

## Supporting Information

### Simple and Effective Catalytic Reaction for the Selective Deuteration of Alcohols

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## General Specifications

All experiments with metal complexes, except for the experiments specified as being carried out under air, were carried out under an atmosphere of purified nitrogen in J. Young NMR tubes that were charged in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier. Deuterated solvents used in the study: CDCl<sub>3</sub> and D<sub>2</sub>O were used as received from Cambridge Isotope Laboratories. The complexes bipyP-RuH(CI)(CO) (**1**) and bipyP\*-RuH(CO) (**2**) were prepared according to literature procedures.<sup>1</sup> Complex **3** could be generated by dissolving **2** in D<sub>2</sub>O or H<sub>2</sub>O.

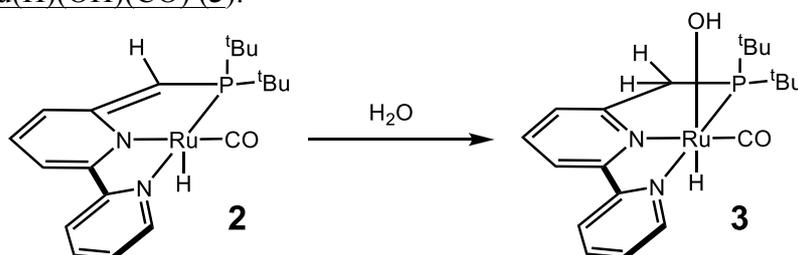
<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded at 250 or 400, 100 and 162 MHz respectively, using a Bruker AMX-250 and AMX-400 NMR spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm downfield from tetramethylsilane. Where products other than the starting alcohol were formed, online NMR library SDBS was consulted for identity confirmation. Locations of deuteration were also determined for cycloheptanol and other complex substrates by consulting SDBS.<sup>2</sup>

## References:

- a) E. Balaraman, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2011**, 50, 11702.
- b) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, 3, 609.
2. [http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre\\_index.cgi?lang=eng](http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng)

## Experimental Procedure

### Synthesis of bipyP-Ru(H)(OH)(CO) (**3**).



Method 1: To a dark black 0.5 ml solution of 10 mg of **2** (~0.02 mmol) in C<sub>6</sub>D<sub>6</sub> was added a large excess of water (50 μL). After mixing for one minute, a dark brown organic phase was obtained alongside a much smaller black aqueous phase. <sup>1</sup>HNMR revealed the presence of one complex (**3**), albeit with broad resonances and a large water peak that obscured the bridge protons. Attempts to obtain pure **3** by drying the mixture under vacuum resulted in decomposition of the complex and partial reversion to **2**.

Method 2: To 10 mg of black solid **2**, 0.5 ml of D<sub>2</sub>O was added. An instant reaction occurred giving a brown, tea-colored solution. Attempts to obtain solid **3** from both methods resulted in some loss of H<sub>2</sub>O under vacuum, giving mixtures of **2** and **3**. A <sup>1</sup>H NMR spectrum quickly obtained after the synthesis of **3** (5 min) showed the location of one of the bridging hydrogens and the hydride signal. These positions were completely deuterated after one hr. The locations of the second bridge hydrogen resonance, as well as the OH, were impossible to determine via this method. The bridging carbon was not observed via <sup>13</sup>C NMR due to deuteration, and subsequent loss of NOE effect and deuteride splitting. <sup>31</sup>P{<sup>1</sup>H} NMR (D<sub>2</sub>O): ) δ ppm 104.1. <sup>1</sup>H NMR (D<sub>2</sub>O): -18.49 (d, 1H, *J*<sub>PH</sub> = 24.7 Hz, Ru-H), 1.11 (d, 9H, *J*<sub>PH</sub> = 13.4 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.32 (d, 9H, *J*<sub>PH</sub> = 14.4 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 3.86 (d, 1H partially deuterated, *J*<sub>PH</sub> = 10.7 Hz, -CH-P), 7.50 (bt, 1H, *J*<sub>HH</sub> = 5.5 Hz, pyridine), 7.74 (bd, 1H, *J*<sub>HH</sub> = 7.21 Hz, pyridine), 8.05 (bm, 2H, pyridine), 8.15 (m, 1H, pyridine), 8.23 (m, 1H, pyridine), 9.05 (bs, 1H, pyridine-ortho). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O): 28.7 (bs, PC(CH<sub>3</sub>)<sub>3</sub>), 28.3 (bs, PC(CH<sub>3</sub>)<sub>3</sub>), 35.8 (vt, 2C *J*<sub>PC</sub> = 16.1 Hz; 24.7 Hz, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 120.2 (pyr), 123.1 (pyr), 124.3 (pyr), 124.4 (pyr), 127.2 (pyr), 138.5 (pyr), 139.5 (pyr), 153.4 (pyr), 155.0 (pyr), 156.3 (pyr), 162.6 (pyr), 206.0 (CO). HRMS unobtained due to rapid conversion to oxidized product (one extra oxygen) even after short times of being exposed to air.

Figure S1: <sup>13</sup>C{<sup>1</sup>H} NMR of **3** in D<sub>2</sub>O.

