Electronic Supplementary Information

Heterogeneous catalytic synthesis of quinoline compounds from aniline and C1-C4 alcohols over zeolite-based catalysts

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1. GC-MS characterization of products mixture

Fig. 1S GC chromatogram and total ions current (TIC) diagram of the products mixture for the reaction of aniline and *n*-propanol over the $ZnCl_2$/Ni-USY-Acid catalyst, and Fig. 2S displays the corresponding mass spectra. There are mainly four peaks, as marked by ***a***, ***b, c*** and ***d***, in both the GC-MS chromatogram (Fig. 1S-A) and TIC diagram (Fig. 1S-B). The peaks ***a***, ***b, c*** and ***d*** are identified by MS spectra (Fig. 2S) to be 2-ethyl-3-methylquinoline, 2,3-dimethylquinoline, N-propylquinoline and aniline, respectively, of which the spectra are well matched with the corresponding standard spectra.

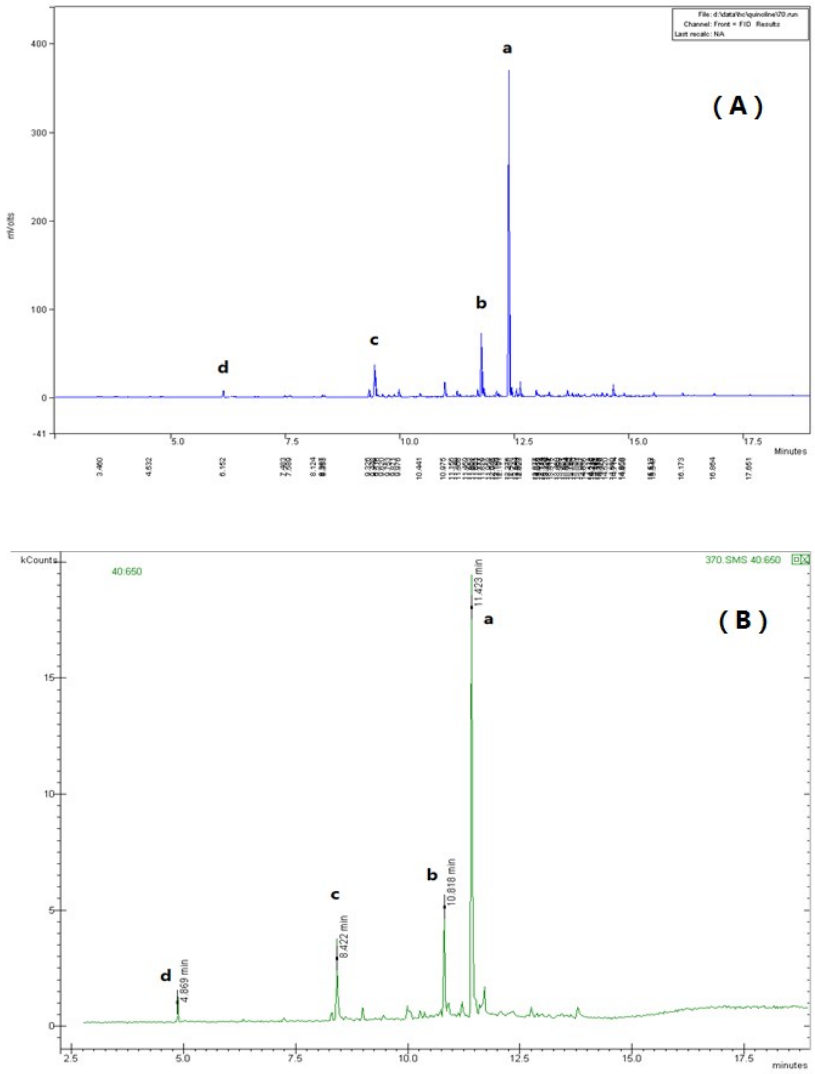

Fig. 1S. GC chromatogram (A) and total ions current (TIC) diagram (B) of the products mixture for the reaction of aniline and *n*-propanol over the $ZnCl_2$/Ni-USY-

Acid catalyst. The reaction conditions: $ZnCl_2$ loading = 10 Wt.%, Ni loading = 4 Wt.%; LHSV (aniline) =0.4 h^{-1}; molar ratio of propanol/aniline = 3; reaction temperature =410 ^oC; carrier gas = H_2.

