

Supporting Information

BF₃/HY as a microporous solid acid catalyst for the regioselective ring-opening of epoxides

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1. General Information

Unless otherwise noted, all manipulations were performed under nitrogen atmosphere, all chemicals were purchased and used as received without any further pretreatments. All reagents were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. and Shanghai Macklin Biochemical Co. Ltd.. HY molecular sieve was supplied by Nanjing Guochang Chemical Technology Co. Ltd.. Gas chromatography (GC) was performed on an Agilent 7820 A instrument equipped with a HP-5 capillary column (30 m×0.25 mm×0.25 μm). GC-Mass spectrometry (GC-MS) was recorded on an Agilent 7890 instrument equipped with an Agilent 5975 mass selective detector. Column chromatography was performed with silica gel (PUKE, type zcx-II, 40-45 μm). The NMR spectra was recorded by a Bruker Avance 400 MHz spectrometer. All chemical shifts in NMR experiments were reported as ppm downfield with Me₄Si (TMS) as internal standard. CDCl₃ δ = 7.26 was used for calibration.

2. Material Characterization

X-ray diffraction (XRD) measurements were performed on X'Pert PRO MPD diffractometer with Cu Kα (λ = 0.1542 nm, 35 kV, 40 mA) radiation, scanning range, 5°-90°, scanning rate, 5°·min⁻¹. X-ray photoelectron spectroscopy (XPS) was studied by Thermo Fisher's ESCALAB 250 X-ray photoelectron spectrometer. The surface area, pore volume and average pore diameter of HY and BF₃/HY were measured by N₂ adsorption using TriStar II automatic adsorption instrument. The morphology of different materials was obtained using Quanta 200 cold field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with a JEM-2100 universal microscope. The acid properties of the solid acid catalyst and molecular sieve were determined by Nicolet-6700 FT-IR spectrometer, pyridine was adsorbed and then desorbed at 150 °C and 350 °C, respectively. FT-IR measurements were carried out on Bruke FT-IR spectrometer. And a Netzsch TG 209 F3 thermal gravimetric analyzer was used to analyze the thermal stability.

3. Additional analysis

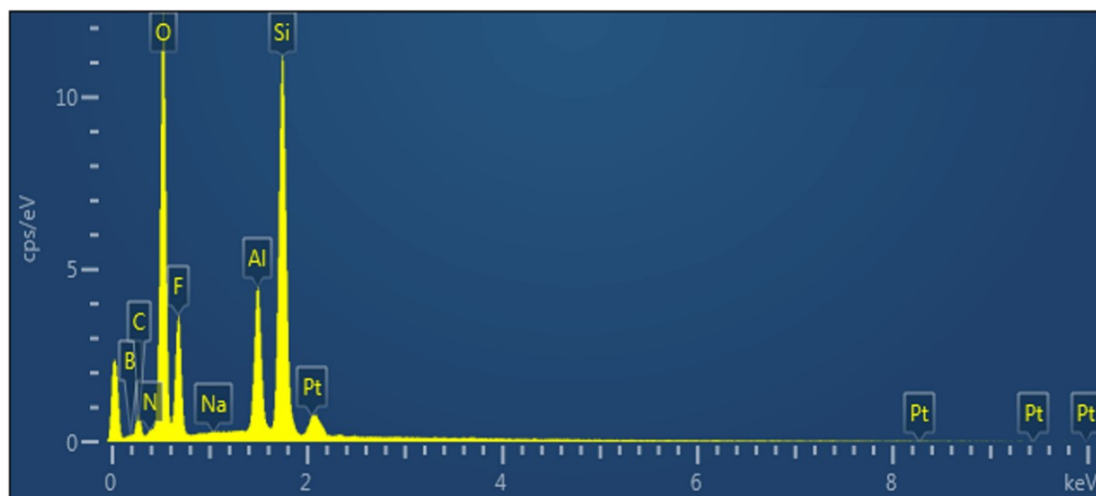


Fig. S1. EDS analysis of BF_3/HY

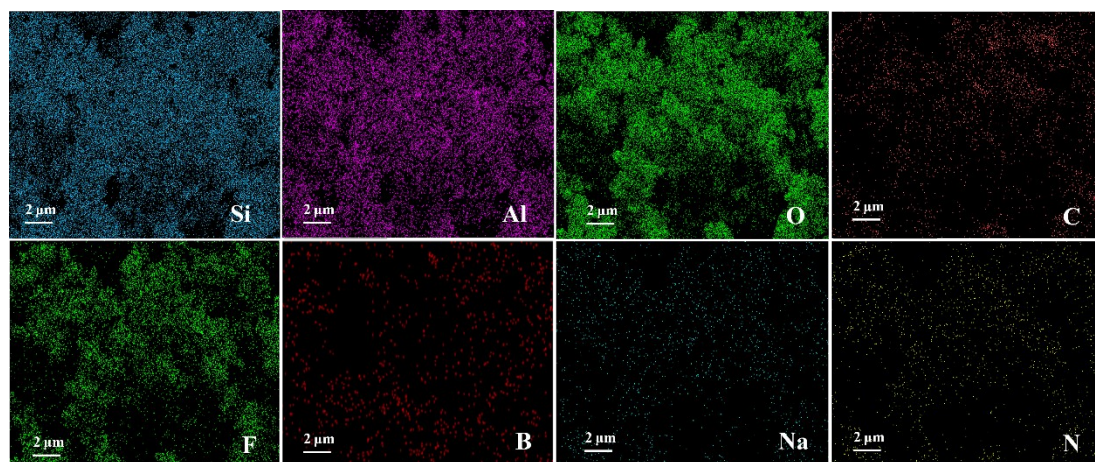


Fig. S2. The EDS mapping images of BF_3/HY

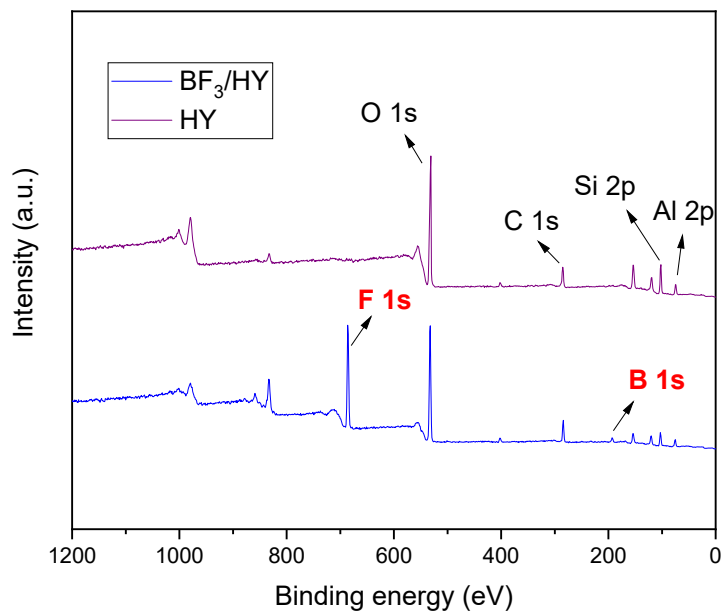


Fig. S3. XPS spectra of HY and BF₃/HY

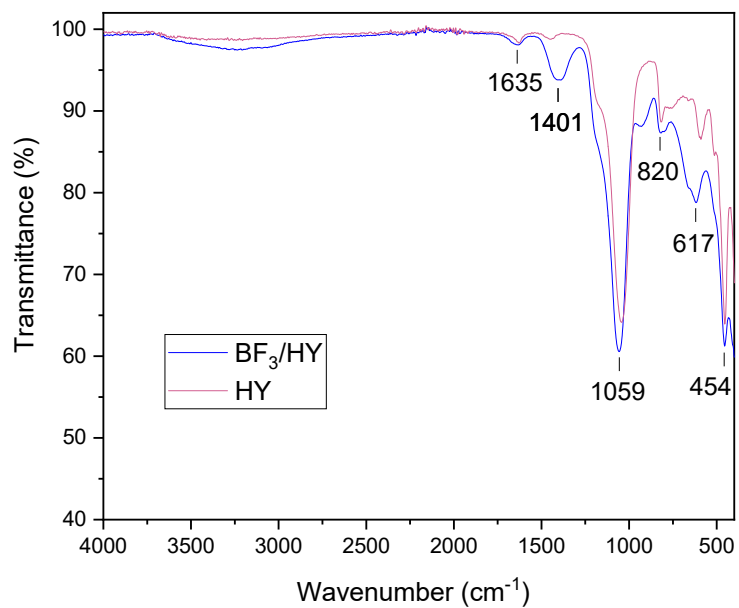


Fig. S4. FT-IR spectra of HY and BF₃/HY

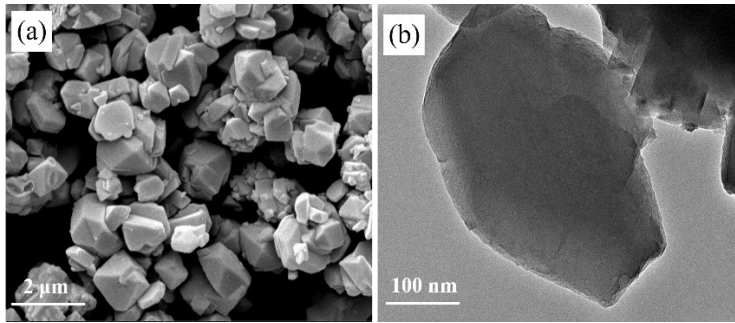


Fig. S5. SEM (a) and TEM (b) images of BF₃/HY after 6 runs

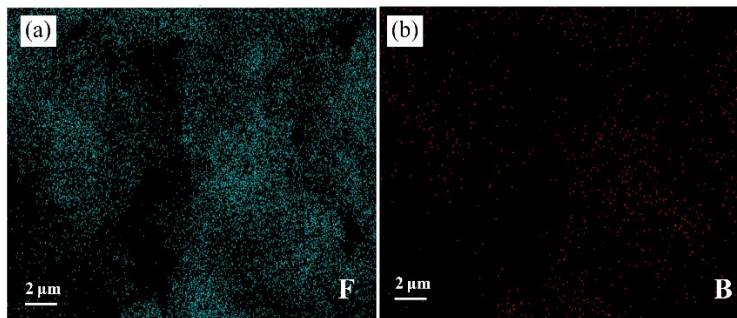


Fig. S6. The EDS mapping images of B and F on BF₃/HY after 6 runs

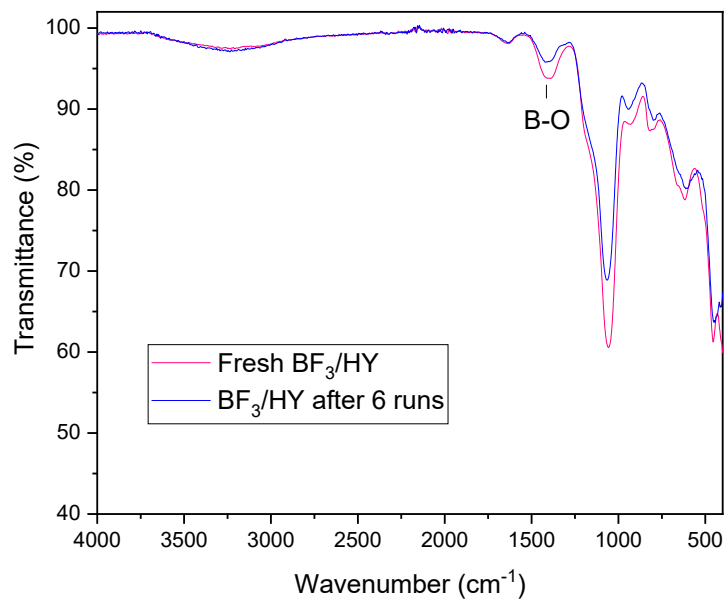
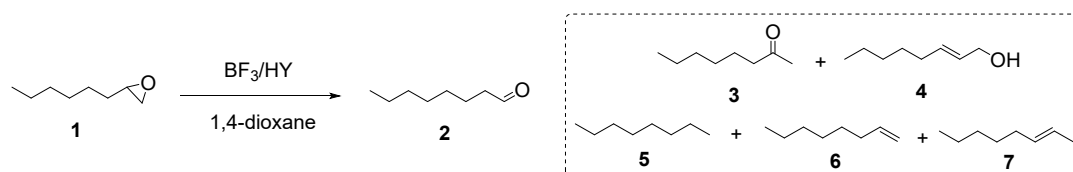


Fig. S7. FT-IR spectra of fresh BF₃/HY and BF₃/HY after 6 runs

4. Additional Tables

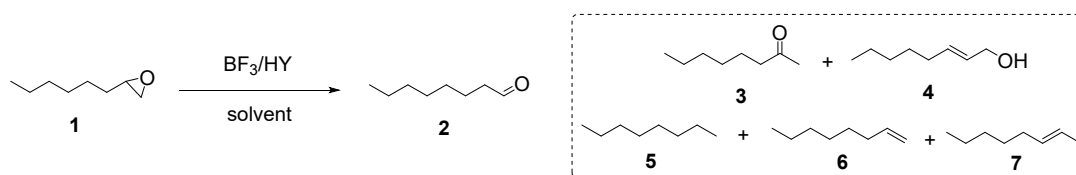
Table S1 Catalytic effects of BF₃/HY impregnated with different solvents ^a



Entry	Impregnating Solvent	Conv. ^b (%)	Yield ^b (%)	
			2	3
1	Ethanol	52	50	2
2	Acetone	61	57	1
3	Water	36	34	3
4	Benzene	70	68	<1

[a] 1,2-epoxyoctane 0.5 mmol, cat. 1 wt.%, 1, 4-dioxane 10 mL, N₂ 0.5 MPa, 80 °C, 12 h. [b] Determined by GC and GC-MS with n-dodecane as an internal standard.

Table S2 BF₃/HY catalyzed ring-opening of epoxides with different solvent amounts ^a

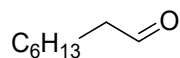


Entry	Solvent (mL)	Conv. ^b (%)	Yield ^b (%)	
			2	3
1	4	52	26	3
2	6	59	42	2
3	8	71	69	<1
4	10	89	87	<1
5	12	89	88	<1

[a] 1,2-epoxyoctane 0.5 mmol, BF₃/HY 1 wt.%, solvent 1, 4-dioxane, N₂ 0.5 MPa, 90 °C, 12 h. [b] Determined by GC and GC-MS with n-dodecane as an internal standard.

5. Analytical Data

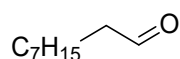
The NMR data of the separated products were consistent with the reported results.¹⁻³



Colorless oil, 62.8 mg, 98%

¹H NMR (400 MHz, CDCl₃): δ = 9.74 (q, J = 2.3 Hz, 1 H), 2.40 (tt, J = 7.4, 2.5 Hz, 2 H), 1.60 (pd, J = 7.3, 2.9 Hz, 2 H), 1.35-1.18 (m, 8 H), 0.86 (td, J = 6.8, 2.8 Hz, 3 H).

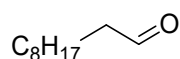
¹³C NMR (101 MHz, CDCl₃): δ = 203.0, 43.9, 31.6, 29.1, 29.0, 22.6, 22.1, 14.0.



Colorless oil, 67.5 mg, 95%

¹H NMR (400 MHz, CDCl₃): δ = 9.76 (t, J = 1.8 Hz, 1 H), 2.42 (td, J = 7.4, 1.9 Hz, 2 H), 1.62 (p, J = 7.2 Hz, 2 H), 1.39-1.15 (m, 10 H), 0.95-0.80 (m, 3 H).

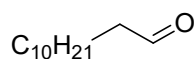
¹³C NMR (101 MHz, CDCl₃): δ = 203.0, 43.9, 31.79, 3.32, 29.2, 29.1, 22.6, 22.1, 14.1.



