Synthesis of microporous polymeric BINOL-derived phosphoric acids and applications in heterogeneous asymmetric organocatalysis

vorgelegt von

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Von der Fakultät II – Mathematik und Naturwissenschaften

der Technischen Universität Berlin

zur Erlangung des akademischen Grades

Doktor der Naturwissenschaften

- Dr. rer. nat. -

vorgelegte Dissertation

Promotionsausschuss:

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Zweiter Berichter:	Jun. -Prof. Dr. rer. nat. Carl Christoph Tzschucke

Tag der wissenschaftlichen Aussprache: 10. September 2012

Berlin, 2012

D 83

Synthesis of microporous polymeric BINOL-derived phosphoric acids and applications in heterogeneous asymmetric organocatalysis

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From the Faculty II – Mathematics and Natural sciences

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To obtain academic grades

Doctor of Natural Science

- Dr. rer. nat. -

Thesis Submitted

Doctoral Committee:

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Second examiner:	Jun. -Prof. Dr. rer. nat. Carl Christoph Tzschucke

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Abstract

This thesis presents synthesis of chiral, catalytically active as well as highly selective organic polymers of intrinsic microporosity for application in asymmetric heterogeneous organocatalysis. To polymerize enantiopure BINOL-derivatives, different organic moieties, containing thiophene unit, were synthesized and substituted on BINOL-backbone. Oxidative coupling reaction under suitable condition provided insoluble solid polymeric materials containing chiral BINOL-phosphoric acid. Other than that, different co-polymers were also synthesized adding organic molecule containing thiophene units, in different proportions. The solid material containing phosphoric acid-functionality showed high specific surface area up to 798 m^2 g^{-1}. The polymers and co-polymers yielded impressive results as heterogeneous catalyst in asymmetric transfer hydrogenation (up to 98% *ee*) as well as Friedel-Crafts type reaction of pyrrole and aza-ene type reaction. This type of heterogeneous catalyst is recoverable by centrifugation after reaction and found to be reusable up to 10 consecutive runs without any loss in activity or selectivity. Again, some kinetic experiments were performed for reaction rate comparison with monomeric catalyst. The porous polymeric catalyst showed much faster reaction rate for asymmetric transfer hydrogenation reaction compared to other reported polymer supported BINOL-derived phosphoric acid catalyst in same reaction condition. This is possibly due to microporous nature of the heterogeneous material. This work not only combines asymmetric organocatalysis with advanced functional material chemistry by revealing easy way to synthesize heterogeneous, microporus BINOL-phosphoric acid but also promises for future applications in large scale industrial processes for asymmetric synthesis.

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Prof. Dr. Siegfried Blechert Dipti Sankar Kundu.

The entire work embodied in this thesis is the result of investigations carried out by me from October 2009 to March 2012 at the Institute of Chemistry, Technical University of Berlin, Germany, under the supervision of Prof. Dr. Siegfried Blechert.

It is with high regards that I thank Prof. Dr. Siegfried Blechert who has given me the opportunity to carry out my doctoral study in his research group and to explore myself by working in the fascinating project combining organocatalysis with advanced functional material chemistry. I am deeply indebted to him for his inspiring guidance, constant encouragement and helpful discussions.

I would like to thank my second supervisor Prof. Dr. Arne Thomas for his constant guidance, and support.

I am sincerely thankful to Jun. -Prof. Dr. Carl Christoph Tzschucke for being my external examiner. I would like to thank Prof. Dr. Marga Cornelia Lensen for being the chair of my doctoral committee.

I am grateful to all of my colleagues, particularly to mention Dr. Christian Bleschke for his help, co-work and invaluable guidance during the initial period.

I am genuinely thankful to Dr. Jean-Philippe Lonjaret, Prof. Dr. Reinherd Schomäcker and Prof. Dr. Matthias Driess for their constant support from UNICAT and BIG-NSE.

My special thanks are due to Dr. Johannes Schmidt for his co-work and contribution to our project.

I would like to thank all the employees of this department, particularly the people of IR and mass divisions, for their help.

It is my pleasure to thank Monalisa Das, my parents and family for their constant love and support.

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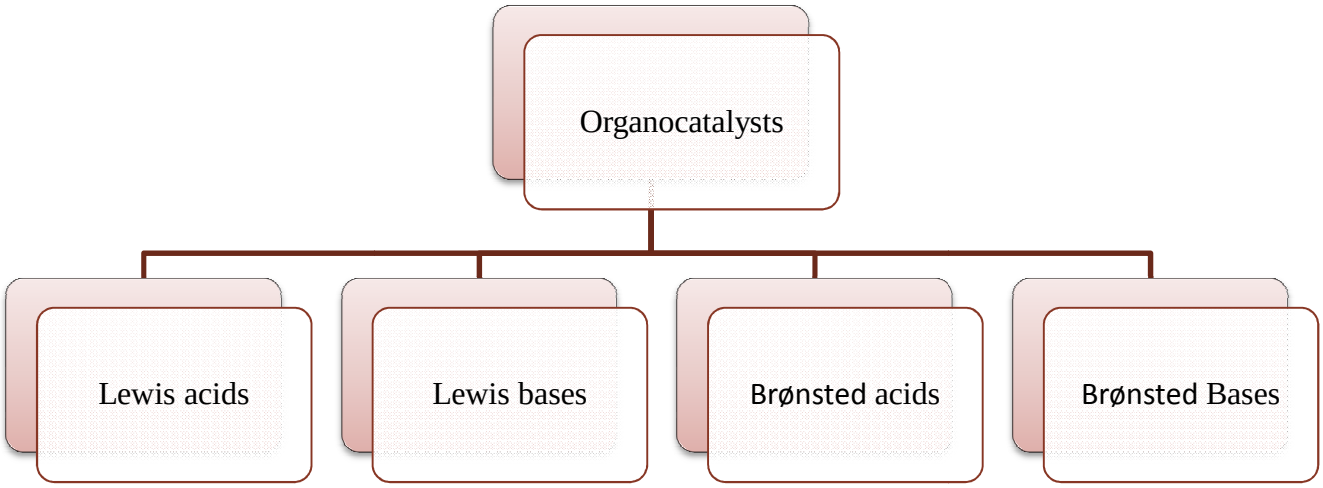
Theoretical background

Organocatalysis

Organocatalysis[1, 2, 3, 4, 5, 6] is the catalysis with small organic molecules, where an inorganic element is not part of the active principle. Besides transition metal catalysis[7] and biocatalysis[8, 9] organocatalysis also provides tremendous opportunities to synthetic organic chemists. Though organocatalysis was known from the work of Leibig in 1859 where acetaldehyde was used as catalyst, it caught the attention of modern chemists only after the pioneering work by List[10, 11] and McMillan[12, 13] in 2000. After that, during last decade organocatalysis rose to prominence as highly useful tool for asymmetric transformations in numerous organic reactions. Primarily all of the organocatalysts can be divided into four broad categories. Lewis bases, Lewis acids, Brønsted bases and Brønsted acids. These catalysts initiate their catalytic cycles by either providing or removing electrons or protons from a substrate or a transition state.

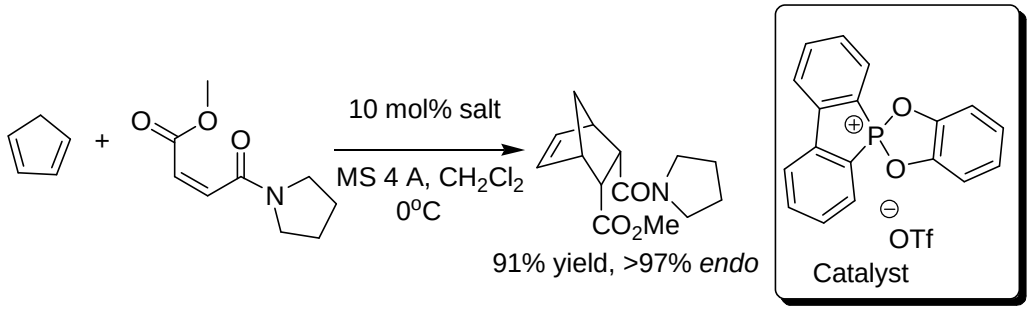


Organocatalysis with Lewis acid

The field of Lewis acid organocatalysis is still unexplored compared to other type of organocatalysis. The number of asymmetric catalyzed examples is small and the obtained enantiomeric excess is often low. But, due to broad variety of possible reactions which are catalyzed by Lewis acids, this research field possesses a large potential to grow. Compounds containing carbenium[14], silylium[15] or phosphonium cations[16, 17] can act as Lewis acid

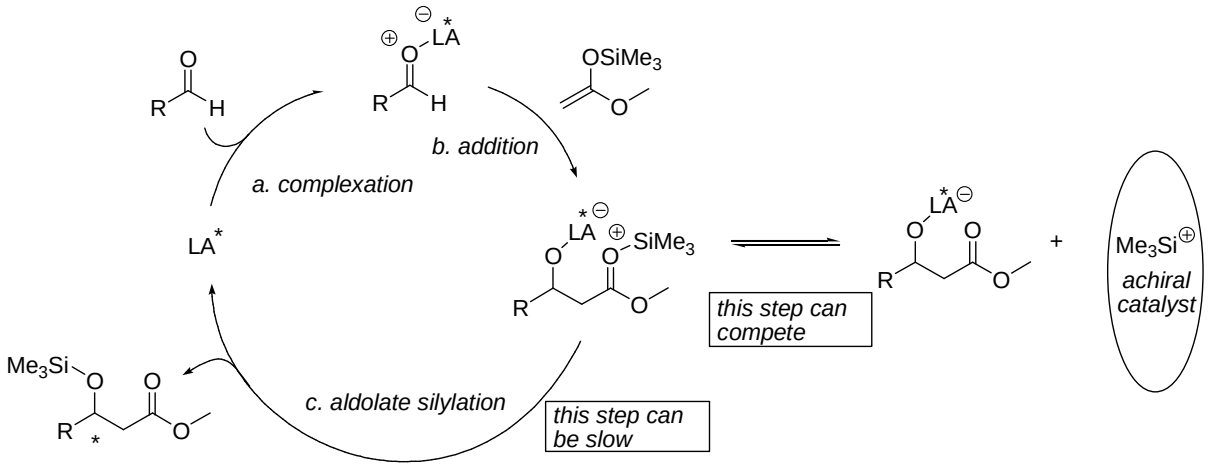
catalysts. Other than that, phosphorous and silicon based hypervalent compounds display Lewis acid catalytic activity [18].

In 2006 *Terada* and *Kouchi* reported use of phosphonium salts as Lewis acid catalysts [19]. They synthesized phosphonium salts containing pentacoordinated hypervalent phosphorous atom attached to electron withdrawing group. They applied various phosphonium salts in the Diels-Alder reaction yielding up to 91% yield and 97% endo selectivity (See Scheme 1).



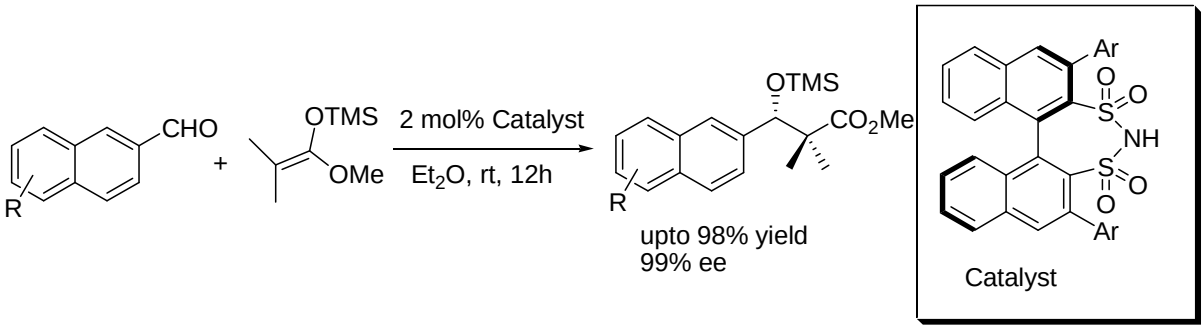
Scheme 1: Use of phosphonium salts as Lewis acid catalyst for Diels-Alder reaction.

Asymmetric Mukaiyama aldol[20] reaction has attracted much interests for years. Though several versions of asymmetric Mukaiyama aldol reactions have been developed most asymmetric variations still require high catalyst loadings of typically 20 mol% or results in lower enantioselectivity[21, 22, 23]. The reason for this high loading is that an achiral yet *catalytically competent* second species is generated during the reaction: a silylium ion equivalent, which can be released if the terminating aldolate silylation step is relatively slow. (See Scheme 2)

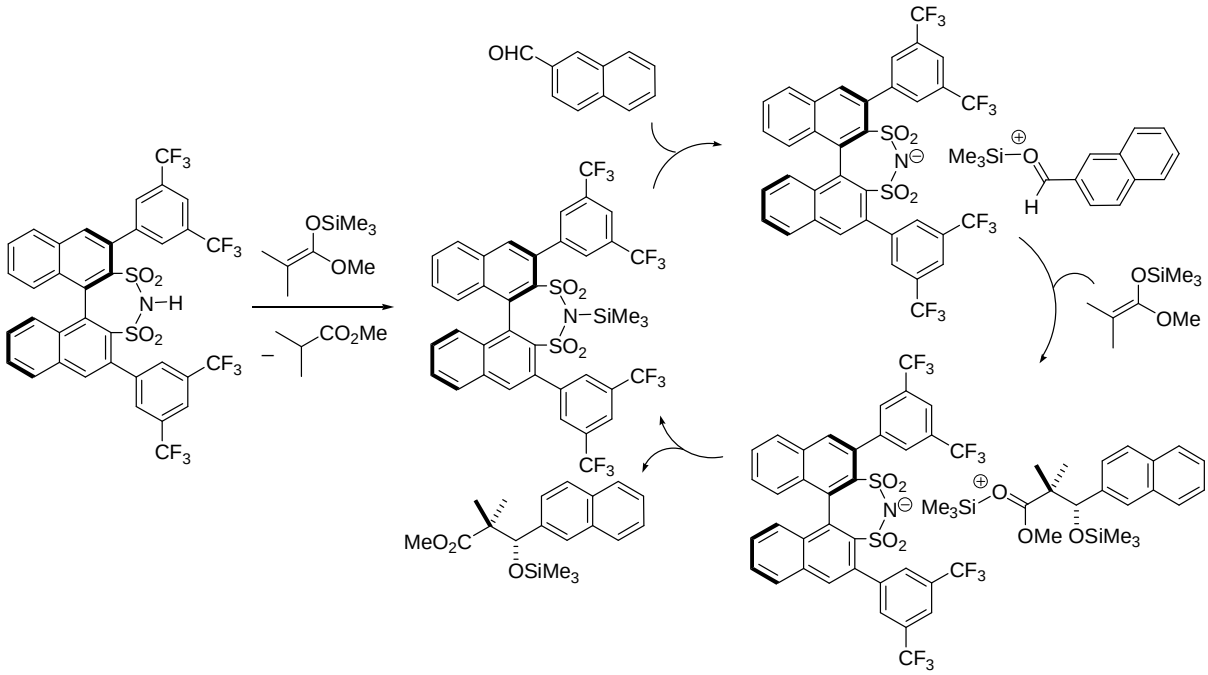


Scheme 2: Trimethyl silylium ion influences enantioselectivity in asymmetric Mukaiyama aldol reaction.

Inspired by the fact that bistriflimide (Tf_2NH) is a powerful achiral Mukaiyama aldol pre-catalyst generating the highly reactive Lewis acid Tf_2NTMS as the actual catalyst *List* and co-workers developed chiral disulfonimides as chiral Tf_2NH equivalents and applied in enantioselective Mukaiyama aldol reactions[24, 25]. They synthesized chiral binaphthyl-based disulfonimides 3, 3'-diaryl substituted (*R*)-BINOL derivatives and achieved up to 99% ee (See Scheme 3 and Scheme 4) .



Scheme 3: Asymmetric Mukaiyama aldol reaction with disulfonamide catalyst.



Scheme 4: Mechanism of asymmetric Mukaiyama aldol reaction using chiral disulfonamide catalyst.

Organocatalysis with Brønsted base

Since their early use in enantiomeric separation [26] processes, chiral Brønsted base catalysis has advanced significantly to include both natural and designed catalysts. Bifunctional catalysts containing both Brønsted base and H-activating functionalities have proven to be very applicable to an array of reaction types (See Figure 1). Initially described in 1913 for enantioselective hydrocyanation to aldehydes[27] and later broadly developed by Wynberg in the 1970s and 1980s, chiral organic Brønsted base catalysis has emerged as the result of mechanistic understanding and observations about Brønsted base and hydrogen bond donor activation of substrates. The first catalytic enantioselective conjugate addition was documented as Wynberg's work[28] on Cinchona alkaloid-catalyzed addition of cyclic ß-keto esters to methyl vinyl ketone.

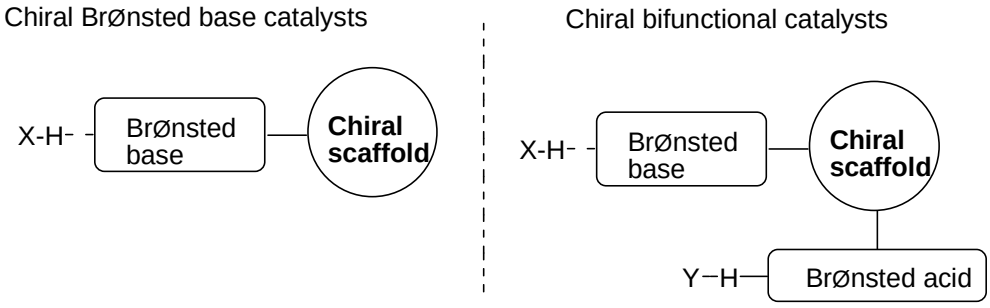


Figure 1: Mode of action for chiral Brønsted base and chiral bifunctional catalyst.

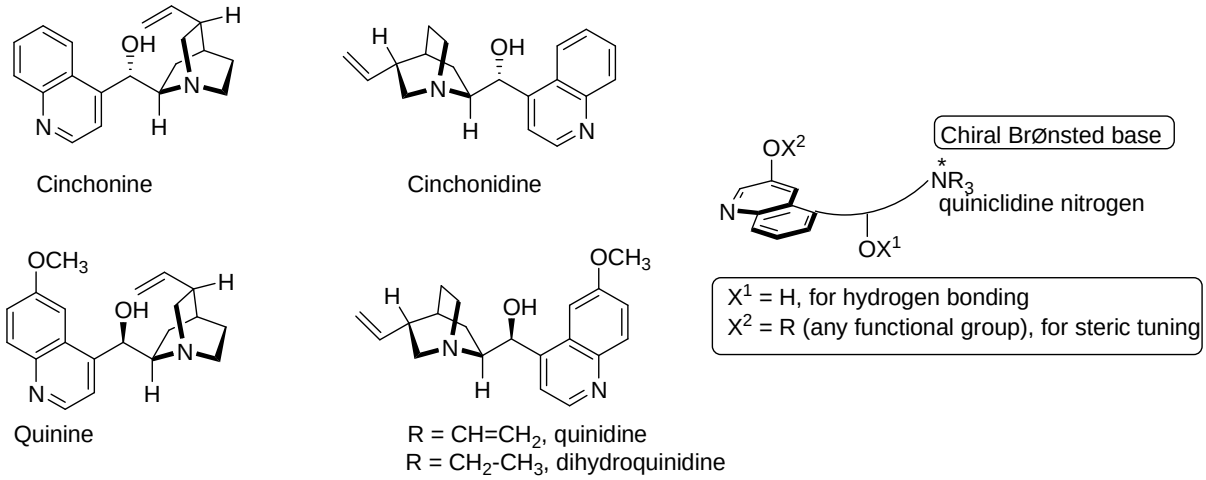
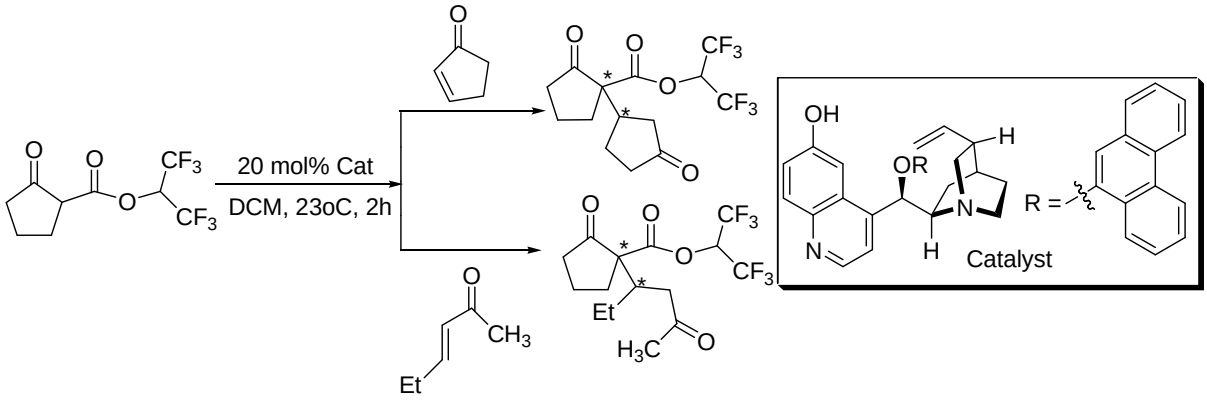


Figure 2: Examples of natural and synthetic alkaloids for Brønsted base catalysis.

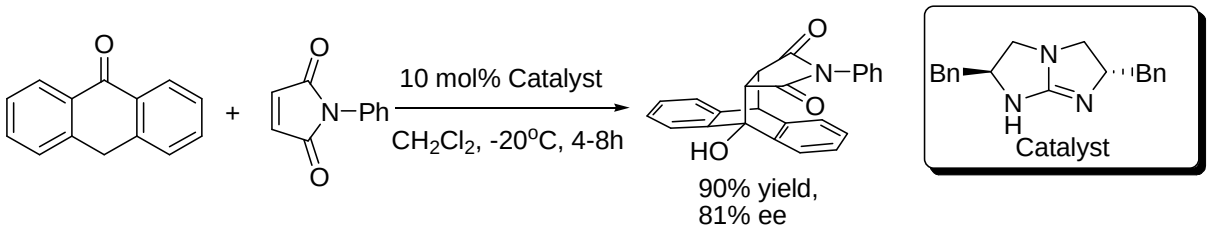
The interesting mode of stereoselectivity of Cinchona alkaloids is presented by its pseudo-enantiomeric pairs which can be employed to generate either enantiomers of chiral product. [29, 30, 31] Again synthetic variations of natural Cinchona alkaloids provide great improvement

of enantioselectivity in many cases (See Figure 2). For example, Deng and co-workers[32] reported the first conjugated addition of α-substituted β-ketoester to α,β-unsaturated ketones using natural cinchona alkaloid with C(9)-OH replaced by an ester group (See Scheme 5).



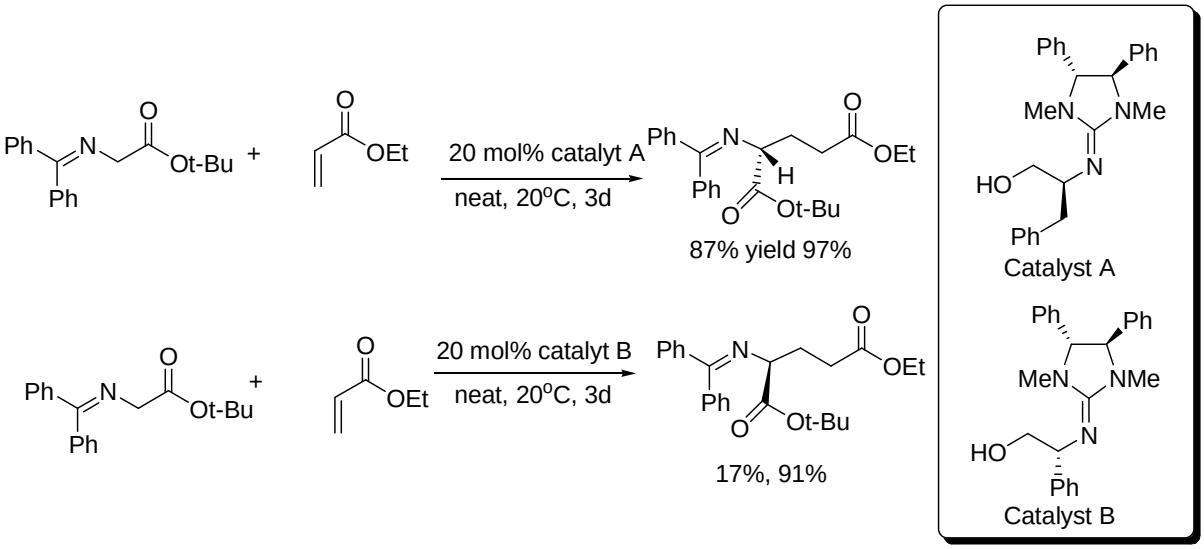
Scheme 5: Conjugated addition of α-substituted β-ketoester to α,β-unsaturated ketones using modified cinchona alkaloid .

While cinchona alkaloids act as bifunctional catalyst there are catalysts which solely act as Brønsted base catalyst. For example, guanidines have been very successful as Brønsted base catalyst. In contrast to bifunctional catalyst, guanidines are basic enough to activate the substrates without the need of the secondary moieties. *Tan* and co-workers, in 2006, reported the first chiral guanidine catalyzed asymmetric Diels-Alder reaction.[33] They used C_2-symmetric bicyclic guanidine catalyst for the addition of anthrone to maleimide.(See Scheme 6)



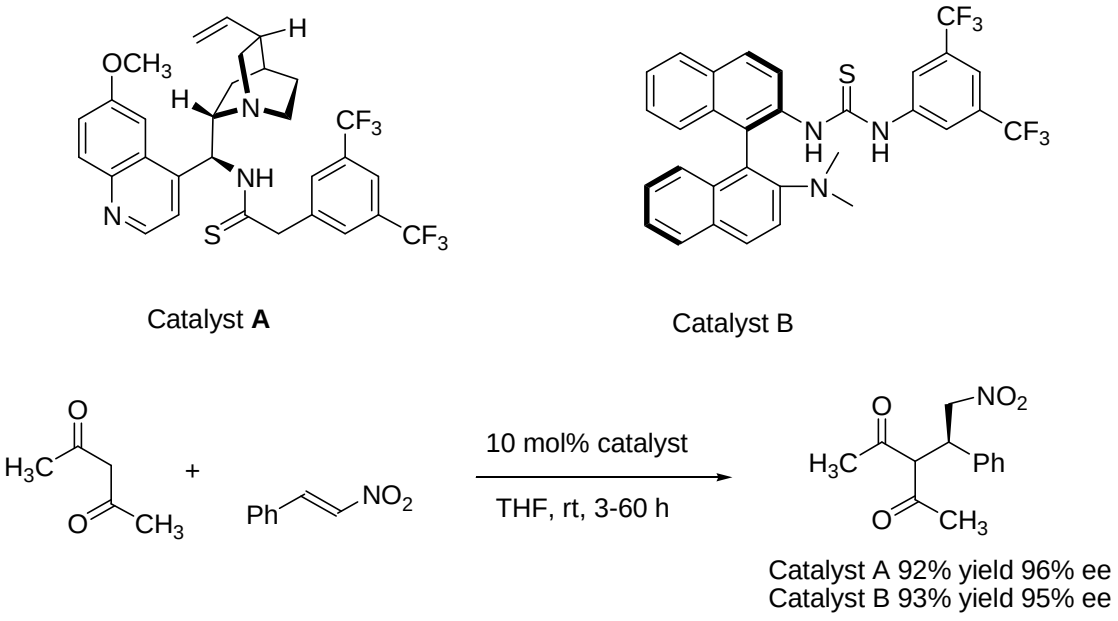
Scheme 6: Chiral guanidine catalyzed asymmetric Diels-Alder reaction.

Ishikawa and co-workers reported asymmetric Michael addition of glycine imines to acrylates using structurally modified chiral guanidine as super base (See Scheme 7).[34]



Scheme 7: Asymmetric Michael addition of glycine imines to acrylates using structurally modified chiral guanidine

Other than bifunctional catalysts and guanidine, more complex catalysts have been developed for Brønsted base catalysis in recent years.[35] Binaphthol-derived amine thioureas have been introduced as a novel class of organocatalysts for asymmetric Michael addition of 2,4-pentadiones to nitro-olefins by Wang and co-workers (See Scheme 8).

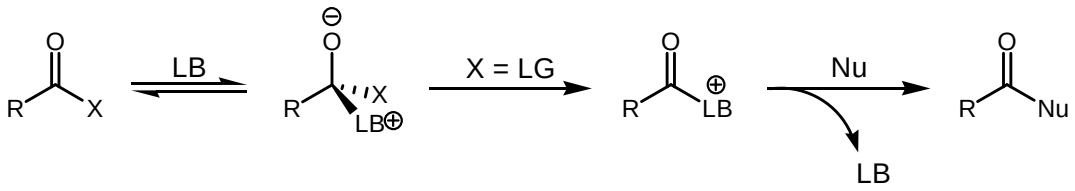


Scheme 8: Examples of complex bifunctional catalysts for Brønsted base catalysis

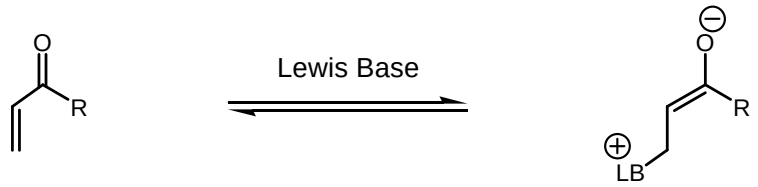
Organocatalysis with Lewis base

Lewis base catalysis is the process by which an electron pair donor increases the rate of a given chemical reaction by interacting with an acceptor atom in one of the reagents or substrates. The binding may enhance either the electrophilic or nucleophilic character of the bound species. The Lewis base should not be consumed or altered during the course of the reaction.

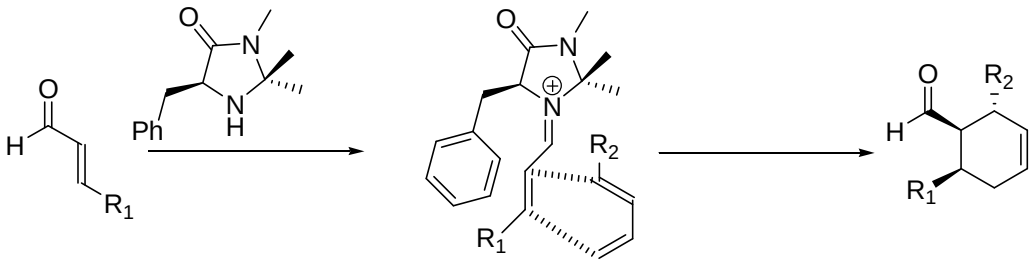
1,2 -addition to carbonyls



Michael-type additions

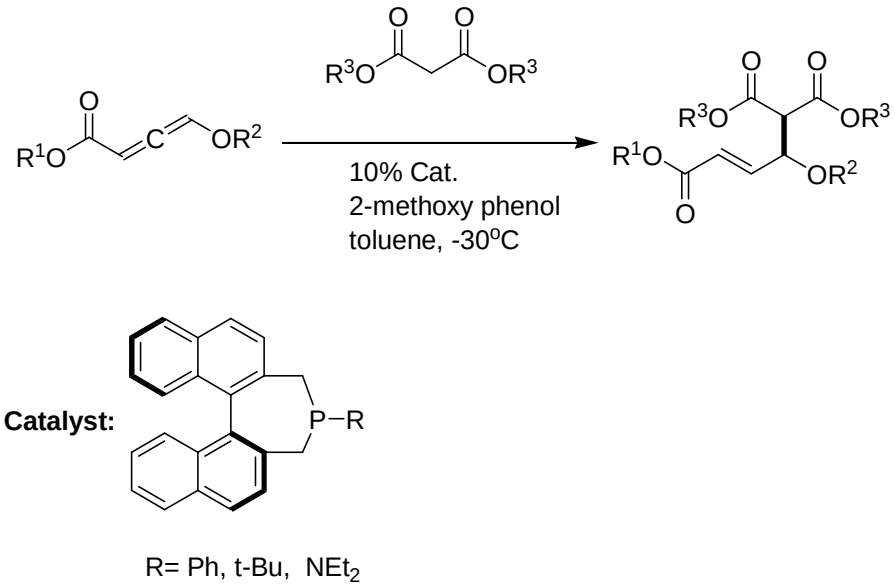


Both primary and secondary amines are useful as Lewis base catalysts. Organocatalysts which display secondary amine functionality can be described as performing either enamine catalysis[36, 37, 38] (by forming catalytic quantities of an active enamine nucleophile) or iminium catalysis[39, 40, 41] (by forming catalytic quantities of an activated iminium electrophile). This mechanism is typical for covalent organocatalysis. Covalent binding of substrate normally requires high catalyst loading (for proline-catalysis typically 20-30 mol%). With secondary amines, aldehydes and ketones may also condense to form iminium cations. Iminium salts are more electrophilic than the corresponding aldehydes or ketones. For this reason, the reversible formation of the iminium salt activates the carbonyl component toward nucleophilic attack (See Scheme 9).



Scheme 9: Mode of action of iminium organocatalyst.

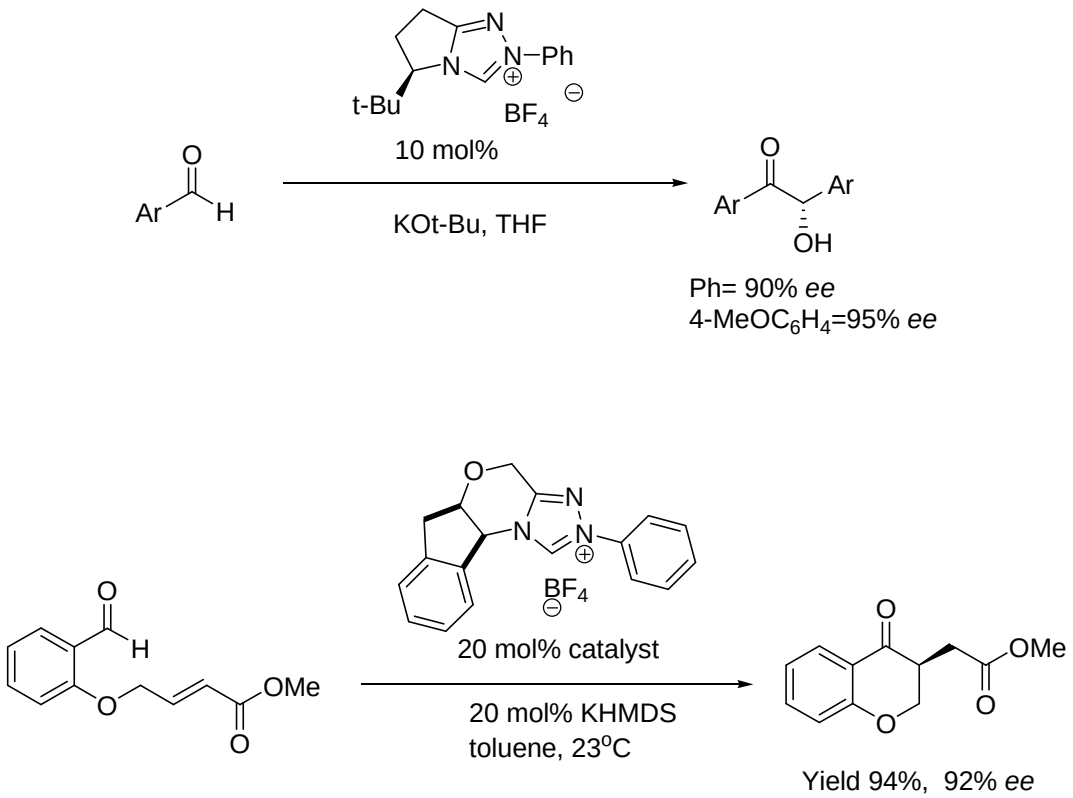
There are not many examples of organocatalysts which function as Lewis base, other than enamine or imminium catalysts. One very good example is use of chiral phosphines as organocatalyst. [42] Fu and co-workers showed that chiral phosphines can be used as organocatalysts for catalytic asymmetric carbon–carbon bond formation at the γ-position of carbonyl compounds [43]. They have developed a straight forward and versatile phosphine catalyzed additions of malonate esters to γ-substituted allenoates and allenamides (See Scheme 10).



Scheme 10: Use of chiral phosphine as Lewis base catalyst

Another very important type of Lewis base organocatalyst is carbene type catalyst. Since the 1950s carbenes have shown great potential in the field of organometallic and organic chemistry. [44] Depending on electronic and steric environment carbene compounds can be nucleophilic or electrophilic in nature. N-heterocyclic carbenes contain heteroatoms on either side of the carbene atom, which donate electron density in the vacant p-orbitol to enhance thermodynamic stability. NHC catalysis mainly useful for their ability to reverse the reactivity or "umpolung"[45] of carbonyl compounds. The concept of umpolung dates back to the

discovery of benzoin condensation reaction by *Wöhler* and *Liebig* in 1832. [46] Recently many groups have attempted to develop asymmetric version of benzoin condensation reaction and Stretter reaction using chiral NHC as catalyst. Most successful of those is the report by *Enders* and co-workers in 2002. [47, 48] They used chiral bicyclic triazolinium NHC salt as pre catalyst to achieve up to 95% ee for a number of benzoin derivatives (See Scheme 11).

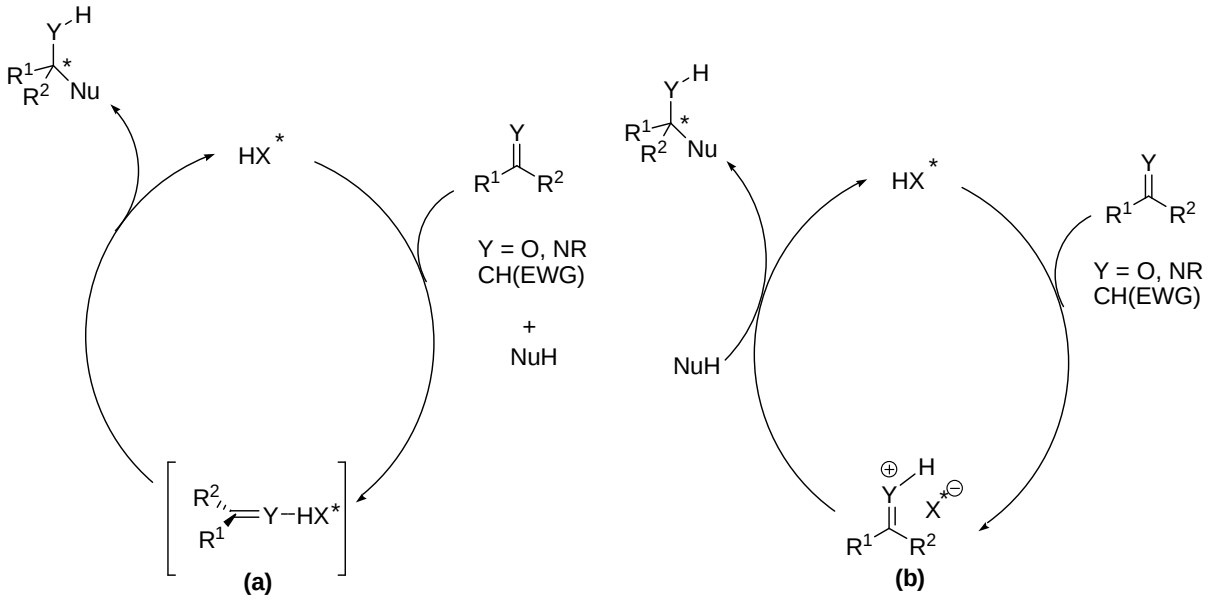


Scheme 11: Intramolecular benzoin condensation and Stretter reaction with chiral NHC

Organocatalysis with Brønsted acid

Chiral BINOL-derived phosphoric acids in asymmetric catalysis

Chiral Brønsted acids have emerged as a new and powerful class of organocatalysts over the last decade. [49, 50, 51, 52] The field of asymmetric Brønsted acid catalysis can be divided into two types, general acid catalysis and specific acid catalysis. General acid catalysis refers to the process where the substrate is activated via hydrogen bonding whereas in case of specific acid catalysis the substrate is activated via protonation. (See Scheme 12)



Scheme 12: Asymmetric Brønsted acid catalysis concept: **(a)** General acid catalysis. (b) Specific acid catalysis.

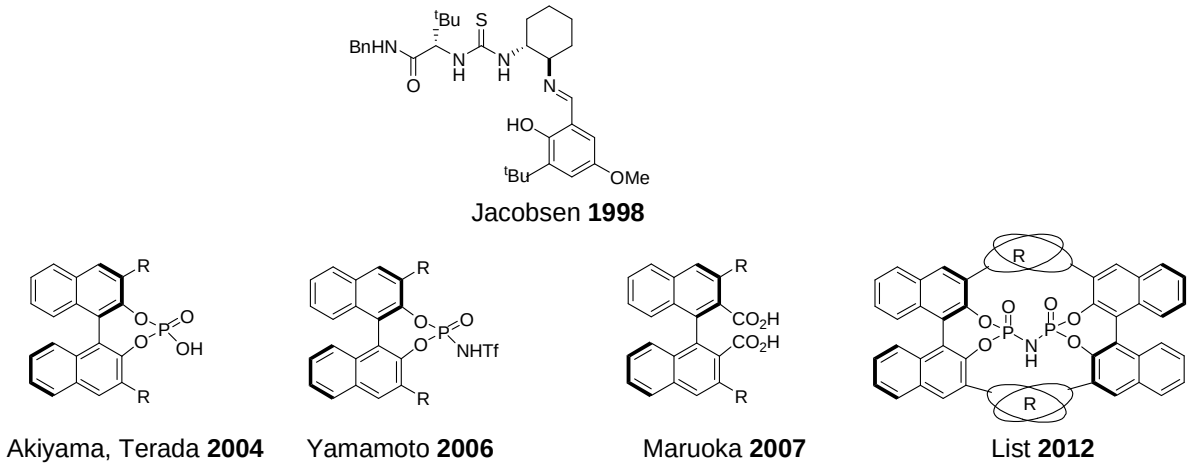
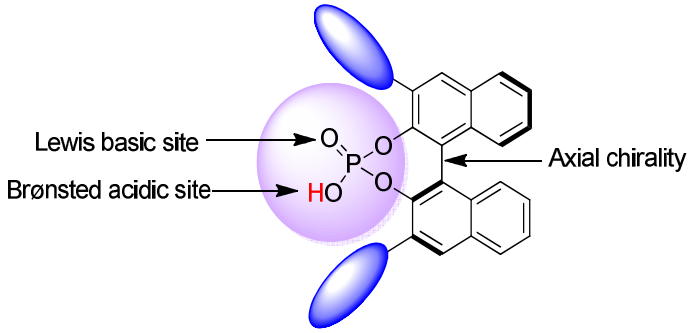
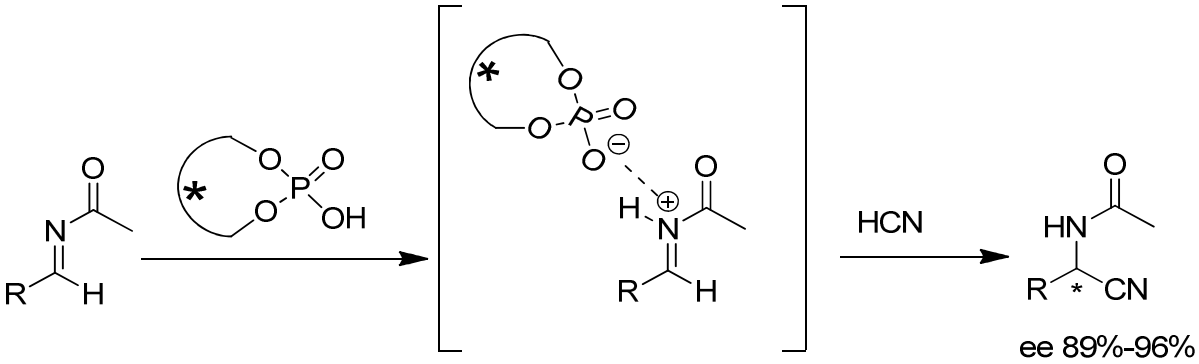


Figure 3: Examples of chiral Brønsted acid catalysts.

