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Supporting Information

A porous metal-organic aerogel based on dirhodium paddle-wheels as an efficient and stable heterogeneous catalyst towards the reduction reaction of aldehyde and ketone

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1. Synthesis of Porphyrin Ligand.

The tetrakis(4-carboxyphenyl)porphyrin (TCPP) ligand was synthesized by the following two steps.

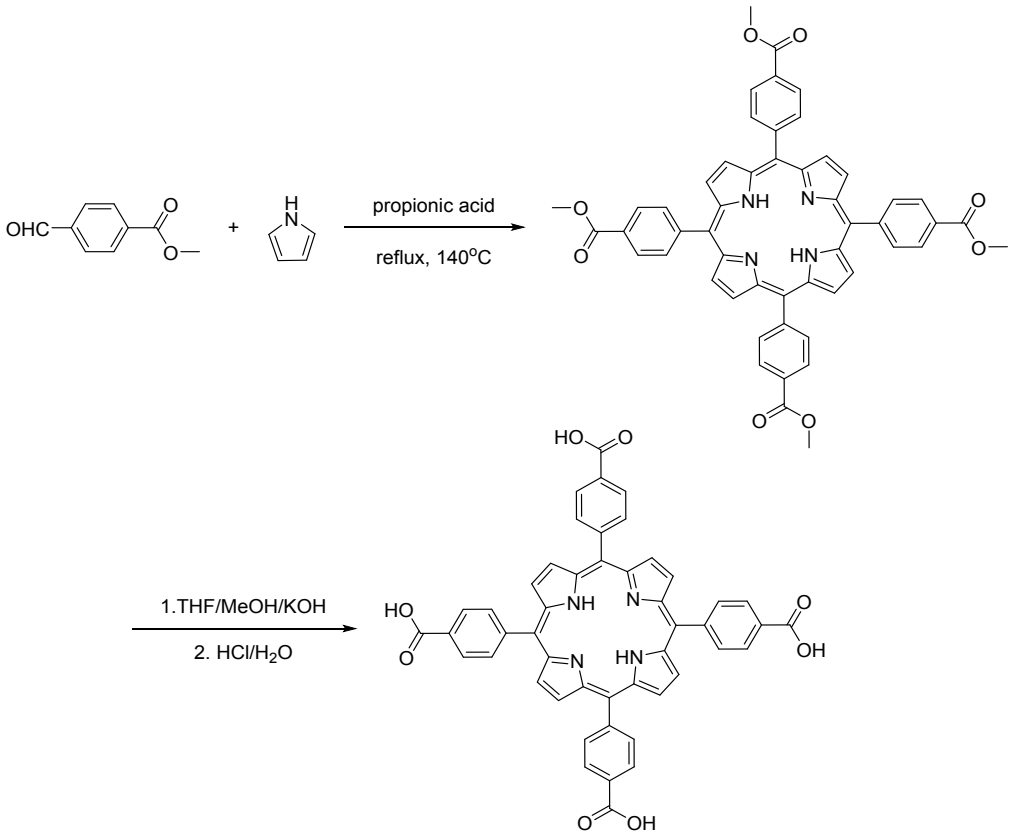


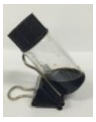
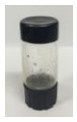
Figure S1. Synthesis of TCPP

Step one: Methyl 4-formylbenzoate (3.0 g, 15.24 mmol) and propionic acid (100 mL) were added to a 250 mL three-necked flask and heated to 100℃. Pyrrole (1 mL, 14.41 mmol) was added into the flask dropwise, the mixture was then heated to 140 ℃. After refluxing for 12 h, the solution was cooled to room temperature and then poured into 200 mL of water. Black purple solid was obtained by filtration, washing with much ethanol and water. The solid was further purified by silica gel column chromatography using CH_2Cl_2 as eluent.

Step two: The obtained ester (1.95 g) in the step one was stirred in a mixed solvent of THF (50 mL) and MeOH (50 mL), to which an aqueous solution of KOH (6.82 g of KOH in 60 mL H_2O) was introduced. This mixture was refluxed for 12 h. After cooling down to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting water phase until the solid was fully dissolved, then the homogeneous solution was acidified with 1M HCl until purple solid was precipitated. The purple solid was collected by filtration, washed with water and dried in vacuum.

