Tetrahedron xxx (2015) 1–6

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Iron oxide-silver magnetic nanoparticles as simple heterogeneous catalysts for the direct inter/intramolecular nucleophilic substitution of π-activated alcohols with electron-deficient amines

Xingzhu Xu, Haibo Wu, Zhengyi Li, Xiaoqiang Sun, Zhiming Wang *

Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu 213164, China

ARTICLE INFO

Article history:
Received 21 March 2015
Received in revised form 4 June 2015
Accepted 6 June 2015
Available online xxx

Keywords:
Iron oxide
Silver
Allylic amine
1,2-Dihydroquinoline

ABSTRACT

The development of bimetallic iron oxide-silver magnetic nanoparticles (Fe_2O_3–Ag MNPs) catalytic system provides an efficient heterogeneous synthetic pathway to allylic amines and 1,2-dihydroquinolines involving the direct inter/intramolecular nucleophilic substitution of π-activated alcohols with electron-deficient amines. The major advantages of the present method are wide substrate scope, simple product separation, low catalyst loading, and magnetically recyclable catalyst.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Allylic amines are valuable intermediates in synthetic strategies to bioactive natural products and pharmaceutically interesting compounds,[1] and also are useful substrates involved ring-closing alkene metathesis[2] and asymmetric isomerization.[3] Among the various synthetic methodologies for allylated nitrogen compounds,[4,5] the direct catalytic nucleophilic substitution reactions of π-activated alcohols with azo compounds such as amines and amides is one of the most efficient and desirable methods in the context of 'Green Chemistry'.[6] The main merits of this transformation are high atom efficiency and producing water as the only by-product by using allylic alcohols rather than their derivatives, such as allylic esters or carbonates, as the starting materials. In 2002, Ozawa group firstly reported an efficient Pd-catalyzed direct conversion of allylic alcohols into allylation products in the absence of activating agents under mild reaction conditions.[7] Since then, the protocols with different kinds of nitrogen nucleophiles have been discovered applying various Lewis acids or Brønsted acids as the catalysts.[8] Moreover, the Lewis acid-catalyzed intramolecular allylic aminations of free π-activated alcohols turn out to be a facile and efficient pathway to synthesize nitrogen-containing heterocycles, such as dihydroquinolines, quinolines, piperidines, indolines, and *etc*.[9] Despite the impressive progress, some examples suffer from the limitation of expensive or toxic catalysts, undesirable regioselectivities, high temperatures, and complicated catalyst recovery. In this regard, the development of efficient, easily recoverable and recyclable catalysts for the direct nucleophilic substitution of π-activated alcohols is still highly desired.

In recent years, magnetic nanoparticles (MNPs) have attracted a great attention as promising catalyst supports because of their facile separation by magnetic force, easy preparation and modification, high surface area-to-volume ratio, as well as low toxicity and cost.[10] Various MNP supported catalysts have been designed and widely used in different kinds of organic reactions, such as coupling reactions, hydrogenation, oxidation, organocatalysis, biocatalysis, and *etc*.[10,11] In particular, MNPs with precious metals such as gold, palladium, or ruthenium provide very useful bimetallic MNPs with high catalytic activities for transition metal-catalyzed reactions. For example, the dumbbell-like gold-coated Fe_3O_4 nanoparticles show superior catalytic activities than either Au or Fe_3O_4 nanoparticles in H_2O_2 oxidation, which was reported by Sun and co-workers in 2010.[12] Surprisingly, compared with the extensive studies of other noble metals MNPs, the research on silver MNPs using as magnetically recyclable catalyst is relatively limited,[13,14] although the silver as a traditional catalyst is widely used in organic synthesis. Furthermore, there are no reports on the use of silver based MNPs as magnetically recyclable catalyst for the direct nucleophilic substitution of π-activated alcohols with

* Corresponding author. Tel./fax: +86 51986330257; e-mail addresses: wzmmol@hotmail.com, zhiming@cczu.edu.cn (Z. Wang).

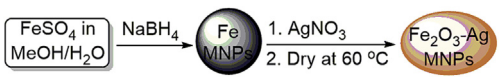
http://dx.doi.org/10.1016/j.tet.2015.06.028
0040-4020/© 2015 Elsevier Ltd. All rights reserved.

Please cite this article in press as: Xu, X.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.06.028

electron-deficient amines. During the course of our ongoing study on the development of nitrogen-containing compound formations,[15] herein, we would like to report a facile and efficient synthetic pathway to allylic amines and 1,2-dihydroquinolines involving the direct inter/intramolecular nucleophilic substitution of π-activated alcohols with electron-deficient amines by using Fe_2O_3–Ag MNPs as simple and recyclable heterogeneous catalysts.

2. Results and discussion

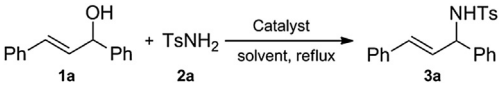
The Fe_2O_3–Ag MNPs catalyst was prepared according to the procedure shown in Scheme 1. The synthetic method used was adapted from the reported literatures.[11g,16,17] As illustrated in Scheme 1, Fe MNPs were prepared by $NaBH_4$ reduction of $FeSO_4$ and the silver decorated iron MNPs (Fe_2O_3–Ag MNPs) were obtained through the Fe–Ag replacement reaction, followed by drying at 60 °C in an oven. The nanocatalyst obtained above was well characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS), and vibrating sample magnetometer (VSM).[18] Interestingly, the XRD data clearly shows that the composition of the catalyst (Fe_2O_3–Ag MNPs) is Ag (0) deposited onto γ-Fe_2O_3 surface, and no Fe (0) peak can be found (Fig. S1). The XPS analysis of Ag3d and Fe2p spectra further conform the existence of Ag (0) and Fe (III) in our Fe–Ag MNPs (Fig. S4 and S5). These suggest that the bare Fe (0) MNPs obtained from $NaBH_4$ reduction are totally oxidized by air during the further treatment after the Fe–Ag replacement reaction. The crystallite size of the Fe_2O_3–Ag MNPs obtained using the Debye-Scherrer equation, on the basis of the (311) line from the XRD, was found to be 14.5 nm, and in agreement with the result observed from the TEM, which shows a size distribution between 10 and 20 nm (Fig. S6). Moreover, the catalyst's weight percentage of Ag was determined to be 5.8% by AAS analysis.[16b] The magnetic properties of as-prepared Fe_2O_3–Ag MNPs was investigated by VSM at room temperature (Fig. S7). Although the saturated magnetization (M_s) value of the Fe_2O_3–Ag MNPs is less than that of commercially available γ-Fe_2O_3 MNPs probably due to the existence of Ag (Table S1), fortunately, the magnetism of the Fe_2O_3–Ag MNPs was still strong enough to be separated easily from the reaction system under an external magnetic field (Fig. S8).



