3-1 Introduction

Organic chemistry is an innovative science and the glory of organic chemistry continues to improve after each discovery. One of such path breaking discovery was Michael reaction\(^1\) which involved a base promoted addition of various active methylene compounds to electron deficient alkenes. In the initial stages, although the reaction was accomplished mostly with carbon nucleophiles\(^2\), the attention was then focused on the use of various other nucleophiles\(^3\) like N (aza-Michael), S (thia-Michael) to design C-N and C-S bond, respectively. The role of aza-Michael reaction in the synthesis of pharmacologically important family of \(\beta\)-amino carbonyl compounds and its derivatives is well documented in the literature\(^4\). Over the last few years there has been increasing interest in the synthesis of such pharmacologically important compounds by reaction of a variety of nitrogen nucleophiles with a range of Michael acceptors employing efficient catalytic systems. Various strategies of aza-Michael reaction have also been proved useful in the synthesis of core intermediates of many natural products\(^5\).

Over the past several years tremendous progress has been achieved by employing new nitrogen nucleophiles and suitable acceptors as well as more efficient catalytic systems for this important transformation. In the following, we have taken a brief account of aza-Michael addition reaction with special emphasis on the development of the new catalysts.

3-2 Catalysts for aza-Michael addition reaction

Catalysis is one of the most intensely studied and pursued in both the chemical engineering and applied chemistry. Indeed, it is more so now because the use of catalysis for environmental management, abatement and to the world’s economic advancement is becoming more crucial. Indeed, the advancement of catalysis is the cornerstone of both economic and environmental sustainability of the world. Today the study of catalytic activity
of catalysts on the design of chemicals and the chemical reactions puts catalysis at the heart of synthetic methodologies. This review gives an overview of catalysis with emphasis on how the field of catalysis can contribute to aza-Michael addition reaction. The subsequent section follows proposed ideas of new synthetic methodologies for aza-Michael addition reaction.

### 3-2a. Metal and metal salt catalyzed aza-Michael addition

Metal and metal salts catalysis has emerged with great activity over homogenous catalytic system. It plays important advantages of easy availability, inexpensiveness and ease of separability. Consequently, a variety of metal and metal salts have been disclosed for aza-Michael addition reaction.

In 1994, K. Utimoto et al. have described highly productive method for conjugate addition catalyzed by oxophilic lanthanide (III) salts. After screening variety of lanthanide salts using a range of solvents, Utimoto et al. inferred lanthanide triflates to be promising catalysts for aza-Michael addition reaction however, for the reason undisclosed, author have established general protocol using Ytterbium triflate as a catalyst which is relatively expensive compared to other lanthanide triflates. The method was further extended to yield optically active β-lactams (Scheme 1).

![Scheme 1](image)

Owing to the unique properties of high catalytic activity coupled with stability as well as easy recoverability from water, indium trichloride has been extensively used in aza-Michael addition of primary as well as secondary amines to α-β unsaturated ethylenic compounds (Scheme 2). The noteworthy feature of the present protocol is, with the methyl acrylate higher percentage of
bisalkylation product was observed while only selective aromatic amines give good yield of Michael addition product in water at room temperature.

![Scheme 2](image)

Both the triflates of lanthanides and the salts of indium are relatively expensive. In another approach, Kawatsura et al. screened various transition metal salts as well as transition metal organometallic complexes. Amongst various organometallic complexes screened, only those with Pd (II), Rh (II) Ru (III) and Ir (III) were found to be effective irrespective of the substitution pattern at the Michael acceptors which is followed by attack of nucleophiles (Scheme 3).

![Scheme 3](image)

Unlike conventional organometallic complexes, ferrocenyl Ni (II) complexes has been demonstrated to be highly efficient catalyst in addition of aromatic amines to conjugated alkenes (Scheme 4).

![Scheme 4](image)
The utility of Bi(NO$_3$)$_2$, as a metal salt catalyst is well established in various organic transformations and Banik et al.\textsuperscript{10} have established a general and solvent-free protocol for carbon as well as aza-Michael addition to various enones using bismuth nitrate as an inexpensive although non reusable catalyst (Scheme 5).

![Scheme 5](image)

In search for a cheaper metal catalyst Xu et al. have reported the use of \textbf{Cu(I) catalyst}\textsuperscript{11a} for the addition of secondary as well as primary amines to various conjugated alkenes (Scheme 6). Subsequently, Xu et al. also disclosed the catalytic activity of other transition metal salts \textit{viz.} \textbf{iron Chloride, chromium chloride and stannous chloride}\textsuperscript{11b} etc. (Scheme 7). Using copper salts although they were not successful in using aromatic amines as nucleophiles, using the aforementioned salts, weakly nucleophilic aromatic amines underwent aza-Michael addition smoothly with a range of Michael acceptors, except α-β unsaturated-N-acyloxyzolidone.

