Review Paper:

Applications of Schiff Bases and their Metal Complexes in Catalytic Transformations

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Abstract

Schiff base ligands can easily coordinate with metal ions and forms stable complexes, which facilitate the utilization of Schiff base metal complexes as catalyst in organic synthesis. Various routes for the synthesis and application of various Schiff base metal complexes in the field of catalytic transformations to synthesize organic compounds economically and more selectively are well-documented. Here we discuss the synthesis of 2-Amino-3-cyano-4H-pyrans or 4H-chromenes, synthesis of polyhydroquinoline derivatives by the Hantzsch reaction, Biginelli reaction, Suzuki–Miyaura and the Sonogashira cross-coupling reactions, synthesis of tetrazoles, synthesis of β-hydroxy-1,2,3-triazole, synthesis of N-aryl amines by Chan–Lam coupling, catalytic epoxidation of alkenes, catalytic reduction of aromatic ketones into alcohol etc.

Numerous Schiff base complexes can withstand higher temperature that provides them extra flexibility for their catalytic action even at higher temperature. Versatile nature of Schiff base (SB) ligands also prompted researchers to focus on studying catalytic activity where metal-SB immobilized on core-shell magnetic nanoparticles as nanocatalyst. The catalytically active Schiff base metal complexes are prerequisite to enhance the yields of stereospecific, regioselective and chemoselective products. This review highlights the Schiff base metal complexes as a catalyst to complicated organic synthesis into a simple one pot synthesis, thus may be beneficial to both researchers and industries in the field of catalytic reaction.

Keywords: Schiff base metal complexes, Nanocatalyst, Catalytic applications, Chemical transformations.

Introduction

Hugo Schiff first discovered Schiff base by the condensation reaction between an aldehyde and an amine yielding a Schiff base in the year 1864[14,43-47]. Schiff base ligands are capable to form coordinate covalent bonds with metal ions via N-atom of imine group and another donor group generally attached to the hydrazone-based system. It stems from observation that various research groups are actively engaged on synthesis of Schiff base and their metal complexes since it is considered as most privileged ligand[9,12,30,31,40,41]. The ease of synthesis and thermal stability enables them a valuable candidate for catalysis reactions. The complexes act as useful synthons to execute a wide range of organic transformations both in small as well as large industrial scale. Schiff base have strong tendency to stabilize various metal ions in oxidation states mainly ranging from II to VI, electric field surrounding the complex ions are responsible for a large extent of useful catalytic reactions.

The organic transformation using novel catalysts is an innovative and exciting area of research. In this study, we focus to introduce the synthesis of some celebrated and eco-friendly Schiff bases metal complexes obtained from reaction between aldehydes/ketones, amines and metal salts, which may act as catalyst for complicated organic synthesis. They have strong tendency to coordinate substrates and intermediates due to vacant coordination site, which is prerequisite to catalyse chemical reactions. Schiff-base complexes acts as the front runner for catalysing a wide range of chemical transformations[11,15,25,26,49].

This review highlights how some selected unsymmetrical Schiff base complexes or Schiff base complex of metal immobilized on core-shell magnetic nanoparticles improving the yield and selectivity of the chemical reactions involving various organic transformations.

As a whole, this review encapsulates a broad and complete survey of the recent work on design, synthesis and catalytic applications of some selected active and useful Schiff base and their metal complexes and may also be helpful for development and discovery of efficient novel catalyst.

Chemistry of Schiff base ligands and their metal complexes: Recently Schiff's base and their metal complexes are versatile about the novel synthesized complexes. Its variable chelating site and ease of preparation give an upper hand. Schiff base metal complexes are generally synthesized using standard procedure by condensation reaction between an aldehyde/ketone and a primary amine/hydrazide in presence of solvent like MeOH or EtOH as solvents at room temperature/microwave or refluxing at particular temperature. The reaction mixture was taken in a round bottom flask. It was heated at reflux with continuous stirring for a specified period. The Schiff's base formed was purified and isolated as a solid crystalline product. The Schiff base ligand was treated with hydrated metal chloride or metal acetate using suitable polar solvents like MeOH, EtOH and refluxed for a specific period.

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The completion of reaction was monitored by TLC. The reaction mixture was cooled down at room temperature and filtered to obtained Schiff's base metal complex. It was washed with cold MeOH or EtOH and recrystallized to obtain pure product dried in vacuo. Finally, it was characterized by using various techniques such as FT IR, ^{1}H and ^{13}C NMR, UV-visible spectroscopy, LC–MS, GC–MS, SEM, EDS, AAS, WDX, XRD, TGA-DTA, elemental analysis, conductivity measurement and melting point. The condensation reaction of aldehydes and amines is carried out in various polar solvents at different reflux temperatures. $MgSO_4$ and Na_2SO_4 are generally considered as a dehydrating agents for synthesizing Schiff bases.

The water is formed as one of the products along with Schiff base, which needs to be expelled using a Dean Stark apparatus, otherwise, there is maximum possibility of reversible reaction. The solvent may be toluene, methanol, ethanol to carry out synthesis of Schiff bases. Purification of the Schiff bases using silica gel column chromatography leads to its decomposition. Therefore, proper way to purify the Schiff base is by recrystallization. Since most of the Schiff bases are insoluble in non-polar solvents, they may be purified by continuous stirring. The impure reaction mixture is dissolved in a minimum amount of a more polar solvent ethanol and DCM, in order to get rid of impurities.

Furthermore, Schiff bases are stable compounds, but to avoid any decomposition, it is common practice to store in desiccator over $CaCl_2$. The condensation reaction is of two equivalents of aromatic aldehydes/aromatic ketones with one equivalent of various hydrazine/hydrazides producing hydrazone-based compound, which is a versatile class of coordinating ligand called as Schiff bases. Generally [O,N,N,O] type tetradentate bis-Schiff base ligands were derived from one equivalent of ethylenediamine/o-phenylenediamine/salen type and two equivalents of aromatic aldehydes having heterocyclic group plus one formyl group plus one OH groups produces H_2L, which on treatment with divalent metal salt gets deprotonated into L^{2-}, forming stable $L^{2-}M^{2+}$ neutral complex as in scheme 1(a). The huge applications of Schiff bases and its metal complexes in the field of biological activity, pharmacological and catalytic activity have motivated researchers to design and synthesize new precursors to make a combinatorial library of Schiff base ligands and their metal complexes.

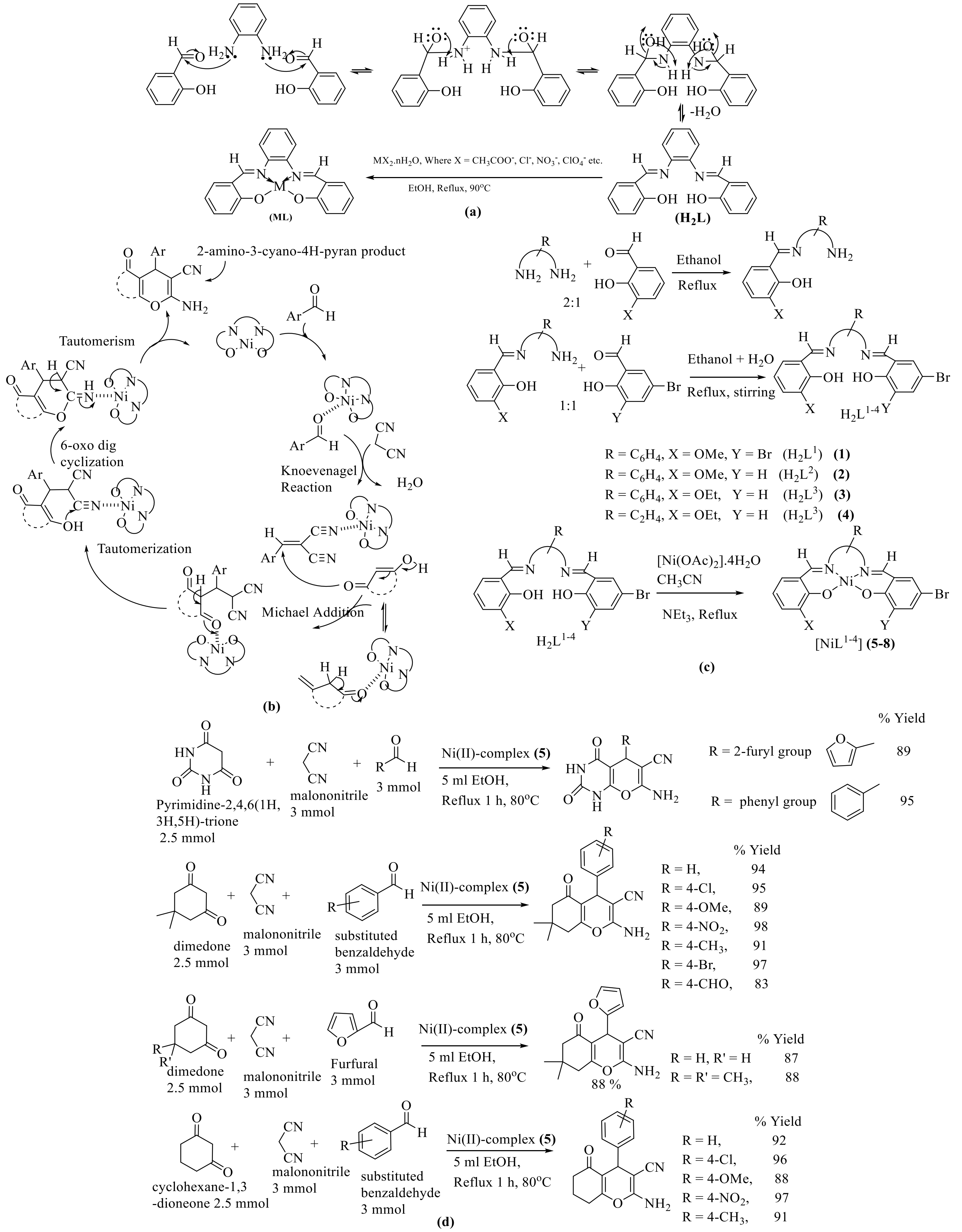
Useful catalyst metal (II)-unsymmetrical salen/MNPs based nanocatalyst for synthesis of biologically active 2-amino-3-cyano-4H-pyrans: Patra et al[32] synthesized four unsymmetrical salen ligands, H_2L^{1-4} (1-4) and their respective novel Ni(II)−salen complexes, [NiL^{1-4}] (5-8). The catalyst [NiL^{1-4}] seems to be economical and environmentally friendly and its activity was demonstrated via one-pot-three-component reactions of 1,3-dicarbonyls, malononitrile, benzaldehyde or substituted benzaldehyde for the synthesis of biologically active 2-amino-3-cyano-4H-pyran derivatives. This method showed a novel and significant development in the synthesis of various chromene-annulated heterocycle compounds as shown in scheme 1(b-d).

The main advantage of these synthesis is of simple procedures, no usage of column chromatography, time span for completion of reaction is 60 minutes, easy to isolate product using green solvent ethanol, small amount of catalyst loading, higher TOF (h^{-1}) values, excellent yields. The catalyst (5) showed excellent yields in a range between 83 to 98 % with TOF values ~ 2800 hr^{-1}.

Furthermore, aromatic aldehyde attached with an electron-withdrawing group as a ring substituent gives maximum yield than the electron-donating group. On comparing catalytic activities of Ni(II) complexes, catalytic efficiency follows the following trends: [NiL^1] > [NiL^3] > [NiL^2] > [NiL^4]. The plausible reaction mechanism for the Ni-catalyzed one-pot multicomponent reaction for the synthesis of 2- amino-3-cyano-4H-pyran derivatives is shown in scheme 1(b-d). Rezayati et al[37] synthesized environmentally friendly novel, nanocatalyst (26 and 45 nm size) of Schiff base copper complex coated over epoxy-modified Fe_3O_4@SiO_2@GPTMS/Schiff base-Cu(II) MNPs (9) by the immobilization of Schiff-base complex on core−shell magnetic nanoparticles followed by treatment with $Cu(NO_3)_2\cdot 3H_2O$. A Schiff base complex acts as a bridge to protect copper nanoparticles to the core-shell Fe_3O_4 exterior by smooth dispersion. The magnetic nanoparticles showed high activity in the synthesis of various biologically active chromene-annulated heterocycles via variety of aromatic aldehydes, various phenols (2-hydroxynaphthalene-1,4-dione/ resorcinol/β-naphthol) and malononitrile in EtOH under reflux condition.