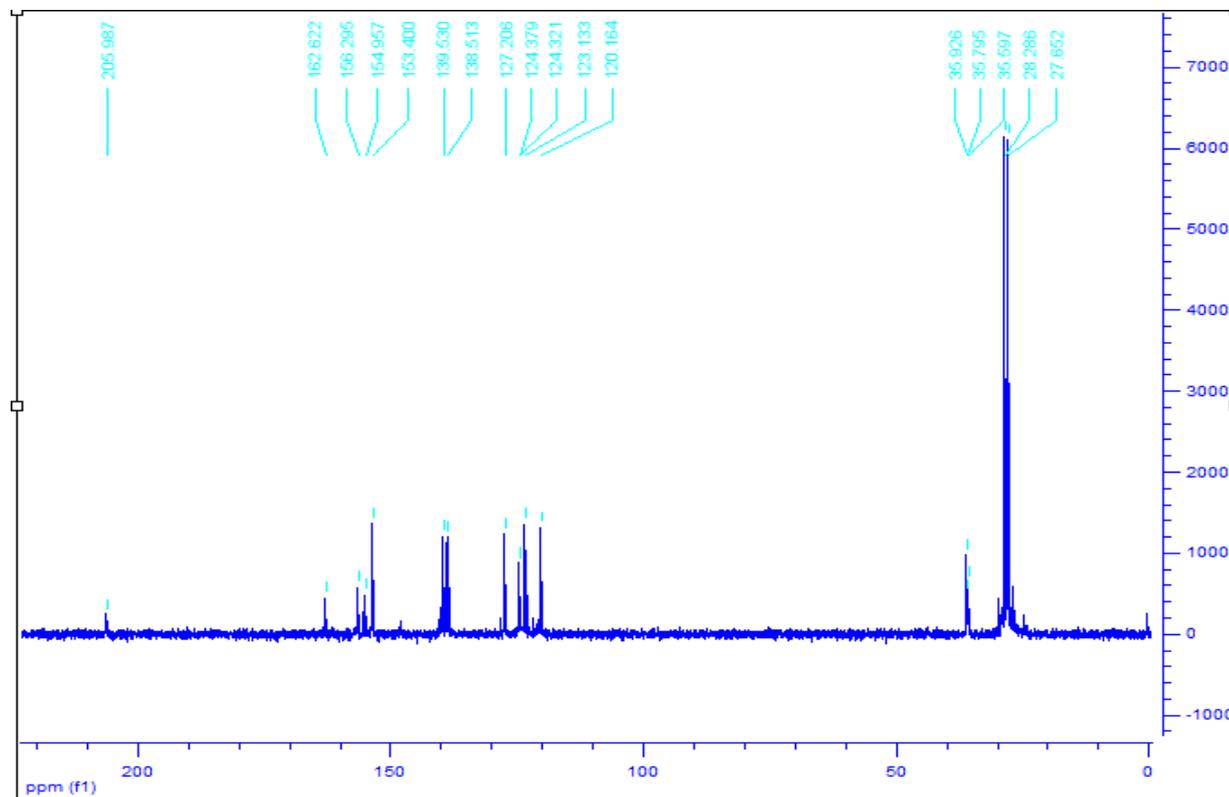


Figure S2: <sup>31</sup>P{<sup>1</sup>H} NMR of **3** in D<sub>2</sub>O.

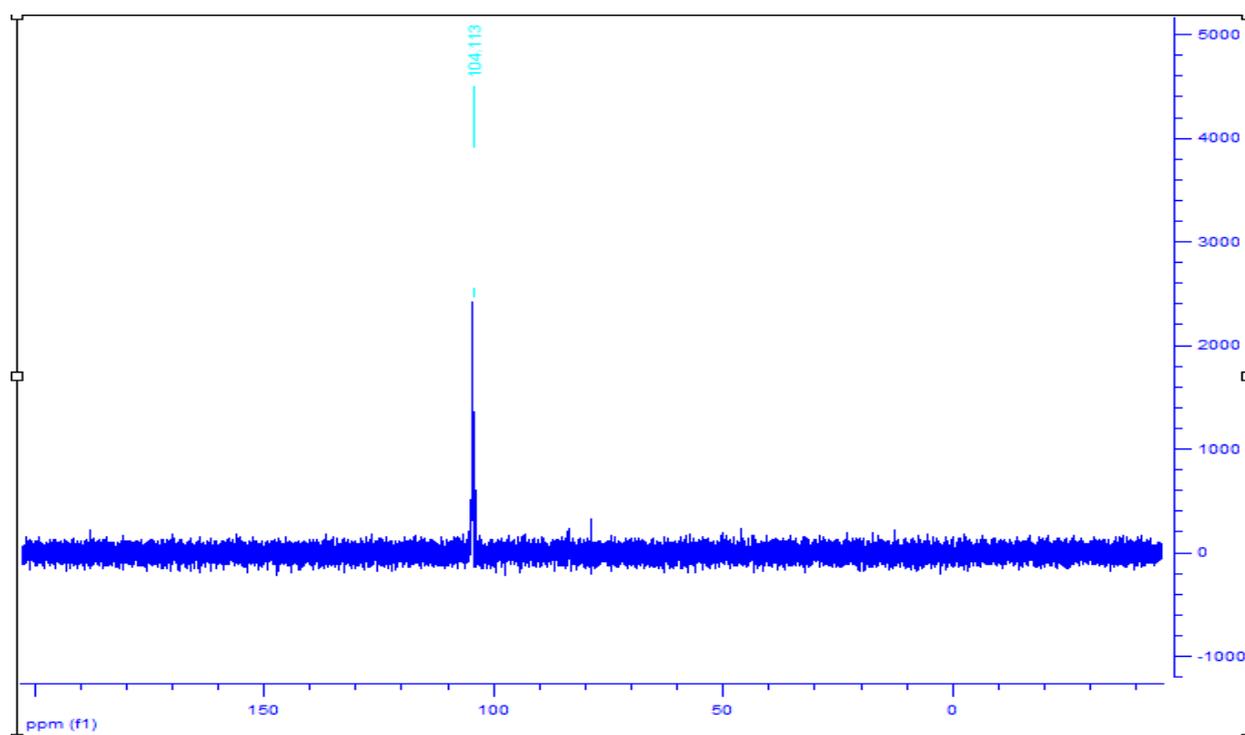


Figure S3:  $^1\text{H}$ NMR of **3** in  $\text{D}_2\text{O}$ .

