DOI: 10.1002/chem.201002801

Direct Hydrogenation of Nitroaromatics and One-Pot Amidation with Carboxylic Acids over Platinum Nanowires

Min Li, Lei Hu, Xueqin Cao, Haiyan Hong, Jianmei Lu,* and Hongwei Gu*[a]

Abstract: A novel ultrathin platinum nanowire with uniform length and a diameter of 1.5 nm was synthesized by acidic etching of FePt nanowire in methanol. This nanowire was characterized by high-resolution transmission electron microscopy (HRTEM). X-ray diffraction (XRD) data indicated that the main plane is (111). The ability of this nanowire to catalyze the heterogeneous hydrogenation of nitroaromatics to give the corresponding amines has been investigated. The catalyst showed satisfactory activity in various solvents under mild conditions and showed excellent stability. The catalytic performance was also evaluated in the one-pot reduction of nitroaromatics and amidation with carboxylic acids under a hydrogen atmosphere at 100 °C. These methods for the hydrogenation of nitroaromatics and the direct amidation of nitroaromatics with carboxylic acids are simple, economical, and environmentally benign, and have practical advantages for the synthesis of amines and amides without the production of toxic byproducts.

Keywords: amides · heterogeneous catalysis · hydrogenation · nanoparticles · platinum

Introduction

The selective reduction of nitrobenzene and its derivatives is one of the most important industrial reactions used for the synthesis of the corresponding amines. These amines are important intermediates in the production of many pharmaceuticals, agrochemicals, dyes, polymers, and rubber materials.[1] Although numerous methods have been developed for amine synthesis, the search for new, facile, chemoselective, cost-effective, and environmentally friendly procedures that avoid the use of expensive and hazardous stoichiometric reducing agents in large excess has still attracted extensive interest.[2] Amides are one of the most prevalent functional groups in both small and complex synthetic or naturally occurring molecules, and they are also used widely by medicinal chemists.[3] Traditional synthetic procedures involve the reaction of amines with pre-activated carboxylic acid derivatives, such as acyl halides, anhydrides, esters, acyl azides, or by dicyclohexylcarbodiimide (DCC)/*N*,*N*′-carbonyldiimidazole[4] type activation. Each of these methods has significant drawbacks, such as toxic reactive reagents, shock sensitivity, poor atom economy, or complex purification procedures.[5] The most desirable solution method for amide synthesis is direct condensation between an amine and a carboxylic acid, which has been known since 1858.[6] The amine used in this process is often obtained by hydrogenation of the corresponding nitro-compound with a catalyst. However, this procedure requires elevated temperatures owing to the formation of unreactive carboxylate-ammonium salts as the intermediates.[7,8] Recently, Whiting and co-workers[8] reviewed the use of efficient boron-based catalysts for this transformation. However, these catalysts also display some disadvantages: synthesis of the boron complex catalysts is not trivial, and separation of the products from the reaction mixture can be difficult because they are homogeneous catalysts. Therefore, it is desirable to perform direct amide condensation reactions between carboxylic acids and amines under mild, catalytic conditions.

Additionally, one-pot reactions have been developed as economical, environmentally friendly, and efficient new synthetic processes in organic chemistry.[9] The reductive amidation process is also one of the most powerful transformations for the direct conversion of carboxylic acids into amides using simple operations.[10]

In the present work, we describe a highly effective platinum nanowire (NW) catalyst for hydrogenation of nitroaromatics to the corresponding amines, and report a one-pot amidation of nitroaromatics with carboxylic acids under a hydrogen atmosphere (1 atm) at 100 °C. This catalyst shows excellent activity and stability for both hydrogenation of nitroaromatics and one-pot amidation reactions under mild conditions. The latter offers compelling advantages over other amide syntheses, because it does not require isolation of the amine intermediate.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002801.

Results and Discussion

Pt NWs with uniform length and a diameter of 1.5 nm were synthesized by acidic etching of FePt NWs, which were prepared by following the methodology described by Sun and co-workers.[11] Transmission electron microscope (TEM) images of the representative FePt and Pt NWs, and high-resolution TEM (HRTEM) images of Pt NWs are shown in Figure 1. The images in Figure 1 A and B show NWs approximately 200 nm in length. The diameters of the FePt and Pt NWs are 1–2 nm. Figure 1 C shows the HRTEM image of Pt NWs. The interplanar distance between the (111) planes is 0.218 nm, which matches that observed in Pt crystals.[12] The X-ray diffraction (XRD) spectrum (Figure 2) also shows that the main plane is (111). An energy dispersive spectrum (EDS) (see Figure S1 in the Supporting Information), collected in different regions, showed that Pt is the main component, with trace amounts of Fe, after acidic etching of FePt NWs.

