

1 **Electronic Supplementary Information**

2 **In-Situ Thermosensitive Hybrid Mesoporous Silica:**
3 **Preparation and the Catalytic Activities for Carbonyl**
4 **Compound Reduction**

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1 **Experimental section**

2 **Materials**

3 Hexadecyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), N-
4 isopropyl acrylamide (NIPAM), 4, azobisisobutyronitrile (AIBN), sodium borohydride
5 (NaBH_4), potassium tetrachloro palladate (K_2PdCl_4), anhydrous dichloromethane (99.9%),
6 anhydrous ethanol (EtOH, 99.8%), benzaldehyde and ethyl acetate were purchased from
7 Sigma-Aldrich. Dichloromethane, diethyl ether, ammonia solution, and HCl were acquired
8 from Dae-Jung Chemical Co. Ltd (Korea). All chemicals were used as received. Throughout
9 the experiment double deionized water was used.

10 **Synthesis of PNIPAM-MCM-41**

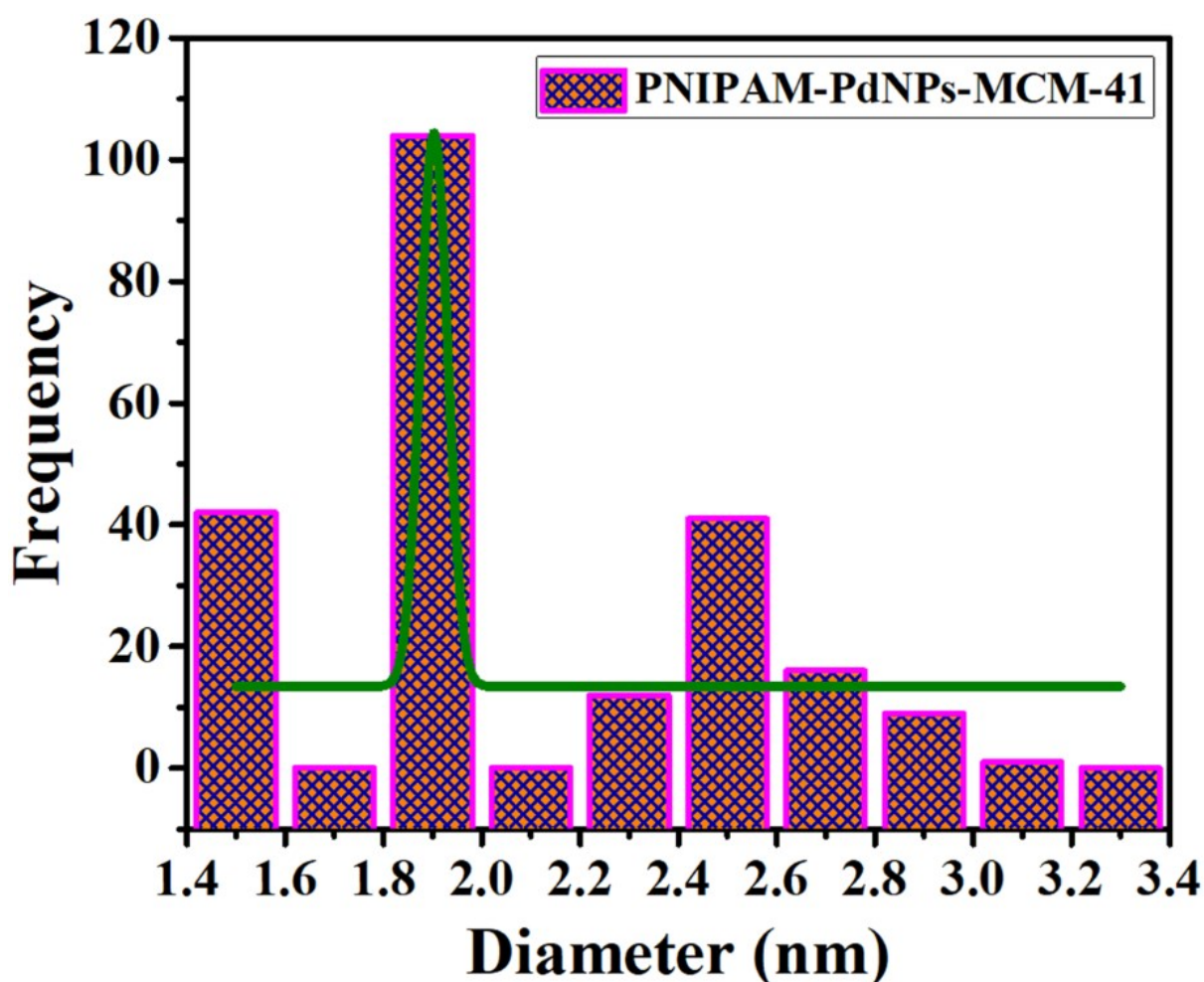
11 0.5 g preheated MCM-41 was introduced, using the wet-impregnation method, into a 1.5 mL
12 dichloromethane solution in a 25 mL Schlenk flask, which contained 0.25 g NIPAM, 0.005 g
13 cross-linker N, N'-Methylenebisacrylamide (MBA), and 0.0164 g AIBN initiator, followed
14 by stirring for about 4 h. Then the mixture was dried at 35 °C in an oven to remove
15 dichloromethane. Subsequently, the obtained product was exposed to conduct three freeze-
16 vacuum-thaw cycles using liquid nitrogen. The monomer incorporated MCM-41 were kept
17 under vacuum for 6 h at 35 °C. For polymerization, the temperature was increased to 80 °C.
18 The obtained product was then soaked in ethanol and acetone to remove unreacted monomers
19 and impurities and dried at 50 °C. The final product obtained was denoted as PNIPAM-
20 MCM-41.

