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Article

Rice husk ash supported $FeCl_2·2H_2O$: A mild and highly efficient heterogeneous catalyst for the synthesis of polysubstituted quinolines by Friedländer heteroannulation

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ABSTRACT

Rice husk ash was used as a new, green, and cheap adsorbent for $FeCl_3$. Characterization of the obtained reagent showed that rice husk ash supported $FeCl_2·2H_2O$ was formed. This reagent is efficient at catalyzing the synthesis of multisubstituted quinolines by the Friedländer heteroannulation of *o*-aminoaryl ketones with ketones or β-diketones under mild reaction conditions. This methodology allows for the synthesis of a broad range of substituted quinolines in high yields and with excellent regioselectivity in the absence of a solvent.

1. Introduction

Quinolines are well-known structural units in alkaloids, therapeutics, and synthetic analogues with interesting biological activities [1–7]. These compounds are also valuable reagents for the synthesis of nano- and mesostructures with enhanced electronic and photonic properties [8–10].

Various procedures such as those of Skraup [11], Conrad-Limpach-Knorr [12,13], Pfitzinger [14,15], Friedländer [16,17], and Combes [18,19] have been developed for the synthesis of quinoline derivatives. Among these, Friedländer reaction is the most popular, which is a condensation reaction followed by a cyclodehydration between an aromatic 2-aminoaldehyde or ketone and an aldehyde or ketone with a methylene function under acidic or basic conditions [20].

Various solid acid catalysts have been used in the Friedländer reaction such as $Ag_3PW_{12}O_{40}$ [21], sulfamic acid [22], $HClO_4$-SiO_2 [23], amberlyst-15 [24], dodecylphosphonic acid [25], *o*-benzenedisulfonimide [26], $SnCl_2$ [27], $FeCl_3$ [28], $Mg(ClO_4)_2$ [29], $Nd(NO_3)_3$ [30], $Y(OTf)_3$ [31], $NiCl_2$ [32], I_2/CAN [33], $NaHSO_4$-SiO_2 [34], poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) [35], and KO*t*Bu [36].

However, many of the reported procedures have significant drawbacks such as low product yields, long reaction time, harsh reaction conditions, difficulties in work-up, and the use of stoichiometric and/or relatively expensive reagents. Moreover, the main disadvantage of almost all existing methods is that the catalysts are spent in the work-up procedure and cannot be recovered or reused. Thus, the development of more efficient procedures for the synthesis of quinolines is still needed.

With growing concern over the environmental impact of chemicals and strict legislation, the development of greener chemical processes in synthetic chemistry is required. Green chemistry is mainly concerned with alternative reaction media.

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These media are the basis of many of the cleaner chemical technologies that have undergone commercial development.

The major goals in green chemistry are to increase process selectivity, maximize the use of starting materials, and to replace hazardous and stoichiometric reagents with eco-friendly catalysts to facilitate the easy separation of final reaction mixtures, including catalyst recovery.

Ferric chloride is a conventional homogeneous acid catalyst, but it has several disadvantages such as a high degree of corrosiveness, long work-up, necessity of stoichiometric quantities, the presence of several undesirable side products, and the single use of catalysts. Therefore, it is highly undesirable from an ecological point of view [36]. Although $FeCl_3$ is very active during the synthesis of polymers, it has low regioselectivity, which can lead to polymers with regioirregular structures and many side products [37,38]. The inhalation of $FeCl_3$ dust can result in gastrointestinal or respiratory tract irritation leading to coughing, sneezing, or a burning sensation. Overexposure can produce lung pain, choking, unconsciousness, or death. This substance is toxic to lungs and mucous membranes, and various methods to mitigate these disadvantages have been considered by researchers.

One method to address these limitations is the preparation of supported solid $FeCl_3$ catalysts and the following supports have been reported: poly(3-alkyithiophenes) [39], NH_3BH_3 [40], polyaniline nanofiber [41], nanopore silica [42], clays and Si-MCM-41 [43], and alumina [44], etc.

Rice husk consists of a thin but abrasive skin, which covers edible rice kernels. It contains cellulose, hemicellulose, lignin, silica, solubles, and moisture [45]. During the combustion of rice husk (RiH), rice husk ash (RiHA) is produced. RiHA is considered to be the most economical source of silica [46], which has been used as an adsorbent for metal ions such as Cd^{2+}, Zn^{2+}, Ni^{2+}, and heavy metals such as lead and mercury from aqueous solutions [47–49]. In this paper, we wish to report the use of RiHA as a green, cheap, and available absorbent for $FeCl_3$ and the applicability of the obtained reagent in the synthesis of multisubstituted quinolines.

2. Experimental

2.1. General

All chemicals were purchased from Fluka, Merck, Aldrich, or Southern Clay Products. Yields refer to isolated products. All the products were fully characterized by spectroscopic methods such as FT-IR, ^{1}H-NMR, and ^{13}C-NMR as well as by melting point. The purity of the substrates and reaction monitoring were accomplished by thin-layer chromatography (TLC) on silica-gel polygram SILG/UV 254 plates.

2.2. Preparation of RiH, RiHA, and $FeCl_2{\cdot}2H_2O$-RiHA

The rice sample (designated Hassani) was obtained from Rasht (Guilan Provience) in the north of Iran. RiH was obtained from a local mill, washed several times with distilled water to remove any adhering materials, and dried at room temperature for 48 h.

RiHA was produced during the combustion of RiH. The ideal temperature is between 600 and 700 °C.

