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An Efficient and Green Catalytic Method for Friedländer Quinoline Synthesis Using Tungstophosphoric Acid Included in a Polymeric Matrix

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Abstract: A new, efficient and green methodology for obtaining quinolines based on the use of tungstophosphoric acid included in a polymeric matrix of polyacrylamide is proposed (APTPOL60). The methodology involves the formation of polysubstituted quinoline compounds using a variety of 2-aminoaryl ketones and β-dicarbonyl compounds, in absolute ethanol as reaction solvent, and a temperature of 78 ºC. The catalyst efficiency is not compromised after its successive use in reactions, and no leaching was observed. Seven examples of quinolone derivatives were obtained with excellent yields (89%–99%). This is the first report about the use of a heteropolyacid included in a polymeric matrix as recyclable catalyst in the Friedländer synthesis of quinoline derivatives (molecules with biological activity potential).

Keywords: Quinolines, friedländer synthesis, tungstophosphoric acid, polymeric matrix, heterogeneous catalysts.

1. INTRODUCTION

Quinolines and their derivatives are very important biological compounds that occur in natural products [1]. Several quinoline derivatives have been found to have useful biological and pharmaceutical activities such as antimalarial [2], antihypertensive [3], antibacterial [4], anti-inflammatory [5], analgesic [6], antitumor [7], antiasthmatic [8], antiplatelet and tyrosine kinase inhibiting agents [9]. In addition, quinolones are valuable synthons used in a variety of nano- and meso-structures with electronic and photonic functions [10] and agrochemical applications [11]. Also, substituted quinolines have been employed in the study of bioorganic and bioorganometallic processes [12].

Because of their importance as substructures in a broad range of natural and semisynthetic products, significant efforts continue to be directed to the development of new and efficient procedures for quinolone synthesis. Various methods such as Doebner, Skraup, Conrad Limpach, Combes, Miller, Friedländer, and Pfitzinger methods have been developed for the preparation of quinilone derivatives [13].

Among these methods, Friedlnder annulation [14], an acid- or base-catalyzed condensation followed by a cyclodehydration between an aromatic 2-aminoaldehyde or ketone and a carbonyl compound containing a reactive α-methylene group, is one of the most simple and straightforward approaches for the synthesis of poly-substituted quinolones [15]. Bronsted acid and Lewis acids, such as hydrochloric acid, perchloric acid, sulfamic acid and oxalic acid, are known to promote this reaction [15, 16].

On the other hand, the preparation of organic compounds involving suitable processes has been

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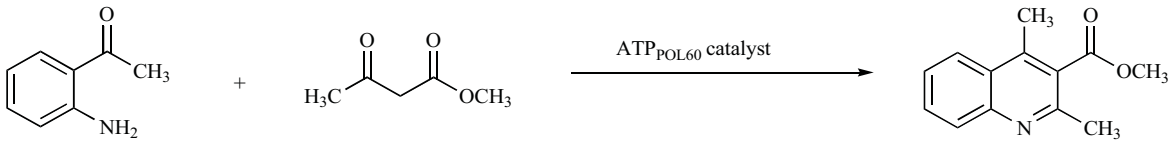


Scheme (1). Model reaction to quinoline synthesis.

investigated worldwide due to stringent environmental regulations. Inorganic solid-catalyzed organic reactions are achieving much importance due to the advantages of heterogeneous catalysis, such as simplified product isolation, mild reaction conditions, easy recovery and catalyst reuse, and reduction of waste by-products. In particular, catalysis by heteropolyacids (HPA) and related compounds is a field of increasing significance worldwide. Many developments have been carried out both in basic research and in fine chemistry processes [17-21].

Following up with the studies directed towards the development of highly expedient methods and the synthesis of diverse heterocyclic compounds, in this paper we report a new procedure for the synthesis of quinolines by Friedländer annulation, using tungstophosphoric acid included in a polymeric matrix as reusable catalyst (Scheme **1**).

