Journal of Materials Chemistry

Cite this: *J. Mater. Chem.*, 2011, **21**, 7350

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PAPER

Functionalization of Fe_3O_4 magnetic nanoparticles for organocatalytic Michael reactions†

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Received 4th February 2011, Accepted 11th March 2011
DOI: 10.1039/c1jm10535c

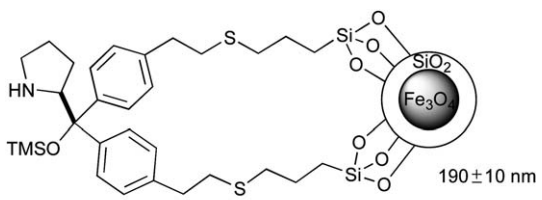
(*S*)-α,α-Diphenylprolinol trimethylsilyl ether supported onto well-defined (5.7 ± 1.1 nm) superparamagnetic Fe_3O_4 nanoparticles was used as a highly active, magnetically recoverable and reusable catalyst for the asymmetric, organocatalytic Michael addition of propanal to nitroolefins leading to high enantioselectivities. The assembly of the catalytic functional nanoparticles involves two successive steps: (i) introduction of a 3-azidopropyl unit through the formation of Si–O bonds, and (ii) integration of the organocatalytic unit by means of a copper-catalysed alkyne–azide cycloaddition reaction leading to a 1,2,3-triazole linker. Neither the process of nanoparticle assembly nor its catalytic use in dichloromethane solution provokes particle growth or agglomeration, this behaviour being key for the observation of high catalytic activity and for recyclability.

Introduction

In recent years magnetic nanoparticles (MNPs) of Fe_3O_4 are attracting an increasing interest in many different fields due to their intrinsic properties such as high surface area, low toxicity and superparamagnetic behaviour, the latter allowing nanoparticle motion control by application of an external magnetic field. In catalytic applications, this is translated into an easy separation and recovery from the reaction medium by magnetic decantation.[1] In addition to that, almost all ferrites behave as metal oxides, presenting a large number of hydroxyl groups on the surface of their particles.[2] This characteristic allows building well-defined shells of different materials around the ferrite core or, when functional materials are targeted, grafting functional groups suitable for the supporting of all kinds of actuators, ligands and/or catalysts by covalent bonds.

For most of their applications, the size of individual nanoparticles and agglomeration processes leading to large size aggregates are important aspects to control during the synthesis and surface modification, since MNPs with small size tend to have a large surface area and are consequently more active.[3] When catalytic applications are considered, agglomeration of MNPs has deleterious effects on reactivity.

Owing to the potential advantages mentioned above, the supporting of organocatalysts for asymmetric applications, onto well-defined, small size MNPs appears as an interesting alternative for the preparation of easily recoverable and recyclable catalysts. Notwithstanding, there are only a few examples in the literature exploring this methodology.[4] Very recently, Wang *et al.* reported on the development of a submicrometric material (*ca.* 200 nm diameter) where a (*S*)-diarylprolinol trimethylsilyl ether was supported onto Fe_3O_4@SiO_2 (A) and studied its catalytic behaviour.[4d] However, the use of small size, superparamagnetic Fe_3O_4 nanoparticles as a substrate in organocatalytic applications remains unexplored.



(A)

Based on our previous experience supporting proline derivatives onto polystyrene (PS) resins[5] and enantiopure β-amino alcohols onto cobalt nanoparticles[6] we decided to extend these approaches by supporting a C-4 substituted (*S*)-α,α-diarylprolinol silyl ether (Jørgensen–Hayashi catalyst)[7] onto well-defined MNPs through a 1,2,3-triazole linker. According to previous experience with the same catalyst on a PS resin,[5f] we expected that anchoring through C-4 position of the pyrrolidine ring will ensure a greater conformational flexibility in the catalytically active moiety and, thus, with minimal perturbation of the active site.

