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Porous Organic Polymers Containing Active Metal Centers as Catalysts for Synthetic Organic Chemistry

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ABSTRACT: Porous organic polymers (POPs) containing catalytically active mononuclear metal centers can bridge the gap between homogeneous and heterogeneous catalysis. These materials offer catalysts with straightforward control over the active site analogously to homogeneous organometallic catalysts; however, just like classical heterogeneous catalysts, they are easy to separate from reaction mixtures and recycle. The main objective of this review is to provide an overview of the different types of reactions for synthetic organic chemistry where metal-POP catalysts have been utilized. In addition, a brief description of different synthesis strategies for accessing metal-POPs is included. We also propose a uniform naming system for metal-POP catalysts. Finally, current challenges, which could advance the field and facilitate industrial application, are discussed.

KEYWORDS: Heterogeneous catalysis, single-site catalysts, porous organic polymers, organic synthesis, metal catalysis, organometallic chemistry.

1. INTRODUCTION

In the view of the continuous environmental and economic challenges in the world there is a pressing need to develop a more sustainable and efficient chemical industry by creating and implementing more efficient chemical transformations. This can be done by developing new highly selective catalysts with increased product yield and therefore lowered process costs. Ideally, catalysts are developed by catalyst-design where the active sites are introduced so that the catalyst selectively drive the reaction to form only the desired products. The uniform active sites accessible in homogeneous catalysis often streamlines this task and allows for rationalization based on computational simulations.¹ In contrast, heterogeneous catalysts may contain multiple active sites which, historically, have led to a greater requirement for trial-and-error experiments in the production of numerous catalysts. Nonetheless, heterogeneous catalysts often displays significant advantages over homogeneous catalysts in terms of sustainability, recyclability, robustness, and ease of catalyst separation.^{2,3,4} One of the reasons for the trial-and-error approach in synthesis of heterogeneous catalysts, may be due to the difficulty in design and synthesis of well-defined uniform active sites in many types of heterogeneous catalysts. This is for instance illustrated in “classic” heterogeneous catalysts consisting of metal nanoparticles on a high surface area support, where several different types of active sites often exist on the metal particles.⁵ Catalyst-design of heterogeneous catalysts has therefore often focused on reducing the size of the active metal particles in order to enhance catalytic performance and efficiency of the heterogeneous nanoparticle catalysts. A reduction of the size of the metal particles in general leads to a more efficient use of metal as the relative surface area of the particles is increased. The ultimate size-reduction of nanoparticles is when each metal “particle” only consist of a single metal atom and

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3 each single metal atom acts as active site. Ideally, this will give a highly efficient use of the metal
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5 but would also lead to more well-defined and uniform active sites as known from homogeneous
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7 catalysis. However, the reduction of particle size enhances the tendency for particle sintering
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9 leading to a decrease in the catalytic activity. Thus, the development of sintering-stable
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11 heterogeneous nanoparticle catalysts has therefore attracted attention over the years and many
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13 strategies have been developed to address the problem of sintering of nanoparticle catalysts.^{6,7,8,9,10}
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15 Many synthesis strategies have also been developed in order to combine the advantages of
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17 molecular homogeneous catalysts and heterogeneous processes, in the aim to obtain the high
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19 reactivity and selectivity of the molecular catalysts, while facilitating product recovery and catalyst
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21 recycling.^{3,4,11,12,13}
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29 Herein, we will focus on the use of porous organic polymers (POPs) containing active
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31 mononuclear metal centers and how they are applied as single-site catalysts for synthetic organic
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33 chemistry (Figure 1). The solid nature of POPs and their high porosity makes them attractive in
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35 heterogeneous catalysis.^{14,15} In addition, the possibility to incorporate ligands in the structures of
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37 POPs makes it possible to design single-atom metal active sites. The active metal sites in POPs
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39 are well-defined and tunable similar to homogeneous catalysts. In this way, POPs containing active
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41 mononuclear metal centers are bridging the gap between homogeneous and heterogeneous
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43 catalysis.
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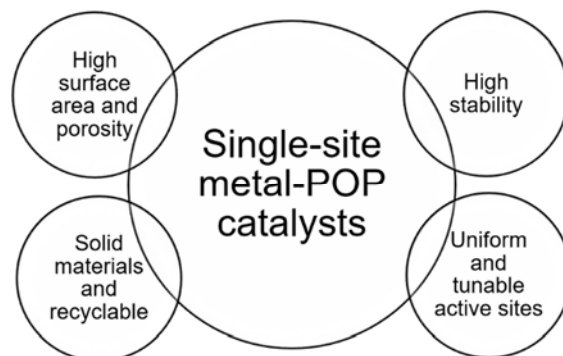


Figure 1. Important properties of porous organic polymers (POPs) containing active mononuclear metal centers for catalysis.

A number of excellent reviews, which focus predominantly on the synthesis and properties of metal-POPs for use in gas storage and catalysis, have been published.^{14,15,16,17,18,19,20,21,22,23} In this review, we will only provide a short overview of the different ways to synthesize POP-catalysts; instead, the main focus will be on the different reaction types – *from the perspective of synthetic organic chemistry* – where POPs containing an active mononuclear metal center have found use as catalysts. We have included as many representative examples as possible in order to demonstrate the variation in reactivity accessible at the current state of research in porous organic polymers containing an active mononuclear metal center. This overview focuses on the development during the last five years with the inclusion of a few illustrative earlier examples. Most of the selected examples utilize amorphous POPs containing robust, non-hydrolyzable carbon backbones. Although characterization of the metal-POP catalysts are an integral part of the research field, this

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3 review focuses on applications of metal-POPs in synthetic organic chemistry, and we refer to
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5 specialized reviews for in-depth discussion of different characterization techniques.²⁴
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10 Synthesis of POPs are done by polymerization of selected building blocks. In section 2 of this
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12 review, six different polymerization categories are briefly described: Radical polymerization,
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14 alkyne trimerization, nitrile trimerization, Sonogashira coupling, Friedel-Crafts reactions, and
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16 miscellaneous reactions (Figure 2). The end of section 2 will also shortly cover examples of
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18 metalation, where metal atoms are incorporated into the synthesized polymers, and the effect of
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20 polymer swelling. The following section 3 describes the different reaction types where POPs
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22 containing an active metal center have found use as catalysts. The reaction types have been
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24 categorized into seven main classes: Lewis acid catalysis, oxidations, reductions, coupling
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26 reactions, oxidative coupling reactions, photocatalysis, and miscellaneous (Figure 2). The final
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28 section discusses current challenges and future possibilities in the field. We hope the broad
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30 overview provided here can help identify current trends in the types of organic reactions that have
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32 been catalyzed by single-site metal-POPs and thus facilitate future advances in the field.
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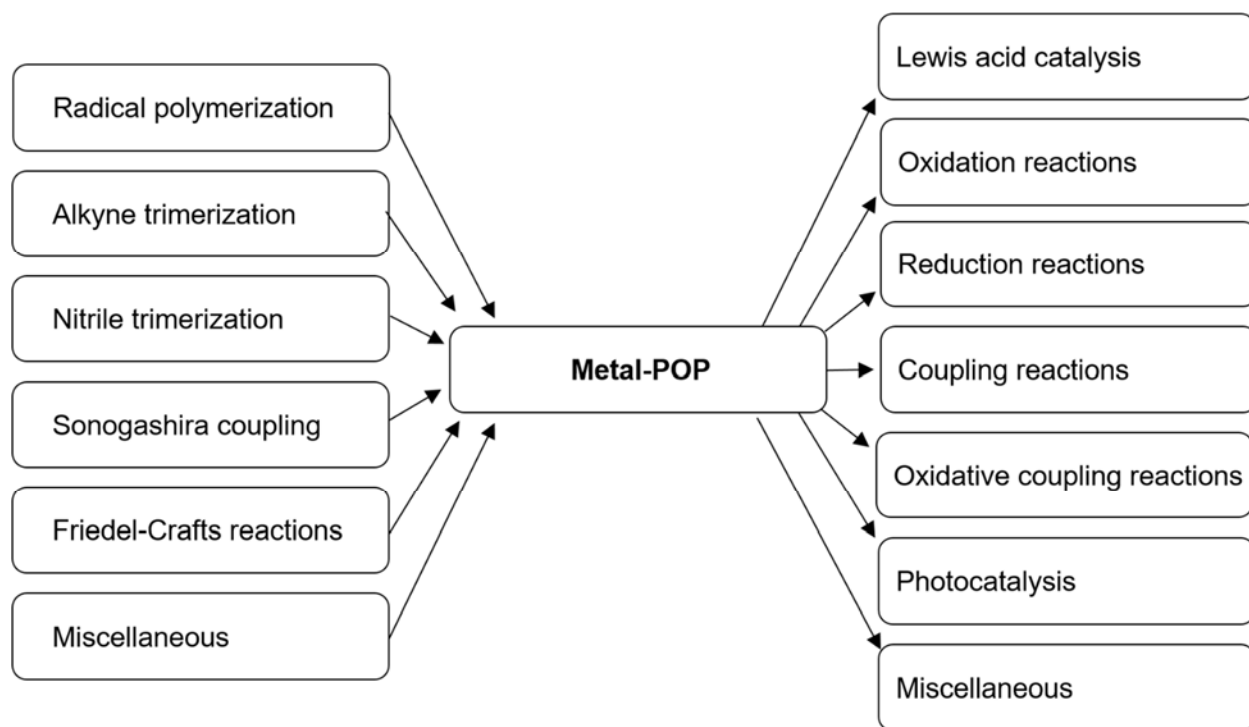
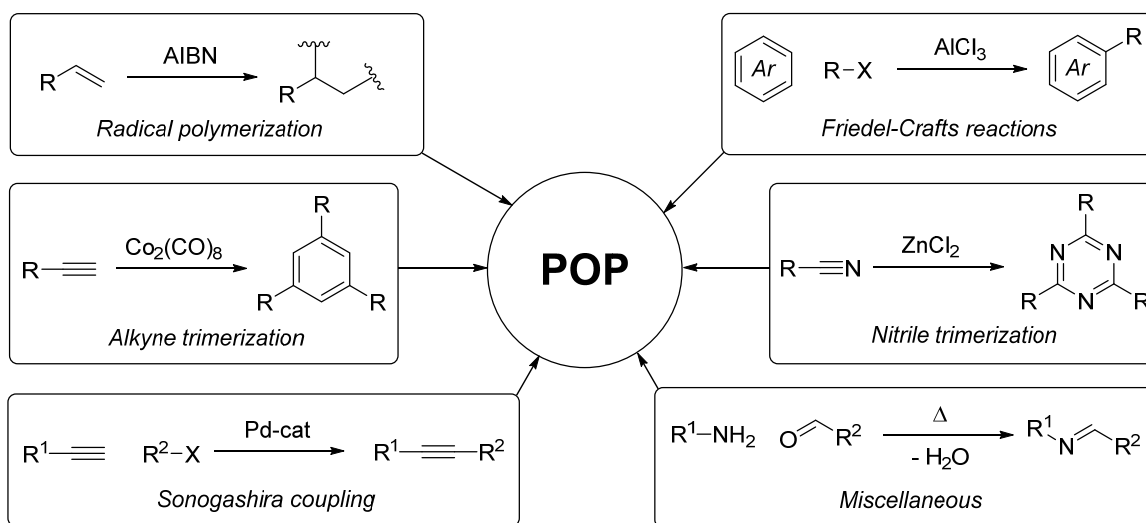


Figure 2. Overview of synthesis of metal-containing porous organic polymers (POPs) and their application in catalysis.

In order to label the different catalysts, we have used the systematic naming: *metal-ligand-POP*. The mentioned ligand is defined as the ligand which coordinates the metal to the polymer. Other ligands around the metal center are not mentioned in this nomenclature. Although the naming system does not take into account linkers and polymerization methods, we believe it is a good indicator for a first prediction of reactivity trends in a similar manner to homogeneous catalytic systems. For inclusion of more information, it is possible to add this in a parenthesis after the systematic name. In contrast to the diversity of catalyst labelling used in the field covered by this review, the application of such a nomenclature provides a concise and accessible overview when browsing through the research literature.

2. SYNTHESIS OF POP-CATALYSTS

For the past decades, surface area and porosity have been crucial properties for heterogeneous catalysis and controlling these parameters have been the target for many researchers.^{25,26,27,28} It is the same case for single-site catalysts incorporated into polymers, where the porosity makes the active sites more accessible and may lead to catalytic selectivity based on which substrates can reach and react with the catalytic sites. The porosity for POPs is most often achieved by having rigid monomers with specific binding sites for polymerization, which form a systematic and rigid porous polymer network. Therefore, the choice of building block(s) when synthesizing POPs has crucial impact on the porosity of the final polymer. This was for instance illustrated in the research by Li *et al.* where a BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthalene) monomer together with different rigid co-building blocks was used.²⁹ These co-building blocks influenced the porosity of the material which in turn affected the catalytic performance of the final catalysts. The porosity of the catalyst is also affected by the ligand-containing building block.^{14,30,31}



1
2
3 **Figure 3.** The different types of polymerization techniques presented in this review. Each
4 technique is represented by a general example.
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10 The chosen building block(s) has to be polymerized in order to obtain the POP, which may be used
11 for single-site catalysis. Polymerization of the building blocks can be achieved in different ways
12 (Figure 3). The polymerization methods have been categorized into six groups: Radical
13 polymerization, alkyne trimerization, nitrile trimerization, Sonogashira coupling, Friedel-Crafts
14 reactions, and miscellaneous reactions. Common for all categories is the possibility to vary the
15 composition of the polymer backbone by modifying the individual ligands/building blocks and/or
16 the ratio in between the used building blocks. Furthermore, it is also possible to change the solvent
17 and the size, type, and denticity of the linkers. All these different possibilities for modifications
18 make it possible to fine-tune the properties of the final catalyst including active site, metal loading,
19 and porosity.
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35 2.1. RADICAL POLYMERIZATION 36 37 38 39

40 A common strategy in the synthesis of single-site catalysts is the polymerization of alkene groups
41 through a radical mechanism. Therefore, ligands, which display the desired selectivity and activity
42 in homogeneous catalysis, are often the first choice for alkene functionalization followed by
43 polymerization to make new heterogeneous catalysts. The mechanism for the polymerization is a
44 free radical chain growth polymerization, which is initiated by a radical initiator. A commonly
45 used radical initiator is azobisisobutyronitrile (AIBN). The polymerization step is often conducted
46 by stirring the monomers and radical initiator together at room temperature before the mixture is
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transferred to an autoclave for solvothermal synthesis.^{30,32,33,34,35,36} The solvent is often *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), or chlorobenzene, but solvents like ethyl acetate³³, 1-methyl-2-pyrrolidinone^{37,38}, and mixtures such as benzotrifluoride/water³⁹ have also been used. The monomers used for this kind of polymerization are usually inspired by phosphine- or nitrogen-based ligands such as PPh₃^{30,40}, BINAP³⁴ or bipyridine⁴¹ (Figure 4).

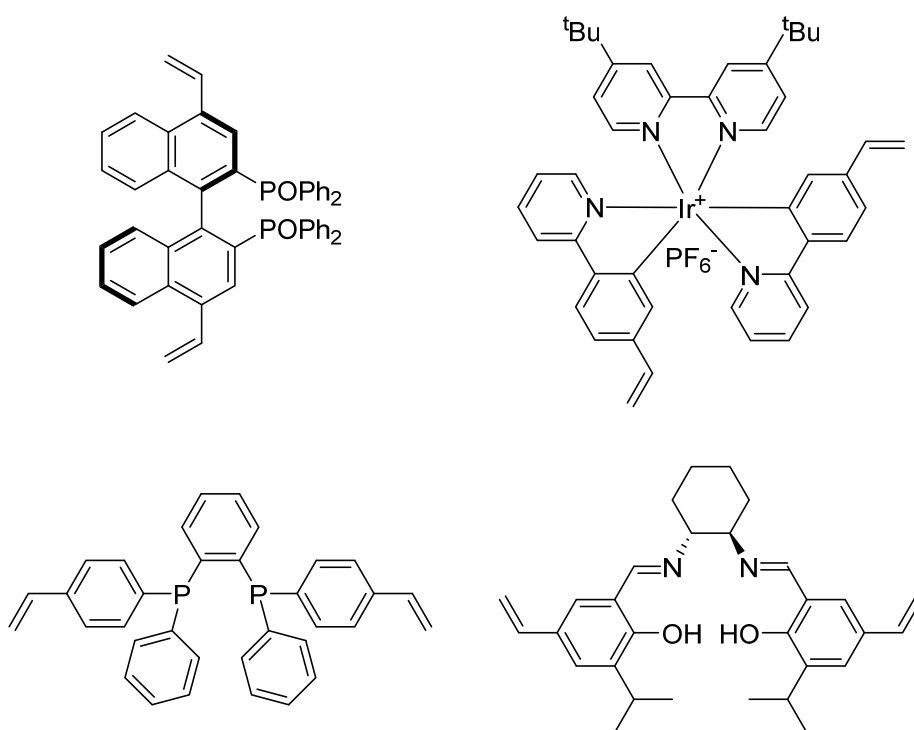


Figure 4. Examples of building blocks used for radical polymerization.

Divinylbenzene, styrene, and derivatives of styrene are common co-building blocks for radical polymerizations. An example of radical polymerization using a mixture of vinyl-functionalized ligand building blocks and co-building blocks was reported by Sawamura and coworkers.⁴² By

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3 mixing divinylbenzene and vinyl-functionalized bis(diphenylphosphino)benzene, a polymer was
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5 obtained where the bisphosphine was incorporated as every 60th unit, on average.
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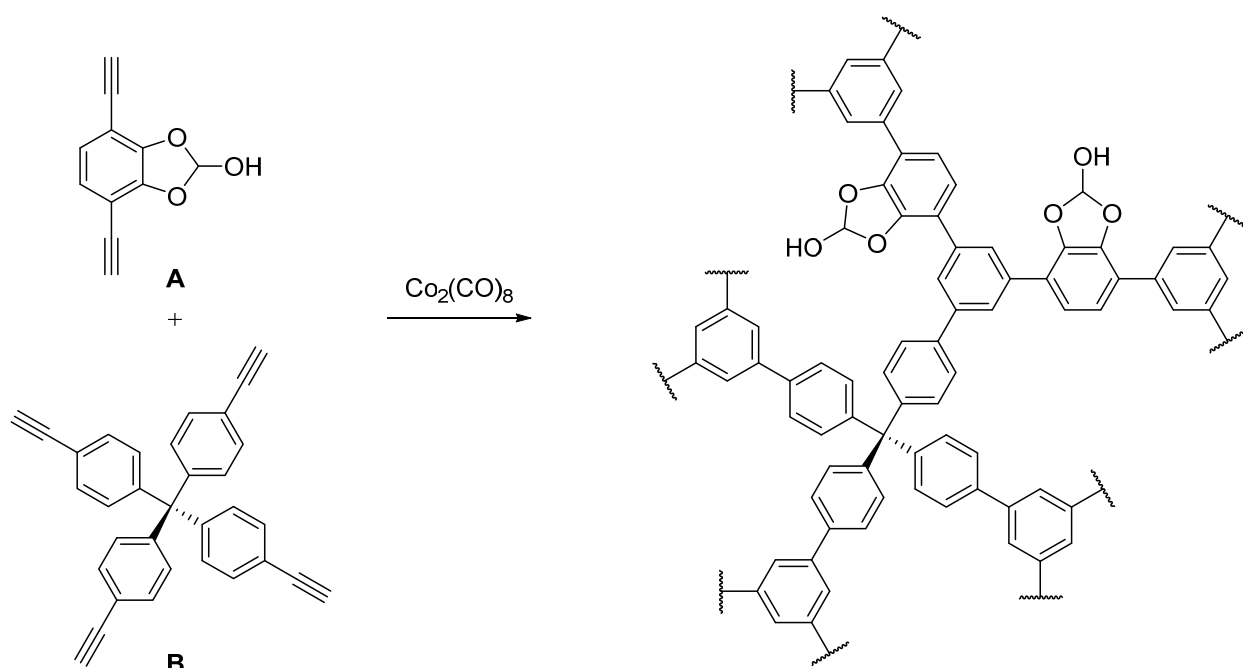
10 One of the advantages of radical polymerization in comparison to most other commonly used
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12 polymerization methods is that the polymerization takes place in the absence of metal catalysts.
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14 Accordingly, this approach removes the risk of metal-contamination in the final metal-POP
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16 catalyst and no precautions in this regard are required. Polymers made by radical polymerization
17
18 are often highly flexible, leading to almost quasi-homogeneous environments. Although these
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20 polymers are robust, the high frequency of benzylic C–H groups in the polymer backbone might
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22 make it prone to oxidation or functionalization under reaction conditions which generate radicals,
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24 e.g. certain oxidations and cross-coupling reactions.
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31 2.2 ALKYNE TRIMERIZATION

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36 Similar to radical polymerization, polymerization through alkyne trimerization, which forms
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38 connecting benzene moieties, is another widespread technique for synthesizing POPs. The
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40 catechol-POP synthesized by Nguyen and coworkers is a representative example of the utilization
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42 of alkyne trimerization (Scheme 1).⁴³ The Co₂(CO)₈-mediated polymerization reaction of 2,3-
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44 (ethoxymethylenedioxy)-1,4-diethynylbenzene (**A**) and tetrakis(4-ethynylphenyl)methane (**B**) is
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46 the foundation of various catalysts reported in literature.^{44,45,46,47,48,49,50,51} The catechol-POP is
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48 capable of coordinating to a large variety of different metals, including Ta⁴⁴, La⁴⁵, and Al⁴⁹.
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51 Furthermore, the composition of the polymer backbone can be modified as the ratio between the
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53 two building blocks, **A** and **B**, can be changed as seen with the **A**₂**B**₁ and **A**₁₀**B**₁ polymers.⁴³
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3 Altering the ratio between building block **A** and **B** gave control over the metal loading. For
4 manganese, a weight percentage of 10.9% was observed for the **A₂B₁** polymer and 21.8% for the
5 **A₁₀B₁** polymer. Similar to the metal loading, the surface area and pore volume changed as well
6 with changing the composition of the polymer. The **A₂B₁** polymer had a Brunauer-Emmett-Teller
7 (BET) surface area of 1050 m²/g and a pore volume of 0.41 cm³/g whereas the **A₁₀B₁** polymer had
8 617 m²/g and 0.25 cm³/g in comparison.
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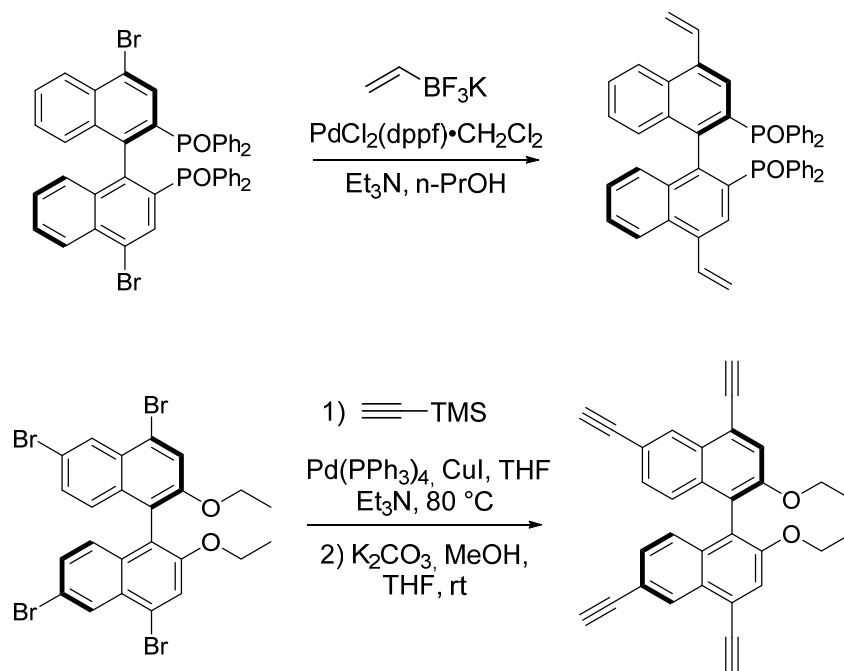


