

Metal Organic Frameworks (MOFs): As multi-purpose catalysts

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

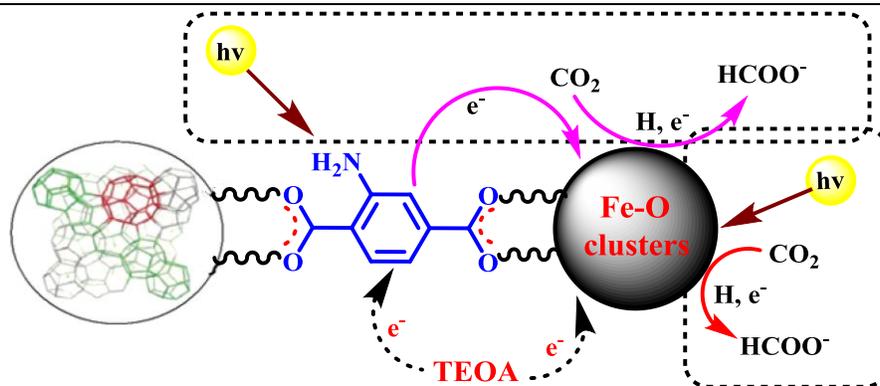
“MOFs” is the abbreviation of Metal Organic Frameworks, which is usually used as a general name for a group of compounds; whenever it is followed by ordinal numbers, means an individual metal organic frameworks [1]. MOFs have emerged as an extensive class of crystalline materials with high porosity in nature. MOFs are a branch of materials having many advantages such as thermal stability, discrete ordered structure, ultra-low densities and ease of synthesis. These striking features led to incessant research for the development of many new porous materials. On an elemental level, MOFs epitomize the elegance of chemical structures and the relevance of the combination of inorganic and organic components. Many scientists across the world have put forward definitions to describe the term MOF. In 2010, Batten *et al.* have conducted an elaborate survey to elicit an opinion on exact definition of MOFs, and as per their investigation, broadly, MOFs were described as proven porous, 3D networks with carboxylate containing materials, but there is no consensus over the strict definition [2-3]. In recent years, metal-organic frameworks (MOFs) are valuable materials because of their applications on the preparation of

various catalysts, sensors, electronics, fuel, cells and industrial products in large scale and other applications in adsorption, petrochemistry, selective separation, and drug delivery (Fig. 1) [4-12].

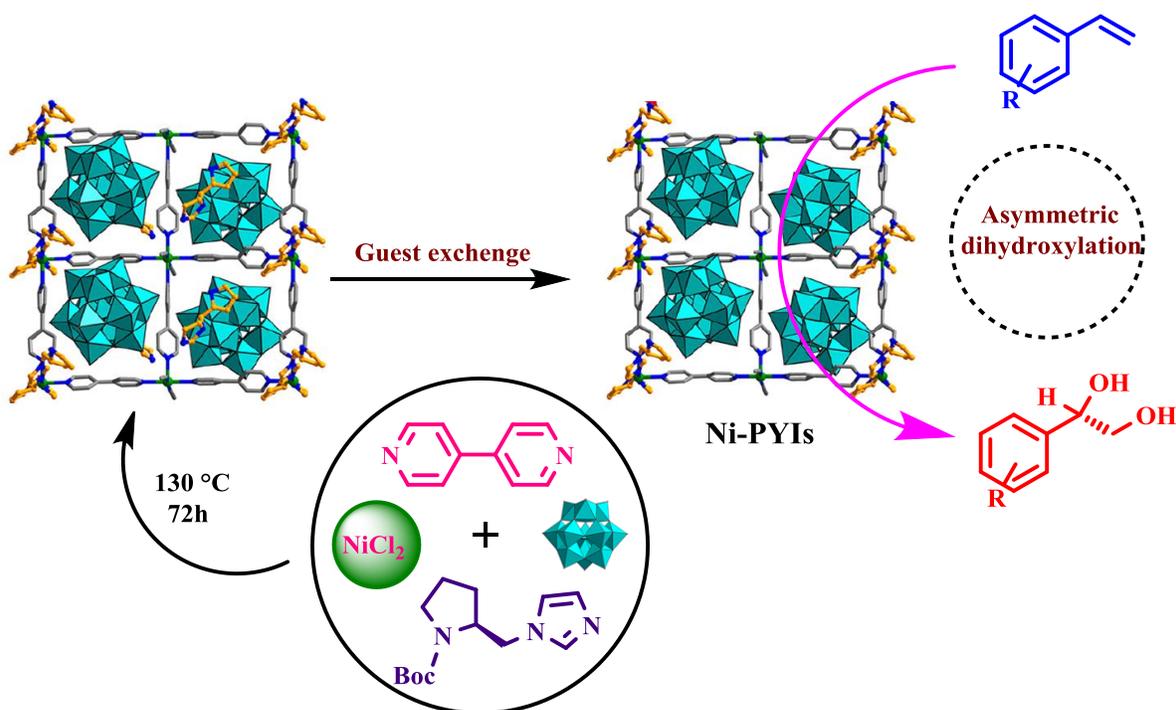


Fig. 1. Different applications of metal organic frameworks

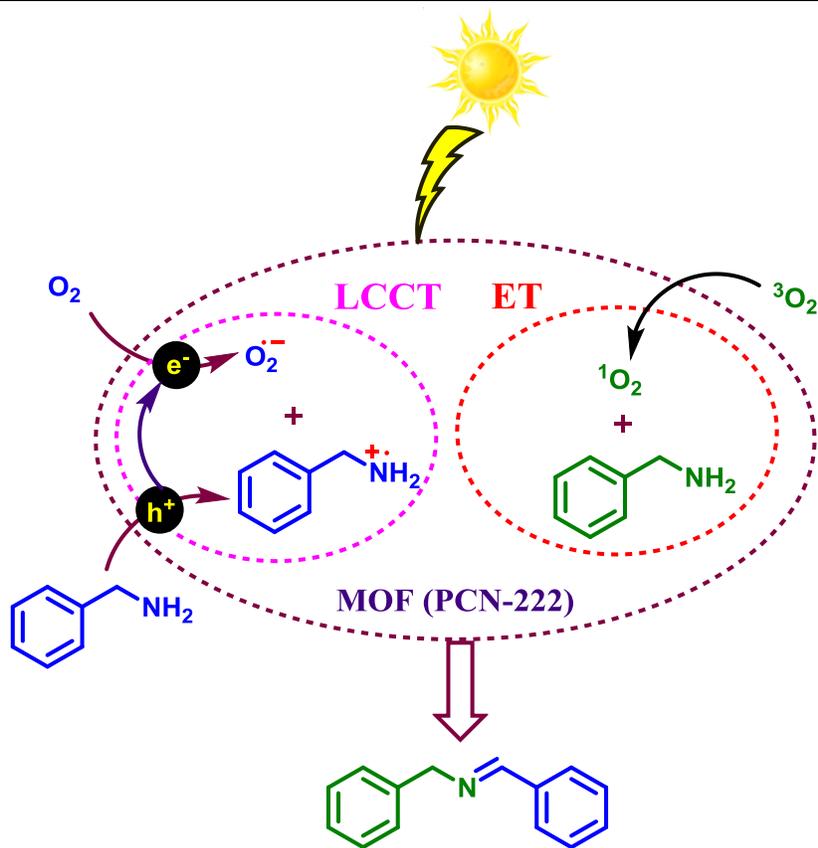
Owing to their specific functional and structural properties, MOFs have currently been recognized as a considerable group of porous compounds. These frameworks are created from bridging organic linkers and metal ion clusters and metal ions. The choice of metal ions and the linkers used ultimately determines



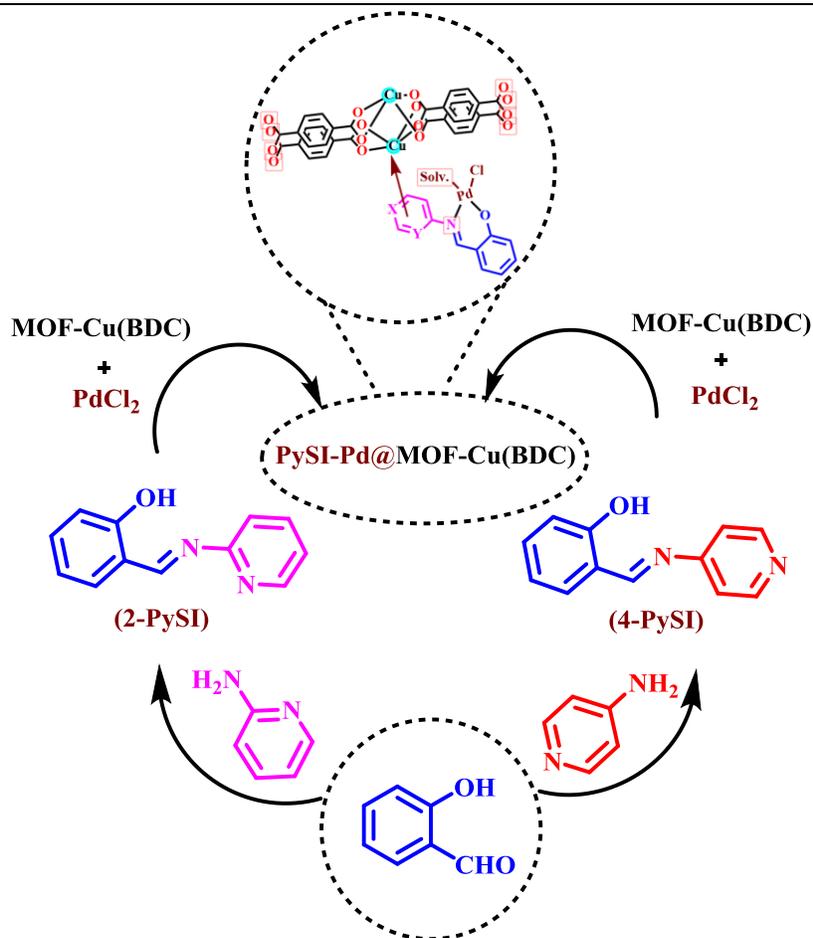
(B) Chiral metal–organic frameworks (MOFs) have been used for performing a variety of chemical reactions as heterogeneous asymmetric catalysts. In one report, the combination of the oxidizing agent $[\text{BW}_{12}\text{O}_{40}]^{5-}$ and the chiral group, L- or D-pyrrolidin-2-ylimidazole (PYI), produced the two enantiomorphs, Ni-PYI1 and Ni-PYI2. The reported MOF has been used as an amphiphatic catalyst to stimulate asymmetric dihydroxylation of aryl olefins with excellent selectivity [31].



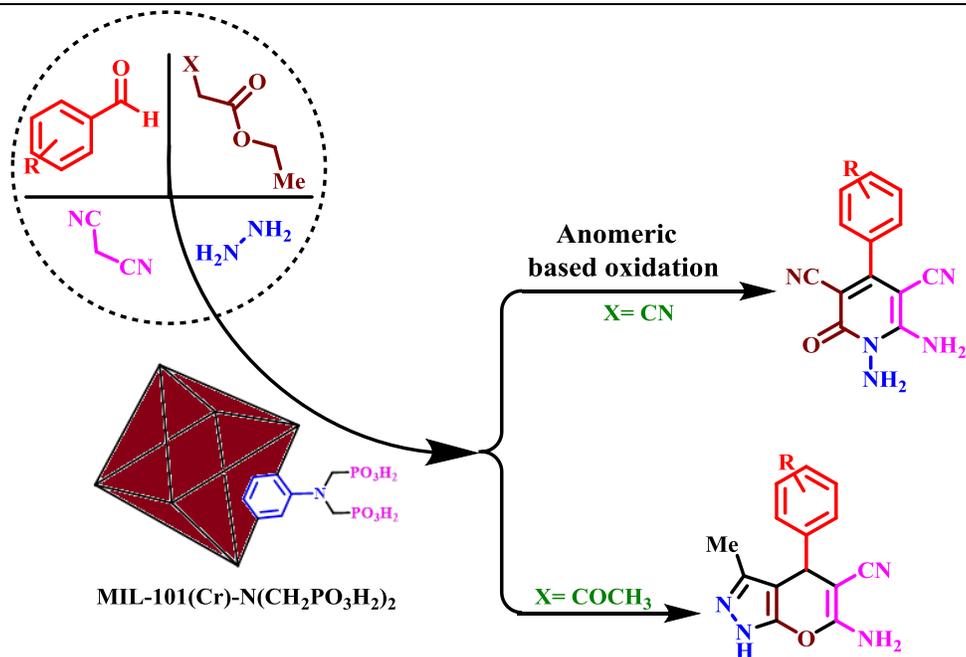
(C) In another discovery, the photocatalytic oxidative pair of various amines was promoted by a porphyrinic-based MOF (PCN-222) under ambient conditions. The results show that the direct oxidative bonding of amines by the porphyrin ligand based on energy transfer as well as the synergistic effect between electrons and the holes caused by charge transfer greatly contributes to the reaction. As a result, PCN-222 has shown excellent photocatalytic activity, selectivity and recyclability in response to this reaction [32].



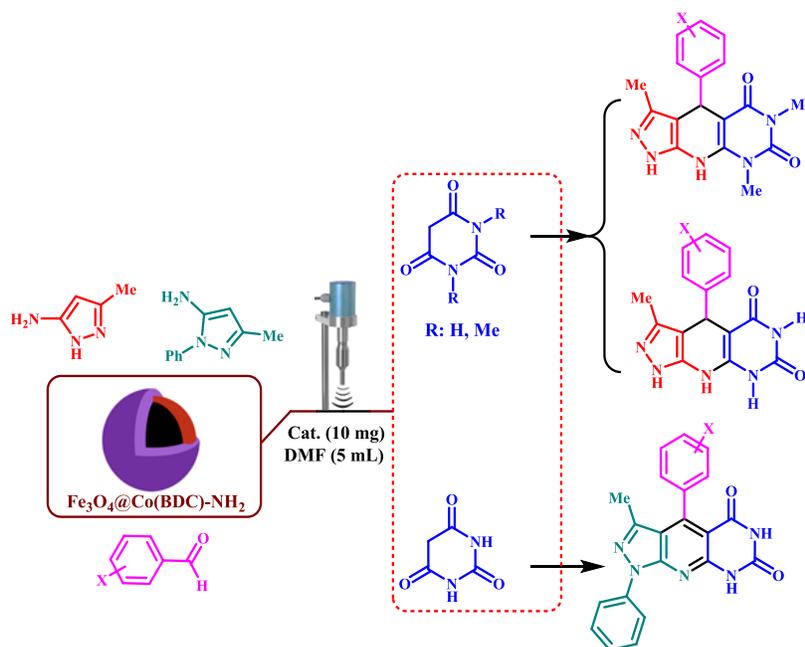
(D) Rostamnia *et al.* have introduced Cu-based MOFs, 4-PySI-Pd@Cu(BDC). They have investigated the effect of metal catalytic and support of Pd@Cu-MOFs on the production of H_2 gas from formic acid. The experiments performed in this paper show the effects of the porous MOF structure and the Schiff-based group presented around the Pd ions, which play an important role in stabilizing the Pd ions and creating a strong interaction between the MOF support and the Pd site. One of the paramount important features of the catalyst presented methodology is that the catalyst can be easily reused through filtration at least three cycles without obvious activity loss [33].