Herein we report the first example of supporting (*S*)-α,α-diphenylprolinol trimethylsilyl ether (**4**) onto azide functionalized MNPs of Fe_3O_4 (**3**), *via* Cu(I) catalyzed alkyne–azide [2 + 3]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1jm10535c

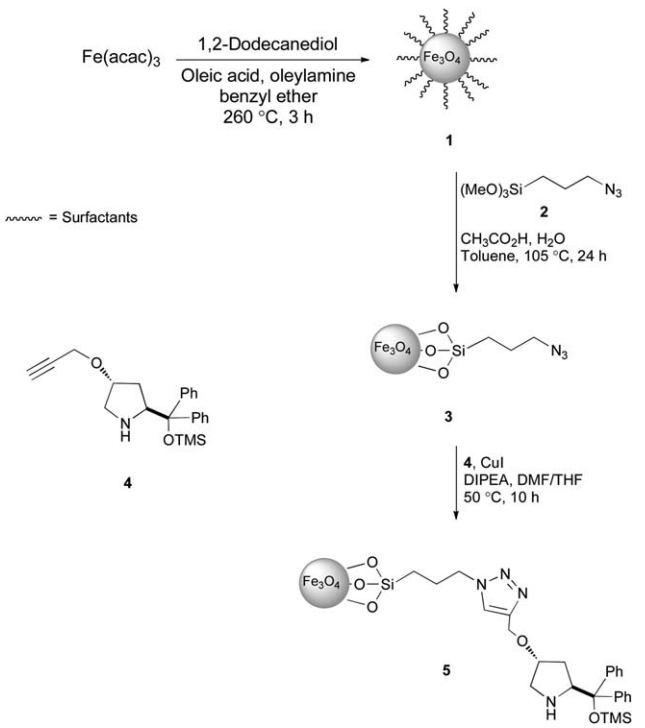
cycloaddition reaction (CuAAC),[8] and the use of the resulting functional nanoparticles for the asymmetric Michael addition[9] of propanal to nitroolefins.

Results and discussion

MNPs of Fe_3O_4 (**1**) were generated by thermal decomposition of $Fe(acac)_3$ (Scheme 1) in the presence of oleic acid and oleylamine as surfactants. In agreement with a previous report by Sun *et al.*,[10] we have found that the synthesis of nanoparticles using thermal decomposition in the presence of 1,2-hydrocarbon diols, as 1,2-dodecanediol, had a notably beneficial effect on the formation of well-defined MNPs with a small diameter when compared with co-precipitation methodology. Transmission electron microscopy (TEM) analysis revealed the formation of spherical, and rather monodisperse nanoparticles (5.6 ± 1.3 nm) (Fig. 1a).

Very interestingly, grafting of a 3-azidopropyl moiety onto MNPs **1** with 3-azidopropyltrimethoxysilane (**2**)[11] took place uneventfully and did not lead to any significant increase in the size of the individual particles (5.7 ± 1.1 nm, according to TEM), nor to agglomeration of the MNPs. This is in sharp contrast with our own observations when the starting MNPs of Fe_3O_4 were prepared by co-precipitation. The loading of azido group in **3** was determined by elemental analysis of nitrogen as 1.9 mmol g^{-1}.

In the IR spectra, of the nanoparticles, the appearance of a characteristic band at 2097 cm^{-1}, corresponding to the stretch vibration of the azido group confirms the incorporation of **2** onto the MNPs (Fig. 2). Finally, the integration of the catalytically active species **4** onto the MNPs was carried out using a CuAAC



Scheme 1 Synthesis of (*S*)-α,α-diphenylprolinol trimethylsilyl ether supported onto MNPs.

