UNVEILING THE POTENTIAL ROLE OF CALIX[4]PYRROLES IN CATALYSIS

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Abstract. *Catalysis is a diverse and interdisciplinary field that spans chemistry, chemical engineering, and material as well as biological sciences. It continues to be a subject of extensive research aimed at developing more efficient catalysts and expanding their applications in various industries. Calix[4]pyrroles (C4Ps) have become increasingly popular topic of interest in catalysis research in past few decades. This unique class of molecules has shown promising results in a wide range of catalytic reactions, especially those involving organic transformations. The framework of C4Ps has been shown to offer high selectivity and activity in various catalytic reactions, making it a valuable tool for the chemists. When comparing C4P-based catalysts with other catalysts in terms of efficiency and selectivity, it becomes evident that C4Ps stands out as a remarkable in the field of catalysis. Their unique structures and functional groups, provide them distinct advantages over traditional catalysts. In terms of efficiency, the C4Ps exhibit high catalytic activity due to its cavity structure that can encapsulate guest molecules, allowing for precise control over reaction pathways. This feature enhances the efficiency of the catalytic process by promoting specific interactions between the catalyst and reactants, leading to faster reaction rates and higher yields. In this chapter, we will delve into this catalytic efficiency of C4Ps in carrying out typical organic transformations. The authors believe that the present chapter will help in better understanding of the knowhows of C4Ps in catalysis and its potential impact in the field of chemistry in general and supramolecular chemistry in particular.*

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1. Introduction

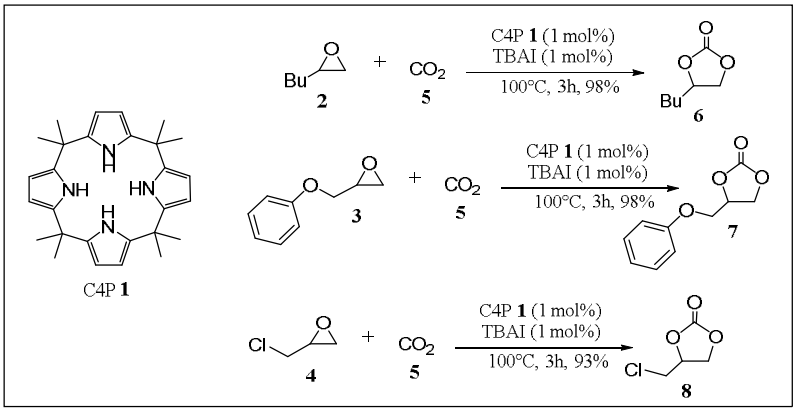
Catalysis play a keynote role in various industrial processes, including petroleum refining, chemical synthesis, environmental remediation, and pharmaceutical production.[1-4] In particular, enzymatic catalysis is essential for numerous biological processes, including metabolism, DNA replication, and protein synthesis. Supramolecular catalysis refers to a branch of catalysis where the catalytic activity arises from the assembly of molecular species through the non-covalent interactions, that is supramolecular interactions such as hydrogen bonding, π-π-interactions, van der Waals forces, and electrostatic interactions, rather than through traditional covalent bonds.[5,6] Supramolecular catalysis is a flexible and potent way to improve and regulate chemical processes, allowing the investigation of intricate reaction networks and the creation of novel synthetic techniques. In this field, the catalyst consists of multiple components that come together to create a highly efficient catalytic organization. These catalysts often exhibit dynamic behavior, where the components can exchange rapidly within the catalytic system. This dynamic nature allows for adaptability and responsiveness to changes in the reaction environment.[7,8] These catalysts can offer high substrate selectivity by virtue of the specific interactions between the catalyst and the substrate molecules. This selectivity can lead to increased efficiency and reduced waste in catalytic reactions.[9,10] Many supramolecular catalysts are designed to self-assemble from their individual components under certain conditions. Self-assembly enables the formation of well-defined catalytic structures and simplifies catalyst synthesis. Supramolecular catalysis has applications in various fields, including organic synthesis, polymerization,

asymmetric catalysis, drug discovery *etc.*[11] Researchers are exploring the potential of supramolecular catalysis in designing of new materials and improving the existing chemical processes.[12]

Among various macrocyclic entities, calix[4]pyrrole (C4P) and related architectures have attracted significant attention in the field of supramolecular catalysis due to their unique structural features and exceptional catalytic properties.[13-16] These intriguing molecule consists of four pyrrole units linked together through four sp^3 *meso*-bridges, generating robust and versatile frameworks.[17-19] One of the key factors that make C4Ps as the prevailing supramolecular catalysts is their ability to encapsulate guest molecules within their cavity (*pocket*), leading to enhanced reactivity and selectivity in various chemical transformations.[20-23] This feature enables the C4Ps to act as molecular containers, facilitating the formation of stable complexes with reactants and promoting specific interactions to drive catalytic activities Moreover, the electron-rich nature of the pyrrole moieties in the C4Ps imparts good nucleophilic character, allowing them for efficient activation of substrates and mediation of diverse catalytic reactions. From Lewis acid catalysis to organocatalysis, C4Ps exhibit remarkable versatility in catalyzing a wide-range of conversions with high efficiency as well as good selectivity.[24-26]

2. Calix[4]pyrroles as organocatalysts

Maeda and co-workers have utilized C4P **1** as an organocatalyst in combination with tetrabutylammonium iodide (TBAI) for the conversion of epoxides **2-4** and CO_2 **5** into cyclic carbonates **6-8** (Scheme 1).[27] Computational studies have shown that C4P **1** in its 1,3-alternate conformation can stabilize anionic species generated during the catalytic process. An essential transition state (TS) that takes place throughout this process is the ring-opening of an epoxide. The activation of the epoxide ring is caused by hydrogen bonding interactions between the pyrrolic NH of C4P **1** and the TBA^+ cation. In contrast, the epoxide ring is activated by the I^- ion guided by an extra NH-group of the C4P **1**.

