Supporting information

Magnetically recyclable magnetite-ceria (NanocatFe-Ce) nanocatalysts - Applications in multicomponent reactions under benign conditions

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1. General Methods

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated were used, respectively. The spots were visualized using UV light.

The X-ray powder diffraction pattern was obtained using a conventional powder diffractometer RIGAKU, model: MiniFlex™ II benchtop X-ray Diffractometer; X-ray tube: Cu-Kα (30 kV / 15 mA) radiation operating in Bragg-Brentano (θ/2θ) geometry. (Sample preparation: grinding when needed and compression in the sample holder with a flat glass. The sample area in the sample holder is about 2 cm²).

Transmission electron microscopy (TEM) experiments were performed on a Hitachi H8100 microscope, with a ThermoNoran light elements EDS detector and a CCD camera for image acquisition. The Fe₃O₄-CeO₂ fine powder was placed on carbon stub and the images were recorded at 5-15 kV using LFD detector under low vacuum.

Elemental analysis was done by using ICP-AES (Inductively coupled plasma-atomic emission spectrometer) using a Horiba Jobin-Yvon, France, Ultima, model equipped with a 40.68 MHz RF generator, Czerny-Turner monochromator with 1.00 m (sequential), autosampler AS500 and CMA (concomitant metals analyzer).

Scanning electron microscopy images were acquired using a JEOL JSM7001F FEG-SEM.

Elemental analysis was performed using a light elements EDS detector from Oxford. The Fe₃O₄-CeO₂ powder was spread on a double-sided carbon tape and analyzed using 25kV acceleration voltage.

For SIMS, (secondary ion mass spectrometry) positive secondary ion spectra were collected in the mass range of 0 -100 m/z (T=10 min) with an upgraded VG Ionex IX23LS TOF-SIMS set-up based on the Poschenrieder design. A focused liquid Ga⁺ gun in pulsed mode (6 kHz) was used as a source of the analytical ions. A beam current in dc mode at 14 keV was ca. 15 nA with a raster size of 300 X 300 μm². Sample potential was 5 kV. Vacuum during the experiments was maintained in the range of (2-3) X10⁻⁹ mbar in the analytical chamber.

XPS measurements were performed on VSW XPS system with the Class 100 energy analyzer being a part of an experimental setup assembled for surface investigation. The
spectra were taken in fixed analyzer transmission mode with the pass energy of 22 eV i.e. FAT 22. Fe3O4-CeO2 fine powder was prepared for XPS by pressing on an Indium plate as a matrix in order to reduce the charging problems and providing a mechanical support. For the energy axis calibration Ag(110) and polycrystalline Au samples (previously cleaned by ion sputtering) were used.

NMR spectra were recorded on a Bruker 400, 5 mm probe at 400 MHz.

2. Characterization of 1,4-dihydropyridines

![1a](image1)

2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1a).

\[ \text{Yield} = 93\% . \]

\[
{^1}H\text{-NMR (CDCl}_3, 400\text{ MHz}) \delta (\text{ppm}): 7.29 (2H, d, J= 8.0 \text{ Hz, ArH}), 7.20 (2H, t, J= 8.0 \text{ Hz, ArH}), 7.10 (1H, t, J= 8.0 \text{ Hz, ArH}), 5.82 (1H, bs, NH), 5.07 (1H, s, CH), 3.61 (3H, s, OCH}_3), 2.39 (3H, s, CH}_3), 2.21-2.14 (4H, m, CH}_2), 1.07 (3H, s, CH}_3), 0.93 (3H, s, CH}_3). \]

\[
{^{13}}C\text{-NMR (CDCl}_3, 100\text{ MHz}) \delta (\text{ppm}): 195.6, 168.0, 147.9, 146.9, 143.8, 128.1, 127.9, 126.2, 112.5, 105.9, 51.2, 50.9, 41.4, 36.4, 32.9, 29.6, 27.3, 19.7. \]