Scheme 1. Synthesis of Fe_2O_3–Ag MNPs.

In order to test the activity of the prepared catalyst as described above, the direct nucleophilic substitution between (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) and *p*-toluenesulfonamide (**2a**) was chosen as the model reaction and a brief screening of the reaction conditions was undertaken (Table 1). Although (*E*)-*N*-(1,3-diphenyl- allyl)-4-methylbenzenesulfonamide (**3a**) was barely detected in the absence of metal catalyst, a reaction yield of 93% was obtained in the present of 3 mol% of bimetallic catalyst Fe_2O_3–Ag MNPs in toluene (entries 1 and 7). Compared with γ-Fe_2O_3 and Ag NPs, the catalyst Fe_2O_3–Ag MNPs was essential or more efficient for the substitution reaction (entries 2–8). The major factor determined the difference between entry 3 and entry 7 may be the nanoparticle size of the catalysts because both the activity and the selectivity of the catalysts usually increase with decreasing size of the catalyst bodies according to the literatures.[10a,10g] It was noteworthy that lowing the catalyst loading to 0.5 or 2 mol% could also get reasonable reaction yields (entries 5 and 6), however, increasing the catalyst loading to 5 mol% could not benefit the reaction time or yield (entry 8). Among the solvents screened, the

Table 1
Optimization of reaction conditions[a]



Entry	Catalyst (loading)	Solvent	Time (h)	Yield (%)[b]
1	None	Toluene	24	Trace[c]
2	γ-Fe_2O_3 NMPs (3 mol%)[d]	Toluene	24	Trace[c]
3	Ag NPs (3 mol%)[e]	Toluene	18	48
4	γ -Fe_2O_3 NMPs (3 mol%)+Ag NPs (3 mol%)	Toluene	18	53
5	Fe_2O_3–Ag NMPs (0.5 mol%)	Toluene	10	82
6	Fe_2O_3–Ag NMPs (2 mol%)	Toluene	10	84
7	Fe_2O_3–Ag NMPs (3 mol%)	Toluene	10	93
8	Fe_2O_3–Ag NMPs (5 mol%)	Toluene	10	92
9	Fe_2O_3–Ag NMPs (3 mol%)	Benzene	48	75
10	Fe_2O_3–Ag NMPs (3 mol%)	DMF[f]	48	70
11	Fe_2O_3–Ag NMPs (3 mol%)	DMSO[f]	48	72
12	Fe_2O_3–Ag NMPs (3 mol%)	CH_2Cl_2	10	Trace[c]
13	Fe_2O_3–Ag NMPs (3 mol%)	THF	10	Trace[c]

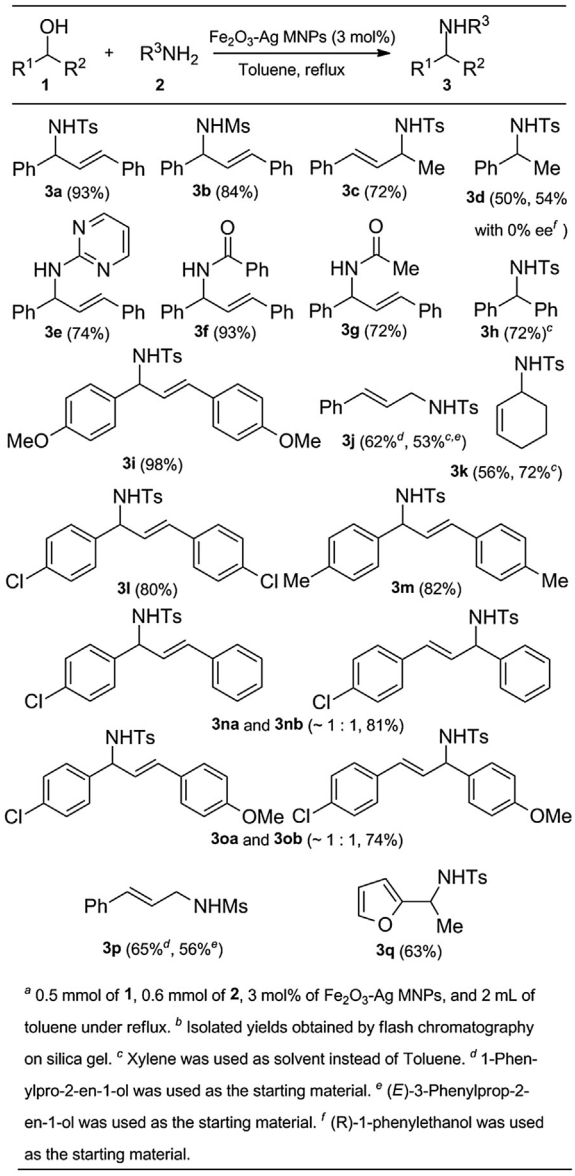
[a] 0.5 mmol of **1a**, 0.6 mmol of **2a**, catalyst, and 2 mL of solvent under reflux.
[b] Isolated yields obtained by flash chromatography on silica gel.
[c] Less than 5% of **3a** was obtained and more than 90% of **1a** was recovered.
[d] 20 nm purchased from Aladdin Reagent.
[e] 20–40 nm purchased from Sigma Aldrich.
[f] At 110 °C.

direct substitution reaction took place in benzene, DMSO, or DMF with moderate yields (entries 9–11), and only little desired product could be detected in CH_2Cl_2 or THF (entries 12 and 13). Moreover, the bimetallic catalyst Fe_2O_3–Ag MNPs could be recovered and reused up to five times with no appreciable decrease in yield (Table S2).[18] At the same time, we note no detectable differences of the catalyst by XPS (Fig. S2–S5) and TEM (Fig. S6). These suggest that the Ag species are strongly attached to the surface of magnetite through van der Waal forces and *etc*.