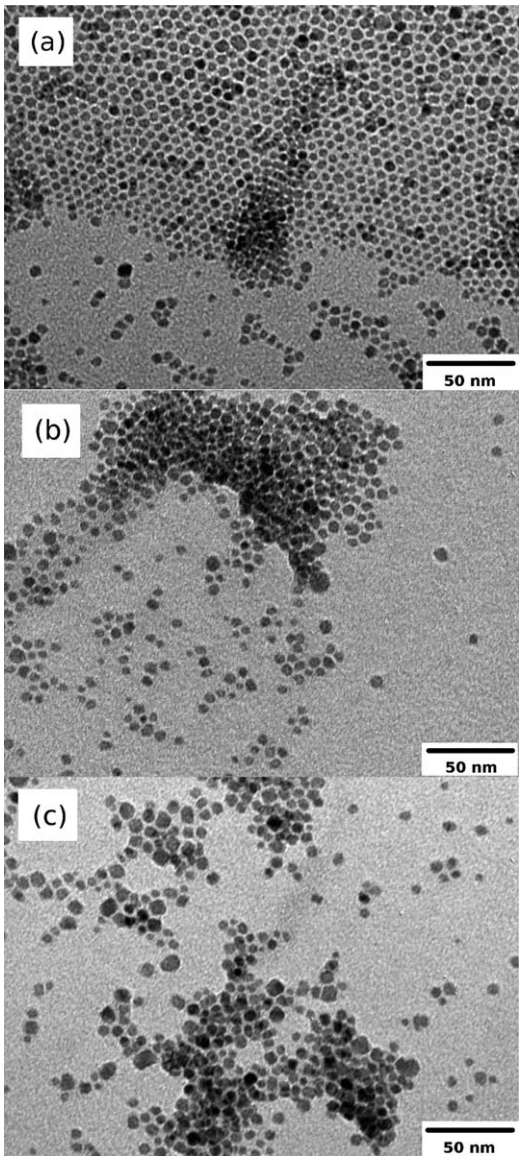


Fig. 1 Micrographs of MNPs determined by TEM. (a) MNPs of Fe_3O_4, **1**; (b) azide functionalized MNPs, **3**; (b) MNPs after functionalization with diphenylprolinol, **5**.

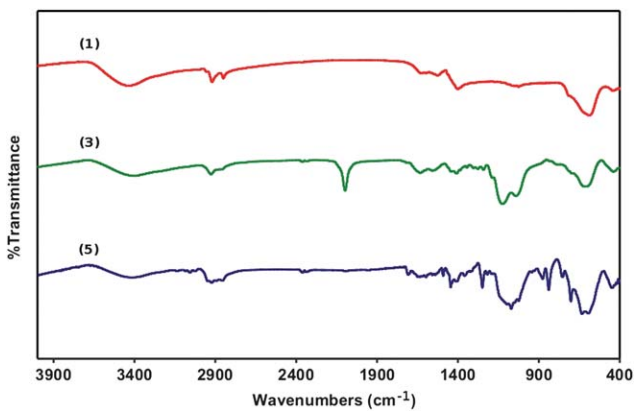


Fig. 2 IR spectrum of MNPs (**1**), azide functionalized MNPs (**3**) and MNPs after functionalization with diphenylprolinol, **5**.

reaction catalyzed by CuI and *N*,*N*-diisopropylethylamine (DIPEA) in a mixture of tetrahydrofuran and dimethylformamide at 50 °C for 10 h. The TEM micrographs of the resulting material show that also in this step the size of the MNPs remains unchanged (4.8 ± 0.8 nm) and that agglomeration processes are avoided (Fig. 1c and Fig. 3). The progress of the CuAAC reaction leading to **5** could be easily monitored by IR spectroscopy, through the disappearance of the azide band at 2097 cm^{-1} and the appearance of new bands at 754, 838, 1070 and 1249 cm^{-1}, corresponding to the diphenylprolinol trimethylsilyl ether.[5f] The diphenylprolinol loading on the ready-to-act, functional MNPs **5** was determined by nitrogen elemental analysis as 0.92 mmol g^{-1}.

With functional MNPs **5** in hand, its catalytic activity was tested on the asymmetric Michael addition of aldehydes to nitroolefins. Since diarylprolinol ethers are highly selective for short chain, linear aldehydes as Michael donors,[9b,d] propanal was mostly used as the donor in our reactivity study. The reaction of propanal with *trans*-β-nitrostyrene was used for the optimization of experimental conditions (Table 1).

The use of 10 mol% of **5** in CH_2Cl_2 showed to be the most effective condition to carry out the reaction (entry 2). Although the reaction in toluene led to the product with high yield and enantioselectivity (entry 3), it took place at a considerably lower rate, requiring up to two days reaction time for the achievement of high conversion. Attempts to further reduce catalyst loading (entry 1) led to unpractical low conversions, while the use of water as a solvent (entry 4) did not lead to any conversion likely, because of the poor dispersibility of the MNPs **5** in this media.

Next, a series of nitroolefins bearing β-aryl or heteroaryl substituent were submitted to the addition of propanal catalyzed by **5** under the optimized reaction conditions. The results of this study have been summarized in Table 2. In general, the corresponding *syn*-adducts were obtained as major stereoisomers in good yields and enantioselectivities. With the only exception of 2-(*p*-tolyl)nitroethylene as an acceptor (entry 2) enantioselectivities above 90% are recorded. These results compare well with those obtained with the Jørgensen–Hayashi catalyst supported on Merrifield type resins,[5f] being clearly superior to those recorded with a diarylprolinol silyl ether supported onto submicrometric Fe_3O_4@SiO_2 particles.[4d]

The asymmetric Michael addition of acetaldehyde to nitrostyrenes represents a more stringent test for organocatalysts.