The $FeCl_2{\cdot}2H_2O$-RiHA catalyst was prepared by the impregnation of RiHA (50 g) with a solution of $FeCl_3$ (0.053 mol, 8.62 g) in acetone. The solvent was evaporated at 60 °C under reduced pressure. The sample was then heated at 120 °C for 8 h to give $FeCl_2{\cdot}2H_2O$-RiHA (55 g).

2.3. Characterization of the catalyst

FT-IR spectra were obtained on a Perkin-Elmer bio-spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) were obtained on a Bruker Avance DPX-250 FT-NMR spectrometer.

Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The RiH was characterized by scanning electron microscopy (SEM-Philips XL30) with a field emission gun and using energy dispersive spectroscopy (EDS). Before placing samples in the microscope the RiH particles were coated with gold under vacuum (SCD 005 sputter coater, Bal-Tec, Swiss) and then examined at an acceleration voltage of 17 kV.

2.4. A typical procedure for Friedländer reaction

A mixture of 2-amino benzophenone (1.0 mmol), dimedone (1.2 mmol), and $FeCl_2{\cdot}2H_2O$-RiHA (0.3 g) was stirred under solvent-free conditions at 90 °C for 35 min. The reaction was monitored by TLC. Upon completion, hot ethanol was added, and the catalyst was removed by filtration. The solution was concentrated, and the product was recrystallized in EtOH-H_2O (4:1). The solid was washed with cold EtOH and dried to afford the desired product in 86% yield. Reaction conversions were determined by GC on a Shimadzu model GC-16A instrument using a 25 m CBPI-S25 (0.32 mm ID, 0.5 m coating) capillary column.

The spectral data of the obtained products are as follows.

1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (Table 4, entry 1). M.p. 107–108 °C. IR (KBr, cm^{-1}): ν 3058, 2902, 1691, 1265; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.92 (s, 3H), 2.61 (s, 3H), 7.27–7.30 (m, 2H), 7.31–7.34 (m, 1H), 7.40–7.45 (m, 3H), 7.51 (dd, J = 1 Hz, 8.1 Hz, 1H), 7.61–7.66 (m, 1H), 8.00 (d, J = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 24.2, 32.9, 124.5, 125.6, 126.7, 128.1, 128.3, 129.0, 129.9, 130.0, 134.2, 135.3, 144.0, 146.8, 153.7, 206.3.

2-Methyl-4-phenyl-quinoline-3-carboxylic acid methyl ester (Table 4, entry 2). M.p. 107–109 °C. IR (KBr, cm^{-1}): ν 3047, 2942, 1735; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.27 (s, 3H), 3.52 (s, 3H), 7.28–7.32 (m, 2H), 7.58–7.65 (m, 3H), 7.69–7.74 (m, 2H), 8.04 (t, J = 6.8 Hz, 1H), 8.63 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 22.6, 52.2, 122.7, 126.1, 127.3, 127.9, 129.0, 129.9, 130.5, 131.8, 133.1, 134.9, 145.0, 146.1, 146.4, 155.1, 171.1.

Ethyl 2-methyl-4-phenylquinoline-3-carboxylate (Table 4, entry 3). M.p. 99–101 °C. IR (KBr, cm^{-1}): ν 3046, 2934, 1716; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.98 (t, J = 7.6 Hz, 3H), 2.74 (s, 3H), 4.02–4.13 (m, 2H), 7.34–7.42 (m, 6H), 7.54 (d, J = 8.4 Hz,

1H), 7.64 (t, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H); ^{13}C-NMR($CDCl_3$, 100 MHz): *δ* 13.8, 22.9, 61.0, 125.1, 126.1, 128.0, 128.4, 128.7, 129.3, 130.0, 135.3, 146.3, 147.8, 153.9, 168.8.

(2-Methyl-4-phenylquinoline-3-yl)(phenyl)methanone (Table 4, entry 4). M.p. 140–143 °C. IR (KBr, cm^{-1}): *ν* 3052, 2908, 1680. ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.67 (s, 3H), 7.21 (m, 7H), 7.34 (m, 2H), 7.58 (m, 3H), 7.70 (m, 1H), 8.08 (d, *J* = 8.4 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 23.9, 124.9, 126.0, 126.4, 127.8, 128.2, 128.3, 128.8, 129.1, 129.6, 129.9, 132.2, 133.3, 134.6, 136.9, 145.3, 147.6, 154.4, 197.5.

9-Phenyl-3,4-dihydroacridin-1(2H)-one (Table 4, entry 5). M.p. 151–153 °C. IR (KBr, cm^{-1}): *ν* 3045, 2956, 1695; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.22 (m, 2H), 2.71 (t, *J* = 6.5 Hz, 2H), 3.29 (t, *J* = 6.20 Hz, 2H), 7.14 (m, 2H), 7.45 (m, 5H), 7.77 (m, 1H), 8.21 (d, *J* = 8.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 22.4, 34.6, 42.7, 123.7, 126.2, 127.4, 127.8, 127.9, 128.0, 128.3, 131.5, 137.5, 148.5, 151.0, 162.0, 197.5.

3,3-Dimethyl-9-phenyl-3,4-dihydro-2H-acridin-1-one (Table 4, entry 6). M.p. 190–191 °C. IR (KBr, cm^{-1}): *ν* 3074, 2901, 1670; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 1.23 (s, 6H), 2.65 (s, 2H), 3.37 (s, 2H), 7.13–7.21 (m, 2H), 7.34–7.38 (m, 1H), 7.43–7.52 (m, 4H), 7.72–7.76 (m, 1H), 8.08 (d, *J* = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 29.1, 29.7, 49.1, 53.8, 123.2, 126.5, 126.9, 127.6, 127.8, 127.9, 128.2, 128.3, 132.3, 137.6, 150.1, 151.2, 161.0, 198.0.

