Supporting Information

Metal- and photocatalyst-free three-component strategy to prepare benzylalcohol-, aldehyde-substituted BCP building blocks

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1. General information

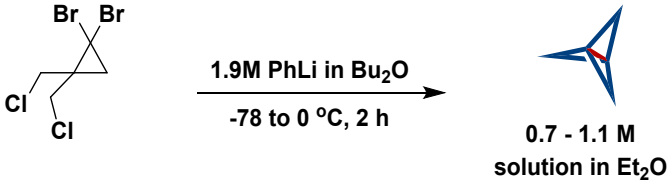
Commercially available reagents were used without further purification unless otherwise stated. All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions, all solvents were purified by VG-P7 solvent drying system from Vigor, or commercial super dry solvents. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (Silica gel 60 F254, Qingdao Haiyang) and visualization on TLC was achieved by UV light or Phosphomolybdic acid. Flash column chromatography was performed on silica gel 200-300 mesh with freshly distilled solvents. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 600, 400 MHz in $CDCl_3$ solvent. All chemical shifts in ^1H NMR spectra were given in parts per million (ppm) relative to the residual or $CDCl_3$ (7.26 ppm) as internal standards and coupling constants (*J*) were given in Hertz (Hz). ^{13}C NMR chemical shifts were reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) as internal standards. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, brs = broad), coupling constant (Hz), and integration. X-Ray crystallographic analyses were performed on Bruker D8 Venture. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS).

The general reactions were carried with the assembled photoreactor (Figure S1). Each of lamp include: 9 W purple LED (390-395 nm, 3 LED lamp beads in series), aluminium radiator with fan, electric driver (XC-8W600-OS). The optical power up to 200 ± 10mw at 1 cm axis distance detected by Thorlabs' Optical Power Meter (PM100D, S120VC). The LED beads were purchased from Zhuhai UV Optoelectronics Co., Ltd. (TH-UV395T3WL-3535 60).

Figure S1. Pictures of assembled photoreactor.

(Notes: the thermal radiation of LEDs increased the temperature of reaction mixture as an average level at 30 °C approximately, and there are no external heating units were equipped.)

2. Preparation of [1.1.1]propellane (solution in Et_2O)[1,2]



The synthesis procedure and concentration determination were based on the Molander's literature.[1] 1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (10.0 g, 33.7 mmol) and Et_2O (20 mL) were added to a 500 mL round-bottomed flask under inert atmosphere. The reaction was cooled to -78 °C, then PhLi (41 mL, 77.5 mmol, 2.3 equiv, 1.9 M in *n*-Bu_2O) was added dropwise to the light brown slurry over 15 min, and the resulting mixture was then stirred at -78 °C for another 30 min and then was allowed to warm to 0 °C. After 2 h, the product propellane is co-distilled with Et_2O as a clear, colorless solution. The receiving flask was submerged in a -78 °C ethanol or liquid nitrogen bath.

Determination of propellane concentration: Add 0.1 mmol of 1,3,5-trimethoxybenzene and 100 μL of [1.1.1]propane solution to an NMR tube containing an appropriate amount of $CDCl_3$. Calculated the concentration of [1.1.1]propellane based on the ratio of 1,3,5-trimethoxybenzene to propellane.

$$c(\text{propellane}) = Int\ (\text{propellane}) \times 0.5\ \text{M} = 1.94 \times 0.5\ \text{M} = 0.97\ \text{M}$$

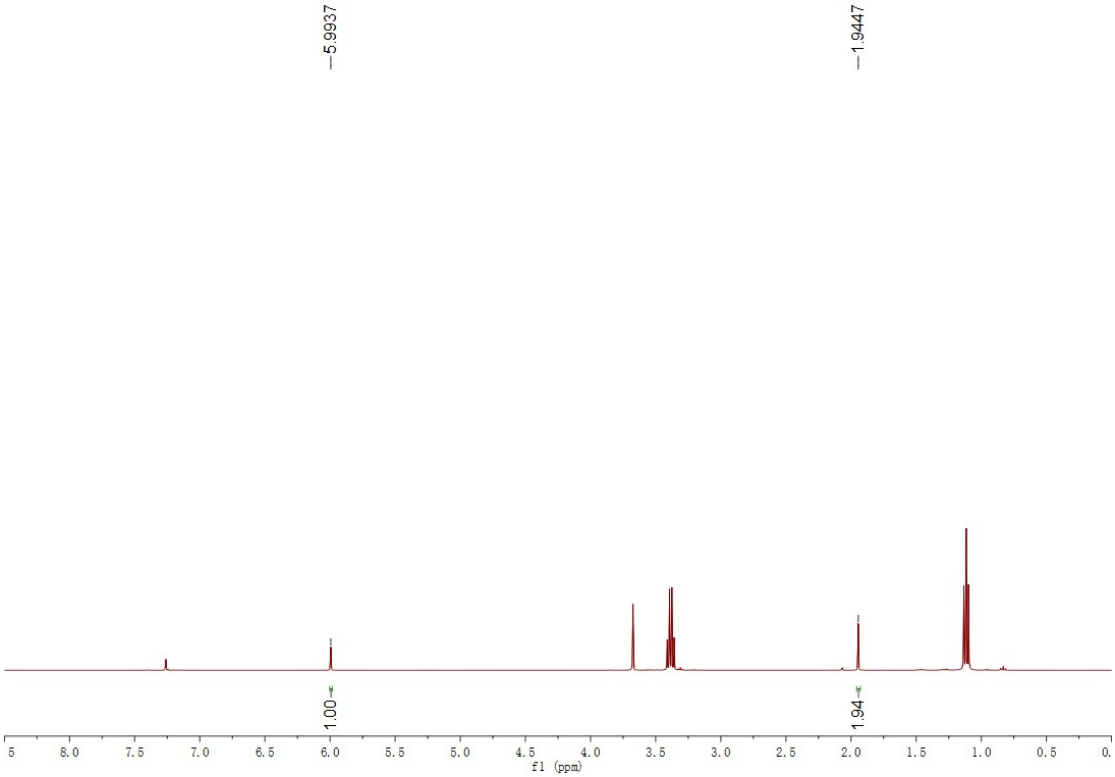
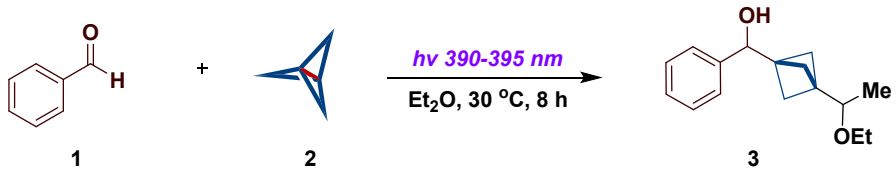


Figure S2. ^{1}H NMR spectrum for the propellane solution with 1,3,5-trimethoxybenzene in $CDCl_3$

3. Optimization of reaction conditions

Table S1. The screening of amount of solvent

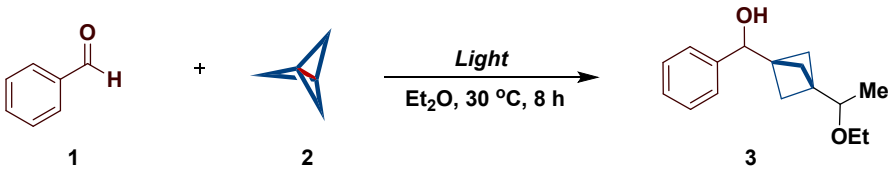


1 **2** **3**

Entry	**Et_2O**	**3** Yield (%)[a]
1	0.5 mL	60%
2	1.0 mL	72%
3	1.5 mL	76%
4	**2.0 mL**	**80%**
5	2.5 mL	80%
6	3.0 mL	80%

Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), Et_2O (X mL), purple LEDs (390-395 nm), 30 °C, Ar, 8 h. [a] Yields determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S2. The screening of light sources

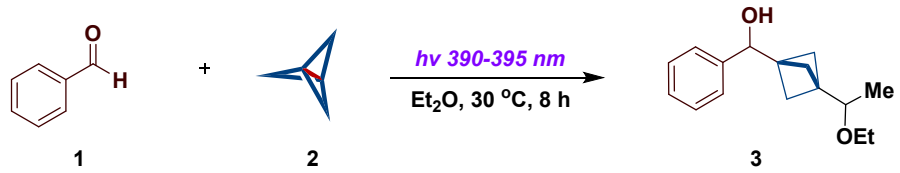


1 **2** **3**

Entry	**Light**	**3** Yield (%)[a]
1	purple LEDs 360-365 nm	68%
2	**purple LEDs 390-395 nm**	**80%**
3	blue LEDs 460-465 nm	10%
4	white 6000 K	trace
5	green LEDs 520-530 nm	NR
6	red LEDs 620-630 nm	NR
7	purple LEDs 390-395 nm, air	78%

Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), Et_2O (2.0 mL), Light, 30 °C, Ar, 8 h. [a] Yields determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S3. The screening of material ratio

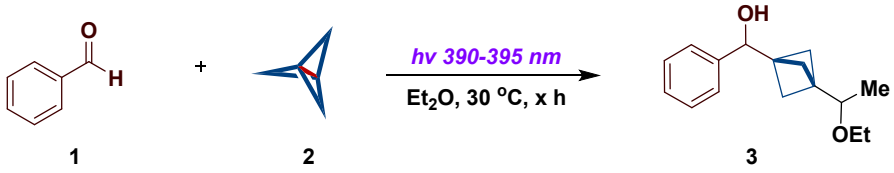


1 **2** **3**

Entry	**1 : 2 (equiv ratio)**	**3** Yield (%)[a]
1	1 : 1	52%
2	1 : 1.5	54%
3	1 : 2.0	48%
4	1 : 3.0	42%
5	1.5 : 1	80%
6	**2.0 : 1**	**82%**
7	2.5 : 1	82%
8	3.0 : 1	82%

Reaction conditions: **1** (x mmol), **2** (y mmol), Et_2O (2.0 mL), purple LEDs (390-395 nm), 30 °C, Ar, 8 h. [a] Yields determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S4. The screening of reaction time

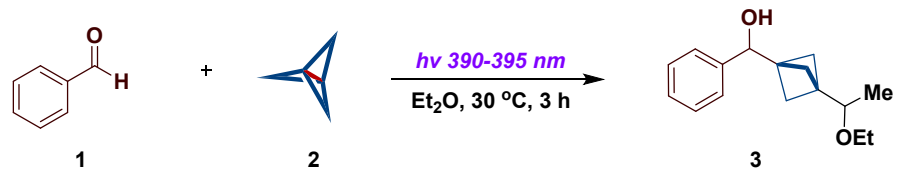


1 **2** **3**

Entry	**time**	**3** Yield (%)[a]
1	1 h	72%
2	2 h	76%
3	**3 h**	**82%/67%[b]**
4	4 h	82%
5	6 h	82%
6	8 h	82%

Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), Et_2O (2.0 mL), purple LEDs (390-395 nm), 30 °C, Ar, x h. [a] Yields determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield.

Table S5. Control experiments



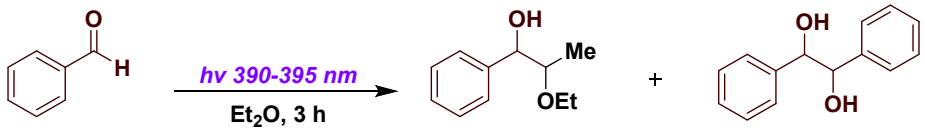
1 2 3

Entry	Variation from the standard conditions	Yield (%)[a][b]
1	**standard conditions**	**82%[a]/67%[b]**
2	UV (365-370 nm)	68%
3	blue LEDs (460-465 nm)	10%
4	green LEDs (530-535 nm)	NR
5	red LEDs (620-630 nm)	NR
6	white LEDs	trace
7	no light, 30 °C	NR
8	air instead of Ar	78%

Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), Et_2O (2.0 mL), purple LEDs (390-395 nm), 30 °C, Ar, 3 h. [a] Yields determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield.

4. Mechanistic studies

4.1 Control experiment

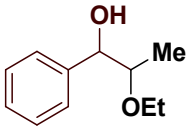


0.2 mmol

1a, 38%
1:1 dr

1b, 42%
d*l*:*meso* = 1.2:1

To a 10 mL glass tube equipped with a magnetic stir bar was added with benzaldehyde (0.2 mmol, 1.0 eq) and Et_2O (2.0 mL) under argon atmosphere. The reaction mixture was placed in a stirrer and irradiated with two 9 W purple LEDs (390-395 nm, approximately 1.0 cm away from the tube, optical power: 200 ± 10 mw/cm^2) at 30 °C for 3 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* to afford crude product. The residue was purified by column chromatography using (PE/EA = 5:1 → 3:1) to afford compound **1a** as a colorless oil (8.0 mg, 38% yield) and compound **1b** as a white solid (9.0 mg, 42% yield).

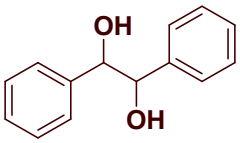


2-ethoxy-1-phenylpropan-1-ol (1a): The product **1a** was purified by column chromatography (PE/EA = 5:1) as a colorless oil (8.0 mg, 38% yield, d.r. = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 5H), 4.89 (d, *J* = 3.5 Hz, 0.5H), 4.38 (d, *J* = 8.0 Hz, 0.5H), 3.75-3.67 (m, 0.5H), 3.66-3.58 (m, 1H), 3.58-3.51 (m, 0.5H), 3.50-3.40 (m, 1H), 3.32 (brs, 0.5H), 2.58 (brs, 0.5H), 1.28-1.19 (m, 3H), 0.98 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.7, 128.4, 128.2, 128.1, 127.4, 127.3, 126.4, 80.2, 79.1, 78.4, 74.9, 64.6, 64.5, 15.7, 15.66, 15.6, 13.4.

HRMS(ESI) m/z calcd. for $C_{11}H_{16}NaO_2$ $[M+Na]^+$: 203.1043, found: 203.1044.



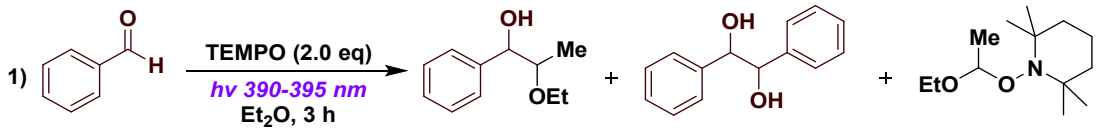
1,2-Diphenylethane-1,2-diol (1b): The product **1b** was purified by column chromatography (PE/EA = 3:1) as a white solid (9.0 mg, 42% yield, *dl:meso* = 1.2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 3H), 7.26-7.20 (m, 5H), 7.15-7.10 (m, 2H), 4.83 (s, 1H), 4.71 (s, 1H), 2.88 (s, 1H), 2.24 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.9, 128.4, 128.3, 128.2, 128.1, 127.2, 127.1, 79.3, 78.3.

HRMS(ESI) m/z calcd. for $C_{14}H_{14}NaO_2$ $[M+Na]^+$: 237,0886, found: 237.0887.

4.2 Radical-trapping experiment

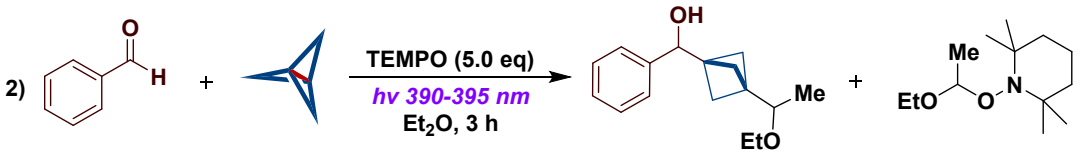


0.2 mmol **1a,** 0% **1b,** 0% **HRMS**

PhCHO remained 20% by HNMR

To a 10 mL glass tube equipped with a magnetic stir bar was added with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (0.4 mmol, 2.0 equiv) and the tube was evacuated and backfilled with argon three times. Then benzaldehyde (0.2 mmol, 1.0 equiv) and Et_2O (2.0 mL) were added under argon atmosphere. The reaction mixture was placed in a stirrer and irradiated with two 9 W purple LEDs (390-395 nm, approximately 1.0 cm away from the tube, optical power: 200 ± 10 mw/cm^2) at 30 °C for 3 h. After cooling to room temperature, the reaction mixture was subjected to HRMS for analysis. Desired product **1a** and **1b** were not detected, and the radical trapping product 1-(1-ethoxyeth-oxy)-2,2,6,6-tetramethylpiperi dine was detected by high-resolution mass spectrometry.

HRMS(ESI) m/z calcd. for $C_{13}H_{27}NNaO_2$ [M+Na]+: 252.1934, found: 252.1932.

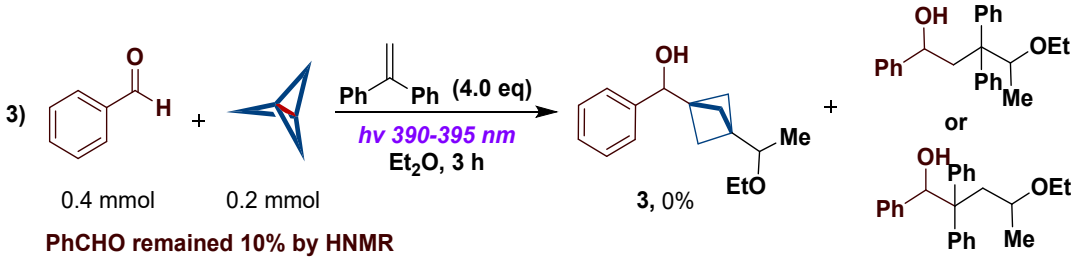


0.4 mmol 0.2 mmol **3,** 0% **HRMS**

PhCHO remained 12% by HNMR

To a 10 mL glass tube equipped with a magnetic stir bar was added with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (1.0 mmol, 5.0 equiv) and the tube was evacuated and backfilled with argon three times. Then [1.1.1]propellane (0.2 mmol, 1.0 equiv, 0.7-1.1 M in Et_2O), benzaldehyde (0.4 mmol, 2.0 equiv) and Et_2O (2.0 mL) were added under argon atmosphere. The reaction mixture was placed in a stirrer and irradiated with two 9 W purple LEDs (390-395 nm, approximately 1.0 cm away from the tube, optical power: 200 ± 10 mw/cm^2) at 30 °C for 3 h. After cooling to room temperature, the reaction mixture was subjected to HRMS for analysis. Desired product **3** was not detected, and the radical trapping product 1-(1-ethoxyeth-oxy)-2,2,6,6-tetramethylpiperi dine was detected by high-resolution massspectrometry.

HRMS(ESI) m/z calcd. for $C_{13}H_{27}NNaO_2$ $[M+Na]^+$: 252.1934, found: 252.1932.

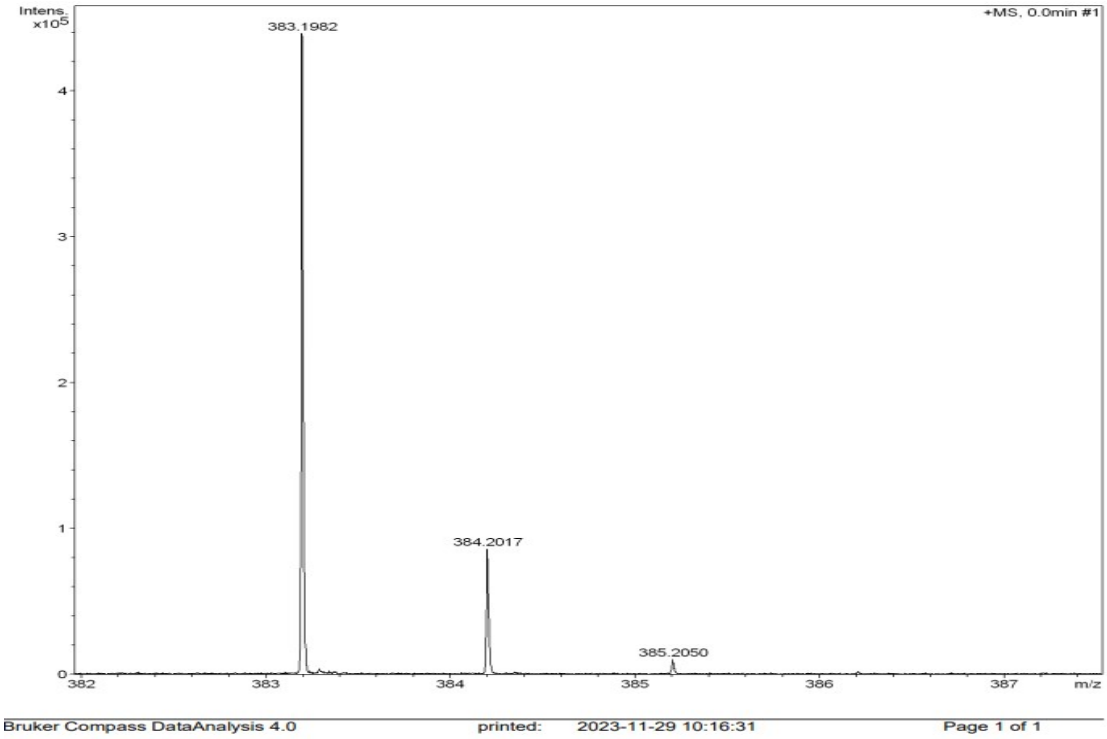


0.4 mmol 0.2 mmol **3,** 0% **HRMS**

PhCHO remained 10% by HNMR

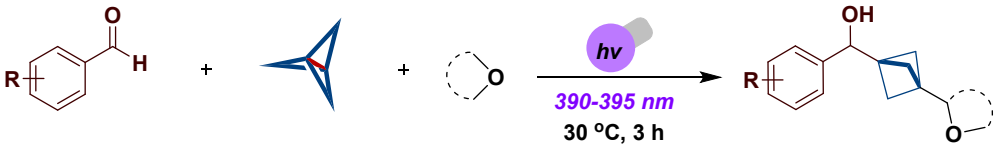
To a 10 mL glass tube equipped with a magnetic stir bar were added with 1,1-diphenylethylene (0.8 mmol, 5.0 equiv), [1.1.1]propellane (0.2 mmol, 1.0 equiv, 0.7-1.1 M in Et_2O), benzaldehyde (0.4 mmol, 2.0 equiv) and Et_2O (2.0 mL) under argon atmosphere. The reaction mixture was placed in a stirrer and irradiated with 9 W pure LEDs (390-395 nm, approximately 1.0 cm away from the tube, optical power: 200 ± 10 mw/cm^2) at 30 °C for 3 h. After cooling to room temperature, the reaction mixture was subjected to HRMS for analysis. Desired product **3** was not detected, and the addition product of ketyl and *α*-oxyalkyl radical was observed by mass spectrometry.

HRMS(ESI) m/z calcd. for $C_{25}H_{28}NaO_2$ $[M+Na]^+$: 383.1982, found: 383.1982.



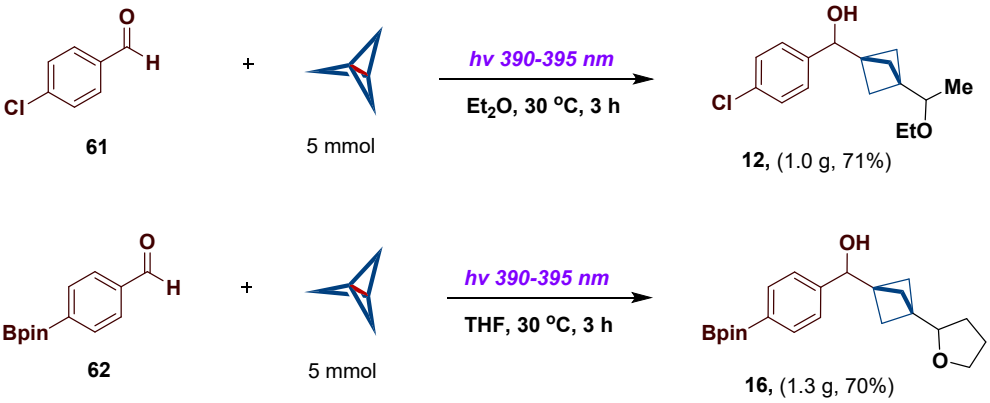
5. General procedure for reactions

5.1 Standard procedure for the synthesis of BCP benzylalcohols



To a 10 mL reaction vial equipped with a magnetic stir bar was added aryl aldehydes (0.4 mmol, 2.0 equiv) and the tube was evacuated and backfilled with argon three times. Then [1.1.1]propellane (0.2 mmol, 1.0 equiv, 0.7-1.1 M in Et_2O) and ether solvents (2.0 mL) were added under argon atmosphere. The reaction mixture was sealed and placed into the assembled photoreactor, stirred and irradiated with two 9 W purple LEDs (390-395 nm, approximately 1.0 cm away from the tube, optical power: 200 ± 10 mw/cm^2) at 30 °C for 3 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* to afford crude product. The crude product was then purified by column chromatography on silica gel to give the desired products.

5.2 Standard procedure for gram-scale synthesis of BCP benzylalcohols



To a 100 mL reaction vial equipped with a magnetic stir bar was added aryl aldehydes (10.0 mmol, 2.0 equiv) and the tube was evacuated and backfilled with argon three times. Then freshly prepared [1.1.1]propellane (5.0 mmol, 1.0 equiv, 0.7-1.1 M in Et_2O) and ether solvents (50.0 mL) were added under argon atmosphere. Then the reaction mixture was irradiated with two 30 W purple LEDs (390-395 nm) at 30 °C for 3 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo to afford crude product. The crude product was then purified by column chromatography on silica gel to give the desired products.

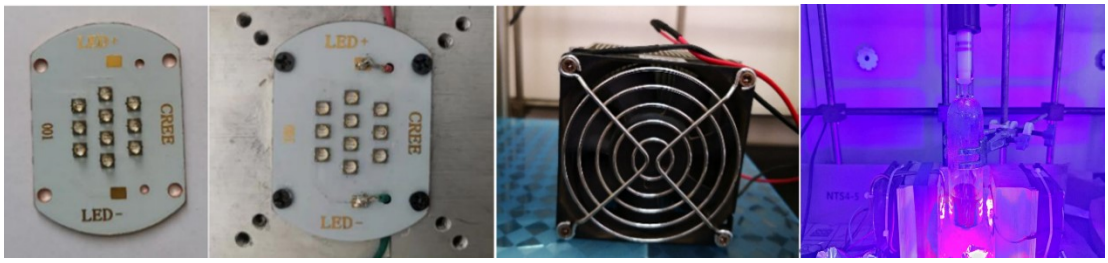
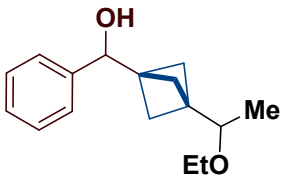


Figure S3. Pictures of gram-scale reaction setup

6. Characterization data of benzylalcohol-, aldehyde-substituted BCPs

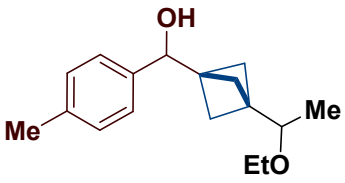


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanol (3)[2]: The product **3** was purified by column chromatography (PE/EA = 6:1) as a colorless oil (33 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 7.28-7.23 (m, 3H), 4.71 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 1.99 (brs, 1H), 1.60-1.44 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 128.2, 127.4, 126.1, 126.0, 74.0, 64.9, 46.4, 42.8, 42.78 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{16}H_{22}NaO_2$ [M+Na]$^+$: 269.1512, found: 269.1509.



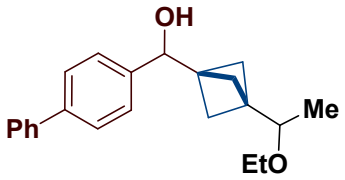
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(p-tolyl)methanol (4): The product **4** was purified by column chromatography (PE/EA = 7:1) as a white solid (28 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 4H), 4.67 (s, 1H), 3.53-3.42 (m, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 1.88 (brs, 1H), 1.60-1.45 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.0, 136.98, 128.9, 126.0, 125.99, 74.0, 73.9, 64.9, 46.4, 42.9, 42.8, 21.3, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{17}H_{24}NaO_2$ $[M+Na]^+$: 283.1669, found: 283.1665.

Melting point: 74 - 75 °C.



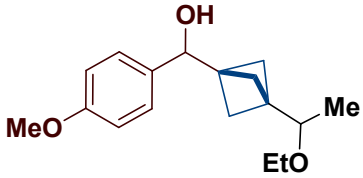
[1,1'-Biphenyl]-4-yl(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (5): The product **5** was purified by column chromatography (PE/EA = 7:1) as a white solid (38 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.55 (m, 4H), 7.46-7.41 (m, 2H), 7.37-7.31 (m 3H), 4.77 (s, 1H), 3.49 (q, *J* = 7.0 Hz, 2H), 3.37 (q, *J* = 6.3 Hz, 1H), 1.97 (brs, 1H), 1.65-1.50 (m, 6H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.04 (dd, *J* = 6.4, 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.9, 140.3, 128.9, 127.3, 127.2, 127.0, 126.5, 126.49, 74.0, 73.8, 64.9, 46.4, 42.9, 42.8, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{22}H_{26}NaO_2$ $[M+Na]^+$: 345.1825, found: 345.1824.

Melting point: 72 - 74 °C

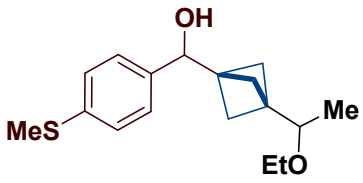


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-methoxyphenyl)methanol (6): The product **6** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (29 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.66 (s, 1H), 3.80 (s, 3H), 3.47 (q, *J* = 6.9 Hz, 2H), 3.35 (q, *J* = 6.3 Hz, 1H), 1.89 (s, 1H), 1.59-1.43 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 134.1, 127.3, 127.2, 113.6, 74.0, 73.7, 64.9, 55.4, 46.4, 43.0, 42.8, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{17}H_{24}NaO_3$ $[M+Na]^+$: 299.1618, found: 299.1614.



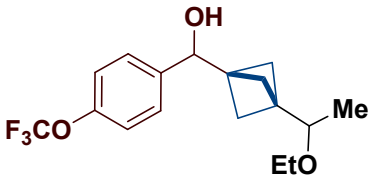
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(methylthio)phenyl)methanol (7): The product **7** was purified by column chromatography (PE/EA = 7:1) as a yellow solid (30 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.66 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.47 (s, 3H), 1.93 (brs, 1H), 1.60-1.41 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 137.2, 126.6, 126.59, 126.5, 73.4, 73.6, 64.9, 46.3, 42.8, 17.2, 16.1, 15.8.

HRMS(ESI) m/z calcd. for $C_{17}H_{24}NaO_2S$ $[M+Na]^+$: 315.1389, found: 315.1387.

Melting point: 55 - 57 °C



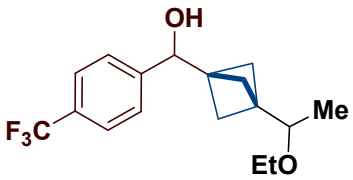
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanol (8): The product **8** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (50 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.72 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 1.96 (brs, 1H), 1.59-1.44 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 140.5, 127.4, 127.38, 120.7, 120.6 (q, *J* = 255.3 Hz, 1H), 73.9, 73.3, 64.9, 46.3, 42.9, 42.7, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87 (s).

HRMS(ESI) m/z calcd. for $C_{17}H_{21}F_3NaO_3$ $[M+Na]^+$: 353.1335, found: 353.1333.



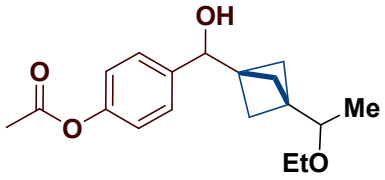
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethyl)phenyl)methanol (9): The product **9** was purified by column chromatography (PE/EA = 6:1) as a colorless oil (50 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.75 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.3 Hz, 1H), 2.12 (brs, 1H), 1.59-1.42 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.4, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 129.6 (q, *J* = 32.1 Hz), 126.3, 126.28, 125.2 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.3 Hz), 73.9, 73.4, 64.9, 46.3, 42.9, 42.6, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.38 (s).

HRMS(ESI) m/z calcd. for $C_{18}H_{24}NaO_3$ $[M+Na]^+$: 311.1618, found: 311.1617.

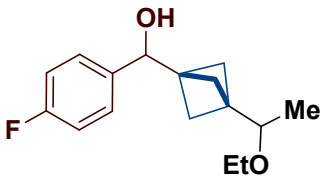


4-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)phenyl acetate (**10**): The product **10** was purified by column chromatography (PE/EA = 5:1) as a colorless oil (37 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.27 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 4.71 (s, 1H), 3.49 (q, *J* = 7.0 Hz, 2H), 3.37 (q, *J* = 6.4 Hz, 1H), 2.30 (s, 3H), 2.02 (brs, 1H), 1.61-1.46 (m, 6H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.03 (dd, *J* = 6.4, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 149.9, 139.4, 127.03, 127.0, 121.3, 74.0, 73.4, 64.9, 46.3, 42.8, 42.7, 21.2, 17.2, 15.7.

HRMS(ESI) m/z calcd. for $C_{18}H_{24}NaO_4$ $[M+Na]^+$: 327.1567, found: 327.1573.



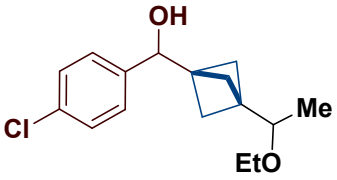
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-fluorophenyl)methanol (11): The product **11** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (34 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 7.05-6.97 (m, 2H), 4.69 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 1.97 (brs, 1H), 1.58-1.43 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 243.3 Hz, 1H), 137.5 (d, *J* = 3.1 Hz), 127.6 (d, *J* = 1.5 Hz), 127.5 (d, *J* = 1.5 Hz), 115.0 (d, *J* = 21.2 Hz), 74.0, 73.4, 64.9, 46.3, 42.8, 42.81, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.53- -115.61 (m).

HRMS(ESI) m/z calcd. for $C_{16}H_{21}FNaO_2$ $[M+Na]^+$: 287.1418, found: 287.1422.



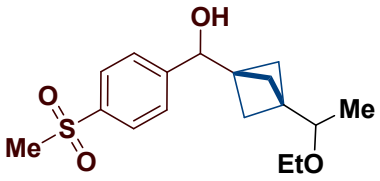
(4-Chlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (12): The product **12** was purified by column chromatography (PE/EA = 7:1) as a yellow solid (40 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.06 (brs, 1H), 1.57-1.40 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.4, 1.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 133.0, 128.4, 127.4, 127.38, 73.9, 73.3, 64.9, 46.3, 42.8, 42.7, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{16}H_{21}ClNaO_2$ $[M+Na]^+$: 303.1122, found: 303.1126.

Melting point: 56 - 58 °C



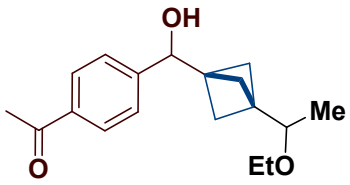
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(methylsulfonyl)phenyl)methanol (13): The product **13** was purified by column chromatography (DCM/EA = 6:1) as a white solid (27 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 4.80 (s, 1H), 3.50-3.40 (m, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 3.04 (s, 3H), 2.23 (brs, 1H), 1.60-1.42 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.4, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 139.4, 127.3, 126.9, 73.8, 73.3, 64.9, 46.3, 44.6, 43.0, 42.6, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{11}H_{24}NaO_4$ $[M+Na]^+$: 347.1288, found: 347.1287.

Melting point: 79 - 81 °C

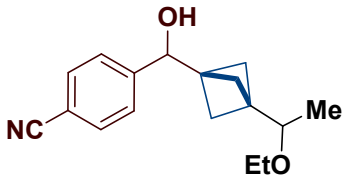


1-(4-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)phenyl)ethan-1-one (14): The product **14** was purified by column chromatography (PE/EA = 6:1) as a colorless oil (30 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.78 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 2.59 (s, 3H), 1.59-1.45 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 147.3, 136.3, 128.3, 126.13, 126.1, 73.9, 73.5, 64.9, 46.3, 42.9, 42.6, 26.7, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{18}H_{24}NaO_3$ $[M+Na]^+$: 311.1618, found: 311.1617.

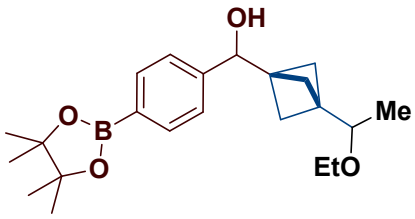


4-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)benzonitrile (**15**): The product **15** was purified by column chromatography (PE/EA = 5:1) as a colorless oil (37 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.77 (s, 1H), 3.51-3.42 (m, 2H), 3.35 (q, *J* = 6.3 Hz, 1H), 2.27 (brs, 1H), 1.60-1.43 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 132.0, 126.7, 119.0, 111.0, 73.8, 73.3, 64.9, 46.3, 42.9, 42.5, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{17}H_{21}NNaO_2$ $[M+Na]^+$: 294,1465, found: 294.1462.



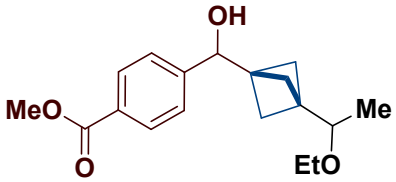
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxabo-rolan-2-yl)phenyl)methanol (**16**): The product **16** was purified by column chromatography (PE/EA = 5:1) as a white solid (50 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 4.72 (s, 1H), 3.46 (q, *J* = 6.9 Hz, 2H), 3.33 (q, *J* = 6.4 Hz, 1H), 1.92 (brs, 1H), 1.58-1.44 (m, 6H), 1.34 (s, 12H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.4, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 134.7, 125.4, 125.3, 83.9, 74.0, 64.8, 46.4, 42.8, 42.7, 25.0, 17.2, 15.7.

HRMS(ESI) m/z calcd. for $C_{22}H_{33}BNaO_4$ $[M+Na]^+$: 395.2364, found: 395.2363.

Melting point: 83 - 85 °C

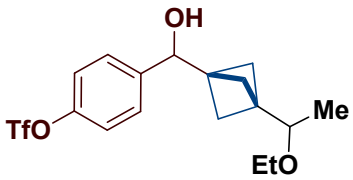


Methyl 4-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)benzoate (**17**): The product **17** was purified by column chromatography (PE/EA = 6:1) as a colorless oil (47 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.78 (s, 1H), 3.91 (s, 3H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.3 Hz, 1H), 1.94 (brs, 1H), 1.58-1.45 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.3, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 147.1, 129.5, 129.1, 125.9, 73.9, 73.5, 64.8, 52.1, 46.3, 42.8, 42.6, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{18}H_{24}NaO_4$ $[M+Na]^+$: 327.1567, found: 327.1563.



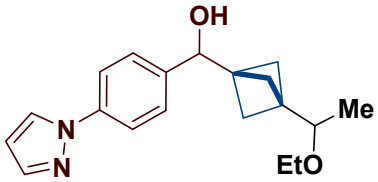
4-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)phenyl trifluoro-methanesulfonate (**18**): The product **18** was purified by column chromatography (PE/EA = 7:1) as a yellow oil (45 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 4.77 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.36 (q, *J* = 6.4 Hz, 1H), 1.89 (brs, 1H), 1.58-1.47 (m, 6H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.02 (dd, *J* = 6.4, 0.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 142.3, 127.8, 127.79, 121.1, 118.9 (q, *J* = 318.8 Hz), 73.9, 73.1, 64.9, 46.3, 42.9, 42.7, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.89 (s).

HRMS(ESI) m/z calcd. for $C_{17}H_{21}F_3NaO_5S$ $[M+Na]^+$: 417.0954, found: 417.0955.



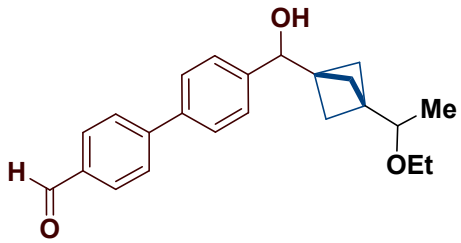
(4-(1*H*-pyrazol-1-yl)phenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**19**): The product **19** was purified by column chromatography (PE/EA = 4:1) as a yellow solid (37 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.47-6.42 (t, *J* = 2.1 Hz, 1H), 4.73 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.3 Hz, 1H), 2.33 (brs, 1H), 1.59-1.43 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.4, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.3, 139.4, 127.05, 127.0, 126.9, 119.1, 107.6, 73.9, 73.4, 64.9, 46.3, 42.83, 42.8, 17.2, 15.7.

HRMS(ESI) m/z calcd. for $C_{19}H_{24}N_2NaO_2$ $[M+Na]^+$: 335.1730, found: 335.1735.

Melting point: 58 - 60 °C

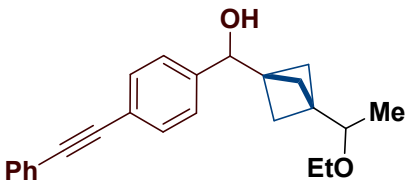


4'-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)-[1,1'-biphenyl]-4-carbaldehyde (**20**): The product **20** was purified by column chromatography (PE/EA = 6:1) as a yellow oil (18 mg, 26% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 4.79 (s, 1H), 3.48 (q, *J* = 7.0 Hz, 2H), 3.37 (q, *J* = 6.3 Hz, 1H), 1.99 (s, 1H), 1.65-1.49 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 147.0, 142.3, 138.7, 135.3, 130.4, 127.7, 127.2, 126.75, 126.7, 74.0, 73.7, 64.9, 46.4, 42.9, 42.8, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{23}H_{26}NaO_3$ $[M+Na]^+$: 373.1774, found: 373.1772.



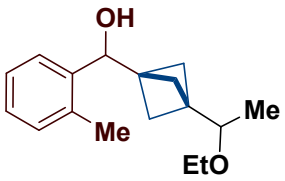
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(phenylethynyl)phenyl)methanol (**21**): The product **21** was purified by column chromatography (PE/EA = 7:1) as a yellow solid (20 mg, 29% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 4H), 7.36-7.31 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.73 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.36 (q, *J* = 6.4 Hz, 1H), 1.96 (brs, 1H), 1.60-1.45 (m, 6H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.02 (dd, *J* = 6.4, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 131.7, 131.5, 128.5, 128.3, 126.1, 126.0, 123.4, 122.3, 89.45, 89.4, 74.0, 73.8, 64.9, 46.4, 42.9, 42.7, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{24}H_{26}NaO_2$ $[M+Na]^+$: 369.1825, found: 369.1828.

Melting point: 60 - 62 °C

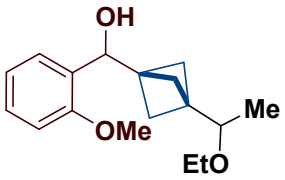


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(*o*-tolyl)methanol (**22**):The product **22** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (27 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.5 Hz, 1H), 7.24-7.07 (m, 3H), 5.03 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.35 (qd, *J* = 6.3, 1.3 Hz, 1H), 2.28 (s, 3H), 1.85 (brs, 1H), 1.63-1.47 (m, 6H), 1.13 (td, *J* = 7.0, 0.7 Hz, 3H), 1.01 (dd, *J* = 6.4, 2.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 134.7, 130.1, 127.1, 126.1, 125.7, 74.0, 69.8, 64.8, 46.6, 42.8, 42.7, 19.4, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{17}H_{24}NaO_2$ $[M+Na]^+$: 283.1669, found: 283.1672.

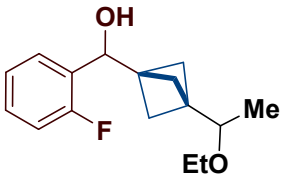


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(2-methoxyphenyl)methanol (**23**): The product **23** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (37 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 6.96-6.91 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.90 (s, 1H), 3.80 (s, 3H), 3.51-3.41 (m, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.68 (brs, 1H), 1.67-1.41 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 129.8, 128.2, 127.6, 127.5, 120.7, 110.5, 74.1, 71.34, 71.3, 64.8, 55.2, 46.8, 42.5, 42.1, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{17}H_{24}NaO_3$ $[M+Na]^+$: 299.1618, found: 299.1623.



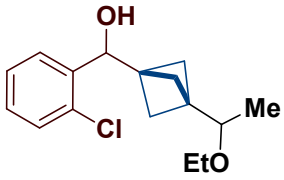
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(2-fluorophenyl)methanol (**24**): The product **24** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (42 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 1H), 7.25-7.18 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03-6.95 (m, 1H), 5.04 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.10 (brs, 1H), 1.61-1.45 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).

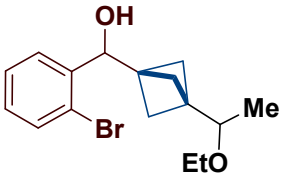
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, *J* = 243.6 Hz), 128.9 (d, *J* = 13.4 Hz), 128.6 (d, *J* = 8.2 Hz), 127.4 (d, *J* = 1.8 Hz), 127.36 (d, *J* = 1.8 Hz), 124.0 (d, *J* = 3.4 Hz), 115.0 (d, *J* = 21.8 Hz), 73.9, 67.8, 64.8, 46.3, 42.3, 42.2, 17.1, 15.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.32 - -119.46 (m).

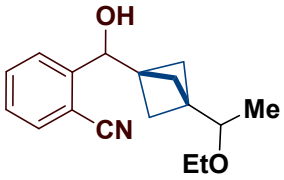
HRMS(ESI) m/z calcd. for $C_{16}H_{21}NaO_2$ $[M+Na]^+$: 287.1418, found: 287.1419.



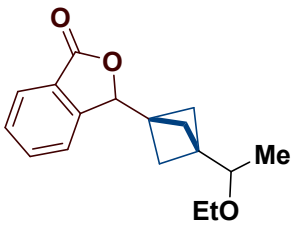
(2-Chlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**25**): The product **25** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (45 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.17 (td, *J* = 7.7, 1.6 Hz, 1H), 5.24 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.11 (brs, 1H), 1.65-1.45 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 132.2, 129.2, 128.3, 127.6, 126.8, 74.0, 69.7, 64.8, 46.6, 42.7, 42.4, 17.2, 15.7.
HRMS(ESI) m/z calcd. for $C_{16}H_{21}ClNaO_2$ $[M+Na]^+$: 287.1418, found: 287.1419.



(2-Bromophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**26**): The product **26** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (52 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.09 (td, *J* = 7.8, 1.7 Hz, 1H), 5.21 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.17 (brs, 1H), 1.65-1.45 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 132.5, 128.7, 127.9, 127.5, 122.3, 74.0, 71.9, 64.8, 46.7, 42.8, 42.4, 17.2, 15.7.
HRMS(ESI) m/z calcd. for $C_{16}H_{21}BrNaO_2$ $[M+Na]^+$: 347.0617, found: 347.0620.



2-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)benzonitrile (**27**): The product **27** was purified by column chromatography (PE/EA = 7:1) as a yellow oil (43 mg, 79% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.53 (m, 3H), 7.33 (td, *J* = 7.4, 2.0 Hz, 1H), 5.15 (s, 1H), 3.44 (qd, *J* = 7.0, 1.8 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.51 (brs, 1H), 1.64-1.46 (m, 6H), 1.10 (td, *J* = 7.0, 1.7 Hz, 3H), 0.99 (dd, *J* = 6.4, 2.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 132.9, 132.5, 127.7, 126.7, 117.8, 110.3, 73.8, 71.6, 64.9, 46.5, 42.8, 42.7, 17.1, 15.7.
HRMS(ESI) m/z calcd. for $C_{17}H_{21}NNaO_2$ $[M+Na]^+$: 294.1465, found: 294.1467.

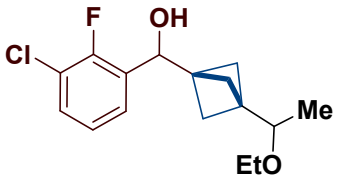


3-(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)isobenzofuran-1(3*H*)-one (**28**): The product **28** was purified by column chromatography (PE/acetone = 7:1) as a colorless oil (20 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.65 (td, *J* = 7.5, 0.7 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 5.43 (s, 1H), 3.51-3.42 (m, 2H), 3.37 (qd, *J* = 6.4, 2.5 Hz, 1H), 1.76-1.58 (m, 6H), 1.16-1.09 (m, 3H), 1.03 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 147.9, 133.8, 129.2, 126.1, 125.9, 122.5, 80.4, 73.7, 64.9, 47.0, 44.0, 39.2, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{17}H_{20}NaO_3$ $[M+Na]^+$: 375.1389, found: 375.1392.



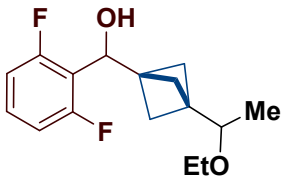
(3-Chloro-2-fluorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methano (**29**): The product **29** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (43 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 2H), 7.07 (t, *J* = 7.9 Hz, 1H), 5.05 (s, 1H), 3.46 (qd, *J* = 7.0, 0.5 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 2.08 (brs, 1H), 1.61-1.45 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1 (d, *J* = 246.3 Hz), 130.8 (d, *J* = 13.6 Hz), 129.3, 125.8 (d, *J* = 3.0 Hz), 125.78 (d, *J* = 3.0 Hz), 124.6 (d, *J* = 4.4 Hz), 120.8 (d, *J* = 18.1 Hz), 73.9, 67.8, 64.9, 46.4, 42.5, 42.2, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.45 (q, *J* = 6.8 Hz).

HRMS(ESI) m/z calcd. for $C_{16}H_{20}ClFNaO_2$ $[M+Na]^+$: 321.1028, found: 321.1032.



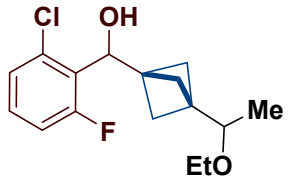
(2,6-Difluorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**30**): The product **30** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (38 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.14 (m, 1H), 6.85 (t, *J* = 8.5 Hz, 2H), 5.06 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.36 (q, *J* = 6.4 Hz, 1H), 2.44 (brs, 1H), 1.72-1.49 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (dd, *J* = 245.6, 8.7 Hz), 129.0 (t, *J* = 10.6 Hz), 117.5 (t, *J* = 16.8 Hz), 111.8 (t, *J* = 26.1 Hz), 73.9, 67.3, 64.9, 46.8, 42.0, 41.9, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.29 (q, *J* = 6.8 Hz).

HRMS(ESI) m/z calcd. for $C_{16}H_{20}F_2NaO_2$ $[M+Na]^+$: 305.1324, found: 305.1325.



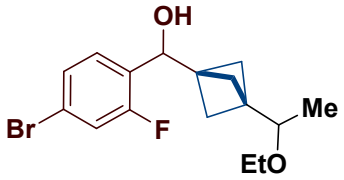
(2-Chloro-6-fluorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**31**): The product **31** was purified by column chromatography (PE/EA = 10:1) as a colorless oil (47 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.07 (m, 2H), 7.01-6.89 (m, 1H), 5.24 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.36 (q, *J* = 6.4 Hz, 1H), 2.67 (brs, 1H), 1.72-1.51 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H).

13C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 246.1 Hz), 133.7 (d, *J* = 7.4 Hz), 129.0 (d, *J* = 10.3 Hz), 127.2 (d, *J* = 14.3 Hz), 125.8 (d, *J* = 3.1 Hz), 114.9 (d, *J* = 23.4 Hz), 73.9, 70.7, 64.9, 47.1, 42.1, 41.8, 17.1, 15.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.12 (d, *J* = 9.6 Hz).

HRMS(ESI) m/z calcd. for $C_{16}H_{20}ClFNaO_2$ $[M+Na]^+$: 321.1028, found: 321.1032.



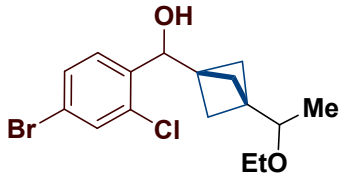
(4-Bromo-2-fluorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**32**): The product **32** was purified by column chromatography (PE/EA = 10:1) as a yellow oil (50 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.19 (d, *J* = 9.9 Hz, 1H), 5.01 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 1.94 (brs, 1H), 1.62-1.45 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, *J* = 248.4 Hz), 128.7 (d, *J* = 4.7 Hz), 128.3 (d, *J* = 13.7 Hz), 127.5 (d, *J* = 3.5 Hz), 120.9 (d, *J* = 9.5 Hz), 118.71 (d, *J* = 25.1 Hz), 118.7 (d, *J* = 25.1 Hz), 73.9, 67.5, 67.4, 64.9, 46.3, 42.5, 42.47, 42.1, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.45- -116.70 (m).

HRMS(ESI) m/z calcd. for $C_{16}H_{20}BrFNaO_2$ $[M+Na]^+$: 365.0523, found: 365.0524.



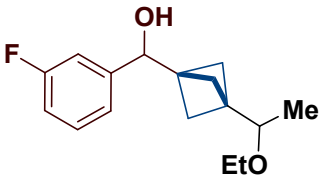
(4-Bromo-2-chlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**33**): The product **33** was purified by column chromatography (PE/EA = 12:1) as a yellow oil (53 mg, 74% yield, d.r. = 3:1. The d.r. value were determined by ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$) mixture of diastereomers, minor diastereomer in brackets [ ]: δ [7.84 (d, *J* = 2.4 Hz, 0.23H)], 7.60 (d, *J* = 2.4 Hz, 0.77H), 7.35-7.27 (m, 1H), 7.16 (d, *J* = 8.5 Hz,

0.81H), [7.10 (d, *J* = 8.5 Hz, 0.23H)], [5.20 (s, 0.24H)], 5.17 (s, 0.76H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.34 (d, *J* = 6.4 Hz, 1H), 2.18 (brs, 1H), 1.65-1.43 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) mixture of diastereomers, minor diastereomer in brackets [ ]: δ 141.6, [139.5], [132.5], [132.3], 131.4, [131.1], [130.8], 130.7, 130.61, 130.6, [128.85], 128.8, 73.9, [72.5], 69.5, 64.9, 46.6, 42.7, 42.2, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{16}H_{20}BrClNaO_2$ $[M+Na]^+$: 381.0227, found: 381.0223.



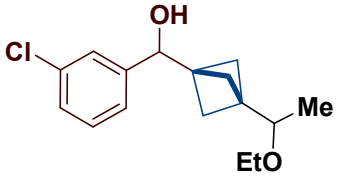
(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(3-fluorophenyl)methanol (**34**): The product **34** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (39 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 1H), 7.02-6.90 (m, 3H), 4.69 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.4 Hz, 1H), 2.03 (brs, 1H), 1.59-1.43 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 244.0 Hz), 144.5 (d, *J* = 6.8 Hz), 129.6 (d, *J* = 8.1 Hz), 121.7 (d, *J* = 2.7 Hz), 114.2 (d, *J* = 21.1 Hz), 112.9 (d, *J* = 21.8 Hz), 112.87 (d, *J* = 21.8 Hz), 73.9, 73.4, 73.38, 64.9, 46.3, 42.8, 42.7, 17.1, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.30- 113.37 (m).

HRMS(ESI) m/z calcd. for $C_{16}H_{21}FNaO_2$ $[M+Na]^+$: 287.1418, found: 287.1419.

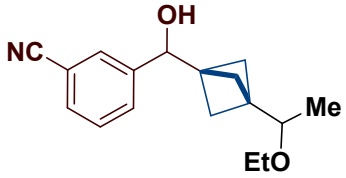


(3-Chlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**35**): The product **35** was purified by column chromatography (PE/EA = 7:1) as a yellow oil (38 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 3H), 7.18-7.11 (m, 1H), 4.71 (s, 1H), 3.50 (q, *J* = 7.0 Hz, 2H), 3.38 (q, *J* = 6.3 Hz, 1H), 2.03 (brs, 1H), 1.62-1.47 (m, 6H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.04 (dd, *J* = 6.3, 0.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 134.2, 129.5, 127.52, 127.5, 126.14, 126.1, 124.3, 124.2, 73.9, 73.4, 64.9, 46.3, 42.8, 42.7, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{16}H_{21}ClNaO_2$ $[M+Na]^+$: 303.1122, found: 303.1124.



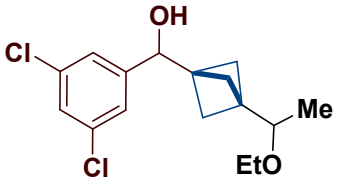
3-((3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)benzonitrile (**36**): The product **36** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (35 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.53 (m, 2H), 7.52-7.40 (m, 2H), 4.76 (s, 1H), 3.53-3.42 (m,

2H), 3.36 (q, *J* = 6.4 Hz, 1H), 1.95 (brs, 1H), 1.59-1.44 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 131.0, 130.5, 129.6, 129.58, 129.0, 119.0, 112.3, 73.8, 73.0, 64.9, 46.2, 43.0, 42.6, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{17}H_{21}NNaO_2$ $[M+Na]^+$: 294.1465, found: 294.1466.

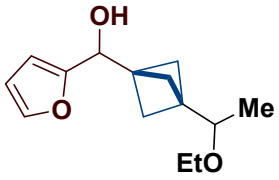


(3,5-Dichlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**37**): The product **37** was purified by column chromatography (PE/EA = 8:1) as a colorless oil (41 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 1H), 7.13 (d, *J* = 1.7 Hz, 2H), 4.65 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.36 (q, *J* = 6.3 Hz, 1H), 2.08 (brs, 1H), 1.61-1.43 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 134.9, 127.52, 127.5, 124.6, 124.5, 73.9, 72.94, 72.9, 64.9, 46.3, 42.9, 42.5, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{16}H_{20}Cl_2NaO_2$ $[M+Na]^+$: 337.0733, found: 337.0738.

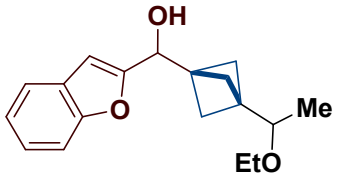


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(furan-2-yl)methanol (**38**): The product **38** was purified by column chromatography (PE/EA = 8:1) as a yellow oil (10 mg, 21% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 6.35-6.29 (m, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 4.70 (s, 1H), 3.51 (q, *J* = 7.0 Hz, 2H), 3.39 (q, *J* = 6.3 Hz, 1H), 1.74-1.59 (m, 6H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 142.1, 110.2, 106.4, 106.3, 74.0, 68.0, 64.9, 47.1, 42.6, 41.4, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{14}H_{20}NaO_3$ $[M+Na]^+$: 259.1305, found: 259.1307.

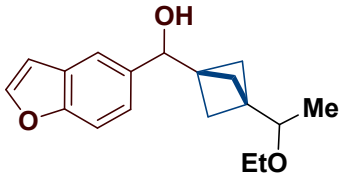


Benzofuran-2-yl(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**39**): The product **39** was purified by column chromatography (PE/EA = 7:1) as a yellow oil (13 mg, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.29-7.18 (m, 2H), 6.62 (s, 1H), 4.84 (s, 1H), 3.50 (q, *J* = 7.0 Hz, 2H), 3.40 (q, *J* = 6.4 Hz, 1H), 2.04 (brs, 1H), 1.78-1.63 (m, 6H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.76, 154.9, 128.3, 124.1, 122.9, 121.1, 111.4, 103.0, 102.9, 73.9, 68.5, 68.47, 64.9, 47.1, 42.6, 41.3, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{18}H_{22}NaO_3$ $[M+Na]^+$: 309.1461, found: 309.1462.



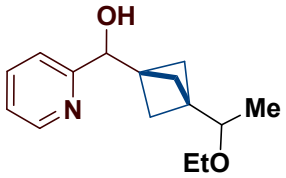
Benzofuran-5-yl(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**40**): The product **40** was purified by column chromatography (PE/EA = 7:1) as a yellow solid (11 mg, 19% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.1 Hz, 1H), 7.50 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 1.1Hz, 1H), 6.75 (d, *J* = 1.3 Hz, 1H), 4.82 (s, 1H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.3 Hz, 1H), 1.92 (brs, 1H), 1.65-1.47 (m, 6H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 145.4, 136.6, 127.4, 122.7, 122.68, 118.6, 118.56, 111.0, 106.8, 74.3, 74.0, 64.9, 46.4, 43.1, 42.8, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{18}H_{22}NaO_3$ $[M+Na]^+$: 309.1461, found: 309.1463.

Melting point: 64 - 65 °C

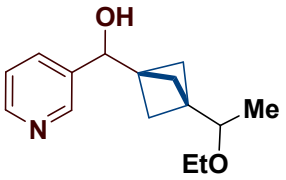


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(pyridin-2-yl)methanol (**41**): The product **41** was purified by column chromatography (PE/acetone = 10:1) as a colorless oil (23 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.7 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.21-7.10 (m, 2H), 4.71 (s, 1H), 4.21 (brs, 1H), 3.50-3.41 (m, 2H), 3.33 (qd, *J* = 6.3, 1.4 Hz, 1H), 1.60-1.47 (m, 6H), 1.11 (td, *J* = 7.0, 2.6 Hz, 3H), 1.00 (dd, *J* = 6.3, 3.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.41, 159.4, 148.3, 136.3, 122.4, 121.1, 74.0, 72.4, 64.8, 46.6, 43.0, 42.4, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{15}H_{21}NNaO_2$ $[M+Na]^+$: 270.1465, found: 270.1469.

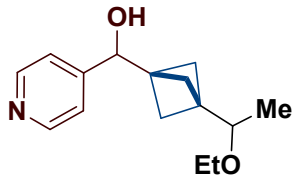


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(pyridin-3-yl)methanol (**42**): The product **42** was purified by column chromatography (PE/acetone = 7:1) as a colorless oil (23 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 2H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.26-7.22 (m, 1H), 4.74 (s, 1H), 3.45 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 6.3 Hz, 1H), 2.97 (brs, 1H), 1.60-1.44 (m, 6H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.00 (dd, *J* = 6.4, 0.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.8, 137.5, 133.9, 123.4, 73.9, 71.7, 64.9, 46.3, 43.1, 42.8, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{15}H_{21}NNaO_2$ $[M+Na]^+$: 270.1465, found: 270.1469.

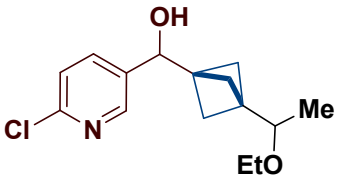


(3-(1-Ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(pyridin-4-yl)methanol (**43**): The product **43** was purified by column chromatography (PE/acetone = 3:1) as a colorless oil (22 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.4 Hz, 2H), 7.17 (d, *J* = 5.3 Hz, 2H), 4.69 (s, 1H), 3.45 (q, *J* = 7.0 Hz, 2H), 3.33 (q, *J* = 6.2 Hz, 1H), 1.60-1.39 (m, 6H), 1.11 (t, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 5.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 121.2, 73.8, 72.5, 64.9, 46.4, 42.9, 42.3, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{15}H_{21}NNaO_2$ $[M+Na]^+$: 270.1465, found: 270.1468.

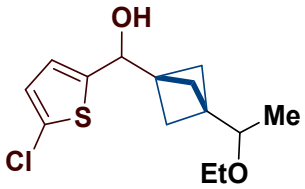


(6-Chloropyridin-3-yl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**44**): The product **44** was purified by column chromatography (PE/EA = 2:1) as a colorless oil (30 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.0 Hz, 1H), 7.58 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 4.74 (s, 1H), 3.45 (qd, *J* = 7.0, 1.7 Hz, 2H), 3.34 (q, *J* = 6.3 Hz, 1H), 2.42 (brs, 1H), 1.60-1.41 (m, 6H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.6, 136.7, 136.3, 124.0, 73.8, 71.1, 64.9, 46.2, 43.1, 42.7, 17.1, 15.7.

HRMS(ESI) m/z calcd. for $C_{15}H_{20}ClNNaO_2$ $[M+Na]^+$: 304.1075, found: 304.1080.

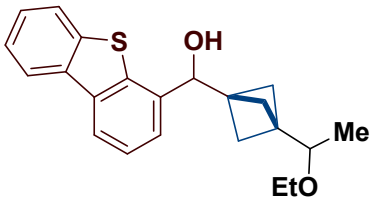


(5-Chlorothiophen-2-yl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**45**): The product **45** was purified by column chromatography (PE/EA = 7:1) as a yellow oil (12 mg, 21% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J* = 3.8 Hz, 1H), 6.68 (d, *J* = 3.7 Hz, 1H), 4.85 (s, 1H), 3.50 (q, *J* = 7.0 Hz, 2H), 3.39 (q, *J* = 6.4 Hz, 1H), 1.99 (brs, 1H), 1.68-1.56 (m, 6H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 129.1, 125.6, 123.3, 123.26, 73.9, 70.7, 65.0, 46.6, 42.5, 42.4, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{14}H_{19}ClNaO_2S$ $[M+Na]^+$: 309.0686, found: 309.0692.

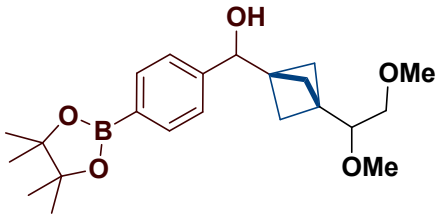


Dibenzo[*b,d*]thiophen-4-yl(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**46**): The product **46** was purified by column chromatography (PE/acetone = 6:1) as a colorless oil (20 mg, 28% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.12 (m, 1H), 8.08 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.88-7.82 (m, 1H), 7.49-7.39 (m, 4H), 5.11 (s, 1H), 3.48-3.40 (m, 2H), 3.32 (qd, *J* = 6.3, 1.2 Hz, 1H), 2.18 (brs, 1H), 1.67-1.52 (m, 6H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.99 (dd, *J* = 6.4, 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.2, 136.5, 136.2, 135.6, 126.9, 124.6, 124.4, 124.1, 122.7, 121.7, 120.7, 73.9, 73.6, 64.9, 47.0, 42.6, 42.3, 17.2, 15.8.

HRMS(ESI) m/z calcd. for $C_{22}H_{24}NaO_2S$ $[M+Na]^+$: 375.1389, found: 375.1392.

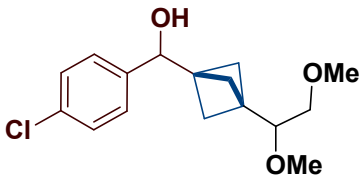


(3-(1,2-Dimethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (**47**): The product **47** was purified by column chromatography (PE/EA = 4:1) as a colorless oil (39 mg, 50% yield, d.r. = 3:1. The d.r. value were determined by ^{13}C NMR).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.72 (s, 1H), 3.59 - 3.22 (m, 9H), 1.91 (brs, 1H), 1.64-1.51 (m, 6H), 1.34 (s, 12H).

13C NMR (100 MHz, $CDCl_3$) mixture of diastereomers, minor diastereomer in brackets [ ]: δ [144.9], 144.8, [134.8], 134.7, [125.4], 125.3, 83.9, 79.0, [74.0], 73.9, 73.8, [72.2], [71.6], [70.6], 59.25, [59.2], 58.8, [47.6], 47.3, [43.8], 43.4, 40.1, [39.0], 25.0.

HRMS(ESI) m/z calcd. for $C_{22}H_{33}BNaO_5$ $[M+Na]^+$: 411.2313, found: 411.2318.

