

# Chapter 8

## Earth-Abundant d-Block Metal Nanocatalysis for Coupling Reactions in Polyols



Marc Camats, Daniel Pla, and Montserrat Gómez

**Abstract** Green Chemistry concepts have directed chemists to conceive and develop sustainable procedures, from the starting materials choice through reaction and analysis conditions, including suitable engineering aspects, to the impact of products, comprising recycling, and waste management. Industrial processes in Fine and Pharmaceutical Chemistry sector have high E factors compared to oil and bulk chemicals industry. Thus, the development of catalytic methods leading to high added value products is crucial, as well as waste minimization through selective transformations. Catalysts from 3d metals, compared to “heavy” metals, are greener, although a combination of different approaches is needed for efficient and viable processes. In contrast to 4d and 5d metals, catalysis with earth-abundant metals is less developed, even less concerning nanocatalysts. Metal nanoparticles (MNPs), due to their unique electronic and structural properties, induce original reactivities allowing a plethora of transformations. Besides, solvents, present in most steps, represent a major economic and environmental concern. In addition, they can have a dramatic influence on the stabilization of MNP and hence, a huge impact on catalytic activity and recycling. This chapter gives a perspective on 3d metal-based nanocatalysts in polyols applied to couplings, reactions present in many methodologies to produce fine chemicals in a sustainable fashion.

**Keywords** 3d metals · Metal nanoparticles · Catalysis · Couplings · Polyols

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Dedicated to Prof. Guillermo Muller for his thorough contributions in Organometallic Chemistry and Homogeneous Catalysis.

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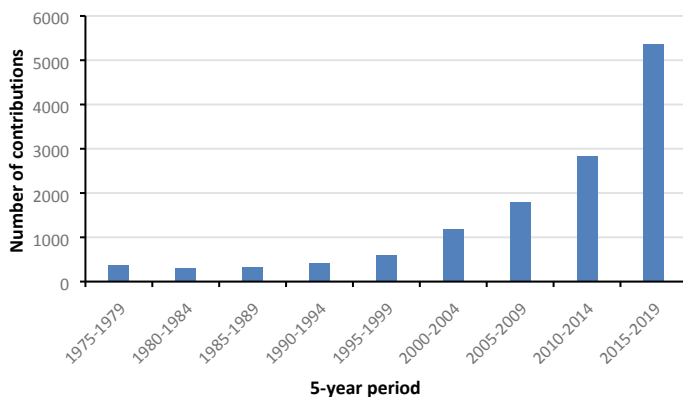
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## 8.1 Introduction

In the 1990s, a ground-breaking movement concerning the Earth preservation for future generations has appeared. In Chemistry, these actions led to the Green Chemistry concept [7, 128] articulated through the 12 Green Chemistry Principles [6]; shortly after, the Sandestin declaration established the bases of the Green Engineering Principles [8]. Notably, catalysis is one of the most important pillars of Green approaches [9]. Analyzing the evolution of metal-based catalysis, involving homogeneous and heterogeneous systems, it is evident to conclude that definitely the twentieth century has been the century of “heavy” metal-based catalysts, *i.e.*, catalytic processes concerning 4d and 5d metals (such as Mo, Ru, Rh, Ir, Pd, Pt, Au ...), as internationally acknowledged by the Nobel Prizes in 2005 (Y. Chauvin, R. H. Grubbs and R. R. Schrock) and 2010 (R. F. Heck, E.-i. Negishi and A. Suzuki) for the development of metathesis processes (mainly Mo- and Ru-based catalysts) and Pd-catalyzed couplings in organic synthesis, respectively ([www.nobelprize.org/prizes/chemistry/2005/summary](http://www.nobelprize.org/prizes/chemistry/2005/summary); [www.nobelprize.org/prizes/chemistry/2010/summary](http://www.nobelprize.org/prizes/chemistry/2010/summary)). Nevertheless, nature has exploited earth abundant 3d metals (Fe, Ni, Cu, Zn ...), leading to metalloenzymes which exhibit a prominent specificity [16]. In coherence to a sustainable development, researches on the design of manufactured catalysts with first-row transition metals have exponentially grown since the 2000s (see the contributions collected in the special issue “First row metals and catalysis” of Chemical Reviews, 2019) [2, 4, 48, 50, 65, 79, 101, 123, 129] (Fig. 8.1).

On the other hand, solvents represent one of the major concerns for chemical transformations (employed in synthesis, extractions, purifications, analyses...), in particular volatile organic compounds which are generally toxic showing different levels of harmfulness and danger, submitted to severe regulations. Alternative solvents (water, ionic liquids and deep eutectic solvents, alcohols, supercritical fluids,



**Fig. 8.1** Published contributions per 5-year period for first-row transition metals used in catalysis (data collected from SciFinder Database since 1975 up to July 2019)

renewable solvents, and combinations thereof ...) and solvent-free chemistry are useful and efficient approaches for many applications, needing investment and effort to adapt the current processes to the new reaction conditions [69]. In the frame of this chapter, we are interested in polyols, largely used in the industrial sector (highlighting the production of polymers such as polyurethanes, polyvinyl alcohol ...), because they present lower environmental impact than low-weight and volatile organic compounds, and they are particularly attractive for the synthesis and stabilization of nano-sized metal clusters.

Focusing on this type of nanomaterials, well-defined metal-based nanoparticles (objects showing dimensions in the range 1–100 nm) have known a huge expansion since the 1980s due to their distinctive properties, both physical and chemical, in comparison to molecular and bulk materials. Actually, this is a consequence of their electronic and structural features, making possible a vast number of applications [111, 90, 133], in particular in catalysis [1, 56, 89, 111, 112]. Even though metal nanoparticles (MNPs) have been largely applied in classical heterogeneous catalysis, with crucial participation in industrial processes mainly those related to oil area [137], nanocatalysis, which concerns MNPs dispersed in a solvent, has only been developed since the end of the last century. This exponential growth has benefited of the recent advances in characterization techniques (including operando approaches) which has permitted the design of catalysts at nanometric scale by means of controlling morphology and surface state of nanoobjects [5, 10, 63, 28]. Noticeably, reproducible synthetic methodologies are crucial for their further applications [107, 122]. The chemical strategies (commonly named bottom-up syntheses) often include solvents, from conventional organic compounds to alternative ones (showing a lower environmental impact), such as water [21, 110], ionic liquids [105],  $\text{scCO}_2$ , [32, 100, 134], and polyols [23, 40, 43]. It is important to mention that solvents may be involved in different aspects, for example, as reducing agents, stabilizers, or medium for trapping, nanocatalysts preserving their morphology during the catalytic transformation and thus facilitating their recycling. This is the case when polyols are present. In 1989, the polyol methodology was for the first time reported by Fiévet and coworkers where metal salts were reduced in ethylene glycol, obtaining well-defined MNPs [44, 45]. In this method, the polyol acts as solvent, reducing agent, and stabilizer when higher polyols are involved (e.g., polyphenols or polysaccharides), which prevents the agglomeration of MNPs in solution [36, 43].

These privileged physicochemical properties favor the preparation of tailor-made first-row transition metal nanocatalysts and derived nanocomposites in a controlled manner. Rational catalyst design is essential for the preparation of well-defined clusters and nanoparticles with optimal properties in terms of redox control, cooperative effects, and increased surface areas, all of them key factors for catalysis. Beyond the dual catalytic behavior related to both surface and reservoir of molecular species, nanocatalysis brings novel reaction manifolds due to the unique structural properties of MNPs, particularly their differential electronic structure as compared to bulk metals (e.g., facilitating single electron transfer processes via the Fermi level for electrons [42]).

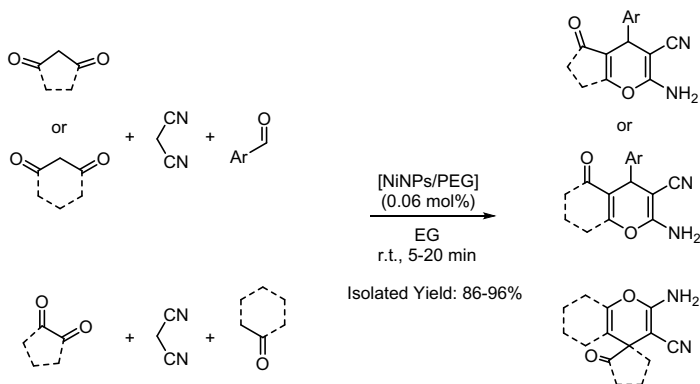
In the present contribution, we focus on the recent advances in 3d metal nanocatalysts (for a recent review, see: [127]), involving polyols acting as stabilizer and/or reaction medium for coupling reactions, Carbon–Carbon and Carbon–Heteroatom bond formation processes, including multicomponent syntheses.

## 8.2 Carbon–Carbon Bond Formation

C–C cross-coupling reactions have been largely dominated by palladium-based catalyzed processes due to their efficiency and versatility. In particular, the ability of this metal to stabilize different kinds of species (complexes, nanoparticles, extended surfaces) and its relatively high robustness under many different reaction conditions has permitted the elucidation of the corresponding mechanisms [18, 120, 124]. From a sustainable chemistry point of view, the use of first-row transition metals is obviously preferred and a huge research has been developed in the last years (for instance, see the contributions published in the Accounts of Chemical Research special issue “Earth Abundant Metals in Homogeneous Catalysis,” [27]).