A plausible mechanism is well illustrated in scheme 2 to synthesize 2-amino-4H-chromene derivatives. It is a three-component condensation of aldehydes, malononitrile and various phenols such as 2-hydroxynaphthalene-1,4-dione/resorcinol/β-naphthol in the presence of the MNPs as catalyst. The first step is the Knoevenagel condensation reaction between various aldehydes (I) and malononitrile (II) in the presence of the magnetic nanocatalyst (9) as a Lewis acid. The second step is the Michael addition of 2-hydroxynaphthalene-1,4-dionein (IV) with Knoevenagel product (III) forming intermediate (V). The final step is enolization of intermediate (V) into intermediate (VI), which undergoes intramolecular nucleophilic cyclization resulting in the formation of 2-amino-3-cyano-4H-pyran derivatives.

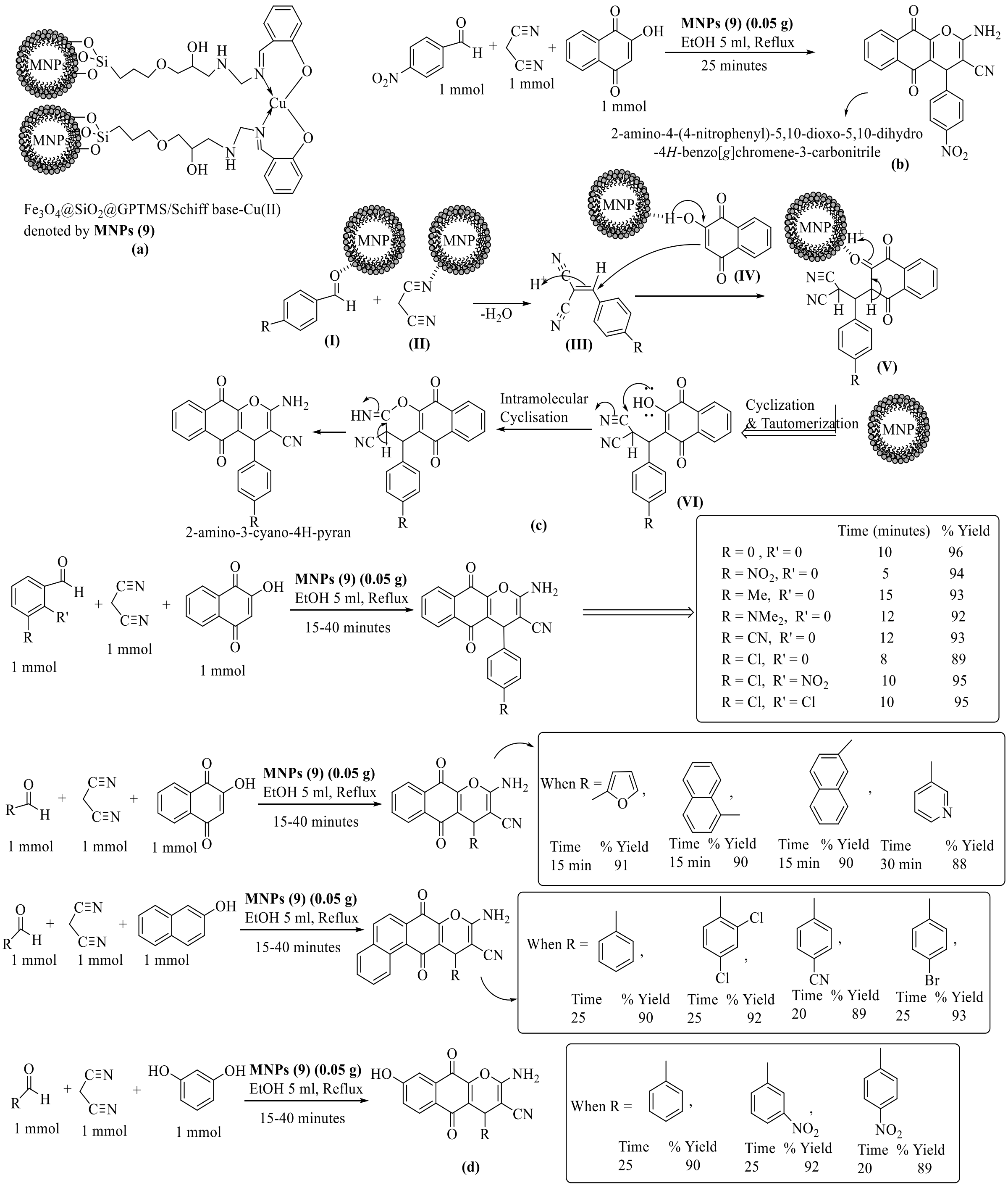
The magnetic nanocatalyst obtained was removed by an external magnet and can be reused further. The catalytic activity (9) was carried out in comparison with the catalytic activities of the Fe_3O_4@SiO_2@GPTMS/Schiff base, Fe_3O_4@SiO_2@GPTMS, Fe_3O_4, Schiff base and the Schiff base complex is depicted in table 1.



Scheme 1: (a) General schemes for synthesis of Schiff bases and their metal complexes (b) Plausible mechanism for the Ni-catalyzed one-pot multicomponent reaction for the synthesis of 2-amino-3-cyano-4H-pyran derivatives, (c) Synthetic pathways of unsymmetrical Salen ligands H_2L^{1-4} (1−4) and Schematic structure of Ni−(unsymmetrical Salen) complexes $[NiL^{1-4}]$ (5−8) and (d) Scheme for the one-pot multicomponent reaction for the synthesis of 2-amino-3-cyano-4H-pyran derivatives

Table 1
Studies of Comparative Catalytic Activity of the (9) under improved Conditions

S.N.	Catalyst	Time	% yield
1.	Fe_3O_4@SiO_2@GPTMS/Schiff base-Cu(II) **(9)**	25 min	94 in scheme 2(b)
2.	Fe_3O_4@SiO_2@GPTMS/Schiff base	6 h	33
3.	Fe_3O_4@SiO_2@GPTMS	4 h	35
4.	Fe_3O_4	1 h	45
5.	Schiff base	3 h	No reaction
6.	Schiff base complex	1.5 h	53



	Time (minutes)	% Yield
R = 0 , R' = 0	10	96
R = NO_2, R' = 0	5	94
R = Me, R' = 0	15	93
R = NMe_2, R' = 0	12	92
R = CN, R' = 0	12	93
R = Cl, R' = 0	8	89
R = Cl, R' = NO_2	10	95
R = Cl, R' = Cl	10	95

Scheme 2: (a) Fe_3O_4@SiO_2@GPTMS/Schiff base-Cu(II) magnetic nanoparticles catalyst (MNPs) (9) (b) Synthesis of 2-amino-4-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]-chromene-3-carbonitrile (c) Plausible mechanism for the Cu-catalyzed one-pot multicomponent reaction for the synthesis of 2-amino-3-cyano-4H-pyran derivatives, (d) Scheme for the one-pot multicomponent reaction for the synthesis of 2-amino-3-cyano-4H-pyran derivatives

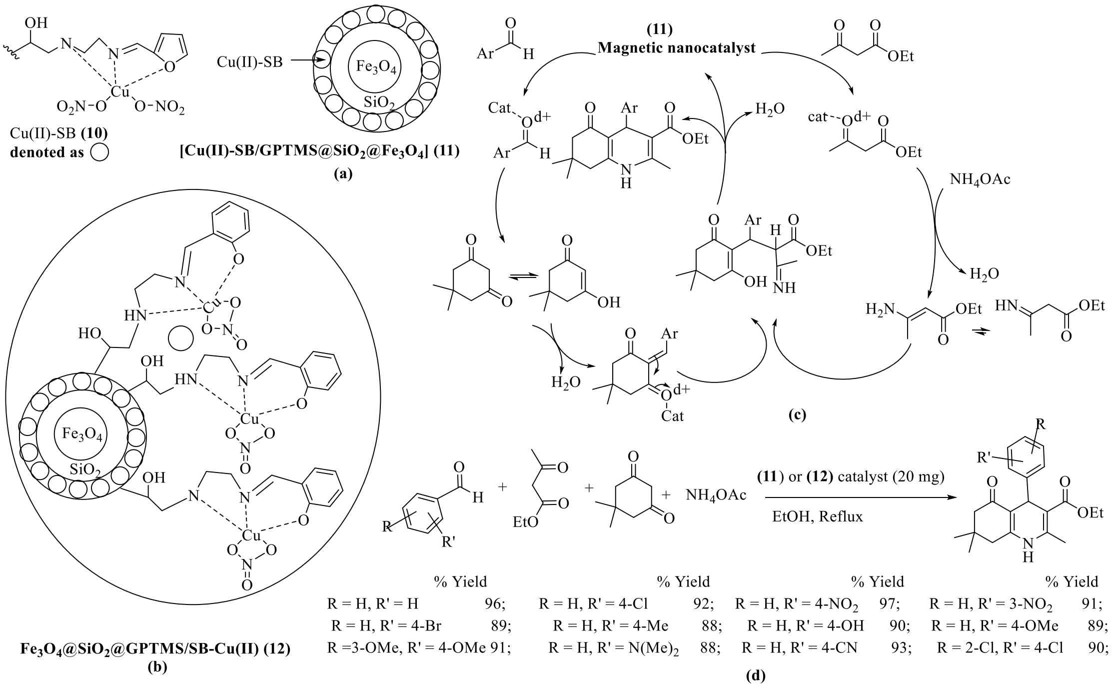
On refluxing ethanolic solution of equimolar amount of 4-nitrobenzaldehydes, 2-hydroxynaphthalene-1,4-dione and malononitrile in presence of nanocatalyst (9) yields 2-amino-4-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]-chromene-3-carbonitrile. The results showed that reaction in presence of the nanocatalyst (9) gives excellent results with 94 % yield after 25 minutes of reaction as in scheme 2(b). The nanocatalyst employed for the preparation of 2-amino-3-cyano-4H-pyran derivatives via one-pot three component reaction mixture of aromatic aldehydes, various phenols(2-hydroxynaphthalene-1,4-dione/resorcinol/β-naphthol) and malononitrile under reflux in ethanol is depicted in scheme 2.

The product isolated by using simple procedure, use of green solvent ethanol, no usage of column chromatography, excellent yields and short reaction time are main advantages of these catalytic reactions. It is worth noting that the nano catalyst can be easily separated from the reaction mixture by using an external magnet and washed with ethanol, dried and can be reused in seven sequential runs without any loss in their catalytic activity.

Useful catalyst metal(II)-SB MNPs based catalyst for synthesis of polyhydroquinoline derivatives by the Hantzsch reaction: Rezayati et al[38] also reported a stable, recyclable, economical and eco-friendly Schiff base complex of copper Cu(II)-SB (10) immobilized on core–shell magnetic nanoparticles [Cu(II)-SB/GPTMS@SiO_2@Fe_3O_4] (11). The nanocatalyst showed excellent catalytic efficiency for the one-pot synthesis of polyhydroquinoline derivatives by the Hantzsch reaction via condensation of dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1 mmol) and various aldehydes (1 mmol) and nanocatalyst (20 mg) in 25 ml of EtOH under reflux (1/2 h to 1.5 h) to obtain the product with excellent yield (88 to 97 %) as shown in scheme 3.

