2.1 ASYMMETRIC SYNTHESIS

In this process, chirality is introduced in a prochiral molecule to bias the synthesis in favour of one stereoisomer over another one, also known as stereoselective synthesis. During the course of reaction, chirality is introduced by chiral reagents. Most of the part of asymmetric synthesis is covered by asymmetric catalysis due to its unique properties such as producing large amounts of the desired chiral product from a minute quantity of a chiral catalyst. A majority of asymmetric catalysis are based on homogeneous and heterogeneous catalysis [Rolison 2003]. In asymmetric processes, catalytic amounts of a chiral molecule or complex are required to transform a prochiral substrate into a chiral product. Transition metals and other organic moieties have good potential for these types of organic transformations in homogeneous and heterogeneous catalysis [Phan *et al*, 2006]. Some general terms used in asymmetric synthesis are explained below.

Chirality

Chirality is a geometric feature of a chiral centre that is bonded to four different groups in a specific arrangement. The molecule that has chirality is not superposed to its mirror image (Figure 2.1). This phenomenon was observed for the first time by Malus in 1809 [Malus 1809] and Biot in 1812 [Biot 1815]. Term was used by Lord Kelvin in 1893 [Kelvin 1904].

Prochiral molecule

In asymmetric synthesis, "prochiral molecule" word is used for molecules which possess a tendency to convert from achiral to chiral in one step synthesis.
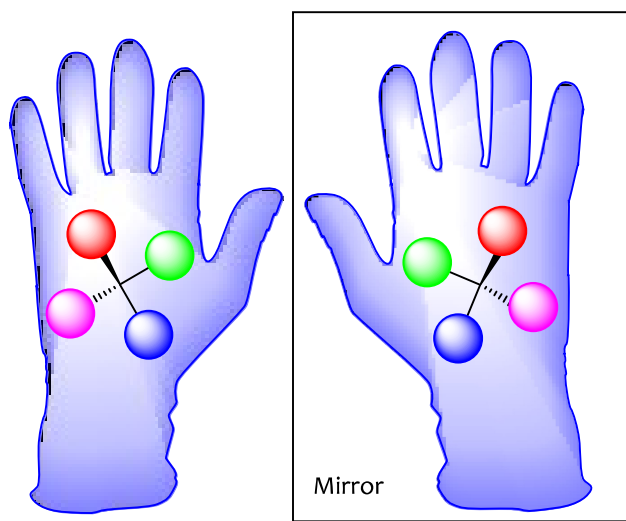

Figure 2.1 Chirality (the mirror image of the molecule is not superimposed to it, just like the two human hands).

Chiral reagents

Chiral reagents are chiral moieties that have the necessary stereocentre to control the induction of chirality into a product. Most of the asymmetric syntheses are carried out in the presence of a chiral reagent. Chiral reagents can be obtained naturally or can be synthesized in a laboratory. Chiral molecules like cinchona, ascorbic acid, amino acid, carbohydrate and terpene are found naturally. In this study, cinchona and camphoric acid are used as chiral reagents. Cinchona alkaloids are obtained from the cinchona plant, found natively in western South America. Cinchona alkaloids include different forms like cinchonine, cinchonidine, quinine, quinidine, dihydroquinine and dihydroquinidine (Figure 2.2). Camphoric acid is also obtained from the camphor plant.
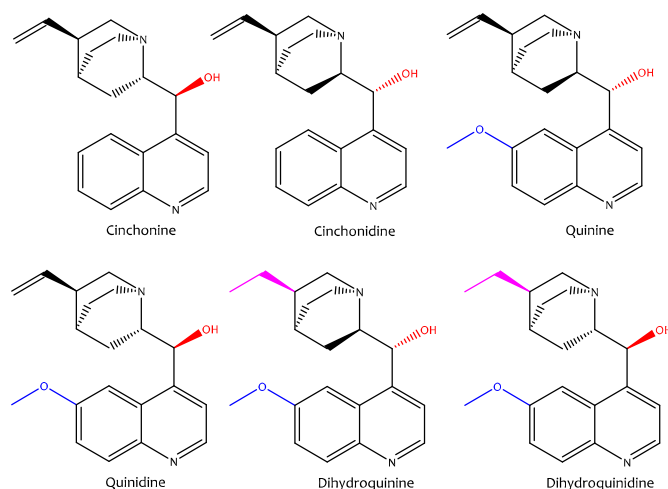

Cinchonine	Cinchonidine	Quinine
Quinidine	Dihydroquinine	Dihydroquinidine

Figure 2.2 Cinchona alkaloids

2.2 ASYMMETRIC CATALYSIS

Traditionally, enantiomerically enriched compounds are produced by the following processes (Figure 2.3).