With the optimized reaction conditions in hand, the reaction scope was explored with a variety of π-activated alcohols and electron-deficient amines. The results were summarized in Table 2. The electron-deficient amines, such as *p*-toluenesulfonamide, methylsulfonamide, pyrimidin-2-amine, benzamide, and acetamide, reacted well with the (*E*)-1,3-diphenylprop-2-en-1-ol under standard reaction condition (**3a**, **3b**, and **3e**–**3g**). When (*E*)-1,3-arylprop-2-en-1-ols with methoxyl, chloro, or methyl groups as the substituents on the aromatic rings were used, the corresponding products were achieved with good to excellent yields (**3i**, **3l**, and **3m**). To expand the reaction scope, the unsymmetrical (*E*)-1,3-arylprop-2-en-1-ols were further examined and the expected products were obtained with poor regioselectivities according to the ^1H NMR and ^{13}C NMR (**3n** and **3o**). It seems clear that the regioisomers (**3nb** and **3ob**) were produced through allylic carbocation rearrangement, thus supporting the mechanism of the current substitution reaction involved an S_N1 pathway, which is quite different from either a borrowing hydrogen or an S_N2 pathway by using alumina-entrapped Ag[19] or iron/amino acid[20] as catalyst. Furthermore, other π-activated alcohols, such as (*E*)-4-phenylbut-3-en-3-ol, 1-phenylethanol, diphenylmethanol, cyclohex-2-enol, and 1-(fura-2-yl)ethanol also worked well for this transformation (**3c**, **3d**, **3h**, **3k**, and **3q**), and the use of xylene as a solvent instead of toluene could improve the reaction efficiency in some cases (**3h** and **3k**). Interestingly, when 1-phenylpro-2-en-1-ol and (*E*)-3-phenylprop-2-en-1-ol were applied as the substrates, the same product **3j** or **3p** was detected. It seems that the regioselectivity of the substitutions is controlled by the steric hindrance of allylic carbocation. When (R)-1-phenylethanol was used as the starting material, the 4-methyl-*N*-(1-phenylethyl) benzenesulfonamide **3d** was obtained in 54% as a racemic mixture, and no chirality transfer was observed. These results also suggest that the Fe_2O_3–Ag MNPs catalyzed nucleophilic substitution reaction goes through an S_N1 pathway.

Please cite this article in press as: Xu, X.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.06.028

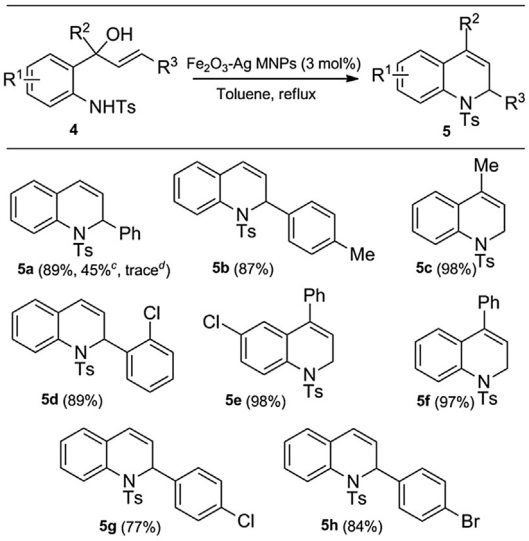
Table 2
Fe_2O_3–Ag MNPs catalyzed intermolecular nucleophilic substitutions with a variety of alcohols and amines[a,b]



[a] 0.5 mmol of **1**, 0.6 mmol of **2**, 3 mol% of Fe_2O_3-Ag MNPs, and 2 mL of toluene under reflux. [b] Isolated yields obtained by flash chromatography on silica gel. [c] Xylene was used as solvent instead of Toluene. [d] 1-Phenylpro-2-en-1-ol was used as the starting material. [e] (*E*)-3-Phenylprop-2-en-1-ol was used as the starting material. [f] (R)-1-phenylethanol was used as the starting material.

Encouraged by the results described above, we decided to apply this new catalytic system to the intramolecular nucleophilic substitution reaction for the synthesis of 1,2-dihydroquinolines. Under the same reaction condition, a number of desired products were also obtained in good to excellent yields, and the representative results were summarized in Table 3. When (*E*)-1-phenyl-3-(2-tosylaminophenyl)prop-1-en-3- ol was used as the substrate, the intramolecular nucleophilic substitution took place smoothly under Fe_2O_3–Ag MNPs catalyzed reaction condition, affording the expected product **5a** with 89% yield. Based on the results of the control experiments, it was found that the catalyst Fe_2O_3–Ag MNPs was essential or more efficient for the intramolecular substitution reaction (Table 3, **5a**). The Fe_2O_3–Ag MNPs catalyzed synthesis of substituted dihydroquinolines could tolerate a methyl group, C–Cl bond, and C–Br bond at the terminal position of the allylic alcohol moiety, providing **5b**, **5d**, **5g**, and **5h** with 77–89% yields. Surprisingly, 4-methyl and 4-phenyl substituted 1,2-dihydroquinolines **5c**, **5e**, and **5f** were achieved by using the standard catalyzed condition with very high reaction yields. In these cases, the reaction efficiency in Fe_2O_3–Ag MNPs

Table 3
Fe_2O_3–Ag MNPs catalyzed intramolecular nucleophilic substitutions for the synthesis of 1,2-dihydroquinilines[a,b]



[a] 0.5 mmol of **4**, 3 mol% of Fe_2O_3-Ag MNPs, and 2 mL of toluene under reflux. [b] Isolated yields obtained by flash chromatography on silica gel. [c] Ag NPs was used as catalyst instead of Fe_2O_3-Ag MNPs. [d] Without catalyst or γ -Fe_2O_3 was used as catalyst instead of Fe_2O_3-Ag MNPs.

heterogeneous catalytic system is even higher than that in $AuCl_3$[9c] or $FeCl_3$[15a] homogeneous catalytic system.

