Preyssler heteropolyacid supported on nano-SiO$_2$, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$: a green and reusable catalyst in the synthesis of polysubstituted quinolines

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Synthesis of polysubstituted quinolines in the presence of silica-supported Preyssler nanoparticles (**SPNP**), H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$, Preyssler H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] and Keggin heteropolyacids, H$_3$PW$_{12}$O$_{40}$, H$_7$[PMo$_8$V$_4$O$_{40}$], H$_6$[PMo$_9$V$_3$O$_{40}$], H$_5$[PMo$_{10}$V$_2$O$_{40}$], H$_4$[PMo$_{11}$VO$_{40}$], H$_3$[PMo$_{12}$O$_{40}$] as catalyst under aqueous conditions is described. The best conditions were observed using Preyssler and silica-supported Preyssler nanoparticles as catalysts. The catalyst is recyclable and reusable.

Keywords: Nano-SiO$_2$-supported; Preyssler; Heteropolyacids; Polysubstituted quinoline; Quinolines; Catalyst

INTRODUCTION

The synthesis of quinoline derivatives has been considered of great interest to organic chemists owning to its wide range of biological and pharmaceutical properties such as anti-malarial, anti-inflammatory, anti-asthmatic, anti-bacterial, anti-hypertensive and tyrosine kinase inhibiting agents [1]. In addition, quinolines are valuable synthones used for the preparation of nano- and meso-structures with enhanced electronic and photonic properties [2]. Consequently, various methods were developed for the synthesis of quinoline derivatives. The Friedländer annulation has been catalyzed by both acids and bases. Under base catalyzed conditions 2-aminobenzophenone fails to react with simple ketones such as cyclohexanone or α-ketoesters [3]. Brønsted acids like hydrochloric acid, sulphuric acid, *p*-toluene sulphonic acid, phosphoric acids are widely used as catalysts for this conversion [4]. However, many of these classical methods require high temperatures, longer reaction times, drastic conditions, and low yields. Therefore, new catalytic systems are continuously explored. As a result, recently Lewis acids such as Ag$_3$PW$_{12}$O$_{40}$, Y(OTf)$_3$, FeCl$_3$ or Mg(ClO$_4$)$_2$, NaAuCl$_4$ .2H$_2$O, SnCl$_2$ or ZnCl$_2$, Bi(OTf)$_3$, NaF, SnCl$_2$.2H$_2$O, CeCl$_3$.7H$_2$O, ZnCl$_2$, and I$_2$ have been used in presence of organic solvent for the synthesis of quinolines [5]. Also, microwave irradiations have been used for the synthesis of these compounds [6]. Quinolines are very important compounds because of their wide

occurrence in natural products [7] and their interesting biological activities such as antimalarial, anti-inflammatory agents, antiasthmatic, antibacterial, antihypertensive, and tyrosine kinase inhibiting agents [8]. In addition, quinolines have been used for the preparation of nanostructures and polymers that combine enhanced electronic, optoelectronic or non-linear optical properties with excellent mechanical properties [9]. As a result of their importance as substructures in a broad range of natural and designed products, significant effort continues to be directed toward the development of new quinoline-based structures and new methods for their construction [10]. Synthesis of the corresponding heterocyclic compounds could be of interest from the viewpoint of chemical reactivity and biological activity. Heteropolyacids are widely used in variety of acid catalyzed reactions [11]. Heteropolyacids as solid acid catalysts are green with respect to corrosiveness, safety, quantity of waste and separability and it is well known that the use of heteropolyacid catalysts for organic synthesis reactions can give a lot of benefits. One of the unique features that make solid heteropoly acids economically and environmentally attractive is their stability and bronsted acidity.

The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds has attracted much attention, particularly in the last two decades [12]. Polyoxametalates (POMs) are a class of molecularly defined organic metal-oxide clusters; they possess intriguing structures and

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diverse properties [12]. These compounds exhibit high activity in acid-base type catalytic reactions, hence they are used in many catalytic areas as homogeneous and heterogeneous catalysts. Numerous attempts to modify the catalytic performance of heteropolyacids, such as supporting them on mobile composition of matter (MCM), silica gel and others have been reported [13]. The application of Preyssler catalysts is highly limited and only a few examples of catalytic activity have been reported [14]. The important advantages of this heteropolyacid are: strong Brønsted acidity with 14 acidic protons, high thermal stability, high hydrolytic stability (pH 0–12), reusability, safety, quantity of waste, ease of separation, corrosiveness, high oxidation potential, and application as a green reagent along with an exclusive structure. All these characteristics have attracted much attention in the recent literature [15,16]. Over the last decade, due to the unique properties of nanoparticles along with their novel properties and potential applications in different fields [17], the synthesis and characterization of catalysts with lower dimension has become an active topic of research. As the particle size decreases, the relative number of surface atoms increases, and thus activity increases. Moreover, due to quantum size effects, nanometre-sized particles may exhibit unique properties for a wide range of applications [18]. In spite of extensive investigations on Keggin-type nanocatalysts [19,20], the synthesis of Preyssler-type nanocatalysts has been largely overlooked. Recently we have explored the application of a Preyssler catalyst in various organic reactions.

