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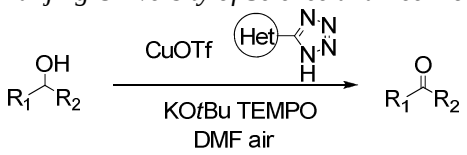

R_1 = H-, Benzyl-. R_2 = Benzyl-, Alkyl-.

Yields up to 98%

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ABSTRACT

An efficient copper-catalyzed aerobic oxidation of alcohols has been established which employed heterocycle-substituted tetrazoles as ligands. The commercially available (S)-5-(pyrrolidin-2-yl)-1*H*-tetrazole proved as the best ligand for this oxidation. Under optimized conditions, the substrate scope was broadened. A plausible mechanism was also proposed.

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Introduction

The oxidation of alcohols to aldehydes and ketones is a fundamental reaction in synthetic chemistry which traditionally relies on stoichiometric hazardous reagents such as Cr(VI) or Mn(VII) derivatives.[1] The environmental concerns prompted chemists to develop green methods. Much attention has been paid to the biomimetic copper/nitroxyl-radical-catalyzed oxidation, in which molecular oxygen is used as the terminal oxidant. First reported in 1966,[2] this kind of oxidation began to draw interest in 1984 when Semmelhack and coworkers demonstrated that Cu/TEMPO (TEMPO=2,2,6,6-tetramethylpiperidine N-oxide) was an efficient system for alcohol oxidation.[3] Chemoselective oxidation of primary alcohols was achieved in several groups.[4] However, the oxidation of secondary alcohols is more challenging. While efficient protocols have been developed, expensive nitroxyl radicals such as ABNO or AZADO have to be used instead of TEMPO.[5] Recently, Ding and coworkers developed a CuI/L-proline-based system, which could promote the oxidation of both primary and secondary benzyl alcohols.[6]

In the past few decades, tetrazoles have found wide applications in medicinal chemistry,[7] material chemistry,[8] coordination chemistry,[9] organocatalysis,[10] and biological science.[11] We have synthesized a series of different heterocycle-substituted tetrazoles (Figure 1, **L1**-**L11**).[12] Herein, we report their application as efficient N,N-bidentate ligands in copper-catalyzed aerobic oxidation of alcohols at room temperature.

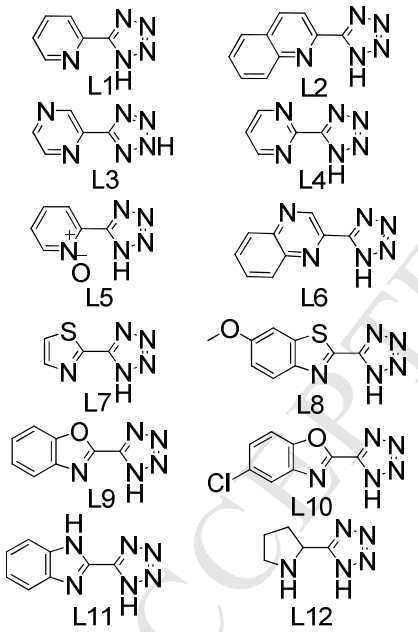
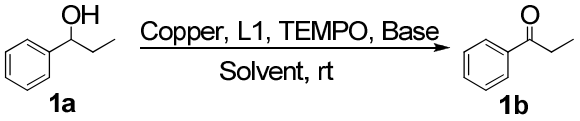


Figure 1. L1-L11, tetrazole ligands synthesized in our laboratory ; L12, a commercially available ligand.

Results and discussion

A simple benzylic sencondary alcohol, 3-phenyl-1-propanol (**1a**) was chosen as the model substrate while 5-(2-pyridyl)tetrazole (**L1**) was selected as the ligand. Compared to Cu(II), the use of Cu(I) as the copper source generally led to higher yields, and the highest yield was obtained when the noncoordinating CuOTf was used (Table 1, entries 1-7). A stoichiometric amount of strong base such as KOtBu was essential for the reaction (Table 1, entries 6 and 9). Different solvents such as toluene, THF or CH_3CN were also tried, and DMF proved to be the best solvent for this oxidation (Table 1, entries 10 and 12).

Table 1 The optimization of copper-catalyzed alcohol oxidation.[a]

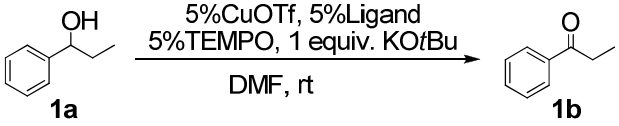


Entry	Copper	Solvent	Base	Time(h)	Yield (%)[b]
1	$CuBr_2$	DMF	KO*t*Bu	12	15
2	$CuSO_4$	DMF	KO*t*Bu	12	17
3	CuOAc	DMF	KO*t*Bu	12	22
4	CuBr	DMF	KO*t*Bu	12	55
5	CuI	DMF	KO*t*Bu	12	64
6	CuOTf	DMF	KO*t*Bu	12	73
7	CuOTf	DMF	KO*t*Bu[c]	12	38
8	CuOTf	DMF	-	12	<5
9	CuOTf	DMF	KOH	12	<5
10	CuOTf	Toluene	KO*t*Bu	12	15
11	CuOTf	THF	KO*t*Bu	12	22
12	CuOTf	CH_3CN	KO*t*Bu	12	21

[a] Reaction conditions: 3-phenyl-1-propanol (2 mmol), copper salt (0.1 mmol), TEMPO (0.1 mmol), L1 (0.1 mmol), KO*t*Bu (2 mmol), DMF (5ml).
[b] Isolated yield.
[c] KO*t*Bu (1 mmol) was used.

With the optimized conditions, other tetrazole ligands (**L2**-**L12**) were also tested and the results were summarized in Table 2. Compared with L-proline, moderate to high yields were obtained with all ligands in which the commercially available (S)-5-(pyrrolidin-2-yl)-1H-tetrazole (**L12**) was the best one. It was found that the alcohol could be fully converted within 1h when **L12** was used. Similar yield was achieved when the reaction was done in gram scale quantity (Table 2, entry 15).

Table 2 Screening of Tetrazole Ligands.[a]



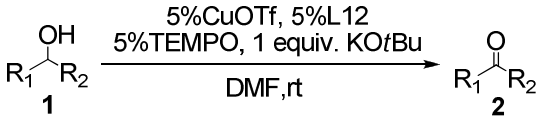
Entry	Ligand	Time	Yield (%)[b]
1	-	12	<5
2	L-proline	12	29
3	**L1**	12	73
4	**L2**	12	46
5	**L3**	12	45
6	**L4**	12	42
7	**L5**	12	51
8	**L6**	12	55
9	**L7**	12	52
10	**L8**	12	65
11	**L9**	12	47
12	**L10**	12	50
13	**L11**	12	52
14	**L12**	1	99

15	**L12**	1.5	97[c]

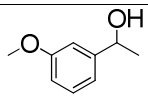
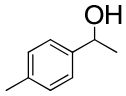
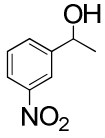
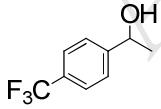
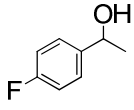
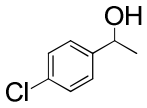
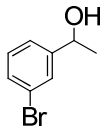
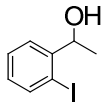
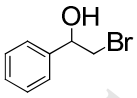
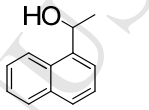
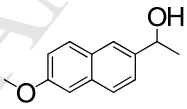
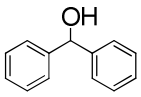
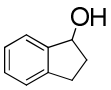
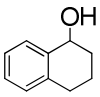
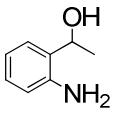
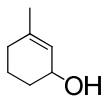
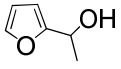
[a] Reaction conditions: 3-phenyl-1-propanol (2 mmol), CuOTf (0.1 mmol), TEMPO (0.1 mmol), Ligand (0.1 mmol), KO*t*Bu (2 mmol), DMF (5ml).
[b] Isolated yield.
c Reaction conditions: 3-phenyl-1-propanol (10 mmol), CuOTf (0.5 mmol), TEMPO (0.5 mmol), Ligand (0.5 mmol), KO*t*Bu (10 mmol), DMF (25ml).

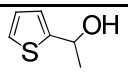
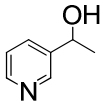
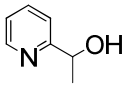
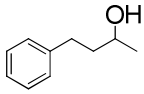
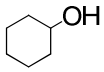
We next explored the substrate scope. Secondary benzyl alcohols bearing either electron-donating or electron-withdrawing group could be oxidized to the corresponding ketones in nearly quantitative yield (Table 3, entries 1-4). Ary and alkyl halogens were tolerated (Table 3, entries 5-9). Naphthyl alcohols could also be oxidized (Table 3, entries 10 and 11). When bulky groups were introduced to the substrate, longer reaction time was needed and slightly lower yields were obtained (Table 3, entries 8, 9, and 12-14). Substrate bearing aniline group was oxidized to the corresponding ketones in moderate yield (Table 3, entry 15). In comparison, the oxidation of an allylic alcohol was much faster and excellent product yield was achieved (Table 3, entry 16). Heterocyclic alcohols such as furanyl and thiophenyl alcohols were also easily oxidized to the corresponding ketones, although prolonged time was required for the oxidation of pyridinyl alcohols (Table 3, entries 17-20). While the oxidation of benzyl and similar alcohols proceeded well, aliphatic alcohols were not suitable substrates(Table 3, entries 21 and 22). This observation was in accordance with what Ding et al described[6].

Table 3 Oxidation of secondary alcohols to ketones.[a]



R1,R2= Aryl-, Alkyl

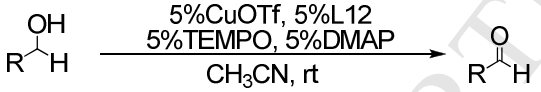
Entry	Substrate	Product	Time(h)	Yield (%)
1	 **1b**	**2b**	1	99
2	 **1c**	**2c**	1	99
3	 **1d**	**2d**	1.5	96
4	 **1e**	**2e**	2	95
5	 **1f**	**2f**	1	96
6	 **1g**	**2g**	1	97
7	 **1h**	**2h**	1	97
8	 **1i**	**2i**	2	95
9	 **1j**	**2j**	2	95
10	 **1k**	**2k**	0.5	97
11	 **1l**	**2l**	0.5	97
12	 **1m**	**2m**	2	95
13	 **1n**	**2n**	3	93
14	 **1o**	**2o**	5	91
15	 **1p**	**2p**	12	78
16	 **1q**	**2q**	0.5	99
17	 **1r**	**2r**	0.5	97

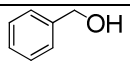
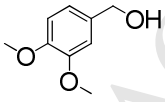
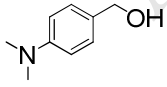
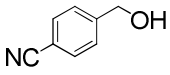
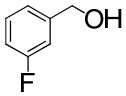
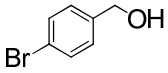
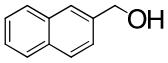
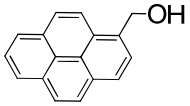
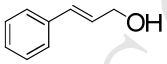
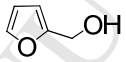
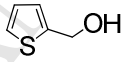
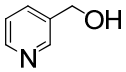
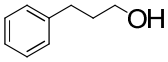
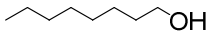
18	 **1s**	**2s**	0.5	95
19	 **1t**	**2t**	5	89
20	 **1u**	**2u**	12	75
21	 **1v**	**2v**	12	-
22	 **1w**	**2w**	12	-

[a] Reaction conditions: secondary alcohol (2 mmol), CuOTf (0.1 mmol), TEMPO (0.1 mmol), L12 (0.1 mmol), KO*t*Bu (2 mmol), DMF (5ml).
[b] Isolated yield.

The oxidation of primary alcohols was also investigated. The reaction was found to be best performed in CH_3CN with catalytic DMAP as base. A variety of benzyl aldehydes were easily prepared (Table 4, entries 1-8). Allylic alcohol was also successfully oxidized to the desired aldehyde (Table 4, entry 9). Alcohols derived from oxygen-, nitrogen-, and sulfur-containing heterocycles are also suitable substrates (Table 4, entries 10-12). Aliphatic primary alcohols were also oxidized to the desired aldehydes, despite the low to moderate yields (Table 4, entries 13-14).

Table 4 Oxidation of primary alcohols to aldehydes.[a]



Entry	Substrate	Product	Time(h)	Yield (%)[b]
1	 **3a**	**4a**	1	95
2	 **3b**	**4b**	1	97
3	 **3c**	**4c**	1	95
4	 **3d**	**4d**	2.5	90
5	 **3e**	**4e**	1.5	95
6	 **3f**	**4f**	1	96
7	 **3g**	**4g**	1	98
8	 **3h**	**4h**	1	93
9	 **3i**	**4i**	1	98
10	 **3j**	**4j**	1.5	95
11	 **3k**	**4k**	2	96
12	 **3l**	**4l**	12	73
13	 **3m**	**4m**	12	75
14	 **3n**	**4n**	12	63

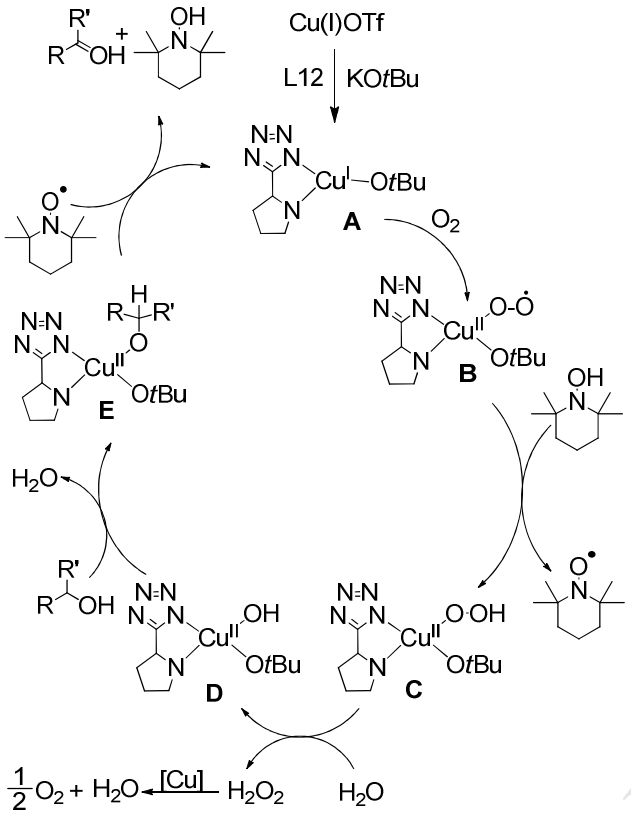
[a] Reaction conditions: primary alcohol (2 mmol), CuOTf (0.1 mmol), TEMPO (0.1 mmol), L12 (0.1 mmol), DMAP (0.1 mmol), CH_3CN (5ml).
[b] Isolated yield.

Based on above experiments and the recent literature, a mechanism was proposed (Scheme 1). The initial step includes the formation of copper alkoxide **A**. It was oxidized by O_2 to form superoxide **B**, which abstracted a hydrogen radical from TEMPOH to generate **C**. **C** reacted with water to give H_2O_2 and **D**. After subsequent condensation with the alcohol substrate, copper alkoxo **E** was formed, which could afford the corresponding ketone upon the transfer of a hydrogen radical to TEMPO, along with the regeneration of **A** and TEMPOH.

Conclusion

In summary, we have developed an efficient method for the copper-catalyzed aerobic oxidation of alcohols at room temperature. Using this protocol, a series of heterocycle-substituted tetrazoles were used as ligands and (S)-5-(pyrrolidin-2-yl)-1*H*-tetrazole was the best ligand. Although the reaction was not compatible for aliphatic secondary alcohols, benzyl

secondary alcohols could be oxidized to the corresponding ketones in moderate to high yields. In addition, both benzyl and aliphatic primary alcohols were oxidized under optimized conditions.



Scheme 1 Proposed mechanism for the copper/(S)-5-(pyrrolidin-2-yl)-1*H*-tetrazolee/TEMPO catalyzed oxidation of alcohols.

Experimental section

General Experiments: Ligands L1-L11 were synthesized according to the literature.[12] Other reagents were purchased from commercial suppliers and used without purification. NMR spectra were obtained with a Bruker Avance 500 spectrometer or Bruker Avance 300 spectrometer. Flash column chromatography was performed by employing 200-300 mesh silica gel. TLC was performed with silica gel HSGF254.

The Oxidation of Secondary Alcohols.

A round-bottom flask was charged with alcohol (2 mmol), CuOTf (0.1 mmol, 0.05 eq) (S)-5-(pyrrolidin-2-yl)-1*H*-tetrazole (0.1 mmol, 0.05 eq), TEMPO (0.1 mmol, 0.05 eq), *t*-BuOK (2 mmol, 1 eq) and DMF (5ml). The reaction mixture was stirred at 25°C open to air until the completion of the reaction, as monitored by TLC. The mixture was then diluted with CH_2Cl_2 (20 ml), washed with water, dried over Na_2SO_4, and evaporated under vacuum to give the crude product, which was purified by column chromatography to give the pure product.

The Oxidation of Primay Alcohols.