Scheme 1. Synthesis of a Catechol-POP through Alkyne Trimerization by Nguyen and Coworkers.⁴³

In contrast to radical polymerization, the alkyne trimerization is metal-catalyzed. Accordingly, an additional step, often acid wash, is necessary to ensure complete removal of this metal catalyst

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3 from the polymer. The absence of functional groups and weak C–H bonds in the final polymer
4 makes it robust to oxidation and radical intermediates.
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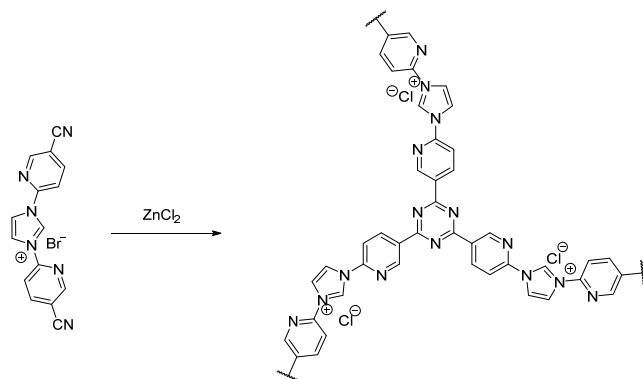
10 While the nature and flexibility of the linker in the final polymer is markedly different for radical
11 polymerization and alkyne trimerization (alkyl vs. phenyl), there are similarities in the building
12 block syntheses. This can be illustrated by comparing the syntheses of the BINAP-containing
13 building block for either radical³⁴ or alkyne⁵⁰ polymerization (Scheme 2). The introduction of the
14 handle for polymerization, vinyl or alkyne group, goes through the bromide-derivative in both
15 cases. Since the steps from the bromide-derivative are equally simple, both polymers are easy to
16 access with the common intermediate in hand.
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53 **Scheme 2. Comparison of Monomer Synthesis for Radical Polymerization and Alkyne**
54 **Trimerization for two BINAP-derivatives (dppf=1,1'-bisphenylphosphino)ferrocene).**
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2.3. NITRILE TRIMERIZATION

Trimerization of nitrile groups, forming triazine linkers, is another option for constructing porous polymers. The trimerization is similar to the alkyne trimerization described earlier but the reaction involves nitrile functionalities instead of alkynes (Scheme 3).⁵² The nitrile trimerization can be facilitated by different reagents and catalysts including ZnCl_2 ⁵³, trifluoromethanesulfonic acid^{54,55}, and nonylphenol.⁵⁶ Triazine-based polymers can also be synthesized directly from moieties of 1,3,5-triazine building blocks through various polymerization techniques such as aromatic electrophilic substitution,⁵⁷ radical polymerization,⁵⁸ condensation,⁵⁹ Sonogashira coupling,⁶⁰ and Friedel-Crafts reactions.^{61,62}



Scheme 3. Polymerization by Trimerization of Nitrile Groups Promoted by ZnCl_2 .⁵²

Triazine-based polymers often have a very high nitrogen content giving them properties that can differ quite significantly from less nitrogen-dense polymers.^{63,64} In terms of metal-POP catalysts containing defined metal-ligand centers, the high nitrogen content provides many alternative binding sites for the metal. In fact, polymers with high triazine content, without any other ligands, may serve as support for metal ions.⁶⁵ Accordingly, caution must be exercised to determine the

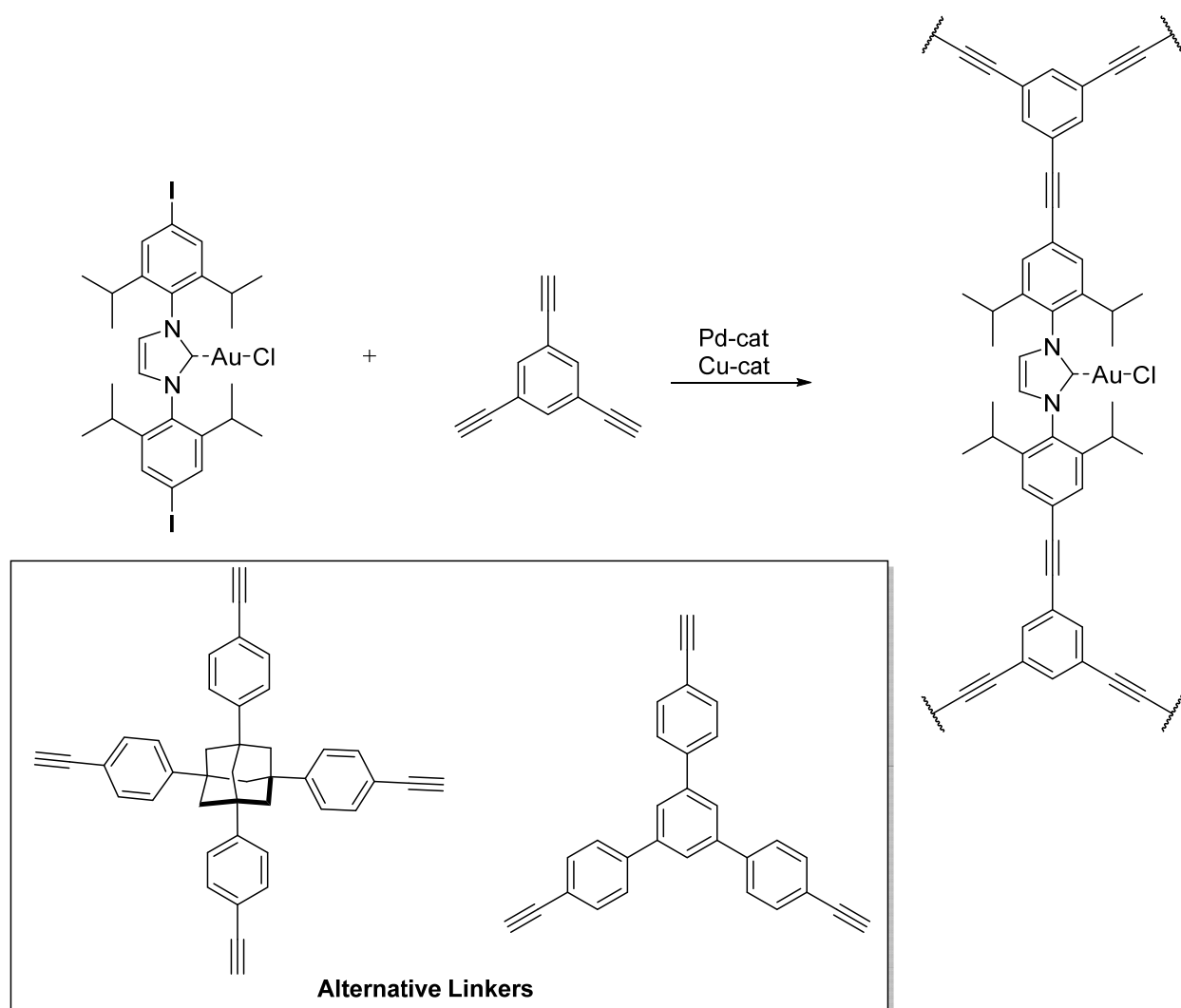
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3 actual metalation site in these polymers. In addition, polymers based on triazine often form
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5 crystalline, highly-ordered materials and, hence, they are outside the scope of this review. A review
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7 on triazine polymers and their application have recently been published by Ahn *et al.*⁶³
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10 11 12 2.4. SONOGASHIRA COUPLING 13 14 15 16

17 The Sonogashira coupling between a terminal alkyne and an arylhalide is another polymerization
18
19 reaction used to synthesize POPs for single-site catalysis.^{29,66,67,68,69,70,71,72,73,74} The reaction is
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21 catalyzed by a palladium/copper catalyst system, typically in THF or DMF and in the presence of
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23 PPh₃ and NEt₃. The coupling between two different functionalities is a useful feature in the
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25 synthesis of POPs as it provides full control over the polymerization process where only polymers
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27 with the ABAB composition can be formed. This is in contrast to the polymerization techniques
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29 described above where the building blocks are randomly incorporated into the polymer backbone.
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31 On the downside, the polymerization requires a precious metal catalyst. The presence of two
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33 transition-metals in the polymerization step using the Sonogashira coupling also necessitates a
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35 reliable method for their removal, in order to circumvent trace metal impurities, which could be
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37 catalytically active, in the final metal-POP.
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45 In the work of Li *et al.*, a single-site catalyst was synthesized by the Sonogashira coupling of 1,3-
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47 bis-(3-iodo-2,6-diisopropylphenyl)-imidazol-2-ylidene (I-IPr) with different rigid alkyne linkers
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49 (Scheme 4).⁶⁷ They studied the effect of altering the amount of solvent used to synthesize their
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51 polymers. The study shows that the pore size, surface area, and catalytic activity can be changed
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53 by using different amounts of solvent in the formation of the POP. Additionally, the effect of
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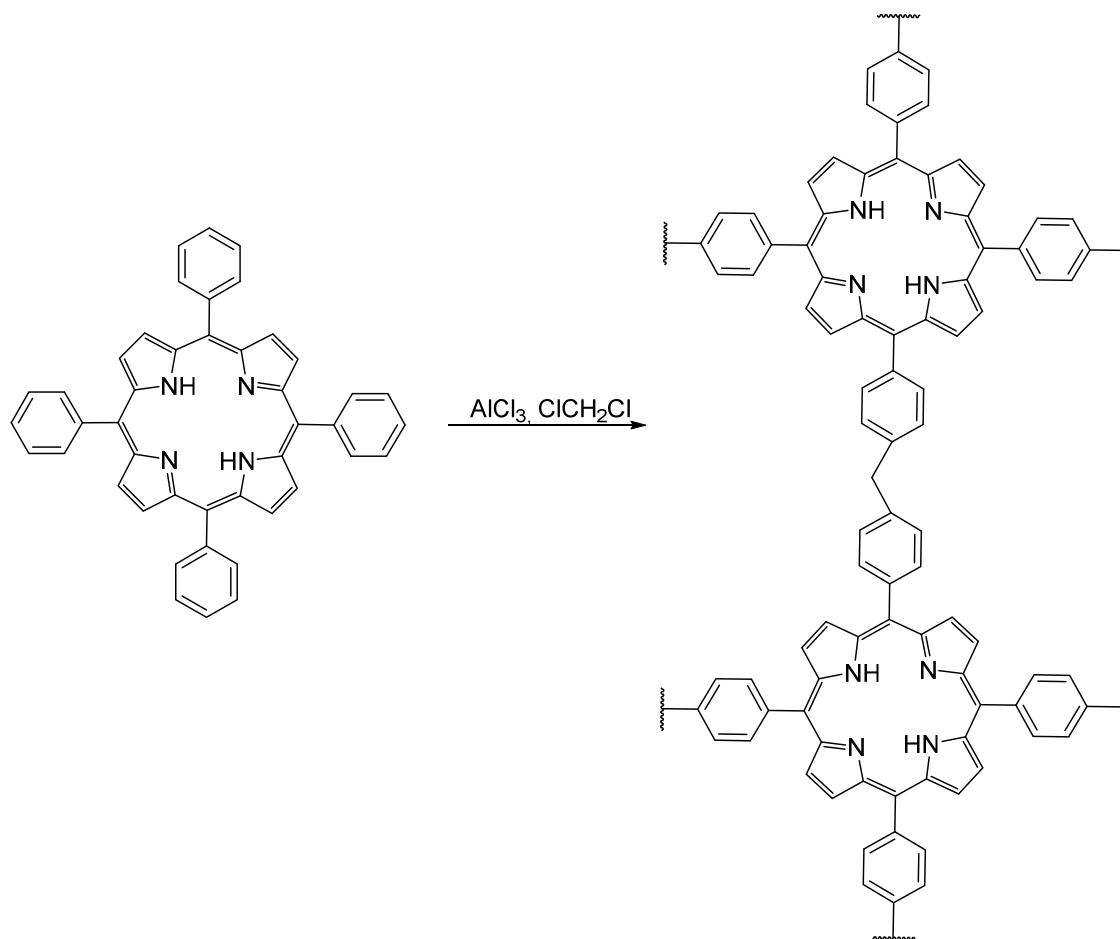
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3 changing size and denticity (3 or 4) of the linker on the resulting catalytic activity and porosity
4 was also investigated. It was concluded that the largest linker with a denticity of 4 yielded the best
5 catalyst. In another study, BINAP was used instead of IPr and either ruthenium or iridium
6 coordinated to the polymer.²⁹ For the polymer with iridium, the authors concluded that iridium did
7 not form any inactive dimers or trimers which are often observed for homogeneous iridium
8 catalysts.²⁹ This made the Ir-BINAP-POP more active than the homogenous Ir-BINAP catalyst
9 when assessed on the asymmetric hydrogenation of quinaldine.⁷⁵
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3 **Scheme 4. Synthesis of Au-IPr-POPs through Sonogashira Coupling by Li *et al.***⁶⁷
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6 2.5. FRIEDEL-CRAFTS REACTIONS
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11 Polymerization by Friedel-Crafts alkylation/acylation is another important method for
12 synthesizing single-site catalysts with polymer supports. The polymerizations are conducted by
13 using stoichiometric or excess amount of either FeCl₃ or AlCl₃ in combination with a linker
14 precursor such as dichloromethane or formaldehyde dimethylacetal.^{76,77,78,79} An advantage of
15 using Friedel-Crafts alkylation/acylation for the formation of POPs is that it does not require the
16 same kind of synthetic modification on the building blocks as the other techniques presented; the
17 Friedel-Crafts reaction can take place directly on aryl moieties without any pre-functionalization.
18 However, this also means that the cross-linking can be unselective and potentially even modify
19 the ligand sites, if they contain nucleophilic aryl groups. Although the metals used for
20 polymerization are cheap, the need for stoichiometric amounts during the polymerization again
21 emphasizes the importance of effective methods for metal removal from the POP. As a
22 representative example of polymerization by Friedel-Crafts reaction, Li, Tan, and coworkers
23 carried out the synthesis of a porphyrin-POP which displayed an excellent BET surface area (1360
24 m²/g) and a pore volume of 1.13 cm³/g (Scheme 5).⁷⁶
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34 **Scheme 5. Synthesis of a Porphyrin-POP by Friedel-Crafts Alkylation Reported by Li, Tan,**
35 **and Coworkers.**⁷⁶

36 2.6. MISCELLANEOUS

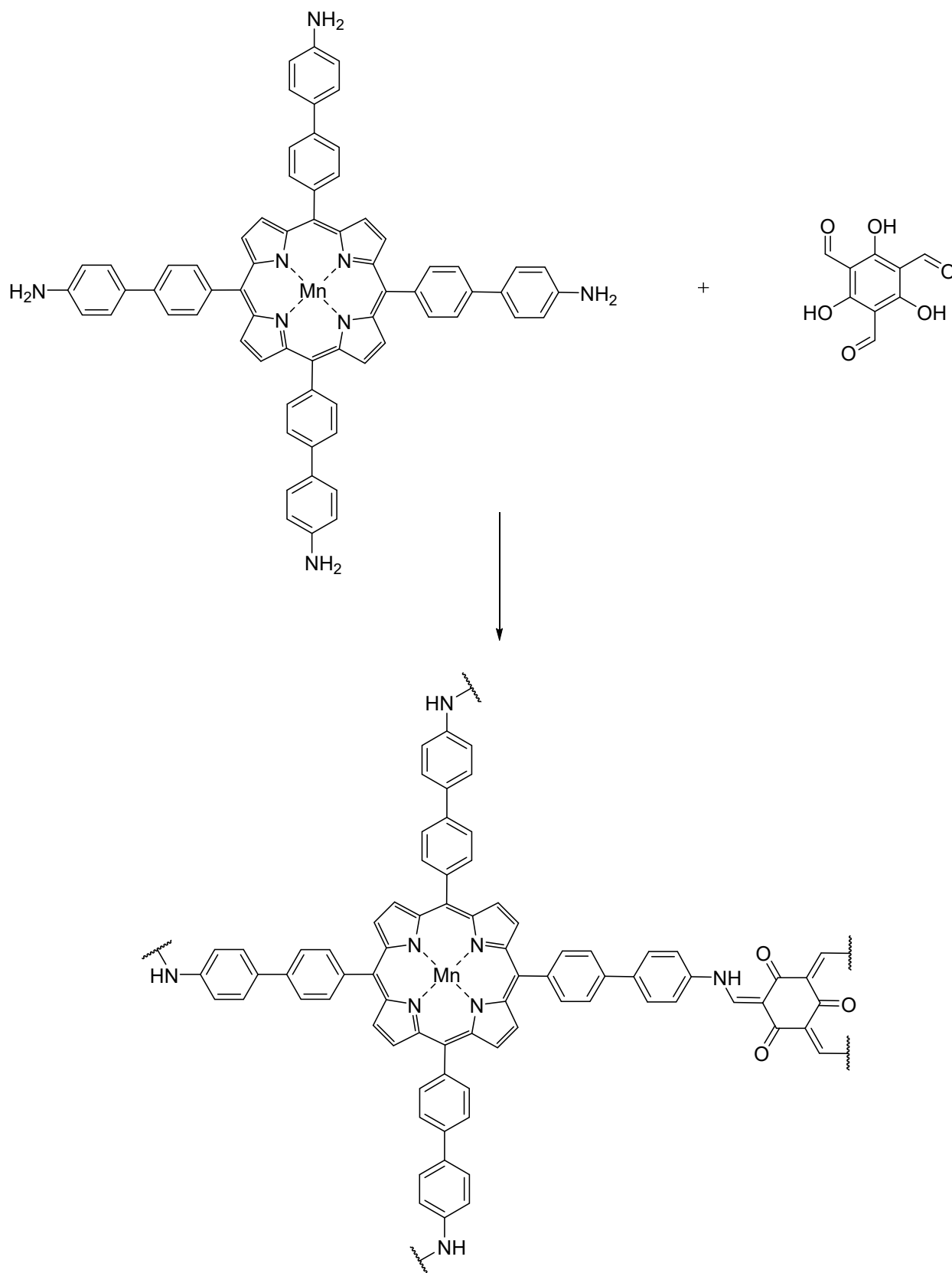
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Polymerization by condensation, where the driving force is release of water, has also been demonstrated.^{80,81} In the work of Gu *et al.*, an approach for the polymerization by a ketoenamine condensation of amino-functionalized porphyrin and 1,3,5-triformyl-phloroglucinol was conducted (Scheme 6).⁸⁰ This type of polymerization technique does not require additives in the form of radical initiators, metal catalysts, or stoichiometric amounts of metal in contrast to the

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3 other methods presented above. However, the condensations are, at least theoretically, reversible,
4 and the resulting polymer may not be as robust as those linked by carbon-carbon bonds.
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8 Condensations forming carbon-carbon bonds have also been demonstrated.⁸²
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12 Polymerization through oxidative coupling has also been reported.^{83,84} In the work by Han *et al.*,
13 two different iridium-based photocatalysts was synthesized by polymerization of polycarbazole-
14 bearing tris(2-phenylpyridine)iridium(III)-complexes.⁸⁴ The corresponding polymer contained a
15 high loading of iridium and proved to be very suitable for photocatalysis. This kind of
16 polymerization technique does not require a linker in contrast to many of the other examples
17 presented here. However, even in the absence of a rigid linker, the BET surface areas for the two
18 iridium-based polymers are still between 460-480 m²/g and the polymers have a defined
19 microporous structure.
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33 Among other methods used for the formation of metal-POPs are nucleophilic aromatic substitution
34 between fluoride-functionalized porphyrins and linkers bearing hydroxy-groups^{85,86}, nickel-
35 catalyzed Ullmann coupling for polymerizing porphyrin moieties⁸⁷, Suzuki cross-coupling
36 between bromide-functionalized porphyrins and aryl boronic esters⁸⁸, and oxidative Eglinton
37 coupling for synthesizing Ru-bpy-POPs³¹.
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Scheme 6. Synthesis of a Mn-Porphyrin-POP by Ketoenamine Condensation.⁸⁰

In the synthesis of polymeric single-site catalysts, many different approaches have been reported in recent years. In this review, the trends have been categorized into five groups with a few additional polymerization techniques mentioned in miscellaneous. The availability of various techniques for the synthesis of metal-POPs provides numerous possibilities for catalyst-design.

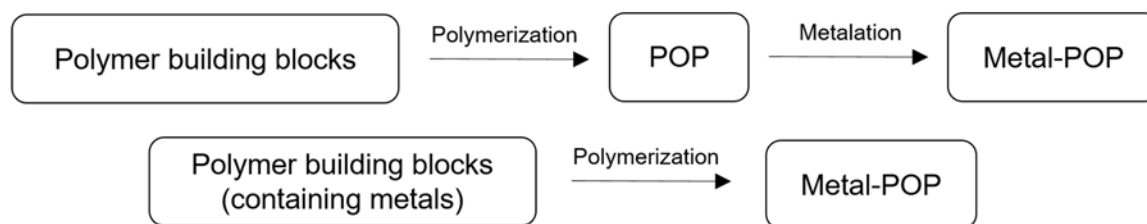
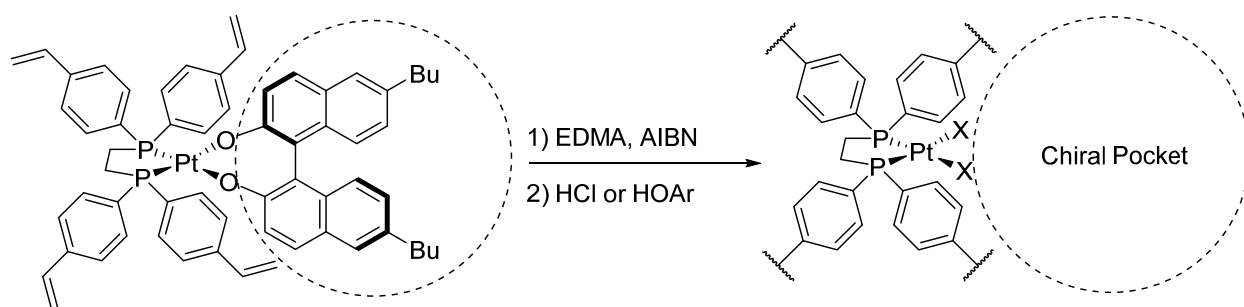
2.7. METALATION

Figure 5. Two different metalation strategies utilized for the syntheses of metal-POPs.

