Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Ni(II)-N′NN′ Pincer Complexes Catalyzed Dehydrogenation of Primary Alcohols to Carboxylic acids and H_2 Accompanied by the Alcohol Etherification

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Supporting Information

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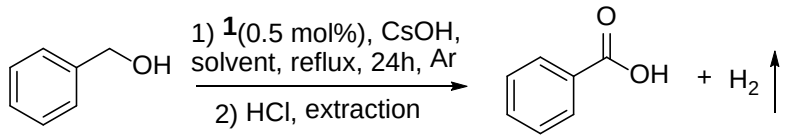
Solvent screening for acceptorless dehydrogenation of benzyl alcohol to benzoic acid catalyzed by complex 1

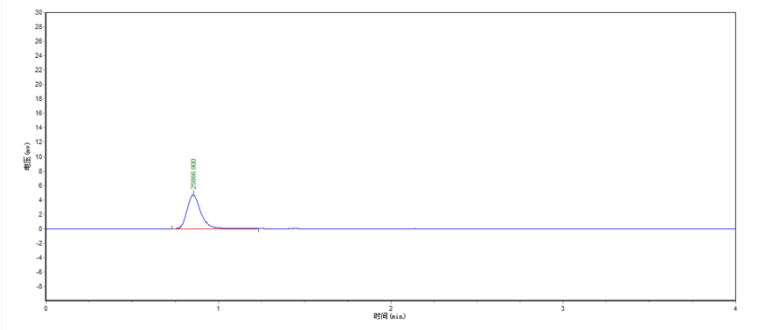
To an oven-dried 25mL schlenk tube, benzyl alcohol (0.54 g, 5 mmol), $CsOH·H_2O$ (5 mmol, 0.84 g) and complex **1** (25 μmol, 11.0 mg) were charged with 1 mL solvent, and the solution was heated at 150°C (oil bath) under argon atmosphere for 24 h. After cooling to room temperature, degassed water (5 mL) was added and the mixture was extracted with diethyl ether (3 × 5 mL). The aqueous phase was acidified with 6M HCl and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate solution were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure, the white solid of the pure benzoic acid was obtained and weighted for calculating the yield. Yield=n(benzoic acid)/n(CsOH).



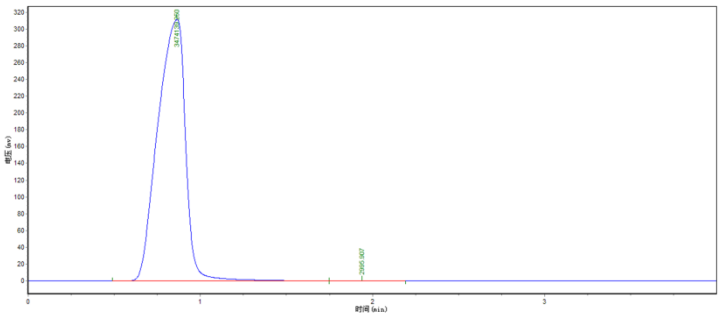
Entry	Solvent	Yield (%)
1	Toluene	6
2	1,4-dioxane	5
3	H_2O	Trace
4	Benzyl alcohol	10

The H_2 detection and production

Under an argon atmosphere, benzyl alcohol (2.16 g, 20 mmol), sodium benzyloxide (5 mmol, 0.65 g) and complex **3** (19.0 mg, 50 μmol) were added to a 25 mL schlenk tube which is connected to a 1000 mL distillation collection ball with one neck sealed by a rubber septum. Then the reaction mixture was heated at 150°C (oil bath). The inner gas was taken out by a 100 μL micro-injector after 6 h, and sent to GC for analysis, hydrogen gas was determined by comparing to the standard sample.



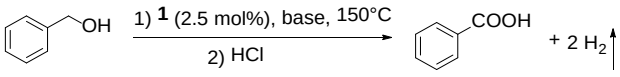
GC spectrum of the produced gas



GC spectrum of standard hydrogen gas

The H_2 gas collection

Under an argon atmosphere, benzyl alcohol (10.8 g, 100 mmol, excess), sodium benzyloxide (1.30 g,10 mmol), and complex **1** (0.11 g, 0.25 mmol, 2.5 mol%) were added to a 100 mL schlenk tube which is connected with a gas collection instrument through gravity drainage method. The reaction mixture was heated at 150°C (oil bath) and the volume of produced gas was recorded in the due time. A blank experiment without catalyst was taken at the same condition.The standard atmospheric pressure P=101.325 kPa; room temperature T=291.15K; the corresponding water saturated vapor pressure under the temperature P_0=2.0644 kPa. The amount of H_2 was calculated by Van der Waals equation: $(P-P_0)V=nRT$ ($R=8.314\ kPa\cdot L\cdot mol^{-1}\cdot K^{-1}$).