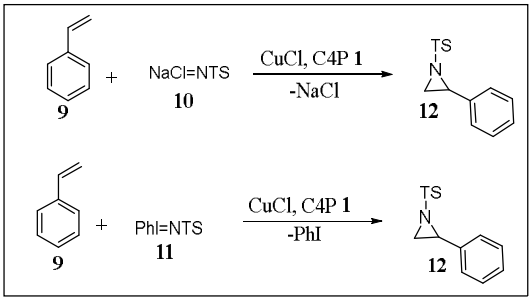


Scheme 1. Synthesis of cyclic carbonates **6-8** from epoxides **2-4** and CO_2 using C4P **1**.

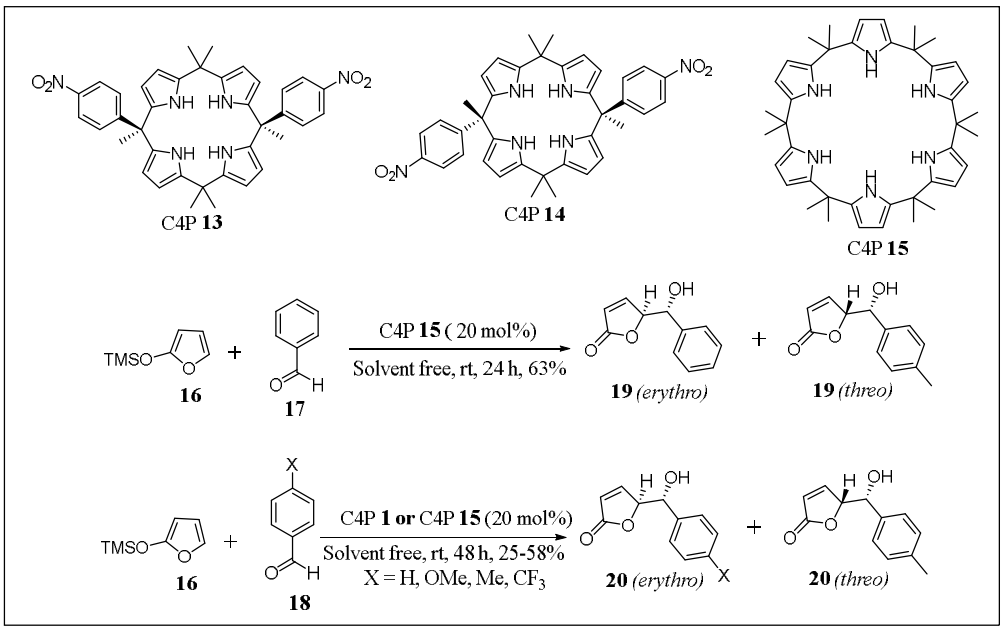
On the other hand, Sessler's research group has employed C4P **1** as a promoter in combination with CuCl catalyst in the aziridination of styrene **9** with chloramine-T **10** and iminoiodinane **11** to produce 1-tosyl-2-phenylaziridine **12** (Scheme 2).[28] Hydrogen bonding interactions between the pyrrolic NHs and the Cl atom of CuCl occur when the anion receptor C4P starts an anion cleavage event. When CuI was used as catalyst instead of CuCl, the presence of C4P **1** had no promoter effect. Interestingly, the enhancement effect stipulated by C4P seems to be unaffected by the presence of small quantities of water.

Using the C4Ps **1**, **13**, and **14** and an expanded calixpyrrole **15** as organocatalysts in the diastereoselective aldol addition reaction of 2-trimethylsilyloxyfuran **16** with different aldehydes **17** and **18**, Kohnke and colleagues have synthesized γ-hydroxybutenolide products **19** and **20** (Scheme 3).[29] The effectiveness of the reaction is highly dependent on the reaction conditions and the molecular structures of the organocatalysts. For the manufacture of the intended γ-hydroxybutenolide products **19** and **20**, expanded

calixpyrrole **15** proved to be the most effective organocatalyst among those that were tested. The reason behind this is its high anion complexation capability and the absence of steric obstacles at the *meso*-positions.



Scheme 2. Synthesis of aziridine **12** using CuCl as a catalyst and C4P **1** as a promoter.