An introduction to different polymerization techniques for synthesizing different POPs has been presented in the previous sections. However, in order to obtain a single-site metal catalyst, a metal has to be incorporated into the structure of the POP. There are essentially two different approaches for metalation: Either metalation is performed after the polymerization step or the desired metal is already ligated to the ligand building block during the polymerization (Figure 5). For the first approach, the metalation is typically conducted by stirring a mixture of the POP and the desired metal precursor.^{37,38,45,76,81,84,89} The second approach is often used for synthesis of metal-containing porphyrin-POPs.^{87,88} A benefit of introducing the metal into the monomers before polymerization

is that the metalation can be almost quantitative whereas complete metalation after the formation of the POP may be difficult in some cases.⁸⁷ A disadvantage of this approach can be encountered if the chosen polymerization technique requires a metal catalyst. In such a case, it can be difficult to ensure complete removal of the metal polymerization catalyst without removal of the desired metal-centers in the metal-POP. For some POPs made from Ru-bpy or Ir-ppy complexes, the metal is crucial during the polymerization as it functions as a template for accessing the desired porous polymer. A different type of metal templating was exploited in a study by Gagné *et al.*, where the metal-coordination helps to induce a chiral cavity (Scheme 7).⁹⁰



Scheme 7. Synthesis of Chiral Pocket by Metal Templating Reported by Gagné *et al.* (EDMA = ethylenedimethacrylate)⁹⁰

Undesired metalation can take place if a transition metal is required during the polymerization step and a coordination site is available. This was indicated in the work by Nguyen and coworkers, where the presence of nickel was required for the polymerization step.⁸⁷ After the polymerization and workup, the POP still retain some nickel and an additional acid treatment was required to completely demetalate the POP. In some cases, complete metalation during the polymerization step is desired. In 2013, Bhaumik and coworkers reported the one-step synthesis of an Fe-porphyrin-POP by mixing FeCl₃, pyrrole, and terephthalaldehyde.⁸²

2.8. SWELLING

Swelling is a common phenomenon when working with polymers and has often been addressed as a drawback of using polymer supports over inorganic supports like oxides, zeolites etc.^{16,91} However, recent studies demonstrate how good swelling properties allows for more accessible catalytic sites and the high degree of flexibility affords catalytic systems which can mimic homogeneous behavior.^{92,93,94,95,96} An example reported by Xiao and coworkers clearly demonstrates this point. When comparing ³¹P static solid-state NMR of a dried dppe-based polymer with a swollen one (dppe = 1,2-bis(diphenylphosphino)ethane), they observed a broad peak for the dried POP (Figure 6a) while the swollen POP gave a sharp signal at almost the same chemical shift as dppe in solution (Figure 6b).⁹⁵ Polymer swelling is also a profound feature in physisorption experiments which may explain unusually behavior in comparison to other porous materials (hysteresis loops, microporosity etc.).⁹⁷

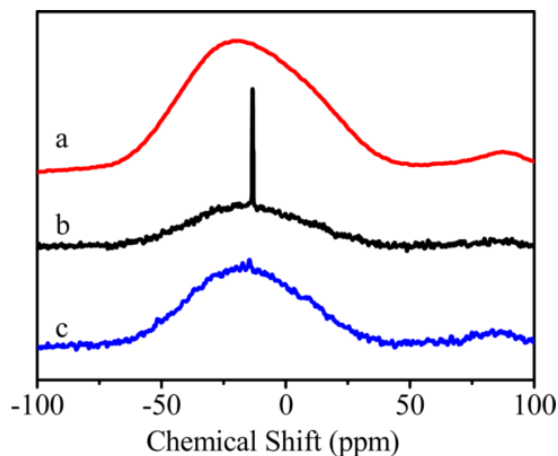


Figure 6. Static solid-state ^{31}P NMR of (a) the dried dppe-based polymer, (b) the dppe-based polymer in the presence of toluene, and (c) an non-porous dppe-based polymer in the presence of toluene. The sharp signal for the swollen polymer indicates homogeneous environment for the ligand in the swollen polymer. Adapted from Xiao and coworkers.⁹⁵

3. CATALYTIC REACTIONS USING METAL-POP-CATALYSTS

The following sections are intended to provide an overview of the different reaction types where porous organic polymers containing an active mononuclear metal center have found use as catalysts. For reaction types with multiple reports, rather than an extensive listing of all the individual reports, representative examples have been selected. However, in many cases, only a single report on a reaction type exists and occasionally even only a single example. The transformations have been categorized into six main classes: Lewis acid catalysis, oxidations, reductions, coupling reactions, oxidative coupling reactions, and photocatalysis. A seventh section for reactions which do not fit well into these categories is also included (Miscellaneous).

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3 Some of the synthesized single-site metal-POPs can catalyze reactions in more than one of the
4 main reaction classes and may accordingly be mentioned more than once.
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10 3.1. LEWIS ACID CATALYSIS 11 12 13 14

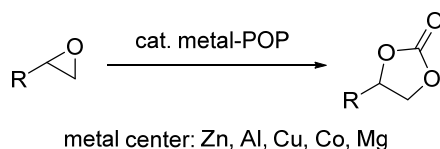
15 The reactions included in this section are redox-neutral reactions where the catalyst can be
16 considered to remain in the same formal oxidation state throughout the catalytic cycle. In
17 general, these reactions involve addition of a nucleophile to a Lewis acid-activated electrophile.
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19 Catalytic activation of both hard and soft electrophiles has been examined. An overview of the
20 reactions discussed in this section is presented in Table 1.
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29 **Table 1. Overview of Lewis Acid Catalysis with Metal-POPs** 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

Entry	Reaction	Catalyst	Reference
1	Cyclic Carbonate formation from CO ₂ and epoxides	Zn-PPh ₃ -POP	93,94,98
	-	Al-porphyrin-POP	38,77
	-	Co-porphyrin-POP	38,76,77
	-	Fe-porphyrin-POP	77
	-	Mg-porphyrin-POP	38
	-	Mn-porphyrin-POP	38,78,99
	-	Co-bpy-POP	41
	-	Cu-bpy-POP	41
2	Nucleophilic addition to epoxides	Fe-porphyrin-POP	85
3	Asymmetric addition of ZnEt ₂ to aldehydes	Ti-BINOL-POP	50
		Ti-TADDOL-POP	71
4	Hetero-Diels-Alder reaction	Fe-porphyrin-POP	78
5	1,3-Dipolar cycloaddition	Cu-Phen-POP	35
6	Methanolysis of organophosphate	La-catechol-POP	45
7	Alkyne hydration	Au-NHC-POP	67
	-	Au-PPh ₃ -POP	108
8	Hydroamination	Au-PPh ₃ -POP	108
9	Enyne rearrangement	Au-PPh ₃ -POP	108
10	Meyer-Schuster rearrangement	Au-PPh ₃ -POP	108
11	3,3-Rearrangement	Au-PPh ₃ -POP	108

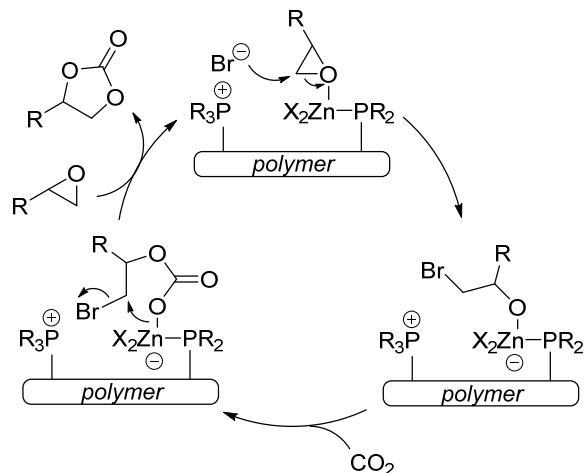
One of the most studied transformations with porous organic polymers containing an active mononuclear metal center is the reactions between epoxides and CO₂ leading to cyclic carbonates (Scheme 8).^{38,41,76,77,93,94,98} POPs with a range of different metals have successfully been used as catalysts for this transformation. The most commonly encountered metal in the active site is zinc, however, many other metals such as cobalt, aluminum, copper, and magnesium can also be used. Concurrent with the variation in metal, several binding sites for the metal have been reported including porphyrins, bipyridine, and phosphines. The two main strategies for assembling the metal-POPs, used for the CO₂-trapping, are radical polymerization

of vinyl-functionalized ligand monomers and Friedel-Crafts alkylation between aryl-containing ligand monomers and simple one- or two-carbon linkers.



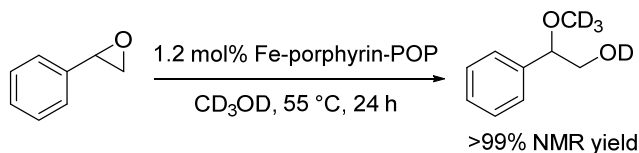
Scheme 8. Formation of Cyclic Carbonates from CO₂ and Epoxides

Interestingly, even though not a requirement, some of the examples of carbonate formation from epoxides and CO₂ suggest a beneficial effect from having a bifunctional active site in the POP. A representative example of this was reported in 2015 by Zhang et al. who copolymerized triphenylphosphine with methyltriphenylphosphonium bromide using a Friedel-Crafts reaction with dimethoxymethane.⁹⁸ The final catalyst was obtained after metalation with ZnBr₂. Similar bifunctional catalysts have been reported by Ding and coworkers, however, using a radical polymerization.^{93,94} The superior activity of catalysts containing both phosphine-coordinated zinc bromide and phosphonium species was explained with a cooperative mechanism involving both moieties (Scheme 9). In 2017, Yan, Ding, and coworkers reported that a bifunctional Mn-porphyrin-POP afforded an impressive TOF of 15,600 h⁻¹ for the carbonate formation from CO₂ and epoxides. They also demonstrated that the catalyst could be recycled at least four times with minimal loss of yield, and essentially no leaching was observed by ICP.⁹⁹



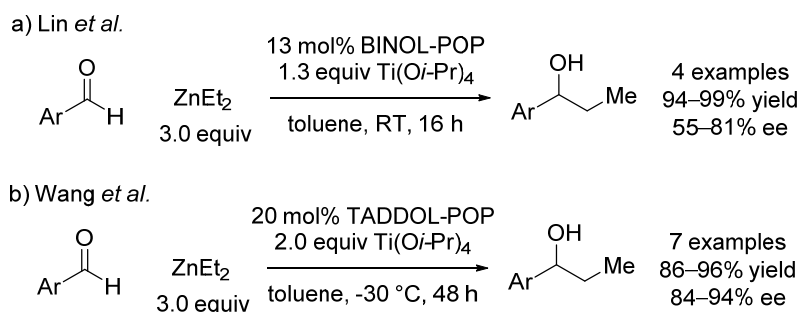
Scheme 9. Proposed Cooperative Mechanism for Cyclic Carbonate Formation using POPs Containing Bifunctional Sites

In addition to reactions with CO_2 , epoxide opening with an alcohol nucleophile using an iron porphyrin-based POP catalyst has also been reported (Scheme 10).⁸⁵ The polymer catalyst was assembled through an $\text{S}_{\text{N}}\text{Ar}$ reaction between hexahydroxytriphenylene and pentafluorophenyl moieties on the porphyrin monomers followed by metalation with FeCl_2 . No leaching was detected by ICP of the reaction mixture and recyclability of the catalyst was also demonstrated.



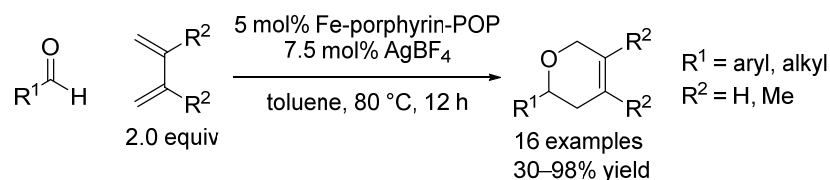
Scheme 10. Nucleophilic Addition to Epoxide Catalyzed by an Iron-Porphyrin-POP

The activation of carbonyl moieties using single-site metal POPs have also been studied. In 2011, Lin and coworkers reported titanium-catalyzed asymmetric addition of diethylzinc to aryl aldehydes (Scheme 11a).⁵⁰ The active metal center is titanium(IV) ligated to the heterogeneous polymer, which was made by cobalt-catalyzed alkyne trimerization of alkyne-bearing BINOL monomers (BINOL = (*R*)-(+)-1,1'-binaphthalene-2,2'-diol). Even though a significant excess of Ti(*Oi*-Pr)₄ is used, the activation of the metal catalyst by coordination to the BINOL-polymer is evidenced by the obtained enantioselectivities (55–81% ee). It was demonstrated that when increasing the catalyst loading to 65 mol%, the BINOL-polymer could be reused nine times without loss of enantioselectivity and consistently providing high yields. Later, Wang and coworkers reported that the use of a TADDOL-based chiral porous polymer (TADDOL = (*4R,5R*)-4,5-bis(diphenylhydroxymethyl)-2,2-dimethyldioxolane) could improve the enantioselectivity of the transformation (Scheme 11b).⁷¹ This polymer catalyst was made by Sonogashira coupling between alkyne-derivatized TADDOL and a C(sp³)-containing aryl bromide linker. The catalyst could be reused 10 times with no loss of yield; however, the enantiomeric excess of the product decreased from 91% ee in the first run to 76% ee in the 11th run. The loss of enantioselectivity was believed to be due to build-up of metal oxides and organic residual in the pores of the polymer.



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3 **Scheme 11. Titanium-Catalyzed Asymmetric Addition of ZnEt₂ to Aldehydes using (a) a**
4 **BINOL-POP Ligand and (b) a TADDOL-POP Ligand**
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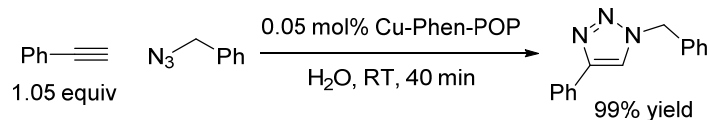
10 In 2016, Dou and Liu *et al.* reported that aldehydes can be activated for hetero-Diels-Alder
11 reactions with simple, unfunctionalized dienes by a combination of a heterogenized iron chloride
12 porphyrin (Fe-porphyrin-POP) and AgBF₄ (Scheme 12).⁷⁸ The heterogeneous catalysts were
13 made by hypercrosslinking iron porphyrins using Friedel-Crafts acylation which led to materials
14 with a high density of catalytic sites. A hot filtration experiment indicated that the catalysis was
15 heterogeneous in nature and it was also established that the catalyst can be reused four times.
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17 Finally, it was demonstrated that the reaction between benzaldehyde and 2,3-dimethylbuta-1,3-
18 diene can be performed on gram-scale with as little as 0.02 mol% Fe-porphyrin-POP, however,
19 the amount of added AgBF₄ was not specified.
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42 **Scheme 12. Hetero-Diels-Alder Reaction Catalyzed by Heterogeneous Iron-Porphyrin-POP**
43 **and AgBF₄**
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49 The powerful “click reaction” between a terminal alkyne and an organic azide can be also be
50 catalyzed by a POP-bound metal.^{100,101} In 2013, Meng, Chen, Xiao, and coworkers published a
51 copper-Phen-POP-catalyzed version of this formal 1,3-dipolar cycloaddition (Scheme 13).³⁵ The
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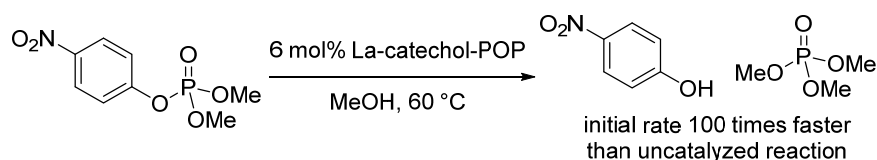
applied catalyst contains $\text{Cu}(\text{OAc})_2$ which is bound to 1,10-phenanthroline in a polydivinylbenzene-polymer. Turnover frequencies were in the range of 1116–2970 h^{-1} .



Scheme 13. Formal 1,3-Dipolar Cycloaddition Catalyzed by a Cu-Phen-POP

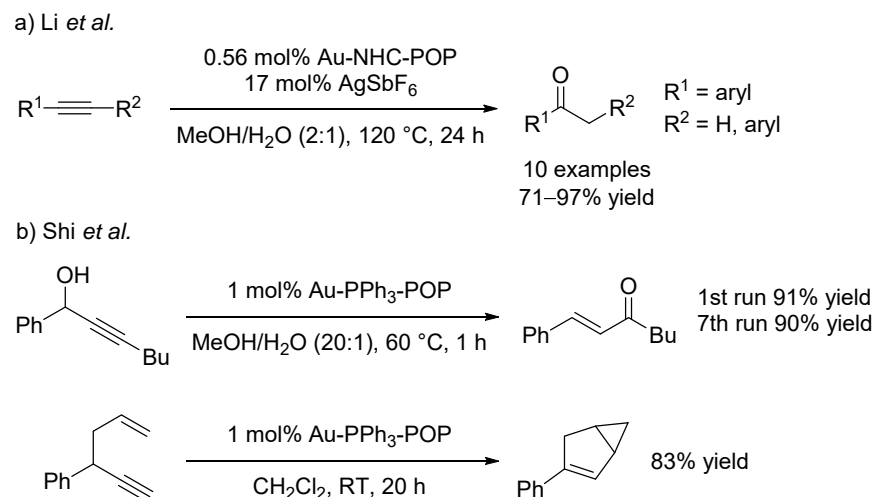
The hydrolysis and methanolysis of the phosphate ester motif in a nerve agent simulant has been demonstrated using a catechol-containing POP with an active lanthanum center (Scheme 14).⁴⁵

The polymer catalyst was made through cobalt-catalyzed alkyne cyclotrimerization between alkyne-functionalized catechol fragments and alkyne-containing linkers followed by postsynthesis metallation. Despite very limited leaching of metal from the best catalyst, significant deactivation was observed for the methanolysis reaction. The deactivation was accompanied by a significant decrease in surface area possibly by clogging of the pores by trapped, degraded lanthanum species. The hydrolysis reaction was much less prone to catalyst deactivation than the methanolysis reaction.



Scheme 14. Methanolysis of an Organophosphate Catalyzed by a Lanthanum-Catechol-POP

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3 In recent years the field of homogeneous gold catalysis has witnessed tremendous
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5 activity.^{102,103,104,105,106,107} Considering the numerous reaction types reported with gold catalysis
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7 and the high price of gold, it is not surprising that strategies for recycling these precious metal
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9 catalysts have also been investigated. In 2014, Li and coworkers reported that a porous organic
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11 polymer containing gold-coordinated NHC ligand sites can efficiently catalyze hydration of
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13 alkynes (Scheme 15a).⁶⁷ The polymer is made through a Sonogashira coupling between an
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15 iodide-functionalized NHC, IPr (IPr = 1,3-bis-(diisopropylphenyl)-imidazole-2-ylidene), and
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17 various alkyne-bearing linkers. Interestingly, a significant influence of the solvent volume used
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19 during polymer synthesis on pore-size and catalytic activity was observed. The catalyst was
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21 recycled five times with essentially constant yield (83–85%). After recycling, it was found that
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23 no hydration of the alkyne-containing linker in the polymer had occurred. While Li et al. only
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25 reported alkyne hydration, last year, Shi and coworkers demonstrated that, along with alkyne
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27 hydration, a range of other typical reactions in homogeneous gold catalysis are also accessible
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29 (Scheme 15b).¹⁰⁸ These reactions included hydroamination, enyne rearrangement, Meyer-
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31 Schuster rearrangement, 3,3-rearrangement, and an example of oxidative alkyne coupling (see
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33 Section 3.5). Instead of using NHC ligand sites in the polymers, Shi et al. used a phosphine-
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35 based polymer made through radical polymerization of vinyl-functionalized triphenylphosphine.
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37 For the majority of the reactions, no loss of yield was observed when recycled catalyst was
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39 utilized.
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Scheme 15. Selected Reactions Catalyzed by Gold-Containing Porous Organic Polymers: (a) Alkyne Hydration by Li *et al.* and (b) Meyer-Schuster Rearrangement and Enyne Rearrangement by Shi *et al.*

3.2. OXIDATION REACTIONS

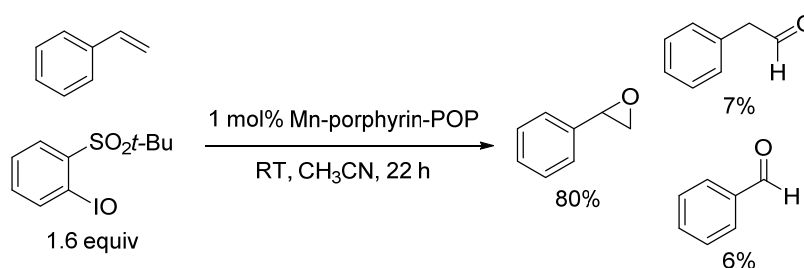
In this section, reactions where the substrate undergoes an overall oxidation are presented. The focus will be on oxidations in a more classical sense i.e. either addition of oxygen or removal of hydrogen (Table 2). Oxidative coupling reactions will be covered in a separate section (Section 3.5).

Table 2. Overview of Oxidation Reactions with Metal-POP Catalysts.

Entry	Reaction	Catalyst	Reference
1	Epoxidation of styrene	Fe-porphyrin-POP	81
	-	Mn-porphyrin-POP	80,81,87
2	Epoxidation of aliphatic alkenes	Mn-salen-POP	70
	-	Mn-porphyrin-POP	80
3	Oxidation of styrene to phenylacetaldehyde	Mn-porphyrin-POP	88
4	Oxidation of primary and secondary alcohols	Fe-porphyrin-POP	82
5	Benzylic oxidation of ethylbenzene	Mn-porphyrin-POP	80
6	Imine formation from benzylic alcohols and anilines	Ru-NHC-POP Ir-NHC-POP	73 73
7	Oxidation of benzylic alcohols	Cu-bpy-POP	79

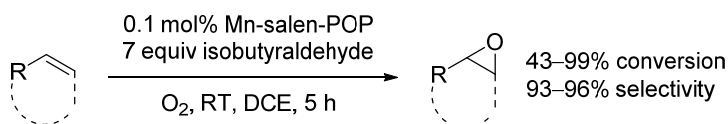
Oxidations of alkenes is among the most studied reactions with porous organic polymers containing an active mononuclear metal center. In 2011, Hupp, Nguyen, and coworkers demonstrated epoxidation of styrene by using a catalyst comprised of a manganese porphyrin complex embedded in a porous organic polymer.⁸¹ The analogous iron catalyst was also investigated but displayed inferior activity. In 2015, the same research group published a more comprehensive study of epoxidation of styrene and divinylbenzene catalyzed by a related manganese-porphyrin-POP.⁸⁷ The catalyst material was made by an Ullmann coupling between bromide-functionalized porphyrins and a tetrabromo-spirobifluorene. Manganese was incorporated into the polymer in a separate step. When styrene was used as the substrate, 80% yield of the corresponding epoxide was obtained. In addition, 7% phenylacetaldehyde and 6% benzaldehyde was observed (Scheme 16). A time-study revealed that benzaldehyde is formed from phenylacetaldehyde under the reaction conditions. Unfortunately, recycling was not possible due to difficulties with removing oxidant degradation products from the polymer. In 2017, Gu and coworkers also reported epoxidation of styrene with a manganese-porphyrin-

POP.⁸⁰ However, the polymer backbone was very different and PhIO was used as oxidant. These changes meant that the catalyst could be recycled as demonstrated by five consecutive runs where only a minor decrease in yield was detected.



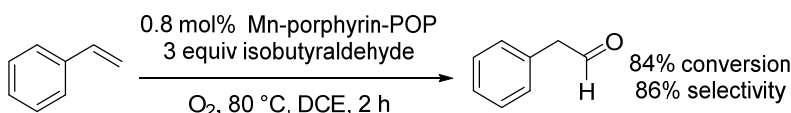
Scheme 16. Epoxidation of Styrene Catalyzed by a Mn-porphyrin-POP

In 2015, epoxidation of aliphatic alkenes, both terminal and internal (cyclic) was reported by Cao and coworkers.⁷⁰ A palladium-catalyzed Sonogashira coupling of a manganese-salen complex bearing arylbromides and 1,3,5-triethynylbenzene afforded the heterogeneous catalyst. In general, high selectivity for the epoxide products were obtained, but the rate was highly substrate dependent (Scheme 17). For cyclohexene, four recycling experiments were performed providing consistently high yield and selectivity. Although the salen complex used for catalyst synthesis was chiral and enantiopure, no enantioselectivity was observed in the epoxidations. Later, Gu and coworkers also reported epoxidation of aliphatic alkenes.⁸⁰



Scheme 17. Aliphatic Alkene Epoxidation Catalyzed by a Mn-Salen-POP

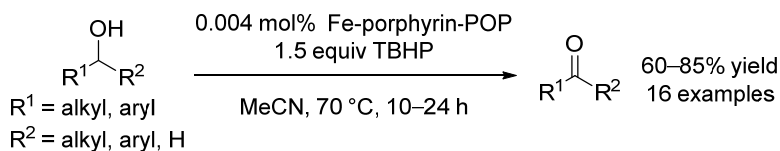
Selective oxidation of styrene to phenylacetaldehyde was published by Zou, Liu, and coworkers (Scheme 18).⁸⁸ The catalyst was similar to the one used by Hupp, Nguyen *et al.* for styrene epoxidation in the sense that it consisted of manganese porphyrins linked by an organic backbone. However, the porous organic polymer was assembled using a Suzuki-Miyaura cross-coupling instead of a Sonogashira cross-coupling. A higher reaction rate was observed for the manganese-metalated POP; however, significant background activity was found when using the manganese-free porphyrin-POP (>99% selectivity for phenylacetaldehyde). It was speculated that traces of residual palladium from the catalyst synthesis could be responsible for the background activity. Finally, it was demonstrated that the catalyst could be recycled four times without any decrease in turnover frequency.



