

## **Chapter 1**

**A detailed introduction on application of N-heterocyclic carbene in organocatalysis, heterogenization of NHC catalysts, zirconium phosphate/phosphonate layered materials as catalyst support and semiconductor based photocatalytic oxidation reactions**

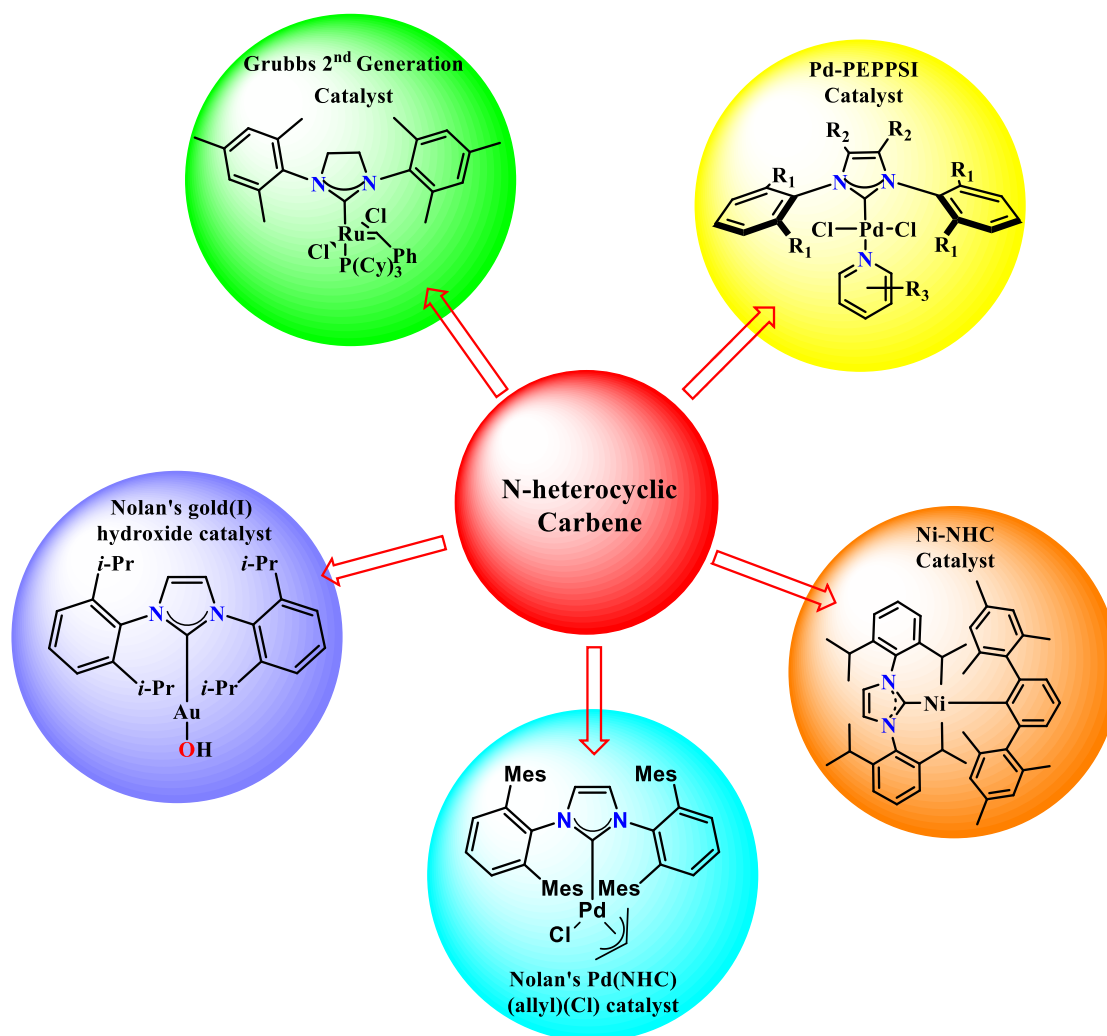
## **1.1. General Introduction**

Catalysis has emerged as a cornerstone in modern chemical synthesis. Use of catalyst for efficient and atom economic chemical conversions of industrial importance is recognized as a primary goal of green and sustainable chemistry. Catalysis in the 21<sup>st</sup> century is multidisciplinary, with ongoing synergistic connections and collaborations among chemists, physicists, biochemists, chemical, mechanical, and electronic engineers, among others. The future of catalysis lies in more extensive and open contacts between industry and academics as well as a long-term vision based on novel concepts, methodologies, and procedures. Contemporary challenges of catalysis primarily involve rational design of catalysts based on a fundamental understanding of their action and reaction mechanism, novel routes to discovery of catalyst using combinatorial methods and high throughput experimentation, and a cheaper and more sustainable catalytic process to increase the selectivity and lifetime of the catalysts, both from an environmental and economic perspective. Majority of catalytical processes employed in industries and laboratories involve homogeneous catalysts owing to their high efficiency and selectivity. Plethora of effective homogeneous catalysts for important chemical conversions have been so far developed and many of them are currently being used in industry [1-3]. However, recovery and separation of homogeneous catalysts have so far remained a challenging task and this not only contaminate reaction products but also make the chemical processes economically unviable. To overcome these drawbacks, heterogeneous solid catalysts are gaining interest because of their reusability, easy separation and thereby reducing chemical waste [4]. These advantages of heterogeneous catalysts over homogeneous catalyst fueled their development and thereby design green and economically profitable chemical technology [5-6]. Major challenges that remain to be addressed for application of heterogeneous catalysts in industries are to enhance their catalytic efficiency and selectivity in comparison to their homogeneous counterparts.

## **1.2. N-heterocyclic carbene: A versatile ligand for catalyst design**

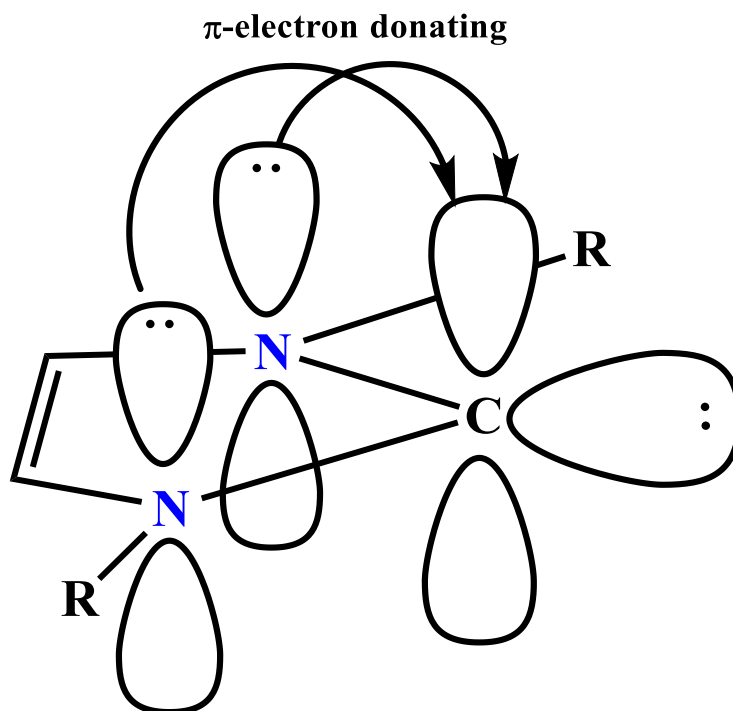
During the last couple of decades, N-heterocyclic carbenes (NHC) have emerged as highly relevant platform in designing efficient catalyst for a wide range of important chemical transformations. NHCs are heterocyclic species containing a divalent carbon atom containing six valence electrons [7-8]. First example of stable, isolable, and 'bottleable' crystalline N-heterocyclic carbene, IAd (1,3-di(adamantyl)imidazol-2-

ylidene) was reported by Arduengo et al. in 1991 [9]. Previous attempt to isolate free NHCs by Wanzlick in 1960 failed because it dimerizes leading to the formation of a C=C bond [10]. Wanzlick and Feile then prepared the first NHC-metal complex with Hg(II) and Cr(III) separately in 1968 [11]. Ever since the synthesis of free NHC by Bernard and Arduengo, this class of ligand has attracted immense attention. NHCs are widely used as ancillary ligands in designing organometallic complexes and many of these complexes act as efficient catalyst in an assortment of important catalytic transformations [12-14]. A few highly celebrated examples of NHC based organometallic catalyst are Grubbs 2<sup>nd</sup> generation metathesis catalyst, [15] Organ groups palladium based Pd-PEPPSI catalyst used in coupling reaction, [16] Nolan's Pd(NHC)(allyl)Cl catalyst used in arylation of ketones, [17] Nolan's gold(I) catalyst which is used in hydroamination reaction [18] and Ni(II) based NHC complex reported by Laskowski [19] etc. (Chart 1.1).



**Chart 1.1.** Selected NHC based organometallic catalysts

N-heterocyclic carbenes are sterically and electronically stable with the electronic stability being provided by nitrogen atoms of the NHC. The nitrogen atom substituents next to the carbene carbon centre shows resonance effect by donating the electron to the empty  $\pi$ -orbital of the carbene carbon centre, thus stabilizing the empty orbital on the carbene (Figure 1.1). The lone pair located on the heterocyclic ring plane of NHCs furnishes these compounds with nucleophilicity. Because of this characteristic of NHCs exhibit a tendency to act as a  $\sigma$ -donors and bind to an extensive array of non-metallic and metallic species. These distinct and unique interactions impact on the structure, stability and reactivity of NHC complexes or NHC adducts and forms the basis for the soaring rise in interest on NHCs [20]. This has eventually led to the widespread employment of NHCs as spectator ligands in transition metal based homogeneous catalysis. NHCs are proved to be excellent ligands efficient in stabilizing alkali, alkaline earth, transition, and inner transition metal complexes.



**Figure 1.1.** Stabilization of NHC by mesomeric effect

### 1.3. NHC in catalysis

NHC based catalysts can be broadly categorized in three classes: NHCs coordinated to metal, adduct of NHC with p-block elements and NHCs organocatalysts. NHCs are excellent  $\sigma$ -donors and therefore capable of forming strong metal carbon bonds. Due to

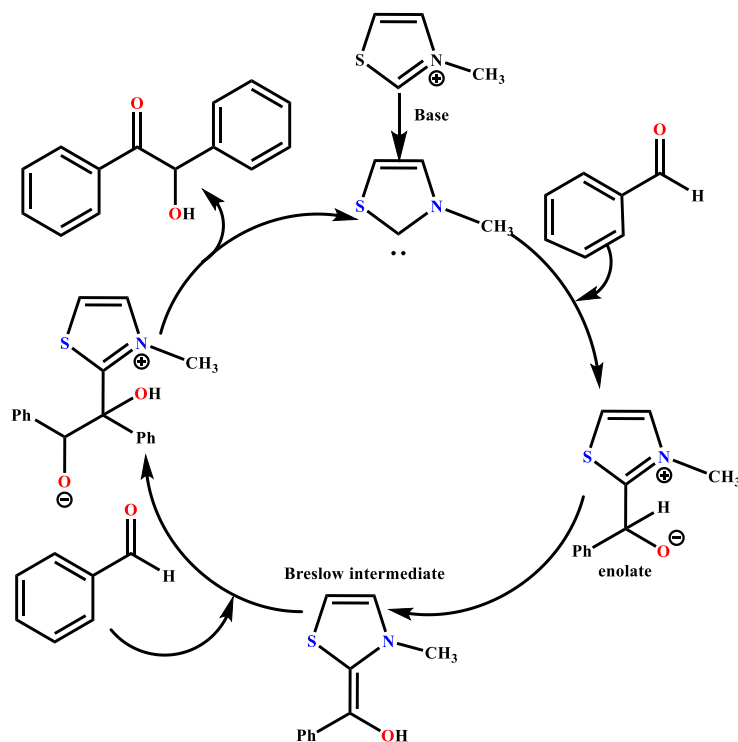
this intrinsic property, metal complexes bearing NHC as ancillary ligands show greater air or thermal stability as compared to conventional metal-phosphine catalysts whereas their catalytic activities are 100-1000 times higher. For example, Herrmann and co-workers reported high catalytic efficacy of imidazole-2-ylidene palladium(II) catalyst in Mizoroki-Heck reaction [21]. NHC-metal complexes have also found several useful applications as organometallic materials and metallo-pharmaceuticals. The high bond strength of the carbene carbon-metal bond in NHC metal complexes accounts for their consideration as a suitable oxidation catalyst. The ease with which NHCs can be incorporated into soft materials, as well as the higher bond strength of the carbon-metal bond in NHCs, facilitates their incorporation into polymeric, dendrimer, and MOF-type materials [22]. These further aids the recyclability of NHC metal complex-based catalysts [23].