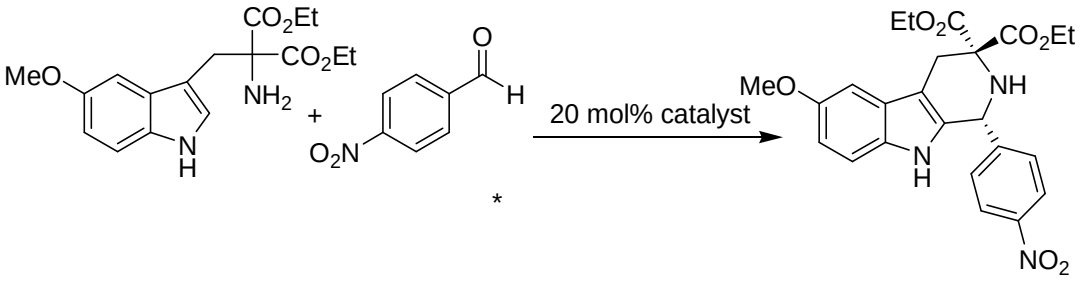
In 2004, research groups of *Akiyama* and *Terada* introduced chiral 1, 1'-Bi 2-naphthol or BINOL-derived phosphoric acids as new organocatalysts. [53,54] Subsequently chiral phosphoric acids found numerous applications as Brønsted acid catalysts in the field of organocatalysis.[55] Early reports using these catalysts relied on the activation of imine electrophiles. Recently, additional discoveries have shown an ability for these catalysts to activate vinyl ether,[56] aziridines, [57] nitroso compounds, [58] enones, [59] and glyoxylates. [60] BINOL-derived chiral phosphoric acid has unique structural features. It has axial chirality, Lewis basic site as well as Brønsted acid site. The steric and electronic properties can be

tuned varying the substituents at the 3 and 3' positions and the range of applications of chiral Brønsted acids could be significantly expanded.[61] BINOL-derived phosphoric and have an acid dissociation constant of about pK_a = 1 and can activate substrates by protonation. For example, asymmetric Strecker reaction is an important way to make chiral amino acids.[62] *Rueping* and co-workers reported chiral phosphoric acid catalyzed highly enantioselective asymmetric Strecker reaction.[63] Suitably substituted imines can be activated by protonation using chiral phosphoric acid. In suitable solvent, the chiral phosphate counter anion stays in the immediate vicinity transferring chiral information to the substrate (See Scheme 13).





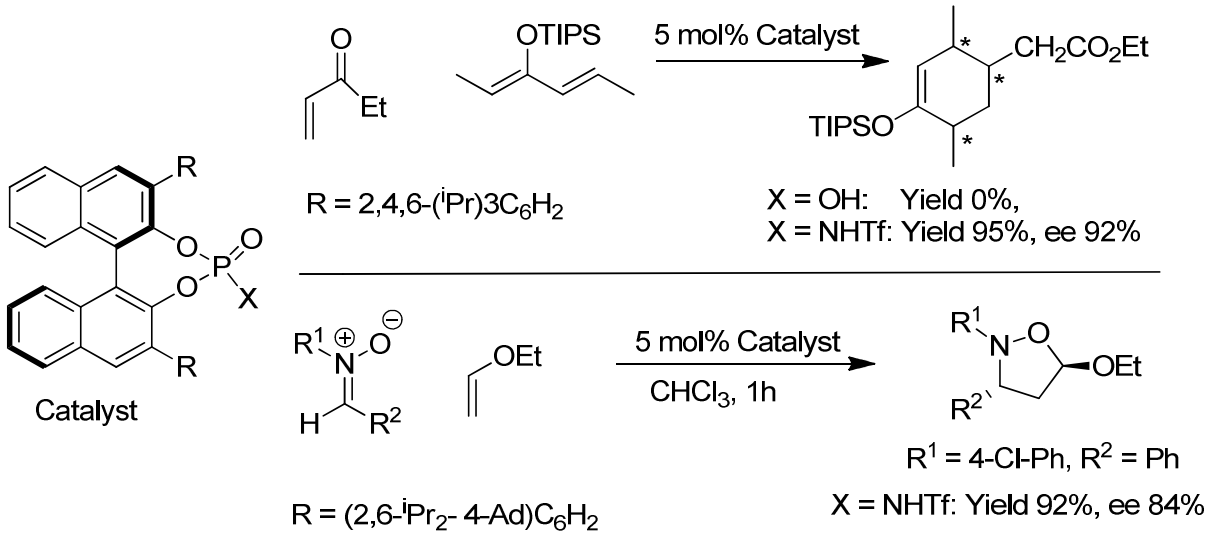
Scheme 13: Asymmetric Strecker reaction using chiral phosphoric acid.



Scheme 14: Asymmetric Pictet-Spengler reaction using chiral phosphoric acid.

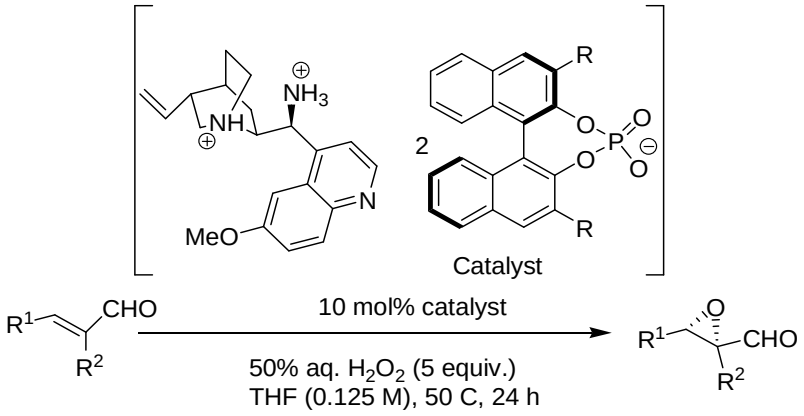
BINOL-derived phosphoric acids are useful to activate basic substrates bearing nitrogen containing electrophiles, including ketamines, aldimines, aziridines, imines or nitrogen heterocycles. However the activation of less basic substrates has been done mainly by Lewis acids. Acid strength of the phosphoric acids is generally not sufficient to activate carbonyl groups. In many cases, therefore, only the respective aza-variant of the reactions could be catalyzed by chiral phosphoric acids. Recently Yamamoto and co-workers have developed a new type of stronger Brønsted acid catalyst [64]. They have introduced strong electron

withdrawing triflylamide groups into the BINOL phosphate structure making it BINOL- N-triflylphosphoramide.(See Scheme 15)

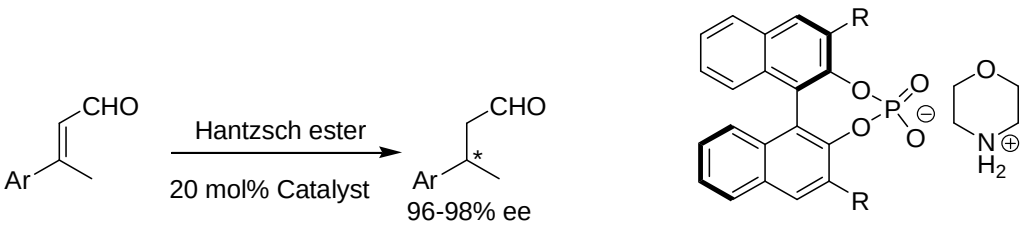


Scheme 15: Use of BINOL- N-triflylphosphoramide as stronger Brønsted acid.

List and co-workers introduced a very interesting concept in asymmetric organocatalysis. They showed, catalytic reactions that proceed via cationic intermediates can be conducted asymmetrically via the use of a chiral enantiomerically enriched anion incorporated into the catalyst. They named this concept as AC-DC (Asymmetric counter anion-directed catalysis) [65]. The underlying concept generalizes the concept of Brønsted acid catalysis, as a substrate, not only by a proton, but generally transferred through an appropriate catalyst in a cationic activated species. The stereo differentiation is continued through the chiral anion. Successful applications of AC-DC concept using chiral phosphoric acids along with ammonium salts are found in the asymmetric epoxidation[66, 67] (See Scheme 16) and transfer hydrogenation[68, 69, 70] of α, β-unsaturated aldehydes and ketones(See Scheme 17).



Scheme 16: Asymmetric epoxidation using AC-DC concept

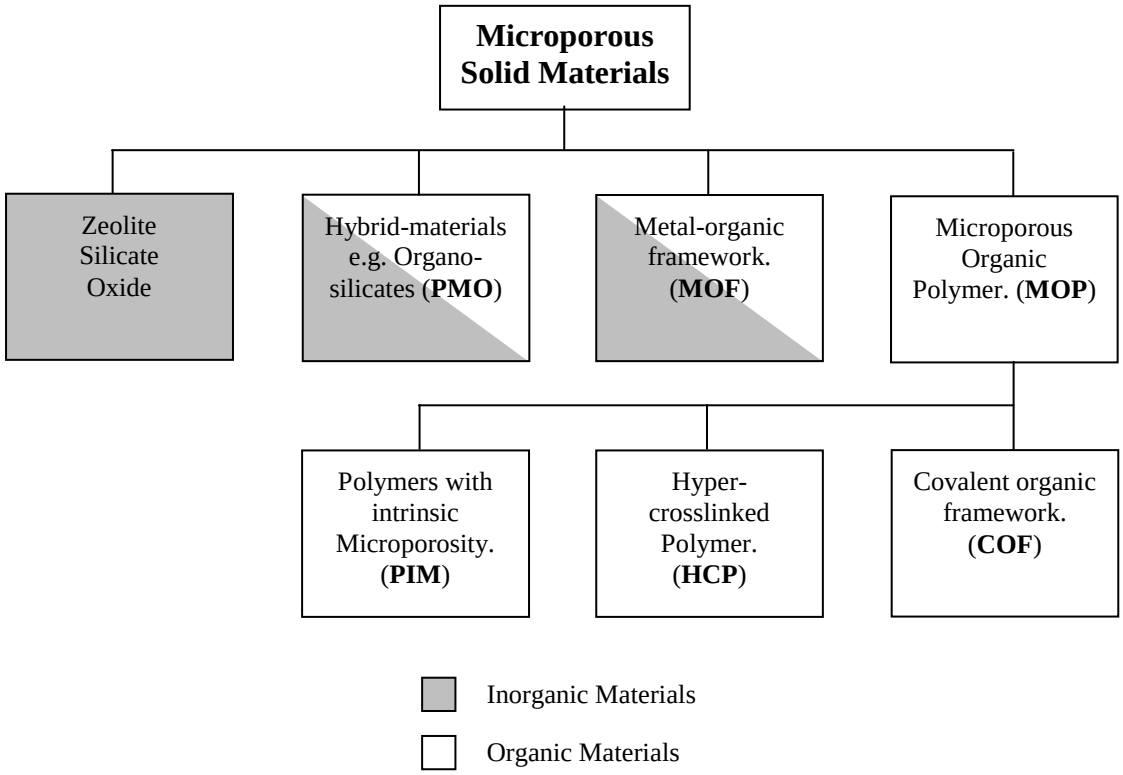


Scheme 17: Asymmetric transfer-hydrogenation using AC-DC concept

The scope of the chiral BINOL-derived phosphoric acids and their modifications now covers an enormous range of reactions. The uniform activation pattern of a protonated or cationic species has also allowed cascade and multi-component reactions with high selectivity in different syntheses. Again, presently Brønsted acids are being used in combination with transition metal catalsyts. Therefore, there is urgent need to commercialize Brønsted acid catalysts for large scale synthesis or industrial use. For that purpose, new materials have to be developed which will be stable enough and cost effective for large scale applications.

Porous polymers

Porous polymeric materials



In last few years a large number of innovative routes to synthesize numerous porous polymeric systems have been developed to generate new materials with wide ranging applications. As the need for porous polymers with more complex structure and functionality has increased so has the ability to synthesize such systems with well-defined pore sizes, tunable mechanical properties, specific pore wall functionality as well as controlled pore size distribution and interconnectivities. According to IUPAC nomenclature, microporous materials are defined as solids containing interconnected pores of less than 2 nm in size, and consequently they possess large and accessible surface areas—typically 300–3000 m^2 g^{-1} as measured by gas adsorption. [71] Mesoporous materials are containing pore size ranging between 2-50 nm and macroporous materials are having pore sizes greater than 50 nm. The specific surface area of these materials can be obtained by measuring the nitrogen adsorption by the Brunauer-Emmett-Teller method (BET method). [72] Conventional microporous materials, such as zeolites (aluminosilicates)[73] and activated carbons [74] are widely used as adsorbents, heterogeneous catalysts and, if the micropores are of uniform size, for molecular separations on the basis of size and shape. Porous materials with large surface areas are among others used in separation processes or adsorption of pollutants and are used for storage

of gases such as hydrogen. [75] Porosity is also an important feature for applications in the field of heterogeneous catalysis, as in functionalized polymers with high surface areas are many active centers within easy reach and this allows a high catalytic activity. Micropores provide about to select out the possibility of different substrate molecules according to size or shape.

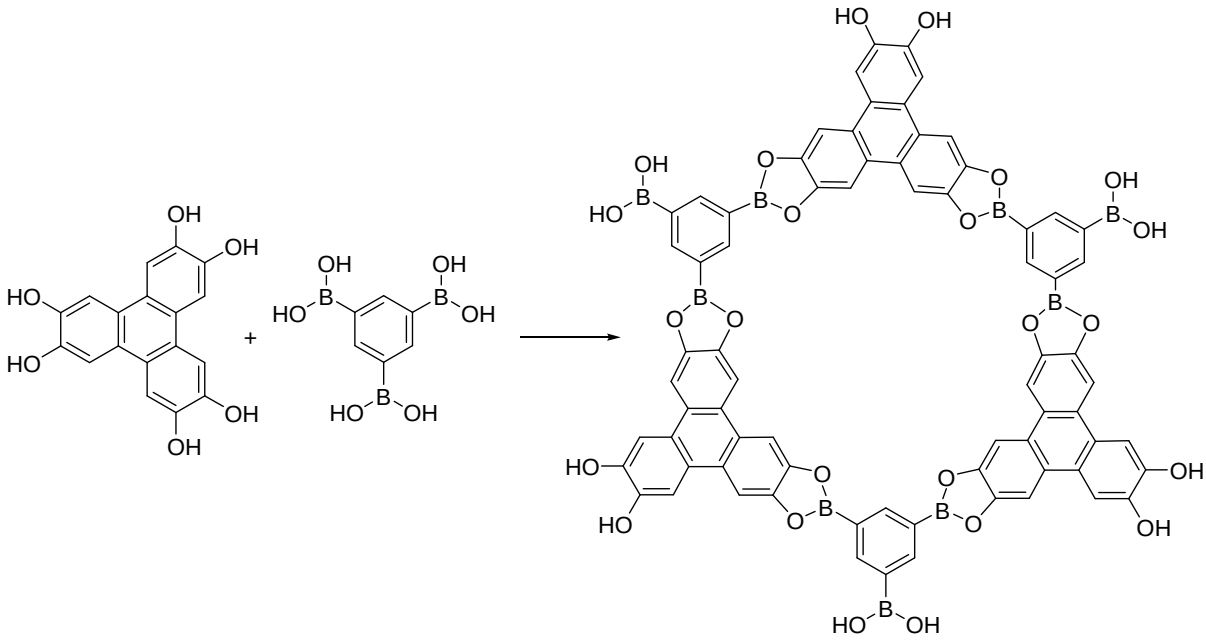
Today a huge number of microporous structures are known to consist of different materials. Inorganic agents, such as zeolites, silicates, metal oxides and activated carbons are among the oldest representatives and have been modified in various ways and used. Zeolites are microporous, aluminosilicate minerals with porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Zeolites are widely used in industry for water purification, as catalysts [76], for the preparation of advanced materials and in nuclear reprocessing. They are also used in medicine and in agriculture.

In the last decade the field of micro-porous polymers consisting organic moieties, increased significantly. [77, 78] The transition to purely organic polymers form porous inorganic materials went through the developments of hybrid materials in which organic part is associated with inorganic components. An example is periodic microporous organosilica (PMO), the silicate precursors are bridged by organic groups.[79]

Another group of polymers that are not entirely of organic components is metal-organic frameworks (MOF). Metal-Organic Frameworks are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. Possible applications of MOFs are in gas purification, in gas separation, in catalysis [80] and as sensors. In some cases, the pores are stable for elimination of the guest molecules (often solvents) and can be used for the storage of gases such as hydrogen and carbon dioxide. However, MOFs are often sensitive to moisture or oxygen. [81]

Another type of organic porous material similar to MOF is Covalent Organic Framework or COF. Covalent Organic Frameworks are porous, crystalline materials made entirely from light elements (H, B, C, N, and O) that are known to form strong covalent bonds in well-established and useful materials such as diamond, graphite, and boron nitride. Just like crystalline MOFs are formed by exploiting the formation of rapidly reversible metal-organic bonds between rigid organic parts and metal ions, *Yaghi* and co-workers [82] prepared COFs

by using the rapidly reversible bonding associated with the facile formation of boronic esters from monomers containing boronic acids and catechol. The design and synthesis of crystalline extended organic structures in which the building blocks are linked by strong covalent bonds are core concepts of covalent organic frameworks (COFs). (See Scheme 18) The successful realization of COF materials through molecular building blocks would provide covalent frameworks that could be functionalized into lightweight materials optimized for gas storage[83, 84], photonic[85], and catalytic applications.

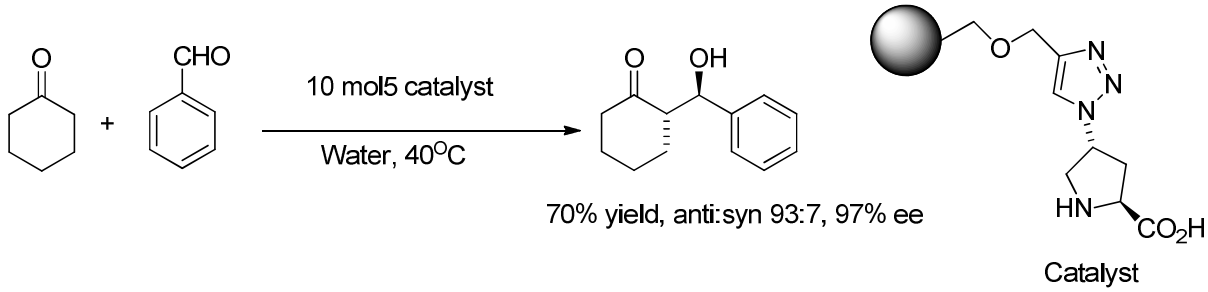


Scheme 18: Example of COF synthesis

Polymer supported organocatalysis

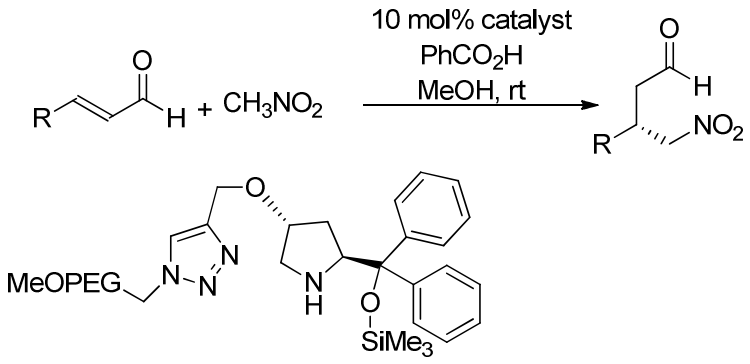
Polymer supported catalysts provide several advantages over homogeneous catalysts. This includes easy separation, recovery, reuse [86, 87] as well as possibility to perform reactions in a continuous flow [88] method. As the field of organocatalysis grows rapidly, it is attracting many approaches to immobilize organocatalysts. However, polymer supported catalysts often suffer from low catalytic activity and enantioselectivity compared to their homogeneous counterparts. So far quite many organocatalysts have been immobilized successfully. For example, *Pericas* and coworkers have reported successful synthesis of polymer bound proline for direct aldol reactions in water. [89] They have bound proline to polystyrene through 1,2,3-triazole linker using *Click chemistry*. [90] Despite the hydrophobicity of the polymer backbone, the resin swells in water with building of an aqueous microenvironment arising from the formation of a hydrogen-bond network connecting the proline and 1, 2, 3-triazole fragments.

This type of catalysts showed high efficiency in direct aldol reactions in water. (See Scheme 19)



Scheme 19: Asymmetrci Aldol reaction in water with polymer bound proline catalyst

Similarly, *Zeitler* and co-workers has reported the design of a soluble-polymer supported diaryl prolinone silyl ether catalyst and its application for the iminium-catalyzed enantioselective synthesis of gamma-nitroaldehydes(See Scheme 20).[91] Starting from trans-L-hydroxy proline (L-Hyp) they prepared the enantiopure alkyne precursor over 5 steps. Then cu-catalyzed (3+2)-cycloaddition to create a stable 1,2,3-triazole resulted the polymer supported aryl prolinol ether catalyst. The catalyst showed indifferent activity and selectivity compared to the monomeric catalyst and it is recyclable. (See Scheme 20)



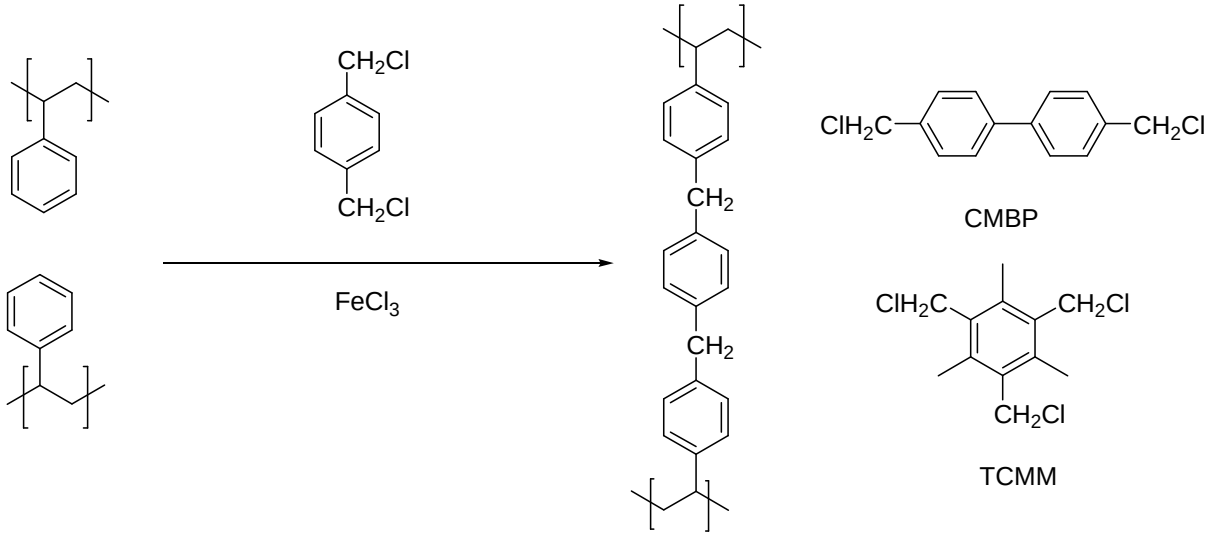
Scheme 20: Polymer supported diaryl prolinone silyl ether catalyst for iminium catalysis

In case of polymer supported catalyst, the support itself is very important. Porous support can provide easy accessibility of the catalytic centers hence leading to faster reaction rate. For that purpose polymer support with high surface area are of great interest. One good example is hypercrosslinked polymer or HCP.

Hyper cross linked polymers

In order to make porous polymers, a large amount of excess free volume can be captured by the formation of hypercrosslinked network polymer within a solvent-swollen polymer gel, which provides a microporous material on removal of the solvent. Hypercrosslinked

polystyrenes are the most investigated class of microporous polymers prepared using this concept. The synthesis involves extensive crosslinking of solvent-swollen, lightly cross linked polystyrene beads prepared previously by suspension polymerization. The cross linking can be achieved by using an efficient Friedel-Crafts alkylation reaction using Lewis acid catalyst such as $FeCl_3$ or $SnCl_4$. Usually the cross links are derived from reactive trichloromethyl or di chloromethyl aromatic compounds. For example compounds such as 4,4'- bis-chloromethylbiphenyl (CMBP), p-xylenedichloride (XDC) or tri-(chloromethyl)mesitylene (TCMM).[92]



Scheme 21: Synthesis of hypercrosslinked polystyrene via Friedel-Crafts alkylation with a di- or trichloromethyl aromatic compound.

The most important property of hypercrosslinked polymers is their tendency and ability to swell in contact with solvent. This property is greatly advantageous for use of hypercrosslinked polymers as adsorbents. They have been used for adsorption of organic vapors and organic contaminants such as phenols, aromatic dye as well as polycyclic aromatic hydrocarbons from water. Hypercrosslinked polymers showed promise for potential application as stationary phase for reverse phase-high performance liquid chromatography due to their hydrophobic nature and swelling properties in highly polar solvents. The high surface area, uniform size of hypercrosslinked polystyrene beads offers potential application as polymer supports for catalysts also.

Polymer with intrinsic microporousity

The term 'intrinsic microporousity' can be defined as "a continuous network of interconnected voids that forms as a direct consequence of the shape and rigidity of the component macromolecules". Polymers with intrinsic microporousity or PIMs belong to a highly versatile class of materials that possess microporosity. [93, 94] The microporosity is directly attributed to the contorted structure and its rigidity. When rigid contorted structures are polymerized they can not pack space efficiently. Other than that the lack of rotational freedom also ensures that the macromolecules can not rearrange their conformation to cause collapse of microporous structure. [95] The lack of rotational freedom and rigidity can be introduced by the polymer backbone consisting solely fused rings. [96, 97] The appropriate sites to induce microporosity in polymers are spiro, bi-naphthyl structure or other rigid nonplanar structure like triptycene. Many different types of bond forming reactions have been used to couple them. One of the most useful may be aromatic nucleophilic substitution (S_NAr) reaction between monomers that lead to catechol type units (See Figure 4).[98, 99]

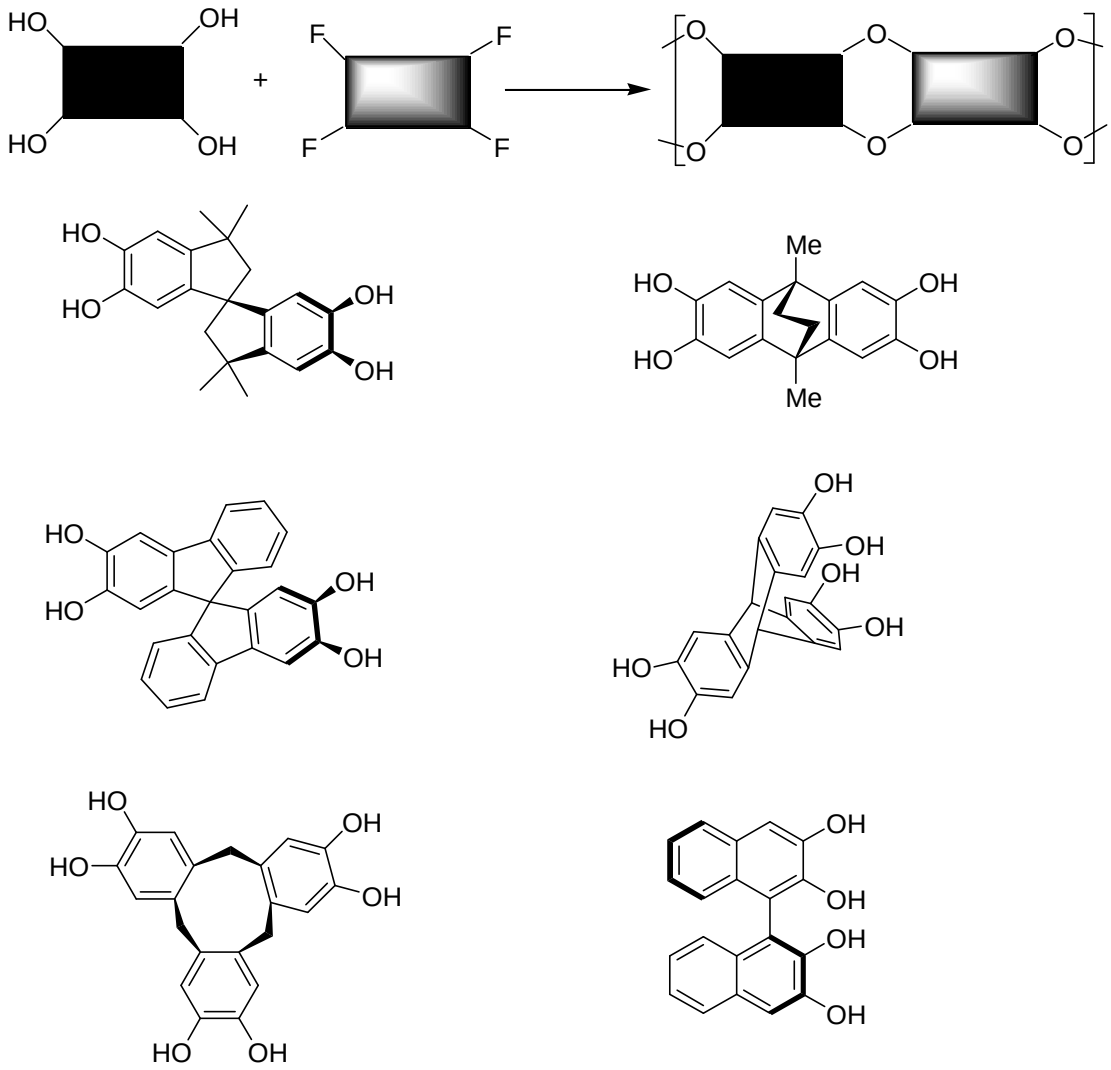
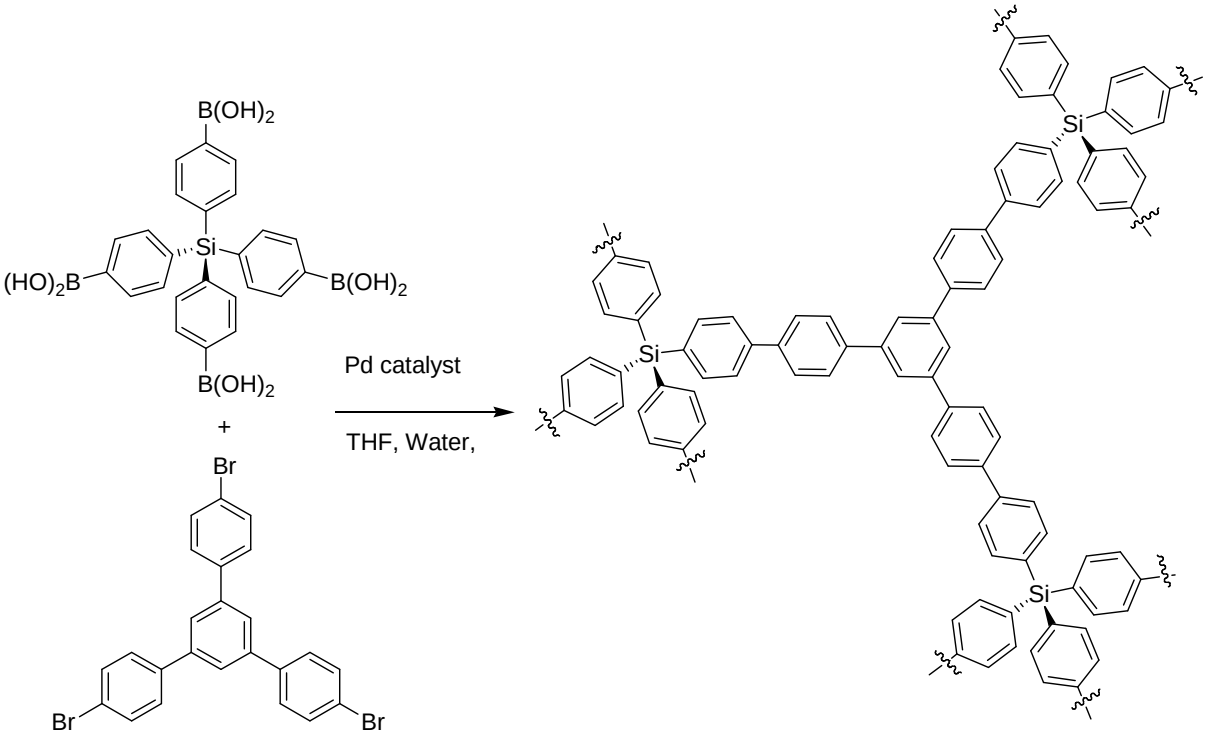


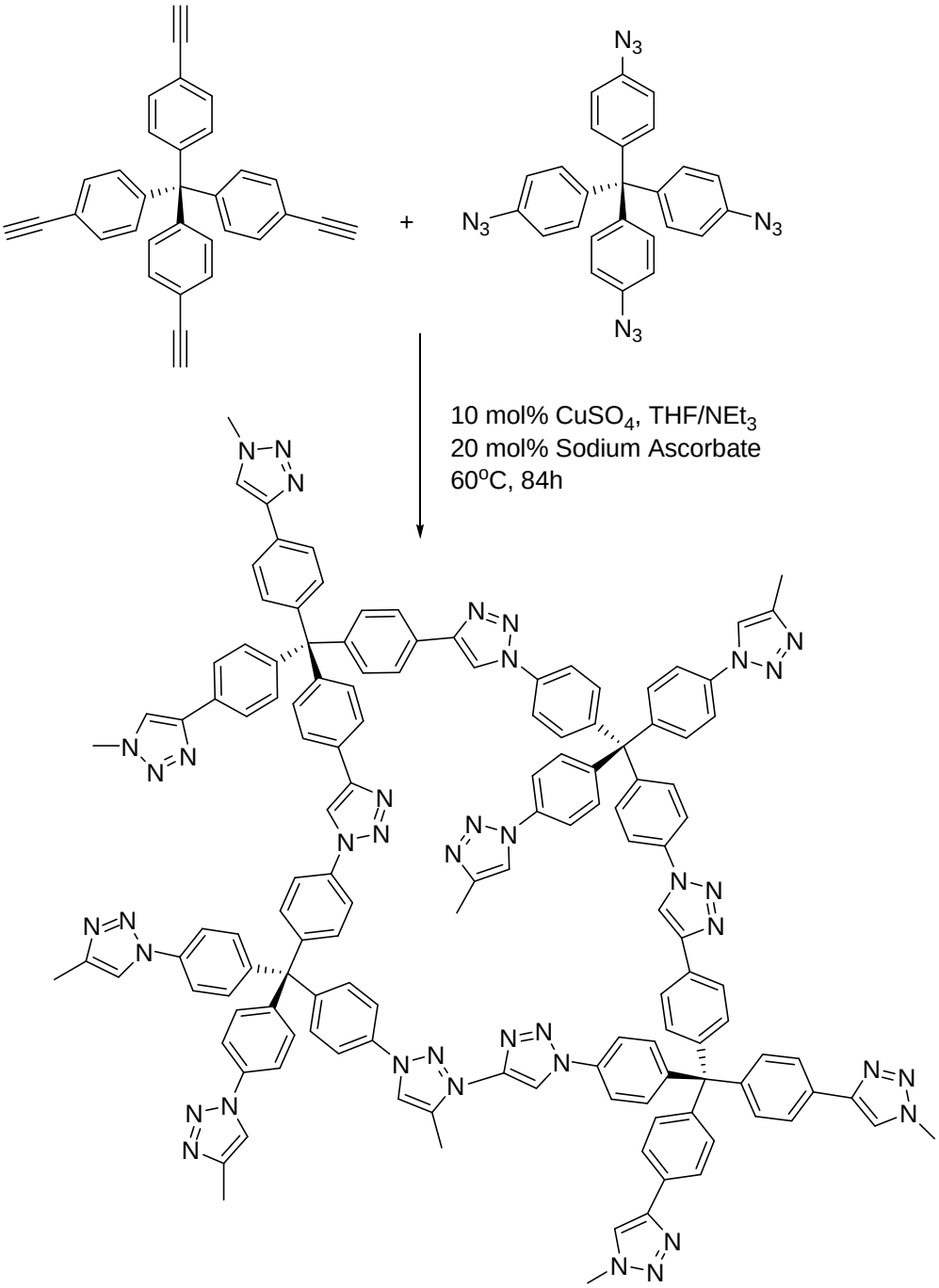
Figure 4: Examples of different rigid or contorted monomeric units containing di-hydroxyl group for PIM synthesis

Other than aromatic nucleophilic substitution (S_NAr) Suzuki coupling reaction and 'Click chemistry'[100] has also found its way into PIM synthesis. *Kaskel* and co-workers used Suzuki coupling reaction to couple tetrahedral silicon centered monomeric unit to couple with boronic acid leading to porous polymeric frameworks with high specific surface areas up to 1380 m^2 g^{-1}.[101] With use of larger aromatic linker a decreasing specific surface area was observed. This effect is due to a higher degree of interpenetration and a higher flexibility of the amorphous structures, allowing a more effective packing in space. (See Scheme 22)



Scheme 22: Porous polymeric frameworks prepared from tetrahedral silicon centered monomeric unit to couple with boronic acid.

Cooper and co-workers prepared a conjugated microporous polymer (CMP) by reacting two complementary azido and alkyne tetrakisphenylmethanes (See Scheme 23). [102] The resulting conjugated microporous polymer has a BET surface area of 1128 m^2 g^{-1}. Independently *Nguyen* and co-workers reported the detailed study of the same "clicked" network—termed this time porous organic polymer (POP). They found that the surface area drastically increased at higher reaction temperature. [103]



Scheme 23: Use of click chemistry to synthesize porous polymer

Porous organic polymers in catalysis:

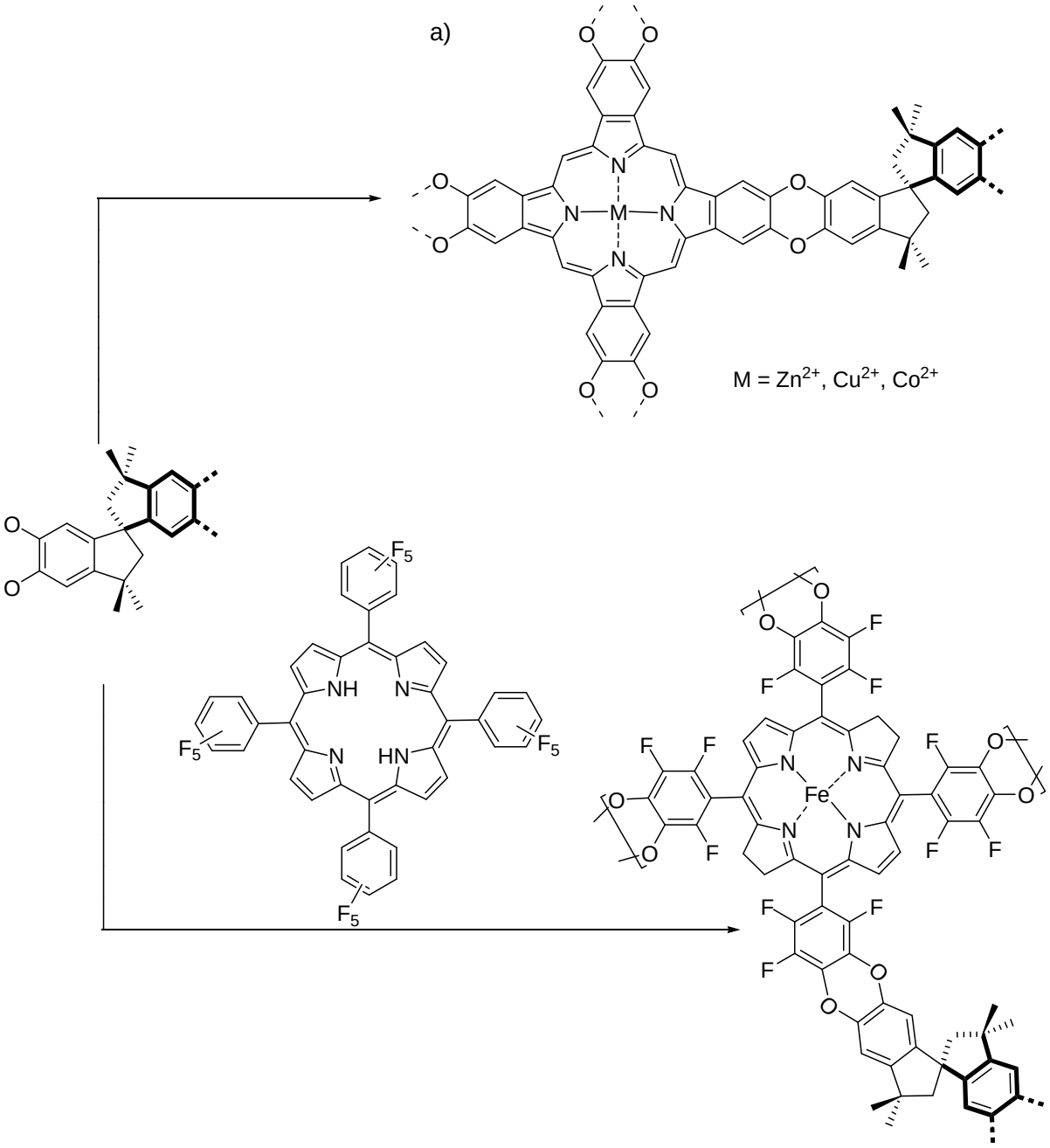
In comparison to polymer supported catalysts, microporous polymers can be interestingly useful in heterogeneous catalysis due to their tunable properties like large specific surface, relatively small pores and other controllable properties. Many successful syntheses have been reported where porous polymer is used to support metal particles and applied as heterogeneous catalyst. *Budd*, *McKeown* and co-workers first reported synthesis of a spiro-

linked phthalocyanamine network and spiro-linked porphyrin network polymers inserting cobalt and iron ions. [104] Polymers containing cboalt phthalocyanamine showed surface area ranging from 120- 612 $m^2 g^{-1}$ while Fe-porphyrin polymer has high surface area of 866 $m^2 g^{-1}$. Compared to monomeric cobalt phthalocyanamine, this type of polymeric catalyst showed an increase in rate constant up to 2 orders of magnitude for decomposition of hydrogen peroxiede. The polymeric catalyst was also tested in oxidation of cyclohexene and hydroquinone.