EXPERIMENTAL

Instrument and chemical materials

All Chemicals were of analytical grade and purchased from Aldrich and Fluka companies. ^1H NMR spectra were recorded on a FT NMR Bruker 400 MHz spectrometer at 298 K. Melting points were recorded on an Electrothermal type 9100 melting point apparatus andwere uncorrected. Chemical shifts were reported in ppm (δ-scale) relative to internal standard TMS (0.00 ppm) and using CDCl₃ as solvent a reference. IR spectra were obtained with a Buck 500 scientific spectrometer (KBr pellets). The products were identified by comparison of their mp., IR and NMR spectra with those of authentic samples. Elemental analyses were preformed on Perkin Elmer 2400, series II microanalyzer.

Synthesis of SiO2 Nanoparticles

The materials used in this work include tetraethyl orthosilicate (TEOS) (Merck, 98%) as the SiO₂ precursor. Besides the main precursor, nitric acid (65%) and double distilled water were used for peptization and solvent, respectively. The sol–gel precursor solution was obtained by mixing tetraethyl orthosilicate (TEOS) and ethanol with specific molar ratios of ethanol to TEOS. The mixture was stirred using magnetic stirring.

Catalyst Preparation

Preyssler catalyst, $H_{14}[NaP_5W_{30}O_{110}]$ was prepared by passage of a solution of the potassium salt (30 mL) in water (30 mL) through a column (50 cm × 1 cm) of Dowex 50w×8 in the H⁺ form. The eluent was evaporated to dryness under vacuum [21,22].

Catalyst Synthesis Procedure

To a solution of the surfactant, sodium bis(2-ethylhexyl) sulphosuccinate, in cyclohexane (0.2 mol L⁻¹), a solution of Preyssler acid in a specified amount of water was added. The molar ratio of water to surfactant was selected to be 3, 5 and 7. Tetraethoxysilane (TEOS) was then added to the micro-emulsion phase. After mixing for various times (8, 12, 18, 25 and 30 h) at room temperature, dispersed Preyssler acid/SiO₂ nanostructures were centrifuged and the particles were rinsed with acetone (4 times) and dried in a vacuum oven. The optimum ratio of water to surfactant was 3:1 and the optimum time was 30 h. The catalysts of $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_7[PMo_8V_4O_{40}]$ and Wells-Dawson, $H_6[P_2W_{18}O_{62}]$ were prepared in according to the literature [23-33]. $H_6[P_2W_{18}O_{62}]$, $H_7[PMo_8V_4O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_4[PMo_{11}VO_{40}]$ and $H_3[PMo_{12}O_{40}]$ were prepared according to the literatures [30-34]. The integrity of the synthesized heteropolyacids has been proven by comparing of spectral data with those reported in literatur [35-38].

General experimental procedure

Preparation of 1-(2-methyl-4-phenylquinolin-3-yl)ethanone and ethyl 2-methyl-4-phenylquinoline-3-carboxylate derivatives:

A mixture of 2-aminoaryl ketone (1.0 mmol), α-methylene ketone (1 mmol) and heteropolyacid as catalyst (0.05 mmol) and water (1.0 mL) was stirred at room temperature for the specified time (Table 2). The progress of the reaction was

monitored by TLC. At the end of the reaction, the catalyst was filtered, washed with dichloromethane, dried at 130 °C for 1 h, and re-used in another reaction. The recycled catalyst was used for five reactions without observation of an appreciable lost in its catalytic activities.

Selected spectra data:

Methyl 2,4-dimethyl quinoline-3-carboxylate (4b): IR (neat, cm^{-1}): 1731, 1612; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.05 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 3.61 (s, 3H), 2.70 (s, 3H), 2.65 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.6, 154.5, 147.0, 141.2, 129.7, 128.9, 127.7, 126.3, 125.8, 123.7, 52.6, 23.9, 15.7; Anal. Calcd for C$_{13}$H$_{13}$NO$_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.40; H, 6.15; N, 6.58. HRMS (EI) Calcd. for C$_{13}$H$_{13}$NO$_2$ [M]$^+$, 215.1003, Found 215.1005;

Methyl 4-(2-chlorophenyl)-2-methylquinoline-3-carboxylate (4c): IR (KBr, cm^{-1}): 1725, 1612; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 7.96 (m, 8H), 3.63 (s, 3H), 2.75 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.6, 154.4, 146.9, 141.5, 133.3, 130.2, 129.8, 129.5, 128.8, 128.5, 128.1, 127.7, 127.1, 126.5, 126.1, 125.3, 52.6, 23.9; Anal. Calcd for C$_{18}$H$_{14}$ClNO$_2$: C, 69.35; H, 4.53; N, 4.49. Found: C, 69.26; H, 4.61; N, 4.59. HRMS (EI) Calcd. for C$_{18}$H$_{14}$ClNO$_2$ [M]$^+$, 311.1003, Found 311.1007;

