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Li^+Modified Nanoporous Na^+-Montmorillonite an Efficient Novel Catalytic System for Synthesis of Quinolines

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Abstract

A simple and efficient method for the synthesis of quinolines and polycyclic quinolines using Li^+ modified nanoporous Na^+-montmorillonite is described. This new nanocatalyst proceeds via Friedlander annulation under solvent-free conditions. It describes our observations about a trend of catalytic activity of Lithium cation in nanoporous Na^+-montmorillonite. In this study, several types of 1,3-diketones such as 1,3-cyclohexanedione, 1,3-cyclopentandione, 5,5-dimethylcyclohexandione (dimedone), acetylacetone and ethyl or methyl acetoacetate and 2-aminoarylketones were rapidly converted to the corresponding substitutedquinoline derivatives in good to excellent yields. The simple experimental procedure, solvent-free reaction conditions, good yields, and utilization of an inexpensive and reusable catalyst are the advantages of the proposed method. To the best of our knowledge, this is the first report on the synthesis of quinoline derivatives using Li^+ modified in nanoporous Na^+-MMT as a novel nanocatalyst under solvent-free conditions.The catalysts can be recovered for the subsequent reactions and reused without any loss of efficiency.

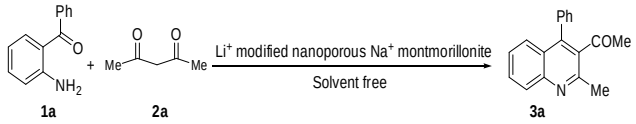
1. Introduction

Quinolines are very important compounds for their wide spectrum of biological activities such as antimalarial, antagonists, antiasthmatic, antitumor, anti-inflamatory, antibacterial, antihypertensive, and tyrosine kinase PDGF-RTK inhibiting agents[1]. In addition to medicinal applications, quinoline derivatives are found to undergo hierarchical self-assembly into a variety of nano-structures and meso-structures with enhanced electronic and photonic functions [2].Moreover, quinolines have been employed in the

study of bioorganic and bioorgano-metallic processes [3]. Considering the significant applications in the fields of medicinal, bioorganic, industrial and synthetic organic chemistry, there has been tremendous interest in developing efficient methods for the synthesis of quinolines. Consequently, various procedures such as the Skraup, Doebner-Von Miller, Friedlander and Combes methods have been developed for the synthesis of quinoline derivatives [4-11]. Among them, the Friedlander annulation [8] is still one of the most simple and straightforward approaches for the synthesis of polysubstituted quinolines. The Friedlander quinoline synthesis consists of the reaction between an aromatic ortho-amino aldehyde and an aldehyde or ketone and an alpha-methylene functionality. Friedlander reactions are generally carried out either by refluxing an aqueous or alcoholic solution of reactants in the presence of base, acid or by heating a mixture of the reactants at high temperatures ranging from 150 to 220°C in the absence of catalyst [12]. Under thermal or base catalysts conditions, o-aminobenzophenone fails to react with simple ketones, such as cyclohexanone and *β*-keto esters [13]. Subsequent work showed that acid catalysts are more effective than base catalysts for the Friedlander annulation. Acid catalysts such as hydrochloric acid, sulfuric acid, *p*-toluenesulfonic acid, and polyphosphoricacid have been widely employed for this conversion [12a,14]. In addition, modified methods employing Wells-Dawson tungsten heteropolyacid [15], Sulfamic acid [16], Phosphotungstic acid ($H_3PW_{12}O_{40}$) [17], Oxalic acid [18], $CeCl_3 \cdot 7H_2O$ [19], $Y(OTf)_3$ [20], $ZnCl_2$, $SnCl_2$[21], HCl [22], $Zr(NO_3)_4$, $Zr(HSO_4)_4$ [23], Amberlyst-15 [24], dodecylphosphonic acid (DPA) [25], Silica supported perchloric acid ($HClO_4$-SiO_2) [26], Silica gel supported sodium hydrogen sulfate ($NaHSO_4$-SiO_2) [27], nanosized MCM-41 [28], Montmorrilonite K-10, zeolite, nano-crystalline sulfated zirconia (SZ) [29], and ionic liquids have been reported for the synthesis of quinolines [30].

