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The untold story of starch as a catalyst for organic reactions†

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Starch is one of the members of the polysaccharide family. This biopolymer has shown many potential applications in different fields such as catalytic reactions, water treatment, packaging, and food industries. In recent years, using starch as a catalyst has attracted much attention. From a catalytic point of view, starch can be used in organic chemistry reactions as a catalyst or catalyst support. Reports show that as a catalyst, simple starch can promote many heterocyclic compound reactions. On the other hand, functionalized starch is not only capable of advancing the synthesis of heterocycles but also is a good candidate catalyst for other reactions including oxidation and coupling reactions. This review tries to provide a fair survey of published organic reactions which include using starch as a catalyst or a part of the main catalyst. Therefore, the other types of starch applications are not the subject of this review.

1. A little bit about starch

Starch or amyllum is the second most abundant natural polysaccharide on earth in terms of quantity after cellulose.¹ Traditionally, this biopolymer has been used in the food industry, however, thanks to the advancement of technology and increasing research, starch is not limited only to the food industry anymore, and there are many other industries like textiles and paper, chemicals, agriculture, medicine, and engineering industries that benefit starch and its applications.²

As the most common carbohydrate in the human diet³ and the main storing carbohydrate in many plants like vascular plants,⁴ this polymeric polyol can be found in many natural sources including grains (wheat, corn, rice, rye, barley, beans, peas, and lentil), fruit (banana peel, apple pulp, kiwi seeds, avocado, pineapple, and mango), plants (sorghum, cassava, potato, sweet potato, taro, amaranth, sago palm), and many other natural sources.¹ Despite the numerous natural sources of starch, about 80% of the global starch production comes from *Zea mays* (corn).²

From a chemical point of view, starch (C₆H₁₀O₅) is a white and tasteless powder that is insoluble in cold water, but if the water is heated beyond the boiling point in a closed container, it can be dissolved.⁵ This hydrocarbon polymer consists of α -D-glucopyranose units as monomers joined together through α -1,4-glycosidic bonds. Although the α -1,4-glycosidic bonds are

the main way of connecting monomeric units and making the chain, there are other common bonds like α -1,6-glycosidic bonds which are responsible for making the connection between chains and creating branches.⁶

Starch is mainly made of two different types of molecules, *i.e.*, amylose (linear and helical structure) and amylopectin (branched structure) (Fig. 1)⁷ that are responsible for about 20–30% and 70–80% of the natural starch composition, respectively.⁸ The chemical structure of starch makes this low-cost natural polymer a wonderful compound with many significant

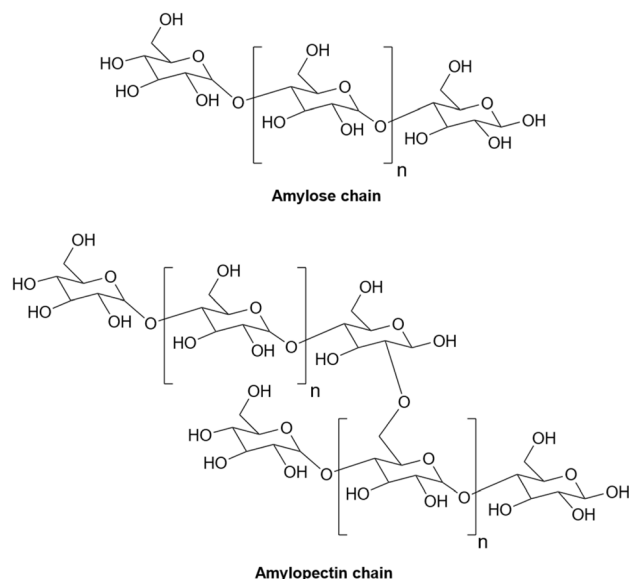


Fig. 1 The chemical structure of two main components of starch.

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† This review is dedicated to the late Prof. Dr Javad Safari for his passion and devotion to educating and leading a new generation of Iranian chemists.



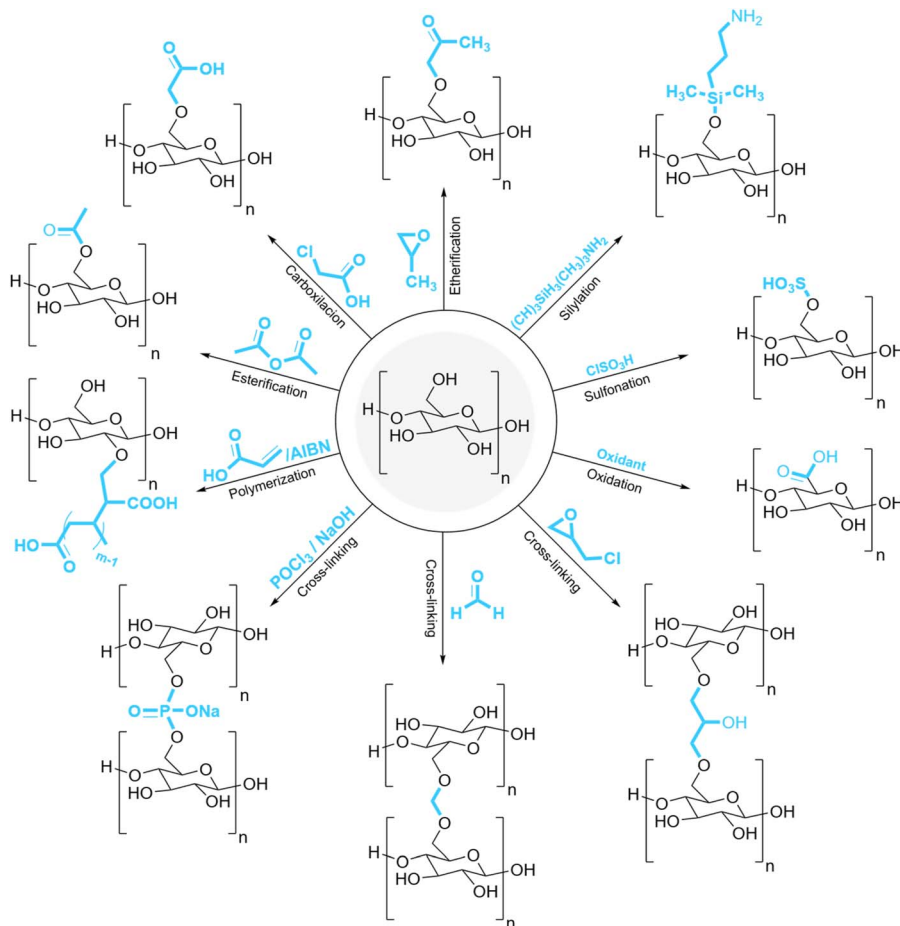


Fig. 2 Some of the common modification reactions for starch.¹⁵⁰

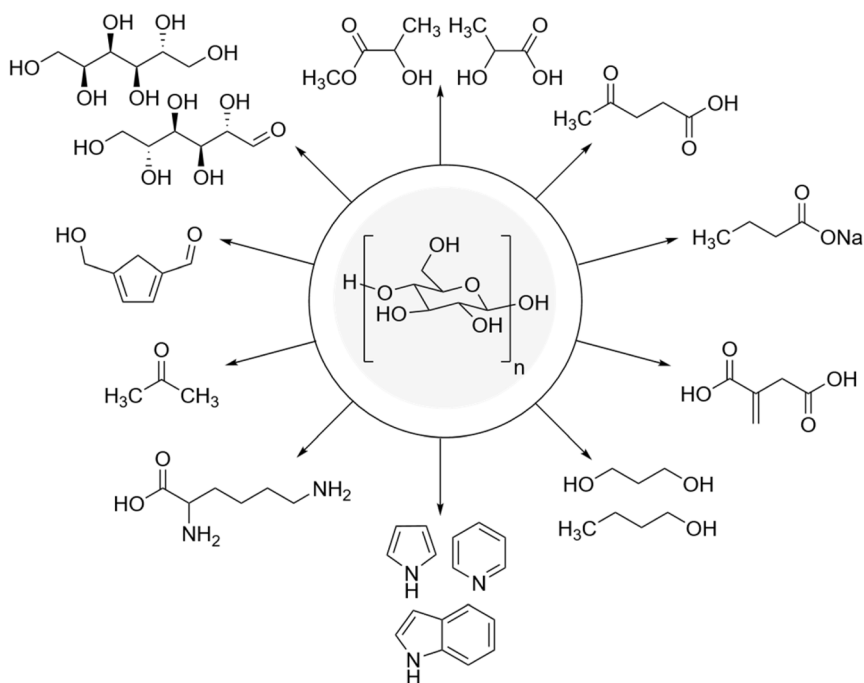


Fig. 3 Some of the important compounds made from starch.⁷



features including biodegradability, safe and convenient usage, annual renewability, and ease of availability.⁸ As a polyol, starch has many hydroxyl groups in its structure which can create a lot of intra and intermolecular hydrogen bonds. The presence of many hydroxyl groups makes starch suitable for many purposes. For example, starch can be converted into many valuable derivatives. Literature review^{9–11} shows that starch can undergo many reactions similar to alcohols including esterification,^{12,13} etherification,^{14,15} oxidation,^{16,17} cross-linking,^{18,19} sulfonation,^{20,21} and so on (Fig. 2). Also, the presence of glycosidic bonds in the structure of starch makes it susceptible to become hydrolyzed under alkaline, acidic, or enzymatic conditions.^{22–24}

In addition to transformations such as depolymerization and modification of the hydroxyl groups on the surface of starch, this polysaccharide can undergo more drastic changes to produce many diverse products (Fig. 3). For instance, the thermal dehydration of starch opens the doors to many carbon-based materials such as porous carbon materials, composite carbon materials, and carbon nanomaterials. Also, starch can be a substrate for many small organic molecules especially industrially manufactured products including 5-hydroxymethylfurfural, levulinic acid, lactic acid, acetone, butanol, ethanol, *etc.*⁷

Apart from the importance of starch as a substrate for the preparation of valuable products, this natural polymer or its slightly modified derivatives can be used as great tools for other purposes.^{25–31} For example, starch with many hydroxyl groups can act like a molecular octopus with many tentacles to remove environmental pollutants such as heavy metals,³² dyes,³³ pesticides,³⁴ anti-biotics,³⁵ and oils.³⁶ Also, there are many reports about starch-based material application as biodegradable and renewable alternatives for current widely used non-renewable resins.³⁷

Besides the application of starch and starch-based materials in the mentioned fields, using starch or modified starch as catalysts has attracted growing attention.^{38–40} Regarding the increasing number of published reports on the use of starch as a catalyst, it is necessary to write a review about the application of starch in organic reactions. To the best of my knowledge, there is no related review about the role of starch as a catalyst in organic reactions and this one would be the first of its kind.

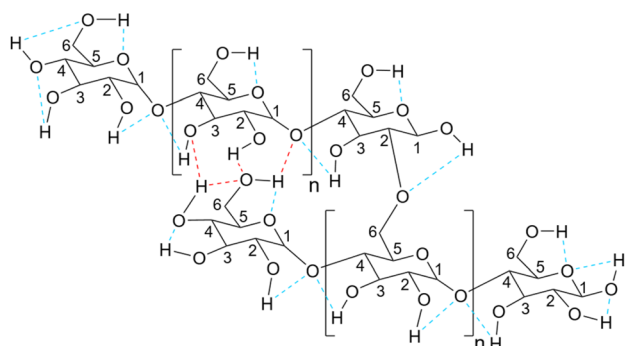


Fig. 4 Intra- (blue) and intermolecular (red) hydrogen bonds in starch (amylopectin chain).

This review aims to comprehensively examine organic reactions that have been carried out using starch or its derivatives as catalysts and categorize them based on the type and structure of the employed starch.

2. Starch as catalyst for organic reactions

Depending on the type and application of the catalyst, there are different mentioned properties for a suitable catalyst in scientific literature. However, for a heterogenous catalyst, we can point out properties like cost, toxicity, stability and durability, volumetric efficiency (good surface area and available active sites), activity (promoting the desired reaction with good yield at a sensible temperature and pressure), selectivity, recoverability and reusability.⁴¹ As a heterogeneous candidate catalyst, starch can fulfill many properties expected of a suitable catalyst. For example, it is cheap, non-toxic, environmentally friendly, reusable, and easy to access and apply, making this biopolymer worth exploring for different organic reactions. Also, with many hydroxyl groups on the surface of this member of the carbohydrate family, it is possible to convert starch to desired functionalized derivatives that can even widen the application of starch as a catalyst.

Regarding the fact that there is no such thing as the perfect catalyst, it is not a big surprise that in addition to the many advantages of starch as a heterogeneous catalyst, there are also some disadvantages. Starch is a hygroscopic substance by nature, so it can absorb up to 17% of moisture.⁴² This means that at least naive starch can not be a good catalyst candidate for water-sensitive reactions. Moreover, naive or simple starch is not capable of coping with some conditions like high temperature, a wide range of pH, or freeze–thaw cycles.⁴² Starch swells when heated in water. As the temperature of heated starch in water reaches the “gelatinization temperature” which depends on the characteristics of its source, swollen starch loses its semi-crystalline structure. When the increasing temperature goes beyond that temperature, the structural integrity decreases. Eventually, this leads the starch structure to break down into its constituent molecules, including amylose, amylopectin, and some other minor components.⁴³ These limitations combined with a natural tendency of naive starch for decomposition and brittleness make it not to be desirable for every reaction condition. However, chemical modification can overcome some of the limitations of simple starch and make it possible to use this inexpensive and environmentally friendly catalyst in reactions with different conditions.

As mentioned before, starch in simple or chemically modified forms can be used for the desired reaction as a catalyst or catalyst support. To describe the mechanism of the action of starch as a catalyst in organic transformations we should resort to non-covalent interactions (NCIs).⁴⁴ For the simple starch, the structural hydrogen bonding interactions are the major NCIs that can promote the conversion of starting materials to the desired products. As a polyhydroxy compound, each ring in the structure of starch has three hydroxyl groups (at C₂, C₄, and C₆) that can



make hydrogen bondings with active sites on substrate molecules and facilitate their transformations to the related products (Fig. 4).⁴⁵ For example, Arabpourian and Behbahani proposed an overall reaction mechanism for the synthesis of pyrrole using starch as a heterogeneous catalyst (Fig. 5).⁴⁶ The authors have shown how starch hydrogen bonding guides the starting materials to the desired product. In the first step, the diketone's carbonyl group is activated by starch's OH-groups to obtain intermediate 1. This hydrogen bonding makes the carbonyl group ready to be attacked by an amine as a nucleophile to produce intermediate 2. The second carbonyl activated by starch hydrogen bonding experiences an intramolecular amine nucleophilic attack which results in intermediate 3. Finally, the desired product 4 is obtained after the dehydration of intermediate 3.

Similar to other polysaccharides,⁴⁷ the hydroxyl groups on the surface of simple starch can be modified and attached to other functional groups to increase the ability of starch and accelerate

organic reactions.⁴⁸ For example, simple starch can be sulfonated using sulfonating agents (sulfuric acid, chlorosulfonic acid, and sulfur trioxide) to convert starch to a suitable brønsted acid.²¹ As another instance, attaching amine groups to these hydroxyl groups by appropriate linkers to prepare related Schiff bases makes starch capable of being like molecular pincers holding metal ions as Lewis acid catalysts.⁴⁹ Depending on the type of chemical functionalization on the surface of starch, the way that these modified starch can promote the reaction will be different but the important point is that the hydrogen bonds of starch with substrates are still considerable. This means when we have an acidic/basic or metal-loaded starch, even if the main driving force from the catalyst is coming from added parts (acid, base, or metal) to the starch, the effect of starch itself to promote the reaction still exists.