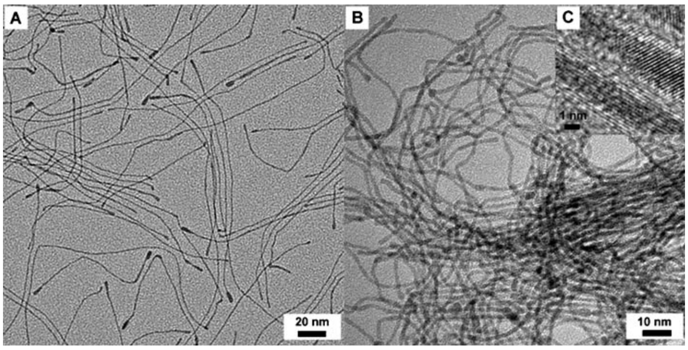


Figure 1. TEM images of A) FePt NWs; B) Pt NWs, and c) HRTEM image of Pt NWs.

Initially, the catalytic efficiency and stability of the Pt NWs were tested in the hydrogenation of nitroaromatics to their corresponding amines. Nitrobenzene was chosen as a model substrate for optimization of the reaction conditions.

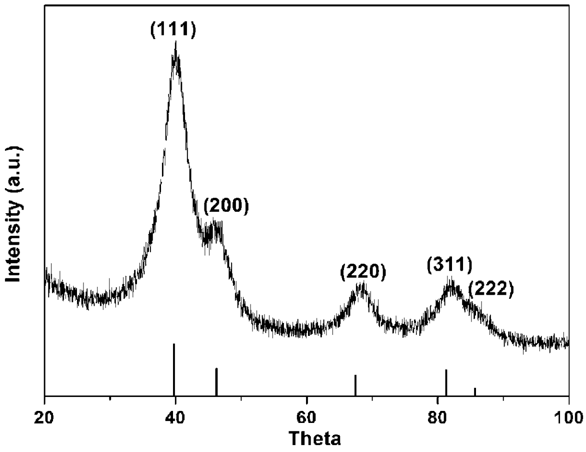


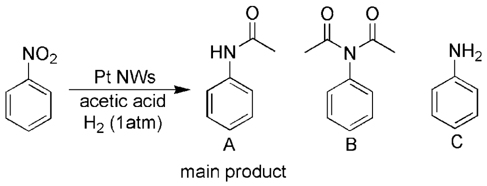
Figure 2. XRD spectrum of Pt NW and the standard powder pattern for Pt.

Table 1. Hydrogenation of nitrobenzene over Pt NW in different solvents.[a]

	Solvent	T [°C]	t [h]	Yield [%][b]
1	CH_3OH	40	1	99
2	C_2H_5OH	40	3	98
3	H_2O	40	3	99
4	$(C_2H_5)_3N$	40	5	98
5	THF	40	17	93
6	CH_2Cl_2	40	17	99
7	toluene	80	19	99
8	*n*-heptane	80	19	99

[a] Reaction conditions: nitrobenzene (1 mmol) and solvent (2 mL) were stirred magnetically under H_2 (1 atm) in a reaction tube in the presence of Pt NW catalyst (0.01 mmol). [b] Determined by GC and GC-MS analysis using 1-*tert*-butylbenzene as internal standard.

Table 1 shows the hydrogenation of nitrobenzene in different solvents. Methanol (Table 1, entry 1) was found to be the best solvent for this reaction, requiring lower temperature (40 °C) and shorter reaction time (1 h) than reactions performed in other solvents. Water, which is clearly an environmentally benign solvent, can also be used for this reaction; in this case, a high yield (99 %) was obtained in 3 h at 40 °C (Table 1, entry 3). Use of Pt NWs as catalyst gave good activity with a high yield of aniline regardless of whether the solvent was polar (Table 1, entries 1–3) or nonpolar (Table 1, entry 8). However, when acetic acid was used as the solvent in the hydrogenation of nitrobenzene at 100 °C, *N*-phenylacetamide (A) was detected as the main product, with a small quantity of aniline (C) and *N*-acetyl-*N*-phenylacetamide (B) (Scheme 1) being observed as minor products. *N*-Phenylacetamide and *N*-acetyl-*N*-phenylacetamide may be obtained through a two-step reaction: 1) the reduction of nitrobenzene to aniline over the Pt NWs, and 2) the amidation of acetic acid with aniline over the Pt NWs under the same reaction conditions. The acetic acid was thus used as both reactant and solvent.