![Scheme 6](image)

![Scheme 7](image)
To address the issue of failure of aromatic amines to undergo aza-Michael reaction, Reboule et al. then demonstrated the utility of samarium iodide as catalyst and depending upon amine to substrate ratio, mixture of β-amino N-acyloxazolidones and β-amino amides were obtained (Scheme 8).

![Scheme 8](image)

R = CO₂Et, CH₃, C₃H₇, H

The use of ceric ammonium salts (especially nitrate over to sulfate) in a variety of organic transformations is well documented in the literature. So it was not at all surprising that one stems out to try ceric ammonium nitrate (CAN) for the aza-Michael reaction. In fact the use of ceric ammonium nitrate (CAN) in aza-Michael reaction was reported by Adapa et al. as well as Duan et al. almost simultaneously. Various primary aliphatic as well as secondary amines including piperazines were demonstrated to undergo aza-Michael addition reaction (Scheme 9). The main difference between the two protocols is the use of ultrasonic waves (Duan et al) to improve yield and to achieve the transformation in less time (Scheme 10).

![Scheme 9](image)

EWG = -CN, COMe, CO₂Et, COOMe, CONH₂

![Scheme 10](image)

EWG = -CN, COMe, CO₂Et, COOMe, CONH₂
Chapter III  

Review on aza-Michael addition reaction

The use of ytterbium triflate in promoting aza-Michael reaction was demonstrated almost a decade ago. However, higher cost of ytterbium triflate was the major limiting factor for the choice of this catalyst. The issue of the cost of this lanthanide triflate has recently been circumvented by Bhanage et al.\textsuperscript{15} They have reported the use of \textit{yttrium nitrate hexahydrate}, especially in addition of aromatic as well as heterocyclic amines to various conjugated alkenes at ambient temperature under solvent free condition in excellent yields (Scheme 11).

\begin{center}
\includegraphics[width=0.5\textwidth]{Scheme11.png}
\end{center}

\textbf{Scheme 11}

\textbf{3-2b. Solid acid catalyzed aza-Michael addition reaction}

Bronsted as well as Lewis acids are well known for their catalytic activity to promote innumerable organic reactions. As a mild Lewis acid, moisture and air sensitive \textit{zirconium oxychloride}\textsuperscript{16} adds as a new catalyst for conjugate addition of amines to $\alpha$-$\beta$ unsaturated ketones under solvent-free condition but at elevated temperature (Scheme 12).

\begin{center}
\includegraphics[width=0.5\textwidth]{Scheme12.png}
\end{center}

\textbf{Scheme 12}

\textbf{Lithium perchlorate} is a well known Lewis acid and its use in aza-Michael reaction of primary aliphatic as well as secondary amines with a variety of Michael acceptors was demonstrated by Saidi \textit{et al.}\textsuperscript{17} The noteworthy
feature of this catalyst is, under kinetically controlled condition, conventional Michael addition product results while under thermodynamic control nucleophilic attack at carbonyl carbon of esters yields corresponding amide as the sole product (Scheme 13).

\[
\begin{align*}
R & \quad \text{COOMe} \\
\text{Ph} & \quad \text{NH}
\end{align*}
\]

Scheme 13

Naturally occurring clays do possess both, Bronsted as well as Lewis acidity and Bedekar \textit{et al.} reported clay catalyzed addition of secondary amines to conjugated alkenes\textsuperscript{18} (Scheme 14). However, the essentiality of organic solvent as well as high temperature appears to be the major limiting factor.

Like clays, the use of silica gel to promote aza-Michael reaction was reported by two different groups viz. Basu \textit{et al.}\textsuperscript{19} and L. You \textit{et al.}\textsuperscript{20} (Scheme 15) Elevated temperature as well as long reaction times are the drawbacks of these protocols.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{Clay, EDC, Reflux} \\
& \quad \text{CO}_2\text{Me} \\
\text{H}_2\text{N} & \quad \text{Clay, EDC, Reflux} \\
& \quad \text{CO}_2\text{Me}
\end{align*}
\]

Scheme 14

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{COOEt, CN}
\end{align*}
\]

Scheme 15
The use of **Amberlyst-15** as a solid acid catalyst in aza-Michael reaction has been reported again by two different groups viz. Das et al\textsuperscript{21} (Scheme 16) and Esteves et al\textsuperscript{22} (Scheme 17) with the only difference that, Stevens et al have used netherto unexplored vinyl sulfones as a Michael acceptors.

