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Ultrathin Platinum Nanowire Catalysts for Direct C−N Coupling of Carbonyls with Aromatic Nitro Compounds under 1 Bar of Hydrogen

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Abstract: Traditionally important in the pharmaceutical, agrochemical, and synthetic dye industries, C−N coupling has proved useful for the preparation of a number of valuable organic compounds. Here, a new method for the direct one-pot reductive C−N coupling from carbonyl and aromatic nitro compounds is described. Employing ultrathin platinum nanowires as the catalyst and hydrogen as the reducing agent, *N*-alkylamines were achieved in high yields. Debenzylation products were not detected after prolonged reaction times. Time-dependent analysis, ReactIR spectroscopy and DFT calculations revealed that the C−N coupling proceeded through a different mechanism than traditional "reductive amination." *N*-Alkylamines were directly obtained by intermolecular dehydration over platinum nanowires under a hydrogen atmosphere, instead of intramolecular water elimination and imine hydrogenation.

Keywords: amination · C−N coupling · heterogeneous catalysis · nanowires · platinum

Introduction

The importance and widespread use of *N*-alkylamines in dye, pharmaceutical, and agrochemical industries have led C−N coupling to become a core interest in organic synthesis.[1] The reaction of amines with alkyl halides or similar alkylation agents is one of the most common methods of C−N coupling.[2] However, these processes have significant drawbacks such as alkylation agent toxicity and a lack of monoalkylation selectivity. The alkylation of amines with alcohols through a hydrogen auto-transfer or oxidation process[3] is an important reaction class that follows three steps to generate the *N*-alkylamines. Reductive amination of amines (or aromatic nitro compounds) with aldehydes (or ketones)[4] is another attractive procedure for *N*-alkylamine formation which includes two synthetic steps: C=N double-bond formation and hydrogenation of the imine derivatives. Several catalysts have demonstrated their efficiency in reductive amination reactions. Yamane et al.[5] reported a direct reduction over Au/Fe_2O_3 under a 2 MPa hydrogen atmosphere. Sreedhar et al.[6] reported that gum-acacia-stabilized Pd nanoparticles could be used as the catalyst with excellent yield. Decaborane Pd/C and $HCOO^-NH_4^+$/Pd/C systems have also been used for C−N bond formation.[7] These methods are encouraging; however, the Au/Fe_2O_3 system needs high pressure and the Pd catalysts system causes debenzylation,[8] which is an side reaction to *N*-alkylamine formation.

Herein, we report on the use of ultrathin platinum nanowires (Pt NW) as nonsupported catalysts for *N*-alkylation from aromatic nitro compounds and various carbonyls in a one-pot reaction under 1 bar of hydrogen. Time-dependent analyses and DFT calculations revealed that C−N bonds are directly formed through intermolecular dehydration instead of C=N intermediate formation through intramolecular water elimination and C=N double-bond hydrogenation. This mechanism is different than previously reported molecular catalysts or "Pd" nanocatalysts. Debenzylation products were not detected even after prolonged reaction times, up to 24 h.

Results and Discussion

Ultrathin Pt NW catalysts were obtained from the acidic etching of FePt NW under an air atmosphere. Compared with the starting material, FePt NW (Fe atomic ratio ≈50%, Figure S1, Supporting Information), Fe not was de-

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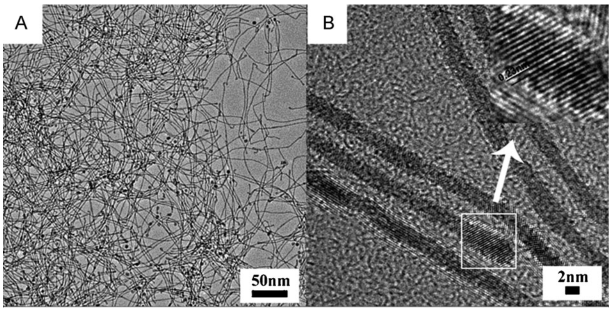
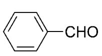
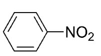
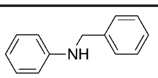
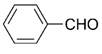
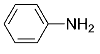
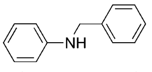
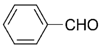
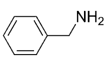
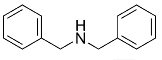
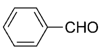
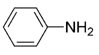
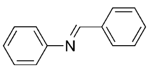
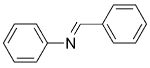
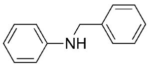


