Polyhedron 199 (2021) 115102

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis of MCM-41 supported cobalt (II) complex for the formation of polyhydroquinoline derivatives

Saurabh Sharma^a, Udai P. Singh^{a,*}, A.P. Singh^b

^a Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India ^b Department of Applied Sciences, National Institute of Technology, Delhi 110 040, India

ARTICLE INFO

Article history: Received 18 December 2020 Accepted 10 February 2021 Available online 20 February 2021

Keywords: Mesoporous material Cobalt (II) complex MCM-41 Catalyst Polyhydroquinoline

ABSTRACT

A new and green heterogeneous **MCM-41@PDCA-Co** catalyst has been prepared via immobilization of cobalt (II) complex onto the surface of MCM-41. This was characterized by different techniques such as FT-IR, TEM, TGA, low angle Powder XRD, MP-AES and nitrogen sorption. The MCM-41@PDCA-Co has been applied in the synthesis of polyhydroquinoline (PHQs) and its derivatives in 98% yield which is four component reaction under solvent free condition at 100 °C. The synthesized catalyst can be easily recovered from the reaction mixture by simple filtration method. This can be reused several times without any significant loss in stability and activity.

© 2021 Published by Elsevier Ltd.

1. Introduction

Polyhydroquinoline and its derivatives are important compounds due to their pharmaceutical properties such as hepatoprotective, geroprotective, bronchodilator, antitumour, vasodilator, cardiovascular and antiartherosclerotic etc [1,2]. Moreover, polyhydroquinoline is used for the treatment of Alzheimer's disease and in the form of chemosensitizer in tumor therapy [3]. Polyhydroquinoline and related compound are generally prepared via condensation of aldehydes, 1,3-cyclohexanedione derivatives, ethyl acetoacetate and ammonium acetate using one-pot fourcomponent Hantzsch reaction [4].

A variety of catalysts like lewis acid, base and nanomaterial such as $Sc(OTf)_3$ [5], GuHCl [6], $Al_2(SO_4)_3$ [7], $Yb(OTf)_3$ [8], $HClO_4$ -SiO₂ [9], $P(4-VPH)HSO_4$ [10], Mn(III) complex [11], $Hf(NPf_2)_4$ [12], $K_7[PW_{11}COO_{40}]$ [13], ceric ammonium nitrate [14], alumina sulfuric acid [15], nickel nanoparticles [16], MgO nanoparticles [17], and palladium (0) nanoparticles [18], have been used. The synthetic methods for above catalytic reaction suffer from various disadvantages such as expensive reagents, harsh reaction conditions, long reaction times, low-product yields and the use of large quantity of volatile, toxic organic solvents. Besides, larger amount of catalyst loading is the main disadvantage, the used catalyst is destroyed during the reaction and cannot be reused [19].

In recent years, researchers have paid considerable attention toward nanomaterials because they show excellent applications in modern synthetic chemistry and industrial chemistry as sensors, adsorbents, CO₂ capture or transformation and energy production [20,21]. The metal catalyst immobilized on solid support materials to incorporate the preponderances of both heterogeneous and homogeneous catalysis has emerged as an efficient catalytic strategy in organic synthesis [22]. Various types of inorganic, organic and metal mix materials for instance mesoporous silica, molecular sieves, magnetic iron oxide, ionic liquids, graphene oxide, polymers, nanocomposite have been reported in the literature [23]. More recently in the material community, interest has been developed towards nanocarrier mesoporous silica nanoparticles (MSNs) with the exposed surface area due to the increasing demands for environmental friendly and economically viable synthetic processes [24]. The development of heterogeneous catalysts that promote one-pot multicomponent reactions (MCRs) for the formation of desired products in the most efficient manner is highly important [25]. For this purpose, Different approaches have been reported time to time for the preparation of heterogeneous catalysts with multiple active sites on various support scaffolds. Hence, mesoporous silica-based materials (MCM) with pore radius of approximately 2-50 nm and very large surface areas (up to 2000 m² g⁻¹) as well as mechanically stable structure have become a new possible candidate for solid supports to immobilize homogeneous catalysts [26] or directly use them alone as heterogeneous catalyst [27]. Dawood Elhamifar et al. developed MCM-41 supported tungstic acid for one-pot synthesis of new pyrrolo[2,1-a]