A round-bottom flask was charged with alcohol (2 mmol), CuOTf (0.1 mmol, 0.05 eq) (S)-5-(pyrrolidin-2-yl)-1*H*-tetrazole (0.1 mmol, 0.05 eq), TEMPO (0.1 mmol, 0.05 eq), DMAP (0.15 mmol, 0.075 eq) and CH_3CN (5ml). The reaction mixture was stirred at 25°C open to air until the completion of the reaction, as monitored by TLC. After completion, CH_3CN was evaporated under vacuum. The residue was then diluted with CH_2Cl_2 (5 ml) and filtered through a plug of silica gel to afford the desired product.

Propiophenone (**2a**)[13] Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01-7.90 (m, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.39, 136.52, 132.50, 128.18, 127.58, 31.38, 7.85.

1-(3-Methoxyphenyl)ethanone (**2b**)[14] Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.48 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.85 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.57, 159.44, 138.11, 129.22, 120.76, 119.22, 111.99, 55.04, 26.36.

4-Methylacetophenone (**2c**)[15] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.33-7.21 (m, 2H), 2.59 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.08, 143.19, 134.01, 128.59, 127.79, 25.85, 20.95.

1-(3-Nitrophenyl)ethanone (**2d**)[16] White crystal; mp 78-79 °C (lit. 78-79 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.43 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.41, 137.79, 133.50, 129.60, 127.01, 122.75, 26.36.

1-(4-(Trifluoromethyl)phenyl)ethanone (**2e**)[17] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.58, 140.22, 134.69, 129.20, 126.20, 27.28.

4-Fluoroacetophenone (**2f**)[18] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.39, 166.71, 164.69, 133.56, 130.93, 130.86, 115.65, 115.48, 26.42.

1-(4-Chlorophenyl)ethanone (**2g**)[16] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6, 2H), 7.44 (d, *J* = 8.6, 2H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.68, 139.40, 135.28, 129.61, 128.75, 26.46.

1-(3-Bromophenyl)ethanone (**2h**)[19] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.60, 138.77, 135.93, 131.32, 130.19, 126.85, 122.92, 26.59.

1-(3-iodophenyl)ethanone (**2i**)[19] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (m, 1H), 7.48 (m, 1H), 7.43 (m, 1H), 7.14 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.80, 144.04, 140.89, 131.83, 128.33, 128.08, 90.96, 29.50.

Phenacyl bromide (**2j**)[20] White solid; mp 45 °C (lit. 47-48 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3, 2H), 7.82 (m, 1H), 7.52 (m, 2H), 4.47 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.20, 133.91, 128.82, 31.07.

1-Acetonaphthone (**2k**)[21] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, *J*=8.4 Hz, 1H), 7.99 (t, *J* = 6.8 Hz, 1H), 7.91 (dd, *J* = 20.0, 7.5 Hz, 2H), 7.68-7.42 (m, 3H), 2.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.02, 135.43, 134.14, 133.27, 130.32, 129.04, 128.64, 128.26, 126.63, 126.22, 124.55, 30.14.

2-Acetyl-6-methoxy naphthalene (**2l**)[21] White solid; mp 106-107 °C (lit. 106-107 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.28-7.08 (m, 2H), 3.93 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.50, 159.39, 136.93, 132.18, 130.78, 129.75, 127.43, 126.76, 124.26, 119.37, 105.38, 55.06, 26.22.

Benzophenone (**2m**)[22] White solid; mp 49-51 °C (lit. 47-48 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 4H), 7.58 (m, 2H), 7.49 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.67, 137.50, 132.37, 129.99, 128.22.

2,3-Dihydro-1H-inden-1-one (**2n**)[23] Yellow solid; mp 38-39 °C (lit. 37.5-38.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7

Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.25 -3.01 (m, 1H), 2.88-2.48 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.96, 155.03, 136.88, 134.45, 127.10, 126.56, 123.50, 36.04, 25.63.

3,4-Dihydronaphthalen-1(2H)-one (**2o**)[24] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13-7.92 (m, 1H), 7.47 (m, 1H), 7.42-7.16 (m, 2H), 2.97 (t, *J* = 5.5 Hz, 2H), 2.66 (m, 2H), 2.25-2.02 (m, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.13, 144.28, 133.17, 132.35, 128.57, 126.87, 126.37, 38.94, 29.46, 23.07.

2-Aminoacetophenone (**2p**)[19] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.28 (m, 1H), 6.67 (m, 2H), 6.30 (br, 2H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.76, 150.36, 134.39, 132.05, 118.19, 117.24, 115.68, 27.83.

3-Methylcyclohex-2-enone (**2q**)[25] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (s, 1H), 2.39-2.32 (m, 2H), 2.29 (t, *J* = 6.0 Hz, 2H), 2.05-1.98 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.56, 162.76, 126.51, 36.91, 30.84, 24.35, 22.47.

2-Acetylfuran (**2r**)[26] Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 6.55 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.66, 152.75, 146.41, 117.24, 112.20, 25.91.

2-Acetylthiophene (**2s**)[27] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 3.7 Hz, 1H), 7.65 (d, *J* = 4.9 Hz, 1H), 7.19-7.07 (m, 1H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.70, 144.52, 133.79, 132.54, 128.15, 26.86.

3-Acetylpyridine (**2t**)[28] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, *J*=1.3 Hz, 1H), 8.90-8.68 (m, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 7.9, 4.8 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.63, 153.40, 149.80, 135.35, 132.15, 123.53, 26.60.

2-Acetylpyridine (**2u**)[29] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.5 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.85 (m, 1H), 7.49 (m, 1H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.85, 153.45, 148.87, 136.70, 126.97, 121.45, 25.61.

Benzaldehyde (**4a**)[4c] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.88 (m, 2H), 7.64 (m, 1H), 7.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.30, 134.40, 129.68, 128.96.

3,4-Dimethoxybenzaldehyde (**4b**)[30] White solid; mp 45-47 °C (lit. 42-45 °C);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.48 (dd, *J* = 8.2 Hz, 1.9 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.83, 154.45, 149.58, 130.10, 126.80, 110.38, 108.91, 56.14, 55.95.

4-Dimethylaminobenzaldehyde (**4c**)[31] White solid; mp 72-73 °C (lit. 71-71.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (d, *J* = 2.5 Hz, 1H), 7.74 (dd, *J* = 9.2, 2.3 Hz, 2H), 6.71 (dd, *J* = 9.2, 2.1 Hz, 2H), 3.21-2.95 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.98, 154.05, 131.67, 124.75, 118.75, 110.71, 39.78.

4-Formylbenzonitrile (**4d**)[32] White solid; mp 83-85 °C (lit. 80-81 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.02 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.47, 138.50, 132.68, 129.66, 117.50, 117.32.

3-Fluorobenzaldehyde (**4e**)[33] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.33- 7.70 (m, 2H), 7.52-6.89 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.76, 167.43, 164.03, 132.24, 131.53, 131.40, 115.71, 115.41.

4-bromobenzaldehyde (**4f**) [34] White solid; mp 56-57 °C (lit. 57 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.71 (dd, *J* = 13.2, 6.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.54, 134.50, 131.88, 130.43, 129.21.

2-Naphthaldehyde (**4g**)[35] White solid; mp 58-59 °C (lit. 58 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.25 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.67 (dd, *J* = 13.8, 6.1 Hz, 1H), 7.59 (q, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.28, 136.48, 134.99, 133.38, 131.00, 130.16, 128.77, 128.22, 126.66, 124.58.

1-Pyrenecarboxaldehyde (**4h**)[36] Yellow solid; mp 122-123 °C (lit. 120-123 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.72 (s, 1H), 9.33 (d, *J* = 9.3 Hz, 1H), 8.36 (d, *J* = 7.9 Hz, 1H), 8.23 (dd, *J* = 5.9, 3.6 Hz, 3H), 8.16 (d, *J* = 8.6 Hz, 2H), 8.04 (dd, *J* = 13.9, 8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.64, 134.82, 130.66, 130.36, 130.14, 129.82, 126.68, 126.44, 126.14, 123.97, 123.79, 123.33, 122.33.

Phenylacrolein (**4i**)[34] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.51 (s, 1H), 7.49-7.37 (m, 4H), 6.73 (dd, *J* = 15.9, 7.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.45, 150.55, 131.77, 129.05, 126.88, 126.29.

2-Furfural (**4j**)[4c] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.70 (s, 1H), 7.26 (s, 1H), 6.77-6.35 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.78, 152.79, 148.08, 121.29, 112.55.

2-Thenaldehyde (**4k**)[4c] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.21-7.58 (m, 2H), 7.52-7.06 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.47, 143.34, 135.90, 134.57, 127.78.

3-Pyridinecarboxaldehyde (**4l**)[37] Colourless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 9.10 (d, *J* = 1.3 Hz, 1H), 8.86 (dd, *J* = 4.7, 1.2 Hz, 1H), 8.19 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50 (dd, *J* = 7.8, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.75, 154.62, 151.89, 135.72, 131.32, 123.99.

3-Phenylpropanal (**4m**)[4c] Slightly Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 8.7 Hz, 3H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.81 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.61, 140.34, 128.62, 128.48, 128.30, 126.32, 45.28, 28.13.

Octanal (**5n**)[4c] Slightly yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (s, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.61 (m, 2H), 1.43-1.13 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.71, 43.72, 31.43, 28.94, 28.83, 22.39, 21.89, 13.84..

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Supplementary Material

Copies of ^{1}H and ^{13}C NMR spectra of all the products.

Click here to remove instruction text...

Supporting Information

Heterocyclic Tetrazole Ligands for Copper-catalyzed Aerobic Oxidation of Alcohols at Room Temperature

Yangyang Liu, Aming Xie, Junjian Li, Xiao Xu, Wei Dong and Boliang Wang*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China

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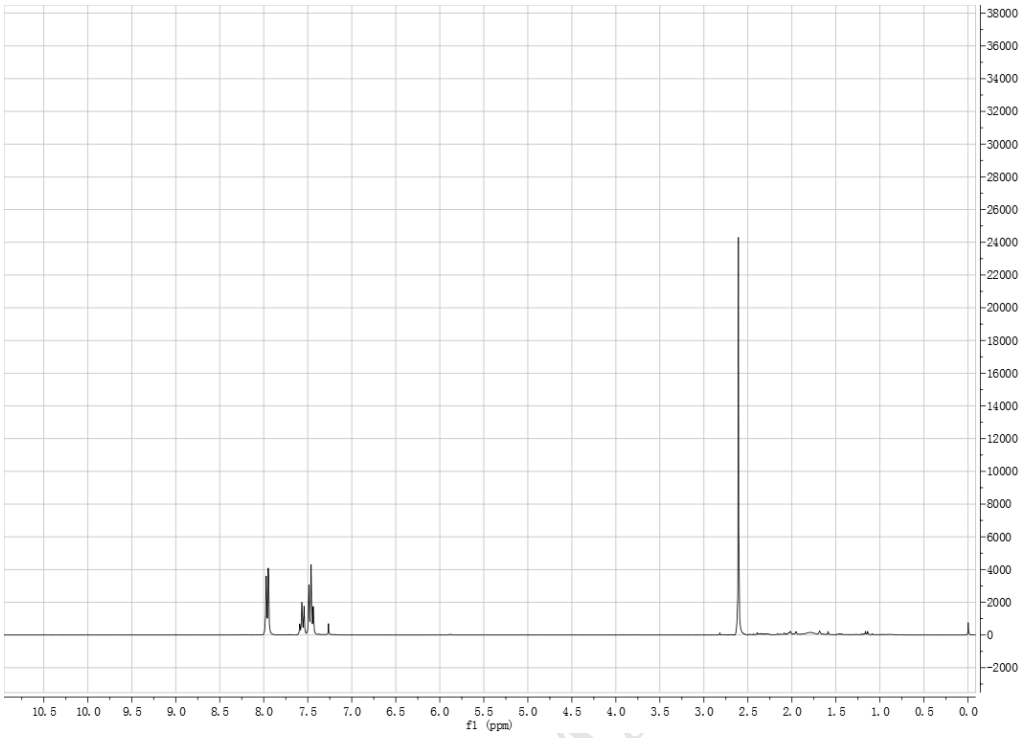
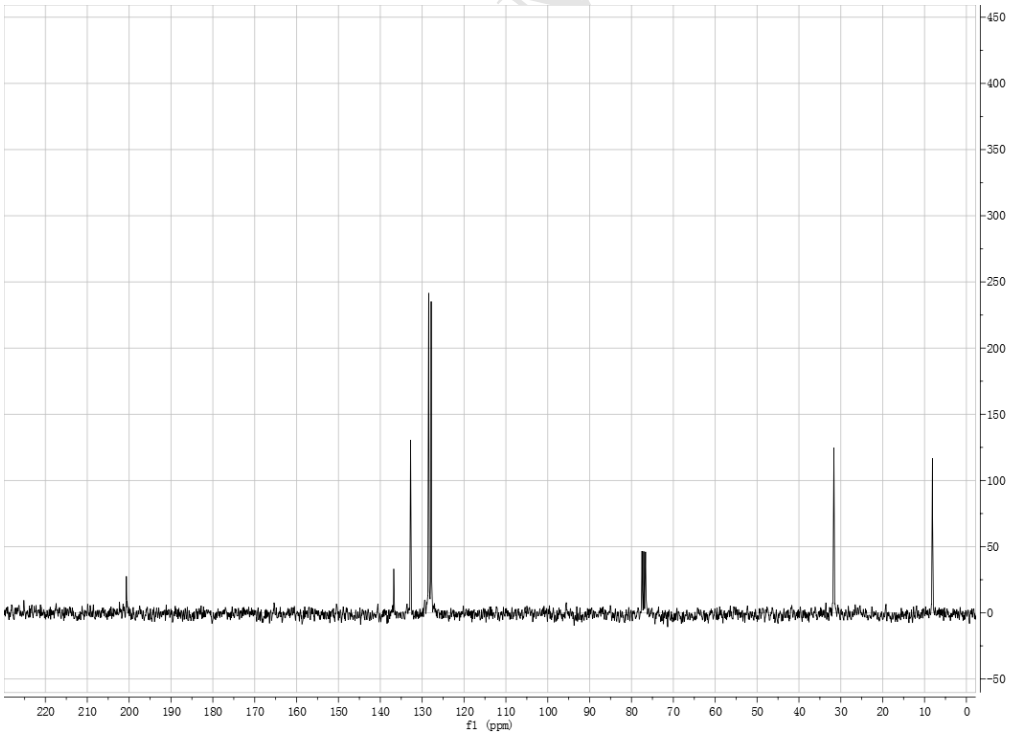
Propiophenone 2a





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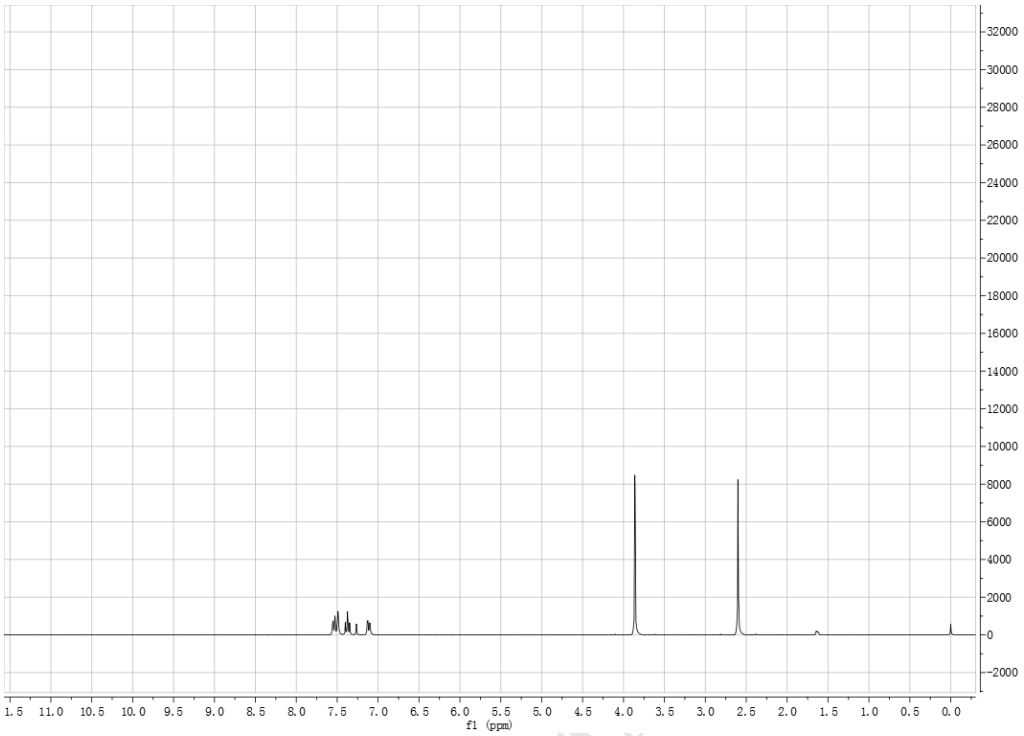

