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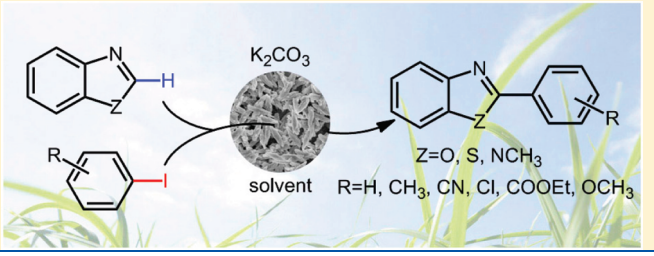
Ligand-Free CuO Nanospindle Catalyzed Arylation of Heterocycle C−H Bonds

Wu Zhang,* Qinglong Zeng, Xinming Zhang, Yujie Tian, Yun Yue, Yujun Guo, and Zhenghua Wang*

Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, People's Republic of China

Supporting Information

ABSTRACT: CuO nanospindles have been developed to efficiently catalyze the direct arylation of heterocycle C−H bonds with moderate to excellent yields. This reaction can be applied to heterocycles such as benzoxazole, benzothiazole, and 1-methylbenzimidazole in the presence of a more environmentally friendly inorganic base like K_2CO_3 under ligand-free catalytic conditions. In addition, the catalyst can be recycled and reused without any significant decrease in catalytic activity.



Heterocycles are one of the most important organic structural motifs in a myriad of pharmaceutically active compounds and organic materials.[1] Therefore, the efficient synthesis of heterocycles and their derivatives has been a topic of great interest from the perspective of medicinal chemistry and organic synthesis.[2] Among these methods, the simplest approach is the arylation of heterocycle C−H bonds. In the past decades, transition metals have been widely used as the efficient catalysts for various cross-coupling reactions,[3] including the rhodium-[4] and palladium-catalyzed[5] direct arylation of various heteroerenes. However, these reactions have limited applications in the industry due to the relatively high cost of the catalyst. Therefore, the development of an inexpensive and efficient catalysts for this reaction has received wide research interest. For example, nickel-catalyzed direct arylation and alkenylation of heterocycle C−H bonds have been successfully developed.[6]

Copper catalysts, as a complementary approach to the conventionally expensive Rh and Pd catalysts, have been receiving much attention in cross-coupling reactions because of their excellent catalytic properties. Recently, Daugulis and co-workers have reported the CuI-catalyzed arylation of heterocycle C−H Bonds using LiO^tBu as the base.[7a] Later on, they extended this CuI-catalyzed reaction to the arylation of arene C−H bonds by introducing phenanthroline into the catalytic system.[7b] Meanwhile, Miura and co-workers have described the CuI/PPh_3-catalyzed direct arylation of benzoazoles with aryl iodides,[7c] and the CuI-catalyzed direct alkenylation of oxazoles with bromoalkenes using *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine as ligand has also been reported by Piguel et al.[7d] In 2009, You and co-workers also reported the CuI-catalyzed direct arylation of heterocycles with aryl bromides using 1,10-phenanthroline as a ligand.[7e] However, these CuI-catalyzed reaction systems require the presence of organic ligands which make it difficult for the separation and purification after the reactions. Considering the preference of modern green chemistry for more environmentally friendly mild base, the development of an efficient ligand-free reaction system with recyclable copper catalysts in the presence of mild inorganic base is highly desirable.

Nanoparticles have emerged as robust and high surface area heterogeneous catalysts,[8] which serve as a sustainable alternatives to conventional materials, especially CuO nanoparticles due to their stability and wild availability. Recently, CuO nanoparticle-catalyzed C−N, C−O, and C−S cross-coupling reactions have been achieved.[9] However, to the best of our knowledge, the application of these CuO nanoparticles in the catalyzed arylations of heterocycle C−H bonds have not been reported. Since the size, shape, and morphology of catalyst particles have significant effects on the catalytical properties of the catalyst,[10] herein we report a general efficient method for the CuO nanospindles-catalyzed arylation of heterocycles with aryl iodides.

