Supplementary Information

Dual reaction pathway catalysis: Base free transfer hydrogenation of aromatic aldehydes by NiAl LDH catalyst via *in situ* Ni(0) formation

Anitya Sharma[a], Sahil Kumar[a,#] Devendra Sharma[a,#]
Ashish Bahuguna[b] and Venkata Krishnan[a*]
[a] School of Chemical Sciences and Advanced Materials Research Center,
Indian Institute of Technology Mandi, Kamand, Mandi 175075, Himachal Pradesh, India.
[b] Dr. Ambedkar Centre of Excellence, Hemvati Nandan Bahuguna Garhwal University (A Central University), Srinagar Garhwal, 246174, Uttarakhand, India.
Email: vkn@iitmandi.ac.in
[#]S.K. and D.S. contributed equally to this work.

S1. Materials characterization

Powder X-ray diffraction (PXRD) measurements were conducted in the 2θ range from 5° to 80° with a scan rate of 2° min^{-1} and a step size of 0.02°, using a Rigaku SmartLab 9 kW rotating anode X-ray diffractometer. The instrument was operated at 45 kV and 100 mA in Bragg-Brentano configuration with a Cu-sealed tube (Cu K_α X-rays of 0.1541 nm). A Rigaku MiniFlex tabletop X-ray spectrometer was also employed for the PXRD measurements operating at 40 kV and 15 mA with a Cu-sealed tube (Cu K_α X-rays of 0.1541 nm). Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed using a PerkinElmer Spectrum 2 spectrometer, covering a range of 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) of the as-synthesized catalysts was carried out from 25 °C to 800 °C under N_2 atmosphere, with a heating rate of 10 °C min^{-1} and a flow rate of 40 mL min^{-1}, using a Netzsch STA 449 F1 Jupiter instrument. Raman analysis was carried out using Renishaw Invia Raman Microscope at excitation wavelength of 532 nm. Thermo Scientific NEXSA X-ray photoemission spectrometer (XPS) with Al-K_α (1486.6 eV) radiation was used to investigate the chemical state and composition of the catalyst. The XPS data were deconvoluted using Avantage software. Surface area, pore size, and pore volume were determined using Quanta chrome Autosorb-iQ-MP-XR system at 77 K. Prior to the analysis, degassing of samples was done at 120 °C for 19 h. The determination of basic sites was performed using organic titration method using bromothymol blue (BTB) as indicator. Morphological analysis of the material was conducted using a scanning electron microscope (SEM) FEI Nova SEM-450. For this, samples were prepared by dispersing 2 mg of powdered material in ethanol, followed by sonication for 15 min, and finally drop-casting them onto a silicon wafer. Technai G 20 (FEI) S-twin microscope operating at 200 kV was used to get transmission electron microscope (TEM) images. For TEM measurement, a highly diluted sample dispersed in ethanol was drop-casted on carbon-coated copper grid. Nuclear magnetic resonance (NMR) spectra were measured using a JEOL-USA (JNMECX500) spectrometer in $CDCl_3$ and DMSO-d6 with TMS (tetramethylsilane) as an internal standard. The ^{1}H and ^{13}C chemical shifts were quantified in ppm, with respect to 7.26 and 77.23 for the $CDCl_3$ solvent and 2.50 and 39.50 for the DMSO-d6 solvent. All ^{1}H NMR spectra were measured at a frequency of 500 MHz, while ^{13}C NMR spectra were measured at a frequency of 125 MHz.

S2. Yield calculation

The yield of benzyl alcohol and its corresponding substrate scope counterparts was calculated by using the NMR method. Typically, 1 mmol (105 µL) of 1,1,2,2-tetrachloroethane was used as an internal standard along with 700 µL $CDCl_3$ and reaction mixture for the NMR analysis. The following formula was used to calculate the yield of the benzyl alcohol relative to internal standard.

$$\text{Yield (\%)} = \frac{Number\ \ of\ moles\ of\ product}{Number\ of\ moles\ of\ reactant} \text{ x } 100$$

$$\frac{Number\ of\ moles\ of\ product}{Number\ of\ moles\ of\ intenal\ standard} = \frac{\frac{Integral\ area\ of\ product\ peak}{Number\ of\ proton\ crossponding\ to\ peak}}{\frac{\text{Integrated area of internal standatd peak}}{Nunber\ of\ proton\ crossponding\ to\ peak\ (Internal\ standard)}}$$

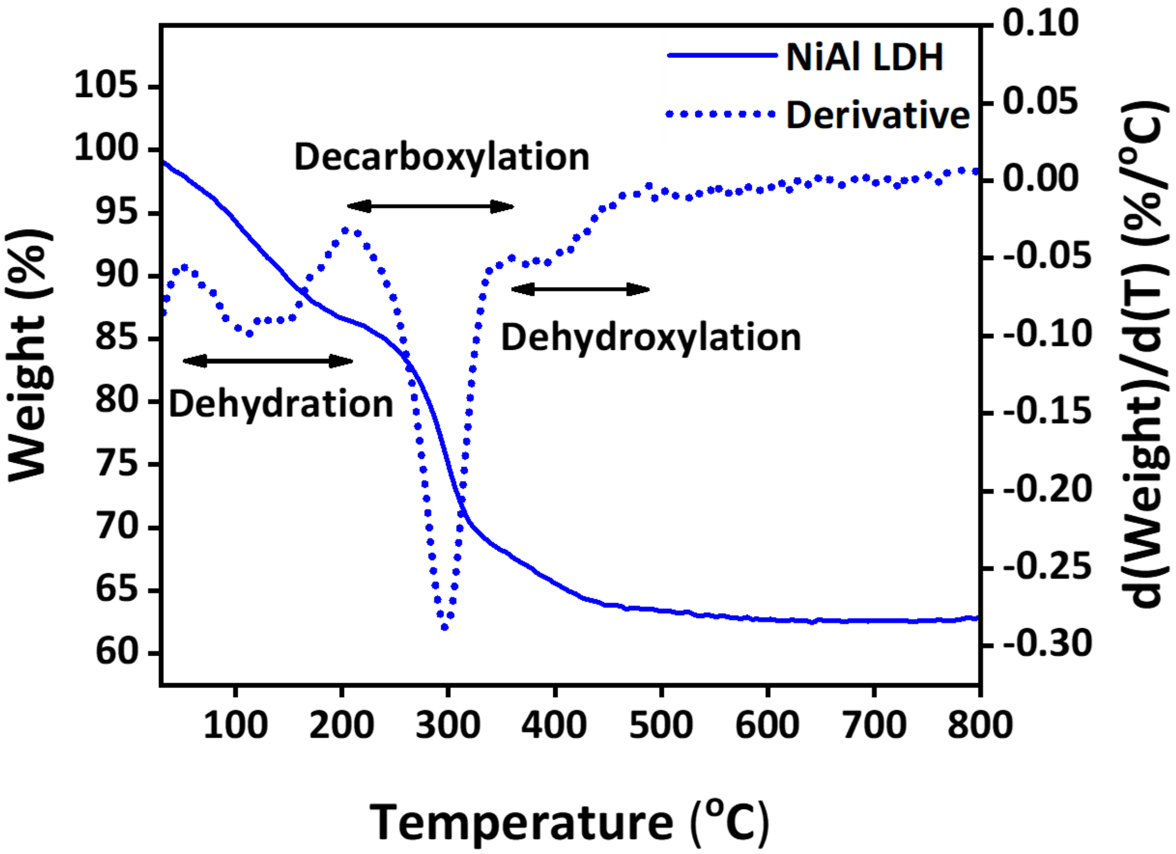
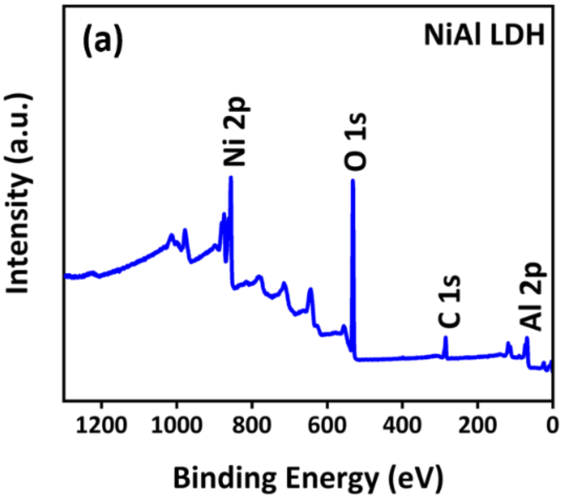


Fig. S1 (a) TGA and DTG plot of NiAl LDH.



(b)

Sl. No.	Element	Atomic percentage
1.	O-1s	56.17
2.	Ni-2p	18.22
3.	C-1s	19.18
4.	Al-2p	6.43

Fig. S2 (a) XPS survey spectrum of NiAl LDH and (b) table showing the atomic percentage of different elements in NiAl LDH.

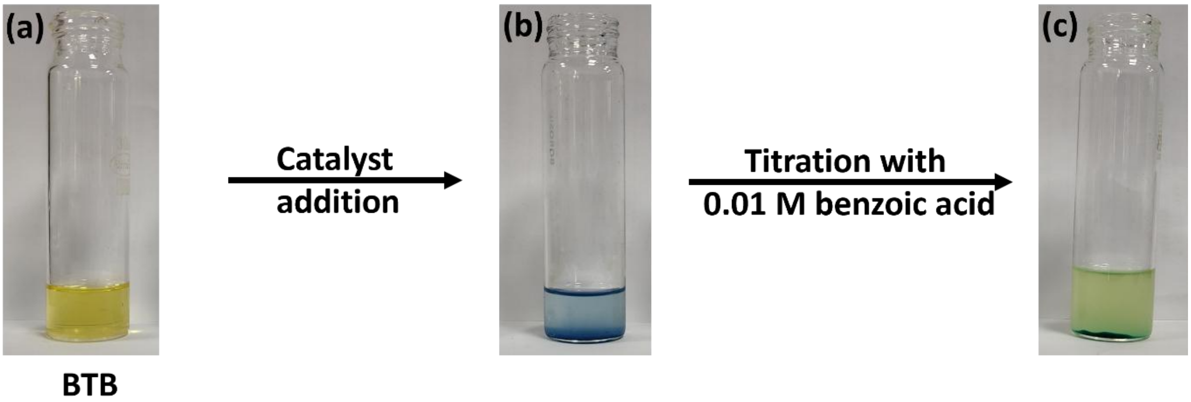


Fig. S3 (a) Pure bromothymol blue (BTB) solution, (b) solution after addition of catalyst, and (c) solution after titration with benzoic acid.