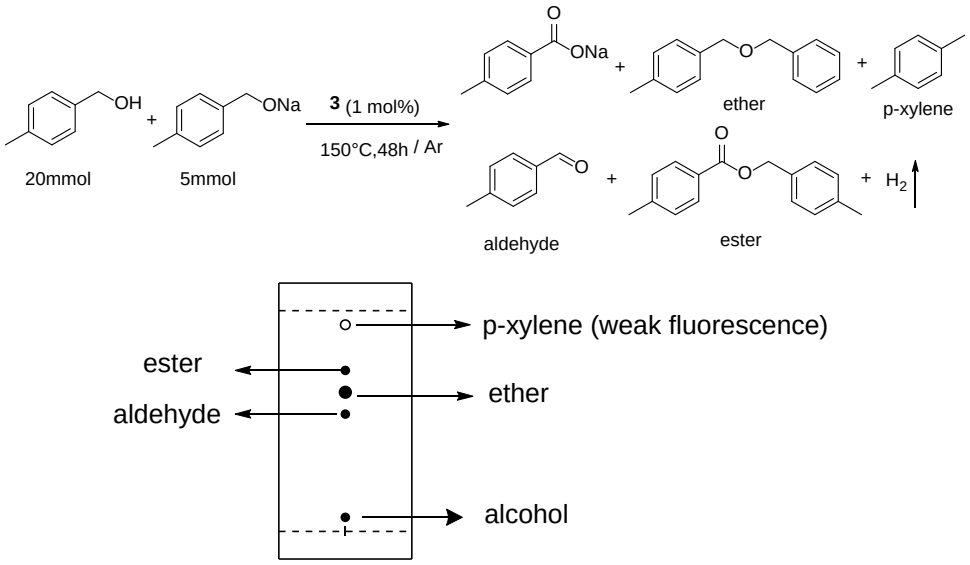
time (h)	V (H_2) (mL)	n(H_2) (mmol)
2	27	1.11
3	42	1.72

4	70	2.87
5	94	3.86
6	98	4.02
7	105	4.31
8	105	4.31
9	111	4.55

After the H_2 collection experiment, the reaction mixture was treated with extraction operation, which afforded 0.24 g pure benzoic acid (1.96 mmol). $n(H_2)/n(\text{benzoic acid}) \approx 2:1$.

Analysis of products in organic phase using 4-methylbenzyl alcohol as the substrate

4-Methylbenzyl alcohol (2.44 g, 20 mmol), sodium 4-methylbenzyloxide (0.72 g, 5.0 mmol) and complex **3** (19.0 mg, 50 μmol) were charged in a 25 mL schlenk tube, and the reaction mixture was heated at 150°C for 48 h under the argon atmosphere. After cooling to room temperature, degassed water (10 mL) was added and the mixture was extracted with diethyl ether (3 ×10 mL). The aqueous phase was acidified with 6M HCl and extracted with ethyl acetate (5 × 20 mL). The combined ethyl acetate solution were washed with brine (25 mL), dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure, in which the pure 4-methylbenzoic acid (0.47g, 69%) was obtained. The products in organic phase were separated by column chromatography using silica gel (elute: petroleum ether/ethyl acetate 40/1 (V/V)). The products were characterized by NMR analysis (relaxation time d1=20 s) with standard samples and weighted for calculating the yields.

