

Hydrothermal Heck reaction catalyzed by Ni nanoparticles

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Received 14th January 2009, Accepted 28th April 2009

First published as an Advance Article on the web 26th May 2009

DOI: 10.1039/b900697d

A novel environmentally benign Heck reaction using Ni nanoparticles as catalysts under hydrothermal conditions has been developed in the absence of phosphine ligands without the protection of an inert atmosphere. The results showed that the aryl iodides and bromides could carry out the coupling reaction with a variety of alkenes by hydrothermal treatment. More importantly, the cheap catalysts are stable under the reaction conditions and retain good to moderate activity for at least six successive runs without any additional activation treatment. This approach would be very useful from a practical viewpoint.

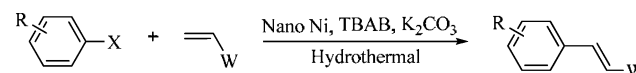
Introduction

The vinylation of aryl and vinyl halides, called the Heck reaction, is extensively used in organic synthesis.¹ Soluble palladium compounds, generally phosphine palladium complexes, are the most efficient catalysts for the Heck reaction. However, phosphine ligands are expensive, toxic, unrecoverable and sensitive to oxygen and water. Additionally, catalyst recycling is often hampered by early precipitation of palladium and recovery of the expensive palladium is difficult. The problems could, in principle, be minimized using heterogeneous catalysts.² Recently, Martínez and Vallribera prepared Ni nanoparticles embedded in silica and carbon aerogels which were active and recoverable catalysts for Mizoroki–Heck reactions.³ Therefore, study on the Heck reaction using much cheaper heterogeneous catalysts such as Ni,⁴ Co⁵ and Cu⁶ is of great importance and significance from industrial and scientific viewpoints.

The Heck reaction is traditionally carried out in organic solvents such as dimethyl formamide (DMF), *N*-methylpyrrolidone (NMP) and acetonitrile, which often creates significant safety, health and environmental issues due to their flammability, toxicity and volatility. From an economic and environmental standpoint, it is desirable to avoid any use of hazardous and expensive organic solvents. There have been a number of reports on C–C bond formations in aqueous medium in recent years,^{7–11} which can be attributed to the development of the field of green chemistry. It is well known that in hydrothermal processes the temperature is much higher than the boiling point of water and the self-engendered high pressure takes the water to a critical or subcritical state. The special properties of supercritical water make it possible to realize organic reactions that cannot be attained in organic solvents. It had also been reported that high-pressure techniques can activate the Heck reaction.^{1b,12} So it is expected that the Heck reaction carried out

in heterogeneous systems may be promoted under hydrothermal conditions.

In this work, we report a hydrothermal Heck reaction using Ni nanoparticles as catalysts which were prepared by direct reduction of NiCl₂ with NaBH₄ in aqueous medium under sonication in the absence of surfactants. The coupling reactions of a variety of aryl halides with different alkenes were investigated under optimum reaction conditions (Scheme 1). More importantly, the cheap catalysts are stable under the reaction conditions and retain good to moderate activity for at least six successive runs without any additional activation treatment in the absence of the phosphine ligands.



R = -H, -OCH₃, -CH₃, -OH, -COOH, -Cl, -NO₂.

X = I, Br, Cl.

W = -CO₂Me, -CO₂Et, -CO₂ⁿBu, -Ph.

Scheme 1 C–C coupling reaction.

Results and discussion

Catalyst characterization

The obtained Ni was characterized by X-ray powder diffraction analysis (XRD). It did not show any peaks that could be associated with a crystalline phase, which indicates that it is poorly crystalline or amorphous. In order to further identify the samples, energy-dispersive spectrometry analysis (EDS, Fig. 1) was carried out. It reveals that the sample is essentially pure nickel and the absence of boron. Only a small amount of oxygen is present, probably due to the existence of air atmosphere or the oxidation of the sample surface. The morphologies of the sample were determined by field emission scanning electron microscopy (FE-SEM) as shown in Fig. 2a. It can be seen that the sample is mainly composed of small nanoparticles.

