Supporting Information

KB_3H_8: an environmental-friendly reagent for the selective reduction of aldehydes and ketones to alcohols

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1. General methods and materials

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Metal borane KB_3H_8 was prepared according to the literature methods[1]. The ^1H and ^{13}C NMR spectra was recorded on a Bruker advance III 400 spectrometer in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^1H, or to chloroform δ = 77.0 for ^{13}C as internal standard. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All reactions were monitored by TLC with GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. All solvents were purified according to literature procedures and stored under nitrogen.

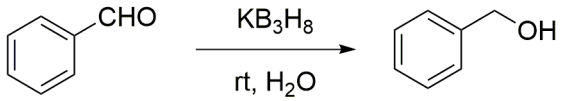
Single-crystal X-ray diffraction data were collected on an Agilent Diffraction SuperNova Atlas using Cu-*K*α radiation (λ = 1.54184 Å). Data reduction were performed using the SAINT software package and an absorption correction was applied using SADABS.[2] The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXT and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. Crystal data and refinement parameters are summarized in Table S1.

2. Synthesis of unsolvated KB_3H_8.

The synthesis of unsolvated KB_3H_8 is following the literature method:[1] Potassium (5.85 g, 150 mmol) was cut by a scissor into a small piece with the size of ~ 3 × 3 × 3 mm^3 in a glovebox and added to a 500 mL Schlenk flask. The flask was connected with a Schlenk line into which $THF{\cdot}BH_3$ (300 mL, 300 mmol) was condensed at -78°C. The reaction mixture was stirred at room temperature until potassium was completely consumed and large amount of KBH_4 white precipitate appeared (about 12 h). The KBH_4 precipitate was filtered out. Removal of THF from the filtrate resulted in a sticky solid, into which 30 mL toluene was added to pruduce a white precipitate. Part of the solvent was removed under dynamic vaccum. The precipitate was filtered, washed with toluene (3 × 30 mL), and then dried under dynamic vacuum to produce a free-flowing unsolvated KB_3H_8 white powder[1] (5.40 g KB_3H_8, 90% yield). ^{11}B NMR (128 MHz, CD_3CN): δ -30.3 (nonet, J = 33 Hz) ppm. ^1H NMR (400 MHZ, CD_3CN): δ 0.11 (decet, J = 33 Hz) ppm.

3. Screening of the reaction conditions

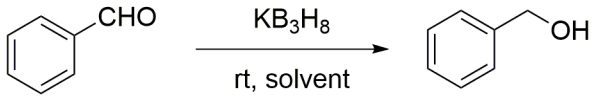
Table S1. Screening of the molar ratio of aldehyde/KB_3H_8 in water



Entry	Benzaldehyde (mmol)	KB_3H_8 (mmol)	Time (h)	Yield[a]
1	1	1	3	94%
2	2	1	5	90%
3	3	1	8	91%
4[b]	4	1	12	70%
5[b]	5	1	36	51%
6[b]	6	1	36	43%
7[b]	7	1	36	35%
8[b]	8	1	36	31%

[a] Yields were determined by NMR. [b] Unreacted benzaldehyde can be separated from the residue.

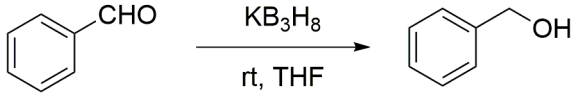
Table S2. Evaluation of organic solvents for the reduction of benzaldehyde with KB_3H_8



Entry	Solvents	Time (h)	Yield[a]
1	DME	15	85
2	CH_3CN	15	79
3	**THF**	**1**	**92**
4	1,2-dioxane	36	48
5	CH_2Cl_2	36	43
6	CH_3OH	19	81

[a] Isolated yields.

Table S3. Screening of the molar ratio of aldehydes/KB_3H_8 in THF



Entry	Benzaldehyde (mmol)	KB_3H_8 (mmol)	Time (h)	Yield[a]
1	1	1	1	94%
2	2	1	3	90%
3	3	1	6	90%
4	4	1	10	85%
5	5	1	12	87%
6	6	1	15	82%
7[b]	7	1	36	79%
8[b]	8	1	36	70%

[a] Yields were determined by NMR. [b] Unreacted benzaldehyde can be separated from the residue.

4. Crystallographic data and crystal structure of $K[B_5O_6(OH)_4] \cdot 2H_2O$

Table S4. Crystallographic data and structure refinement results for $K[B_5O_6(OH)_4]\cdot 2H_2O$

Empirical formula	$B_5H_8K_1O_{12}$
Formula weight	293.21
Temp, K	100.15
Crystal system	orthorhombic
Space group	Aea2
a, Å	11.0495(2)
b, Å	11.1733(2)
c, Å	8.9600(2)
α (°)	90
β (°)	90
γ (°)	90
Volume, $Å^3$	1106.20(4)
Z	4
d_{calc}, g cm^{-3}	1.761
λ, Å	1.54184
μ, mm^{-1}	4.795
Reflections collected	2575
Independent reflections	848
R_{int}	0.0231
Goodness-of-fit on F^2	1.093
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0227$, $wR_2 = 0.0586$
R_1, wR_2 (all data)	$R_1 = 0.0227$, $wR_2 = 0.0586$

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; [b] $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

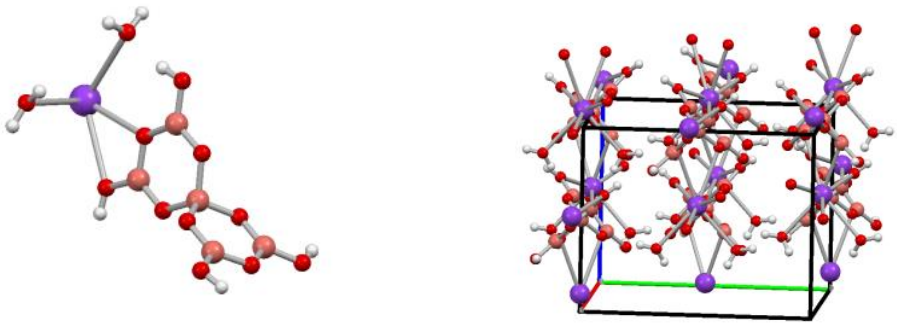


Figure S1. Crystal structure of $K[B_5O_6(OH)_4]\cdot 2H_2O$

5. General procedure for the reduction of aldehydes and ketones to alcohols using KB_3H_8

3.1 In water. In a 5 mL flask, KB_3H_8 (0.5 mmol) was added to the solution of carbonyl compound (0.5 mmol) in neat water (2 mL) under air atmosphere. Then the reaction mixture was stirred at room temperature for **1-30, 41** or under reflux for **31-40**. The reaction was monitored by TLC. Upon completion, the forming alcohols were extracted with ethyl acetate (3 × 10 mL) from the reaction mixture. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated by rotary evaporation, the residue was purified by silica gel column chromatography to obtain the product.

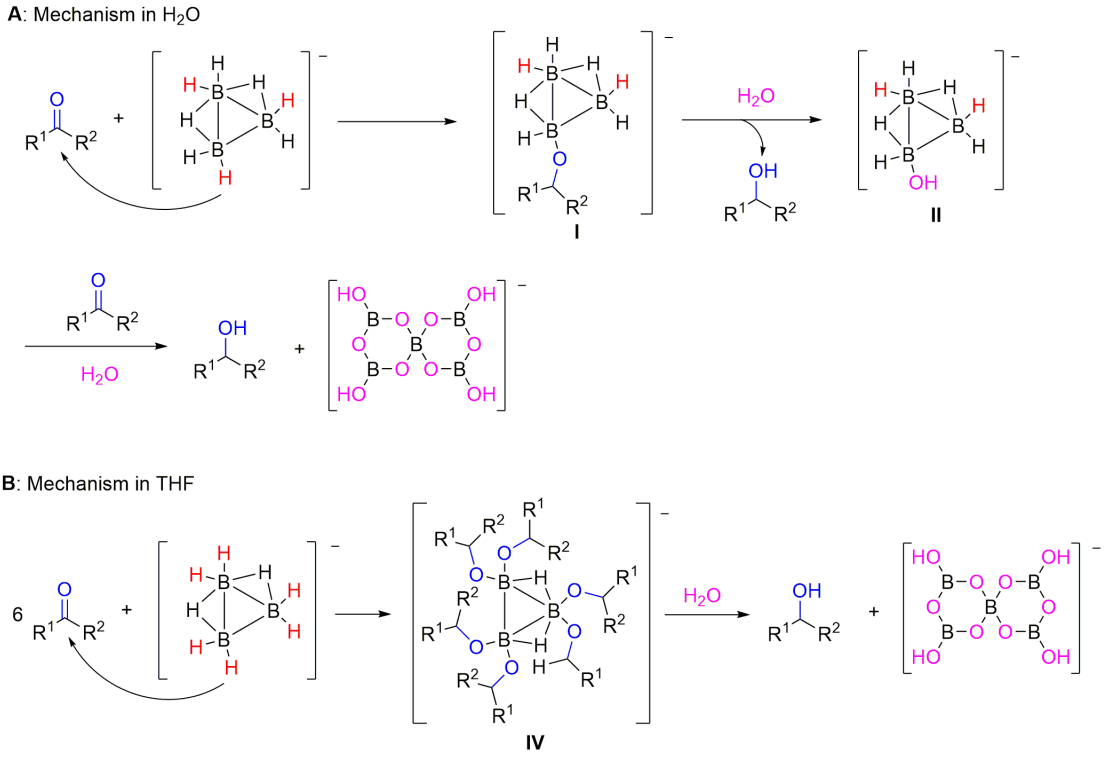
3.2 In THF. In a 5 mL flask, KB_3H_8 (0.5 mmol) was added to the solution of carbonyl compound (0.5 mmol) in THF (2 mL) under air atmosphere. Then the reaction mixture was stirred at room temperature for **1-30, 41** or under reflux for **31-40**. The reaction was monitored by TLC. Upon completion, 2 mL H_2O was added and then the forming alcohols were extracted with ethyl acetate (3 × 10 mL) from the reaction mixture. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated by rotary evaporation, the residue was purified by silica gel column chromatography to obtain the product.

6. Proposed mechanisms

The molar ratio of aldehydes/KB_3H_8 screening procedure reveals that three hydrides of KB_3H_8 participate in the reduction of aldehydes and ketones in water and six hydrides in THF. So, it is believed that the mechanisms in water and THF are different but they are not fully understood. The proposed mechanisms are depicted in Scheme S1.

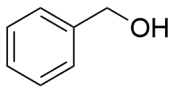
In water: firstly, the hydride of the $B_3H_8^-$ anion attacks the carbonyl carbon to form intermediate **I**, which can transform to intermediate **II** by immediately hydrolysis under the effect of water. Intermediate **II** further reacts with aldehydes/ketones following hydrolysis to produce alcohol and $B(OH)_3$, $B(OH)_4^-$ or polyborate. Alternatively, one of the hydrides of each B atom in $B_3H_8^-$ anion interact with the C atom of carbonyl in the same time and then hydrolysis to polyborate.

In THF: all the six terminal hydrides except the two bridge hydrogens can participate in the reduction to form intermediate **IV**, which can be further transformed to alcohol and $B(OH)_3$, $B(OH)_4^-$ or polyborate after hydrolysis. On the other hand, the interactions between all six B-H bonds of the $B_3H_8^-$ anion and the six carbonyl may take place step by step, which can not be ruled out currently.

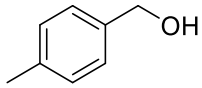


Scheme S1. Proposed mechanisms

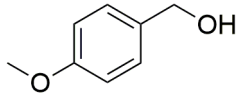
7. Characterization data



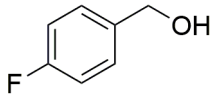
benzyl alcohol (**1**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.31 (m, 3H), 7.28-7.26 (m, 2H), 4.61 (s, 2H), 2.37 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.79, 128.44, 127.51, 126.91, 65.08.[3]



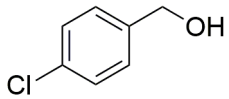
p-tolylmethanol (**2**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.64 (s, 2H), 2.35 (s, 3H), 1.73 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.91, 137.42, 129.26, 127.14, 65.27, 21.15.[3]



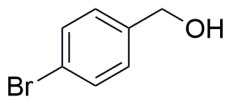
4-methoxybenzyl alcohol (**3**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 1H), 3.60 (s, 3H), 3.40 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.99, 133.33, 128.63, 113.86, 64.45, 55.25.[3]



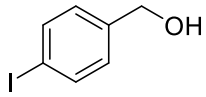
(4-fluorophenyl)methanol (**4**): ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.25 (dd, *J* = 7.8, 5.8 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 4.54 (s, 2H), 2.89 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.27 (d, *J* = 244.6 Hz), 136.57 (d, *J* = 2.7 Hz), 128.75 (d, *J* = 9.0 Hz), 115.32 (d, *J* = 22.7 Hz), 64.31.[3]



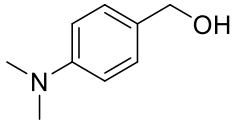
(4-chlorophenyl)methanol (**5**): ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.32-7.31 (m, 2H), 7.28-7.26 (m, 2H), 4.63 (s, 2H), 1.98 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.20, 133.30, 128.62, 128.23, 64.45.[3]



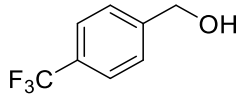
(4-bromophenyl)methanol (**6**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.62 (s, 2H), 1.97 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.71, 131.57, 128.54, 121.39, 64.48.[3]



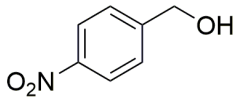
(4-iodophenyl)methanol (**7**)**:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 2H), 1.97 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.45, 137.60, 128.82, 93.00, 64.61.[11]



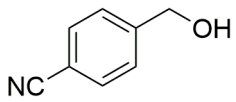
(4-(dimethylamino)phenyl)methanol (**8**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 4.44 (s, 2H), 2.84 (s, 6H), 1.90 (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.39, 129.10, 128.64, 112.75, 65.25, 40.73.[3]



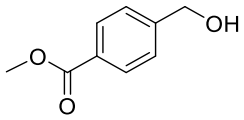
(4-(trifluoromethyl)phenyl)methanol (**9**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.17 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.72, 129.79 (d, *J* = 32.3 Hz), 126.83, 125.45 (d, *J* = 4.0 Hz), 124.17 (d, *J* = 272.7 Hz), 64.43.[15]



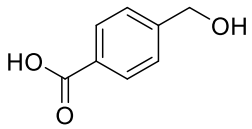
4-nitrobenzyl alcohol (**10**): ^{1}H NMR (600 MHz, $CDCl_3$) δ8.21 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 4.84 (d, *J* = 3.3 Hz, 2H), 2.02 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.19, 147.23, 126.96, 123.69, 63.93.[3]



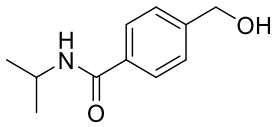
4-cyanobenzyl alcohol (**11**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.57 (s, 2H), 3.90 (d, *J* = 47.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.47, 131.77, 126.59, 118.55, 109.94, 63.20.[6]



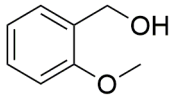
methyl 4-(hydroxymethyl)benzoate (**12**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 4.77 (s, 2H), 3.92 (s, 3H), 1.90 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.96, 145.97, 129.86, 129.36, 126.47, 64.71, 52.10.[10]



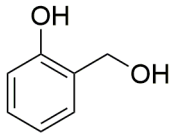
4-(hydroxymethyl)benzoic acid (**13**): ^{1}H NMR (400 MHz, DMSO) δ 12.81 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 5.34 (s, 1H), 4.58 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 167.73, 148.30, 129.63, 129.56, 126.65, 62.85.[10]



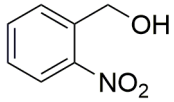
4-(hydroxymethyl)-N-isopropylbenzamide (**14**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.44 (d, *J* = 7.7 Hz, 1H), 4.60 (d, *J* = 5.9 Hz, 2H), 4.20 (dq, *J* = 13.3, 6.6 Hz, 1H), 3.97 (t, *J* = 5.9 Hz, 1H), 1.21 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.06, 144.77, 133.59, 133.57, 126.95, 126.56, 64.17, 41.97, 22.68.



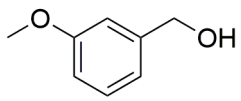
2-methoxybenzyl alcohol (**15**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 4.65 (s, 2H), 3.81 (s, 3H), 2.67 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.20, 129.02, 128.68, 128.47, 120.47, 110.04, 61.61, 61.58, 55.08.[5]



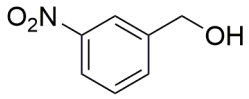
2-hydroxybenzyl alcohol (**16**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.23-7.17 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.90-6.83 (m, 2H), 4.82 (s, 2H), 2.66 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.85, 129.46, 127.92, 124.73, 120.12, 116.42, 64.39.[4]



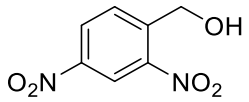
2-nitrobenzyl alcohol (**17**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.70-7.63 (m, 1H), 7.50-7.43 (m, 1H), 4.96 (s, 2H), 2.64 (br, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.57, 136.77, 134.10, 129.87, 128.44, 124.96, 62.44.[3]



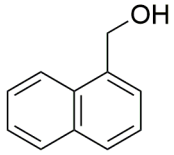
3-methoxybenzyl alcohol (**18**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (t, *J* =7.9 Hz, 1H), 6.74-6.68 (m, 2H), 6.65-6.61 (m,1H), 4.37 (s, 2H), 3.60 (s, 1H), 3.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.37, 142.41, 129.16, 118.86, 112.72, 111.93, 64.33, 54.81.[4]



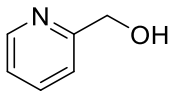
3-nitrobenzyl alcohol (**19**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 4.76 (s, 2H), 3.55 (br, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.00, 142.84, 132.57, 129.23, 122.14, 121.16, 63.44.[5]



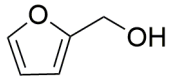
(2,4-dinitrophenyl)methanol (**20**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.2 Hz, 1H), 8.53 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 5.19 (s, 2H), 2.41 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.15, 146.93, 143.87, 130.33, 127.96, 120.39, 61.79.[3]



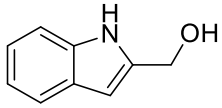
1-naphthalenemethanol (**21**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.59-7.48 (m, 3H), 7.45 (dd, *J* = 8.0, 7.1 Hz, 1H), 5.14 (d, *J* = 4.6 Hz, 2H), 1.93 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.22, 133.75, 131.18, 128.63, 128.53, 126.30, 125.84, 125.36, 125.29, 123.60, 63.62.[4]



pyridin-2-ylmethanol (**22**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.7 Hz, 1H), 7.68 (m, *J* = 7.7, 1.7 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.23-7.17 (m, 1H), 4.76 (s, 2H), 4.24 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.29, 148.53, 136.75, 122.34, 120.65, 64.25.[5]

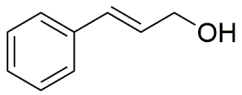


furfuryl alcohol (**23**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 0.9 Hz, 1H), 6.39-6.22 (m, 2H), 4.59 (s, 2H), 2.12 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.95, 142.53, 110.31, 107.71, 57.38.[3]

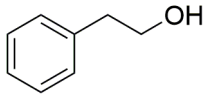


(1*H*-indol-2-yl)methanol (**24**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.22-7.17 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.31 (s, 1H), 4.61 (d, *J* = 12.0 Hz,

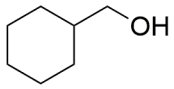
2H), 2.70 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.56, 136.44, 128.04, 122.23, 120.66, 119.98, 111.14, 100.64, 58.46.[12]



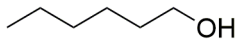
cinnamyl alcohol (**25**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 9.5, 5.1 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.34 (m, *J* = 15.9, 5.7 Hz, 1H), 4.30 (dd, *J* = 5.7, 0.8 Hz, 2H), 1.95 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.72, 131.12, 128.62, 128.55, 127.71, 126.50, 63.66.[3]



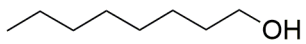
phenethyl alcohol (**26**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 8.2 Hz, 3H), 3.68 (t, *J* = 7.0 Hz, 2H), 3.12 (s, 1H), 2.74 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.43, 128.71, 128.15, 126.00, 63.09, 38.83.[3]



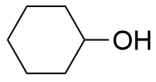
cyclohexanemethanol (**27**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.33 (d, *J* = 6.5 Hz, 2H), 2.51 (s, 1H), 1.75-1.56 (m, 5H), 1.44-1.33 (m, 1H), 1.24-1.03 (m, 3H), 0.91-0.78 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 63.38, 40.31, 29.50, 26.49, 25.74.[8]



1-hexanol (**28**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.61 (d, *J* = 6.8 Hz, 2H), 1.72 (br, 1H), 1.57-1.52 (m, 2H), 1.36-1.25 (m, 6H), 0.87 (d, *J* = 12.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 62.95, 32.69, 31.59, 25.38, 22.58, 13.96.[9]

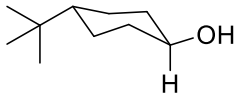


1-octanol (**29**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.51 (t, *J* = 6.8 Hz, 2H), 3.12 (s, 1H), 1.54-1.43 (m, 2H), 1.24 (m, *J* = 19.2, 10.6, 4.5 Hz, 9H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 62.48, 32.57, 31.73, 29.34, 29.24, 29.20, 25.69, 22.53, 13.89.[10]

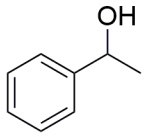


oyclohexanol (**30**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.59 (td, *J* = 9.0, 4.2 Hz, 1H), 1.86 (dd, *J* = 23.4, 18.2 Hz, 2H), 1.79-1.59 (m, 3H), 1.59-1.47 (m, 1H), 1.31-1.08 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$)

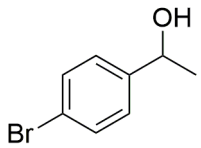
δ 70.26, 35.49, 25.41, 24.10.[3]



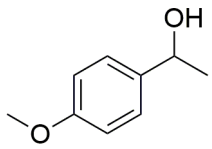
4-(*tert*-butyl)cyclohexan-1-ol (**31**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (m, 1H), 2.06-1.98 (m, 2H), 1.84-1.76 (m, 2H), 1.22 (m, 2H), 1.12-0.97 (m, 3H), 0.87 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 71.24, 47.20, 36.10, 32.28, 27.65, 25.61.[13]



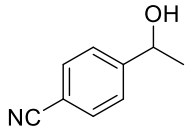
1-phenethylalcohol (**32**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 10.1, 3.3 Hz, 4H), 7.17-7.11 (m, 1H), 4.69 (q, *J* = 6.5 Hz, 1H), 2.57 (s, 1H), 1.33 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.75, 128.29, 127.22, 125.29, 70.08, 24.98.[4]



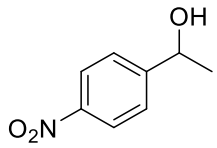
1-(4-bromophenyl)ethanol (**33**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.64 (q, *J* = 6.5 Hz, 1H), 2.92(s, 1H)1.28 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.61, 131.30, 127.02, 120.87, 69.39, 25.00.[3]



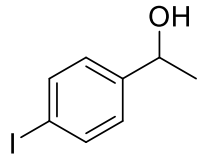
1-(4-methoxyphenyl)-1-ethanol (**34**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16-7.05 (m, 2H), 6.75-6.65 (m, 2H), 4.63 (q, *J* = 6.4 Hz, 1H), 3.62 (s, 3H), 2.91 (s, 1H), 1.29 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.80, 138.27, 126.73, 113.77, 69.68, 55.24, 25.09.[3]



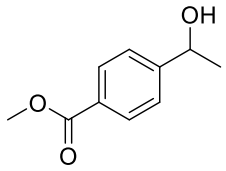
4-(1-hydroxyethyl)benzonitrile (**35**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 4.95 (q, *J* = 6.2 Hz, 1H), 2.41 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.24, 132.33, 126.09, 118.89, 110.94, 69.59, 25.38.[15]



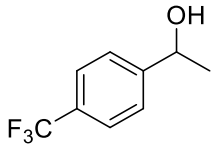
1-(4-nitrophenyl)ethan-1-ol (**36**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 4.93 (q, *J* = 6.4 Hz, 1H), 2.38 (s, 1H), 1.43 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.21, 147.12, 126.14, 123.73, 69.46, 25.45.[14]



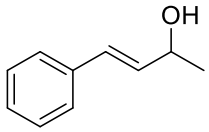
1-(4-iodophenyl)ethan-1-ol (**37**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.76 (q, *J* = 6.3 Hz, 1H), 1.95 (s, 1H), 1.38 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.48, 137.54, 127.43, 92.72, 69.85, 25.23.[16]



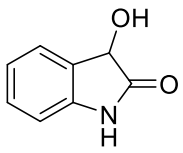
methyl 4-(1-hydroxyethyl)benzoate (**38**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 4.94 (q, *J* = 6.3 Hz, 1H), 3.90 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.02, 150.99, 129.84, 129.16, 125.30, 69.95, 52.10, 25.29.[14]



1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**39**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 4.96 (q, *J* = 6.4 Hz, 1H), 2.03 (s, 1H), 1.50 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.70, 129.64 (d, *J* = 32.3 Hz), 125.65, 125.45 (d, *J* = 4.0 Hz), 124.17 (d, *J* = 272.7 Hz), 69.83, 25.38.[15]

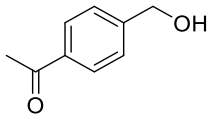


(E)-4-phenylbut-3-en-2-ol (**40**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.45 (p, *J* = 6.4 Hz, 1H), 2.15 (s, 1H), 1.35 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.66, 133.54, 129.23, 128.49, 127.51, 126.37, 68.74, 23.31.[5]

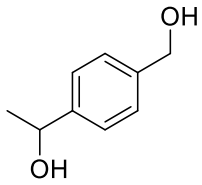


3-hydroxyindolin-2-one (**41**): ^{1}H NMR (400 MHz, DMSO) δ 10.21 (s, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.16 (d, *J* = 7.6 Hz, 1H), 4.83

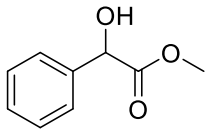
(d, J = 7.5 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 177.97, 142.19, 129.32, 128.94, 124.79, 121.52, 109.50, 69.19.[17]



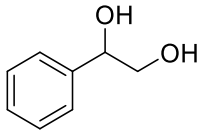
1-(4-(hydroxymethyl)phenyl)ethan-1-one (**42**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.48-7.40 (m, 2H), 4.76 (d, J = 2.9 Hz, 2H), 2.58 (dd, J = 2.9, 2.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.18, 198.12, 146.45, 146.40, 136.27, 136.23, 128.61, 126.62, 64.50, 64.46, 26.61.[10]



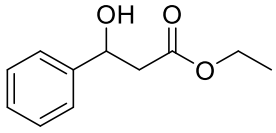
1-(4-(hydroxymethyl)phenyl)ethan-1-ol (**43**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 4H), 4.84 (q, J = 6.4 Hz, 1H), 4.60 (s, 2H), 1.46 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.14, 140.03, 127.12, 125.56, 70.01, 64.71, 25.11.[18]



methyl 2-hydroxy-2-phenylacetate (**44**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J = 7.2 Hz, 2H), 7.28 (t, J = 7.3 Hz, 2H), 7.24 (dd, J = 8.5, 5.8 Hz, 1H), 5.10 (d, J = 2.9 Hz, 1H), 3.67 (s, 3H), 3.49 (d, J = 3.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.13, 138.29, 128.63, 128.52, 126.62, 72.94, 52.99.[3]



1-phenylethane-1,2-diol (**45**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.24 (m, 5H), 4.79 (dd, J = 8.2, 3.0 Hz, 1H), 3.74-3.61 (m, 2H), 3.57 (s, J = 30.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.54, 128.50, 127.91, 126.11, 74.74, 68.04.[3]



ethyl 3-hydroxy-3-phenylpropanoate (**46**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.22 (m, 5H), 5.13 (dd, J = 8.7, 3.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.73 (m, J = 10.4, 6.4 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.43, 142.56, 128.55, 127.81, 125.72, 70.38, 60.92, 43.41, 14.14.[3]

8. References

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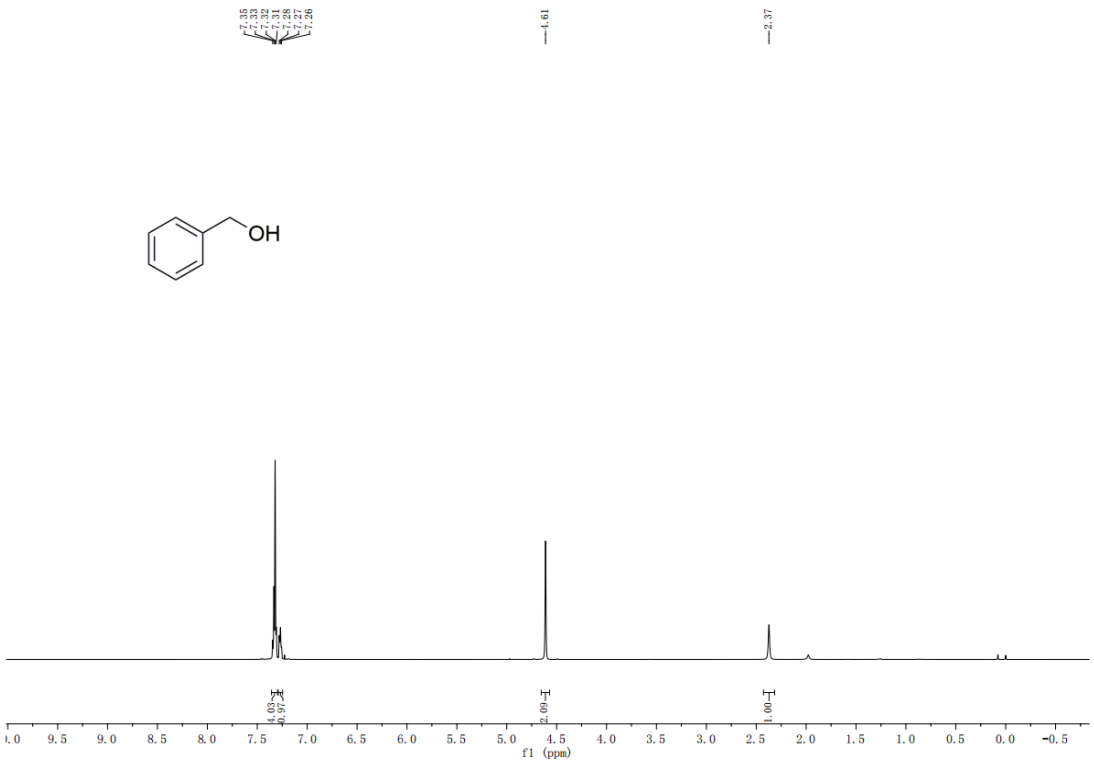
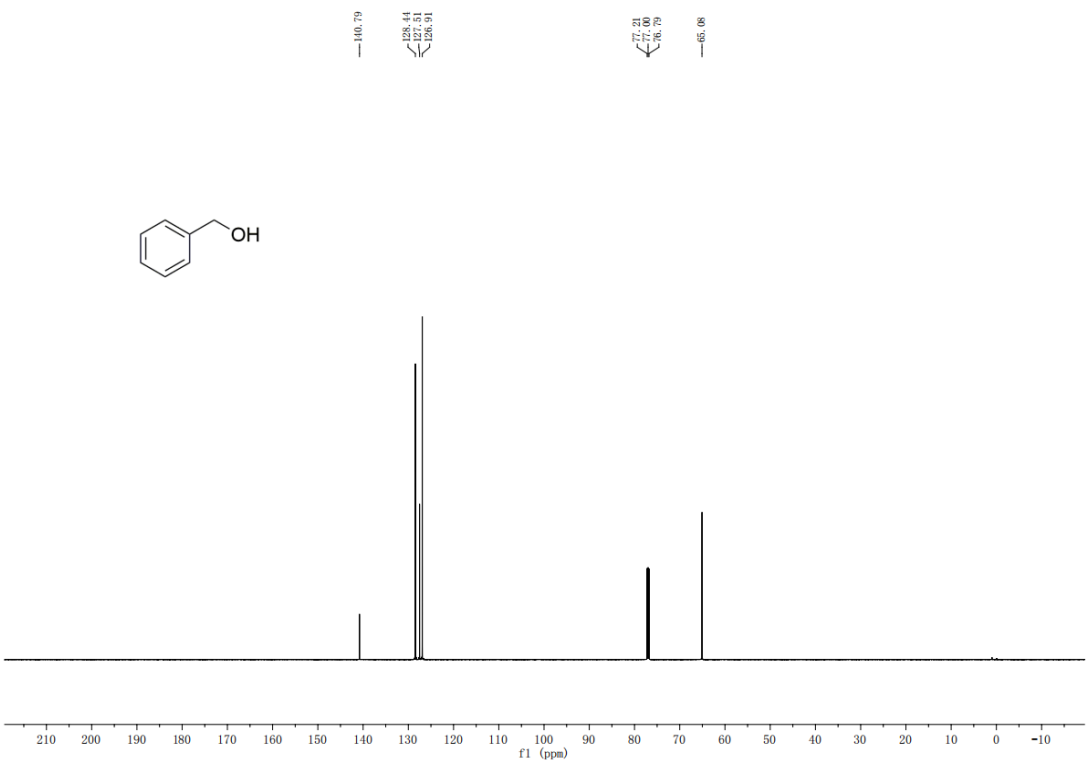
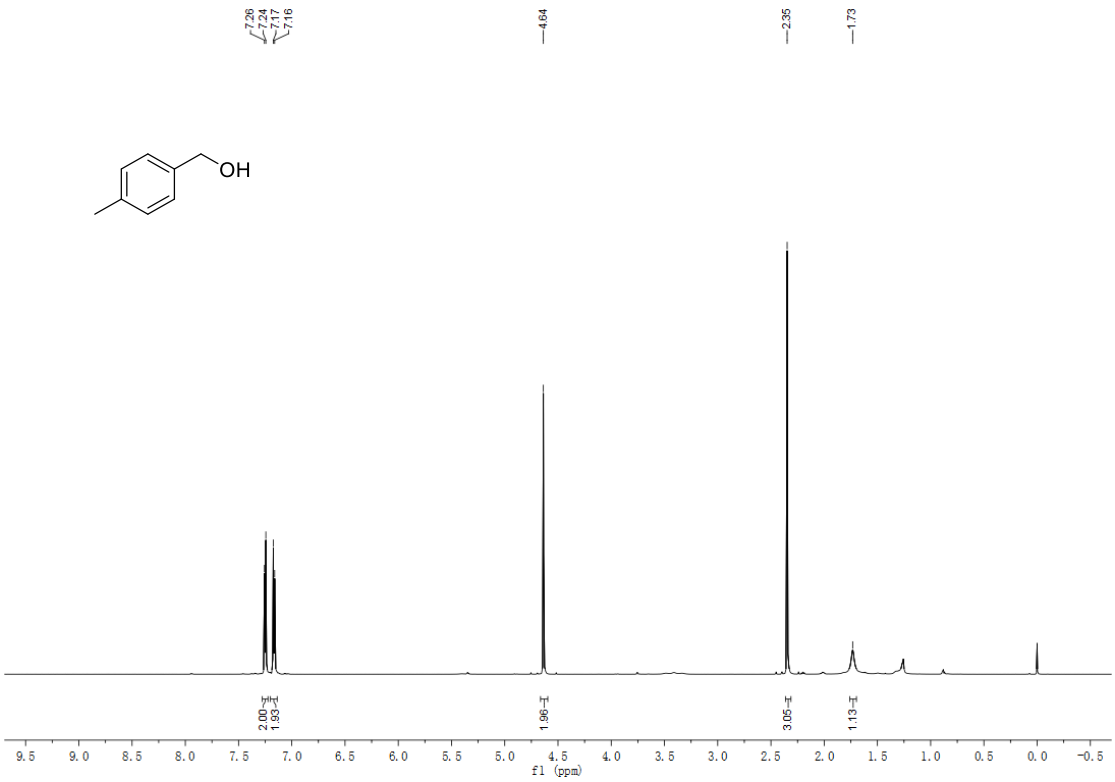
9. NMR spectra of all the forming alcohol products