### 8.2.1 Lewis Acid-Catalyzed Coupling Reactions

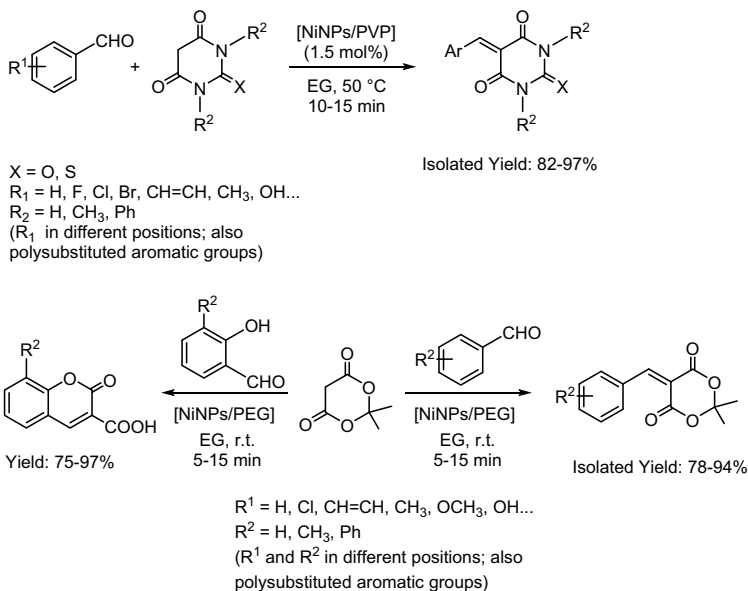
Heterocyclic motifs are present in a large variety of naturally occurring products along with industrial compounds [37, 59, 66, 102]. Multicomponent reactions represent an environmentally friendly approach to prepare polyfunctional compounds, in particular heterocycle derivatives, via one-pot processes involving three or more reactants, with high atom economy and easy implementation [19, 130, 138]. These transformations are often promoted by Lewis acids, which favor the kinetics directing the reaction pathway and in consequence improving the selectivity [51]. In this frame, Khurana and coworkers reported nickel nanoparticles (NiNPs) stabilized by polyethylene glycol (PEG-4000) and prepared by polyol-based methodology using ethylene glycol (EG) in the presence of NaBH<sub>4</sub>, which were applied in the synthesis of spiropyrans [73], interesting materials particularly due to their unique molecular switch properties that can trigger structural isomerization under the effect of different external stimuli (light, mechanical stress, temperature...) [75, 83, 131]. They were synthesized by a multicomponent reaction, constituted of a tandem Knoevenagel-cyclo-condensation involving ninhydrin (or related cyclic dicarbonyl compounds), malonitrile, and dimedone (or related 1,3-dicarbonyl derivatives) (Scheme 8.1). The role of the nanocatalyst (mean size: ca. 7 nm determined by TEM) was evidenced by different control tests; in the absence of nickel, the reaction was much slower (some hours vs. some minutes) and the use of Ni powder (particle size <150 μm) led to moderate yields after 8 h of reaction. Ethylene glycol was a convenient solvent permitting a straightforward extraction of products by a biphasic system (using ethyl acetate as immiscible solvent with ethylene glycol), preserving the catalyst dispersed



**Scheme 8.1** Synthesis of spiroyrans by a multicomponent reaction catalyzed by NiNPs and stabilized by PEG in ethylene glycol [73]

in the diol. NiNPs were efficiently reused up to 3 times. Authors postulated that nickel activates both carbonyl and nitrile groups.

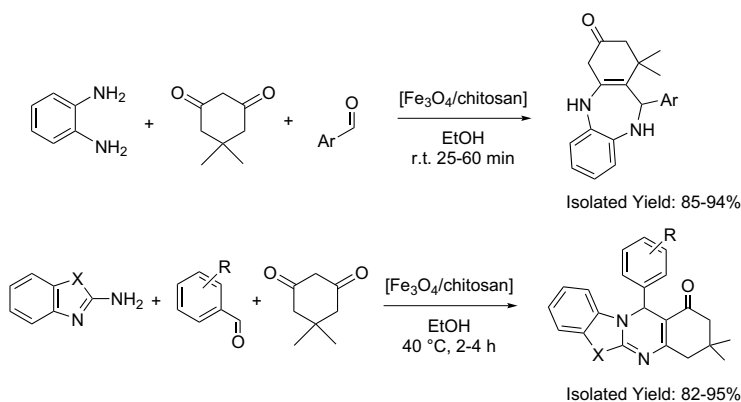
The same authors previously reported Knoevenagel condensations of barbituric or Meldrum acid and aromatic aldehydes in EG, catalyzed by NiNPs and stabilized by PVP (polyvinylpyrrolidone) [71] and PEG [72], respectively (Scheme 8.2).



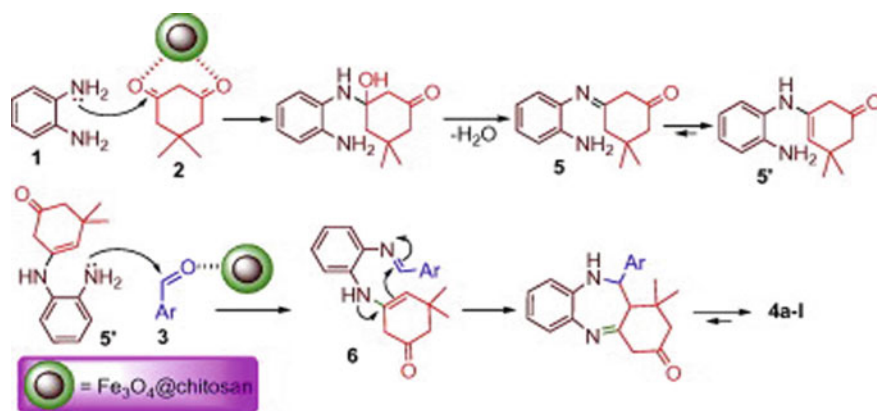
**Scheme 8.2** NiNPs stabilized by polymers catalyzed Knoevenagel condensations in ethylene glycol [71, 72]

Maleki and coworkers synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles stabilized by the biopolymer chitosan coming from chitin (polymer of *N*-acetylglucosamine) to be applied in three-component reactions yielding benzodiazepines [86] and benzimidazoloquinazolinones [84] (Scheme 8.3), which present biological and pharmacological activities [25, 58]. For both types of reactions, the catalyst was recycled up to four times preserving its catalytic performance, being ethanol the most appropriate solvent for these catalytic reactions. Authors proposed a similar pathway for both transformations.

In Fig. 8.2, the postulated mechanism for the synthesis of benzimidazo[2,3-*b*]quinazolinones is illustrated. The reaction most likely starts by a Knoevenagel



**Scheme 8.3** Three-component reactions catalyzed by  $\text{Fe}_3\text{O}_4$  nanoparticles stabilized by chitosan [84, 86]



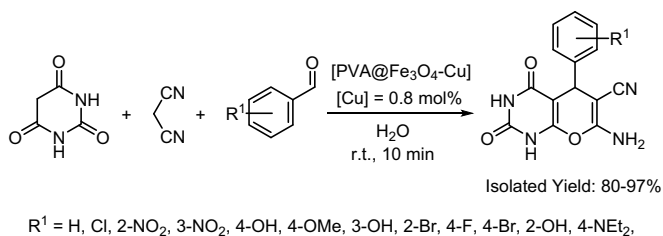
**Fig. 8.2** Proposed mechanism for Fe-based catalyzed synthesis of benzimidazo[2,3-*b*]quinazolinones. Reprinted from [84] with permission from Elsevier 2015, license no. 4639401066332

condensation between the aromatic aldehyde and dimedone; the resulting  $\alpha,\beta$ -unsaturated ketone reacts with the 2-aminobenzimidazole or its corresponding thio-derivative via a Michael addition, giving an acyclic compound which undergoes a further intramolecular cyclization. Similar catalysts were also applied for the synthesis of 2-amino-4H-chromenes [108] and highly substituted pyridines [85].

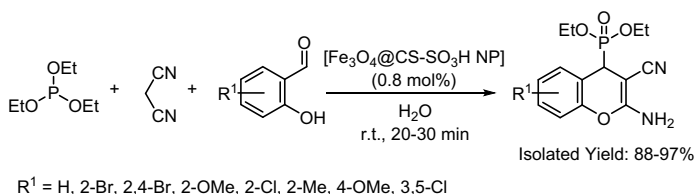
Although the Lewis acid properties of  $\text{Fe}_3\text{O}_4$  have proven to be useful for the synthesis of heterocycles, these properties seem to be enhanced in the presence of Cu(II) (Scheme 8.4) [87]. This catalytic system was reused 6 times with slight yield loss (first run: 98%; sixth run: 91%).

An interesting variant of this reactivity was reported by Mohammadi and Kassaei, showing that chromenylphosphonates could also be prepared in a similar manner in water with high yields and short reaction times (20–30 min), using functionalized magnetite with modified sulfo-chitosan (Scheme 8.5) [93].