^{*} Corresponding author. E-mail address: udaipfcy@iitr.ac.in (U.P. Singh).

isoquinolines [28]. Ghorbani-Choghamarani et. al. discovered a new cobalt (II) complex immobilised on the surface of SBA-15 as an efficient catalyst for the oxidation of sulphide and preparation of polyhydroquinoline [29]. Ehsan Valiey et al. prepared hydrogen-bond-enriched 1,3,5-tris(2-hydroxyethyl)isocyanurate covalently functionalized MCM-41 for synthesis of acridinedione derivatives [30]. Khanmoradi et al. reported zirconium@guanine@MCM-41 nanoparticles that catalysed one-pot, multicomponent tandem Knoevenagel condensation Michael addition-cyclization reactions [31].

The present paper reports a green approach for the synthesis of polyhydroquinoline via multicomponent reactions using an inexpensive, eco-friendly and recyclable MCM-41 supported cobalt (II) catalyst under the solvent-free condition in less reaction time.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were of analytical grade and used without further purification. Co(Cl)₂ anhydrous was purchased from Merck. The MCM-41 mesoporous nanoparticle was synthesized by Juarez method [32]. Melting points were determined with a capillary point apparatus equipped with a digital thermometer. IR spectra were recorded as KBr pellets with Perkin Elmer FT-IR spectrometer in the range of 4000–400 cm⁻¹. MP-AES (Agilent Technologies 4210) was used to measure the metal content of the catalyst. Powder X-ray diffraction (PXRD) data were collected on Bruker AXS D8 Advance diffractometer. The thermogravimetric analysis was performed with EXSTAR TG/DTA 6300 instrument under air atmosphere. The surface morphology of the synthesized material was analysed with the help of transmission electron microscope (Technai G2 20 S-TWIN). BET surface area, pore volume and pore diameter were analysed using Autosorb IQ2 (Quantachrome Instrument). NMR spectra were recorded with Jeol ECX 400 MHz and Bruker spectrospin DPX 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants are expressed in Hz. ¹H NMR chemical shifts are given relative to residual chloroform or DMSO in deuteriated solvent or with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as internal standard. ¹³C NMR spectra are referenced to CDCl₃ and [D₆] DMSO. The following abbreviations denote the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. HRMS were recorded with a micro TOF-Q II mass spectrometer in ESI mode.

2.2. Synthesis of MCM-41@PDCA-Co catalyst

2.2.1. Synthesis of N², N⁶-bis(3-(triethoxysilyl)propyl)pyridine-2,6dicarboxamide (PDCA)

3-aminopropyltriethoxysilane (1.32 g, 6.00 mmol) and triethyl amine (0.65 g, 6.50 mmol) was dissolved in 20 ml of dry THF and degassed under nitrogen. Then a solution of 2,6-pyridinedicarboxylic acid chloride (0.61 g, 3.00 mmol) in 30 ml of dry THF was added drop wise with constant stirring and the resulting solution was further stirred for 2 h at room temperature under nitrogen. The white precipitate was obtained and separated by filtration. The filtrate was evaporated and the ligand was obtained as yellow oil with yield 97.73% (1.68 g, 2.93 mmol). ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 7.7 Hz, 2H), 8.02 (m, 2H), 7.94 (t, *J* = 7.2 Hz,1H), 3.45 (q, *J* = 6.8 Hz, 4H), 3.76 (t, *J* = 7.0 Hz, 12H), 1.72 (m, *J* = 7.6 Hz, 4H), 1.15 (t, *J* = 6.9 Hz, 18H), 0.66 (t, *J* = 8.0 Hz, 4H), ¹³C NMR (100 MHz, CDCl₃): 163.65 (s), 149.06 (s), 138.56 (s), 124.88 (s), 58.52 (s), 42.80 (s), 23.33 (s), 18.29 (s), 7.95 (s).