However, most of the earlier methods suffer from different disadvantages such as harsh reaction conditions, long reaction times, harmful organic solvents, low yields, and difficulties in the work-up procedures. The recovery of the catalyst is also a problem. Although different methods are available for the synthesis of quinolines, the development of an easy convenient, and environmentally benign methods for the preparation of quinoline derivatives is still a challenging task. For these reasons, in the recent years, the use of solid and heterogeneous catalysts in organic reactions has drawn the attention of chemists for the Friedlander quinoline synthesis. This extensive application of heterogeneous catalysts in synthetic organic chemistry can make the synthetic process more efficient from both the environmental and economical points of view and used-catalyst can be easily recycled [31]. Montmorrilonite clay is an efficient solid acid catalyst in organic transformations with excellent product, regio- and stereo-selectivity [32]. The main reasons for utilizing clays are accessibility, easy modification, cheapness, non- corrosiveness, and recyclability. Montmorillonite minerals have very small micron-sized particles, and they are extremely fine-grained and thin-layered [33]. Layers of MMT have a thickness of about 1 nm and a length of 100 nm or a little more. Broken bonds on the edge of MMT layers are common phenomena for layered silicates and lead to the free formation of hydroxyl groups [34], which can be used for chemical modification. The first attempt may be traced back to 1941 when Berger found that hydroxyl groups of

montmorillonite could be methylated with diazomethane [35]. Many scientists then used this property for different modifications on the surface of montmorillonite [36].Due to the acidic properties of nano catalysts derivatives of Na^+-montmorillonite in recent years, Li^+ modified nanoporous Na^+-montmorillonite has been used as an efficient, novel and recyclable catalyst. Since the reaction is heterogeneous in nature, the catalyst can conveniently be separated by simple filtration. The use of Li^+ modified nanoporous Na^+-montmorillonite as a recyclable catalyst makes the process convenient, economic, and environmentally benign. Therefore, we were interested in using new nano catalysts for Friedlander synthesis of quinolines (Scheme 1).



Scheme 1. Synthesis of quinoline **3a** using by Li^+ modified nanoporous Na^+-MMT.

2. Experimental procedure

2.1. Chemicals and apparatus

Chemicals were purchased from Fluka and Merck Chemical Companies. All yields refer to the isolated products. The products were characterized by their physical constants, comparison with authentic samples. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silica-gel polygram SILG/UV 254 plates.Melting points were measured with an Electrothermal 9200 apparatus. IR spectra were recorded on a FT-IR 102MB BOMEM apparatus. ^1H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300AVANCE spectrometer at 300.13 and 75.47MHz. ^1H and ^{13}C NMR spectra were obtained on solutions in $CDCl_3$using TMS. All products showed the same physical, analytical, and spectral data with those reported in the literature.Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Philips Analytical X-Ray PW1800, using Cu-Kα radiation (λ = 0.15418 nm). The characterization of Na^+-MMT and Li^+ modified nanoporous Na^+-MMT was obtained using scanning electron microscopy (SEM-LEO 1430VP). Inductively coupled plasma optical emission spectrometry (ICP-OES), measurements were performed on an ICP Varian 735-ES.

2.2. Catalyst preparation

A 100 mL suction flask charged with 4.0 g Na^+-montmorillonite (Southern Clay Products) and 50 mL H_2O was stirred for 4 h slowly at room temperature. In the second step, 5 g LiCl was added to the mixture and stirred for 24 h at room temperature. Then, the mixture was filtered and the solid residue washed with methanol (20 mL) and dried at 100 ^oC to obtain Li^+ modified nanoporous Na^+-montmorillonite powder (3.9 g).

2.3. Catalyst characterization

2.3.1. IR analysis

The infrared spectra of Na^+-MMT and Li^+ modified nanoporous Na^+-MMT are presented in Fig.1. The spectra are virtually identical. This implied that FTIR is not sensitive to changes in the system. In the stretching region, a peak at 3610-3640 cm^{-1} is observed in both of spectra. The broadband in the range 3610-3640 cm^{-1} is due to the stretching vibration of OH units bonded to the aluminum and/or magnesium in Na^+-MMT and aluminum and/or magnesium and Lithium in Li^+ modified nanoporous Na^+-MMT.The peaks at 3461, 3444 and 1647 cm^{-1}corresponds to the -OH stretching vibration of the adsorbed water and the bands at 1047, 1045 and 918 cm^{-1} can

becollectively attributed to Si-O stretching vibrations.