Methyl 6-chloro-2,4-dimethylquinoline-3-carboxylate (4d): IR (KBr, cm^{-1}): 1726, 1615; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.12 (d, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 3.62 (s, 3H), 2.75 (s, 3H), 2.65 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.5, 154.4, 146.2, 135.5, 132.6, 130.3, 129.4, 128.5, 127.7, 124.9, 52.8, 24.4, 16.6; Anal. Calcd for C$_{13}$H$_{12}$ClNO$_2$: C, 62.53; H, 4.84; N, 5.61. Found: C, 62.47; H, 4.92; N, 5.52. HRMS (EI) Calcd. for C$_{13}$H$_{12}$ClNO$_2$ [M]$^+$, 249.1003, Found 249.1008;

Methyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (4e): IR (KBr, cm^{-1}): 1735, 1587; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.04 (d, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.0 Hz, 1H), 7.50 (m, 4H), 7.34 (m, 2H), 3.57 (s, 3H), 2.76 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.2, 154.9, 148.2, 145.5, 135.0, 132.1, 131.0, 130.4, 129.4, 128.9, 128.4, 127.5, 125.7, 125.3, 52.5, 24.8; Anal. Calcd for C$_{18}$H$_{14}$ClNO$_2$: C, 69.35; H, 4.53; N, 4.49. Found: C, 69.29; H, 4.48; N, 4.41. HRMS (EI) Calcd. for C$_{18}$H$_{14}$ClNO$_2$ [M]$^+$, 311.1002, Found 311.1004;

Methyl 6-chloro-4-(2-chlorophenyl)-2-methyl-quinoline-3-carboxylate (4f): IR (KBr, cm^{-1}): 1733,

1606; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.06 (d, *J* = 9.2 Hz, 1H), 7.49 (m, 6H), 3.56 (s, 3H), 2.78 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.1, 154.7, 139.5, 135.5, 134.6, 133.4, 132.4, 130.5, 129.8, 129.1, 128.7, 128.3, 128.0, 127.5, 126.5, 125.7, 52.5, 23.9; Anal. Calcd for C$_{18}$H$_{13}$Cl$_2$NO$_2$: C, 62.45; H, 3.78; N, 4.05. Found: C, 62.38; H, 3.67; N, 4.10. HRMS (EI) Calcd. for C$_{18}$H$_{13}$Cl$_2$NO$_2$ [M]$^+$, 345.0005, Found 345.1008;

Methyl 6-nitro-2,4-dimethylquinoline-3-carboxylate (4g): IR (KBr, cm^{-1}): 1736, 1615; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.45 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 3.65 (s, 3H), 2.76 (s, 3H), 2.65 (s, 3H), ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.4, 154.5, 148.4, 135.5, 132.7, 130.5, 129.6, 128.6, 127.5, 125.3, 52.7, 24.3, 16.8; Anal. Calcd for C$_{13}$H$_{12}$N$_2$O$_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.91; H, 4.46; N, 10.66. HRMS (EI) Calcd. for C$_{13}$H$_{12}$N$_2$O$_4$ [M]$^+$, 260.1006, Found 260.1008;

Methyl 2-methyl-6-nitro-4-phenylquinoline-3-carboxylate (4h): IR (KBr, cm^{-1}): 1731, 1620, 1525; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 7.95 (m, 8H), 3.65 (s, 3H), 2.72 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.4, 155.2, 148.5, 145.7, 135.5, 132.5, 131.0, 130.6, 129.4, 128.9, 128.6, 127.8, 125.5, 124.7, 52.6, 24.9; Anal. Calcd for C$_{18}$H$_{14}$N$_2$O$_4$: C, 67.08; H, 4.38; N, 8.69. Found: C, 66.97; H, 4.67; N, 8.60. HRMS (EI) Calcd. for C$_{18}$H$_{14}$N$_2$O$_4$ [M]$^+$, 322.1002, Found 322.1006;

Methyl 4-benzyl-2-methylquinoline-3-carboxylate (4i): IR (KBr, cm^{-1}): 1725, 1567; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.05 (d, *J*= 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.30 (m, 5H), 3.97 (s, 2H), 3.54 (s, 3H), 2.60 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.2, 154.6, 147.4, 141.5, 131.2, 129.7, 128.8, 128.5, 128.2, 127.9, 127.7, 126.6, 126.2, 124.3, 51.9, 37.7, 23.6; Anal. Calcd for C$_{19}$H$_{17}$NO$_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.24; H, 5.82; N, 4.97. HRMS (EI) Calcd. for C$_{19}$H$_{17}$NO$_2$ [M]$^+$, 291.1002, Found 291.1006;