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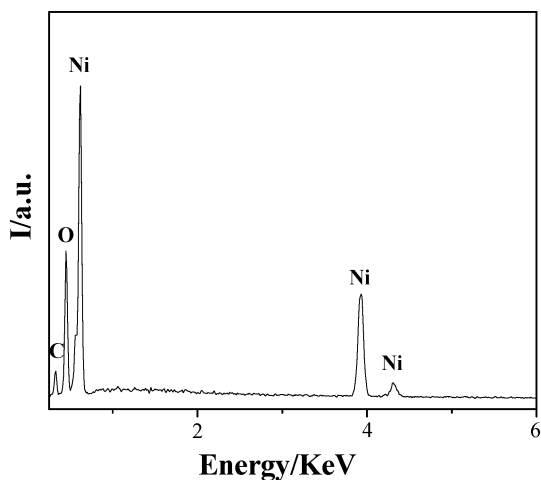


Fig. 1 EDS image of the Ni nanoparticles.

Testing of the catalysts

During the course of further optimization of our reaction conditions, the vinylation of iodobenzene with ethyl acrylate was studied as model reaction using the as-prepared Ni nanoparticles as catalysts in an autoclave. The effects of solvent, base, temperature, amount of catalyst and reaction time were investigated and the results are summarized in Table 1. It can be seen that 84% of the product was obtained in pure water in an autoclave (Table 1, entry 1). A parallel experiment was carried out in aqueous medium under reflux conditions (Table 1, entry 2), but only a trace of the product was obtained due to the lower temperature and pressure compared to hydrothermal conditions. However, we obtained comparatively better yields with mixed solvent (Table 1, entry 3) possibly due to the increased solubility of the organic substrates. Although a better yield was observed in DMF/H₂O = 1/2, water was chosen as the solvent of choice for our reaction system for economic and environmental reasons. The basic environment is indispensable for the Heck reaction and among the bases examined (Table 1, entries 1 and 4–8), K₂CO₃ showed the best effect on the coupling reaction. It is well-known that heterogeneous Heck reactions can run better at higher temperatures if reagents, products, and catalyst can survive such a harsh treatment. As expected, the yield significantly increased from 20% to 84% as the temperature increased from 100 °C to

140 °C (Table 1, entries 1 and 9, 10). When the temperature was raised to 150 °C, the yield did not increase significantly (Table 1, entry 11) and hence 140 °C was chosen for the further study. Experiments showed that 2 mol% of catalyst provided the best yield of product (Table 1, entries 1 and 12–14). Time-dependent experiments indicated that the reaction time has a strong influence on the yield (Table 1, entries 1 and 15–17), 16 h was chosen as the ideal reaction time for the coupling of iodobenzene with ethyl acrylate. Superior results were obtained when the molar ratio of iodobenzene with ethyl acrylate was 1 : 1.2. All results were obtained without the protection of an inert atmosphere.

Thus, the optimized reaction conditions for this Heck reaction were aryl halide (1 mmol), alkene (1.2 mmol), catalysts (0.02 mmol), K₂CO₃ (1 mmol), tetrabutylammonium bromide (TBAB) (0.5 mmol) and water (10 mL) at 140 °C in a 15 mL Teflon-lined stainless-steel autoclave for 16 h.

We next explored the scope and limitations of this hydrothermal Heck reaction for different substrates using Ni nanoparticles as catalyst under the optimum reaction conditions, and the results are summarized in Table 2. The yields depended on the nature of halides and their substituents. It was found that the yields were generally high for both electron-donating and electron-withdrawing aryl iodides (Table 2, entries 5–13) and all of the products were easily separated by the extraction with ether. The results were comparable to the results obtained with palladium catalysts in water.^{8c} Furthermore, the yields in heterogeneous systems were even higher than the yields obtained in homogeneous ones with nickel catalysts in the presence of phosphine ligands.^{4b} It is worth mentioning that the hydrothermal system could tolerate a broad range of functional groups, such as OMe, OH, NO₂ and COOH.

In the case of aryl bromides the catalytic system presented moderate activity for activated aryl bromobenzenes (Table 2, entries 14, 15), but only 35% yield of the product was obtained with bromobenzene (Table 2, entry 16) although the reaction time was prolonged and a higher reaction temperature was necessary for the electron-rich aryl bromides (Table 2, entry 17). Unfortunately, the catalytic system was inactive for aryl chlorides (Table 2, entry 18) and only trace product was observed. All coupling products were purified and characterized; only *E*-isomers were obtained which was confirmed by NMR (³J_{H-H} = 16 Hz).