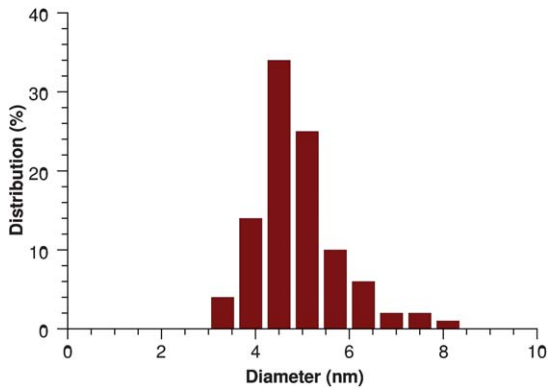
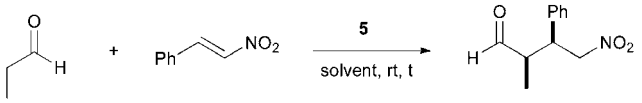


Fig. 3 Size distribution of MNPs after functionalization with diphenylprolinol **5**.

Table 1 Screening of reaction conditions for the Michael addition of propanal to *trans*-β-nitrostyrene[a]



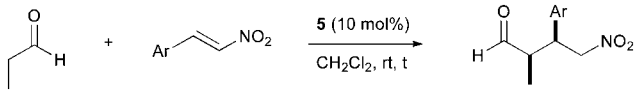
Entry	Catalyst (mol%)	Solvent	*t*/h	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1	5	CH_2Cl_2	24	<15	—	—
2	10	CH_2Cl_2	22	89	89 : 11	97
3	10	Toluene	48	83	87 : 12	96
4	10	H_2O	—	0	—	—

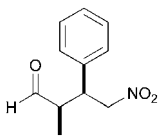
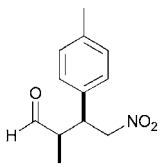
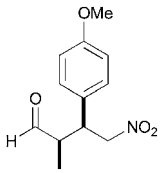
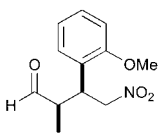
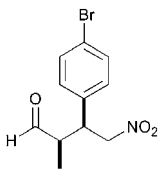
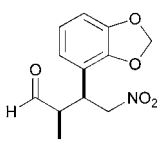
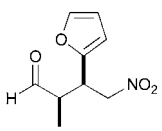
[a] *Trans*-β-nitrostyrene (0.2 mmol), propanal (0.3 mmol), **5** (0.02 mmol), solvent (0.5 mL), rt. [b] Isolated yield after column chromatography. [c] Determined by ^1H NMR. [d] Determined by chiral HPLC analysis.

This particular aldehyde exhibits a dual character as a pronucleophile and as an electrophile that makes difficult the control of its reactivity. According to this, most catalysts acting by formation of reactive enamine intermediates become deactivated through the formation of unreactive, acetal-type species. Only a few examples of this reaction, catalyzed by either a polymer-supported (*S*)-α,α-diphenylprolinol trimethylsilyl ether[5f] or by the Jørgensen–Hayashi homogeneous catalyst,[12] have been reported in the literature with results far from optimal. In view of the behaviour exhibited by the functional magnetic nanoparticles **5**, we wanted to test them as catalysts for the Michael addition of acetaldehyde to *trans*-β-nitrostyrene. Very gratifyingly, the reaction led to the formation of the corresponding Michael product in good yield (58%). However, this product was obtained in racemic form (Scheme 2). This result seems to obey to a lack of clear conformational preferences in the putative acetaldehyde enamine intermediate, since it could be established that MNPs **1**, lacking the functional diarylprolinol unit, fail to catalyse the considered Michael reaction.