Figure 1. A) TEM and B) high resolution TEM images of the as-synthesized Pt NW. (Insert: Pt NW atomic lattice).

tected in the ultrathin Pt NW by inductive coupling plasma (ICP) and X-ray photoelectron spectroscopy (XPS, Figure S2 in the Supporting Information). Figure 1 A shows representative transmission electron microscopic (TEM) images of the as-synthesized Pt NW several hundred nanometers in length and less than 2 nm in average diameter (Figure 1 B). The high-resolution TEM image in Figure 1 B (insert) shows that the Pt NW are single crystals, and the plane distance is 0.23 nm, which is in agreement with that of the (111) plane of the face-centered cubic (fcc) phase of bulk Pt crystals.[9] The powder X-ray diffraction (XRD) pattern (Figure S3, Supporting Information) also showed that (111) is the predominant plane.

The catalytic activity of the Pt NW was first investigated with nitrobenzene and benzaldehyde as reactants under a hydrogen atmosphere (1 bar). Table S1 (Supporting Information) compares the catalytic performance in different solvents. In methanol, ethanol, or toluene (Table 1, entry 1), the reaction gives high yields (>90 %) after 12 h. A completely green process for the C−N coupling (Table S1, entry 4, Supporting Information) was also tested, and a yield of about 88 % of *N*-benzylbenzenamine was obtained when using water as the solvent.

Table 1. The control experiments for the preparation of *N*-benzylbenzenamine from direct reductive amination in toluene at 100 °C.

	Substrate 1	Substrate 2	Product	*t* [h]	Yield [%][e]
1[a]				12	92.4
2[b]				24	48.8
3[c]				24	67.6
4[a]				24	99.4
5[a]				24	97.6
6[d]				0.8	95.0
7[a]				24	4.6

[a] Pt nanowires, 1 bar of H_2. [b] Pt nanoparticles, 1 bar of H_2. [c] Pt nanorods, 1 bar of H_2. [d] Pt nanowires, 1 bar of N_2. [e] GC yield.

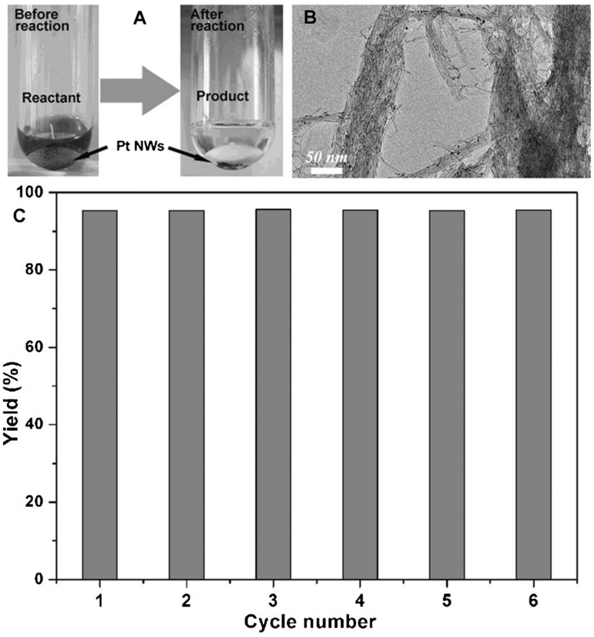
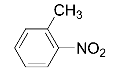
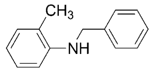
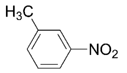
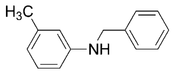
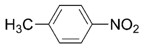
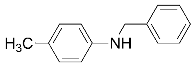
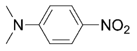
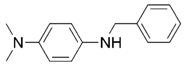
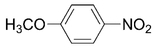
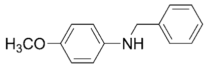
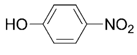
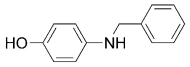
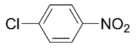
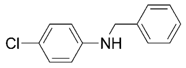
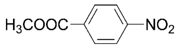
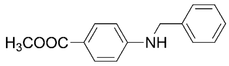
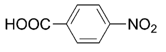
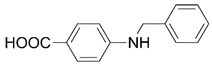