The most important feature of the adducts formed by NHC with p-block elements is the  $\sigma$ -donation from the N-heterocyclic carbene carbon into an empty  $\sigma$ -electron accepting orbital of the low-valent p-block elements. The unique strength of this dative coordination is attributed to the high stability, non-lability of the adducts and their exotic properties and reactivity. The strong  $\sigma$ -donation ability of NHCs allows for the unprecedented stabilization of their adducts with p-block elements even in the low-oxidation state. NHCs can also act as component of Lewis acid-base adducts and thereby activate small molecules [20].

The immense affinity NHCs for carbon-electrophiles has resulted another prime area of applications, namely NHCs as organocatalysts. The reactions resulting from the nucleophilic attack of NHCs on aldehydes have led to the development of a broad and diverse range of NHC organocatalyzed reactions. NHCs can also combine with alcohols to produce transesterification products [24]. Reactions of these type have found widespread application in ring-opening and step growth polymer synthesis as an substitute to convention organometallic catalysts and initiators [20]. A few important organic transformations in which NHCs find application as catalyst are Benzoin condensation [25], metathesis [15], Stetter reaction [26], photochromic reaction [27] etc. The synthetic value of many of these reactions have been significantly augmented by the introduction of asymmetric variants using chiral NHCs [28].

### 1.3.1. NHC based Organocatalysis

NHC based organocatalysis is recognized one of the most important fields in organic synthesis for the unconventional formation of carbon-heteroatom and carbon-carbon bonds. Thiazolium catalyzed benzoin condensation reaction reported by T. Ugain et al in 1943 is considered as the first example of NHC based organocatalysis [29]. Soon it was discovered that triazolium salts also act as highly efficient catalyst in benzoin condensation reaction and good enantioselectivity can be achieved when chiral bicyclic thiazolium salts are employed [30]. In a landmark article published in 1958, Breslow suggested a mechanistic pathway for the thiazolium salt catalyzed benzoin reaction which involved NHC promoted umpolung of carbonyl carbon center from electrophilic to nucleophilic [31] (Scheme 1.1). Initially suggested by Breslow in 1958, nucleophilic

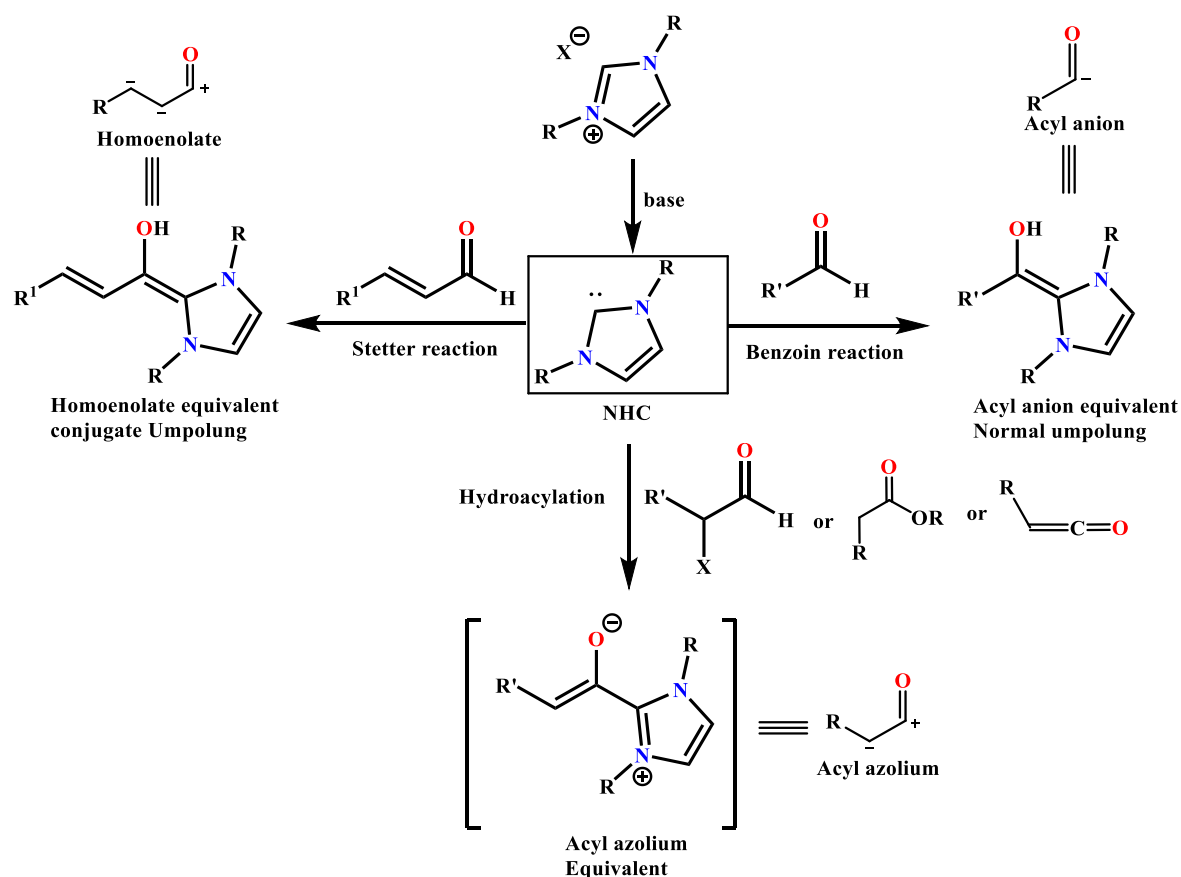


**Scheme 1.1.** Formation of Breslow Intermediate

addition of a NHC to a carbonyl group produces an enaminol which in present literature is referred as Breslow intermediate and remains a common thread that operates in NHC catalyzed reactions. Whereas a zwitterionic intermediate is initially produced by the action of NHC on the carbonyl carbon atom, a crucial proton transfer from the aldehydic carbon to the geminal oxygen atom result the diamino enol which is known as Breslow intermediate. The carbonyl carbon of the Breslow intermediate behaves as a nucleophile

and therefore merge with a second molecule of the carbonyl carbon to form the benzoin product. Thus, umpolung of the carbonyl carbon atom, which signifies reversible of polarity occur.

Reversing the electrophilic polarity of carbonyl carbon atom is a highly desirable yet reasonably challenging task that typically necessitates a strong base under harsh reaction conditions. Traditionally, dithianes or protected cyanohydrin derivatives have been used to generate acyl anion equivalents. However, umpolung of carbonyl functionality by employing NHCs under moderate reaction conditions propelled the interest in NHC based organocatalysis. Thus, a thiazolium based NHC catalyzed selective conjugate addition of aliphatic, aromatic and heteroaromatic aldehyde with Michael acceptor resulting in 1,4-bifunctional compounds was discovered by H. Stetter et. al in 1974 [32]. This reaction, currently known as the Stetter reaction remains one of the extensively developed NHC catalyzed reaction due to its immense potential in organic synthesis (Scheme 1.2) [33]. Even though a Breslow intermediate is involved in Stetter reaction,

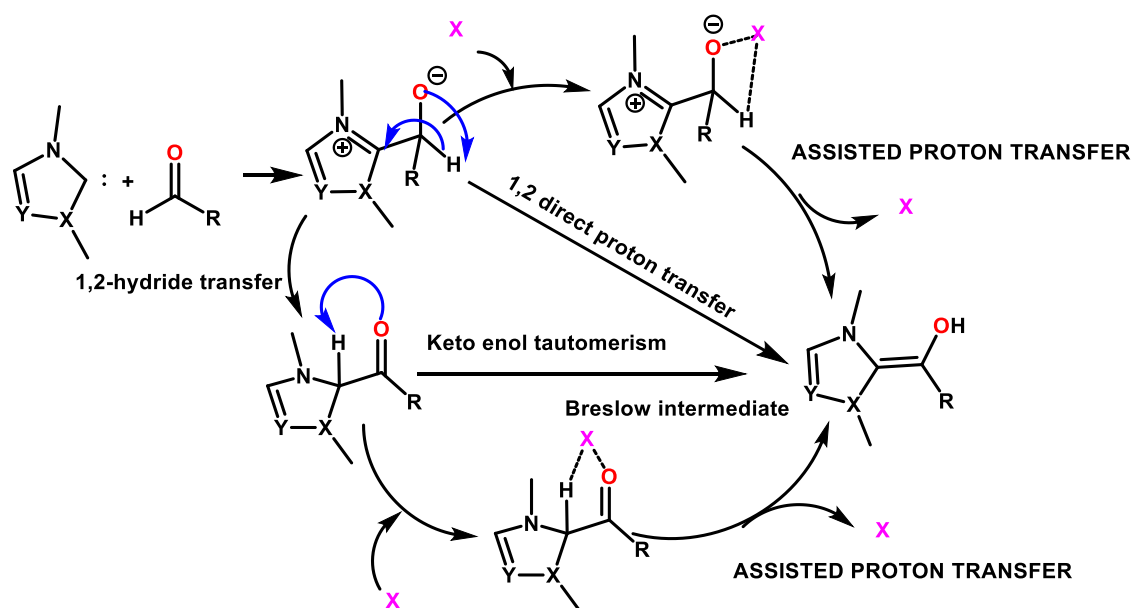


**Scheme 1.2.** Benzoin condensation and Stetter reaction

the mode of reactivity is markedly different from that observed in case of NHC catalyzed Benzoin condensation. While the mode of reactivity in NHC catalyzed Benzoin condensation is formation of an acyl anion through the Breslow intermediate, presence of  $\alpha,\beta$ -unsaturation in the Breslow intermediate formed in case of Stetter reaction instead generate a homoenolate.

Another important mode of reactivity observed in NHC based organocatalytic reaction is formation of acyl azolium equivalent through attack of NHC on  $\alpha$ -functionalized aldehydes or esters. This mode of reactivity has been widely employed in e.g. [2+2], [4+2] and [3+2] cycloadditions reactions as well as in enolate chemistry of  $\alpha$ -functionalized aldehydes [34-36].

Computational investigations have advocated that a direct 1,2-proton transfer within the original zwitterionic intermediate is energetically unreasonable and therefore the involvement of other species capable of facilitating an assisted proton transfer is more likely. The proton transfer facilitated by additives (such as bases, acids, other species such as solvents) thereby facilitate the kinetics of formation of Breslow intermediate. The choice of additive has a direct influence on the formation of Breslow intermediate and consequently on its subsequent catalytic activity. Substituents on imidazole nitrogen play a crucial role in stability as well as electronic characteristics of NHCs (Scheme 1.3). The geometric proximity and the capability of the substituents to alter the electron donating capacity of the nitrogen to carbene carbon are of great significance to the energetics of generation of Breslow intermediate [37].