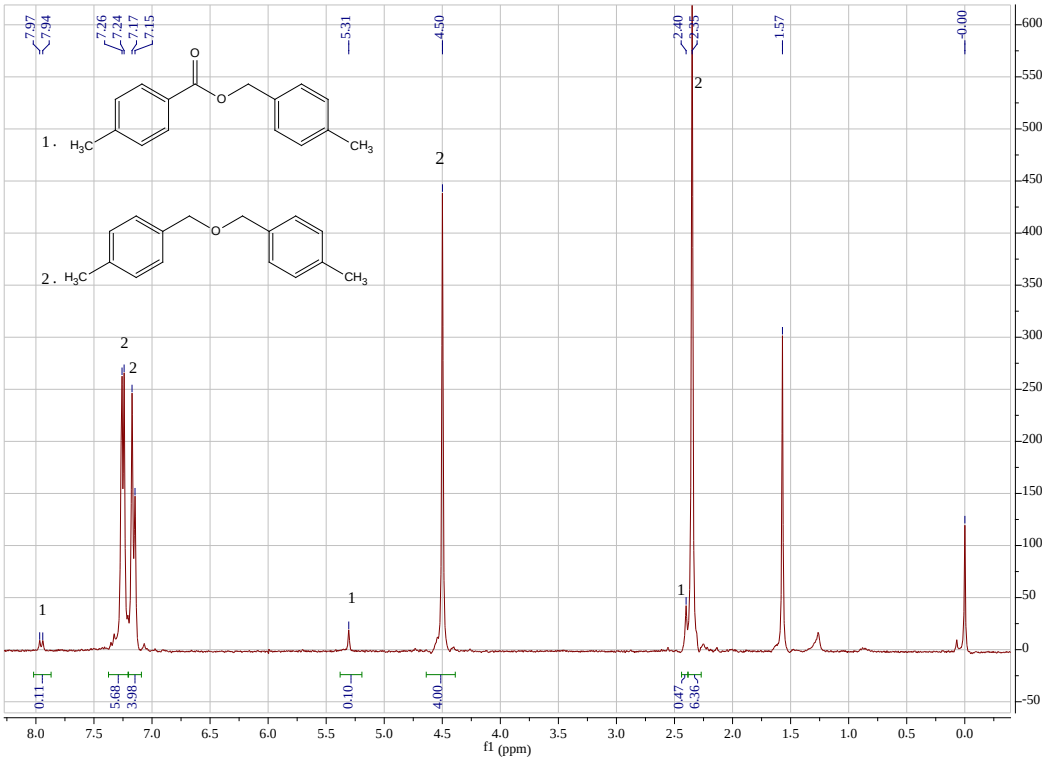


TLC analysis of products in organic phase

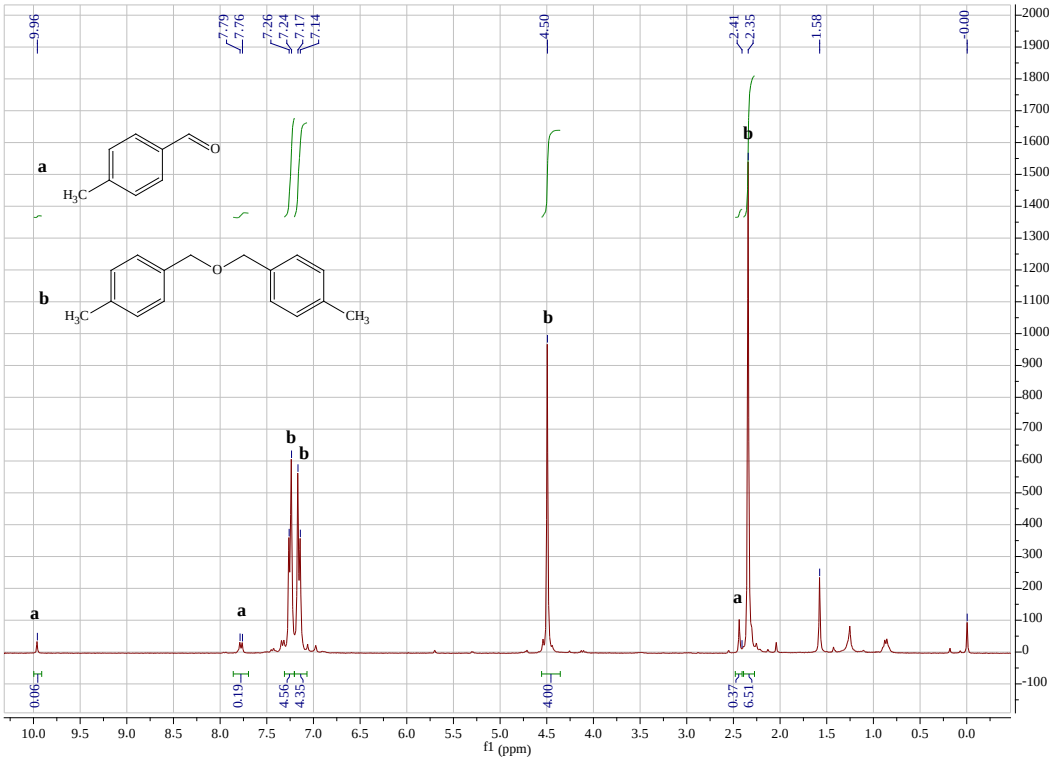
P-xylene was obtained as a colorless oil weighted 0.11 g (1.03 mmol);

