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# A mild and highly efficient Friedländer synthesis of quinolines in the presence of heterogeneous solid acid nano-catalyst

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**KEYWORDS**

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Zeolite;
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**Abstract** A simple highly versatile and efficient synthesis of various poly-substituted quinolines in the Friedländer condensation of 2-aminoarylketones with carbonyl compounds and β-keto esters using Montmorrilonite K-10, zeolite, nano-crystalline sulfated zirconia (SZ) as a catalyst in ethanol at moderate temperature. The advantages of methods are short reaction times and milder conditions, easy work-up and purification of products by non-chromatographic methods. The catalysts can be recovered for the subsequent reactions and reused without any appreciable loss of efficiency.


## 1. Introduction

Quinoline is a well-known structural unit in alkaloids and their derivatives are very important compounds that show a broad range of biological and pharmaceutical activities such as antagonists (Bennacef et al., 2007), analgesic agents (Gopalsamy and Pallai, 1997), $5HT_3$ (Anzini et al., 1995), NK-3 receptors (Giardian et al., 1997), anti-malarial (Larsen et al., 1996; Chauhan and Srivastava, 2001), antitumor (Myers et al., 1997; Comins et al., 1994; Shen et al., 1993), anti-inflammatory (Roma et al., 2000), anti-bacterial (Chen et al., 2001), anti-asthmatic (Dube et al., 1998), anti-hypertensive (Ferrarini et al., 2000) and anti-platelet agents, and as tyrosine kinase inhibiting agents. (Larsen et al., 1996; Kalluraya and Sreenivasa, 1998). In addition, quinolines are valuable synthons used in a variety of nano-structures and meso-structures with enhanced electronic and photonic functions (Agarwal and Jenekhe, 1991; Zhang et al., 2000; Jenekhe et al., 2001). Moreover, quinolines are advantageously employed in the fields of natural products (Larsen et al., 1996; Chauhan and Srivastava, 2001), bioorganic (Saito et al., 2001), bioorganometallic processes (He and Lippard, 2001; Nakatani et al., 2000) and industrial organic chemistries (Jenekhe et al., 2001). Because of their importance as substructures in a broad

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range of natural and designed products, significant effort continues to be directed into the development of new quinoline based structures (Hoemann et al., 2000) and new methods for their construction (Du and Curran, 2003; Lindsay et al., 2002; Dormer et al., 2003). Various methods such as Skraup, Doebner von Miller, Friedländer, Pfitzinger, Conrad-Limpach, and Combes methods have been developed for the preparation of quinoline derivatives (Abass, 2005; Kouznetsov et al., 2005; Jones et al., 1996; Skraup, 1880; Friedländer, 1882; Mansake and Kulka, 1953; Arisawa et al., 2001). Among them, the Friedländer annulation (Marco-Contelles et al., 2009) appears to be still one of the most simple and straightforward approaches for the synthesis of quinolines. This method involves the acid or base catalyzed or thermal condensation between a 2-aminoaryl ketone and an other carbonyl compound possessing a reactive α-methylene group followed by cyclodehydration.

Brønsted acids catalysts, such as sulfamic acid, hydrochloric acid, sulfuric acid, *p*-toluene sulfonic acid, PEG-supported sulfonic acid, propylsulfonic silica, sulfonic acid-functionalized ionic liquids, oxalic acid, dodecylphosphonic acid (DPA) and o-benzenedisulfonimide were widely used for Friedländer annulation (Yadav et al., 2005; Wang et al., 2006; Strekowski et al., 2000; Zhang et al., 2009; Akbari et al., 2010; Dabiri et al., 2007; Barbero et al., 2010). Lewis acids such as $FeCl_3$, $ZnCl_2$, $SnCl_2$, $CuSO_4{\cdot}5H_2O$, $FeSO_4{\cdot}7H_2O$, $AuCl_3$, $CeCl_3{\cdot}7H_2O$, $Zr(NO_3)_4$ or $Zr(HSO_4)_4$, $GdCl_3{\cdot}6H_2O$, $BiCl_3$, $Yb(PFO)_3$, $Bi(OTf)_3$, $Sc(OTf)_3$, $Y(OTf)_3$, $I_2$, NaF, TMSCl, Sulfonated cellulose starch, Silica supported perchloric acid ($HClO_4$–$SiO_2$), $NaHSO_4$–$SiO_2$, $H_2SO_4$–$SiO_2$, Amberlyst-15 and $HClO_4$–$SiO_2$ have also recently been utilized for this synthesis (Das et al., 2007; Narasimhulu et al., 2007; Zolfigol et al., 2007; Prabhakar Reddy et al., 2008; Jia and Wang, 2006; Wang et al., 2009; Shaabani et al., 2008).

