Hantzsch reaction on free nano-Fe$_2$O$_3$ catalyst: Excellent reactivity combined with facile catalyst recovery and recyclability

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrumentation, Analysis and Starting Materials</td>
<td>3</td>
</tr>
<tr>
<td>Experimental</td>
<td>3</td>
</tr>
<tr>
<td>General procedure for the synthesis of nano-$\gamma$-Fe$_2$O$_3$</td>
<td>4</td>
</tr>
<tr>
<td>XPS spectrum of nano Fe$_3$O$_4$</td>
<td>5</td>
</tr>
<tr>
<td>XPS spectrum of nano-$\gamma$-Fe$_2$O$_3$</td>
<td>6</td>
</tr>
<tr>
<td>XPS spectrum of nano-$\gamma$-Fe$_2$O$_3$ after reuse five times</td>
<td>7</td>
</tr>
<tr>
<td>XRD pattern of the nano-$\gamma$-Fe$_2$O$_3$</td>
<td>8</td>
</tr>
<tr>
<td>VSM pattern of the nano-$\gamma$-Fe$_2$O$_3$</td>
<td>8</td>
</tr>
<tr>
<td>FTIR spectrum of nano-$\gamma$-Fe$_2$O$_3$</td>
<td>9</td>
</tr>
<tr>
<td>Photographs of suspension of nano-$\gamma$-Fe$_2$O$_3$</td>
<td>9</td>
</tr>
<tr>
<td>X-ray structure of 4g..</td>
<td>10</td>
</tr>
<tr>
<td>Spectral data</td>
<td>11</td>
</tr>
<tr>
<td>References</td>
<td>32</td>
</tr>
</tbody>
</table>
**Instrumentation, Analysis and Starting Materials:**

**Experimental:**

**General:** All chemicals were purchased from Merck, Fluka or Acros companies and used without any further purification. Nano-$\gamma$-Fe$_2$O$_3$ was prepared with the reported method.$^1$-$^2$ NMR spectra were recorded with a Bruker Avance 300 spectrometer ($^1$HNMR 300 MHz and $^{13}$CNMR 75 MHz) in pure deuteriated chloroform, acetone and dimethyl sulfoxide with tetramethylsilane (TMS) as the internal standard. X-ray data was measured on a STOE IPDS-II two circle diffractometer at 120 K, using graphite monochromated Mo Ka X-ray radiation ($\lambda = 0.7107$ Å), Suitable crystal was obtained from ethanol solution by the slow evaporation of the solvent over several days. Scanning electron microscope (SEM, Philips, XL30, Netherlands) was used for preparation of SEM images. Transmission electron microscope, TEM (Philips CM10) was also used to obtain TEM images. The crystal structure of synthesized materials was determined by an X-ray diffractometer (XRD) (38066 RIVA, d/G. Via M. Misone, 11/D (TN), Italy) at ambient temperature. XPS spectra were acquired using a Kratos Axis ULTRA “DLD” X-ray photoelectron spectrometer equipped with a monochromatic Al-KR X-ray source. The pass energies were 160eV for the survey scans and 20 eV for the high
resolution scans. The instrument was operated in electrostatic mode as the samples were magnetic. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (4 inch, Daghighe Meghnatis Kashan Co., Kashan, Iran) at room temperature.

**General procedure for the synthesis of nano-\(\gamma\)-Fe\(_2\)O\(_3\):**

Magnetite (Fe\(_3\)O\(_4\)) nanoparticles were prepared by partial reduction coprecipitation method based on the procedure of S.C. Qu, H.B. Yang, S.H. Kan, et al.\(^2\) 3 mL FeCl\(_3\) (2 mol L\(^{-1}\) dissolved in 2 mol L\(^{-1}\) HCl) was added to 10.33 mL double distilled water, and 2 mL Na\(_2\)SO\(_3\) (1 mol L\(^{-1}\)) was added to the former solution dropwise in 1 min under magnetic stirring. When the color of the solution turned back from red to light yellow, the solution was added to 80 mL NH\(_3\)·H\(_2\)O solution (0.85 mol L\(^{-1}\)) under vigorous stirring. After 30 min, the magnetite precipitates were washed to pH<7.5 by deoxygenated water. The black precipitate obtained above was diluted to a volume of 168 mL with a mass concentration of 6 mg mL\(^{-1}\). The pH of the suspension was adjusted to 3.0 with HCl (0.1 mol L\(^{-1}\)) and the pH was kept stable for 5 min. The temperature of the suspension was raised to 90 °C in 5 min, and was stirred under aeration (with air) for 60 min at about 100 °C. The reddish-brown solution was washed with water by magnetic decantation four times.\(^1\)
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#### Fe 2p/20