The optimization of the reaction conditions for our CuO nanospindle-catalyzed arylation reaction was performed using benzoxazole and iodobenzene as substrates as summarized in Table 1. The absence of either CuO nanospindles or bases fails to generate the desired products, and all the starting materials were recovered from the reaction system (Table 1, entries 13 and 14). Decreasing the catalyst loading from 10 to 5 mol % resulted in the decrease of the yield even under extended reaction time conditions (Table 1, entry 15). In contrast, no significant improvement of the yield was observed by increasing the catalyst loading to 20 mol % (Table 1, entries 16 and 17). Reaction temperature also has some effect on this reaction (for example, 41% yield at 150 °C and 13% yield at 140 °C). In addition, the size of the CuO was observed to affect the reaction, and the substitution of CuO nanospindles with the commercial CuO powder (about 200 mesh) only gave the desired product in 39% yield (Table 1, entry 20). Thus, by varying the solvents and bases, the optimal reaction

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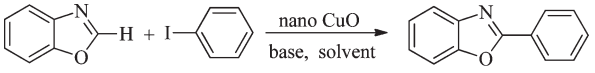
Table 1. Optimization of the Arylation Conditions[a]



entry	CuO (mol %)	base	solvent	T/°C	yield (%)
1	10	K_2CO_3	DMF	reflux	56
2	10	K_2CO_3	DMSO	reflux	44
3	10	K_2CO_3	dioxane	reflux	trace
4	10	K_2CO_3	NMP	160	
5	10	K_2CO_3	toluene	reflux	
6	10	K_2CO_3	diglyme	reflux	93
7	10	Na_2CO_3	diglyme	reflux	81
8	10	Cs_2CO_3	diglyme	reflux	trace
9	10	NaOAc	diglyme	reflux	
10	10	NEt_3	diglyme	reflux	
11	10	K_3PO_4	diglyme	reflux	53
12	10	KO^tBu	diglyme	reflux	11
13		K_2CO_3	diglyme	reflux	
14	10		diglyme	reflux	
15[b]	5	K_2CO_3	diglyme	reflux	71
16	15	K_2CO_3	diglyme	reflux	95
17	20	K_2CO_3	diglyme	reflux	96
18	10	K_2CO_3	diglyme	150	41
19	10	K_2CO_3	diglyme	140	13
20[c]	10	K_2CO_3	diglyme	reflux	39

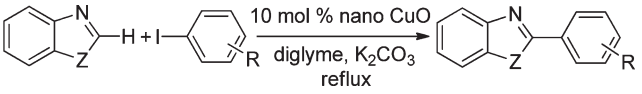
[a] Reaction conditions: benzoxazole (1 equiv), iodobenzene (2 equiv), base (2 equiv), solvent (2 mL), under reflux in argon for 3 h. [b] Reaction time of 48 h. [c] CuO (200 mesh) was used instead of CuO nanospindles.

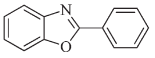
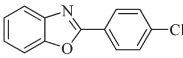
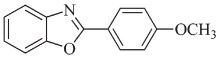
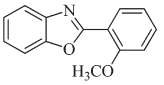
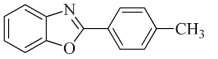
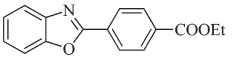
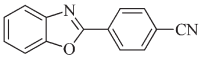
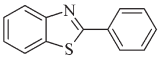
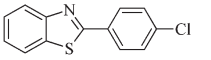
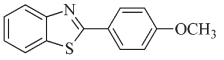
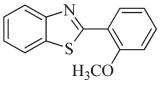
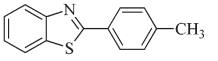
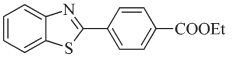
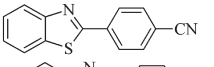
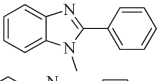
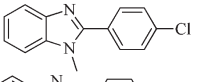
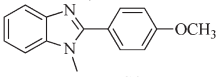
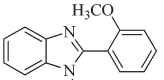
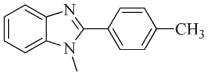
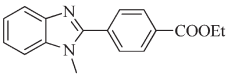
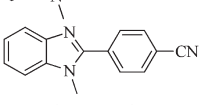
conditions were set to be 10 mol % of CuO nanospindles in the presence of 2 equiv of K_2CO_3 in refluxing diglyme for 3 h. Under these optimized reaction conditions, the desired arylation product was obtained in 93% yield.