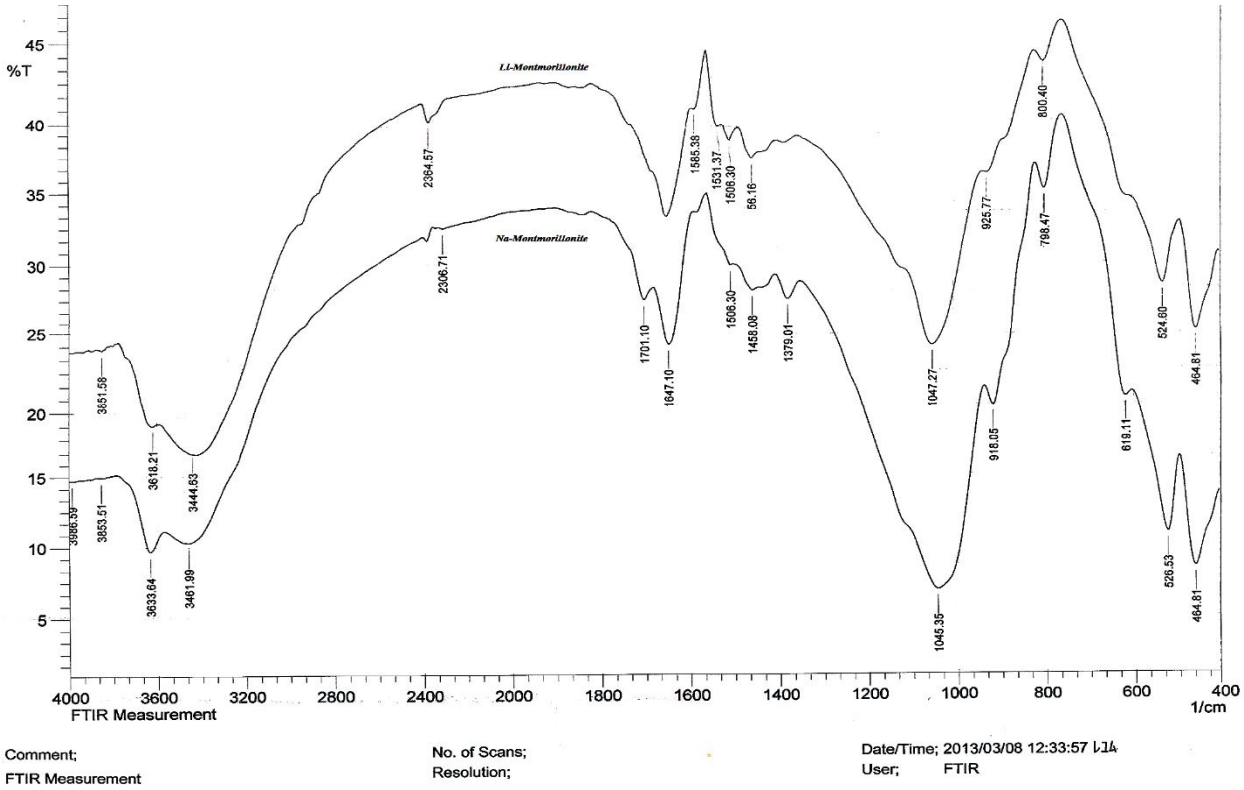


Fig.1. IR spectra of Na^+-MMT and Li^+ modified nanoporous Na^+-MMT.

2.3.2. SEM analysis

The representative SEM micrographs of the Na^+-MMT and Li^+ modified nanoporous Na^+-MMTare shown in Fig.2, respectively. This technique can't provide any evidence that Lithium has been intercalated into montmorillonite interlayer spaces.

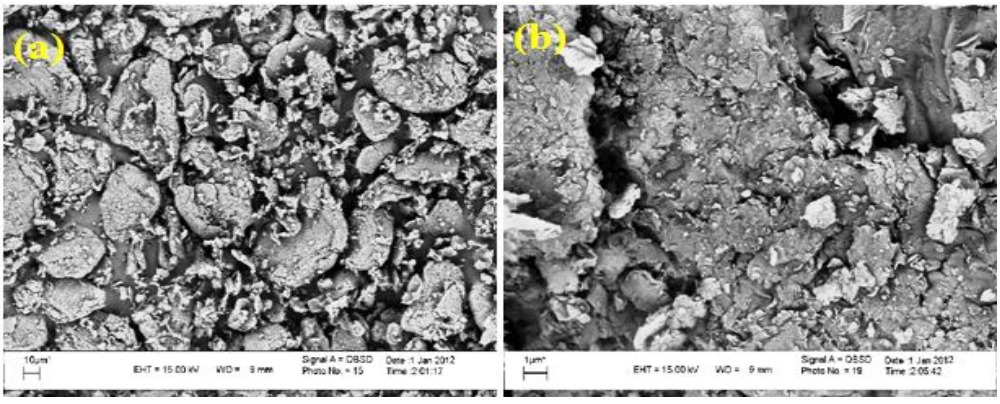


Fig.2. SEM images of (a) Na^+-MMT and (b) Li^+ modified nanoporous Na^+-MMT.

