

Supporting Information

Efficient Dehydrogenation of Amines and Carbonyl Compounds Catalyzed by a Tetranuclear Ruthenium- μ -Oxo- μ -Hydroxo-Hydride Complex

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et₂O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic substrates were received from commercial sources and used without further purification. The ¹H, ²H, ¹³C and ³¹P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer. Mass spectra were recorded from a Agilent 6850 GC/MS spectrometer. The TON of the products was measured from a Hewlett-Packard HP 6890 GC spectrometer.

Representative Procedure of the Catalytic Reaction. In a N₂ filled glove box, complex **1** (5 mg, 2.9 μmol) was charged with indoline (0.71 g, 6.0 mol) and TBE (0.53 g, 6.0 mol; contained 5% TBA) in a 10 mol Schlenk tube equipped with a Teflon stopcock and a stirring bar. The tube was closed and was brought out of the box. The reaction tube was fully immersed into a silicone oil bath, which was preset at 200 °C, and the reaction mixture was stirred for 1 h. The tube was cooled to room temperature, and was open to air. The crude product mixture was analyzed by GC and GC/MS. Analytically pure organic product **2a** was isolated after a simple column chromatography on silica gel (Et₂O/hexane).

For **Phosphate Inhibition Experiments:** PCy₃ (2-10 mg) was added to the reaction tube containing the same amount of substrates, and the reaction mixture was analyzed after 20 min of heating at 200 °C.

Deuterium Labeling Study. Indoline-N-*d*₁ (72 mg, 0.60 mol) and indoline-α-*d*₂ (73 mg, 0.60 mol) were added to a separate J-Young NMR tube containing TBE (53 mg, 0.60 mol) and **1** (1 mg, 0.60 μmol), and the mixture was dissolved in toluene (0.3 mol). The reaction tubes were brought out of the box, and were immersed in a silicone oil bath set at 200 °C. The deuterium content of the products was measured by both ¹H NMR (toluene-*d*₈) and ²H NMR (toluene). The distribution of deuterium measured from the reaction of indoline-N-*d*₁ with TBE in toluene after

18 h: Ar (15%), N-D (20%), C_α (17%) and C_β (29%) of indole; methyl (12%) and methylene (7%) of *t*-butylethane. From the reaction of indoline- α -*d*₂ with TBE in toluene after 18 h: Ar (6%), N-D (12%), C_α (40%) and C_β (18%) of indole; methyl (15%) and methylene (9%) of *t*-butylethane.

Preparation of Labeled Indoline Compounds. Indoline-N-*d*₁ was prepared by following a reported procedure.¹ In a 25 mL Schlenk tube, indoline (5.0 g, 42 mmol) was added to a NaOD (40 wt% in D₂O, 1.0 g, 10 mmol) solution in D₂O (5 mL), and the reaction mixture was stirred at 110 °C for 16 h. The tube was cooled to room temperature, and 20 mL of CH₂Cl₂ was added to reaction tube. Organic layer was separated from the aqueous layer, and the solution was washed two times with brine solution. The extracted solution was dried in anhydrous MgSO₄, and was concentrated under vacuum. The product was isolated after distillation under high vacuum (4.7 g, 94% yield; 93% deuterium as determined by both ¹H and ²H NMR).

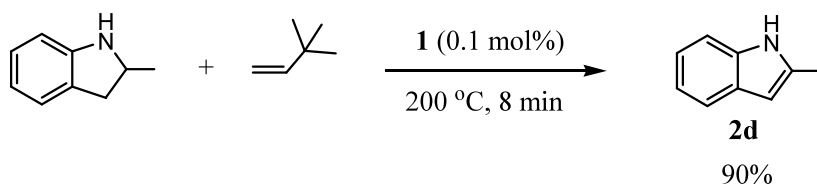
N-Nitrosoindoline- α -*d*₂ was prepared by following a reported procedure.¹ In a 25 mL Schlenk tube containing NaOD (40 wt% in D₂O, 1.0 g, 10 mmol) in D₂O (5 mL), was added N-nitrosoindoline (3.0 g, 20 mmol),² and the reaction mixture was stirred at 110 °C for 16 h. The tube was cooled to room temperature, and 20 mL of CH₂Cl₂ was added to the reaction tube. Organic layer was separated from aqueous layer, and the solution was washed two times with brine solution. The solution was dried in anhydrous MgSO₄, and was concentrated under vacuum. The product (2.7 g, 90% yield), which was isolated after recrystallization in CH₂Cl₂ and hexanes, was found to contain 94% of deuterium as determined by both ¹H and ²H NMR.