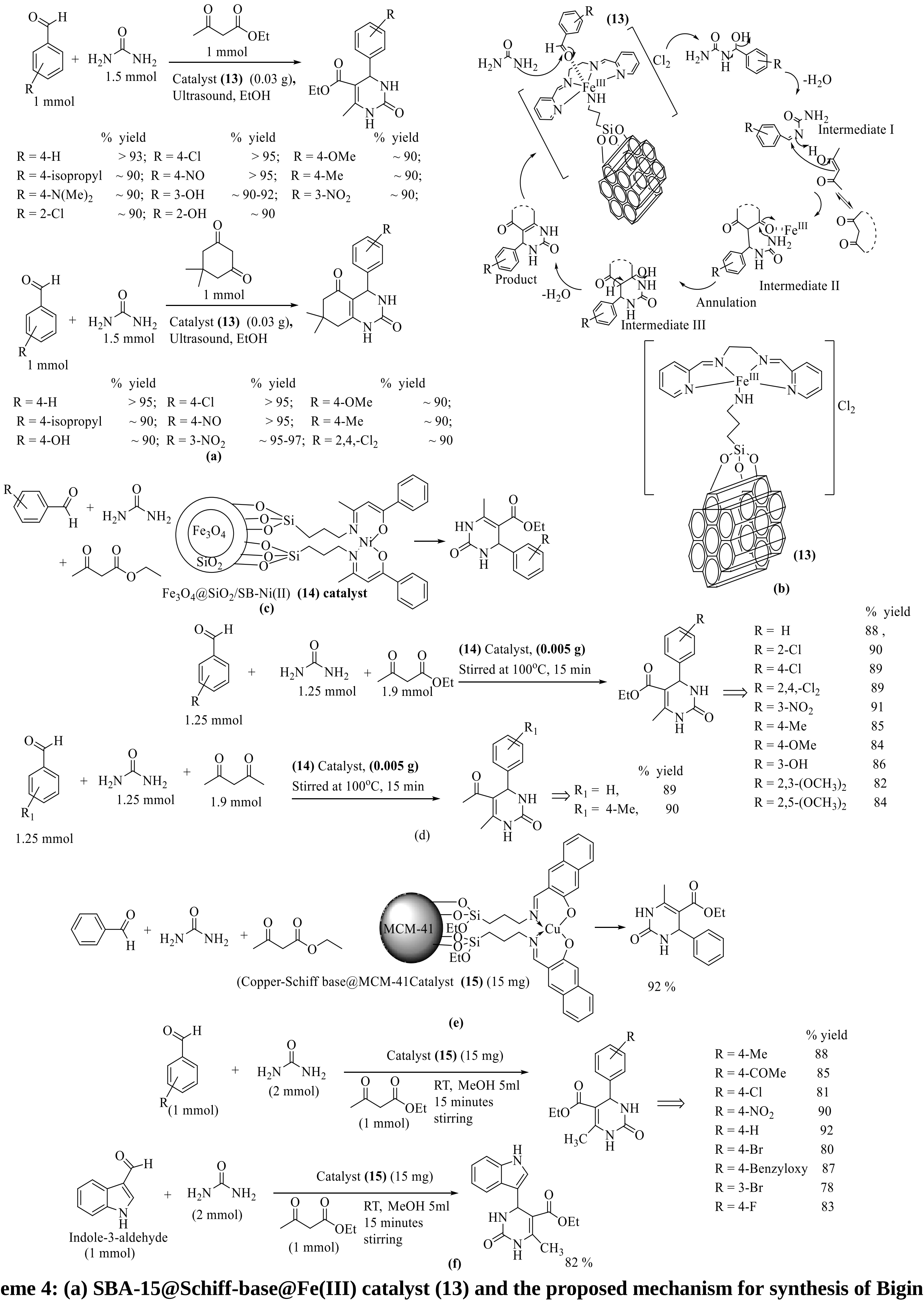
Rezayati et al[39] also synthesized a new heterogeneous nanocatalyst system including core/shell nanostructure Fe_3O_4@SiO_2@GPTMS/ Schiff base-Cu(II) nanocatalyst (12). The nanocatalyst acts as synthons for the one-pot synthesis of polyhydroquinoline derivatives of a wide range of aldehydes, dimedone, ethyl acetoacetate and ammonium acetate and Knoevenagel condensation product with high yields. Both the nanocatlysts (11) and (12) display identical organic transformations as shown in scheme 3.

Useful nanocatalyst based on metal (II)-Schiff base for synthesis of 3,4-dihydropyrimidin-2(1H)-ones and octahydroquinazoline-2,5-diones derivatives by the Biginelli-type reaction: Balali et al[8] synthesized Schiff base N,N′-bis-(pyridin-2-ylmethylene)-ethane-1,2-diamine by condensation reaction between ethylenediamine and pyridine-2-carbaldehyde, which on treatment with $FeCl_3.6H_2O$ gives SAB-15@Schiff-base@Fe(III) catalyst (13). They also synthesized Biginelli-type heterocyclic compounds comprising of 3,4-dihydropyrimidin-2(1H)-ones and octahydroquinazoline-2,5-diones using aryl aldehyde (1 mmol), ethyl acetoacetate or dimedone (1 mmol), urea (1.5 mmol) and SBA-15@Schif-base@Fe(III) (0.03 g) as a catalyst under ultrasound in EtOH at room temperature as shown in scheme 4a with excellent yields, easier and simple workup and reduced reaction times.



R, R'	% Yield	R, R'	% Yield	R, R'	% Yield	R, R'	% Yield
R = H, R' = H	96;	R = H, R' = 4-Cl	92;	R = H, R' = 4-NO_2	97;	R = H, R' = 3-NO_2	91;
R = H, R' = 4-Br	89;	R = H, R' = 4-Me	88;	R = H, R' = 4-OH	90;	R = H, R' = 4-OMe	89;
R =3-OMe, R' = 4-OMe	91;	R = H, R' = N$(Me)_2$	88;	R = H, R' = 4-CN	93;	R = 2-Cl, R' = 4-Cl	90;

Scheme 3: (a) Cu(II)-SB (10) (b) Schiff base complex of copper immobilized on core–shell magnetic nanoparticles catalyst [Cu(II)-SB/GPTMS@SiO_2@Fe_3O_4] (11) (c) Plausible mechanism for the Cu-catalyzed one-pot multicomponent reaction for synthesis of polyhydroquinoline derivatives by the Hantzsch reaction (d) One-pot multicomponent reaction for the synthesis of polyhydroquinoline derivatives by the Hantzsch reaction.



Scheme 4: (a) SBA-15@Schiff-base@Fe(III) catalyst (13) and the proposed mechanism for synthesis of Biginelli heterocycles by Ramos et al (b) Synthesis of 3,4-dihydropyrimidin-2(1H)-ones and octahydroquinazoline-2,5-diones using (13) (c) Fe_3O_4@SiO_2/SB-Ni(II) catalyst (14) (d) Synthesis of 3,4-dihydropyrimidine-2-(1H)-one derivatives by Biginelli reaction (e) Copper-Schiff base@MCM-41 catalyst (15) (f) Synthesis of 3,4-dihydropyrimidin-2(1H)-ones derivatives by the Biginelli reaction

After five successive runs, it showed no significant loss of activity, which can be proven on the basis of comparison of their FE-SEM image and FT-IR spectrum with the fresh catalyst. It is three component reaction as proposed earlier by Ramos et al[36] in scheme 4b. In this work, Fe(III) immobilized SBA-15 (13) acts as a catalyst based on Lewis acid causing activation of the aldehyde by coordinating with aldehydic O-atom, followed by nucleophilic attack of urea molecule yielding the intermediate I. The β-diketo enolate interacts to the imine bond of intermediate I forming an open-chain intermediate ureide II, which further activated on coordinating via O atom of one of the keto groups to the empty orbitals of Fe^{3+}.

Furthermore, NH_2 attack to the carbonyl carbon yielded cyclic intermediate III, followed by dehydration of intermediate III forming a six membered expected product dihydropyrimidines and octahydroquinazolinones.

Abravi et al[1] synthesized a general and aliphatic Schiff base immobilized on magnetite nanoparticles, a new core–shell nanocatalyst, Fe_3O_4@SiO_2/Schiff base of Ni(II), formulated as Fe_3O_4@SiO_2/SB-Ni (14), a magnetic nanoparticles catalyst. It showed significant catalytic activity to synthesize 3,4-dihydropyrimidine-2-(1H)-one.

This reaction is a substitute of the solvent-free Biginelli reaction, a multicomponents chemical reaction between an aldehyde, β-keto ester and urea and was carried out with excellent yields (82–91%) within 15 minutes yielding dihydropyrimidones as depicted in scheme 4 (c) and (d).

Biginelli products occupy a superb position in drug discoveries and they can be frequently utilized as library products for screening and can be further modified into significant bioactive compounds. Arumugam et al[5] reported Schiff base (15) by condensation of 3-aminopropyltriethoxysilane and 2-hydroxy-1-naphthaldehyde and their Cu^{II} complex.

They also investigated Schiff-base complex immobilized mesoporous silica-41 (Copper-Schiff base@MCM-41) using the ultrasonication method. It showed that copper-Schiff base@MCM-41 is superior and effective heterogeneous catalyst towards the Biginelli reaction for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) derivatives with high yield in shorter time at room temperature. Furthermore, the catalyst showed remarkable stability and was utilized five times without loss of catalytic activity.

The above results established that the newly synthesized catalyst may be used as a promising and sustainable tool for catalysing organic transformations. The nanocatalyst showed excellent catalytic efficiency for the one-pot synthesis of DHPMs derivatives by the Bignelli reaction via condensation of substituted benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (2 mmol) and nanocatalyst (15 mg) in 5 ml of MeOH under RT stirring for 15 minutes to obtained the product with excellent yield (80 to 92 %) as shown in scheme 4 (e) and (f). Paul et al[33] demonstrated the synthesis of nanostructured metal oxides, produced from the thermal breakdown of two new Schiff base metal complexes of Zn(II) and Cu(II) acting as inexpensive precursor.

Using ZnO (16) and CuO (17) nanoparticles, the optimal conditions achieved are 2 mol% catalysts at 75 ◦C with ethanol as solvent under reflux conditions which yield 94% and 96% Biginelli adducts respectively as depicted in scheme 5 (a) and 5 (b). Ethanolic medium gives products obtained with maximum yields for both the nanocatalysts ZnO (94%) and CuO (96%). After four successive runs, it showed no significant loss of activity.

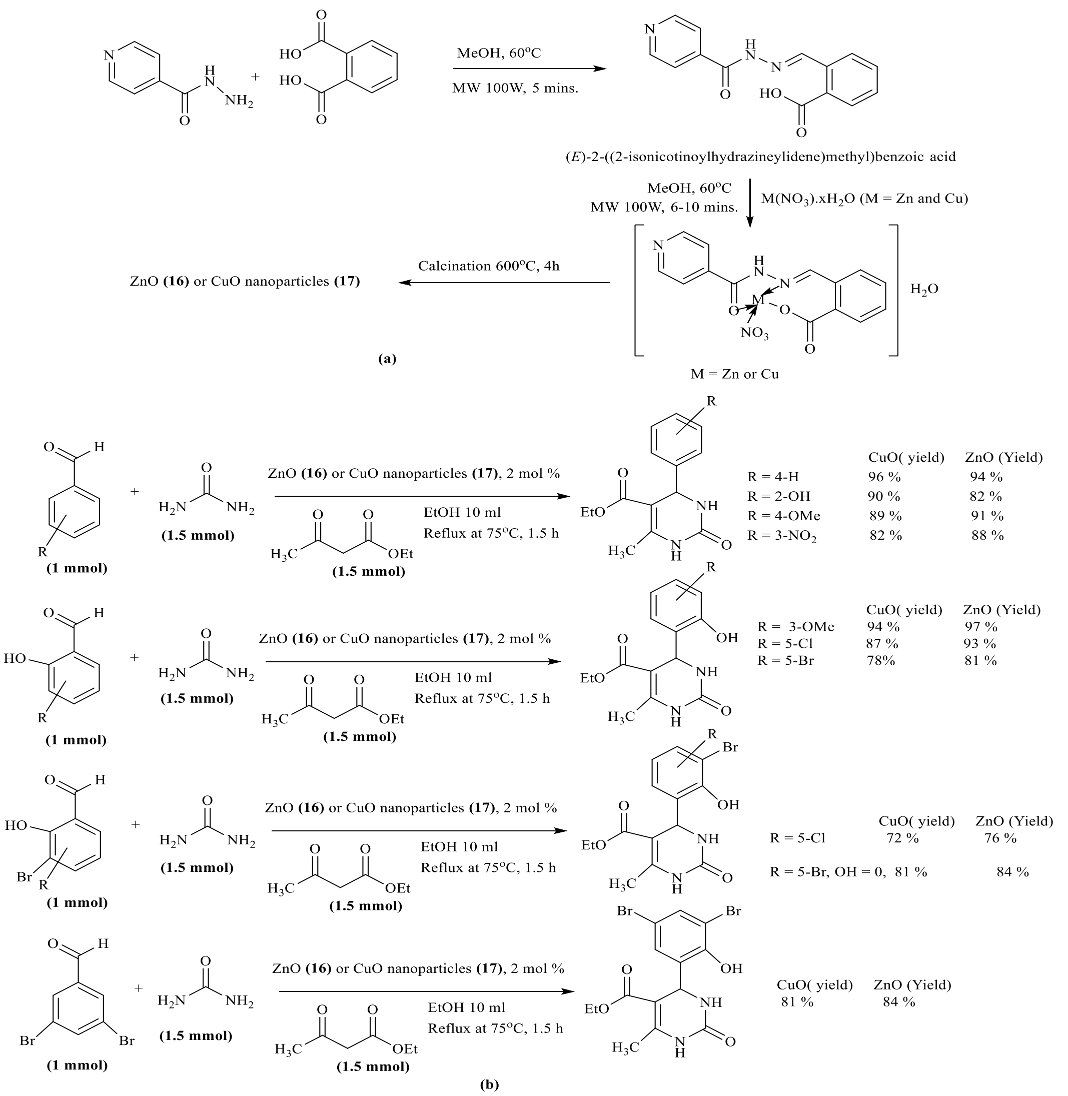
Useful metal(II)-Schiff base or nanocatalyst based on metal (II)-Schiff base for Suzuki–Miyaura cross-coupling: Ease of synthesis and higher yield have made Schiff bases an attractive target for the development of novel ligands in coordination chemistry of transition metal ions. Neshat et al[28] reported novel Schiff base (18-25) by condensing aromatic amines with pyridoxal-5'-phosphate as in scheme 6 (a).