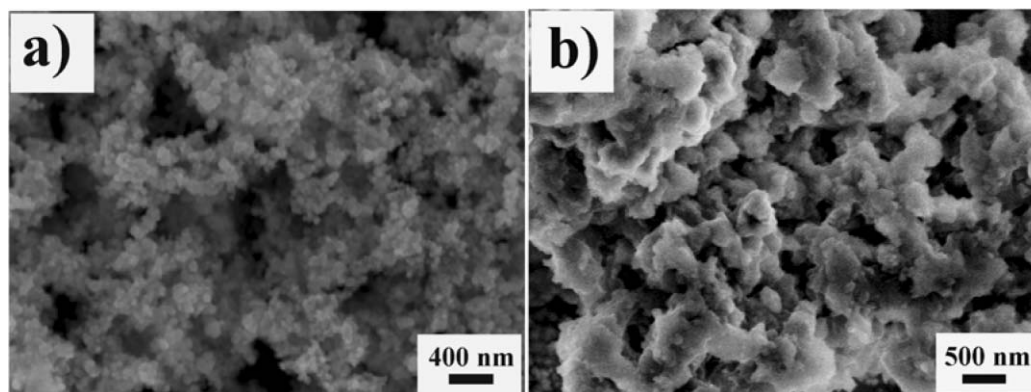
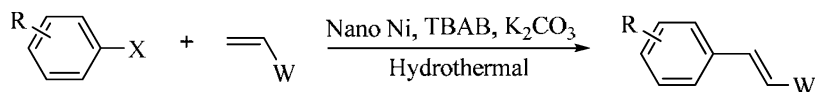


Fig. 2 (a) FE-SEM image of the Ni nanoparticles; (b) FE-SEM image of the Ni catalyst after the sixth cycle.

Table 1 The effects of solvent, base, temperature, amount of catalyst and reaction time on the Heck coupling of iodobenzene and ethyl acrylate

Entry	Solvent	Base	T/°C	Ni (mol%) ^c	Time/h	Yield (%) ^a
1	H ₂ O	K ₂ CO ₃	140	2	16	84
2 ^b	H ₂ O	K ₂ CO ₃	100	2	16	trace
3	DMF/H ₂ O = 1/2	K ₂ CO ₃	140	2	16	89
4	H ₂ O	KOH	140	2	16	62
5	H ₂ O	NaOH	140	2	16	55
6	H ₂ O	Na ₂ CO ₃	140	2	16	71
7	H ₂ O	NaOAc	140	2	16	72
8	H ₂ O	Et ₃ N	140	2	16	64
9	H ₂ O	K ₂ CO ₃	120	2	16	65
10	H ₂ O	K ₂ CO ₃	100	2	16	20
11	H ₂ O	K ₂ CO ₃	150	2	16	85
12	H ₂ O	K ₂ CO ₃	140	1	16	72
13	H ₂ O	K ₂ CO ₃	140	1.5	16	79
14	H ₂ O	K ₂ CO ₃	140	4	16	86
15	H ₂ O	K ₂ CO ₃	140	2	8	68
16	H ₂ O	K ₂ CO ₃	140	2	12	76
17	H ₂ O	K ₂ CO ₃	140	2	20	85

^a Isolated yields. ^b Under reflux conditions. ^c The amount of the catalysts was relative to the amount of iodobenzene.

Table 2 Heck reactions of aryl halides with alkenes catalyzed by Ni nanoparticles^a

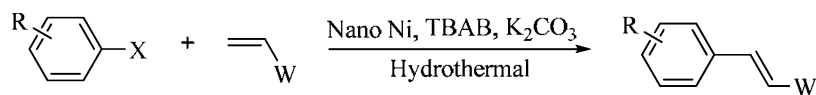
R = -H, -OCH₃, -CH₃, -OH, -COOH, -Cl, -NO₂.

X = I, Br, Cl.

W = -CO₂Me, -CO₂Et, -CO₂ⁿBu, -Ph.

Entry	Aryl halide	Alkene	Product	Time/h	Yield (%) ^b
1				16	81
2				16	84
3				16	80
4				16	78
5				16	79
6				16	83

Table 2 (Contd.)