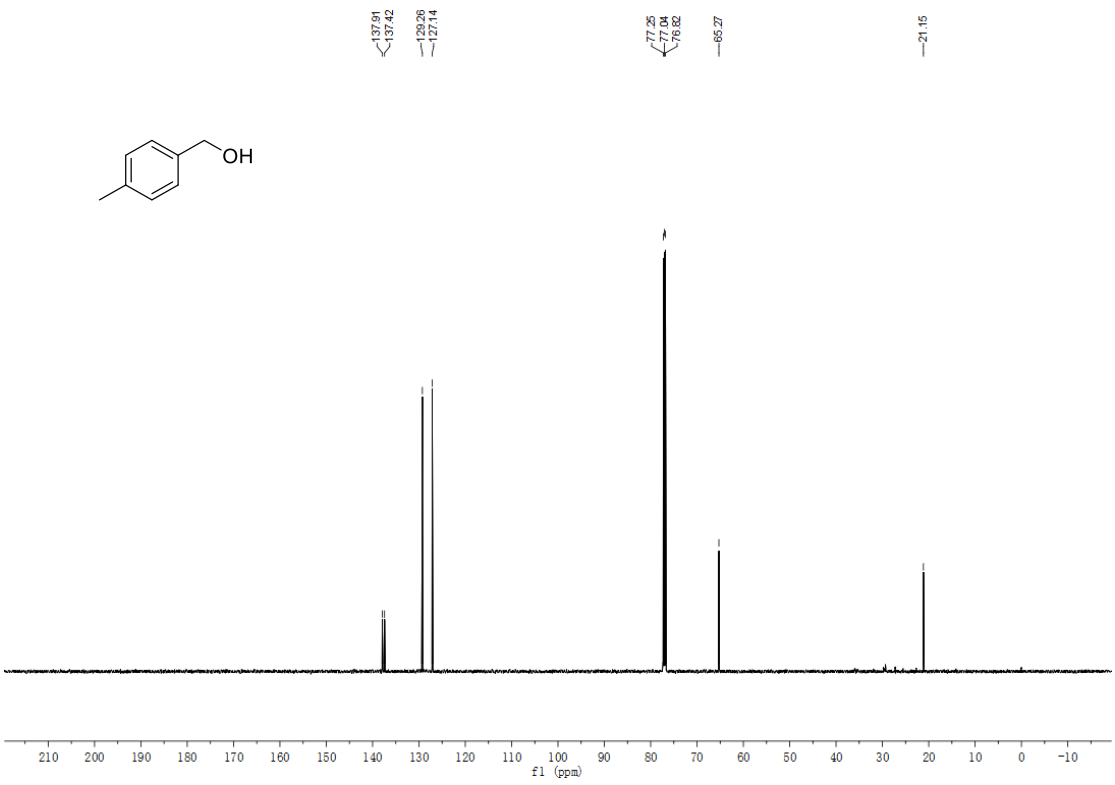
^{1}H NMR spectrum of **1** (600MHz, $CDCl_3$)



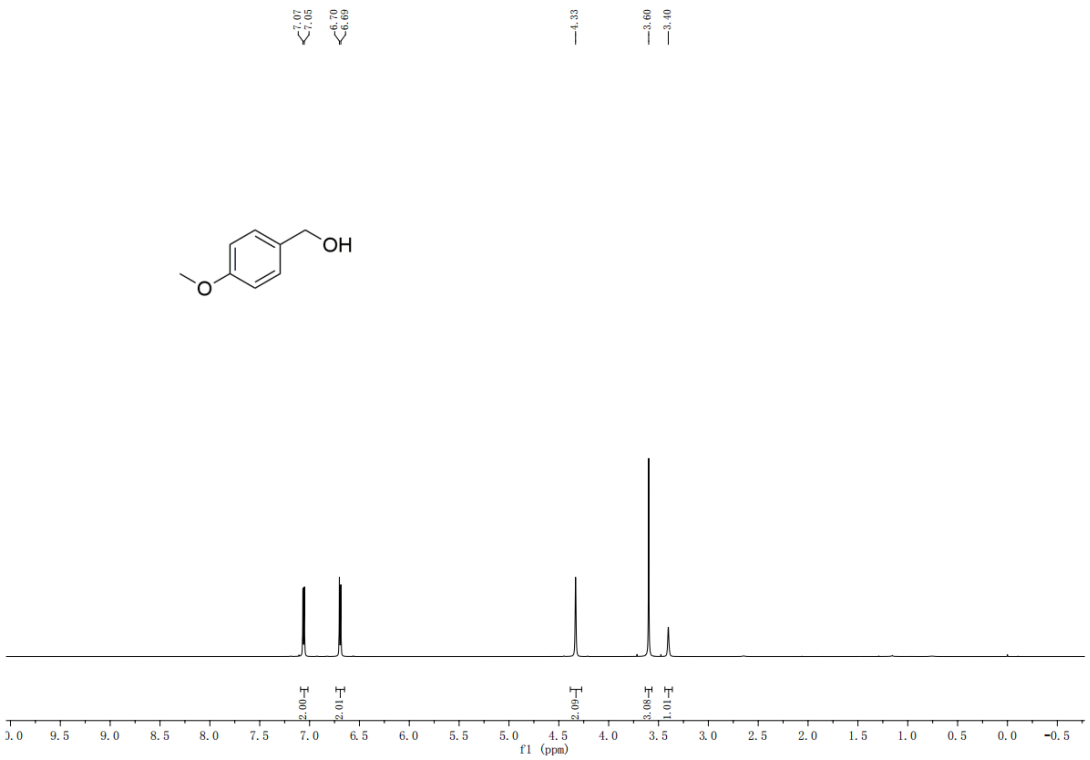
^{13}C NMR spectrum of **1** (151MHz, $CDCl_3$)



^{1}H NMR spectrum of **2** (600MHz, $CDCl_3$)



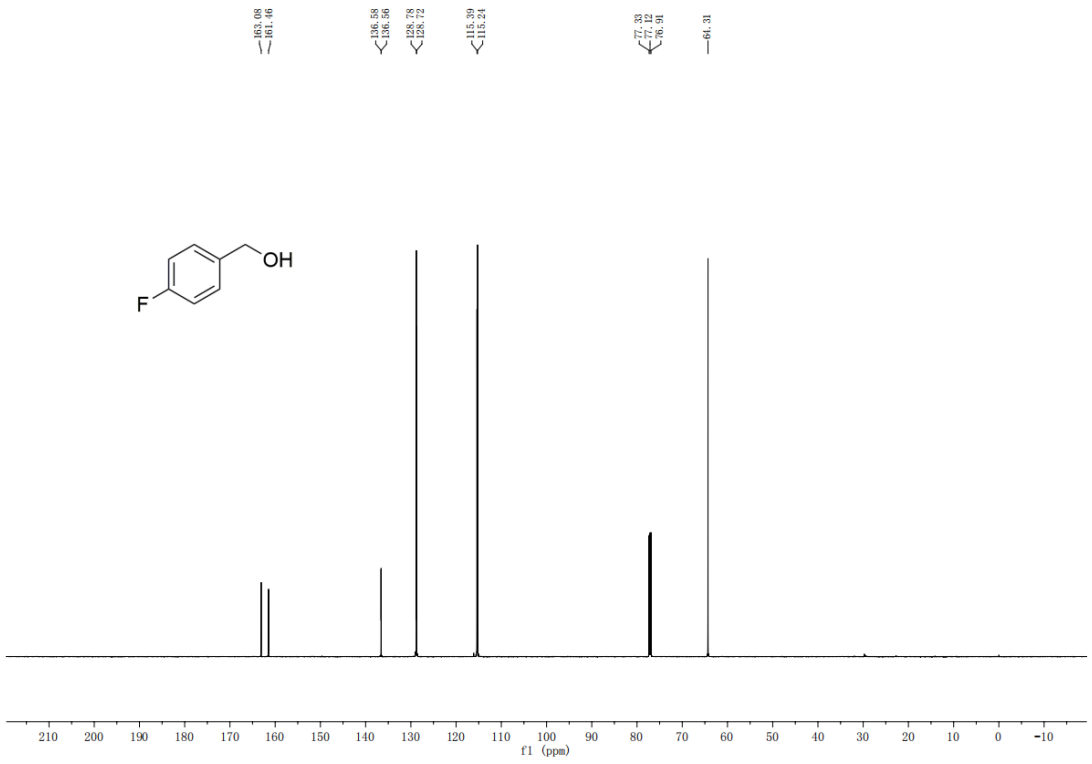
^{13}C NMR spectrum of **2** (151MHz, $CDCl_3$)



^{1}H NMR spectrum of **3** (600MHz, $CDCl_3$)

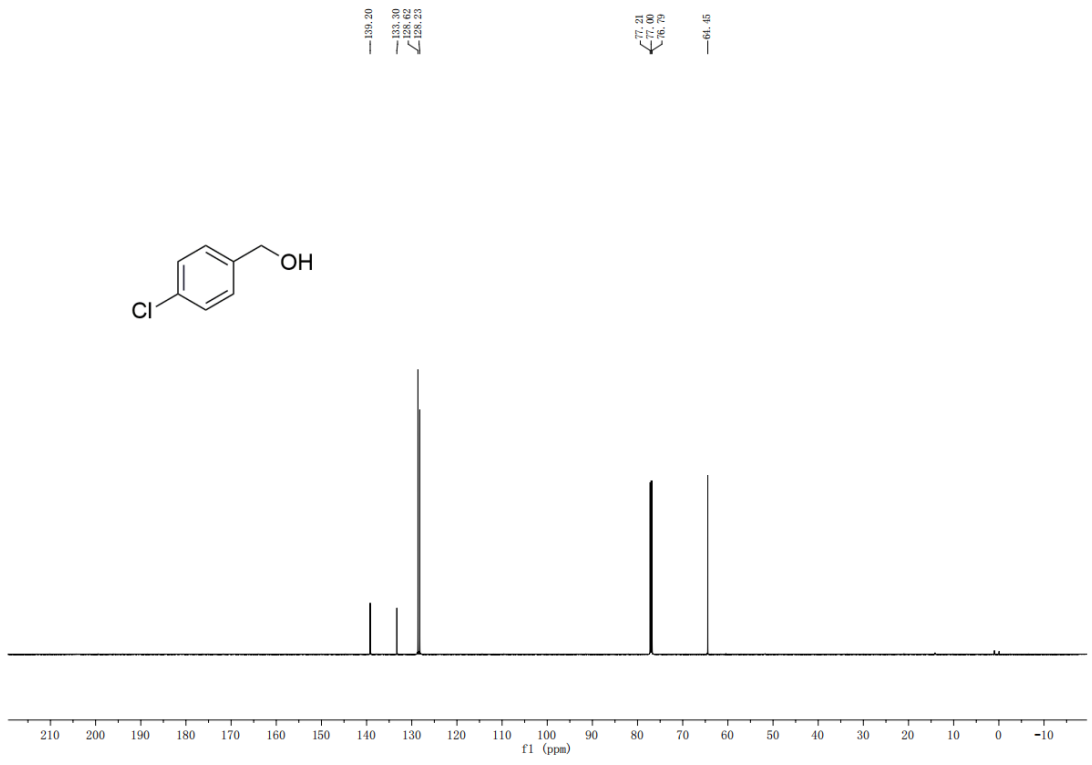
^{13}C NMR spectrum of **3** (151MHz, $CDCl_3$)

^{1}H NMR spectrum of **4** (600MHz, $CDCl_3$)

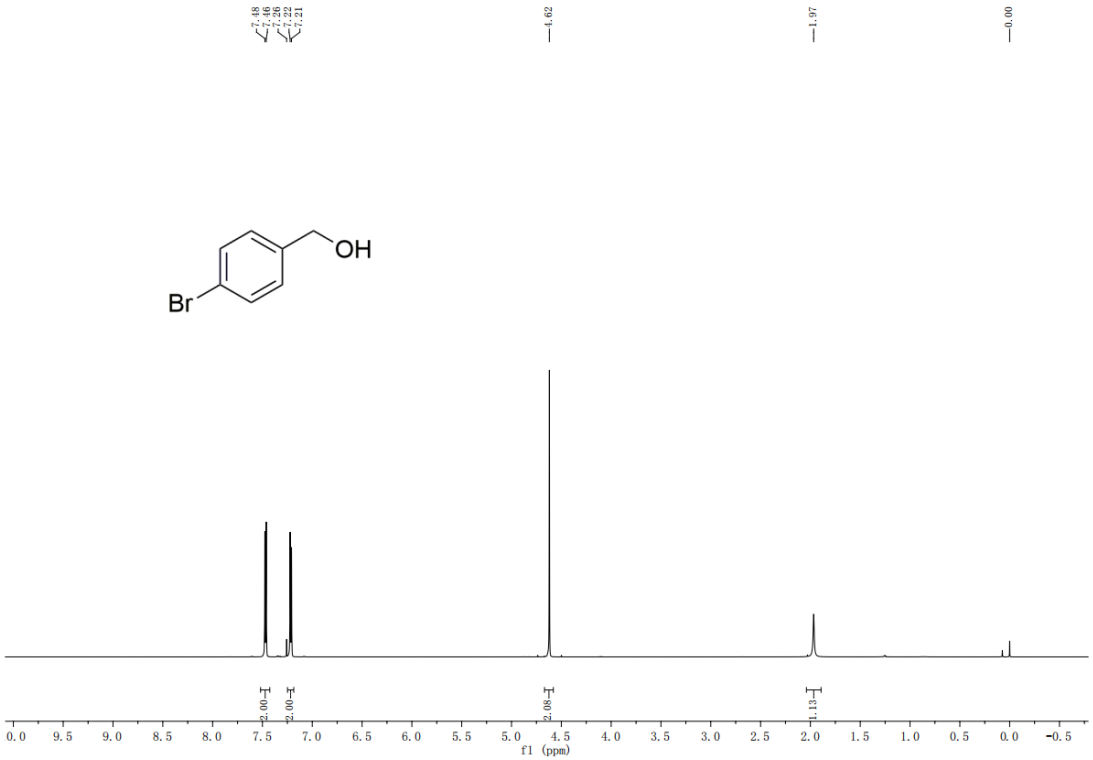


^{13}C NMR spectrum of **4** (151MHz, $CDCl_3$)

^{1}H NMR spectrum of **5** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **5** (151MHz, $CDCl_3$)



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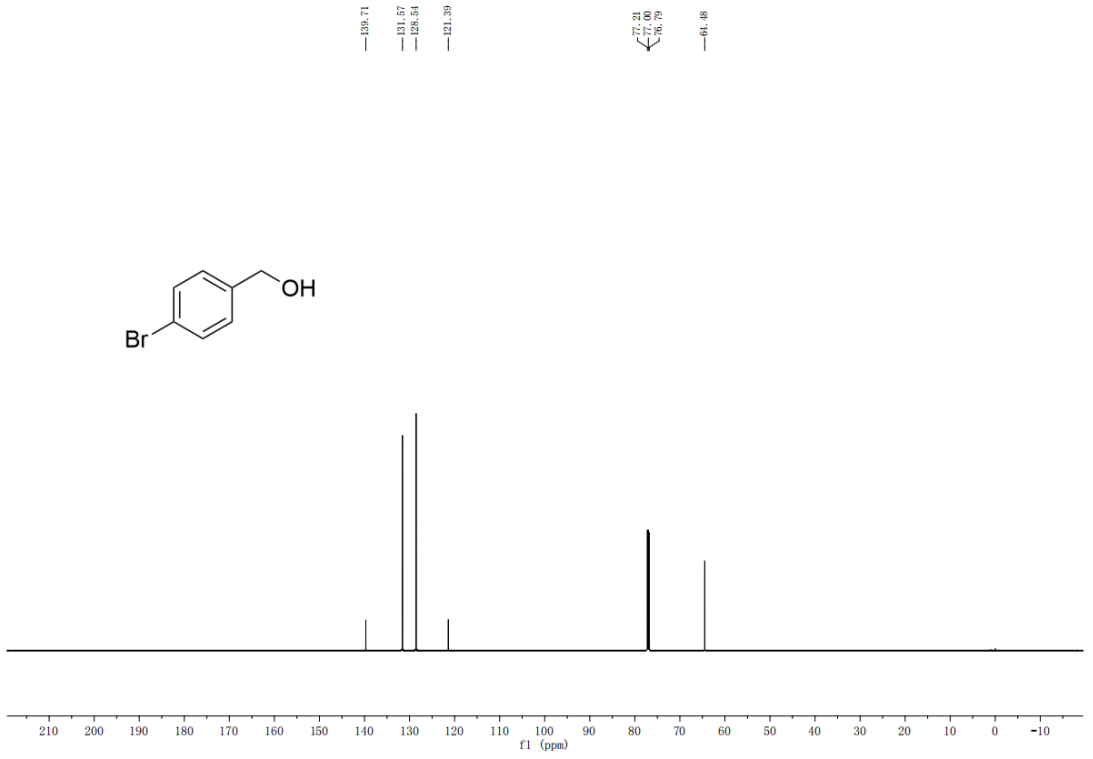
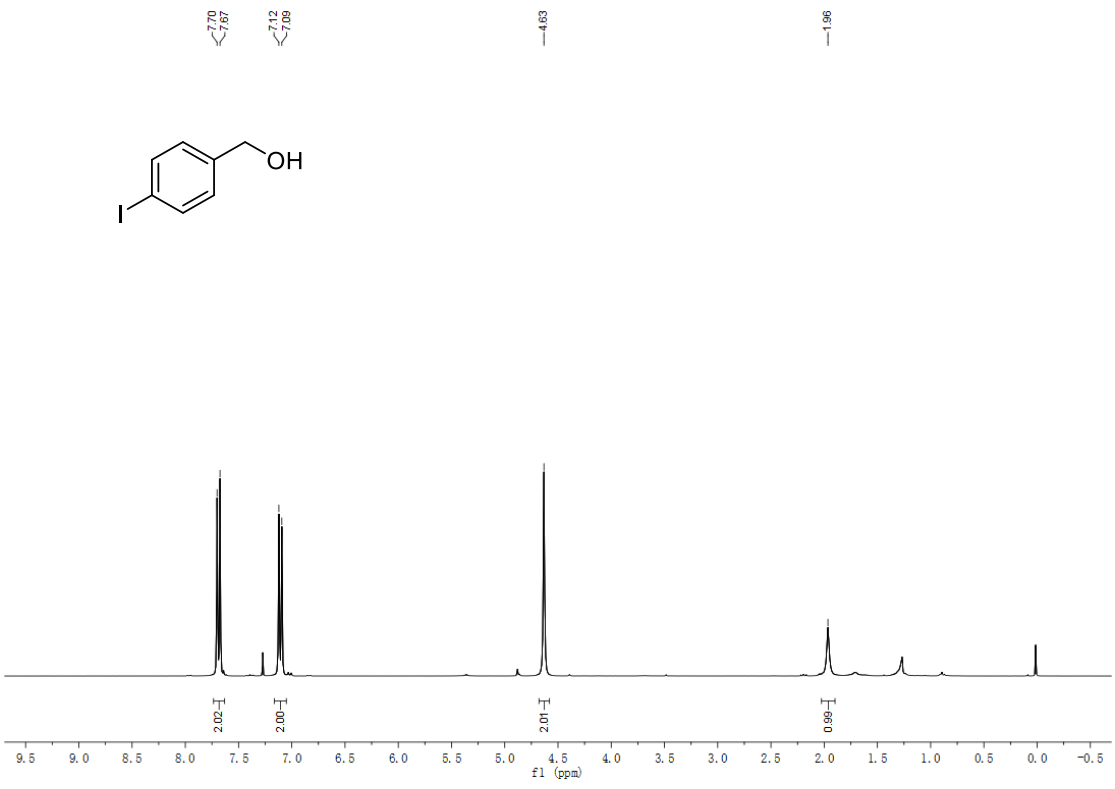
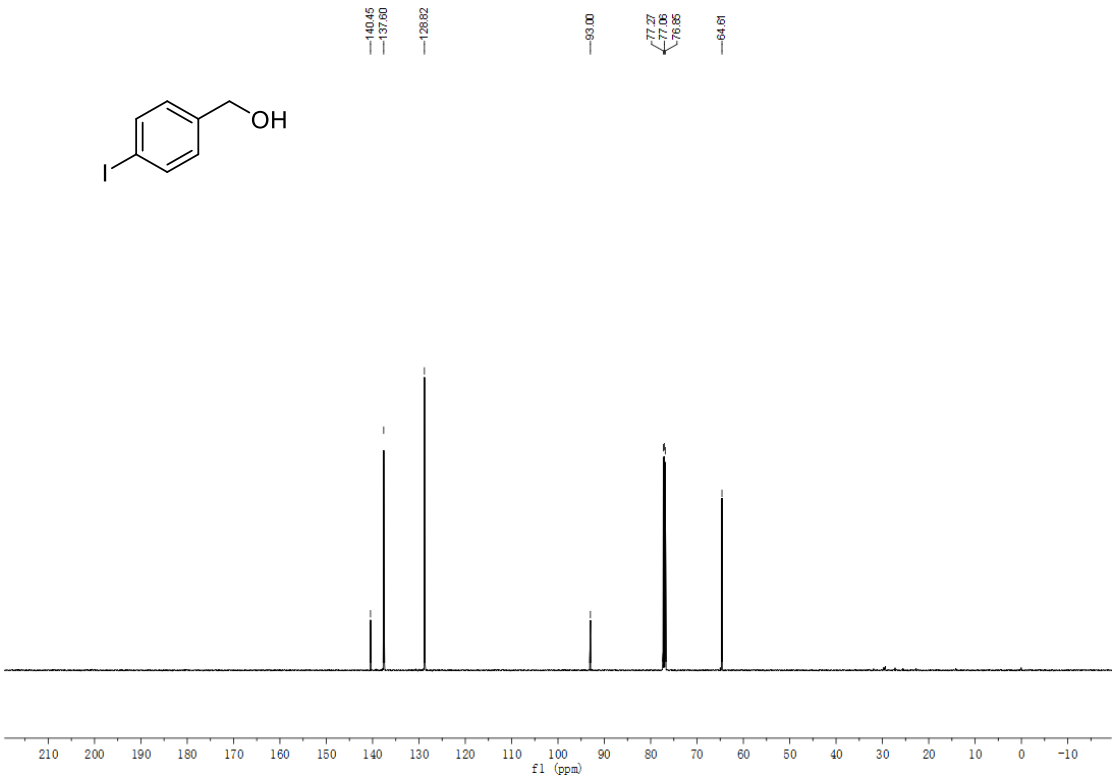


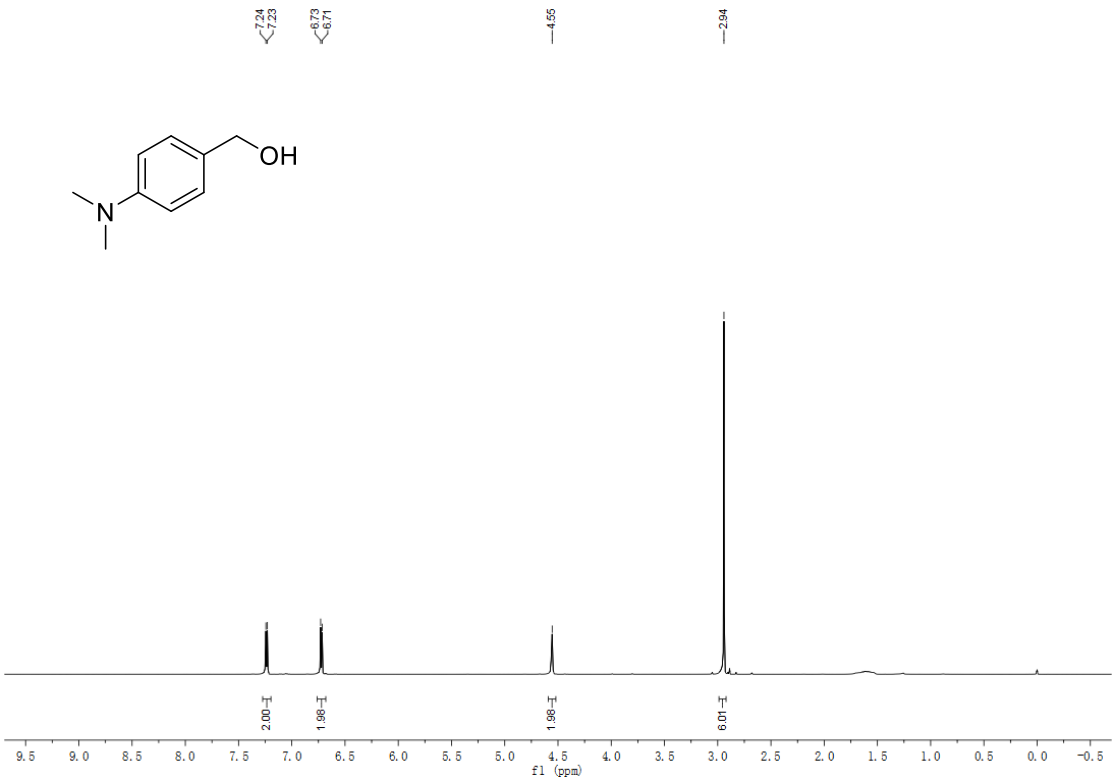
^{13}C NMR spectrum of **6** (151MHz, $CDCl_3$)



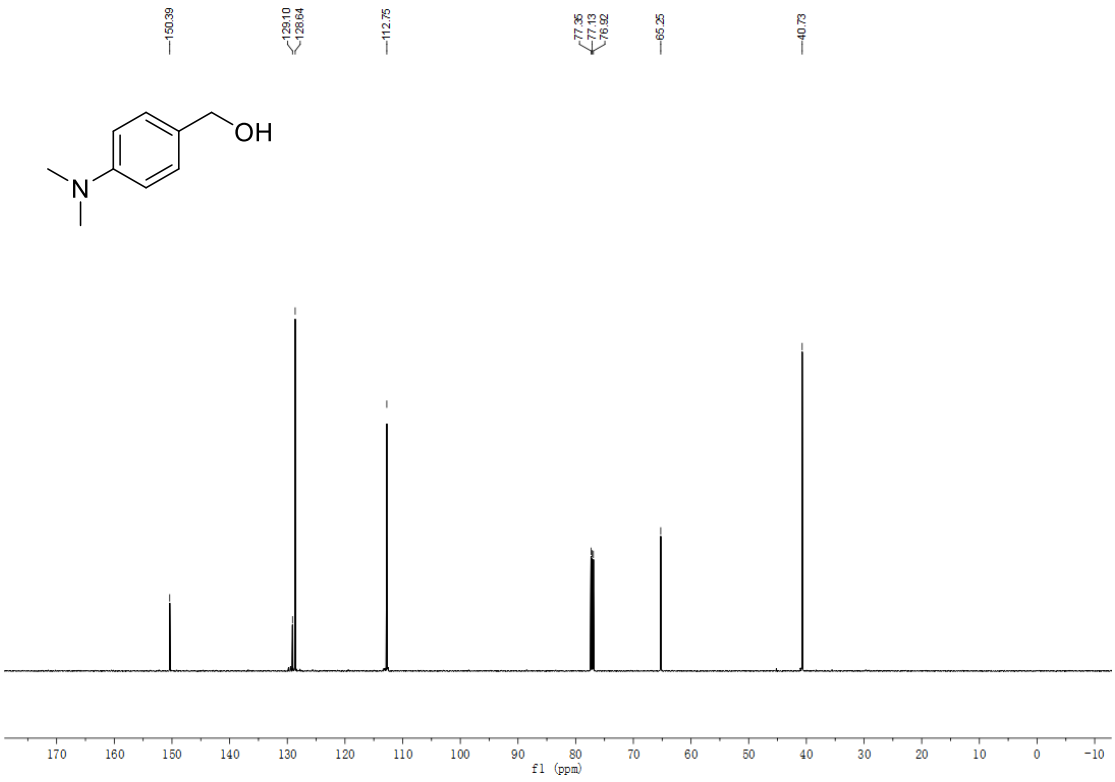
^{1}H NMR spectrum of **7** (600MHz, $CDCl_3$)



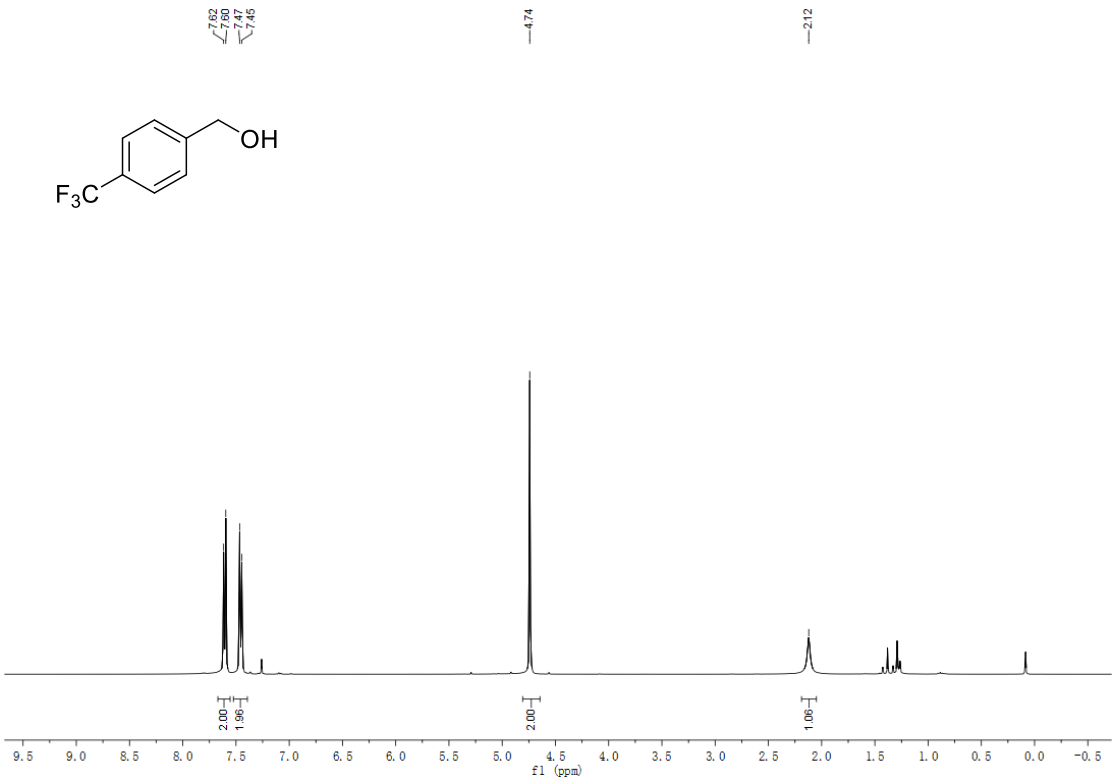
^{13}C NMR spectrum of **7** (151MHz, $CDCl_3$)



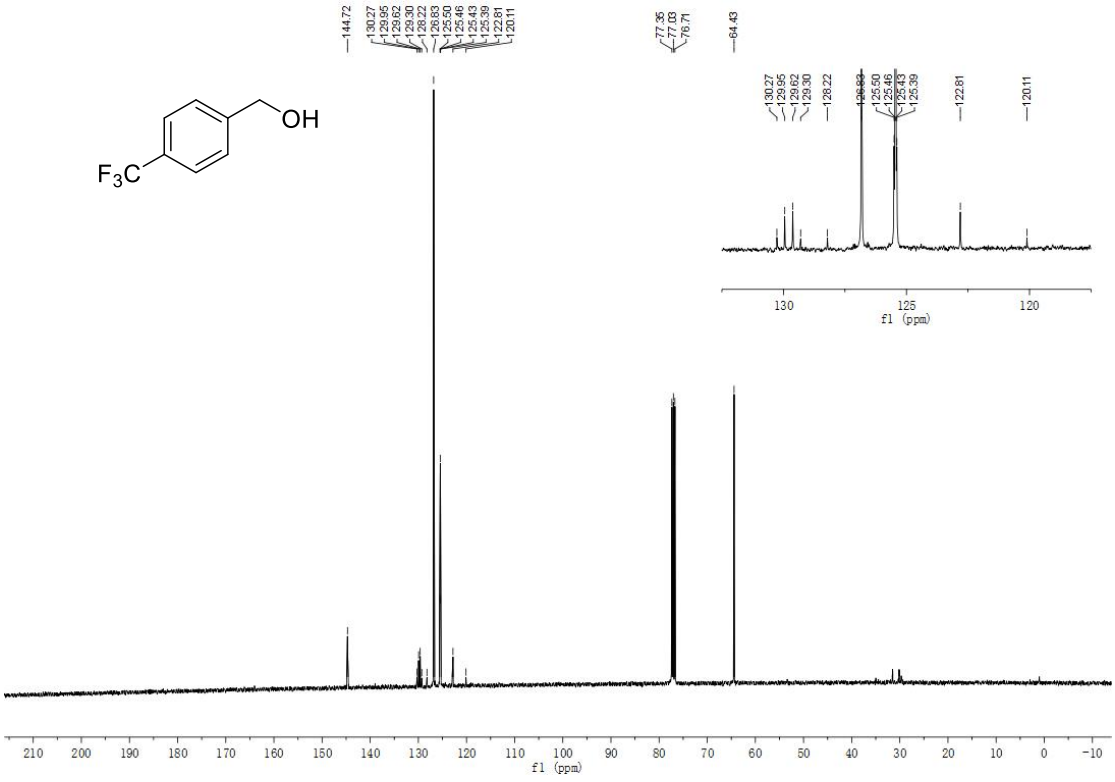
^{1}H NMR spectrum of **8** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **8** (151MHz, $CDCl_3$)