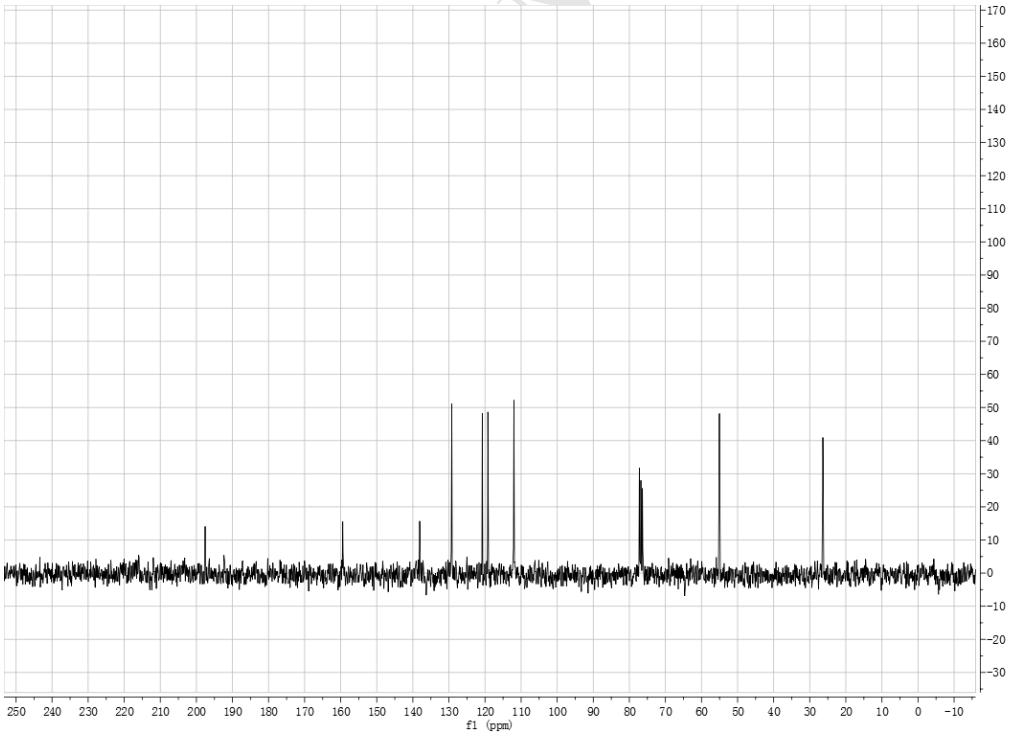

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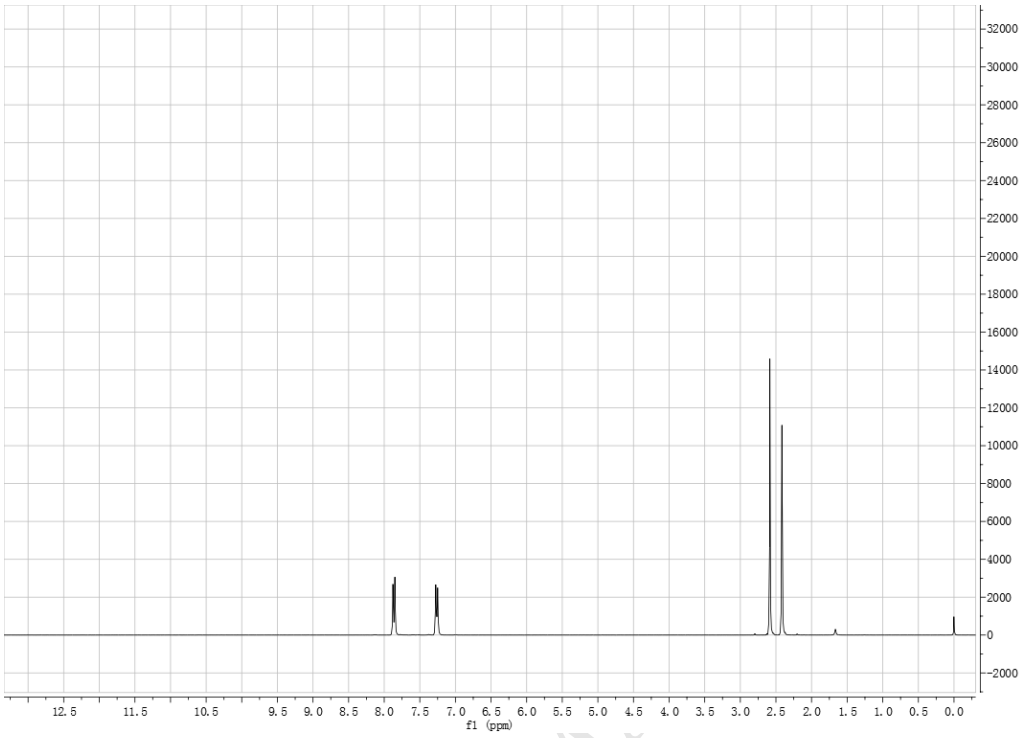

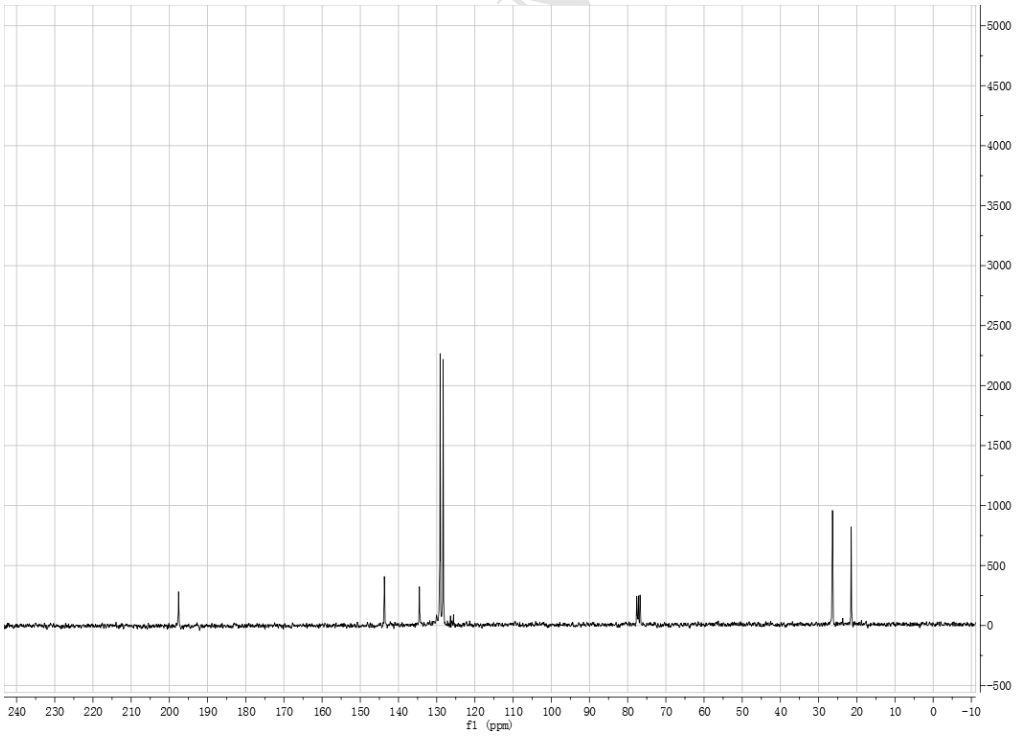

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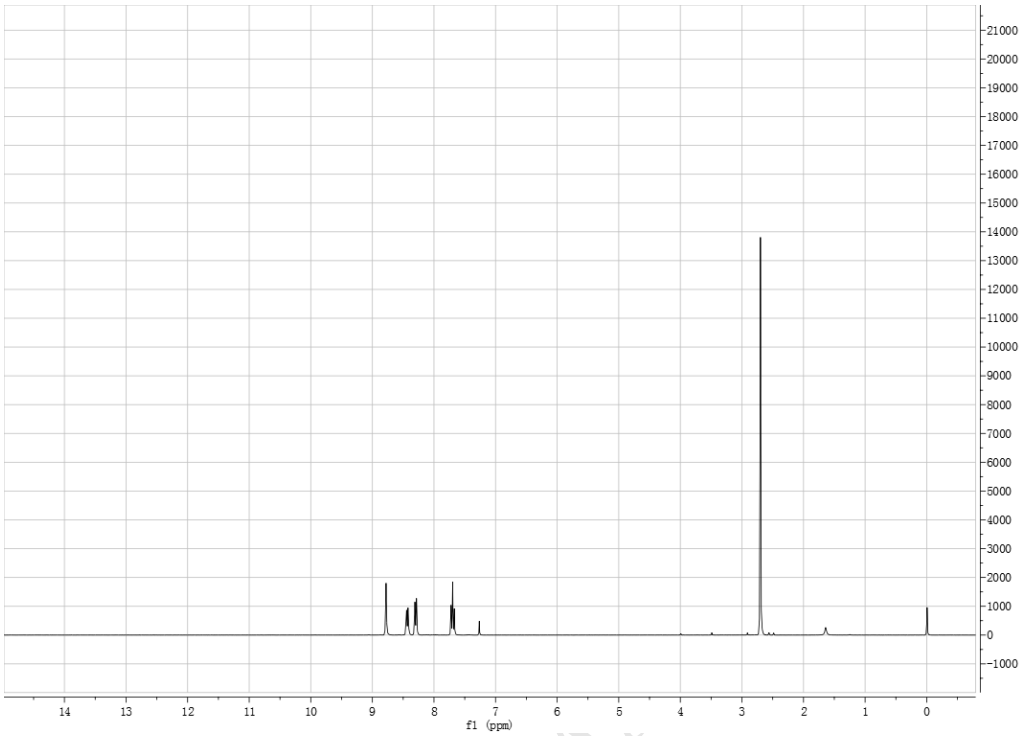

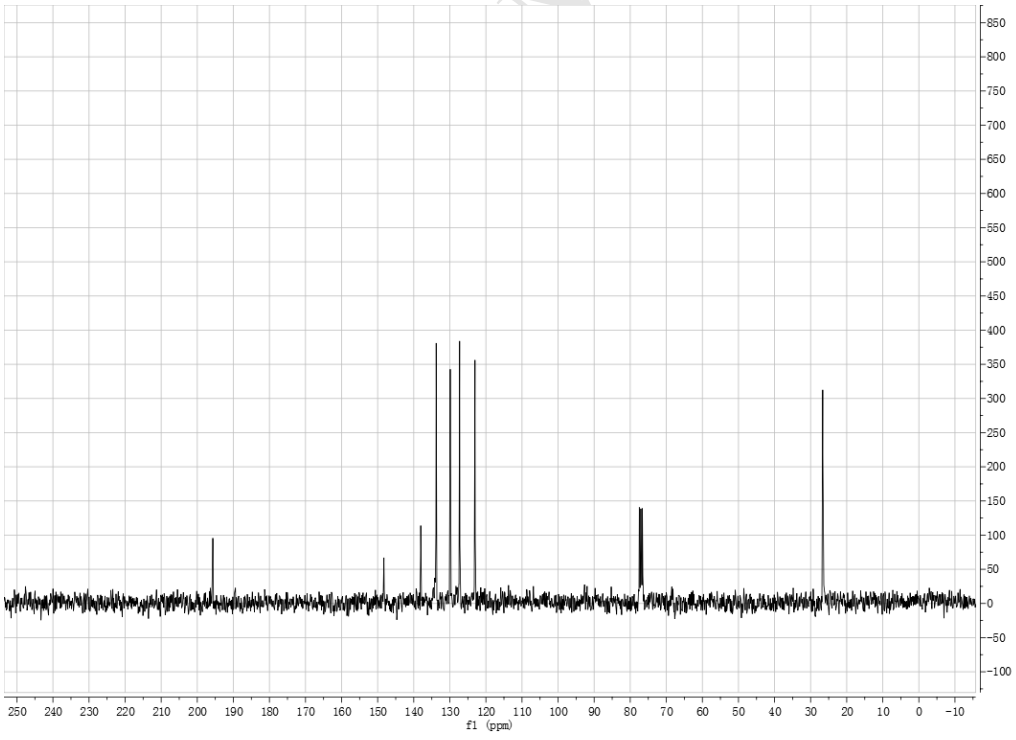

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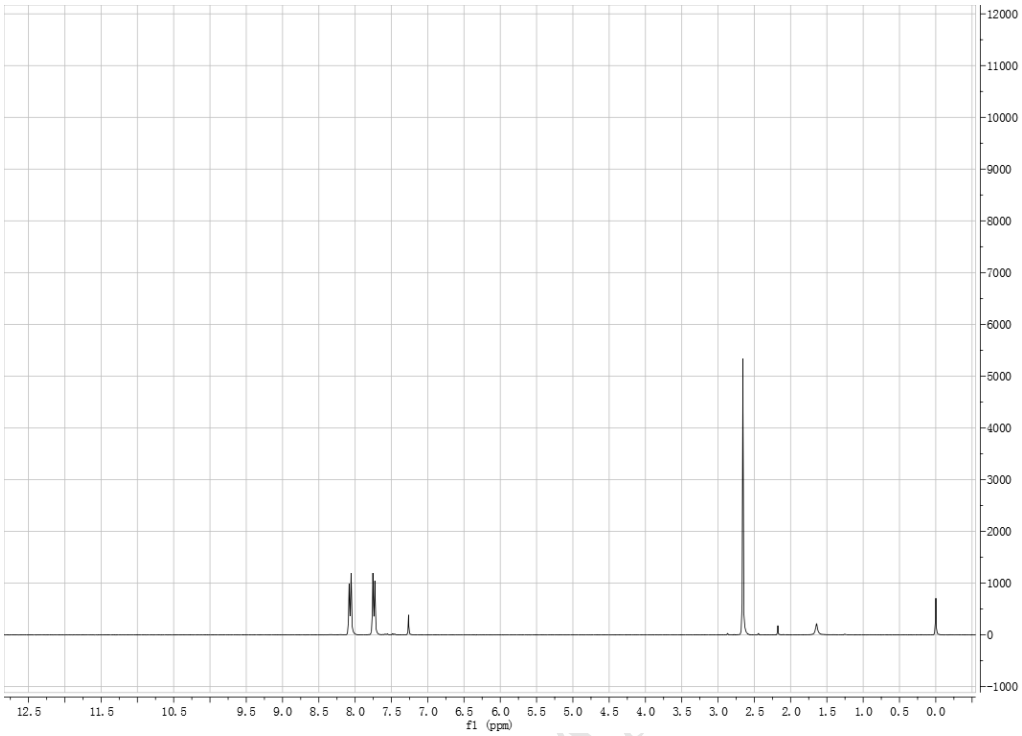

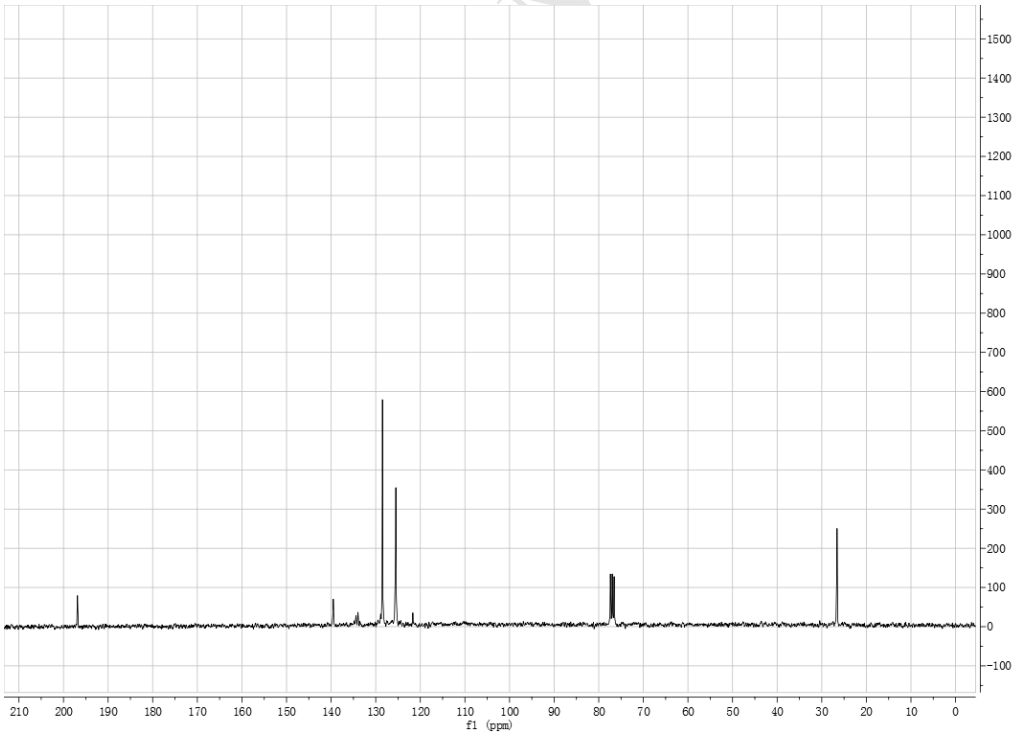

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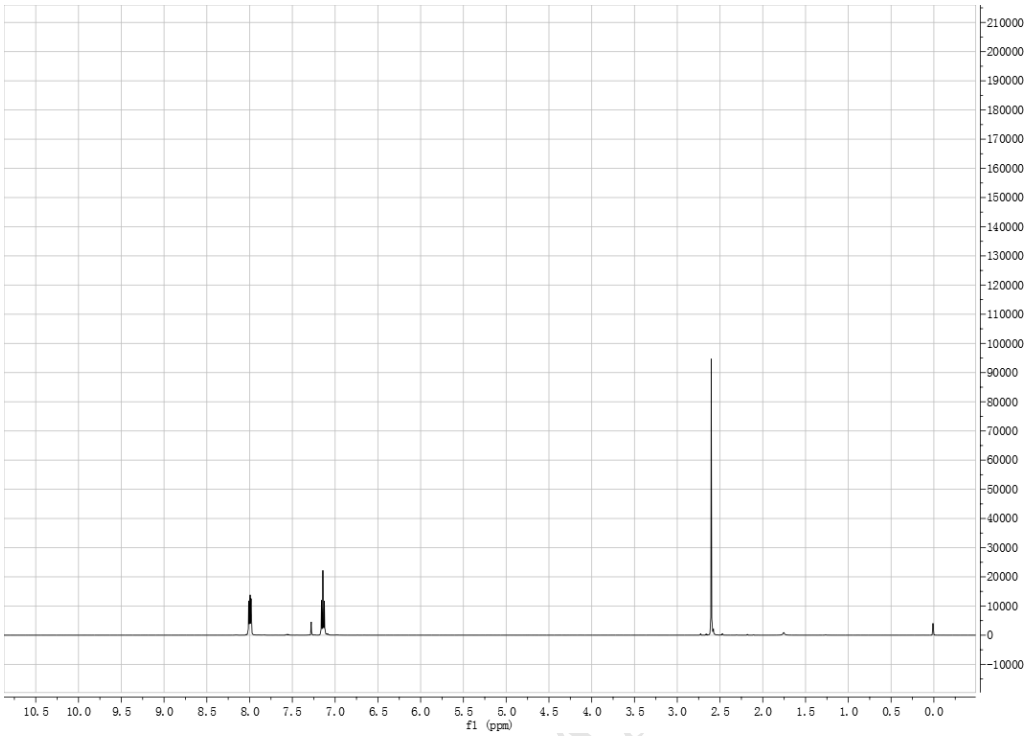