2. Gelation Study

Table S1. Gelation tests of TCPP and $Rh_2(OAc)_4$ with different reactant concentrations.[a]

Entry	TCPP		C_L[b]	$Rh_2(OAc)_4$		C_M[c]	Result[d]	Photo
	(mmol)	(mg)	(mol/L)	(mmol)	(mg)	(mol/L)		
1	0.0075	6.0	0.0034	0.0075	3.3	0.0034	S	
2	0.015	11.9	0.0068	0.015	6.6	0.0068	G	
3	0.03	23.7	0.0136	0.03	13.3	0.0136	G	
4	0.045	35.6	0.0205	0.045	19.9	0.0205	G	

[a]A 1:1 molar ratio mixture of $Rh_2(OAc)_4$ and TCPP was dissolved in 2.2 mL of DMF/H_2O (10:1 v/v) with sonication. The resultant homogeneous solution was then left to stand at 85°C for *ca* 50 h. [b]C_L = the molar concentration of TCPP. [c]C_M = the molar concentration of $Rh_2(OAc)_4$. [d]G = gel, S = solution.

Table S2. Gelation tests of TCPP and $Rh_2(OAc)_4$ in different solvents.[a]

Entry	Solvent	Result[b]	Photo
1	MeOH (2 mL)	S	
2	DMF (2 mL)	S	
3	DMSO (2 mL) + H_2O (0.2 mL)		
4	DMF (2 mL) + H_2O (0.2 mL)	G	

[a]A mixture of $Rh_2(OAc)_4$ (13.3 mg, 0.03 mmol) and TCPP (23.7 mg, 0.03 mmol) was dissolved in different solvent with sonication. The resultant homogeneous solution was then left to stand at 85°C for *ca* 50 h. [b]G = gel, S = solution.

3. Physical Characterizations

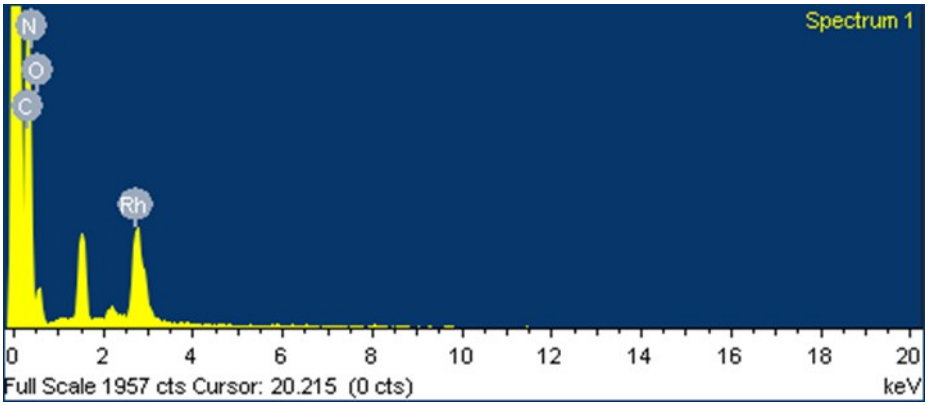
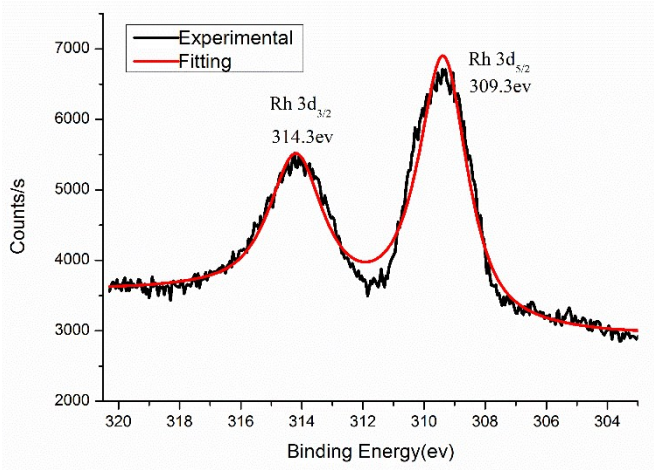
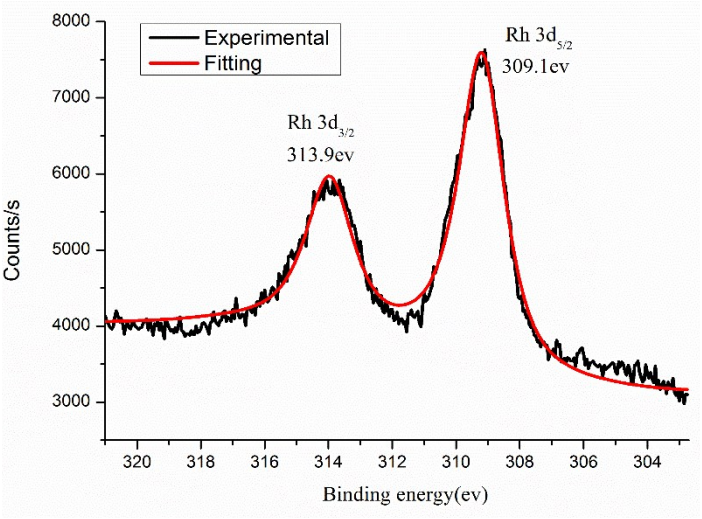