**Scheme 1.3.** Scheme showing various pathways involving the Breslow intermediate



### 1.3.2. NHC catalyzed direct aerobic esterification of benzaldehyde

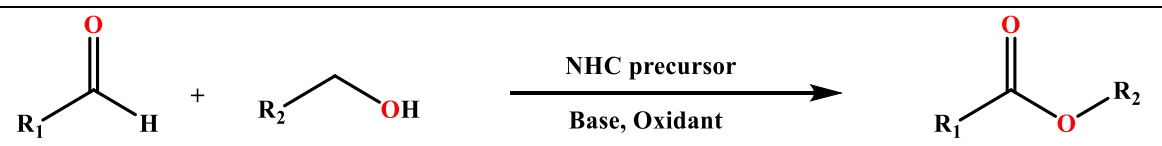
Esterification is a pivotal class of reaction due to the ubiquitous nature of the ester functionality in various natural and synthetic molecules, as well as their utility as a building block of natural product and active pharmaceutical ingredients [38]. Conventional esterification is accomplished through nucleophilic substitution of carboxylic acid derivatives with alcohols. Because these derivatives are derived from corresponding carboxylic acids, esterification necessitates several steps that produce undesirable by-products, which is incompatible with the current requirement of developing environmentally friendly process. Direct ester formation from aldehydes is also possible via oxidation of intermediate hemiacetals in alkaline alcoholic solutions, but the formation of methyl ester is limited due to selectivity factors [39].

Aromatic esters are very useful and important class of compounds with a lot of potential due to their numerous applications in pharmaceuticals, agrochemicals, solvents, lubricants, plasticizing agents, perfumes and so on [40,41]. Aromatic esters can be synthesized using a variety of methods including Fischer esterification, the Mitsunobu reaction, the Favorskii rearrangement, the Baeyer-villiger oxidation and the Pinner reaction [42-46]. Furthermore, the halogen-metal exchange of aryl halides with carbon monoxide, ethyl chloroformate, or DMF is known to be an alternative method of synthesis [47]. Despite this several limitations such as the use of expensive Pd catalysts, reversibility of the traditional esterification reaction, the involvement of poisonous CO, and inconsistent yields achieved in some cases have limited their use [48]. Due to their wide and vivid importance in the synthesis of natural products, scientist devised a new strategy for synthesizing esters that involved direct esterification of aromatic aldehydes to aromatic esters under mild condition [49]. However, some drawbacks remained, such as the need for more than stoichiometric amounts of oxidants such as ozone, hypervalent iodine,  $V_2O_5-H_2O_2$  and so on, and more reaction time is required [50-52].

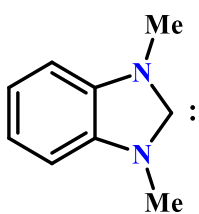
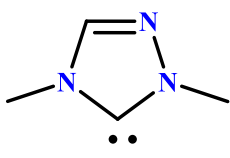
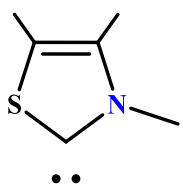
With the emergence of N-heterocyclic carbenes (NHCs) as potent and powerful class of organocatalysts having enormous applications in synthetic transformations as a versatile ligand, the direct esterification of aldehydes in presence of catalytic amount of base became possible under most convenient conditions. Many esters obtained in oxidative or oxygenative reactions promoted by N-heterocyclic carbenes can be interesting precursors in advanced organic synthesis [53]. The catalytic efficacy of azolium salts in oxidative esterification of benzaldehyde was initially realized by the Miyashita group in 1997 [54].

Their work revealed that benzimidazolium or thiazolium salts can effectively catalyse the direct oxidative esterification of aromatic aldehydes into the corresponding esters in presence of a suitable base e.g. DBU and an oxidant e.g. nitrobenzene. However, the importance of this reaction as well as involvement of NHC in this reaction is not realized until 2007 when Scheidt *et al.* reported NHC catalyzed oxidative esterification of aldehydes into the corresponding esters [55]. Tandem oxidation of allylic, propargylic and benzylic alcohols to aldehyde which subsequently undergo NHC catalyzed oxidative esterification reaction to form corresponding esters was reported in this study. Catalytic efficacy of several imidazolium, thiazolium and triazolium based NHCs were screened and a simple imidazolium based NHC (**L1**) provided highest yield of the ester when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is used as a base and MnO<sub>2</sub> as the oxidant. Subsequent studies explored the utility of a varied range of oxidants and azolium salts in this esterification reaction involving both activated as well as inactivated aldehydes (Table 1.1).

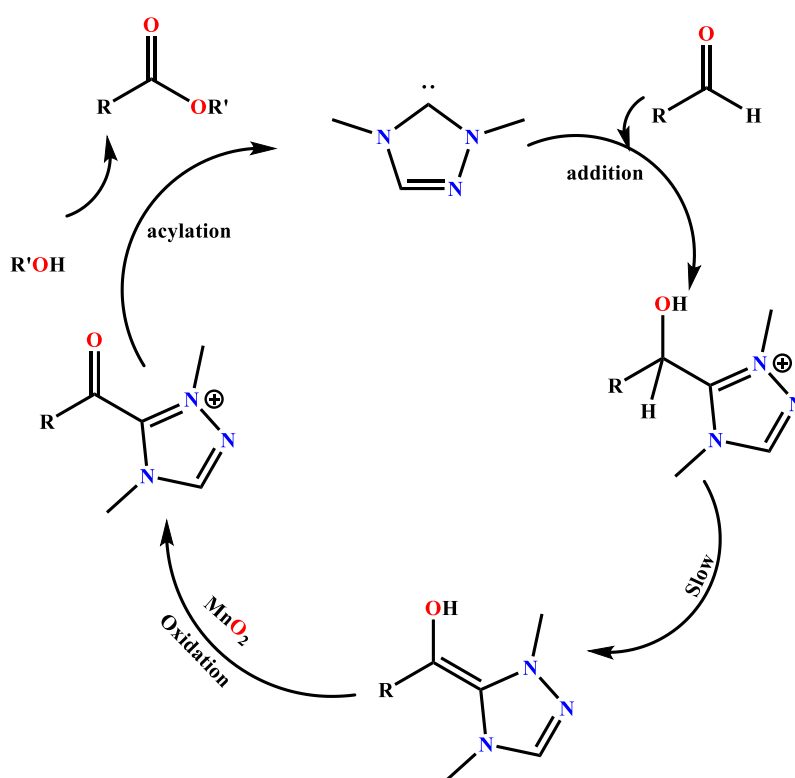
**Table 1.1.** Examples of NHC catalyzed oxidative esterification of aldehydes with alcohols

					
NHC	Base	Oxidant	Reaction Conditions (Solvent/Temperature/Time)	% Yield	Reference
<b>L1</b>	DBU	p-nitroaniline	THF, RT/reflux, 1-5 h	95%	54
<b>L2</b>	DBU	MnO <sub>2</sub>	DCM/25 °C/0.5-3 h	98%	55
<b>L2</b>	DBU	TEMPO	THF/RT/6-12 h	98%	56
<b>L2</b>	DBU	diphenone	THF/RT/2 h	98%	57
<b>L3</b>	triethylamine	nitrobenzene	CH <sub>3</sub> OH/60 °C/4 days	79%	58
<b>L2</b>	Rb <sub>2</sub> CO <sub>3</sub>	Bisquinone	THF/RT-60 °C/6-42 h	89%	59

<b>L1:</b>		<b>L2:</b>		<b>L3:</b>	
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Mechanistic investigation of the above NHC catalyzed esterification of aldehydes with alcohols reveal the involvement of Breslow intermediate (Scheme 1.4) upon addition of NHC to the aldehyde substrate. Once formed, the Breslow intermediate is oxidized into an electrophilic acyl azolium ion by stoichiometric quantity of oxidant e.g. nitrobenzene,  $\text{MnO}_2$ , TEMPO, quinone etc. in the next step. Transfer of the acyl group from the acyl azolium ion to a nucleophile, e.g. alcohol then generate the desired ester as well as regenerate the NHC catalyst. Due to the involvement of stoichiometric amount of an oxidant for oxidation of the Breslow intermediate into the key acyl azolium synthon, this pathway is typically termed as oxidative NHC catalysis.



**Scheme 1.4.** Proposed mechanistic pathway for NHC catalyzed oxidative esterification of aldehydes with alcohols

Within a couple of years after the discovery of oxidative NHC catalysis, it was realized that such reactions can proceed even via a different pathway via direct transfer of oxygen atoms (Table 1.2). In 2013, Kiran *et al.* reported that the NHC catalyzed direct esterification of aromatic aldehydes also proceed efficiently when atmospheric oxygen is used instead of  $\text{MnO}_2$  [60]. Out of several NHCs screened, imidazolium based NHC containing bulky aromatic substituent (**L2**) gave the highest yield of the ester. Further,

**Table 1.2.** Examples of NHC catalyzed oxygenative esterification of aldehydes with alcohols

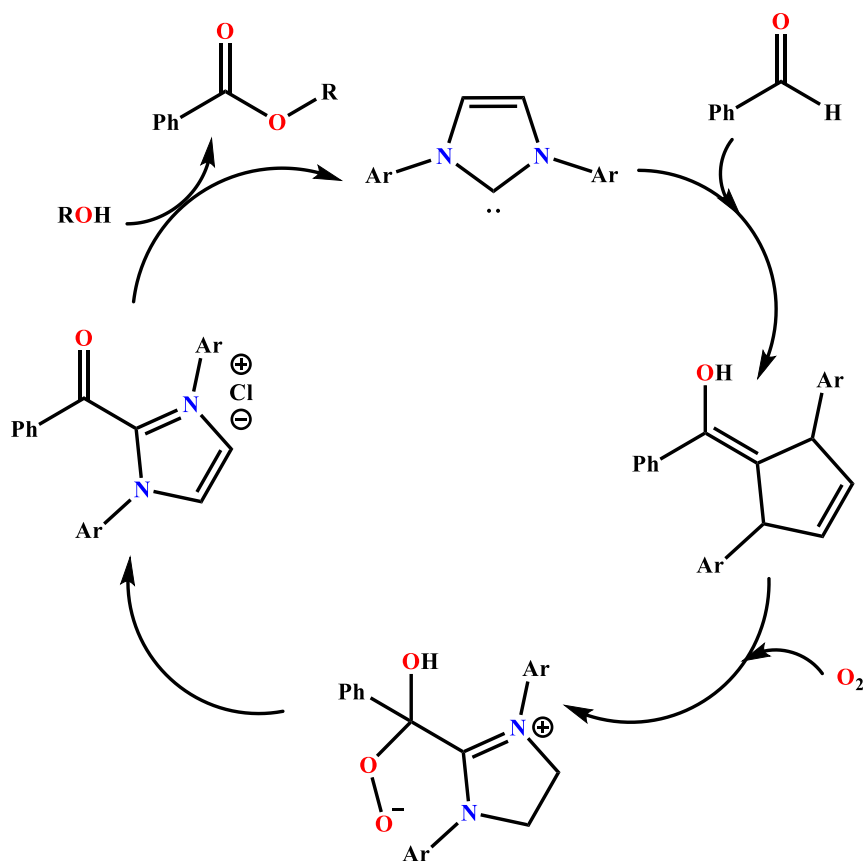
NHC	Base	Oxidant	Reaction Conditions (Solvent/Temperature/Time)	% Yield	Reference
<b>L4</b>	DBU	O <sub>2</sub>	THF/25 °C/4 h	82%	60
<b>L5</b>	DBU	Air	THF/RT/ 24 h	94%	61
<b>L6-L9</b>	DBU	Air	THF/55 °C/16 h	93%	62
<b>L10</b>	DBU	Air	THF/ RT/24 h	97%	63

<b>L4:</b>		<b>L5:</b>		<b>L10:</b>	
<b>L6:</b>		<b>L7:</b>			
<b>L8:</b>		<b>L9:</b>			

the reactivity of substrates with electron-withdrawing substituents was reasonably higher as compared to substrates containing electron-releasing substituents. Based on the outcomes of their work and on precedents set by the literature, they suggested a catalytic cycle where the peroxy anion generated from the reaction between the Breslow intermediate and O<sub>2</sub> was portrayed as the key intermediate in the esterification process (Scheme 1.5). In the same year Connon and co-workers reported an efficient method for NHC-catalyzed esterification of aldehydes using different alcohols and molecular O<sub>2</sub> as the oxidant at ambient temperature [61]. They found out that carrying out the reaction by employing triazolium salt as the precatalyst gave the most promising results with better yields. Also, the emergence of DBU as the most prominent base among many others was highlighted in the paper. They then studied the compatibility of their process using different aldehydes and found out that electron-neutral and deactivated aldehydes gave

excellent conversion results while activated benzaldehydes showed varying degrees of yield. Further, aliphatic aldehydes gave poor yields of the ester and resulted in a complex product mixture (Scheme 1.5). Mechanistic studies on the above type of NHC organocatalysis involving molecular oxygen reveal formation of a peroxy zwitterion upon addition of O<sub>2</sub> to the Breslow intermediate. The peroxy zwitterion decomposes momentarily to result acyl azolium ion, which can efficiently transfer the acyl to a nucleophile e.g. alcohol and thereby result the corresponding ester.

