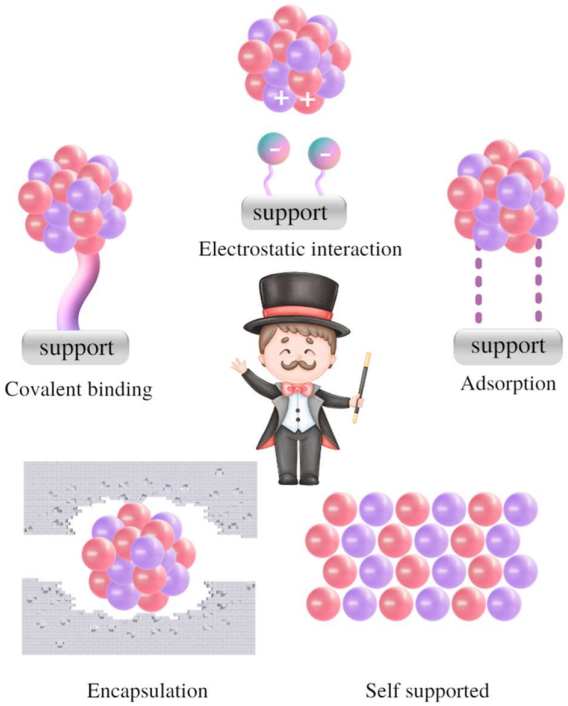
Chapter 1

Introduction



1.1. Asymmetric synthesis

In the realm of modern organic chemistry, the art of crafting complex molecules with precision and expertise has garnered profound attention. Asymmetric synthesis, a captivating and intricate facet of chemical synthesis, holds the key to manipulating molecules in a profoundly selective manner, bestowing upon them unique three-dimensional structures and, consequently, distinct properties. This profound scientific discipline, sometimes referred to as enantioselective synthesis, stands as a testament to the astonishing intricacies that govern the interactions between matter on a molecular scale.[1,2] At its core, asymmetric synthesis is a branch of chemical synthesis that is dedicated to the construction of molecules possessing chirality – a property intrinsic to many organic compounds that results in their mirror-image isomers, known as enantiomers (*Figure 1.1*).

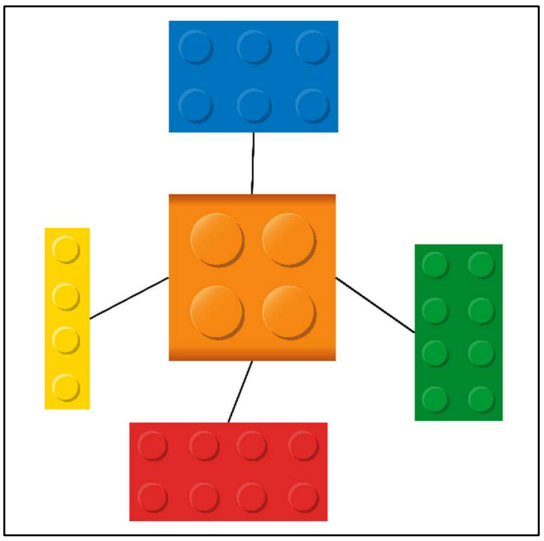


Figure 1.1 How does a chiral molecule function?

The enantiomers are characterized by their non-superimposable nature, akin to left and right hands, and possess the remarkable ability to exhibit vastly different biological, pharmaceutical, and chemical behaviors. The driving force behind asymmetric synthesis lies in the pursuit of harnessing this chirality to selectively access a single enantiomer, thereby unlocking the potential to engineer compounds with enhanced efficacy, reduced side effects, and improved functional properties. As one delves deeper into the intricate tapestry of asymmetric synthesis, a myriad of strategic approaches emerges, each representing a unique

thread in the grand fabric of enantioselective molecular construction. Transition metal-catalyzed reactions, organocatalysis, biocatalysis, and kinetic resolution stand as but a few of the pivotal techniques that have been deftly woven into the discipline's landscape. These methodologies, often characterized by their ingenuity and creative design, offer chemists an expansive toolkit to navigate the challenging terrain of chirality control.[3–6]

The significance of asymmetric synthesis extends beyond the confines of the laboratory bench, permeating diverse scientific domains. From the realms of drug discovery and development, where enantiopure compounds hold the promise of minimizing adverse effects and maximizing therapeutic potential, to the realm of materials science, where chirality-driven properties are harnessed to engineer cutting-edge materials with tailored functionalities, the impact of asymmetric synthesis distinguishes no bounds. As our understanding of the fundamental principles governing asymmetric synthesis deepens, researchers continue to push the boundaries of what is achievable. The interplay of theory and experiment has paved the way for the elucidation of intricate mechanistic pathways and the development of novel strategies for controlling stereochemistry. Furthermore, the sustainable and environmentally conscious aspects of asymmetric synthesis have come to the forefront, spurring the development of greener methodologies that align with the principles of green chemistry.[7,8]

Asymmetric synthesis, an exquisite branch of chemical artistry, casts a spotlight on the intriguing phenomenon of chirality. Within the realm of enantioselective molecular construction, the quest for crafting single-handed molecules – those that exist exclusively in either a left- or right-handed form – fuels an unquenchable curiosity to unravel the profound implications of such seemingly subtle differences. These enantiomers, resembling mirror images, carry the potential to exhibit dramatically distinct behaviors in biological, medicinal, and chemical contexts. Enter the virtuoso of asymmetric catalysis, a pivotal player that elegantly guides the transformation of prochiral substrates into enantioenriched products, while sparingly consuming the catalyst itself. At its essence, asymmetric catalysis stands as a testament to the ingenious manipulation of molecular interactions. Catalysis, a concept rooted in the principles of accelerating chemical reactions, receives a refined twist when coupled with chirality. Asymmetric catalysts, often fashioned from chiral ligands, navigate the intricate dance of molecular substrates with finesse, steering them toward a specific enantiomer while rejecting its mirror image counterpart. This intricate choreography embodies the heart of

asymmetric synthesis, crafting molecules that exhibit newfound properties and behaviors, catalyzing advancements in diverse scientific domains.[9,10]

1.2 Asymmetric catalysis

In the captivating realm of modern organic chemistry, a remarkable synergy between theory and experimentation has yielded a profound understanding of the intricate dance of atoms and bonds. Among the many virtuosic performances on this chemical stage, the art of asymmetric catalysis stands as a resplendent masterpiece, casting a luminous spotlight on the manipulation of molecular chirality and the orchestration of intricate transformations. Within this symphonic overture, the concept of privileged chiral ligands emerges as a pivotal motif, weaving an enchanting melody of selectivity and efficiency, while unlocking the door to a captivating array of enantioselective reactions. At the heart of asymmetric catalysis lies a quest to harness chirality's exquisite intricacies to create molecules of distinct handedness, where a single enantiomer takes center stage, while its mirror image counterpart languishes in the wings. This pursuit is fueled by the realization that these enantiomers, though near-identical in composition, can possess dramatically different chemical, physical, and biological properties. Asymmetric catalysis elevates this endeavor to new heights, employing catalysts as chemical conductors that guide reactions toward a preferred enantiomer, akin to a maestro skillfully directing an orchestra.[11,12] The virtuosity of asymmetric catalysis is elegantly showcased through the utilization of privileged chiral ligands (*Figure 1.2*).

