

Supporting Information
for

**Cooperative Interplay between a Flexible PNN-Ru(II) Complex and a NaBH₄
Additive in the Efficient Catalytic Hydrogenation of Esters**

Zheng Wang,^{a,b,f} Xiangyang Chen,^{c,e,f} Bo Liu,^a Qing-bin Liu,^{*,a} Gregory A. Solan,^{b,d} Xinzheng Yang,^{*,c} and Wen-Hua Sun^{*,b,e}

^a College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China

^b Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^c Beijing National Laboratory for Molecular Science, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^d Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK

^e University of Chinese Academy of Sciences, Beijing 100049, China

^f These authors contributed equally to this work

[†] Corresponding Authors: whsun@iccas.ac.cn; liuqingb@sina.com;

Tel: +86-10-62557955

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1. Experimental Section

Unless otherwise stated, all manipulations were performed under an atmosphere of argon or using standard Schlenk techniques. Hydrogen gas (99.99%) was purchased from Shijiazhuang Xisanjiao. Solvents were dried using standard procedures and degassed with nitrogen. For example, tetrahydrofuran (THF) was distilled over sodium/benzophenone, 1,4-dioxane was distilled over sodium and diglyme (diethylene glycol dimethyl ether) was

distilled over sodium under reduced pressure. Analytical grade isopropanol, ethanol, methanol, toluene and hexane were degassed by bubbling argon through them before use. NMR spectra were recorded on a Bruker Avance-III (500 MHz) spectrometer. All ^{31}P chemical shifts are relative to 85% H_3PO_4 . ^1H and ^{13}C chemical shifts were measured relative to the solvent peaks but they are reported relative to TMS. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^1H NMR spectra and relative to CDCl_3 (77.0 ppm) for ^{13}C NMR spectra. Column chromatography was performed using silica gel (200-300 mesh). GC analysis was carried out on Agilent 6820 Series instrument using a capillary column (part number 19091N-113 HP-INNOWAX). GC-MS analysis was carried out on a Bruker SCION TQ GC-MS/MS. The purity of all ester substrates was greater than 97% and these were purchased from Beijing Innochem, Science & Technology. All the liquid substrates and solid substrates were used directly.

1.1 Syntheses

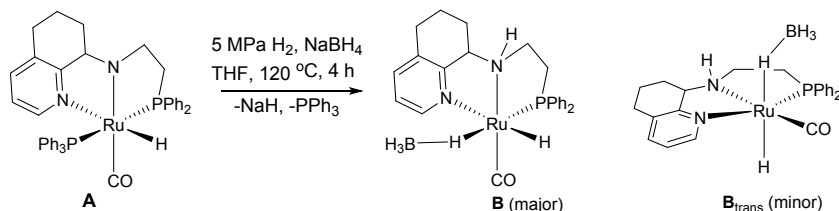
1.1.1 Preparation of [*fac*-PNN]RuH(PPh₃)(CO) (**A**)

Based on the literature procedure,¹ a mixture of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (3.20 g, 3.36 mmol) and N-(2-(diphenylphosphino)ethyl)-5,6,7,8-tetrahydroquinolin-8-amine (1.20 g, 3.36 mmol) in toluene (60 mL) was stirred and heated to reflux for 12 h. The resultant solution was then cooled to 30 °C and stirred for an additional 2 h. The precipitate formed was collected by filtration, washed with toluene and dried under reduced pressure to give **A** as an off-white solid (1.80 g, 71% yield). On standing in deuterated chloroform for 4 h a mixture of two isomers is apparent by ^1H NMR spectroscopy: **A** (90%) and **A'** (10%). If the spectrum is recorded immediately following dissolution only **A** is observed.

A and **A'**. ^1H NMR (500 MHz, CDCl_3) δ 7.79 (dd, J = 12.1, 7.1 Hz, 2H), 7.51 (t, J = 9.0 Hz, 6H), 7.37 (d, J = 7.3 Hz, 4H), 7.30 – 7.21 (m, 13H), 7.00 (d, J = 8.0 Hz, 2H), 6.44 (t, J = 6.5 Hz, 1H), 4.00 – 3.75 (m, 1H), 3.65 (q, J = 7.1 Hz, 1H), 3.53 (d, J = 10.9 Hz, 1H), 2.49 – 2.36 (m, 1H), 2.36 – 2.17 (m, 2H), 1.78 – 1.48 (m, 3H), 1.17 (t, J = 7.0 Hz, 1H), 1.00-0.96 (m, 1H), -11.72 (t, J = 20.7 Hz, 1H, **A**), -12.37 (dd, J = 24.0, 16.0 Hz, **A'**). ^{13}C NMR (126 MHz, CDCl_3) δ 204.02 (d, J = 14.4 Hz) Ru-CO), 155.38, 150.16, 136.39, 135.34, 133.61, 133.50, 133.41, 133.30, 133.14, 130.74, 130.63, 129.75, 129.68, 128.81, 128.78, 128.73, 128.70, 128.58, 128.52, 128.49, 122.81, 58.26, 45.79, 31.69 (d, J = 25.3 Hz), 27.35 (d, J = 105.6 Hz), 26.93, 20.91. **A**: ^{31}P NMR

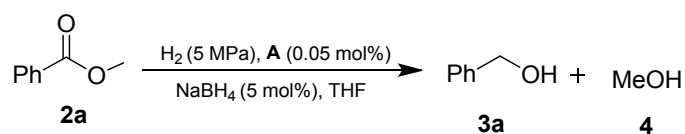
(CDCl₃) δ 66.85 (d, J = 257.3 Hz), 47.66 (d, J = 257.8 Hz). **A**¹: ³¹P NMR (CDCl₃) δ 58.75 (d, J = 261.7 Hz), 49.91 (d, J = 263.6 Hz). Anal. Calcd for C₄₂H₄₀N₂ORuP₂: C, 67.10; H, 5.36; N, 3.73. Found: C, 67.21; H, 5.27; N, 3.75.

1.1.2 Syntheses of [*fac*-PN_HN]RuH(η^1 -BH₄)(CO) (**B**).



To a solution of freshly prepared **A** (0.25 g, 0.33 mmol) in THF (10 mL) was added a solution of NaBH₄ (0.25 g, 6.75 mmol) in THF (10 mL) and the mixture transferred into a stainless steel 100 mL autoclave equipped with a magnetic stir bar. The autoclave was purged by three cycles of pressurization/vent with hydrogen and then finally pressurized with hydrogen (5 MPa) and sealed. The reaction mixture was stirred at 120 °C for 4 h. The autoclave was allowed to cool to room temperature and the hydrogen gas released. The resulting suspension was filtered through a pad of celite and the filtrate separated. Addition of pentane (50 mL) to the filtrate resulted in precipitation of a solid, which was collected and dried under reduced pressure forming **B** as a grey solid (0.08 g, 47%). **B** is obtained as a mixture of two isomers, **B** (90%) and **B**_{trans} (10%) on dissolution in CD₂Cl₂ as revealed by ¹H NMR spectroscopy.

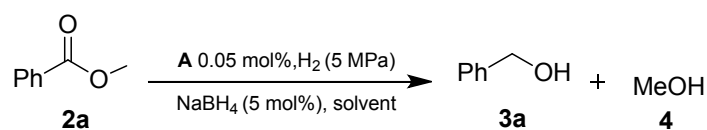
B and **B**_{trans}: ¹H NMR (500 MHz, CD₂Cl₂) δ 7.76 – 7.71 (m, 2H), 7.67 – 7.59 (m, 2H), 7.38 – 7.29 (m, 8H), 7.10 (dd, J = 7.9, 5.3 Hz, 1H), 4.64 – 4.51 (m, 1H), 4.01–3.95 (m, 1H), 3.89 – 3.59 (m, 2H), 2.95 (t, J = 11.8 Hz, 1H), 2.77–2.73 (m, 2H), 2.66–2.62 (m, 2H), 2.55–2.52 (m, 1H), 2.06 (dd, J = 10.0, 4.2 Hz, 1H), -1.92 (br, J = 110.5 Hz, 4H, BH₄), -12.01 (d, J = 23.5 Hz, 1H, Ru-H (**B**)), -16.28 (d, J = 25.4 Hz, Ru-H (**B**_{trans})). ¹³C NMR (126 MHz, CD₂Cl₂) δ 202.93 (d, J = 15.2 Hz, Ru-CO (**B**)), 202.50 (d, J = 14.4 Hz, Ru-CO (**B**_{trans})), 171.55, 159.43, 151.40, 138.01, 135.21, 132.97, 132.90, 131.66, 131.60, 130.27, 129.65, 128.24, 128.17, 128.13, 128.06, 124.25, 61.79, 46.03, 31.91 (d, J = 26.5 Hz), 28.63, 27.60, 21.17. **B**: ³¹P NMR (202 MHz, CDCl₃) δ 69.90 (s). **B**_{trans}: ³¹P NMR (202 MHz, CDCl₃) δ 67.77 (s). Anal. Calcd for C₂₄H₃₀BN₂OPRu: C, 57.01; H, 5.98; N, 5.54. Found: C, 57.41; H, 5.97; N, 5.24.

Table S2 Hydrogenation of methyl benzoate at different temperatures.^[a]

Entry	Time (h)	Benzyl alcohol conversion (%) by GC ^[b]		
		80 °C	100 °C	120 °C
1	3	15	34	89
2	6	56	78	99
3	12	85	99	99
4	24	90	99	99
5	36	95	99	99

^[a] Conditions: methyl benzoate (20 mmol), **A** (0.01 mmol), NaBH_4 (1 mmol), THF (50 mL), H_2 (5 MPa), T (80-120 °C).

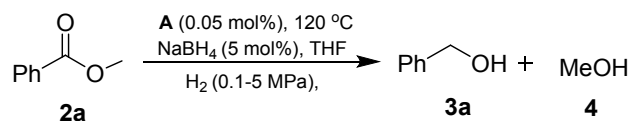
^[b] The conversion was determined by GC respect to benzyl alcohol.

Table S3 Effect of solvent on the hydrogenation of methyl benzoate.^[a]

Time (h)	Benzyl alcohol conversion (%) by GC ^[b]			
	THF	1,4-Dioxane	Ethanol	Toluene
1	20	18	1	2
3	89	75	10	10
6	99	95	12	15
12	99	99	14	20
24	99	99	15	25
36	99	99	15	25

^[a] Conditions: Methyl benzoate: 20 mmol, **A** (0.01 mmol), NaBH_4 (1 mmol), solvent (50 mL), H_2 (5 MPa), T (120 °C)

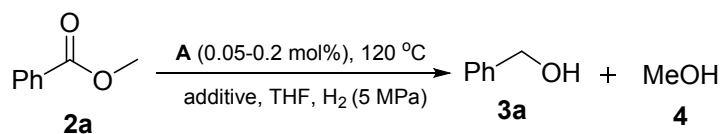
^[b] The conversion was determined by GC respect to benzyl alcohol.

Table S4 Hydrogenation of methyl benzoate under different pressures.^[a]

Entry	Time (h)	Benzyl alcohol conversion (%) by GC ^[b]			
		H ₂ (0.1 MPa)	H ₂ (1 MPa)	H ₂ (3 MPa)	H ₂ (5 MPa)
1	3	3	16	35	89
2	6	5	20	45	99
3	12	6	34	95	99
4	24	10	45	99	99
5	36	10	60	99	99

^[a] Conditions: methyl benzoate (20 mmol), **A** (0.01 mmol), NaBH₄ (1 mmol), THF (50 mL), H₂ (0.1-5 MPa), T (120 °C).

^[b] The conversion was determined by GC respect to benzyl alcohol.

Table S5 Effect of S/C ratio on the hydrogenation of methyl benzoate.^[a]

Entry	S/C ratio	Additive (mol%)	Time (h)	Conv. (%) ^[b]
1	500	NaBH ₄ (5)	3	99
2	2000	NaBH ₄ (5)	4	99
3	2000	<i>t</i> -BuOK (10) / NaBH ₄ (5)	24	59
4	8000	NaBH ₄ (5)	16	93
5	20000	NaBH ₄ (5)	36	48

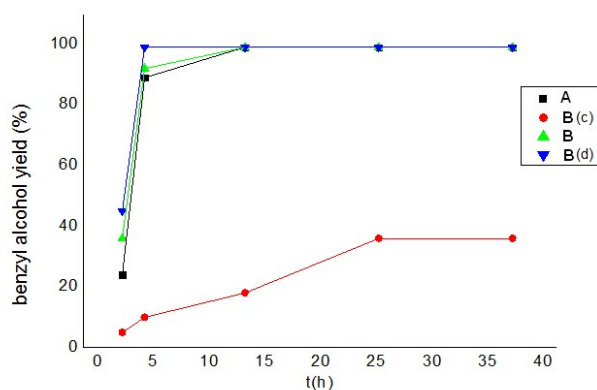
^[a] Conditions: methyl benzoate (20 mmol), **A** (0.04-0.001 mmol), NaBH₄ (1 mmol), THF (50 mL), H₂ (5 MPa), T (120 °C).

^[b] The conversion was determined by GC respect to benzyl alcohol.

Table S6 Hydrogenation of methyl benzoate under different reaction conditions.^[a]

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{O}-\text{CH}_3 \\ \textbf{2a} \end{array} \xrightarrow[\text{NaBH}_4(5 \text{ mol\%}), \text{THF}, \text{H}_2 (5 \text{ MPa})]{\text{A or B (0.05 mol\%)}, 120^\circ \text{C}} \begin{array}{c} \text{Ph}-\text{CH}_2-\text{OH} \\ \textbf{3a} \end{array} + \text{MeOH} \textbf{4} $					
Entry	Time (h)	benzyl alcohol conversion (%) by GC ^[b]			
		A	B ^[c]	B	B ^[d]
1	1	24	5	36	45
2	3	89	10	92	99
3	12	99	12	99	99
4	24	99	36	99	99
5	24	99	36	99	99

^[a] Conditions: methyl benzoate (20 mmol), **A/B** (0.01 mmol), NaBH₄ (1 mmol), THF (50 mL), H₂ (5 MPa), T (120 °C).^[b] The conversion was determined by GC respect to benzyl alcohol.^[c] Conditions: in the absence of NaBH₄.^[d] Conditions: in the presence of 1 equiv of (20 mmol) NaBH₄ with respect to methyl benzoate in the absence of H₂.

Figure S1 Effect of NaBH₄ concentration and hydrogen pressure on the conversion rate of methyl benzoate.^b

^[a] Conditions: methyl benzoate (20 mmol), **A or B** (0.01 mmol), NaBH₄ (1 mmol), THF (50 mL), H₂ (5 MPa), T (120 °C).^[b] The conversion was determined by GC respect to benzyl alcohol.^[c] Conditions: in the absence of NaBH₄.^[d] Conditions: 1 equiv of NaBH₄ (20 mmol) with respect to methyl benzoate and in the absence of H₂.

2.2 Reduction of methyl benzoate by hydrogen in the presence of NaBD₄

Experimental: Under an atmosphere of argon, a stainless steel 100 mL autoclave, equipped with a magnetic stirring bar, was charged with **A** (0.05 mmol), NaBD₄ (1.0 mmol) and THF (50

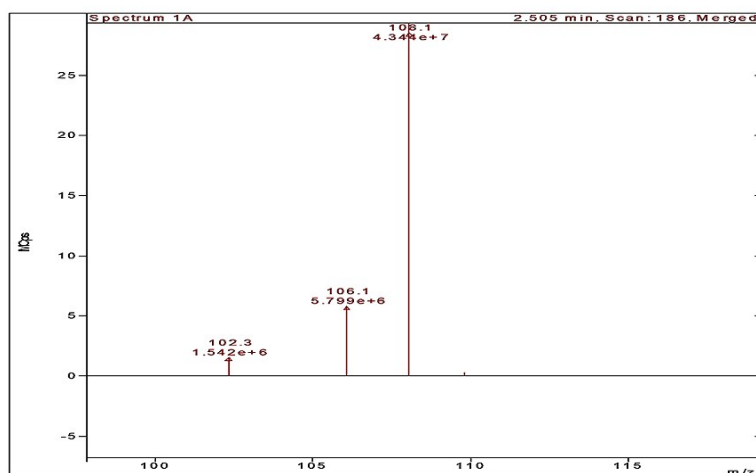
mL). Then a solution of methyl benzoate (20 mmol) in THF (4 mL) was added by syringe. The autoclave was purged by three cycles of pressurization/venting with hydrogen (1 MPa), then pressurized with hydrogen (5 MPa), sealed and disconnected from the hydrogen source. The vessel was stirred and heated to 120 °C (bath temperature). After four hours, the autoclave was cooled to room temperature and the pressure was released slowly. The reaction mixture was filtered through a plug of silica gel and then analyzed by GC. The crude product was purified by column chromatography¹. GC-MS analysis was carried out on a Bruker SCION TQ GC-MS/MS.

Table S7. Reduction of methyl benzoate by hydrogen in the presence of NaBD₄

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{OCH}_3 \\ \mathbf{2a} \end{array} \xrightarrow[\text{NaBD}_4 (5 \text{ mol\%}), \text{THF}]{\text{A} (0.05 \text{ mol\%}), \text{H}_2 (5 \text{ MPa})} \begin{array}{c} \text{Ph}-\text{CH}_2-\text{OH} \\ \mathbf{3a_1} \end{array} + \begin{array}{c} \text{D} \\ \\ \text{Ph}-\text{CH}-\text{OH} \\ \mathbf{3a_2} \end{array} + \begin{array}{c} \text{D} \\ \\ \text{Ph}-\text{C}-\text{OH} \\ \\ \text{D} \\ \mathbf{3a_3} \end{array} $			
Products	3a₁	3a₂	3a₃
Relative percentage (%)	90	9.25	0.75

2.3 GC-MS spectra of non-labeled benzyl alcohol and the products (3a₁, 3a₂ and 3a₃)

(a) GC-MS spectrum of non-labeled benzyl alcohol



Spectrum

* File: wz-1.xms

* Retention Time: 2.505 min

* Scan: 186

* Data: Merged

* RIC: 2785490551

* Background Correction: Yes

* Edited Data: No

* Data Type: Centroid

* BP: 30.0

* BP Amount: (1.989e+9=100%)

* Name: 2.505 min, Scan: 186

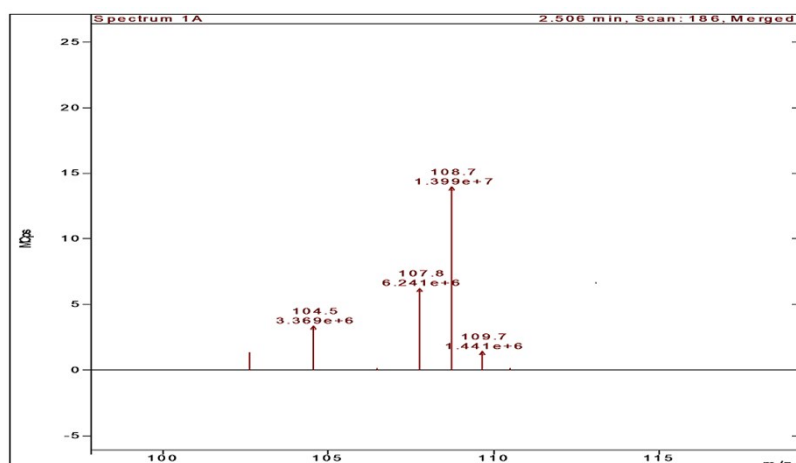
* Comment: WZ-1.xms

* Pair Count = 43

108.0565 43439480

109.7945 312358

(b) GC-MS spectrum of the products (3a₁, 3a₂ and 3a₃)



Spectrum

* File: wz-2.xms

* Retention Time: 2.506 min

* Scan: 186

* Data: Merged

* RIC: 2204557847

* Background Correction: Yes

* Edited Data: No

* Data Type: Centroid

* BP: 28.3

* BP Amount: (1.789e+9=100%)

* Name: 2.506 min, Scan: 186

* Comment: WZ-2.xms

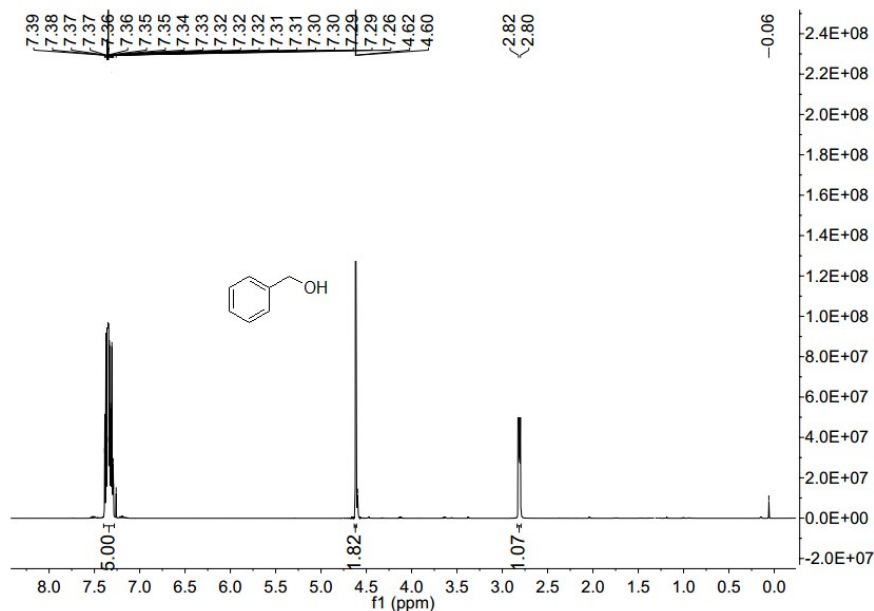
* Pair Count = 59

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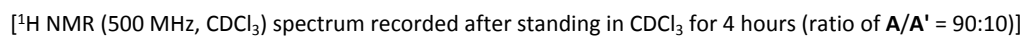
109.6601 1440779