21 **Characterisation techniques**

22 X-ray diffraction (XRD, XPERT-PRO and Bruker AXN) was performed by Cu-K α radiation
23 in the range of $2\theta = 1.2^\circ$ to 10° and $2\theta = 10^\circ$ to 90° . Fourier transform infrared spectroscopy

1 (FTIR, JASCO FTIR-4100) was used for the analysis of surface functional groups at a
2 scanning range of 400-4000 cm^{-1} using potassium bromide (KBr) pellets. The surface
3 morphology of the samples was studied by using field emission scanning electron microscopy
4 (FE-SEM, ZEISS SUPRA 25 VP), which was conducted at an accelerating voltage of 20 kV,
5 and field emission transmission electron microscopy (FE-TEM, JEM-2011) was performed at
6 an accelerating voltage of 200 kV with an attached energy-dispersive X-ray spectroscopy
7 (EDX). Elemental mapping was carried out on FE-TEM images with a high-angle annular
8 dark-field (HAADF) detector. In addition, the average particle size of the samples was
9 measured by using the inbuilt measuring tool in the FE-SEM and FE-TEM instruments and
10 confirmed further by using 'Image J' software. Thermogravimetric analysis (TGA, Q50 V6.2,
11 Build 187, TA instrument, US) was used to check the thermal stability of the material at a
12 heating rate of 10 $^{\circ}\text{C min}^{-1}$ under N_2 atmosphere. Surface area and pore size distribution of
13 the synthesized material were measured by using nitrogen adsorption and desorption isotherm
14 (MICROMERETICS ASAP 2020 V3.04G), which were calculated by using Braunauer-
15 Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively. Before doing
16 N_2 sorption measurement all samples are degassed at 80 $^{\circ}\text{C}$. In the case of MCM-41, after the
17 synthesis, the obtained samples are calcined at 550 $^{\circ}\text{C}$ for 8 h and then preheated at 100 $^{\circ}\text{C}$ in
18 a vacuum oven for further degassing. For the polymer grafted samples, obtained samples are
19 vacuum dried at 80 $^{\circ}\text{C}$ and then degassed at 80 $^{\circ}\text{C}$ before the measurements. X-ray
20 photoelectron spectroscopy (XPS) analysis was used to examine the chemical composition of
21 the synthesized material. XPS spectra were obtained using a Theta Probe AR-XPS system
22 (Thermo Fisher Scientific, UK) employing monochromated Al K α X-rays ($h\nu=1486.6$ eV) at
23 an electron take-off angle of 45 $^{\circ}$. The base pressure of the spectrophotometer was 10^{-9} mbar.
24 The X-ray gun was operated at 15 kV (power 100 W). The analyzer was operated in fixed
25 analyzer transmission mode with a pass energy 300 eV (survey) and 50 eV (narrow). The

1 hydrodynamic diameter of the sample was measured by dynamic light scattering (DLS, Zeta
2 sizer NANO-S90, Malvern) at a series of different temperatures. Gas Chromatography (GC;
3 DS Science IGC 7200) with a flame ionization detector was used to measure the conversion
4 and selectivity for the coupling reaction. We have quantified the conversion and selectivity
5 through GC results and then isolated them through column chromatographic techniques,
6 followed by again confirming the molecular structure of products with ^1H NMR studies. We
7 could not be able to isolate those bi-product complexes in the column chromatographic
8 techniques because of the high selectivity of our catalyst, which converts to our
9 desired product.



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11 **Fig. S2.** (a) Particle size histogram of PdNPs in PNIPAM-PdNPs-MCM-41.

1 **Table S1** Comparison of PNIPAM-PdNPs-MCM-41 catalytic activity with previously
2 reported ones

Entry	Catalyst	H ₂ source	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref.
1	BCA-Pd	10 bar H ₂	Toluene	100	6	85	[1]
2	Ni-Cu	4 MPa H ₂	H ₂ O	160	4	99	[2]
3	Pd(0)-EDA/SC-2	H ₂	H ₂ O/EtOH	25	1	95	[3]
4	Cu-Mg-Al	--	IPA	150	6	100	[4]
5	Wet-SiO ₂	NaBH ₄	--	75	0.7	97	[5]
6	PNIPAM- PdNPs-MCM-41	NaBH ₄	H ₂ O	25	1	99	This work