![1a'](image2)

Bis-adduct

2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (1a').

\[ \text{Yield} = 25\% . \]

\[
{^1}H\text{-NMR (CDCl}_3, 400\text{ MHz}) \delta (\text{ppm}): 7.24-7.07 (5H, m, ArH), 5.07 (1H, s, CH), 2.46-2.27 (8H, m, CH}_2), 1.21 (6H, s, CH}_3), 1.08 (6H, s, CH}_3). \]

\[
{^{13}}C\text{-NMR (CDCl}_3, 100\text{ MHz}) \delta (\text{ppm}): 190.5, 189.5, 138.2, 128.3, 126.9, 125.9, 115.7, 47.2, 46.6, 32.9, 31.6, 29.8, 27.6. \]
2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1b).\(^{[1,3]}\) Yield= 95%. \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) (ppm): 7.27 (2H, d, \(J=\) 8.0 Hz, ArH), 7.16 (2H, t, \(J=\) 8.0 Hz, ArH), 7.06 (1H, t, \(J=\) 8.0 Hz, ArH), 6.07 (1H, bs, NH), 5.02 (1H, s, CH), 4.01 (2H, m, \(CH_2CH_3\)), 2.33 (3H, s, CH\(_3\)), 2.27-2.10 (4H, m, CH\(_2\)), 1.16 (3H, t, \(J=\) 8.0 Hz, \(CH_2CH_3\)), 1.04 (3H, s, CH\(_3\)), 0.90 (3H, s, CH\(_3\)). \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm): 195.6, 167.6, 148.3, 147.2, 143.6, 128.1, 128.0, 126.1, 112.3, 106.2, 59.9, 50.9, 41.2, 36.7, 32.8, 29.6, 27.3, 19.5, 14.4.

Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (1c).\(^{[4]}\) Yield = 92%. \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) (ppm): 7.49 (2H, d, \(J=\) 8.0 Hz, ArH), 7.42 (2H, d, \(J=\) 8.0 Hz, ArH), 6.11 (1H, bs, NH), 5.09 (1H, s, CH), 4.04 (2H, m, \(CH_2CH_3\)), 2.39 (3H, s, CH\(_3\)), 2.33-2.11 (4H, m, CH\(_2\)), 1.16 (3H, t, \(J=\) 8.0 Hz, \(CH_2CH_3\)), 1.07 (3H, s, CH\(_3\)), 0.90 (3H, s, CH\(_3\)). \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) (ppm): 195.4, 167.0, 152.4, 148.6, 144.4, 1321.0, 129.0, 119.4, 111.4, 109.7, 105.1, 60.2, 50.7, 41.2, 37.4, 29.5, 27.2, 19.6, 14.3.
4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1d). \[^{[3]}\] Yield = 90%. \(^1\)H-NMR (CDCl\(_3\), 400 MHz) δ (ppm): 7.31 (2H, d, \(J = 8.0\) Hz, ArH), 7.18 (2H, d, \(J = 8.0\) Hz, ArH), 5.97 (1H, bs, NH), 5.01 (1H, s, CH), 4.05 (2H, m, CH\(_2\)CH\(_3\)), 2.37 (3H, s, CH\(_3\)), 2.30-2.12 (4H, m, CH\(_2\)), 1.19 (3H, t, \(J = 8.0\) Hz, CH\(_2\)CH\(_3\)), 1.07 (3H, s, CH\(_3\)), 0.92 (3H, s, CH\(_3\)). \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) δ (ppm): 195.5, 167.3, 148.1, 146.2, 143.7, 131.1, 130.0, 119.9, 112.0, 105.8, 60.1, 50.8, 41.3, 32.9, 29.6, 27.3, 19.6, 14.4.