9-Pheyl-1,2,3,4-tetrahydroacridine (Table 4, entry 7). M.p. 138–139 °C. IR (KBr, cm^{-1}): *ν* 3071, 2952, 1568, 1470, 1451; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 1.73–1.82 (m, 2H), 1.94–2.00 (m, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 7.23–7.32 (m, 4H), 7.42–7.56 (m, 3H), 7.64–7.66 (m, 1H), 8.17 (d, *J* = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 22.5, 22.8, 28.0, 33.1, 126.1, 126.2, 127.4, 127.9, 128.7, 128.8, 129.1, 136.6, 144.8, 150.3, 159.0.

2,3-Dihydro-9-phenyl-1H-cyclopenta[b]uinolone (Table 4, entry 8). M.p. 129–131 °C. IR (KBr, cm^{-1}): *ν* 3062, 2915, 1575, 1485; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.16–2.20 (m, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 3.27 (t, *J* = 7.6 Hz, 2H), 7.37–7.43 (m, 3H), 7.48–7.56 (m, 3H), 7.62–7.66 (m, 2H), 8.07–8.09 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 24.0, 29.9, 35.3, 124.9, 125.7, 126.4, 128.6, 128.3, 129.3, 133.7, 137.0, 142.5, 148.0, 167.6.

6-Phenyl-7H-indeno[1,2-b]quinolin-7-one (Table 4, entry 9). M.p. 180–182 °C. IR (KBr, cm^{-1}): *ν* 3074, 2929, 1621, 1455; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 7.44 (t, *J* = 8.0 Hz, 2H), 7.50–7.59 (m, 4H), 7.60–7.74 (t, *J* = 8.0 Hz, 3H), 7.81–7.85 (t, *J* = 8.0 Hz, 1H), 8.32 (s, 2H) ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 29.7, 123.0, 124.1, 127.0, 127.7, 128.1, 128.7, 128.9, 129.3, 131.7, 140.0, 133.0, 135.4, 137.7, 163.1.

1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)ethanone (Table 4, entry 10). M.p. 159–160 °C. IR (KBr, cm^{-1}): *ν* 3056, 2938, 1675 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 1.94 (s, 3H), 2.68 (s, 3H), 7.31–7.34 (m, 2H), 7.49–7.56 (m, 4H), 7.60–7.64 (m, 1H), 7.99 (d, *J* = 9.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 23.5, 31.9, 124.6, 125.8, 128.7, 129.2, 129.7, 130.2, 130.6, 132.4, 134.5, 135.6, 143.1, 145.6, 153.9, 205.0.

Methyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (Table 4, entry 11). M.p. 131–133 °C; IR (KBr, cm^{-1}): *ν* 3063, 2945, 1735; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.56 (s, 3H), 3.54 (s, 3H), 7.26–7.92 (m, 8H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 23.4, 52.62, 125.1, 125.9, 127.9, 128.6, 128.9, 129.1, 130.4, 131.1, 132.5, 134.9, 145.6, 146.1, 154.8, 168.7.

Ethyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (Table 4, entry 12). M.p. 98–100 °C. IR (KBr, cm^{-1}): *ν* 3042, 2936, 1712; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 0.90 (t, *J* = 7.0 Hz, 3H), 2.73 (s, 3H), 3.88 (q, *J* = 7.0 Hz, 2H), 7.30–7.47 (m, 6H), 7.51 (dd, J_1 = 8.8 Hz, J_2 = 2.4, 1H), 7.88 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 13.5, 23.8, 59.9, 124.5, 125.8, 127.9, 128.4, 128.2, 128.9, 130.1, 130.8, 132.2, 134.6, 144.9, 145.4, 154.7, 167.8.

(6-Chloro-2-methyl-4-phenylquinolin-3-yl)(phenyl)methanone (Table 4, entry 13). M.p. 209–211 °C. IR (KBr, cm^{-1}): *ν* 2925, 2851, 1680, 1240; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.49 (s, 3H), 7.12 (m, 7H), 7.41 (m, 1H), 7.46 (m, 3H), 7.66 (d, *J* = 2.40 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 23.8, 124.7, 125.9, 128.1, 128.3, 128.4, 129.0, 129.7, 130.4, 130.8, 132.3, 133.0, 133.5, 133.9, 136.7, 144.6, 146.0, 154.8, 199.9.

7-Chloro-9-phenyl-3,4-dihydro-1-2H-acridinone (Table 4, entry 14). M.p. 187–189 °C. IR (KBr, cm^{-1}): *ν* 3032, 2967, 2875, 1688, 1549. ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.24 (q, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 3.32 (t, *J* = 6.4 Hz, 2H), 7.15 (t, 2H), 7.41 (s, H), 7.52 (m, 3H), 7.59 (d, *J* = 8.4 Hz, 1H,), 7.98 (d, *J* = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 20.9, 34.2, 40.3, 124.2, 126.3, 127.8, 130.0, 132.2, 136.6, 146.7, 149.9, 162.2, 197.0.

