Chapter 1

A Brief Overview: Imidazolium- and Pyridinium-based Metal Catalysts and Chemosensors

1.1 Imidazolium-based metal catalyst

Catalysis is one of the important pillars of green chemistry, and there has been an ever-increasing demand for environmentally friendly catalytic processes. Catalysis offers various green chemistry benefits including lower energy requirements, catalytic versus stoichiometric amounts of materials, increased selectivity, elimination or reduction of waste, and prevention of toxic or hazardous reagents and solvents [1-3]. Organometallic complexes based on transition-metal are powerful catalysts for various organic transformations [4-5]. When suitable ligands are associated with these metal centres, they can offer excellent chemoselectivity, regioselectivity, or stereoselectivity under mild conditions [6]. Despite the attractive properties such as activity and selectivity, these homogeneous catalysts are associated with limitations of separating the products from the catalyst and the catalyst recyclability [7-9]. The use of recoverable and recyclable catalysts over expensive homogeneous catalysts is an important task due to environmental concerns and economic demands. There has been considerable interest in the development of catalytic systems that can be reused efficiently whilst keeping the inherent activity of the catalytic centre [10-12].

Supporting a homogeneous catalyst on a material is a straightforward approach for developing cost-effective, and environmentally benign catalytic systems to facilitate recovery and reusability of the catalyst [13-14]. The most classical approach is to use insoluble support such as silica gel or a cross-linked polymer leading to so-called heterogeneized catalysts. These supported catalysts are always insoluble before, during, and after a reaction [15-16]. However, despite many exciting results in terms of catalyst recovery and recycling, solid-phase supported catalysts are often characterized by reduced activity and selectivity compared to their homogeneous counterparts [17]. An alternative approach is to insert organic moieties into the catalyst structure whose solubility differs from the reaction substrates and products [18]. The catalytic reaction can thus be either run in liquid-liquid biphasic conditions or, in pure aqueous medium or, in a homogeneous solvent suitable for both supported catalyst and the reaction substrates. The recovery of the catalyst then occurs in a later stage, the extraction process depends on the difference in solubility of the catalyst, reagents, and products of the reaction [19-20]. Numerous types of soluble supports are used for this purpose, [21] such as soluble polyethylene glycol polymers [22-26], perfluorous [27-29], and ionic tags [30-32].

Among them, attaching ionic tags in catalyst structure has received special attention in terms of activity, stability, and reusability of catalyst. Water or ionic liquids can be used as an anchoring medium leading to effective sustainability [33]. Due to low molecular weight, supported catalysts provide a higher catalytic activity per gram as compared to polymer-based catalysts. Moreover, the solubility of the catalyst can be finely tuned by the choice of a proper counter ion [34-35].

The ionic catalysts most often contain imidazolium as a cationic tag [36-38]. The common way for the introduction of such moieties is a nucleophilic substitution of a halogen derivative with imidazole resulting in the quaternization of the imidazole nitrogen. The subsequent metathesis reactions with either organic or inorganic salts yield various imidazolium-based catalysts bearing different types of anions. The commonly employed counter anions are chloride, nitrate, bromide, sulfonate, acetate, hexafluorophosphate, tetrafluoroborate, and trifluoromethane, etc. The catalysts with imidazolium cations and organic/inorganic anions possess excellent chemical and physical properties (**Figure 1.1**) [39-40].

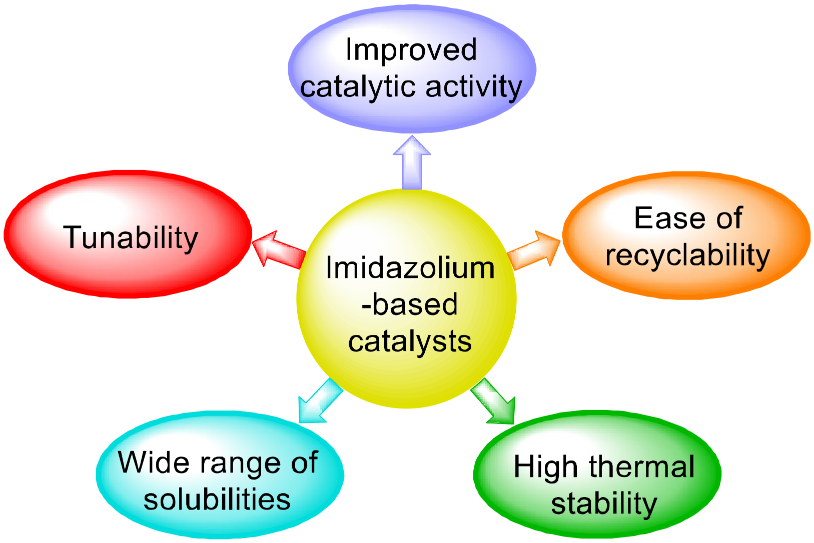


Figure 1.1 Properties of imidazolium-based catalysts

The imidazolium-based catalysts have shown great potential in different organic reactions such as olefin metathesis [41], hydrogenation [42], hydroformylation [43], cross-coupling [44], epoxidation of chalcone [45], ester synthesis [46], etc. These imidazolium-based catalysts can be characterized by using analytical techniques such as IR, NMR spectroscopy, mass spectrometry, and X-ray crystallography. The reaction progress can be easily monitered by TLC (thin layer chromatography) and the purification of the product can be achieved by simple washing with an appropriate solvent [47]. The recycling and reusability of these catalysts make organic synthesis more efficient, economic and environmentally benign. Selected examples of imidazolium-based catalysts are given in **Figure 1.2** [48-51].

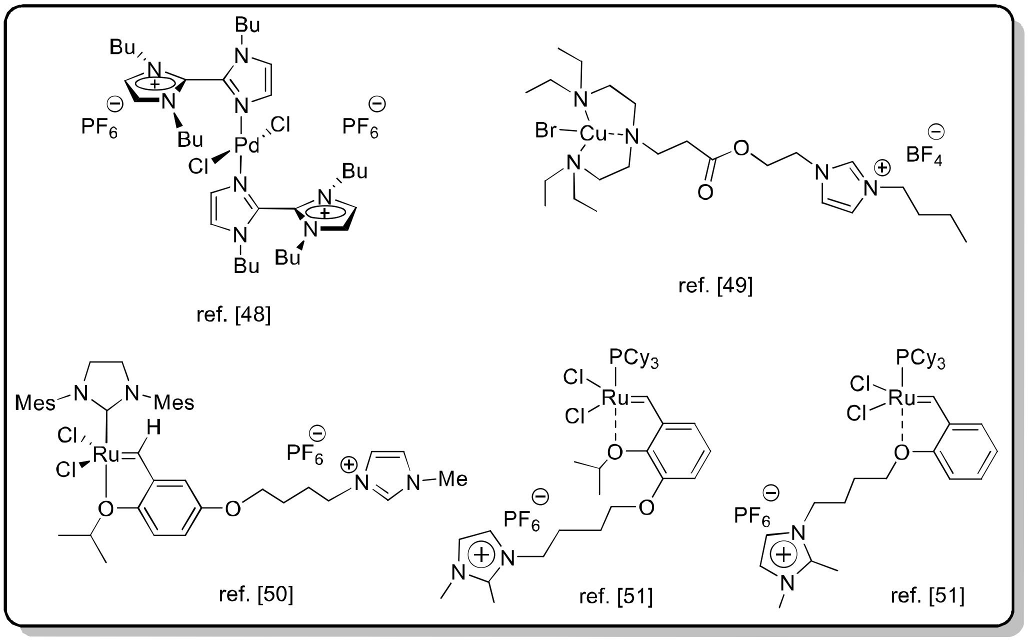
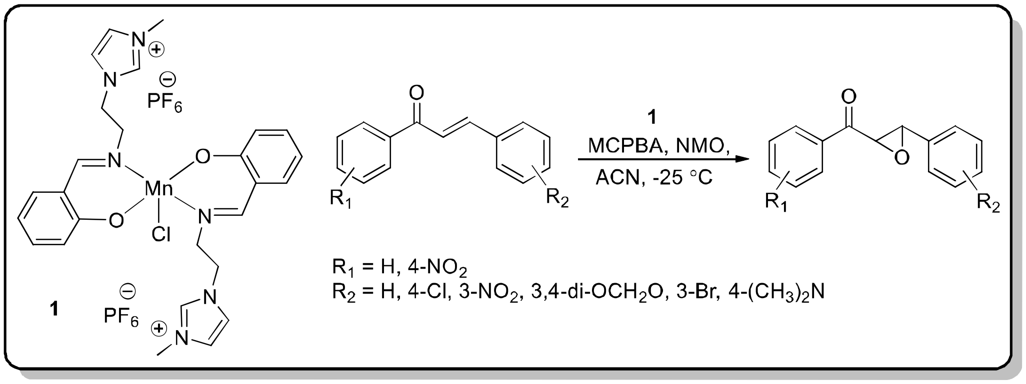


Figure 1.2 Selected examples of imidazolium-based catalysts

In the forthcoming part, literature reports on different imidazolium-based Schiff base and N-heterocyclic carbene (NHC) catalysts used in different organic transformations are discussed in detail.

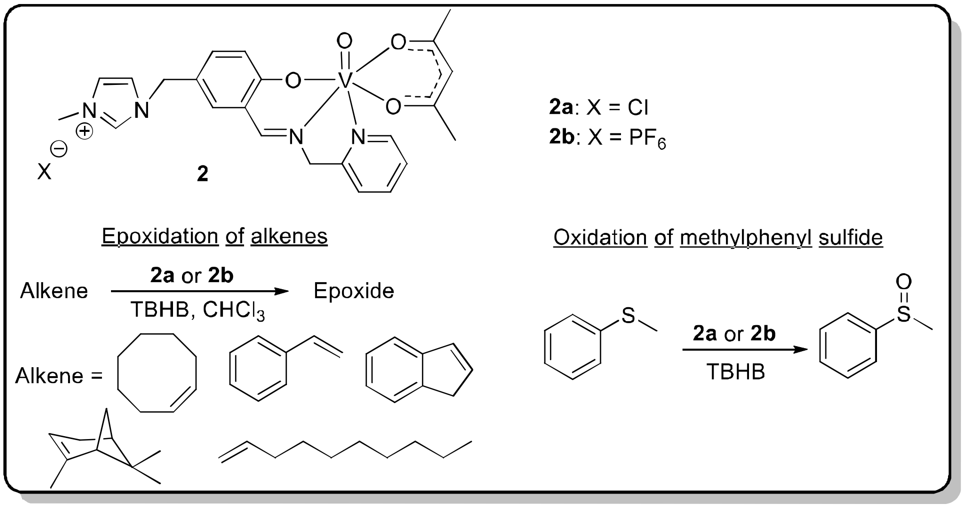
1.1.1 Imidazolium-based Schiff base metal catalyst

A German chemist, Hugo Schiff, in 1864 presented a new class of organic compounds termed as Schiff bases. They can be easily synthesized by the condensation of a carbonyl compound with a primary amine [52]. Schiff base as ligands in metal complexes can stabilize metals in various oxidation states and control the activities of metals in various organic transformations like polymerization [53], oxidation [54], epoxidation [55], transfer hydrogenation of ketones [56], hydrosilylation of ketones [57], Michael addition [58], Henry reaction [59], etc. Typically used traditional homogeneous Schiff base metal catalysts work well for many organic reactions but suffer from the problem of recyclability, product isolation, and purification [60-61]. To overcome these problems, the use of imidazolium-based Schiff base metal catalysts has emerged as alternatives to conventional catalysts. These catalysts not only exhibit good catalytic activity but also show efficient recycling after the completion of the reaction, addressing environmental concerns and economic demands. Moreover, imidazolium-based metal catalysts retain their properties during the extensive mechanical degradation which is generally experienced by solid-supported catalysts at high stirring rates. Peng *et al.* reported an imidazolium-based Schiff base Mn(III) complex **1** as an efficient and recyclable catalyst for the epoxidation of chalcones with MCPBA/NMO in acetonitrile (**Scheme 1.1**). This reaction failed in neat [bmim][PF_6] ionic liquid due to the increased viscosity of ionic liquids at low temperature. Also, in the absence of NMO, poor results were obtained due to the formation of unidentified by-products. The reaction was more facile in the presence of electron-donating substituents, whereas phenyl rings with two electron-withdrawing groups provided good yields when the reaction time was extended to 2.5 hours. Catalyst **1** was reused even after 5 runs without any significant loss of activity [62].