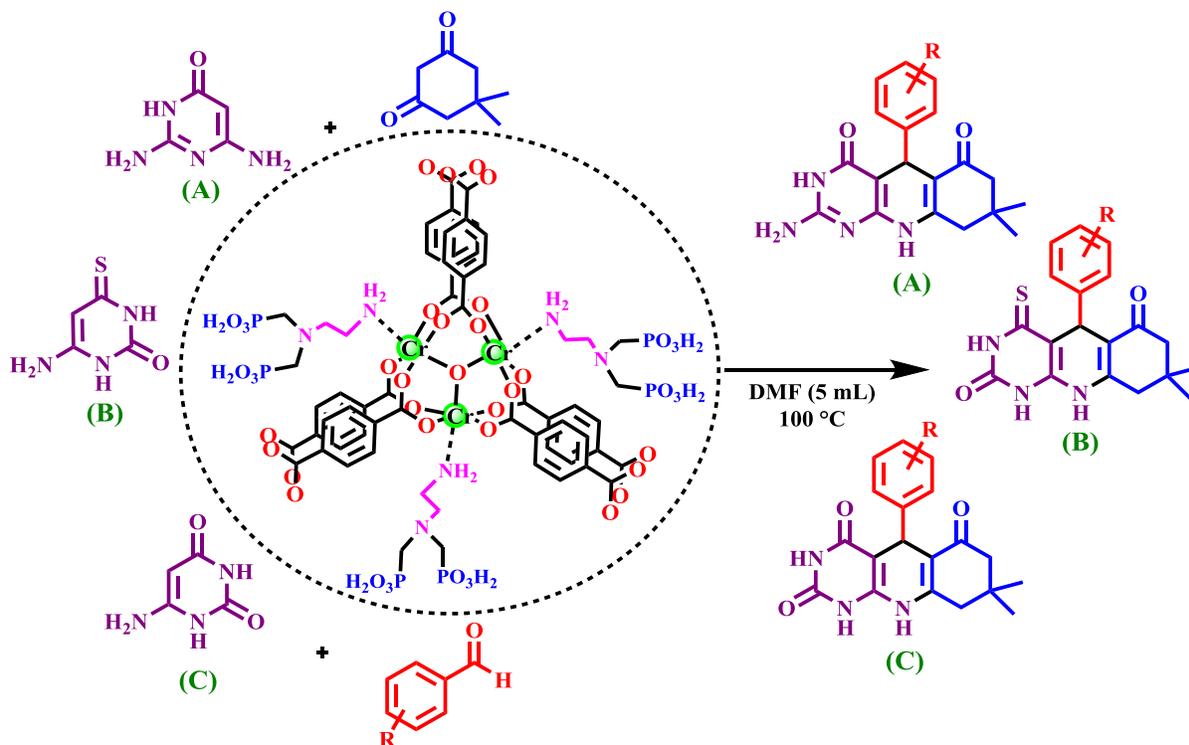
(E) The MIL-101(Cr)-NH₂ organic-metal framework has been synthesized with phosphorous acid functional groups and its structure has been confirmed by various techniques. The synthesized catalyst has been successfully used to produce a range of pyranol [2,3-*c*] pyrazole and *N*-amino-2-pyridone derivatives via a cooperative vinylogous anomeric-based oxidation mechanism. Short reaction time, clean reaction properties, easy performance, recyclability and reuse of the catalyst are the advantages of the method presented in this report [34].



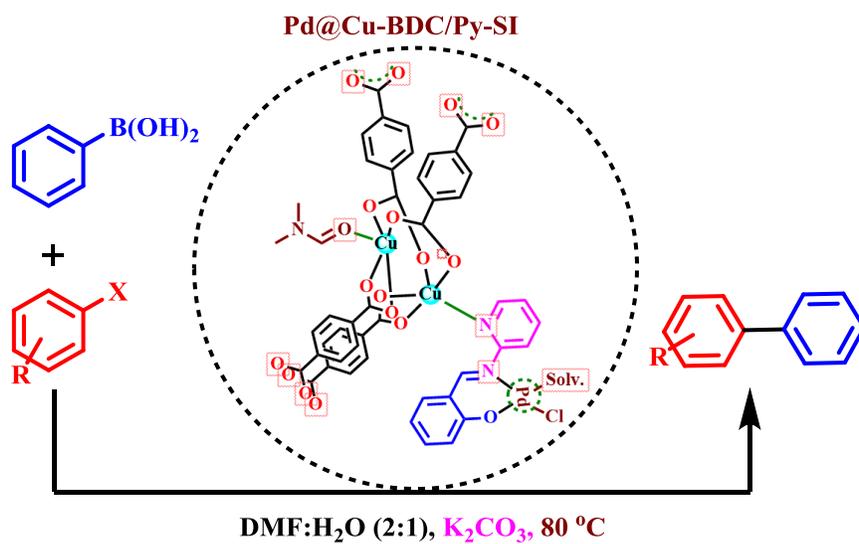
(F) In another discovery, a core shell nano-magnetic metal-organic framework of $\text{Fe}_3\text{O}_4@\text{Co}(\text{BDC})\text{-NH}_2$ has been reported as a new catalyst. This catalyst has also been used for synthesis of a wide range of novel fused pyridines and 1,4-dihydropyridine with good yields *via a* cooperative vinylogous anomeric based oxidation mechanism under ultrasonic irradiation. The synthesized catalyst is reusable and can be easily removed from reaction mixture by an external magnet [35].