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<td>4.31692</td>
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<td>718.84</td>
<td>4.31692</td>
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#### Fe 2p3/2

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### Electronic Supplementary Material (ESI) for Chemical Communications

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Figure S1. XPS spectrum of nano Fe₃O₄.

Figure S2. XPS spectrum of nano-γ-Fe₂O₃.
Figure S3. XPS spectrum of nano-\(\gamma\)-Fe\(_2\)O\(_3\) after reuse five times.
Figure S4. XRD patterns of the nano-$\gamma$-Fe$_2$O$_3$.\(^{4-5}\)

Figure S5: Magnetization curve for the Fe$_2$O$_3$ nanoparticles at room temperature.

The room-temperature magnetization curve of the magnetic nanoparticles proves that the magnetic nanoparticles are superparamagnetic. The saturation magnetization of ~60 emu/g was determined for the fine Fe$_2$O$_3$ nanoparticles.
Figure S6: Photographs of suspension of nano-\(\gamma\)-Fe\(_2\)O\(_3\) before (a, b) and after (c, d) magnetic capture.

The particles suspended smoothly by eccentricity force after the magnet bar start to stir, so that, the suspended Fe\(_2\)O\(_3\) particles turned the reaction color into smooth brown during the reaction. Because of the reaction carried out in solvent free condition and the product is in viscose form, in order to make separation easier, at the end of the reaction, the mixture was triturated with ethyl acetate and after 10 s suspended particles moved on to the stirrer bar. Using an external magnet can make the separation of Nps easier during the cycling.

Figure S7: FTIR spectra of \(\gamma\)-Fe\(_2\)O\(_3\) nanoparticles.\(^6\)
Figure S8. X-ray structure of 4g.
Spectral data:

**Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate**

\[ \text{O} \quad \text{O} \quad \text{C} \quad \text{H} \]

**Mp:** 157-159 °C; \( ^1H \) NMR (CDCl\(_3\), 300 MHz): \( \delta \) (ppm): 1.15 (t, 6 H), 2.22 (s, 6 H), 4.0 (q, 4 H), 4.93 (s, 1 H), 6.2 (b, 1 H), 7.04-7.22 (m, 5 H); \( ^13C \) NMR (CDCl\(_3\), 75 MHz): \( \delta \) (ppm): 14.26, 19.40, 39.63, 59.74, 103.93, 126.1, 127.84, 127.98, 144.23, 147.85, 167.81; Elemental Analysis: Calcd. C: 69.28, H: 7.04, N: 4.25, O: 19.43, Found. C: 69.12, H: 7.00, N: 4.21, O: 19.39.
Diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

\[
\text{Mp: 144-146 °C; } \text{H NMR (CDCl}_3, 300 \text{ MHz): } \delta \text{ (ppm): 1.16-1.11 (t, 6 H), 2.19 (s, 6 H), 4.03-5.96 (q, 4 H), 4.89 (s, 1 H), 6.30 (s, 1 H), 7.15-7.06 (q, 4 H); } \text{C NMR (CDCl}_3, 75 \text{ MHz): } \delta \text{ (ppm): 14.27, 19.31, 39.24, 59.85, 103.50, 127.92, 129.36, 131.66, 144.56, 146.45, 167.68;}
\]

1H NMR of 4c

Expanded 1H NMR of 4c
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Expanded $^1$H NMR of 4c