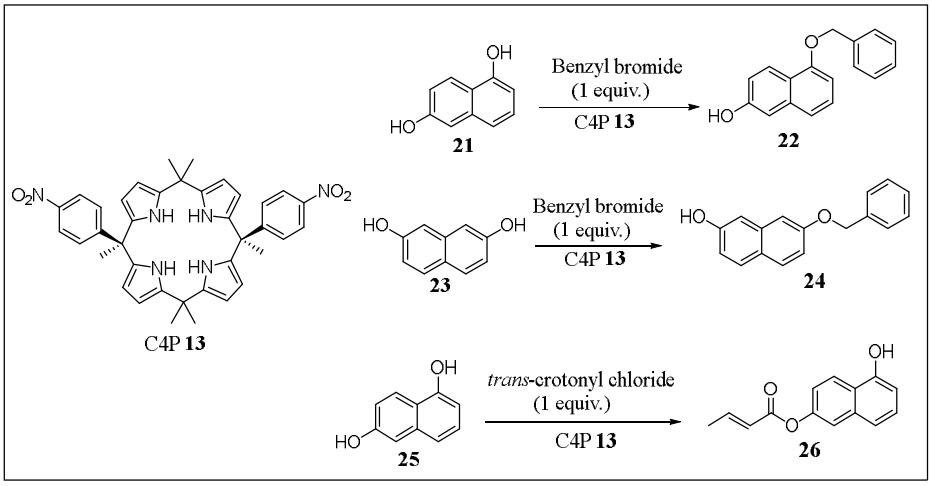


Scheme 3. Diastereoselective synthesis of γ-hydroxybutenolides **19** and **20** using C4Ps **1**, **13**, **14**, and **15**.

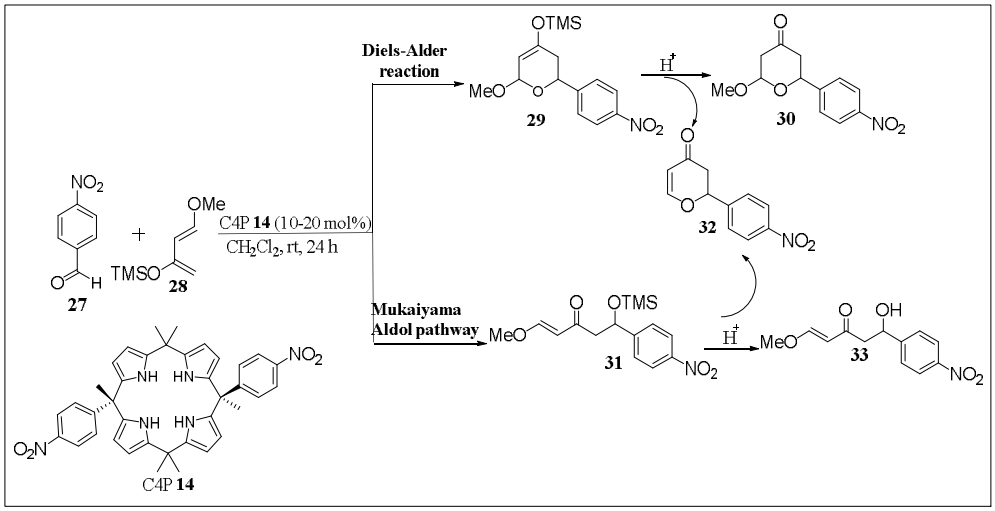
In another study, Kohnke and coworkers have utilized C4P **13** as an organocatalyst in selective *o*-alkylation/acylation of polyphenolic aromatic compounds.[30] As an example, dihydroxy naphthalenes **21** and **23** were treated with one equiv. of benzyl bromide to preferentially produce *mono*-benzyl ethers **22** and **24** in the presence of a C4P catalyst **13** (Scheme 4). Similarly, dihydroxy naphthalene **25** was treated with one equiv. of *trans*-crotonyl chloride to preferentially produce the *mono*-acylated product **26** in the presence of **13** (Scheme 4). It was revealed that the C4P organocatalyst **13** could differentiate between molecules containing two phenolate groups.

Cafeo *et al.* documented a Mukaiyama aldol condensation and hetero-Diels Alder reaction using *p*-nitrobenzaldehyde **27** and Danishefsky's diene **28** (Scheme 5), which were facilitated by an organocatalyst based on two-walled C4P **14**.[31] Organocatalyst **14** concentration and solvent volume determined the relative

amounts of aldolic adduct **33** and cycloadduct **30** *via* the formation of respective intermediates **29** and **31**, which were produced during a 1:2 ratio reaction between diene **28** and aldehyde **27**. Construction of the dihydropyrone product **32** was not detected when 10 mol% of the catalyst **24** was utilized in the aforementioned reaction. The most important byproduct was the cycloadduct product **30**, which was detected when the organocatalyst **24** concentration was increased from 10 to 20 mol%. This further indicates that the reaction is taking place *via* a concerted cycloaddition route. However, cycloadduct **30** was the most abundant product when 2 mL of CH_2Cl_2 and 10 mol% of catalyst **24** were employed, indicating that the cycloaddition mechanism was the main route. Nevertheless, a significant quantity of aldolic adduct **33** was seen when 4 mL of CH_2Cl_2 was utilized while maintaining the 10 mol% concentration of catalyst **24**. Because of this, Mukaiyama aldol condensation seems to be the main route.