7-Chloro-3,3-dimethyl-9-phenyl-3,4-dihydro-2H-acridin-1-one (Table 4, entry 15). M.p. 207–209 °C. IR (KBr, cm^{-1}): *ν* 3071, 2946, 1693; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 1.12 (s, 6H), 2.53 (s, 2H), 3.25 (s, 2H), 7.13–7.16 (m, 2H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.42–7.55 (m, 3H), 7.71 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 28.4, 32.3, 48.4, 54.3, 123.5, 126.8, 127.7, 127.9, 128.1, 128.2, 130.0, 132.3, 132.5, 136.8, 147.2, 150.2, 161.2, 197.5.

7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (Table 4, entry 16). M.p. 160–163 °C. IR (KBr, cm^{-1}): *ν* 3060, 2944, 1604, 1572, 1481, 1215, 703; ^{1}H-NMR($CDCl_3$, 400 MHz): *δ* 1.71–1.83 (m, 2H), 1.92–1.96 (m, 2H), 2.58 (t, *J* = 6.2 Hz, 2H), 3.30 (t, *J* = 6.2 Hz, 2H), 7.21–7.32 (m, 4H), 7.48–7.69 (m, 3H), 7.94 (d, *J* = 8.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 22.6, 27.7, 35.6, 124.2, 126.9, 128.1, 128.8, 128.9, 129.0, 129.5, 130.4, 131.6, 136.8, 144.9, 145.9, 129.8.

7-Chloro-2,3-dihydro-9-phenyl-1H-cyclopenta[b]uinolone (Table 4, entry 17). M.p. 97–98 °C. IR (KBr, cm^{-1}): *ν* 3043, 2941, 1608, 1481; ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* 2.23 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 3.24 (t, *J* = 7.4 Hz, 2H), 7.41–7.32 (m, 2H), 7.41–7.55 (m, 5H), 7.96 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 23.3, 31.4, 36.2, 126.5, 128.0, 128.1, 128.6, 128.8, 129.0, 130.2, 131.3, 134.7, 136.0, 141.9, 146.9, 168.5.

8-Chloro-10-phenyl-11H-indeno[1,2-b]quinolin-11-one (Table 4, entry 18). M.p. 240–243 °C. IR (KBr, cm^{-1}): *ν* 3045, 2917, 1717, 1611.51, 1572, 1442; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43–7.46 (m, 2H), 7.51–7.55 (td, J_1 = 7.60 Hz, J_2 = 0.80 Hz, 1H), 7.60–7.634 (m, 3H), 7.66–7.67 (d, *J* = 2.00 Hz, 1H), 7.69–7.70 (d, *J* = 2.40 Hz, 1H), 7.72–7.75 (m, 1H), 8.10-8.15 (t, *J* = 9.80 Hz, 2H) ^{13}C-NMR ($CDCl_3$, 100 MHz): *δ* 121.7, 123.3, 124.0, 127.4, 128.4, 128.7, 129.3, 129.4, 131.3, 131.8, 132.4, 133.1, 135.5, 137.5, 143.1, 147.1, 148.8, 162.2, 189.9.

3. Results and discussion

3.1. Characterization results

3.1.1. FT-IR analysis

Figure 1 shows the FT-IR spectra of RiHA and $FeCl_2{\cdot}2H_2O$-RiHA catalysts. The broad band at 3430–3480 cm^{-1} comes from O–H stretching vibrations of silanol OH groups and adsorbed water bound to the silica surface [50]. The band at 1620–1640 cm^{-1} comes from the bending vibration of water molecules, which are trapped in the matrix of the adsrorbent. The strong peak at 1095 cm^{-1} comes from the structural siloxane bond, Si–O–Si. This peak is observed in both RiHA and metal incorporated RiHA. The bands at 800–805 and 465–475 cm^{-1} in all spectra come from Si–O bond deformation [51]. In $FeCl_2{\cdot}2H_2O$-RiHA the shoulder at 1002.16 cm^{-1} comes from the Fe–O–Si vibration [52].

3.1.2. SEM analysis

SEM was used to investigate the structures of both the bare RiHA support and the $FeCl_2{\cdot}2H_2O$-RiHA catalyst precursors. A clean and smooth RiHA support surface is evident in Fig. 2(a–c). Images of the $FeCl_2{\cdot}2H_2O$-RiHA catalyst precursors are shown in Fig. 2(d–e). They clearly reveal the presence of structures with different diameters after metal ion sorption. These structures were absent on the RiHA before the sorption process. The $FeCl_2{\cdot}2H_2O$ particles that cover the substrate are 0.5–3 μm in diameter. The surface morphology and spherical structure of the particles are retained even when the RiHA sample was modified with $FeCl_3$. These SEM observations prove that the RiHA supported $FeCl_2{\cdot}2H_2O$ catalyst was successfully prepared. These results are in accordance with an earlier report [53].

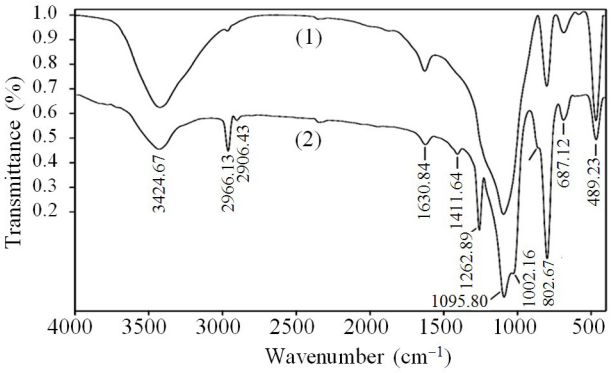


Fig. 1. FT-IR spectra of RiHA (1) and $FeCl_2{\cdot}2H_2O$-RiHA (2).

