

### Supplementary Information for

### Recyclable and efficient heterogenized Rh and Ir catalysts for the transfer hydrogenation of carbonyl compounds in aqueous medium

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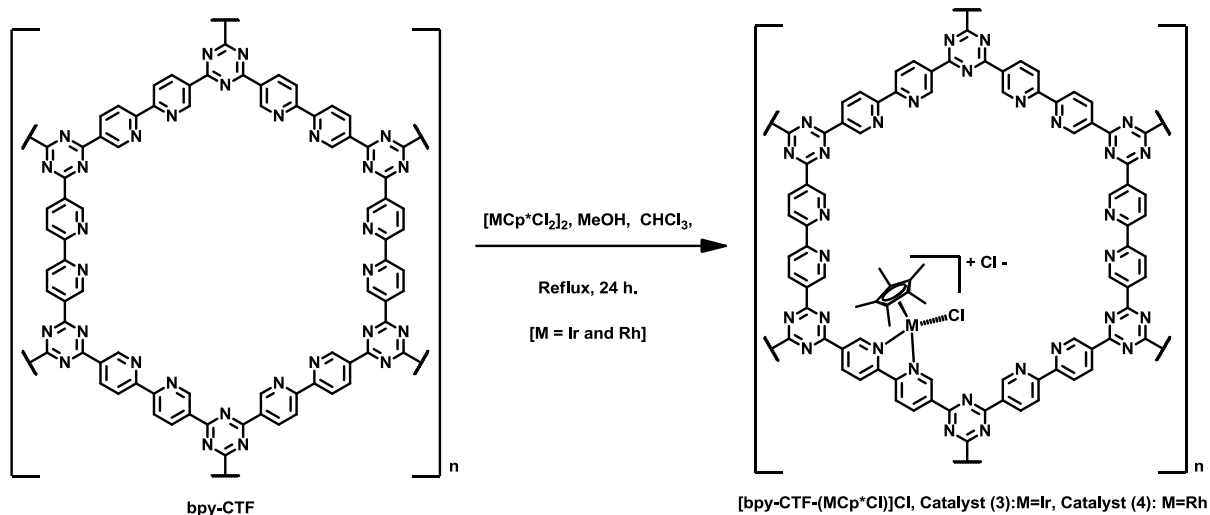
#### General Considerations:

All reagents and materials used in this study were obtained from commercial sources and used as received unless mentioned otherwise. The catalyst 1, 2 and the metal precursors [IrCp\*Cl<sub>2</sub>]<sub>2</sub> and [RhCp\*Cl<sub>2</sub>]<sub>2</sub> were synthesized by following a published procedure.<sup>1,2</sup> Bpy-CTF was synthesized according to a reported procedure.<sup>3</sup> FT-IR spectra were recorded on a Nicolet iS 50 instrument from Thermo Fischer Scientific. A JEOL LTD (JAPAN) JEM-7610F operated at an accelerating voltage of 20.0 kV was used for the Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) measurements. X-ray photoelectron Spectroscopy (XPS) analysis was performed on an ESCA 2000 (VG microtech) at a pressure of  $\sim 3 \times 10^{-9}$  mbar using Al K $\alpha$  as the excitation source ( $h\nu=1486.6$  eV) with concentric hemispherical analyzer. Metal contents in complex 3 and 4 were determined by ICP-MS (iCAP-Q, Thermo fisher scientific) using microwave assisted acid digestion system (MARS6, CEM/U.S.A). BET surface area and N<sub>2</sub> adsorption-desorption measurements were conducted at 77 K using an automated gas sorption system (Belsorp II mini, BEL Japan, Inc.,). The conversions of the ketones into alcohols were determined by <sup>1</sup>H-NMR spectroscopy using an ASCEND 400MHZ (BRUKER) instrument. pH of the solutions were measured using a Metrohm 780 pH meter with a glass electrode probe. pH values were adjusted using 1M solutions of HCOOH and HCOONa. pD values were adjusted using DCOOD and DCOONa in D<sub>2</sub>O and the pH meter readings were converted to pD values by adding a conversion factor of 0.4 (pD = pH + 0.4).

#### General Procedure for the transfer hydrogenation of carbonyl compounds:

The [bpy-CTF-(MCp\*Cl)]Cl catalyst (1 equivalent) was taken in a 25 mL double neck round bottom flask. To this 200 equivalents of ketone were added followed by 2.50 mL of degassed aq. HCOOH/HCOONa mixture (pH =3.504). The reaction was performed at 40 °C for allowed reaction times and then the reaction mass was filtered through a filter paper and the catalyst was washed well with water and then dried at 100 °C for 8 h. The dried catalyst was directly used in the recycling experiments.