2.2.2. Synthesis of MCM-41@PDCA

1.00 g of MCM-41 was dispersed in 30 ml of dry chloroform for 30 min with vigorous stirring. Then the solution of 0.50 g (0.87 mmol) of PDCA in 20 ml of dry chloroform was added and the reaction mixture was stirred at room temperature under nitrogen atmosphere for 24 h. After completion of reaction, the reaction mixture was centrifuged to get the white solid, which was washed with chloroform and ethanol several times. The resulting white solid was dried in a hot air oven at 60 °C for 8 h.

2.2.3. Preparation of MCM-41@PDCA-Co

0.50 g of MCM-41@PDCA was dispersed in 40 ml ethanol for 30 min with constant stirring. Then an ethanolic solution (10 ml) of cobalt chloride (0.10 g, 0.7 mmol) was added. The resulting solution was refluxed for 24 h under nitrogen atmosphere and cooled to room temperature. The bluish solid was separated, washed with ethanol (4 \times 5 ml) and dried at 70 °C for 5 h (Scheme 1).

2.2.4. General method for the synthesis of polyhydroquinoline

Aldehyde (1.00 mmol), 1,3-cyclohexanedione or dimedone (1.00 mmol), ethylacetoacetate (1.00 mmol), ammonium acetate (1.20 mmol) and MCM-41@PDCA-Co (10.00 mg) were taken in a 25 ml round bottom flask and the reaction mixture was stirred at 100 °C for 10 min. The formation of the product was monitored by TLC using ethyl acetate:*n*-hexane (3:7 ratio) solvent. After completion of reaction as indicated by TLC, the solid product was dissolved in 10 ml ethanol by refluxing, filtered and cooled. The yellow precipitate was obtained by adding ice to the filtrate and washing with cold ethanol.

3. Results and discussion

3.1. Characterization of complex

3.1.1. FT-IR spectroscopy

The FT-IR spectra of MCM-41, MCM-41@PDCA and MCM-41@PDCA-Co are shown in Fig. 1. The FT-IR spectrum of MCM-41 shows bands at 3400 and 1634 cm⁻¹ which are associated with O-H stretching and bending vibration of surface hydroxyl groups and physisorbed water. The spectrum also shows bands at 1230 and 1080 cm⁻¹ due to Si–O–Si asymmetric stretching mode, 800 cm⁻¹ due to Si–O–Si symmetric stretching mode, 463 cm⁻¹ due to Si–O–Si bending vibration and the peak at 960 cm⁻¹ due to the Si-O stretching of Si-OH (Fig. 1a). After grafting of PDCA on to MCM-41, new peaks appeared at 2940 and 1454 cm⁻¹ due to C—H stretching and bending vibration, 1650 cm⁻¹ due to C=O stretch, 1549 cm⁻¹ due to NH bending of amide (Fig. 1b). The characteristic band for amide carbonyl group at 1650 \mbox{cm}^{-1} shifted to lower wave number upon the coordination of cobalt chloride with PDCA immobilized on MCM-41, confirms the coordination of cobalt (II) ion with the carbonyl oxygen of PDCA (Fig. 1c) in resultant catalyst, MCM-41@PDCA-Co.

3.1.2. Powder XRD studies

The XRD patterns of MCM-41, MCM-41@PDCA and MCM-41@PDCA-Co are shown in the Fig. 2. The XRD pattern of MCM-41 showed one intense peak at $2\theta = 2.68^{\circ}$ assigned to 100 reflection plane of MCM-41 structure and three weak peaks at $2\theta = 4.48^{\circ}$, 5.12° and 6.64° assigned to 110, 200 and 210 planes respectively. This demonstrated the well-ordered hexagonal mesoporous structure of MCM-41 (Fig. 2a) [33,34]. The intensity of the peaks corresponding to 100, 110 and 200 planes decreased while the peak corresponding to 210 reflection plane disappeared in the XRD pattern of MCM-41@PDCA-Co (Fig. 2c). Besides, all the peaks slightly shifted towards higher angle from their position. All these changes



Scheme 1. Synthesis of MCM-41@PDCA-Co.