110.5073 130867

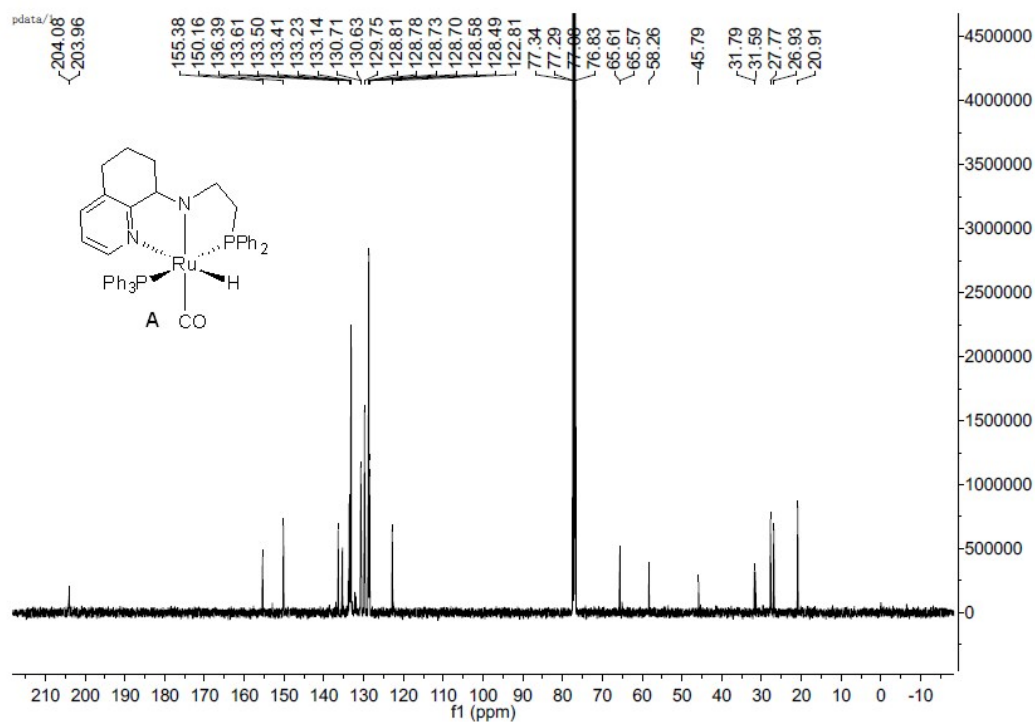
2. 3 ¹H NMR spectrum of the products (3a₁, 3a₂ and 3a₃)



3.1 The ^1H NMR spectrum of A in CDCl_3 ; spectrum recorded following dissolution^{1(b)}

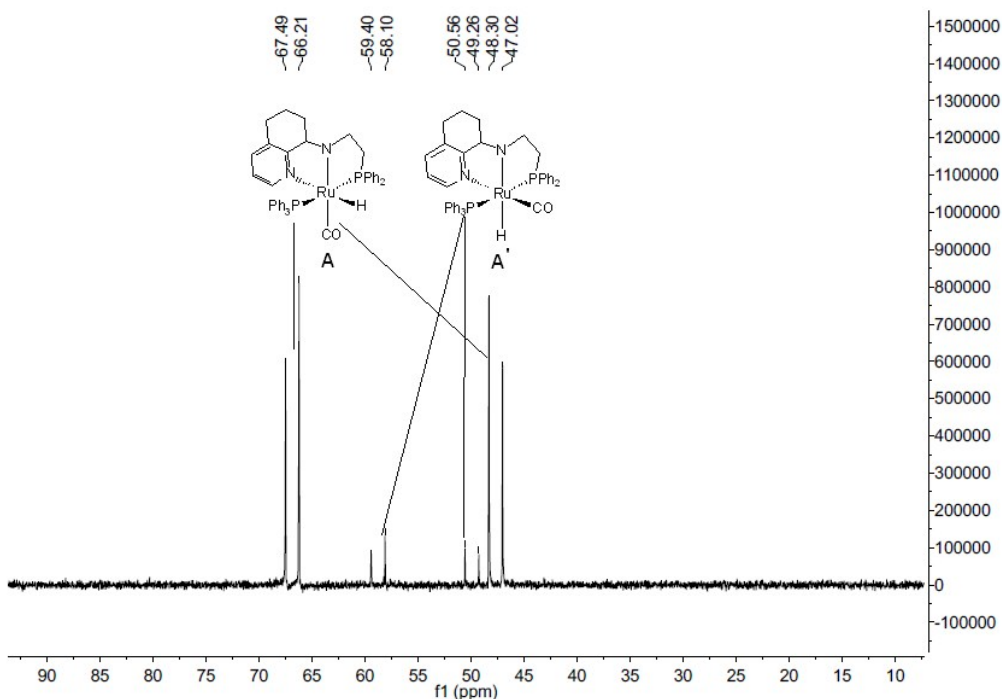


3.3 The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of A in CDCl_3 ; spectrum recorded after 4 hours in solution



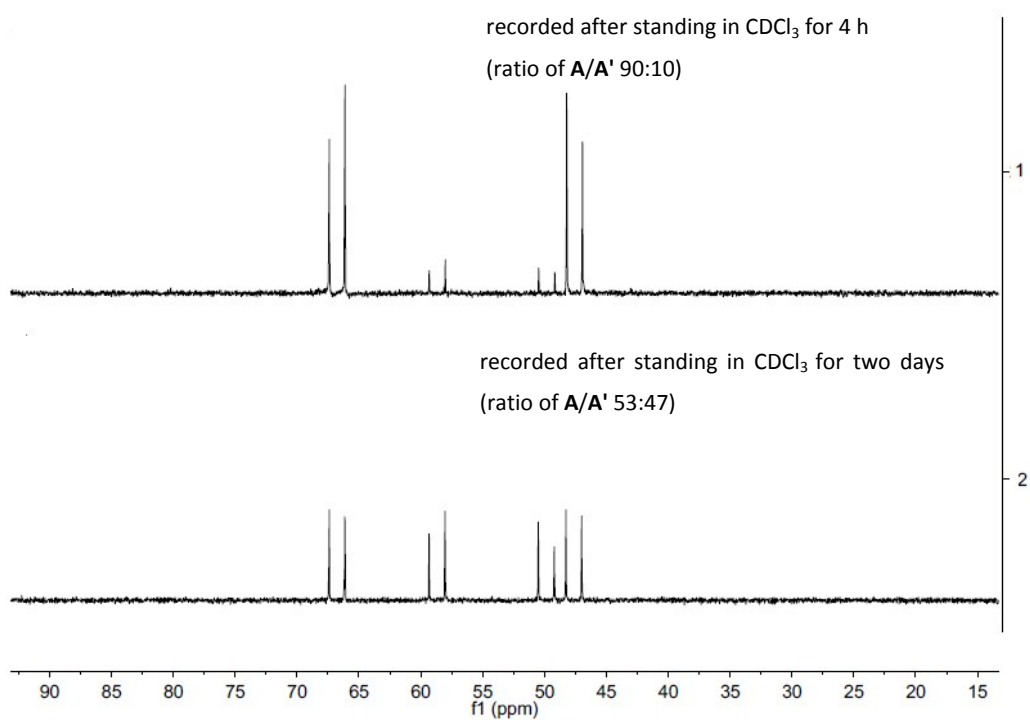
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) spectrum recorded after standing in CDCl_3 for 4 hours (only A observable)]

3.4 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of A in CDCl_3 ; spectrum recorded after 4 hours in solution

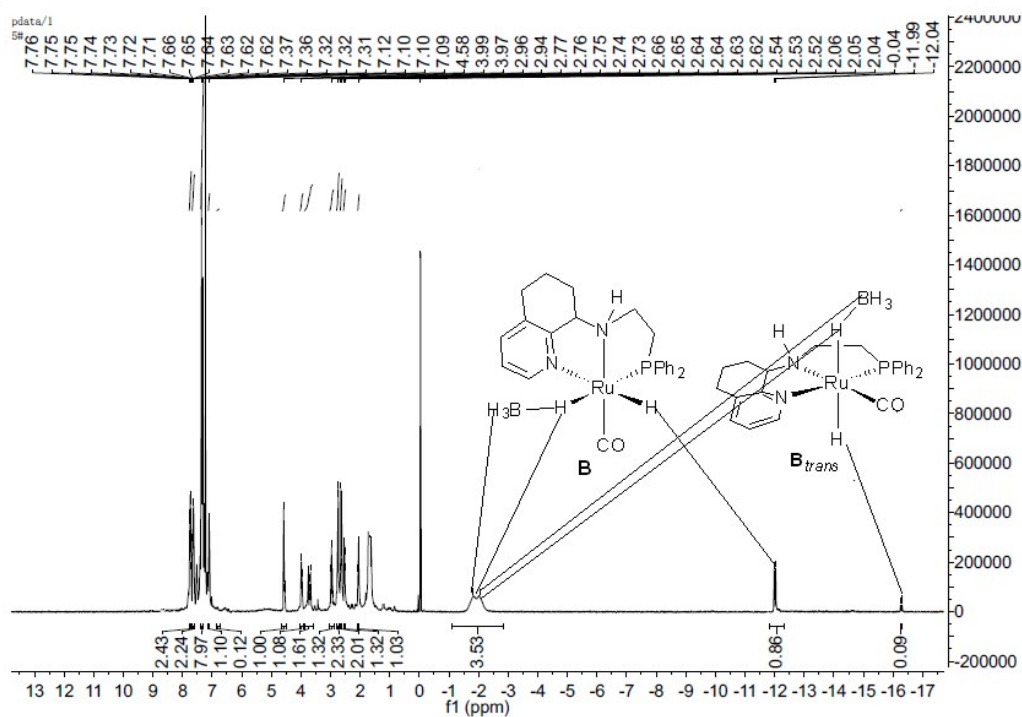


$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum recorded after standing in CDCl_3 for 4 hours (ratio of A/A' = 90:10)]

3.5 Comparison of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **A** recorded over time

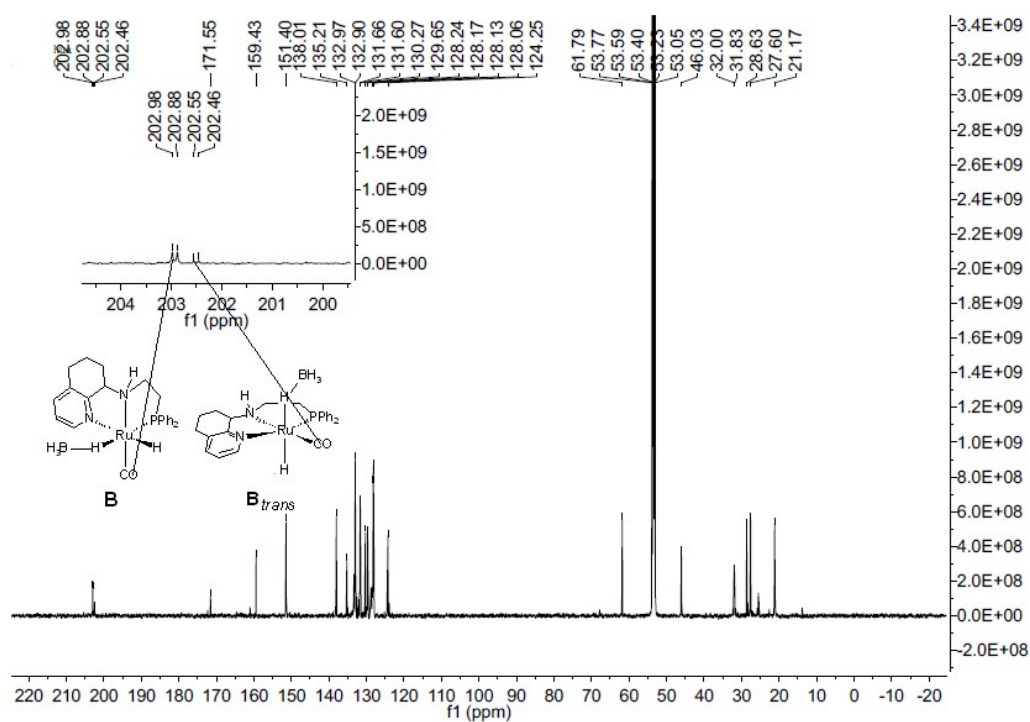


3.6 The ^1H NMR spectrum of **B** in CDCl_3



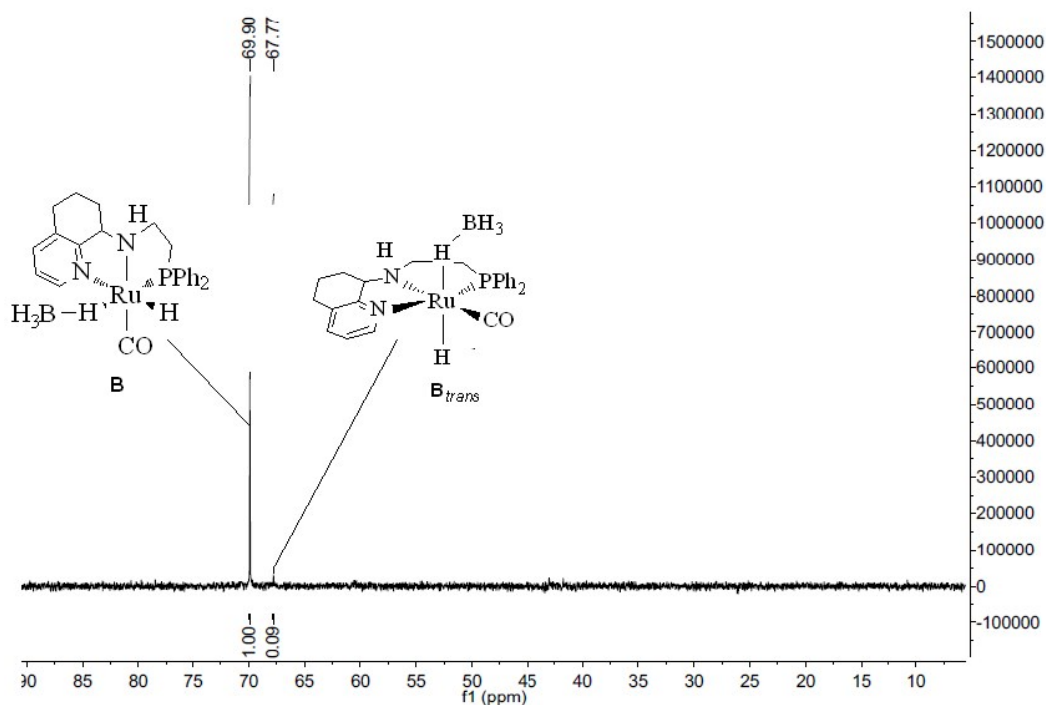
^1H NMR (500 MHz, CDCl_3) spectrum recorded on dissolution in CDCl_3 (ratio of **B**:**B_{trans}** = 90:10)]

3.7 The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **B** in CD_2Cl_2



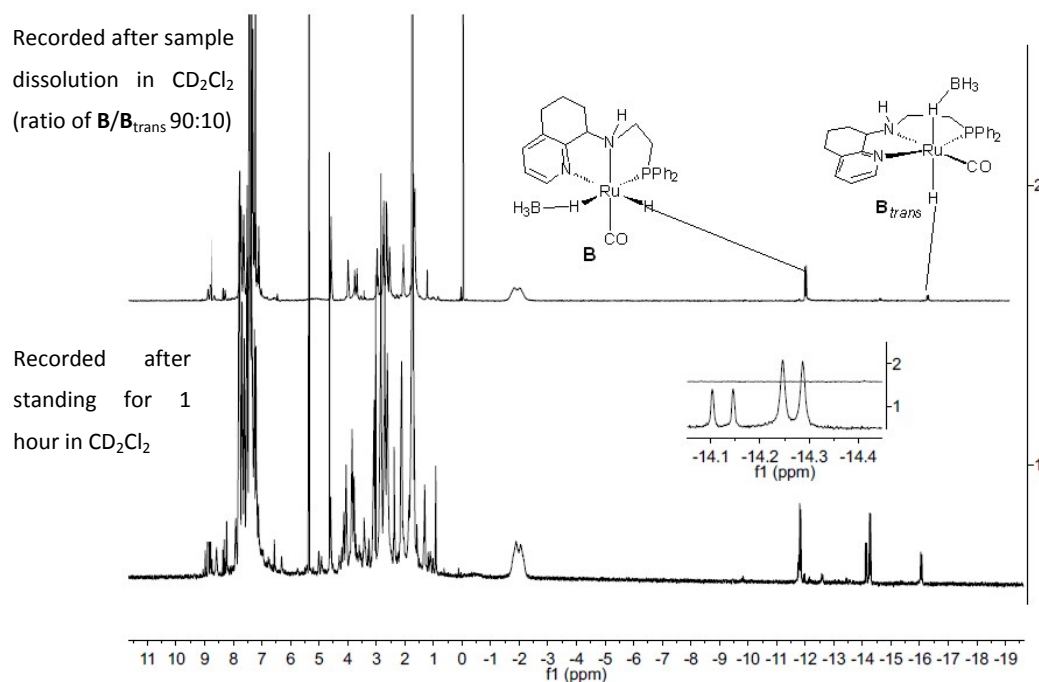
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) spectrum recorded on dissolution in CD_2Cl_2 (ratio of **B**:**B_{trans}** = 90:10)

3.8 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **B** in CDCl_3



$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum recorded on dissolution in CDCl_3 (ratio of **B**:**B_{trans}** = 90:10)

3.9 Comparison of the ^1H NMR spectra of **G** recorded over time in CD_2Cl_2



3.10 NMR data for the alcohols (**3**)

Benzyl alcohol (3a)^{3,5} (Table 1): ^1H NMR (500 MHz, CDCl_3) δ 7.46–7.22 (m, 5H), 4.67 (s, 2H), 2.66 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.86, 128.55, 127.63, 127.04, 65.17.

2-Fluorobenzyl alcohol (3b)³: ^1H NMR (500 MHz, CDCl_3) δ 7.40 (t, $J=7.5$ Hz, 1H), 7.31–7.24 (m, 1H), 7.13 (t, $J=7.5$ Hz, 1H), 7.04 (t, $J=9.2$ Hz, 1H), 4.70 (s, 2H), 3.09 (s, 1H). ^{13}C NMR (CDCl_3) δ 160.55 (d, $J_{\text{C-F}}=246.0$ Hz), 129.26 (d, $J_{\text{C-F}}=4.4$ Hz), 129.19, 127.88 (d, $J_{\text{C-F}}=14.7$ Hz), 124.18 (d, $J_{\text{C-F}}=3.5$ Hz), 115.16 (d, $J_{\text{C-F}}=21.2$ Hz), 58.90.

2-(Trifluoromethyl)benzyl alcohol (3c)⁴: ^1H NMR (500 MHz, CDCl_3) δ 7.69 (d, $J=7.7$ Hz, 1H), 7.64 (d, $J=7.8$ Hz, 1H), 7.55 (t, $J=7.5$ Hz, 1H), 7.38 (t, $J=7.6$ Hz, 1H), 4.85 (s, 2H), 2.95 (s, 1H). ^{13}C NMR (CDCl_3) δ 139.25, 132.09, 128.62, 127.33, 125.65, 123.34, 121.16, 61.08.

2-Chlorobenzyl alcohol (3d)³: ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, $J=7.4$ Hz, 1H), 7.38 (d, $J=7.8$ Hz, 1H), 7.32–7.21 (m, 2H), 4.79 (s, 2H), 2.27 (s, 1H). ^{13}C NMR (CDCl_3) δ 138.18, 132.72, 129.35, 128.83, 128.73, 127.03, 62.80. White solid Mp 70–72 $^\circ\text{C}$.

2-Bromobenzyl alcohol (3e)⁵: ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J=8.0$ Hz, 1H), 7.51 (d, $J=7.6$ Hz, 1H), 7.36 (t, $J=7.5$ Hz, 1H), 7.19 (t, $J=7.6$ Hz, 1H), 4.78 (s, 2H), 2.02 (s, 1H). ^{13}C NMR (CDCl_3) δ 139.74, 132.61, 129.13, 128.93, 127.66, 122.59, 65.10. White solid Mp 78–79 $^\circ\text{C}$.

2-Iodobenzyl alcohol (3f): ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J=7.9$ Hz, 1H), 7.51–7.44 (m, 1H), 7.38 (t, $J=7.5$ Hz, 1H), 7.01 (t, $J=7.1$ Hz, 1H), 4.69 (s, 2H). ^{13}C NMR (CDCl_3) δ 142.59, 139.21, 130.19, 129.30, 128.48, 97.46, 69.28. White solid Mp 90–92 $^\circ\text{C}$.

3-Fluorobenzyl alcohol (3g): ^1H NMR (500 MHz, CDCl_3) δ 7.29–7.35 (m, 1H), 7.04–7.09 (m, 2H), 6.9 (t, $J=8.5$ Hz, 1H), 4.64 (s, 2H), 2.63 (s, 1H). ^{13}C NMR (CDCl_3) δ 163.99 (d, $J_{\text{C-F}}=245.4$ Hz), 143.49 (d, $J_{\text{C-F}}=6.9$ Hz), 130.01 (d, $J_{\text{C-F}}=8.2$ Hz), 122.21 (d, $J=2.7$ Hz), 114.40 (d, $J_{\text{C-F}}=21.2$ Hz), 113.72 (d, $J_{\text{C-F}}=21.8$ Hz), 64.30.

3-(Trifluoromethyl)benzyl alcohol (3h): ^1H NMR (500 MHz, CDCl_3) δ 7.61 (s, 1H), 7.54 (d, $J=7.6$ Hz, 1H), 7.50

(d, $J=7.6$ Hz, 1H), 7.45 (t, $J=7.6$ Hz, 1H), 4.69 (s, 2H), 3.44 (s, 1H). ^{13}C NMR (CDCl_3) δ 141.74, 130.02, 128.89, 125.22, 124.23 (d, $J_{\text{C-F}}=3.8$ Hz), 123.43 (d, $J_{\text{C-F}}=3.7$ Hz), 123.06, 64.16.

3-Chlorobenzyl alcohol (3i)³: ^1H NMR (500 MHz, CDCl_3) δ 7.35 (s, 1H), 7.30–7.23 (m, 2H), 7.21 (d, $J=7.0$ Hz, 1H), 4.65 (s, 2H), 1.95 (s, 1H). ^{13}C NMR (CDCl_3) δ 142.85, 134.42, 129.81, 127.68, 126.95, 124.86, 64.42.

3-Bromobenzyl alcohol (3j): ^1H NMR (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.44 (d, $J=7.7$ Hz, 1H), 7.29 (d, $J=6.0$ Hz, 1H), 7.24 (t, $J=7.7$ Hz, 1H), 4.67 (s, 1H), 1.99 (s, 1H). ^{13}C NMR (CDCl_3) δ 143.12, 130.63, 130.11, 129.89, 125.33, 122.65, 64.44.

4-Fluorobenzyl alcohol (3k)^{3,5}: ^1H NMR (500 MHz, CDCl_3) δ 7.36 (m, 2H), 7.07 (m, 2H), 4.68 (s, 2H), 1.79 (s, 1H). ^{13}C NMR (CDCl_3) δ 163.25 (d, $J_{\text{C-F}}=245.4$ Hz), 136.57 (d, $J_{\text{C-F}}=3.1$ Hz), 128.73 (d, $J_{\text{C-F}}=8.1$ Hz), 115.38 (d, $J_{\text{C-F}}=21.1$ Hz), 64.28.

