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# PAPER



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## Efficient and robust superparamagnetic copper ferrite nanoparticle-catalyzed sequential methylation and C–H activation: aldehyde-free propargylamine synthesis†

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We have described a method for oxidative cross-coupling reactions between *N*-alkyl anilines and terminal alkynes forming *N*-aryl-*N*-methylpropargylamines. Superparamagnetic  $CuFe_2O_4$  nanoparticles were employed as efficient and robust catalyst. The optimum conditions involved the use of *tert*-butyl hydroperoxide (TBHP) as oxidant and methylating reagent in dimethylacetamide (DMA) solvent at 140 °C. The two-step reaction, methylation and C–C cross-coupling, proceeds efficiently and has high selectivity, and good conversions were achieved in short reaction times. Preliminary mechanistic investigation was conducted. The  $CuFe_2O_4$  nanoparticles could be facilely separated from the reaction mixture by magnetic decantation and could be reused several times with only a slight decrease in catalytic activity.

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## 1. Introduction

The demand for developing sustainable chemical processes has encouraged the discovery of more environmentally friendly methodology, especially in organic synthesis. In recent years, the employment of heterogeneous catalysts has received increasing interest.<sup>1</sup> Generally, a major issue associated with low activity limits their applications.<sup>1</sup> The solution to address this problem is to keep the particle size of the catalyst in the nanometer scale to improve its dispersability in the reaction medium.<sup>2</sup> However, for such suspensions of nanoparticles, conventional catalyst separation methods are ineffective in recyclability studies.<sup>3</sup> Superparamagnetic nanoparticles have emerged as an alternative due to their unique magnetically separable features.<sup>4</sup> Over the past few years, catalysts supported on magnetic nanoparticles have been utilized for various organic transformations including carbon-carbon cross-coupling reactions,5 Friedel-Crafts formylation,6 hydrogenation,<sup>7</sup> and polymerization.<sup>8</sup> In most cases, the catalyst was accommodated on the functionalized surface of magnetic nanoparticles.9 Recently, unfunctionalized CuFe2O4 superparamagnetic nanoparticles have been reported to be active for a variety of important chemical processes.<sup>10</sup> With

simple synthesis and facile recovery, the use of unfunctionalized CuFe<sub>2</sub>O<sub>4</sub> superparamagnetic nanoparticles in organic transformations is highly desirable, especially in practical applications.

Propargylamines are frequently found to be versatile intermediates for the synthesis of many nitrogen-containing biologically active compounds.<sup>11</sup> Traditional routes to synthesize these substrates exploited the nucleophilic attack of lithium acetylides or Grignard reagents to imines or their derivatives.<sup>12</sup> Subsequently, poor functional group tolerance and strictly controlled reaction conditions were observed. The one-pot three-component reactions of formaldehyde, terminal alkynes, and secondary amines, Mannich-type reactions (Scheme 1, eqn (1)), and dehydrogenative cross-coupling reactions (Scheme 1, eqn (2)) have recently become the most attractive methods for the synthesis of propargylamines.<sup>13</sup> Over the past decades, enormous progress has been devoted to expanding the reaction scope by employing various metal catalysts such as silver,<sup>14</sup> gold,<sup>15</sup> copper,<sup>16</sup> iron,<sup>17</sup> and indium.<sup>18</sup> Despite the advantages of homogeneous metal catalysts, difficulties in catalyst recovery severely hamper their wide use in industry.<sup>19</sup> Notably, in homogeneous catalysis, purification of products contaminated with transition metals represents a serious problem.19b This issue further increases the cost of the process and limits their industrial applications, especially in pharmaceutical processes. Thus, the development of efficient and reusable heterogeneous catalysts for the synthesis of propargylamines is highly needed. A few supported reactions or reactions using heterogeneous catalyst systems have recently been demonstrated for this three-component reaction.<sup>20</sup>



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Previous works (Ref. 14-17)

In comparison with other heterogeneous catalysts, along with advantages in the ease of handling, simple workup, recyclability and reusability, superparamagnetic nanoparticles could minimize the difference in the reaction rate of homogeneous and heterogeneous reactions due to their particle sizes.<sup>21</sup> Herein, we present the use of unfunctionalized CuFe<sub>2</sub>O<sub>4</sub> superparamagnetic nanoparticles as an efficient heterogeneous catalyst for aldehyde-free Mannich type reactions between N-alkyl anilines and arylacetylenes forming tertiary propargylamines as major products (Scheme 1). Interestingly, the tert-butyl hydroperoxide oxidant was found to serve as a methylating reagent. The superparamagnetic catalyst could be easily separated from the reaction mixture by simple magnetic decantation and reused several times without significant degradation in activity. To the best of our knowledge, the above coupling reactions were not previously described in the literature under any catalysis.