Figure S2. EDS spectra of the aerogels: MOA-Rh-**2**.



(a)



(b)

Figure S3. XPS curves of MOA-Rh-**2** : (a) before the reaction and (b) after the reaction.

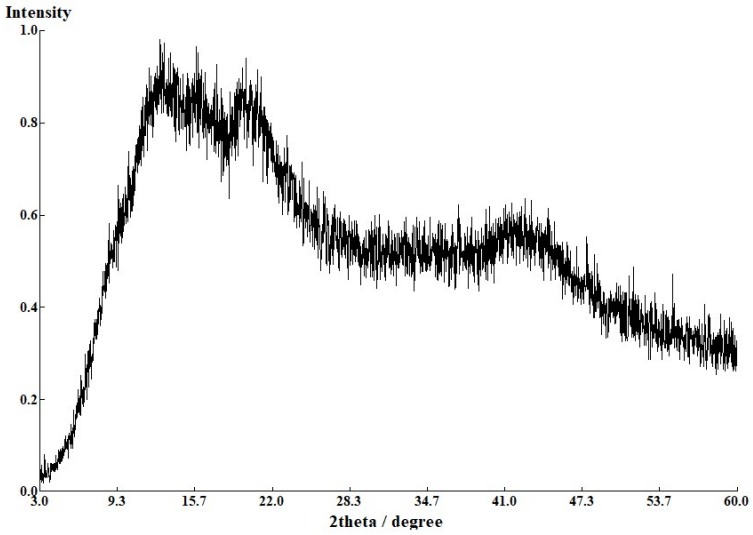


Figure S4. Powder XRD patterns of MOA-Rh-**2**.

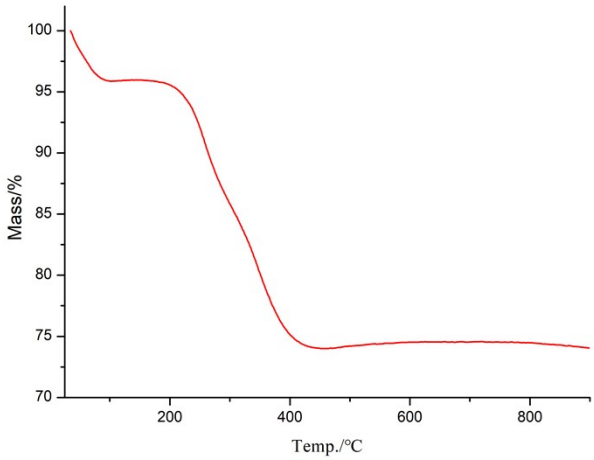


Figure S5. Thermogravimetric analysis of MOA-Rh-**2**.

4. N_2 Adsorption

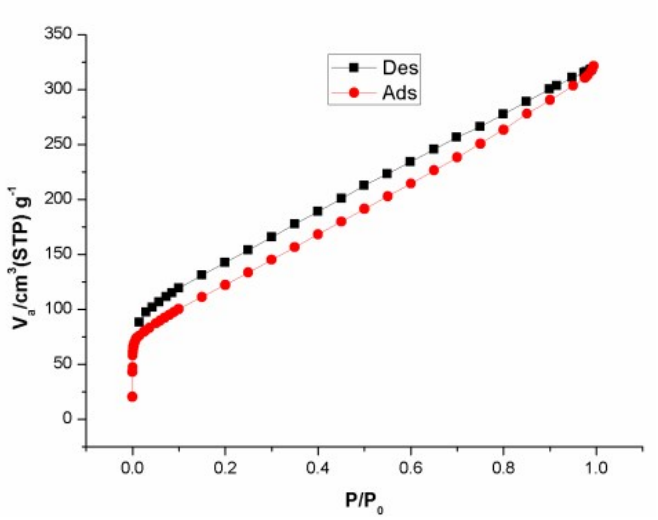


Figure S6. N_2 adsorption/desorption of MOA-Rh-**2** at 77 K.