3. Conclusions

In summary, we have developed a facile and efficient methodology for the direct inter/intramolecular nucleophilic substitution reaction between π-activated alcohols and electron-deficient amines catalyzed by Fe_2O_3–Ag MNPs, achieving the corresponding allylic amines and 1,2-dihydroquinolines in yields up to 98%. The wide substrate scope, simple product separation, low catalyst loading, and magnetically recyclable catalyst make this protocol attractive to the chemistry community.

4. Experimental section

4.1. Preparation of Fe_2O_3–Ag MNPs

To a solution of 2.0 g $FeSO_4$ in MeOH–H_2O (30 mL/70 mL) was added dropwise aqueous $NaBH_4$ (0.4 g in 10 mL H_2O) for 30 min under ultrasound at pH 6 (achieved by addition of 5 N NaOH). The obtained Fe MNPs were washed by H_2O for five times. Then aqueous $AgNO_3$ (1.0 mL in H_2O, 0.5 N) was added dropwise for 5 min to the sonicating solution of the obtained Fe MNPs in 20 mL H_2O. The reaction mixture was left to sonicate for 20 min after addition of $AgNO_3$. The Fe_2O_3–Ag MNPs were obtained after washed by H_2O for three times and dried for 2 h at 60 °C in an oven before being used for catalysis.

4.2. General procedure for the direct nucleophilic substitutions of π-activated alcohols and electron-deficient amines catalyzed by Fe_2O_3–Ag MNPs

To a solution of alcohol (0.5 mmol) and amine (0.6 mmol) in toluene (2 mL) was added Fe_2O_3–Ag MNPs (28 mg). The reaction mixture was stirred under reflux at nitrogen atmosphere until

Please cite this article in press as: Xu, X.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.06.028

the substrate alcohol was consumed (TLC monitored). The Fe_2O_3–Ag MNPs was magnetically separated, and washed with acetone (2.0 mL X 3) and H_2O (2.0 mL X 3), then dried, and could be used directly for the next run. The reaction supernatant and acetone washings were collected together, evaporated, and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product (**3a**–**3o** and **5a**–**5h**).

*4.2.1. (E)-N-(1,3-Diphenylallyl)-4-methylbenzenesulfonamide (**3a**).*[15b] Light yellow solid; mp 137–139 °C (lit.[15b] 133–135 °C); 93% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, J=8.4 Hz, 2H), 7.31–7.15 (m, 12H), 6.36 (d, J=15.9 Hz, 1H), 6.09 (dd, J=6.6, 15.9 Hz, 1H), 5.16–5.07 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 59.8, 126.5, 127.1, 127.3, 127.8, 127.9, 128.2, 128.5, 128.7, 129.5, 132.2, 136.0, 137.7, 139.7, 143.3.

*4.2.2. (E)-N-(1,3-Diphenylallyl)methanesulfonamide (**3b**).*[8h] Light yellow solid; mp 125–127 °C (lit.[8h] 127 °C); 84% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.24 (m, 10H), 6.63 (d, J=15.6 Hz, 1H), 6.33 (dd, J=6.6, 15.6 Hz, 1H), 5.31–5.27 (m, 1H), 4.89 (br, 1H), 2.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.3, 59.9, 126.8, 127.3, 128.3, 128.4, 128.5, 128.8, 129.2, 132.6, 136.0, 134.0.

*4.2.3. (E)-4-Methyl-N-(4-phenylbut-3-en-2-yl)benzenesulfonamide (**3c**).*[8d] White solid; mp 90–92 °C (lit.[8d] 88–89 °C); 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J=8.4 Hz, 2H), 7.28–7.12 (m, 7H), 6.28 (d, J=16.2 Hz, 1H), 5.83 (dd, J=6.9, 15.6 Hz, 1H), 4.91–4.87 (br, 1H), 4.11–4.04 (m, 1H), 2.33 (s, 3H), 1.26 (d, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 22.0, 51.8, 126.5, 127.4, 127.8, 128.5, 129.7, 130.2, 130.6, 136.4, 138.1, 143.4.

*4.2.4. 4-Methyl-N-(1-phenylethyl)benzenesulfonamide (**3d**).*[8a] White solid; mp 82–84 °C (lit.[8a] 81–82 °C); 50% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J=8.4 Hz, 2H), 7.19–7.16 (m, 5H), 7.10–7.08 (m, 2H), 5.06 (br, 1H), 4.48–4.43 (m, 1H), 2.38 (s, 3H), 1.41 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 23.7, 53.8, 126.2, 127.2, 127.6, 128.6, 129.6, 137.7, 142.2, 143.2.

*4.2.5. (E)-N-(1,3-Diphenylallyl)pyrimidin-2-amine (**3e**).*[15b] Light yellow oil; 74% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J=4.8 Hz, 2H), 7.45–7.19 (m, 10H), 6.63 (d, J=15.6 Hz, 1H), 6.53 (t, J=4.8 Hz, 1H), 6.44 (dd, J=5.4, 15.9 Hz, 1H), 5.96–5.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.7, 111.2, 126.7, 127.3, 127.6, 127.8, 128.7, 128.8, 130.0, 130.8, 136.8, 141.7, 158.2, 161.7.