## 2. Experimental

#### 2.1. Synthesis of superparamagnetic CuFe<sub>2</sub>O<sub>4</sub> nanoparticles

Superparamagnetic CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized using a modified literature procedure.<sup>22</sup> In a typical preparation, CuCl<sub>2</sub>·2H<sub>2</sub>O (0.3444 g, 2 mmol) and Fe(acac)<sub>3</sub> (1.4269 g, 4 mmol) were added to a round-bottomed flask containing triethylene glycol (80 mL). The mixture was magnetically stirred at room temperature for 60 min and then placed in an ultrasonic bath for another 30 min. The resulting dark red mixture was heated to 270 °C for 8 hours. The reaction mixture was cooled down naturally to room temperature, and the particles were recovered by using a magnet. The final product was washed several times with diethyl ether/ethyl acetate (1:4) (3 times), ethanol (2 times), deionized water (10 times), and ethanol (5 times) followed by magnetic decantation, and dried under a vacuum at 200 °C for 6 h to yield the superparamagnetic CuFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.413 g, 85%).

#### 2.2. Catalytic studies

The superparamagnetic  $CuFe_2O_4$  nanoparticles were used as a catalyst for sequential methylation and carbon-carbon

coupling reactions between N-methylaniline and phenylacetylene in tert-butyl hydroperoxide. In a typical procedure, phenylacetylene (1.0 mmol; 0.11 mL), diphenyl ether as the internal standard (0.10 mL), a predetermined amount of the catalyst, N-methylaniline (3 mmol; 0.34 mL), TBHP (3 mmol; 0.41 mL), and DMA (4 mL) were added to a 25 mL three-necked reaction flask. Catalyst percentage was calculated based on the molar ratio of copper to phenylacetylene. The reaction mixture was heated and stirred at indicated temperatures under an argon atmosphere for 180 min. In kinetic studies, the reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals. Samples were quenched with water (1 mL), diluted with diethyl ether (4 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, analyzed by GC with reference to diphenyl ether, and confirmed by GC-MS. The product was then isolated by flash chromatography to further determine its structure by NMR.

To investigate the recyclability of the catalyst, the reaction liquid phase was removed from the reaction vessel by decantation while an external magnet held the superparamagnetic nanoparticles stationary inside the vessel. The catalyst was washed several times with copious amounts of deionized water, ethanol, ethyl acetate, and diethyl ether, separated by magnetic decantation, dried under a vacuum at 140 °C for 180 min, and reused if necessary.

For the leaching test, the catalyst was separated from the reaction mixture after 30 min by magnetic decantation. The reaction solution was reacted under identical conditions for another 150 min with aliquots being sampled at different time intervals and analyzed by GC.

## 3. Results and discussion

#### 3.1. Catalyst synthesis and characterization

The superparamagnetic  $CuFe_2O_4$  nanoparticles were successfully synthesized and characterized using various techniques. Elemental analysis of the nanoparticles by AAS showed a Cu: Fe molar ratio of approximately 1:2 (see the ESI†). Magnetic properties of the nanoparticles were examined at room temperature using a vibrating sample magnetometer (VSM) with

an applied field in the range of -15 000 Oe to 15 000 Oe. The results showed that the as-synthesized copper ferrite nanoparticles were superparamagnetic at room temperature. In particular, no hysteresis was observed and the magnetization curve was completely reversible at room temperature (Fig. 1). The saturation magnetization of the copper ferrite nanoparticles was found to be 26 emu g<sup>-1</sup>, which is similar to that of other CuFe<sub>2</sub>O<sub>4</sub> nanoparticles previously mentioned in the literature.<sup>23</sup> This indicated that magnetic separation at room temperature is possible, referring to the ease in catalyst recovery and recycling as well as in product separation. In addition, XRD patterns of the superparamagnetic nanoparticles are in good agreement with those in previous reports and consistent with the standard XRD pattern JCPDS 01-077-0010 (Fig. 2).<sup>24</sup> Furthermore, SEM (Fig. S2<sup>†</sup>) and TEM (Fig. S3<sup>†</sup>) images showed approximate diameters of the synthesized CuFe<sub>2</sub>O<sub>4</sub> nanoparticles. It should be noted that aggregation often occurs on TEM grids for most metal oxide



Fig. 1 Magnetization curve of the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles measured at room temperature.