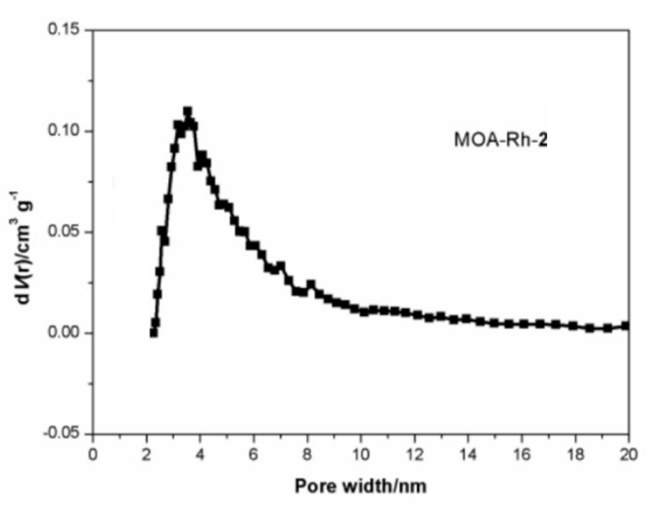
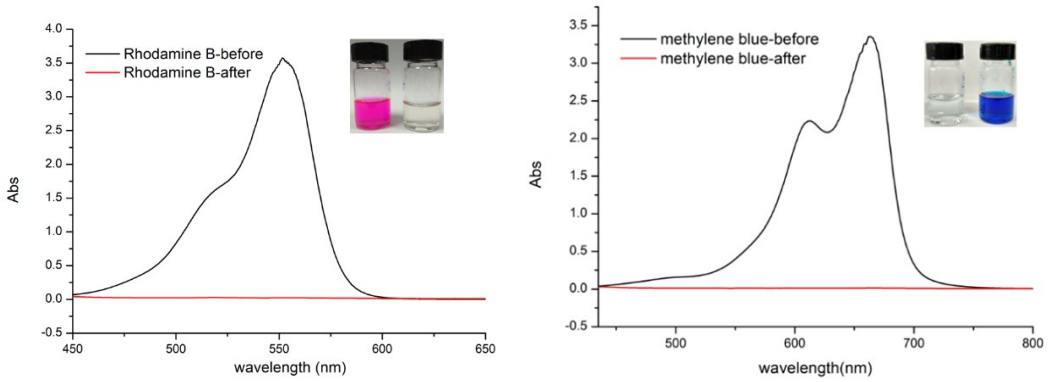


Figure S7. The mesoporous distribution of MOA-Rh-**2**.

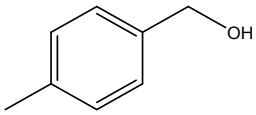
5. Dye Uptake Experiments



(a) (b)

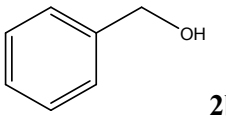
Figure S8. The UV-vis spectra for the dye uptake experiments of MOA-Rh-**2**: (a) Rhodamine B and (b) methylene blue. The inserts show the picture of the dye solution before (light colour) and after (deep colour) dye adsorption.

6. NMR Data of the Products



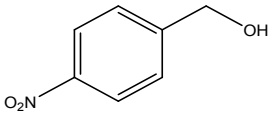
2a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 2H), 4.62 (s, 2H), 2.35 (s, 3H), 1.80 (br, 1H).



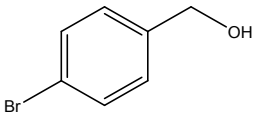
2b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.46 (m, 5 H), 4.61 (d, 2 H, J = 4 Hz), 4.06 (br, 1 H).



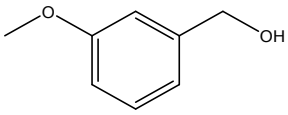
2c

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8 Hz, 2H), 7.56 (d, J = 8 Hz, 2H), 4.86 (d, J = 4 Hz, 2H), 2.10 (t, J = 4 Hz, 1H).



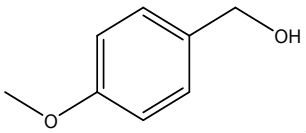
2d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 4.65 (d, J = 8 Hz, 2H), 1.83 (t, J = 8 Hz, 1H).