*4.2.6. (E)-N-(1,3-Diphenylallyl)benzamide (**3f**).*[15b] Light yellow solid; mp 156–158 °C (lit.[15b] 150–152 °C); 93% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85–7.82 (m, 2H), 7.55–7.24 (m, 13H), 6.63 (d, J=16.8 Hz, 1H), 6.51–6.42 (m, 2H), 6.03 (t, J=6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 126.7, 127.2, 127.4, 127.9, 128.0, 128.7, 128.8, 128.9, 129.0, 131.8, 131.9, 134.4, 136.5, 140.9, 166.6.

*4.2.7. (E)-N-(1,3-Diphenylallyl)acetamide (**3g**).*[8e] White solid; mp 135–136 °C (lit.[8e] 136–138 °C); 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.24 (m, 10H), 6.54 (d, J=15.9 Hz, 1H), 6.34 (dd, J=5.7, 15.9 Hz, 1H), 5.84–5.82 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.7, 54.9, 126.7, 127.4, 127.9, 128.0, 128.7, 129.0, 131.5, 136.6, 141.0, 169.2.

*4.2.8. N-Benzhydryl-4-methylbenzenesulfonamide (**3h**).*[8a] White solid; mp 157–159 °C (lit.[8a] 156–158 °C); 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, J=8.4 Hz, 2H), 7.24–7.16 (m, 6H), 7.11–7.07 (m, 6H), 5.56 (d, J=7.2 Hz, 1H), 5.30–5.23 (br, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 61.4, 127.3, 127.5, 127.7, 128.7, 129.5, 137.4, 140.6, 143.3.

*4.2.9. (E)-N-(1,3-bis(4-Methoxyphenyl)allyl)-4-methylbenzenesulfonamide (**3i**).* White solid; mp 124–125 °C; 98% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, J=8.1 Hz, 2H), 7.25–7.08 (m, 6H), 6.79–6.74 (m, 4H), 6.26 (d, J=15.9 Hz, 1H), 5.91 (dd, J=6.6, 16.5 Hz, 1H), 5.11–5.00 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 55.4, 59.4, 113.9, 114.0, 126.3, 127.4, 127.8, 128.4, 129.0, 129.5, 131.4, 132.1, 137.9, 143.2, 159.2, 159.4; HRMS (EI): m/z calcd for $C_{24}H_{25}NO_4S$ (M^+): 423.1504, Found, 423.1509.

*4.2.10. N-Cinnamyl-4-methylbenzenesulfonamide (**3j**).*[8f] Light yellow solid; mp 104–106 °C (lit.[22] 103–105 °C); 62% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J=8.4 Hz, 2H), 7.33–7.23 (m, 7H), 6.44 (d, J=15.9 Hz, 1H), 6.02 (td, J=6.3, 15.9 Hz, 1H), 4.48 (br, 1H), 3.76 (dt, J=1.5, 7.8 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 45.7, 124.2, 126.6, 127.4, 128.1, 128.7, 129.9, 133.3, 136.2, 137.2, 143.7.

*4.2.11. N-(Cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (**3k**).*[8d] White solid; mp 101–102 °C (lit.[8d] 102–103 °C); 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J=7.8 Hz, 2H), 7.30 (d, J=7.8 Hz, 2H), 5.80–5.73 (m, 1H), 5.37–5.31 (m, 1H), 4.46 (d, J=8.4 Hz, 1H), 3.85–3.78 (br, 1H), 2.43 (s, 3H), 1.96–1.90 (m, 2H), 1.80–1.72 (m, 1H), 1.64–1.51 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4, 21.7, 24.6, 30.4, 49.1, 127.1, 127.2, 129.8, 131.8, 138.5, 143.4.

*4.2.12. (E)-N-(1,3-bis(4-Chlorophenyl)allyl)-4-methylbenzenesulfonamide (**3l**).* White solid; mp 137–139 °C; 80% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, J=8.4 Hz, 2H), 7.32–7.09 (m, 10H), 6.29 (d, J=15.6 Hz, 1H), 6.02 (dd, J=6.6, 15.9 Hz, 1H), 5.08 (t, J=6.9 Hz, 1H), 5.00 (d, J=6.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 59.2, 127.4, 127.9, 128.4, 128.6, 128.9, 129.0, 129.7, 131.5, 133.9, 134.0, 134.4, 137.6, 137.9, 143.7; HRMS (EI): m/z calcd for $C_{22}H_{19}Cl_2NO_2S$ (M^+): 431.0514, Found, 431.0512.

*4.2.13. (E)-N-(1,3-di-p-Tolylallyl)-4-methylbenzenesulfonamide (**3m**).*[21] White solid; mp 128–130 °C; 82% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, J=8.1 Hz, 2H), 7.17–7.06 (m, 10H), 6.33 (dd, J=0.6, 15.9 Hz, 1H), 6.06 (dd, J=6.9, 15.9 Hz, 1H), 5.48–5.46 (br, 1H), 5.10 (t, J=7.2 Hz, 1H), 2.35 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 21.2, 21.4, 59.7, 126.5, 127.0, 127.3, 127.4, 129.2, 129.3, 129.4, 131.7, 133.5, 136.9, 137.4, 137.6, 137.9, 143.1.

*4.2.14. N-Cinnamylmethanesulfonamide (**3p**).*[23] White solid; mp 73–75 °C (lit.[23] 74–76 °C); 65% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H), 6.61 (d, J=15.9 Hz, 1H), 6.20 (dt, J=15.9, 6.3 Hz, 1H), 4.63 (br, 1H), 3.93 (td, J=6.3, 1.5 Hz, 2H), 2.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.2, 45.4, 124.4, 126.5, 128.2, 128.7, 133.4, 136.0.