Furthermore *McKeown* and co-workers have synthesized nanoporous network polymer incorporating 5,6,11,12,17,18-hexaazatrinapthylene (Hatn) as the rigid functional.[105, 106] This material exhibits a high BET surface area (775 $m^2 g^{-1}$). similar to that obtained from related nanoporous networks based on phthalocyanine and porphyrin macrocycles. The ability of the Hatn unit to bind to metal ions was shown by the sequential binding of three palladium(II) dichloride moieties. The resulting material retains porosity (BET surface area around 347 $m^2 g^{-1}$) and should be useful as a heterogeneous catalyst in Suzuki coupling reaction.

Similarly heterogeneous version of *Periana* catalyst showed enhanced activity for oxidation of methane to methanol (See Figure 5). [107] Apart from loading metal on porous polymer, there is possibility of direct polymerization of metal containing polymerizable units into porous materials. In an example, *Lin* and co-workers reported that porous cross-linked polymers (PCPs) with phosphorescent $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$ building blocks were obtained via octacarbonyldicobalt (Co_2-$(CO)_8$)-catalyzed alkyne trimerization reactions.[108] The resultant

Ru- and Ir- PCPs exhibited high porosity with specific surface areas of 1348 $m^2 g^{-1}$ and 1547 $m^2 g^{-1}$, respectively. This type of insoluble porous materials is thermally stable at up to 350^o C in air. The photoactive PCPs were shown to be highly effective, recyclable, and reusable heterogeneous photocatalysts for aza-Henry reactions and oxyamination of an aldehyde, with catalytic activities comparable to those of the homogeneous $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$ photocatalysts. (See Scheme 25)



Scheme 24 Synthesis anduse of PIM as metal support

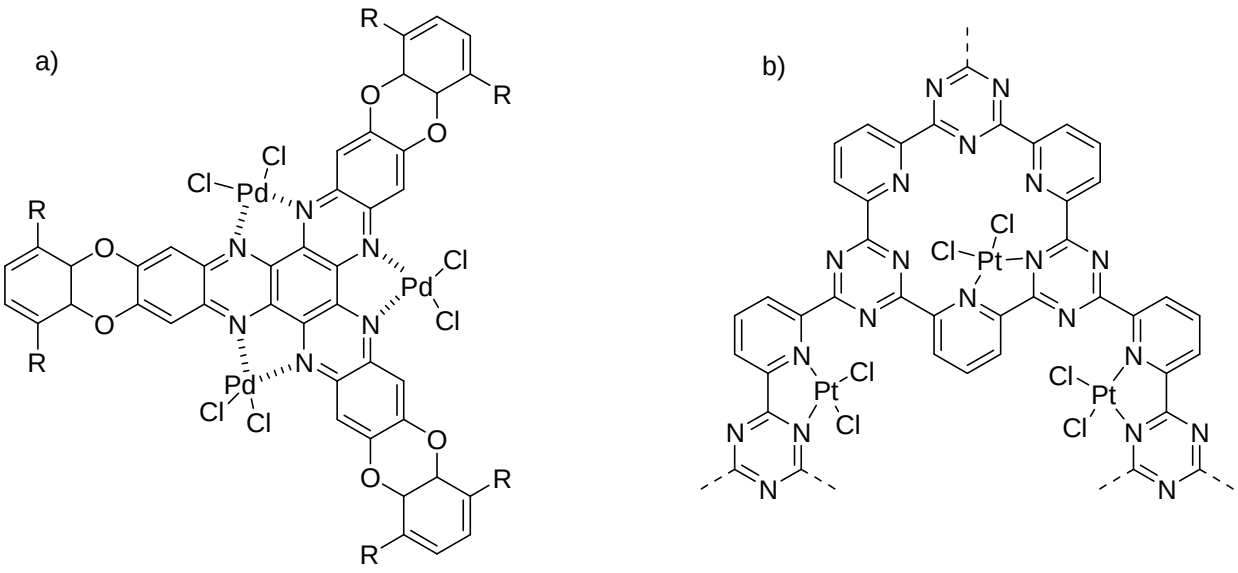
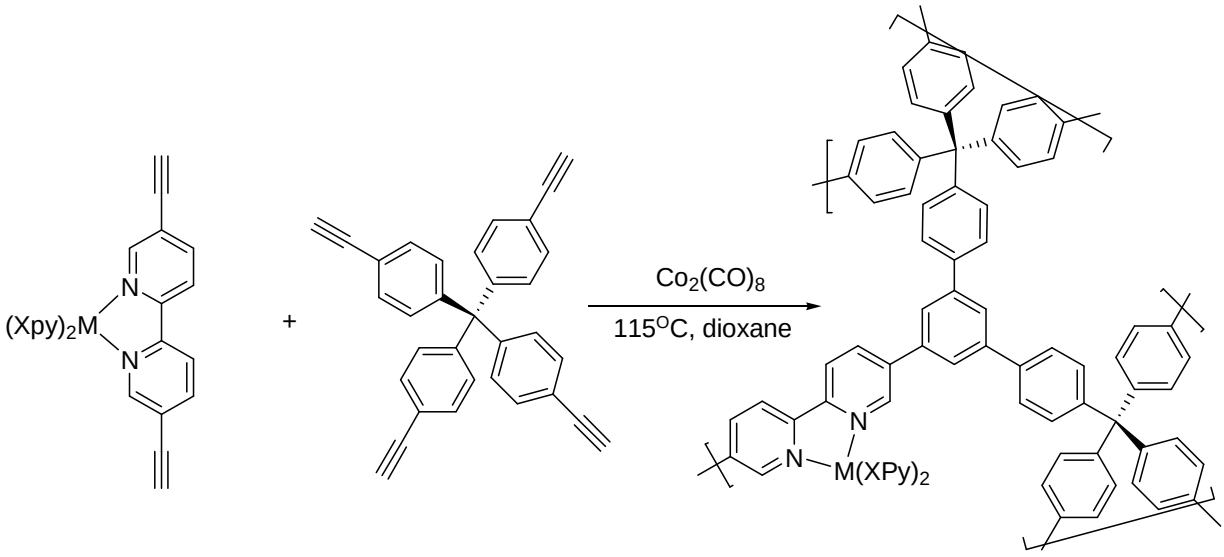


Figure 5: (a) and (b) variants of heterogeneous Periana catalyst .



Scheme 25: Synthesis of cross-linked polymer by trimerization reaction

In a recent example *Lin* and co-workers have synthesized chiral cross-linked polymers (CCPs) based on 1,1' binaphthyl building blocks via trimerization reaction of terminal alkyne groups. [109] These cross linked polymers have porosity ranging from 689 $m^2 g^{-1}$ to 974 $m^2 g^{-1}$. They have used their polymers as ligand system for Lewis acid catalyzed asymmetric diethyl zinc addition to aldehydes with high yield and moderate *ee* (55-81% *ee*). (See Figure 6)

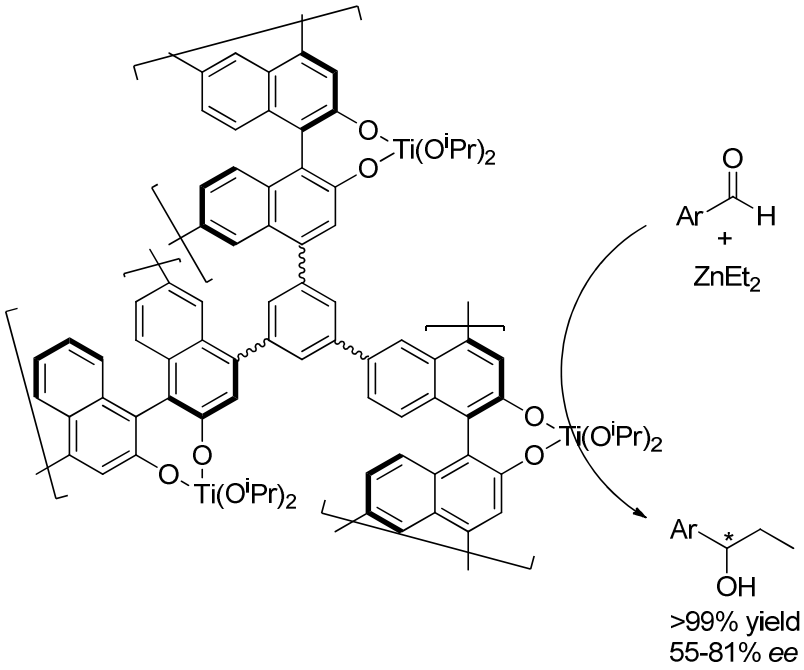
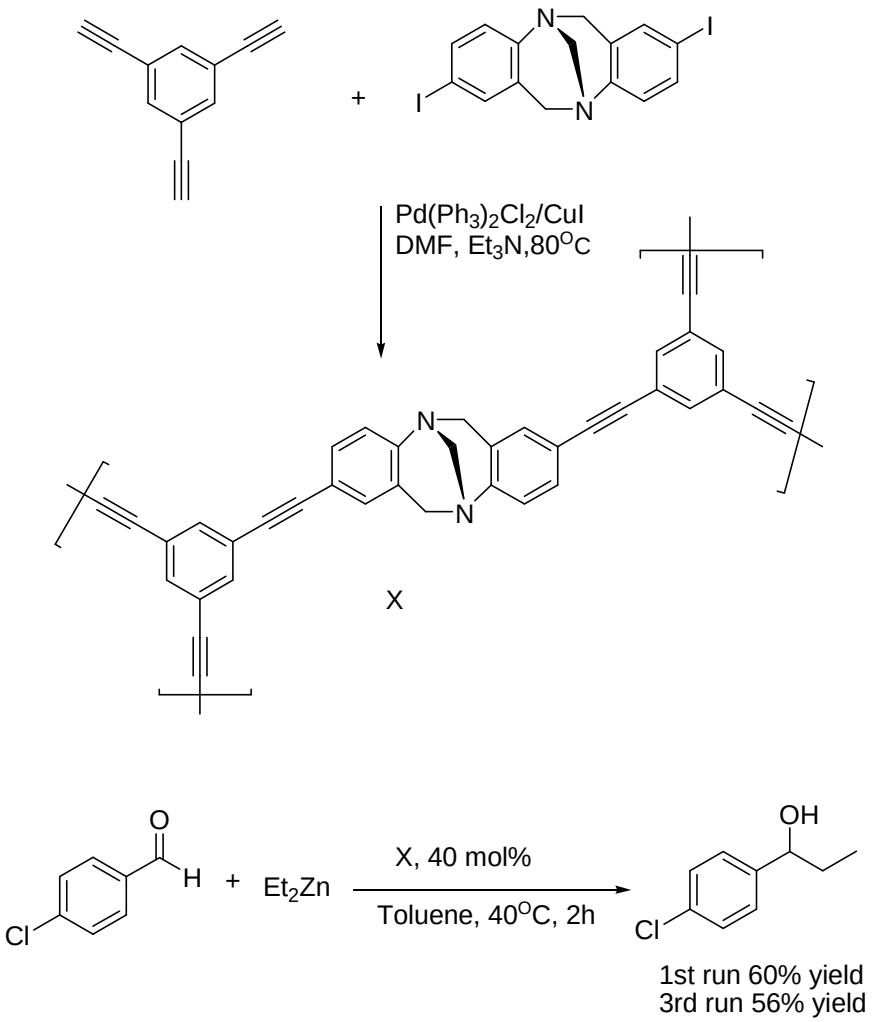


Figure 6: Porous BINOL-polymer as ligand for asymmetric catalysis

Porous organic polymer as heterogeneous organocatalyst

Although porous organic polymers have been used mainly as a support for metal catalysts few attempts has been also made to use porous polymer for organocatalysis.[110] When suitable active sites are incorporated into porous frame work, it can be used as heterogeneous organocatalyst. For example, in 2010, *Wang* and co-workers [111] reported Troger's base functionalized porous organic polymers. They have used as heterogeneous organocatalyt for diethyl zinc addition to aromatic aldehydes. The synthesis of the organocatalyst was performed using Sonoghasira coupling of diazocine and 1,3,4-triethylbenezene units. The resulting polymer showed BET surface area of 750 m^2 $g^{-1}$and pore volume of 0.74 cm^3 g^{-1} (See Scheme 26).



Scheme 26: Immobolized Troger's base

Although the catalytic performance tends to be diminishing after 3 repeating runs, this was possibly first example of using insoluble porous polymer as organocatalyst.

In 2011, *Glorius* and co-workers reported direct installation of N-heterocyclic carbene into porous polymers. [112] N-heterocyclic carbene was copolymerized with a structuring tecton using Suzuki coupling reaction (See Figure 7 and Scheme 27). The catalytically active, microporous network could then be used successfully as organocatalyst in N-heterocyclic carbene-catalyzed conjugated umpolung of α, β-unsaturated cinnamaldehyde.

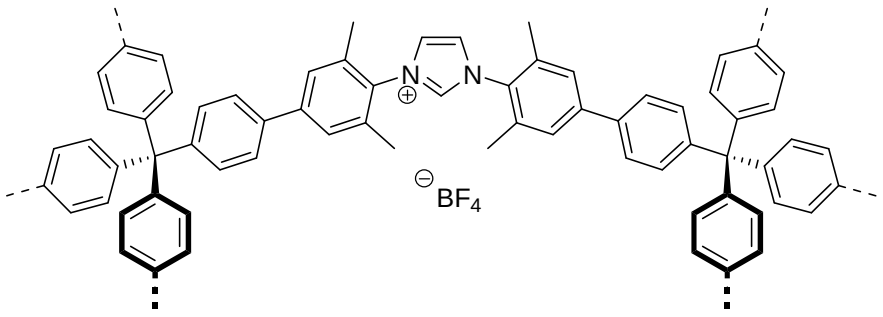
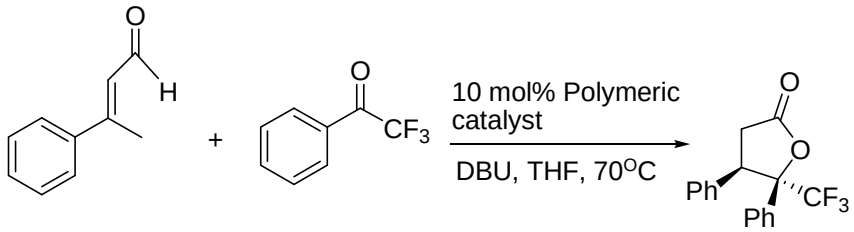
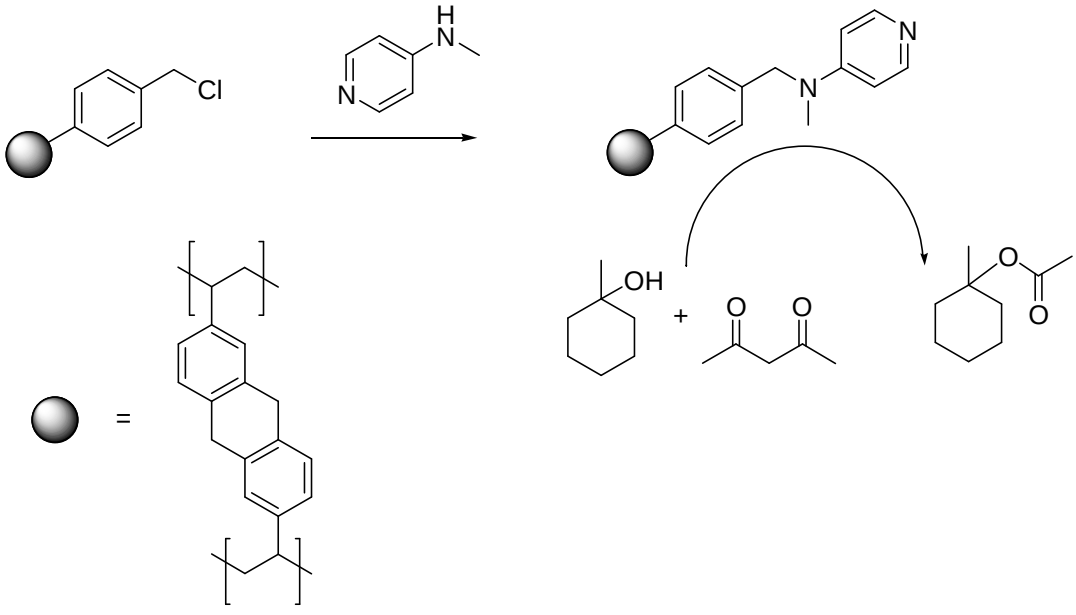


Figure 7: Porous polymer containing N-heterocyclic carbene



Scheme 27 Use of immobilized NHC ligand as organocatalyst

4-Dimethylaminopyridine (DMAP) is a highly efficient and important organocatalyst used for a variety of organic reactions, including the acylation and silylation of hindered alcohols, the Baylis–Hillman reaction and the ring opening polymerization of lactide. In 2010, a hypercrosslinked polystyrene with a DMAP analog catalyst has been used in the acylation reaction by *Pulko* and co-workers. [113] The activity of the microporous system was significantly higher than that of comparable conventional polystyrenes with smaller specific surface areas. (See Scheme 28)

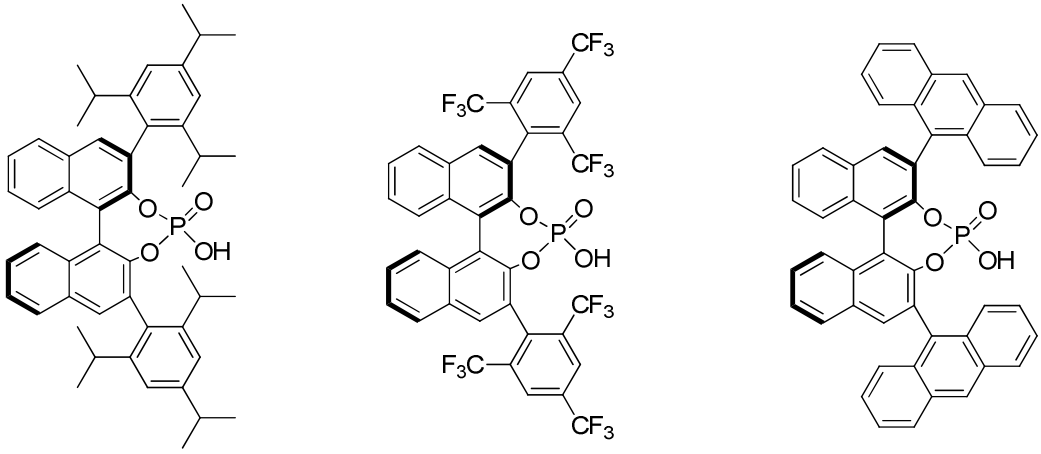


Scheme 28: Hypercroslinked DMAP as heterogeneous organocatalyst

Synthesis and Catalysis

Goal and concept

Goal of this PhD work was to combine organocatalysis with advanced functional material chemistry by making new heterogeneous Brønsted acid catalysts for asymmetric orgnaocatalysis. Many BINOL-derived phosphoric acids are commercially available but they are quite expensive. Their prices are in the range of 1800 to 2000 euro per gram. As they are quite efficient in numerous organocatalytic reactions and usually stable, it is highly desirable to heterogenize BINOL-derived phosphoric acid structures.



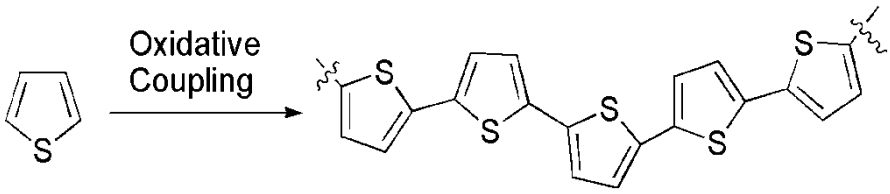
1
265 € / 100 mg

2

3
234 € /100 mg

Figure 8: Examples of commercially available BINOL-phorphoric acid catalyst.

In BINOL, the two naphthol parts have dihedral angle of 80.8^{o} which is primary requirement for inefficient packing, leading to porous structure after polymerization. The question was how to conveniently interconnect BINOL-phosphoric acid monomers into porous polymeric structure. We focused on a very well explored polymerization reaction: polymerization of thiophenes into polythiphene. Thiophenes can be polymerized either chemically or electrochemically into polythiophene chain. In 1988 *Sugimoto* and co-workers reported oxidative coupling of thiophenes into polythiophene under mild condition using $FeCl_3$ as oxidative reagent. [114] (See Scheme 29)



Scheme 29: Oxidative coupling of thiophenes to polythiophene

We thought about attaching thiophene units at the 3 and 3' positions of BINOL structure and then polymerizing them using oxidative coupling reaction with $FeCl_3$. (See Figure 9)

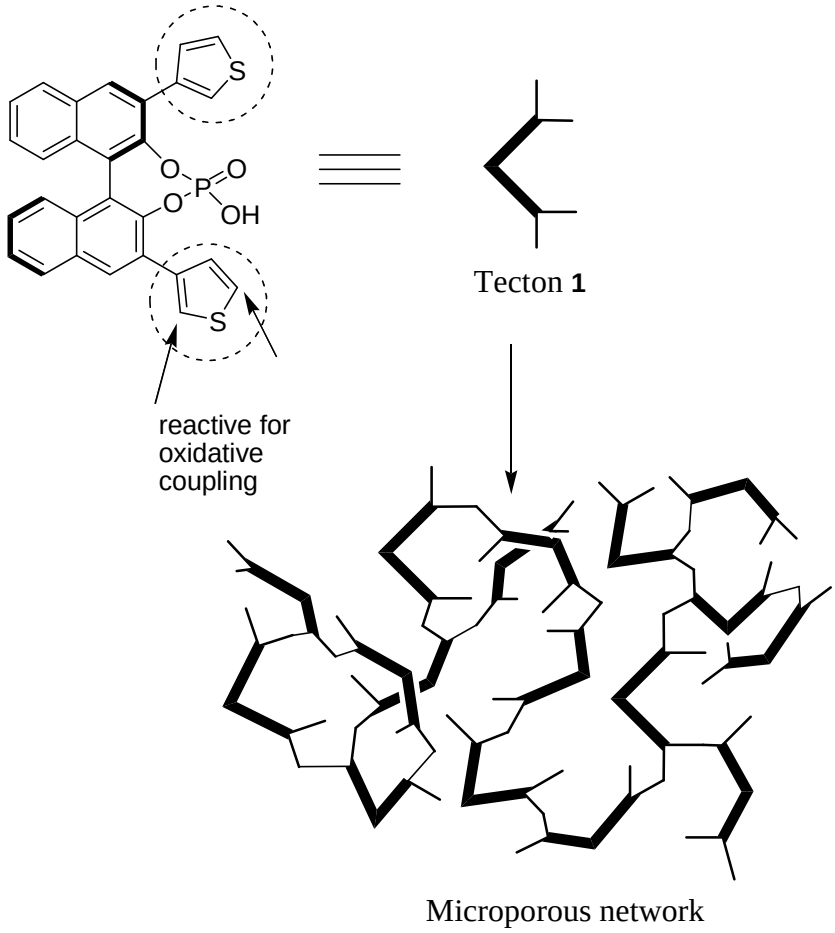


Figure 9: Use of oxidative coupling reaction to make microporous network containing BINOL-phosphoric acid

With this concept several polymerizable BINOL-derived phosphoric acid structures were envisioned to be synthesized (See Figure 10).

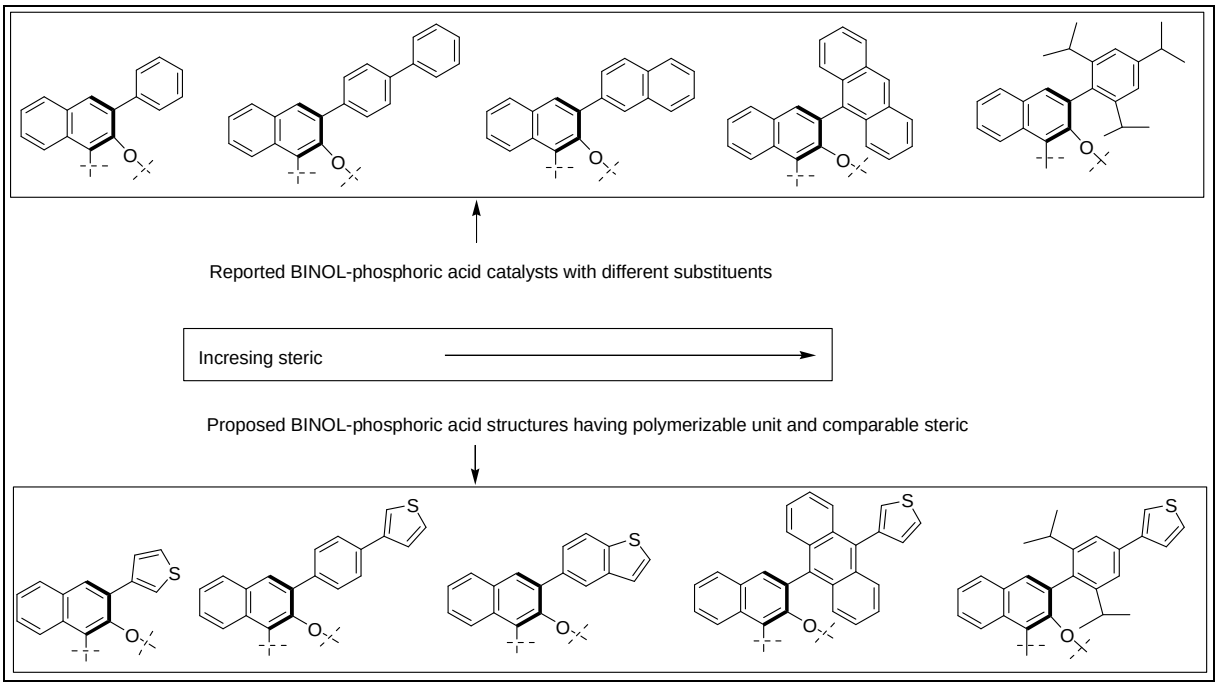
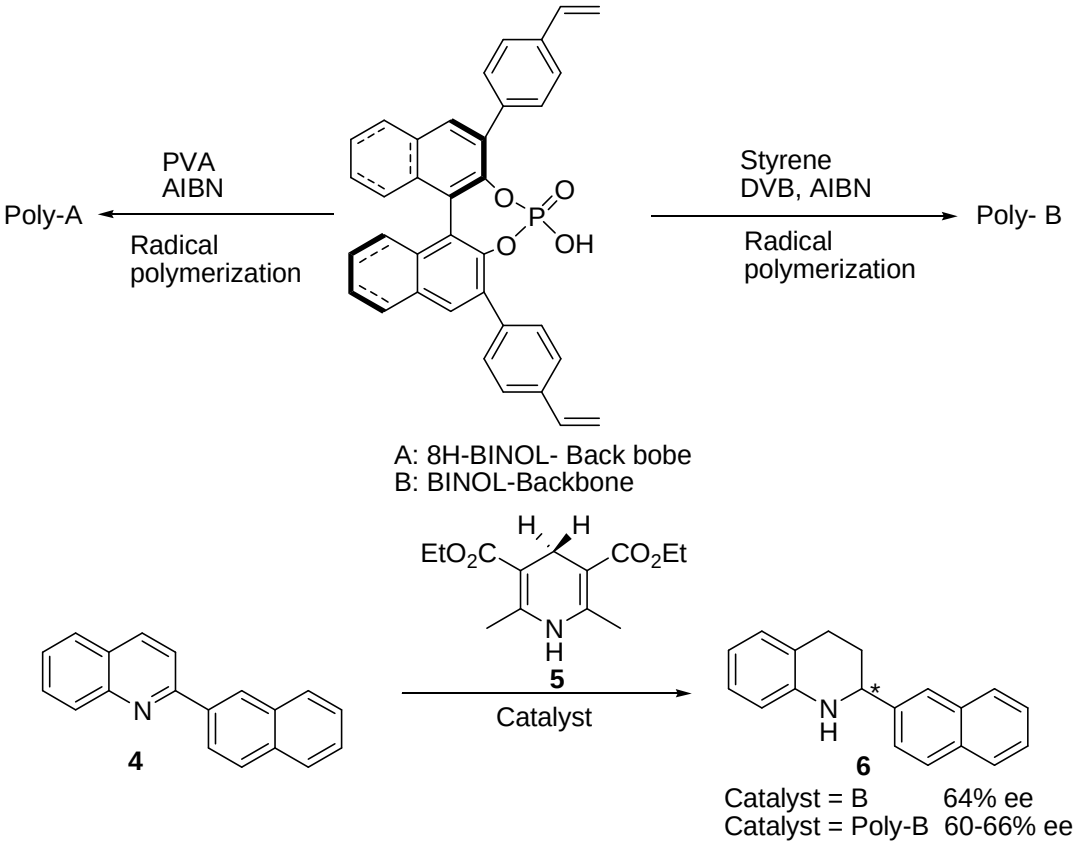


Figure 10: Designing polymerizable BINOL-derived phosphoric acid with different steric.

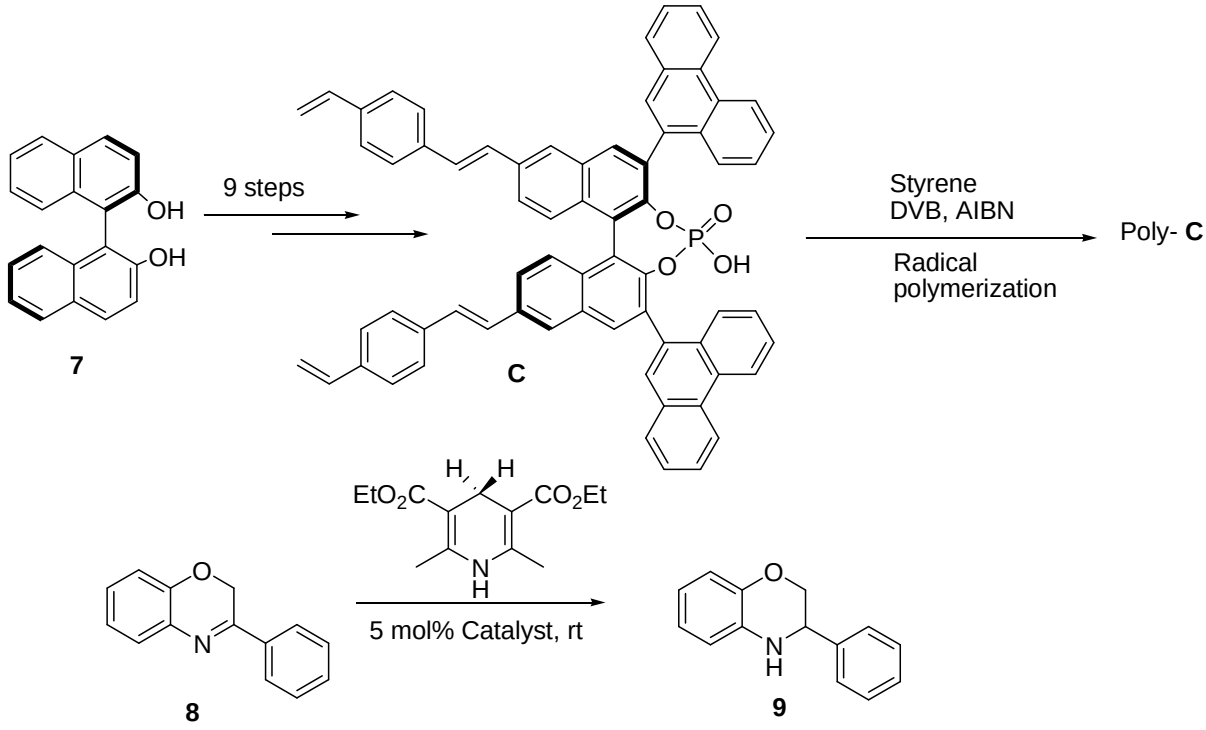
Chiral heterogeneous phosphoric acid catalyst

In 2008, *Beller* and co-workers reported attempts to immobilize BINOL-phosphoric acid first time.[115] The styrene-substituted phosphoric acid monomer **A** polymerized together with polyvinyl alcohol (PVA) by a radical reaction (See Scheme 30). Poly-A showed a very small specific surface area of less than 4 m^2/g and found to be catalytically inactive in achiral test reactions as opposed to a simple acid catalyst Amberlyst-36.[116]



Scheme 30: Synthesis of heterogeneous chiral BINOL-Phosphoric acid by radical polymerization and application in asymmteric transfer hydrogenation

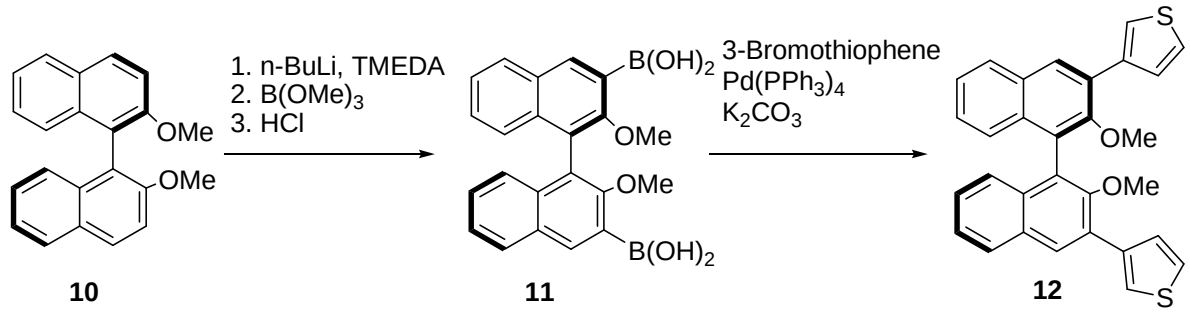
In 2010, *Rueping* and co-workers used a similar strategy to synthesize heterogeneous BINOL-derived phosphoric acid polymer. Starting from chiral (R)-BINOL they synthesized polymerizable BINOL-phosphoric acid unit. First, the polymerized the monomer **B** to polymer Poly-**B** by radical polymerization and applied in asymmetric transfer hydrogenation of 2-naphthyl quinoline substrate with Hantzsch ester reaching 60-66% ee (See Scheme 30). They also synthesized BINOL-phosphoric acid structure with bulkier (phenanthryl) substituents at 3,3' positions and successfully polymerized the monomers with divinyl benzene (DVB) and styrene again using free radical polymerization (See Scheme 31).[117] They used their monomer **C** and polymer poly-**C** in asymmetric transfer hydrogenation of benzoxazine. For the monomer, they got an *ee* of 96% and the polymer Poly-**C** catalyst yielded an *ee* of 94%. They are able to recover their polymer supported catalyst easily and reuse it up to 10 times without any significant loss of enantioselectivity. But, in their case, the reaction rate with the polymer supported catalyst for transfer hydrogenation reaction of benzoxazine is quite slow. They required 20-24 hours reaction time to achieve full conversion of the substrate. This can be explained by low catalyst density and diffusion difficulty.



Scheme 31: Polymerization of substituted BINOL-backbone and application as heterogeneous catalyst.

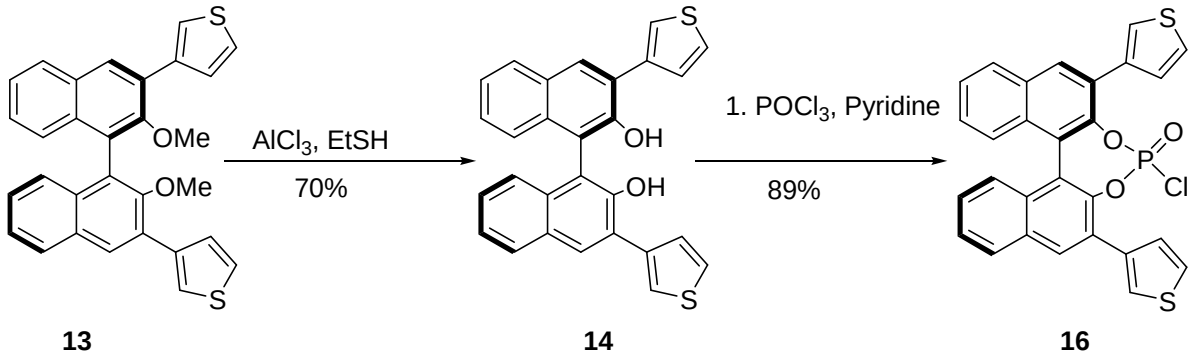
In our group, *Christian Bleschke* showed that homogeneous and heterogeneous BINOL derived phosphoric acid catalyst can be synthesized from the same precursor, BINOL phosphoric acid chloride. [118, 119] In the pretext of this thesis, the discussion of *Bleschke's* work is very relevant.

According to *Bleschke's* report, synthesis of the monomer was started with enantiomerically pure (R) (+) 1, 1'-Bi 2-naphthol, (R) –BINOL **7**. For functionalization of BINOL scaffold, it was protected with dimethoxy group leading to monomer **10.** In structure **10,** 3 - and 3'-positions were selectively deprotonated by n-butyllithium and was reacted with trimethylborate. The subsequent hydrolysis gave the diboronic acid **11** as a coupling partner for Suzuki cross-coupling reaction (See Scheme 32). The BINOL-derivative **12** was then synthesized by the Suzuki cross-coupling of diboronic acid **11** with 3-bromothiophene in 70% yield.



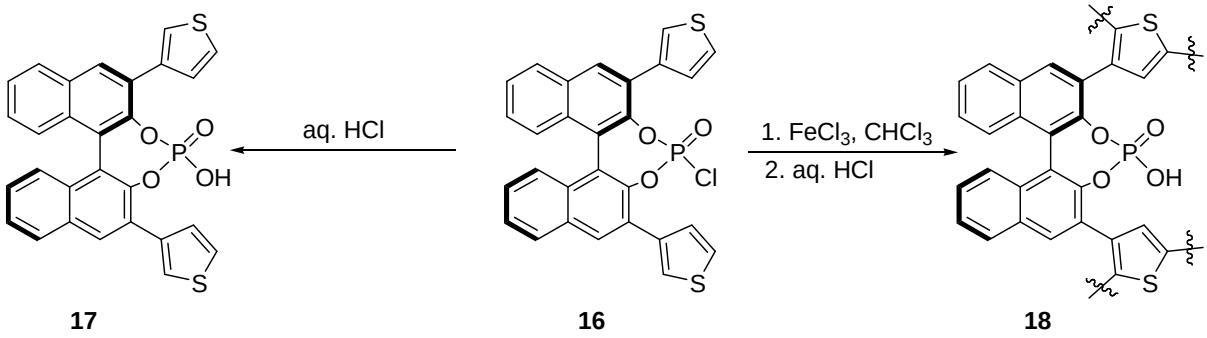
Scheme 32: Synthesis of di-methoxy protected 3,3'(3-thienyl)-BINOL

The following deprotection of the methyl ether using strong Lewis acid aluminium trichloride and strong nucleophile thioethanol yielded very good results at 0°C for 2 h, the desired product without the formation of side products. The isolated yield was about 70% (See Scheme 33). The reaction with phosphorus oxychloride in pyridine afforded the product **16** in good yield.



Scheme 33: Synthesis of the phosphoric oxychloride

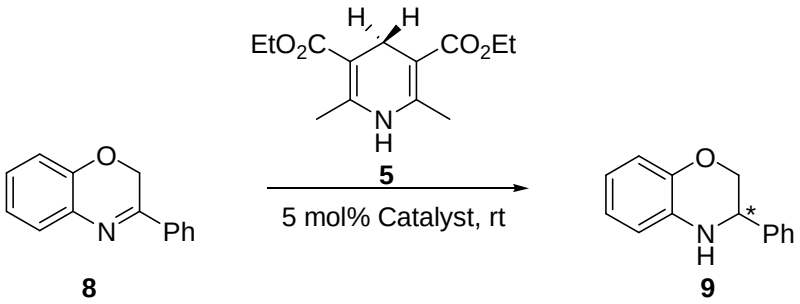
Hydrolysis of the acid chloride **16** gives the monomeric phosphoric acid **17** (in overall 29% yield over 5 steps) which is used as homogeneous catalyst. Again, the acid chloride was polymerized by oxidative coupling reaction using $FeCl_3$ in organic solvent leading to insoluble polymeric material **18** (See Scheme 34).



Scheme 34: Synthesis of the monomeric and polymeric phosphoric acid

The homogeneous catalyst **17** and polymeric catalyst **18** were used in asymmetric transfer hydrogenation of benzoxazine with Hantzsch ester (see Table 1). The monomer yielded 34% *ee* whereas the polymer resulted in about 60% *ee* with the other enantiomer as major.