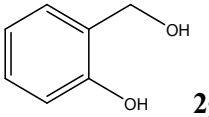
2e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, J = 8 Hz, 1H), 6.89 (d, J = 8 Hz, 2H), 6.82 (s, 1H), 4.60 (s, 2H), 3.77 (s, 3H), 2.43 (br, 1 H).



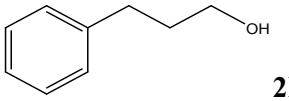
2f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8 Hz, 2H), 6.90 (d, J = 8 Hz, 2H), 4.57 (s, 2H), 3.81 (s, 3H), 2.60 (br, 1 H).



2g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (br, 1H), 7.23 (t, 1H), 7.05 (d, 1H), 6.88 (m, 2H), 4.86 (s, 2H), 2.60 (br, 1 H).



2h

^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.38 - 7.19 (m, 5H), 3.70 (t, J = 6.4 Hz, 2H), 2.74 (t, 2H), 2.26 (br, 1H), 1.93 (m, J = 13.4, 6.8 Hz, 2H).

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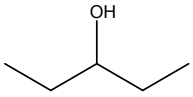
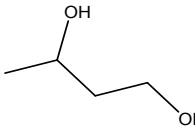


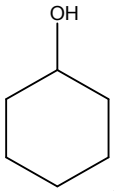
2i

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (m, 1H), 1.58 (m, 4H), 0.94 (t, 6H).



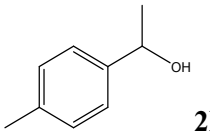
2j

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (m, 1H), 3.67 (t, 2H), 1.52 (q, 2H), 1.08 (d, 3H).



2k

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (m, 1H), 1.46 (m, 4H), 1.33 (m, 4H), 0.89 (m, 2H).



2l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 4.89 (q, 1H), 2.38 (s, 3H), 1.59 (d, 3H).

NMR Data of the Products

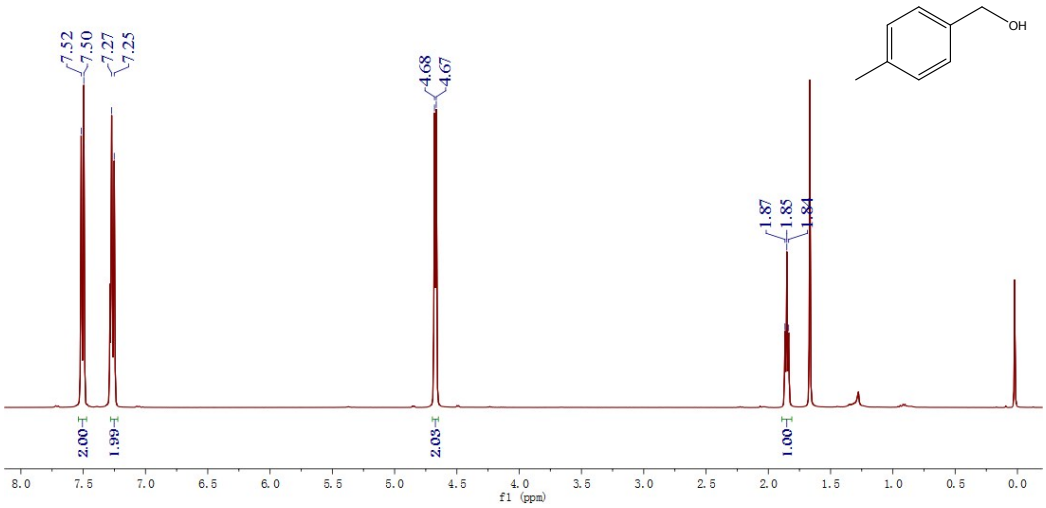


Figure S9a. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *p*-tolylmethanol (**2a**).

