



Synthesis of quinoline derivatives from anilines and aldehydes catalyzed by Cp_2ZrCl_2 and recyclable $\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$ system

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ABSTRACT

A facile method for the synthesis of quinoline derivatives using catalytic amount of Cp_2ZrCl_2 or Cp_2ZrCl_2 supported on MCM-41 ($\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$) in reaction of anilines and aldehydes is described. When $\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$ was used as catalyst, the yields of quinolines were enhanced by 5–15% compared with Cp_2ZrCl_2 as catalyst alone under the same reaction conditions. More importantly, $\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$ catalyst can be reused at least thrice by simple recover via filtration in air. Moreover, both Cp_2ZrCl_2 and $\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$ showed good catalytic activities to generate corresponding quinoline derivatives in moderate to good yields by varying the substituent of aniline and aldehyde. And the reaction conditions were optimized by studying the influences of reactant ratio, additives, solvent effect and reaction temperatures.

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1. Introduction

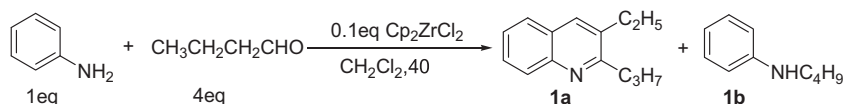
Quinolines have always been received great attention because of their broad chemical and biological activities. Five known methods are used to synthesize substituted quinoline derivatives including the Skraup reaction [1], the Doebner–von Miller reaction [2], the Conrad–Limpach reaction [3], the Friedländer reaction [4] and the Pfitzinger reaction [5]. The Doebner–von Miller reactions which are generally carried out in the presence of strong acid without any oxidants are particularly useful for large-scale synthesis of quinolines using simple substrate (anilines and aldehydes). Matsugi et al. [6] and Baba et al. [7] reported that quinoline could be synthesized in a two-phase solvent system which consists of an organic phase and an aqueous acid phase in order to avoid the tedious isolation procedure. In our previous work, we also found that yields of 2,3-dialkylquinoline derivatives could be efficiently promoted by H_2O_2 in the presence of AlCl_3 at mild conditions without by-product formation [8]. Xi [9] and Ghorai [10] reported synthesis of variously substituted quinolines via transition-metal-free cyclization reaction. However, as all methods have several disadvantages such as special substrate, unfriendly strong acid or base, high temperatures

or harsh conditions, tedious isolated procedure, waste production and no reusability which need to be overcome. Moreover, in terms of catalyst, various precious metals such as palladium, iridium, rhodium, ruthenium, lanthanum, bismuth, indium and gold nanoparticles have been used for the synthesis of quinoline derivatives [11–19]. Many of the catalysts are not fully satisfactory with regard to cost of catalysts, operational simplicity and catalyst stability. Therefore, to avoid these limitations, the exploration of new catalyst with good catalytic activity, reusability, simple work-up and isolated procedure for the synthesis of quinoline derivatives is highly required.

On the other hand, zirconocene dichloride (Cp_2ZrCl_2) catalyzed organic transformation and zirconium-mediated syntheses are widely used in organic chemistry. In the past years, Takahashi et al. [20] have reported 2,3-dihalopyridine such as 2-bromo-3-iodopyridine reacted with zirconacyclopentadienes to give 5,6,7,8-tetrasubstituted quinoline derivatives in good to high yields. In 2005, Wang reported nano-polyethylene fibers were prepared via in situ ethylene extrusion polymerization, with MCM-41 or SBA-15 supported zirconocene dichloride (Cp_2ZrCl_2) catalytic systems [21]. So far the applications of Cp_2ZrCl_2 have focused mainly on stereoselectivity of the reaction or syntheses of zirconium cation compounds and not on the construction of carbon–nitrogen bonds using aniline and aldehyde. Based on the high catalytic activity of Cp_2ZrCl_2 and the lower price than precious metals, we would like to report the synthesis of quinoline

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Scheme 1. Cp_2ZrCl_2 -catalyzed reaction of aniline with *n*-butyraldehyde.

derivatives from aniline and aldehyde using Cp_2ZrCl_2 or Cp_2ZrCl_2 supported on MCM-41 ($\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$) as catalyst in this paper. It is worth noting that the latter catalyst has good catalytic activity, reusability and simple procedure.

2. Experimental

2.1. Materials

Zeolite Y, ZSM-5, H β and MCM-41 were synthesized in our laboratory according to the methods in the literatures [22–25]. Supported Cp_2ZrCl_2 catalysts used in this work were prepared by a conventional impregnation method. Typically, at room temperature, 3.75 mmol (1.095 g) Cp_2ZrCl_2 was dissolved in 20 mL tetrahydrofuran under gentle magnetic stirring. Next, the solution was dropped into 2.5 g MCM-41 and stirred for 24 h. Then the solution was dried in a conventional oven with air circulation at 75 °C for 24 h, after the impregnation pale yellow solids ($\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$) were obtained. THF was purified by distillation under nitrogen from sodium. Other starting materials were obtained from commercial supplies and used without further purification.

2.2. Characterization of the catalyst

Power X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 advance X-ray diffractometer. The texture property was determined by measuring the N_2 isotherm at –196 °C on a Micromeritics ASAP 2020 automated system. Elemental analysis was performed on a Rigaku ZSX 100e X-ray fluorescence (XRF) spectrometer. ^1H and ^{13}C spectra were measured by JEOL JNM-ECA600.