These optimized reaction conditions were then applied to the arylation of a series of aryl halides as summarized in Table 2, and moderate to excellent yields were achieved for substituted aryl iodides with both electron-donating and electron-withdrawing substituents (Table 2, entries 1−7). In general, the presence of electron-withdrawing groups on aryl iodides leads to higher arylation yields than those with electron-donating groups. This may be due to the fact that the rate-determining step is the oxidative addition process in this reaction, thus rendering a faster reaction rate for the substrate with electron-withdrawing group. Interestingly, even aryl iodide with the steric hindrance substituent at ortho position was tolerated in this reaction (Table 2, entry 4). It is noteworthy that this reaction system could tolerate various functional groups such as COOEt and CN. Unfortunately, the substitution of aryl iodides with aryl bromides fails to generate the desired products.

We then investigated the reaction of other heterocycles such as benzothiazole and 1-methylbenzimidazole with aryl iodides, and the results are summarized in Table 2 (entries 8−21). Increasing the reaction time leads to an increase of the product yield, with the best results obtained at 8 and 16 h, respectively. The yields for the arylation of 1-methylbenzimidazole with aryl iodides were lower than that for benzoxazole, which may arise from the different acidities of hydrogen at C-2 of heterocycles.[11]

Table 2. Arylation Scope with Respect to Aryl Iodides and Heterocycles[a]



entry	Z	R	Product	Yield
1	O	H		93
2	O	4-Cl		84
3	O	4-OCH_3		81
4	O	2-OCH_3		80
5	O	4-CH_3		75
6	O	4-COOEt		82
7	O	4-CN		90
8	S	H		70
9	S	4-Cl		61
10	S	4-OCH_3		55
11	S	2-OCH_3		52
12	S	4-CH_3		51
13	S	4-COOEt		60
14	S	4-CN		66
15	NCH_3	H		90
16	NCH_3	4-Cl		83
17	NCH_3	4-OCH_3		79
18	NCH_3	2-OCH_3		75
19	NCH_3	4-CH_3		70
20	NCH_3	4-COOEt		80
21	NCH_3	4-CN		88

[a] Reaction conditions: heterocycle (1 equiv), aryl halide (2 equiv), K_2CO_3 (2 equiv), diglyme (2 mL), under reflux in argon. The reaction times are 3, 8, and 16 h for benzoxazole, benzothiazole, and 1-methylbenzimidazole, respectively.

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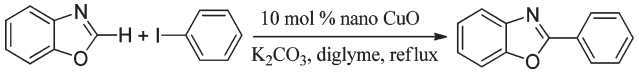
Table 3. Successive Tests by Using Recycled CuO Nanospindles[a]



test	yield (%)
1	93
2	91
3	88

[a] Reaction conditions: benzoxazole (1 equiv), iodobenzene (2 equiv), 10 mol % of CuO nanospindles, K_2CO_3 (2 equiv), diglyme (2 mL), under reflux in argon for 3 h.