Scheme 1. One-pot reductive amidation of acetic acid with nitrobenzene.

To elucidate the reaction mechanism, the reaction of nitrobenzene and acetic acid was monitored by GC analysis using 1-*tert*-butylbenzene as internal standard (Figure 3). Nitrobenzene was first reduced to aniline as the reaction intermediate. Amidation proceeded through the reduction of nitrobenzene. Upon completion of the reduction, a small quantity of *N*-acetyl-*N*-phenylacetamide was detected as a byproduct (see Figure S2 in the Supporting Information). Increasing the reaction time did not increase the yield of *N*-acetyl-*N*-phenylacetamide.

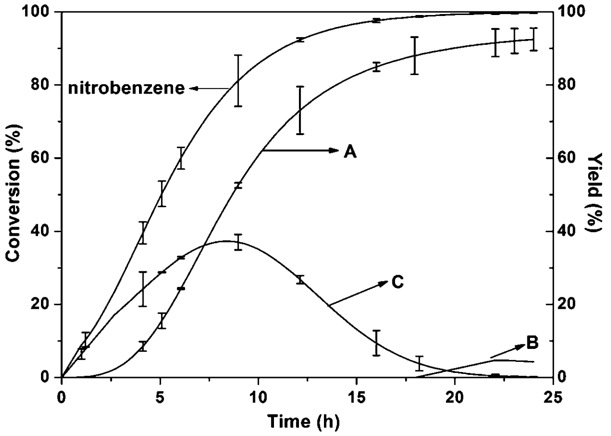


Figure 3. Reaction of nitrobenzene and acetic acid at 100 °C under a hydrogen atmosphere over Pt NW (the structures of A, B, C are shown in Scheme 1).

Water was considered to be an excellent solvent for the reduction of nitrobenzene to aniline (Table 1, entry 3); therefore, several experiments were conducted using various amounts of water in acetic acid as the solvent for the one-pot reduction and amidation of nitrobenzene to *N*-phenylacetamide (Table 2). The addition of water generated aniline as a byproduct but did not deactivate the hydrogenation of nitrobenzene. Acetic acid was found to be the most suitable solvent for high selectivity of *N*-phenylacetamide (Table 2, entry 1). When the molar ratio of acetic acid and nitrobenzene was 1:1 in water, 21 % of *N*-phenylacetamide was obtained as the product (Table 2, entry 5).

Table 2. Hydrogenation of nitrobenzene on Pt NW in acetic acid.[a]

	Acetic acid [mmol]	Conversion [%][b]	Selectivity (A/B/C) [%][b]
1	35	100	99:1:0
2	23	100	86:1:13
3	17	100	87:1:12
4	7	100	61:1:38
5	1	98	21:0:77
6[c]	1	95	19 (A)
7[d]	1	trace	trace

[a] Reaction conditions: nitrobenzene (1 mmol) and solvent (acetic acid and water 2 mL), H_2 (1 atm), Pt NW catalyst (0.01 mmol), 100 °C, 24 h. [b] Determined by GC and GC-MS analysis using 1-*tert*-butylbenzene as an internal standard. [c] Aniline (1 mmol) was used as the substrate. [d] Aniline (1 mmol) was used as the substrate without Pt nanowire catalyst.

Nitrobenzene and acetic acid were used to probe the activity of the Pt NW catalyst at different temperatures. It was found that the reaction temperature is critical in the range of 40–100 °C (Table 3) with higher temperatures favoring the one-pot amidation of nitrobenzene. A reaction temperature of 100 °C resulted in a yield of 99 % *N*-phenylacetamide. At 40 °C, the main product was aniline. The selectivity of *N*-phenylacetamide increased with increasing temperature. Temperature thus mainly influences the later amidation step rather than the former hydrogenation step.