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4 **References**

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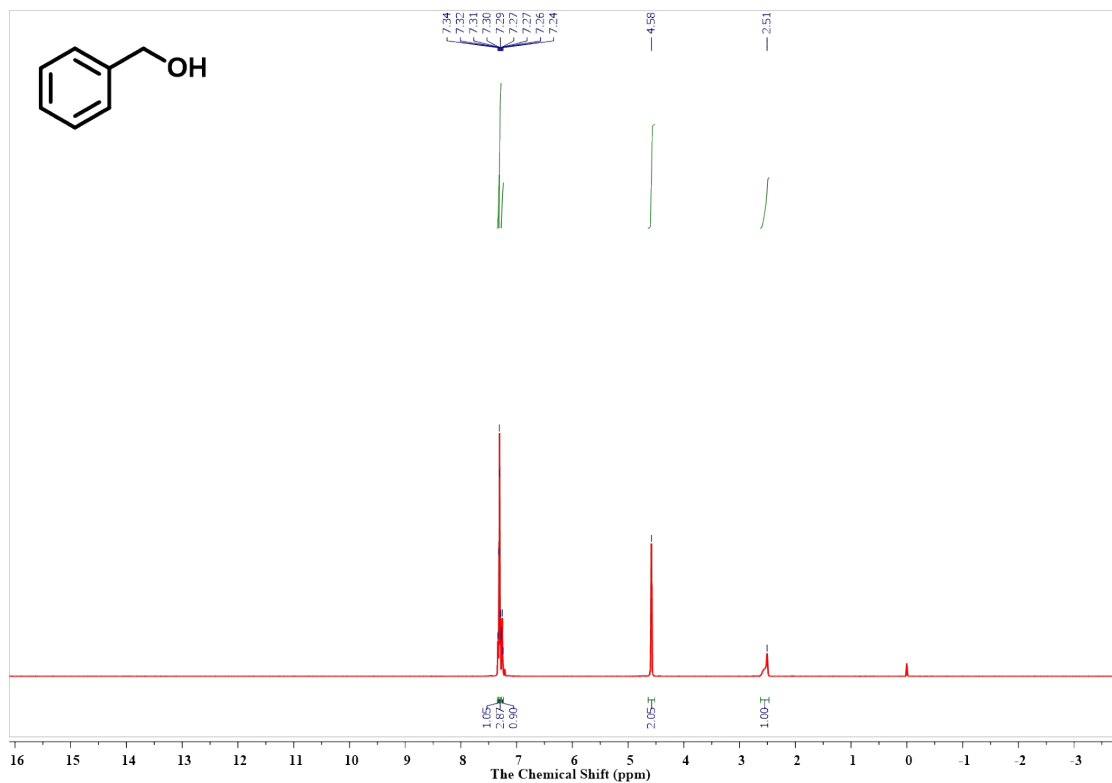
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1 Benzyl alcohol

- 2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.33 (d, $J = 7.4$ Hz, 1H), 7.32 – 7.28 (m, 3H), 7.26 (dd, $J =$
3 11.0, 4.2 Hz, 1H), 4.58 (s, 2H), 2.51 (s, 1H).



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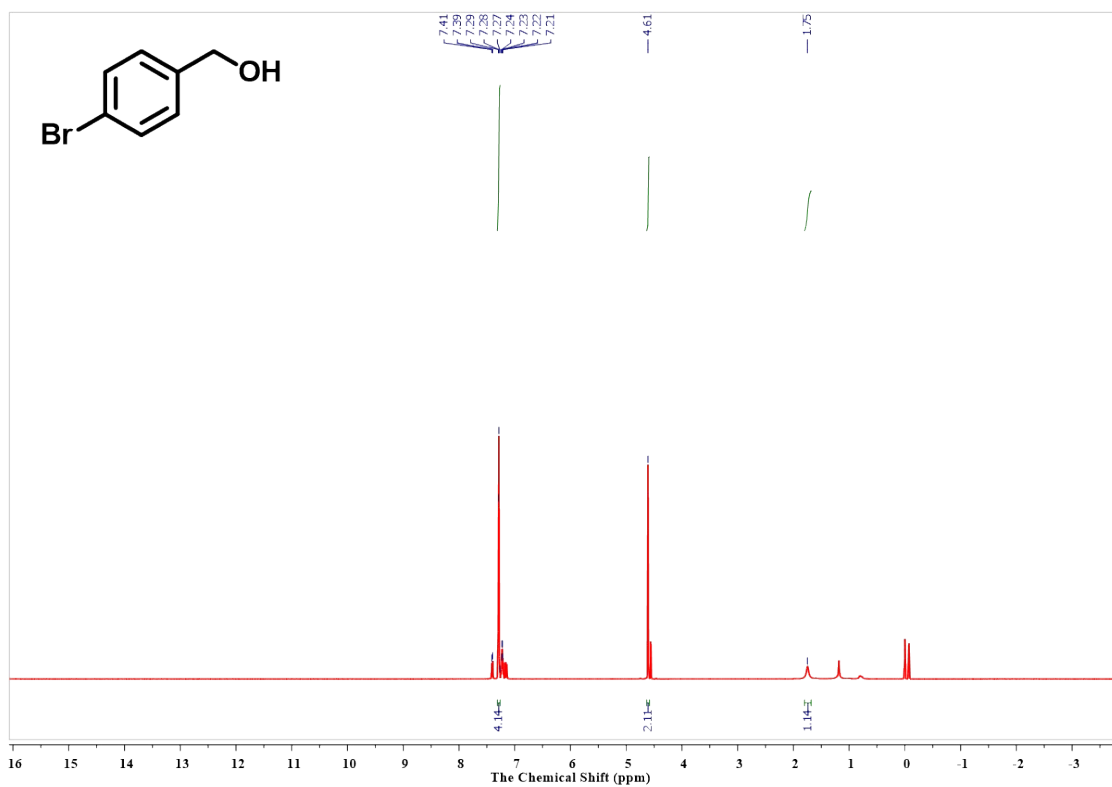
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1 4-Bromobenzyl alcohol

- 2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.33 (d, $J = 7.4$ Hz, 1H), 7.32 – 7.28 (m, 3H), 7.26 (dd, $J =$
3 11.0, 4.2 Hz, 1H), 4.58 (s, 2H), 2.51 (s, 1H).