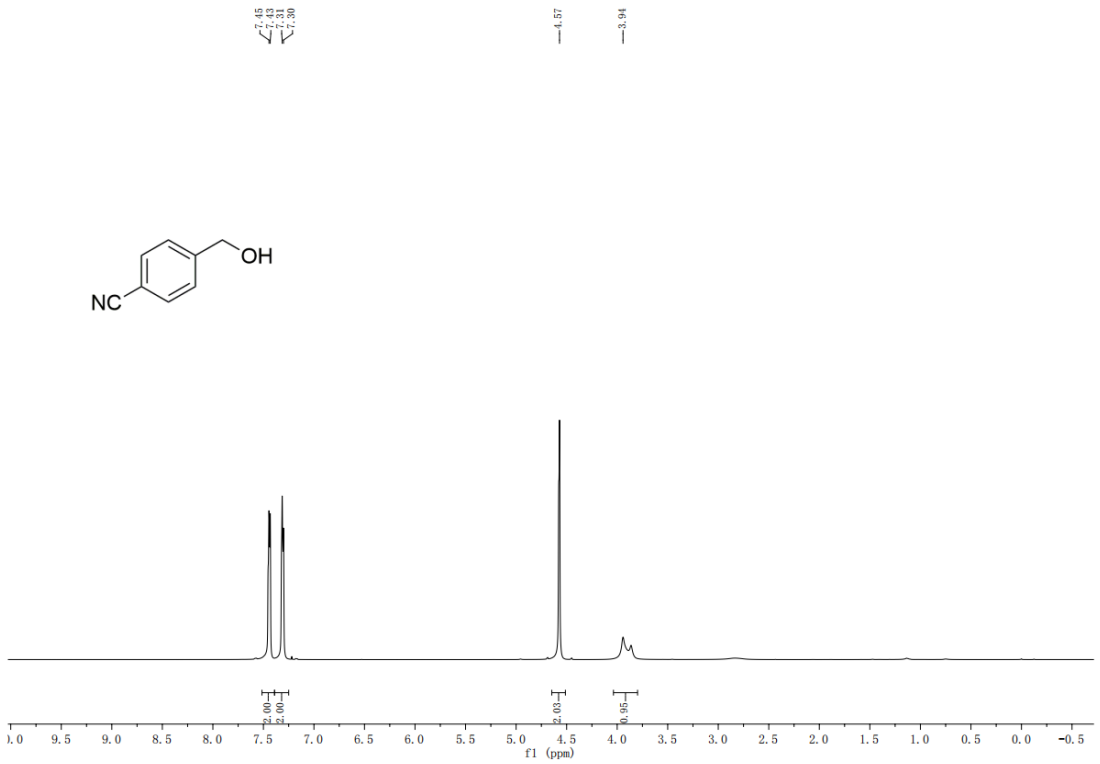
^{1}H NMR spectrum of **9** (400MHz, $CDCl_3$)



^{13}C NMR spectrum of **9** (101MHz, $CDCl_3$)

^{1}H NMR spectrum of **10** (600MHz, $CDCl_3$)

^{13}C NMR spectrum of **10** (151MHz, $CDCl_3$)



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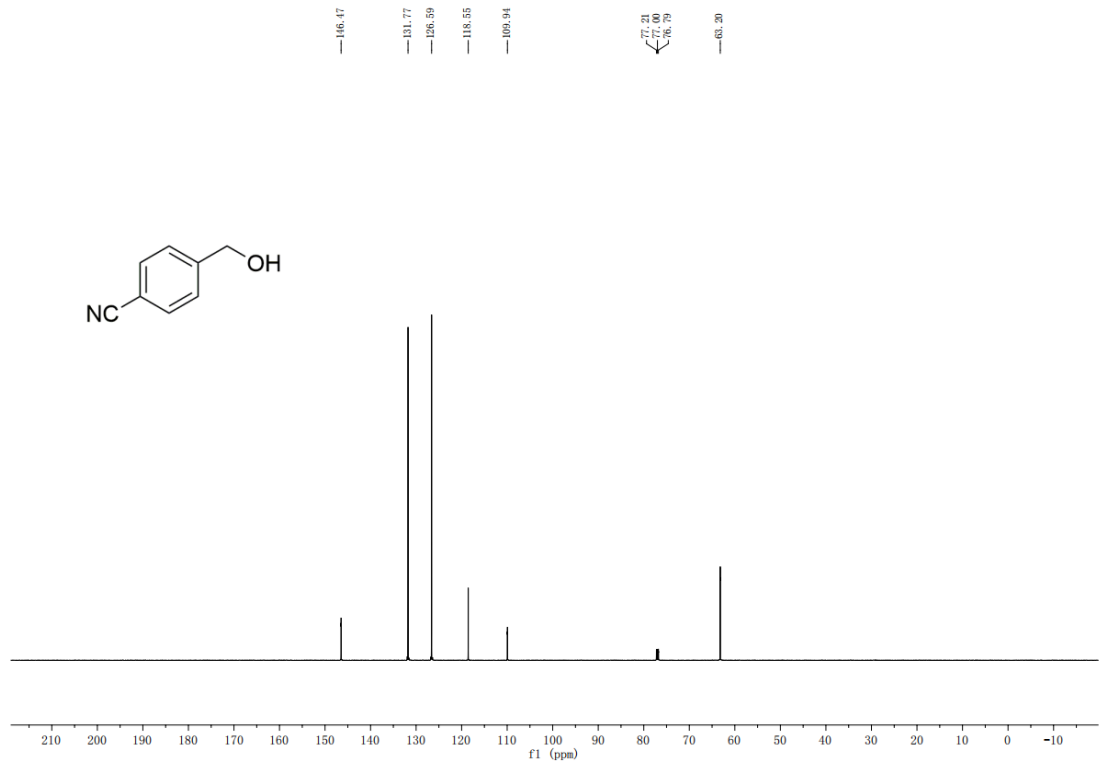
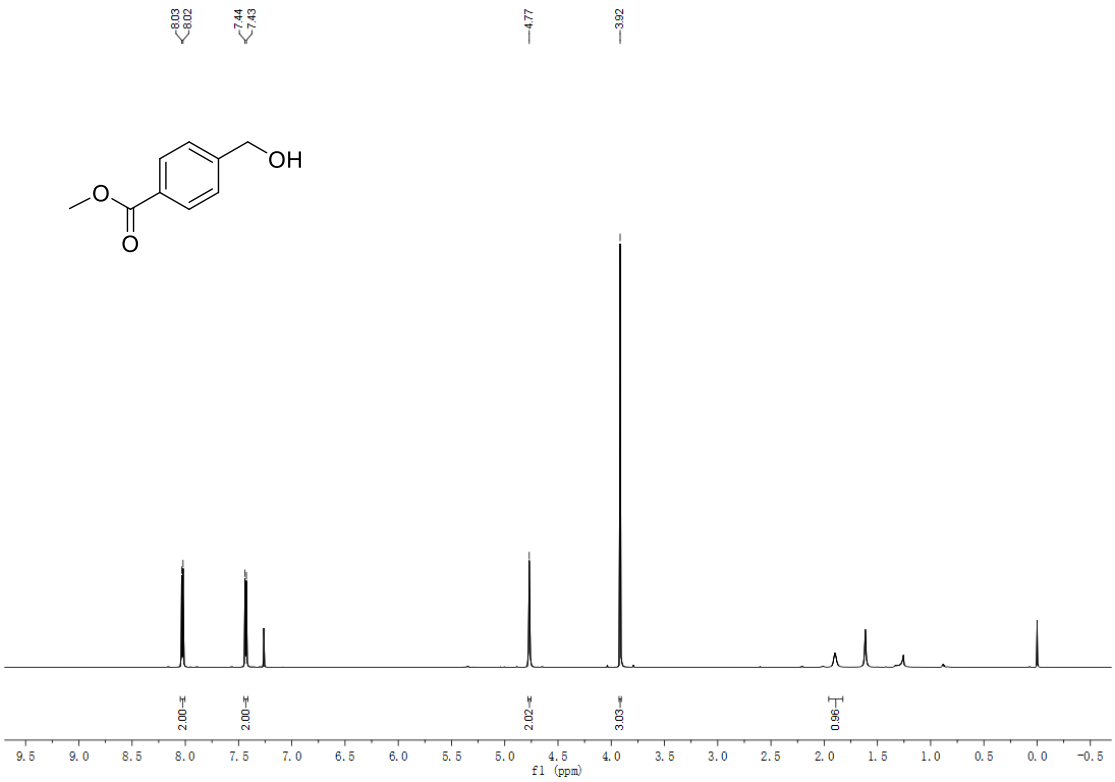
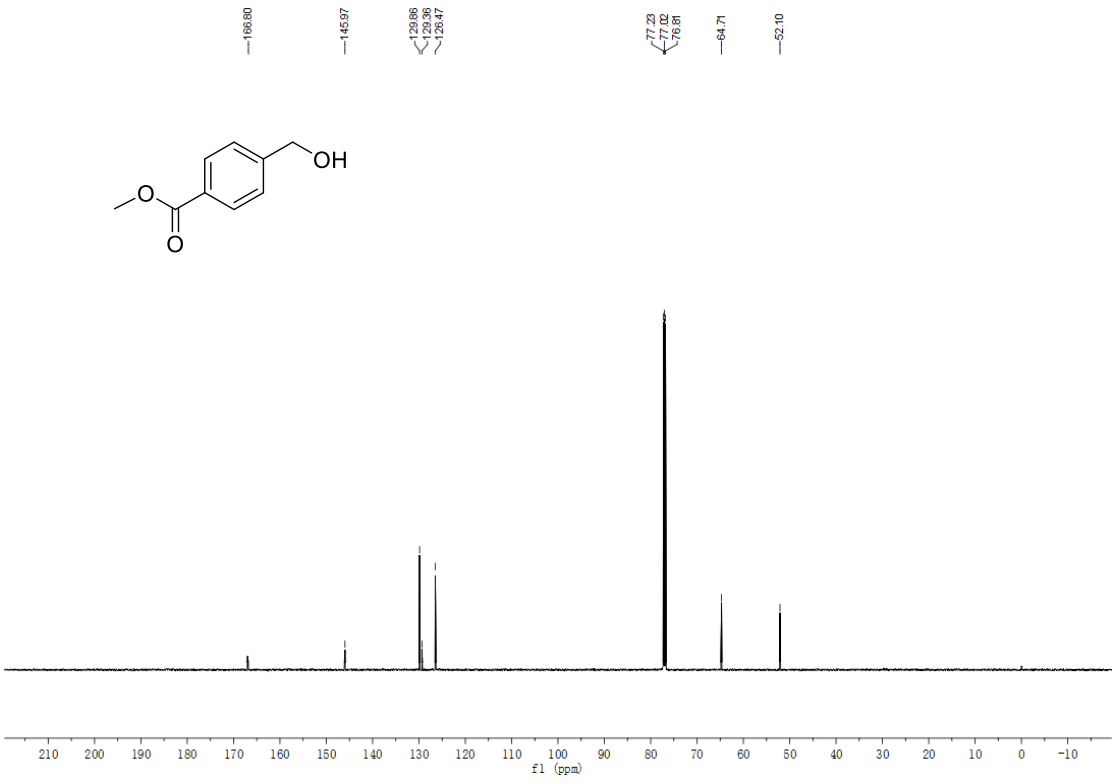


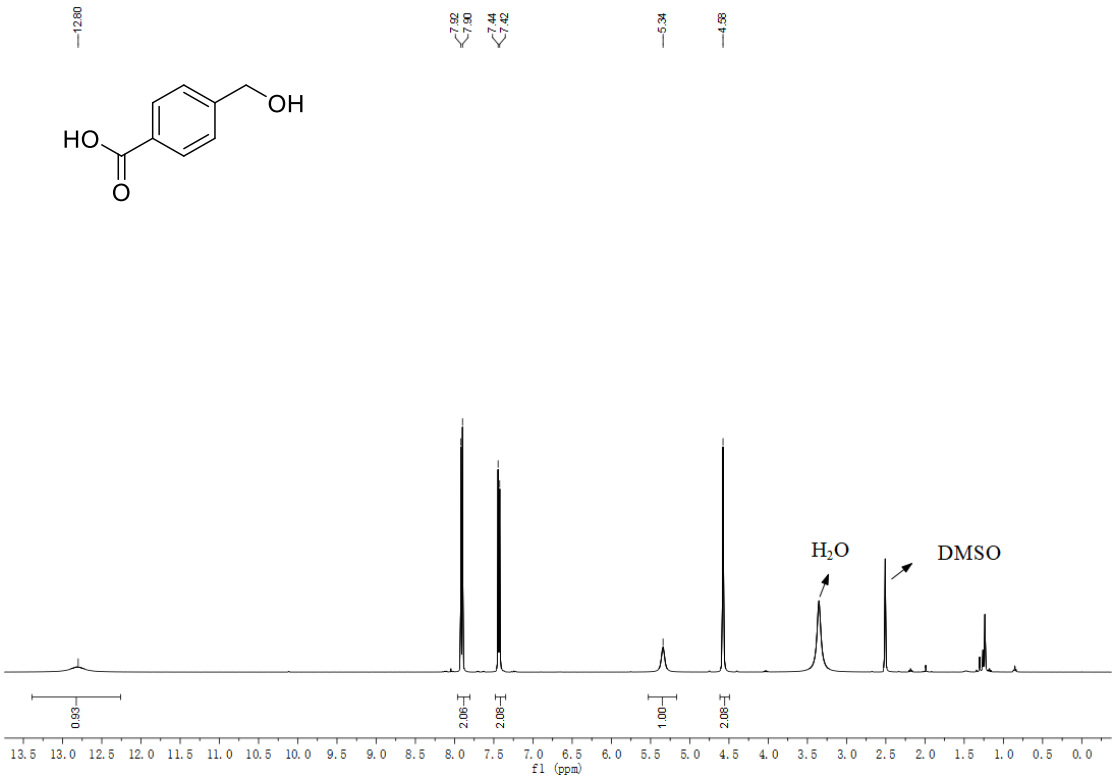
^{13}C NMR spectrum of **11** (151MHz, $CDCl_3$)



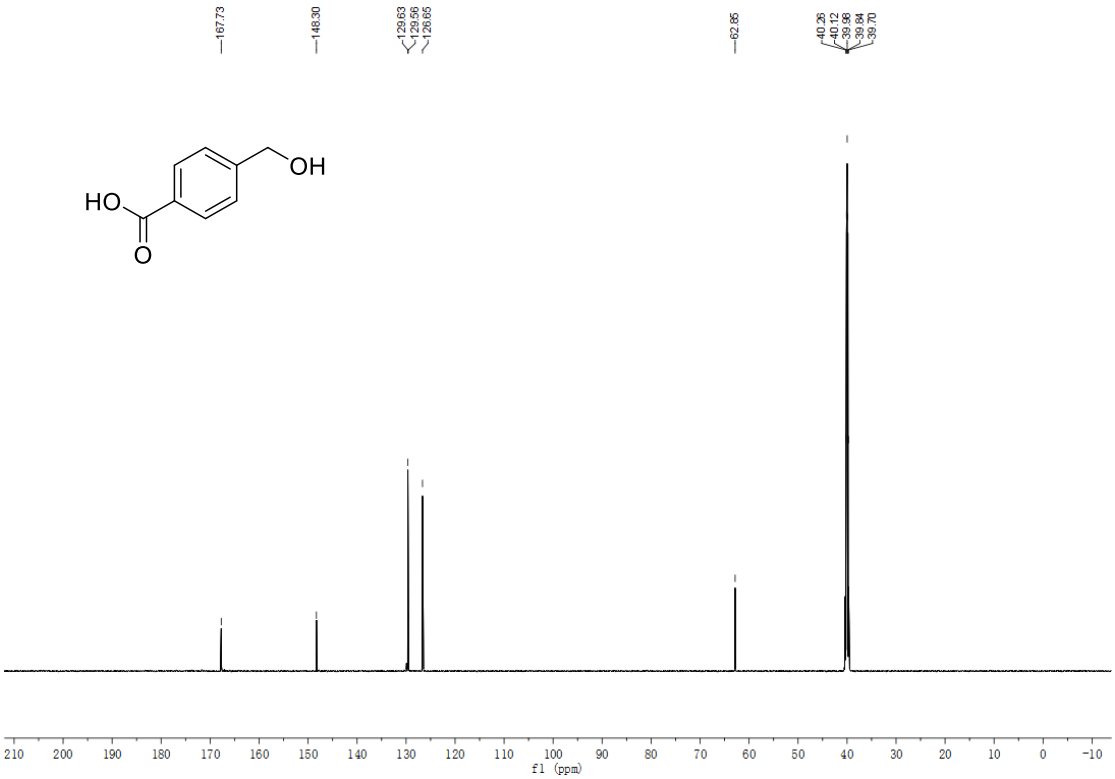
^{1}H NMR spectrum of **12** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **12** (151MHz, $CDCl_3$)



^{1}H NMR spectrum of **13** (400MHz, DMSO)



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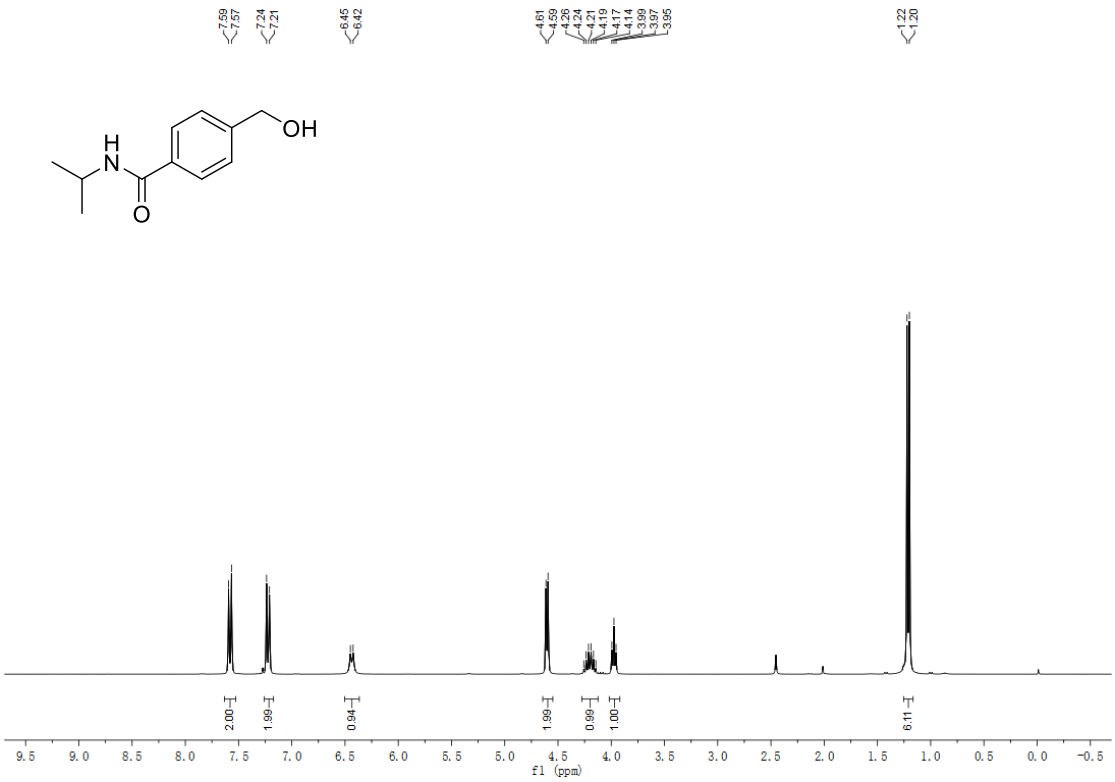
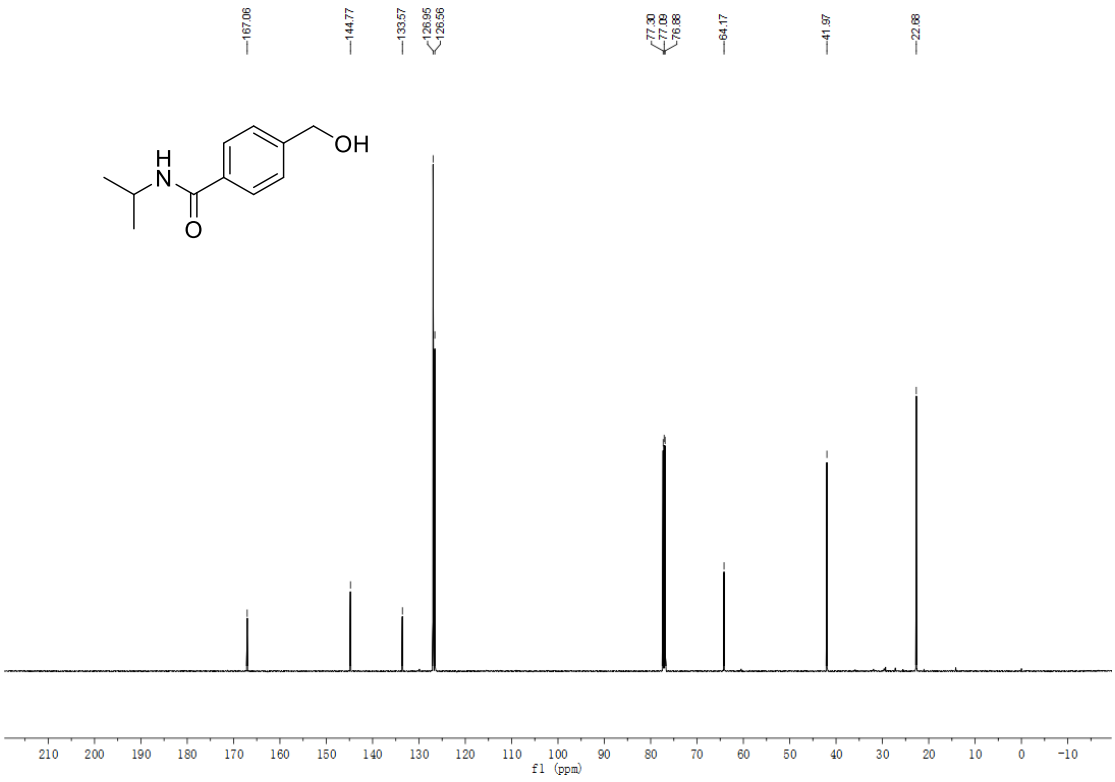
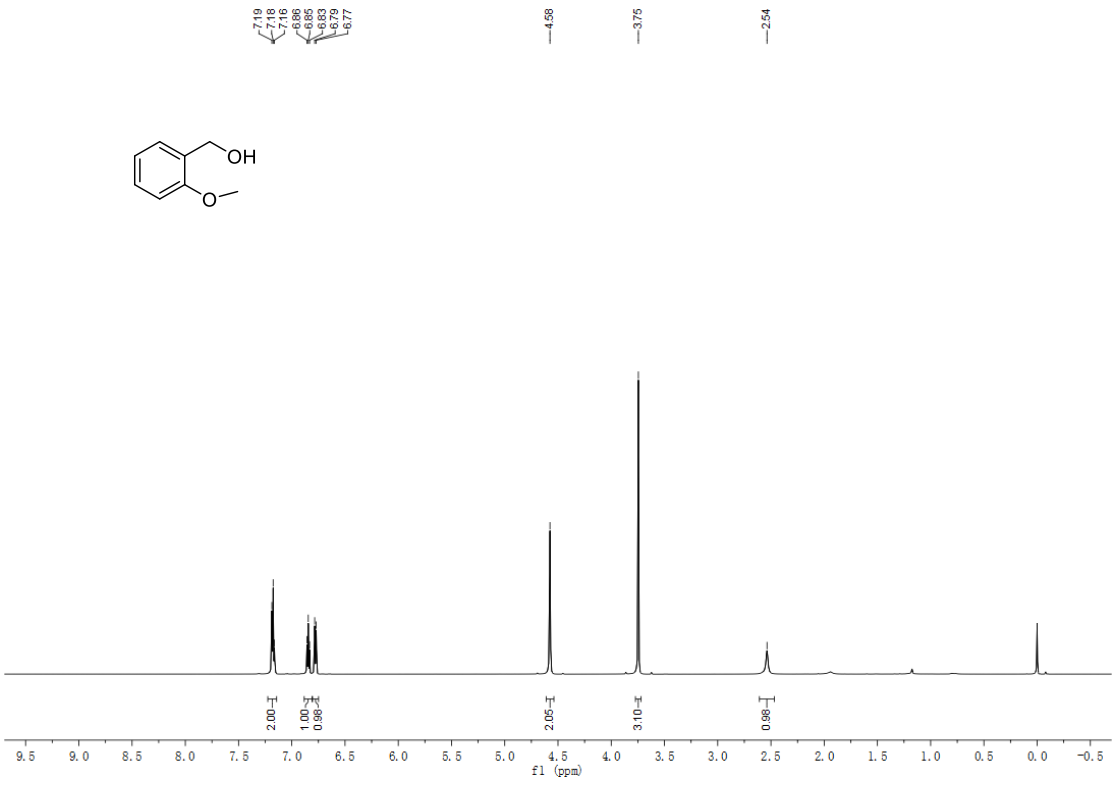


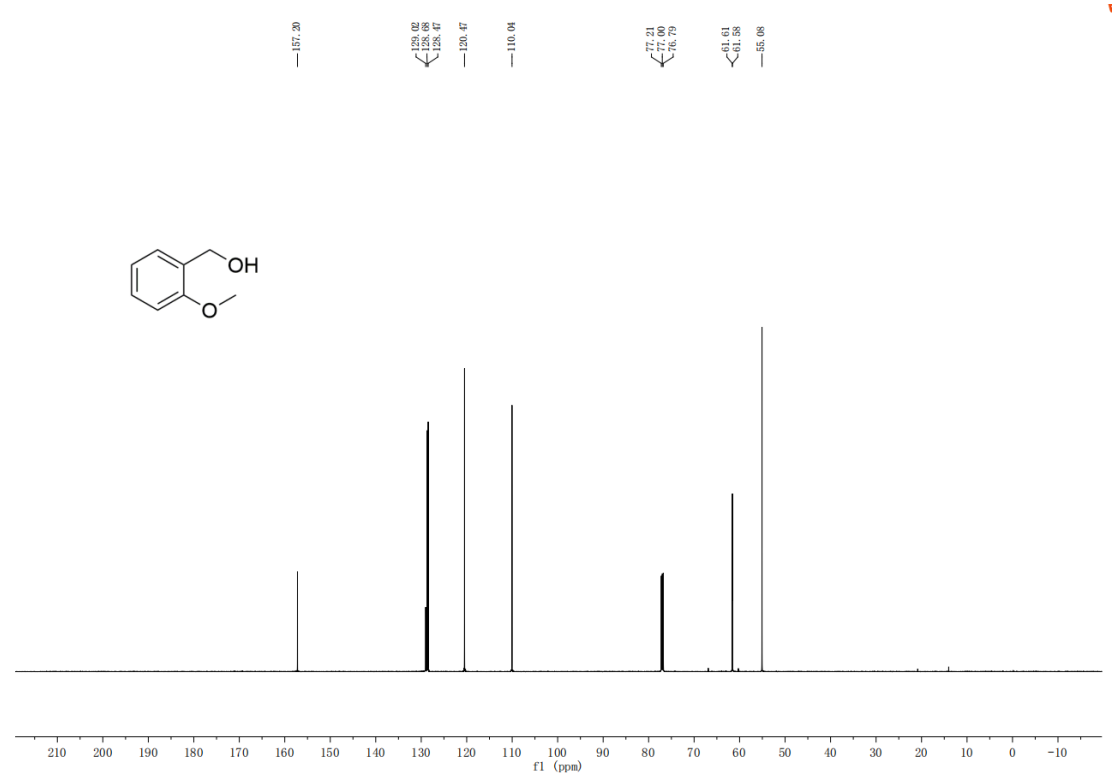
^{1}H NMR spectrum of **14** (600MHz, $CDCl_3$)



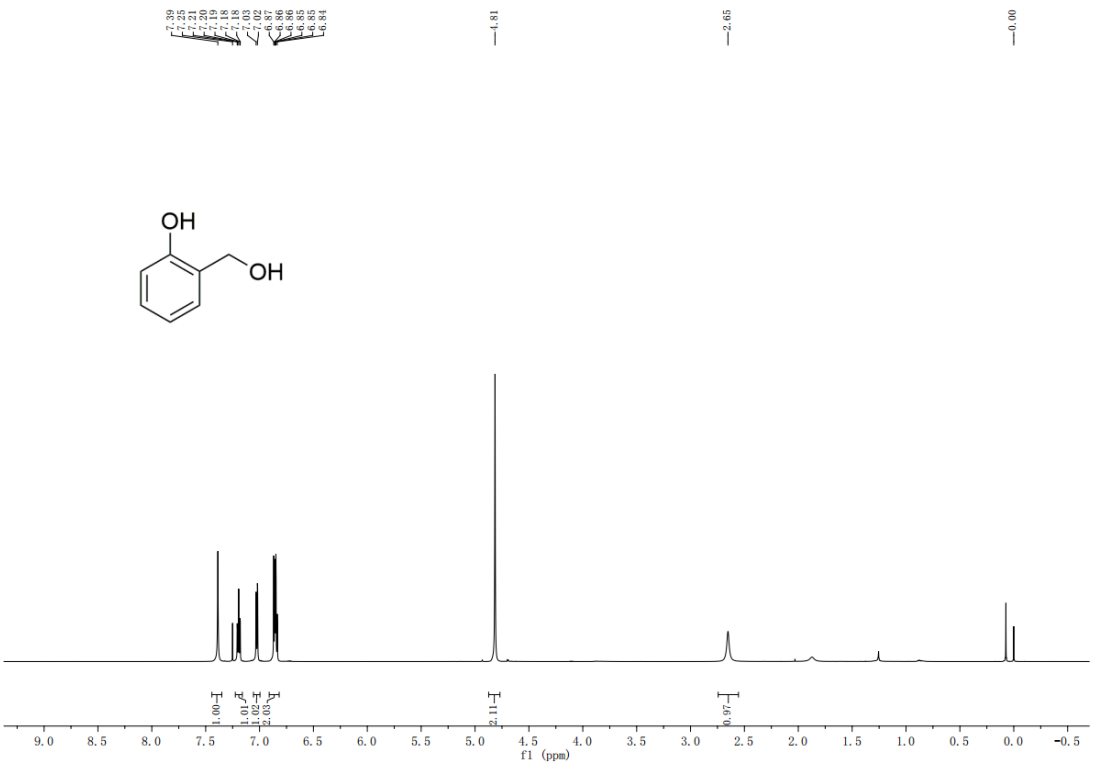
^{13}C NMR spectrum of **14** (151MHz, $CDCl_3$)



^{1}H NMR spectrum of **15** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **15** (151MHz, $CDCl_3$)