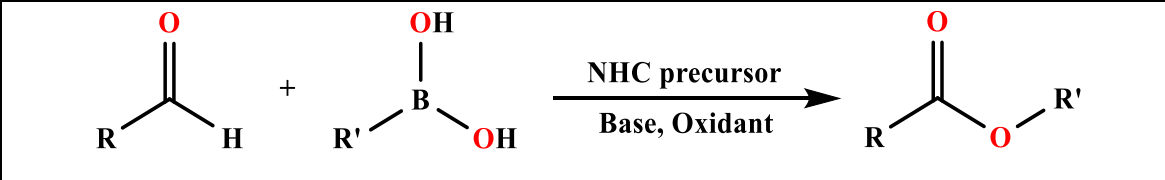


**Scheme 1.5.** Plausible mechanism for oxygenative NHC catalyzed esterification involving aldehyde and alcohols

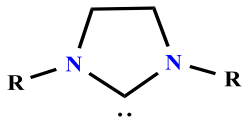
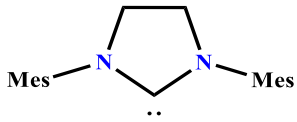
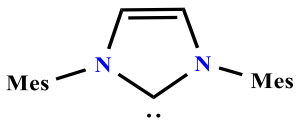
The above oxidative or oxygenative NHC catalyzed esterification of aldehydes also proceeds with several other nucleophiles e.g. aryl boronic acid, aryl halides etc. olefins etc. For example, Arde et al. in the year 2012 reported the aerobic oxidation of aryl aldehydes in the presence of boronic acids to furnish the corresponding esters. Results of this study show that electron rich boronic acids reacted faster than electron deficient boronic acids while electron poor aldehydes reacted at a faster rate when compared to electron rich aldehydes [64].

Subsequently, scope of this NHC catalyzed esterification reaction of aldehydes with aryl boronic acid is explored by using different azolium precursors and base (Table 1.3). Furthermore, dioxygen was found to play a significant role in the reaction mechanism. No desired product was observed under the N<sub>2</sub> atmosphere. The reaction proceeded to give moderate to good yields for aromatic aldehydes of various functional groups such as cyano, nitro, fluoro etc. Electron-rich aldehydes reacted with aromatic boronic acids readily to result the desired esters in excellent yields. However, the reaction is sluggish with aldehyde substituted with electron-withdrawing groups. Moreover, aliphatic aldehydes did not prove to be an efficient substrate for this reaction. Aryl boronic acids with electron withdrawing substituents also did not give us the desired products.

**Table 1.3.** NHC catalyzed oxygenative esterification of aldehydes with aryl boronic acid

					
NHC	Base	Oxidant	Reaction Conditions (Solvent/Temperature/Time)	% Yield	Reference
<b>L9</b>	Cs <sub>2</sub> CO <sub>3</sub>	air	Toluene/RT/5 h	99%	64
<b>L10</b>	DBU	air	DMSO/80 °C/30 mins	99%	65
<b>L10</b>	Cs <sub>2</sub> CO <sub>3</sub>	O <sub>2</sub>	Toluene/50 °C/3 h	63%	66
<b>L9</b>	KO <sup>t</sup> Bu	air	Dioxane/90 °C/24 h Fe(OTf) <sub>2</sub>	97%	67
<b>L2</b>	CsF	air	Toluene/120 °C/24 h Pd(OAc) <sub>2</sub>	68%	68

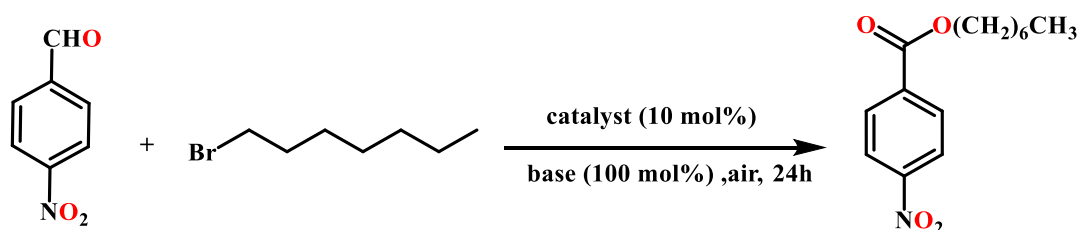
  

<b>L9:</b>	 <b>R = 2,6-Diisopropylphenyl</b>	<b>L10:</b>		<b>L2:</b>	
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Gois et al. have designed an effective methodology to synthesize benzoates and amides by the aerobic oxidative aromatic esterification of aldehydes with aryl boronic acid catalyzed by NHC-Fe complexes. Their method utilizes equimolar amounts of both the aldehyde and the boronic acids resulting the corresponding benzoates in yields amounting up to 97%. The reaction conditions applied are relatively mild in

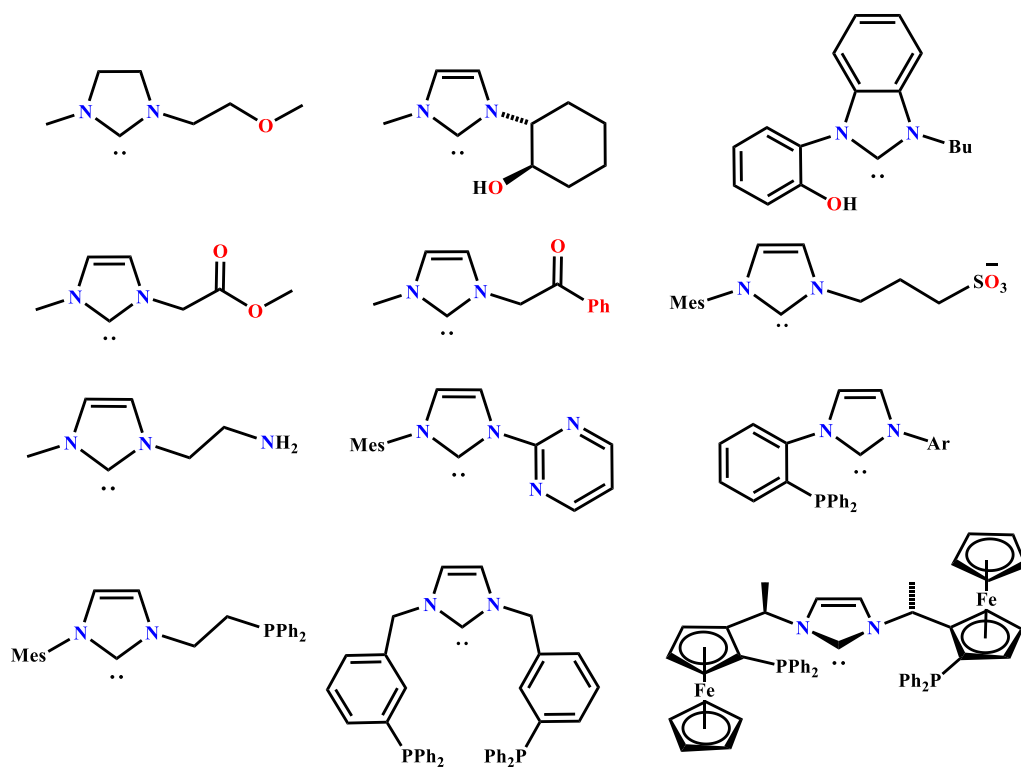
consideration to traditional processes. The reaction conditions were optimized for the iron sources ( $\text{Fe}(\text{OTf})_2$  is proved to be the best source], and temperature ( $90\text{ }^\circ\text{C}$  gave maximum yield). The presence of air as the oxidant is indispensable for the reaction. The scope of using various aldehydes as the substrate was also investigated. The reaction was exceptionally tolerant irrespective of the electronic characteristics of the aldehyde. Good to excellent results were obtained for the various boronic acids used. A probable mechanism for formation of the benzoate esters was also suggested. In the suggested mechanism, the in-situ formation of phenol species from boronic acid was the initial step. The NHC is presumed to participate in the formation of a catalytic active NHC-iron complex. It was followed by the oxidative esterification of the aldehyde to give the desired product [68].

Xin et al. in the year 2011 reported a direct oxidative esterification reaction of alkyl halides or alkyl 4-methylbenzenesulfonates with aldehydes organocatalyzed by NHCs (Scheme 1.6). The reaction progressed efficiently even under mild reaction conditions with complete inversion of stereochemistry and a wide assortment of esters were obtained in reasonably good yields. While the organocatalytic efficacy of a wide range of precatalysts are investigated, the N-mesityl substituted imidazolium salts showed the best activity and afforded the corresponding ester in good yield. It was observed that increasing the ratio of 1-bromoheptane (reactant) to 3.0 equivalent considerably enhanced the yield. Elevation of reaction temperature to  $50\text{ }^\circ\text{C}$ , increased the reaction yield to 75%. However, under nitrogen atmosphere the reaction resulted only trace amounts of the product. Realizing the importance of atmospheric oxygen in the progress of the reaction, the NHC catalyzed esterification reaction is performed in less than 1 atm oxygen pressure. As anticipated, in presence of molecular oxygen the reaction afforded 83% yield of the corresponding ester. While aromatic aldehydes bearing electron-withdrawing substituents showed good reactivity, aromatic aldehydes with electron-donating groups resulted inferior yields [69].