They studied catalytic activity of some of the selected palladium complexes (26-29). They performed Suzuki cross-coupling reaction of a series of aryl halides with boronic acids as depicted in scheme 6 (b).

$Pd(L_8)_2$ (29) has L comprising of methoxy group on para position of aryl imine displaying the highest activity at low catalyst loading (0.75% mol) at RT. Different reaction conditions are: aryl iodides (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (0.75 mmol), $Pd(L_8)_2$ (0.65 mol %) and H_2O:EtOH (1:1 mL), R.T. 24 h, all the components are same as (a), except aryl bromides (0.5 mmol) and the concentration of $Pd(L_8)_2$ is 0.75 mol %.

Puzari et al[35] reported Schiff base ligand (30) by condensation reaction between two equivalents of sodium salicylaldehyde-5-sulfonate with one equivalent of 2-aminobenzylamine in EtOH and their water-soluble palladium (II) complex (31) as shown in scheme 6c. The catalytic activity of the complex (31) was carried out based on Suzuki–Miyaura cross-coupling reactions of aryl/heteroaryl chlorides with arylboronic acids in water but addition of cetyltrimethylammonium bromide a phase-transfer agent increases the yield of diaryls as depicted in table 2.

They also demonstrated the catalytic activity of (31) based on Sonogashira cross-coupling reactions of phenylacetylene (0.65 mmol), aryl bromide (0.5 mmol), Et_3N (1.3 mmol), CuI as cocatalyst (0.5 mol%), catalyst (31) (0.5 mol%), H_2O (4 mL) and [b]CTAB (0.5 mmol) to generate conjugated arylalkynes as depicted in scheme 6c and table 2 with excellent yield.

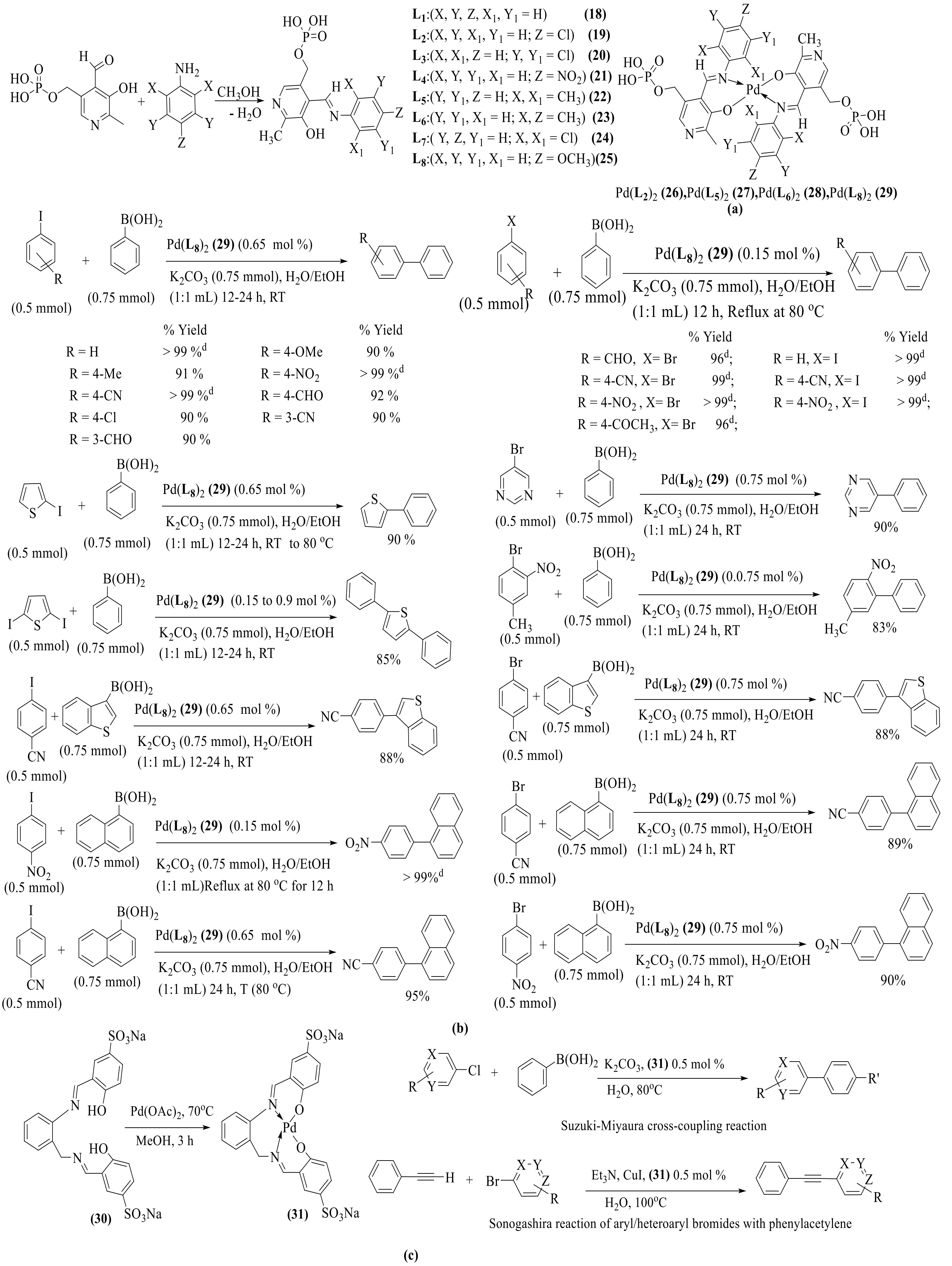


Scheme 5: (a) ZnO (16) and CuO (17) nanocatalyst (10) (b) One-pot multicomponent reaction for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones derivatives by the Biginelli reaction

Table 2
Suzuki–Miyaura cross-coupling reaction of aryl/heteroaryl chlorides with arylboronic acids in water

S.N.	R	X	Y	R’	Time(h)	% Yield
1	4-NO_2	CH	CH	H	5	97
2	4-OCH_3	CH	CH	H	8	83 (86)^c
3	H	CH	CH	H	4	98
4	4-CHO	CH	CH	H	8	79
5	2-CHO	CH	CH	H	8	71
6	4-NO_2	CH	CH	4-CH_3	6	82
7	4-NO_2	CH	CH	4-Cl	6	89
8	4-OCH_3	CH	CH	4-CH_3	8	77
9	4-OCH_3	CH	CH	4-Cl	7	83
10	2,5-di-OCH_3	CH	C	H	8	66
11	H	N	CH	H	6	89
12	H	N	N	H	7	83
13^d	3-CH_3	S	-	H	8	78
14	3-OCH_3	CH	CH	H	8	80
15	4-CH_3	CH	CH	H	8	84

Reaction Conditions: boronic acid: 0.65 mmol, aryl halide: 0.5 mmol, K_2CO_3: 1.3 mmol, Catalyst **(30)**: 0.5 mol%. H_2O: 4 mL. ^{b}GC yield. ^{c}CTAB was used (0.5 mmol). ^{d}aryl halide: 2-chloro-3-methylthiophene.



Scheme 6: (a) Active catalyst Pd(L_8)$_2$ (29) (b) One-pot reaction for the synthesis of Suzuki coupling reactions catalyzed by Schiff base based palladium complex (29) (c) Synthesis of diaryls and arylalkynes using Suzuki-Miyaura cross-coupling and Sonogashira reaction by catalyst (31).

Table 3
Sonogashira reaction of aryl/heteroaryl bromides with phenylacetylene in water

S.N.	R	X	Y	Z	Time(h)	% Yield
1	4-$COCH_3$	CH	CH	C	7	81 (84)[b]
2	H	CH	CH	N	6	97
3	4-CHO	CH	CH	C	7	94
4	H	N	CH	CH	6	82
5	4-NO_2	CH	CH	C	6	98
6	4-CH_3	CH	CH	C	8	65
7	2,5-di-OCH_3	C	CH	CH	9	47
8	3-NO_2	CH	C	CH	7	82
9	H	CH	N	CH	6	87
10	2-CH_2OH	C	CH	CH	8	37

Reaction Conditions: Phenylacetylene: 0.65 mmol, aryl bromide: 0.5 mmol, Et_3N: 1.3 mmol, CuI: 0.5 mol%, Catalyst(C1): 0.5 mol%. H_2O: 4 mL. [b]CTAB was used (0.5 mmol)

Table 2 demonstrate that aryl bromides bearing electron-withdrawing substituents such as –$COCH_3$, –CHO, –NO_2 at para positions (Table 2, S.N. 1, 3, 5) have excellent yield of the expected aryl-alkynes products whereas aryl bromides containing electron-donating groups such as –CH_3, –OCH_3, –CH_2OH etc. yielded moderate-to-low products. The catalytic reaction as depicted in scheme 6c and table 3, entries 2, 4, 9. 4, 2 and 3-bromopyridines undergo coupling reaction easily with phenylacetylene yields of 97, 82 and 87% (Table 2, entries 2, 4, 9). Schiff-base complex acts as catalyst in both the Suzuki–Miyaura and the Sonogashira cross-coupling reactions with excellent yields.

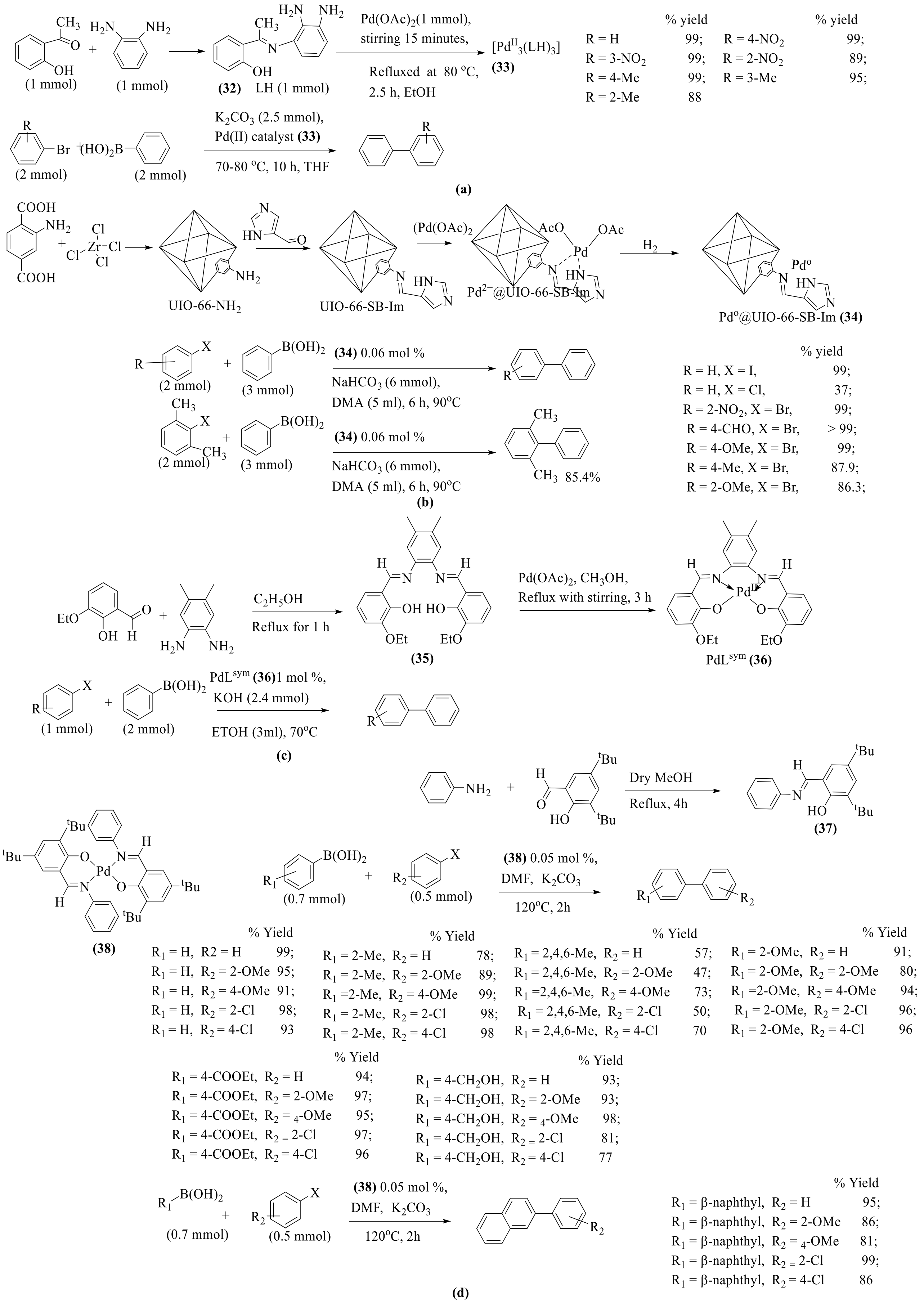
Mandal et al[22] reported Schiff base 2-(1-(2-aminophenylimino)ethyl)phenol (LH_3) (32) and their $[Pd^{II}{}_3(LH)_3]$ complex (33), acting as efficient catalyst and undergoes Suzuki-Miyaura coupling reaction on treatment of bromobenzene or substituted bromobenzene's with phenylboronic acid yielding biphenyl or substituted biphenyls, respectively *viz.* Biphenyl, 1-Phenyl-4-nitrobenzene, 1-phenyl-5-nitrobenzene, 1-phenyl-6-nitrobenzene, 1-phenyl-4-methylbenzene, 1-phenyl-5-methylbenzene and 1-phenyl-6-methylbenzene with product yield 88 to 90 % as in scheme 7a.