3.1.3. XRD analysis

The XRD patterns of the samples are shown in Fig. 3. As indicated by the featureless diffractograms and the appearance of a diffuse maximum at 2θ = 25°, which is typical for amorphous silica [54], it can be concluded that the RiHA and the $FeCl_2{\cdot}2H_2O$-RiHA are completely amorphous and do not have a crystalline structure. This XRD pattern indicates that one of the Cl atoms from Fe has been removed and that $FeCl_2{\cdot}2H_2O$-RiHA was obtained after final heating. The interaction of the Fe species with the Brönsted and the silanol sites of the support results in HCl formation during the reaction [55].

3.1.4. XRF analysis

XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited upon bombardment with high energy X-rays or gamma rays. XRF technology provides one of the simplest, most accurate, and

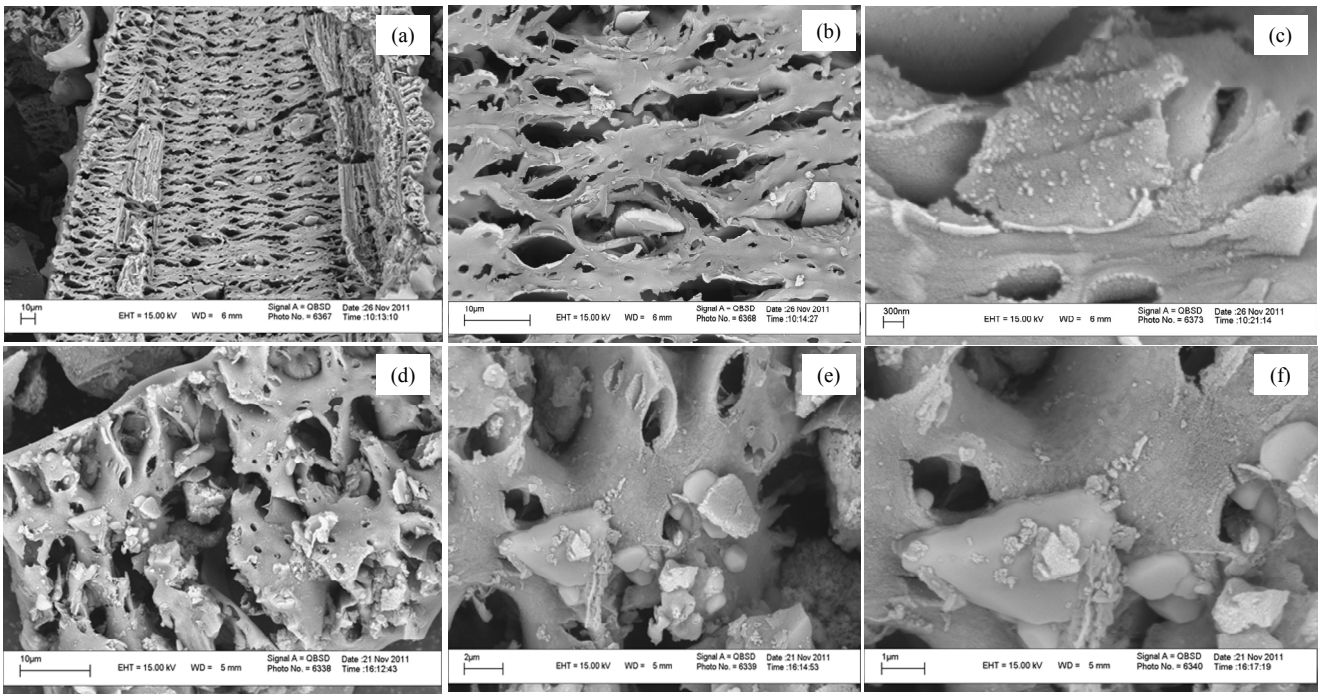


Fig. 2. SEM micrographs of RiHA (a–c) and $FeCl_2{\cdot}2H_2O$-RiHA (d–f).

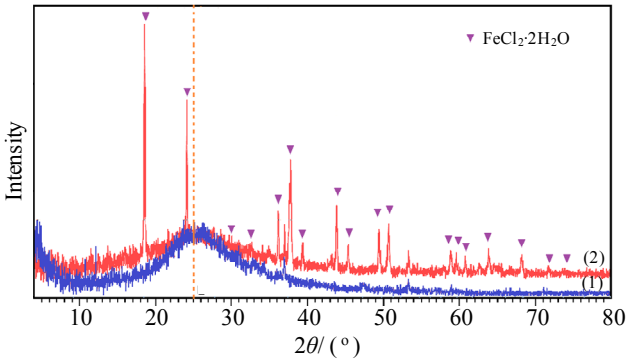


Fig. 3. XRD patterns of RiHA (1) and $FeCl_2·2H_2O$-RiHA (2).

most economic analytical methods for the determination of the chemical composition of many types of materials.

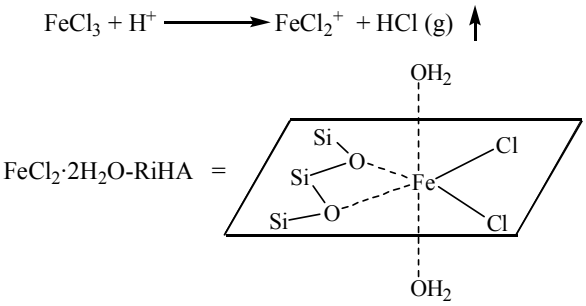
The loss on ignition (L.O.I) of RiHA and $FeCl_2·2H_2O$-RiHA was determined by heating 3 g of each sample at 1000 °C for 1 h in air to remove moisture and any coexistent unburned carbon. Table 1 shows the elemental composition of the obtained RiHA with silica as the major component (~80.82%). Other metallic elements are also present in the RiHA as minor elements. The composition of the $FeCl_2·2H_2O$ supported on RiHA as determined by XRF is also listed in Table 1. The results clearly show that the Fe content is higher in the $FeCl_2·2H_2O$-RiHA (Table 1).