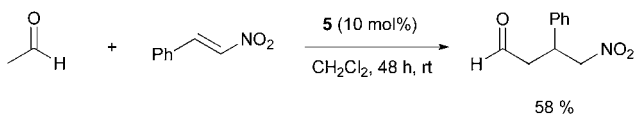
One of the main advantages associated with supporting a catalyst onto MNPs is the possibility of recovery by simple magnetic decantation and reuse. Through the assembling process, the magnetic properties of the support nanoparticles are transmitted to the rather expensive (chiral) ligand supported onto them, so that the catalyst can be separated from the reaction media and subsequently recovered and reused by simple application of an external magnetic field. For success of this strategy, it is also required that the binding between the ligand responsible for the catalytic behaviour and the support nanoparticle be stable enough under the employed reaction conditions to minimize ligand leaching. We have studied the possibility of reuse of **5** in the reaction between propanal and *trans*-β-nitrostyrene using magnetic decantation (neodymium magnets) as the strategy for catalyst separation. Interestingly, the magnetic decantation of the catalyst could be easily performed thanks to the high magnetisation of the Fe_3O_4 nanoparticles. Not less important, the magnetic nanoparticles could be readily redispersed in dichloromethane after each separation. We have collected in Table 3 the results obtained in four consecutive cycles using the same sample of **5**. We were pleased to find that the catalyst can be used in four consecutive cycles without significant deterioration of its stereochemical performance. Although after the first run an

Table 2 Michael addition of propanal to nitroolefins catalyzed by **5**[a]



Entry	Product	*t*/h	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1		22	89	89 : 11	97
2		48	80	80 : 20	75
3		24	80	74 : 26	91
4		30	75	85 : 15	94
5		48	85	80 : 20	94
6		48	70	75 : 25	90
7		48	74	84 : 16	91

[a] Nitroolefin (0.2 mmol), propanal (0.3 mmol), **5** (0.02 mmol), CH_2Cl_2 (0.5 mL), rt. [b] Isolated yield after column chromatography. [c] Determined by ^{1}H NMR. [d] Determined by chiral HPLC analysis.



Scheme 2 Michael addition of acetaldehyde to *trans*-β-nitrostyrene catalyzed by **5**.

increase in reaction time was necessary for the completion of the reaction, yields remained essentially constant in the next three 48 h runs. After the third run, we could observe a significant decrease in catalytic activity, although enantioselectivity was maintained. According to precedents with polymer-supported Jørgensen–Hayashi catalysts, the main reason for deactivation of the α,α-diarylprolinol silyl ether lies on hydrolysis of the labile silyl ether group.[13] We think that this phenomenon together with some ligand leaching, indicated by elemental analysis ($f = 0.74$ mmol g^{-1}, after 4 runs), is responsible for the partial deactivation of **5** since, by TEM (see ESI†), we didn't observe any agglomeration of **5** after four runs.

Table 3 Recycling experiments of catalyst **5** in the Michael addition of propanal to *trans*-β-nitrostyrene[a]

Run	*t*/h	Yield[b] (%)	*syn*/*anti*[c]	ee[d]
1	22	89	89 : 11	97
2	48	83	76 : 24	90
3	48	81	78 : 22	94
4	48	57	72 : 28	92

[a] *Trans*-β-nitrostyrene (0.2 mmol), propanal (0.3 mmol), **5** (0.02 mmol), CH_2Cl_2 (0.5 mL), rt. [b] Isolated yield after column chromatography. [c] Determined by ^{1}H NMR. [d] Determined by chiral HPLC analysis.

Experimental

General information

Unless otherwise stated, all commercial reagents were directly used without any purification. All starting materials 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 μS. NMR spectra were registered in a Bruker Advance 400 Ultrashield spectrometer in $CDCl_3$ at room temperature, operating at 400.13 MHz (^{1}H) and 100.63 MHz (^{13}C{1H}). TMS was used as internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR. IR spectra of nanoparticles were recorded on a Thermo Nicolet 5700 FTIR spectrometer, using KBr pellets. High performance liquid chromatography (HPLC) was performed on Agilent Technologies Chromatographs (Series 1100 and 1200), using Chiralpak IC columns using guard column. 3-Azidopropyltrimethoxysilane (**2**)[14] and (2*S*,4*R*)-2-(diphenyl-(trimethylsilyloxy)methyl)-4-(prop-2-ynyloxy)-pyrrolidine (**4**)[5f] are known and were characterized by comparison of their physical and spectroscopic properties with those described in the literature. TEM images were recorded using a JEOL JEM 1011 microscope equipped with a lanthanum hexaboride filament, operated at an acceleration voltage of 100 kV, at Microscopy Unit, Universitat Rovira i Virgili, Tarragona, Spain.