**Scheme 1.6.** Direct oxidative esterification reaction of alkyl halides with aldehydes

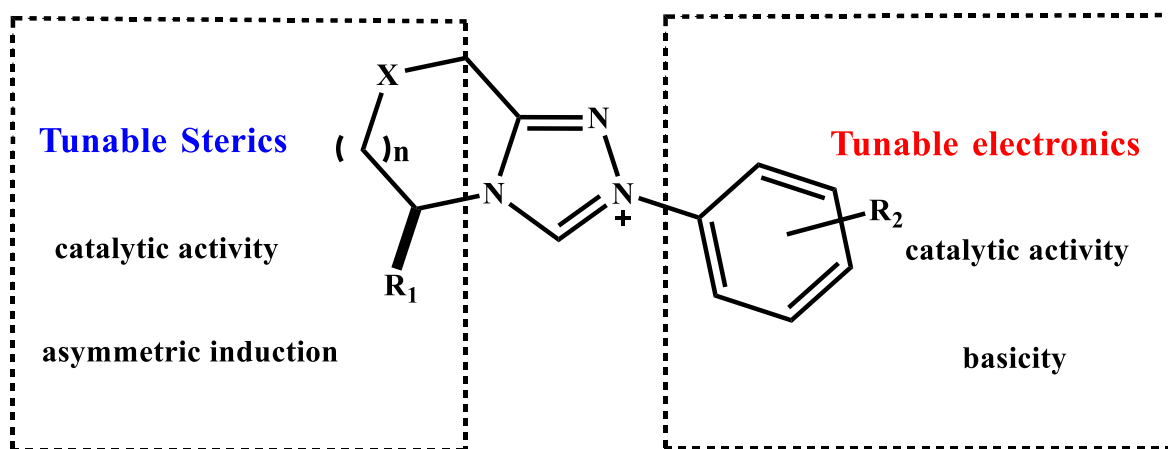
*1.3.3. Functionalized N-heterocyclic carbenes:* NHCs have found wide application in catalysis due to their strong  $\sigma$ -donation ability and introduction of any other functionality NHCs can potentially mitigate this advantage of NHCs over other conventional ligands. Nevertheless, anchoring an additional functionality on NHCs can greatly augment their catalytic behaviour and thus this approach has emerged as a versatile tool to design NHC based organocatalysts. Apart from that, functionalization of NHCs can facilitate anchoring of free carbenes to metal sites which are otherwise not prone to bind with NHCs. Conversely, by employing metal sites which bind strongly with NHCs but weakly with the additional functionality present, one can design hemilabile catalysts. Functionalization of NHCs by using suitable functional group is also a viable strategy to introduce chirality and thereby design NHC based asymmetric catalysts. Additional functionalities present on NHC can also be utilized to immobilize free NHCs or NHC based transition metal complexes on solid supports for designing heterogeneous NHC catalysts. Most examples of functionalized N-heterocyclic carbenes involve functional groups containing nitrogen or oxygen, as well as phosphanes. Thus, NHC ligands containing pendant amino, amido, ether, thioether, aryloxy, alkoxy and cyclopentadienyl functional groups have been designed and some of these examples are listed in Chart 1.2.



**Chart 1.2.** Examples of functionalized NHCs



Functionalization of NHC using other donor functionality imparts hemilability and this characteristic has been extensively explored in designing NHC metal complexes with improved catalytic efficacy. In this regard, N, O, S and P based donor functionalized NHCs are of particular interest due to their unique ability to coordinate with transition metals. By employing N/O/S/P donor functionalized NHCs, plethora of metal complexes are prepared and many of these complexes serve as excellent catalysts [70-74]. Functionalization of NHC using chiral substituents is an established strategy to impart enantioselectivity in NHC catalyzed transformations. Asymmetric benzoin condensation reaction catalyzed by employing thiazolium salts containing chiral substituents was initially reported by Sheehan and co-workers in 1966 [75]. Similarly, development of N-aryl-bicyclic triazoliums led the way to improved catalyst efficiency by easy tunability of steric and electronic characteristics (Figure 1.2) [76]. For example, Connon et al demonstrated that N-aryl-bicyclic triazolium salts containing alcohol directing group provide exceptional level of enantio-induction [77]. These studies reveal the importance of incorporating additional functional groups on NHC skeleton and thereby augment their catalytic efficacy.



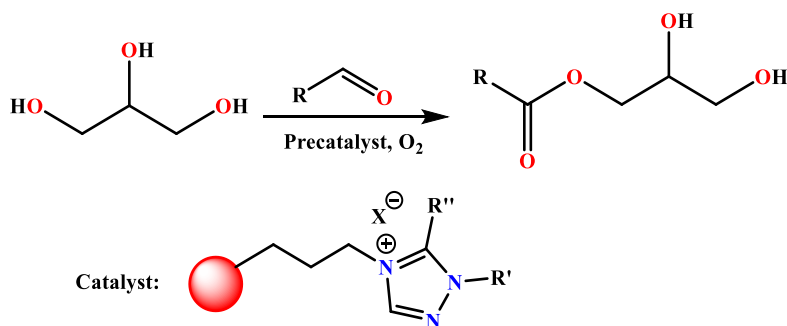
**Figure 1.2.** N-aryl-bicyclic functionalized triazolium salt

#### 1.4. Heterogeneous NHC organocatalysts

Homogeneous catalysts are preferred over heterogeneous catalysts because of their better efficiency and selectivity. However, separating homogeneous catalyst from the reaction mixture has remained a difficult task, preventing their recyclability. Furthermore, unlike heterogeneous catalysts, homogeneous catalysts typically perform reactions at lower temperatures, whereas a robust solid catalyst can perform reactions at higher temperature

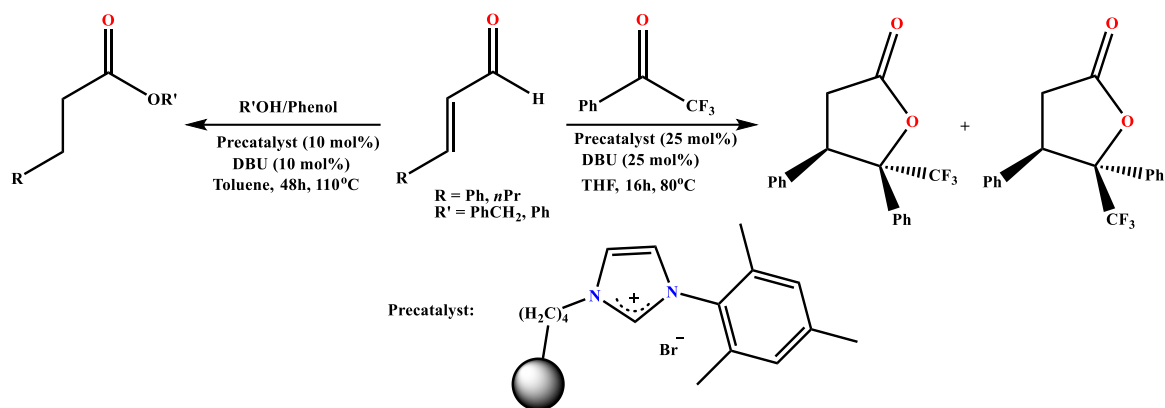
opening the door to a wider range of reactions [78-79]. Heterogeneous solid catalysts are gaining popularity due to their ease of post-reaction separation, recyclability, and thus waste reduction [80]. Furthermore, optimizing catalysts activity for maximum productivity has remained a major challenge for heterogeneous catalytic systems. Apart from that, the behaviour of organocatalysts immobilized over a solid support, i.e., heterogeneous organocatalysts is poorly understood in comparison to their homogeneous counterparts. This has restricted their development and application in both academia as well as in industry. While many NHC based on homogeneous organocatalysts are known, the above considerations facilitated the development of heterogeneous NHC organocatalysts for different important organic transformations. Majority of these heterogeneous NHC catalyst are designed by employing different polymer matrices, silicious materials and metal organic frameworks as solid supports. Apart from that, examples of a few self-supported NHCs are also reported in the literature.

Alessandro Massi and coworkers reported a set of supported azolium salt pre-catalysts and their application in the oxidative NHC catalyzed production of monoesters of glycerol and solketal via batch and continuous-flow approaches (Scheme 1.7) [81].



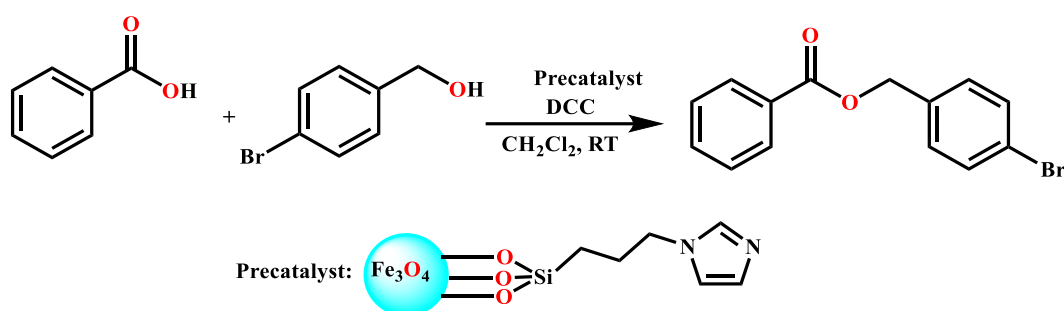
**Scheme 1.7.** Glycerol valorization by heterogeneous NHC-catalysis

Ana C. Albéniz and coworkers described polynorbornene supported imidazolium salts as heterogeneous NHC organocatalysts. The catalytic efficacy of the polynorbornene supported N-heterocyclic carbenes were explored in two model reactions: the synthesis of saturated esters from  $\alpha,\beta$ -unsaturated aldehydes and the conjugate umpolung reaction of  $\alpha,\beta$ -unsaturated aldehydes to produce  $\gamma$ -butyrolactones (Scheme 1.8). The supported catalyst showed high catalytic efficacy, fully recyclable from the reaction mixture and can be recovered and stored as an imidazolium salt for future use [82].



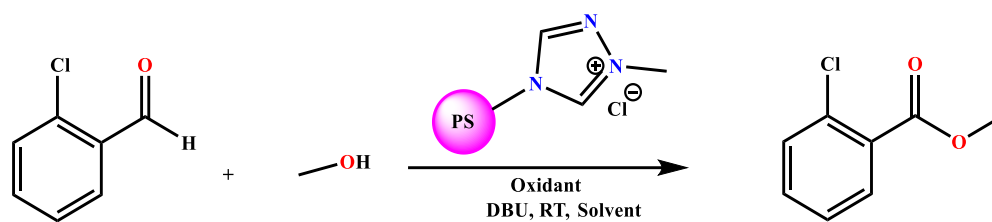
**Scheme 1.8.** Synthesis of saturated esters and  $\gamma$ -butyrolactones as a mixture of *cis* (like) and *trans* (unlike) diastereoisomers catalyzed by polymer supported imidazolium salt

Vasyl Kinzhyalo and coworkers reported an imidazole salt supported onto  $\text{Fe}_3\text{O}_4$ /Chloro-silane core-shell nanoparticles in 2017 (Scheme 1.9). Under mild reaction conditions, this was used as an efficient heterogeneous organocatalyst for the esterification of carboxylic acids with alcohols in the presence of *N,N'*-dicyclohexyl carbodiimide as a coupling reagent [83].



**Scheme 1.9.** Esterification reaction of benzoic acid and 4-bromobenzyl alcohol in presence of imidazole salt supported onto  $\text{Fe}_3\text{O}_4$ /Chloro-silane core-shell nanoparticles

In the year 2020, Carmine D'Agostino screened the efficiency of a polystyrene-supported *N*-heterocyclic carbene catalyzed oxidative coupling of 2-chlorobenzaldehyde with methanol in a variety of solvents (Scheme 1.10) [84]. Investigation of the strength of solvent-surface interactions in this NHC promoted oxidative coupling of aldehyde by employing  $T_1/T_2$  NMR relaxation measurements revealed a significant reduction in catalyst activity in solvents with high surface affinity. Thus, the importance of the adsorption properties of the solid matrix in design of suitable heterogeneous NHC organocatalysts is highlighted in this study.