*4.2.15. N-(1-(Furan-2-yl)ethyl)-4-methylbenzenesulfonamide (**3p**).*[24] White solid; mp 72–73 °C (lit.[24] 72–73 °C); 63% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, J=8.4 Hz, 2H), 7.23 (d, J=8.4 Hz, 2H), 7.16 (dd, J=1.8, 0.9 Hz, 1H), 6.15 (dd, J=3.3, 2.1 Hz, 1H), 5.98 (dd, J=3.0, 0.6 Hz, 1H), 5.10 (d, J=8.1 Hz, 1H), 4.59–4.49 (m, 1H), 2.40 (s, 3H), 1.44 (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 21.5, 47.4, 106.1, 110.1, 127.0, 129.5, 137.7, 141.9, 143.1, 154.1.

*4.2.16. 2-Phenyl-1-tosyl-1,2-dihydroquinoline (**5a**).*[9c] White solid; mp 124–126 °C (lit.[25] 125 °C); 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J=8.0 Hz, 1H), 7.34–7.33 (m, 4H), 7.24–7.18 (m, 4H), 7.14–7.08 (m, 3H), 6.96 (d, J=7.2 Hz, 1H), 6.28 (d, J=9.6 Hz, 1H),

Please cite this article in press as: Xu, X.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.06.028

6.02 (d, *J*=6.0 Hz, 1H), 5.88 (dd, *J*=9.6, 6.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.5, 57.0, 125.5, 126.3, 126.4, 126.5, 127.2, 127.4, 127.6, 127.9, 128.2, 128.4, 128.6, 129.1, 132.9, 136.1, 138.4, 143.4.

*4.2.17. 2-(p-Tolyl)-1-tosyl-1,2-dihydroquinoline (**5b**).*[9c] White solid; mp 123–125 °C (lit.[9c] 124–127 °C); 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J*=8.0 Hz, 1H), 7.33 (d, *J*=8.0 Hz, 2H), 7.23–7.18 (m, 3H), 7.14–7.08 (m, 3H), 7.04 (d, *J*=8.0 Hz, 2H), 6.96 (d, *J*=7.6 Hz, 1H), 6.26 (d, *J*=9.6 Hz, 1H), 5.98 (d, *J*=6.0 Hz, 1H), 5.87 (dd, *J*=9.6, 6.0 Hz, 1H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 21.6, 56.8, 125.4, 126.2, 126.4, 126.7, 127.3, 127.4, 127.7, 128.2, 128.7, 129.1, 129.2, 132.9, 135.3, 136.2, 137.7, 143.3.

*4.2.18. 4-Methyl-1-tosyl-1,2-dihydroquinoline (**5c**).*[9c] White solid; mp 80–82 °C (lit.[26] 82 °C); 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J*=8.0 Hz, 1H), 7.32–7.28 (m, 1H), 7.26–7.16 (m, 3H), 7.11 (d, *J*=7.6 Hz, 1H), 7.05 (d, *J*=8.0 Hz, 2H), 5.32 (br, 1H), 4.34–4.33 (m, 2H), 2.33 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 21.4, 45.3, 120.3, 123.3, 126.7, 127.2, 127.4, 127.8, 128.8, 131.4, 131.6, 135.2, 136.1, 143.2.

*4.2.19. 2-(2-Chlorophenyl)-1-tosyl-1,2-dihydroquinoline (**5d**).*[15a] White solid; mp 147–149 °C; 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.0 Hz, 1H), 7.39–7.34 (m, 3H), 7.30 (t, *J*=7.6 Hz, 1H), 7.18–7.09 (m, 5H), 7.01 (t, *J*=7.6 Hz, 1H), 6.95 (d, *J*=7.6 Hz, 1H), 6.45 (d, *J*=5.6 Hz, 1H), 6.15 (d, *J*=9.6 Hz, 1H), 6.01 (dd, *J*=9.6, 5.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 55.2, 124.6, 126.0, 126.5, 126.6, 127.1, 127.5, 128.1, 128.3, 128.6, 129.0, 129.1, 129.9, 131.3, 134.0, 135.8, 137.3, 143.6.

*4.2.20. 6-Chloro-4-phenyl-1-tosyl-1,2-dihydroquinoline (**5e**).*[9c] White solid; mp 168–170 °C (lit.[9c] 167–170 °C); 98% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J*=8.8 Hz, 1H), 7.34 (d, *J*=8.4 Hz, 2H), 7.31–7.23 (m, 4H), 7.06 (d, *J*=7.8 Hz, 2H), 6.84 (d, *J*=2.4 Hz, 1H), 6.71–6.68 (m, 2H), 5.61 (t, *J*=4.5 Hz, 1H), 4.53 (d, *J*=4.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 45.4, 122.9, 125.8, 127.5, 127.9, 128.1, 128.2, 128.4, 129.0, 129.2, 132.3, 132.4, 134.0, 135.8, 137.3, 137.9, 143.7.

*4.2.21. 4-Phenyl-1-tosyl-1,2-dihydroquinoline (**5f**).*[9c] White solid; mp 128–130 °C (lit.[9c] 129–131 °C); 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J*=8.0 Hz, 1H), 7.35–7.32 (m, 3H), 7.25–7.22 (m, 3H), 7.14 (t, *J*=7.6 Hz, 1H), 7.03 (d, *J*=8.0 Hz, 2H), 6.87 (d, *J*=7.6 Hz, 1H), 6.71 (d, *J*=7.0 Hz, 2H), 5.58 (t, *J*=4.4 Hz, 1H), 4.54 (d, *J*=4.4 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 45.5, 121.6, 126.0, 126.6, 127.57, 127.61, 127.64, 127.9, 128.3, 128.5, 129.1, 131.0, 135.5, 136.1, 138.1, 138.7, 143.4.

*4.2.22. 2-(4-Chlorophenyl)-1-tosyl-1,2-dihydroquinoline (**5g**).*[9c] White solid; mp 129–130 °C (lit.[9c] 128–131 °C); 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J*=8.0 Hz, 1H), 7.32 (d, *J*=8.0 Hz, 2H), 7.27 (d, *J*=8.0 Hz, 2H), 7.24–7.19 (m, 3H), 7.16–7.08 (m, 3H), 6.97 (d, *J*=7.6 Hz, 1H), 6.28 (d, *J*=9.6 Hz, 1H), 5.98 (d, *J*=6.0, 1H), 5.85 (dd, *J*=9.6, 6.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 56.2, 125.9, 126.0, 126.4, 126.6, 127.2, 127.6, 128.5, 128.6, 128.9, 129.2, 132.7, 133.8, 136.0, 136.9, 143.6.