Colorless oil, 71.8 mg, 92%

¹H NMR (400 MHz, CDCl₃): δ = 9.74 (d, J = 2.0 Hz, 1 H), 2.40 (td, J = 7.4, 1.9 Hz, 2 H), 1.60 (p, J = 7.2 Hz, 2 H), 1.26 (d, J = 12.7 Hz, 12 H), 0.85 (t, J = 6.7 Hz, 3 H).

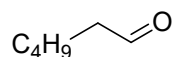
¹³C NMR (101 MHz, CDCl₃): δ = 203.0, 43.9, 31.9, 29.4, 29.4, 29.2, 29.2, 22.7, 22.1, 14.1.



Colorless oil, 84.7 mg, 92%

¹H NMR (400 MHz, CDCl₃): δ = 9.74 (s, 1 H), 2.39 (td, J = 7.4, 1.8 Hz, 2 H), 1.60 (p, J = 7.2 Hz, 2 H), 1.26 (d, J = 15.5 Hz, 16 H), 0.86 (t, J = 6.7 Hz, 3 H).

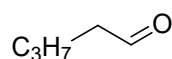
¹³C NMR (101 MHz, CDCl₃): δ = 201.9, 42.9, 30.9, 28.6, 28.4, 28.3, 28.3, 28.1, 21.7, 21.1, 13.1, 13.1.



Colorless oil, 48.0 mg, 96%

¹H NMR (400 MHz, CDCl₃): δ = 9.74 (t, J = 1.8 Hz, 1 H), 2.40 (td, J = 7.4, 1.9 Hz, 2 H), 1.68-1.54 (m, 2 H), 1.29 (tq, J = 6.4, 3.7, 2.9 Hz, 4 H), 0.91-0.82 (m, 3 H).

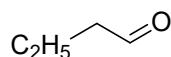
¹³C NMR (101 MHz, CDCl₃): δ = 203.0, 43.8, 31.3, 22.4, 21.7, 13.8.



Colorless oil, 38.7 mg, 90%

¹H NMR (400 MHz, CDCl₃): δ = 9.74 (q, J = 2.1 Hz, 1 H), 2.41 (tt, J = 7.5, 2.0 Hz, 2 H), 1.65-1.53 (m, 2 H), 1.34 (hd, J = 7.4, 2.0 Hz, 2 H), 0.90 (td, J = 7.4, 2.0 Hz, 3 H).

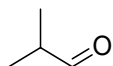
¹³C NMR (101 MHz, CDCl₃): δ = 202.9, 43.6, 24.1, 22.3, 13.8.



Colorless oil, 29.9 mg, 83%

¹H NMR (400 MHz, CDCl₃): δ = 9.72 (q, J = 1.7 Hz, 1 H), 2.37 (td, J = 7.3, 1.7 Hz, 2 H), 1.62 (hd, J = 7.3, 1.3 Hz, 2 H), 0.92 (td, J = 7.4, 1.2 Hz, 3 H).

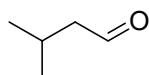
¹³C NMR (101 MHz, CDCl₃): δ = 202.9, 45.7, 15.6, 13.7.



Colorless oil, 25.2 mg, 70%

¹H NMR (400 MHz, CDCl₃): δ = 9.63 (d, J = 1.3 Hz, 1 H), 2.42 (pd, J = 7.1, 1.1 Hz, 1 H), 1.11 (d, J = 7.1 Hz, 6 H).

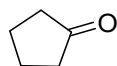
¹³C NMR (101 MHz, CDCl₃): δ = 205.2, 41.0, 15.4.



Colorless oil, 12.5 mg, 29%

¹H NMR (400 MHz, CDCl₃): δ = 9.71 (p, J = 2.0 Hz, 1 H), 2.26 (dt, J = 6.8, 1.9 Hz, 2 H), 2.22-2.11 (m, 1 H), 0.94 (dt, J = 6.7, 1.7 Hz, 6 H).

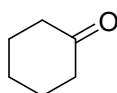
¹³C NMR (101 MHz, CDCl₃): δ = 203.0, 52.6, 23.5, 22.6.



Colorless oil, 12.2 mg, 29%

¹H NMR (400 MHz, CDCl₃): δ = 2.12-1.99 (m, 4 H), 1.86 (dp, J = 7.0, 3.5 Hz, 4 H).

¹³C NMR (101 MHz, CDCl₃): δ = 220.7, 38.4, 23.2.



Colorless oil, 13.7 mg, 28%

¹H NMR (400 MHz, CDCl₃): δ = 2.27 (t, J = 6.7 Hz, 4 H), 1.80 (p, J = 6.3 Hz, 4 H), 1.65 (p, J = 6.0, 5.5 Hz, 2 H).

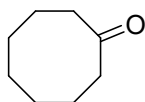
¹³C NMR (101 MHz, CDCl₃): δ = 212.3, 42.0, 27.0, 25.0.



Colorless oil, 11.2 mg, 20%

¹H NMR (400 MHz, CDCl₃): δ = 2.44-2.21 (m, 3 H), 2.06 (tq, J = 10.0, 6.0, 4.6 Hz, 2 H), 1.88-1.77 (m, 1 H), 1.66 (tq, J = 12.0, 6.7, 4.2 Hz, 2 H), 1.36 (qd, J = 12.3, 3.9 Hz, 1 H), 1.01 (dd, J = 6.5, 1.7 Hz, 3 H).

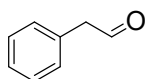
¹³C NMR (101 MHz, CDCl₃): δ = 213.6, 45.4, 41.8, 36.2, 28.0, 25.28, 14.7.



White solid, 10.7 mg, 17%

¹H NMR (400 MHz, CDCl₃): δ = 2.43-2.35 (m, 4 H), 1.92-1.80 (m, 4 H), 1.59-1.48 (m, 4 H), 1.41-1.30 (m, 2 H).

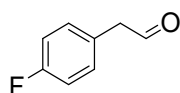
¹³C NMR (101 MHz, CDCl₃): δ = 218.4, 42.0, 27.2, 25.7, 24.7.



Slight-yellow oil, 59.4 mg, 99%

¹H NMR (400 MHz, CDCl₃): δ = 9.78 (t, *J* = 2.4 Hz, 1 H), 7.46-7.30 (m, 3 H), 7.29-7.19 (m, 2 H), 3.72 (d, *J* = 2.4 Hz, 2 H).

¹³C NMR (101 MHz, CDCl₃): δ = 199.5, 131.9, 129.6, 129.0, 127.4, 50.6.

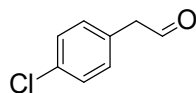


Slight-yellow oil, 57.9 mg, 84%

¹H NMR (400 MHz, CDCl₃): δ = 9.82 (t, *J* = 2.1 Hz, 1 H), 7.35-7.21 (m, 2 H), 7.14 (t, *J* = 8.6 Hz, 2 H), 3.76 (d, *J* = 2.1 Hz, 2 H).

¹³C NMR (101 MHz, CDCl₃): δ = 199.0, 162.2 (d, *J* = 246.0 Hz), 131.2, 127.6, 115.9 (d, *J* = 21.5 Hz), 49.6.

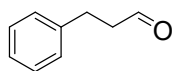
¹⁹F NMR (376 MHz, CDCl₃): δ = -115.14 (tt, *J* = 9.2, 5.2 Hz, 1 F).



White solid, 63.2 mg, 82%

¹H NMR (400 MHz, CDCl₃): δ = 9.74 (t, *J* = 2.1 Hz, 1 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.15 (d, *J* = 8.1 Hz, 2 H), 3.68 (d, *J* = 2.0 Hz, 2 H).

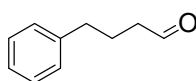
¹³C NMR (101 MHz, CDCl₃): δ = 198.6, 133.5, 130.9, 130.3, 129.1, 49.8.



Yellow oil, 57.0 mg, 85%

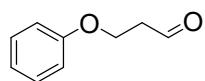
¹H NMR (400 MHz, CDCl₃): δ = 9.87 (t, *J* = 1.4 Hz, 1 H), 7.39-7.30 (m, 2 H), 7.29-7.19 (m, 3 H), 3.01 (t, *J* = 7.5 Hz, 2 H), 2.84 (td, *J* = 7.8, 1.2 Hz, 2 H).

¹³C NMR (101 MHz, CDCl₃): δ = 201.6, 140.3, 128.6, 128.3, 126.3, 45.3, 28.1.



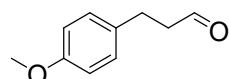
Yellow oil, 59.2 mg, 80%

¹H NMR (400 MHz, CDCl₃): δ = 9.76 (t, *J* = 1.6 Hz, 1 H), 7.34 – 7.27 (m, 2 H), 7.25 – 7.13 (m, 3 H), 2.67 (t, *J* = 7.6 Hz, 2 H), 2.46 (td, *J* = 7.3, 1.6 Hz, 2 H), 1.98 (p, *J* = 7.4 Hz, 2 H).
¹³C NMR (101 MHz, CDCl₃): δ = 202.3, 141.2, 128.5, 126.1, 43.2, 35.0, 23.7.



Colorless oil, 42.8 mg, 57%

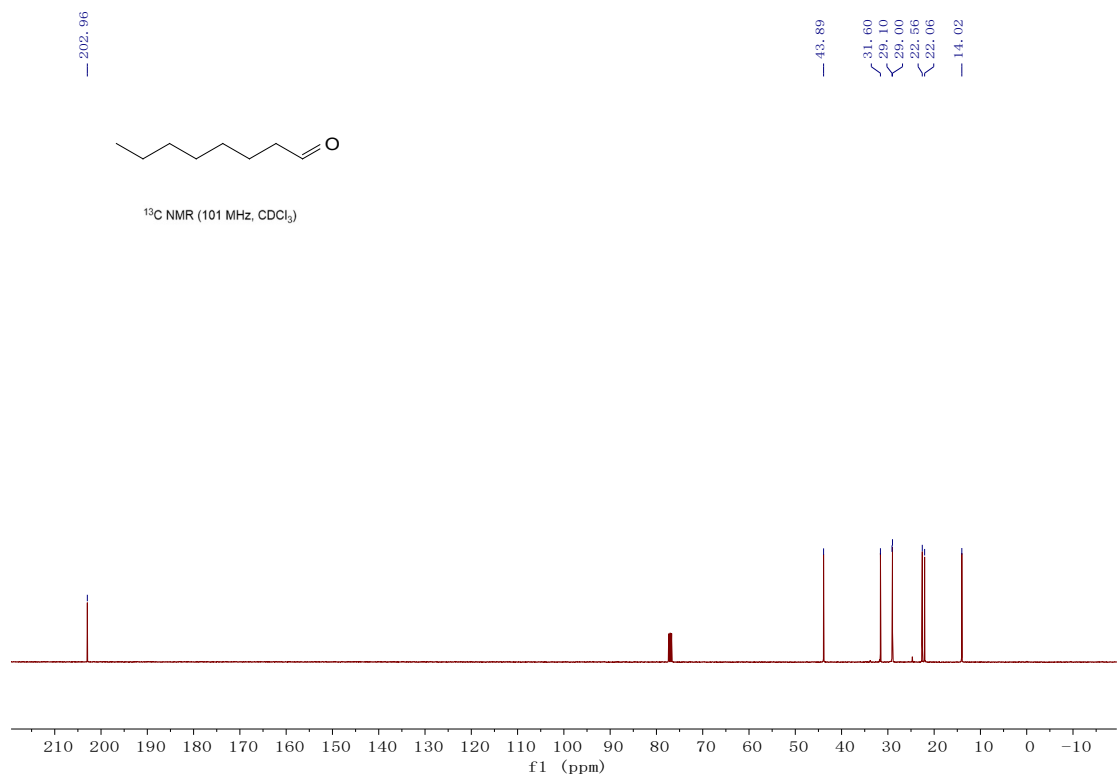
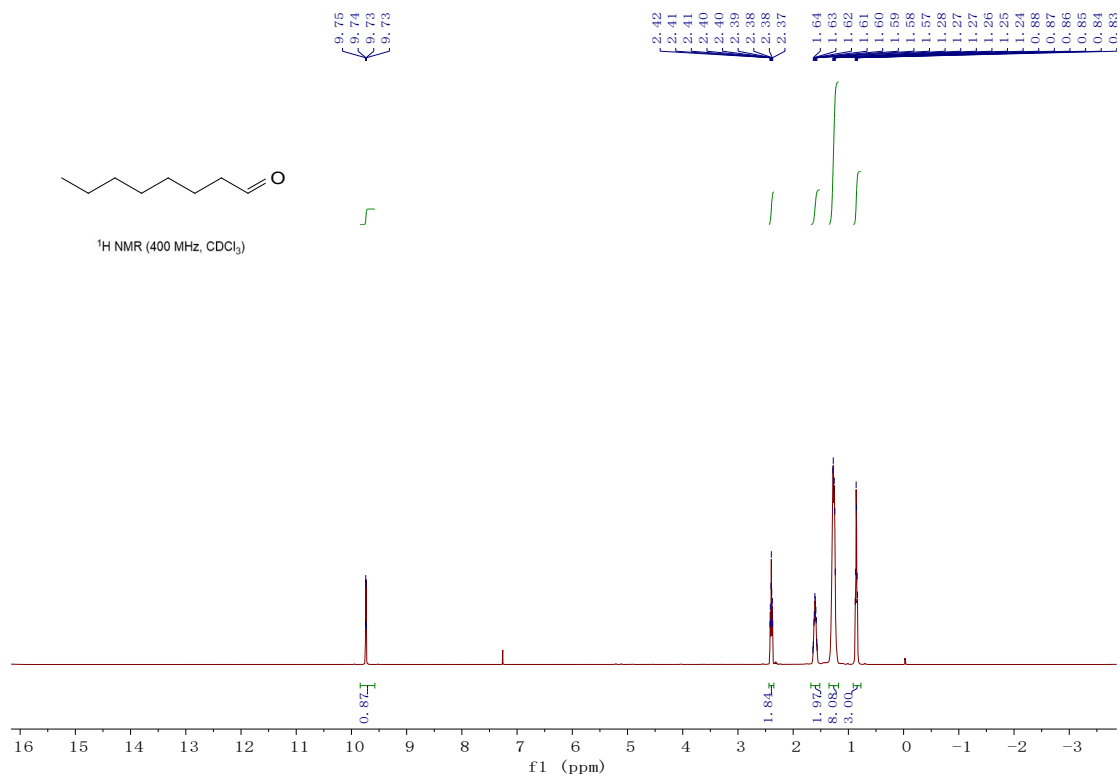
¹H NMR (400 MHz, CDCl₃): δ = 9.87 (t, *J* = 1.6 Hz, 1 H), 7.29 (dt, *J* = 8.7, 7.1 Hz, 2 H), 7.07-6.81 (m, 3 H), 4.32 (t, *J* = 6.1 Hz, 2 H), 2.90 (td, *J* = 6.1, 1.6 Hz, 2 H).
¹³C NMR (101 MHz, CDCl₃): δ = 200.3, 158.4, 129.5, 121.2, 114.6, 61.6, 43.3.

