

***Supporting Information***

**Functionalization of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles for organocatalytic Michael reactions**

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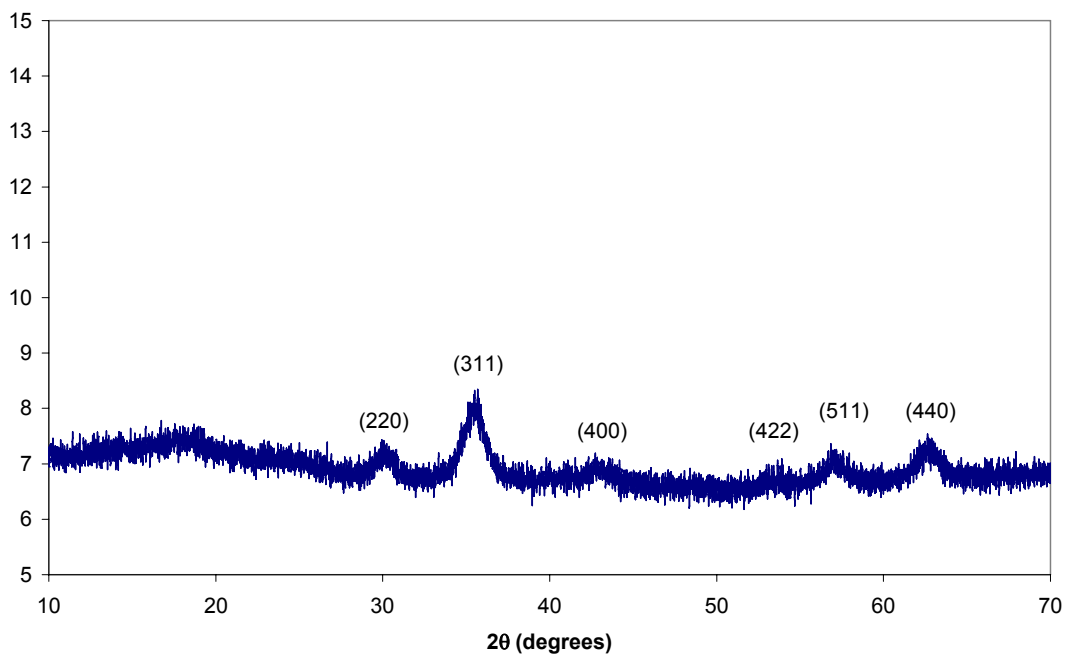
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General	<b>S2</b>
XRD spectrum of the MNPs of Fe <sub>3</sub> O <sub>4</sub> ( <b>1</b> )	<b>S3</b>
Size distribution of the MNPs of Fe <sub>3</sub> O <sub>4</sub> ( <b>1</b> )	<b>S3</b>
Size distribution of the azide functionalized MNPs ( <b>3</b> )	<b>S4</b>
TEM micrograph and size distribution of diphenyl prolinol supported onto MNPs ( <b>5</b> ) after four runs	<b>S4</b>
Synthesis of ( <i>S</i> )- $\alpha,\alpha$ -diphenylprolinol trimethylsilyl ether	<b>S5</b>
Physical data for Michael adducts	<b>S7</b>