Ester, ether, aldehyde were collected as mixtures.

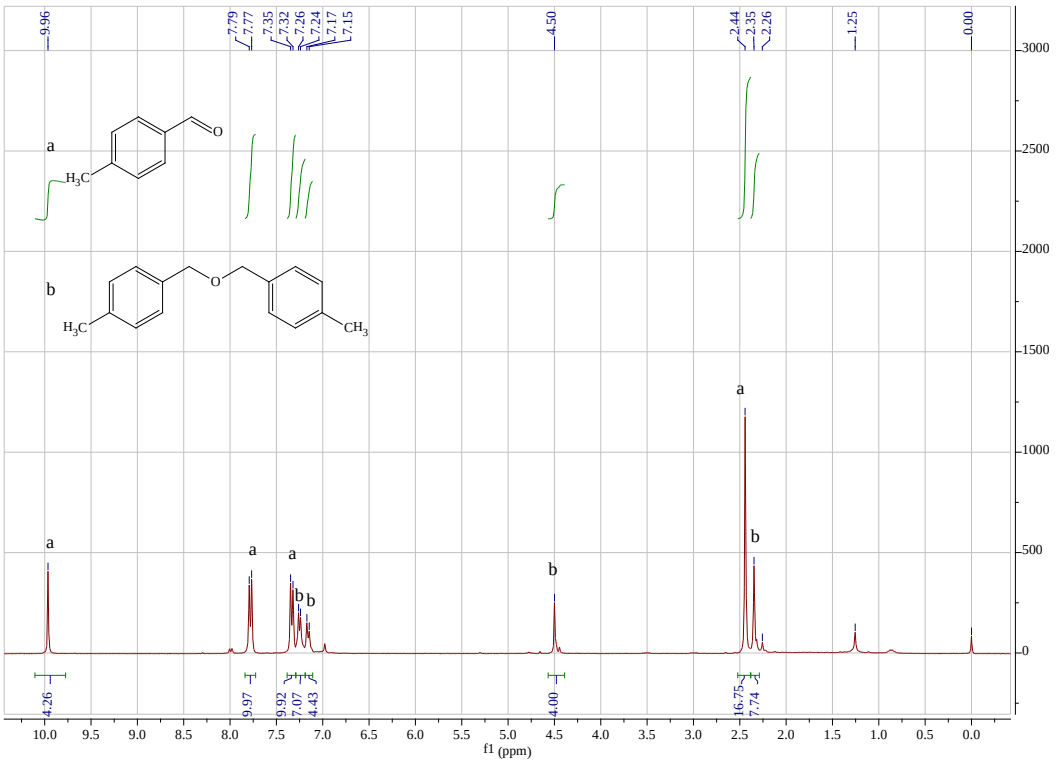
1) Mixture of ether and trace amount of ester, weighted 0.09 g (deuterated solvent: $CDCl_3$);



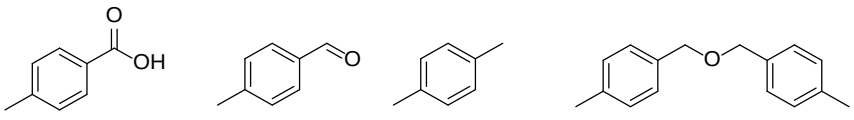
2) Mixture of ether and aldehyde, weighted 0.37 g (deuterated solvent: $CDCl_3$);



3) Mixture of ether and aldehyde, weighted 0.16 g (deuterated solvent: $CDCl_3$).



The amounts of products were listed below according to the calculation:



3.45 mmol 1.10 mmol 1.03 mmol 2.15 mmol