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MAGHNITE-H$^+$ CLAY AS A GREEN CATALYST WAS USED FOR THE SYNTHESIS OF NEW 1,4- DIHYDROPYRIMIDO[1,2-*A*]BENZIMIDAZOLE DERIVATIVES

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ABSTRACT
A series of new 1, 4- dihydropyrimido[1,2-*a*]benzimidazole derivatives (DHPBz) has been successfully synthesized by one-pot three compounds reaction of an aromatic aldehydes, ketones and 2-aminobenzimidazole in presence of Maghnite-H$^+$, a proton exchanged Algerian montmorillonite clay as a green catalyst. The Magnite-H$^+$ is an efficient catalyst, it is cheap, recyclable and eco-friendly catalyst. The catalytic effect of the Maghnite-H$^+$ for the condensation reaction is very considerable giving a high yield (72-84%) in short time.
All the synthesized 1,4-dihydropyrimido[1,2-*a*]benzimidazole derivatives compounds were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR.

KEYWORDS
1,4-dihydropyrimido[1,2-*a*]benzimidazole, Multi-compounds reaction, Benzaldehyde, ketone, 2-Aminobenzimidazole, Maghnite-H$^+$.

INTRODUCTION
In organic synthesis, researchers are always interested in the shortest synthetic methods. Indeed, multi-compounds reactions (MCRs) offer the possibility of synthesizing new compounds from three reagents in one step. In addition, the compounds elaborated by (MRCs) containing the structural units of all the reagents. In this context, the chromeno[4,3-d] pyrimidinone derivatives[i], the 1,2- dihydro- pyrimido [1,2-*a*] - benzimidazole -3-carbonitrile[ii], the benzoquinazolinone derivatives[iii], 3,4-dihydropyrimidin-2-(1H)-ones and thiones [iv] were synthesized by one-pot three-compounds condensation.
The cyclic and heterocyclic compounds, in particular pyrimido [1,2-a] benzimidazole and its

derivatives, are very interesting since they have a biological activity and therefore, they have played a very important role in the synthesis of various agents and pharmaceutical chemistry. 1,4-Dihydropyrimido [1,2-a] benzimidazoles derivatives (DHPBz) containing substituted imidazole and pyrimidine. Further, these functions can increase the biological activities of its compounds. The DHPBz have given satisfactory and encouraging results as antimicrobial [v], antimalarial [vi], antiproliferative [vii] also, pyrimido [1,2-a] benzimidazoles have significant biological activity, they have been used as antibacterial [viii] and anticancer [ix].

The synthesis of pyrimido [1,2-a] benzimidazoles derivatives was generally catalyzed by a Brosted acid or Lewis acid. In this context, a series of pyrimido[1,2-a]benzimidazoles were synthesized using refluxing protocol without catalyst in DMF[x], also, the synthesis of chromenopyrimidobenzimidazolones was catalyst by zinc chloride, in the presence of HCl [xi], a nanoporous sodium montmorillonite clay (Na^+–MMT) modified with 1-methyl -3-(trimethoxysilylpropyl)-imidazolium hydrogen sulfate (Na^+–MMT–[pmim]HSO_4) was used as a catalyst for synthesis of pyrimido[1,2-a]Benzimidazoles and ethyl pyrimido[1,2-a] benzimidazole-3-carboxylates [xii].

In this present work, we have used an eco-friendly catalyst for the synthesis of new 1,4-dihydropyrimido [1,2-a] benzimidazoles (DHPBz) derivatives **(4a-f)** (figure 1) via one-pot chemo-selective synthesis using three reagents aldehyde **1**, ketones compounds **2** and 2-aminobenzimidazole **3** in the presence of methanol. The catalyst used in this study is green catalyst, non toxic, no expensive which can be recycled and not polluting based on clay of the montmorillonitic type called Maghnite-H^+ [xiii]. Recently it was used in the synthesis of bis-schiff bases [xiv], it was also used in the synthesis of macromonomers and in the synthesis of polymers by cationic polymerization [xv-xviii]. Maghnite-H^+ provides a novel and potential route for the synthesis of 1,4-dihydropyrimido [1,2-a] benzimidazoles (DHPBz) with moderate to excellent yields and an integrated approach to synthetic access currently available to 1,4-dihydropyrimido [1,2-a] benzimidazoles (DHPBz).