2. EXPERIMENTAL

2.1. General

Chemicals were purchased from Aldrich, Fluka and Merck chemical companies and were freshly used after purification by standard procedures (distillation and recrystallization). All the reactions were monitored by TLC on precoated silica gel plates (254 mm). Flash column chromatography was performed with 230–400 mesh silica gel. All the yields were calculated from crystallized products. All the products were identified by comparison of physical data (mp, TLC and NMR) with those reported or with those of authentic samples prepared by the respective conventional methods using sulfuric acid as catalyst. Melting points of the compounds were determined in sealed capillary tubes and are uncorrected. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz instrument as $CDCl_3$ solutions, and the chemical shifts were expressed in δ units with Me_4Si (TMS) as the internal standard.

2.2. Catalyst Preparation

The catalyst (TPA_{Pol60}) was prepared following a procedure reported in the literature by us, and properly characterized [22]. The process for the synthesis of the catalyst described below: 7.5 ml of a solution by dissolving polyacrylamide (Aldrich, MW = 15 x 10^5) in a mixture of 180 ml of formamide and 7.5 ml of water was prepared. To the solution was added 5 g of ATP ($H_3PW_{12}O_{40}.23H_2O$, Fluka pa) dissolved in 12.5 ml of distilled water, stirring continuously until a homogeneous mixture was formed. In order to obtain spherical catalyst particles, the solution was placed in a 25 ml burette and allowed to drip slowly in concentrated hydrochloric acid (12 M) placed in a 1000 ml beaker. The spheres are separated for filtration, washed with distilled water, and then dried in at 70°C, 5 h. The relation between TPA and the polymeric matrix (polyacrylamide, PAM) in the catalyst was 60/40.

2.3. Representative Procedure for the Synthesis of Quinoline Derivatives

In a 10 mL reaction tube 2-aminoaryl ketone (1 mmol, 135 mg) and methyl acetoacetate (1.2 mmol, 115 mg) were thoroughly mixed in ethanol (5 mL), then the catalyst (100 mg) was added and the solution was refluxed for an appropriate time. The progress of the reaction was monitored by GC analysis and TLC. After completion of the reaction, the catalyst was filtered, and the organic layer was dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crude product 1, which was purified by silica gel recrystallization to give the pure product with a yield of 96 % (206 mg). All products 1-7 are known compounds, and they were characterized by melting point and ^{13}C-NMR and ^{1}H-NMR spectroscopy.

3.4. Catalyst Reuse

Stability tests of the catalysts were carried out running four consecutive experiments, under the

same reaction conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed with absolute ethanol (2 x 2 mL), dried under vacuum, and then reused.

3.5. Characterization of Synthesized Compounds

M.P. (o C)[Lit.]

Compound 1: Yield: 96 %; mp 76-78 °C (lit[23]. 77-78 °C); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.2 (CH_3-C4), 15.2 (CH_3-C2), 51.6 (CH_3O-), 123.8 (C3), 125.6 (C6), 126.2 (C4a), 127.9 (C8), 129.3 (C5), 129.7 (C7), 141.9 (C4), 147.5 (C8a), 154.2 (C2), 167 (C=O); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.60 (s, 3H, CH_3-C4). 2.72 (s, 3H, CH_3-C2), 3.81 (s, 3H, CH_3O-), 7.60-7.70 (m, 2H, H6, H7), 7.95 (d, 1H, J = 8 Hz, H8), 8.10 (d, 1H, J = 8 Hz, H5).

Compound 2: Yield: 90 %; mp 270-272 °C (lit[24]. 270-272 °C); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.1 (CH_3-C4), 15.5 (CH_3-C2), 23.7 (**CH_3**-CH_2O-) 60.8. (CH_3**CH_2**O-), 123.9 (C3), 125.6 (C6), 126.3 (C4a), 127.8 (C8), 129.4 (C5), 129.8 (C7), 141.8 (C4), 147.4 (C8a), 154.8 (C2), 168.5 (C=O); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.40 (t, 3H, J = 7 Hz, **CH_3**-CH_2O-), 2.61 (s, 3H, CH_3-C4). 2.73 (s, 3H, CH_3-C2), 4.45 (q, J = 6 Hz, 2H, CH_3**CH_2**O-), 7.50-7.70 (m, 2H, H6, H7), 7.98 (d, 1H, J = 8 Hz, H8), 8.11 (d, 1H, J = 8 Hz, H5).