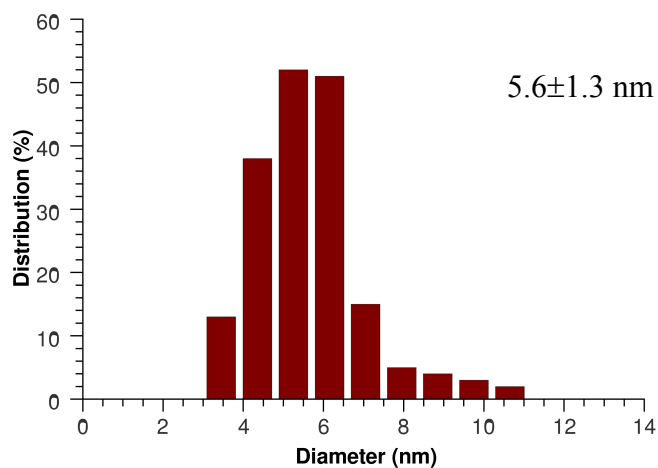
**General:**

Unless otherwise stated, all commercial reagents were directly used without any purification. All starting materials, 3-iodopropyltrimethoxysilane (Aldrich), *N*-Boc-*trans*-4-hydroxy-L-proline methyl ester (Aldrich) and iron(III) acetylacetonate (TCI) were commercially available of the best grade and were used without further purification. Ultrapure water was obtained from an SG Water Ultra Clear system that provides water with conductivity at 25 °C of 0.055  $\mu$ S. All flash chromatography was carried out using 60 mesh silica gel and dry-packed columns. NMR spectra were registered in a Bruker Advance 400 Ultrashield spectrometer in CDCl<sub>3</sub> at room temperature, operating at 400.13 MHz (<sup>1</sup>H) and 100.63 MHz (<sup>13</sup>C{<sup>1</sup>H}). TMS was used as internal standard for <sup>1</sup>H-NMR and CDCl<sub>3</sub> for <sup>13</sup>C-NMR. Chemical shifts are reported in ppm referred to TMS. IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer fitted with an ATR cell. IR spectra of nanoparticles were recorded on a Thermo Nicolet 5700 FTIR spectrometer, using KBr pellets. Potassium bromide used in the preparation of the pellets was kept in an oven at 50 °C. Elemental analysis (C; H; N) were performed in LECO CHNS-model 932 by C.A.I. microanálisis elemental, Departamento de Química Orgánica y Farmacéutica, Universidad Complutense de Madrid, Madrid, Spain. ESI mass spectra were obtained on a Waters LCT Premier instrument. High performance liquid chromatography (HPLC) was performed on Agilent Technologies Chromatographs (Series 1100 and 1200), using Chiralpak IC columns using guard column. Racemic standard products were prepared using DL-proline as catalyst in order to establish HPLC conditions. All products are known and were characterized by comparison of their physical and spectroscopic properties with those described in the literature. TEM images were recorded using JEOL JEM 1011 microscope equipped with lanthanum hexaboride filament, operated at an acceleration voltage of 100 kV, at Microscopy Units, Universitat Rovira i Virgili, Tarragona, Spain. A drop of the MNPs suspension was added to a holey-carbon coated 200 mesh copper grid allowing the solvent to evaporate before being introduced into the microscope. X-Ray diagrams were collected in the  $\theta$ - $\theta$  mode using a Bruker D8 Advance X-ray diffractometer: Cu K $\alpha$ <sub>1</sub> irradiation,  $\lambda = 1.5406$  Å; room temperature (25 °C);  $2\theta = 4$ -70.

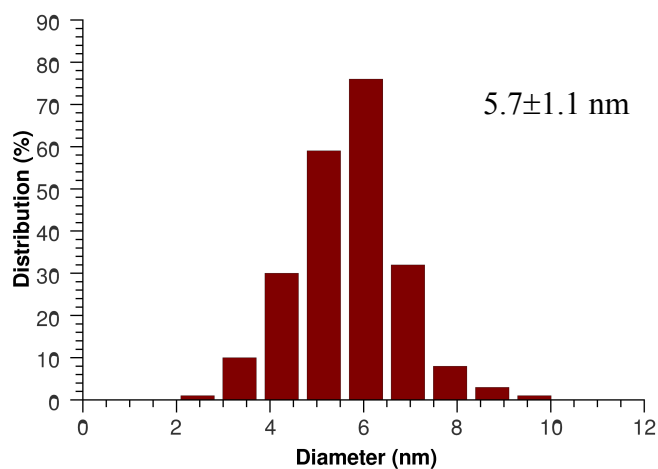
**Figure S1.** XRD spectrum of the MNPs of Fe<sub>3</sub>O<sub>4</sub> (**1**).



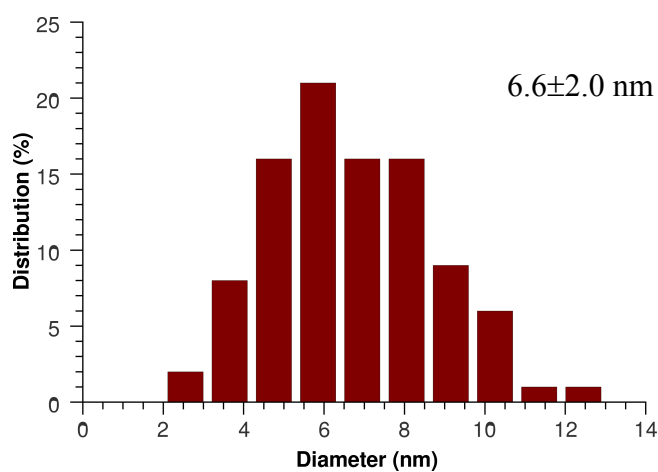
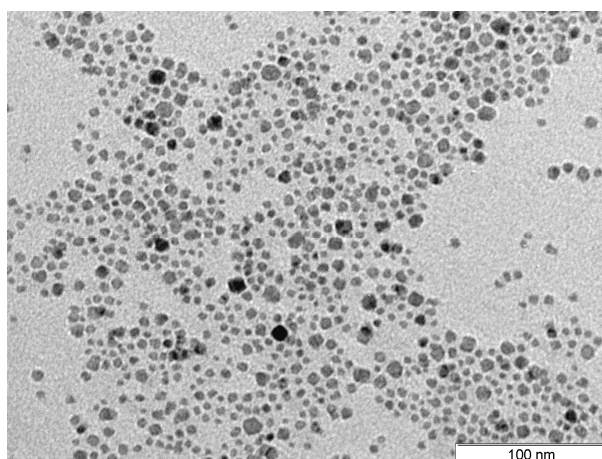
**Figure S2.** Size distribution of the MNPs of Fe<sub>3</sub>O<sub>4</sub> (**1**) determined by TEM.