2.3.3. Powder X-ray diffraction

The SEM result is supported by XRD results. The XRD pattern of the catalyst (Fig 3) indicates that the basic sodium montmorillonite structure is maintained after modification. In the reaction between sodium montmorillonite and Lithium Chloride, the intensity of the montmorillonite layers was demonstrated by X-ray diffraction is decreased. The basal spacing for the Na^+-MMT is 12.13°Å with 2θ=7.3°. It is shown by the XRD patterns that the basal spacing of the Li^+ modified nanoporous Na^+-MMT has obviously lower intensity than that of Na^+-MMT (12.04°Å). This decrease in the basal spacing verifies that the Lithium has been intercalated into montmorillonite interlayer spaces.

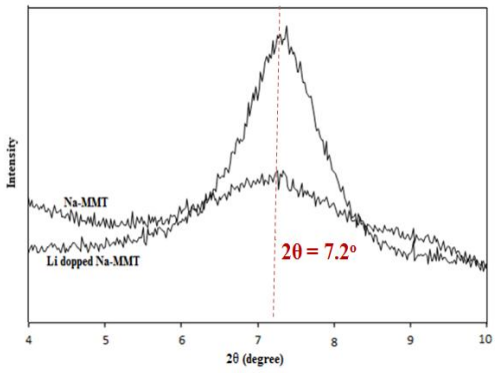


Fig.3. XRD patterns of Na^+-MMT and Li^+ modified nanoporous Na^+-MMT.

2.3.4. ICP analysis

Inductively coupled plasma optical emission spectrometry (ICP-OES) indicates the leachable portion of the elements Li^+modifiednanoporous Na^+-MMT catalyst (Table 1). This method proves that Lithiumhas been intercalated into montmorillonite interlayer spaces.

Table 1.ICP analysiswithME-01 Elements Method.

Element	DL [a]	Leachable Portion
Li	1	5836

[a] DL: Detection Limit (in ppm).

2.4. General procedure for preparation of quinoline derivative

A mixture of 2-aminoarylketones **1a** or **1b** (1 mmol), 1,3-diketones or ketones (1mmol), and 0.06 g Li^+ modified nanoporous Na^+-MMT was heated at 100 °C. The reaction was monitored by TLC. After completion, the reaction mixture was washed with 10 cm^3EtOAc and filtered to recover the catalyst. Evaporation of the solvent followed by purification by column chromatography (silica gel, EtOAc:n-hexane, 1:8) afforded the corresponding pure quinoline derivative.

2.4. Spectroscopic data of selected compounds

*2.4.1. Methyl-2-methyl-4-phenylquinoline-3-carboxylate(**3a**)*

White powder (0.25 g, 95%), mp 147-149°C. IR (KBr): 3030, 2958, 1704, 1615 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.84 (s, CH_3), 3.58 (s, OCH_3), 7.27–8.22 (m, H-Ar), ^{13}C NMR (75 MHz, $CDCl_3$): δ= 23.25, 52.30, 125.19, 126.61, 126.87, 127.43, 128.10, 128.36, 128.71, 129.15, 130.93, 135.35, 146.64, 147.46, 154.57, 168.54 ppm.

*2.4.2.Methyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (**3b**)*

White powder (0.28 g, 96%), mp 131-133°C. IR (KBr): 3027, 2964, 1701, 1617 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.81 (s,CH_3), 3.59 (s, OCH_3), 7.26-8.13 (m, H-Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ= 23.34, 52.40, 125.34, 126.02, 128.20, 128.57,129.01, 129.08, 129.92, 131.69, 132.83, 134.70, 145.24, 146.42, 154.94, 168.27 ppm.

3. Results and discussion

Over recent years, clays as nanostructured materials have been widely utilized in organic transformations as solid acid catalysts. The main reasons for the use of clays are accessibility, easy modification, cheapness, non-corrosively, and recyclability. Montmorillonite (MMT) and its derivatives have very small micron-sized particles, so they are extremely fine grained and thin layered. With this background in mind, and in line with our

interest in the synthesis of heterocyclic compounds [37], we wish to report a simple, convenient, and high-yielding method for the synthesis of polysubstituted quinolines via Friedlander annulation using Li^+ modified nanoporous Na^+-MMT as a reusable eco-friendly nanocatalyst under solvent-free conditions. Accordingly, treatment of 2-aminobenzophenone **1a** with acetylacetone **2a** in the presence of 0.06 g of Li^+ modified nanoporous Na^+-MMT resulted in the formation of quinoline **3a** in 95% yield (Table 2, Entry 7). It is noteworthy to mention that in the absence of acatalyst, no product was found even after 12 h (Table 2, Entries 1, 2). Higher amounts of catalyst did not improve the result to any greater extent (Table 2, Entry 8). These results indicate that the catalyst exhibits a high catalytic activity in this transformation. The generality and substituent scope of this new method was investigated by employing several examples. Various 1,3-diketones such as 1,3-cyclohexanedione, 1,3-cyclopentandione, 5,5-dimethylcyclohexandione (dimedone), acetylacetone and ethyl or methyl acetoacetate reacted with 2-aminobenzophenone **1a**, 2-amino-5-chloro-benzophenone **1b** or 2-aminoacetophenone **1c** to produce the corresponding substituted quinolines for reaction times of 0.5 up to 2 h (Table 4). Interestingly, cyclic ketones such as cyclopentanone and cyclohexanone under smooth condensation with 2-aminoaryl ketones afford the respective tricyclic quinolines. In most cases, the products were isolated by simple filtration. The crude products were purified either by recrystallization from a mixture of EtOAc/n-hexane. In addition, this method is equally effective for both cyclic and acyclic ketones (Table 4).