4-(Trifluoromethyl)benzyl alcohol (3l): ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J=8.1$ Hz, 2H), 7.50 (d, $J=8.0$ Hz, 2H), 4.79 (s, 2H), 1.88 (s, 1H). ^{13}C NMR (CDCl_3) δ 144.74, 129.87, 126.80, 125.40 (q, $J_{\text{C-F}}=3.8$ Hz), 123.08, 64.29.

4-Chlorobenzyl alcohol (3m)^{3,5}: ^1H NMR (500 MHz, CDCl_3) δ 7.33 (d, $J=8.1$ Hz, 2H), 7.31 (d, $J=8.5$ Hz, 2H), 4.68 (s, 2H), 2.37 (s, 1H). ^{13}C NMR (CDCl_3) δ 139.20, 133.35, 128.66, 128.29, 64.41. White solid Mp 69–72 °C.

4-Bromobenzyl alcohol (3n)^{3,5}: ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, $J=8.1$ Hz, 2H), 7.18 (d, $J=8.1$ Hz, 2H), 4.57 (s, 2H), 2.84 (s, 1H). ^{13}C NMR (CDCl_3) δ 139.74, 131.59, 128.59, 121.40, 64.32. White solid Mp 77–78 °C.

4-Methoxybenzyl alcohol (3o)^{3,5}: ^1H NMR (500 MHz, CDCl_3) δ 7.31 (d, $J=8.7$ Hz, 2H), 6.92 (d, $J=8.4$ Hz, 2H), 4.63 (s, 2H), 3.83 (s, 3H), 1.76 (s, 1H). ^{13}C NMR (CDCl_3) δ 159.11, 133.25, 128.63, 113.91, 64.76, 55.28.

4-Methylbenzyl alcohol (3p)^{3,5}: ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, $J=8.1$ Hz, 2H), 7.19 (d, $J=7.9$ Hz, 2H), 4.65 (s, 2H), 2.37 (s, 3H), 1.87 (s, 1H). ^{13}C NMR (CDCl_3) δ 137.95, 137.36, 129.23, 127.13, 65.21, 21.14.

Isobenzofuran-1(3H)-one (3r): ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, $J=7.7$ Hz, 1H), 7.71 (t, $J=7.5$ Hz, 1H), 7.57 (t, $J=7.5$ Hz, 1H), 7.52 (d, $J=7.6$ Hz, 1H), 5.35 (s, 2H). ^{13}C NMR (CDCl_3) δ 171.11, 146.54, 134.02, 129.04, 125.81, 125.76, 122.12, 69.66. White solid Mp 68–70 °C

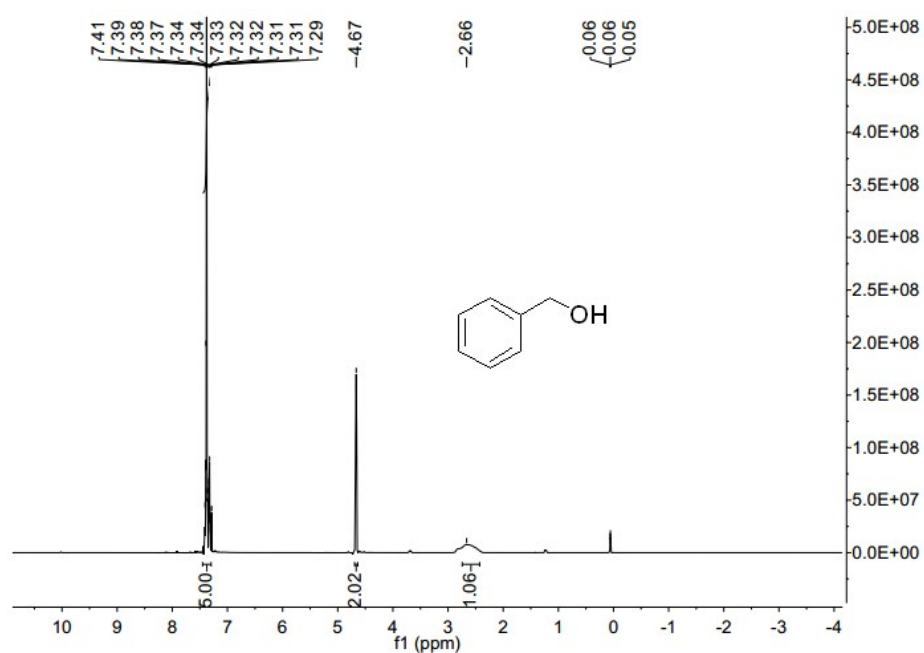
3,4-Difluorobenzyl alcohol (3s): ^1H NMR (500 MHz, CDCl_3) δ 7.85–7.65 (m, 1H), 7.25–7.14 (m, 1H), 7.01 (t, $J=8.4$ Hz, 1H), 3.92 (s, 2H), 1.66 (s, 1H). ^{13}C NMR (CDCl_3) δ 165.78 (d, $J_{\text{C-F}}=2.6$ Hz), 153.01, 126.52 (d, $J_{\text{C-F}}=3.4$ Hz), 117.62 (d, $J_{\text{C-F}}=27.5$ Hz), 116.45, 114.27, 52.19.

2,3,4,5,6-Pentafluorobenzyl alcohol (3t): ^1H NMR (500 MHz, CDCl_3) δ 4.79 (s, 2H), 2.54 (s, 1H). ^{13}C NMR (CDCl_3) δ 146.72, 144.48, 142.20, 140.17, 138.47, 136.39 (d, $J_{\text{C-F}}=16.4$ Hz), 52.33. White solid Mp 38–40 °C.

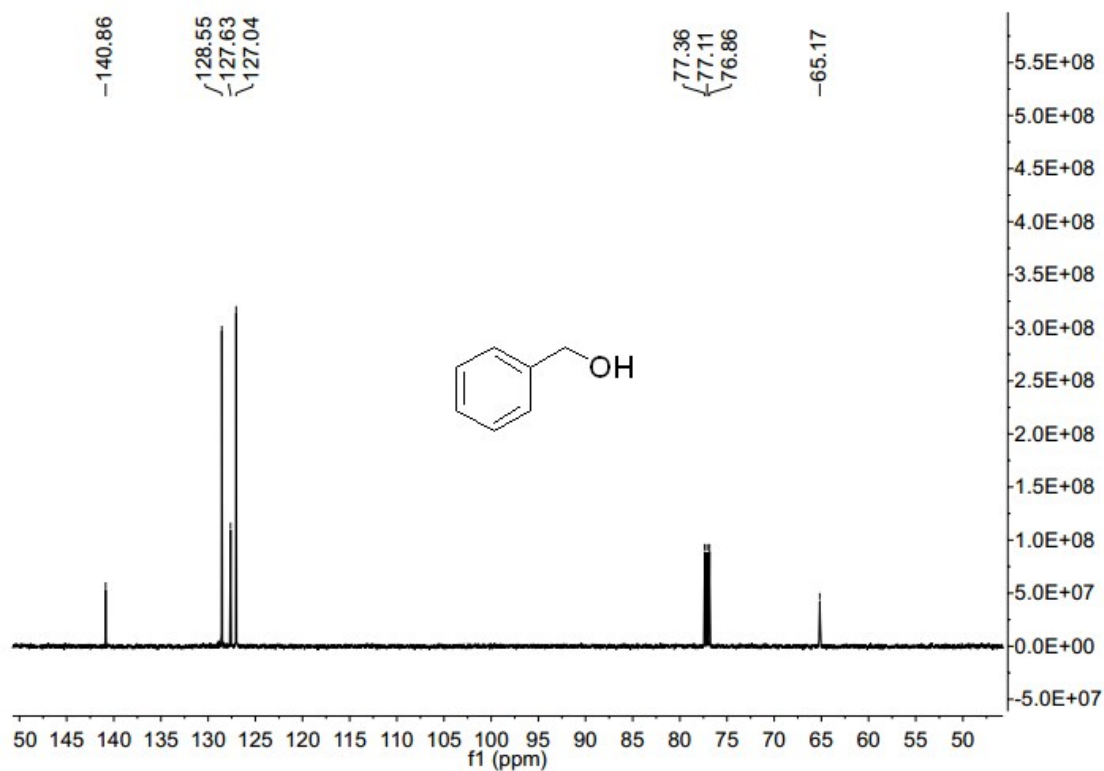
3-Phenyl-1-propanol (3t) (Table 4, entry 9): ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, $J=7.5$ Hz, 2H), 7.26–7.19 (m, 3H), 3.71 (t, $J=6.4$ Hz, 2H), 2.75 (t, $J=7.7$ Hz, 2H), 1.94 (m, 2H), 1.72 (s, 1H). ^{13}C NMR (CDCl_3) δ 141.86, 128.46, 128.43, 125.89, 62.21, 34.20, 32.10.

3.11 NMR spectra for the alcohols (3)

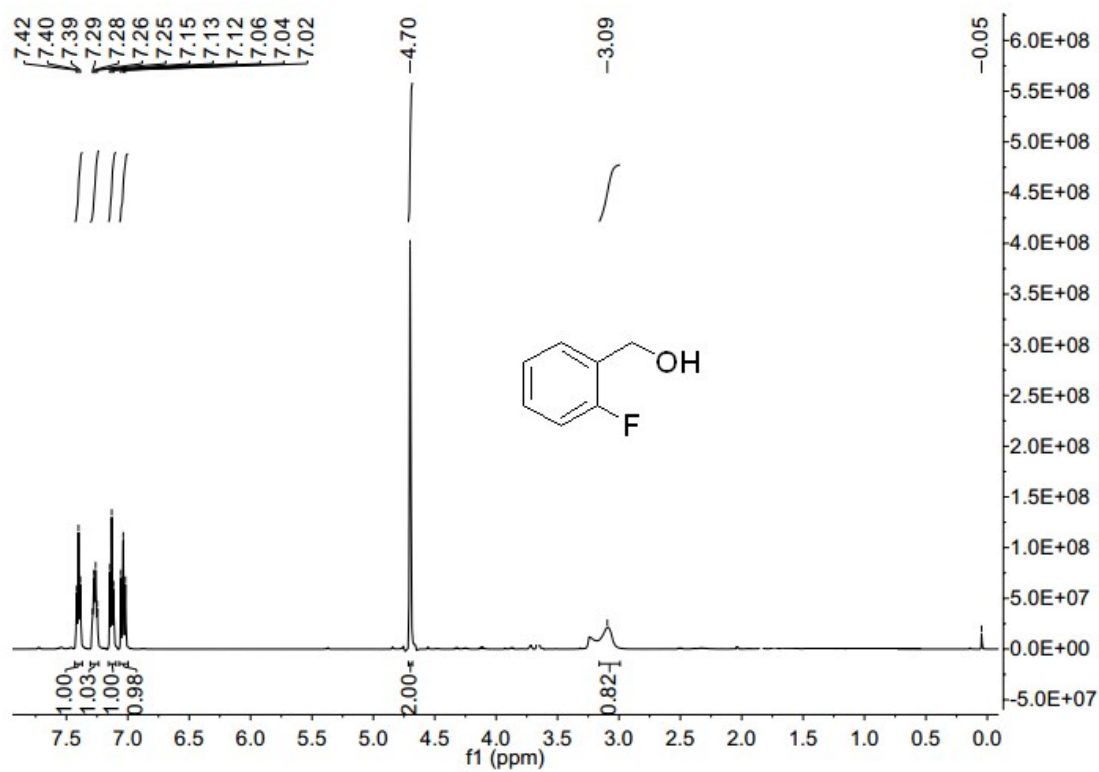
^1H NMR spectrum of benzyl alcohol (**3a**)



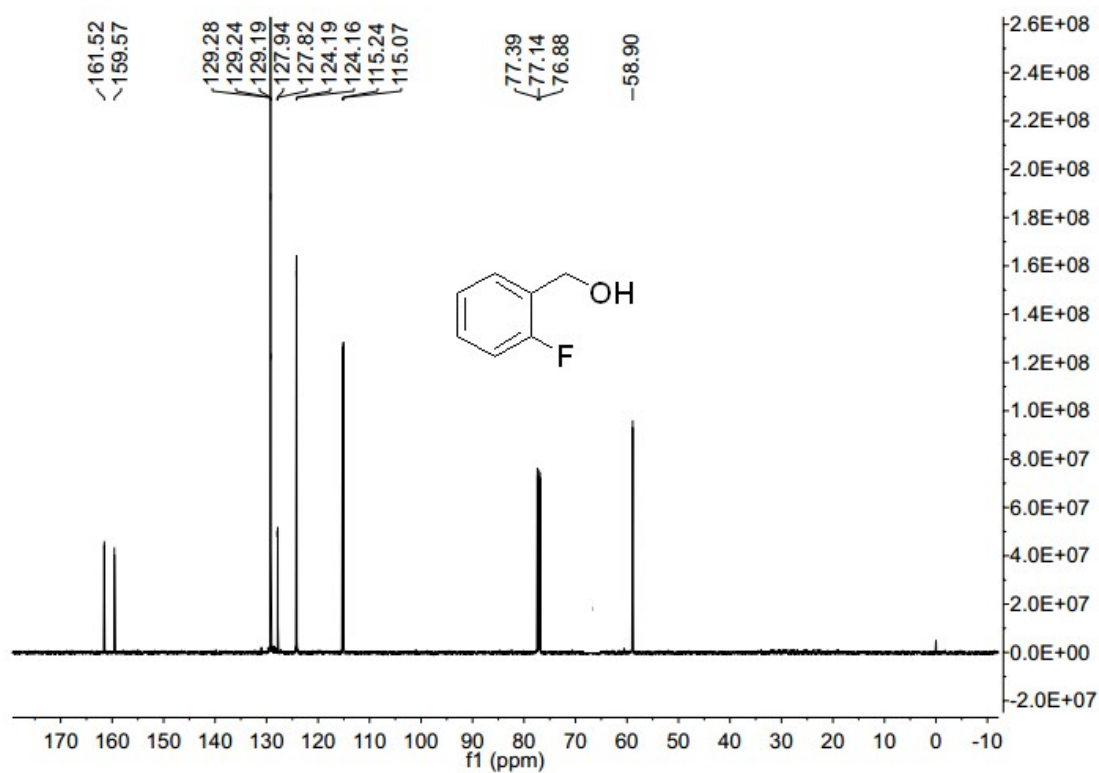
^{13}C NMR spectrum of benzyl alcohol (**3a**)



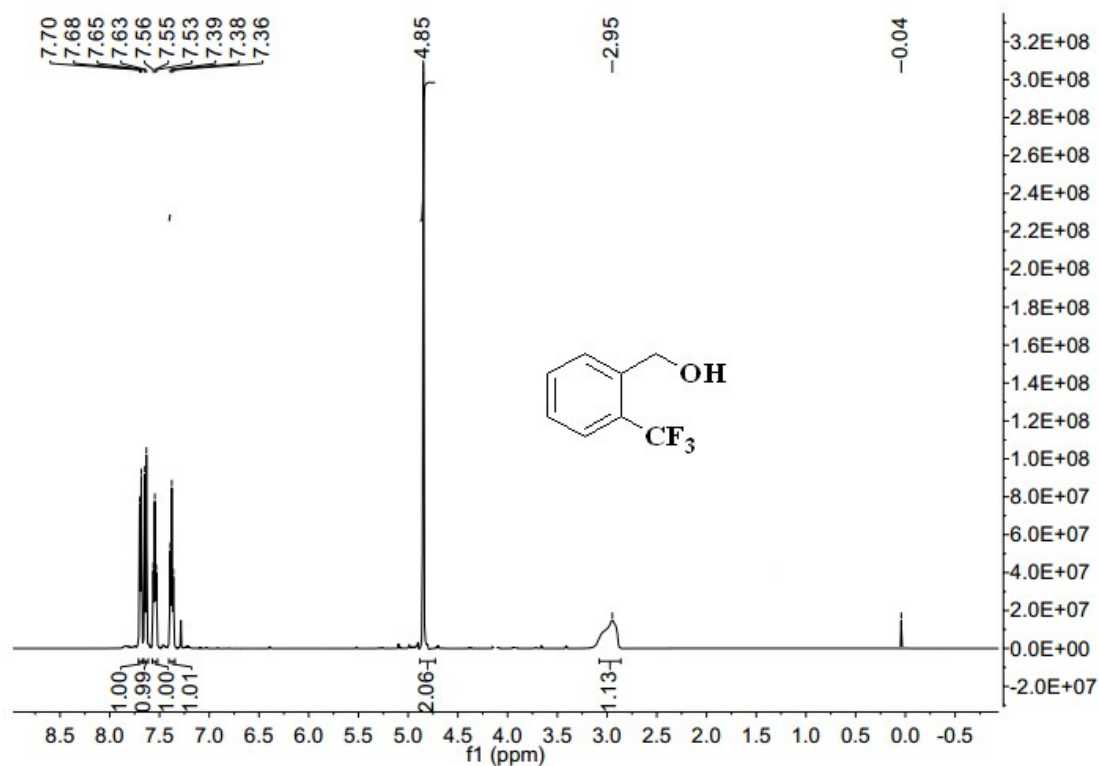
^1H NMR spectrum of 2-fluorobenzyl alcohol (**3b**)



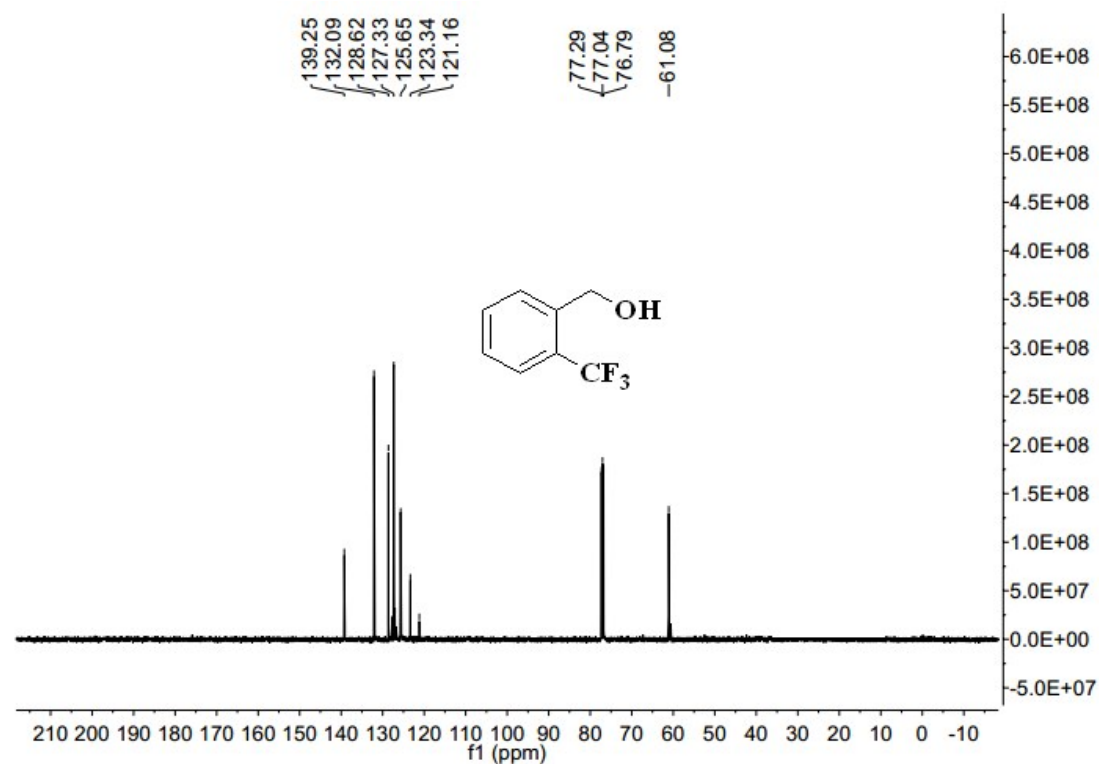
^{13}C NMR spectrum of 2-fluorobenzyl alcohol (**3b**)



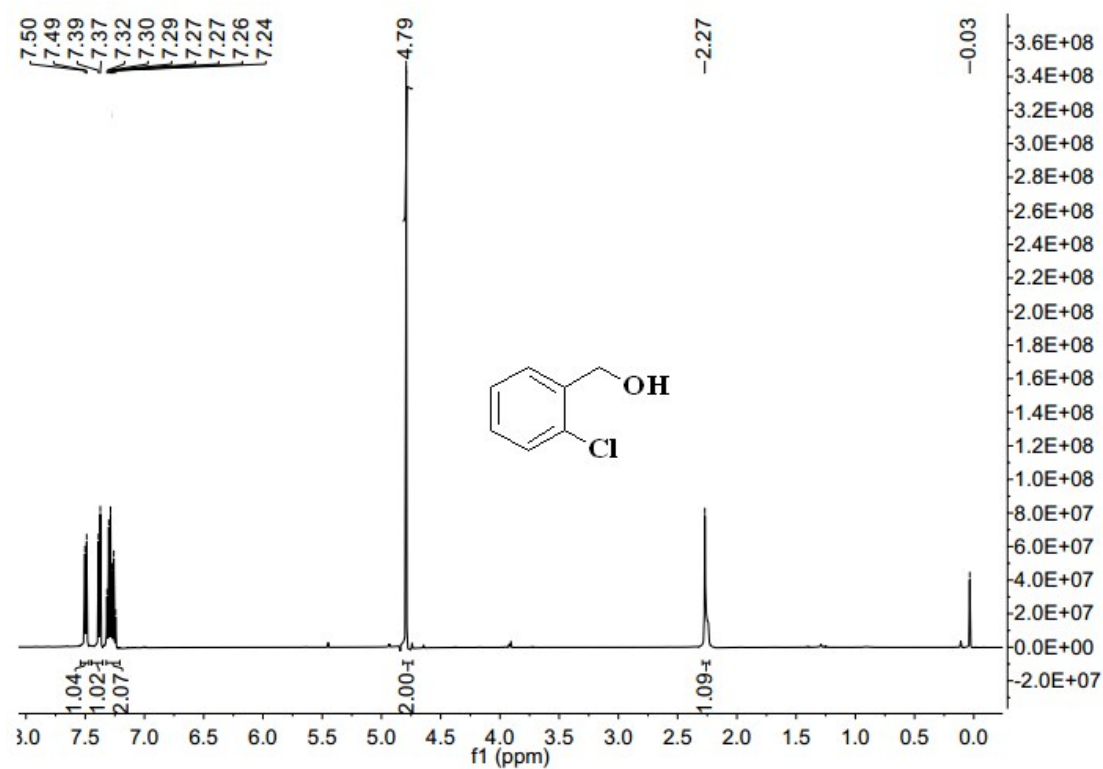
^1H NMR spectrum of 2-(trifluoromethyl)benzyl alcohol (**3c**)