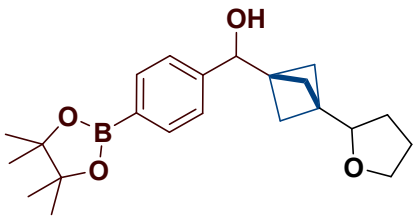


(4-Chlorophenyl)(3-(1,2-dimethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**48**): The product **48** was purified by column chromatography (PE/EA = 3:1) as a colorless oil (30 mg, 51% yield, d.r. = 3:1. The d.r. value were determined by ^{13}C NMR).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 4.67 (s, 1H), 3.58-3.44 (m, 2H), 3.40-3.36 (m, 2H), 3.35-3.27 (m, 5H), 2.03 (brs, 1H), 1.63-1.50 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) mixture of diastereomers, minor diastereomer in brackets [ ]: δ [140.2], 140.17, [133.1], 133.07, 128.4, [128.38], [127.4], 127.36, 78.9, 73.6, [73.3], 73.2, [72.1], [71.5], [70.6], 59.2, [59.0], 58.8, [47.5], 47.2, [43.7], 43.4, 40.1, [39.0].

HRMS(ESI) m/z calcd. for $C_{16}H_{21}ClNaO_3$ $[M+Na]^+$: 319.1071, found: 319.1067.



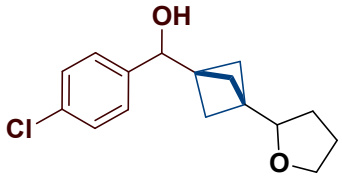
(3-(Tetrahydrofuran-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (**49**): The product **49** was purified by column chromatography (DCM/EA = 8:1) as a white solid (51 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 1H), 3.85-3.74 (m, 2H), 3.72-3.65 (m, 1H), 1.92 (brs, 1H), 1.86-1.72 (m, 3H), 1.58-1.42 (m, 7H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 134.7, 125.4, 83.9, 78.0, 74.0, 68.5, 46.1, 43.3, 41.5, 28.1, 26.0, 25.0.

HRMS(ESI) m/z calcd. for $C_{22}H_{31}BNaO_4$ $[M+Na]^+$: 393.2208, found: 393.2214.

Melting point: 118 - 120 °C



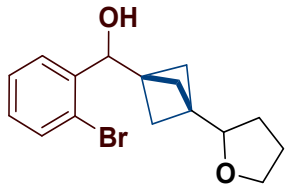
(4-Chlorophenyl)(3-(tetrahydrofuran-2-yl)bicyclo[1.1.1]pentan-1-yl)methanol (**50**): The product **50** was purified by column chromatography (PE/EA = 3:1) as a white solid (40 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 3.85-3.74 (m, 2H), 3.73-3.63 (m, 1H), 2.13 (brs, 1H), 1.87-1.73 (m, 3H), 1.58-1.39 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 133.0, 128.4, 127.4, 77.9, 73.3, 68.5, 46.0, 43.3, 41.5, 28.1, 26.0.

HRMS(ESI) m/z calcd. for $C_{16}H_{19}ClNaO_2$ $[M+Na]^+$: 301.0966, found: 301.0959.

Melting point: 81 - 83 °C

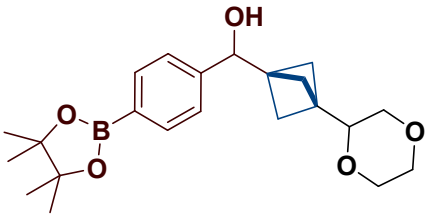


(2-Bromophenyl)(3-(tetrahydrofuran-2-yl)bicyclo[1.1.1]pentan-1-yl)methanol (**51**): The product **51** was purified by column chromatography (DCM/EA = 10:1) as a colorless oil (45 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 5.24 (s, 1H), 3.87-3.75 (m, 2H), 3.74-3.66 (m, 1H), 1.87 (s, 1H), 1.86-1.77 (m, 3H), 1.66-1.48 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 132.5, 128.7, 127.91, 127.9, 127.5, 122.3, 78.0, 71.9, 68.4, 46.4, 42.9, 41.5, 28.1, 26.0.

HRMS(ESI) m/z calcd. for $C_{16}H_{19}BrNaO_2$ $[M+Na]^+$: 345.0461, found: 345.0460.



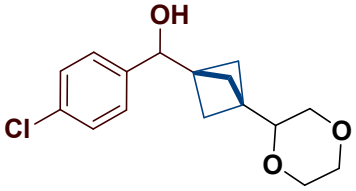
(3-(1,4-Dioxan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxa-borolan-2-yl)phenyl)methanol (**52**): The product **52** was purified by column chromatography (PE/EA = 4:1) as a white solid (38 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.70 (s, 1H), 3.74-3.57 (m, 4H), 3.54-3.43 (m, 2H), 3.23-3.14 (m, 1H), 2.01 (brs, 1H), 1.60-1.46 (m, 6H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 134.8, 125.3, 83.9, 73.9, 73.8, 68.9, 66.8, 66.4, 46.6, 43.3, 38.9, 25.0.

HRMS(ESI) m/z calcd. for $C_{22}H_{31}BNaO_5$ $[M+Na]^+$: 409.2157, found: 409.2163.

Melting point: 97 - 99 °C



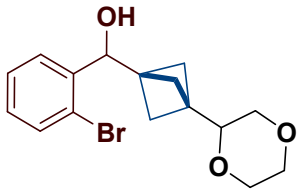
(3-(1,4-Dioxan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanol (**53**): The product **53** was purified by column chromatography (PE/acetone = 4:1) as a white solid (35 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 3.74-3.59 (m, 4H), 3.51 (m, 2H), 3.24-3.16 (m, 1H), 1.97 (brs, 1H), 1.62-1.45 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 133.2, 128.5, 127.4, 73.8, 73.1, 68.8, 66.8, 66.4, 46.5, 43.3, 39.0.

HRMS(ESI) m/z calcd. for $C_{16}H_{19}ClNaO_3$ $[M+Na]^+$: 317.0915, found: 317.0914.

Melting point: 92 - 94 °C

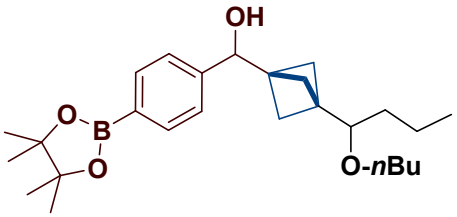


(3-(1,4-Dioxan-2-yl)bicyclo[1.1.1]pentan-1-yl)(2-bromophenyl)methanol (**54**): The product **54** was purified by column chromatography (PE/EA = 5:1) as a colorless oil (42 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.30 (td, *J* = 7.7, 0.9 Hz, 1H), 7.10 (td, *J* = 7.8, 1.7 Hz, 1H), 5.20 (s, 1H), 3.74-3.58 (m, 4H), 3.54-3.44 (m, 2H), 3.27-3.15 (m, 1H), 2.20 (brs, 1H), 1.66-1.52 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 132.5, 128.8, 127.8, 127.5, 122.3, 73.9, 71.6, 68.9, 66.8, 66.4, 46.9, 42.9, 38.9.

HRMS(ESI) m/z calcd. for $C_{16}H_{19}BrNaO_3$ $[M+Na]^+$: 361.0410, found: 361.0409.

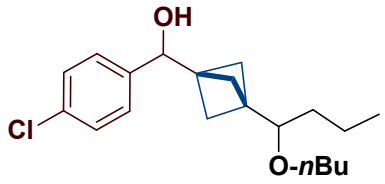


(3-(1-Butoxybutyl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxa-borolan-2-yl)phenyl)methanol (**55**): The product **55** was purified by column chromatography (PE/EA = 9:1) as a white solid (43 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 1H), 3.55-3.45 (m, 1H), 3.36-3.28 (m, 1H), 3.13-3.07 (m, 1H), 1.97 (brs, 1H), 1.58-1.43 (m, 9H), 1.34 (s, 12H), 1.31-1.20 (m, 5H), 0.92-0.82 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 134.7, 125.4, 125.35, 83.9, 78.3, 74.0, 70.7, 46.9, 43.0, 42.4, 34.6, 32.5, 25.0, 19.5, 19.2, 14.2, 14.1.

HRMS(ESI) m/z calcd. for $C_{26}H_{41}BNaO_4$ $[M+Na]^+$: 451.2990, found: 451.2997.

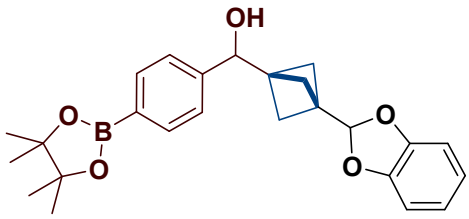


(3-(1-Butoxybutyl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanol (**56**): The product **56** was purified by column chromatography (PE/EA = 7:1) as a colorless oil (40 mg, 59% yield, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 3.56-3.46 (m, 1H), 3.37-3.29 (m, 1H), 3.14-3.08 (m, 1H), 1.98 (brs, 1H), 1.56-1.46 (m, 8H), 1.37-1.23 (m, 6H), 0.91-0.84 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 133.1, 128.4, 127.4, 127.38, 78.3, 73.4, 70.7, 46.8, 43.0, 42.5, 34.6, 32.5, 19.5, 19.2, 14.2, 14.1.

HRMS(ESI) m/z calcd. for $C_{20}H_{29}ClNaO_2$ $[M+Na]^+$: 359.1748, found: 359.1743.



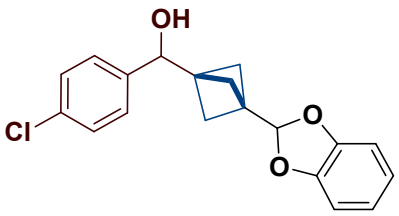
(3-(Benzo[*d*][1,3]dioxol-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (**57**): The product **57** was purified by column chromatography (DCM/EA = 40:1) as a white solid (38 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.81-6.68 (m, 4H), 5.99 (s, 1H), 4.75 (s, 1H), 1.96 (brs, 1H), 1.68 (qd, *J* = 9.5, 1.3 Hz, 6H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 144.5, 134.9, 125.3, 121.4, 108.34, 108.3, 83.9, 73.7, 46.0, 43.9, 39.4, 25.0.

HRMS(ESI) m/z calcd. for $C_{25}H_{29}BNaO_5$ $[M+Na]^+$: 443.2000, found: 443.2002.

Melting point: 110 - 112 °C



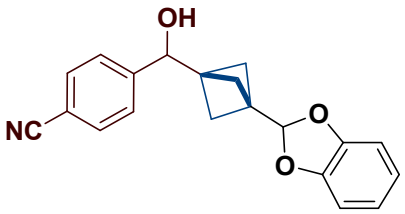
(3-(Benzo[*d*][1,3]dioxol-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanol (**58**): The product **58** was purified by column chromatography (DCM/EA = 40:1) as a white solid (34 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.81-6.70 (m, 4H), 6.00 (s, 1H), 4.72 (s, 1H), 1.94 (brs, 1H), 1.68 (q, *J* = 9.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 139.8, 133.4, 128.5, 127.3, 121.5, 108.4, 108.2, 73.1, 45.9, 43.9, 39.5.

HRMS(ESI) m/z calcd. for $C_{19}H_{17}ClNaO_3$ $[M+Na]^+$: 351.0758, found: 351.0761.

Melting point: 79 - 81 °C



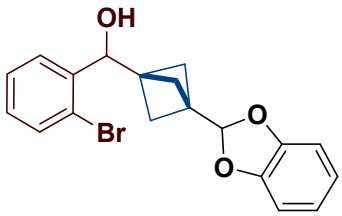
4-((3-(Benzo[*d*][1,3]dioxol-2-yl)bicyclo[1.1.1]pentan-1-yl)(hydroxy)methyl)ben-zonitrile (**59**): The product **59** was purified by column chromatography (DCM/EA = 60:1) as a white solid (42 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.57 (m, 2H), [7.46 (d, *J* = 8.1 Hz, 0.18H)], 7.35 (d, *J* = 8.2 Hz, 1.82H), 6.86-6.69 (m, 4H), 6.00 (s, 1H), 4.80 (s, 1H), 2.30 (brs, 1H), 1.73-1.63 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 146.6, 132.2, 126.7, 121.5, 118.9, 111.3, 108.4, 107.9, 72.9, 45.9, 43.7, 39.5.

HRMS(ESI) m/z calcd. for $C_{20}H_{17}NNaO_3$ $[M+Na]^+$: 342.1101, found: 342.1097.

Melting point: 110 - 112 °C



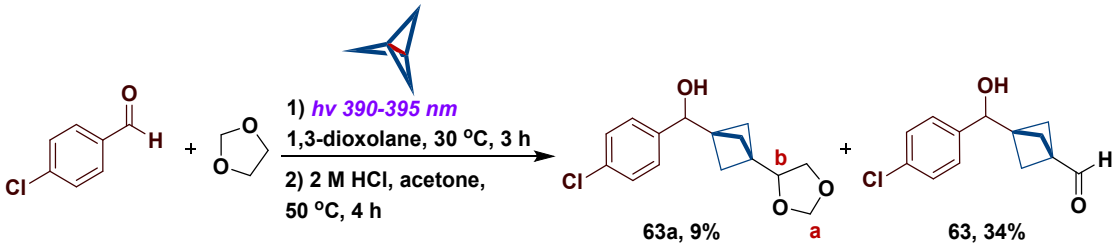
(3-(Benzo[*d*][1,3]dioxol-2-yl)bicyclo[1.1.1]pentan-1-yl)(2-bromophenyl)methanol (**60**): The product **60** was purified by column chromatography (DCM/EA = 100:1) as a colorless oil (52 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.12 (td, *J* = 7.9, 1.7 Hz, 1H), 6.85-6.68 (m, 4H), 6.00 (s, 1H), 5.27 (s, 1H), 1.98 (s, 1H), 1.82-1.69 (m, 6H).

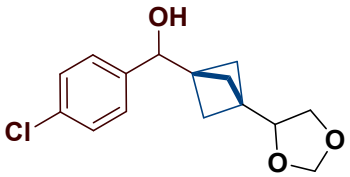
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 140.7, 132.67, 129.0, 127.8, 127.6, 122.3, 121.4, 108.3, 108.27, 71.7, 46.3, 43.6, 39.4.

HRMS(ESI) m/z calcd. for $C_{19}H_{17}BrNaO_3$ $[M+Na]^+$: 395.0253, found: 395.0251.

7. Synthesis and characterization of BCP aldehyde 63



To a 250 mL reaction vial equipped with a magnetic stir bar was added 4-chlorobenzaldehyde (2.8 g, 20.0 mmol, 2.0 equiv), the tube was evacuated and backfilled with argon for three times. Then freshly prepared [1.1.1]propellane (10.0 mmol, 1.0 equiv, 0.7-1.1 M solution in Et_2O) and 1,3-dioxolane (100.0 mL) were added under argon atmosphere. The reaction mixture was sealed and placed in an assembled photoreactor, stirred and irradiated with two 30 W purple LEDs at 30 °C for 3 hours. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* to afford the crude product (**Note**: The crude product obtained mainly contains coupled products at positions **a** and **b**. Due to the similar polarity of these two products, they cannot be separated by column chromatography). The crude product was crudely separated by short column chromatography. Then the separated mixture was dissolved in 30 mL of acetone and 2 M HCl (v:v=1:1), and the reaction mixture was heated to 50°C for 4 hours. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* to afford the crude product. The crude product was purified by column chromatography using (DCM : MeOH = 200 : 1 → 80 : 1) to afford compound **61a** as a colorless oil (258 mg, 9% yield) and compound **63** as a white solid (803 mg, 34% yield).

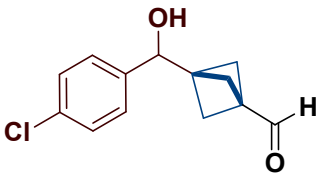


(3-(1,3-Dioxolan-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanol (**63a**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.21-7.16 (m, 2H), 4.93 (s, 1H), 4.85 (s, 1H), 4.71 (s, 1H), 4.02-3.97 (m, 1H), 3.84 (t, *J* = 7.3 Hz, 1H), 3.57-3.51 (m, 1H), 1.89 (brs, 1H), 1.63-1.48 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 133.3, 128.5, 127.4, 127.37, 95.6, 74.6, 73.2, 66.8, 46.2, 43.9, 39.7.

HRMS(ESI) m/z calcd. for $C_{15}H_{17}ClNaO_3$ $[M+Na]^+$: 303.0758, found: 303.0763.



3-((4-Chlorophenyl)(hydroxy)methyl)bicyclo[1.1.1]pentane-1-carbaldehyde (**63**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H),

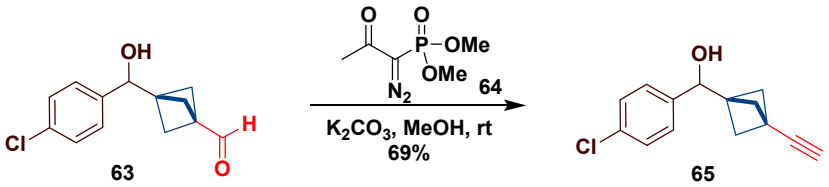
4.74 (s, 1H), 1.88 (qd, *J* = 9.6, 1.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 139.5, 133.5, 128.7, 127.3, 72.9, 48.2, 44.4, 43.9.

HRMS(ESI) m/z calcd. for $C_{13}H_{13}ClNaO_2$ $[M+Na]^+$: 259.0496, found: 259.0495.

8. Post-functionalizations

8.1 Further functionalization of BCP aldehyde **63**

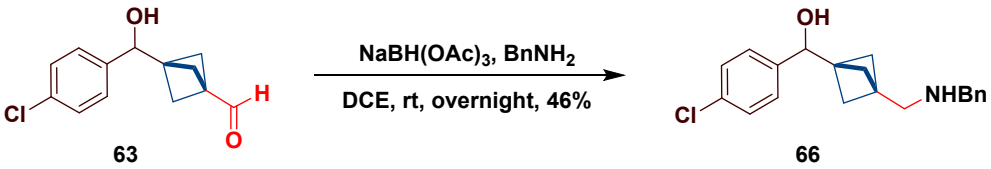


(4-Chlorophenyl)(3-ethynylbicyclo[1.1.1]pentan-1-yl)methanol (**65**):To an oven-dried 10 mL storage tube with a high vacuum valve, a magnetic stir bar, K_2CO_3 (28 mg, 0.2 mmol, 2.0 equiv.), compound **63** (24 mg, 0.10 mmol, 1.0 equiv.) were added. The tube was evacuated and backfilled with argon for three times. Then Ohira−Bestmann reagent **64** (23 mg, 0.12 mmol, 1.2 equiv) and MeOH (1.0 mL) were added under argon atmosphere. And the reaction was stirred for 2 h at room temperature. TLC analysis indicated the complete conversion, the reaction mixture was concentrated under vacuum to afford the crude product. The crude product was purified by column chromatography using (PE/EA = 5:1) to afford compound **65** as a colorless oil (16 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 1H), 7.19-7.14 (m, 1H), 4.68 (s, 1H), 2.09 (s, 1H), 1.90 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 133.5, 128.6, 127.3, 82.9, 72.8, 68.6, 52.4, 45.2, 28.5.

HRMS(ESI) m/z calcd. for $C_{14}H_{14}ClO$ $[M+H]^+$:233,0728 found: 233.0720.

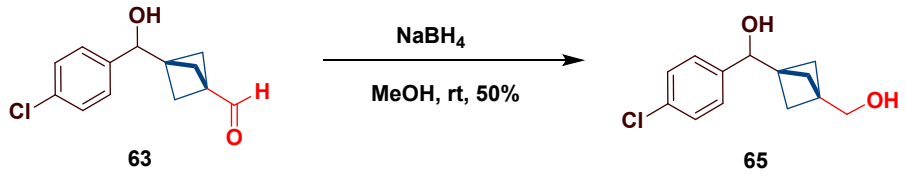


(3-((Benzylamino)methyl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanol (**66**): Under nitrogen atmosphere, compound **63** (47 mg, 0.20 mmol, 1.0 eq.), $BnNH_2$ (32 mg, 0.3 mmol, 1.5 eq.), $NaBH(OAc)_3$ (212 mg, 1.0 mmol, 1.5 eq.) and DCE (3.0 mL) were added to a 10 mL reaction vial equipped with a magnetic stir bar. The reaction mixture was allowed to stir at room temperature for overnight. TLC analysis indicated the complete conversion, the mixture was quenched with saturated $NaHCO_3$ (aq), the mixture was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by column chromatography using (DCM/MeOH = 40:1) to afford compound **66** as a yellow oil (30 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 7H), 7.16 (d, *J* = 8.3 Hz, 2H), 4.65 (s, 1H), 3.78 (s, 2H), 2.66 (s, 2H), 2.46 (brs, 2H), 1.59-1.48 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 133.1, 128.6, 128.4, 127.4, 127.3, 73.2, 53.8, 50.0, 47.6, 43.4, 39.4.

HRMS(ESI) m/z calcd. for $C_{20}H_{22}ClNNaO$ $[M+Na]^+$:350.1282, found: 350.1288.

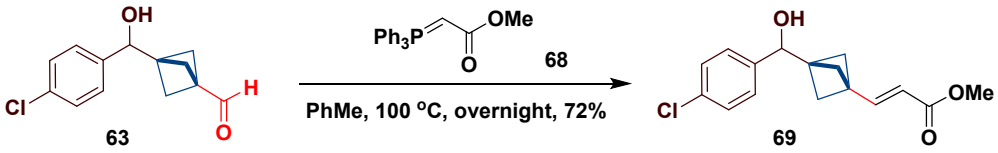


(4-Chlorophenyl)(3-(hydroxymethyl)bicyclo[1.1.1]pentan-1-yl)methanol (**65**): To an oven-dried 10 mL glass tube equipped with a Teflon septum and a magnetic stir bar were added compound **63** (47 mg, 0.20 mmol, 1.0 eq.), $NaBH_4$ (16 mg, 0.40 mmol, 2.0 eq.) and MeOH (3.0 mL). The reaction was stirred for 2 h at room temperature. TLC analysis indicated the complete conversion, the reaction was quenched with (aq) NH_4Cl (10 mL), then the aqueous phase was extracted with (2 × 10 mL) EtOAc. The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography using (PE/EA = 2:1) to afford compound **65** as a colorless oil (24 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 1H), 3.56 (s, 2H), 2.03 (brs, 1H), 1.58-1.48 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 133.2, 128.4, 127.4, 73.3, 63.3, 46.5, 43.4, 40.4.

HRMS(ESI) m/z calcd. for $C_{13}H_{15}ClNaO_2$ $[M+Na]^+$:261.0653, found: 261.0655.



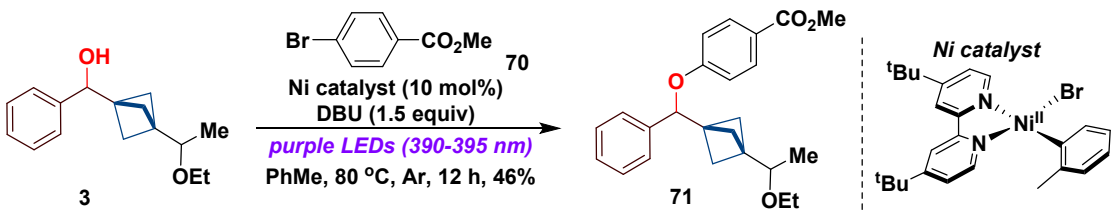
Methyl (*E*)-3-(3-((4-chlorophenyl)(hydroxy)methyl)bicyclo[1.1.1]pentan-1-yl)acrylate (**69**): To an oven-dried 10 mL glass tube equipped with a Teflon septum and a magnetic stir bar were added ethyl (triphenylphosphoranylidene)acetate **68** (40 mg, 0.12 mmol, 1.2 equiv), compound **63** (24 mg, 0.10 mmol, 1.0 equiv) and PhMe (1.0 mL). The reaction mixture was heated to stir at 100 °C for overnight. TLC analysis indicated the complete conversion, the reaction mixture was concentrated under vacuum to afford the crude product. The crude product was purified by column chromatography using (PE/EA = 5:1) to afford compound **69** as a colorless oil (21 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 15.6 Hz, 1H), 5.72 (d, *J* = 15.6 Hz, 1H), 4.72 (s, 1H), 3.71 (s, 3H), 1.95 (brs, 1H), 1.77-1.67 (m, 6H).

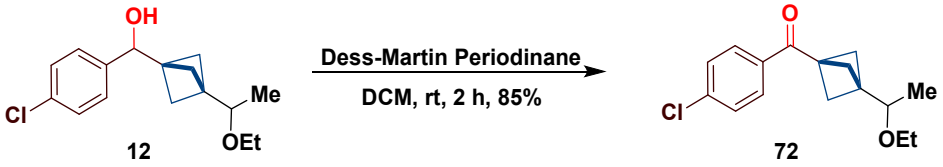
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 146.6, 139.9, 133.4, 128.6, 127.4, 121.3, 73.0, 51.7, 49.7, 43.6, 40.3.

HRMS(ESI) m/z calcd. for $C_{16}H_{17}ClNaO_3$ $[M+Na]^+$:315.0758, found: 315.0756.

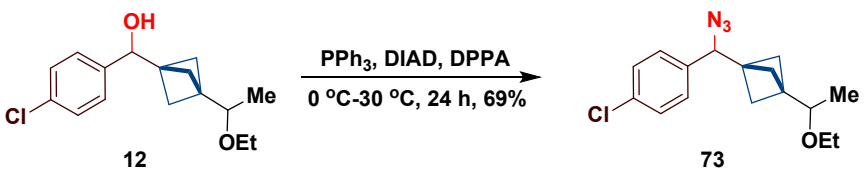
8.2 Further functionalization of BCP benzylalcohols



Methyl4-((3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methoxy)benzoate (**3**):
To an oven-dried 10 mL storage tube with a high vacuum valve, a magnetic stir bar, Methyl 4-bromobenzoate (44 mg, 0.20 mmol, 1.0 equiv), Ni catalyst (10 mol %, 0.02 mmol), and alcohols **3** (98 mg, 0.4 mmol, 2.0 equiv) were added. The tube was evacuated and backfilled with argon for three times. Then DBU (0.30 mmol, 1.5 equiv,) and toluene (1.0 mL) were added under argon atmosphere. The reaction mixture was then irradiated with two purple LED lamps (1.0 cm from the tube, optical power: 200 ± 10mw/cm^2) for 24 hours at 80 °C. After cooling to room temperature, the reaction mixture was concentrated under vacuum to afford the crude product. The crude product was purified by column chromatography using (PE/EA = 10:1) to afford compound **71** as a yellow solid (35 mg, 46% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.35-7.28 (m, 2H), 7.27-7.21 (m, 3H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.19 (s, 1H), 3.83 (s, 3H), 3.48 (q, *J* = 7.0 Hz, 2H), 3.36 (q, *J* = 6.2 Hz, 1H), 1.67-1.53 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (dd, *J* = 6.4, 1.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 162.3, 138.6, 131.5, 128.5, 127.7, 126.2, 126.18, 122.5, 115.5, 79.5, 74.0, 64.9, 51.9, 47.0, 43.7, 41.7, 17.2, 15.8.
HRMS(ESI) m/z calcd. for $C_{24}H_{28}NaO_4$ [M+Na]$^+$: 403.1880, found: 403.1879.
Melting point: 84 - 86 °C



(4-Chlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methanone (**72**): To a 25 mL reaction vial equipped with a magnetic stir bar was added compound **12** (83 mg 0.30 mmol, 1.0 equiv.), Dess-Martin periodinane (255 mg 0.60 mmol, 2.0 equiv.) and dry DCM (5.0 mL), the reaction was stirred for 2 hours at room temperature. TLC analysis indicated the complete conversion, the reaction was quenched with (aq) $NaHCO_3$ (10 mL) and (aq) $Na_2S_2O_3$ (10 mL), then the aqueous phase was extracted with (2 × 10 mL) DCM. The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography using (PE/EA = 10:1) to afford compound **72** as a colorless oil (71 mg, 85% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 3.58-3.46 (m, 2H), 3.43 (q, *J* = 6.4 Hz, 1H), 2.22-2.12 (m, 6H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.09 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 139.4, 134.9, 130.4, 128.9, 73.5, 65.0, 51.8, 43.9, 43.3, 16.9, 15.8.
HRMS(ESI) m/z calcd. for $C_{16}H_{19}ClNaO_2$ [M+Na]$^+$: 301.0966, found: 301.0964.

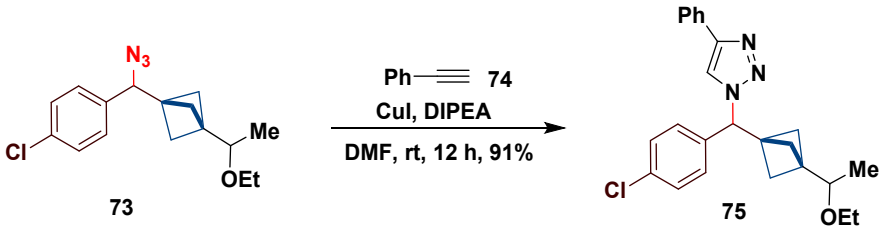


1-(Azido(4-chlorophenyl)methyl)-3-(1-ethoxyethyl)bicyclo[1.1.1]pentane (**73**): Under nitrogen atmosphere, alcohols **12** (120 mg, 0.43 mmol, 1.0 eq.), PPh_3 (224 mg, 0.86 mmol, 2.0 eq.) and dry THF (5.0 mL) were added to a 25 mL reaction vial equipped with a magnetic stir bar and cooled to 0 °C, then DIAD (172 mg, 0.86 mmol, 2.0 eq.) was added slowly added and the mixture was stirred for 20 minutes. DPPA (244 mg, 0.86 mmol, 2.0 eq.) was then added by syringe, and the reaction was heated to 35°C for 24 hours. TLC analysis indicated the complete conversion, the reaction mixture was concentrated under vacuum to afford the crude product. The crude product was purified by column chromatography using (PE/acetone = 300:1) to afford compound **73** as a yellow oil (90 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.55 (s, 1H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.35 (q, *J* = 6.3 Hz, 1H), 1.63-1.51 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.01 (dd, *J* = 6.4, 1.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 133.8, 128.8, 128.33, 128.3, 73.7, 65.8, 64.9, 47.3, 43.4, 42.2, 17.1, 15.8.

HRMS(ESI) m/z calcd. for $C_{16}H_{20}ClN_3NaO$ $[M+Na]^+$: 328.1187, found: 328.1195.



1-((4-Chlorophenyl)(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)methyl)-4-phenyl-1*H*-1,2,3-triazole (**75**): To an oven-dried 10 mL glass tube equipped with a Teflon septum and a magnetic stir bar were added CuI (2.0 mg, 0.01 mmol, 0.1 eq) The tube was evacuated and backfilled with argon for three times. Compound **73** (31mg, 0.10 mmol, 1.0 eq), Phenylacetylene **74** (14 mg, 0.13 mmol, 1.3 eq), DIPEA (26 mg, 0.20 mmol, 2.0 eq) and DMF (2 mL) were added under argon atmosphere. The reaction mixture was allowed to stir at room temperature for 12 hours. After this time, the mixture was extracted with EtOAc (3 × 10 mL), and each extract was washed with water (3 × 10 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by column chromatography using (PE/EA = 5:1) to afford compound **75** as a yellow solid (37 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36-7.24 (m, 5H), 5.69 (d, *J* = 2.0 Hz, 1H), 3.52-3.41 (m, 2H), 3.38 (q, *J* = 6.2 Hz, 1H), 1.84-1.68 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (dd, *J* = 6.3, 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.45, 135.5, 135.4, 134.51, 134.5, 130.6, 129.1, 128.94, 128.9, 128.3, 125.8, 119.3, 73.5, 65.6, 64.9, 48.3, 43.7, 41.2, 17.1, 15.7.

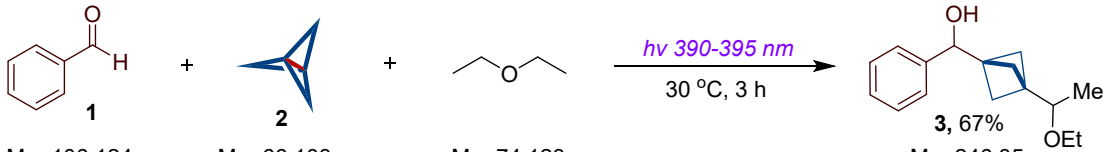
HRMS(ESI) m/z calcd. for $C_{24}H_{26}ClN_3NaO$ $[M+Na]^+$: 430.1657, found: 430.1655.

Melting point: 98 - 100 °C

9. Calculation of Atom efficiency and EcoScale of the reaction

From the perspective of green chemistry, we evaluated the reaction for its atom economy and environmental friendliness.[3] The calculation results as follows:

9.1 Calculation of atom efficiency.



M = 106.124 M = 66.103 M = 74.123 M = 246.35

Atom efficiency = 246.35/106.124 + 66.103 + 74.123 = 246.35/246.35 = 100%

9.2 Calculation of EcoScale.

Table: The penalty points to calculate the EcoScale

Parameter	Penalty	Parameter	Penalty
1. Yield	(100 - %yield)/2	5. Temperature/time	
2. Price of reaction components (to obtain 10 mmol of end product)		Room temperature, < 1 h	0
		Room temperature, < 24 h	1
Inexpensive (< $10)	0	Heating, < 1 h	2
Expensive (> $10 and < $50)	3	Heating, > 1 h	3
Very expensive (> $50)	5	Cooling to 0 °C	4
3. Safety[a]		Cooling, < 0 °C	5
N (dangerous for environment)	5	6. Workup and purification	
T (toxic)	5	None	0
F (highly flammable)	5	Cooling to room temperature	0
E (explosive)	10	Adding solvent	0
F+ (extremely flammable)	10	Simple filtration	0
T+ (extremely toxic)	10	Removal of solvent with bp < 150 °C	0
4. Technical setup		Crystallization and filtration	1
Common setup	0	Removal of solvent with bp > 150 °C	2
Instruments for controlled addition of chemicals[b]	1	Solid phase extraction	2
Unconventional activation technique[c]	2	Distillation	3
Pressure equipment, > 1 atm[d]	3	Sublimation	3
Any additional special glassware	1	Liquid-liquid extraction[e]	3
(Inert) gas atmosphere	1	Classical chromatography	10
Glove box	3		

[a]Based on the hazard warning symbols. [b]Dropping funnel, syringe pump, gas pressure regulator, etc. [c]Microwave irradiation, ultrasound or photochemical activation, etc. [d]$scCO_2$, high pressure hydrogenation equipment, etc. [e]If applicable, the process includes drying of solvent with desiccant and filtration of desiccant.

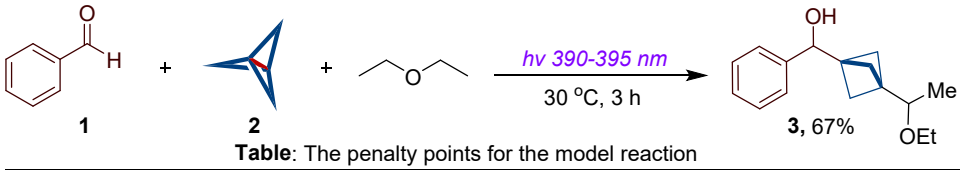


Table: The penalty points for the model reaction

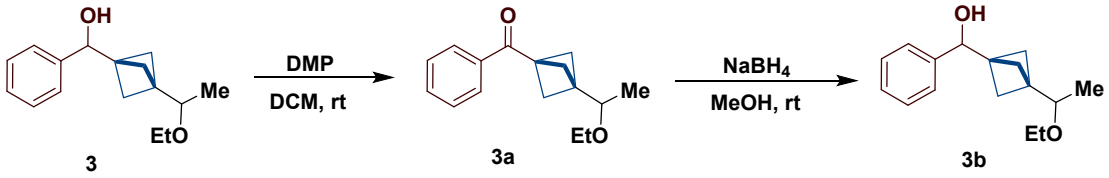
# **1-6** from Table Parameter	Penalty
1 Yield: 67	16.5
2 Benzaldehyde (30 mmol) [1.1.1]propellane (15 mmol) Et_2O (150 mL)	3
3 Benzaldehyde (F) Et_2O (F+)	15
4 Photoreactor	1
5 Room temperature, 3 h	1
6 Silica gel chromatography	10
Penalty points total:	46.5

In summary, the model reaction was calculated to have an 100% atomic efficiency and an EcoScale score of 53.5 (acceptable).

10. Diastereoisomer ratio (d.r.) determination studies

Due to the ratio of diastereoisomers in this reaction could not be determined by ^{1}H NMR, it was only recognized in part of the carbon in some ^{13}C NMR. Therefore, we tried to identify the ratio of diastereoisomers by the following methods.

10.1 Oxidation of BCP-benzylalcohol **3** followed by $NaBH_4$ reduction.



(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone (3a): To a 25 mL reaction vial equipped with a magnetic stir bar was added compound **3** (100 mg 0.40 mmol, 1.0 equiv.), Dess-Martin periodinane (340 mg 0.80 mmol, 2.0 equiv.) and dry DCM (6.0 mL), the reaction was stirred for 2 hours at room temperature. TLC analysis indicated the complete conversion, the reaction was quenched with (aq) $NaHCO_3$ (10 mL) and (aq) $Na_2S_2O_3$ (10 mL), then the aqueous phase was extracted with (2 × 10 mL) DCM. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using (PE/EA = 10:1) to afford compound **3a** as a colorless oil (75 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.55 (qd, *J* = 7.0, 3.7 Hz, 2H), 3.46 (q, *J* = 6.4 Hz, 1H), 2.20 (q, *J* = 9.4 Hz, 6H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.12 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 136.7, 132.9, 129.0, 128.5, 73.6, 65.0, 51.8, 44.0, 43.3, 17.0, 15.8.

(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanol (3b): To an oven-dried 10 mL glass tube equipped with a Teflon septum and a magnetic stir bar were added compound **3a** (36 mg, 0.14 mmol, 1.0 eq.), $NaBH_4$ (8.0 mg, 0.21 mmol, 2.0 eq.) and MeOH (2.0 mL). The reaction was stirred for 2 h at room temperature. TLC analysis indicated the complete conversion, the reaction was quenched with (aq) NH_4Cl (10 mL), then the aqueous phase was extracted with (2 × 10 mL) EtOAc. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography using (PE/EA = 2:1) to afford compound **3b** as a colorless oil (24 mg, 70% yield).

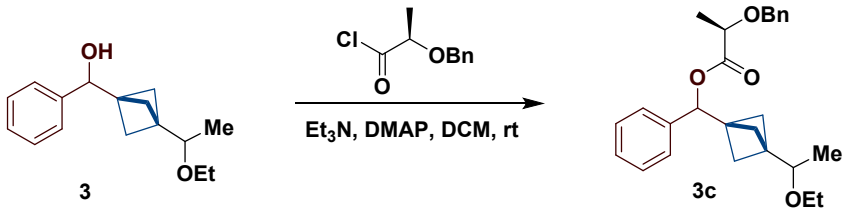
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 7.28-7.23 (m, 3H), 4.71 (s, 1H), 3.48 (q, *J* = 6.9 Hz, 2H), 3.36 (q, *J* = 6.3 Hz, 1H), 1.96 (s, 1H), 1.64-1.43 (m, 6H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 128.2, 127.4, 126.1, 126.0, 74.0, 64.9, 46.4, 42.8, 42.78 17.2, 15.8.

Note: We oxidized alcohol and then reduced the ketone with $NaBH_4$ to form the two diastereoisomers and checked the NMR, we found only one set of peaks in ^{1}H NMR, proving that diastereoisomers are not distinguishable in the NMR. We observed that the NMR of compound **3** is as same as **3b**. Moreover, it was also difficult to distinguish the ratios of

diastereoisomers by HPLC and GC.

10.2 Esterification of BCP benzyl alcohol **3** with [*R*, (+)]-2-(Benzyloxy)propionyl chloride.



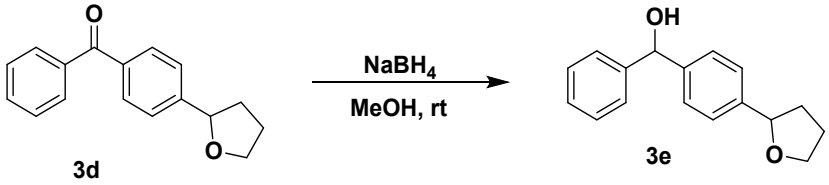
(3-(1-ethoxyethyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methyl(2R)-2-(benzyloxy) propanoate (3c) Under argon atmosphere, compound **3** (20 mg, 0.08 mmol, 1.0 equiv.), Et_3N (12 mg, 0.12 mmol, 1.5 equiv.) and DMAP (1.0 mg, 0.008 mmol, 0.1 equiv) were dissolved in 1.5 mL DCM. (*R*)-2-(benzyloxy)propanoyl chloride (19 mg, 0.1 mmol, 1.2 equiv) was added, the reaction was stirred for 3 hours at room temperature. The reaction mixture was concentrated under vacuum to afford the crude product. The residue was purified by thin layer chromatography using (PE/EA = 8:1) to afford compound **3c** as a colorless oil (22 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 10H), 5.89 (d, *J* = 3.1 Hz, 1H), 4.70 (t, *J* = 12.0 Hz, 1H), 4.42 (t, *J* = 11.2 Hz, 1H), 4.13 (q, *J* = 6.8 Hz, 1H), 3.52-3.41 (m, 2H), 3.40-3.29 (m, 1H), 1.61-1.52 (m, 6H), 1.48 (dd, *J* = 18.0, 6.8 Hz, 3H), 1.13 (dd, *J* = 11.0, 6.9 Hz, 3H), 1.00 (t, *J* = 5.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.53, 172.5, 137.9, 137.8, 128.6, 128.4, 128.38, 128.1, 128.05, 1280.0, 127.94, 126.6, 126.54, 126.0, 75.5, 75.47, 74.4, 74.36, 74.11, 73.9, 73.84, 73.8, 72.12, 72.1, 64.93, 64.9, 47.2, 47.1, 43.33, 43.3, 41.2, 41.1, 19.2, 19.0, 17.2, 15.8.

Note: By esterification of BCP benzyl alcohol **3** with chiral (*R*)-2-(benzyloxy)propionic acid, we found that these diastereoisomers remain indistinguishable in NMR.

10.3 Benzophenone compound **3d** reduced by $NaBH_4$.



Phenyl(4-(tetrahydrofuran-2-yl)phenyl)methanol (3e): To an oven-dried 10 mL glass tube equipped with a Teflon septum and a magnetic stir bar were added compound **3d** (25 mg, 0.1 mmol, 1.0 eq.), $NaBH_4$ (6.0 mg, 0.15 mmol, 1.5 eq.) and MeOH (1.0 mL). The reaction was stirred for 2 h at room temperature. TLC analysis indicated the complete conversion, the reaction was quenched with (aq) NH_4Cl (5 mL), then the aqueous phase was extracted with (2 × 5 mL) EtOAc. The combined organicc phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by thin layer chromatography using (PE/EA = 3:1) to afford compound **3e** as a colorless oil (20 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 9H), 5.83 (s, 1H), 4.86 (t, *J* = 7.2 Hz, 1H), 4.07 (dd, *J* = 15.0, 6.9 Hz, 1H), 3.92 (dd, *J* = 14.5, 7.6 Hz, 1H), 2.35-2.25 (m 2H), 2.04-1.93 (m, 2H), 1.83-1.73 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 143.97, 143.0, 142.93, 142.9, 128.6, 127.7, 127.65, 126.7, 126.65, 126.0, 80.6, 76.2, 68.8, 34.6, 26.2.

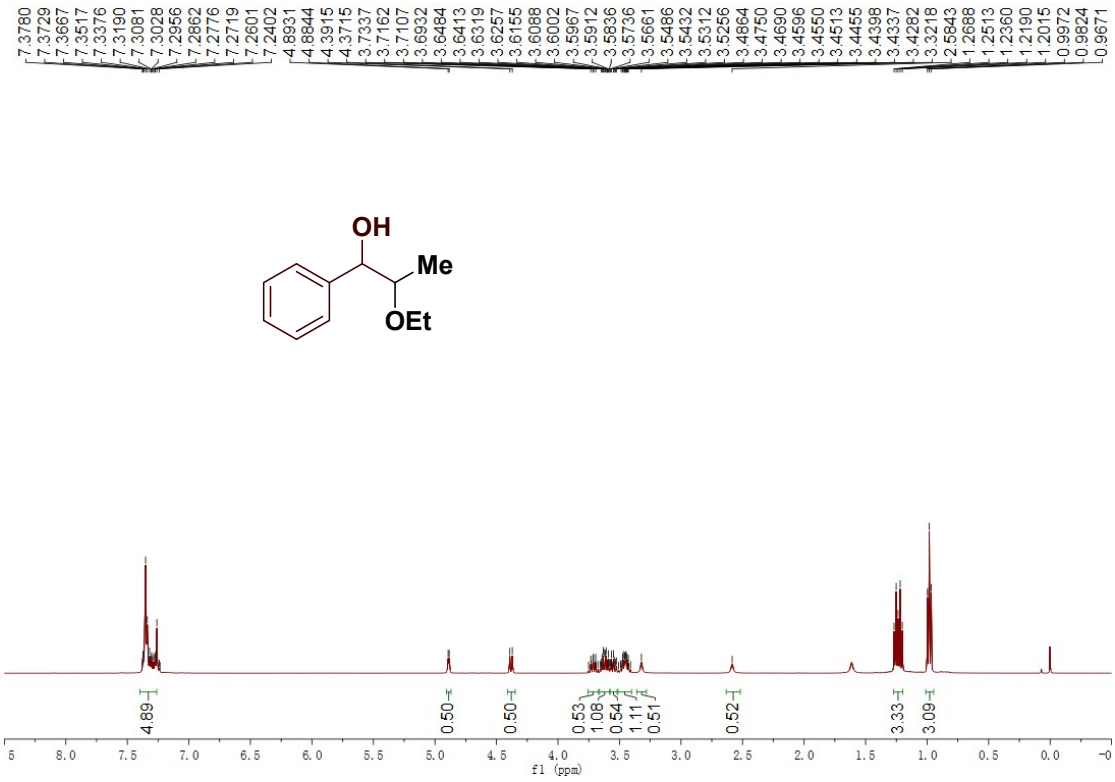
Compound 3d was synthesized with reference to Ruben Martin's report (*J. Am. Chem. Soc.* **2018**, *140*, 12200–12209).

In summary, we are not able to determine the ratios of diastereoisomers of reaction products in NMR using the above methods, and it was also difficult to distinguish the ratios of diastereoisomers by HPLC and GC. However, we could see the peaks of the diastereoisomers in part of the carbon in some ^{13}C NMR. Although the peaks are very close and they cannot be separated, it can be seen that the ratio is close to 1:1 in ^{13}C NMR. And we believe that there is no diastereoselectivity for this reaction.

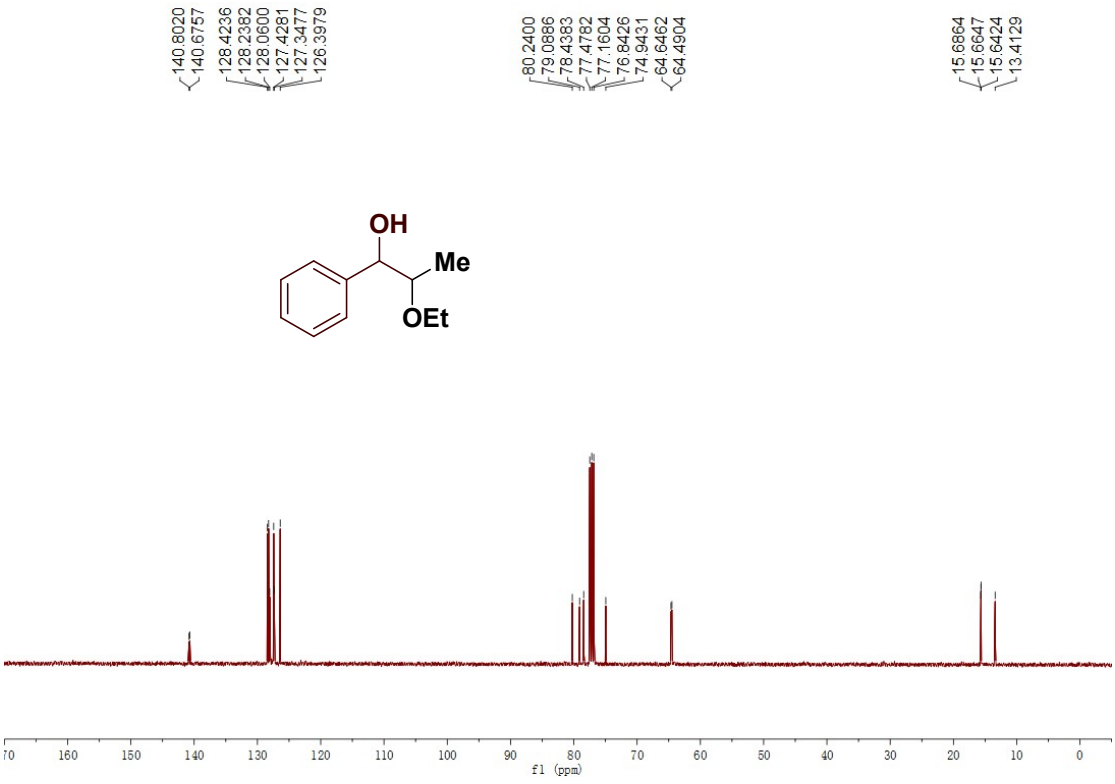
11. References

1. (a) R. Gianatassio, J. M. Lopchuk, J. Wang, C.-M. Pan, L. R. Malins, L. Prieto, T. A. Brandt, M. R. Collins, G. M. Gallego, N. W. Sach, J. E. Spangler, H. Zhu, J. Zhu, P. S. Baran, *Science* 2016, **351**, 241–246; (b) W. Dong, E. Yen-Pon, L. Li, A. Bhattacharjee, A. Jolit, G. A. Molander, *Nat. Chem.* 2022, **14**, 1068–1077.
2. P. Kaszynski, A. C. Friedli, J. Michl, *J. Am. Chem. Soc.* 1992, **114**, 601-620.
3 a) B. Trost, The Atom Economy—A Search for Synthetic Efficiency. *Science* 1991, **254**, 1471–1477; b) K. V. Aken, L. Strekowski, L. Patiny, EcoScale, a Semi-Quantitative Tool to Select an Organic Preparation Based on Economical and Ecological Parameters. *Beilstein J. Org. Chem.* 2006, **2**, 3; c) R. A. Sheldon, The E Factor: Fifteen Years On. *Green Chem.* 2007, **9**, 1273–1283.

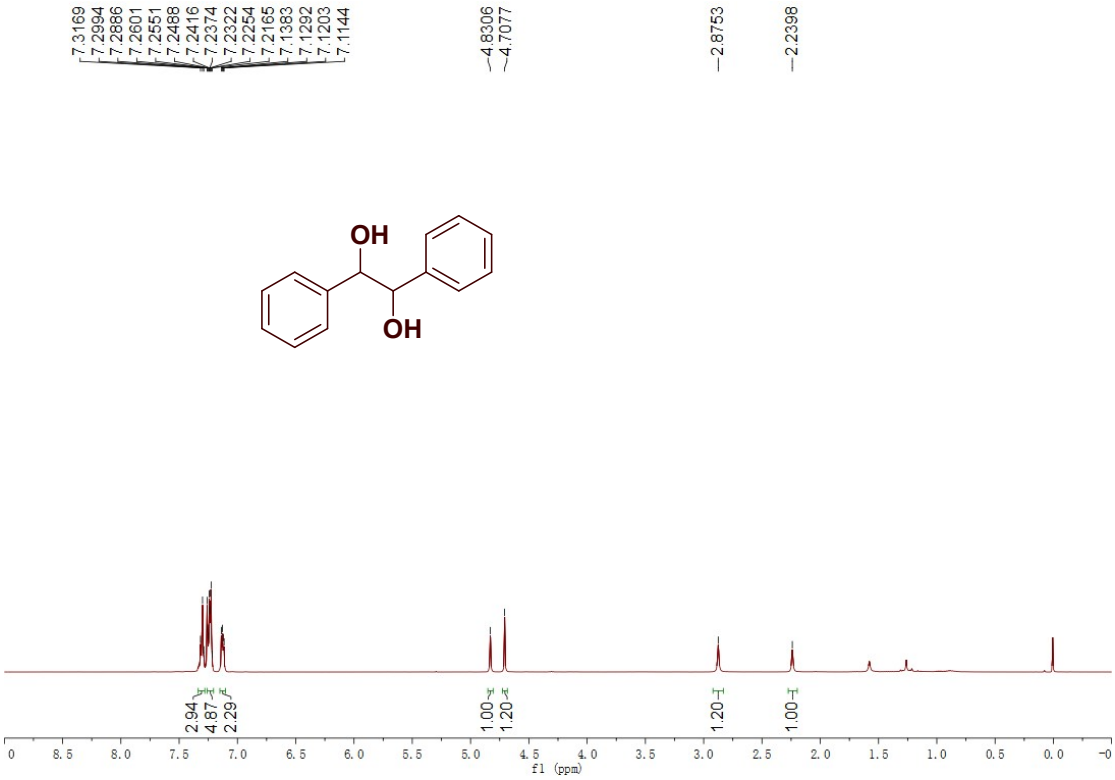
12. Copies of NMR spectra for products



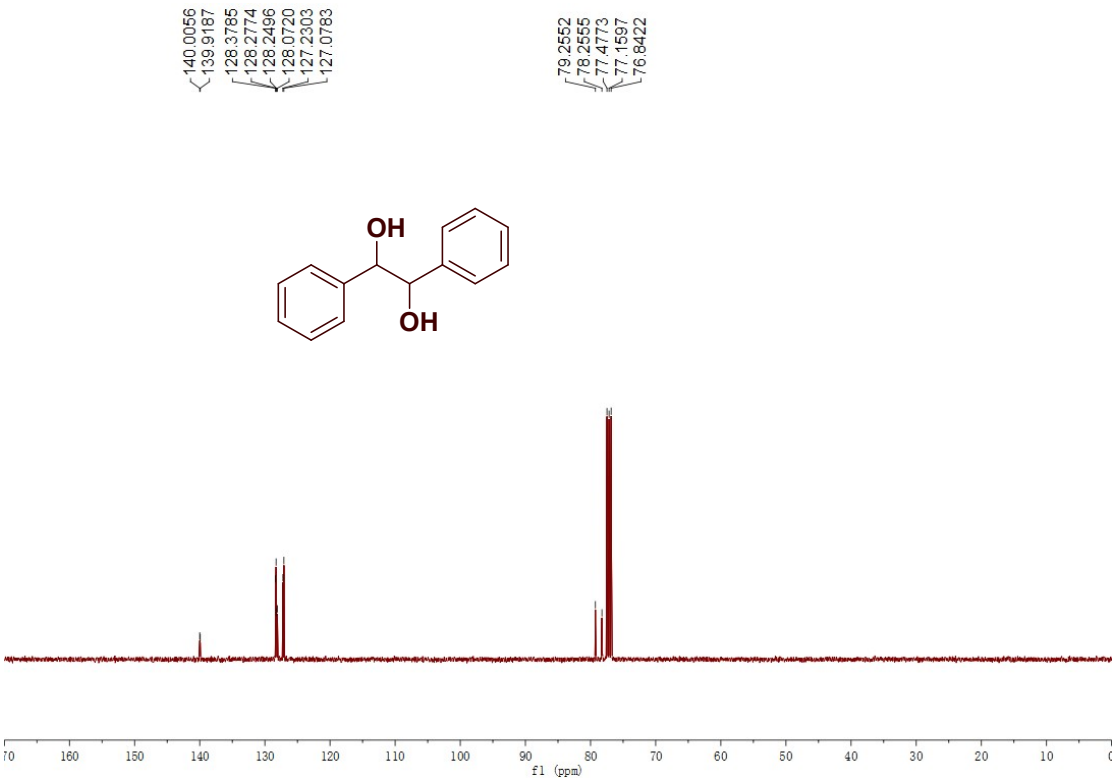
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1a**



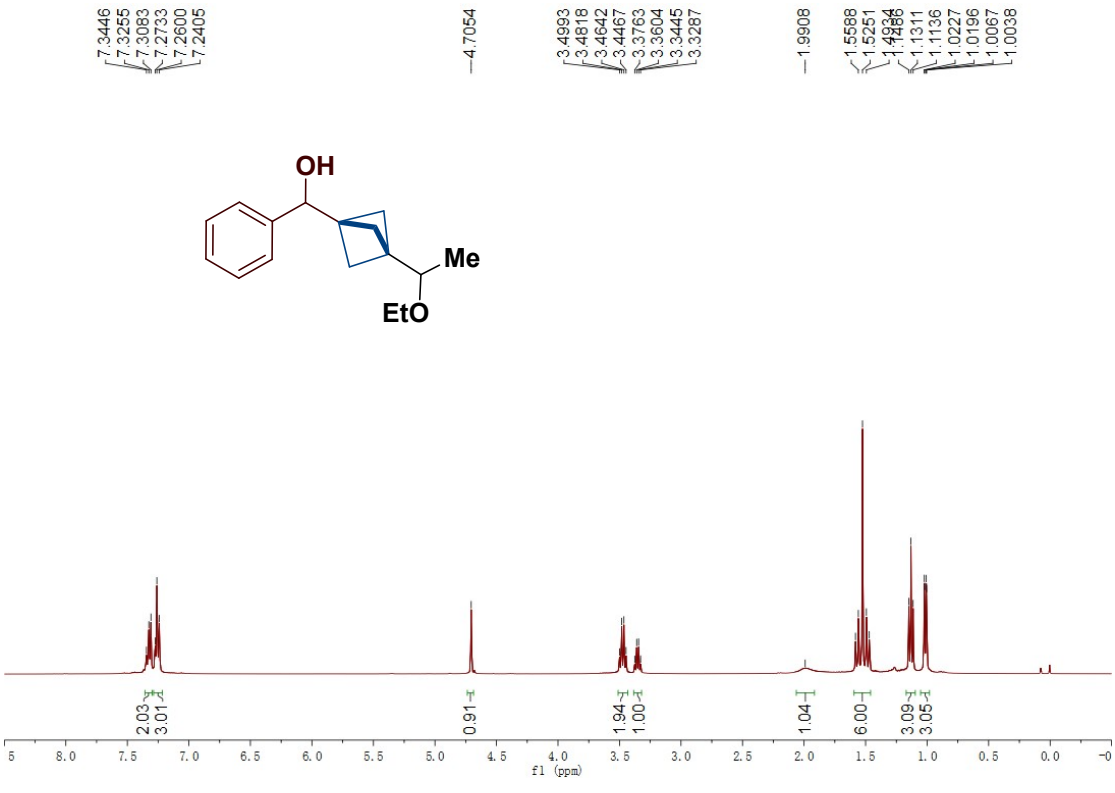
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1a**



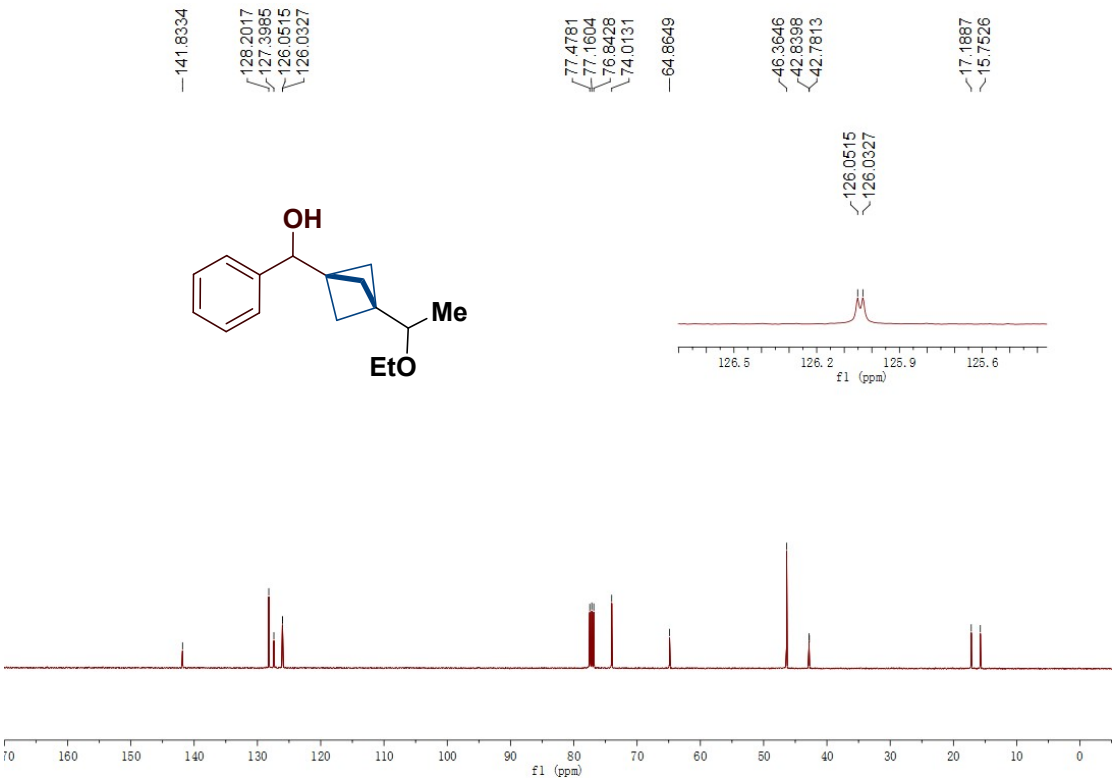
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1b**



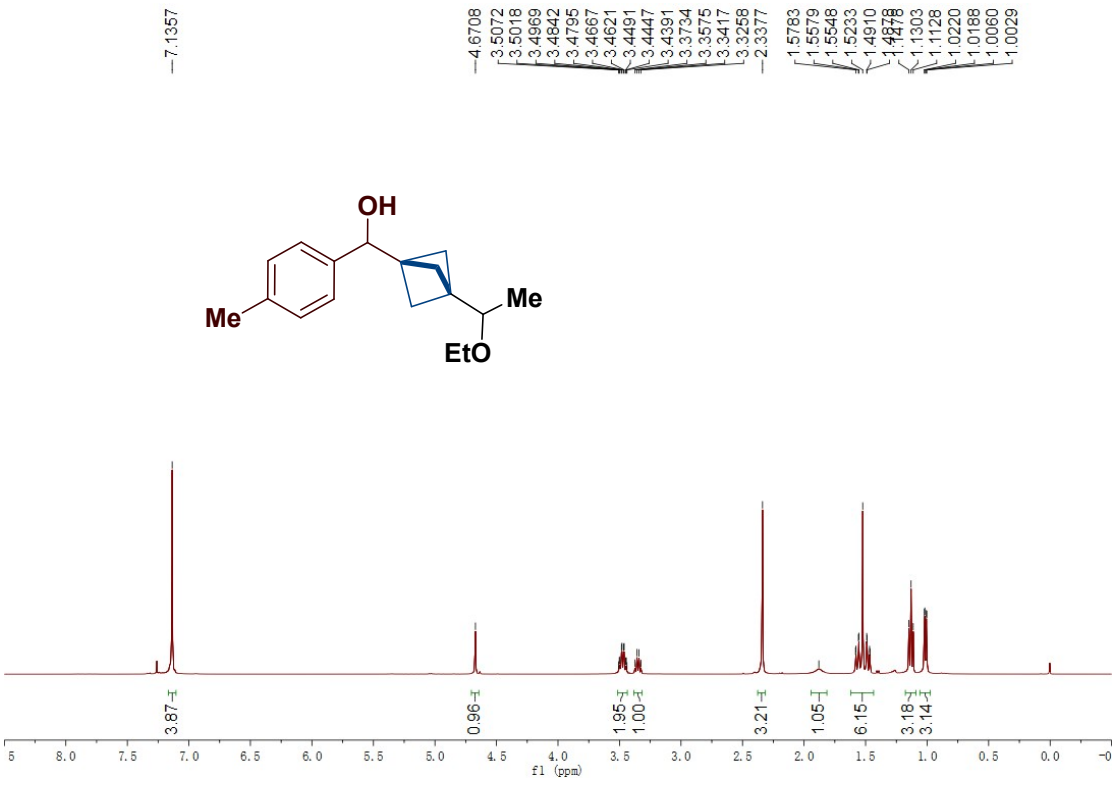
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1b**



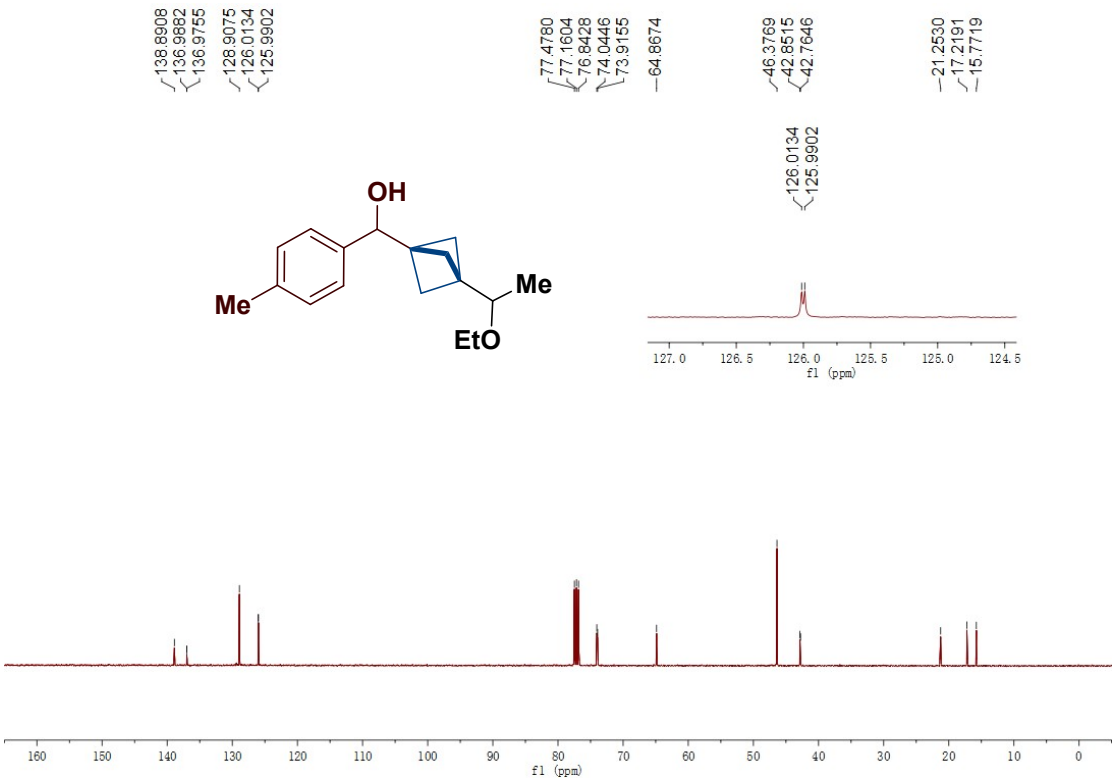
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