(a) Chemical transformation of an enantiomerically precursor (using natural chiral pool)
(b) Resolving the racemic mixture of the two enantiomers
(c) Asymmetric synthesis

The first two processes suffer from a few drawbacks, such as, the former requires stoichiometric amounts of a suitable precursor, and the latter yields only 50 % of a particular isomer. Asymmetric catalysis is successful in overcoming these problems. In asymmetric catalysis processes, a chiral complex and catalysts promote the conversion of an achiral substrate to a chiral product, with the preference of a single enantiomer. The chiral catalysts are successfully regenerated after reaction completion without any loss of activity. This is a significant advantage of asymmetric synthesis to generate chiral compounds with lesser amounts of catalysts.

Asymmetric homogeneous and heterogeneous catalysis play a vital role in the synthesis of chiral compounds. Homogeneous catalysis is a process in which substrate and catalysts are in the same phase (liquid-liquid, solid-solid and gas-gas) during the catalytic reaction, while in heterogeneous catalysis, substrate and catalyst are in different phases (Figure 2.4).
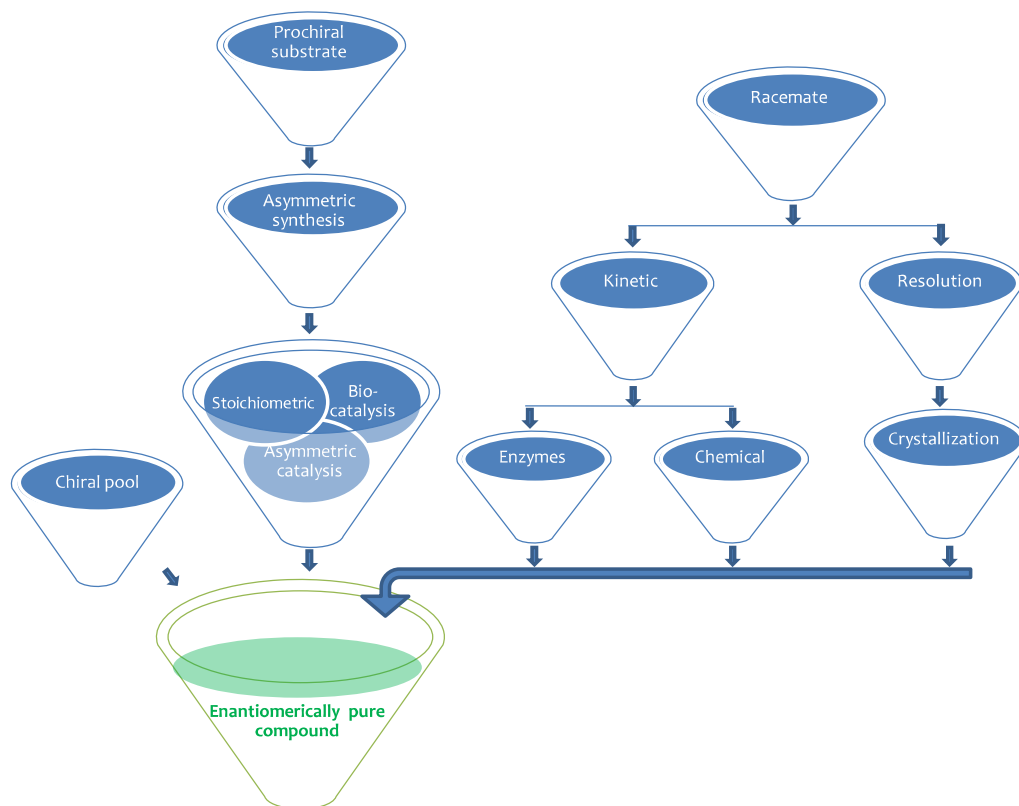
Figure 2.3 Processes for obtaining enantiopure compounds

In most of the studies, homogeneous catalysis allows high conversion and enantioselectivity. Despite these excellent results, it has some problems like separation, purification and recycling of catalysts. Heterogeneous catalysis is a viable option to overcome these problems. Most of the heterogeneous catalysts are solid and reactants are in liquid or gaseous form. The success of heterogeneous catalysis came into knowledge when Fritz Haber and Carl Bosch in 1918, Irving Langmuir in 1932, and Gerhard Ertl in 2007 won Nobel prizes for the heterogeneous catalysis. Out of various heterogeneous catalytic transformations, asymmetric hydrogenation and allylation reaction will be carried out in detail in this thesis.
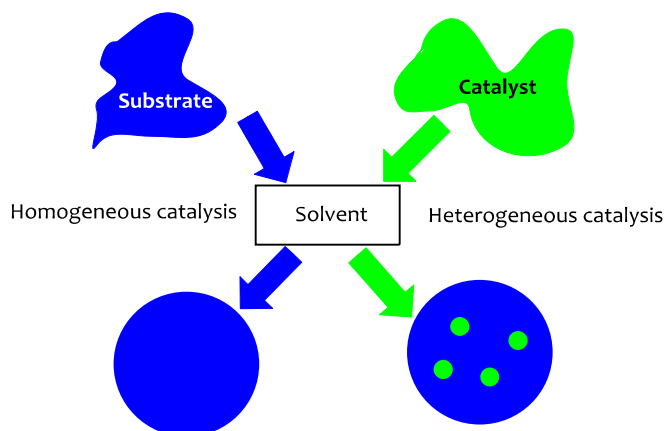