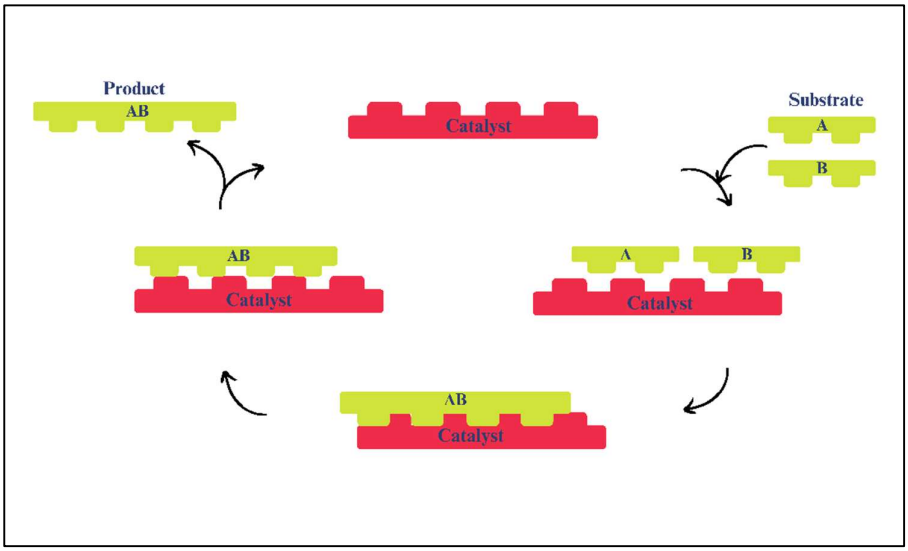


Figure 1.2 Catalytic cycle

These ligands, akin to expert musicians, demonstrate an inherent ability to harmonize molecular transformations, driving reactions with remarkable precision and efficiency.

1.3 Privileged chiral ligands

Privileged chiral ligands possess a unique blend of structural features that render them exceptionally adept at steering reactions towards desired enantiomers, effectively serving as guiding stars in the constellation of asymmetric catalysis.[13] Within the realm of privileged chiral ligands, diverse structural motifs have emerged as focal points of exploration. From the salen and bi-2-naphthol-based ligands, which have orchestrated transformations through transition metal catalysts with unparalleled finesse, to the proline and thiourea-based ligands (*Figure 1.3*), which have conducted symphonies of organocatalysis with exquisite control, these privileged architectures exemplify the marriage of creativity and functionality.

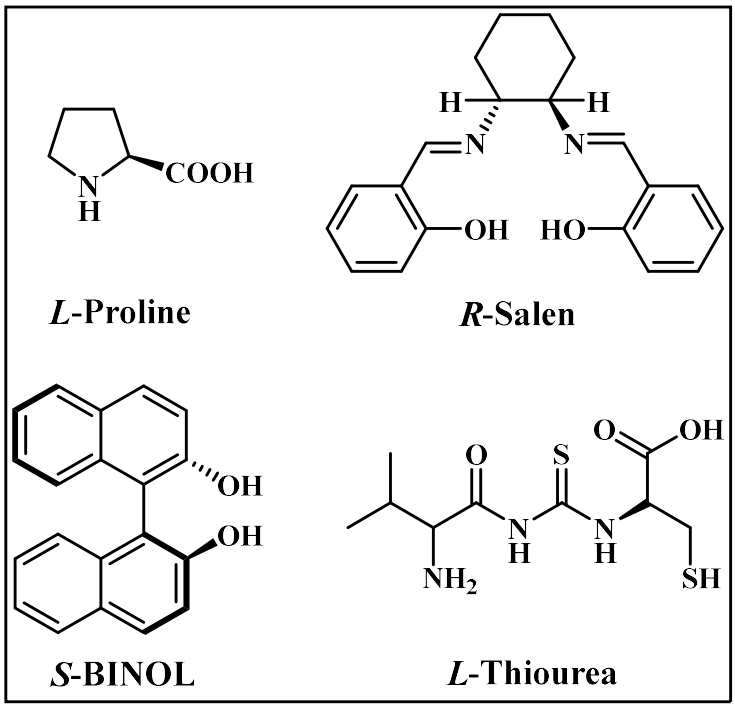


Figure 1.3 Examples privileged chiral ligands

Such ligands, often imbued with modularity and tunability, empower chemists to choreograph intricate reactions with precision, affording an exceptional level of control over product enantioselectivity. This synergistic interplay enables chemists to craft catalysts that are finely tailored to the demands of specific transformations, thereby amplifying the impact and scope of asymmetric catalysis.

1.3.1 Proline

Proline, an essential component of proteins, holds a distinct position in the realm of chiral ligands due to its unique structural characteristics and its versatile applications in asymmetric catalysis. Proline, formally known as pyrrolidine-2-carboxylic acid, is an amino acid with a five-membered ring structure. Its exceptional conformational rigidity, arising from its cyclic structure, imparts significant stereochemical control when employed as a ligand in asymmetric synthesis. The inherent chirality of proline allows it to act as a catalyst in various chemical transformations, promoting the formation of enantioselective products by influencing the reaction pathways.

In asymmetric catalysis, proline-based ligands often serve as organocatalysts, facilitating reactions that traditionally required transition metal complexes. This organocatalytic approach has gained substantial attention due to its environmental friendliness and mild reaction conditions. The distinct mode of action of proline involves its interaction with reactants through hydrogen bonding, leading to the creation of chiral transition states that guide the reaction toward the desired enantiomer. Proline-based ligands find wide application in a plethora of reactions, such as aldol reactions, Mannich reactions, and Michael additions, among others. These transformations allow chemists to construct complex molecular architectures with high levels of stereocontrol, making proline a powerful tool in the synthesis of pharmaceuticals, natural products, and functional materials.[14–18]

1.3.2 BINOL

BINOL, an acronym for 1,1'-bi-2-naphthol, possesses a distinctive structure characterized by two naphthalene rings connected by a central axis. This symmetrical yet chiral arrangement allows BINOL to engage in intricate interactions with metal catalysts and substrates, steering reactions toward the formation of enantiomerically enriched products. BINOL's chiral environment influences the pathways of chemical transformations, leading to the selective synthesis of molecules with specific laterality. Asymmetric catalysis, the cornerstone of chiral ligand applications, capitalizes on BINOL's ability to differentiate between mirror-image molecules. BINOL-based ligands, often in combination with metal catalysts, orchestrate a symphony of molecular interactions, inducing a desired stereochemistry in a variety of chemical reactions. These reactions range from classic transformations like asymmetric hydrogenation and allylation to more intricate processes such as Diels-Alder and Michael reactions.

BINOL's effectiveness lies in its role as a chiral scaffold, facilitating the creation of intricate transition states that dictate the outcome of reactions. Its ability to fine-tune molecular recognition and substrate orientation imparts an extraordinary level of control, enabling chemists to access specific enantiomers with remarkable efficiency.[19–23]

1.3.3 Salen

The chiral ligand salen (salen: (−)-1,2-*trans*-N,N'-bis(salicylidene)diaminocyclohexane) emerges as a compelling architect of chirality, orchestrating transformative reactions through asymmetric catalysis. Salen ligands are valued for their remarkable ability to selectively influence the formation of enantiomers – molecules with distinct mirror-image arrangements. These ligands, bearing a metal center coordinated by a symmetrically designed framework, act as precise navigators, steering chemical reactions towards desired three-dimensional outcomes. At the heart of salen's elegance lies its ingenious construction. The carefully designed ligand framework incorporates two salicylaldehyde moieties linked by a diaminocyclohexane bridge. This arrangement presents a platform for tailored interactions with metal catalysts and substrates, an essential facet of asymmetric catalysis. Salen's chiral backbone dictates the spatial orientation of reactants, directing their engagement in a manner that endows the final product with enantioselectivity.

Through a symphony of electrostatic forces, steric hindrance, and molecular recognition, salen ligands sculpt transition states with unparalleled precision. These transition states govern the path of reactions, ushering the formation of chiral products that hold distinct biological, pharmaceutical, and material applications. Salen's influence is tangible across a spectrum of reactions, ranging from oxidation and epoxidation to cycloadditions and polymerizations.[24–29]

1.3.4 Thiourea

Thiourea ligands, characterized by a sulfur-nitrogen double bond, possess an inherent asymmetry that resonates deeply with the concept of chirality. This structural peculiarity allows thiourea to engage in selective interactions with a wide array of substrates and catalysts, steering reactions toward the production of molecules with specific handedness. With precision reminiscent of an artisan's touch, thiourea ligands orchestrate the transformation of reactants into enantioenriched products. By virtue of their chiral structure, they influence the arrangement of atoms during chemical reactions, guiding the formation of distinct enantiomers with elegant finesse.