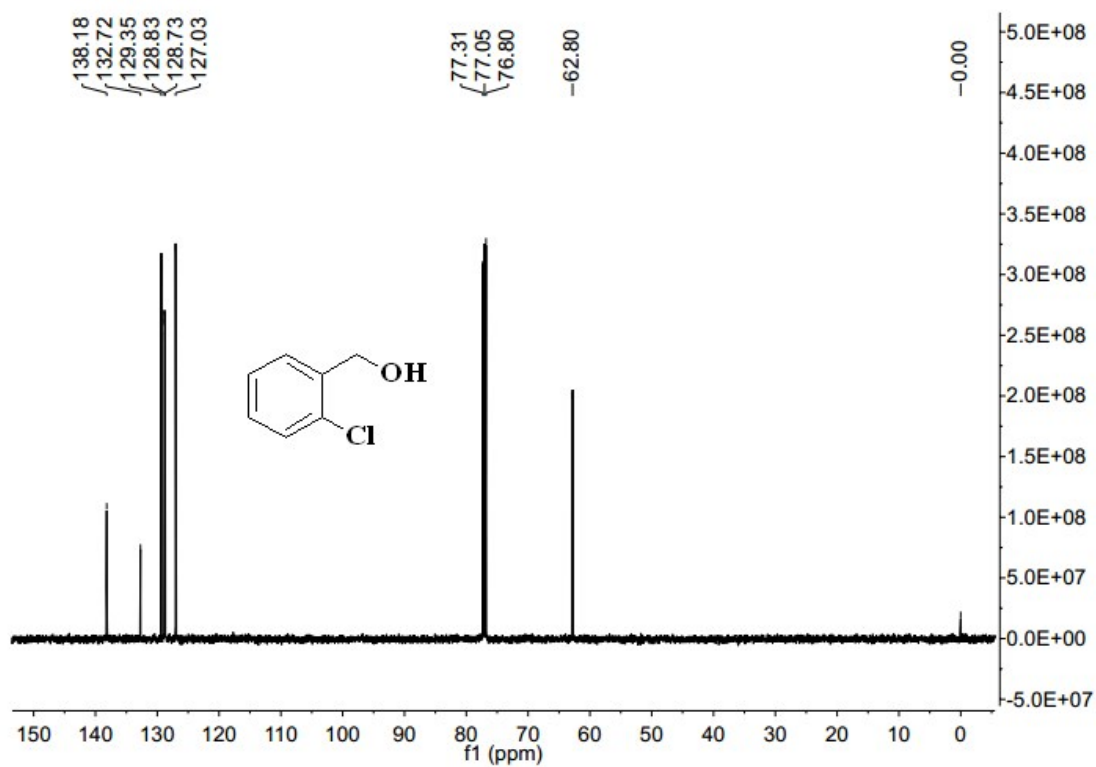
^{13}C NMR spectrum of 2-(trifluoromethyl)benzyl alcohol (**3c**)



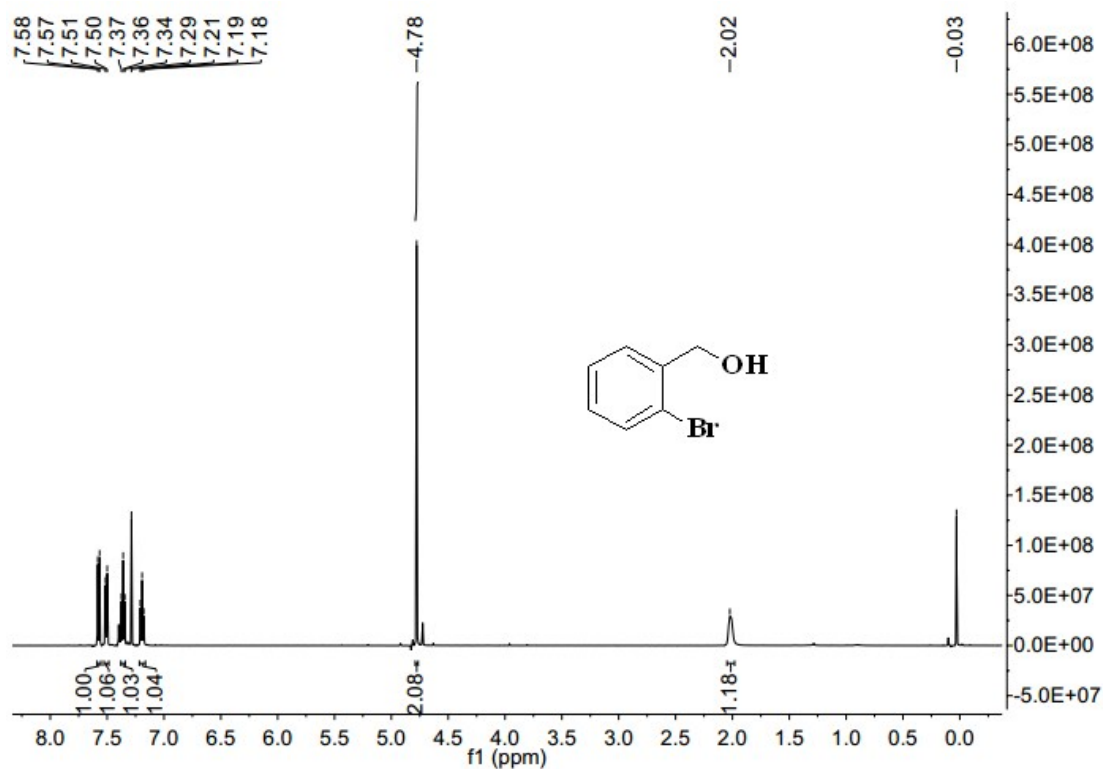
^1H NMR spectrum of 2-chlorobenzyl alcohol (**3d**)



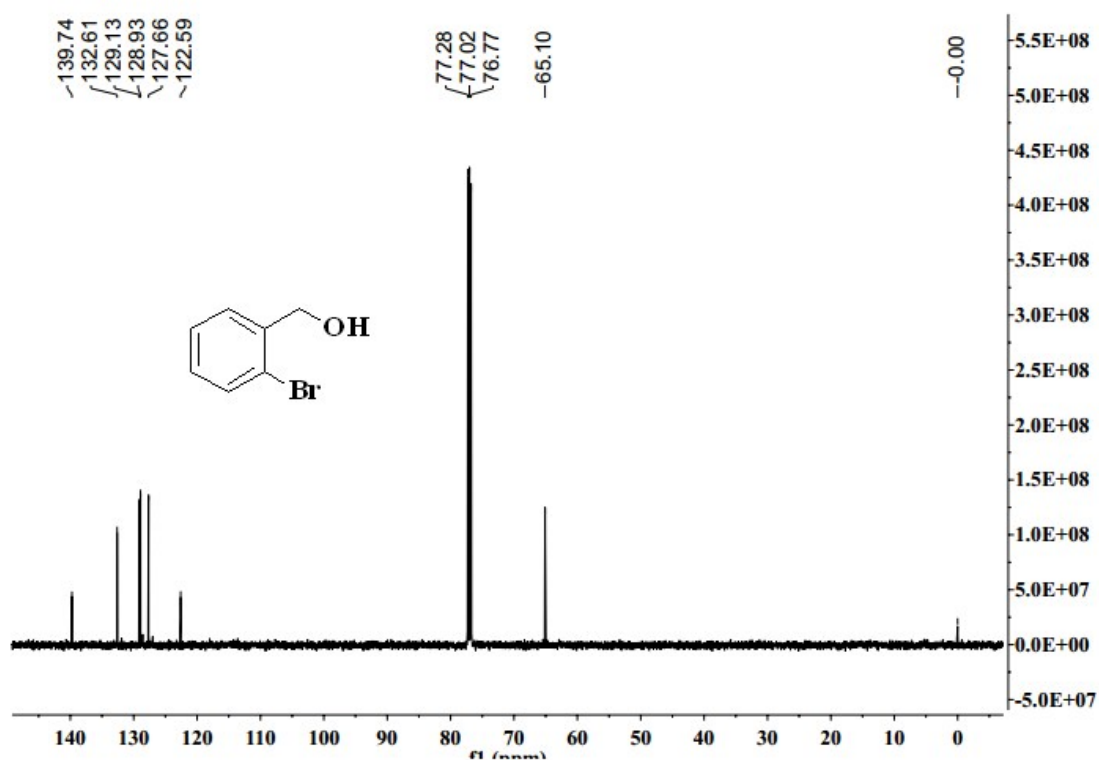
^{13}C NMR spectrum of 2-chlorobenzyl alcohol (**3d**)



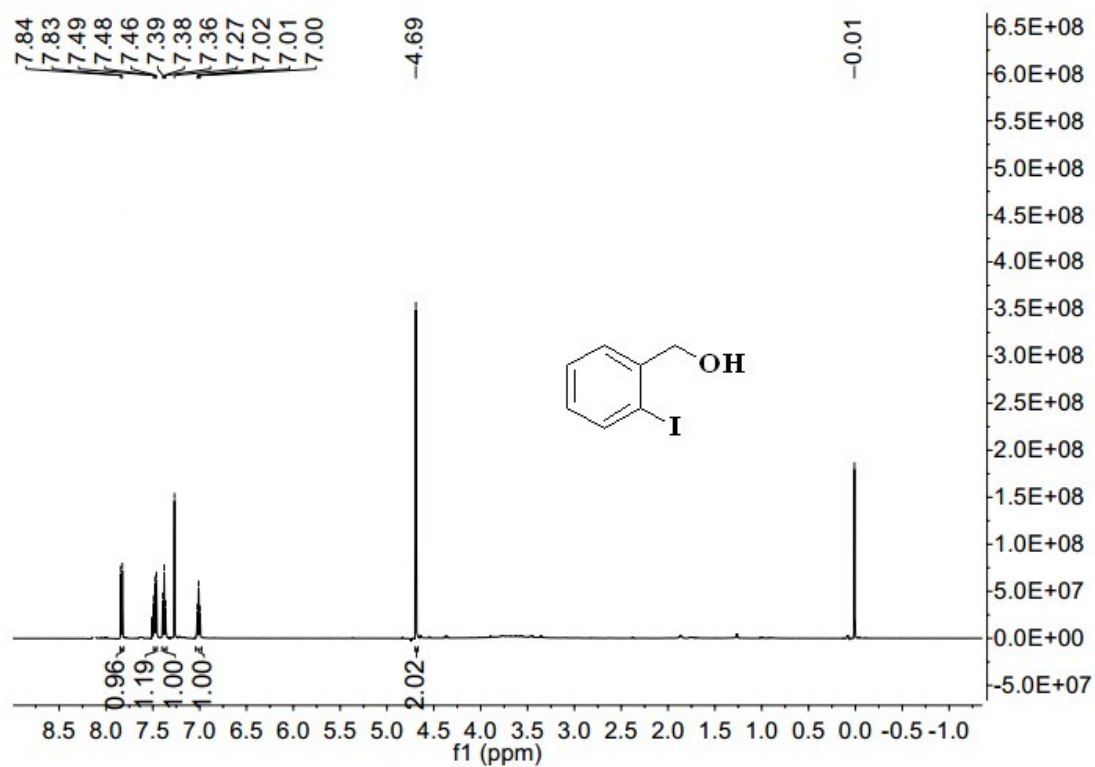
^1H NMR spectrum of 2-bromobenzyl alcohol (**3e**)



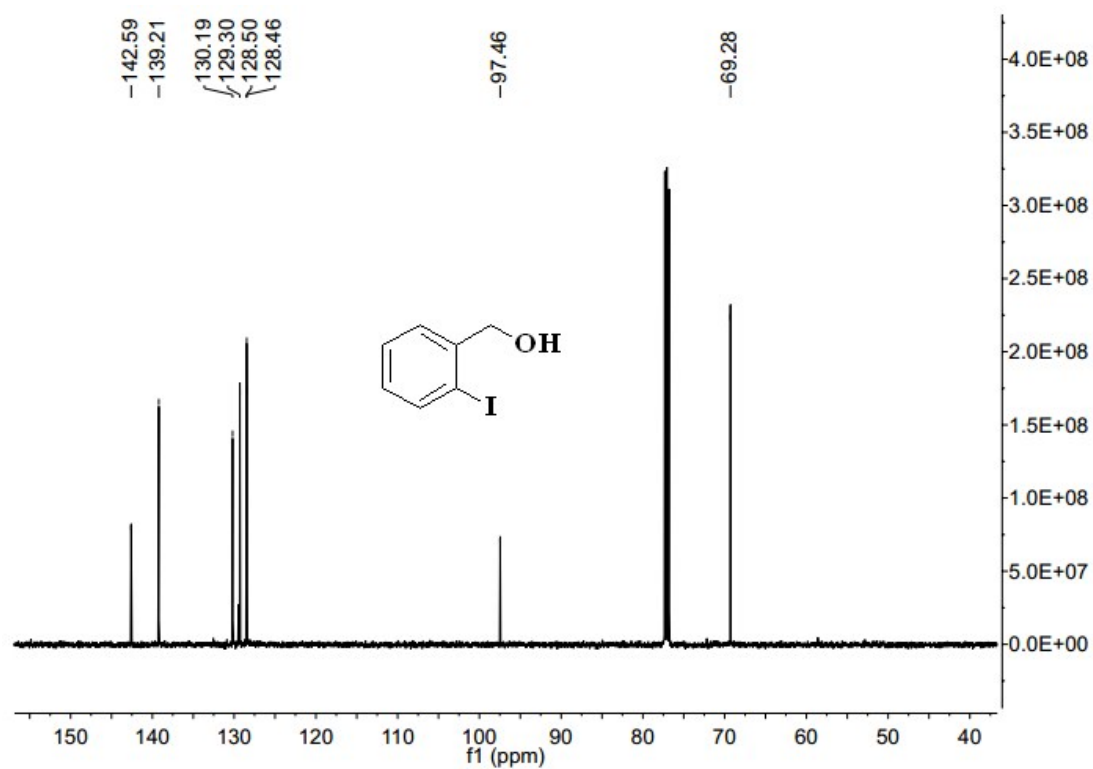
^{13}C NMR spectrum of 2-bromobenzyl alcohol (**3e**)



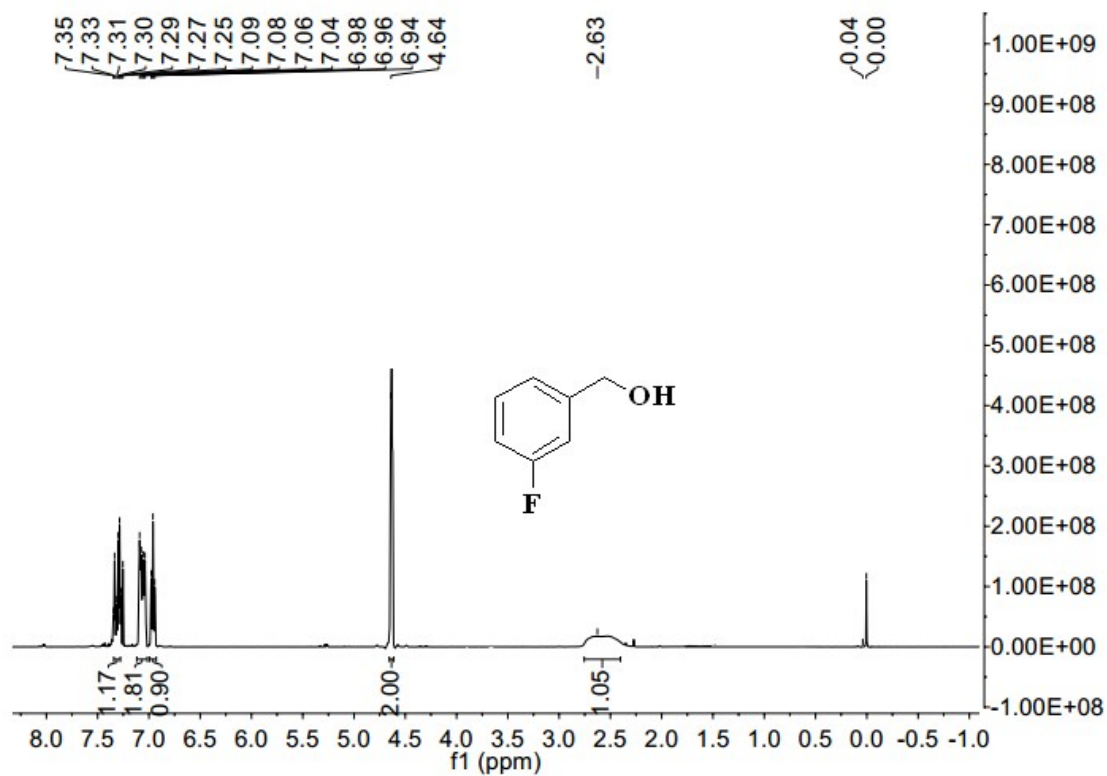
^1H NMR spectrum of 2-iodobenzyl alcohol (**3f**)



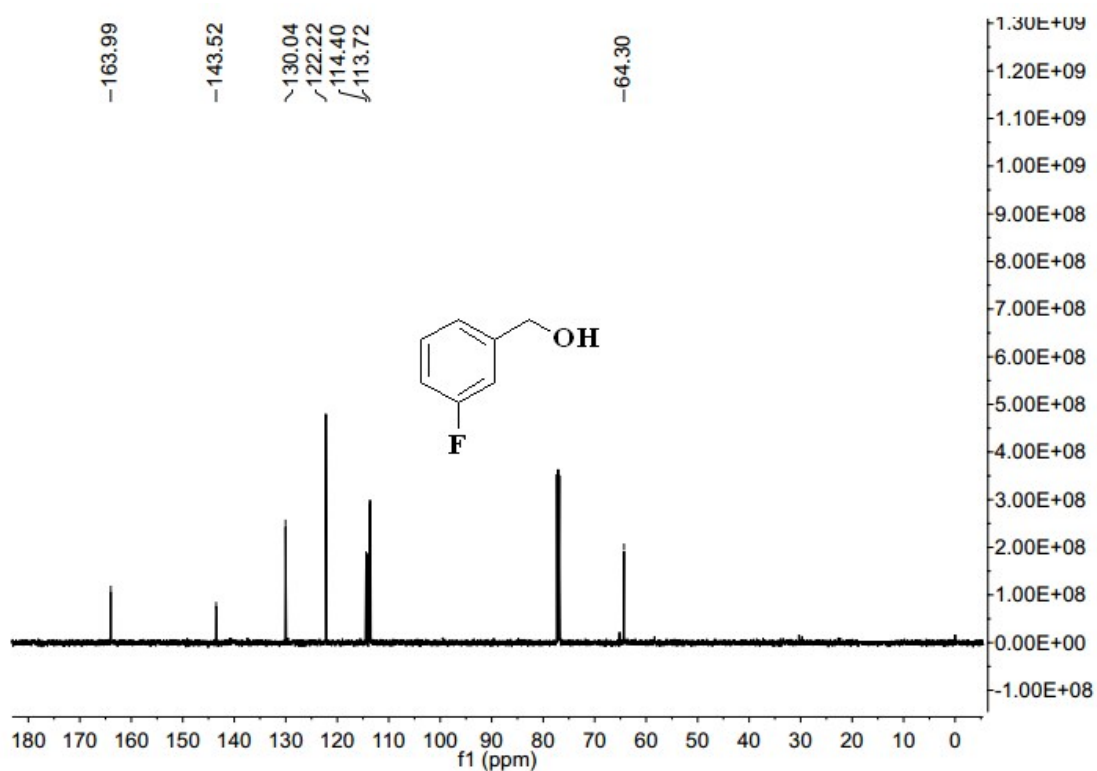
^{13}C NMR spectrum of 2-iodobenzyl alcohol (**3f**)



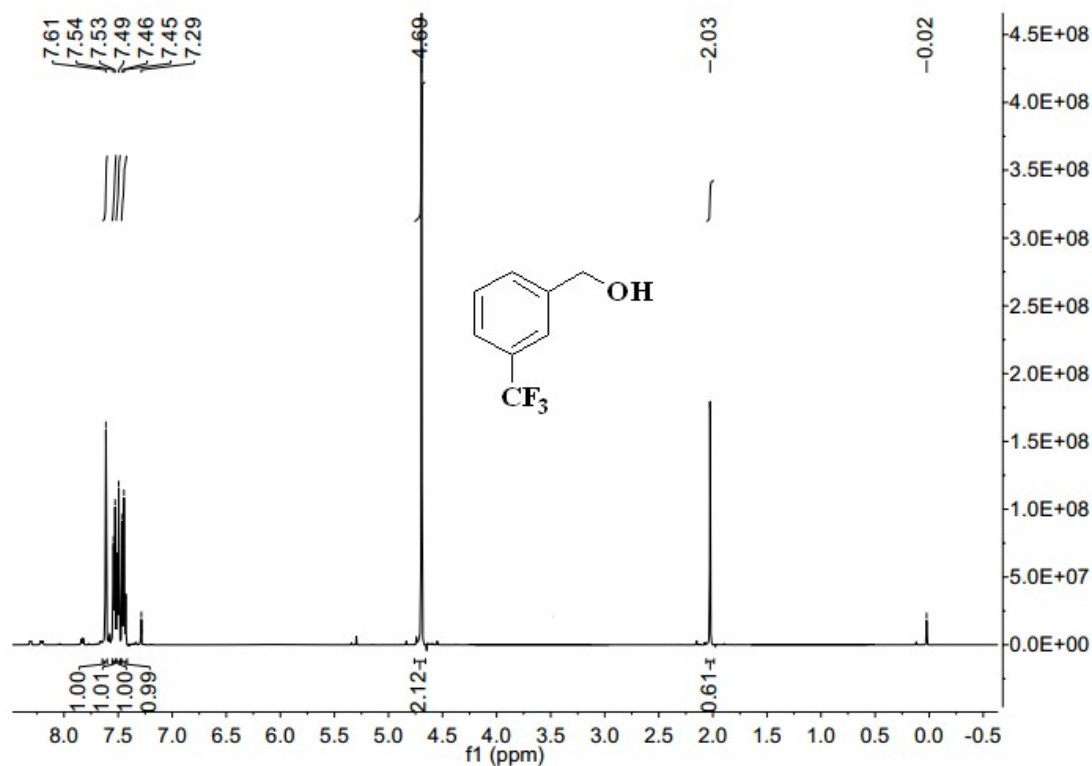
^1H NMR spectrum of 3-fluorobenzyl alcohol (**3g**)