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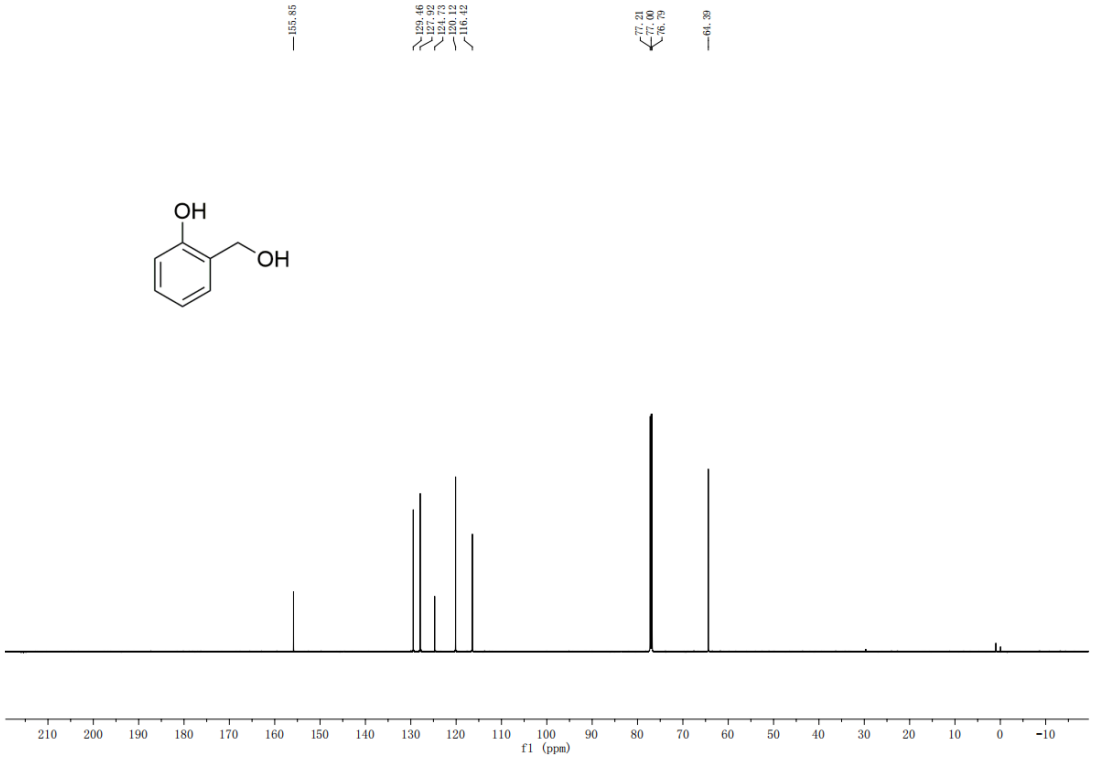
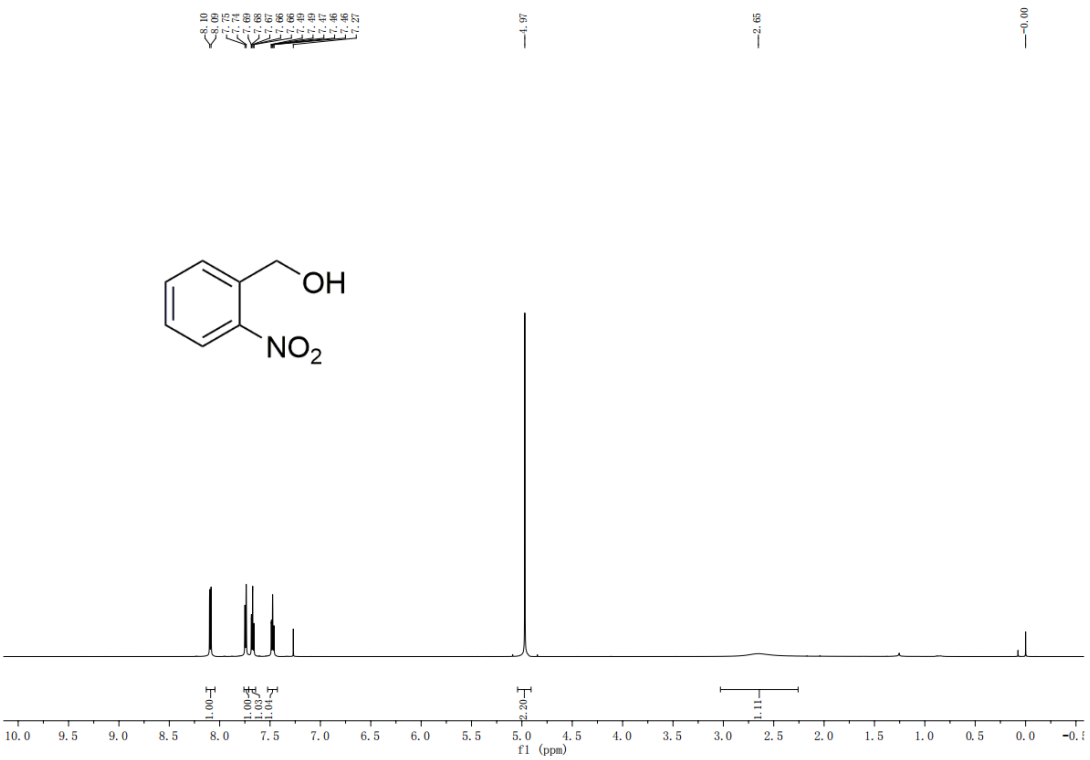
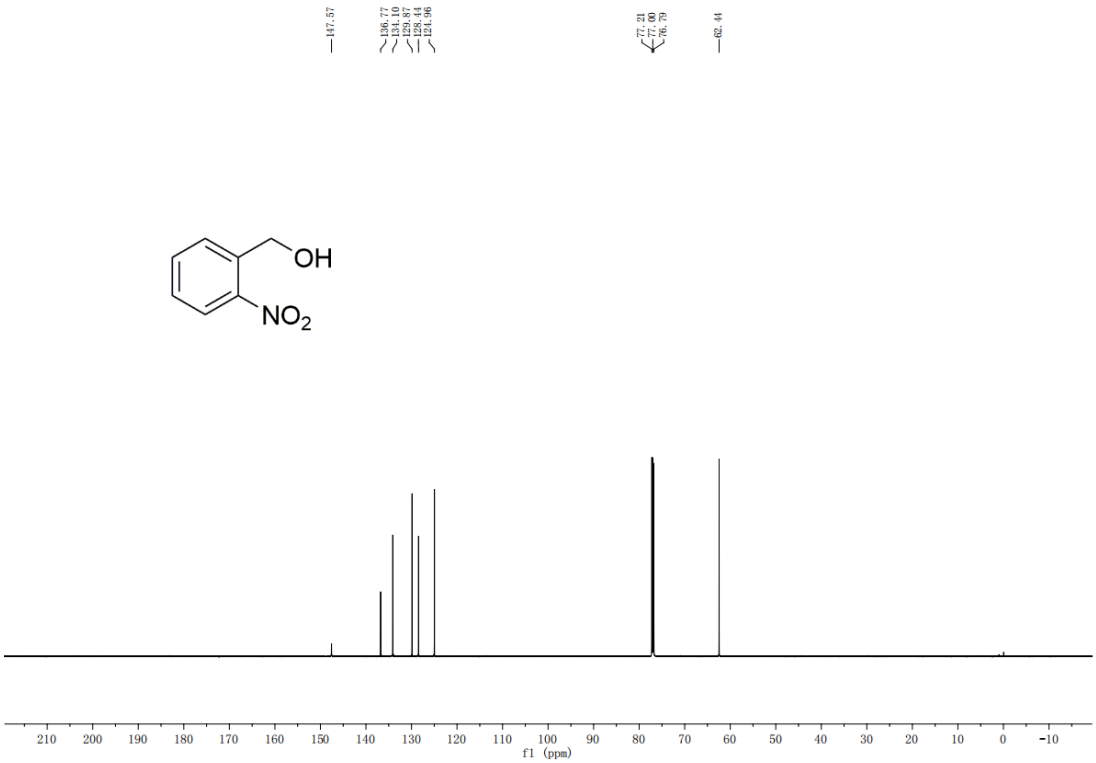


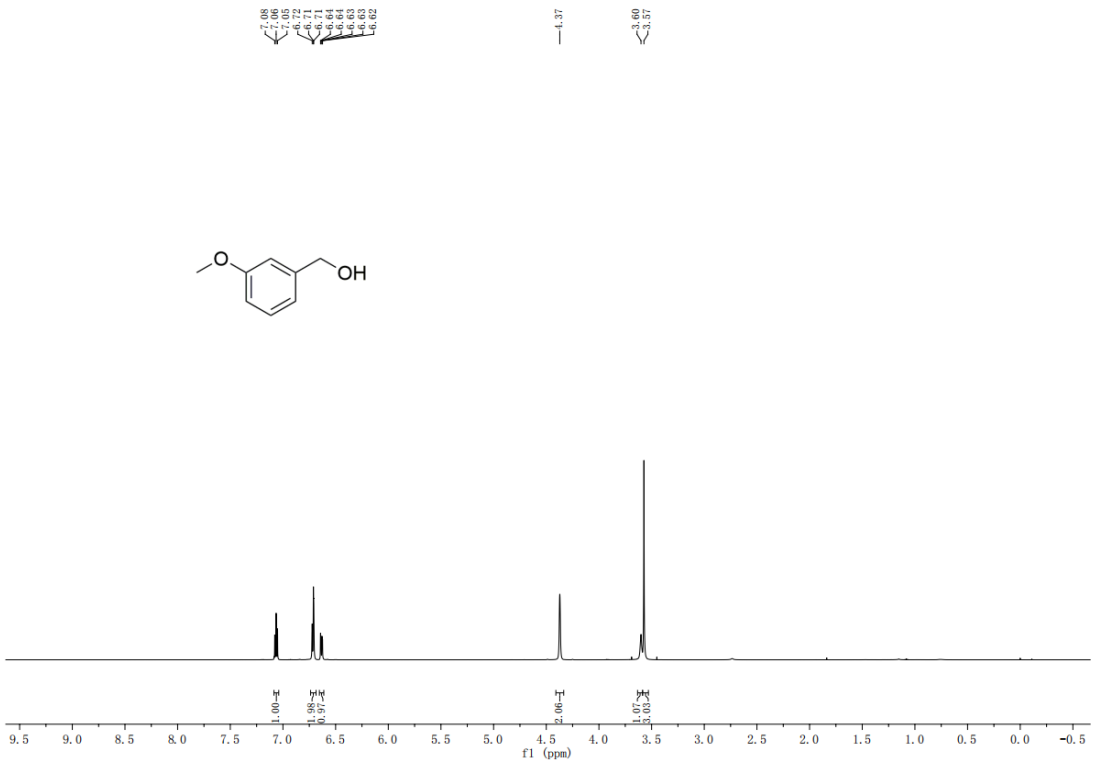
^{13}C NMR spectrum of **16** (151MHz, $CDCl_3$)



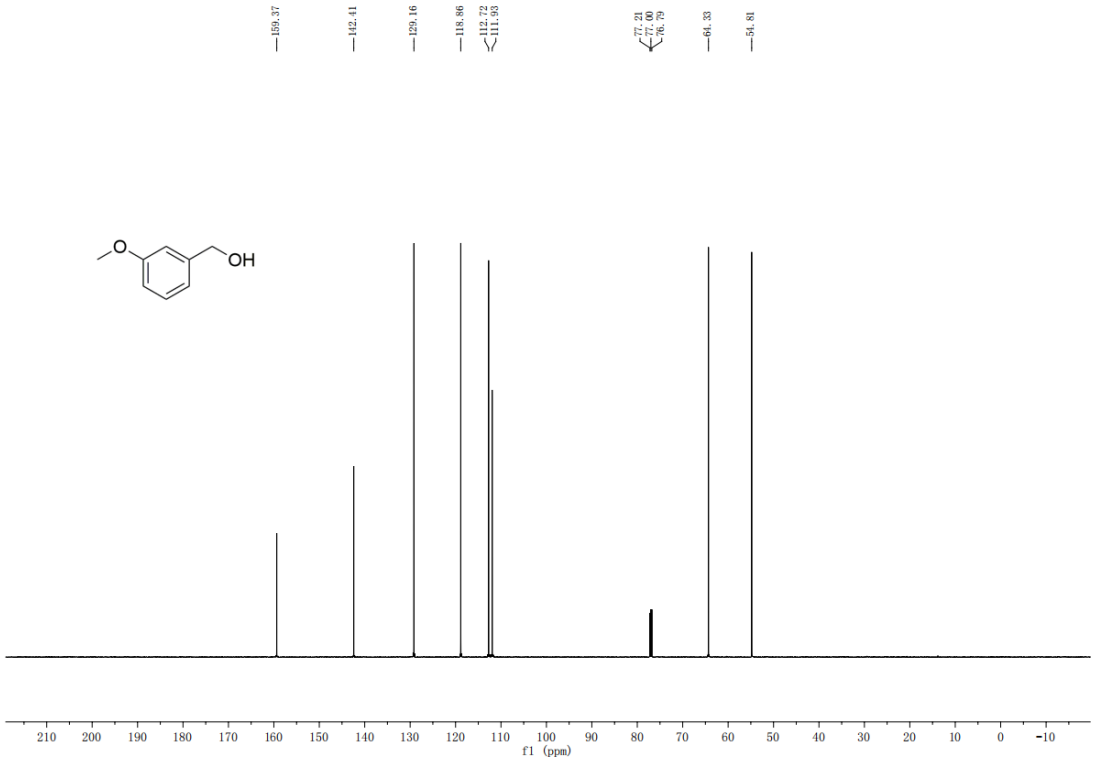
^{1}H NMR spectrum of **17** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **17** (151MHz, $CDCl_3$)



^{1}H NMR spectrum of **18** (600MHz, $CDCl_3$)



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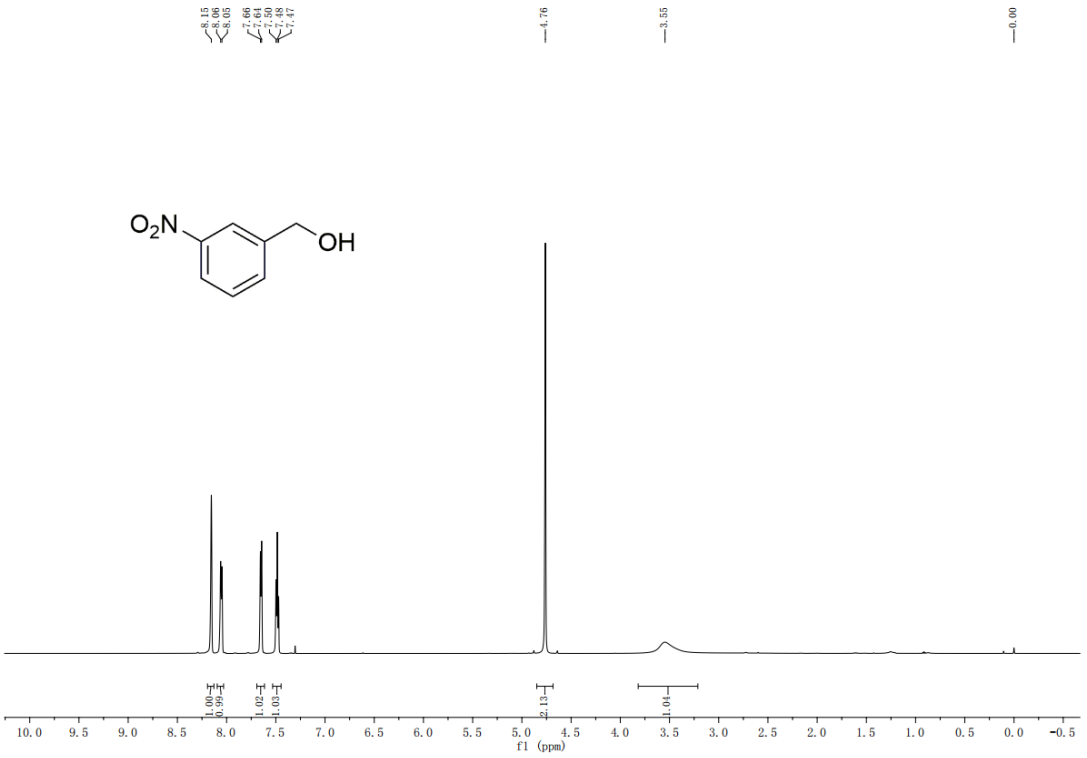

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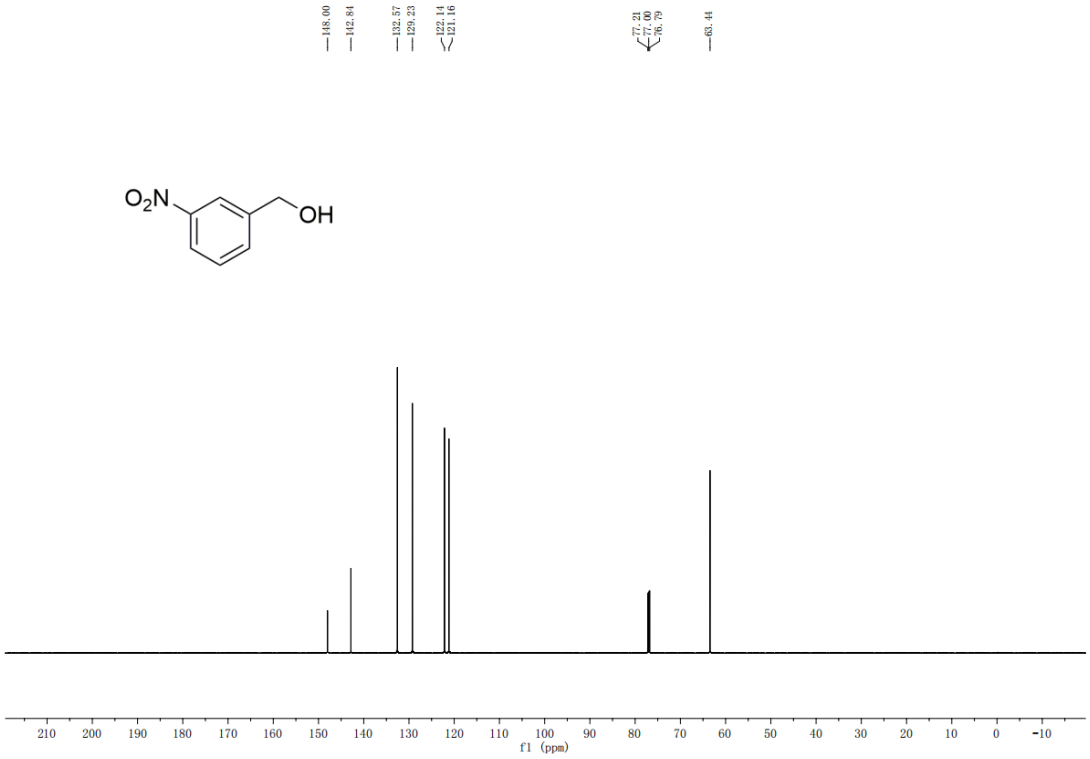

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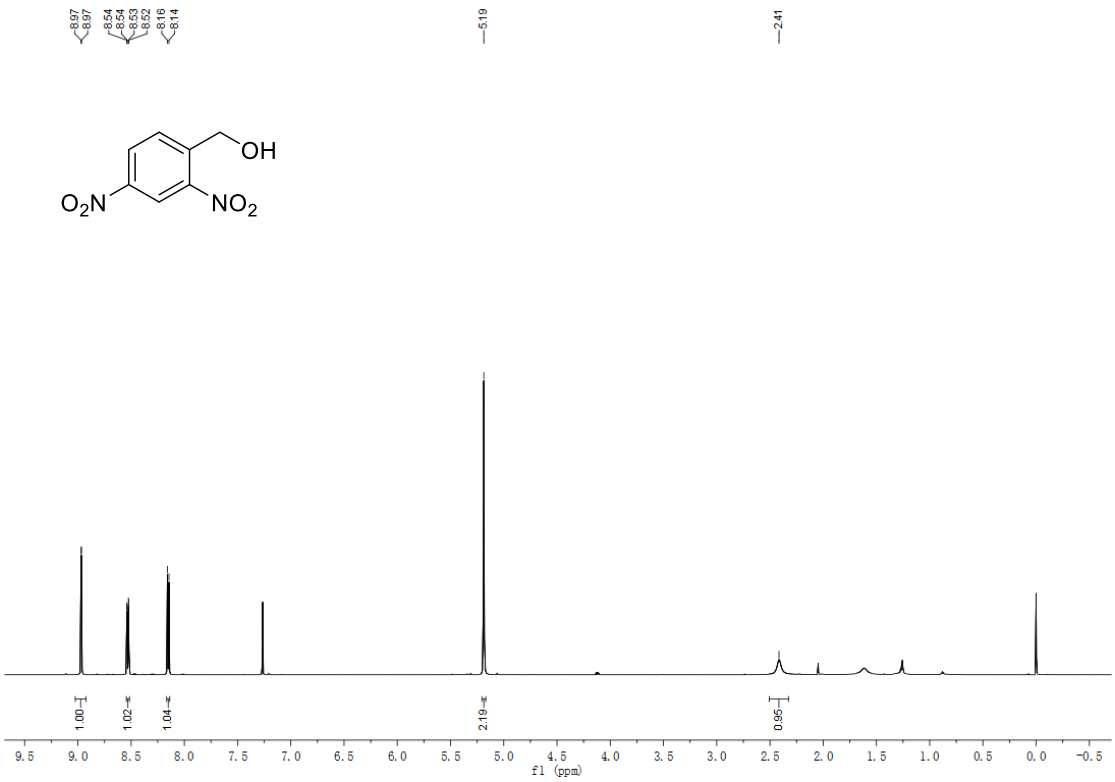

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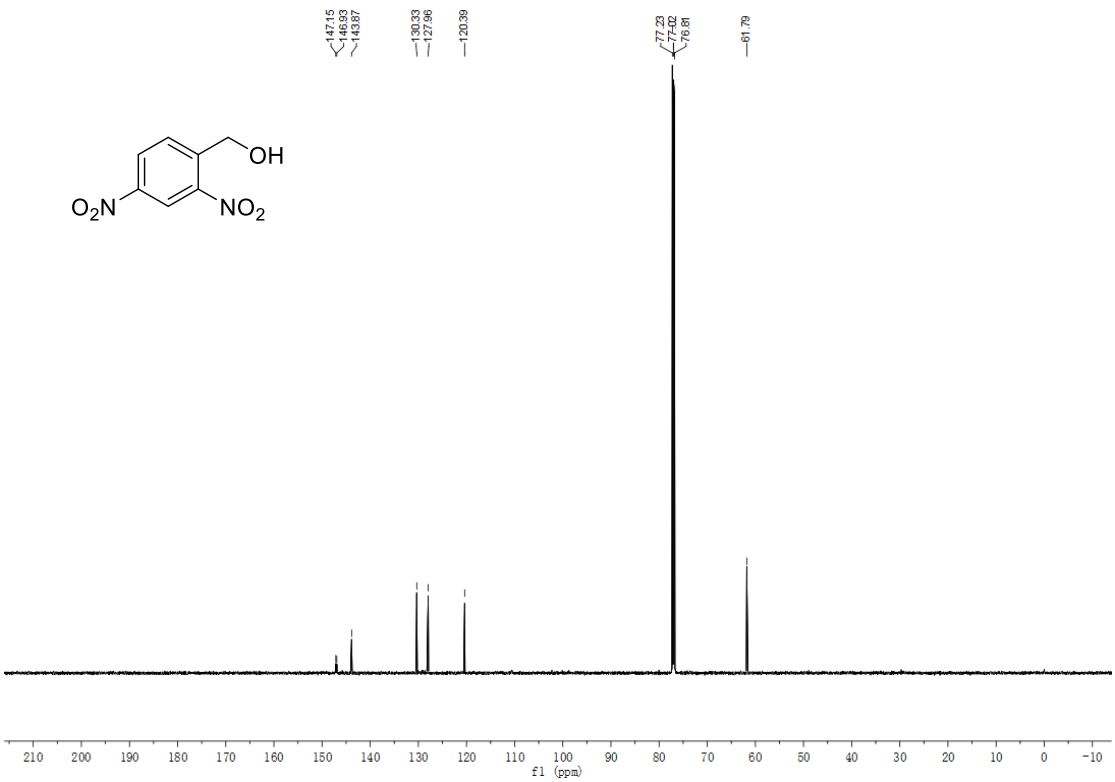
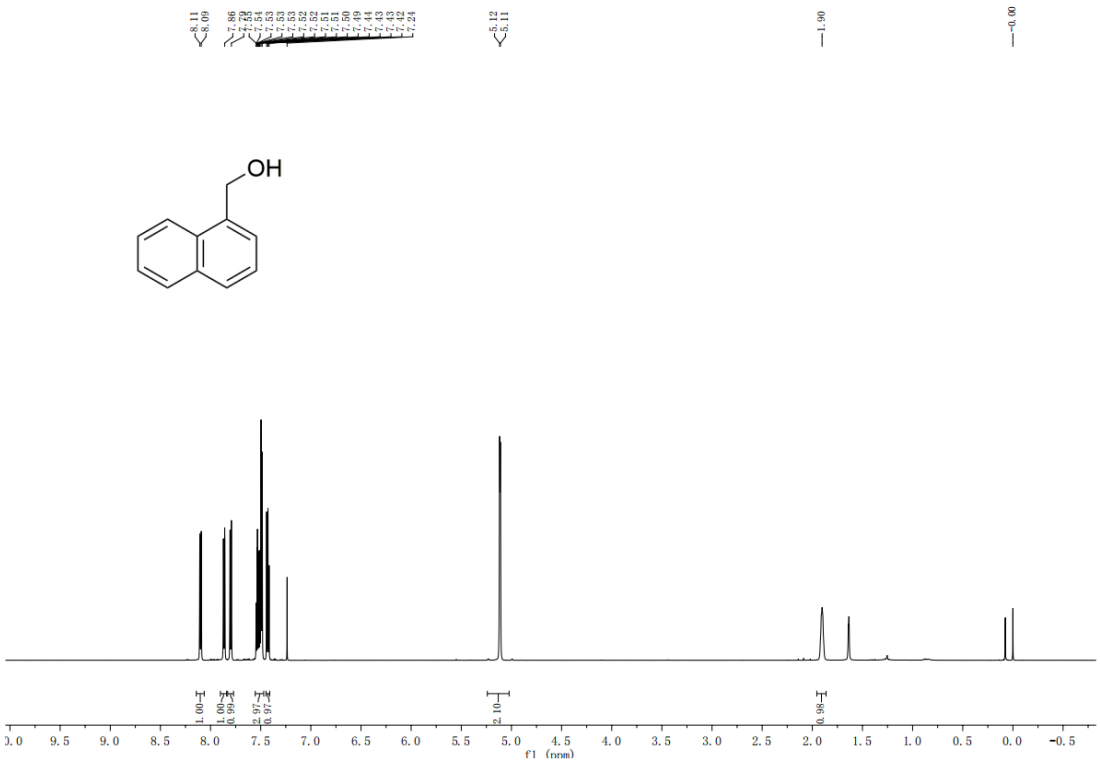
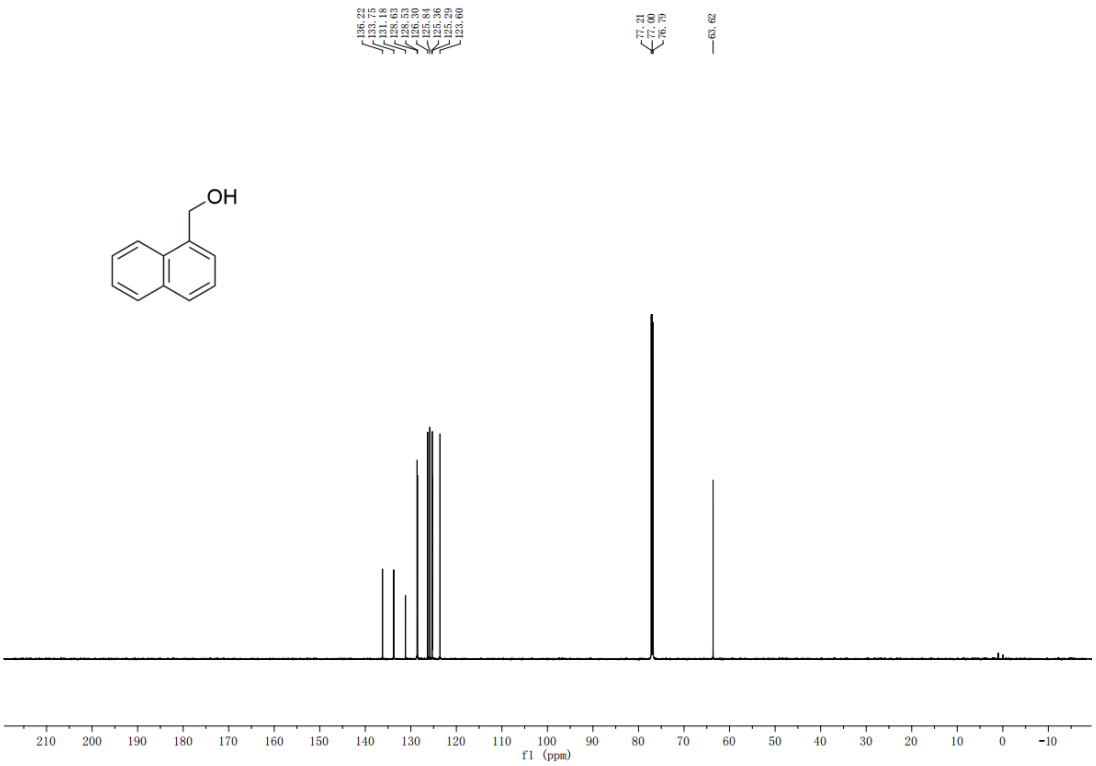


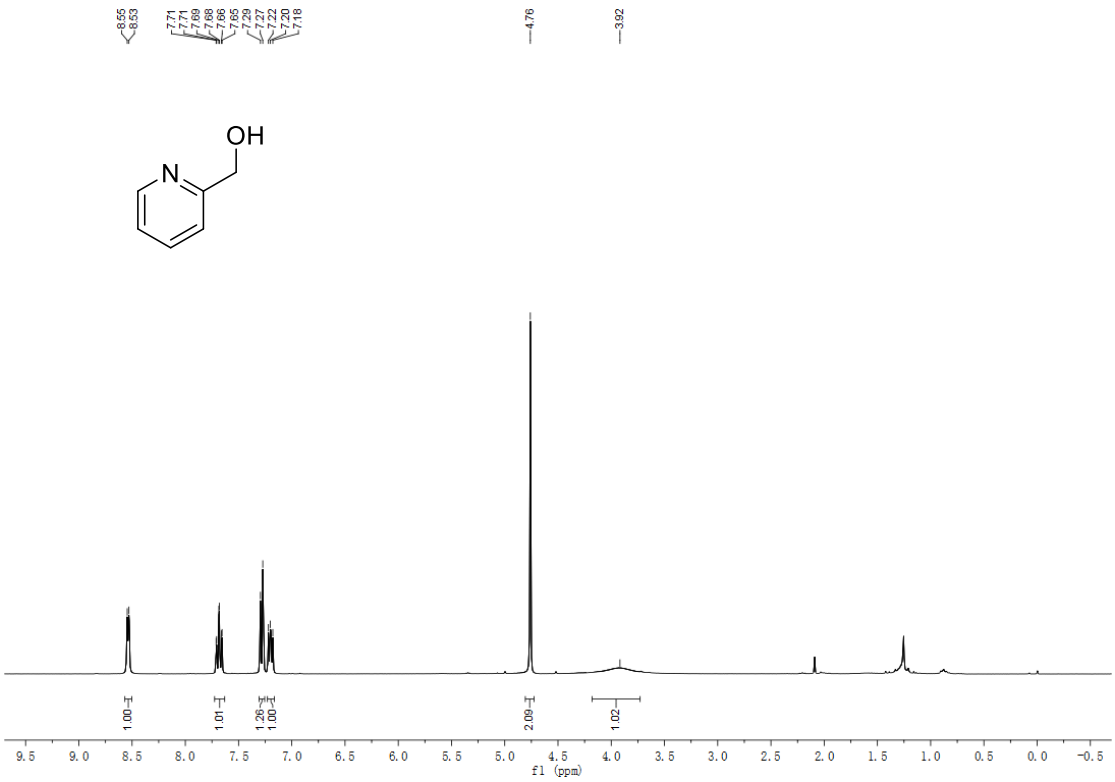
^{13}C NMR spectrum of **20** (151MHz, $CDCl_3$)



^{1}H NMR spectrum of **21** (600MHz, $CDCl_3$)



^{13}C NMR spectrum of **21** (151MHz, $CDCl_3$)



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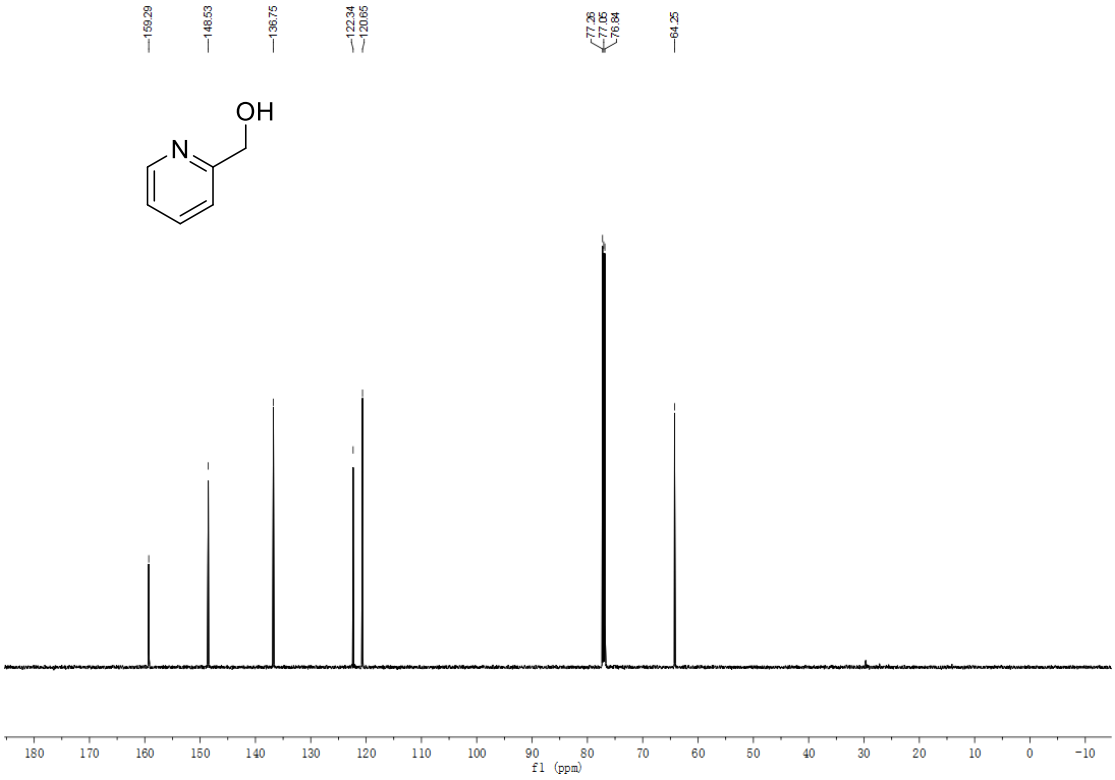