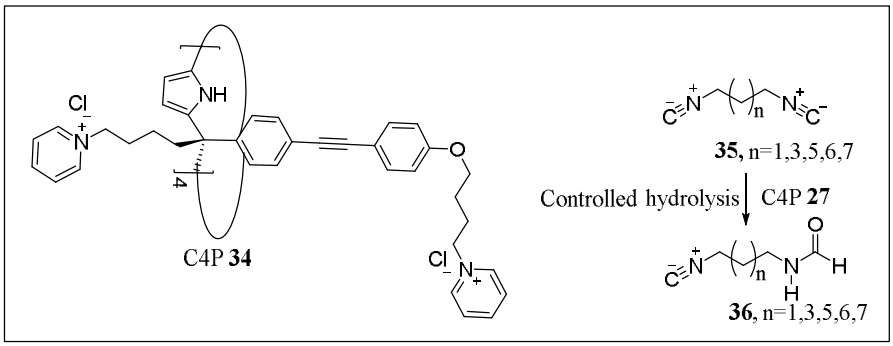


Scheme 4. C4P organocatalyst **13** assisted selective synthesis of *mono*-benzyl ethers **22** and **24** and *mono*-acylated product **26**.



Scheme 5. Schematic drawing of the construction of cycloadduct **30** and aldolic adduct **33** using two-walled C4P-based organocatalyst **24**.

The research group led by Ballester has developed a superaryl extended C4P-based organocatalyst **34**, that may be used to modulate the hydrolysis of symmetrical *bis*-isonitriles **35** to unsymmetrical monoformamides **36** (Scheme 6).[32] Compared to other symmetrical *bis*-isonitrile based guest entities **35**, the *bis*-isonitrile guest molecule with five methylene groups has been shown to be more susceptible to selective hydrolysis of one of the distal isonitrile functional groups to a monoformamide group. Consequently, this is a reflection of the fact that the hydrolysis rate of symmetrical *bis*-isonitriles bound with C4P **34** is lower than their hydrolysis rate in free solution.



Scheme 6. Controlled hydrolysis of symmetrical *bis*-isonitriles **35** to unsymmetrical monoformamides **36** by means of superaryl extended C4P **34** as an organocatalyst.

3. Heterogeneous catalysts based on calix[4]pyrrole nanoparticles

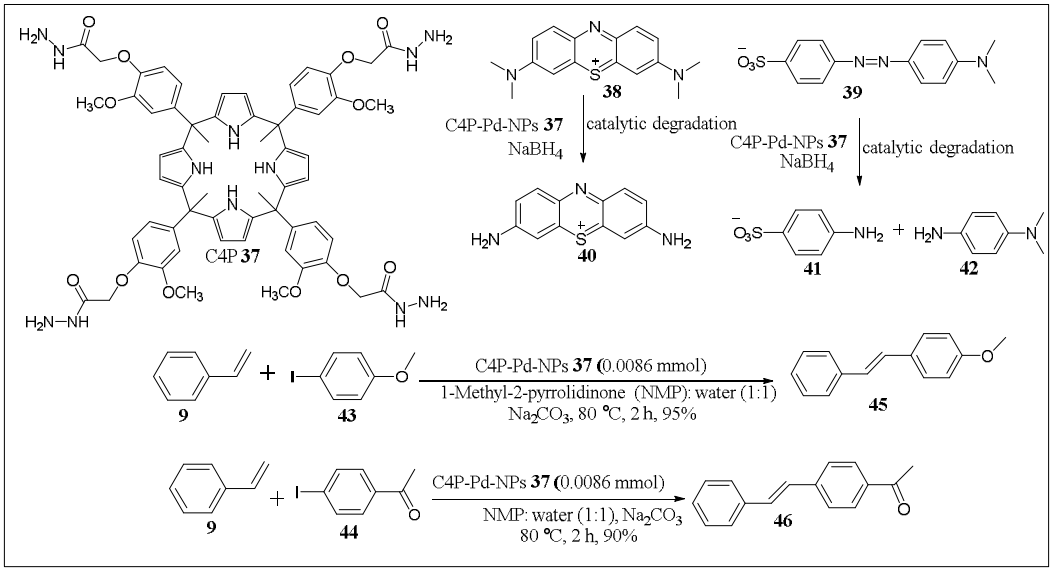
Kongor *et al.* have synthesized Pd-nanoparticles (Pd-NPs) by employing four-walled aryl extended C4P (C4P-Pd-NPs **37**) as a reducing as well as stabilizing/capping agent (Scheme 7).[33] To speed up the breakdown of water-soluble *azo*-dyes like methylene blue **38** into **40** and methyl orange **39** into **41** and **42**, the C4P-Pd-NPs **37** acts as a heterogeneous catalyst in the presence of $NaBH_4$. In another study, they have also revealed the catalytic use of this C4P-Pd-NPs **37** in C–C bond formation through Heck coupling, generating the desired C–C coupled products **45** and **46** from styrene **9** and iodophenyl derivatives **43** and **44**.[34]

As a further progress, Desai and teammates have reported Pd-NPs capped with octahydrazide C4P **47** as an effective nano-catalyst for various C–C coupling reactions like Heck coupling, Stille coupling, and Suzuki-Miyaura cross-coupling *etc.* to produce C–C coupled products **52** and **53** from starting materials **9** and **48-51** (Scheme 8).[35] The newly created C4P-based nano-catalyst exhibited no discernible activity degradation even after five reuse cycles.