3.1.5. *Surface area and pore distribution measurements*

N_2 adsorption is a powerful tool for nano- or mesoporous material characterization and was carried out in this study to obtain information about the modified porous silica materials. The textural properties of the RiHA were substantially altered upon reaction with $FeCl_3$. When the RiHA was converted to $FeCl_2·2H_2O$-RiHA a decrease of surface area from 250 to 190 m^2/g occurred. This suggests that $FeCl_2·2H_2O$ may be well-confined in the pores of the RiHA and indicates the ordered mesoporosity of the support even after modification.

3.1.6. *Catalyst structure*

On the basis of the above-mentioned characterization, especially XRD analysis, we conclude that $FeCl_2·2H_2O$-RiHA is the prepared catalyst. This result can be explained by considering that the interaction of the Fe species with the Brönsted and the silanol sites of the support results in HCl formation during the reaction [55]. After this interaction, Fe is stabilized by the RiHA matrix in the form of isolated mononuclear complexes located at the Brönsted sites. These Fe complexes consist of tetrahedrally coordinated Fe^{3+} bound to the framework by two O atoms and are further surrounded by two Cl atoms (Scheme 1).



Scheme 1. Removal of Cl from $FeCl_3$.

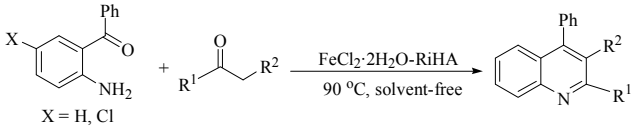
3.2. *Catalytic performance of $FeCl_2·2H_2O$-RiHA for Friedländer reaction*

We recently reported the preparation of RiH supported $FeCl_3$ nanoparticles and its application in the 1,1-diacetate protection and deprotection of aldehydes [56] as well as application in multi-component reactions [57]. In a continuation of these studies we were interested in the preparation of $FeCl_3$ supported RiHA and the influence of a change in support on this type of reaction. Our investigations, especially XRD analysis, showed that when RiHA was used instead of RiH, $FeCl_2·2H_2O$-RiHA was obtained as the product. After the preparation and identification of $FeCl_2·2H_2O$-RiHA, we found that this reagent efficiently catalyzed the synthesis of uinolone derivatives by the Friedländer reaction (Scheme 2).

To optimize the amount of catalyst and the temperature, reaction between 5-chloro-2-amino uinoloneon and dimedone as a model one was performed in the presence of varying amounts of catalyst $FeCl_2·2H_2O$-RiHA (Table 2). The product yield increased, and the time for reaction completion decreased upon an increase in the amount of $FeCl_2·2H_2O$-RiHA up to 0.3 g catalyst and 90 °C. Any further increase in the amount of $FeCl_2·2H_2O$-RiHA or the temperature did not significantly improve the results. It is important to note that in the absence of catalyst no product was observed (Table 2, entry 14).

The role of the solvent in the synthesis of 7-chloro-3,4-dihydro-3,3-dimethyl-9-phenylacridin-1(*2H*)-one was investigated in the presence of $FeCl_2·2H_2O$-RiHA as the catalyst. We established that solvent-free conditions were the best (Table 3).

After the optimization of the reaction conditions and to show the generality of the method we used the optimized conditions for the synthesis of different types of uinolone deriva-



Scheme 2. Friedländer reaction catalyzed by $FeCl_2·2H_2O$-RiHA.

Table 1
XRF analysis of RiHA and $FeCl_2·2H_2O$-RiHA.

Sample	Element composition (%)									
	L.O.I [a]	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	Cl	Na_2O
RiHA	12.70	0.25	80.82	0.44	0.39	1.25	0.82	0.38	1.99	0.96
$FeCl_2·2H_2O$-RiHA	30.15	0.14	45.75	0.25	0.27	0.62	0.48	9.54	12.16	0.64

[a] Loss on ignition.

Table 2
Effect of the amount of catalyst and temperature on the reaction time and conversion to 7-chloro-3,4-dihydro-3,3-dimethyl-9-phenylacridin-1(*2H*)-one.

Entry	Catalyst amount (g)	Temperature (°C)	Time (min)	Conversion (%)
1	0.1	25	90	20
2	0.1	50	90	35
3	0.1	90	90	50
4	0.1	100	90	50
5	0.2	25	60	40
6	0.2	50	60	60
7	0.2	90	60	80
8	0.2	100	60	80
9	0.3	50	60	80
10	0.3	90	45	100
11	0.3	100	45	100
12	0.4	50	50	90
13	0.4	90	45	100
14	0.0	100	90	0