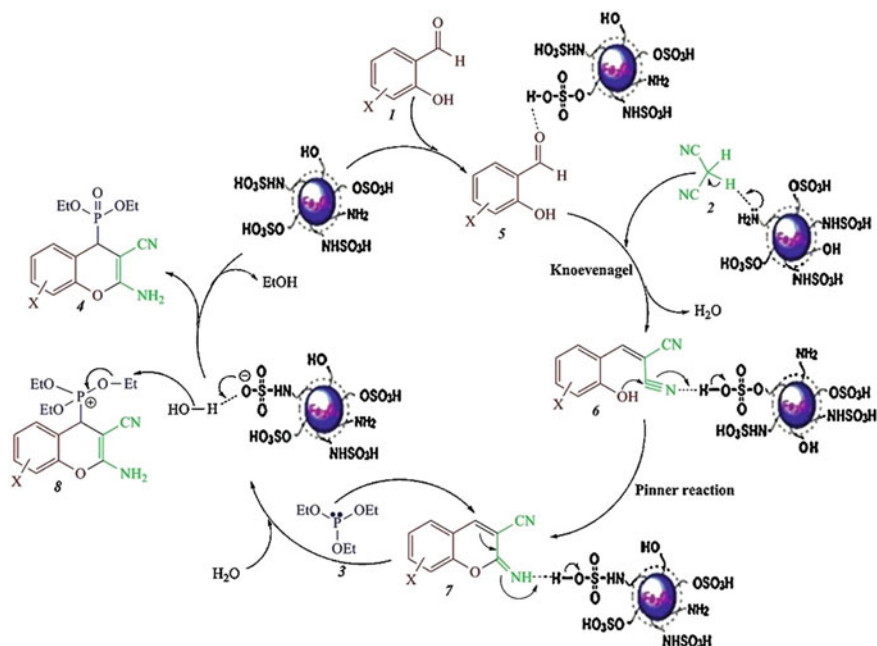
These authors proposed a mechanism catalyzed by hydrogen–heteroatom (nitrogen or oxygen) interactions, where water is not an innocent solvent (Fig. 8.3) [93]. Similar behavior has been observed with magnetite functionalized with sulfo-PEG,  $\text{Fe}_3\text{O}_4@\text{PEG-SO}_3\text{H}$  [88].



**Scheme 8.4** Synthesis of pyrano[2,3-*d*]pyrimidines catalyzed by  $\text{Fe}_3\text{O}_4$  modified with polyvinyl alcohol (PVA) and doped with Cu(II) salts [87]



**Scheme 8.5** Synthesis of 2-amino-4H-chromen-4-ylphosphonates catalyzed by  $\text{Fe}_3\text{O}_4@\text{CS-SO}_3\text{H}$  nanoparticles [93]



**Fig. 8.3** Plausible mechanism for the synthesis of 2-amino-4H-chromen-4-ylphosphonates catalyzed by functionalized magnetite, Fe<sub>3</sub>O<sub>4</sub>@CS-SO<sub>3</sub>H nanoparticles. Reprinted from [93], Copyright 2013, with permission from Elsevier, license no. 4640241387630

## 8.2.2 Cross-Coupling Reactions

The upbringing of d-block transition metals in catalyzed cross-coupling reactions is gaining ground against palladium thanks to their larger abundance than noble metals. The Sonogashira–Hagihara cross-coupling reaction enables the formation of a C–C bond between an sp<sup>2</sup>-carbon halide (aryl or vinyl) and a terminal alkyne [117]. This transformation was initially described with a Pd(0) catalyst and a Cu(I) co-catalyst, but Cu alone [76, 80, 121] and other 3d transition metals have been reported as efficient catalysts for this transformation (Ni [15, 103, 104], Fe [67], Co [116]), fueling the important role of abundant metals in C–C bond forming reactions. Gaining a better understanding on the physicochemical processes leading to the formation of MNPs is key for the design of nanocatalysts with defined morphology [52, 97], notably when catalyst heterogenization with solid supports such as zeolites, titania, montmorillonite and carbonaceous materials is required. Robustness and catalytic activity of tailor-made nanostructured catalysts outperform in many cases classical ones [91].

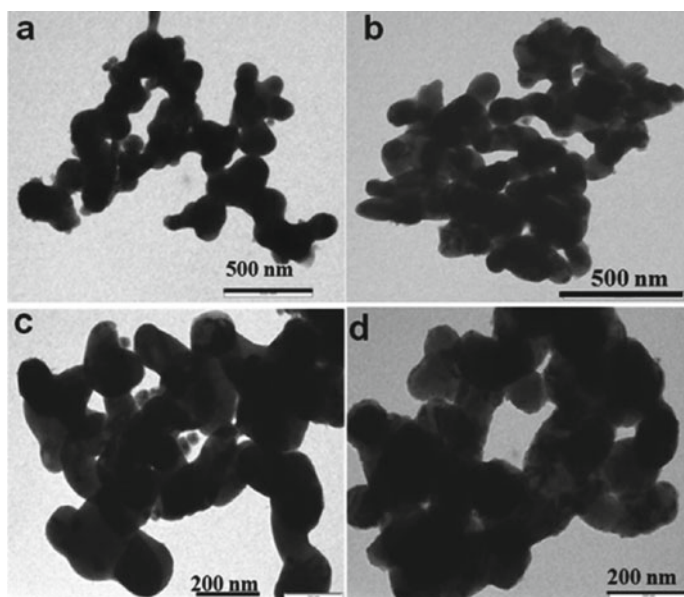
**C(sp)-C(sp<sup>2</sup>) Sonogashira cross-coupling** Since synthesis of copper(I) acetylide, the first organometallic copper complex described in 1859 [20], the reactivity of copper toward the activation of terminal alkyne groups has yielded a number of



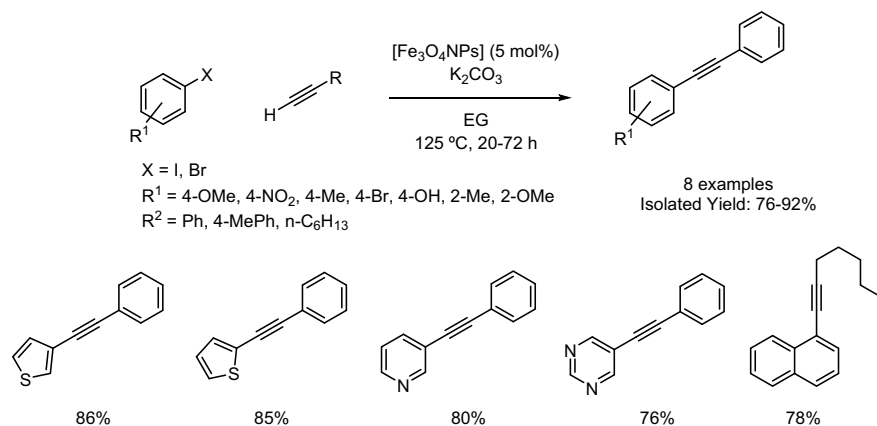
interesting transformations for the synthesis of propargylic compounds [35]. The search of catalytic versions is key for exploiting the privileged reactivity of this metal from the point of view of sustainability [38]. Recent reports on the singular  $\pi$ -activation of alkynes leveraged by zero-valent CuNPs reveal the importance of this coordination in catalysis [33, 97].

In this context, the cross-coupling of terminal alkynes and acyl chlorides has been reported by Bhosale et al. using a Cu/Cu<sub>2</sub>O catalyst prepared from Cu(OAc)<sub>2</sub> in one-step under microwave irradiation (3 min, 600 W) in 1,3-propanediol. The as-prepared catalytic material exhibited an irregular morphology that combines tubular domains and spherical particles ranging from 70 to 110 nm in size (Fig. 8.4) of a mixture of Cu(0) and Cu<sub>2</sub>O as confirmed by high-resolution XPS analysis [17].

Taking into account the paramount importance that metal traces might have in catalysis, it is crucial to determine their contribution and potential cooperative effects. Firouzabadi et al. described the use of spherical paramagnetic Fe<sub>3</sub>O<sub>4</sub> NPs (<30 nm in diameter) in ethylene glycol under ligand-free conditions for the Sonogashira–Hagihara reaction for the synthesis of (hetero)aryl alkynes from terminal alkynes and haloarenes (e.g., heteroaryl bromides, aryl iodides, Scheme 8.6) [46, 47]. In order to ascertain the role of Fe<sub>3</sub>O<sub>4</sub> NPs as catalyst, the authors determined the traces of Pd, Ni, Cu, and Co present both in the reagents and solvent. Thus, the contamination concerning the above-mentioned metals was found to be 130 ppb Pd, 45 ppb Ni, 24 ppb Cu, and 21 ppb Co for K<sub>2</sub>CO<sub>3</sub>; as well as 20 ppb Pd, 33 ppb Cu, 27 ppb Ni,



**Fig. 8.4** TEM micrographs of Cu/Cu<sub>2</sub>O NPs. Reproduced with permission from Royal Society of Chemistry 2014, license no. 4639380035278