Fig. 1. IR spectra of (a) MCM-41; (b) MCM-41@PDCA and (c) MCM-41@PDCA-Co.



Fig. 2. XRD patterns of (a) MCM-41; (b) MCM-41@PDCA and (c) MCM-41@PDCA-Co.

indicated that cobalt (II) complex of PDCA was successfully immobilized on the surface of mesoporous MCM-41 and the mesoporous structure of MCM-41 was intact. The PXRD gives no information about the catalyst degradation (physical damage) (Fig. 3).

3.1.3. Thermo gravimetric analysis (TGA)

TGA study of MCM-41 (Fig. 4a) revealed 10-11 wt - % weight loss in the region of 25–100 °C due to the removal of adsorbed water. A further weight loss by 1 wt - % in the region of 100– 300 °C was observed due to the desorption of the chemisorbed water on the silica surface [35]. In comparison with MCM-41,



Fig. 3. XRD patterns of (a) MCM-41@PDCA-Co and (b) Recovered MCM-41@PDCA-Co.



Fig. 4. TGA patterns of (a) MCM-41; (b) MCM-41@PDCA-Co.

MCM-41@PDCA-Co (Fig. 4b) showed a significant weight loss by 22.5 wt - % between 25 and 125 °C besides a weight loss by 7.9 wt - % between 300 and 450 due to loss of organic group in ligand. This suggested that cobalt (II) complex was successfully immobilized onto the mesopores of MCM-41.

3.1.4. N₂ sorption

The nitrogen sorption isotherms for MCM-41 and MCM-41@PDCA-Co are shown in the Fig. 5. The MCM-41 exhibited a type-IV isotherm with hysteresis loop, which is the characteristic



Fig. 5. N₂ adsorption-desorption isotherms of (a) MCM-41; (b) MCM 41@PDCA-Co.

of mesoporous structure [36]. BET (Brunauer-Emmett-Teller) surface area and pore volume of MCM-41 were found to be 788 m² g⁻¹ and 0.569 cm³ g⁻¹ respectively (Fig. 5a). The pore diameter of MCM-41 is 3.55 nm, calculated by DFT (density functional theory). The BET surface area, pore volume and the pore diameter of MCM-41@PDCA-Co are 542 m² g⁻¹, 0.264 cm³ g⁻¹

and 2.049 nm respectively (Fig. 5b). This decrease in surface area, pore volume and pore diameter demonstrated that cobalt (II) complex has been immobilized of onto the mesopores of MCM-41.

3.1.5. SEM

SEM images of MCM-41, MCM-41@PDCA-Co catalyst and spent catalyst are all shown in Fig. 6. This illustrates that there is no significant change in the morphology of mesoporous material MCM-41 and MCM-41@PDCA-Co and used catalyst. However, minor agglomeration of particles is observed in the spent catalyst which may lead to a little decrease in the surface area. This might be the reason for the gradual decrease in the catalytic efficiency from 98% to 91% after six successive runs.

3.1.6. TEM

The mesoporosity of MCM-41 and MCM-41@PDCA-Co was evaluated by transmission electron microscopy (TEM) (Fig. 7). It was observed that both materials exhibited an arrangement of wellordered mesopores with a narrow pore size distribution suggesting no significant change in the *meso* structure of MCM-41 after the loading of cobalt (II) complex

on MCM-41.

3.1.7. MP-AES analysis

The cobalt loading in catalyst was measured by microwave plasma atomic emission spectroscopy MP-AES analysis. The experiment revealed that the cobalt content of the catalyst is 0.22 mmol per gram of MCM-41@PDCA-Co.





Fig. 6. SEM image of (a) MCM-41; (b) MCM-41@PDCA-Co; (c) recovered catalyst MCM-41@PDCA-Co.



Fig. 7. TEM micrographs of (a) MCM-41; (b) MCM-41@PDCA-Co.