EXPERIMENTAL

Materials

All research chemical reagents: 2-aminobenzimidazole, Aldehydes (Benzaldehyde, 3-hydroxy-5-methoxybenzaldehyde, 4-methoxybenzaldehyde) and ketones (Sigma aldrich) were purchased from (Sigma-Aldrich) and they are used as received. Raw-Maghnite, Algerian montmorillonite clay was procured from "BENTAL" (Algerian Society of Bentonite).

The progress of the reactions was monitored by thin layer chromatography (TLC) on silica gel plates (TLC Silica gel 60 F_{254}) using éluants (hexan/AcOEt). Melting points of all synthesized compounds were measured by Kofler bench method (HEIZBANK System Kofler Type WME N° 6973), and visualizing by iodine as agent. FT-IR spectra were recorded on FT-IR spectrophotometer (Atlas Manual Hydraulic Press 15T, GS15011) using KBr pellets technique. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz (BRUKER Avance spectrometers) in DMSO-d6 using as internal standards the residual DMSO signal for 1H NMR (δ = 2.50 ppm), and the following multiplicity abbreviations were used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet.

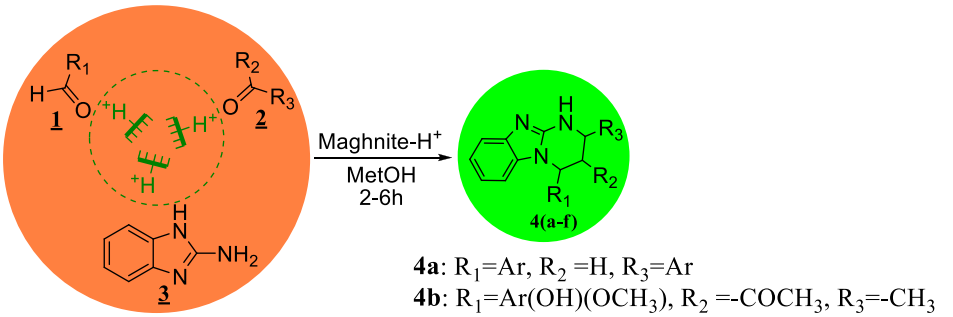
General procedure for the preparation of Maghnite-H^+ catalyst

All the reactions were catalyst by Maghnite-H^+. It was prepared according to the following method [xix-xx]: An amount of 20g of raw-Maghnite in powder form was dried for two hours at a temperature of 105°C to remove any traces of water. After drying, the Maghnite was put in an Erlenmeyer containing 500 ml distilled water, then 0.23M sulfuric acid solution was added at once to the mixture Maghnite / water and agitated by a mechanical stirrer for about two days

at room temperature. After that, the mineral part of the whole mixture was washed by distilled water until it become a free from sulfate and finally dried at 105°C for about 2hours.

General method for synthesis of 1,4-dihydropyrimido [1,2-a] benzimidazoles (DHPBz) derivatives

To a mixture of aldehyde **1** (1mmol), ketone compounds **2** (1mmol) and 2-amino benzimidazole **3** (1 mmol) in 5ml methanol with 10% of Maghnite-H^+, the mixture was refluxed at 60°C. After the completion of the reaction (monitored by TLC). The crude product was dissolved in MetOH at 50°C and then filtered to remove the solid catalyst. The mixture was cooled to room temperature to give the pure product, the precipitated product was filtered, washed and dried to afford compounds **4a-f** (figure 1).



4a: R_1=Ar, R_2 =H, R_3=Ar
4b: R_1=Ar(OH)(OCH_3), R_2 =-$COCH_3$, R_3=-CH_3
4c: R_1=Ar, R_2 =-$COOCH_3$, R_3=-OCH_3
4d: R_1=Ar(OCH_3), R_2 =-$COOCH_3$, R_3=-OCH_3
4e: R_1=Ar, R_2 =Ar($COCH_3$), R_3=-CH_3
4f: R_1=Ar(OH)(OCH_3), R_2 =-$COOCH_3$, R_3=-CH_3