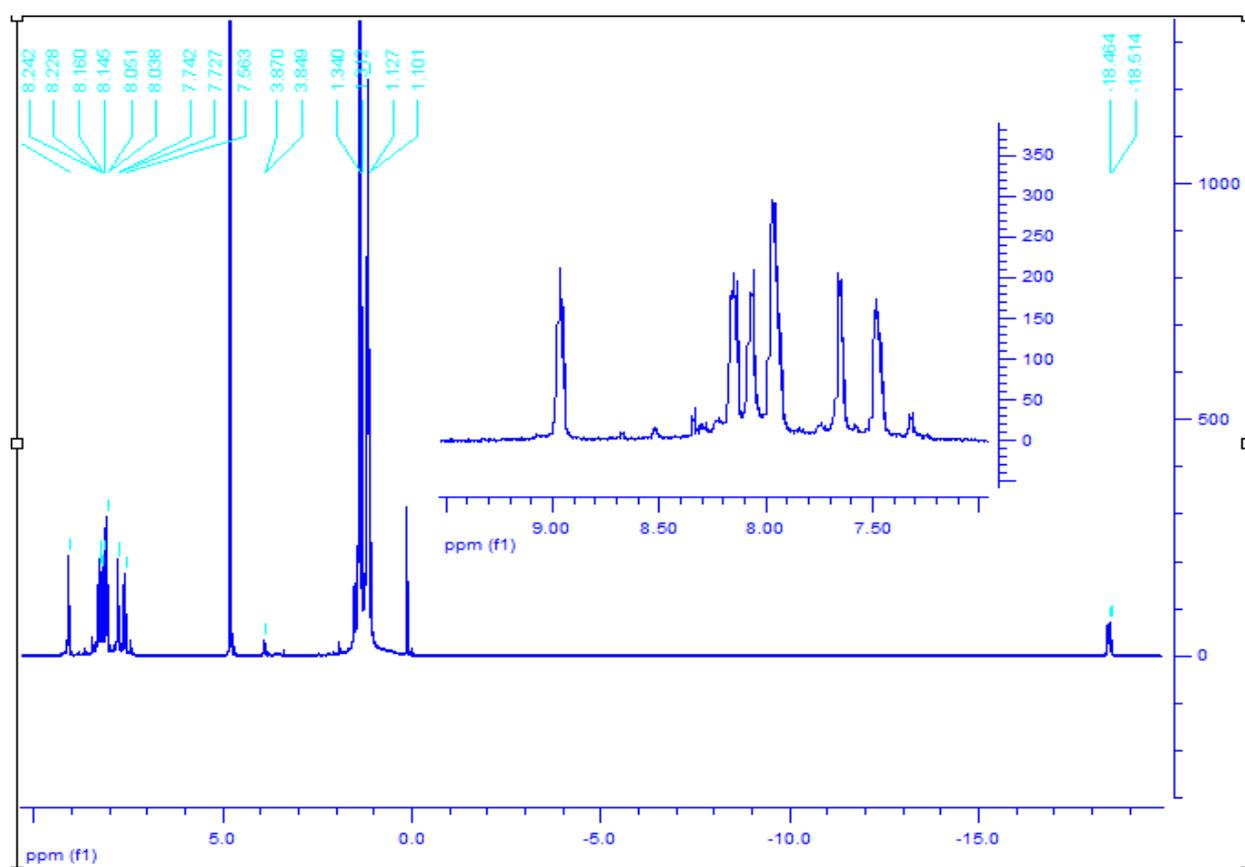


Figure S4:  $^1\text{H}$ NMR ( $\text{D}_2\text{O}$ ) of deuteration of ethanol (Table 2, entry 3). Initial spectrum.

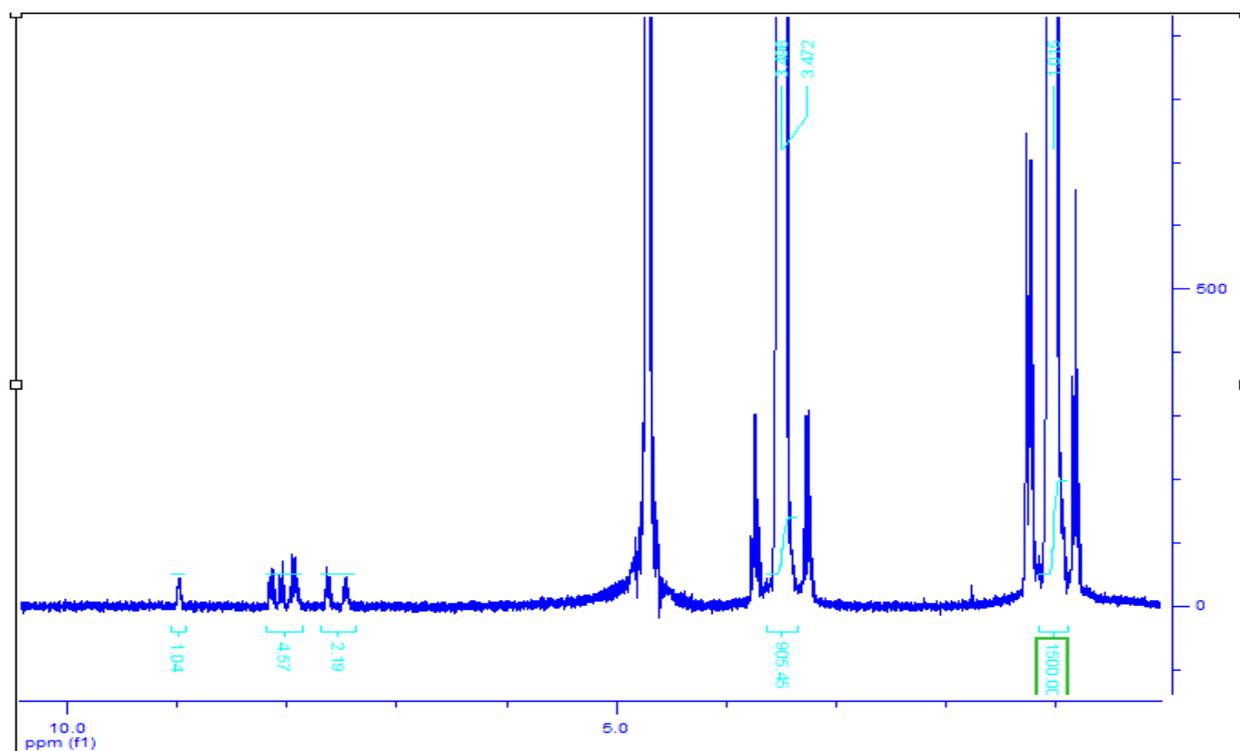


Figure S5:  $^1\text{H}$ NMR ( $\text{D}_2\text{O}$ ) of deuteration of ethanol (Table 2, entry 3). Final spectrum after 40 hrs with 20 eq. of dioxane internal standard.