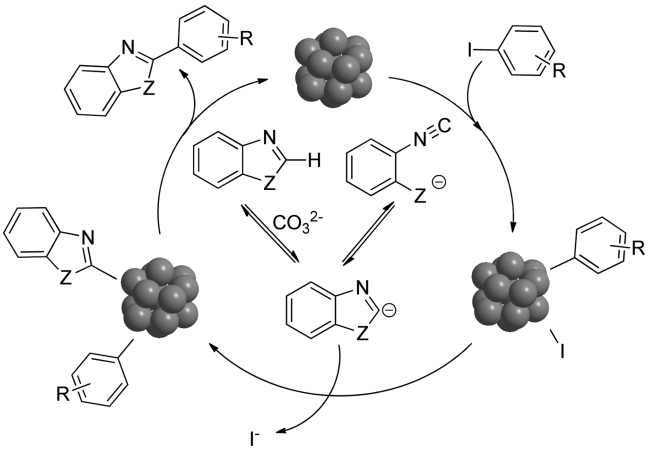
However, the yields of benzothiazole with aryl iodides were the lowest in the reaction system, which could be attributed to the fact that there is a equilibrium between the ring-opened isomer with azole anion upon deprotonation.[12] The resulting phenthiol species could have a relative higher reactivity with aryl iodides to generate the byproduct *N*,*N*-diphenyl-2-phenylthioaniline[7c] because of the stronger nucleophilicity of phenthiol species compared to phenol species. The detailed ring-opening process of benzothiazole in this reaction is still under the investigation.

The recyclability of the CuO nanospindles was also tested as shown in Table 3. No significant decrease in the catalytic activity for the arylation of benzoxazole with iodobenzene was observed for the recovered CuO nanospindles. XRD of the catalysts after the reaction demonstrated that the catalysts did not change during the reaction process (Figure S1, Supporting Information), and SEM of the catalysts after the reaction implied slight assemblage of the CuO nanospindles (Figure S2, Supporting Information). To further identify the recycled catalyst, energy-dispersive spectrometry (EDS) analysis was also performed, which reveals that the sample is essentially pure copper oxide without the presence of iodine (Figure S3, Supporting Information).

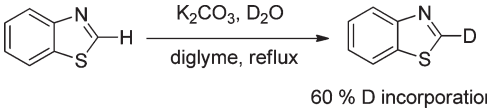
It is very necessary to further investigate whether this observed active catalysis is derived either from CuO nanospindles or the leached copper species.[13] The arylation of benzoxazole was then performed under the optimized conditions, and the catalyst was removed from the mixture by centrifugation after 1 h (at this time, approximately 50% yield was obtained). The "catalyst-free" mixture was continued to react under the same reaction conditions, which showed no further reaction progress even after 3 h. Leaching of the copper from the CuO nanospindles during the reaction was examined by AAS analysis, and a slight leaching (<1 ppm) was observed. Therefore, the reaction was believed to occur on the surface of the CuO nanospindles via a heterogeneous process.

A possible mechanism for this CuO nanospindles-catalyzed direct arylation of heterocycle was proposed. The reaction may undergo through an oxidative addition subsequent anion substitution, followed by a reductive elimination process on the surface of the CuO nanospindles (Scheme 1), similar to that for many of the heterogeneous processes reported in the literature.[9] To further check the alternative mechanism through σ-adduct formation at the metal center followed by elimination,[14] the H/D exchange of the benzothiazole has also been carried out with K_2CO_3 in the absence of CuO catalysts (Scheme 2). The result indicated that the hydrogen at C-2 of the heterocycle can be

Scheme 1. Proposed Catalytic Cycle



Scheme 2. H/D Exchange Experiment



removed in the presence of K_2CO_3 without the copper catalyst, which is consistent with the previous report.[12b]

In summary, CuO nanospindles can effectively catalyze the arylation of the C−H bond of heterocycles, such as benzoxazole, benzothiazole and 1-methylbenzimidazole, in a ligand-free coupling reaction system, to form the corresponding heterocycle compounds in moderate to excellent yields. A more environmentally friendly mild base can be used instead of a strong base such as LiO^tBu. It is also noteworthy to point out that the catalyst can be recycled and reused without any significant decrease in the catalytic activity.