Liu et al[21] synthesized Pd^o@UIO-66–SB–Im (34) Pd Clusters on new Schiff Base–Imidazole-Functionalized MOFs having 1.5 nm size and studied their enhanced catalytic activity in the Suzuki coupling reaction by yielding identical product as found in Suzuki coupling reactions, where treatment of phenyboronic acid and bromobenzene obtained gives biphenyl (>99%) under mild reaction conditions.

Furthermore, the catalyst can be actively used six times. The coupling of bromobenzene having electron-withdrawing groups such as nitro, aldehyde, or methoxy group gives more yield in their respective biphenyl products whereas coupling of bromobenzene with electron-donating groups such as methyl group gives low yields of products suggesting that the withdrawing groups in bromobenzene facilitate weakening of C-Br bond while the electron-donating groups in bromobenzene strengthen C-Br bond. The bond dissociation energy of C–X (X = Cl, Br, I) bond is in the order C–Cl > C–Br > C–I. The coupling of aryl iodobenzene with phenylboronic acid yield is > 99% of biphenyl, while coupling of chlorobenzene only yields 37% of biphenyl. Kargar et al[18] reported a new ONNO-tetradentate chelating ligand (H_2L^{Sym}) (35) by condensation reaction between 4,5-dimethyl-1,2-phenylenediamine and 3-ethoxysalicylaldehyde and their Pd(II) (36) complex. The palladium complex (36) demonstrates excellent catalytic activity when coupling reaction between different aryl halides and phenylboronic acid was carried out under optimized conditions and the results are shown in table 4.

Aryl iodide yields better results than aryl bromide and aryl bromide yields better results than aryl chloride. PdLSym catalyzed the Suzuki-Miyaura cross-coupling reactions where the following stoichiometric conditions are followed: aryl halide (1 mmol), phenylboronic acid (2 mmol), KOH (2.4 mmol), EtOH (3 mL), PdLSym (1 mol %) at 70 °C to synthesize various biphenyls. As compared to conventional Suzuki coupling reaction, this catalytic coupling process offers many benefits such as mild reaction conditions, high selectivity and simple work-up. In the presence of catalyst, the electron-withdrawing and electron-donating groups on aryl halide facilitate the coupling products in excellent yield as depicted in scheme 7.

Meena et al[23] reported the novel Schiff base **(37)** by condensing aniline with 3,5-di-tert-butylsalicylaldehyde and their Pd(II) complex (38). They also studied catalytic activity of Pd(II) complex (38) by performing Suzuki-Miyaura coupling of a series of aryl halides with boronic acids as depicted in scheme 7d, when catalyst (38) (0.05 mol%) was treated with K_2CO_3 (5.0 mmol) base, iodobenzene (2.5 mmol) and phenylboronic acid (3.5 mmol) and refluxed at 120°C in DMF for 2-4 h yields C–C coupling products. The catalyst (38) shows a significant activity against a variety of substituted phenyl or β-naphthyl boronic acids and substituted phenyl halide having electron donating/electron withdrawing substituents. Products formed were obtained in excellent yields.



% yield
R = H 99; R = 4-NO$_2$ 99;
R = 3-NO$_2$ 99; R = 2-NO$_2$ 89;
R = 4-Me 99; R = 3-Me 95;
R = 2-Me 88

% yield
R = H, X = I, 99;
R = H, X = Cl, 37;
R = 2-NO$_2$, X = Br, 99;
R = 4-CHO, X = Br, > 99;
R = 4-OMe, X = Br, 99;
R = 4-Me, X = Br, 87.9;
R = 2-OMe, X = Br, 86.3;

% Yield
R$_1$ = H, R2 = H 99;
R$_1$ = H, R$_2$ = 2-OMe 95;
R$_1$ = H, R$_2$ = 4-OMe 91;
R$_1$ = H, R$_2$ = 2-Cl 98;
R$_1$ = H, R$_2$ = 4-Cl 93

% Yield
R$_1$ = 2-Me, R$_2$ = H 78;
R$_1$ = 2-Me, R$_2$ = 2-OMe 89;
R$_1$ =2-Me, R$_2$ = 4-OMe 99;
R$_1$ = 2-Me, R$_2$ = 2-Cl 98;
R$_1$ = 2-Me, R$_2$ = 4-Cl 98

% Yield
R$_1$ = 2,4,6-Me, R$_2$ = H 57;
R$_1$ = 2,4,6-Me, R$_2$ = 2-OMe 47;
R$_1$ =2,4,6-Me, R$_2$ = 4-OMe 73;
R$_1$ = 2,4,6-Me, R$_2$ = 2-Cl 50;
R$_1$ = 2,4,6-Me, R$_2$ = 4-Cl 70

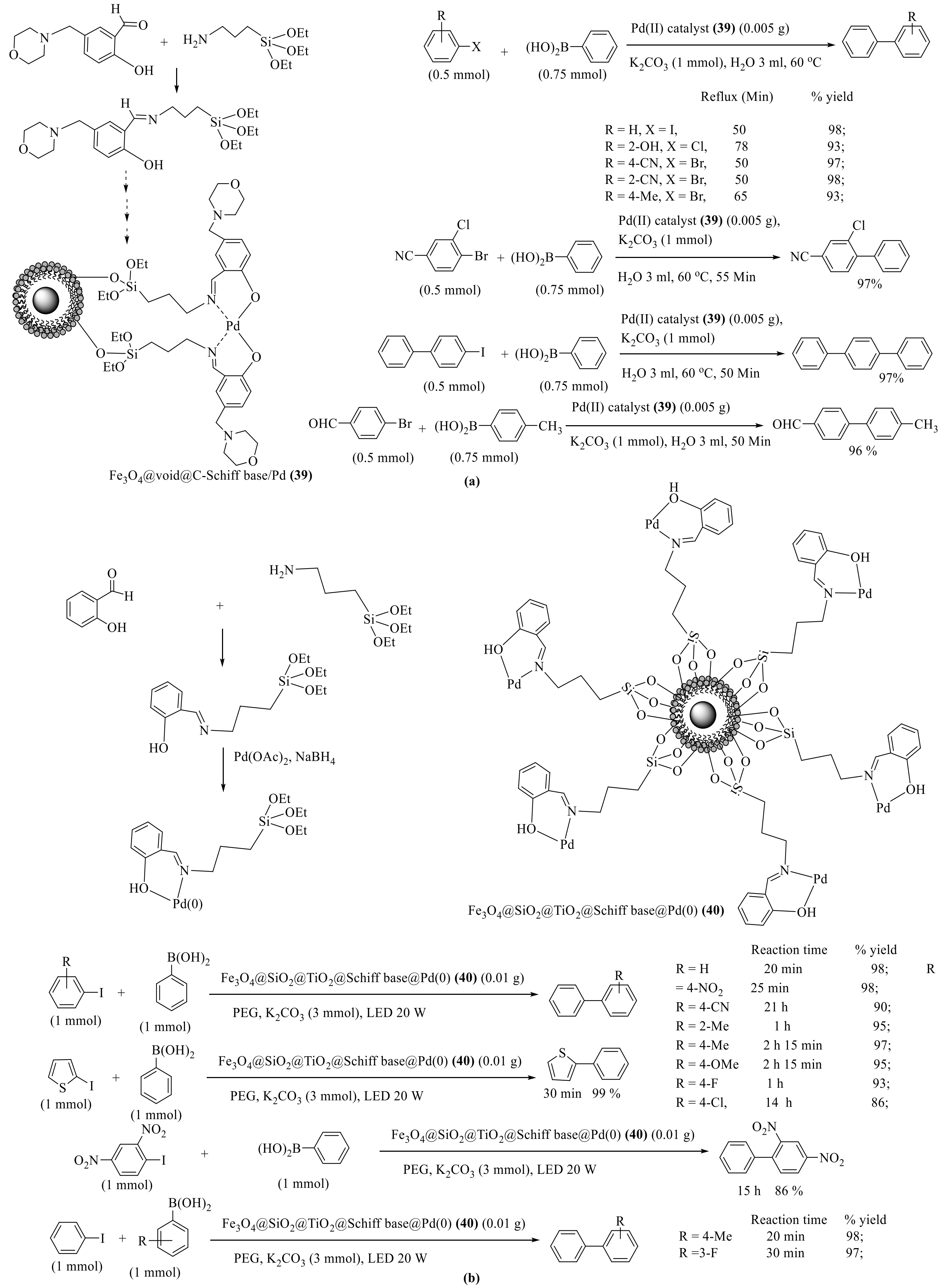
% Yield
R$_1$ = 2-OMe, R$_2$ = H 91;
R$_1$ = 2-OMe, R$_2$ = 2-OMe 80;
R$_1$ =2-OMe, R$_2$ = 4-OMe 94;
R$_1$ = 2-OMe, R$_2$ = 2-Cl 96;
R$_1$ = 2-OMe, R$_2$ = 4-Cl 96

% Yield
R$_1$ = 4-COOEt, R$_2$ = H 94;
R$_1$ = 4-COOEt, R$_2$ = 2-OMe 97;
R$_1$ = 4-COOEt, R$_2$ = $_4$-OMe 95;
R$_1$ = 4-COOEt, R$_2$ = 2-Cl 97;
R$_1$ = 4-COOEt, R$_2$ = 4-Cl 96

% Yield
R$_1$ = 4-CH$_2$OH, R$_2$ = H 93;
R$_1$ = 4-CH$_2$OH, R$_2$ = 2-OMe 93;
R$_1$ = 4-CH$_2$OH, R$_2$ = $_4$-OMe 98;
R$_1$ = 4-CH$_2$OH, R$_2$ = 2-Cl 81;
R$_1$ = 4-CH$_2$OH, R$_2$ = 4-Cl 77

% Yield
R$_1$ = β-naphthyl, R$_2$ = H 95;
R$_1$ = β-naphthyl, R$_2$ = 2-OMe 86;
R$_1$ = β-naphthyl, R$_2$ = $_4$-OMe 81;
R$_1$ = β-naphthyl, R$_2$ = 2-Cl 99;
R$_1$ = β-naphthyl, R$_2$ = 4-Cl 86