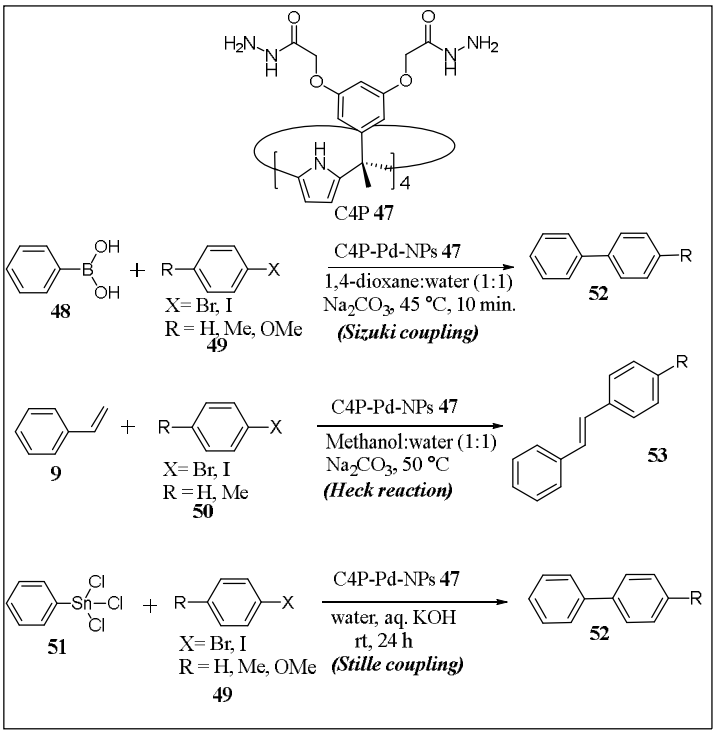
The research team led by Jain has made significant strides in the field of nano-catalysts by generating stable spherical gold nanoparticles (Au-NPs) with a *meso*-tetrahydrazide substituted C4P **54**, template for stabilization and reduction reaction (Scheme 9).[36] The resulting C4P templated Au-NPs **54** has been utilized as a heterogenous catalyst in the presence of $NaBH_4$ to carry out an efficient reduction of 4-nitrophenol **55** into 4-aminophenol **56**. On the other hand, they have also synthesized Pt-NPs using four-walled aryl extended C4P **57** as a reducing, stabilizing, and capping agent.[37] These C4P based Pt-NPs **58** catalyze the chemoselective hydrogenation reaction of nitroarenes **58** into aminoarenes **59** when exposed to room temperature with H_2.

4. Catalysis through calix[4]pyrrole-based organometallic complexes

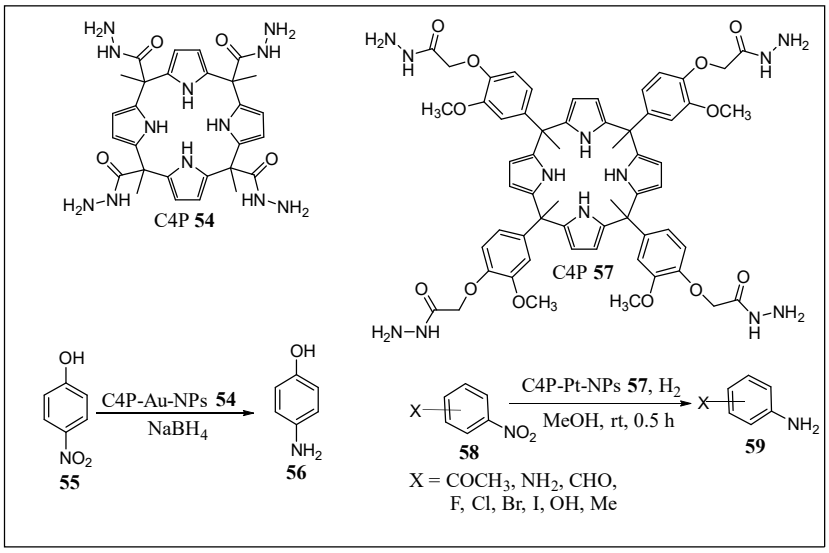
A catalyst for the reduction of nitrobenzene to aniline was created by Anjali *et al.* by grafting C4P-Rh **60** onto the surface of diamino functionalized SBA 15 molecular sieve material (Scheme 10).[38] The catalytic efficiency of SBA 15 heterogenized C4P-Rh **61** remained unchanged even after many catalytic cycles. Using SBA 15 heterogenized C4P-Rh **61** (C4P-Rh-SBA 15 **61**) as a catalyst, they have reduced a wide variety of functionalized nitrobenzenes **62-64** into functionalized anilines **65-67** (Scheme 10**)**.