S3. Basicity calculation

The total basicity of NiAl LDH was calculated using organic acid method. Typically, 50 mg catalyst was added to 5 mL of 2 x 10^{-5} M bromothymol blue solution. The solution was stirred for about 30 min and then titrated against 0.01 M benzoic acid solution. The following formula was used for the calculation of basicity.

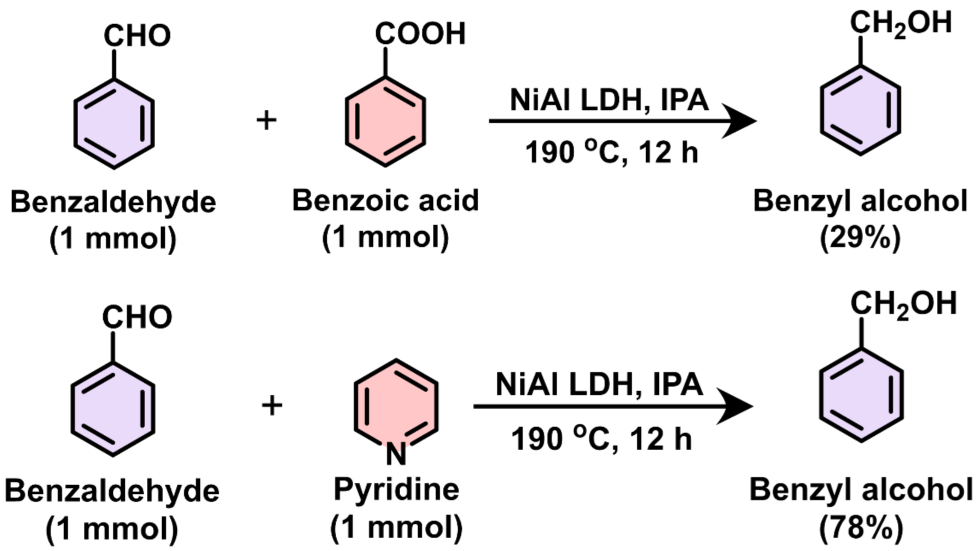
$$\text{Total basicity (mmol g}^{-1}\text{)} = \frac{Concentration\ of\ benzoic\ acid\ (M) \times Volume\ (L)}{Amount\ of\ catalyst\ (g) \times 1000}$$

Table S1 Comparison of as-synthesized catalyst with reported catalysts for hydrogenation of benzaldehyde.

SI. No.	**Catalyst**	**Hydrogen source**	**Additive**	**Temp. (°C)**	**Time (h)**	**Solvent**	**Yield (%)**	**Ref.**
1.	Ru-ED-POM	HCOONa (3 mmol)	1 MPa N_2	110	1	H_2O	98	[1]
2.	Ni-Sac/NC	2-ProOH (8 mL)	2 MPa N_2	140	4	2-ProOH	93.2	[2]
3.	Pt_2/mpg-C_3N_4	H_2:N_2 (1:1) (8 MPa)	1 MPa N_2	120	7	IPA	99	[3]
4.	5 wt% Pt/C	MeOH (3 mL)	NaOH (2 mmol)	130	16	MeOH	85	[4]
5.	Ni-GCN	NaH_2PO_2 (37.5 mg)	-	150	16	H_2O + EtOH	96	[5]
6.	0.3 wt% Ir/ZnO (1 mol% Ir)	MeOH (1.5 mL)	0.5 MPa N_2	110	7	MeOH	95	[6]
7.	MgCoMo HT	H_2 (10 bar)	-	120	8	EtOH	96	[7]
8.	Fe-ZIF-8-800	IPA (3 mL)	-	120	6	IPA	93.5	[8]
9.	Ru-MSP-II	HCOOK (6 mmol)	-	82	1	H_2O	100	[9]
10.	NiO (P)-300	IPA (10 mL)	-	140	3 h	IPA	95.7	[10]
11.	SnO-MgO	IPA (30 mL)	0.1 MPa (N_2)	100	3 h	IPA	99.8	[11]
12.	Zr-HTC	IPA (24.5 g)	-	110	4 h	IPA	98.8	[12]
13.	Mg_3-Al_1@C	IPA (30 mL)	0.1 MPa (N_2)	100	1 h	IPA	99.1	[13]

14.	NiAl LDH	IPA (5 mL)	-	190	12	IPA	94	This work

Description: Ru-ED-POM = Composite between cationic Ru complexes and Wells-Dawson polyoxometalate anion, Ni-Sac/NC = Ni single-atoms supported on nitrogen doped carbon, Pt_2/mpg-C_3N_4 = mesoporous graphitic carbon nitride (mpg-C_3N_4) supported dual-atom Pt_2 catalyst, 5 wt% Pt/C = Pt loaded on carbon support, Ni-GCN = Ni metal supported on graphitic carbon nitride, 0.3 wt% Ir/ZnO = zinc oxide-supported iridium, MgCoMo HT= MgCoMo Hydrotalcite, Fe-ZIF-8-800= Fe single atoms (SA) loaded onto ZIF-8, Ru-MSP-II = Ru-based metallo-supramolecular polymers , NiO (P)-300= NiO prepared viacalcination at 300 ^{O}C SnO-MgO= reduced Sn-Mg based catalyst, Zr-HTC= Zr-coordinated Hydrothermal carbon, Mg_3-Al_1@C= carbon coated MgO-Al_2O_3.



Scheme S1 Control reactions for the determination of the role of acidic and basic sites. Transfer hydrogenation of benzaldehyde with (a) benzoic acid and (b) pyridine.

S4. Green metrics calculations

Environmental impact and sustainability of a reaction is determined using green metric parameters. Here, different green metrics parameters have been calculated for the CTH of benzaldehyde. It is pertinent to state here that in this reaction, as we were able to quantify only the main product (benzyl alcohol), while the byproduct (acetone) was not quantified. The green metrics parameters are discussed as follows:

(1) Environmental factor (E-factor): E-factor is the ratio between the mass of waste to the mass of product. It governs the amount of waste that is generated in a chemical process. An ideal green chemical reaction is expected to have an *E*-factor equals to 0. A higher *E*-factor corresponds to higher generation of waste material, which can have a detrimental impact on the environment.

$E - \text{factor} = (\text{mass of waste }) / (\text{mass of product})$

Mass of waste = Total mass of raw material – Total mass of product

(i) Yield of benzyl alcohol (IPA) = 94%

Mass of product (IPA)= (0.10812*0.94) = 0.101 g

(ii) Yield of benzyl alcohol (ethanol) = 85.5%

Mass of product (ethanol)= (0.10812*0.855) = 0.092 g

(iii) Yield of benzyl alcohol (2-butanol) = 71.5%

Mass of product (2-butanol) = (0.10812*0.715) = 0.077 g

(iv) Yield of benzyl alcohol (methanol) = 28%

Mass of product (methanol)= (0.10812*0.28) = 0.030 g

(i) *E* – factor (IPA) = (Total mass of reactant- Mass of product)/mass of product

= ((0.106+0.060) - 0.101)/0.101

= 0.644

(ii) *E* – factor (ethanol) = (0.106+0.046) – 0.092)/0.092

=0.652

(iii) *E* – factor (2-butanol) = (0.106+0.074) – 0.077)/0.077

=1.337

(iv) *E* – factor (methanol) = (0.106+0.032) – 0.030)/0.030

=3.6

(2) Atom economy (AE): AE of a reaction describes the total number of atoms present in the reactant that could be found in the product. It is an important parameter to determine the efficiency of any synthesis protocol. Ideally, AE should be 100%.

$$\mathrm{AE} = \mathrm{Mol.\,wt.\,of\,product}/\sum(\mathrm{Mol.\,wt.\,of\,stoichiometric\,reactants}) \times 100$$

Mol wt. of product (benzyl alcohol) = 108.4

Mol. wt. of reactant (benzyl aldehyde) = 106.821

Mol. wt. of isopropyl alcohol = 60.10

AE = (108.40/(106.12 + 60.10))* 100

= (108.40/166.22)* 100

= 65%

(3) Process mass intensity (PMI): PMI is the total mass used in a chemical process including the mass of the solvents used divided by the mass of the product.

$$\mathrm{PMI} = [\mathrm{Total\,mass\,in\,process\,(including\,solvent)}]/(\mathrm{Mass\,of\,product})$$

PMI = (3.93 + 0.050 + 0.106)/0.101

= 4.086/0.101

= 40

(4) Carbon Economy (CE): Carbon Economy (CE) relates to the number of carbon atoms in the reactant that can be found in the product. It is the ratio of carbon atoms in the product w.r.t. to the product.

CE (%) = [Carbon in product] / [Total carbon in reactant] * 100

CE (%) = {[Number of moles of product*Number of Carbon in product] / [Number of moles of reactant*Number of C in reactant]} * 100

CE (%) = {[1*7] / [1*7 + 1*3]} * 100

CE (%) = 70%

(5) Solvent intensity (SI): SI is the total mass of the solvent involved in process divided by the mass of product. Lower the solvent intensity value, lower will be the cost and the process will be more sustainable.

$$\mathrm{SI}\ \ (\%) = \mathrm{Mass\,of\,solvents}/\mathrm{Mass\,of\,product} \times 100$$

SI (%) = 0/0.101

= 0

(6) Renewable intensity (RI): RI is the total mass of all renewable material involved in the process divided by the mass of product.

$\mathrm{RI}\ \ (\%) = \text{Mass of renewable material}/\text{Mass of product}$

RI (%) = (3.93/0.101)* 100

= 39

(7) Renewable percentage (RP): it is defined as the ratio of the RI to the PMI.

$\mathrm{RP}\ \ (\%) = \mathrm{RI}/\mathrm{PMI} \times 100$

RI = 39

PMI = 40

RP = (39/40)* 100

= 98%

(8) Reaction mass efficiency (RME): Reaction mass efficiency is defined as the mass of product divided by the sum of total mass of stoichiometric reactants. RME measures the "cleanness" of a chemical reaction. The values of RME range from 0-100%. Higher value of RME is considered better for an ideal green chemical reaction.

$\mathrm{RME}\ (\%) = \text{Mass of product}/\sum(\text{Mass of stoichiometric reactants}) \times 100$

RME = (0.101)/(0.106 + 0.0471)* 100

= 66%

(9) Mass intensity (MI): MI refers to the total mass involved in the process divided by the mass of product. Lower is mass intensity value suggests an economically and sustainably benign process.