*4.2.23. 2-(4-Bromophenyl)-1-tosyl-1,2-dihydroquinoline (**5h**).*[9c] White solid; mp 152–154 °C (lit.[9c] 154–156 °C); 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J*=8.0 Hz, 1H), 7.36 (d, *J*=8.4 Hz, 2H), 7.32 (d, *J*=8.0 Hz, 2H), 7.24–7.20 (m, 3H), 7.16–7.08 (m, 3H), 6.97 (d, *J*=7.2 Hz, 1H), 6.29 (d, *J*=9.6 Hz, 1H), 5.96 (d, *J*=5.6 Hz, 1H), 5.85 (dd, *J*=9.6, 5.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6, 56.3, 122.0, 125.8, 126.0, 126.4, 126.7, 127.2, 127.6, 128.4, 128.5, 129.1, 129.2, 131.5, 132.6, 135.9, 137.4, 143.6.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (Grant no. 21372033), the Priority Academic Program Development of Jiangsu Higher Education Institutions, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology (BM2012110), the Qing Lan Project, and the National Natural Science Foundation of Jiangsu Province (Grant no. 12KYB150002 and no. 14KJA150002).

Supplementary data

Supplementary data (Copies of the ^{1}H NMR and ^{13}C NMR spectra of all key intermediates and final products) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.06.028. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943; (b) Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, NY, 1999.
2. Nicolaou, K. C.; Bulger, P. G.; Sarlar, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490–4527.
3. Akutagawa, S.; Tani, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, NY, 2000.
4. For selected reviews on allylic amine synthesis, see: (a) Breder, A. *Synlett* **2014**, 899–904; (b) Ramirez, T. A.; Zhao, B.; Shi, Y. *Chem. Soc. Rev.* **2012**, *41*, 931–942; (c) Collet, F.; Lescot, C.; Dauban, P. *Chem. Soc. Rev.* **2011**, *40*, 1926–1936; (d) Hartwig, J. F.; Stanley, L. M. *Acc. Chem. Res.* **2010**, *43*, 1461–1475; (e) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689–1708.
5. For recent selected examples on allylic amine synthesis, see: (a) Kawatsura, M.; Terasaki, S.; Minakawa, M.; Hirakawa, T.; Ikeda, K.; Itoh, T. *Org. Lett.* **2014**, *16*, 2442–2445; (b) Lee, J. H.; Lee, S. *Chem. Sci.* **2013**, *4*, 2922–2927; (c) Beck, J. F.; Samblanet, D. C.; Schmidt, J. A. R. *RSC Adv.* **2013**, *3*, 20708–20718; (d) Wei, Y.; Liang, F.; Zhang, X. *Org. Lett.* **2013**, *15* 5189-5189; (e) Sun, M.; Wu, H.; Bao, W. *Org. Biomol. Chem.* **2013**, *11*, 7076–7079; (f) Souto, J. A.; Zian, D.; Muñiz, K. *J. Am. Chem. Soc.* **2012**, *134*, 7242–7245; (g) Xie, Y.; Hu, J.; Wang, Y.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 20613–20616; (h) Jiang, B.; Li, Y.; Tu, M. S.; Wang, S. L.; Tu, S. J.; Li, G. *J. Org. Chem.* **2012**, *77*, 7497–7505.
6. For recent reviews on nucleophilic substitution reactions of π-activated alcohols with nitrogenated compounds, see: (a) Muzart, J. *Eur. J. Org. Chem.* **2007**, 3077–3089; (b) Muzart, J. *Tetrahedron* **2008**, *64*, 5815–5849; (c) Emer, E.; Sinisi, R.; Guiteras-Capdevila, M.; Petruzzielo, P.; De Vicentiis, F.; Cozzi, P. G. *Eur. J. Org. Chem.* **2011**, 647–666; (d) Bandini, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 994–995; (e) Biannic, B.; Aponick, A. *Eur. J. Org. Chem.* **2011**, 6605–6617.
7. Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968–10969.
8. For recent selected examples on nucleophilic substitution reactions of π-activated alcohols with nitrogenated compounds, see: (a) Li, L.; Zhu, A.; Zhang, Y.; Fan, X.; Zhang, G. *RSC Adv.* **2014**, *4*, 4286–4291; (b) Fan, G. P.; Liu, Z.; Wang, G. W. *Green Chem.* **2013**, *15*, 1659–1664; (c) Trillo, P.; Baeza, A.; Nájera, C. *ChemCatChem* **2013**, *5*, 1538–1542; (d) Trillo, P.; Baeza, A.; Nájera, C. *J. Org. Chem.* **2012**, *77*, 7344–7354; (e) Gopal Das, B.; Nallagonda, R.; Ghorai, P. *J. Org. Chem.* **2012**, *77*, 5577–5583 and references cited therein; (f) Trillo, P.; Baeza, A.; Nájera, C. *Eur. J. Org. Chem.* **2012**, 2929–2934 and references cited therein; (g) Han, F.; Yang, L.; Li, Z.; Xia, C. *Adv. Synth. Catal.* **2012**, *354*, 1052–1060; (h) Giner, X.; Trillo, P.; Nájera, C. *J. Organomet. Chem.* **2011**, *696*, 357–361.
9. (a) Guerinot, A.; Serra-Muns, A.; Gnamm, C.; Bensoussan, C.; Reymond, S.; Cossy, J. *Org. Lett.* **2010**, *12*, 1808–1811; (b) Yamamoto, H.; Ho, E.; Namba, K.; Imagawa, H.; Nishizawa, M. *Chem.—Eur. J.* **2010**, *16*, 11271–11274; (c) Kothandaraman, P.; Foo, S. J.; Chan, P. W. H. *J. Org. Chem.* **2009**, *74*, 5947–5952.
10. For recent reviews, see; (a) Cheng, T.; Zhang, D.; Li, H.; Liu, G. *Green Chem.* **2014**, *16*, 3401–3427; (b) Rossi, L. M.; Costa, N. J. S.; Silva, F. P.; Wojcieszak, R. *Green Chem.* **2014**, *16*, 2906–2933; (c) Kainz, Q. M.; Reiser, O. *Acc. Chem. Res.* **2014**, *47*, 667–677; (d) Mrówczyński, R.; Nan, A.; Liebscher, J. *RSC Adv.* **2014**, *4*, 5927–5952; (e) Nasir Baig, R. B.; Varma, R. S. *Chem. Commun.* **2013**, 752–770; (f) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J. M. *Chem. Rev.* **2011**, *111*, 3036–3075; (g) Shylesh, S.; Schunemann, V.; Thiel, W. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 3428–3459.
11. For recent selected examples, see: (a) Shen, C.; Xu, J.; Yu, W.; Zhang, P. *Green Chem.* **2014**, *16*, 3007–3012; (b) Khalafi-Nezhad, A.; Nourisefat, M.; Panahi, F. *RSC Adv.* **2014**, *4*, 22497–22500; (c) Song, J.-M.; Zhang, S.-S.; Yu, S.-H. *Small* **2014**, *10*, 717–724; (d) Wang, D.; Etienne, L.; Echeverria, M.; Moya, S.; Astruc, D. *Chem.—Eur. J.* **2014**, *20*, 4047–4054; (e) Baig, R. B. N.; Varma, R. S. *RSC Adv.* **2014**, *4*, 6568–6572; (f) Baig, R. B. N.; Varma, R. S. *Green Chem.* **2013**, *15*, 398–417; (g)