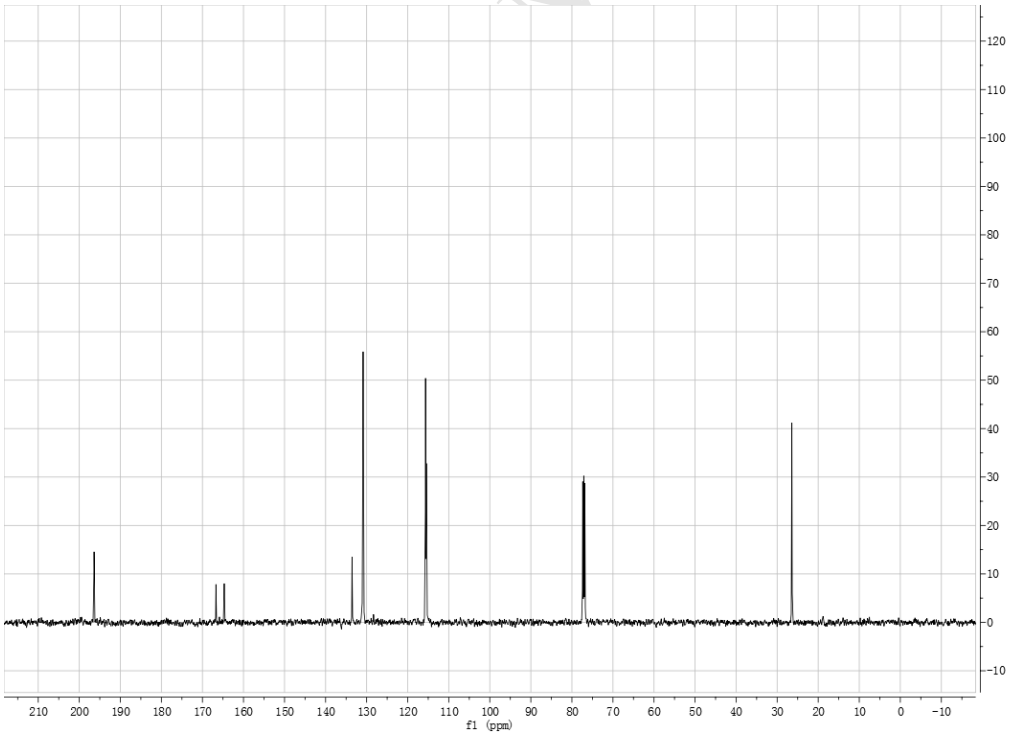

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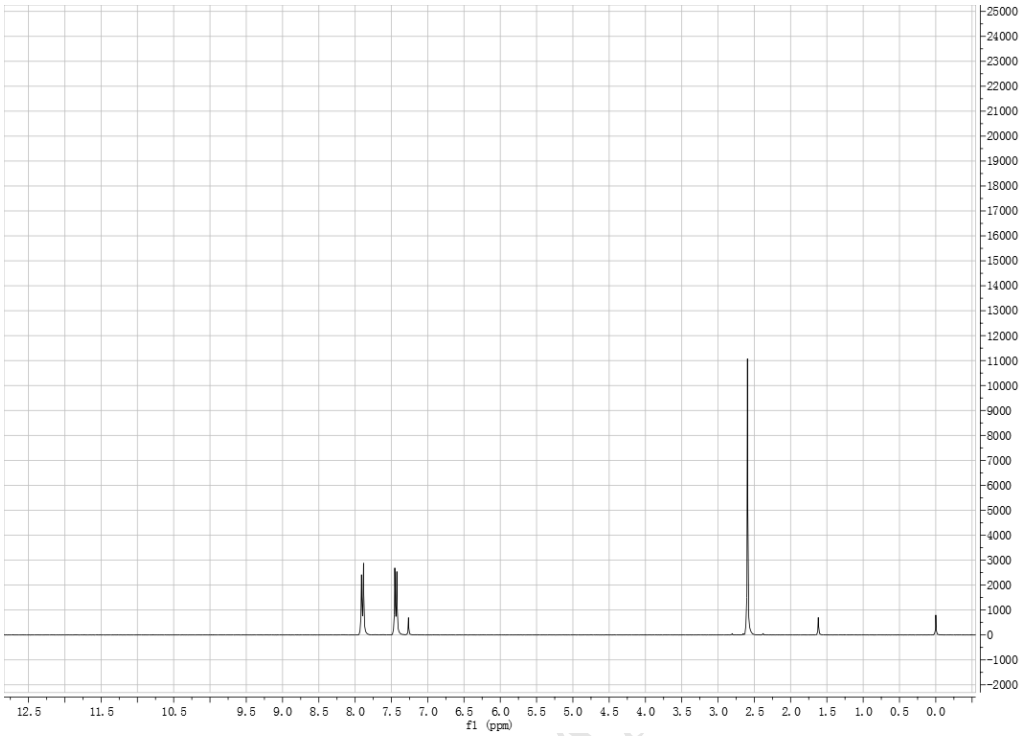

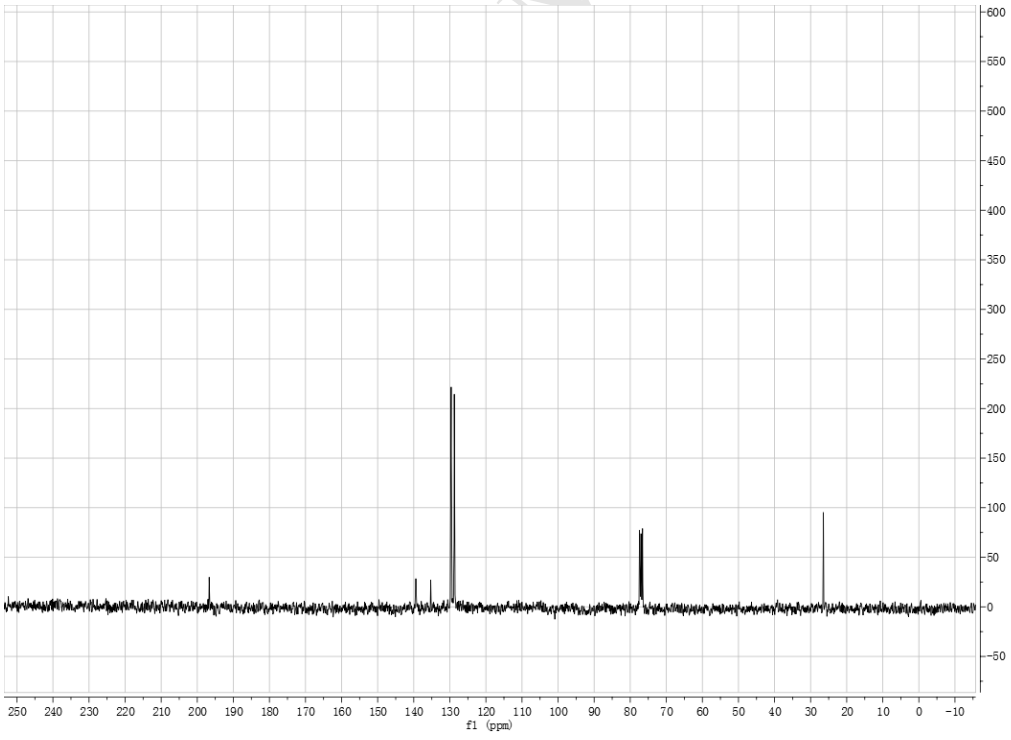

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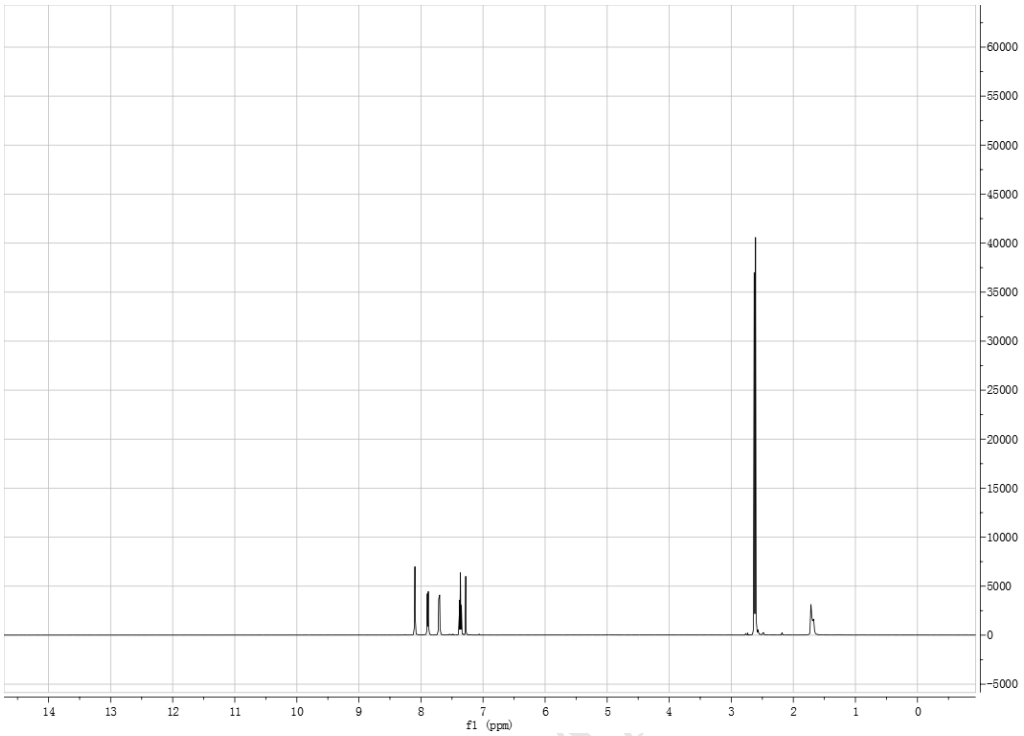

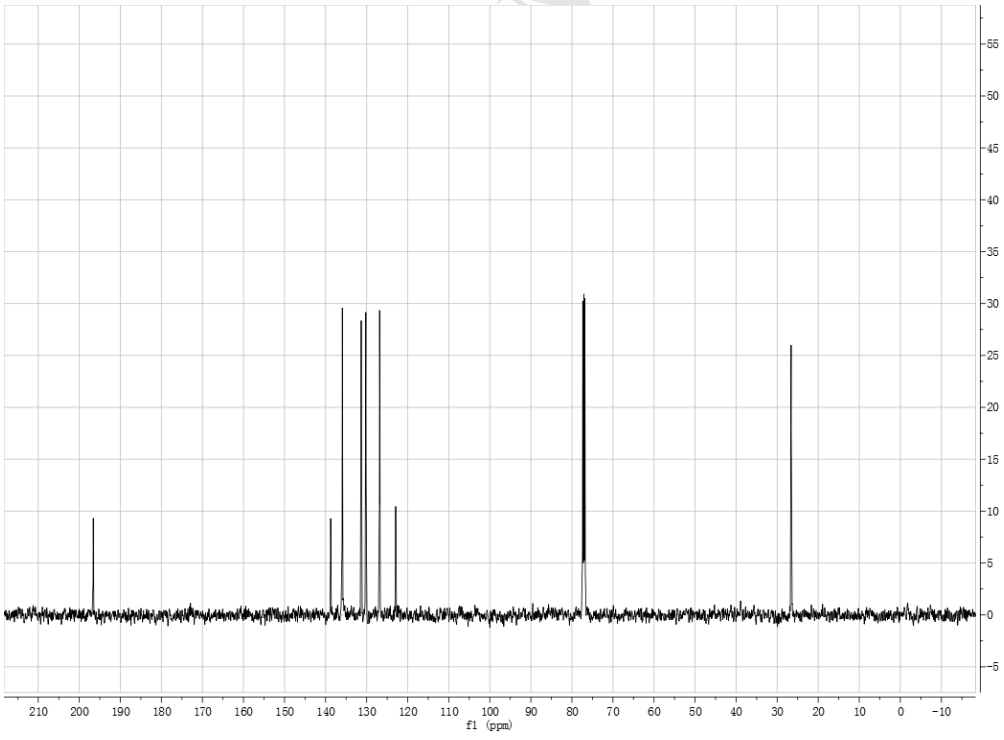

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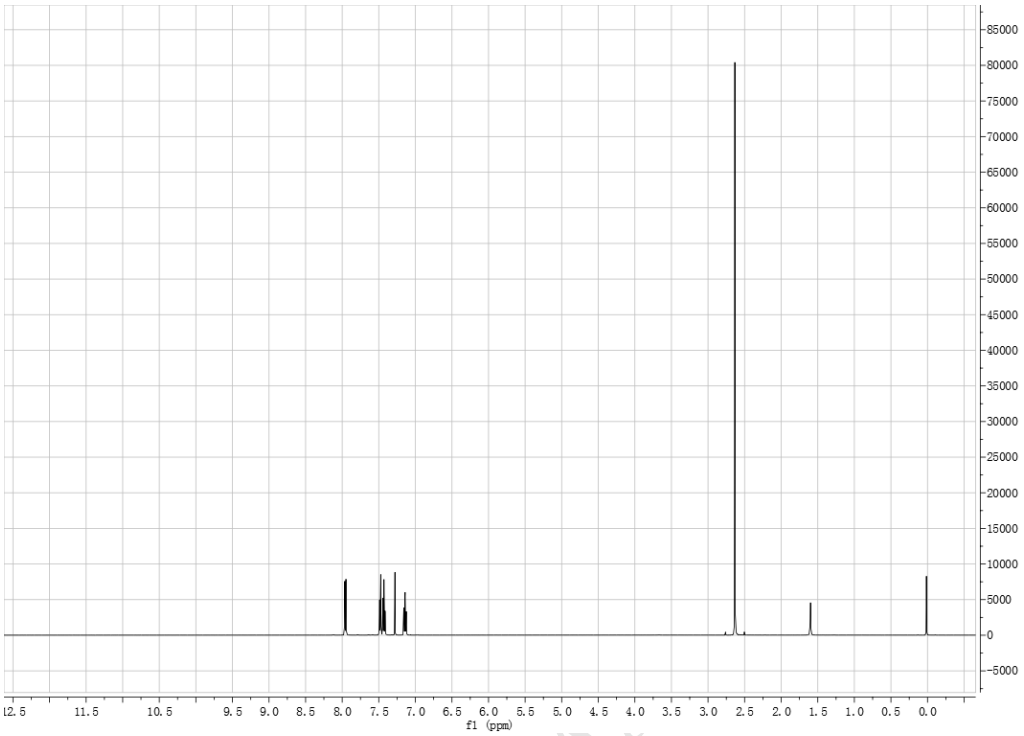