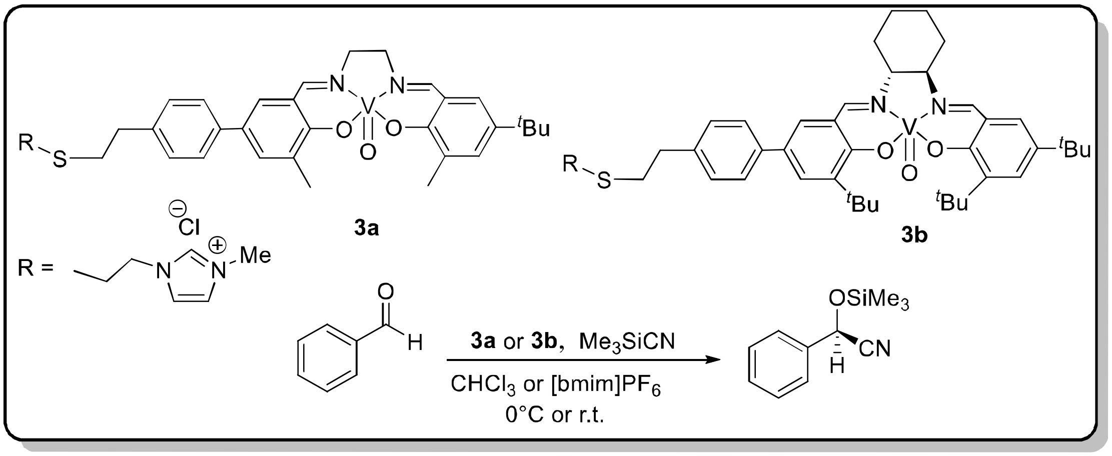
Scheme 1.1 Mn(III) complex (**1**) for epoxidation of chalcones

Talouki *et al.* also reported six coordinated vanadium(IV) Schiff base complexes **2a-b** and used them as a catalyst in the epoxidation of cyclooctene and oxidation of methylphenyl sulfide (**Scheme 1.2**). It was found that counter anion variation greatly influenced the catalytic activity and the activity of **2a** was higher as compared to **2b** for both the reactions [63].



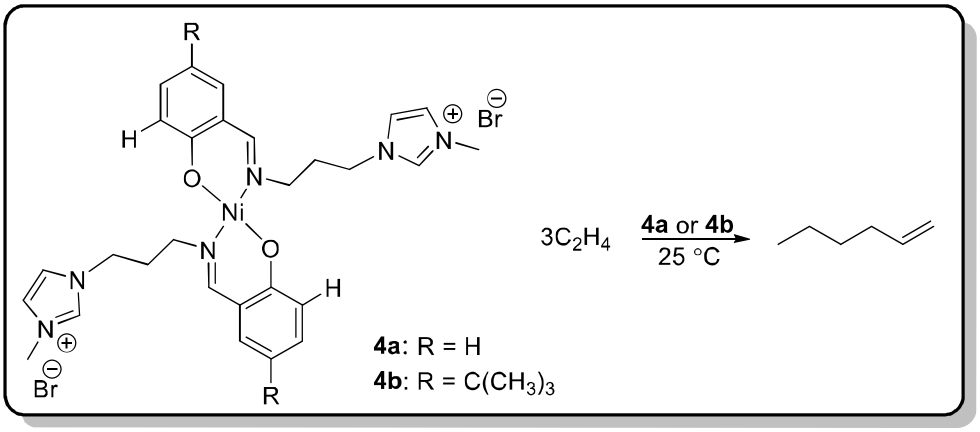
Scheme 1.2 Vanadium(IV) complexes (**2a-b**) for epoxidation and oxidation reactions

Baleizaõ *et al.* proposed imidazolium-based vanadyl salen complexes **3a-b** for the cyanosilylation of benzaldehyde (**Scheme 1.3**). With complex **3a**, high conversion and selectivity of cyanohydrin were obtained in [bmim]PF_6 solvent at room temperature with the recyclability up to six cycles. Moderate enantiomeric excesses were obtained using the complex **3b** [64].



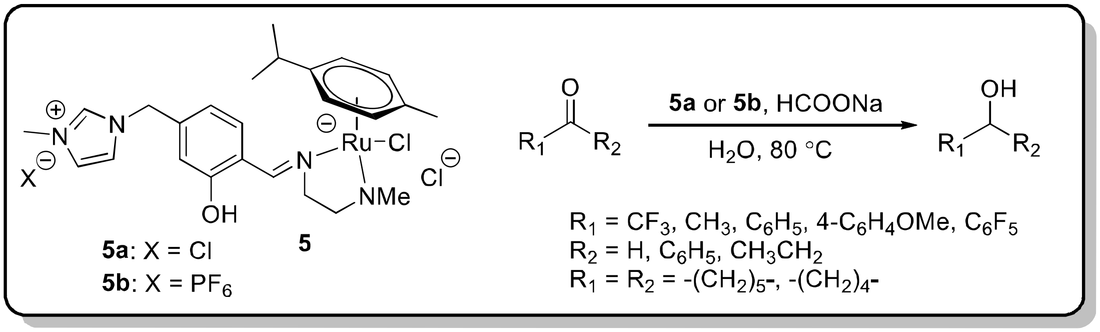
Scheme 1.3 Vanadyl salen complexes (**3a-b**) for cyanosilylation

Gao *et al.* synthesized two imidazolium-based bis-(salicylaldimine) Ni(II) complexes **4a-b** and used them as a catalyst for the ethylene oligomerization reactions in biphasic solvent systems consisting of chloroaluminate ionic liquid and toluene or *n*-heptane (**Scheme 1.4**). The obtained oligomers mainly contained C4, C6, and C8 units that are linear *α* or branched or internal olefins. The composition analysis suggested that active nickel species catalyzed olefin oligomerization and isomerization concurrently. The olefinic product was easily separated by simple decantation and catalysts were reused up to three successive catalytic cycles [65].



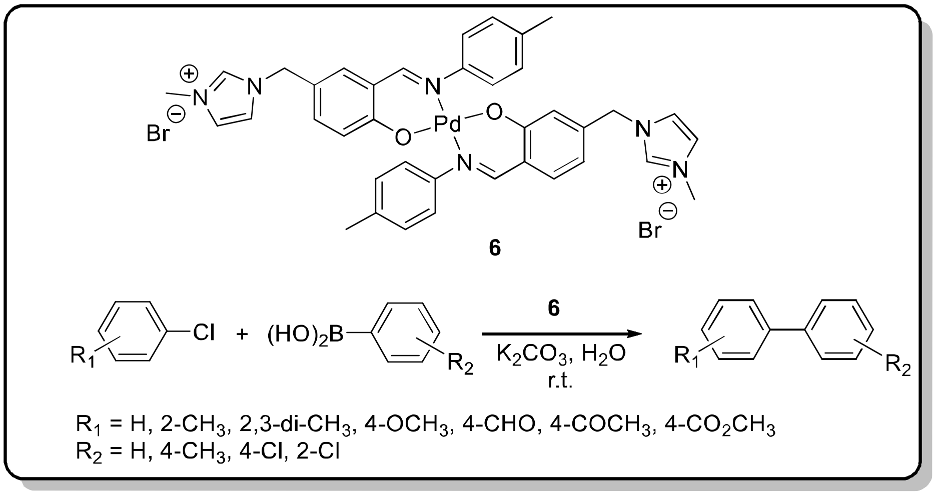
Scheme 1.4 Ni(II) complexes (**4a-b**) for ethylene oligomerization

Grivani and coworkers documented the synthesis of imidazolium-based Schiff base mononuclear Ru(II) complexes **5a-b**, that showed high catalytic activity in the transfer hydrogenation of 2,2,2-trifluoroacetophenone using HCOONa as the hydrogen source under aqueous conditions (**Scheme 1.5**). In aqueous medium, these complexes exhibited excellent catalytic activity as compared to non-imidazolium-based catalyst with similar structures [66].



Scheme 1.5 Half-sandwich ruthenium(II) complexes (**5a-b**) for transfer hydrogenation of carbonyl compounds

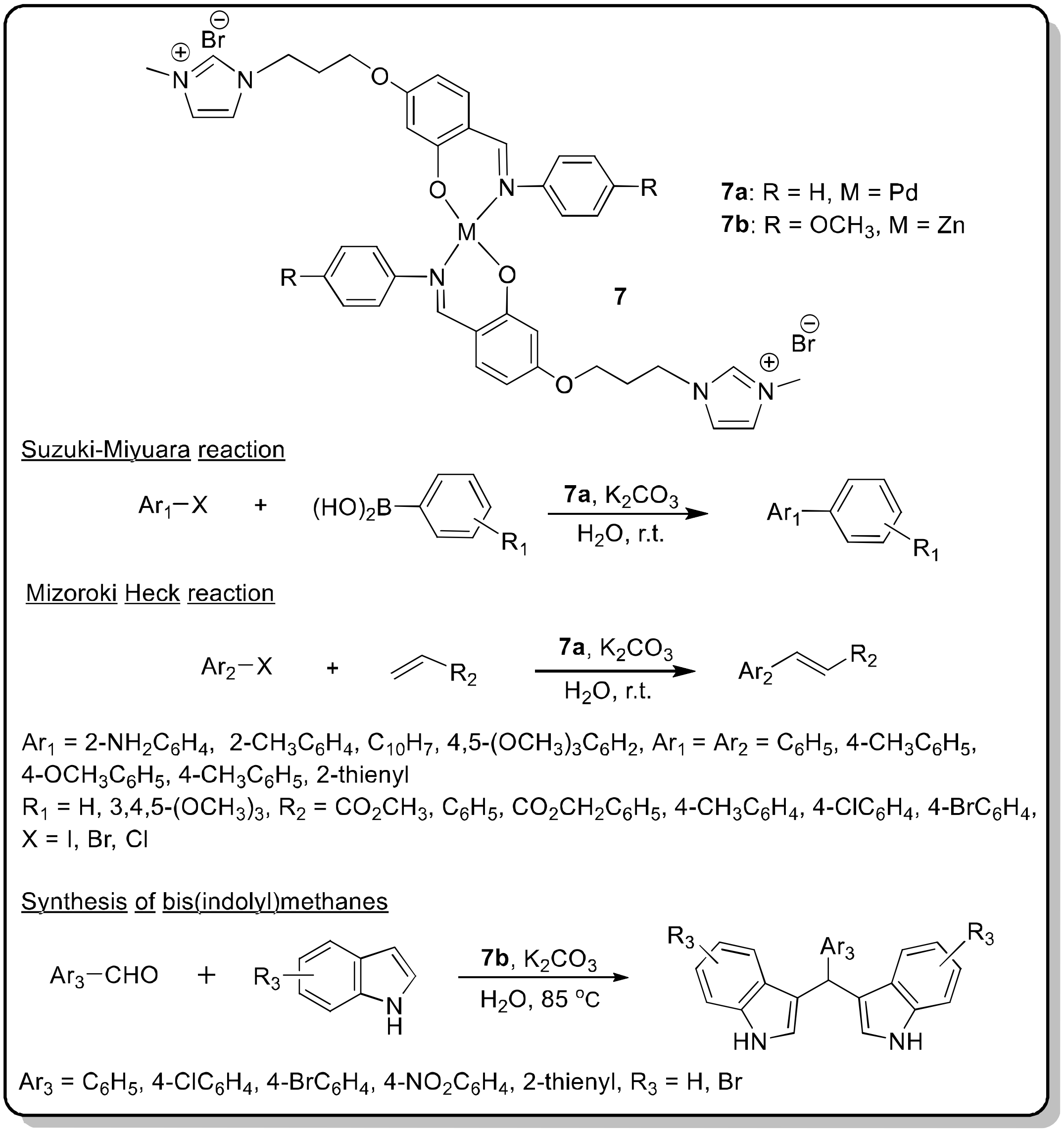
Zong *et al.* reported imidazolium-based Pd(II) complex **6** as a catalyst for the Suzuki-Miyaura reaction in aqueous medium (**Scheme 1.6**). Complex **6** efficiently catalyzed the reaction of aryl iodides and bromides with differently substituted boronic acids. However, *ortho*-substituted aryl bromides and arylboronic acids provided lower yields even if the reaction time was extended, which indicated that steric hindrance influences the coupling reaction. Complex **6** was recycled six times without much loss in the activity [67].