Compound 3: Yield: 92 %; mp 99-101 °C (lit[24]. 98-99 °C); ^{13}C NMR (50 MHz, $CDCl_3$): δ ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.9 (**CH_3**-CH_2-O), 24.0 (CH_3-C2), 61.5 (CH_3**CH_2**O-), 125.4 (C4a), 126.6 (C3), 126.7 (C5), 126.37 (C6), 128.4 (C2′), 128.7 (C8), 129.1 (C3′), 129.6 (C4′), 130.4 (C7), 136.0 (C1′), 146.4 (C4), 147.9 (C8a), 154.8 (C2), 168.3 (C=O); ^{1}H-NMR (200 MHz, $CDCl_3$): 0.95 (t, 3H, J = 7.3 Hz, (**CH_3**-CH_2O-), 2.80 (s, 3H, CH_3-C2), 4.05 (q, 2H, J = 7.3 Hz, CH_3**CH_2**O-), 7.24-7.76 (m, 8H, H2′, H3′, H4′, H6, H7, H8), 8.07, (d, 1H, J = 8.1 Hz, H5).

Compound 4: Yield: 96 %; mp 130-132 °C (lit[25]. 131-133 °C), ^{13}C NMR (50 MHz, $CDCl_3$): δ ^{13}C NMR (200 MHz, $CDCl_3$): δ 24.1 (CH_3-C2), 64.2 (CH_3O-), 125.3 (C4a), 126.4(C3), 128.6(C5) , 128.7 (C6), 129.1 (C2′), 129.6 (C4), 130.9 (C3′), 131.4 (C8), 132.6 (C7), 135.3 (C1′), 145.7 (C1), 146.5 (C8a), 155.3 (C2), 168.3 (C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.77 (s, 3H, CH_3-C2), 4.11 (s, 3H, OCH_3) , 7.30-7.69 (m, 7H, H2′, H3′, H4′, H7, H8), 8.11 (d, 1H, J= 9.0 Hz, H5).

Compound 5: Yield: 95 %; mp 98-100 °C (lit[25]. 98-100 °C); ^{13}C NMR (50 MHz, $CDCl_3$): δ ^{13}C NMR (200 MHz, $CDCl_3$): δ 13.8(**CH_3**-CH_2-O), 24.0 (CH_3-C2), 61.7 (CH_3**CH_2**O-), 125.4 (C4a), 126.2(C3), 128.4(C5) , 128.6 (C6), 129.0 (C2′), 129.5 (C4), 130.8 (C3′), 131.3 (C8), 132.5 (C7), 135.2 (C1′), 145.6 (C1), 146.3 (C8a), 155.2 (C2), 168.3 (C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, 3H, J= 7.1 Hz), 2.77 (s, 3H), 4.05 (q, 2H, J= 7.1 Hz), 7.28-7.67 (m, 7H, H2′, H3′, H4′, H7, H8), 8.01 (d, 1H, J= 9.0 Hz, H5).

Compound 6: Yield: 89 %; mp 108-110 °C (lit[26]. 108-110 °C); ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.3 (CH_3C2), 125.5 (C4a), 126.5(C5), 126.7(C6), 128.3(C2′), 128.5(C8), 128.7 (C3′′), 129.2(C3′), 129.5(C4′), 130.3 (C2′), 130.4(C3), 132.7(C7), 133.8(C4′′), 135.1 (C1′), 137.5(C1′′), 146.0(C4), 148.4(C8a), 154.6(C2), 197.3 (C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.61 (s, 3H), 7.17-7.77 (m, 13 H), 8.15 (d, 1H, J= 8.3 Hz).

Compound 7: Yield: 99 %; mp 210-211 °C (lit[25]. 209-211 °C); ^{13}C NMR (50 MHz, $CDCl_3$): δ ^{13} 24.2(CH_3C2), 123.9 (C4a), 125.2(C5), 128.5(C6), 128.7(C2′), 128.8(C8), 129.5(C3′′), 130.1 (C3′), 130.8(C4′), 131.2(C2′), 132.7(C3), 133.5(C7), 133.9(C4′′), 134.4(C1′), 137.1(C1′′), 145.0(C4), 146.5(C8a), 155.3(C2), 197.9(C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.62 (s, 3H), 7.15-7.72 (m, 12 H), 8.07 (d, 1H, J= 8.4 Hz).