### Synthesis of catalysts 3 and 4:



### Scheme S1. Synthesis of catalyst 3 and 4.

To a suspension of bpy-CTF (0.2 g) in 1:1 mixture of methanol and chloroform (15.0 mL) was added metal dimer (10 wt%) under N<sub>2</sub> atm. The resulting suspension was refluxed under N<sub>2</sub> atm for 24 h. After 24 h, the black solid was filtered and washed with excess of dichloromethane (10 X 25 mL) to remove the unreacted metal precursor. The as-synthesized catalyst was dried under vacuum for 16 h.

### FT-IR of bpy-CTF, Catalyst 3 and 4:

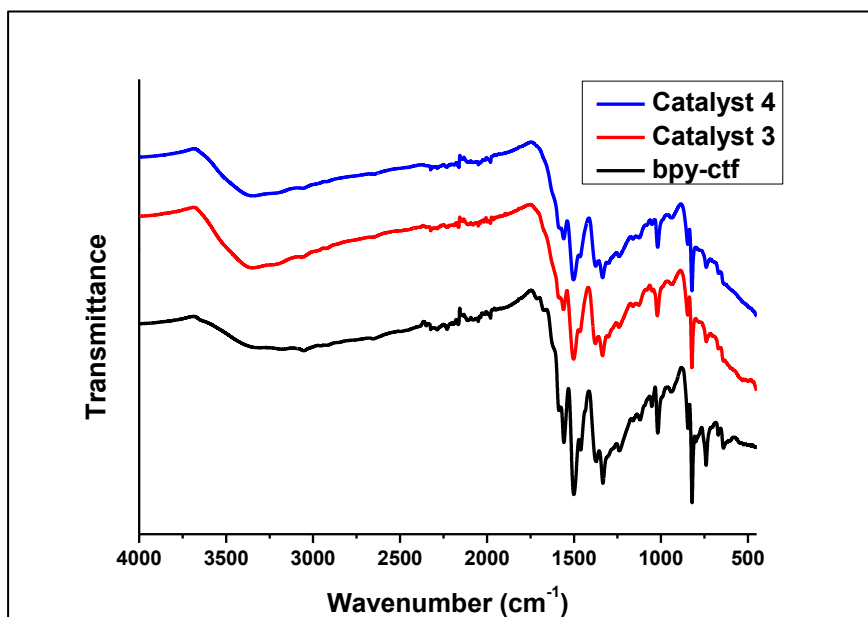


Fig. S1. The FT-IR spectra of bpy-CTF, catalyst 3 and 4.

Scanning Electron Microscopic (SEM) Images.

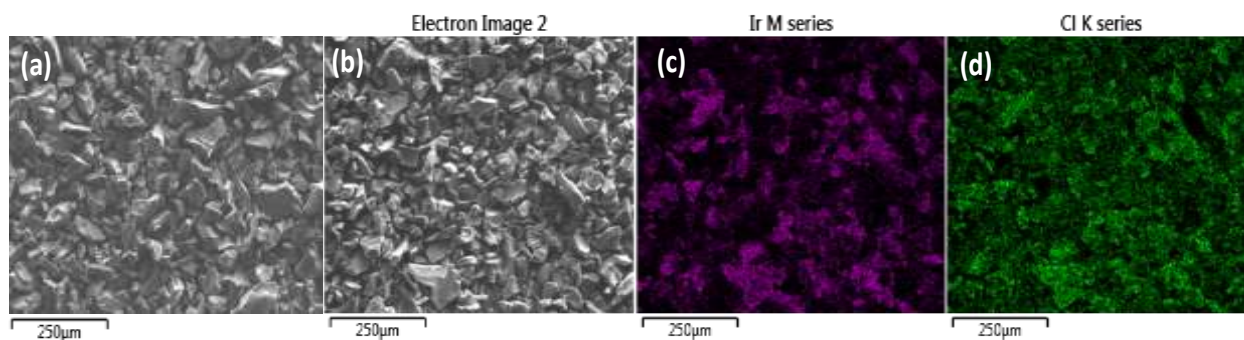


Fig. S2. SEM image of (a) bpy-CTF, (b) catalyst 3; EDS mapping of (c) Iridium and (d) Chlorine in catalyst 3.

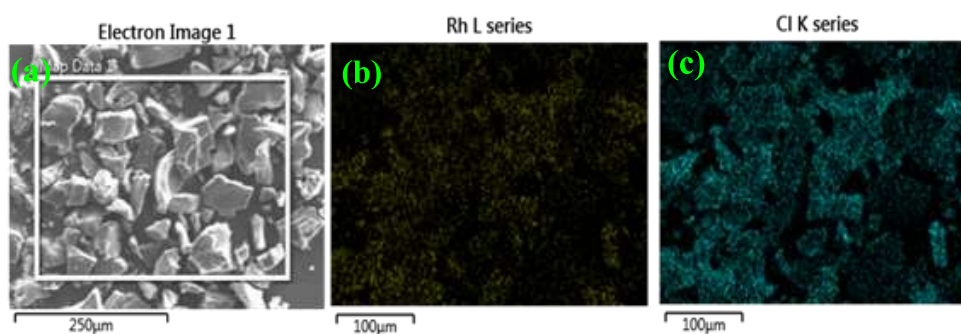


Fig. S3. SEM image of (a) catalyst 4; EDS mapping of (b) Rhodium and (c) Chlorine in catalyst 4.