Based on published papers about using starch or modified starch as a catalyst for organic transformations, they can be placed in two categories: (1) unfunctionalized and (2) functionalized starch. The first type of starch is related to the ones with no surface functionalization which includes either simple starch or magnetic/composite starch. The second one indicates catalysts with chemical surface functionalization including acidic/basic, and metal-loaded starch. From the structural point of view, these two types of starch can have a simple or complex structure like a core-shell structure where starch is wrapped around a specific core usually a magnetic one, functionalized with desired groups (Fig. 6). In the following sections, this review deals with the reactions that employed simple and functionalized starch as a catalyst or catalyst support.

2.1 Simple starch

Simple or raw starch without any chemical modification could be used directly as a catalyst for the synthesis of many heterocyclic compounds. Published reports show that this cheap polysaccharide has been successfully used as a catalyst for the preparation of pyrrole, 2-aminothiazole, dihydropyranopyrazole, tetrahydrobenzopyran, and dihydropyranochromene derivatives. In the following, these reactions will be discussed.

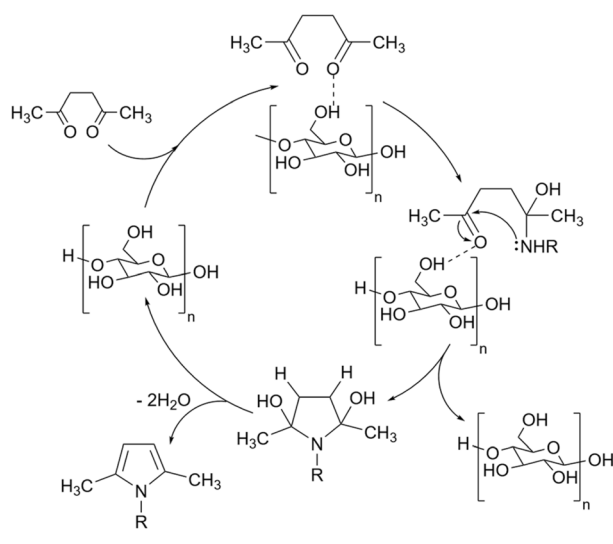


Fig. 5 The proposed mechanism for the synthesis of *N*-substituted pyrroles using starch as a catalyst.⁴⁶

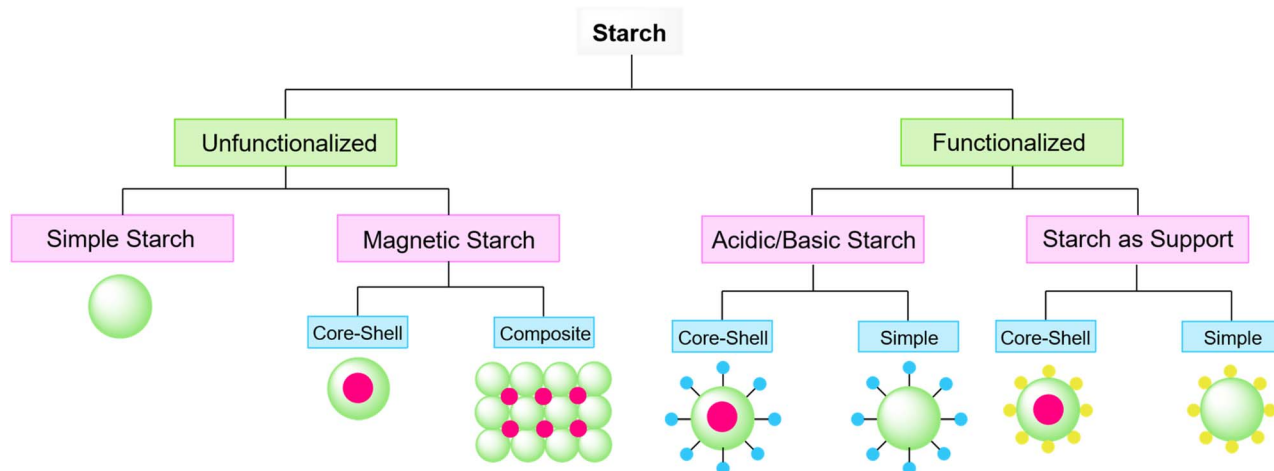


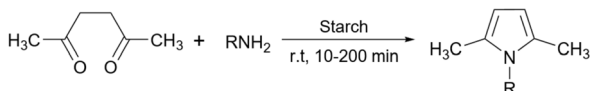
Fig. 6 Different types of starch used as catalyst.



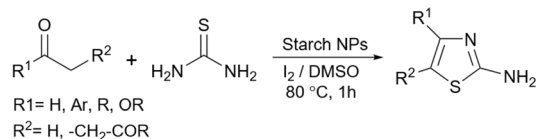
2.1.1 Synthesis of pyrroles. Pyrroles are five-membered rings with many known applications in synthetic chemistry as an interesting scaffold for the construction of many valuable compounds.^{51,52} The most general approach for the synthesis of pyrroles is the Paal–Knorr reaction. Very recently, Arabpourian and Behbahani disclosed a novel method for the Paal–Knorr synthesis of different pyrroles.⁴⁶ They successfully managed to prepare different 2,5-dimethyl-1-phenyl-1*H*-pyrrole derivatives from the reaction of 2,5-hexadione with a variety of amines at room temperature using simple starch as a catalyst (Scheme 1).

2.1.2 Synthesis of 2-aminothiazoles. Structures containing 2-aminothiazole moiety are an important class in the family of heterocyclic compounds and have many potential applications especially in medicinal chemistry because of their anti-cancer and anti-tumor, anti-viral, anti-inflammatory, and anti-microbial activities.^{53–55} Moreover, these compounds can be used as convenient substrates to prepare more complex products like corresponding azo derivatives⁵⁶ and many polycyclic heterocyclic compounds.^{57,58} In 2017, our team at the University of Kashan found that simple starch can promote the synthesis of 2-aminothiazole derivatives in the presence of molecular iodine as a halogenating agent (Scheme 2).⁵⁹ However, we soon found that using starch nanoparticles (starch NPs) instead of bulk starch increases the reaction yield by 1.5 times and also decreases the required starch for the reaction.

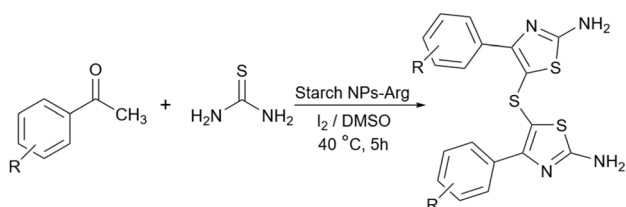
In search for new capabilities of starch as catalyst in the preparation of 2-aminothiazole derivatives, two years later our group succeeded in finding a similar protocol to produce some diheteroaryl thioether derivatives containing 2-aminothiazole units (Scheme 3).⁶⁰ Compared to our previous protocol for the



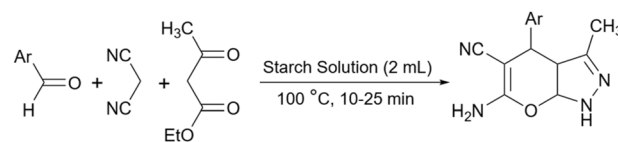
Scheme 1 Synthesis of *N*-aryl pyrroles using simple starch.



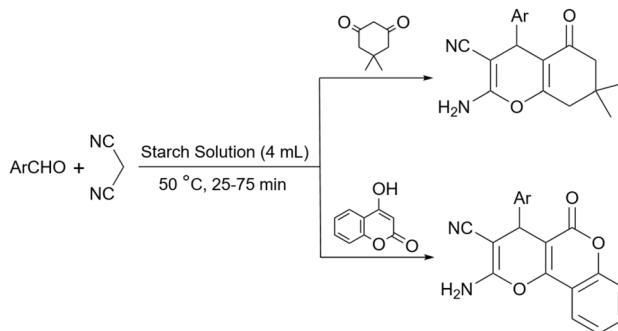
Scheme 2 Synthesis of 2-aminothiazoles using starch nanoparticles.



Scheme 3 Synthesis of diheteroaryl thioethers using starch nanoparticles.



Scheme 4 Synthesis of dihydropyrano[2,3-*c*]pyrazoles using starch solution.



Scheme 5 Synthesis of tetrahydrobenzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes using starch solution.

synthesis of 2-aminothiazoles, this one proceeded at a much slower speed and a lower temperature.

2.1.3 Synthesis of dihydropyrano[2,3-*c*]pyrazoles. As one of the significant fused heterocyclic compounds, dihydropyrano[2,3-*c*]pyrazoles have diverse bioactivities including anti-inflammatory, anti-cancer, anti-oxidant, analgesic, and anti-microbial properties.⁶¹ In 2015, Kangani and colleagues used starch solution to prepare a wide range of dihydropyrano[2,3-*c*]pyrazole derivatives from aryl aldehydes, hydrazine monohydrate, ethyl acetoacetate, and malononitrile as precursors (Scheme 4).⁶² To prepare the starch solution, they added starch to the magnetically stirred water, and after 30 minutes the achieved solution was filtered out and used as a solution containing starch.

2.1.4 Synthesis of tetrahydrobenzopyrans and dihydropyrano[*c*]chromenes. Tetrahydrobenzopyrans and dihydropyrano[*c*]chromenes not only have similar structures but also have many pharmaceutical and biological activities. For instance, prepared tetrahydrobenzo compounds can be used as an effective anti-cancer, anti-coagulant, diuretic, spasmolytic, and anti-anaphylactic agents⁶³ and dihydropyrano[*c*]chromenes are similarly known for their anti-coagulant, anti-cancer, anti-bacterial, anti-microbial, anti-alzheimer, and anti-malaria properties.⁶⁴ Hazeri *et al.* succeeded in achieving a protocol for the synthesis of both tetrahydrobenzo[*b*]pyrans and 3,4-dihydropyrano[*c*]chromenes using starch solution as a catalyst (Scheme 5).⁶⁵ They prepared the starch solution as mentioned before⁶² and carried out these two three-component reactions at 50 °C with a very good yield for the products.

2.2 Magnetic starch

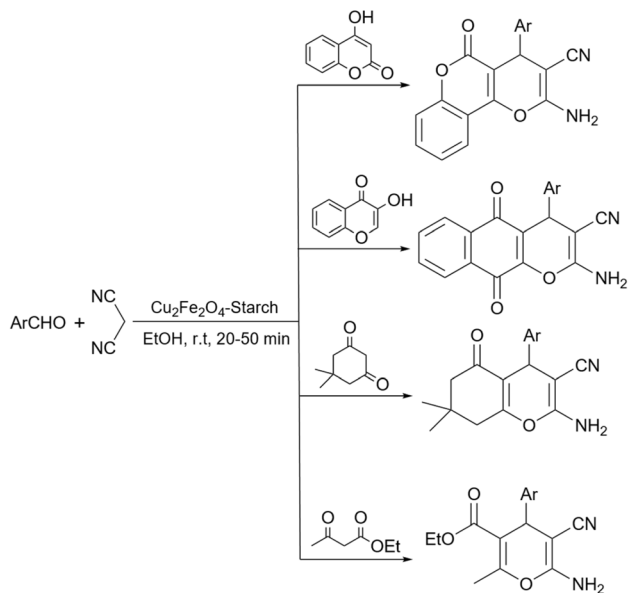
The recovery of the catalyst after the end of the reaction is one of the important problems with using simple starch as a catalyst in organic reactions. However, there are some solutions to fix this



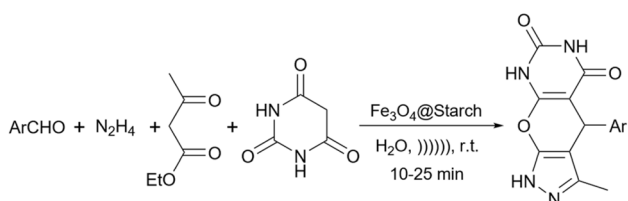
weakness. One of them is magnetizing the simple starch using iron oxide particles. The papers that used this technique will be presented, in the next sections.

2.2.1 Synthesis of pyran. As an oxygen-containing heterocyclic compound, pyrans are a known family of organic compounds with great importance in synthetic chemistry.^{66,67} Among the members of this family, fused benzo 4*H*-pyrans like 4*H*-chromene derivatives have been well-known because they are extensively present in nature including plants, vegetables, and fruits.⁶⁸ In 2020, Kamalzare and colleagues introduced a novel starch composite for the synthesis of the 4*H*-pyran derivatives (Scheme 6).⁶⁹ They prepared CuFe₂O₄-starch as a magnetically recyclable nanocatalyst and used it to facilitate a three-component reaction between aldehydes, malononitrile, and dimedone or ethyl acetoacetate (as C-H activated acidic compounds). The authors employed a simple dispersion technique to impregnate the starch with CuFe₂O₄. The resulting mixture was stirred for 8 hours and then dried on a glass plate for the next 48 hours to form the desired CuFe₂O₄-starch nanocomposite.

2.2.2 Synthesis of chromenoquinolines. Pyranopyrazoles, pyranopyrimidines, and pyrazolopyranopyrimidines scaffolds can be found in the structure of many biologically active compounds.^{70,71} Recently, the Ameta research group



Scheme 6 4*H*-Pyran synthesis catalyzed by CuFe₂O₄@starch.



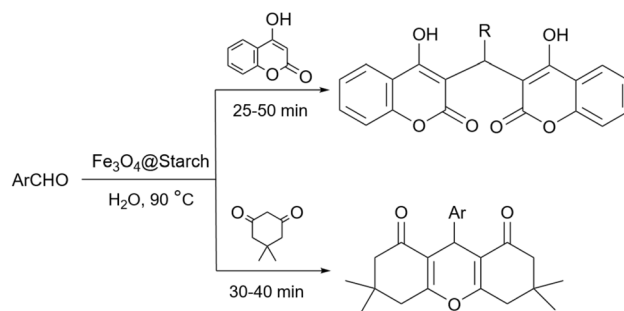
Scheme 7 Chromenoquinoline synthesis catalyzed by Fe₃O₄@starch.

successfully managed to prepare different pyrazolopyranopyrimidines from ethyl acetoacetate, hydrazine hydrate, barbituric acid, and various benzaldehydes as substrates (Scheme 7).⁷² To proceed with the reaction they used Fe₃O₄@starch as catalyst. Based on the proposed mechanism proposed by the authors, the reaction is facilitated by the hydrogen bond between substrates and the hydroxyl groups on the surface of the catalyst.

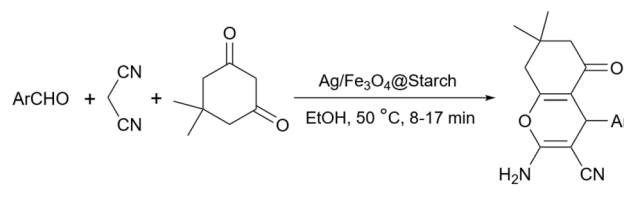
2.2.3 Synthesis of bis-coumarin and xanthenes. In 2018, Razikazemi *et al.* reported a procedure for the synthesis of bis-coumarin and xanthenes derivatives from 4-hydroxycoumarin and dimedone, respectively (Scheme 8).⁷³ They prepared a magnetic starch from Fe₃O₄ and hot-water-soluble starch and used this nanocomposite as the catalyst. To prepare hot-water-soluble starch, they used a previously reported method⁷⁴ including heating wheat starch with ethanol at 98 °C, centrifuging the achieved solution, and drying the prepared solid. The authors proposed that both reactions can proceed through a consecutive proton exchange on the surface of starch.

2.2.4 Synthesis of 4*H*-pyran and tetrahydro-4*H*-chromene. Similar work to Hazeri's research⁶⁵ has been done by Marjani and colleagues in 2020 (Scheme 9). They prepared Ag/Fe₃O₄@starch and used that as a catalyst for the synthesis of 4*H*-pyran and tetrahydro-4*H*-chromene derivatives.⁷⁵ Authors reported that their magnetic nanocatalyst can be still reused even after up to five runs.