Table 1



Catalyst	Type	Conversion	ee
Monomer **17**	Homogeneous	>99	-34%
Polymer **18**	Heterogeneous	>99%	60%

This enhancement in enantioselectivity can be explained by the fact that, the monomeric phosphoric acid catalyst **17** has thiophene units attached to the 3, 3' positions which has low steric influence to the catalytic center. When the monomers polymerizes, the polymer grows near the catalytic center increasing the steric effect and hence enhancing enantioselectivity with the polymeric catalyst **18**. (See Figure 11)

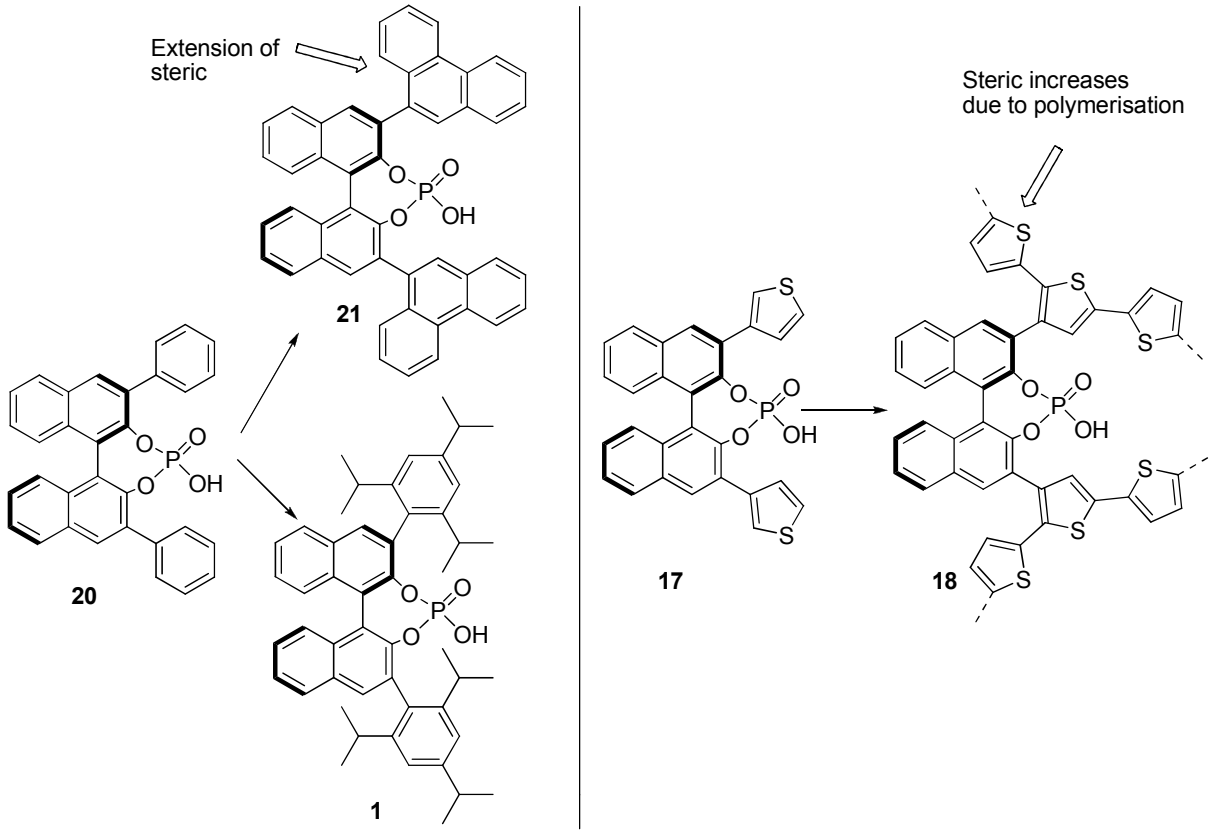


Figure 11: Explanation for enhancement of enantioselectivity from monomeric catalyst to polymeric catalyst.

Synthesis of helical polymeric phosphoric acid

In our group, we thought that attaching thiophene units through 2 position at the 3, 3' position of BINOL-phosphoric acid monomer and then polymerizing will lead to polymeric chain. We expected to find helical structure and hence enhanced enantioselectivity.

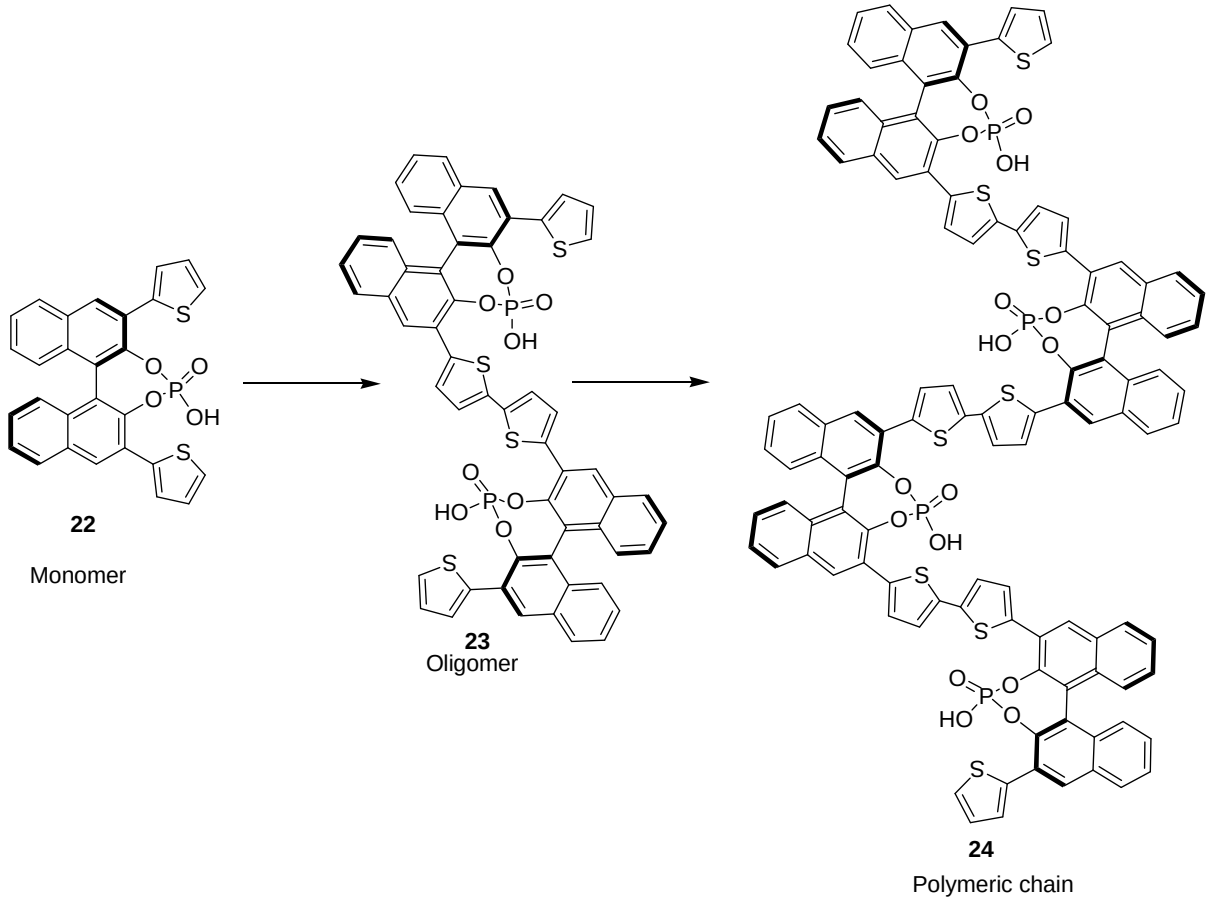
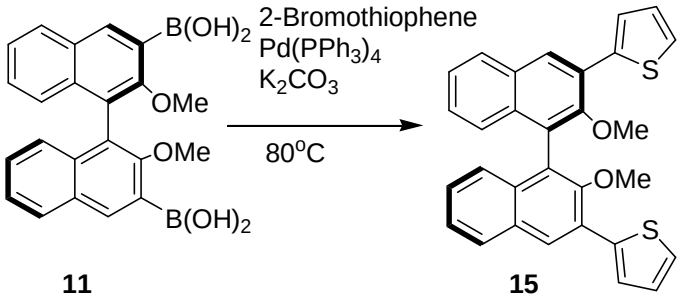


Figure 12: Helical polymeric chain from polymerizable monomer

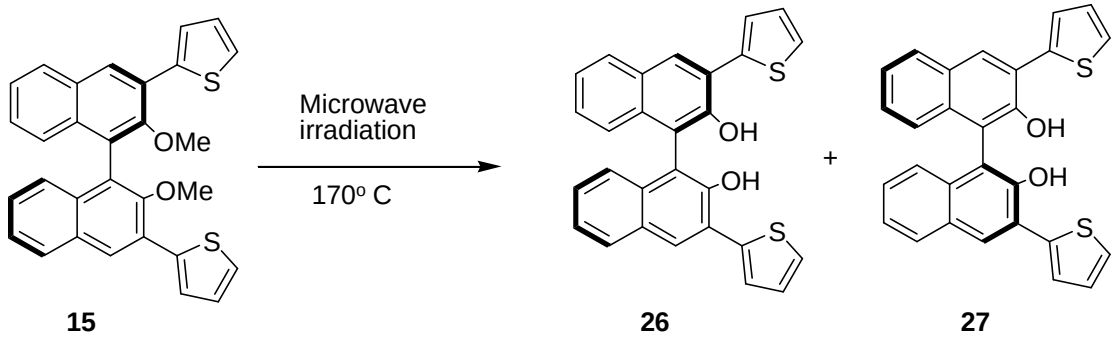
Bleschke reported the possible synthesis starting from chiral (R) -BINOL. First, the free –OH groups in BINOL were protected to methoxy groups. From dimethylated (R)-BINOL, the diboronic acid was synthesized as precursor for Suzuki-coupling reaction. [23] Double coupling with 2-bromothiophene led to structure **15** in good yield. (See Scheme 35)



Scheme 35: Synthesis of 3,3‘ bis (2-thinyl) dimethoxy BINOL

Subsequent cleavage of the methyl ether group proved to be challenging. Usually deprotection of aryl methoxy group is done using Lewis acid BBr_3. In our case this reaction condition did not work. We tried combination of stronger Lewis acid $AlCl_3$ and stronger nucleophile thioethanol but this reaction condition too did not provide desired results. Then careful study of literature revealed the information that use of pyridinium hydrochloride and microwave irradiation can cleave aryl methoxy group.

Subsequently pyridinium hydrochloride was synthesized mixing hydrochloric acid and pyridine under low temperature. Pyridinium hydrochloride as a white semi solid was yielded after evaporation of water. Microwave irradiation of 2,2'-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)dithiophene provided the cleavage of methoxy protecting groups. Feasibility of this deprotection reaction condition was proved by a 90% yield of 3,3'-di(thiophen-2-yl)-[1,1'-binaphthalene]-2,2'-diol.

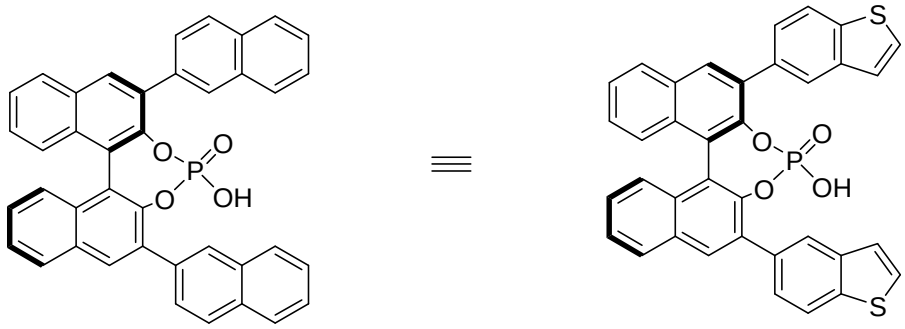


Scheme 36: Racemization due to microwave irradiation

Next treatment of the thiophene substituted diol dissolving in pyridine with phosphorous oxy chloride yielded the phosphoric acid chloride. Subsequent hydrolysis of the phosphoric acid chloride resulted pure phosphoric acid as white solid. Before attempt of polymerization, the catalytic performance of the monomer was tested in asymmetric hydrogenation reaction of benzoxazine. Use of 5 mol% phosphoric acid catalyst led to 99% conversion but racemic product. Hence the enantiopurity of the catalyst was checked by chiral HPLC. It was found

that microwave irradiation led to racemization of the BINOL structure. As no other way was found to deprotect the di-methoxy protected 2-thiophenyl substituted structure **15**, the idea of making helical structure out of linear polymeric chain had to be abandoned.

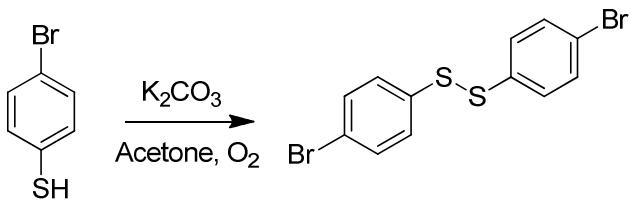
In order to synthesize other phosphoric acids containing polymerizable unit, benzothiophene unit was in our focus. Benzothiophene has one possible polymerization site and can be polymerized using oxidative coupling condition leading to polymeric chain. BINOL-phosphoric acid structure **29** containing benzothiophene substituents at 3, 3' positions should have steric effect comparable to 2-naphthyl substituted BINOL-phosphoric acid **28** (See Figure 13).



28 **29**

Figure 13

The synthetic sequence for bromobenzothiophene was started reacting 4-bromo thiophenol **30** with 2-bromo-1,1-diethoxyethane **32.** This reaction was attempted in open air condition first. It was found that, presence of oxygen leads to homo coupling of 4-bromo thiophenol **30** to bis(4-bromophenyl)sulfane **31** exclusively (See Scheme 37).



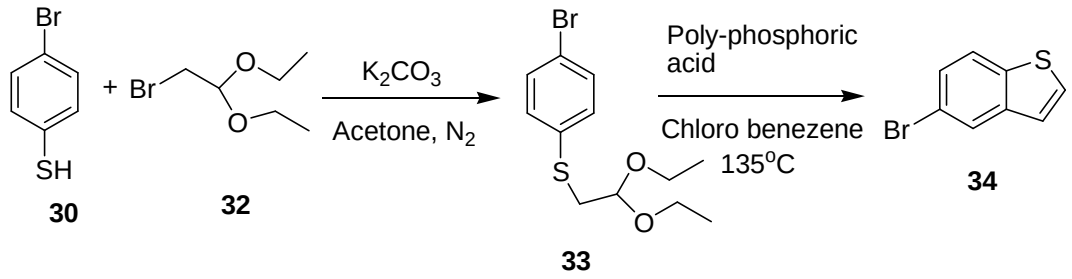
30 **31**

bis(4-bromophenyl)sulfane

Scheme 37: homo coupling of 4-bromo thiophenol to bis(4-bromophenyl)sulfane in presence of oxygen

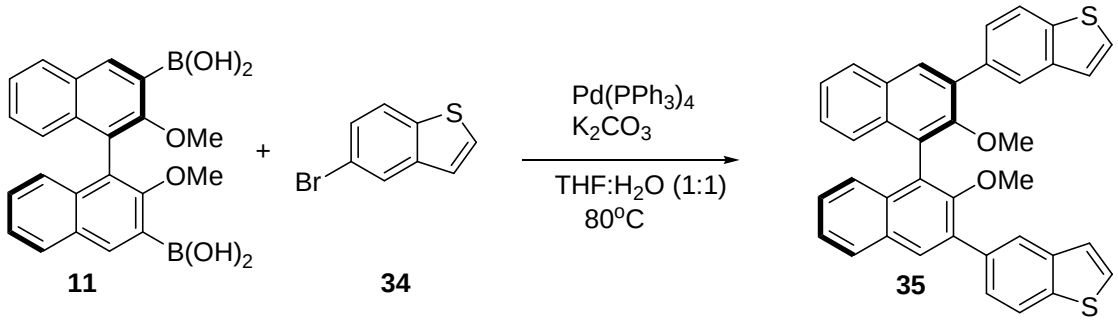
To solve this problem the reaction was performed under nitrogen atmosphere. (4-bromophenyl)(2,2-diethoxyethyl)sulfane **33** was synthesized in very good yield (98%) as

color less liquid. Heating **33** with polyphosphoric acid does electrophilic cyclization to give 5-bromobenzothiophene **34**. (See Scheme 38)



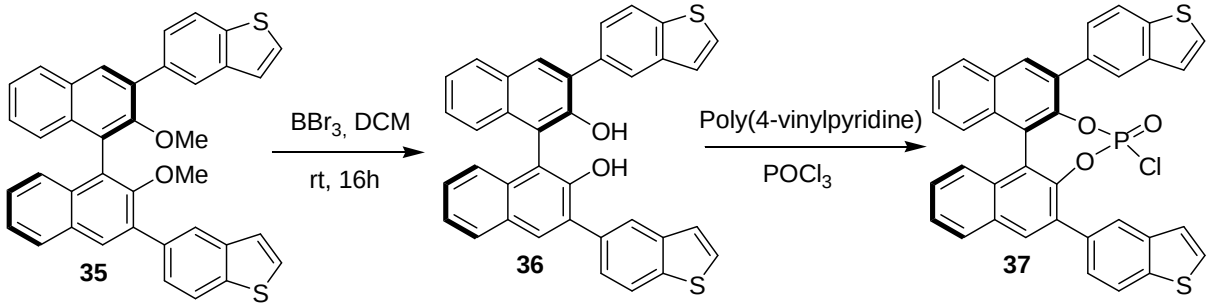
Scheme 38: Synthesis of 5-bromobenzothiophene

With 5-bromobenzothiphene in our hand, Suzuki coupling between BINOL di boronic acid gave the compound bis5-(1-(2-(benzothiophen-5-yl)-di-methoxy-BINOL **35**.



Scheme 39

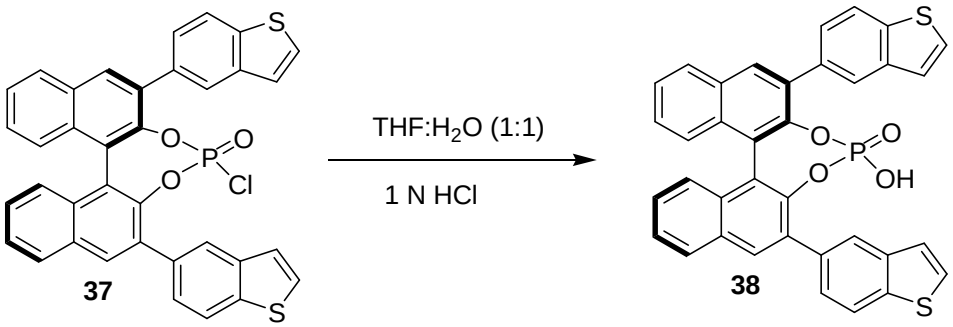
Deprotection of the di-methoxy group worked smoothly using borontribromide in CH_2Cl_2.



Scheme 40

The synthesis of the corresponding phosphoric acid chloride was performed stirring **36** with Poly(4-vinylpyridine) in DCM and adding phosphorous oxychloride. In this step polymeric pyridine instead of pyridine was used to avoid tedious separation of pyridine after the reaction. Polymeric pyridine base is separated easily by filtration affording the desired compound in good yield. Stirring the compound (R)-3,3'-(benzothiophen-5-yl)-BINOL-

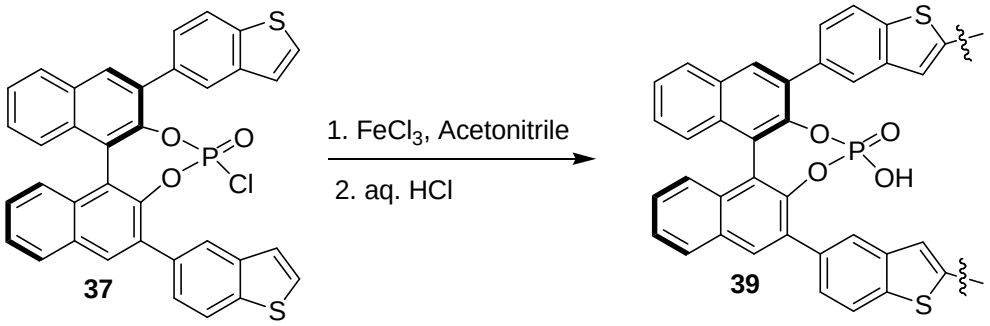
phosphoric acid chloride **37** with aqueous HCl in tetrahydrofuran yielded the monomeric phosphoric acid catalyst **38** (see Scheme 41).



Scheme 41: Hydrolysis of phosphoric acid chloride to phosphoric acid

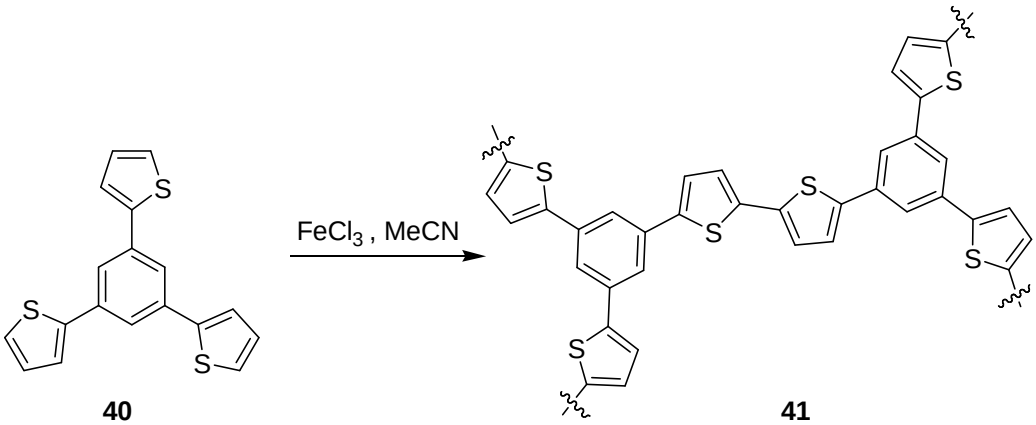
Synthesis of polymer and copolymers from benzothiophene substituted BINOL posphoric acid chloride

The polymerization of the monomers and the characterization of the synthesized polymers were performed by *Johannes Schmidt* in the *Thomas* group at the TU Berlin. The surfaces of the materials were determined by the BET method by measuring the absorption over nitrogen at low temperatures. Phosphoric acid chloride **37** was dissolved in dry toluene and heated to 60 °C. Under vigorous stirring 8 equivalent of $FeCl_3$, dissolved in dry acetonitrile, was added to the solution. The reaction mixture was stirred for 4 hours at 60 °C and quenched with ethanol. Due to oxidative coupling the monomers **37** polymerizes and grows as polymeric chain. After a growth of certain chain length it precipitates. The resulting insoluble polymer chain was separated by centrifugation (4000 rpm), washed several times with ethanol, a mixture (1:1) of aqueous HCl and THF, and $CHCl_2$ to remove residues of the monomer and reactants. The product was dried in high vacuum for 24 h.



Scheme 42: Polymerization of phosphoric acid chloride to phosphoric acid chain

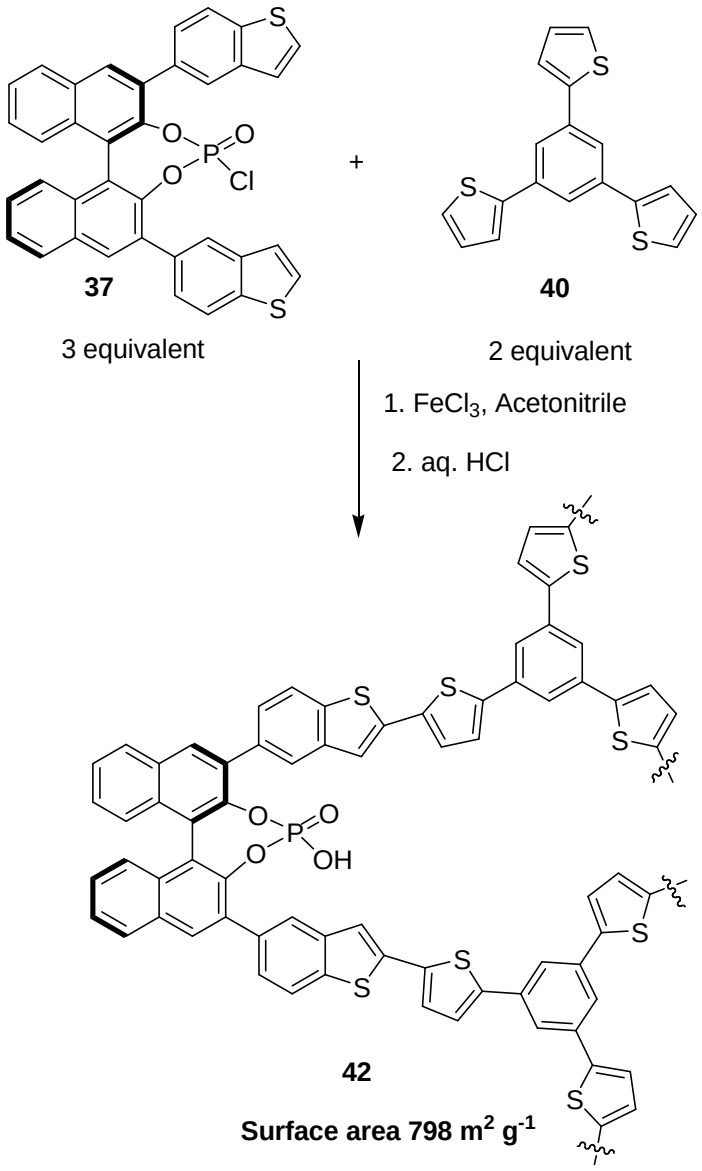
In 2009, *Thomas*, *Antonietti*, and co-workers have reported synthesis of conjugated microporous polymer or CMP **41** based on the poly(arylenethienylene) motif via the oxidative polymerization of 1,3,5-tris(2-thienyl)benzene (see Scheme 43).[120] The resulting CMP has comparatively high surface area of 577 $m^2 g^{-1}$ and porosity (0.61 $cm^3 g^{-1}$) with relatively large pore sizes (average diameter = 1.6 nm). The high density of thiophene functionalities in this framework makes the CMP also suitable for encapsulation of metal clusters.



40 **41**

Scheme 43: Synthesis of CMP from 1,3,5-tris(2-thienyl)benzene

In order to synthesize polymeric network structure we decided to add 1,3,5-tris(2-thienyl)benzene **40** during the polymerization process of the phosphoric acid chloride **37** to get co-polymer network structure containing phosphoric acid units.



Scheme 44: Synthesis of co-polymer

Addition of 2 equivalent of 1,3,5-tris(2-thienyl)benzene **40** to 3 equivalent phosphoric acid chloride **37** led to co-polymer **42** with network structure. The surface area of the co-polymer was found to be 798 $m^2 g^{-1}$ using the BET method (See Scheme 44).

Application of monomer 38 and co-polymer 42 in asymmetric transfer hydrogenation:

The asymmetric transfer hydrogenation of prochiral quinoline or benzoxazine derivatives provides access to important structural motifs that are found in many natural products and pharmacological agents. [121, 122]

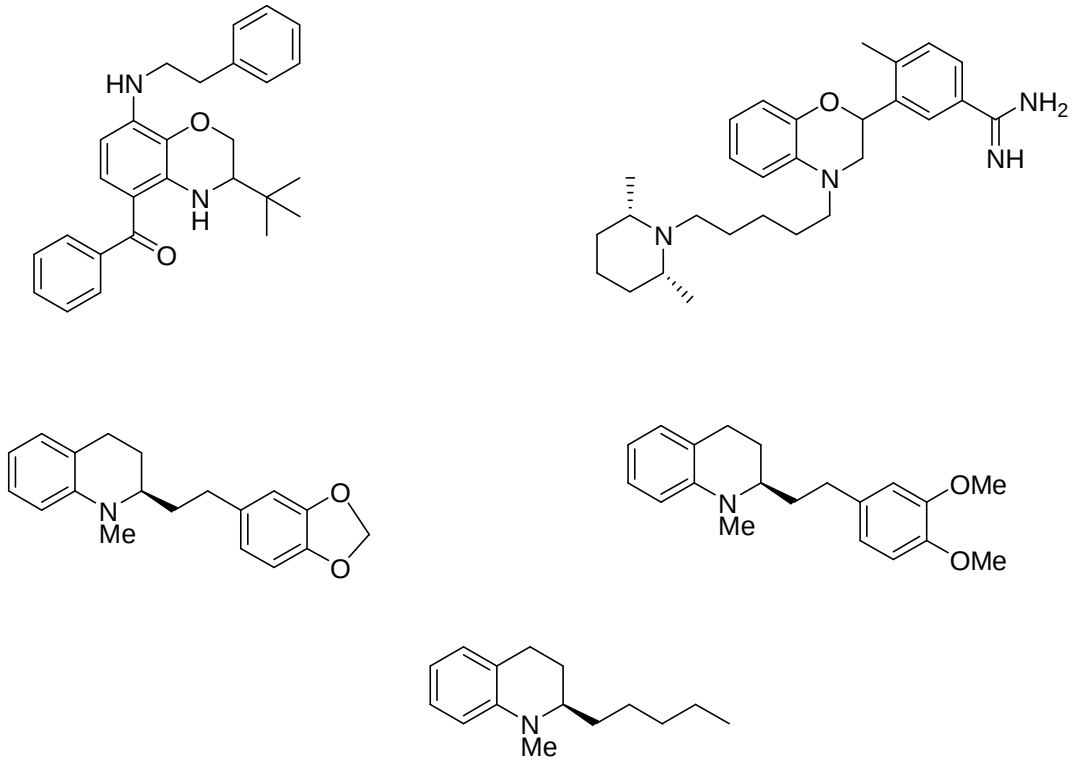
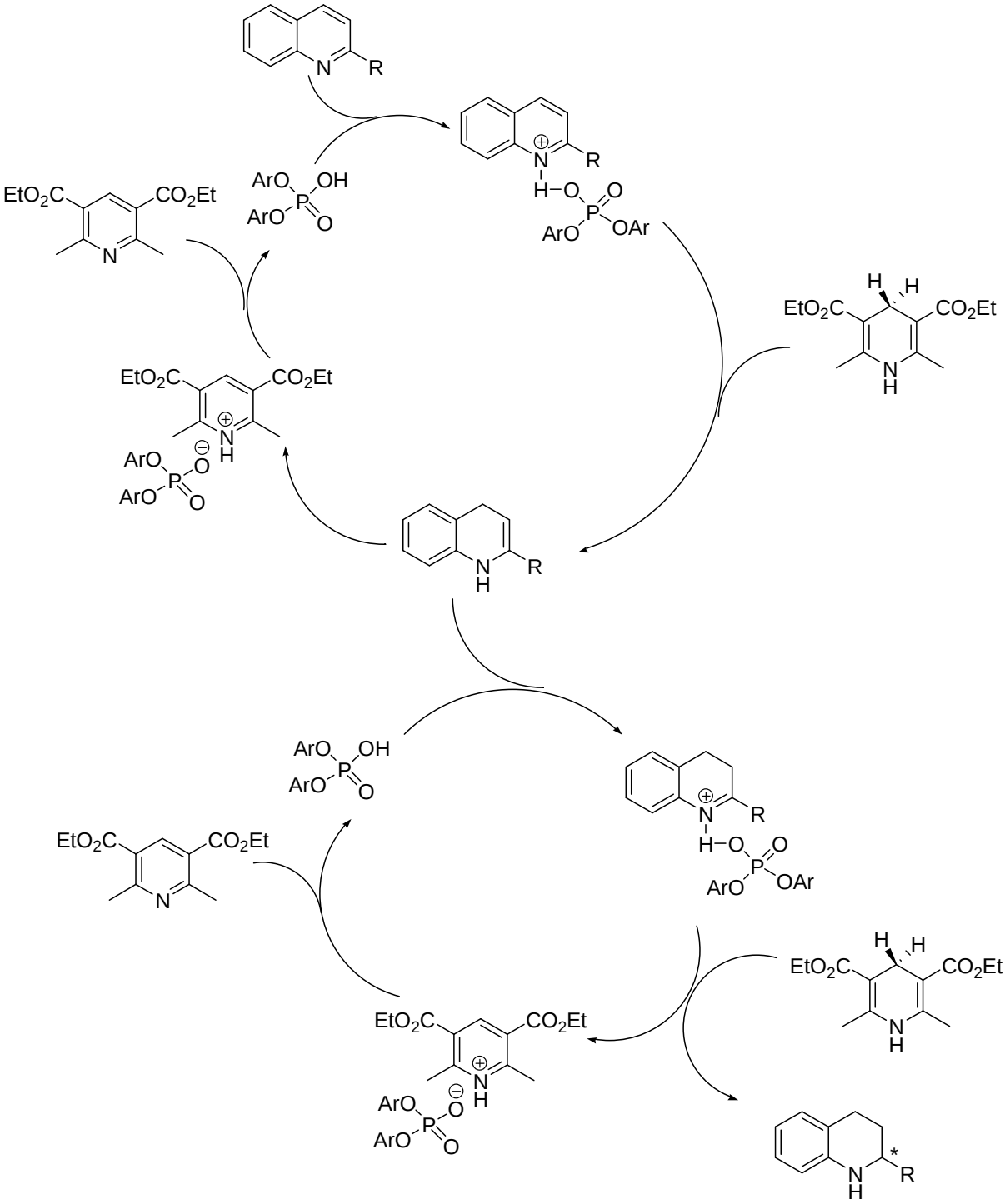


Figure 14: Examples of natural products and bio-active molecules containing tetrahydro quinoline and benzoxazine core.

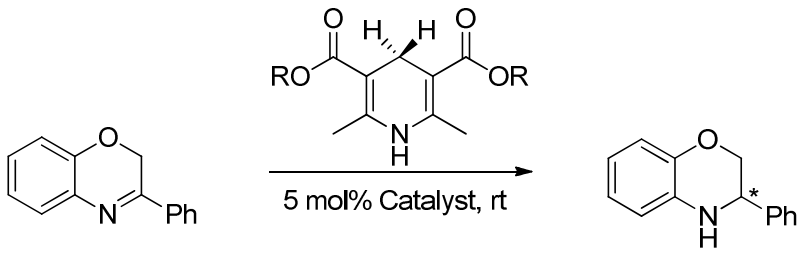
The reaction is catalyzed by chiral BINOL-phosphoric acid with excellent enantioselectivity and Hantzsch ester or benzothiazolidinone can be used as hydride source. In order to check the catalytic performance our newly synthesized monomer **38** and co-polymer **42**, first transfer hydrogenation of benzoxazine was performed using two different Hantzsch-ester as hydride source. In a reaction with 1.25 equivalents of ethyl-Hantzsch ester **5**, the product was



Scheme 45: Possible mechanism of asymmetric transfer hydrogenation of 2-aryl quinoline

obtained after full conversion within 2 h without the formation of any byproduct. The enantioselectivity was determined by chiral HPLC and was 45% *ee* (Table 2, entry 1). In subsequent experiments the selectivity could be enhanced by the use of bulky tert-butyl substituted Hantzsch ester as the hydride source to 60% *ee* (entry 3).

Table 2

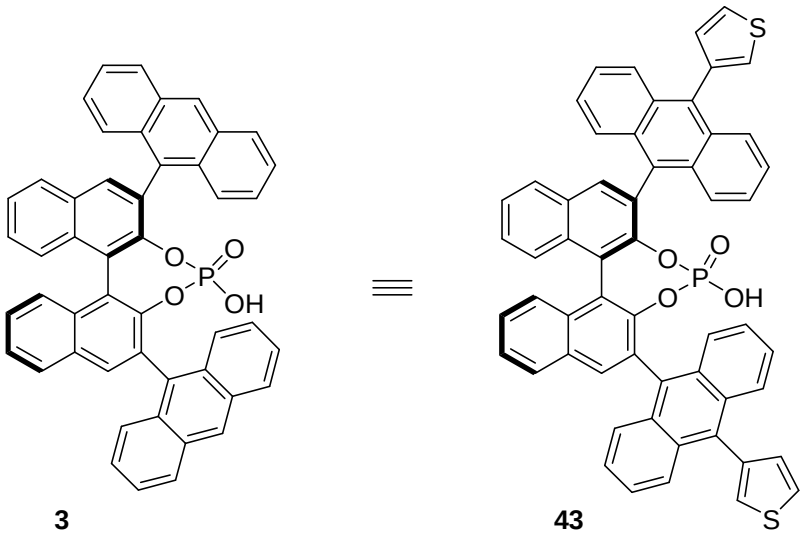


Entry	Type	Catalyst	Hantzsch ester	Time (h)	Conversion	*ee*
1	Homogeneous	**38**	R = ethyl	2	>99%	45%
2	Heterogeneous	**42**	R = ethyl	2	>99%	39%
3	Homogeneous	**38**	R = ^{t}butyl	4	>99%	60%
4	Heterogeneous	**42**	R = ^{t}butyl	4	>99%	50%

Next, the reaction was performed with insoluble co-polymer **42** in $CDCl_3$. This time, the selectivity was observed to be slightly lower in comparison to the monomeric catalyst **38**. Using the 1.25 eq. ethyl-Hantzsch ester 39% enantioselectivity was observed and using the 1.25 eq. of tert-butyl Hantzsch ester yielded 50% ee. After the reaction, centrifugation of the reaction mixture led to precipitation of the polymeric catalyst at the bottom of the centrifuge tube. The polymer was washed with chloroform and recovered. After drying the polymeric catalyst it is reused in same fashion and no significant change in reactivity or selectivity was observed.

Although the results with polymeric catalyst **42** is not better than that of the monomer **38** like our previous results with 3,3' thiophene substituted BINOL-phosphoric acid polymer , this ultimately motivated us to synthesize BINOL-phosphoric acid structure with even bulkier substituents at the 3,3' positions.

Synthesis of monomers with large steric groups at 3,3' positions:

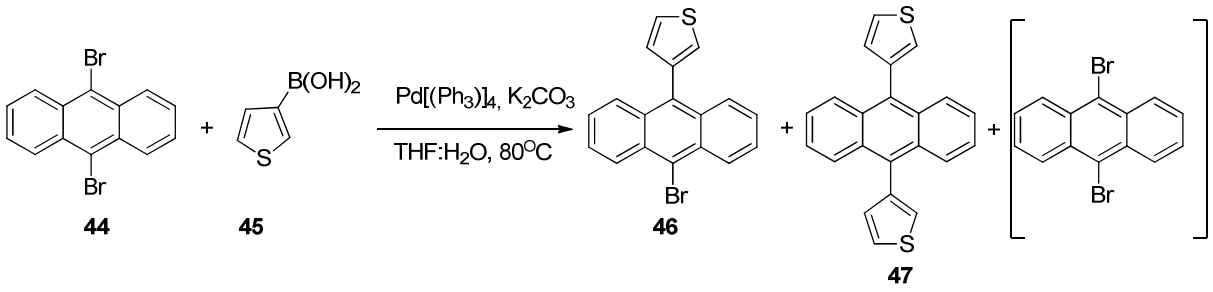


3 **43**

Figure 15

BINOL-phosphoric acid structure with anthracenyl substituents at 3, 3' positions is well known as very selective Brønsted acid catalyst in several asymmetric reactions.[123] We envisioned that designing the polymerizable structure such a way that overall steric effect at the catalytic center remains same may lead to very similar activity and selectivity. In order to do so, structure containing 3-thiophenyl anthracenyl substituents was on our focus. Starting from 9,10 di bromo anthracene, Suzuki coupling with 3-thienyl boronic acid was performed.

Table 3

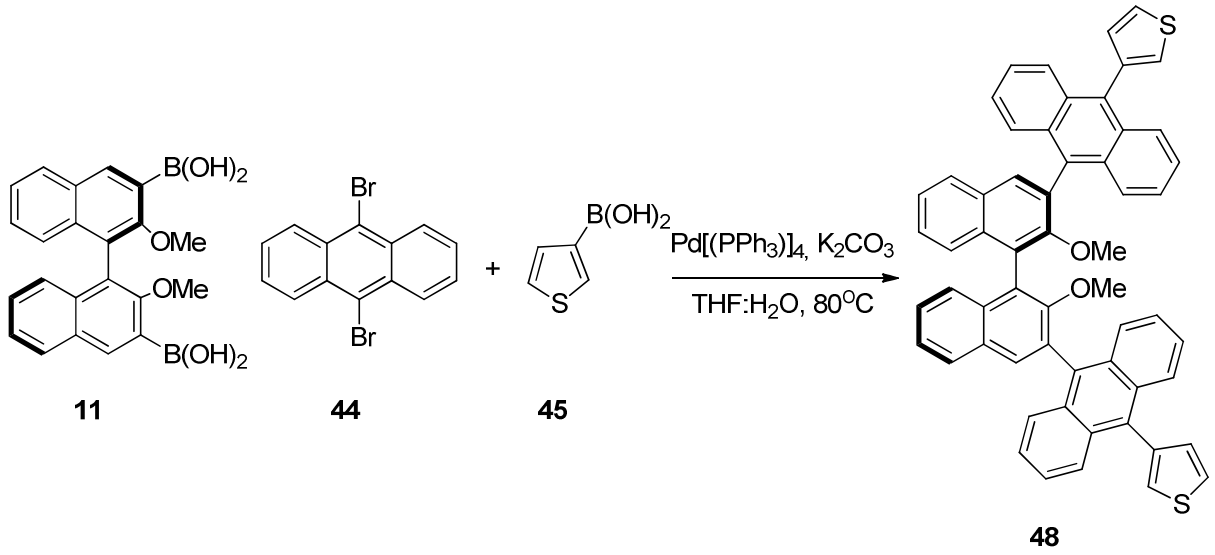


44 **45** **46** **47**

Entry	44	45	Time (h)	46	47
1	1 eq.	1 eq.	24	60%	40%
2	1.5eq.	1 eq.	10	40%	20%
3	2 eq.	1 eq.	24	65%	35%
4	2 eq.	1 eq.	10	45%	10%

Following literature procedure, it was found that there is tendency to form significant amount 9,10 di (3-thienyl) antracene. When less equivalent of thienyl boronic acid was used, the product mixture was very difficult to separate as changing Br-substituent to thiophene substituent on anthracene structure does not change overall polarity of the molecule significantly. (See Table 3)

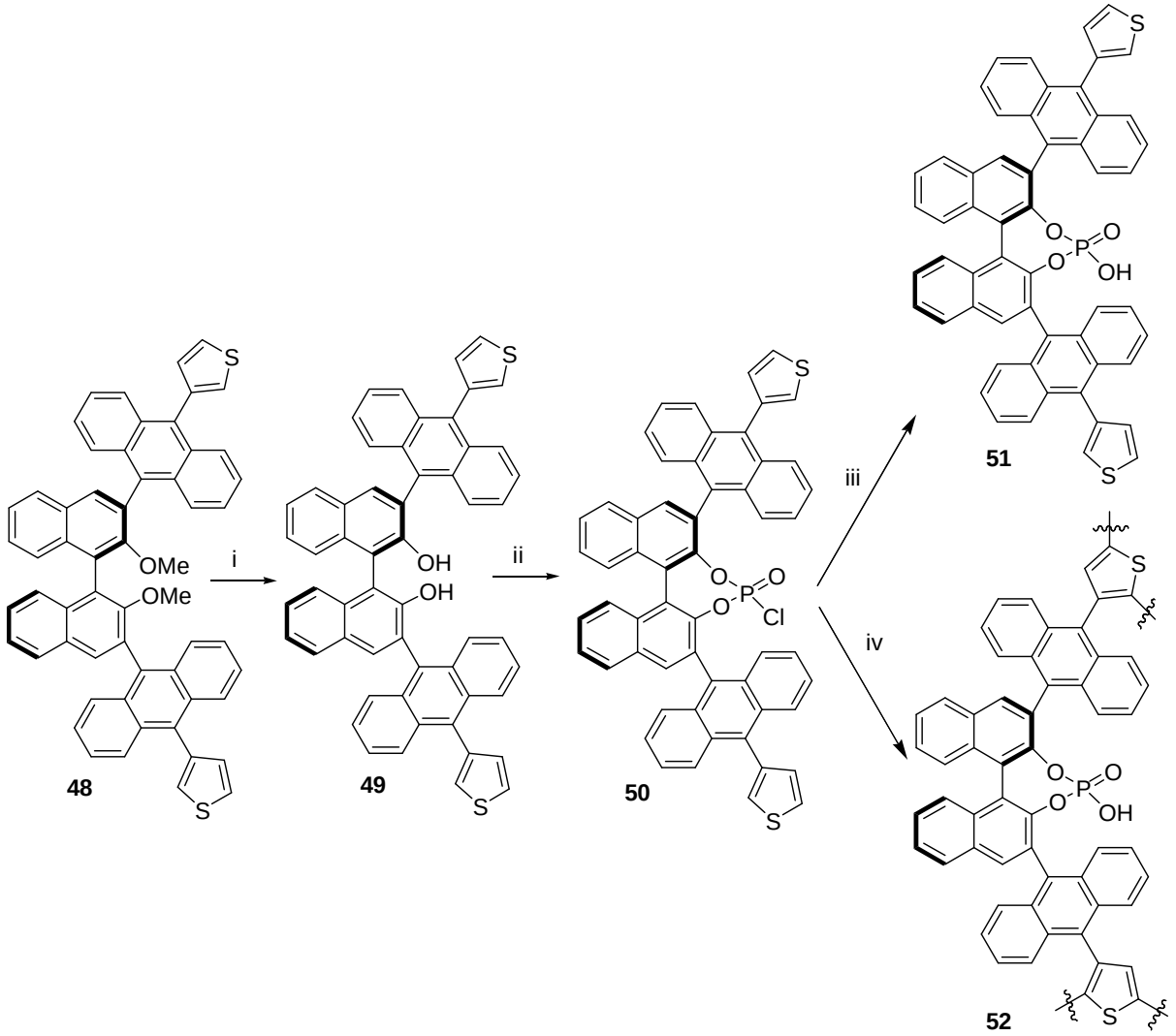
To solve this problem we came up with the idea of one pot three component Suzuki coupling reaction. Taking 3, 3' BINOL-di-boronic acid, 9,10 di-bromo anthracene and 3-thienyl boronic aicd in 1:1:1 ratio and using 10 mol% $Pd(PPh_3)_4$ in 1:1 THF:Water mixture led to 85 % yield of the desired product (See Scheme 46).