Figure 2.4 Homogeneous catalysis versus heterogeneous catalysis

In heterogeneous catalytic transformations, metal nanoparticles dispersion and support materials play important roles. The agglomeration behaviour of metal nanoparticles reduces the active sites of a catalyst. Thus, the binding of a catalyst to a solid support has become the most employed method to increase the active site of the catalysts [Tai *et al,* 2000]. In practice, there are various supporting materials [Vankelecom and Jacobs 2000], like alumina (Al_2O_3), silica (SiO_2) and titanium oxide (TiO_2) that have been used for heterogeneous catalysis (Figure 2.5). These supporting materials produce acidic or basic poisoning in chemical reaction and are being replaced by carbon materials. Carbon materials [Sharma and Sharma 2015] such as activated carbon, graphene, carbon fibers and carbon nanotubes [Chen *et al,* 2011] proved to be the best supporting materials, due to their high surface area, commercial availability and ease of chemical modification. A detailed study of supports and catalysts is carried out here.
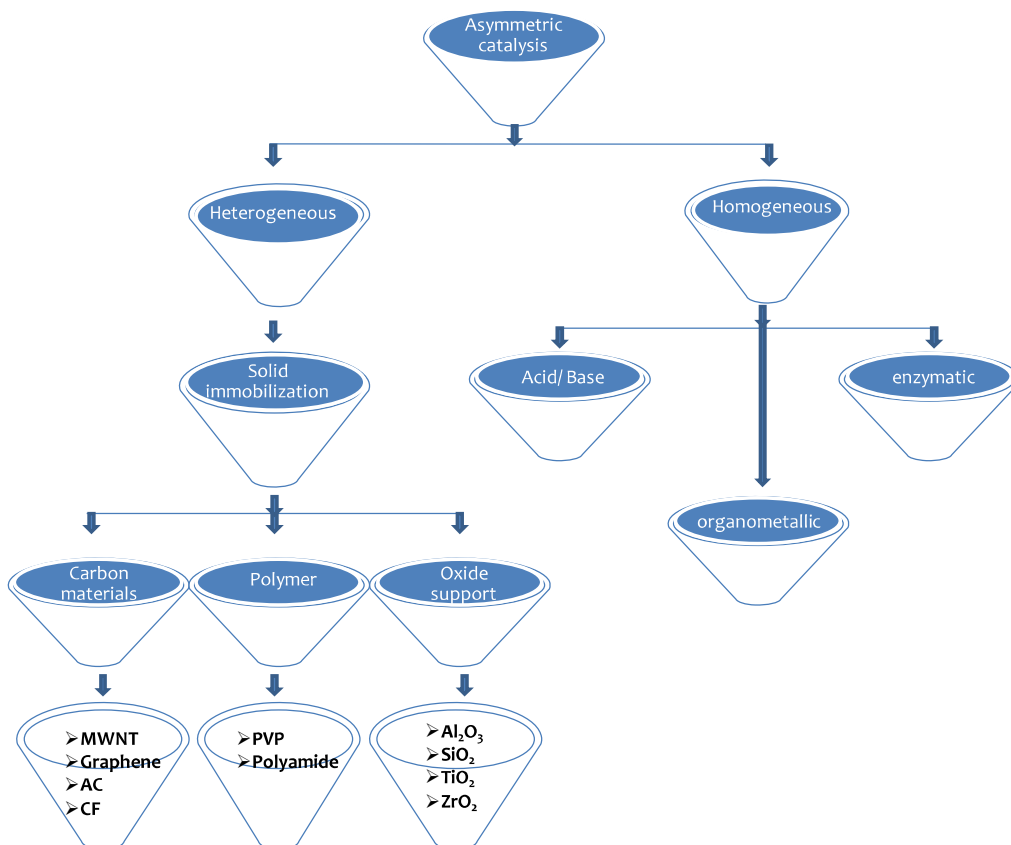