![Scheme 16](image1)

![Scheme 17](image2)

Heteropoly acids (HPAs), apart from their high acidity (Bronsted) acidity offer advantages such as of reusability, environmental compatibility, non toxicity and operational simplicity. Chen et al\textsuperscript{23} have recently reported the use of **12-tungustophosphoric acid** in water medium to promote conjugate addition of aliphatic as well as aromatic amines to $\alpha$-$\beta$ unsaturated esters and nitriles at room temperature (Scheme 18).

![Scheme 18](image3)
Kotsuki et al.\textsuperscript{24} have reported the use of p-toluenesulphonic acids to promote the aza-Michael reaction between conjugated enones and ureas under high pressure conditions (Scheme 19).

As an inorganic solid acid, the use of sulfated zirconia to promote aza-Michael reaction of $\alpha$-$\beta$ unsaturated ketone with a range of amines has been demonstrated by Reddy et al.\textsuperscript{25} (Scheme 20).

3-2c. Solid supported heterogeneous catalysts

Heterogeneous catalysts conventionally offer the prime advantage of high catalytic activity due to improved surface area, reusability, easier separation from the reaction mixture, (availing the isolation of product easier,) etc. Taking clues from earlier reports on use of indium chloride to promote aza-Michael reaction, Kantam et al.\textsuperscript{26} have reported recently polyaniline supported indium chloride as a heterogeneous and reusable catalyst to promote the conjugate addition of primary aliphatic as well as secondary amines to conjugate alkenes (Scheme 21). Typically, with the use of excess of Michael acceptors, bis-Michael addition product results. However, with aromatic amines, corresponding Michael addition products result only in moderate yields.
To circumvent the high cost of indium chloride, quite recently Saidi et al.\textsuperscript{27} have reported the use of \textit{silica supported aluminium chloride} as an efficient catalyst to promote aza-michael reaction of both secondary as well as aromatic amines with a variety of Michael acceptors (Scheme 22).

\textbf{CeCl}_3.7\text{H}_2\text{O}-\text{NaI system supported on SiO}_2 has been found to be one of the efficient and easily separable catalysts in Michael addition of secondary amines to $\alpha$-$\beta$ unsaturated enones\textsuperscript{28} (Scheme 23). Surprisingly, cerium chloride alone is unable to promote this reaction suggesting that during the preparation of the catalyst halide exchange reaction might be taking place and cerium iodide (?) is a true catalyst in this reaction.
Misra et al.\textsuperscript{29a} in 2007 have reported \textit{silica supported perchloric acid} while Sing \textit{et al.}\textsuperscript{29b} have reported \textit{silica impregnated perchloric acid} for aza-Michael addition of a series of secondary amines (Scheme 24). Primary amines were also effectively added to electron deficient alkene to furnish corresponding Michael addition product in moderate to satisfactory yield. Chaudhary \textit{et al.}\textsuperscript{30} reports \textit{phosphate impregnated titania} as a new catalyst to promote the same reactions (Scheme 25).

\begin{align*}
\text{R}_1\text{NH}_2 + \text{R}_2\text{Y} \xrightarrow{\text{HClO}_4 / \text{SiO}_2} \text{MW 540 W, 2-7 min} & \rightarrow \text{R}_3\text{N} - \text{R}_4 X \\
\text{X} = \text{COOMe, CN, COMe, CONH}_2
\end{align*}

\textit{Scheme 24}

\begin{align*}
\text{R}_1\text{NH}_2 + \text{R}_2\text{Y} \xrightarrow{\text{Phosphate impregnated titania}} \text{rt} & \rightarrow \text{R}_3\text{N} - \text{R}_4 X
\end{align*}

\textit{Scheme 25}

Very recently, Guo \textit{et al.}\textsuperscript{31} have reported the use of \textit{silica sulphuric acid} as a highly efficient catalyst for Michael addition of secondary amines and aliphatic as well as aromatic amines on selective Michael acceptors (Scheme 26). Satisfactory results have been obtained within short reaction times. However, the authors have not extended reaction with Michael acceptors like conjugated nitriles, esters, amides, etc.
3-2d. Organocatalytic aza-Michael addition reaction

During the last decade, organocatalysis has been one of the most rapidly growing and competitive field in catalytic systems. It offers several advantages such as, mild reaction conditions, operational simplicity and easily accessible catalytic system.