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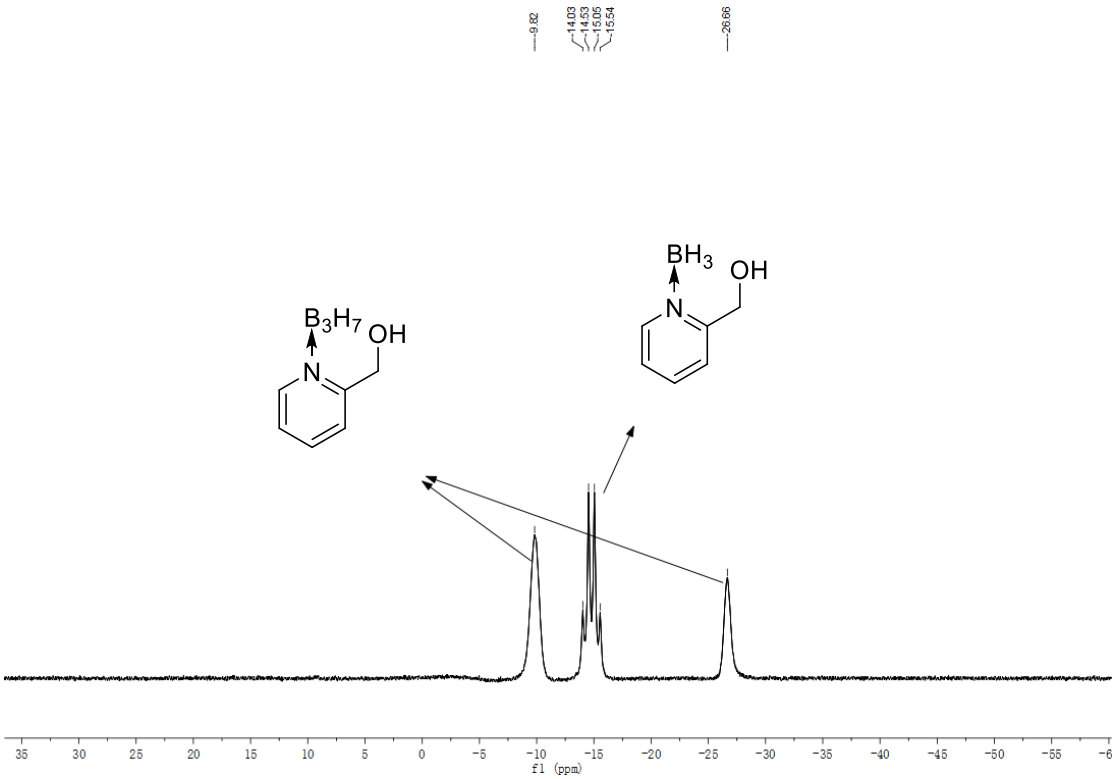
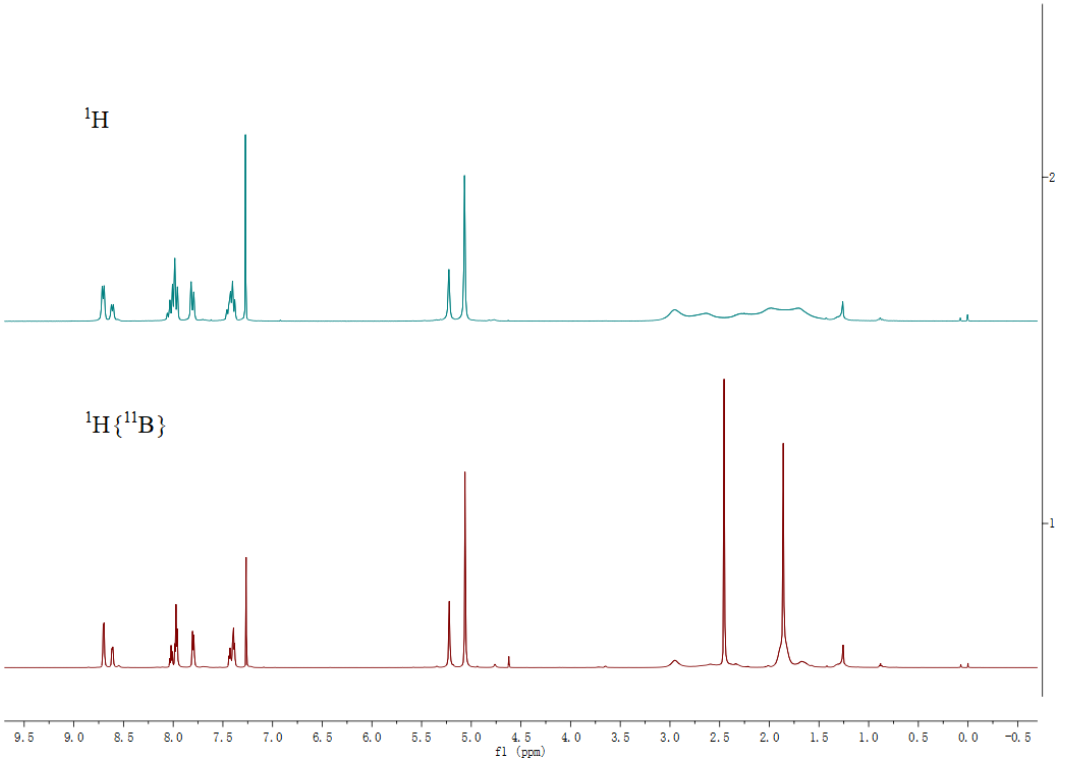
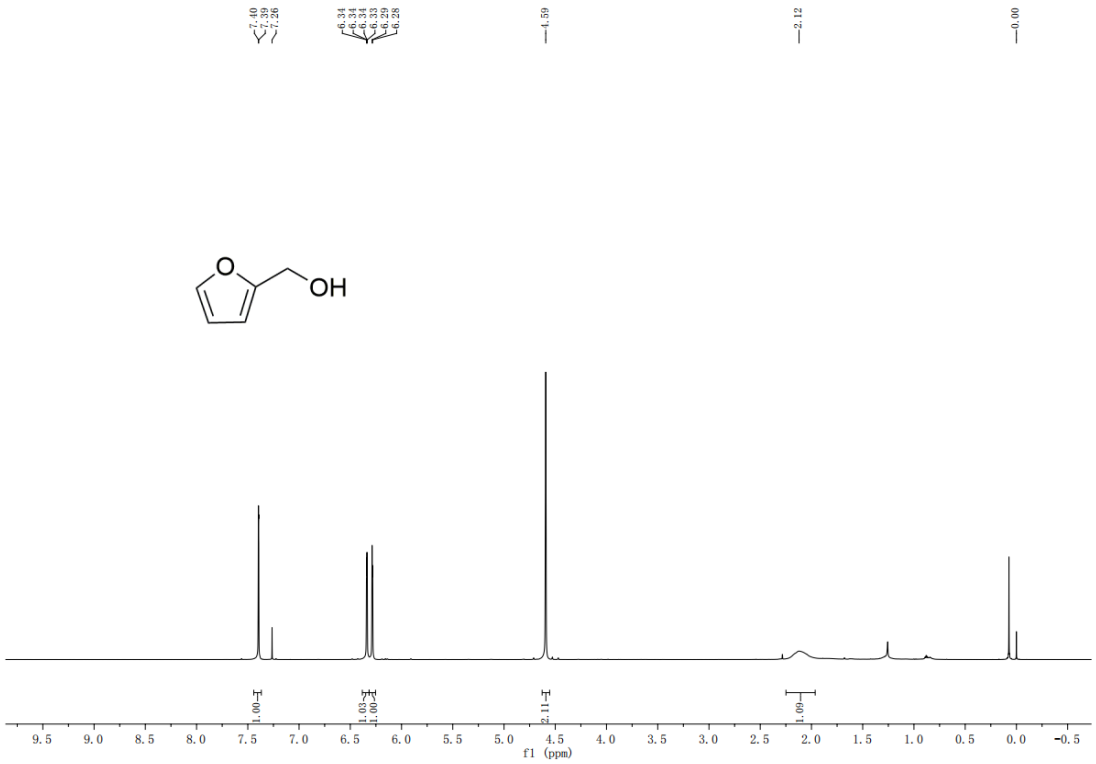


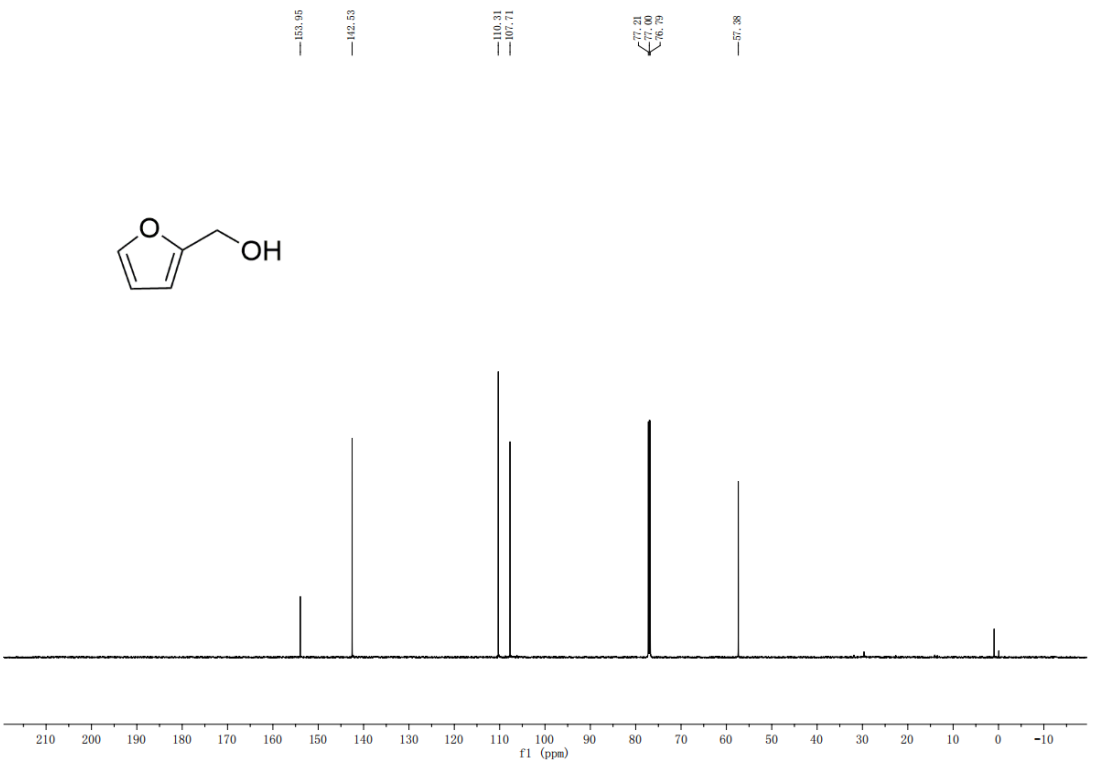
^{11}B NMR spectrum of pyridin-2-ylmethanol borane complexes (600MHz, $CDCl_3$)



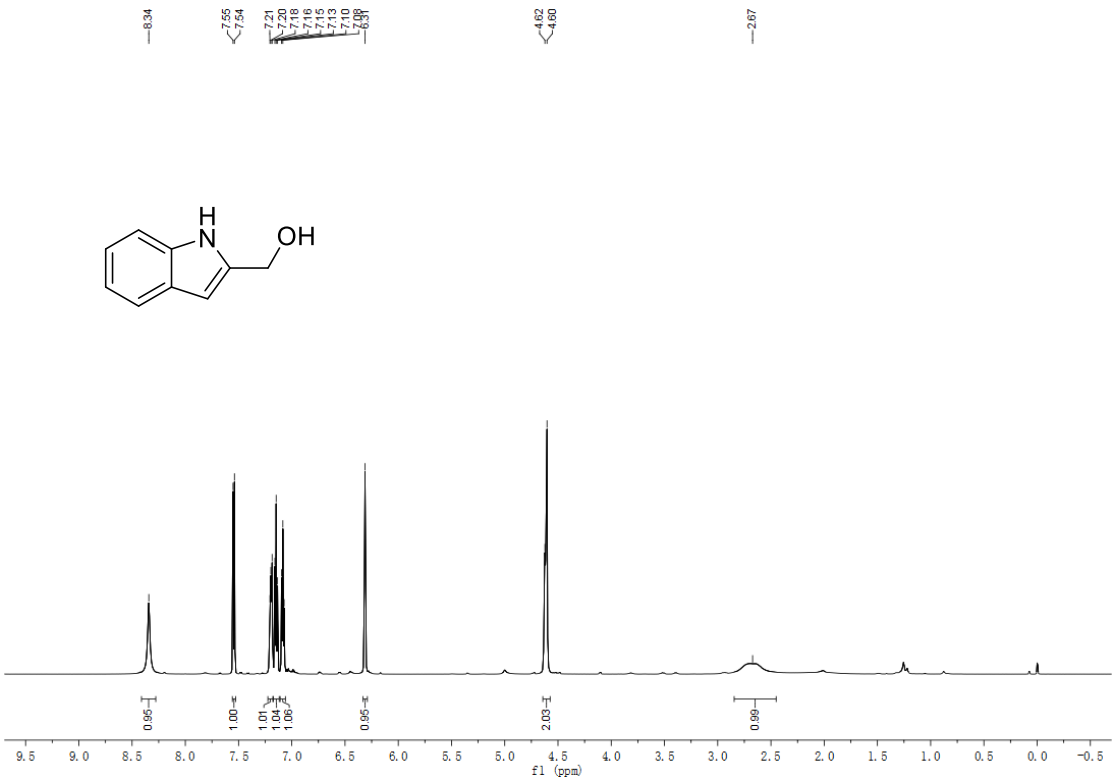
^{1}H NMR and ^{1}H{^{11}B} NMR spectrum of pyridin-2-ylmethanol borane complexes (600MHz, $CDCl_3$)



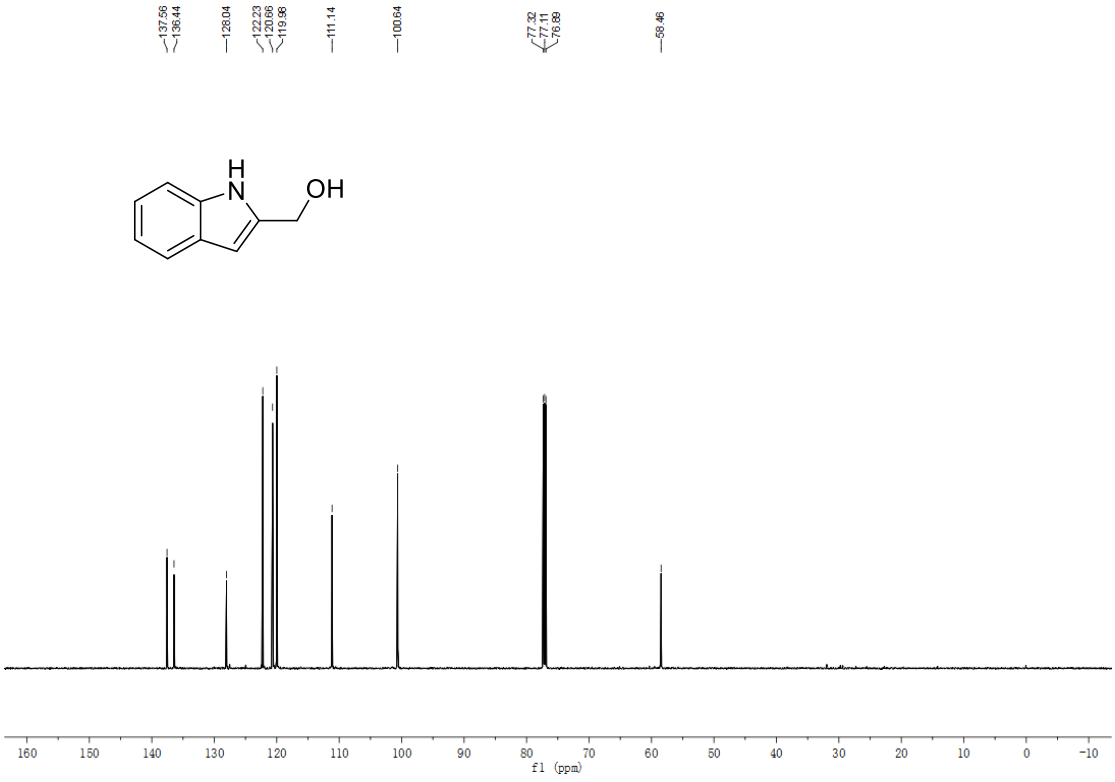
^{1}H NMR spectrum of **23** (600MHz, $CDCl_3$)



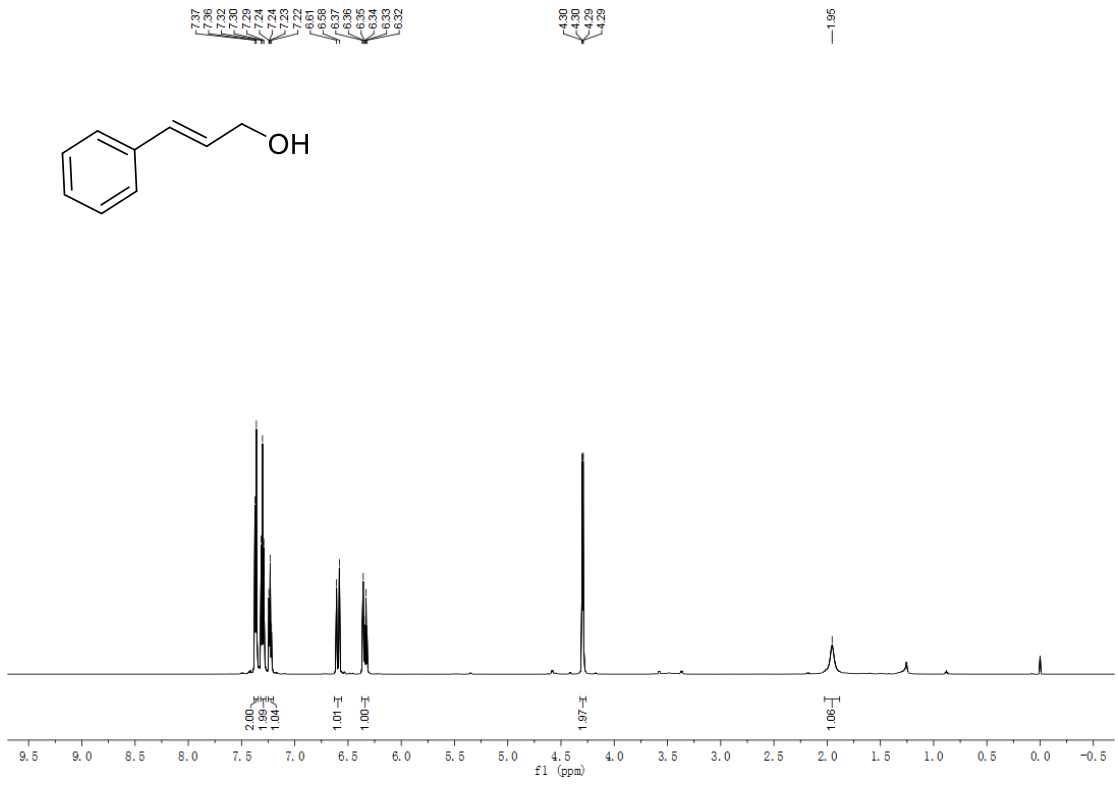
^{13}C NMR spectrum of **23** (151MHz, $CDCl_3$)



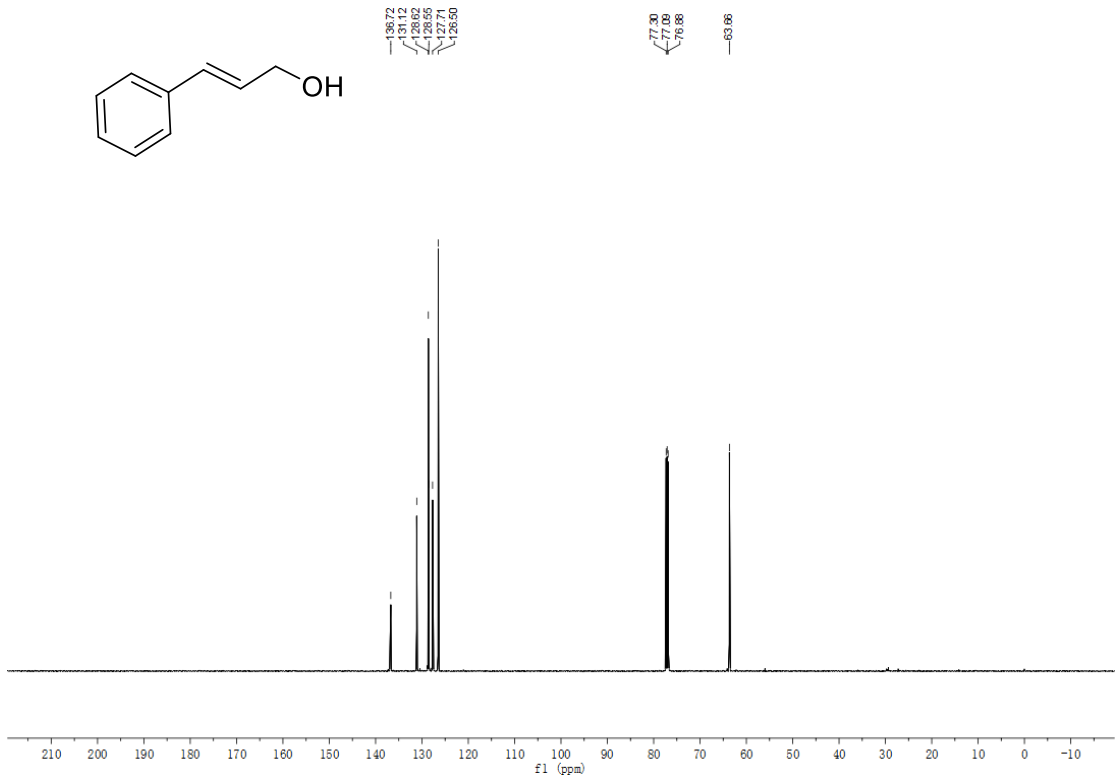
^{1}H NMR spectrum of **24** (600MHz, $CDCl_3$)



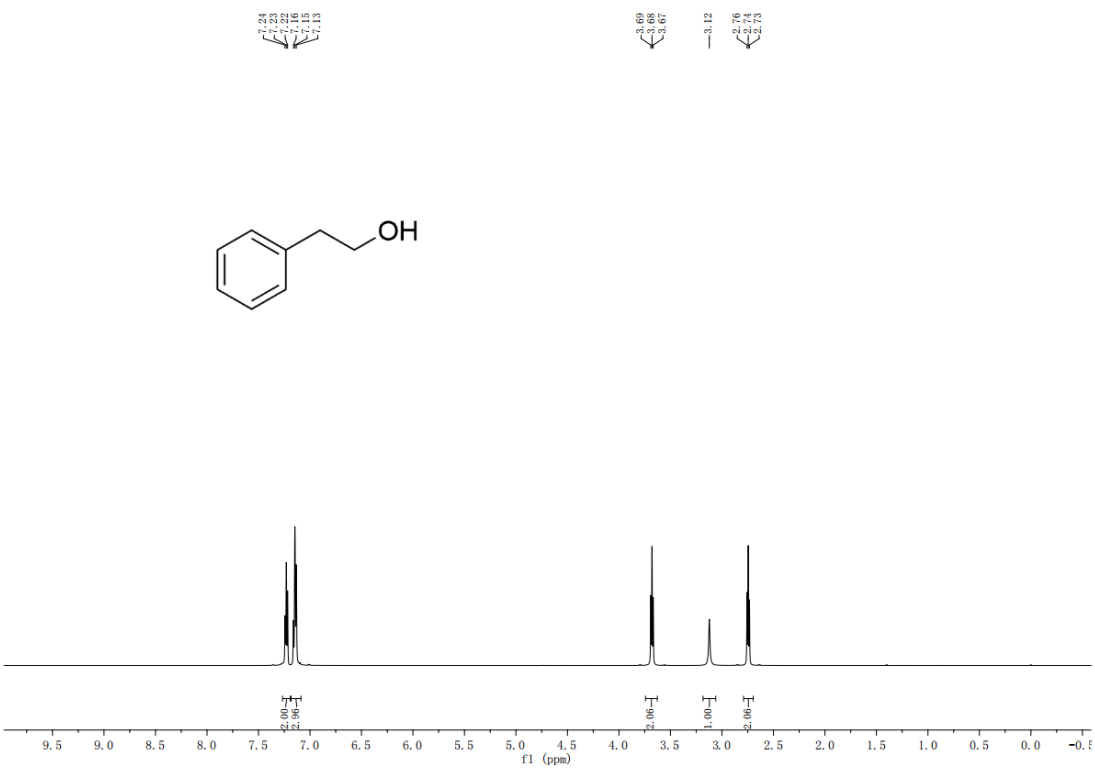
^{13}C NMR spectrum of **24** (151MHz, $CDCl_3$)



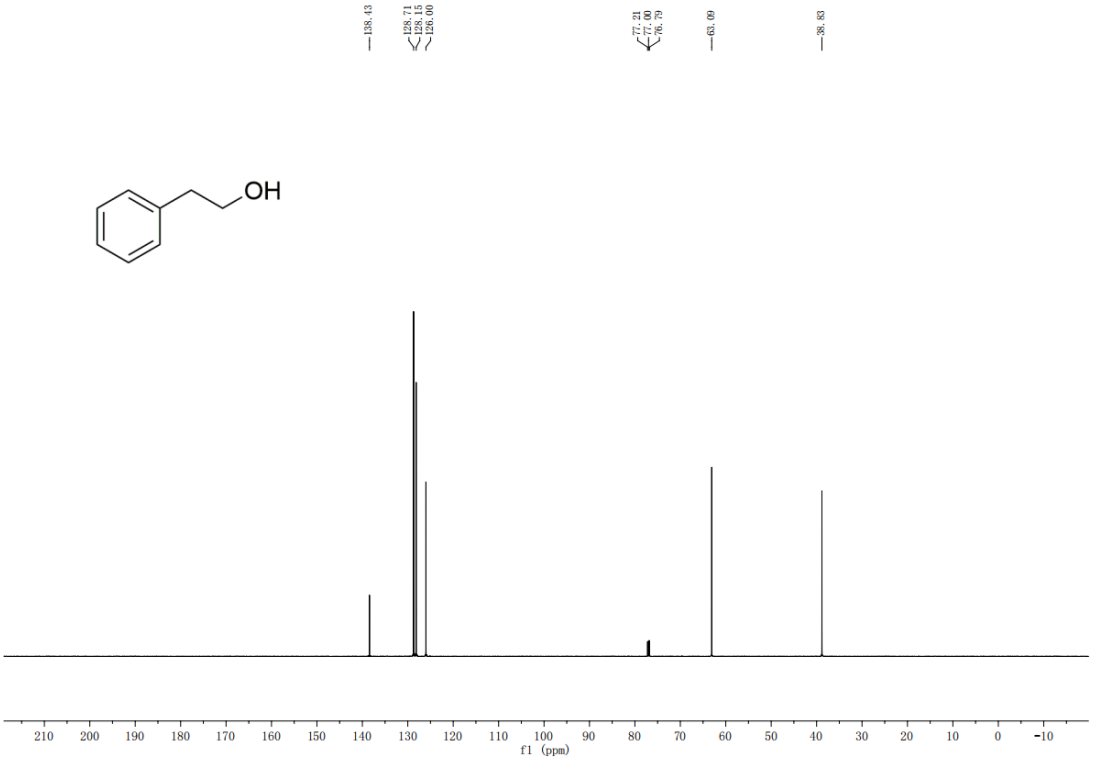
^{1}H NMR spectrum of **25** (600MHz, $CDCl_3$)



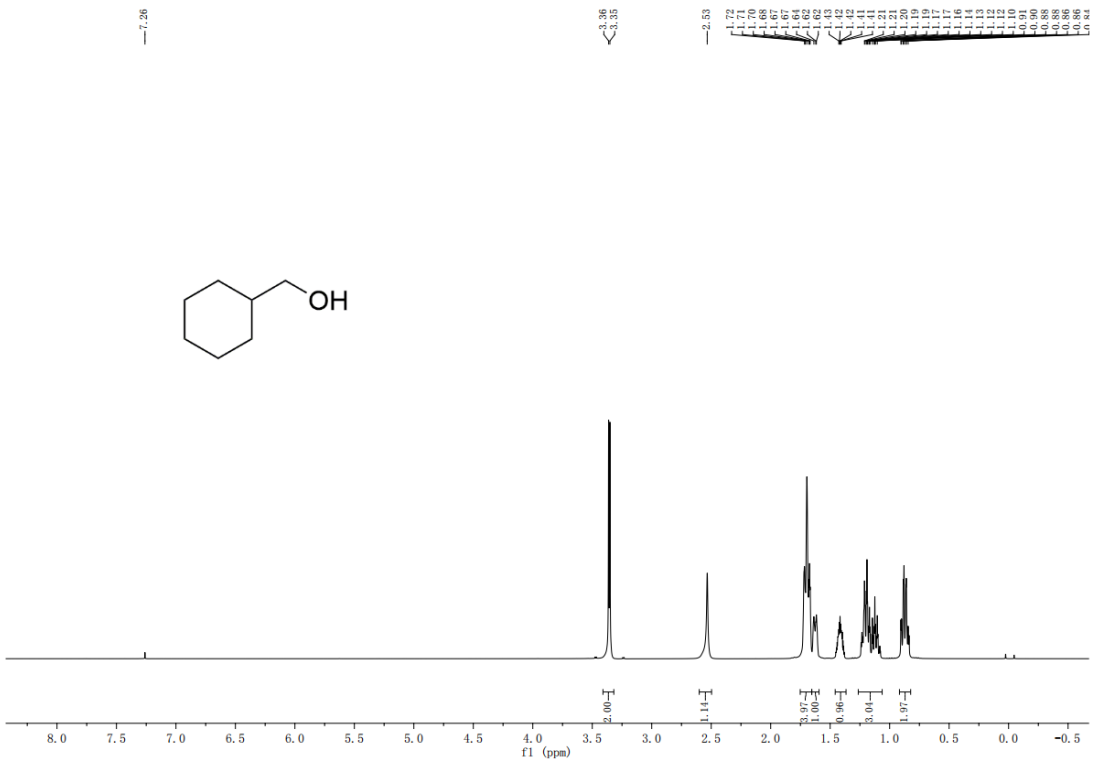
^{13}C NMR spectrum of **25** (151MHz, $CDCl_3$)



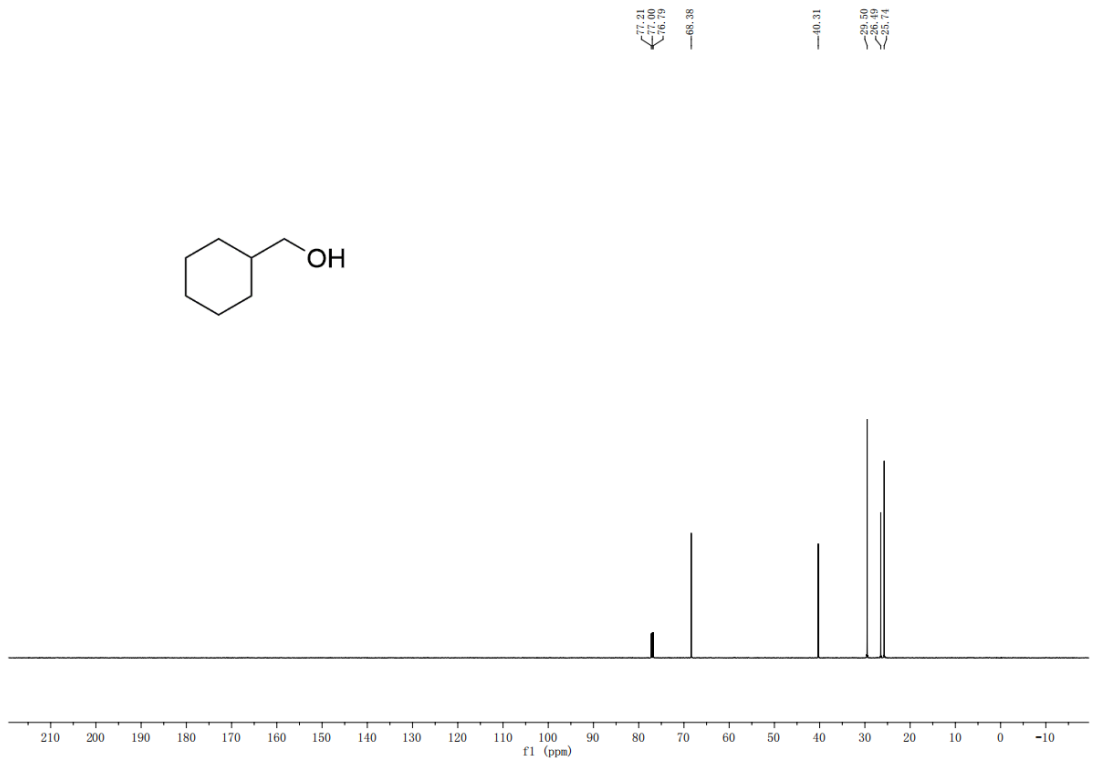
^{1}H NMR spectrum of **26** (600MHz, $CDCl_3$)



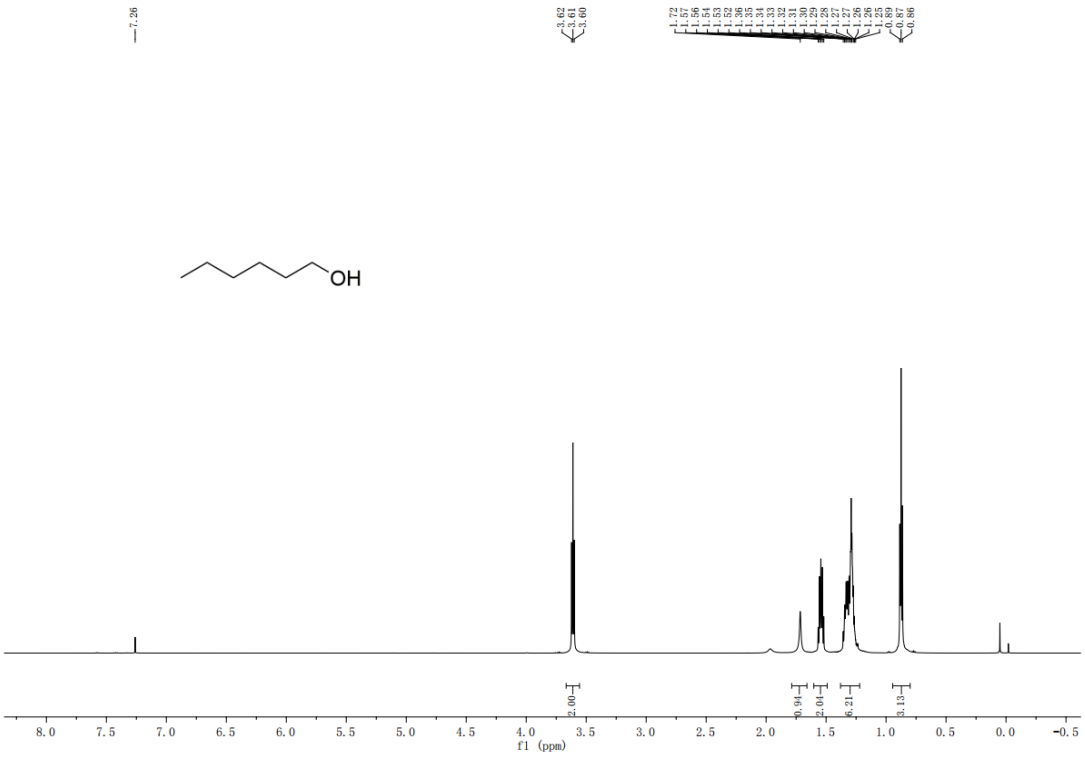
^{13}C NMR spectrum of **26** (151MHz, $CDCl_3$)



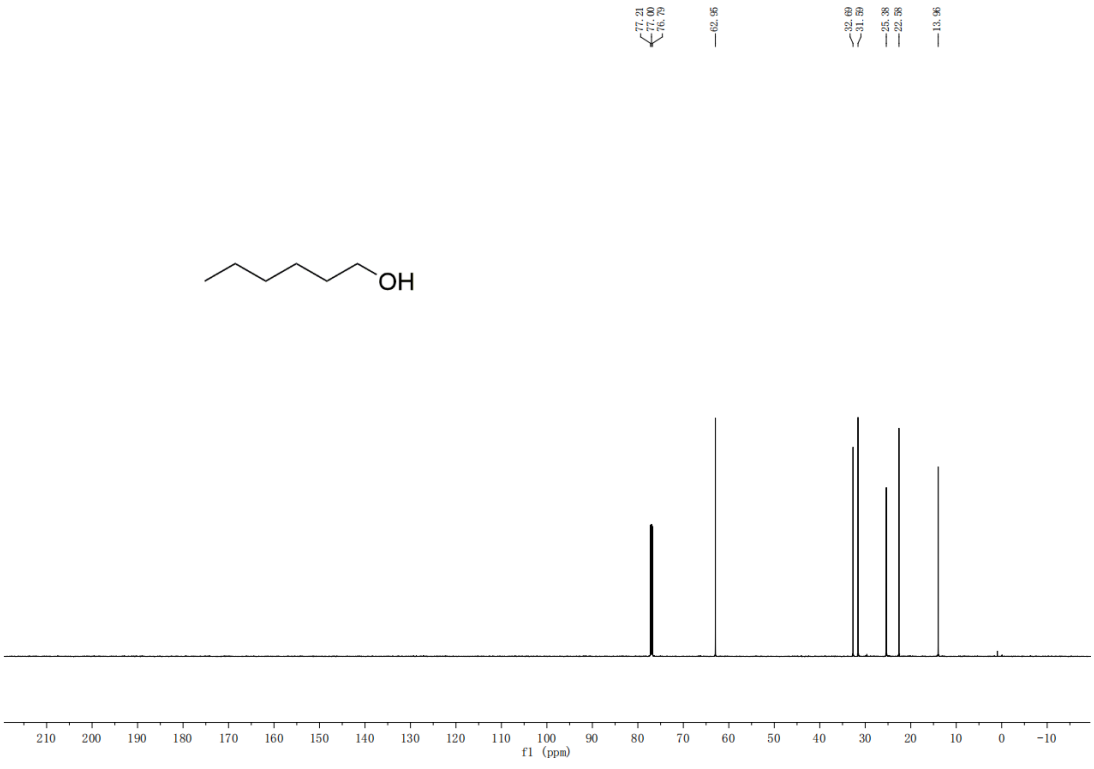
^{1}H NMR spectrum of **27** (600MHz, CD_3Cl)