The allure of thiourea lies not only in its structural simplicity but also in its remarkable versatility. It finds a place of prominence in various catalytic processes, ranging from asymmetric synthesis to metal complexation. As a catalyst, thiourea engages in hydrogen bonding, π-π interactions, and other subtle forces, creating a chiral environment that serves as a gateway to chemo-, regio-, and stereoselectivity. Thiourea's impact extends across a broad spectrum of reactions, encompassing Michael additions, Mannich reactions, and more. Its contributions span beyond the laboratory bench, as industries harness its power to craft complex molecules with precision and efficiency.[30–34]

1.4 Asymmetric homogeneous catalysis

These catalysts, soluble within the reaction medium, possess inherent chirality, a characteristic that enables them to wield control over the formation of enantiomerically enriched products. At its core, asymmetric homogeneous catalysis employs both transition metal complexes and organocatalysts as the catalysts of choice. These chiral agents interact harmoniously with reactants, choreographing a precise dance of molecular interactions that guides the synthesis of specific mirror-image molecules. Transition metal complexes, often adorned with intricate chiral ligands, play the role of conductors in this intricate symphony. These ligands meticulously orchestrate the trajectory of reactants, ensuring that they align in a manner that leads to the desired enantiomeric outcome. On the other hand, organocatalysts wield their chiral influence through non-covalent interactions like hydrogen bonding, enacting their role as artistic directors of diverse chemical transformations.[35]

While the elegance of asymmetric homogeneous catalysis is undeniable, challenges abound. Catalyst stability and selectivity form a dynamic duet, each influencing the other. Ensuring the recovery and recycling of precious catalysts presents logistical intricacies. Moreover, orchestrating a harmonious interplay of catalysts, ligands, and reactants can be akin to conducting a complex symphony, requiring meticulous coordination.[36–39]

1.5 Asymmetric heterogeneous catalysis

Asymmetric heterogeneous catalysis stands as a captivating branch of modern chemistry, offering a distinctive approach to crafting chiral molecules with precise three-dimensional arrangements. This field harnesses solid catalysts, each possessing a carefully

designed chiral environment, to orchestrate enantioselective transformations. In contrast to its homogeneous counterpart, asymmetric heterogeneous catalysis involves catalysts existing as solids while the reactants remain in liquid or gaseous phases. These solid catalysts, often derived from modified or immobilized chiral homogeneous catalysts, interact with substrates at their surface, guiding reactions towards producing specific enantiomers. Solid catalysts in asymmetric heterogeneous catalysis showcase a fascinating array of surface properties that facilitate chirality-induced selectivity. Immobilized chiral ligands on the catalyst surface establish a platform for strategic interactions with reactants, enabling the creation of chiral transition states that favor desired enantiomeric outcomes.[40–44]

This thesis embarks on an exploration of the captivating work of asymmetric heterogeneous catalysis, delving into the arrangement of chiral surfaces, the intricacies of catalyst design, and the mechanistic tones that underscore enantioselective transformations.

1.5.1 Methodologies for immobilizing homogeneous asymmetric catalysts

In this, it is noted that the challenging task of separating the catalyst from the reaction medium in a way that is both simple and affordable is a significant barrier to the commercial utilization of chiral homogeneous catalysis. One of the most methodical solutions to this problem is the confinement of the catalyst-active substance on a hard support.[45] Many researchers have offered alternative techniques for immobilizing chiral compounds. Based on the catalyst-solid support interaction, covalent binding, electrostatic interaction, adsorption, and encapsulation are four key methods for immobilizing homogeneous catalysts as depicted in *Figure 1.4*

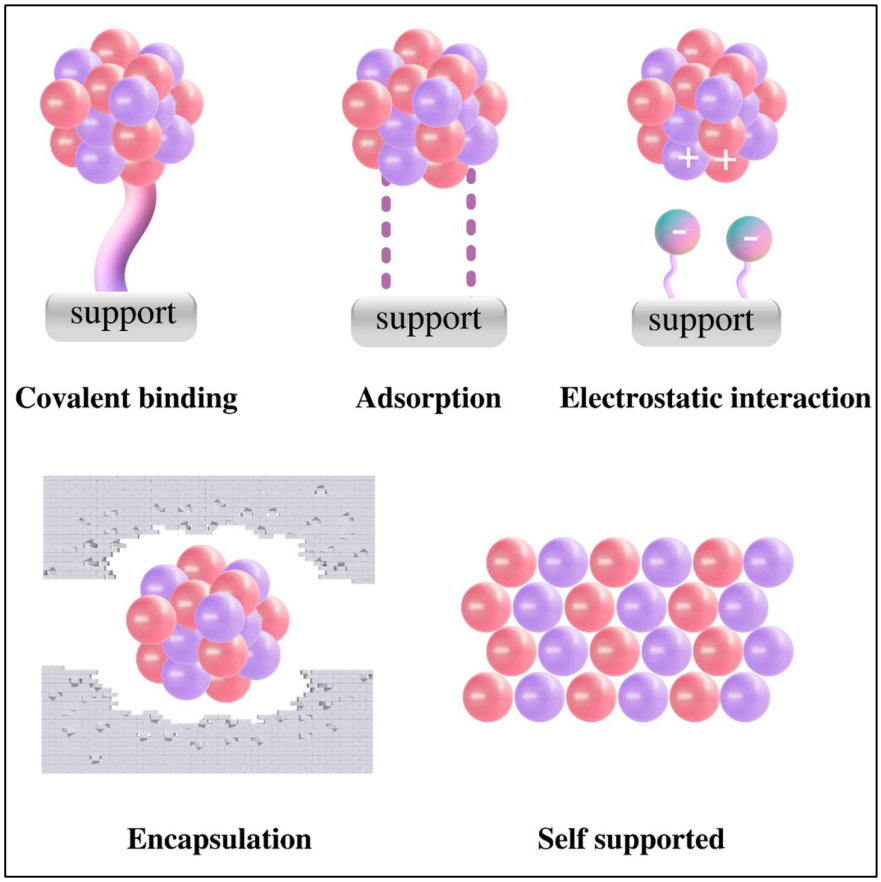


Figure 1.4 Various tactics for the confinement of homogeneous chiral catalysts.

(A) Encapsulation

This strategy involves entrapping a homogeneous catalyst within a porous support structure, preventing substantial physical or chemical association. The two techniques utilized are a flexible polymeric matrix or a rigid inorganic structure, with zeolites being preferred for their internal cavities. The catalyst is synthesized within the support's voids or trapped by it. Due to their internal cavities and narrow apertures, zeolites are the preferred material for this procedure, also known as the "ship-in-a-bottle" technique. Drawbacks include the challenge of finding materials with precise pore distribution and potential catalyst loss during the surface cleaning or Soxhlet extraction. While successful recycling preserves enantioselectivity, repeated regeneration reduces activity. The catalyst possesses short side chains and an inorganic backbone. This immobilization approach offers promising possibilities for enhancing catalytic processes in various applications.[46–54]

(B) Covalent binding

Functional groups are covalently attached to solid supports using the tethering technique, creating catalysts suitable for diverse reaction conditions and reducing leaching risks compared to non-covalent interactions. Silica and organic polymers are commonly used as support materials, with two main methods: post-grafting and co-condensation for incorporating active sites into silica materials. Post-grafting modifies silica surfaces through silylation, avoiding unwanted side reactions. Co-condensation yields materials with uniformly distributed functional groups. Polymer-supported catalysts are prepared using similar techniques like copolymerization or post-grafting onto pre-formed resins. These approaches enhance catalytic processes, providing stable catalysts with defined structures for various applications.[55–61]

(C) Electrostatic interaction

Enantioselective catalysts can be immobilized non-covalently on solid supports using electrostatic interactions. Positively or negatively charged enantioselective scaffolds can be immobilized on solid supports containing cationic or anionic species through electrostatic interactions. Layered materials (LMs) like anionic compounds and cationic clays, such as montmorillonite or hectorite like hydrotalcite (LDH), are excellent substrates due to their high surface area and ion-exchange capacity. Heterogeneous LDH catalysts with enantioselective organic scaffolds or complexes can be synthesized through different methods, including direct incorporation by mixing a freshly made anionic organic catalyst solution with LDH in an inorganic host. During the process, the organic and inorganic ionic counterparts reform, facilitating the insertion of the organocatalyst into the inorganic matrix.[62–68]