Figure 2. A) Optical images of the nanowire catalysts before and after the reactions; B) TEM image of the Pt nanowire catalysts after 6 reaction cycles; C) stabilities of Pt NW catalysts. Reaction conditions: nitrobenzene (1.1 mmol), benzaldehyde (1.0 mmol), and toluene (2 mL) in H_2 (1 bar) with Pt NW (0.005 mmol). Product yields were determined by GC using *tert*-butylbenzene as an internal standard.

The Pt NW catalysts could be conveniently recycled and reused. As shown in Figure 2 A, Pt NW served as heterogeneous catalysts and could be recovered by simple centrifugation. This recycled catalyst could be directly reused without losing any catalytic activity (Figure 2 C). The Pt NW were relatively stable. Evident morphology changes were not found (Figure 2 B), and Pt leaching was not detected by ICP after six cycles. It is interesting to note that the catalytic activities were highly depended on the morphology of the catalysts. When using Pt nanoparticles (Figure S4, ≈3 nm in diameter), the yields of C−N and C=N products were 48.8 and 3.9 %, respectively (Table 1, entry 2), but when using Pt nanorods (Figure S5, Supporting Information, ≈2 nm in diameter and ≈20 nm in length), the yields of C−N and C=N products were 67.6 and 22.3 % respectively (Table 1, entry 3). Compared to nanoparticles or nanorods, Pt NW show much higher catalytic activity. This was also demonstrated in the nitrobenzene hydrogenation and several other kinds of reactions.[10]

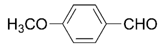
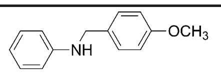
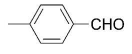
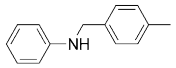
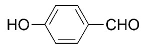
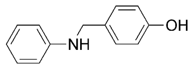
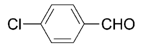
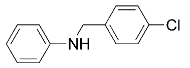
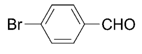
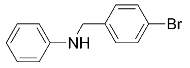
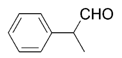
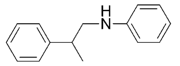
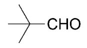
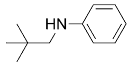
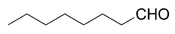
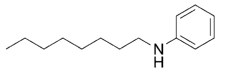
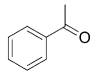
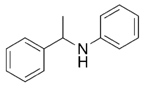
The scope of the reaction was then explored using a number of aromatic nitro and benzaldehyde reactants. As shown in Table 2, various aromatic nitro compounds were coupled with benzaldehyde to form C−N bonds under ambient hydrogen pressure in toluene. High yields from *o*-, *m*-, and *p*-methyl nitrobenzene (Table 2, entries 1–3) showed good regioselectivity, and the yields of the corresponding *N*-alkylamines were higher than 85 %. The functional groups showed little influence on the formation of the C−N coupling products (Table 2, entries 4–9).

Table 2. The Pt NW catalyzed reductive C–N coupling of benzaldehyde with different aromatic nitro compounds and amines under a H_2 (1 bar) atmosphere.[a]

	R–NO_2	Product	*t* [h]	Yield [%][b]
1			22	89.5
2			22	85.0
3			22	92.2 (92)
4			24	75.9
5			24	94.7 (94)
6			24	71.8 (67)
7			22	92.6
8			24	91.4 (87)
9			24	83.9 (79)

[a] Reaction conditions: benzaldehyde (1 mmol), nitro aromatic compound (1.1 mmol), toluene (2 mL), and Pt NW catalyst (0.005 mmol) at 100 °C. [b] GC yield. The values in parentheses are the yields of the isolated products.

Table 3. The Pt NW catalyzed reductive C–N coupling of nitrobenzene with different carbonyl compounds under a H_2 (1 bar) atmosphere.[a]

	$R^1R^2C{=}O$	Product	*t* [h]	Yield [%][b]
1			24	94.9 (94)
2			24	93.1
3			24	89.1
4			24	95.0 (95)
5			24	94.7
6			24	90.8 (90)
7[c]			24	88.3
8			24	71.2 (68)
9			24	76.9 (75)

[a] Reaction conditions: Carbonyl compound (1 mmol), nitrobenzene (1.1 mmol), toluene (2 mL), and Pt NW catalyst (0.005 mmol) at 100 °C. [b] GC yield. [c] 60 °C. The values in parentheses are the yields of the isolated products.