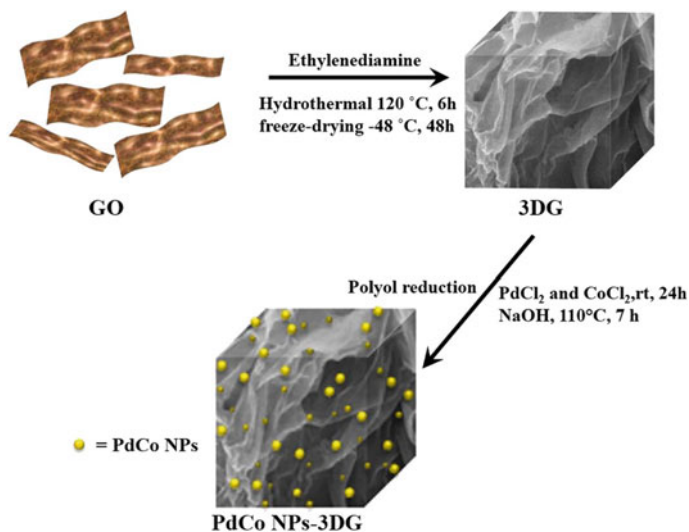


**Scheme 8.6** Fe<sub>3</sub>O<sub>4</sub> NPs catalyzed Sonogashira-Hagihara coupling reaction in EG [46]

and 24 ppb Co for ethylene glycol by ICP analyses. As catalyst controls, different metal salts [e.g., Pd(OAc)<sub>2</sub>, CuCl, NiCl<sub>2</sub>, CoCl<sub>2</sub>] at concentrations ranging from 200 to 1500 ppb were tested, but the catalytic activity of Fe<sub>3</sub>O<sub>4</sub> NPs at 5 mol% loadings proved to be superior [46]. The magnetic properties of Fe<sub>3</sub>O<sub>4</sub> NPs allowed an easy catalyst recycling with only an overall 2% yield decrease after five consecutive runs.

An example of bimetallic nanocatalyst for Sonogashira cross-coupling reaction featuring PdCo NPs supported on graphene has been described by Dabiri and Vajargahy [31]. The synthesis of this nanocomposite was carried out following the polyol methodology. In particular, the co-reduction of PdCl<sub>2</sub> and CoCl<sub>2</sub> was performed in ethylene glycol, which acted as reducing and stabilizing agent for the immobilization of NPs on the 3D graphene support (Fig. 8.5). XPS analysis of the as-prepared nanocomposite revealed the presence of zero-valent Pd and Co (binding energies at 335.67 and 341.49 eV corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>; as well as 781.53 and 798.16 eV corresponding to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>), which match the literature values for PdCo alloys. Higher oxidation states, namely Pd(II), Co(II), and Co(III) were also detected, the latter arising from an oxidation on the NPs surface [31]. The prepared PdCo nanocomposite exhibited high catalytic activity for Sonogashira and Suzuki cross-coupling reactions of aryl halides with terminal alkynes and boronic acids, respectively, in water. Moreover, the catalyst was recycled up to seven times without loss in catalytic activity.

Aluminosilicate-based materials such as montmorillonite are largely used as catalyst supports. Liu et al. have recently described the co-immobilization of Cu and Pd on a montmorillonite-chitosan matrix. According to the authors, the resulting bimetallic CuPd nanocomposite features Pd coexisting in both Pd(0) and Pd(II) valence states, as well as Cu mainly in its Cu(II) as determined by XPS. However, the presence of Cu(0) and Cu(I) cannot be excluded relying solely on this technique. The as-prepared



**Fig. 8.5** Synthesis of PdCo NPs supported on graphene. Reproduced with permission from Ref. [31]. Copyright 2016 Wiley, license no. 4639270206261

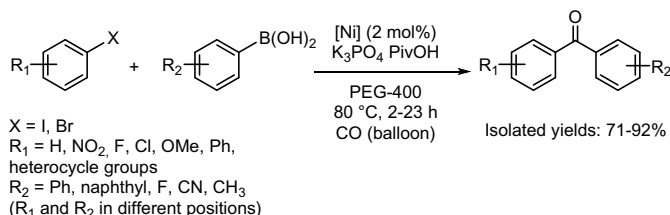
nanocomposite containing spherical PdNPs below 3 nm in diameter catalyzed Sonogashira couplings of haloarenes and alkynes in 1,2-dimethoxyethane/H<sub>2</sub>O, although Cu leaching resulted in an activity decrease upon recycling [81].

Alternatively, the stabilization of Pd at higher oxidation states could be achieved via the formation of stable Pd-*N*-heterocyclic carbene complexes. Yavuz et al. have recently reported Sonogashira cross-coupling reaction catalyzed by in situ generated Pd-1*H*-benzo[*d*]imidazolium complexes [from Pd(OAc)<sub>2</sub> and Cs<sub>2</sub>CO<sub>3</sub>], and CuNPs in PEG300 [132]. However, authors did not characterize the catalyst employed.

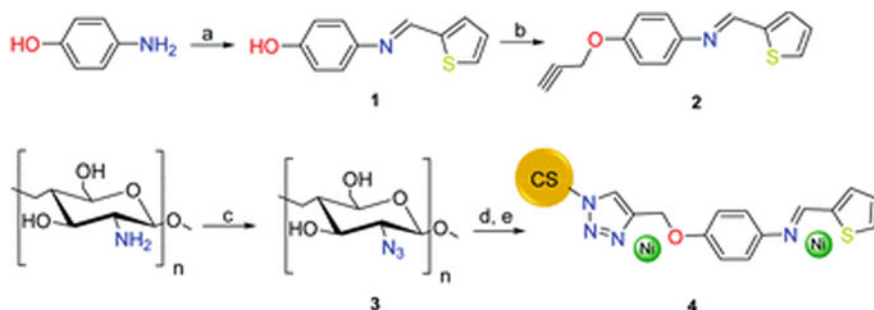
**Suzuki–Miyaura-type cross-coupling** During the last years, the controlled synthesis of NiNPs has drawn attention to several research groups, the main challenge being the exclusive preparation of zero-valent nickel nanomaterials due to the facile oxidation of Ni(0) species. Consequently, the lack of control of nickel oxidation in preformed nanoparticles is a persistent issue, as shown by several authors. Among them, one finds Tilley and coworkers in the synthesis of nickel nanocubes from Ni(acac)<sub>2</sub> under H<sub>2</sub> [78]; Hyeon's group in the preparation of NiNPs under thermal decomposition [99]; and Zarbin and coworkers in the synthesis of NiNPs following the polyol approach [98]. Chaudret and coworkers published an efficient method for the synthesis of nickel(0) nanorods, from [Ni(COD)<sub>2</sub>] under hydrogen atmosphere [29]. More recently, zero-valent NiNPs were successfully prepared in neat glycerol, without exhibiting any oxide shell on their surface thanks to the low solubility of molecular oxygen in glycerol; these nanocatalysts were, in particular, highly efficient for the semi-hydrogenation of alkynes [106]. However, Ni-based nanoparticles have been scarcely applied in C–C cross-coupling reactions. Their efficiency is particularly remarkable when they are formed in situ, as proven by Lipshutz and coworkers using

NiNPs generated in water in the presence of appropriate surfactants (acting as stabilizers) and the Grignard reagent MeMgBr to activate the pre-catalyst ( $[\text{NiCl}_2\text{L}_n]$ , where L is a (di)phosphine and  $n = 1$  or 2), which were successfully applied in Suzuki–Miyaura couplings [62]. Simultaneously, Han and coworkers reported Ni-catalyzed carbonylative Suzuki-based reactions in PEG (Scheme 8.7) [135], process leading to biaryl ketones, motif present in different types of compounds (drugs, photosensitizers ...). They compared the reactivity between preformed and in situ generated NiNPs, evidencing that those formed in situ were more active, probably because the latter are smaller, showing less aggregation than the preformed ones. Authors carried out control tests (with Hg and  $\text{CS}_2$ ) in order to prove the nature of the catalytically active species (in the presence of these additives, the reaction did not work), concluding that the activity observed agrees with a surface-like reactivity.

Preformed NiNPs stabilized by triazole-modified chitosan were active nanocatalysts for Suzuki–Miyaura reactions between aryl halides and phenyl boronic acid derivatives (Scheme 8.8) [60].