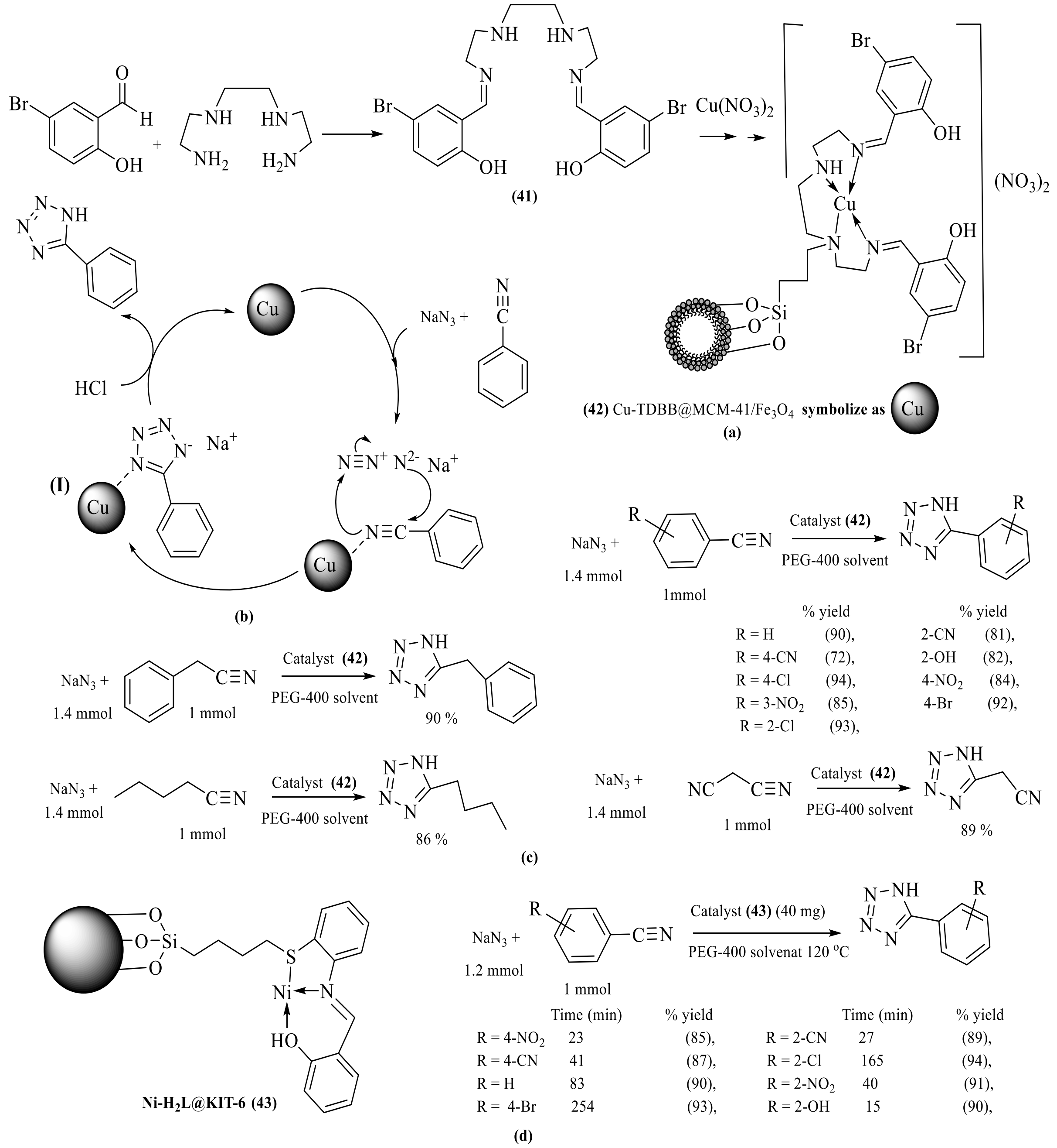
Scheme 7: Suzuki-Miyaura cross-coupling reaction of aryl halide with phenylboronic acid in presence of (a) catalyst (33), (b) catalyst (34) and (c) catalyst (36) (d) Catalyst (38)



Scheme 8: Suzuki-Miyaura cross-coupling reaction of aryl halide with phenylboronic acid in presence of (a) catalyst (39), (b) catalyst (40)

Table 4
PdLSym catalyzed the Suzuki-Miyaura cross-coupling reactions

S.N.	R	X	Time(h)	% Yield
1	H	I	3.5	99
2	H	Br	4	97
3	H	Cl	7	94
4	4-NO_2	Cl	8	39
5	2-NO_2	Cl	7	41
6	3-$COCH_3$	Cl	24	60
7	4-CN	Cl	24	59
8	4-$COCH_3$	Br	6	82
9	3-CN	Br	6	85
10	4-CH_3	I	4.5	91
11	4-OCH_3	I	4	97



Scheme 9: (a) Cu-TDBB@MCM-41/Fe_3O_4 (42) (b) A proposed mechanism of formation of 5-aryl-1H-tetrazoles using (42) (c) Synthesis of tetrazole derivatives using (42) (d) Synthesis of tetrazole derivatives using (43)

Barzkar et al[10] synthesized a novel magnetic nanomaterial modified by functionalized carbon shell with Schiff-base/Palladium, written as Fe_3O_4@void@C-Schiff-base/Pd (39). They performed Suzuki coupling reactions in the presence of nanocatalyst Fe_3O_4@Void@C-Schiff-base/Pd (39) (0.005 g), aryl halide (0.5 mmol,), phenylboronic (0.75 mmol), K_2CO_3 (1 mmol) and H_2O (3 mL) and efficiently synthesized Suzuki coupling products in excellent yield within a short span of time as shown in scheme 8a. It has been observed that the (39) showed large activity and can be reused for 10 runs without loss in its efficiency. Azadi et al[6] demonstrated a novel Nano photocatalyst complex $Fe_3O_4@SiO_2@TiO_2$@Schiff-base@Pd(0) (40) by treatment of $Fe_3O_4@SiO_2@TiO_2$, 3-aminopropyltriethoxysilane, salicylaldehyde, followed by addition of $Pd(OAc)_2$ and $NaBH_4$. They obtained substituted biphenyls by reaction of aryl bromide (1 mmol), aryl boronic acid (1 mmol), K_2CO_3 (3 mmol), Solvent: PEG-400, $Fe_3O_4@SiO_2@TiO_2$@Schiff-base@Pd(0) (40) (0.01 g, 0.9×10^{-3} mol%, 0.159 wt%) as depited in scheme 8b.

The catalyst (40) is the example of efficient magnetic nano photocatalyst for the synthesis of biphenyl compounds and can be recyclable for eight consecutive times. As the catalyst acts as magnetic nanoparticles, thereby showed high dispersion and activity, thereby, producing Suzuki-Miyaura coupling products in excellent yields.

Useful metal(II)-Schiff base or nanocatalyst based on metal (II)-Schiff base for synthesis of tetrazoles: Nikoorazm et al[29] synthesized 2,2′-((1Z,11Z)-2,5,8,11-tetraazadodeca-1,11-diene-1,12-diyl)bis(4-bromophenol) (TDBB) as a new Schiff-base ligand (41), magnetic MCM-41 nanoparticles (MCM-41/Fe_3O_4), TDBB @MCM-41/Fe_3O_4 nanoparticles and their copper Schiff-base complex Cu-TDBB@MCM-41/Fe_3O_4 (42). It is noted that the nanocatalyst can be easily separated from the reaction mixture with the help of an external magnet and it was washed with ethanol, dried and finally, reused in six sequential runs without any loss in activity. Most importantly, environmentally friendly valuable and reusable nanocatalysts were utilized for the synthesis of 5-substituted 1H-tetrazoles derivatives via one-pot two component reaction mixture of aromatic benzonitrile (1 mmol), sodium azide (1.4 mmol), Cu-TDBB@MCM-41/Fe_3O_4 (0.040 g) and PEG-400 solvent (1 mL) in a sealed container with continuous stirring and heating at 120°C for time span in the range between 145 minutes to 570 minutes.

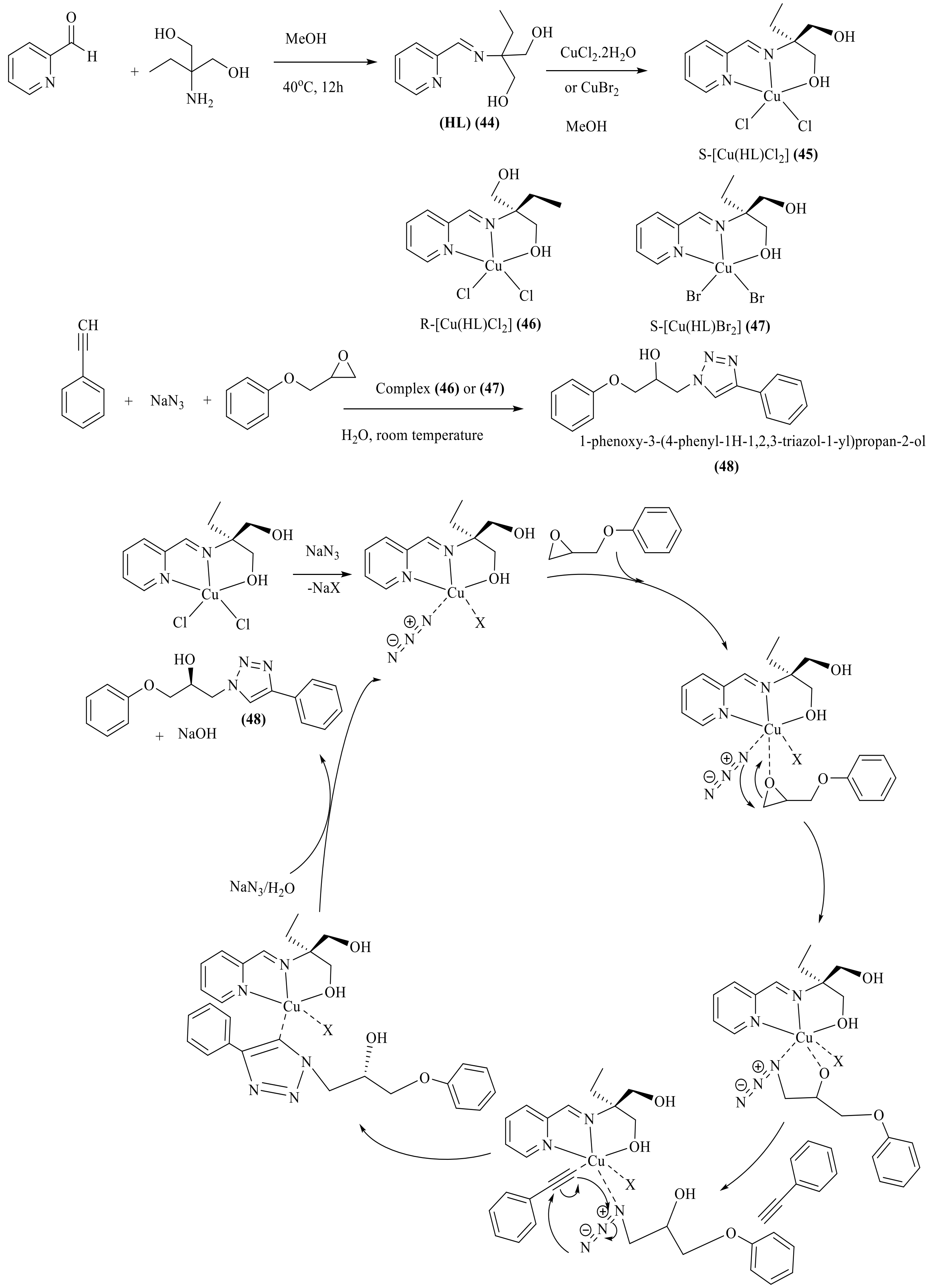
The catalyst (42) first activates the benzonitrile, followed by [3+2] cycloaddition of the cyanide group of nitriles with azide ion leading to the formation of intermediate (I), which on protonation yields the 5-substituted 1H-tetrazole[16] as shown in scheme 9 (a-c). Akbari et al[3] demonstrated the synthesis of Ni-Schiff base catalyst stabilized on 3D KIT-6 mesoporous silica named as Ni-H_2L@KIT-6 (43) (40 mg), which on treatment with benzonitrile (1 mmol), Ni-H_2L@KIT-6 catalyst and NaN_3 (1.2 mmol) in PEG at 120 °C undergoes [3+2] cycloaddition reaction to produce various substituted homo-selective tetrazoles in excellent yields as given in scheme 9d. The catalytic efficiency remains effective for five successive runs without any loss in its activity.