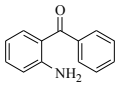
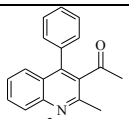
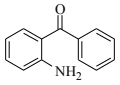
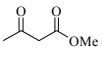
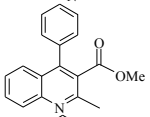
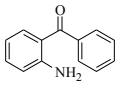
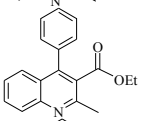
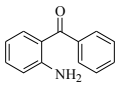
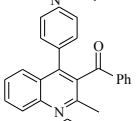
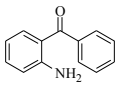
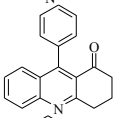
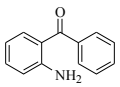
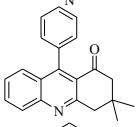
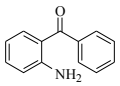
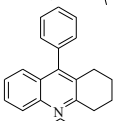
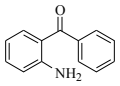
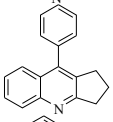
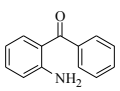
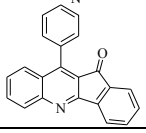
tives. The results are summarized in Table 4. Various 1,3-diketones were reacted with 2-aminoaryl ketones to give the corresponding substituted uinolone. Interestingly, cyclic ketones such uinoloneone and cyclopentanone reacted with 2-aminoaryl ketones to afford the respective tricyclic quinolines. The reaction is fairly general, clean, rapid, and efficient. The experimental procedure is very simple and the products are obtained in high yields in relatively short reaction times.

Table 3
Effect of the solvent on the preparation of 7-chloro-3,4-dihydro-3,3-dimethyl-9-phenylacridin-1(*2H*)-one in the presence of $FeCl_2·2H_2O$-RiHA.

Entry	Solvent	Time (min)	Yield (%)
1	solvent-free	45	92
2	ethanol	120	65
3	CH_2Cl_2	120	trace
4	CH_3CN	120	30

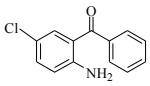
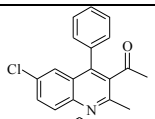
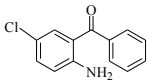
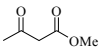
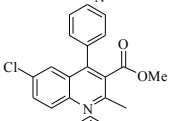
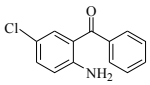
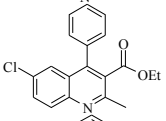
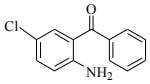
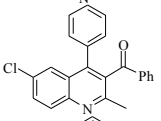
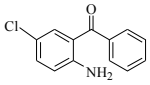
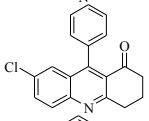
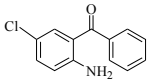
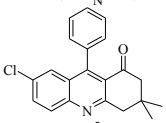
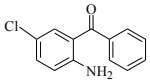
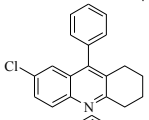
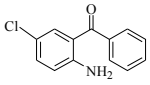
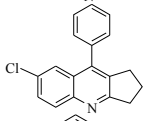
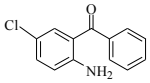
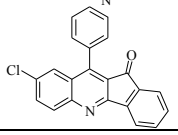
After the completion of the reaction, the catalyst was separated and washed well with ethyl acetate and then dried at 100 °C before activity testing in a subsequent run and thus fresh catalyst was not added. It was found that the catalyst had very good reusability (Fig. 4).

Table 4
Preparation of uinolone derivatives using $FeCl_2·2H_2O$-RiHA as the catalyst.

Entry	Substrate	Ketone	Product	Time (min)	Yield [a] (%)	Melting point (°C)	Ref.
1				30	88	107–108	[58]
2				20	91	107–109	[59]
3				25	93	99–101	[59]
4				75	86	140–143	[25]
5				25	94	154–156	[59]
6				35	86	190–191	[59]
7				40	89	138–139	[59]
8				35	90	129–131	[59]
9				45	95	180–182	[59]

(To be continued)

Table 4 (continued)

Entry	Substrate	Ketone	Product	Time (min)	Yield [a] (%)	Melting point (°C)	Ref.
10				50	93	159–160	[59]
11				35	92	131–133	[59]
12				40	90	98–100	[53]
13				90	87	209–211	[59]
14				35	94	187–189	[59]
15				40	85	207–209	[59]
16				90	89	160–163	[60]
17				45	91	97–98	[59]
18				60	94	240–243	this work

[a] Isolated yield.

We compared the results obtained from the reaction between 5-chloro-2-amino benzophenone and acetylacetone in the presence of $FeCl_2{\cdot}2H_2O$-RiHA with other catalysts in similar reactions (Table 5). This comparison clearly shows that with our method the desired product is obtained in a shorter reaction time and under relatively milder reaction conditions.

