One-pot multicomponent reaction synthesis of Spirooxindoles promoted by guanidine-functionalized magnetic Fe$_3$O$_4$ nanoparticles

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Thermogravimetric analysis (TGA) evaluates the thermal stability of the MNPs-CPTMS and MNPs-Guanidine. These nanoparticles show suitable thermal stability without significantly decreasing in weight (Fig. S1). The weight loss at temperatures below 200 ºC is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The curve shows a weight loss about 10% from 250 to 600 ºC, resulting from the decomposition of organic spacer grafting to the MNPs surface.

Fig. S1. TGA curve of MNPs-Guanidine.
X-ray photoelectron spectroscopy (XPS) analysis was used to investigate the chemical binding in the synthesized MNPs-Guanidine. In the wide-scan spectrum of functionalized MNPs (Fig. S2) the predominant components are Si 2p (103 eV), Si 2s (150 eV), C 1s (284 eV), N 1s (400 eV), O 1s (530 eV), and Fe 2p (710 eV).

Fig S 2. XPS spectrum of MNPs-Guanidine
In order to investigate the size distribution of nanoparticles, DLS (dynamic light scattering) graph of the nanoparticles are presented in Fig. S3. This size distribution is centered at a value of 44 nm.

![DLS data of MNPs-Guanidine in ethanol](image)

Fig S3. DLS data of MNPs-Guanidine in ethanol
Meanwhile, the reusability of MNPs-Guanidine was studied for the reaction of 5-chloroisatin, hydrazine hydrate, ethyl acetoacetate and dimedone or malononitrile. After completion of the reaction, the nanocatalyst was easily separated using an external magnet. The recovered magnetite nanoparticles were washed several times with acetone and then dried at room temperature. Figure S4 indicates that the catalyst could be reused for seven times with a minimal loss of activity.

**Fig S4.** Reusability of MNPs-Guanidine as catalyst for the synthesis of 6b and 7f
$^1$H NMR: 3,7,7-Trimethyl-7,8-dihydro-$1^H$-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5($6^H$)-dione (6a)
$^{13}$C NMR: 3,7,7-Trimethyl-7,8-dihydro-1$H$-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5(6$H$)-dione(6a)
'H NMR: 3,7,7-Trimethyl-7,8-dihydro-5'-chloro-1H-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5(6H)-dione (6b)
$^{13}$C NMR: 3,7,7-Trimethyl-7,8-dihydro-5'-chloro-1$H$-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5(6$H$)-dione (6b)
$^1$H NMR: 3,7,7-Trimethyl-7,8-dihydro-5'-bromo-1$H$-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5(6$H$)-dione (6c):
$^{13}$CNMR: 3,7,7-Trimethyl-7,8-dihydro-5'-bromo-1$H$-spiro[chromeno [2, 3-$c$]pyrazole-4,3'-indoline]-2', 5(6$H$)-dione (6c):
$^1$H NMR: 3,7,7-Trimethyl-7,8-dihydro-5'-nitro-1$H$-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5(6$H$)-dione(6d)
$^{13}$C NMR: 3,7,7-Trimethyl-7,8-dihydro-5'-nitro-1H-spiro[chromeno [2, 3-c]pyrazole-4,3'-indoline]-2', 5(6H)-dione (6d)
H NMR: Methyl 6'-Amino-3'-methyl-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (7a):
$^{13}$C NMR: Methyl 6'-Amino-3'-methyl-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (7a):
\(^1\text{H NMR: Methyl 6'}-\text{Amino-3'}-\text{methyl-2-oxo-5-chloro-2}'H\text{-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'}-\text{carboxylate(7b)}}\)
$^{13}$C NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-chloro-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate(7b)
$^1$H NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-bromo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate(DMSO-$d_6$, 400 MHz)(7c):
1H NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-bromo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (DMSO-\(d_6\) + D\(_2\)O, 400 MHz): (7c):
$^{13}$C NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-bromo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (7c):
$^1$H NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-nitro-2'H-spiro[indoline-3,4'-pyrano[2,3-c|pyrazole]-5'-carboxylate(DMSO-$d_6$, 400 MHz): (7d):
$^1$H NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-nitro-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (DMSO-$d_6$ + D$_2$O, 400 MHz) (7d):
$^{13}$C NMR: Methyl 6'-Amino-3'-methyl-2-oxo-5-nitro-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (DMSO-$d_6$, 100 MHz): (7d):