(D) Adsorption

Noncovalent immobilization occurs through physisorption or chemisorption. Physisorption relies on weaker forces like Van der Waals, while chemisorption involves stronger interactions like hydrogen bonding for stable adsorption. Silica is an effective host for physisorption of chiral metal complexes. Hydrophobicity affects adsorption characteristics. Immobilization on supports with free OH groups can be done via hydrogen bonding or using a "linker" or direct immobilization of the chiral catalyst. The approach serves as a counterion for

cationic enantioselective catalysts, enabling immobilization of various cationic substrates. Enantioselectivity for hydrogenation reactions improved after immobilization on diverse silicas due to structural constraints. The distinction between supporting approaches and chemisorption involving hydrogen bonds remains a debated topic.[69–77]

(E) Self-supported

Enantioselective catalysts can be self-supported through noncovalent or covalent anchoring to soluble or insoluble supports. One method involves using coordination bonds to create homochiral metal-organic solids by linking chiral scaffolds with metal centers, forming ditopic or polytopic structures. Another approach utilizes chiral polyfunctional scaffolds as connectors with metal ions or groups as junctions to produce metal-organic based homochiral solids with active sites on the main chain. These modular materials can be chemically modified for fine-tuning catalytic performance. These self-supported enantioselective catalysts offer strong enantioselectivity and efficiency in asymmetric transformations and can be easily recycled after the reaction without losing activity or selectivity.[78–82]

In summary, identifying a heterogeneous catalyst can be challenging. Immobilization processes and support materials are used to enhance catalytic activity and selectivity under optimal conditions. Immobilization prevents deactivation due to dimerization and cluster formation. However, additional synthetic pathways and methods are needed, potentially increasing catalyst costs. Weak metal complex-support interactions, like dipole-dipole and hydrogen bonding, can be used for immobilization. Supported catalysts come in various forms, such as physisorption, zeolite entrapped coordination compounds, polymer matrices, and supported ionic liquid phase catalysts. Alternatively, complex-support interaction can occur through ionic or covalent bonds via metal-ligand complex chemisorption, covalent anchoring, or ionic bonding.

1.5.2 Immobilization of chiral catalyst on organic polymers

Polymer-supported ligands and catalysts are gaining popularity due to their ease of separation and recyclability. They are considered as powerful tool for sustainable chemistry as they can be easily retrieved and recycled. However, in heterogeneous catalysis using a polymer support, the organic yield of a nonnatural process may decrease due to inefficient substrate-

supported catalyst interactions. Polymeric-supported catalysts have become popular choices in recent years, due to their easy recovery and recyclability. While polymer-supported catalysts can sometimes result in lower chemical yields, the development of highly reactive and chiral catalysts has enabled excellent enantioselectivities in asymmetric reactions. In fact, polymeric catalysts have demonstrated higher enantioselectivities compared to low-molecular-weight catalysts. The polymer network microenvironment can also benefit asymmetric processes. Common polymer substrates for chiral catalyst immobilization include crosslinked polystyrene and poly(ethylene glycol) (PEG). Soluble PEG-supported catalysts, for example, exhibit high reactivity and can be utilized in aqueous conditions. Polyethylene fibers, polymeric monoliths, polynorbornenes, and methacrylates are effective substrates for immobilizing homogeneous asymmetric catalysts as well.

Enantioselective catalysts have been immobilized on organic polymer supports in large numbers due to the effectiveness of supported catalysts and substrates in diverse organic transformations. Polymeric chiral catalysts achieve higher enantioselectivities. Amphiphilic polymer supports allow organic polymer-supported catalysts to perform in aqueous and organic solvents. As polymeric chiral catalysts are insoluble, they can be readily recovered and reused.[83–89]

1.5.3 Chiral catalysts supported by a dendrimer

Catalyst recovering is an essential experiential purpose in assisted catalyst development, especially for dendrimer catalysts. Various approaches are used to separate and recycle chiral dendrimer catalysts. In general, two methods can be employed to manufacture dendrimer catalysts: (i) incorporating a chiral organocatalyst (or metal complex) into the dendrimer's core; and (ii) inserting several chiral metal complexes at the dendrimer's periphery.

The innovative supramolecular dendritic catalysis method offers several advantages over traditional covalent techniques for synthesizing catalysts. It simplifies the process of catalyst synthesis and makes it easier to recycle the precious dendrimer support. Furthermore, by attaching different catalytic units to the supports at specific locations, supramolecular dendritic catalysis can also enable tandem and/or multicomponent asymmetric catalysis. Chiral dendrimer catalysts are thus poised to link the aperture between asymmetric homogeneous and heterogeneous catalytic systems, with a highly promising future. However, creating stable,

active, and efficient hyperbranched polymeric (or enantioselective dendrimer) catalysts remains a challenging task.[61,90–95]

1.5.4 Self-supported chiral catalysts

A new generation of immobilized chiral catalysts based on self-supporting chiral molecules showed exceptional enantioselectivity and activity in heterogeneous asymmetric catalytic processes. Self-sustaining chiral catalysts can be categorized as either organic-inorganic hybrid polymers or metal-organic coordination polymers, depending on the skeleton constitutions they possess. Polyfunctional (polytopic) organic molecules link metal atoms and clusters in MOCPs and MOFs to form extended arrays of metal-ligand complexes. In terms of their compositions, these compounds can either be classified as metal-ligand coordination polymers or metal-organic frameworks. The simplest coordination polymer comprises one metal ion and one bridging ligand with two coordination sites. Coordination sites produce polymeric chains, layers, or networks. In organic-inorganic hybrid polymers, the inorganic units consist of infinite arrays of metal-to-metal, which are modified by organic ligands or functionalities. These compounds combine the structural properties of both organic and inorganic materials, resulting in a unique class of materials with tunable properties and diverse applications. Due to versatile synthetic methods for synthesis from molecular building blocks, this self-supported chiral catalyst may preserve their structural solidarity during mild reactions. By assembling molecular building blocks, the self-supported chiral catalyst can be designed systematically with the required physical and chemical properties such as catalytic aptness and chirality. Polyfunctional chiral ligands that have multiple sites and catalytically operative metals are used to form coordination polymers or modify inorganic-organic composites, such as hybrid metal oxides, to create a self-supported chiral catalyst assemblage with catalytic ability and chiral topography.

In the recent years, innovative methods for the immobilization of soluble chiral chemicals in homochiral metal-organic hybrid polymers have been developed, offering a potential solution for heterogeneous asymmetric catalysis. These techniques have not only improved the activity and selectivity of MOCP catalysts but have also enhanced their stability and compatibility with reaction systems. As a result of the multifaceted challenges associated with MOCPs, several concepts and methods have been explored in catalysis, inorganic, polymers, supramolecular, and organometallic chemistry. With their potential applications in

numerous organic processes and materials chemistry, it is anticipated that MOCPs for catalyst immobilization will inspire more industrial and academic research community.[54,96–100]

1.5.5 Phase-transfer catalysis

Phase transfer catalysis (PTC) is today a key synthetic technique, valued in many areas of organic chemistry and used widely in industry. While asymmetric PTC derived structurally lucid nonracemic, chiral catalysts has been developed gradually, despite its potential to create a new domain in contemporary asymmetric catalysis by using structurally and stereochemically modulated tetraalkylonium cations (Q+). Massive efforts have recently enabled a number of bond-forming reactions to be achieved under gentle phase-transfer catalyst conditions. Interestingly, this shows the limits of prevailing systems but also drives the growth of innovative methods to expand asymmetric PTC. The strategy of rational chiral phase-transfer catalysts and synthetically useful conversions is to be emphasized in the near future. As a result, sustainable chemical processes could be developed around the world to produce industrially important compounds.[101–107]

1.5.6 Immobilization of chiral catalyst on inorganic materials

In the wide-ranging field of heterogeneous asymmetric catalysis research, the use of inorganic support in the sketching of entrapped catalysts favored reusability, and the potential application of this strategy is growing. In enabling easy catalyst reuse, the heterogenization of chiral catalysts onto inorganic materials also significantly improves the catalytic performances (activity, stability, and enantioselectivity), mostly as a result of site isolation and confinement effects.