However, most of the earlier methods are associated with 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 and efficient method for the preparation of quinoline derivatives is still a challenging task. Thus, the development of simple, convenient, and environmentally benign methods for the synthesis of quinolines is still required. For these reasons, the use of solid and heterogeneous catalysts in organic reactions in aqueous media and solvent-free conditions has drawn the attention of chemists for the Friedländer quinoline synthesis.

In the recent years, the use of heterogeneous catalysts has received considerable interest in organic synthesis (Corma and Garcia, 2003). This extensive application of heterogeneous catalysts in synthetic organic chemistry can make the synthetic process more efficient from both the environmental and economic point of view (Santor et al., 2004) and used-catalyst can be easily recycled. Montmorrilonite clay, enable to function as an efficient solid acid catalyst in organic transformations with excellent product, regio- and stereo-selectivity (Binitha and Sugunan, 2006; Joseph et al., 2005, 2006; Shanbhag and Halligudi, 2004; Albertazzi et al., 2005; Jagtap and Ramaswamy, 2006; Lal et al., 2006; Reddy et al., 2004, 2005, 2007; Sharma et al., 2006).

Nowadays, more and more heterogeneous Bronsted acids, e.g., zeolites are preferred from an economical perspective as well as from an ecological viewpoint. Due to its high protonic acidity and unique shape-selective behavior, HZSM-5, has been shown to be a highly active and stable catalyst for reactions (Marques and Moreira, 2003; Mavrodinova et al., 2003; Corma and Orchilles, 2000; Ingelsten et al., 2005; Zhao et al., 2006; Thomas, 1994; Heravi et al., 2006; Hegedus et al., 2006). Zirconia is attracting considerable interest on account of its potential use as a catalyst support. Recent investigations reveal that promoted zirconia is an exceptionally good solid acid catalyst for various organic synthesis and transformation reactions having enormous industrial applications (Indovina et al., 2002; Pietrogiacomi et al., 2003; Li et al., 2003; Tsyntsarski et al., 2003; Demirci and Garin, 2002).

As a part of our continuing effort toward the development of useful synthetic methodologies (Dabbagh et al., 2007; Najafi Chermahini et al., 2010; 30) herein, we report the synthesis of substituted quinolines from 2-amino acetophenone or benzophenone and α-methylene carbonyl compounds in the presence of heterogeneous solid acid catalysts including Montmorrilonite K-10, zeolite, nano-crystalline sulfated zirconia (SZ) in ethanol under reflux condition.

## 2. Experimental

### 2.1. Instruments and characterization

All reagents were purchased from Merck and Aldrich and used without further purification. Products were characterized by spectroscopy data (IR, FTIR, $^1$H NMR and $^{13}$C NMR spectra), elemental analysis (CHN) and melting points. A JASCO FT/IR-680 PLUS spectrometer was used to record IR spectra using KBr pellets. NMR spectra were recorded on a Bruker 400 Ultrasheild NMR and DMSO-d6 was used as solvent. Melting points reported were determined by open capillary method using a Galen Kamp melting point apparatus and are uncorrected. Mass Spectra were recorded on a Shimadzu Gas Chromatograph Mass Spectrometer GCMS-QP5050A/Q P5000 apparatus.