**Scheme 1.10.** Oxidative coupling of 2-chlorobenzaldehyde with methanol by using polystyrene-supported NHC

### 1.5. Metal organic frameworks supported NHCs

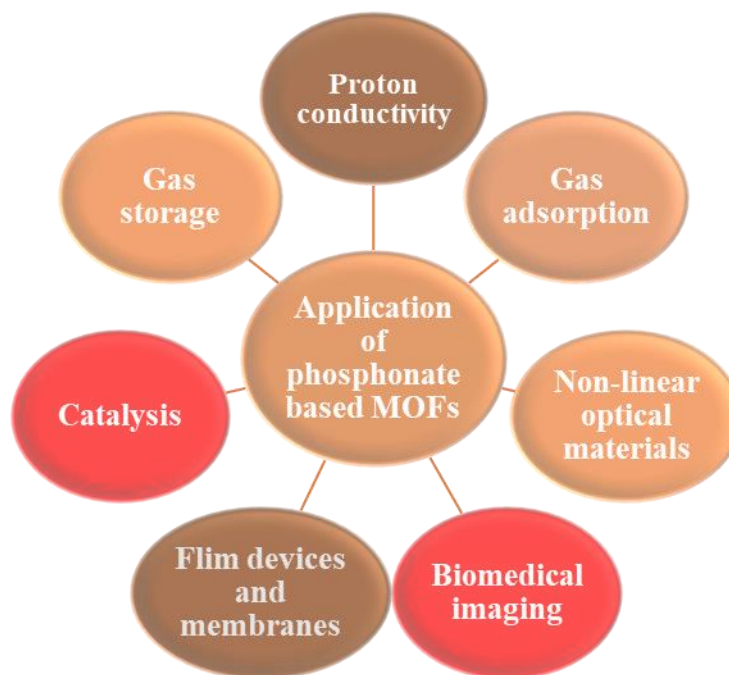
Metal organic frameworks are a class of porous and hybrid supramolecular solid material network. MOFs are composed of a substantial number of organic and inorganic linkers that are organized and bound to metal ions. MOFs have received a lot of attention because of their well-defined molecular building blocks that are able to assemble into periodic frameworks. These compounds have a larger surface area with the advantage of changing pore sizes, as well as a diverse and well modified structure. The research group of Omar M Yaghi began investigating MOF in the early 1990s. Yaghi coined the term MOF in the year 1995 [85]. MOF-5m a Zn<sub>4</sub>O(terephthalate)<sub>3</sub> polymer, was first reported in 1999 [86]. Because of its numerous advantages, MOF has the potential to replace the widely used material zeolites. The structure of zeolites is highly rigid, and organo-functionalization of zeolites to tune the acidity/basicity of the pores is a challenging task, whereas MOFs are composition of organic and inorganic components with the consistency of inorganic material and the versatility of organic materials. As a result, MOF are used as a support for various reaction. They are also used as a support for NHC or metal-NHC complexes [87]. The Yaghi group reported one such example in the year 2010, in which NHCs are embedded on MOF-5 framework. The advantage of using MOFs as support is that the electronic environment can be chemically controlled, and the catalytic sites are more exposed due to the crystalline and porous nature of MOFs [88]. Carboxylate-based MOFs are the most preferred choice of linker for MOF synthesis. Furthermore, carboxylate-based MOFs have a high surface area and a uniform pore size distribution, making them suitable for a wide range of catalytic application. The high crystallinity of the final polymeric frameworks greatly aids in structural characterization.

Although carboxylate-based MOFs have many advantages, there are several major drawbacks that have seriously limited their utility in catalysis. Due to the liability of the metal carboxylate bonds, carboxylate-based MOFs are usually hydrolytically unstable

which tends to hydrolyse under ambient conditions, most carboxylate -based MOFs are moisture sensitive [89-93]. Aside from hydrolytic instability, a lack of high thermal stability is another major concern that must be addressed before they can be used in industrial catalysis. Such example where MOF undergo hydrolytic cleavage was reported by Matzger and co-worker in the year 2019 where the drug loaded MOF undergoes hydrolytic cleavage to release the drug embedded in it [94].

### **1.6. Metal phosphonates: A suitable alternative to MOFs**

High valent metal organophosphonates are considered as a potential alternative to metal organic frameworks because of their layered structure and inherent chemical robustness. Due to the above two characteristics, organophosphonate based hybrid frameworks have received significant attention during the last few decades [95]. The presence of three donor oxygen atoms in the phosphonate group increases the possibility of various coordination modes and therefore the resulting metallic frameworks more intact and stable than carboxylate-based frameworks. Therefore, polyphosphonate based MOFs are comparatively denser and less porous than carboxylate-based MOFs. Moreover, each oxygen atom can bind up to three metal ions, implying that each phosphonate group can bind up to nine metal ions [96]. Thus, phosphonate-based MOFs are more stable in presence of air and moisture than carboxylate-based MOFs and are less sensitive to acidic or basic conditions. Thus, lack of porosity, lack of coordination unsaturation within the metal ions and inherent robustness, phosphonate-based frameworks are unlikely to find use in catalysis. In spite of these intriguing characteristics, only a few studies employing metal organophosphonate as catalyst support have been reported so far [97]. Particularly phosphonate-based frameworks with high valent metal ions e.g. Sn(IV) and Zr(IV) are highly porous, stable, robust, insoluble in most widely used solvents such as methanol, acetone, water etc. and are also stable in highly acidic conditions even in aqua regia [98-101]. Due to the robust character of high valent metal phosphonate-based frameworks they have found application in numerous areas such as catalysis [102-103], gas storage [104], proton conduction [105-108], gas adsorption [109-111] and non-linear optical materials (Figure 1.3). They have also gained significant interest in the field of biomedical imaging, film devices and membranes [112-114].

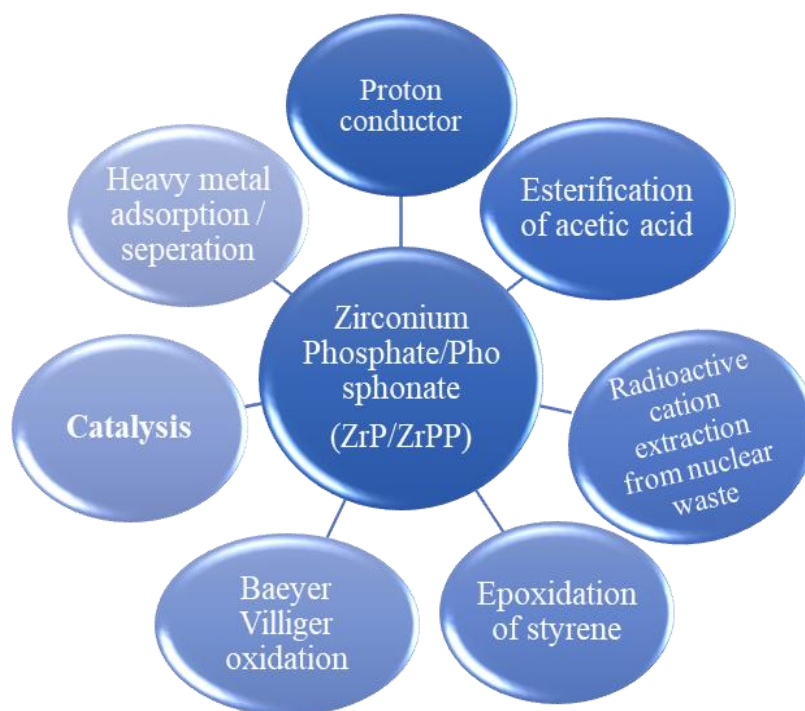


**Figure 1.3.** Application of phosphonate-based MOFs

#### 1.6.1. Layered zirconium(IV) phosphate/phosphonate (ZrP) Framework as support

In 1964, Abraham Clearfield first studied about zirconium(IV) phosphates/phosphonates, where the crystal structure of Zr(IV) phosphate was discussed [115]. Zirconium(IV) has been found to form a layered compound when combined with phosphonic acid. Based on the reaction conditions, two types of structures are possible with Zr and phosphonic acid:  $\alpha$ -ZrP and  $\gamma$ -ZrP with chemical formulas,  $\alpha$ -Zr(HPO<sub>4</sub>).2H<sub>2</sub>O and  $\gamma$ -ZrPO<sub>4</sub>(H<sub>2</sub>-PO<sub>4</sub>).2H<sub>2</sub>O respectively [116-117]. Zirconium(IV) has the unusual property of forming layered compounds with phosphonates. After, Abraham Clearfield discovered  $\alpha$ -ZrP and  $\gamma$ -ZrP, G. Alberti reported the synthesis of Zr(IV) phenyl phosphonate framework in 1978 with structure similar to  $\alpha$ -ZrP [118]. Following that, numerous reports of various substituted Zr(IV) phenyl phosphonate were published and their applications in photochemistry, catalysis and molecular and chiral recognition were investigated (Figure 1.4). Apart from that,  $\alpha$ -ZrP phosphonate framework has been widely used as a proton conductor. The addition of acidic groups to the phosphonate ligands, such as -SO<sub>3</sub>H and -COOH, results in the formation of a material with a higher proton conductivity than the parent  $\alpha$ -ZrP [119-120]. The Zr- phosphate/phosphonate can be used as heterogeneous catalysts as well as support for various catalytically active complexes or metal nanoparticles. The free dangling -OH groups pointed between the framework's interplanar layer give the

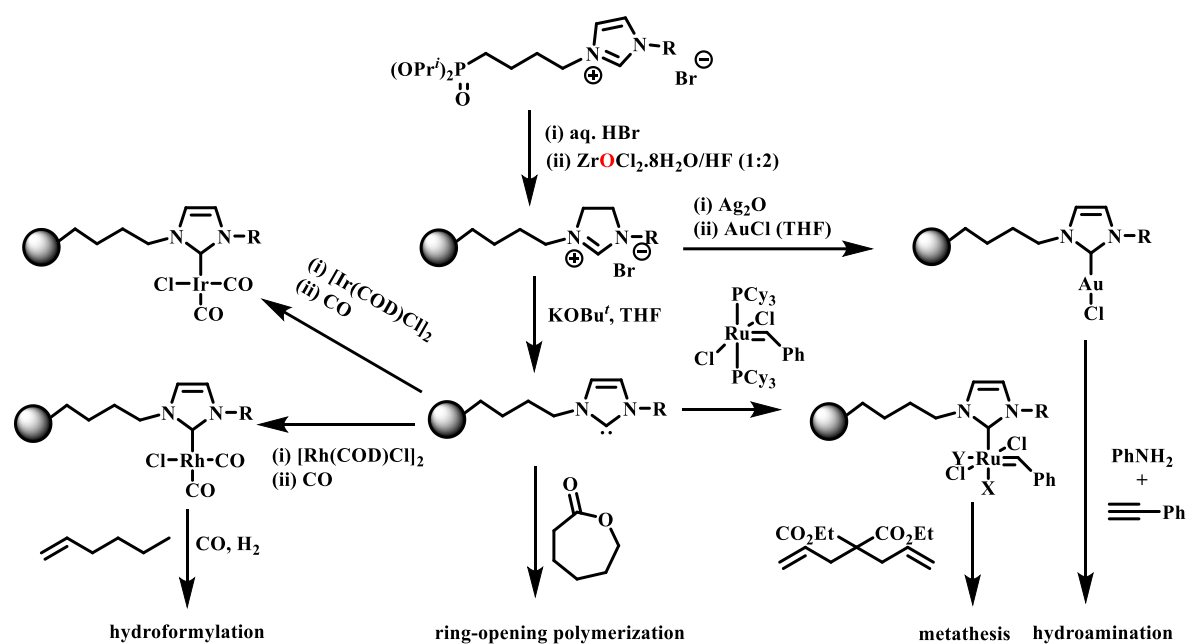
ZrP framework high proton conductivity. Furthermore, through systematic design, Zirconium(IV) Phosphate/Phosphonate frameworks can be employed in effective cation exchange and selective cation adsorbent material. In 2012, Qinghong Xu and co-worker reported the synthesis of a mesoporous Zr(IV)-phosphonate with  $ZrOCl_2$  using nitrilotris(methylene)-triphosphonic acid (ATMP) as a ligand. This high surface area material was used as an adsorbent for the efficient removal of heavy metal ions like  $Pd^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  [121]. Zirconium(IV) phosphonate-based material have found application in wide range of domains e.g. catalysis, adsorption, exchange material, proton conductivity and so on. Because of its chemical robustness as well as the layered structure, this class of material have emerged as potential candidate for many industrial applications. The salient features of the material include its (i) typical layered structure with mono and bis-phosphonates (ii) broad range of catalytic applications by pristine zirconium(IV) Phosphate/Phosphonate materials (iii) thermal and chemical stability (iv) ease of functionalization by employing suitable phosphonate ligand (v) stability in presence of radioactive material.