Fig. 2 X-ray powder diffractogram of the synthesized  $CuFe_2O_4$  nanoparticles.

nanoparticles. TEM images, therefore, do not imply the real size of particles dispersed in the liquid phase.<sup>3</sup>

#### 3.2. Catalytic studies

In optimization screening, the reactions between N-methylaniline and phenylacetylene were performed over superparamagnetic CuFe<sub>2</sub>O<sub>4</sub> nanoparticle catalyst using TBHP as an oxidant and DMA as solvent at 140 °C (Scheme 2). Interestingly, isolation and the subsequent spectroscopic analysis including GC-MS and NMR revealed that the formation of expected product (1) was negligible. Specifically, N-methyl-N-(3-phenylprop-2-ynyl)benzenamine (2) was found as the major product in 70% isolated yield. Analysis of the reaction product showed that the propargylamine was formed by one-pot sequential methylation and oxidative C-C formation. Similar products were obtained by Mannich reactions of N-methylanilines, phenylacetylenes, and formaldehyde over palladium or copper catalyst.<sup>25</sup> It is worth mentioning that the N-methylation of N-H amines by the TBHP methylating reagent has not been described in the literature.

The conditions employing TBHP and DMA (4 mL) were used to investigate the effect of other reaction parameters (Table 1). It was observed that temperature possesses an important impact on reaction efficiency. In particular, optimum results were obtained at 140 °C with 94% conversion in 3 hours (entry 4). Lower conversion (85%) was obtained when the temperature was decreased to 130 °C (entry 3). As expected, reactions at 110 °C and 120 °C afforded 46% and 67% conversion, respectively (entries 1, 2). It should be noted that reaction selectivity of (1): (2) ratio was unchanged when reaction temperature increased with around 80% in all cases. With respect to catalyst loading, it was found that decreasing the amount of catalyst, in general, resulted in the drop in reaction conversions. In detail, a conversion of 82% was achieved when 3% catalyst was employed (entry 6). It is worth mentioning that the reaction using 7% catalyst gave 85% conversion, which is lower than that of the reaction with 5% catalyst (entry 5). Furthermore, comparable reaction selectivity was observed under most reaction conditions. Noticeably, less than 10% conversion was detected when no catalyst was added into the reaction mixture, supporting the necessity of CuFe<sub>2</sub>O<sub>4</sub> (entry 7). Additionally, increasing the ratio of N-methylaniline to phenylacetylene resulted in a minor change in reaction conversion, while a significant drop in conversion was observed when a 2:1 ratio was employed (entries 12, 13). Furthermore, it was observed that two equivalents of TBHP are insufficient and only 82% conversion was obtained in 3 hours (entry 9). Formation of products was not detectable in the reaction without TBHP (entry 11). Although quantitative conversion was obtained with 4 equivalents of TBHP in 2 hours, the reaction afforded lower selectivity (entry 10).

Mechanistically, one should be able to argue that dimethylacetamide solvent can act as a methylating reagent.<sup>26</sup> Consequently, organic solvents that are unlikely to act as methylating reagents were also examined on reaction conversions (Table 2).

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Scheme 2 Propargylamine formation via a one-pot three-component reaction of N-alkyl anilines, terminal alkynes, and TBHP over CuFe<sub>2</sub>O<sub>4</sub>.

 Table 1
 Optimization of the reaction conditions<sup>a</sup>



<sup>*a*</sup> Volume of solvent 4 mL, 1.0 mmol scale, aniline/alkyne = 2:1, 3 h. Conversion by GC analysis. <sup>*b*</sup> Aniline/alkyne = 1:2. <sup>*c*</sup> Aniline/alkyne = 4:1. Numbers in parentheses indicate the isolated yields. Kinetic studies of all entries were placed in Supporting Information.