Indoline- α -*d*₂ was prepared by a modified reported method.¹ In a 100 mL Schlenk flask, N-nitrosoindoline- α -*d*₂ (2.7 g, 18 mmol) was added slowly to a diluted 6 N HCl (10.5 g, 54 mmol) in water solution (30 mL). After refluxing the reaction mixture for 3 h, the reaction flask was cooled to room temperature. The black precipitate was filtered through a fritted funnel, and

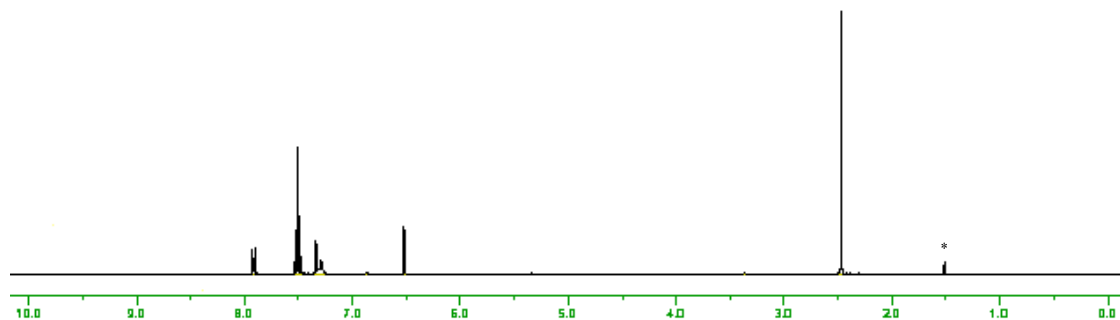
was washed 3 times with water. Saturated aqueous NaHCO_3 solution was slowly added to neutralize the solution. Ethyl ether (100 mL) was added to the reaction mixture, was extracted from the aqueous solution, and the ether solution was washed two times with brine solution. The solution was dried in anhydrous MgSO_4 , and was concentrated under vacuum. The product was isolated after distillation under high vacuum (1.0 g, 46% yield; 94% deuterium as determined by both ^1H and ^2H NMR).

- (1) Lautie, M. F. *J. of Labeled Compounds and Radiopharmaceuticals* **1979**, *16*, 735-744.
- (2) Ohwada, T.; Miura, M.; Tanaka, H.; Sakamoto, S.; Yamaguchi, K.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **2001**, *123*, 10164-10172.

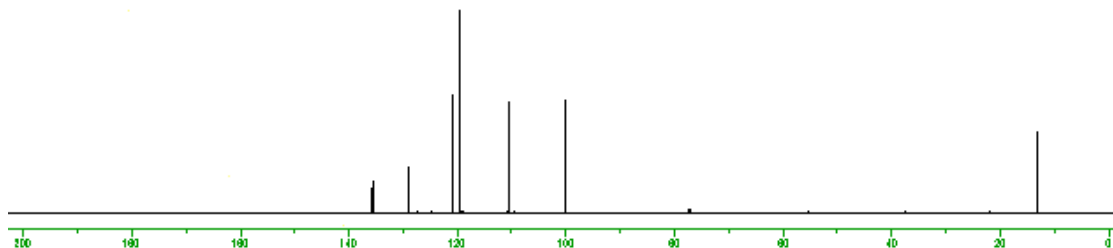
The ^1H and ^{13}C NMR Spectra of Selected Crude Product Mixture



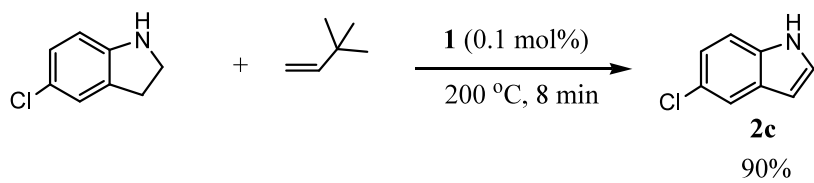
^1H NMR (CDCl_3 , 400 MHz)