Scheme 1.6 Pd(II) complex (**6**) for the Suzuki-Miyaura reaction

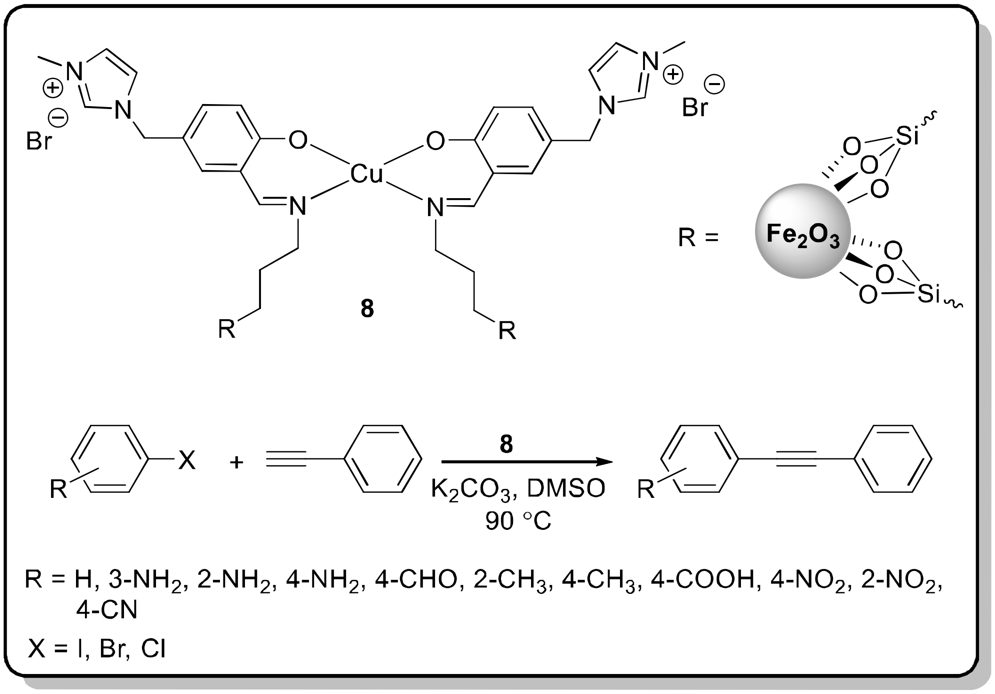
Khungar and coworkers reported two imidazolium-based Schiff base Pd(II) and Zn(II) complexes **7a-b**. Complex **7a** showed excellent activity for the Suzuki-Miyaura and Mizoroki-

Heck reaction in water at room temperature by using a modest amount of the catalyst (**Scheme 1.7**). The catalyst worked well for water-insoluble aryl halides in both reactions. The catalyst can be easily reused and recycled for six cycles without much loss in the activity. Complex **7b** was found to be a good catalyst for the synthesis of bis(indolyl)methanes for the reaction of an aromatic aldehyde with indole substrates (**Scheme 1.7**). Electron-donating aldehydes resulted in good yields of product, whereas electron-withdrawing and heterocyclic aldehydes provided moderate yields in water with the effective recycling of catalyst up to six cycles [68-69].



Scheme 1.7 Pd(II) complex (**7a**) for the Suzuki-Miyaura/Mizoroki-Heck reaction and Zn(II) complex (**7b**) for the synthesis of bis(indolyl)methanes

Kazemnejadi *et al.* synthesized imidazolium-based Cu(II) Schiff base complex **8** decorated on γ-Fe_2O_3 magnetic nanoparticles for base/Pd free Sonogashira coupling reaction (**Scheme 1.8**). Complex **8** worked efficiently for a variety of aryl halide substrates bearing sterically hindered, electron-withdrawing, and electron-donating groups. There was no considerable difference in reaction yields when I, Br, or Cl were used as leaving groups, however, the reaction was slow for Br and Cl derivatives. Aryl halides bearing electron-withdrawing groups gave excellent yields, whereas electron-donating groups showed lower efficiency and imidazolium moiety participated in the reaction as a base. The catalyst could be recycled up to eight consecutive runs [70].

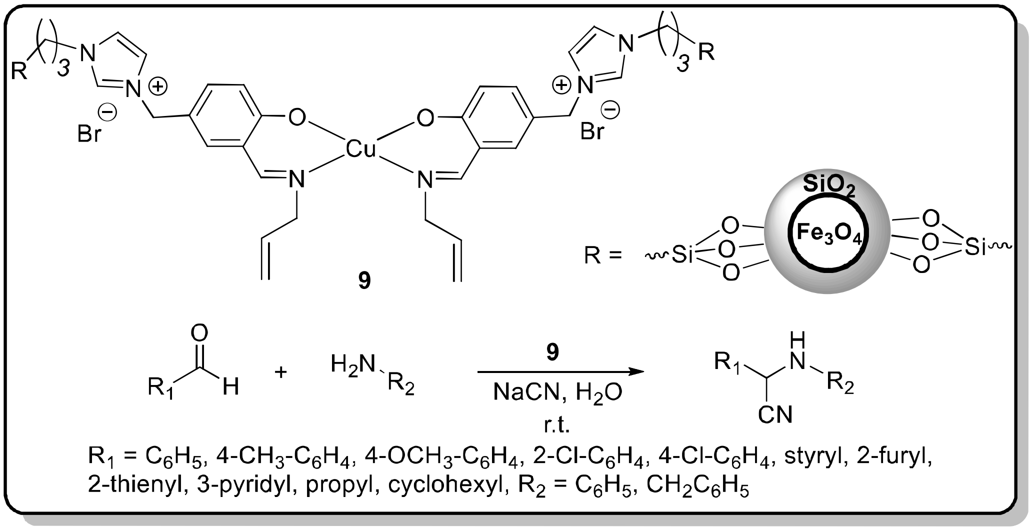


R = H, 3-NH_2, 2-NH_2, 4-NH_2, 4-CHO, 2-CH_3, 4-CH_3, 4-COOH, 4-NO_2, 2-NO_2, 4-CN
X = I, Br, Cl

Scheme 1.8 Magnetic Cu(II) Schiff base complex (**8**) for Sonogashira coupling reaction

Kazemnejadi *et al.* proposed another imidazolium-based Cu(II) Schiff base complex **9** supported on Fe_3O_4@SiO_2 nanoparticles and employed it as a magnetic nanocatalyst for the one-pot preparation of α-aminonitriles (Strecker reaction) (**Scheme 1.9**). Using catalyst **9**, desired α-aminonitriles were obtained from the reaction of aromatic or aliphatic aldehydes and aniline or benzylamine in the water at room temperature with good to excellent yields. The efficiency of the catalyst was also evaluated for the preparation of α-aminonitrile from ketones, but the steric hindrance of ketones produced only the Schiff base compounds.

The catalyst could be quickly separated from the reaction mixture with an external magnet and reused for at least seven successive reaction cycles [71].



$R_1 = C_6H_5$, 4-CH_3-C_6H_4, 4-OCH_3-C_6H_4, 2-Cl-C_6H_4, 4-Cl-C_6H_4, styryl, 2-furyl, 2-thienyl, 3-pyridyl, propyl, cyclohexyl, $R_2 = C_6H_5$, $CH_2C_6H_5$

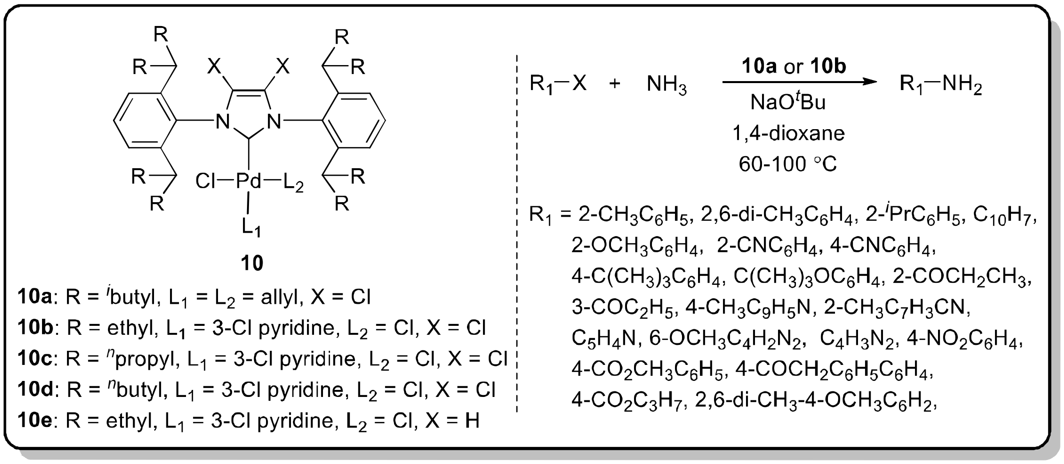
Scheme 1.9 Magnetic Cu(II) complex (**9**) for Strecker reaction

1.1.2 Imidazolium-based NHC metal catalyst

N-heterocyclic carbenes have become an exceptionally important class of compounds that are regarded as flexible carbon-donor ligands in catalysis. NHC ligands are two-electron σ-donors with little π-accepting ability and the σ-donor strength depends on the composition of the respective derivative. In its ground-state, the lone pair of the carbene carbon atom exists in the plane of the heterocyclic ring and due to this nucleophilic character (good σ-donors) they can bind to many metallic and non-metallic species. Further studies revealed that π-interactions also contribute to the NHC-metal bond. It was found that there is a significant π-donor contribution and also a π^* back-donation from the *d*-orbital of the metals to the entire NHC-metal bonding. N-Heterocyclic carbenes form strong bonds with metal centres, which prevents the decomposition of catalyst and makes them air-stable [72-75].

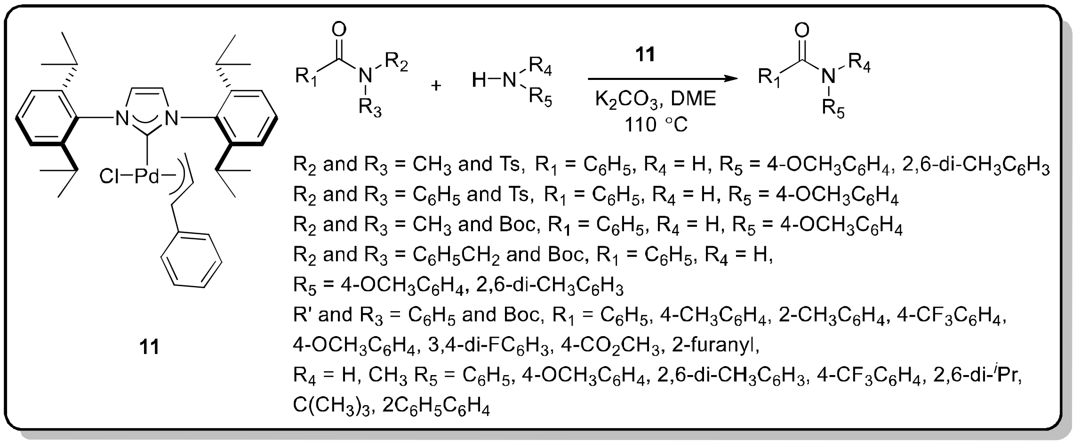
Imidazolium-based NHC metal complexes are efficient catalyst precursors for a great variety of reactions including cross-coupling [76], olefin metathesis [77], cyclization [78], hydrogenation [79], transfer hydrogenation [80], hydrosilylation of aldehydes [81], alcohol oxidation [82], water oxidation [83], etc. Cross-coupling reactions are indispensable tools in modern organic synthesis providing versatile routes for the construction of carbon-carbon/carbon-heteroatom bonds. NHC metal complexes have been widely utilized in numerous cross-coupling reactions. Lombardi *et al.* investigated the catalytic efficiency of Pd-

NHC complexes **10a-e** in the selective cross-coupling of aryl halides with ammonia to synthesize primary arylamines (**Scheme 1.10**). The air and moisture stable precatalysts **10a** and **10b** presented superior activity in selective aminations of electron-rich, electron-deficient, and *ortho*-substituted aryl halides in high yields. Nitrogen-containing heterocycles and base-sensitive functionalities were also coupled with NH_3 in excellent yields and high selectivity [84].