Table 1

Optimization of the reaction condition for the synthesis of ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate catalysed by MCM-41@PDCA-Co under various conditions with 10.00 mg of the catalyst, the product yield increased to 94% within 10 min (Table 1, entry 6) at 100 °C but further increase in catalyst amount (i.e. 12.00 mg) did not affect the yield of the product (Table 1, entry 7). The experiment was tried with other solvents system, such as ethanol, 2-ethoxy ethanol, glycol, glycerol, THF, water, DMF and DMSO but the yields of polyhydroquinoline was not very encouraging.



Entry	Solvent	Temp.	Catalyst (mg)	Time	Yield ^b
1	Solvent free	rt & 100 °C	-	24 h	NR
2	Solvent free	rt	3	24 h	Trace
3	Solvent free	100 °C	3	12 h	42
4	Solvent free	100 °C	5	4 h	57
5	Solvent free	100 °C	8	30 min	78
6	Solvent free	100 °C	10	10 min	94
7	Solvent free	100 °C	12	10 min	94
8	Ethanol	reflux	10	10 min	82
9	2-ethoxy ethanol	reflux	10	10 min	86
10	Glycol	reflux	10	10 min	79
11	Glycerol	reflux	10	10 min	76
12	THF	reflux	10	10 min	46
13	H ₂ O	reflux	10	10 min	76
14	DMF	reflux	10	10 min	35
15	DMSO	reflux	10	10 min	32
16	Solvent free	130 °C	10	10 min	90

Reaction condition: demidone (1.00 mmol), benzaldehyde (1.00 mmol), ethylacetoacetate (1.00 mmol), NH₄OAc (1.20 mmol) and catalyst (10.00 mg) at 100 °C for 10 min, neat. ^bfinal yield.

3.1.8. Catalytic performance of MCM-41@PDCA-Co in the synthesis of polyhydroquinoline

tested. We performed our reaction as proposed in the experimental section.

In order to optimize the reaction condition, various factors such as amount of catalyst, solvent and effect of temperature have been According to the optimized result, it has been found that in the absence of catalyst at room temperature to 100 °C, the reaction

S. Sharma, U.P. Singh and A.P. Singh

Table 2

Synthesis of different polyhydroquinolines using optimized conditions.





Table 2 (continued)



(continued on next page)



2q N H



Reaction condition: active methylene compound (1.00 mmol), benzaldehyde (1.00 mmol), ethylacetoacetate (1.00 mmol), NH4OAc (1.20 mmol) and catalyst (10.00 mg) at 100 °C for 10 min, neat.

Table 3	
Comparison of Co-catalyst with other reported catalysts for the synthesis of polyhydrod	juinolines.

Entry	Substrate	Catalyst	Catalyst (mg)	Time(min)	Yield%	Reference
1	p-chloro benzaldehyde	Fe ₃ O ₄ -Adenine-Ni	50	145	96	[37]
2	<i>p</i> -chloro benzaldehyde	Fe ₃ -xTixO ₄ -SO ₃ H	20	5	87	[38]
3	<i>p</i> -chloro benzaldehyde	TEDETA@BNPs	20	60	95	[39]
4	<i>p</i> -choloro benzaldehyde	MCM-41@Serine@Cu(II)	8	170	96	[40]
5	<i>p</i> -chloro benzaldehyde	Ni-dithiazone@boehmite	25	280	96	[41]
6	p-chloro benzaldehyde	SBA-15@AMPD-Co	7	35	97	[29]
7	<i>p</i> -chloro benzaldehyde	Fe3O4@MCM-41@Cu-P ₂ C	20	180	96	[42]
8	p-chloro benzaldehyde	MCM-41@PDCA-Co	10	10	98	This work

failed to give the product (**2j**) and the starting materials were recovered quantitatively (Table 1, entry 1). Furthermore, it was found that the use of catalyst (3.00 mg) at room temperature was also inactive for the production of polyhydroquinoline (Table 1, entry 2). Even an increase in reaction temperature with 3.00 mg catalyst loading produced only 42% yield of the desired product (**2j**) in 12 h (Table 1, entry 3). When the catalyst amount was increased to 5.00 mg and 8.00 mg, the product yield was enhanced by 57% and 78% respectively in a short time (Table 1, entry 4, 5).