4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1e). \[^{[5]}\] Yield = 92%. \(^1\)H-NMR (CDCl\(_3\), 400 MHz) δ (ppm): 6.90 (1H, s, ArH), 6.83 (1H, s, NH), 6.77 (1H, d, \(J = 8.0\) Hz, ArH), 6.68 (1H, d, \(J = 8.0\) Hz, ArH), 4.99 (1H, s, CH), 4.06 (2H, m, CH\(_2\)CH\(_3\)), 3.80 (3H, s, OCH\(_3\)), 3.77 (3H, s, OCH\(_3\)), 2.33 (3H, s, CH\(_3\)), 2.27-2.11 (4H, m, CH\(_2\)), 1.20 (3H, t, \(J = 8.0\) Hz, CH\(_2\)CH\(_3\)), 1.02 (3H, s, CH\(_3\)), 0.92 (3H, s, CH\(_3\)). \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) δ (ppm): 195.90, 167.67, 148.90, 148.33, 147.26, 143.62, 140.25, 119.86, 110.87, 106.06, 59.86, 55.83, 50.87, 40.89, 36.07, 32.67, 29.59, 27.09, 19.30, 14.41.
4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1f).[^6] Yield = 83%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.04 (1H, t, $J=8.0$ Hz, ArH), 6.85 (2H, m, ArH), 6.59 (1H, d, $J=8.0$ Hz, ArH), 5.84 (1H, bs, NH), 5.28 (1H, bs, OH), 5.03 (1H, s, CH), 4.09 (2H, m, CH$_2$CH$_3$), 2.38 (3H, s, CH$_3$), 2.22 (4H, m, CH$_2$), 1.19 (3H, t, $J=8.0$ Hz, CH$_2$CH$_3$), 1.07 (3H, s, CH$_3$), 0.94 (3H, s, CH$_3$). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 193.8, 166.4, 156.0, 148.4, 148.1, 143.6, 127.7, 118.5, 114.2, 111.9, 110.4, 104.1, 58.3, 49.9, 39.4, 35.4, 31.5, 25.9, 17.5, 13.2.

![1g](image)

4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1g).[^1,7] Yield = 90%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.20 (2H, d, $J=8.0$ Hz, ArH), 6.72 (2H, d, $J=8.0$ Hz, ArH), 6.68 (1H, s, NH), 4.98 (1H, s, CH), 4.04 (2H, m, CH$_2$CH$_3$), 3.71 (3H, s, OCH$_3$), 2.33 (3H, s, CH$_3$), 2.28-2.10 (4H, m, CH$_2$), 1.20 (3H, t, $J=8.0$ Hz, CH$_2$CH$_3$), 1.04 (3H, s, CH$_3$), 0.92 (3H, s, CH$_3$). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 195.9, 167.7, 157.9, 148.8, 143.8, 143.6, 139.8, 129.0, 113.3, 112.2, 106.3, 59.9, 55.2, 50.9, 41.0, 35.9, 32.8, 29.6, 27.3, 19.4, 14.4.

![1h](image)

4-(3-hydroxy-4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ester (1h). Yield = 86%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 6.86 (1H, d, $J=8.0$ Hz, ArH), 6.82 (1H, s, ArH), 6.68 (1H, d, $J=8.0$ Hz, ArH), 6.00 (1H, bs, NH), 5.56 (1H, bs, OH), 4.97 (1H, s, CH), 4.07 (2H, q, $J=8.0$ Hz, CH$_2$CH$_3$), 1.98 (3H, t, $J=8.0$ Hz, CH$_2$CH$_3$), 1.20 (3H, s, CH$_3$), 1.19 (3H, s, CH$_3$), 0.92 (3H, s, CH$_3$). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 196.9, 167.7, 157.9, 148.8, 143.8, 143.6, 139.8, 129.0, 113.3, 112.2, 106.3, 59.9, 55.2, 50.9, 41.0, 35.9, 32.8, 29.6, 27.3, 19.4, 14.4, 14.4.