EXPERIMENTAL SECTION

General Methods. The prepared CuO products were characterized by X-ray powder diffraction with graphite-monochromatized Cu Kα radiation (λ = 0.154060 nm), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 10° to 80°. The field-emission scanning electron microscopy (FE-SEM) images were obtained with an accelerating voltage of 5 kV. NMR spectra were obtained at 300 MHz for ^{1}H and at 75 MHz for ^{13}C NMR, and chemical shifts for ^{1}H and ^{13}C were both referenced to $CDCl_3$. High-resolution mass spectral (HRMS) data were obtained with an ionization mode of ESI.

All starting materials and reagents were commercially available and used without further purification. All products were purified and characterized by ^{1}H NMR and ^{13}C NMR. The spectroscopic data of the known compounds are in accordance with those reported in the literatures.[15]

Recycling Procedure of the Catalysts. The separated precipitates in the above procedure were washed sufficiently with deionized water and ethanol three times each and then dried under vacuum at 50 °C for 8 h, and then the CuO nanospindles were recovered.

Typical Procedure for CuO-Catalyzed Arylation of Benzoxazole and 4-Iodoanisole. The CuO nanospindles were prepared by thermal dehydration of the freshly prepared $Cu(OH)_2$ in solution.[16]Benzoxazole (0.5 mmol), 4-iodoanisole (1 mmol), CuO

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nanospindles (10 mol %), and K_2CO_3 (1 mmol) were stirred in diglyme (2 mL) under reflux in argon for 3−16 h. The resulting mixture was cooled to room temperature and then centrifuged. The organic phase was separated; the precipitate was washed thoroughly with EtOAc and then centrifuged. The organic phases were combined, washed with brine (3 × 10 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/petroleum = 1/3) to afford the product 2-(2-methoxyphenyl)benzo[*d*]oxazole (Table 2, entry 4): white solid; yield 80%; mp 46−47 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15−8.12 (d, J = 7.6 Hz, 1H), 7.84−7.82 (m, 1H), 7.59−7.48 (m, 2H), 7.36−7.35 (m, 2H), 7.13−7.08 (m, 2H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 158.5, 150.4, 142.1, 132.8, 131.3, 124.9, 124.3, 120.7, 120.2, 116.2, 112.1, 110.5, 56.2. HRMS (ESI) calcd for $C_{14}H_{12}NO_2$ ($[M + H]^+$) 226.0868, found 226.0858.

Ethyl 4-(benzo[*d*]oxazol-2-yl)benzoate (Table 2, entry 6): white solid; yield 82%; mp 160−161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33−8.31 (d, J = 7.7 Hz, 2H), 8.20−8.17 (d, J = 7.5 Hz, 2H), 7.81−7.80 (m, 1H), 7.60−7.59 (m, 1H), 7.40−7.38 (m, 2H), 4.45−4.38 (q, J = 6.9 Hz, 2H), 1.44−1.40 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 162.0, 150.9, 142.0, 132.9, 130.9, 130.1, 127.5, 125.7, 124.9, 120.4, 110.8, 61.4, 14.3; HRMS (ESI) calcd for $C_{16}H_{14}NO_3$ ($[M + H]^+$) 268.0974, found 268.0958.

Ethyl 4-(benzo[d]thiazol-2-yl)benzoate (Table 2, entry 13): white solid; yield 60%; mp 135−136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15−8.08 (m, 5H), 7.92−7.90 (d, J = 7.8 Hz, 1H), 7.53−7.48 (m, 1H), 7.43−7.38 (m, 1H), 4.44−4.37 (q, J = 7.0 Hz, 2H), 1.44−1.39 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 165.9, 154.1, 137.4, 135.3, 132.4, 130.2, 127.4, 126.6, 125.7, 123.6, 121.7, 61.3, 14.3; HRMS (ESI) calcd for $C_{16}H_{14}NO_2S$ ($[M + H]^+$) 284.0745, found 284.0732.