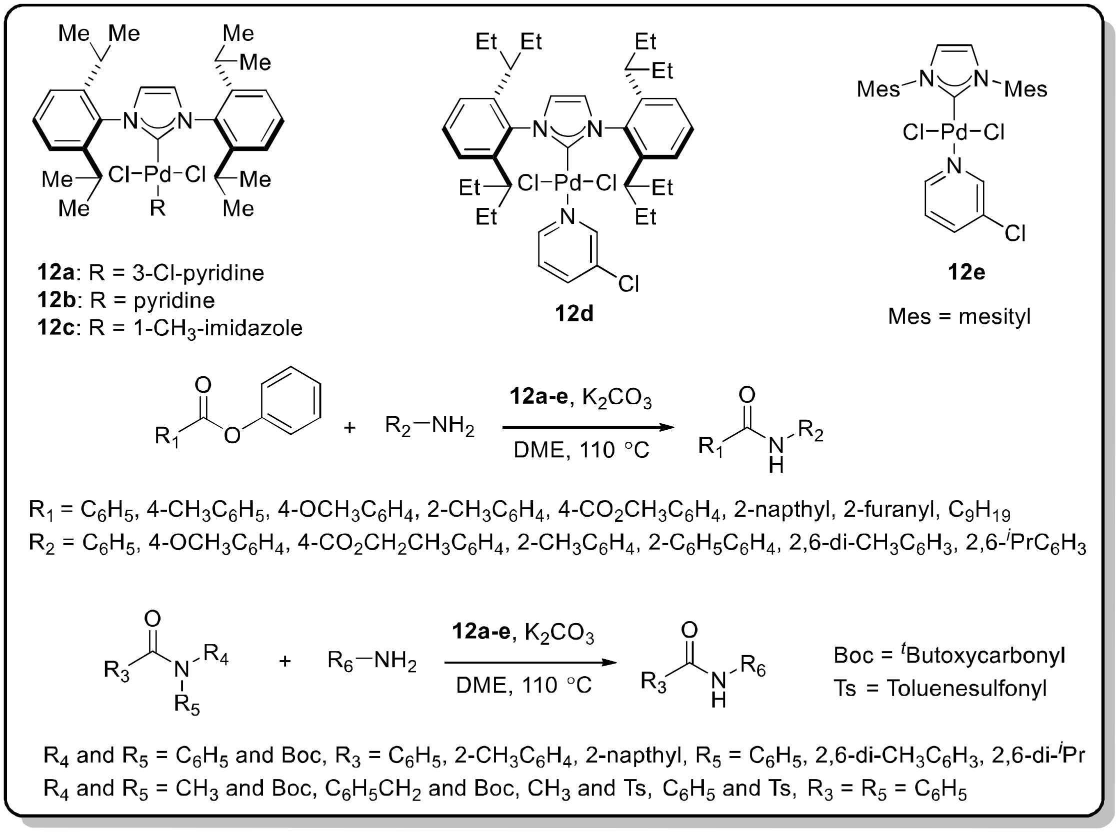
Scheme 1.10 Monoligated Pd(II) complexes (**10a-e**) for selective cross-coupling of aryl halides with ammonia

Meng *et al.* proposed a transamidation of secondary carboxamides catalyzed by Pd-NHC complex **11**. Complex **11** catalyzed the cross-coupling of a variety of non-nucleophilic neutral, electron-rich, electron-poor, sterically hindered, and secondary anilines with amides which furnished the desired C-N amination products in high yields (**Scheme 1.11**). Sterically hindered, electron-deficient, electron-rich, acyclic, aliphatic, fluorine-, ester-containing and heterocyclic amides were used [85].



Scheme 1.11 Pd(II) complex (**11**) for transamidation of secondary amides

Shi *et al.* reported a series of air and moisture stable NHC based palladium PEPPSI (pyridine enhanced precatalyst preparation stabilization and initiation) precatalysts (**12a-e**) that were prepared in a single step. Their catalytic activity was demonstrated in Buchwald-Hartwig cross-coupling of esters and amides with amines (transamidation) (**Scheme 1.12**). Different neutral, electron-rich, sterically-hindered, polyaromatic, and electron-withdrawing esters provided a diverse range of amides. The electron-rich heterocycles conjugated at the deactivating 2-position and aliphatic esters were also selectively cross-coupled. Different N-activated amides, including alkyl and aryl N-Boc-carbamates and alkyl and aryl N-sulfonamides provided good to excellent yields of product. It was suggested that Pd(II)-NHC precatalysts bearing pyridine ‘‘throw-away’’ ligand improved the yields of the product due to the nucleophilicity of Pd centre to promote the oxidative addition [86].



12a: R = 3-Cl-pyridine
12b: R = pyridine
12c: R = 1-CH$_3$-imidazole

Mes = mesityl

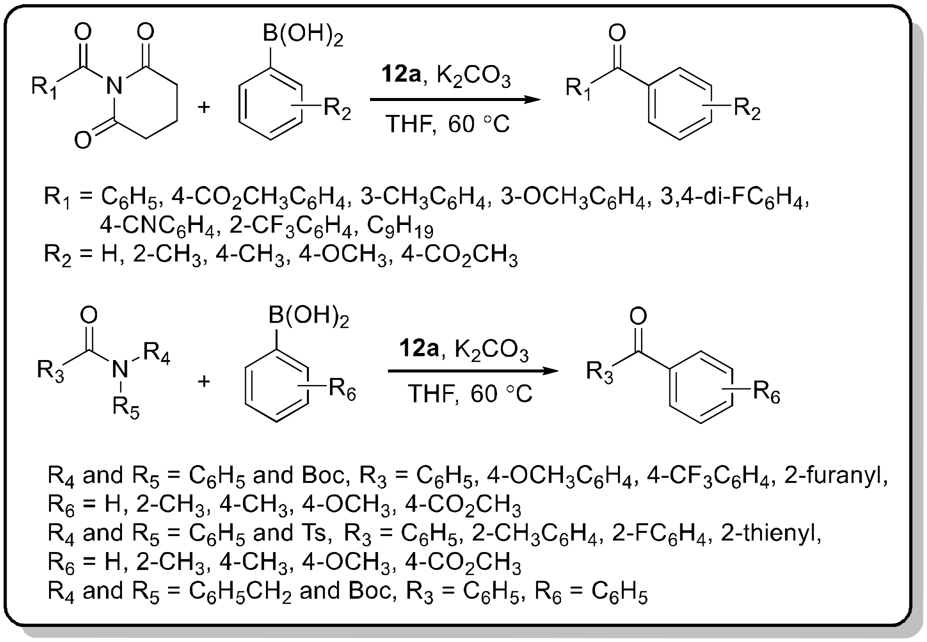
R_1 = C_6H_5, 4-$CH_3C_6H_5$, 4-$OCH_3C_6H_4$, 2-$CH_3C_6H_4$, 4-$CO_2CH_3C_6H_4$, 2-napthyl, 2-furanyl, C_9H_{19}
R_2 = C_6H_5, 4-$OCH_3C_6H_4$, 4-$CO_2CH_2CH_3C_6H_4$, 2-$CH_3C_6H_4$, 2-$C_6H_5C_6H_4$, 2,6-di-$CH_3C_6H_3$, 2,6-^{i}PrC_6H_3

Boc = ^{t}Butoxycarbonyl
Ts = Toluenesulfonyl

R_4 and R_5 = C_6H_5 and Boc, R_3 = C_6H_5, 2-$CH_3C_6H_4$, 2-napthyl, R_5 = C_6H_5, 2,6-di-$CH_3C_6H_3$, 2,6-di-^{i}Pr
R_4 and R_5 = CH_3 and Boc, $C_6H_5CH_2$ and Boc, CH_3 and Ts, C_6H_5 and Ts, R_3 = R_5 = C_6H_5

Scheme 1.12 Pd(II)-PEPPSI complexes (**12a-e**) for Buchwald-Hartwig cross-coupling of esters and amides with amines

Szostak *et al.* used Palladium-NHC complex **12a** which served as a reactive precatalyst in the Suzuki-Miyaura cross-coupling of amides (**Scheme 1.13**). A library of electron-rich, electron-withdrawing, sterically hindered and heterocyclic amide substrates were efficiently cross-coupled with a variety of arylboronic acids in good yields. Some challenging N-alkyl and *α*-alkyl amide substrates also afforded the cross-coupling products in modest to good yields [87].

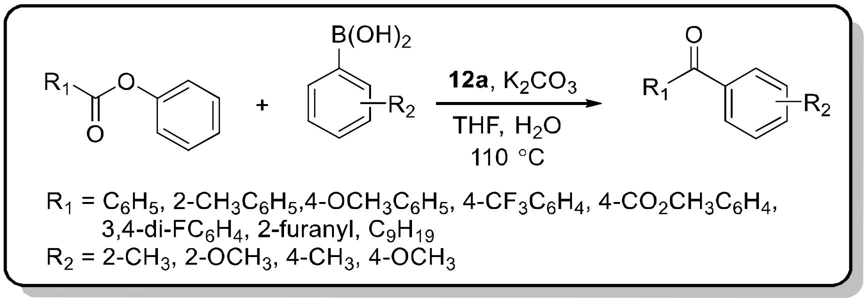


R_1 = C_6H_5, 4-$CO_2CH_3C_6H_4$, 3-$CH_3C_6H_4$, 3-$OCH_3C_6H_4$, 3,4-di-FC_6H_4, 4-CNC_6H_4, 2-$CF_3C_6H_4$, C_9H_{19}
R_2 = H, 2-CH_3, 4-CH_3, 4-OCH_3, 4-CO_2CH_3

R_4 and R_5 = C_6H_5 and Boc, R_3 = C_6H_5, 4-$OCH_3C_6H_4$, 4-$CF_3C_6H_4$, 2-furanyl,
R_6 = H, 2-CH_3, 4-CH_3, 4-OCH_3, 4-CO_2CH_3
R_4 and R_5 = C_6H_5 and Ts, R_3 = C_6H_5, 2-$CH_3C_6H_4$, 2-FC_6H_4, 2-thienyl,
R_6 = H, 2-CH_3, 4-CH_3, 4-OCH_3, 4-CO_2CH_3
R_4 and R_5 = $C_6H_5CH_2$ and Boc, R_3 = C_6H_5, R_6 = C_6H_5

Scheme 1.13 Pd(II) complex (**12a**) for the Suzuki-Miyaura coupling of amides

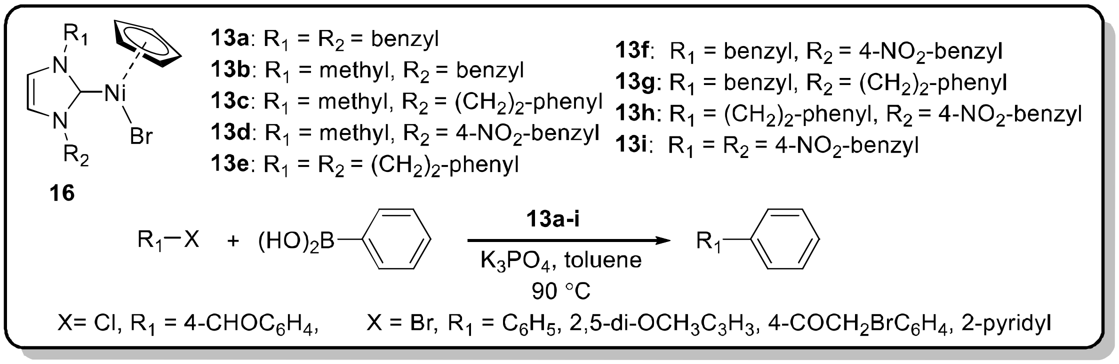
Li *et al.* proposed another application of complex **12a** for the water-assisted Suzuki-Miyaura cross-coupling of aryl esters *via* selective C-O bond cleavage at room temperature (**Scheme 1.14**). A wide range of electronically and sterically diverse aryl esters and boronic acids generated biaryl ketones in good to excellent yields. Electron-deficient polyfluorinated, electron-rich 5-membered heterocycles substituted at the deactivating 2-position and alkyl amides were also well-tolerated. Experimental studies suggested the use of water was crucial for achieving high reactivity [88].