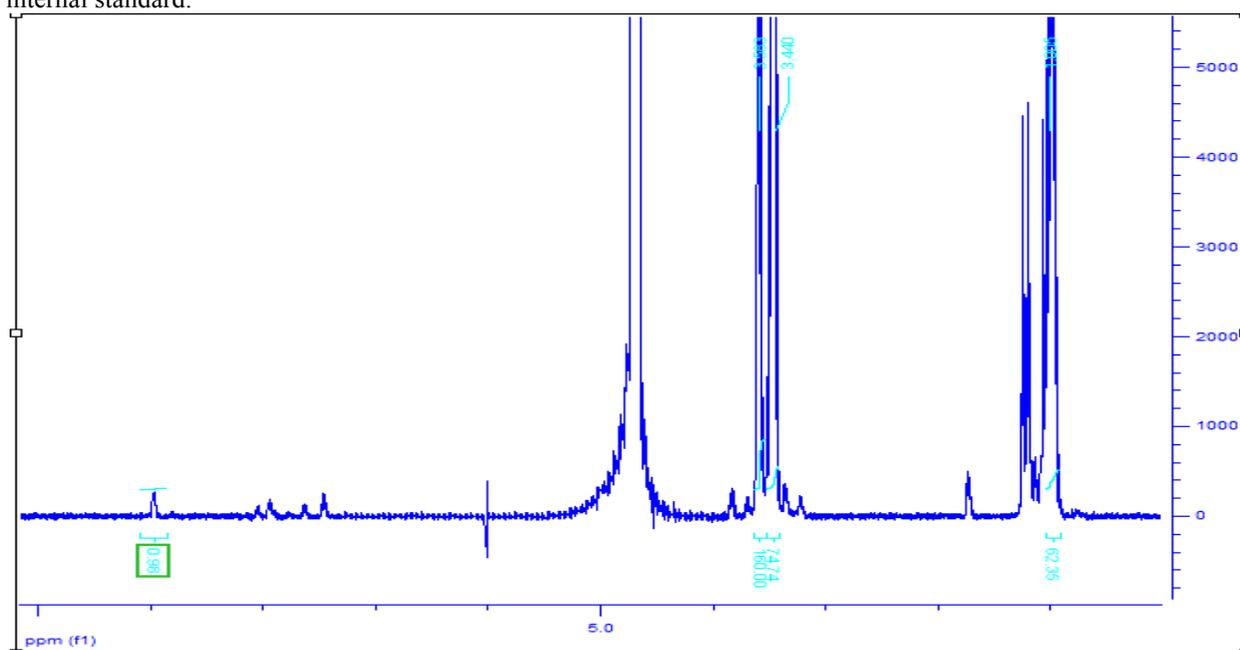


Figure S6:  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) of the decomposition reaction of cinnamic alcohol (Scheme 2) under the catalytic conditions, with aldehyde and aliphatic region peaks growing in prominence.

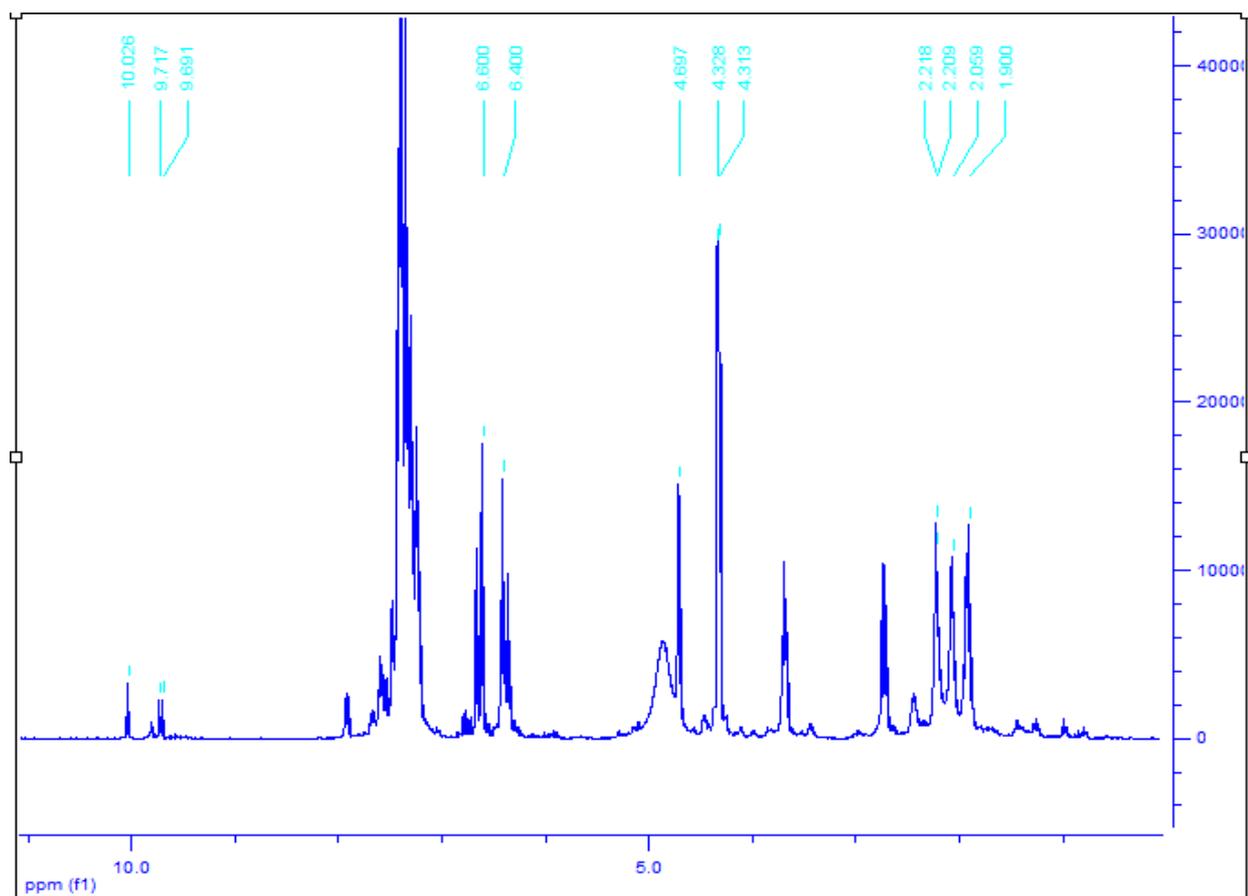


Figure S7: <sup>1</sup>H NMR (D<sub>2</sub>O) Deuteration of dibenzoic alcohol (Table 2; entry 5). Initial spectrum.