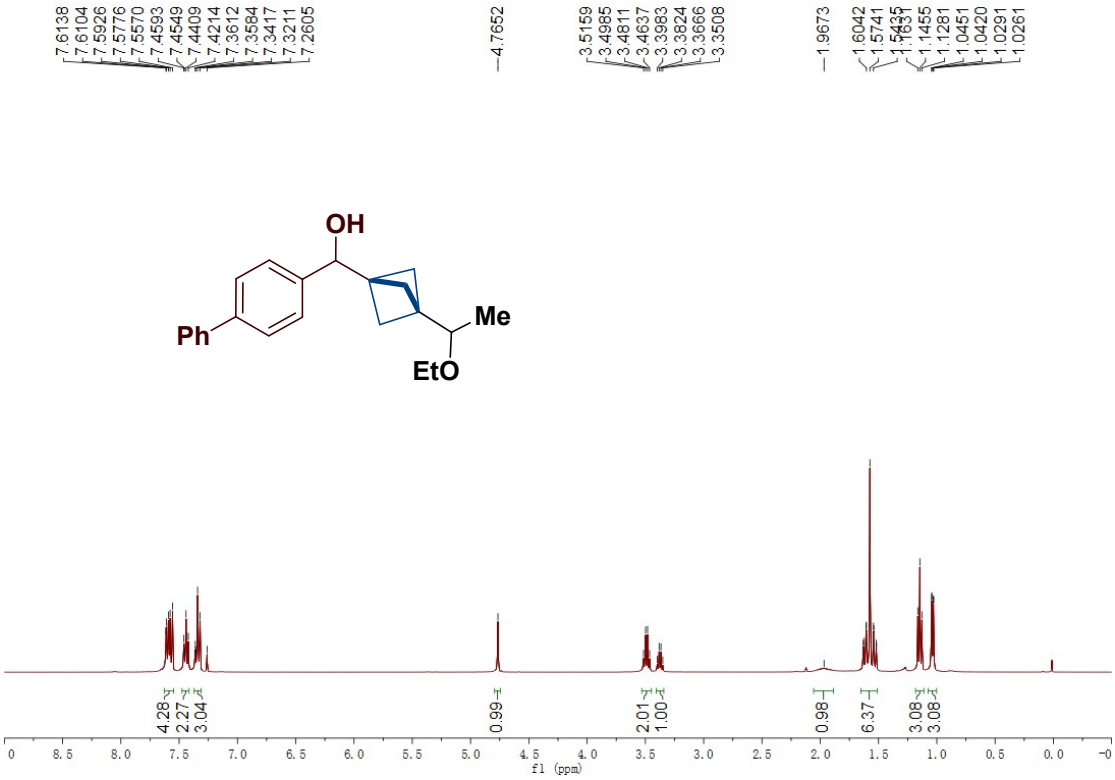
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3**



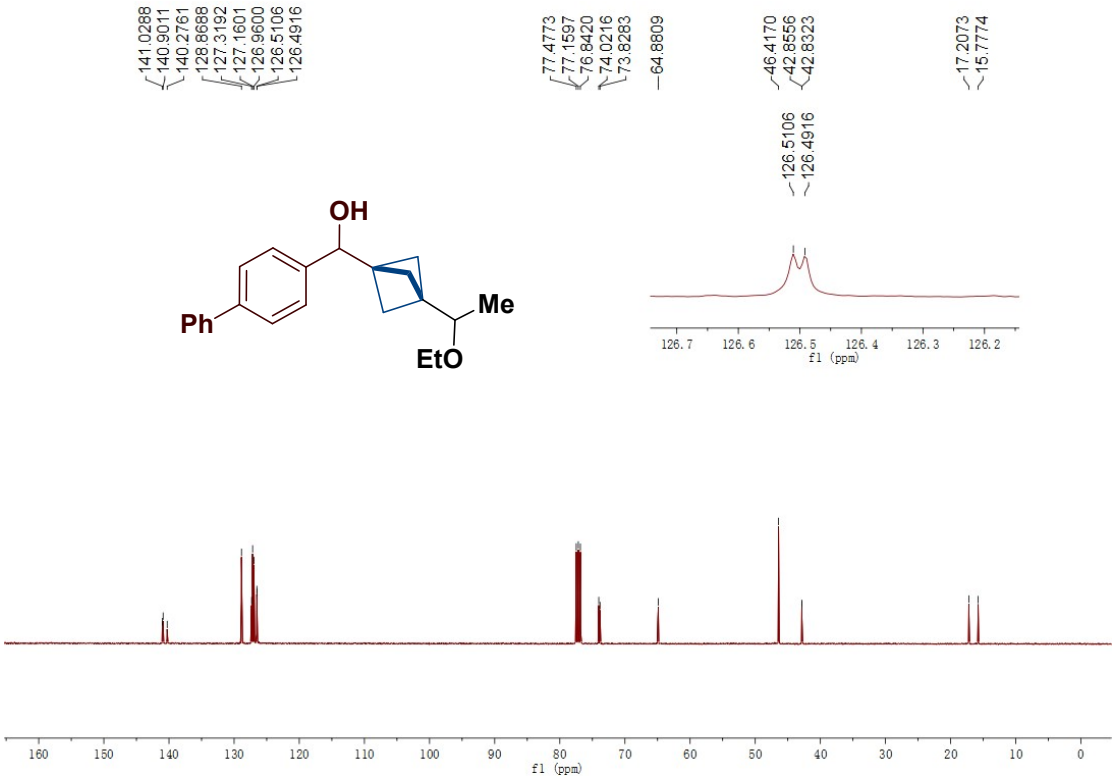
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**



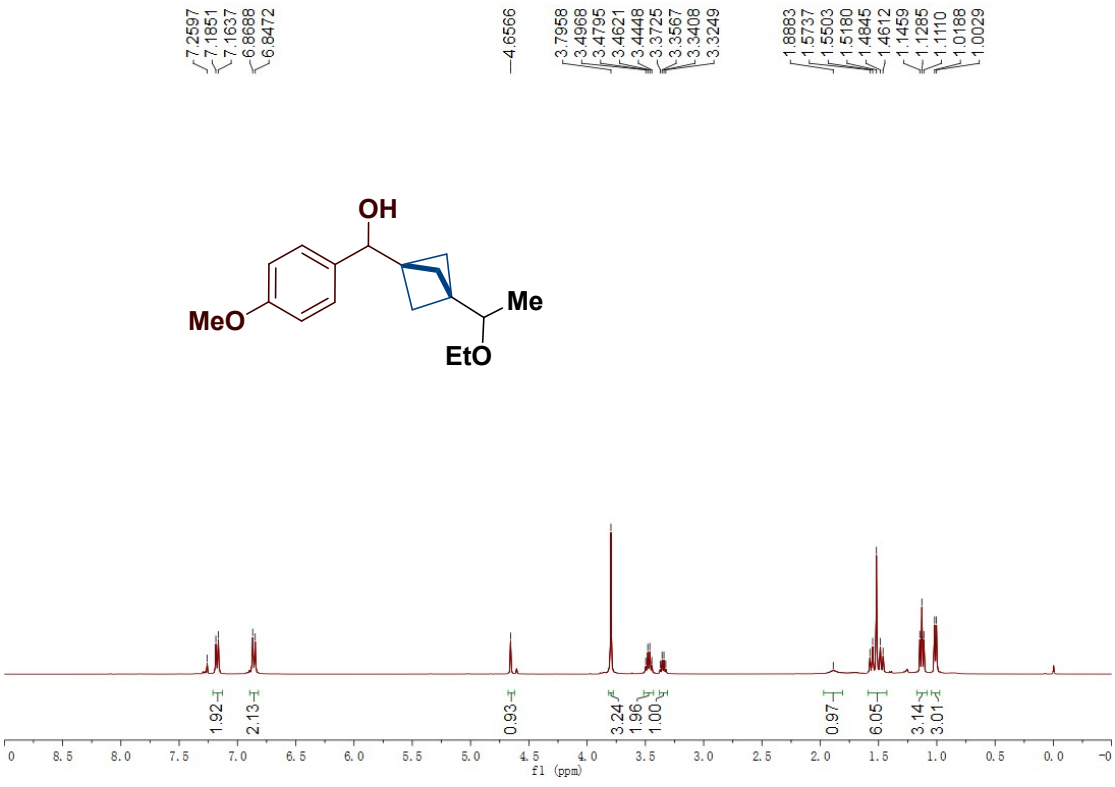
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4**



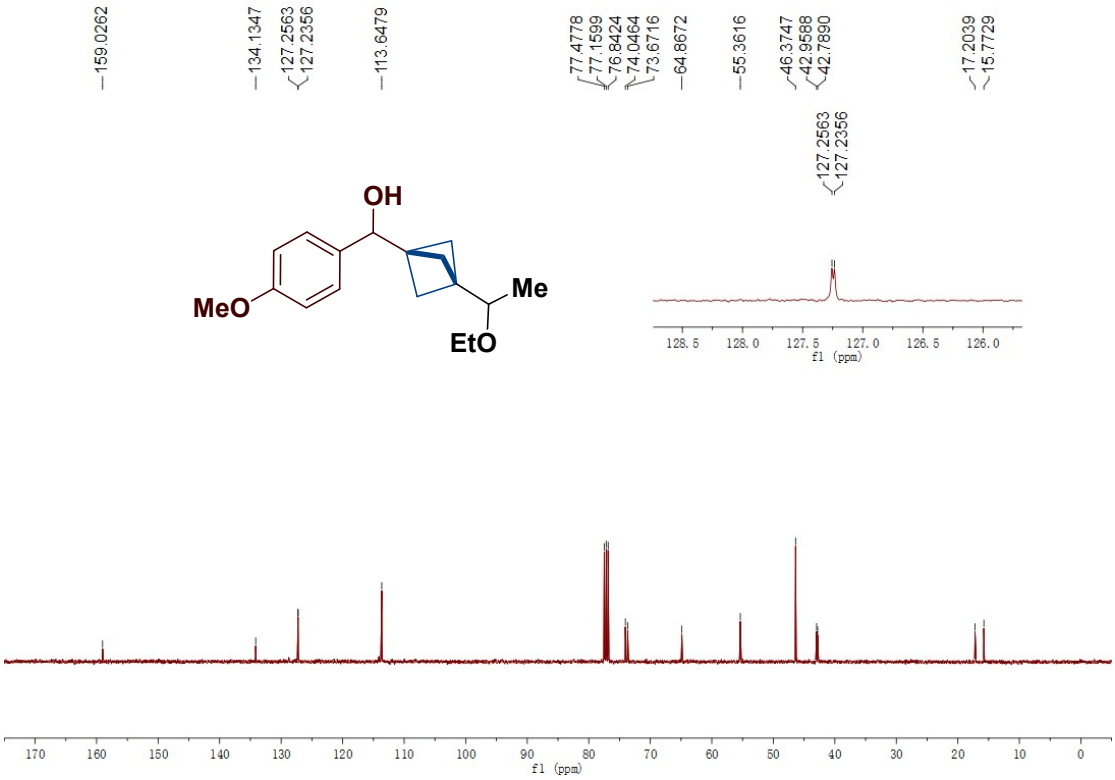
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**



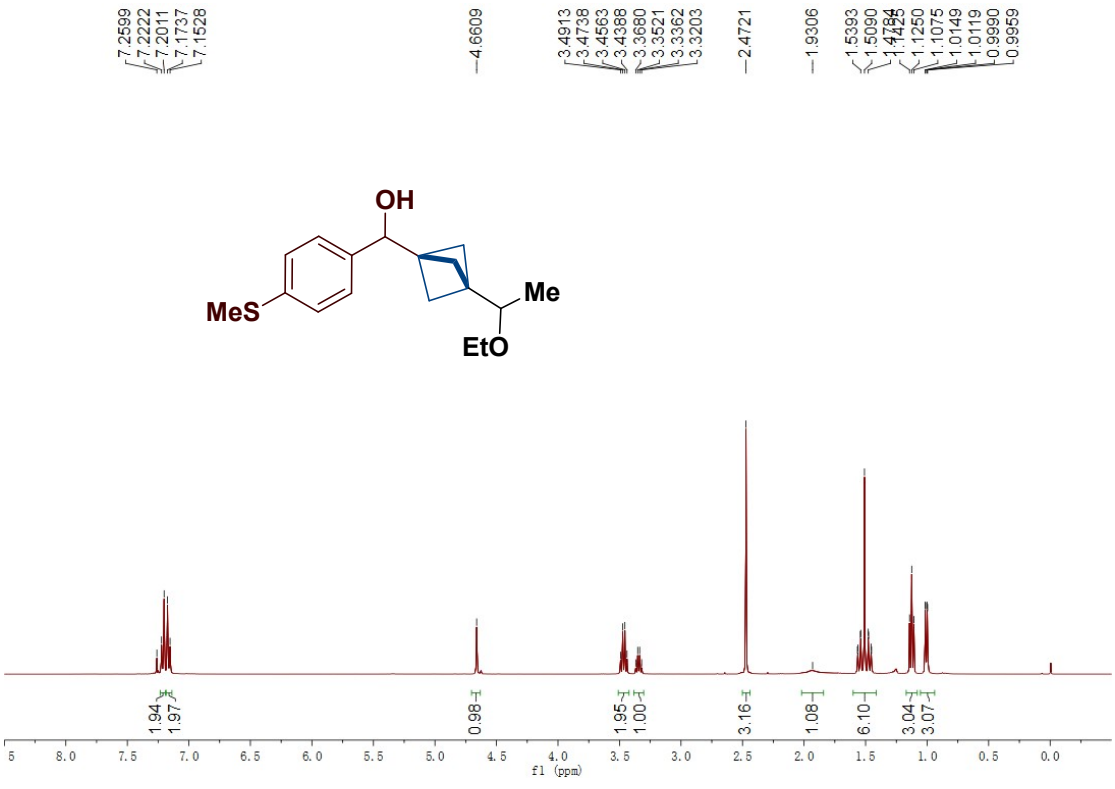
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5**



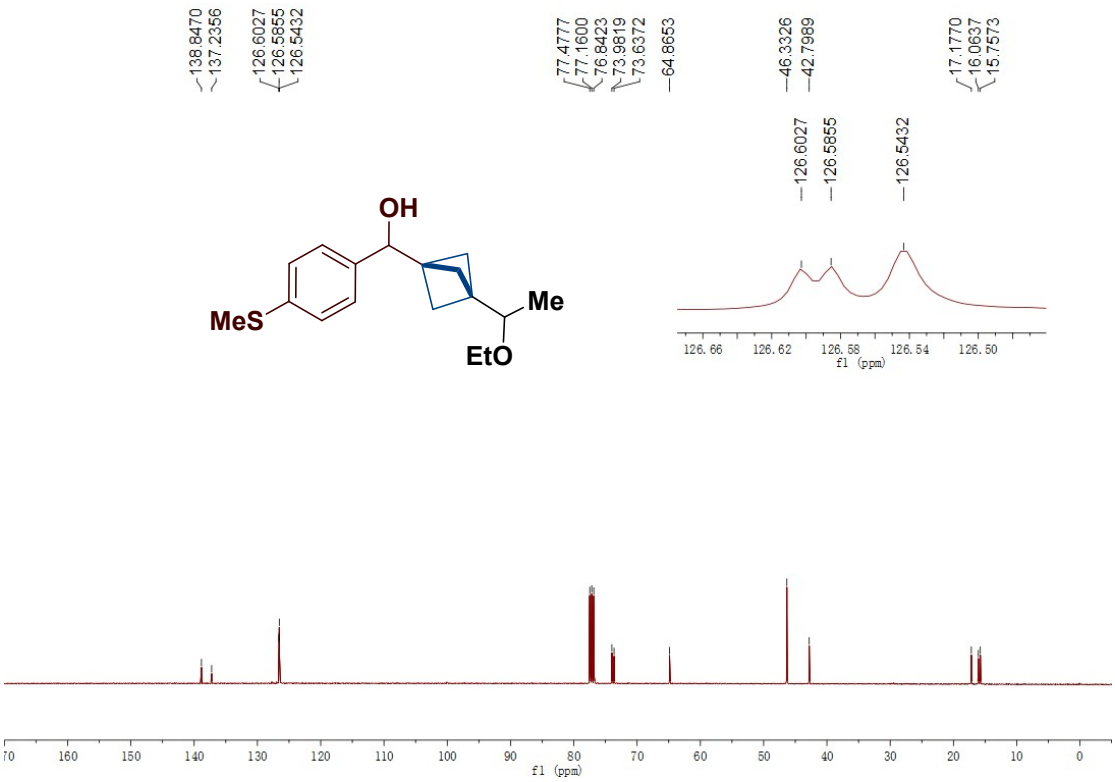
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



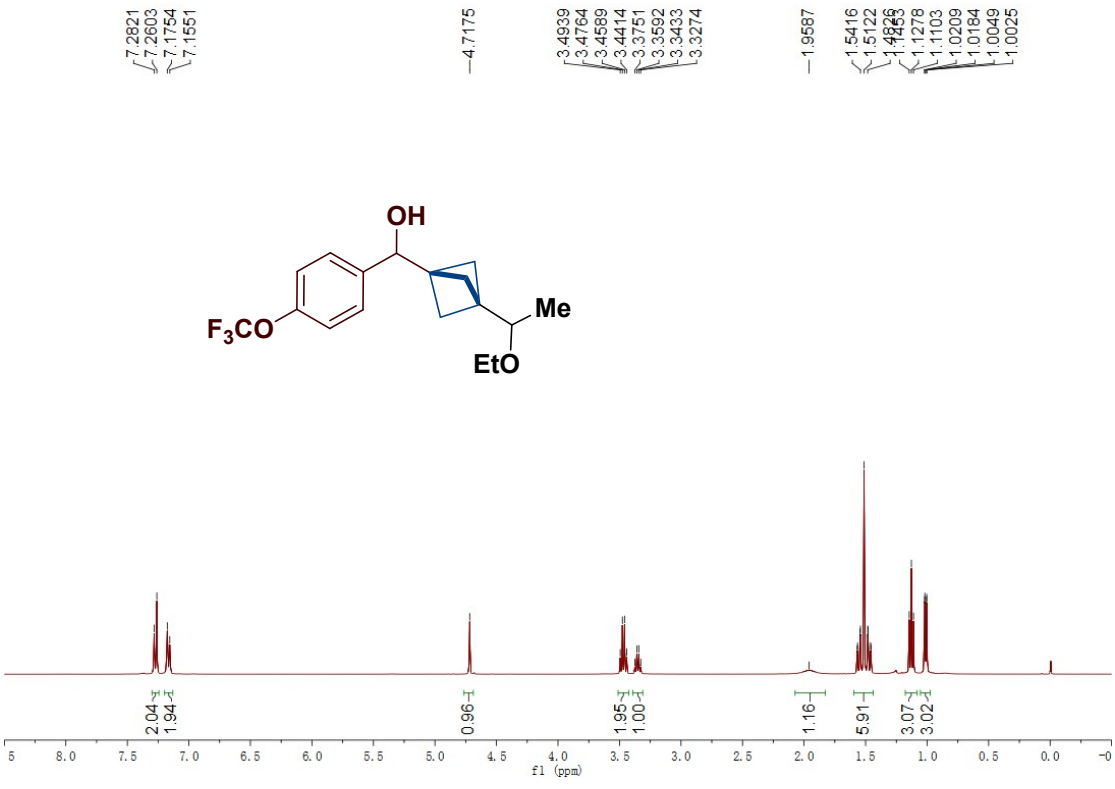
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6**



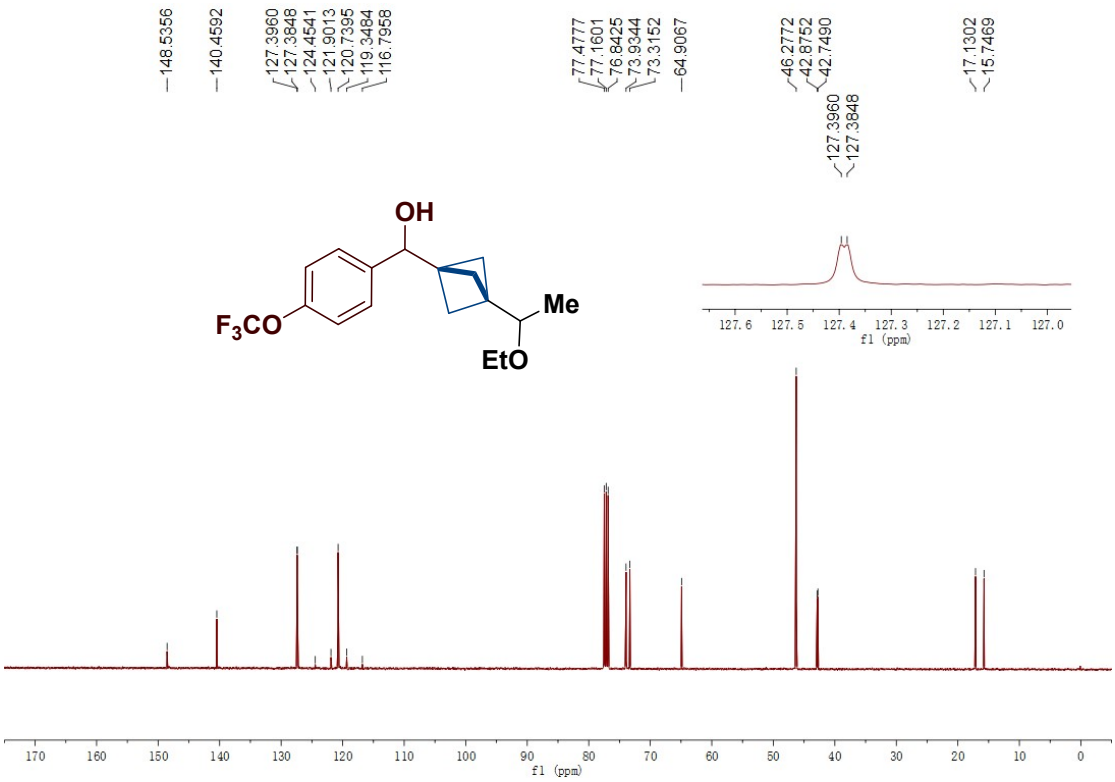
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



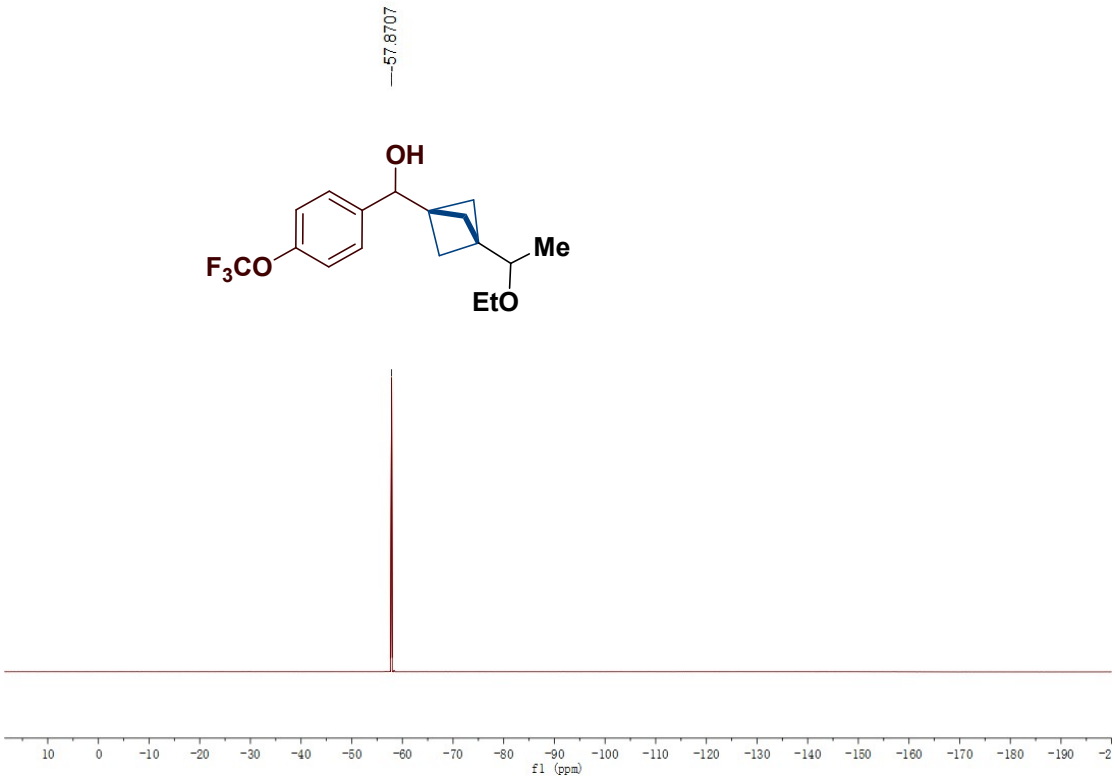
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**



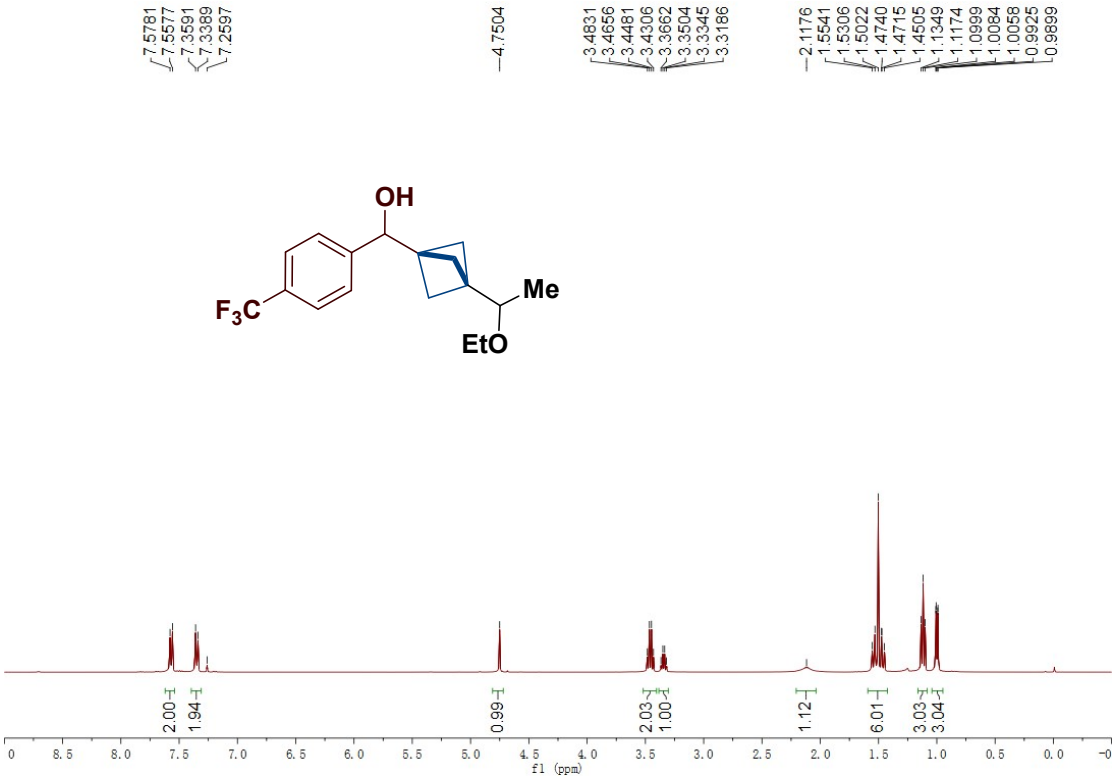
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



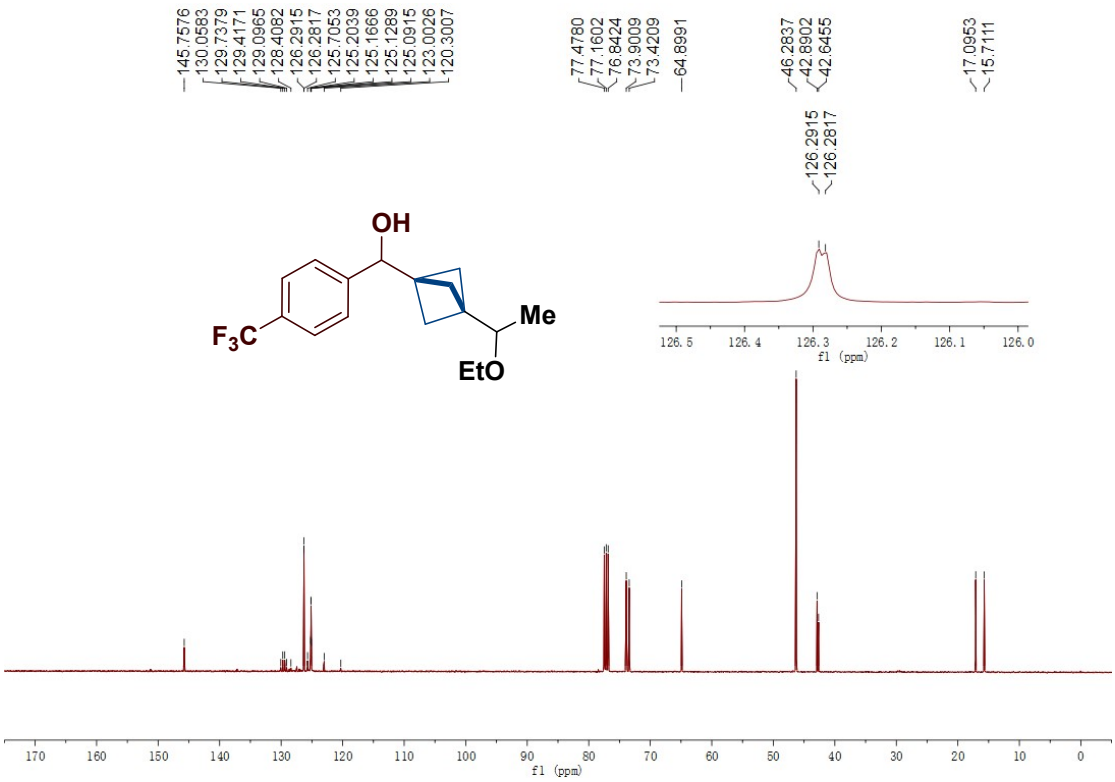
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**



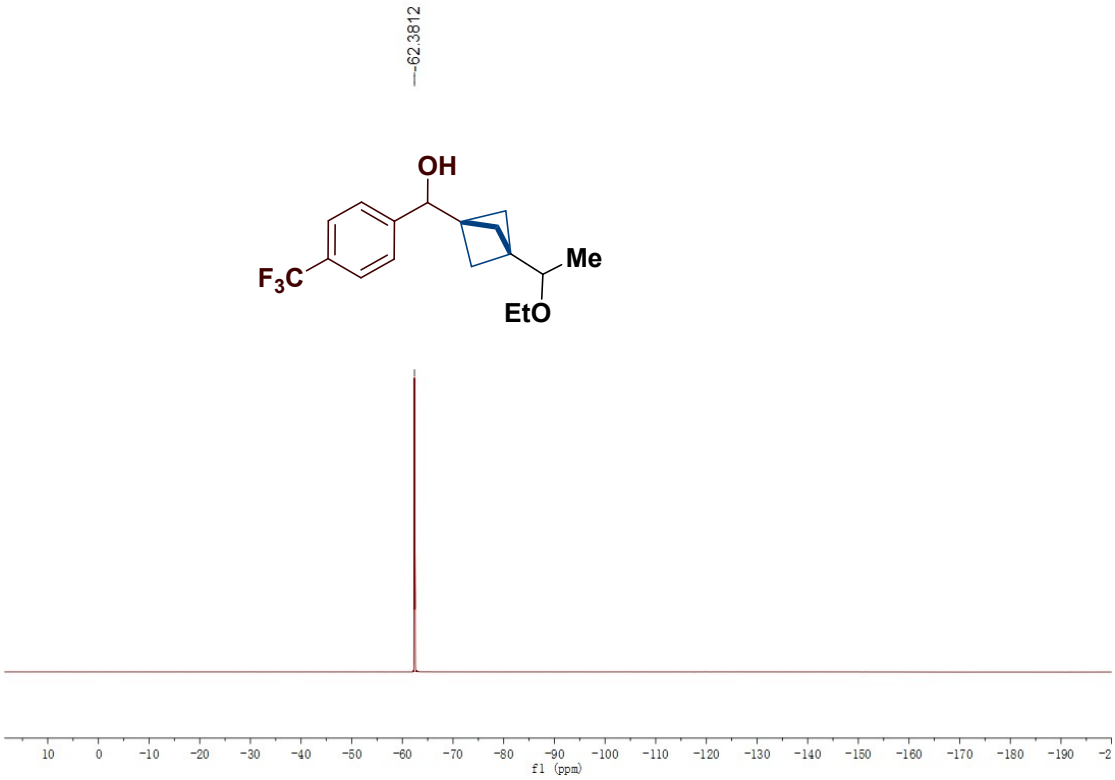
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **8**



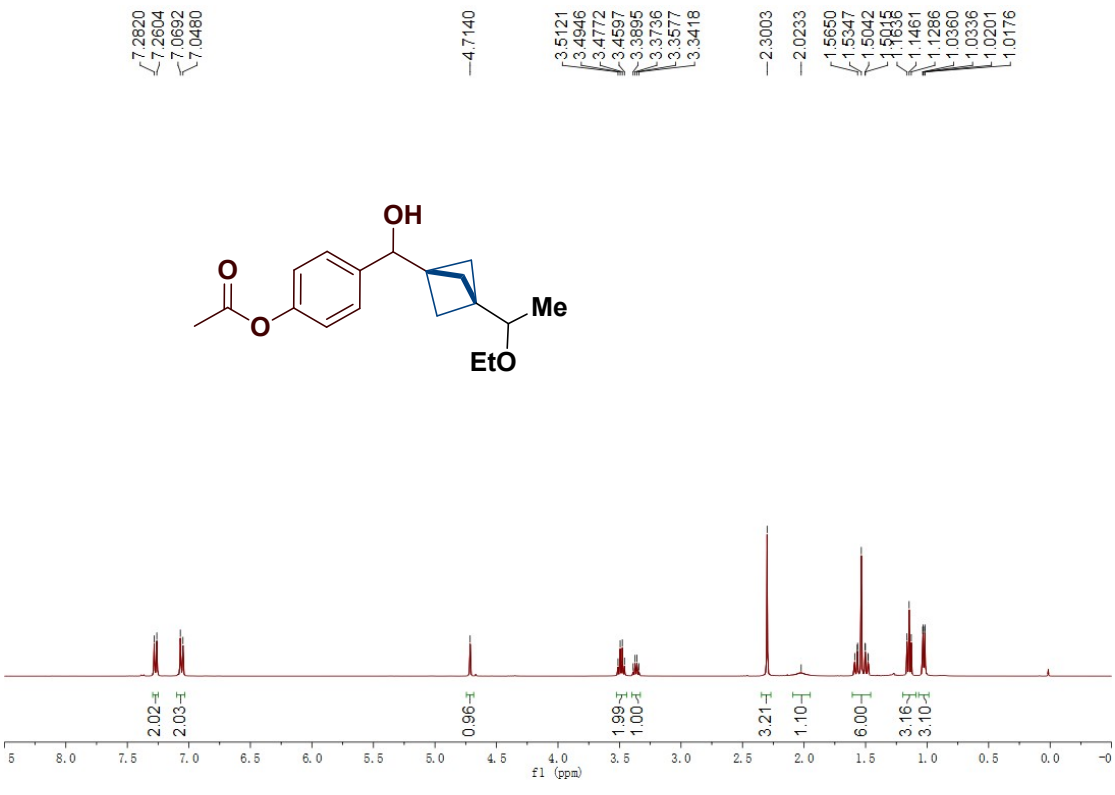
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**



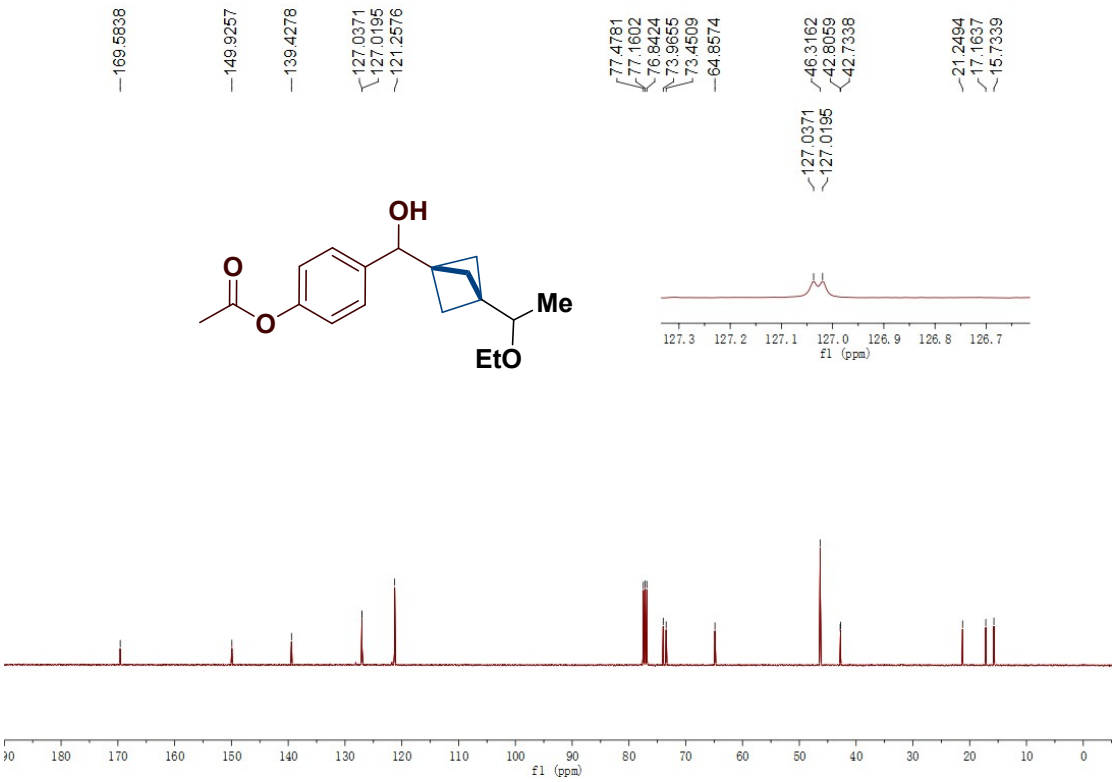
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**



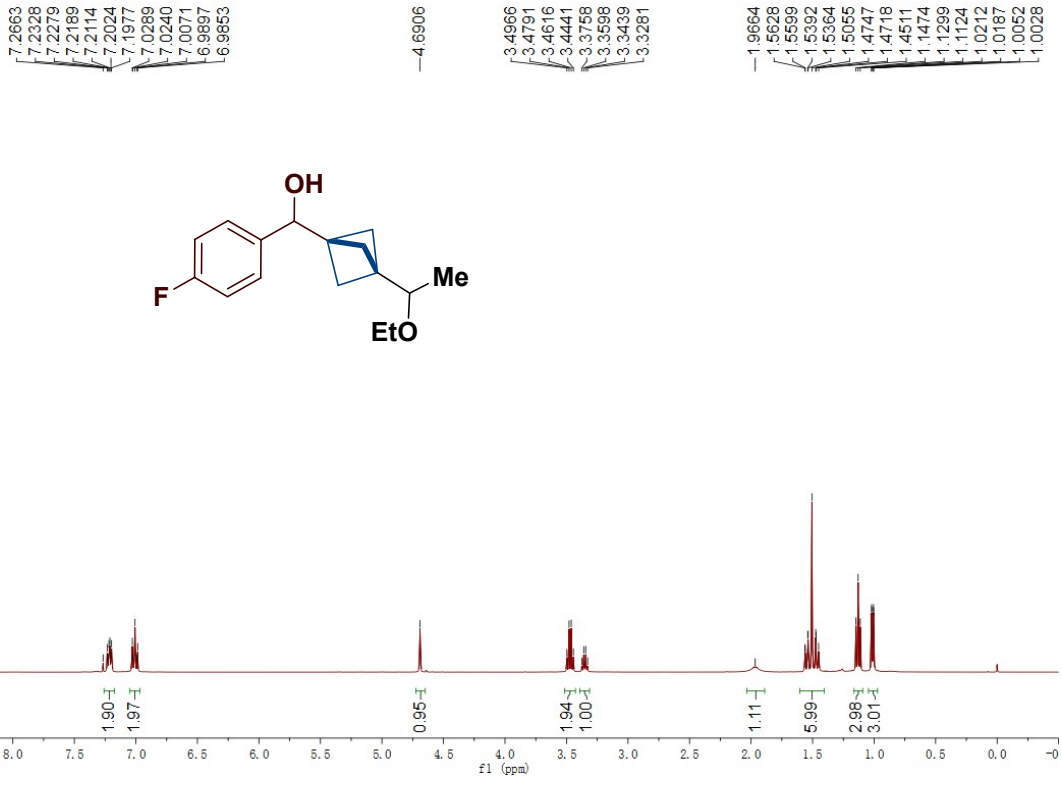
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **9**



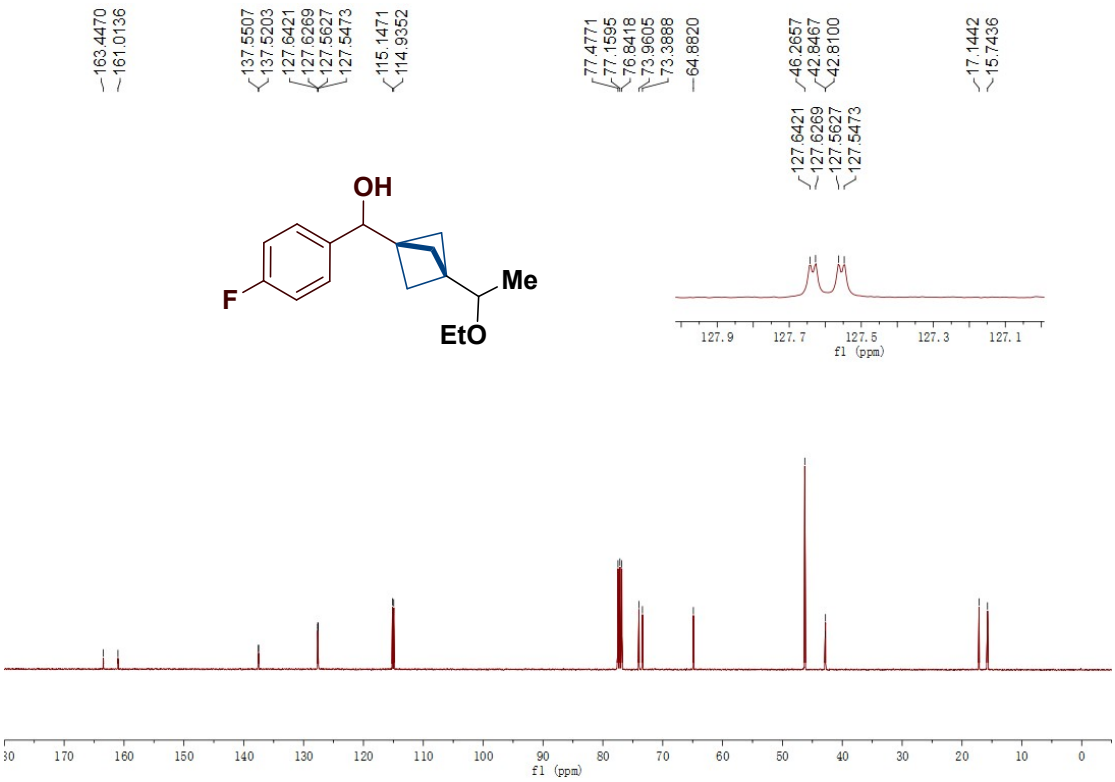
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**



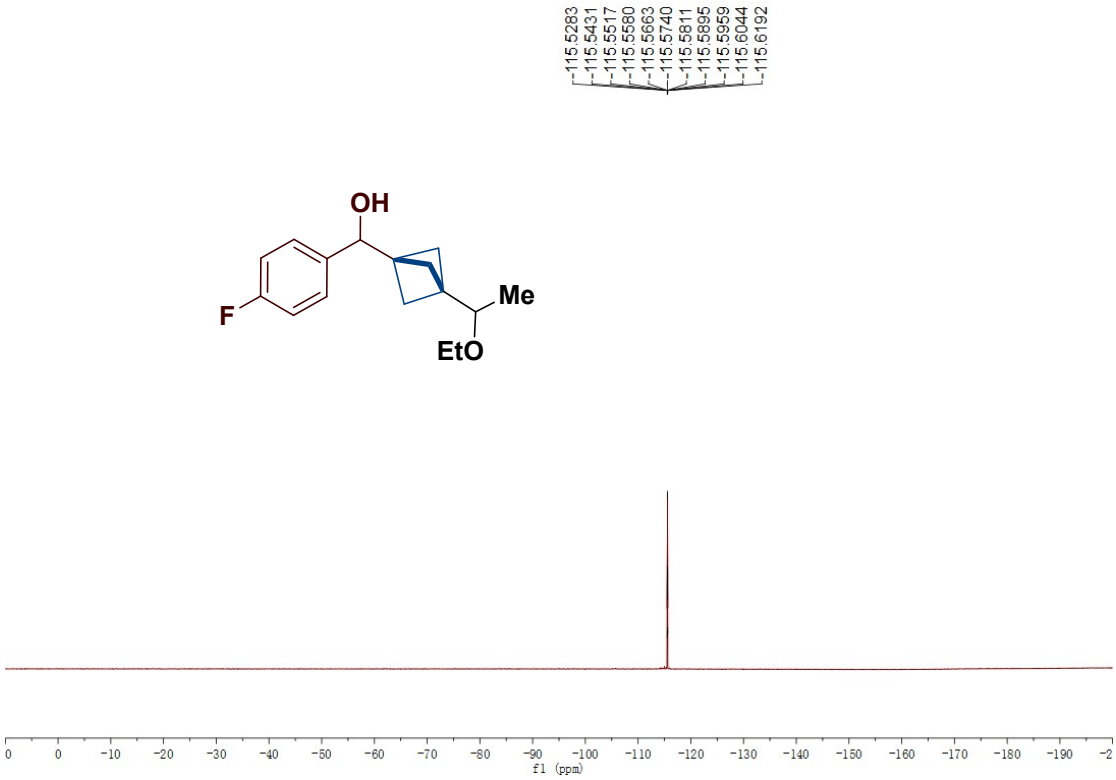
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **10**



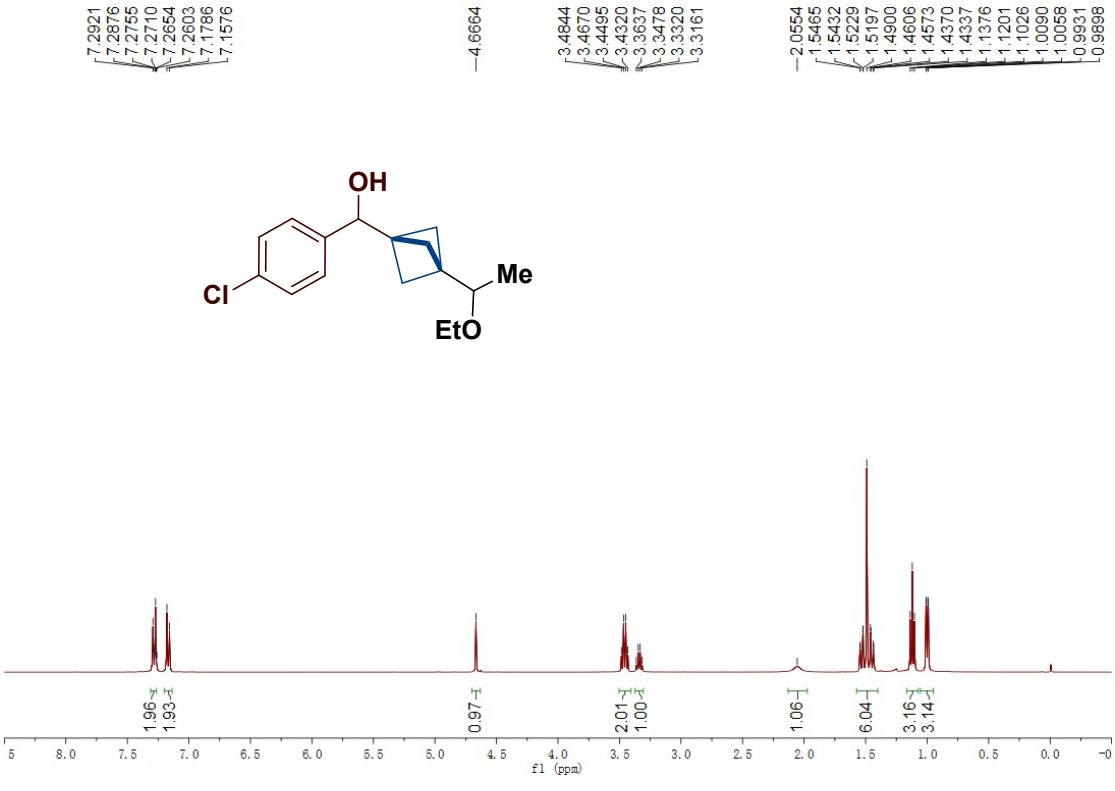
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**



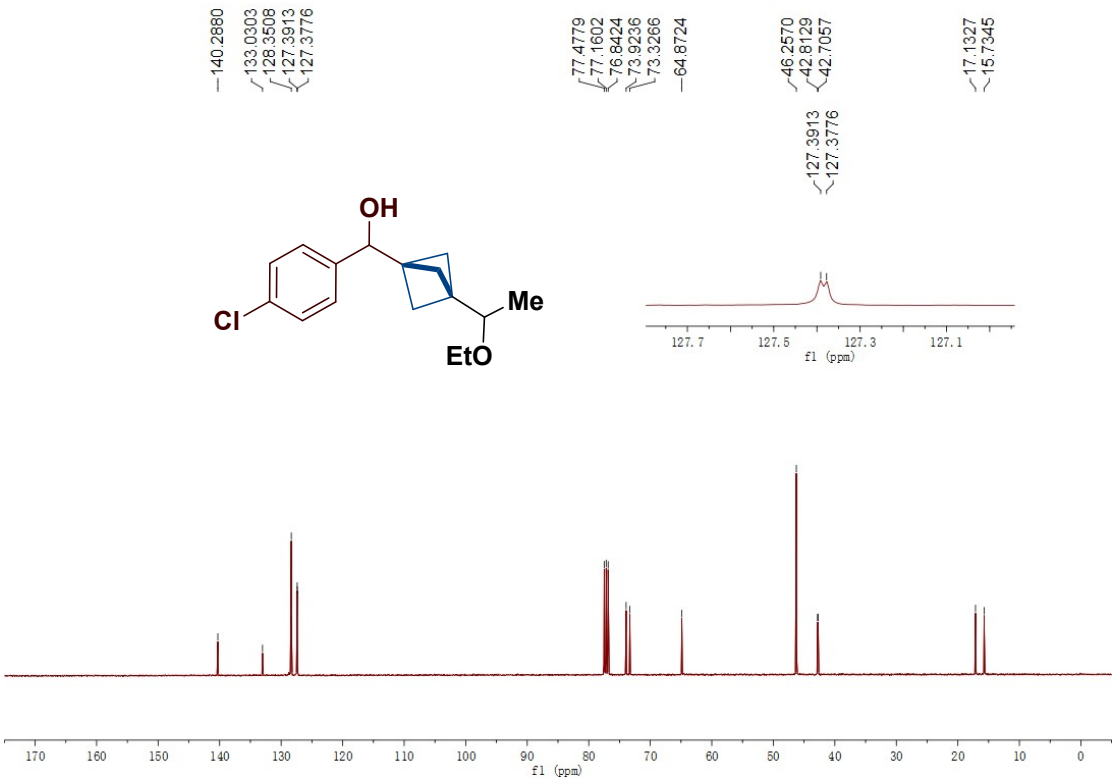
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**



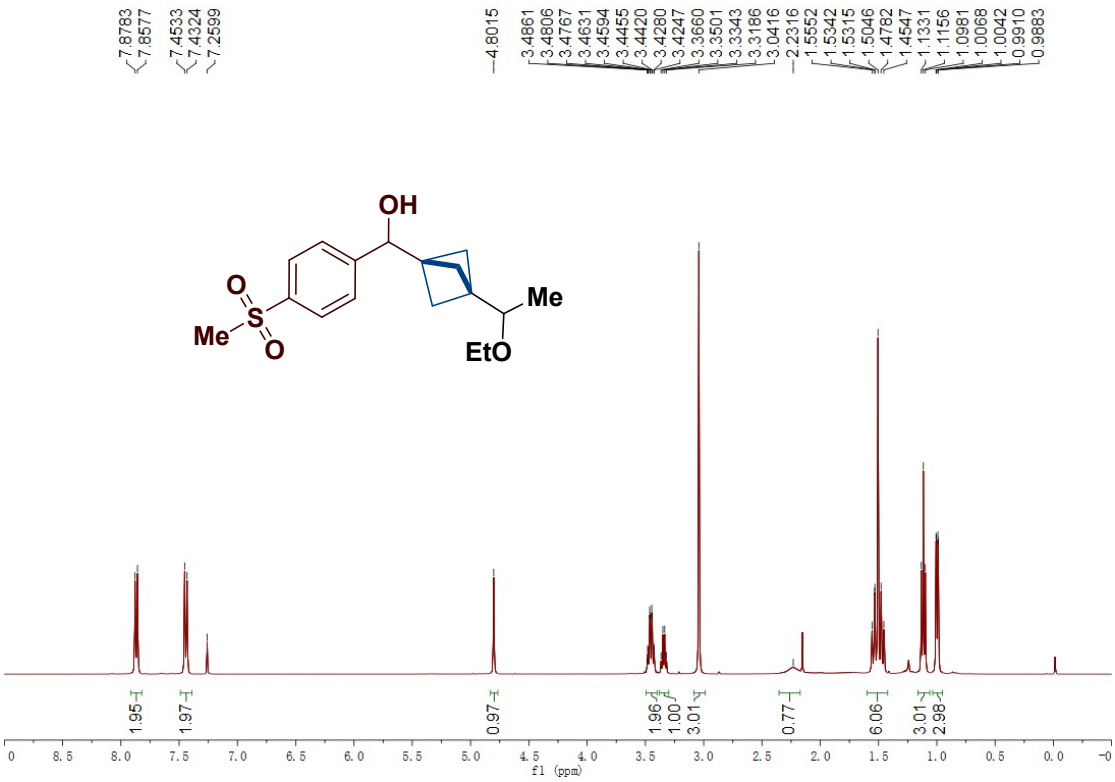
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **11**



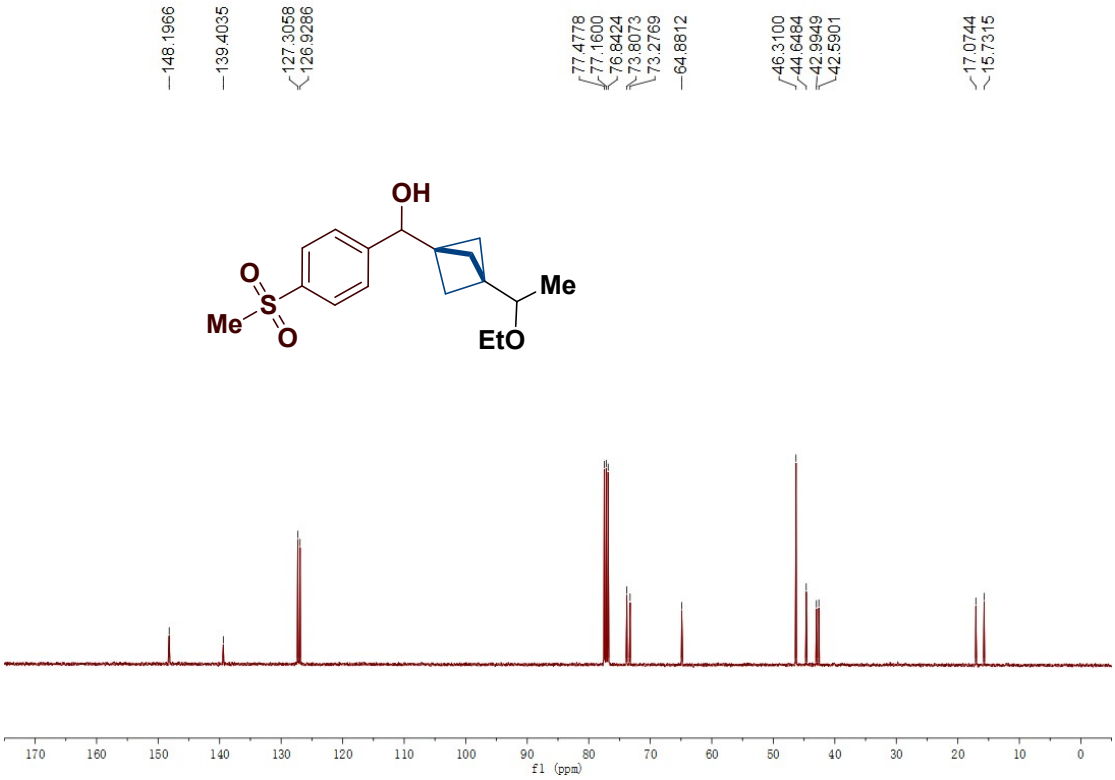
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **12**



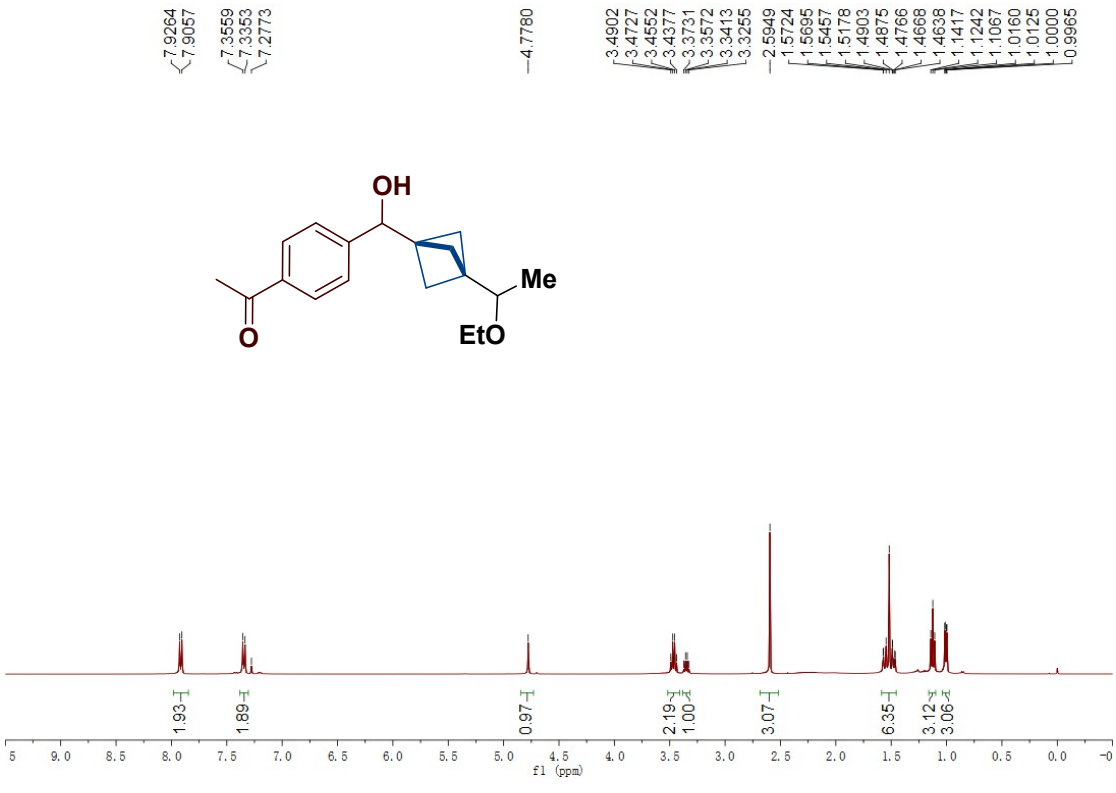
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **12**



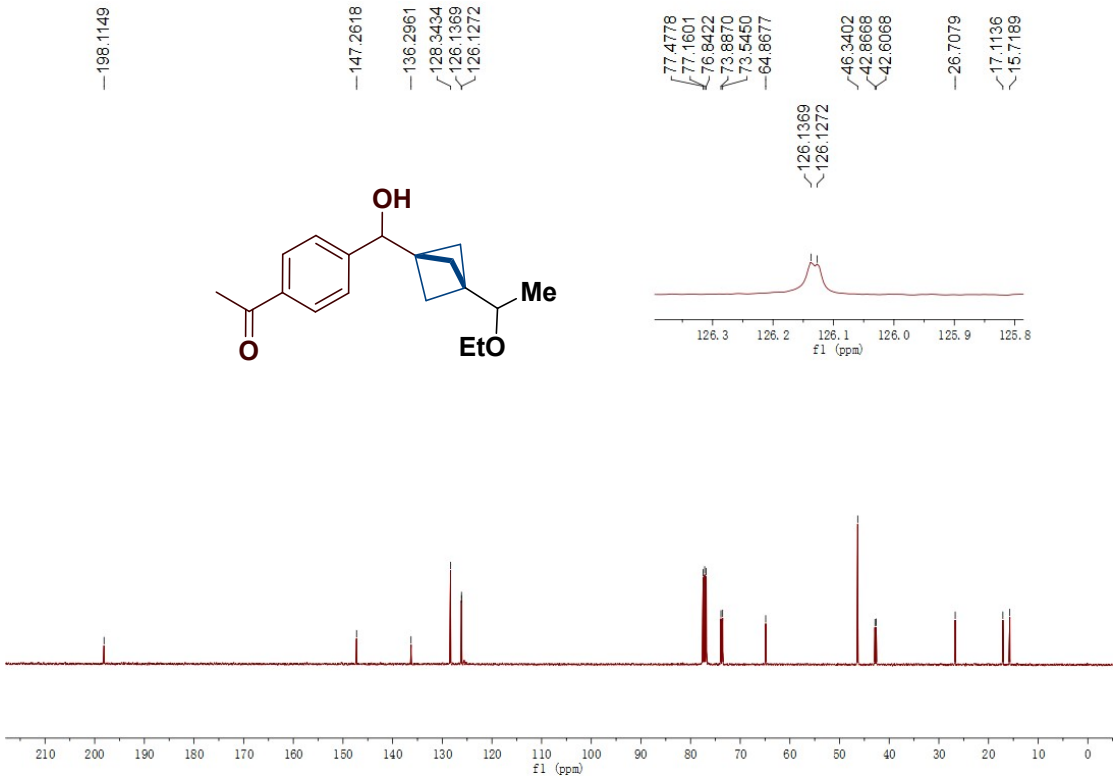
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13**



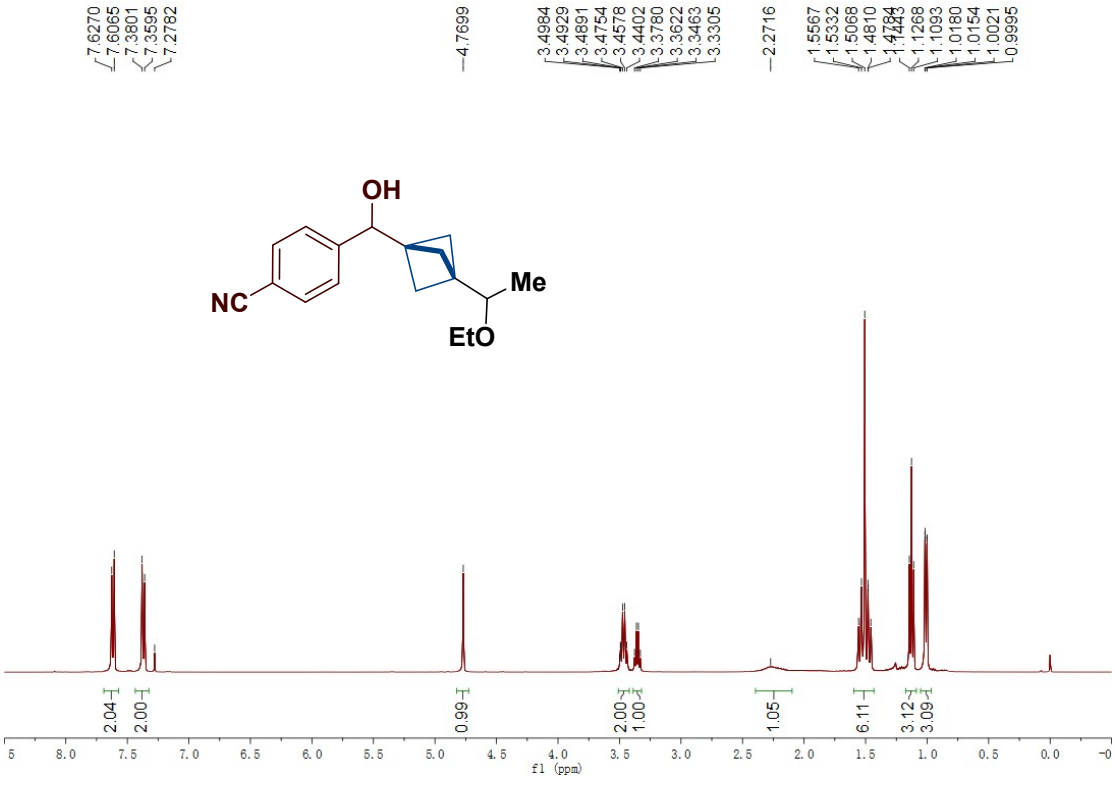
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13**



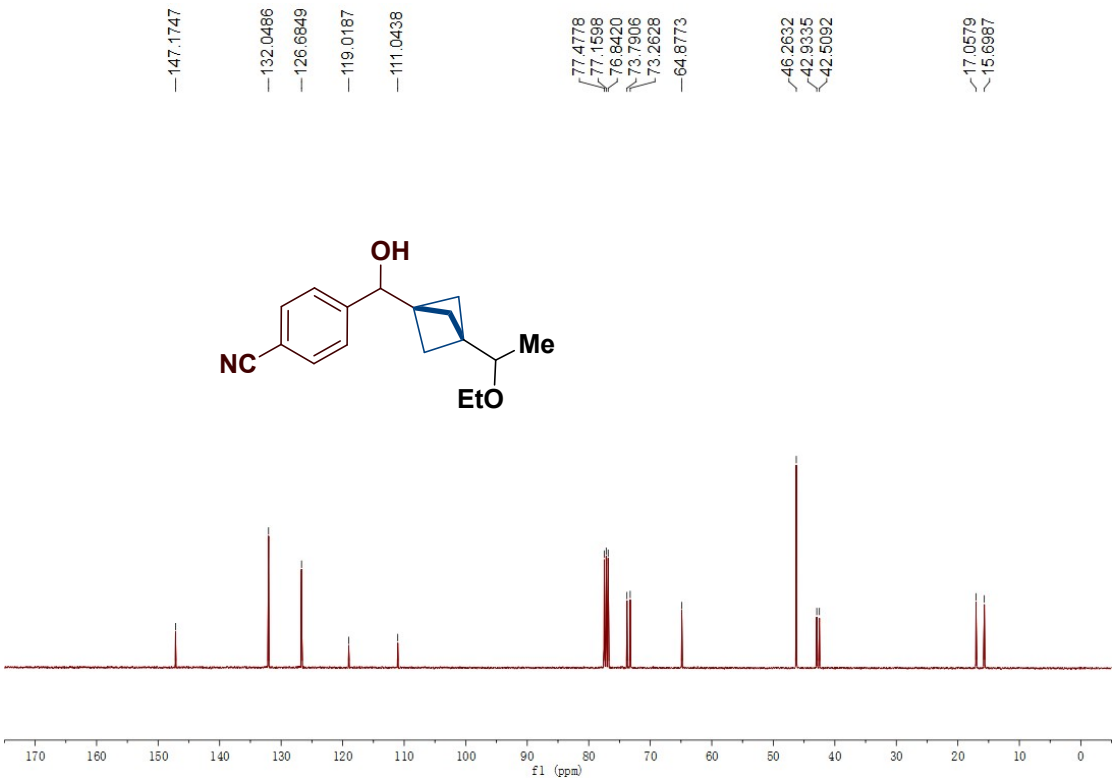
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**