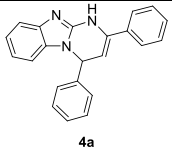
Figure1. One-pot three compounds reaction for synthesis of 1,4-dihydropyrimido[1,2-a]benzimidazole derivatives using Maghnite-H^+

RESULTS AND DISCUSSION

In this work, a green, non-toxic and recyclable catalyst was used for the synthesis of new 1,4-dihydropyrimido [1,2-a] benzimidazole derivatives by one-pot three compounds reaction (Figure 1)

To investigate the catalytic effect on the reaction yield, tests are carried out with different amounts of catalyst for the compound (4a). The results shown (Table 1) show that the use of 10% of catalyst referring to 2-aminobenzimidazole at 60°C. is the most effective and the yield obtained was 82% for 2 h in methanol (scheme 1).

Table 1. Catalytic effect on the one-pot synthesis of 1,4-dihydropyrimido[1,2-a]benzimidazole derivatives catalyst by Maghnite-H^+.

Entry	Cat (%)	Time(h)	T(°C)	Yield(%)
 4a	**10**	2	Reflux	**81.53**
	20			74.9
	30			67.29

Cat: Maghnite-H^+

We found that combining aldehyde (**1**) with ketone (**2**) and 2-aminobenzimidazole (**3**) in

methanol as a solvent and a amount of 10% of Maghnite-H^+, the mixture was refluxed between 2 to 4hours to give 1,4-dihydropyrimido[1,2-*a*] benzimidazole derivatives (Table 2). The desired products precipitate upon cooling of the reaction mixture and a filtration provides analytically pure material.

Table 2. One-pot synthesis of 1,4-dihydropyrimido[1,2-a]benzimidazole derivatives catalyst by 10% of Maghnite-H^+.

Compounds mp(°C)	R_1, R_2 and R_3	Time(h)	Yield (%)
4a 260<	R_1= Ar, R_2 =H, R_3 =Ar	2	81,53
4b	R_1= -CH_2-C(O)-CH_3, R_2 =Ar, R_3 =Ar	4 80	260<
4c	R_1= -CH_2-C(O)-O-CH_3, R_2 = -OCH_3, R_3 =Ar	4 75	246
4d	R_1= -CH_2-C(O)-CH_3, R_2 =-CH_3, R_3 =	4 75	250
4e	R_1= -CH_2-C(O)-O-CH_3, R_2 = -OCH_3, R_3 = 4-hydroxy-3-methoxybenzyle	3 72	260<
4f	R_1= -CH_2-C(O)-O-CH_3, R_2 = -OCH_3, R_3 = 4-methoxybenzyle	4 79	244

Characterization

FT-IR spectroscopic analysis

The FT-IR spectrums of all obtained products have a wide band between 3500 and 3400 cm^{-1} due to the elongation vibration of the N-H bond, a strong band between 1598 and 1701cm^{-1}. The carbonyl groups (C=O) band of some products (**4b-f**) is observed between 1747 and 1653cm^{-1}. The peaks associated to H-C= (aromatic) of all synthesized products were observed between 3026-3228cm^{-1}. Moreover, the bands of C=C (aromatic) were observed about 1635cm^{-1}. The C–H symmetric and asymmetric stretching due to the (-CH_3) of products (**4b-f**) were observed around 2957cm^{-1}. A large band at 3414 cm^{-1} appeared in the spectra of product (**4d**) and (**4e**) due to the hydroxyl group (O-H).

^{1}H-NMR spectroscopic analysis

In the ^{1}H-NMR spectra of all synthesized products show a singlet between 9.22 and 12.01 ppm due to the proton resonance of N-H of pyrimidine. The ^{1}H-NMR spectrum of (**4d**) and (**4e**) show also a singlet respectively at 8.97 and 9.25ppm corresponding to the proton of hydroxyl groups O-H. The protons of all aromatic cycles show a multiplets in the area of δ 6.50-7.50 ppm. All spectral data from FTIR, ^{1}H-NMR and ^{13}C-NMR confirmed the structure of the 1,4-dihydropyrimido [1,2-a] benzimidazole derivatives.