Table 2. Optimization of the reaction conditions.[a]

Entry	Conditions	Time (h)	Yield(%) [b]	Ref.
1	-/ 80 °C	12	-	-
2	-/ 100 °C	12	-	-
3	Na^+-MMT (0.06 g)/ 100 °C	6	78	-
4	Li^+ modified nanoporous Na^+-MMT (0.04 g)/ 100 °C	2	89	-
5	Li^+ modified nanoporous Na^+-MMT (0.05 g)/ 100 °C	1.5	90	-
6	Li^+ modified nanoporous Na^+-MMT (0.06 g)/ 100 °C	1	95	-
7	Na^+-MMT (0.06 g)/ LiCl/ 100 °C	4	79	-
8	Li^+ modified nanoporous Na^+-MMT (0.07 g)/ 100 °C	1	96	-
9	K-10/ EtOH/ 80 °C	2	83	28
10	$CeCl_3 \cdot 7H_2O$/ CH_3CN/ rt	2.5	88	19
11	NH_2SO_3H/ 70 °C	0.75	89	16
12	$Y(OTf)_3$/ CH_3CN/ rt	5	85	20
13	HCl/ H_2O/ 60 °C	0.5	94	22
14	$NaHSO_4$/ SiO_2/ 80 °C	1	87	27a
15	Amberlyst-15/ EtOH/ reflux	2	93	24
16	$NaHSO_4$-SiO_2/ CH_3CN/ 60 °C	3	92	26

[a] Reaction conditions: A mixture of 2-aminobenzophenone**1a** (1 mmol), acetylacetone**2** (1 mmol).[b]isolated yield.

In order to optimize the reaction conditions, we conducted this reaction in different solvents suchas H_2O, EtOH, MeOH, CH_3CN, CH_2Cl_2, and toluene. (Table 3, Entries 1-6). Reaction in toluene and dichloromethane solvent gave low product yields even after 6 h up to 7 h (Table 3, Entries 5, 6). In the case of ethanol and water under reflux condition, the yields were moderate (Table 3,

Entries 1, 2). However, the results showed that the efficiency and the yield of the reaction in solution were much less than those obtained under solvent-free conditions (Table 2). The best result was obtained with 0.06 g of catalyst under solvent-free conditions at 100 ^{o}C. The insolubility of the catalyst Li^{+} modified nanoporous Na^{+}-MMTindifferent organic solvents provides an easy method for its separation from the product. The catalyst was separated by filtration and reused after activation with only a gradual decrease in itsactivity. The presented method provides an easy access to the preparation of substituted quinolines with a wide range of substitution patterns.

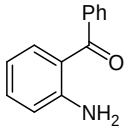
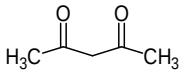
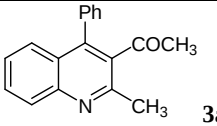
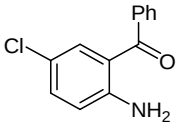
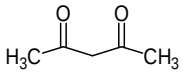
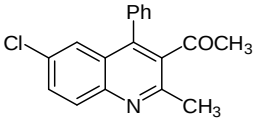
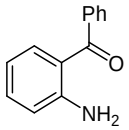
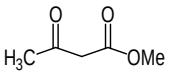
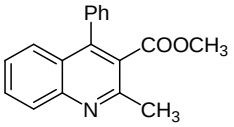
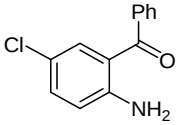
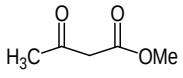
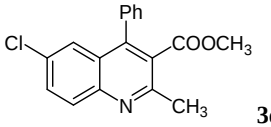
Table 3. Optimization of the reaction conditions in different solvents.[a]