Table S1. BET analysis of bpy-CTF, Complex 3, Complex 4 and ICP-MS data:

Material	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Ir content by ICP-MS (Wt%)
bpy-CTF	684.6	0.400	--
Catalyst 3	170.24	0.095	4.70
Catalyst 4	151.8	0.126	1.72

Table S2. Pore volume of bpy-CTF with various metal contents:

Compound/ Ir content (Wt%)	Surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )
bpy-CTF400	684.59	0.400
Ir/1.4	479.98	0.280
Ir/4.7	170.24	0.095
Ir/10.6	9.74	0.010

**Table S3.** TH of carbonyl compounds using catalysts **3** and **4**.<sup>a</sup>

Entry	Substrate		S/C	Catalyst 3					Catalyst 4				
	R	R'		Time (h)	Conversion <sup>b</sup> (%)	TON <sup>c</sup>	TOF <sup>d</sup> (h <sup>-1</sup> )	Yield <sup>e</sup> (%)	Time (h)	Conversion <sup>b</sup> (%)	TON <sup>c</sup>	TOF <sup>d</sup> (h <sup>-1</sup> )	Yield <sup>e</sup> (%)
1	Ph	Me	100	24	99.0	99	4.1	76.1	8	99.0	99	12.4	72.1
2	Ph	Me	200	30	99.0	198	6.6	78.4	12	99.0	198	16.5	77.6
3	p-OMe- Ph	Me	200	30	59.2	118	3.9	41.1	24	98.3	197	8.1	92.1
4	p-Me- Ph	Me	200	30	52.6	105	3.5	40.7	24	94.3	189	7.8	75.8
5	p-Cl-Ph	Me	200	24	99.0	198	8.3	85.4	10	99.0	198	19.8	84.3
6	Me	Me	200	30	30.1	60	2.0	10.4	12	56.4	113	9.3	18.1
7	R,R' = -(CH <sub>2</sub> ) <sub>5</sub> -		200	30	96.4	193	6.4	64.1	12	96.8	194	16.2	79.2
8	Ph	H	200	12	86.0	172	14.3	65.2	12	95.4	191	15.8	73.5

<sup>a</sup>Reaction Conditions: 40 °C, pH = 3.5, HCOOH/HCOONa = 2.5 mL. <sup>b</sup>Determined by <sup>1</sup>H-NMR. <sup>c</sup>Based on <sup>1</sup>H-NMR conversion; No. of moles of product/No. of moles of metal. <sup>d</sup>TON/h. <sup>e</sup>isolated crude yield.

<sup>1</sup>H-NMR spectra:

Reaction of acetophenone with DCOOD/DCOONa in D<sub>2</sub>O

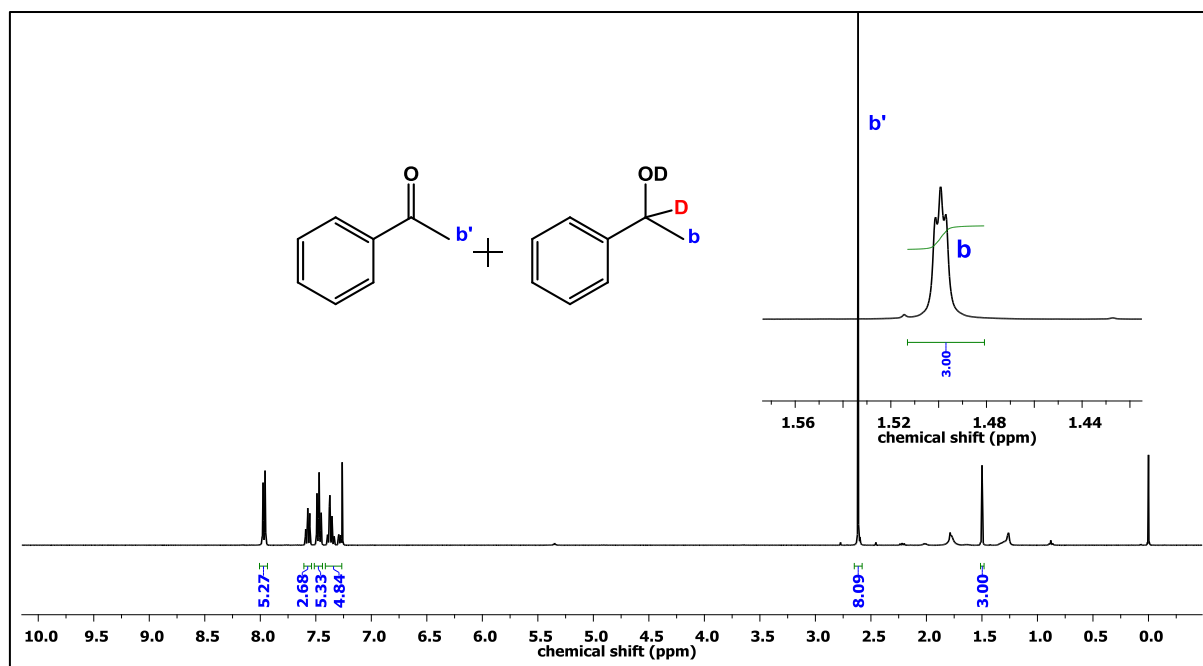


Fig. S4. <sup>1</sup>H-NMR spectrum of crude product (in D<sub>2</sub>O) resulted in the reaction of acetophenone with DCOOD/DCOONa using catalyst **4** in D<sub>2</sub>O

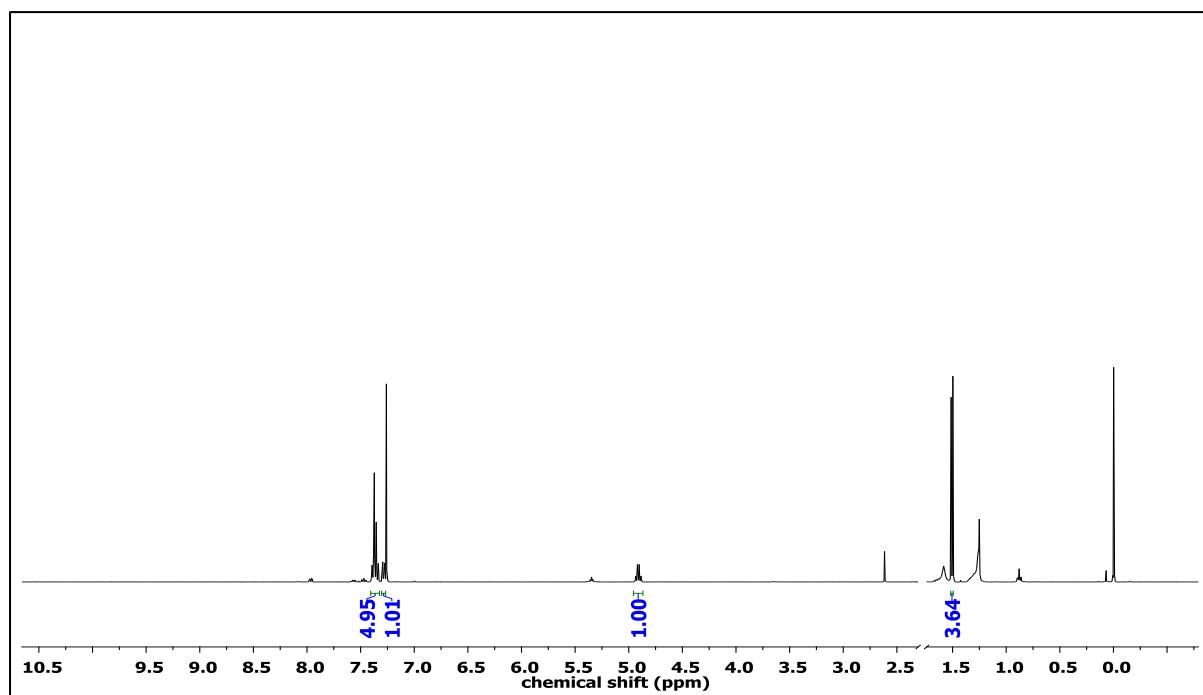


Fig. S5. <sup>1</sup>H-NMR spectrum of crude product (in D<sub>2</sub>O) resulted in the reaction of acetophenone with HCOOH/HCOONa using catalyst **4** in D<sub>2</sub>O as a reaction medium.