R_1 = C_6H_5, 2-$CH_3C_6H_5$,4-$OCH_3C_6H_5$, 4-$CF_3C_6H_4$, 4-$CO_2CH_3C_6H_4$, 3,4-di-FC_6H_4, 2-furanyl, C_9H_{19}
R_2 = 2-CH_3, 2-OCH_3, 4-CH_3, 4-OCH_3

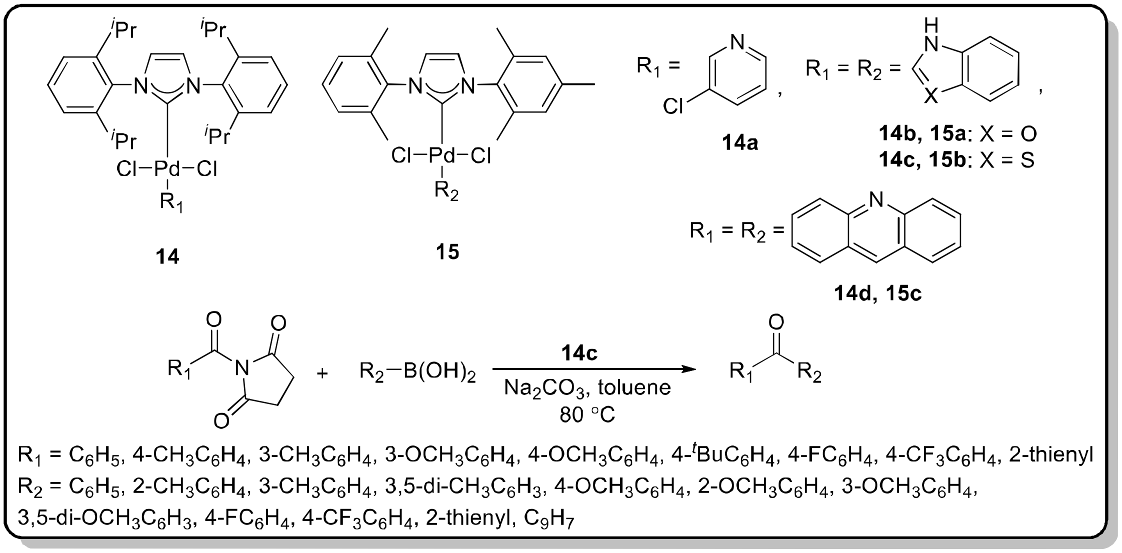
Scheme 1.14 Pd(II) complex (**12a**) for the Suzuki-Miyaura coupling of aryl esters

Malan *et al.* reported the synthesis of nine nickel-NHC complexes **13a-i** and studied their catalytic activity in the Suzuki-Miyaura coupling of aryl bromides and chlorides with phenylboronic acid in toluene solvent (**Scheme 1.15**). The Ni-NHC complexes bearing electron-donating groups were more efficient in coupling as compared to the complexes bearing the electron-withdrawing group. The electron-donating ancillary ligands stabilized the intermediates and suppressed the catalyst decomposition [89].



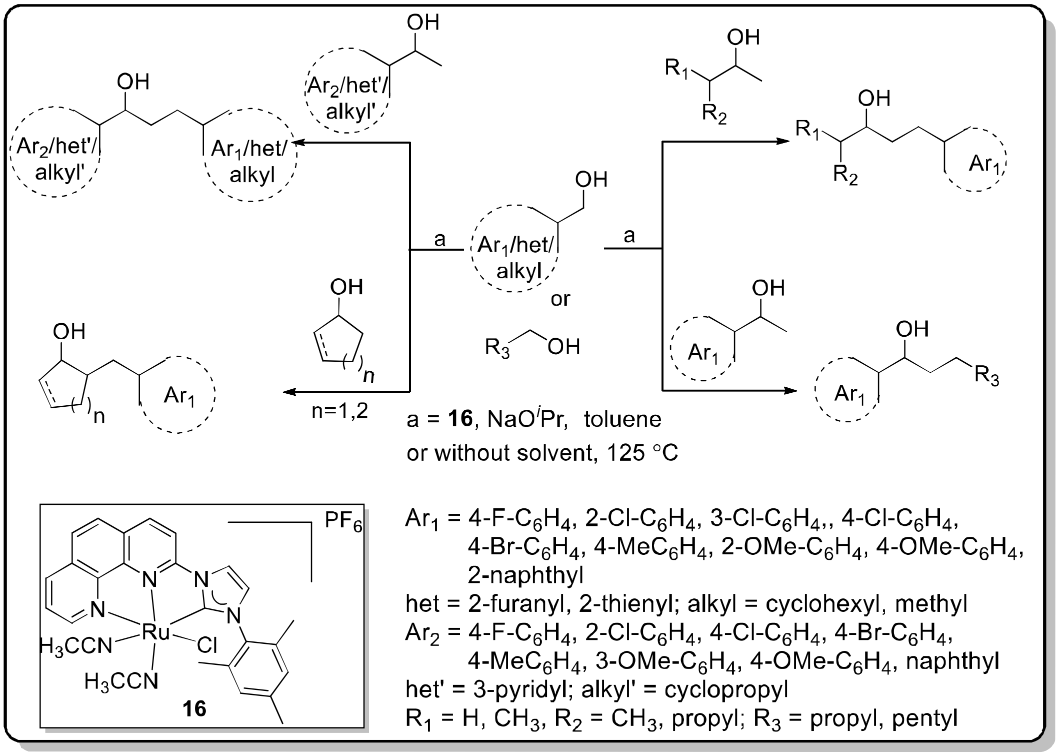
Scheme 1.15 Ni(II) complexes (**13a-i**) for the Suzuki-Miyaura reaction

Wang *et al.* prepared a series of NHC palladium complexes **14a-d** and **15a-c** and tested their activity for the Suzuki-Miyaura cross-coupling of N-acylsuccinimides with arylboronic acids *via* C-N bond cleavage (**Scheme 1.16**). Both electron-donating and electron-withdrawing groups in the phenylboronic acids were well tolerated and good results were obtained. Complex **14c** exhibited higher catalytic activity and generated a broad array of diaryl ketones in high yields [90].



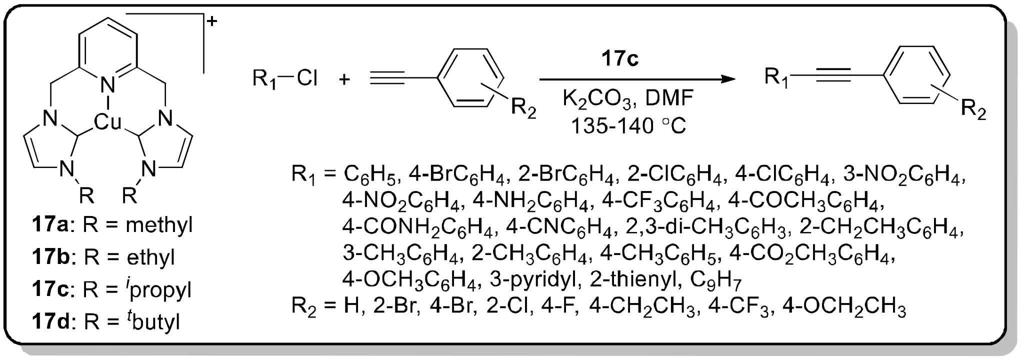
Scheme 1.16 Pd(II) complexes (**14a-d**) and (**15a-c**) for the Suzuki-Miyaura reaction of N-acylsuccinimides with arylboronic acids

Kundu *et al.* proposed a Ru(II) NHC complex **16** catalyzed cross-coupling of a broad range of aromatic, aliphatic and heterocyclic alcohols using NaO^{i}Pr base under solvent-free condition or using toluene as a solvent (**Scheme 1.17**). By utilizing this methodology, biologically active flavan derivatives in a one-pot manner were also synthesized. The plausible mechanism was supported by DFT calculations and kinetic experiments. The lower activation energy barriers for the dehydrogenation of alcohols as well as hydrogenation of the *α,β*-unsaturated ketones indicated higher efficiency with good selectivity of this catalytic system [91].



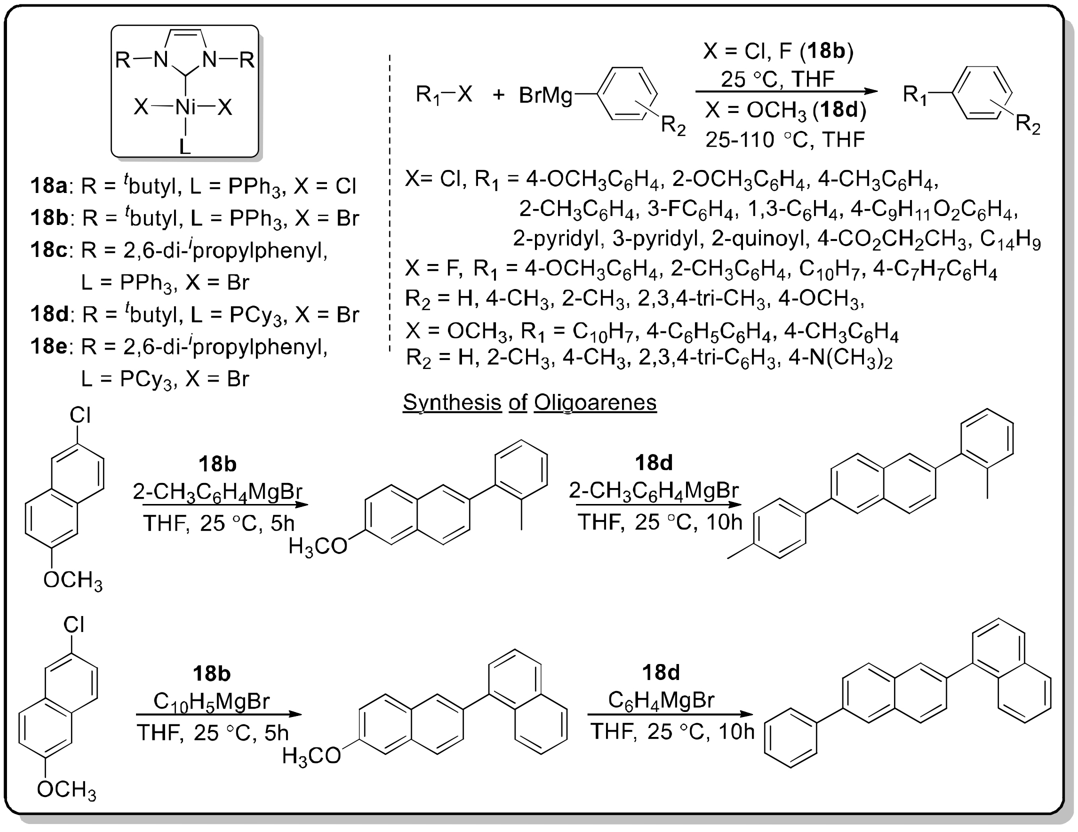
Scheme 1.17 Ru(II) complex (**16**) for tandem cross-coupling reaction of alcohols

Domyati *et al.* proposed pincer N-heterocyclic carbene copper complexes **17a-d** and compared their catalytic activity for the Sonogashira-type cross-coupling reaction under oxidative conditions (**Scheme 1.18**). Complex **17c** showed greater activity and was used to construct a library of internal alkynes. The *o*-substituted aryl iodides afforded greater yields than their *p*-substituted derivatives. The cross-coupled product yields were higher in the air than under the argon atmosphere. The radical trap and UV-visible experiments suggested the formation of high-valent Cu-oxygen adduct in the reaction [92].



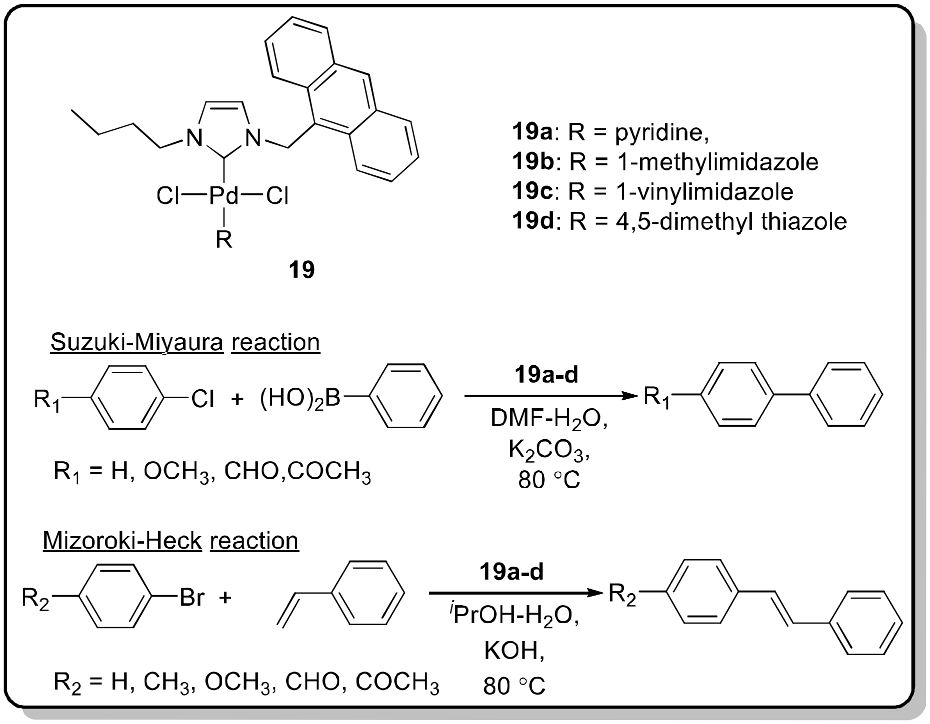
Scheme 1.18 Pincer NHC Cu(II) (**17a-d**) for Sonogashira-type reaction

Zhang *et al.* reported the synthesis of NHC based nickel complexes **18a-e** and investigated their efficiency in the cross-coupling of aryl Grignard reagents with a wide range of electrophiles (aryl chlorides/fluorides and aryl methyl esters) (**Scheme 1.19**). Complex **18b** exhibited the highest catalytic activity for aryl chlorides/fluorides while complex **18d** showed great potential for aryl methyl ethers. This difference in catalytic activity between **18b** and **18d** was further utilized for the selective cross-coupling of the chloride or the methoxy group with a Grignard reagent for the construction of oligoarenes [93].