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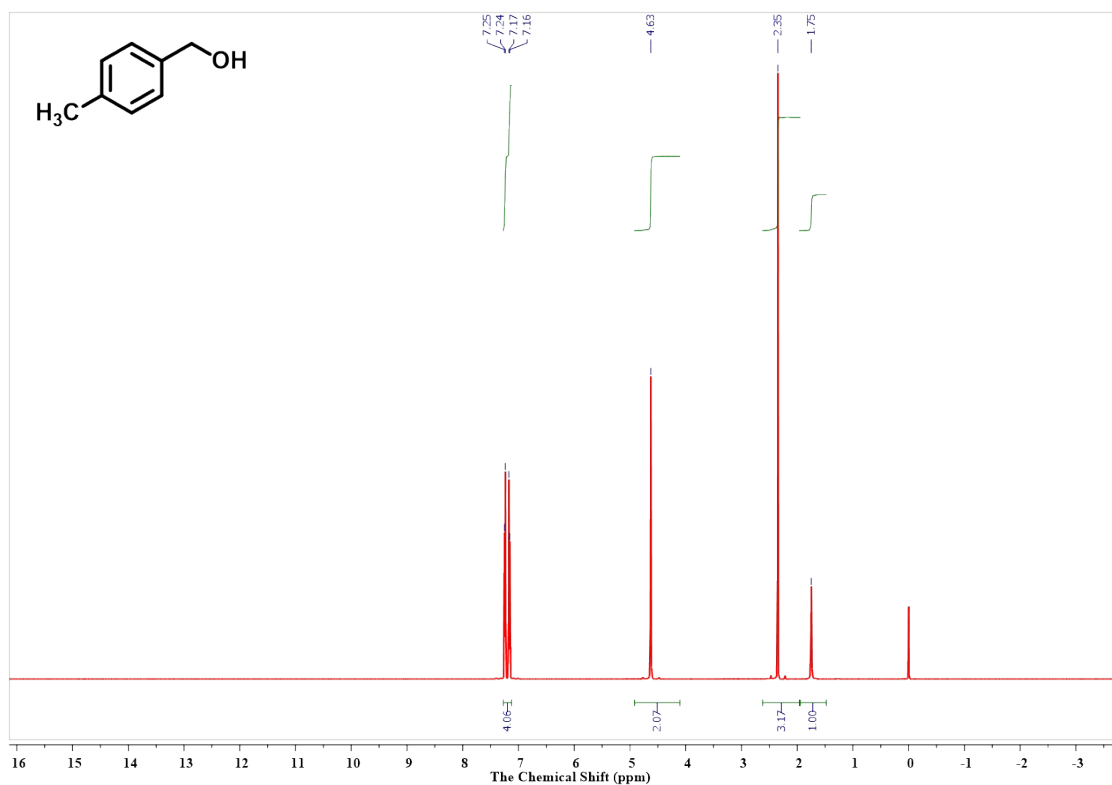
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1 **4-Methylbenzyl alcohol**

2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.20 (dd, $J = 40.4, 7.8$ Hz, 4H), 4.63 (s, 2H), 2.35 (s, 3H), 1.75

3 (s, 1H).



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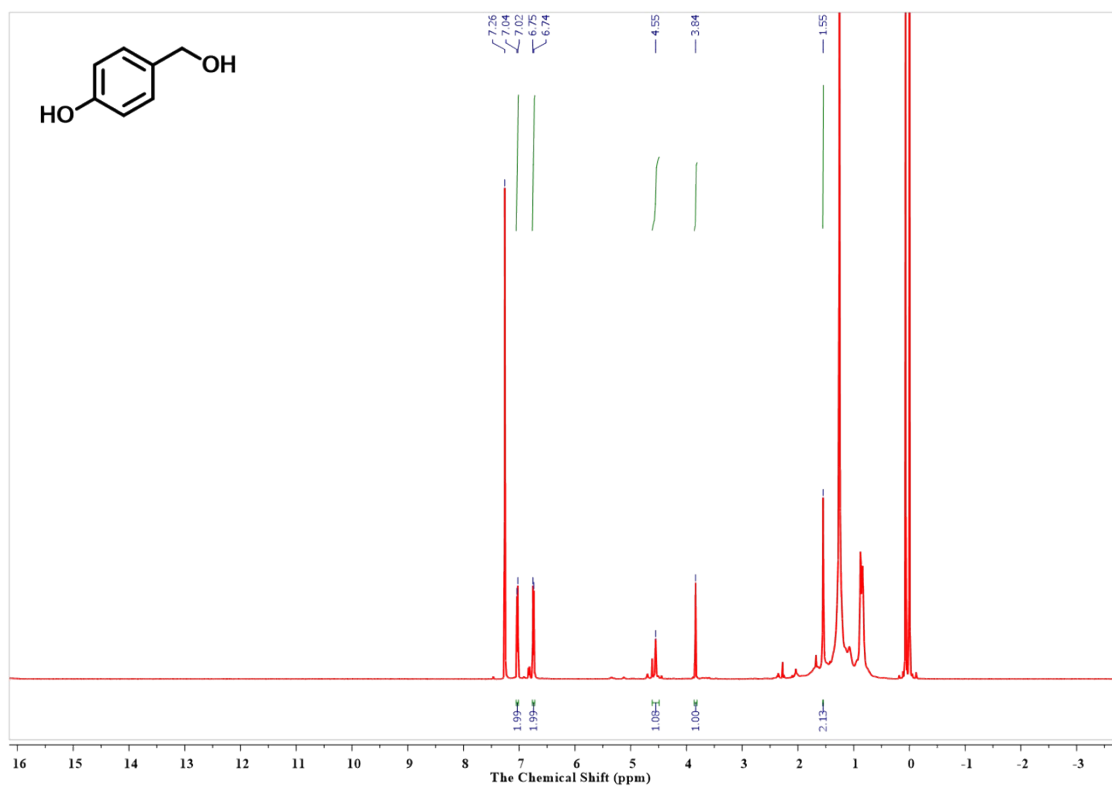
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1 4-Hydroxybenzyl alcohol