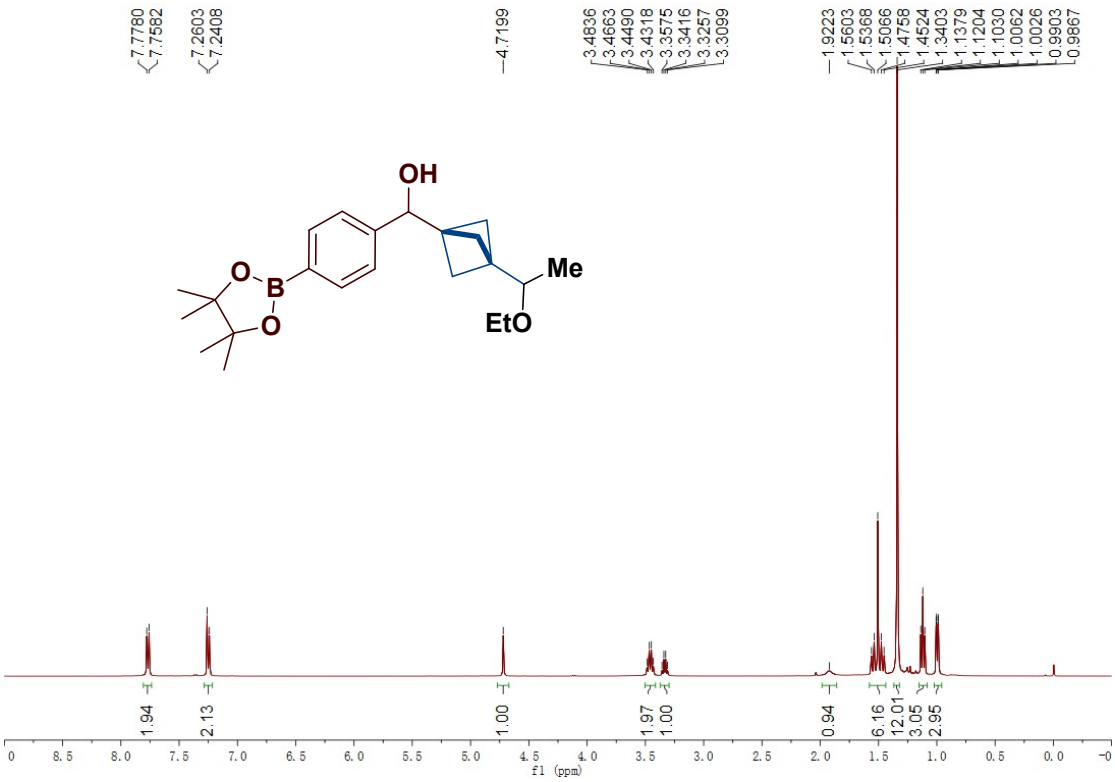
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**



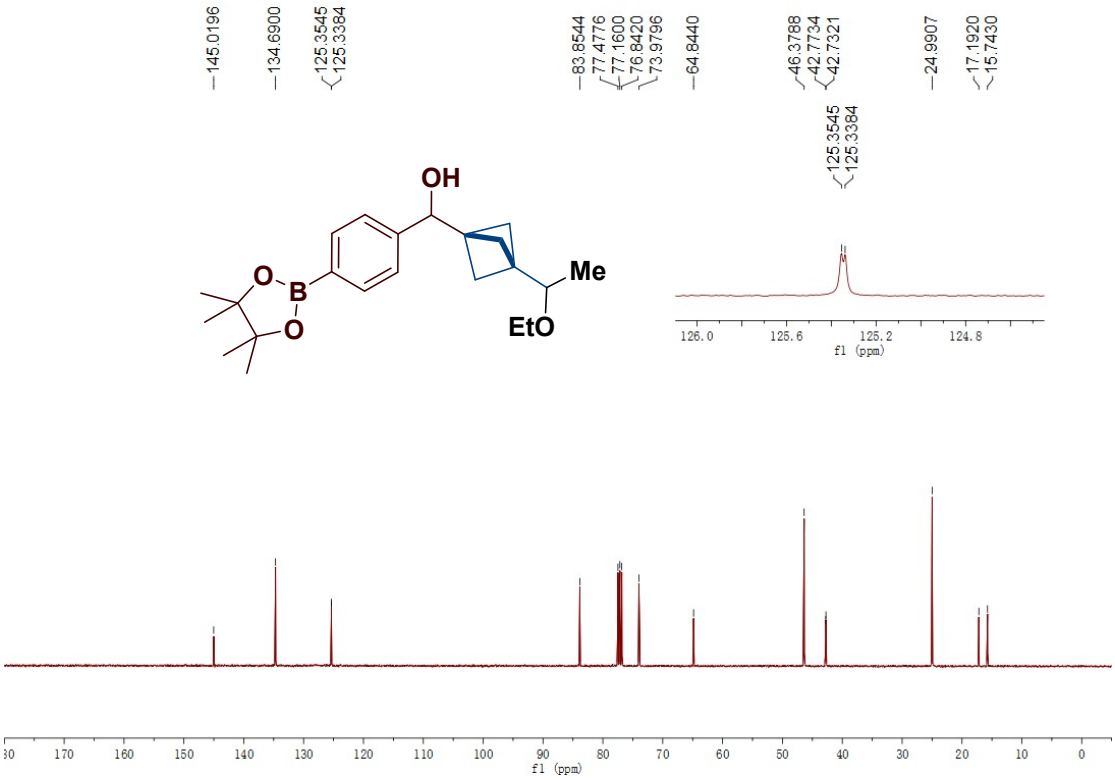
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**



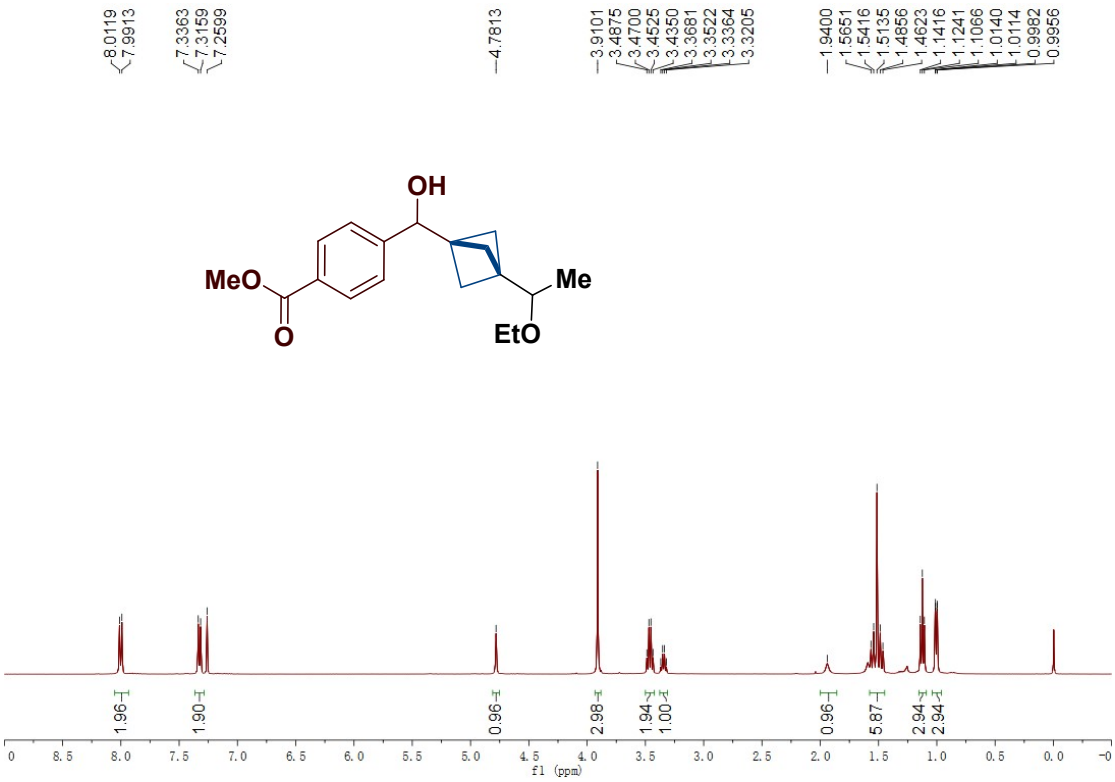
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **15**



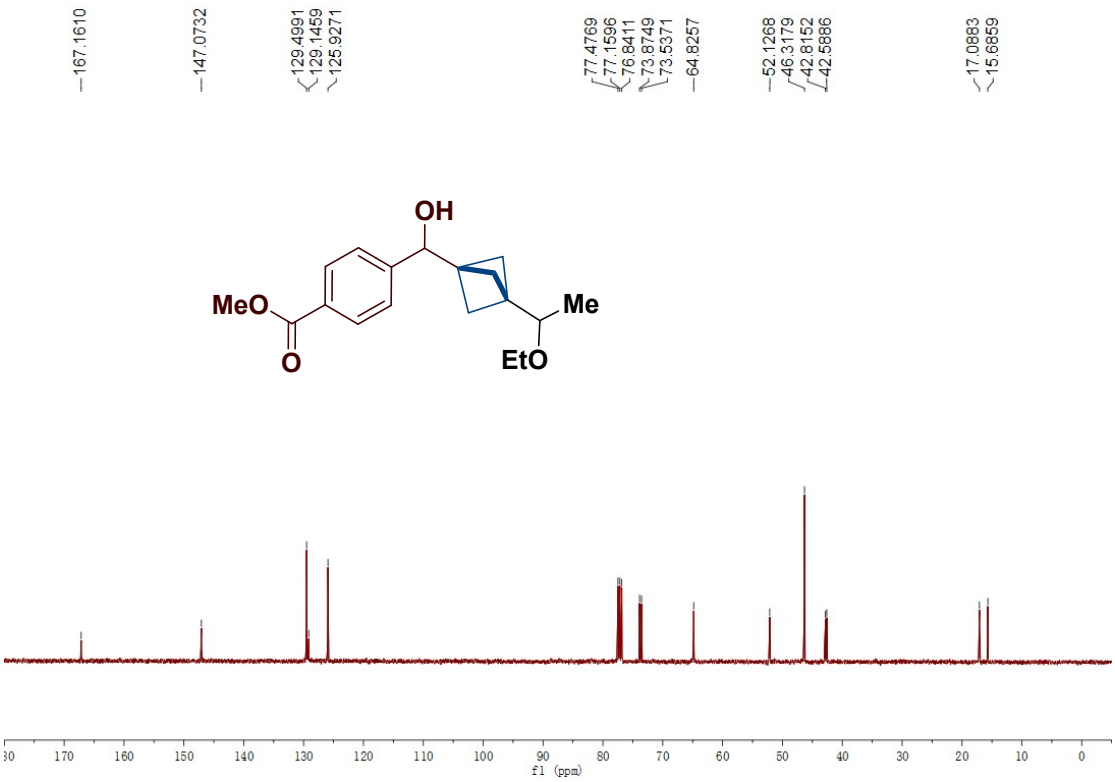
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **16**



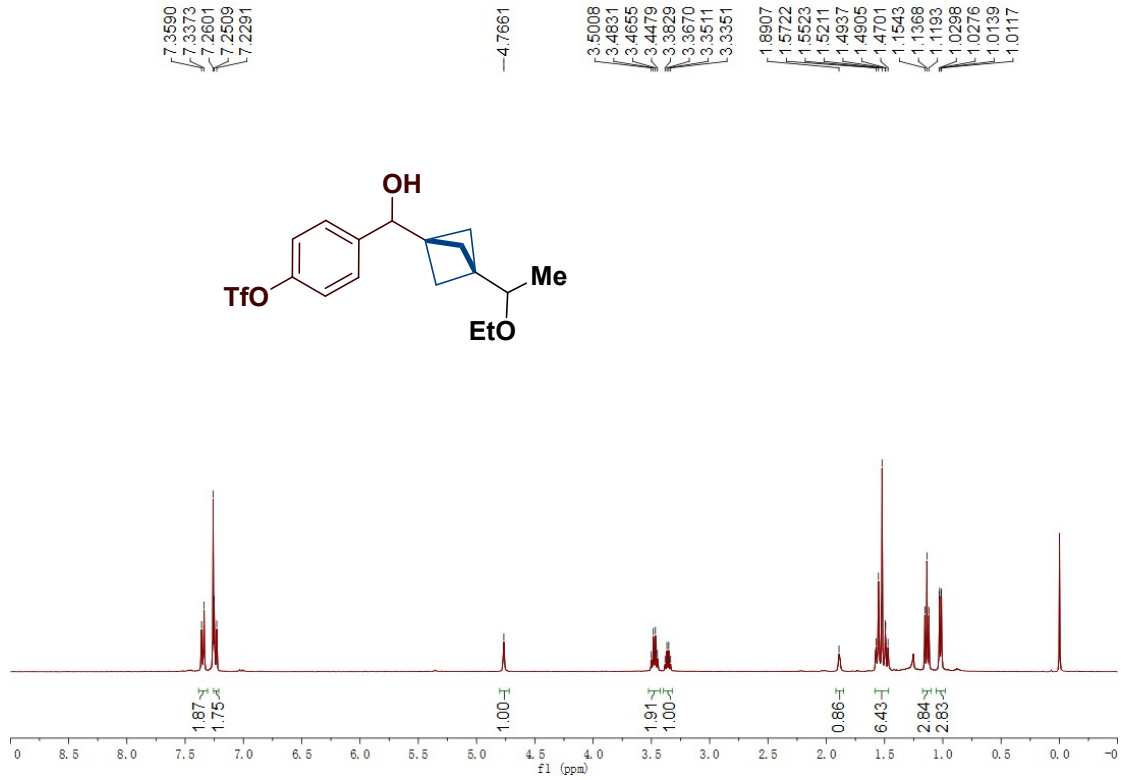
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **16**



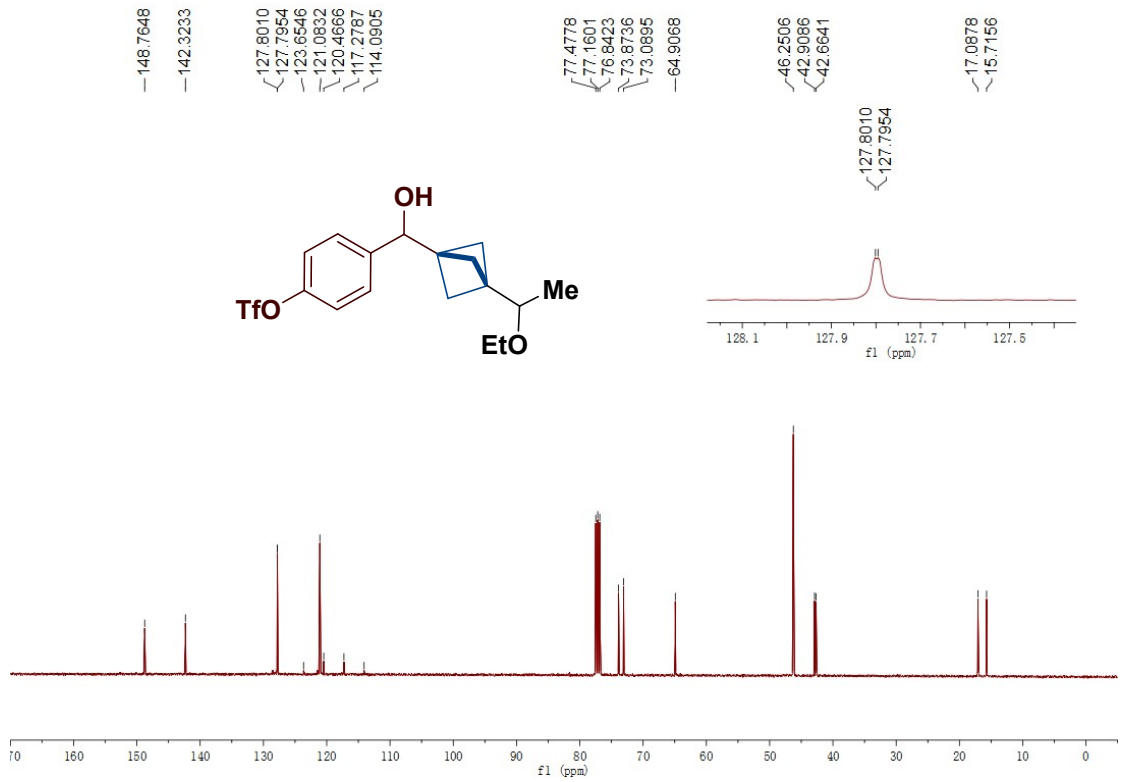
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **17**



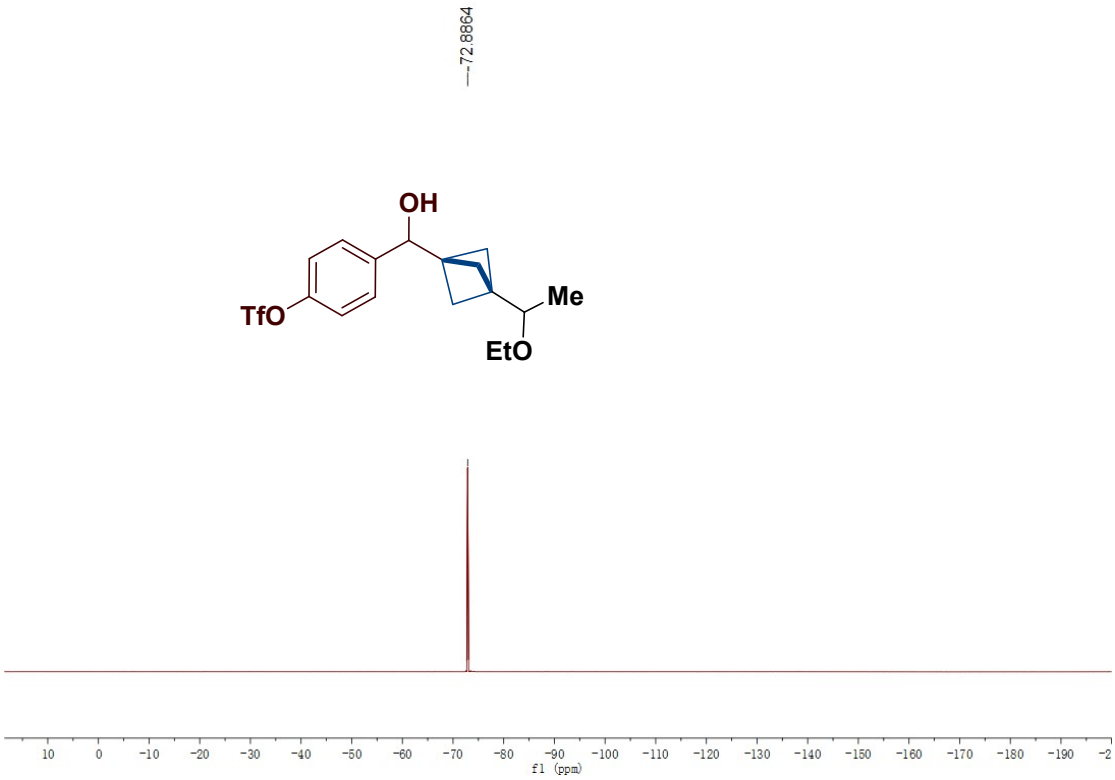
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **17**



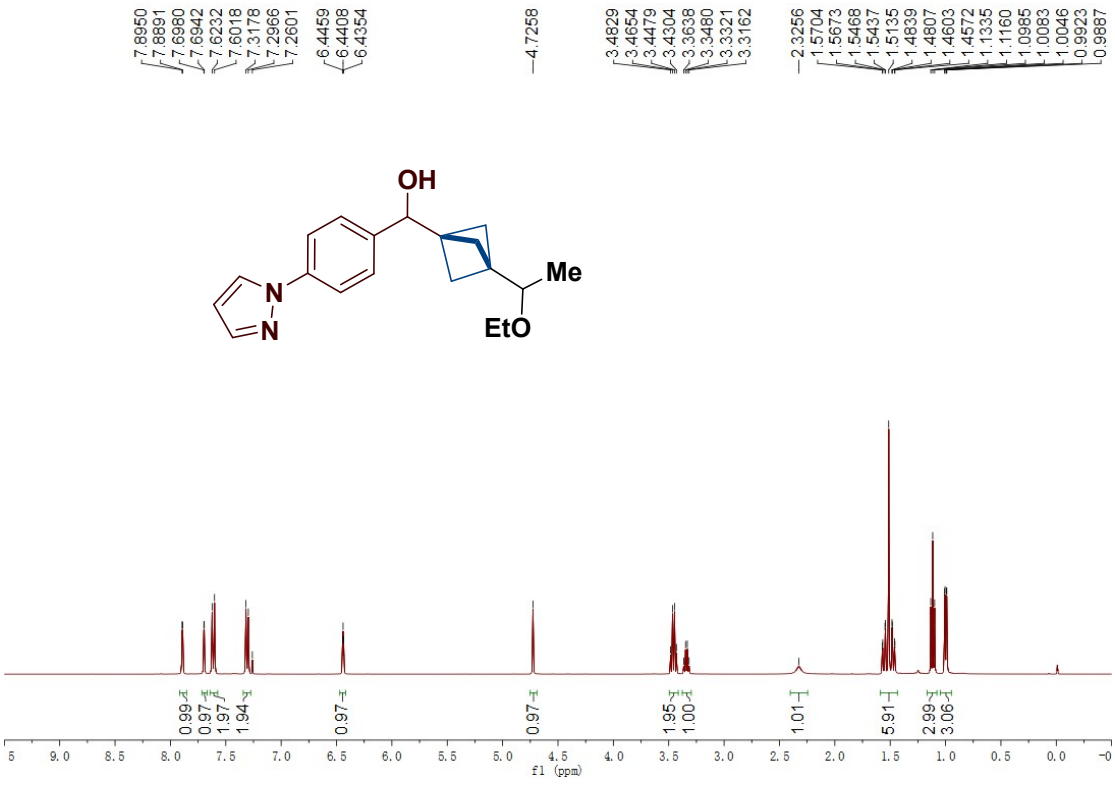
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **18**



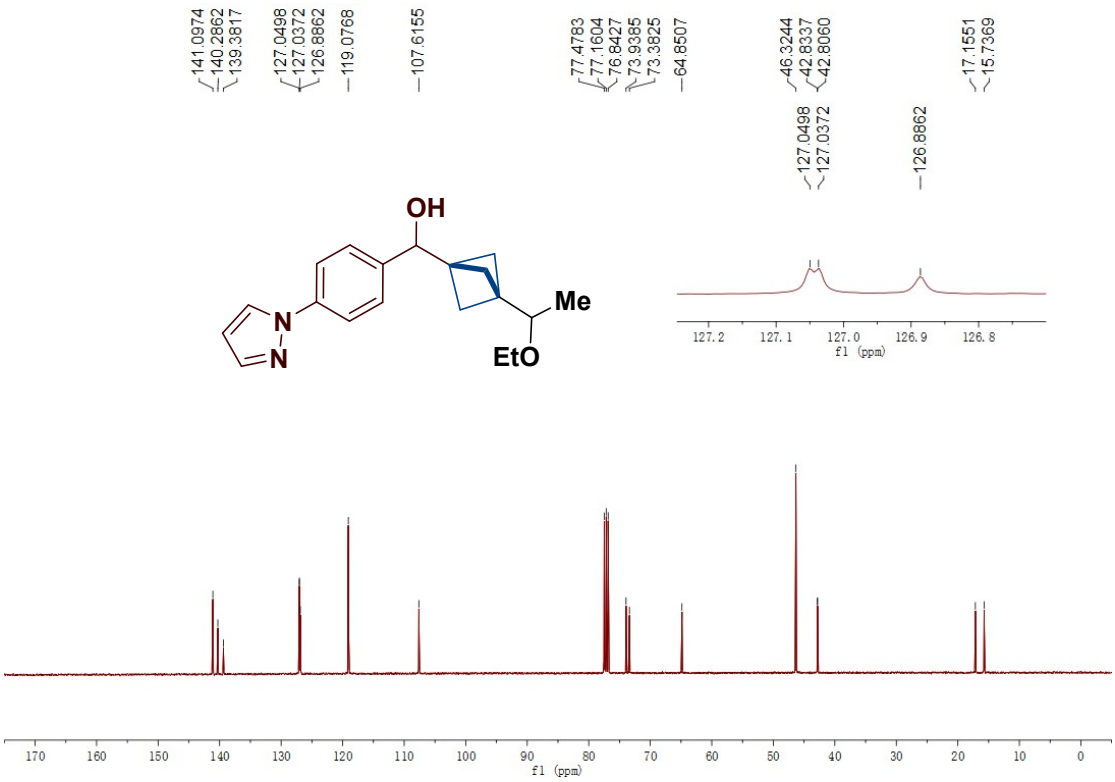
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **18**



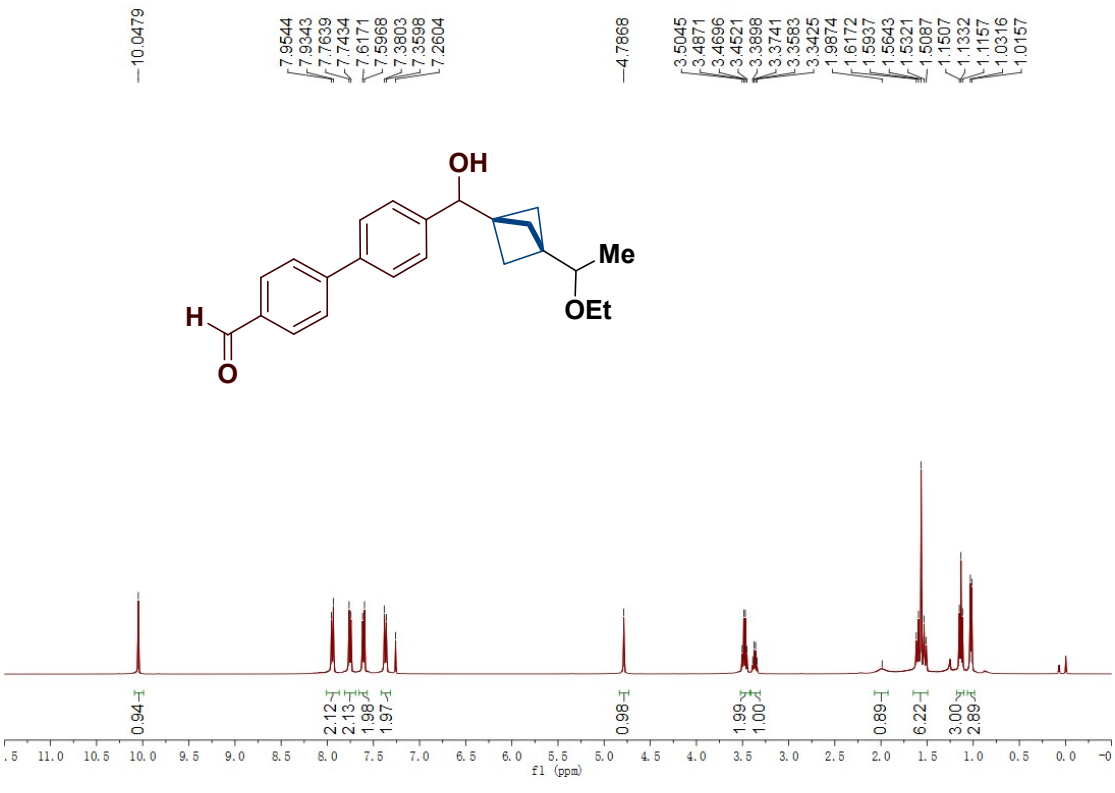
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **18**



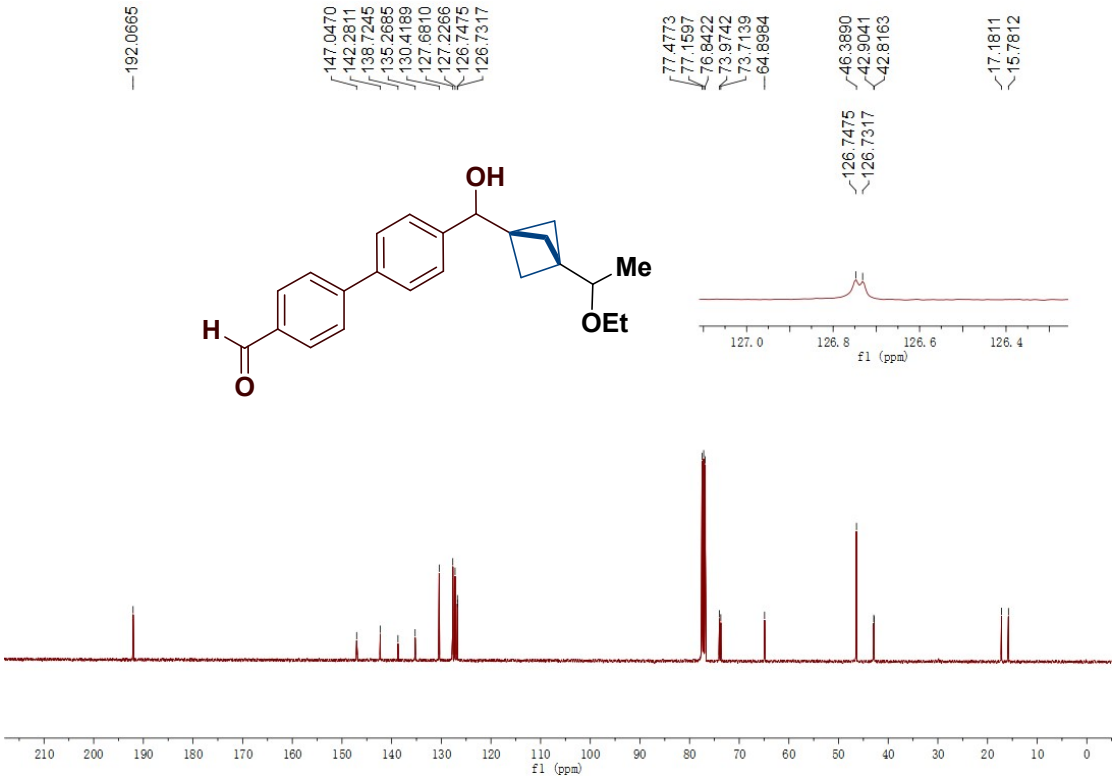
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **19**



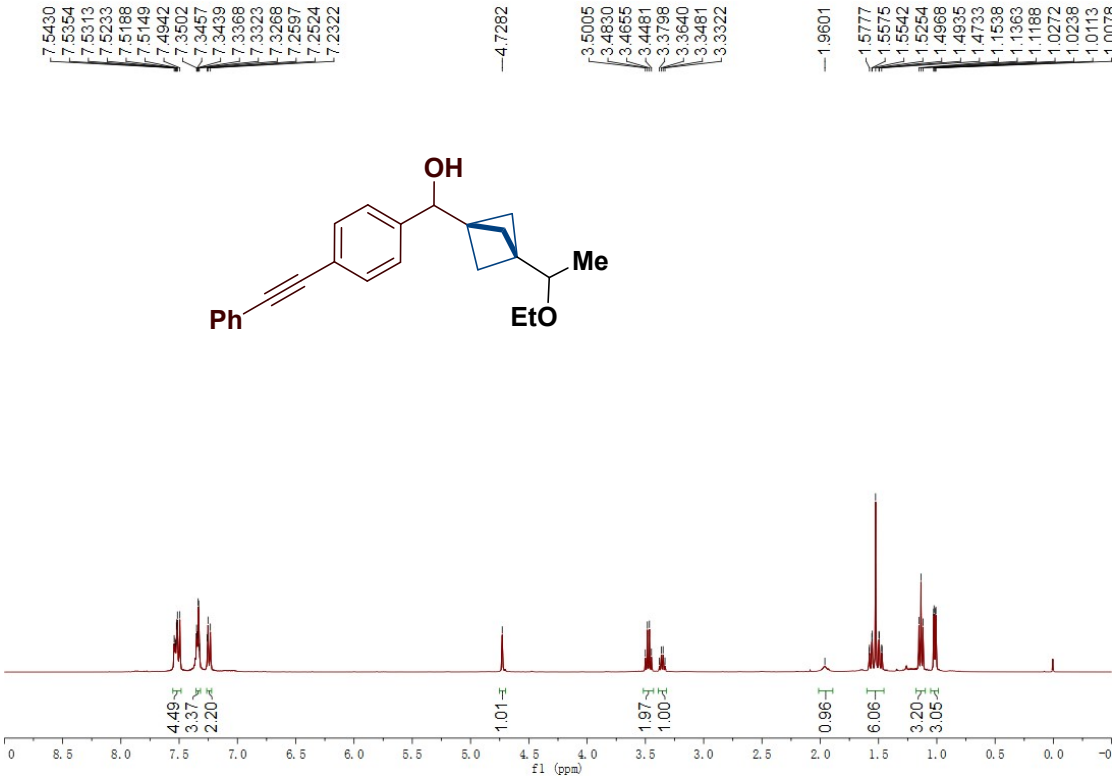
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **19**



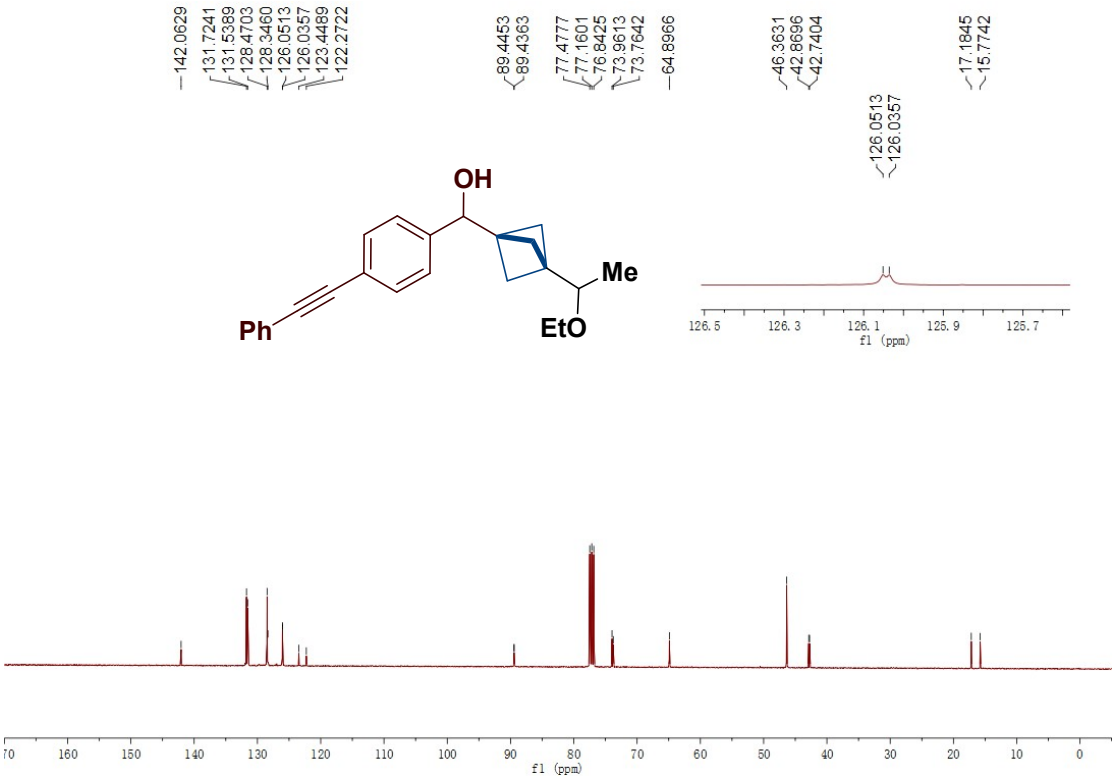
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **20**



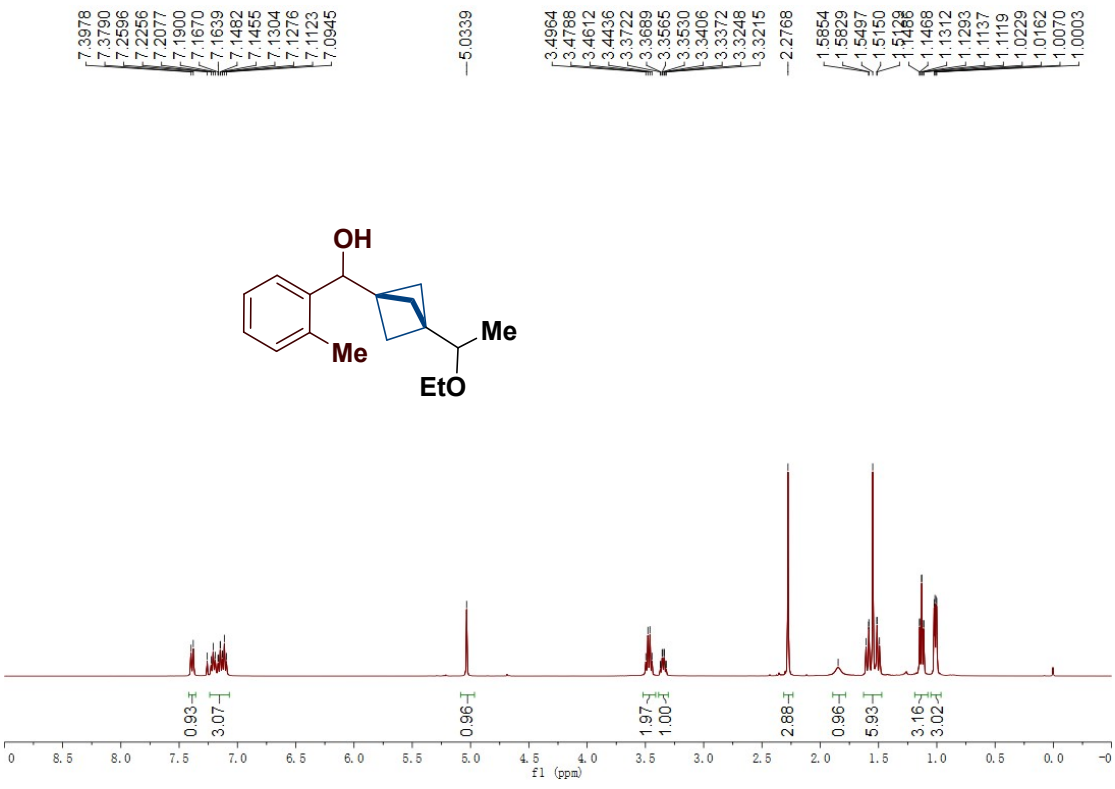
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **20**



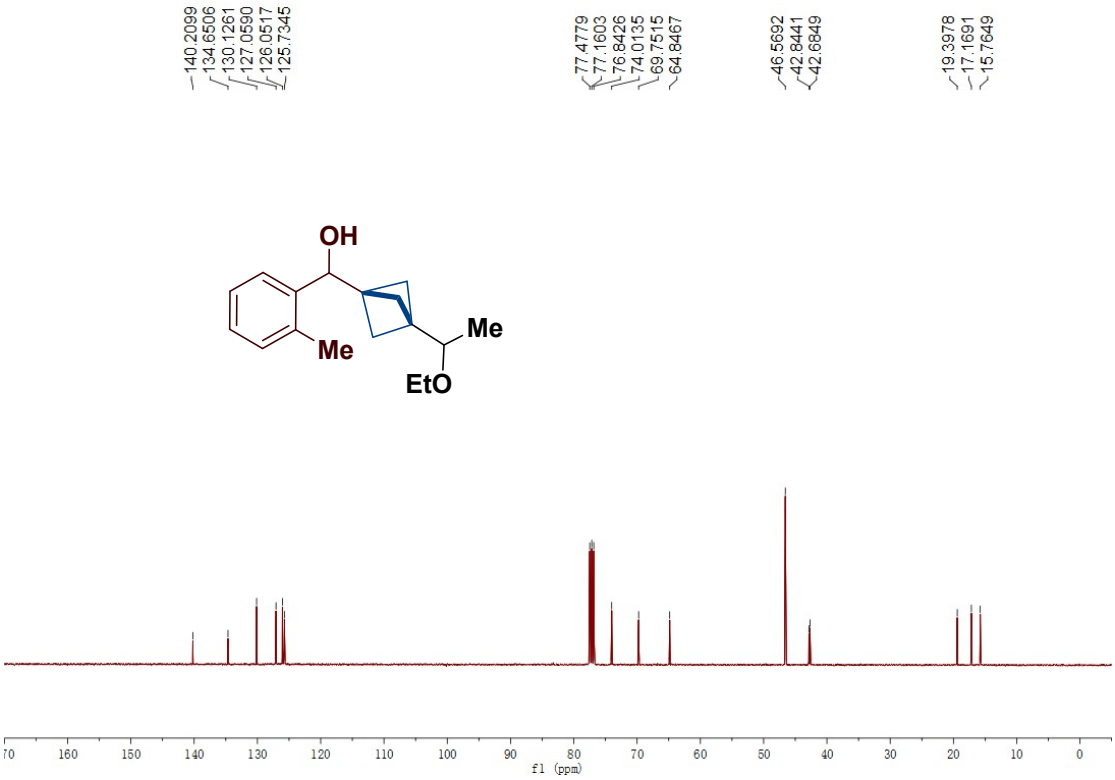
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **21**



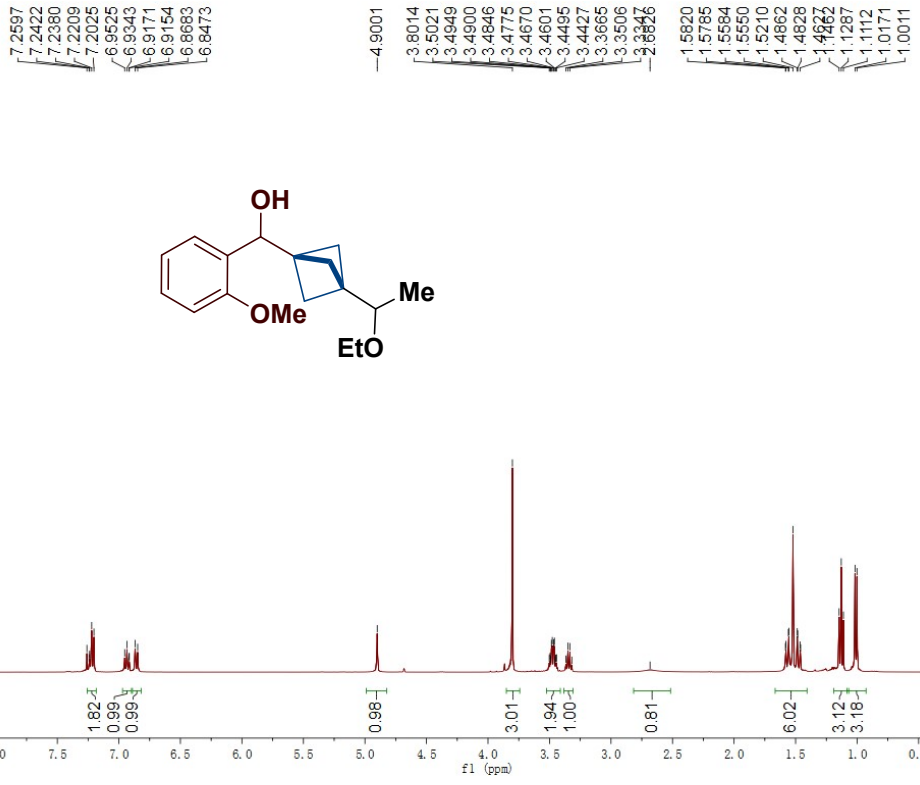
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **21**



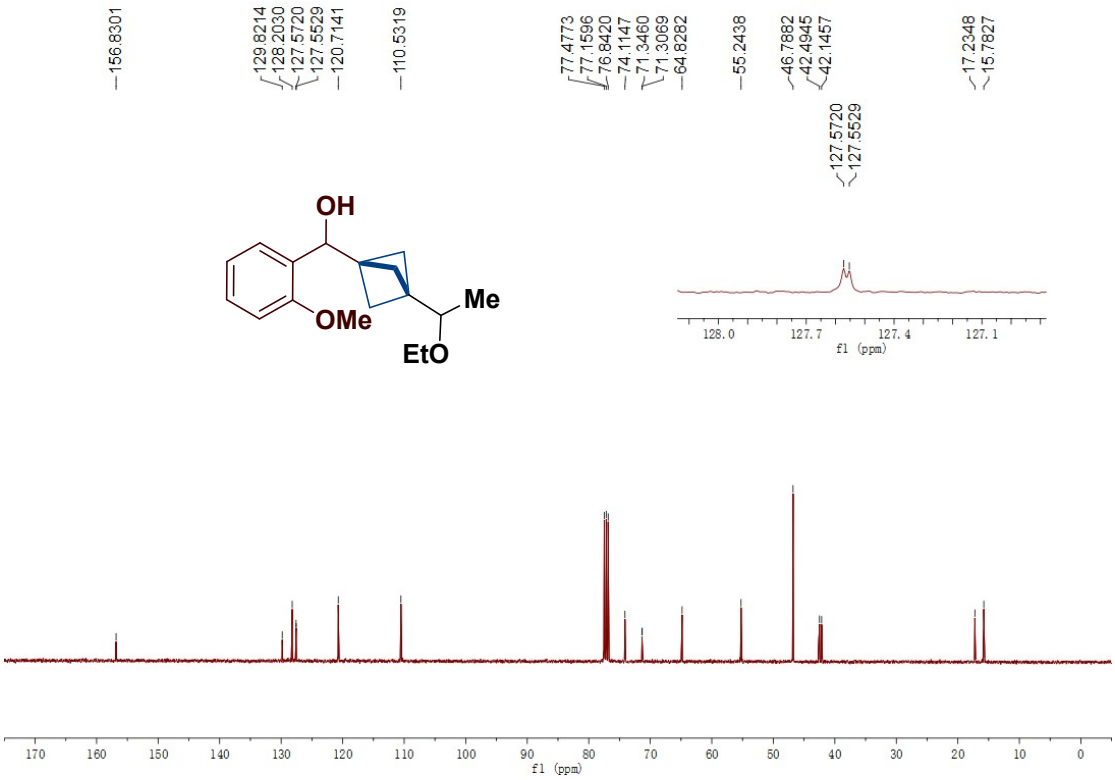
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **22**



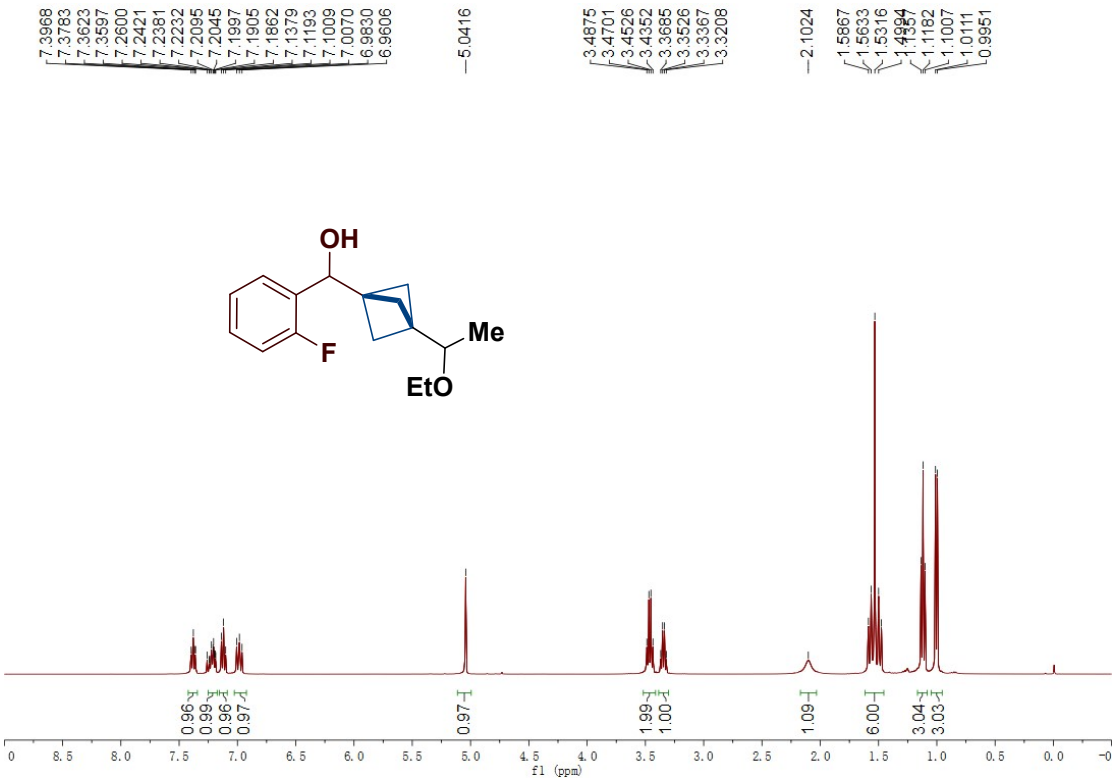
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **22**



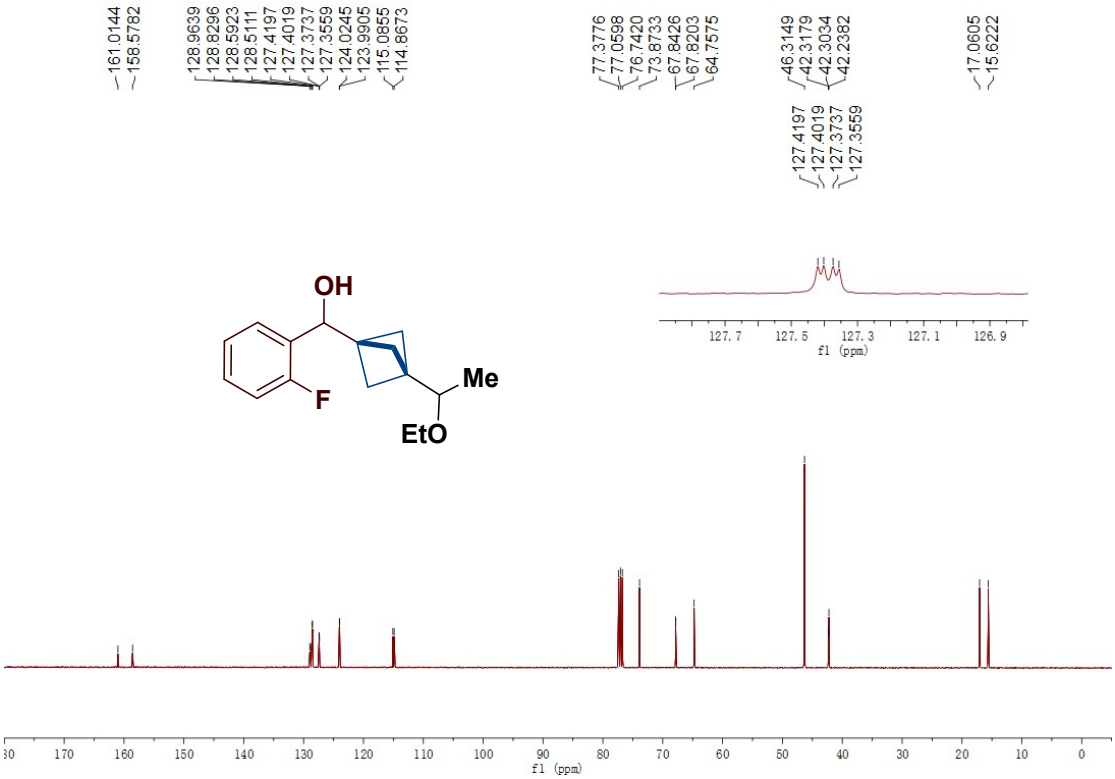
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **23**



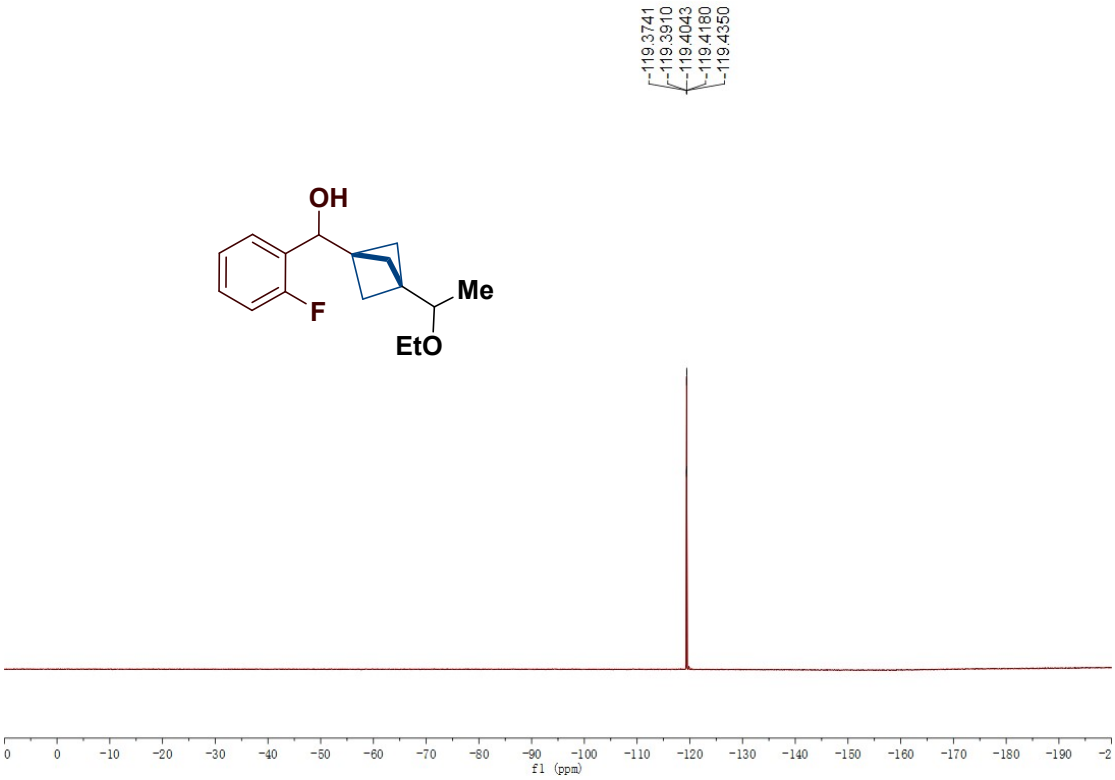
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **23**



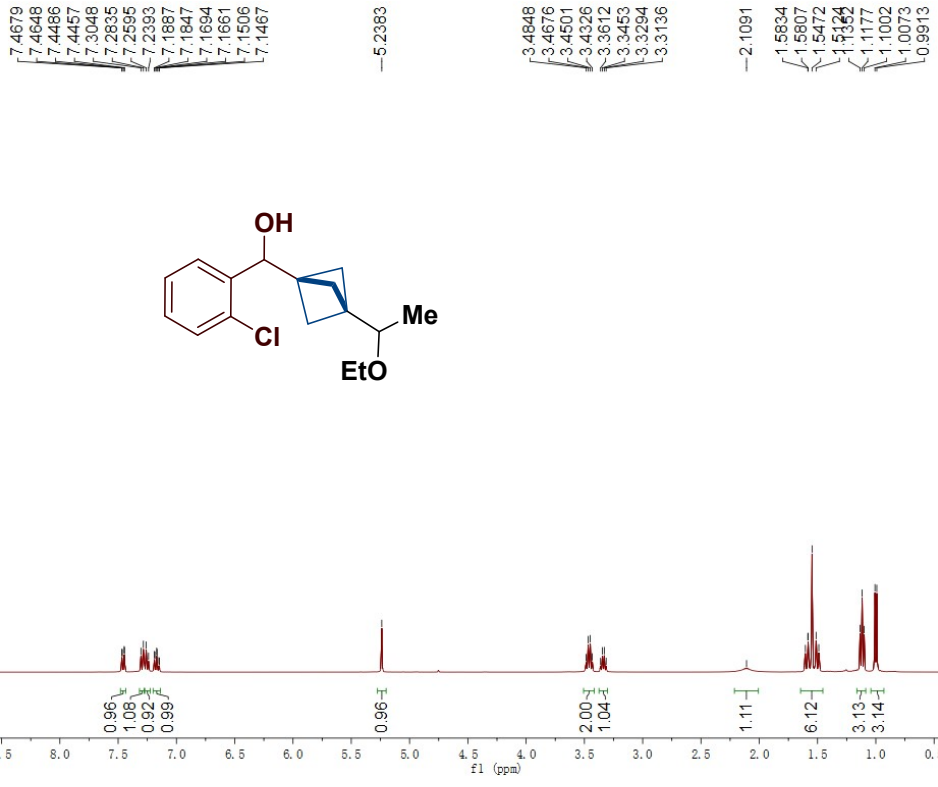
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **24**



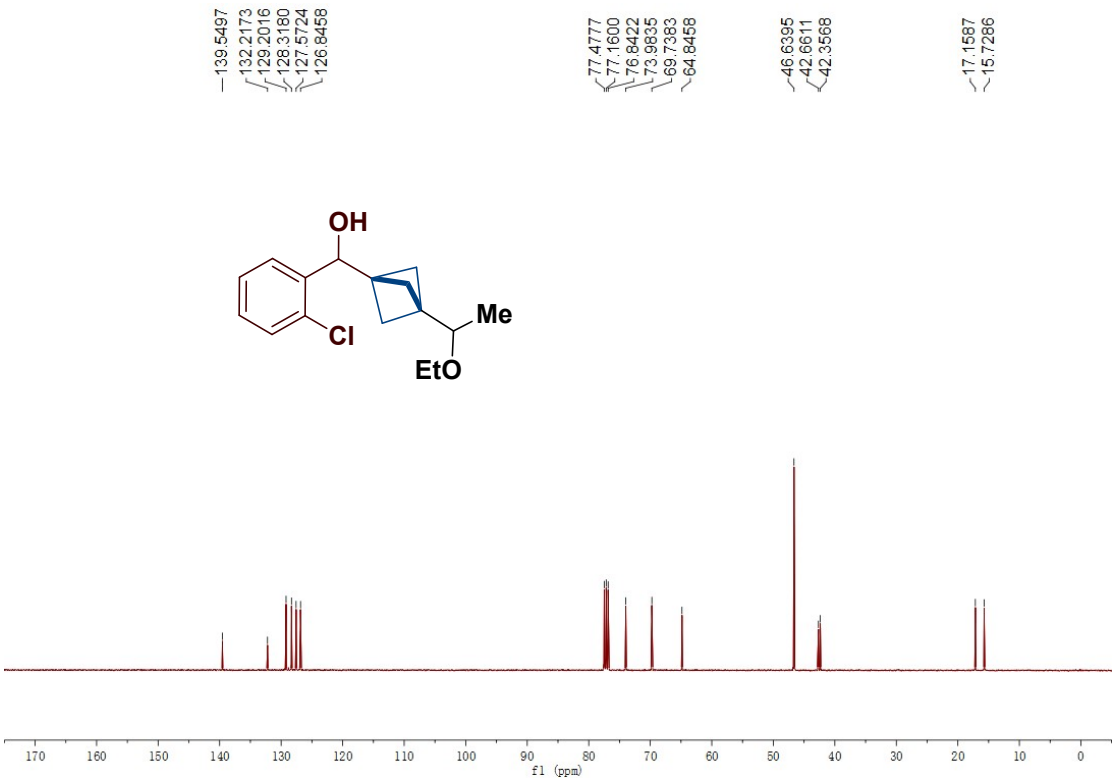
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **24**



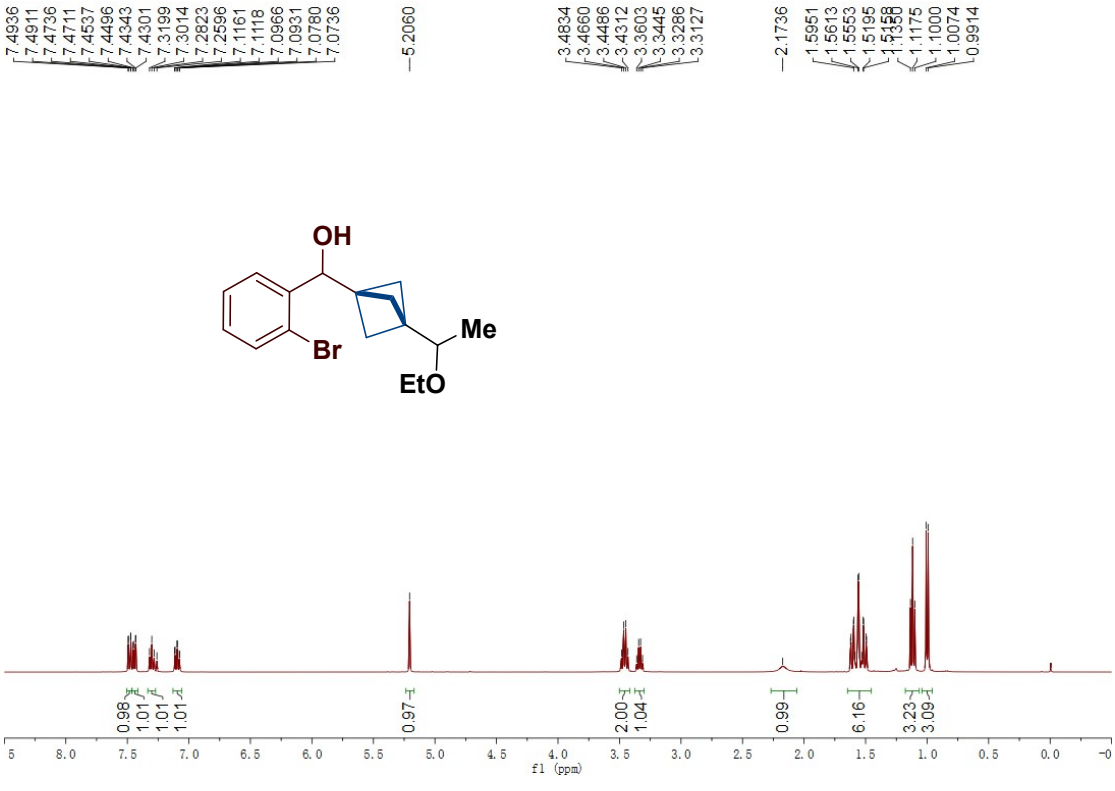
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **24**



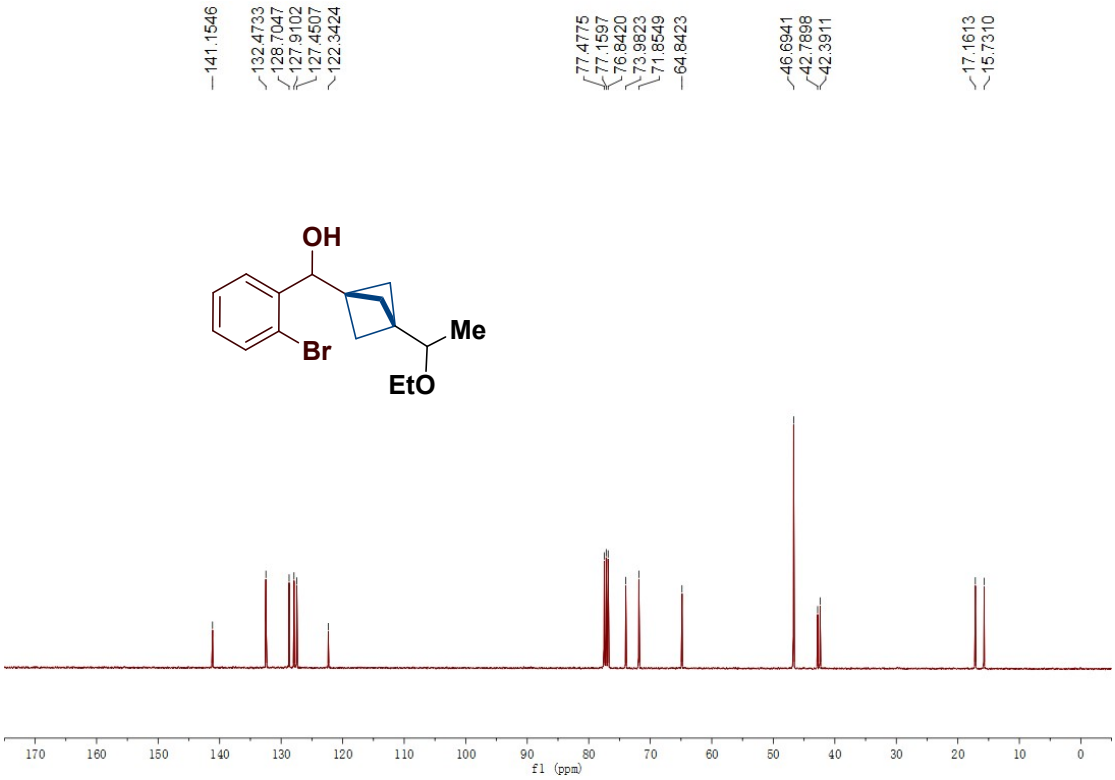
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **25**



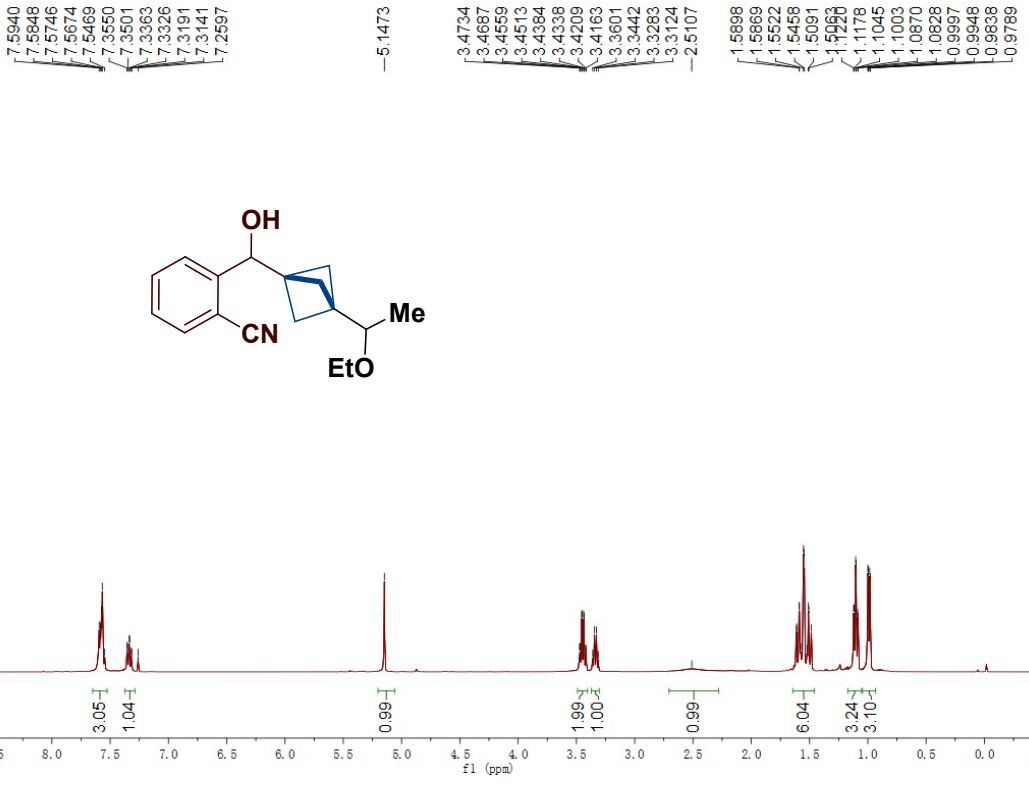
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **25**