$\mathrm{MI} = (\text{Total mass in process})/(\text{Mass of product})$

MI = (0.106 + 0.05 + 3.93)/0.101

= 4.086/0.101

= 40

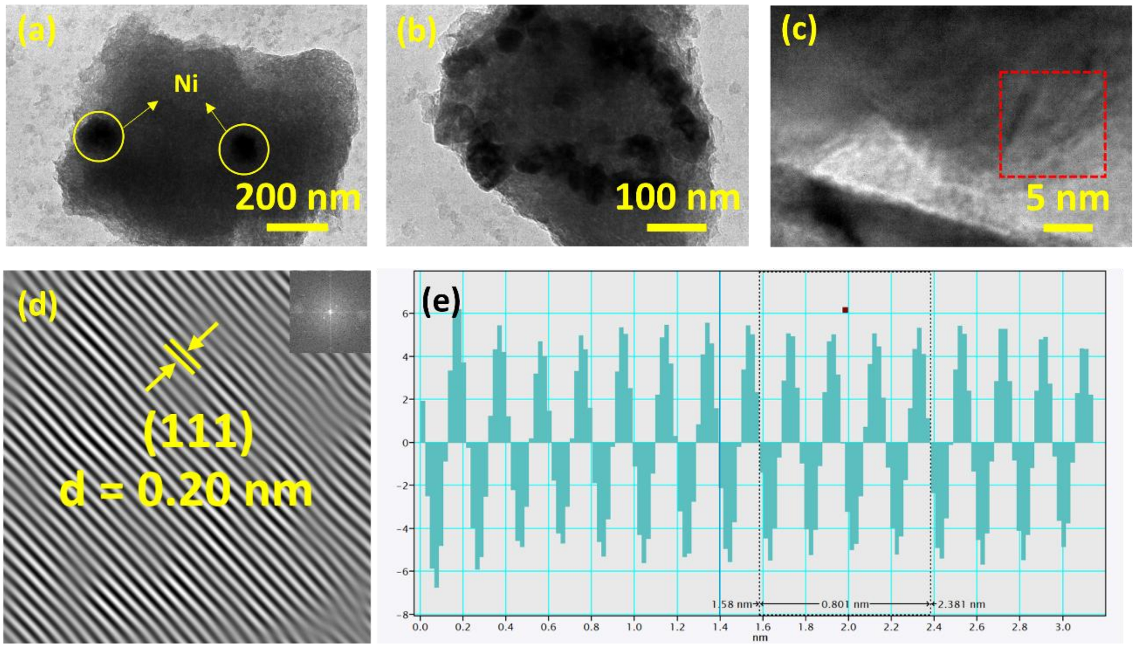


Fig. S4 (a-b) TEM images, (c) HRTEM image, (d) IFFT (inset FFT), and (e) line profiling of catalyst recovered after last cycle.

S5. Compounds characterization

Phenyl methanol (3a).[14] ^{1}H NMR (500MHz, DMSO-d$_6$) *d* (ppm) 7.32-7.31 (m, 4H, *j*=4.15 Hz), 7.24-7.21 (m, 1H, *j*=4.4 Hz), 5.15, (s, 1H), 4.50 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) *d* (ppm) 142.4, 127.9, 126.5, 126.3 62.8.

(4-Methyl phenyl)methanol (3b).[14] ^{1}H NMR (500MHz, CDCl$_3$) *d* (ppm) 7.26 (d, 2H, *j*=8.25 Hz), 71.17 (d, 2H, *j*=7.8 Hz), 4.65 (d, 2H, *j*= 6.15 Hz), 2.35 (s, 3H), 1.65 (t, 1H, *j*= 6.15). ^{13}C NMR (125 Hz, CDCl$_3$) *d* (ppm) 137.9, 137.4, 129.2, 127.1, 65.3 and 21.1.

(4-Methoxy phenyl)methanol (3c).[15] ^{1}H NMR (500MHz, DMSO-d$_6$) *d* (ppm) 7.25 (d, 2H, *j*= 8.9 Hz), 6.89 (d, 2H, *j*= 8.9 Hz) 5.07 (t, 1H, *j*= 5.5 Hz), 4.44 (d, 2H, *j*= 5.5 Hz). ^{13}C NMR (125 MHz, DMSO-d$_6$) *d* (ppm) 158.2, 134.5, 128.0, 113.5, 62.6 and 55.0.

(3,4-Dimethoxy)phenyl methanol (3d). ^{1}H NMR (500MHz, DMSO-d$_6$) *d* (ppm) 6.88 (m, 2H, *j*=2.75 Hz), 6.82 (d, 1H, *j*= 8.25 Hz), 5.01 (t, 1H, *j*= 5.85 Hz), 4.41 (d, 2H, *j*= 500 Hz). ^{13}C NMR (125 MHz, DMSO-d$_6$) *d* (ppm) 148.6, 147.6, 135.1, 118.5, 111.6, 110.6, 62.7, 55.5.

(3-Bromo phenyl)methanol (3e).[14] ^{1}H NMR (500MHz, DMSO-d$_6$) *d* (ppm) 7.52 (s, 1H), 7.41 (d, 1H, *j*= 7.55 Hz), 7.32-7.26 (m, 2H), 5.29 (t, 1H, *j*= 5.5 Hz), 4.51 (d, 2H, *j*= 5.5 Hz). ^{13}C NMR (125 MHz, DMSO-d$_6$) *d* (ppm) 145.4, 130.1, 129.3, 128.9, 125.2, 121.5 and 62.1.

(4-Bromo phenyl)methanol (3f).[16] ^{1}H NMR (500MHz, CDCl$_3$) *d* (ppm) 7.48 (d, 2H, *j*= 8.25 Hz), 7.23 (d, 2H, *j*=8.25 Hz), 4.64 (s, 2H), 1.88 (s, 1H). ^{13}C NMR (125 Hz, CDCl$_3$) *d* (ppm). ^{13}C NMR (125 Hz, CDCl$_3$) *d* (ppm) 139.71, 131.6, 128.6, 121.4 and 64.5.

(4-Chloro phenyl)methanol (3g).[14] ^{1}H NMR (500MHz, CDCl$_3$) *d* (ppm) 7.33 (d, 2H, *j*=8.25 Hz), 7.30 (d, 2H, *j*= 8.25 Hz), 4.66 (d, 2H, *j*=5.1 Hz), 1.85 (t, 1H, *j*=3.4 Hz). ^{13}C NMR (125 Hz, CDCl$_3$) *d* (ppm) 139.2, 133.3, 128.6, 128.6, 128.2 and 64.5.

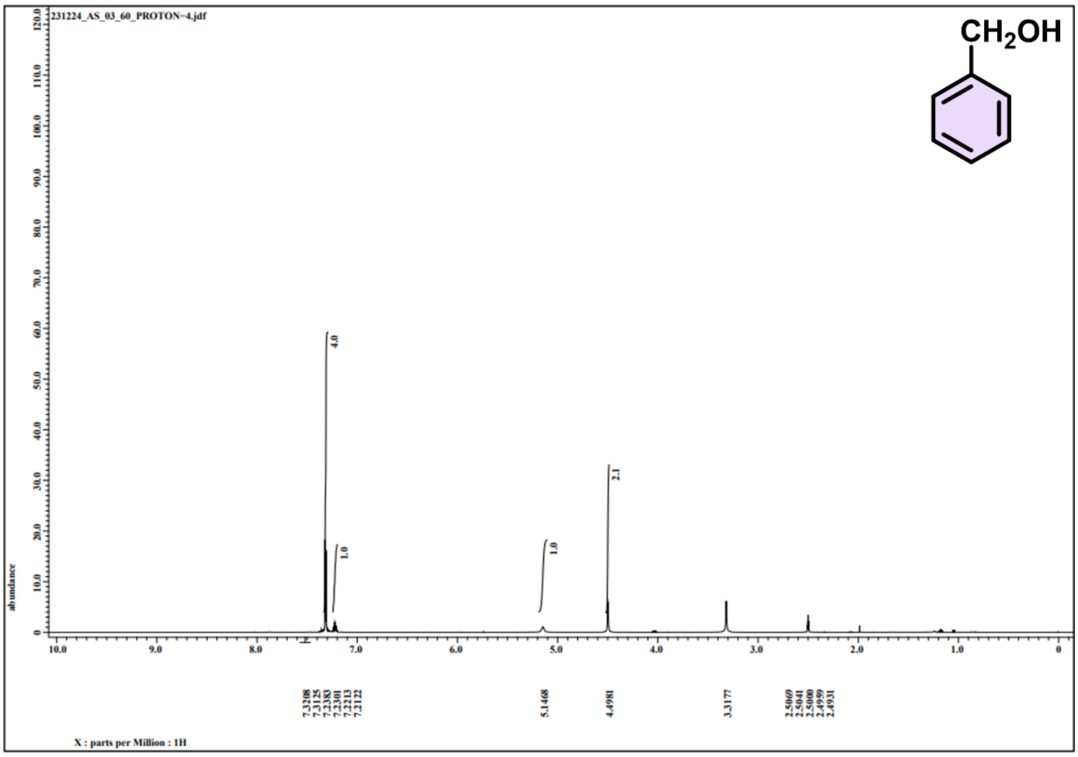
(4-Cyano phenyl)methanol (3h). ^{1}H NMR (500MHz, DMSO-d$_6$) *d* (ppm) 7.79 (d, 2H, *j*= 8.25 Hz), 7.51 (d, 2H, *j*=8.25 Hz), 5.44 (t, 1H, *j*= 7.55 Hz), 4.59 (d, 2H, *j*= 5.5Hz). ^{13}C NMR (125 MHz, DMSO-d$_6$) *d* (ppm) 148.5, 132.0, 126.9, 119.0, 109.2 and 62.2.

(2-Nitrophenyl)methanol (3i).[16] ^{1}H NMR (500MHz, CDCl$_3$) *d* (ppm) 8.09 (d, 1H, *j*= 8.25 Hz), 7.74 (d, 2H, *j*= 6.85 Hz), 7.67 (t, 1H, *j*= 7.55 and 7.6 Hz), 7.48 (t, 1H, *j*= 7.48 and 7.55 Hz) 4.97 (d, 2H, *j*= 4.8 Hz), 2.80 (t, 1H, *j* = 6.2 Hz). ^{13}C NMR (125 Hz, CDCl$_3$) *d* (ppm) 147.5, 136.8, 134.1, 129.8, 128.4, 125.0, and 62.4.