Scheme 46

The deprotection of the methoxy groups in **48** worked smoothly with Lewis acid boron tribromide in DCM. Subsequently, treatment of the diol **49** dissolved in DCM with poly(4-vinyl)pyridine with phosphorous oxy chloride yielded the phosphoric acid chloride **50**. Hydrolysis of the (R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-BINOL-phosphoric acid chloride **50** with aqueous HCl yielded the pure (R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-BINOL-phosphoric acid **51** as dark brown solid. Like the previous synthesis of microporous polymer from (R)-3,3'-(benzothiophen-5-yl)-BINOL-phosphoric acid chloride **37**, the polymerization of the bulky substituted phosphoric acid chloride **50** was performed. (R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-BINOL-phosphoric acid chloride **50** was dissolved in dry toluene and heated to 60 °C. Under vigorous stirring $FeCl_3$ (8 eq.), dissolved in dry acetonitrile, was added to the solution. The reaction mixture was stirred for about 4 h at 60 °C and quenched with ethanol. The resulting polymer network was separated by

centrifugation (4000 rpm), washed several times with ethanol, a mixture (1:1) of aqueous HCl (c = 2 mol/L) and THF, and $CHCl_2$ to remove residues of the monomer and reactants. The polymeric phosphoric acid network **52** was dried in high vacuum for 24 h. (Yield, 80%) (See Scheme 47). The pure polymer showed BET surface area of 386 $m^2 g^{-1}$.



i) BBr_3, DCM, ii) poly(4-vinyl pyridine), $POCl_3$, DCM; iii) THF, 1N HCl rt; iv) (a) $FeCl_3$, toluene, acetonitrile, (b) aqueous HCl.

Scheme 47

Synthesis of co-polymers from phosphoric acid chloride 50:

In a similar fashion like the synthesis of phosphoric acid polymer **52**, different co polymers were synthesized mixing phosphoric acid chloride **50** and 1,3,5 –tris(2-thienyl)benzene **40** in different ratios. When used in same equivalent of both, it provided co-polymer **53** having BET surface area of 577 $m^2 g^{-1}$. Again using 5 equivalent of 1,3,5 –tris(2-thienyl)benzene **40**

and 1 equivalent of phosphoric acid chloride **50** it resulted in co-polymer with BET surface area 668 $m^2 g^{-1}$ (see Table 4).

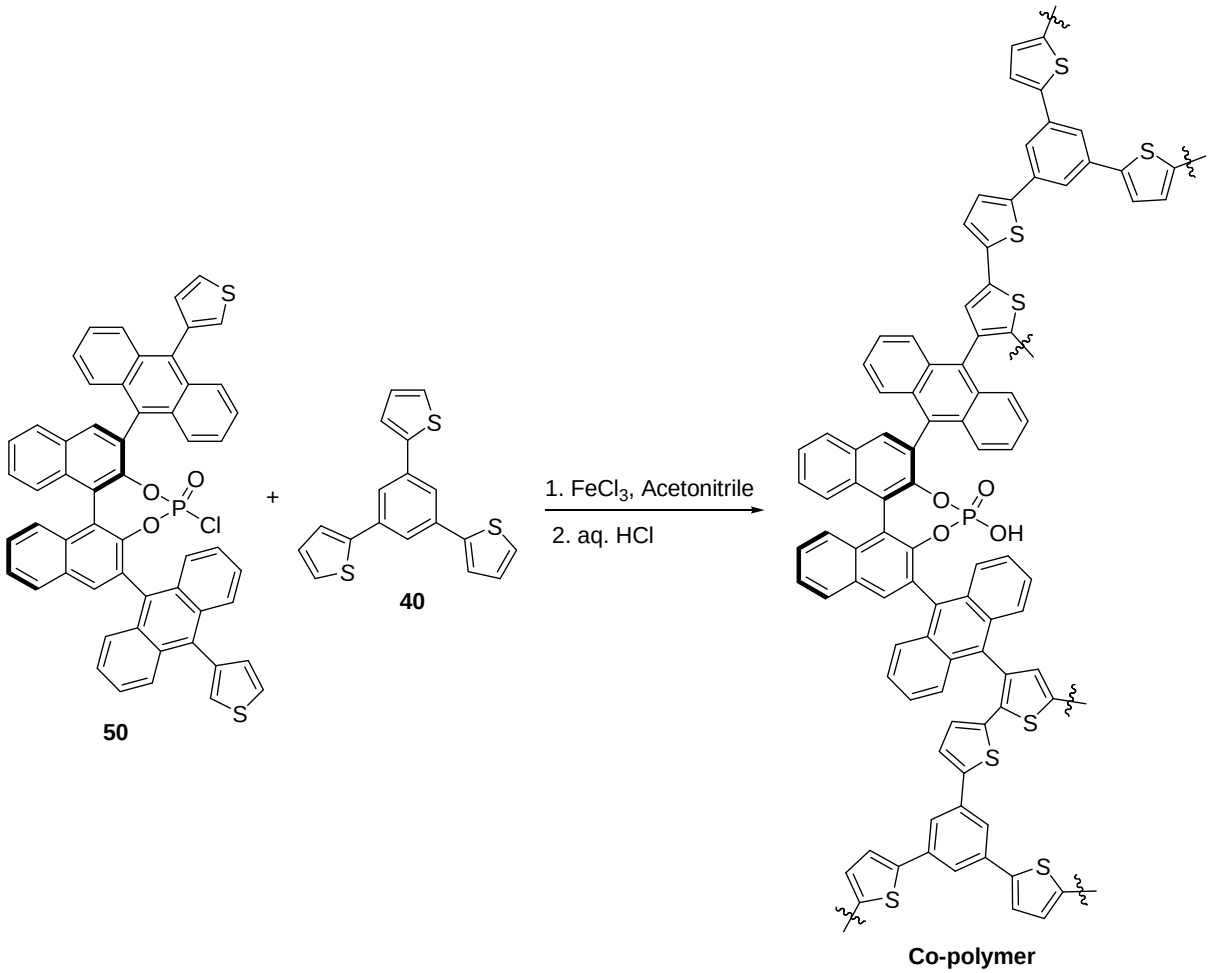


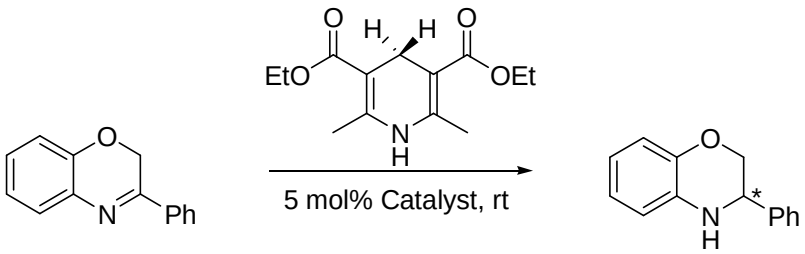
Table 4

Entry	Monomer 50	Linker 40	Product	BET surface
1	1 eq.	NIL	Polymer **52**	386 $m^2 g^{-1}$
2	1 eq.	1 eq.	Co-polymer **53**	577 $m^2 g^{-1}$
3	1 eq.	5 eq.	Co-polymer **54**	668 $m^2 g^{-1}$

Catalysis with monomer 51 and polymer 52:

Newly synthesized phosphoric acid catalyst **51** was tried first in asymmetric transfer hydrogenation of benzoxazine substrate. To our great delight it showed excellent enantioselectivity. When 5 mol% of the monomer is used in $CHCl_3$ or $CDCl_3$ solvent with 1.25 eq. Hantzsch ester is used it resulted 99% enantioselectivity (see Table 5).

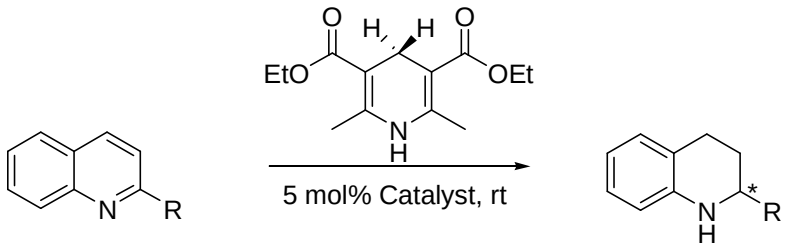
Table 5



Type	Entry	Catalyst	Time(h)	Conversion	ee
Homogeneous	1	**51**	2	>99%	99%
Heterogeneous	Run 1	**52**	2	>99%	98%
Heterogeneous	Run 2	**52**	2	>99%	98%
Heterogeneous	Run 3	**52**	2	>99%	98%
Heterogeneous	Run 4	**52**	2	>99%	98%
Heterogeneous	Run 5	**52**	2	>99%	98%
Heterogeneous	Run 6	**52**	2	>99%	98%
Heterogeneous	Run 7	**52**	2	>99%	98%
Heterogeneous	Run 8	**52**	2	>99%	98%
Heterogeneous	Run 9	**52**	2	>99%	98%
Heterogeneous	Run 10	**52**	2	>99%	98%

Next, to compare, the polymeric phosphoric acid network **52** was used for the same reaction under same reaction conditions. The polymer **52** resulted in full conversion and 98% ee. As the polymer is insoluble, after the reaction it can be recovered. The polymer can be filtered using filter paper or can be centrifuged out. It was realized that centrifugation of the polymer is more convenient way to recover the polymeric catalyst compared to filtration as some amount of the polymeric material stick and remains on the filter paper hence can lead to loss of material. To check the recyclability of our polymeric catalyst, after the reaction it was recovered by centrifugation and washed with chloroform 3 times. After drying it was used for the same reaction next time. It was found that the reuse of the polymeric catalyst does not diminish its performance. Both conversion of the substrate and enantioselectivity in the product remains stable each time. This result clearly fulfills one of our goals of recyclability of polymeric catalyst without any loss in activity or selectivity.

Table 6



Entry	Type	Catalyst	R	Conversion [%]	ee [%]
1	Homogeneous	**51**	Phenyl	>99%	98 (***S***)
2	Heterogeneous	Polymer **52**	Phenyl	>99%	97 (***S***)
3	Heterogeneous	Polymer **52**	1-naphthyl	>99%	94 (***S***)
4	Heterogeneous	Polymer **52**	3-methoxy phenyl	>99%	87 (***S***)

As reduction of 2-aryl quinoline substrate to 1,2,3,4, tetrahydroquinoline can be performed in similar fashion like benzoxazine; we tried our monomeric phosphoric acid catalyst **51** and polymeric network **52** for that purpose. The complete conversion is achieved within 2 hours of reaction time. Again with same reaction condition different 2-aryl quinoline substrates were reduced. Asymmetric hydrogenation of 2-phenyl quinoline gave >99% conversion and 98% ee with homogeneous catalyst **51**. With this result in hand the pure polymer **52** was used in same reactions. Using 5 mol% of the polymeric catalyst and 1.25 eq. Hantzsch ester

resulted in full conversion of substrate to desired product and 97% *ee*. Again, with same reaction condition and polymeric catalyst **52**, transfer hydrogenation of 2-(1-naphyl) quinoline and 2-(3-methoxy phenyl) quinoline resulted in 94% and 87% *ee* respectively (see Table 6).

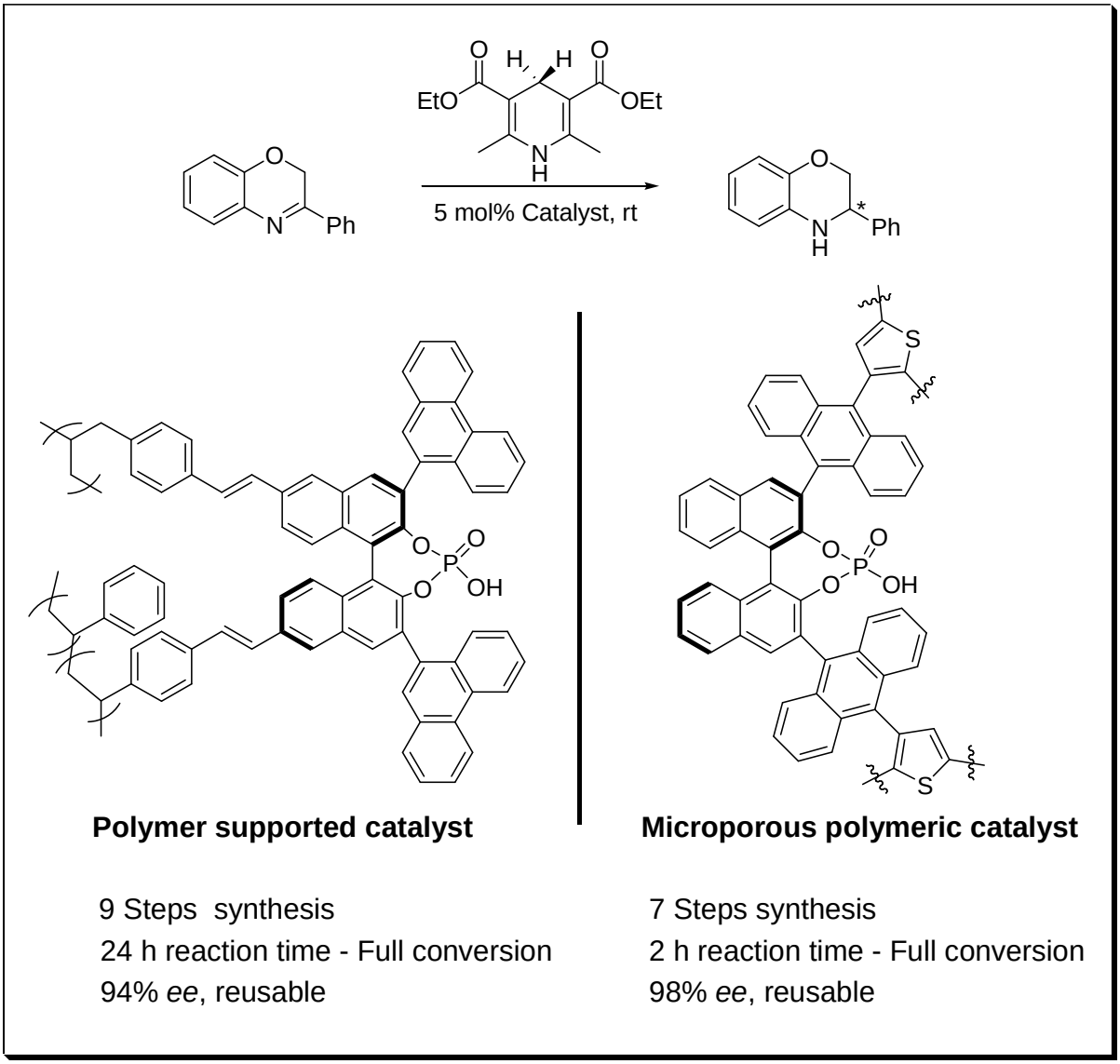


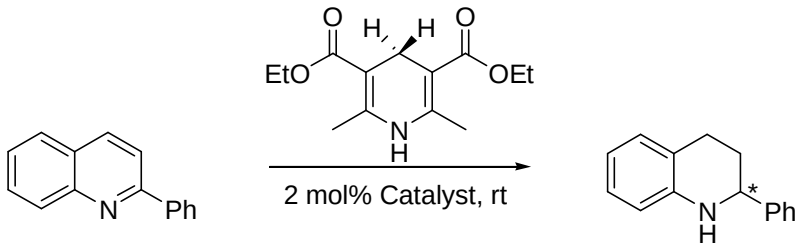
Figure 16: Comparison of our microporous polymeric phosphoric acid catalyst **52** with reported polymer supported phosphoric acid catalyst.

Rueping's polymer supported BINOL-phosphoric acid is one successful example of heterogenization of chiral phosphoric acid catalyst. It required 9 steps synthesis and resulted full conversion of benzoxazine substrate in 24 hours when 5 mol% of the catalyst was used. Compared to that, our microporous polymer **52** showed fast reaction rate in transfer hydrogenation reaction of benzoxazine. When 5 mol% of catalyst was used it resulted in full conversion within 2 hours reaction time. This is due to the fact that the porous nature allows

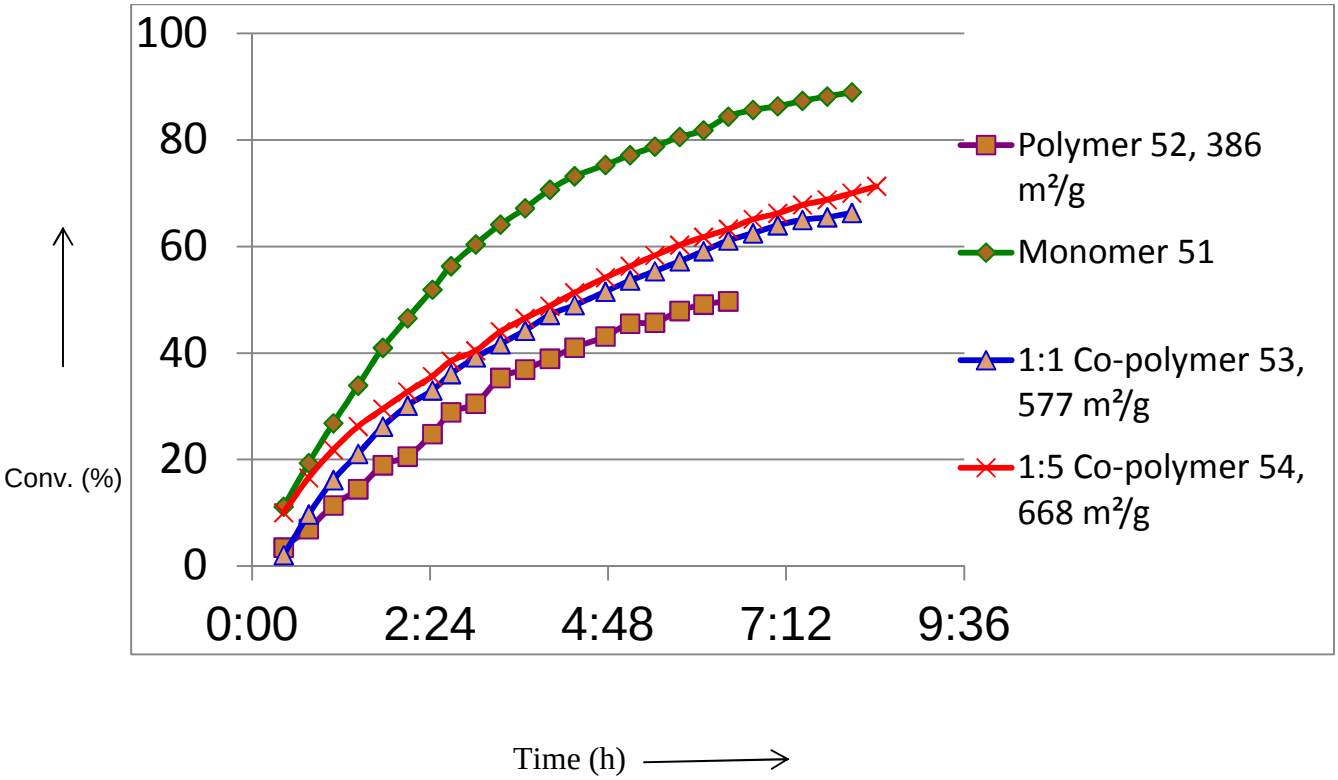
substrate and product molecules to be diffused through the catalytic center efficiently as well the microporous polymer has high catalyst density.[124] (See Figure 16).

Kinetic experiment to compare catalysis rate of homogeneous and heterogeneous catalysts:

As we found that, the rate of transfer hydrogenation for benzoxazine substrate with polymer **52** is much faster compared to the reported rate with polymer supported catalyst (see Figure 16) by *Rueping*, we desired to do kinetic experiments to exactly compare our homogeneous and heterogeneous catalysts. We chose the transfer hydrogenation of 2-phenyl quinoline substrate as standard for our study as it has slower reaction rate compared to benzoxazine substrate hence easier to monitor by NMR studies at normal condition. We also went down with our catalyst loading to 2 mol% only to make the catalytic process even slower. In order to measure exact catalyst content in co-polymer, ICP-OES experiment was performed. The ICP-OES of co-polymer **53**, prepared by adding monomer **50** and 1,3,5 -tris (2-thienyl) benzene **40** in 1:1 proportion, showed that the co-polymer contains 1.15 wt% (weight percentage) of phosphorous whereas the complete incorporation of the monomer **50** would have led to co-polymer containing 1.26 wt% of phosphorous. This shows about 90% incorporation of the monomer into co-polymer structure. This information was used for quantitative calculation of required co-polymer as catalyst. The kinetic experiment was done in NMR tube using about 30-40 μ-mol scale in $CDCl_3$ solvent at room temperature. Each time 16 scans of 400 MHz NMR machine for ^1H NMR showed the progress of the catalytic process.



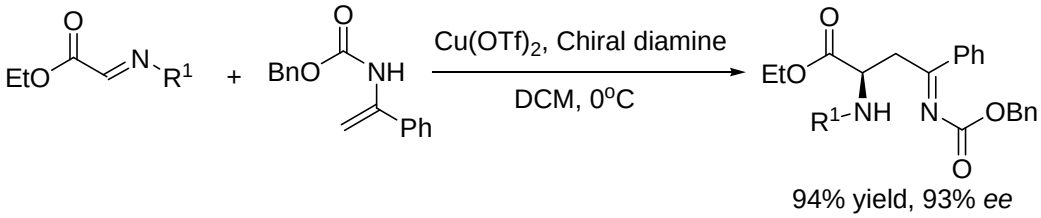
Graph 1



The plotted graph (see Graph 1) clearly shows that though the polymeric catalyst **52** is not as fast as the homogeneous catalyst **51**, the co-polymers **53** and **54** with higher surface area enhanced rate of conversion. The enantiomeric excess in each case was measured and no significant difference was found between results of polymers and co-polymers. Conclusion from this result can be drawn as higher surface area of the microporous co-polymer leads to faster catalysis hence in future synthesis of different co-polymers with even higher surface area will be of much interest.

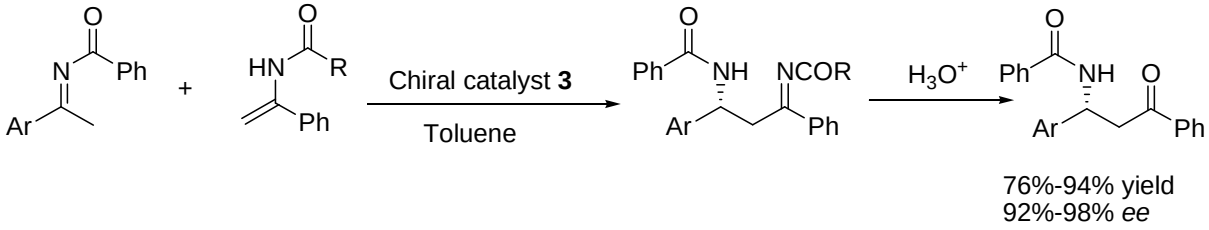
Other reactions:

In order to prove the versatility of our polymeric catalyst we focused on other reactions which are known to be catalyzed by BINOL-derived phosphoric acids efficiently. Recently Kobayashi and co-workers [125] successfully reported the first use of enamides and enecarbamates as nucleophiles in enantioselective reactions with glyoxylates or glyoxylate-derived imines catalyzed by chiral copper complexes. (See Scheme 48)



Scheme 48: Chiral Cu complex catalyzed asymmetric enamide addition to glyoxylate-derived imines

The proposed mechanism by Kobayashi group was that the reaction proceeds by an aza-ene-type pathway. This work inspired Terada and coworkers to further explore and develop a highly efficient organocatalytic reaction using a BINOL derived phosphoric acid catalyst (see Scheme 49). They showed that BINOL-derived phosphoric acid is capable of catalyzing addition of enamides or enecarbamates to N-benzoylimines with high enantioselectivity. Hydrolysis of the addition product leads to chiral β-keto amines which are structurally useful moiety in several important bioactive molecules.



Scheme 49: Organocatalytic addition of enamides to N-benzoylimines.

In this publication *Terada* and co-workers proposed that BINOL phosphoric acid acts as dual catalyst. [126] In one hand it activates electrophilically the N-benzoylimine by protonation and again on the other hand it activates the N-acyl ene through the Lewis basic phosphoryl oxygen atom via abstraction of the NH proton (see Figure 17).

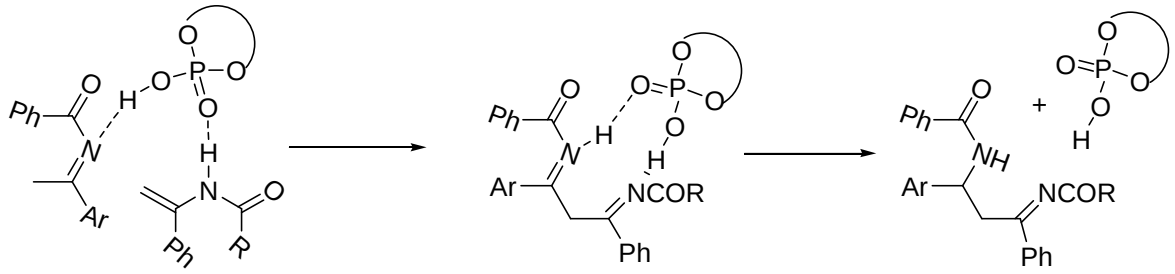
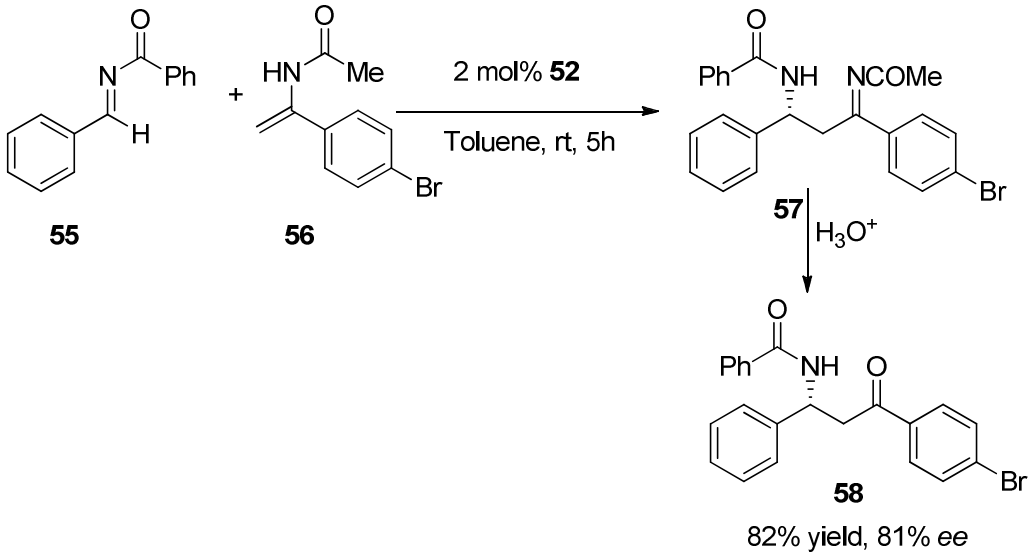


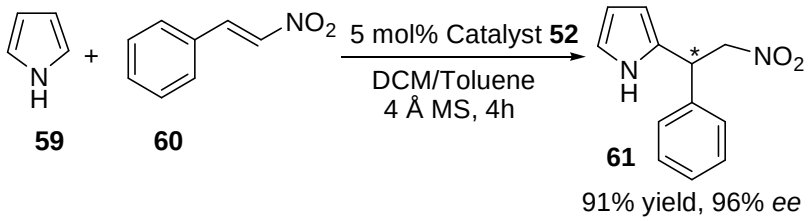
Figure 17: Dual mode of action of BINOL-derived phosphoric acid

To demonstrate the broader scope of polymer network **52**, we also made aza-ene-type reaction. Addition of enecarbamate **56** to freshly prepared N-benzoylaldimine **55** and subsequent hydrolysis afforded the β-amino ketone **58** in 82% yield and 81% *ee*. (See Scheme 50)



Scheme 50: Organocatalytic Aza-ene type reaction using polymer **52** as catalyst.

Sheng and co-workers reported an efficient Brønsted acid catalyzed asymmetric Friedel-Crafts alkylation of pyrroles. [127] Pyrroles are often present as core in many natural products and pharmaceuticals. [128, 129] We used 5 mol% of our polymeric catalyst **52** for asymmetric Friedel-Crafts alkylation of unprotected pyrrole with nitroalkene **60**. The reaction in a mixture of DCM and Toluene at room temperature afforded yield of 91% with a selectivity of 96% *ee*.



Scheme 51: Friedel-Crafts alkylation of unprotected pyrrole with nitroalkene.

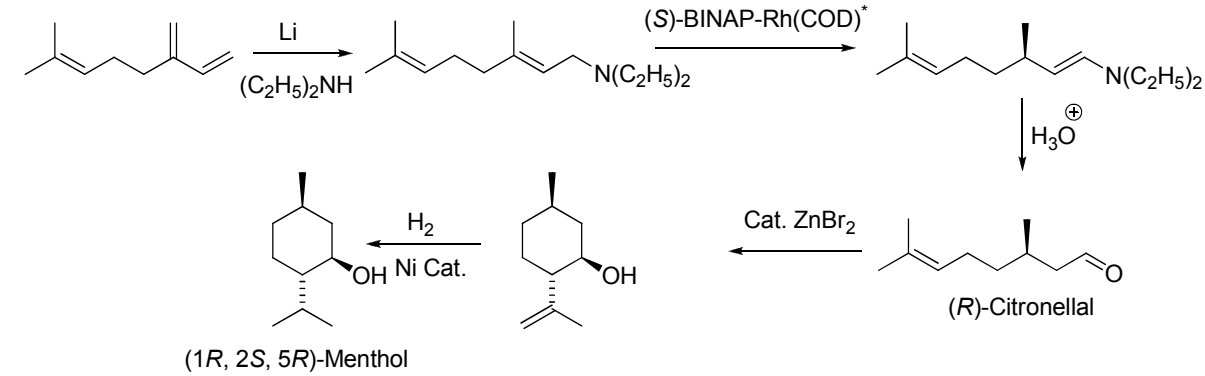
These two reactions showed that polymeric network **52** not only limited for catalytic use in asymmetric transfer hydrogenation reaction.

Heterogeneous organocatalyst comparable to TRIP catalyst:

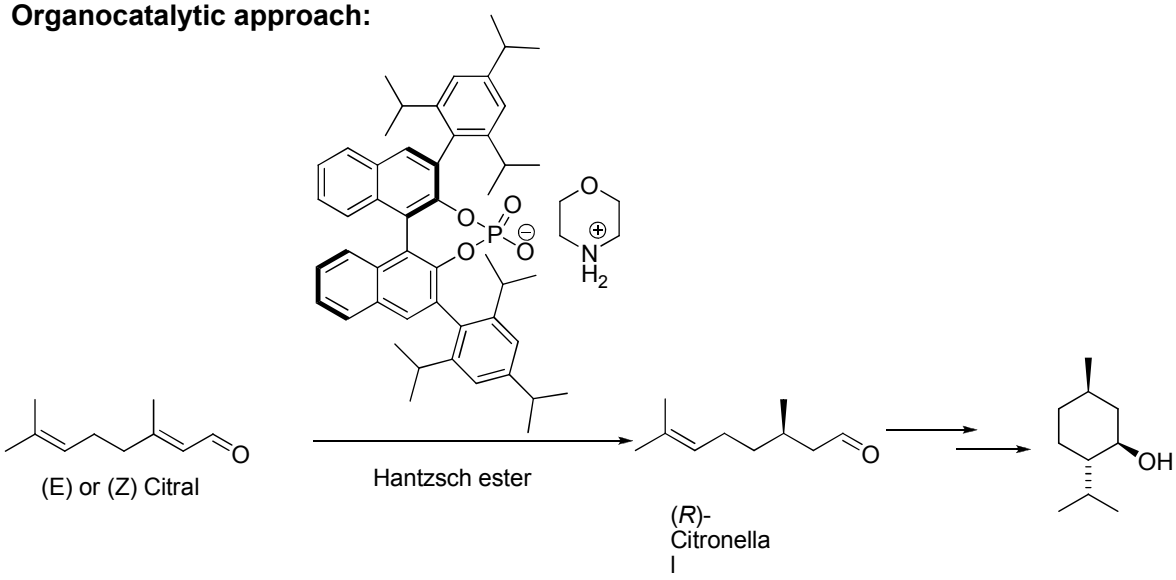
Menthol is manufactured as a single enantiomer (94% ee) 3000 tons per year by Takasago International Corporation in Japan. The process involves an asymmetric synthesis developed by *Noyori* and co-workers. [130] The process begins by forming an allylic amine from myrcene, which undergoes asymmetric isomerisation in the presence of a BINAP rhodium complex to give (after hydrolysis) enantiomerically pure (*R*)-citronellal. This is cyclized by a carbonyl-ene-reaction initiated by zinc bromide to isopulegol which is then hydrogenated to give pure (*1R, 2S, 5R*)-menthol.

In a new approach developed by List group, the key precursor for menthol synthesis (R)-citronellal can be synthesized from naturally occurring citral by asymmetric transfer hydrogenation using TRIP catalyst **1**. TRIP catalyst, which is BINOL derived phosphoric acid with 2, 4, 6 tri isopropyl benezene substituent at the 3, 3' positions, has been proved to be very successful in a wide range of organocatalytic transformations. Therefore it will be beneficial to make polymeric network out of polymerizable monomers with similar steric comparable to TRIP catalyst.

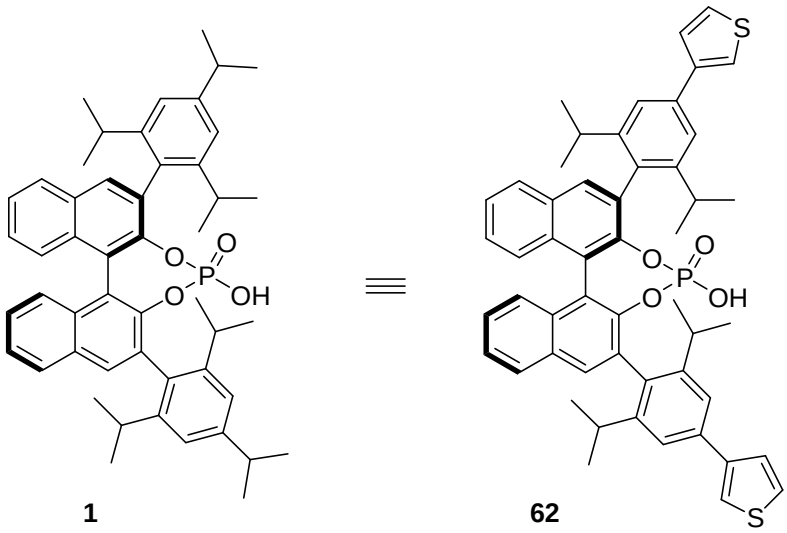
Takasago process:



Organocatalytic approach:

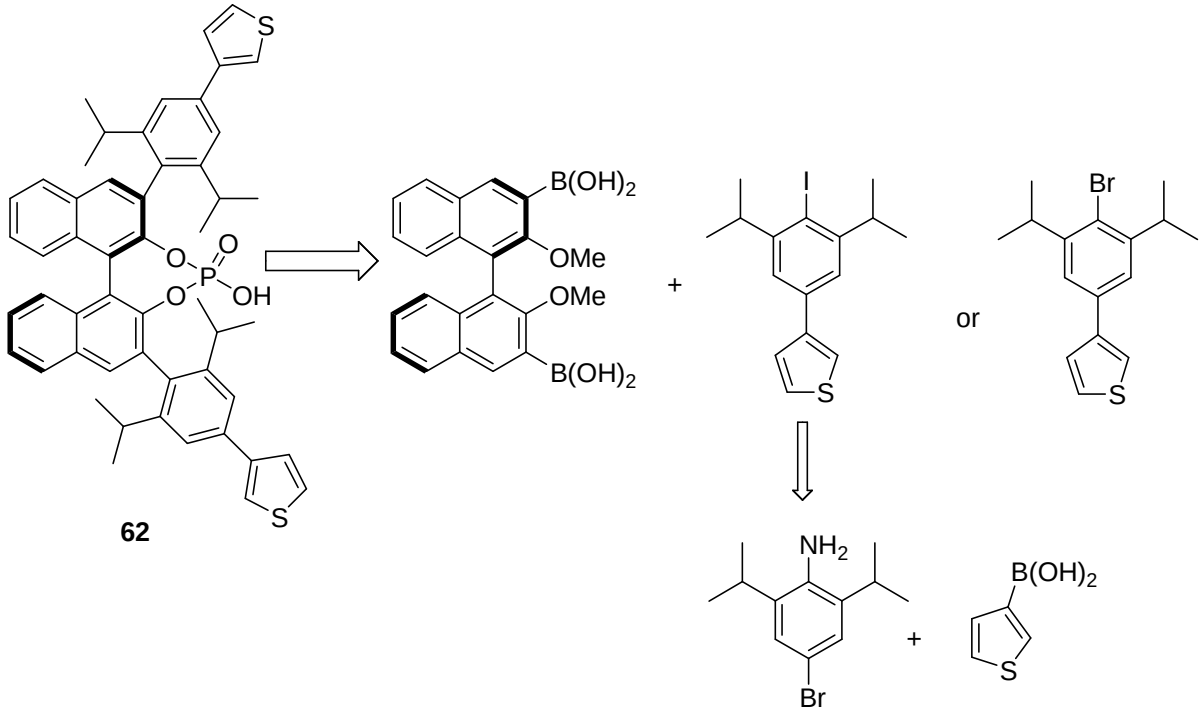


Scheme 52: Synthesis of menthol



1 **62**

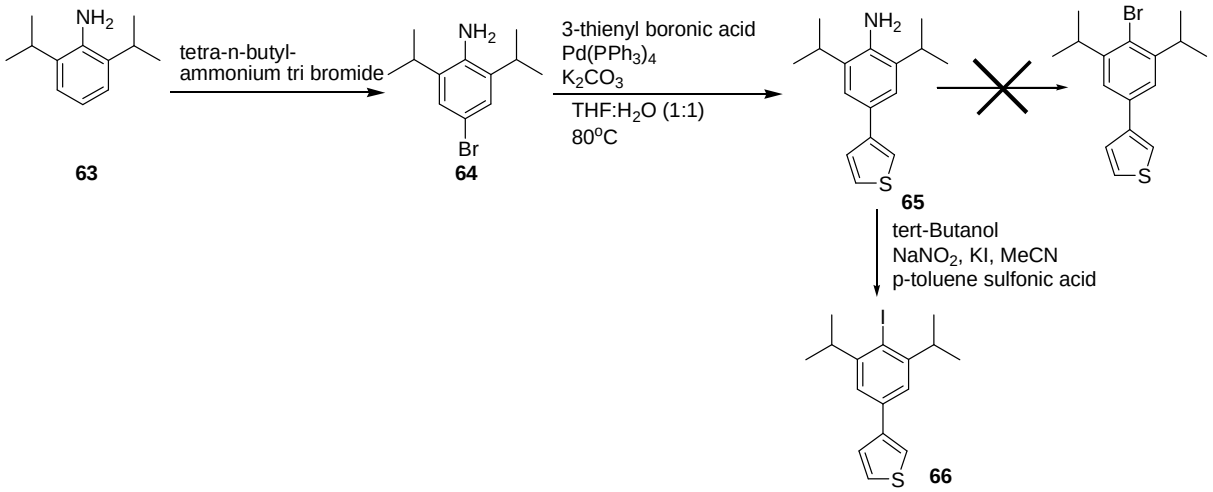
Retro synthetic analysis:



Starting from 2,6-diisopropylbenzenamine **63**, 4-bromo-2,6-diisopropylbenzenamine **64** was synthesized using tetra-n-butyl-ammonium tri bromide as brominating agent (see Scheme 53). Instead of using molecular bromine, this approach provides much safer bromination reaction and the yield was also high (99%). Suzuki coupling reaction between 4-bromo-2,6 -diisopropylbenzenamine and 3-thienyl boronic acid using 5 mol% tetrakis triphenyl phosphine palladium catalyst, potassium carbonate base in 1:1 THF:H_2O mixture and heating at 80^oC overnight resulted the desired product 2,6-diisopropyl-4-(thiophen-3-yl)benzenamine **65** in 78 % isolated yield. Next, the sandmayer diazotization followed by bromination reaction to convert 2,6-diisopropyl-4-(thiophen-3-yl)benzenamine to 3-(4-bromo-3,5-diisopropylphenyl)thiophene was tried dissolving the compound **65** into 48% HBr water solution and adding solid sodium nitrite to this mixture at a low temperature, -15^oC. But this reaction condition did not resulted in the desired product and led to decomposition of the starting material into several by products. This is due to the fact that, $Br^{\oplus}$ attacks not only diazo group but also the thiophene part leading to several byproducts. Failure of this pathway led us to try to make the 3-(4-Iodo-3,5-diisopropylphenyl)thiophene compound.