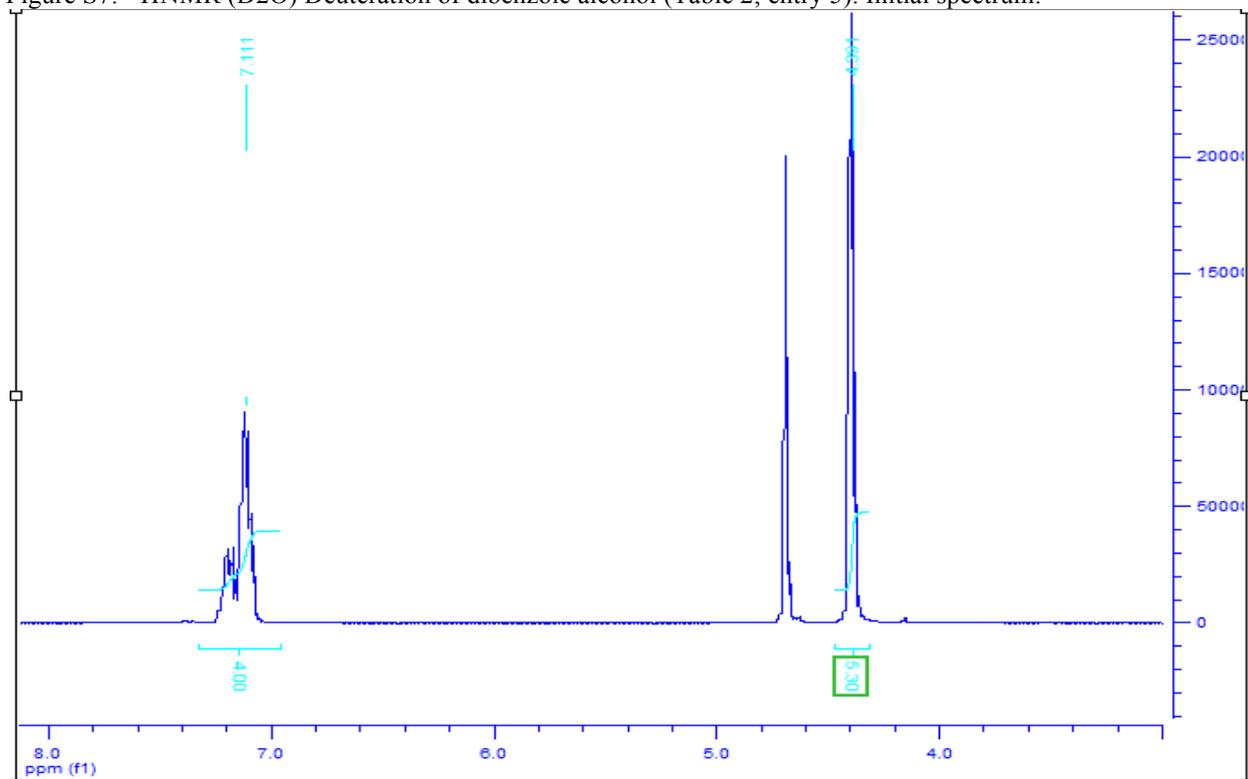


Figure S8: <sup>1</sup>H NMR (D<sub>2</sub>O) Deuteration of dibenzoic alcohol (Table 2; entry 5). Final spectrum.

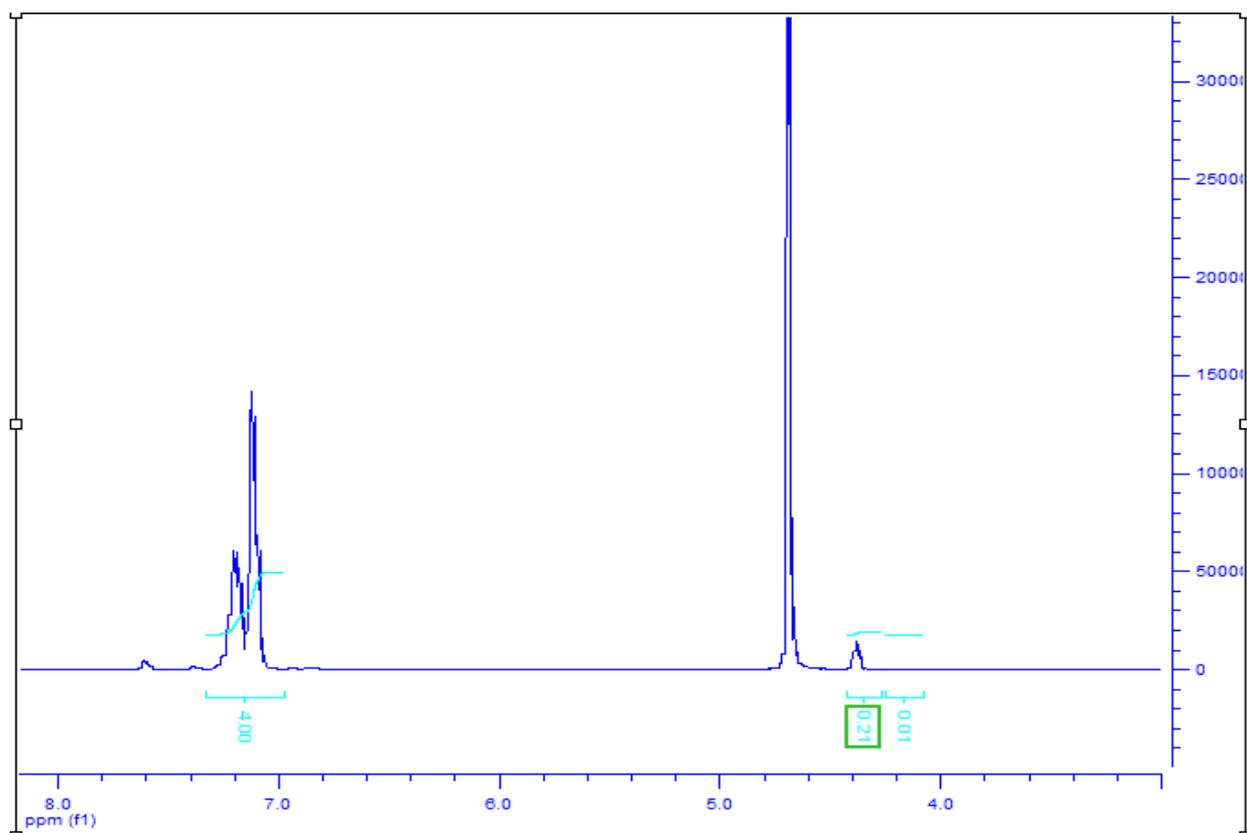


Figure S9:  $^1\text{H}$ NMR ( $\text{D}_2\text{O}$ ) Deuteration of cycloheptanol (Table 3; entry 3). Initial spectrum.