2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.03 (d, $J = 7.9$ Hz, 2H), 6.75 (d, $J = 7.6$ Hz, 2H), 4.55 (s, 1H),

3 3.84 (s, 1H), 1.55 (s, 2H).



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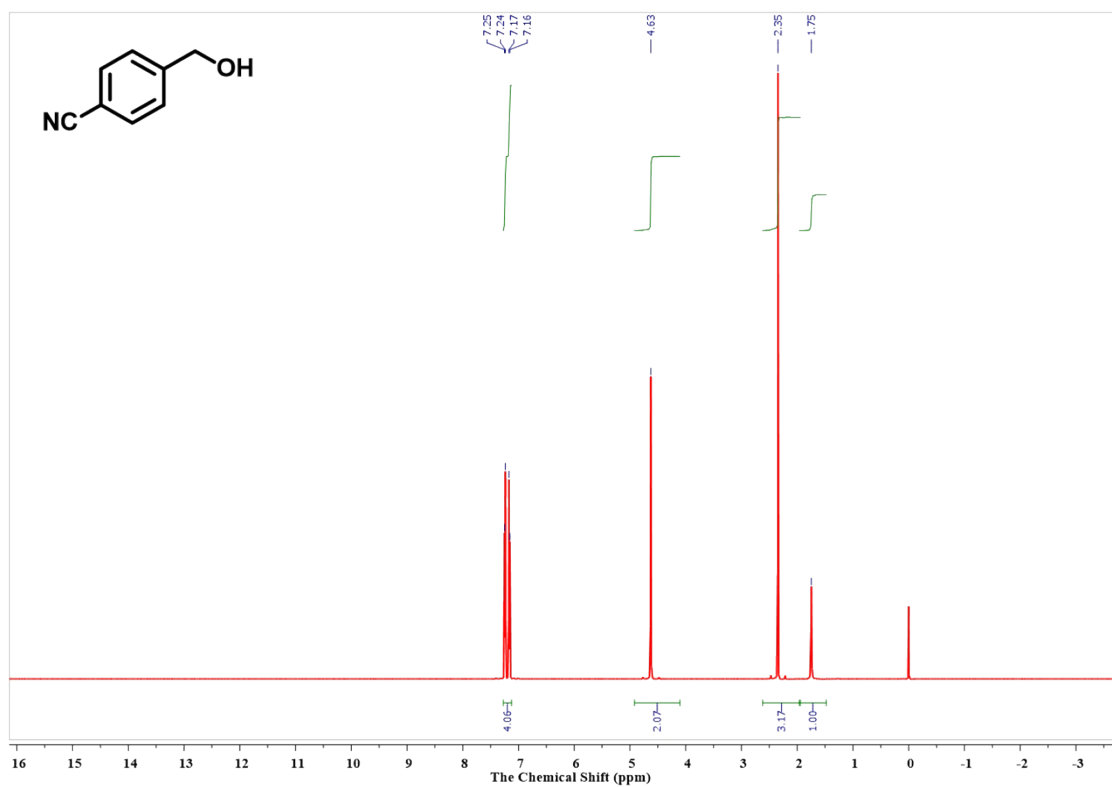
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1 4-Cyanobenzyl alcohol

2 ^1H NMR (500 MHz, CDCl_3) δ 7.63 (d, $J = 7.9$ Hz, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 4.77 (s, 1H),