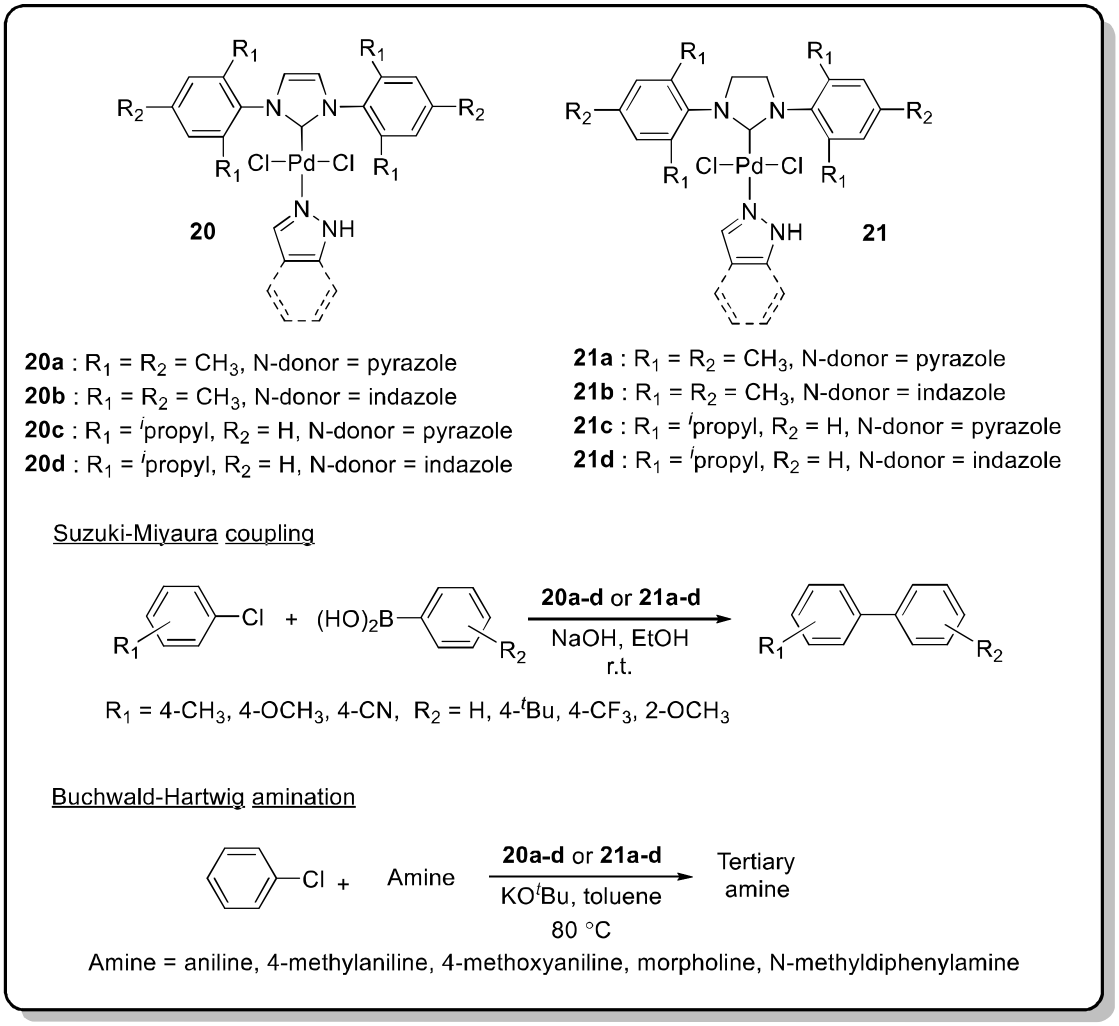
Scheme 1.19 Ni(II) complexes (**18a-e**) for cross-coupling reaction of aryl Grignard reagents with aryl chlorides/fluorides and aryl methyl esters

Karataş *et al.* reported anthracene substituted NHC palladium complexes **19a-d** with different N-coordinated ligands and tested their catalytic activity for the Suzuki-Miyaura and the Mizoroki-Heck cross-coupling reactions in the aqueous medium (**Scheme 1.20**). In the Suzuki-Miyaura reaction, aryl chloride derivatives bearing electron-withdrawing groups coupled more efficiently with phenylboronic acid as compared to electron-donating groups. In the Mizoroki-Heck reaction, aryl bromides with electron-withdrawing groups did not react whereas derivatives with electron-donating groups provided good yields. The most active catalyst for the Suzuki-Miyaura reaction was **19a** and for the Mizoroki-Heck reaction was **19d** [94].



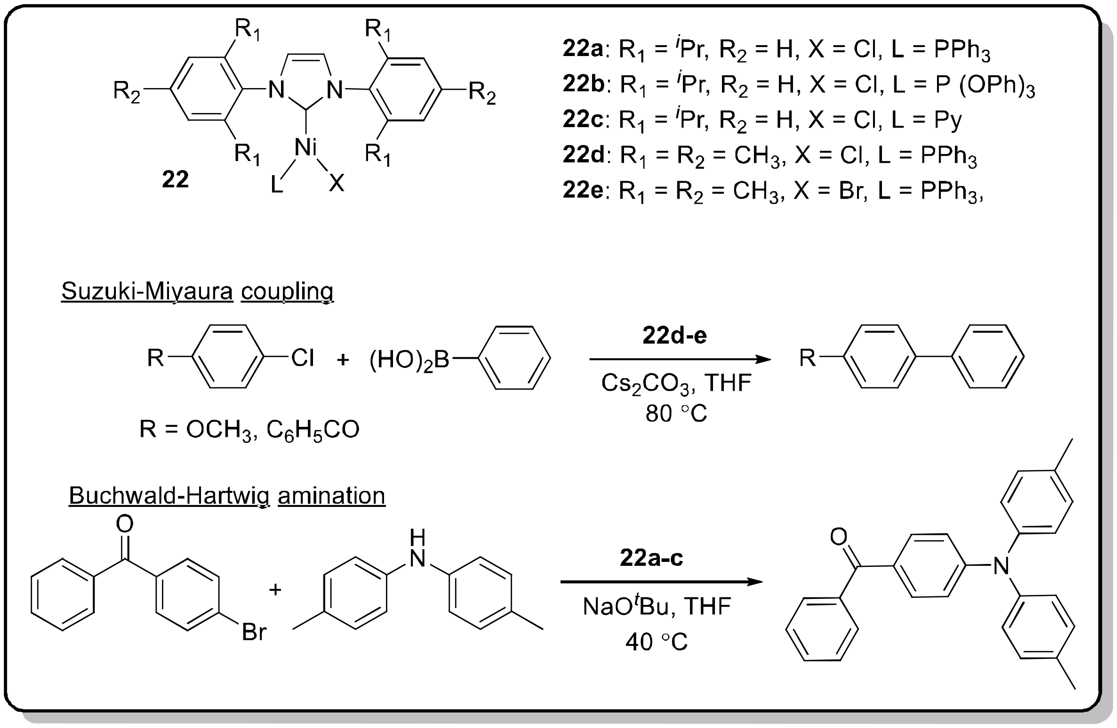
Scheme 1.20 Pd(II) complexes (**19a-d**) for the Suzuki-Miyaura and Mizoroki-Heck reaction

Yang proposed eight heteroleptic palladium complexes **20a-d** and **21a-d** containing both NHC and NH-heterocycle azoles (pyrazole and indazole). The obtained complexes exhibited good catalytic activity for the Suzuki-Miyaura reaction and Buchwald-Hartwig amination employing aryl chlorides as a halide source (**Scheme 1.21**). However, the recovered catalysts were found to be unreactive for the next run due to palladium black deposition in the reactions [95].



Scheme 1.21 Heteroleptic Pd(II) complexes (**20a-d**) and (**21a-d**) for the Suzuki-Miyaura coupling and Buchwald-Hartwig amination

Matsubara *et al.* prepared a series of three-coordinate monovalent nickel halide complexes **22a-e** bearing NHC ligands. These complexes exhibited three-coordinate Y-shaped geometries in both the solid and solution states. The catalytic efficiency of the complexes was compared for the Suzuki-Miyaura cross-coupling and Buchwald-Hartwig amination of aryl bromides (**Scheme 1.22**). Buchwald-Hartwig aminations using the complexes **22a-c** as catalysts proceeded efficiently to yield triarylamines, whereas complex **22d** and **22e** catalyzed the Suzuki cross-coupling reactions with high efficiency [96].



Scheme 1.22 Monovalent Ni(II) complexes (**22a-e**) for the Suzuki-Miyaura and Buchwald Hartwig amination reactions

1.2 Imidazolium- and pyridinium-based chemosensors

Fluorescent chemosensors are widely employed for both analytical sensing and optical imaging with advantages of good sensitivity, quick response, and procedural simplicity. The fluorescence sensing systems provide reliable results for chemical, environmental, as well as biological analytes. Chemosensor is a system with either purely organic or organometallic frameworks that on interaction with target analyte produces a fluorogenic signal due to the alteration in its photophysical properties. Chemosensor can bind to the analyte *via* non-covalent interactions including metal coordination, electrostatic interactions, and hydrogen bonding [97-99].

The fluorescence results from the emission of a photon from the lowest energy singlet excited state S_1 to the singlet ground state S_0 [100-101]. These chemosensors function *via* two processes, fluorescence “turn-on” (fluorescence enhancement) and “turn-off” (fluorescence quenching) response on selective analyte binding (**Figure 1.3**) [102]. Resonance energy transfer (RET), photo-induced electron transfer (PET) and chelation induced enhanced fluorescence (CHEF) phenomenon are examples of some mechanisms related to fluorescence sensing.

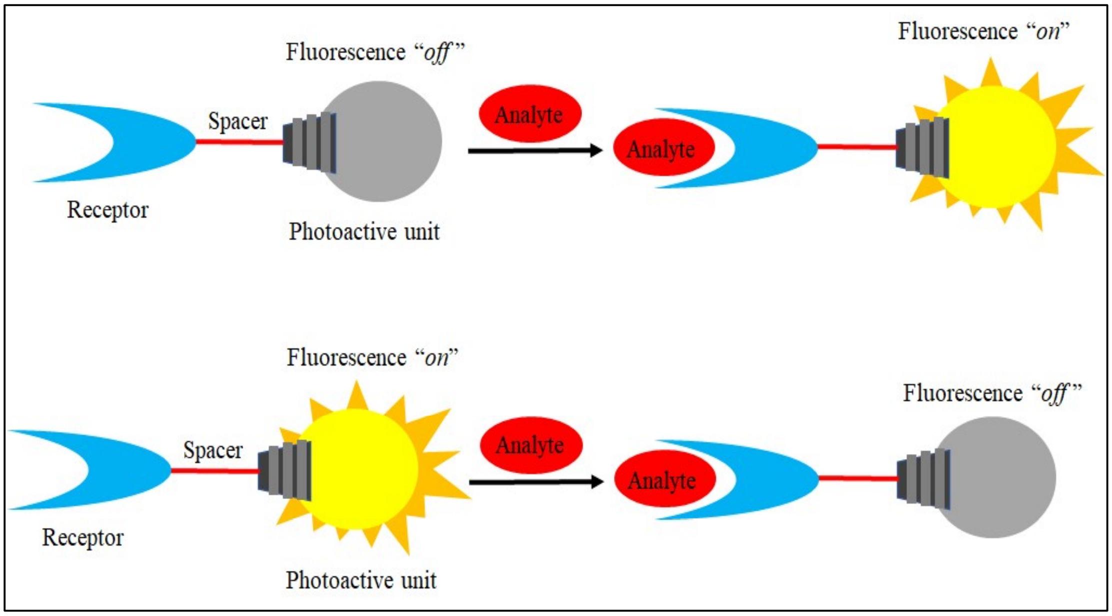
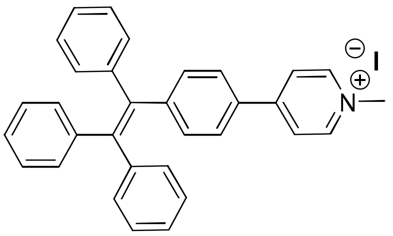


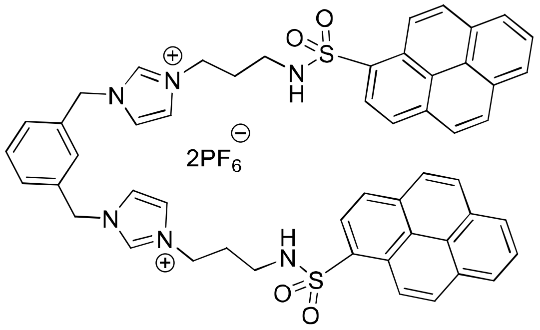
Figure 1.3 Pictorial representation of a chemosensor response on analyte binding

The fluorometric chemosensors find applications in biochemistry, analytical chemistry, medical and environmental sciences [103-104]. The detection of hazardous and noxious metal ions, anions, and nitroaromatics has been investigated extensively due to their potential negative impact on human health and the environment. A wide variety of chemosensors have been reported by several research groups for the selective and rapid detection of these analytes [105-106]. However, many of these chemosensors suffer from some challenges such as high cost, interference from other analytes, and detection only in organic solvents [107]. Improving the sensitivity of chemosensors is highly desirable to detect analytes at very low concentrations in aqueous medium.