In light of these results, various aldehydes were subjected to the reaction for *N*-alkylamine formation. Both aromatic and aliphatic aldehydes were investigated (Table 3). Irrespective of the electronic nature of the substituent, aromatic aldehydes always reacted smoothly to give the corresponding products in excellent yields (Table 3, entries 1–5). Regardless of whether the aliphatic aldehyde compounds were linear or α-branched, the reactions always gave good yields without any apparent byproducts (Table 3, entries 6–8). Acetophenone, which is known to be an inert reactant,[11] was successfully converted to the C–N product with a yield of 76.9 % (Table 3, entry 9).

The time-dependent conversion plot of the reductive C–N coupling is shown in Figure 3 A. Only trace amounts of *N*-benzylidenebenzenamine, phenylmethanol, and aniline were detected in the reaction by gas chromatograph (GC) analysis. Debenzylation products were not detected when the reaction time was prolonged to 24 h (Figure S6, Supporting Information). ReactIR technology (Figure 3 B) was also employed to monitor the reaction. The intensity of the C–N bond (1329 cm^{-1}) increased, but the intensities of the $-NO_2$ group (1352 cm^{-1}) and the C=O group (1709 cm^{-1}) decreased. Figure 3 C shows the initial conversion speeds (from ReactIR) of the NO_2 and C=O groups, that is 0.02 $mol\,L^{-1}\,min^{-1}$. The C–N bond formation speed was 0.004 $mol\,L^{-1}\,min^{-1}$, which is shown in Figure 3 D.

We conducted a series of experiments to gain information on the reaction mechanism (Table 1, entries 4–7). Under the same reaction conditions (1 bar of H_2, 100 °C, Pt NW as the catalyst), a 99.4 % yield of *N*-benzylbenzenamine was achieved in the reaction between benzaldehyde and aniline, instead of nitrobenzene. We separated this reaction into two steps. First, aniline reacted with benzaldehyde without the catalyst giving *N*-benzylidenebenzenamine in 95 % yield. Second, reduction of *N*-benzylidenebenzenamine occurred to form *N*-benzylbenzenamine in the fresh catalytic system with only 4.6 % yield (1 bar of H_2, 100 °C, 24 h, Pt NW as the catalyst, Figure S7, Supporting Information). This result demonstrated that *N*-benzylbenzenamine was not formed by *N*-benzylidenebenzenamine hydrogenation.

Compared with the previously reported C–N bond formation in the “reductive amination” procedure, the reaction underwent a new pathway in our nanocatalytic system. Based on this result, a proposed mechanism for the direct reductive C–N coupling is given in Scheme 1. Under a hydrogen atmosphere, nitrobenzene (**A**) was first reduced to nitrosobenzene and then to *N*-phenylhydroxylamine (**C**)[12] with the help of the Pt NW catalyst. *N*-Phenylhydroxylamine (**C**) reacts with benzaldehyde (**B**)[13] to give a dihydroxy intermediate, then this dihydroxy intermediate eliminates a water molecule over the Pt nanowire to form phenyl(phenylamino)methanol (**D**) under a hydrogen atmosphere. When hydrogen and Pt were removed, this dihydroxy