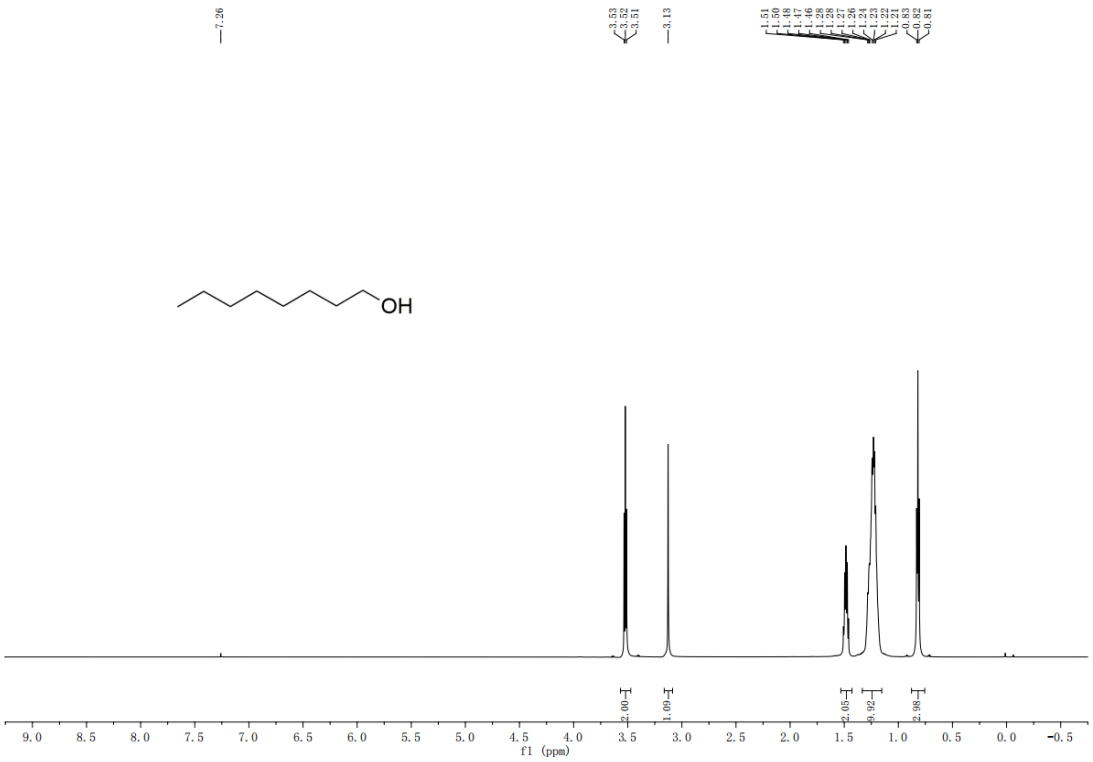
^{13}C NMR spectrum of **27** (151MHz, $CDCl_3$)



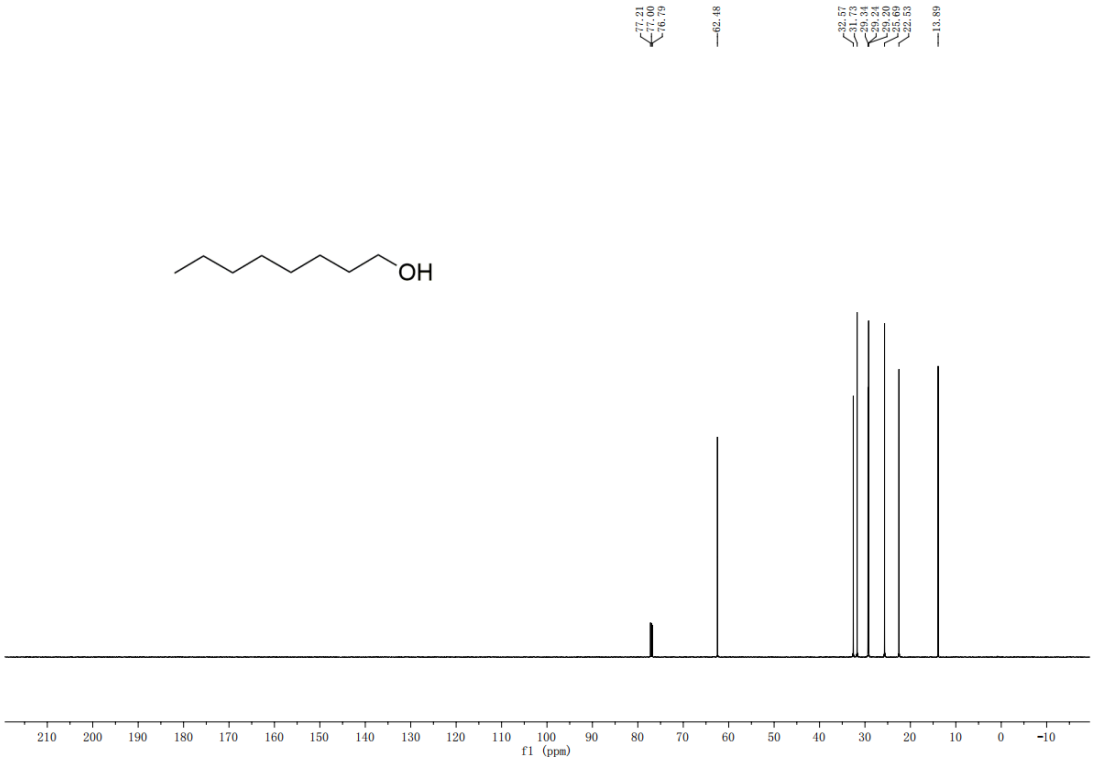
^{1}H NMR spectrum of **28** (600MHz, CD_3Cl)



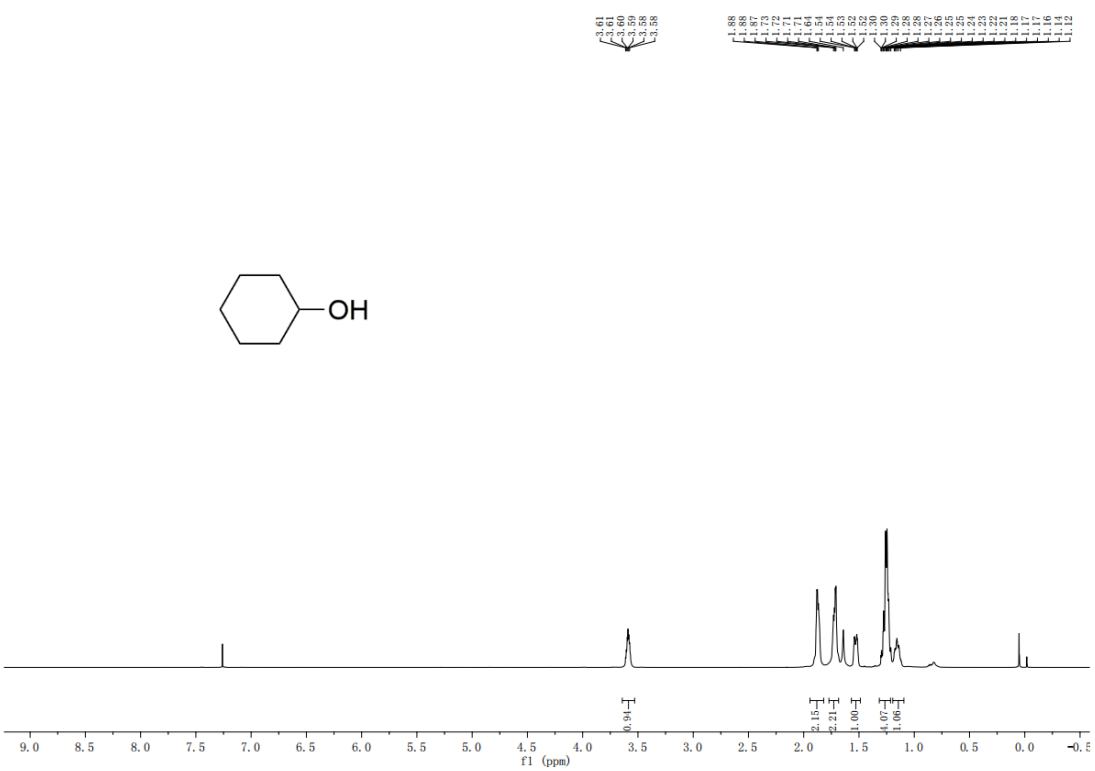
^{13}C NMR spectrum of **28** (151MHz, $CDCl_3$)



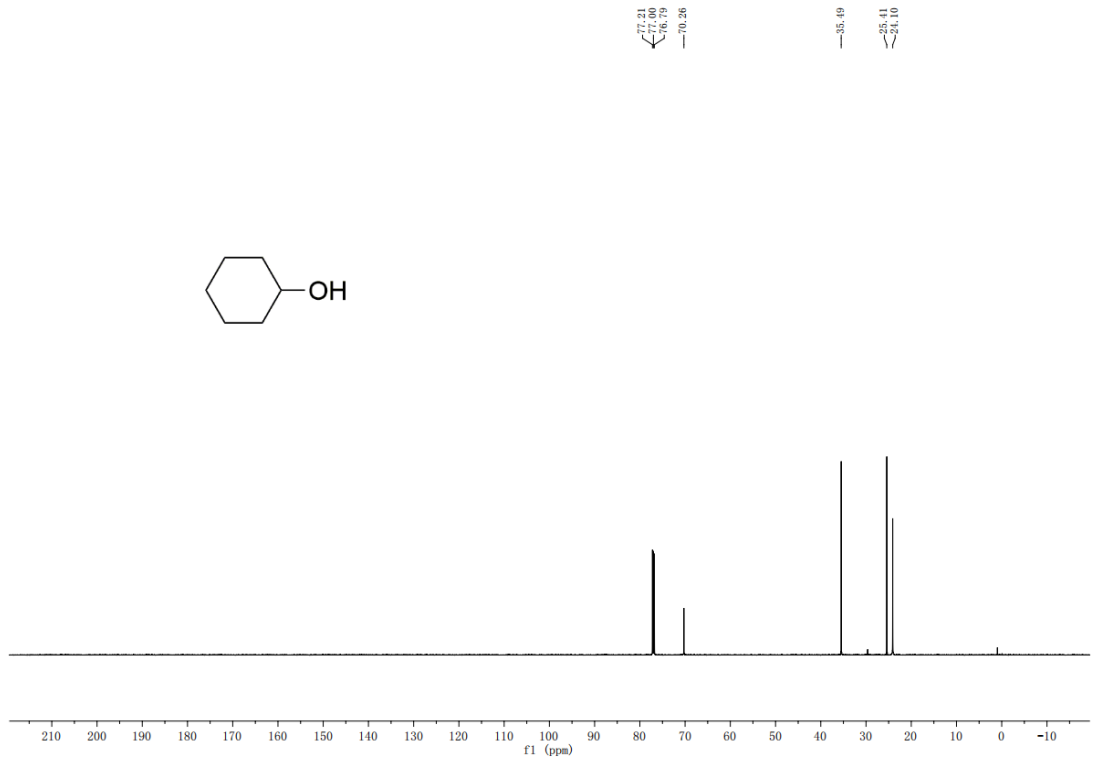
^{1}H NMR spectrum of **29** (600MHz, $CDCl_3$)



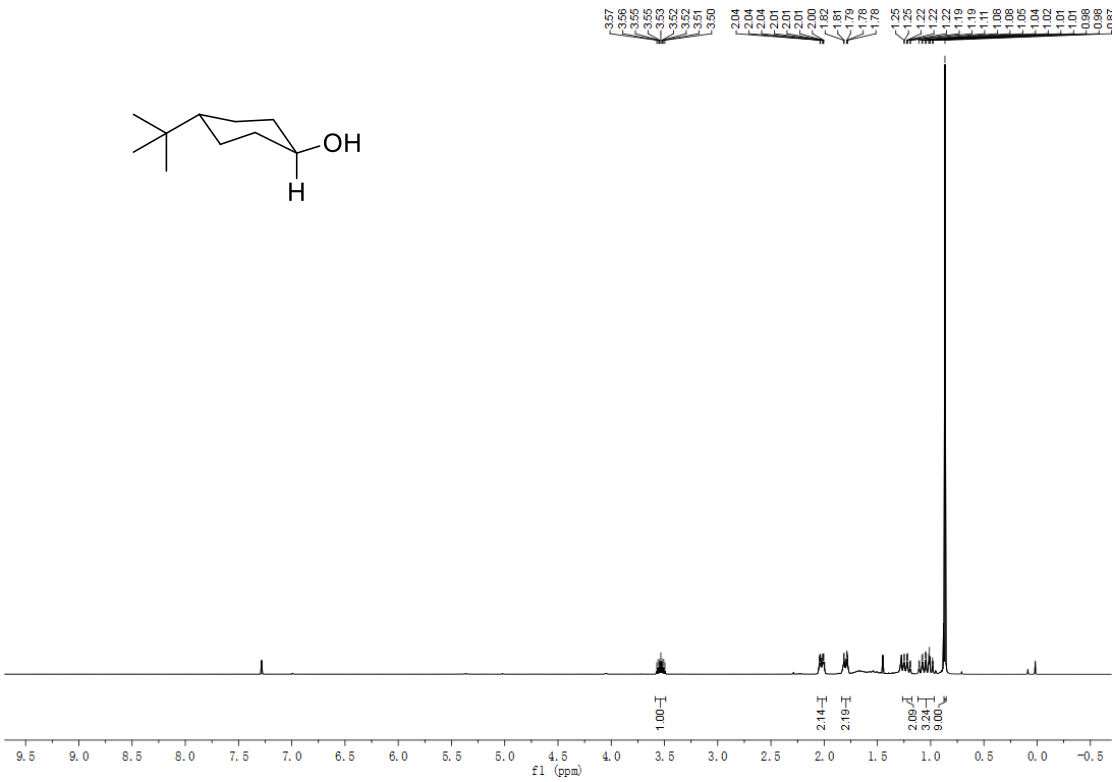
^{13}C NMR spectrum of **29** (151MHz, $CDCl_3$)



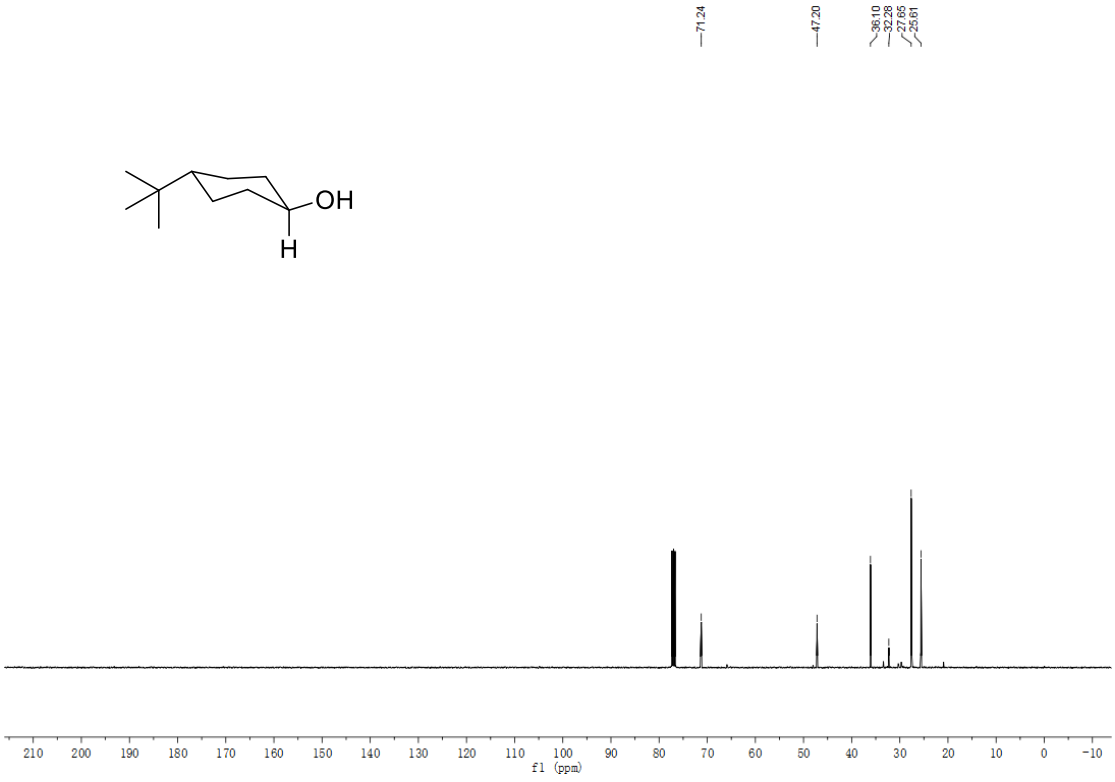
^{1}H NMR spectrum of **30** (600MHz, $CDCl_3$)



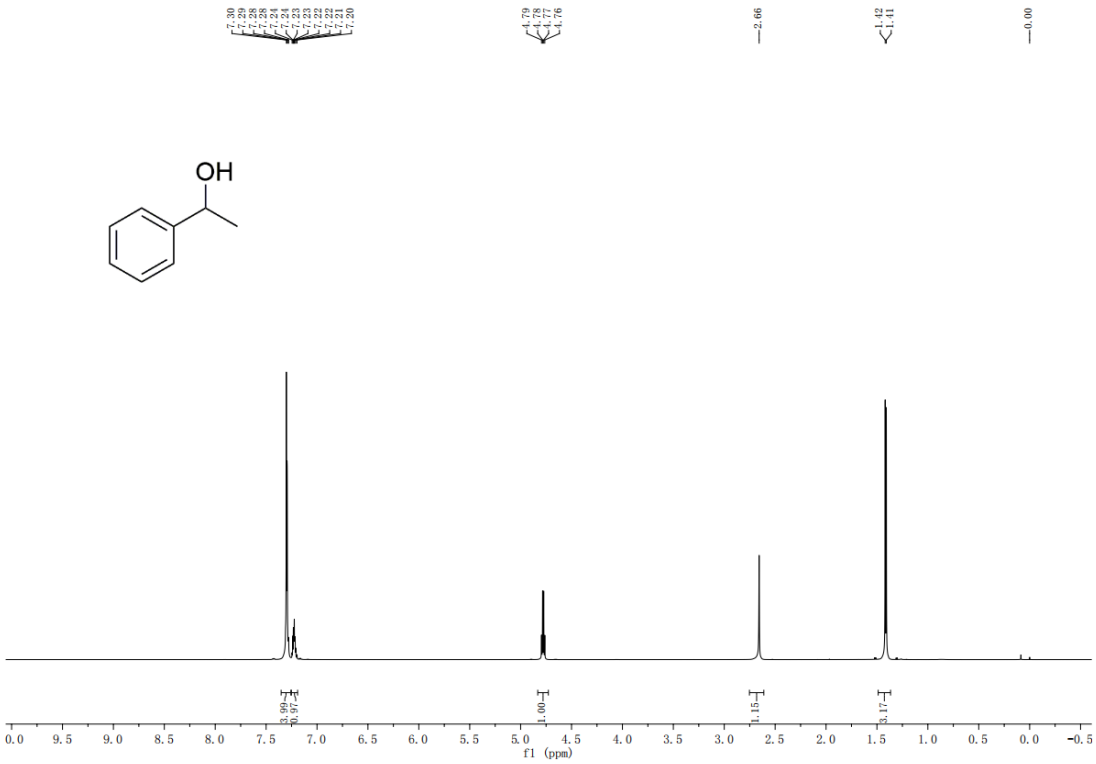
^{13}C NMR spectrum of **30** (151MHz, $CDCl_3$)



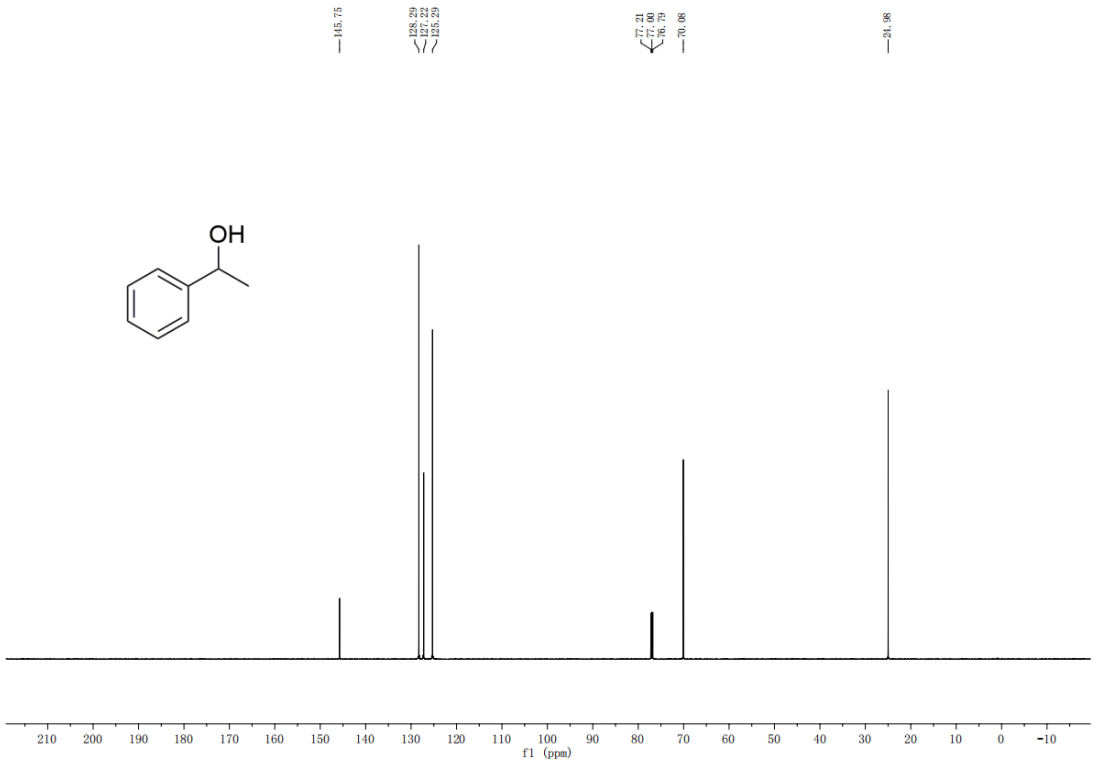
^{1}H NMR spectrum of **31** (400MHz, $CDCl_3$)



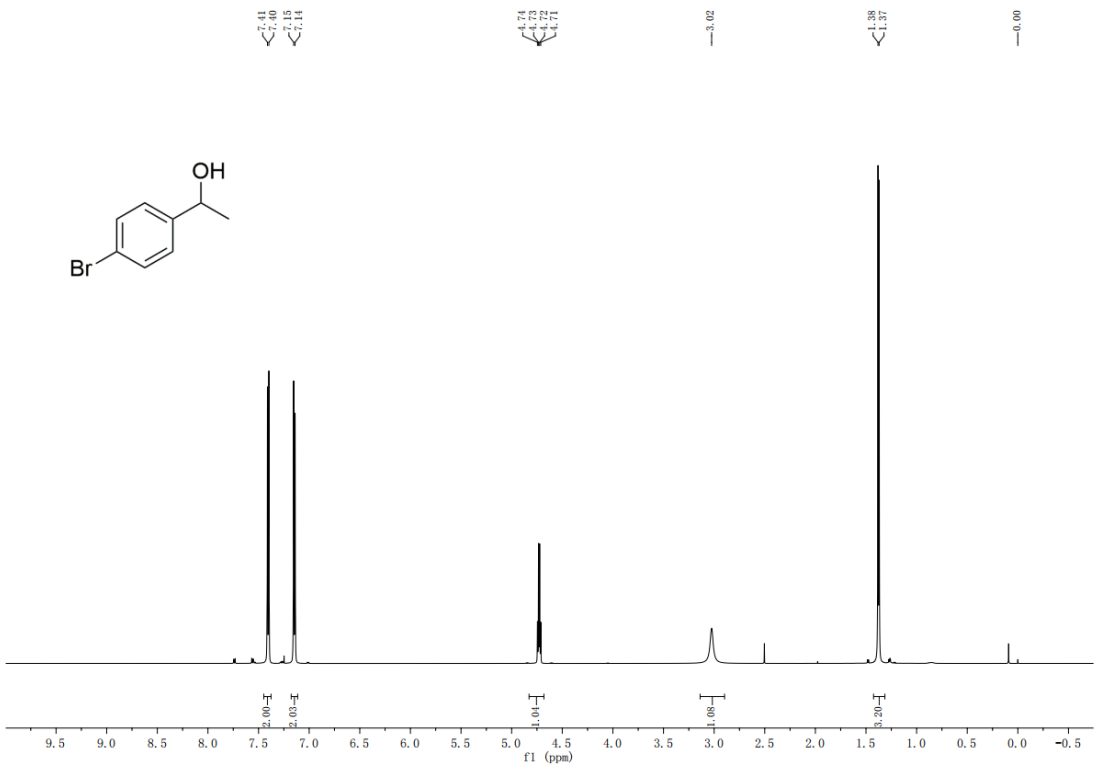
^{13}C NMR spectrum of **31** (101MHz, $CDCl_3$)



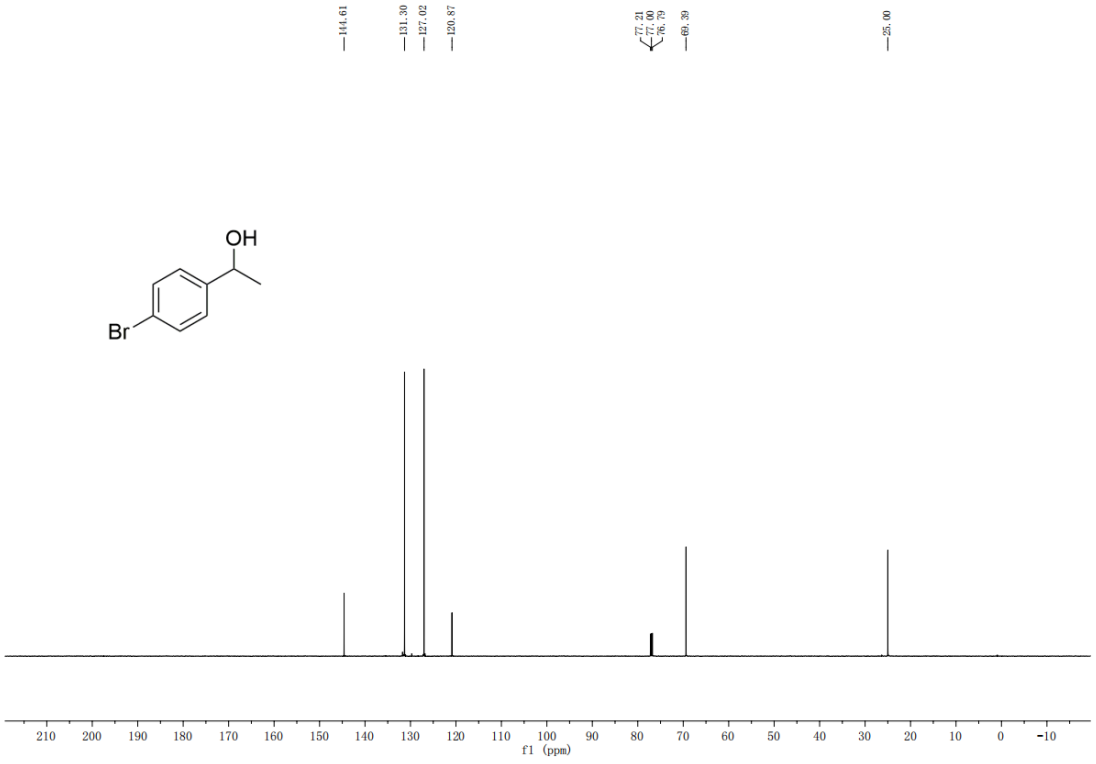
^{1}H NMR spectrum of **32** (600MHz, $CDCl_3$)



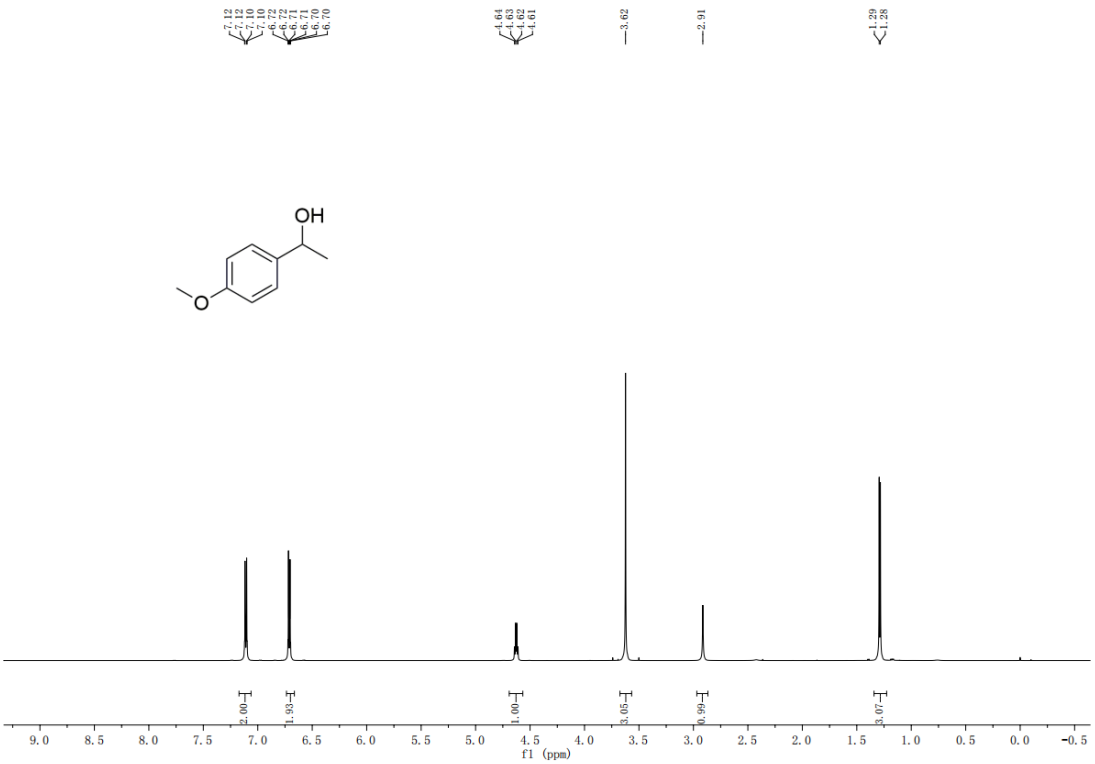
^{13}C NMR spectrum of **32** (151MHz, $CDCl_3$)



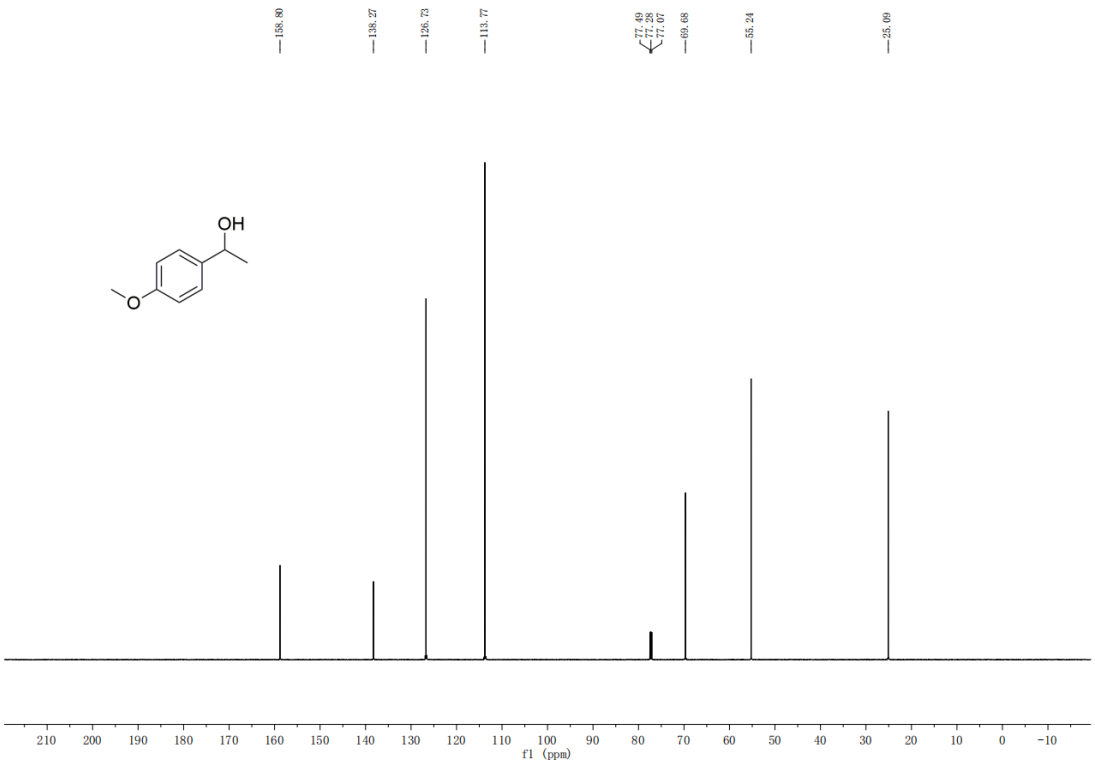
^{1}H NMR spectrum of **33** (600MHz, $CDCl_3$)