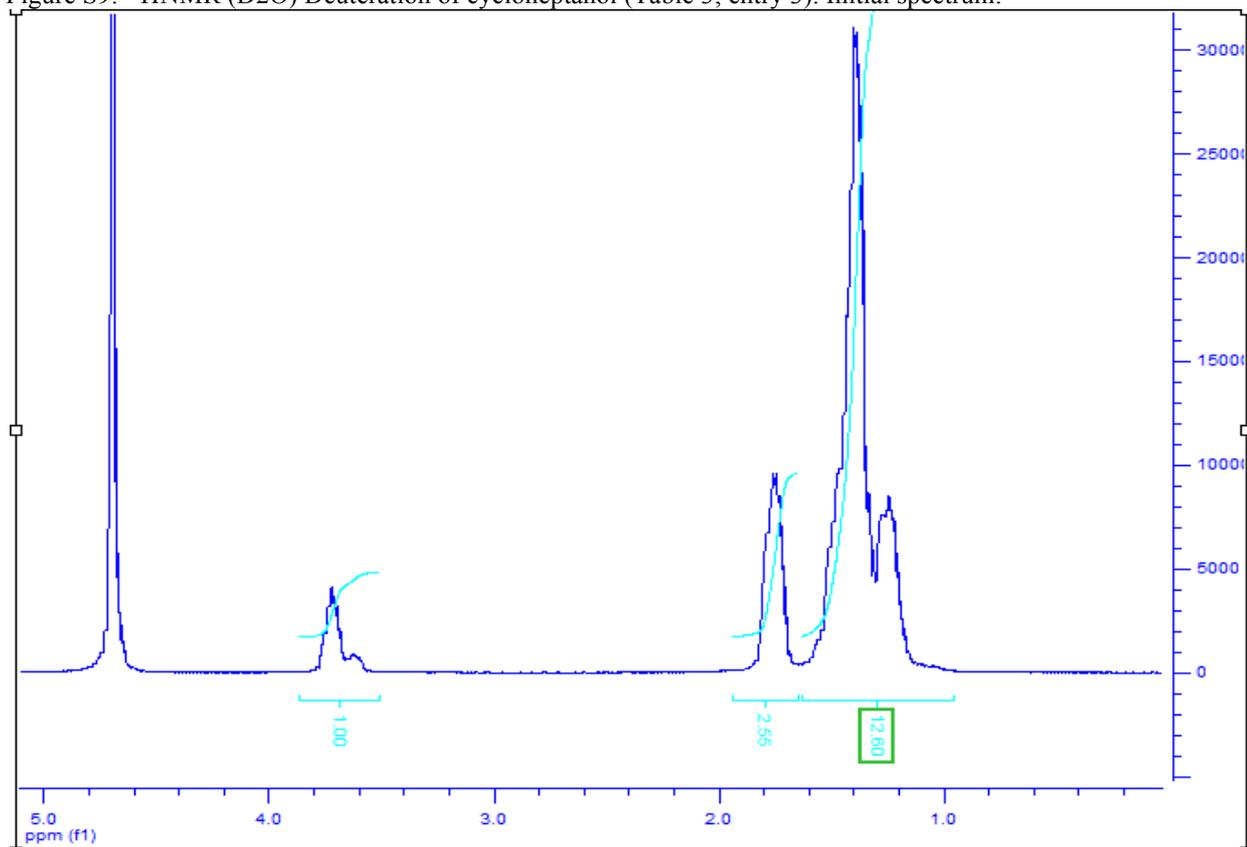


Figure S10:  $^1\text{H}$ NMR ( $\text{D}_2\text{O}$ ) Deuteration of cycloheptanol (Table 3; entry 3). Final spectrum.

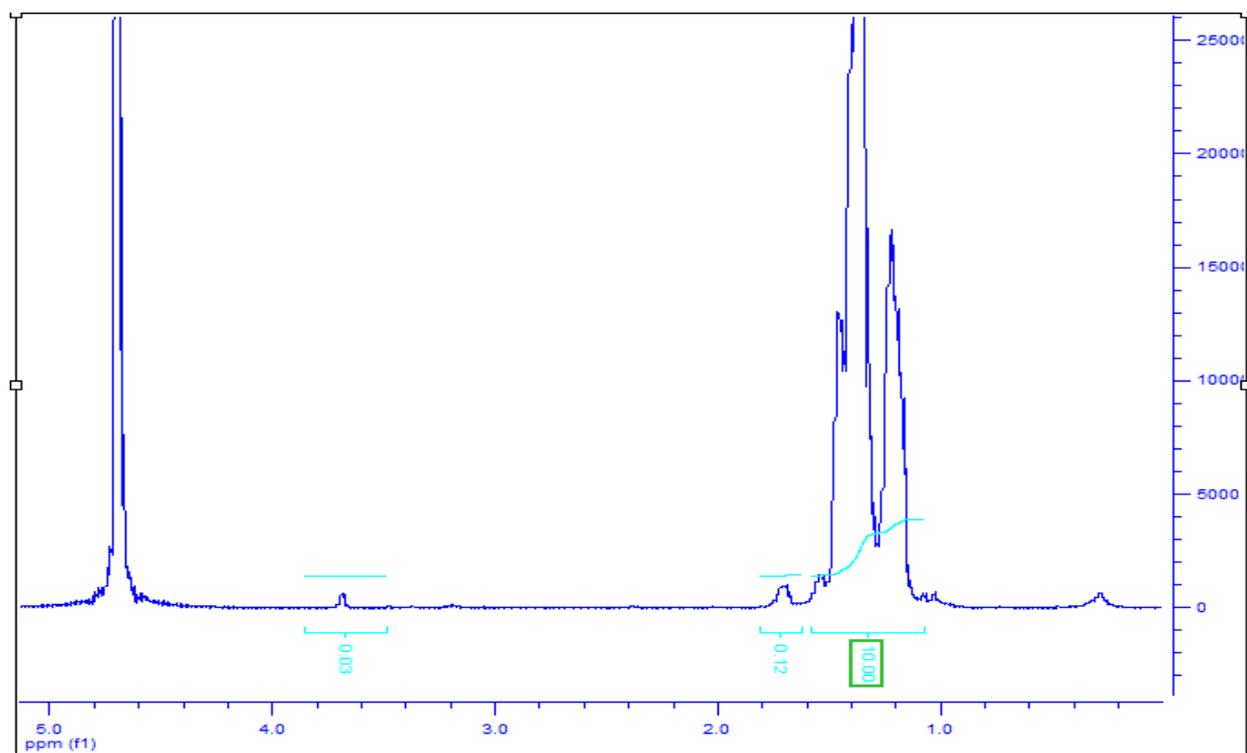


Figure S11:  $^{13}\text{C}$ NMR (D<sub>2</sub>O) Deuteration of cycloheptanol (Table 3; entry 3). Final spectrum.