**Figure 1.4.** Application of Zr(IV)-phosphate/phosphonate framework

In 2009, Manfred Bochmann, Joseph A. Wright, and co-workers published a study in which a Zr(IV)-phosphonate framework was immobilized with imidazolium functionalized ligands (Scheme 1.11). It was then used in assembling various N-

heterocyclic carbene complexes, and the catalytic activities of these complexes were investigated for various reactions. The raw carbene formed from the imidazolium group participated in the ring opening polymerization reaction as a radical initiator, whereas the Ir(I) and Rh(I)-NHC complexes participated in the hydroformylation reaction. The NHC-Ag(I) catalyst was used for hydroamination reactions between aryl amine and phenyl acetylene with Ag, whereas with Ru, it formed heterogeneous 3<sup>rd</sup> generation Grubb's catalyst and was investigated for metathesis reaction. This provides a complete set of catalysts from a single parent support (Scheme 1.11) and the large surface area and layered structure resulted in higher activity of these systems [122].



**Scheme 1.11.** Synthesis of Zr(IV) phosphonate supported NHC and its application in preparation of Zr(IV) phosphonate supported NHC complexes

### 1.6.2. Heterogeneous catalyst in photochemical reaction

Photochemistry, which means chemical changes caused by light absorption, is the branch of chemistry that studies the chemical effects caused by electromagnetic waves in the visible range. Photochemistry is extremely important in nature because it is the foundation of photosynthesis, vision, and the formation of vitamin D with sunlight. As a result, it is not surprising that the Sun was worshipped as a God in the earliest human cultures. Similarly, photocatalysis is an old phenomenon, and its existence is evident from common observations such as the fading of painted walls after prolonged exposure



to sunlight. However, it was not until 1972, when Fujishima and Honda made a groundbreaking discovery of photo-electrocatalysis of water molecules using an n-type rutile TiO<sub>2</sub> anode against a platinum cathode, that photocatalysis came to the forefront of scientific attention [123]. This discovery sparked an explosion of activity in this field, and a plethora of photocatalytic applications have since been developed [115-152]. Indeed, several applications of photocatalysis can be found in everyday life.

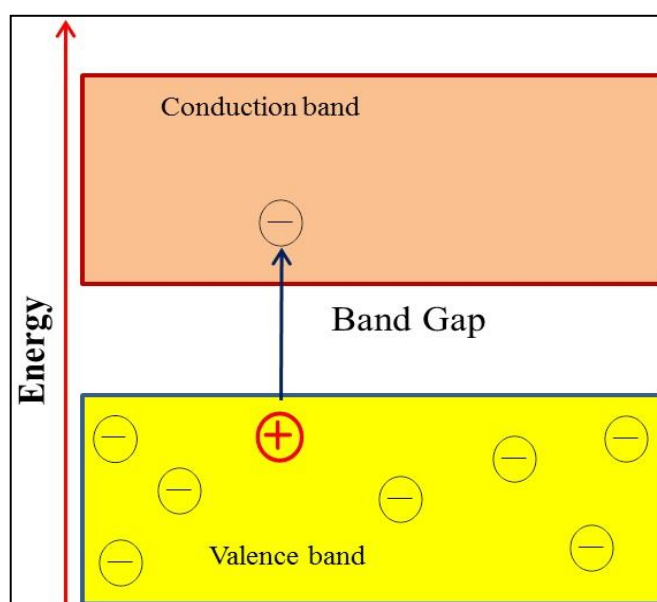
Photocatalysis can be classified into two broad types: photocatalytic synthesis and photocatalytic degradation. The classification is based on the fact that photocatalytic reactions can be directed toward either the formation of new substances or the decomposition of reacting material. Photocatalytic degradation includes photo-splitting of water, photo-disinfection, and photo-detoxification of inorganic materials, whereas photocatalytic synthesis includes photocatalytic CO<sub>2</sub> reduction, organic synthesis, and photocatalytic fixation. The chemical nature of the substrate and the reaction conditions influence photocatalytic reactions. In both cases, dioxygen is invariably required for oxidation [124]. Photocatalytic synthesis by reduction processes, on the other hand, can take place in the absence of oxygen. Several steps were involved in the mechanism for photocatalytic reactions, including hydrogen abstraction, hydroxylation, and bond scission, which resulted in functional group conversion.

#### *1.6.3. Semiconductor quantum dots as photocatalyst*

Photocatalysis on semiconductor surfaces has grown at an exponential rate in recent decades [123-160]. Semiconductors' utility can be attributed to their band structure and associated ability to absorb light of a specific frequency. Semiconductors have a band structure with a characteristic width band gap separating the conduction band from the valence band (Figure 1.5). When the incident light's energy exceeds the energy of a band gap, electrons and holes are generated in the conduction and valence bands, respectively. The band-gap energy of semiconductors decreases as temperature rises. Each semiconductor has a unique energy band structure. The wide range of electrical properties observed in various materials is due to variation in the band gap structure.

#### *1.6.4. Semiconductor quantum dots supported on 2D materials as photocatalyst*

Heterogeneous photocatalysis using semiconductors and solar energy has been regarded as one of the most promising processes for addressing both the global energy supply and environmental pollution crises. To make better use of solar energy, it is necessary to



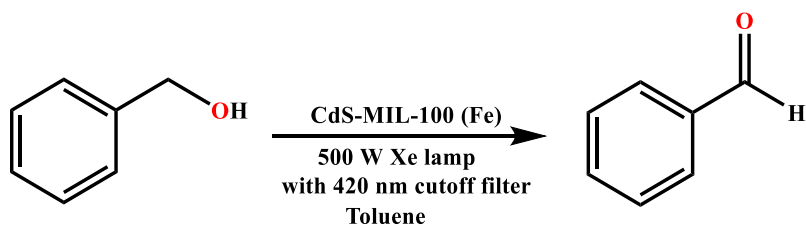
**Figure 1.5.** Semiconductor band gap structure

create visible light-driven photocatalysts by modifying wide band gap semiconductors. The major challenges are photo-corrosion and photo-stability of semiconductor quantum dots. To address this issue, novel CdS photocatalysts with controlled nanostructures and morphologies, such as 0D, 1D, 2D, and 3D hierarchical structures, could increase their surface to volume ratio and shorten charge carrier lateral diffusion pathways to the surface. Because of their superior electron conductivity, unique 2D structure with a large surface to volume ratio, structural flexibility, biocompatibility, and chemical stability, graphene oxide (GO) and its derivatives have been used in a variety of applications in recent years. Graphene, as a member of the carbon family, provides an exciting opportunity to build highly efficient photocatalysts by coupling with other semiconductors. Because of their superior photocatalytic activity and photostability under visible-light irradiation, CdS/grapheme nanocomposites have received a great deal of attention as an important type of photocatalyst in chemical and material science. The induced charges could be separated using graphene as a conductive channel, good acceptors, and reservoir of photo-generated electrons. Because of its electron conductivity, it can also improve interfacial charge transfer and increase the lifetime of photo-generated  $e^-h^+$  pairs. As a result, the photoactivity of semiconductor graphene nanocomposites is increased. Liu and colleagues [129] achieved one-step synthesis of graphene-CdS quantum dot nanocomposite in 2010. They studied fluorescence spectroscopy in real time. A picosecond rate ultrafast transfer of the photoexcited electron from CdS to graphene was discovered, indicating that graphene as an electron

acceptor and transporter could reduce the recombination rate of photoexcited electrons and holes in CdS photocatalysts. Since then, CdS/graphene nanocomposites have received a great deal of attention in the field of photochemistry. CdS/graphene nanocomposites have a wide range of applications in the field of light-driven photocatalytic reactions, including H<sub>2</sub> production from water [130-132], hydrocarbon production from CO<sub>2</sub> reduction [133], environmental remediation [134-137], organic synthesis [138-140] etc. As a good supporter, graphene effectively suppresses CdS cluster aggregation and overgrowth, increases photo-activity and surface area, and also the number of surface-active sites of CdS nanoparticles, reducing bulk recombination of electron-hole pairs. Although many CdS/graphene nanocomposite have been well-designed, their ability to meet the demands of industrial applications is inadequate. To some extent, graphene improves the photo-stability of CdS material, but the long-term durability and efficiency of CdS/graphene are unsatisfactory. The amount of graphene in the CdS/graphene composite should be carefully controlled at a suitable level because too much graphene can reduce light absorption and shield the active sites on the CdS surface. Also, the photo-catalytic efficiency of CdS/graphene nanocomposite is too low to meet the practical demand.

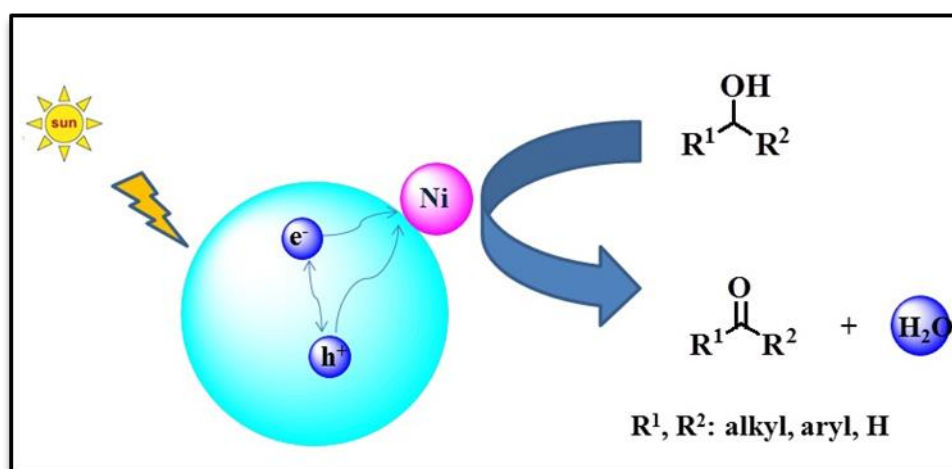
Another cocatalyst which has gain importance in photochemistry is nanosized layered-structured MoS<sub>2</sub>/graphene nanosheet loaded with CdS nano particles with 3D hierarchical configuration [141]. It provides an abundance of reactive sites for hydrogen evolution while also increasing charge transport and decreasing the recombination probability of photo-excited charge carriers. Graphene, as a good two-dimensional layered conductor, could significantly match with layered MoS<sub>2</sub> and improve its conductivity, facilitating first charge transfer. Because of the rapid recombination of photogenerated electrons and holes, pure CdS has a very low photocurrent density. However, when MoS<sub>2</sub> or graphene cocatalysts are added, photocurrent densities increase, indicating that electron-hole pair recombination is delayed. A semiconductor with small particle size and high crystallinity is thought to have good photocatalytic activity and stability. MoS<sub>2</sub>/G-CdS composite has a wide range of applications as a promising photocatalyst with high efficiency and low cost for the photocatalytic H<sub>2</sub> evolution reaction. MoS<sub>2</sub>/G-CdS composite has a wide range of applications as a promising photocatalyst with high efficiency and low cost for photocatalytic H<sub>2</sub> evolution reactions.