Scheme 18. Catalytic Oxidation of Styrene to Phenylacetaldehyde

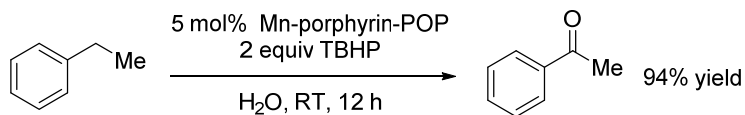
In 2013, Bhaumik and coworkers reported oxidation of primary and secondary alcohols to aldehydes and ketones using an iron-porphyrin-POP catalyst and *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant (Scheme 19).⁸² The reaction conditions could successfully be applied to a range of substrates. In addition, only a small decrease in yield was observed after

two recycles (from 85% yield to 80% yield) and no metal leaching was detected in the filtrate of a completed reaction.



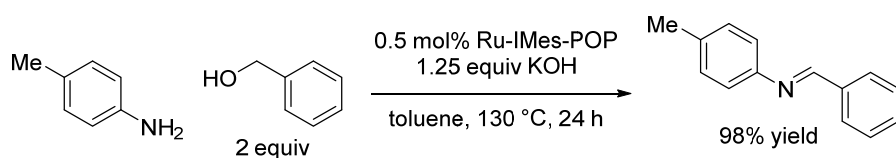
Scheme 19. Oxidation of Primary and Secondary Alcohols Catalyzed by an Iron-Porphyrin-POP

In 2017, Gu and coworkers demonstrated that the manganese-porphyrin-POP they used for olefin epoxidation could also catalyze benzylic oxidation of ethylbenzene and related unfunctionalized substrates.⁸⁰ In the presence of TBHP, ketones were obtained in mostly high yields and selectivity (Scheme 20). For ethylbenzene, over the course of five consecutive runs with the same catalyst, the yield of acetophenone only decreased from 94% to 86%.



Scheme 20. Acetophenone Synthesis from Ethylbenzene Catalyzed by a Manganese-Porphyrin-POP

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3 Another oxidation by removal of benzylic hydrogen has been reported by Iglesias, Sanchez, and
4 coworkers.⁷³ Using a porous organic polymer containing NHC ligands bound to either ruthenium
5 or iridium, it was demonstrated that imines could be formed directly from benzyl alcohols and
6 anilines, likely through arylaldehyde intermediates (Scheme 21). By modification of the catalyst
7 and reaction conditions, the selectivity could be altered favoring amine instead of imine
8 products. This is an example of a hydrogen-borrowing reaction and it will be discussed in more
9 detail in Section 3.6. Huang and coworkers have also reported oxidation of three benzylic
10 alcohols to arylaldehydes using a porous organic polymer containing copper-2,2'-bipyridine
11 active sites.⁷⁹



35 **Scheme 21. Oxidation/Condensation Sequence Catalyzed by a Ruthenium-IMes-POP (IMes**
36 **= 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene)**

3.3. REDUCTION REACTIONS

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46 Porous organic polymers containing an active mononuclear metal center have also catalyzed a
47 number of reactions where the substrate undergoes an overall reduction. These reactions include
48 alkene and alkyne reduction by H₂; carbonyl reduction by H₂, transfer hydrogenation, or
49 hydrosilylation; asymmetric carbonyl reduction; reductive amination; and hydrogenation of nitro
50 groups (Table 3).
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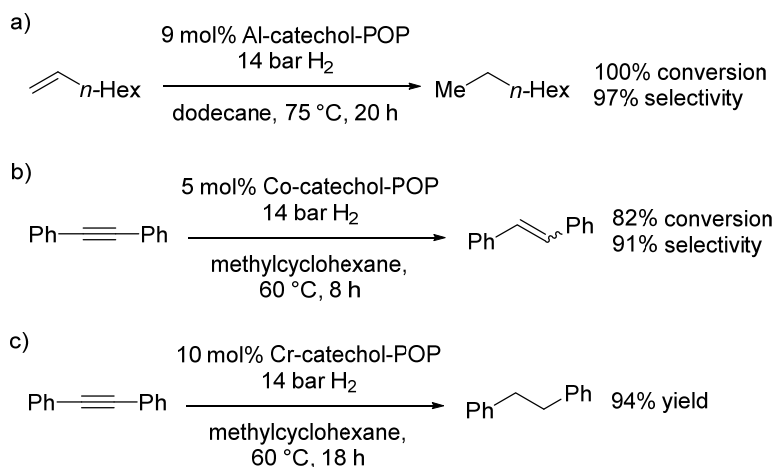
Table 3. Overview of Reduction Reactions with Metal-POP Catalysts.

Entry	Reaction	Catalyst	Reference	
1	Alkene and alkyne hydrogenation	Ta-catechol-POP	44,48	
		Ru-catechol-POP	109	
		-	Al-catechol-POP	48,49
		-	Co-catechol-POP	46,48
		-	Cr-catechol-POP	48
		-	Fe-catechol-POP	48
		-	Mn-catechol-POP	48
-	Ni-catechol-POP	48		
-	V-catechol-POP	48		
2	Reductive amination	Ir-ppy-POP	110	
3	Hydrogenation of β -keto esters	Ru-BINAP-POP	29,34,111	
4	Hydrogenation of quinoline		29	
5	Transfer hydrogenation	Ru-NHC-POP	73	
6	Carbonyl hydrosilylation	Fe-catechol-POP	47	

Most hydrogenations of carbon–carbon multiple bonds use simple alkenes or alkynes and rarely is functional group tolerance investigated. These reactions frequently use catalysts where the metal is bound to a catechol ligand in the porous organic polymer. The catechol-POP is typically made first by a cobalt-catalyzed cyclotrimerization between a (tetrakis)alkyne-bearing linker and protected catechol units also containing alkynes. After deprotection of the catechol moiety, the catechol-POP is finally metalated.

In an early report, Mader, Johnson, Nguyen, and coworkers demonstrated hydrogenation of cyclohexene to cyclohexane using a tantalum-catechol-POP catalyst and later Hock and coworkers used a rhodium-catechol-POP for propylene hydrogenation.^{44,109} In 2017, Stair and coworkers reported an aluminum-catechol-POP for use in hydrogenation of eight different alkenes and alkynes (Scheme 22a).⁴⁹ While monosubstituted alkenes led to high conversions,

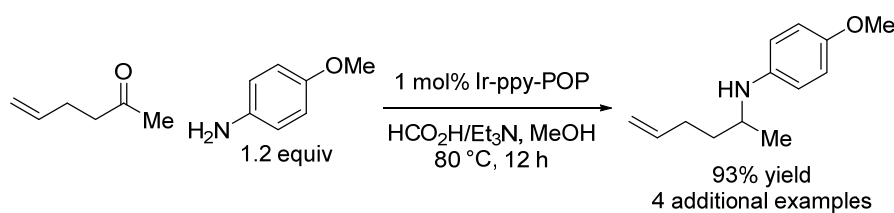
1,1-disubstituted as well as tri- and tetrasubstituted alkenes reacted very sluggishly. In contrast, both terminal and internal alkynes were highly reactive, however, only moderate selectivity was observed leading to a mixture of *cis/trans*-alkenes and alkane from overreduction. It was shown that a ketone and an imine did not react under the reaction conditions.



Scheme 22. Alkene and Alkyne Hydrogenation Catalyzed by Metal-Catechol-POPs. (a) Aluminum Catalyst, (b) Cobalt Catalyst, and (c) Chromium Catalyst.

Miller, Hock, Nguyen, and coworkers have also studied hydrogenation of diphenylacetylene using different first-row metal-catechol-POPs. First, semihydrogenation of diphenylacetylene was investigated using six different metal-catechol-POP catalysts.⁴⁸ For cobalt-catechol-POP, 91% selectivity for stilbenes was obtained at 82% conversion (Scheme 22b). In a different study, Hock and coworkers demonstrated that while a mixture of semi- and fully hydrogenated products were obtained with 5 mol% of chromium-catechol-POP catalyst, an increase in catalyst loading afforded 94% yield of the fully hydrogenated product (Scheme 22c).⁴⁶

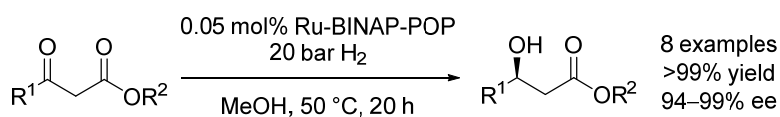
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3 Reductive elimination, i.e. hydrogenation of imines formed in situ, catalyzed by an iridium-
4 containing POP was reported by Cooper and coworkers.¹¹⁰ A palladium-catalyzed Sonogashira
5 coupling between 1,3,5-triethynylbenzene and Cp*IrCl cyclometalated onto a bis-
6 bromophenylpyridine afforded the Ir-ppy-POP. The application of 1 mol% of this catalyst in the
7 presence of formic acid led to high yields of the amine products (Scheme 23). The reaction
8 worked well with a primary and secondary amine and an aniline.
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Scheme 23. Reductive Amination Catalyzed by an Iridium-ppy-POP

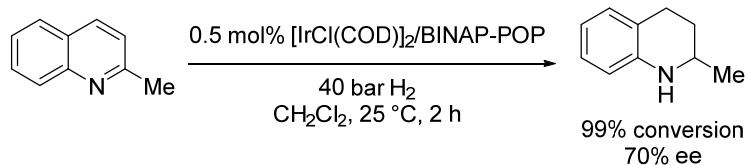
34 A few reports on direct reduction of carbonyl groups to alcohols have also appeared.
35
36 Asymmetric hydrogenation of β -keto esters using ruthenium-BINAP-POPs has been studied by
37 several groups. In 2012, Meng, Yang, Xiao, and coworkers synthesized a porous organic
38 polymer by radical copolymerization of 1,4-divinylbenzene and acrylamide-functionalized
39 BINAP (as the bis-phosphine oxide).¹¹¹ After reduction of the phosphine oxides, the polymer
40 was metalated with $[\text{RuCl}_2(\text{benzene})]_2$. Application of this material as catalyst for asymmetric
41 hydrogenation of eight different β -keto esters afforded the corresponding β -hydroxy esters in
42 high yields and with high enantioselectivity (Scheme 24). For one substrate, it was demonstrated
43 that the catalyst could be reused six times without any decrease in yield or enantioselectivity.
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55 Furthermore, an experiment with 0.02 mol% Ru-BINAP-POP also provided quantitative yield
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with only a small decrease in enantioselectivity (from 95% ee to 90% ee). In 2017, Ding *et al.* reported a related catalyst which was made by radical dimerization of 1,4-divinylbenzene and vinyl-functionalized BINAP followed by metalation with $[\text{RuCl}_2(\text{benzene})]_2$.³⁴ This catalyst also displayed good activity and enantioselectivity for hydrogenation of different β -keto esters. A hot filtration experiment showed that no catalytic activity was present in the liquid phase after the hot filtration, thus indicating the heterogenous nature of the catalyst.



Scheme 24. Asymmetric Hydrogenation of β -Keto Esters

In 2015, Liu, Li, and coworkers accessed a ruthenium-BINAP-POP through a different route.²⁹ The ligand-containing polymer was synthesized by a palladium-catalyzed Sonogashira coupling between different alkyne-linkers and 4,4'-dibromo-BINAP oxide. Subsequent reduction of the phosphine oxides and metalation with $[\text{RuCl}_2(\text{benzene})]_2$ afforded the ruthenium-BINAP-POP. Also this catalyst provided highly enantioenriched β -hydroxy esters in quantitative yields. Interestingly, a BINAP-POP, without ruthenium incorporation, was also combined with $[\text{IrCl}(\text{COD})]_2$ for the asymmetric hydrogenation of 2-methyl quinoline (Scheme 25). While the same degree of enantioselectivity was observed for $[\text{IrCl}(\text{COD})]_2/\text{BINAP-POP}$ and a homogeneous $[\text{IrCl}(\text{COD})]_2/\text{BINAP}$ system, the porous organic polymer catalyst displayed superior activity (99% conversion vs. 23% conversion).

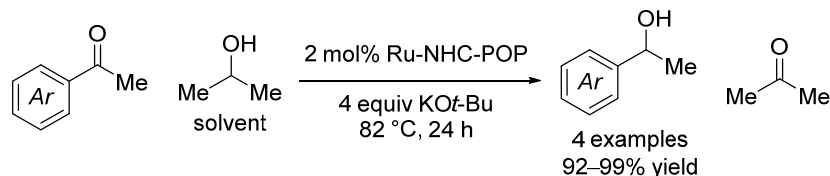


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Scheme 25. Asymmetric Hydrogenation of 2-Methyl Quinoline

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Iglesias, Sanchez, and coworkers reported that transfer hydrogenations from *iso*-propanol to acetophenones are also possible (Scheme 26).⁷³ This approach avoids the need for high hydrogen pressures for hydrogenation of the carbonyl moiety. It was demonstrated that the catalyst could be recycled six times providing continuously high yields of the alcohol product.



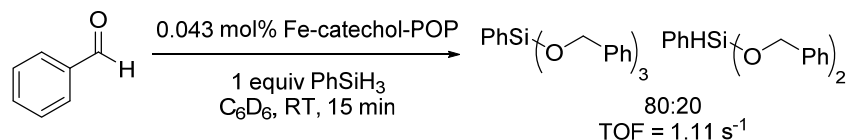
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Scheme 26. Transfer Hydrogenation for Reduction of Acetophenones

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Besides reduction of carbonyl groups by addition of hydrogen, hydrosilylation has also been demonstrated.⁴⁷ Hock and coworkers reported the use of an iron-catechol-POP as a highly active catalyst for addition of phenylsilane and diphenylsilane to ketones and aldehydes (Scheme 27). The applied catalyst was a porous organic polymer containing mono-catechol-complexed iron(II) centers. Interestingly, the mono-catechol complex was unattainable by mixing the iron-precursor and 3,6-di-*tert*-butylbenzene-1,2-diol in a homogeneous solution. It was suggested that it is the

spacial separation of catechol units in the polymer that allows for the formation of the coordinatively unsaturated iron complexes. The catalyst was highly air sensitive but very active for the hydrosilylation reactions. A filtration experiment revealed no catalytic activity in the filtrate.



Scheme 27. Hydrosilylation of Carbonyl Groups Catalyzed by an Fe-Catechol-POP

In addition to reduction of C=C, C=N, and C=O bonds, an example of nitro-group reduction in *para*-nitrophenol with NaBH₄ catalyzed by a ruthenium-POP has also been reported.⁷⁹

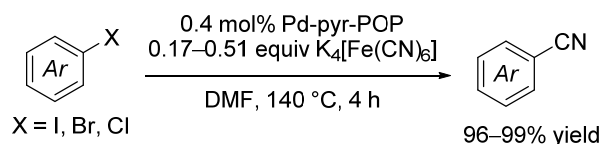
3.4. COUPLING REACTIONS

Coupling reactions are very powerful since they can form a variety of bonds such as carbon–carbon, carbon–nitrogen, and carbon–oxygen bonds.^{112,113} These reactions typically connect an aryl or vinyl halide electrophile with an appropriate nucleophile (amines, sulfides, organometallic reagents, etc.). An overview of the reactions discussed in this section is presented in Table 4. A few examples of oxidative coupling between two nucleophiles, in the presence of an oxidant have also been reported and will be discussed in a separate section (Section 3.5.).

Table 4. Overview of Coupling Reactions with Metal-POP Catalysts.

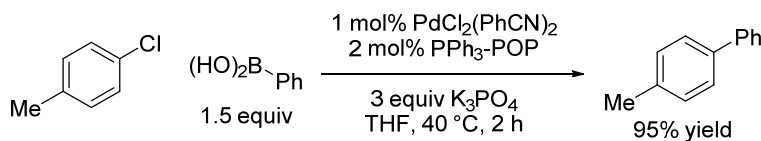
Entry	Reaction	Catalyst	Reference
1	Cyanation of aryl halides	Pd-pyr-POP	83
2	Suzuki-Miyaura cross-coupling	Pd-PPh ₃ -POP	96
	-	Pd-salen-POP	74
	-	Pd-bpy-POP	79
	-	Pd-IP-POP	116
3	Mizoroki-Heck reaction	Pd-salen-POP	74
4	Coupling of aryl pivalates and benzoxazoles	Ni-dppbz-POP	42
5	Amination of aryl chlorides	Ni-dppbz-POP	42
6	Ullmann coupling	Cu-IP-POP	89
7	Alkoxycarbonylation of terminal alkynes	Pd-PyPPH ₂ -POP	92

In 2017, Zhu, Zhang, Dai, and coworkers reported an efficient palladium-POP-catalyzed cyanation of various aryl halides (iodides, bromides, and chlorides) with K₄[Fe(CN)₆] as cyanide source (Scheme 28).⁸³ The catalyst was made by crosslinking dicarbazolpyridines using Friedel-Crafts alkylation with CH₂Cl₂ followed by metalation with Pd(OAc)₂, which coordinates to the pyridine-nitrogens. It was demonstrated that the catalyst could be used in four consecutive reactions providing continuously high yields. In addition, a hot filtration test also supported the intended heterogeneous nature of catalysis.



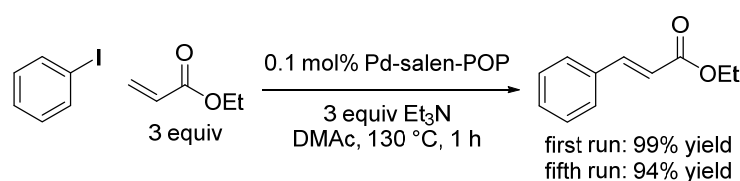
Scheme 28. Cyanation of Aryl Halides using a Palladium-Containing Porous Organic Polymer

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3 One of the most widely used homogeneous reactions in medicinal chemistry is the Suzuki-
4 Miyaura cross-coupling which connects aryl halides and aryl boron species.¹¹⁴ In 2013,
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6 Sawamura and coworkers reported the use of a phosphine-containing POP as a heterogeneous
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8 ligand for palladium-catalyzed Suzuki-Miyaura coupling.⁹⁶ The heterogeneous ligand was made
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10 by radical polymerization of vinyl-functionalized triphenylphosphine and 4-*tert*-butylstyrene
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12 leading to polystyrene-PPh₃. Interestingly, the rigid spacing of phosphine ligands leads
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14 exclusively to mono-phosphine-ligated palladium complexes, which is a key necessity for
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16 oxidative addition to aryl chlorides.¹¹⁵ Accordingly, a high yield of the desired biaryl product
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18 was obtained for the reaction between an unactivated aryl chloride and phenylboronic acid
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20 (Scheme 29). The use of POPs made from triphenylphosphines bearing vinyl-moieties on all the
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22 aryl groups provided the best yields for the Suzuki-Miyaura cross-coupling. Catalyst recycling
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24 was also examined. While the first four recycles of the catalyst provided continuously high
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26 yields, after reusing the catalyst seven times, only 24% yield was obtained. The apparent
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28 explanation for the deactivation was the formation of Pd(0)-nanoparticles, which was observed
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30 by HRTEM. ICP-AES showed negligible palladium leaching and a hot filtration test revealed no
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32 catalytic activity in the liquid phase. Other groups have reported on the Suzuki-Miyaura coupling
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34 catalyzed by other metal-POPs.^{74,79,116}



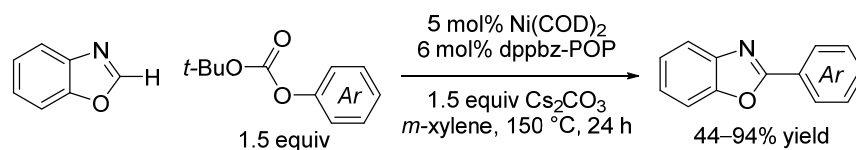
53 **Scheme 29. Suzuki-Miyaura Coupling Catalyzed by a Palladium-POP Complex**

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3 A palladium-POP has also been used to catalyze the widely-used Mizoroki-Heck reaction
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5 (Scheme 30).^{74,117} In a convenient synthetic approach, Liu, Mu, and coworkers prepared their
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7 catalyst by a Sonogashira coupling between 1,3,5-triethynylbenzene and palladium-complexes
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9 bearing bromide-functionalized salen ligands.⁷⁴ The palladium-salen complex catalyzes the
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11 incorporation of itself into the polymer, hence, the synthesis requires no separate metalation step.
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13 The application of this palladium-POP as catalyst in Suzuki-Miyaura and Mizoroki-Heck
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15 reactions was examined. Both aryl iodides and activated aryl bromides could be used as
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17 substrates for the reaction with acrylates. In addition, good recyclability of the catalyst was also
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19 demonstrated (Scheme 30).
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Scheme 30. Mizoroki-Heck Reaction Catalyzed by a Palladium Porous Organic Polymer.

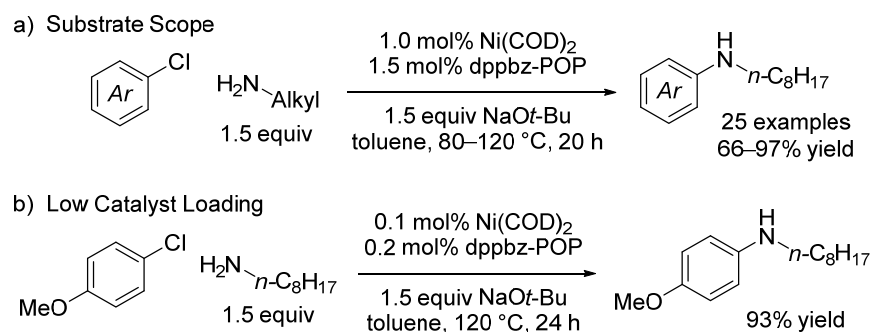
In 2017, Iwai, Sawamura, and coworkers reported another example of carbon-carbon bond formation, this time through a nickel-catalyzed coupling of aryl pivalates and benzoxazoles (Scheme 31).⁴² The heterogeneous ligand for nickel was made by the same radical polymerization procedure as for their PPh₃-POP but now using vinyl-functionalized 1,2-bis(diphenylphosphino)benzene (dppbz) leading to the polystyrene polymer. The yields were mostly moderate-to-good but in one case 94% yield was isolated.