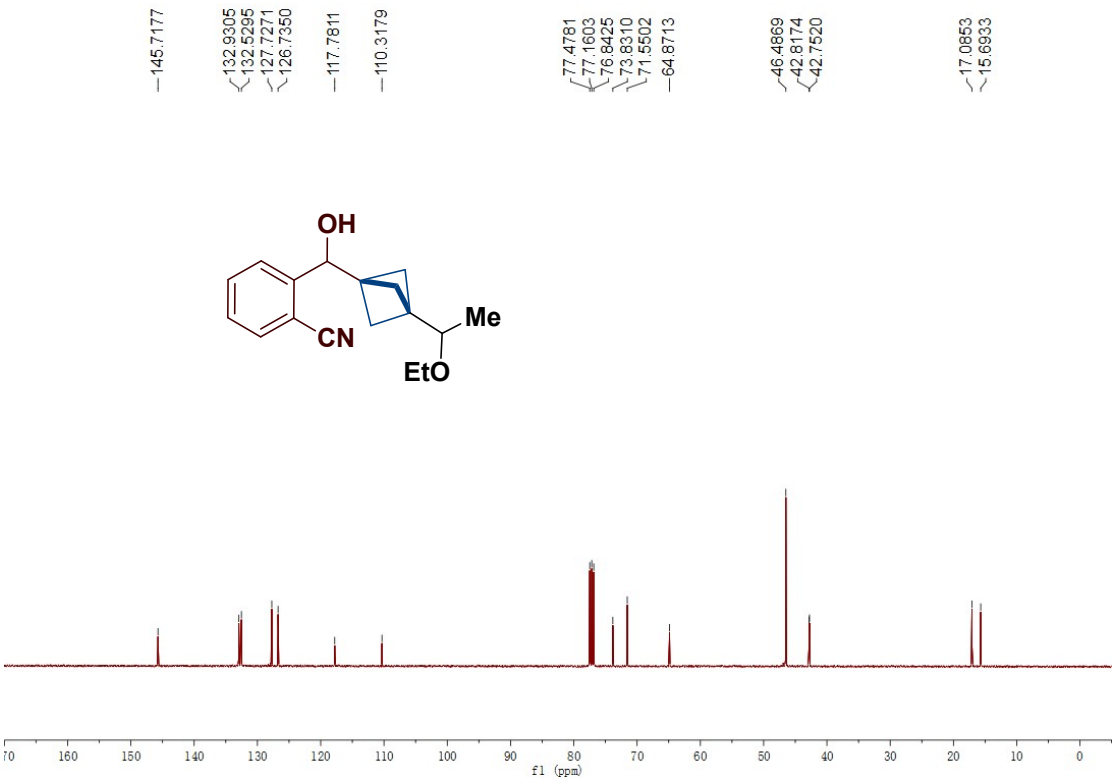
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **26**



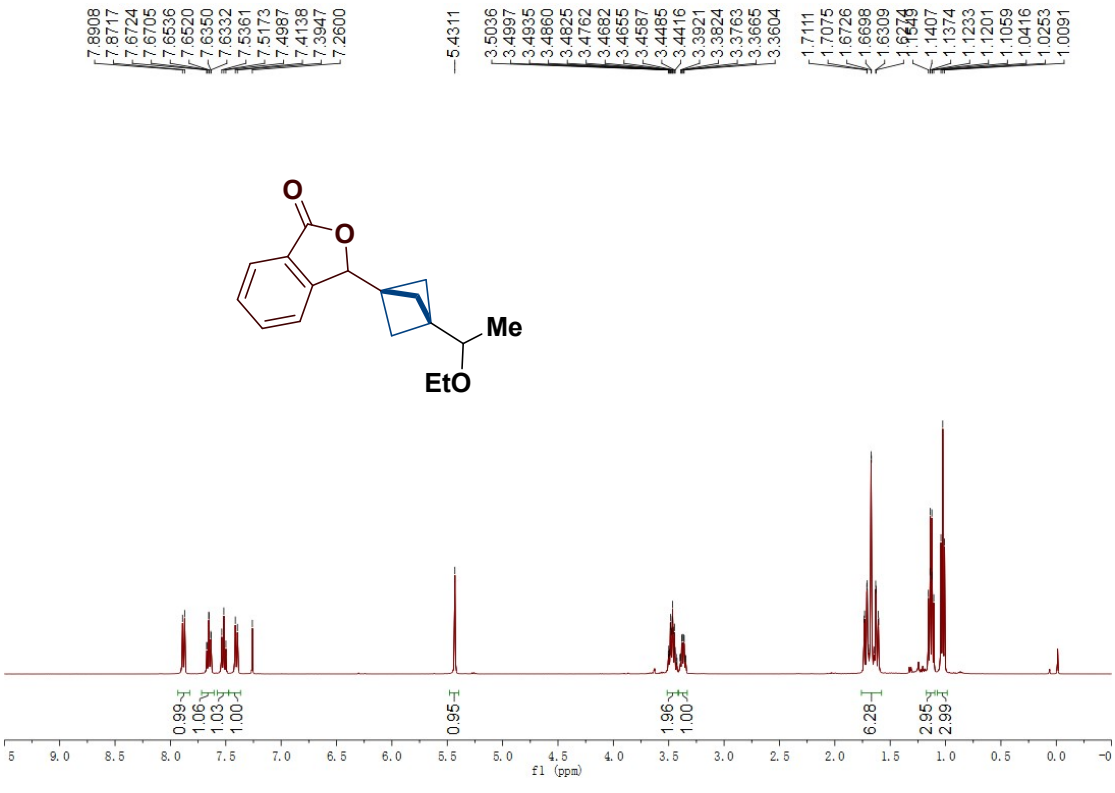
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **26**



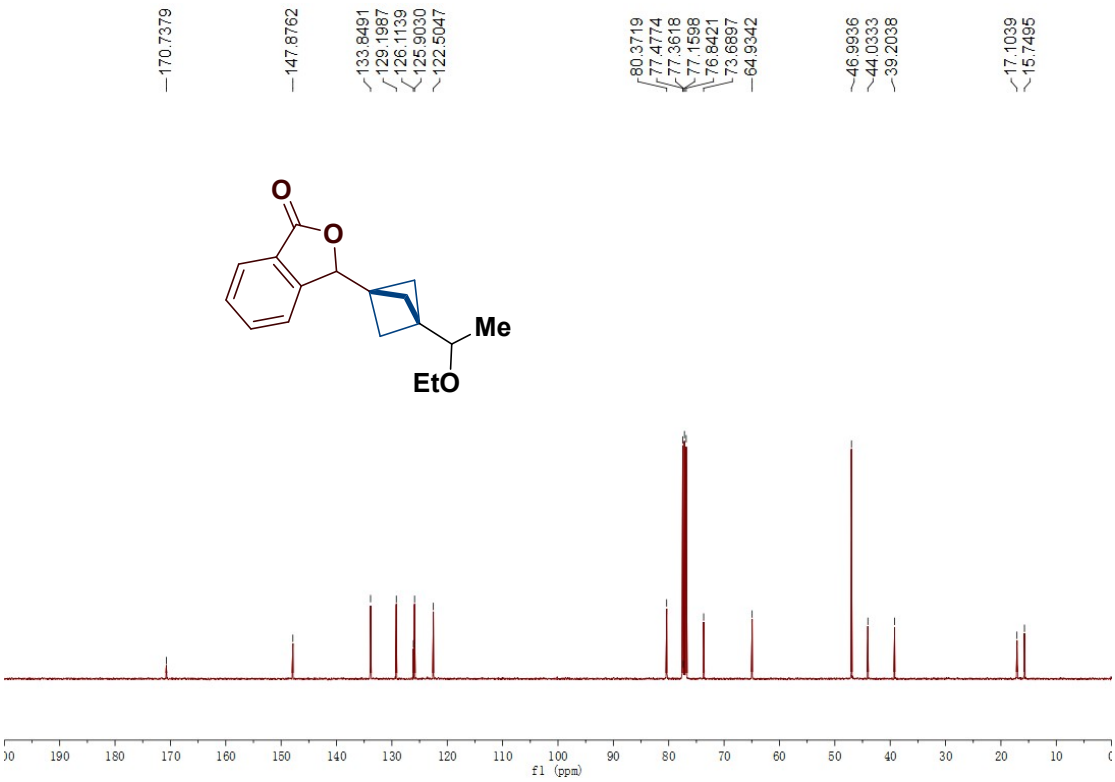
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **27**



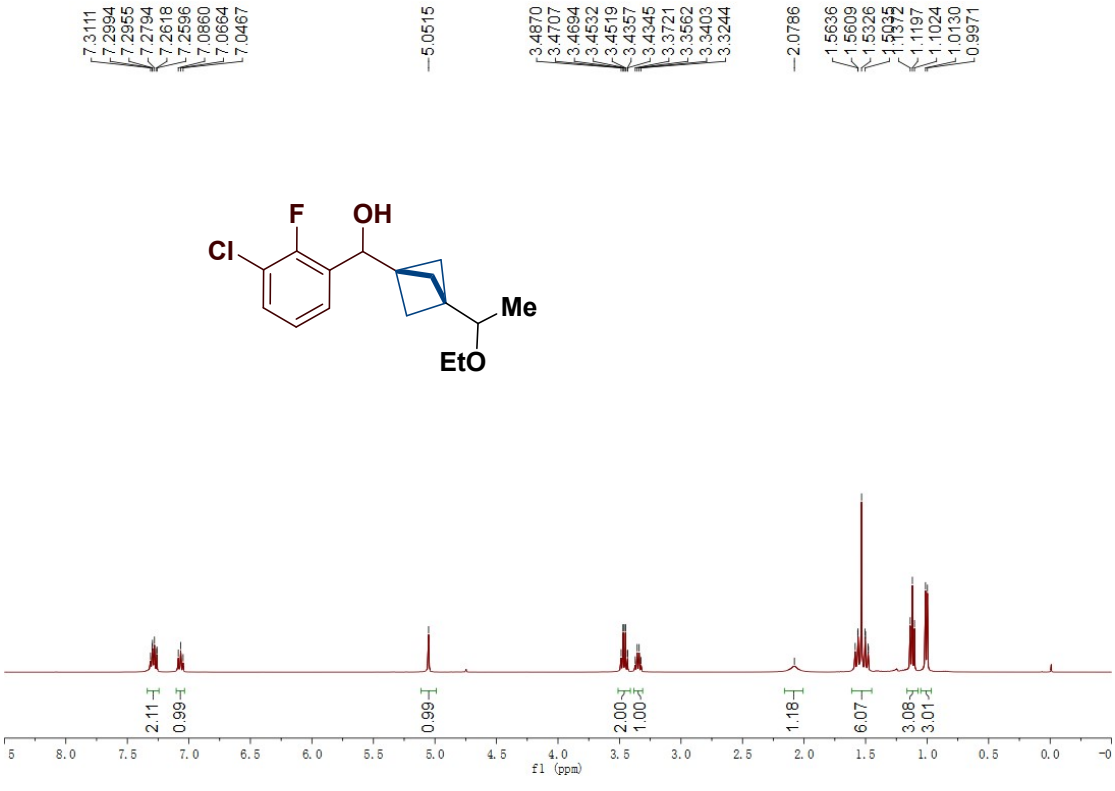
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **27**



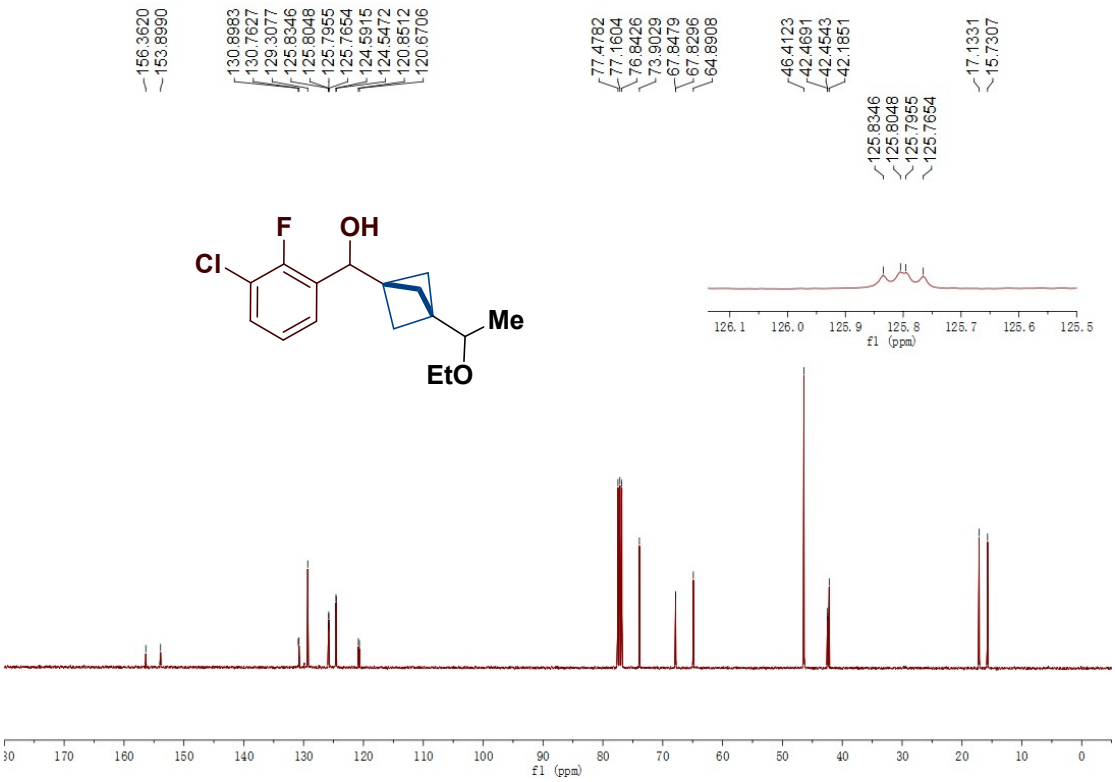
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **28**



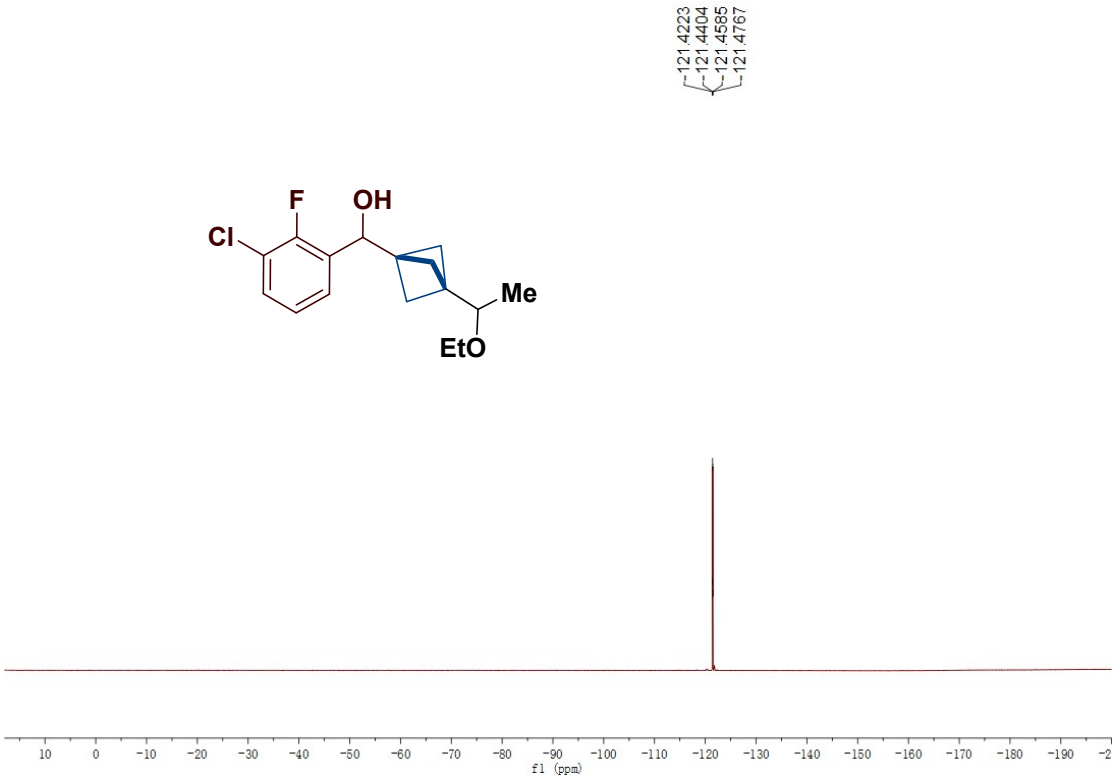
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **28**



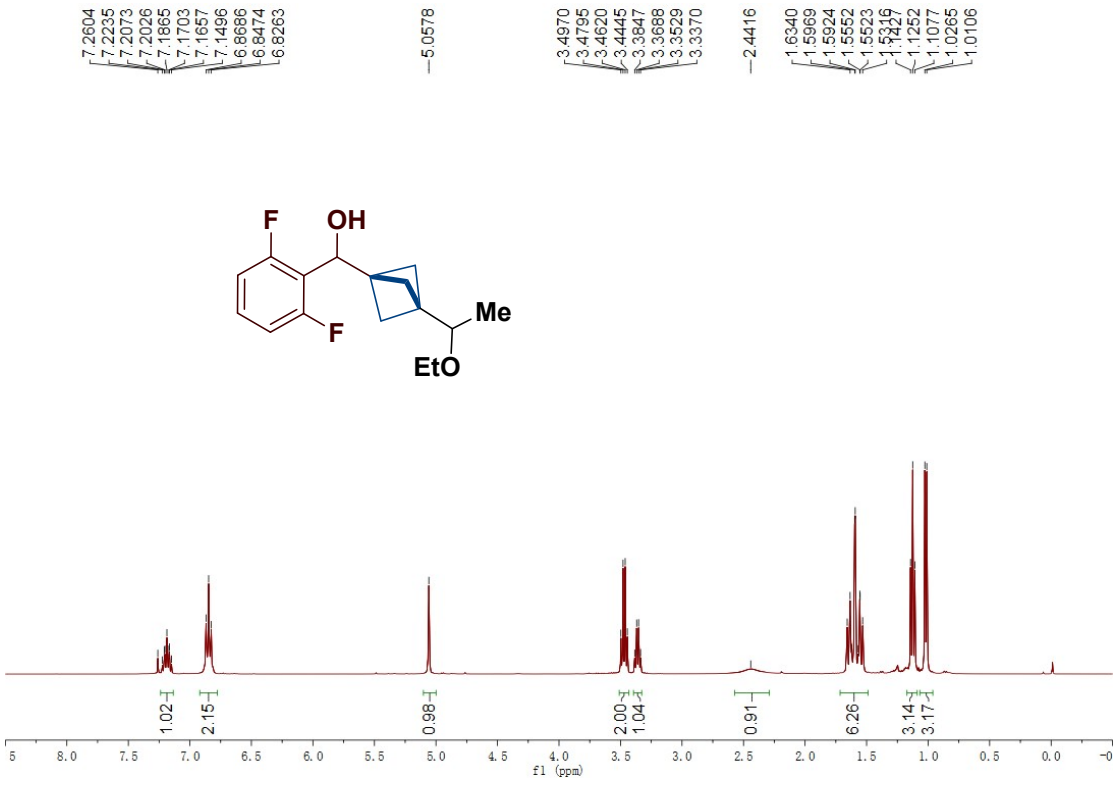
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **29**



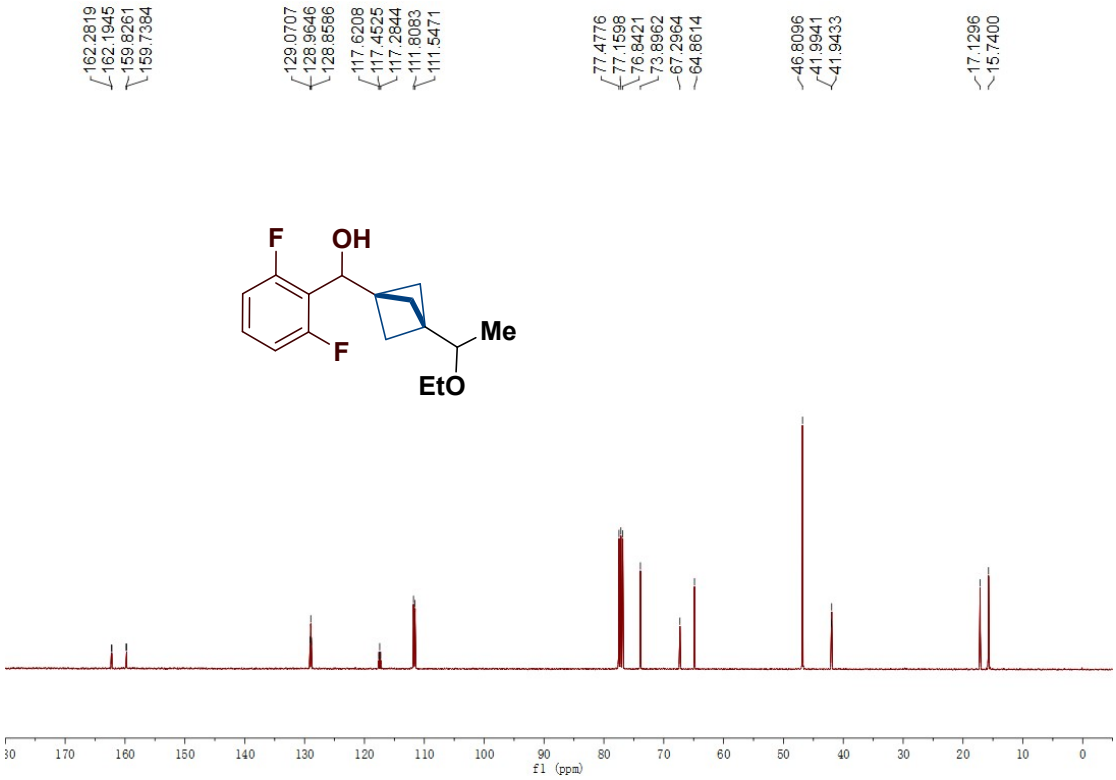
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **29**



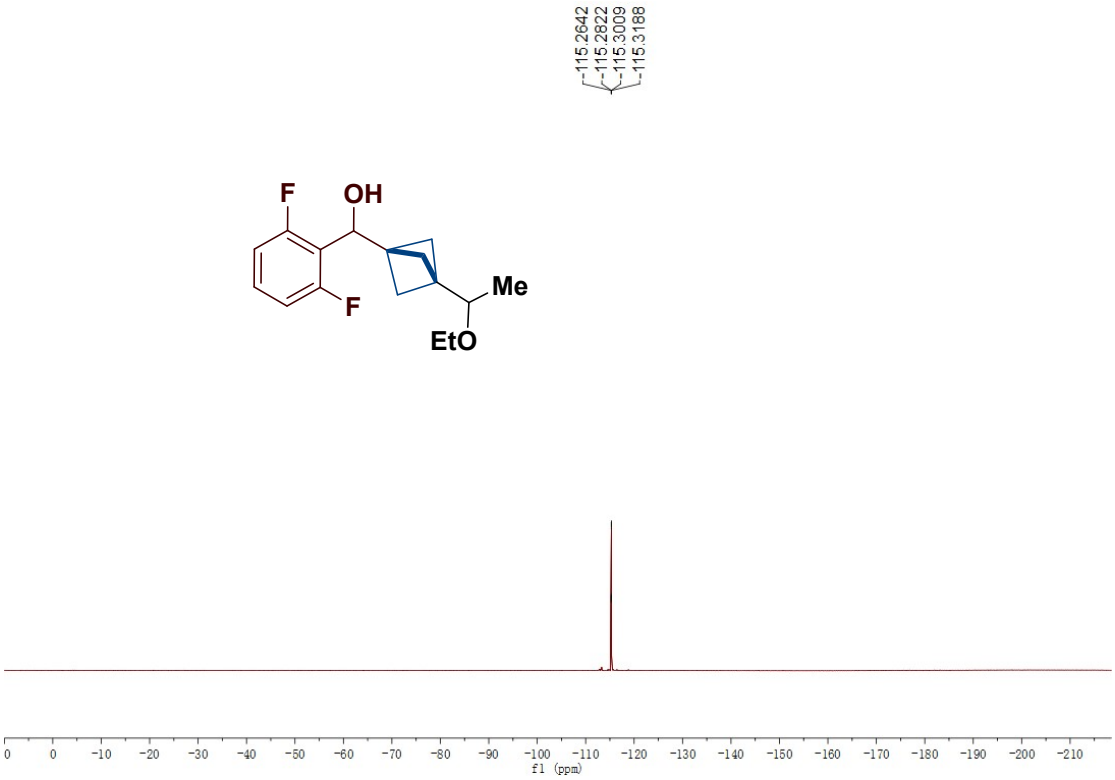
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **29**



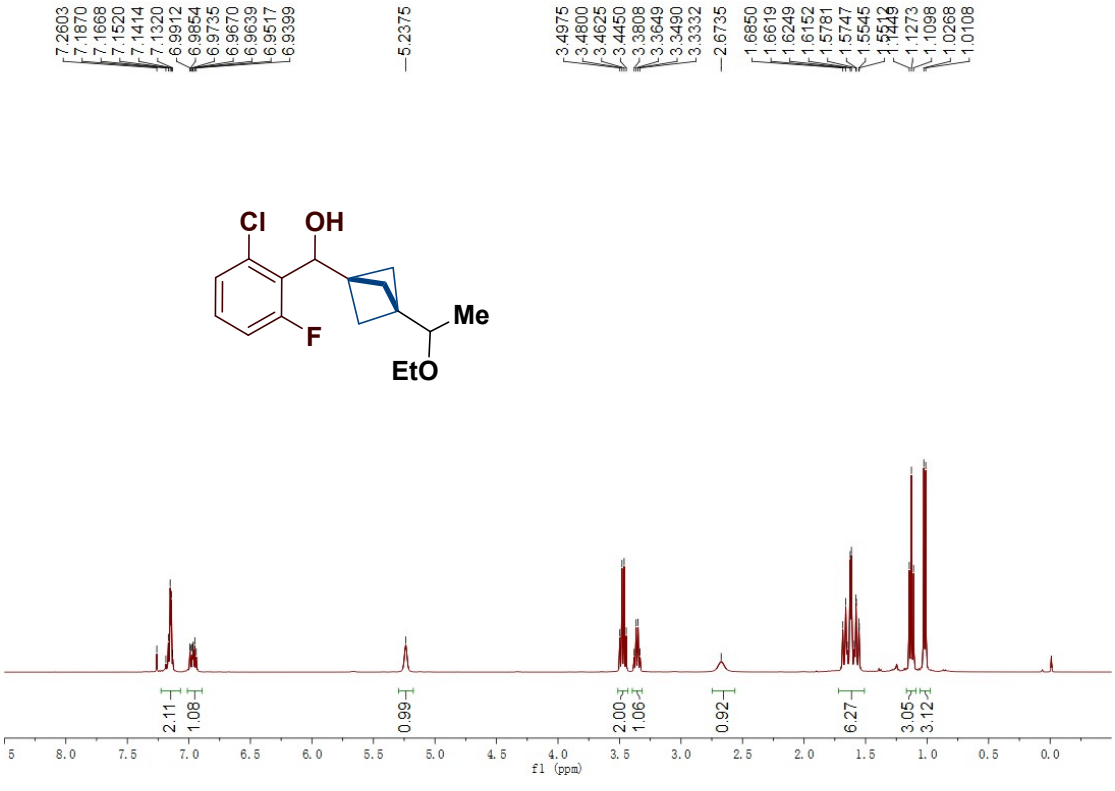
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **30**



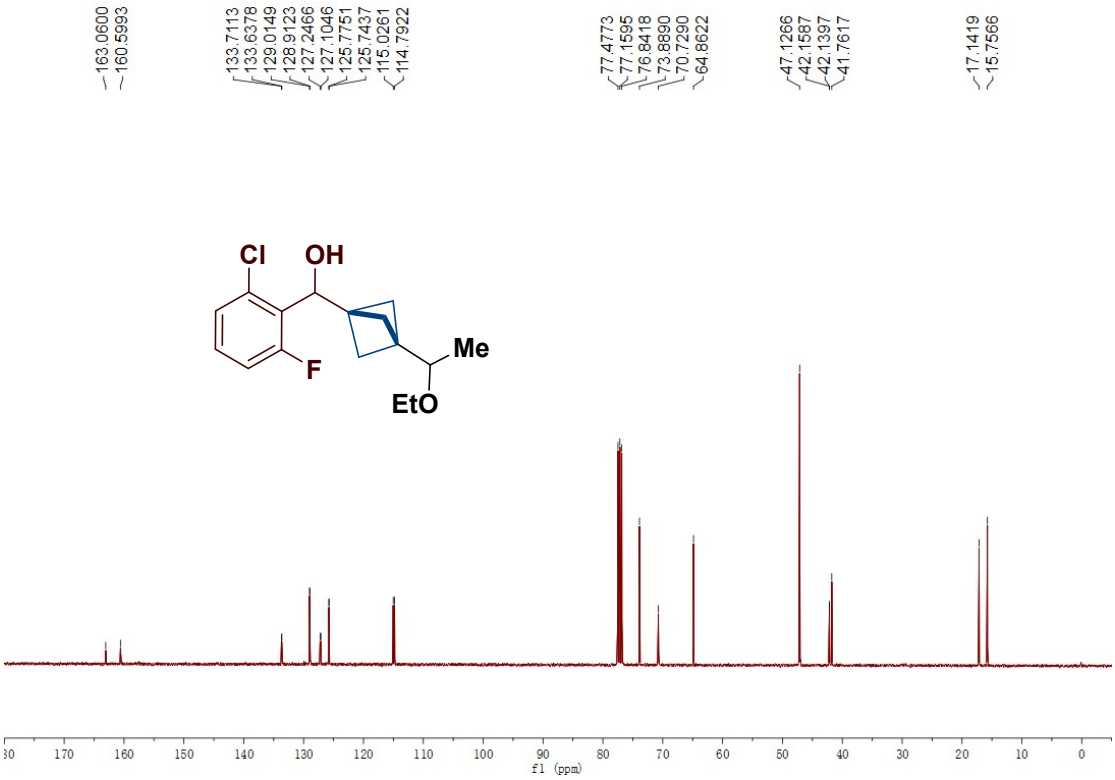
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **30**



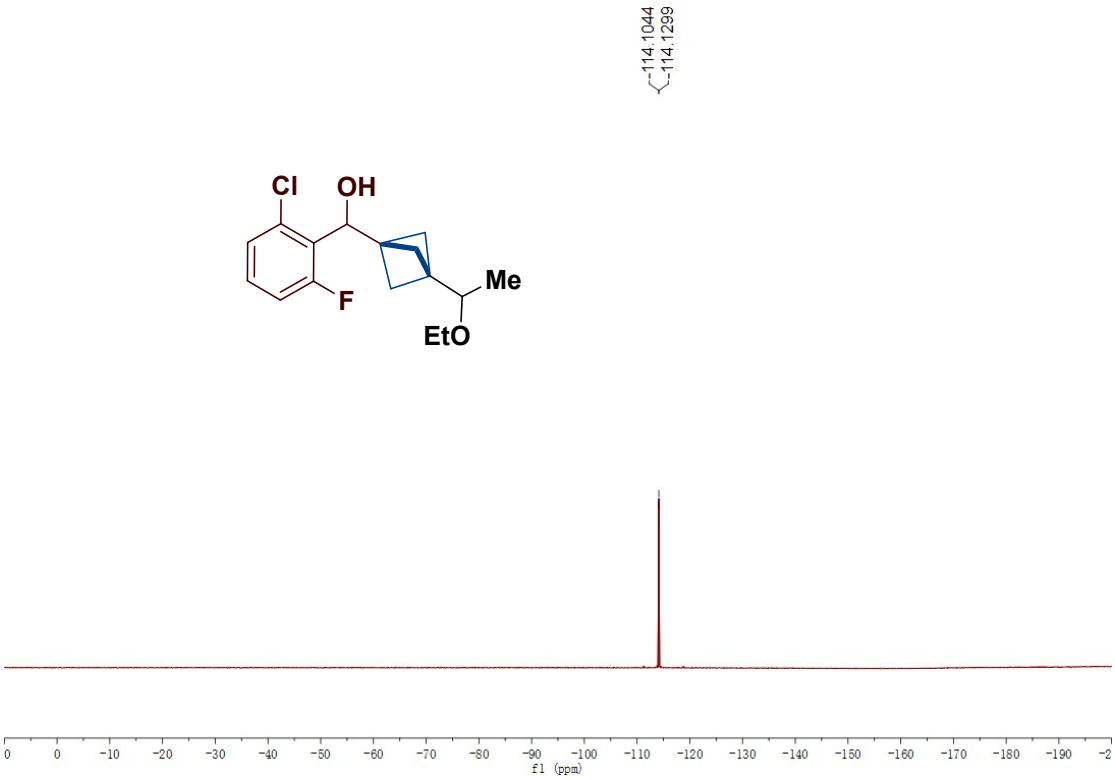
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **30**



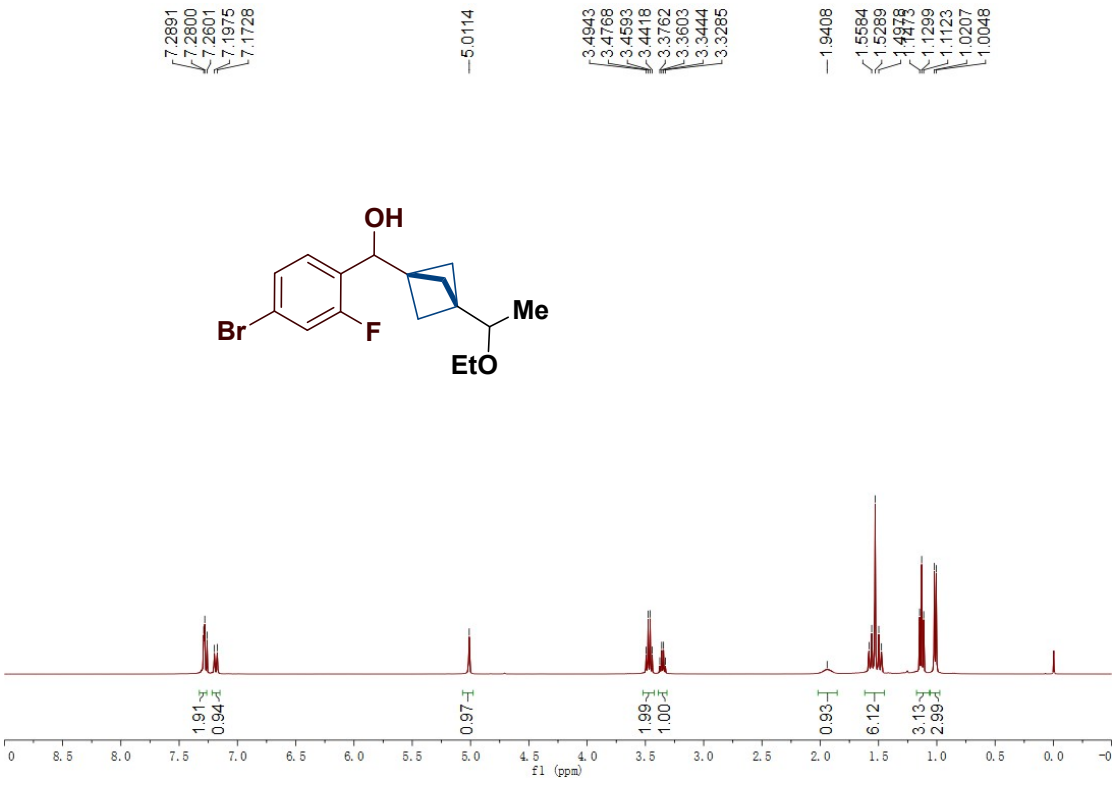
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **31**



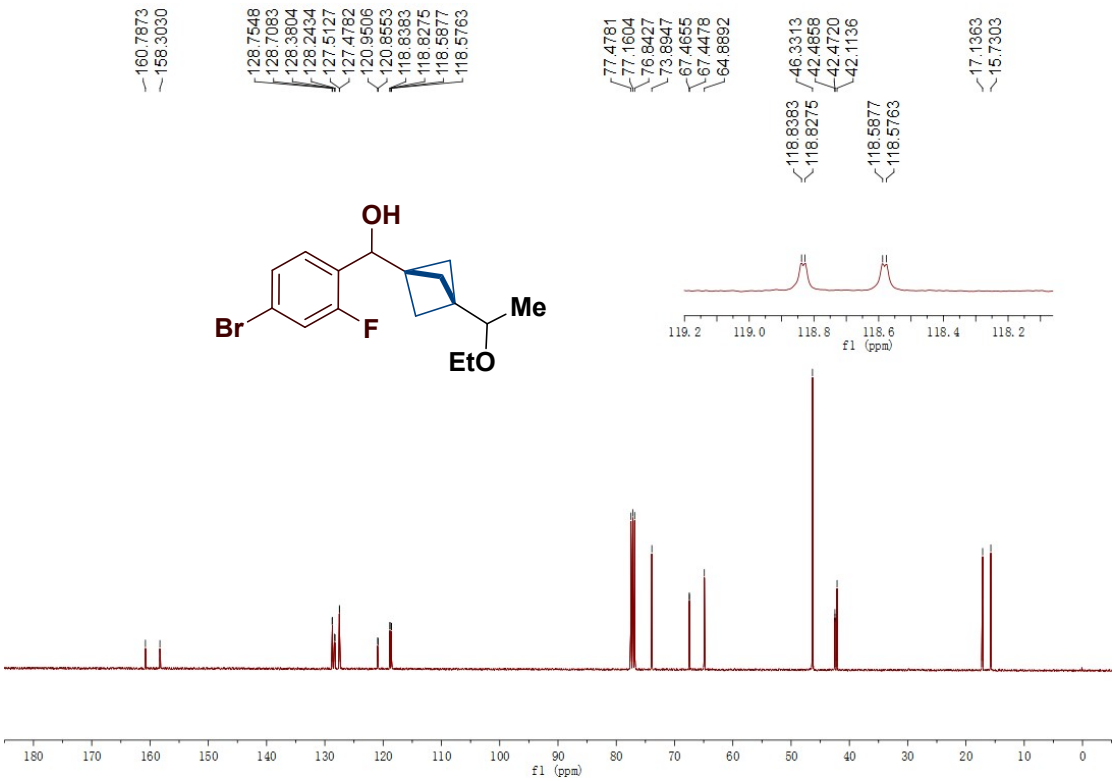
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **31**



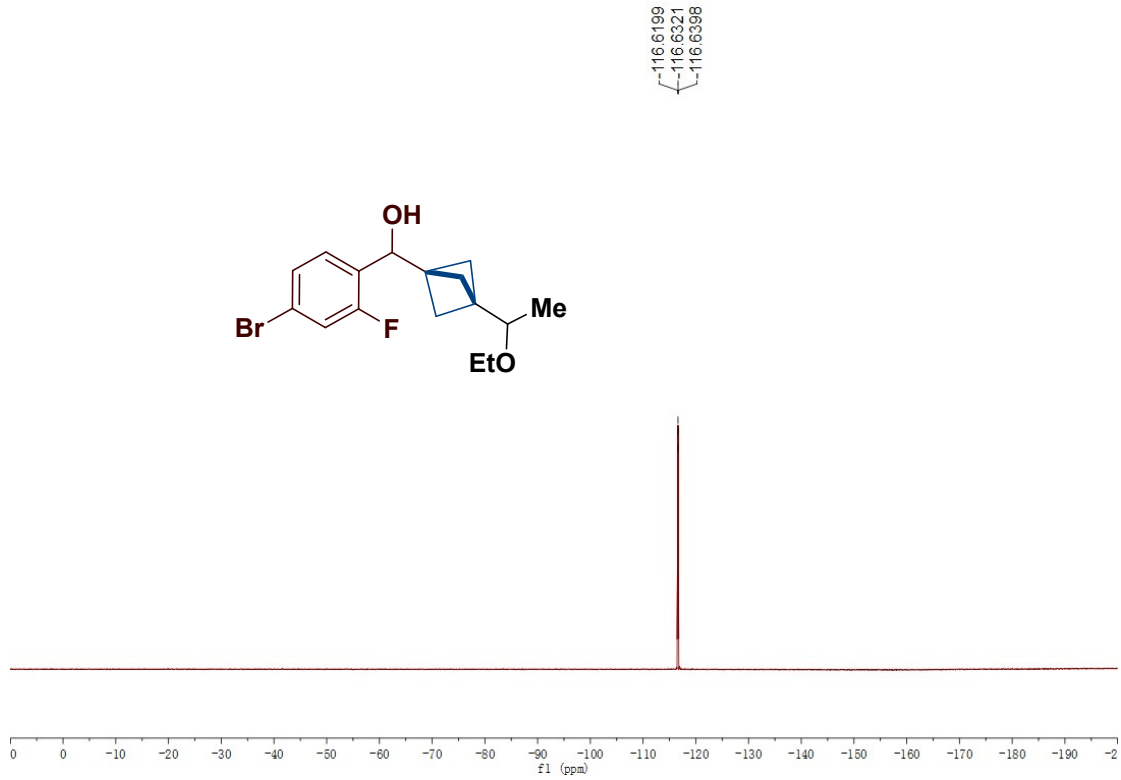
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **31**



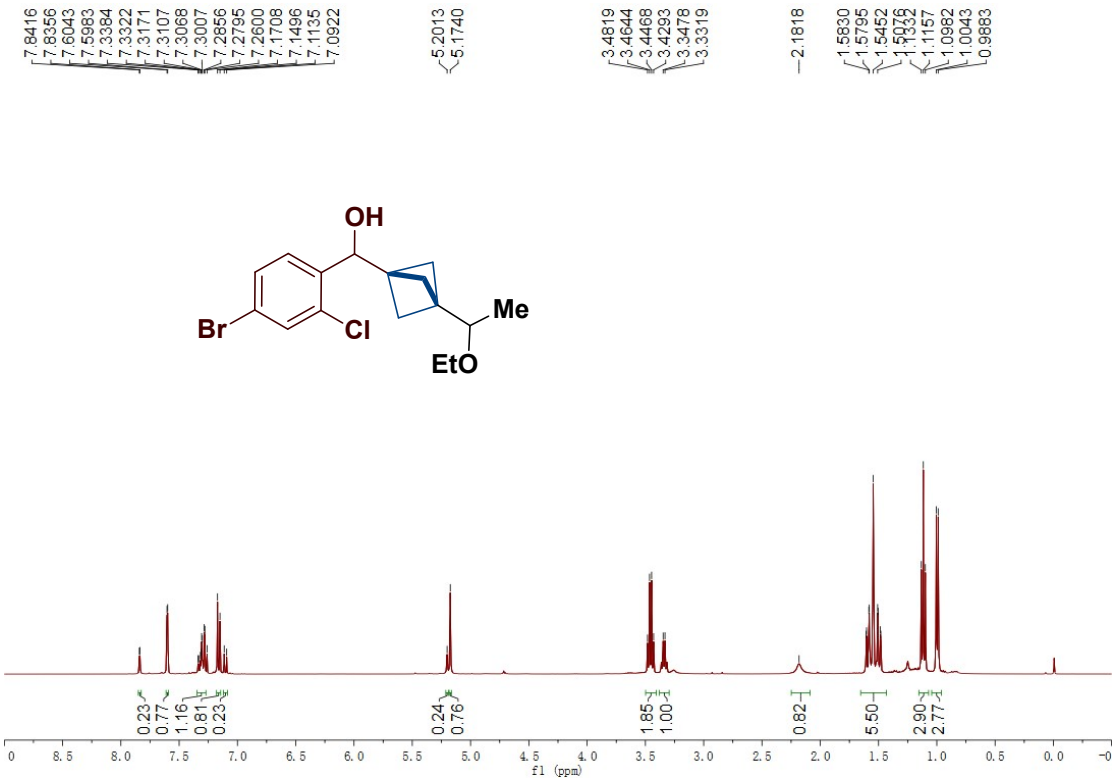
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **32**



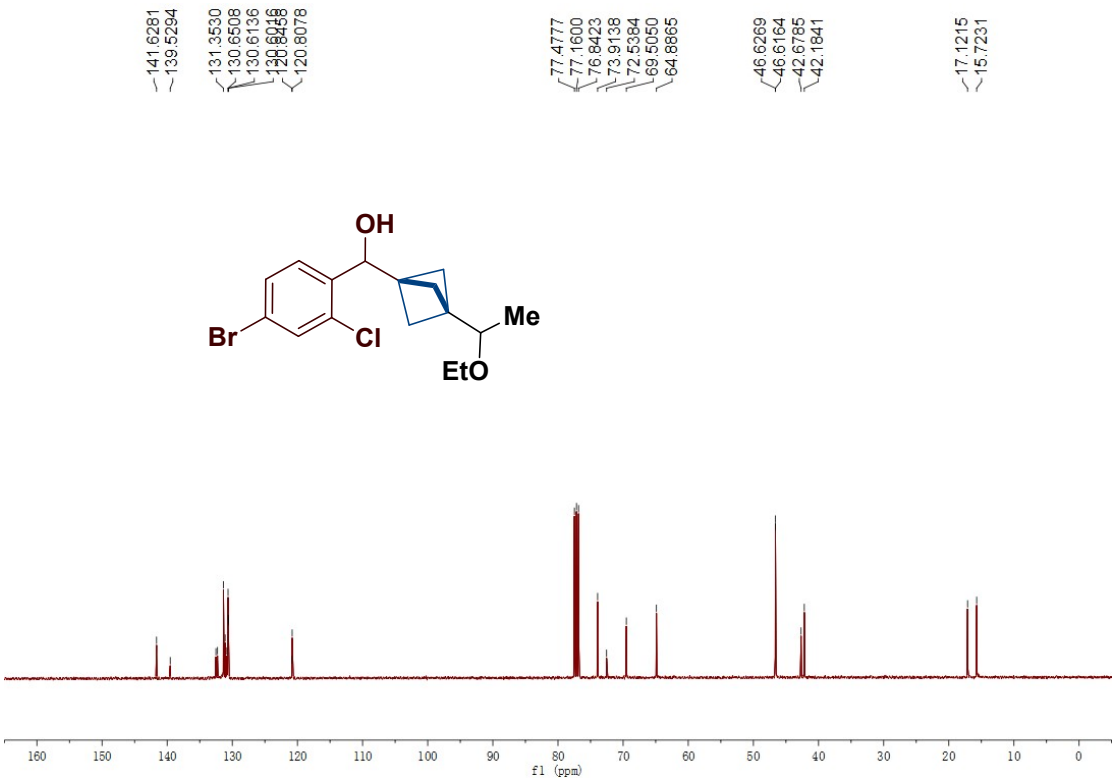
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **32**



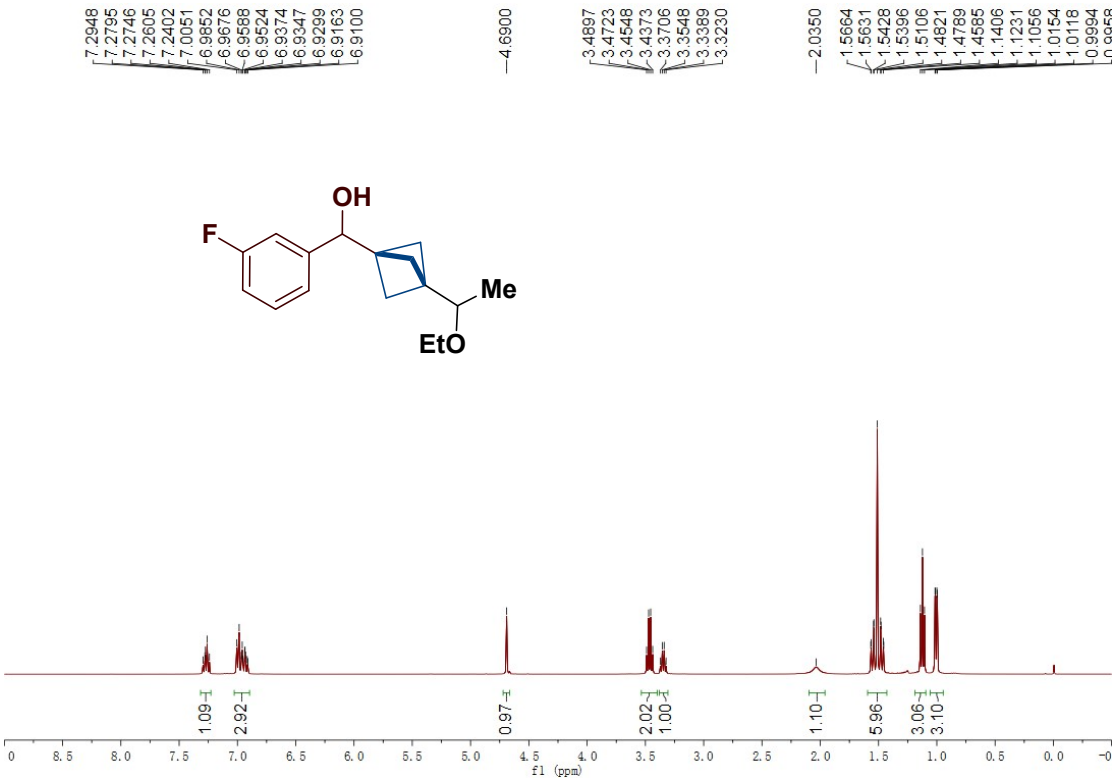
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **32**



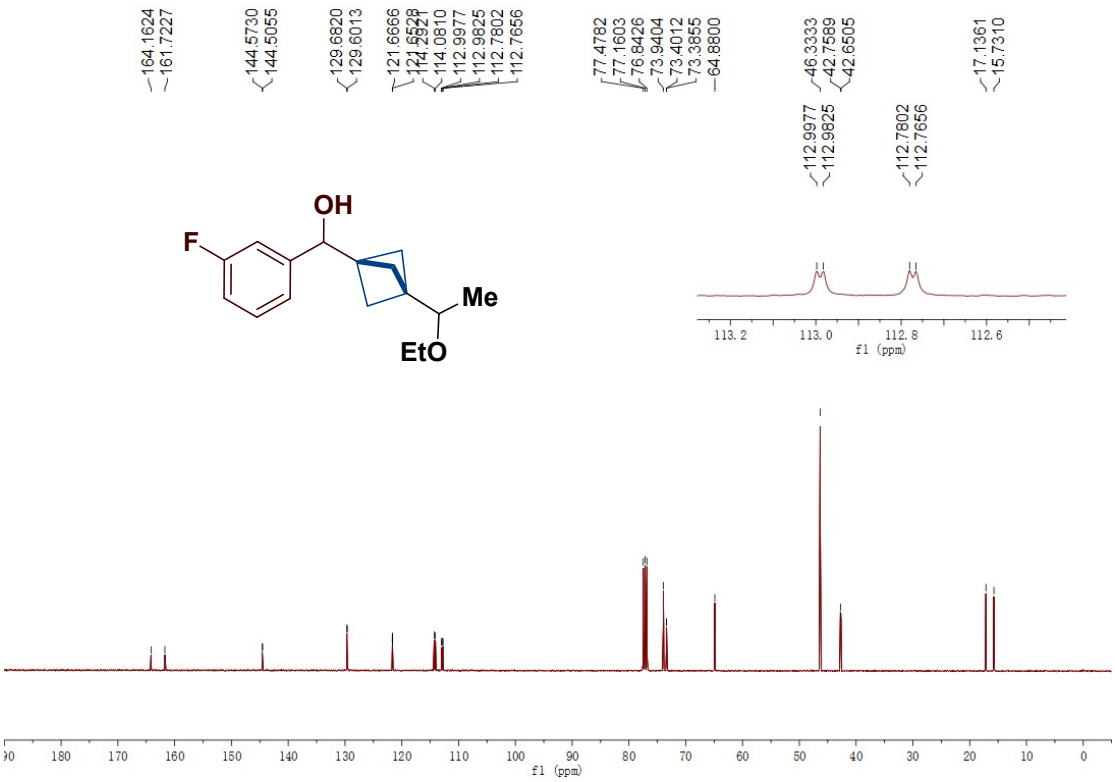
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **33**



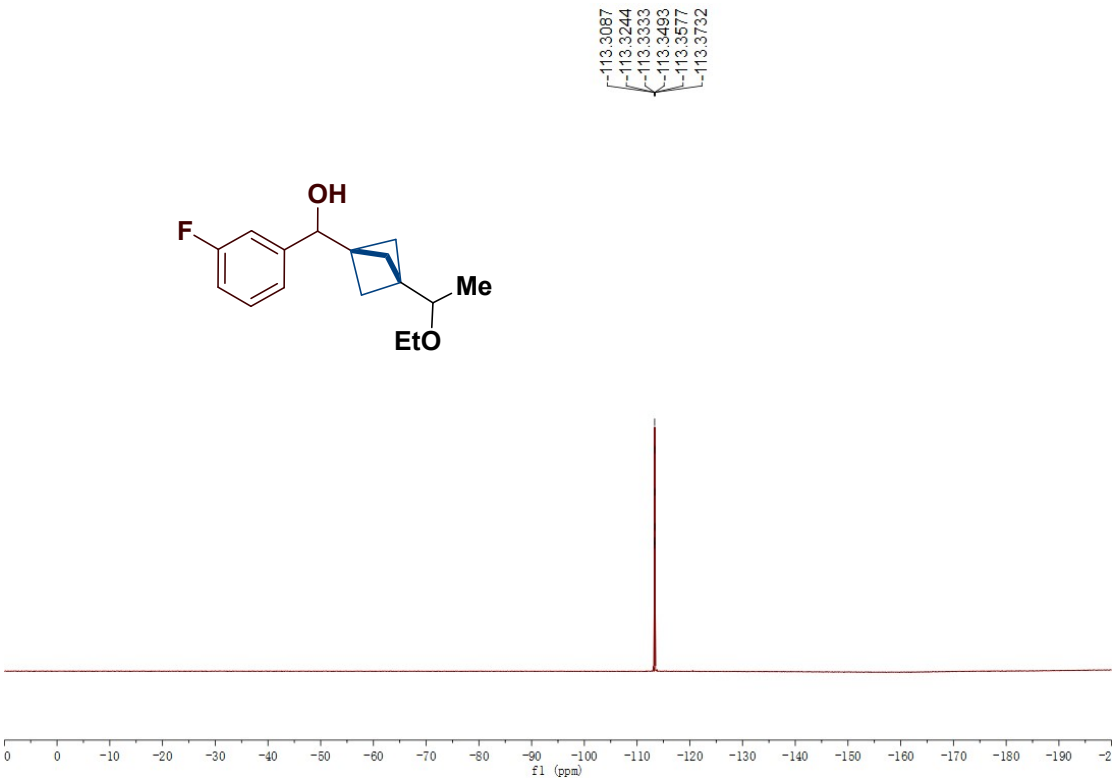
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **33**



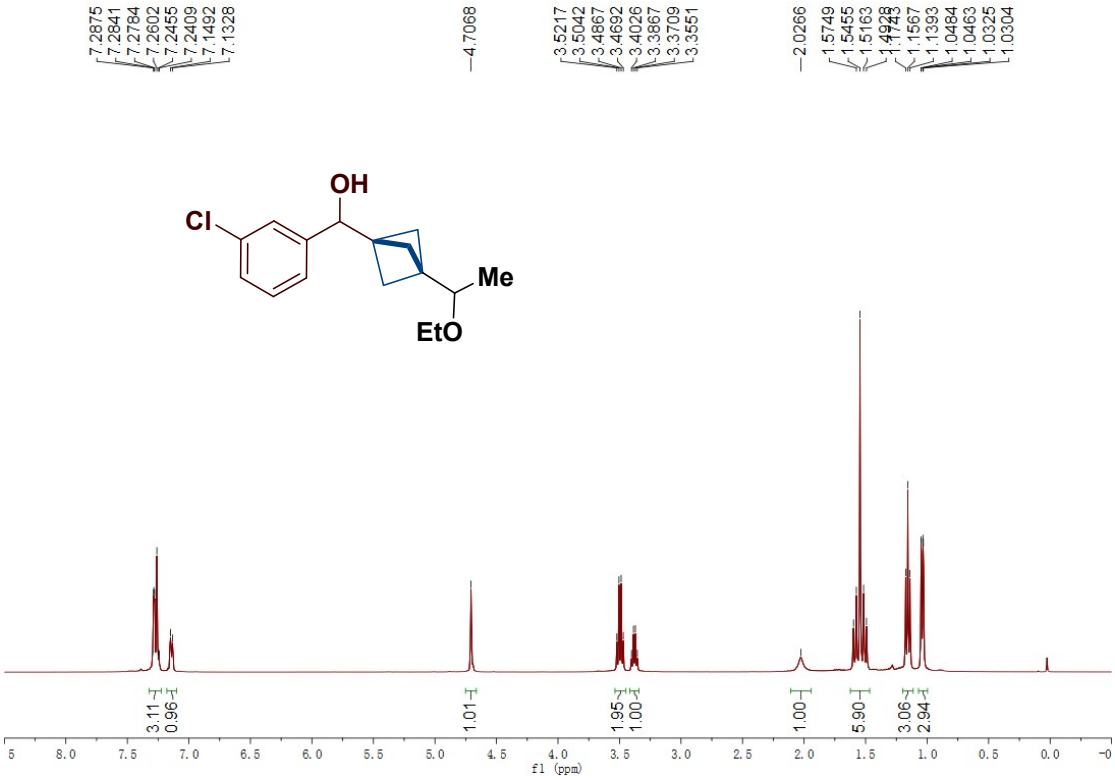
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **34**



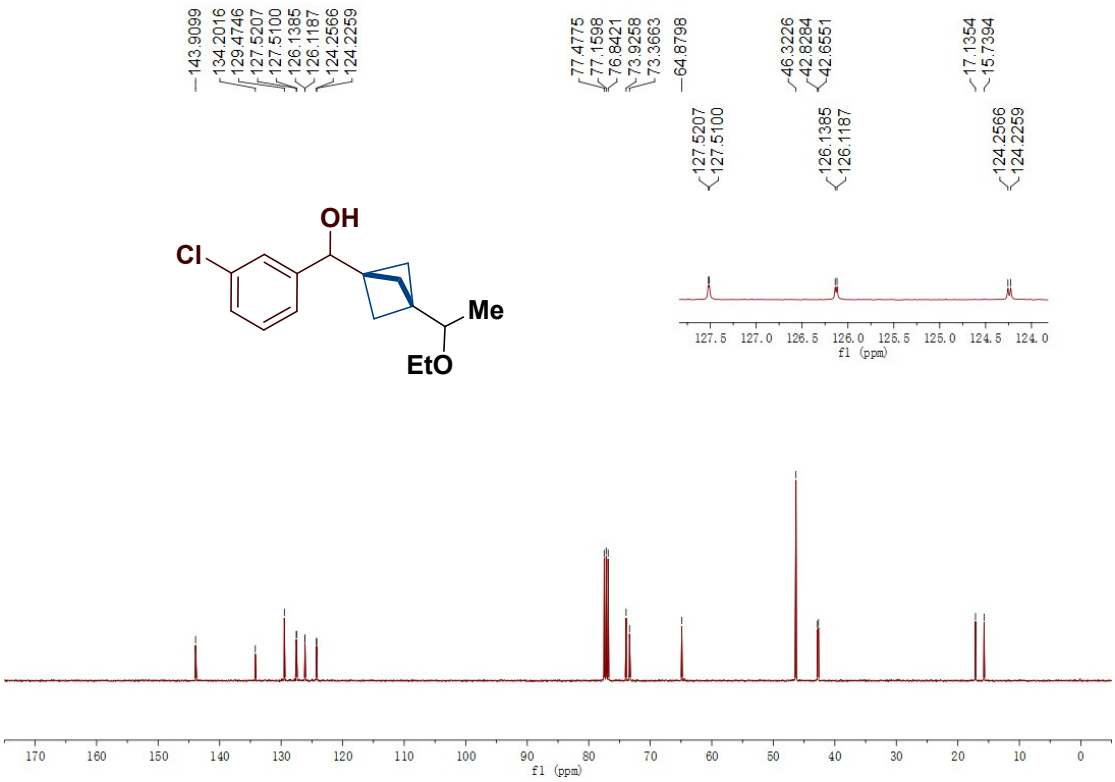
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **34**



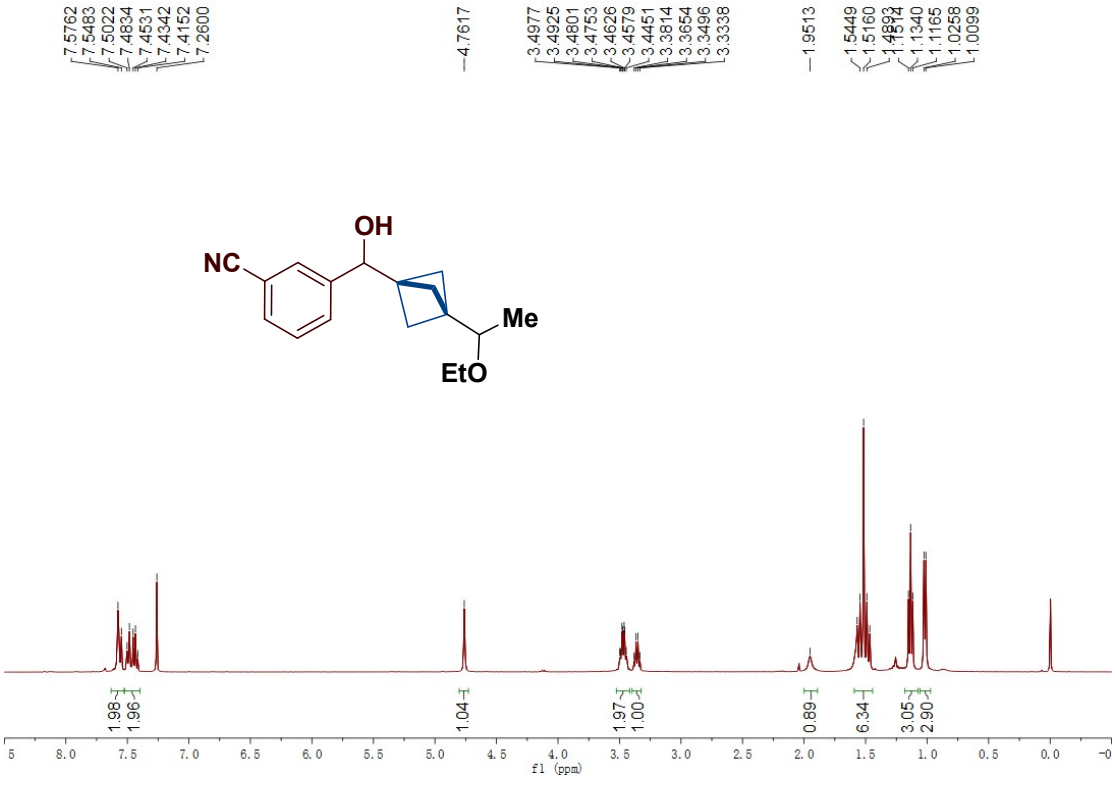
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **34**



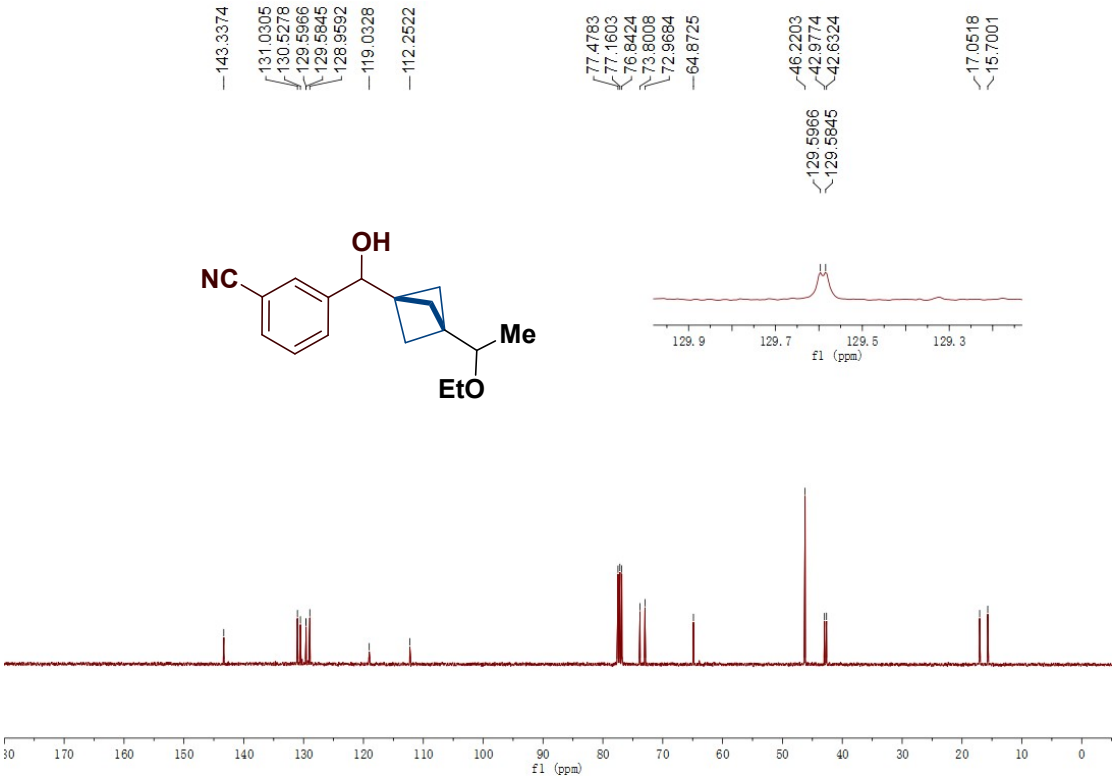
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **35**



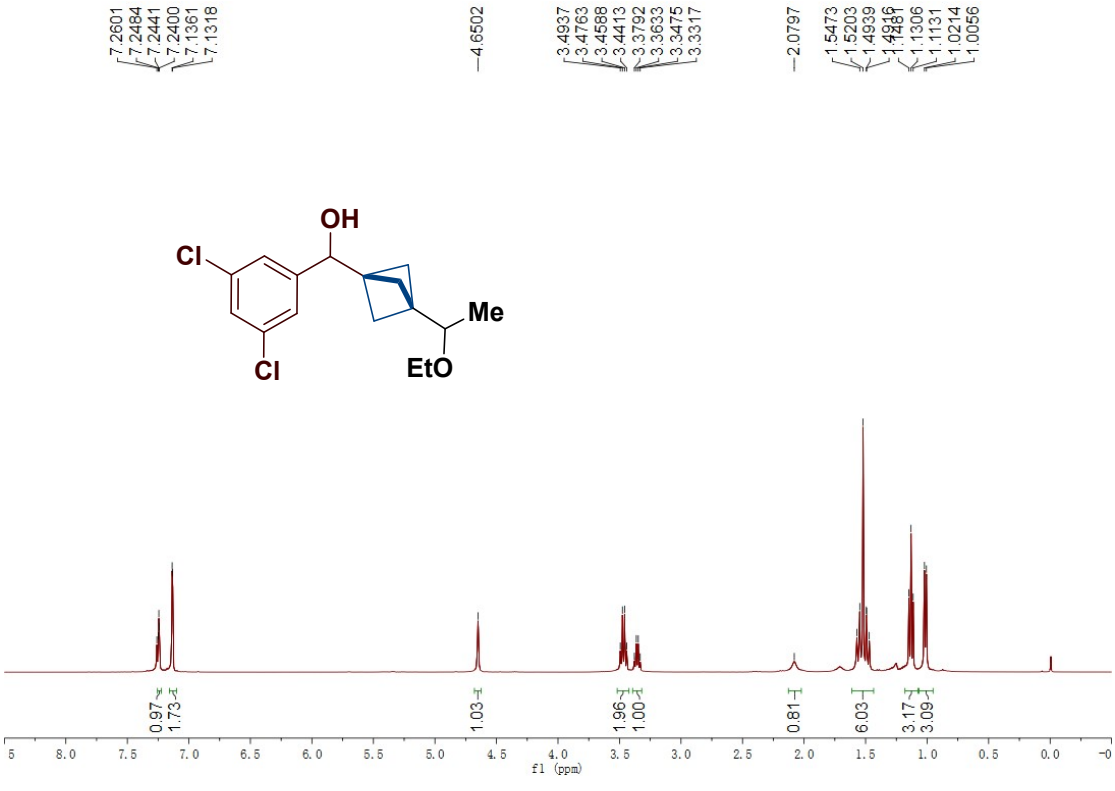
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **35**