ARTICLE IN PRESS

Reuben, H.; Li, C. J.; Moores, A. *Green Chem.* **2012**, *14*, 622–624; (h) Li, P.; Wang, L.; Zhang, L.; Wang, G. W. *Adv. Synth. Catal.* **2012**, *354*, 1307–1318.
12. Lee, Y.; Garcia, M. A.; Huls, N. A. F.; Sun, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 1271–1274.
13. Silver based MNPs as recyclable catalysts for the reduction of nitrophenols, methylene blue, and Rhodamine B, see: (a) Shin, K. S.; Cho, Y. K.; Choi, J. Y.; Kim, K. *Appl. Catal., A* **2012**, *413–414*, 170–175; (b) Zhu, M.; Wang, C.; Meng, D.; Diao, G. *J. Mater. Chem. A* **2013**, *1*, 2118–2125; (c) Duan, B.; Liu, F.; He, M.; Zhang, L. *Green Chem.* **2014**, *16*, 2835–2845; (d) Ai, L.; Zeng, C.; Wang, Q. *Catal. Commun.* **2011**, *14*, 68–73.
14. Silver based MNPs as recyclable catalysts for the epoxidation of styrene, see: (a) Zhang, D. H.; Li, H. B.; Li, G. D.; Chen, J. S. *Dalton Trans.* **2009**, 10527–10533; (b) Zhang, D. H.; Li, G. D.; Li, G. D.; Chen, J. S. *Chem. Commun.* **2008**, 3414–3416.
15. (a) Wang, Z.; Li, S.; Yu, B.; Wu, H.; Wang, Y.; Sun, X. *J. Org. Chem.* **2012**, *77*, 8615–8620; (b) Wang, Z.; Mo, H.; Cheng, D.; Bao, W. *Org. Biomol. Chem.* **2012**, *77*, 4249–4255; (c) Wang, Z.; Yu, B.; Yuan, C.; Sun, X.; Bao, W. *Chin. J. Chem.* **2011**, *29*, 2769–2774; (d) Wang, Z.; Yu, B.; Zhang, X.; Sun, X.; Bao, W. *Chin. J. Chem.* **2011**, *29*, 2775–2780.
16. (a) Wang, Y.; He, J.; Wang, W.; Shi, J.; Mitsuzaki, N.; Chen, Z. *Appl. Surf. Sci.* **2014**, *292*, 462–468; (b) Wang, Y.; Zhou, Y.; Wang, W.; Chen, Z. *J. Electrochem. Soc.* **2013**, *160* D199-D123; (c) Wang, Y.; He, J.; Wang, W.; Mitsuzaki, N.; Chen, Z. *J. Electrochem. Soc.* **2013**, *160*, D295–D299.
17. Zhou, S.; Johnson, M.; Veinot, J. G. C. *Chem. Commun.* **2010**, 2411–2413.
18. See electronic supplementary information for more details.
19. Liu, H.; Chuah, G. K.; Jaeniche, S. *J. Catal.* **2012**, *292*, 130–137.
20. Zhao, Y.; Foo, S. W.; Saito, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 3006–3009.
21. Wu, W.; Rao, W.; Er, Y. Q.; Loh, J. K.; Poh, C. Y.; Chan, P. W. H. *Tetrahedron Lett.* **2008**, *49*, 2620–2624.
22. Zhang, C.; Zhang, S. Q.; Cai, H. J.; Cui, D. M. *Beilstein J. Org. Chem.* **2013**, *9*, 1045–1050.
23. Zhang, W.; Liu, N.; Schienebeck, C. M.; Zhou, X.; Izhar, I. I.; Guzei, I. A.; Tang, W. *Chem. Sci.* **2013**, *4*, 2652–2656.
24. Padwa, A.; Zanka, A.; Cassidy, M. P.; Harris, J. M. *Tetrahedron* **2003**, *59*, 4939–4944.
25. Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, *61*, 3584–3585.
26. Theeraladanon, C.; Arisawa, M.; Nishida, A.; Nakagawa, M. *Tetrahedron* **2004**, *60*, 3017–3035.

Please cite this article in press as: Xu, X.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.06.028