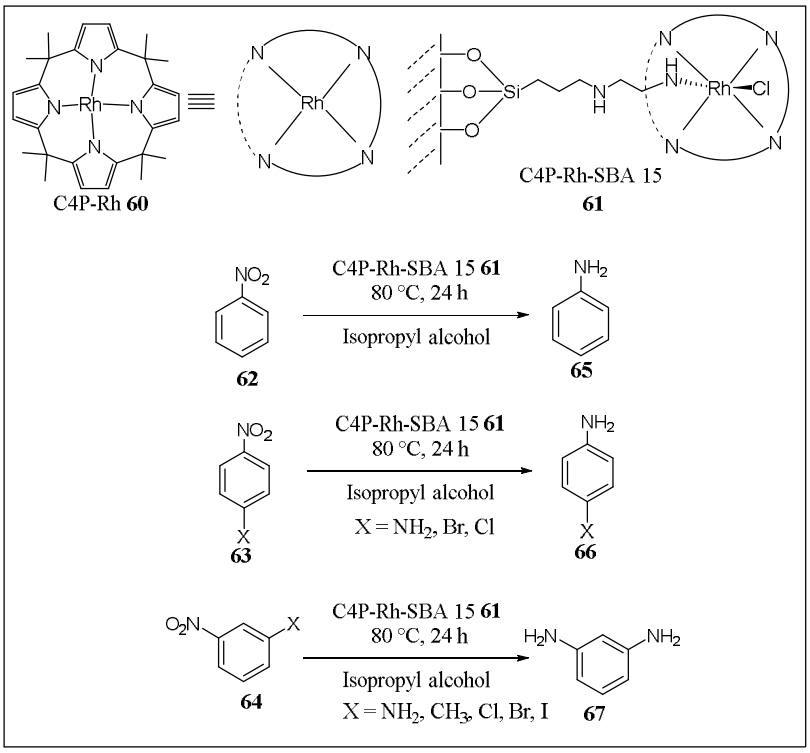
Scheme 7. Catalytic degradation of *azo*-dyes **38** and **39**, and also formation of C–C coupled Heck products **45** and **46** by means of Pd-NPs based C4P **37**.



Scheme 8. Schematic illustration of C4P-Pd-NPs **47** assisted coupling reactions *via* Heck reaction, Suzuki-Miyaura coupling, and Stille coupling.

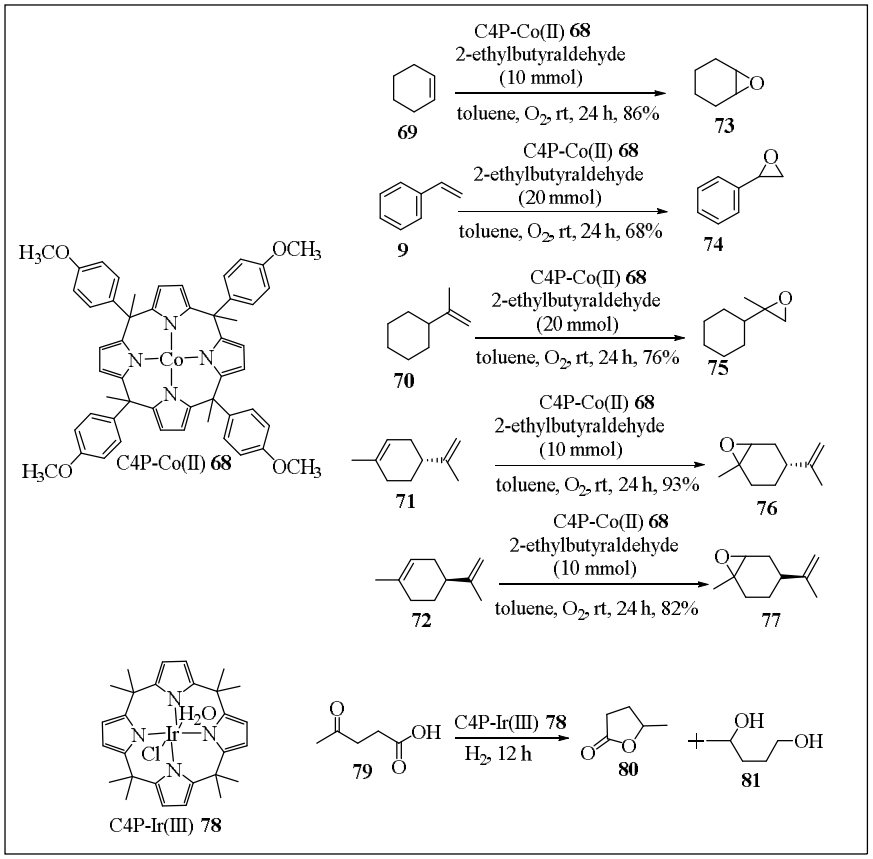


Scheme 9. Reduction of 4-nitrophenol **55** into 4-aminophenol **56** by means of C4P **54** templated Au-NPs, and chemoselective hydrogenation of nitroarenes **58** using C4P **57** based Pt-NPs as heterogenous catalyst.