### 2.2. Catalyst preparation

#### 2.2.1. Synthesis of ZSM-5 and HZSM-5

For synthesis of ZSM-5, hydrated aluminum sulfate and sodium silicate solution were the sources of aluminum and silicon, respectively. The tetrapropylammonium bromide was used as the structure-directing template (Argauer and Landolt, 1972; Dwyer, 1984; Guth, 1992; Choudhary et al., 2002). ZSM-5 zeolite was synthesized according to the procedure described earlier. The solid phase obtained was filtered, washed with distilled water several times, dried at 120 °C for 12 h and then calcined at 550 °C for 6 h and followed by ion exchange with $NH_4NO_3$ solution (three times). The acid hydrogen form of the compound is prepared by transferring the oven-dried compound to a tube furnace. Heat the ammonium zeolite for 3 h to ensure the thermal decomposition of $NH_4^+$ ions. Over the course of this process, zeolite should turn from white to brown/black color (Guth, 1992; Choudhary et al., 2002).

#### 2.2.2. Synthesis of sulfated zirconia

Amorphous hydrated zirconia synthesized by hydrolysis of $ZrCl_4$ with a concentrated (25%) solution of ammonia

according to the procedure described earlier (Tichit et al., 1996). The obtained hydrous zirconia sample was dried at 120 °C for 12 h. Sulfated zirconia (SZ) was prepared by suspending $ZrO_2$ in a solution of 0.5 M $H_2SO_4$. After 90 min stirring the mixture was filtered and washed with 0.05 M $H_2SO_4$. The precipitate was dried at 120 °C and calcined for 2 h at 600 °C with subsequent cooling in either a desiccator or under ambient conditions. (Tichit et al., 1996).

### 2.2.3. Synthesis of nano-crystalline sulfated zirconia

Nano-crystalline sulfated zirconia has been prepared by one step sol–gel technique (Mishra et al., 2004; Tyagi et al., 2006). A typical synthesis involves the addition of concentrated sulfuric acid (1.02 ml) to zirconium n-propoxide precursor (30 wt%) followed by the hydrolysis with water. After 3 h aging at room temperature, the resulting gel was dried at 110 °C for 12 h followed by calcination at 600 °C for 2 h.

### 2.3. General procedure for the synthesis of quinoline derivatives

In a 50 mL round bottomed flask 2-aminoaryl ketone (1 mmol) and α-methylene carbonyl compound (1.2 mmol) were thoroughly mixed in ethanol (10 mL), then catalyst (50 mg) was added, and the solution was refluxed for appropriate time (Table 2). The extent of the reaction was monitored by TLC. After completion of the reaction, the resulting solid was collected by filtration and dissolved in 20 mL dichloromethane and the combined organic layer was dried over anhydrous calcium chloride and filtered. Evaporation of the solvent gave a crude product, which was purified by silica gel column chromatography with cyclohexane and ethyl acetate (4:1) to give the pure product.

### 2.3.1. Ethyl 2-methyl-4-phenylquinoline-3-carboxylate (*4a*)

Mp 100–102 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3060, 2976, 1728, 1587, 1484, 1265, 1065 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-d6): δ 0.94 (t, 3H), 2.76 (s, 3H), 4.04 (q, 2H), 7.30–7.48 (m, 7H), 7.72 (t, $^1H$), 8.04 (d, $^1H$); MS (m/z): 291.13 ($M^+$); Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.12; H, 5.46; N, 4.87.

### 2.3.2. Methyl 2-methyl-4-phenylquinoline-3-carboxylate (*4b*)

Mp 86–88 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3060, 2966, 1738, 1608, 1588, 1387, 1235, 1176, 1065 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-d6): δ 2.76 (t, 3H), 3.54 (s, 3H), 7.24–7.88 (m, 8H), 8.08 (d, $^1H$). MS (m/z): 277.11 ($M^+$). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.44; N, 5.04. Found: C, 77.68; H, 5.26; N, 4.77.

### 2.3.3. 1-(2-Methyl-4-phenylquinolin-3-yl) ethanone (*4c*)

Mp 108–110 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3046, 2962, 1716, 1606, 1574, 1388, 1218, 1062 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-d6): δ 1.96 (t, 3H), 2.61 (s, 3H), 7.28–7.74 (m, 8H), 8.02 (d, 1H); MS (m/z): 261.12 ($M^+$); Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.58; H, 5.56; N, 5.11.