**Scheme 8.7** In situ generated NiNPs in PEG-400 applied in carbonylative Suzuki coupling reactions [135]

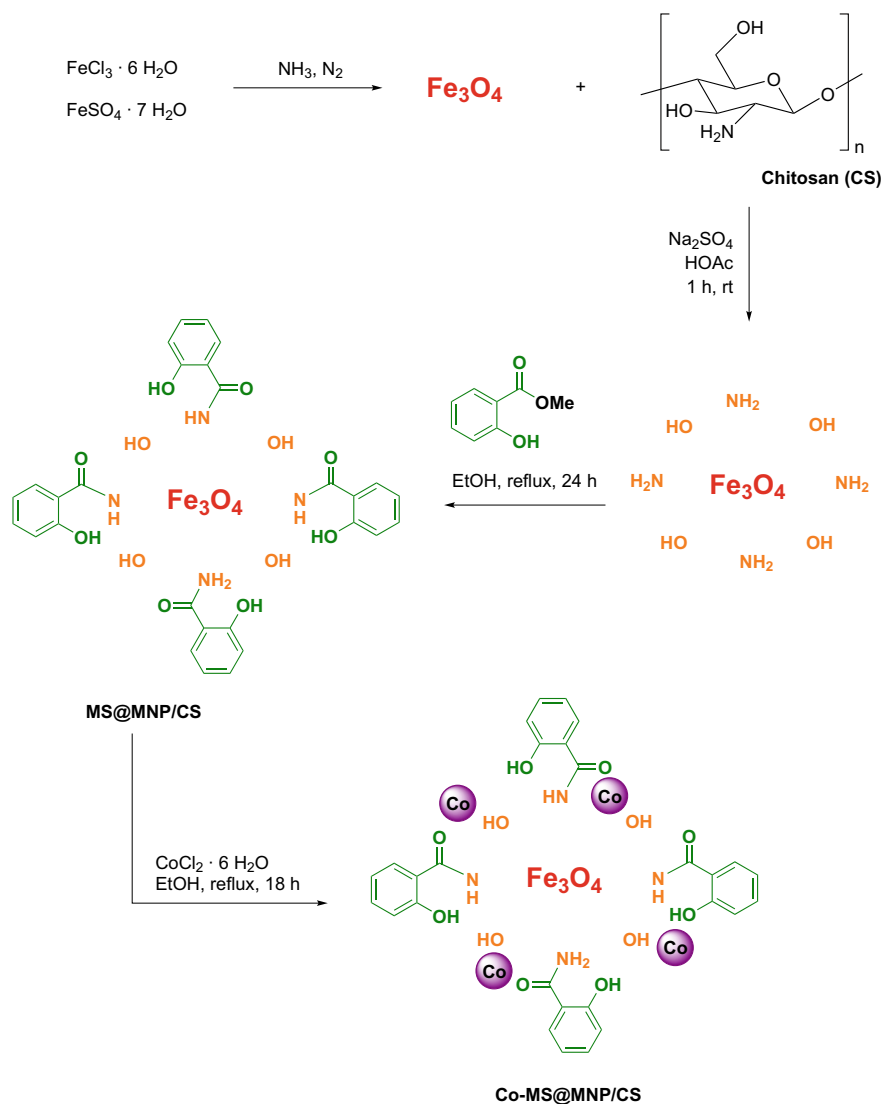


**Scheme 8.8** Synthetic path for the synthesis of NiNPs stabilized by modified chitosan: **a** thiophene-2-carbaldehyde, MeOH, reflux, 3 h; **b** propargyl bromide,  $\text{K}_2\text{CO}_3$ , acetone, 50 °C, 24 h; **c** tris(4-aminophenoxy)amine, aqueous  $\text{HCl} \cdot \text{NaHCO}_3$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , MeOH, r.t., 5 d; **d**  $\text{CuI}$ , **2**, DMF/THF (1 : 1), r.t., 72 h; **e**  $\text{NiCl}_2/\text{EtOH}$  solution, 12 h, r.t., then hydrazine hydrate, r.t., 2 h. New Journal of Chemistry by Center National de la Recherche Scientifique (France); Royal Society of Chemistry (Great Britain) Reproduced with permission of ROYAL SOCIETY OF CHEMISTRY in the format Book via Copyright Clearance Center, license no. 4639350882762 [60]

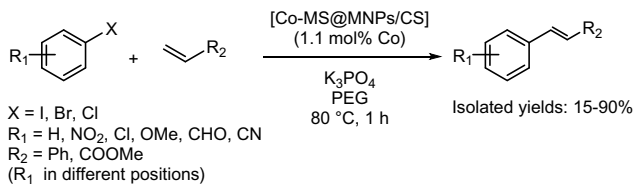
**Heck–Mizoroki-type cross-coupling** Since the pioneering and independent works from Gilman and Lichtenwalter [57], and Kharasch and Fields [70] in the 1930s and 1940s respectively, concerning the homocoupling reaction of Grignard reagents promoted by cobalt(II) salts, scarce works were carried out up to the 1990s ([22] and references therein). Cobalt complexes have proven their efficiency for the formation of  $C(sp^2)–C(sp^2)$  bonds; particularly, Co-based catalysts are interesting for cross-couplings where alkyl halides are involved, because  $\beta$ -hydrogen elimination of alkyl intermediates is not favored in contrast to the analogous Pd and Ni organometallic species. In the frame of the present contribution, Co(II) anchored to chitosan-functionalized  $Fe_3O_4$  NPs has found applications in Heck- and Sonogashira-type couplings [61].  $Fe_3O_4$  NPs containing chitosan were modified by reaction with methyl salicylate to give amide-phenol groups at their surface, which coordinate  $CoCl_2$  (Scheme 8.9).

This represents an example of molecular-like catalytic reactivity using functionalized nanoparticles as support. For the Heck-type reaction, the catalyst was efficient for the coupling of aryl halides (chloro, bromo, iodo) with styrene or methyl acrylate using PEG as solvent (Scheme 8.10). In contrast to the non-functionalized  $Fe_3O_4$  NPs, the functionalized ones were more active and could be recycled up to five times preserving their efficiency, without metal leaching. The Sonogashira-type coupling between aryl halides (bromo, iodo) and phenylacetylene derivatives gave moderate yields under harsher conditions than those used for the Heck couplings.

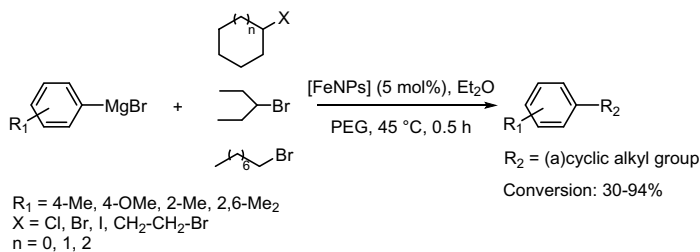
**Kumada-type cross-coupling** Kumada–Tamao–Corriu reaction, coupling between a Grignard reagent and an organic halide, was initially reported using Ni-based catalysts [30, 119]; other efficient systems such as those based on palladium and iron, have proven their efficacy, the main part of them involving molecular catalysts, but more recently copper, nickel, and palladium nanoparticles have been used as well ([64, 92] and references therein). Iron, representing the second more abundant metal in the Earth's crust, has found interesting applications in C–C couplings [3, 13, 96]. The main part of reported works assumes the contribution of molecular intermediate species in the catalytic transformation, but also nanoparticles have been identified for low oxidation states (zero-valent FeNPs should be more stable under catalytic conditions than organometallic Fe(0) complexes) and it has been postulated that they act as a reservoir of molecular species exhibiting higher oxidation state [11]. Bedford and coworkers studied the reaction of alkyl halides with aryl Grignard compounds catalyzed by in situ generated FeNPs from  $FeCl_3$  in the presence of PEG-14000 (Scheme 8.11 and Fig. 8.6) [12]. Authors proved that the Grignard reagent acted as reducing agent. Preformed FeNPs/PEG (diameter in the range 7–13 nm, determined by TEM) afforded the same reactivity as those formed in situ.



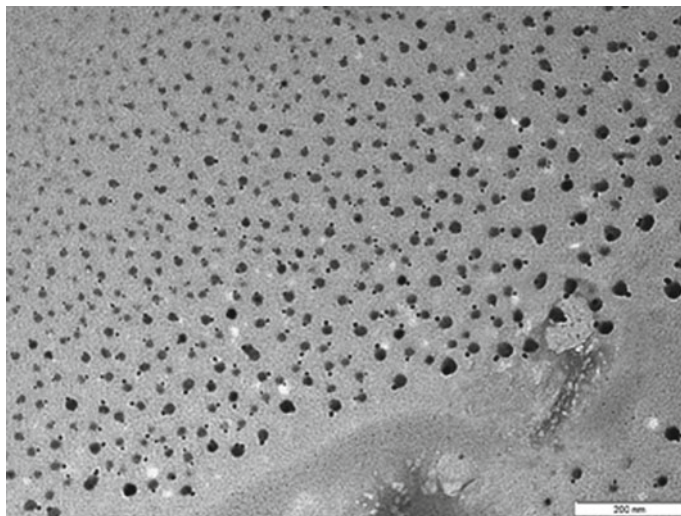
**Scheme 8.9** Preparation of co-based nanocatalyst immobilized on  $\text{Fe}_3\text{O}_4$  nanoparticles modified by chitosan. Green Chemistry by Royal Society of Chemistry (Great Britain) Reproduced with permission of ROYAL SOCIETY OF CHEMISTRY in the format Book via Copyright Clearance Center, license no. 4639360400827 [61]



**Scheme 8.10** Heck–Mizoroki-type couplings catalyzed by Co(II) supported on functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles (see Scheme 8.9) [61]