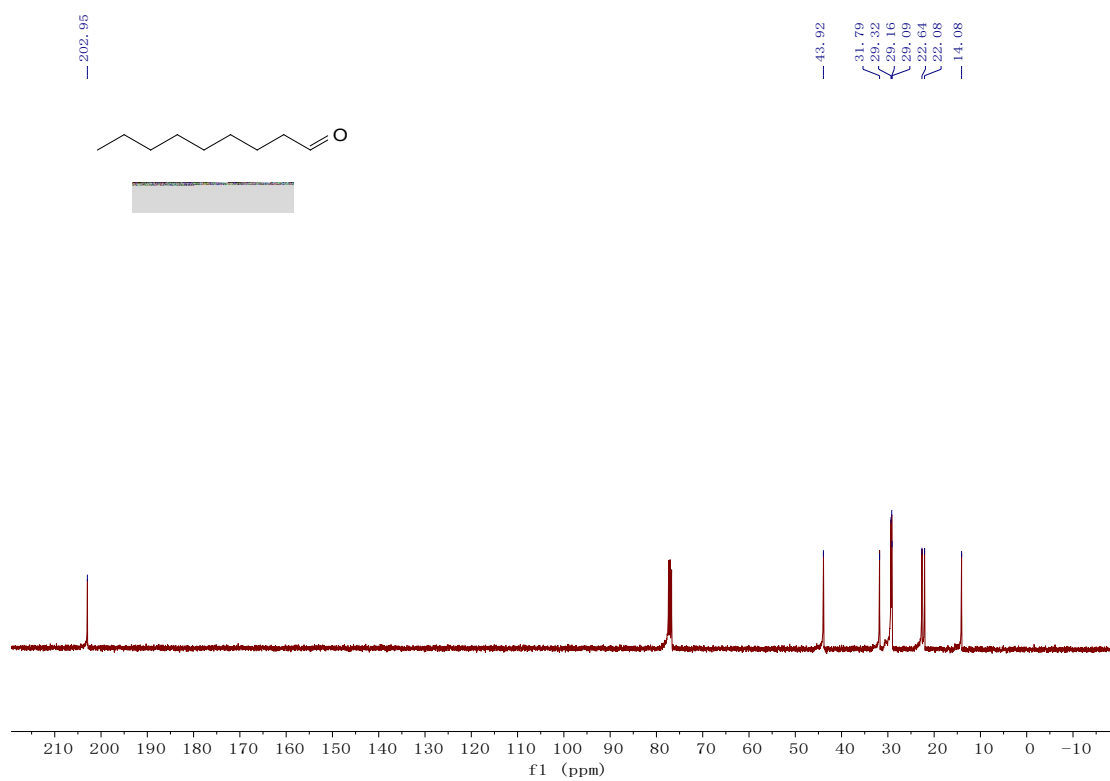
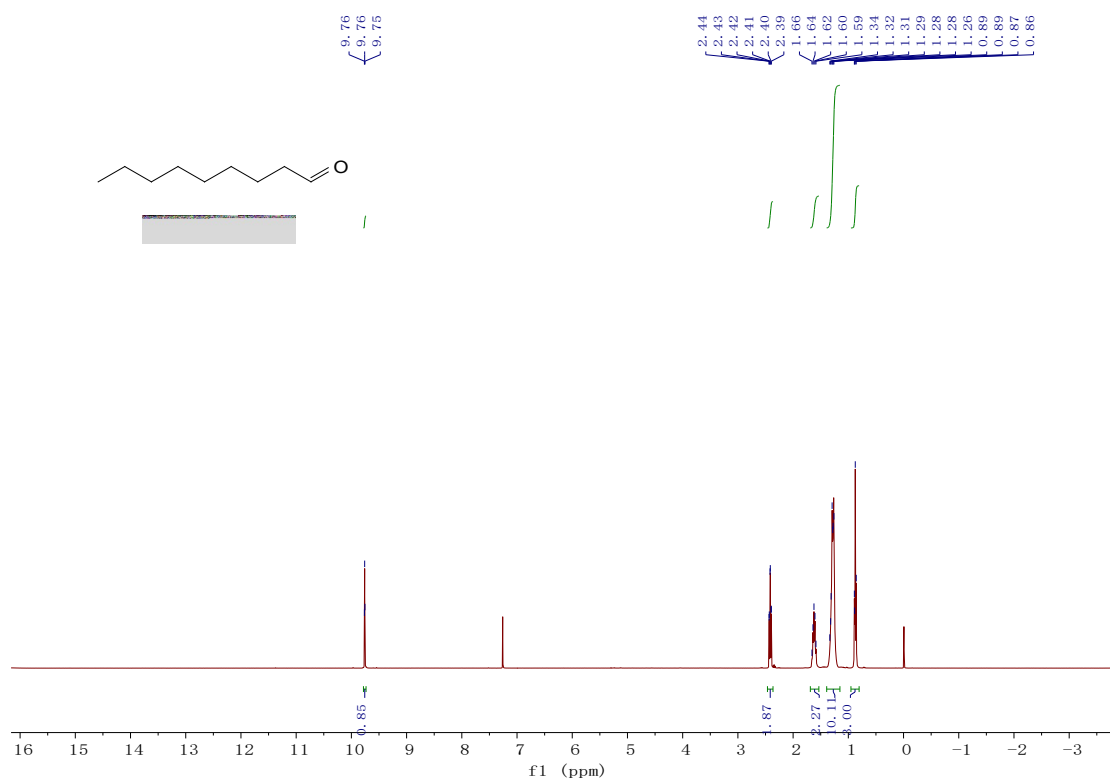


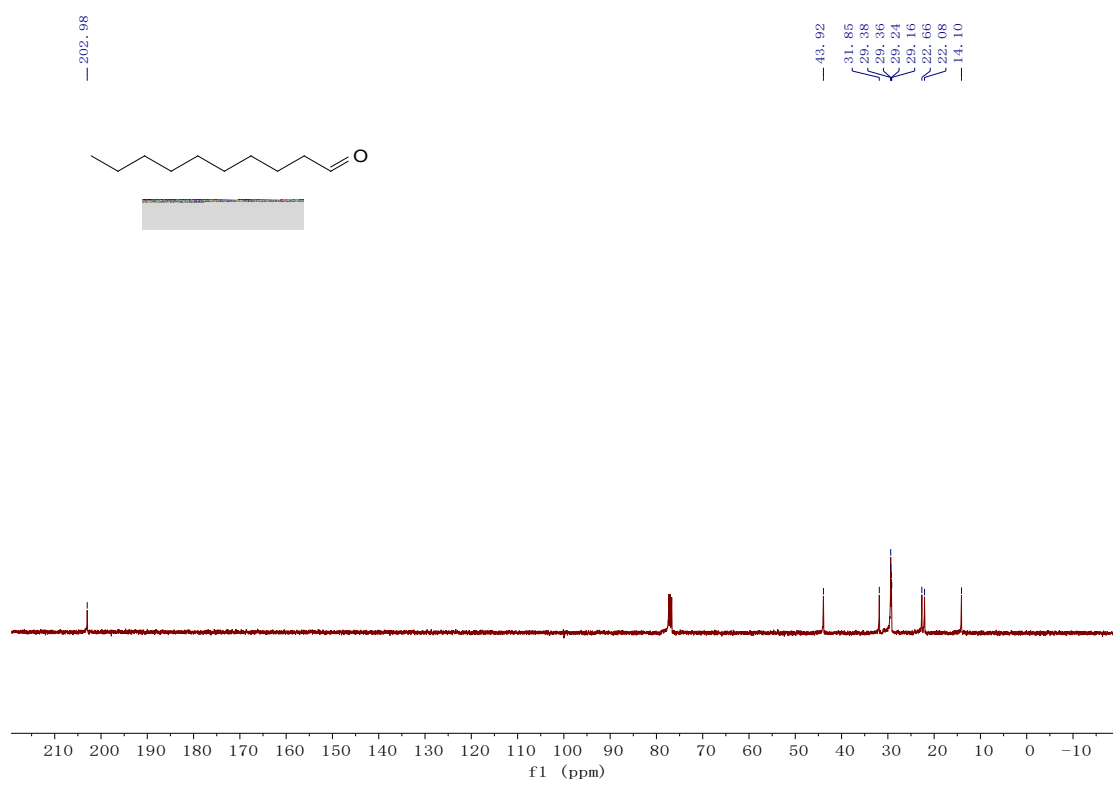
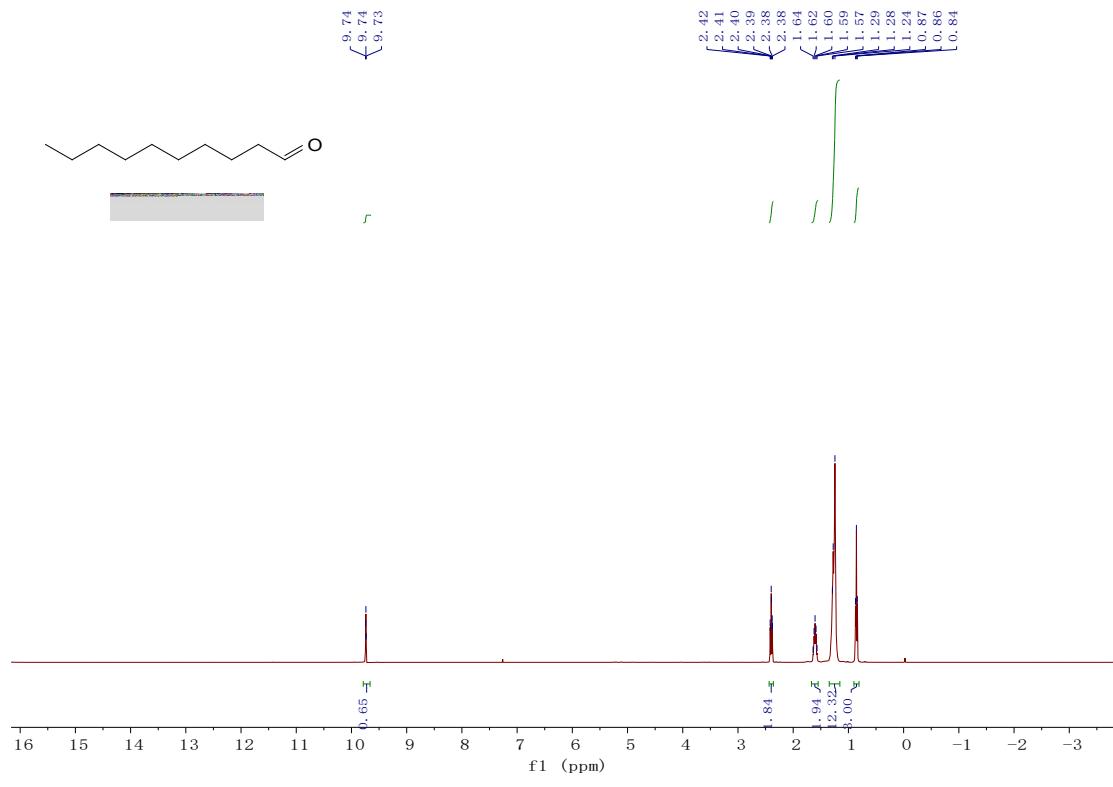
Yellow oil, 48.4 mg, 59%

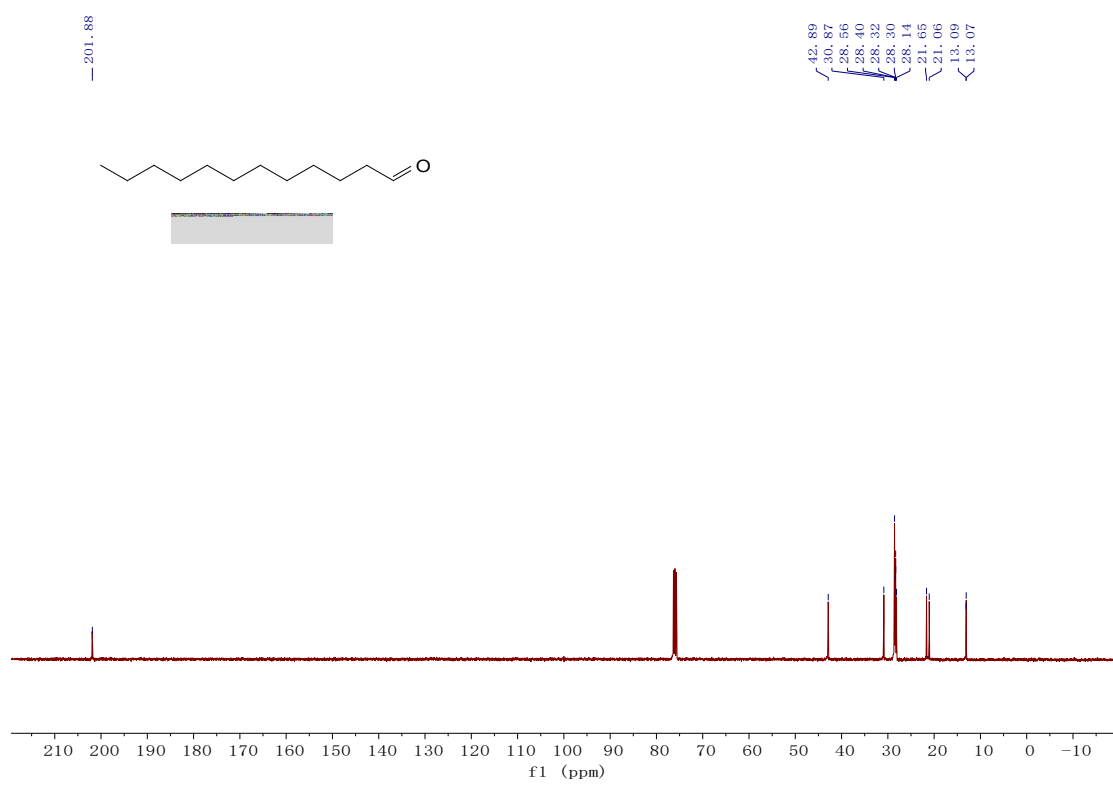
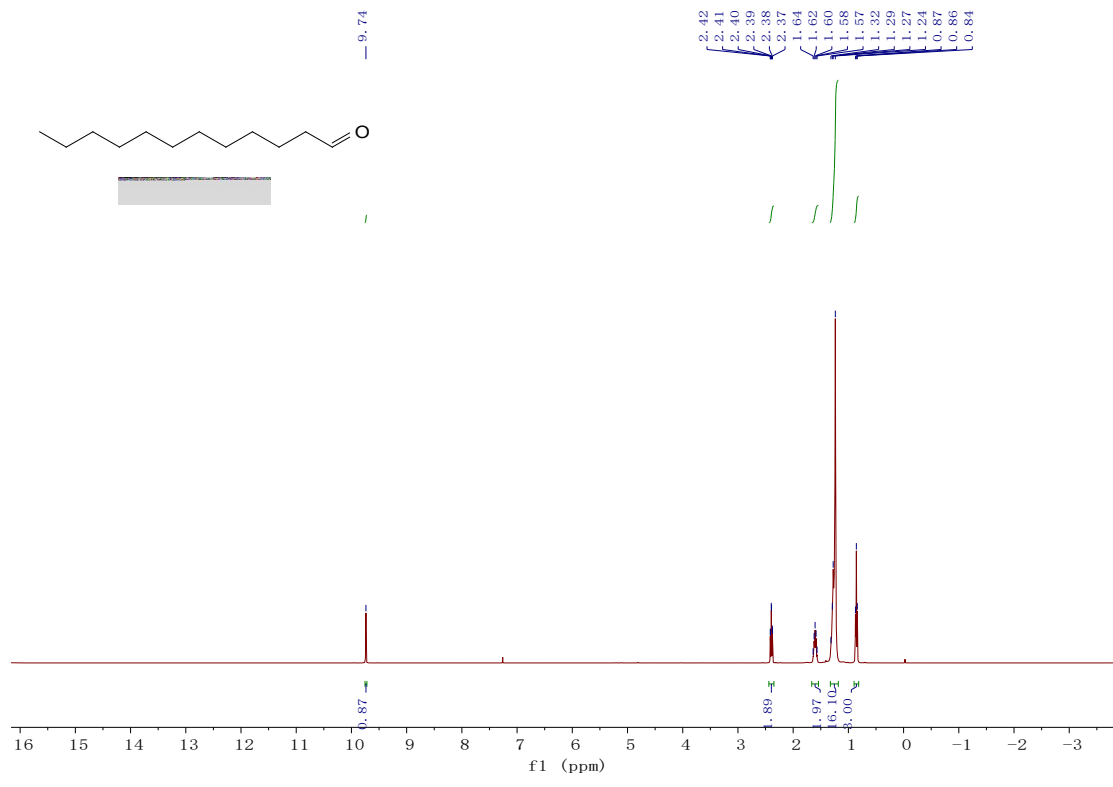
¹H NMR (400 MHz, CDCl₃): δ = 7.12 (d, *J* = 8.2 Hz, 2 H), 6.83 (d, *J* = 8.1 Hz, 2 H), 4.79 (t, *J* = 5.4 Hz, 1 H), 3.79 (s, 3 H), 2.72 (q, *J* = 8.9, 7.9 Hz, 2 H), 2.07-1.91 (m, 2 H).
¹³C NMR (101 MHz, CDCl₃): δ = 157.9, 133.4, 129.3, 113.8, 100.7, 55.3, 35.9, 28.7.