First 2,6-diisopropyl-4-(thiophen-3-yl)benzenamine was dispersed in a mixture of tert-butanol and water. The mixture was cooled to -15^oC and stirred for 30 mins. To this dispersion, first sodium nitrite solution was added. Next, 1 equivalent p-toluenesulfonic acid solution in

acetonitrile followed by 1.2 equivalent potassium iodide solution was added slowly and the mixture was brought to room temperature. Stirring at room temperature for 6 hours led to the desired product 3-(4-Iodo-3,5-diisopropylphenyl)thiophene **66** in 63% yield. Here to be mentioned, if higher equivalent of potassium iodide is used it leads to iodination of at the 2-position of the thiophene ring hence compound 2-iodo-3-(4-iodo-3,5-diisopropylphenyl)thiophene is formed .



63 **64** **65** **66**

Scheme 53: synthesis of 3-(4-Iodo-3,5-diisopropylphenyl)thiophene

In future the thiophene containing moiety **66** can be coupled to BINOL backbone.

Outlook

Continuous flow method provides opportunity for reaction and separation of catalyst simultaneously. In case of polymer supported catalysts, the mechanical degradation of the support material can lead to significantly shortened lifetime of the supported reagent. In continuous flow method, no mechanical stirring or agitation is required, hence avoiding such problem, which can lead to overall higher productivity. Proper design of continuous flow method using supported catalyst offers production of valuable organic compounds in large scale. For example, enantioselective addition of diethyl zinc to aldehyde has been performed successfully using continuous flow method by several groups (see Figure 18). [131]

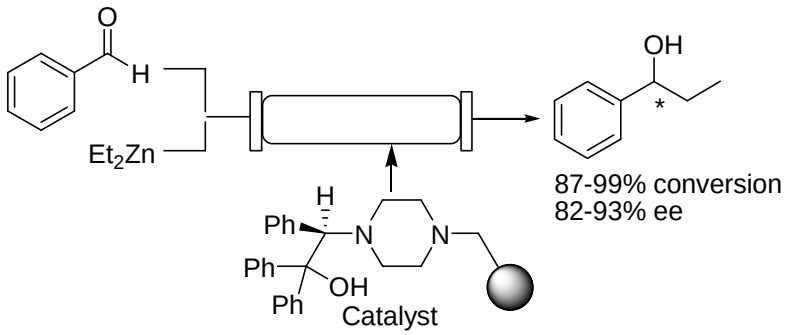


Figure 18: Continuous flow method for polymer supported organocatalysis

In future, our porous polymeric BINOL-derived phosphoric acid catalyst can be used in continuous flow method for asymmetric transformations in large scale. Our catalyst is heterogeneous as well as we did not observe any decrease in either selectivity or activity up to 10 times consecutive runs. This approach can make pathway for asymmetric chiral Brønsted acid catalysis in large scale industrial processes.

Experimental Section

Supporting information

^{1}H-NMR: ^{1}H-NMR spectra were recorded with the devices DRX 400 or DRX 500 Bruker at 400 MHz and 500 MHz. The spectra were, unless otherwise stated, recorded at room temperature. The solvents are indicated for the respective substances. The chemical shifts are reported as dimensionless δ values in ppm, given relative to internal solvent peak. In parentheses are the number of protons determined by electronic integration, the signal multiplicity and coupling constants J are in Hz. The multiplicities are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), m (multiplet), br (broad singlet).

^{13}C-NMR: ^{13}C-NMR spectra were recorded on the DRX 400 spectrometer from Bruker at 100 MHz and 125 MHz. The solvents are indicated for the respective substances. The chemical shifts are reported as dimensionless δ values in ppm. The number of directly bound protons was determined by DEPT measurements and is cited in parentheses, quaternary carbon atoms are abbreviated as C_q.

IR: IR spectra were recorded with a Nicolet Magna 750 FTIR spectrometer as ATR (Attenuated Total Reflectance) was added. The position of the bands is given in wave numbers (cm-1). The intensities are relative to the strongest peak (100%) identified as follows: vs (very strong, 75-100%), s (strong, 50-75%), m (medium, 25-50%), w (weak, <25%), br (broad). The measurements were carried out by employees of the TU Berlin.

Elemental analyzes were performed with a Vario EL elemental analysis of the company Jena. The measurements were carried out by employees of the TU Berlin.
Mass spectra (EI-MS) and high resolution mass spectra (HRMS) were recorded on the spectrometers Finnigan MAT 95 SQ or Varian MAT 711th. Ionization of the samples was performed by electron impact (EI) at 70 ° C and an ionization potential of 70 eV. The relative signal intensities are in percent based on the most intense signal (100%).
The measurements were carried out by employees of the TU Berlin.

ESI-MS: ESI-MS spectra were recorded on a LTQ XL FTMS from Thermo Scientific. The ionization was performed at 5 kV through electron spray ionization. The samples were dissolved in MeCN. For measurements on the auto sampler were following conditions:

MeOH + 0.1% HCOOH, flow rate 200 µL / min. The measurements were carried out by employees of the TU Berlin.

GC/MS: GC / MS measurements were performed with a HP6980 Series GC system of the type system from Hewlett Packard. Served as an HP5973 Mass Selective detector is a detector. As a column, a Supelco 28482-U was used 30mx0.32mm with helium as carrier gas.

HPLC: HPLC analyzes were performed on a system of type *Agilent Technologies* 1200 Series (UV / Vis detector G1315D DAD, *Varian Prostar* chiral HPLC (Chiracel IB column 4.6 mm ø x 250 mm) auto sampler G1329A ALS, G1312A Bin Pump, Agilent 6130 Quadrupole mass spectrometer LC / MS) performed. As the columns were a Chiracel OD-H (0.46 cm diameter, 25 cm), a Chiralcel OJ (0.46 cm diameter, 25 cm) and a Waters Symmetry C18 (0.39 cm diameter, 15 cm). HPLC grade eluents were purchased from Fisher Scientific. Enantiomeric excesses were determined by comparison with the corresponding racemic samples.)

Glove box: Inert reactions were carried out either using Schlenk techniques or in a glove box MB 120 BG company MBraun under nitrogen atmosphere.

Solvents were distilled prior to use and optionally dried. As a desiccant for diethyl ether, tetrahydrofuran and toluene was sodium. Dichloromethane was dried over CaH_2 or Sicapent ®. DMF and pyridine were stored over CaH_2 and then distilled over 4 Å molecular sieves. All other commercially available materials were used without further purification.

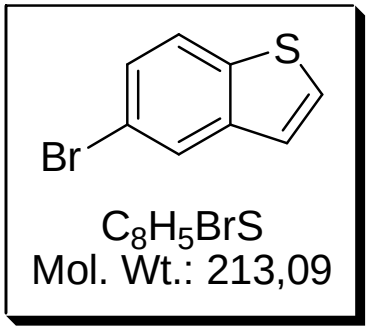
Microwave: Microwave reactions were performed with a device of the type performed Discover the CEM.

TLC: Thin-layer chromatograms were made on aluminum foils with fluorescent indicator 254 of the Merck (silica gel, Merck 60 F254 plates, layer thickness 0.2 mm) or created from Macherey-Nagel (silica gel 60 with fluorescent indicator UV254, layer thickness 0.2 mm). For the evaluation was carried out after UV detection (λ = 254 nm) a treatment with the Seebach reagent (sulphate 1.00 g of cerium (IV) and 2.50 g of phosphomolybdic acid in 4 mL of concentrated sulfuric acid and 96 mL H_2O).

Column chromatography: Column chromatography was performed with Merck silica gel (particle size 0:03 to 0:06 mm).

Chemical name for all the synthesized products were created using “Chem Draw Ultra” Version.10.0.

5-bromobenzothiophene(34):



Under nitrogen atmosphere a round bottom flask was charged with (4-bromophenyl)(2,2-diethoxyethyl)sulfane (6.1g, 20mol%), Chlorobenezene solvent and poly phosphoric acid. The mixture was refluxed at 130°C for 12 hours. After that, the mixture was cooled to room temperature, washed 4 times with excess saturated sodium bi carbonate. After evaportation of chlorobenezene solvent the the crude product was purified by column chromatography (SiO_2, cyclo-hexane) to give compound 5-bromobenzothiophene as color less amorphous solid (4.05g 95% yield).

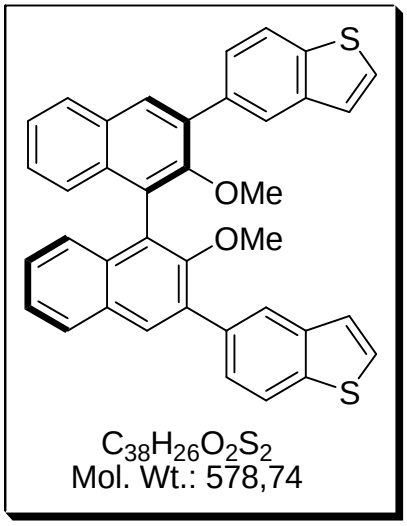
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.97(1H, d, J= 1.92), 7.73 (1H, d, J=8.56), 7.47(1H, d, J=5.52), 7.44 (1H, dd, J1= 8.6, J2= 1.88), 7.27(1H, d, J=5.44)

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 141.26 (1C, C_q), 138.38 (1C, C_q), 128.19, (1C, CH), 127.3 (1C, CH), 126.28 (1C, CH), 123.8 (1C, CH), 123.15 (1C, CH), 118.28 (1C, C_q).

IR: 3103 (w), 3078(w), 2952(w), 2924(m), 2851(w), 1876 (w), 1772(w), 1733(w), 1635 (w), 1623 (w), 1581 (m), 1576 (m), 1546 (m), 1489(m), 1470 (s), 1430 (s), 1415 (m), 1402 (vs), 1386 (m), 1338 (w), 1312 (w), 1308 (w), 1273 (w), 1223 (w), 1250 (m), 1191 (s), 1176 (w), 1150 (s), 1094 (m), 1086 (m), 1077 (m), 1063 (vs), 1055 (s), 1048 (m), 1006 (s), 940 (w), 884 (s), 865 (m), 812 (vs), 797 (vs), 749 (vs), 690 (vs).

ESI Mass: 211.9290

5-(1-(2-(benzothiophen-5-yl)-3-methoxynaphthalen-4-yl)-2-methoxynaphthalen-3 yl)benzothiophene (35)



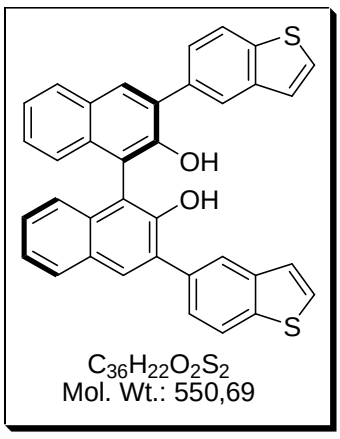
Under nitrogen atmosphere, a two neck round bottom flask was charged with 5-bromobenzothiophene (2.62 g, 7.8 mmol, 2.5 eq.), thienyl-3-boronic acid (2 g, 15.6 mmol, 1 eq.) tetrakis(tri-phenylphophine)palladium (496 mg, 429 µmol, 5.5 mol%) and potassium carbonate (3.2 g, 23.4 mol, 3 eq.). The flask was protected against light. Degassed water (75 ml), degassed THF (75 ml) were added via syringe. The mixture was heated at 80 °C for 24 h and then diluted with CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclo-hexane) to give compound as a light brown solid (3.6 g, 6.24 mmol, 80%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.24 (2H, J= 1.36), 8.05 (2H, s), 7.97 (2H, d, J= 8.4), 7.94 (2H, d, J= 8.2), 7.78 (2H, dd, J1= 6.9, J2= 1.6), 7.49 (2H, d, J= 5.4), 7.43-7.4 (4H), 7.29-7.27 (4H), 3.19 (6H, s).

IR: 3621(w), 3100 (w), 3057(w), 2969 (m), 2934 (m), 2899(w), 2855(w), 2833(w), 1952(w), 1928(w), 1900(w), 1702 (m), 1621(w), 1591(w), 1543(w), 1492 (m), 1456 (s), 1435(m), 1407 (s), 1395 (s), 1354 (s), 1332(m), 1395 (vs), 1291 (w), 1267(m), 1248 (vs), 1217 (m), 1207 (m), 1178 (m), 1165 (m), 1148 (s), 1127 (s), 1079 (w), 1088 (m), 1054 (m), 1049 (m), 1038 (vs), 1018 (vs), 933 (m), 954 (w), 920 (w), 891 (s), 855 (s), 815 (s), 803 (m), 789 (w), 772 (w), 752 (vs), 741 (m), 701 (vs), 679 (w), 661(w).

ESI-MS: APCI 579.1446 ($C_{38}H_{26}O_2S_2$+H).

3-(benzothiophen-5-yl)-1-(2-(benzothiophen-5-yl)-3-hydroxynaphthalen-4-yl)naphthalen-2-ol (36):



In a flame dried Schlenk tube was charged with compound **5**-(1-(2-(benzothiophen-5-yl)-3-methoxynaphthalen-4-yl)-2-methoxynaphthalen-3 yl)benzothiophene **35** (3.47 g, 6 mmol)

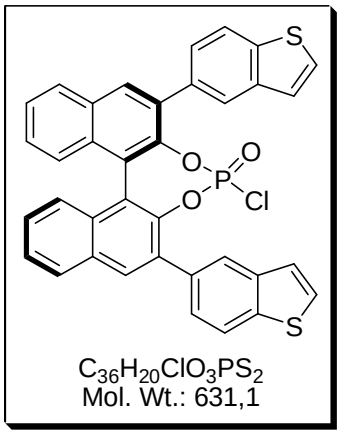
under nitrogen atmosphere and dry CH_2Cl_2 was added. The mixture was cooled at 0 °C and boron tri bromide (1 M solution in DCM, 18 ml, 18 mmol, 3 eq.) was added. The mixture was stirred at 0 °C for 2 h. Then the mixture was stirred at room temperature overnight. Next morning, water was added slowly drop by drop at 0 °C. After separation, the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layer was washed with water and dried over dry sodium sulfate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclohexane / ethyl acetate = 97:3) to give the compound 3-(benzothiophen-5-yl)-1-(2-(benzothiophen-5-yl)-3-hydroxynaphthalen-4-yl)naphthalen-2-ol **36** as a light yellow solid (3.13 g, 5.7 mmol, 95%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.19 (2H, d, J= 1.5), 8.09 (2H, s), 7.99 (2H, d, J= 8.4), 7.94 (2H, d, J= 7.8), 7.72 (2H, dd, J1= 7, J2= 1.68), 7.5 (2H, d, J=5.4), 7.41-7.4 (4H), 7.34 (2H, dt, J1= 5.6, J2= 1.4), 7.29-7.24 (2H), 5.41 (2H, s).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 150.28 (2C, C_q), 139.99 (2C, C_q), 139.28 (2C, C_q), 133.68 (2C, C_q), 133.03 (2C, C_q), 131.64 (2C, CH), 130.77 (2C, C_q), 129.56 (2C, C_q), 128.49 (2C, CH), 127.39 (2C, CH), 127.1 (2C, CH), 126.02 (2C, CH), 124.6 (2C, CH), 124.42 (4C, CH), 124.11 (2C, CH), 122.49 (2C, CH), 112.63 (2C, C_q).

IR: 3506 (s), 3368 (m), 3102 (m), 3058 (m), 2970 (m), 2926 (m), 2853 (w), 1949 (w), 1921 (w), 1897 (w), 1770 (w), 1700 (vs), 1672 (m), 1620 (m), 1594 (m), 1543 (w), 1497 (m), 1452 (s), 1443 (s), 1429 (vs), 1401 (vs), 1380 (vs), 1361 (vs), 1326 (s), 1302 (m), 1259 (vs), 1238 (vs), 1216 (s), 1201 (vs), 1180 (vs), 1166 (vs), 1146 (vs), 1123 (vs), 1089 (s), 1068 (s), 1053 (s), 1026 (m), 1012 (m), 984 (m), 951 (m), 937 (m), 893 (s), 855 (w), 815 (s), 802 (s), 791 (m), 781 (m), 752 (vs), 722 (s), 701 (vs), 659 (w).

ESI MS: 511.1132 ($C_{36}H_{22}O_2S_2$ +H)



$C_{36}H_{20}ClO_3PS_2$
Mol. Wt.: 631,1

(R)-3,3'-(benzothiophen-5-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid chloride (37):

In a flame dried Schlenk tube was charged with poly (4-vinylpyridine) (1.25 g, excess). Dry CH_2Cl_2 was added under nitrogen atmosphere. The mixture was cooled to 0 °C, compound 3-(benzothiophen-5-yl)-1-(2-(benzothiophen-5-yl)-3-hydroxynaphthalen-4-yl)naphthalen-2-ol **36** (247.8 mg, 0.45 mmol) was dissolved in dry CH_2Cl_2 and added into the Schlenk via syringe. Next, $POCl_3$ was added

slowly into the Schlenk via syringe. The mixture was stirred at room temperature overnight. The mixture was filtered through glass crucible to remove poly(4-vinylpyridine). Evaporation of the solvent gave a light yellow solid compound (284 mg, 0.45 mmol, quant.) and used for next step without further purification.

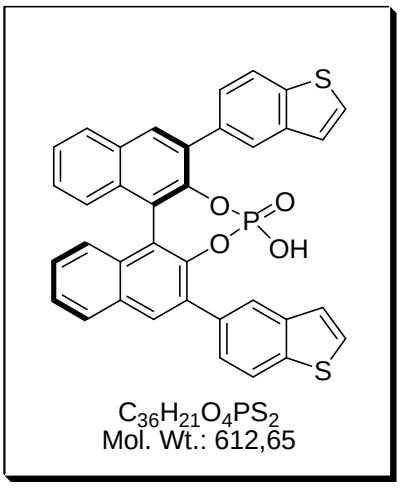
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.19 (2H, s), 8.14(2H, d, J=4), 8.03(2H, t, J= 7.16), 7.99(1H, d, J= 4.8), 7.97(1H, d, J= 4.8), 7.72(1H, dd, J1= 8.48, J2= 1.72), 7.67 (1H, dd, J^1= 8.48, J^2= 1.72), 7.57 (2H, t, J= 6.76), 7.51(1H, d, J=5.39), 7.48(1H, d, J=5.48), 7.44(1H), 7.42-7.37 (5H)

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 144.24 (1C, C_q), 144.18(1C, C_q), 144.05(1C, C_q), 143.89(1C, C_q), 139.85 (1C, C_q), 139.83 (1C, C_q), 139.59 (1C, C_q), 139.55 (1C, C_q), 134.03 (1C, CH), 133.57 (1C, CH), 132.58 (1C, CH), 132.45 (2C, CH), 132.2 (1C, CH), 132.04 (1C, CH), 131.97 (1C, CH), 131.86 (1C, CH), 128.63 (1C, CH), 128.57 (1C, CH), 127.2 (1C, CH), 127.17 (1C, CH), 127.07 (2C, CH), 127.02 (1C, CH), 126.95 (1C, CH), 126.72 (3C, CH), 126.08 (2C, CH), 124.96 (2C, CH), 124.27 (1C, CH), 124.19 (1C, CH), 122.63 (1C, CH), 122.41 (1C, CH).

IR: 3100 (w), 3070 (w), 2960 (m), 2925 (m), 2854 (m), 1726 (m), 1648 (m), 1596 (m), 1568 (w), 1545 (w), 1497 (m), 1451(m), 1436 (m), 1413 (m), 1399 (m), 1375 (m), 1362 (m), 1310 (vs), 1262 (s), 1242 (s), 1200 (vs), 1180 (s), 1149 (vs), 1131 (vs), 1125 (vs), 1089 (vs), 1077 (vs), 1051 (vs), 1007 (vs), 982 (vs), 966 (vs), 928 (vs), 913 (s), 899 (vs), 864 (s), 838 (s), 821 (vs), 812 (vs), 803 (vs), 775 (s), 753 (vs), 729 (s), 704 (vs), 665 (s).

(R)-3,3'-(benzothiophen-5-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid (38):

A flame dried Schlenk tube was charged with (R)-3,3'-(benzothiophen-5-yl)-BINOL-phosphoric acid chloride **37** (189.3 mg, 0.3 mmol) and dissolved into THF/HCl-solution. The mixture was stirred overnight. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. Evaporation of the solvent gave a white solid. (R)-3,3'-(benzothiophen-5-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid **38** was obtained as crude product (183.7 mg, 0.3 mmol, quant.).



$C_{36}H_{21}O_4PS_2$
Mol. Wt.: 612,65

^{1}H-NMR (400 MHz, DMSO): δ [ppm] = 8.37 (2H, s), 8.2 (2H, s), 8.1 (2H, d, J= 8.12), 8.04 (2H, d, J=8.4), 7.94 (2H, d, J= 8.4), 7.78 (2H, d, J= 5.4), 7.51-7.47 (4H), 7.33 (2H, t, J= 7.72), 7.16 (2H, d, J= 8.56).

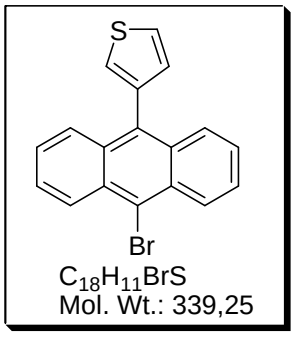
^{13}C-NMR (100 MHz, DMSO): δ [ppm] = 146.6 (2C, C_q), 146.52 (2C, C_q), 144.21 (1C, C_q), 144.07 (1C, C_q), 144.0 (1C, C_q), 143.94 (1C, C_q), 139.58 (1C, CH), 138.29 (1C, CH), 134.19 (1C, CH), 133.95 (1C, CH), 131.67 (1C, CH), 130.9 (2C, CH), 130.58 (1C, CH), 128.63 (2C, CH), 127.79 (1C, CH), 126.66 (2C, CH), 126.52 (2C, CH), 126.1 (4C, CH), 125.34 (2C, CH), 125.09 (2C, CH), 124.33 (2C, CH), 122.64 (1C, CH), 122.05 (2C, CH).

IR: 3508 (s), 3325 (m), 3102 (w), 3058 (m), 2972 (m), 2929 (w), 2894 (w), 2853 (w), 1948 (w), 1922 (w), 1899 (w), 1800 (w), 1701 (s), 1620 (m), 1594 (m), 1577 (w), 1543 (w), 1497 (s), 1443 (s), 1429 (s), 1414 (s), 1401 (vs), 1381 (vs), 1361 (vs), 1325 (s), 1301 (m), 1258 (s), 1237 (s), 1201 (vs), 1180 (vs), 1166 (vs), 1146 (vs), 1122 (vs), 1089 (s), 1068 (m), 1053 (s), 1026 (m), 1012 (m), 984 (m), 951 (m), 940 (w), 893 (s), 854 (w), 830 (m), 815 (s), 802 (s), 791 (m), 780 (m), 752 (vs), 722 (s), 701 (vs).

ESI -MS: Anionic measurement, 611.0546 (C_{36} H_{20} O_4 PS2)

3-(10-bromoanthracen-9-yl)-thiophene (46):

Under nitrogen atmosphere a two neck round bottom flask was charged with 9,10-dibromo-antracene (2.62 g, 7.8 mmol), thienyl-3-boronic acid (2 g, 15.6 mmol, 2 eq.) tetrakis(tri-phenylphophine)palladium (496 mg, 429 µmol, 5.5 mol%) and potassium carbonate (3.2 g, 23.4 mol, 3 eq.). The flask was protected against light. Degassed water (75 ml), degassed THF (75 ml) were added via syringe. The mixture was heated at 80 °C for 24 h and then diluted with CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclo-hexane) to give compound 3-(10-bromoanthracen-9-yl)-thiophene as a yellow solid (2.12 g, 6.24 mmol, 85%).

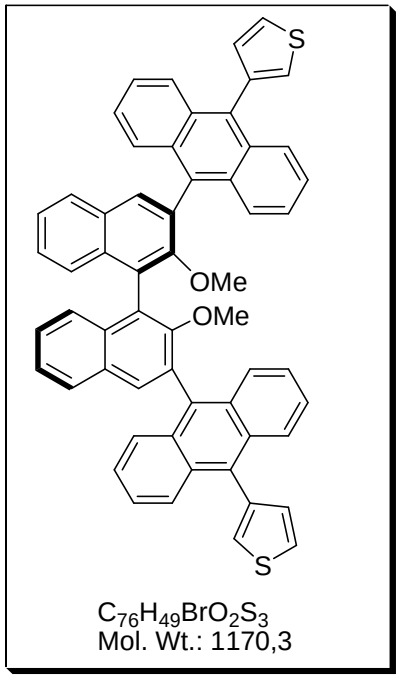


^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.60 (2H, d, *J* = 8.9 Hz), 7.77 (2H, d, *J* = 8.8 Hz), 7.62-7.57 (3H, m), 7.43-7.37 (3H, m), 7.20 (1H, dd, *J* = 6.0 Hz, *J* = 1.2 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 138.05, 132.78, 131.58, 130.75, 130.24, 127.88, 127.22, 127.02, 125.72, 125.34, 123.07.

(R)-3,3'-(10,10'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(anthracene-10,9-diyl))-dithiophene (48)

Under nitrogen atmosphere a two neck round bottom flask was charged with *R*-2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyldiboronic acid (804.04 mg, 2 mmol), 3-(10-bromoanthracen-9-yl)thiophene (2 g, 6 mmol, 3 eq.) tetrakis-(triphenylphophine)-palladium (231.1 mg, 200 µmol, 10 mol%) and potassium carbonate (829 mg, 6 mol, 3 eq.). The flask was protected against light. Degassed water (50 ml), degassed THF (50 ml) were added via syringe. The mixture was heated at 80 °C for 24 h and then diluted with CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulphate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclohexane) to give the desired product **48** as a light yellow solid (1.99 g, 1.7 mmol, 85%).



$C_{76}H_{49}BrO_2S_3$
Mol. Wt.: 1170,3

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm = 8.03 (2H, s), 7.98-7.94 (4H, m), 7.87 (2H, d, *J* = 9.3 Hz), 7.82 (4H, d, *J* = 9.1 Hz), 7.66-7.61 (4H, m), 7.53-7.49 (4H, m), 7.47-7.45 (4H, m), 7.44-7.42 (2H, m), 7.32-7.28 (4H, m), 7.22-7.18 (2H, m), 3.07 (6H, s).

^{13}C-NMR(100 MHz, $CDCl_3$): δ [ppm] = 155.73 (2C, C_q), 138.73(2C, C_q), 134.36(2C, C_q), 133.90(2C, C_q), 132.96(2C, CH), 132.53(2C, C_q), 132.42(2C, C_q), 131.03(2C, CH), 130.75(2C, C_q), 130.59(4C, C_q), 130.38(2C, C_q), 130.26(2C, C_q), 128.21(2C, CH), 127.02(4C, CH), 126.91(4C, CH), 126.79(2C, CH), 126.00(2C, CH), 125.55(2C, C_q), 125.53(2C, CH), 125.48(2C, CH), 125.26(4C, CH), 125.22(2C, CH), 125.20(4C, CH), 61.16(2C, CH_3).

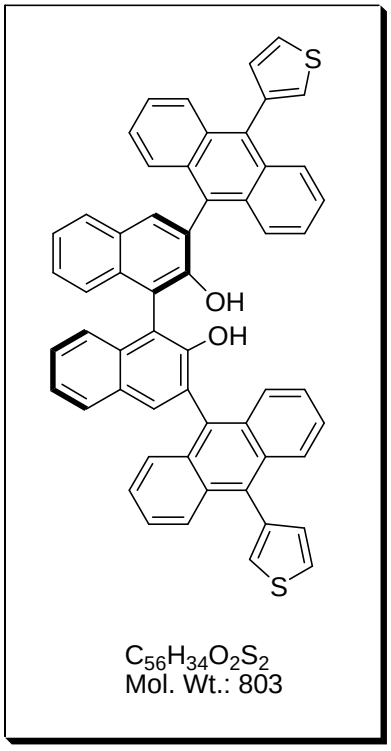
IR: 3549 (w), 3101 (w), 3062 (w), 3941 (w), 2963 (m), 2932 (m), 2870 (w), 2852 (w), 1951 (w), 1928 (w), 1805 (w), 1753 (w), 1704 (w), 1667 (w), 1621 (w), 1593 (w), 1519 (w), 1493

(m), 1485 (w), 1457 (s), 1440 (m), 1422 (m), 1401 (m), 1353 (m), 1321 (m), 1307 (m), 1260 (s), 1232 (s), 1175 (m), 1149 (m), 1094 (vs), 1041 (s), 1027 (s), 1014 (vs), 955 (w), 930 (w), 900 (w), 866 (w), 847 (s), 795 (vs), 767 (vs), 756 (vs), 720 (w), 693 (m), 674 (m).

HR-MS (ESI): $[C_{58}H_{38}O_2S_2]^+$: 830.23127

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthyl-2,2'-diol (49)

In a flame dried Schlenk tube was charged with compound **48** (1.25 g, 1.5 mmol) under nitrogen atmosphere and dry CH_2Cl_2 was added. The mixture was cooled at 0 °C and boron tri bromide (4.45 ml, 4.5 mmol, 3 eq.) was added. The mixture was stirred at 0 °C for 2 h. Then the mixture was stirred at room temperature overnight. Water was added slowly drop by drop at 0 °C. After separation, the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over dry sodium sulfate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclohexane / ethyl acetate = 97:3) to give the compound as a light yellow solid (939.5 mg, 1.17 mmol, 93%).



$C_{56}H_{34}O_2S_2$
Mol. Wt.: 803

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.07 (2H, s), 7.96 (2H, dd, *J* = 7.4 Hz, *J* = 2.0 Hz), 7.91 (2H, dd, *J* = 9.0 Hz, *J* = 1.24 Hz), 7.88 (2H, d, *J* = 7.9 Hz), 7.83 (2H, d, *J* = 8.8 Hz), 7.71 (2H, d, *J* = 8.7 Hz), 7.64-7.61 (4H, m), 7.54-7.40 (10H, m), 7.35-7.23 (6H, m), 5.19 (2H, s).

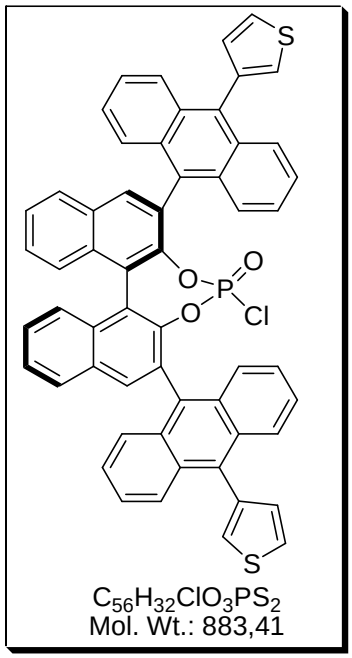
^{13}C-NMR(100 MHz, $CDCl_3$): δ [ppm] = 151.10(2C, C_q), 138.53(2C, C_q), 133.97(2C, C_q), 133.37(2C, C_q), 133.25(2C, CH), 131.13(2C, C_q), 130.89(2C, CH), 130.73(2C, C_q), 130.68(2C, C_q), 130.54(2C, C_q), 130.49(2C, C_q), 129.39(2C, C_q), 128.55(2C, CH), 127.50(2C, CH), 127.44(2C, C_q), 127.23(2C, CH), 127.13(2C, CH), 126.31(2C, CH), 126.23(2C, CH), 126.00(2C, CH), 125.97(2C, CH), 125.58(2C, CH), 125.45(4C, CH), 125.31(2C, CH), 124.97(2C, CH), 124.38(2C, CH), 113.47(2C, C_q).

IR: 3533 (m), 3365 (w), 3101(w), 3062 (s), 2971(w), 2929 (w), 2872(w), 2852 (w), 1948 (w), 1928 (w), 1820 (w), 1806 (w), 1702 (m), 1674 (w), 1621 (m), 1598 (w), 1518 (w), 1495 (m), 1455 (m), 1439 (s), 1423 (w), 1400 (w), 1378 (m), 1358 (m), 1352 (m), 1330 (m), 1284 (w), 1260 (m), 1247 (m), 1229 (m), 1208 (s), 1174 (m), 1147 (m), 1133(m), 1101 (w), 1093 (w), 1080 (w), 1026 (m), 1011 (w), 976 (w), 951 (w), 938 (w), 930 (w), 904 (w), 873 (w), 848 (s), 819 (w), 811 (w), 785 (m), 768 (vs), 751 (s), 727 (w), 701 (w), 689 (w), 677 (m).

HR-MS (ESI): $[C_{56}H_{33}O_2S_2]^-$: 801.1932

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid chloride (50)

In a flame dried Schlenk tube was charged with poly(4-vinylpyridine) (1.25 g, excess). Dry CH_2Cl_2 was added under nitrogen atmosphere. The mixture was cooled to 0 °C, compound **49** (286 mg, 0.45 mmol) was dissolved in dry CH_2Cl_2 and added into the Schlenk via syringe. Next $POCl_3$ was added slowly into the Schlenk via syringe. The mixture was stirred at room temperature overnight. The mixture was filtered through glass crucible to remove poly(4-vinylpyridine). Evaporation of the solvent gave a light yellow solid compound (397.5 mg, 0.45 mmol, quant.) and used for next step without further purification.



^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.24 (1H, s), 8.13 (1H, s), 8.09 (1H, d, *J* = 7.9 Hz), 8.03 (1H, d, *J* = 8.2 Hz), 7.91 (1H, d, *J* = 8.4 Hz), 7.86-7.68 (10H, m), 7.65-7.56 (5H, m), 7.51 (1H, d, *J* = 7.6 Hz), 7.41 (1H, s, br), 7.35-7.24 (10H, m).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 146.2 (1C, Cq), 146.07 (1C, Cq), 145.96 (1C, Cq), 145.85 (1C, Cq), 138.81 (1C, Cq), 138.56, (2C, Cq), 138.43 (2C, Cq), 135.14 (2C, CH), 133.78 (1C, Cq), 133.46 (1C, Cq), 132.69 (1C, Cq), 132.64 (1C, Cq), 132.08 (1C, Cq), 131.79 (1C, Cq), 131.12 (2C, CH), 130.94 (1C, CH), 130.7 (1C, Cq), 130.59 (1C, Cq), 130.39 (2C, Cq), 130.2 (1C, Cq), 130.16 (1C, Cq), 129.94 (1C, Cq), 128.75 (2C, CH), 127.77 (1C, CH),

127.62 (1C, CH), 127.56 (2C, CH), 127.36 (1C, CH), 127.26 (1C, CH), 127.23 (2C, CH), 127.11 (1C, CH), 126.89 (2C, CH), 126.65 (1C, CH), 126.31 (1C, CH), 126.1 (1C, CH), 125.89 (1C, CH), 125.75 (1C, CH), 125.45 (2C, CH), 125.35 (3C, CH), 125.23 (1C, CH), 125.14 (1C, CH), 125.03 (1C, CH), 124.96 (1C, CH), 122.65 (2C, Cq).

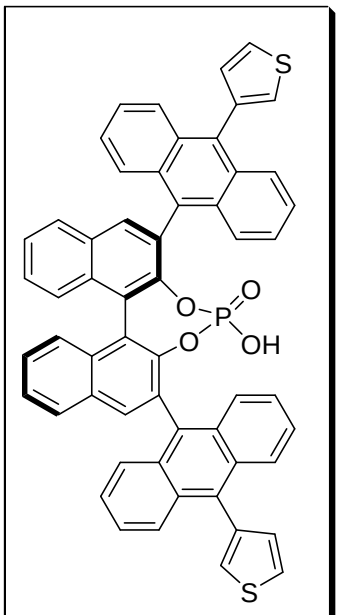
HR-MS (ESI): $[C_{56}H_{32}ClO_3PS_2Na]^+$: 905.11141

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid polymer network (52)

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid chloride **50** (1.13 g, 1.25 mmol, 1 eq.) was dissolved in 500 mL dry toluene and heated to 60 °C. Under vigorous stirring $FeCl_3$ (1.63 g, 10 mmol, 8 eq.), dissolved in 100 mL dry acetonitrile, was added to the solution. The reaction mixture was stirred for 4 h at 60 °C and quenched with ethanol. The resulting polymer network was separated by centrifugation (4000 rpm), washed several times with ethanol, a mixture (1:1) of aqueous HCl (c = 2 mol/L) and THF, and $CHCl_2$ to remove residues of the monomer and reactants. The product was dried in high vacuum for 24 h. (Yield 860 mg, 80%)

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid (51)

A Schlenk tube was charged with Compound **50** (397.5 mg, 0.45 mmol) and dissolved into THF/HCl-solution. The mixture was stirred overnight. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. Evaporation of the solvent gave a brown solid. Compound **51** was obtained as brown product (388.9 mg, 0.45 mmol, quant.).



$C_{56}H_{33}O_4PS_2$
Mol. Wt.: 864,96

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.00-7.98 (3H), 7.96 (2H, d, *J* = 7.8 Hz), 7.82-7.77 (4H, m), 7.71 (2H, d, *J* = 5.6 Hz), 7.64 (2H, s, br), 7.57-7.54 (3H, m), 7.51-7.47 (4H, m), 7.35 (1H, s), 7.29-7.27 (3H, m), 7.20-6.96 (9H, m).

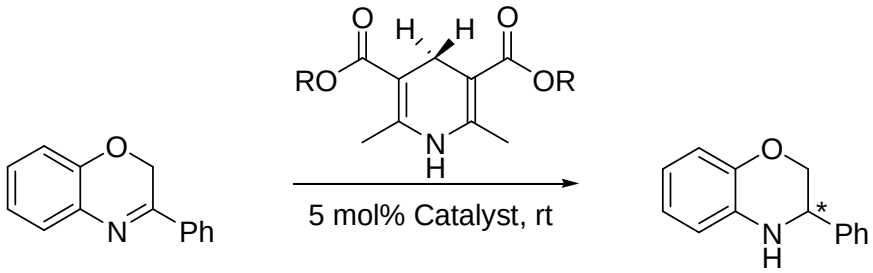
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 148.45 (2C, C_q), 143.89 (4C, C_q), 140.73 (2C, CH), 133.56 (2C, CH), 133.21 (2C, C_q), 131.9 (2C, C_q), 131.73 (2C, C_q), 131.06 (2C, C_q), 131.06 (2C, CH), 130.77 (2C, C_q), 130.41 (2C, C_q), 130.2 (2C, C_q), 130.13 (2C, C_q), 129.0 (2C, CH), 128.39 (2C, CH), 127.48 (2C, CH), 127.26 (2C, CH), 126.57 (2C, CH), 126.53 (2C, CH), 125.93 (2C, CH), 125.67 (2C, CH), 125.42 (2C, CH), 125.37 (2C, CH), 125.22 (2C, CH), 125.07 (2C, CH), 124.36 (2C, CH), 123.2 (2C, C_q).

IR: 3392 (br, w), 3103 (w), 3066 (m), 3039 (w), 2972 (m), 2855 (w), 1951 (w), 1701 (s), 1666(s), 1626 (m), 1601 (m), 1519 (w), 1498 (m), 1478 (m), 1456 (s), 1441 (m), 1422 (m), 1399 (m), 1377 (m), 1362 (s), 1319 (vs), 1271 (s), 1208 (s), 1183 (s), 1150 (s), 1122 (m), 1100(s), 1028 (m), 1013 (m), 972 (s), 946 (s), 902 (s), 878 (m), 855 (s), 821 (m), 785 (m), 767 (s), 755 (s), 715 (m), 734 (m), 705 (m), 687 (m), 668 (m).

HR-MS (ESI): $[C_{56}H_{32}ClO_4PS_2]^-$: 863.14774

Catalysis:

General procedure for the transfer hydrogenation of 3-phenyl-2H-1,4 benzoxazine



A 2 ml glass vial was charged with 3-phenyl-2H-1,4 benzoxazine **8** (10.5 mg, 50 µmol, 1 equiv.), Hantzsch ester (15.8 mg, 62.5 µmol, 1.25 equiv.), phosphoric acid catalyst (5 mol%), 1 ml $CHCl_3$ and was stirred at room temperature for 2 h. ^{1}H NMR analysis showed complete conversion of substrate. In case of the homogeneous catalysis the solvent was evaporated. In

case of the heterogeneous catalysis using polymeric catalyst **52**, the catalyst was separated by centrifugation after washing with $CHCl_3$ for three times. Crude product was purified by column chromatography (SiO2, cyclohexane/EtOAc = 40:1). In repeating runs the polymeric catalyst was reused after drying as obtained from the previous run.

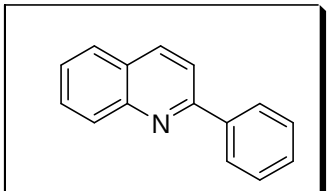
3-phenyl-3,4-dihydro-2H-benzoxazine (9):

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.40-7.32 (5H, m, ph), 6.84-6.86 82H, m, Ar), 6.69-6.65 (2H, m, Ar), 4.5 (1H, dd, J= 8.6 Hz, J= 3.0 Hz), 4.26 (1H, dd, J= 10.6 Hz, J=3.0 Hz), 3.9781H, dd, J=10.6 Hz, J=8.6 Hz)

HPLC: Chiracel OD-H, n-Hex / ^{i}PrOH = 80:20, flow 0.6 mL /min, 254nm

Synthesis of 2-aryl quinolones:

2-Phenyl quinoline:



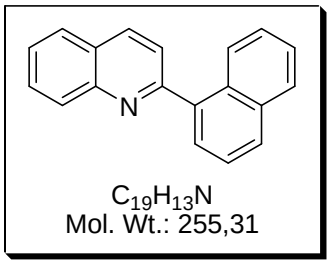
$C_{15}H_{11}N$
Mol. Wt.: 205,25

Under nitrogen atmosphere a two neck round bottom flask was charged with phenyl boronic acid (120 mg, 1 mmol, 1 eq.), 2-Chloroquinoline (164 mg, 1 mmol, 1 eq.) tetrakis-(triphenylphophine)-palladium (57.5 mg, 5 mol%) and potassium carbonate (414 mg, 3 mmol, 3 eq.). The flask was protected against light. Degassed benzene (2.5 ml), degassed ethanol (2.5 ml) were added via syringe. The mixture was heated at 80°C for 24 h and then diluted with CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. After removal of solvent the crude product was recrystallized dissolving in ethanol to give 2-phenyl quinoline as a light pink solid (184.72 mg, 0.9 mmol, 90%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.23 (1H, d, J = 8 Hz), 8.18-8.16 (3H), 7.89 (1H, d, J = 8 Hz), 7.84 (1H, dd, J = 8 Hz, J = 4 Hz), 7.73 (1H), 7.55-7.52 (3H), 7.48-7.45(1H)

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 157.4 (1C, C_q), 148.29 (1C, C_q), 139.69 (1C, C_q), 136.84 (1C, CH), 129.75 (1C, CH), 129.71 (1C, CH), 129.37 (1C, CH), 128.88 (2C, CH), 127.62 (2C, CH), 127.50 (1C, CH), 127.21 (1C, C_q), 126.33 (1C, CH), 119.06 (1C, CH).