**Scheme 8.11** C(sp<sup>2</sup>)-C(sp<sup>3</sup>) cross-coupling catalyzed by FeNPs stabilized by PEG [12]

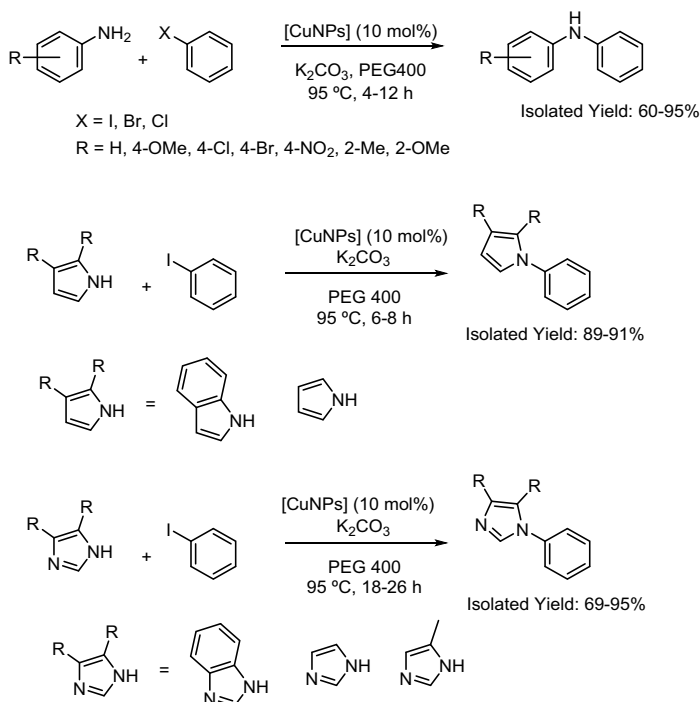


**Fig. 8.6** TEM image corresponding to FeNPs generated in situ from FeCl<sub>3</sub> in the presence of 1,6-bis(diphenylphosphino)hexane with 4-MeC<sub>6</sub>H<sub>4</sub>MgBr. Reproduced with permission of ROYAL SOCIETY OF CHEMISTRY in the format Book via Copyright Clearance Center, license no. 4640081165587 [12]

### 8.3 Carbon–Heteroatom Bond Formation

The activation of C–halogen bonds has been overwhelmingly used in the functionalization of arenes. Since the discovery of Ullmann’s coupling in 1901, copper has been one of the most used earth-abundant metals in both C–C and C–heteroatom couplings (original paper of Ullmann: [125]; recent reviews: [14, 94, 109]). However, many applications of this reactivity are especially limited due to the use of hazardous solvents such as DMF and DMSO. A lot of interest has been put into transforming this reactivity into greener approaches. In this context, considerable efforts have been recently developed in nanocatalytic systems capable of working in friendly environmental conditions [68, 127], polyols being alternative solvents of interest [41].

This strategy has been successfully applied in a wide range of C–N couplings using many different nitrogen-based reagents. Kidwai and coworkers applied preformed unsupported CuNPs in the *N*-arylation of aryl halides with anilines using PEG400 as solvent (Scheme 8.12) [74]. A large scope of aniline derivatives and also NH heterocycles was carried out.

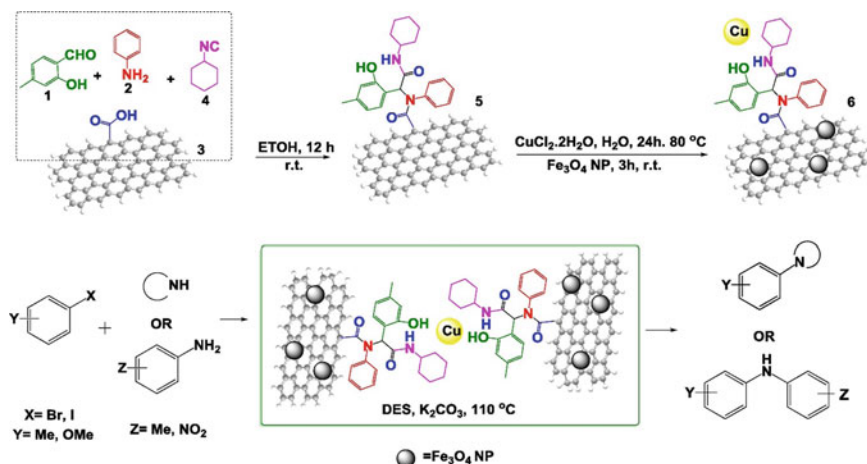


**Scheme 8.12** CuNPs catalyzed C–N cross-couplings of anilines and NH heterocycles with aryl halides in PEG400 [74]

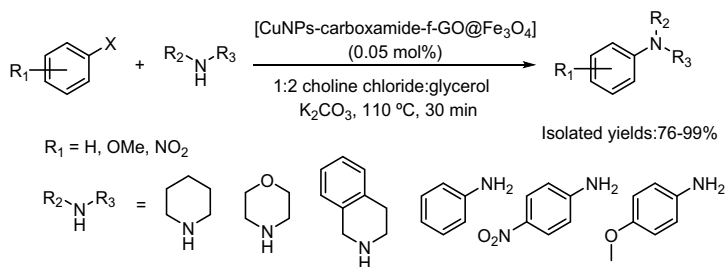


Graphene oxide functionalized with carboxamide groups (f-GO) was an efficient support to coordinate Cu(II) salts and further reducing them to give CuNPs immobilized on the solid. This CuNPs on f-GO were then treated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles leading to a magnetic catalytic material, which enhanced the catalyst recyclability (Fig. 8.7) [113].

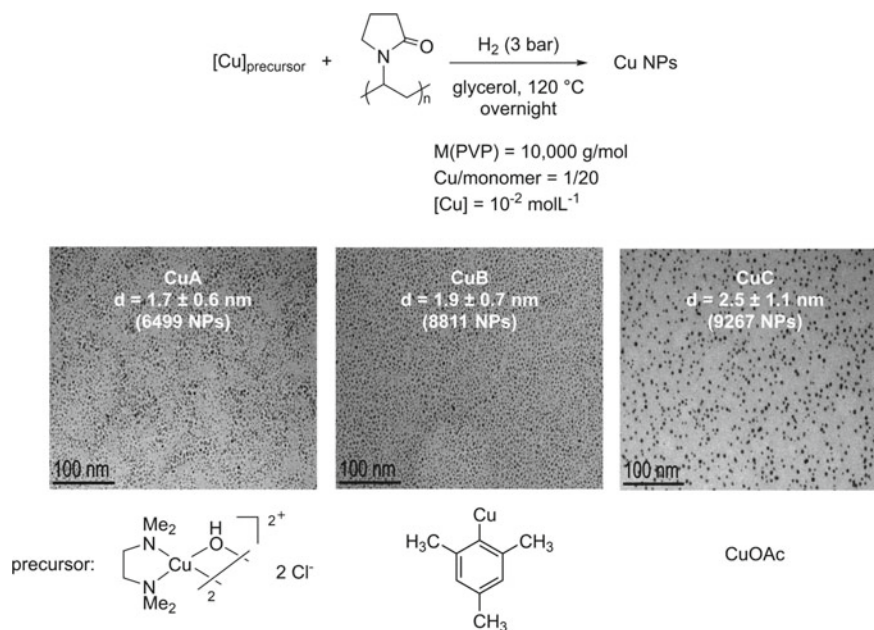
The as-prepared heterogenized nanocatalyst was applied to Ullmann-type coupling for the synthesis of *N*-aryl amines using a deep eutectic solvent (choline chloride:glycerol = 1:2) (Scheme 8.13). Authors compared the efficiency of this catalytic system with other CuNPs, both supported and unsupported, concluding that their catalyst led to higher yields under smoother conditions. However, the recycling was moderate (up to 3 times without loss of activity).



**Fig. 8.7** Illustration of the synthesis of CuNPs immobilized on f-GO containing Fe<sub>3</sub>O<sub>4</sub> NPs (top) with the application in C–N bond formation processes (bottom). Reprinted from [113], Copyright 2018, with permission from Elsevier, license no. 4640121432056



**Scheme 8.13** CuNPs immobilized on a magnetic-modified graphene oxide (see Fig. 8.7) catalyzed C–N couplings of secondary amines and anilines [113]



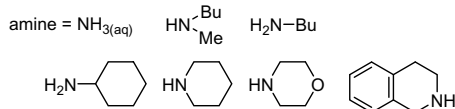
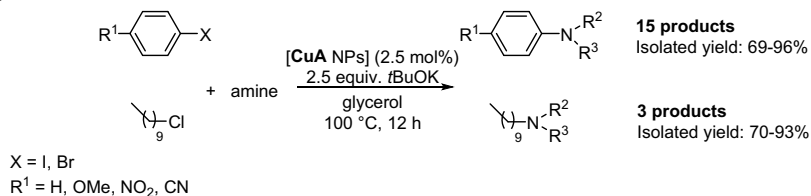
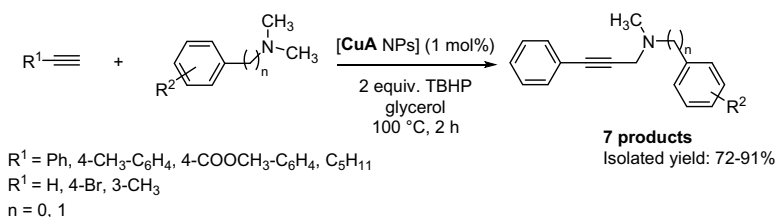
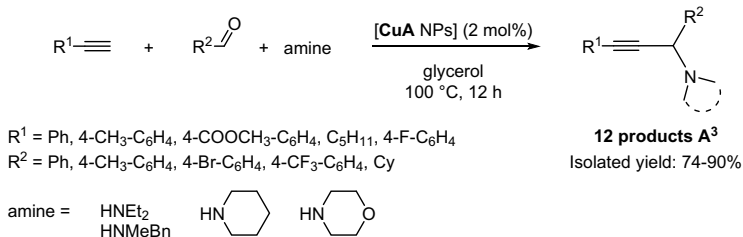
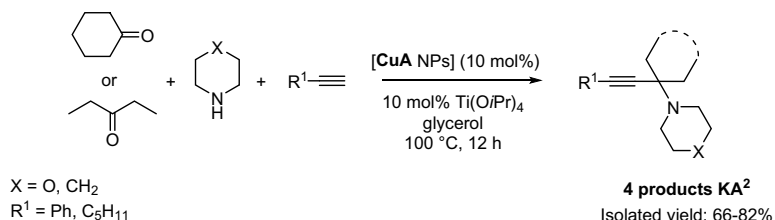
**Fig. 8.8** Synthesis of CuNPs in glycerol from different copper precursors stabilized by the polymer PVP (top) and the corresponding TEM images of the different nanoparticles (bottom). Adapted with permission from [33], Copyright 2017 Wiley, license no. 4640130742799