$^{13}$C NMR of 4c
Diethyl 4-(4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate\(^8\)

\[
\begin{align*}
&\text{Mp: 230-231 °C; } \text{H NMR (CDCl}_3, 300 MHz): \delta (ppm): 1.13-1.9 (t, 6 H), \\
&2.23 (s, 6 H), 3.99-3.93 (q, 4 H), 4.86 (s, 1 H), 7.04-6.56 (m, 4 H), 7.90(s, 1H), 7.98(s,1H); \text{C NMR (Acetone D, 75 MHz): } \delta (ppm): 13.77, 17.87, \\
&38.54, 58.87, 103.39, 114.40, 128.83, 139.76, 144.38, 155.54, 167.23; \\
\end{align*}
\]
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**$^1$H NMR of 4d**

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**$^{13}$C NMR of 4d**
Diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 165-167 ºC; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ (ppm): 1.10 (t, 6 H), 2.20 (s, 6 H), 4.0 (q, 4 H), 4.95 (s, 1 H), 6.22 (b, 1 H), 7.30-7.43 (m, 4 H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ (ppm): 14.25, 19.36, 40.4, 59.93, 102.93, 109.52, 119.35, 128.87, 131.87, 145.03, 163.28, 167.27; Elemental Analysis: Calcd. C: 67.78, H: 6.26, N: 7.90, O: 18.06, Found. C: 67.71, H: 6.22, N: 7.89, O: 18.01.
Diethyl 4-(3-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 141-142 °C; $^1$H NMR (CDCl$_3$, 300 MHz): δ (ppm): 1.15 (t, 6 H), 2.23-2.09 (s, 6 H), 4.04-3.96 (q, 4 H), 4.89 (s, 1 H), 6.2 (s, 1 H), 7.16-7.03 (m, 4 H); $^{13}$C NMR (CDCl$_3$, 75 MHz): δ (ppm): 14.21, 19.47, 39.68, 59.86, 103.50, 126.24, 126.30, 128.23, 129.06, 133.56, 144.45, 149.81, 167.49; Elemental Analysis: Calcd. C: 62.72, H: 6.09, N: 3.85, O: 17.59, Found. C: 62.68, H: 6.01, N: 3.78, O: 17.52.
**Diethyl 4-(4-hydroxy-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate**

Mp: 159-161°C; \( ^1 \)H NMR (DMSO, 300 MHz): \( \delta \) (ppm): 1.07 (t, 6 H), 2.18 (s, 6 H), 3.61 (s, 3 H), 3.88-3.95 (q, 1 H), 4.69 (s, 1 H), 6.44-6.56 (dd, 2 H), 6.63 (s, 1 H), 8.57 (s, 1 H), 8.65 (s, 1 H); \( ^{13} \)C NMR (DMSO, 75 MHz): \( \delta \) (ppm): 14.68, 18.65, 38.64, 55.84, 59.13, 102.64, 112.24, 115.24, 120.09, 140.03, 145.16, 145.32, 147.15, 167.58; Elemental Analysis: Calcd. C: 63.99, H: 6.71, N: 3.73, O: 25.57, Found. C: 63.90, H: 6.70, N: 3.71, O: 25.50.
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$^{13}$C NMR of 4l

Expanded $^{13}$C NMR of 4l
Diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate\textsuperscript{7}

\begin{化学式}
\begin{center}
\includegraphics[width=0.3\textwidth]{diethyl-dicarboxylate.png}
\end{center}
\end{化学式}

Mp: 161-162 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \( \delta \) (ppm): 1.17 (t, 6 H), 2.21 (s, 6 H), 4.07 (q, 4 H), 5.11 (s, 1 H), 5.83-6.12 (m, 2H), 6.29 (s,1H), 7.10-7.11 (t, 1 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): \( \delta \) (ppm): 143.31, 19.29, 33.82, 59.82, 100.41, 104.39, 110.00, 140.78, 145.51, 158.76, 167.65; Elemental Analysis: Calcd. C: 63.94, H: 6.63, N: 4.39, O: 25.05, Found. C: 63.91, H: 6.59, N: 4.32, O: 25.01.
Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 196–197 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) (ppm): 2.23 (s, 6 H), 3.75 (s, 6 H), 4.95 (s, 1 H), 6.09 (b, 1 H), 7.14-7.21 (m, 4 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) (ppm): 19.41, 38.28, 51.03, 103.64, 126.23, 127.60, 128.05, 144.61, 147.48, 168.22; Elemental Analysis: Calcd. C: 67.76, H: 6.36, N: 4.65, O: 21.24, Found. C: 67.43, H: 6.31, N: 4.56, O: 21.20.
1H NMR of 5a