Methyl 4-benzyl-6-chloro-2-methylquinoline-3-carboxylate (4j): IR (KBr, cm^{-1}): 1725, 1580; ^{1}H-NMR (400 MHz, CDCl$_3$, δ/ppm): 8.06 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.32 (m, 2H), 7.20 (m, 3H), 3.96 (s, 2H), 3.62 (s, 3H), 2.65 (s, 3H); ^{13}C-NMR (400 MHz, CDCl$_3$, δ/ppm): 168.6, 154.2, 146.5, 135.8, 132.5, 131.6, 130.4, 129.4, 128.9, 128.4, 128.2, 127.9, 127.6, 125.6, 52.4, 37.8, 24.4; Anal. Calcd for C$_{19}$H$_{16}$ClNO$_2$: C, 70.05; H, 4.95; N, 4.30. Found: C, 69.86; H, 4.87;

N, 4.38. HRMS (EI) Calcd. for $C_{19}H_{16}ClNO_2$ [M]⁺, 325.1002, Found 325.1007;

Methyl 4-benzyl-2-methyl-6-nitroquinoline-3-carboxylate (4k): IR (KBr, cm⁻¹): 1733, 1619; ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 8.44 (d, J= 8.4 Hz, 1H), 7.85 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.36 (m, 5H), 4.01 (s, 2H), 3.64 (s, 3H), 2.65 (s, 3H); ¹³C-NMR (400 MHz, CDCl₃, δ/ppm): 168.6, 154.5, 148.6, 135.1, 133.1, 131.4, 130.7, 129.5, 129.2, 128.6, 128.2, 127.9, 127.8, 126.1, 52.7, 37.9, 24.8; Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.80; N, 8.33. Found: C, 67.72; H, 4.73; N, 8.40. HRMS (EI) Calcd. for $C_{19}H_{16}N_2O_4$ [M]⁺, 336.1002, Found 336.1004;

1-(2-methyl-4-phenylquinolin-3-yl)ethanone (3q): IR (KBr, cm⁻¹): 3027, 2963, 1708, 1615, 1573, 1480, 705; ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 1.80 (s, 3H), 2.02 (s, 3H), 7.12 (m, 2H), 7.23 (t, J = 8.4 Hz, 1H), 7.26 (m, 3H), 7.30 (d, J = 8.6 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H); ¹³C-NMR (400 MHz, CDCl₃, δ/ppm): 23.2, 29.1, 31.4, 124.5, 125.4, 126.0, 128.1, 128.4, 129.6, 134.8, 147.0, 153.1, 205.5; Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.78; N, 5.36. Found: C, 82.71; H, 5.80; N, 5.33. HRMS (EI) Calcd. for $C_{18}H_{15}NO$ [M]⁺, 261.1004, Found 261.1009;

1-(6-chloro-2-methyl-4-phenylquinolin-3-yl) ethanone (4l): IR (KBr, cm⁻¹): 3030, 2962, 1702, 1606, 1569, 1485, 909, 695; ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 1.91 (s, 3H), 2.62 (s, 3H), 7.32 (m, 2H), 7.56 (m, 5H), 7.92 (d, J = 8.7 Hz, 1H); ¹³C-NMR (400 MHz, CDCl₃, δ/ppm): 23.5, 31.7, 124.6, 125.7, 128.6, 129.2, 129.8, 130.7, 132.4, 134.5, 135.6, 142.8, 145.8, 153.8, 204.7; Anal. Calcd for $C_{18}H_{14}ClNO$: C, 73.09; H, 4.77; N, 4.73. Found: C, 73.05; H, 4.74; N, 4.77. HRMS (EI) Calcd. for $C_{18}H_{14}ClNO$ [M]⁺, 295.1000, Found 295.1006;

RESULTS AND DISCUSSION

Herein we wish to report the catalytic ability of this catalyst in the synthesis of Polysubstituted Quinolines by the reaction of a variety of α-methyleneketones and or 2-aminoaryl ketones and dimedones under mild reaction conditions with the use of heteropolyacids (HPAs) as a catalyst in the synthesis of quinolines with excellent yields. The effects of various parameters such as solvent, catalyst type, temperature (under relux and room temperature) and times of the reactions were studied.