2.3. Synthesis of quinoline derivatives

The first typical reaction was carried out with 1 mmol aniline and 4 mmol *n*-butyraldehyde added to the solution of 0.1 mmol Cp_2ZrCl_2 catalysts dissolved in 8 mL dichloromethane (DCM) in a dry Schlenk tube under nitrogen atmosphere at 40 °C. Dodecane was added as an internal standard. The mixture was stirred at 40 °C until the reaction was completed. The reaction mixture was then quenched with 3 M ammonia solution, and extracted with diethyl ether, then the combined organic layer was washed with water, brine, dried over sodium sulfate and concentrated to get a crude product, which was purified by column chromatography over silica gel using ether/petroleum ether (1/30) as eluent.

The second typical reaction was carried out with aniline (1.5 mmol), *n*-butyraldehyde (6 mmol), and $\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$ (0.1 g) in CH_2Cl_2 (12 mL). The mixture was stirred for 5 h at 40 °C in a dry Schlenk tube under nitrogen atmosphere. After cooling the reaction mixture, the catalyst was separated from the liquid product by filtration. It was concentrated and then purified by column chromatography over silica gel. The reaction was monitored by gas chromatograph to determine the yield of the product.

Catalytic activity was determined by the yield of quinoline derivatives using dodecane as an internal standard. The structures of the products were identified by ^1H , ^{13}C NMR spectra and HRMS. The catalytic reaction was carried out with aniline (3 mmol), *n*-butyraldehyde (12 mmol), and $\text{Cp}_2\text{ZrCl}_2/\text{MCM-41}$ (0.2 g) in CH_2Cl_2 (24 mL). The mixture was stirred for 7 h at 40 °C under nitrogen atmosphere. After cooling the reaction mixture to room

temperature, the catalyst was separated from the liquid product by filtration. The recovered catalyst was washed with DCM, and dried at room temperature overnight under aerobic conditions, and then reused for the next reaction under the same conditions mentioned above.

3. Results and discussion

3.1. Synthesis of quinoline derivatives catalyzed by Cp_2ZrCl_2

When 1.5 mmol aniline reacted with 6 mmol *n*-butyraldehyde in the presence of 0.15 mmol Cp_2ZrCl_2 (0.1 equiv.) under nitrogen atmosphere, 3-ethyl-2-propylquinoline (**1a**) was obtained as a major product in 60% yield (Scheme 1). For the structure of 3-ethyl-2-propylquinoline was determined by NMR spectrum shown in supporting information, no other isomer products could be isolated.

In addition, *N*-butylbenzamine (**1b**) was obtained in 20% yield as a by-product. Considering the influence of temperature and solvents, we investigated this double carbon–nitrogen bond formation under various conditions. The optimal reaction conditions were 40 °C in DCM. Lower yields of **1a** were obtained, when the reaction temperature was decreased to 25 °C or raised to 50 °C. A broad number of solvents were tested for the reaction. Dichloromethane, toluene, acetonitrile, chloroform, dimethyl sulfoxide and 1,2-dichloroethane gave comparable yields of **1a** whereas lower yields were obtained with tetrahydrofuran.

In the further work, the amount of the reactants and the dosage of catalysts were varied. As shown in Table 1, an optimal aniline/aldehyde ratio of 1/4 is obtained. At lower ratios, the aldehyde tends to condense and product isolation becomes difficult. Also, we obtained good results when 0.1 equiv. of Cp_2ZrCl_2 was used. Treatment of 1 equiv. aniline and 4 equiv. *n*-butyraldehyde with 0.1 equiv. of Cp_2ZrCl_2 afford 60% quinoline and 20% *N*-butylaniline (entry 4). It shows essentially same yields compared to 1 equiv. of Cp_2ZrCl_2 as the catalyst (entry 7). This indicated that the overall transformation should be catalytic to Cp_2ZrCl_2 . The reactions were also checked by using 0.05 equiv. catalyst, the yield of quinoline was 55% (entry 6), but the reaction time of 0.05 equiv. case was 32 h, as a result, 0.1 equiv. Cp_2ZrCl_2 was the best as the catalytic amount. In this reaction, firstly, the nucleophilic addition reaction of aniline with aldehyde occurs to give imine after elimination of

Table 1
 Cp_2ZrCl_2 catalyzed of aniline with *n*-butyraldehyde.^a

Entry	Aniline: <i>n</i> -butyraldehyde: Cp_2ZrCl_2	Conditions	Yield [%] ^b	
			Quinoline	<i>N</i> -Butylbenzamine
1	1:1:0.1	40 °C, 1 h	21	Trace
2	1:2:0.1	40 °C, 18 h	53	14
3	1:3:0.1	40 °C, 7 h	47	20
4	1:4:0.1	40 °C, 5 h	60	20
5	1:5:0.1	40 °C, 8 h	59	27
6	1:4:0.05	40 °C, 32 h	55	19
7	1:4:1	40 °C, 4 h	63	37

^a 12 mL DCM was used as solvent.

^b The yields are relative to aniline and were determined by gas chromatography with dodecane as an internal standard.

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