Useful chiral copper(II)-Schiff base for synthesis of β-hydroxy-1,2,3-triazole: Ajormal et al[2] reported synthesis of chiral Schiff base ligand (HL) (44) by the reaction of equimolar ratio of 2-amino-2-ethyl-1,3-propanediol and pyridine-2-carbaldehyde in methanol. HL on treatment with $CuCl_2\cdot 2H_2O/CuBr_2$ in MeOH yields Cu(II) complexes with general formula of S-[Cu(HL)Cl_2] (45) and R-[Cu(HL)Cl_2] (46) and S-[Cu(HL)Br_2] (47) respectively. Both enantioselective catalysts (46) and (47) catalytically transform epoxy, acetylene and azide into asymmetric click synthesis of β-hydroxy-1,2,3-triazole under mild condition as shown in scheme 10a. The first step is the azide and epoxide are ligated with the Cu(II) center, where azide acts as a nucleophile, attacks the less substituted carbon of the epoxide ring forming alkyl-azide intermediate.

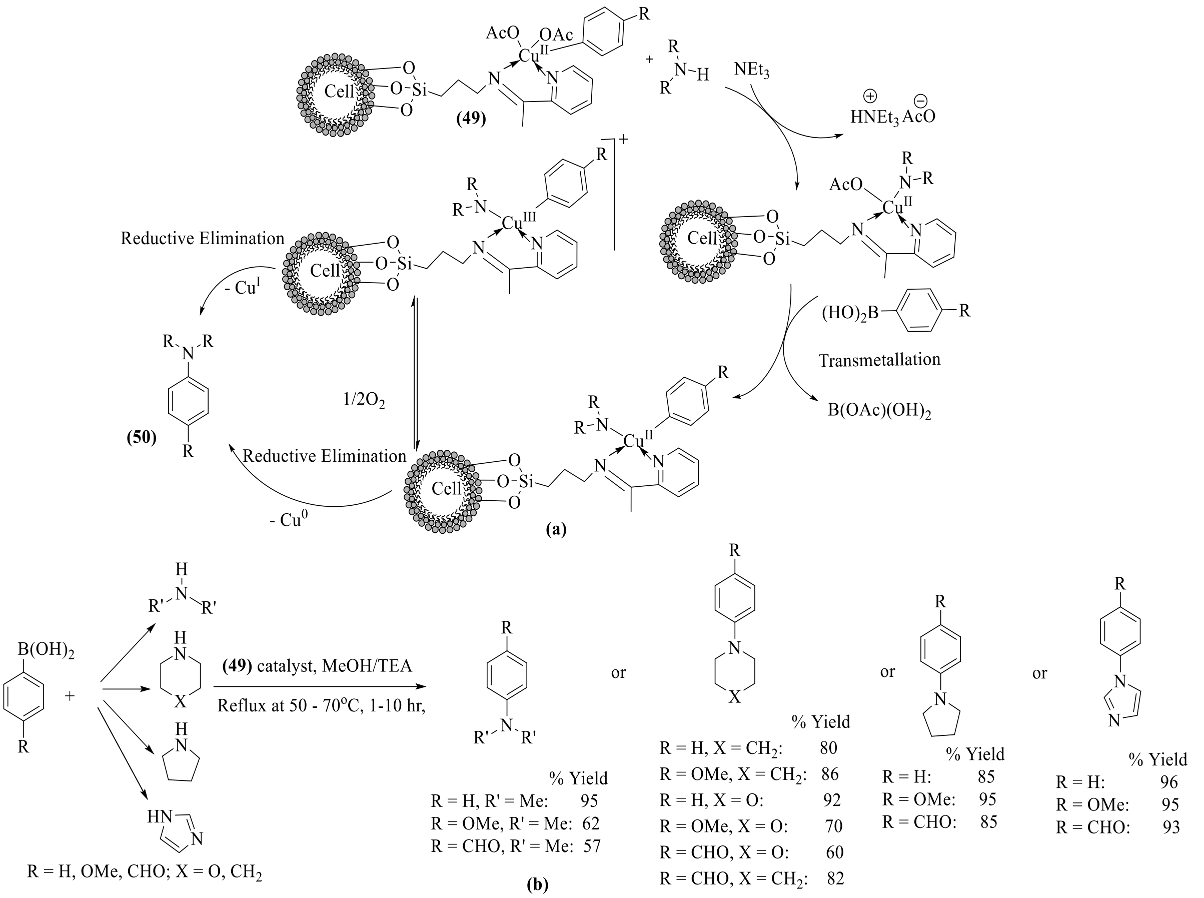
A chiral Cu(II) complex facilitates ring opening reaction followed by the formation of chiral 1,2,3-triazole. The phenyl acetylene ligates to the Cu(II) and the cycloaddition reaction of copper(II) acetylide with alkyl-azide intermediate producing a triazole ring via. click reaction. Finally, protonation of the Cu–C centre in the presence of water solvent and NaN_3 gives β-hydroxy-1,2,3-triazole (48), followed by regeneration of catalyst as shown in scheme 10b.

Useful copper(II)-Schiff base for Synthesis of N-aryl amines by Chan–Lam coupling: Pharande et al[34] designed and synthesized cellulose-immobilized Cu(II) Schiff base complex [Cell-AP-Cu(II)] (49) by the reaction of Schiff base functionalized cellulose (Cell-AP) with $Cu(OAc)_2$ in ethanol under reflux. The catalytic activity of [CellAP-Cu (II)] was carried in accordance with the most promising and versatile Chan–Lam coupling reactions[13] where phenylboronic acids (1 mmol), secondary amines (1.5 mmol), triethylamine (1 mmol, 0.139 ml in 5 mL MeOH) plus (49) 0.11 mol % (40 mg) were taken in a 10 ml round bottomed flask with continuous stirring at ambient temperature for the well-defined time. The organic transformation caused due to faster reductive elimination from Cu(III) species forming product is well illustrated in scheme 11a.

Consequently, oxidative coupling of boronic acids with N-H/O-H/S-H containing compounds in the presence of O_2 undergoes organic transformation producing carbon-heteroatom bonds especially of C–O, C–N and C–S type products (50) as in scheme 11 (b). The prime importance of using (49) catalyst is eco-friendliness with minimal catalyst loading (0.11 mol %), recyclability of the catalyst (up to 5 times), moderate reaction conditions, high yield of the products and finally the greener approaches in the synthesis may pave the way for future research.



Scheme 10: (a) synthesis of β-hydroxy-1,2,3-triazole using catalyst (46) and (47), (b) Mechanism for Click synthesis of β-hydroxy-1,2,3-triazole using catalyst (46) and (47)



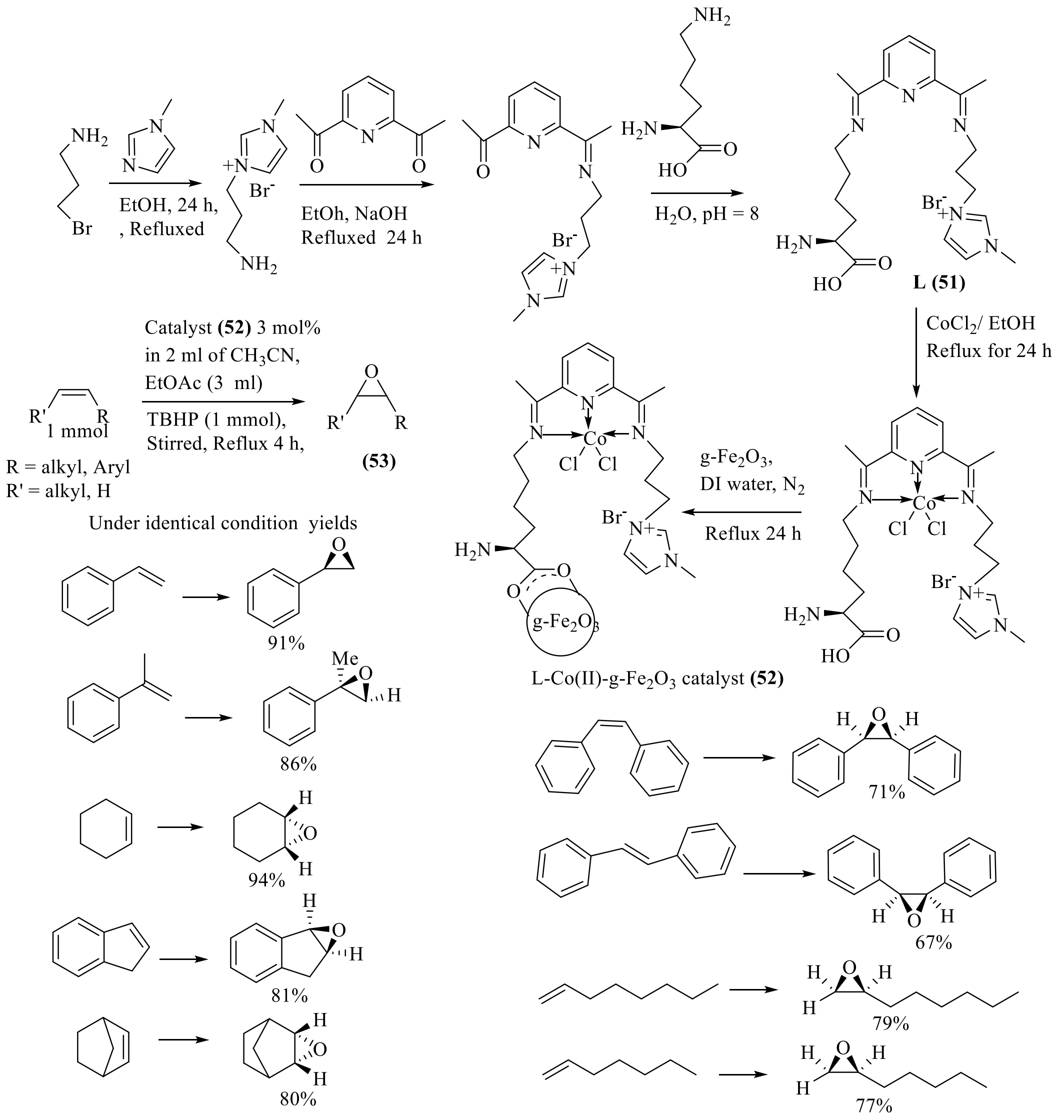
Scheme 11: (a) Mechanism for Cham Lam Coupling using [Cell-AP-Cu(II)] (49) as catalyst (b) Chan–Lam coupling of phenylboronic acids and secondary amines

Useful cobalt(II)-Schiff base for catalytic epoxidation of alkenes: The epoxidation of alkenes is highly carried out due to their significant role as essential starting materials for a wide variety of products. Mohammadian et al[27] investigated a new unsymmetrical Schiff base (51) and their chiral magnetic Co^{II}-complex as catalyst, L-Co(II)-γ-Fe_2O_3 (52) containing ionic liquid groups as a reusable green catalyst in the epoxidation of alkenes. The catalytic reaction was carried out by treatment of alkene (1 mmol), ter-butyl hydroperoxide (TBHP 1 mmol) and 3 mol% of catalyst in 2 ml of acetonitrile, followed by continuous stirring at 70 °C for 4 h giving epoxidation of various alkenes (53) as depicted in scheme 12.

The catalyst (52) can be easily recovered separated using an external magnet and also can be reused for five runs without significantly loss of efficiency and activity. The catalyst demonstrates significant catalytic activity, in addition to stereo, regio and chemoselectivity enantioselectivity, making it a promising candidate for alkene epoxidation reactions in terms of excellent products yield, recyclability, eco-friendly and economically feasible.

Useful ruthenium(II)-Schiff base for catalytic reduction of aromatic ketones into alcohol: Turan et al[51] synthesized two new Schiff base ligands, (E)-ethyl 2-(2-hydroxybenzylideneamino)-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate (L^1H) (54) and (E)-ethyl2-(2-hydroxy-3-methoxybenzylideneamino)-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrothieno[2,3 -c] pyridine-3-carboxylate (L^2H) (55) and their respective Ru^{II} complexes, $[L^1Ru(p\text{-cymene})]Cl{\cdot}2.5H_2O$ (56) and $[L^2RuCl(p\text{-cymene})]1.5H_2O$ (57). They studied the catalytic activities of the Ru^{II}-p-cymene complexes (56) and (57) for reduction of acetophenone derivatives into corresponding alcohol by transfer hydrogenation as shown in scheme 13 (a). The -Br is an electron withdrawing group at 4-position of the aryl ring of the acetophenone derivatives, pulls electron density from C=O bond, thereby, enhancing catalytic activity and facilitating the reduction of ketone, followed by the formation of corresponding alcohol in higher yield whereas CH_3O- an electron-donating substituent in the aryl ring possess slightly poor activity in reducing ketones.