2-(Naphthalen-1-yl)-quinoline:



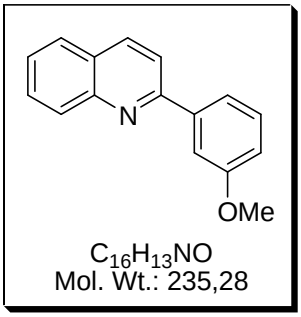
$C_{19}H_{13}N$
Mol. Wt.: 255,31

Under nitrogen atmosphere a two neck round bottom flask was charged with naphthalen-1-yl-boronic acid (172 mg, 1 mmol, 1 eq.), 2-Chloroquinoline (164 mg, 1 mmol, 1 eq.) tetrakis-(triphenylphophine)-palladium (57.5 mg, 5 mol%) and potassium carbonate (414 mg, 3 mmol, 3 eq.). The flask was protected against light. Degassed water (2.5 ml), degassed THF (2.5 ml) Toluene (5ml) were added via syringe. The mixture was heated at 80°C for 40 h and then diluted with CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclohexane : EtOAc = 99:1) to give pure 2-(Naphthalen-1-yl)-quinoline as a white solid (107 mg, 0.6 mmol, 62%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.29 (1H,d, *J* = 8Hz), 8.25 (1H, d, J = 8 Hz), 8.14 (1H, d, J = 8 Hz), 7.96 (1H, d, *J* = 8 Hz), 7.94 (1H, d, *J* = 8 Hz), 7.92 (1H, d, *J* = 8 Hz), 7.79 (1H, t, *J* = 8), 7.74-7.71 (2H), 7.63-7.59 (2H), 7.54-7.46 (2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 159.43 (1C, C_q), 148.08 (1C, C_q), 138.67 (1C, C_q), 136.34 (1C, CH), 134.03 (1C, C_q), 131.28 (1C, C_q), 129.83 (1C, CH), 129.71 (1C, CH), 129.17 (1C, CH), 128.43 (1C, CH), 127.80 (1C, CH), 127.60 (1C, CH), 127.03 (1C, C_q), 126.61 (2C, CH), 125.99 (1C, CH), 125.70 (1C, CH), 125.41 (1C, CH), 123.30 (1C, CH).

2-(3-Methoxyphenyl)-quinoline



$C_{16}H_{13}NO$
Mol. Wt.: 235,28

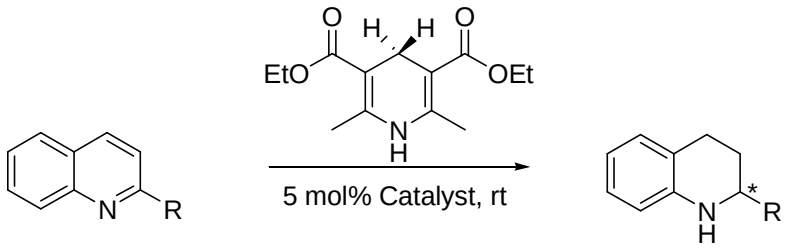
Under nitrogen atmosphere a two neck round bottom flask was charged with 3-methoxyphenylboronic acid (152 mg, 1 mmol, 1 eq.), 2-chloroquinoline (164 mg, 1 mmol, 1 eq.) tetrakis-(triphenylphophine)-palladium (57.5 mg, 5 mol%) and potassium carbonate (414 mg, 3 mmol, 3 eq.). The flask was protected against light. Degassed water (2.5 ml), degassed THF (2.5 ml) Toluene (5ml) were added via syringe. The mixture was heated at 80°C for 40 h and then diluted with

CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulphate. After removal of solvent the crude product was purified by column chromatography (SiO_2, cyclohexane : EtOAc = 99:1) to give pure 2-(3-Methoxyphenyl)-quinoline as a white solid (141 mg, 0.6 mmol, 60%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.21 (1H, d, J = 8 Hz), 8.20 (1H, d, J = 8 Hz), 7.86 (1H, d, J = 8 Hz), 7.82 (1H, dd, J = 8 Hz, J = 4 Hz), 7.79 (1H), 7.76-7.70 (2H, m), 7.55-7.51 (1H), 7.44 (1H, t, J = 8 Hz), 7.03 (1H, dd, J = 8 Hz, J = 4 Hz), 3.94 (3H, s).

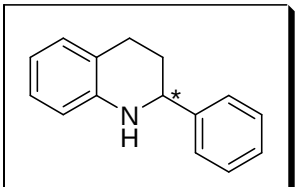
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 160.16 (1C, C_q), 157.14 (1C, C_q), 148.17 (1C, C_q), 141.11 (1C, C_q), 136.86 (1C, CH), 129.86 (1C, CH), 129.73 (2C, CH), 127.50 (1C, CH), 127.30 (1C, C_q), 126.39 (1C, CH), 120.06 (1C, CH), 119.15 (1C, CH), 115.45 (1C, CH), 112.74 (1C, CH), 55.46 (1C, CH).

General procedure for organocatalytic transfer hydrogenation of 2-aryl quinoline:



A 2 ml glass vial was charged with 2-aryl quinoline (0.1 mmol, 1 eq.), Hantzsch-Ester (67 mg, 0.3 mmol, 2.5 eq.), catalyst 5**1** or polymeric catalyst **52** (5 mol%) and $CHCl_3$ (1.5 ml). The mixture was stirred at room temperature for 4 h. Completion of reaction was confirmed by NMR and after removal of solvent the crude product was purified by column chromatography (SiO_2, cyclo-hexane : EtOAc = 98:2) to afford pure 2-aryl 1,2,3,4 tetrahydroquinoline in good yield (83%-90%).

2-Phenyl 1,2,3,4-tetrahydroquinoline



$C_{15}H_{15}N$
Mol. Wt.: 209,29

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] =7.41-7.25 (5H), 7.04-6.99

(2H), 6.66 (1H, t, *J* = 6.4 Hz), 6.55 (1H, d, *J* = 8.0 Hz), 4.45 (1H, dd, J = 11.0 Hz, J = 4.0 Hz), 2.97-2.91 (1H, m), 2.78-2.71 (1H, m), 2.13-1.98 (2H, m).

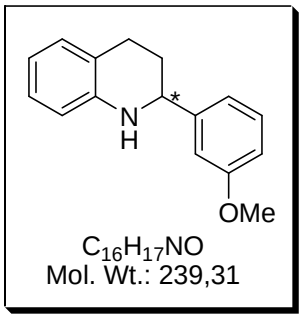
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 144.79 (1C, C_q), 144.71 (1C, C_q), 129.32 (1C, CH), 128.59 (2C, CH), 127.46 (1C, CH), 126.92 (1C, CH), 126.56 (2C, CH), 120.91 (1C, C_q), 117.19 (1C, CH), 114.00 (1C, CH), 56.28 (1C, CH), 30.99 (1C, CH_2), 26.40 (1C, CH_2).

IR: 3355(w), 2955(s), 2923(vs), 2853 (m), 1684 (vs), 1600 (m), 1444 (m), 1437 (m), 1419 (m), 1377 (m), 1321 (m), 1283 (m), 1209 (vs), 1183 (s), 1138 (vs), 1047 (w), 842 (s), 802 (s), 770 (w), 755 (w), 724 (m), 695 (w).

HPLC: Chiracel OD-H, n-Hex / ^{i}PrOH = 80:20, flow 0.6 mL /min, 254nm

2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline:

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.29-7.24 (1H), 7.03-6.97 (4H), 6.84-6.81 (1H), 6.67 (1H, t, *J* = 6.4 Hz), 6.56 (1H, d, *J* = 8.0 Hz), 4.41 (1H, dd, J = 11.0 Hz, J = 4.0 Hz), 3.80 (3H, s), 2.97-2.88 (1H, m), 2.74 (1H, td, J = 16.4 Hz, J = 4.7 Hz), 2.17-1.99 (2H, m).



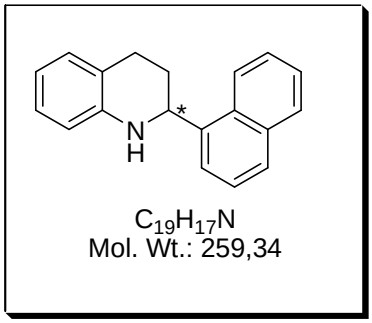
$C_{16}H_{17}NO$
Mol. Wt.: 239,31

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 159.85 (1C, C_q), 146.2, 144.7, 129.59 (1C, CH), 129.30 (1C, CH), 126.91 (1C, CH), 120.91, 118.91 (1C, CH), 112.83 (1C, CH), 112.06 (1C, CH), 56.28 (1C, CH), 55.26 (1C, CH_3), 30.97 (1C, CH_2), 26.44 (1C, CH_2).

HPLC: Chiracel IB, n-Hex / ^{i}PrOH = 90:10, flow 0.4 mL /min, 254nm

2-(Naphthalen-1-yl)-1,2,3,4-tetrahydroquinoline

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.16 (1H, d, *J* = 8.0 Hz), 7.91 (1H, dd, *J* = 8.7 Hz, *J* = 2.0 Hz), 7.79 (1H, d, *J* = 8.1 Hz), 7.68 (1H, d, *J* = 7.1 Hz), 7.57-7.45 (3H, m), 7.08-7.04 (2H), 6.70 (1H, dt, *J* = 7.6 Hz, *J* = 1.1 Hz), 6.62 (1H, d, *J* = 8.1 Hz), 5.29 (1H, dd, *J* = 8.6 Hz, *J* = 3.4 Hz), 3.03-2.95 (1H, m), 2.79-2.72 (1H, m), 2.37-2.29 (1H, m), 2.23-



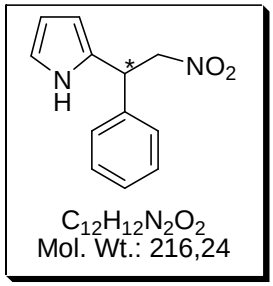
$C_{19}H_{17}N$
Mol. Wt.: 259,34

2.14 (1H, m).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 144.85 (1C, C_q), 139.98 (1C, C_q), 133.96 (1C, C_q), 130.52 (1C, C_q), 129.39 (1C, CH), 129.10 (1C, CH), 127.82 (1C, CH), 126.99 (1C, CH), 126.15 (1C, CH), 125.62 (1C, CH), 125.59 (1C, CH), 123.60 (1C, CH), 122.79 (1C, CH), 120.95 (1C, C_q), 117.19 (1C, CH), 114.05 (1C, CH), 52.11 (1C, CH), 29.21 (1C, CH_2), 26.26 (1C, CH_2).

HPLC: Chiracel OD-H, n-Hex / ^{i}PrOH = 80:20, flow 0.6 mL /min, 254nm

2-(2-nitro-1-phenylethyl)-1H-pyrrole (61)



$C_{12}H_{12}N_2O_2$
Mol. Wt.: 216,24

Under nitrogen atmosphere a dry Schlenk tube was charged with pyrrole (59.4 mg, 3 equiv.), polymeric catalyst **52** (5 mol%) and 4Å molecular sieves. 1:1 mixture of dry DCM/benzene (1 ml) was added and the mixture was stirred at room temperature for 30 minutes. A solution of nitrostyrol (44.7 mg, 1 equivalent) in 1:1 mixture of dry DCM/benzene (1 ml) was added drop wise. The mixture was stirred at room temperature for 4 hours. After completion, catalyst and molecular sieves were filtered out and (brown) organic solvent part was concentrated. The crude product was purified by flash chromatography (DCM/methanol = 99:1 to 95:5) to afford **2**-(2-nitro-1-phenylethyl)-1H-pyrrole as brown solid in 91% yield and 96% ee.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 7.84 (1H, s, br), 7.37-7.22 (5H), 6.69 (1H), 6.16 (1H), 6.09 (1H), 4.99 (1H), 4.9(t, 1H J = 8 Hz), 4.81 (1H).

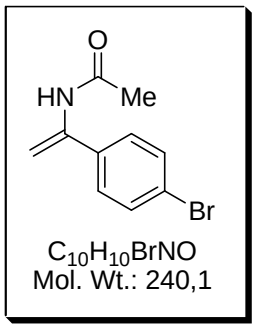
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] 138.17, 129.19(2C), 129.15, 128.03, 127.92(2C), 118.24, 108.50, 105.77, 79.21, 42.95

IR: 3358 (w), 3109 (m), 3082 (w), 3059 (w), 3044 (w), 3005 (w), 2959 (w), 2924 (w), 2852 (w), 2596 (w), 2304 (w), 1969 (w), 1934 (w), 1917 (w), 1898 (w), 1816 (w), 1704 (m), 1632 (s), 1601(m), 1594(m), 1577(m), 1544 (s), 1514 (vs), 1495 (vs), 1449 (s), 1425 (w), 1400 (w), 1377 (w), 1342 (vs), 1292 (m), 1262 (s), 1201 (m), 1184 (m), 1163 (m), 1110 (m), 1093 (m),

1075(m), 1030 (w), 1014 (w), 1002 (w), 995 (w), 967 (s), 887 (w), 870 (w), 847 (m), 840 (w), 787 (w), 767 (s), 737 (s), 706 (s), 682 (m).

HPLC: Chiracel IB, n-Hex / ^{i}PrOH = 80:20, flow 0.5 mL /min, 254nm

N-(1-(4-bromophenyl)-vinyl)-acetamide (56):

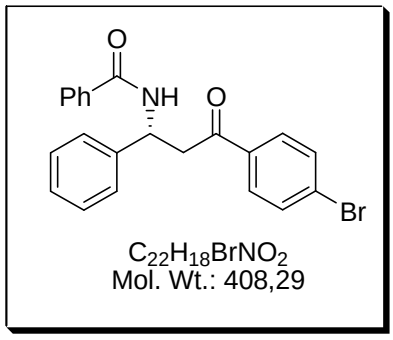


The compound was prepared in good yield using the reported literature procedure. [132]

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.47-7.44 (2H), 7.27-7.25 (2H), 7.15 (1H, s, br), 5.71 (1H, s), 5.06 (1H, s), 2.06 (3H, s).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.42 (1C, C_q), 139.80 (1C, C_q), 137.09 (1C, C_q), 131.69 (2C, CH), 127.73 (2C, CH), 122.59 (1C, C_q), 103.83 (1C, CH), 24.29 (1C, CH).

N-(3-(4-bromophenyl)-3-oxo-1-phenylpropyl)benzamide (58):



A dry Schlenk tube was charged with freshly prepared N-benzoylaldimine (0.1 mmol, 1equivalent) and polymeric catalyst **52** (2 mol%) in nitrogen atmosphere. Dry toluene was added and the mixture was stirred at room temperature for 30 minutes. Enamide (0.12 mmol, 1.2 equivalent) dissolved in dry toluene was added to the Schlenk tube and the mixture was stirred at room temperature for 5 hours. The solid catalyst was filtered out and washed with toluene. Saturated $NaHCO_3$ solution was added to the organic part and was extracted with dichloromethane. The organic part was dried over Na_2SO_4 and evaporated. The residue after evaporation was dissolved in methanol and HBr (48% aqueous solution) was added. The mixture was stirred at room temperature for 4 h and then was quenched with saturated $NaHCO_3$ solution at 0^{o} c. The mixture was extracted with dichloromethane and dried over Na_2SO_4. The crude product was purified by column chromatography (Cyclohexane:EtOAc =90:10-70:30) to afford white solid (82% yield, 81% ee).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.83-7.77 (4H), 7.60-7.58 (2H), 7.51-7.49 (1H), 7.46-7.42 (3H), 7.39-7.37 (2H), 7.33-7.30 (2H), 5.77-5.72 (1H), 3.86 (1H, dd, *J* = 17.1 Hz, *J* = 5.9 Hz), 3.49 (1H, dd, *J* = 17.1 Hz, *J* = 6.2 Hz).

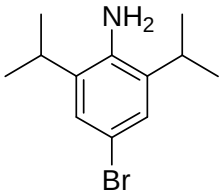
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 198.05 (1C, C_q), 166.73 (1C, C_q), 140.64 (1C, C_q), 135.36 (1C, C_q), 134.18 (1C, C_q), 132.08 (2C, CH), 131.71 (1C, CH), 129.70 (2C, CH), 128.92 (1C, C_q), 128.82 (2C, CH), 128.65 (2C, CH), 127.68 (1C, CH), 127.05 (2C, CH), 126.50 (2C, CH), 50.43 (1C, CH), 43.02 (1C, CH).

IR: 3309 (m), 3083 (w), 3016 (m), 3061 (m), 3030 (m), 3005 (w), 2961 (w), 2925 (m), 2853 (w), 1959 (w), 1901 (w), 1810 (w), 1725 (w), 1686 (vs), 1636 (vs), 1602 (s), 1585 (vs), 1568 (s), 1536 (vs), 1490 (s), 1453 (m), 1397 (s), 1362 (s), 1316 (s), 1294 (s), 1267 (s), 1227 (m), 1202 (m), 1177 (m), 1157 (w), 1146 (w), 1112 (w), 1102 (w), 1071 (s), 1028 (m), 1010 (m), 1002 (m), 989 (s), 929 (w), 892 (w), 816 (w), 772 (m), 758 (m), 700 (vs).

HPLC: Chiracel OD-H, n-Hex / ^{i}PrOH = 75:25, flow 1 mL /min, 254nm

4-bromo-2,6-diisopropylbenzenamine:

In a dry flask 2, 6 di-isopropyl aniline (M.W 177.29, 20 mmol, 3.545g, d= 3.2 g/ml) was dissolved in 20 ml dry dichloromethane and stirred at room temperature. Tetraethyl tribromide dissolved in 10 ml dichloro methane was added to the flask slowly over 15 mins. The mixture was stirred at room temperature overnight. Next morning, saturated solution of sodium bi sulphite was added to the mixture and the organic phase was separated using separatory funnel. After evaporation the desired product 4-bromo-2,6-diisopropylbenzenamine was obtained as thick brown liquid.

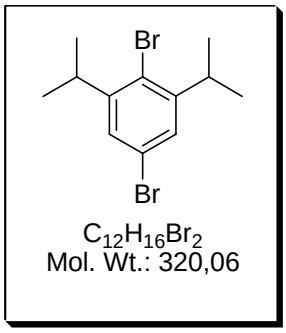


$C_{12}H_{18}BrN$
Mol. Wt.: 256,18

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.10 (s, 2H,), 3.54 (s, 2H, br), 2.6 (sept. J= 6.8 Hz, 2H), 1.23 (d, J= 6.8 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 140.1, 134.5, 125.6, 111.0, 28.6, 22.4.

2,5-dibromo-1,3-diisopropylbenzene:

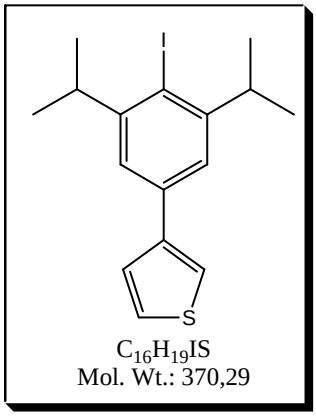


Into a 50 ml flask 2.00 g 4-bromo-2,6-diisopropylaniline (7.81 mmol, 1.00 eq) were added to 15 ml hydrobromic acid. This mixture was stirred in a ultrasonic bath for one minute. Then the suspension was cooled to -50°C. Afterwards 1.6 g solid sodium nitrite (23.88 mmol, 3.06 eq) was added in the space of five minutes. The color of the suspension changed from yellow to brown. After stirring at -50°C for an hour, 15 ml pre-cooled diethyl ether was added to the reaction mixture. The solution was warmed to -15°C. During the warming process, brown gases originated. After the gas producing, the reaction mixture was cooled once more to -50°C. Then, 0.5 ml water was added drop wise and sodium carbonate decahydrate were added to the mixture. The ice bath was removed and the reaction mixture was stirred at room temperature for 12 h. Afterwards,. The aqueous phase was extracted twice with diethyl ether. The solvent of the organic phases were removed under pressure. g 2,5-dibromo-1,3-diisopropylbenzene (5.08 mmol, 65 %) of an red liqiid fluid was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 1.23-1.22 (12H, d, J = 4 Hz, CH3), 3.48-3.44 (2H, sept, J = 8 Hz, CH), 7.23 (1H, s, CH).

13C-NMR (100 MHz, CDCl3) δ [ppm] = 22.87 (2C, CH) 33.63 (4C, CH3), 1121.88 (1C, C_q), 125.13 (1C, C_q), 127.35 (2C, CH), 149.95 (2C, C_q).

3-(4-Iodo-3,5-diisopropylphenyl)thiophene (66):



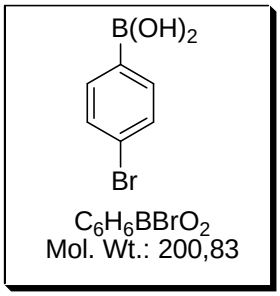
2,6-diisopropyl-4-(thiophen-3-yl)benzenamine was dispersed in a mixture of tert-butanol and water. The mixture was cooled to -15^{o}C and stirred for 30 mins. To this dispersion, first sodium nitrite solution was added. Next, 1 equivalent p-toluenesulfonic acid solution in acetonitrile followed by 1.2 equivalent potassium iodide solution was added slowly and the mixture was brought to room temperature. Stirring at room temperature for 6 hours led to the desired product 3-(4-Iodo-3,5-diisopropylphenyl)thiophene **66** in 63% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.48 (1H, s), 7.42-7.39 (2H), 7.3 (2H, s), 3.47 (2H, sept, J= 6.8), 1.3 (12H, d, J= 6.8).

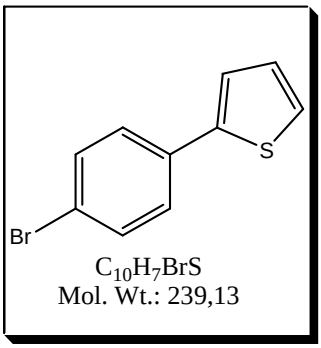
^{13}C-NMR (100 MHz, DMSO): δ [ppm] = 151.52 (2C, C_q), 142.0 (1C, C_q), 136.06 (1C, C_q), 126.5 (1C, CH), 126.38 (1C, CH), 122.13 (2C, CH), 120.62 (1C, CH), 107.6 (1C, C_q), 39.37 (2C, CH), 23.46 (4C, CH_3).

IR: 3103 (w), 3053 (w9, 2960 (s), 2925 (m), 2886 (w), 2867 (m), 1751 (w), 1653 (w), 1591 (w), 1561 (m), 1526 (w), 1460 (s), 1429 (s), 1401 (w), 1383 (m), 1361 (m), 1323 (m), 1031 (w), 1277 (w), 1254 (w), 1217 (w), 1189 (w), 1168 (w), 1139 (w), 1113 (w), 1106 (w), 1082 (w), 1070 (m), 1046 (w), 1000 (s9, 958 (w), 934 (m), 885 (m), 877 (m), 863 (m), 837 (m), 817 (m), 777 (vs), 750 (w), 733 (m), 684 (w), 660 (s).

4-bromophenylboronic acid:



To a flame-dried 250 mL flask, under nitrogen was added 1,4-dibromobenzene (2.36 g, 10.0 mmol) followed by anhydrous diethyl ether (50 mL). The solution was cooled to –78 °C and 1.6 M *n*-BuLi (7 mL, 11 mmol) was added drop wise over 10 min. The reaction was stirred at –78 °C for 1 h then allowed to warm to room temperature over the course of 1 h, then again cooled to –78 °C. Triisopropylborate (3.5 mL, 15 mmol) was added and the reaction was stirred for a further 10 min. and allowed to warm to r.t., during which time precipitate formed. The reaction was cooled to 0 °C, quenched with 1 M hydrochloric acid (20 mL) and diluted with 20 mL diethyl ether (precipitate dissolved). The two phases were separated and the organic phase was washed with water (2 × 15 mL) and brine (10 mL). The resulting aqueous phase was extracted with ether (2 × 15 mL) and the combined organic extracts were dried over sodium sulfate, filtered and concentrated *in vacuo*, affording 1.12 g (62% yield) of an off-white solid.

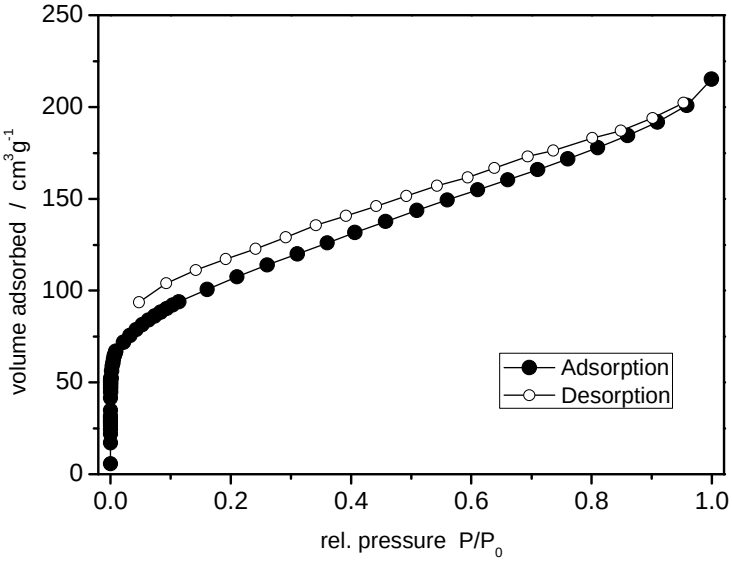


2-(4-Bromophenyl)thiophene: To a mixture of manganese(III) acetate (3.3 g, 12.4 mmol $Mn(OAc)_3 \cdot 2H_2O$) in 10 mL of toluene was added 4-bromo phenyl boronic acid (500 mg, 4.1 mmol), and the resulting mixture was refluxed for 30 min . After the completion of the reaction, the mixture was filtrated through a pad of silica using hexane or petroleum ether as the eluent. Concentration under reduced pressure furnished the biphenyl 2-(4-Bromophenyl)thiophene (600 mg, 93%, solid).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.08 (t, *J* = 4.3 Hz, 1H), 7.29 (d, *J* = 4.3 Hz, 2 H), 7.49 (d, *J* = 9.0 Hz, 2 H), 7.47 (d, *J* = 9.0 Hz, 2 H).

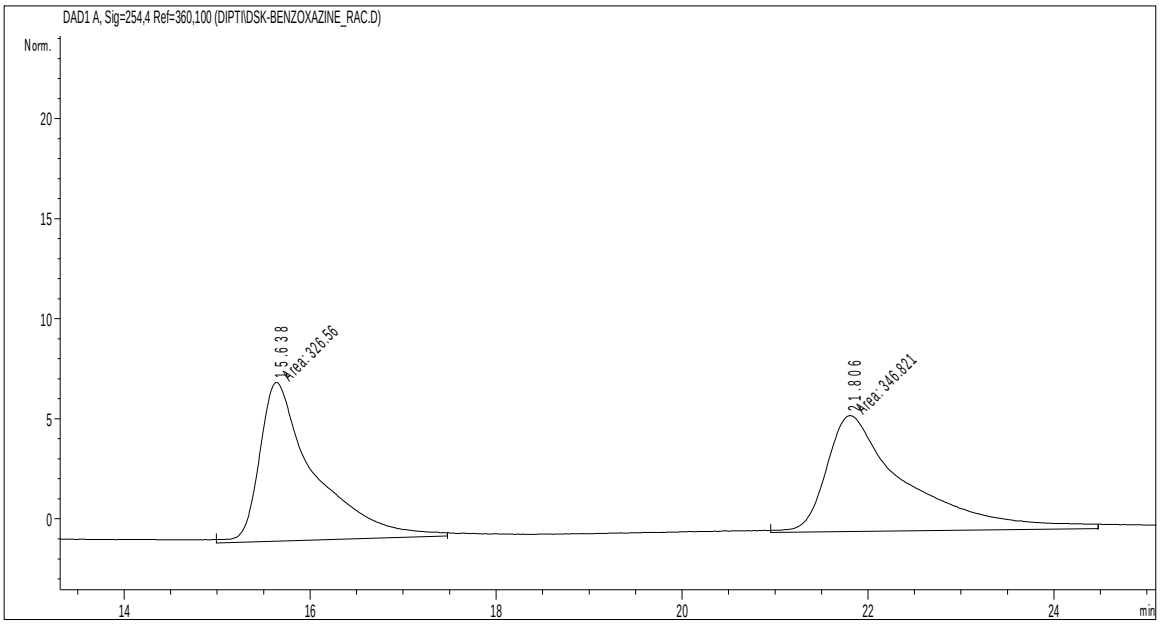
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 138.31 (Cq), 132.78 (2C), 129.72 (2C), 127.84, 127.65, 125.41, 123.1(Cq), 121.13.

Nitrogen adsorption isotherm of the polymer network 52:

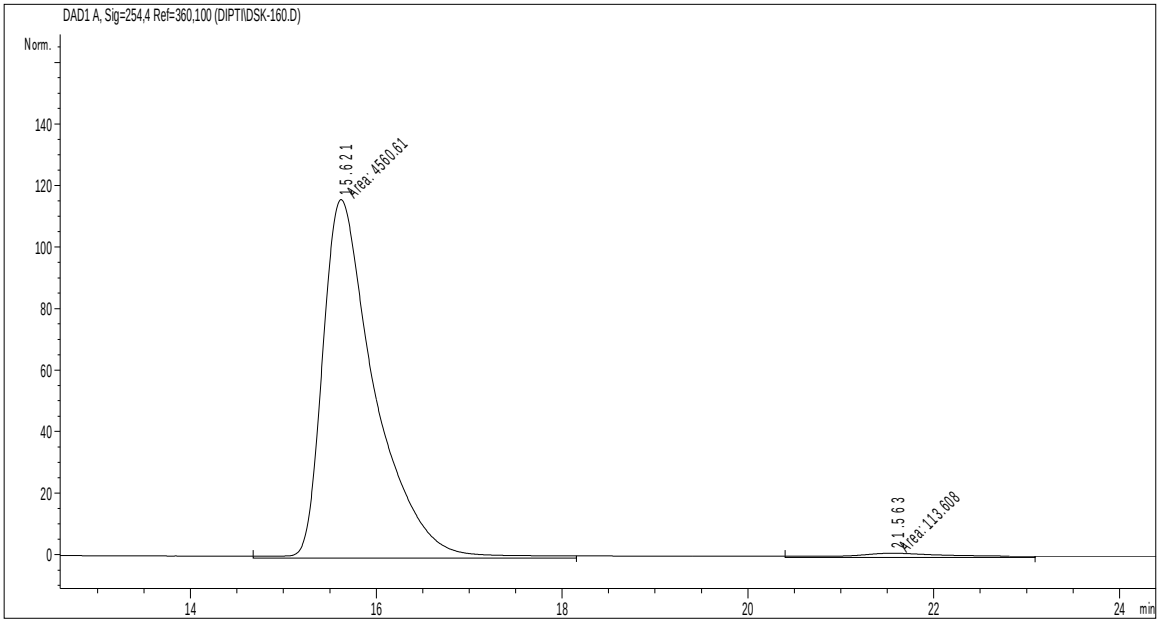


3-phenyl-3,4-dihydro-2H-benzoxazine:

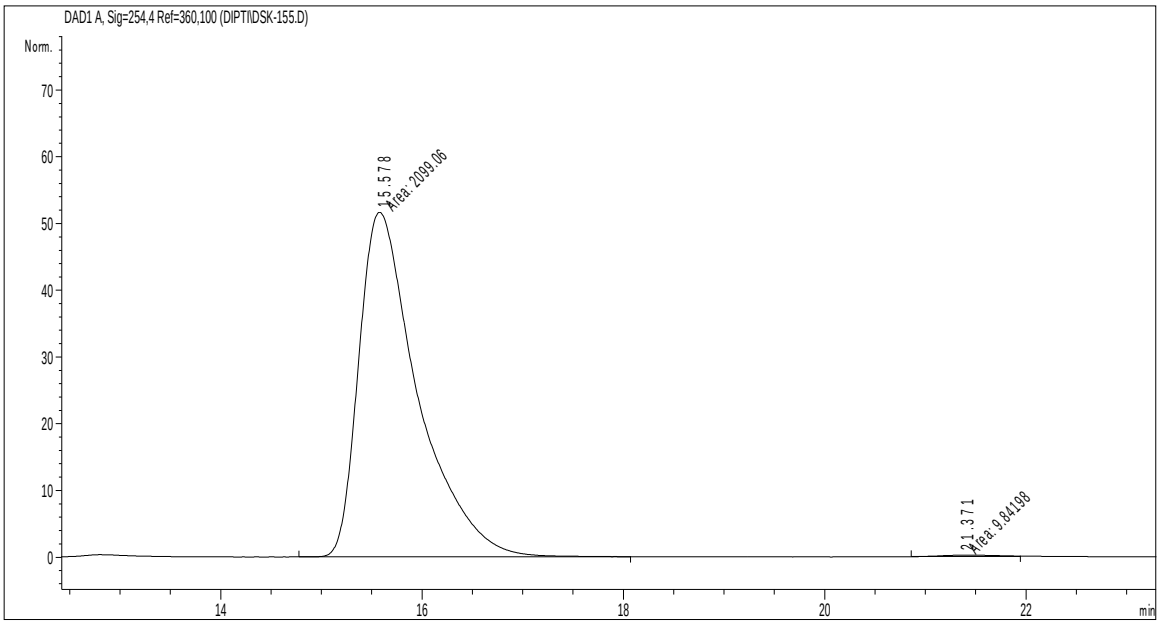
Racemic



Homogeneous catalysis using catalyst 3: (95% ee)

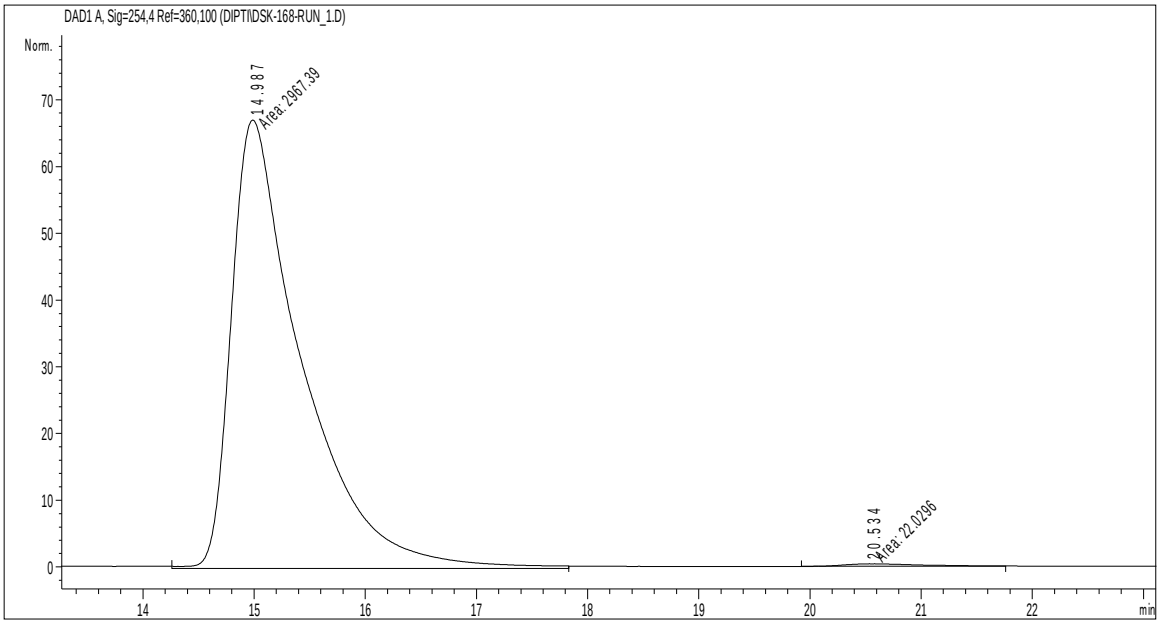


Homogeneous catalysis using catalyst 51: (99% ee)

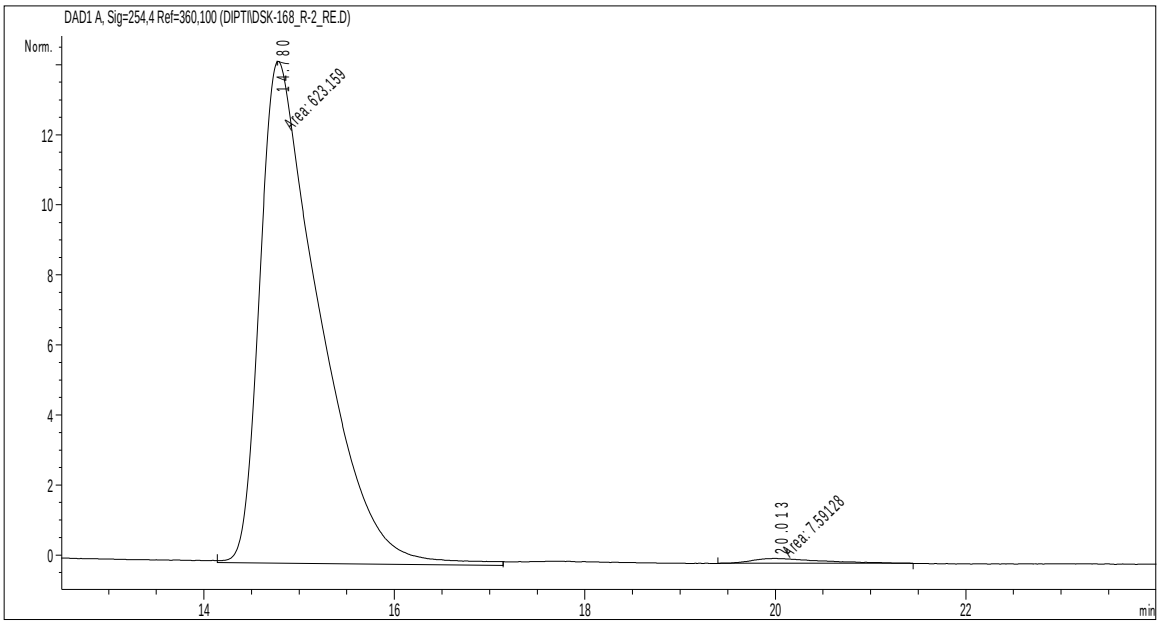


Heterogeneous catalysis using polymeric catalyst 52:

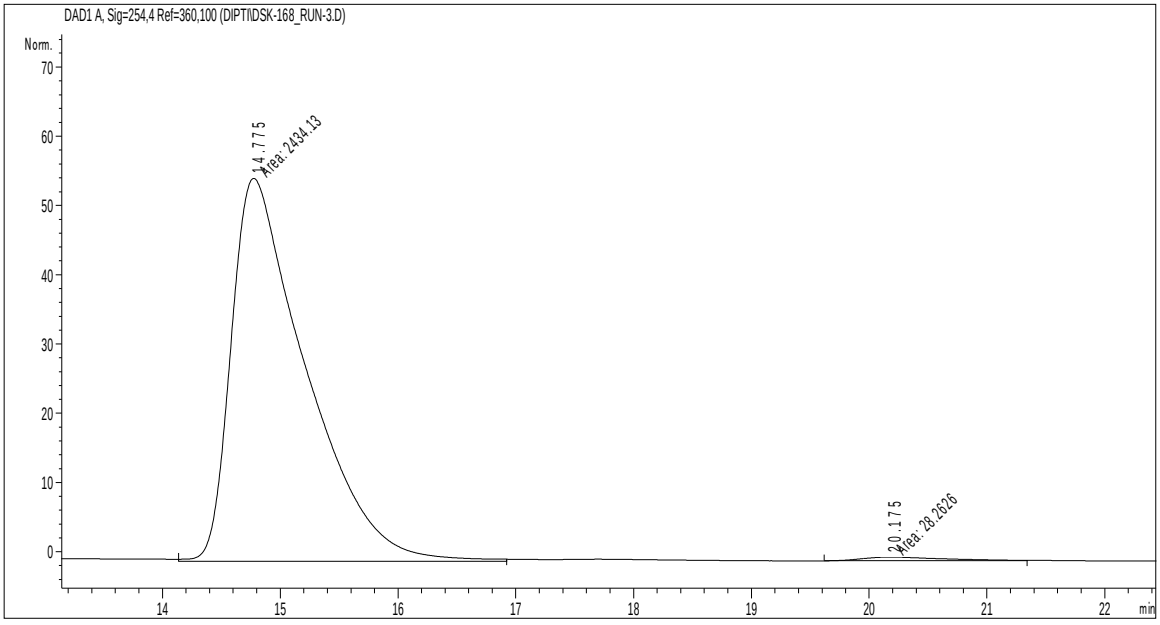
Run 1 (98% ee)



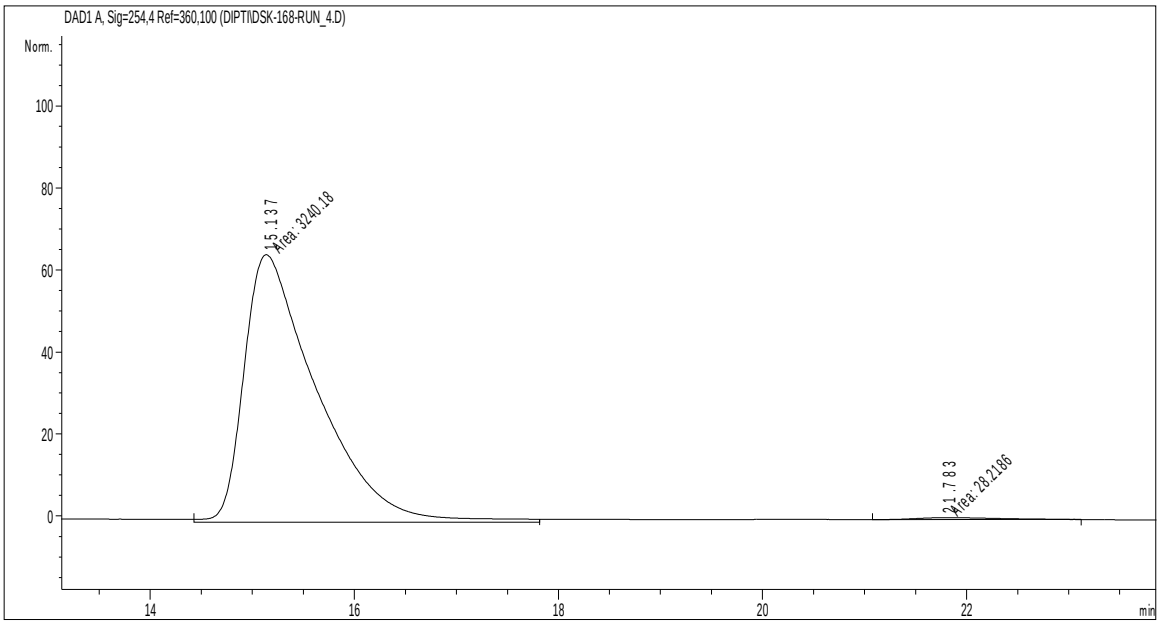
Run 2 (98% ee)