R = -H, -OCH₃, -CH₃, -OH, -COOH, -Cl, -NO₂.

X = I, Br, Cl.

W = -CO₂Me, -CO₂Et, -CO₂ⁿBu, -Ph.

Entry	Aryl halide	Alkene	Product	Time/h	Yield (%) ^b
7				16	78
8				16	75
9				16	78
10				16	79
11				24	76
12				24	77
13				24	72
14				20	61
15				20	55
16				30	35
17				30 (150 °C)	20
18				30 (150 °C)	trace

^a Reaction conditions: aryl halide (1 mmol), alkene (1.2 mmol), Ni catalysts (0.02 mmol), K₂CO₃ (1 mmol), TBAB (0.5 mmol), water (10 mL) at 140 °C in a 15 mL Teflon-lined stainless-steel autoclave. ^b Isolated yields.

Table 3 Successive trials using recycled Ni^a catalysts

Trial	Yield (%) ^b	Trial	Yield (%) ^b
1	84	4	78
2	82	5	76
3	81	6	75

^a Reaction conditions: iodobenzene (1 mmol), ethyl acrylate (1.2 mmol), recycled Ni catalysts, K₂CO₃ (1 mmol), TBAB (0.5 mmol), water (10 mL) at 140 °C in a 15 mL Teflon-lined stainless-steel autoclave. ^b Isolated yields.

Catalysts recycling

Experiments were also conducted to examine the recyclability of Ni catalysts. As can be seen from Table 3, Ni nanoparticles were reused successfully and minor decreases in reaction yields were observed after the fourth catalytic coupling reactions of iodobenzene with ethyl acrylate (Table 3). Elemental analysis of the filtrate after the reaction demonstrated no leaching of Ni, implying that the reaction proceeded through a heterogeneous catalytic process. After the sixth cycle, Ni nanoparticles were much larger in size (Fig. 2b) because of aggregation and precipitation of the catalysts.

Conclusions

In summary, Ni nanoparticles were prepared by a facile method under sonication. It was found that the as-prepared Ni nanoparticles exhibited superior catalytic activity in the Heck reaction simply by environmental benign hydrothermal treatment and provides the corresponding coupling products with moderate to good yields in the absence of phosphine ligands. Furthermore, the cheap catalysts are stable under the reaction conditions and retain good to moderate activity for at least six successive runs without any additional activation treatment. Fortunately, it was found that other metals such as Fe and Cu nanostructures prepared by the same method also show the similar activities under hydrothermal conditions. The results of these studies will be reported in due course.

Experimental

Chemicals

All starting materials and reagents were commercially available and used without further purification. All products have been previously reported and characterized. All known products gave satisfactory analytical data corresponding to the reported literature values.

Apparatus

The as-prepared Ni products were characterized by X-ray powder diffraction (Shimadzu XRD-6000) with graphite monochromatized Cu-K α radiation ($\lambda = 0.154060$ nm), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range from 10° to 80° . All the experiments were conducted in a 15 mL Teflon-lined stainless-steel autoclave. The field-emission scanning electron microscopy

(FE-SEM) image and the energy-dispersive spectrometry (EDS) were obtained on an S-4800 field-emission scanning electron microscope with an accelerating voltage of 5 kV. NMR spectra were obtained at 25 °C on a Bruker Avance-300 at 300 MHz for ¹H, and at 75 MHz for ¹³C NMR, chemical shifts for ¹H and ¹³C were both referenced to CDCl₃.

Preparation of the catalysts

In a typical synthetic process 0.0952 g NiCl₂·6H₂O (0.4 mmol) and 0.012 g NaBH₄ (0.3 mmol) were each dissolved in 10 mL de-ionized water to form aqueous solutions. Then the NiCl₂ solution was injected dropwise into the NaBH₄ solution under sonication at 30–40 °C. After the addition was complete, the mixture was sonicated continuously for 10 min. Finally, the mixture was separated by centrifugation. The black precipitate was collected and washed with de-ionized water several times, then dried in a vacuum oven at 60 °C for 4 h.