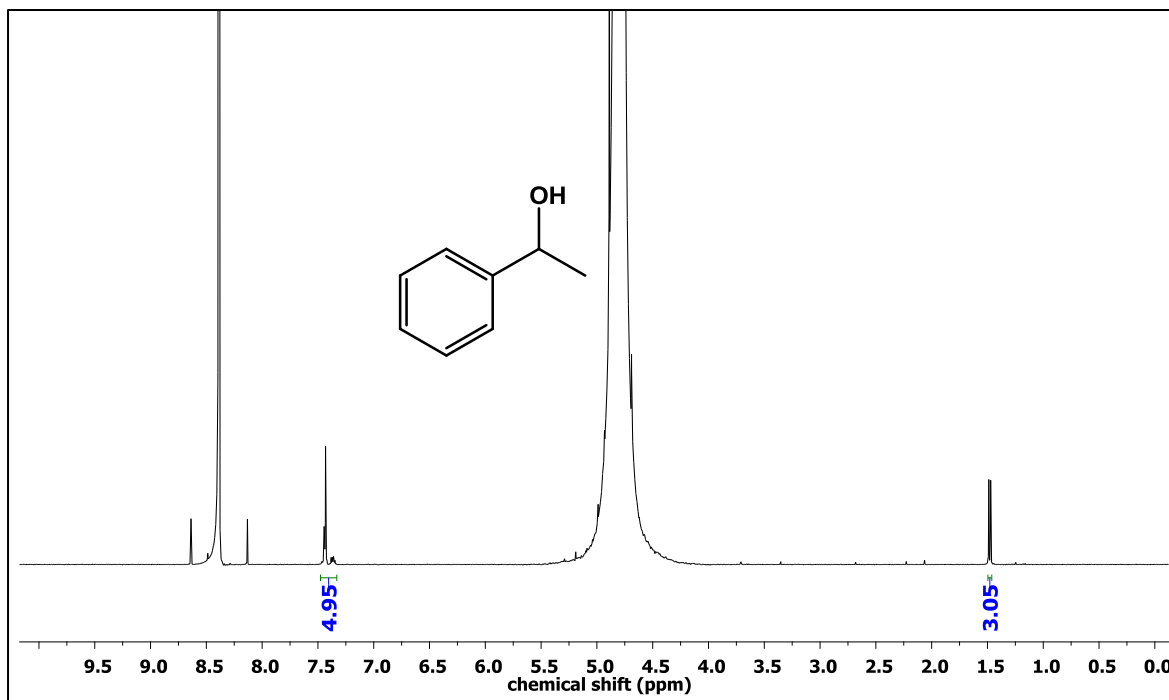


Fig. S6. <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of 1-phenyl ethanol in D<sub>2</sub>O.

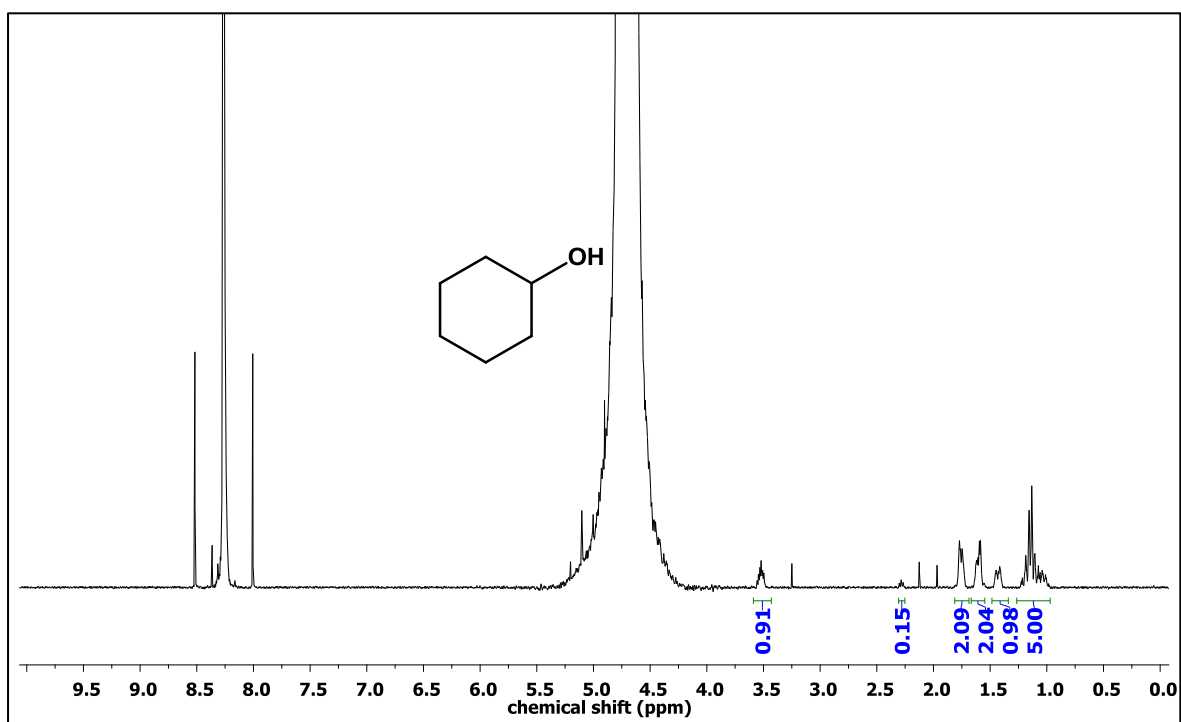


Fig. S7. <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of cyclohexylalcohol in D<sub>2</sub>O:

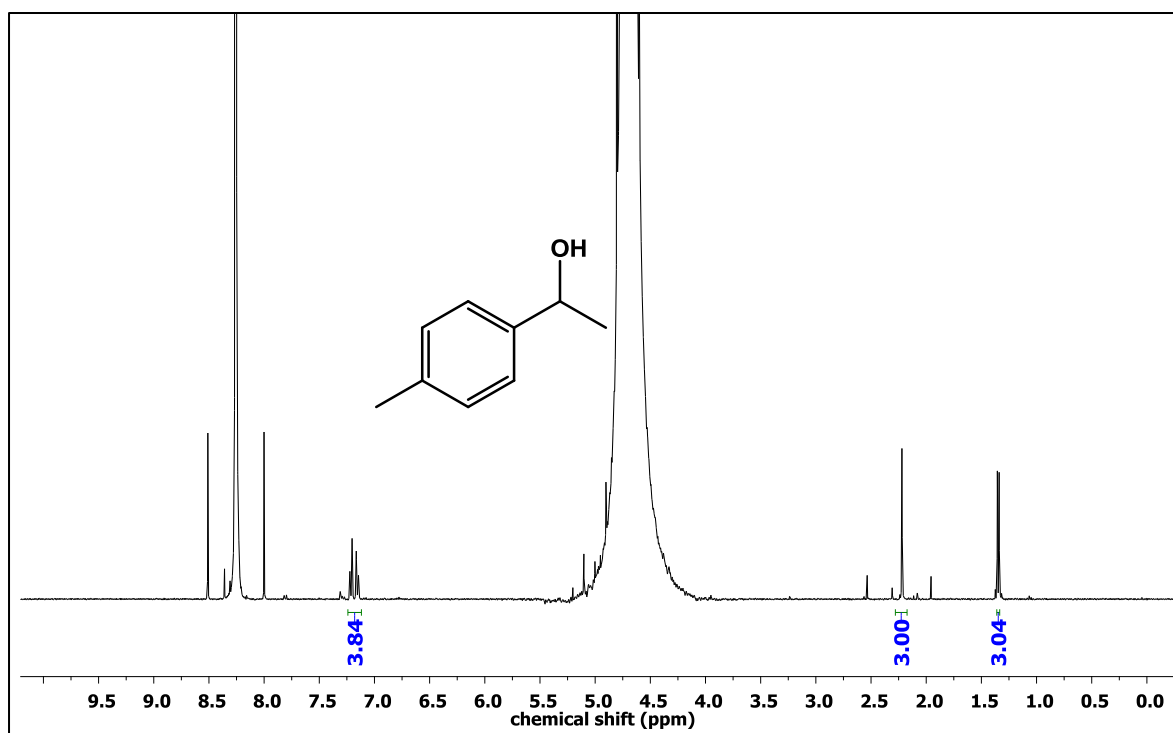


Fig. S8. <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of 1-(4'-methylphenyl)-ethanol in D<sub>2</sub>O.

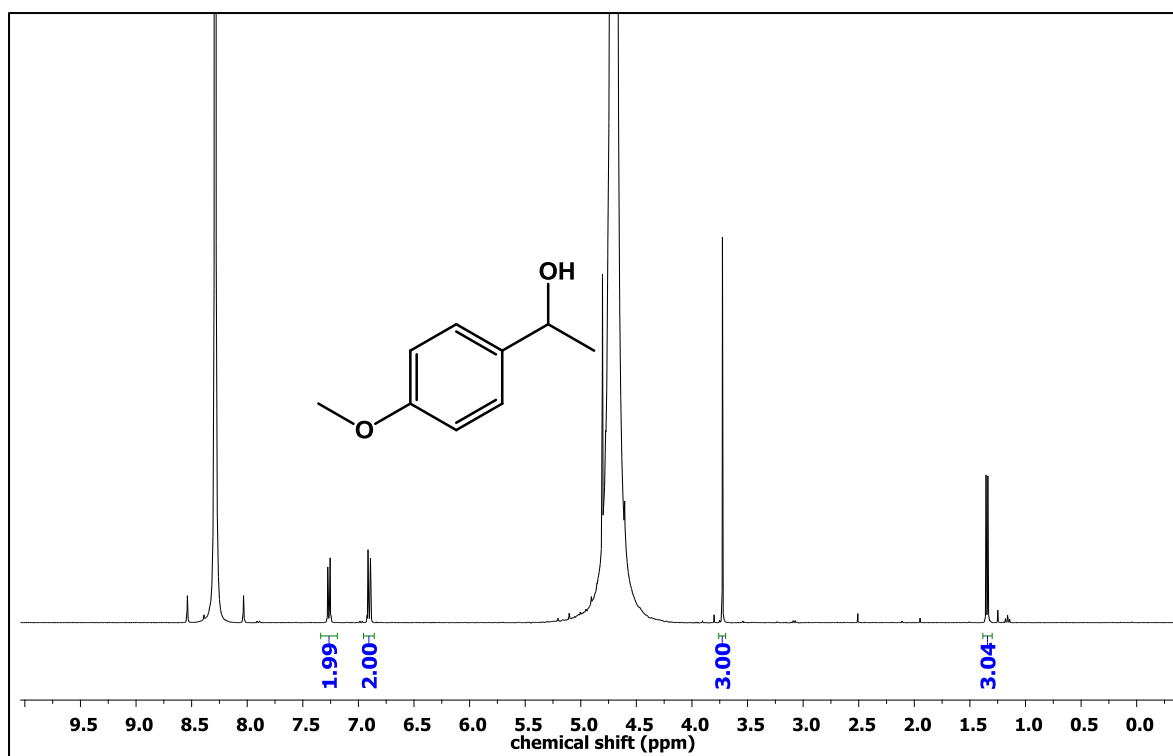


Fig. S9. <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of 1-(4'-methoxyphenyl)-ethanol in D<sub>2</sub>O.