Spectroscopic Data

Data for 2,4-diphenyl-1,4-dihydropyrimido[1,2-a]benzimidazole (**4a**) : white powder, (lit. mp. 249°C), IR (KBr in cm^{-1}); 3419 (NH), 3034 (aromatic C-H), 1627.92 (C = N), 1573.91 (aromatic C-C). ^{1}H NMR (400 MHz, DMSO) δ 10.02 (s, -NH-), 8.12 (2H,dd, H_6,H_3, *J* = 15.8,7.8 Hz, Ar-H), 7.64 (1H,d, H_2, *J* = 6.6 Hz, Ar-H), 7.41 (2H,d, H_{14},H_{18}, *J* = 7.0 Hz, Ar-H),

7.35 (2H,d, H_{21}, H_{25}, *J* = 6.1 Hz, Ar-H), 7.25 (2H,t, H_{14}, H_{16}, *J* = 7.4 Hz, Ar-H), 7.15 (2H,H_{22},H_{24},t, *J* = 6.9 Hz, Ar-H), 7.01 (2H,d, H_{16},H_{23}, *J* = 8.4 Hz, Ar-H), 6.87 (1H,H_{26},d, *J* = 3.9 Hz, -C=C-H), 6.33 (1H,H_{10}, d, *J* = 3.9 Hz,=C-C-H), 5.28 (1H,d,H_1, *J* = 7.7 Hz, -C=C-H). ^{13}C NMR (100 MHz, DMSO) δ 148.62, 143.00, 142.32, 134.89, 132.19, 129.30, 128.98, 128.37, 126.91 , 126.32 , 121.86 , 116.41, 98.03, 57.19.

Data for 1-(2-methyl-4-phenyl-1,4-dihydropyrimido[1,2-*a*]benzimidazol-3-yl) ethanone (4b) : yellow powder, IR (KBr in cm^{-1}); 3471 (NH), 3037 (aromatic C-H), 1653 (C = O), 1610.56 (C = N), 1562.34 (aromatic C-C), 1521.84 (-CH_3),. ^{1}H-NMR (δ, ppm): 10.79 (s, 1H,-NH-), 7.42 (3H, d, H_{10},H_{13}, *J*= 7.4Hz, Ar-H), 7.33 (1H, t,H_8,H_9, *J*= 7.8Hz , Ar-H), 7.27 (2H, t, H_6,H_4, *J*= 7.6Hz, Ar-H), 7.17 (1H, d, H_7,H_3, *J* = 7.2 Hz, Ar-H), 7.04 (1H, s,H_5, Ar-CH), 6.98 (1H, s,H_5, Ar-CH), 6.59 (1H, s,H_6, Ar-CH), 2.50 (1H, s,-CH_3) 2.23 (3H, s,-CH_3).^{13}C NMR (DMSO-d_6, 100 MHz): 129.07, 128.31, 127.65, 122.23,120.63, 117.32, 110.47, 56.17, 31.14, 20.18.

Data for Methyl-2-methoxy-4-phenyl-1,4-dihydropyrimido[1,2-*a*]benzimidazole- 3-carboxylate (**4c**): white powder, IR (KBr in cm^{-1}); 3417.86 (NH), 3061.03 (aromatic C-H), 1749.44 (C = O), 1604 (C = N), 1583.56 (aromatic C-C), 1456.26 (-CH_3),. ^{1}H-NMR (δ, ppm): 12.08 (s, 1H,-NH-), 7.45 (d, 1H, H_3, H_6, J=7.9Hz, Ar-H), 7.38 (d, 3H, $H_1H_2H_4$, *J* = 6.4 Hz,Ar-H), 7.19 (t, 3H, H_4, H_5, H_7, *J* = 7.3 Hz, Ar-H), 7.11 (t, 1H, H_{22}, *J* = 7.5 Hz, Ar-H), 6.99 (d, 1H, H_{23}, *J* = 7.9 Hz, Ar-H), 6.88 (d, 1H, H_{10}, *J* = 4.4 Hz, -C=C-H), 6.14 (d, 1H, H_8, *J* = 4.3 Hz, -C=C-H), 3.65 (s, 3H,-CO-CH_3), 3.46(s, 3H,-CH_3. ^{13}C NMR (101 MHz, DMSO) δ 167.69, 166.59, 164.27, 148.00, 137.21, 132.81, 129.63, 129.30, 126.84 , 122.43, 121.73 , 117.83, 110.20, 55.69 , 55.31 , 53.41.