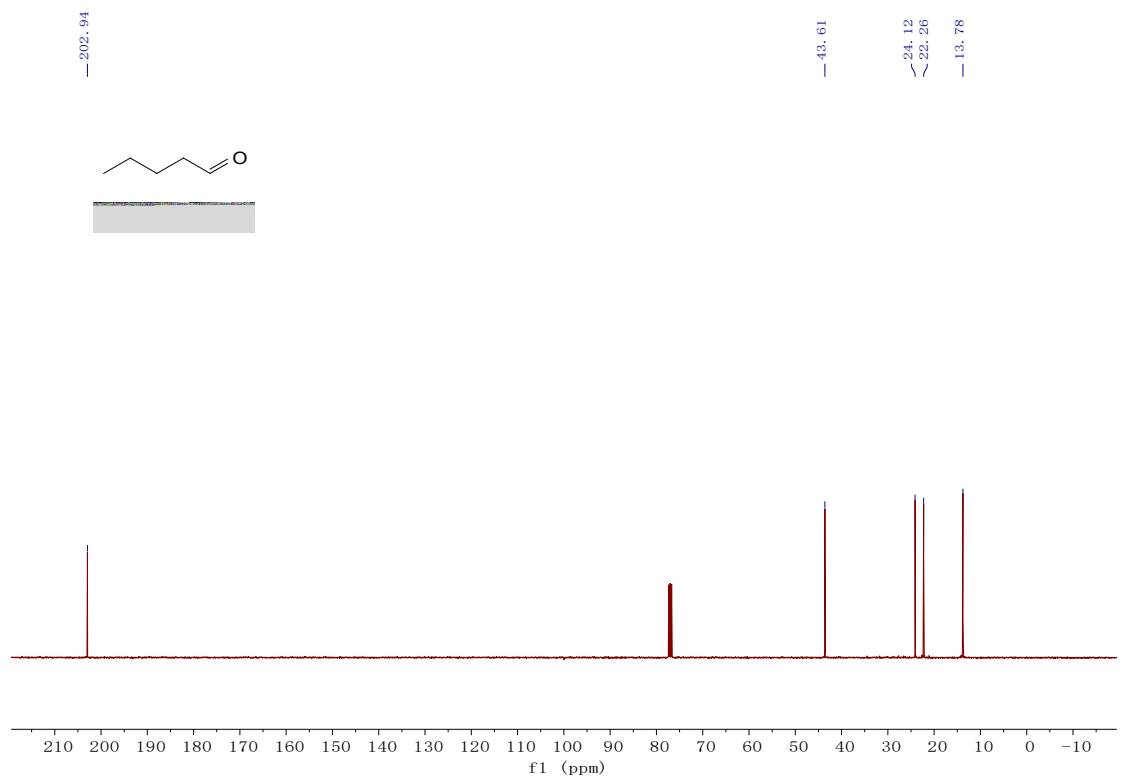
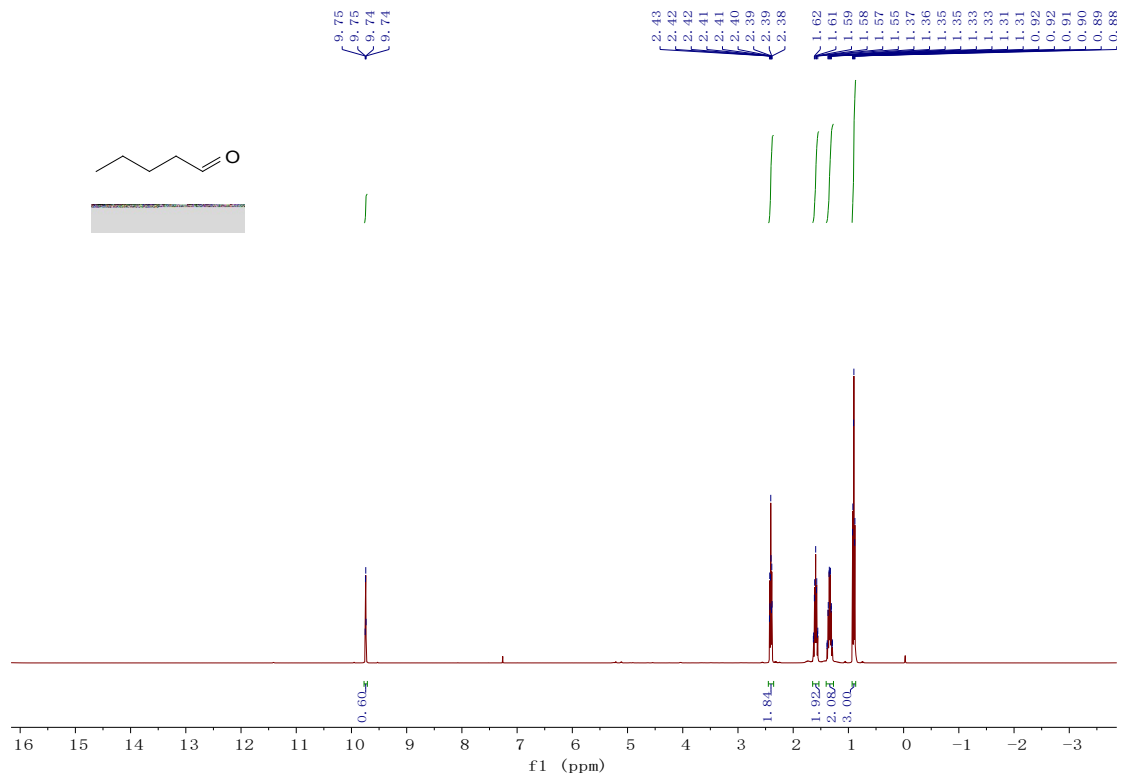
6. NMR Spectra

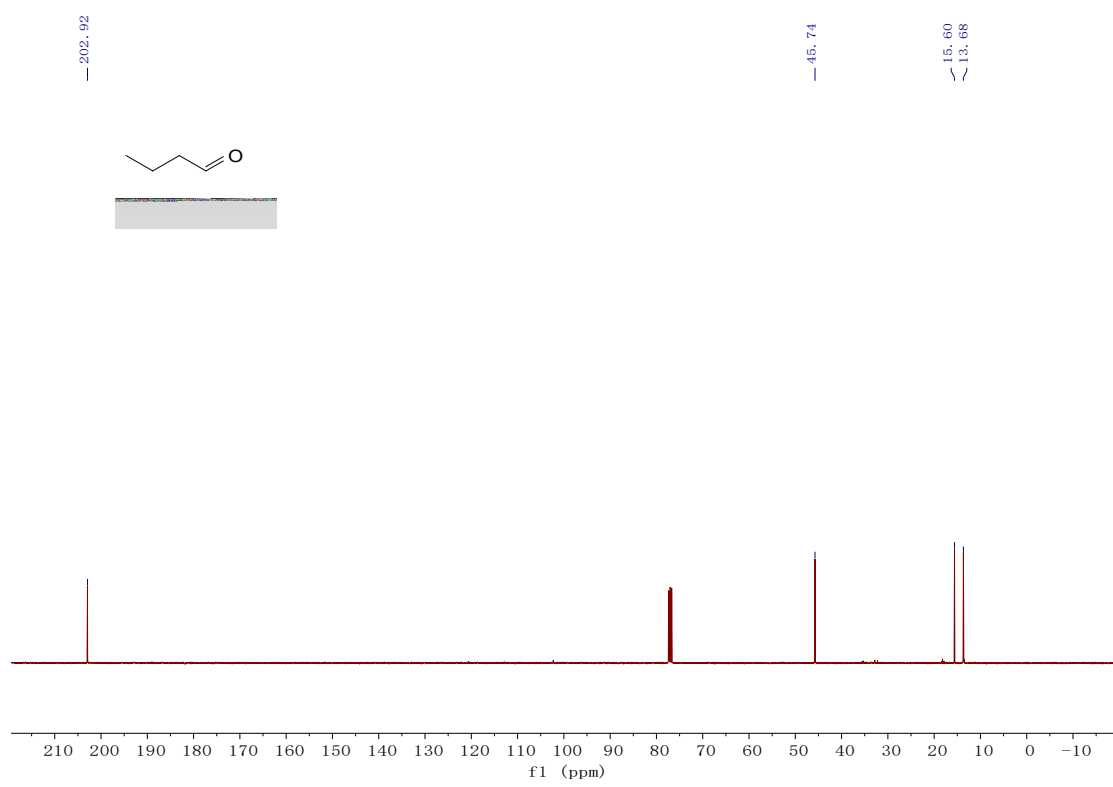
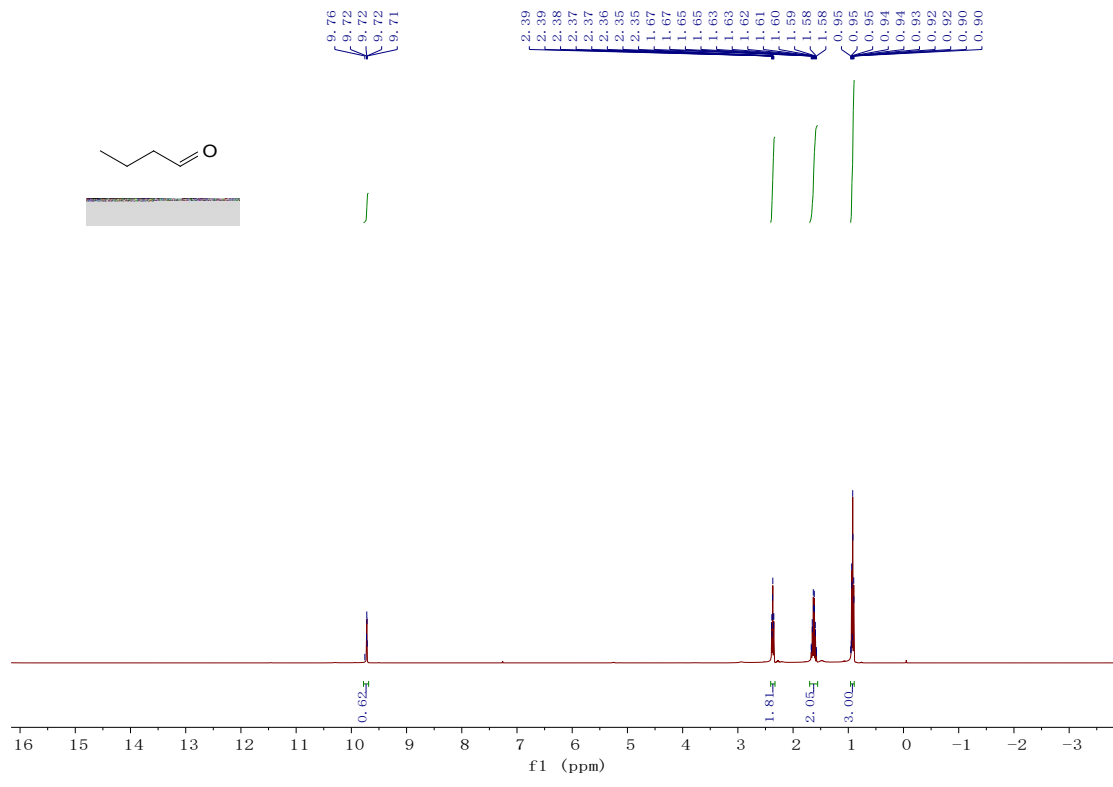


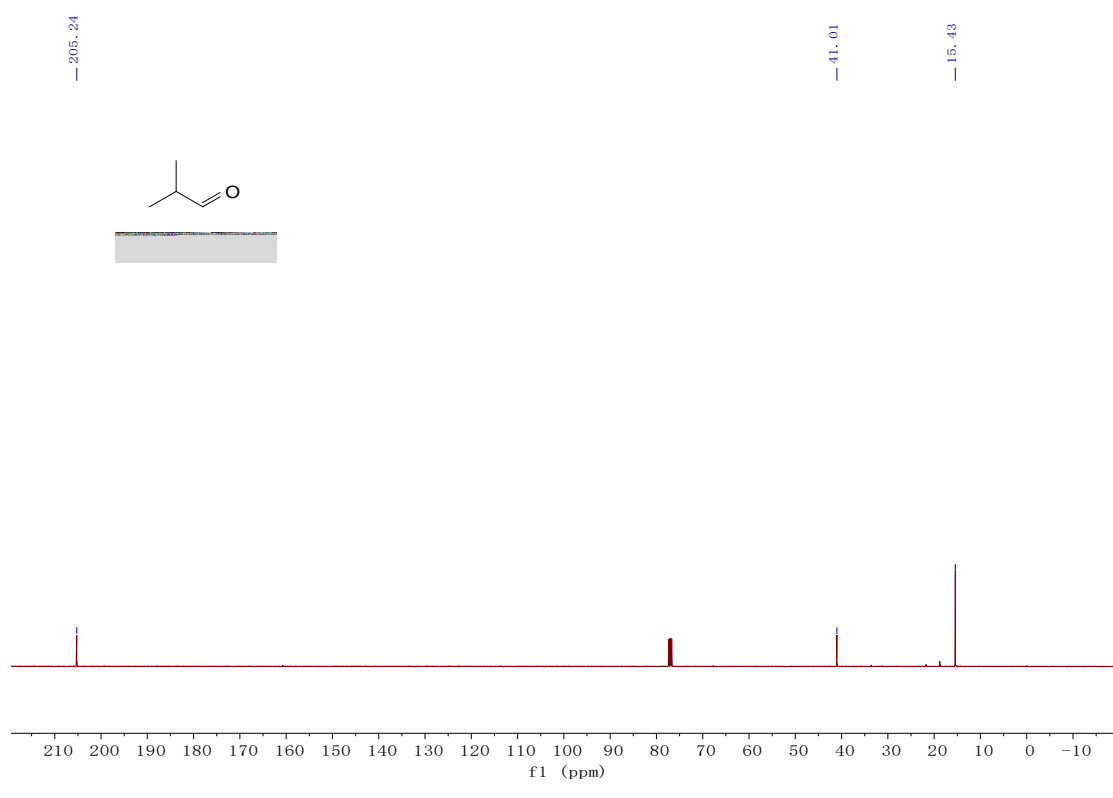
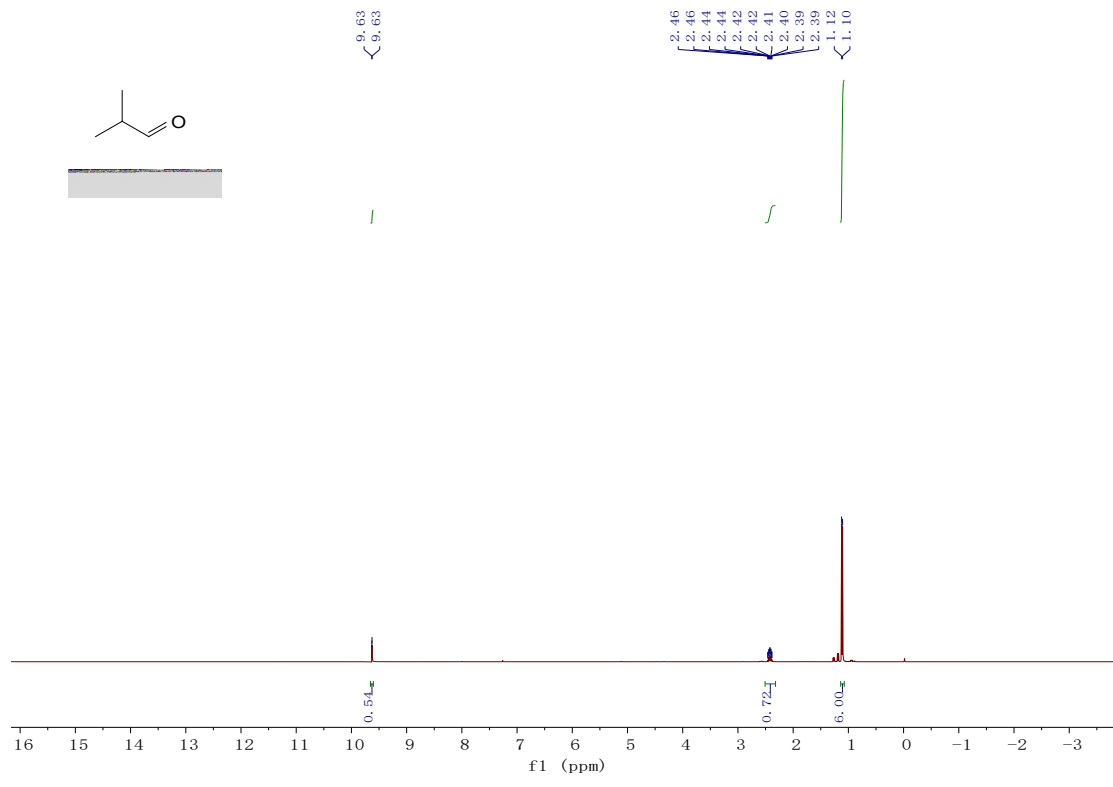