Many of the Bronsted acid catalysts discussed earlier are capable to promote aza-Michael addition with secondary amines or primary aliphatic amines which are sufficiently nucleophilic and they either fail or furnish aza-Michael addition products with weakly nucleophilic aromatic amines. However, Amore et al.\textsuperscript{32} have developed acetic acid mediated microwave assisted protocol to promote addition of aromatic amines to a range of conjugated alkenes (Scheme 27). The striking feature of the protocol is the temperature (200 °C) of the reaction mixture at which both the starting materials are expected to boil off.
Like heterogeneous solid acid catalyst, the use of polyvinyl pyridine (Scheme 28) as well as borax (Scheme 29) to promote the aza-Michael reaction has been reported by two different research groups, viz. Samant et al. 33 and Chaudhuri et al.34

\[
\text{N} + \text{COOMe} + \text{PVP} \xrightarrow{\text{rt}} \text{N-COOMe}
\]

\textbf{Scheme 28}

\[
\text{R}_1\text{N} + \text{EWG} \xrightarrow{\text{Borax 10 mol \% rt, Water}} \text{R}_1\text{N-EWG}
\]

\text{EWG = CO2Me, CN, CONH2, COMe, COPh}

\textbf{Scheme 29}

Biomolecular modeling of organic chemical reactions involves cyclodextrins as supramolecular catalysts. Like enzymes, cyclodextrins show reversible formation of host guest complexes without covalent bonding. Surendra et al.35 have reported the catalytic activity of β-cyclodextrin for aza Michael addition reaction in aqueous medium (Scheme 30). This methodology permits the use of amines of almost every class as Michael donors.

\[
\text{R}_1\text{NH} + \text{R}_2\text{R}_3\text{N} \xrightarrow{\beta-\text{CD/H}_2\text{O}} \text{R}_1\text{R}_2\text{R}_3\text{N}
\]

\textbf{Scheme 30}

3-2e. Ionic Liquids

Until recently, most of the organic reactions were carried out in molecular solvents. However, in the last decade, ionic liquids have emerged as novel reaction media to promote a variety of organic transformations.
Yadav et al.\textsuperscript{36} have reported the use of both hydrophilic (1-butyl-3-methyl imidazolium tetrafluoroborate) as well as hydrophobic (1-butyl-3-methyl imidazolium hexafluorophosphate) ionic liquids to promote aza-Michael reaction (Scheme 31). Although the reaction medium is reusable, the advantage of its use over to other conventional solvents is definitely questionable because the time required for the reaction is too long.

\[ \text{NH} \text{EWG} \text{N} \text{EWG} \text{R}_1 \text{R}_2 + [\text{bmim}]\text{PF}_6 / [\text{bmim}]\text{BF}_4 \text{rt} \]

\text{EWG = CN, COCH}_3, \text{CO}_2\text{Et, CO}_2\text{Me, COPh}

\textbf{Scheme 31}

After this first report, Xu et al.\textsuperscript{37} have reported the use of simple quaternary ammonium salt for the same purpose (Scheme 32). Commercial availability as well as high yield are the prime advantages of quaternary ammonium salts. The report also shows the catalytic activity of hydrophilic ionic liquid [bmim]BF\textsubscript{4}. The only limitation with the present protocol is the reaction fails with aromatic amines.

\[ \text{\text{O}} \text{Et} + \text{Catalyst} \text{H}_2\text{O/rt/7hr} + \text{EWG = CN, COOEt, COOCH}_3, \text{COCH}_3 \]

\textbf{Scheme 32}

To overcome this incompleteness, recently, Xu et al.\textsuperscript{38} reported basic ionic liquid [Emim]OH as a catalyst and green solvent for conjugate addition.
of aromatic amines to α-β unsaturated ketones (Scheme 33). The protocol shows less reactivity towards α-β unsaturated ester.

Based upon similar philosophy Xu et al.\textsuperscript{39} has also reported the use of [bmim]OH as a reusable, basic ionic liquid to promote the same reactions (Scheme 34).

EWG = CN, COCH₃, CO₂CH₃

For the same reaction, Ying \textit{et al.} have recently reported both, DBU-derived and DBU-based task specific ionic liquids. Firstly, they reported [DBU][Ac] as a efficient catalytic system for the solvent free conjugate addition of secondary amines to α-β unsaturated ester, nitrile and amide\textsuperscript{40} (Scheme 35) in excellent yields and in acceptable results for the weak nucleophiles like aromatic amines.