Both complex (56) and (57) act as effective catalyst for the transfer hydrogen reactions of 4-bromoacetophenone to corresponding alcohols with a maximum transformation of 93% and 96% respectively. Sarıdağ et al[42] investigated the synthesis of ruthenium-p-cymene-Schiff base complexes $[Ru(p\text{-cymene})L_1]{\cdot}Cl{\cdot}0.5H_2O$ (58), $[RuCl(p\text{-cymene})L_2]{\cdot}Cl$ (59) and studied catalytic activity for the transfer hydrogen (TH) reactions of a series of ketones into corresponding alcohols as shown in scheme 13 (b).

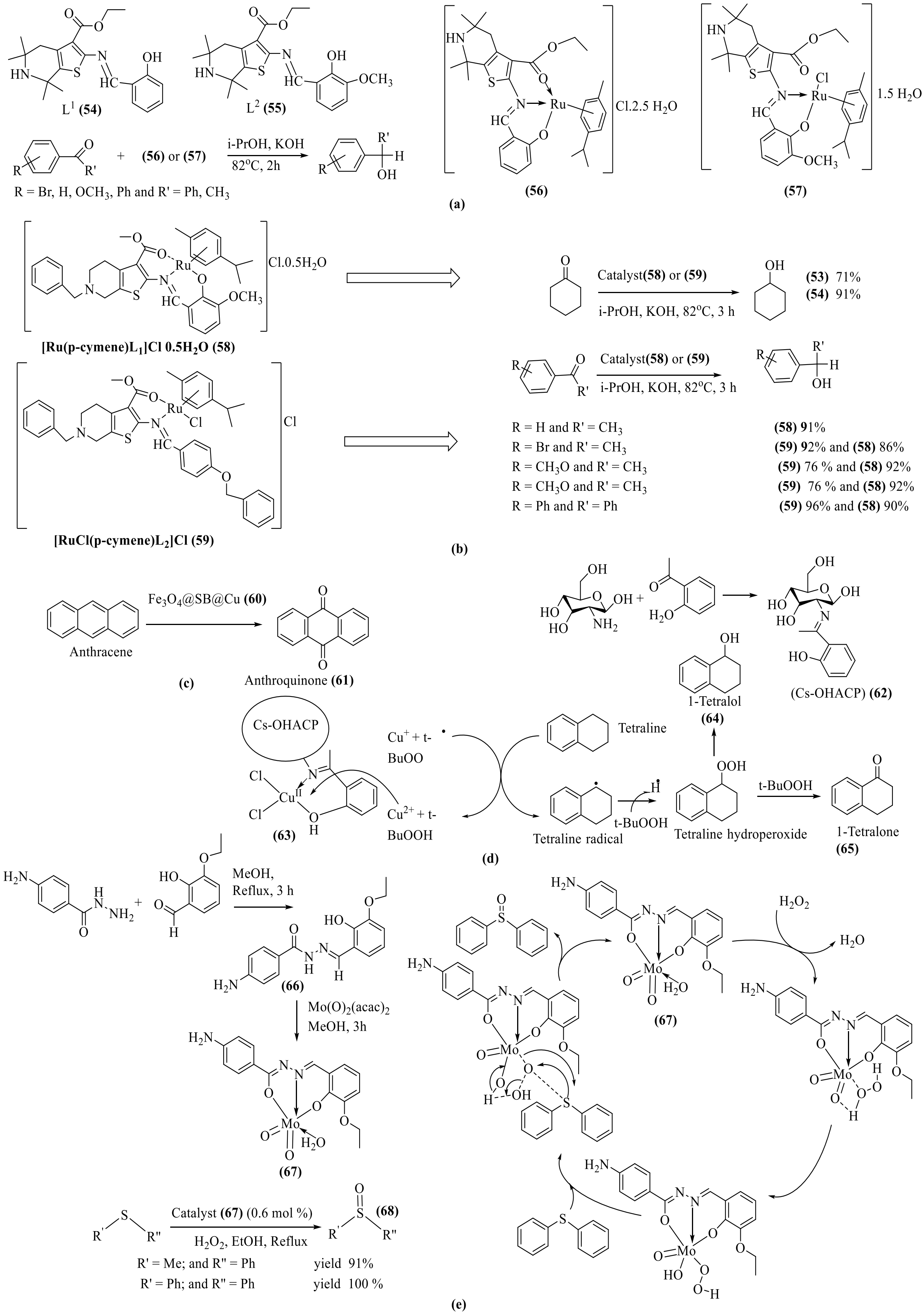


Scheme 12: (a) Synthesis of L-Co(II)-γ-Fe_2O_3 catalyst (52) from Schiff base (51)
(b) One-pot synthesis for the epoxidation of alkenes using catalyst (52)

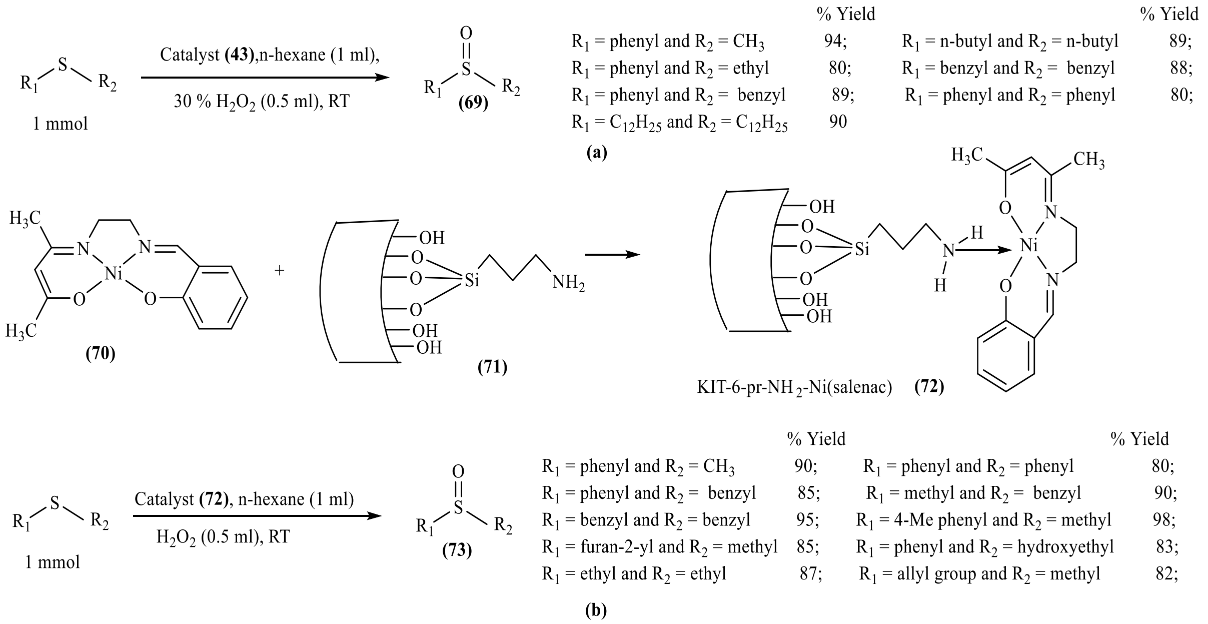
Useful metal(II)-Schiff base for catalytic oxidation of anthracene, tetraline and aromatic sulphides: Megha et al[24] demonstrated novel magnetic heterogeneous catalyst Fe_3O_4@SB@Cu (60) that comprises of Cu(II) Schiff base complex covalently immobilised on Fe_3O_4 nanoparticles. [SB novel Schiff base 3-(1λ^2-indol-3-yl)-2-((2-oxoindolin-3-ylidene)amino)propanoic acid]. The synthesised catalyst (60) in presence of H_2O_2 oxidized anthracene into anthraquinone (61), when refluxed in acetonitrile medium at 70 ^oC for 36 min as shown in scheme 13c. Khare et al[20] reported synthesis of [Cs-OHACP] (62), by condensation of chitosan (Cs) with ortho-hydroxyacetophenone (OHACP) and its Cu^{II}[Cs-OHACP]Cl_2 complex (63). Tetraline was treated with 70% TBHP catalysed in presence of (63) yielding 1-tetralol (64) and 1-tetralone (65).

The oxidation of tetralin followed free radical mechanism. The catalyst and tert-butyl hydroperoxide interact to form tert-butoxyl free radical, which abstracts proton from tetraline molecule and generates tetraline free redical. The activated tetraline free radical was attacked by another tert-butoxyl free radical and converts it into intermediate species, tetralin hydroperoxide, decomposing into 1-tetralol and 1-Tetralone. Kargar et al[19] synthesized an ONO donor Schiff base ligand H_2L (66), (E)-4-amino-N'-(3-ethoxy-2-hydroxybenzylidene)benzohydrazide by the condensation of 4-aminobenzohydrazide and 3- ethoxysalicylaldehyde and their novel dioxomolybdenum Schiff base complex, [MoO_2(L)(H_2O)] (67).

It was found that the important source of oxygen in the reaction is H_2O_2 and the formation of sulfoxide failed in absence of catalyst (67). The catalyst worked efficiently at 0.6 mol% under reflux in ethanolic medium and oxidizes methyl phenyl sulphide and diphenyl sulphide into their respective sulfoxides (68). Akbari et al[3] also reported the efficient synthesis of sulfoxides (69) as depicted in scheme 14a, by treatment of catalytic amount of Ni-H_2L@KIT-6 (43) (10 mg) in normal hexane with 1 mmol of sulfide substrates and 0.5 mL of H_2O_2 (30%) at room temperature.



Scheme 13: (a) Synthesis of Schiff base ligand (L^{1}H) (54), (L^{2}H) (55) and their corresponding complexes (56) and (57) acting as catalyst for transfer hydrogen reactions (b) Transfer hydrogenation reactions catalysed by (58) and (59) (c) Conversion of anthracene into anthraquinone by Fe_3O_4@SB@Cu (60) (d) Synthesis of 1-tetralol (64) and 1-tetralone (65) using catalyst (63) (e) Organic transformation of methyl phenyl sulphide and diphenyl sulphide into their respective sulfoxides by Mo^{VI} catalyst (67) and the proposed mechanism of sulfoxidation



Scheme 14: (a) Sulfoxidation by catalyst (43) (b) Sulfoxidation reaction catalysed by (72)

The catalyst can be reused successfully for several cycles, without any significant loss of initial activity. Ardakani et al[4] treated methanolic solution of Ni(II) Schiff-base complex (70) and fresh KIT-6-pr-NH_2 (71) and on refluxing for 24 h with continuous stirring and successfully synthesizing a new Ni(II) unsymmetrical Schiff-base catalyst KIT-6-pr-NH_2-Ni(salenac) (72). The oxidation of various aromatic sulphide, mixed aromatic-aliphatic sulphides and aliphatic sulphides into their respective sulfoxides (73) as shown in scheme 14 (b), was carried out by reaction of 100 mg (72) in 4 ml ethanol and 1 mmol aliphatic or aromatic or mixed sulphides followed by addition of 2 mmol of 30% H_2O_2 at room temperature.

Conclusion

The review will facilitate for transition metal ‘salen type’ complexes. The Schiff base complexes when immobilized with magnetic nanoparticles act as a promising and sustainable tool for catalysing complicated organic transformations as well as the synthesis of various biologically active molecules in the simplest way that too in excellent yield. Specifically, the study of Schiff base complexes in catalysis has demonstrated tremendous potential as an efficient catalysts for various organic transformation such as synthesis of 4H-chromenes, synthesis of polyhydroquinoline derivatives, Biginelli reaction, Suzuki–Miyaura and the Sonogashira cross-coupling reactions, synthesis of tetrazoles, synthesis of β-hydroxy-1,2,3-triazole, synthesis of N-aryl amines, catalytic epoxidation of alkenes, oxidation, reduction of aromatic ketones into alcohol. Various research groups have been continuously engaged on studying catalytic activity and their potential for various organic transformations. In addition, investigating novel Schiff bases metal complexes and exploring their applications in the field of biological activity, green chemistry, pharmacological and catalytic activity are the need of the hour.

Acknowledgement

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