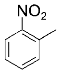
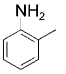
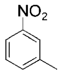
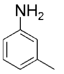
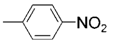
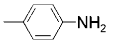
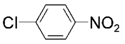
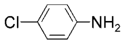
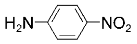
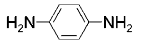
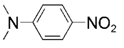
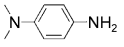
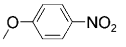
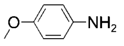
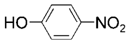
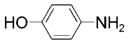
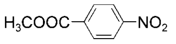
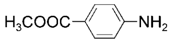
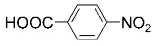
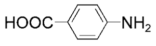
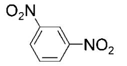
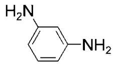
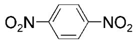
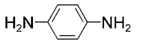
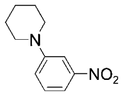
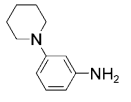
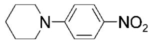
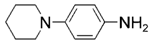
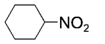
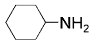
Table 3. Hydrogenation of nitrobenzene on Pt NW in acetic acid at different temperatures.[a]

	T [°C]	Conversion [%]	Selectivity (A/B/C) [%][b]
1	40	11	0:0:100
2	60	100	6:3:91
3	80	100	81:6:13
4	100	100	99:1:0

[a] Reaction conditions: nitrobenzene (1 mmol), acetic acid (2 mL), H_2 (1 atm), Pt NW catalyst (0.01 mmol), 24 h. [b] Determined by GC and GC-MS analysis using 1-*tert*-butylbenzene as internal standard.

Conditions for the hydrogenation of nitrobenzene to aniline were optimized with methanol as solvent. Using a reaction temperature of 40 °C, the effect of substrate type was investigated; Table 4 summarizes the main products and yields under these conditions. Nitroaromatics containing functional groups were also successfully reduced under these reaction conditions. High yields from *o*-, *m*-, and *p*-methyl nitrobenzene (Table 4, entries 1–3) showed the good regioselectivity obtained with the Pt NWs as catalysts, and the yields of the corresponding anilines were higher than

Table 4. Hydrogenation of nitroaromatics on Pt NW in methanol.[a]

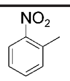
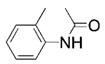
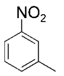
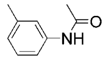
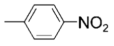
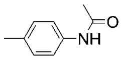
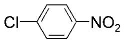
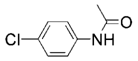
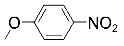
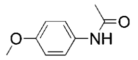
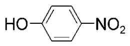
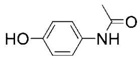
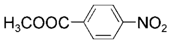
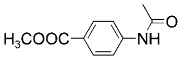
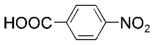
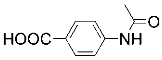
	Substrate	Product	*t* [h]	Yield [%][b]
1			5	99
2			5	97
3			5	99
4			5	78
5			5	98
6			5	98
7			5	99
8			5	98
9			5	96
10			5	99
11			5	98
12			5	99
13			5	97
14			5	99
15[c]			24	88

[a] Reaction conditions: nitroaromatics (1 mmol), methanol (2 mL), H_2 (1 atm), Pt NW catalyst (0.01 mmol), 40 °C. [b] Determined by GC and GC-MS analysis using 1-*tert*-butylbenzene as internal standard. [c] Reaction conducted at 9 atm.

97 %. Functional groups did not influence the reduction of the nitroaromatics significantly because good chemoselectivity was observed for substrates containing electron-donating or electron-withdrawing groups (Table 4, entries 4–10). Hydrogenation of *m*- and *p*-dinitrobenzene also gave excellent yields and produced the corresponding dianilines (Table 4, entries 11 and 12) with yields of 98 and 99 %, respectively. Nitroaromatics with a sterically bulky group also produced high yields (Table 4, entries 13 and 14). Moreover, hydrogenation was possible using unactivated aliphatic nitro compounds, with the corresponding amine being obtained with an excellent yield of 88 % (Table 4, entry 15).