	Me NH	Ph CuFe <sub>2</sub> O <sub>4</sub> (5 %) Oxidant (3 equiv.) Solvent 140 °C, 3 h	HN Ph (1)	+ (2)
Entry	Solvent	Oxidant	Conversion (%)	Selectivity (2)/[(1) + (2)] (%)
1	o-xylene	ТВНР	48	
2	diglyme	TBHP	58	75
3	DMF	TBHP	88	82
1	NMP	TBHP	92	77
5	DMA	tert-Butylbenzoylperoxide	84	78
5	DMA	Dicumyl peroxide	86	80
7	DMA	Hydrogen peroxide	0	
3	DMA	Dilauroyl peroxide	0	
)	DMA	СН <sub>3</sub> СОООН	0	
10	DMA	$K_2S_2O_8$	0	

The results indicated that *o*-xylene and diglyme afforded 48% and 58%, respectively (entries 1, 2). The formation of the product in these solvents supports our hypotheses that solvents are unlikely to be involved in the methylation step. In

addition, similar conversions and selectivity were achieved when DMF and NMP were applied (entries 3, 4).

To further gain evidence of the reaction pathway, various types of oxidants were employed (Table 2). Interestingly, oxidants

possessing methyl groups such as *tert*-butylbenzoylperoxide and dicumyl peroxide were also active and approximately 85% of phenylacetylene was converted to the desired product for both cases (entries 5, 6). On the other hand, peroxides that do not contain methyl groups such as hydrogen peroxide or dilauroyl peroxide gave no trace amount of the principal product (entries 7, 8). Additionally, peroxy acids such as peracetic acid were not suitable under our conditions (entry 9). For the inorganic  $K_2S_2O_8$  oxidant, even though 55% conversion was observed, no peak of the desired product was detected by GC-MS (entry 10). Therefore, it is most likely that TBHP is the methylating reagent of the reaction.

Methylation of arenes, N-H amides, and carboxylic acids using TBHP is known.<sup>27</sup> However, the methylation of N-H amine by peroxides is unknown. We decided to conduct the reaction under optimized conditions with the absence of phenylacetylene. About 10% of N,N-dimethylaniline was detected in the reaction mixture. Gratifyingly, reactions of N.N-dimethylaniline with phenylacetylene afforded the desired product in good yield (Scheme 3). Similar to the reaction of N-methylaniline, only a trace amount of the product was detected when side-product (1) was applied in the reaction conditions. Addition of TEMPO (2,2,6,6-tetramethylpiperidinyloxy) inhibited the reaction, and the generation of the coupling product between methyl radical and TEMPO was confirmed by GC-MS (Scheme 4). Formation of the methyl radical from TBHP or structurally similar oxidants has been described.<sup>28</sup> Furthermore, a control experiment using magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles failed to give the desired product. Based on previous reports<sup>27,28</sup> and the aforementioned experimental results, the plausible mechanism was then depicted (Scheme 5). Formation of the tert-butoxy radical from TPHB over copper catalyst is well known.<sup>29</sup> Facile decomposition of

the *tert*-butoxy radical *via* a unimolecular fashion generated a methyl radical.<sup>26</sup> Carbon–carbon bond formation between methyl radicals with *N*-methylaniline over copper catalyst resulted in *N*,*N*-dimethylaniline or an iminium in the presence of an oxidant. The copper-catalyzed nucleophilic attack of phenylacetylide to iminium gave the desired product (2). Generation of 1 followed a similar reaction pathway. However, more studies such as isotope effects as well as experiments using atom labeling are required to support the reaction mechanism.

The reaction scope with respect to coupling components is described in Table 3. Phenylacetylenes with methyl and methoxy substituents are active and the corresponding propargylamine products were obtained in good yields (entries 2, 3). It is well known that isomerization of aliphatic terminal alkynes in the presence of a base and a strong oxidant occurs steadily.<sup>30</sup> Consequently, their uses are limited to organic transformations, especially in cross-coupling reactions. Gratifyingly, our conditions can be also employed for aliphatic alkynes, and the reaction of 1-octyne afforded product in 56% yield (entry 4). With respect to aniline components, the cross-coupling of *N*-methylaniline with an electron-donating group as well as an electron-withdrawing group is possible and products were obtained in good yields (entries 5, 6).