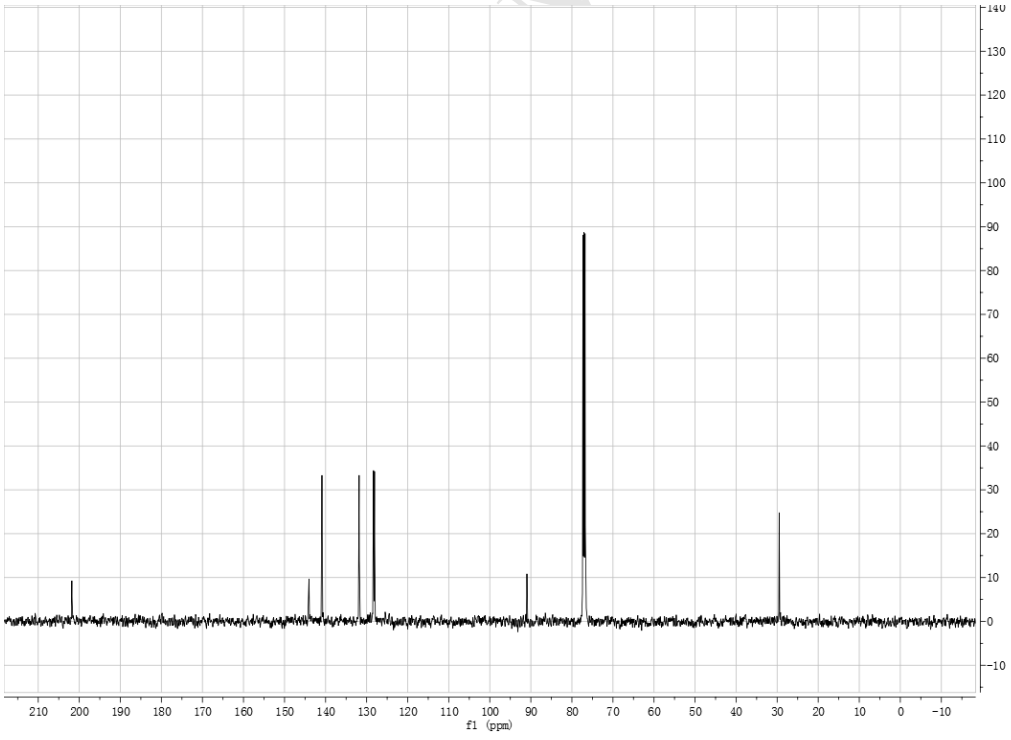

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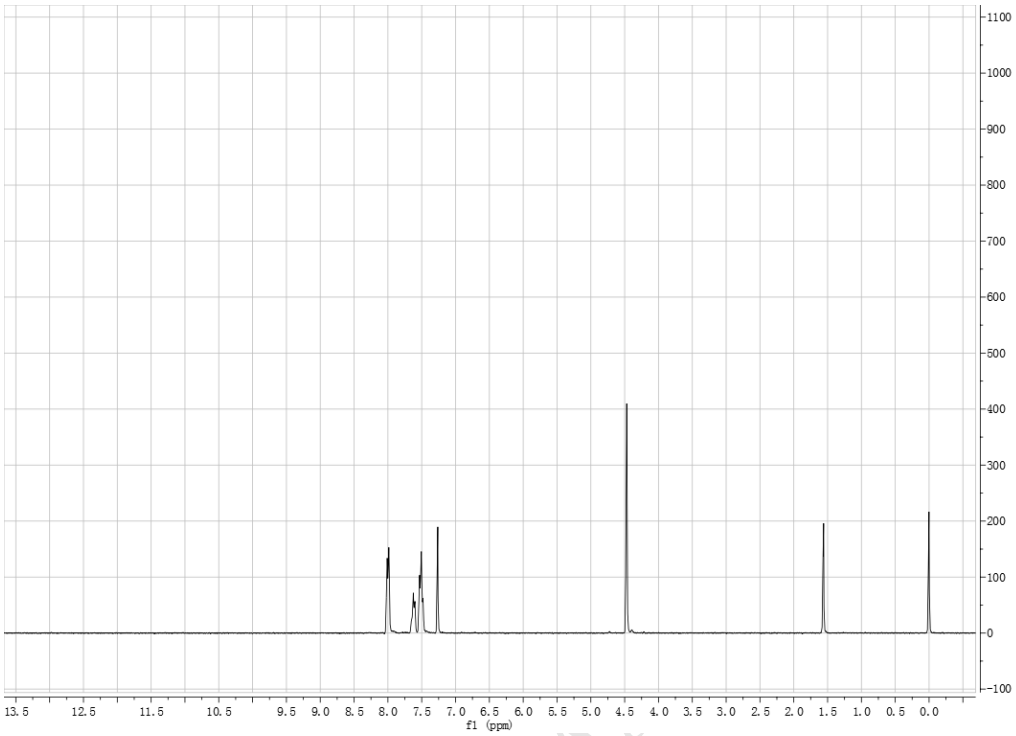

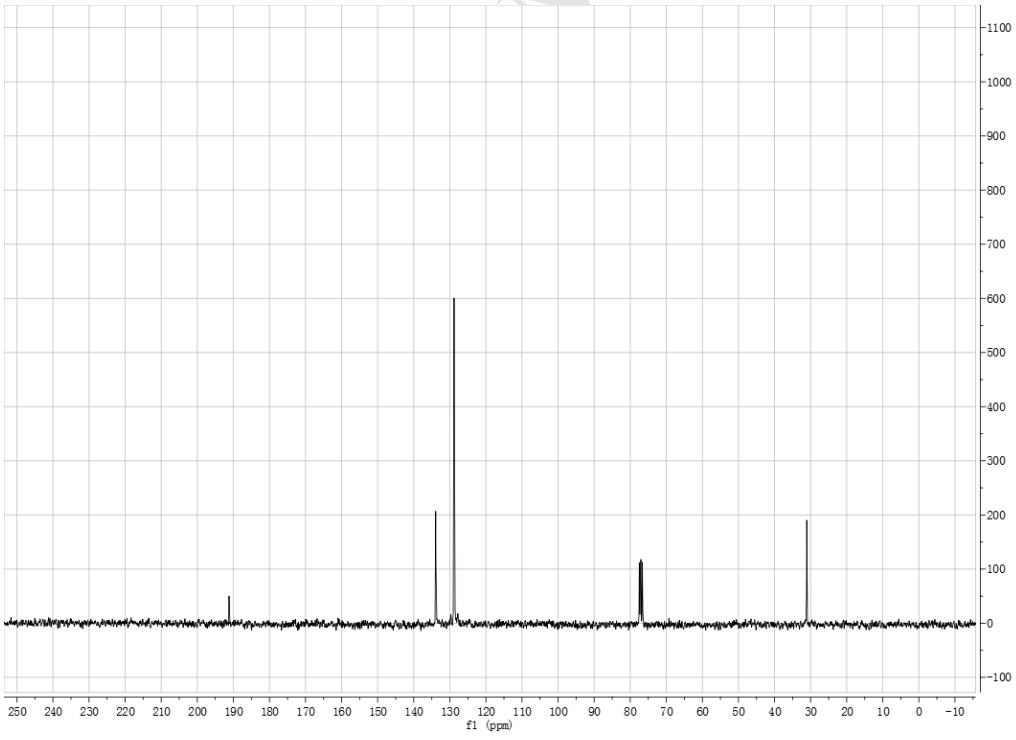

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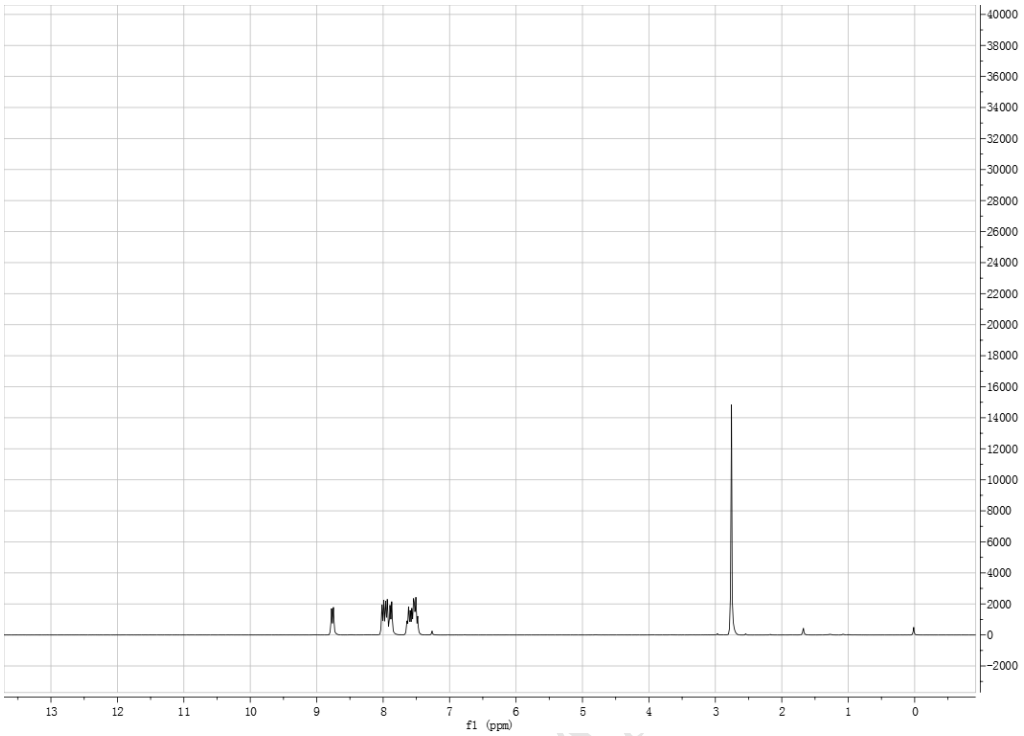
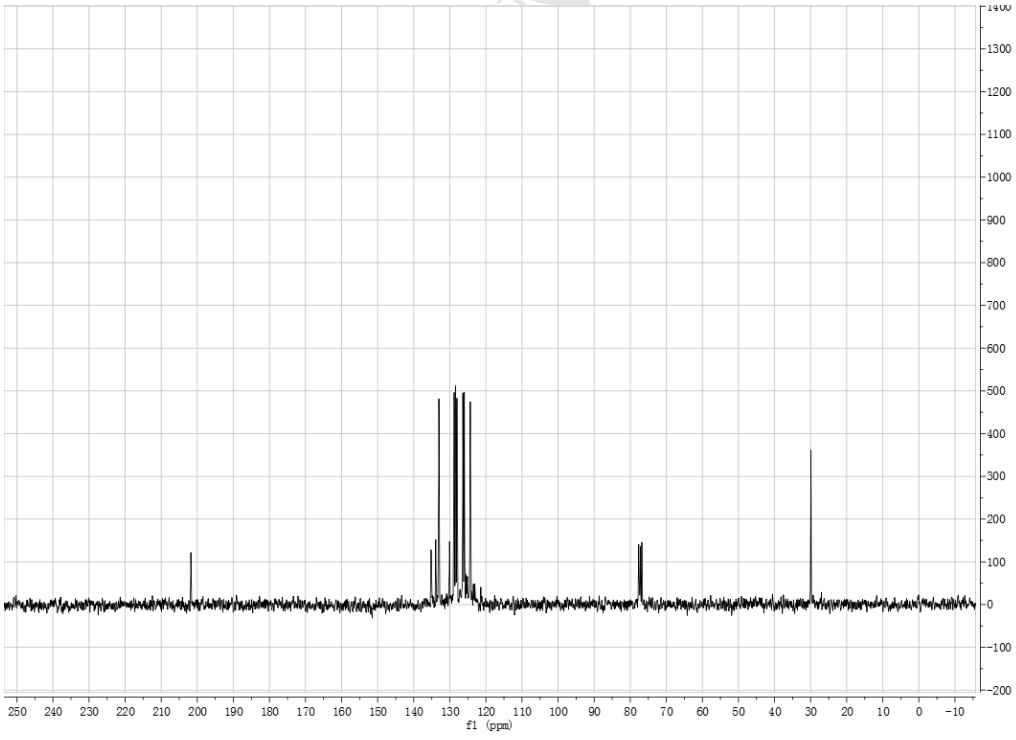
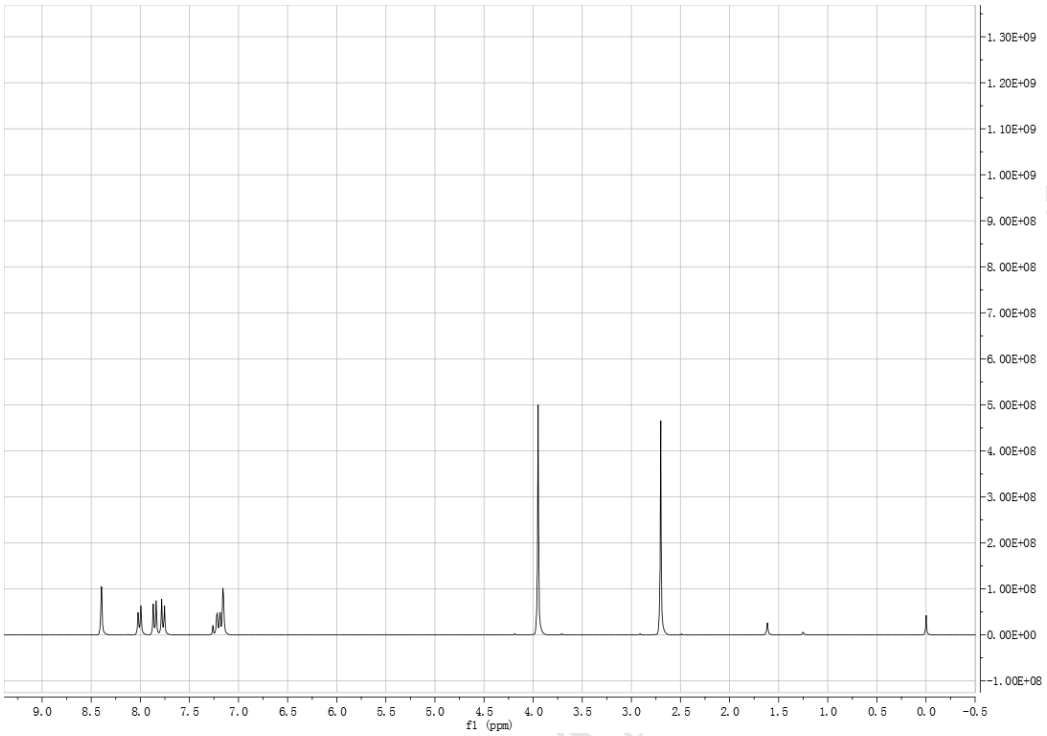
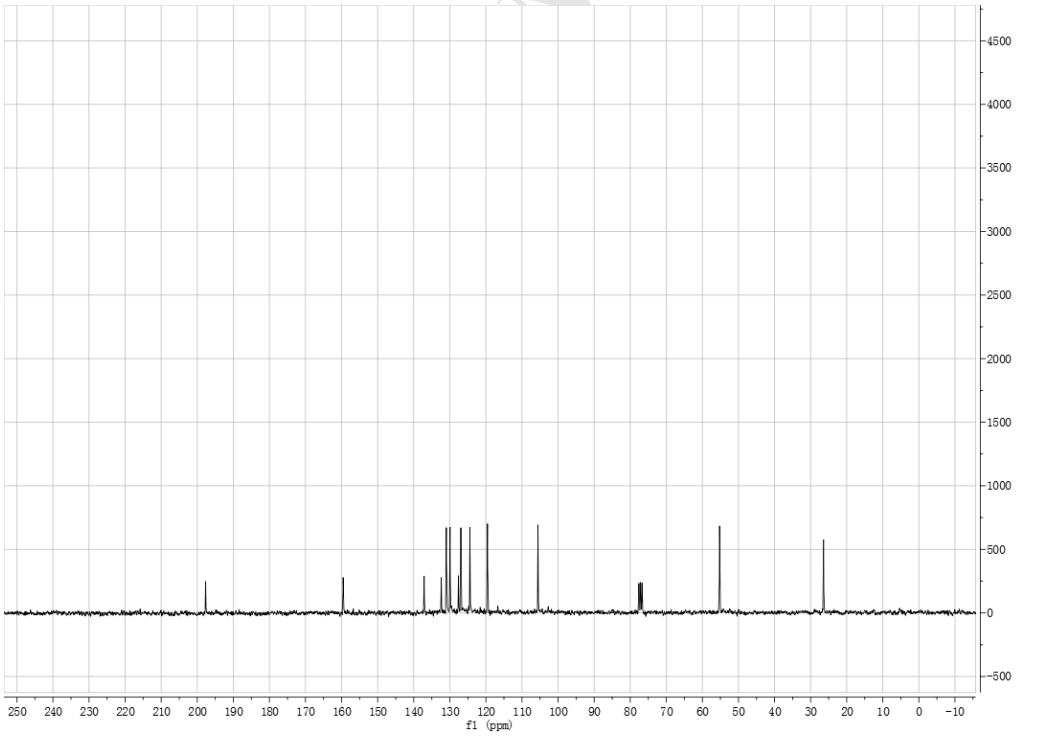