2-(4-Chlorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (Table 2, entry 16): white solid; yield 83%; mp 112−113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−7.80 (m, 1H), 7.69−7.66 (d, J = 7.5 Hz, 2H), 7.49−7.46 (d, J = 7.5 Hz, 2H), 7.33−7.31 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 142.9, 136.6, 136.0, 130.7, 129.0, 128.7, 123.0, 122.6, 119.9, 109.7, 31.7; HRMS (ESI) calcd for $C_{14}H_{12}N_2Cl$ ($[M + H]^+$) 243.0689, found 243.0678.

2-(4-Methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (Table 2, entry 17): white solid; yield 79%; mp 118−119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−7.80 (m, 1H), 7.70−7.67 (d, J = 7.6 Hz, 2H), 7.32−7.28 (m, 3H), 7.03−7.00 (d, J = 7.6 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 153.8, 142.9, 136.6, 130.8, 122.5, 122.3, 119.5, 114.1, 109.5, 55.4, 31.7; HRMS (ESI) calcd for $C_{15}H_{15}N_2O$ ($[M + H]^+$) 239.1184, found 239.1172.

2-(2-Methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (Table 2, entry 18): yellow oil; yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.81 (m, 1H), 7.58−7.56 (d, J = 7.1 Hz, 1H), 7.49−7.44 (m, 1H), 7.35−7.28 (m, 3H), 7.11−7.06 (m, 1H), 7.00−6.97 (d, J = 8.1 Hz, 1H), 3.76 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 152.2, 143.1, 136.1, 132.3, 131.6, 122.5, 122.0, 121.0, 119.8, 119.6, 111.1, 109.5, 55.6, 30.9; HRMS (ESI) calcd for $C_{15}H_{15}N_2O$ ($[M + H]^+$) 239.1184, found 239.1177.

1-Methyl-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (Table 2, entry 19): white solid; yield 70%; mp 127−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.81 (m, 1H), 7.66−7.63 (d, J = 7.2 Hz, 2H), 7.33−7.30 (m, 5H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 143.0, 139.9, 136.6, 129.4, 129.3, 127.3, 122.6, 122.4, 119.7, 109.6, 31.7, 21.5; HRMS (ESI) calcd for $C_{15}H_{15}N_2$ ($[M + H]^+$) 223.1235, found 223.1224.

Ethyl 4-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)benzoate (Table 2, entry 20): white solid; yield 80%; mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21−8.19 (d, J = 8.0 Hz, 2H), 7.88−7.85 (m, 3H), 7.40−7.35 (m, 3H), 4.46−4.39 (m, 2H), 3.89 (s, 3H), 1.45−1.40 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 152.6, 136.7, 134.3, 131.5, 129.9, 129.4, 123.3, 122.8, 120.1, 109.8, 61.3, 31.8, 14.3; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_2$ ($[M + H]^+$) 281.1290, found 281.1284.

4-(1-Methyl-1*H*-benzo[*d*]imidazol-2-yl)benzonitrile (Table 2, entry 21): white solid; yield 88%; mp 208−209 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94−7.91 (d, J = 7.8 Hz, 2H), 7.85−7.83 (m, 3H), 7.42−7.37 (m, 3H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 142.9, 136.7, 134.6, 132.5, 130.0, 123.7, 123.1, 120.2, 118.3, 113.4, 109.9, 31.9; HRMS (ESI) calcd for $C_{15}H_{12}N_3$ ($[M + H]^+$) 234.1031, found 234.1019.

■ ASSOCIATED CONTENT

Supporting Information. Catalyst characterization (XRD, SEM, and EDS) and NMR (^{1}H and ^{13}C) spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangwu@mail.ahnu.edu.cn; zhwang@mail.ahnu.edu.cn.

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