Scheme 31. Nickel-Catalyzed Coupling of Aryl Pivalates and Benzoxazole

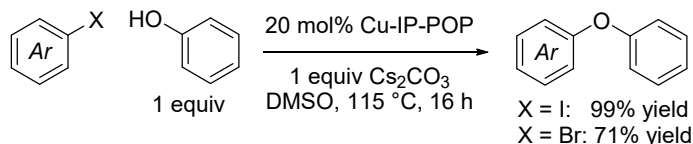
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Iwai, Sawamura, and coworkers also demonstrated that their porous organic polymer containing dppbz-ligand sites (dppbz-POP) could be used for aminations of aryl chlorides, which is another frequently used transformation in medicinal chemistry.^{42,114} By using dppbz-POP in combination with Ni(COD)₂, high yields of the aniline products were obtained for a range of primary amines as well as both electron rich and electron poor aryl chlorides (Scheme 32a). Furthermore, in one case, it was demonstrated that as little as 0.1 mol% nickel and 0.2 mol% dppbz-POP is sufficient to provide 93% yield of the desired aniline (Scheme 32b). The heterogeneous nature of catalysis was supported by a hot filtration test and a mercury poisoning experiment. However, slow leaching of nickel was found to hamper multiple reuses of the Ni-dppbz-POP catalyst (decrease from 90% to 73% yield over four consecutive reactions). An interesting feature of the various methodologies developed by Sawamura and coworkers is the use of *in situ* formation of metal-ligand complexes – a method which mirrors the one used in homogeneous catalysis. This approach allows for expedited screening of combinations of metal precursors and ligands. Another example of carbon–nitrogen bond formation (Chan-Lam coupling) has been reported; however, the applied catalyst is better described as a crystalline COF rather than an amorphous, porous organic polymer.¹¹⁸



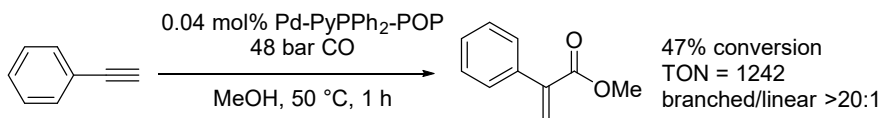
Scheme 32. Nickel-Catalyzed Amination of Aryl Chlorides (a) displays Broad Substrate Scope, and (b) can be performed with Low Catalyst Loading.

Porous organic polymers containing an active metal center have also found use for the formation of carbon–oxygen bonds. In 2013, Shi, Xiao, and coworkers reported the use of a Cu-POP as catalyst for Ullmann coupling between phenols and aryl halides (Scheme 33).⁸⁹ The catalyst was made by installing iminopyridine (IP) ligand motifs on a porous polydivinylbenzene polymer followed by metalation with Cu(OAc)₂. Seven different substrate combinations of various aryl iodides and phenols were examined, all providing good yields of the desired biaryl ether. Aryl chlorides were unreactive, but a reaction with bromobenzene highlighted the compatibility of these electrophiles. For all the substrates examined, the catalyst could be recycled at least four times without significant loss of yield relative to the first run.



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3 **Scheme 33. Cu-IP-POP-Catalyzed Ullmann Coupling for the Formation of Biaryl Ethers (IP**
4 **= iminopyridine)**
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10 In 2016, Zhu, Ding, and coworkers reported the use of a palladium-POP for alkoxy carbonylation
11 of terminal alkynes with good selectivity for the branched product (Scheme 34).⁹² The catalyst
12 was prepared by radical copolymerization of *para*-styrene sulfonic acid and a vinyl-
13 functionalized pyridyl-phosphine (PyPPh₂) followed by metalation with Pd(OAc)₂. The authors
14 demonstrated that, in the absence of acid additives, the presence of both pyridine and sulfonic
15 acid moieties is crucial for obtaining good activities. A hot filtration experiment supported that
16 the palladium-PyPPh₂-POP is operating as a heterogeneous catalyst and ICP-OES also showed
17 very limited palladium leaching. Furthermore, the catalyst could be recycled at least four times
18 with only a minor decrease in activity.
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41 **Scheme 34. Alkoxy carbonylation of Terminal Alkynes using a Palladium-PyPPh₂-POP**
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48 **3.5. OXIDATIVE COUPLING REACTIONS**
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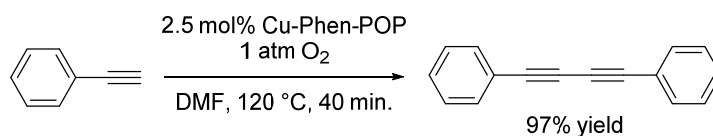
52 In addition to coupling reactions between an electrophile and a nucleophile, a few examples of
53 oxidative coupling reactions, i.e. reactions between two nucleophiles, have been reported.
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Although these reactions could be classified as oxidations, we have chosen the classification oxidative coupling reactions since the products often are related to products from coupling reactions. Typically, these reactions involve C–H functionalization of one or both coupling partners. At the current state, it has been demonstrated that metal-ligand-POPs can catalyze coupling reactions which functionalize C(sp)–H, C(sp²)–H, and C(sp³)–H bonds (Table 5).

Table 5. Overview of Oxidative Coupling Reactions with Metal-POP Catalysts.

Entry	Reaction	Catalyst	Reference
1	Alkyne C–H homocoupling	Cu-Phen-POP	35
	-	Au-PPh ₃ -POP	108
2	Aryl C–H homocoupling	Pd-OAc-POP	119
3	Aryl C–H acetoxylation	Pd-NHC-POP	120
4	Alkyl C–H arylation	Pd-Pyr-POP	121

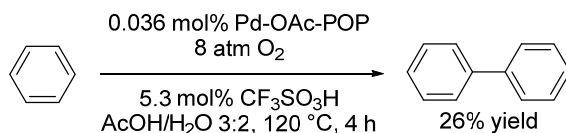
In 2013, Meng, Chen, Xiao, and coworkers demonstrated the use of a copper-containing POP for the oxidative coupling of terminal alkynes using O₂ as oxidant, i.e. Glaser coupling (Scheme 35).³⁵ Through the use of vinyl acrylamide-functionalized phenanthroline building blocks, this ligand was incorporated into a polymer by radical polymerization with 1,4-divinylbenzene. In a subsequent step, Cu(OAc)₂ was ligated to the phenanthroline sites. The obtained single-site Cu-Phen-POP was successfully applied as a catalyst for the oxidative coupling of terminal alkynes and it was demonstrated that the catalyst could be recycled nine times without loss of yield (97% in 10th run). In addition, ICP showed no copper in the filtrate after a reaction.



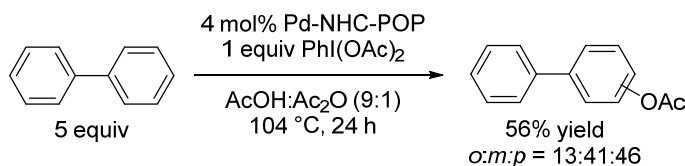
Scheme 35. Glaser Coupling using a Copper-Phen-POP Catalyst

Later, Ma, Shi, and coworkers reported that the Au-PPh₃-POP, which they used for Lewis acid catalysis (Scheme 15 and corresponding text), could also effectively catalyze the oxidative coupling of two terminal alkynes using PhI(OAc)₂ as oxidant.¹⁰⁸ A small decrease in activity was observed during four consecutive reactions with the same catalyst.

Oxidative homocoupling of benzene, toluene, and xylenes catalyzed by a palladium-POP was reported last year by Yan, Wang, and coworkers.¹¹⁹ Radical polymerization of maleic anhydride, sodium *para*-styrene sulfonate, and 1,4-divinylbenzene, followed by hydrolysis, afforded a polymer containing both carboxylic and sulfonic acids. An ensuing ion exchange with Pd(OAc)₂ produced the palladium-OAc-POP catalyst. By using 0.036 mol% of Pd-OAc-POP, biphenyl was produced in 26% yield after 4 hours (Scheme 36). The reaction was stopped at partial conversion and the selectivity for the biphenyl product over phenol was high. Attempts to reuse the Pd-OAc-POP twice showed a small decrease in activity which was accompanied by a significant loss of palladium content, as detected by ICP of the reused polymer.

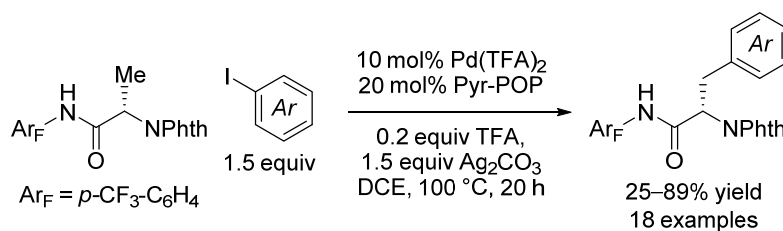
**Scheme 36. Oxidative Homocoupling of Benzene using a Pd-OAc-POP**

Another example of palladium-catalyzed oxidative C–H functionalization also appeared in 2017 when Wendt and coworkers reported on the acetoxylation of aromatic compounds.¹²⁰ The catalyst was accessed by radical polymerization of 1,4-divinylbenzene and NHC-palladium complexes containing vinyl moieties on the NHC-ligand. In the presence of the oxidant $\text{PhI}(\text{OAc})_2$, biphenyl and other simple unfunctionalized aromatic compounds could be acetoxyated (Scheme 37). A hot filtration experiment indicated heterogeneous nature of catalysis. In addition, similar kinetic profiles were observed for four consecutive runs demonstrating that the catalyst is highly recyclable. Interestingly, the same regioselectivity was observed with palladium-NHC-POP catalysis and with a related homogeneous palladium catalyst which suggests that the two systems have a similar mode of operation.



Scheme 37. Aryl C–H Acetoxylation Catalyzed by a Palladium-NHC-POP

In 2016, a rare example in heterogeneous catalysis of oxidative coupling by activation of a $\text{C}(\text{sp}^3)\text{--H}$ bond was demonstrated by Yu, Jones, and coworkers (Scheme 38).¹²¹ The transformation was catalyzed by palladium(II) bound to a 2-methylpyridine ligand in the porous organic polymer. The developed conditions display good functional group tolerance. Although the first catalyst recycling gave essentially the same result as the fresh catalyst, complete loss of activity was observed when the catalyst was reused a second time.



14 **Scheme 38. Oxidative C(sp³)-H Arylation Catalyzed by a Palladium-Pyr-POP (TFA =**
15 **trifluoroacetic acid)**

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21 **3.6. PHOTOCATALYSIS**

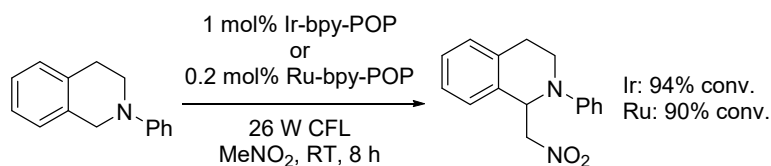
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23 The ability of a combination of visible light and a photocatalysts to drive known and novel
24 transformations under mild conditions have received considerable interest in recent
25 years.^{122,123,124} Although certain organic molecules, minerals, and first row transition-metal
26 complexes also display photocatalytic properties, at the present, the most widely-used
27 photocatalysts for organic synthesis are based on precious metals, especially ruthenium and
28 iridium. Even though the catalyst loadings are often low, facile recycling and reuse the expensive
29 metal catalysts would be a significant advantage. In this regard, a few reports have appeared on
30 heterogenization of ruthenium- and iridium-based photocatalysts by incorporation into a porous
31 organic polymer and their use in organic synthesis (Table 6).
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46 **Table 6. Overview of Photocatalysis Reactions using Metal-POP Catalysts.**

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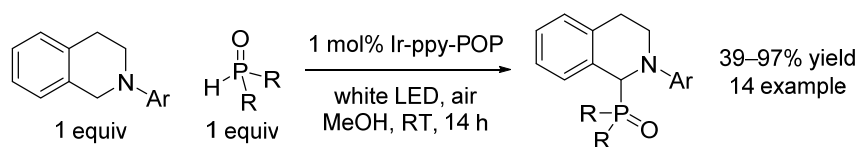
Entry	Reaction	Catalyst	Reference
1	Aza-Henry reaction	Ir-ppy-POP	51,84
	-	Ru-bpy-POP	31,51
	-	Ru-dipyrrin-POP	68
2	Coupling of tetrahydroisoquinolines and P-H nucleophiles	Ir-ppy-POP	39

In 2011, Lin and coworkers published the synthesis and use of two POP-photocatalysts.⁵¹ A cobalt-catalyzed cyclotrimerization between a linker bearing four terminal alkynes and bis-alkyne-functionalized Ru(bpy)₃Cl₂ or bis-alkyne-functionalized Ir(ppy)₂(bpy)Cl afforded the heterogeneous photocatalysts. Although the Ru-bpy-POP was also used for α -oxygenation of an imine (one example) and addition of bromomalonates to nucleophilic heterocycles (two examples), most of the study focused on aza-Henry reactions (Scheme 39). Both catalysts increased the rate significantly compared to the background reaction for the aza-Henry reaction between different tetrahydroisoquinolines and nitromethane or nitroethane. The ruthenium catalyst could be recycled at least four times with only minimal decrease in conversion. In addition, a filtration experiment supported the heterogeneous nature of the photocatalyst. In general, the most frequently examined reaction with POP-photocatalysts is the aza-Henry reaction.^{31,68,84}



Scheme 39. Photocatalytic Aza-Henry Reaction using Ruthenium- and Iridium-bpy-POPs

In 2014, Kobayashi and coworker reported a transformation related to the photocatalyzed aza-Henry reaction.³⁹ Instead of addition of a carbon nucleophile to tetrahydroisoquinolines, different phosphorus-based nucleophiles were utilized (Scheme 40). The catalyst was made by radical polymerization of different acrylates and iridium complexes carrying vinyl moieties on the ligands. High yields were obtained for a number of substrates and it was demonstrated that the catalyst could be recycled four times with only minimal decrease in yield and iridium leaching.



Scheme 40. Photocatalytic Coupling of Tetrahydroisoquinolines and P-H Nucleophiles

In addition to reactions involving addition of nucleophiles to an oxidized form of tetrahydroisoquinoline, examples of photocatalytic dehalogenation of an α -bromo ketone and oxidative imine formation have also been described but only very limited substrate scope was reported.³¹

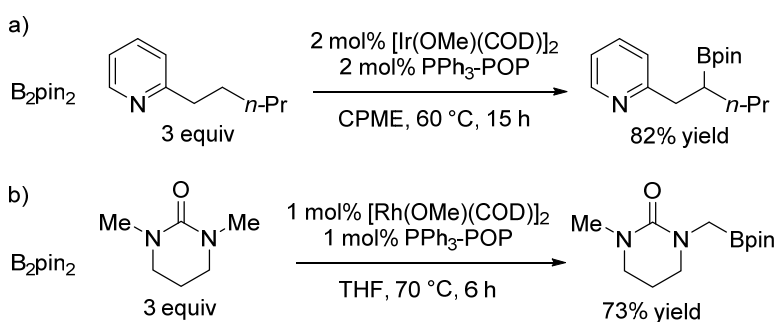
3.7. MISCELLANEOUS

The reactions in this section either fit more than one of the five main categories listed above or they do not fit into the main categories. These transformations include borylation, hydroboration, hydroformylation, ethylene dimerization, and hydrogen-borrowing reactions (Table 7).

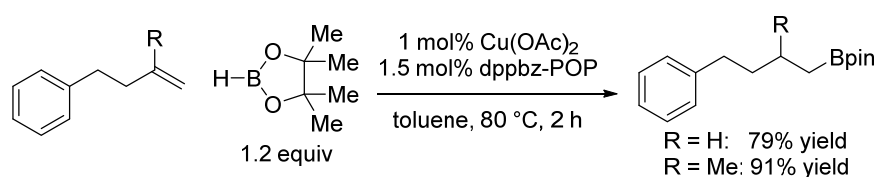
Table 7. Overview of Miscellaneous Reactions using Metal-POP Catalysts.

Entry	Reaction	Catalyst	Reference
1	C(sp ³)–H borylation	Ir-PPh ₃ -POP	96
	-	Ru-PPh ₃ -POP	96
2	Hydroboration of aliphatic alkenes	Cu-dppbz-POP	42
3	Alkene hydroformylation	Rh-dppe-POP	95
	-	Rh-PPh ₃ -POP	30,40,125
	-	Rh-PPh ₃ /Xantphos-POP	36
	-	Rh-phosphine/phoshite-POP	32,128
4	Ethylene dimerization	Ni-bpy-POP	129
5	Hydrogen-borrowing reaction	Ir-IMes-POP	73

Sawamura and coworkers reported rare examples of borylation of C(sp³)–H facilitated by a heterogeneous catalyst.⁹⁶ Using a directing group strategy, they demonstrated that an iridium-PPh₃-POP catalyst could effectively install a pinacolboronic ester group on 2-pentyl-pyridine (Scheme 41a). Furthermore, borylation of N-adjacent C(sp³)–H using a rhodium-PPh₃-POP was also included (Scheme 41b).

**Scheme 41. Borylation of C(sp³)–H Catalyzed by (a) Ir-PPh₃-POP and (b) Rh-PPh₃-POP**

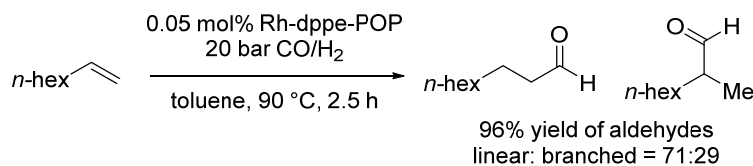
In 2017, Sawamura and coworkers reported another method for incorporating boron-functionalities into organic molecules using a metal-containing porous organic polymer catalyst. Metalation of their dppbz-POP (dppbz = 1,2-bis(diphenylphosphino)benzene) with $\text{Cu}(\text{OAc})_2$ afforded a highly active catalyst for hydroboration of both mono-substituted and 1,1-disubstituted alkenes (Scheme 42), thus adding another transformation to this versatile heterogeneous ligand (see amination and cross-coupling reaction in Section 3.4).⁴² Furthermore, it was demonstrated that CoI_2 could be used as metal source for hydroboration of α -methylstyrene. Interestingly, for the heterogeneous cobalt-based system, 63% yield was obtained while the analogous homogeneous $\text{CoI}_2/\text{dppbz}$ system afforded none of the hydroboration product.



Scheme 42. Hydroboration of Aliphatic Alkenes using a Copper-dppbz-POP Catalyst

Xiao and coworkers published a thorough investigation of alkene hydroformylation catalyzed by a rhodium-dppe-POP made by radical polymerization of vinyl-functionalized 1,2-bis(diphenylphosphino)ethane (dppe) and metalation with $\text{Rh}(\text{CO})_2(\text{acac})$.⁹⁵ This catalyst, containing a 1:10 metal to bis-phosphine ratio, was able to provide excellent yields and selectivities for the aldehyde products (Scheme 43). The regioselectivity (linear vs. branched) was highly substrate dependent. Among the various parameters investigated was the influence of ligand density in the polymer. It was found that the highest ligand density led to the highest

activity and selectivity, which was also observed in a later study on the same reaction.¹²⁵ Finally, it was demonstrated that a fresh catalyst batch and a catalyst that had been used in 10 recycles provided essentially identical kinetic profiles. The maintained catalytic activity highlights the excellent recyclability of the Rh-dppe-POP catalyst in the hydroformylation reaction.



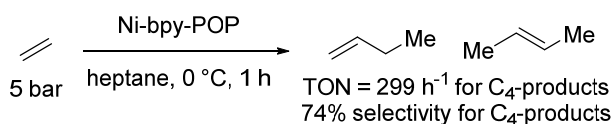
Scheme 43. Hydroformylation of 1-Octene with a Rh-dppe-POP Catalyst

A few additional reports on the use of rhodium-POPs for hydroformylation of alkenes have also appeared. In 2014, Meng, Ding, Xiao, and coworkers reported a triphenylphosphine-based polymer catalyst and later Yan, Ding, and coworkers utilized a mixed triphenylphosphine/Xantphos polymer.^{30,36} While all the above methodologies rely on phosphine-POPs, Yan, Ding, and coworkers made a mixed phosphine/phosphite polymer which was also used for hydroformylation of various terminal and internal olefins.³²

Continuous flow production have received considerable attention within recent years as an advantageous production method for the chemical industry.^{126,127} Interestingly, Ding, Liu, and coworkers demonstrated the successful application of a Rh-PPh₃-POP for continuous flow hydroformylation of ethylene in a fixed-bed reactor.⁴⁰ During the stability test, a TOF of approximately 4500 h⁻¹ was maintained over 1000 hours on stream with a corresponding 96% selectivity for propanal. Minimal leaching was detected during the stability test as the rhodium

content only decreased from 0.125 wt% in the fresh catalyst to 0.121 wt% at the end of the test. Further catalyst development lead to a highly active catalyst for hydroformylation of 1-butene.¹²⁸ It was demonstrated that a rhodium catalyst on a mixed phosphine/phosphite porous organic polymer afforded a TOF of 11,200 h⁻¹ with 94% selectivity for pentanal and a linear:branched ratio of 62:1 during 24 hours on stream. After 300 hours on stream a small decrease in activity to 5400 h⁻¹ was observed, however, this was not accompanied by any significant metal leaching.

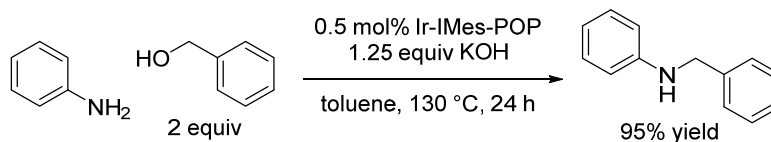
In 2017, Farha, Lee, and coworkers reported that ethylene dimerization could be catalyzed by a nickel-bpy-POP (Scheme 44).¹²⁹ The catalyst was made by a copper-catalyzed click reaction between alkyne-functionalized bipyridine and azide-containing linkers, followed by metalation with NiCl₂. The best selectivity for butene was obtained at 0 °C and 5 bar ethylene pressure. During four consecutive reactions with the same catalyst a ten-fold decrease in activity was observed. The deactivation was caused by significant formation of polyethylene on the catalyst.



Scheme 44. Ethylene Dimerization Catalyzed by a Ni-bpy-POP

In 2016, Iglesias, Sanchez, and coworkers reported an example of a hydrogen-borrowing reaction.⁷³ The reaction was catalyzed by an iridium-IMes-POP (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene) and proceeds through removal of H₂ from benzyl alcohol, condensation with an aniline, and then re-addition of H₂ to the formed imine (Scheme 45).

