

Supporting Information

Rhodium(III)-Catalyzed C(sp³)-H bond Aminocarbonylation with Isocyanates

Huaiqing Zhao,^{*,†} Xi Zhou,[†] Bo Li,[†] Xiufen Liu,[†] Ningxin Guo,[†]
Zhengliang Lu,[†] Shoufeng Wang[‡]

[†]Key Laboratory of Interfacial Reaction & Sensing Analysis in
Universities of Shandong, School of Chemistry and Chemical
Engineering, University of Jinan, Jinan, Shandong, 250022, P. R. China

[‡]Shandong Provincial Key Laboratory of Fluorine Chemistry and
Chemical Materials, School of Chemistry and Chemical Engineering,
University of Jinan, Jinan 250022, P. R. China

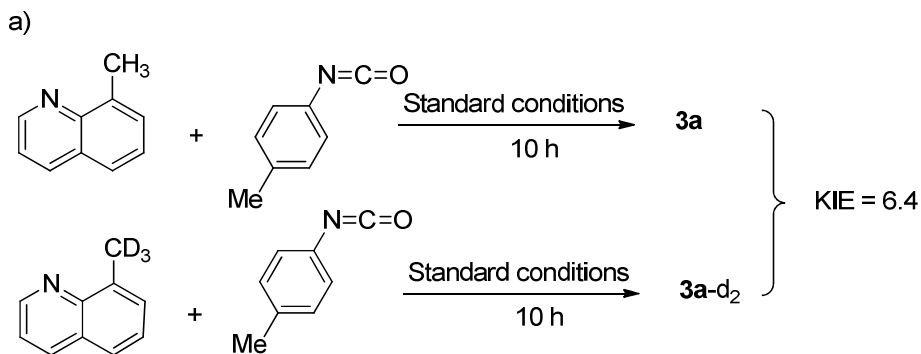
E-mail: chm_zhaohq@ujn.edu.cn

Contents	Page Number
1. Experimental Procedures of Mechanistic Studies	S2
2. ¹ H and ¹³ C NMR spectra.....	S5

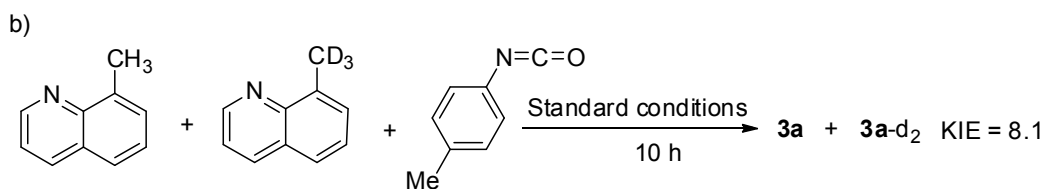
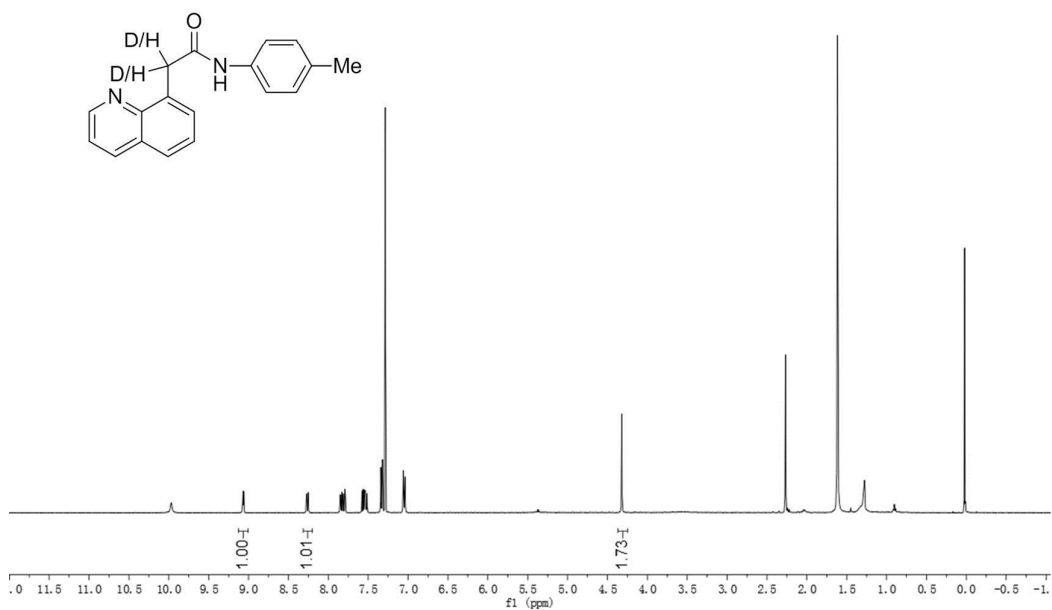
Experimental Procedures of Mechanistic Studies

1. Deuteration experiments (Scheme 2a and 2b)

a. Parallel reactions.