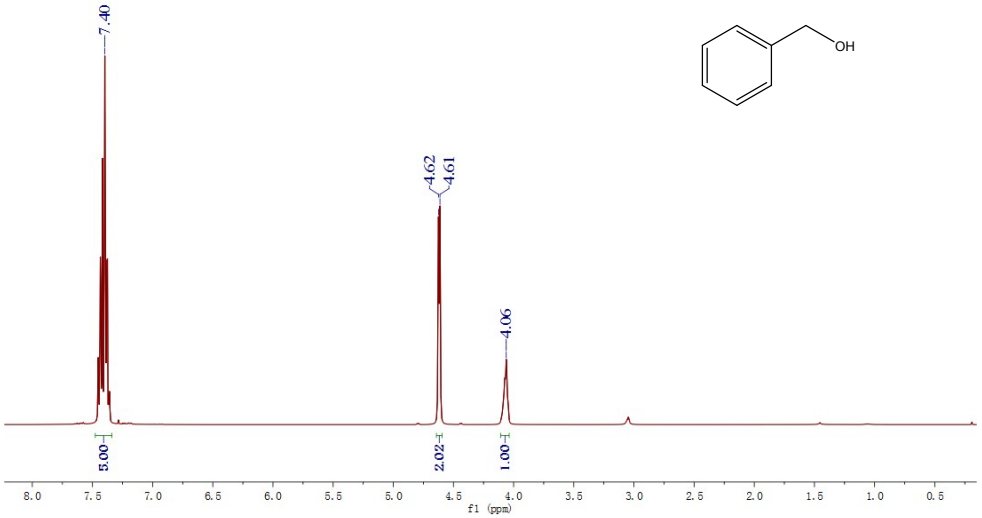


Figure S9b. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of benzyl alcohol (**2b**).

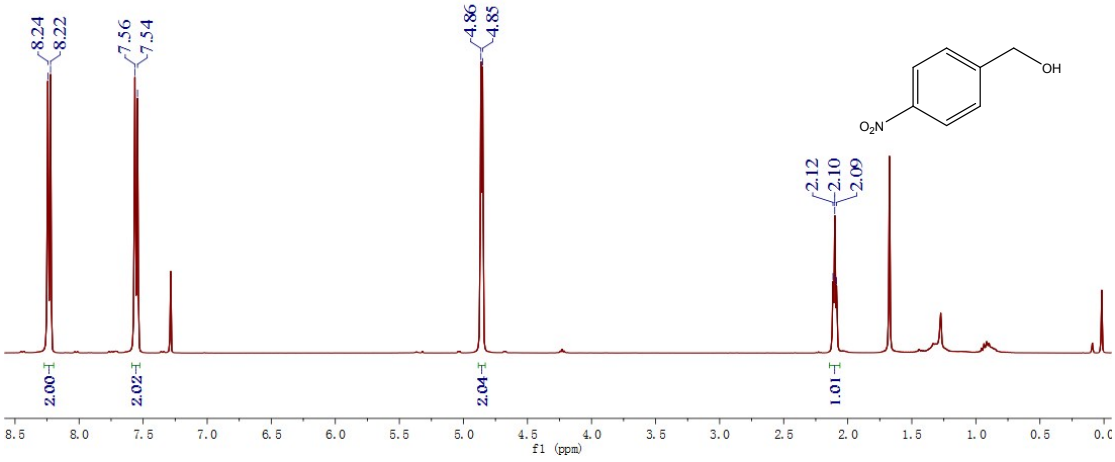


Figure S9c. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (4-nitrophenyl)methanol (**2c**).

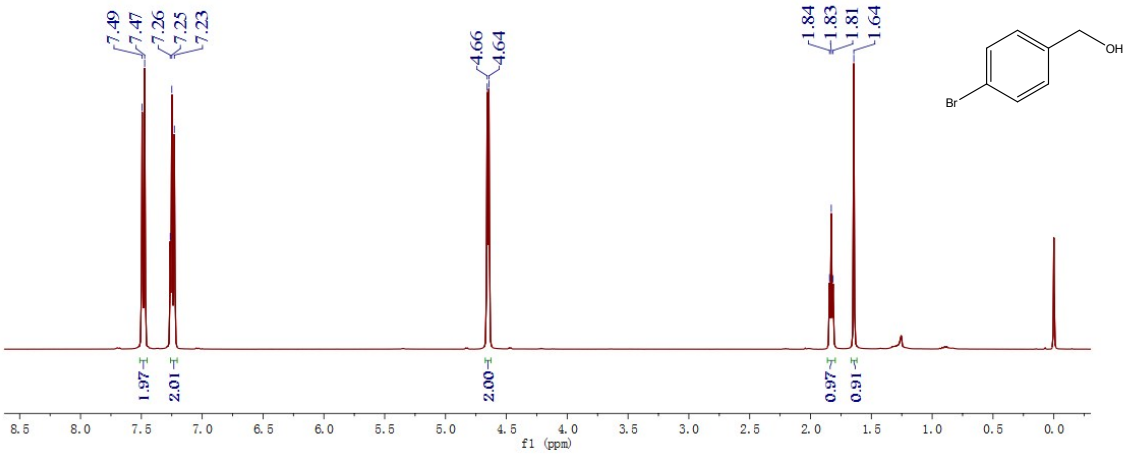


Figure S9d. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of methyl (4-bromophenyl)methanol (**2d**).