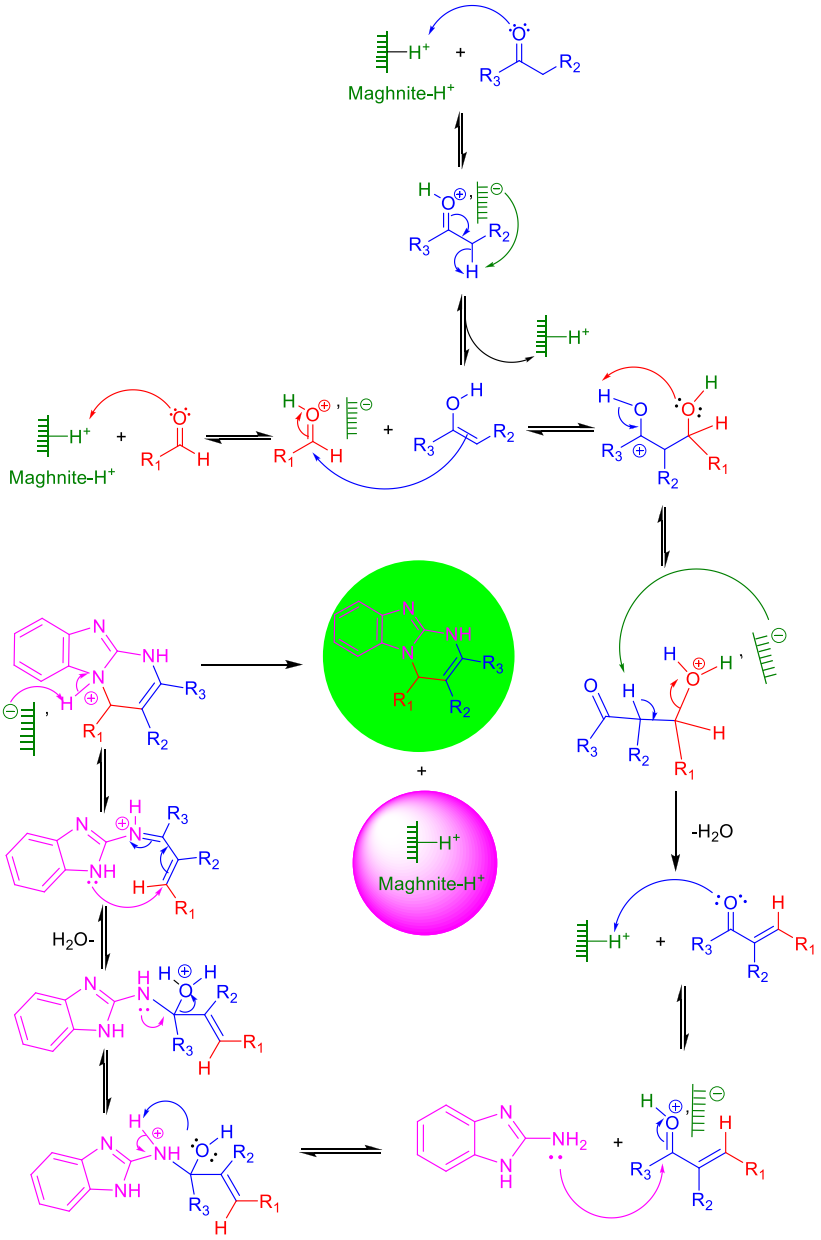
Data for 1-[4-(4-hydroxy-3-methoxyphenyl)-2-methyl-1,4-dihydropyrimido[1,2-*a*]benzimi dazole -3-yl]ethanone (**4d**) : yellow powder, IR (KBr in cm^{-1}); 3527.80 (NH), 3101.54 (aromatic C-H) ,1653(C=O), 1598.99 (C = N), 1556.55 (aromatic C-C), 1516.05 (-CH_3). ^{1}H-NMR (δ, ppm): 10.66 (s, 1H,-NH-), 8.97 (s, 1H,-OH), .750 (d, J=7.5Hz, 1H, H_7 , Ar-H), 7.34 (d, 1H, H_6 , Ar-H), 7.06 (d, J=7.5Hz, 1H, H_5 ,Ar-H), 6.77 (d, J=7.9Hz, 1H, H_4 ,Ar-H), 6.65 (d, 1H,Ar-H), 6.51 (s, 1H, Ar-CH),3.72 (s, 3H,-CH_3), 2.47 (s, 3H,-CH_3), 2.21 (s, 3H,-CH_3). ^{13}C NMR (100 MHz, DMSO) δ 196.00, 147.72, 146.77, 145.99, 142.83, 133.07, 132.18, 122.11, 120.47, 120.18, 117.23 , 115.99 , 112.48 , 110.69 , 109.05, 56.20, 31.13, 20.05.