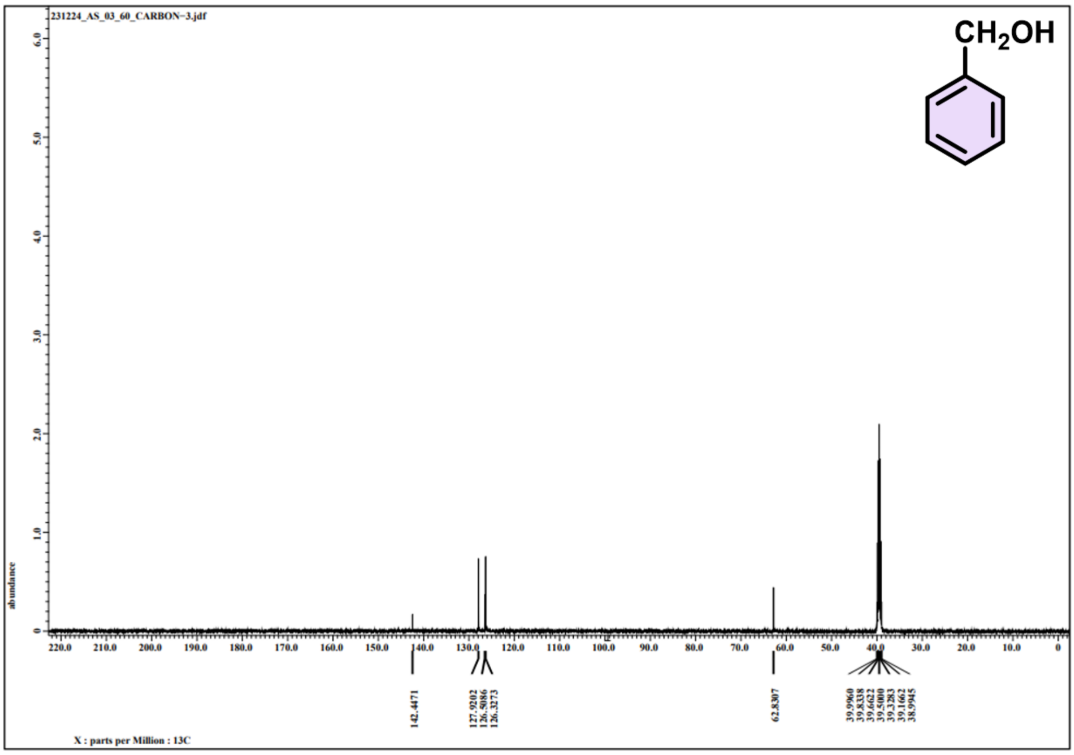
(3-Nitrophenyl)methanol (3j).[16] ^{1}H NMR (500MHz, CDCl$_3$) *d* (ppm) 8.18 (s, 1H), 8.08 (d, 1H, *j*=7.55 Hz), 7.66 and 7.65 (d, 1H, *j*=7.6 Hz), 7.49 (t, 1H, *j*= 7.6 Hz), 4.77 (s, 2H), 2.78 (s, 1H). ^{13}C NMR (125 Hz, CDCl$_3$) *d* (ppm) 148.2, 142.9, 132.6, 129.3, 122.3, 121.3 and 63.7.

S6. NMR spectra of compounds

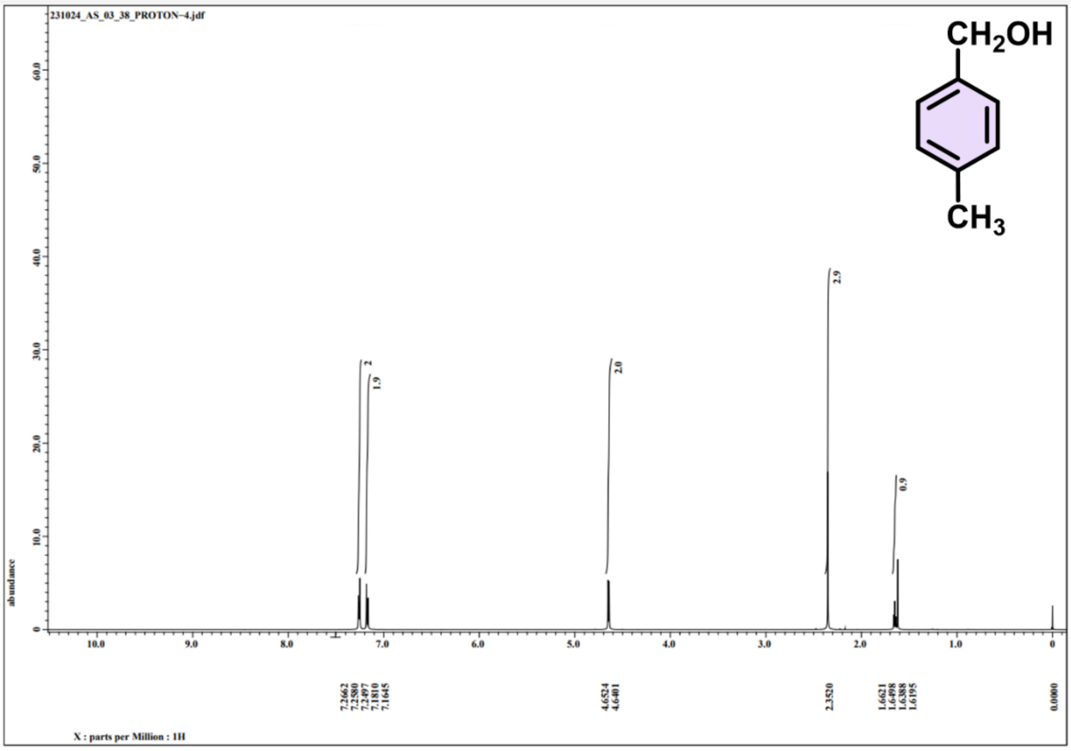
^{1}H-NMR spectrum of Benzyl alcohol [500 MHz, DMSO-D_6]



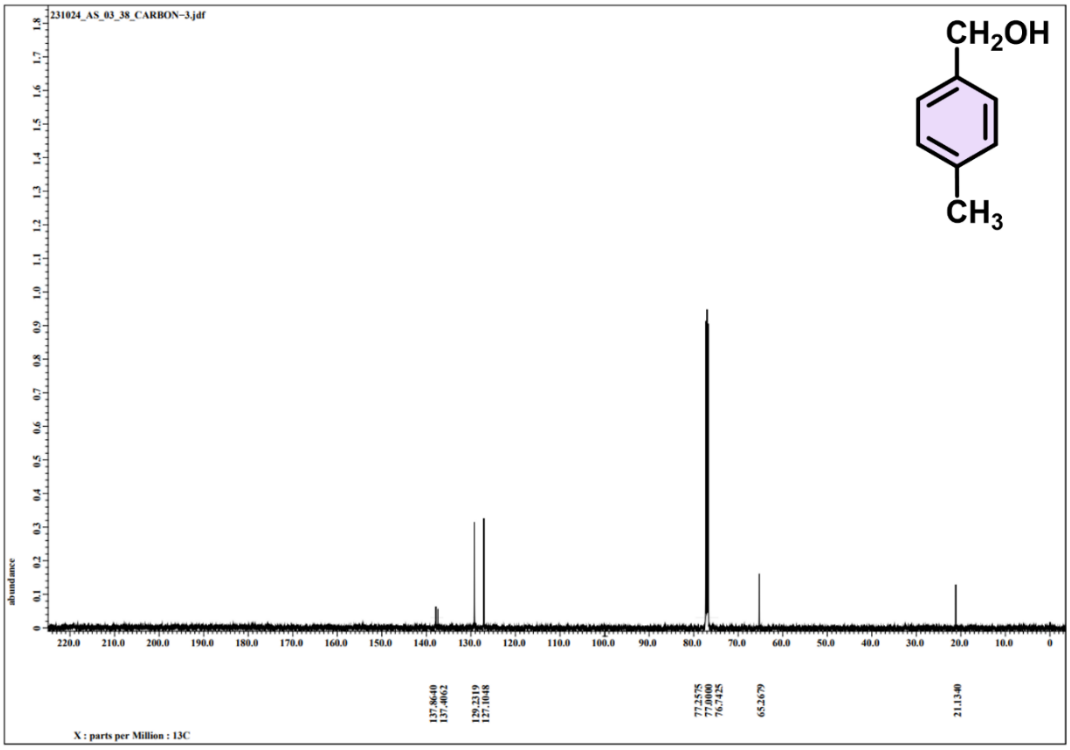
^{13}C-NMR spectrum of Benzyl alcohol [125 MHz, DMSO-D_6]



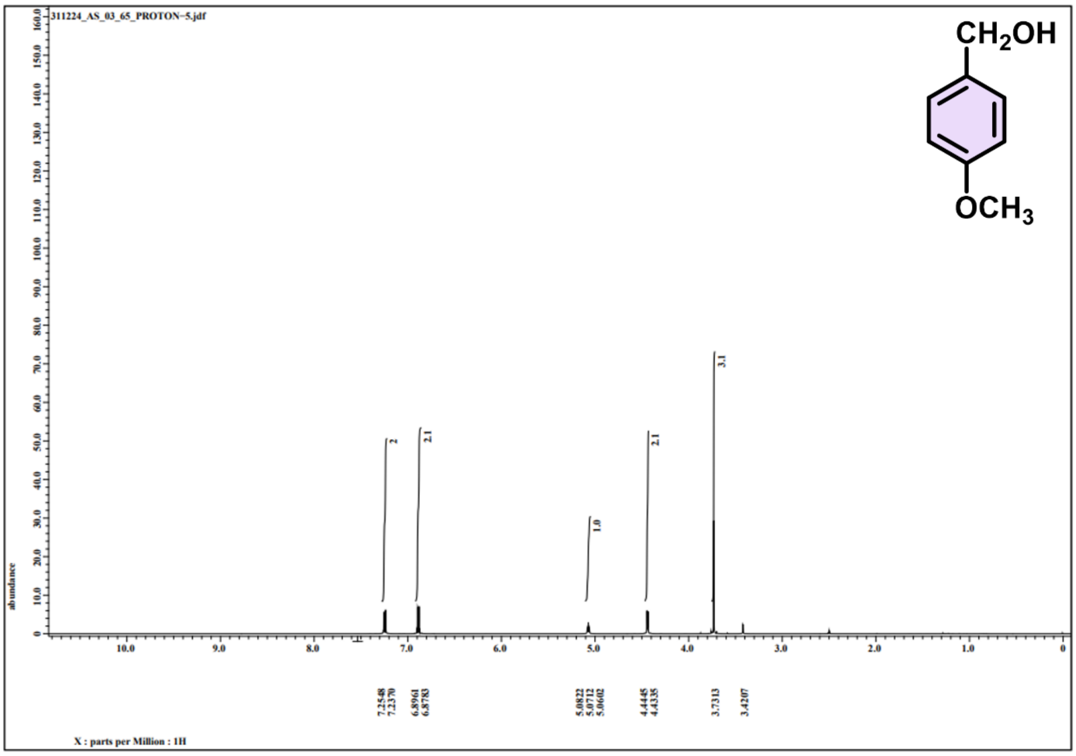
^{1}H-NMR spectrum of 4-Methyl benzyl alcohol [500 MHz, CDCl$_3$]