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3 Overall this is a redox-neutral reaction facilitated by removal and recycling of H₂. It was
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5 demonstrated that the catalyst could be recycled although a steady decrease in selectivity was
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7 observed beyond the fourth recycling. Tests for catalytic activity and for iridium leaching in the
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9 filtrate of a filtered reaction mixture indicated that the catalysis was heterogeneous in nature.
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Scheme 45. Hydrogen-Borrowing Reaction Catalyzed by an Iridium-IMes-POP

4. OUTLOOK

Heterogeneous catalysis is typically preferred by the chemical industry due to advantages such as facile removal and recycling of the catalyst material. However, designing heterogeneous catalysts which contain only one type of active site is a great challenge. Unfortunately, the presence of different catalytically active sites can lead to decreased product selectivity. In contrast, organometallic complexes used for homogeneous catalysis contains only one type of active metal center. The incorporation of organometallic catalysts into porous organic polymers combines the advantages of both catalyst classes as it affords heterogeneous catalysts which allows stringent control over the active site analogously to homogeneous catalysis. Accordingly, metal-POP catalysts are expected to be well-suited for industrial applications. While the reactions highlighted in this review clearly demonstrates the large potential of this emerging

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3 field, there are still several challenges to address in order to move from an academic curiosity to
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5 a widely applicable tool for organic synthesis and chemical production.
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10 Although examples of many different reaction types catalyzed by metal-POPs have been
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12 described here, sometimes only a single example of a reaction type is reported and, in many
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14 cases, very limited substrate scope investigation is performed. Expanded examination of
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16 substrate scope and limitations would be very useful information for researchers interested in
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18 applying the reported reactions, and thus facilitate more widespread use of these catalyst
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20 systems. Furthermore, for some industrially relevant reaction classes, such as asymmetric
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22 catalysis and C–H functionalizations, there are very few reports. Further investigations into these
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24 important reaction types would be highly valuable.
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31 In spite of the simple conceptual idea of heterogeneous organometallic catalysts, there are
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33 examples of differences in activity and distribution of catalyst species between metal-POPs and
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35 the analogous homogeneous systems. For example, incorporation of the ligand into a polymer in
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37 some cases prevents the formation of resting states where additional ligands are bound to the metal.
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39 In general, a better understanding of the catalytic cycles with metal-POP catalyst as well as the
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41 differences and potential advantages compared to the analogous homogeneous systems is
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43 warranted. In this regard, it is also important to be able to distinguish formation of discrete metal-
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45 ligand-POP complexes versus much less defined catalysts where the metal ions are randomly
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47 distributed at different types of ligand sites on a polymer support. These points could be addressed
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49 by experimental reaction mechanism elucidation and thorough characterization of the metal-POP
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51 catalysts.
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3 From an industrial point of view, there are several issues to consider. Significant advantages over
4 homogeneous catalytic systems are necessary to justify building block and polymer synthesis. A
5 straightforward comparison can be made based on TOF and TON for the metal-POP catalysts and
6 the corresponding homogeneous catalyst, when data are available. For large scale production of
7 bulk chemicals, these parameters are often decisive. For pharmaceutical production, other aspects
8 could also be relevant such as the facilitation of toxic metal catalyst removal from active
9 pharmaceutical ingredients.
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21 In terms of bulk chemical production, continuous flow reactors are typically preferred over batch
22 reactors. Due to the immobilized nature of the metal complexes in the metal-POPs, they could be
23 well-suited for such applications. Indeed, as presented in this review, a few successful reports on
24 this topic have appeared, however, reports are still scarce and additional research efforts would be
25 beneficial for the chemical industry. One of the key challenges in this field is the development
26 catalysts for a broad range of reactions which maintain activity and selectivity over extended time
27 on stream.
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38 Deactivation is a significant issue for recycling of heterogeneous catalysts as well as for
39 successful applications in continuous flow production. For the majority of reports in this review,
40 metal leaching seems to be a limited issue; nonetheless, catalyst deactivation is still observed
41 upon extended recycling. Only in a few cases have the changes in catalyst material
42 accompanying the deactivation been thoroughly investigated. Further insight into deactivation
43 pathways is necessary for developing more robust catalysts with extended lifetimes. This point
44 should be addressed by detailed analysis and characterization of deactivated catalysts. In fact, the
45 deactivated catalysts should undergo the same scrutiny as the fresh catalyst, for example
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3 nanoparticle formation in the used catalyst could be examined by TEM as a cause of deactivation
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5 despite minimal metal leaching.
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10 Significant advances have been made in the use of metal-ligand-POP catalysts for synthetic
11 organic chemistry and the current state-of-the-art has moved beyond proof-of-principle. However,
12 as listed above, there are still several challenges to address in order to obtain a better understanding
13 of these catalyst systems (e.g., catalytic cycles and deactivation pathways), improve catalyst
14 stability, as well as examine the suitability of these catalysts for real chemical production. Finally,
15 further investigations which target new reaction types and improve substrate scopes are needed for
16 obtaining a broader and more robust foundation for addressing synthetic challenges in the
17 production of fine and bulk chemicals. We hope the overview of reactions presented here will help
18 identify unexplored territory and guide future research efforts to focus on unsolved issues.
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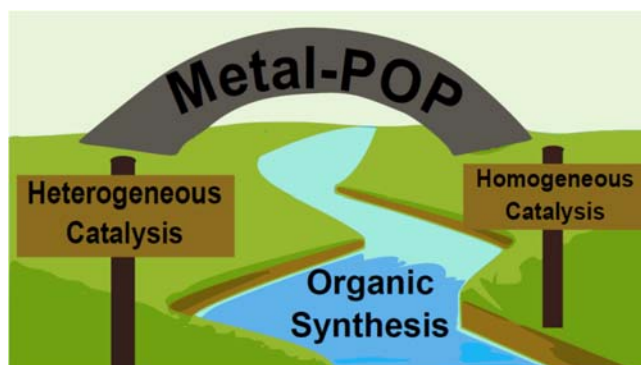
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22 copolymer supported Rh catalysts for heterogeneous hydroformylation of butenes. *Appl.*
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28 Complex on a Bispyridine-Based Porous Organic Polymer as a Heterogeneous Catalyst for
29 Ethylene Oligomerization. *Catal. Sci. Technol.* **2017**, *7*, 4351–4354.
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TOC-Graphic



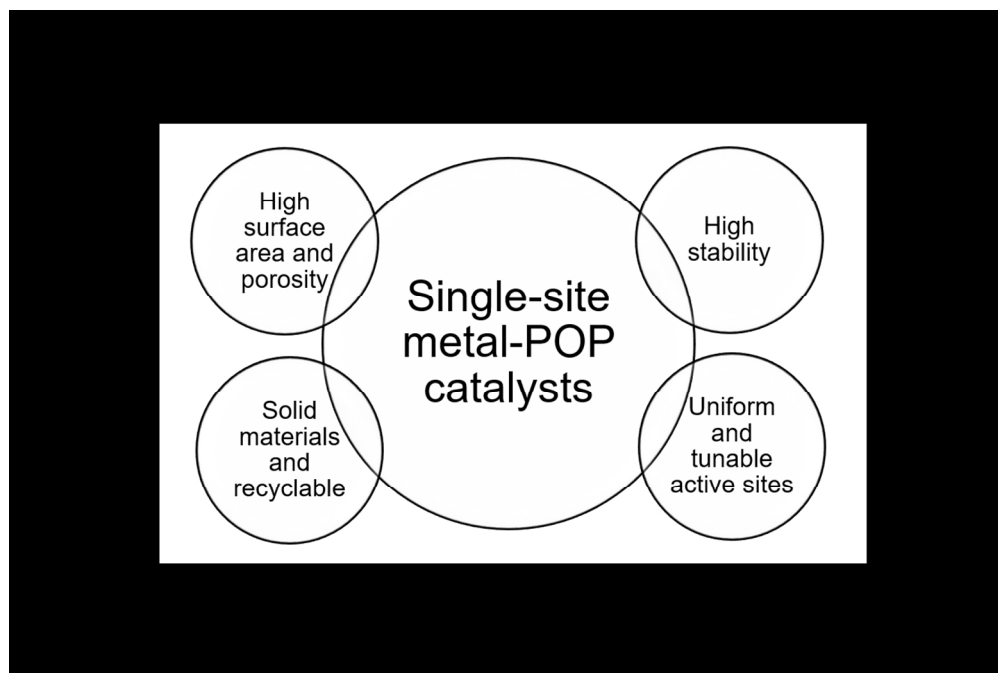


Figure 1. Important properties of porous organic polymers (POPs) containing active mononuclear metal centers for catalysis.

225x150mm (150 x 150 DPI)

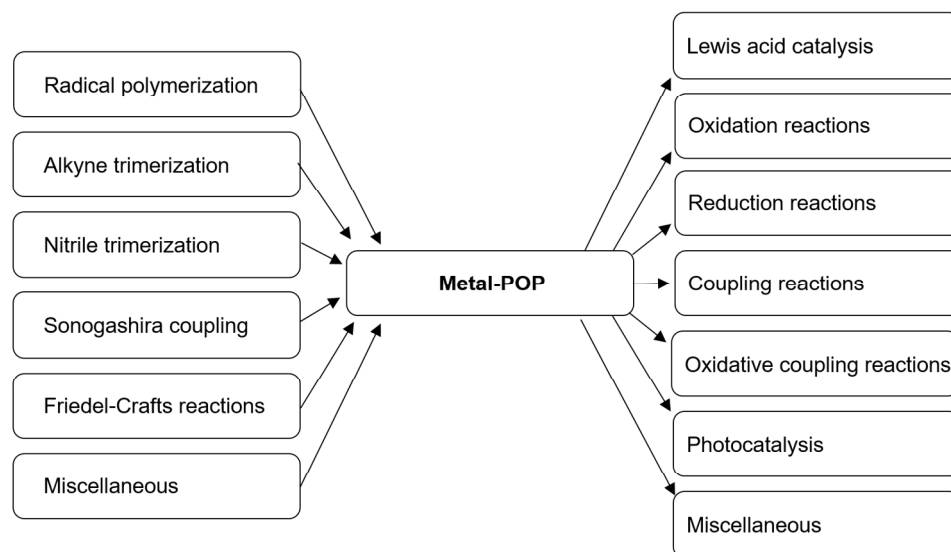
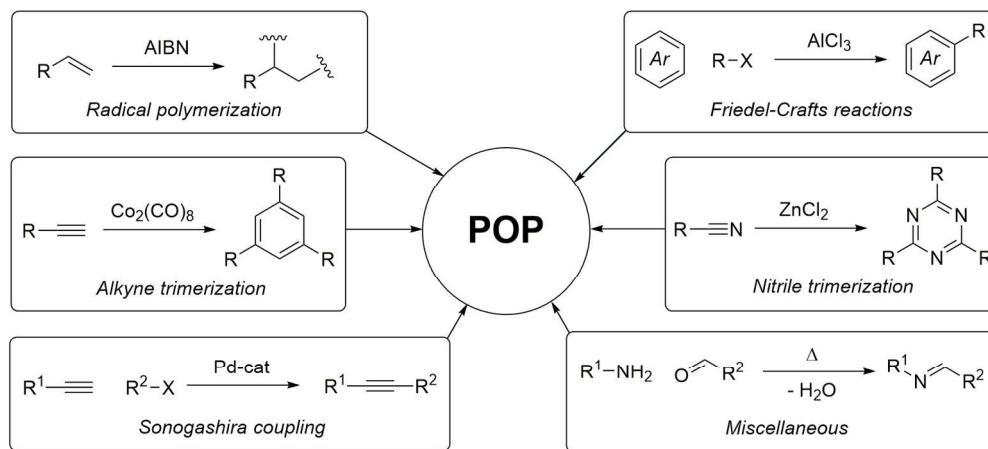


Figure 2. Overview of synthesis of metal-containing porous organic polymers (POPs) and their application in catalysis.

298x169mm (150 x 150 DPI)



22 Figure 3. The different types of polymerization techniques presented in this review. Each technique is
23 represented by a general example.

24 154x69mm (300 x 300 DPI)

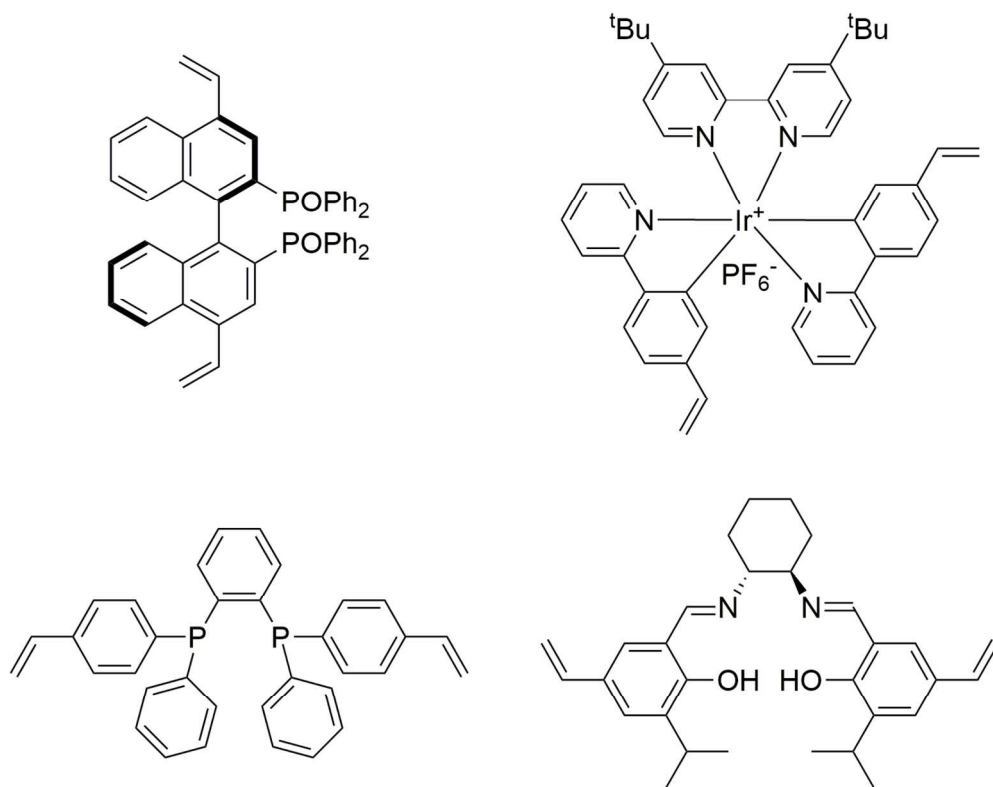
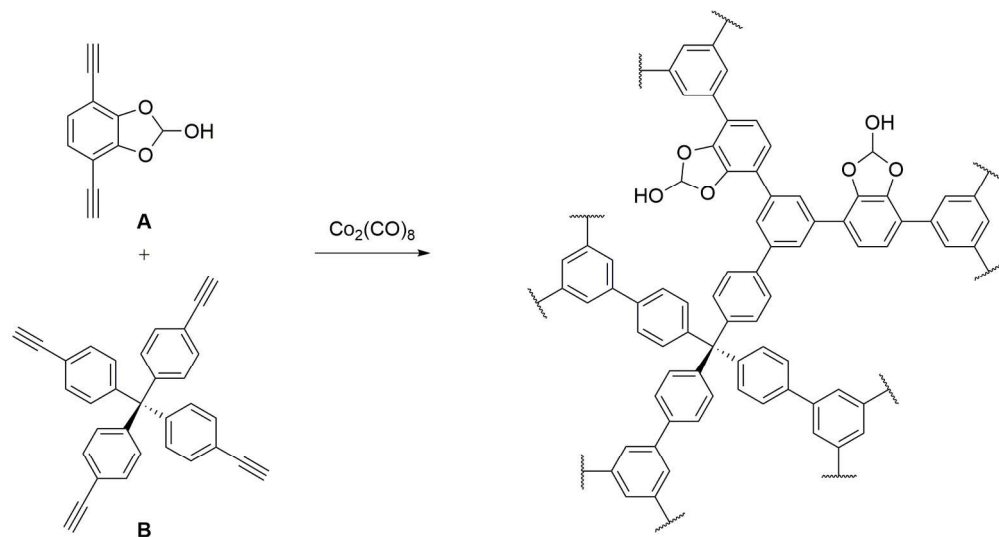


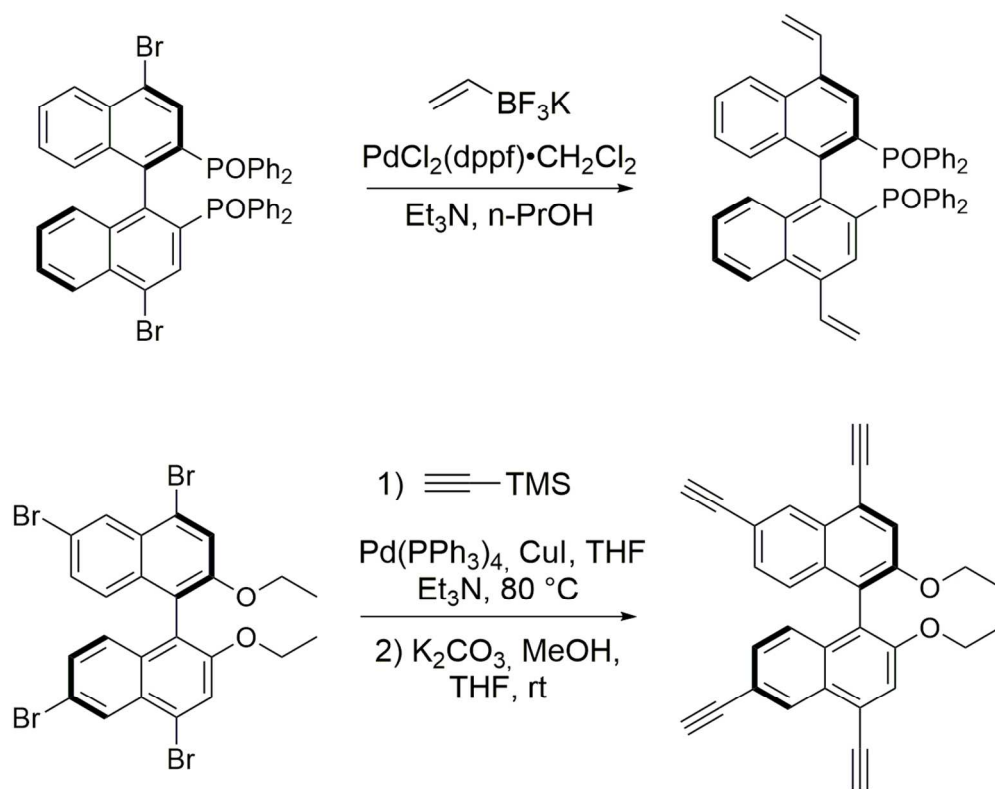
Figure 4. Examples of building blocks used for radical polymerization.

122x97mm (300 x 300 DPI)



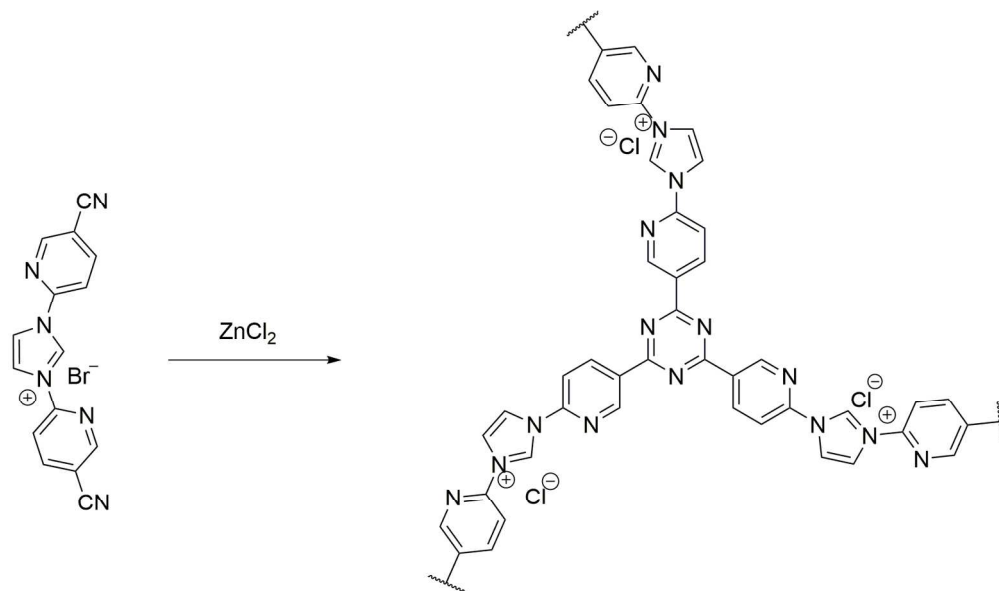
24 Scheme 1. Synthesis of a Catechol-POP through Alkyne Trimerization by Nguyen and Coworkers.⁴³

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26 175x94mm (300 x 300 DPI)



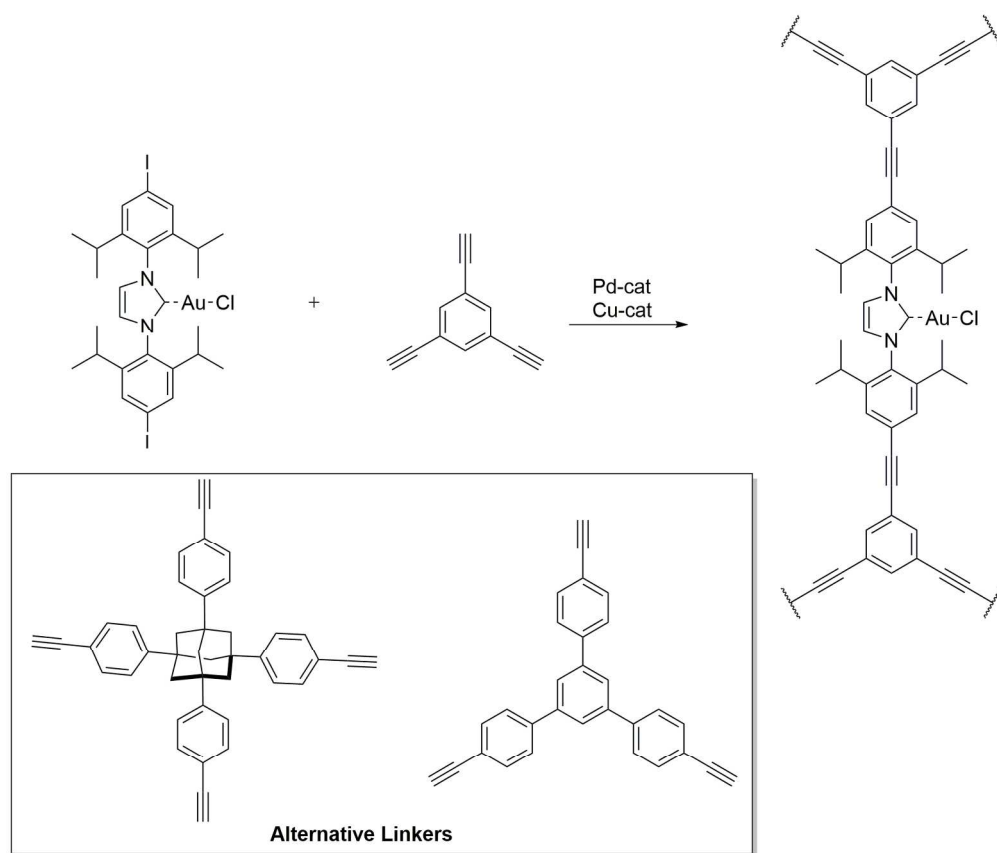
Scheme 2. Comparison of Monomer Synthesis for Radical Polymerization and Alkyne Trimerization for two BINAP-derivatives (dppf=1,1'-bisphenylphosphino)ferrocene).