2.2.5 Synthesis of tetraketones and pyranopyrazoles. Tetraketones are important precursors for the preparation of many organic molecules including heterocyclic compounds. Also, these compounds have shown interesting biological activities including lipoxygenase and tyrosinase-inhibiting properties.⁷⁶ Very recently, Matloubi Moghaddam and colleagues introduced

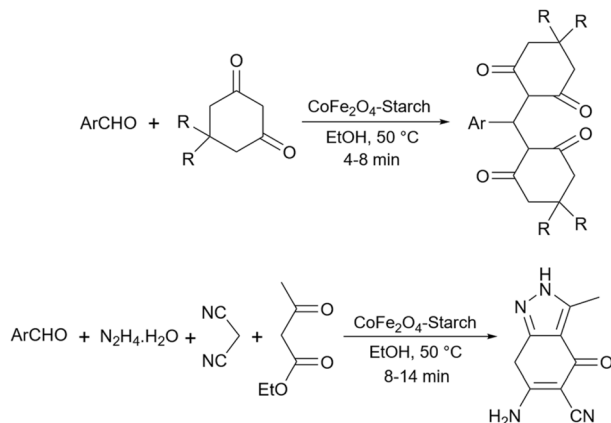


Scheme 8 Synthesis of bis-coumarins and xanthenes using Fe₃O₄@starch.



Scheme 9 Synthesis of tetrahydro-4*H*-chromene catalyzed by Ag/Fe₃O₄@starch.





Scheme 10 Synthesis of tetraketones and pyranopyrazoles using CoFe_2O_4 -starch nanocomposite.

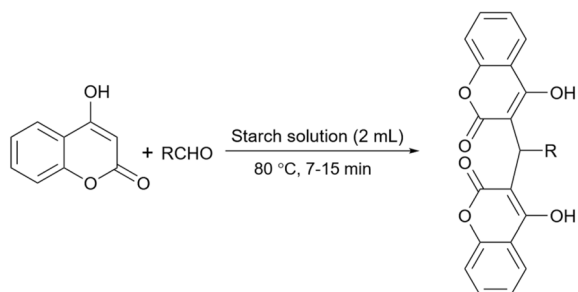
a method for the preparation of magnetic starch and using it as a catalyst for the synthesis of tetraketone and pyranopyrazole derivatives (Scheme 10).⁷⁷ They used bread waste as the source of starch and then modified the prepared starch with CoFe_2O_4 nanoparticles.

2.3 Acidic starch

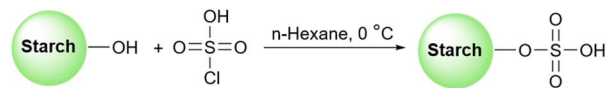
Simple starch has many hydroxyl groups and is capable of helping the reaction process through hydrogen bondings with substrates and intermediates, but sometimes these groups are not effective enough to help the reaction. Therefore, the functionalization of simple starch by acidic groups is used to increase the ability of starch to create more hydrogen bonds and the activation of substrates. The related papers will be discussed in the coming parts.

2.3.1 Synthesis of coumarin. Coumarin derivatives similar to many other heterocyclic compounds have shown interesting pharmacological properties. Based on published research papers, this family that belongs to lactones shows significant properties like anti-fungal, anti-coagulant, insecticidal, and anti-helminthic activities, HIV protease inhibition, and even some potential applications in the treatment of Alzheimer's disease.⁷⁸

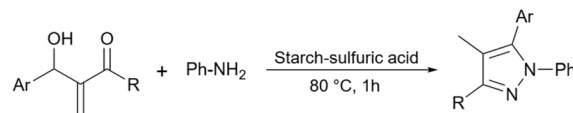
To prepare bis-coumarins commonly known as coumarin derivatives (Scheme 11), Rezaei and Sheikhi used starch-sulfuric acid as a catalyst. Instead of modifying starch with linkers and



Scheme 11 Synthesis of bis-coumarin using starch-sulfuric acid.



Scheme 12 Preparation of starch-sulfuric acid.

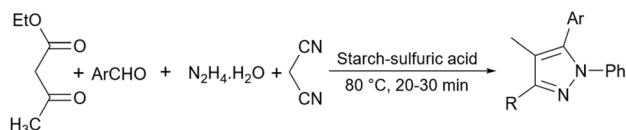


Scheme 13 Synthesis of the 1,5-diaryl-1H-pyrazoles using starch-sulfuric acid.

attaching the sulfonate group to the linker,⁷⁹ they just synthesized starch-sulfuric acid by adding chlorosulfonic acid to the starch in *n*-hexane as solvent at 0 °C (Scheme 12).⁸⁰ In their provided protocol, the transformation of aldehydes and coumarins as substrates to the corresponding bis-coumarin derivatives involves a Knoevenagel reaction followed by a Michael addition which both reactions can be facilitated by Brønsted acids like sulfuric acid.

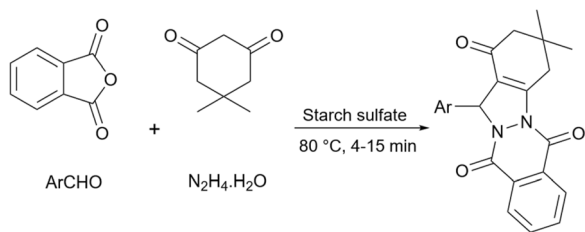
2.3.2 Synthesis of pyrazoles. Studies show that pyrazoles could stop many cancer cell types from developing including lung, brain, prostate, colorectal, renal, and pancreatic cancer.⁸¹ In 2013, Hatamjafari published a paper on *Helvetica Chimica Acta* reporting a new method for the synthesis of 1,5-diaryl-1H-pyrazoles catalyzed by starch-sulfuric acid (Scheme 13).⁸² The provided method was based on the condensation of Baylis-Hillman adducts of an α,β -unsaturated, and phenyl hydrazine as substrates. Two years later, Vekariya and his co-workers used the same catalyst to speed up a 4-component reaction to prepare related 1,4-dihydropyranopyrazoles (Scheme 14).⁸³ They came up with an efficient way to convert ethyl acetoacetate, hydrazine, benzaldehyde, and malononitrile nitrile to the corresponding 1,4-dihydropyranopyrazoles in less than 30 minutes with pretty good yields.

2.3.3 Synthesis of phthalazines. Phthalazines, benzopyridazines, or benzo-orthodiazines are members of heterocyclic families that are present in many natural products with extensive proven or potential biological applications like anti-cancer activity.⁸⁴ With this in mind, in 2011, Shaterian and Rigi disclosed another application for starch-sulfuric acid as a novel catalyst for the preparation of 2H-indazolo[2,1-*b*]phthalazine-trione derivatives (Scheme 15).⁸⁵ Their presented four-component reaction included hydrazine, phthalic anhydride, dimedone, and benzaldehyde as substrates.



Scheme 14 Synthesis of 1,4-dihydropyranopyrazole-5-carbonitriles using starch-sulfuric acid.

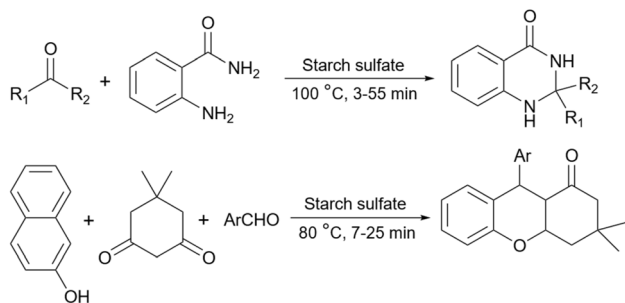




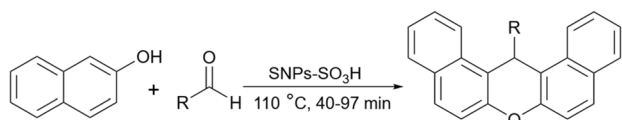
Scheme 15 Synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones using starch-sulfuric acid.

2.3.4 Synthesis of xanthene. Compounds containing xanthene and benzoxanthene units have shown many diverse properties like anti-bacterial and anti-inflammatory activities, the ability to be used as fluorescent dyes, and promising applications in laser technology.^{86–88} In 2015, Shaterian and Rigi unveiled a new method for the synthesis of xanthene and quinazoline derivatives (Scheme 16).⁸⁹ Apart from different precursors, the presented protocols for the two reactions were almost similar including using starch sulfate as a biodegradable solid acid.

In 2017, our team at the University of Kashan proposed an effective procedure for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes using sulfonated starch nanoparticles as a promising heterogeneous catalyst (Scheme 17).⁹⁰ The reaction proceeded in a solvent-free condition at 110 °C with satisfactory yields for a wide range of substrates. To prepare starch nanoparticles, the bulk starch went through a two-step process. In the first step starch was treated with acid and then base under an argon atmosphere and rigorous stirring. Then, potassium persulfate was added to the resulting mixture, and in the end, the starch nanoparticle was separated from the solution using an ice bath.



Scheme 16 Synthesis of xanthene and quinazoline derivatives using starch-sulfuric acid.



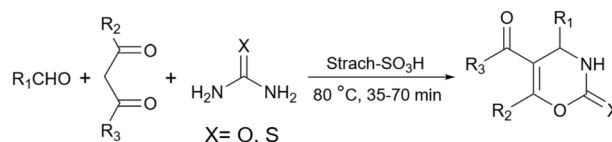
Scheme 17 Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes using sulfonated starch nanoparticles.

2.3.5 Synthesis of dihydropyrimidinone. Since Biginelli's first report about the condensation of dicarbonyl compounds with aldehydes and urea or thiourea for the synthesis of dihydropyrimidinones in 1893,⁹¹ there have been many reports about these important compounds in medicinal chemistry.⁹² In 2013, Rezaei *et al.* disclosed a novel catalytic method for the preparation of these compounds using starch-sulfuric acid as a catalyst (Scheme 18). They used their modified starch as an eco-friendly and reusable catalyst for the famous Biginelli reaction.⁹³

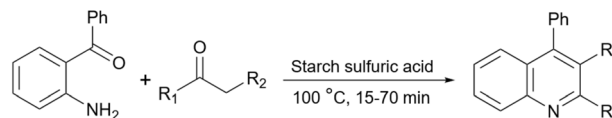
2.3.6 Synthesis of quinolines. Quinoline or benzopyridine is one the most important N-based heterocyclic compounds with many medicinal, bioorganic, and industrial chemistry applications.⁹⁴ Shaabani and co-workers proposed a sulfonated starch-catalyzed Friedländer reaction for the synthesis of quinoline derivatives using 2-amino aryl ketones and β -diketones as substrates (Scheme 19).⁹⁵ They also prepared and used sulfonated cellulose for this reaction, but no significant difference between the catalytic effects of cellulose sulfuric acid and starch sulfuric acid was observed.

2.3.7 Synthesis of quinoxalines and benzimidazoles. Quinoxalines and benzimidazoles like many other nitrogen-containing heterocycles have a great place in synthetic and medicinal chemistry. Literature review shows that there are many reports about the synthesis of quinoxalines^{96,97} and benzimidazole derivatives.^{98,99} For instance, in 2018, Farrokhi and co-workers disclosed a new method for the synthesis of quinoxalines and benzimidazoles using Fe_2O_3 @starch-1,4-piperazinediylbis(methylene)bisphosphonic acid as Brønsted acid (Scheme 20).¹⁰⁰

2.3.8 Synthesis of chromenoquinoline. Quinolines and chromenes are considered important families in heterocyclic chemistry. However, the literature review shows that chromenoquinoline compounds that contain both these units at their structure have many interesting properties.⁶⁸ For example, some of these compounds have shown the ability to act like fluorescence sensors.¹⁰¹ Recently, Sayahi *et al.* reported a sulfonic acid functionalized magnetic starch as a novel and efficient catalyst for the synthesis of chromeno[4,3-*b*]quinoline-6,8(9*H*)-dione derivatives (Scheme 21).¹⁰² To prepare the catalyst they prepared

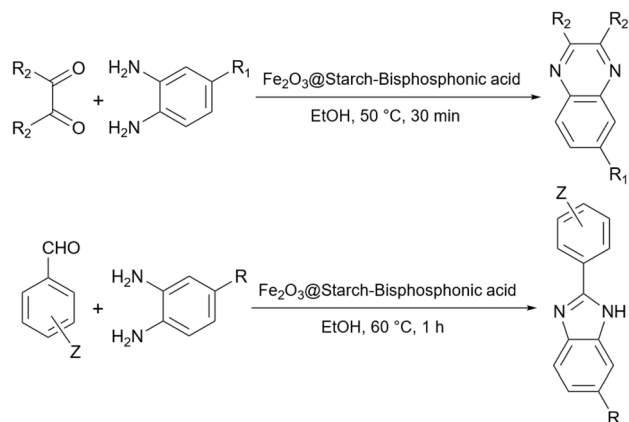


Scheme 18 Synthesis of dihydropyrimidinones using starch sulfuric acid.

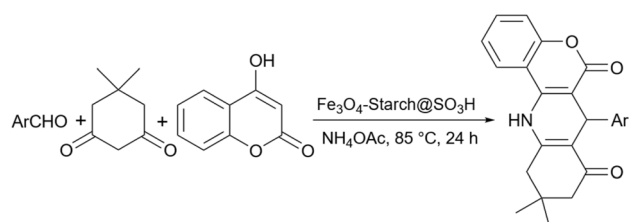


Scheme 19 Synthesis of quinolines using starch sulfuric acid.





Scheme 20 Synthesis of quinoxalines and benzimidazoles using Fe_2O_3 @starch-1,4-piperazinediylbis (methylene) bisphosphonic acid.



Scheme 21 Synthesis of chromenoquinoline using Fe_3O_4 -starch@ SO_3H .

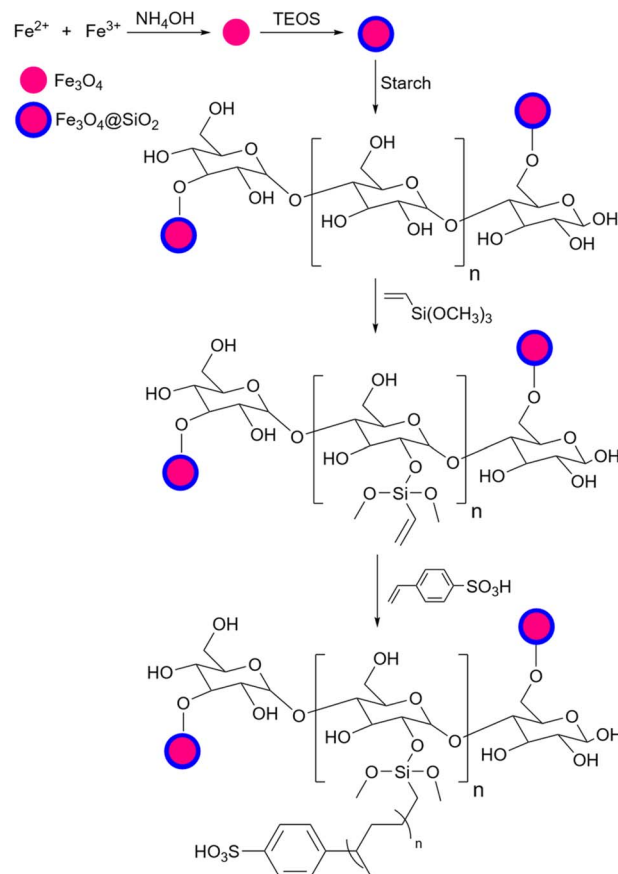
Fe_3O_4 nanoparticles, modified its surface with tetraethyl orthosilicate (TEOS), and attached these nanoparticles to the surface of starch. In the next step, the surface of the prepared magnetic starch was coated with allyltrimethoxysilane. Finally, the 4-styrenesulfonic acid was attached to the surface as the last layer through polymerization (Scheme 22).