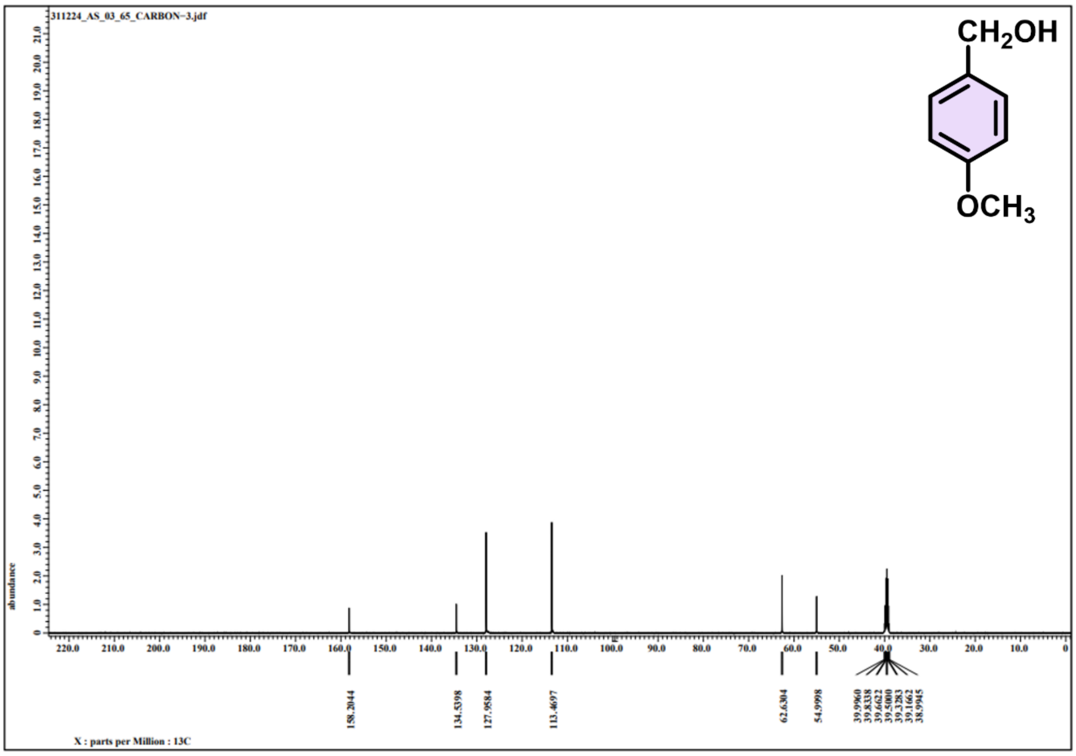
^{13}C-NMR spectrum of 4-Methyl benzyl alcohol [125 MHz, CDCl$_3$]



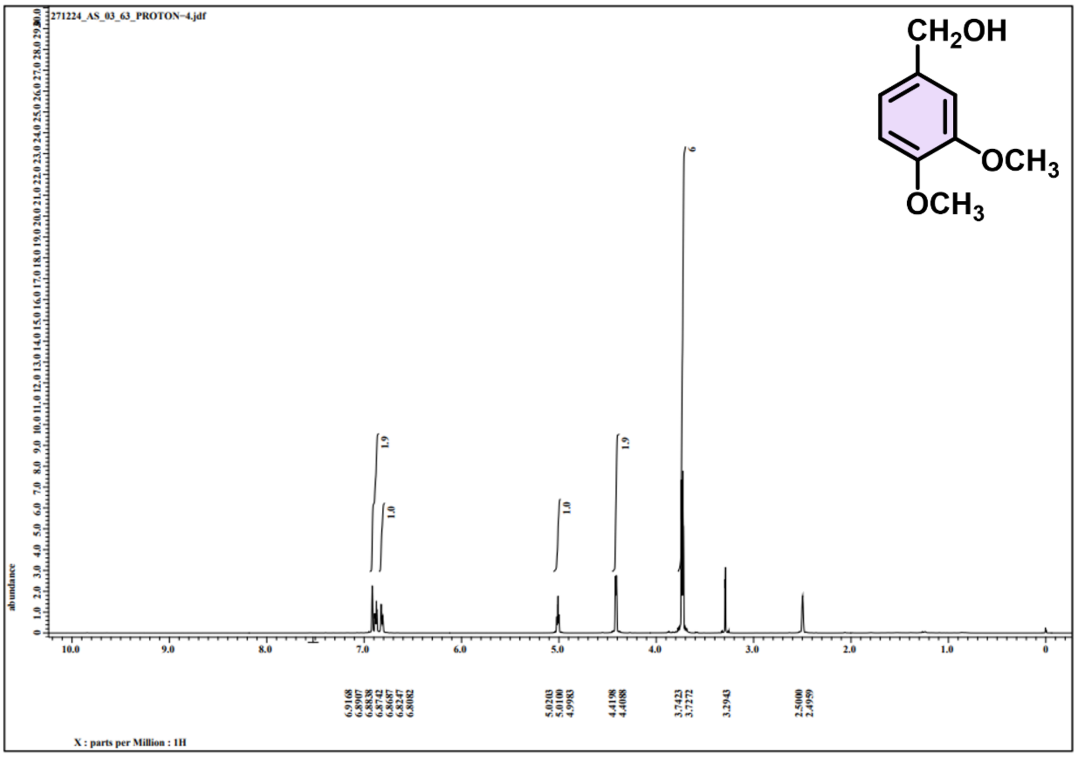
^{1}H-NMR spectrum of 4-Methoxy benzyl alcohol [500 MHz, DMSO-D$_6$]



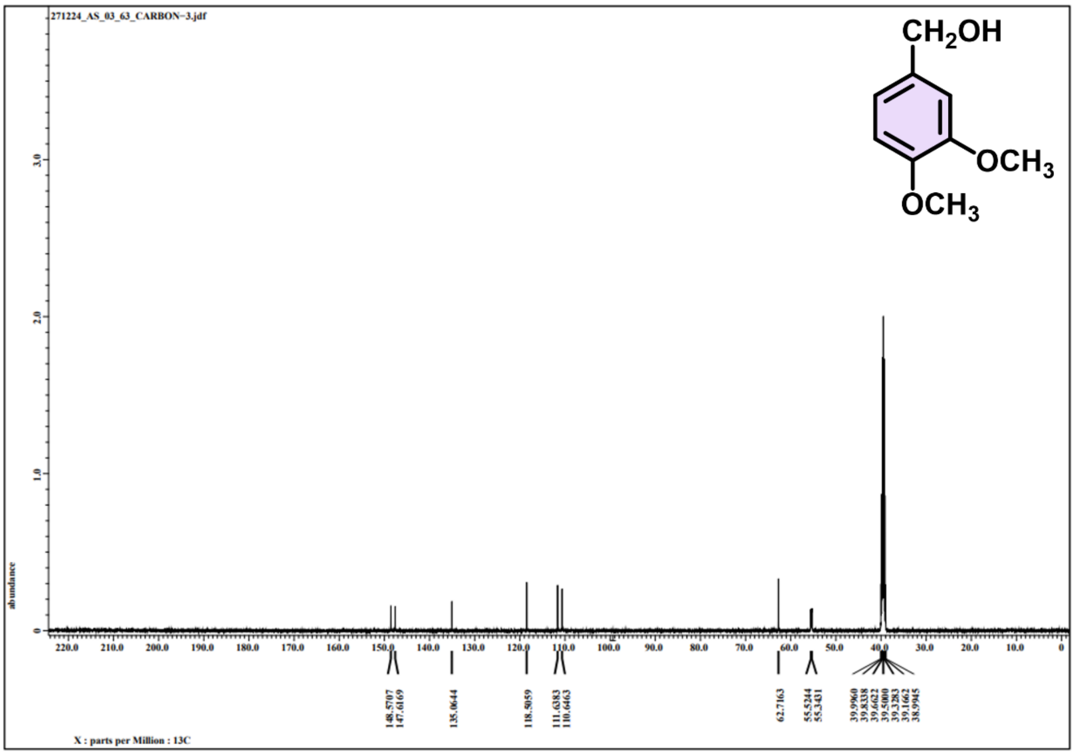
^{13}C-NMR spectrum of 4-Methoxy benzyl alcohol [125 MHz, DMSO-D$_6$]