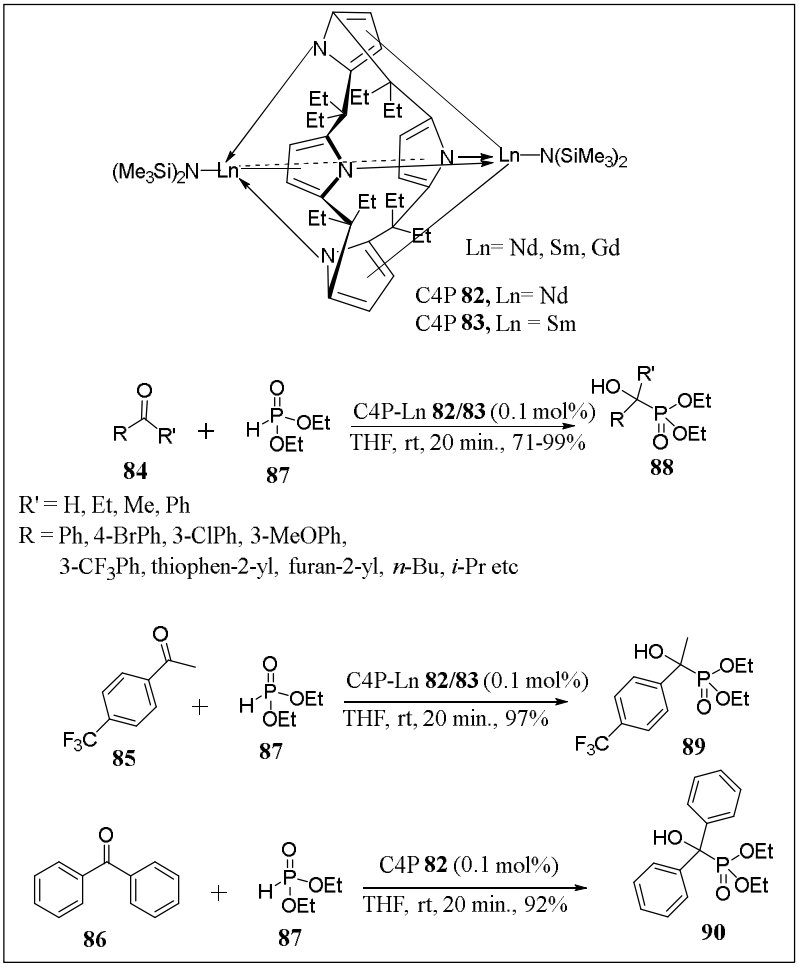
Scheme 10. Reduction of simple/functionalized nitrobenzenes **62-64** into aniline/functionalized anilines **65-67** using SBA 15 heterogenized C4P-Rh **61**.

Conversely, it has been revealed by Chavasiri and colleagues that a catalyst based on C4P-Co(II), **68** when combined with aldehydes and O_2, provides enhanced chemoselectivity for the oxidation of alkenes **9**, and **69**-**72** to epoxides **73**-**77** at room temperature in combination of an oxidant 2-ethylbutyraldehyde (Scheme 11).[39] It was discovered that the amount of oxidant determined the production of the required epoxides. For example, increasing from 10 mmol to 20 mmol of 2-ethylbutyraldehyde resulted in a 34% to 68% increase in the styrene oxide yield. Endocyclic double bonds are far more likely to undergo epoxidation than their exocyclic counterparts. One example is the high yield of diastereomers **76** and **77** produced when *R*-(+)- and *S*-(-)-limonenes **71** and **72** are epoxidized at endocyclic double bonds. Alternatively, Anjali *et al.* have also developed C4P-Ir(III) complex **78** that efficiently hydrogenates levulinic acid **79** to γ-valerolactone **80** and 1,4-pentanediol **81**.[40]



Scheme 11. Epoxidation of numerous cyclic alkenes using C4P-Co(II)-based organometallic catalyst **68** and oxidant 2-ethylbutyraldehyde. Moreover, hydrogenation of levulinic acid **79** using C4P-Ir(III) complex **78** as a catalyst is also given.

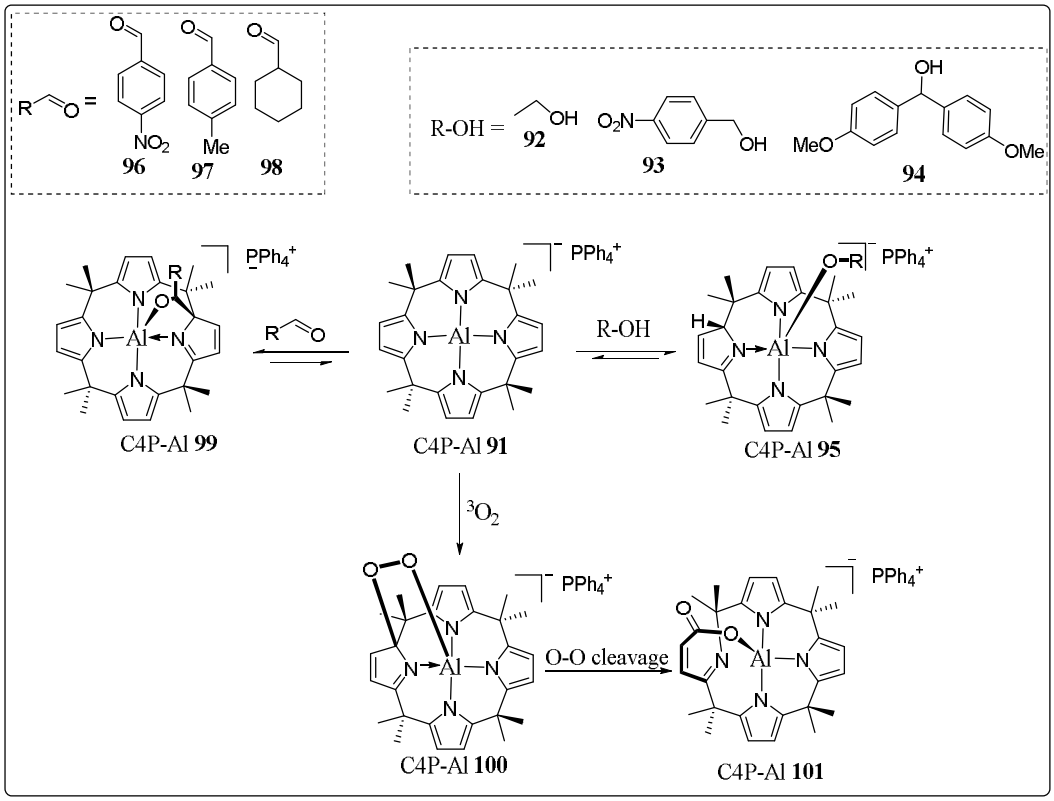
In another work, Zhang and coworkers have employed C4P-based dinuclear trivalent lanthanide amido complexes C4P-Ln **82** and **83** as efficient catalysts in the hydrophosphonylation with **87** of unactivated aldehydes and ketones **84**-**86** to desired products **88**-**90** (Scheme 12).[41] In many different organic solvents, the C4P-based catalytic complexes **82** and **83** work well with aliphatic, aromatic, and heteroaromatic aldehydes and ketones. They have taken it a step further by using these complexes **82** and **83** in the catalytic activities of *L*-lactide ring opening polymerization.[42]