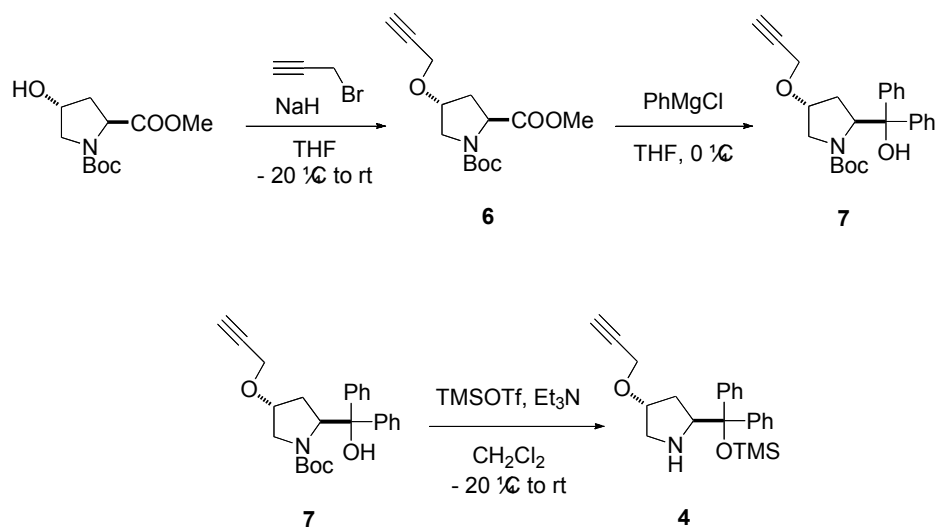
**Figure S3.** Size distribution of the azide functionalized MNPs (**3**).



**Figure S4.** TEM micrograph and size distribution of diphenyl prolinol supported onto MNPs (**5**) after four runs.



**Synthesis of (*S*)- $\alpha,\alpha$ -diphenylprolinol trimethylsilyl ether (**4**):<sup>1</sup>**



**(2*S*,4*R*)-1-*tert*-butyl 2-methyl 4-(prop-2-ynoxy)pyrrolidine-1,2-dicarboxylate (**6**)**

A solution of *N*-Boc-*trans*-4-hydroxy-L-proline methyl ester (2 g, 7.9 mmol) in anhydrous THF (20 mL) was added *via canula* to a suspension of sodium hydride (475 mg, 11.8 mmol) in anhydrous THF (35 mL) at -20 °C under N<sub>2</sub>. The resulting mixture was stirred for 20 min and then a solution of propargyl bromide (1.3 mL, 11.8 mmol) in THF was added. The reaction mixture was stirred at -20 °C for 1 h and then was allowed to reach room temperature and stirred overnight. Once the reaction was completed MeOH (10 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The combined organic layers were washed with brine (50 mL), dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting crude was purified by flash chromatography through deactivated silica (2.5% Et<sub>3</sub>N v/v) (hexane/EtOAc 2:1), to afford the desire product as an orange oil (1.8 g, 80% yield).

<sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta_{\text{H}}$  = 1.44 (9H, s), 2.04 - 2.12 (1H, m), 2.24 - 2.46 (2H, m), 3.47 - 3.65 (2H, m), 3.68 - 3.74 (3H, brs), 4.11 - 4.17 (2H, m), 4.28 - 4.45 (2H, m). <sup>13</sup>C-NMR (100 MHz; CDCl<sub>3</sub>; 328 K):  $\delta_{\text{C}}$  = 28.4 (CH<sub>3</sub>), 36.6 (CH<sub>2</sub>), 51.3 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 56.5 (CH<sub>2</sub>), 57.8 (CH), 74.8 (CH), 75.9 (CH), 79.4 (C), 80.1 (C), 153.8

<sup>1</sup> E. Alza and M. A. Pericàs, *Adv. Synth. Catal.*, 2009, **351**, 3051.