Figure 2.5 Systematic representation of asymmetric catalysis

Carbon materials

Carbon is a chemical element of the P block, having atomic number 6. It is non-metallic and has a valency of four to make covalent bonds. It has many allotropes like carbon nanotubes, diamond, fullerenes, graphene, activated carbon and carbon fibers. Hybridization of carbon in carbon allotropes varies from sp^3 to sp. Among the various carbon allotropes, carbon fibers, graphene, activated carbon and carbon nanotubes are the most commonly used in catalysis [Schloegl 2013]. Carbon materials are found in all forms, from powder to fibers and have all dimensions (Figure 2.6). Carbon materials also show electrical, mechanical and optical properties that have opened new doors for others future applications [Parish 2011]. The carbon nanomaterials can be produced using several different methods including arc discharge, laser ablation and chemical vapour deposition.
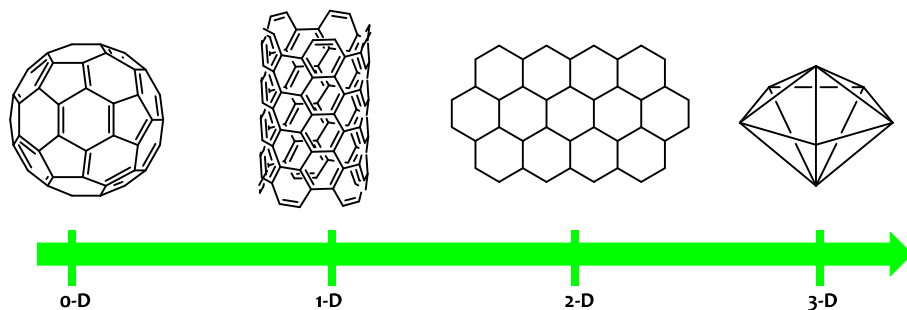
Figure 2.6 Dimensions of carbon materials

Activated carbon

Activated carbon is a solid, porous and carbonaceous material with high surface area. That characteristic makes it useful in catalytic applications. Other applications include food, pharmaceuticals, water treatment, hydro metallurgy, gold recovery and pollutants removal (both gaseous and liquid) [Soleimani and Kaghazchi 2008]. Due to porous structure, it is used as filter and adsorbent.

Carbon fibers

Carbon fibers are light weighted, containing approximately 99 % of fibrous carbon. Carbon fibers are prepared at high temperature from organic matters [Endo 1988]. The properties of carbon fibers, such as high stiffness, high tensile strength, low weight and chemical resistance make them important in the field of catalysis, aerospace, civil engineering, military and motorsports.

Graphene

Graphene is a thin layered structure of carbon atoms having hexagonal honeycomb lattice [Allen *et al,* 2009]. The carbon atom is sp^2 bonded in graphene layers with a molecule length of 0.142 nm. It is a conducting, transparent and flexible material with high surface area. These properties make it utile in various applications [Zhou *et al,* 2014], such as solar cells, light-emitting diodes (LED), touch panels, as a support, and in smart windows or phones.

Carbon nanotubes

For the first time in 1991, Iijima introduced a significant nanoparticles and reported a tabular structure of carbon [Iijima 1991]. A carbon nanotube is a cylindrical array of hexagons, made of carbon in the nanosized scale. There are numerous unique properties of carbon nanotubes that make it valuable in many applications [Endo *et al,* 2007]. Properties like mechanical strength, electrical and thermal conductivity opened an era in industrial application and material science. High surface area and inert nature of carbon nanotubes make them useful for catalysis. There are different types of carbon nanotubes like single walled, double walled and multi-walled.

Polymer (polyamide)

Similar and different monomers connect by a special bond, in a repetitive way, to make a macromolecule. These macromolecules are called polymers and the process of making a polymer is called polymerization. These polymers have broad properties like high molecular weight, toughness, viscoelasticity and semi-crystalline nature, making them useful for everyday life [Rodriguez *et al,* 2014]. Out of various polymers, polyamide containing polymers play an important role as supporting materials in heterogeneous asymmetric catalysis [Michalska *et al,* 2002]. In polyamide containing polymers, the linkage between two monomers is made up of the amide bond. The functionalities of the amide group help in the interaction with the catalyst.

Selectfluor
        First time Selectfluor has been synthesized by Banks [Banks 1992]. It is a white crystalline, free flowing, nonhygroscopic and high melting point solid. Selectfluor is the most reactive electrophilic reagent with stable, safe and easy handleability. Due to the ionic character, it is soluble in CH_3CN, water, and nitro methane [Vincent *et al*, 1999] and DMF [Banks 1998].