3. RESULTS AND DISCUSSION

Initially, the reaction of 2-aminoacetophenone and methyl acetoacetate was chosen as a model for finding the optimization conditions and obtaining very good yields of the desired product (Scheme **1**). From this point onwards, different conditions were checked for the reaction, such as temperature, time or calcination temperature of the catalyst, and in all cases, absolute ethanol was used as solvent. In a blank experiment, 2-aminoacetophenone (1 mmol) and methyl acetoacetate (1.2 mmol) were thoroughly mixed in absolute ethanol (5 mL), and the solution was refluxed (78 ºC) for the appropriate time. The results indicate that without the presence of catalyst, the quinoline yields were low (Table **1**. Entry 1: 5 h, traces, and Entry 2: 24 h, 10%).

Then the reaction was monitored by TLC and GC analysis at different temperatures ranging from 25 to 78 ºC, using 100 mg of the catalyst. Our re-

Table 1. APT_{POL60}-catalyzed reactions of 2-aminoacetophenone and methyl acetoacetate.

Entry	Temperature (ºC)	Time (h)	Catalyst calcination temperature: (ºC)	Yields (%)[a]
1[b]	78	5	25	-
2[b]	78	24	25	10
3	25	24	25	21
4	55	24	25	61
5	78	24	25	97
6	78	15	25	93
7	78	10	25	91
8	78	5	25	90
9	78	1	25	44
10	78	24	100	85
11	78	24	200	40
12	78	24	300	32
13[c]	78	24	25	97
14[c]	78	24	25	98

[a] Yields % of pure compounds, [b] Reaction without catalyst, [c] First and second reuse respectively

sults indicate that after stirring the reaction mixture at 25 ºC for 24 h, the yields of the corresponding product was low (Table **1**, Entry 3: 21%). The next experiments were performed at 55 and 78 ºC respectively, and the obtained yields were 61% and 97% (Table **1**, Entries 4 and 5). Therefore, 78 ºC was selected as the reaction temperature for all further reactions.

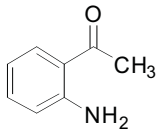
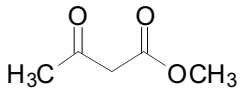
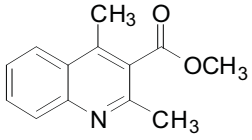
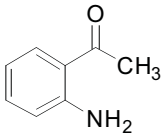
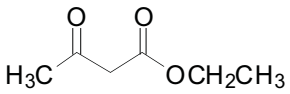
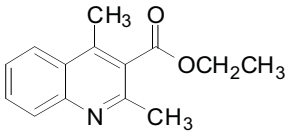
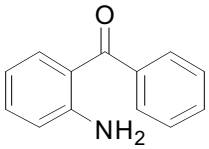
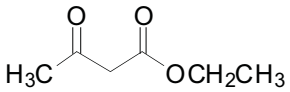
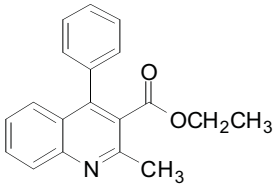
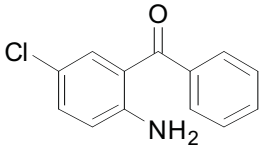
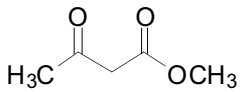
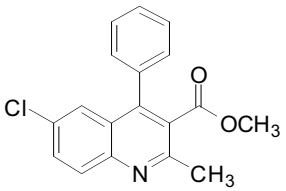
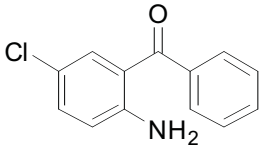
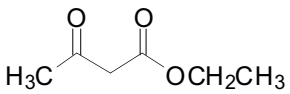
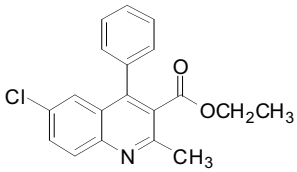
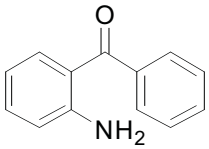
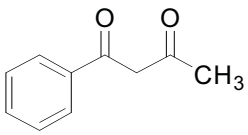
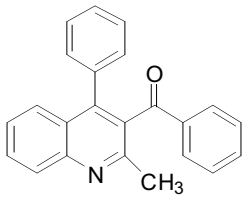
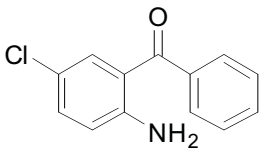
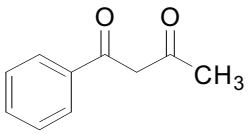
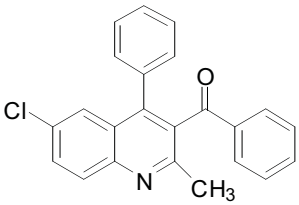
The reaction time was also tested at the selected optimal temperature of 78 ºC, using five different times of 1, 5, 10, 15 and 24 h (Table **1**, Entries 5–9). A good yield was obtained at 5 h of reaction (Table **1**, Entry 7: 91%), without considerable variation at longer reaction times such as 24 h (Table **1**, Entry 5: 97%).