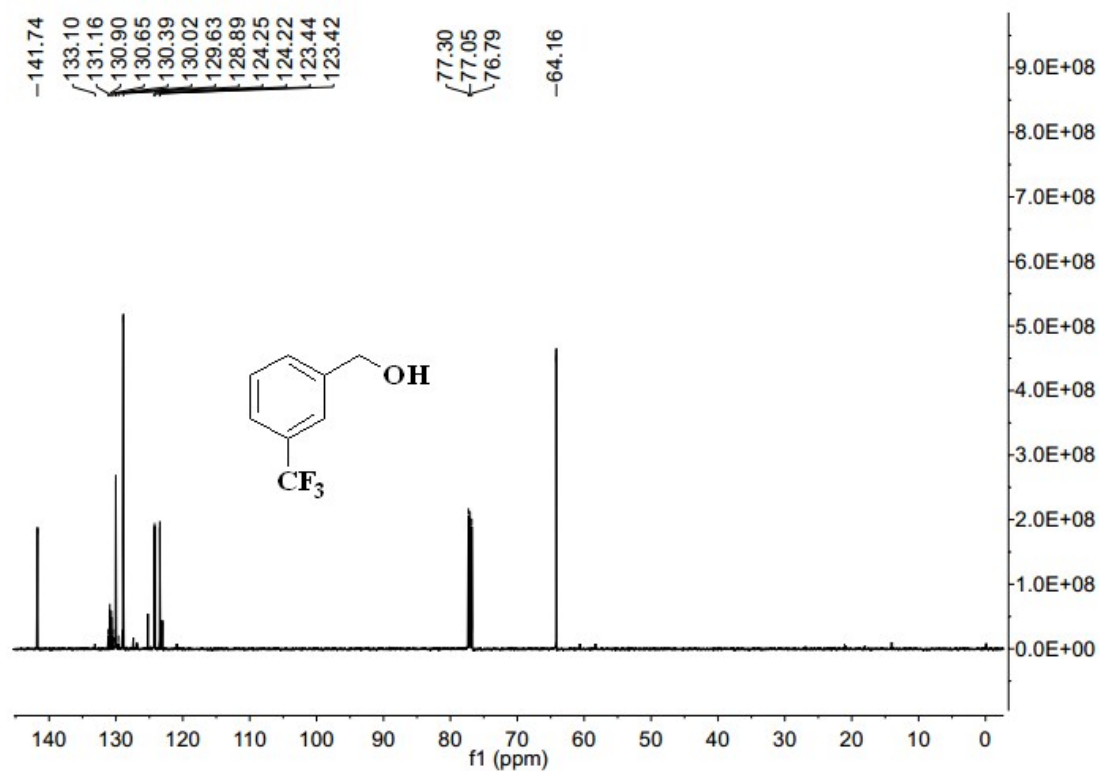
^{13}C NMR spectrum of 3-fluorobenzyl alcohol (**3g**)



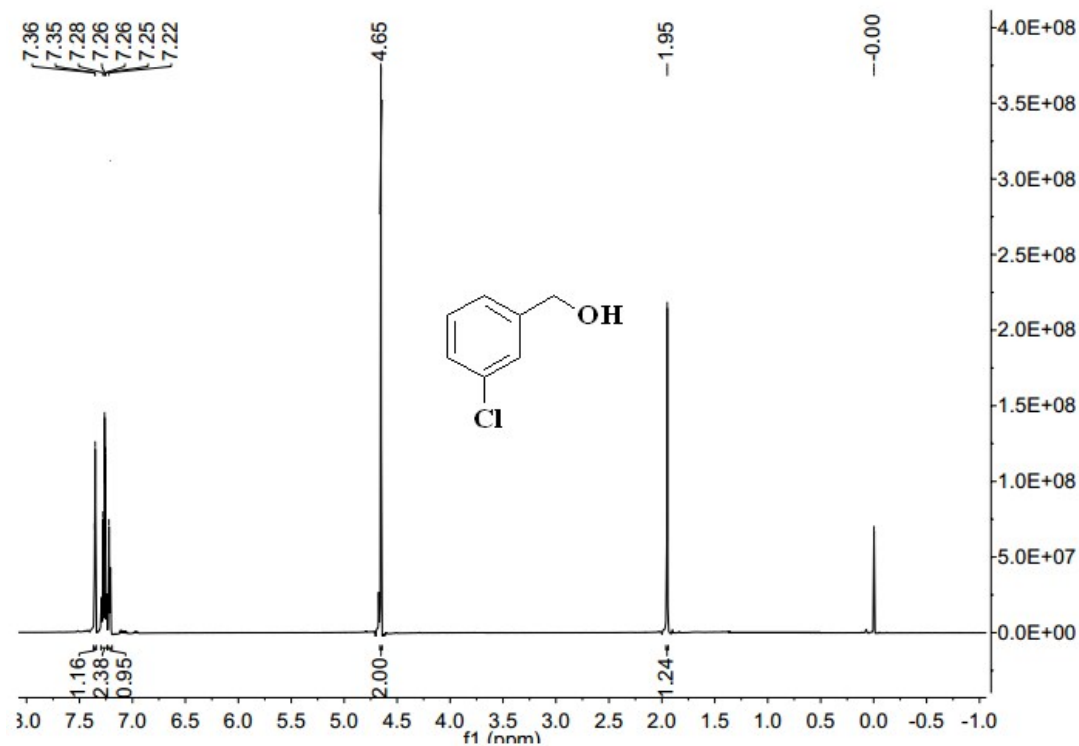
^1H NMR spectrum of 3-(trifluoromethyl)benzyl alcohol (**3h**)



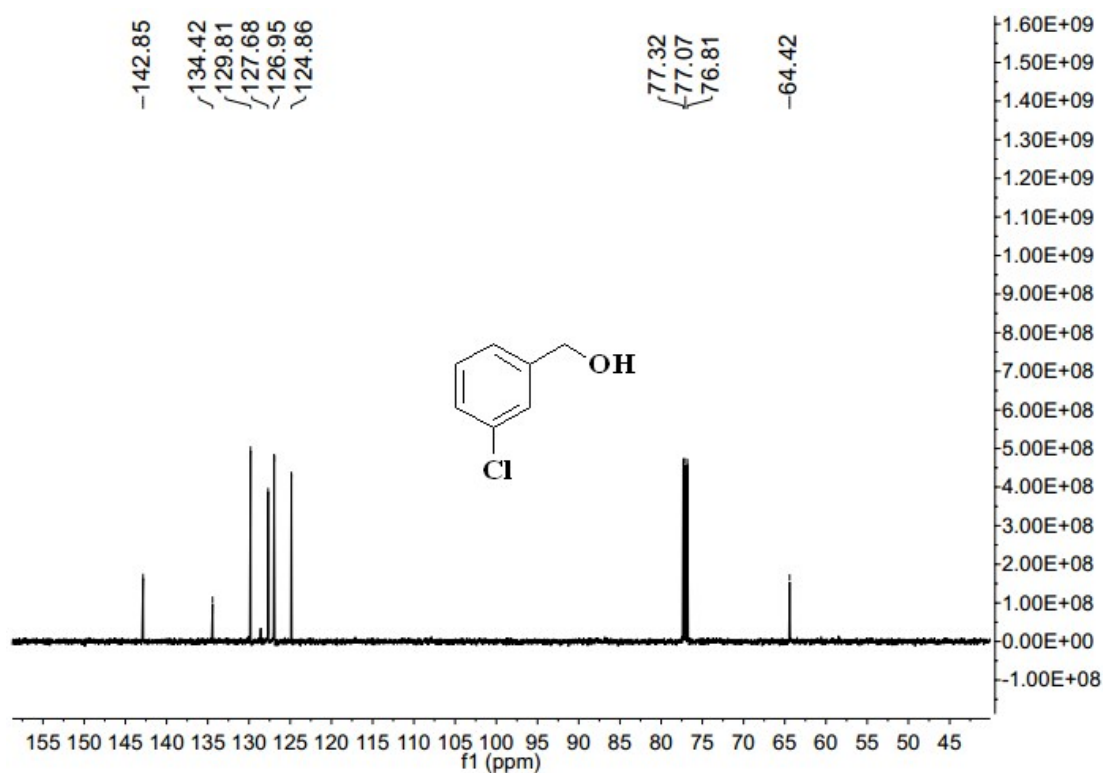
^{13}C NMR spectrum of 3-(trifluoromethyl)benzyl alcohol (**3h**)



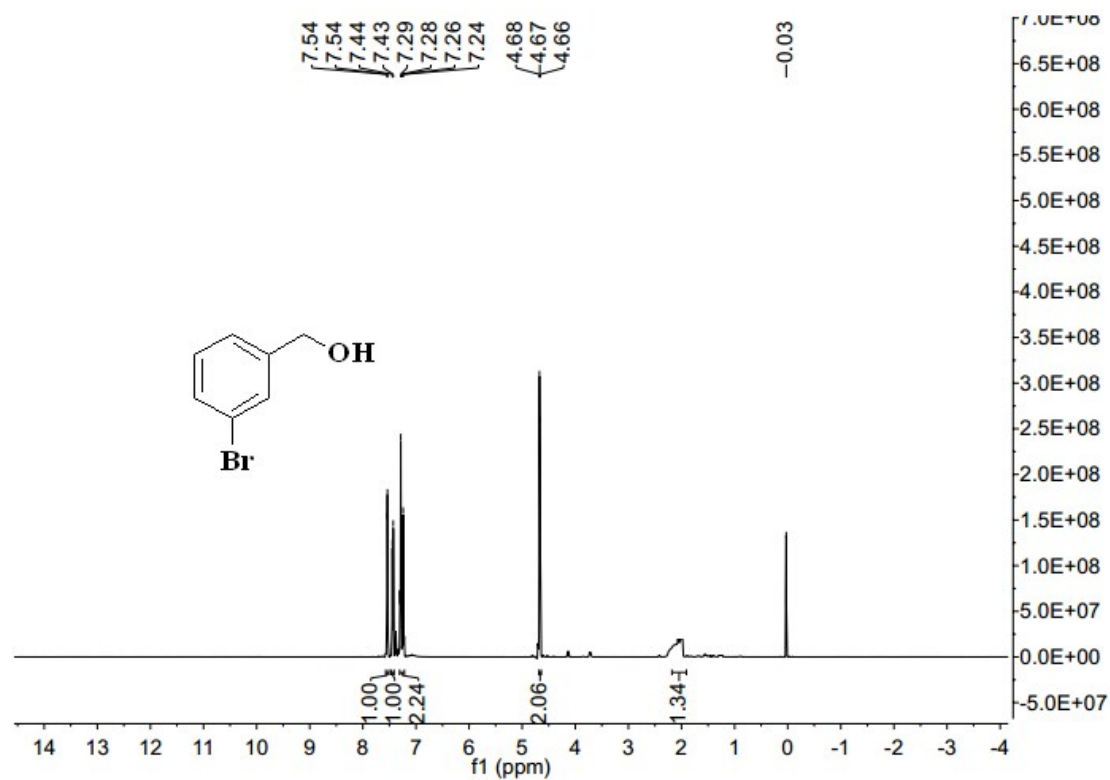
^1H NMR spectrum of 3-chlorobenzyl alcohol (**3i**)



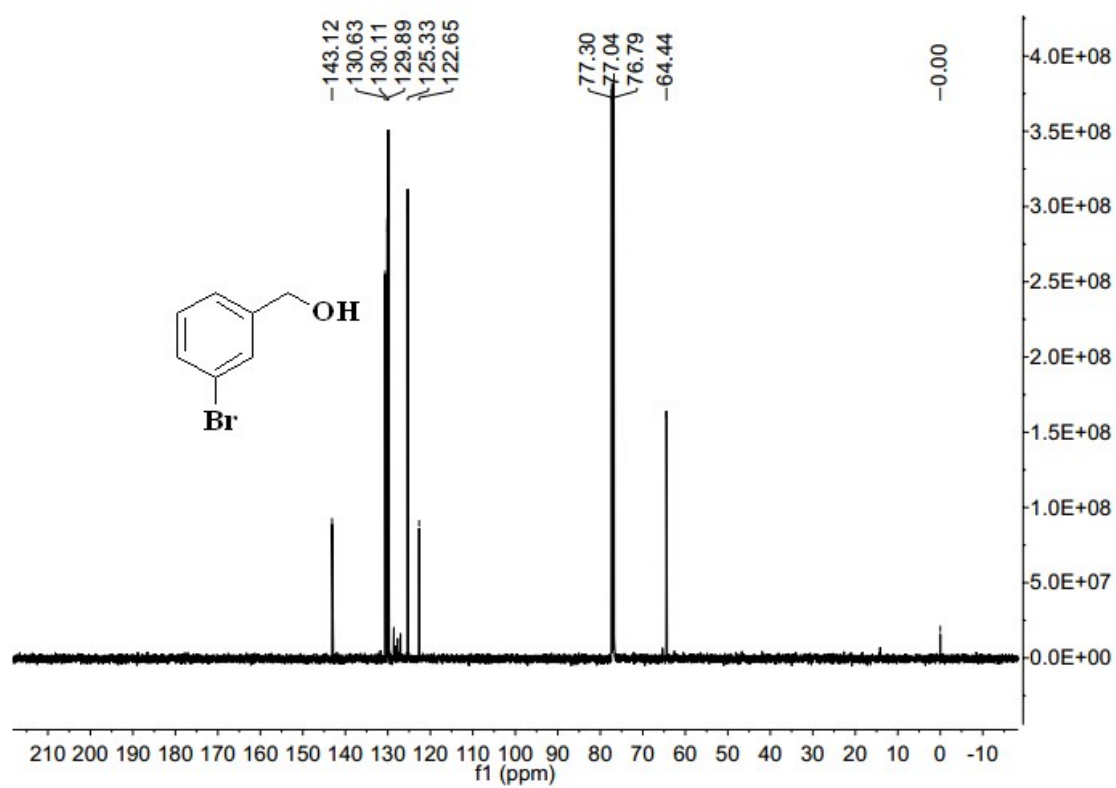
^{13}C NMR spectrum of 3-chlorobenzyl alcohol (**3i**)



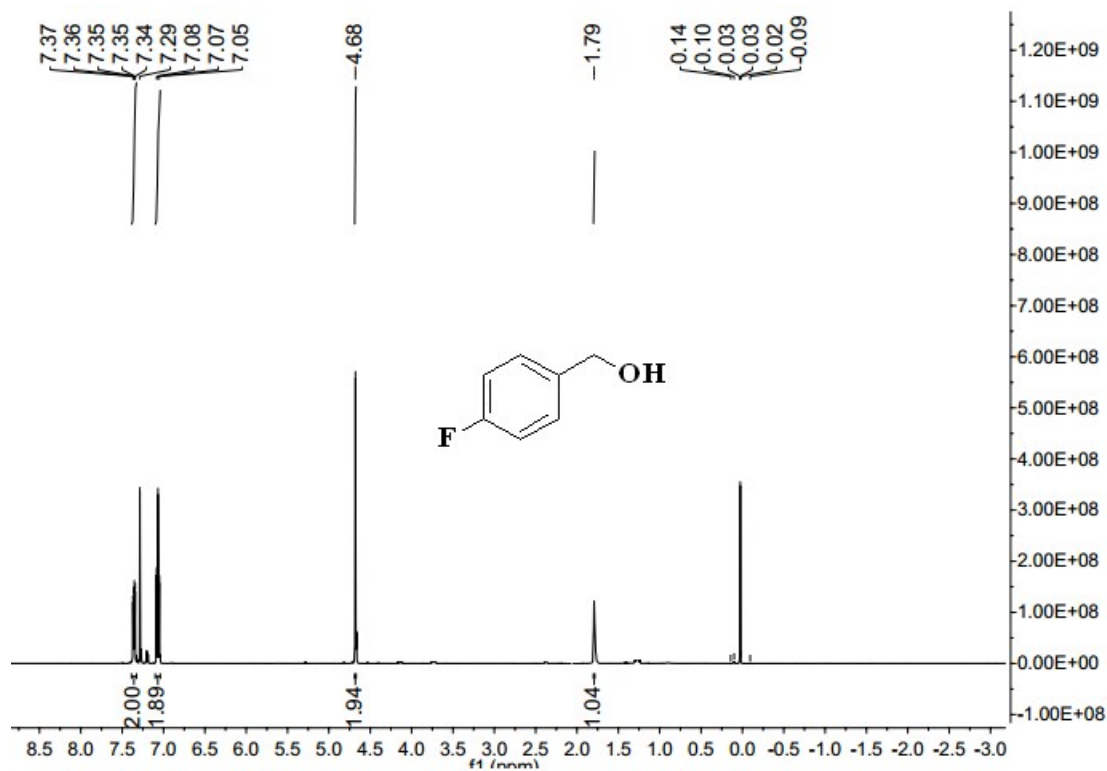
^1H NMR spectrum of 3-bromobenzyl alcohol (**3j**)



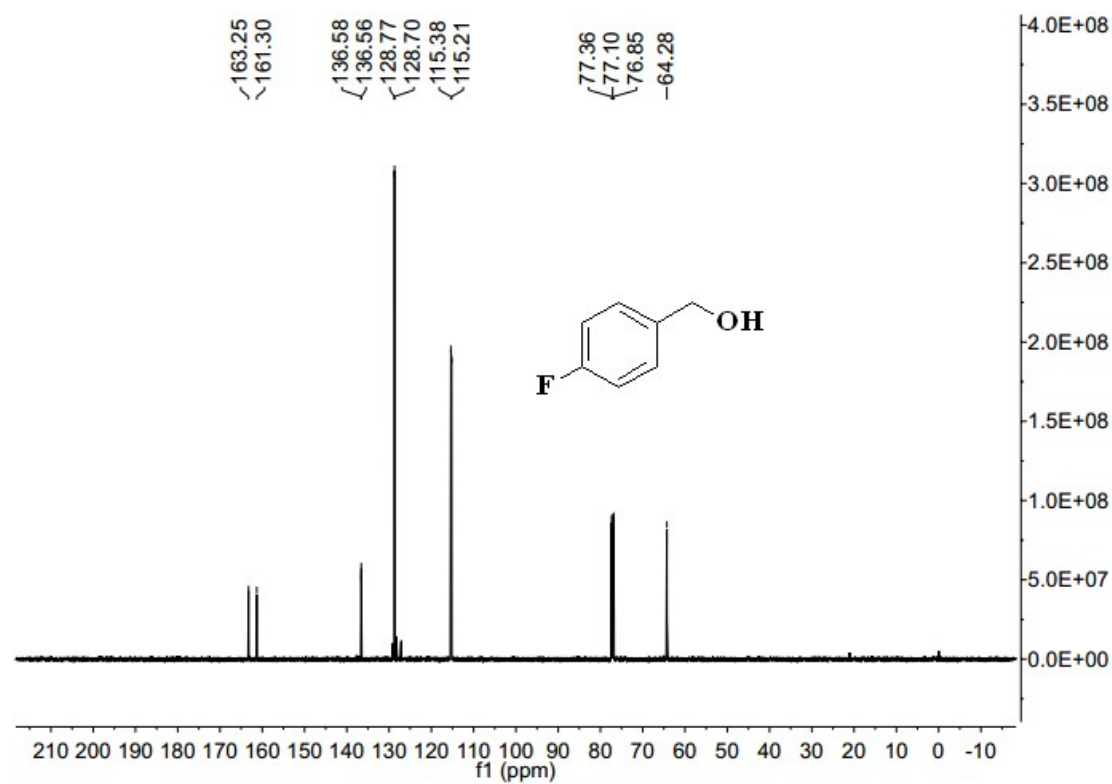
^{13}C NMR spectrum of 3-bromobenzyl alcohol (**3j**)



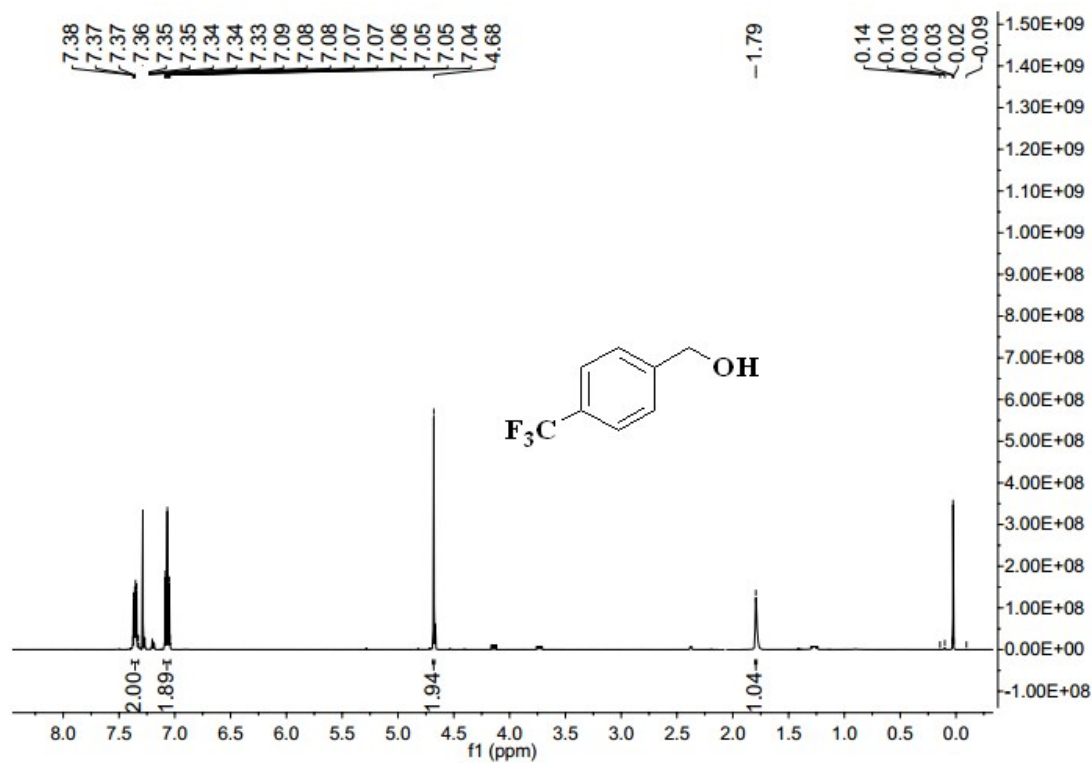
^1H NMR spectrum of 4-fluorobenzyl alcohol (**3k**)