13C NMR of 5a
Dimethyl 4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 171-172 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) (ppm): 2.20 (s, 6 H), 3.56 (s, 6 H), 4.91 (s, 1 H), 6.39 (s, 1 H), 7.16-6.76 (m, 4 H); \(^1\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) (ppm): 19.28, 38.71, 51.03, 103.49, 114.55, 114.83, 129.01, 129.12, 143.49, 144.78, 159/75, 162.98, 168.21; Elemental Analysis: Calcd. C: 63.94, H: 5.68, N: 4.39, O: 20.04, Found. C: 63.73, H: 5.65, N: 4.33, O: 20.02.
Dimethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 225-227 °C; $^1$H NMR (CDCl$_3$, 300 MHz): δ (ppm): 2.26 (s, 6 H), 3.50 (s, 6 H), 4.97 (s, 1 H), 6.00 (s, 1 H), 7.48-7.19 (m, 4 H); $^{13}$C NMR (CDCl$_3$, 75 MHz): δ (ppm): 19.50, 39.93, 51.13, 102.87, 109.73, 119.30, 128.55, 131.99, 145.09, 152.81, 167.61; Elemental Analysis: Calcd. C: 66.25, H: 5.56, N: 8.58, O: 19.61, Found. C: 66.18, H: 5.55, N: 8.54, O: 19.58.
Dimethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate\textsuperscript{11}

Mp: 200-201 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): δ (ppm): 2.32 (s, 6 H), 3.63 (s, 6 H), 4.88 (s, 1 H), 6.08 (s, 1 H), 7.05-7.26 (m, 4 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): δ (ppm): 19.45, 20.88, 39.01, 51.08, 103.33, 119.98, 129.48, 131.08, 144.69, 146.56, 167.97; Elemental Analysis: Calcd. C: 53.70, H: 4.77, N: 3.68, O: 16.83, Found. C: 53.40, H: 4.71, N: 3.62, O: 16.82.

\begin{center}
\textbf{1\textsuperscript{H} NMR of 5j}
\end{center}
Dimethyl 4-(4-hydroxy-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 227-228 °C; $^1$H NMR (CDCl$_3$, 300 MHz): δ (ppm): 2.26 (s, 6 H), 3.65 (s, 6 H), 3.77 (s, 3 H), 4.87 (s, 1 H), 5.30 (s, 1H), 5.40(s, 1H), 6.77-6.65 (m, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz): δ (ppm): 19.64, 38.82, 50.99, 55.76, 104.04, 110.54, 113.95, 120.10, 139.65, 143.89, 168.10; Elemental Analysis: Calcd. C: 62.24, H: 6.09, N: 4.03, O: 27.64, Found. C: 62.01, H: 6.04, N: 4.01, O: 27.59.
Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

Mp: 187-190 ºC; \( ^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta \) (ppm): 2.26 (s, 6 H), 3.56 (s, 6 H), 5.02 (s, 1 H), 6.29 (s, 1 H), 8.01-7.26 (m, 4 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \( \delta \) (ppm): 19.44, 39.60, 51.16, 102.88, 121.39, 122.69, 128.76, 134.24, 145.37, 148.31, 149.65, 167.67; Elemental Analysis: Calcd. C: 58.96, H: 5.24, N: 8.09, O: 27.72, Found. C: 58.66, H: 5.21, N: 8.01, O: 27.70.

\( ^1\)H NMR of 5o
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$^{13}$C NMR of 5o

References: