

Recent developments in coupling reactions catalyzed by copper ferrite nanoparticles (CuFe₂O₄ NPs)

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ABSTRACT: Coupling reactions are one of the most important transformations in organic chemistry. These reactions are powerful tools for the construction of C-C, C-S, C-O and C-N bonds. The utilization of magnetic nanoparticles as catalyst have recently received great attention in chemistry science especially in organic synthesis. In recent times, copper ferrite nanoparticles (CuFe₂O₄ NPs) have attracted the profound attention of many chemists or researchers due to unique properties such as high stability, high activity and simple separation. In recent years, numerous methods have been reported based on copper ferrite nanoparticles (CuFe₂O₄ NPs) catalyzed coupling reactions. In this mini-review, we discussed on copper ferrite nanoparticles (CuFe₂O₄ NPs) and their catalytic activity in a library of coupling reactions.

KEYWORDS: Coupling reactions, Copper ferrite nanoparticles (CuFe₂O₄ NPs), Organic Synthesis, Recoverable catalysts.

■ Introduction

Nanocatalysts are the heart of scientific field because of their vast applications in multidisciplinary sciences¹. Nanocatalysts stand at the boundary between homogeneous and heterogeneous catalysts, in the sense that in many cases they offer advantages from both, in terms of activity, selectivity, efficiency and re-usability²⁻⁴. In this library, copper ferrite nanoparticles (CuFe₂O₄ NPs) have received profound attention due to their valuable properties such as selectivity, ease in separation, eradicating the expensive materials and hazardous chemicals^{3,5,6}. When synthesizing magnetic nanoparticles, some key conditions such as intrinsic magnetic properties, size and shape of nanoparticles, surface coating and surface charge of nanoparticles, stability in aqueous medium as well as their non-toxicity must be considered⁷⁻⁹. Copper ferrite nanoparticles (CuFe₂O₄ NPs) easily separated and recovered from the reaction mixture using an external magnet.¹⁰⁻¹²

Coupling reactions have a long history in organic chemistry and are of considerable importance due to their numerous applications in various fields such as industrial, biological and medicinal processes¹³⁻¹⁵. Coupling reactions are widely used in industrial and petrochemical processes to produce dyes, pigments and polymers¹⁶⁻¹⁸. The products of coupling reactions are usually a building block in the structure of most pharmaceutical and biological molecules^{19,20}. According to the described points, many efforts are being made to find simple, gentle, economical and environmentally friendly approaches for the performance of coupling reactions.

■ Copper ferrite nanocatalysts

During the last decade, many methods have been reported for the performance of coupling reactions catalyzed by copper ferrite nanoparticles (CuFe₂O₄ NPs). In this mini-review, we discussed on copper ferrite nanoparticles (CuFe₂O₄ NPs) and their catalytic activity in a library of coupling reactions.

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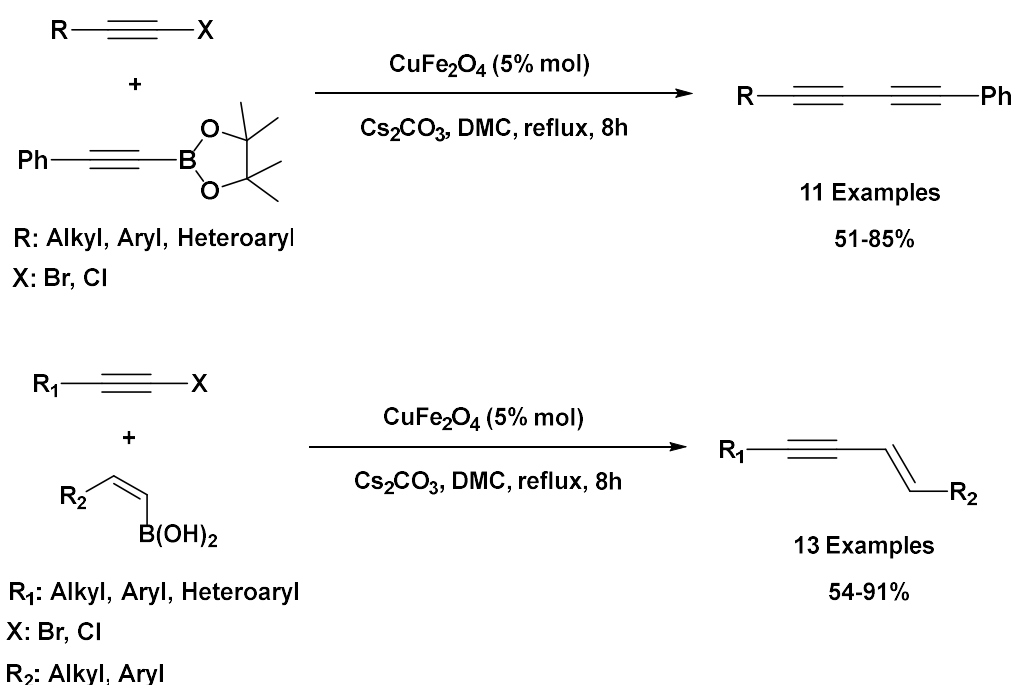
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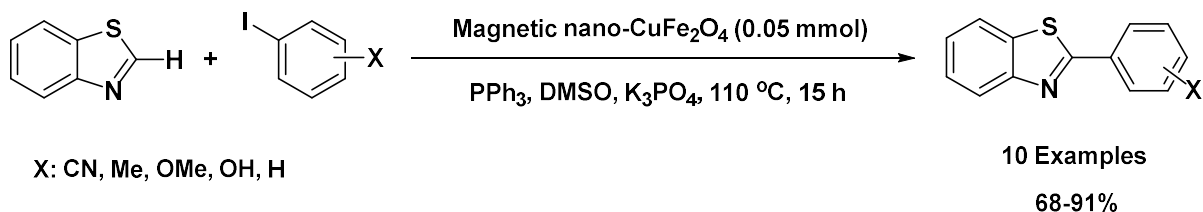
Carbon-Carbon bond formation

The research group of Ranu have described an attractive and efficient methodology for the preparation of conjugated 1,3-enynes in the presence of copper ferrite nanoparticles as the catalyst via Csp-Csp cross-coupling of alkynylbromide and pinacol ester of alkynylboronic acid (**Scheme 1**)²¹. The structure of copper ferrite nanocatalyst is characterized by a number of spectroscopic techniques. In order to standardize conditions, the effect of catalyst loading, base and temperature was evaluated. The copper catalyst was recovered for several times without significant loss of activity.



Scheme 1. Synthesis of 1,3-diynes and enynes catalyzed by CuFe₂O₄ NPs

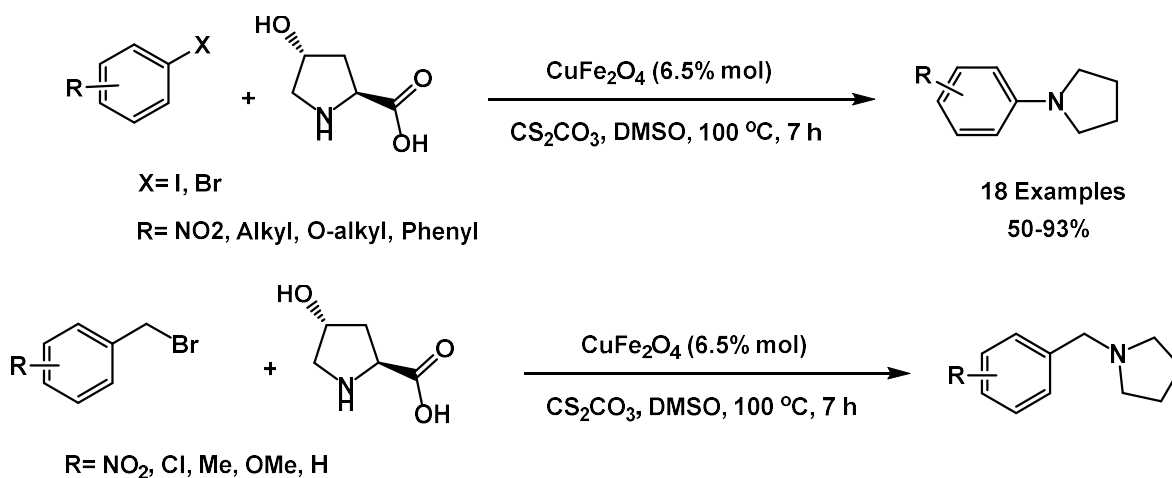
Satish and his coworkers found that the utilization of copper ferrite nanoparticles in the presence of PPh₃ and K₃PO₄ as base is a novel and effective methodology for the one-pot reaction of different aryl iodides with benzothiazoles in DMSO under thermal conditions²². The model reaction is not accomplished in the absence of copper ferrite nanocatalyst. Under the standardized conditions, a nice library of benzothiazole derivatives were synthesized with high to excellent yields; the copper ferrite nanocatalyst was recovered for four times without significant loss of activity (**Scheme 2**).



Scheme 2. CuFe₂O₄ NPs catalyzed direct C-H arylation of benzothiazoles.