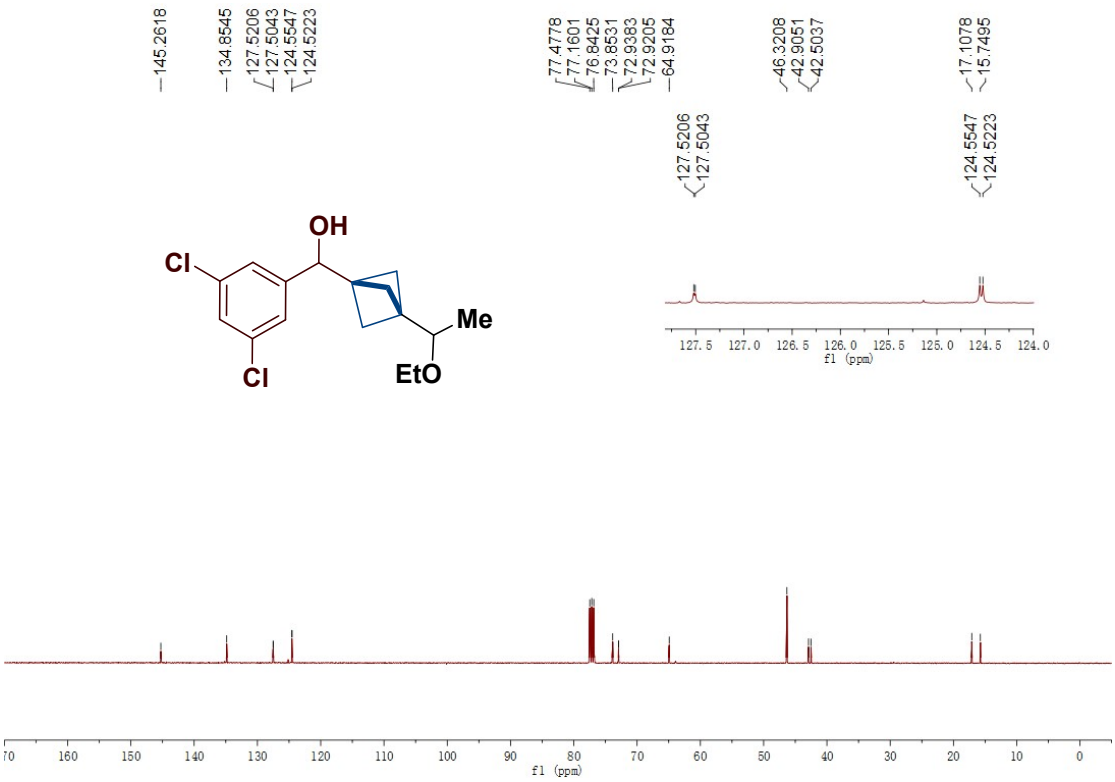
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **36**



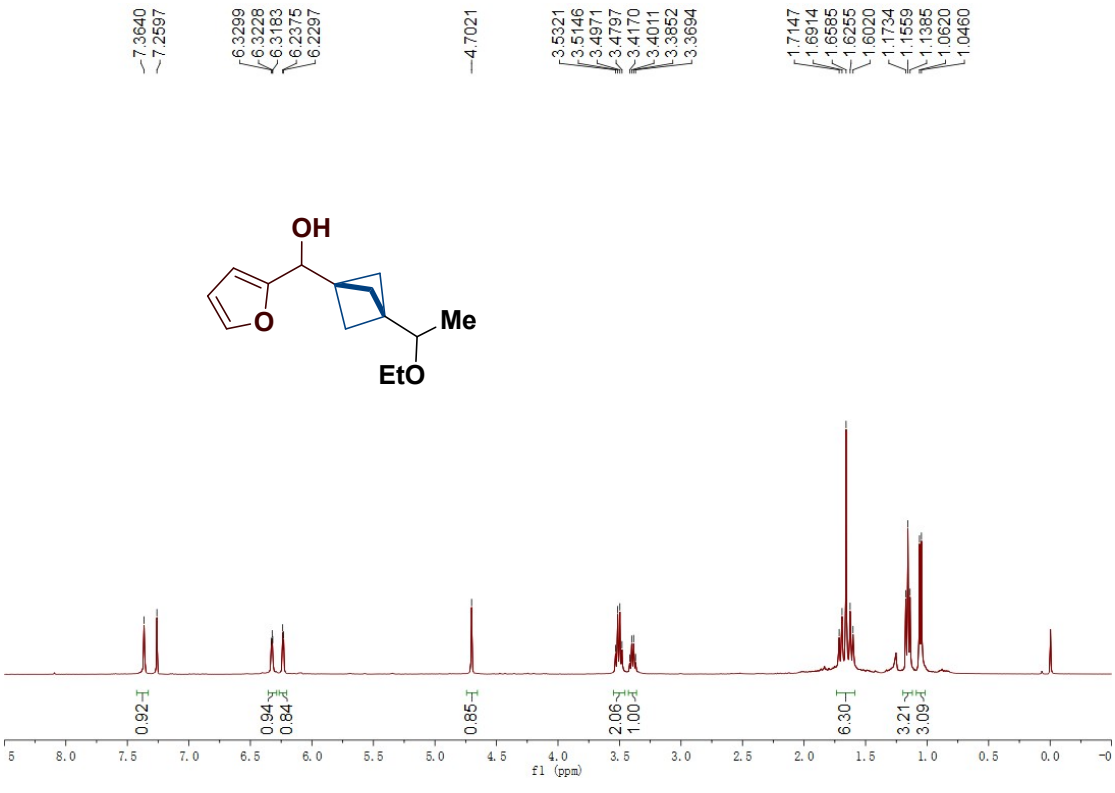
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **36**



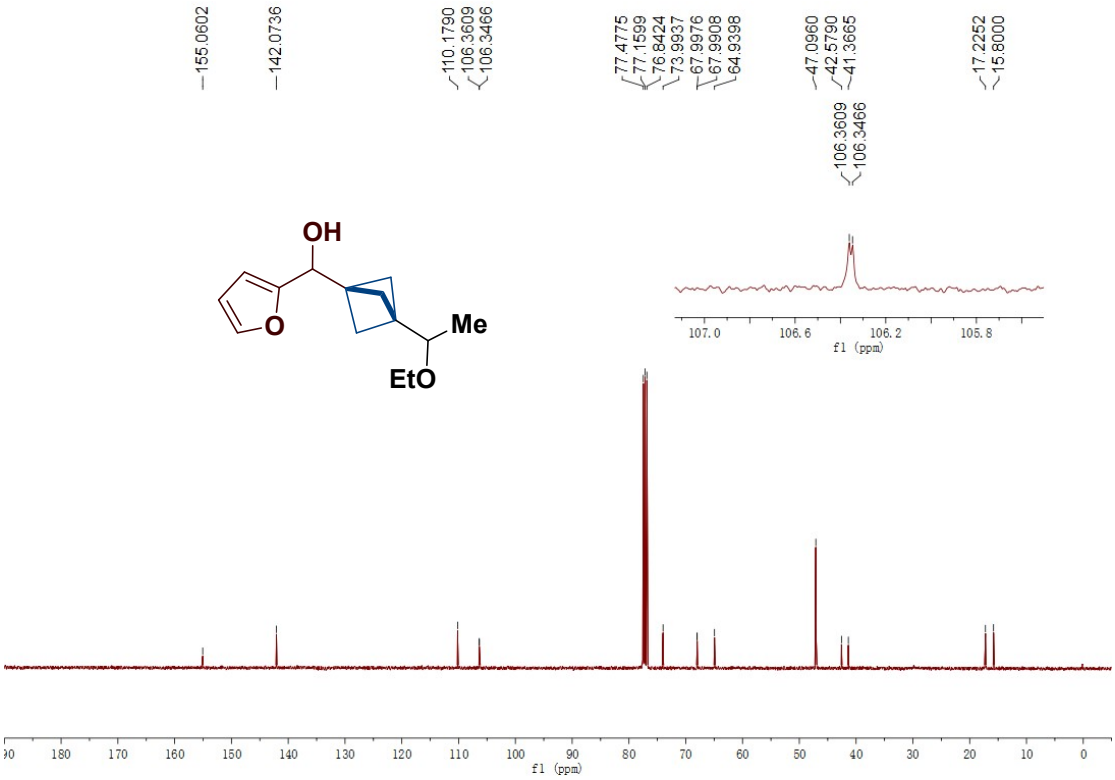
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **37**



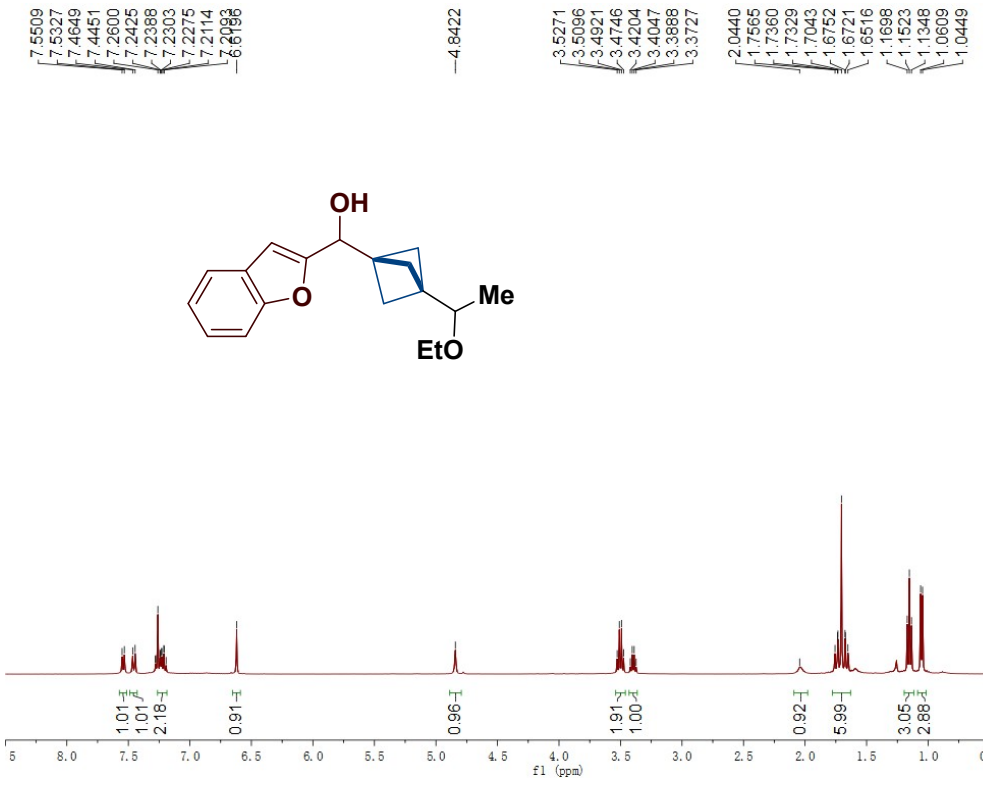
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **37**



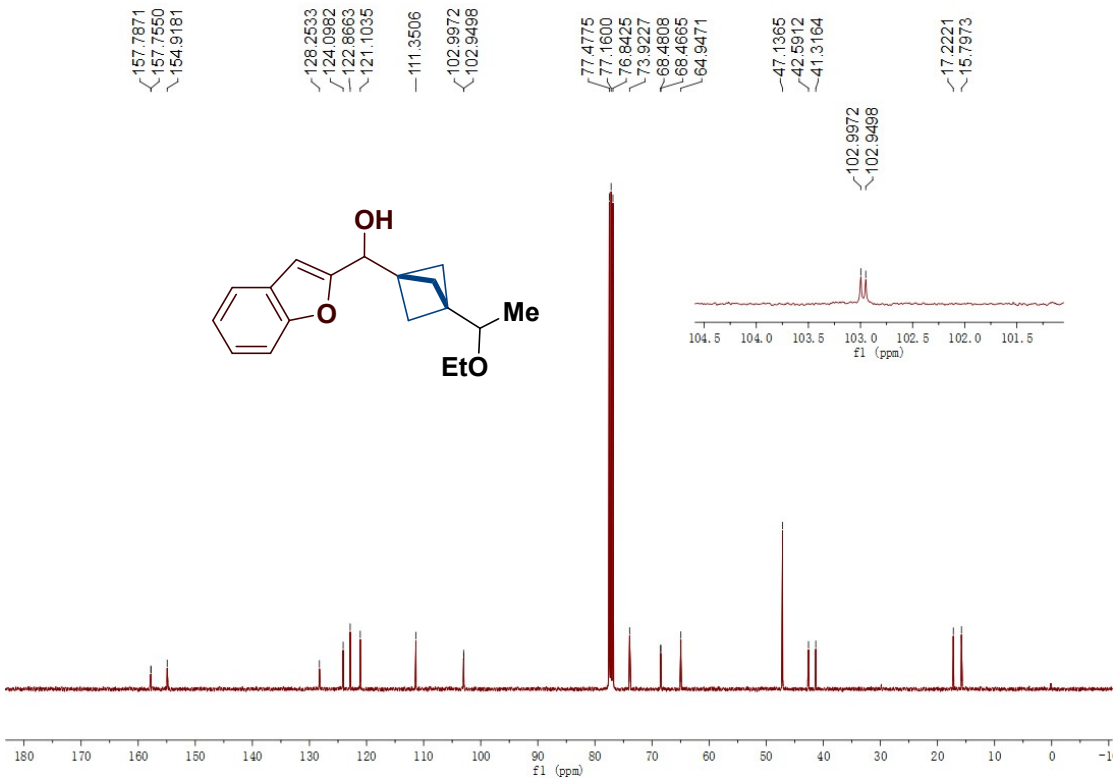
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **38**



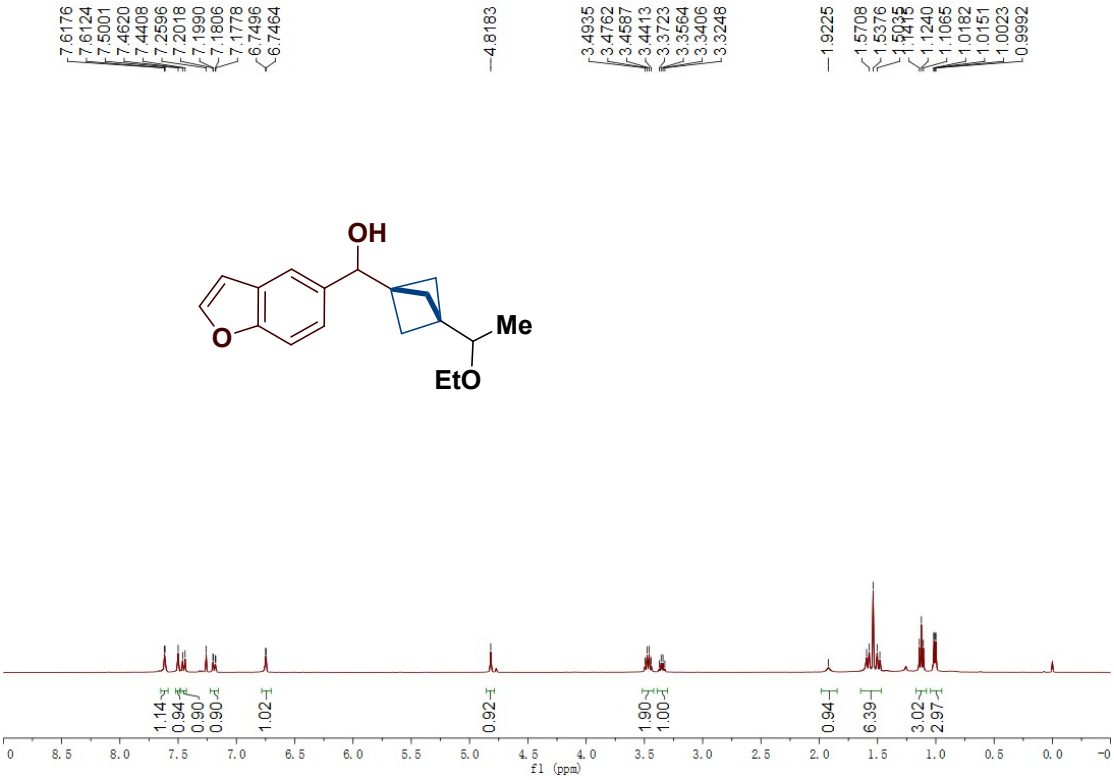
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **38**



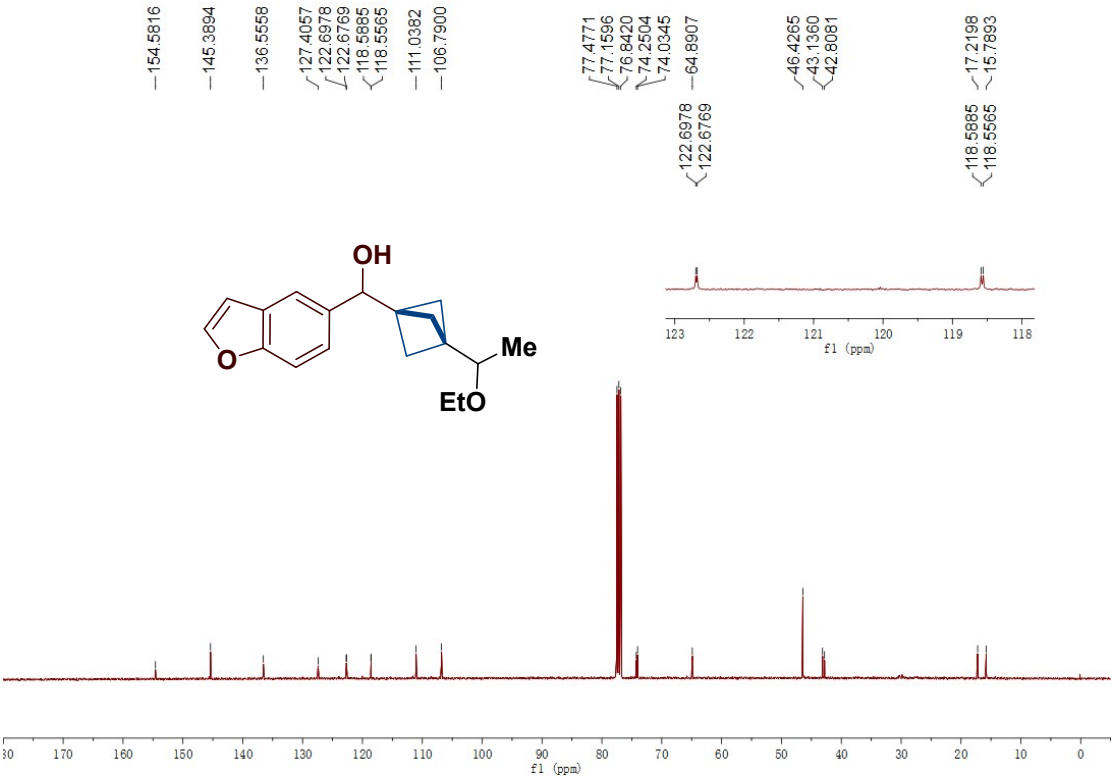
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **39**



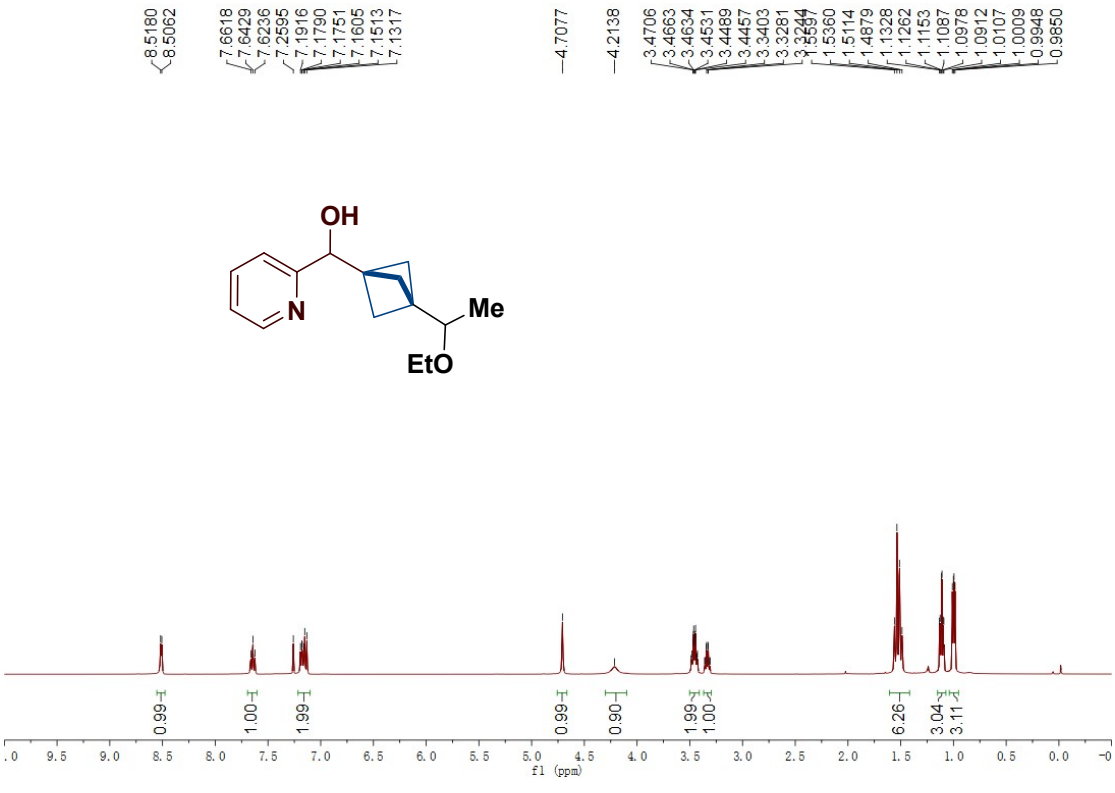
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **39**



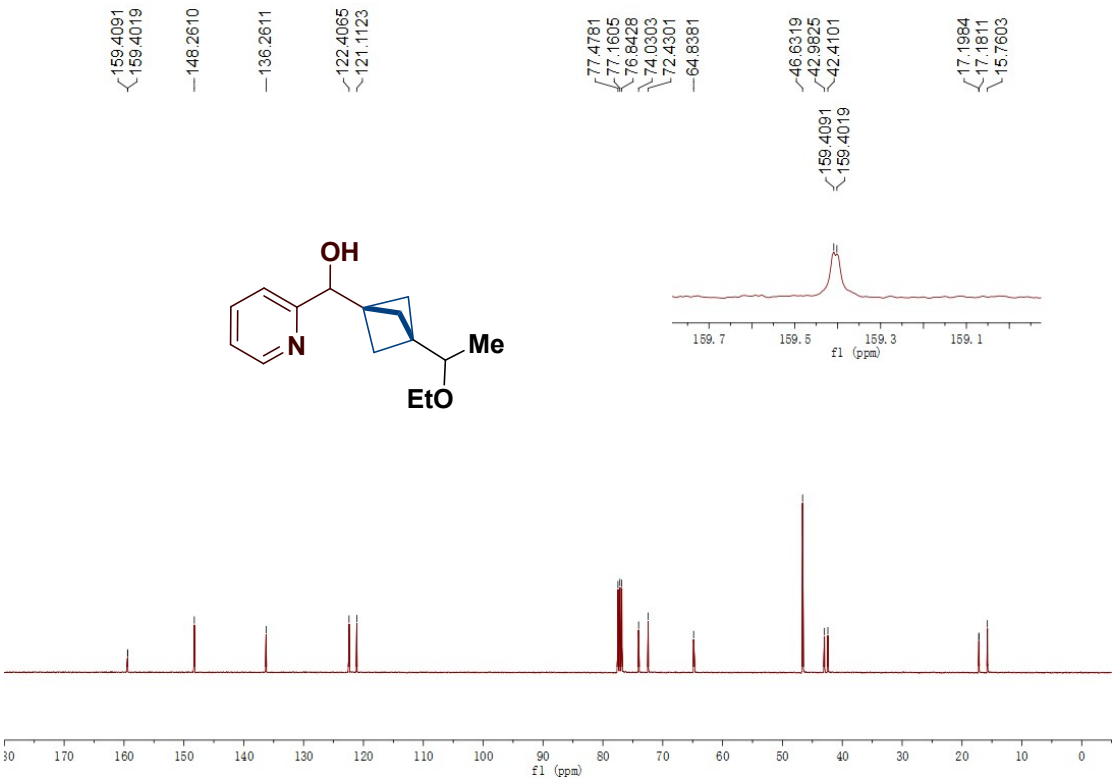
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **40**



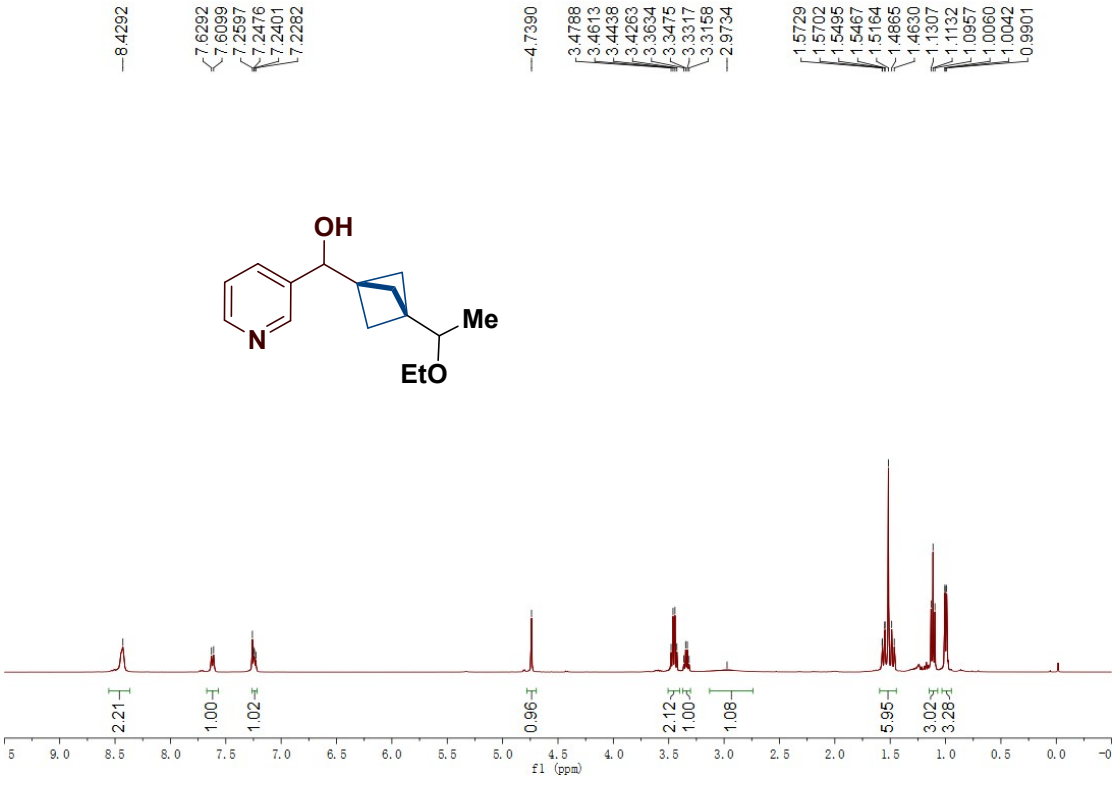
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **40**



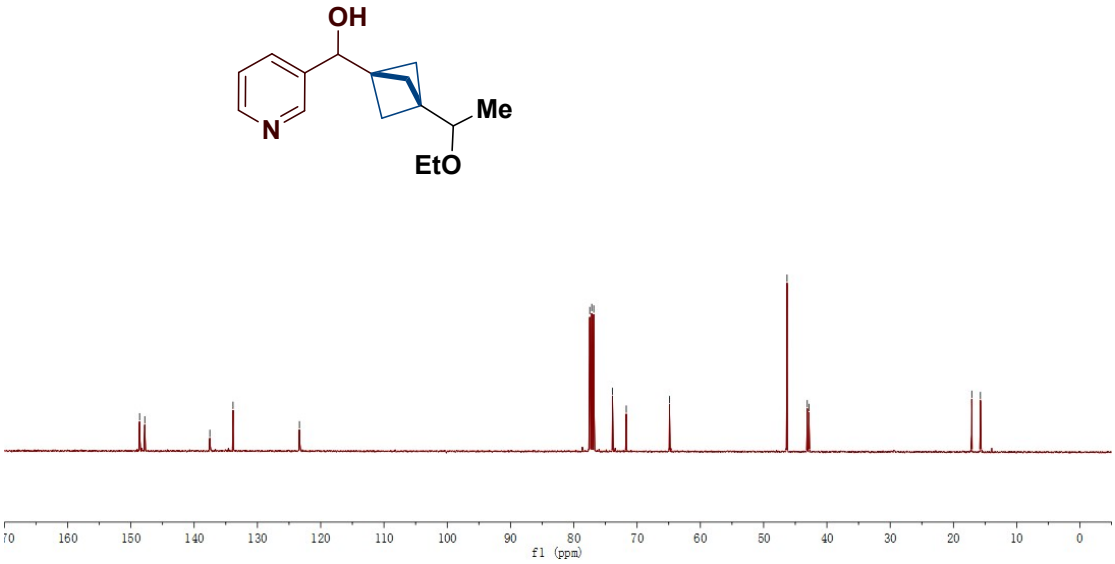
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **41**



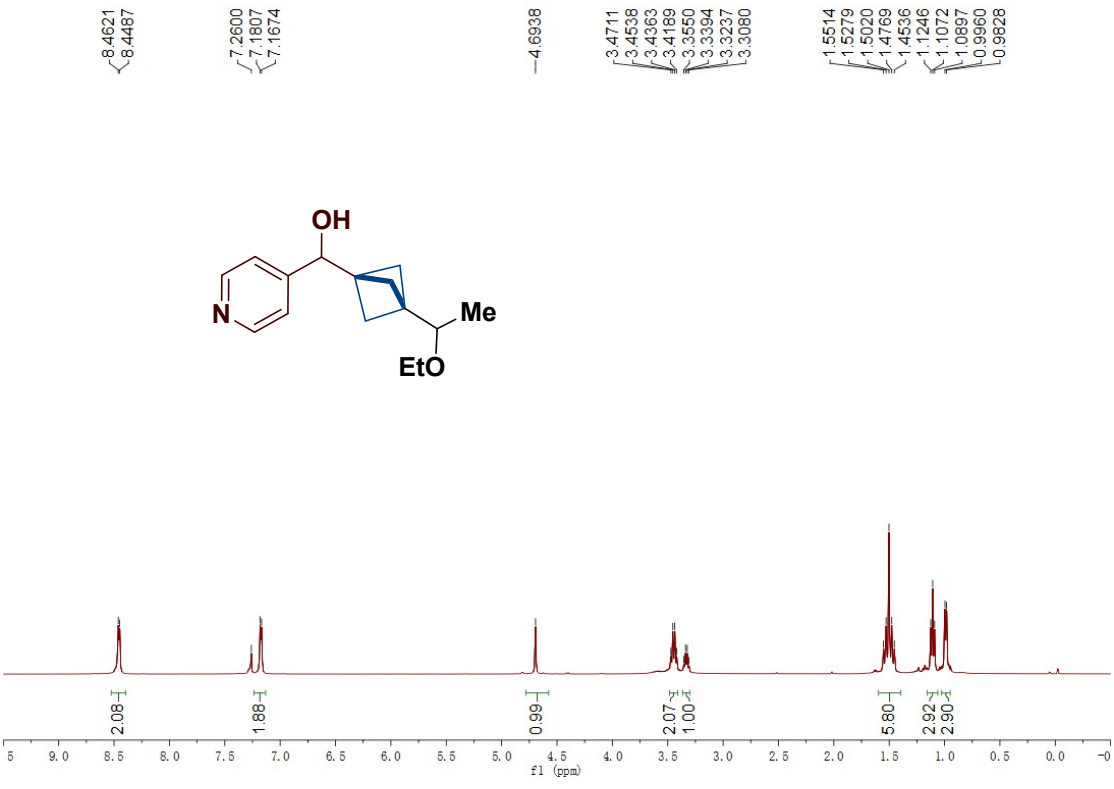
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **41**



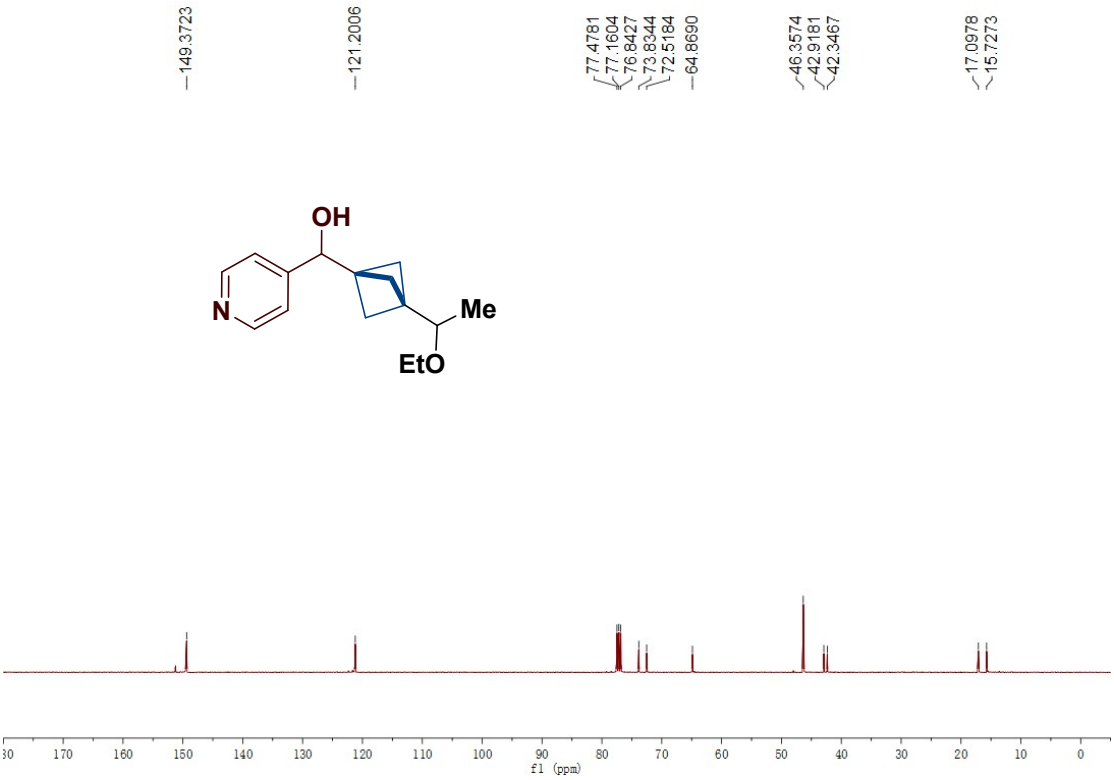
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **42**



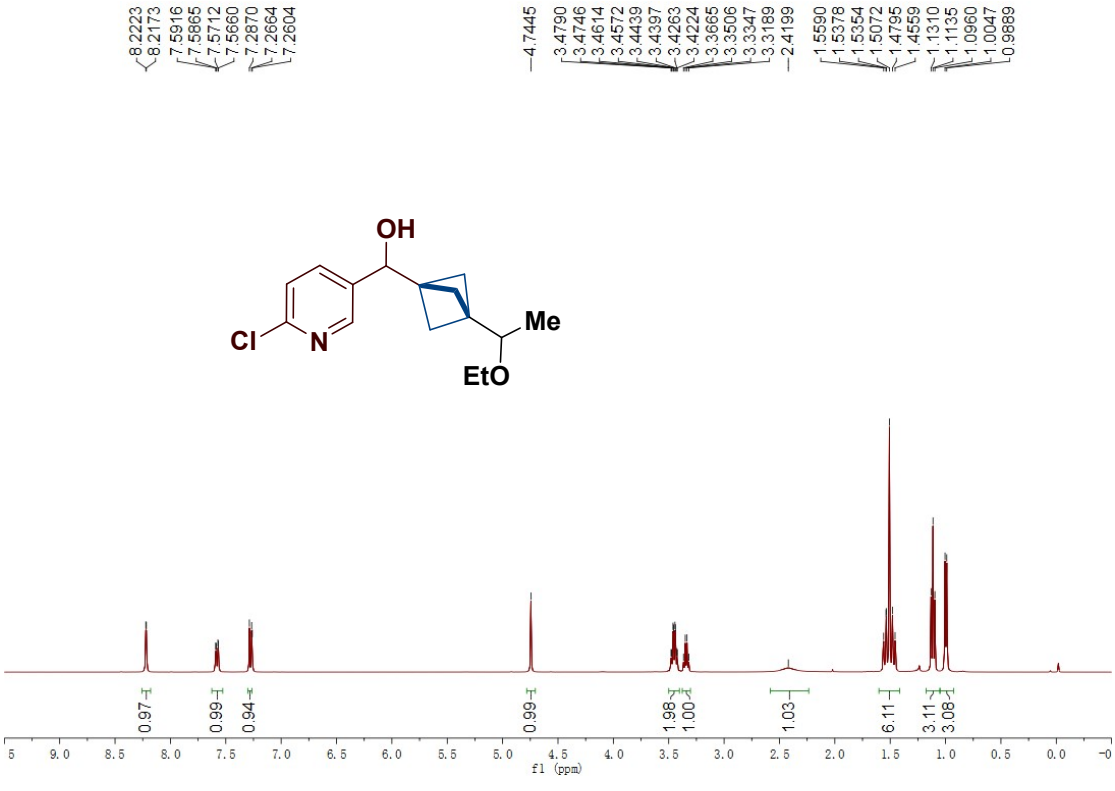
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **42**



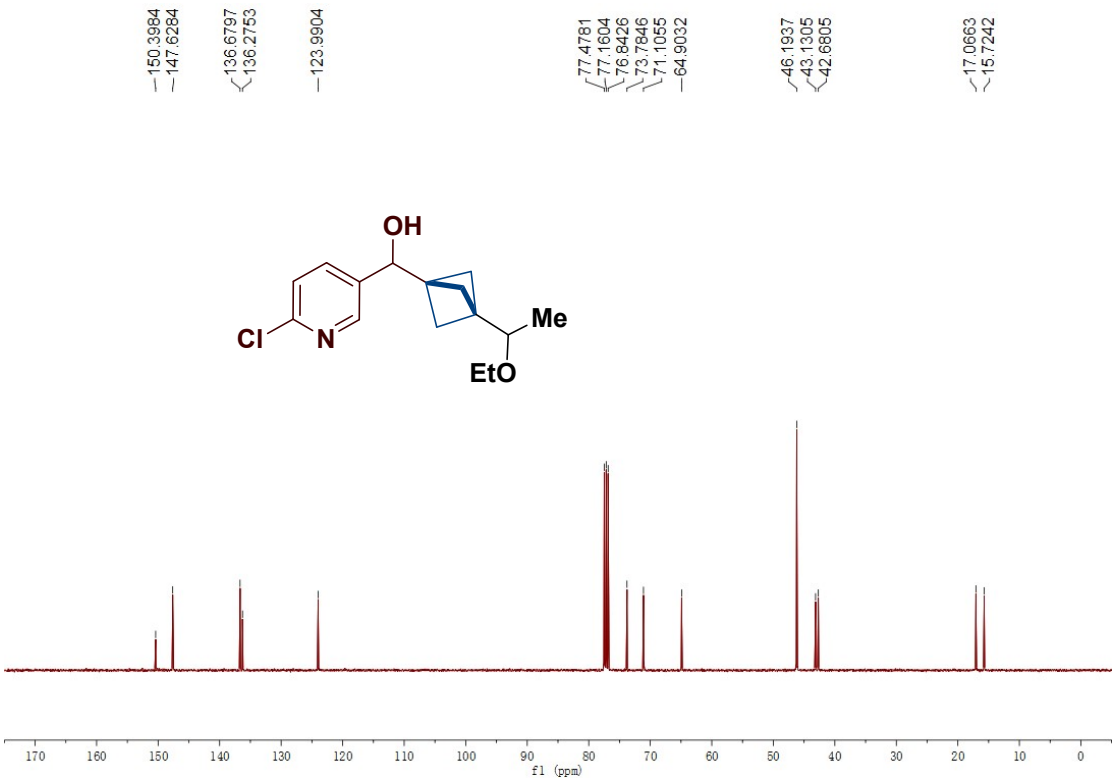
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **43**



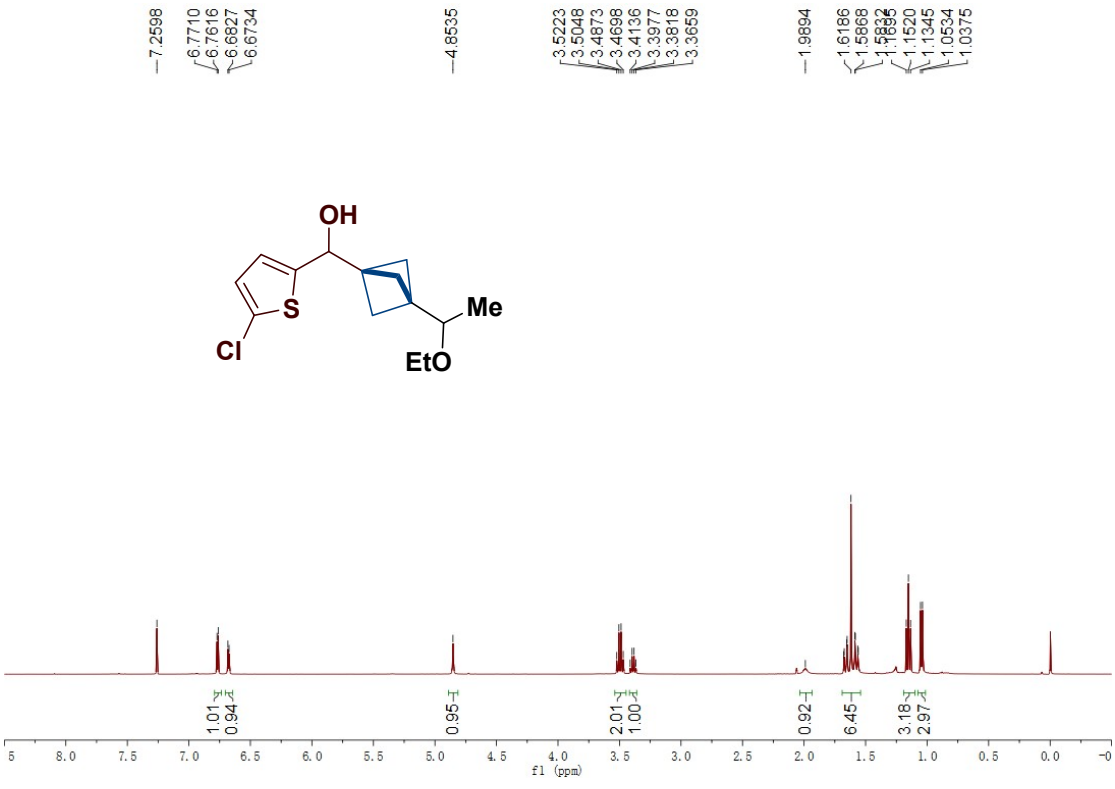
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **43**



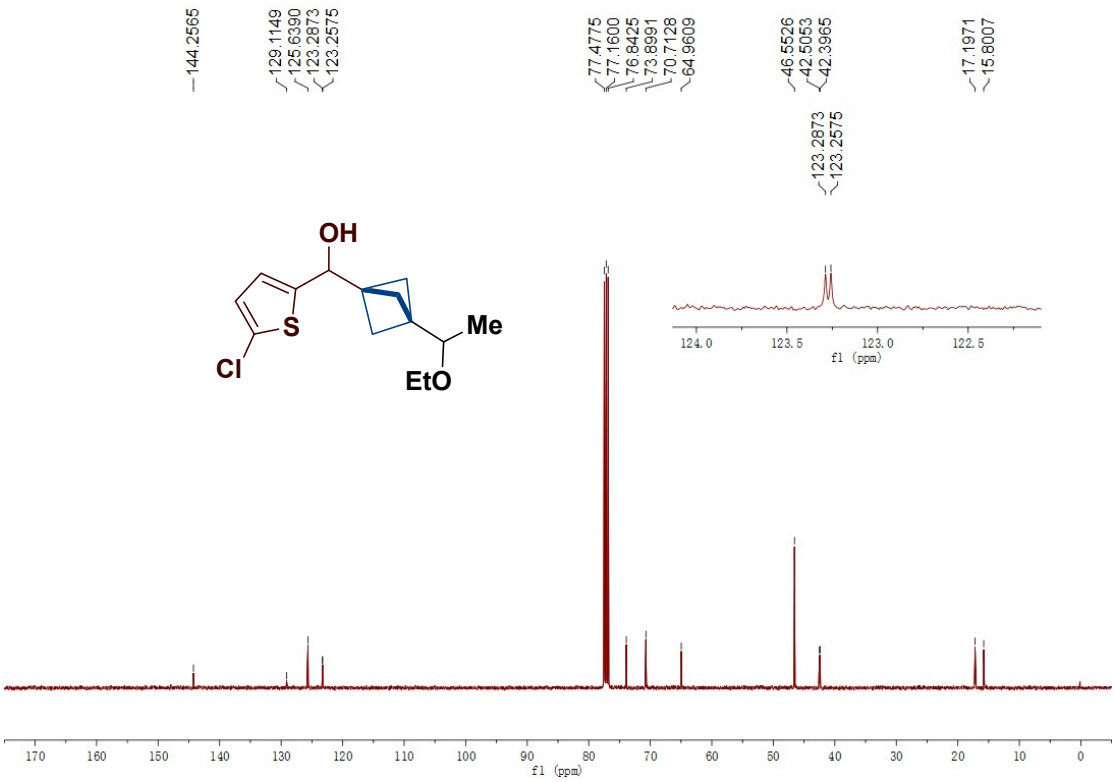
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **44**



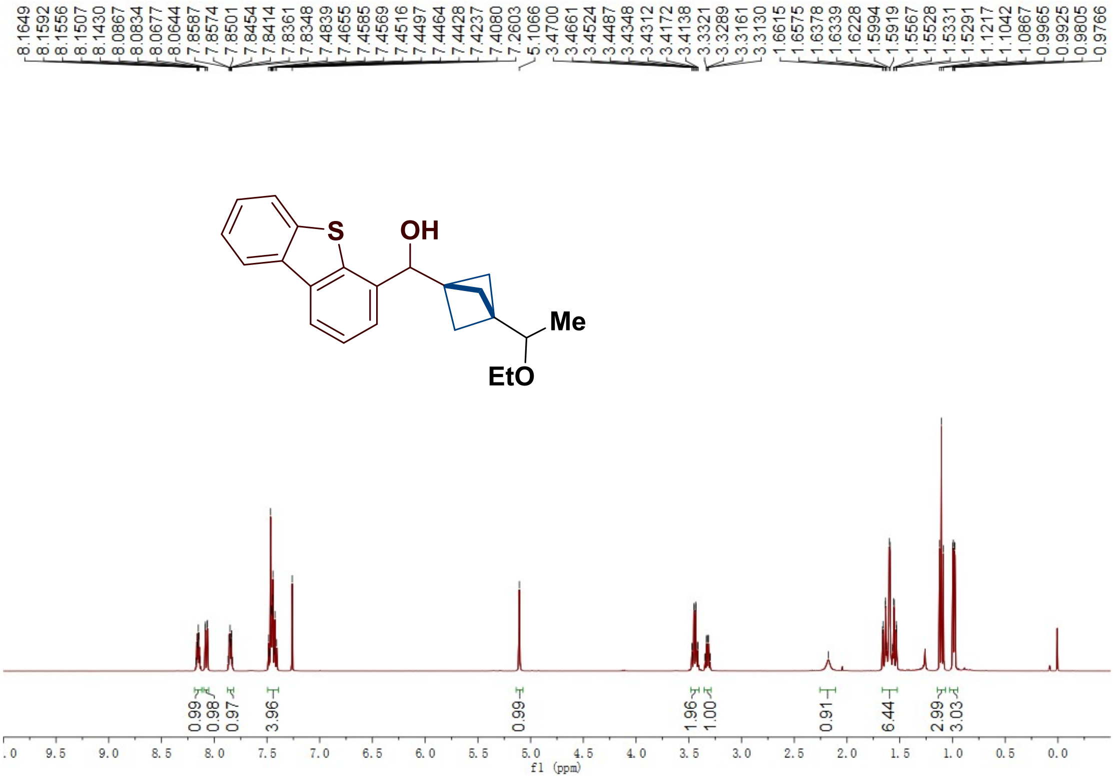
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **44**



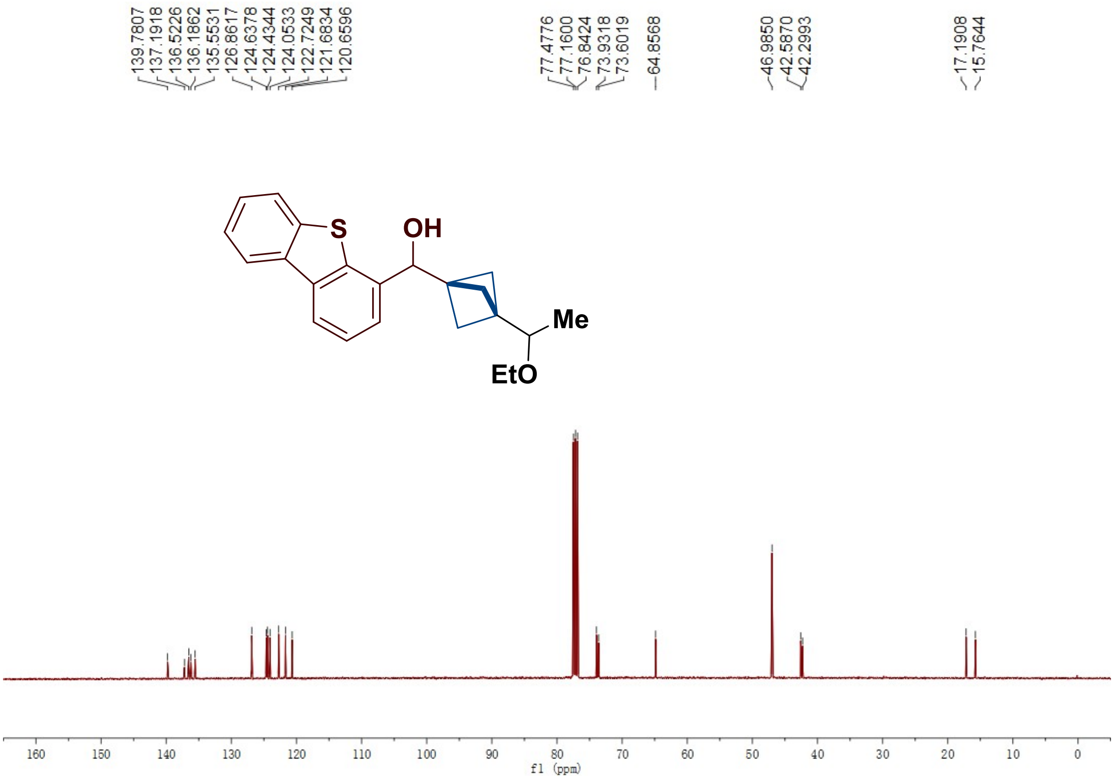
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **45**



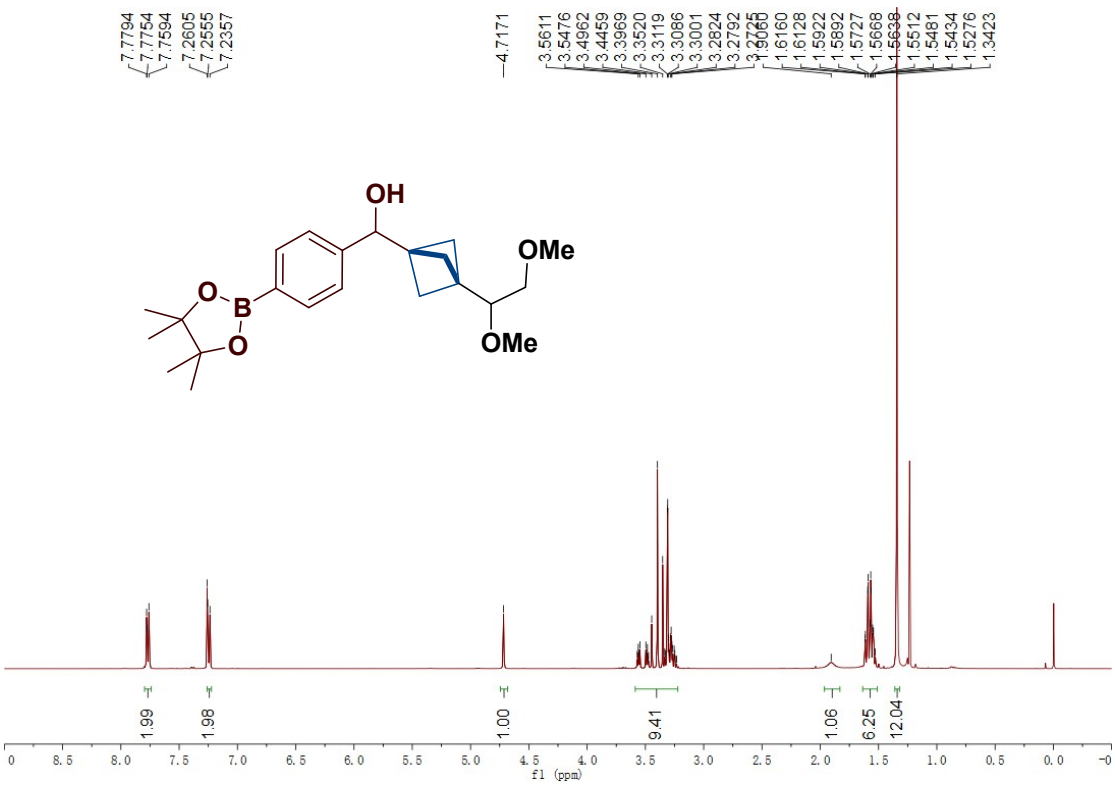
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **45**



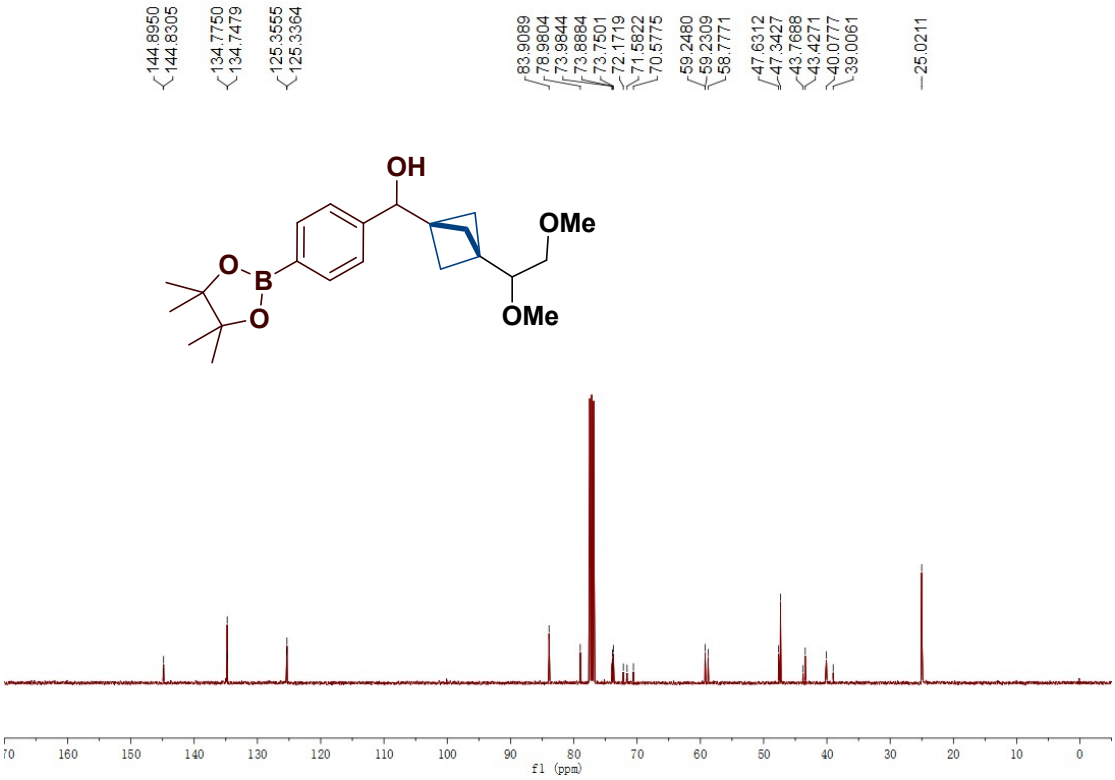
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **46**



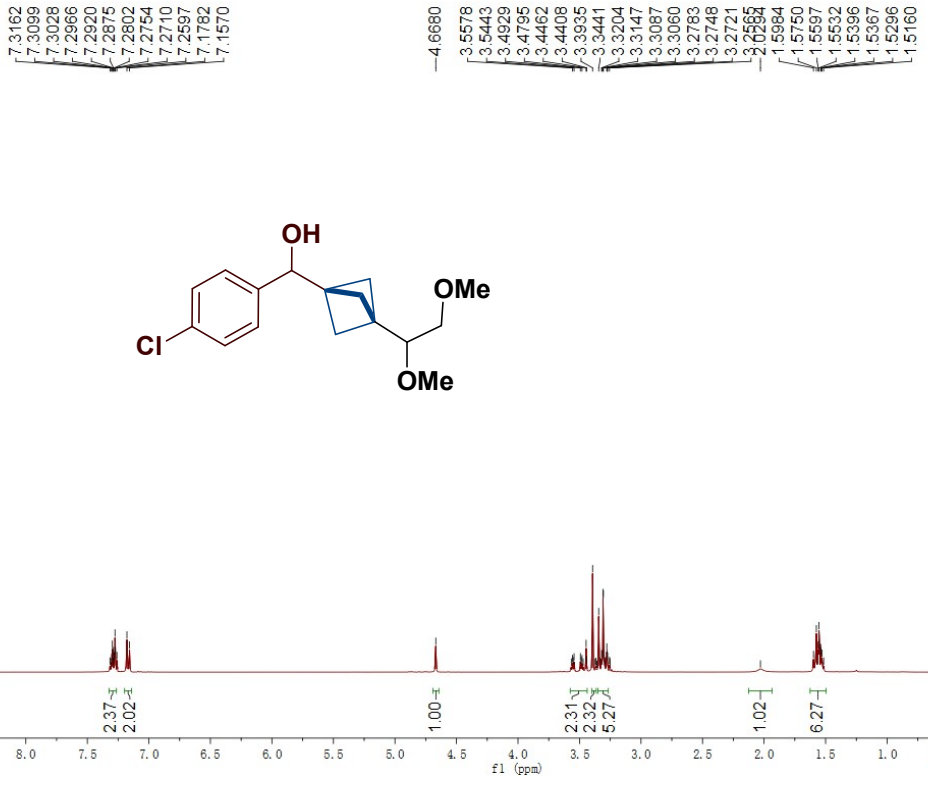
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **46**



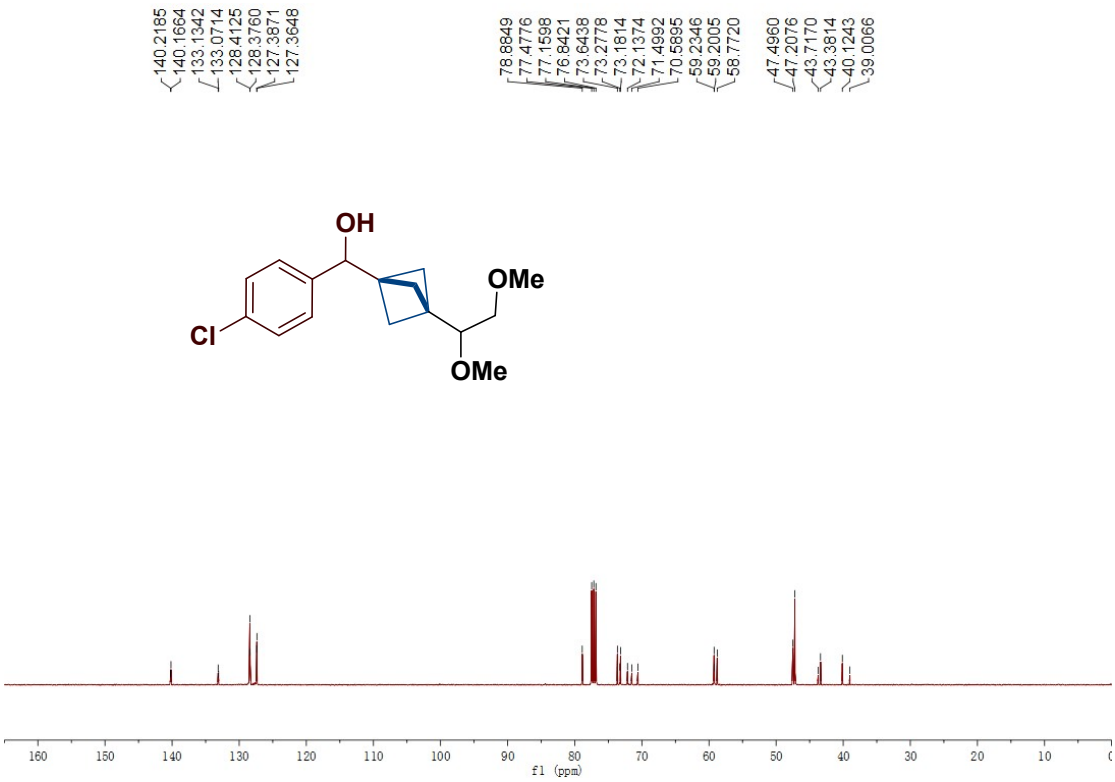
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **47**



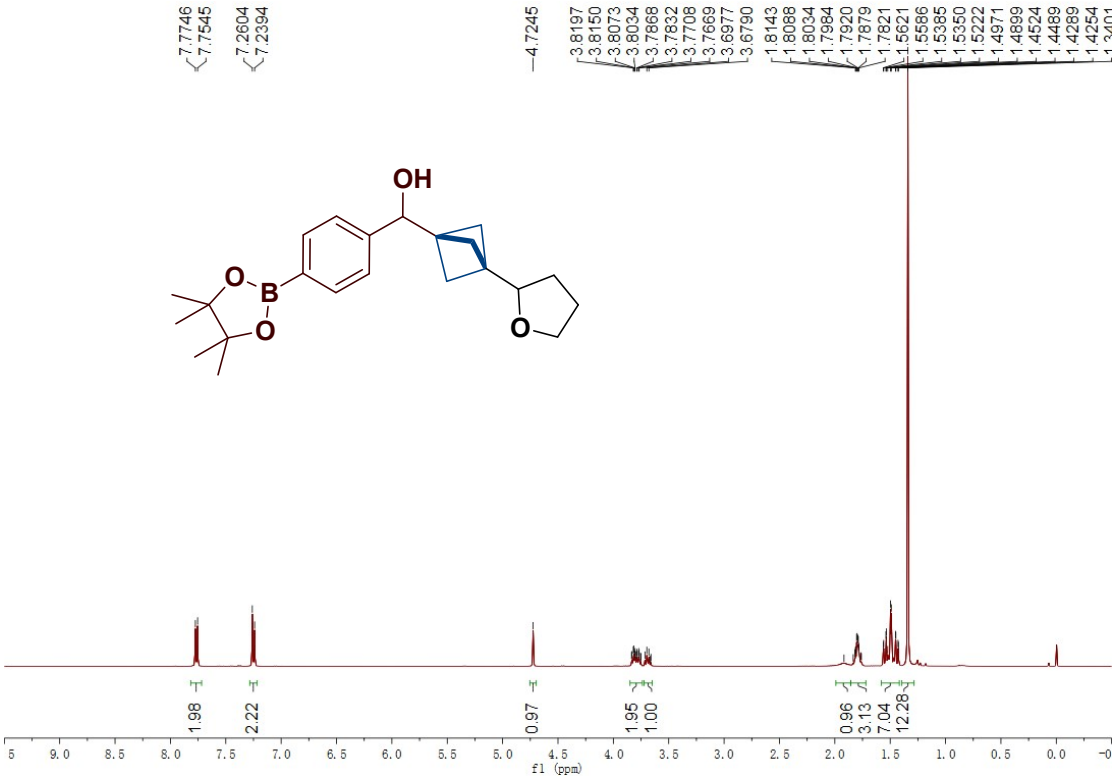
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **47**



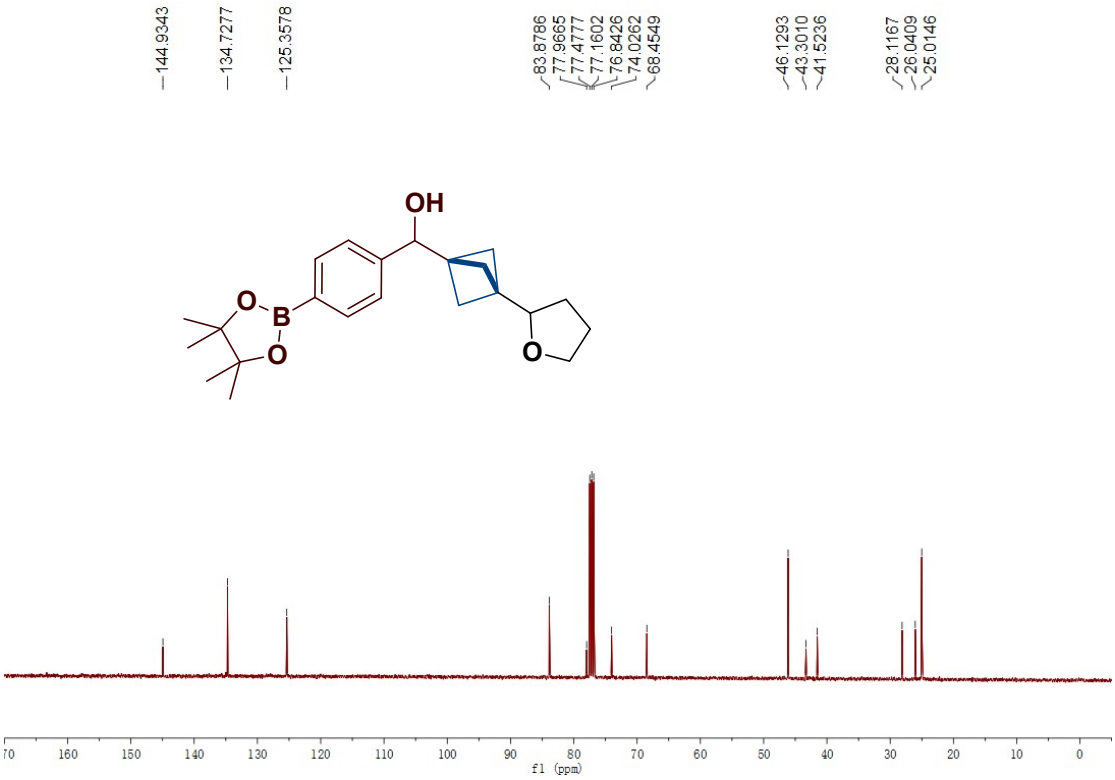
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **48**