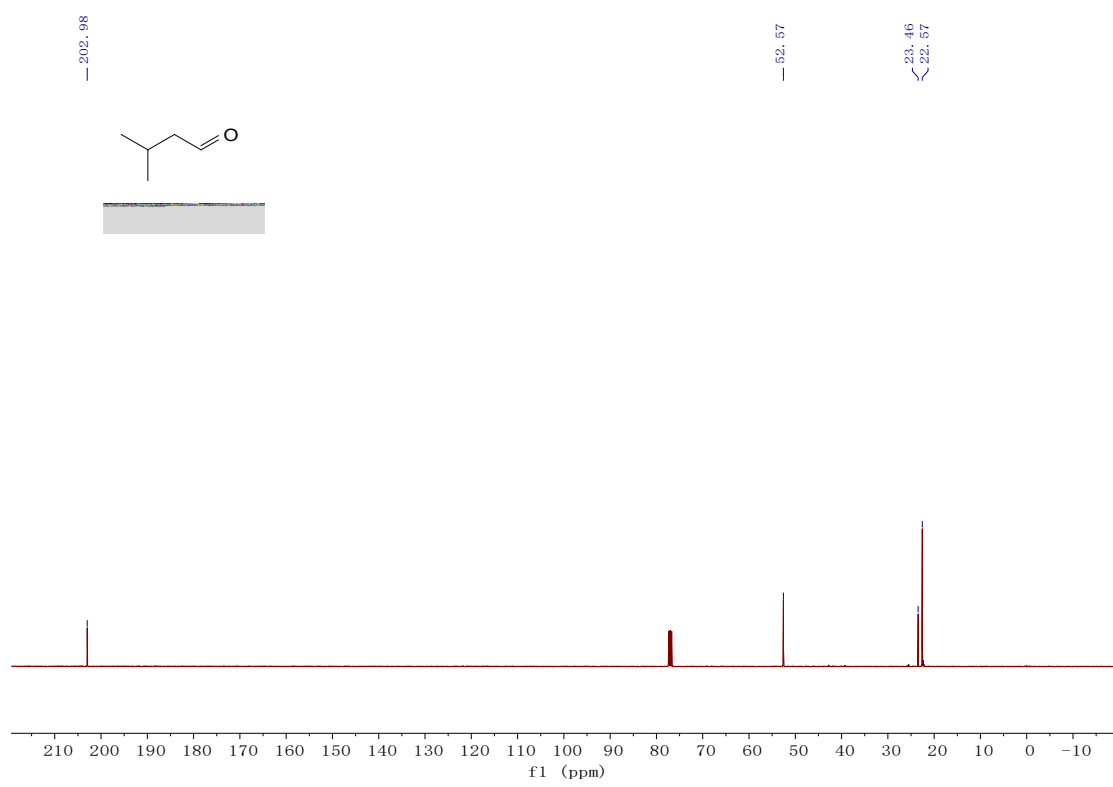
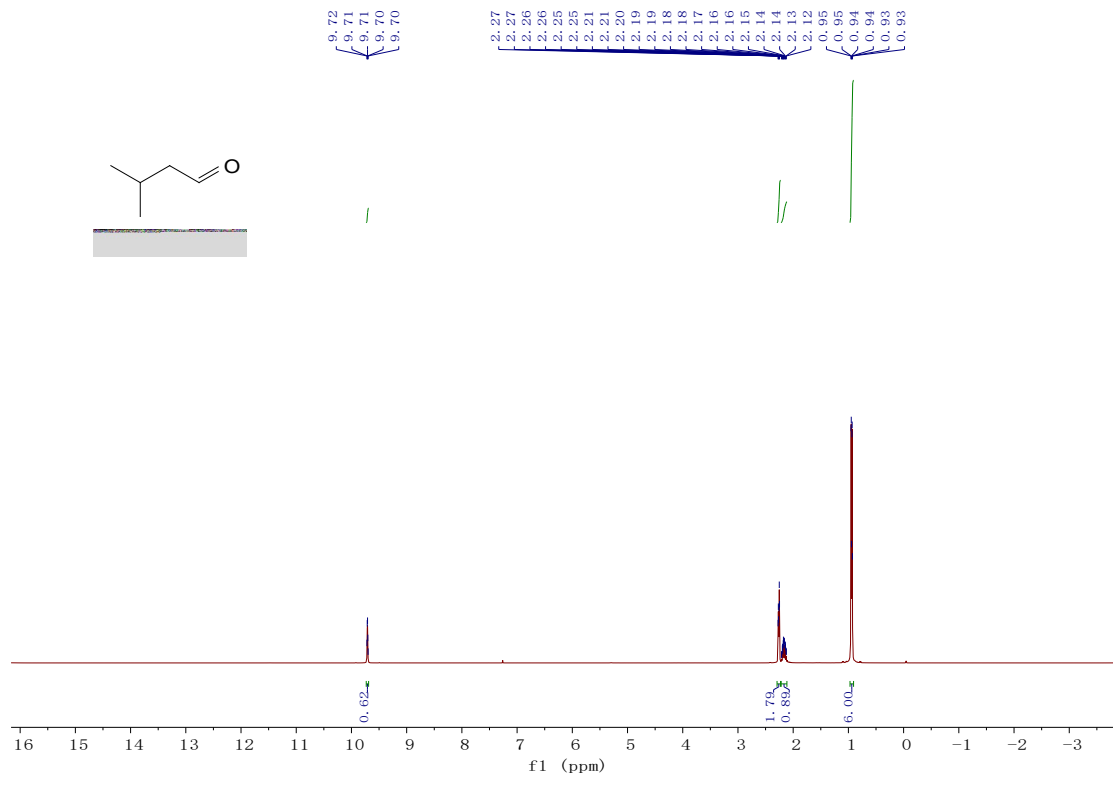


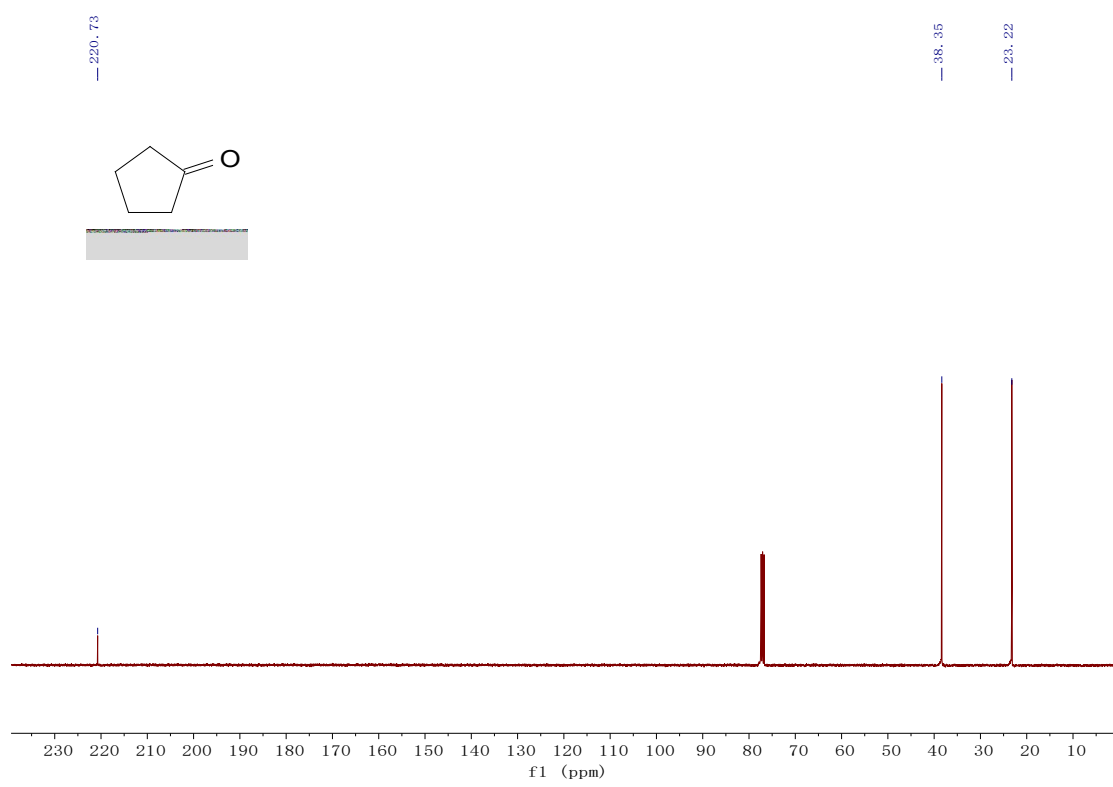
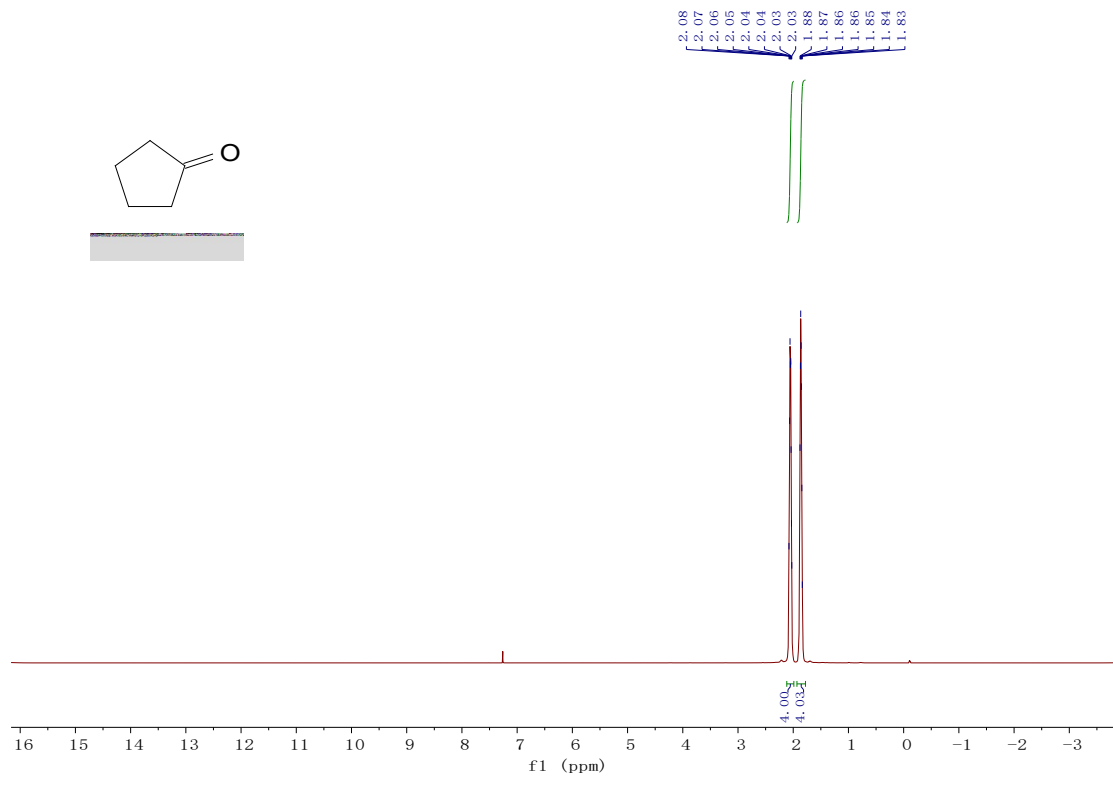