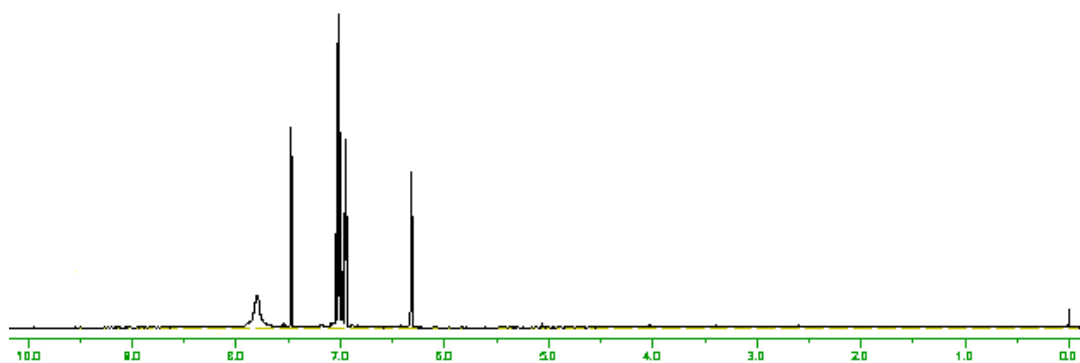
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



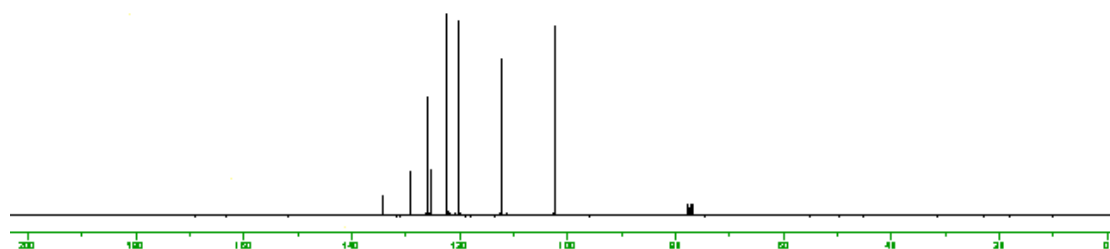
* denotes starting material.

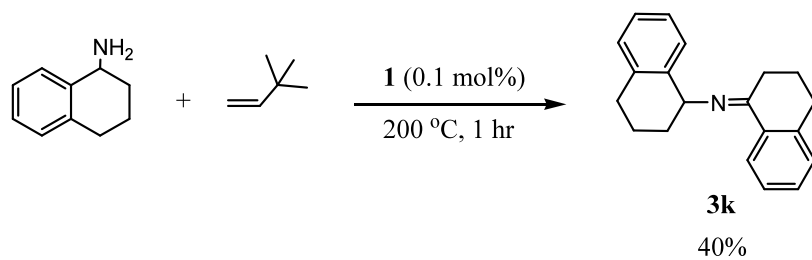


^1H NMR (CDCl_3 , 400 MHz)