### 2.3.4. Ethyl 2,4-dimethylquinoline-3-carboxylate (*4d*)

Oil. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3066, 2946, 1726, 1611, 1584, 1212, 1072 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-d6): δ 1.44 (t, 3H), 2.61 (s, 3H), 2.70 (s, 3H), 4.44 (q, 2H), 7.52 (t, 1H), 7.67 (t, 1H), 7.94 (d, 1H), 7.97 (d, 1H). MS (m/z): 229.11 ($M^+$); Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.08; H, 6.26; N, 6.16.

### 2.3.5. Methyl 2,4-dimethylquinoline-3-carboxylate (*4e*)

Oil. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3065, 2954, 1729, 1614, 1581, 1382, 1228, 1063 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-d6): δ 2.60 (t, 3H), 2.65 (s, 3H), 3.72 (s, 3H), 7.36 (t, 1H), 7.63 (t, 1H), 7.92 (d, 1H), 8.01 (d, 1H). MS (m/z): 215.09 ($M^+$). Anal.

**Table 1** Effect of catalyst type and amount of catalyst on the synthesis of compounds.

| Entry | Catalyst | Catalyst loading (mg) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | K-10 | 10 | 120 | 79 |
| 2 | | 25 | 120 | 83 |
| 3 | | 50 | 90 | 81 |
| 4 | ZMS-5 | 10 | 120 | 83 |
| 5 | | 25 | 90 | 85 |
| 6 | | 50 | 95 | 80 |
| 7 | SZ | 10 | 120 | 81 |
| 8 | | 25 | 90 | 92 |
| 9 | | 50 | 95 | 85 |

[a] Yields after isolation of products.

**Table 2** Effect of solvent on the reaction times and yields.

| Entry | Solvent | Time (min) | Yield (%)[a] |
|---|---|---|---|
| 1 | $H_2O$ | 180 | 55 |
| 2 | EtOH | 70 | 90 |
| 3 | MeOH | 85 | 75 |
| 4 | $CH_3CN$ | 110 | 70 |
| 5 | DCM | 100 | 65 |
| 6 | Toluene | 120 | 60 |

Reaction condition: 2-Amino acetophenone or benzophenone (2.0 mmol), α-methylene carbonyl compounds (2.0 mmol) in the presence of catalyst (25 mg) under reflux condition in various solvents.

[a] Yields after isolation of products.

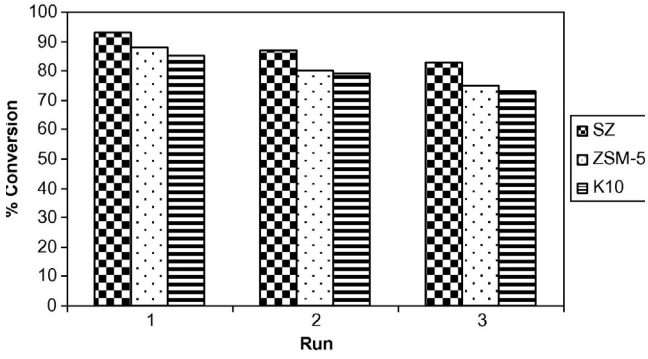



**Figure 1** The results obtained from catalyst reuse nano-crystalline sulfated zirconia (black bars), Zeolite (white bars) and Montmorrilonite K-10 (dash bars) in the quinoline formation.

Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.21; H, 5.86; N, 6.34.

*2.3.6. 1-(2,4-Dimethylquinolin-3-yl) ethanone (**4f**)*

Oil. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3064, 2957, 1714, 1618, 1583, 1375, 1223 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-d6): δ 2.52 (t, 3H), 2.56 (s, 3H), 3.62 (s, 3H), 7.43 (t, 1H), 7.61 (t, 1H), 7.92 (d, 1H), 7.98 (d, 1H); MS (m/z): 199.10 ($M^+$); Anal. Calcd for $C_{13}H_{13}NO$: C, 78.34; H, 6.58; N, 7.03. Found: C, 78.06; H, 6.38; N, 6.84.