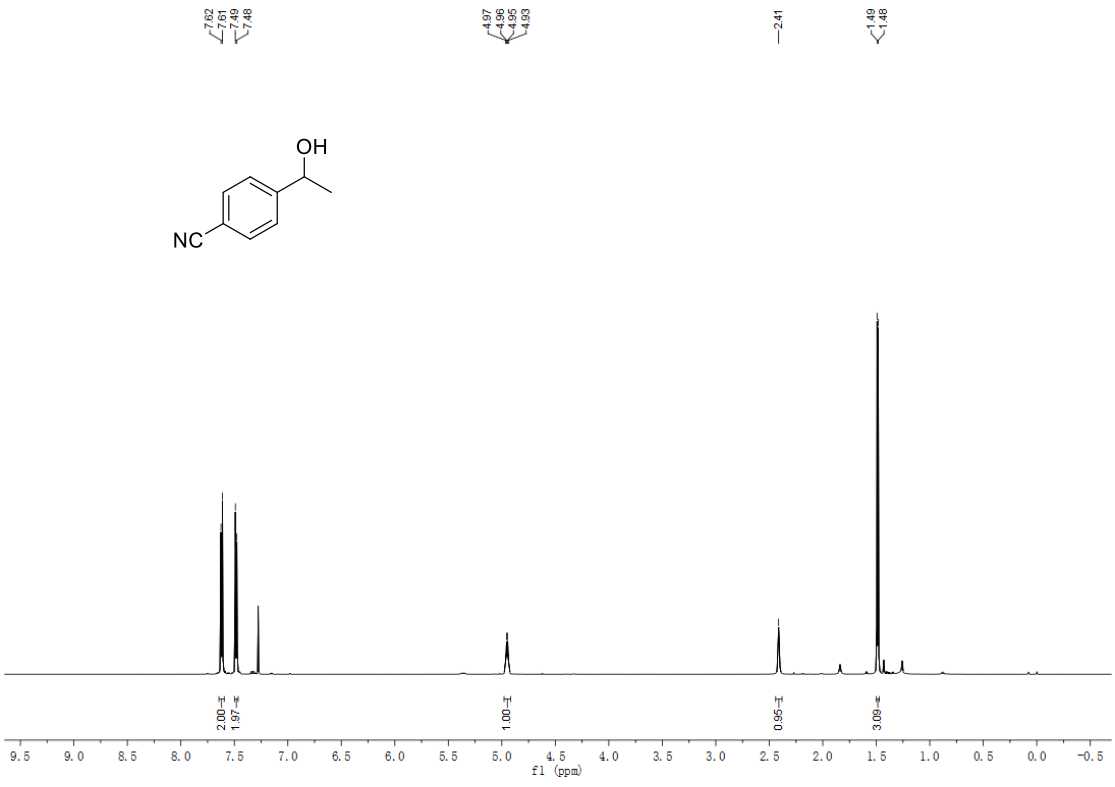
^{13}C NMR spectrum of **33** (151MHz, $CDCl_3$)



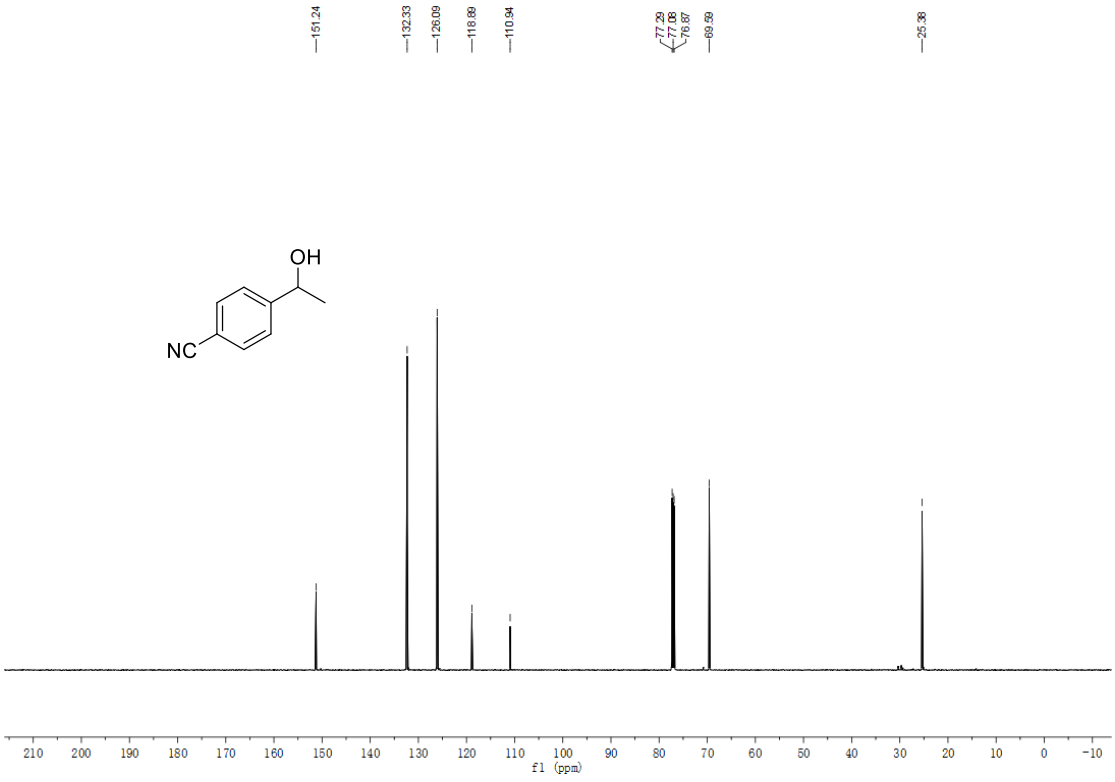
^{1}H NMR spectrum of **34** (600MHz, $CDCl_3$)



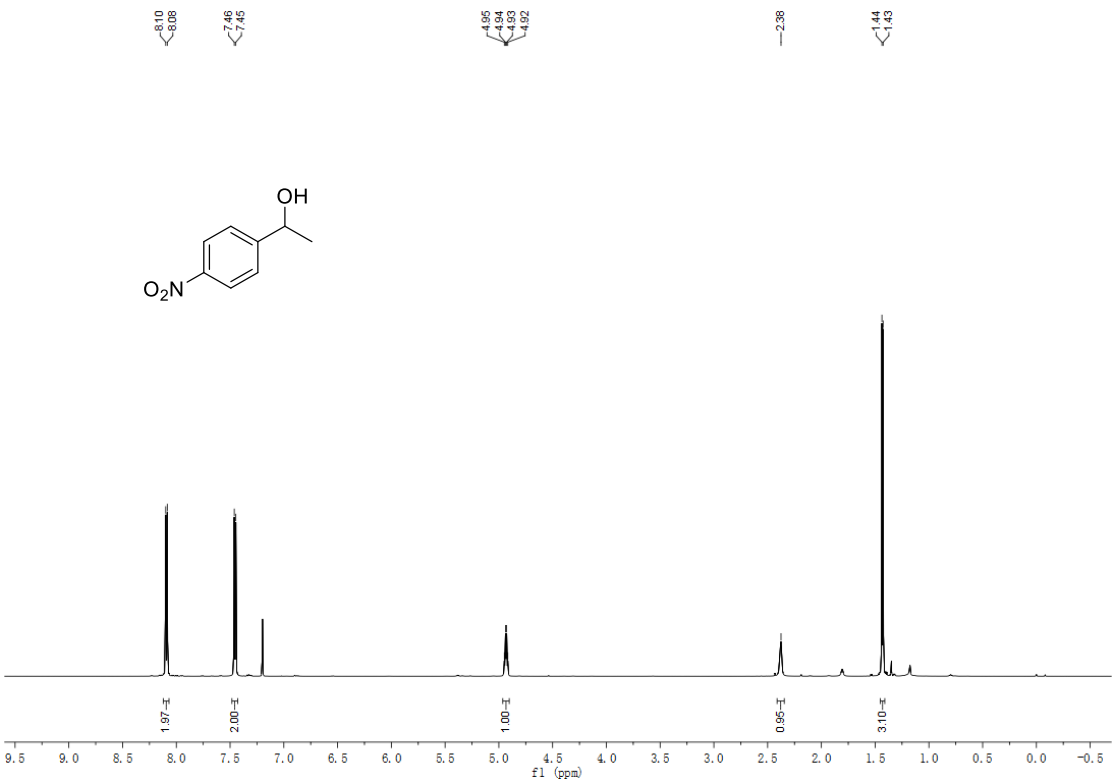
^{13}C NMR spectrum of **34** (151MHz, $CDCl_3$)



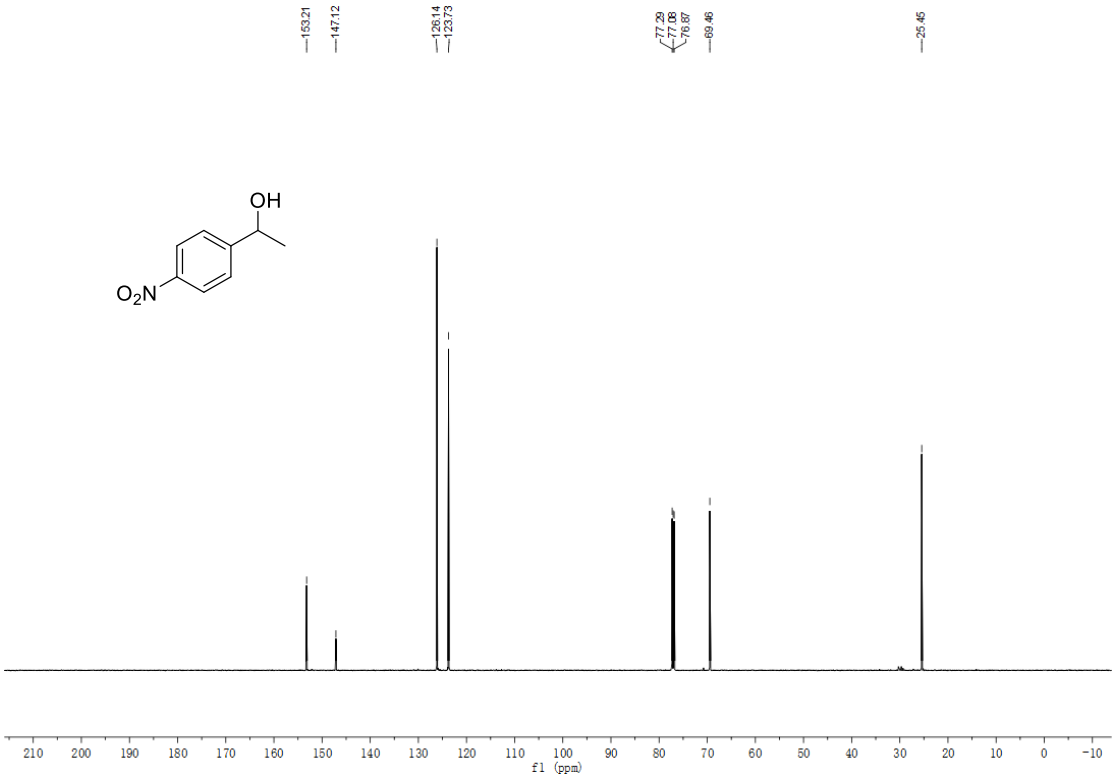
^{1}H NMR spectrum of **35** (600MHz, $CDCl_3$)



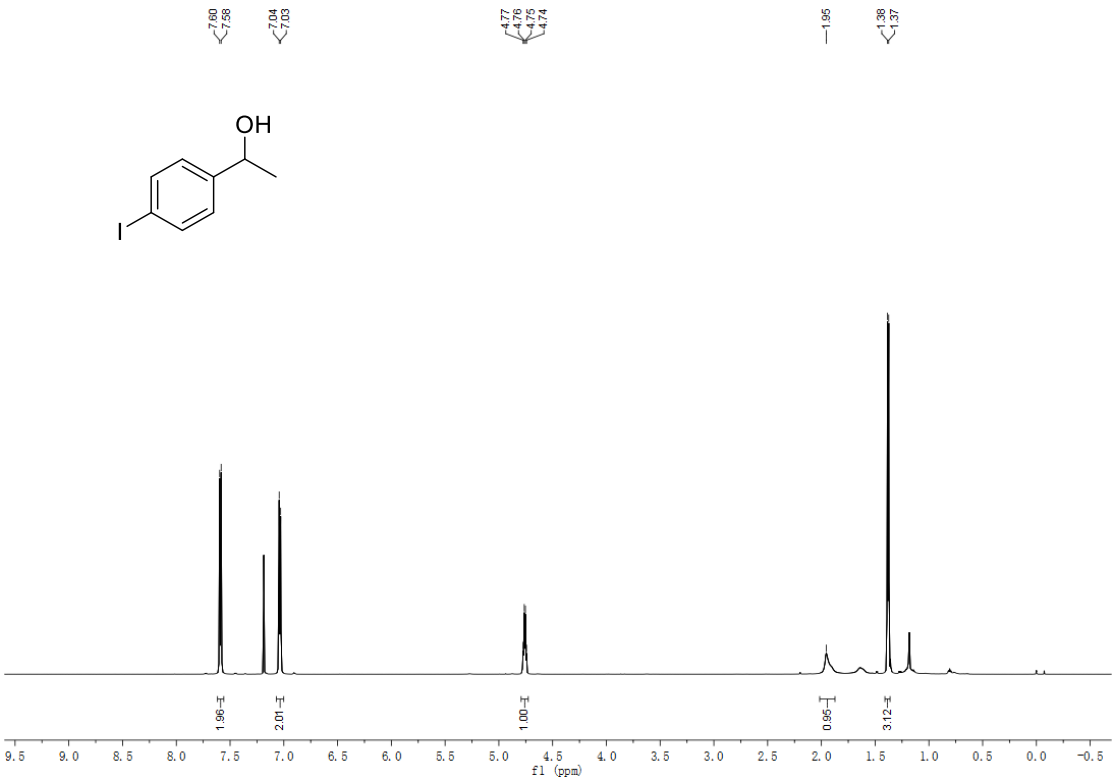
^{13}C NMR spectrum of **35** (151MHz, $CDCl_3$)



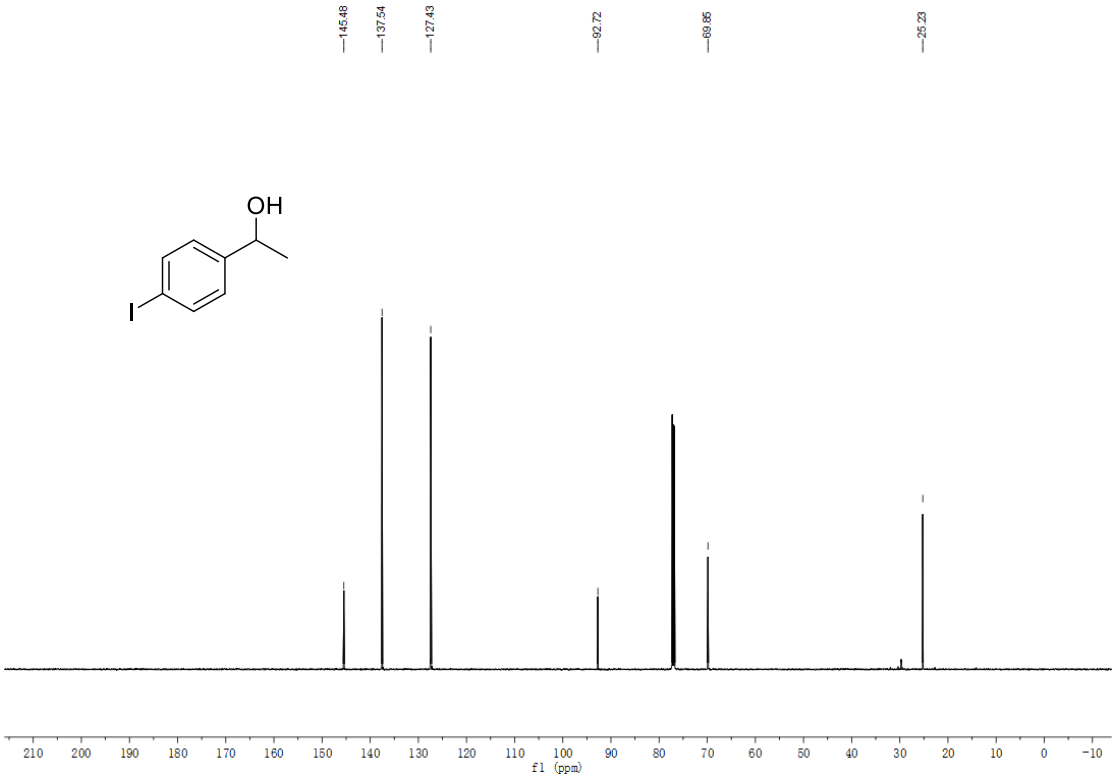
^{1}H NMR spectrum of **36** (600MHz, $CDCl_3$)



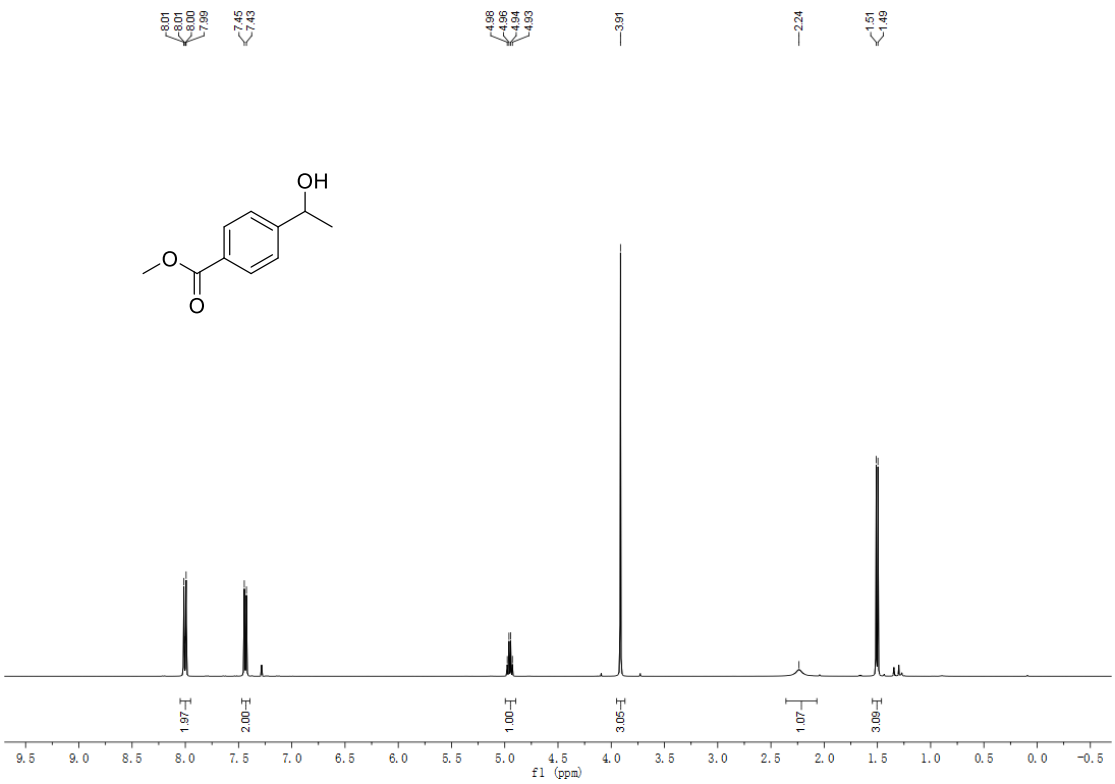
^{13}C NMR spectrum of **36** (151MHz, $CDCl_3$)



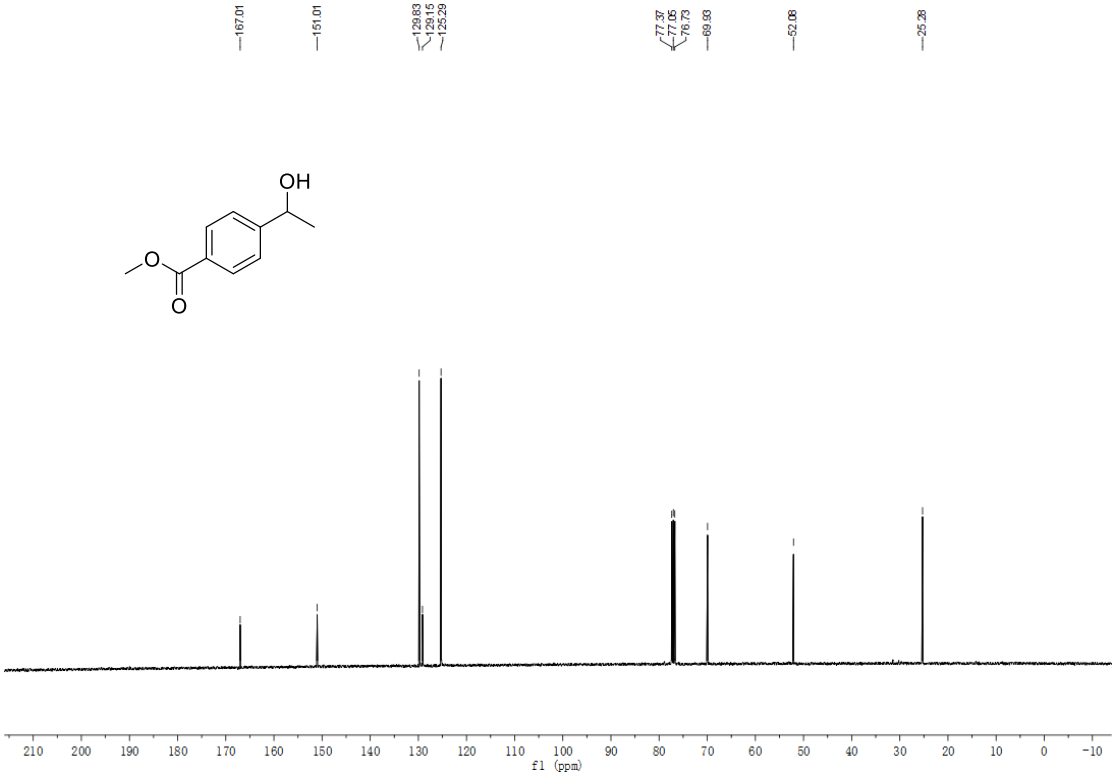
^{1}H NMR spectrum of **37** (600MHz, $CDCl_3$)



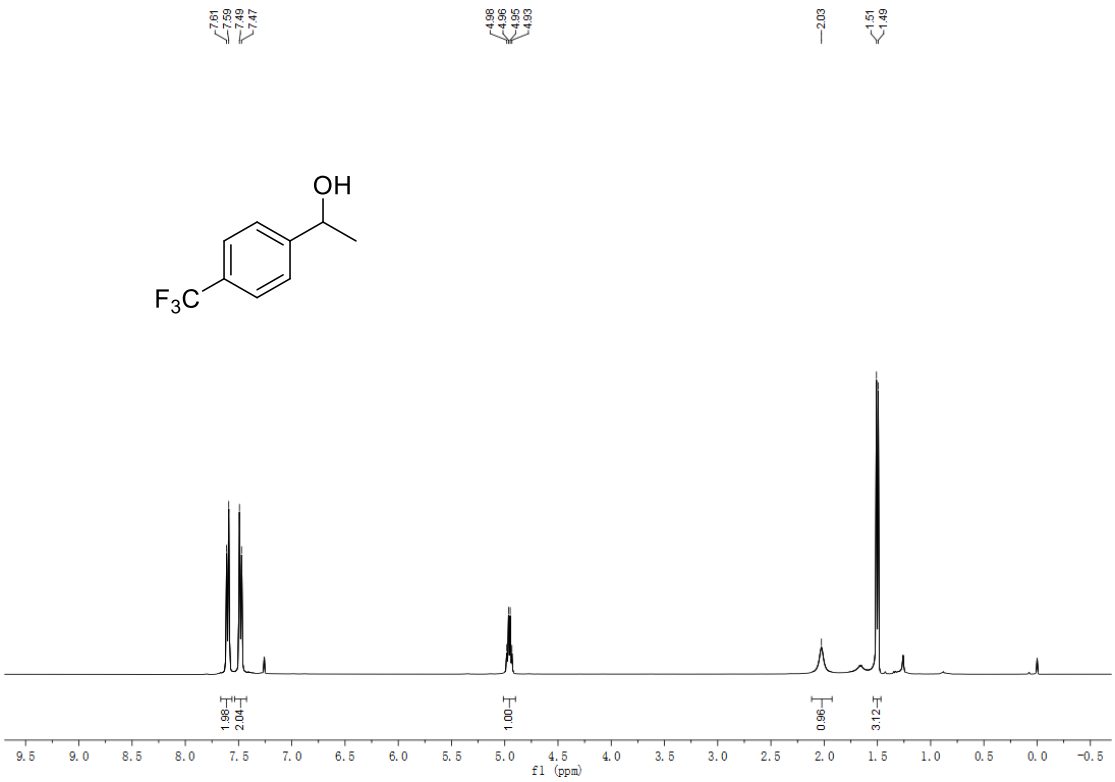
^{13}C NMR spectrum of **37** (151MHz, $CDCl_3$)



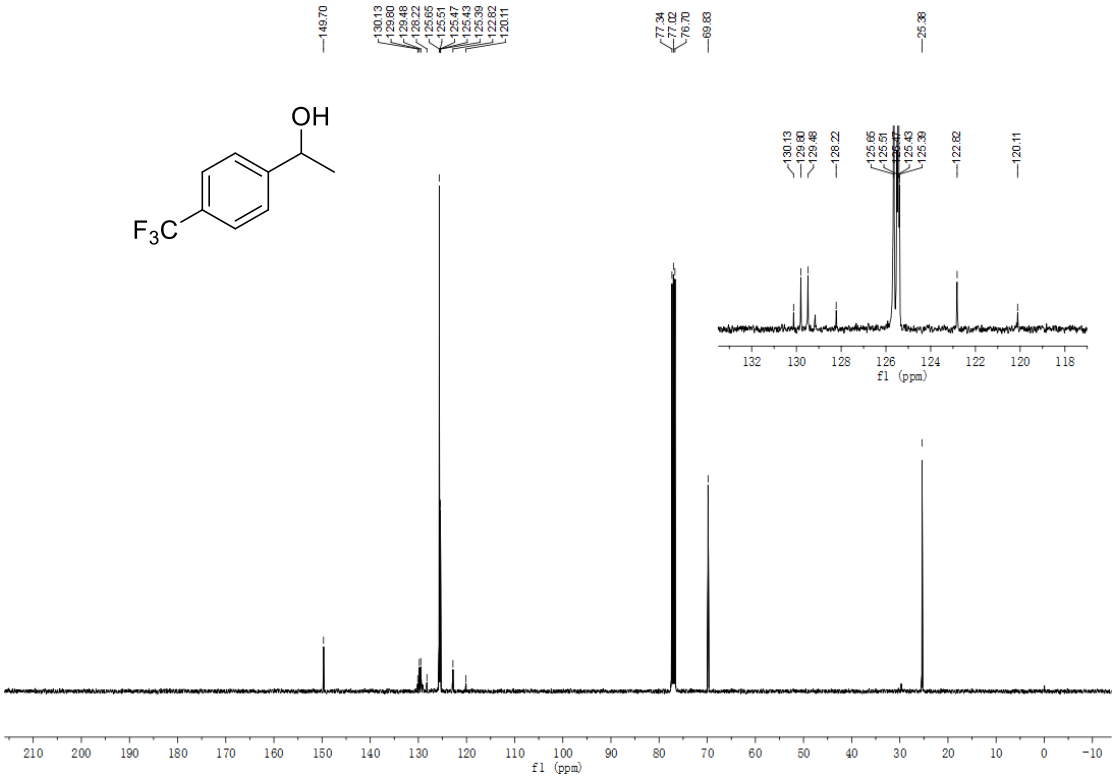
^{1}H NMR spectrum of **38** (400MHz, $CDCl_3$)



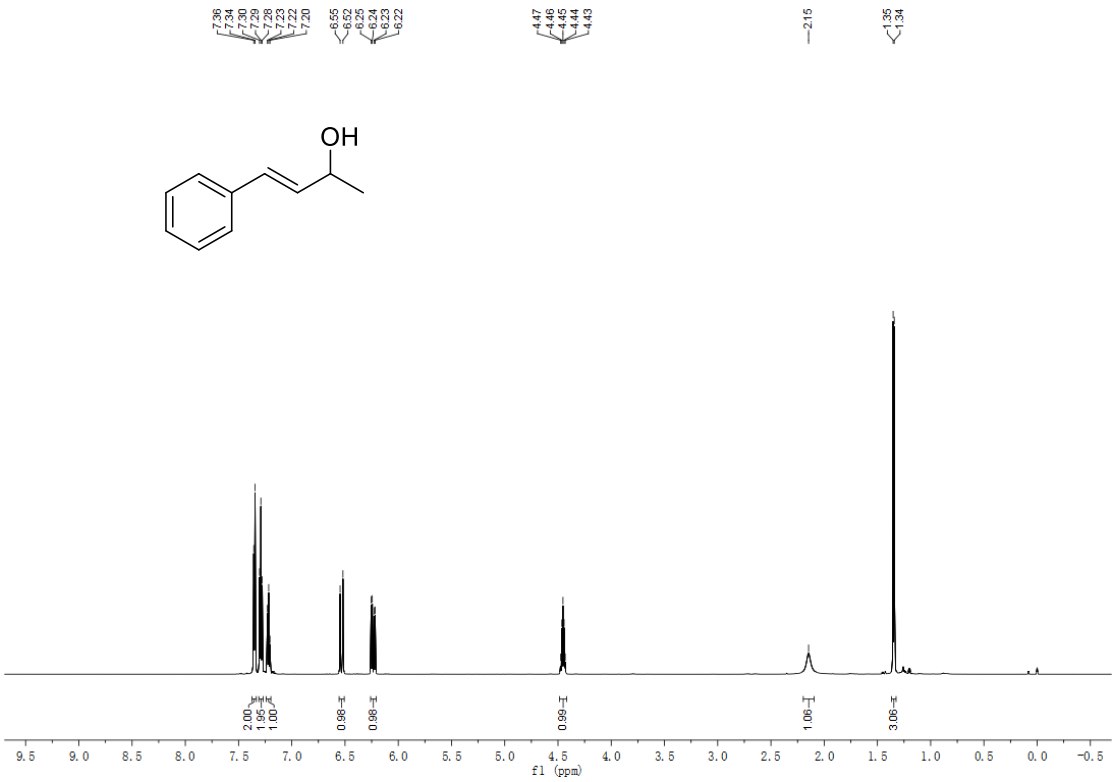
^{13}C NMR spectrum of **38** (101MHz, $CDCl_3$)



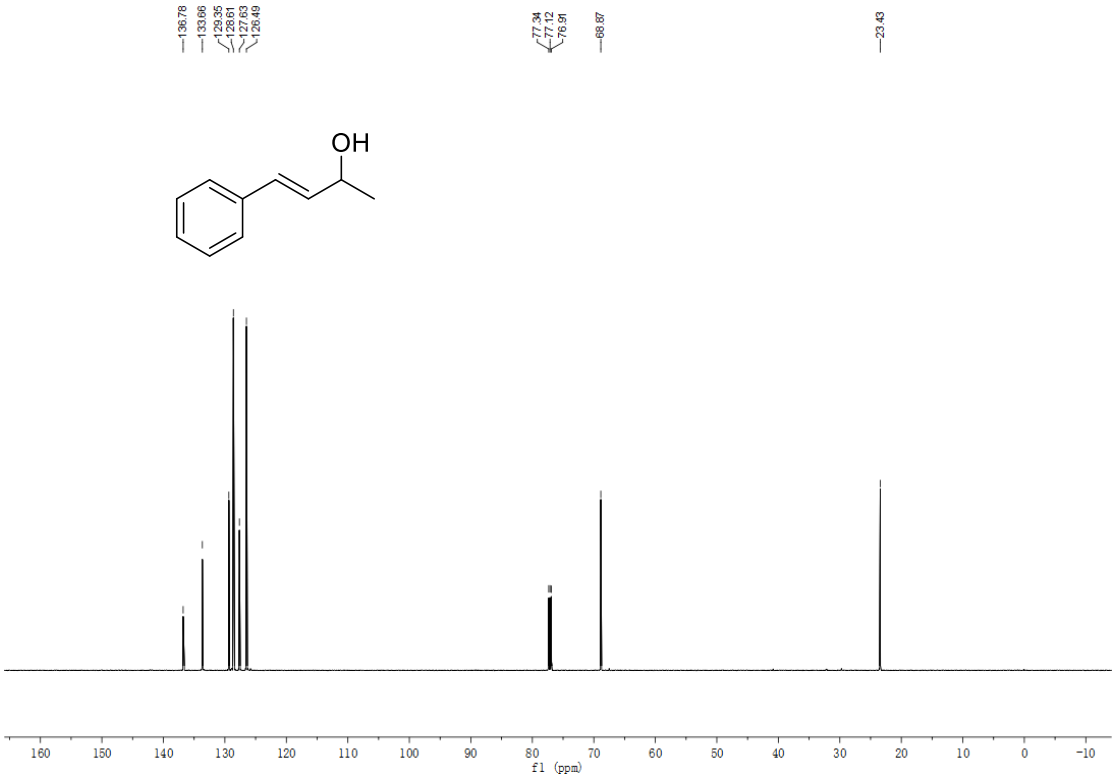
^{1}H NMR spectrum of **39** (400MHz, $CDCl_3$)



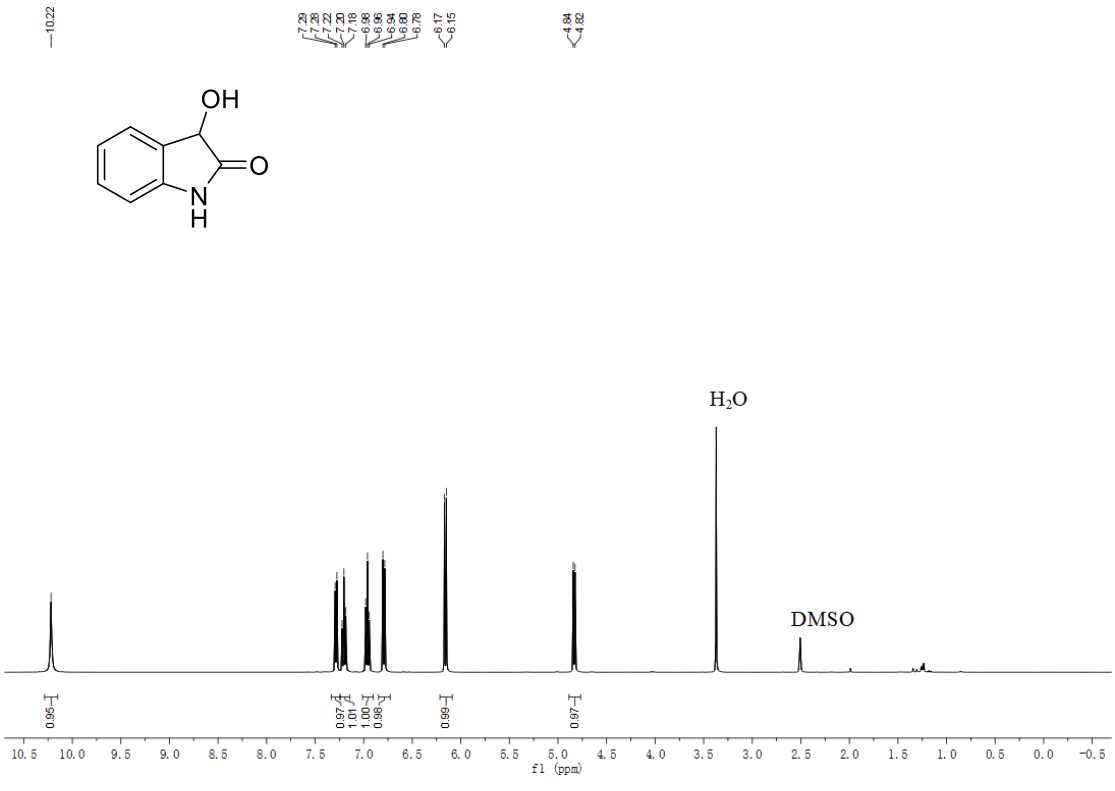
^{13}C NMR spectrum of **39** (101MHz, $CDCl_3$)