In the leaching test, an experiment under optimum conditions was performed with the magnetic separation of the catalyst after 30 minutes. The reaction solution was transferred to a new reaction flask and the resulting mixture was stirred for an additional 150 min at 140 °C with samples taken at regular intervals. It was observed that no further conversion was detected for the reaction after the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were removed from the reaction mixture (Fig. 3). In addition,













<sup>a</sup> Conditions: DMA (4 mL), anilines (0.5 mmol). See the ESI<sup>†</sup> for details.



ICP-MS revealed less than 30 ppm of copper in the filtrate from the reaction mixture. According to the result from entry 8 in Table 1 (when 0.5% of Cu catalysts was used), it is unlikely that there was a contribution from leached active copper species.

The recoverability and reusability of CuFe2O4 nanoparticles were also investigated. After each run, an external magnetic field generated by a small permanent magnet was applied on the outer surface of the glass reaction flask containing CuFe<sub>2</sub>O<sub>4</sub> nanoparticles. The liquid phase of the reaction mixture was decanted from the reaction flask. The catalyst was washed several times with copious amounts of deionized water, ethanol, ethyl acetate, and diethyl ether, separated by magnetic decantation, dried under a vacuum at 140 °C for 2 hours and applied in the next reactions under identical conditions to those in previous runs. The results exhibited that a conversion of 95% was still achieved after 180 min in the 6th run (Fig. 4). Interestingly, reaction selectivity was retained during recycling studies. Furthermore, PXRD (Fig. 5), SEM and TEM (Fig. S4, S5<sup>†</sup>) of the reused nanoparticles after the 6th run indicated that the change in catalyst crystallinity and pattern is trivial.



Fig. 4 Catalyst recycling studies.

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Fig. 5 PXRD patterns of fresh (a) and reused (b)  $CuFe_2O_4$  nanoparticles after the 6th run.

## 4. Conclusions

The superparamagnetic CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were successfully prepared and characterized by several techniques, including VSM, XRD, SEM, TEM, and AAS. The CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were shown to be an efficient catalyst for new cross-coupling reactions between *N*-alkyl anilines and arylacetylenes in the aldehyde-free Mannich type reactions. The optimum conditions employed TBHP as oxidant and methylating reagent in DMA solvent at 140 °C for 3 hours. The reaction scope with good to excellent yields along with the leaching test was also studied. Preliminary mechanistic studies were investigated to elucidate the reaction pathway. The CuFe<sub>2</sub>O<sub>4</sub> nanoparticles could be facilely separated from the reaction mixture by magnetic decantation and could be reused several times without remarkable loss in catalytic activity.

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### References

- 1 J. A. Gladysz, Chem. Rev., 2002, 102, 3215.
- 2 W. Yan, S. M. Mahurin, Z. Pan, S. H. Overbury and S. Dai, J. Am. Chem. Soc., 2006, 127, 10480.
- 3 N. T. S. Phan and C. W. Jones, *J. Mol. Catal. A: Chem.*, 2006, 253, 123.
- 4 N. T. S. Phan, C. S. Gill, J. V. Nguyen, Z. J. Zhang and C. W. Jones, *Angew. Chem., Int. Ed.*, 2006, 45, 2209.
- 5 (a) P. D. Stevens, G. F. Li, J. D. Fan, M. Yen and Y. Gao, *Chem. Commun.*, 2005, 4435; (b) Z. F. Wang, B. Shen, A. H. Zou and N. Y. He, *Chem. Eng. J.*, 2005, 113, 27.
- 6 R. Abu-Reziq, H. Alper, D. S. Wang and M. L. Post, J. Am. Chem. Soc., 2006, 128, 5279.