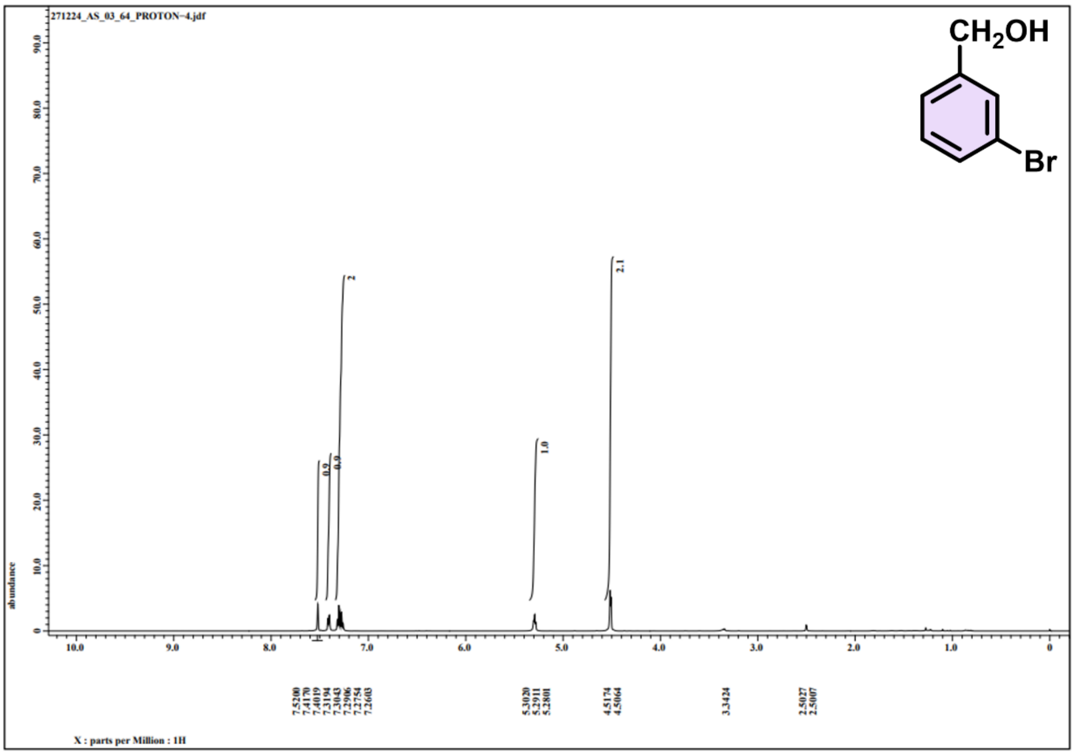
^{1}H-NMR spectrum of 3,4-Dimethoxy benzyl alcohol [500 MHz, DMSO-D$_6$]



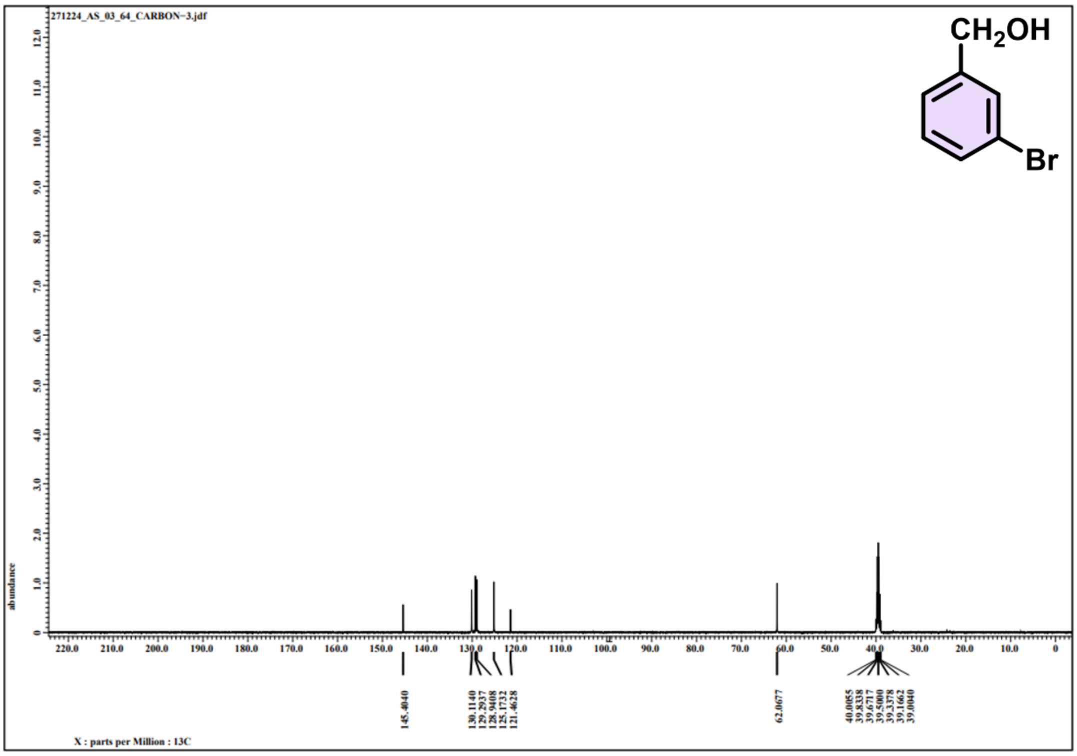
^{13}C-NMR spectrum of 3,4-Dimethoxy benzyl alcohol [125 MHz, DMSO-D$_6$]



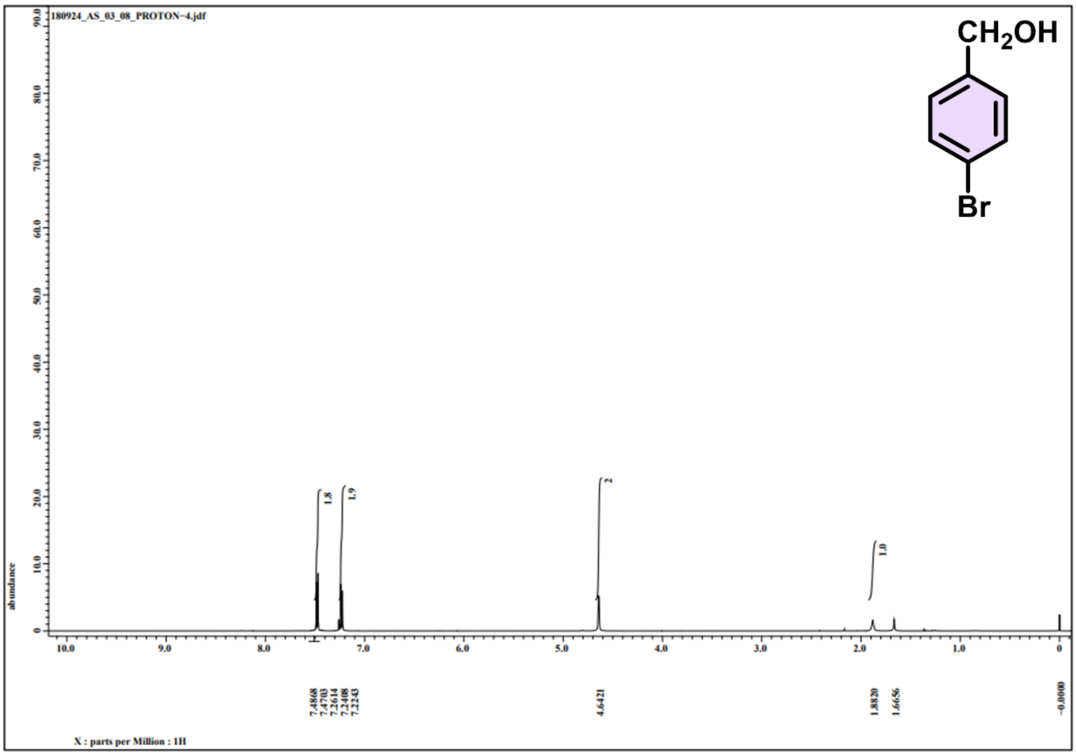
^{1}H-NMR spectrum of 3-Bromo benzyl alcohol [500 MHz, DMSO-D$_6$]



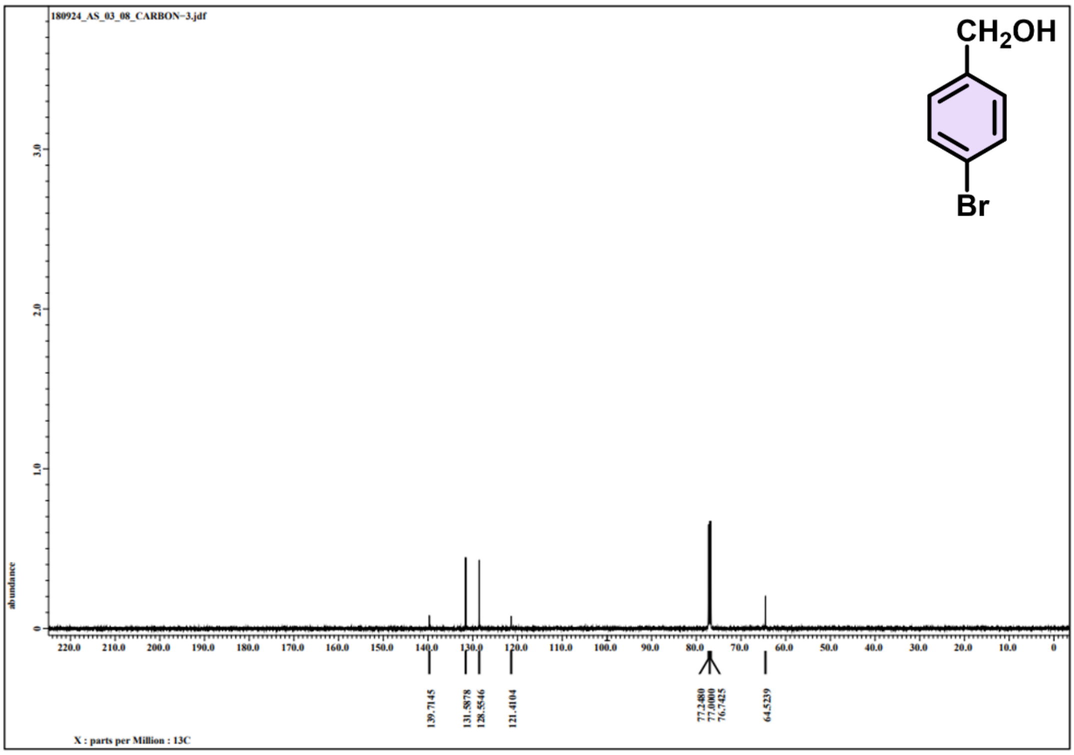
^{13}C-NMR spectrum of 3-Bromo benzyl alcohol [125 MHz, DMSO-D$_6$]