112x88mm (300 x 300 DPI)



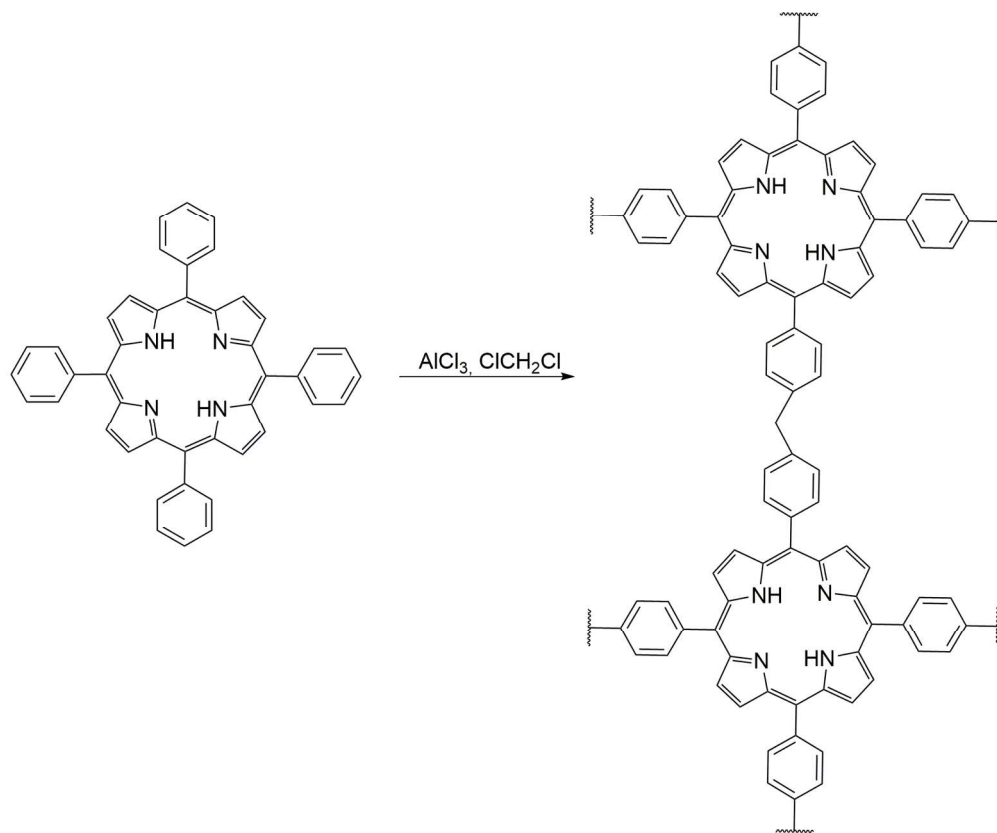
Scheme 3. Polymerization by Trimerization of Nitrile Groups Promoted by ZnCl_2 .⁵²

155x92mm (300 x 300 DPI)



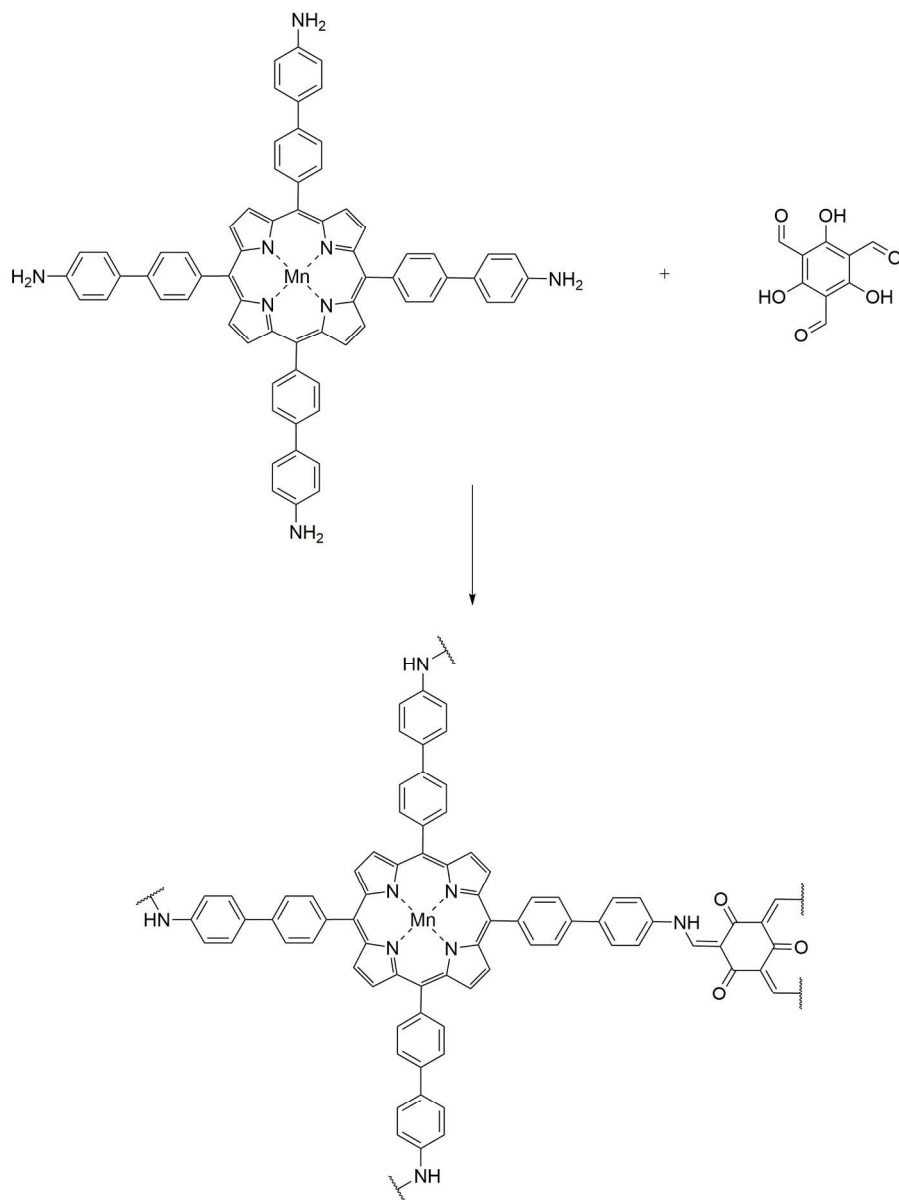
Scheme 4. Synthesis of Au-IPr-POPs through Sonogashira Coupling by Li et al.⁶⁷

174x148mm (300 x 300 DPI)



34 Scheme 5. Synthesis of a Porphyrin-POP by Friedel-Crafts Alkylation Reported by Li, Tan, and Coworkers.⁷⁶

35 161x133mm (300 x 300 DPI)



45 Scheme 6. Synthesis of a Mn-Porphyrin-POP by Ketoenamine Condensation.⁸⁰

46 168x225mm (300 x 300 DPI)

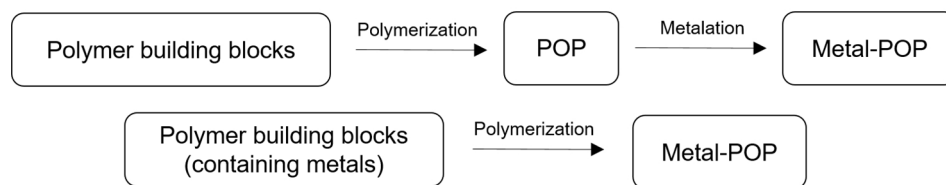
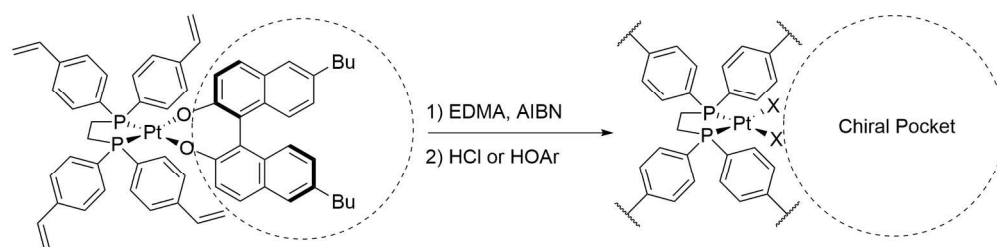


Figure 5. Two different metalation strategies utilized for the syntheses of metal-POPs.

268x57mm (150 x 150 DPI)



Scheme 7. Synthesis of Chiral Pocket by Metal Templating Reported by Gagné et al. (EDMA = ethylenedimethacrylate)⁹⁰

179x44mm (300 x 300 DPI)

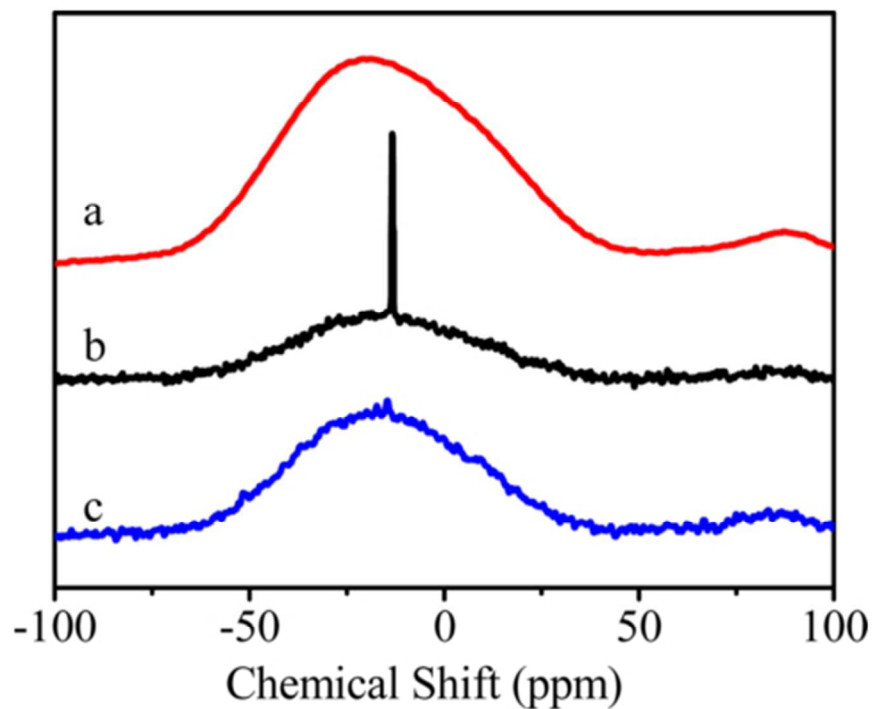


Figure 6. Static solid-state ^{31}P NMR of (a) the dried dppe-based polymer, (b) the dppe-based polymer in the presence of toluene, and (c) an non-porous dppe-based polymer in the presence of toluene. The sharp signal for the swollen polymer indicates homogeneous environment for the ligand in the swollen polymer. Adapted from Xiao and coworkers.⁹⁵

150x110mm (96 x 96 DPI)



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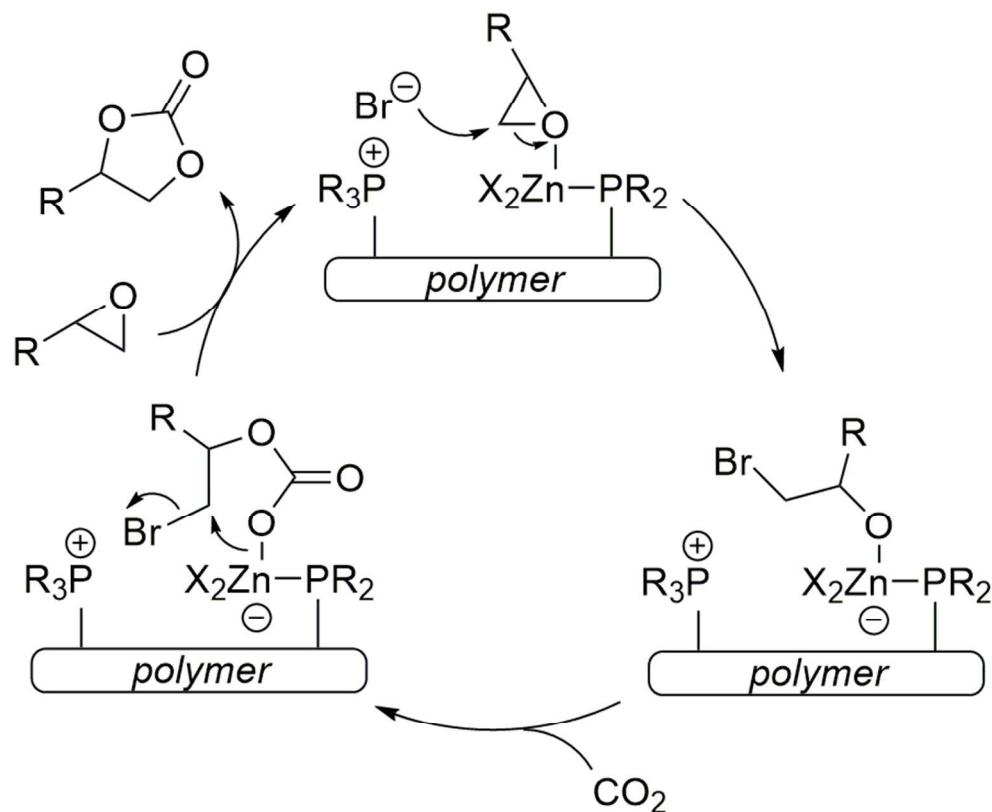
metal center: Zn, Al, Cu, Co, Mg

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Scheme 8. Formation of Cyclic Carbonates from CO₂ and Epoxides

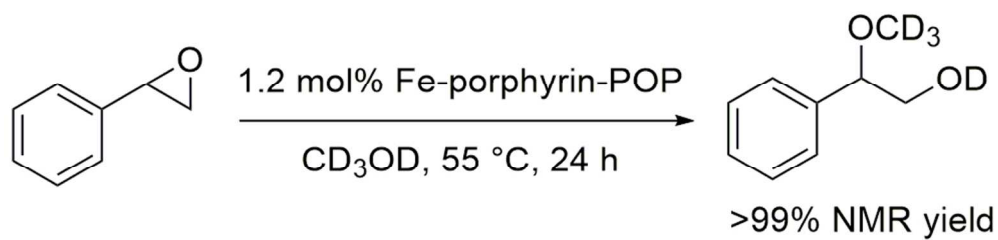
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58x20mm (300 x 300 DPI)



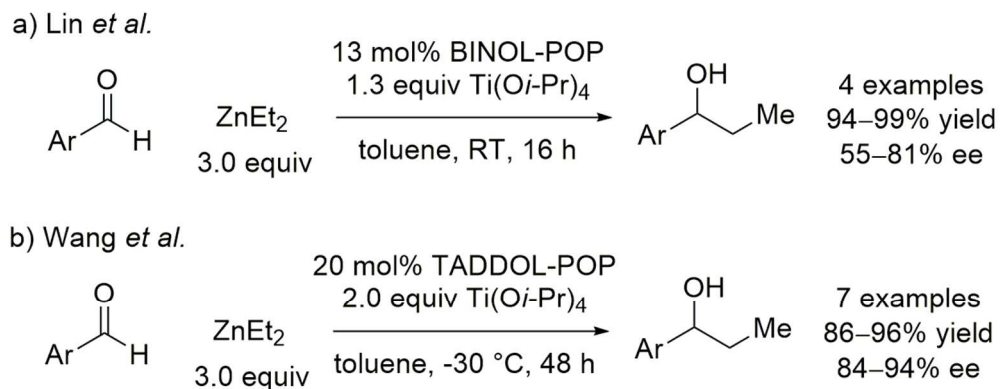
Scheme 9. Proposed Cooperative Mechanism for Cyclic Carbonate Formation using POPs Containing Bifunctional Sites.

77x63mm (300 x 300 DPI)



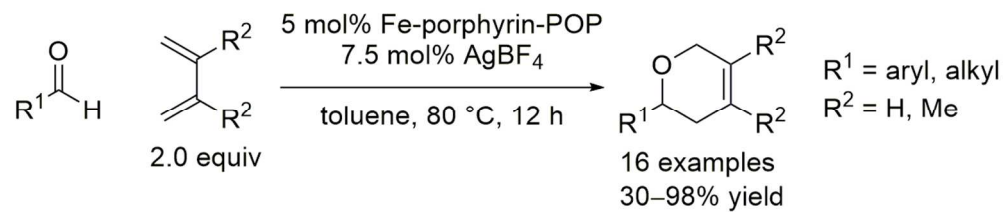
Scheme 10. Nucleophilic Addition to Epoxide Catalyzed by an Iron-Porphyrin-POP.

84x21mm (300 x 300 DPI)



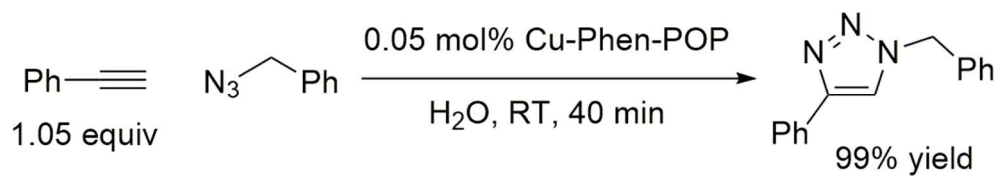
20 Scheme 11. Titanium-Catalyzed Asymmetric Addition of ZnEt₂ to Aldehydes using (a) a BINOL-POP Ligand
21 and (b) a TADDOL-POP Ligand

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23 105x42mm (300 x 300 DPI)



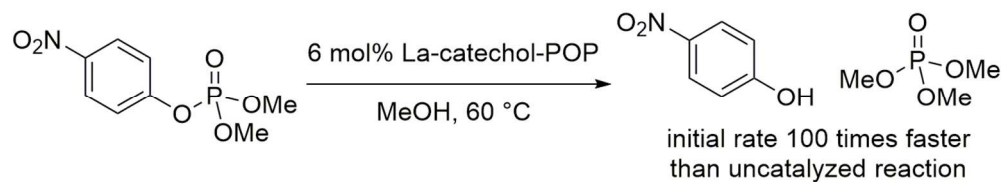
Scheme 12. Hetero-Diels-Alder Reaction Catalyzed by Heterogeneous Iron-Porphyrin-POP and AgBF_4 .

109x23mm (300 x 300 DPI)



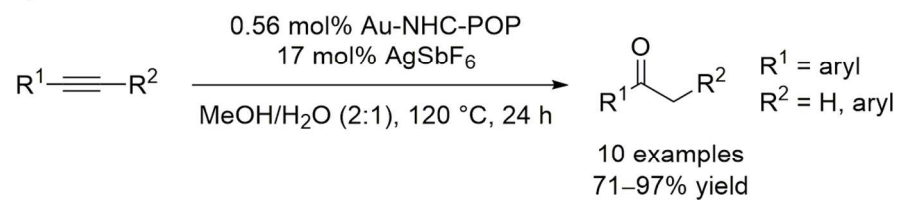
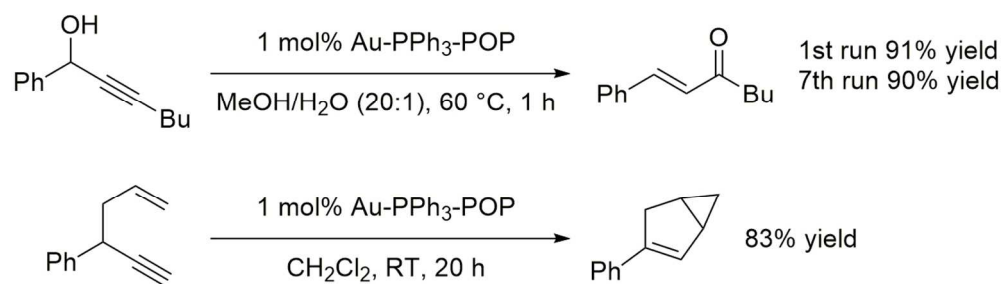
Scheme 13. Formal 1,3-Dipolar Cycloaddition Catalyzed by a Cu-Phen-POP.

93x17mm (300 x 300 DPI)

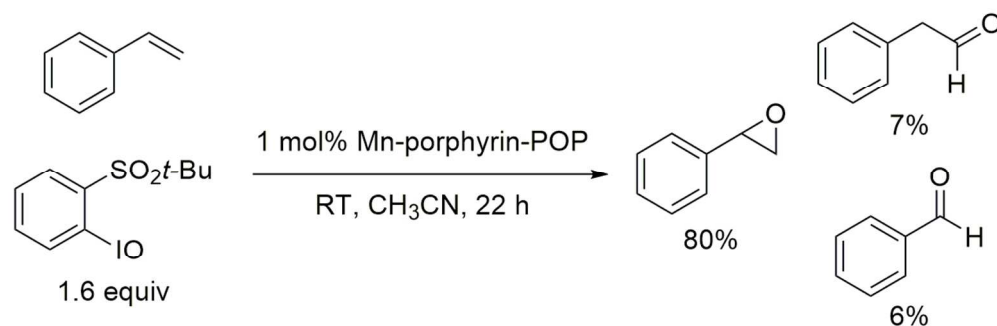


Scheme 14. Methanolysis of an Organophosphate Catalyzed by a Lanthanum-Catechol-POP.

115x21mm (300 x 300 DPI)

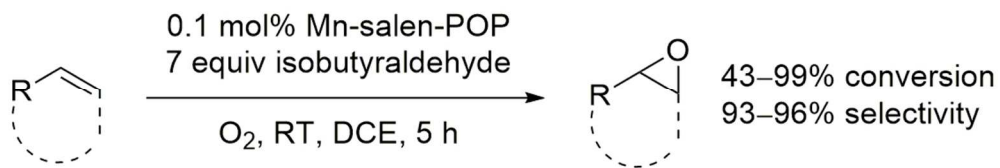
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7 a) Li *et al.*b) Shi *et al.*Scheme 15. Selected Reactions Catalyzed by Gold-Containing Porous Organic Polymers: (a) Alkyne Hydration by Li *et al.* and (b) Meyer-Schuster Rearrangement and Enyne Rearrangement by Shi *et al.*

115x66mm (300 x 300 DPI)



Scheme 16. Epoxidation of Styrene Catalyzed by a Mn-porphyrin-POP.

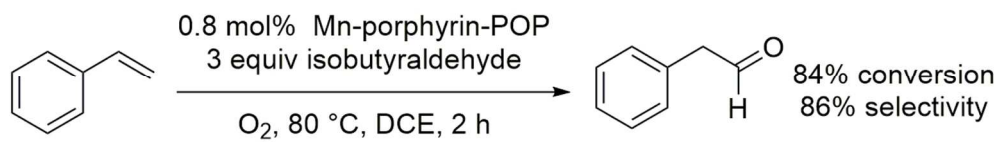
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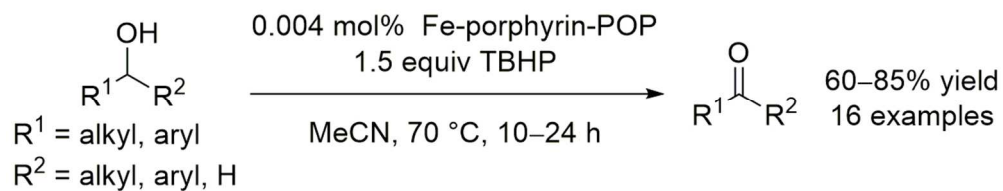
Scheme 17. Aliphatic Alkene Epoxidation Catalyzed by a Mn-Salen-POP.

96x16mm (300 x 300 DPI)



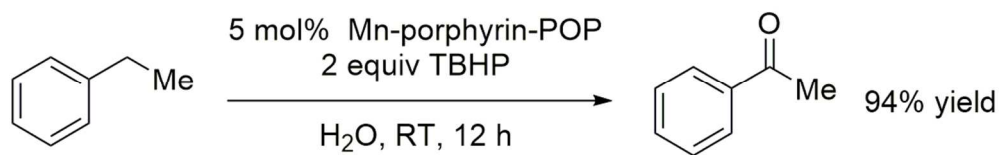
Scheme 18. Catalytic Oxidation of Styrene to Phenylacetaldehyde.