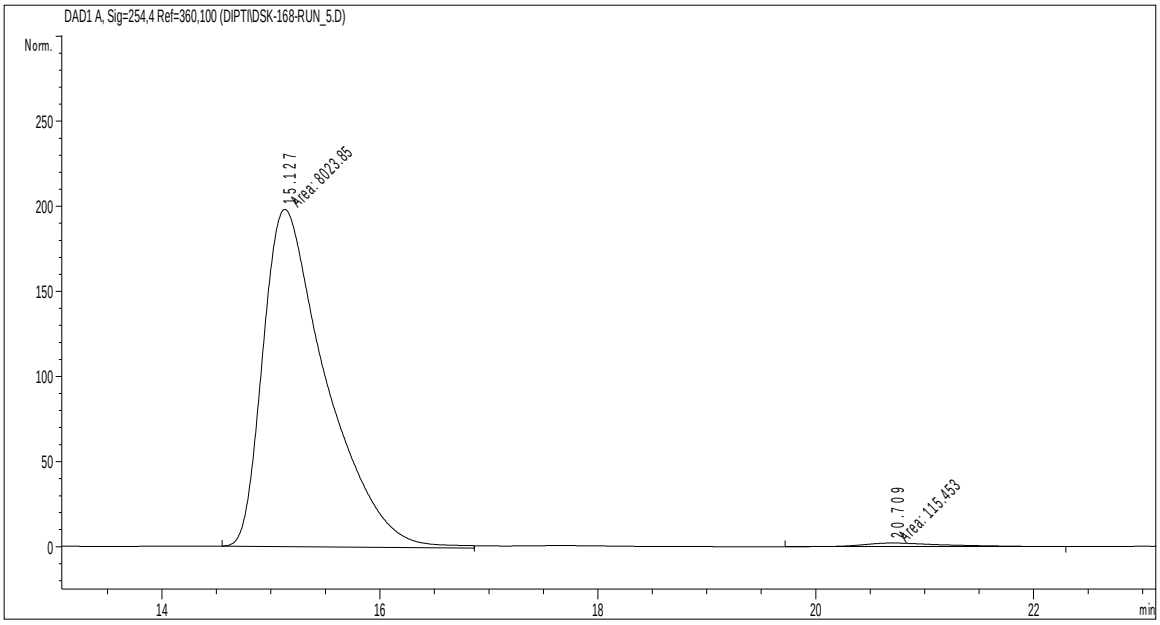
Run 3 (98% ee)



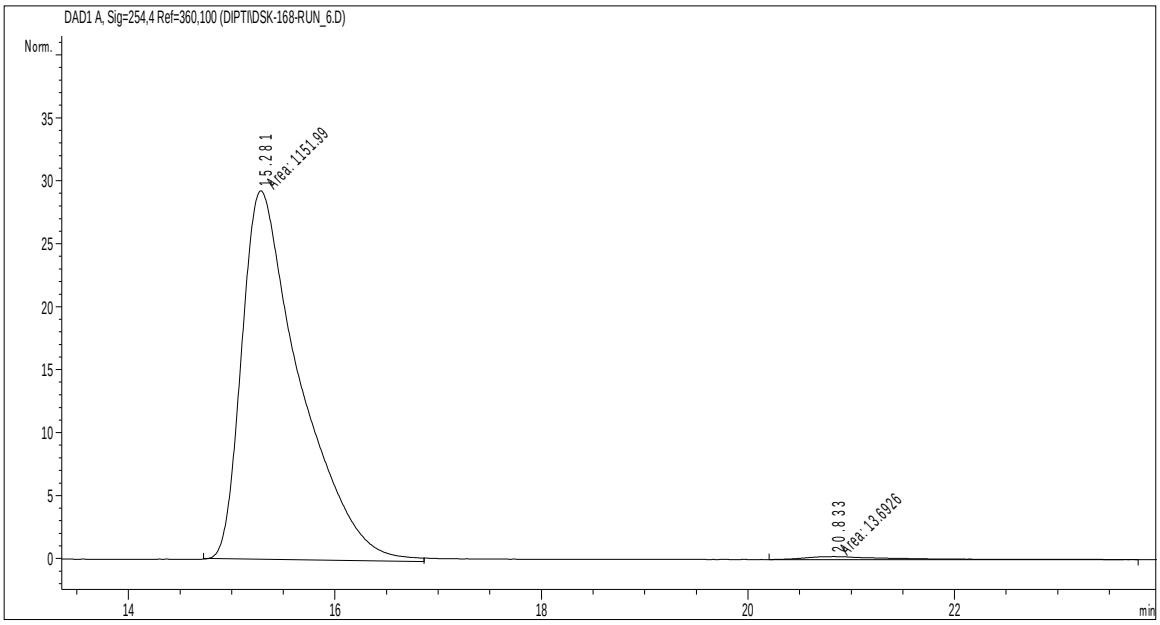
Run 4 (98% ee)



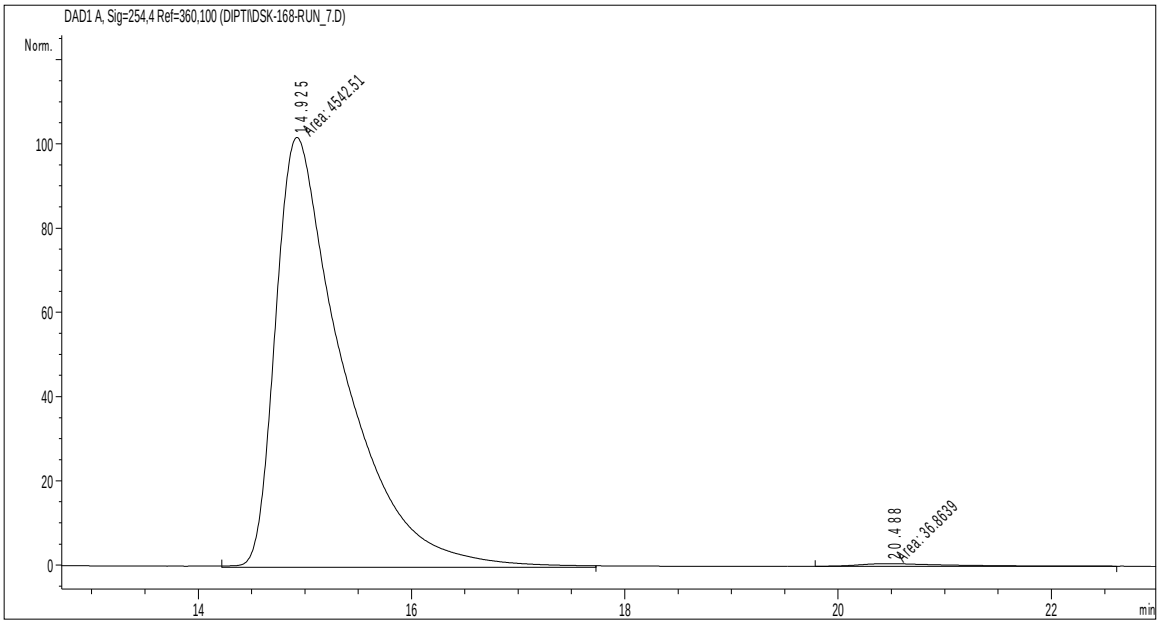
Run 5 (98% ee)



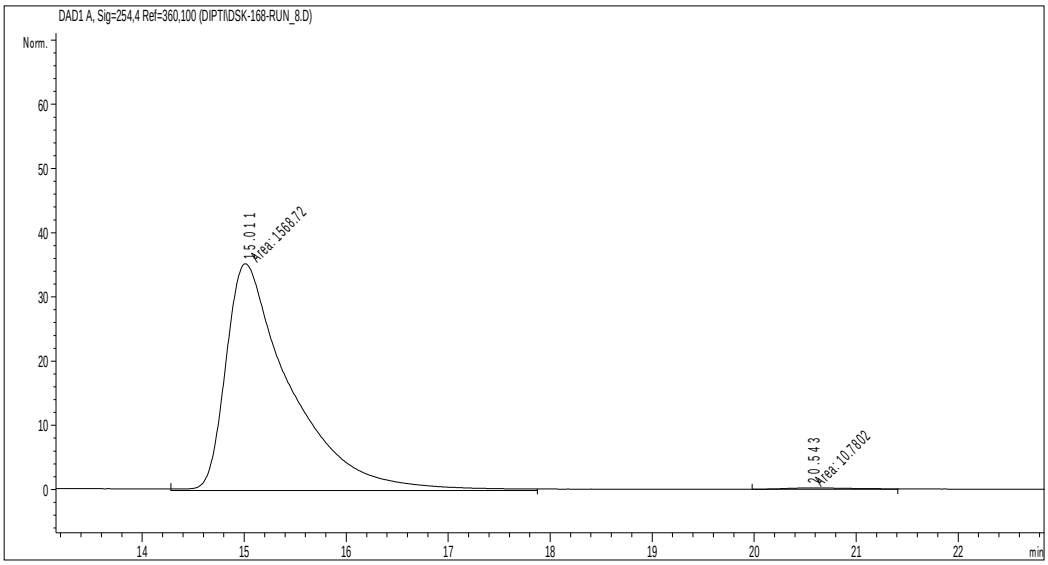
Run 6 (98% ee)



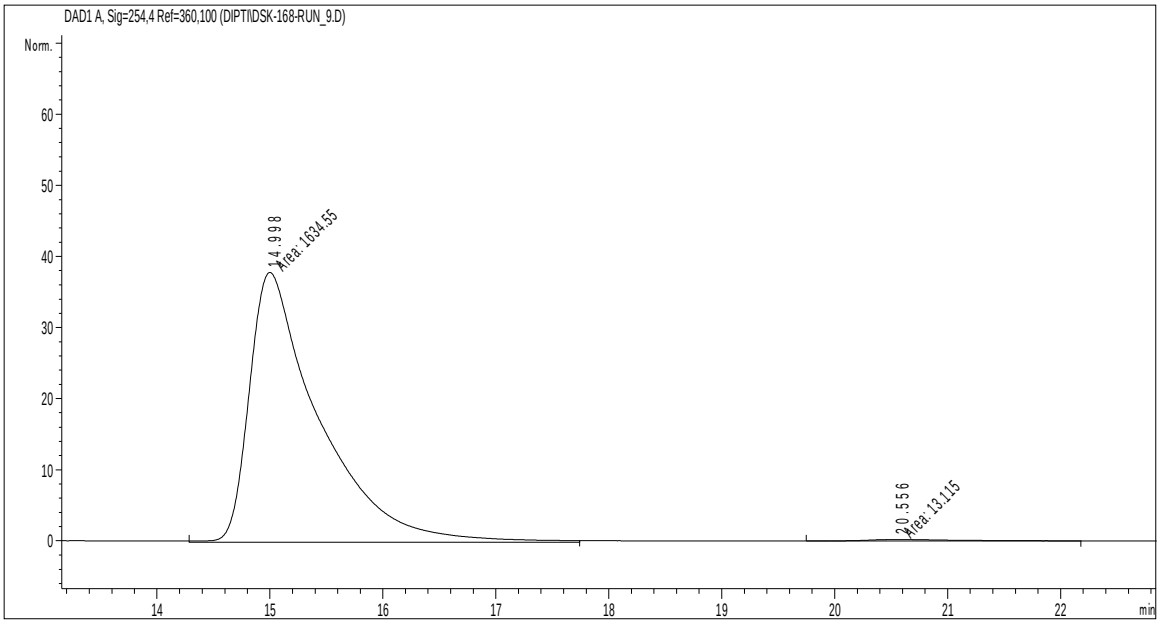
Run 7 (98% ee)



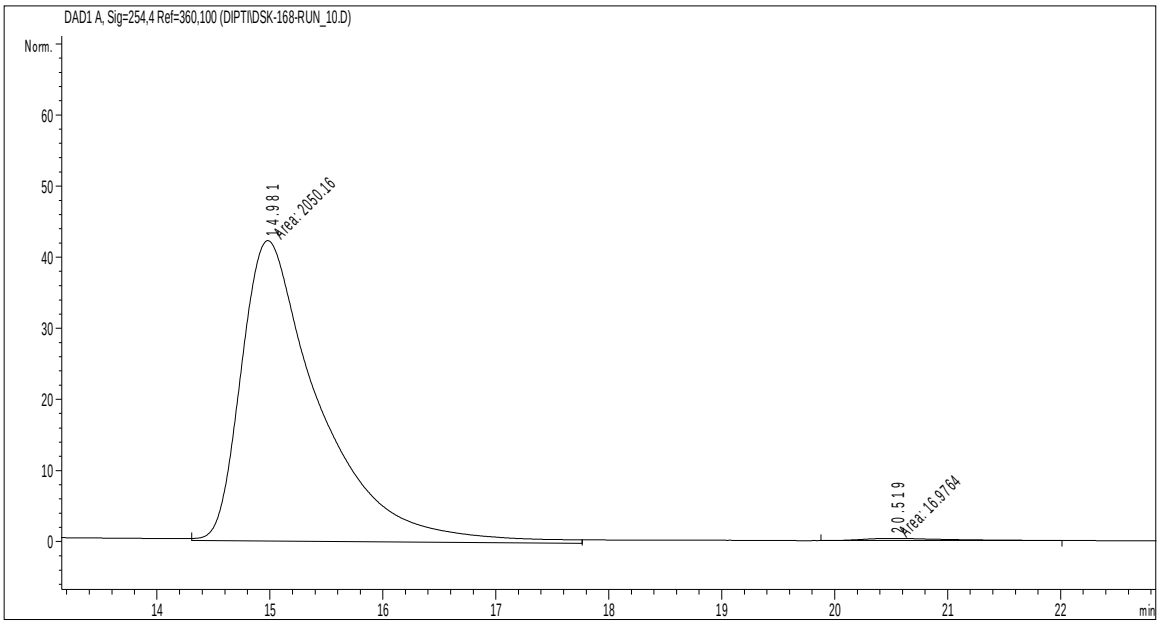
Run 8 (98% ee)



Run 9 (98% ee)

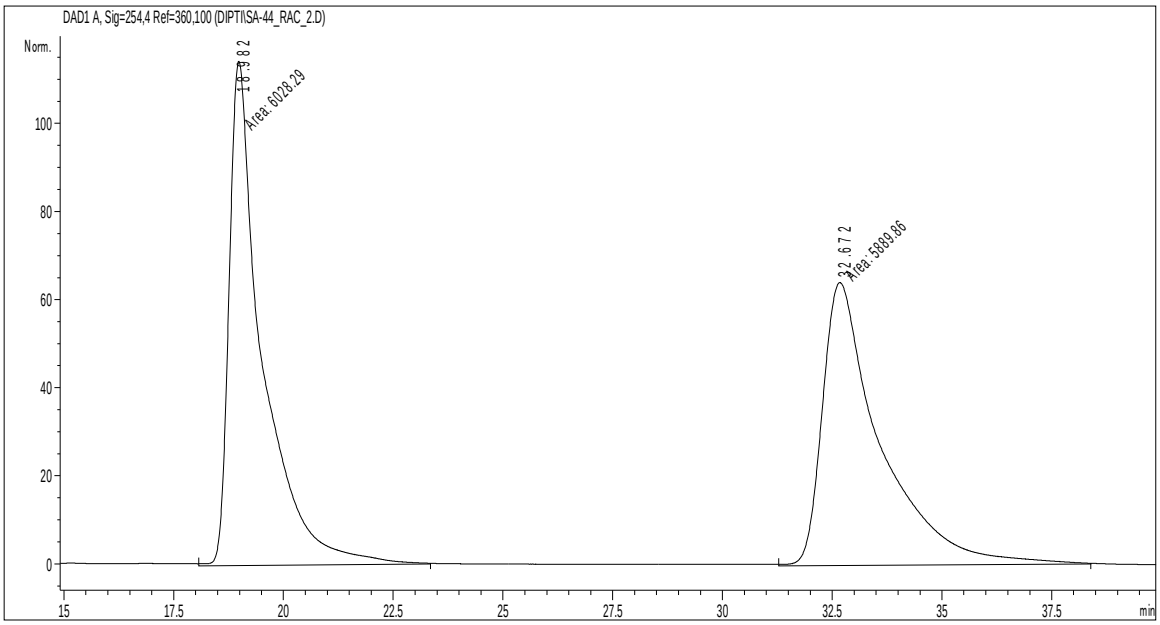


Run 10 (98% ee):

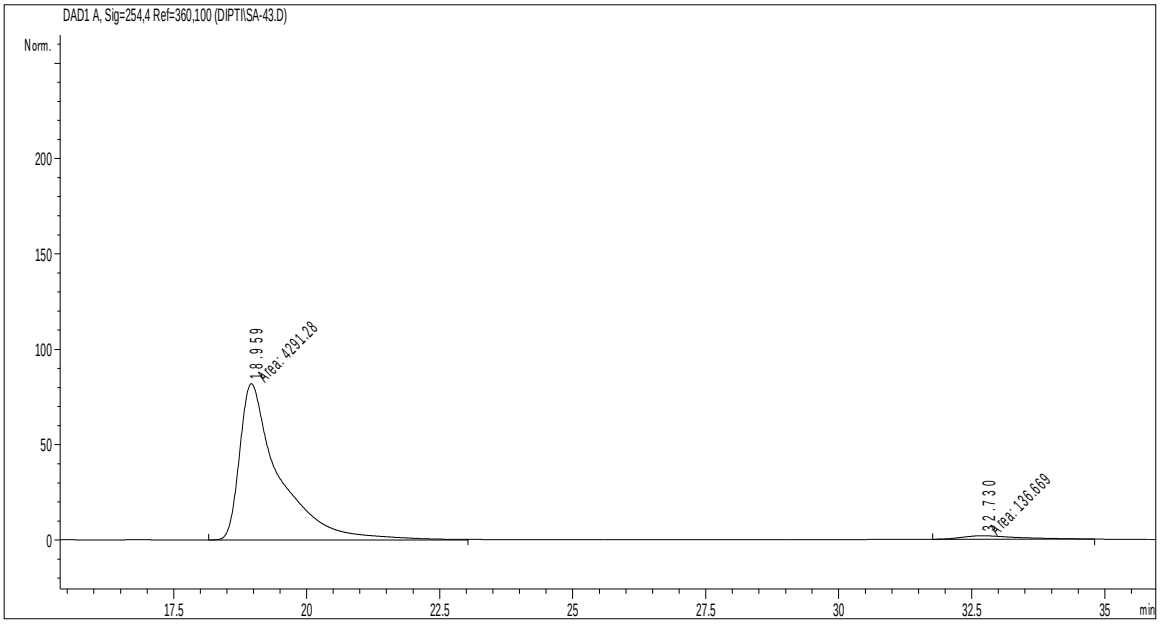


2-(Naphthalen-1-yl)-1,2,3,4-tetrahydroquinoline (94% ee):

Racemic

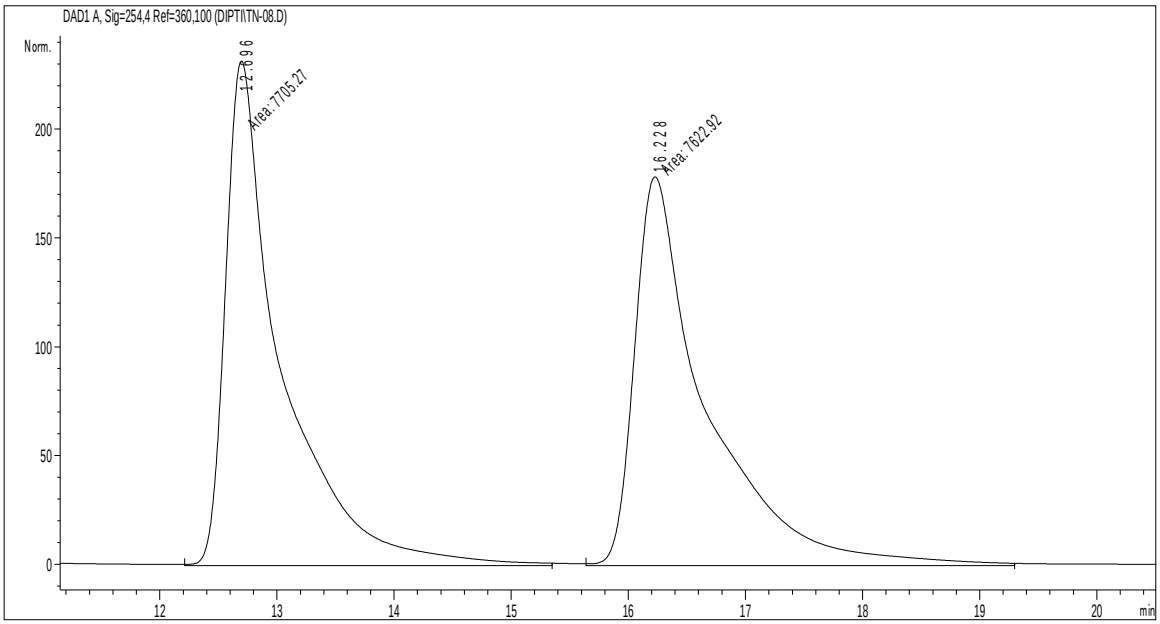


94% ee :

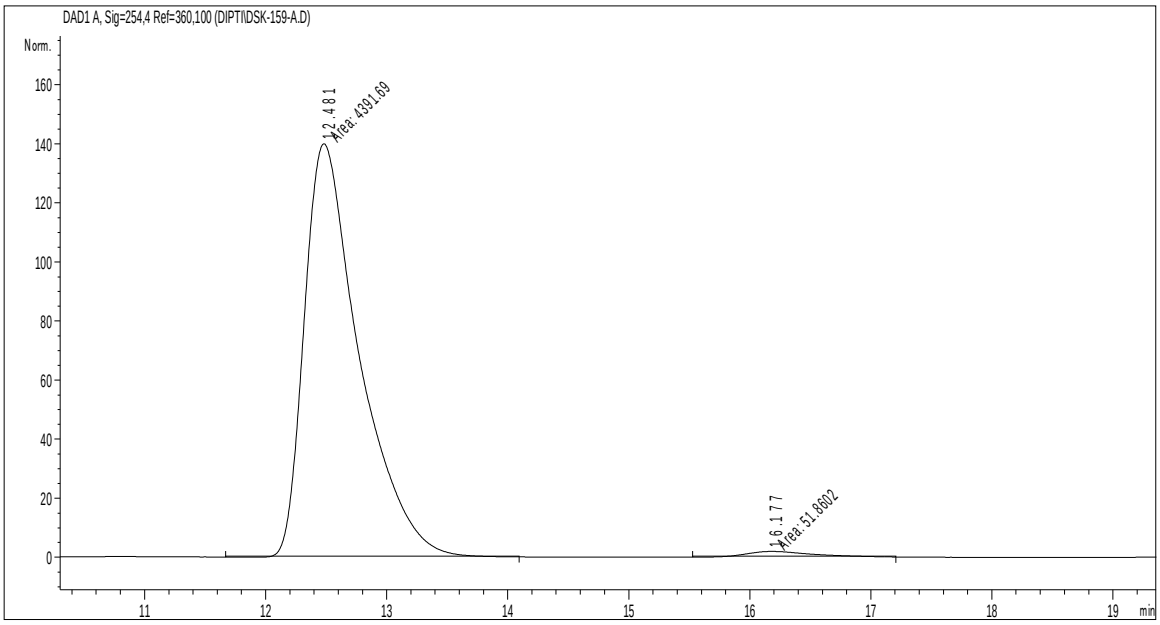


2-Phenyl 1,2,3,4-tetrahydroquinoline:

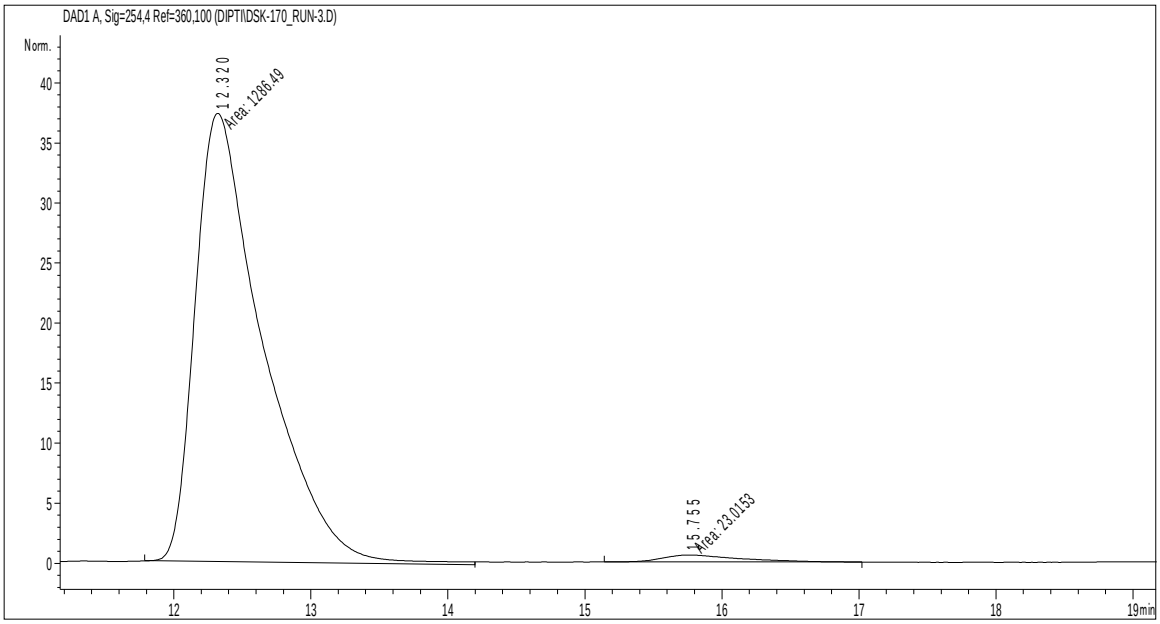
Racemic:



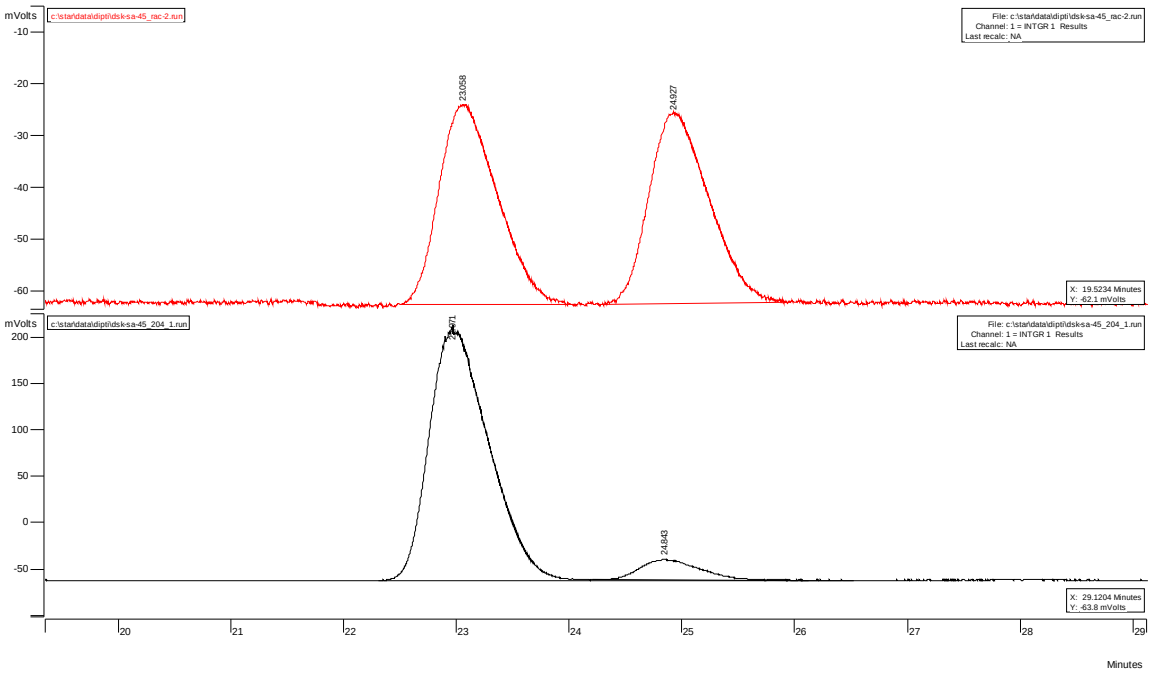
Homogeneous catalysis using catalyst 51 (98% ee)



Heterogeneous catalysis using polymeric catalyst 52 (97% ee)

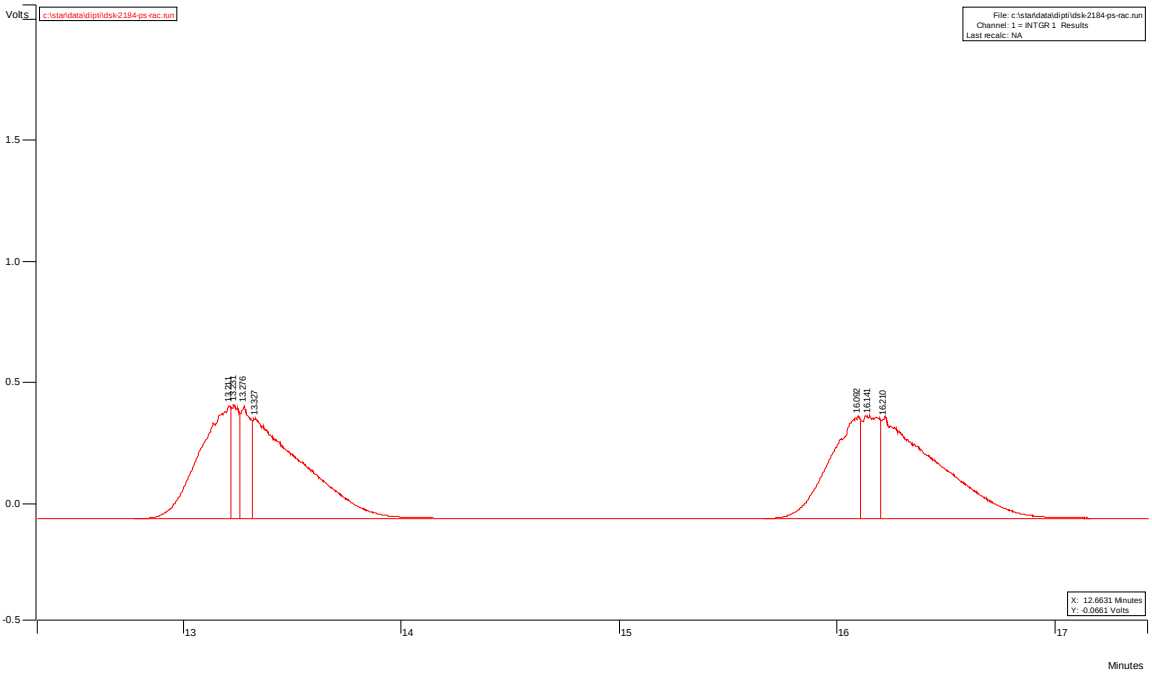


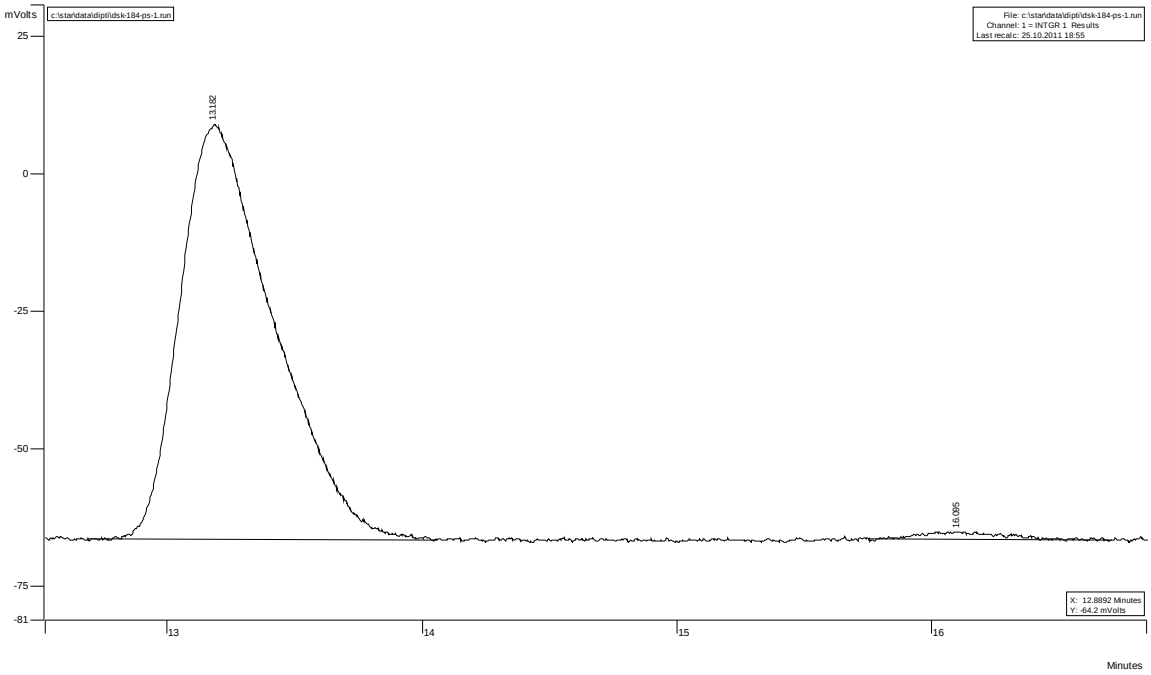
2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline using polymeric catalyst 52 (87% ee)



Time	Area
16.598	14039823
17.762	971228

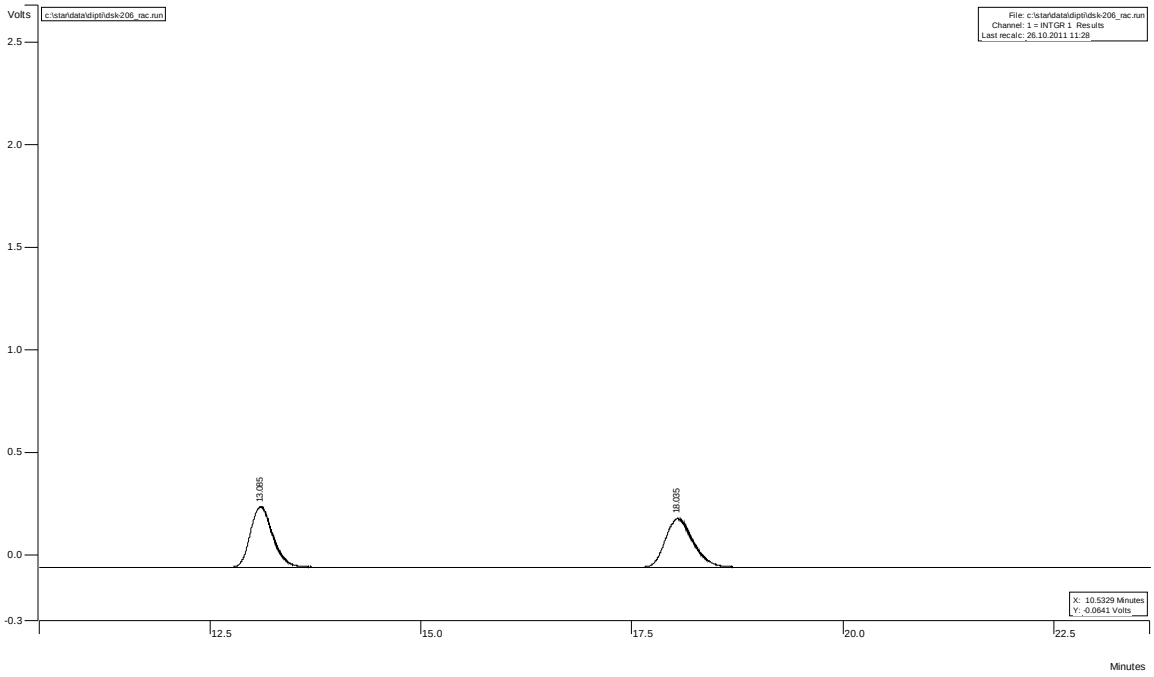
2-(2-nitro-1-phenylethyl)-1H-pyrrole 61 (96% ee):

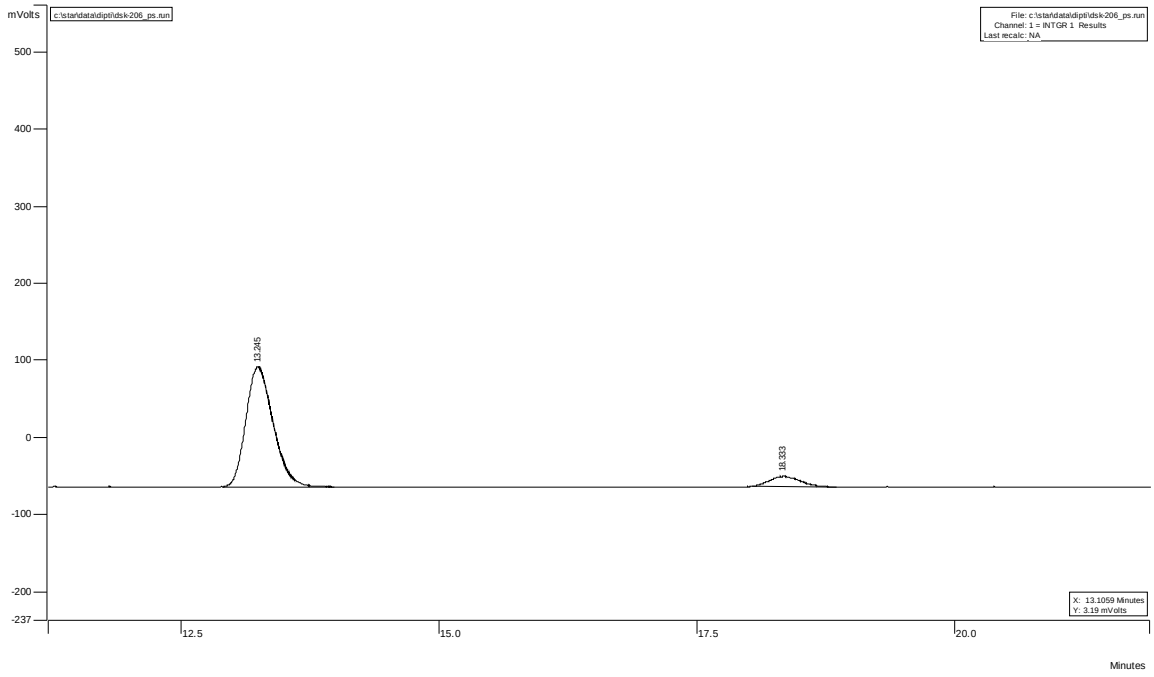




Time	Area
13.182	1936830
16.095	35066

N-(3-(4-bromophenyl)-3-oxo-1-phenylpropyl)benzamide 58 (81% ee):





Time	Area
13.242	2878201
18.335	299459

Å	Ångstrom
abs.	absolute
Ac	Acyl
ACDC	Asymmetric counterion-directeded catalysis
APCI	atmospheric-pressure chemical ionization
BET	*Brunauer-Emmett-Teller* / spezifische Oberfläche
BINOL	1,1´ -Bi-2-naphthol
Bn	Benzyl
br	broad Signal
Bu	Butyl
BuLi	Butyllithium
c	*cyclo*
CMP	Conjugierted microporous Polymer
COF	Covalently-bound organisc framework
Conv.	Conversion
C_q	Quartret carbon atom
d	Doublett
DCM	Dichlormethane
δ	chemiscal shift
δ	Difference
DEPT	distortionless enhancement by polarization transfer
DMAP	4-(Dimethylamino)-pyridine
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethylsulfoxide
DVB	Divinylbenzene
EE	Ethylacetate
ee	Enantiomerenüberschuss
EI	electron impact (ionization)
eq.	equivalent

ESI	electrospray-ionization
Et	Ethyl
eV	Electronvolt
GC	Gas chromatography
h	hour
HCP	Hyper Crosslinked Polymer
HPLC	high performance liquid chromatography
HR-MS	hochauflösende Massenspektrometrie
Hx	Hexane
Hz	Hertz
i	*iso*
ICP	induktively coupled Plasma
IR	Infrarred spektroscopy
IUPAC	International Union of Pure and Applied Chemistry
Cat.	Catalyst
kV	Killovolt
λ	Wavelength
M	mol / L
m	mideam Signal
m	Multiplett
m/z	Mass /Charge
Me	Methyl
MeCN	Acetonitrile
min.	Minutes
MOF	Metal Organic Framework
MOP	Microporous Organic Polymer
MS	Mass spectrometry
MTBE	*tert*-Butyldimethylether
MW	Microwave

n	normal
NHC	*N*-heterocyclic Carbene
NMR	Kernspinresonanzspektroskopie
OES	Optiscal Emissions spectroscopy
Ph	Phenyl
PIM	Polymer with intrinsisc Mikroporosity
pin	Pinacolyl
PMB	*para*-Methoxybenzyl
PMO	periodisc mikroporous Organosilicate
ppm	parts per million
Pr	Propyl
PV	Porenvolumen
PVA	Polyvinylalcohol
Py	Pyridine
q	Quartett
qn	Quintett
quant.	quantitative
R	organic group
rac	racemic
R_f	Retentions factor
RT	Room temperature
s	strong Signal
s	Singlet
T	Temperature
t	*tert*
t	Triplet
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMEDA	*N*,*N*,*N*,*N*-Tetramethylethylendiamin

vs	Very strong signal
ṽ	Wave length
w	weak signal

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