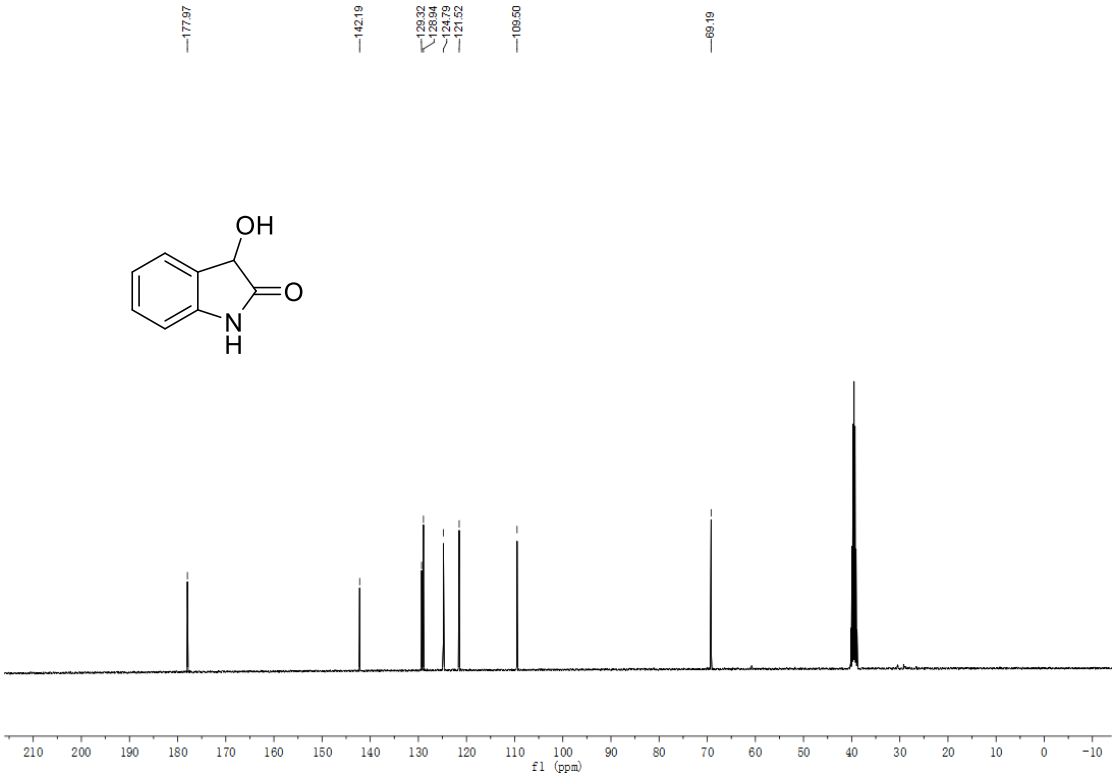
^{1}H NMR spectrum of **40** (600MHz, $CDCl_3$)



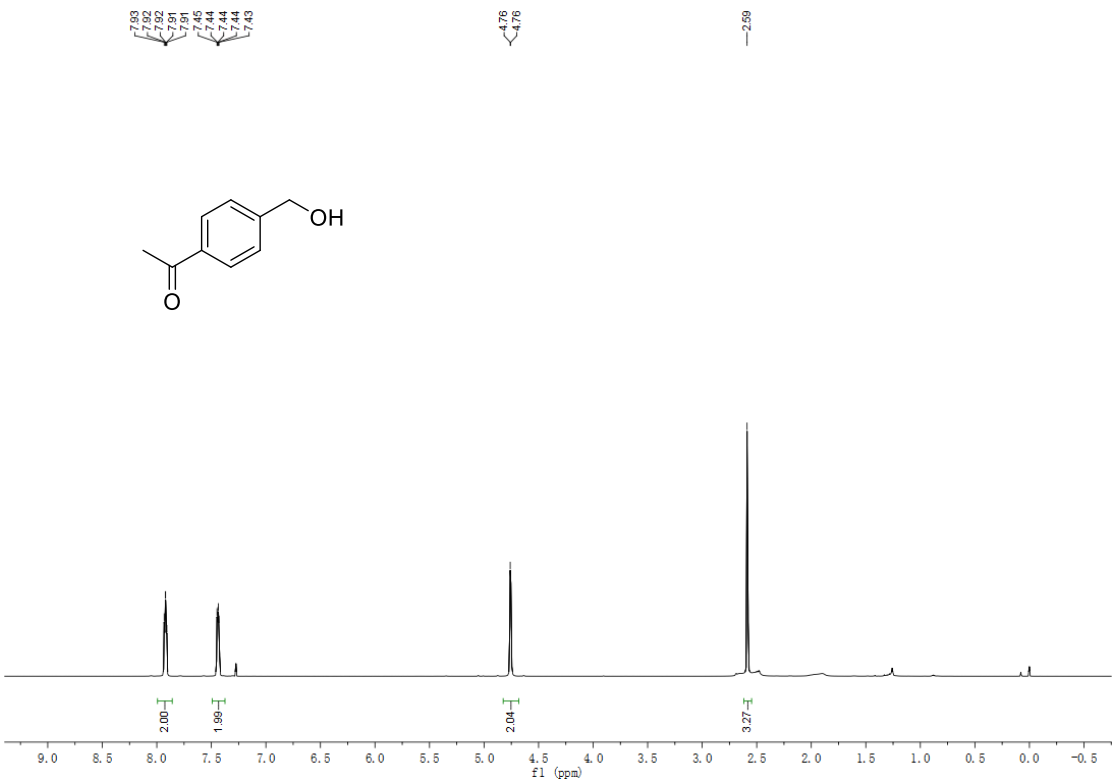
^{13}C NMR spectrum of **40** (151MHz, $CDCl_3$)



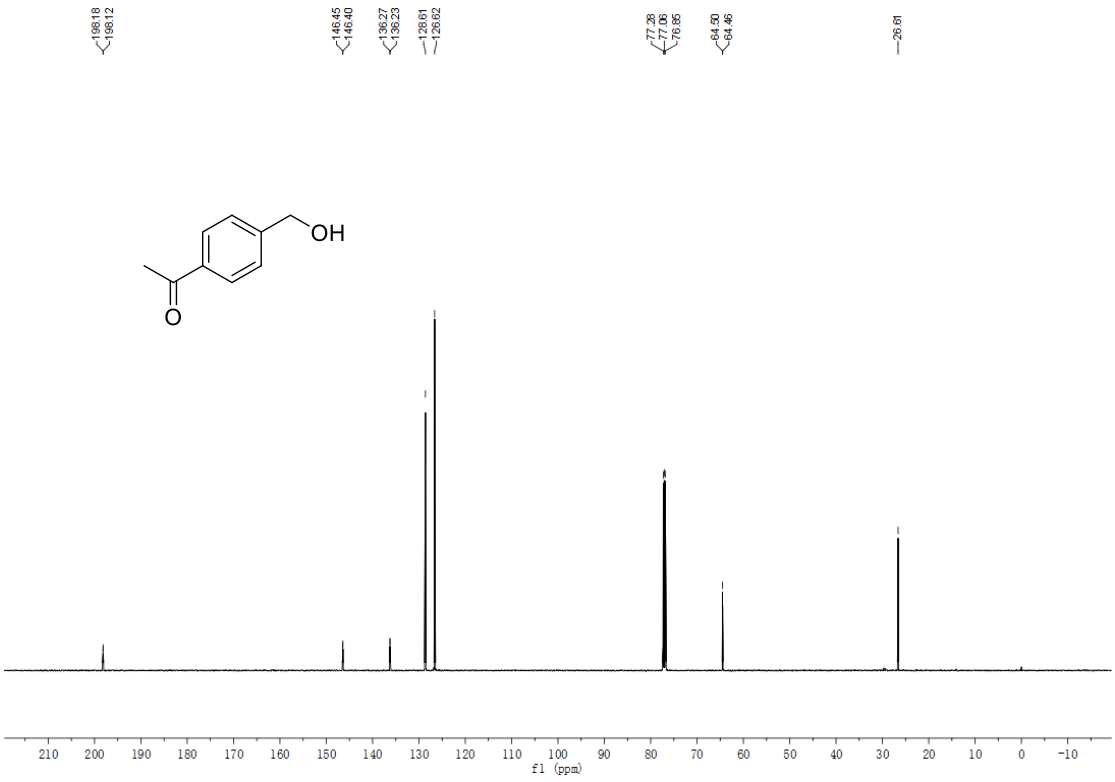
^{1}H NMR spectrum of **41** (400MHz, DMSO)



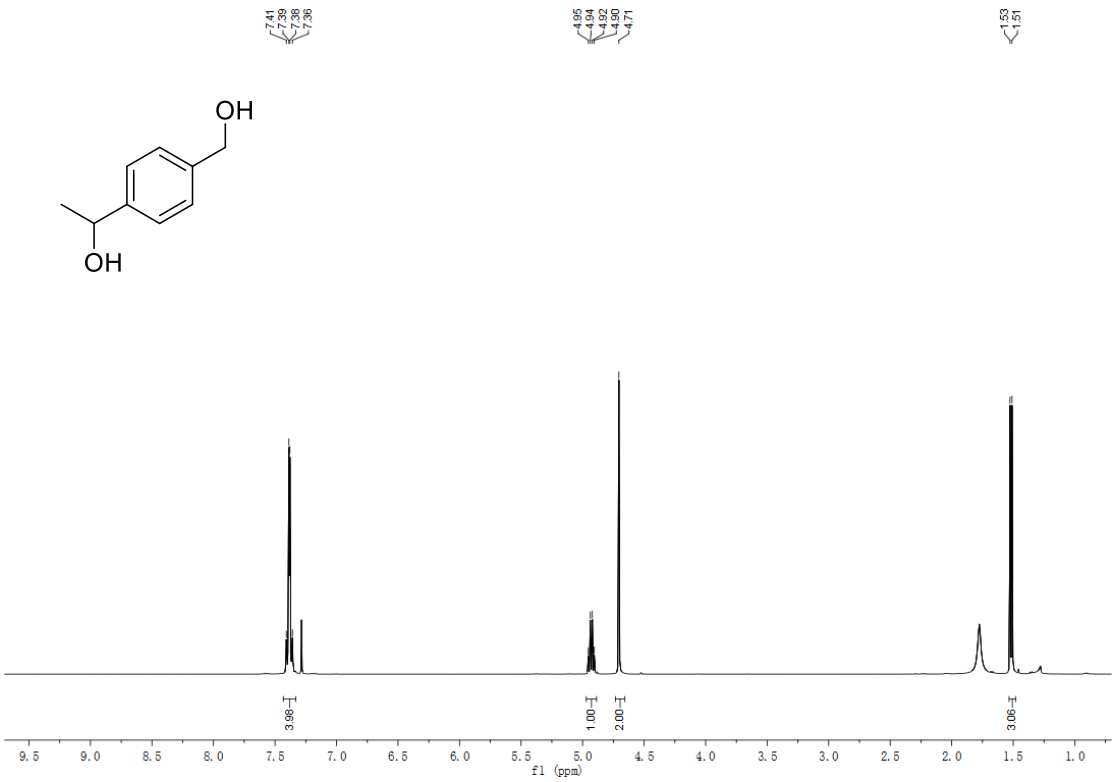
^{13}C NMR spectrum of **41** (101MHz, DMSO)



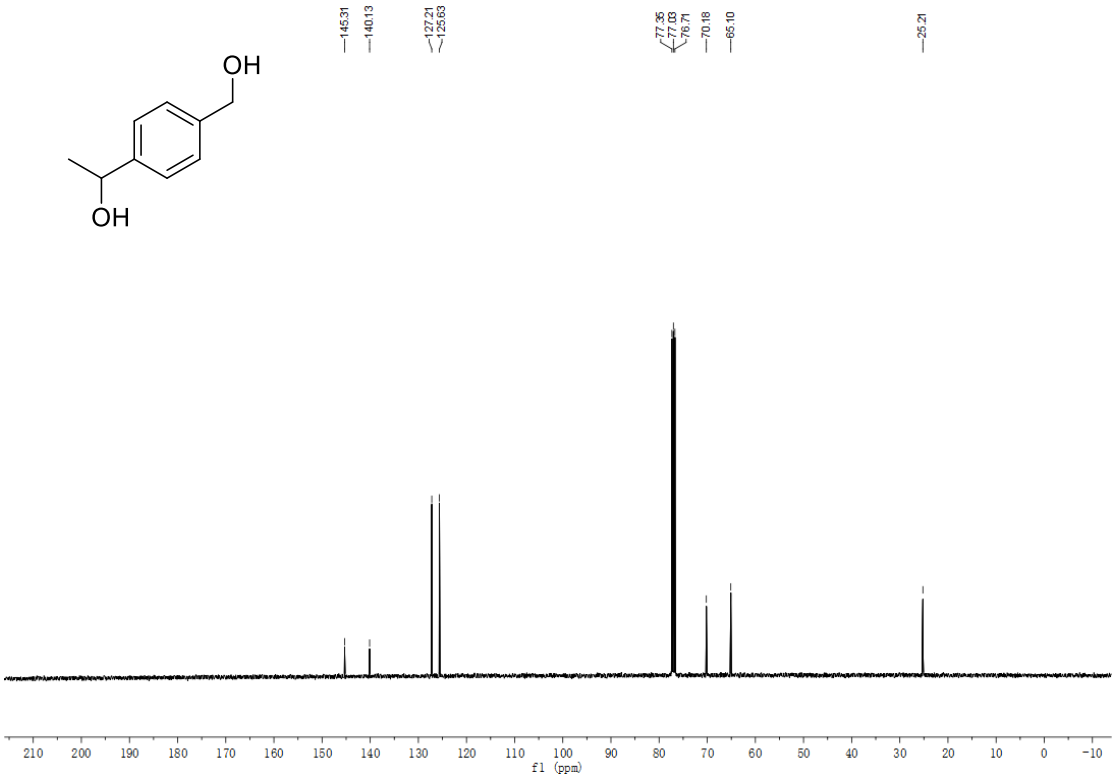
^{1}H NMR spectrum of **42** (600MHz, $CDCl_3$)



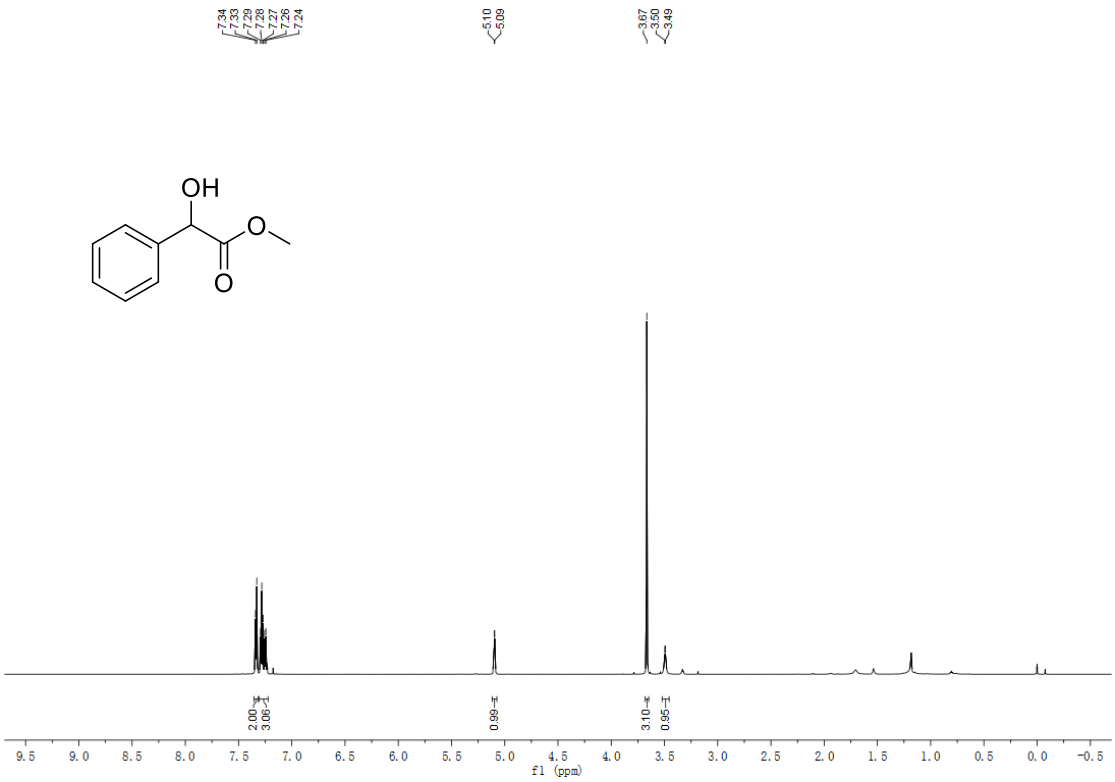
^{13}C NMR spectrum of **42** (151MHz, $CDCl_3$)



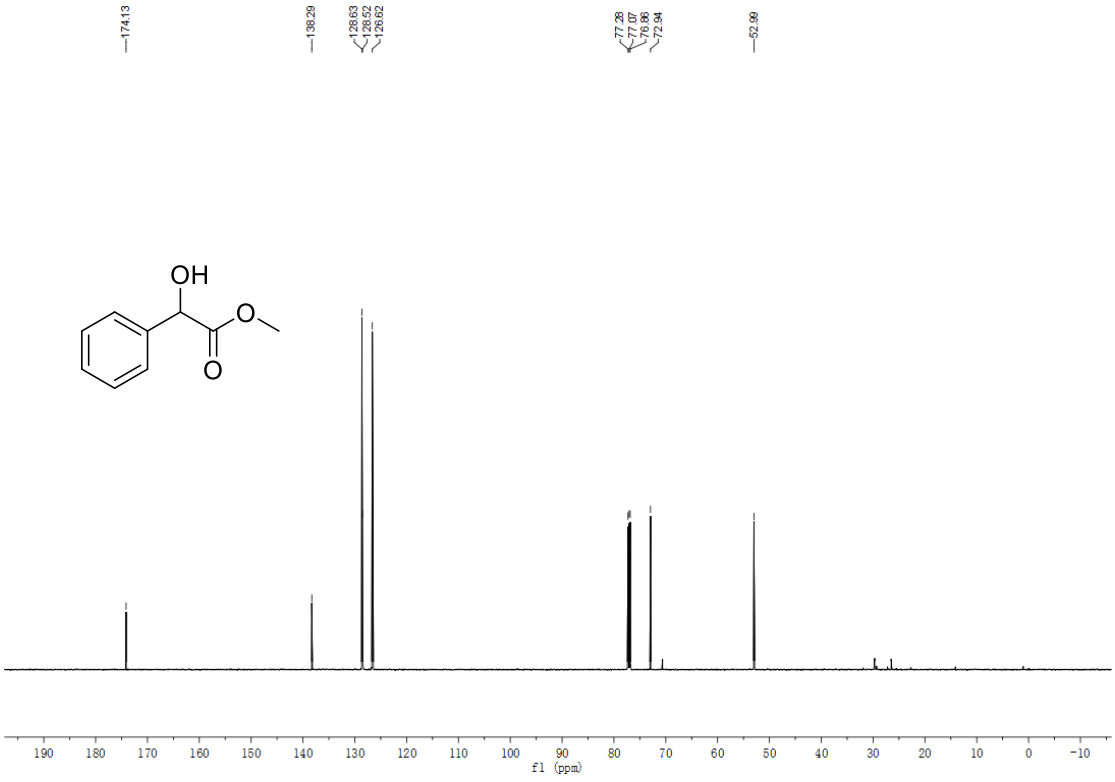
^{1}H NMR spectrum of **43** (400MHz, $CDCl_3$)



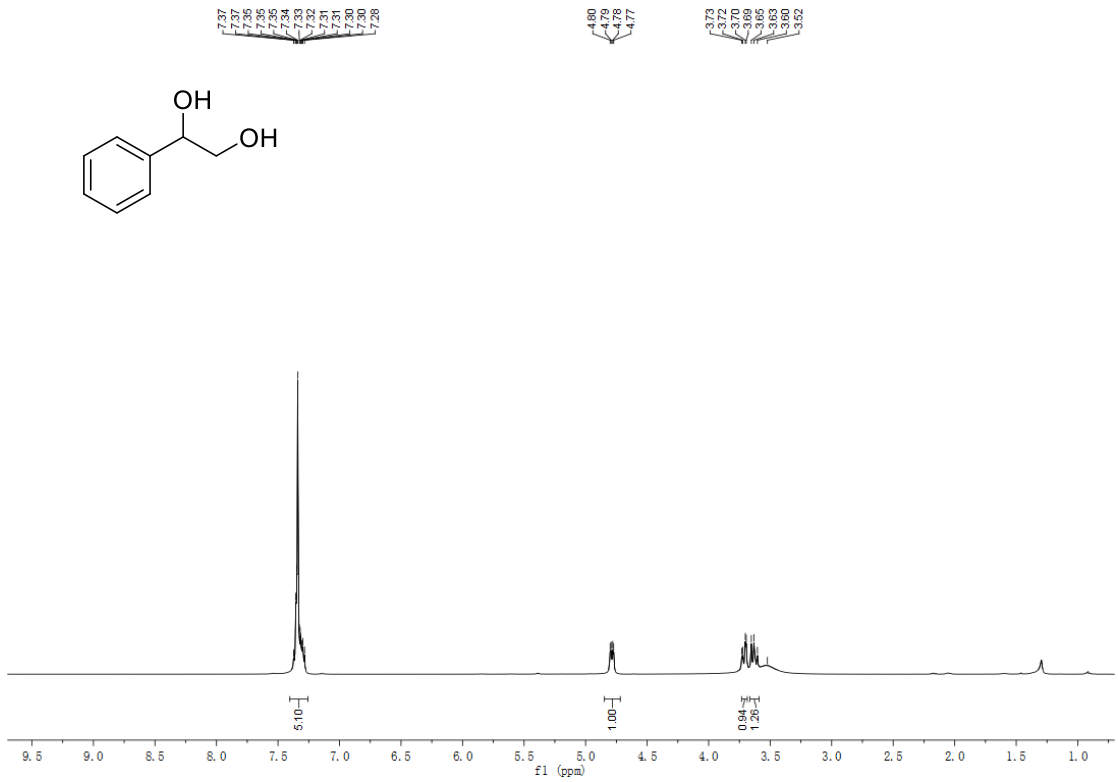
^{13}C NMR spectrum of **43** (101MHz, $CDCl_3$)



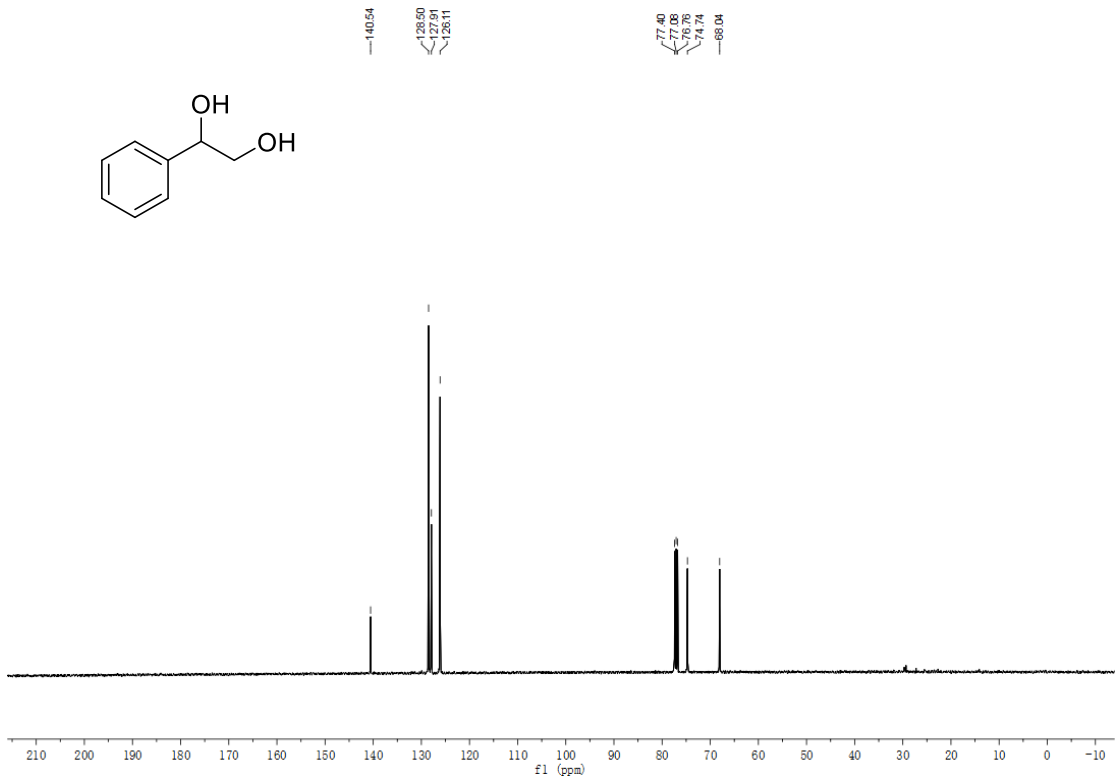
^{1}H NMR spectrum of **44** (600MHz, $CDCl_3$)



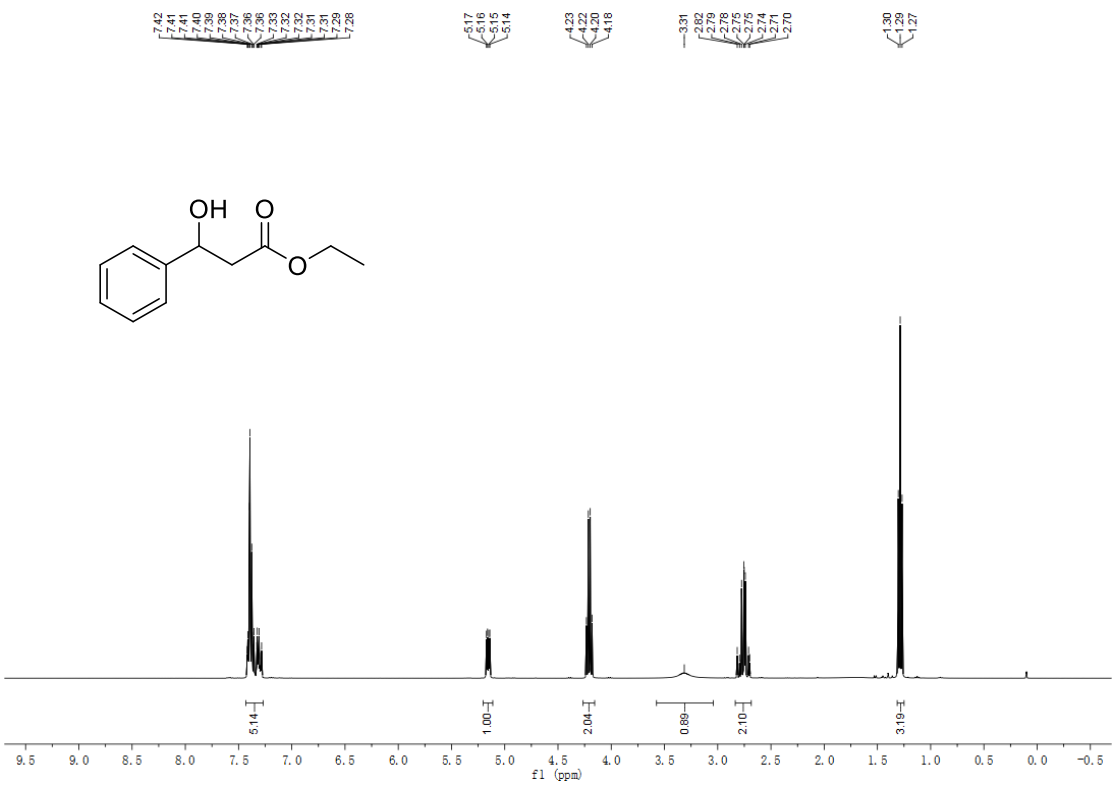
^{13}C NMR spectrum of **44** (151MHz, $CDCl_3$)



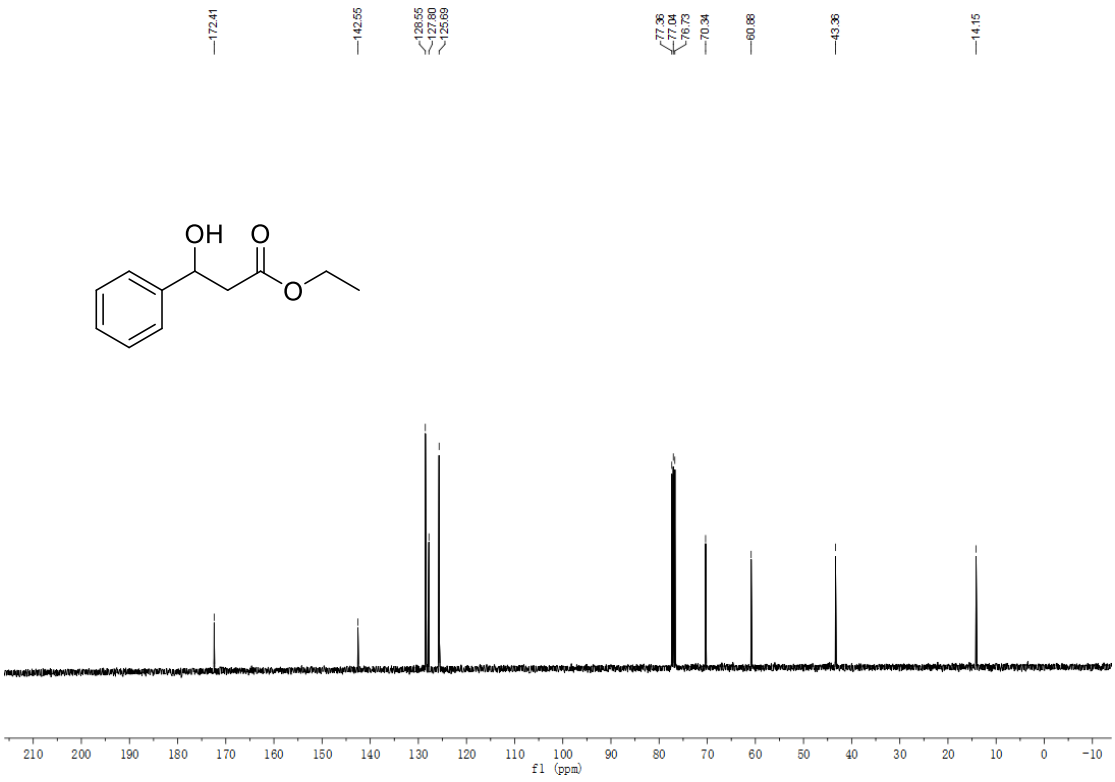
^{1}H NMR spectrum of **45** (400MHz, $CDCl_3$)



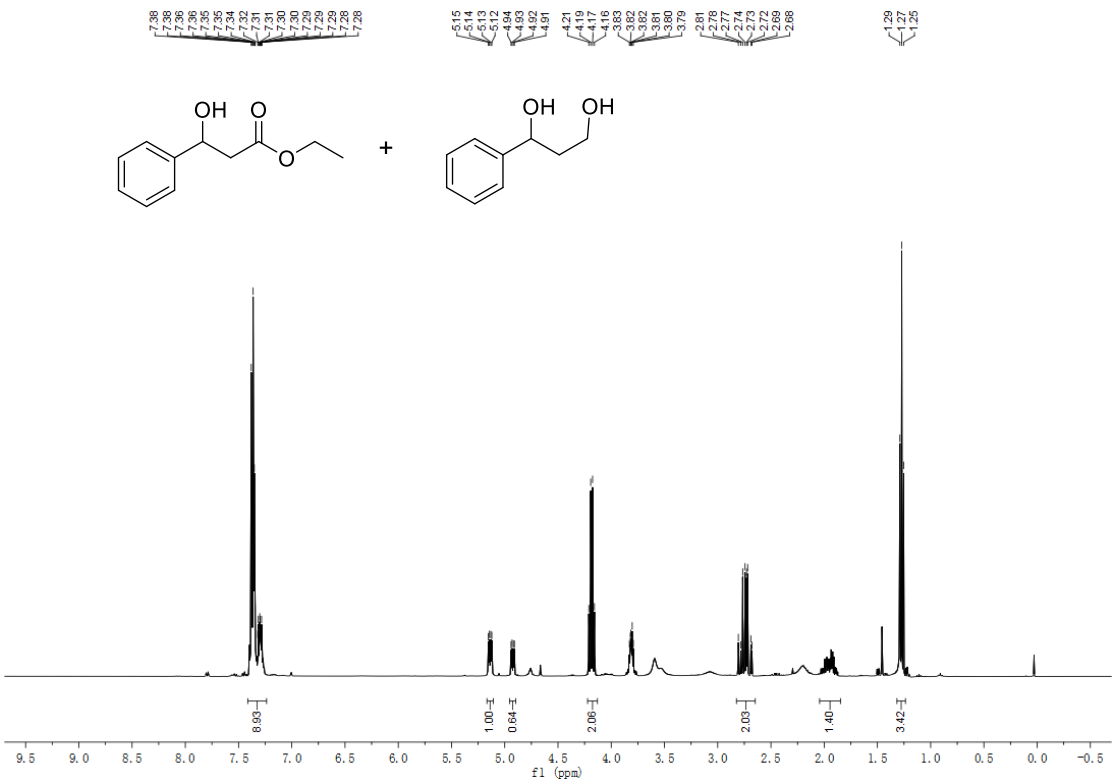
^{13}C NMR spectrum of **45**(101MHz, $CDCl_3$)



^{1}H NMR spectrum of **46** (400MHz, $CDCl_3$)



^{13}C NMR spectrum of **46** (101MHz, $CDCl_3$)



^{1}H NMR spectrum of **46**, **47** (600MHz, $CDCl_3$)