- 7 D. Guin, B. Baruwati and S. V. Manorama, *Org. Lett.*, 2007, 9, 1419.
- 8 S. J. Ding, Y. C. Xing, M. Radosz and Y. Q. Shen, Macromolecules, 2006, 39, 6399.
- 9 A.-H. Lu, E. L. Salabas and F. Schüth, *Angew. Chem., Int. Ed.*, 2007, 46, 1222.
- 10 (a) A. Dandia, A. K. Jain and S. Sharma, RSC Adv., 2013, 3, 2924; (b) A. T. Nguyen, L. T. M. Nguyen, C. K. Nguyen, T. Truong and N. T. S. Phan, ChemCatChem, 2014, 6, 815.
- 11 M. Konishi, H. Ohkuma, T. Tsuno, T. Oki, G. D. VanDuyne and J. Clardy, *J. Am. Chem. Soc.*, 1990, **112**, 3715.
- 12 L. Zani and C. Bolm, Chem. Commun., 2006, 4263.
- (a) M. B. Smith and J. March, Advanced Organic Chemistry, Wiley, New York, 5th edn, 2001; (b) W.-J. Yoo, L. Zhao and C.-J. Li, in Science of Synthesis: Multicomponent Reactions 1, ed. T. J. J. Mueller, Thieme, Stuttgart, 2014, p. 189.
- 14 C. Wei, Z. Li and C.-J. Li, Org. Lett., 2003, 5, 4473.
- 15 C. Wei and C.-J. Li, J. Am. Chem. Soc., 2003, 125, 9584.
- 16 (a) Z. Li and C.-J. Li, J. Am. Chem. Soc., 2004, 126, 11810; (b)
  C. E. Meyet, C. J. Pierce and C. H. Larsen, Org. Lett., 2012, 14, 964; (c) A. Bisai and V. K. Singh, Org. Lett., 2006, 8, 2405.
- 17 Z.-P. Zhan, J.-L. Yu, Y.-Y. Cui, R.-F. Yang, W.-Z. Yang and J.-P. Li, *J. Org. Chem.*, 2006, 71, 8298.
- 18 M. Lin, L. Hao, X.-T. Liu, Q.-Z. Chen, F. Wu, P. Yan, S.-X. Xu, X.-L. Chen, J.-J. Wen and Z.-P. Zhan, *Synlett*, 2011, 665.
- (a) C. J. Welch, J. Albaneze-Walker, W. R. Leonard, M. Biba, J. DaSilva, D. Henderson, B. Laing, D. J. Mathre, S. Spencer, X. Bu and T. Wang, *Org. Process Res. Dev.*, 2005, 9, 198;

(b) C. E. Garrett and K. Prasad, Adv. Synth. Catal., 2004, 346, 889.

- 20 (a) M. L. Kantam, V. Balasubrahmanyam, K. B. S. Kumar and G. T. Venkanna, *Tetrahedron Lett.*, 2007, 48, 7332; (b) P. Li and L. Wang, *Tetrahedron*, 2007, 63, 5455; (c) T. Zeng, W.-W. Chen, C. M. Cirtiu, A. Moores, G. Song and C.-J. Li, *Green Chem.*, 2010, 12, 570.
- 21 K. P. De Jong, *Synthesis of solid catalysts*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009.
- 22 E. Solano, L. Perez-Mirabet, F. Martinez-Julian, R. Guzmán, J. Arbiol, T. Puig, X. Obradors, R. Yañez, A. Pomar, S. Ricart and J. Ros, *J. Nanopart. Res.*, 2012, 14, 1034.
- 23 (a) N. Panda, A. K. Jena and S. Mohapatra, *Appl. Catal.*, *A*, 2012, 433–434, 258; (b) R. Zhang, C. Miao, Z. Shen, S. Wang, C. Xia and W. Sun, *ChemCatChem*, 2012, 4, 824.
- 24 J. E. Tasca, A. N. Ponzinibbio, G. Diaz, R. D. Bravo, A. Lavat and M. A. G. Gonza'lez, *Top. Catal.*, 2010, 53, 1087.
- 25 T. Okamura, K. Asano and S. Matsubara, Synlett, 2010, 3053.
- 26 Y. Li, D. Xue, W. Lu, C. Wang, Z.-T. Liu and J. Xiao, Org. Lett., 2014, 16, 66.
- 27 Q. Xia, X. Liu, Y. Zhang, C. Chen and W. Chen, Org. Lett., 2013, 15, 3326.
- 28 Q. Dai, J. Yu, Y. Jiang, S. Guo, H. Yanga and J. Cheng, *Chem. Commun.*, 2014, **50**, 3865.
- 29 Z. Liu, J. Zhang, S. Chen, E. Shi, Y. Xu and X. Wan, *Angew. Chem., Int. Ed.*, 2012, **51**, 1.
- 30 Y. Makioka, Y. Taniguchi, T. Kitamura, Y. Fujiwara and A. Saiki, *Bull. Soc. Chim. Fr.*, 1997, 134, 349.