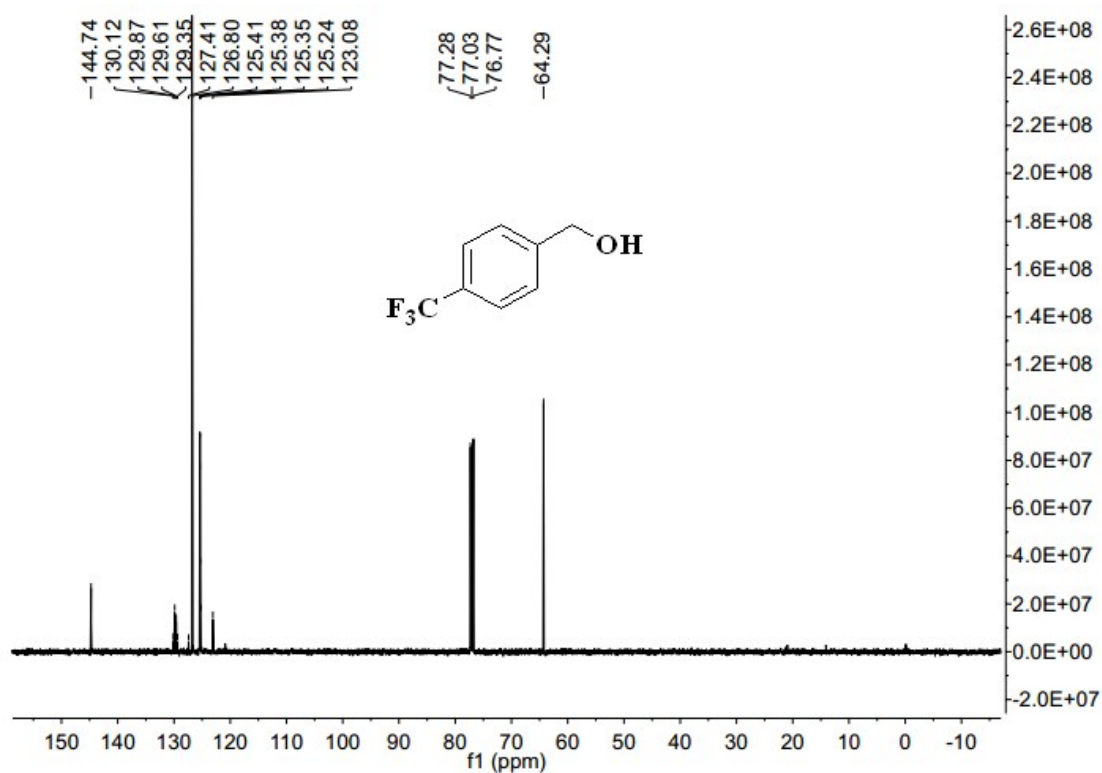
^{13}C NMR spectrum of 4-fluorobenzyl alcohol (**3k**)



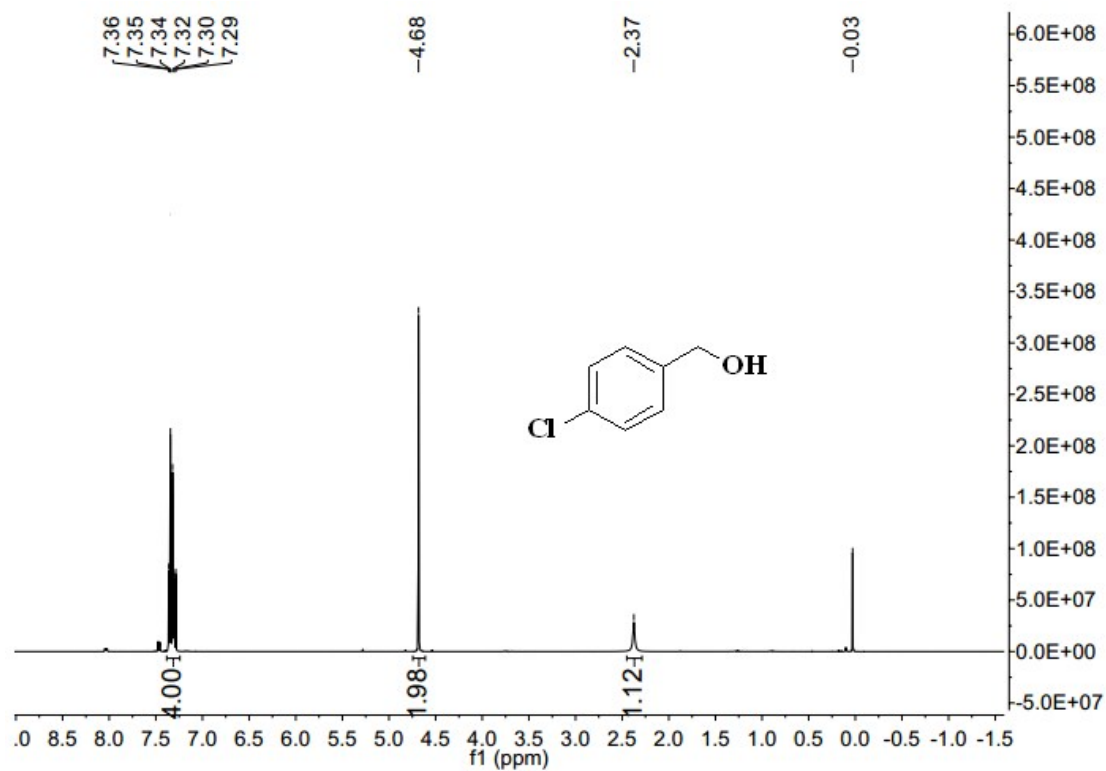
^1H NMR spectrum of 4-(trifluoromethyl)benzyl alcohol (**3l**)



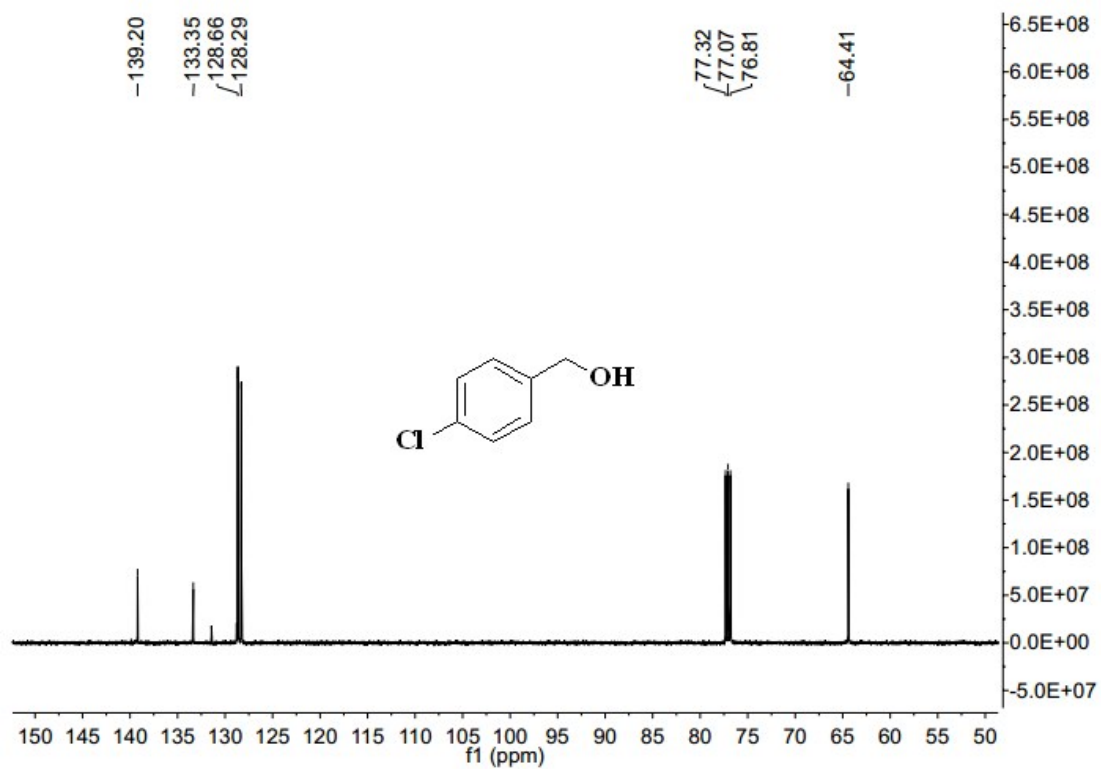
^{13}C NMR spectrum of 4-(trifluoromethyl)benzyl alcohol (**3l**)



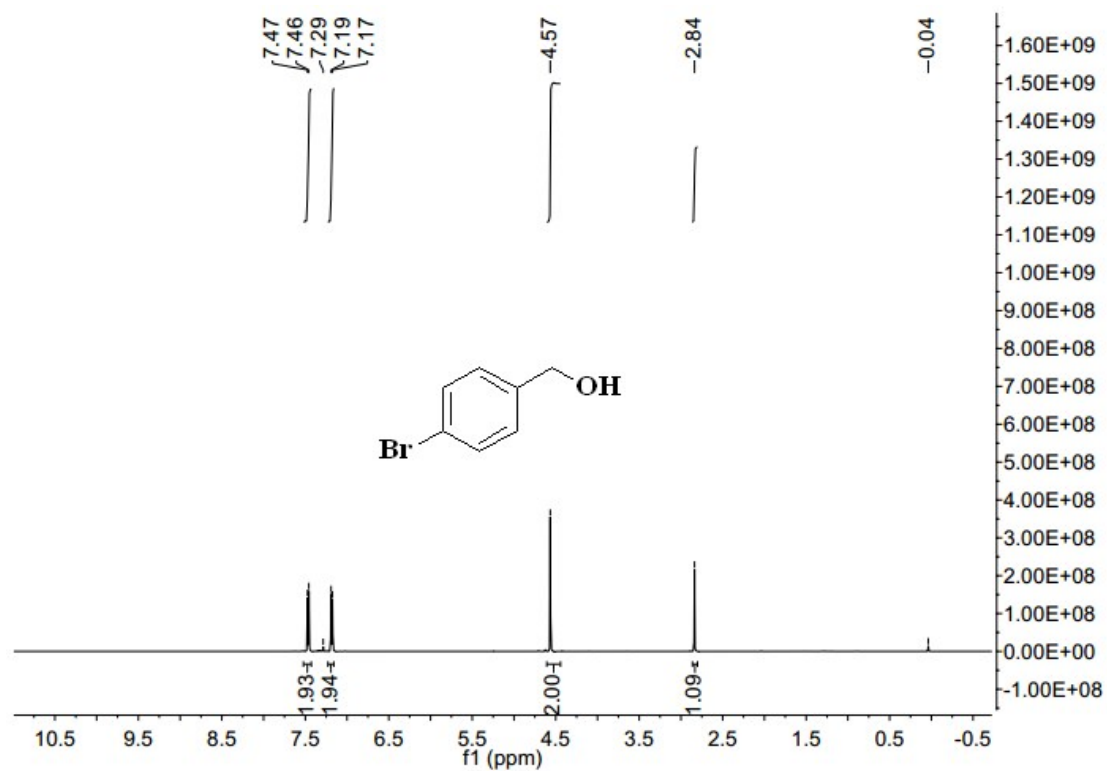
^1H NMR spectrum of 4-chlorobenzyl alcohol (**3m**)



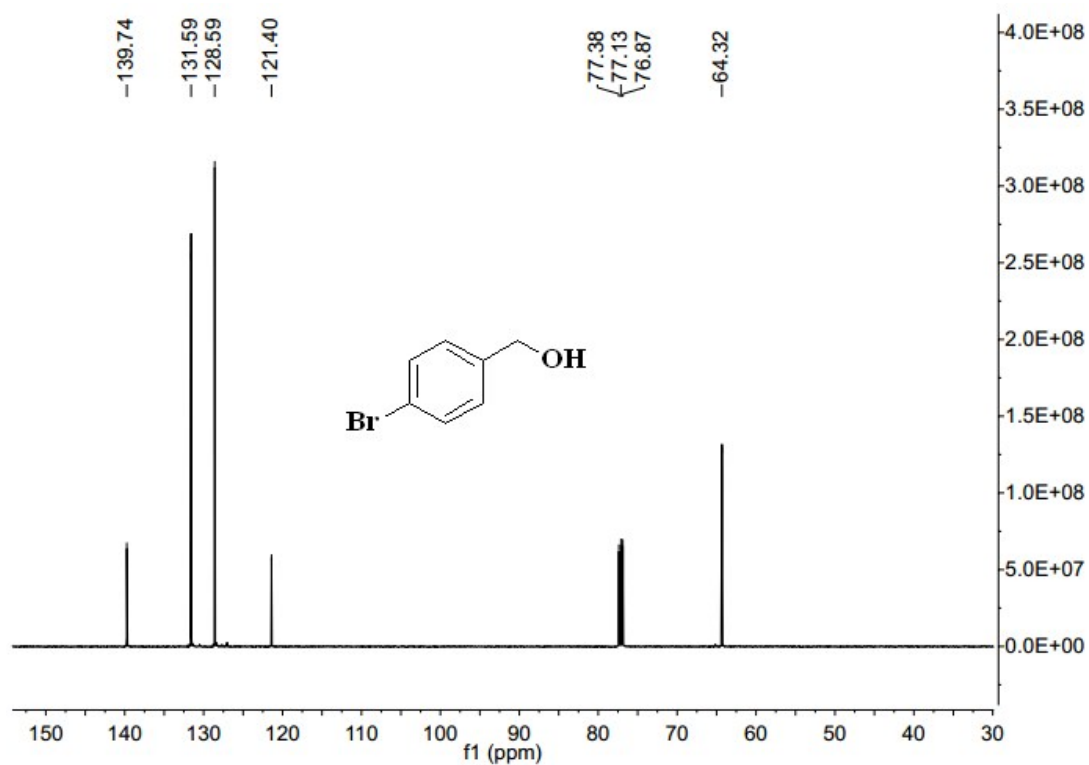
^{13}C NMR spectrum of 4-chlorobenzyl alcohol (**3m**)



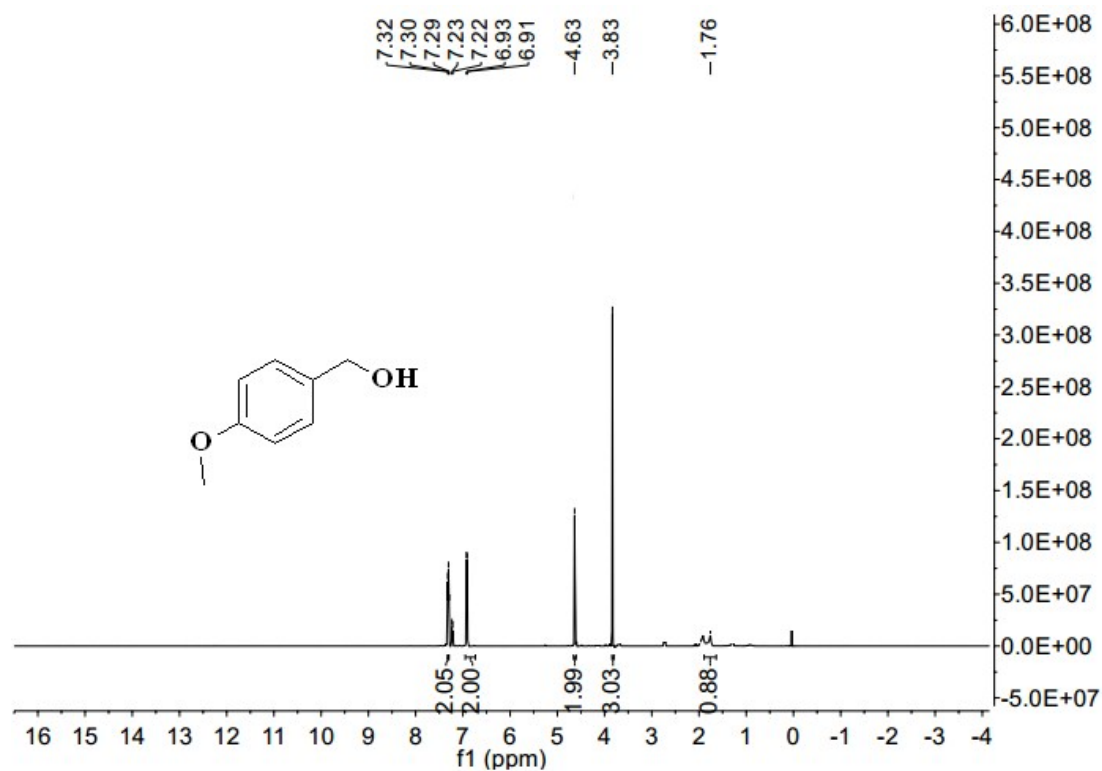
^1H NMR spectrum of 4-bromobenzyl alcohol (**3n**)



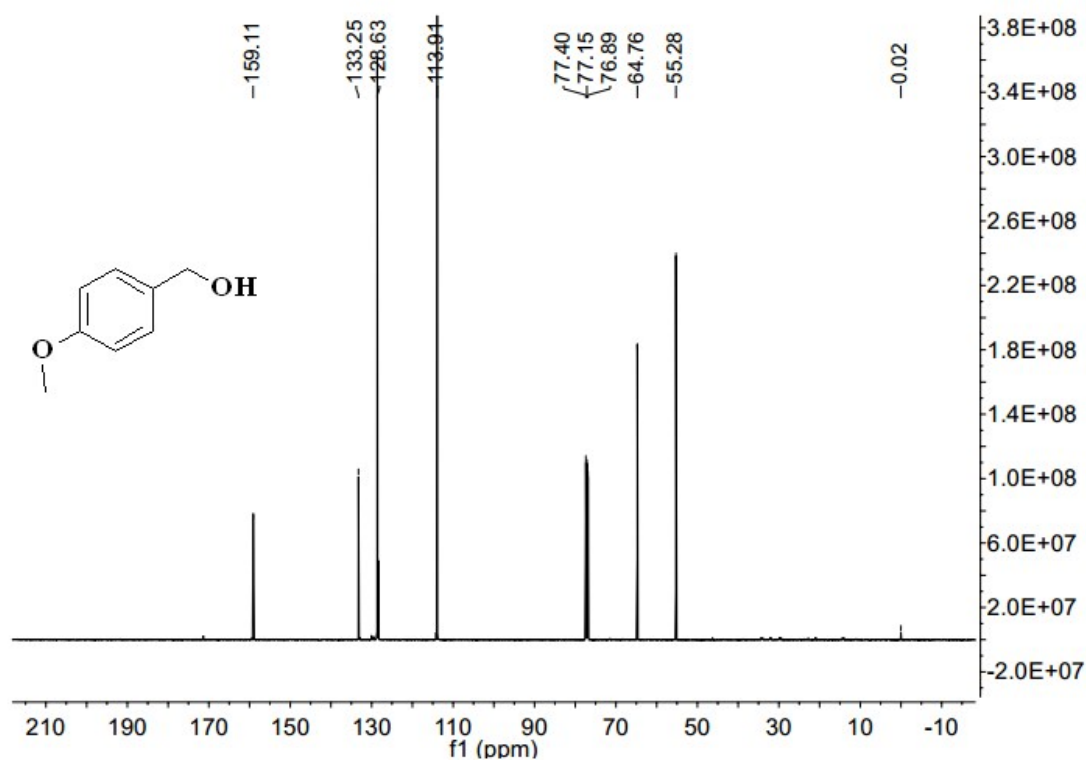
^{13}C NMR spectrum of 4-bromobenzyl alcohol (**3n**)



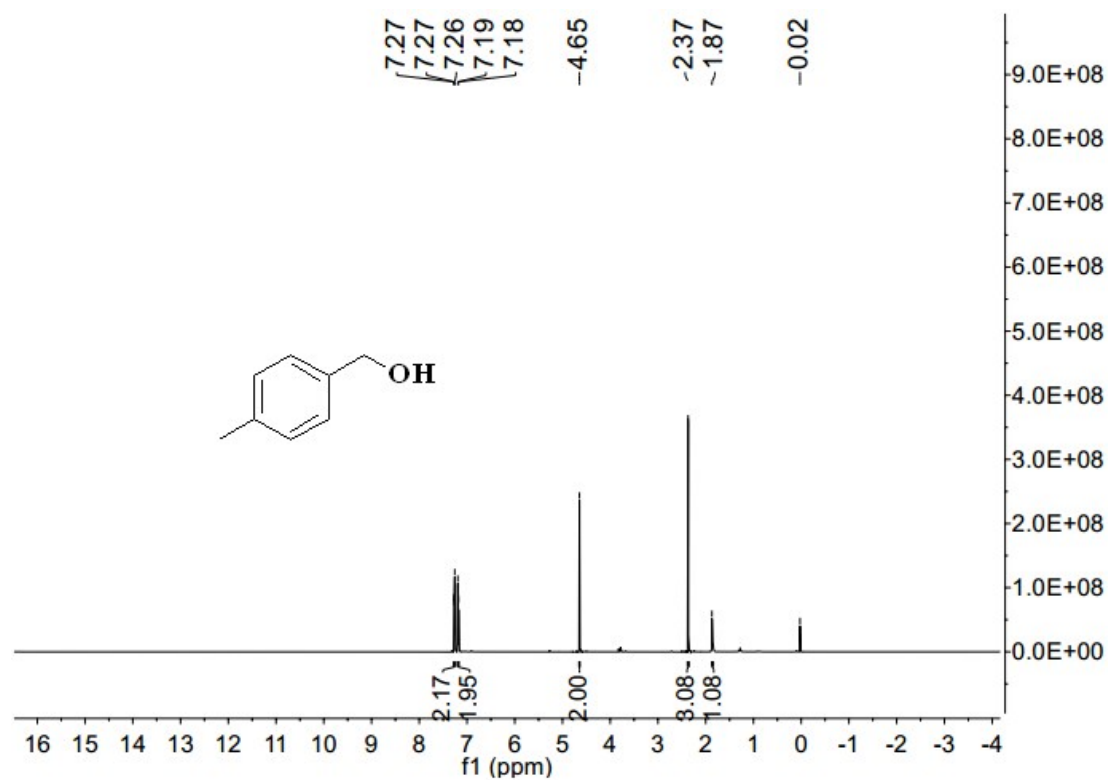
^1H NMR spectrum of 4-methoxybenzyl alcohol (**3o**)