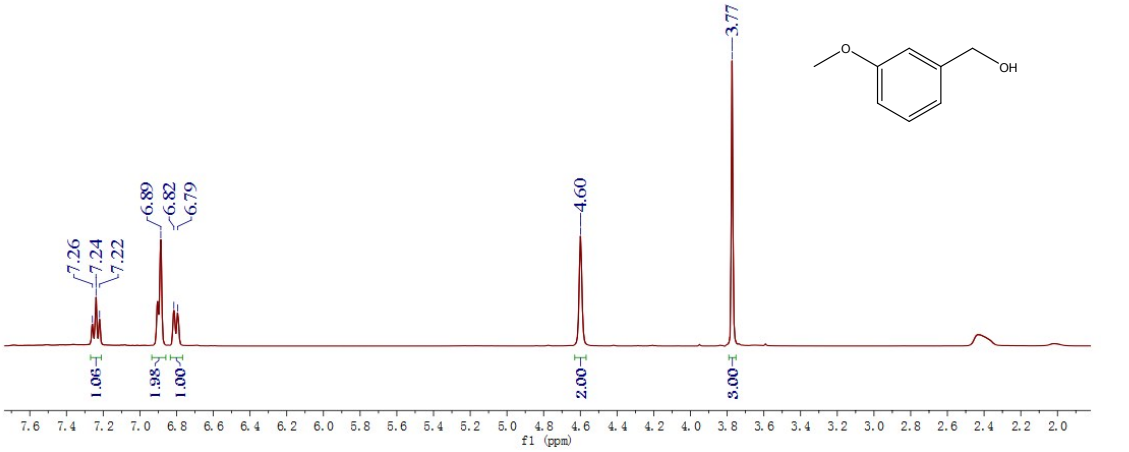


Figure S9e. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of methyl (3-methoxyphenyl)methanol (**2e**).

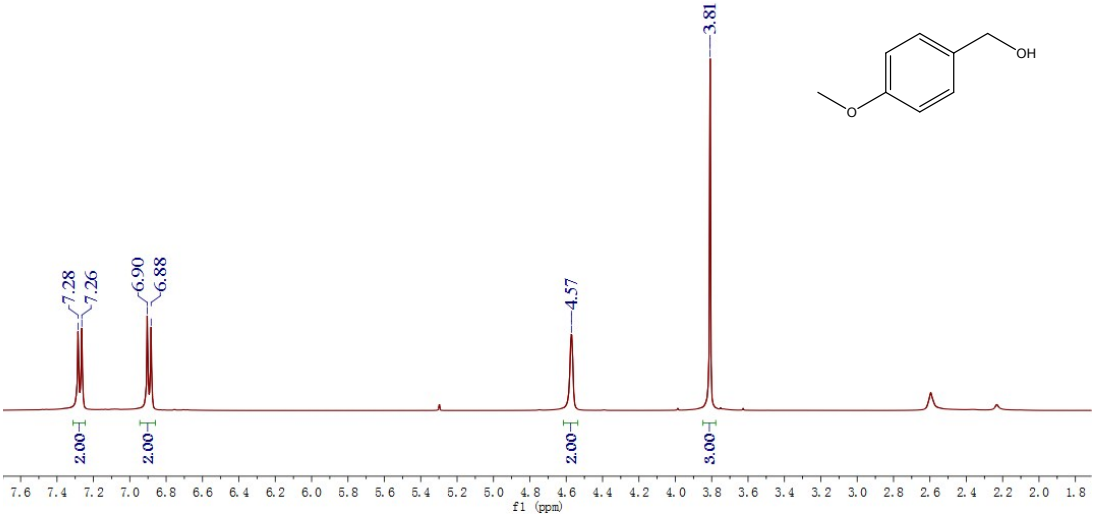


Figure S9f. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (4-methoxyphenyl)methanol (**2f**).