In other set of experiment, we tried the reaction with a wide range of benzaldehyde and active methylene compound to determine the effect of electronic and steric factors on the efficiency of the catalyst. It is noteworthy that the reaction tolerated diverse substituent on the benzaldehyde and the electronic properties of aryl substituent bearing either electron- withdrawing or electron releasing groups have a negligible effect on the reaction efficiency (Table 2). It was observed that the presence of electron-donating groups like methyl and methoxy slightly lowers the yield of the product but the electron-withdrawing groups such as nitro, fluoro and chloro slightly increase the yields of the product. In the case of 2, 6 dichloro benzaldehyde, the product yield slightly decreases due to steric hindrance (see Table 3). 3.1.9. Mechanism

The suggested mechanism for the synthesis of polyhydroquinoline is shown in Scheme 2. According to literature, the formation of product goes by two different paths. In the mechanism, MCM-41@PDCA-Co acts as a Bronsted acid that activates carbonyl compounds (**1a**, **1b** and **1c**) for amine formation (**B**, **F**) and Knoevenagel condensation product (**A**, **G**) as a key intermediate. According to path **I**, demidone **1a** react with ammonia (NH₃) to form amine **F**. The resulting amine reacts with adduct **G** in a conjugate manner to produce adduct **H**. The adduct **H** tautomarizes into adduct **I** which converts into the final product polyhydroquinoline **2j** by intramolecular cyclization followed by dehydration. In the path **II** all steps are same as path **I** except the formation of Knoevenagel adduct **A** and amine **B**.

3.1.10. Catalyst reusability

The reusability and stability are the most important properties of any new prepared heterogeneous catalyst. These properties were investigated in the synthesis of polyhydroquinoline. After the reaction, ethanol was added in the reaction vessel and refluxed till the suspension was formed. The catalyst was filtered, washed with DCM (4×10) and ether (3×10), dried in a hot air oven at







Fig. 8. Recovery of the catalyst in the synthesis of polyhydroquinoline.

 $60~^\circ$ C for 3 h. The separated catalyst was reused for 6 successive runs in the synthesis of polyhydroquinoline as shown in Fig. 8. It showed that catalyst worked efficiently without loss of catalytic activity. Moreover, in order to confirm that no cobalt leaching

occurred, MP-AES analysis was carried out for the catalyst recovered from the six successive runs and it was found that cobalt content in the recovered catalyst was 0.217 mmol/g which is very close to 0.22 mmol/g, a cobalt loading on the fresh catalyst. This indicates that no significant leaching of cobalt occurred during the reaction.

4. Conclusion

In summary, an efficient heterogeneous MCM-41@PDCA-Co catalyst was prepared via a simple method. The catalyst revealed very high activity for the synthesis of polyhydroquinolene (98%) through one-pot multi-component reaction under solvent free condition. Low catalyst loading, very short reaction time, high yield, easy separation by simple filtration and reusability for at least six successive runs are among the main advantages of the catalyst.

CRediT authorship contribution statement

Saurabh Sharma: Conceptualization, Investigation, Methodology, Original draft preparation. **Udai P. Singh:** Formal analysis, Funding acquisition, Supervision, Writing - Reviewing and Editing. **A.P. Singh:** Reviewing and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors are grateful to the Board of Research in Nuclear Sciences, India, Grant No. 37018 (DAE), Mumbai, India for financial assistance. S. Sharma is thankful to UGC for fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115102.