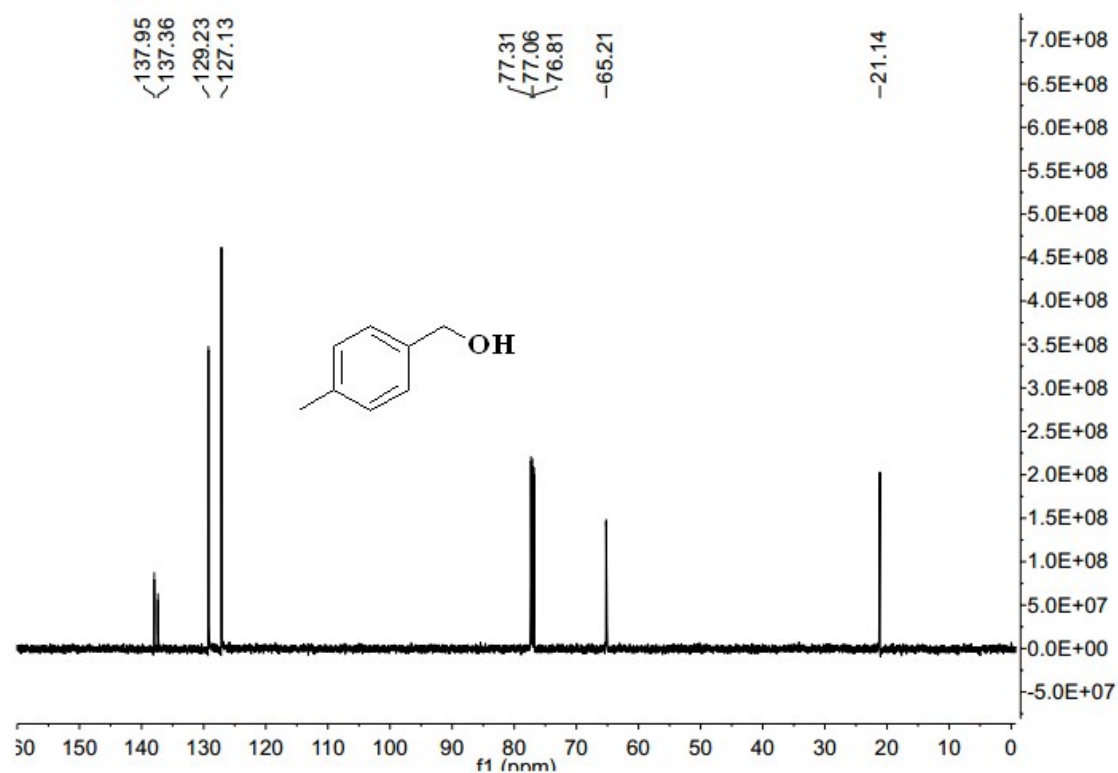
^{13}C NMR spectrum of 4-methoxybenzyl alcohol (**3o**)



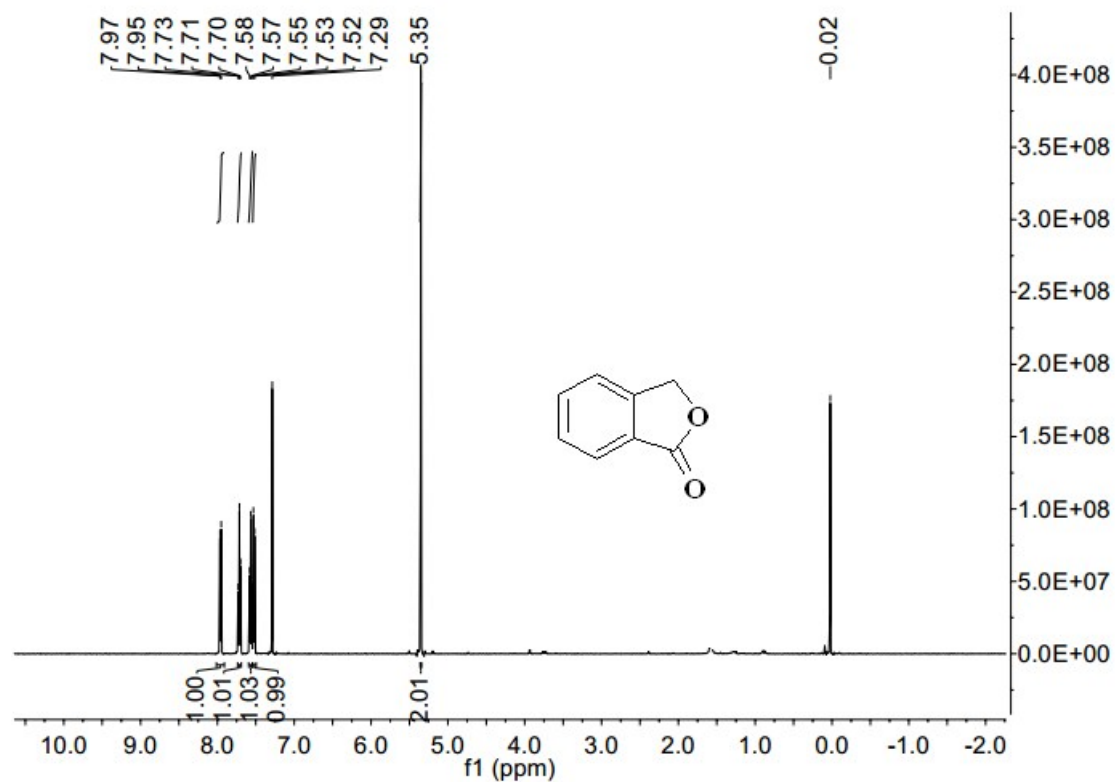
^1H NMR spectrum of 4-methylbenzyl alcohol (**3p**)



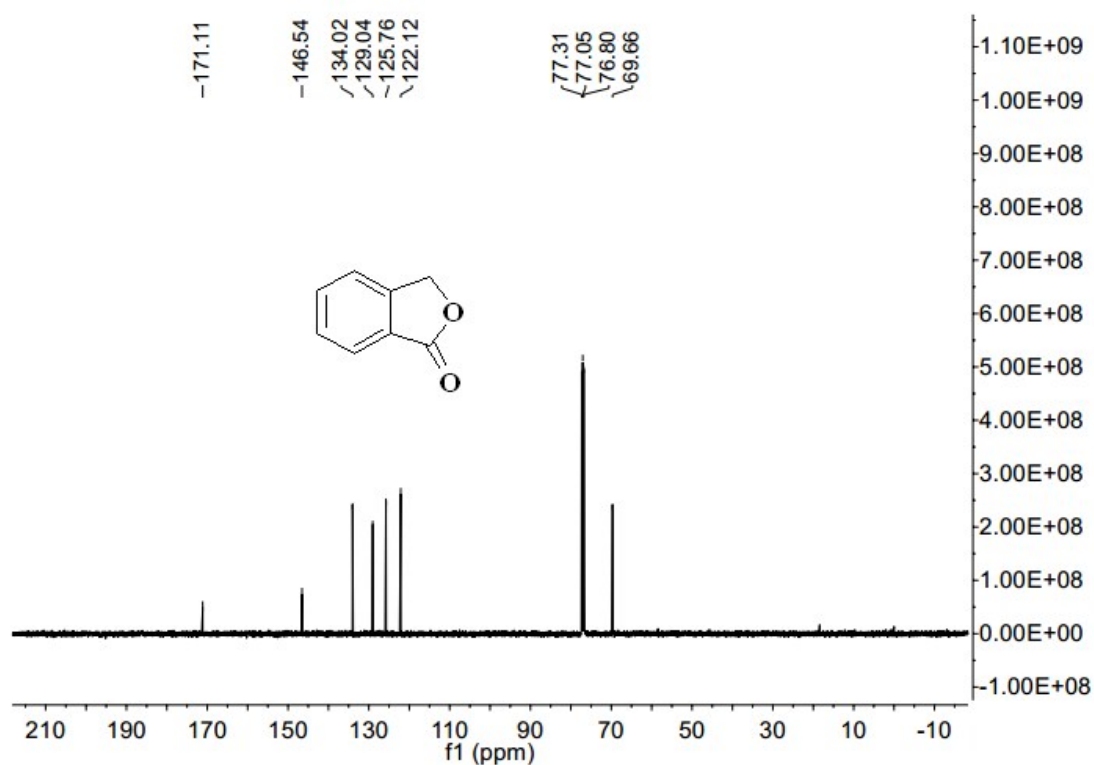
^{13}C NMR spectrum of 4-methylbenzyl alcohol (**3p**)



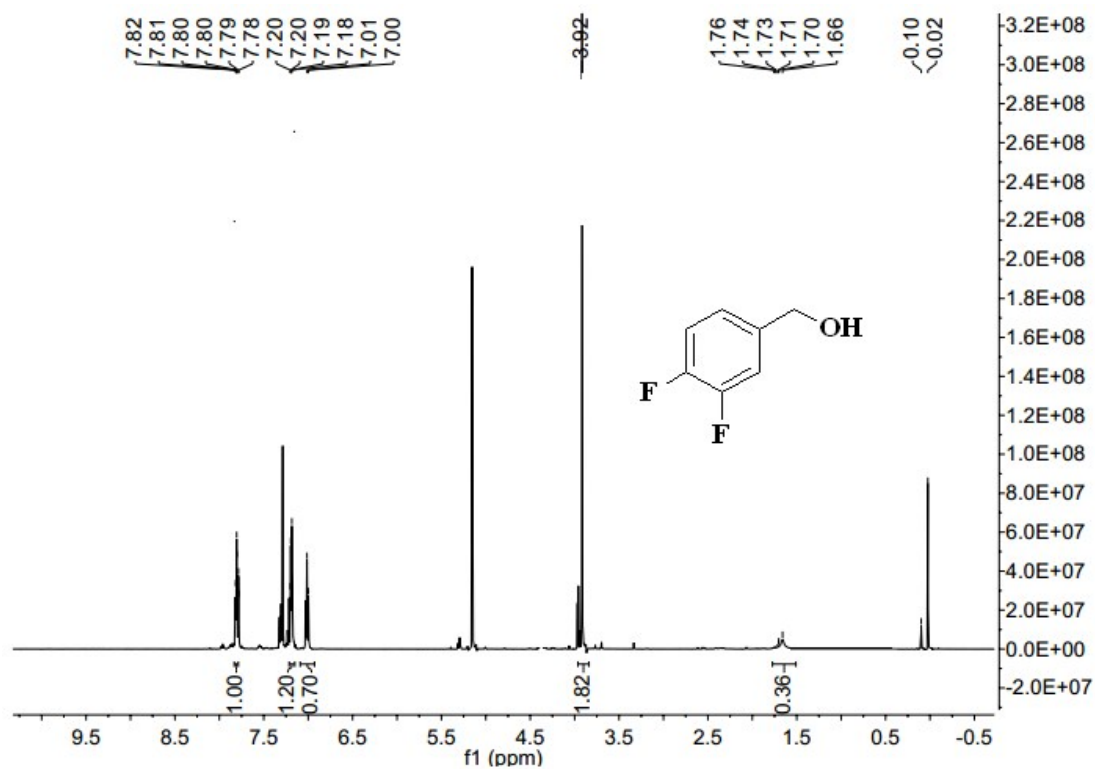
^1H NMR spectrum of isobenzofuran-1(3H)-one (**3r**)



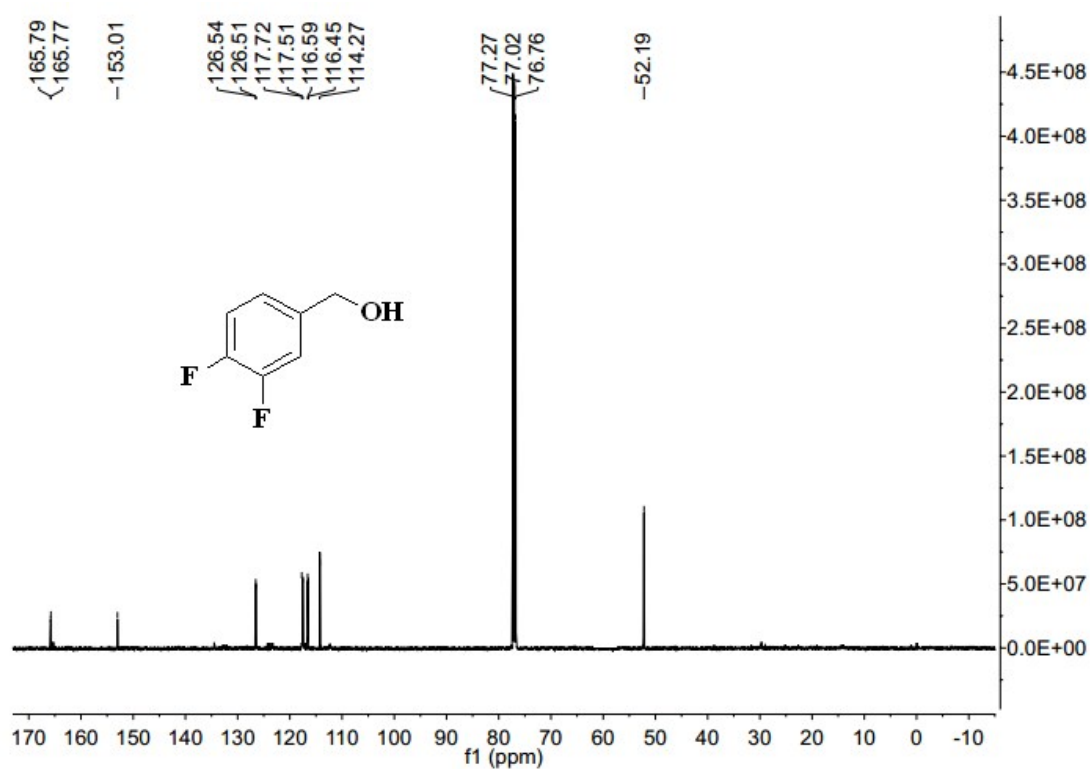
^{13}C NMR spectrum of isobenzofuran-1(3H)-one (**3r**)



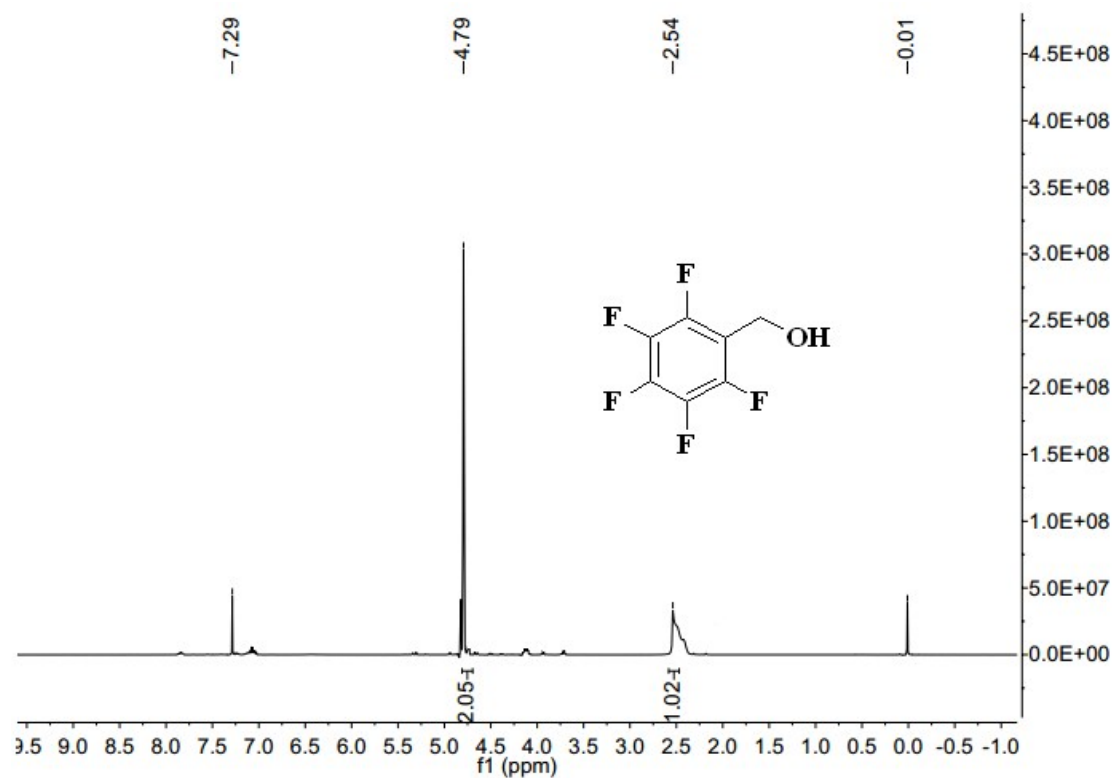
^1H NMR spectrum of 3,4-difluorobenzyl alcohol (**3s**)



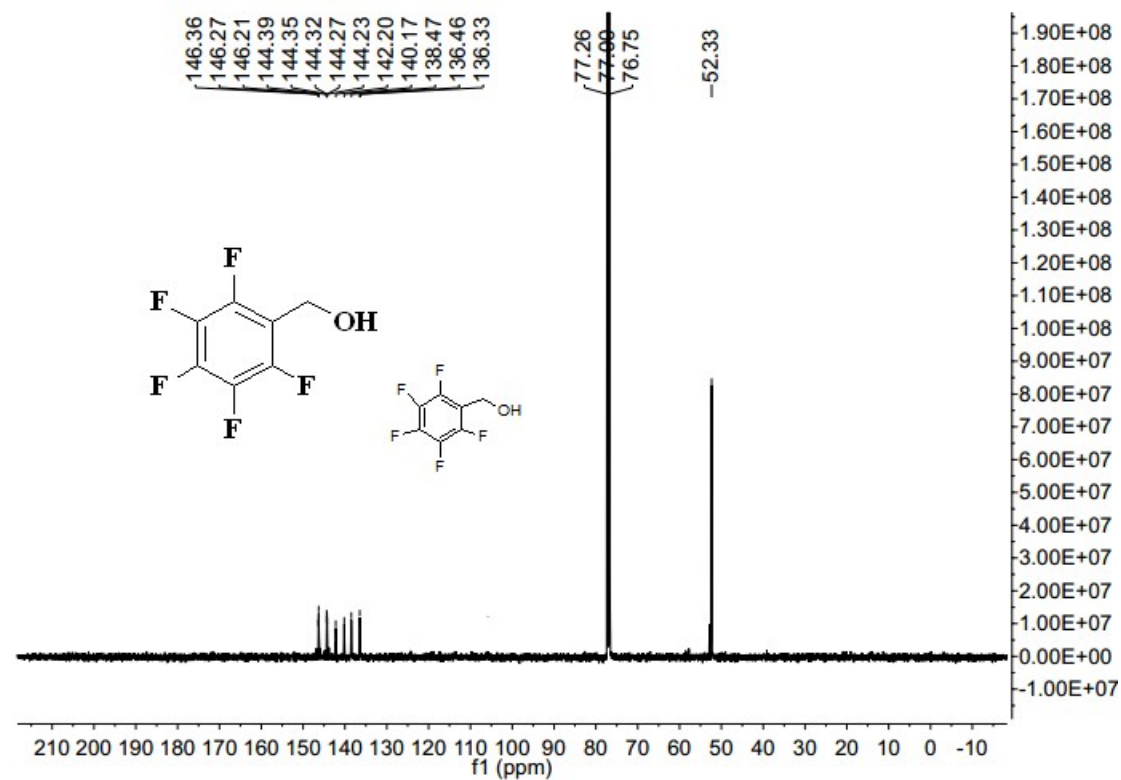
^{13}C NMR spectrum of 3,4-difluorobenzyl alcohol (**3s**)



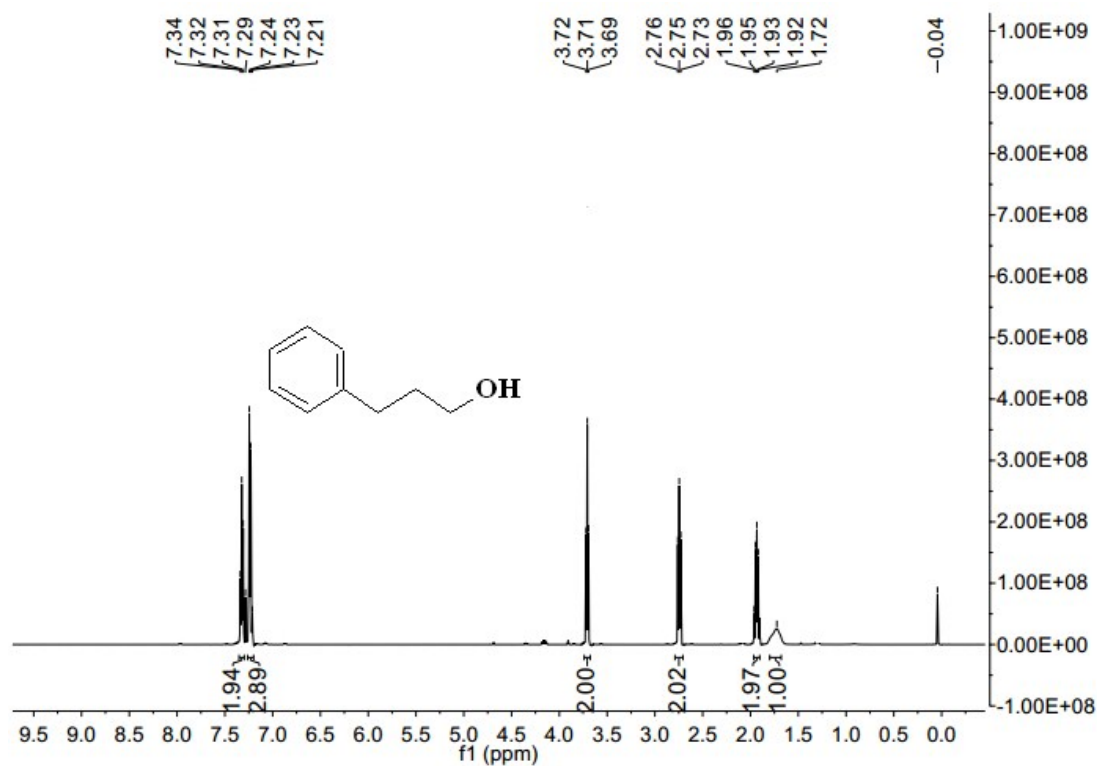
^1H NMR spectrum of 2,3,4,5,6-pentafluorobenzyl alcohol (**3t**)



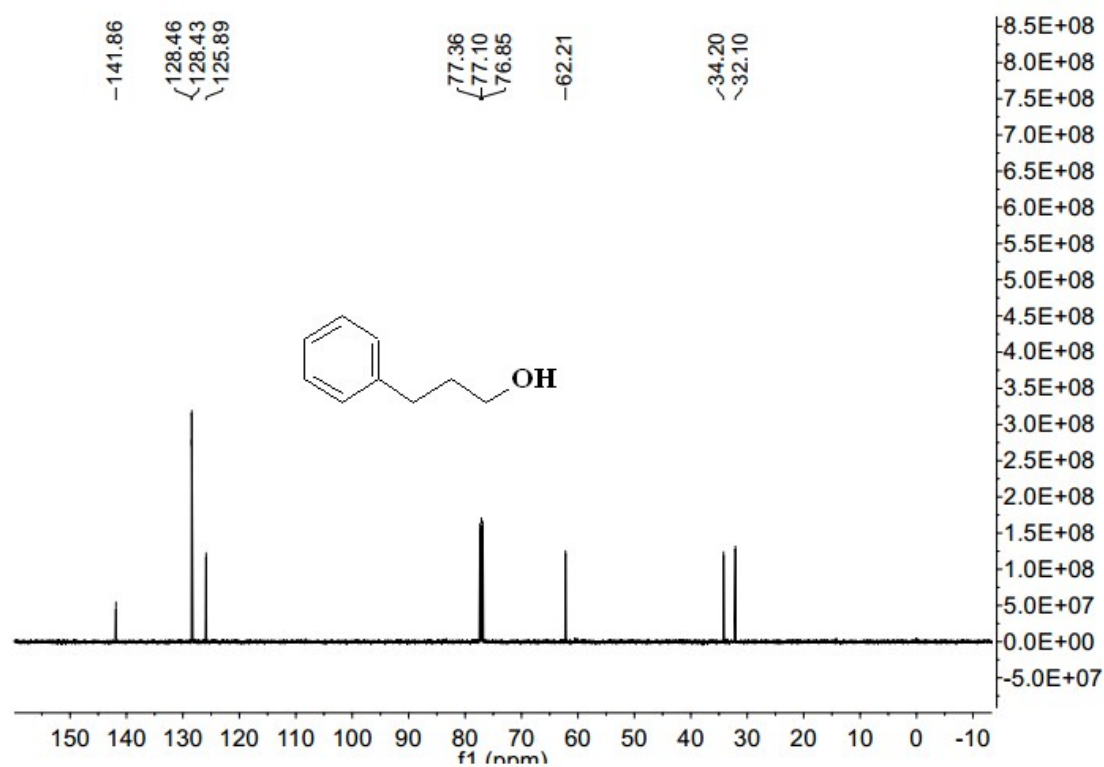
^{13}C NMR spectrum of 2,3,4,5,6-pentafluorobenzyl alcohol (**3t**)



^1H NMR spectrum of 3-phenyl-1-propanol (**3t**)



^{13}C NMR spectrum of 3-phenyl-1-propanol (**3t**)



4. GC analysis

All the GC analysis were carried out on Angilent 6820 Series instrument using polar capillary column (part number 19091N-113 HP-INNOWAX Capillary Column, 30 m).