The work of our group on the preparation of small CuNPs (mean diameter: 1.7–2.4 nm) in glycerol from the reduction of Cu(II) and Cu(I) precursors with PVP as stabilizer and under low pressure of H<sub>2</sub> (3 bar) avoided the formation of oxidized by-products coming from the solvent (Fig. 8.8). This approach represents the first report toward the synthesis of well-defined and stable CuNPs by a bottom-up strategy thanks to the low solubility of O<sub>2</sub> in this medium, circumventing the formation of oxide shells [33].

CuNPs nanoparticles were successfully applied in C–N couplings and in the synthesis of propargyl amines through different strategies, such as cross-dehydrogenative couplings and multicomponent reactions, both A<sup>3</sup> (aldehyde–alkyne–amine) and KA<sup>2</sup> (ketone–alkyne–amine) (Scheme 8.14). Authors carried out spectroscopic monitoring (UV-vis and FTIR analyses) concluding that the C–N coupling follows a surface reactivity, without formation of Cu(I) molecular species, like phenylethynylcopper(I), which would be poisoned by the presence of amines.

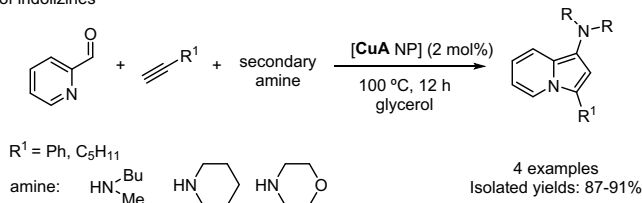
The selection of alternative aldehydes bearing heteroatoms in position 2 of the ring (e.g., 2-aminobenzaldehyde, 2-hydroxybenzaldehyde and 2-pyridinecarbaldehyde) provided a direct entry to the synthesis of heterocycles, namely indolizines, benzofurans and quinolines via a CuNP-catalyzed A<sup>3</sup>-cycloisomerization tandem processes (Scheme 8.15).

## a) Synthesis of amines and anilines

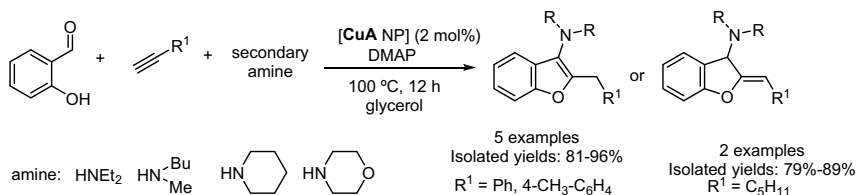
b) Cross-dehydrogenative coupling catalyzed by **CuA** NPs in glycerolc) A<sup>3</sup> coupling catalyzed by **CuA** NPs in glycerold) **CuA**-catalyzed KA<sup>2</sup> multicomponent processes

**Scheme 8.14** **CuA** nanoparticles catalyzed C–N couplings and multicomponent reactions [33] (for **CuA**, see Fig. 8.8)

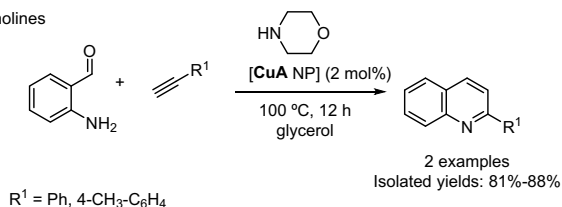
## a) Synthesis of indolizines



## b) Synthesis of benzofurans

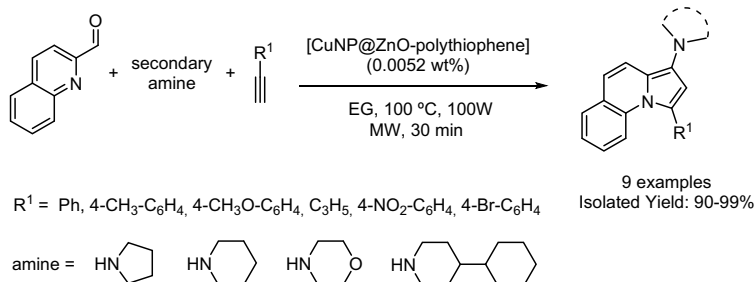


## c) Synthesis of quinolines



**Scheme 8.15** Synthesis of indolizines, benzofurans, and quinolines catalyzed by **CuA** nanoparticles in glycerol [33] (for **CuA**, see Fig. 8.8)

Moreover, Shah et al. have recently reported the  $\text{A}^3$ -coupling reaction for the synthesis of propargylamines and pyrrolo[1,2-*a*]quinolines using a heterogenized Cu catalyst ( $\text{CuNPs@ZnO-polythiophene}$ ) at low catalyst loadings (Scheme 8.16)



**Scheme 8.16**  $\text{CuNPs@ZnO-polythiophene}$  catalyzed synthesis of pyrrolo[1,2-*a*]quinolines in EG under microwave irradiation [114]

[114]. Notably, the cyclization only takes place in an intramolecular fashion and no Cu leaching was detected in the EG reaction medium after catalyst filtration (ICP analyses).

Preformed  $\text{Cu}_2\text{O}$  nanoparticles (mean diameter: ca. 5 nm, Fig. 8.9) were applied in the coupling between iodoaryl derivatives and different nitrogen-based reagents, such as aryl and alkyl amines, but also aqueous ammonia, in glycerol [24]. This nanocatalyst was also efficient for the synthesis of thioethers through C–S couplings.

This catalytic system has also been applied for the activation of terminal alkyne groups toward azide–alkyne cycloaddition reaction (CuAAC) in glycerol (Scheme 8.17) [24].

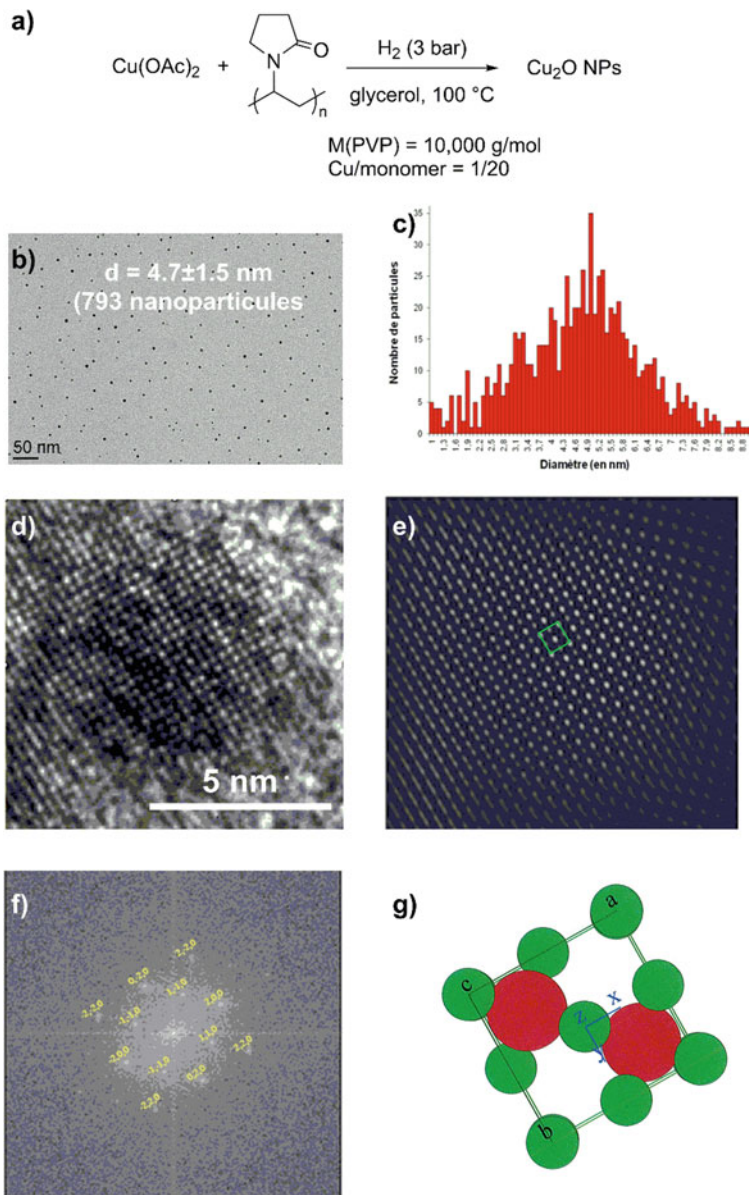
Furthermore, Sharghi and Aberi reported the application of  $\text{Cu}_2\text{O}$  NPs in the synthesis of indazole derivatives through a three-component strategy in PEG300 (Scheme 8.18) [115].