2.3.9 Synthesis of formamides and acetamides. Converting primary and secondary amines to their related formamide and acetamide products has always been interesting to chemists.^{103,104} This is because amide bonds are a significant part of many compounds including some important polymers, drugs, dyes, and agrochemical compounds.^{105–108} Very recently, Wani *et al.* employed sulfated starch as an efficient catalyst to transform the simple amines to their corresponding amides (Scheme 23).¹⁰⁹

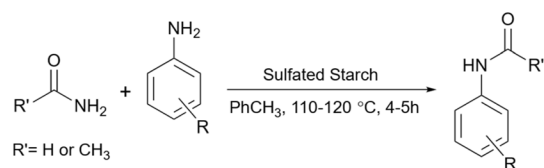
2.4 Basic starch

Although simple starch can act like a Brønsted acid to advance the reaction this is not very helpful for those reactions that need basic catalysts. To use starch as a catalyst for these types of reactions, researchers have used basic agents including NaOH, and *p*-phenylenediamine (PPD) to give basic properties to the starch. The papers in which basic starch has been used as a catalyst will be presented in the next sections.

2.4.1 Synthesis of hydroquinazolines. Quinazolines are interesting heterocyclic compounds with a wide range of biological and pharmaceutical activities.^{110,111} For example,



Scheme 22 Preparation of Fe_3O_4 -starch@ SO_3H .

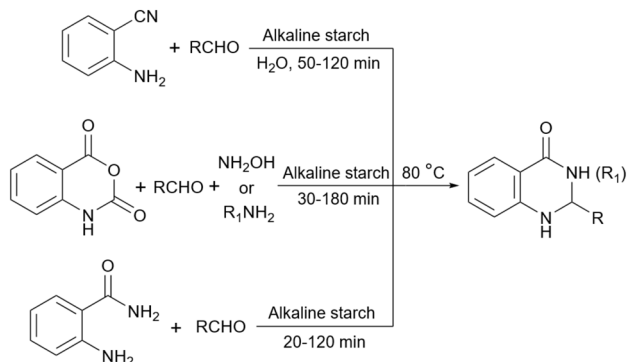


Scheme 23 Synthesis of formamides and acetamides using sulfated starch.

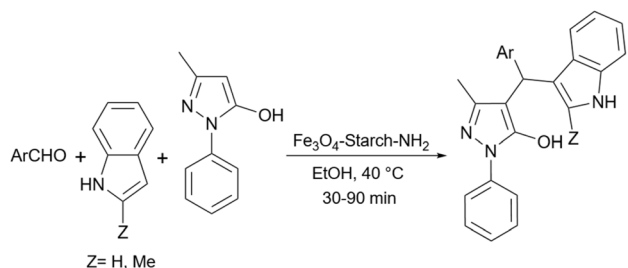
there are many drugs containing quinazolines such as quinethazone, metolazone, raltitrexed, and fenquizone.¹¹² Tamaddon and co-workers reported two protocols for the synthesis of dihydroquinazolines using alkaline starch as a catalyst (Scheme 24).^{113,114} In their reports, they used 2-aminobenzonitrile, 2-aminobenzamide, and isatoic anhydride as precursors. To prepare alkaline starch, they ground corn starch with NaOH to achieve a yellowish powder. The achieved powder was washed with ethanol, dried in a vacuum oven, and used in the mentioned reactions.

2.4.2 Synthesis of pyrazolones. Like many heterocyclic compounds, there are many reports about pyrazolones as useful compounds.^{115,116} For example, there is a wide range of FDA-approved drugs containing pyrazolone nucleus including edaravone, matamizole, nifenazone, and eltrombopag.¹¹⁷ Very recently, Ramshini and his co-workers published a paper about



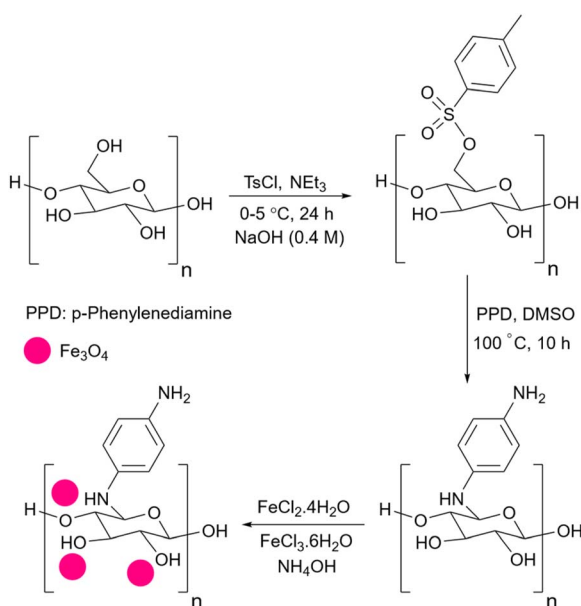


Scheme 24 Synthesis of hydroquinazolinones using alkaline starch.



Scheme 25 Synthesis of diheteroaryl thioethers using starch NPs-arginine.

using magnetic aminated starch as a suitable catalyst for the synthesis of 4-[(indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolone derivatives (Scheme 25).¹¹⁸ The authors used Fe_3O_4 -starch-*p*-phenylenediamine nanocomposites to convert indole, 1-phenyl-1*H*-pyrazol-5-ol, and different aldehydes to the related pyrazolones. To prepare the catalyst, the researcher



Scheme 26 Preparation of magnetic aminated starch nanocomposite.

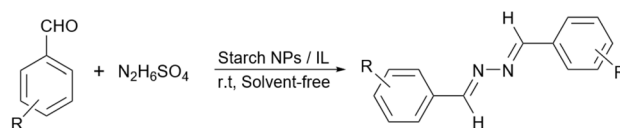
converted the simple starch to the tosylated starch and then used *p*-phenylenediamine as a nucleophile to substitute the tosylate groups. Finally, the intended catalyst was prepared using the precipitation of iron nanoparticles onto the aminated starch prepared from the last step (Scheme 26).

2.5 Starch as support

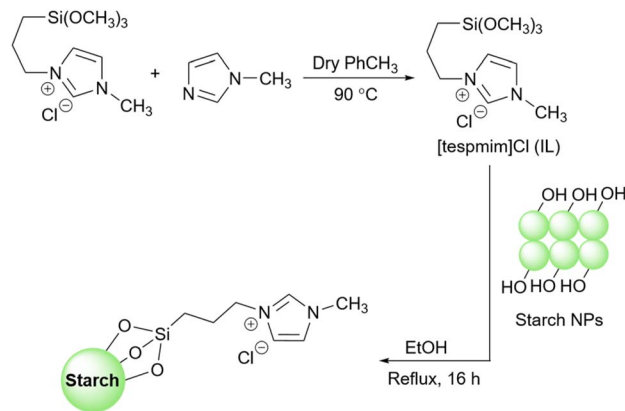
As mentioned in previous sections, simple starch can be used for many organic reactions, however, there are still some reactions including coupling, reduction, and oxidation, and some heterocyclic reactions that simple starch can not cope with. For this reaction, researchers have used starch as catalyst support to help the catalyst increase the reaction yield of the reaction. These catalytic systems will be introduced in the coming parts.

2.5.1 Synthesis of azines. Very recently, our group reported another starch-based structure as a catalyst for organic reaction.¹¹⁹ We successfully converted some aldehydes and hydrazine sulfate as substrates to the desired azines using starch nanoparticles modified with 1-propyl-3-methylimidazolium chloride ([PMIM]Cl) as catalysts (Scheme 27). The yield of products was satisfying and the reaction proceeded well at room temperature. To prepare the catalyst, first, we created *N*-methyl-*N*-propyltriethoxysilane imidazolium chloride (IL) part from the reaction between methyl imidazole and 3-chloropropyltriethoxysilane under reflux conditions. Then, we attached the prepared ionic liquid from the last step to the surface of the starch to reach the starch-IL NPs under reflux conditions in ethanol as solvent (Scheme 28).

2.5.2 Synthesis of diheteroaryl thioethers. After proving the capabilities of starch nanoparticles as good catalysts for the synthesis of heteroaryl thioethers,⁶⁰ our group screened some functionalized starch nanoparticles to find another suitable

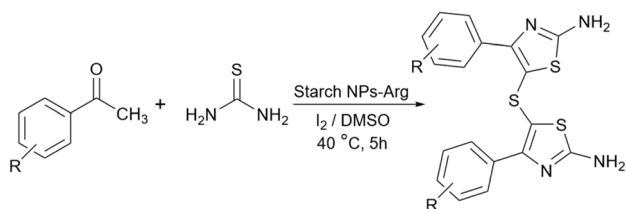


Scheme 27 Synthesis of diheteroaryl thioethers using starch-IL NPs.

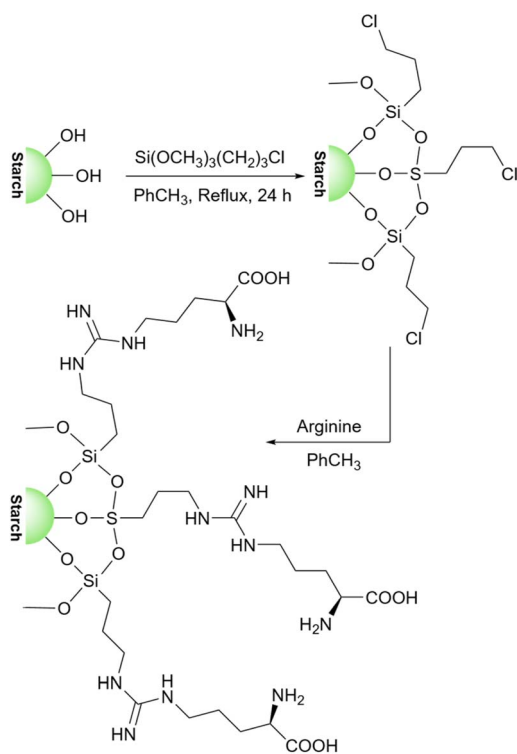


Scheme 28 Preparation of starch-IL NPs.





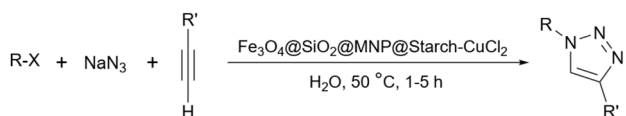
Scheme 29 Synthesis of diheteroaryl thioethers using starch NPs-Arginine.



Scheme 30 The steps for the synthesis of arginine-nanostarch.

catalyst for this interesting disulfide product. In the same year, we unveiled another similar protocol based on using arginine-decorated starch nanoparticles as a novel catalyst for the same reaction (Scheme 29).¹²⁰ We used 3-chloropropyl-trimethoxysilane as a linker to connect arginine amino acid to the surface of starch nanoparticles (Scheme 30).

2.5.3 Synthesis of triazoles. Triazoles(1,2,3-triazole and 1,2,4-triazole) and their derivatives are well-known compounds in synthetic chemistry.¹²¹ Many important properties have been attributed to these compounds such as anti-viral, anti-microbial, anti-cancer, anti-depressant, analgesic, and anti-

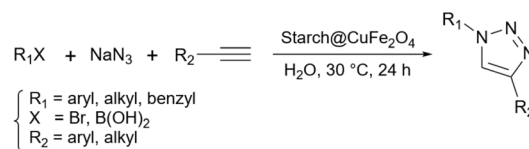


Scheme 31 Synthesis of triazoles using $\text{Fe}_3\text{O}_4@SiO_2@MNP@starch-CuCl_2$.

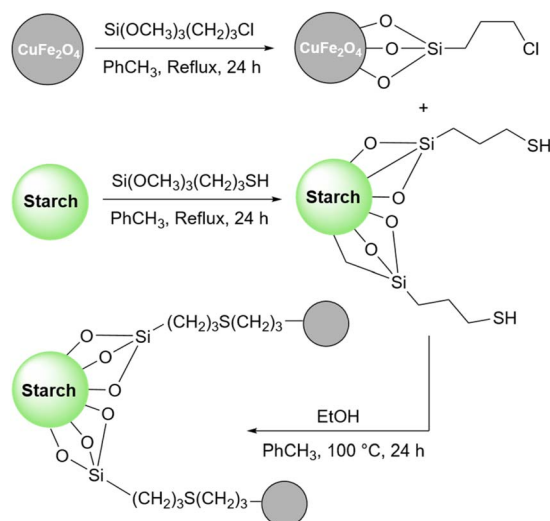
inflammatory activities.¹²² To the best of my knowledge, there are three published papers about the synthesis of triazoles using starch as catalyst support. As the first one, Pourjavadi *et al.* published copper 1,2,3-triazoles synthesis using a magnetic starch nanocomposite (Scheme 31).¹²³ The results were good and they managed to reach good to excellent yields. To prepare the catalyst, they synthesized silica-coated Fe_3O_4 nanoparticles as the core of the catalyst and functionalized its surface by 3-(trimethoxysilyl)propylmethacrylate (MPS). Then, alongside starch, a mixture of acrylamide and *N,N*-methyl-enebisacrylamide was used to provide a $\text{Fe}_3\text{O}_4@SiO_2@cross-linked polymeric starch$ nanocomposite. Finally, CuCl_2 was added to the prepared magnetic starch to provide the intended $\text{Fe}_3\text{O}_4@SiO_2@starch-CuCl_2$.

In 2018, Bonyasi *et al.* proposed starch@ CuFe_2O_4 as a magnetic reusable catalyst for the synthesis of 1,2,3-triazoles from benzyl bromide, sodium azide, and phenylacetylene (Scheme 32).¹²⁴ To attach the prepared CuFe_2O_4 nanoparticles to the surface of starch, they functionalized the nanoparticles and starch using (3-chloropropyl)triethoxysilane and (3-mercaptopropyl)triethoxysilane, respectively (Scheme 33).

Inspired by previous work, very recently, Gupta *et al.* used surface functionalized starch with copper(II) acetate as a heterogeneous catalyst to promote the synthesis of 1,4-disubstituted-1,2,3-triazoles (Scheme 34).¹²⁵ To stabilize the copper salt on the surface of the starch, they modified the surface of the starch with a Schiff base. To do this, first, they attached a 3-aminopropyl(trimethoxy)silane molecule to the

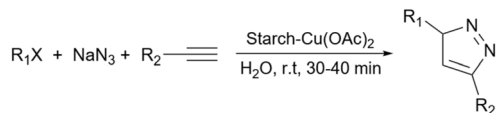
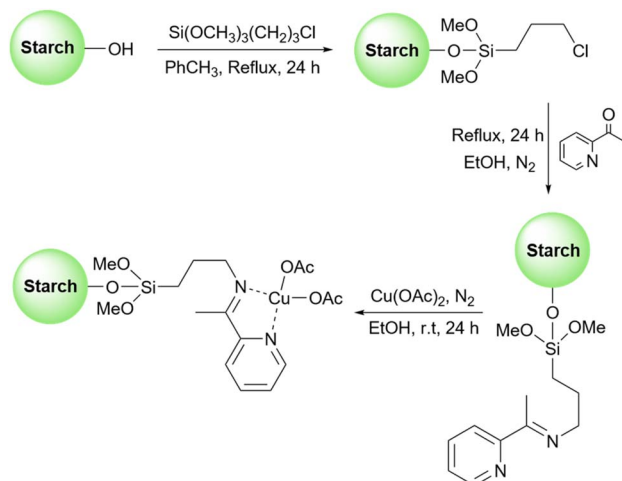


Scheme 32 4H-Pyran synthesis catalyzed by starch@ CuFe_2O_4 .



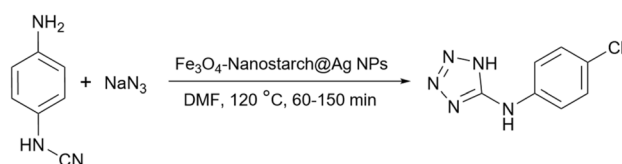
Scheme 33 Steps for the preparation of starch@ CuFe_2O_4 .