Procedures for the Heck reaction

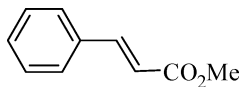
In a typical experimental procedure 0.02 mmol Ni was added to 5 mL de-ionized water in a 10 mL beaker, and then 1 mmol of aryl halide and 1.2 mmol of alkene, followed by 0.5 mmol TBAB and 1 mmol of K₂CO₃ were added sequentially, mixed with vigorous stirring. After five minutes, the mixture was transferred into a 15 mL Teflon-lined stainless-steel autoclave and de-ionized water was added up to 80% of the total volume. The autoclave was maintained at 140 °C for an appropriate time, then cooled down to room temperature and then centrifuged. The aqueous solution was separated and the precipitate was washed sufficiently with ethyl ether. The solutions were combined and extracted with ethyl ether (3 × 5 mL). The organic phases were then dried with anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent.

Recycling procedure of the catalysts

In the recycling experiment, when the reaction was complete and allowed to cool down to room temperature naturally, the precipitate was separated by centrifugation and washed sufficiently with ether and de-ionized water, each three times, then dried in a vacuum oven at 60 °C for 4 h. The catalysts were recovered and reused in the next run without further activation treatment.

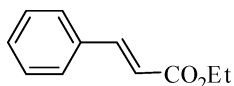
The NMR data of the products are presented below

1.



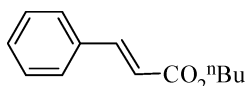
(*E*)-Methyl cinnamate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.70 (d, $J = 16.1$ Hz, 1H), 7.53–7.50 (m, 2H), 7.38–7.36 (m, 3H), 6.45 (d, $J = 16.1$ Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 167.5, 144.9, 134.4, 130.5, 128.9, 128.2, 117.8, 51.7.

2.



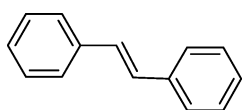
(*E*)-Ethyl cinnamate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.68 (d, $J = 16.0$ Hz, 1H), 7.49–7.47 (m, 2H), 7.35–7.33 (m, 3H), 6.42 (d, $J = 16.0$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 166.9, 144.5, 134.5, 130.1, 128.9, 128.0, 118.3, 60.4, 14.3.

3.



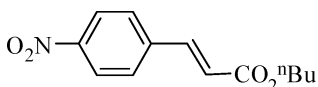
(*E*)-*n*-Butyl cinnamate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.69 (d, $J = 16.0$ Hz, 1H), 7.53–7.50 (m, 2H), 7.38–7.36 (m, 3H), 6.44 (d, $J = 16.0$ Hz, 1H), 4.21 (t, $J = 6.6$ Hz, 2H), 1.74–1.64 (m, 2H), 1.50–1.40 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 167.0, 144.5, 134.5, 130.2, 128.9, 128.0, 118.3, 64.4, 30.8, 19.2, 13.8.

4.



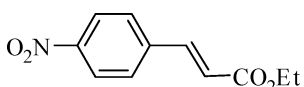
(*E*)-1,2-Diphenylethene: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.61 (d, $J = 7.2$ Hz, 4H), 7.46 (t, $J = 7.2$ Hz, 4H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.21 (s, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 137.4, 128.8, 128.6, 127.7, 126.7.

5.



(*E*)-Butyl 3-(4-nitrophenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 8.25 (d, $J = 8.6$ Hz, 2H), 7.70 (d, $J = 16.0$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 2H), 6.56 (d, $J = 16.0$ Hz, 1H), 4.24 (t, $J = 6.6$ Hz, 2H), 1.75–1.66 (m, 2H), 1.48–1.38 (m, 2H), 0.97 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 166.1, 146.6, 141.5, 140.6, 128.6, 124.1, 122.7, 64.9, 30.7, 19.1, 13.7.

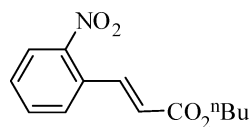
6.



(*E*)-Ethyl 3-(4-nitrophenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 8.25 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 16.0$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 2H), 6.59 (d, $J = 16.0$ Hz, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 ,

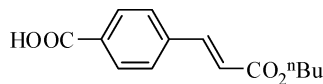
75 MHz) δ : 170.9, 157.9, 148.1, 141.6, 128.6, 123.2, 117.5, 61.0, 14.3.

7.