Using the best conditions reported in Table 1, we then continued to study the reaction by using variety of 2-aminoaryl and α-methylene ketones respectively. The results were summarized in Table 1 indicating that both cyclic and acyclic ketones underwent smooth reaction with 2-aminoaryl ketones to give high yields of products. The present protocol is highly effective for substituted 2-aminoaryl ketones such as 2-aminobenzophenone and 2-amino-5-chlorobenzophenone. In general, the yields of the quinoline dervetives were high. It is noteworthy to mention that the method is clean and free form side reactions which normally observed under basic conditions.
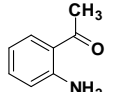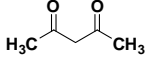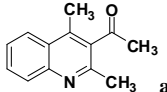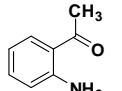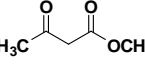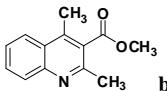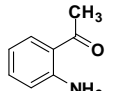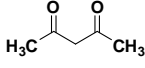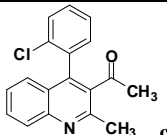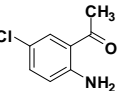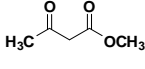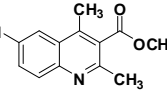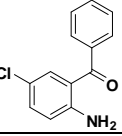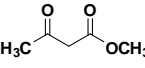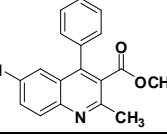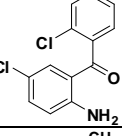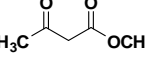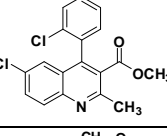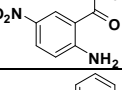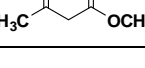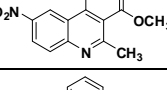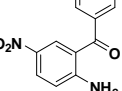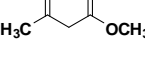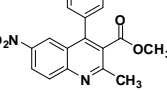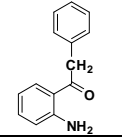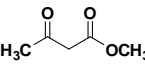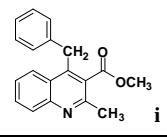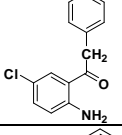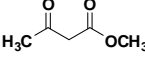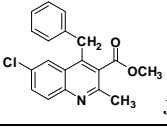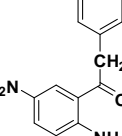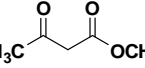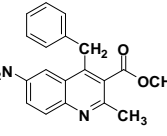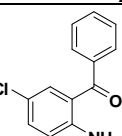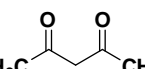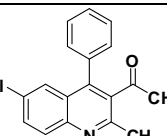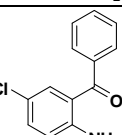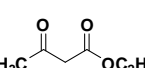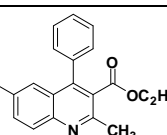
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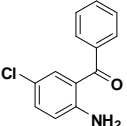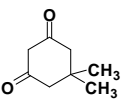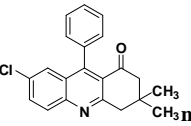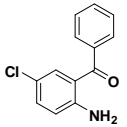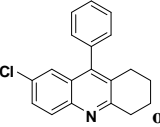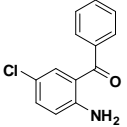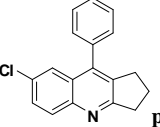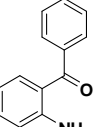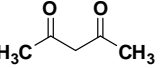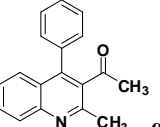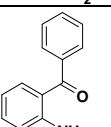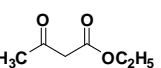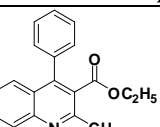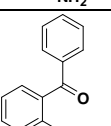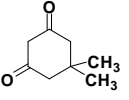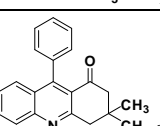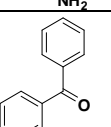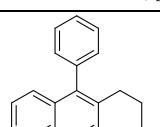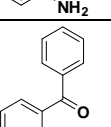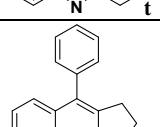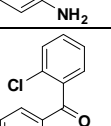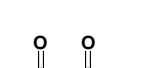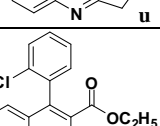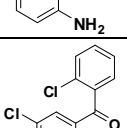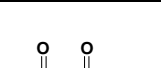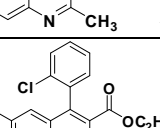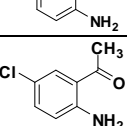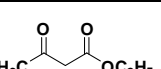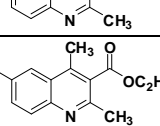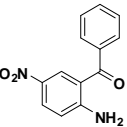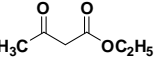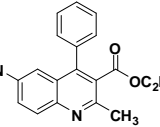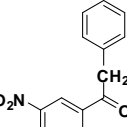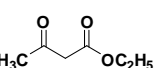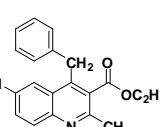
As could be seen in Table 3, the best result was obtained in the presence of silica-supported Preyssler nanoparticles heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ under reflux and room temperatures and any further increase in the reaction time did not have any effect on the yield. Furthermore, we also tested the catalytic activity of different catalysts such as HClO₄, *p*-toluenesulfonic acid (T*s*OH), H₂SO₄, silica sulfuric acid (SSA), and ZnCl₂, and obtained only moderate yields at reflux and room temperatures conditions. One of the most interesting points in this work is the difference of the catalytic activity between simple mineral acids (HClO₄ and H₂SO₄, Table 3, entries 10, 11), silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, Preyssler heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$ and other keggin heteropolyacids
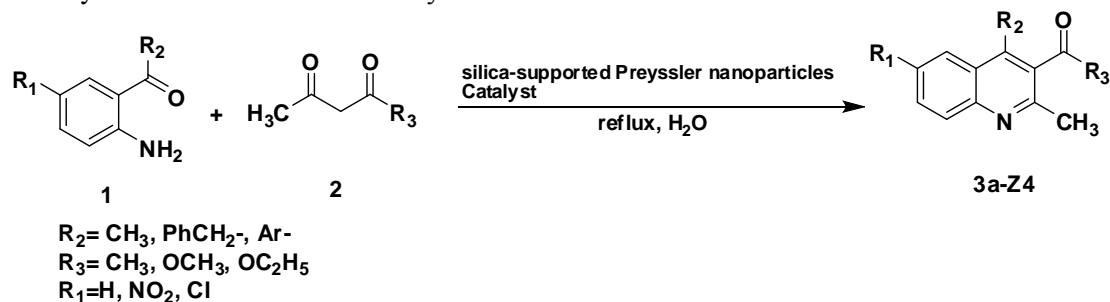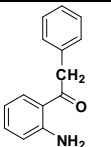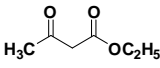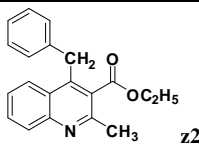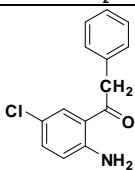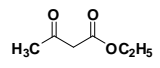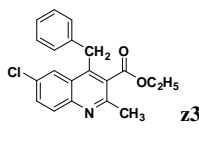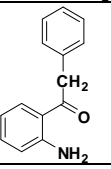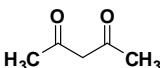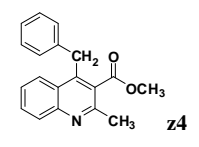