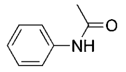
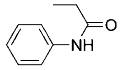
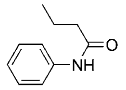
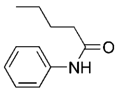
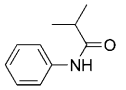
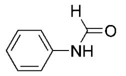
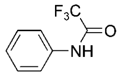
Use of the Pt NWs as catalyst also showed good regioselectivity in the one-pot amidation, and the yield of the corresponding amide was higher than 92 % (Table 5, entries 1–3). Nitroaromatics containing both electron-donating and electron-withdrawing groups were converted into the corresponding amides in good to high yields (Table 5, entries 4–8).

Table 5. One-pot reductive amidation of nitroaromatics with acetic acid over Pt NW.[a]

	Substrate	Product	Conversion [%]	Yield [%][b]
1[c]			99	94
2			100	96
3			100	92
4			100	91 (88)
5			99	94 (94)
6			100	82
7			82	– (78)
8			100	98

[a] Reaction conditions: nitroaromatic (1 mmol), acetic acid (2 mL), H_2 (1 atm), Pt NW catalyst (metal/nitrobenzene mol ratio 1 %), 100 °C, 24 h. [b] Determined by GC and GC-MS analysis using 1-*tert*-butylbenzene as internal standard. The values within parentheses are the yields of the isolated products. [c] Reaction time: 40 h.

Table 6. One-pot reductive amidation of nitrobenzene with carboxylic acid over Pt NW.[a]

	Carboxylic acid (pK_a)	Product	Conversion [%]	Yield [%][b]
1	CH_3COOH (4.76)		100	99 (95)
2	CH_3CH_2COOH (4.88)		98	90 (88)
3	$CH_3(CH_2)_2COOH$ (4.82)		100	95
4	$CH_3(CH_2)_3COOH$ (4.82)		97	96
5	$(CH_3)_2CH_2COOH$ (4.84)		100	84 (82)
6[c]	HCOOH (3.77)		99	70
7[d]	CF_3COOH (0.23)		99	41

[a] Reaction conditions: nitrobenzene (1 mmol), carboxylic acid (2 mL), H_2 (1 atm), Pt NW catalyst (0.01 mmol), 100 °C, 24 h. [b] Determined by GC and GC-MS analysis using 1-*tert*-butylbenzene as internal standard. The values within parentheses are the yields of the isolated products. [c] Reaction conducted at 80 °C. [d] Reaction conducted at 60 °C.

To determine the scope and limitations of the use of carboxylic acids in the reduction of nitrobenzene and the one-pot amidation under a hydrogen atmosphere over Pt NW catalyst, some of the liquid acids were chosen as substrates (Table 6). The Pt NW catalyst showed excellent activity when acetic acid, propanoic acid, *n*-butyric acid, or *n*-pentanoic acid were used, and high yields of the corresponding amides (>90 %) were obtained (Table 6, entries 1–4). 2-Methylpropanoic acid gave a yield of 84 % (Table 6, entries 5). Aniline was formed as a byproduct instead of the inactive carboxylate salt or unreacted nitrobenzene. However, acids with lower pK_a values, such as formic acid (3.77) and trifluoroacetic acid (0.23), gave lower yields of the corresponding amides; this is because the stronger acids easily formed inactive carboxylate salts with anilines. The lower reaction temperatures, which were determined according to the boiling points of the acids used, may also have influenced the yield of the amide.

We attempted to use nitrobenzene with different functional groups (including 1-methoxy-4-nitrobenzene and 1-chloro-4-nitrobenzene) as the substrate in a range of carboxylic acids under the same reaction conditions. Good yields were obtained from 1-methoxy-4-nitrobenzene (88–98 %; see Table S1 in the Supporting Information). However, the yields were lower for the 1-chloro-4-nitrobenzene (47–91 %; see Table S2 in the Supporting Information), especially when 2-methylpropanoic acid was used in the reaction, and 47 % amide was obtained with a higher quantity of amine.