The use of inorganic materials for catalyst heterogenization will remain a significant technique in the future for producing highly efficient chiral catalysts. Incorporating the distinct characteristics of inorganic substances in conjunction with a combinatorial strategy and advanced catalyst screening methods may enhance the potential for the growth of efficient chiral systems. This approach is expected to further facilitate the heterogenization of catalysts and improve the success rate of screening for highly efficient catalysts. Since the thesis primarily focuses on porous silica material as the support, a concise overview of mesoporous silica is provided below.[108–113]

1.6. Porous silica materials

In the realm of catalysis, where molecular transformations are orchestrated with finesse, catalyst supports play an instrumental role in shaping the performance and efficacy of catalytic systems. Among these, porous silica materials stand as architecturally exquisite platforms, poised at the intersection of structural versatility and catalytic prowess. This thesis embarks on a profound exploration into the multifaceted realm of porous silica materials as catalyst supports, delving into their design, impact on catalytic efficiency, and their role in tailoring selectivity across diverse reactions. At the heart of porous silica materials lies a complex network of interconnected pores and channels, akin to a scaffold that cradles catalytic species. This structural intricacy, reminiscent of an artful framework, provides a high surface area and a three-dimensional milieu for the deposition and immobilization of catalytically active species. The porous domains not only serve as repositories for active counterparts but also influence the accessibility of reactants to the catalytic sites, thereby orchestrating a delicate balance between reactivity and selectivity.[114–116]

The design and synthesis of porous silica catalyst supports involve a choreography of chemistry and engineering. The controlled adjustment of pore size and distribution, akin to tuning an instrument, governs the diffusion of reactants and products, thus influencing the rate and outcome of catalytic reactions. Additionally, the surface modification of these materials with functional groups or other catalytic promoters acts as a conductor's baton, orchestrating the interactions between the support and the catalytic species. Porous silica materials have graced the catalytic stage across a panorama of reactions, including hydrogenation, oxidation, cross-coupling, and beyond. Their remarkable stability, compatibility with diverse catalytic species, and facile surface engineering enable them to serve as ideal scaffolds for both homogeneous and heterogeneous catalysis. As catalyst supports, these materials not only enhance catalytic activity but also influence stereoselectivity and regioselectivity, akin to a director guiding the performance of each performer on a dramatic stage. Furthermore, the synergy between porous silica materials and catalysts extends beyond the confines of laboratory-scale reactions. These materials have found applications in industrial catalysis, where factors like stability, scalability, and recyclability is paramount. Their ability to accommodate high catalyst loadings, withstand harsh reaction conditions, and facilitate catalyst recovery aligns with the pragmatic demands of large-scale processes, rendering them as

indispensable components of sustainable and efficient industrial catalytic methodologies.[117–120]

This thesis illuminates the captivating role of porous silica materials as catalyst supports, delving into their structural intricacies, synthesis methodologies, and catalytic impact. By scrutinizing their influence on reaction mechanisms, selectivity patterns, and their contributions to sustainable chemistry, we uncover the underlying work that governs catalysis on these architecturally diverse platforms. As we traverse through diverse applications, from fine chemical synthesis to industrial processes, a panoramic view of porous silica materials as catalyst supports emerges, spotlighting their pivotal role in catalytic innovation and their significance in the quest for sustainable and selective chemical transformations.

This summary indicates the potential of heterogeneous chiral catalysis to greatly influence the academia and industrial research on chiral compounds. Several noteworthy instances have showcased the importance of solid support surfaces and pores. However, there remains a considerable need to enhance the enantioselectivity, activity, and stability of most heterogeneous chiral catalysts before their extensive integration into the industrial production of chiral compounds.

1.7 References

1. Collins A.N., Sheldrake G.N. and Crosby J. Chirality in Industry: The Commercial Manufacture and Applications of Optically Active Compounds, *John Wiley & Sons, Ltd.* **1992**.
2. Collins A.N., Sheldrake, G.N. and Crosby, J. () Chirality in Industry II: Developments in the Commercial Manufacture and Applications of Optically Active Compounds, *John Wiley & Sons, Ltd.* **1997**.
3. Noyori R. Asymmetric Catalysis In Organic Synthesis, *John Wiley & Sons, Ltd.* **1993**.
4. Rothenberg G. Catalysis Concepts and Green Applications, *John Wiley & Sons, Ltd.* **2008**.
5. Ojima I., Catalytic Asymmetric Synthesis, *John Wiley & Sons, Ltd.* **2010**.
6. Jacobsen E. N., Pfaltz A., Yamamoto H. & Jacobsen E. N. Comprehensive Asymmetric Catalysis I–III, *Springer-Verlag Berlin Heidelberg,* **2000**.
7. Yamamoto H., Lewis Acids in Organic Synthesis, *John Wiley & Sons, Ltd,* **2000**.

8. Blaser H. U., Schmidt E. Asymmetric Catalysis on Industrial Scale, *John Wiley & Sons, Ltd,* **2004**.
9. Heitbaum M., Glorius, F. & Escher I. Catalysis Asymmetric Heterogeneous Catalysis *Angew. Chem. Int. Ed.*, **2006**, 45, 4732–4762.
10. Blaser H. U., Pugin B. & Spindler F. Progress in enantioselective catalysis assessed from an industrial point of view. *J. Mol. Catal. A Chem.* **2005**, 231, 1–20.
11. Baleiza C. Chiral Salen Complexes : An Overview to Recoverable and Reusable Homogeneous and Heterogeneous Catalysts. *Chem. Rev.* **2006**,106, 3987−4043.
12. Gladysz J. A. Introduction : Recoverable Catalysts and Reagents s Perspective and Prospective. *Chem. Rev.* **2002**, 102, 9–10.
13. Thomas J. M. Constrained chiral catalysts. *J. Mol. Catal. A Chem.* **1999**, 141, 139–144.
14. Emma M. G., Tamburrini A., Martinelli A., Lombardo M., Quintavalla A., and Trombini C., A Simple and Efficient Protocol for Proline-Catalysed Asymmetric Aldol Reaction, *Catalysts,* **2020**, 10, 649.
15. Lustosa D. M., Barkai S., Domb I., and Milo A., Effect of Solvents on Proline Modified at the Secondary Sphere: A Multivariate Exploration, *J. Org. Chem.* **2022**, 87, 1850.
16. Mukherjee S., Yang J. W., Hoffmann S., and List B., Asymmetric Enamine Catalysis, *Chem. Rev.,* **2007**, 107, 5471.
17. List B., Lerner R. A., and Barbas C. F., Proline-Catalyzed Direct Asymmetric Aldol Reactions, *J. Am. Chem. Soc.*, **2000**, 122, 2395.
18. Tang Z., Jiang F., Cui X., Gong L. Z., Mi A. Q., Jiang Y. Z., and Wu Y. D., Enantioselective Direct Aldol Reactions Catalyzed By L-Prolinamide Derivatives, *Proc. Natl. Acad. Sci. U.S.A.* **2004**, 101, 5755.
19. Cheng J. K., Xiang S. H., Li S., Ye L., and Tan B., Recent Advances in Catalytic Asymmetric Construction of Atropisomers, *Chem. Rev.*, **2021**, 121, 4805.
20. Yue Q., Liu B., Liao G., and Shi B. F., Binaphthyl Scaffold: A Class of Versatile Structure in Asymmetric C–H Functionalization, *ACS Catal.*, **2022**, 12, 9359.
21. Chen Y., Yekta S., and Yudin A. K., Modified BINOL Ligands in Asymmetric Catalysis, *Chem. Rev.*, **2003**, 103, 3155.
22. Brunel J. M., BINOL: A Versatile Chiral Reagent, *Chem. Rev.*, **2005**, 105, 857.
23. Krajnc M. and Niemeyer J., BINOL as a Chiral Element in Mechanically Interlocked Molecules, Beilstein *J. Org. Chem.,* **2022**, 18, 508.
24. Baleizão, C. & Garcia, H. Chiral salen complexes: An overview to recoverable and reusable homogeneous and heterogenous catalysts. *Chem. Rev.,* **2006**, 106, 3987–4043.