Transition metal as catalysts
        Transition metals are able to exchange electrons from other moieties due to their variable oxidation state. By doing this, these metals can change the rate of a reaction. There are various successful examples in which transition metals behave like a catalyst, such as, the Haber process (Vanadium), contact process (Iron), catalytic hydrogenation (Nickel, Palladium and Platinum), etc [Giacalone *et al,* 2016]. Platinum is used as a catalyst since the 19th century. It is used in hydrogenation, dehydrogenation, isomerisation, catalytic converters and oxidation reactions [Reith *et al,* 2014]. Platinum is more expensive due to its limited abundance (about 0.005 ppm), but other properties, like having resistance towards corrosion and less reactivity, make it precious for use [Stellman 1998]. Therefore, it is important to maximize the efficiency of the applications of platinum in order to reduce the loss of this valuable metal and recycle it, whenever possible.

        For successful catalytic reactions, it is necessary that the reactant is absorbed on the catalyst surface and, according to the Sabatier principle, the interaction between the reactant and the catalyst should neither be too weak and nor too strong. Weak interactions lead to desorption of reactants before completion of reaction. In other hand, strong interactions will poison the catalyst. The interaction behaviour of a metal can be explained by the d-band model, which indicates that the Pt metal has the right electronic structure to interact with a reactant and it can be modified in order to suit the different catalytic processes [Nørskov *et al,* 2011].

2.3 ASYMMETRIC HETEROGENEOUS HYDROGENATION REACTION

Hydrogenation reaction
        An addition of molecular hydrogen to an unsaturated moiety in the presence of a catalyst is called hydrogenation reaction (Figure 2.7). A homogeneous catalytic hydrogenation reaction was reported by Calvin, Wilkinson's and Noyori [Noyori 2002]. A number of studies in this field have been carried out by numerous research groups, using transition metal complexes [Itooka *et al,* 2003, Wang *et al,* 2003, Mäki-Arvela *et al,* 2005, Kong *et al,* 2006, Ikariya and Blacker 2007, Lu and Bolm 2008, Baruwati *et al,* 2009]. Nickel, palladium and platinum and their compounds are the most common catalysts for hydrogenation. Out of these metals, Pt has been used widely as catalyst for hydrogenation reactions [Rylander 2012].
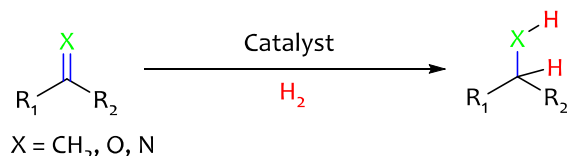

Figure 2.7 Hydrogenation reaction

        This study focuses on the asymmetric hydrogenation reaction of carbonyl compounds. The asymmetric hydrogenation of carbonyls is well studied in the literature [Schrock and Osborn 1976, Pettinari *et al,* 2004]. In 2001, Noyori [Noyori *et al,* 1987] and Knowles [Knowles 2002] won Nobel Prizes for implementing a practical catalytic study of asymmetric

hydrogenation of ketones in the presence of BINAP-Ru complex [Knowles and Sabacky 1968, Mashima *et al,* 1994, Ohta *et al,* 1995, Noyori and Ohkuma 2001]. Further, detailed experimental and theoretical studies on heterogeneous catalysis of α-ketoesters are explained by various research groups [Wehrli *et al,* 1989, Blaser *et al,* 1993, Minder *et al,* 1994, Minder *et al,* 1995, Blaser *et al,* 1997, Studer *et al,* 2000]. In these studies, most of the Pt is supported on inorganic oxides like alumina [Minder *et al,* 1996, Köhler and Bradley 1998, Weng and Zaera 2014], silica [Török *et al,* 1997, Toukoniitty and Murzin 2004, Xiong *et al,* 2005], polymer [Huang *et al,* 2001] and zeolite [Gamez *et al,* 1998]. The effect of changes in pressure, temperature, solvent, catalyst and modifier on reaction rate and enantioselectivity were reported in earlier studies [Minder and Schürch *et al,* 1996].

The heterogeneous hydrogenation reaction of α-ketoesters is examined using transition metal catalysts. The relevant literature studies are tabulated in Table 2.1.

Table 2.1 Literature review of asymmetric hydrogenation reactions of α-ketoesters