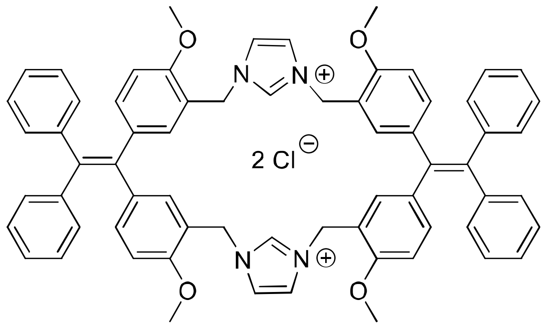
Imidazolium- and pyridinium-based chemosensors are good candidates for chemosensory applications in aqueous medium due to their high water solubility. These chemosensors are widely studied for the recognition of environmentally relevant anions like halides, cyanide, perchlorate, carboxylic acids, phosphate, sulfate, etc. Some selective examples of these chemosensors used for various anions detection are given in **Figure 1.4**.



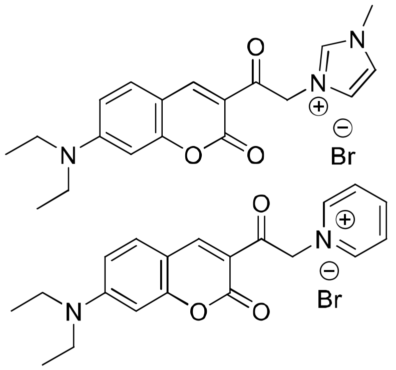
Detection of F^- [108]
Sensing solvent = CH_3CN-H_2O (v/v = 1:99)



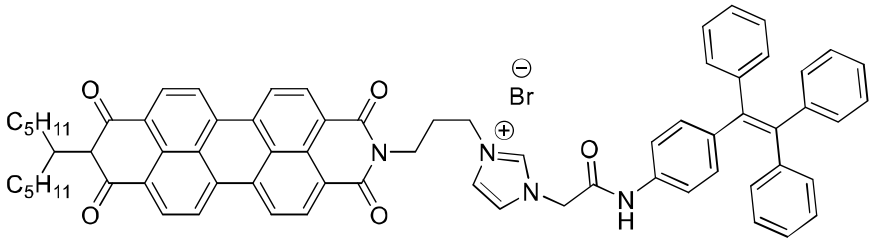
Detection of CN^- [109]
Sensing solvent = PBS-EtOH (v/v = 5:95)



Detection of $P_2O_7^{4-}$ [110]
Sensing solvent = H_2O with 0.5% DMSO



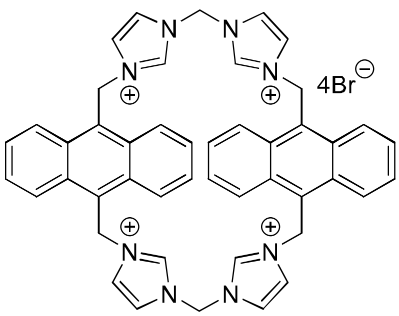
Detection of HSO^{3-} and SO_3^{2-} [111]
Sensing solvent = THF-PBS (v/v = 3:1)



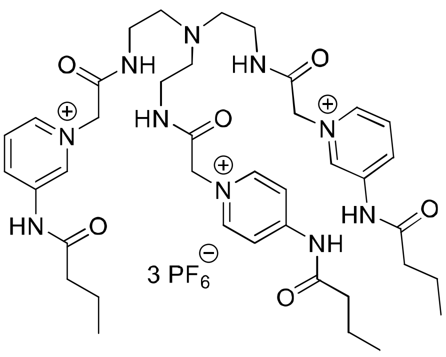
Detection of H_2PO_4 and $HP_2O_7^{3-}$ [112]
Sensing solvent = CH_3CN

Figure 1.4 Selected examples of imidazolium- and pyridinium-based chemosensors for various anion detection

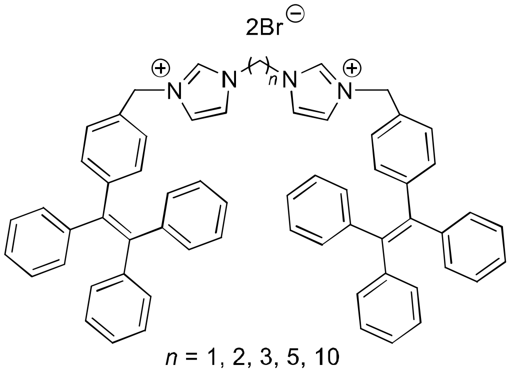
Due to their low human toxicity imidazolium- and pyridinium-based chemosensors find valuable applications in detecting biologically important anionic analytes like nucleotides, DNA, RNA, proteins, etc. (**Figure 1.5**).



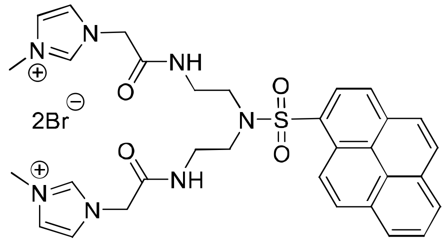
Detection of GTP and I^- [113]
Sensing solvent = H_2O



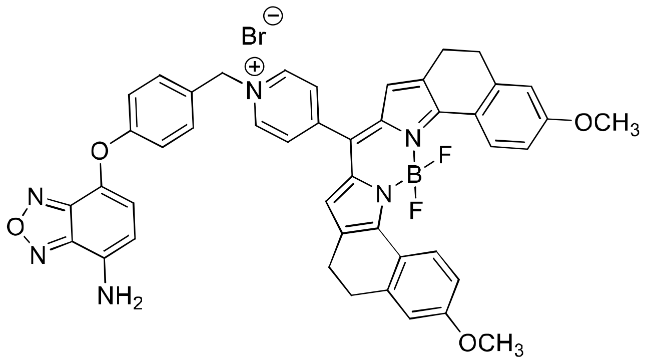
Detection of AMP [114]
Sensing solvent = H_2O



Detection of ATP [115]
Sensing solvent = H_2O



Detection of Heparin [116]
Sensing solvent = H_2O



Detection of hydrogen sulphide/glutathione and cysteine/homocysteine [117]
Sensing solvent = DMSO-PBS buffer (v/v = 1:1)

Figure 1.5 Selected examples of imidazolium- and pyridinium-based chemosensors for biologically relevant analytes

1.2.1 Imidazolium- and pyridinium-based chemosensors for metal ions and nitroaromatic compounds (NACs) detection

Imidazolium- and pyridinium-based fluorescent chemosensors have been employed for the detection of toxic metal ions and nitroaromatic compounds. Saleh *et al.* reported pyridinium-based Schiff base chemosensor **23** (**Figure 1.6**) for the selective and sensitive detection of Ca^{2+} ions in an aqueous medium over other physiological relevant alkali, alkaline-earth, and transition metal ions. The selectivity and sensitivity of **23** for Ca^{2+} was due to internal charge transfer (ICT) process [118]. Prabphal *et al.* synthesized a pyridinium-based porphyrin chemosensor **24** (**Figure 1.6**) that exhibited a selective fluorescence “turn-off” response on complexation with Cu^{2+} ion. They constructed a simple paper-based sensor by depositing **24** onto pre-patterned papers and used it for Cu^{2+} detection with good selectivity and sensitivity. The determination of Cu^{2+} was also conducted in drinking water and tap water with satisfactory results [119].

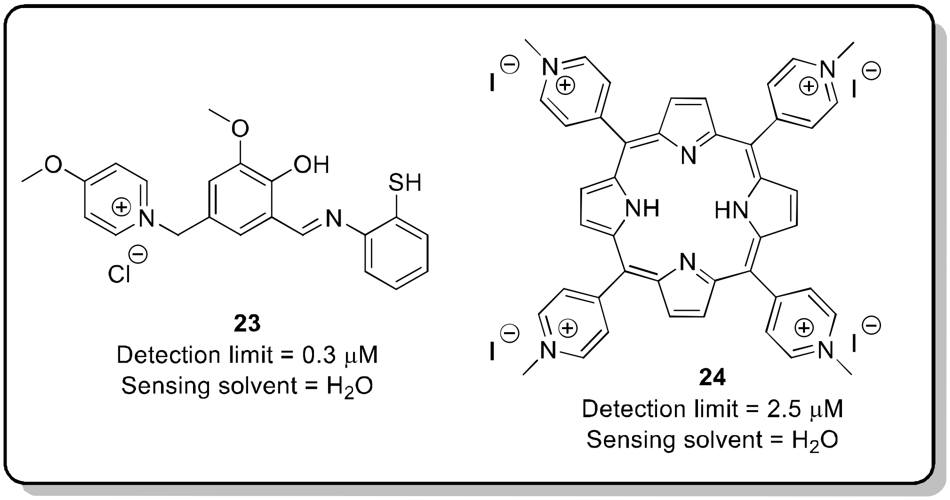
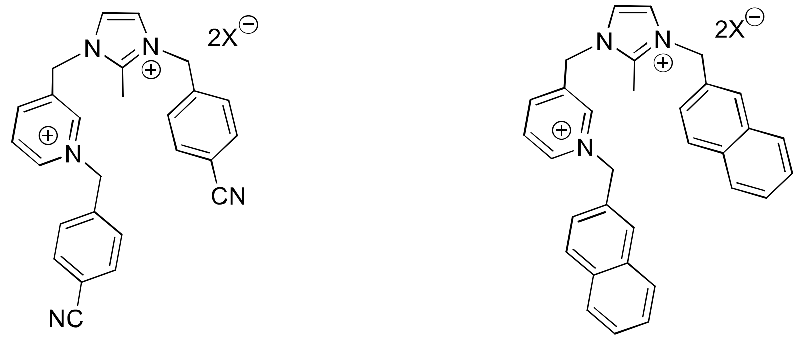


Figure 1.6 Pyridinium-based Schiff base (**23**) and porphyrin (**24**) chemosensors

Milton *et al.* proposed a water-soluble aryl-functionalized imidazolium bromide chemosensors **25a** and **26a**, their metathesis products (counter anion exchange by hexafluorophosphate) **25b** and **26b** (**Figure 1.7**). These chemosensors selectivity detected Fe^{3+} ion over other metal ions in aqueous media by fluorescence “turn-off” mechanism. Fluorescence quenching was also observed in the case of Fe^{2+}, Cr^{3+}, and Cu^{2+} ions to some extent but the emission intensities of **25a** and **25b** were quenched by Fe^{3+} to 92% and 99%, respectively. The Stern-Volmer (S-V) plot indicated the static quenching mechanism [120].