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CH$_2$CH$_3$), 3.80 (3H, s, OCH$_3$), 2.34 (3H, s, CH$_3$), 2.28-2.13 (4H, m, CH$_2$), 1.22 (3H, t, $J$= 8.0 Hz, CH$_2$CH$_3$), 1.06 (3H, s, CH$_3$), 0.95 (3H, s, CH$_3$). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 195.7, 167.6, 148.0, 145.0, 143.2, 140.7, 120.1, 114.1, 112.4, 110.1, 106.3, 60.0, 56.0, 50.9, 41.3, 36.1, 32.9, 29.5, 27.5, 19.6, 14.4.

![Structure 1i](image)

**4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1i).**[8] Yield= 92%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.31 (2H, d, $J$= 8.0 Hz, ArH), 7.17 (2H, t, $J$= 8.0 Hz, ArH), 6.73 (1H, bs, NH), 5.01 (1H, s, CH), 3.60 (3H, s, OCH$_3$), 2.34 (3H, s, CH$_3$), 2.30-2.11 (4H, m, CH$_2$), 1.19 (3H, t, $J$= 8.0 Hz, CH$_2$CH$_3$), 1.05 (3H, s, CH$_3$), 0.90 (3H, s, CH$_3$). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 195.9, 167.8, 149.2, 146.1, 144.5, 131.1, 129.8, 120.0, 113.5, 111.6, 105.3, 51.2, 50.9, 40.9, 36.3, 32.8, 29.6, 27.2, 19.4.

![Structure 1j](image)

**4-(3,4-bis(benzyloxy)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1j).**[9] Yield= 85%. $^1$H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.42-7.28 (10H, m, PhH), 6.90 (1H, s, ArH), 6.82-6.76 (2H, m, ArH), 6.77 (1H, d, ArH), 5.87 (1H, bs, NH), 5.09 (4H, d, OCH$_2$Ph), 4.96 (1H, s, CH), 4.02 (2H, q, OCH$_2$CH$_3$), 2.31 (3H, s, CH$_3$), 2.28-2.11 (4H, m, CH$_2$), 1.15 (3H, t, OCH$_2$CH$_3$), 1.05 (3H, s, CH$_3$), 0.90 (3H, s, CH$_3$).
4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1k).\[10]\ Yield = 92%. $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.49 (2H, d, $J=8.0$ Hz, ArH), 7.41 (2H, t, $J=8.0$ Hz, ArH), 6.80 (1H, bs, NH), 5.09 (1H, s, CH), 3.59 (3H, s, OCH$_3$), 2.33 (3H, s, CH$_3$), 2.32-2.10 (4H, m, CH$_2$), 1.06 (3H, s, CH$_3$), 0.88 (3H, s, CH$_3$).

4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1l).\[8]\ Yield = 95%. $^1$H-NMR (DMSO-d$_6$, 400 MHz) $\delta$ (ppm): 9.05 (1H, bs, NH), 7.04 (2H, d, $J=8.0$ Hz, ArH), 6.73 (2H, t, $J=8.0$ Hz, ArH), 4.79 (1H, s, CH), 3.67 (3H, s, OCH$_3$), 3.52 (3H, s, OCH$_3$), 2.41 (1H, d, $J=20.0$, CH), 2.27 (4H, m, CH+CH$_3$), 2.16 (1H, d, $J=20.0$, CH), 1.97 (1H, d, $J=16.0$, CH), 1.00 (3H, s, CH$_3$), 0.84 (3H, s, CH$_3$). $^{13}$C-NMR (DMSO-d$_6$, 100 MHz) $\delta$ (ppm): 195.0, 168.1, 157.9, 149.9, 145.6, 140.5, 128.9, 113.8, 110.9, 104.2, 55.5, 51.3, 50.9, 35.4, 32.8, 29.8, 27.1, 18.9.
3. $^1$H NMR and $^{13}$C NMR spectra of 1,4-dihydropyridines
References