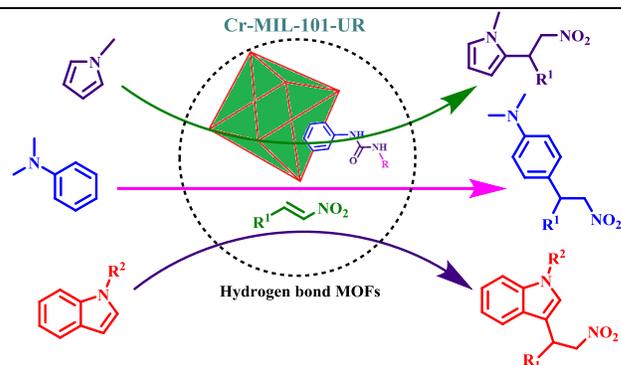
(G) In 2019, Zolfigol *et al.* have introduced a new multifunctional metal-organic framework MIL-100(Cr)/En with phosphorous acid MIL-100(Cr)/NHEtN(CH₂PO₃H₂)₂ as an effective nanoporous catalyst. They have used this catalyst to successfully synthesize some new biological active *N*-heterocyclic compounds. The main advantages of the described work are high productivity, short reaction time, easy operation and catalyst reuse [36].



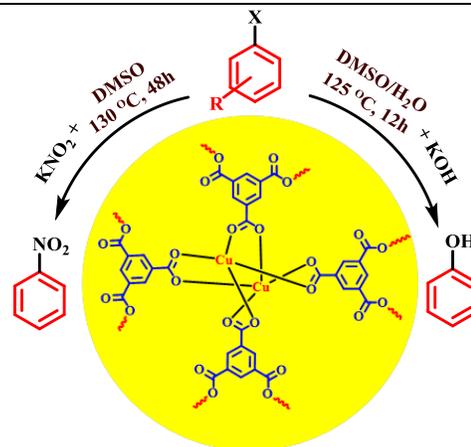
(H) In 2013, Cu-BDC/Py-SI has been reported with the reaction of pyridine salicylaldehyde (Py-SI), copper nitrate trihydrate and terephthalic acid in DMF solvent. Pd supported on Cu-BDC/Py-SI and Pd-complexes generated an efficient catalytic heterogeneous system for Suzuki coupling reaction. Rostamnia *et al.* has showed that Pd@Cu-BDC/Py-SI as a new nanoporous MOF with hydrophobic nature that has efficiently catalyzed the Suzuki-Miyaura crosslinking reaction. In the described method, chemoselective C-C cross-coupling products have been produced [37].



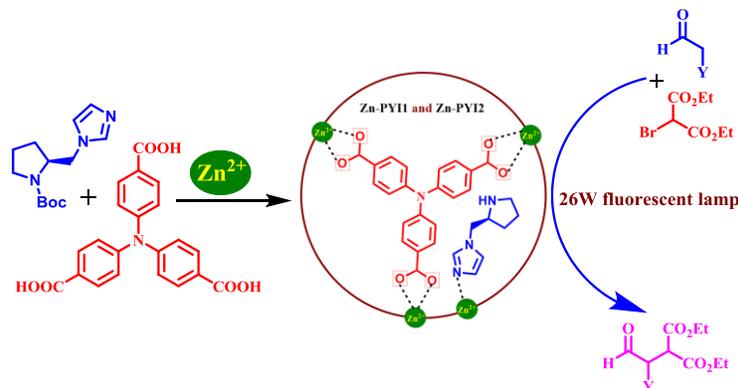
(I) Hydrogen bond (H-bond) catalysis is a type of organocatalyzed that relies on use of hydrogen bonding interactions to accelerate and control organic reactions. During the course of a reaction, hydrogen bonding can be used to stabilize anionic intermediates and transition states. In recent years, H-bond MOFs has been developed. In 2013, a simple and efficient method for the synthesis of new urea-derived heterogeneous MOF catalysts through post-synthetic modification has been reported. The MOFs with large pores and H-bond ability has been used as an efficient catalyst for Friedel-Crafts reactions [38].



(J) Ipso reactions has been defined as a substitution of an aromatic leaving group with a suitable nucleophile. Kantam *et al.* have introduced Cu-based MOF, Cu₃(btc)₂. They have used copper MOF as an efficient catalyst for hydroxylation and nitration of aryl halides *via* the ipso substitution method [39].



(K) In 2013, a new approach for obtaining an asymmetric MOF-based photocatalyst has been developed by combination of tri-phenylamine and proline-based asymmetric ligand in a single MOF structure. Synthesized photocatalysts have been used successfully for photocatalytic α -alkylation reaction with excellent catalytic efficiency [40].



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