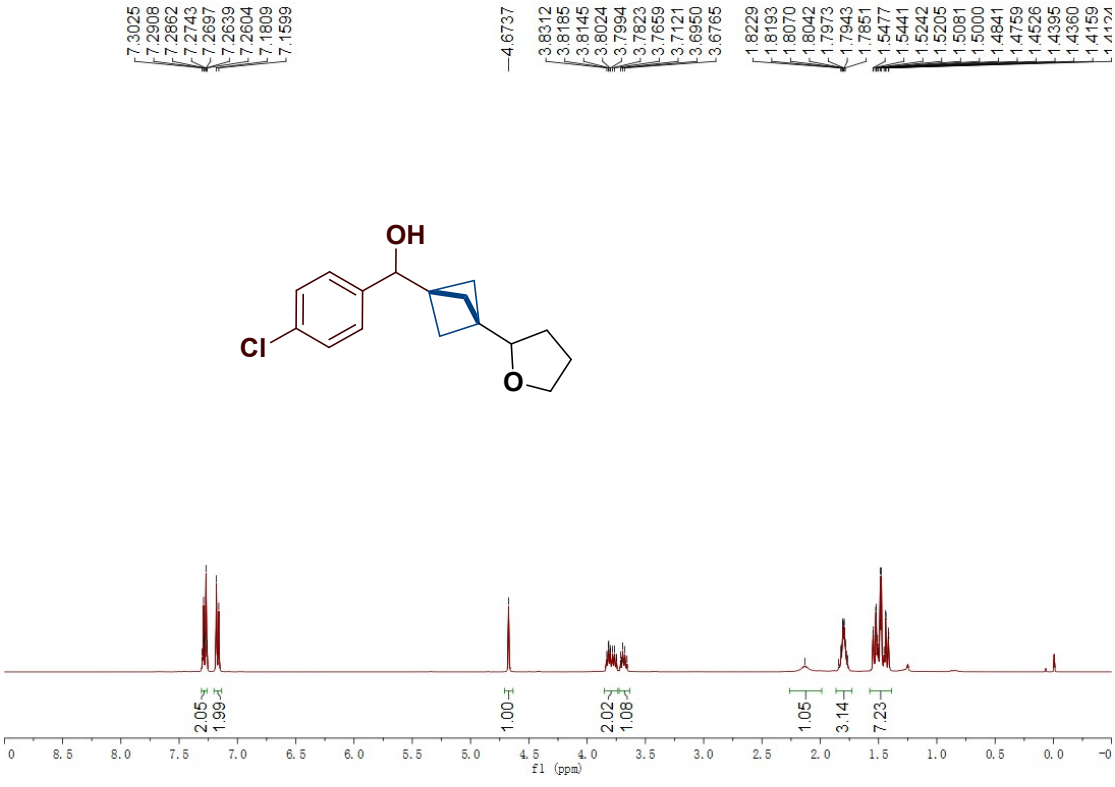
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **48**



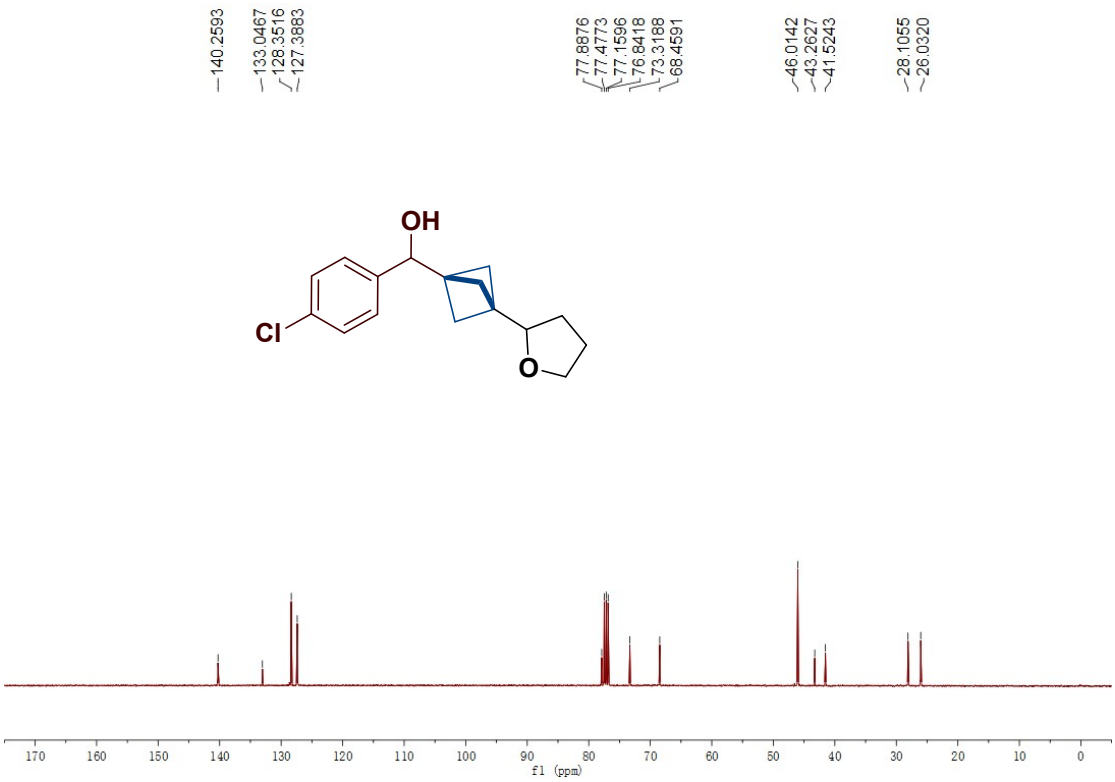
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **49**



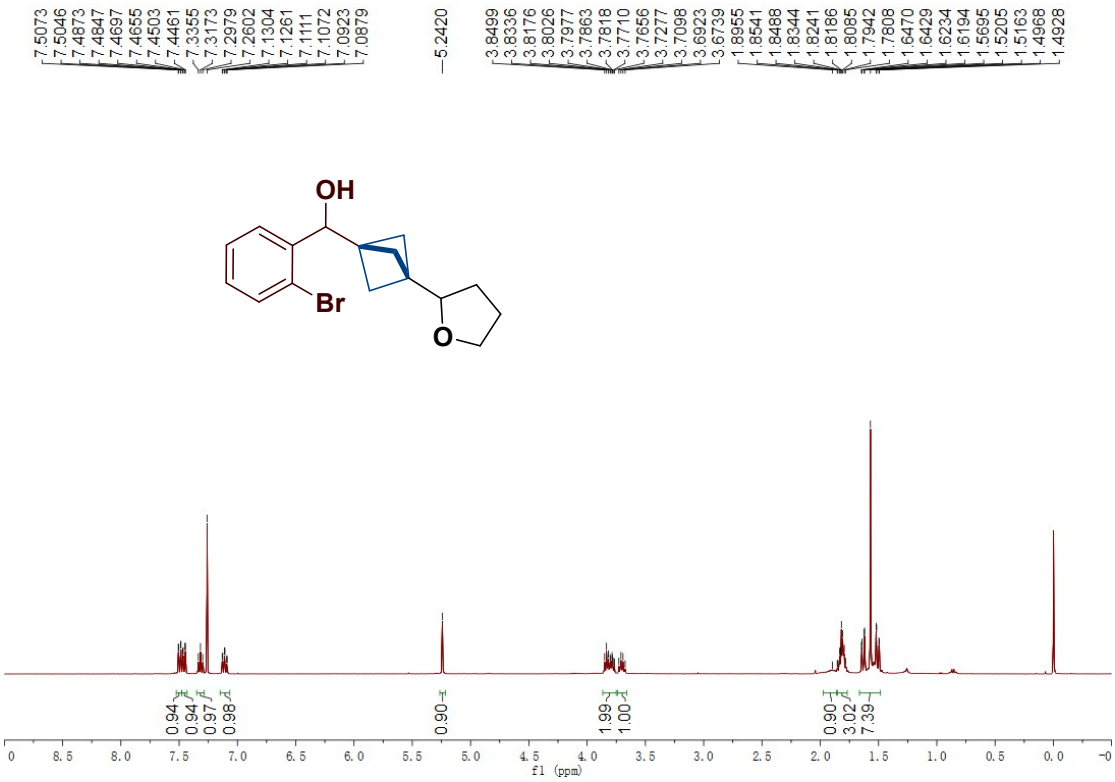
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **49**



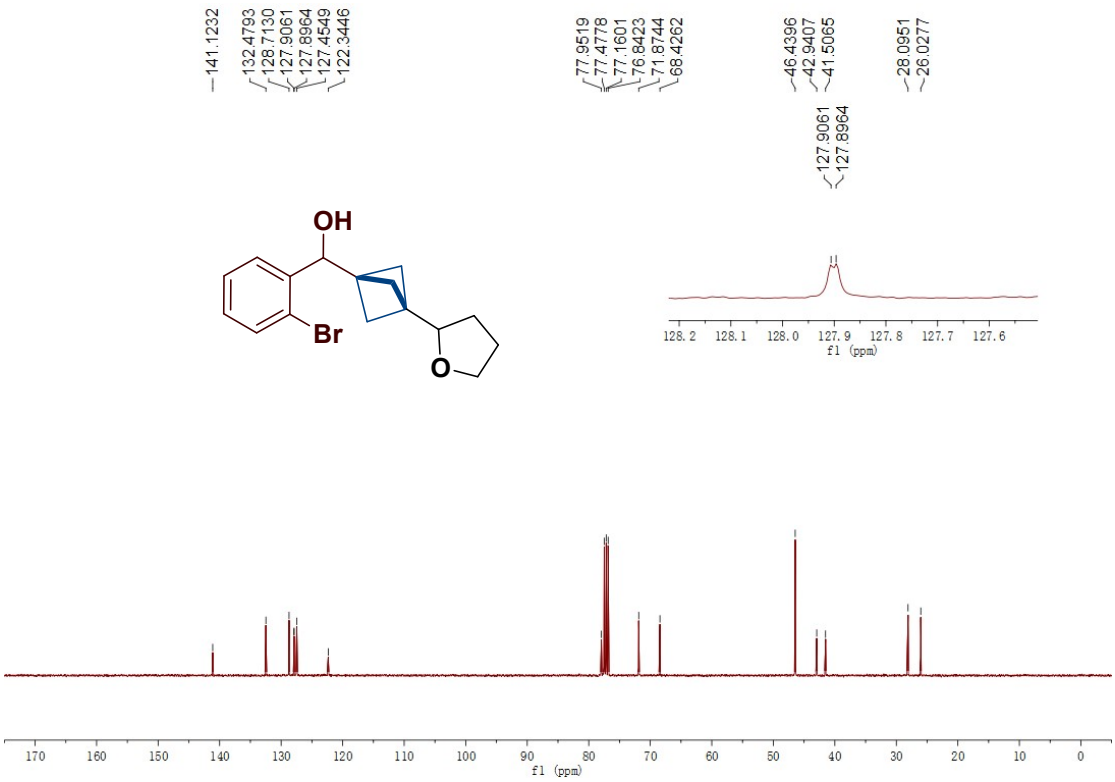
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **50**



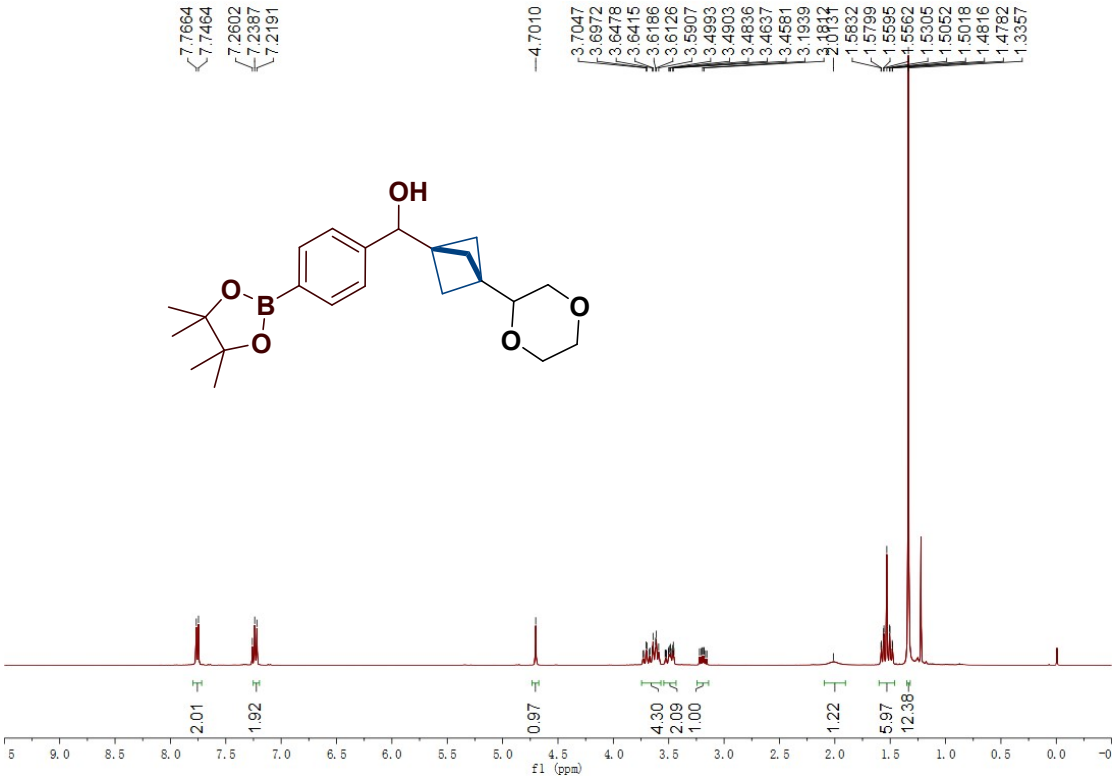
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **50**



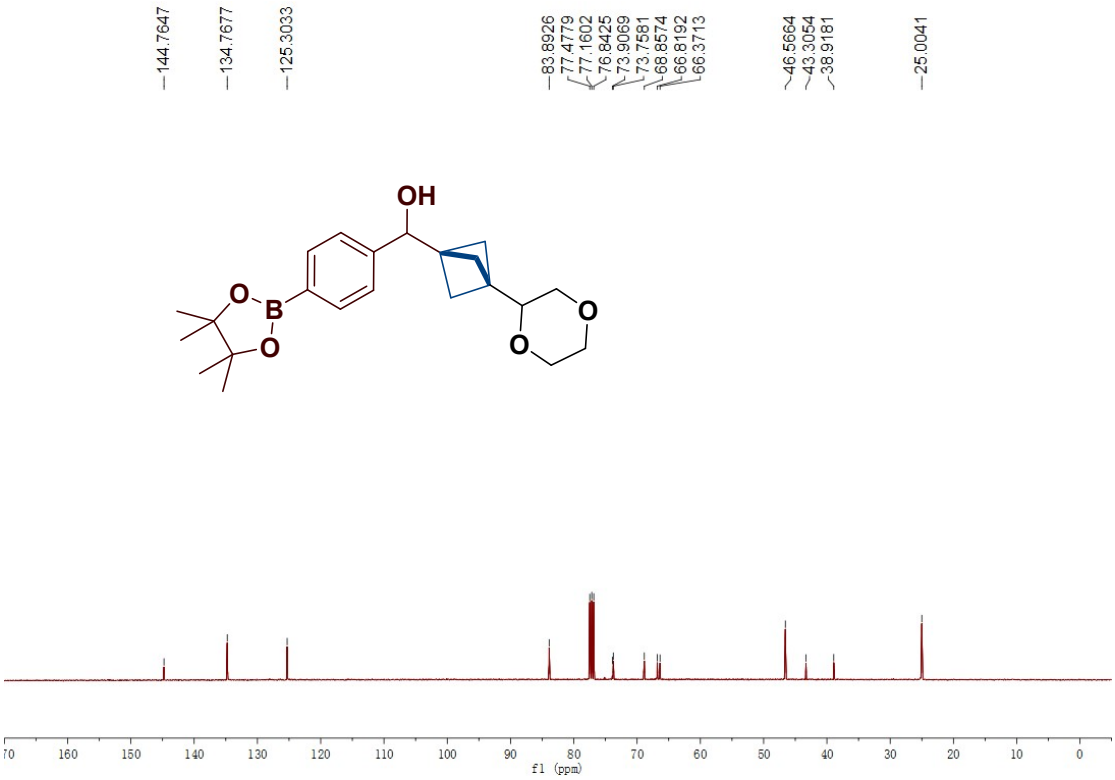
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **51**



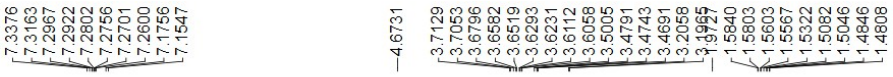
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **51**

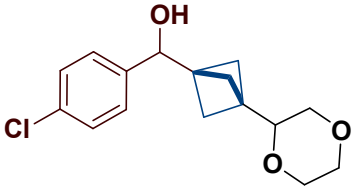


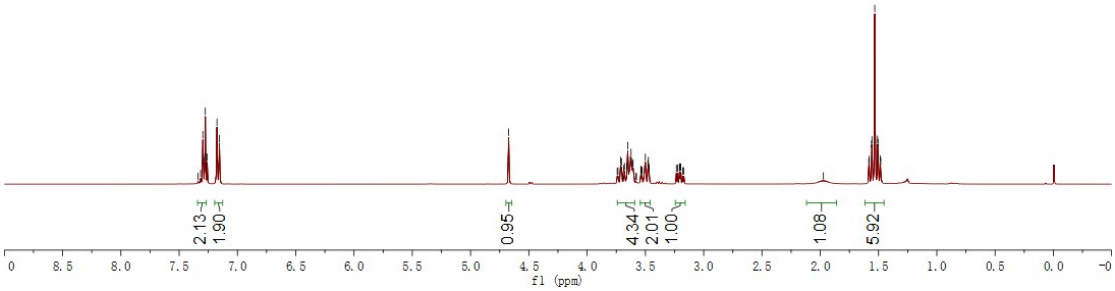
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **52**



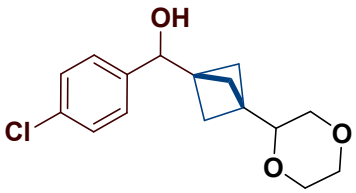
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **52**

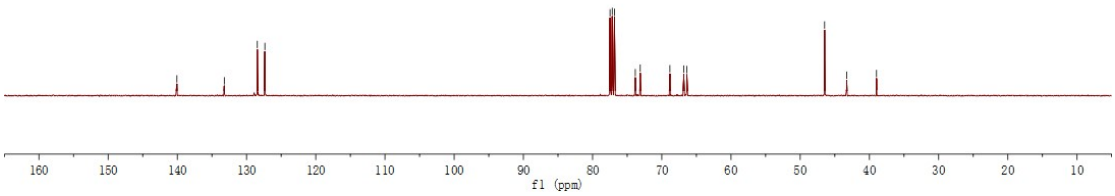




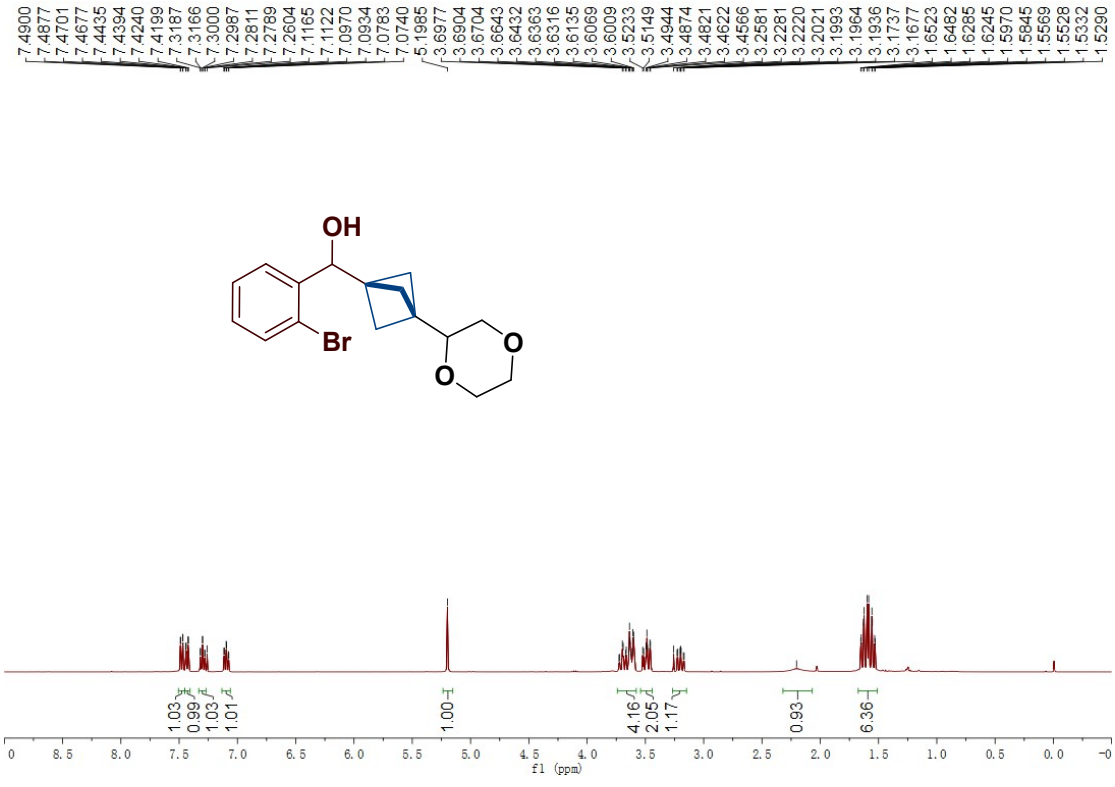


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **53**

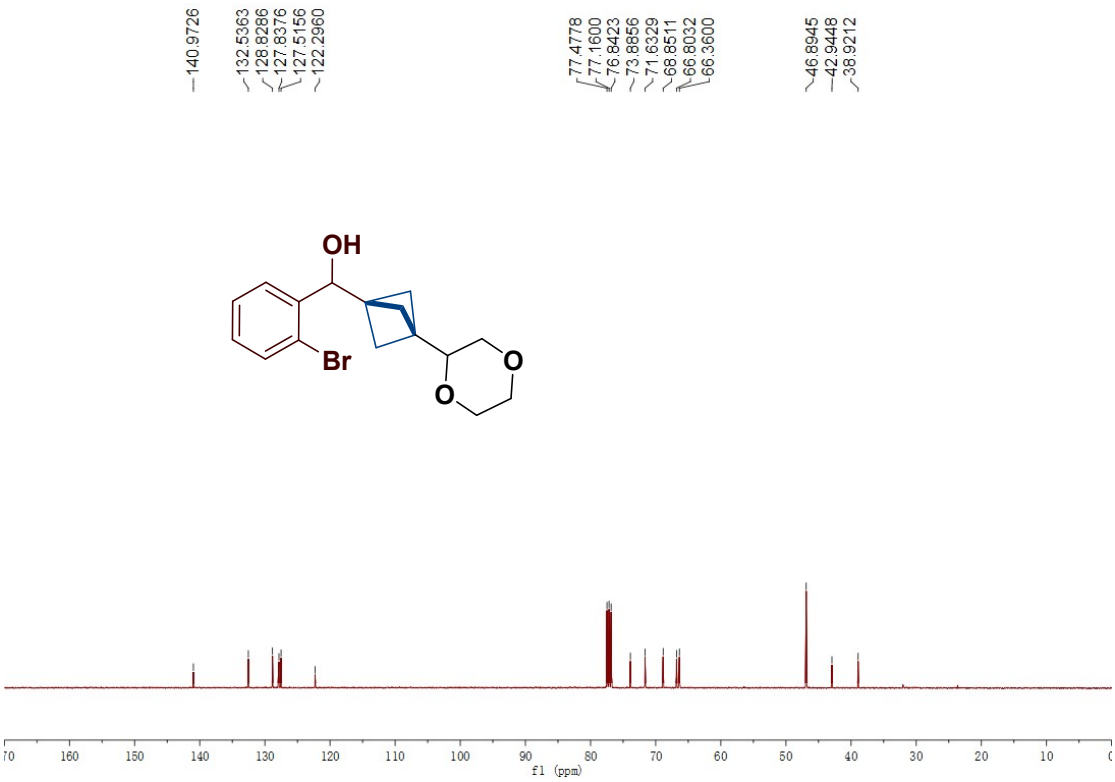




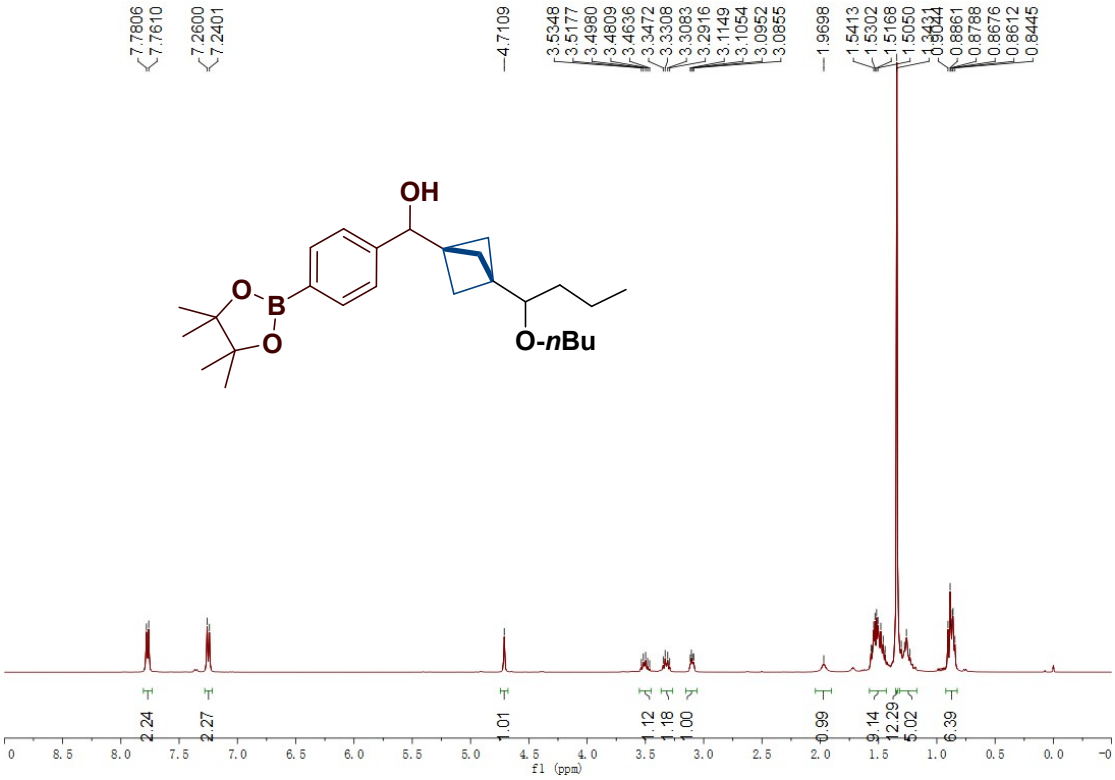
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **53**



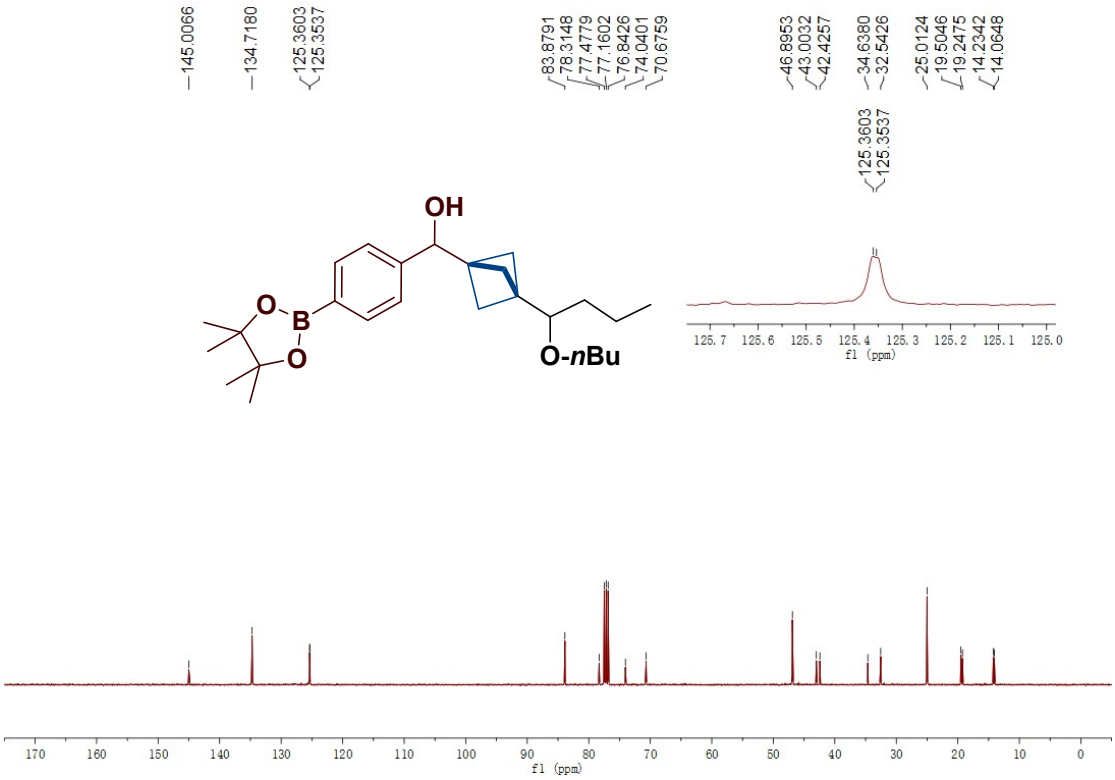
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **54**



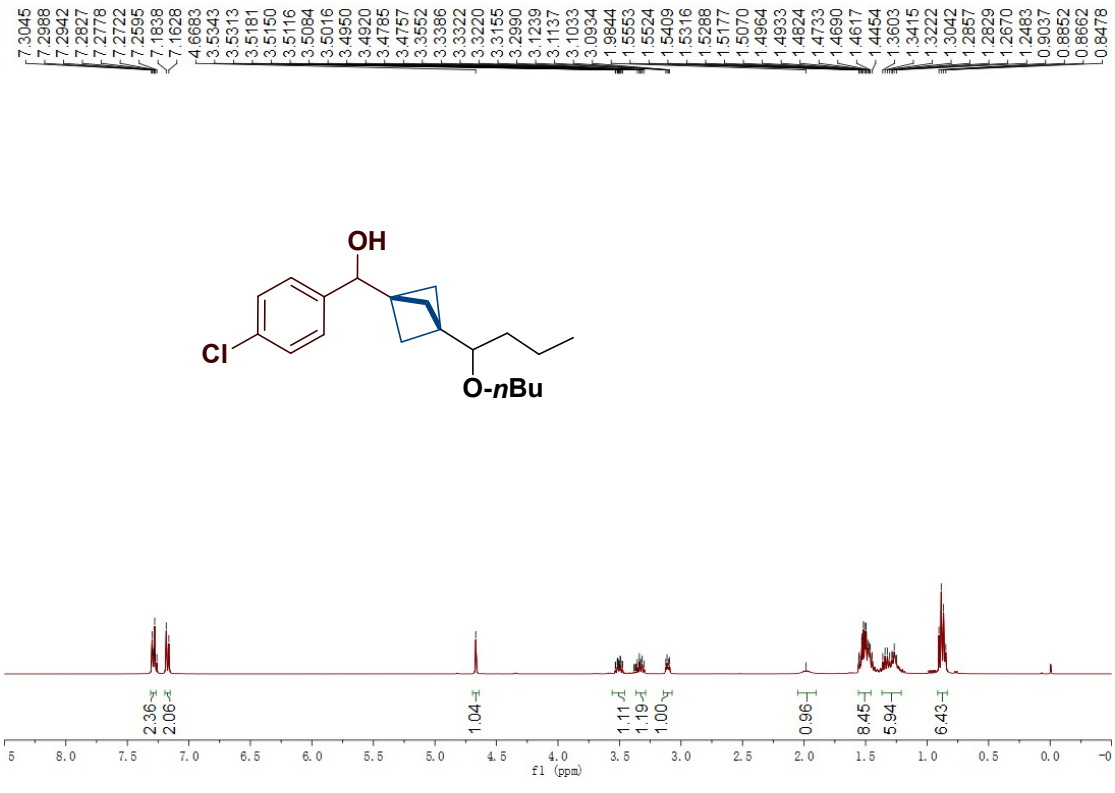
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **54**



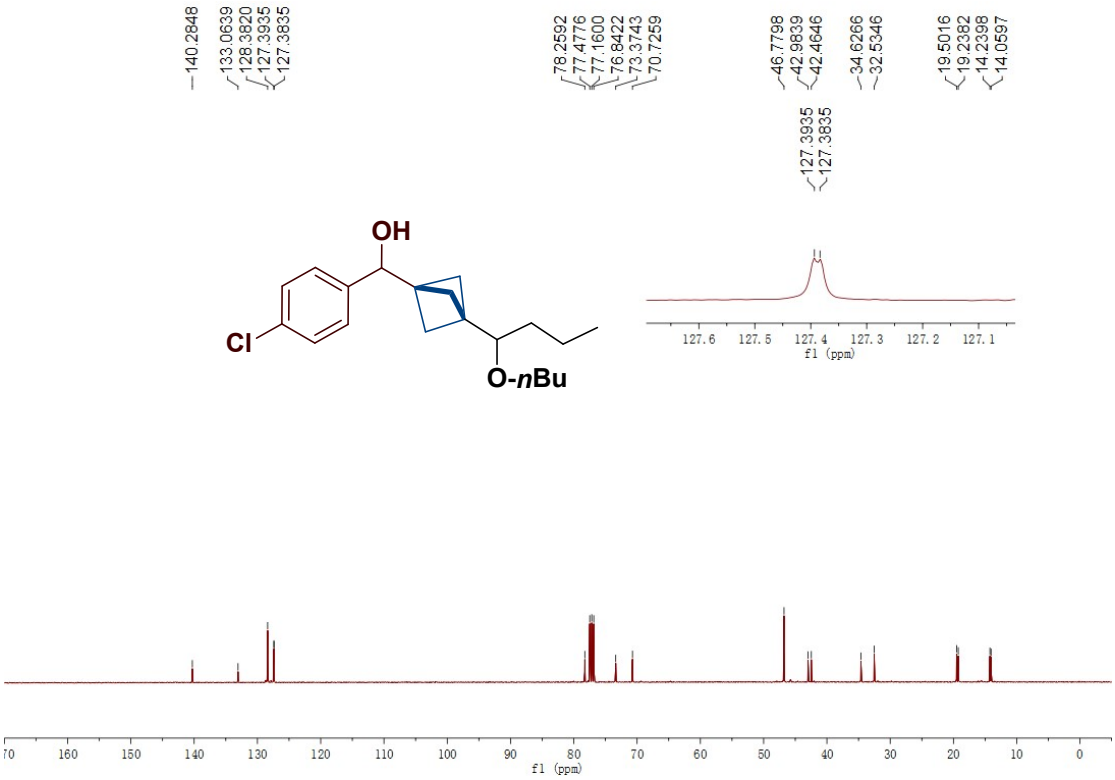
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **55**



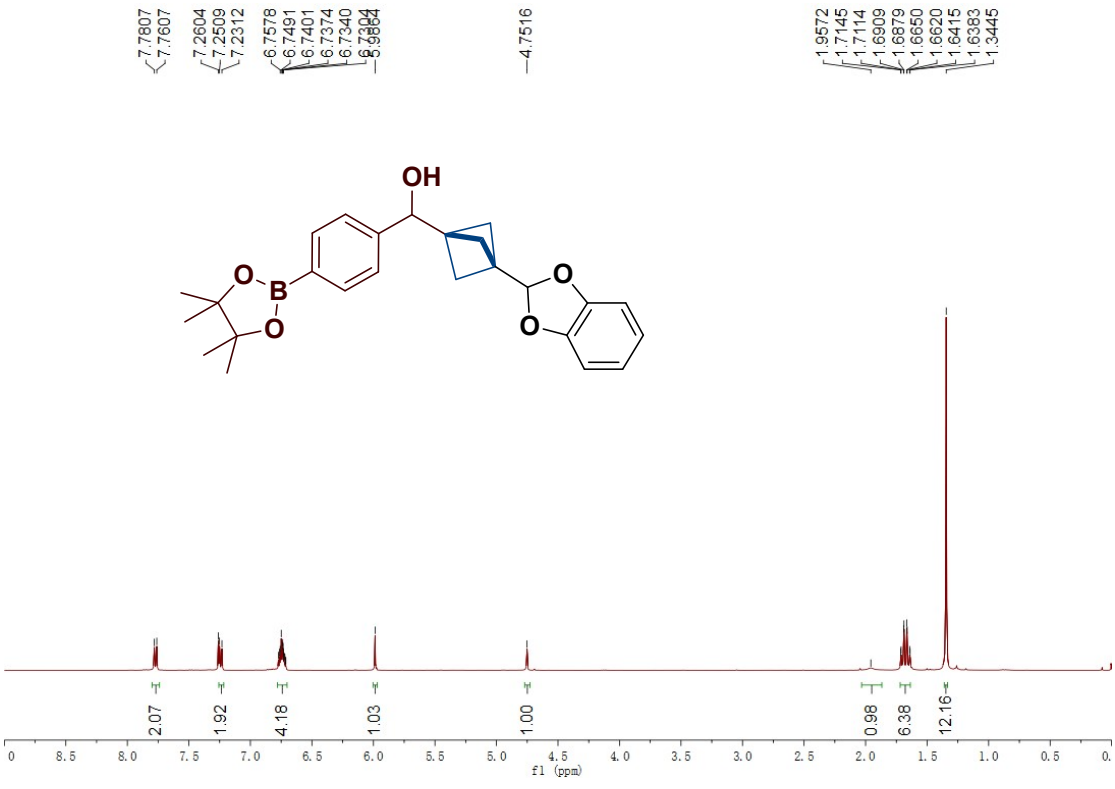
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **55**



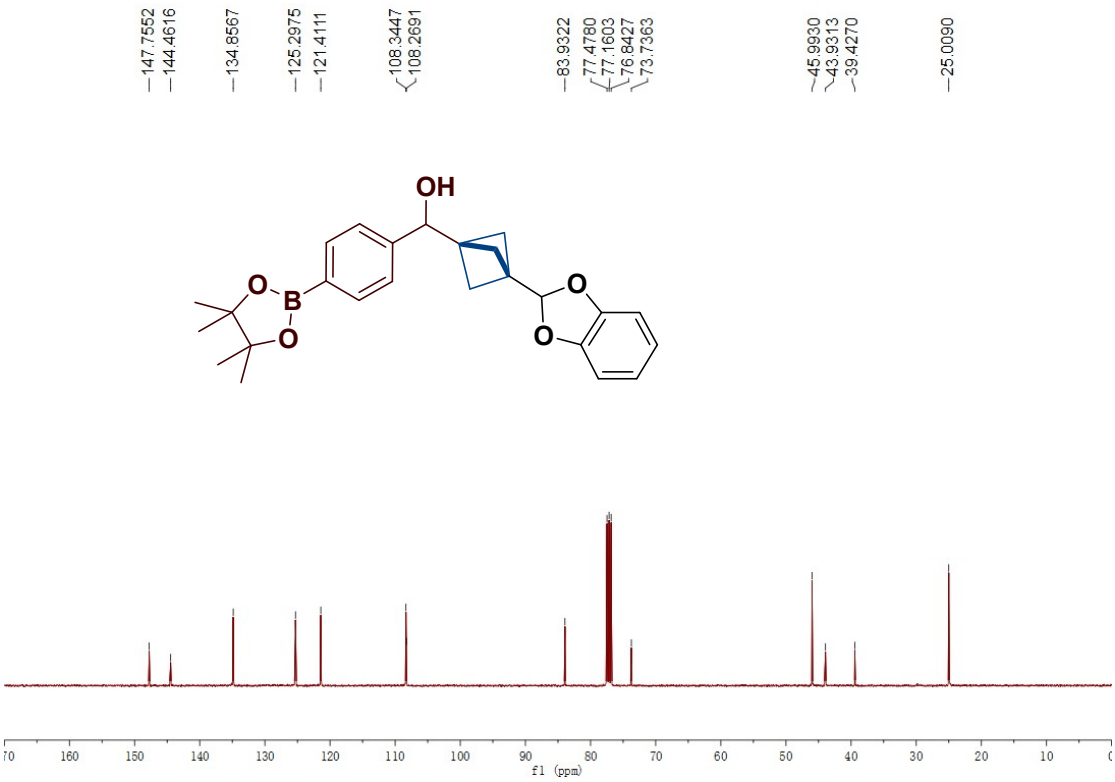
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **56**



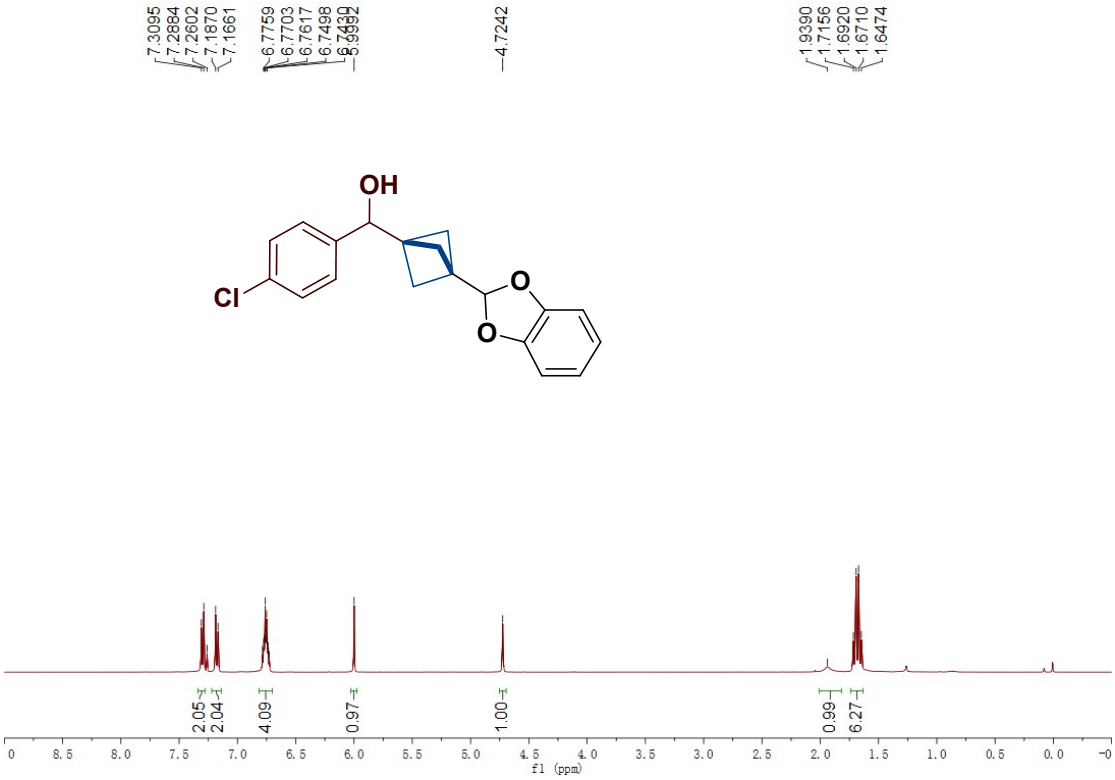
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **56**



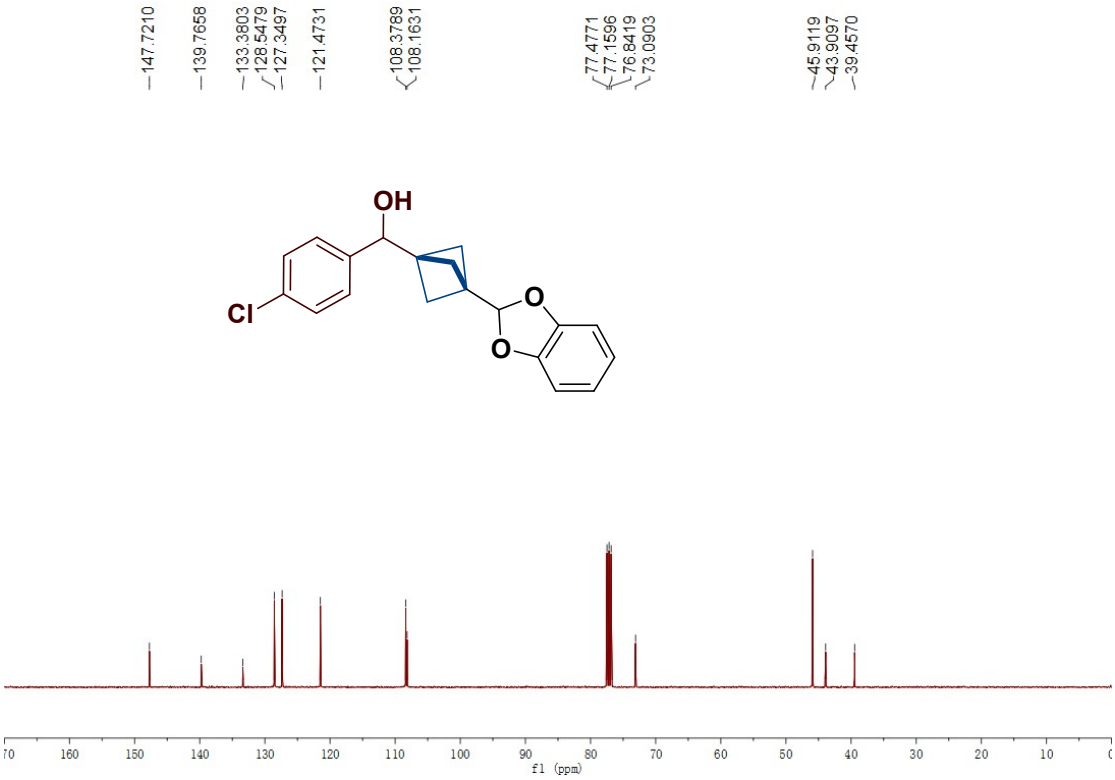
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **57**



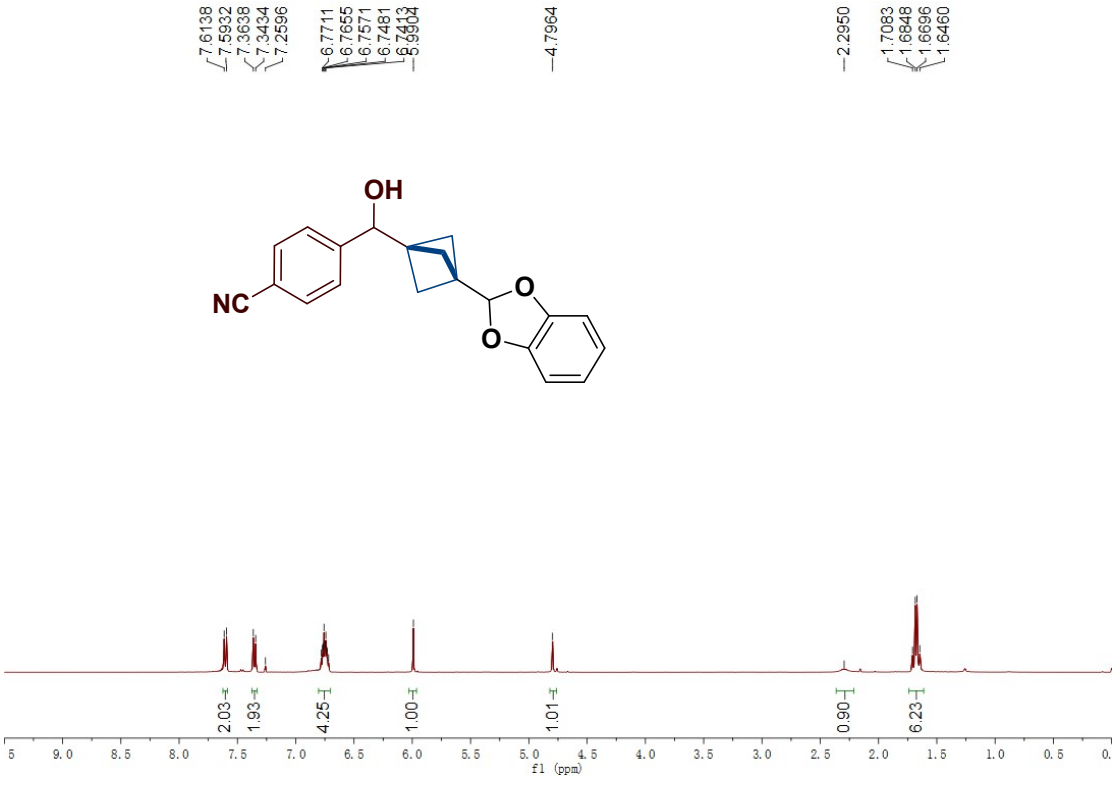
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **57**



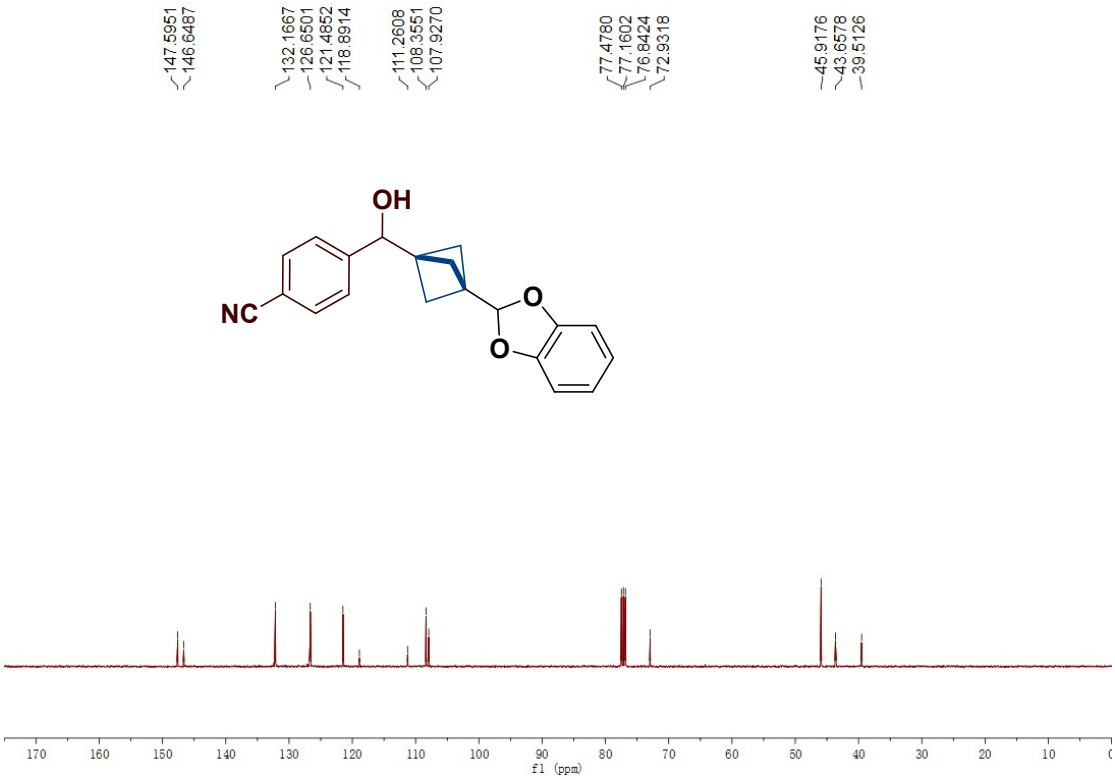
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **58**



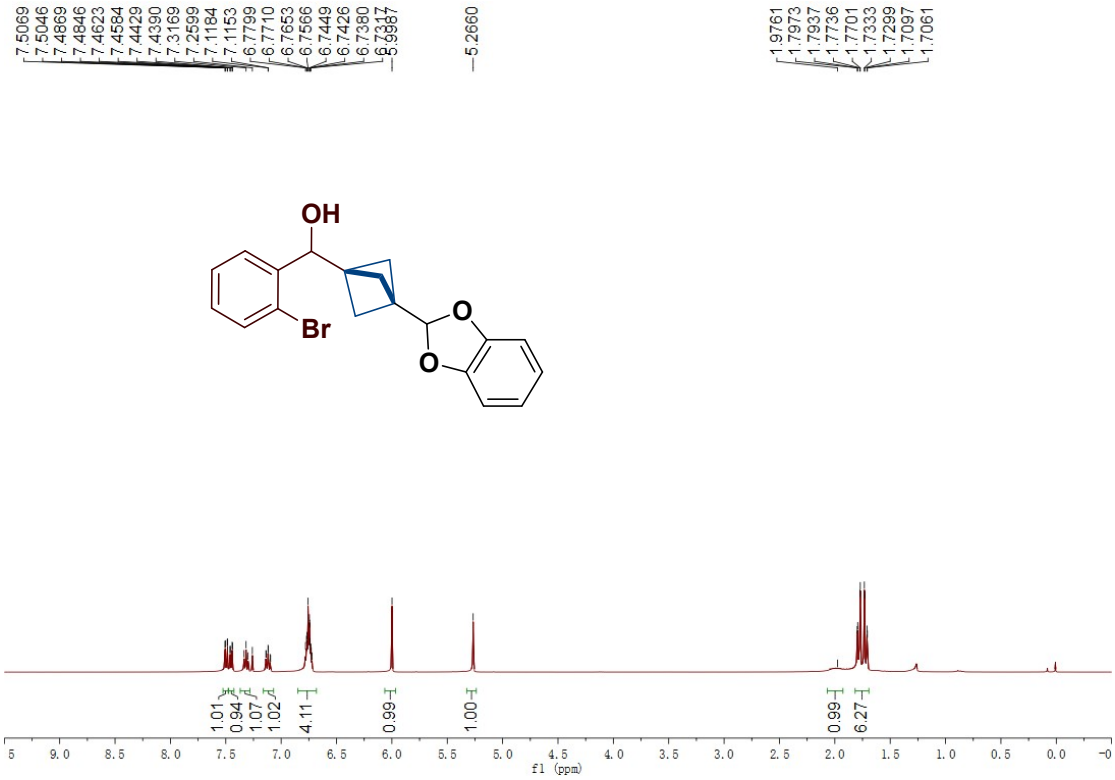
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **58**



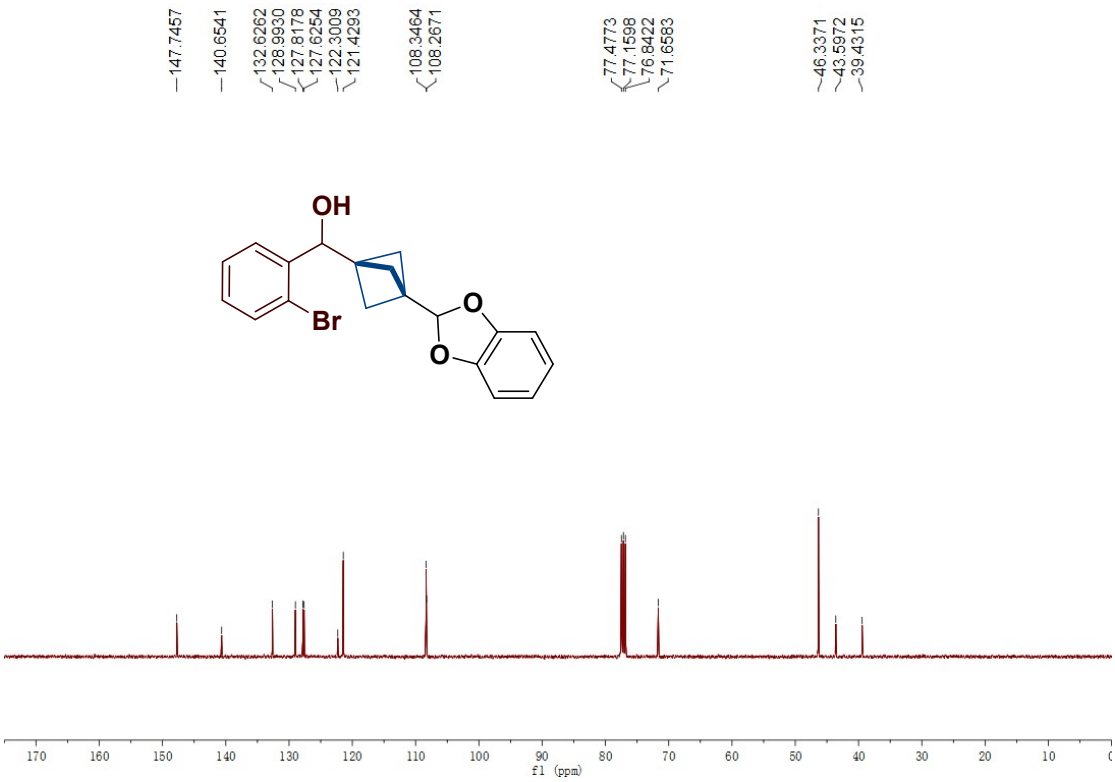
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **59**



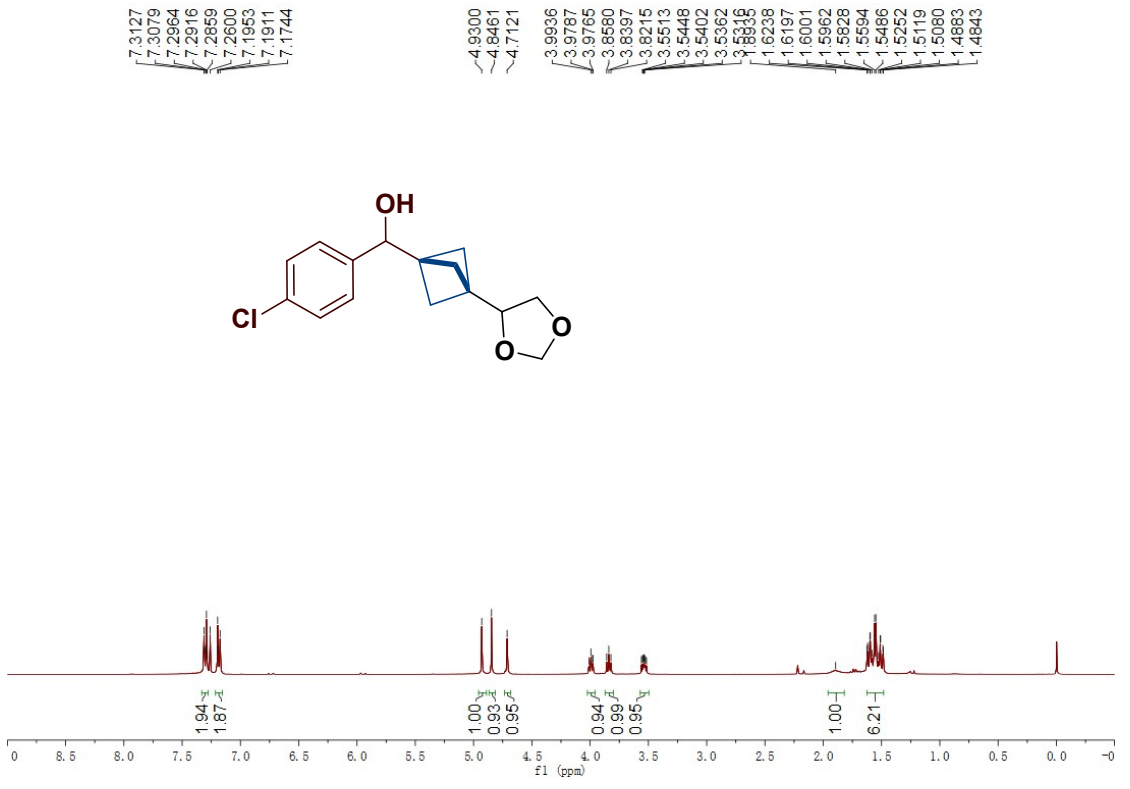
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **59**



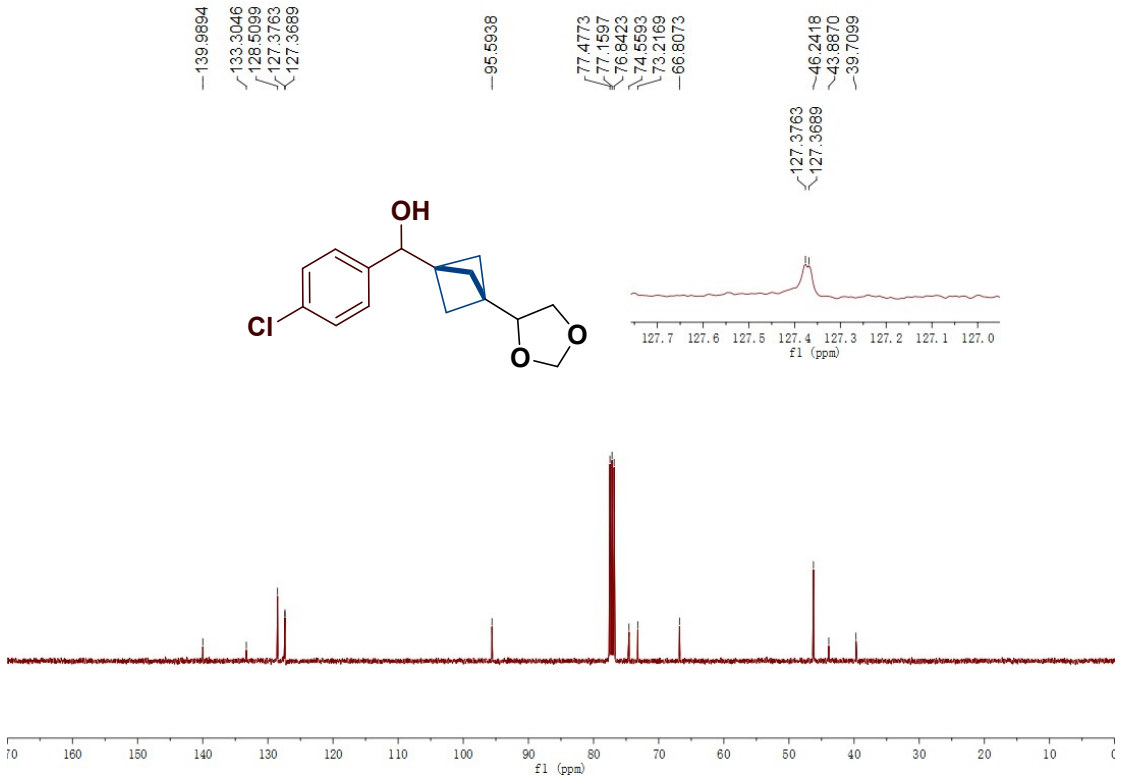
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **60**



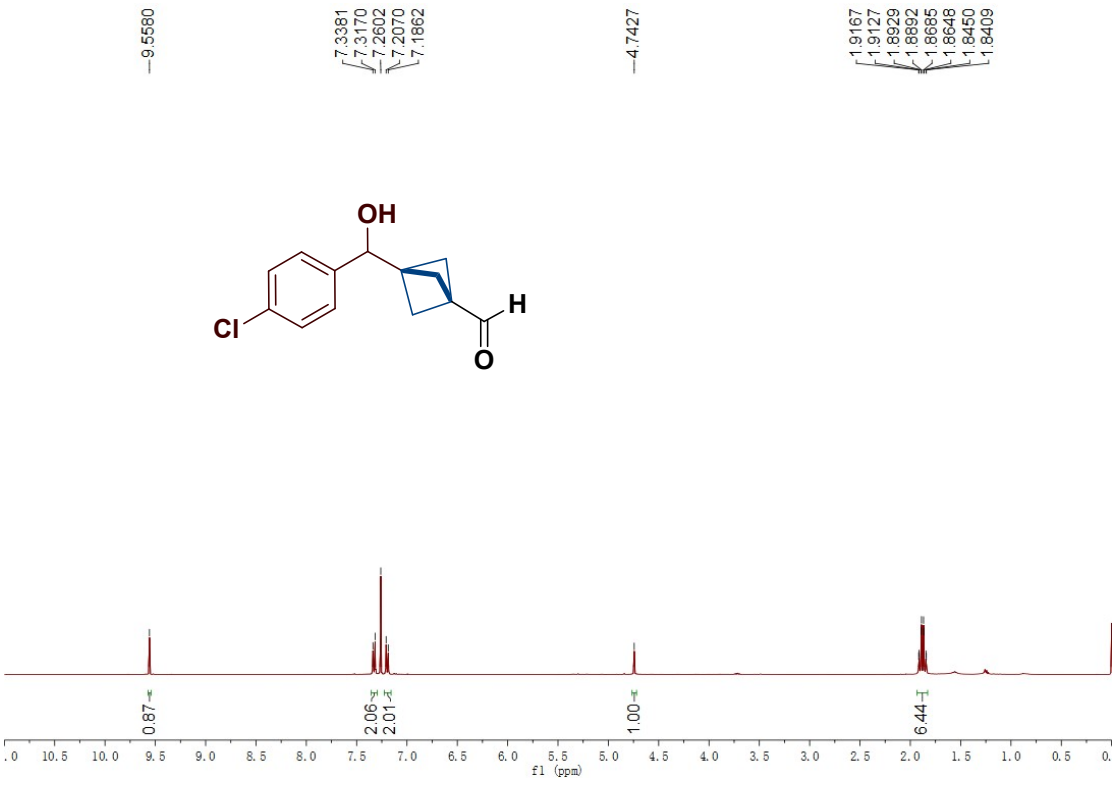
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **60**