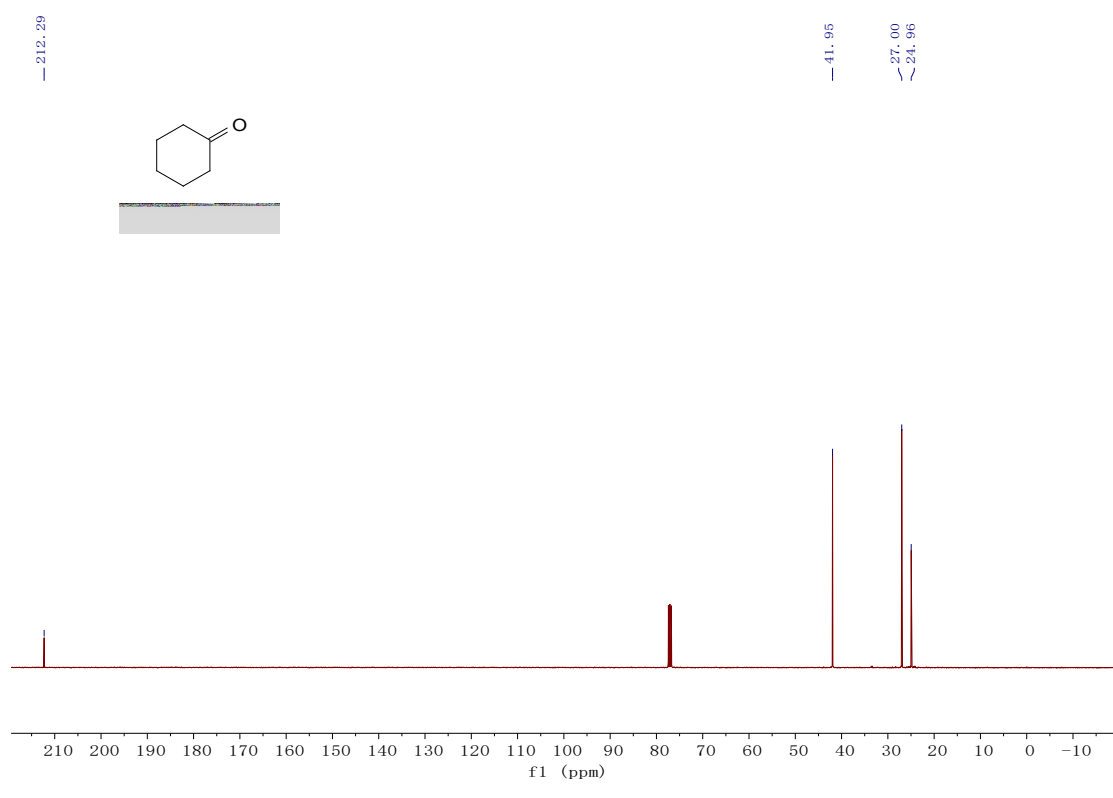
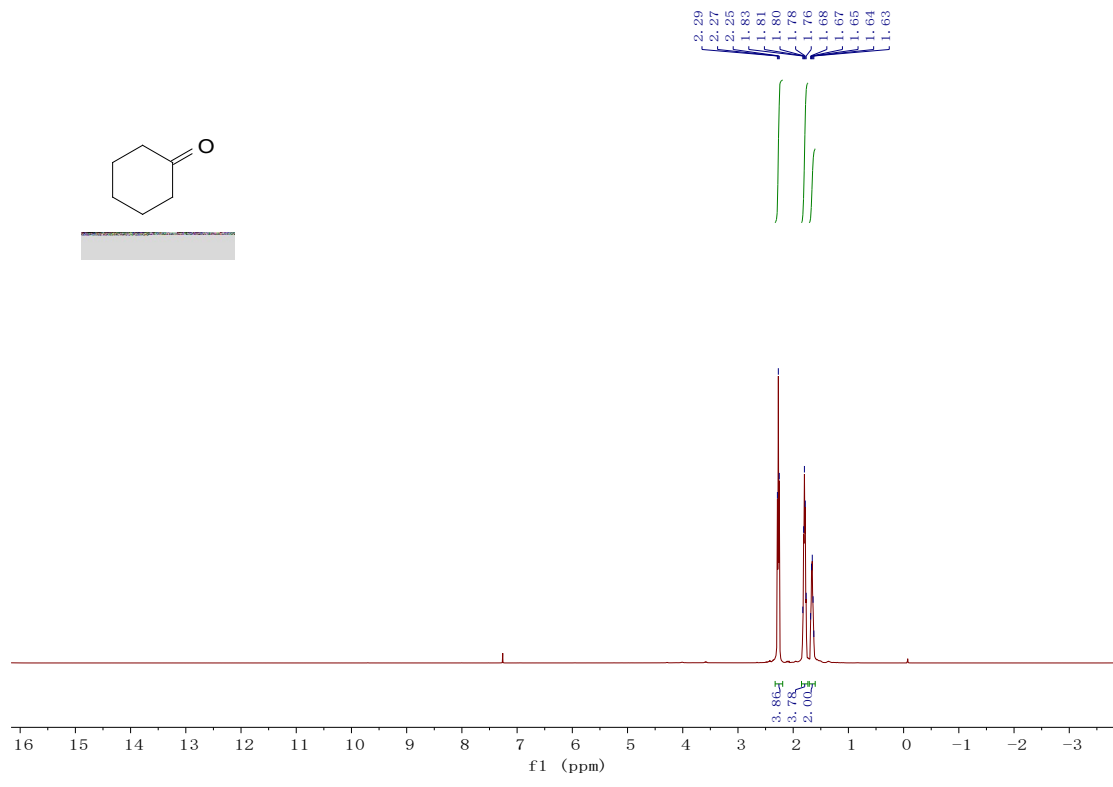


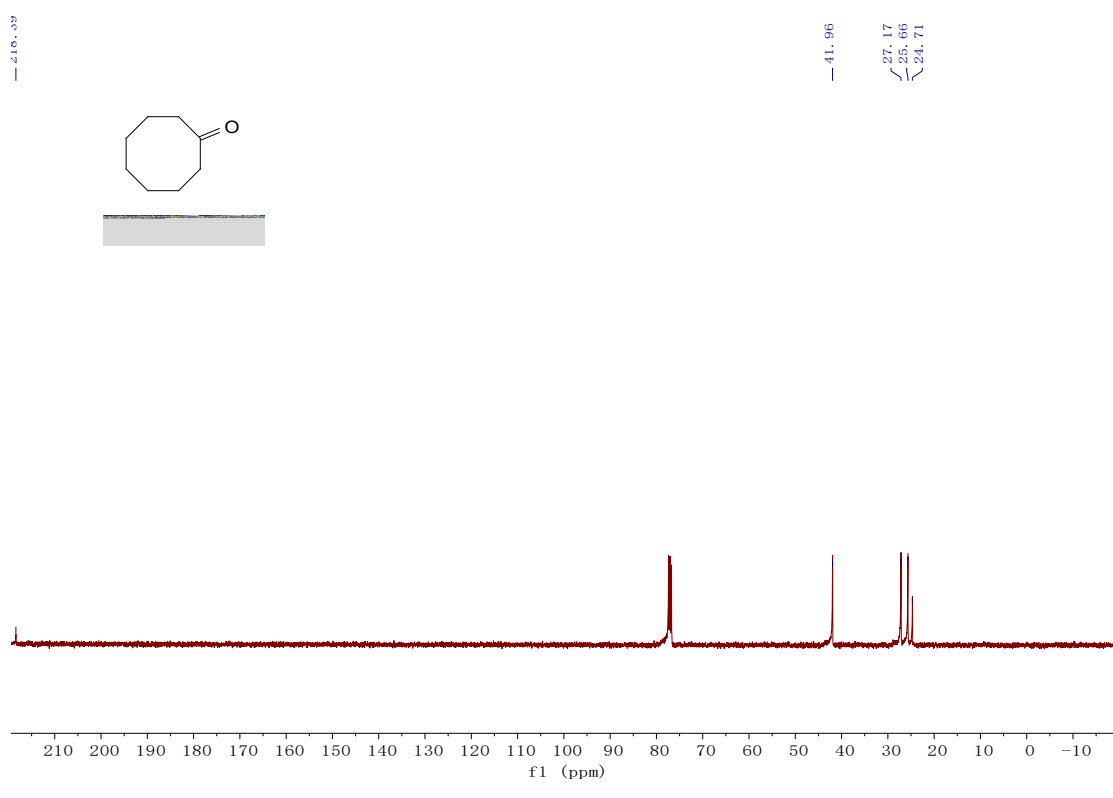
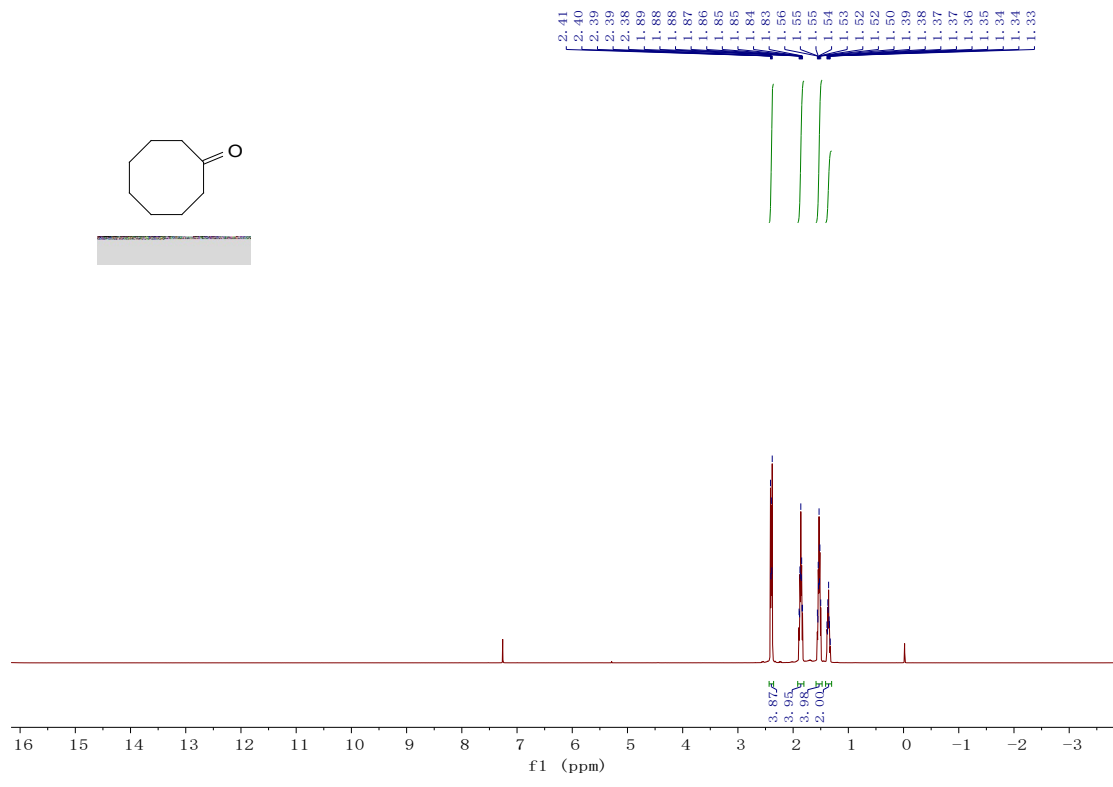


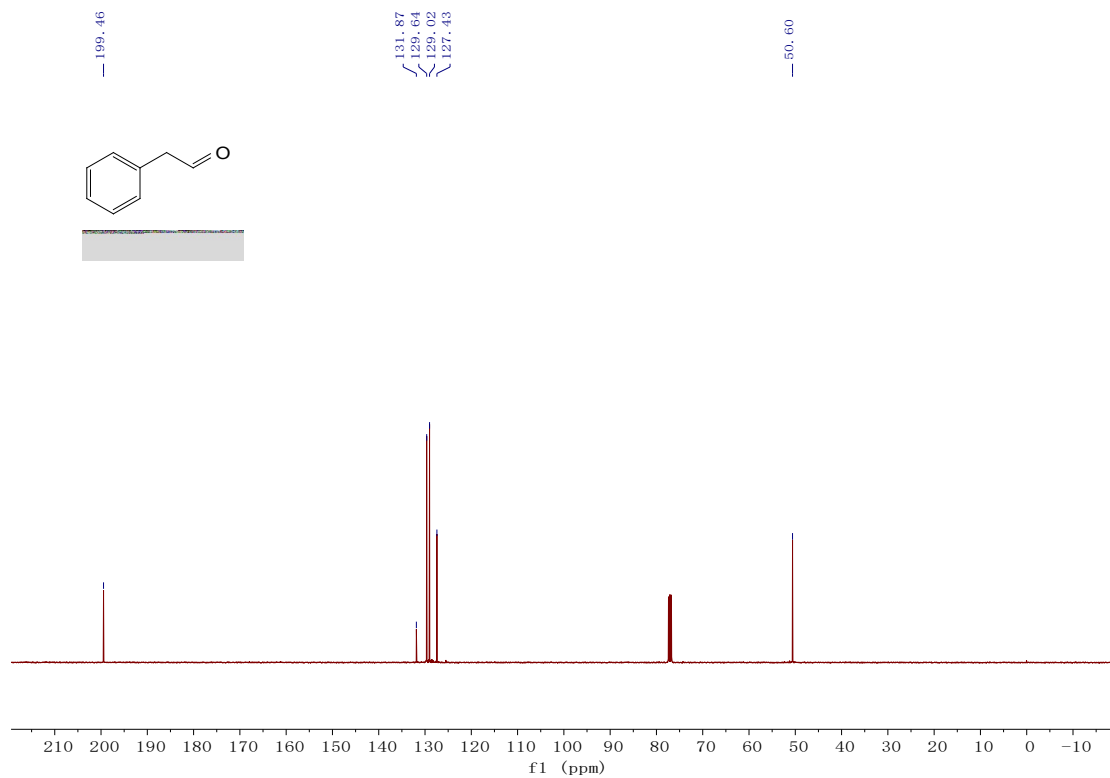
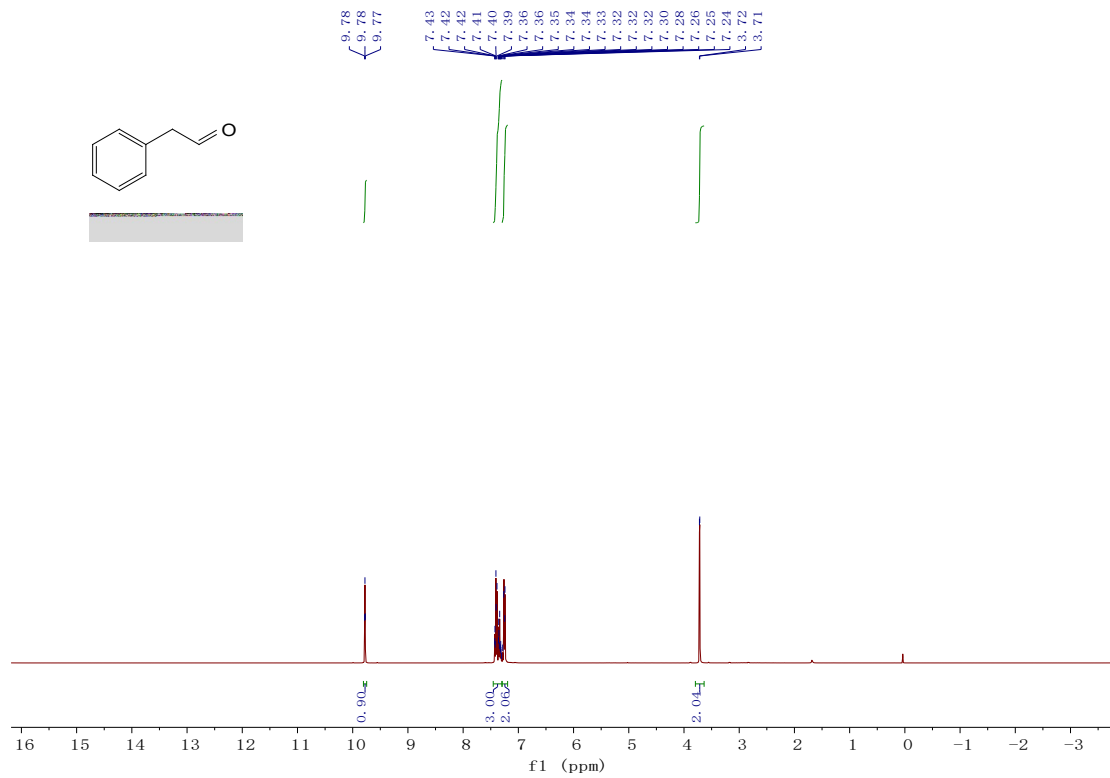