Scheme 34 Synthesis of triazoles using starch-Cu(OAc)₂.Scheme 35 Steps for the preparation of modified starch@Schiff base-Cu(OAc)₂.

starch and then converted the amine group on this molecule to the corresponding imine by adding 2-acetylpyridine to the prepared 3-aminopropyl starch (Scheme 35). Based on the proposed mechanism by authors for the synthesis of triazoles, the key step in this transformation is the reduction of Cu(II) to Cu(I) which facilitates the connection between an azide and terminal alkyne substrates to produce the related triazole derivatives.

2.5.4 Synthesis of aminotetrazoles. 5-Aminotetrazole derivatives have been used as important synthons in some multicomponent reactions to achieve more complex polycyclic compounds.¹²⁶ Recently, Nasiri and co-workers published a paper about preparing and using Fe₃O₄-nanostarch@AgNPs as a catalyst for the synthesis of various arylaminotetrazole derivatives (Scheme 36).¹²⁷ To prepare the starch nanoparticles, the authors employed an acidic hydrolysis method using H₂SO₄ as the acid. In addition to the synthesis of different 5-aminotetrazoles, they tested their catalyst for some other reactions including the oxidation of benzyl alcohol to benzaldehyde by hydrogen peroxide as oxidant and the reduction of 4-

Scheme 36 Synthesis of 5-aryl-amino-1H-tetrazole using Fe₃O₄-nanostarch@AgNPs.

nitrophenol, Congo red, rhodamine B, and methylene blue using NaBH₄ as reductant.

2.5.5 Synthesis of allyl indoles. Because indoles are a pharmacologically important class of compounds, converting simple indoles to their more complex derivatives has attracted significant attention.¹²⁸⁻¹³¹ Indole alkaloids are among the important indole derivatives that can be prepared by the alkylation reaction at the indole C₃ position.^{132,133} In 2019, the Mallik research group developed a new protocol including using starch-supported cuprous iodide nanoparticles as catalysts for the 3-allylation reaction of *N*-substituted indoles (Scheme 37).¹³⁴ The authors proposed that the reaction proceeds with an electrophilic mechanism assisted by CuI nanoparticles as a catalyst.

2.5.6 Synthesis of indazoles. There are usually two tautomeric forms for indazoles: 1*H*-indazole and 2*H*-indazole. From a thermodynamical point of view, the first one is more stable (Fig. 7).¹³⁵ Apart from stability, not only these compounds are prevalent in nature but also the synthetic compounds containing these structures have shown considerable biological properties.¹³⁶ In 2014, Sodhi and colleagues presented a new starch-based catalyst for the synthesis of 2*H*-indazoles from the reaction between 2-bromo-benzaldehydes, various primary amines, and sodium azide.¹³⁷ The catalyst they used was an amine-functionalized silica/starch-Cu(acac)_n (Scheme 38). To prepare this catalyst, in the first step, they bound the starch to the surface of silica which was activated by SOCl₂. Then, 3-amino-propyl(trimethoxy)silane is attached to the surface of starch and silica to prepare the support for the final step. Finally, amine-functionalized silica/starch was treated with M(acac)_n to reach

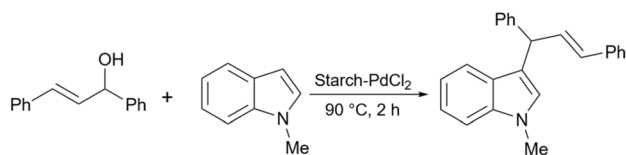
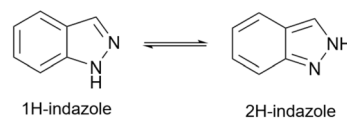
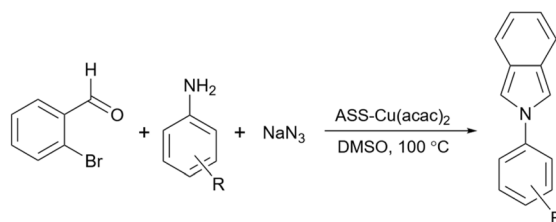
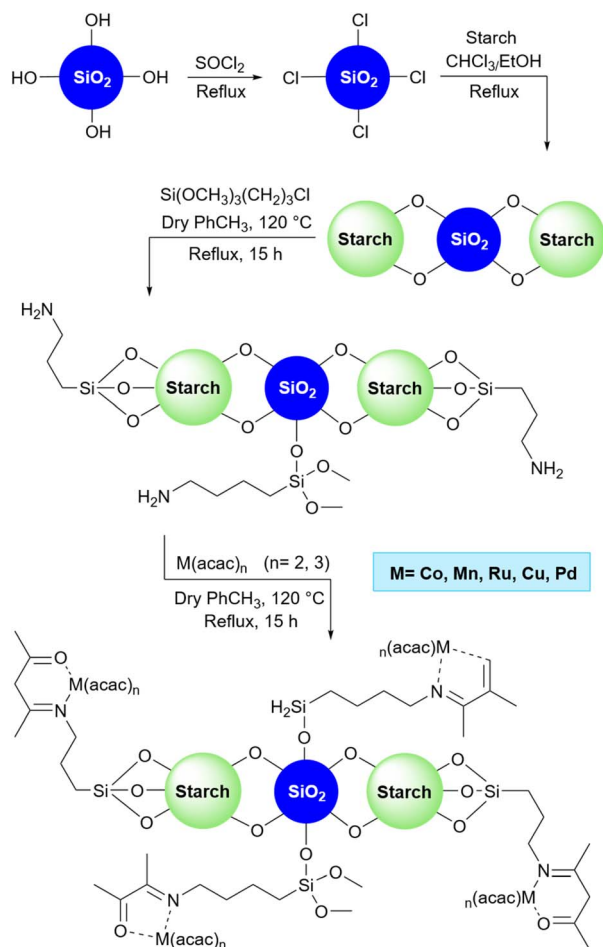
Scheme 37 Synthesis of allyl indoles using alkaline starch-PdCl₂.

Fig. 7 Two tautomeric forms of indazoles.

Scheme 38 Synthesis of indazole derivatives using amine-functionalized silica/starch-Cu(acac)_n.

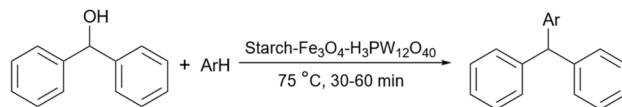


Scheme 39 Preparation of amine-functionalized silica/starch- $M(acac)_n$.

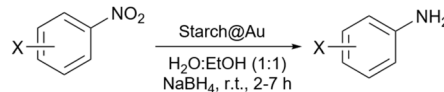
the desired amine-functionalized silica/starch- $M(acac)_n$ catalyst (Scheme 39). In addition to indazoles, the authors used this catalyst for the catalyzed thioetherification of different aryl halides using thiourea and the results were promising.

2.5.7 Synthesis of triarylmethane. The triarylmethane unit is an important structural part of triarylmethane dyes.¹³⁸ Among synthetic methods, the Friedel-Crafts alkylation reaction is probably the most common method for the synthesis of triarylmethanes.^{139,140} In 2015, Rafiee and Khodayari reported a novel method for the Friedel-Crafts alkylation of benzhydrols substrates using starch- $Fe_3O_4-H_3PW_{12}O_{40}$ composite as an efficient catalyst (Scheme 40).¹⁴¹

2.5.8 Synthesis of 4-aminotoluenes. As one of the earliest research about using starch as a catalyst for the synthesis of aniline from nitrobenzene,¹⁴² one can refer to Liu's paper. His research group prepared and used a silica-supported starch-L-glutamic acid-Fe complex for the hydrogenation of nitrobenzene, cyclohexanone, and octene.¹⁴³ After Liu's work about the hydrogenation of nitrobenzenes using silica-supported starch-glutamic acid-Fe as a catalyst, there have been more published papers about this reaction. For example, in 2017, Chairam and co-workers showed the reduction of 4-nitrophenol to 4-aminophenol using mung bean starch-Au nanoparticles and $NaBH_4$ as



Scheme 40 Synthesis of triarylmethane using starch- $Fe_3O_4-H_3PW_{12}O_{40}$.



Scheme 41 Synthesis of 4-aminotoluenes using starch@Au.

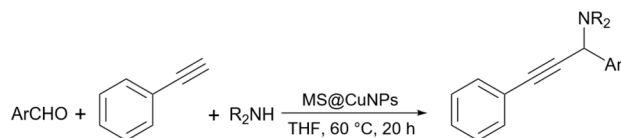
the catalyst and reducing agent, respectively.¹⁴⁴ In 2018, Luo's research group modified maize starch with 2-(dimethylamino) ethyl methacrylate and N,N' -methylenebisacrylamide by using a free radical polymerization process. Then, they used this modified starch as a support to precipitate gold nanoparticles. They employed the prepared catalyst for the hydrogenation reaction of *p*-nitro anisole (Scheme 41).¹⁴⁵

In 2019, Gholinejad and colleagues prepared starch support containing gold nanoparticles for the reduction of nitroarenes to their corresponding amines using $NaBH_4$ as the reducing agent.¹⁴⁶ To stabilize the gold nanoparticle on the surface of starch they modified the surface of starch with (3-chloropropyl) triethoxysilane so that it can act as a linker and hold the gold nanoparticles.

As another example of converting of nitroaromatic compounds to the corresponding amines, Nasiri *et al.* prepared and employed nanocomposites containing Fe_3O_4 -starch-Cu nanoparticles as catalysts.¹⁴⁷ The authors also tested their catalyst for the reduction of some dyes such as Congo red, rhodamine B, and methylene blue and the results were promising. Recently, Heravi's research group published another protocol for the hydrogenation of nitroaromatics using sulfur-doped graphitic carbon nitride decorated with starch, Fe_3O_4 , and Ag.¹⁴⁸ They managed to proceed with the reaction in aqueous media with excellent yield for many different nitrobenzene derivatives. Very recently, Lan *et al.* showed the potential catalytic activity of kaolin@chitosan-starch-Au for the reduction of nitrobenzene derivatives under mild conditions using sodium borohydride as a reductant.¹⁴⁹

2.5.9 Synthesis of propargylamines. Propargylamines have many applications in synthetic and medicinal chemistry. For example, they are essential building blocks for the synthesis of many biologically active compounds and also natural products such as lactams, and peptides.¹⁵⁰ To the best of my knowledge, there are only two reports about using starch as support for the synthesis of propargylamines. The first one belongs to Gholinejad's group (Scheme 42).¹⁵¹ In 2016, they reported copper nanoparticles supported starch microparticles as a catalyst for the synthesis of propargylamines from the reaction of benzaldehyde, phenylacetylene, and piperidine. To prepare the catalyst, the authors dissolved corn starch in distilled water and acetone to prepare the starch microparticles. Then, they



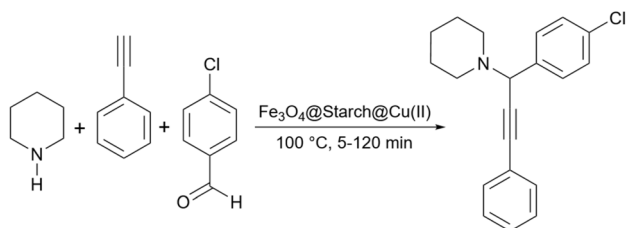
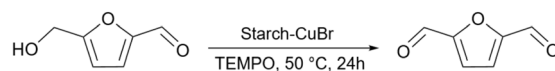


Scheme 42 Synthesis of propargylamines using MS@CuNPs.

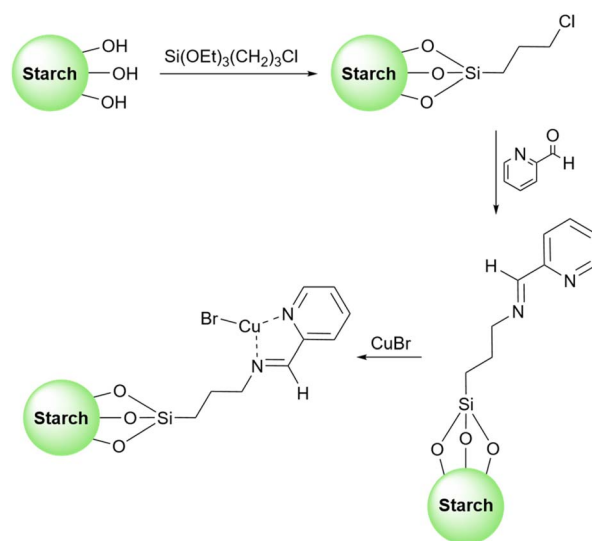
separated high molecular weight starch, dissolved it in acidic water (pH = 2.5), and added acetone to the prepared solution. Finally, they added glutaraldehyde to the solution and after stirring for 12 hours, dried the achieved solution to reach the starch microparticles.

In the second report about using starch as support for the synthesis of propargylamines, Saadati *et al.* presented a modified starch with a linker to stabilize copper nanoparticles and use this copper-loaded support as a catalyst for the synthesis of propargylamine derivatives.¹⁵² Very recently, Tajbakhsh and co-workers provided a protocol for the synthesis of propargylamines through a one-pot coupling reaction using copper(II)-immobilized on starch-coated nanomagnetite (Scheme 43).¹⁵³ Based on the optimization data reported by the authors, the simple starch can proceed with this reaction with 70% yield, an efficiency even better than simple Fe₃O₄. However, when Fe₃-O₄@starch-Acr@Cu(II) was used as the catalyst, the yield of the reaction increased to 99% and the consuming time for the reaction to be complete decreased to about half an hour. The authors proposed a plausible mechanism in which Cu(II) is first coordinated with π electrons of acetylene to produce the acetylide-Cu(II) complex. In this condition, copper promotes the attack of acetylide on the reactive iminium intermediate to obtain the desired propargylamine.

2.5.10 Synthesis of 2,5-diformylfuran. 2,5-Diformylfurans, which can be prepared from different methods like the oxidation 5-hydroxymethylfurfural, have many potential applications in pharmaceuticals, organic conductors, and polymer chemistry.¹⁵⁴ In 2019, Hong and co-workers prepared corn starch-anchored CuBr as a recyclable catalyst for the oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran (Scheme 44).¹⁵⁵ To stabilize the CuBr on the surface of starch, first, they attached a 3-aminopropyltriethoxysilane to the surface of starch to obtain an amine-functionalized surface. Then, they added 2-pyridinecarboxaldehyde to the achieved amine from the previous step to make a Schiff base to anchor the CuBr particles (Scheme 45). Almost simultaneously with this report, they

Scheme 43 Synthesis of propargylamines using Fe₃O₄@starch-Acr@Cu(II).

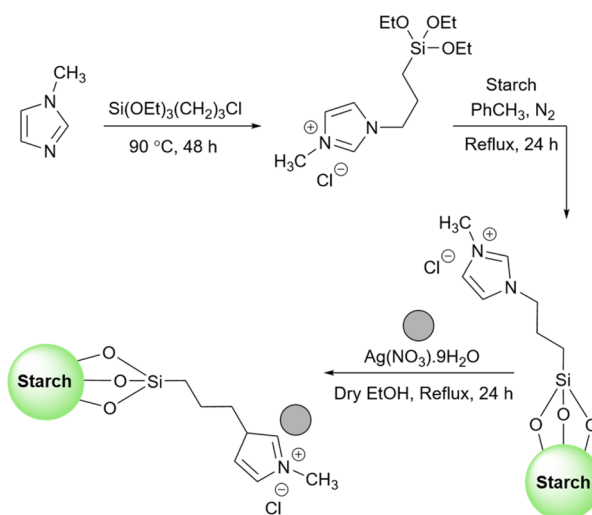
Scheme 44 Synthesis of 2,5-diformylfuran using starch-CuBr.



Scheme 45 Synthesis of expanded starch@Schiff base-CuBr.

published another protocol for the oxidation of 5-(hydroxymethyl)furfural using a starch-supported catalyst.¹⁵⁶ This time, they modified with 1-(triethoxysilyl)propyl-3-methylimidazolium chloride as an ionic liquid. Then, they used Al(NO₃)₃ as a metallic ion to stabilize the surface of the modified starch and employed the final product as a catalyst for the synthesis of 2,5-diformylfuran (Scheme 46).