Similarly, we studied the effect of the calcination temperature of the catalyst on the reaction activity. The calcination temperatures were: 25, 100, 200 and 300 ºC, respectively. A continuous decline in the conversion with increasing calcination temperature can be seen, in accordance with the decrease in the number of sites confirmed by potentiometric titration (reported result in reference 22), (Table **1**, Entries 10–12).

The reusability of the catalyst was checked by separating the catalyst from the reaction mixture by simple filtration, washing with absolute ethanol, and drying in a vacuum oven at room temperature for 4 h prior to its reuse in subsequent reactions without significant loss in product yields (Table **1**, Entries 13–14).

In order to evaluate the possible catalyst solubilization, an additional test was performed. The catalyst sample was refluxed in absolute ethanol for 24 h, filtered at high temperature and dried in vacuum till constant weight. The activity of the so-treated catalyst was the same as that of the fresh catalyst (98% yields in 24 h). The refluxed absolute ethanol was used as solvent for attempting the reaction without adding the catalyst. After 24 h only traces of quinoline were detected, and the starting material was quantitatively recovered.

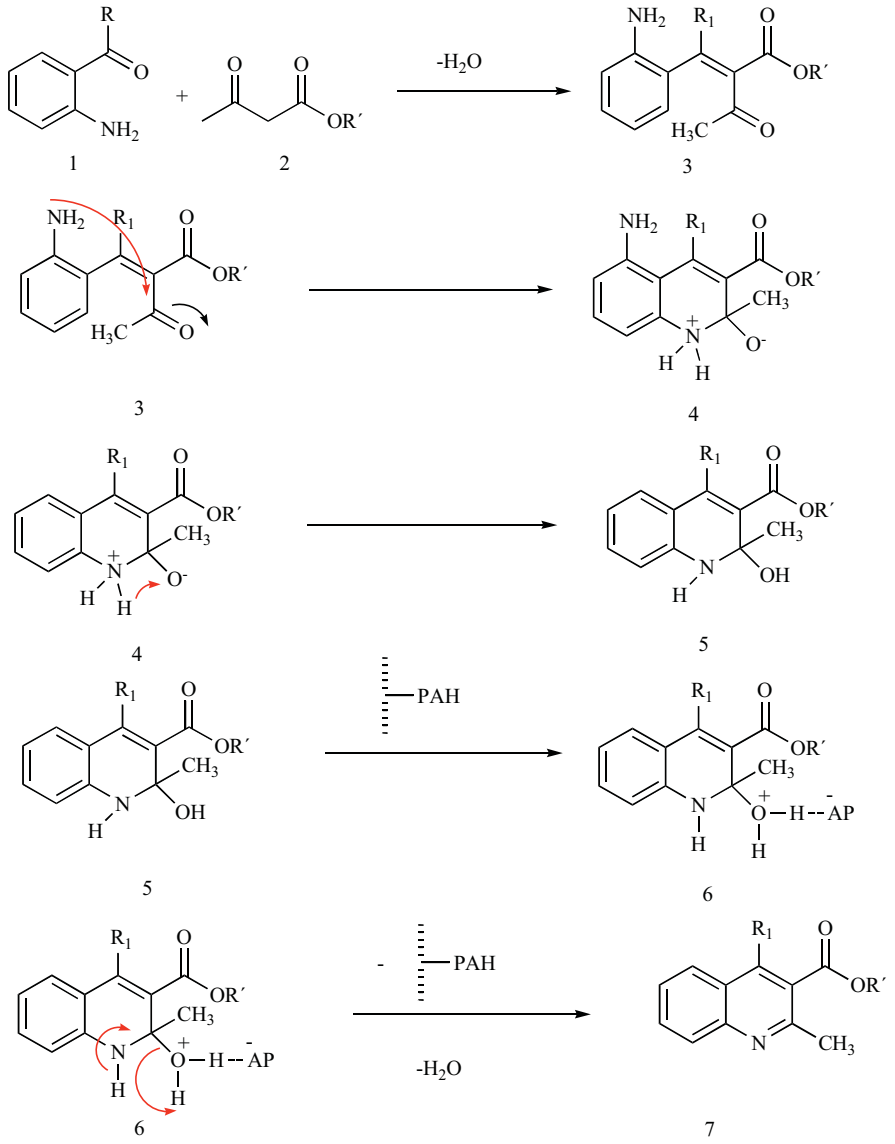
Table 2. Preparation of quinoline derivatives by the reaction 2-amino-ketones and β-dicarbonyl compounds using APT_{POL60} catalyst.