25. Shaw S. & White J. D. Asymmetric Catalysis Using Chiral Salen-Metal Complexes: Recent Advances. *Chem. Rev.,* **2019**, 119, 9381–9426.
26. Yuan G., Jiang H., Zhang L., Liu Y. & Cui Y. Metallosalen-based crystalline porous materials: Synthesis and property. *Coord. Chem. Rev.,* **2019**, 378, 483–499.
27. Abd M., Sater E., Jaber N. & Schulz E. Chiral Salen Complexes for Asymmetric Heterogeneous Catalysis : Recent Examples for Recycling and Cooperativity. *ChemCatChem*, **2019**, 11, 3662.
28. Yuan Y. C., Mellah M., Schulz E., and David O. R. P., Making Chiral Salen Complexes Work with Organocatalysts, *Chem. Rev.*, **2022**, 122, 8841.
29. Mondal K. & Mistri S., Comments on Inorganic Chemistry A Journal of Critical Discussion of the Current Literature Schiff Base Based Metal Complexes : A Review of Their Catalytic Activity on Aldol and Henry Reaction. *Comments Inorg. Chem.* **2022**, 00, 1–29.
30. Sicignano M., Rodríguez R. I., Capaccio V., Borello F., Cano R., De Riccardis F., Bernardi L., Díaz-Tendero S., Della Sala G., and Alemán J., Asymmetric Trifluoromethylthiolation of Azlactones under Chiral Phase Transfer Catalysis, *Org. Biomol. Chem.* **2020**, 18, 2914.
31. Lafzi F., Kilic H., Tanriver G., Avcı Ö. N. & Catak S., Design and synthesis of novel indoline- (thio) urea hybrids. *Synth. Commun.* **2019**, 49, 3510–3527.
32. Vera S., García-Urricelqui A., Mielgo A., and Oiarbide M., Progress in (Thio)Urea- and Squaramide-Based Brønsted Base Catalysts with Multiple H-Bond Donors. *Eur J Org Chem*., **2023**, 26, 1-31.
33. Steppeler F., Iwan D., Wojaczyńska E., and Wojaczyński J., Chiral Thioureas-Preparation and Significance in Asymmetric Synthesis and Medicinal Chemistry, *Molecules*, **2020**, 25, 401.
34. Sun Y. L., Wei Y., and Shi M., Applications of Chiral Thiourea-Amine/Phosphine Organocatalysts in Catalytic Asymmetric Reactions, *ChemCatChem*, **2017**, 9, 718.
35. Tóth I., and Paul C. van Geem. The Handbook of Homogeneous Hydrogenation, *John Wiley & Sons, Ltd,* **2007**.
36. Li C. Chiral Synthesis on Catalysts Immobilized in Microporous and Mesoporous Materials. *Catalysis Reviews*, **2011**, 46, 419-492.
37. Zhao D. and Ding K. Recent Advances in Asymmetric Catalysis in Flow. *ACS Catal.* **2013**, 3, 928−944.
38. Trindade A. F., Gois P. M. P. & Afonso C. A. M. Recyclable Stereoselective Catalysts.

Chem. Rev. **2009**, 109, 418–514.

39. Mcmorn P. and Hutchings G. J. Heterogeneous enantioselective catalysts : strategies for the immobilisation of homogeneous catalysts. *Chem. Soc. Rev.* **2004**, 33, 108–122.
40. De Vos D. E., Van-kelecom I. F. J. and Jacobs P. A. Chiral Catalyst Immobilization and Recycling, *John Wiley & Sons, Ltd,* **2000**.
41. Bein T., Asymmetric catalysis on solids. *Current Opinion in Solid State & Materials Science*, **1999**, 4, 85-96.
42. Hutchings G. J., New approaches to rate enhancement in heterogeneous catalysis. *Chem. Commun.* **1999**, 4, 301–306.
43. Fan Q. & Chan A. S. C. Polymer-Supported Chiral Catalysts with Positive Support Effects. *Bioorganic Med. Chem. Lett*., **2002**, 12, 1867–1871.
44. Fan Q., Li Y. and Chan A. S. C. Recoverable Catalysts for Asymmetric Organic Synthesis. *Chem. Rev.,* **2002**, 102, 3385−3466.
45. Wan K. T. and Davis M. E., Design and Synthesis of a Heterogeneous Asymmetric Catalyst. *Nature,* **1994**, 370, 449.
46. Traa Y., Murphy D. M., Farley R. D. and Hutchings G. J., An EPR study on the enantioselective aziridination properties of a CuNaY zeolite. *Phys. Chem. Chem. Phys*. **2001**, 3, 1073–1080.
47. Formentin P. & Dome A. Combined Electrochemical and EPR Studies of Manganese Schiff Base Complexes Encapsulated within the Cavities of Zeolite Y. *Eur. J. Inorg. Chem.* **2000**, 1339-1344.
48. Frunza L., Kosslick H., Landmesser H., Hijft E. and Fricke R., Host/guest interactions in nanoporous materials I. The embedding of chiral salen manganeset (III) complex into mesoporous silicates. *J. Mol. Catal. A Chem.,* **1997**, 123, 179-187.
49. Domenech A., On the Existence of Different Zeolite-Associated Topological Redox Isomers. Electrochemistry of the Y Zeolite-Associated Mn (Salen) N3 Complex. *J. Phys. Chem. B,* **2002**, 106, 574-582.
50. Yao W., Zhang N., Xiong R., Kankala R., Liu Y. & Wang S., Highly-active platinum nanoparticle-encapsulated alumina-doped resorcinol–formaldehyde carbon composites for asymmetric hydrogenation. *React. Chem. Eng.* **2021**, 6, 1277–1284.
51. Li Y., Wang Ji., Kan J., Li F., Dong Y., and Dong Y., Combination of a Metal-N -Heterocyclic-Carbene Catalyst and a Chiral Aminocatalyst within a Covalent Organic Framework: a Powerful Cooperative Approach for Relay Asymmetric Catalysis. *Inorg. Chem.* **2022**, 61, 2455−2462.

52. Chen M., Zhang J., Liu C., Li H., Yang H., Feng Y., and Zhang B. Construction of Pyridine-Based Chiral Ionic Covalent Organic Frameworks as a Heterogeneous Catalyst for Promoting Asymmetric Henry Reactions. *Org. Lett.* **2021**, 23, 1748−1752.
53. Jiang H., Zhang W., Kang X., Cao Z., Chen X., Liu Y., and Cui Y. Topology-Based Functionalization of Robust Chiral Zr-Based Metal − Organic Frameworks for Catalytic Enantioselective Hydrogenation. *J. Am. Chem. Soc.* **2020**, 142, 9642−9652.
54. Newar R., Akhtar N., Antil N., Kumar A., Shukla S., Begum W., and Manna K., Amino Acid-Functionalized Metal-Organic Frameworks for Asymmetric Base – Metal Catalysis *Angew. Chem. Int. Ed*. **2021**, 4, 10964–10970.
55. Adima A., Moreau J. E. & Chi Man Michel W.. Chiral organic – inorganic solids as enantioselective catalytic materials. *J. Mater. Chem.* **1997**, 7(12), 2331–2333.
56. Tada M., Kojima N., Izumi Y., Taniike T. and Iwasawa Y., Chiral Self-Dimerization of Vanadium Complexes on a SiO2 Surface for Asymmetric Catalytic Coupling of 2-Naphthol : Structure , Performance , and Mechanism. *J. Phys. Chem. B,* **2005,** 109, 9905-9916.
57. Kureshy R. I., Ahmad I., Khan N. H., Sayed H.R. Abdi, Singh S., Pandia P. H., Jasra R. V. New immobilized chiral Mn (III) salen complexes on pyridine N-oxide-modified MCM-41 as effective catalysts for epoxidation of nonfunctionalized alkenes. *J. Catal.*, **2005**, 235, 28–34.
58. Luo Y., Xu Zi-Yue Wang H., Sun Xing-Wen Li Z., and Zhang D., Porous $Ru(bpy)_3^{2+}$-Linked Polymers for Recyclable Photocatalysis of Enantioselective Alkylation of Aldehydes. *ACS Macro Lett.,* **2020**, 9, 90−95.
59. Bakangura E., *et al.* Post-Modification of Copolymers Obtained by ATRP for an Application in Heterogeneous Asymmetric Salen Catalysis. *Molecules,* **2022**, 27, 4654.
60. Landeros J. M., Suchy L., Ávila C. G., Nuno O. and Juaristi E. Dendrimeric α, β - dipeptidic conjugates as organocatalysts in the asymmetric Michael addition reaction of isobutyraldehyde to N-phenylmaleimides. *Monatshefte für Chemie - Chem. Mon.,* **2019**, 150, 777–788.
61. Chen Y., Tan R., Zhang Y., Zhao G. and Yin D., Dendritic Chiral Salen Titanium (IV) Catalysts Enforce the Cooperative Catalysis of Asymmetric Sulfoxidation. *ChemCatChem,* **2015**, 7, 4066–4075.
62. Kureshy R. I. *et al.* Dicationic chiral Mn (III) salen complex exchanged in the interlayers of montmorillonite clay: a heterogeneous enantioselective catalyst for epoxidation of nonfunctionalized alkenes. *J. Catal.,* **2004**, 221, 234–240.