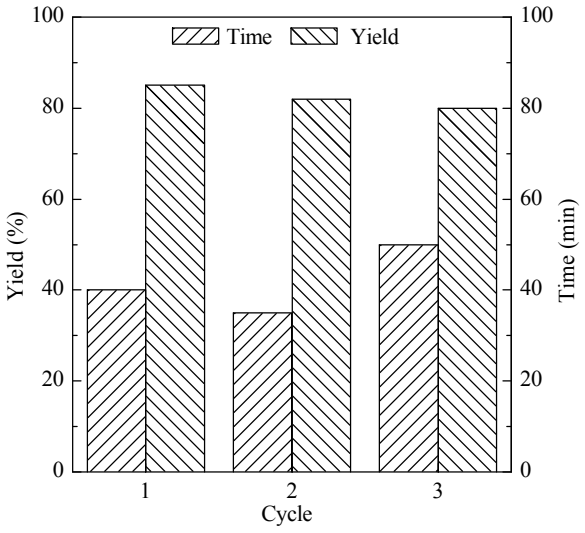
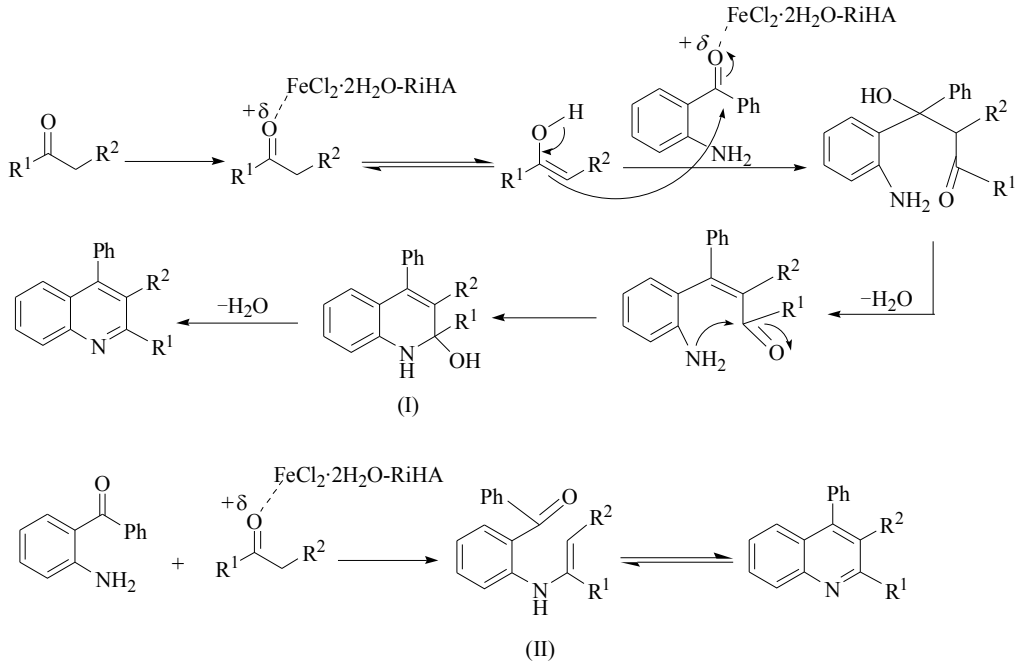


Fig. 4. Reusability of $FeCl_2{\cdot}2H_2O$-RiHA in the synthesis of 7-chloro-3,4-dihydro-3,3-dimethyl-9-phenylacridin-1(*2H*)-one (Table 3, entry 15).

Two possible reaction mechanisms may explain our results and these are shown in Scheme 3. On the basis of these mechanisms the carbonyl group is activated in the first step by $FeCl_2{\cdot}2H_2O$-RiHA in a cross-aldol reaction creating an amino ketone (I or II). This intermediate subsequently condenses with itself and produces a ring with the concomitant formation of a C=N bond.

Table 5
Effect of different catalysts in the preparation of 1-(6-chloro-2-methyl-4-phenylquinolin-3-yl)ethanone compared with $FeCl_2{\cdot}2H_2O$-RiHA.

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
1	$Y(OTf)_3$	CH_3CN, r.t.	360	81	[30]
2	$[Hbim]BF_4$	100 °C/solvent-free	198	93	[61]
3	TBBDA	H_2O/reflux	300	94	[34]
4	Amberlyst-15	EtOH/reflux	120	90	[62]
5	$Zr(NO_3)_4$	H_2O/reflux	360	86	[63]
6	$FeCl_2{\cdot}2H_2O$-RiHA	90 °C/solvent-free	50	93	this work



Scheme 3. Proposed mechanisms of the synthesis of quinoline derivatives by Friedländer reaction using $FeCl_2·2H_2O$-RiHA catalyst.

4. Conclusions

We have developed an environmentally friendly, high yielding and mild condition protocol for the synthesis of quinoline derivatives by the Friedländer reaction using $FeCl_2·2H_2O$-RiHA as a catalyst. This method has several advantages compared to those reported in the literature, i.e., the introduction of a new, green and cheap adsorbent for $FeCl_3$, the promotion of Friedländer heteroannulation under mild reaction conditions, high product yields, the heterogeneous nature of the reaction, reusability of the catalyst as well as a simple procedure. It is thus a useful and attractive strategy for the synthesis of quinoline derivatives.

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Graphical Abstract

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Rice husk ash supported $FeCl_2·2H_2O$: A mild and highly efficient heterogeneous catalyst for the synthesis of polysubstituted quinolines by Friedländer heteroannulation

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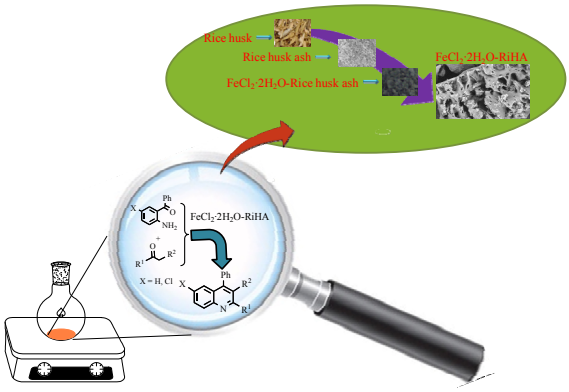

A new, green, and efficient catalyst $FeCl_2·2H_2O$-rice husk ash was prepared and used in the synthesis of polysubstituted quinoline derivatives by Friedländer heteroannulation.

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