Scheme 1. The reaction of 2-aminobenzophenone (**1**), and ethyl acetoacetate (**2**) under solvent-free condition at reflux conditions in the presence of silica-supported Preyssler nanoparticles catalyst, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$

Table 1. Synthesis of quinolines in the presence of silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ under reflux and solvent-free conditions in 2 hours (**3a-Z4**). ([a]Isolated yield)

Entry	Substrate (1)	Substrate (2)	Product	[a]Yield (%)	Mp(°C) Found	Mp(°C) Reported
1	2-aminoacetophenone	H_3C—CO—CH_2—CO—CH_3	**a**	93	112	-
2	2-aminoacetophenone	H_3C—CO—CH_2—CO—OCH_3	**b**	97	oil	Oil,(lit .39)
3	2-aminoacetophenone	H_3C—CO—CH_2—CO—CH_3	**c**	95	123-126	-
4	5-chloro-2-aminoacetophenone	H_3C—CO—CH_2—CO—OCH_3	**d**	93.5	65-67	-
5	2-amino-5-chlorobenzophenone	H_3C—CO—CH_2—CO—OCH_3	**e**	92	132-133	134-136, (lit.40)
6	2-amino-2',5-dichlorobenzophenone	H_3C—CO—CH_2—CO—OCH_3	**f**	91.5	134-137	-
7	2-amino-5-nitroacetophenone	H_3C—CO—CH_2—CO—OCH_3	**g**	94.5	79-81	-
8	2-amino-5-nitrobenzophenone	H_3C—CO—CH_2—CO—OCH_3	**h**	93.5	160-162	-
9	2-aminophenyl benzyl ketone	H_3C—CO—CH_2—CO—OCH_3	**i**	92	103-105	-
10	5-chloro-2-aminophenyl benzyl ketone	H_3C—CO—CH_2—CO—OCH_3	**j**	93	118-120	-
11	2-amino-5-nitrophenyl benzyl ketone	H_3C—CO—CH_2—CO—OCH_3	**k**	94	165-166	-
12	2-amino-5-chlorobenzophenone	H_3C—CO—CH_2—CO—CH_3	**l**	94	152-153	150-151,(lit.39)
13	2-amino-5-chlorobenzophenone	H_3C—CO—CH_2—CO—OC_2H_5	**m**	95.5	125-127	-

#						
14			**n**	95	206-207	208-209
15			**o**	92	164-166	164-165
16			**p**	85	106-108	106-107
17			**q**	94	110-112	111-112
18			**r**	96	102-103	100-101
19			**s**	97.5	192-194	190-192
20			**t**	92	153-154	156-157
21			**u**	90.5	130-131	130-132
22			**w**	94	128-131	-
23			**x**	95	139-141	-
24			**y**	93	137-138	-
25			**z**	89	122-124	-
26			**z1**	92	127-128	-