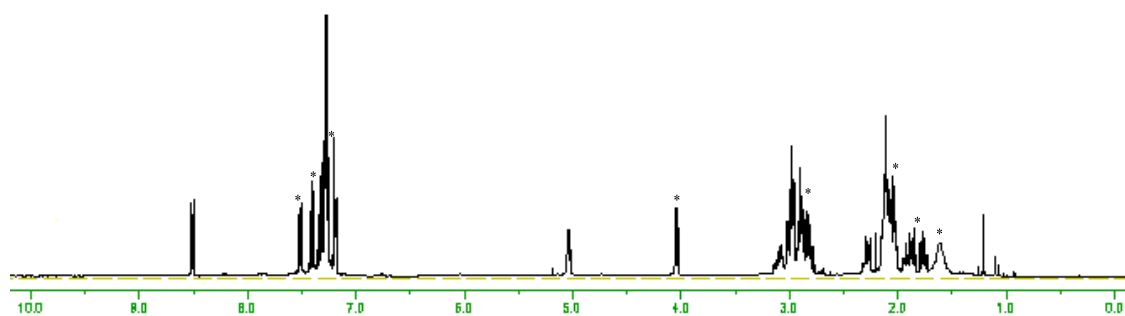


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

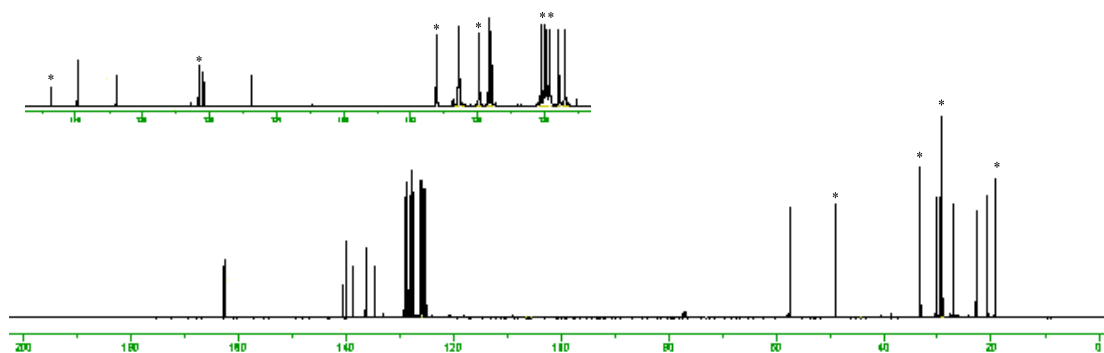




^1H NMR (CDCl_3 , 400 MHz)

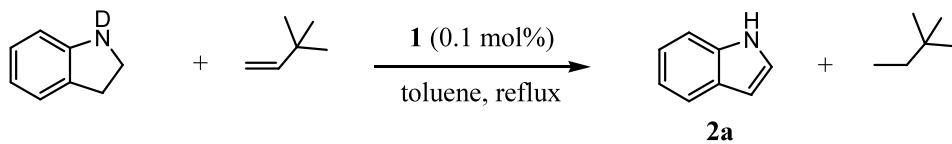


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

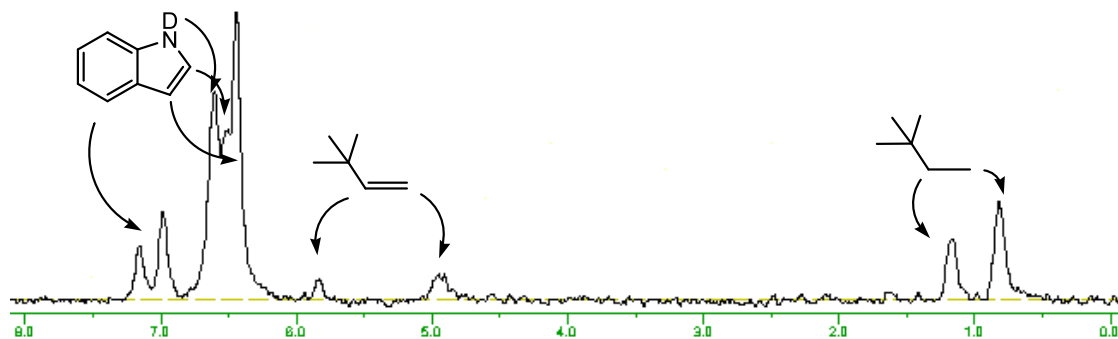


* denotes starting material.