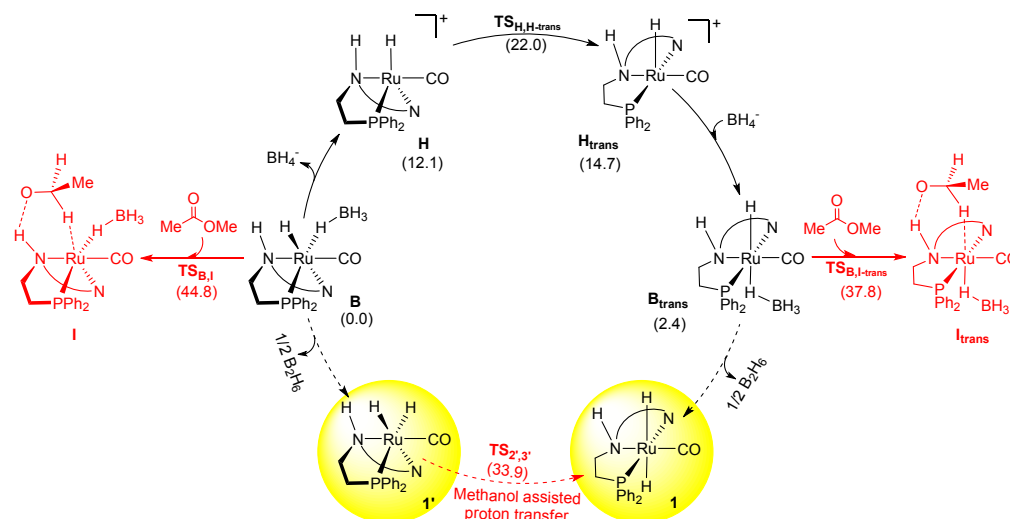
5. Mechanistic and Computational information

5.1 Mechanistic and structural aspects. In order to shed some light on the mechanism of catalysis and gain an insight into the role of the NaBH_4 , a set of experiments was performed. It was first considered likely that complex $[\text{fac-PN}_\text{H}\text{N}]\text{RuH}(\eta^1\text{-BH}_4)(\text{CO})$ (**B**) would be formed when $[\text{fac-PNN}]\text{RuH}(\text{PPh}_3)(\text{CO})$ (**A**) is treated with NaBH_4 , as related $\eta^1\text{-BH}_4$ complexes have been prepared and reported as effective catalysts for hydrogenation of esters by Kuriyama⁶ and Beller.⁷ However, before carrying out this experiment we noticed that **A**, reported in our earlier work,^{1(b)} slowly undergoes some isomerization on standing in deuterated chloroform and after four hours a mixture of two geometrical isomers (**A/A'** = 90:10) is evident (see spectra in 3.1.2 – 3.1.4). In both isomers a *fac*-coordinated monoanionic PNN ligand is apparent with mutually coupled *trans* phosphines observed in each ($^2J(\text{PP}) = \text{ca. } 260 \text{ Hz}$: **A** and **A'**), while $^2J(\text{PH})_{\text{cis}}$ couplings of between 16-24 Hz are seen in the ^1H NMR spectrum for the distinct hydride resonances; an X-ray structure of the **A** isomer has been reported elsewhere.^{1(b)}

5.2 Results of the DFT calculations

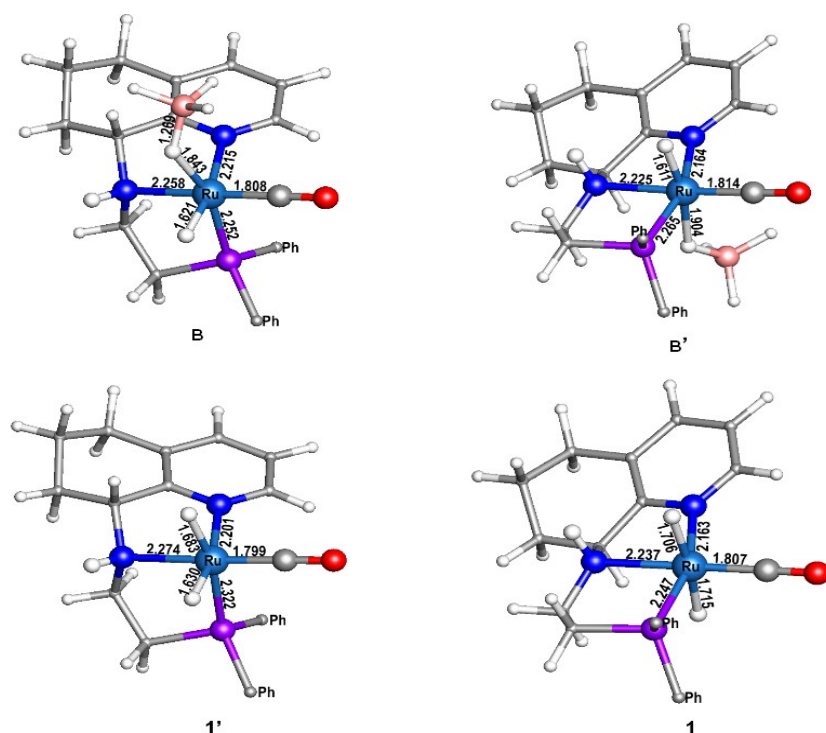
5.2.1 Computed pathway to the active catalyst **1** from **B**

Scheme S1. Computed pathway to the active catalyst **1** from **B**. The less favorable pathways with higher barriers are shown in red. The numbers in parenthesis are the relative free energies given in kcal/mol.



The generation of the active catalyst **1** from **B** is illustrated in Scheme S1. The optimized structures of **B**, **B_{trans}**, **1'** and **1** are displayed in Figure S3. In agreement with the experimental result, it was found that **B** cannot hydrogenate methyl acetate directly as the barrier **TS_{B,I}** is too high at 44.8 kcal/mol (Scheme S1). **B** can however undergo loss of 1/2B₂H₆ to give *cis*-dihydride **1'**, but again the hydrogenation of methyl acetate using **1'** is unlikely as the barrier is similarly large at 45.7 kcal/mol (**TS_{1,6'}**). A more energetically feasible (free energy barrier of 22.0 kcal/mol) pathway involves the conversion of **B** to its 2.4 kcal/mol less stable isomer **B_{trans}** via a series of steps based on BH₄[−] dissociation, a *fac-mer* isomerization of the PN_HN ligand and re-association of the BH₄[−]. Following the release of 1/2B₂H₆ from **B_{trans}**, *trans*-dihydride complex **1** is formed and considered as the actual catalyst for the hydrogenation of methyl acetate. An alternative pathway to **1** from **1'** involving the assistance of methanol,⁸ is less likely due to the relatively high free energy barrier of **TS_{2',3'}** (33.9 kcal/mol).

Figure S2. Optimized structures of **B**, **B_{trans}**, **1'** and **1**. Phenyl groups are omitted for clarity. Bond lengths are in Å.



5.2.2 The methanol assisted isomerization of **1'** to **1**

An alternative pathway to **1** from **1'**, shown in red in Scheme S2, has also been calculated as a similar self-promotion mechanism has been proposed by us previously,⁸ indicating a calculated reaction pathway for the isomerization of **1'** to **1** with the assistance of the methanol. The corresponding free energy profile is shown in Figure S4.

Scheme S2. Predicted reaction pathway for the isomerization of **1'** to **1**.

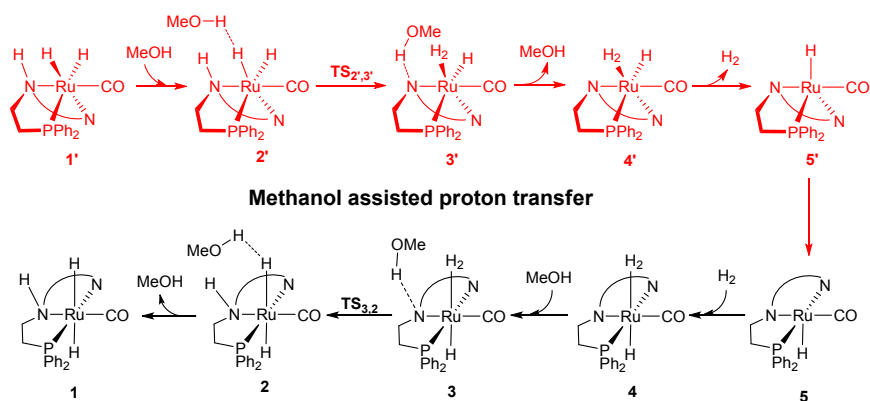
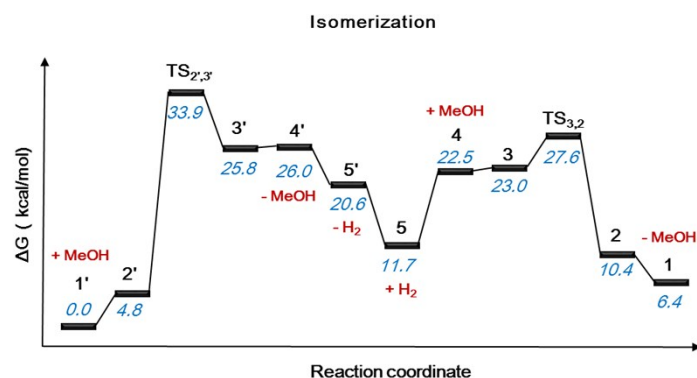


Figure S3. Free energy profile for the isomerization of **1'** to **1**.



In this pathway, an extra methanol molecule can act as a proton transfer tunnel to promote the isomerization of **1'** to **1**, with a relatively high free energy barrier of 33.9 kcal/mol (**TS_{2',3'}**). We also examined the direct formation of H₂ and found that the relative free energy of **TS_{1',4'}** is 40.0 kcal/mol, which is too high for a reaction under 120 °C.

5.2.3 Free energy profiles and key optimized structures for the hydrogenation of methyl acetate to acetaldehyde and methanol and the hydrogenation of acetaldehyde to ethanol

Scheme S3. Predicted reaction pathway for the hydrogenation of methyl acetate to acetaldehyde and methanol (Cycle 1).

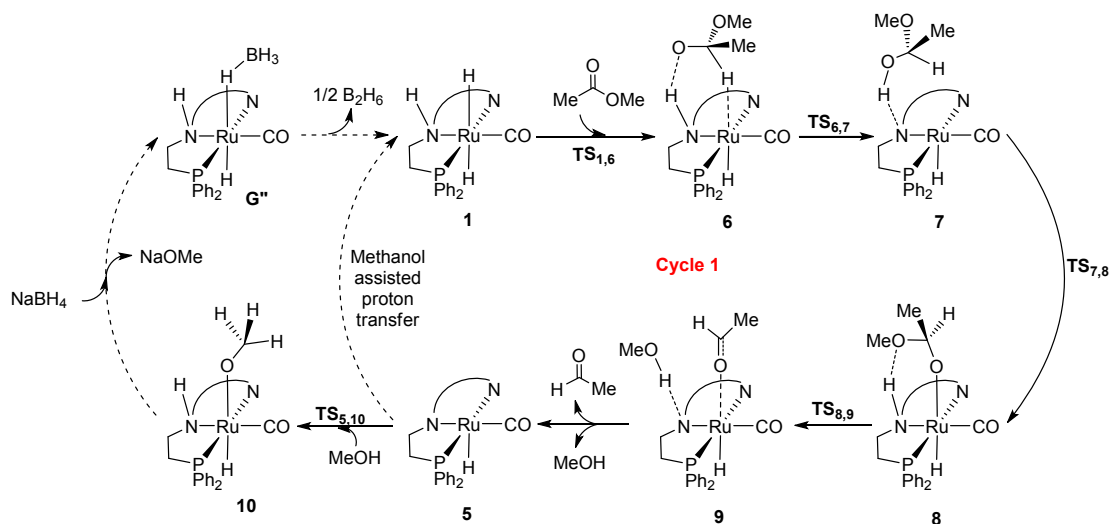


Figure S4. Free energy profile for the hydrogenation of methyl acetate to acetaldehyde and methanol (Cycle 1).

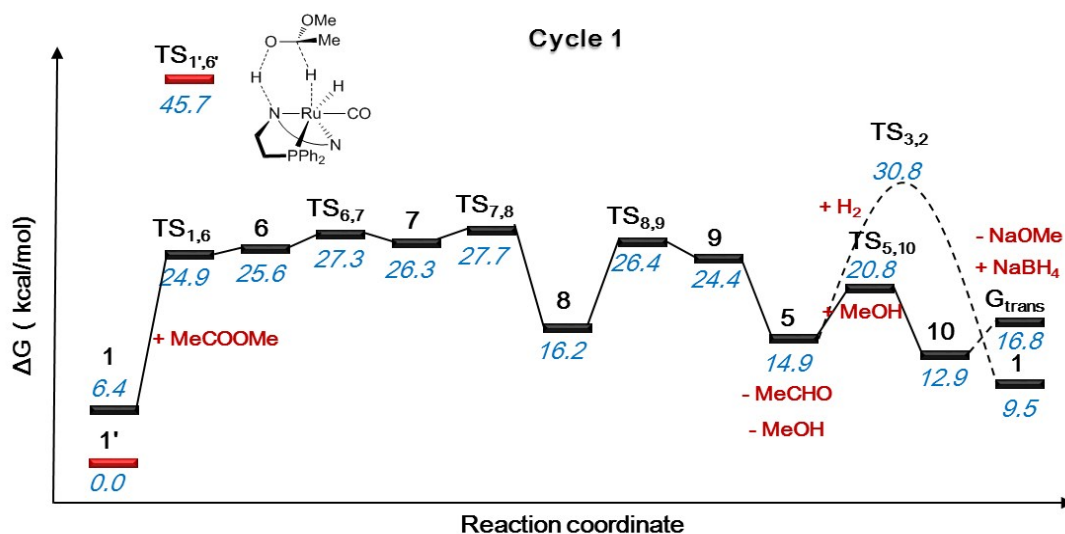
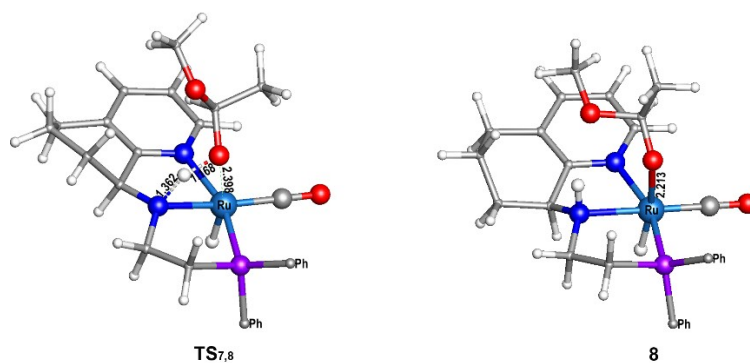


Figure S5. Optimized structures of **TS_{7,8}** (730i cm⁻¹) and **8**. Phenyl groups are omitted for clarity. Bond lengths are in Å.



Scheme S4. Predicted reaction pathway for the hydrogenation of acetaldehyde to ethanol (Cycle 2).

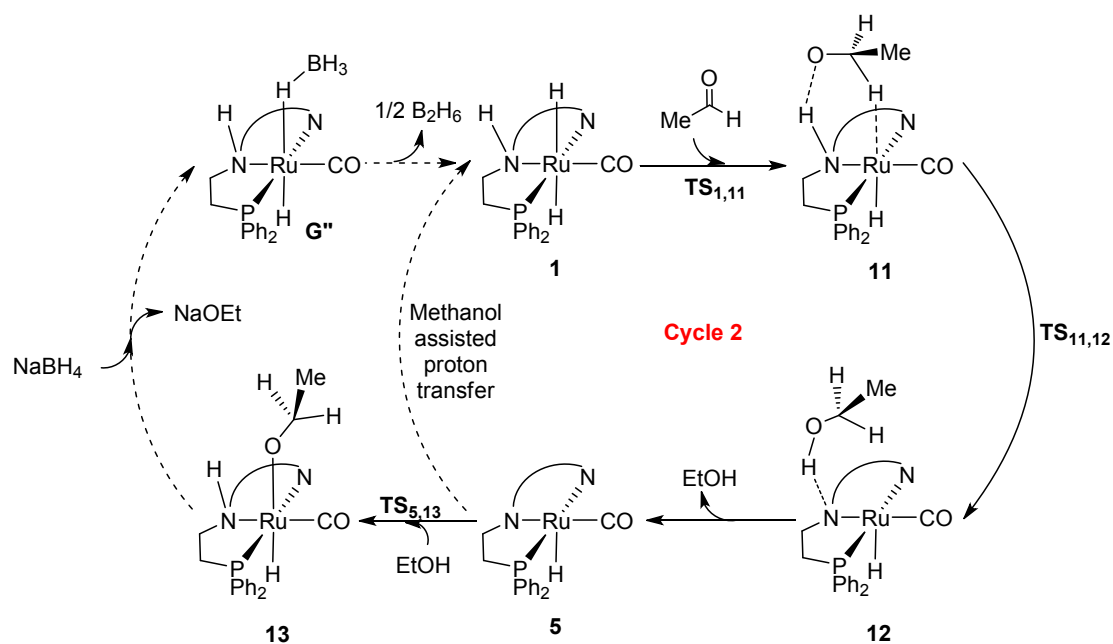


Figure S6. Free energy profile for the hydrogenation of acetaldehyde to ethanol (Cycle 2).

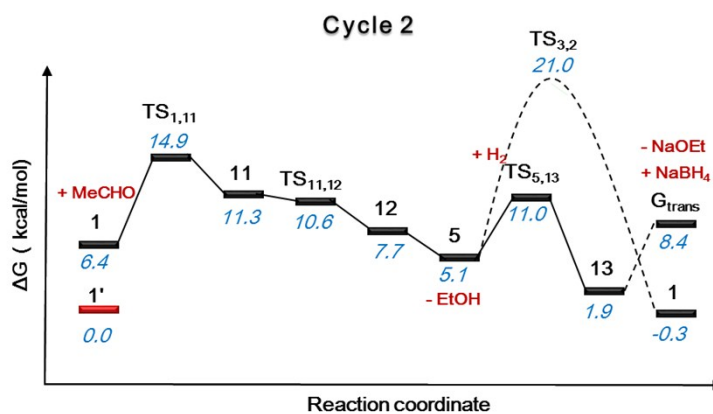
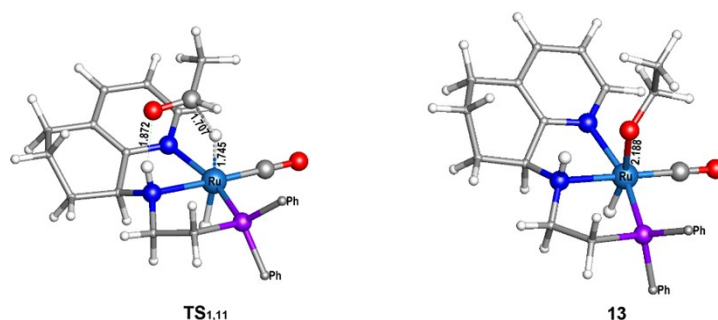


Figure S7. Optimized structures of **TS_{1,11}** (451/ cm⁻¹) and **13**. Phenyl groups are omitted for clarity. Bond lengths are in Å.



5.3 Computational methods

All DFT calculations were performed in Gaussian 09⁹ using the M06L functional¹⁰ and an ultrafine integration grid (99,590) in conjunction with the all-electron 6-31G(d,p) basis set for H and C atoms and the 6-31+G(d) basis set for all other non-metal atoms. The Stuttgart relativistic effective core potential basis set was used for the Ru (ECP28MWB)^{11,12} atom. All structures were optimized in solvent by using the integral equation formalism polarizable continuum model (IEFPCM)¹³ with radii and cavity-dispersion-solvent-structure terms in the SMD solvation model¹⁴ for the experimental solvent of THF. Thermal corrections were calculated within the harmonic potential approximation on optimized structures under T = 298.15 K and 1 atm pressure. Unless otherwise noted, the energies reported in the text are solvent corrected free energies. The calculated structures were verified to have no imaginary frequency (IF) for all intermediates and only one IF for each transition state structure. All transition states were also confirmed to connect reactants and products by intrinsic reaction coordinate (IRC) calculations. The JIMP2 molecular visualizing and manipulating program was employed to draw the 3D molecular structures.¹⁵

6. References

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