Cu-based catalysts in polyol medium have also found interesting applications in C–S bond formation processes, as proved by our group using  $\text{Cu}_2\text{O}$  nanoparticles [24]. Primo, García, and coworkers reported the synthesis of Cu-based nanoparticles stabilized by chitosan, mainly constituted of Cu(0) but surrounded by a thin layer of copper oxides as proven by XPS [49]. This nanocatalyst was applied in the C–S coupling of aryl halides and thiophenol, being more active for iodo than bromo and chloro arenes, for the latter ones they were only active for aryl halides containing electron withdrawing substituents (Scheme 8.19). Authors observed that halide anions released to the medium during the catalytic reaction can act as poison for CuNPs, in addition to promoting metal leaching.

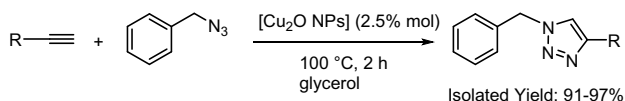
Generally speaking, C–O couplings are more challenging reactions mainly due to the limited functional compatibilities and the need of activated substrates [77, 118]. Besides, the use of polyol medium adds another difficulty because the solvent can compete with the substrate. In this frame, Biegi and Ghiasbeigi have recently reported the synthesis and full characterization of functionalized magnetite with isonicotinic acid with the aim of coordinating Cu(I) precursors (Fig. 8.10) [53]. The resulting catalytic material was efficiently applied to the synthesis of phenol and aniline derivatives (TOF up to  $4494 \text{ h}^{-1}$ ), using a mixture of PEG and water as solvent (PEG:H<sub>2</sub>O = 2:1) (Scheme 8.20). The catalytic phase was recycled up to 5 times with slight loss of yield, although the 30% copper loss reported by the authors after the fourth run was substantial (Cu content of catalyst before use: 57,037.8 ppm; after 4th run: 40,297.3 ppm).

## 8.4 Conclusions and Outlook

This chapter describes the use of nanocatalysts from Earth-abundant metals in polyol media applied in C–C and C–heteroatom coupling reactions. Despite the interesting reports mentioned in this contribution, nanocatalysis based on d-block transition metals in polyols is still in its infancy. This is an exponentially growing research

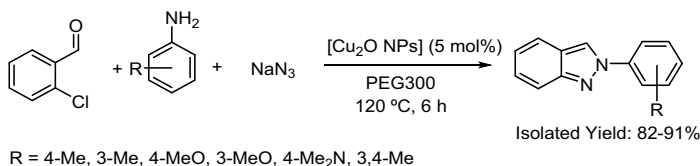


**Fig. 8.9** Synthesis of  $\text{Cu}_2\text{O}$  NPs in glycerol and characterization after isolation at solid state and re-dispersion in glycerol. **a** Synthesis scheme; **b** TEM micrograph in glycerol; **c** size distribution histogram; **d** HR-TEM micrograph of one single particle of  $\text{Cu}_2\text{O}$ ; **e** electronic diffraction spots by fast Fourier transform of a single particle; **f** filtered image showing the zone axis [0 0 1]; **g** cartoon of  $\text{Cu}_2\text{O}$  cubic structure. Adapted with permission from [24], Copyright 2014 Wiley, license no. 4640200545968



R = Ph, Cy, n-Bu, t-Bu, (CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-OH, CH<sub>2</sub>CH<sub>2</sub>-OH, (CH<sub>3</sub>)<sub>2</sub>C-OH, (CH<sub>2</sub>)<sub>5</sub>-CH<sub>2</sub>OH, CH<sub>2</sub>-NMe<sub>2</sub>,

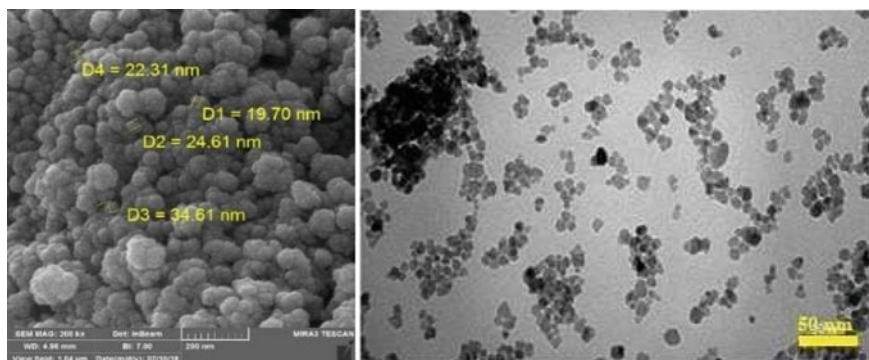
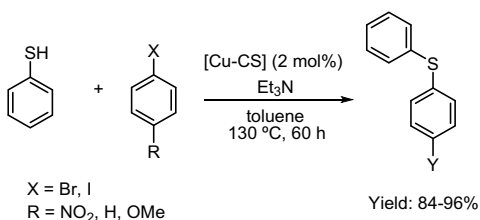
**Scheme 8.17** Cu<sub>2</sub>O NPs catalyzed azide-alkyne cycloaddition in glycerol [24]



R = 4-Me, 3-Me, 4-MeO, 3-MeO, 4-Me<sub>2</sub>N, 3,4-Me

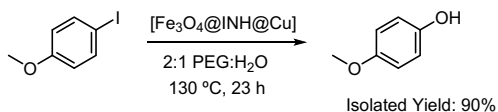
**Scheme 8.18** Cu<sub>2</sub>O nanoparticles catalyzed the synthesis of 2H-indazoles [115]

**Scheme 8.19** CuNPs stabilized by chitosan applied in C-S couplings [49] (CS stands for chitosan)



**Fig. 8.10** SEM (left) and TEM (right) images of Cu(I) grafted to Fe<sub>3</sub>O<sub>4</sub> modified by isonicotinic groups. Reprinted with permission from [53], Copyright 2019 Wiley, license no. 4640160235060

**Scheme 8.20** Synthesis of phenols catalyzed by Cu-based catalyst supported on modified Fe<sub>3</sub>O<sub>4</sub> [53]



field that exploits the non-innocent physicochemical properties of polyols as reducing, stabilizing, and dispersing agents in the quest for tailor-made nanocatalysts and nanocomposites with enhanced properties as compared to classical ones. In the framework of the development of greener and more sustainable processes, Cu, Ni, Co, and Fe nanocatalysts in polyol media represent key alternatives to overcome the dependence on the scarcity of noble metals in use currently for both academic and industrial purposes.

The Lewis acidity properties of 3d-transition metals confer them suitable properties as (co)catalysts to achieve new transformations by means of (i) Lewis acid base-adduct formation, thereby accelerating slow elementary steps, (ii) pK<sub>a</sub> of the reaction modulation (e.g., release of a Brønsted acid, proton transfer processes), or (iii) activating the catalyst precursors or off-cycle catalyst species by tuning its coordination sphere by anion abstraction. This chapter describes the reports on Ni, Cu, and Fe Lewis acid mediated transformations in polyol medium, but contributions from other abundant metals will surely appear in the literature in the years to come.

On the other hand, the abundance and redox properties of 3d-metal-oxide-based materials confer them large applicability as supports for catalysts. In particular, the magnetic properties of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> as supports enable the recovery of the prepared composite materials. For instance, the use of such supports for the preparation of heterogenized Pd catalysts for C–C cross-coupling reactions and hydrogenations in polyol medium has been widely reported (for selected articles, see: [39, 54, 55, 82, 126, 136]). Other supports based on 3d-transition metals such as TiO<sub>2</sub> [95], CuO [26], and ZnO [114] have also been used for the same purpose. This heterogenization strategy efficiently enables the recoverability of the catalytic materials by magnetic separation, and also in some cases, the enhancement of TON is observed due to the synergy between catalyst and support. Furthermore, polymetallic systems merit further studies to exploit the cooperative effects between active metal centers in polyol medium [34]. The intrinsic properties of polyols in terms of favoring 3D organization via supramolecular interactions, their suitable oxidation potentials for the reduction of transition metal salts and organometallic complexes, as well as their dispersing abilities via solvation interactions, which often trigger an activity increase, confer them unique properties in nanocatalysis.

From a structural point of view, 3d -metals based-species present several oxidation states, often leading to paramagnetic intermediates of challenging elucidation. Given the specificity developed by nature in biocatalyzed transformations involving 3d-transition metals and the demonstrated efficiency of nanocatalysts discussed herein (e.g., Cu NPs for Sonogashira and C–heteroatom couplings, Ni NPs for Suzuki, Co NPs for Heck–Mizoroki, Fe NPs for Kumada-like couplings . . .), the fundamental and applied research in this field foresees new reactivities and deep mechanistic insights taking advantage of the cutting-edge in operando techniques available nowadays.



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