As mentioned earlier, 5-hydroxymethylfurfural (HMF) can be used as a precursor for the synthesis of 2,5-diformylfuran. However, the literature review shows using HMF as substrates is

Scheme 46 Synthesis of expanded starch-IL-Al(NO₃)₃ catalyst.

not always the case and there is a good number of reports about preparing HMF as the final product.^{157,158} One of these reports is about preparing 5-hydroxymethylfurfural using a starch-based catalyst. In 2017, Matharu *et al.* published a paper about the conversion of fructose to HMF using expanded starch@ionic liquid-FeCl₃ as a catalyst.¹⁵⁹ To expand the surface of starch, the authors used *N,N'*-disuccinimidyl carbonate and to attach iron chloride to the surface of expanded starch, they modified the surface of expanded starch with *N*-(3-aminopropyl), *N*-aryl imidazolium chloride.

2.5.11 Synthesis of imidazothiadiazoles. Imidazothiadiazoles and their derivatives have gained much attention in recent years, especially because of their wide biological activities.^{160–162} In 2019, Bahadorikhalili and colleagues provided a protocol for the preparation of magnetic starch as a support for ionic liquid-β-cyclodextrin (βCD-IL-starch-Fe₃O₄) (Scheme 47).¹⁶³ They used this catalyst for the synthesis of imidazo[2,1-*b*][1,3,4]thiadiazol-5-amine derivatives. The authors proposed that the ionic liquid part of the catalyst has the main catalytic role in this transformation (Fig. 8).

2.5.12 Synthesis of dihydropyrimidine. Dihydropyrimidines are widely considered the “privileged structures”, some molecular frameworks with versatile binding properties.¹⁶⁴ There are many biologically active pyrimidine-based compounds and alongside purine, pyrimidine is one of the building blocks of DNA and RNA.^{165,166} These structures can be found in several candidate drugs.¹⁶⁷ To facilitate the preparation of these important heterocyclic compounds, Foroughifar's research group introduced magnetic starch support loaded with aspartic acid (Scheme 48).¹⁶⁸ To prepare the mentioned catalyst, MnFeCaFe₂O₄@starch@aspartic acid, first, they prepared a MnFeCaFe₂O₄ as the core of the catalyst through the coprecipitation of related salts. To attach the starch to the surface of the prepared core, they activated MnFeCaFe₂O₄ by NH₄OH and have the activated magnetic core stirred with starch in boiling water. To load the aspartic acid on the prepared magnetic starch support, the authors put the aspartic acid and the magnetic support under reflux conditions for 24 hours and dried the product in a vacuum (Scheme 49).

2.5.13 Synthesis of quinoxalines. As mentioned before, the synthesis of quinoxalines from 1,2-dicarbonyl and 1,2-diamine substrates can be catalyzed by acidic starch.¹⁰⁰ However, 3 years

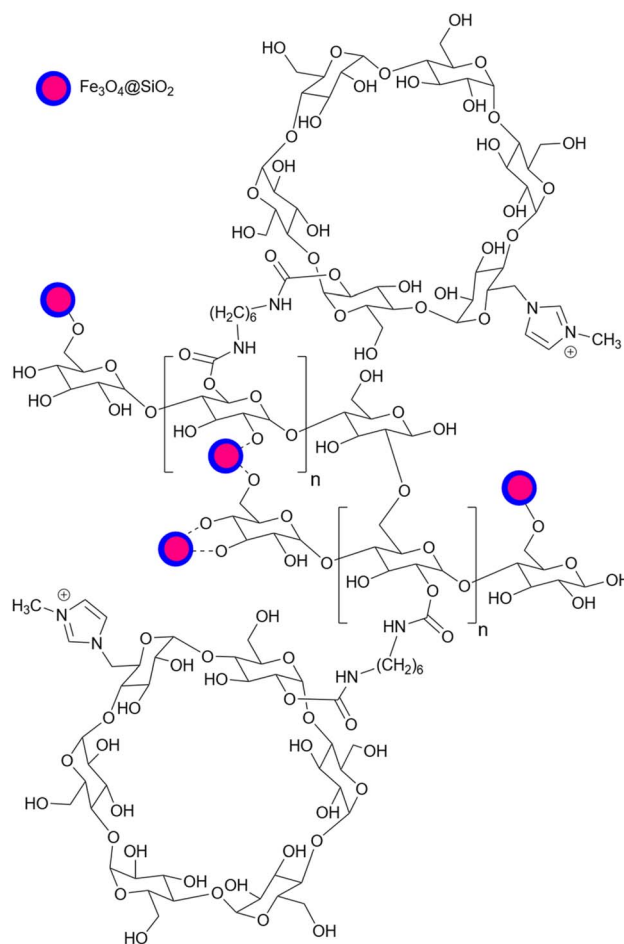
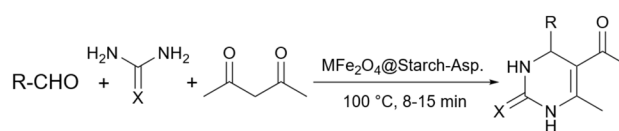


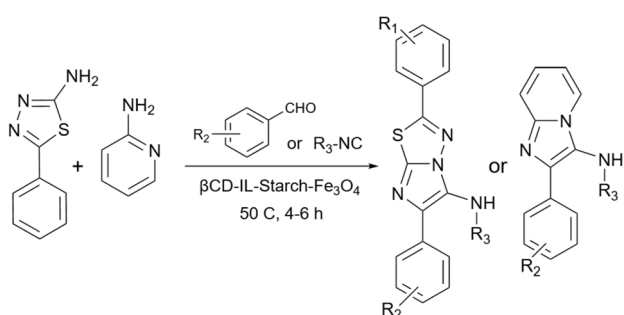
Fig. 8 The proposed structure of βCD-IL-starch-Fe₃O₄.



Scheme 48 Synthesis of dihydropyrimidine derivatives using MnFeCaFe₂O₄@starch@aspartic acid.

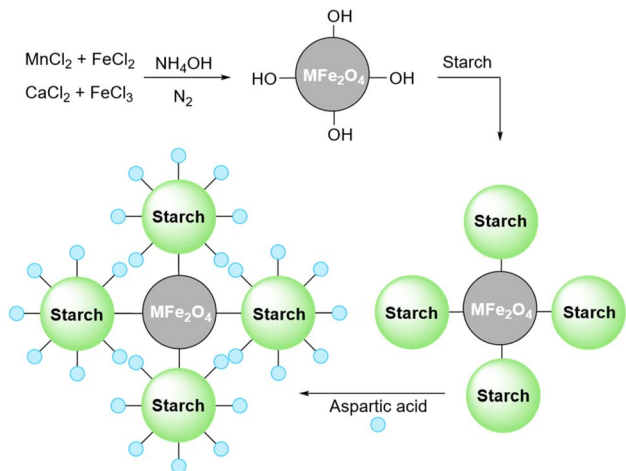
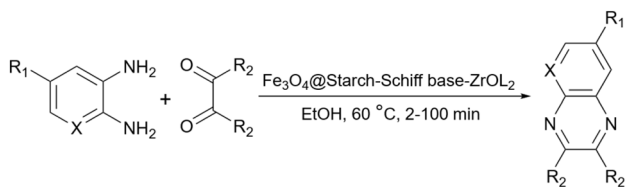
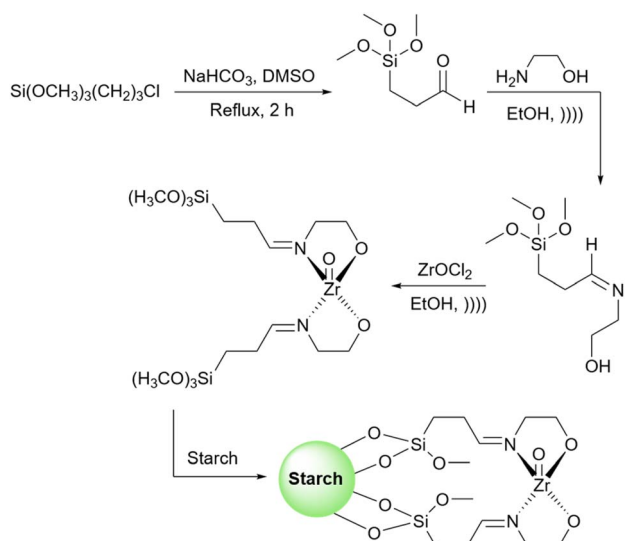
before that research, the same research group had reported a paper about facilitating this reaction by a starch-Schiff base catalyst containing oxo zirconium (Scheme 50).¹⁶⁹ Based on the table the authors provided to compare their work with previous research about using zirconium for the synthesis of quinoxaline, Fe₃O₄@starch-Schiff base-ZrOL₂ was the best catalyst in terms of efficiency and the amount of required catalyst. The steps for the synthesis of the catalyst have been shown in Scheme 51.

2.5.14 Synthesis of isocoumarins. Isocoumarins are a type of lactonic natural product that can be widely found in different parts of nature such as fungi, lichens, liverworts, bacteria, molds, higher plants, marine sponges, and even insect pheromones, and venom.¹⁷⁰ Recently, Marandi and co-workers presented an indium-loaded Fe₃O₄@starch core-shell as a green



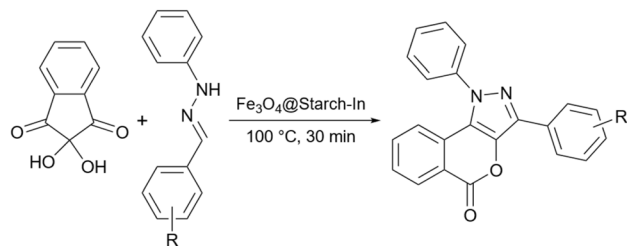
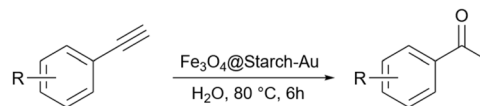
Scheme 47 Synthesis of imidazothiadiazoles using βCD-IL-starch-Fe₃O₄ as a catalyst.



Scheme 49 Preparation of MnFeCaFe₂O₄@starch@aspartic acid.Scheme 50 Synthesis of quinoxaline derivatives using Fe₃O₄@starch-Schiff base-ZrOL₂.Scheme 51 Preparation of MnFeCaFe₂O₄@starch@aspartic acid.

biocatalyst for the synthesis of pyrazole-fused isocoumarins derivatives (Scheme 52).¹⁷¹ They used apple seeds as a cheap source of starch.

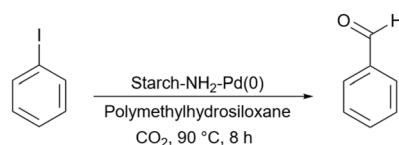
2.5.15 Hydration of terminal alkynes. The hydration of terminal alkynes is one of the common methods for preparing carbonyls. There are many published research papers about converting terminal alkynes to their related methyl carbonyl

Scheme 52 Synthesis of isocoumarin derivatives using Fe₃O₄@starch-In.Scheme 53 Synthesis of methyl carbonyls from terminal alkynes derivatives using Fe₃O₄@starch-Au.

compounds.^{172–174} Recently, Mousavi-Mashhadi and Shiri successfully managed to prepare Fe₃O₄@starch-Au and use this core-shell structure as a heterogeneous catalyst for the hydration of terminal alkynes and nitriles (Scheme 53).¹⁷⁵

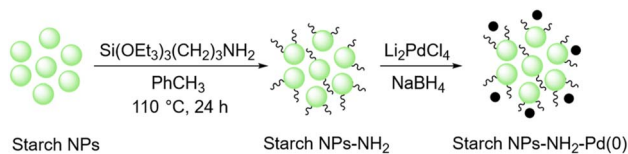
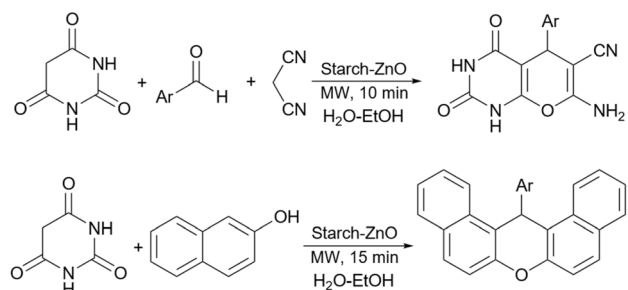
2.5.16 Formylation of iodo benzene. As a greenhouse gas, the increase of environmental carbon dioxide is one of the main causes of global warming.¹⁷⁶ With this fact in mind, the chemical fixation of carbon dioxide is an attractive research field.^{177–181} To provide another useful method to consume carbon dioxide, the research group of Jian came up with a new method to convert iodo benzene to the corresponding benzaldehyde using Pd-nanoparticles grafted onto amino-functionalized nanostarch as a catalyst (Scheme 54).¹⁸² To prepare the catalyst, first, the author functionalized the surface of starch with 3-aminopropyltrimethoxysilane. Then, the Li₂-PdCl₄ solution was added to the amino starch followed by adding NaBH₄ to the mixture to convert Pd(II) to Pd(0) (Scheme 55).

2.5.17 Synthesis of pyranopyrimidinone and xanthene. Similar to xanthene, pyranopyrimidines have attracted much attention because of their application as anti-tumor, anti-bacterial, and anti-Alzheimer agents.¹⁸³ In 2020, the Amininia research group presented a nano starch-ZnO composite as a novel heterogeneous catalyst for the synthesis of pyranopyrimidinone and xanthene derivatives under microwave irradiation (Scheme 56).¹⁸⁴ In addition to the synthetic protocol, the authors tested prepared pyranopyrimidines and xanthene



Scheme 54 Synthesis of benzaldehyde from iodo benzene using starch-Pd(0).



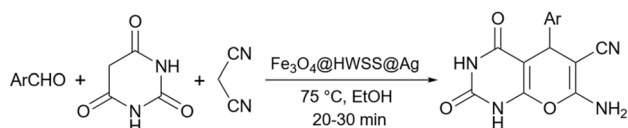
Scheme 55 Preparation of starch-NH₂-Pd(0).

Scheme 56 Synthesis of pyrano pyrimidinones and xanthenes using starch-ZnO composite.

derivatives against *M. luteus* and *P. aeruginosa* and the results were promising. Very recently, Azad Poshtmakhi and colleagues reported another protocol for the synthesis of pyranopyrimidines using silver-loaded magnetic starch composite (Scheme 57).⁷² To prepare the catalyst they coated Fe₃O₄ nanoparticles with hot water starch solution (HWSS) and then decorated the product with Ag nanoparticles through heating it in a solution of Ag ion and glucose.