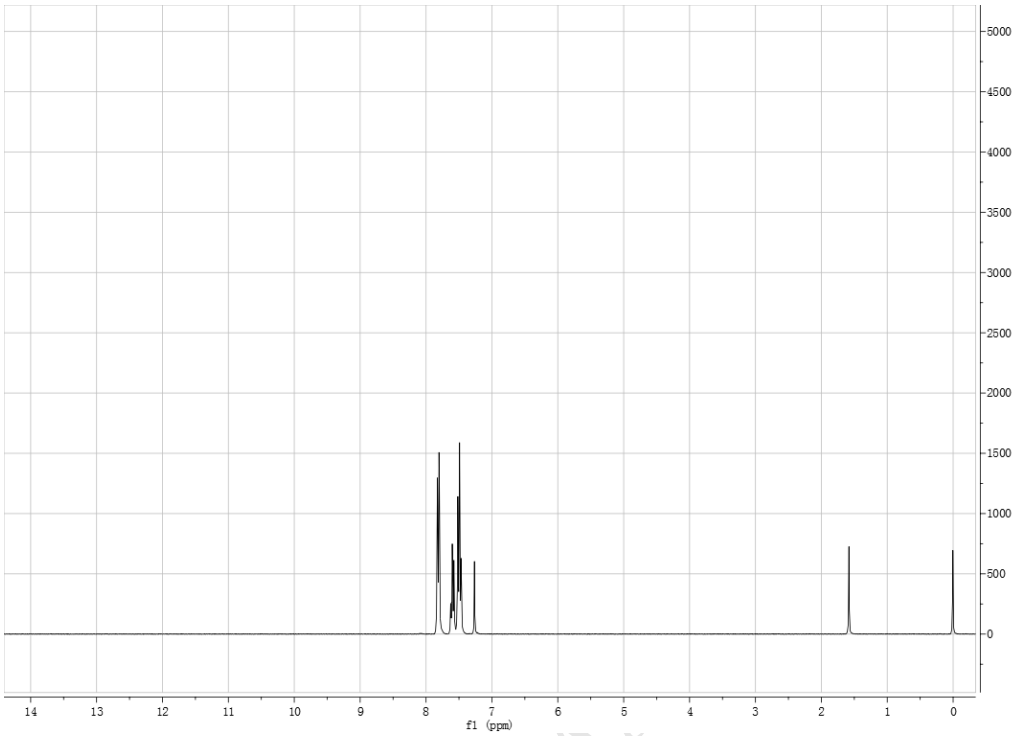


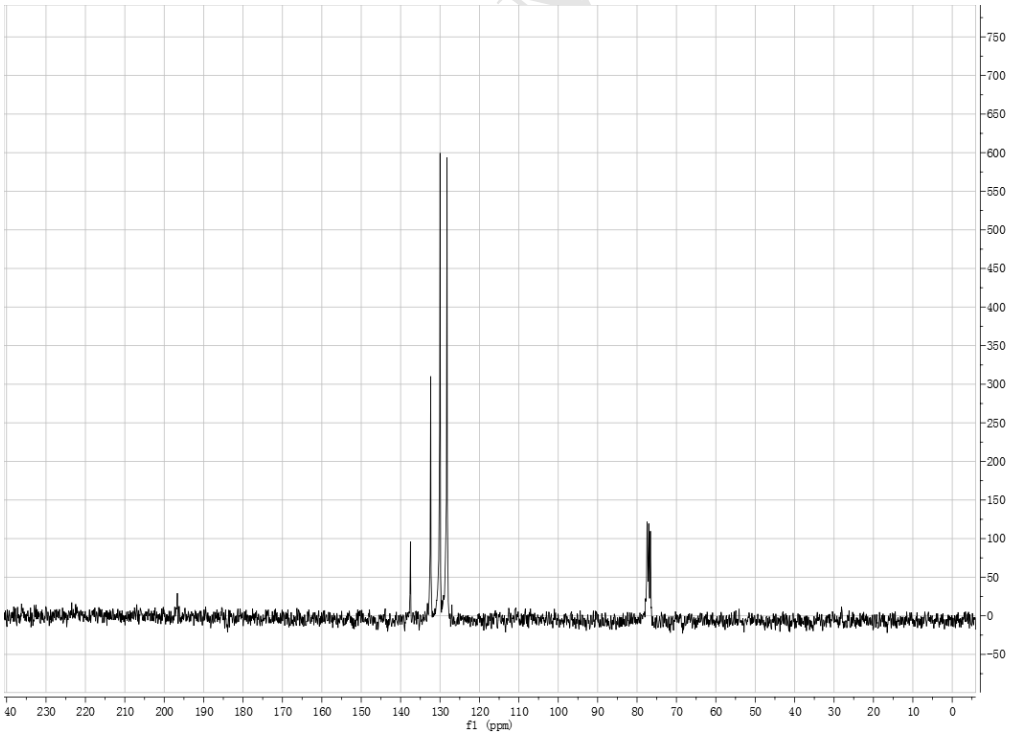
2-Acetyl-6-methoxy naphthalene (**2l**)





Benzophenone (**2m**)





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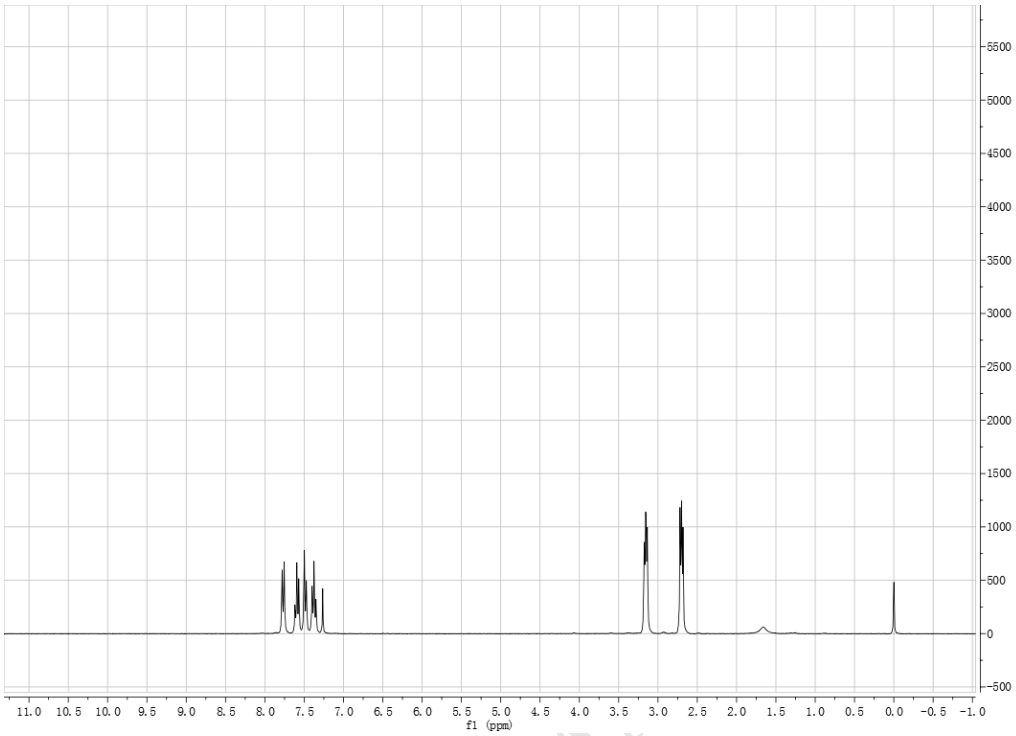

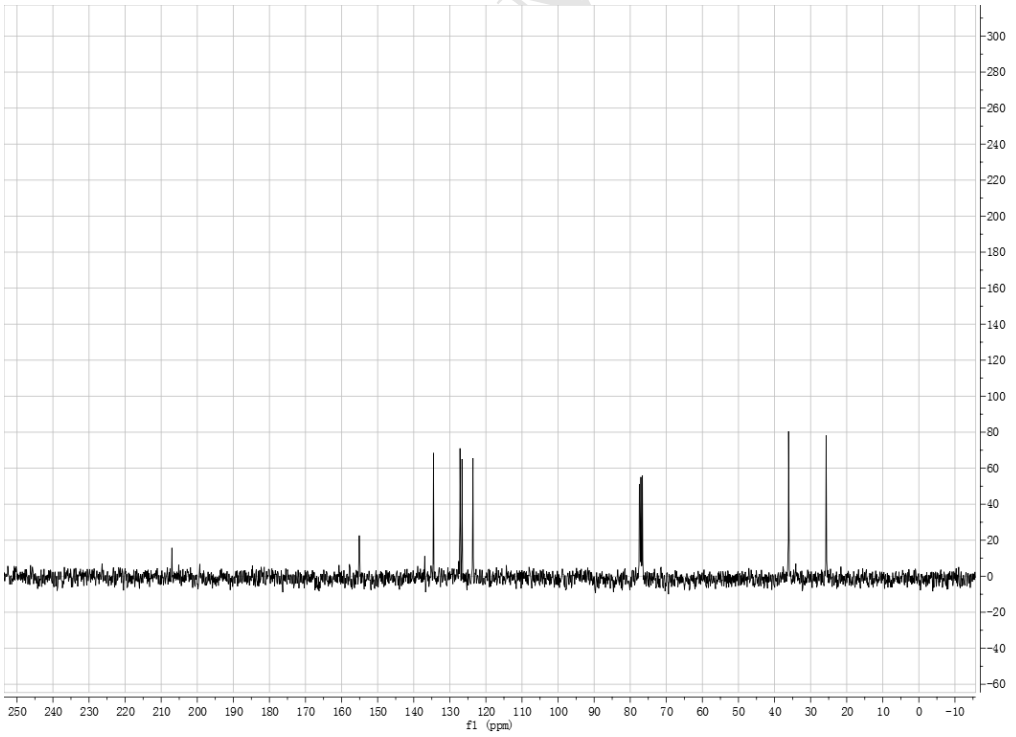

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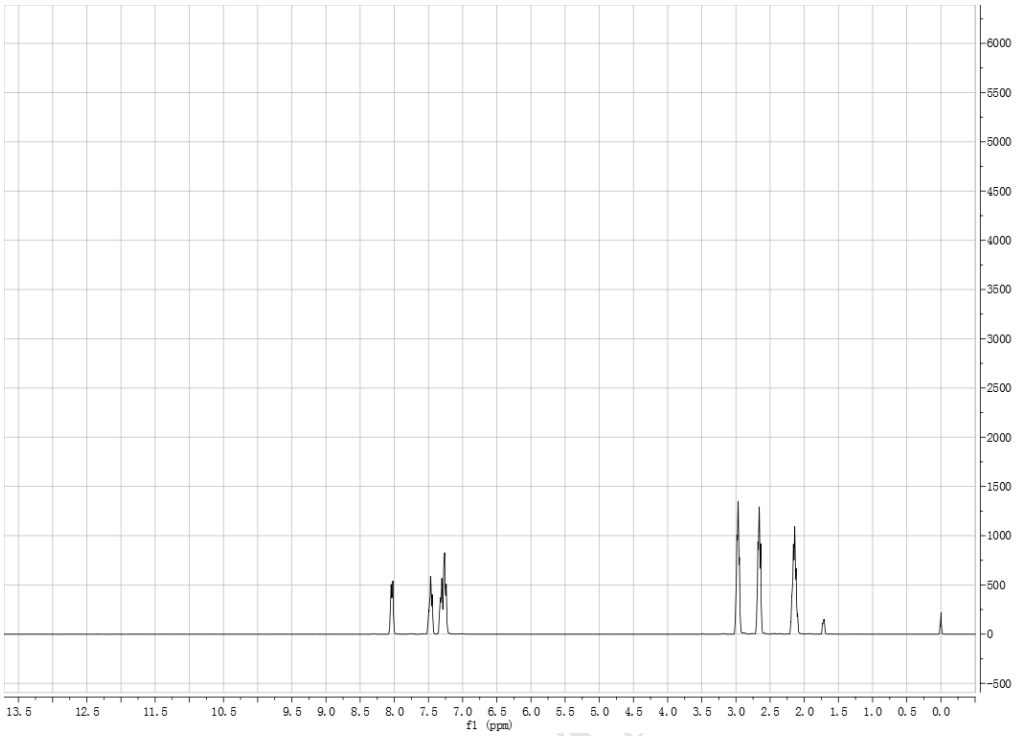

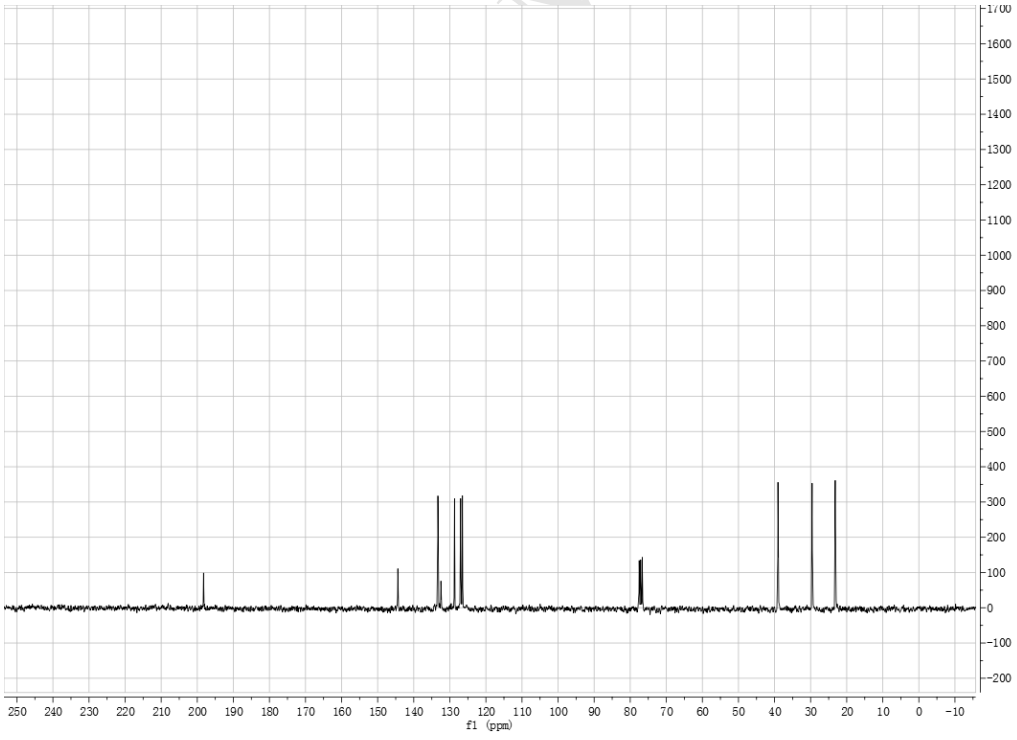

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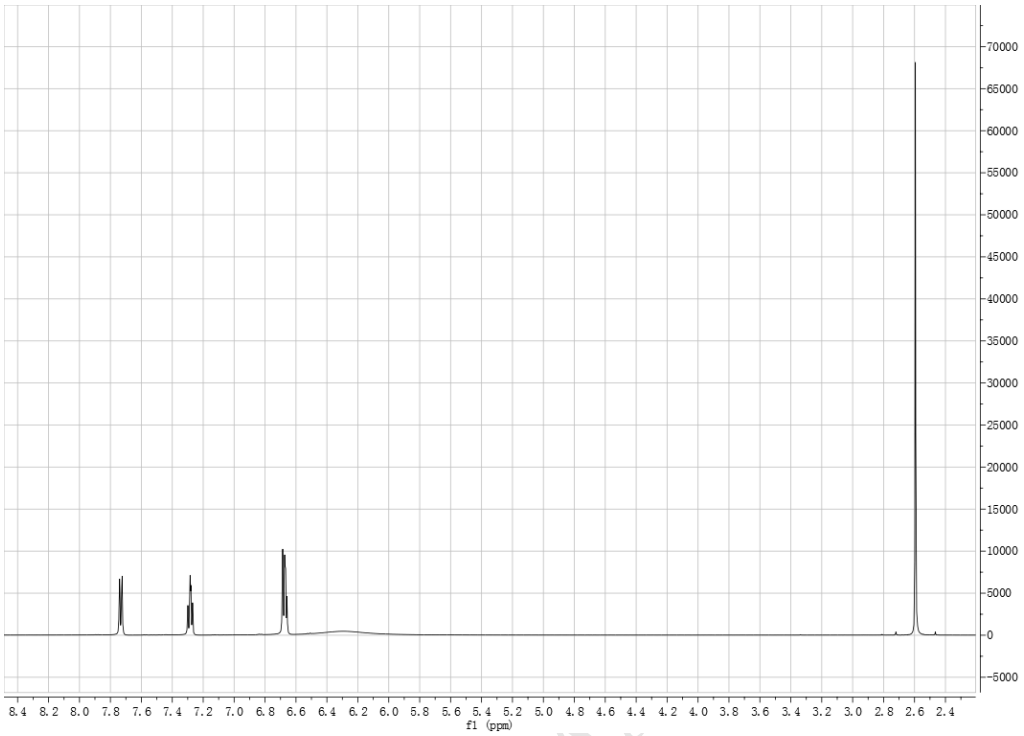