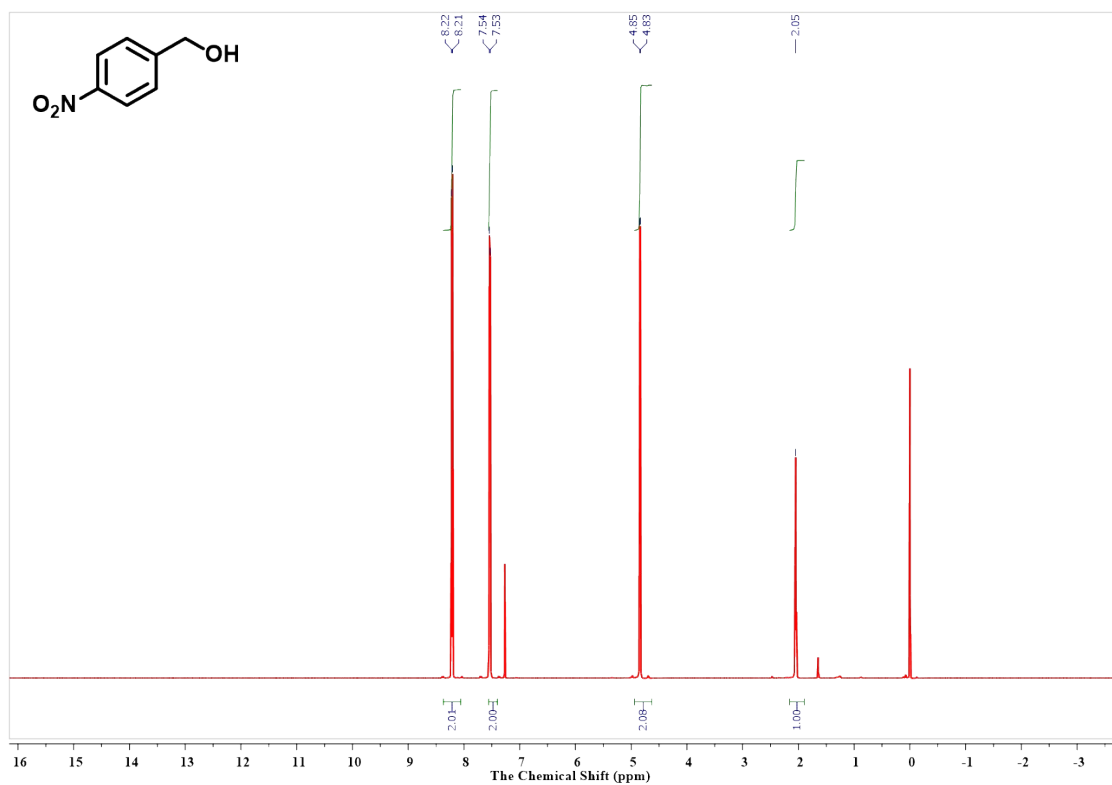
3 2.27 (s, 1H).



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1 4-Nitrobenzyl alcohol

- 2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.21 (d, $J = 8.7$ Hz, 2H), 7.54 (d, $J = 8.7$ Hz, 2H), 4.84 (d, $J =$
3 5.5 Hz, 2H), 2.05 (s, 1H).

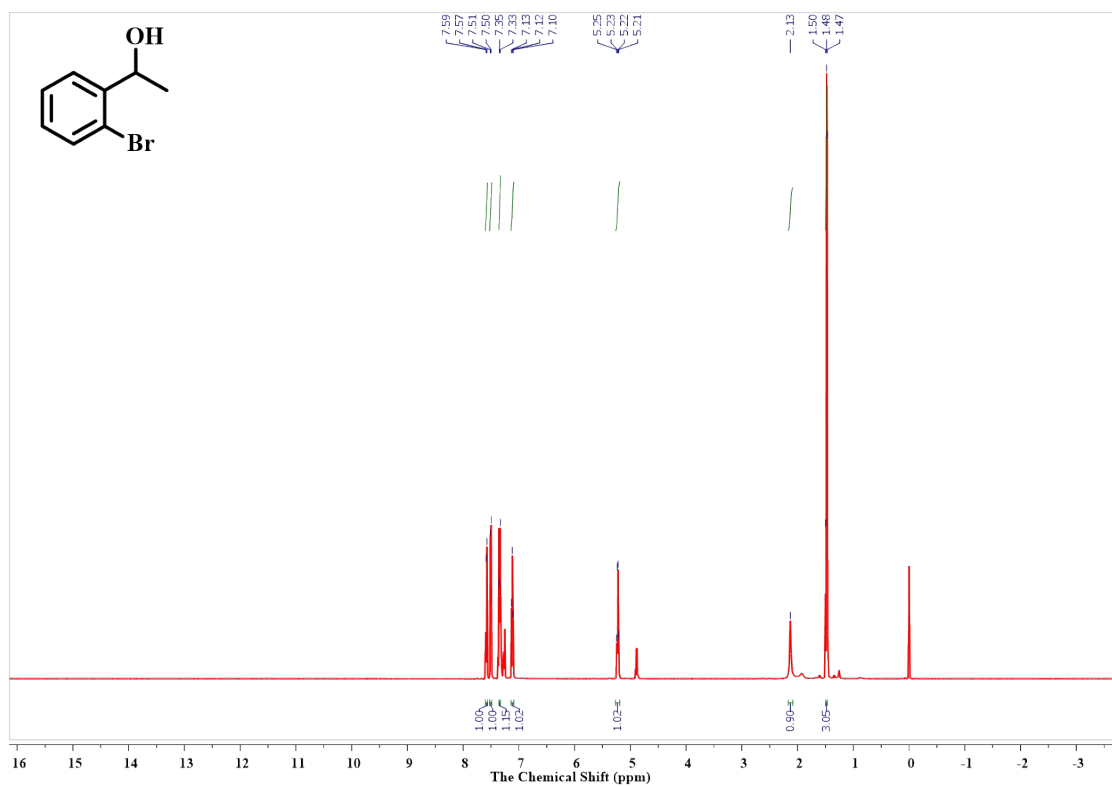


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1 **1-(2-Bromophenyl)ethanol**

2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.76 – 7.00 (m, 1H), 5.23 (q, $J = 6.4$ Hz, 1H), 2.13 (s, 1H),

3 1.48 (t, $J = 7.1$ Hz, 1H).