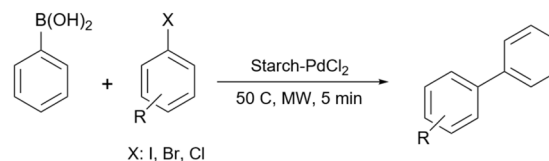
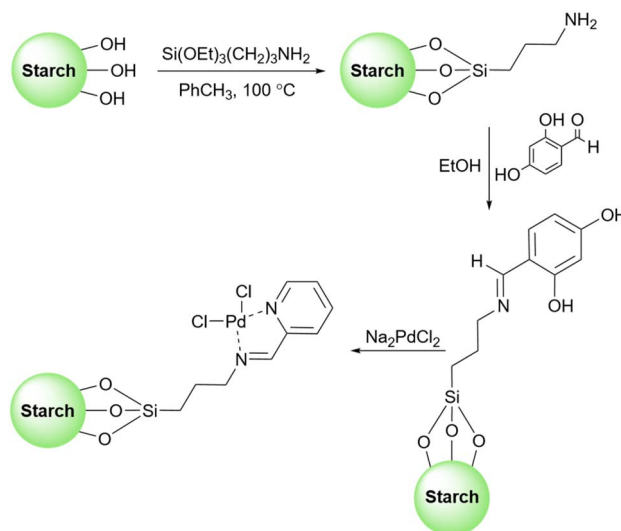
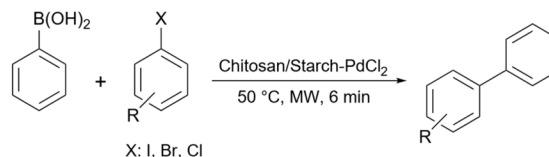
2.5.18 Coupling reactions. Coupling reactions are a class of organic transformations that allow two hydrocarbons to join together through the creation of a new C–C sigma bond. The reaction between an organic halide (R–X) and a main group organometallic compound (R'M) is the backbone of cross-coupling reactions. If R and R' are the same this reaction is called a homo-coupling reaction and otherwise it is called a hetero-coupling reaction.^{185,186}

Biphenyl derivatives are one the most common products of coupling reactions. There are many synthetic methods for the synthesis of biphenyl compounds because of their synthetic and biological importance.¹⁸⁷ Simple biphenyls are pretty non-reactive because they don't have any active functional group. However, their derivatives with active functional groups are more reactive, and because of this higher reactivity, they have a wide range of applications in different fields.¹⁸⁸ Among synthetic protocols for coupling reactions, the Suzuki reaction is one of the famous methods for the synthesis of biphenyl compounds.¹⁸⁹

Scheme 57 Synthesis of pyranopyrimidinones using Fe₃O₄@HWSS@Ag composite.

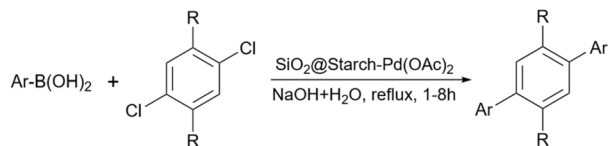
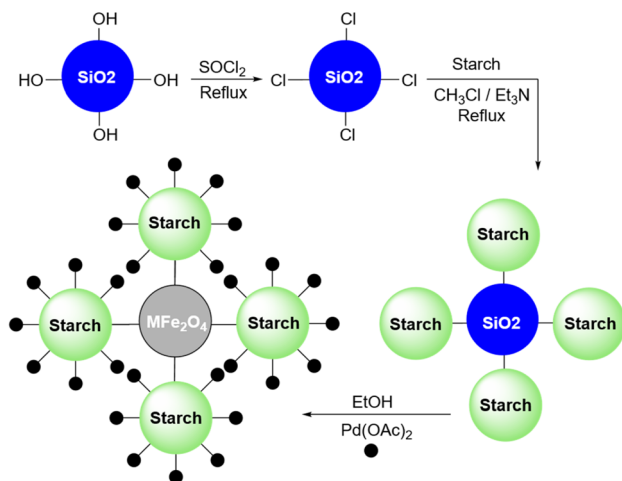
In 2017, Baran introduced a starch-based palladium catalyst for the Suzuki coupling reactions (Scheme 58).¹⁹⁰ His protocol includes making the connection between the surface of starch and 3-aminopropyltriethoxysilane (APTES) as an amine linker. Then, 2,4-dihydroxybenzaldehyde as an aldehyde agent can be added to the prepared starch-APTES to reach the desired Schiff base. Finally, adding Na₂PdCl₄ to the prepared Schiff base from the last step leads to the starch-PdCl₂ catalyst (Scheme 59).

In 2018, Baran's group disclosed another method for the palladium-catalyzed synthesis of biphenyls through a Suzuki-cross-coupling reaction (Scheme 60).¹⁹¹ They prepared a mixed composition of starch and chitosan by adding starch to the acidic solution containing chitosan. Then, the Na₂PdCl₄ was added dropwise to a mixture containing the prepared composite of starch/chitosan, and the solution was stirred for the next 3 hours. Finally, NaNBH₄ was added to the solution to reduce the Pd(II) to Pd(0) and palladium nanoparticles precipitated on the surface of the mixed carbohydrate composite.

Scheme 58 Synthesis of biphenyls using starch-PdCl₂.Scheme 59 Steps for the preparation of starch-PdCl₂.

Scheme 60 Synthesis of hydroquinazolinones using alkaline starch.

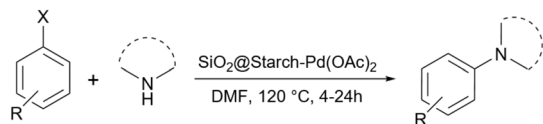
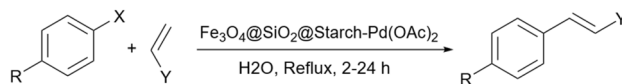


Scheme 61 Synthesis of hydroquinazolones using $\text{SiO}_2\text{@starch-Pd(OAc)}_2$.Scheme 62 Preparation of $\text{SiO}_2\text{@starch-Pd(OAc)}_2$.

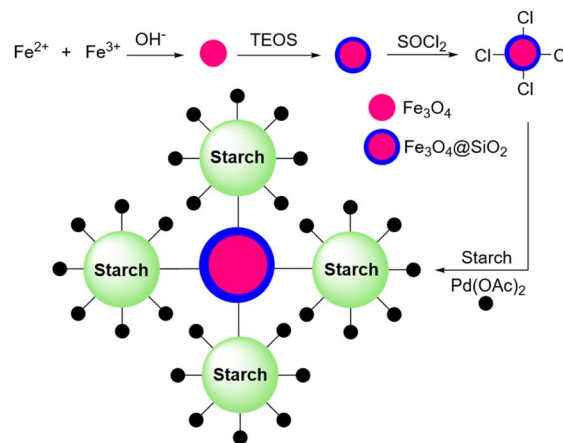
In 2012, Khalafi-Nezhad and Panahi reported a silica starch loaded with palladium nanoparticles as an efficient heterogeneous catalyst for the synthesis of *p*-teraryls using the Suzuki reaction (Scheme 61).¹⁹² They attached the starch to the silica chloride which was prepared by the reaction between silicon dioxide (silica gel) and thionyl chloride. Then, they added the palladium acetate to the achieved silica starch from the previous step to obtain the palladium nanoparticles-loaded silica starch (Scheme 62).

Five years later, this research group used the same catalyst for the Pd-catalyzed Buchwald–Hartwig C–N cross-coupling reaction (Scheme 63).¹⁹³ They showed that Pd nanoparticles on silica-starch were powerful enough to promote the C–N cross-coupling reaction between aryl halides and amines almost as good as the carbon–carbon coupling reaction that they reported 5 years ago.

In 2018, Khalafi and Panahi reported another application for their Pd nanoparticles on the silica-starch catalyst (Scheme 64).¹⁹⁴ This time the authors used a magnetic version of their catalyst by replacing simple silica with magnetic silica ($\text{Fe}_3\text{O}_4\text{@SiO}_2$) (Scheme 65). They used this magnetic version of the

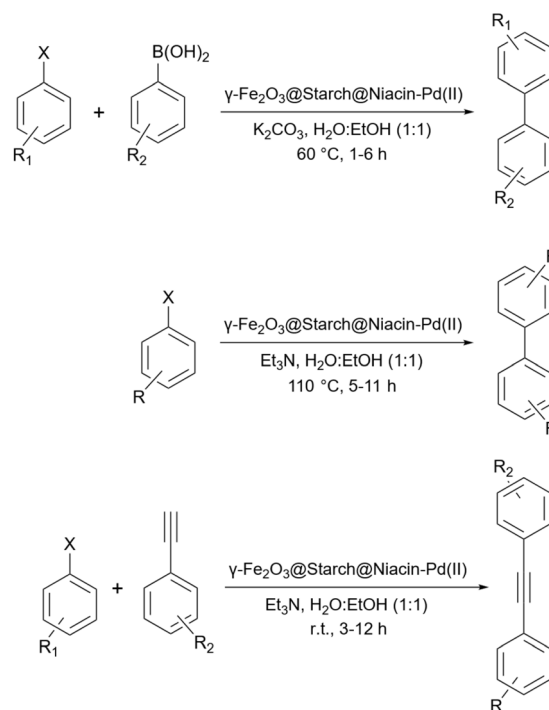
Scheme 63 Synthesis of *N*-aryl amines using $\text{SiO}_2\text{@starch-Pd(OAc)}_2$.

Scheme 64 Palladium-catalyzed Heck reaction between iodobenzene and styrene.

Scheme 65 Preparation of $\text{SiO}_2\text{@starch-Pd(OAc)}_2$.

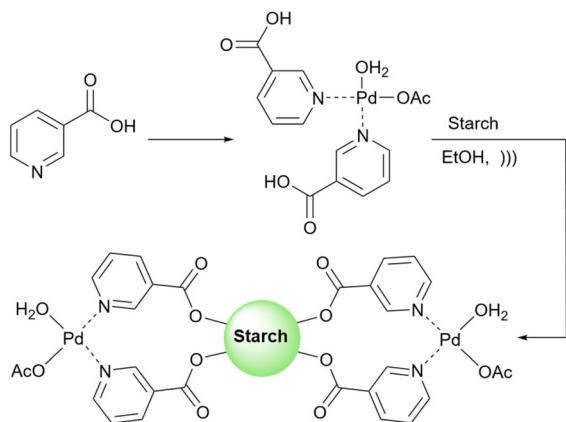
palladium nanoparticles-loaded silica-starch as a catalyst for the Heck reaction between iodobenzene and styrene.

Rezapor *et al.* reported another palladium-loaded starch catalyst for the cross-coupling reaction (Scheme 66).¹⁹⁵ This research group used a palladium niacin complex immobilized



Scheme 66 Palladium-catalyzed Suzuki, Ullmann, and Sonogashira reactions.





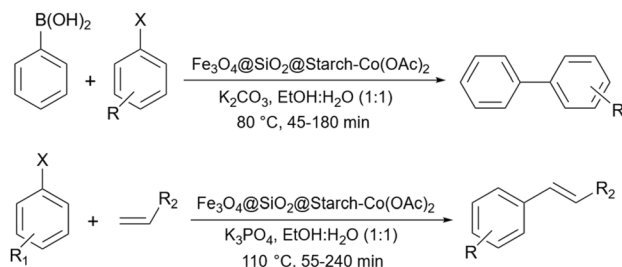
Scheme 67 Preparation of $\gamma\text{-Fe}_2\text{O}_3\text{@starch@niacin-Pd(II)}$ as a catalyst for coupling reactions.

on starch-coated maghemite nanoparticles ($\gamma\text{-Fe}_2\text{O}_3\text{@starch@niacin-Pd(II)}$) for some of the homo- and cross-coupling reactions (Suzuki, Ullmann, and Sonogashira reactions (Scheme 67)).

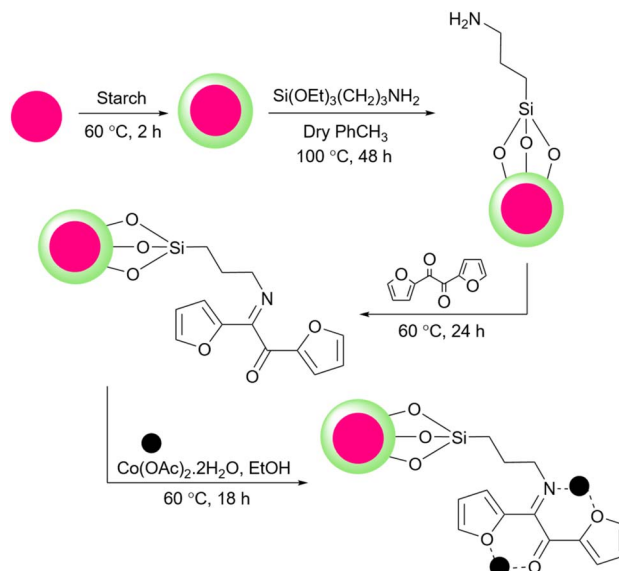
Arghan and colleagues reported a magnetic starch loaded with cobalt nanoparticles as a catalyst for the Mizoroki–Heck and the Suzuki–Miyaura reactions (Scheme 68).¹⁹⁶ To prepare the catalyst they coated the Fe_3O_4 nanoparticles with starch and then modified the surface of starch with APTES. Using 2,2'-fural, they managed to achieve the related Schiff base. Finally, they added cobalt salt as $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ to the solution containing the Schiff base and prepared the desired catalyst (Scheme 69).

Veisi *et al.* presented another starch-based palladium catalyst for the coupling reaction. They prepared a $\text{Fe}_3\text{O}_4\text{@chitosan-starch}$ core–shell decorated with palladium nanoparticles as a versatile for the Suzuki–Miyaura coupling and also reduction of nitrophenol to aminophenol reactions under ultrasonic conditions (Scheme 70).¹⁹⁷ Based on the mechanism proposed by the authors, the key role in these transformations is on the palladium's shoulder which can be changed from Pd(0) to Pd(II) and make the coupling and reduction reactions possible.

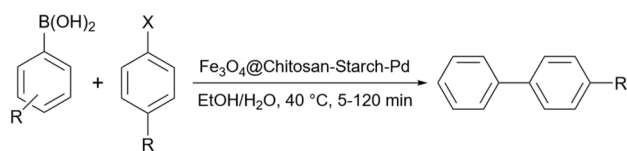
Recently, Koukabi and Arghan used a little bit different magnetic catalyst compared to their previous work¹⁹⁶ to promote Mizoroki–Heck and Suzuki–Miyaura reactions.¹⁹⁸ They prepared the $\text{Fe}_3\text{O}_4\text{@starch}$ core–shell like before, however, instead of modifying it with a linker they just added



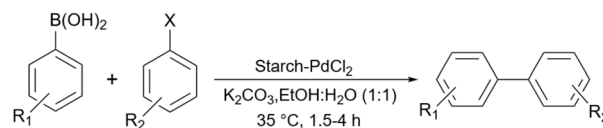
Scheme 68 Cobalt-catalyzed Suzuki–Miyaura and Mizoroki–Heck coupling reactions.



Scheme 69 Preparation of $\text{Fe}_3\text{O}_4\text{@starch-Co(OAc)}_2$.



Scheme 70 Suzuki reaction of 4-methylbromobenzene with phenyl boronic acid using $\text{Fe}_3\text{O}_4\text{@Chitosan-starch/Pd}$.



Scheme 71 Suzuki–Miyaura coupling reactions of aryl halides with arylboronic acids using starch- PdCl_2 as a catalyst.

$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ to the solution containing this magnetic structure to prepare their intended $\text{Fe}_3\text{O}_4\text{@starch-Co(II)}$ catalyst. As we expect and also the authors proposed in their paper, Co(II) can change to Co(IV), to disconnect the Ar–X bond and help the coupling reaction to occur. Very recently, Li *et al.* another starch Schiff base as a support for palladium for the Suzuki coupling reactions (Scheme 71).⁴⁹ They used almost the same technique that we have seen before for the preparation of starch Schiff base¹⁹⁰ using APTES as a linker and 2-aminobenzaldehyde as a required carbonyl group.

In addition to the mentioned examples of published work about using starch as support for coupling reactions, there is more work in this field that we can talk about. These protocols are gathered in Table 1.