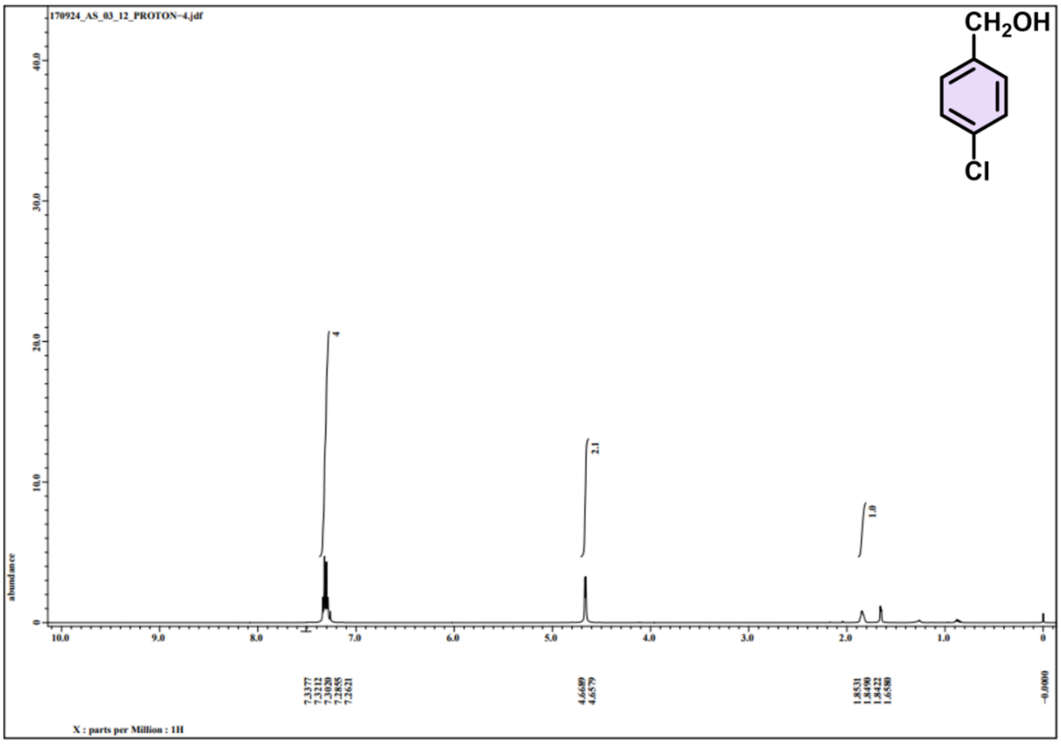
^{1}H-NMR spectrum of 4-Bromo benzyl alcohol [500 MHz, $CDCl_3$]



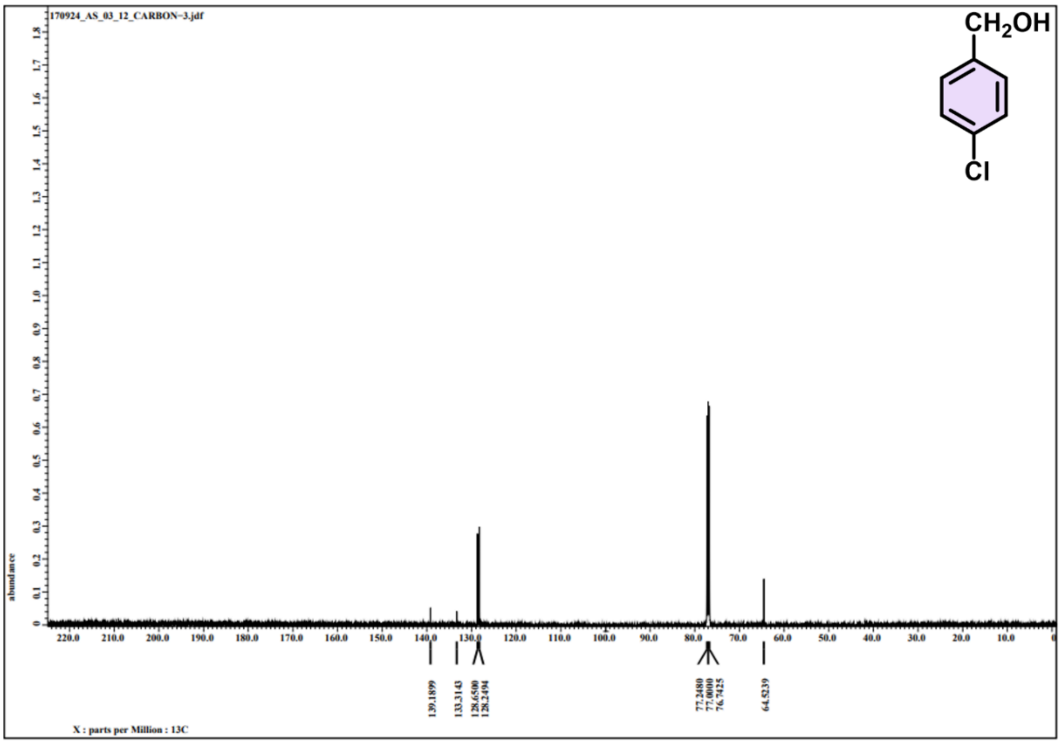
^{13}C-NMR spectrum of 4-Bromo benzyl alcohol [125 MHz, $CDCl_3$]



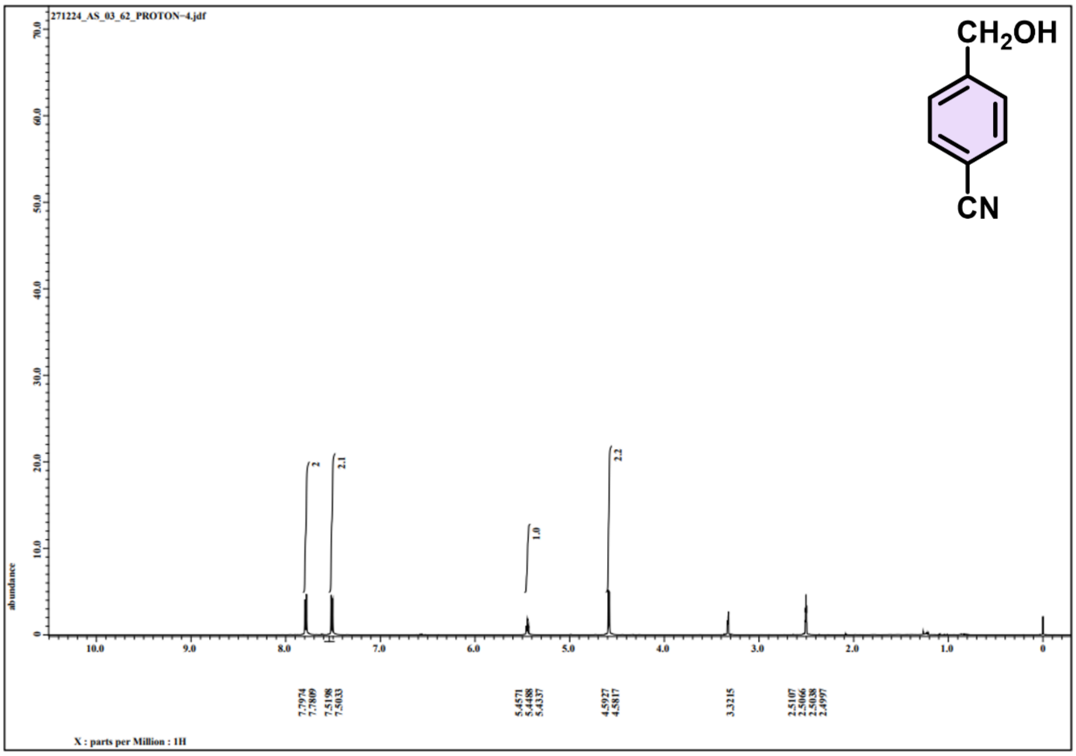
^{1}H-NMR spectrum of 4-Chloro benzyl alcohol [500 MHz, $CDCl_3$]



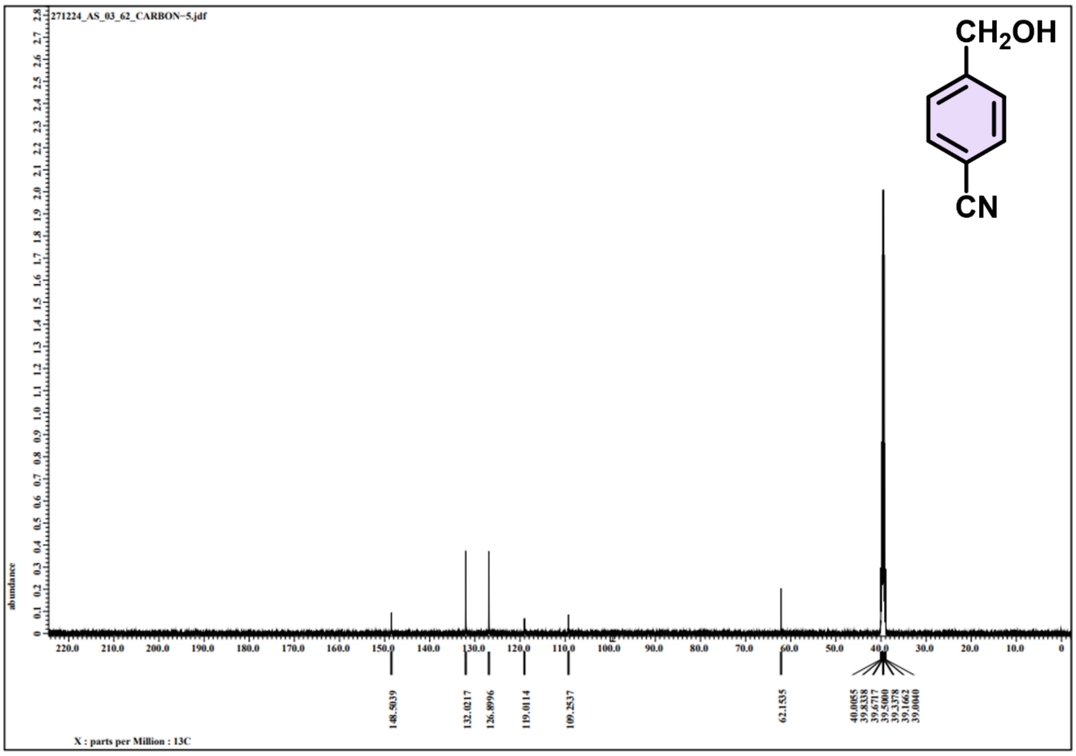
^{13}C-NMR spectrum of 4-Chloro benzyl alcohol [125 MHz, $CDCl_3$]