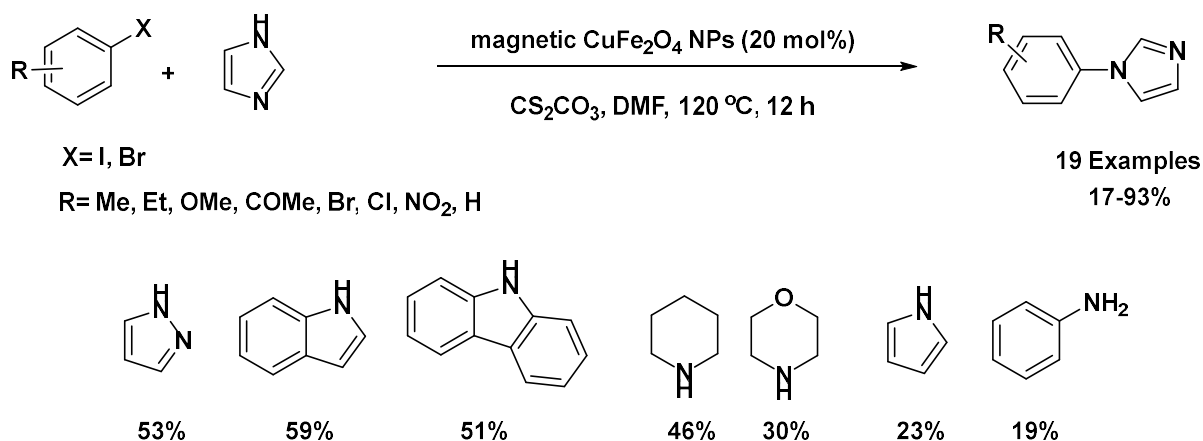
C-N bond formation

Nageswar and his research team reported that ligand-free C-N cross-coupling of aryl halides with trans-4-hydroxy-L-proline could be successfully catalyzed by copper ferrite nanoparticles (CuFe₂O₄ NPs) in the presence of cesium carbonate as base in DMSO under thermal conditions (**Scheme 3**)²³. Under this catalytic system, a broad range of N-substituted pyrroles were synthesized with high yields.



Scheme 3. CuFe₂O₄ NPs catalyzed ligand-free C-N cross-coupling of aryl halides with trans-4-hydroxy-L-proline.

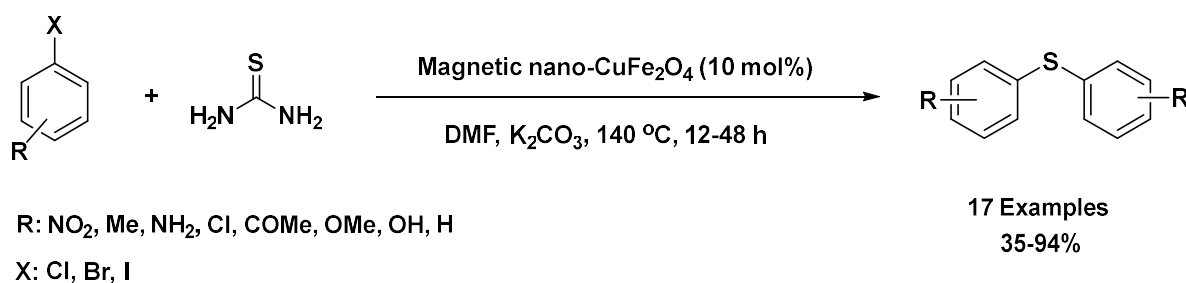
Research group of Sun have developed an efficient approach for the C-N coupling of imidazole with iodobenzene derivatives in the presence of catalytic amount of copper ferrite nanoparticles (CuFe₂O₄ NPs) and cesium carbonate as base in DMF under thermal conditions (**Scheme 4**)²⁴. The structure of the copper ferrite nanoparticles (CuFe₂O₄ NPs) was characterized by FT-IR, TEM, XRD and BET techniques.



Scheme 4. CuFe₂O₄ NPs catalyzed N-arylation of imidazole or various nitrogen derivatives with different substituted aryl halides.