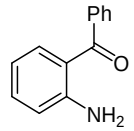
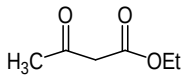
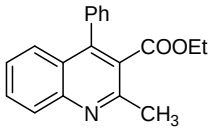
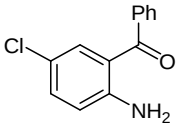
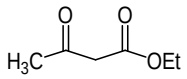
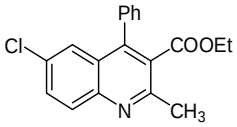
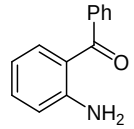
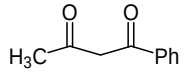
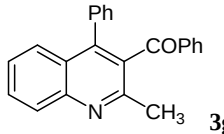
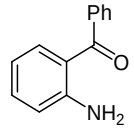
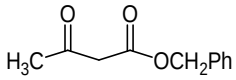
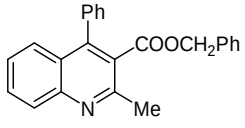
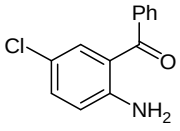
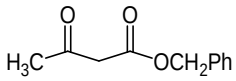
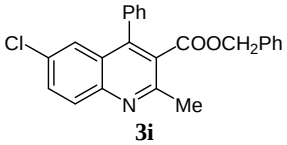
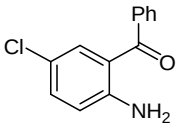
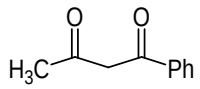
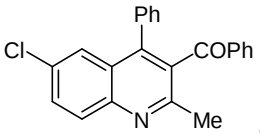
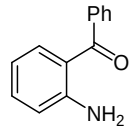
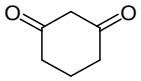
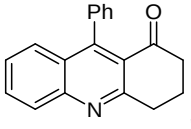
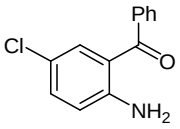
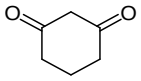
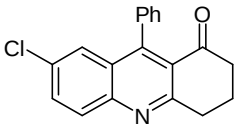
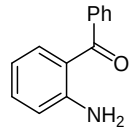
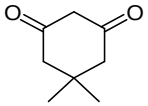
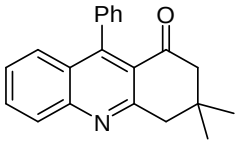
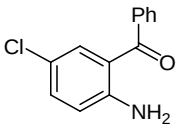
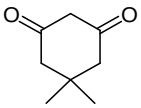
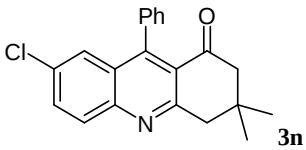
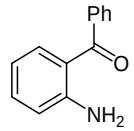
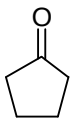
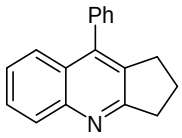
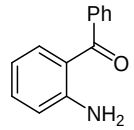
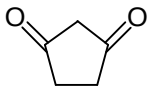
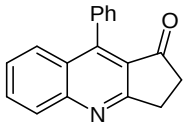
Entry	Solvent	Time(h)	Yield(%)	Ref.
1	EtOH	4	80	---
2	H_2O	3.5	82	---
3	CH_3CN	4	78	---
4	MeOH	4	75	---
5	CH_2Cl_2	6	63	---
6	Toluene	7	56	---