(C=O), 173.4 (C=O).

**(2*S*,4*R*)-tert-butyl 2-(hydroxydiphenylmethyl)-4-(prop-2-ynyloxy)pyrrolidine-1-carboxylate (7)**

To a solution of **6** (1.3 g, 4.6 mmol) in 20 mL of anhydrous THF was added dropwise by an addition funnel a solution of phenyl magnesium chloride 2M in THF (11.5 mL, 22.9 mmol) at 0 °C under argon. After the addition was completed, the reaction mixture was stirred for 6 h and then was quenched with 10 mL of saturated aqueous solution of NH<sub>4</sub>Cl. The resulting solution was diluted with Et<sub>2</sub>O (150 mL) and the organic layer was washed with a saturated aqueous solution of NH<sub>4</sub>Cl (80 mL x 3), dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography through deactivated silica (2.5% Et<sub>3</sub>N v/v) (hexane/EtOAc 2:1) to afford the desire product as colourless oil (704 mg, 38 % yield).

<sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), mixture of rotamers: δ<sub>H</sub>= 1.28 (9H, s), 1.94 - 2.15 (2H, m), 2.28 - 2.38 (1H, m), 2.91 (1H, br, OH), 3.56 (2H, br), 3.96 - 4.30 (3H), 4.93 - 5.03 (1H), 7.15 - 7.57 (10H, m). <sup>13</sup>C-NMR (100 MHz; CDCl<sub>3</sub>; 328 K), mixture of rotamers: δ<sub>C</sub>= 28.2, 28.5, 35.9, 36.5, 53.1, 53.2, 56.3, 57.1, 65.3, 65.4, 74.5, 75.2, 76.7, 79.1, 79.8, 80.2, 80.9, 81.2, 81.8, 126.9 - 128.1, 143.8, 145.4, 145.9, 157.3

**(2*S*,4*R*)-2-(diphenyl(trimethylsilyloxy)methyl)-4-(prop-2-ynyloxy)pyrrolidine (4)**

To a solution of **7** (460.3 mg, 1.13 mmol) in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> at -20 °C was added triethylamine (0.31 mL, 2.15 mmol) and trimethylsilyl trifluoromethanesulfonate (0.39 mL, 2.15 mmol). The solution was then allowed to reach 0 °C and was stirred for 3 h at this temperature. The reaction was quenched with water and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The resulting crude was purified by flash chromatography through deactivated silica (2.5% Et<sub>3</sub>N v/v) (hexane/EtOAc 1:1) to afford the desire product as pale yellow oil (288.4 mg, 68% yield).

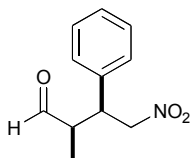
<sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ<sub>H</sub> = -0.11 (9H, s), 1.67 - 1.70 (2H, m), 1.74 (1H, br, NH), 2.36 (1H, t, *J* = 2.39 Hz), 2.79 (1H, dd, *J* = 11.82, 4.85 Hz), 2.95 (1H, dd, *J* =

11.82, 2.42 Hz), 3.91 to 3.95 (1H, m), 4.05 (2H, dd,  $J = 2.35, 1.23$  Hz), 4.32 (1H, t,  $J = 7.94$  Hz), 7.18 - 7.47 (10H, m).  $^{13}\text{C-NMR}$  (100 MHz;  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 2.3$  ( $\text{CH}_3$ ), 34.2 ( $\text{CH}_2$ ), 52.8 ( $\text{CH}_2$ ), 56.2 ( $\text{CH}_2$ ), 63.7 (CH), 74.1 (CH), 79.4 (CH), 80.2 (C), 83.0 (C), 127.0 - 128.6 (CH, Ar), 145.5 (C, Ar), 146.8 (C, Ar).

### **Physical data of the Michael products:**

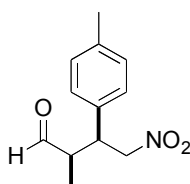
All the products are known and all the spectroscopic data matched those reported in the literature.

#### **(2*R*, 3*S*)-2-Methyl-4-nitro-3-phenylbutanal**<sup>2</sup>



Title compound was prepared from *trans*- $\beta$ -nitrostyrene and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with an IC column (hexane/EtOH 95:5,  $0.8 \text{ mL}\cdot\text{min}^{-1}$ , 214 nm):  $t_{\text{r}} = 27.0$  min (minor, *syn*), 32.4 min (major, *syn*).