Catalysts	ee % /Modifier	Substrate	References
$Pt/\Upsilon\text{-}Al_2O_3$	65 % / Cinchonidine	Ethyl pyruvate	[Wehrli and Baiker *et al,* 1989]
Pt/Al_2O_3	10,11-ihydrocinchonidine	Ethyl pyruvate	[Garland and Blaser 1990]
Pt/C and Pd/C	34 % / Cinchonidine	Ethyl pyruvate	[Tungler *et al,* 1991]
Pt/Al_2O_3	95 % / 10,11 dihydro-o-methylcinchonidine	α–ketoesters	[Blaser *et al,* 1991]
5 % Pt/Al_2O_3	95 % / HCD, O-methyl-HCD	Ethyl pyruvate	[Blaser and Garland *et al,* 1993]
5 % Pt/Al_2O_3	Cinchona	α–ketoesters	[Schwalm *et al,* 1993]
Pt/Al_2O_3	Dihydrocinchonidine	Ethyl pyruvate	[Augustine *et al,* 1993]
$Ir/(Sio_2, Al_2O_3, CaCO_3)$	39 % / Cinchonidine	Methyl pyruvate	[Simons *et al,* 1994]
Pt/Al_2O_3	75– 87 % / Cinchonidine		[Minder and Mallat *et al,* 1994]
Pt catalysts	Cinchona	α-ketoesters	[Schwalm *et al,* 1994]
Pt/Al_2O_3	75 % / 2-(1-pyrrolidinyl)-l-(l-naphthy1) ethanol	Ethyl pyruvate	[Wang *et al,* 1994]
Pt Catalysts	75 % / Chiral amino alcohols	Ethyl pyruvate	[Simons *et al,* 1995]
Pt/Al_2O_3	75 % / R-2-(1-pyrrolidinyl)-1-(1-naphthyl) ethanol (PNE)	Ethyl pyruvate	[Minder and Mallat *et al,* 1995]
$Pt/Al_2O_3\text{-}$ and Pt /carbon	67 % / Heterocyclic N-compounds	Ethyl pyruvate	[Minder *et al,* 1995]
Pt/Al_2O_3	Cinchona	α-ketoesters	[Schwalm *et al,* 1995]
Pt/Al_2O_3	82 % / (R)- or (S)-l-(l-naphthyllethylamine	Ethyl pyruvate	[Heinz *et al,* 1995]

Pt (111)	10,11-dihydrocinchonidine	Methyl pyruvate	[Carley et al, 1995]
5 wt % Pt/ Al$_2$O$_3$	82 % / (R)-1-(1-naphthyl)ethylamine	Ethyl pyruvate	[Minder and Schürch et al, 1996]
Pt catalysts	60 % / Cinchona	Ethyl pyruvate	[Sun et al, 1996]
Pt/ Al$_2$O$_3$	~ 75 % / Cinchonidine	Ethyl pyruvate	[Margitfalvi et al, 1996]
Pt/C, Pt/SiO$_2$ and Pt/K-10	Cinchonidine	α-ketoester	[Török and Felföldi et al, 1997]
Pt/ Al$_2$O$_3$	10,11 dihydrocinchonidine	Ethyl pyruvate	[Blaser et al, 1998]
Pt/ Al$_2$O$_3$	70 % / α-isocinchonine	Ethyl pyruvate	[Bartók et al, 1998]
Pt/ Al$_2$O$_3$	70 % / α-isocinchonine	Ethyl pyruvate	[Bartók and Felföldi et al, 1998]
Colloidal Pt	Cinchonidine	Ethyl pyruvate	[Köhler and Bradley 1998]
Platinum catalysts	87 % / 1-(9-anthracenyl)-2-(1-pyrrolidinyl) ethanol	Ethyl pyruvate	[Schürch et al, 1998]
5 wt % Pt/Zeolite	Cinchonidine	Ethyl pyruvate	[Gamez and Köhler et al, 1998]
Platinum catalysts	95 % / Cinchonidine	Carbonyl compounds	[Török et al, 1999]
1 % Pt/ Al$_2$O$_3$	94 % / DHCD	α-ketoesters	[LeBlond et al, 1999]
stabilized Pt and Pd NPs	36 % / Cinchona	Ethyl pyruvate	[Collier et al, 1999]
Pt/ Al$_2$O$_3$	Cinchonidine	α-ketoesters	[Margitfalvi and Tfirst 1999]
5 wt % Pt/ Al$_2$O$_3$	Cinchonidine	Ethyl pyruvate	[Ferri et al, 2000]
Platinum catalysts	92 % / Cinchonidine	s-trans-methyl pyruvate	[Buergi and Baiker 2000]
Pt/ Al$_2$O$_3$	70 % / Cinchonidine	Ethyl pyruvate	[Morawsky et al, 2000]
Rh / PVP	42.2 % / Cinchona	Ethyl pyruvate	[Huang and Chen et al, 2001]
Pt/ Al$_2$O$_3$	43 % / (S)-3-(1-methyl-indol-3-yl)-2-methylamino-propan-1-ol	Ethyl pyruvate	[Szöllösi et al, 2001]
Pt/C	25-35 % / Cinchonidine	Methyl pyruvate	[Fraga et al, 2002]
Pt/Al$_2$O$_3$	Dihydrocinchonidine	Ethyl pyruvate	[Bartók et al, 2002]