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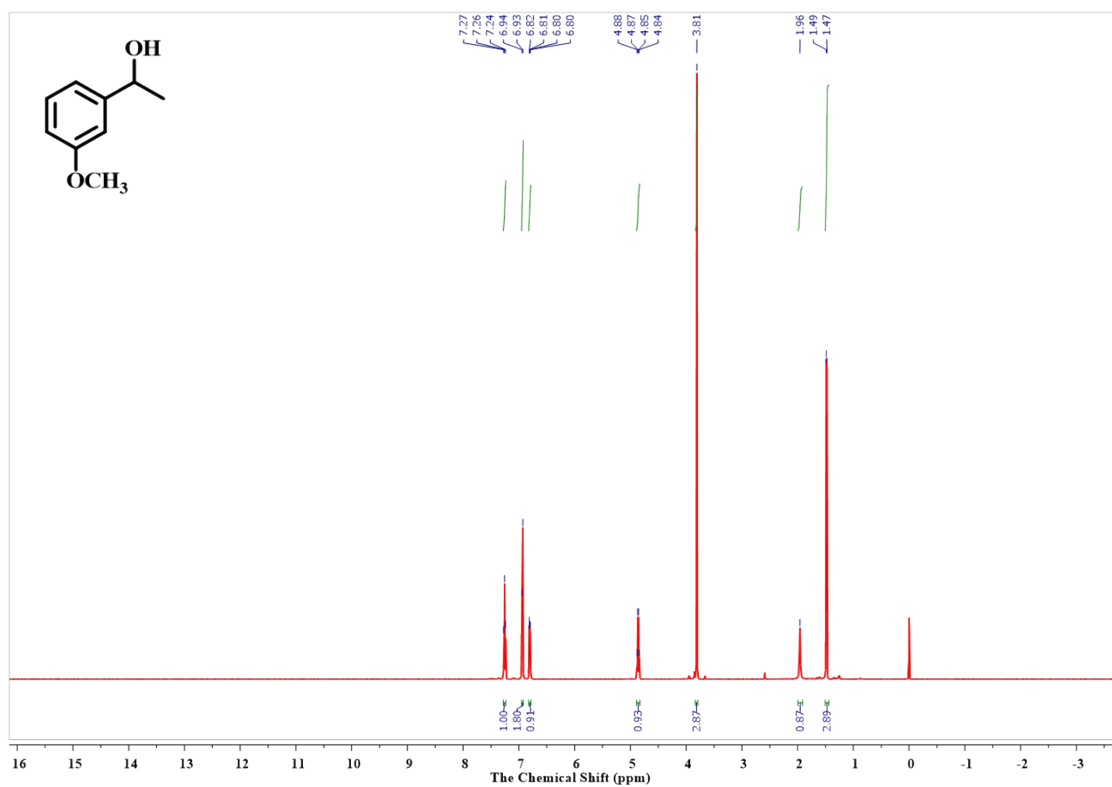
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1 1-(3-Methoxyphenyl)ethanol

- 2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.26 (t, $J = 8.1$ Hz, 1H), 6.94 (d, $J = 6.5$ Hz, 2H), 6.81 (dd, $J =$
3 8.1, 1.4 Hz, 1H), 4.86 (q, $J = 6.4$ Hz, 1H), 3.81 (s, 1H), 1.96 (s, 1H), 1.48 (d, $J = 6.5$ Hz, 1H).



