Supplementary Information

N-Propyl Benzoguanamine Sulfonic acid supported on magnetic Fe₃O₄ nanoparticles: A novel and efficient magnetically heterogeneous catalyst for the synthesis of 1, 8-dioxo-decahydroacridine derivatives

Masoumeh Gholami Dehbalaei a, Naser Foroughifar a,*, Hoda Pasdar a, Alireza Khajeh-Amiri b

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General experimental procedure:

All chemicals were purchased from Merck or Fluka and were used without further purification. The melting points were uncorrected and measured using capillary tubes on an electrothermal digital apparatus. IR spectra were recorded on a Shimadzo (FT)-IR 300 spectrophotometer in KBr. $^1$H-NMR 500 MHz and $^{13}$C-NMR spectra were obtained on Brucker 125 MHz spectrometers in CDCl$_3$ or DMSO-d$_6$ as the solvent with TMS as an internal standard. The progress of the reaction was monitored by TLC (thin-layer chromatography) using n–hexane/EtOAc as an eluent. Nanoparticles were characterized using a X-Pert Pro MPD X-ray diffraction (XRD) diffractometer (Cu-K$_\alpha$, k = 0.154056 nm) over the range $2\theta = 10$–80 using 0.04$^0$ as the step length. The scanning electron microscope measurement was carried out on a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). TEM analysis of the catalyst was recorded using Zeiss-EM10C transmission electron microscope. The thermogravimetric analysis (TGA) curves were recorded using Diamond TGA/DTA SII Perkin Elmer Company. The magnetization was measured at room temperature using a vibrating sample magnetometer (Model 7300 VSM system, Lake Shore Cryotronic, Inc., Westerville, OH, USA). Inductively coupled mass spectroscopy (ICP-MS) was also done in order to confirm the iron loading ICP-MS (Model Elan 6000 DRC). The iron content in the catalyst supernatant was estimated by atomic absorption spectroscopy (AAS) on a Model novAA-400p atomic absorption spectrometer.

General procedure for preparation of MNPs-N-Propyl-Benzoguanamine-SO$_3$H

Fe$_3$O$_4$ MNPs were prepared by chemical co-precipitation of Fe$^{3+}$ and Fe$^{2+}$ ions as described in the literature. The Fe$_3$O$_4$ coated with SiO$_2$ was prepared through a modified sol–gel method.
Chloropropyl-modified silica-coated MNPs were prepared according to a reported procedure. To a magnetically stirred mixture of the prepared Fe₃O₄/SiO₂-Chloropropyl (1 g) was added benzoguanamine (10 mmol, 1.87 g) and triethylamine (10 mmol, 1.39 ml) in dried toluene (50 mL) and the mixture was sonicated for 2 h under N₂ atmosphere, then stirred for 48 h under reflux conditions. The obtained solid was magnetically collected from the solution and washed with water/ethanol (20:10 mL) for three times and dried in vacuum for 5 h. To a mixture of benzoguanamine-modified silica-coated Fe₃O₄ MNPs (1 g) in dried CHCl₃ (3 mL), chlorosulfonic acid (ClSO₃H, 1 mL) was added dropwise at 0 °C over 2 h and then the mixture was filtered and washed with ethanol (5 mL) and dried at room temperature to afford the title compound.

**General procedure for synthesis of 1, 8-dioxo-decahydroacridin derivatives**

To a mixture of dimedone (2 mmol), aromatic benzaldehyde (1 mmol) and ammonium acetate or aniline (1.2 mmol) was added MNPs-N-Propyl-Benzoguanamine-SO₃H (6 mg) in 2 mL aqueous ethanol [V (ethanol): V (H₂O) = 3 : 1] as the solvent and the reaction mixture stirred magnetically under reflux (100 °C) conditions. The progress of the reaction was followed by thin layer chromatography (TLC). After the completion of the reaction, mixture was added 0.5 mL water and stirred for a moment. Then, the reaction mixture was cooled to room temperature and the catalyst was easily separated by an external magnet. The solvent was evaporated to afford the crude solid. Finally, the resulting solid was filtered, then washed with 30% aqueous ethanol without further purification and dried in an oven at 60 °C. The pure 1, 8-dioxo-decahydroacridin derivatives were obtained in excellent yields.
Spectral data for selected of 1, 8-dioxo-decahydroacridin derivatives:

3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (Entry 1, Table 2): White solid; m.p: 288–290 °C; Yield 93%; IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 1591 (C=O), 2879-2961 (CH$_3$ str.), 3068 (NH); $^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$ ppm: 1.11 (s, 6H, 2CH$_3$), 1.24 (s, 6H, 2CH$_3$), 2.30-2.49 (m, 8H, 4CH$_2$), 7.10-7.29 (m, 5H, Ar-H), 11.91 (s,1H, NH); $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ ppm: 27.4, 29.6, 31.4, 32.7, 46.4, 47.0, 115.6, 125.8, 126.7, 128.2, 138.0, 189.4, 190.5.