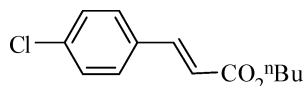
(*E*)-Butyl 3-(2-nitrophenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 8.10 (d, $J = 15.9$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 7.56–7.54 (m, 1H), 7.54–7.52 (m, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 1.71–1.66 (m, 2H), 1.46–1.37 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 166.2, 148.3, 146.2, 139.6, 133.9, 130.5, 128.9, 124.8, 123.2, 64.5, 30.8, 19.2, 13.7.

8.



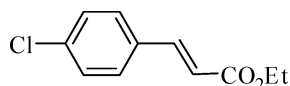
(*E*)-4-(3-Butoxy-3-oxoprop-1-enyl)benzoic acid: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 12.8 (s, 1H), 8.13 (d, $J = 7.9$ Hz, 2H), 7.72 (d, $J = 16.0$ Hz, 1H), 7.63 (d, $J = 7.9$ Hz, 2H), 6.56 (d, $J = 16.0$ Hz, 1H), 4.24 (t, $J = 6.5$ Hz, 2H), 1.73–1.66 (m, 2H), 1.48–1.41 (m, 2H), 0.97 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 169.3, 166.7, 143.0, 139.6, 130.7, 130.3, 128.0, 121.1, 64.8, 30.7, 19.2, 13.8.

9.



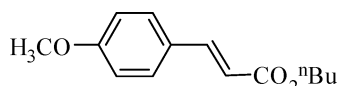
(*E*)-Butyl 3-(4-chlorophenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.59 (d, $J = 16.0$ Hz, 1H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.31 (d, $J = 7.5$ Hz, 2H), 6.37 (d, $J = 16.0$ Hz, 1H), 4.18 (t, $J = 6.4$ Hz, 2H), 1.68–1.64 (m, 2H), 1.44–1.37 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 166.7, 143.0, 136.1, 132.9, 129.1, 128.8, 118.8, 64.9, 30.7, 19.2, 13.7.

10.



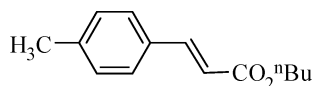
(*E*)-Ethyl 3-(4-chlorophenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.63 (d, $J = 15.9$ Hz, 1H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 6.41 (d, $J = 15.9$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 166.2, 142.5, 135.6, 132.5, 128.8, 128.7, 118.5, 61.4, 14.3.

11.



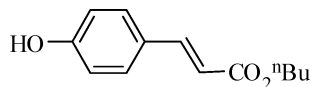
(*E*)-Butyl 3-(4-methoxyphenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.62 (d, $J = 16.0$ Hz, 1H), 7.45 (d, $J = 8.3$ Hz, 2H), 6.87 (d, $J = 8.3$ Hz, 2H), 6.29 (d, $J = 16.0$ Hz, 1H), 4.18 (t, $J = 6.6$ Hz, 2H), 3.79 (s, 3H), 1.71–1.62 (m, 2H), 1.46–1.38 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 167.3, 161.3, 144.2, 129.6, 127.1, 115.7, 114.3, 64.2, 55.3, 30.8, 19.2, 13.7.

12.



(*E*)-Butyl 3-*p*-tolylacrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.67 (d, $J = 16.0$ Hz, 1H), 7.42 (d, $J = 7.2$ Hz, 2H), 7.18 (d, $J = 7.2$ Hz, 2H), 6.40 (d, $J = 16.0$ Hz, 1H), 4.30 (t, $J = 6.6$ Hz, 2H), 2.36 (s, 3H), 1.74–1.65 (m, 2H), 1.50–1.41 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 167.3, 144.6, 140.6, 129.6, 128.9, 128.1, 117.2, 64.4, 30.8, 21.5, 19.2, 13.8.

13.



(*E*)-Butyl 3-(4-hydroxyphenyl)acrylate: ^1H NMR (CDCl_3 , 300 MHz, ppm) δ : 7.69 (d, $J = 16.0$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 6.45 (d, $J = 16.0$ Hz, 1H), 4.22 (t, $J = 6.3$ Hz, 2H), 1.72–1.65 (m, 2H), 1.48–1.41 (m, 2H), 0.97 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.5, 30.8, 19.2, 13.8.

Acknowledgements

Financial support from the National Natural Science Foundation of China (20701001, 20872001) and a grant from the Education Department of Anhui province (TD200707) are appreciated.

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