Pt/ Al$_2$O$_3$	90 % / Cinchona	Ethyl pyruvate	[Bartók et al, 2002]
Pt/Al$_2$O$_3$	98 % / Dihydrocinchonidine	Ethyl benzoylformate	[Sutyinszki et al, 2002]
5 wt % Pt/ Al$_2$O$_3$	93–94 % / isocinchonine	Ethyl pyruvate	[Bartók et al, 2003]
Pt/ Al$_2$O$_3$	88 % / Dihydrocinchonidine	Ethyl pyruvate	[Bartók et al, 2003]
Pt/ Al$_2$O$_3$	Cinchona	α-ketoesters	[Bürgi and Baiker 2004]
Platinum nanoparticles	55 % / Cinchonidine	Ethyl pyruvate	[Mévellec et al, 2004]
Pt/SiO$_2$ fiber	60 % / Cinchonidine	Ethyl pyruvate	[Toukoniitty and Murzin 2004]
Rh/Υ-Al$_2$O$_3$	71.6 % / Quinine	Ethyl pyruvate	[Xiong and Ma et al, 2005]
Pt/ Al$_2$O$_3$	88 -93 % Cinchona	Ethyl pyruvate	[Bartók et al, 2005]
Pt/graphite	63 % / Cinchonidine	Ethyl pyruvate	[Attard et al, 2006]
Platinum catalysts	Cinchona	methyl pyruvate	[Taskinen et al, 2007]
Pt/MWCNT	96 % / Cinchonidine	Ethyl pyruvate	[Chen and Guan et al, 2011]
Pt/Al$_2$O$_3$	92–93% / Cinchona alkaloid	Methyl benzoylformate	[Sano et al, 2012]
Pt/MIL-101	76.5%/ Cinchona alkaloid	Ethyl pyruvate	[Pan et al, 2013]
Pt/CNTs	95 % / Cinchonidine	α-ketoesters	[Guan et al, 2013]
Pt/15 % Al-C	87.5 % / Cinchonidine	Ethyl pyruvate	[Zhang et al, 2014]
Pt/SiO$_2$	63 %/(S)-(+)-1-aminoindan	Ethyl pyruvate	[Ruggera et al, 2016]
Stabilized Pt nanoparticle	80% / Cinchonidine	Ethyl pyruvate	[Yu et al, 2016]

2.4 SYNTHESIS OF METAL NANOCRYSTALS AND HYDROGENATION ON Pt (111)

Various shape control synthesis have been reported [Ahmadi et al, 1996]. Metal NCs with different shapes have different crystallographic facets, which makes them an interesting topic to study for catalysis [Somorjai and Park 2008]. Among various NCs, noble metal NCs attracted great attention, due to their fascinating properties and especially their excellent catalytic performance in a wide range of organic reactions. A variety of shapes such as spheres, cubes, cuboctahedra, octahedra, tetrahedra, bipyramids, and rods have been explored in last decade, with successful control over the crystal-plane [Xia et al, 2009]. Theoretical studies also revealed the shape and crystal plane of noble metal NCs effects on the catalytic activity [Demers-Carpentier et al, 2013]. Among various planes, Pt (111) has high exposure site and good enantioselectivity. The performance of Pt (111) for hydrogenation on Pt/Al$_2$O$_3$ (5 wt % Pt) was

reported by Baiker *et al.* [Schmidt *et al,* 2009]. A number of investigations based on scanning tunneling microscopy (STM) and theoretical studies have shown the role of Pt (111) plane in asymmetric synthesis [Laliberté *et al,* 2008, Schmidt *et al,* 2009]. The role of exposed face in chirality transfer and high coordination of Pt (111) edges has been explained by experimental studies [Demers-Carpentier and Rasmussen *et al,* 2013]. Li *et al.* [Zhou and Li 2012] synthesized the highly faceted Pt NCs enclosed with (111) plan, which were supported on carbon nanotubes. This catalytic system showed outstanding performances for oxygen reduction, owing to the effect of 111 facets [Lin *et al,* 2009]. In addition, El-Sayed and Narayanan investigated the catalytic performance of tetrahedral (111), cubic (110), spherical (111) and (100) Pt NPs towards electron-exchange reactions [Narayanan and El-Sayed 2004]. Zaera and co-workers also reported a catalytic system where reaction selectivity was successfully tuned through the specific control of particle shape [Lee *et al,* 2009]. Temperature-programmed desorption data on single crystals shows the isomerisation of trans olefins to cis olefins which is promoted by Pt (111) facets and such selectivity gets reversed on more open surfaces (557) and (100) [Lee and Delbecq *et al,* 2009].

2.5 ALLYLATION REACTION OF IMINES AND ALDEHYDES

Imine and aldehydes are common building blocks for the synthesis, by stereoselective allylation, of chiral organic compounds which are important in the synthesis of pharmaceutical, and biological active compounds [Yamamoto and Asao 1993, Huo *et al,* 2014]. The first allylation reaction involving aqueous media was carried out in 95% ethanol and butanol, using activated zinc dust [Killinger *et al,* 1977]. Numerous studies were reported for allylation reaction of imines and aldehydes with good results. Platinum and palladium allylic substitution is one of the most studied catalytic reactions. This is because it is an efficient synthetic tool for the formation of carbon-carbon and carbon-heteroatom bonds, which is one of the main objectives in modern organic synthetic chemistry. Relevant literature of asymmetric allylation reactions is listed below (Table 2.2).