105x15mm (300 x 300 DPI)



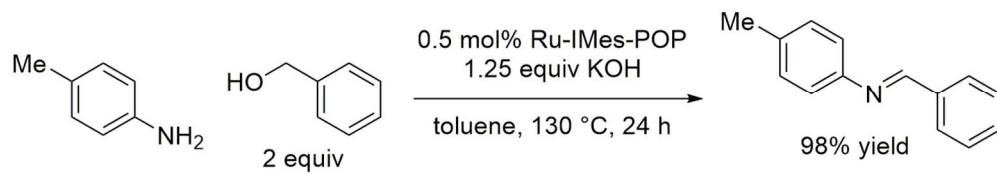
14 Scheme 19. Oxidation of Primary and Secondary Alcohols Catalyzed by an Iron-Porphyrin-POP

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16 103x20mm (300 x 300 DPI)



13 Scheme 20. Acetophenone Synthesis from Ethylbenzene Catalyzed by a Manganese-Porphyrin-POP

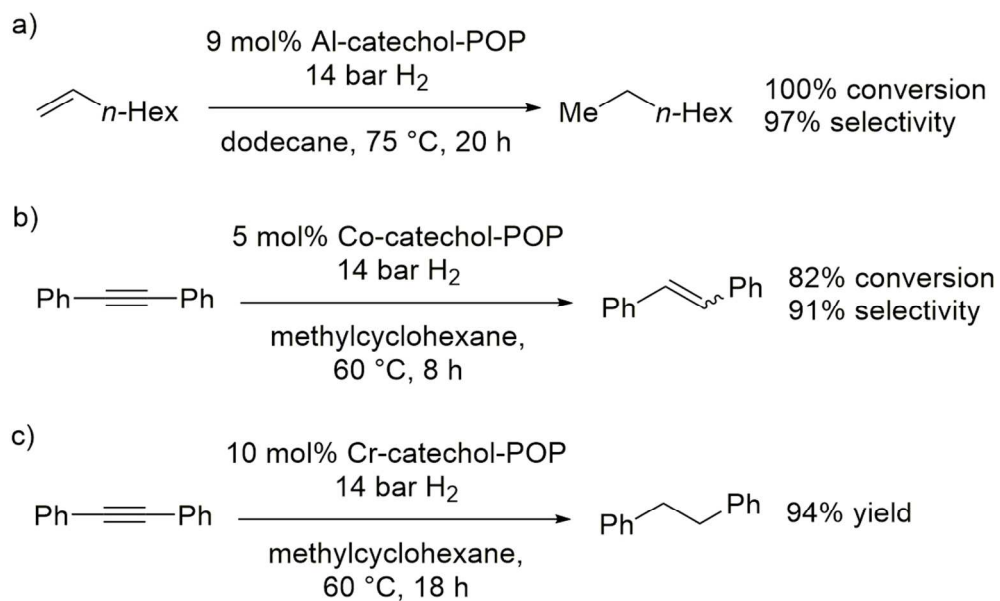
14 98x15mm (300 x 300 DPI)



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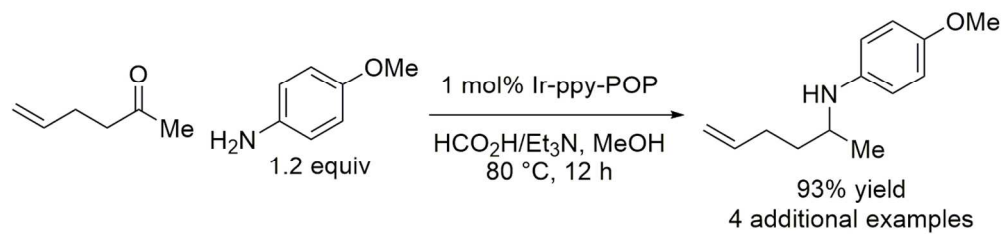
Scheme 21. Oxidation/Condensation Sequence Catalyzed by a Ruthenium-IMes-POP (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene).

118x21mm (300 x 300 DPI)



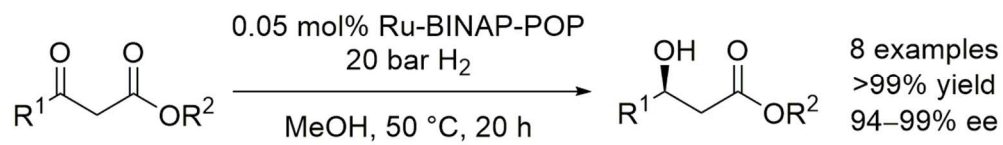
Scheme 22. Alkene and Alkyne Hydrogenation Catalyzed by Metal-Catechol-POPs. (a) Aluminum Catalyst, (b) Cobalt Catalyst, and (c) Chromium Catalyst.

102x62mm (300 x 300 DPI)

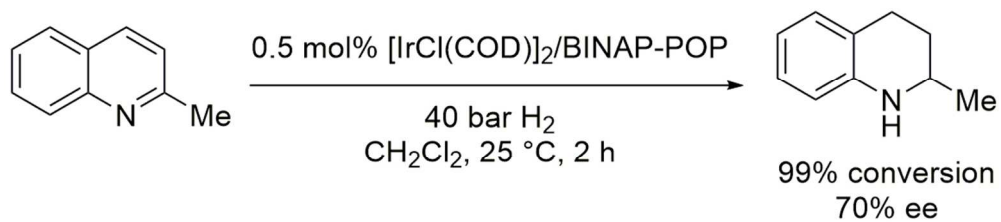


15 Scheme 23. Reductive Amination Catalyzed by an Iridium-ppy-POP

16 118x28mm (300 x 300 DPI)

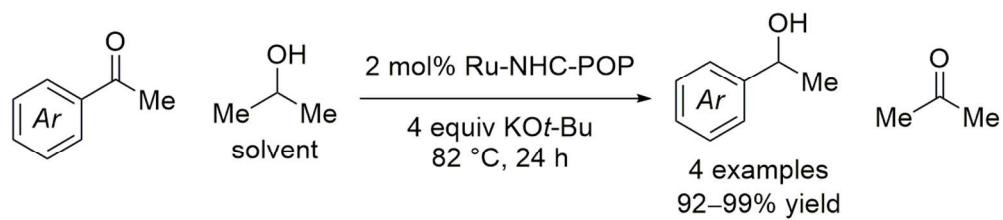
Scheme 24. Asymmetric Hydrogenation of β -Keto Esters.

102x15mm (300 x 300 DPI)



Scheme 25. Asymmetric Hydrogenation of 2-Methyl Quinoline.

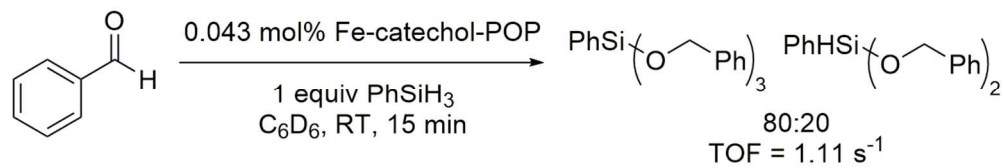
98x22mm (300 x 300 DPI)



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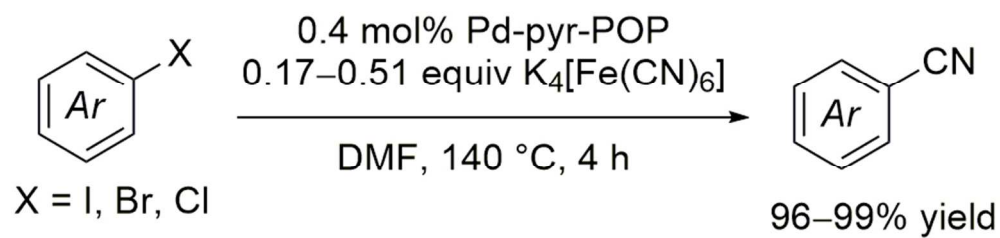
Scheme 26. Transfer Hydrogenation for Reduction of Acetophenones.

109x24mm (300 x 300 DPI)



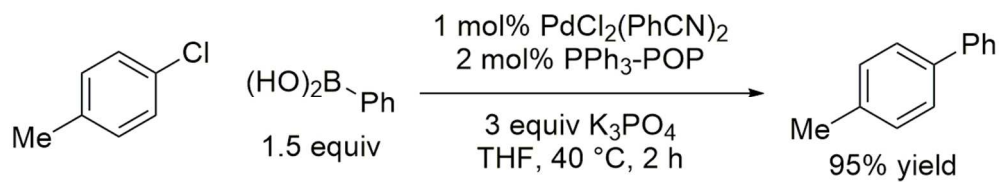
Scheme 27. Hydroosilylation of Carbonyl Groups Catalyzed by an Fe-Catechol-POP.

111x19mm (300 x 300 DPI)



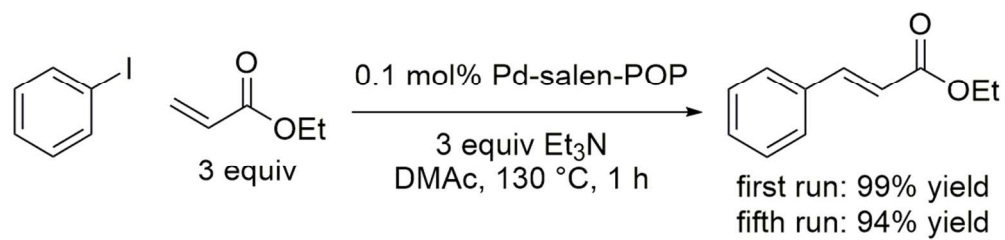
Scheme 28. Cyanation of Aryl Halides using a Palladium-Containing Porous Organic Polymer.

79x19mm (300 x 300 DPI)



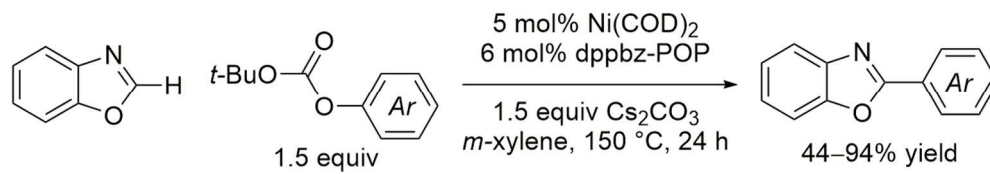
Scheme 29. Suzuki-Miyaura Coupling Catalyzed by a Palladium-POP Complex.

101x18mm (300 x 300 DPI)



Scheme 30. Mizoroki-Heck Reaction Catalyzed by a Palladium Porous Organic Polymer.

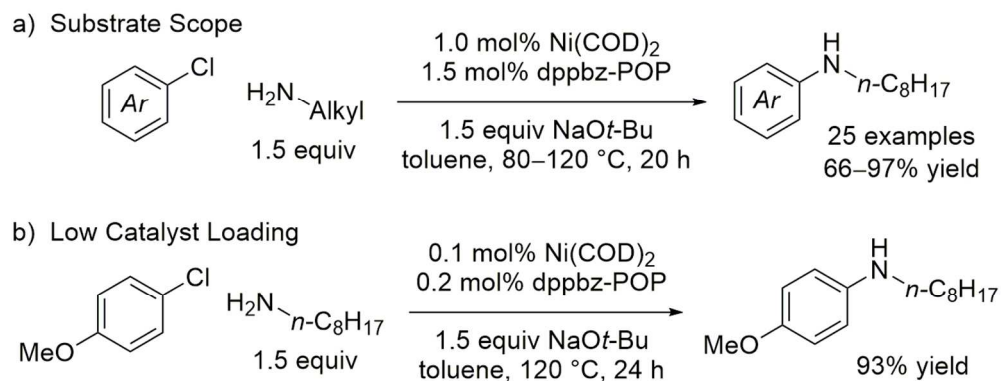
97x24mm (300 x 300 DPI)



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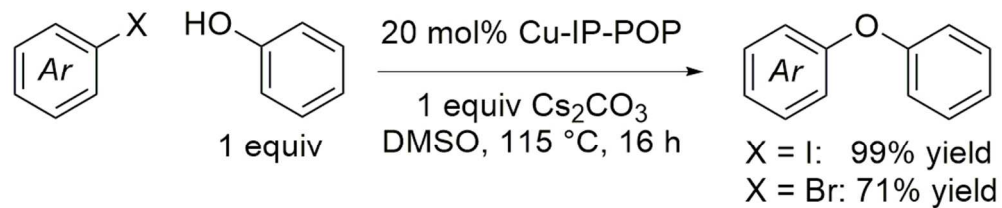
Scheme 31. Nickel-Catalyzed Coupling of Aryl Pivalates and Benzoxazole.

114x20mm (300 x 300 DPI)



20 Scheme 32. Nickel-Catalyzed Amination of Aryl Chlorides (a) displays Broad Substrate Scope, and (b) can be
21 performed with Low Catalyst Loading.

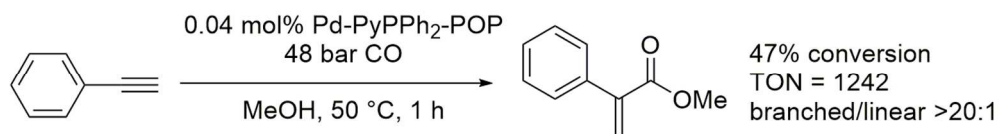
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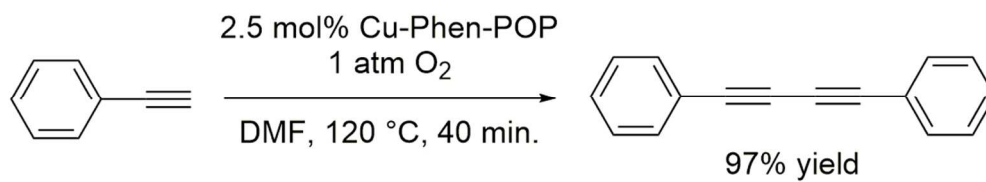
Scheme 33. Cu-IP-POP-Catalyzed Ullmann Coupling for the Formation of Biaryl Ethers (IP = iminopyridine)

91x20mm (300 x 300 DPI)



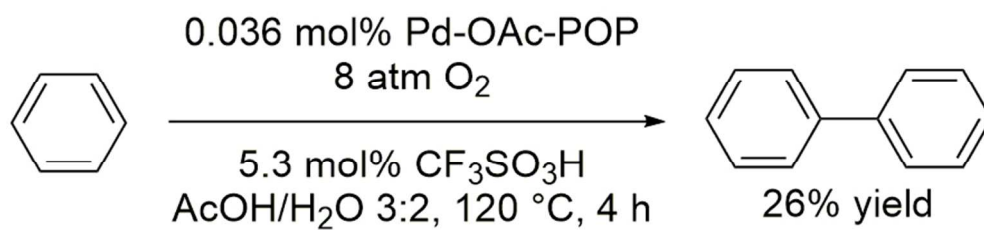
12 Scheme 34. Alkoxycarbonylation of Terminal Alkynes using a Palladium-PyPPh₂-POP Catalyst

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14 117x16mm (300 x 300 DPI)



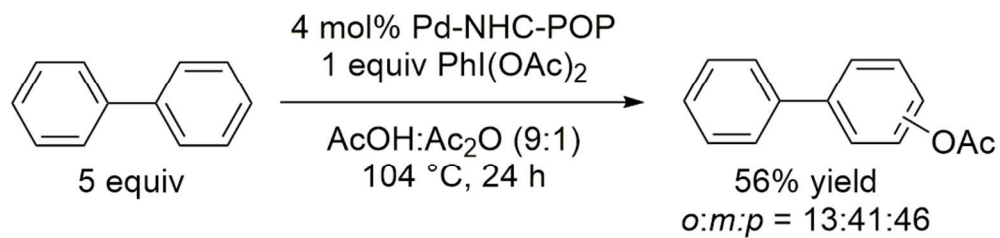
Scheme 35. Glaser Coupling using a Copper-Phen-POP Catalyst.

96x17mm (300 x 300 DPI)



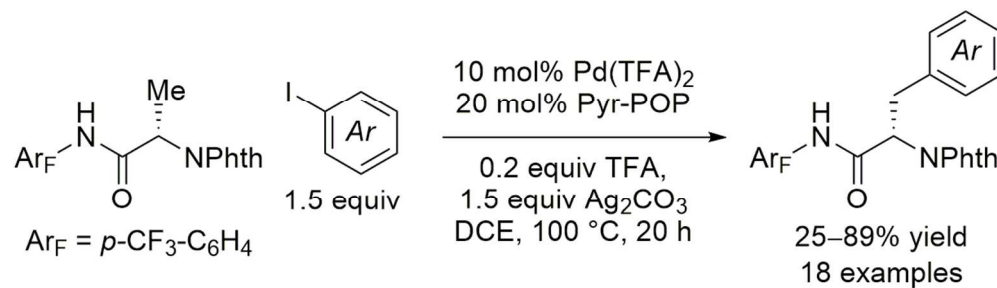
Scheme 36. Oxidative Homocoupling of Benzene using a Pd-OAc-POP.

75x18mm (300 x 300 DPI)



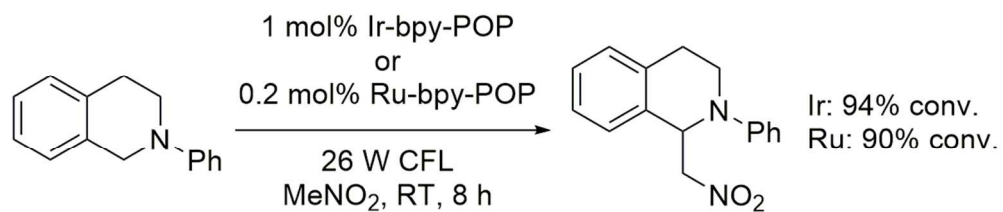
Scheme 37. Aryl C-H Acetoxylation Catalyzed by a Palladium-NHC-POP.

90x22mm (300 x 300 DPI)



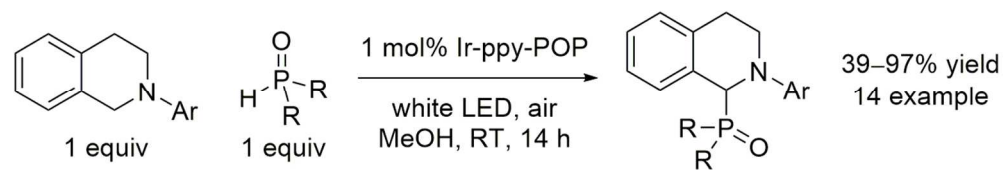
17 Scheme 38. Oxidative C(sp³)-H Arylation Catalyzed by a Palladium-Pyr-POP (TFA = trifluoroacetic acid).

18 103x30mm (300 x 300 DPI)



Scheme 39. Photocatalytic Aza-Henry Reaction using Ruthenium- and Iridium-bpy-POPs.

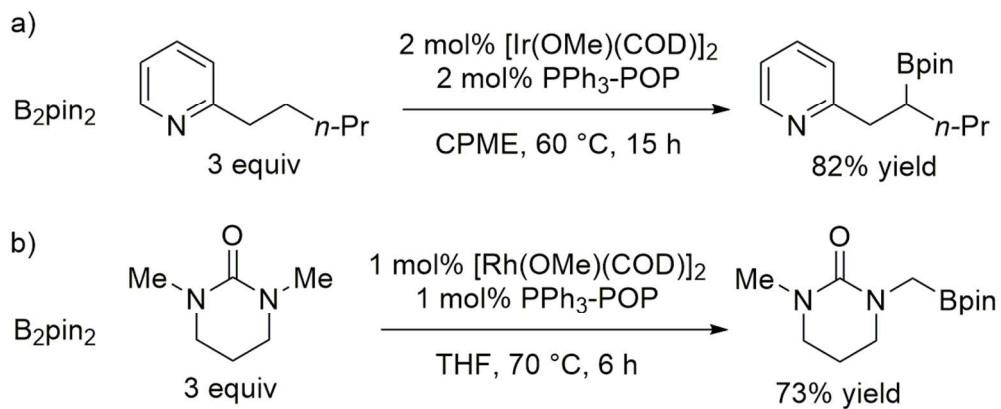
102x22mm (300 x 300 DPI)



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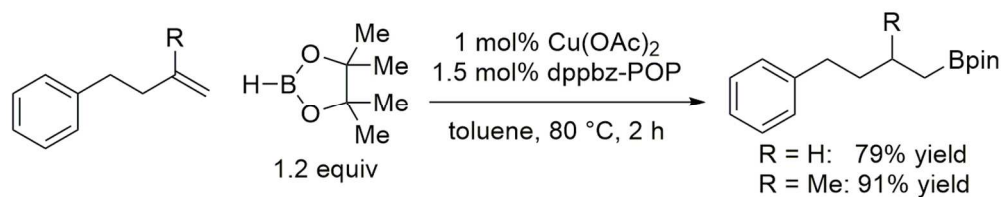
Scheme 40. Photocatalytic Coupling of Tetrahydroisoquinolines and P-H Nucleophiles.

113x19mm (300 x 300 DPI)



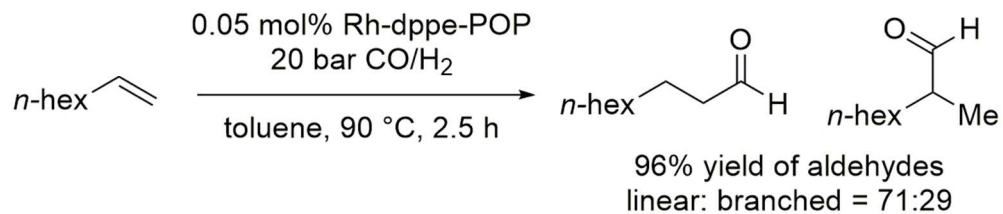
Scheme 41. Borylation of $\text{C}(\text{sp}^3)\text{-H}$ Catalyzed by (a) Ir- $\text{PPh}_3\text{-POP}$ and (b) Rh- $\text{PPh}_3\text{-POP}$.

103x43mm (300 x 300 DPI)



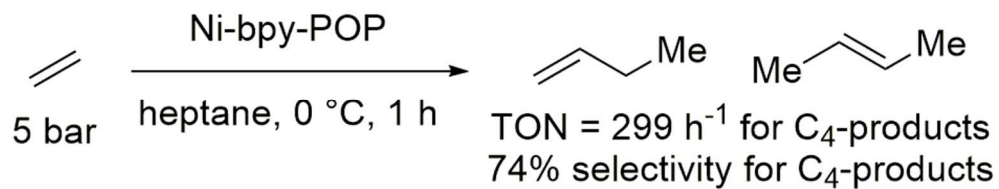
Scheme 42. Hydroboration of Aliphatic Alkenes using a Copper-dppbz-POP Catalyst.

115x23mm (300 x 300 DPI)



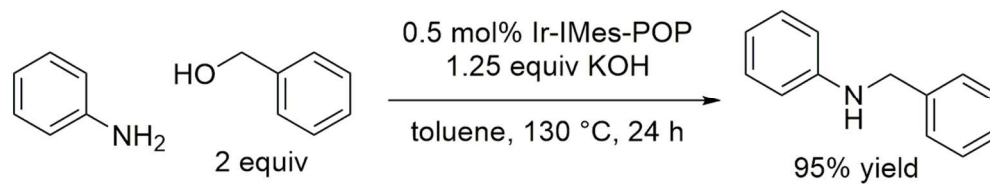
Scheme 43. Hydroformylation of 1-Octene with a Rh-dppe-POP Catalyst.

99x22mm (300 x 300 DPI)



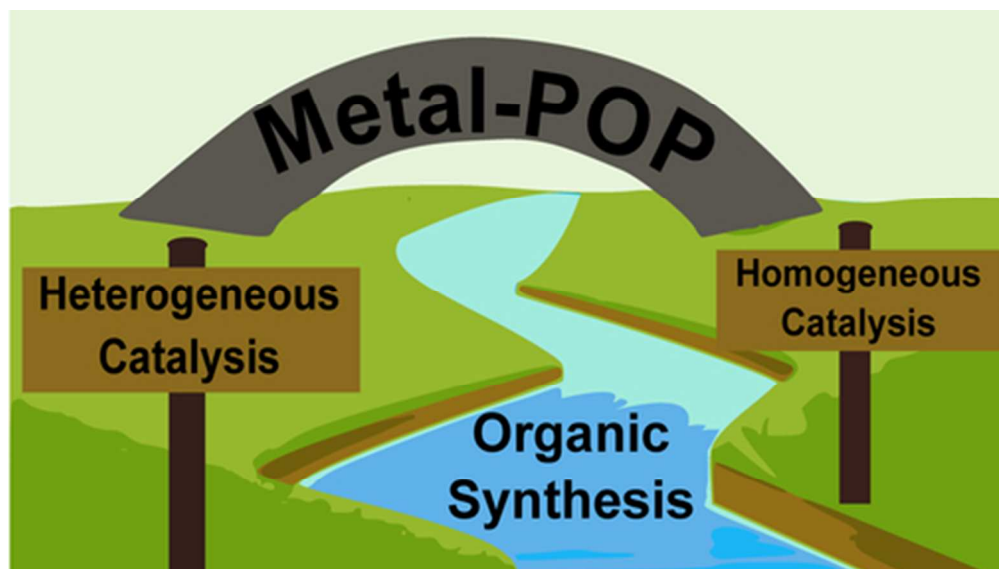
Scheme 44. Ethylene Dimerization Catalyzed by a Ni-bpy-POP.

80x16mm (300 x 300 DPI)



Scheme 45. Hydrogen-Borrowing Reaction Catalyzed by an Iridium-IMes-POP.

103x19mm (300 x 300 DPI)



21x12mm (600 x 600 DPI)