63. Bhattacharjee S. & Anderson J. A. Synthesis and characterization of novel chiral sulfonato–salen–manganese(III)complex in a zinc–aluminium LDH host. *Chem. Commun.,* **2004**, 5, 554–555.

64. Sento T., Shimazu S., Ichikuni N. & Uematsu T., Asymmetric hydrogenation of itaconates by hectorite-intercalated Rh-DIOP complex. *Journal of Molecular Catalysis A: Chemical,* **1999**, 137, 263–267.

65. Choudary B. M., Pal U., Kantam M. L. & Ranganath K. V. S., Asymmetric Epoxidation of Olefins by Manganese (III) Complexes Stabilised on Nanocrystalline Magnesium Oxide. *Adv. Synth. Catal.,* **2006**, 348, 1038–1042.

66. Majdecki M., Niedbala P. & Jurczak J., Amide-Based Cinchona Alkaloids as Phase-Transfer Catalysts: Synthesis and Potential Application. *Org. Lett.,* **2019**, 22, 8687−8691.

67. Gao Z., Qian J., Yang H., Zhang J. & Jiang G., Enantioselective Construction of C − C Axially Chiral Quinazolinones via Chirality Exchange and Phase-Transfer Catalysis. *Org. Lett.,* **2021**, 23, 1731−1737.

68. Guo Y., Wu L. & Qiu F. G., Highly Diastereo- and Enantioselective Formal [4+2] Cyclization of Nitroalkenes and Unsaturated Ketoesters under Phase-Transfer Catalysis. *Org. Lett.,* **2022**, 24, 8370−8374.

69. Wagner H. H. & Hausmann H., Immobilization of Rhodium Diphosphine Complexes on Mesoporous Al-MCM-41 Materials : Catalysts for Enantioselective Hydrogenation. *J. Catal.,* **2001**, 156, 150–156.

70. Heckel A. & Seebach D., Enantioselective Heterogeneous Epoxidation and Hetero-Diels-Alder Reaction with Mn- and Cr-salen Complexes Immobilized on Silica Gel by Radical Grafting. *Helvetica Chimica Acta.,* **2002**, 85, 913–926.

71. Baleizão C., Gigante B., Das D.,b Álvaro M., Garcia H., & Corma A., Periodic mesoporous organosilica incorporating a catalytically active vanadyl Schiff base complex in the framework. *J. Catal.,* **2004**, 223, 106–113.

72. Samadi S., Ashouri A., Rashid H. I., Majidiana S. & Mahramasrara M., Immobilization of (*L*)-valine and (*L*)-valinol on SBA-15 nanoporous silica and their application as chiral heterogeneous ligands in the Cu-catalyzed asymmetric allylic oxidation of alkenes. *New J. Chem.*, **2021**, 45, 17630-17641.

73. Stephenson P., Licence P., Ross S. K., Poliakoff M. and Swan T., Continuous catalytic asymmetric hydrogenation in supercritical. *Green Chem.,* **2004**, 6, 521–523.

74. Hu A., Yee G. T., and Lin W., Magnetically Recoverable Chiral Catalysts Immobilized

on Magnetite Nanoparticles for Asymmetric Hydrogenation of Aromatic Ketones. *J. Am. Chem. Soc.,* **2005**, 127, 12486-12487.

75. Lizandara-pueyo C., Fan X., Ayats C. and Pericàs M. A. Calcium Carbonate as Heterogeneous Support for Recyclable Organocatalysts. *J. Catal.,* **2020,** 393, 107-115.
76. Varga G., Kozma V., Judit V., Kukovecz Á. & Kónya Z., β -Isocupreidinate – CaAl-layered double hydroxide composites-heterogenized catalysts for asymmetric Michael addition. *Mol. Catal.,* **2020**, 482, 110675.
77. Wang J., Li K., He Y., Wang Y., Yan J., Xu L., Han X., and Yan Y., Lipase Immobilized on a Novel Rigid−Flexible Dendrimer-Grafted Hierarchically Porous Magnetic Microspheres for Effective Resolution of (R,S)-1-Phenylethanol. *ACS Appl. Mater. Interfaces.,* **2020**, 12, 4906−4916.
78. Wang X. & Ding K., Self-Supported Heterogeneous Catalysts for Enantioselective Hydrogenation. *J. Am. Chem. Soc.,* **2004**, 126, 10524-10525.
79. Ding K., Wang Z., Wang X., Liang Y., and Wang X., Self-Supported Chiral Catalysts for Heterogeneous Enantioselective Reactions, *Chem. Eur. J.,* **2006**, 12, 5188.
80. Bellemin-laponnaz S., Achard T. & Bissessar D. Synthesis and application of dynamic self-supported enantioselective catalysts. *Coord. Chem. Rev.,* **2017**, 332, 38.
81. Jiang J., Ouyang G., Zhang L., & Liu M., Self-Assembled Chiral Nanostructures as Scaffolds for Asymmetric Reactions. *Chem. Eur. J.,* **2017**, 23, 9439.
82. Wang Z., Chen G. & Ding K., Self-Supported Catalysts. *Chem. Rev.,* **2009**, 109, 322–359.
83. Ochiai H., Nishiyama A., Haraguchi N. & Itsuno S., Polymer-Supported Chiral Cis-Disubstituted Pyrrolidine Catalysts and Their Application to Batch and Continuous-Flow Systems. *Org. Process Res. Dev.,* **2020**, 24, 2228–2233.
84. Wang J., Li J., Wang Y., He S., You H., & Chen Fen-Er,. Polymer-Supported Chiral Heterogeneous Copper Catalyst for Asymmetric Conjugate Addition of Ketones and Imines under Batch and Flow. *ACS Catal.,* **2022**, 12, 9629−9637.
85. Monterde C., Navarro R., Iglesias M. & Sánchez F., Adamantyl-BINOL as platform for chiral porous polymer aromatic frameworks. Multiple applications as recyclable catalysts. *J. Catal.,* **2019**, 377, 609–618.
86. Md. Wali U. & Haraguchi N., Ionic, Core-Corona Polymer Microsphere-Immobilized MacMillan Catalyst for Asymmetric Diels-Alder Reaction. *Catalysts,* **2019**, 9, 960.
87. Li X., Sun Y., Wang S. & Jia X. Stable Chiral Ruthenium Complex Catalyst Based on Polymer Ionic Liquid for Asymmetric Transfer Hydrogenation of Aliphatic Ketones in

Water. *ACS Appl. Polym. Mater.,* **2020**, 2, 1268–1275.