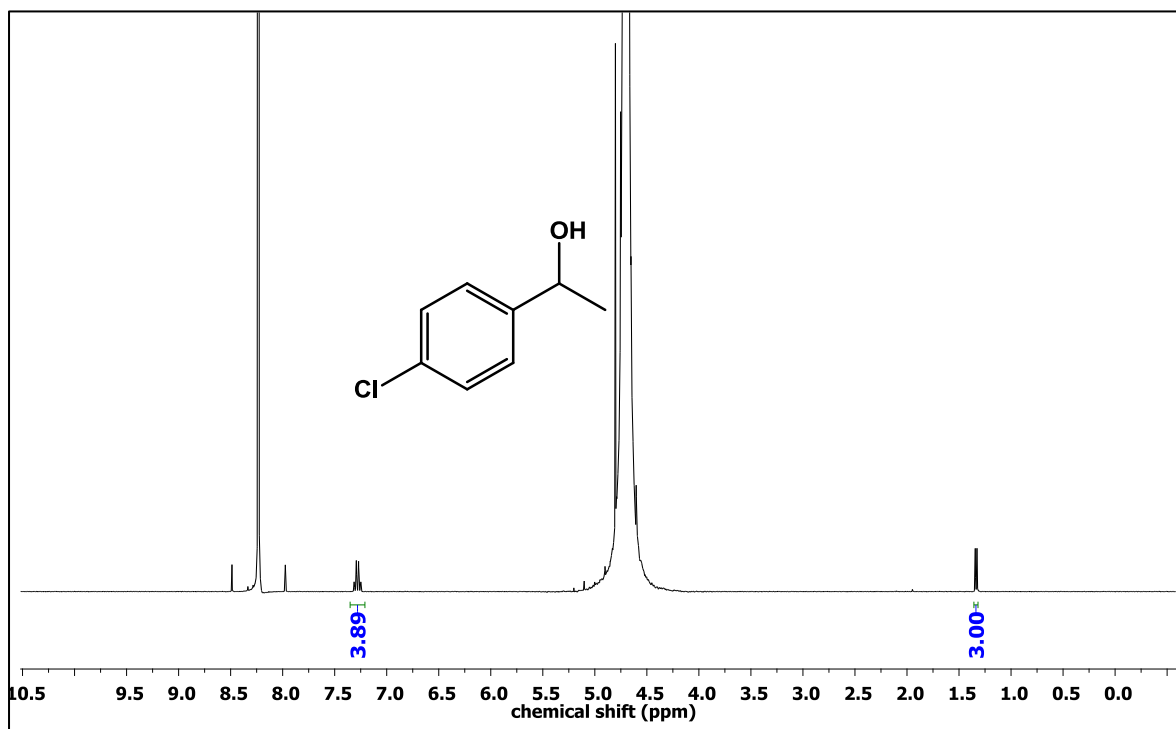


Fig. S10. <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of 1-(4'-chlorolphenyl)-ethanol in D<sub>2</sub>O.