References

- [1] (a) F. Bossert, H. Meyer, E. Wehinger, Angew. Chem. Int. Ed. Engl. 20 (1981) 762-769
 - (b) H. Nakayama, Y. Kasoaka, Heterocycles 42 (1996) 901-909;
 - (c) Y. Sawada, H. Kayakiri, Y. Abe, T. Mizutani, N. Inamura, M. Asano, C. Hatori, I. Aramori, T. Oku, H. Tanak, J. Med. Chem. 47 (2004) 2853-2863;
 - (d) D. Mauzeral, F.H. Westheimer, J. Am. Chem. Soc. 77 (1955) 2261-2264.
- [2] (a) T. Godfaid, R. Miller, M. Wibo, Pharmacol. Rev. 38 (1986) 321–416;
- (b) A. Sausins, G. Duburs, Heterocycles 27 (1988) 279-289;
- (c) P.P. Mager, R.A. Coburn, A.J. Solo, J. Trigle, H. Rothe, Drug Des. Discov. 8 (1992) 273-286; (d) R. Mannhold, B. Jablonka, W. Voigdt, K. Schoenafinger, K. Schravan, Eur. J.
- Med. Chem. 27 (1992) 229-235;
- (e) R. Shan, C. Velazquez, E.E. Knaus, J. Med. Chem. 47 (2004) 254-261.
- [3] H. Khabazzadeh, F.T. Kermani, D. Afzali, A. Amiri, A. Jalaladini, Arabian J. Chem. 5 (2012) 167–172.
- [4] P.P. Ghosh, S. Paul, A.R. Das, Tetrahedron Lett. 54 (2013) 138-142.
- [5] J.L. Donelson, R.A. Gibbs, S.K. De, J. Mol. Catal. A: Chem. 256 (2006) 309-311. [6] S.M. Baghbanian, S. Khaksar, S.M. Vahdat, M. Farhang, M. Tajbakhsh, Chin.
- Chem. Lett. 21 (2010) 563–567. [7] P. Kulkarni, J. Chil. Chem. Soc. 59 (2014) 2319-2321.
- [8] L.M. Wang, J. Sheng, L. Zhang, J. Han, Z. Fan, H. Tian, C. Qian, Tetrahedron 61 2005) 1539-1543. [9] M. Maheswara, V. Siddaiah, G. Lakshmi, V. Damu, C.V. Rao, ARKIVOC 2 (2006)
- 201-206.
- [10] B. Janardhan, B. Rajitha, P.A. Crooks, J. Saudi Chem. Soc. 18 (2014) 722-727.
- [11] E. Mosaddegh, A. Hassankhani, Arabian J. of Chem. 5 (2012) 315–318. [12] M. Hong, C. Cai, W. Yi, J. Fluorine Chem. 131 (2010) 111-114.
- [13] M.M. Heravi, K. Bakhtiari, N.M. Javadi, F.F. Bamoharramb, M. Saeedi, H.
- Oskooie, J. Mol. Catal. A: Chem. 264 (2006) 50-52. [14] S. Ko, C.F. Yao, Tetrahedron 62 (2006) 7293-7299.
- [15] M. Arslan, C. Faydali, M. Zengin, M. Kucukislamoglu, H. Demirhan, Turk. J. Chem. 33 (2009) 769–774.

- [16] S.B. Sapkal, K.F. Shelke, B.B. Shingate, M.S. Shingare, Tetrahedron Lett. 50 (2009) 1754-1756.
- [17] H. Mirzaei, A. Davoodnia, Chin. J. Catal. 33 (2012) 1502–1507.
- [18] M. Saha, A.K. Pal, Tetrahedron Lett. 52 (2011) 4872-4877.
- [19] S. Sajjadifar, Z. Azmoudehfard, Appl. Organometal. Chem. 33 (2019) 1-9.
- [20] F. Lu, J. Ruiz Aranzaes, D. Astruc, Angew. Chem., Int. Ed. 44 (2005) 7399-7404. [21] (a) D. Astruc, Inorg. Chem. 46 (2007) 1884–1894;
- (b) D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem., Int. Ed. 44 (2005) 7852-7872; (c) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009–3066.
 [22] N. Pal, A. Bhaumik, RSC Adv. 5 (2015) 24363–24391.
- [23] (a) M. Nikoorazm, A. Ghorbani-Choghamarani, F. Ghorbani, H. Mahdavi, Z. Karamshahi, J. Porous Mater. 22 (2015) 261-267; (b) Y.-S. Feng, X.-Y. Lin, J. Hao, H.-J. Xu, Tetrahedron 70 (2014) 5249-5253; (c) T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, New J. Chem. 41 (2017) 11714-11721; (d) A. Fodor, Z. Hell, L. Pirault-Roy, Appl. Catal. A: Gen. 484 (2014) 39-50; (e) B. Atashkar, A. Rostami, B. Tahmasbi, Catal, Sci. Technol. 3 (2013) 2140-2146 (f) M. Darabi, T. Tamoradi, M. Ghadermazi, Asian J. Chem. 30 (2018), 2429-
 - 2432, Trans. Met. Chem. 42 (2017) 703-710.;