Preparation of MNPs of Fe_3O_4 (1)[10]

Iron(III) acetylacetonate (1.8 g, 5 mmol), 1,2-dodecanediol (5.6 g, 25 mmol), oleic acid (5.3 mL, 15 mmol), oleylamine (7 mL, 15 mmol) and benzyl ether (20 mL) were mixed at room temperature under argon. The reaction mixture was warmed at 260 °C for 3 h and was cooled at room temperature. The MNPs were removed using an external magnetic field and washed several times with MeOH and acetone and dried under vacuum.

Preparation of azide functionalized MNPs (3)

To a suspension of MNPs **1** (402 mg) in degassed toluene (10 mL) under argon were added 3-azidopropyltrimethoxysilane (**2**) (482.4 mg, 2.35 mmol), glacial acetic acid (50.3 μL, 0.87 mmol) and ultrapure water (69 μL, 3.86 mmol). The reaction mixture was warmed at 105 °C for 24 h and then cooled at room temperature. The MNPs were removed using an external magnetic field, washed several times with MeOH, hexane, acetone and dried under vacuum.

Preparation of (*S*)-α,α-diphenylprolinol trimethylsilyl ether supported onto azide functionalized MNPs (5)

Azide functionalized MNPs (**3**) (0.17 mmol), (*S*)-α,α-diphenylprolinol trimethylsilyl ether (**4**) (115 mg, 0.24 mmol), CuI (6.61 mg, 0.034 mmol), DIPEA (386 μL, 2.21 mmol) and a mixture of dry THF/DMF (1 : 1), under argon, were warmed at 50 °C for 10 h. The ligand supported onto MNPs was removed using an external magnetic field, washed several times with MeOH, acetone and dried under vacuum.

General procedure for the Michael reaction

The corresponding nitroolefin (0.2 mmol), catalyst **5** (10 mol%), aldehyde (0.3 mmol) and CH_2Cl_2 (0.5 mL) were mixed and stirred at room temperature and monitored by TLC until completion. The catalyst **5** was removed using an external magnetic field. The organic mixture was concentrated and was purified by column chromatography (silica gel, hexane/EtOAc) to afford the Michael adduct. The enantiomeric excess was determined by HPLC on a chiral stationary phase (Chiralpak IC column and IC guard column) and the diastereoisomeric ratio by ^{1}H NMR.

Procedure for the Michael reaction for acetaldehyde catalyzed by 1

Trans-β-nitrostyrene (13.5 mg, 0.09 mmol), MNP **1** (15 mg) acetaldehyde (7.6 μL, 0.135 mmol) and CH_2Cl_2 (0.5 mL) were mixed and stirred at room temperature and monitored by TLC.

Recycling of catalyst 5

Trans-β-nitrostyrene (0.2 mmol), catalyst **5** (10 mol%), propionaldehyde (0.3 mmol) and CH_2Cl_2 (0.5 mL) were mixed and stirred at room temperature and monitored by TLC until completion. The catalyst **5** was removed using an external magnetic field, was washed several times with MeOH, acetone and was dried under vacuum, then another portion of reactants was added.

Conclusions

In conclusion, we have reported for the first time the support of C-4 propargyloxy substituted (*S*)-α,α-diphenylprolinol trimethylsilyl ether onto azide functionalized MNPs of Fe_3O_4 using the CuAAC reaction for the construction of 1,2,3-triazole linkers on the nanoparticles. The functional, magnetic nanoparticles prepared in this manner, spherical in size and depicting a narrow size distribution (4.8 ± 0.8 nm), have been successfully used to promote the highly enantioselective Michael addition reaction of propanal to β-arylsubstituted nitroolefins. The nanoparticles showed good stability in front of agglomeration in dichloromethane, and could be easily separated from the reaction media by magnetic decantation and easily redispersed for reuse. In this manner, the MNPs could be used in 4 consecutive runs without any reactivation of the catalyst.

Acknowledgements

This work was supported by *MICINN* (grant CTQ2008-00947/BQU) and Consolider Ingenio 2010 (grant CSD2006-0003), DURSI (grant 2009SGR623), and the ICIQ foundation. P.R. thanks *MICINN* for a Torres Quevedo posdoctoral grant. We also thank ICIQ Support Units and Universitat Rovira i Virgili for TEM images.

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