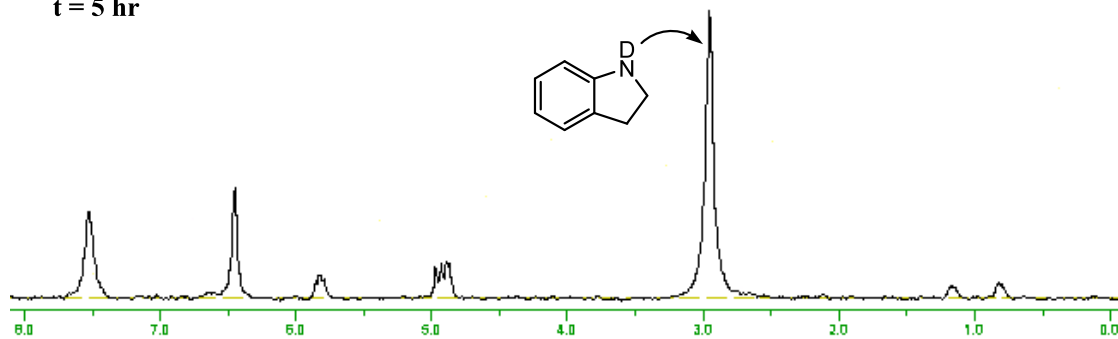
^2H NMR (61.36 MHz) spectra in toluene



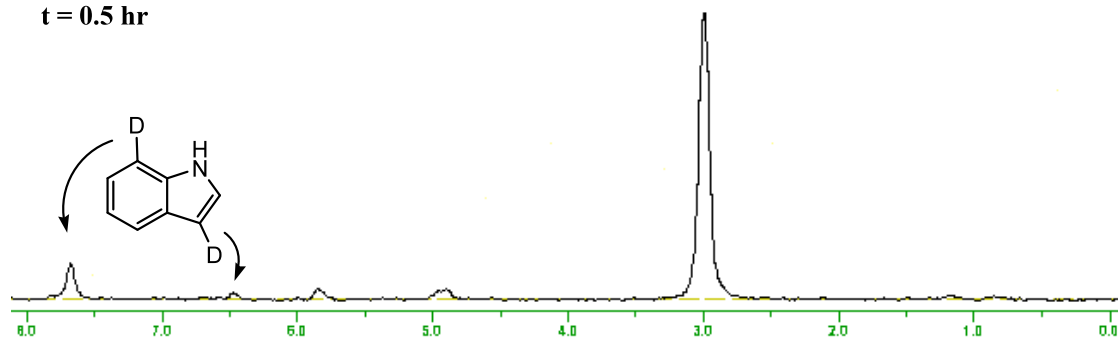
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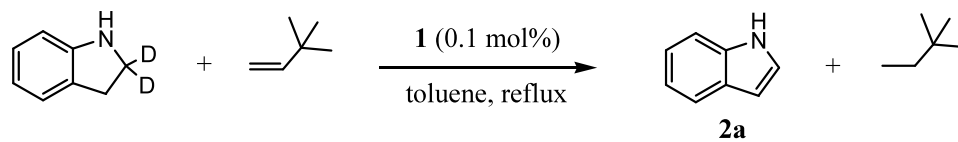
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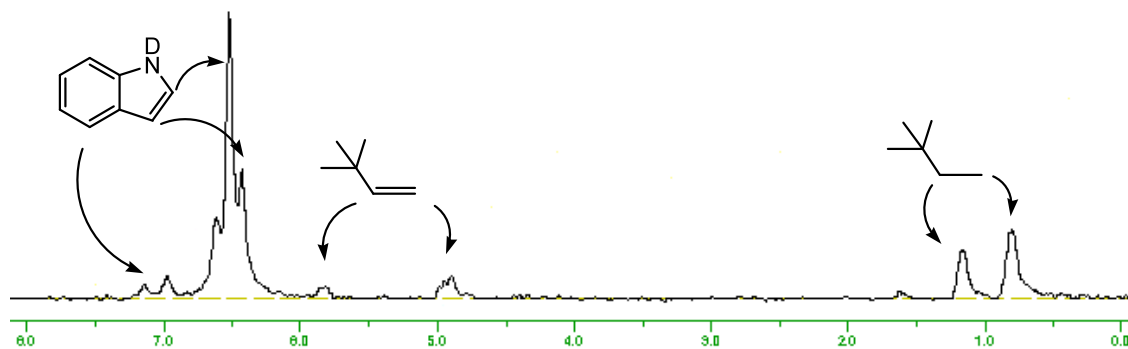
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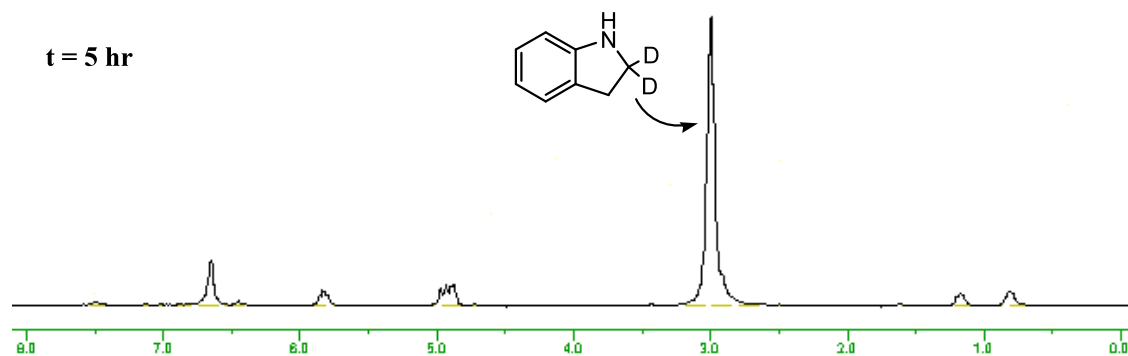
^2H NMR (61.36 MHz) spectra in toluene



$t = 18 \text{ hr}$



$t = 5 \text{ hr}$



$t = 0.5 \text{ hr}$