27	[structure: 1-(2-aminophenyl)-2-phenylethanone]	H3C—C(O)—CH2—C(O)—OC2H5	[product **z2**]	94.5	117-119	-
28	[structure: 5-chloro substituted]	H3C—C(O)—CH2—C(O)—OC2H5	[product **z3**]	94	120-121	-
29	[structure]	H3C—C(O)—CH2—C(O)—CH3	[product **z4**]	93	114-116	-

catalysts at reflux and room temperatures conditions (Table 3). Encouraged by this result, we turned our attention to various substituted substrates. The procedure gave the products in high yields and avoids problems associated with solvents and liquid acids use (cost, handling, safety, pollution, corrosiveness, separation, and recovery) (Tables 1 and 3). In a control experiment, it was observed that in the absence of the catalyst, the reaction did not proceed even at higher temperatures. Lowering the reaction temperature was detrimental to the efficiency of this procedure. Usually positional isomers are possible and coexist when two or more vanadium atoms are incorporated into the Keggin structure (for example 5 and 13 isomers for x=2 and 3, respectively) [39]. Studies on these isomers in catalytic reactions indicate that different isomers cause to show different reactivities [40]. Because the metal substitution may modify the energy and composition of the LUMO and redox properties, for mentioned heteropolyacids with different charges, the energy and composition of the LUMOs have significant effects on the catalytic activity [41]. Substitution of vanadium ions into the molybdenum framework stabilize the LUMOs because these orbitals derive, in part from vanadium d-orbitals which have been assumed to be more stable than those of molybdenum and tungsten [41]. The abundance of different isomers may also play an important role in catalytic performance. In addition, different positional Mo atom(s) substituted by the V atom(s) in $[PMo_{12}O_{40}]^{3-}$ may create different vanadium chemical environments, thus causing these catalysts to exhibit varying catalytic performances. By variation of the addenda atoms, the electrochemical character of them can be widely changed. The addenda atoms can be ordered by decreasing oxidizing ability in the following way: V(V) > Mo(VI) > W(VI) [33].

In order to confirm the utility of HPAs, as effective catalysts, this reaction was repeated in the absence of the HPAs.

Effect of the solvent

The effect of solvent on the model reaction was studied by carrying out the reaction in a solvent-free system and in a variety of solvents including chloroform, dichloromethane, and acetonitrile at different temperatures. As shown in (Table 2) the best results in terms of yield and time have been achieved in solvent-free systems. The synthesis of quinoline derivatives at reflux temperature was carried out using various common solvents such as acetic acid, ethanol, methanol, THF and acetonitrile. The results are shown in Table 2. With using all of the catalysts the highest yield of products was obtained under solvent-free condition.

Table 2. Synthesis of methyl 2,4-dimethylquinoline-3-carboxylate (**3b**) and ethyl 2-methyl-4-phenylquinoline-3-carboxylate (**3r**) in the presence of silica-supported Preyssler nanoparticles heteropolyacid catalyst and different solvents under reflux conditions.

Entry	Solvent	Temperature (°C)	Time (h)	[a]Yield (%) 3b	[a]Yield (%) 3r
1	Free	Reflux	2	98.5	97.5
2	Water	Reflux	2.5	92	90.5
3	C2H5OH	Reflux	2.5	88	83
4	CHCl3	Reflux	3.5	77.5	74.5
5	CCl4	Reflux	4.5	73	70
6	THF	Reflux	5	70	66.5
7	CH3CN	Reflux	4	90	88
8	CH2Cl2	Reflux	4.5	76	73.5
9	CH3COOH	Reflux	3	86.5	82

[a]Isolated yield.

In addition, the time required for completion of the reaction was found to be less under solvent-free condition. In our studies, we investigated the activity of silica-supported Preyssler nanoparticles

Table 3. Effect of silica-supported Preyssler nanoparticles, Preyssler and various Keggin-type heteropolyacids on the yields of Polysubstituted Quinolines (**3b** and **3r**) under reflux and room temperatures and in solvent-free conditions

Entry	Catalyst	Time (h)		[a]Yield (%) at Room Temperature		[a]Yield (%)at reflux	
		Reflux	Room	3b	3r	3b	3r
1	Silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$	2	14	51.5	59.5	98.5	97.5
2	$H_{14}[NaP_5W_{30}O_{110}]$	2	16	45.5	46	97	96
	$H_7[PMo_8V_4O_{40}]$	3	16	42.5	44.5	92.5	94
2	$H_6[PMo_9V_3O_{40}]$	3	16	39	43.5	90.5	92.5
3	$H_5[P Mo_{10}V_2O_{40}]$	3	16	41	43	88.5	90.5
4	$H_4[PMo_{11}V_1O_{40}]$	3	16	40.5	42	86	88
5	$H_3[PW_{12}O_{40}]$	3	16	37.5	39	83.5	84
6	$H_4[SiW_{12}O_{40}]$	4	18	34	32.5	80	81.5
7	$H_3[PMo_{12}O_{40}]$	4	18	29	32	77	79
8	$H_4[SiMo_{12}O_{40}]$	4	18	31.5	30.5	75	76
9	$H_6[P_2W_{18}O_{62}]$	4	18	40	41	91	93
10	$HClO_4$	6	21	19.5	20	41	43
11	H_2SO_4	6	21	10.5	10	35	36.5
12	T*s*OH	6	21	31	30	53.5	52
13	SSA	6	19	28.5	31	64	63
14	$ZnCl_2$	6	21	12	11	37	37.5
15	Free	10	24	-	-	-	-