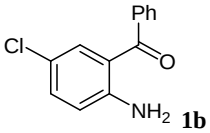
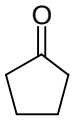
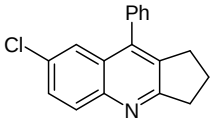
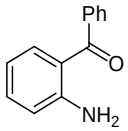
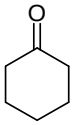
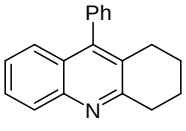
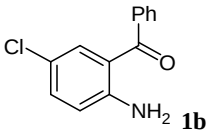
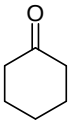
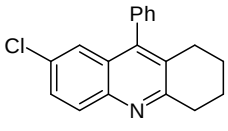
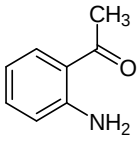
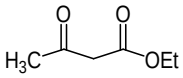
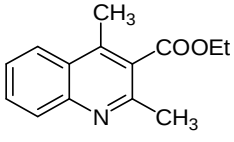
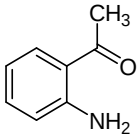
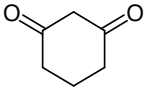
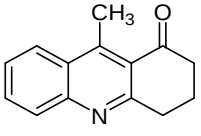
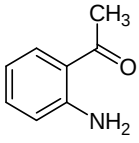
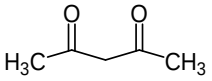
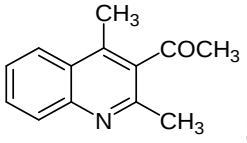
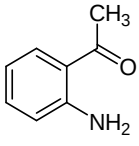
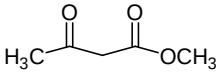
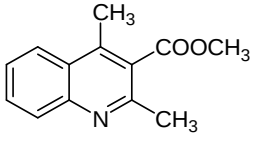
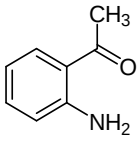
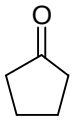
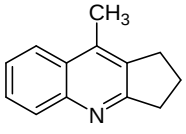
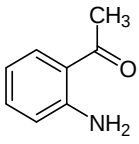
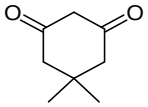
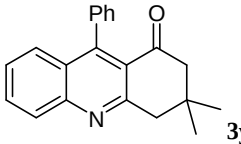
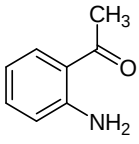
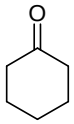
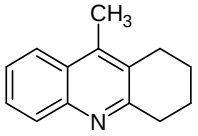
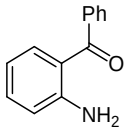
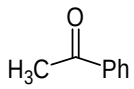
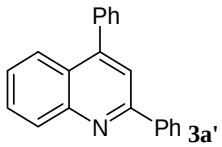
[a] Reaction conditions: A mixture of 2-aminobenzophenone**1a** (1 mmol), acetylacetone**2** (1 mmol) and Li^{+} modified nanoporous Na^{+}-MMT (0.06 g).[b] isolated yield.

Moreover, it offers several advantages such as higher yields, shorter reaction times, cleaner reaction profiles and simple experimental and work up procedures. All the products were characterized by ^{1}H NMR, ^{13}C NMR, IR and mass spectroscopy and also compared with authentic samples. The scope and generality of this process are illustratedwith respect to various 2-aminoaryl ketones and α-methylene ketones and the results are summarized in Table 4.To the best of our knowledge, this is the first report on the synthesis of polysubstituted quinolines using Li^{+} modified nanoporous Na^{+}-MMT as a novel nanocatalyst under solvent-free conditions.

Table 4. Synthesis of quinoline derivatives catalyzed by Li^{+} doped in nanoporous Na^{+}-MMT**.**

Entry	2-Aminoaryl ketone	Ketone	Quinoline[a]	Time (h)	Yield (%)[b]	Mp^{o}C [Lit]
1	 **1a**		 **3a**	1	95	108-109 [28]
2	 **1b**		 **3b**	0.5	96	154-156 [28]
3	 **1a**		 **3c**	1	94	147-149 [27a]
4	 **1b**		 **3d**	1.5	93	131-133 [27a]

5	 **1a**		 **3e**	1	95	100-102 [28]
6	 **1b**		 **3f**	1.5	92	97-99 [28]
7	 **1a**		 **3g**	1	94	132-133 [25]
8	 **1a**		 **3h**	1.5	92	90-93 [25]
9	 **1a**		 **3i**	0.5	89	120-122 [25]
10	 **1b**		 **3j**	1	93	208-210 [25]
11	 **1a**		 **3k**	1.5	88	157-159 [30b]
12	 **1b**		 **3l**	1.5	94	184-186 [28]
13	 **1a**		 **3m**	1	91	190-192 [30b]
14	 **1b**		 **3n**	1.5	93	207-209 [18]
15	 **1a**		 **3o**	1.5	96	133-135 [28]
16	 **1a**		 **3p**	1	94	170-173 [25]

17	 **1b**		 **3q**	1.5	95	96-98 [28]
18	 **1a**		 **3r**	1.5	93	141-142 [28]
19	 **1b**		 **3s**	1.5	91	161-162 [28]
20	 **1c**		 **3t**	1	93	Oil [29]
21	 **1c**		 **3u**	1.5	94	76-77 [30b]
22	 **1c**		 **3v**	1.5	91	Oil [29]
23	 **1c**		 **3w**	1.5	89	Oil [29]
24	 **1c**		 **3x**	2	92	56-58 [22]
25	 **1c**		 **3y**	0.5	96	105-106 [22]
26	 **1c**		 **3z**	1	94	76-77 [27b]
27	 **1a**		 **3a'**	1.5	96	102-103 [17]

[a] Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy.[b] Isolated yields.

We have found that Li^+ modified nanoporous Na^+-MMT can be easily recovered by filtration, washing with EtOAc and $CHCl_3$ and drying at 100 ^oC. The reusability of this reagent is exemplifiedby thereaction of 2-aminobenzophenone**1a**, acetylacetone**2**in the presence of the recycled reagent, which gave the requested product in 95, 94, 94, 92, 91 and 89% yields after six runs. It retains almost the initial activity after recovery when reused in the next successive cycles (Fig.4).