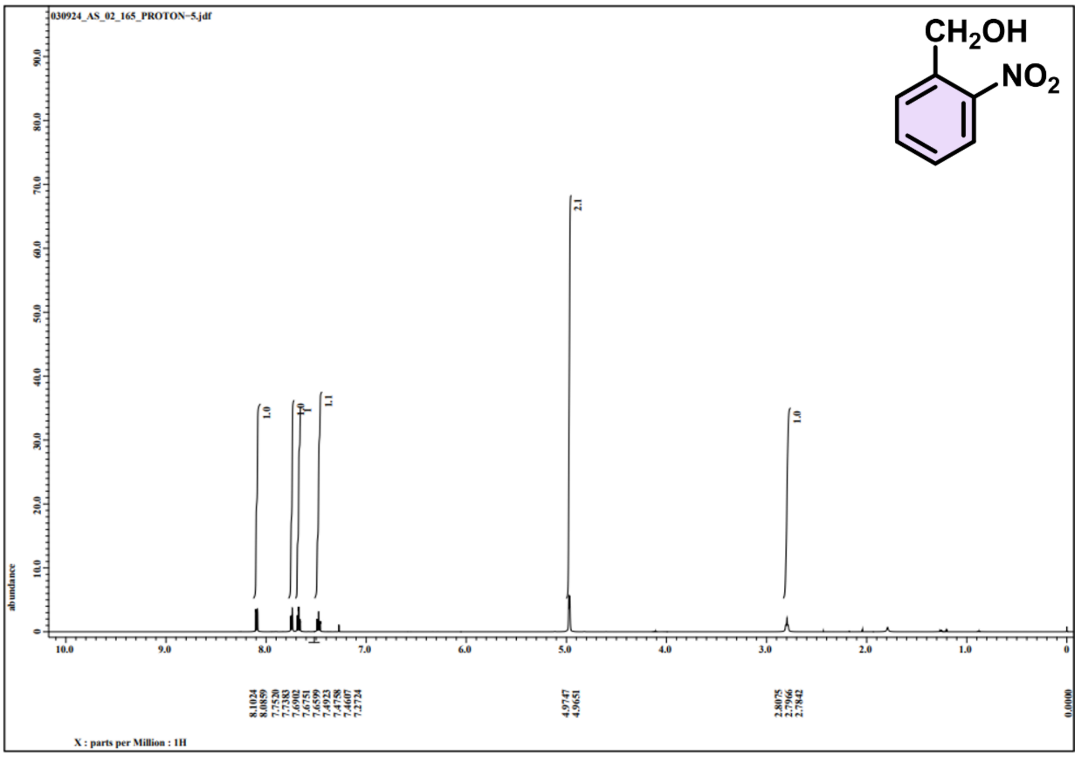
^{1}H-NMR spectrum of 4-Cyano benzyl alcohol [500 MHz, DMSO-D$_6$]



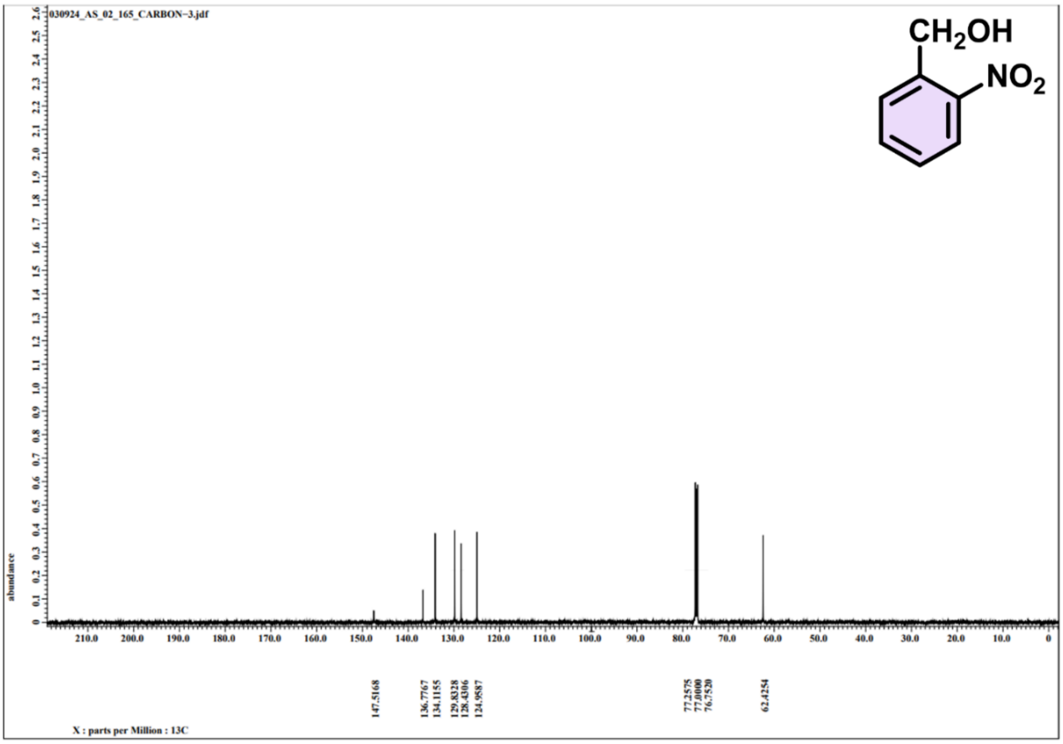
^{13}C-NMR spectrum of 4-Cyano benzyl alcohol [125 MHz, DMSO-D$_6$]



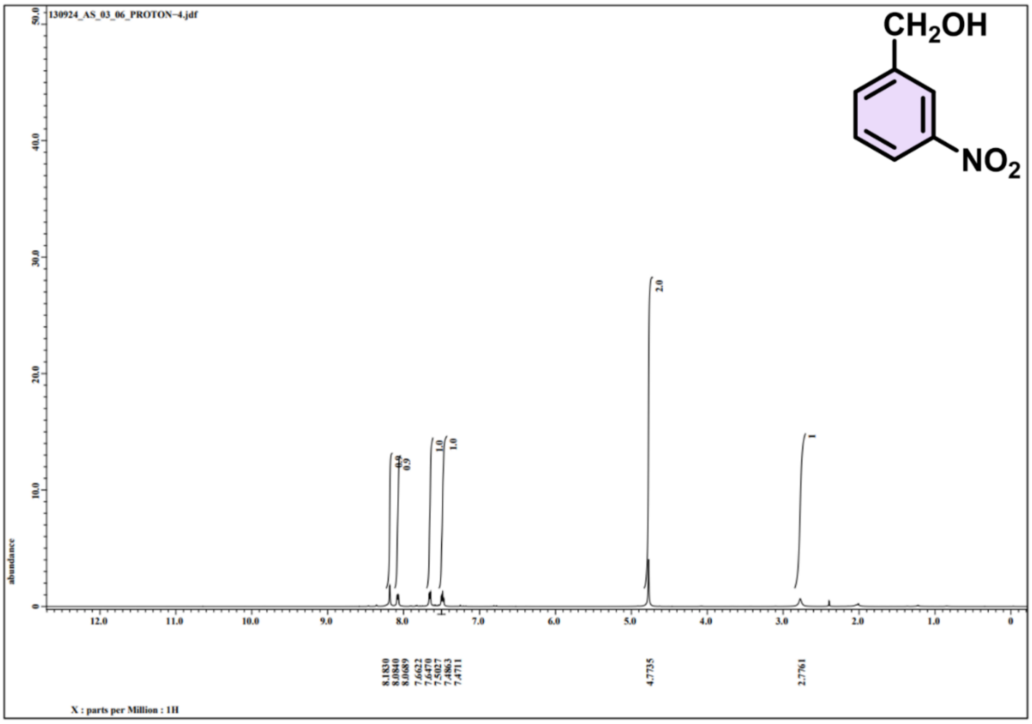
^{1}H-NMR spectrum of 2-Nitro benzyl alcohol [500 MHz, $CDCl_3$]



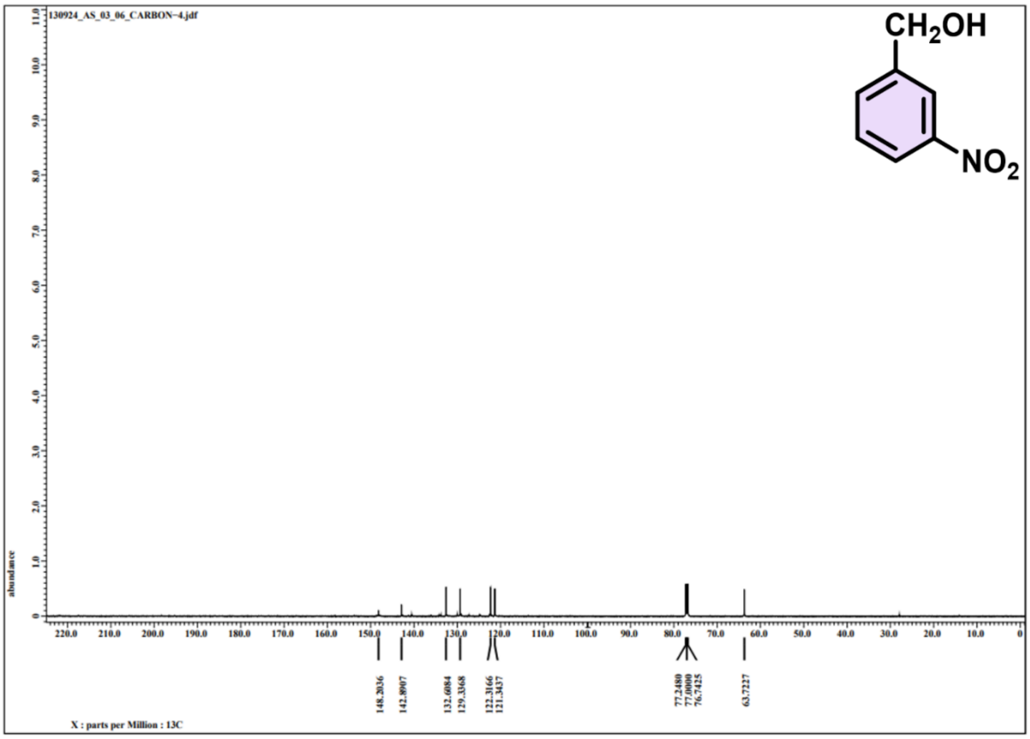
^{13}C-NMR spectrum of 2-Nitro benzyl alcohol [125 MHz, $CDCl_3$]



^{1}H-NMR spectrum of 3-Nitro benzyl alcohol [500 MHz, $CDCl_3$]



^{13}C-NMR spectrum of 3-Nitrobenzyl alcohol [125 MHz, $CDCl_3$]



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