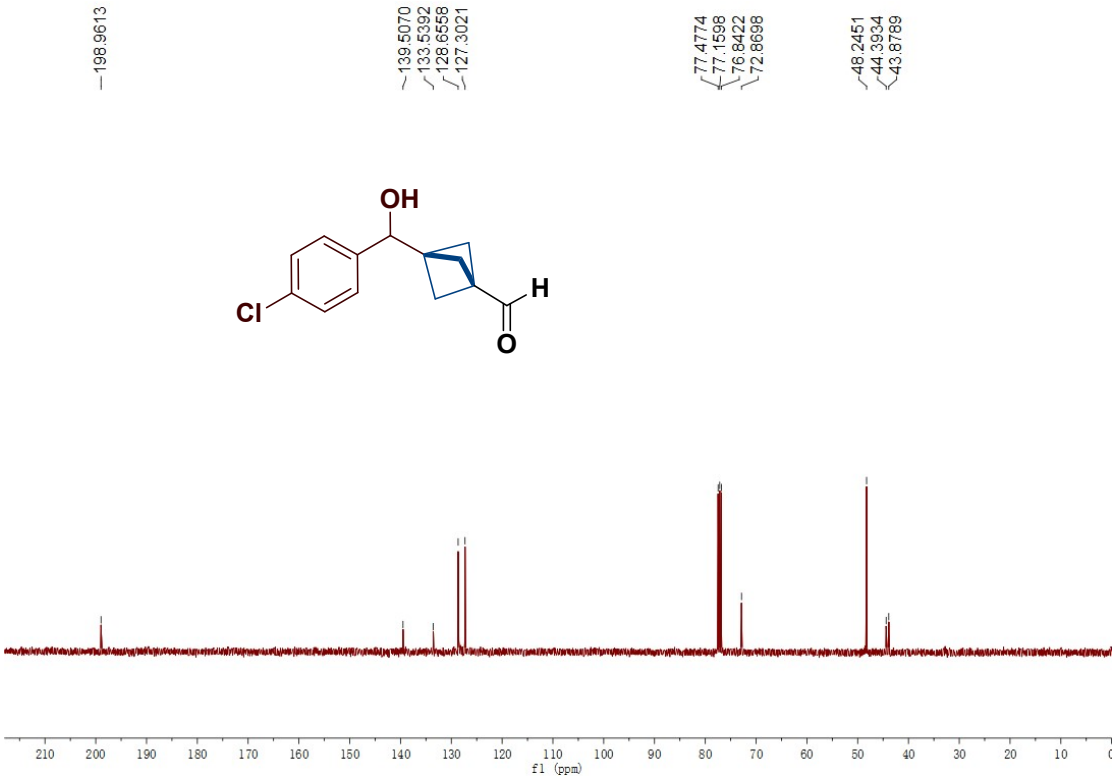
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **63a**



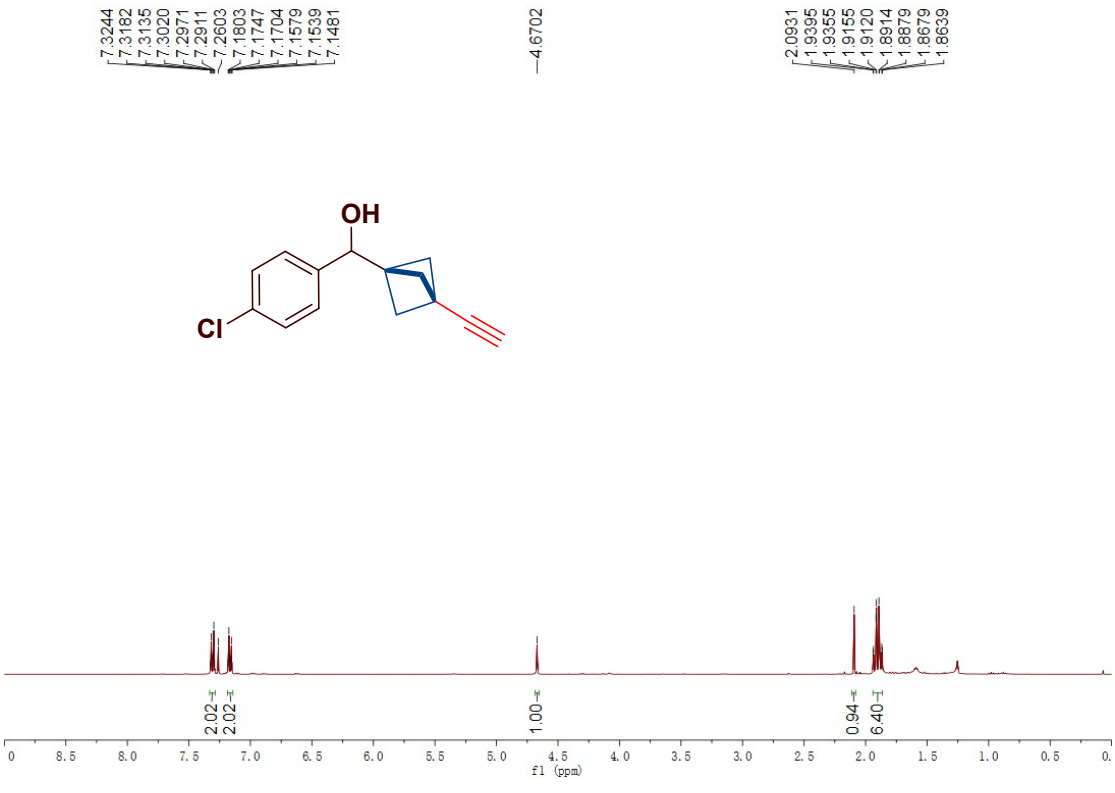
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **63a**



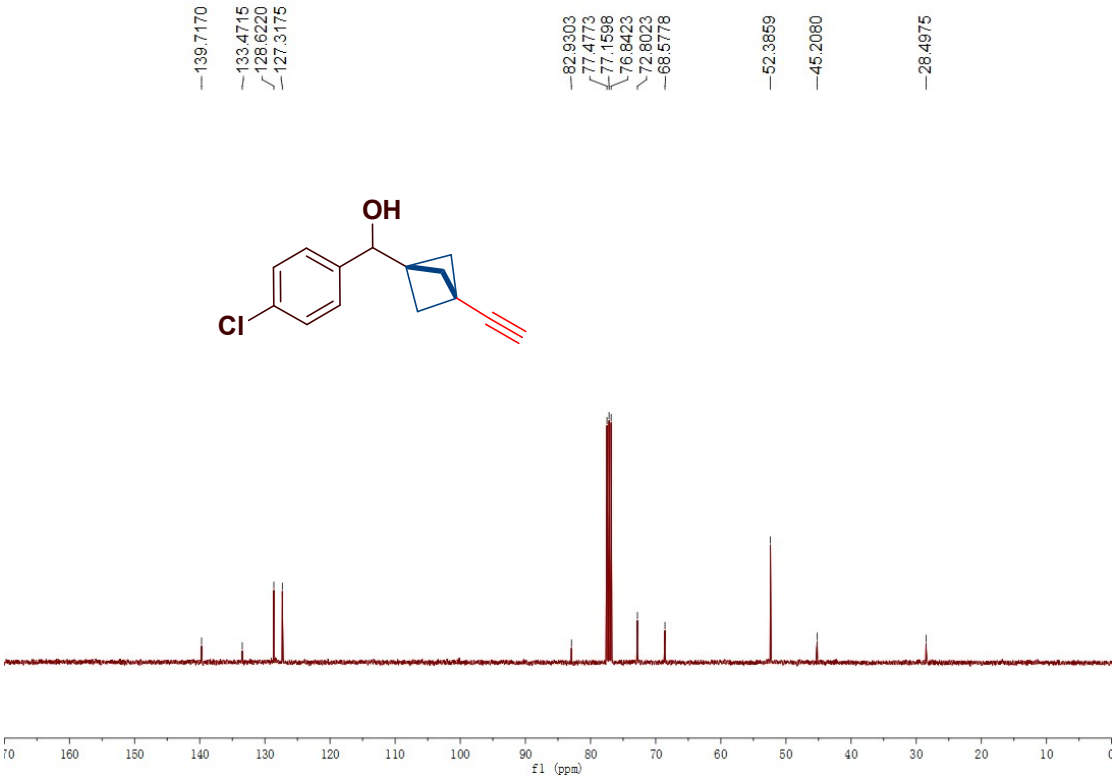
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **63**



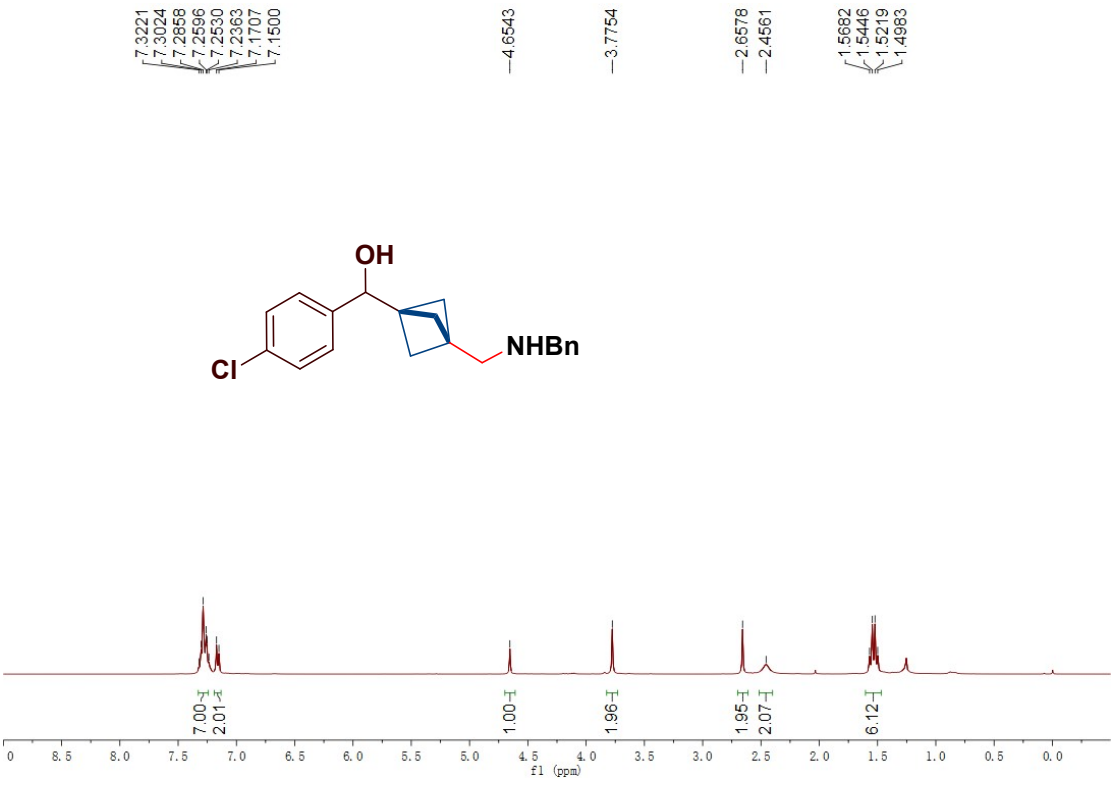
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **63**



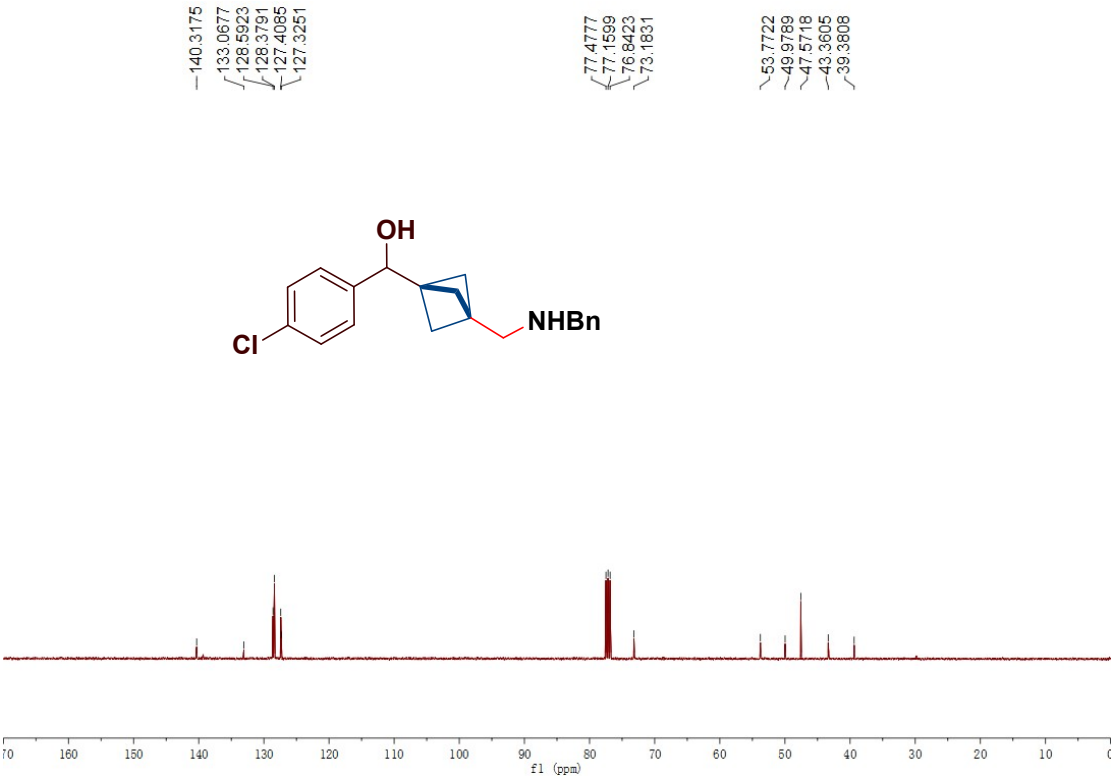
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **65**



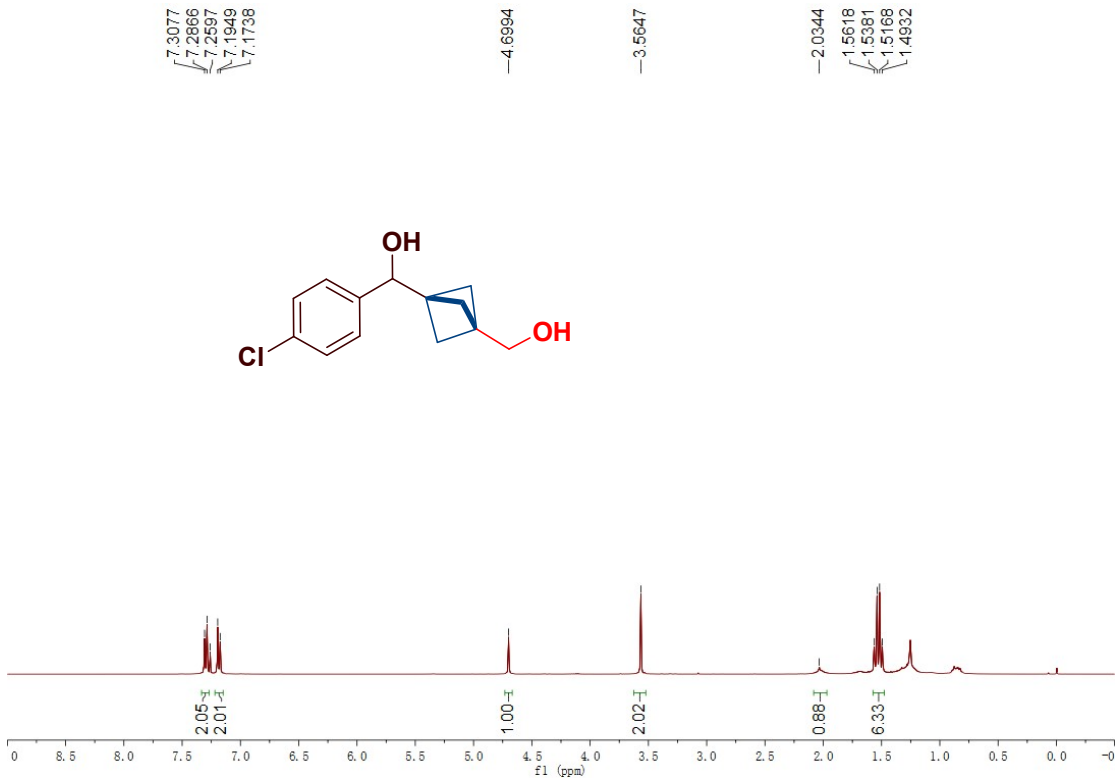
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **65**



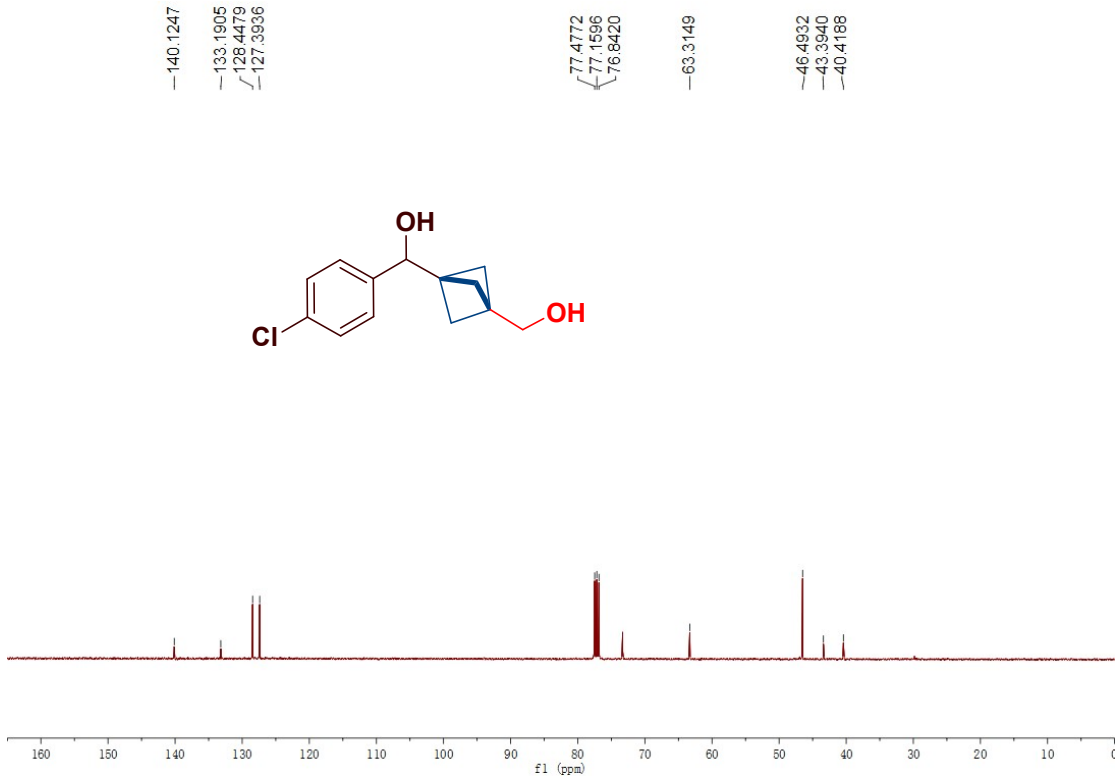
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **66**



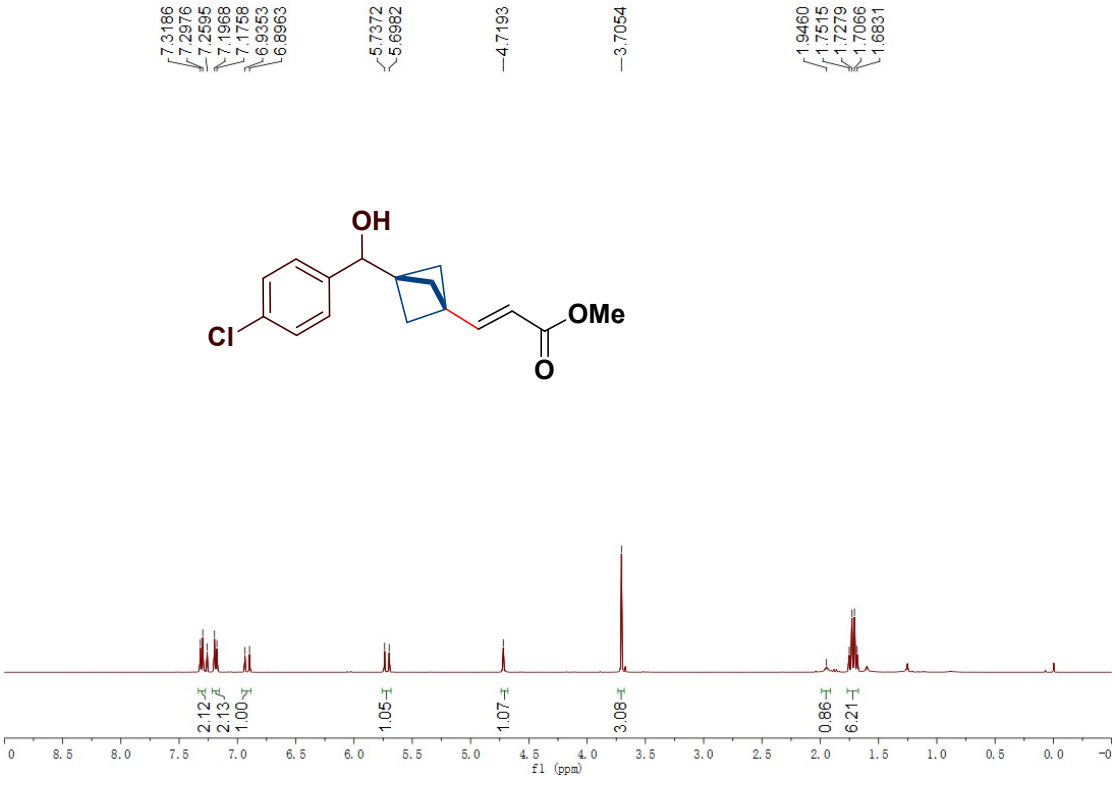
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **66**



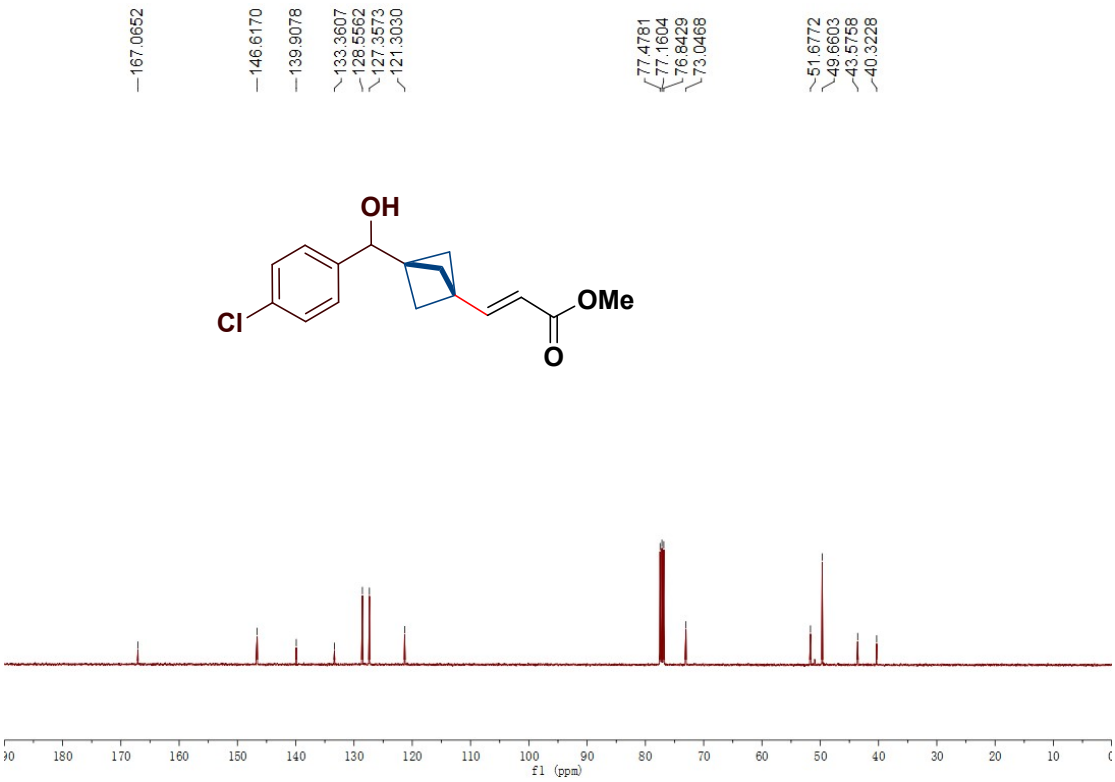
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **67**



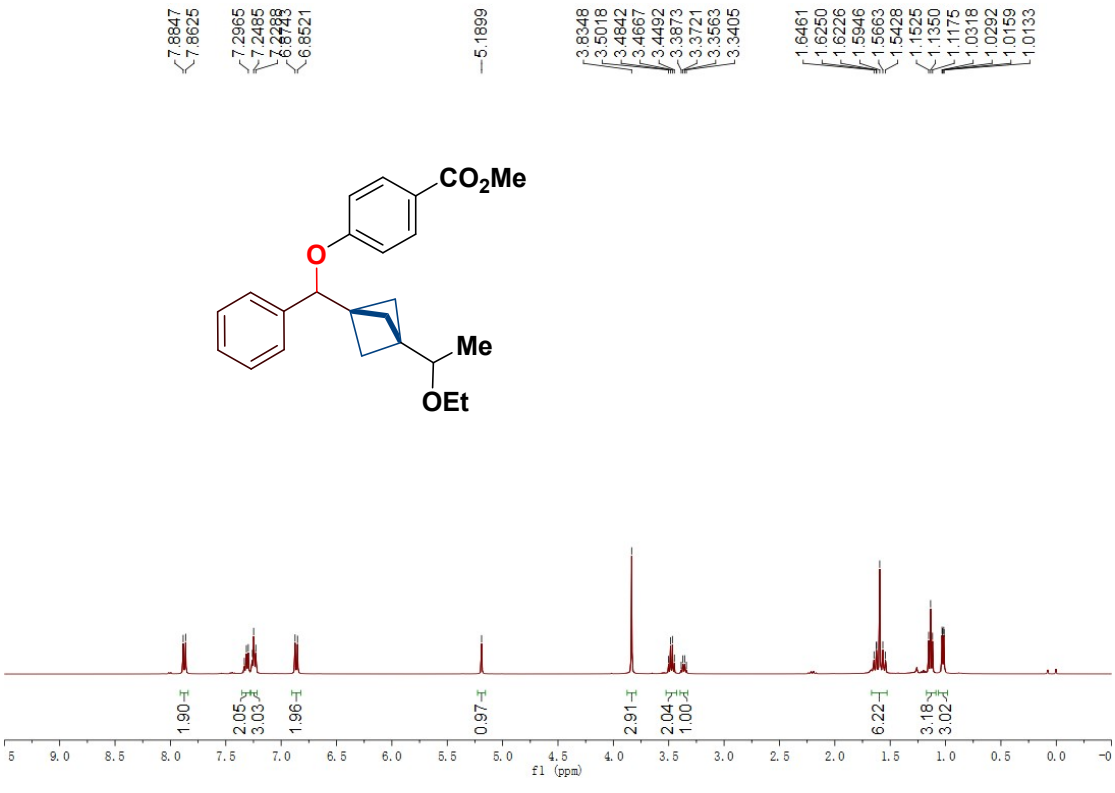
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **67**



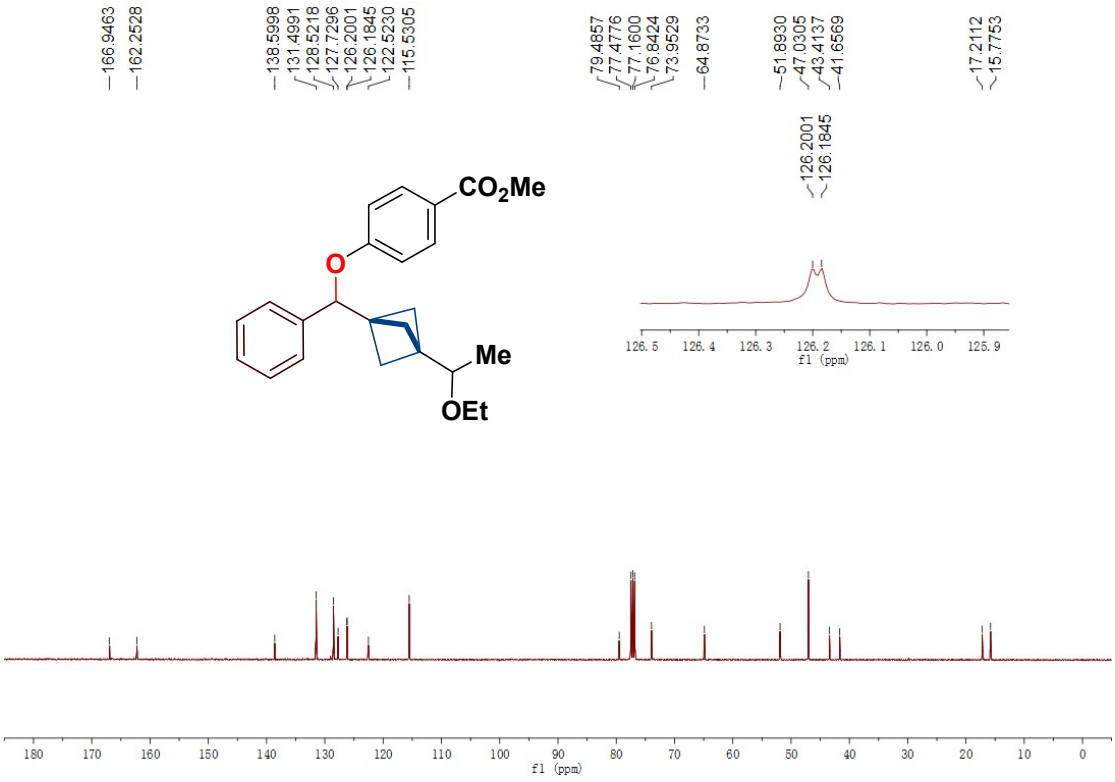
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **69**



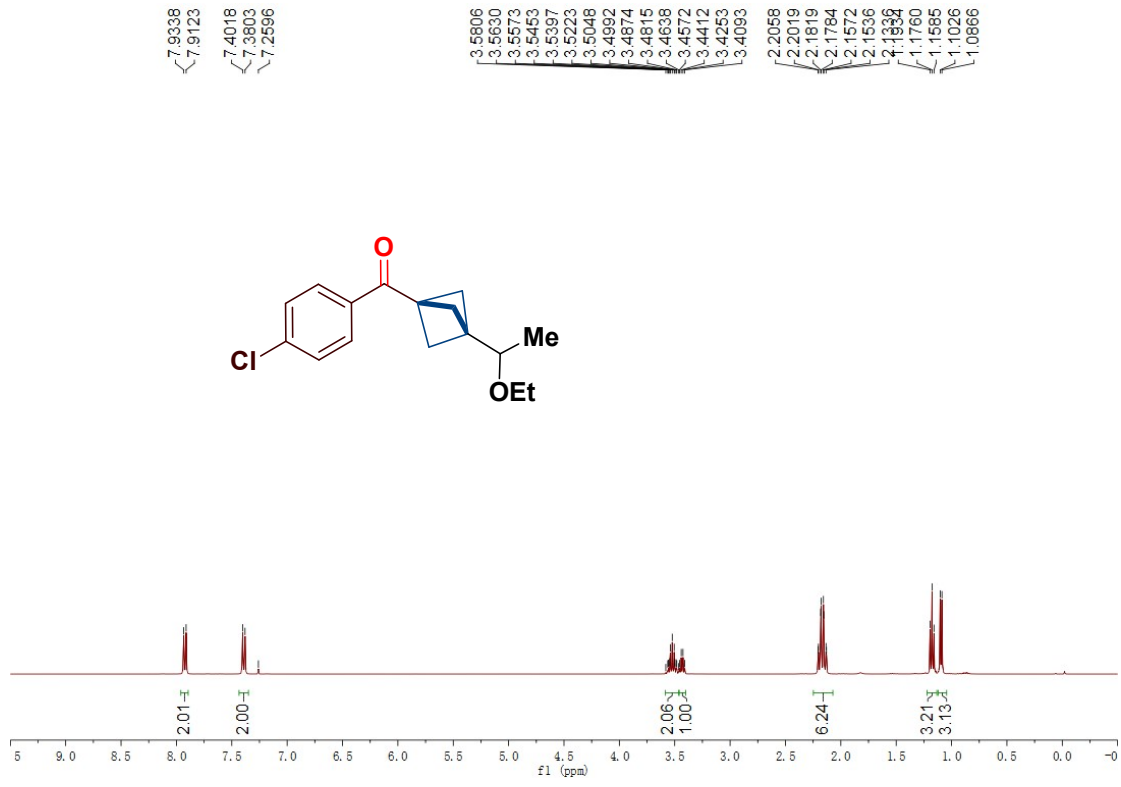
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **69**



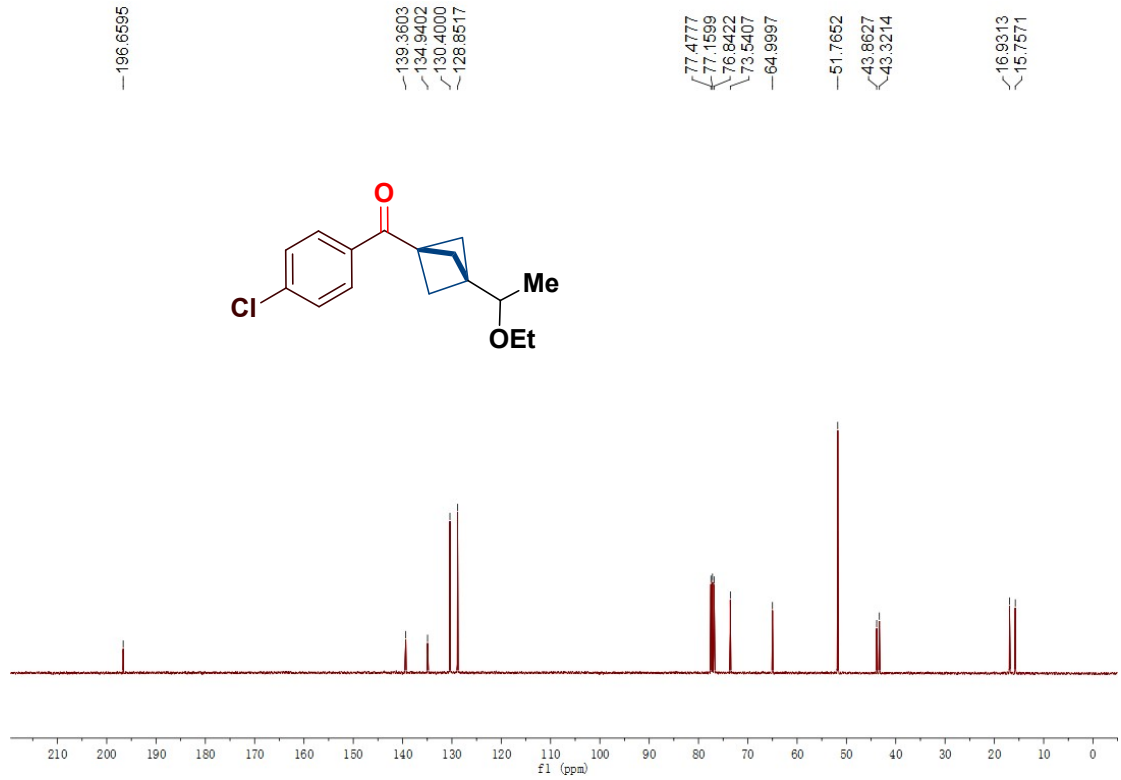
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **71**



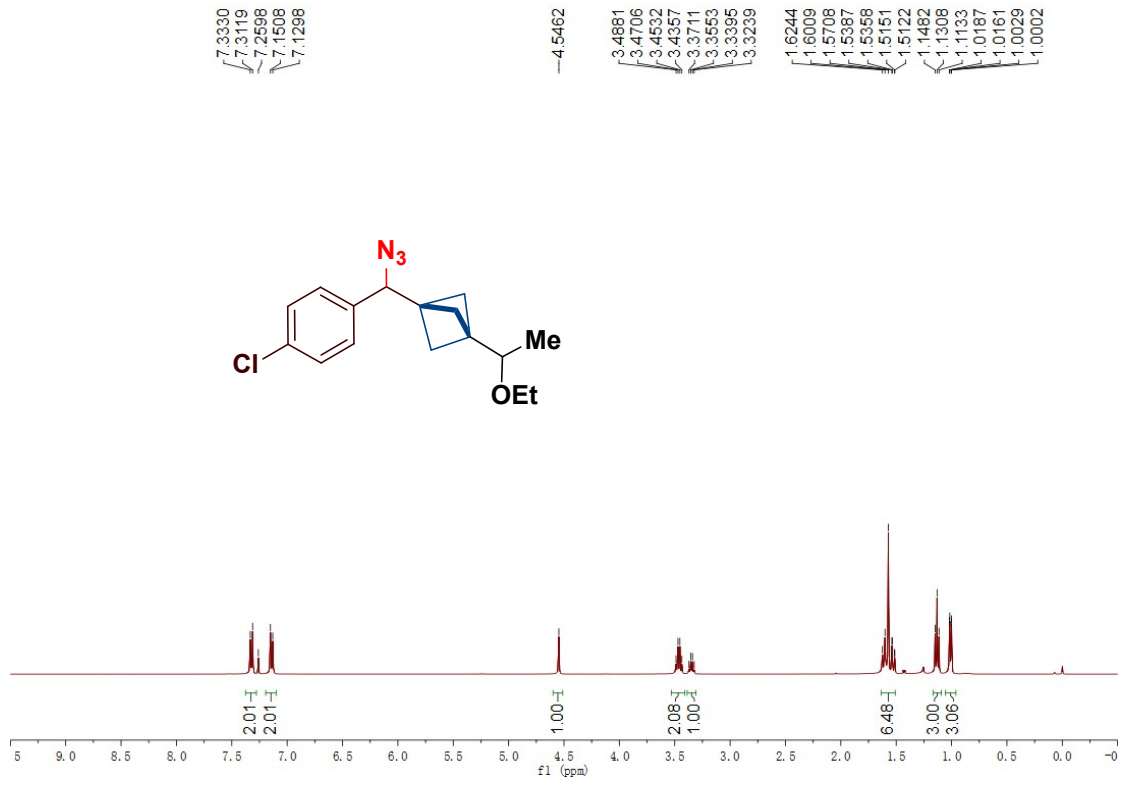
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **71**



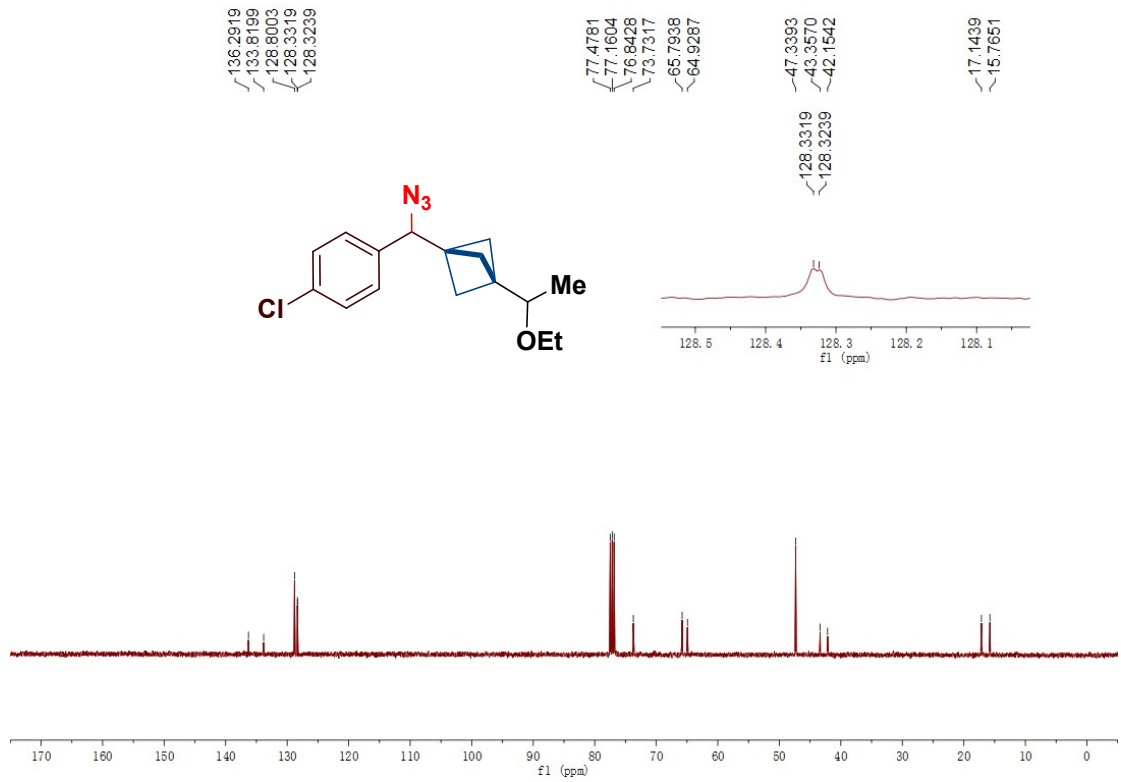
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **72**



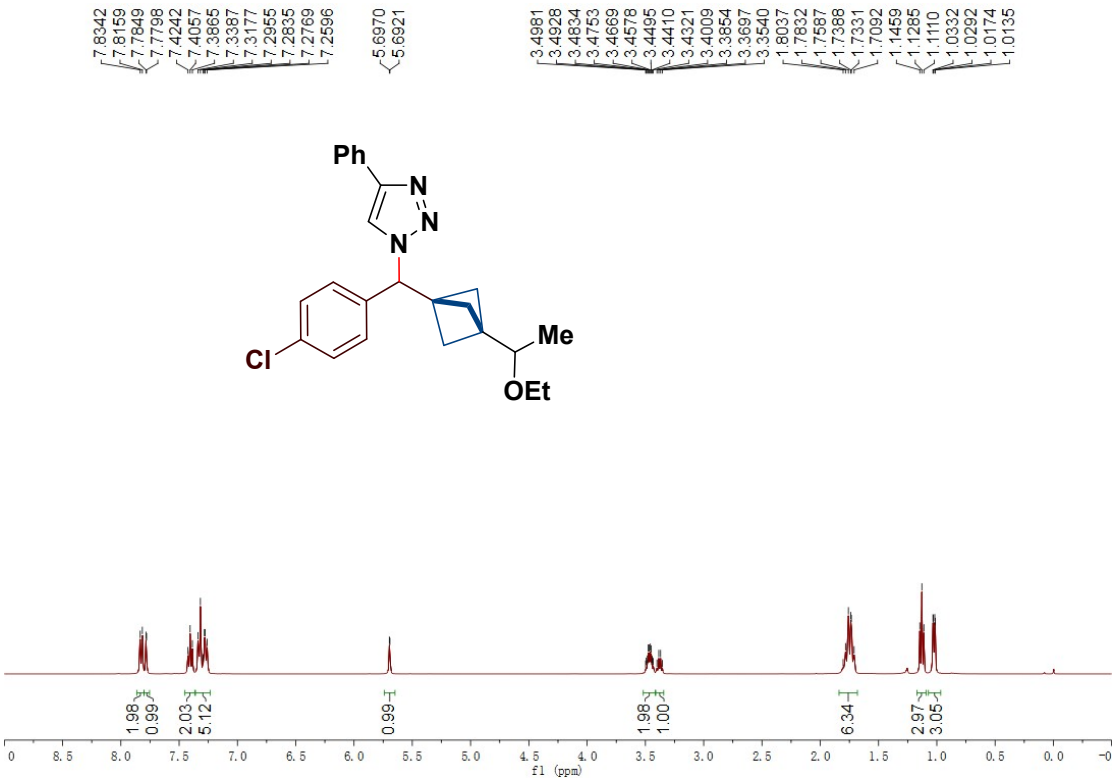
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **72**



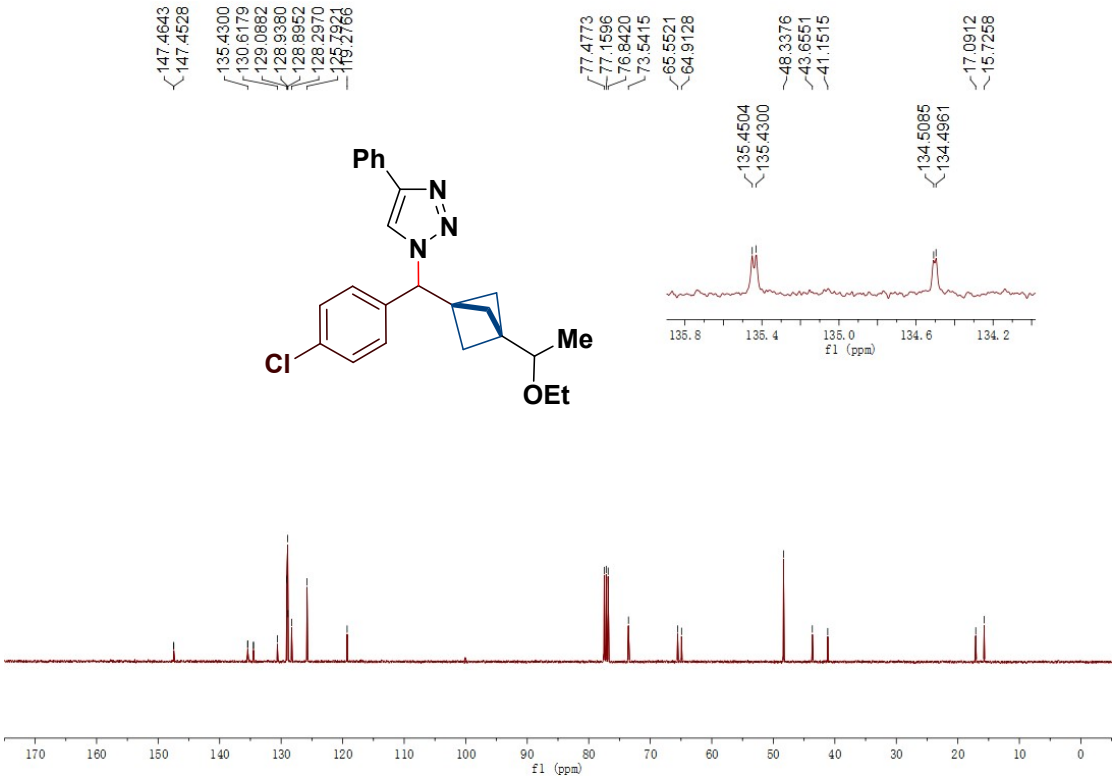
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **73**



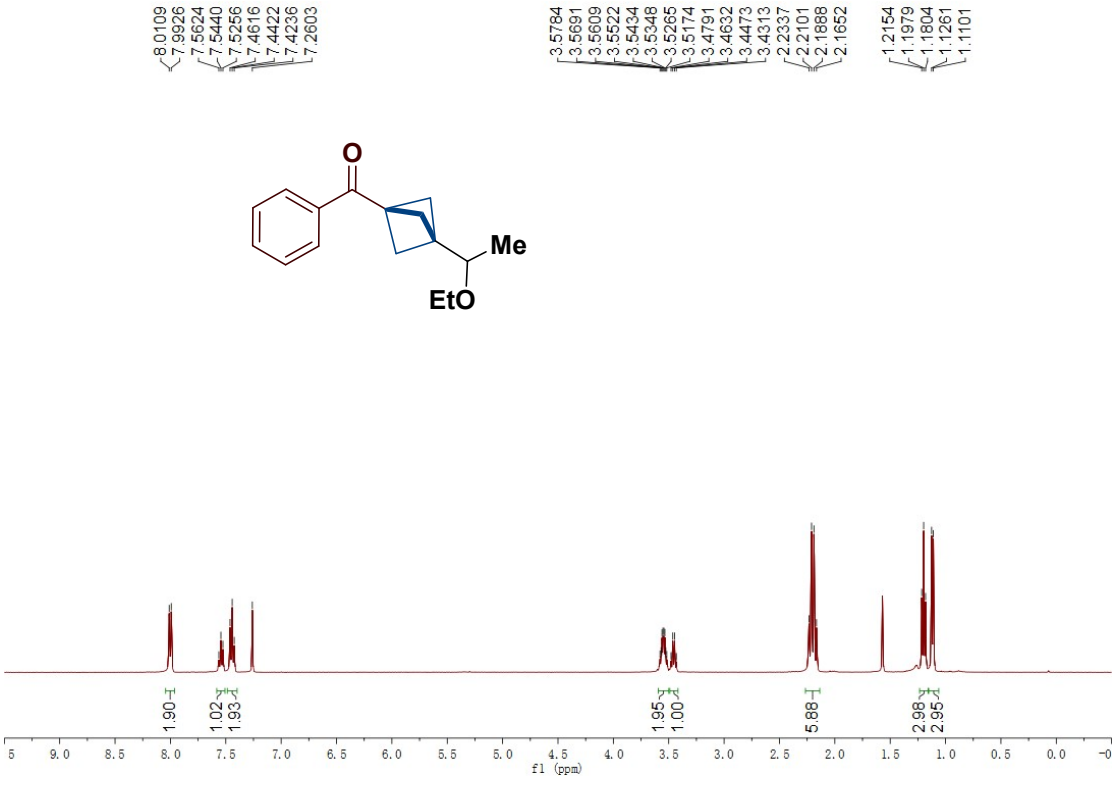
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **73**



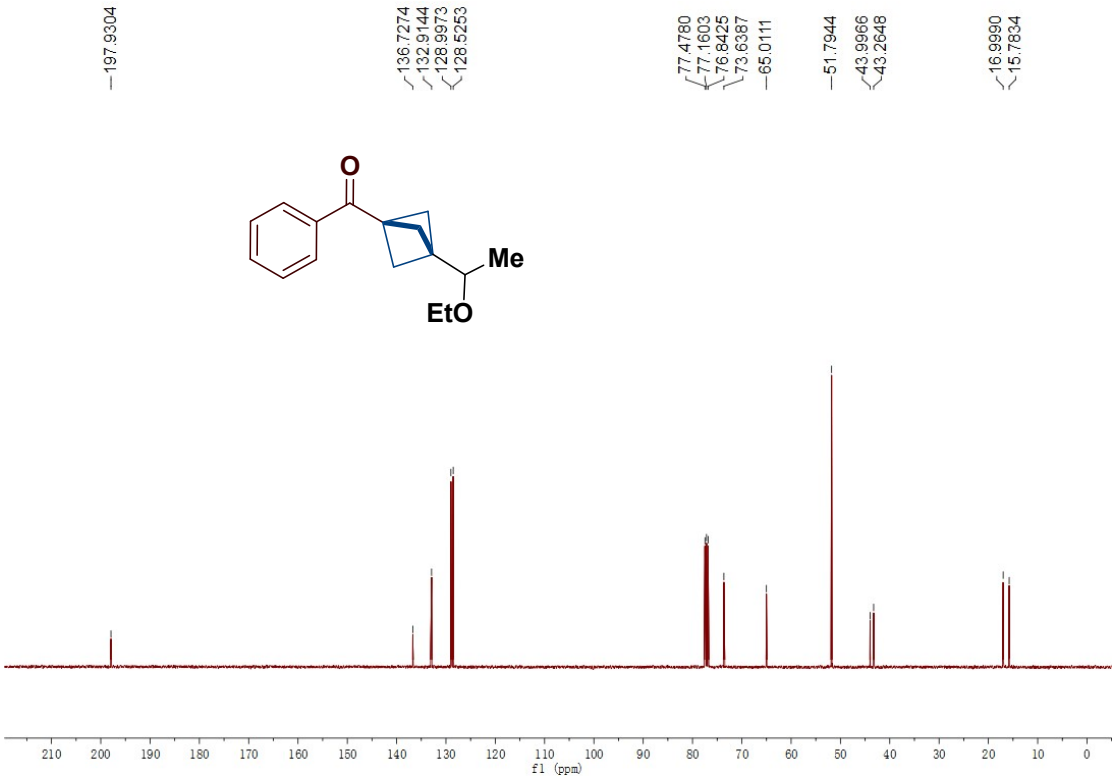
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **75**



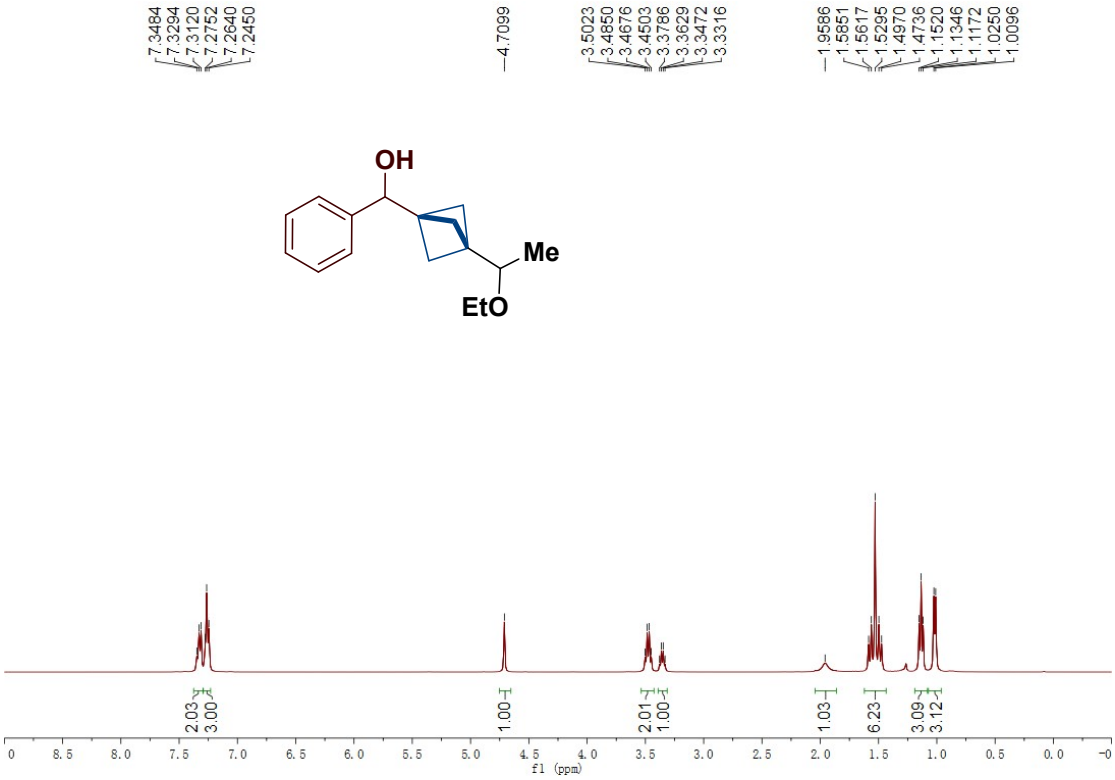
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **75**



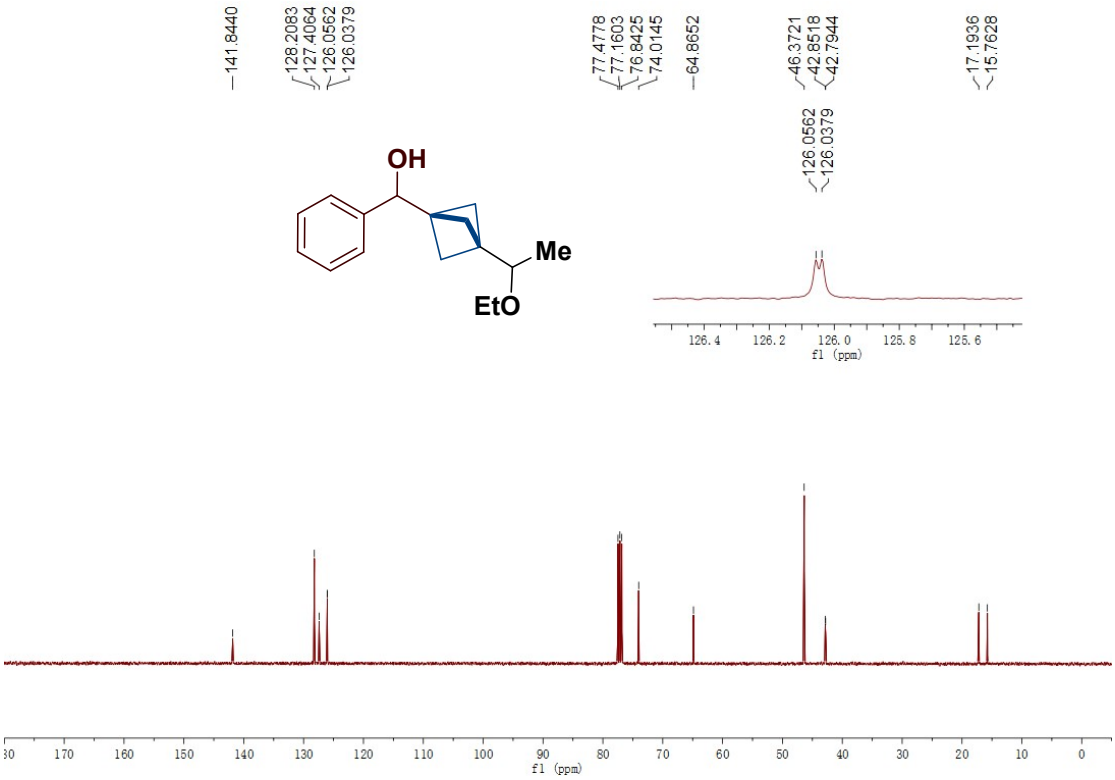
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



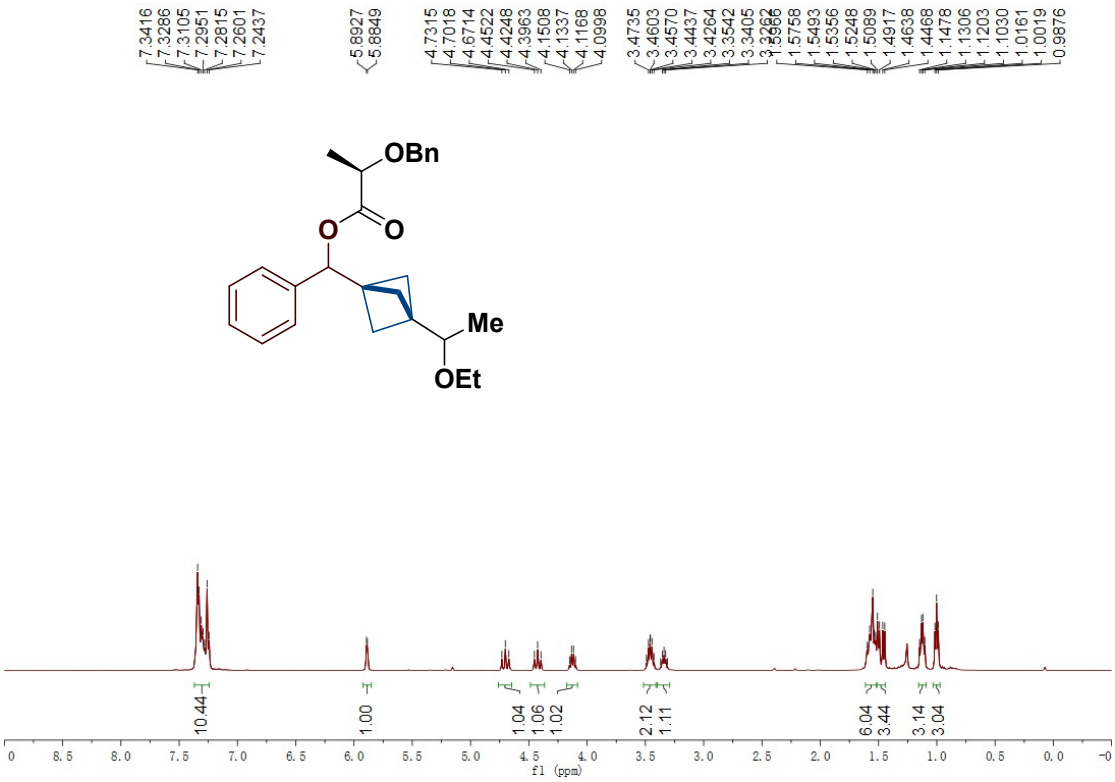
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**



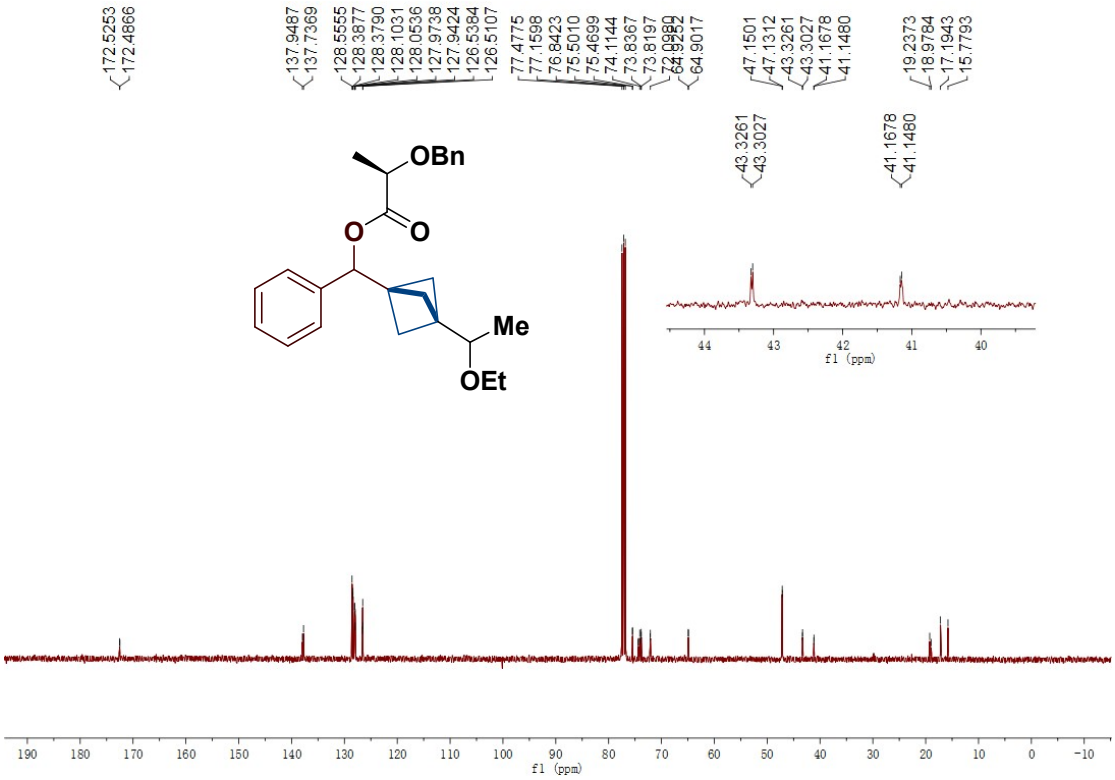
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



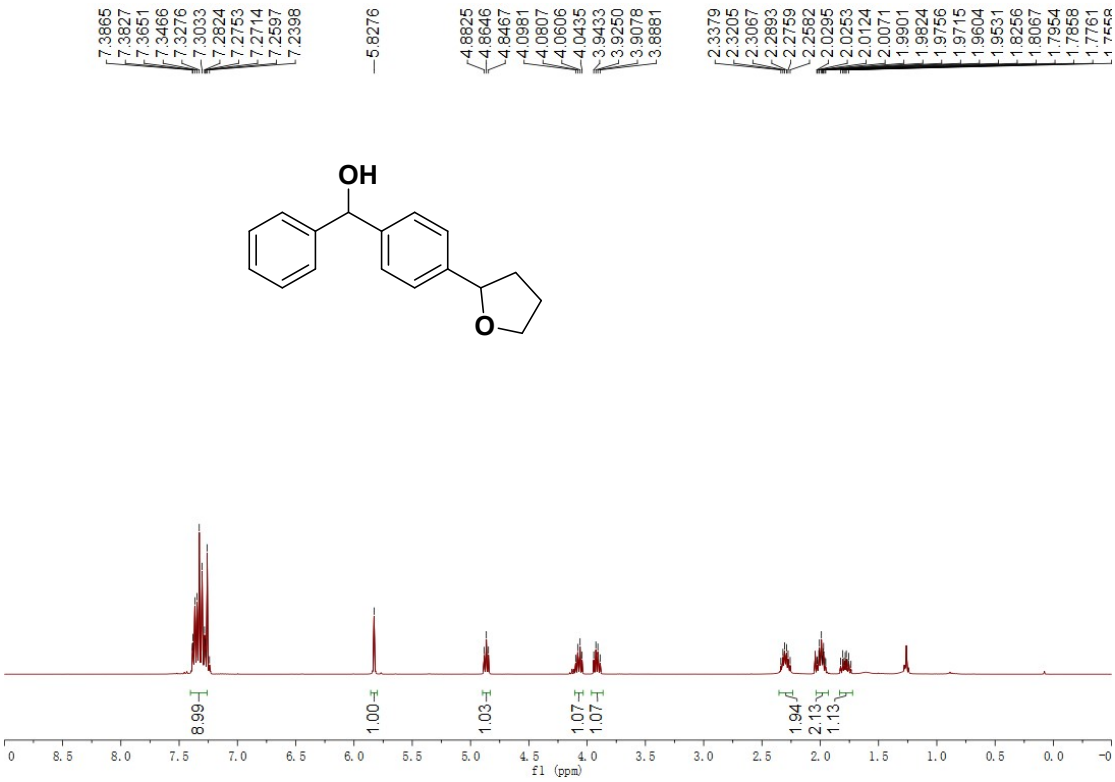
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**



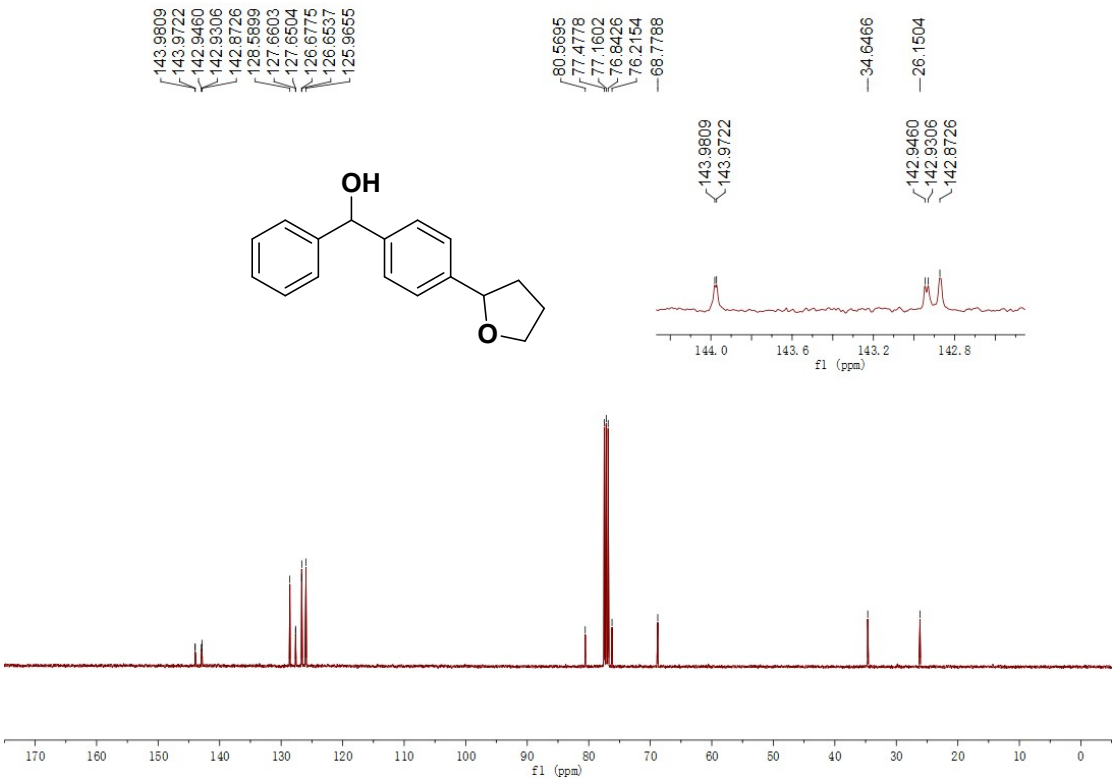
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**