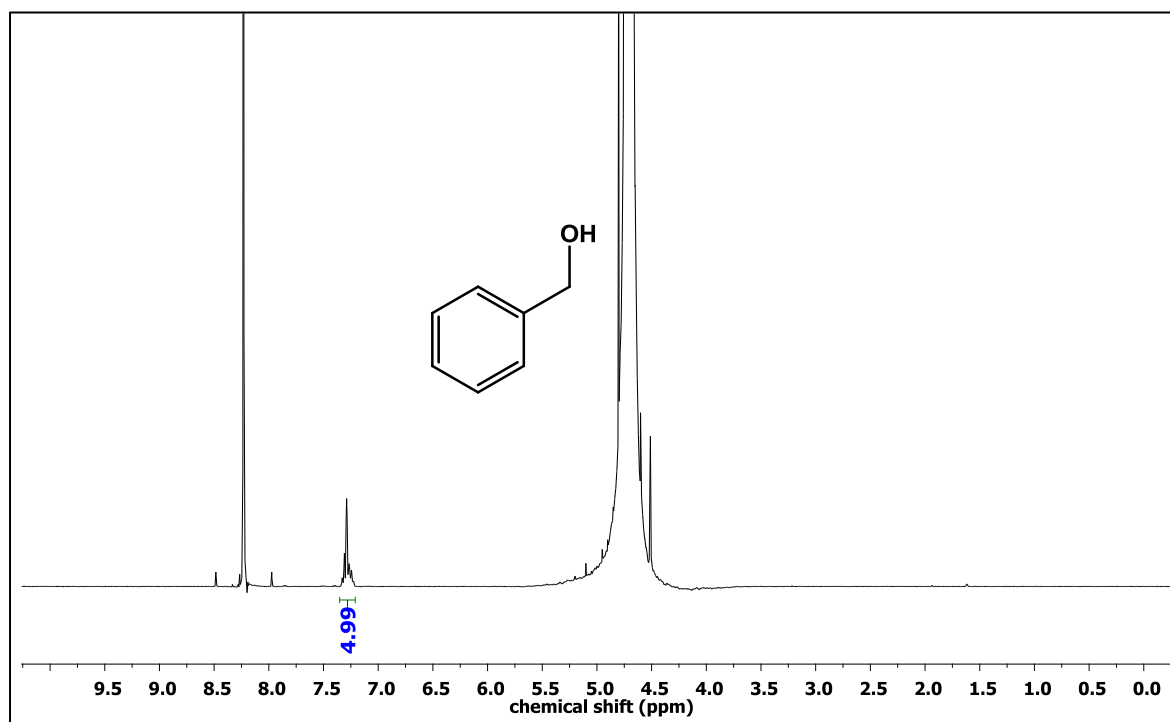
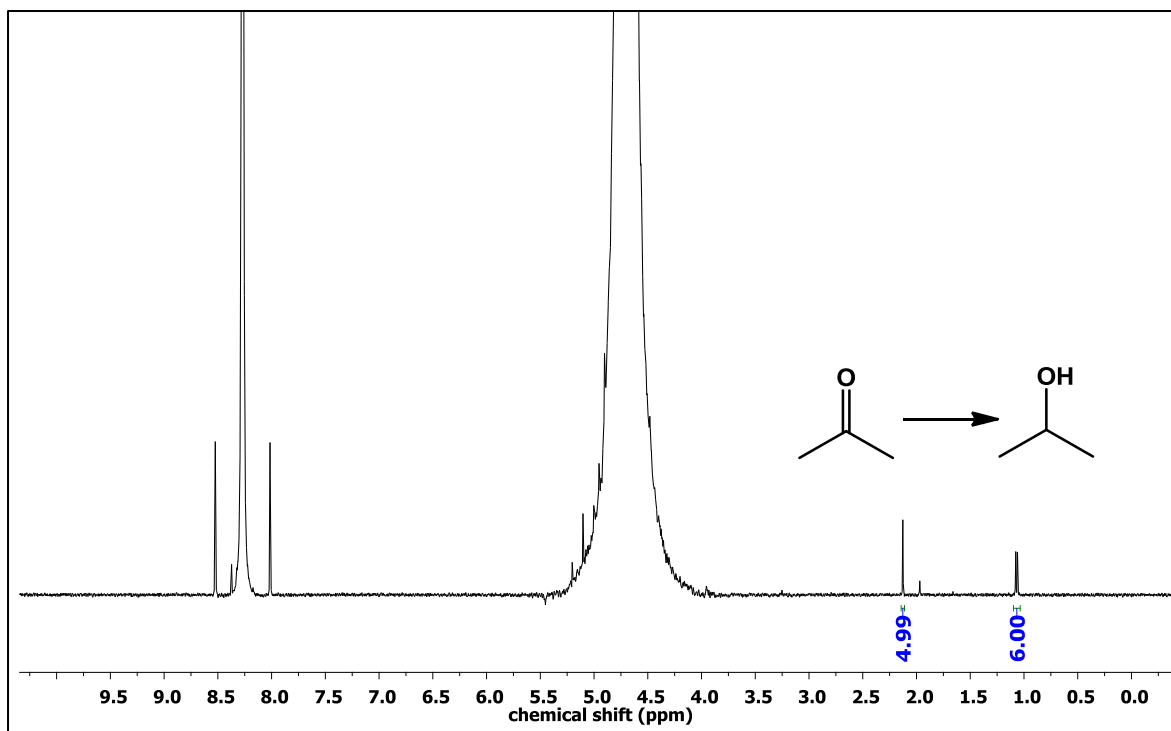


Fig. S11. <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of benzyl alcohol in D<sub>2</sub>O





**Fig. S12.** <sup>1</sup>H-NMR spectrum of reaction mass that shows the formation of isopropyl alcohol (55 % conversion) in D<sub>2</sub>O.

1. Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa and K. Kasuga, *J Mol Catal A-Chem*, 2003, **195**, 95-100.
2. R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, and S. T. Michel, *Inorg. Chem.* 1990, **29**, 2023-2025
3. K. Park, G. H. Gunasekar, N. Prakash, K. D. Jung and S. Yoon, *Chemsuschem*, 2015, **8**, 3410-3413.