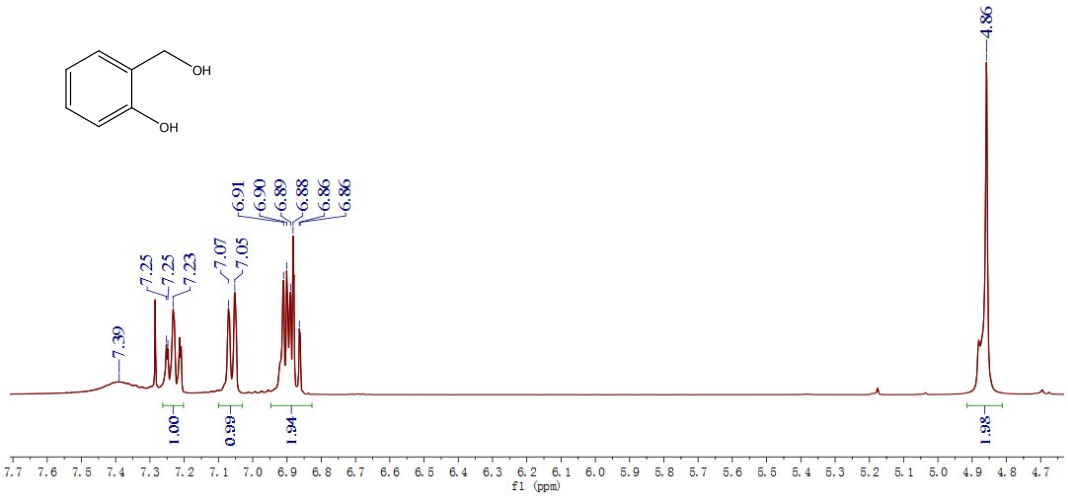


Figure S9g. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(hydroxymethyl)phenol (**2g**).

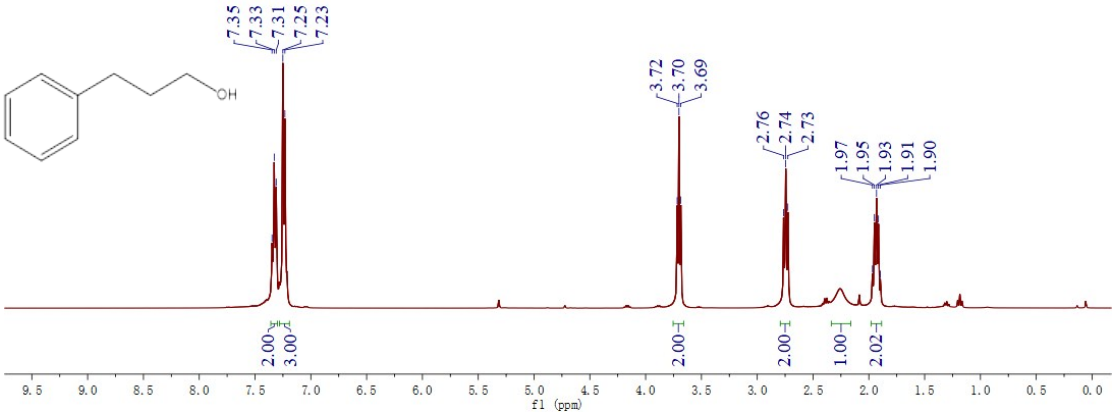


Figure S9h. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of phenylpropanol (**2h**).

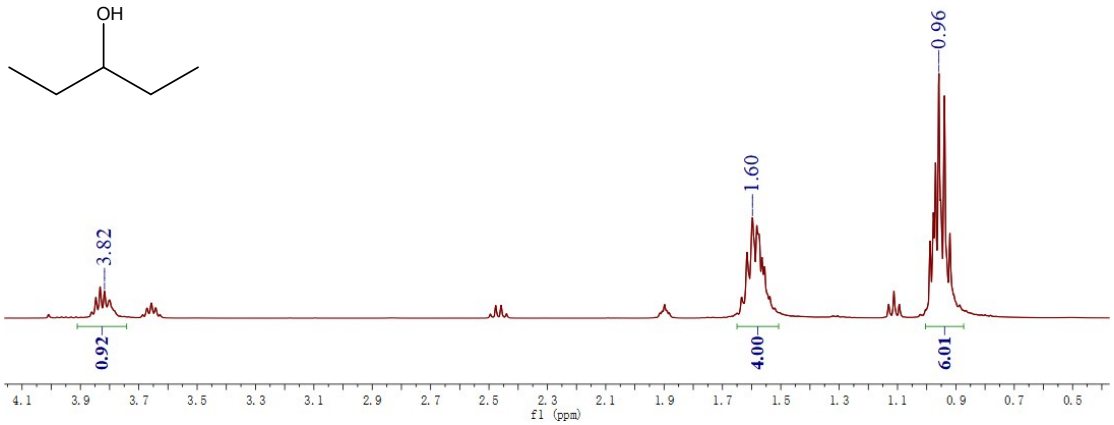


Figure S9i. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-pentanol (**2i**).