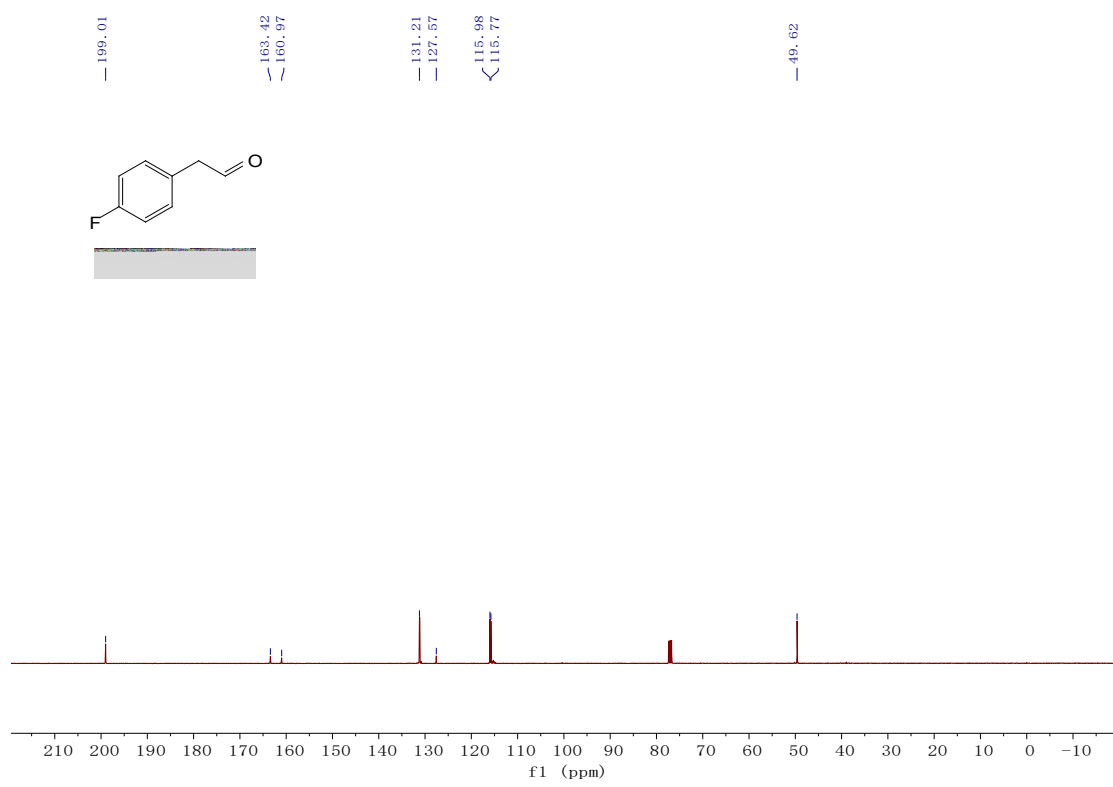
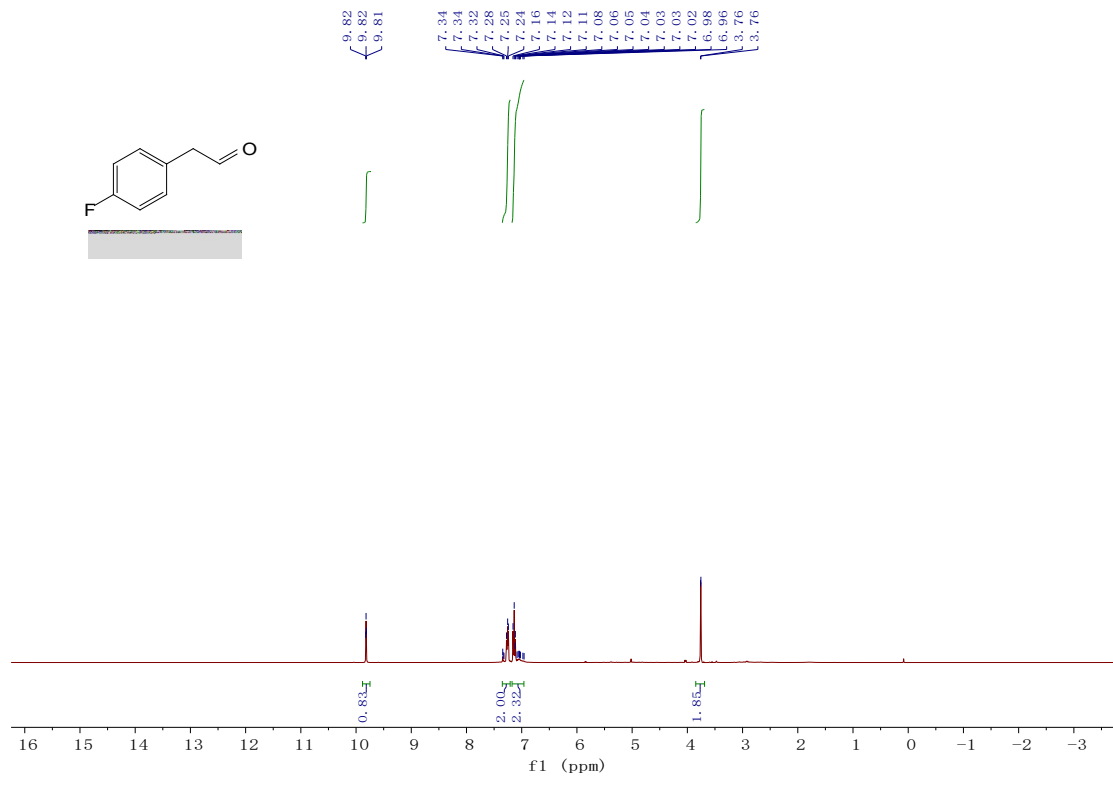


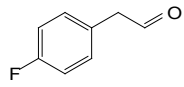






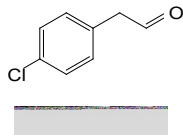
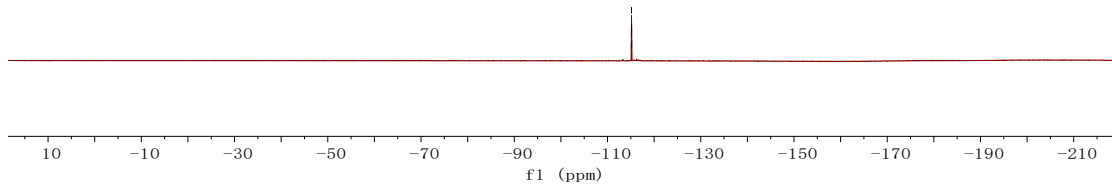






^{19}F NMR (376 MHz, CDCl_3)

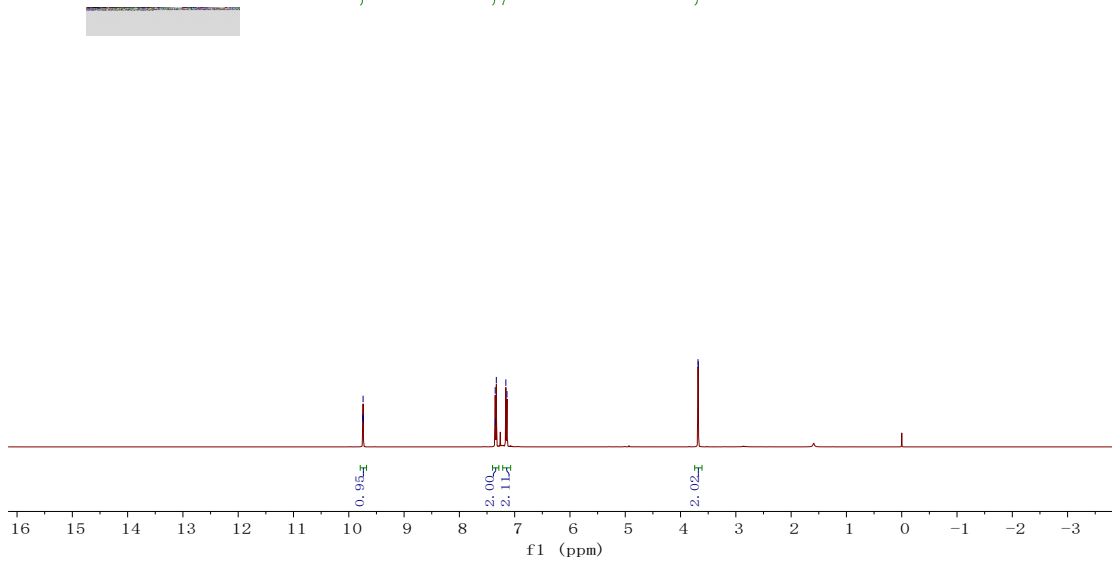
-115.11
-115.12
-115.13
-115.14
-115.16
-115.17
-115.18

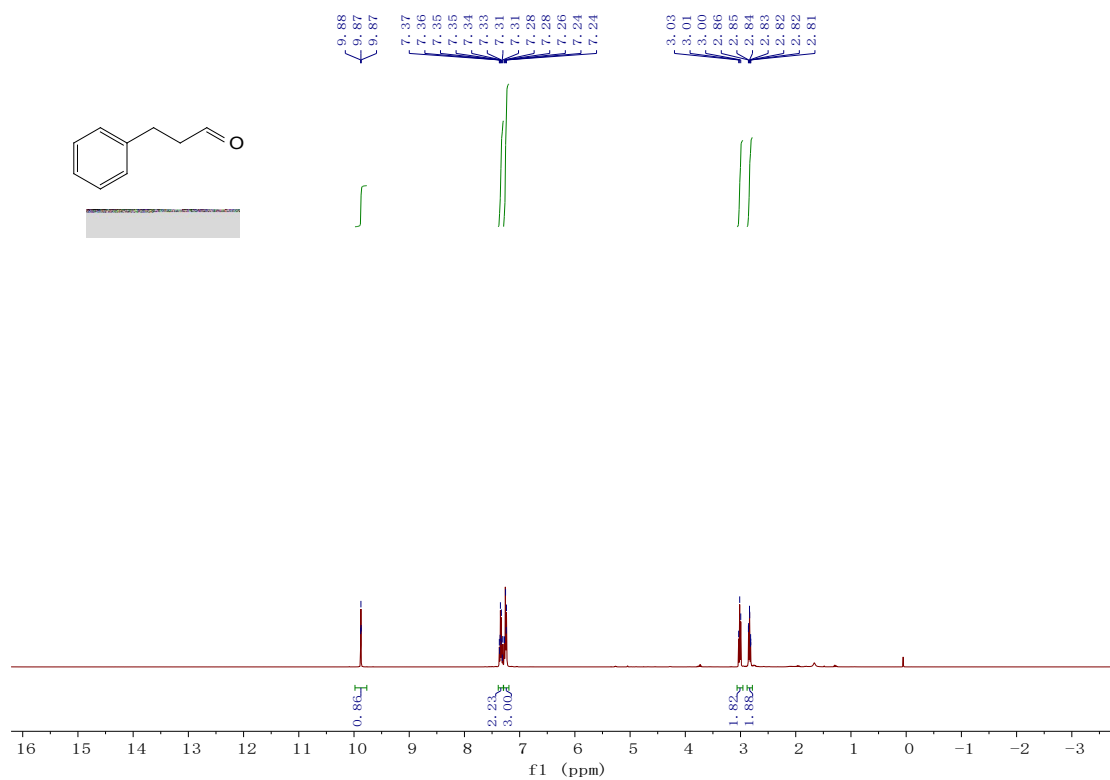
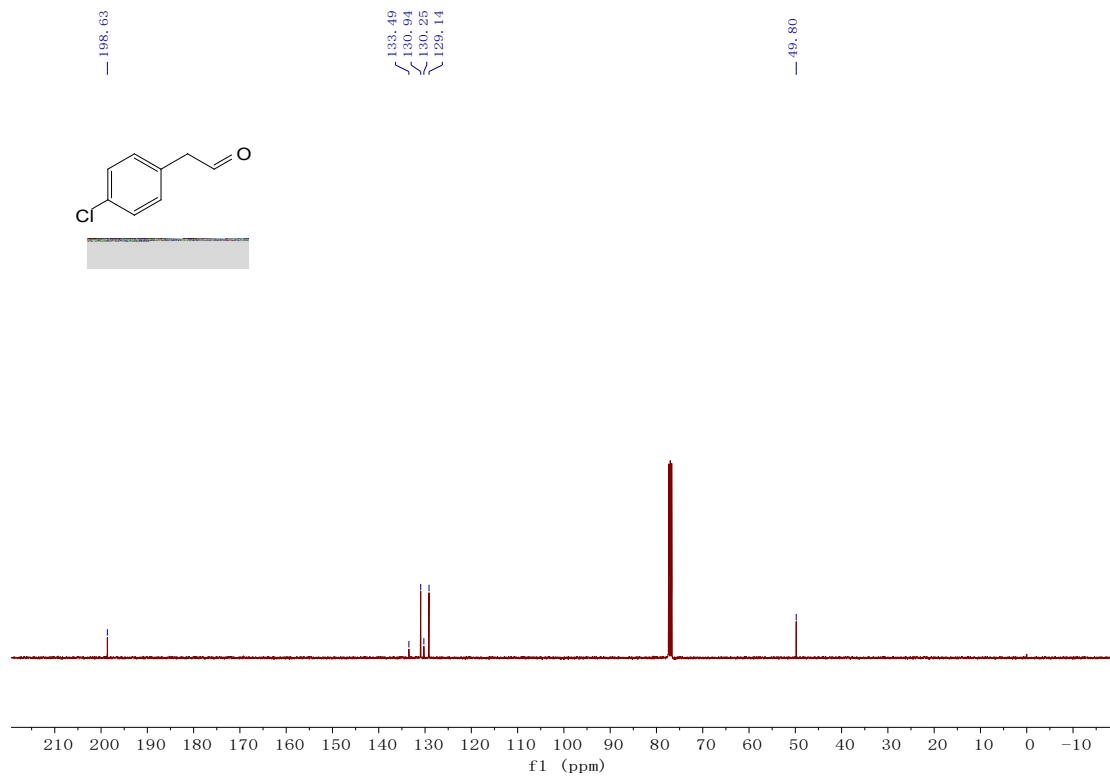


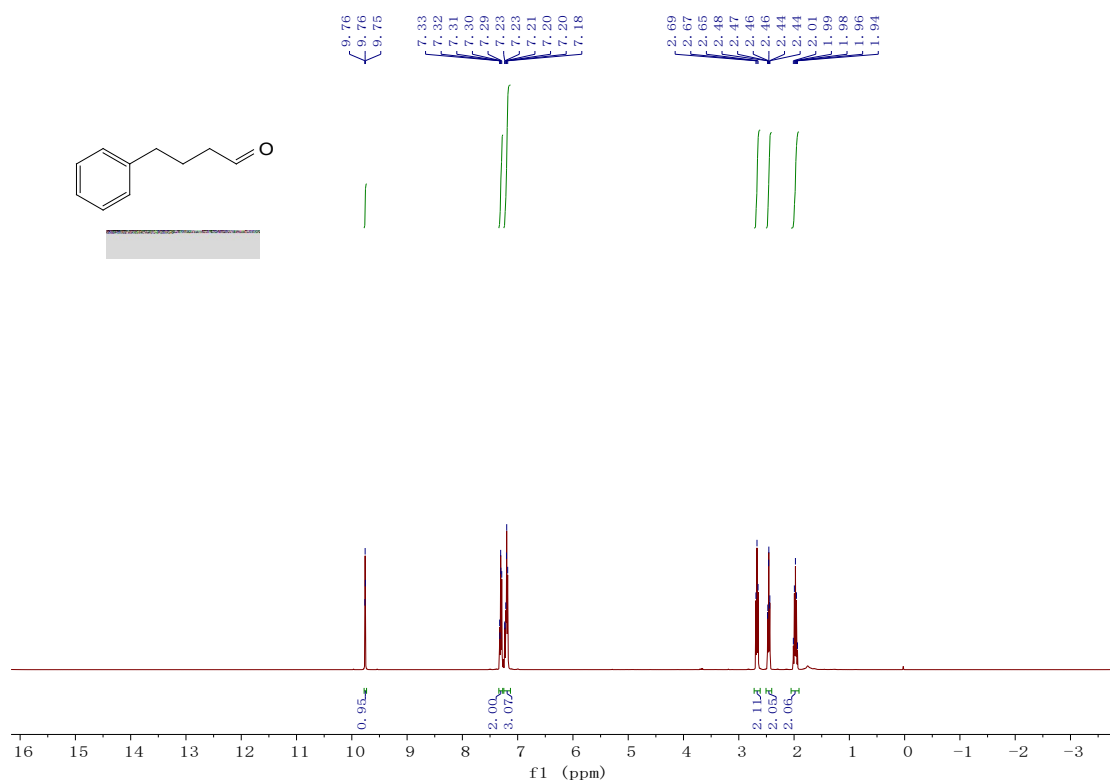
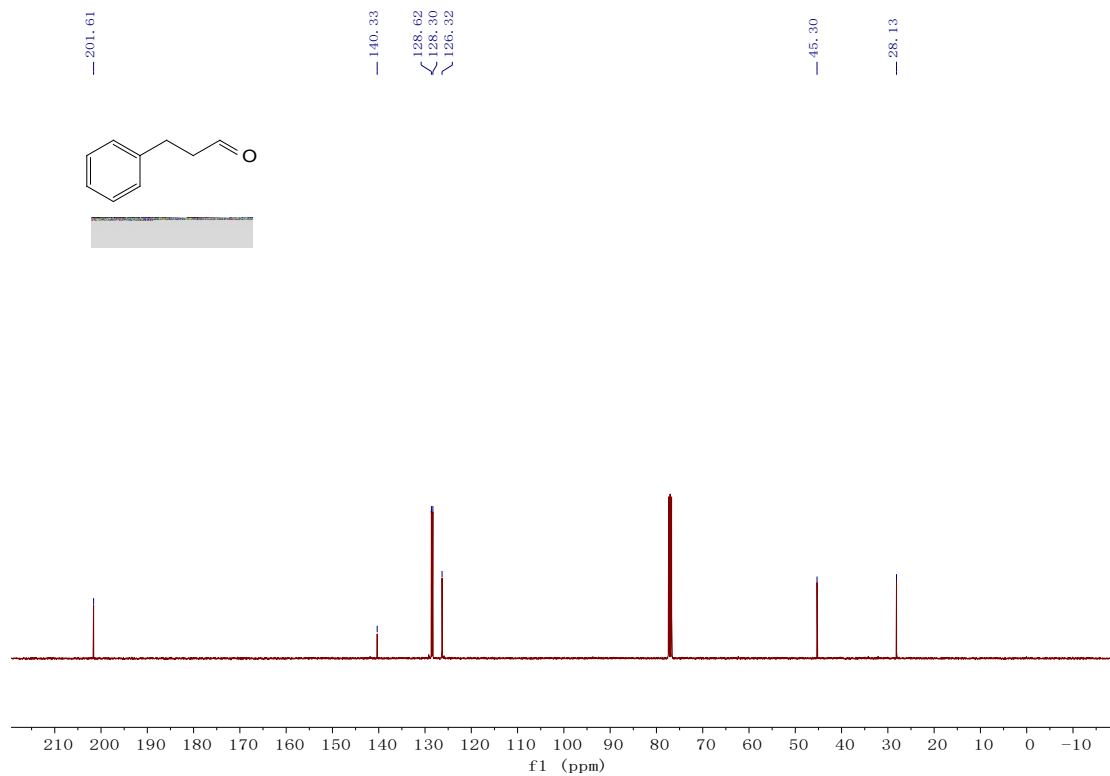
9.75
9.74
9.74