Data for methyl 4-(4-hydroxy- 3-methoxyphenyl) -2-methoxy- 1,4-dihydropyrimido [1,2-*a*] benzimi dazole- 3- carboxylate (**4e**) : yellow powder, IR (KBr in cm^{-1}); 3552.08 (NH), 3057.17 (aromatic C-H), 1701.22 (C = O), 1635.64(C = N), 1570.06 (aromatic C-C). ^{1}H NMR (400 MHz, DMSO) δ 9.22 (s, H,-NH-), 7.44(d, 2H, H_{10}, H_{13} , *J* = 7.8 Hz, Ar-H), 7.09 (t, 2H, H_8, H_9, *J* = 7.3 Hz, 2H), 7.02 (s, 1H,H_{24},-OH), 6.97 (d,2H, *J* = 7.6 Hz, Ar-H), 6.77 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.73 (d, 2H, Ar-H), 6.41 (d, 2H, H_1, -C=C-H), 5.93 (d, 2H, -(CO)-O-CH_3), 3.71 (s, 3H, -O-CH_3), 3.64 (s, 3H, -CH_3).^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.78, 148.54, 147.54, 132.90, 127.62, 122.24, 121.56, 119.30, 117.73, 116.03, 111.69, 110.41, 56.20, 55.51, 53.25.

Data for methyl 2-methoxy-4-(4-methoxyphenyl)-1,4-dihydropyrimido[1,2-*a*] benzimidazole -3-carboxylate(**4f**) : yellow powder, IR (KBr in cm^{-1}); 3446.79 (NH), 3055.24 (aromatic C-H), 1747.51 (C = O), 1701.22 (C = N), 1612.49 (aromatic C-C), 1456.26 (CH_3),. ^{1}H-NMR (δ, ppm): 12.07 (s, 1H,-NH-), 7.43 (d, 1H, *J* = 7.9 Hz , H_{10}, Ar-H), 7.15 (t, 1H, *J* = 8.3 Hz, H_8, Ar-H), 7.10 (d,1H , *J* = 7.6 Hz, H_3, Ar-H), 6.96 (d, 1H , *J* = 7.9 Hz ,H_4, Ar-H), 6.79 (d, 1H, -C=C-H), 6.03 (d, 1H, Ar-H), 3.74 (s, 3H,-CH_3), 3.64 (s, 3H,-CH_3), 2.50 (s, 3H,-CH_3). ^{13}C NMR (101 MHz, DMSO) δ: 167.72, 164.55, 159.99, 148.00, 132.83, 128.89, 128.48, 122.32, 121.63,

117.77, 114.98, 110.32 , 55.65, 53.30, 14.29.

A proposed mechanism is presented in (Scheme 1) for the synthesis of 1,4-dihydropyrimido[1,2-*a*]benzimidazole derivatives via one-pot three compounds in one step and in short reaction time (2-4h).



Scheme1. Proposed mechanism of the synthesis of 1,4-dihydropyrimido[1,2-a]benzimidazole derivatives using Maghnite-H^+

CONCLUSION

In conclusion, the synthesis reactions of 1,4-dihydropyrimido [1,2-a] benzimidazole (DHPBz) using three reagents aldehydes with ketones derivatives and 2-aminobenzimidazole, in the presence of a catalytic amount of Maghnite-H^+ in methanol as solvent is an extremely effective and chemo-selective method for the synthesis of DHPBz derivatives. In addition, Maghnite-H^+

is a catalyst, non-toxic, inexpensive, environmentally friendly. The products have been obtained in good yield (72-82%) without further purification.

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