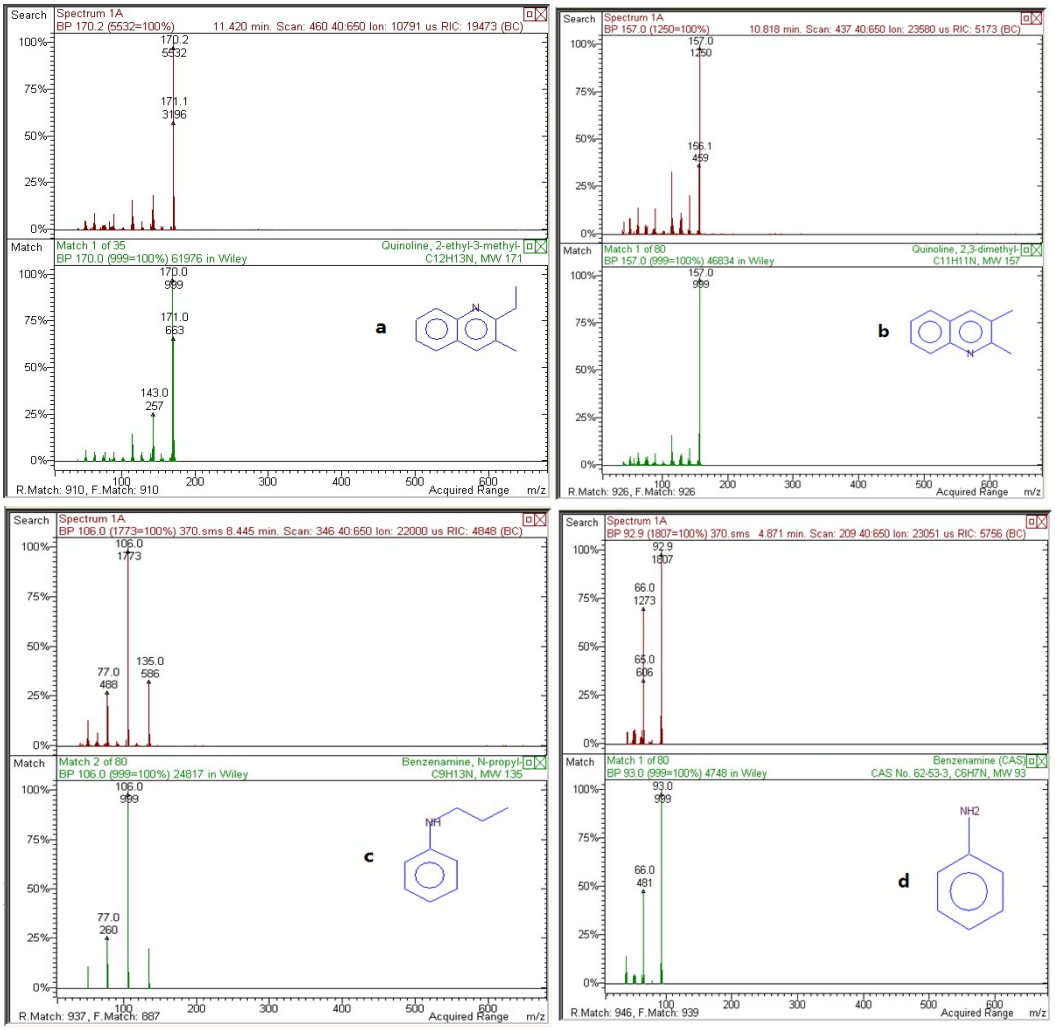

Fig. 2S. Recorded (upper) and matched (lower) mass spectra for the peaks marked in Fig. 1S.

2. Separation and purification of products mixture

The products mixture for the reaction of aniline and *n*-propanol over the $ZnCl_2$/Ni-USY-Acid catalyst, under the conditions of LHSV (aniline) =0.4 h^{-1}, molar ratio of propanol/aniline = 3, reaction temperature =410 ^oC and carrier gas = H_2, was first distilled at 270 - 273 ^oC by batch fractionating process (reflux ratio = 8, steam flow = 30 kg/h) with electric heating fractionating system. The resultant distillate was collected and recrystallized from 60% HCl solution for

refining. Then, the received product was treated by molecular sieve absorption process (4A zeolite) for dehydration. The thus-purified product was employed in the NMR characterization.

3. NMR characterization of purified product

The above-purified product was analyzed by both ^{1}H NMR and ^{13}C NMR spectroscopies over a Bruker DRX 600 MHz NMR spectrometer. The ^{1}H NMR spectrum was recorded in 1mL of $CDCl_3$, under the conditions as follows: ^{1}H signal was observed at 400 MHz, relaxation time was 5.0 s and integral process was repeated for 5 times. In the quantitative analysis by ^{1}H NMR, ammonium formate was added as external standard material (δ = 8.44). The ^{13}C NMR spectrum was recorded in 1mL $CDCl_3$, under the operation conditions as follows: ^{13}C signal was observed at 100 MHz, relaxation time was 6.0 s and integral process was repeated for 5 times. The ^{13}C NMR spectrum was processed by applying an exponential line broadening of 1.0 Hz for sensitivity enhancement before Fourier transforms and was accurately phased and baseline adjusted.