*2.3.7. 9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (**6a**)*

Mp 132–134 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3061, 2958, 1714, 1610, 1563, 1348, 1172, 1067 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-d6): δ 2.15–2.20 (m, 2H), 2.65 (t, 2H), 3.12 (t, 2H), 7.28–7.71 (m, 8H), 8.03 (d, 1H); MS (m/z): 245.12 ($M^+$); Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.84; H, 5.78; N, 5.78.

*2.3.8. 9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (**6b**)*

Mp 136–138 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3063, 2951, 1611, 1573, 1481, 1226 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-d6): δ 1.75 (m, 2H), 1.83 (m, 2H), 2.55 (t, 2H), 2.65 (t, 2H), 3.16 (t, 2H), 7.15–7.45 (m, 8H), 7.98 (d, 1H); MS (m/z): 259.14 ($M^+$); Anal. Calcd for $C_{19}H_{17}N$: C, 88.03; H, 6.63; N, 5.40. Found: C, 87.77; H, 6.38; N, 5.18.

*2.3.9. 9-Methyl-2,3-dihydro-1H-cyclopenta[b]quinoline (**6c**)*

Mp 58–60 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3062, 2954, 1612, 1573, 1351, 1173 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-d6): δ 2.15–2.22 (m, 2H), 2.56 (s, 3H), 3.03 (t, 2H), 3.25 (t, 2H), 7.43–7.97 (m, 4H); MS (m/z): 183.11 ($M^+$); Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 84.94; H, 6.89; N, 7.32.

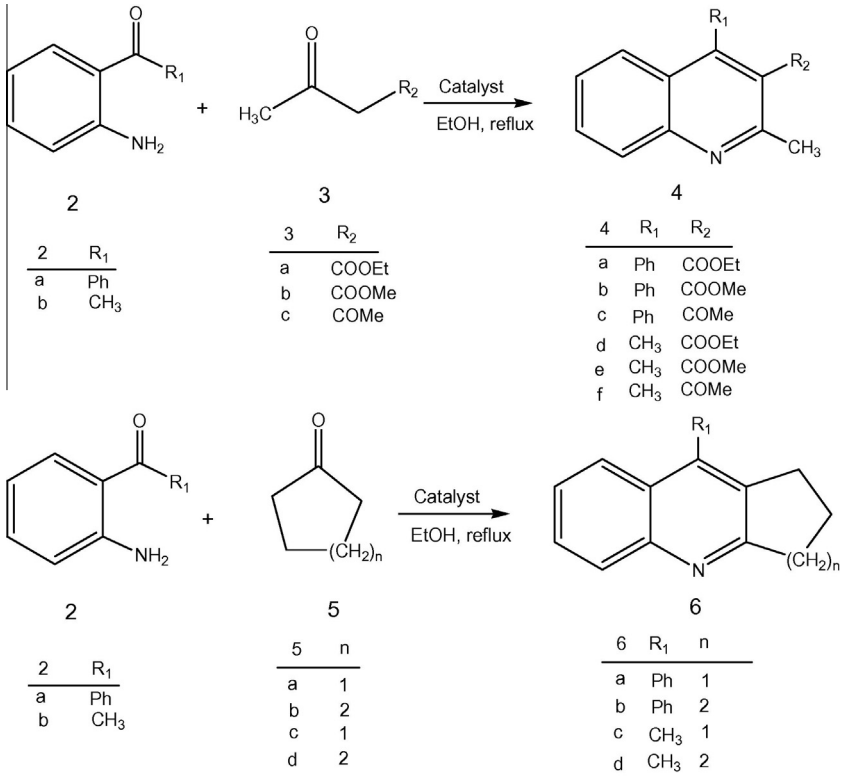
*2.3.10. 9-Methyl-1,2,3,4-tetrahydroacridine (**6d**)*

Mp 76–78 °C. FTIR (KBr, $cm^{-1}$) $\nu_{max}$: 3063, 2945, 1613, 1578, 1353, 1170 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-d6): δ 1.71–1.73 (m, 4H), 2.28 (s, 3H), 2.66 (t, 2H), 2.93 (t, 2H), 7.23–7.87 (m, 4H); MS (m/z): 197.21 ($M^+$); Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.98; H, 7.23; N, 7.02.