#### **(2*R*,3*S*)-2-Methyl-3-(4-methylphenyl)-4-nitrobutanal**<sup>3</sup>

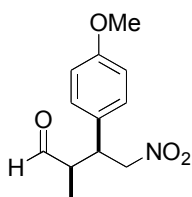


Title compound was prepared from *trans*-4-methyl- $\beta$ -nitrostyrene and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with an IC column (hexane/EtOH 95:5,  $0.8 \text{ mL}\cdot\text{min}^{-1}$ , 214 nm):  $t_{\text{r}} = 22.0$  min (minor, *syn*), 26.1 min (major, *syn*).

<sup>2</sup> Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem.*, 2005, **117**, 4284; *Angew. Chem. Int. Ed.* 2005, **44**, 4212.

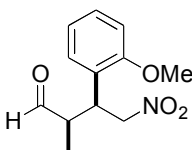
<sup>3</sup> W. -H. Wang, X. -B. Wang, K. Kodama, T. Hirose and G. -Y. Zang, *Tetrahedron*, 2010, **66**, 4970.

**(2*R*, 3*S*)-2-Methyl-4-nitro-3-(4-methoxyphenyl)-butanal**<sup>4</sup>



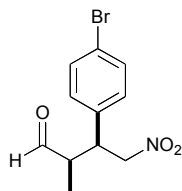
Title compound was prepared from *trans*-4-methoxy- $\beta$ -nitrostyrene and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with an IC column (hexane/EtOH 95:5, 0.8 mL·min<sup>-1</sup>, 214 nm):  $t_r$  = 45.1 min (major, *syn*), 38.9 min (minor, *syn*).

**(2*R*, 3*S*)-2-Methyl-4-nitro-3-(2-methoxyphenyl)-butanal**<sup>4</sup>



Title compound was prepared from *trans*-2-methoxy- $\beta$ -nitrostyrene and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with an IC column (hexane/EtOH 95:5, 0.8 mL·min<sup>-1</sup>, 214 nm):  $t_r$  = 23.4 min (major, *syn*), 21.1 min (minor, *syn*).

**(2*R*, 3*S*)-(4-Bromophenyl)-2-methyl-4-nitrobutyraldehyde**<sup>4</sup>



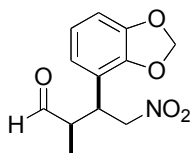
Title compound was prepared from *trans*-4-bromo- $\beta$ -nitrostyrene and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC

<sup>4</sup> R. -S. Luo, J. Weng, H. -B. Ai, G. Lu and A. S. C. Chan, *Adv. Synth. Catal.*, 2009, **351**, 2449.



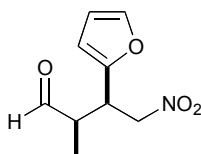
with an IC column (hexane/EtOH 95:5, 0.8 mL·min<sup>-1</sup>, 214 nm):  $t_r = 26.9$  min (major, *syn*), 24.3 min (minor, *syn*).

**(2*R*, 3*S*)-3-(benzo[d][1,3]dioxol-4-yl)-2-methyl-4-nitrobutanal**



Title compound was prepared from 5-[(*E*)-2-nitroethenyl]-1,3-benzodioxole and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with an IC column (hexane/EtOH 95:5, 0.8 mL·min<sup>-1</sup>, 214 nm):  $t_r = 36.84$  min (minor, *syn*), 41.9 min (major, *syn*). <sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta_H$  1.0 (3H, d,  $J = 7.3$ , Me), 2.6-2.8 (1H, m, CHCH<sub>3</sub>), 3.7-3.8 (1H, m, CHCH<sub>2</sub>NO<sub>2</sub>), 4.6-4.8 (2H, m, CH<sub>2</sub>NO<sub>2</sub>), 5.9 (2H, s, CH<sub>2</sub>O), 6.6-6.8 (3H, m, ArH), 9.7 (1H, s, CHO). <sup>13</sup>C-NMR (100MHz; CDCl<sub>3</sub>):  $\delta_C$  12.2, 43.8, 44.8, 48.5, 78.3, 101.3, 107.9, 108.6, 121.6, 130.1, 148.2, 202.1. HRMS(TOF MS ES<sup>-</sup>): Calculated for C<sub>12</sub>H<sub>12</sub>NO<sub>5</sub>, 250.0715; found 250.0716.

**(2*R*, 3*S*)-3-Furyl-2-methyl-4-nitrobutyraldehyde**<sup>4</sup>



Title compound was prepared from 2-(2-nitrovinyl)-furan and propionaldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with an IC column (hexane/EtOH 95:5, 0.8 mL·min<sup>-1</sup>, 214 nm):  $t_r = 29.5$  min (minor, *syn*), 41.21 min (major, *syn*).