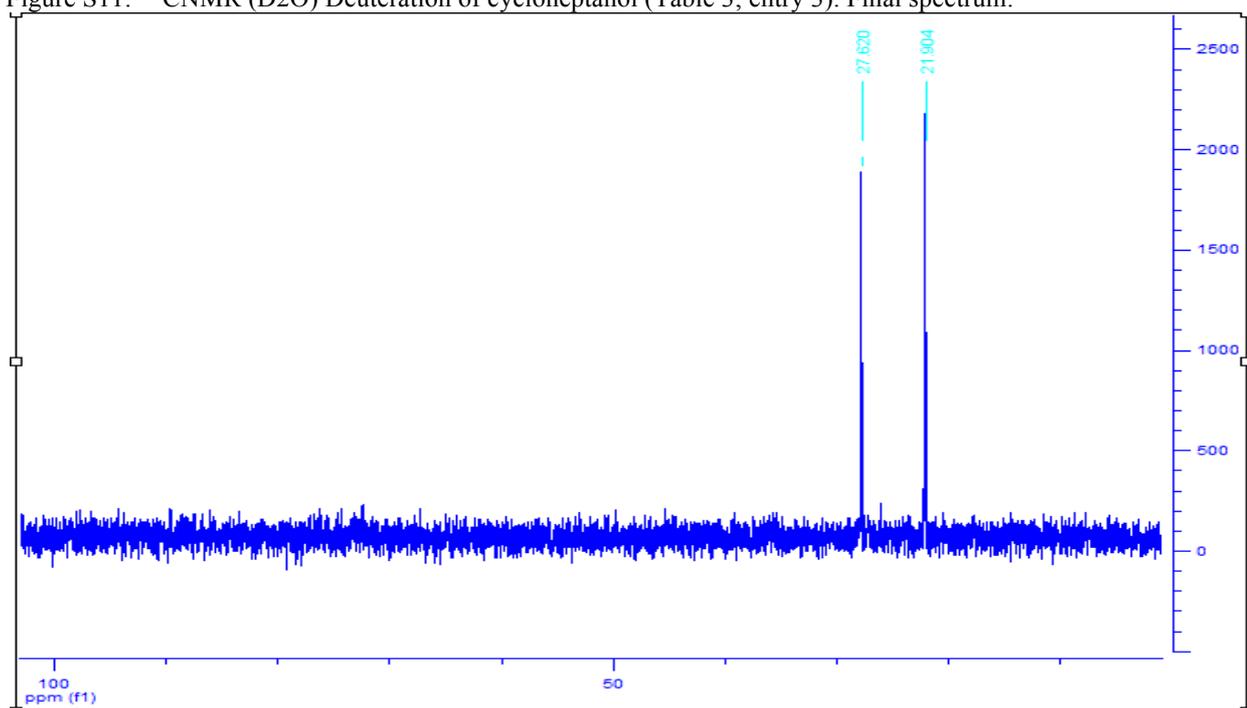


Figure S12:  $^1\text{H}$ NMR (D<sub>2</sub>O) Deuteration of p-fluorobenzyl alcohol (Table 2; entry 8). Initial spectrum with 10mol% dioxane. Doubling of peaks due to poor solubility.

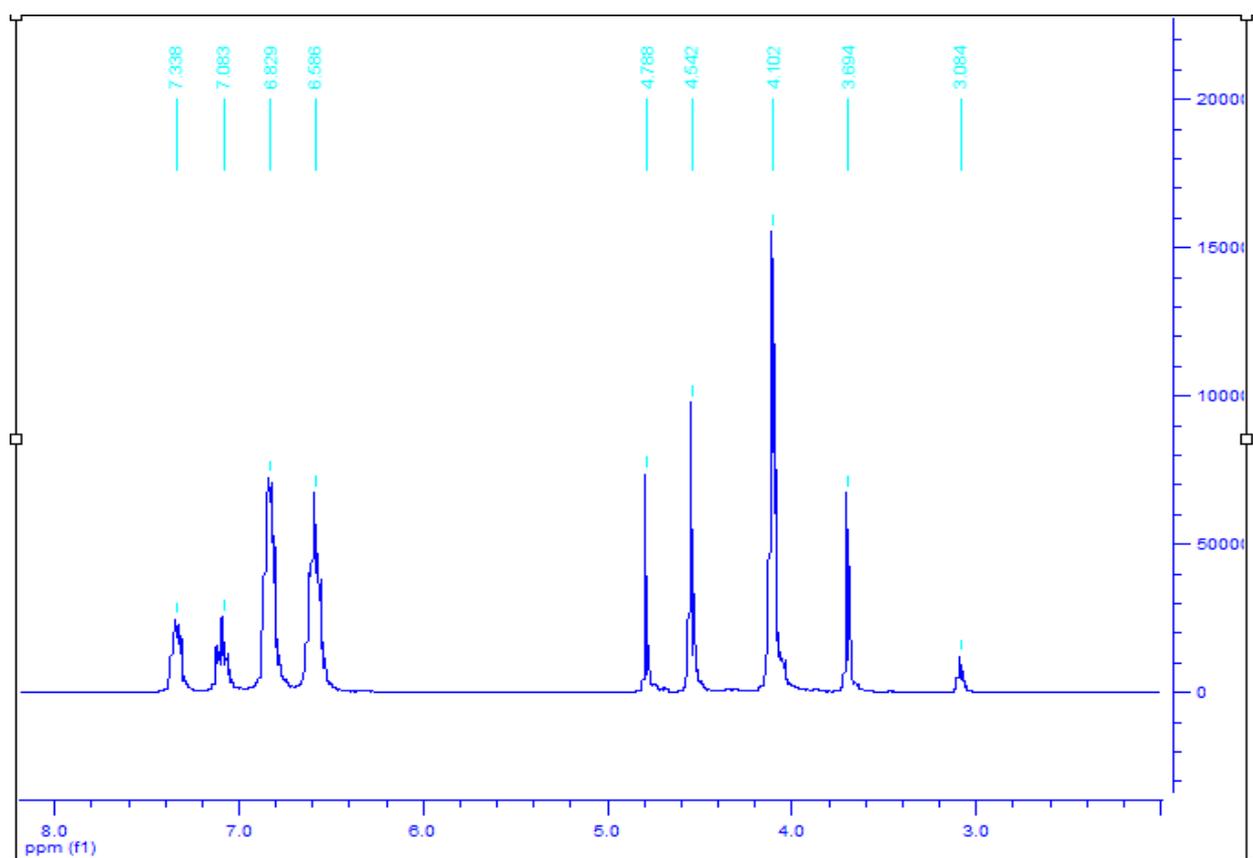


Figure S13:  $^1\text{H}$ NMR ( $\text{D}_2\text{O}$ ) Deuteration of p-fluorobenzyl alcohol (Table 2; entry 8). Final spectrum with 10mol% dioxane. Doubling of peaks due to poor solubility.