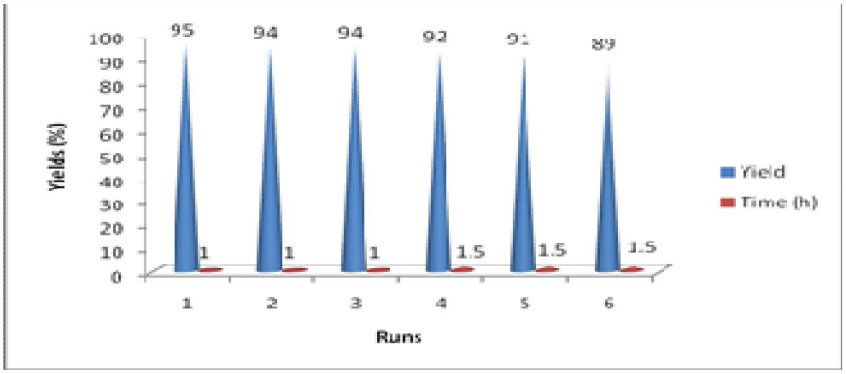
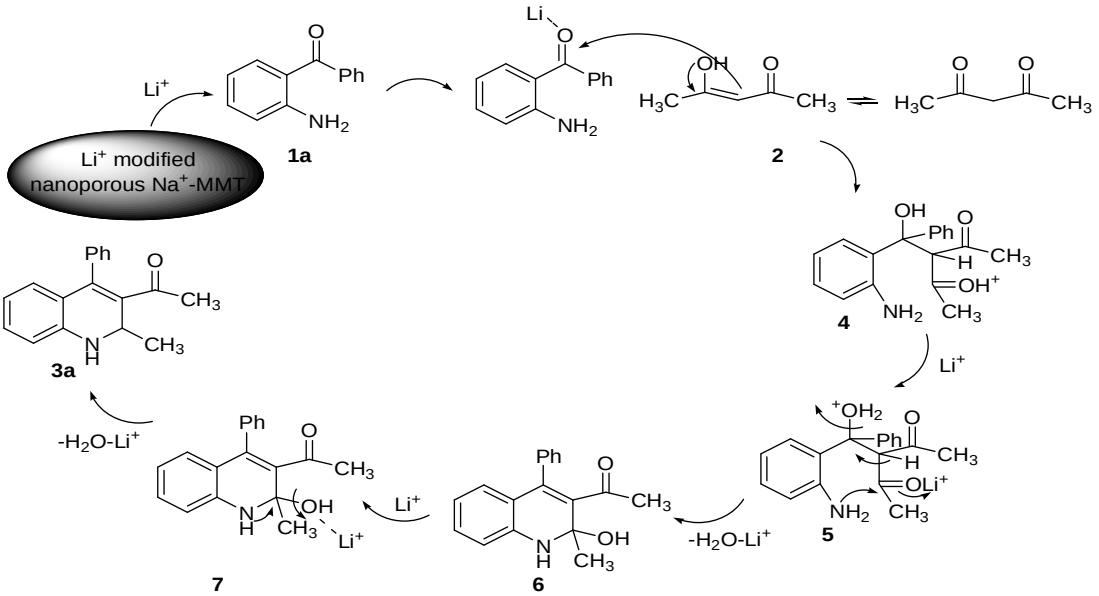


Fig.4. Reusability of the catalyst.

A possible mechanism for the synthesis of quinolines using the proposed method is shown in Scheme 2. The quinoline synthesis is presumably initiated by the nuleophilic addition of the substrate Ketone **2** on the reactant 2-Aminoaryl ketone **1a** activated by Lithium cation. The resulting adduct **4**undergoes dehydration to give the key enone intermediate **5** which is likely activated by Lithium cation. Then, the intermediate **5** was converted to intermediate **6** and followed by cyclization afforded the corresponding quinoline **3a**andwater (Scheme 2).



Scheme 2. A plausible mechanism for the synthesis of products **3a-a'**.

4. Conclusion

In summary, we have described a mild and efficient protocol for the synthesis of quinolines and polycyclic quinolines via Friedlander condensation in 2-aminoarylketones with α-methylene ketones using Li^+ modified nanoporous Na^+-MMT as a recyclable heterogeneous catalyst. The simple experimental procedure combined with the ease of recovery and reusability of this novel catalyst makes this method quite simple, convenient and environmentally benign for the synthesis of highly functionalized quinolines.

Acknowledgment

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