## 3. Results and discussion

In the reaction between 2-aminoaryl ketones and α-methylene carbonyl compounds to minimize the formation of byproducts and to achieve good yield of the desired product, the reaction is optimized by varying the amount of catalyst (10, 25 and 50 mg), the percentage yield of the product with 10, 25 and 50 mg of SZ as a catalyst are 81%, 92% and 85%, respectively (Table 1, entries 7–9). The same reaction when performed without catalyst for 6 h gave no product. When the catalyst content was increased to 50 mg, the product yield decreased to 85% (Table 1, entry 6). Therefore, it was found that the use of 25 mg of the catalyst was sufficient to promote the reaction, and greater amounts of the catalyst did not improve the yields.

We found that ethanol and 25 mg of zeolite catalyst and K-10 an efficient reaction medium in terms of reaction time as well as yield (Table 1, entries 1–6). It is noteworthy to mention that in the absence of catalyst, no product was found even

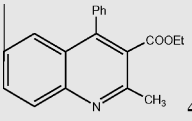
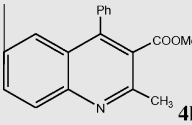
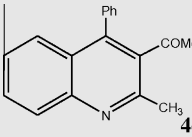
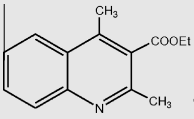
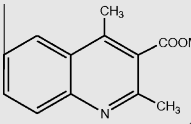
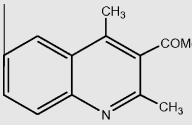
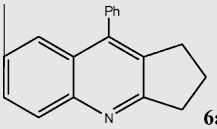
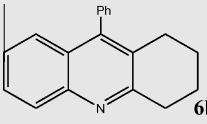
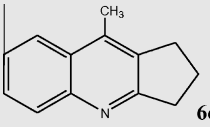
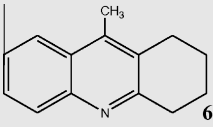



**Scheme 1** Friedländer synthesis of quinolines **4** and **6**.

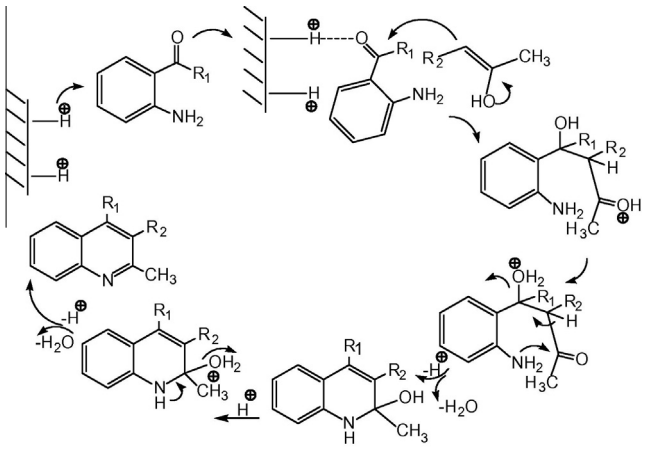
after 12 h. These results indicate that the catalyst exhibits a high catalytic activity in this transformation.

To optimize the reaction conditions, we first conducted the Friedländer condensation of 2-aminobenzophenone (**2a**) with ethyl acetoacetate (**3a**) to the desired quinoline in the presence of a catalytic amount of catalyst in different solvents such as EtOH, MeOH, $CH_3CN$, and toluene. (Table 2, entries 1–6). Reaction in toluene and dichloromethane (DCM) solvent gave low product yields even after 100 min and 120 min (Table 2, entries 5 and 6). Although the yields were moderate in case of methanol and acetonitrile under reflux condition (Table 2, entries 3 and 4).