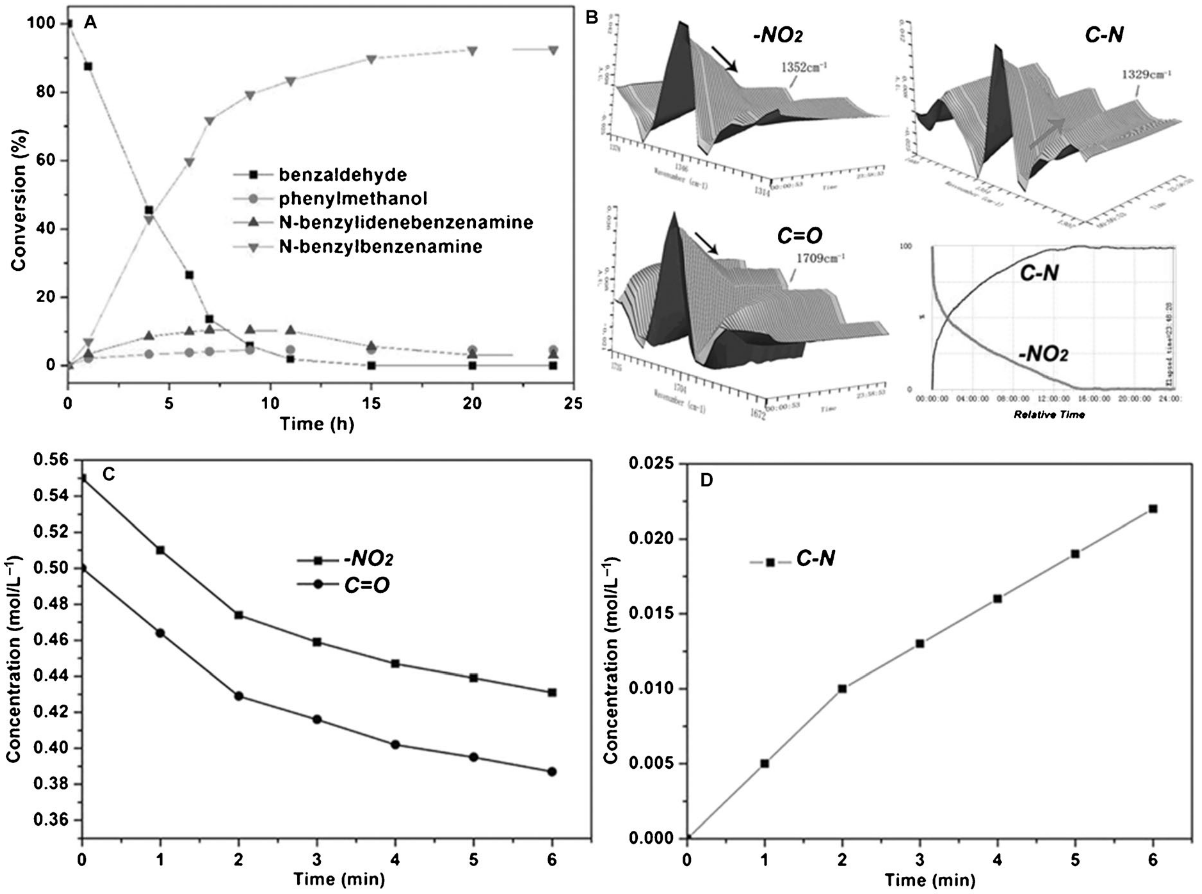
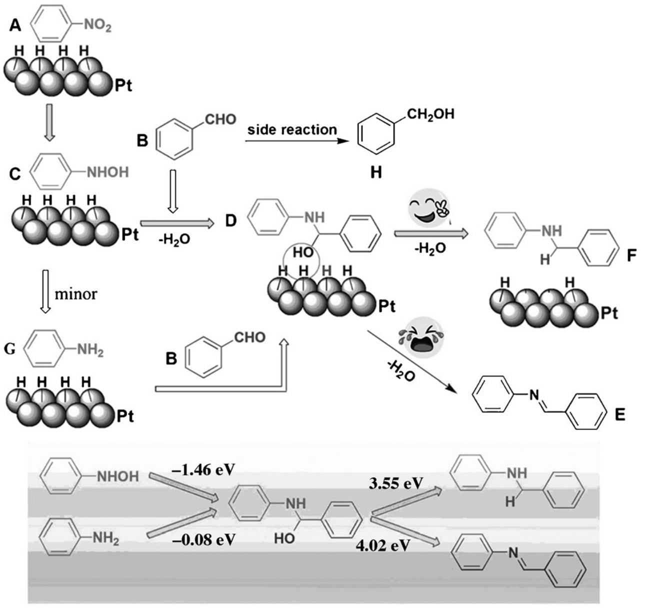


Figure 3. A) GC and B) ReactIR profiles for C−N coupling reactions; the kinetic plots for the reactions of C) $-NO_2$, C=O and D) C−N bonds. Reaction conditions: nitrobenzene (5.5 mmol), benzaldehyde (5 mmol), toluene (10 mL), catalyst (0.025 mmol), and H_2 (1 bar) at 100 °C. Product yields were determined by GC using *tert*-butylbenzene as an internal standard.