88. Yan Z., Xie G., Zhang J. & Ma X., Hollow organic polymeric nano-bowls-supported BINOL-derived chiral phosphoric acid: enhanced catalytic performances in the enantioselective allylation of aromatic aldehydes. *Mol. Catal.,* **2019**, 464, 39–47.
89. Huang J., Liu S., Ma Y. & Cai J. Chiral salen Mn (III) immobilized on ZnPS-PVPA through alkoxyl-triazole for superior performance catalyst in asymmetric epoxidation of unfunctionalized olefins. *J. Organomet. Chem.,* **2019**, 886, 27–33.
90. Ley S. V. *et al.* Multi-step organic synthesis using solid-supported reagents and scavengers: A new paradigm in chemical library generation. *J. Chem. Soc. Perkin Trans.,* **2000***,* 1, 3815–4195.
91. Lee W., Li L., and Kim B., SuFEx-Click Approach for the Synthesis of Soluble Polymer-Bound MacMillan Catalysts for the Asymmetric Diels–Alder Reaction. *Catalysts,* **2021**, 11, 1044.
92. Chhanda S. A. & Itsuno S., Design and synthesis of chiral hyperbranched polymers containing cinchona squaramide moieties and their catalytic activity in the asymmetric Michael addition reaction. *J. Catal.,* **2019**, 377, 543–549.
93. Anandhan R., Reddy M. B. and Sasikumar M., Development of novel triazole based dendrimer supported spiroborate chiral catalysts for the reduction of (E)-O-benzyl oxime: an enantioselective synthesis of (S)-dapoxetine. *New J. Chem.,* **2019**, 43, 15052-15056.
94. Peng M., Chen Y., Tan R., Zhenga W. & Yin D., A Highly Efficient and Recyclable Catalyst—Dendrimer Supported Chiral salen Mn(III) Complex for Asymmetric Epoxidation. *RSC Adv.,* **2013**, 3, 20684-20692.
95. Zhao W., *et al.* Synthesis of dendrimer-supported ferrocenylmethyl aziridino alcohol ligands and their application in asymmetric catalysis. *Green Chem.* **2015**, 17, 2924–2930.
96. Valverde-González A., *et al.* Porous aromatic frameworks containing binaphthyl-dihydroazepine units (cBAPAFs) as catalytic supports for asymmetric reactions. *J. Catal.* **2022**, 413, 434–442.
97. Zhu J., Meng X., Liu W., Qi Y., Jina S. & Huo S., Regulated synthesis of Zr-metal – organic frameworks with variable hole size and its influence on the performance of novel MOF-based heterogeneous amino acid–thiourea catalysts. *RSC Adv.*, **2022**, 12, 21574.
98. Berijani K., Morsali A. and Hupp J. T., An effective strategy for creating asymmetric MOFs for chirality induction : a chiral Zr-based MOF for enantioselective epoxidation.

Catal. Sci. Technol., **2019**, 9, 3388.

99. Ma H., Sun Y., Chen G., & Dong Y., A BINOL-phosphoric acid and metalloporphyrin derived chiral covalent organic framework for enantioselective α-benzylation of aldehydes. *Chem. Sci.,* **2022**, 13, 1906-1911.
100. Lirio S., *et al.* Fast multipoint immobilization of lipase through chiral L-proline on a MOF as a chiral bioreactor. *Dalton Trans.,* **2021**, 50, 1866–1873.
101. Sicignano M., *et al.* An Entry to Enantioenriched 3,3-Disubstituted Phthalides through Asymmetric Phase-Transfer-Catalyzed γ-Alkylation. is: *J. Org. Chem.,* **2020**, 85, 7476−7484.
102. Li J., Wei Z., Cao J., Liang D., Lin Y., & Duan H., Aymmetric Aza-Friedel − Crafts Reaction of Isatin-Derived Ketimines with Indoles Catalyzed by a Chiral Phase-Transfer Catalyst. *Org. Biomol. Chem.*, **2022**, 18, 2914-2920.
103. Xu C., Qi Y., Yang X., Li X., Li Z., & Bai L., Development of C2-Symmetric Chiral Spirocyclic Phase-Transfer Catalysts: Synthesis and Application to Asymmetric Alkylation of Glycinate Schiff Base. *Org. Lett.,* **2021**, 23, 2890−2894.
104. Long H., Li Y., Zhang B., Xiao W., Zhang X., He L., & Deng J., Asymmetric Bromoaminocyclization and Desymmetrization of Cyclohexa-1,4-dienes through Anion Phase-Transfer Catalysis. *Org. Lett.,* **2021**, 23, 8153−8157.
105. Lee J., *et al.* Asymmetric Phase-Transfer Catalytic aza-Michael Addition to Cyclic Enone: Highly Enantioselective and Diastereoselective Synthesis of Cyclic 1,3-Aminoalcohols. *Org. Lett.,* **2022**, 24, 1647−1651.
106. Zhu P., Yang Y., Liu Y. & Peng Y., Asymmetric Addition of α- Diazomethylphosphonate to Alkylideneindolenine Catalyzed by a Trifunctional BINAP-Based Monophosphonium Salt. *Org. Lett.,* **2022**, 24, 1657−1661.
107. Majdecki M., Tyszka-gumkowska A. & Jurczak J., Highly Enantioselective Epoxidation of α , β -Unsaturated Ketones Using Amide-Based Cinchona Alkaloids as Hybrid Phase-Transfer Catalysts. *Org. Lett.,* **2020**, 21, 8085−8090.
108. Ren Y., Wang M., Yang Q. & Zhu J., Merging Chiral Diamine and Ni/SiO2 for Heterogeneous Asymmetric 1,4-Addition Reactions. *ACS Catal.* **2023**, 13, 1974-1982.
109. Yuan Y., El A. & Mellah M., Enantiopure isothiourea@carbon-based support: stacking interactions for recycling a lewis base in asymmetric catalysis. *Org. Chem. Front,* **2021,** 8, 4693-4699.
110. Samadi S., Ashouri A. & Samadi M. Synthesis of Chiral Allylic Esters by Using the New Recyclable Chiral Heterogeneous Oxazoline-Based Catalysts. *ACS Omega,* **2020,**

5, 22367-22378.

111. Deimling M., Kousik S. R., Abitaev K., Frey W., Sottmann T., Koynov K., Laschat S., & Atanasova P., Hierarchical Silica Inverse Opals as a Catalyst Support for Asymmetric Molecular Heterogeneous Catalysis with Chiral Rh-diene Complexes. *ChemCatChem,* **2021**, 13, 2242–2252.
112. Shukla M., Barick K. C., Salunke H. G. & Chandra S., Chiral salen - Ni (II) based spherical porous silica as platform for asymmetric transfer hydrogenation reaction and synthesis of potent drug intermediate montekulast. *Mol. Catal.* **2021**, 502, 111367.
113. Zou X., Wang Y., Wang C., Shi K., Ren Y. & Zhao X., Chiral Mn^{III} (Salen) Immobilized on Organic Polymer/Inorganic Zirconium Hydrogen Phosphate Functionalized with 3-Aminopropyltrimethoxysilane as an Efficient and Recyclable Catalyst for Enantioselective Epoxidation of Styrene. *Polymers,* **2019**, 11, 212.
114. Narayan R. & Nayak U. Y,. Mesoporous Silica Nanoparticles : A Comprehensive Review on Synthesis and Recent Advances. *Pharmaceutics*, **2018**, 10, 118.
115. Ghaedi H. & Zhao M., Review on Template Removal Techniques for Synthesis of Mesoporous Silica Materials. *Fuels,* **2022**, 36, 2424–2446
116. Xu H. & Wu P., Two-dimensional zeolites in catalysis : current state-of-the- art and perspectives. *Catal. Rev.,* **2021,** 63, 234–301.
117. Wu S. H. & Lin H. P. Synthesis of mesoporous silica nanoparticles. *Chem. Soc. Rev.,* **2013**, 42, 3862–3875.
118. Shinde P. S., *et al.* A brief overview of recent progress in porous silica as catalyst supports. *J. Compos. Sci.,* **2021**, 5, 1–17.
119. Eduardo P., Valencia S. & Rey F. Zeolites in Adsorption Processes : State of the Art and Future Prospects. *Chem. Rev.*, **2022,** 122, 17647–17695.
120. Gong X., *et al.* First-Generation Organic Reaction Intermediates in Zeolite Chemistry and Catalysis. *Chem. Rev.*, **2022**, 122, 14275.