**Table 3** Acid-catalzed synthesis of quinoline derivatives[a].

| Entry | Reactants | Products | Time (min)/yield (%)[b] | | | MP °C (lit.) | References |
|---|---|---|---|---|---|---|---|
| | | | Montmorrilonite K-10 | Zeolite | Nano-crystalline SZ | | |
| 1 | **2a**, **3a** |  **4a** | 120/70 | 110/84 | 90/92 | 100–102 [100–101] | Shaabani et al. (2008) |
| 2 | **2a**, **3b** |  **4b** | 120/75 | 95/82 | 90/90 | 86–88 [87–88] | Zhang et al. (2009) |
| 3 | **2a**, **3c** |  **4c** | 130/75 | 100/83 | 90/89 | 108–110 (112–113) | Shaabani et al. (2008) |
| 4 | **2b**, **3a** |  **4d** | 130/75 | 95/81 | 90/88 | oil (oil) | Zhang et al. (2009) |
| 5 | **2b**, **3a** |  **4e** | 120/75 | 95/80 | 85/88 | oil (oil) | Zhang et al. (2009) |
| 6 | **2b**, **3a** |  **4f** | 120/83 | 90/85 | 80/91 | oil (oil) | Zhang et al. (2009) |
| 7 | **2a**, **5a** |  **6a** | 120/75 | 100/81 | 90/90 | 132–134 (139–141) | Shaabani et al. (2008) |
| 8 | **2a**, **5b** |  **6b** | 120/70 | 110/78 | 90/88 | 136–138 (138–141) | Akbari et al. (2010) |
| 9 | **2a**, **5c** |  **6c** | 120/75 | 95/80 | 90/89 | 58–60 (60–61) | Akbari et al. (2010) |
| 10 | **2a**, **5d** |  **6d** | 120/73 | 100/78 | 90/86 | 76–78 (78–79) | Akbari et al. (2010) |

[a] The products were characterized by IR, $^1$H NMR, $^{13}$C NMR and mass spectroscopy.
[b] Isolated yields.



**Scheme 2** A plausible mechanism for the synthesis of quinolines by catalyst.

The best results were obtained when the reaction was carried out in ethanol at reflux 85 min in the presence of catalyst (Table 2, entry 2). Therefore, ethanol was selected as a solvent for this reaction. Although water is a desirable solvent for chemical reactions for reasons of cost, safety and environmental concerns, we found that using water in this reaction gave moderate yields of products under reflux condition after long reaction times.

After the completion of the reaction, the catalyst was separated by centrifugation, washed with doubly distilled water and acetone, and the centrifugate was treated with 6 M HCl (20 mL) and while being stirred vigorously. The aqueous solution finally obtained was extracted twice with ethyl acetate; the combined organic phase was washed with water and concentrated to precipitate the crude solid crystalline.

One of the most important advantages of heterogeneous catalysis over the homogeneous counterpart is the possibility of reusing the catalyst by simple filtration, without loss of activity. The recovery and reusability of the catalyst was investigated in the product formation. After completion of the reaction, the catalyst was separated by filtration, washed three times with 5 mL acetone, then with doubly distilled water several times and dried at 110 °C. Then the recovered catalyst was used in the next run. The results of three consecutive runs showed that the catalyst can be reused several times without significant loss of its activity (see Fig. 1).

A possible mechanism for the synthesis of quinolines using this method is shown in Scheme 2, based on the literature (Arcadi et al., 2003) and the obtained results.

Considering the reaction time and yield nano-crystalline SZ was found to be most effective. Subsequently a series of substituted quinolines were prepared following the same method using this catalyst (Scheme 1, Table 3).

A possible mechanism for the synthesis of quinolines using this method is shown in Scheme 2, based on the literature (Arcadi et al., 2006) and the obtained results.

## 4. Conclusion

In conclusion, a one-pot, mild, efficient, and environmentally benign protocol has been developed for the synthesis of, quinoline derivatives catalyzed by Montmorrilonite K-10, zeolite, nano-crystalline SZ in high yields. Compared to previously reported methods, Moreover, the mild reaction conditions, easy work-up, clean reaction profiles, lower catalyst loading and cost efficiency render this approach as an interesting alternative to the existing methods.

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