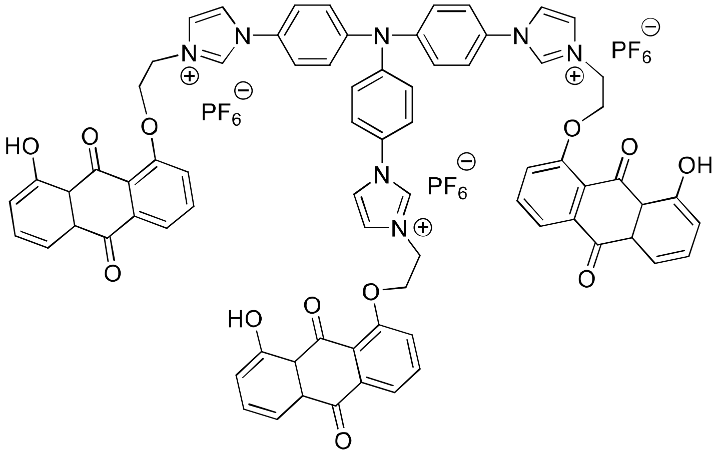


25a: X = Br, Detection limit = 28.1 μM
Sensing solvent = H_2O
25b: X = PF_6, Detection limit = 27 μM
Sensing solvent = CH_3CN-H_2O (v/v = 1:9)

26a: X = Br, Detection limit = 19.9 μM
Sensing solvent = H_2O
26b: X = PF_6, Detection limit = 30.2 μM
Sensing solvent = CH_3CN-H_2O (v/v = 1:9)

Figure 1.7 Dicationic chemosensors (**25a-b** and **26a-b**)

Zhao *et al.* prepared an imidazolium-based fluorescent and colorimetric chemosensor **27** (**Figure 1.8**) for Cu^{2+} ion detection. The colour of the chemosensor solution changed from yellow to orange under sunlight within 1 minute and a decrease in fluorescence emission was observed. Furthermore, **27** was also used in detecting Cu^{2+} by employing a smartphone with the detection limit of 0.51 μM [121].

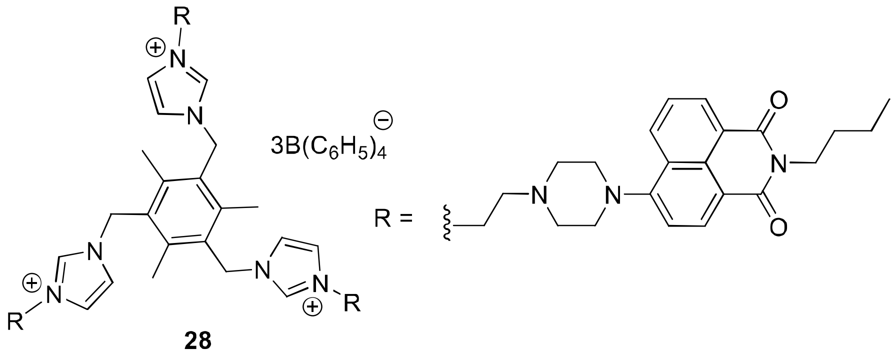


27
Detection limit = 0.049 μM
Sensing solvent = DMSO-DCM (v/v = 1:49)

Figure 1.8 Tri-imidazolium-based chemosensor (**27**)

Wang *et al.* synthesized a tripodal chemosensor **28** based on imidazolium and 1,8-naphthalimide dye (**Figure 1.9**) that displayed high selectivity for copper(II) ion pairs,

$Cu(ClO_4)_2$ and $Cu(NO_3)_2$ *via* fluorescence "turn on" response over a wide range of tested metal ions, anion, and other Cu^{2+} salt ion pairs. On the addition of $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ to the chemosensor solution, a blue-shifted emission from 518 nm to 496 nm with a significant colour change from yellow-green to bright blue was observed [122].

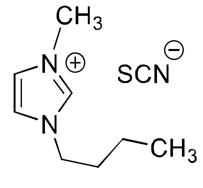


28

Sensing solvent = CH_3CN

Figure 1.9 Imidazolium-based tripodal chemosensor (**28**)

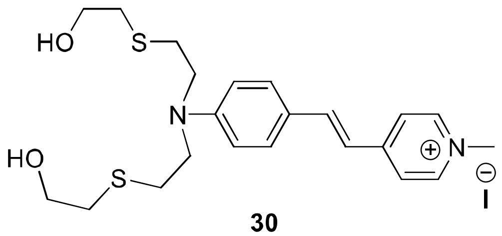
Coldur *et al.* reported an imidazolium-based fluorescent chemosensor **29** (**Figure 1.10**) that exhibited a selective and sensitive response to Fe^{3+} in acidic aqueous solutions. The chemosensor **29** was encapsulated in the ethyl cellulose matrix to form a continuous thin film and detected Fe^{3+} efficiently. Limit of detection values from absorption and emission methods were found to be 2.48×10^{-5} M and 2.4×10^{-8} M, respectively [123]. Patel and coworkers demonstrated chromogenic and fluorogenic applications of pyridinium-based chemosensor **30** (**Figure 1.10**) for the detection of Hg^{2+} ions in the methanol-water system. The orange-coloured solution of **30** became colourless upon the addition of Hg^{2+} ion with the generation of a new absorption band and ~ 10 fold emission enhancement along with a blue-shifted emission peak. The fluorescence of **30** was quenched on Hg^{2+} addition which was regained on S^{2-} ion addition, indicating the reversible nature of **30** [124].



29

Detection limit = 24 μM

Sensing solvent = H_2O



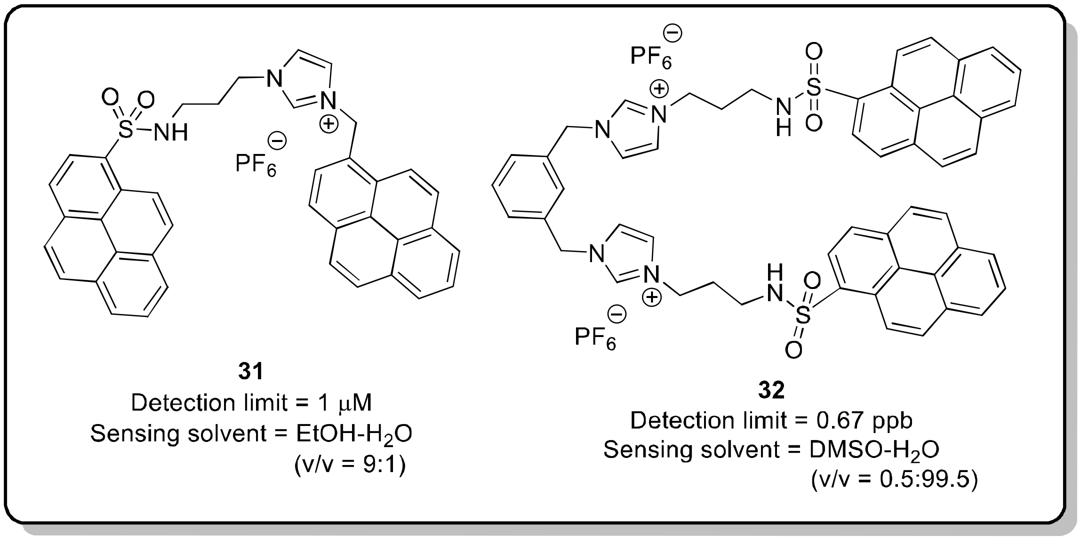
30

Detection limit = 4.8 μM

Sensing solvent = MeOH-H_2O (v/v = 4:1)

Figure 1.10 Imidazolium-based thiocyanate (**29**) and styrylpyridinium (**30**) chemosensors

Kim *et al.* synthesized a bisimidazolium-based pyrenesulfonamide chemosensor **31** (**Figure 1.11**) for the sensing of 3,5-dinitrosalicylic acid (DNSA) in 10% ethanol-water system. The fluorescence quenching of the chemosensor was due to the energy transfer from electron-rich pyrene to electron-deficient DNSA. The detection was also conducted on a paper strip and the bright emission was quenched on the addition of DNSA [125]. The same group also proposed another imidazolium appended pyrenesulfonamide chemosensor **32** (**Figure 1.11**) for TNP detection in water. The bright green emission of **32** was quenched selectively on TNP addition due to the loss *of π-π* interactions between the pyrene rings and energy transfer from electron-rich pyrene to electron-deficient TNP [126].



31
Detection limit = 1 μM
Sensing solvent = EtOH-H$_2$O
(v/v = 9:1)

32
Detection limit = 0.67 ppb
Sensing solvent = DMSO-H$_2$O
(v/v = 0.5:99.5)

Figure 1.11 Bisimidazolium-based pyrenesulfonamide chemosensors (**31**) and (**32**)

Kolekar and coworkers synthesized 3-(2-amino-2-oxoethyl)-1-methylimidazolium chloride **33** (**Figure 1.12**) as a fluorescent chemosensor for the detection of trinitrophenol (TNP) and *p*-nitrophenol (NP) in the aqueous medium. Significant quenching in fluorescence was observed due to the formation of the ground-state charge-transfer complex between chemosensor and TNP/NP [127]. Zheng *et al.* reported two imidazolium-based fluorescent chemosensor **34a** and **34b** containing Eu(III) and Dy(III) with a 1-(2-methoxyethyl)-3-methylimidazolium cation (**Figure 1.12**) and used them for the detection of nitrotoluenes (NTs). Among the three isomeric nitrotoluenes (*o*-, *m*- and *p*-), *p*-nitrotoluene provided the most significant fluorescence quenching [128]. Liu *et al.* proposed a series of imidazolium-based anthracene chemosensors **35a** and **35b** (**Figure 1.12**) for the selective recognition of 2,4-dinitrophenylhydrazine (DNPH). On the interaction of DNPH with **35a** or **35b**, the photoinduced electron transfer (PET) process from imidazolium moieties to anthracene ring was switched-on due to the influence of nitro groups of DNPH that resulted in the decrease in fluorescence intensity [129].

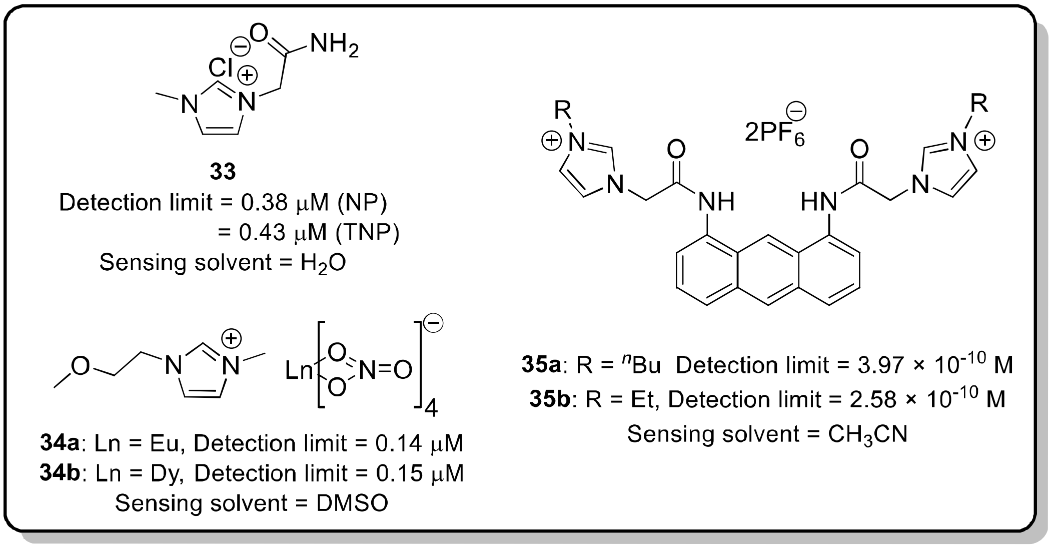


Figure 1.12 Imidazolium-based amide (**33**), lanthanide (**34a-b**) and anthracene (**35a-b**) chemosensors

1.3 Aim of present study

In the quest for efficiency and sustainability in catalysis the concept of supported homogeneous catalysts is a rapidly growing area. The imidazolium ionic tags Schiff base metal complexes possess unique chemical and physical properties and also aid to perform different organic transformations in pure aqueous medium. After the completion of reaction, the catalyst can be reused and recycle again with little loss in its activity. Imidazolium-based compounds are also used as precursors for N-heterocyclic carbenes (NHCs) and are widely employed ligands for transition metal complexes due of their strong σ-donation capabilities. These complexes show excellent catalytic activities for different organic transformations. The imidazolium- and pyridinium-based compounds also exhibit excellent photophysical properties. Due to their higher water solubility and excellent stability in aqueous medium they are also used as fluorescent chemosensors which can detect toxic analytes *via* fluorescence “turn on” or “turn off” response.

The present thesis deals with the synthesis and characterization of imidazolium- and pyridinium-based compounds and using them as a ligand to synthesizing metal catalyst for C-S and C-C cross coupling reactions. These compounds are also used for chemosensory application to detect several hazardous analytes with excellent sensitivity and selectivity in the aqueous medium.

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