Fig. 3S and Fig. 4 S show respectively the ^{1}H NMR and ^{13}C NMR spectra of the purified product, which are both consistent with 2-ethyl-3methylquinoline. The ^{1}H NMR spectrum is also employed in the quantitative analysis of the purity (content) of 2-ethyl-3methylquinoline. The H in CH_2 group is selected as a target signal in the ^{1}H NMR spectrum, since its only presence for 2-ethyl-3-methylquinoline but not for other quinolines formed in the reaction of aniline and propanol. The purity of 2-ethyl-3-methylquinoline can be calculate by the equation shown as follows:

$$Purity_{2-ethyl-3-methylquinoline} = \frac{A_x/n_x}{A_s/n_s} \times \frac{m_s}{M_s} \times M_x \times V \times 100\%$$

, where n_x and n_s refer to the proton numbers of the selected signal for the product and external standard material, respectively; m_s and M_s denote the quality (1.5×10^{-3} g) and molar mass (63.06 g/mol) of external standard material, and Mx and V represent the product molar mass (171.24 g/mol) and volume (5×10^{-4} L), respectively. The

calculation indicates that the purified 2-ethyl-3-methylquinoline possesses a purity of 98.6 %.

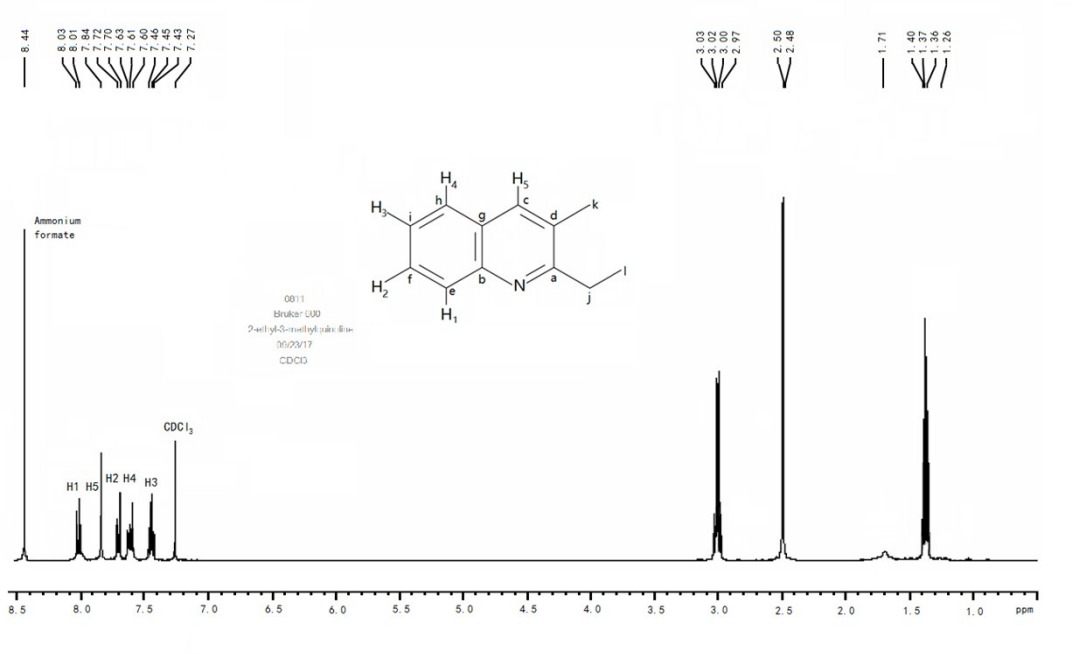

Fig. 3S. [1]H NMR of the purified 2-ethyl-3methylquinoline.

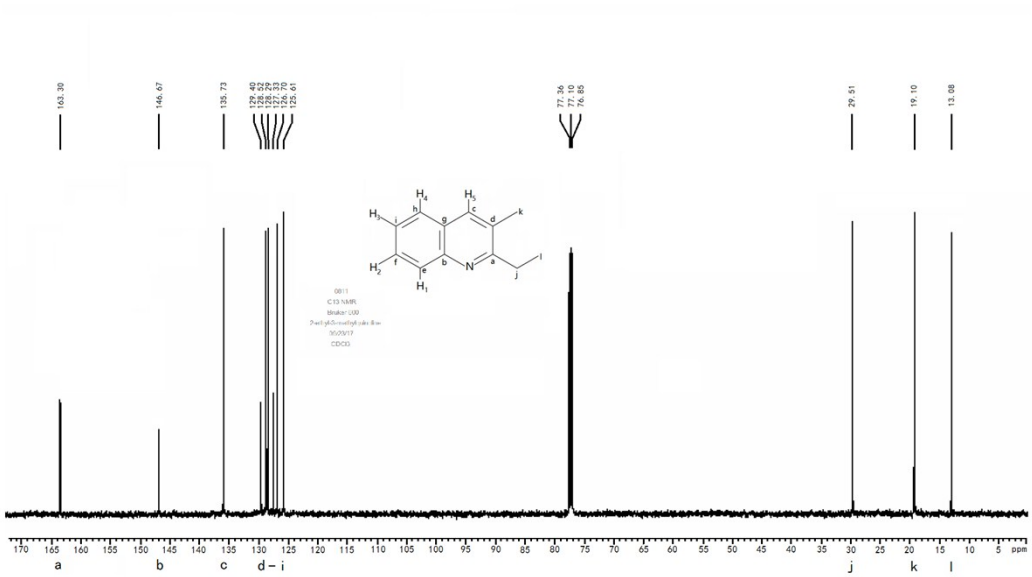

Fig. 4S. [13]C NMR of the purified 2-ethyl-3methylquinoline.