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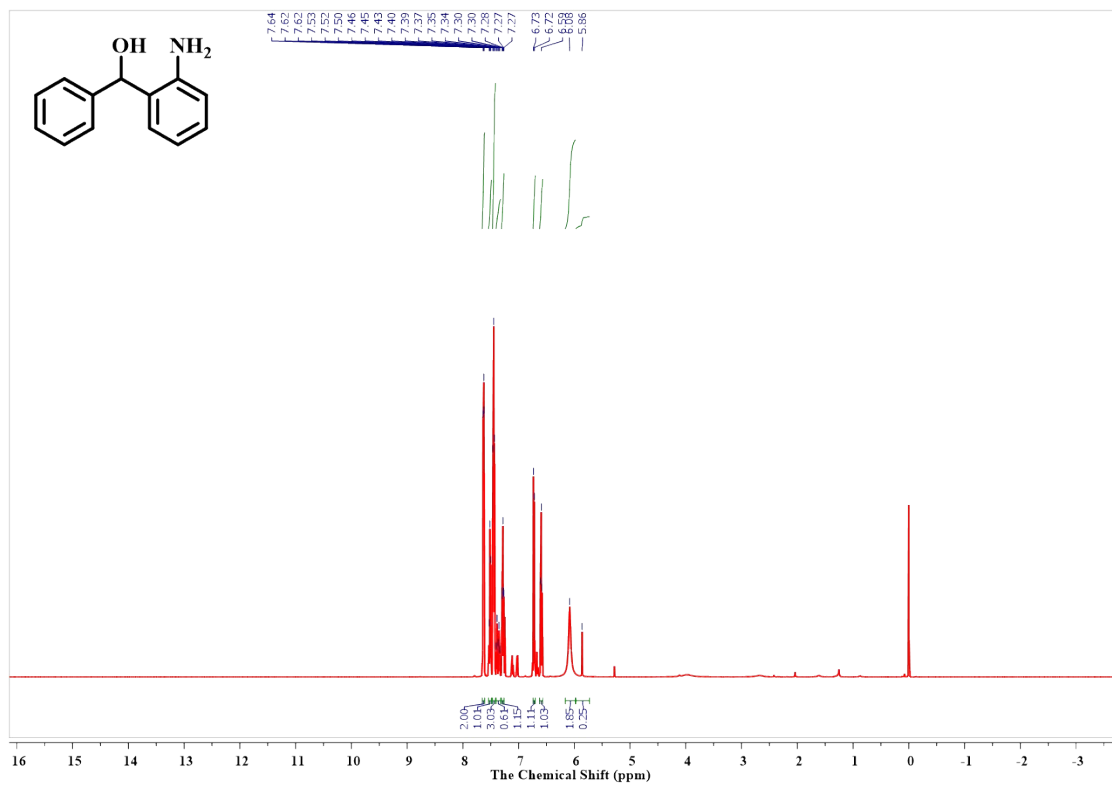
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1 **(2-Aminophenyl)(phenyl)methanol**

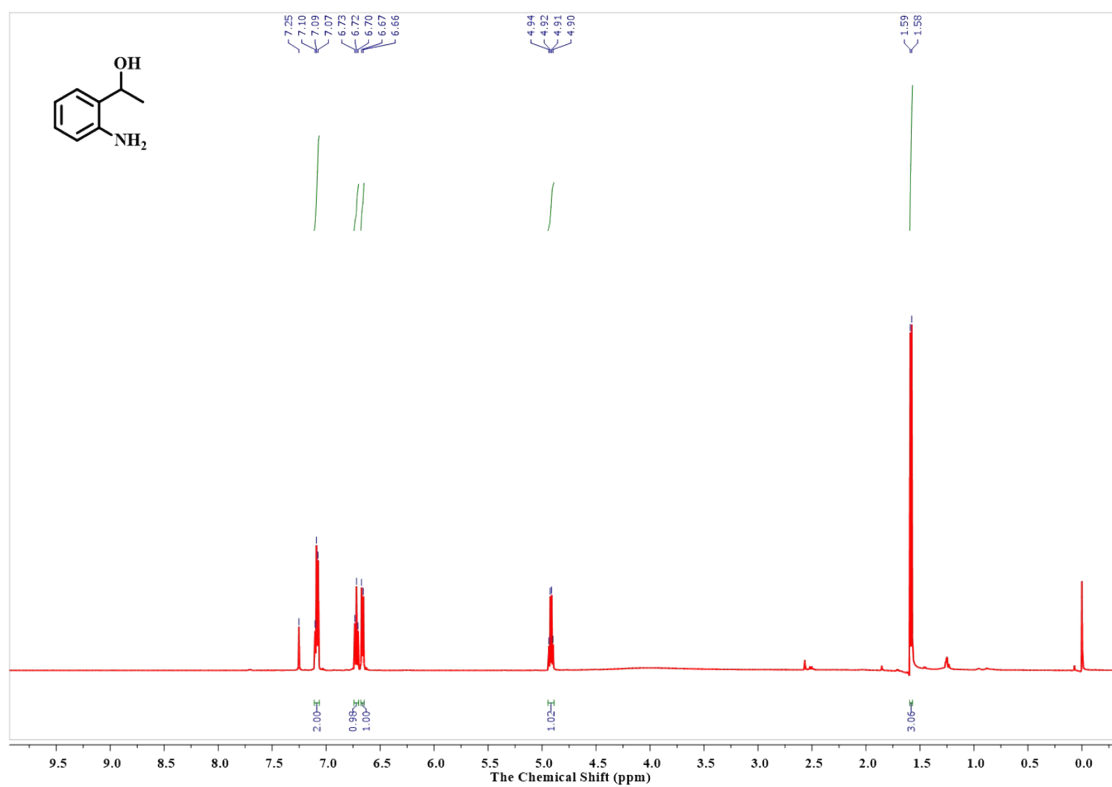
- 2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.26 (t, $J = 8.1$ Hz, 1H), 6.94 (d, $J = 6.5$ Hz, 2H), 6.81 (dd, $J =$
3 8.1, 1.4 Hz, 1H), 4.86 (q, $J = 6.4$ Hz, 1H), 3.81 (s, 1H), 1.96 (s, 1H), 1.48 (d, $J = 6.5$ Hz, 1H).



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1 1-(2-aminophenyl)ethanol

- 2 $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.09 (t, $J = 6.8$ Hz, 2H), 6.72 (t, $J = 7.4$ Hz, 1H), 6.66 (d, $J = 8.1$ Hz, 1H), 4.92 (q, $J = 6.6$ Hz, 1H), 1.58 (d, $J = 6.6$ Hz, 3H).



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