To demonstrate the unique reactivity and selectivity of this Pt NW catalyst, two alternative types of Pt nanomaterials, nanoparticles and nanorods were synthesized as control catalysts for the amide formation using nitrobenzene and acetic acid as the reactants (see Figure S3 and S4 in the Supporting Information). The amide yield was 72 % in the nanoparticle system (ca. 2 nm in diameter[13]), and 87 % in the nanorod system (ca. 2 nm in diameter and ca. 20 nm in length; see Table S3 in the Supporting Information). When acetic acid was used as the solvent and substrate without the

Pt NW catalyst, the amide was also obtained as the main product (see Table S4, entry 3 in the Supporting Information). When *n*-butyric acid was used as the solvent and substrate without the Pt NW catalyst, the yield of amide was decreased and only 70 % amide was obtained (see Table S4, entry 6 in the Supporting Information). However, when the molar ratio of aniline and acetic acid was 1:1 in water (Table 2, entries 6 and 7), aniline could react with the carboxylic acid over Pt NW catalyst with a 19 % yield, but no amide was detected by GC analysis without Pt NW catalyst. Aniline was also used as the substrate in the reaction. When aniline (the intermediate) was used as the substrate instead of nitrobenzene in acetic acid (or *n*-butyric acid; see Table S4, entries 2 and 5 in the Supporting Information), the amides were also formed as the main product with yields of 96 % (90 %), which is slightly lower than observed when nitrobenzene was used (see Table S4, entries 1 and 4 in the Supporting Information). These results demonstrate that the nitroaromatics are first reduced to amines and then to amides as the final product over Pt NW catalyst in one-pot, without isolation of the amine intermediates.

The catalyst could be recovered by simple centrifugation and washing with methanol. It could be reused at least six times without significant loss of activity (98 %) and there were no measurable amounts of Pt in the reaction solution as determined by atomic absorption spectrometry (Figure 4).

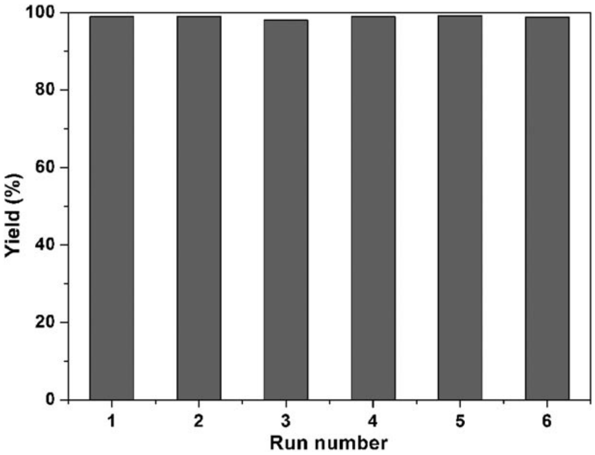


Figure 4. Cycling of Pt NWs from the one-pot reaction. Reaction conditions: Pt NWs (0.01 mmol), nitrobenzene (1 mmol), acetic acid (2 mL), 100 °C; reaction time of each cycle: 24 h.

Conclusion

The Pt NW developed here was found to be a useful heterogeneous catalyst for the hydrogenation of nitroaromatics and direct amide synthesis from nitroaromatics and carboxylic acids in a one-pot reaction. Whereas most of the reported direct amidation reactions of amines and acids require harsh conditions, such as high temperature, it is worth noting that the reactions in this new approach proceeded under very mild conditions. Moreover, the reduction of nitroaromatics to the corresponding amines and the one-pot amidation of nitroaromatics with carboxylic acids under a hydrogen atmosphere were carried out in one-pot without isolating the amine intermediates. Further studies on the reaction process have revealed that the reduction of nitroaromatics was faster than the amidation and resulted in high yields of the corresponding amides.

Experimental Section

Typical procedure for reductive amidation of carboxylic acids with nitroaromatics: Catalyst testing was carried out in a sealed tube. Pt NWs in hexane were added and the hexane was evacuated by pressure reduction. Nitroaromatics, carboxylic acid and 1-*tert*-butylbenzene were added to the reaction tube and the tube was sealed. The reaction tube was thrice evacuated and flushed with hydrogen and the reaction was carried out at the appropriate temperature under a hydrogen atmosphere. The resulting product mixtures were analyzed by gas chromatography (GC) (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and gas chromatography mass spectrometry (GC-MS) (VARIAN 450-GC and VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. Some amides were purified by flash chromatography and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and TOF-MS.

Acknowledgements

H.W.G. acknowledges financial support from the National Natural Science Foundation of China(21003092), the National Science Foundation of Jiangsu Province (BK2008158), and the New Faculty Start Foundation of Soochow University; J.M.L. acknowledges financial support from the National Natural Science Foundation of China (20876101).

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Received: September 30, 2010