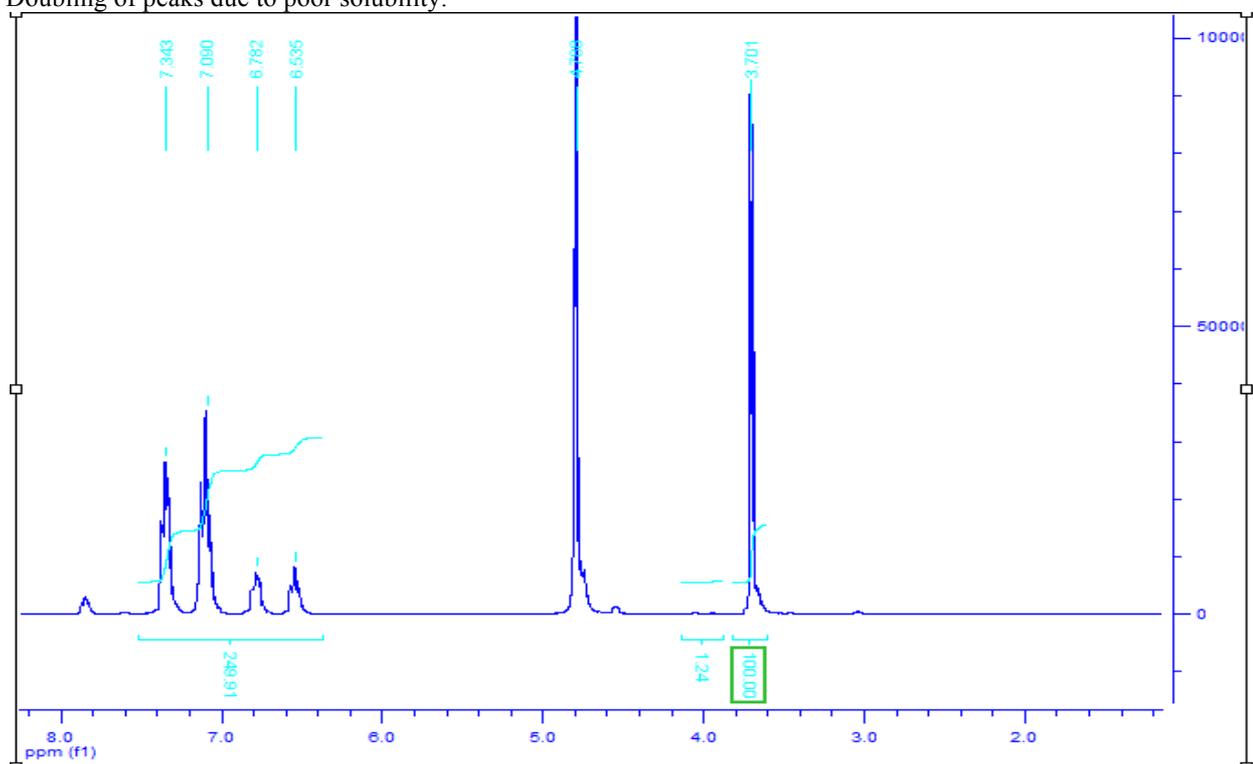


Figure S14:  $^1\text{H}$ NMR ( $\text{CDCl}_3$  extract of the reaction mixture) Deuteration of p-fluorobenzyl alcohol (Table 2; entry 8). Final spectrum with 10mol% dioxane.

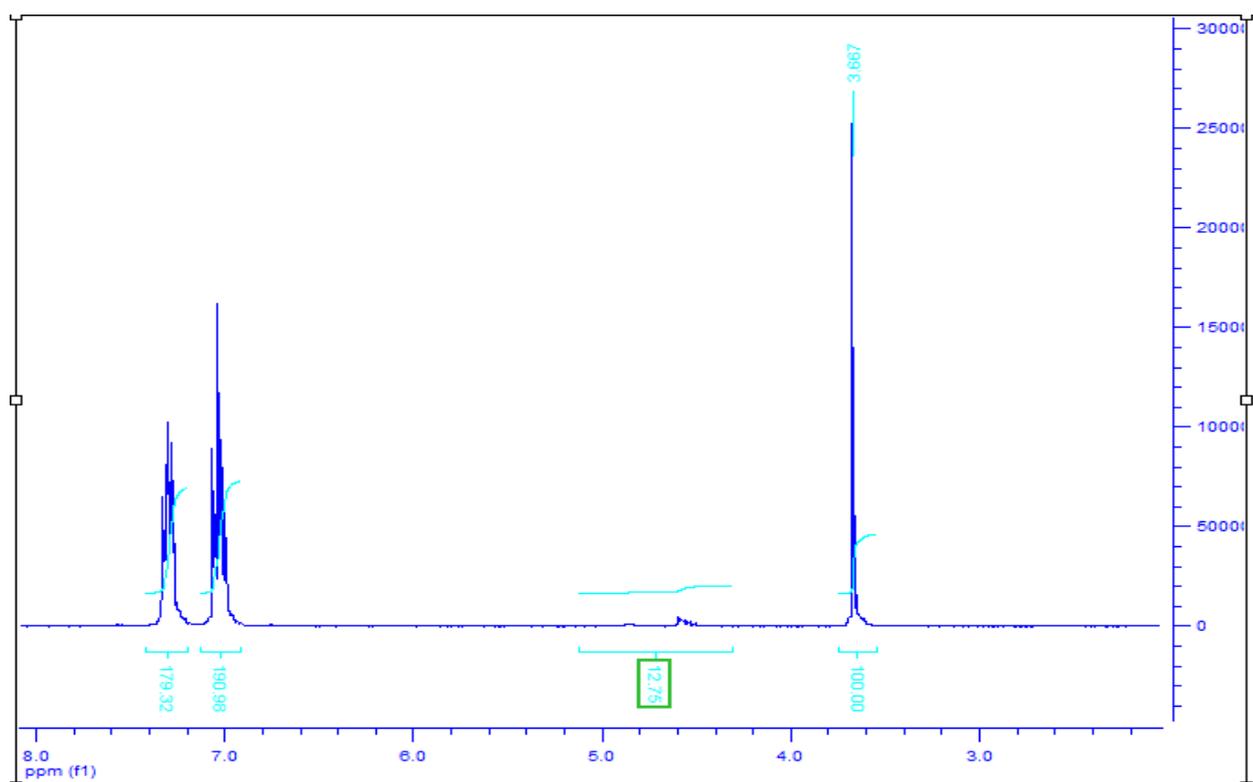


Figure S15:  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) Deuteration of 1-hexanol under air (Table 1; entry 8). Final spectrum after quenching with 1M HCl and extraction in  $\text{CDCl}_3$  with  $\text{CH}_3$  peak as internal standard.