Later on, they described [DBU][Lac] as a better catalyst compared to [DBU][Ac] while examining the catalytic activity towards addition of primary aromatic amines\textsuperscript{41} (Scheme 36) to various α-β unsaturated ketones.
3-2f. Solvent promoted aza-Michael addition reaction

**Reaction media** plays an important role in organic synthetic chemistry. The medium considered for reaction should include the advantage of recyclability or easy removal with energy conservation. It should have much of catalytic activity to promote the reaction. Most of the solvents can be easily removed by water solubility and should be extensively employed for green context. Thus, according to environmental impact, the reaction media can be recycled with efficient number of cycles, non inflammable, high polarity for homogeneity and also with low vapour pressure. Various reaction media like supercritical fluids, fluorous based systems, ionic liquids and water have been extensively used in organic transformations.

The Michael addition of anilines to electron deficient olefins proceeds easily in **water, trifluoroethanol and hexafluoroisopropanol** without any assisting agent\(^{42}\) (Scheme 37). Moreover, according to the nature of the solvent and that of the electrophile, the selectivity of the reaction can be finely tuned to afford mono-or bis-addition products, or even quinolines, in a one pot fashion. De. *et al.* has extensively studied the effect of polar protic solvents in 1,4 addition of anilines on to Michael acceptors.
Kumar et al.\textsuperscript{43} described the use of inexpensive and nontoxic polyethylene glycol (400) as the reaction medium of aza-Michael reaction of amines as well as monoalkylated piperazine derivatives with electron deficient alkenes (Scheme 38).

Today the point of view of researchers continues with the green chemical concept. The choice of solvent is the heart of the chemical reaction and should be parallel with the reactivity as well as green nature of solvent. Various reactions have been carried out in aqueous media due to its environmental acceptability, abundance and low cost. Ranu et al have reported rate accelerated aza-Michael reaction in water\textsuperscript{44a} (Scheme 39). Surprising thing is that scientist himself has reported the same protocol\textsuperscript{44b} operable at elevated temperature and the report was not so far extended to generalization. The latest report shows the aza-Michael addition over $\alpha$-$\beta$ unsaturated esters, nitriles, ketones and amides.
3-3 Application of aza-Michael reaction

Aza-Michael addition reaction has been extensively studied using a variety of catalysts as well as solvents as summarized earlier and various researchers have also reported the utility of aza Michael addition towards the synthesis of various pharmacological active compounds as well as natural products like colchicine, podophylotoxin and combretastatine A-4, etc. Noteworthy applications of intramolecular aza-Michael addition lies in the synthesis of 6,7,2',3',4'-substituted-1,2,3,4-tetrahydro-2-phenylquinolone which shows potent cytotoxic and antitubuline effects.

Verma et al. have reported microwave assisted isomerisation of 2'-amino chalcone on clay (Scheme 40.1). Microwave heating is used for induction of the reaction under dry condition with salient features of rapid reaction rate and cleaner reactions. Various 2'-aminochalcones have been used. The isolated yield was 70-80%.
Subsequently, Perumal *et al.*\textsuperscript{49} reported **indium trichloride supported on silica gel** to effect the same transformations using microwave dielectric heating technique in almost same yields (Scheme 40.2).

Later on, two more procedures for intramolecular aza-Michael reaction were reported. Van Lier *et al.* reported **tantalum pentabromide adsorbed on silica gel** as a lewis acid catalyst (Scheme 40.3). in this protocol, instead of microwave dielectric heating reaction was carried out under conventional heating\textsuperscript{50}.

Later on, **alumina supported cerium chloride heptahydrate-sodium iodide**\textsuperscript{51} was reported to be relatively less expensive catalyst for the synthesis of targeted dihydroquinilines in improved yields (Scheme 40.4).

For developing both the solution phase reaction as well as solid supported reactions, Bhattacharya *et al.*\textsuperscript{52} have reported **antimony trichloride** as an effective catalyst for isomerization of 2’-amino chalcones. The catalyst is effective in cost, handling and yield of the product (Scheme 40.5).
3-4 Concluding remarks

Last few years have witnessed tremendous achievements in the field of catalytic aza-Michael additions. The reaction has great potential in organic synthesis, primarily because of the ubiquitous presence of β-amino acids or alcohols in many natural products as partial structures or in designed hybrid scaffolds containing β-amino acids/alcohols, due to their role played in bioprocesses as isosteres of α-amino acids. Although there is still no any report for “universal” catalyst (and will probably never be one) for all types of nucleophiles and Michael acceptors, in this chapter an impressive number of highly efficient systems has been compiled by us. By this compilation we are inspired to contribute towards aza-Michael addition, which is developing in multitude.
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