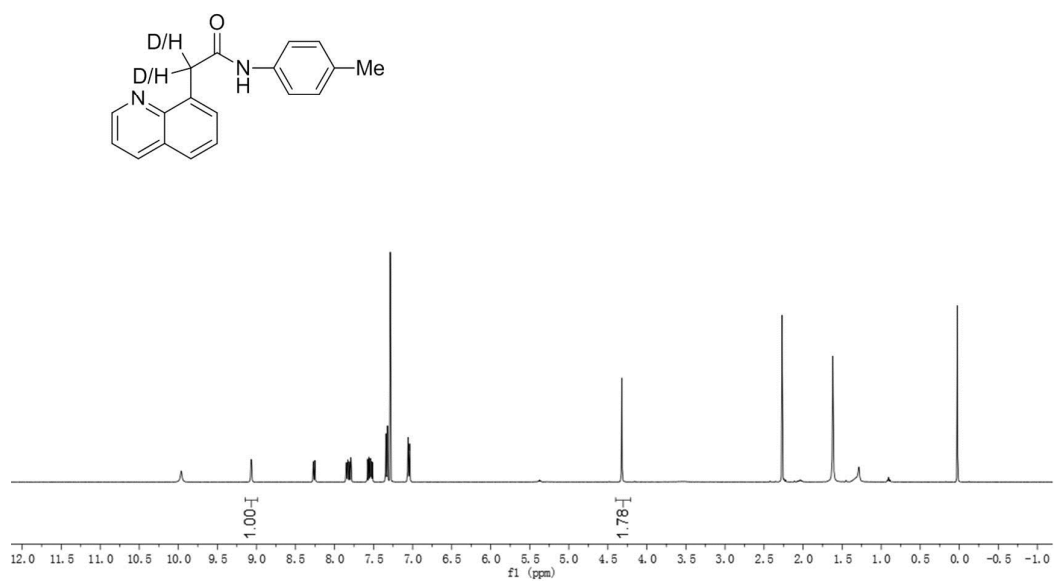


In a glove box, two 25 mL Schlenk tubes equipped with stir bars were charged with [Cp*RhCl₂]₂ (3.1 mg, 5 mol %), AgSbF₆ (6.9mg, 20 mol %), p-tolylisocyanate (0.2 mmol), respectively. The tube was separately fitted with a rubber septum, and removed out from the glove box. Then 8-methylquinoline (0.1 mmol) and 8-methylquinoline-d₃ (0.1 mmol) were separately added through the rubber septum using syringe under the atmosphere of N₂. 1,2-Dichloroethane (2 mL) was added to the Schlenk tube though the rubber septum using syringes. The septum was replaced by a Teflon screwcap under N₂ flow. The reaction mixture was stirred at 60 °C (pre-heated to 60 °C) for 10 h. After cooling down, the reaction mixture of the two parallel tubes was mixed together. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel (eluent: EtOAc/PE) to provide the corresponding products (**3a** and **3a-d₂**), and then analyzed by NMR.



In a glove box, a 25 mL Schlenk tube equipped with a stir bar was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (6.2 mg, 5 mol %), AgSbF_6 (13.8 mg, 20 mol %), p-tolylisocyanate (0.4 mmol). The tube was separately fitted with a rubber septum, and removed out from the glove box. Then 8-methylquinoline (0.1 mmol) and 8-methylquinoline-d₃ (0.1 mmol) were separately added through the rubber septum using syringe under the atmosphere of N_2 . 1,2-Dichloroethane (2 mL) was added to the Schlenk tube though the rubber septum using syringes. The septum was replaced by a Teflon screwcap under N_2 flow. The reaction mixture was stirred at 60 °C (pre-heated to 60 °C) for 10 h. After cooling down, the solvent was

removed in vacuo and the residue was purified by chromatography on silica gel (eluent: EtOAc/PE) to provide the corresponding products (**3a** and **3a-d2**), and then analyzed by NMR.



¹H and ¹³C NMR spectra