Table 2.2 Literature review of asymmetric allylation reaction of imine and aldehydes

Catalysts	ee % / Yield % / Allylic reagent	Substrate	References
Chiral titanium complex (BINOL-Ti)	86 % / Allylic stannanes and 80 % /Allylic silanes	Glyoxylate	[Furuta *et al,* 1991]
Chiral (acyloxy) borane	95 % / (E) -tributyl (2-methyl-2-pentyl)stannane	Crotonoaldehyde	[Marshall and Tang 1992]
Cd/Bu4NBr/THF	Allyl bromide	Carbonyl compound/Imine	[Sain *et al,* 1992]
Chlorotrlmethylsilane	Allylstannane	Aldimines	[Wang *et al,* 1995]
Lanthanide triflate	Allyltributylstannane	Imines	[Bellucci *et al,* 1995]
Cerium trichloride	Vinyimagnesium bromide	Imines	[Betz and Heuschmann 1995]
$PdCl_2(PPh_3)$	Allylstannanes	Imines	[Nakamura *et al,* 1996]

Mg and Zn mediated	Allyl Bromide	imines	[Wang *et al*, 1996]
SnCl$_2$	Allylictributyltin	Aldehydes, imines	[Yasuda *et al*, 1996]
[BINOL-Zr(OiPr)$_2$]	92 % , /Allyltributyltin	Aldehydes	[Bedeschi *et al*, 1995]
BINAP silver (I) complex	Methallyltributyltin or Crotyltributyltin	Aldehydes	[Yanagisawa *et al*, 1997]
Chiral bipyridine zinc (II) complex	60 % / Allyltributyltin	Aldehydes	[Kwong *et al*, 1999]
Cinchonine with indium	90 % / Allyl bromide	Aldehydes	[Loh *et al*, 1999]
Chiral bis (oxazalinyl) zinc complexes	40- 46 % / Allyl-tributyltin	Aldehydes	[Cozzi *et al*, 1997]
Chiral isoxazoline ligands complexes with (Cu, Zn, Pd and Ag)	35-69 % / Allyltri-n-butyltin	Aldehydes	[Imai and Zhang *et al*, 2000]
RhCl$_2$ (Phebox) (H$_2$O) complexes	Allyltributyltin	Aldehydes	[Motoyama *et al*, 2001]
Cadmium perchlorate	Allyltributyltin	Aldehydes and Ketones	[Aoyama and Manabe 2002]
Ceric ammonium nitrate	Allyltributylstannane	Aldehydes	[Yadav *et al*, 2003]
Indium trichloride	Allytributyltin	Aldehydes	[Lu *et al*, 2004]
MgO as a promoter	Allylictantalum	Imines	[Shibata *et al*, 2004]
L-aspartic acid	40 % / Tetraallyltin and other allylstannanes	Aldehydes	[Yanagisawa *et al*, 2004]
Pd (OAc)$_2$ (10 mol %)–P(n-Bu)$_3$ (20 mol %)–Et$_3$B (360 mol %)	Allylic alcohols	Anisidineimines	[Shimizu *et al*, 2005]
Bisphophinite complexes of Pd or Pt	Allyltributylstannane	Imines	[Sharma and Samuelson 2006]
Platinum phosphinite complexes	88 % / Allyltributyltin	Aldehyde	[Sharma and Samuelson 2007]
Chiral palladium-bisphosphinite	97 % / Dimethyl malonate	1,3-diphenylpropene	[Sharma *et al*, 2008]

complexes		-2-yl acetate	
Activated zinc powder	Allylbromide	Imines	[Zhang *et al*, 2009]
Palladium-catalyst	70-80 % / Allylic alcohols	Imines	[Qiao *et al*, 2010]
Zinc electrodes	70 -95 % /Benzyl bromide or alkyl iodide	Imine	[Huang *et al*, 2011]
π-allylpalladium	98 % / Allyltributyl stannane	Imine	[Fernandes and Nallasivam 2012]
3,3-disubstituted allylic pinacol boronic esters	Allylic compounds	Imine	[Chen and Aggarwal 2014]
CuCl (5 mol %), chiral ligand	90–99 % / Allylboronic acid pinacol ester	Aldimines and ketimines	[Zhao *et al*, 2015]
Ir(COD)Cl$_2$	Tert-butyl cinnamyl carbonate	Imine	[Liu *et al*, 2016]