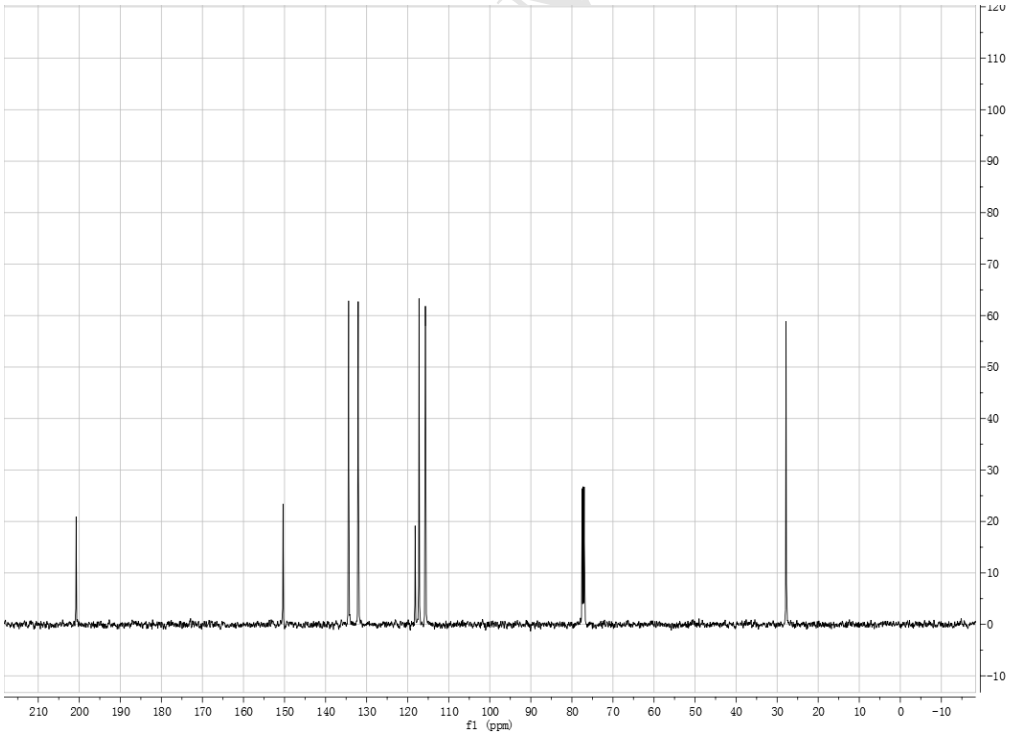

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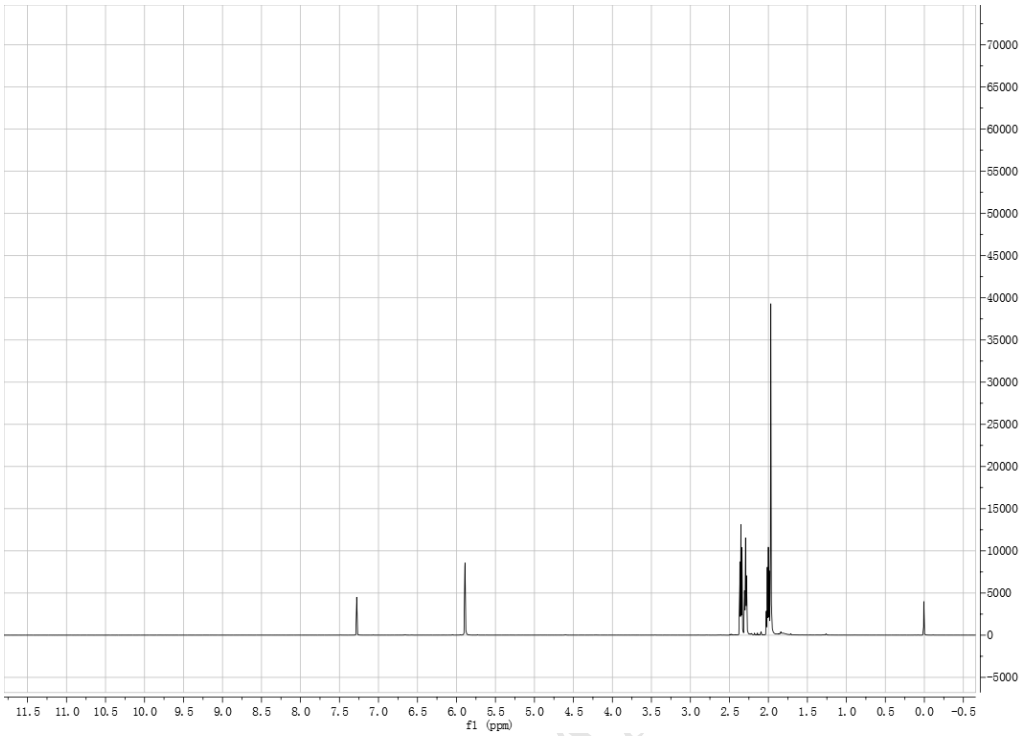

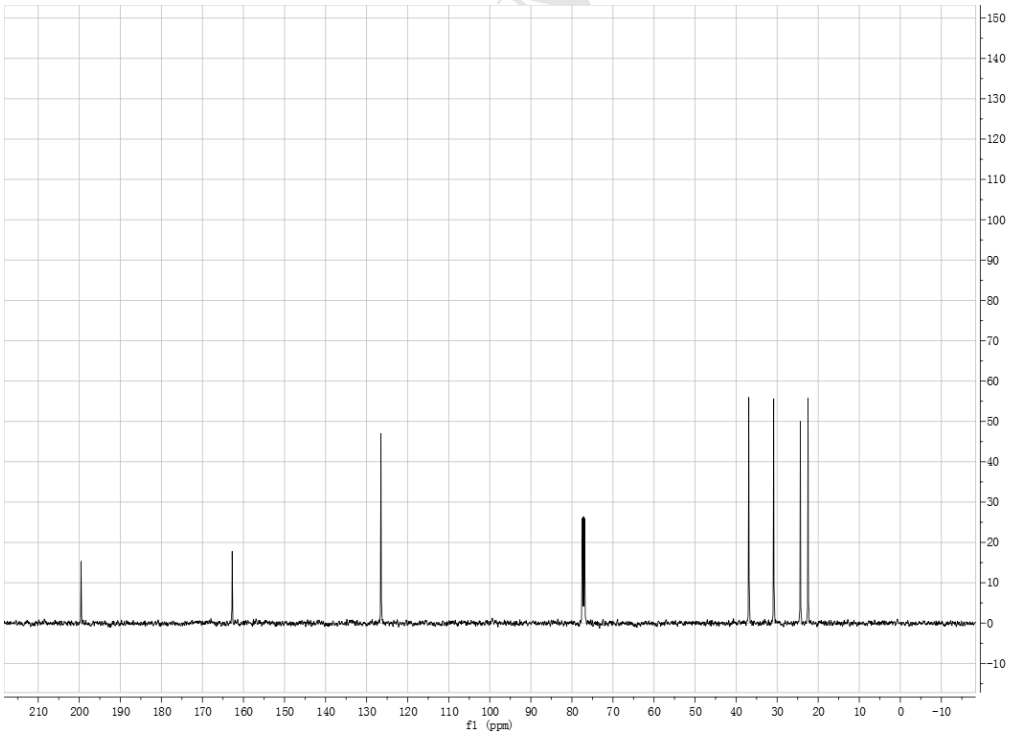

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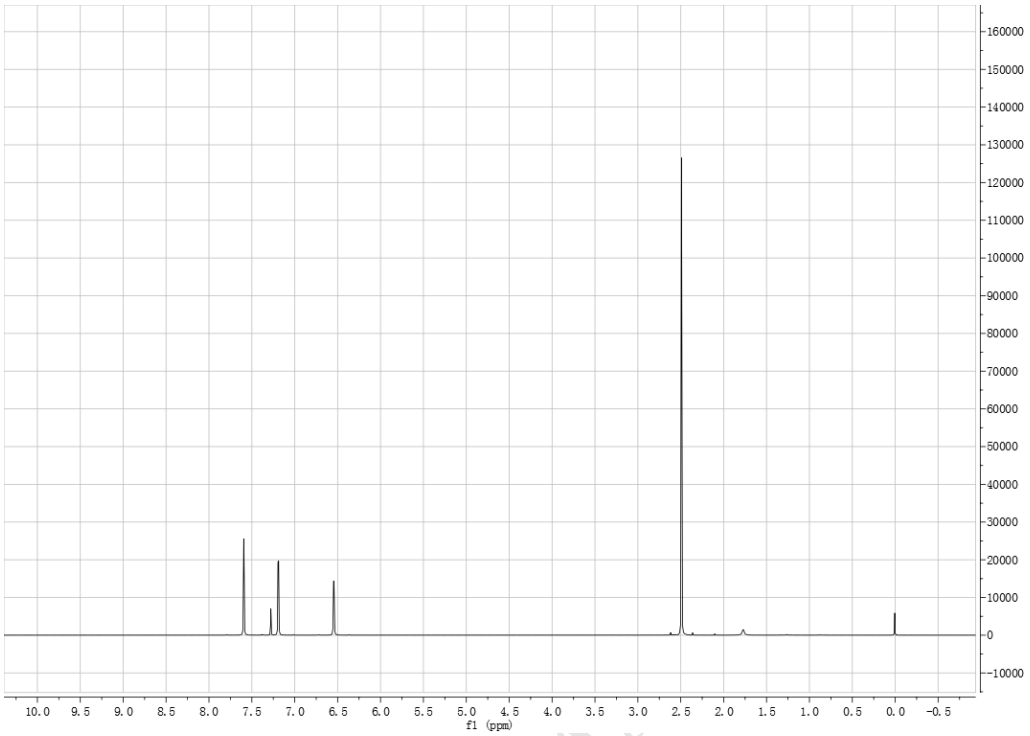

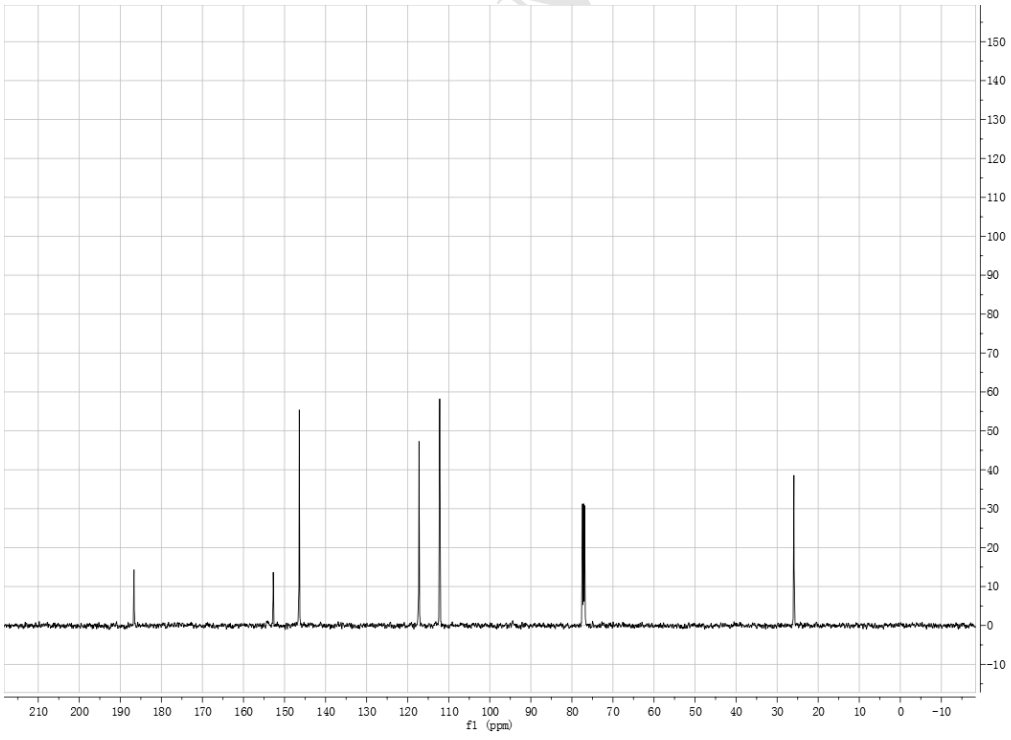

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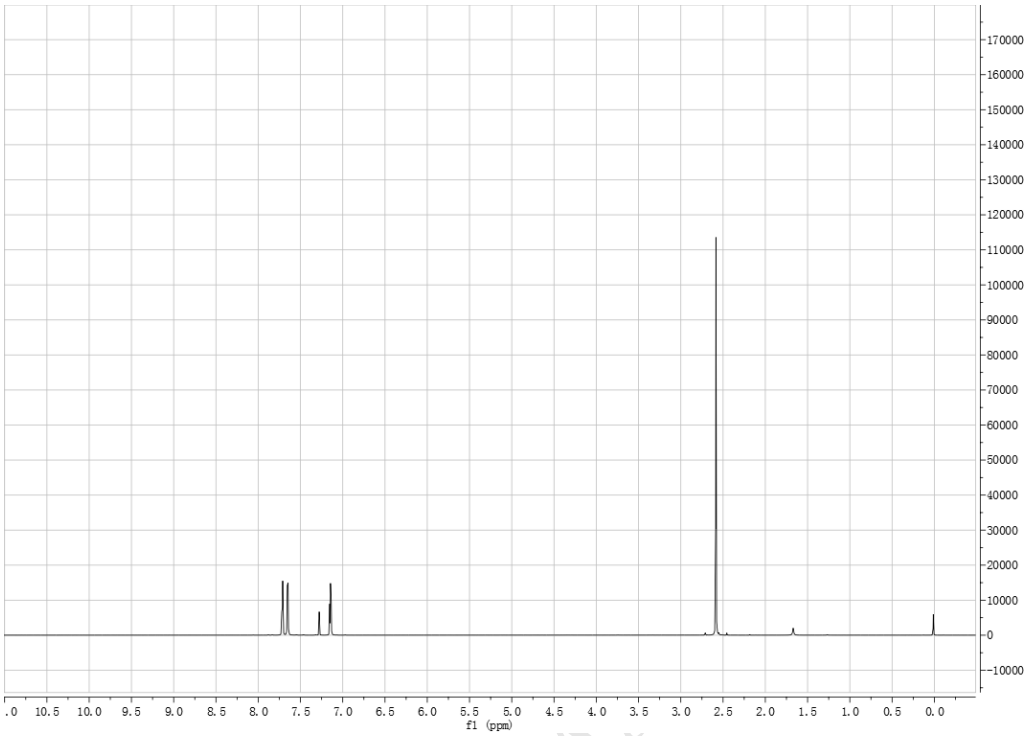

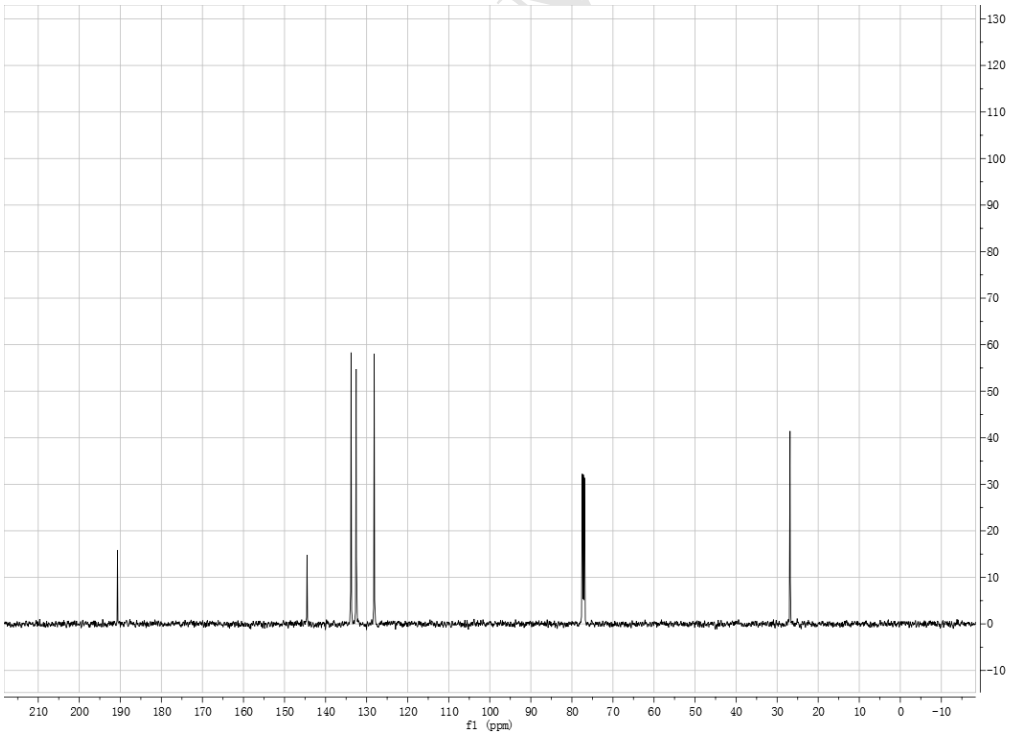

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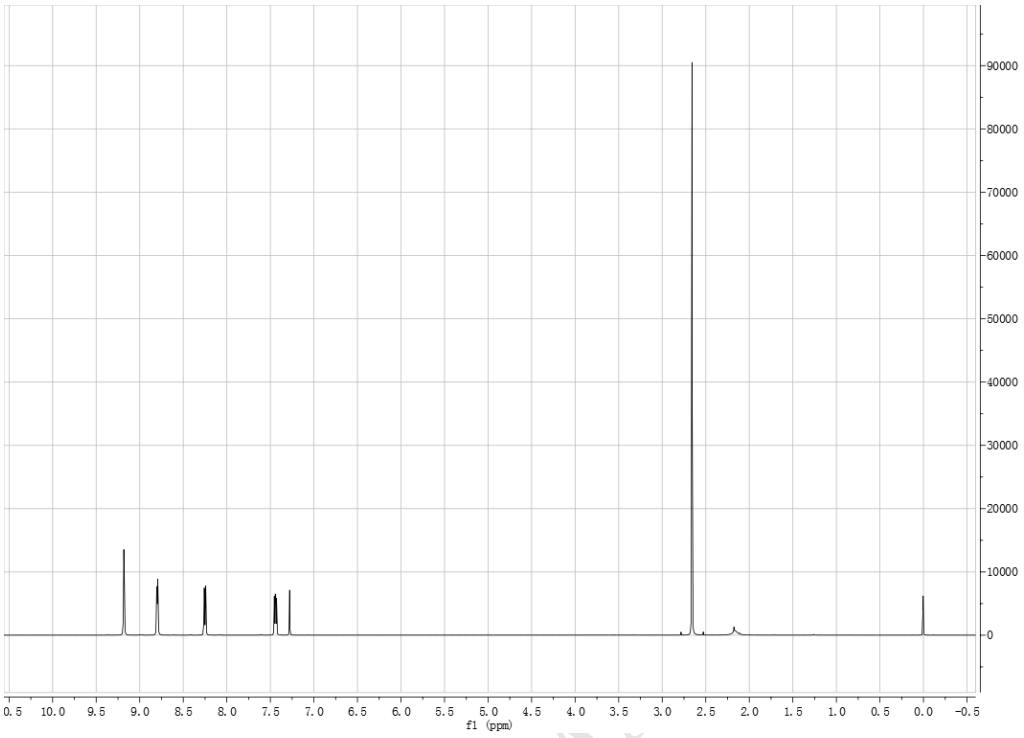