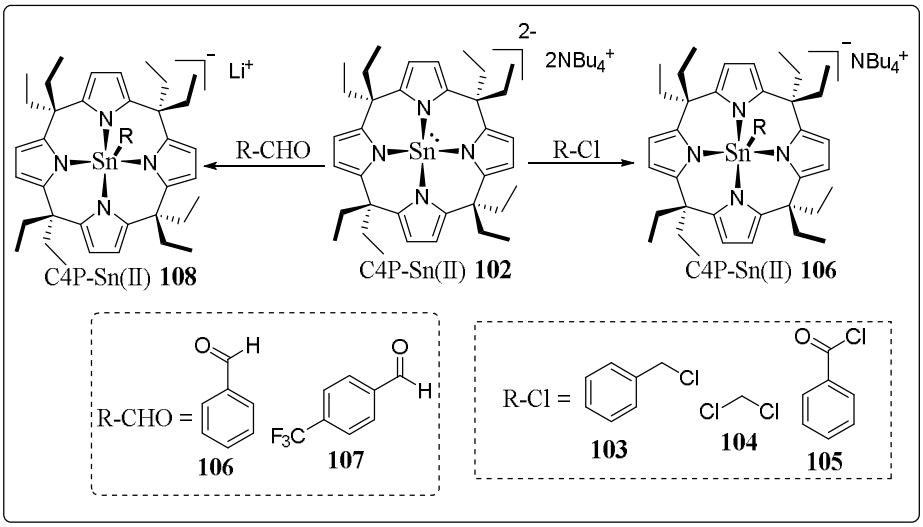
Scheme 12. Hydrophosphonylation reactions of unactivated aldehydes and ketones by means of catalysis by C4P-based catalytic complexes **82** and **83**.

In an elegant work, Greb and teammates recently described a C4P-Al complex **91** as an efficient catalyst for the activation of O–H bond of primary, secondary, and tertiary alcohols **92-94** to produce the activated products **95** (Scheme 13).[43] The unique anti-vant Hoff-Le Bel square planar arrangement at the Al-metal center in the C4P-Al complex caused the pyrrolic unit to undergo reversible dearomatization/aromatization (Scheme 13). Through metal-ligand cooperativity, the dearomatization of the pyrrole unit in catalyst **91** is also observed when it interacts with carbonyl compounds **96-98**, resulting in the formation of Al–O and C–C bonds **99**.[44] In another study, these authors have also carried out the activation of triplet dioxygen for selective peroxide formation **100** by using calix[4]pyrrolato aluminate complex **91** (Scheme 13). The peroxides are stable against many external substrates, however the oxidative α-cleavage of the pyrrole unit in **100** was observed to produce **101** when the authors heated that complex.[45]

The catalytic effectiveness and nucleophilic reactivity of C4P-Sn(II) **102** was investigated in a separate experimental study by the Greb's group. Curiously, **106** is produced when ligand **102** combines with chloro derivatives **103** and **104** and acyl chloride **105** (Scheme 14**)**. Catalyst **102** also produces acyl stannates **108** *via* hydride substitution when it combines with aldehydes **106** and **107** (Scheme 14).[46]



Scheme 13. Schematic illustration of O–H bond activation, C–C/Al–O bond formation, and peroxide formation **100**/cleavage **101** by means of calix[4]pyrrolato aluminate complex **91**.



Scheme 14. Synthesis of acyl stannates **106** and **108** using calix[4]pyrrolato Sn(II) **102** as a catalyst.

5. Conclusions

In summary, C4Ps have shown a huge potential in advancing catalytic processes through their unique structural properties and versatile reactivity. The significance of C4Ps lies in their ability to enhance reaction rates, improve selectivity, and enable the synthesis of complex molecules with precision. The rigid framework and tunable functional groups make them versatile platform for designing custom catalysts tailored to specific chemical transformations. Furthermore, the ease of functionalization and modification of C4Ps allows for fine-tuning its catalytic properties to suit different reaction conditions and substrates. By harnessing the power of C4Ps, researchers can unlock new possibilities in synthetic chemistry, green catalysis, and sustainable manufacturing. As we delve deeper into the realm of catalysis, the unique properties of C4Ps are sure to play a pivotal role in shaping the future of intricate chemical transformations and catalytic methodologies.

Acknowledgements

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