Entry	2-Aminoketones	β-Dicarbonyl Compounds	Quinolines	Yields (%)[b]
1				96
2				90
3				92
4				96
5				95
6				89
7				99

[a] Reaction conditions: 2-aminoaryl ketone (1-mmol), α–methylene carbonyl compound (1.2 mmoles), solvent: absolute ethanol 5 ml, catalyst: APT_{POL60}, temperature: 78 ºC, time: 24 h.

[b] Yields of recrystallized product

Finally, other test to verify the catalysis leaching was performed. Before the reaction is done (1 h.), the reaction is stopped and the catalyst filtered off. Then, the reaction are continued for 5 h, and the yield was similar to obtained in 1 h. (44 vs 46 % respectively). The experiment confirm that the catalyst have not leached into the reaction solution.



Scheme (2). Plausible reaction mechanism for the formation quinolone derivatives.

The scope and generality of this procedure is illustrated by various examples using different amino ketones and β-dicarbonyl compounds, and the results are summarized in Table **2**. According to the results of optimization experiments for the reaction conditions, the reactions were carried out in the presence of catalyst (100 mg) at 78 ºC using absolute ethanol as solvent reaction, and the corresponding quinolines were obtained in excellent yields (Table **1**, Entries 1–7).

The workup and catalyst recovery are simple and all reactions have very high selectivity toward the corresponding quinolones. The TLC analysis shows only trace amounts of by-products. After completion of the reaction (monitored by TLC, eluent; EtOAc: *n*-hexane mixtures), the catalyst was separated by centrifugation and washed with absolute ethanol. After evaporation of absolute ethanol, the crude product was easily isolated in almost pure state. Further purification was performed by recrystallization from ethanol. All of the yields reported in Table **2** are isolated yields after recrystallization. The products are known compounds and were characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The characterization details of selected compounds are shown in the experimental methods section.

A plausible mechanism for the synthesis of quinolones using this methodology is shown in Scheme (**2**). The mechanism involves the condensation of 2-aminoacetophenone with the corresponding β-dicarbonyl compound to form the in-

termediary 5, and then cyclodehydratation catalyzed by TPA supported catalyst gives the corresponding quinoline 7.

CONCLUSION

In this paper we have demonstrated that tungstophosphoric acid could be highly dispersed on the surface of a polymeric matrix based on polyacrylamide. The materials can be used as solid acid catalyst for the Friedländer synthesis of quinolines. A mild, efficient and environmentally benign methodology has been developed for the synthesis of quinolone derivatives in high yields. Moreover, the mild reaction conditions, easy workup, and clean reaction profiles make this approach an alternative to existing methods. The solid acid catalysts can be recovered and reused at least two times with negligible loss in their activity. Further investigations into the scope and other applications of tungstophosphoric acid included in a polymeric matrix are now in progress in our laboratory and will be reported in due course.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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