(g) E.R. Nezhad, R. Tahmasebi, Asian J. of, Green Chem. 3 (2019) 34-42; (h) J.K. Oleiwi, R.A.M. Anaee, S.H. Radhi, Asian J. of Chem. 30 (2018) 2429-2432.

- [24] (a) J. Florek, R. Caillard, F. Kleitz, Nanoscale 9 (2017) 15252-15277;
- (b) S.-H. Wu, Y. Hung, C.-Y. Mou, Chem. Commun. 47 (2011) 9972–9985. [25] (a) J. Tang, M. Yang, M. Yang, J. Wang, W. Dong, G. Wang, New J. Chem. 39 (2015) 4919-4923;
- (b) S. Azizi, J. Soleymani, M. Hasanzadeh, Nanocomposites 6 (2020) 31–40. [26] (a) A. Corma, H. Garcia, Adv. Synth. Catal. 348 (2006) 1391-01412;
- (b) J. Nowicki, K. Jaroszewska, E. Nowakowska-Bogdan, M. Szmatoła, J. llowska, Mol. Catal. 454 (2018) 94-103.
- [27] D.J. Macquarrie, R. Maggi, A. Mazzacani, G. Sartori, R. Sartorio, Appl. Catal. A. 246 (2003) 183-188.
- [28] B. Karami, M. Farahi, S. Akrami, D. Elhamifar, RSC Adv. 4 (2014) 28238–28248. [29] A. Ghorbani-Choghamarani, M. Mohammadi, T. Tamoradi, M. Ghadermazi, Polyhedron 158 (2019) 25-35.
- [30] Z. Alirezvani, M.G. Dekamin, E. Valiey, ACS Omega 4 (2019) 20618-20633.
- [31] M. Nikoorazm, M. Mohammadi, M. Khanmoradi, Appl. Organomet. Chem. 34 (2020) 5704-8724.
- [32] L.A. Juárez, A.M. Costero, M. Parra, P. Gaviña, S. Gil, F. Sancenón, R. Martínez-Máñez, Chem. Comm. 53 (2017) 585-588.
- [33] S. Jana, B. Dutta, R. Bera, S. Koner, Langmuir 23 (2007) 2492-2496.
- [34] M. Niakan, Z. Asadi, S. Zare, Chem. Sel. 5 (2020) 40-48.
- [35] D. Perez-Quintanilla, I. del Hierro, M. Fajardo, I. Sierra, J. Environ. Monit. 8 (2006) 214-222.
- [36] S. Gregg, K. Sing, Adsorption, Surface Area, and Porosity, Academic Press, New York, 1982.
- [37] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, Appl. Organometal. Chem. 32 (2017) 3974-3988.
- [38] D. Azarifar, R. Asadpoor, O. Badalkhani, M. Jaymand, E. Tavakoli, M. Bazouleh, Chem. Sel. 3 (2018) 13722-13728.
- [39] A. Ghorbani-Choghamarani, Z. Heidarnezhad, B. Tahmasbi, G. Azadi, J. Iran. Chem. Soc. 15 (2018) 2281–2293.
- [40] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, Catal. Lett. 148 (2018) 857-872.
- A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasbi, J. Iran. Chem. Soc. 16 [41] (2019) 511-521.
- [42] M. Nikoorazm, Z. Erfani, Chem. Phys. Lett. 737 (2019) 1367842.