Carbon-Sulfur bond formation

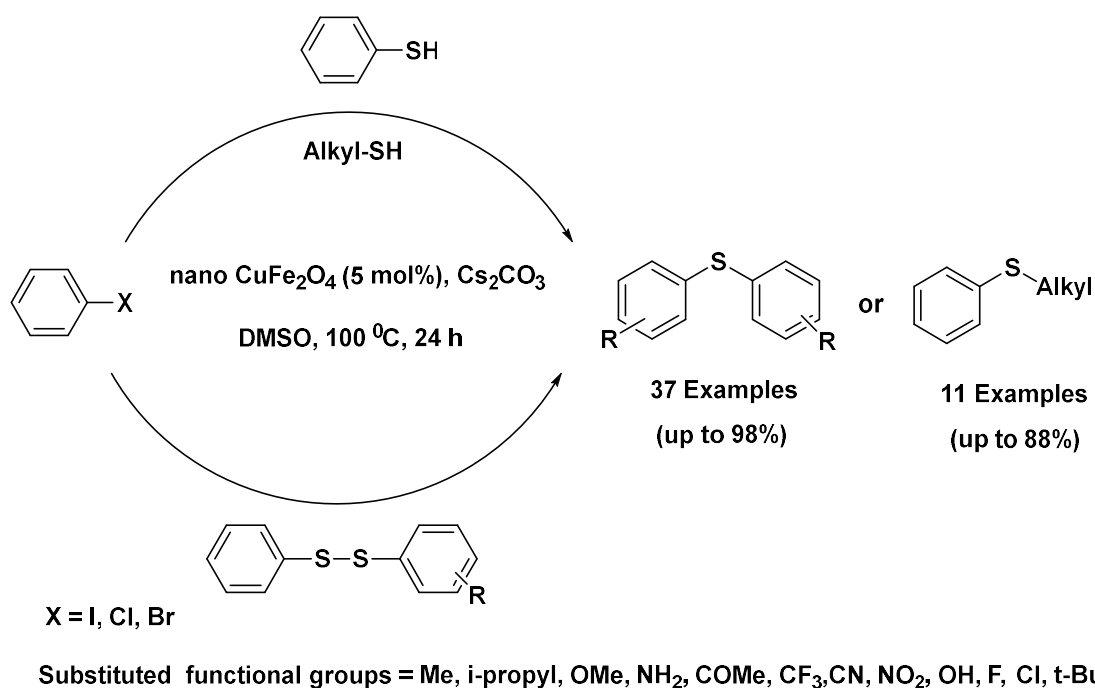
Research team of Hajipour have reported a general and effective methodology for the preparation of symmetrical aryl sulfides via C-S cross-coupling of thiourea with different aryl halides (including aryl chlorides, bromides and iodides) in the presence of copper ferrite nanoparticles (CuFe₂O₄ NPs) as magnetically recoverable catalyst²⁵. As shown in **Scheme 5**, C-S cross-coupling of thiourea with different aryl halides (including aryl chlorides, bromides and iodides) were accomplished in the presence of potassium carbonate in DMF under thermal conditions.



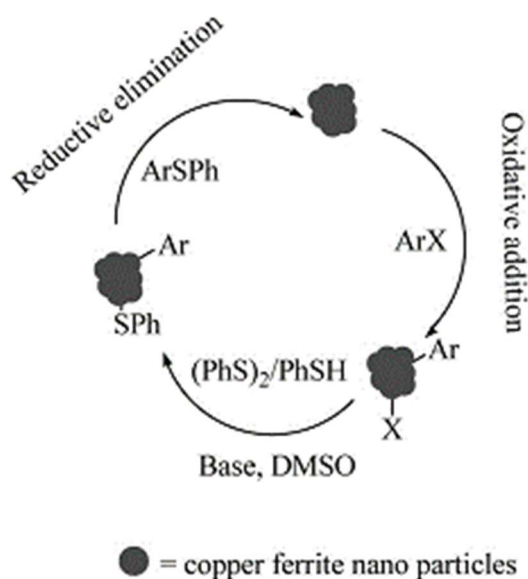
Scheme 5. CuFe₂O₄ NPs catalyzed C-S coupling between thiourea with a wide variety of aryl halides.

In another publication, research team of Nageswar have reported that the utilization of CuFe₂O₄ NPs in the presence of cesium carbonate in DMSO is an highly efficient for the synthesis of diaryl and alkyl aryl sulfides with high yields through the C-S coupling reaction of various commercially available aliphatic/aromatic iodides and aryl bromides with aromatic/aliphatic thiols under ligand-free conditions

(Scheme 6)²⁶. The copper nanocatalyst could be recovered for several runs without significant loss of activity. Synthetic mechanism for the C-S coupling reaction of various commercially available aliphatic/aromatic iodides and aryl bromides with aromatic/aliphatic thiols under the optimized conditions is drawn in Scheme 7.



Scheme 6. CuFe₂O₄ NPs catalyzed C-S coupling between aryl halides with thiols or disulfides.



Scheme 7. Presented mechanism for CuFe₂O₄ NPs catalyzed C-S coupling between aryl halides with thiols or disulfides.

■ Summary and Outlook

Coupling reactions have a long history in organic chemistry and are of considerable importance due to their numerous applications in various fields such as industrial, biological and medicinal processes. Coupling reactions are widely used in industrial and petrochemical processes to produce dyes, pigments and polymers. During the last decade, many methods have been reported for the performance of coupling reactions catalyzed by copper ferrite nanoparticles (CuFe₂O₄ NPs). In this mini-review, we discussed on copper ferrite nanoparticles (CuFe₂O₄ NPs) and their catalytic activity in a library of coupling reactions. In most cases the products were synthesized with high yields and copper nanocatalyst could be recovered for several runs without significant loss of activity.

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