A solvothermal approach to synthesized CdS-MIL-100 (Fe) nanocomposites was reported by Junfa Zhu and his group in 2015. The prepared MOF function as an excellent supporting matrix for the evenly distributed CdS nanoparticles. Under visible-light irradiation, the resulting CdS-MIL-100(Fe) nanocomposites exhibit excellent photostability and enhanced photocatalytic activity in the selective oxidation of benzyl alcohol to benzaldehyde (Scheme 1.12) [155].



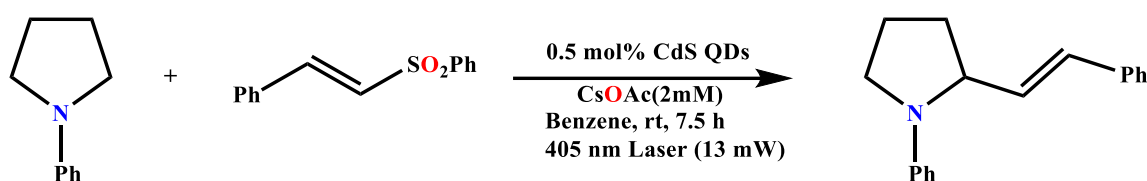
**Scheme 1.12.** Photocatalytic oxidation of benzyl alcohol to benzaldehyde using CdS nanoparticles.

Xu et al. in the year 2016 has reported a Ni modified CdS quantum dot. They have reported a heterogeneous photocatalyst could efficiently split alcohols into hydrogen and corresponding aldehydes or ketones in a stoichiometric manner under visible light irradiation. They reported a photocatalytic oxidation of alcohols using Ni-modified CdS nanoparticles as photocatalysts under visible light irradiation (Scheme 1.13). Both aliphatic and aromatic alcohols were converted into corresponding carbonyl compounds with a high selectivity and along with the evolution of hydrogen under mild conditions [156].



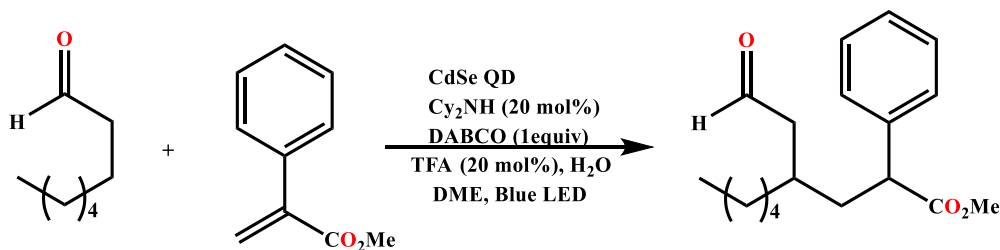
**Scheme 1.13.** Visible light-driven oxidation of alcohol over a Ni-modified CdS photocatalyst

Weiss et al. reported colloidal CdS quantum dot in 2017. They demonstrated photoredox catalysis of a C-C coupling reaction between 1-phenyl pyrrolidine (PhPyr) and phenyl trans-styryl sulfone (PhSO<sub>2</sub>) using visible light-absorbing colloidal CdS quantum dots (QDs), without the use of a sacrificial oxidant or reductant, and without the use of a co-catalyst. The rate-limiting step in this reaction is hole transfer from QDs to 1-phenyl pyrrolidine (Scheme 1.14). They created QDs with easily tunable surface chemistry, allowing them to control reaction kinetics without covalent synthetic modification of the catalyst and without jeopardizing the catalyst's absorption and electrochemical properties [128].



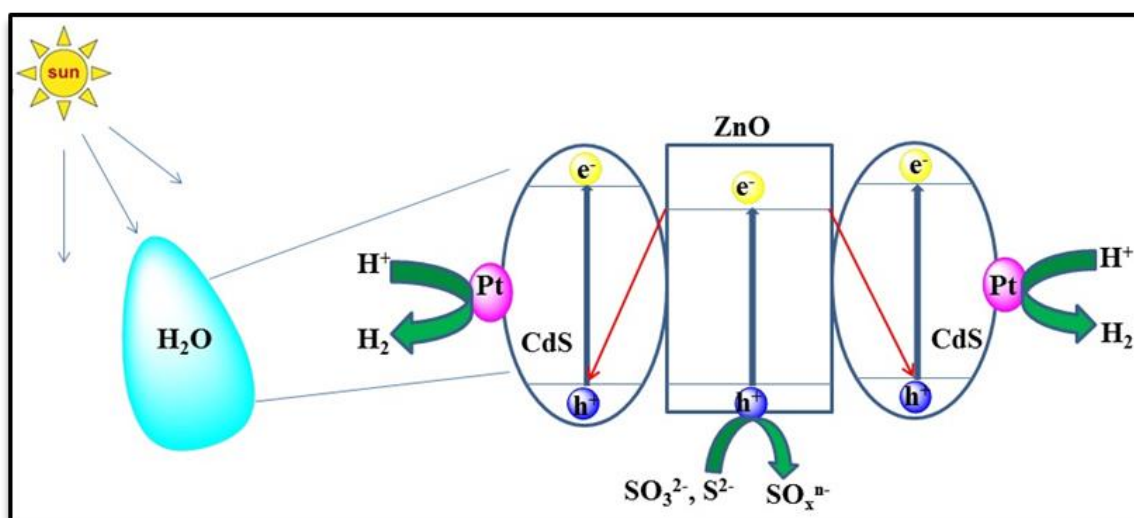
**Scheme 1.14.** Coupling reaction of 1-phenylpyrrolidine, and phenyl trans-styryl sulfone

In the year 2017 Weix et al. reported the synthesis of colloidal nanocrystal quantum dots (QDs). They used a single-sized CdSe quantum dot to perform five different photoredox reactions:  $\alpha$ -alkylation,  $\alpha$ -amino-alkylation, dehalogenation, amine arylation, and decarboxylative radical formation (Scheme 1.15). They discovered that CdSe QDs are versatile catalysts for the formation of C-C bonds, even at very low loadings. Their findings show that a single size of easily made CdSe QDs can be an advantageous replacement for two of the most used photoredox catalyst classes, Ru(bpy)<sub>3</sub>X<sub>2</sub> and Ir(ppy)<sub>2</sub>(dtbbpy)X [157].



**Scheme 1.15.**  $\beta$ -alkylation of octanal with CdSe QD photocatalysts

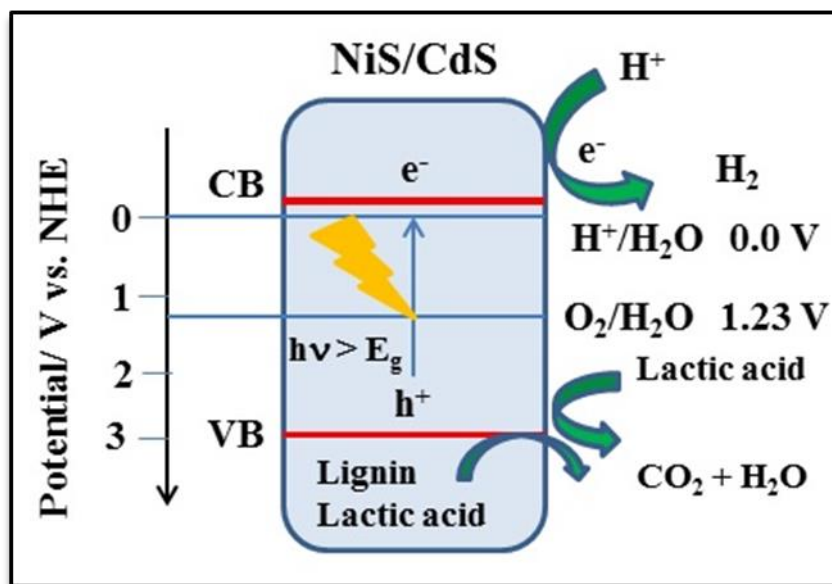
Niu et al. published the first report on the synthesis of zero-dimensional CdS quantum dots and two-dimensional ZnO nanosheets in 2017. The 2D ZnO nanosheets were assembled into ZnO microflowers using an ultrasonic-assisted hydrothermal procedure (100 °C, 12 h) in the presence of a 0.06 M NaOH solution, and CdS QDs were deposited on both sides of each ZnO nanosheet in situ using the successive ionic-layer absorption and reaction method. They discovered that ultrasonic treatment was important in the formation of ZnO nanosheets, whereas NaOH was responsible for the formation of a flower-like structure (Scheme 1.16). The obtained CdS/ZnO 0D/2D heterostructures exhibited remarkably enhanced photocatalytic activity for hydrogen evolution from water splitting in comparison with other CdS/ZnO heterostructures with different dimensional combinations such as 2D/2D, 0D/three-dimensional (3D), and 3D/0D [158].



**Scheme 1.16.** Proposed mechanism for the photocatalytic hydrogen evolution over the CdS/ZnO heterostructures

In 2018, Fang et al. reported the synthesis of uniform one dimensional NiS/CdS nanocomposites using CdS nanowires and NiS nanoparticles via a two-pot solvothermal synthetic procedure. The synergistic interaction between CdS and NiS which can be attributed to proximity, efficiently enhance the charge carrier separation with (Scheme 1.17). The photocatalytic H<sub>2</sub> evolution activity of NiS/CdS nanocomposites in presence of lignin and lactic acid as hole scavenger was significantly higher comparison to pristine CdS [159]. Ultrafast dynamics studies based on femtosecond transient absorption technique reveal that NiS improve the average charge carrier

lifetime of CdS nanowires by 97 times and this eventually leads to more efficient charge separation and transfer.



**Scheme 1.17.** Scheme for the photocatalytic hydrogen production over NiS/CdS nanocomposites under visible light

### 1.7. Objectives of the present work

The preceding discussion on NHCs and Zr(IV) phosphate/phosphonate frameworks respectively established their importance as homogeneous catalyst and heterogeneous support for catalytically active species. While the relevance of NHCs in organocatalysis is well established, the decisive role of electronic nature of the substituents present on the NHCs in their organocatalytic activity is well recognized. The present study primarily focused on designing NHCs containing additional functional groups and thereby augment their organocatalytic efficacy. For this purpose, phosphonate ester functionalized NHCs are preferred mainly due the ability of phosphonate oxygen atoms to act as strong sigma donor and thereby influence the organocatalytic behaviour of the NHCs. Moreover, the phosphonate group can be further employed to anchor the NHCs on solid surfaces and thereby design heterogeneous NHC based catalysts. The high thermal and chemical stability of zirconium phosphonate/phosphate frameworks impart tremendous potential to act as a support for catalytically active and functional materials in a variety of applications. Furthermore, given the versatile properties of MOFs in bridging the appealing qualities of both homogeneous and heterogeneous catalysis, developing robust zirconium phosphonate/phosphate based heterogeneous catalysts have

been prioritized throughout the course of this work. Thus, the efficacy of zirconium phosphate based solid support in enhancing the recyclability as well as efficiency of semiconductor based photocatalyst is explored during the course of this work,

In a nutshell, the objectives of the thesis are:

1. Design phosphonate ester functionalized imidazolium salts and investigate their applications in NHC based organocatalysis.
2. Employ the phosphonate ester functionalized imidazolium salts to fabricate zirconium(IV) organophosphonate framework containing covalently anchored imidazolium functionality and investigate their applications in NHC based organocatalysis.
3. Employ  $\alpha$ -zirconium(IV) phosphate as a solid support to immobilize CdS semiconductor quantum dots and investigate the photocatalytic activity of the resulting composite.

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