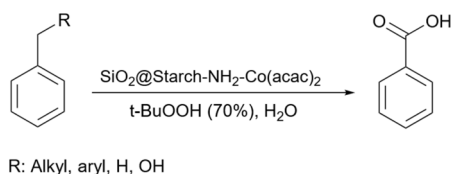
2.5.19 Oxidation reactions

2.5.19.1 Oxidation of alkanes. Because of the presence of the carbonyl group, aryl carbonyls can be used as synthetic



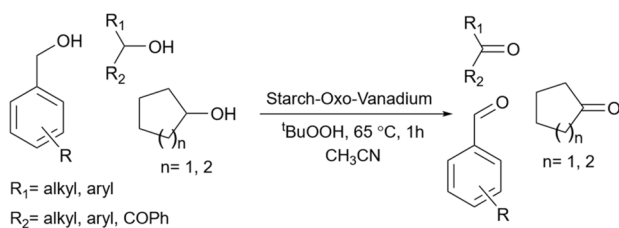
Table 1 Coupling reactions catalyzed by metal-supported starch

Entry	Year	Reaction type	Catalyst	Refs.
1	2005	Suzuki, Heck, and Sonogashira	Starch@Schiff base-Pd(OAc) ₂	199
2	2008	Suzuki, Heck, and Sonogashira	Mesoporous starch-Pd(OAc) ₂	200
3	2010	Miyaura-Suzuki	Starch-PdCl ₂	201
4	2011	Sonogashira	SiO ₂ @starch@Pd(OAc) ₂	202
5	2013	Miyaura-Heck	Starch@ethylene diamine-PdCl ₂	203
6	2017	Suzuki-Miyaura	Starch@polyethylenimine@Pd(0)	204
7	2020	Heck and Tsuji-Trost	Fe ₃ O ₄ @starch-PdCl ₂	205

Scheme 72 Oxidation of aryl alkane using silica/starch-NH₂-Co(acac)₂ as a catalyst.

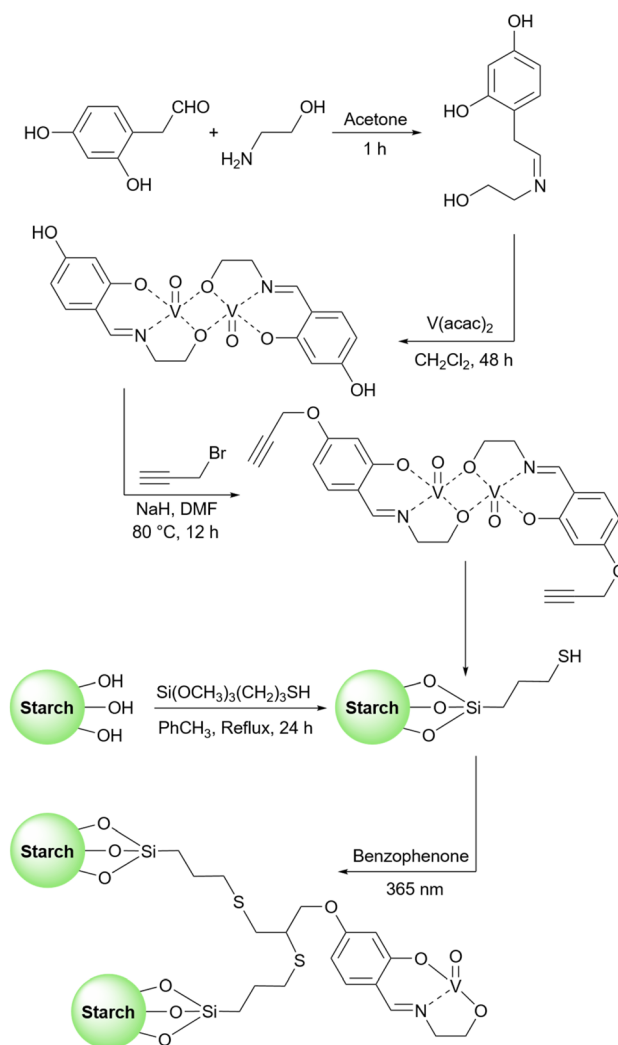
precursors to reach many products.²⁰⁶ There are many reports about the synthesis of aryl carbonyl from aryl alkanes^{207–209} including our previous work.²¹⁰ In 2018, Sodhi and Paul prepared a starch-based catalyst to convert aryl alkane substrates to related aryl carbonyls. To do the job, they prepared and used a Co(acac)₂ supported amine-functionalized silica/starch as a catalyst alongside *t*-BuOOH as an oxidant agent (Scheme 72).²¹¹

2.5.19.2 Oxidation of alcohols. The oxidation of alcohol is one of the most popular and key reactions in organic chemistry and many related reports are published every year.^{212–216} The literature review shows there are some published research papers about using starch as catalyst support for the oxidation reactions of alcohol.²¹⁷ For example, one could point out the work that has been done by Yang's research group. This group introduced a novel method for the preparation of the starch-Schiff base Co(II) complex and used this complex as a catalyst to oxidize cyclohexanes.²¹⁸ Another starch-based catalyst for the oxidation of alcohols emerged in 2013. Verma and colleagues published a research paper about the vanadium-catalyzed oxidation reaction of alcohols (Scheme 73).²¹⁹ They used an oxo-vanadium Schiff base grafted on the surface of a functionalized starch as support. To prepare the catalyst, the authors functionalized the hydroxyl groups of the corn starch with 3-mercaptopropyltrimethoxysilane. Then, they prepared a Schiff



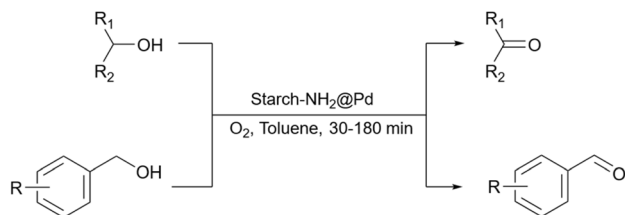
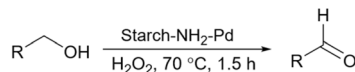
Scheme 73 Preparation of starch-oxo-vanadium Schiff base.

base from amino ethanol and 2,4-dihydroxy benzaldehyde and added Vo(acac)₂ to reach the related vanadium complex. After modifying the prepared vanadium complex with propargyl bromide, they connect this modified vanadium complex to the modified starch prepared in the first step (Scheme 74). In the same year, this group provided another catalyst for the oxidation reaction of alcohols. They prepared palladium nanoparticles grafted on nanocrystalline starch to convert primary



Scheme 74 Preparation of starch-oxo-vanadium Schiff base.



Scheme 75 Preparation of silica/starch-NH₂@Pd(0).Scheme 76 Preparation of Fe₃O₄@starch-NH₂-Pd.

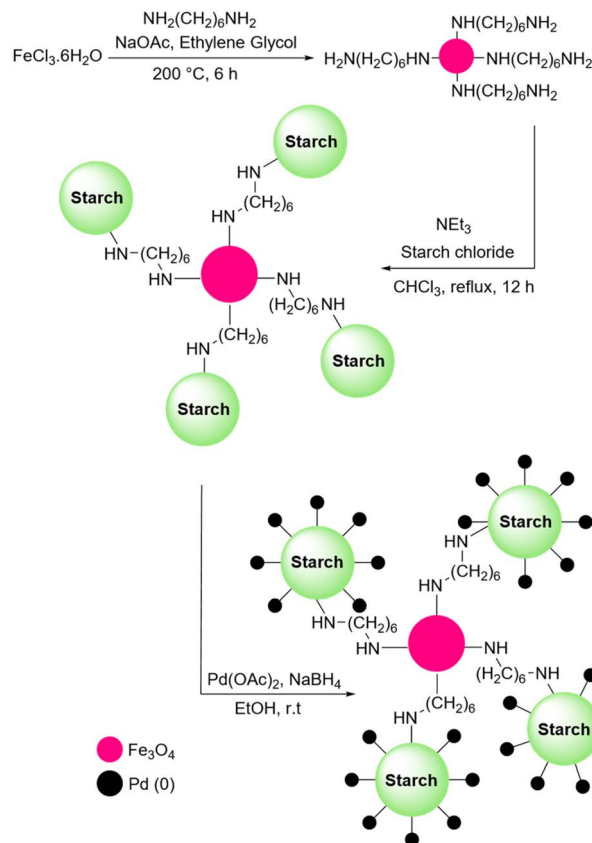
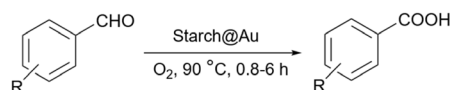
and secondary alcohols to the related aldehydes and ketones (Scheme 75).²²⁰

Sharma *et al.* proposed another method to produce grafted metallic palladium on the surface of starch and used this structure as a catalyst for the oxidation of alcohols (Scheme 76).²²¹ First, they prepared Fe₃O₄ particles and then modified their surface using 1,6-hexanediamine. Next, they coated the amine-functionalized magnetic nanoparticles from the last step with starch chloride. Finally, Pd(OAc)₂ was added to the solution containing starch-coated Fe₃O₄ particles and used NaBH₄ to reduce Pd(II) to Pd(0). The authors also used the prepared catalyst for other reactions including reduction of nitroarenes and synthesis of functionalized amines from aldehydes at room temperature (Scheme 77).

Again in 2013, another method based on using starch as support was proposed, this time by the research group of Ebittani.²²² They prepared some kind of platinum/gold alloy nanoparticles-supported hydroxalite and used this catalyst to oxidize polyols at room temperature. The results showed the different percentages of Pt/Au can affect the amount of conversion of glycerol substrate to its oxidized forms like glyceric acid, tartronic acid, glycolic acid, and oxalic acid.

2.5.19.3 Oxidation of aldehydes. In 2019, Li's research group proposed a novel way for the synthesis of benzoic acid derivatives based on using starch as support (Scheme 78).²²³ They added HAuCl₄·4H₂O to the solution containing starch to reach a gold nanoparticle-supported starch and used that as a catalyst alongside H₂O₂ as an oxidant to convert benzaldehydes to their corresponding benzoic acids. According to the authors, in this catalytic system, starch doesn't have any specific direct influence on the outcome but works as a ligand and reducing agent for gold nanoparticles which play the main role as a catalyst.

Very recently, Ravichandran *et al.* introduced another starch-based catalyst to convert benzaldehyde to corresponding carboxylic acid.²²⁴ They prepared Fe₃O₄@starch@Ag *via* the grinding method and used this nanocomposite as a catalyst for the oxidation of benzaldehyde. Also, the published results indicate that the catalyst is capable of decreasing some common dyes including Methylene blue and Methyl red.

Scheme 77 Preparation of Fe₃O₄@starch-NH₂-Pd(0).

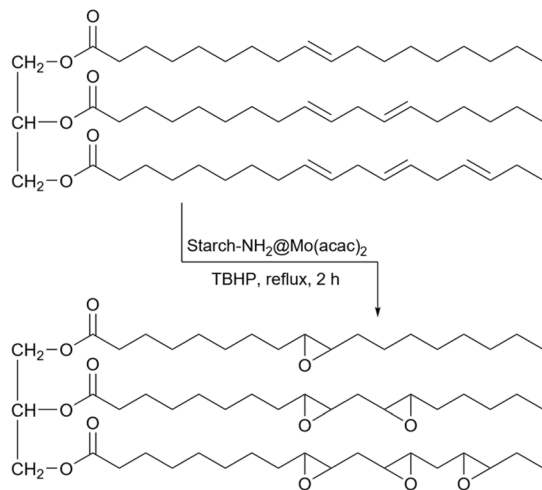
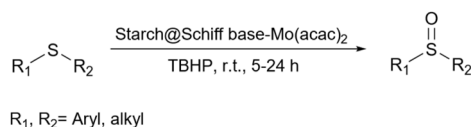
Scheme 78 Oxidation of benzaldehyde using of starch@Au.

2.5.19.4 Epoxidation of alkenes. Epoxides can be very common intermediates in many organic reactions and alkenes are one of the major sources to reach epoxide.^{225,226} Vegetable oils are one of those compounds that contain double bonds and from a commercial point of view, the epoxidation of these bonds is very important. The reason is that epoxidized vegetable oils have many applications for the synthesis of polyurethane foams, synthetic detergents, coatings agents, and lubricant compounds.²²⁷ In 2015, Pan's research group presented a starch-Schiff base-Mo(acac)₂ catalyst for the epoxidation of stillingia oil as a vegetable oil using *tert*-butyl hydroperoxide (TBHP) as an oxidizing agent (Scheme 79).²²⁸

2.5.19.5 Oxidation of sulfoxides. Sulfoxides are valuable targets in synthetic and medicinal chemistry and the oxidation of sulfide is one of the easiest ways to prepare these compounds. In 2017, Hong and Yan prepared a starch@Schiff base-Mo(acac)₂ as a catalyst to convert sulfides to sulfoxide using *t*-BuOOH as an oxidant (Scheme 80).²²⁹

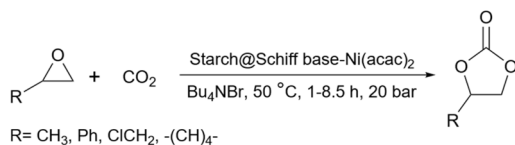
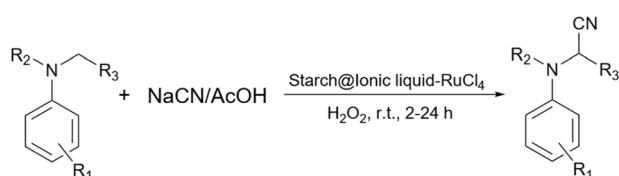
2.5.19.6 Synthesis of cyclic carbonates. There are many reports about using carbon dioxide as an undesirable molecule



Scheme 79 Epoxidation of stilingia oil using starch-NH₂@Mo(acac)₂.Scheme 80 Oxidation of sulfides to sulfoxides using starch@Schiff base-Mo(acac)₂.

to prepare much more precious compounds. One of these reactions is converting epoxides to their related cyclic carbonate.²³⁰⁻²³³ In 2012, Kumar *et al.* prepared and employed a starch-based catalyst to convert substituted epoxides to cyclic carbonates (Scheme 81). To do that, they prepared a starch Schiff base and attached Ni(acac)₂ to the surface of the Schiff base.²³⁴

2.5.19.7 Oxidative cyanation of tertiary amines. The oxidative cyanation of tertiary amines is an interesting method for the synthesis of α -aminonitriles.²³⁵⁻²³⁷ In 2011, Verma *et al.* reported

Scheme 81 Synthesis of cyclic carbonates from epoxides using starch@Schiff base-Ni(acac)₂.Scheme 82 Oxidative cyanation of tertiary amines using starch@ionic liquid-RuCl₄.

a ruthenium-catalyzed cyanation of aromatic tertiary amines (Scheme 82).²³⁸ They prepared a starch@ionic liquid-RuCl₄ as a novel catalyst for this transformation. To prepare the ionic liquid layer around the starch, the authors took advantage of the reaction between 1-methylimidazole and 3-trimethoxysilylpropyl chloride. Then, they attached the prepared 1-methyl-3-(silylpropyl)imidazolium chloride from the last step to the surface of starch under reflux conditions in toluene and used the achieved starch@ionic liquid to reach the intended starch@ionic liquid-RuCl₄.

3. Conclusion

In this review, the applications of starch as catalyst and catalyst support have been discussed. Literature review shows that starch has been used in different forms for a wide range of organic reactions. The application of starch in these reactions as a catalyst can be summarised based on the type of starch, *i.e.*, unfunctionalized and functionalized starch. Unfunctionalized starch could be used as simple or attached to magnetic particles and functionalized starch could be employed with simple acidic/basic modification of the surface of starch or anchored to a complex structure using an appropriate linker. In either case, starch can have a simple or core-shell structure. Based on what is presented here, simple starch like raw starch or starch nanoparticles are good candidates to promote acid-base reactions like multi-component organic transformations. Also, modified starch with suitable functional groups like acidic or basic starch can do the same job even with greater efficiency in some cases. However, to do more difficult reactions including coupling and oxidation reactions that the presence of metals is almost necessary, starch or its modified versions can be used as efficient support to hold the desired metal or metal oxide like molecular pincers and facilitate the process. Like any other catalyst starch has its disadvantages including low tolerance to a wide range of temperatures, and its tendency to absorb and hold water. However, properties such as being cheap, environmentally friendly, and easy to prepare can help balance the situation. All in all, regardless of whether we use starch, as a catalyst or catalyst support, this biodegradable and environmentally friendly biopolymer is a very good option for accelerating many organic reactions.

Conflicts of interest

There are no conflicts to declare.

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