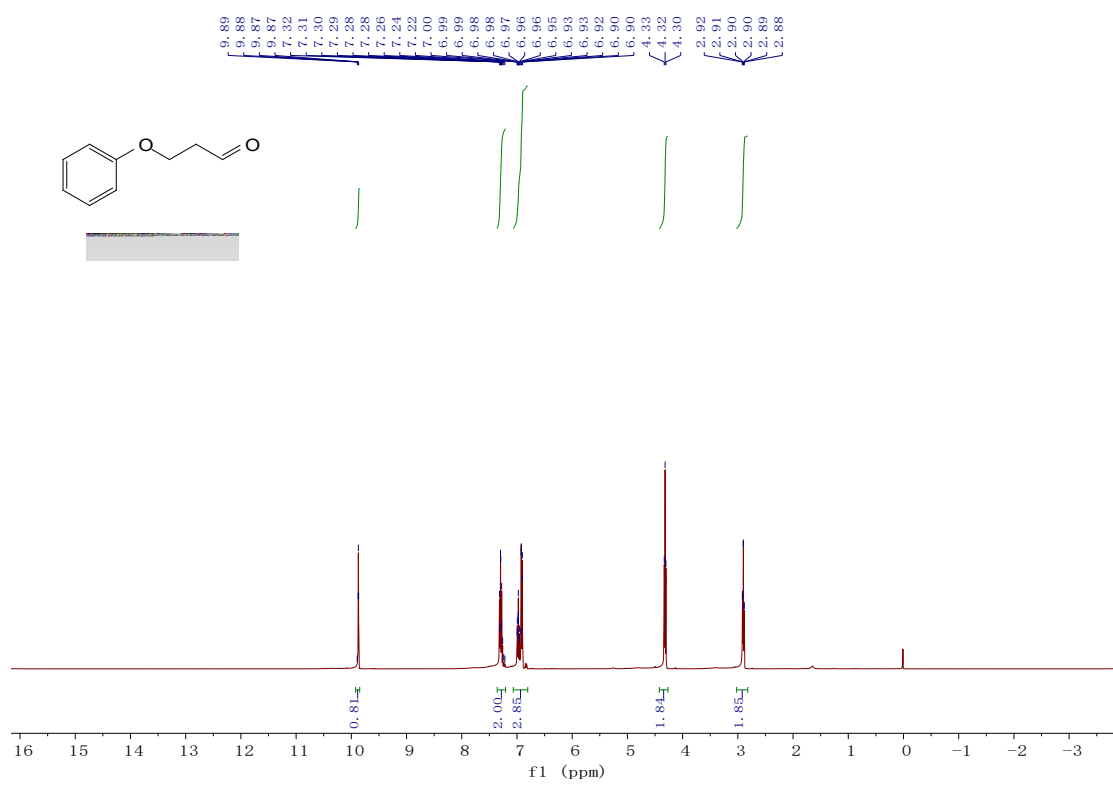
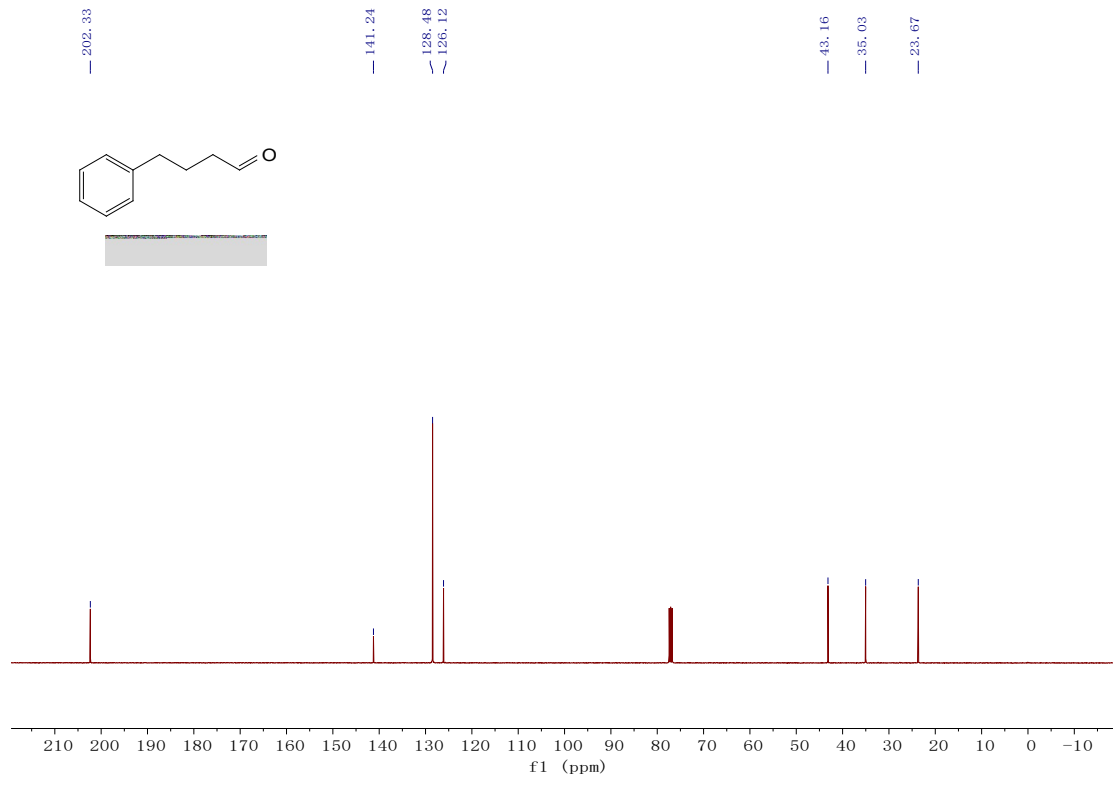
7.35
7.33
7.16
7.14

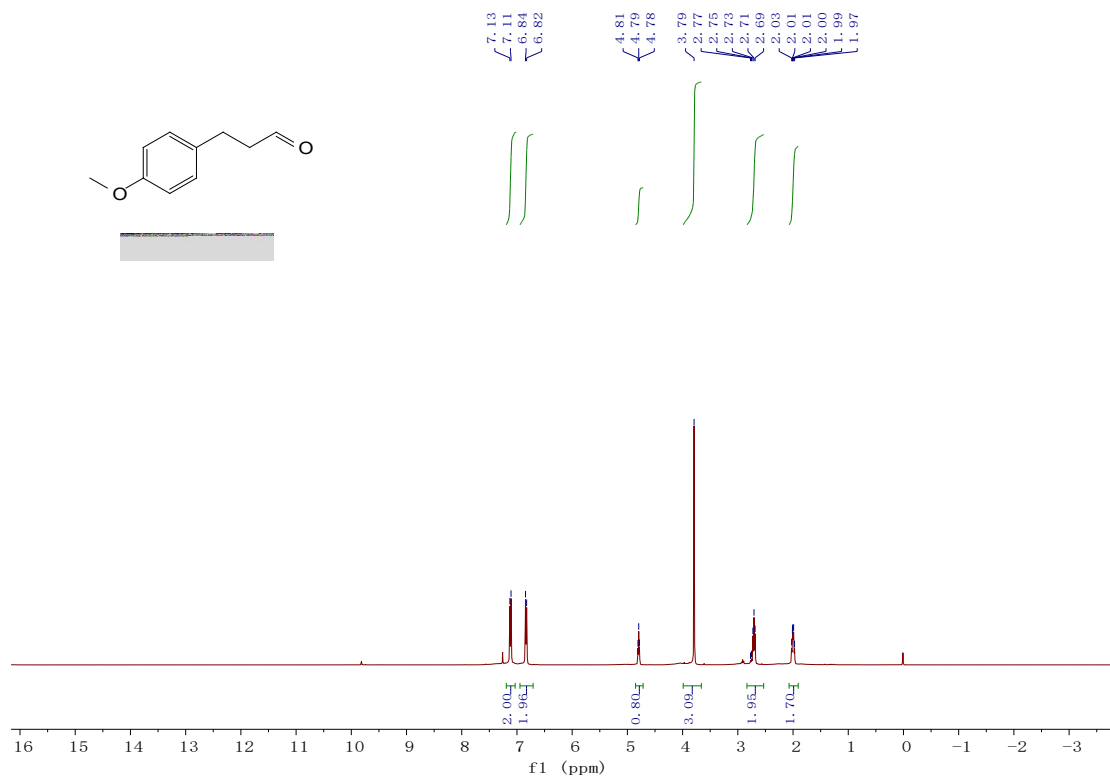
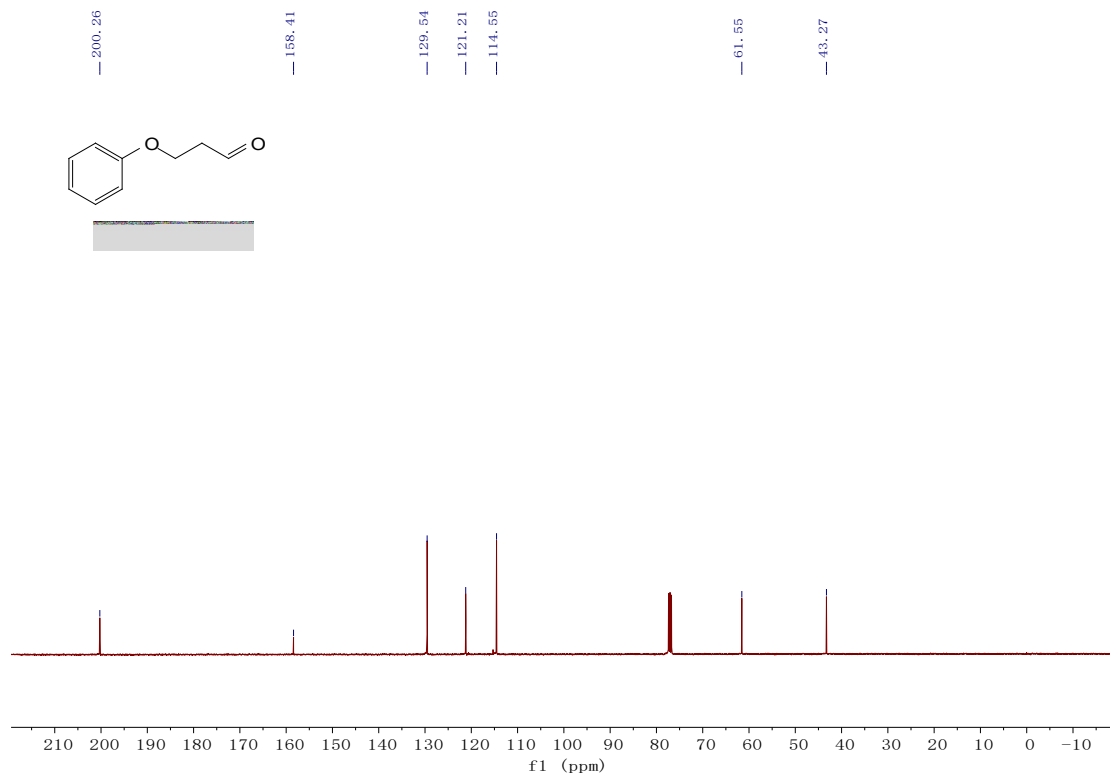
3.68
3.68

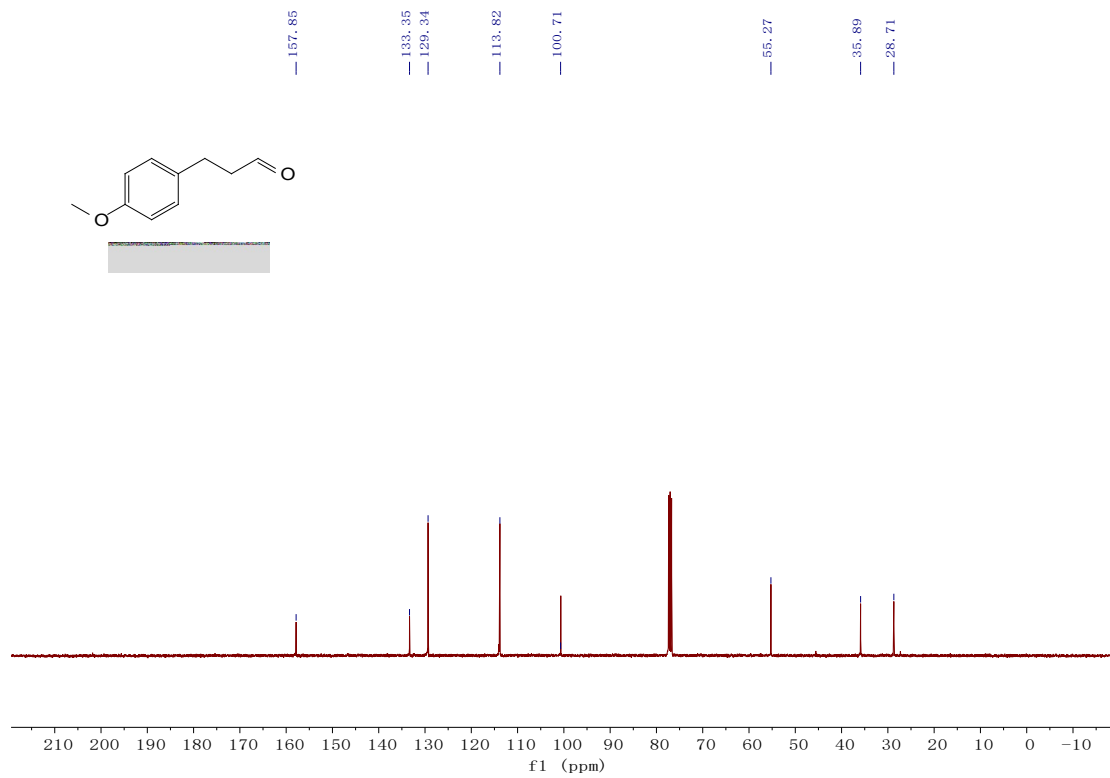












7. References

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