Scheme 1. The proposed mechanism for the direct reductive C−N coupling of nitrobenzene and benzaldehyde.

intermediate was intramolecularly dehydrated to obtain *N*-benzylideneaniline and *N*-oxide.[14,13c] *N*-Phenylhydroxylamine (**C**) also can be reduced to aniline (**G**) under these reaction conditions. However, the aniline product (**G**) can also reacted with benzaldehyde (**B**)[15] to give phenyl(phenylamino)methanol (**D**). The phenyl(phenylamino)methanol (**D**) is quickly transformed to *N*-benzylbenzenamine (**F**) through intermolecular dehydration and subsequent H addition on the Pt NW surface under a hydrogen atmosphere.

ReactIR technology was employed to monitor the conversion. By analysis of two bands at 1411 (δ_{OH}) and 1533 cm^{-1} (δ_{NH}), phenyl(phenylamino)methanol (**D**, Scheme 1) was proved to be the intermediate product of the reaction (Figure S8, Supporting Information), and most of the nitrobenzene and benzaldehyde was first converted to phenyl(phenylamino)methanol (**D**). However, trace amounts of *N*-benzylidenebenzenamine (**E**) could also be obtained through intramolecular elimination of water from phenyl(phenylamino)methanol (**D**). These two steps are competitive reactions (from **D** to **F** and from **D** to **E**, Scheme 1).[16] DFT calculations offer a simple explanation for this proposed mechanism. Hydrogen molecules are extremely easier to dissociate to form the active hydrogen species at a low energies (0.7 eV) on the surface of Pt (111). The binding energy of this active hydrogen species to the Pt (111) surface (Pt–H) is about 2.6 eV, which is much lower than the bonding energy of N–H (4.02 eV). While undergoing a dehydration process (the bonding energy of C–OH is 3.55 eV), the **D** to **F** pathway has priority (Scheme 1).

Conclusion

In summary, we have described a new and efficient synthetic methodology for *N*-alkylamine formation from aromatic nitro and carbonyl compounds. Pt NW were used as catalysts and applied in C–N coupling reactions. The reactions were carried out under very mild conditions to generate a diverse range of *N*-alkylamine compounds with remarkably high yields. The new mechanism, in contrast with the traditional reductive amination route, was further supported by ReactIR and GC analyses and DFT calculations. The simple procedure for catalyst preparation, the ease of catalyst recovery and reusability, the high *N*-alkylamine yield, and environmentally friendly chemical processes are of interest to the scientists who work in the areas of synthetic chemistry and material science.

Experimental Section

Synthesis of Pt nanowires: Ultrathin Pt nanowires were achieved by acidic etching FePt nanowires, which were synthesized according to the procedure described by S. H. Sun et al.[17] FePt nanowires (100 g) were first treated by bubbling air at 100 °C in methanol (100 mL), to which HCl (15 mL) solvent mixture was added. The solution was heated and stirred at 60 °C for 1 hour. The resulting precipitate was obtained following 10 min of centrifugation (3000 rpm). The dark solid was washed at least twice with methanol and stored in hexane.

Typical procedure for catalytic C–N bond formation: Catalyst testing was carried out in a sealed tube. Pt nanowires (0.005 mmol) in hexane (0.2 mL) were added and the hexane was evacuated under reduced pressure. Aromatic nitro compounds (1.1 mmol), carbonyls (1 mmol), toluene (2 mL), and 1-*tert*-butylbenzene (0.1 mL) were added to the reaction tube and then sealed. The reaction tube was evacuated and flushed with hydrogen three times. The reaction was conducted at a certain temperature and under a hydrogen atmosphere (Supporting Information). The resulting product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC; equipped with a CP8944 capillary column, 30 m × 0.25 mm, and a FID detector). Some *N*-alkylamine compounds were purified by flash chromatography and characterized by ^{1}H and ^{13}C NMR spectroscopy.

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