$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, Preyssler and various Keggin-type heteropolyacids. Representative results in (Table 2) are shown. The results indicate that the nature of the catalyst plays an important role on their catalytic activities. The highest yield of products has been achieved in the presence of silica-supported Preyssler nanoparticles $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ as catalyst, and H_2SO_4 gave the lowest yields. Due to the complicated nature of the reaction, obtaining the variety of products, it seemed rather difficult to make an exact assessment of the catalyst role. The Keggin anion has an assembly of 12 cornershared octahedral MoO_6 from trimetallic groups $[Mo_3O_{13}]$ around a heteroatomtetrahedron PO_4. The introduction of vanadium (V) into the Keggin framework of $[PMo_{12}O_{40}]^{3-}$ is beneficial for catalysis reactions [42].

Effect of the catalyst type

To study the effect of catalyst type, the synthesis of Polysubstituted Quinolines was selected as a model reaction and the efficiency using Preyssler and four Keggin-type heteropolyacids ($H_{14}[NaP_5W_{30}O_{110}]$, $H_7[PMo_8V_4O_{40}]$, $H_6[PMo_9V_3O_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_4[PMo_{11}VO_{40}]$, $H_6[P_2W_{18}O_{62}]$ and $H_3[PMo_{12}O_{40}]$) was studied. The results are reported in Table. 3 with the order of efficiency as follows: silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2>$ $H_{14}[NaP_5W_{30}O_{110}]>H_7[PMo_8V_4O_{40}]>H_6[P_2W_{18}O_{62}]$ $>H_6[PMo_9V_3O_{40}]>H_5[PMo_{10}V_2O_{40}]>H_4[PMo_{11}VO_{40}]>H_3[PMo_{12}O_{40}]$.

Reusability of the catalyst

In order to know whether the catalysts would succumb to poisoning and lose of catalytic activity during the reaction, we investigate the reusability of the catalyst. For this purpose, we first carried out the reaction in the presence of the catalyst. After completion of the reaction, the catalyst was removed and washed with diethyl ether, dried at 80 °C for 1 h, and subjected to a second run of the reaction process with the same substrate. The results of the first experiment and subsequent experiments were almost consistent in yields. We have found that silica-supported Preyssler nanoparticles catalyst can be reused several times without any appreciable loss of activity. The several time recoveries had only slightly decreased the catalytic activity, pointing to the stability and retention capability of this useful polyanion. In Table **4** the comparison of efficiency of the catalyst after five times reuse is reported.

Table 4. Reuse of the silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ for the synthesis of **3r** (ethyl 2-methyl-4-phenylquinoline-3-carboxylate) in solvent-free under reflux conditions. [a]Isolated Yields.

Entry	Run	Time (h)	[a]Yield (%)
1	1	2	97
2	2	2	97
3	3	2	95.5
4	4	2	95
5	5	2	94

CONCLUSIONS

In conclusion, we have developed a simple, convenient and efficient protocol for the synthesis of wide range of quinolines under solvent-free conditions is reported. The high yields of products, easy work up procedure, and use of a very small amount of heteropolyacid make it the preferred procedure for the preparation of different kind of quinolines. In our studies, we investigated the activity of various Keggin-type heteropolyacids. The highest yield of products has been achieved in the presence of silica-supported Preyssler nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ and $H_7[PMo_8V_4O_{40}]$ as catalyst, and H_2SO_4 gave the lowest yields.

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PREYSSLER'ОВИ ХЕТЕРОПОЛИКИСЕЛИНИ H$_{14}$[NAP$_5$W$_{30}$O$_{110}$], НАНЕСЕНИ ВЪРХУ НАНОЧАСТИЦИ ОТ СИЛИЦИЕВ ДИОКСИД: ЗЕЛЕН И РЕЦИКЛИРУЕМ КАТАЛИЗАТОР ЗА СИНТЕЗАТА НА ПОЛИ-ЗАМЕСТЕНИ ХИНОЛИНИ

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(Резюме)

Описани са синтезите на поли-заместени хинолини в присъствие на катализатори от наночастици, нанесени върху подложка от силициев диоксид (**SPNP**): H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$, Preyssler'ови H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] и Keggin'ови хетерополикиселини, H$_3$PW$_{12}$O$_{40}$, H$_7$[PMo$_8$V$_4$O$_{40}$], H$_6$[PMo$_9$V$_3$O$_{40}$], H$_5$[PMo$_{10}$V$_2$O$_{40}$], H$_4$[PMo$_{11}$VO$_{40}$], H$_3$[PMo$_{12}$O$_{40}$] във водна среда. Най-добри условия са наблюдавани при използването на Preyssler'ови хетерополикиселини като катализатор. Катализаторите са рециклируеми и годни за многократна употреба.