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (Entry 2, Table 2): White solid; m.p: 279–281 °C; Yield 85%; IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 1596 (C=O), 2878-2961 (CH$_3$ str.), 3021 (NH); $^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$ ppm: 1.11 (s, 6H, 2CH$_3$), 1.24 (s, 6H, 2CH$_3$), 2.31 (s, 3H, CH$_3$), 2.32-2.49 (m, 8H, 4CH$_2$), 5.52 (s, 1H, CH), 6.99-7.09 (dd, 4H, Ar-H, J= 7.7 Hz), 11.93 (s, 1H, NH); $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ ppm: 20.7, 20.9, 27.2, 27.3, 29.1, 29.4, 31.2, 31.3, 32.0, 32.3, 40.7, 46.3, 46.9, 50.6, 115.5, 115.6, 126.5, 128.1, 128.6, 128.8, 134.8, 135.1, 135.5, 141.1, 161.9, 189.2, 190.2, 196.2.

9-(3-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (Entry 6, Table 2): Yellow solid; m.p: 308–310 °C; Yield 89%; IR (KBr, cm$^{-1}$) $\nu_{\text{max}}$: 1617 (C=O), 2878-2928 (CH$_3$ str.), 3282 (NH), 3447 (OH); $^1$H-NMR (DMSO-d$_6$, 500 MHz) $\delta$ ppm: 0.87 (s, 6H, 2CH$_3$), 0.99 (s, 6H, 2CH$_3$), 1.97-2.00 ( d, 2H, CH$_2$, J= 16.1 Hz), 2.14-2.17 (d, 2H, CH$_2$, J= 16.1 Hz), 2.28-2.31 (d, 2H, CH$_2$, J= 17.0 Hz), 2.41-2.44 (d, 2H, CH$_2$, J= 17.0 Hz), 4.73 (s, 1H, CH), 6.39-6.42 (d, 1H, Ar-H, J= 11.0 Hz), 6.55-6.57 (d, 1H, Ar-H, J= 7.65 Hz), 6.61 (s, 1H, Ar-H), 6.89-6.92 (t, Ar-H, J= 7.5 Hz), 9.03 (s, 1H, NH), 9.23 (s, 1H, OH); $^{13}$C-NMR (DMSO-d$_6$, 125 MHz) $\delta$ ppm: 26.5, 26.6, 27.9, 28.8, 31.9, 32.2, 32.6, 40.0, 46.6, 50.1, 50.3, 111.5, 112.5, 114.5, 114.7, 118.4, 128.7, 148.5, 149.3, 156.7, 157.1, 162.9, 194.5, 196.1.
3,3,6,6-tetramethyl-9-(2-nitrophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (Entry 7, Table 2): Yellow solid; m.p: 297–299 °C; Yield 92%; IR (KBr, cm⁻¹) ν_max: 1343 and 1520 (NO₂), 1723 (C=O), 2900-2955 (CH₃ str.), 3381 (NH); ¹H-NMR (CDCl₃, 500 MHz) δ ppm: 1.02 (s, 6H, 2CH₃), 1.15 (s, 6H, 2CH₃), 2.20-2.51 (m, 8H, 4CH₂), 6.04 (s, 1H, CH), 7.24-7.55 (m, 4H, Ar-H), 11.6 (s, 1H, NH); ¹³C-NMR (CDCl₃, 125 MHz) δ ppm: 28.1, 28.5, 30.0, 31.9, 46.2, 46.8, 114.6, 124.3, 127.2, 129.6, 131.3, 132.1, 149.7, 189.4, 190.4.

9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (Entry 8, Table 2): White solid; m.p: 298–301 °C; Yield 91%; IR (KBr, cm⁻¹) ν_max: 673-885 (Cl), 1590 (C=O), 2881-3005 (CH₃ str.), 3049 (NH); ¹H-NMR (CDCl₃, 500 MHz) δ ppm: 1.09 (s, 6H, 2CH₃), 1.21 (s, 6H, 2CH₃), 2.29-2.47 (m, 8H, 4CH₂), 5.47 (s, 1H, CH), 7.00-7.02 (d, 2H, Ar-H, J= 8.0 Hz), 7.21-7.23 (d, 2H, Ar-H, J= 8.0 Hz), 11.87 (s, 1H, NH); ¹³C-NMR (CDCl₃, 125 MHz) δ ppm: 27.2, 27.4, 29.2, 29.5, 31.3, 31.4, 32.1, 32.4, 40.8, 46.4, 47.0, 50.6, 115.2, 115.3, 128.1, 128.3, 129.7, 131.5, 131.9, 136.7, 142.6, 162.4, 189.3, 190.5, 196.2.

3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (Entry 1, Table 3): White solid; m.p: 253–255 °C; Yield 95%; IR (KBr, cm⁻¹) ν_max: 1595 (C=O), 2873-2962 (CH₃ str.); ¹H-NMR (CDCl₃, 500 MHz) δ ppm: 1.10 (s, 6H, 2CH₃), 1.24 (s, 6H, 2CH₃), 2.30-2.48 (m, 8H, 4CH₂), 5.55 (s, 1H, CH), 7.09-7.28 (m, 10H, 2 Ar-H); ¹³C-NMR (CDCl₃, 125 MHz) δ ppm: 27.3, 29.5, 31.3, 32.7, 46.4, 47.0, 115.5, 125.7, 126.7, 128.1, 138.0, 189.3, 190.4.
FIGURE 1
FIGURE 2

FIGURE 3
FIGURE 4
FIGURE 5
FIGURE 6

FIGURE 7
FIGURE 10