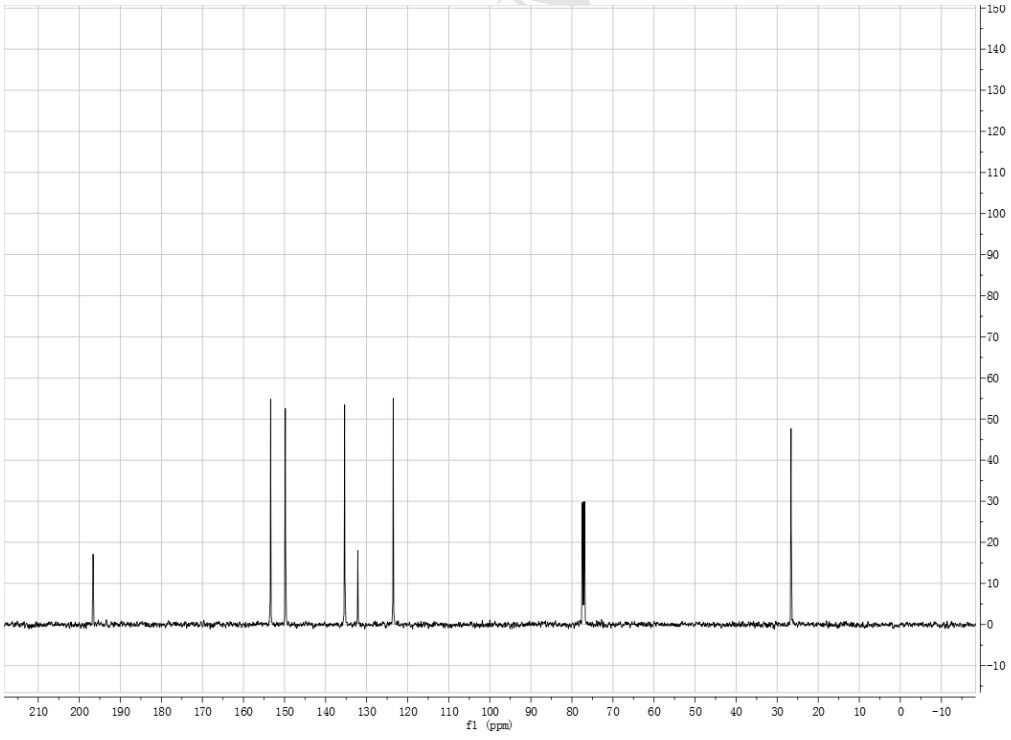

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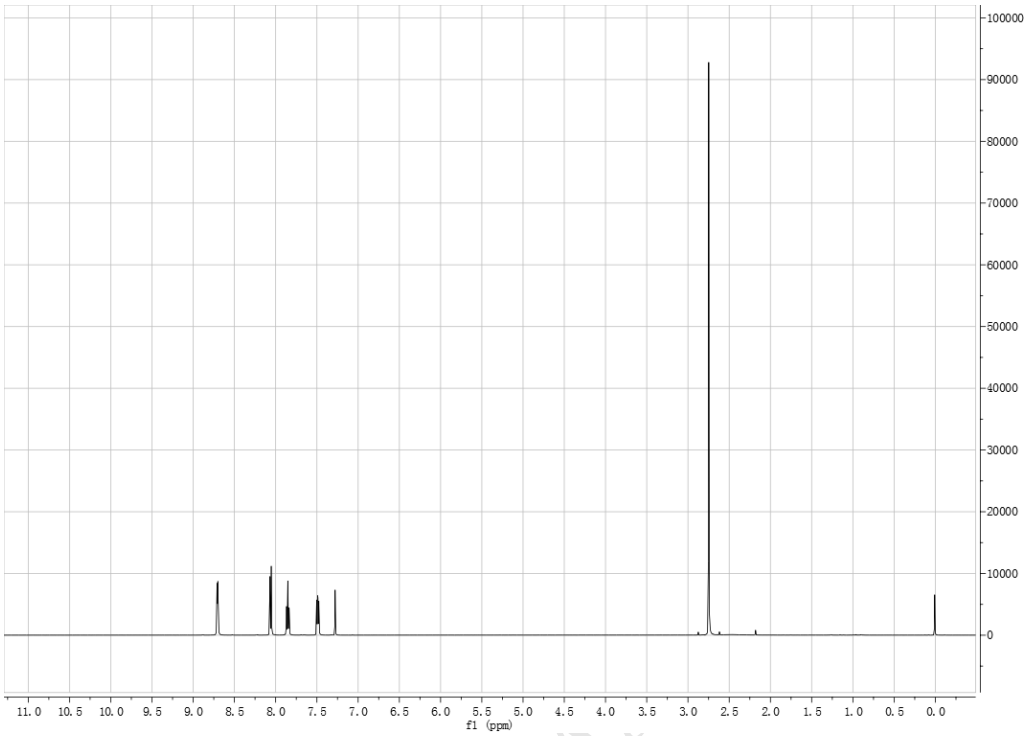

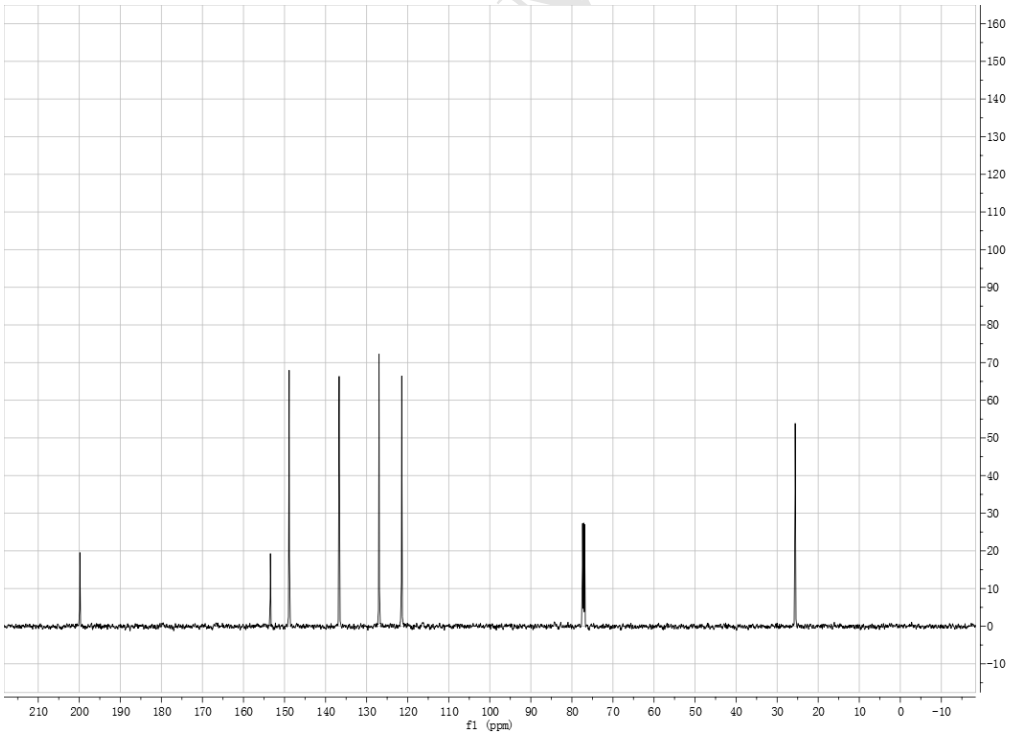

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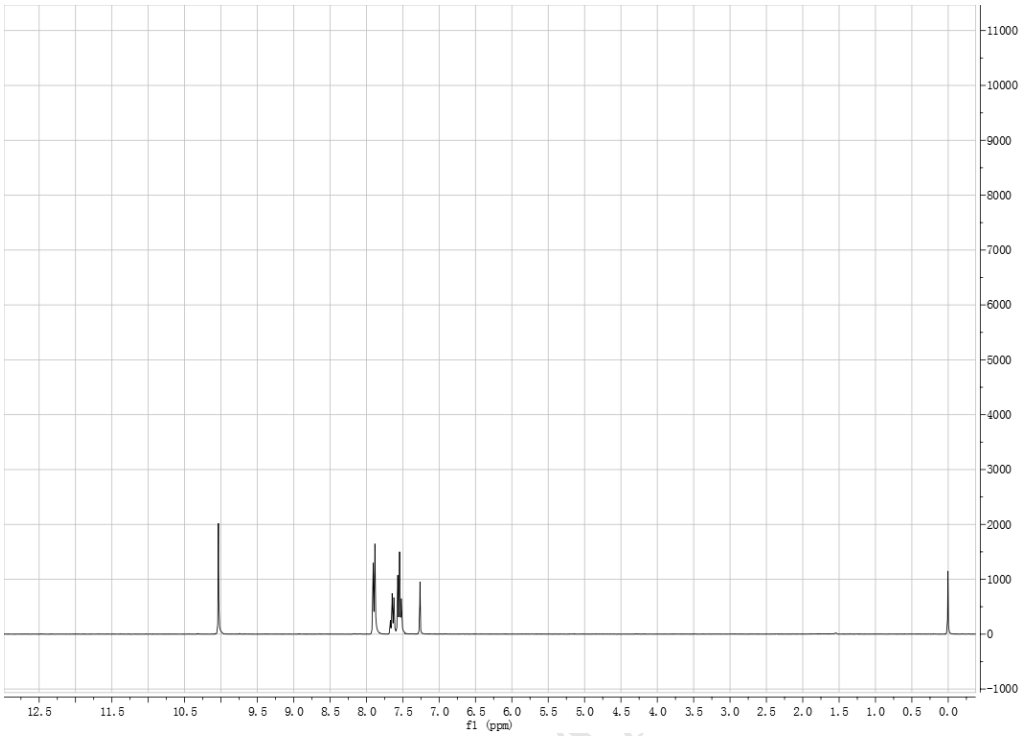

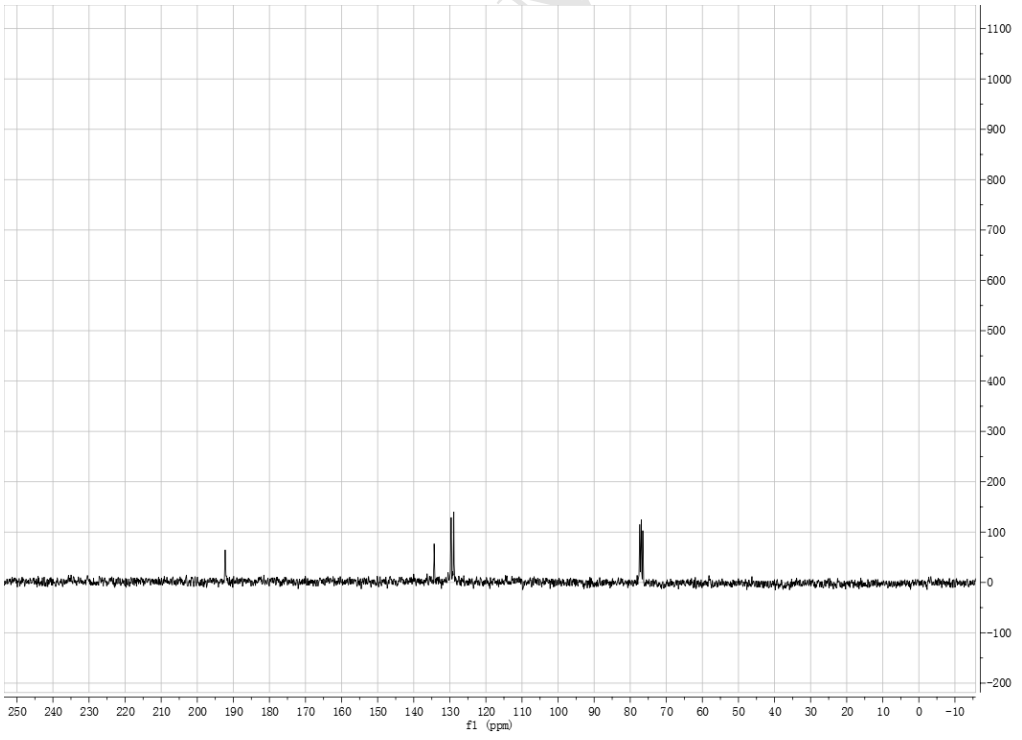

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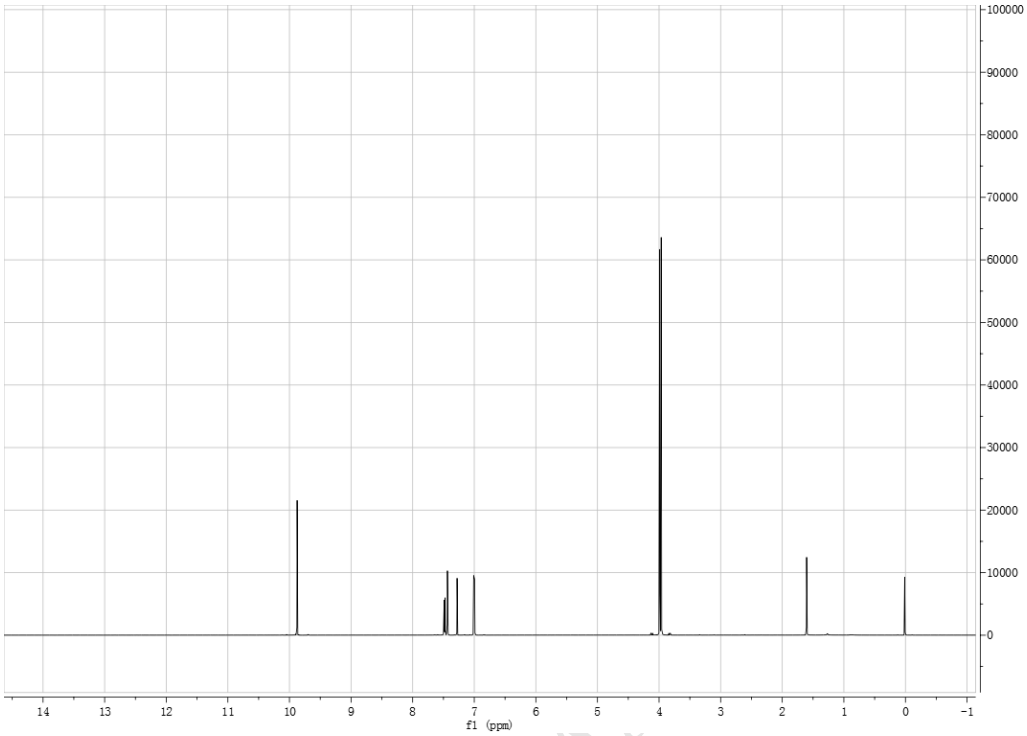
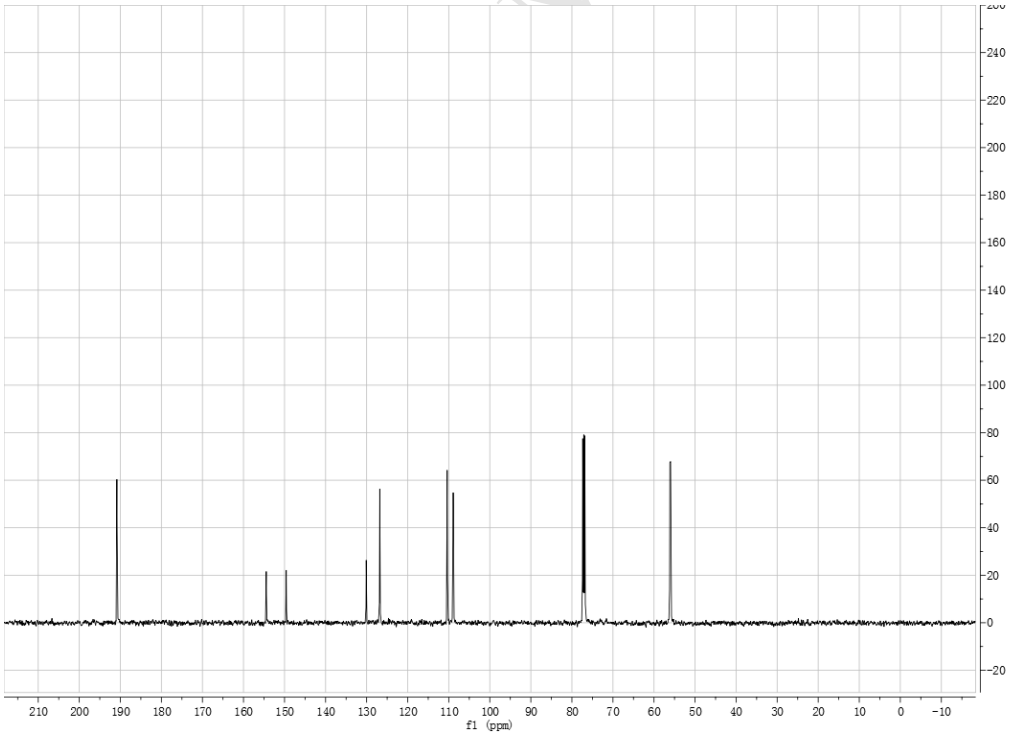
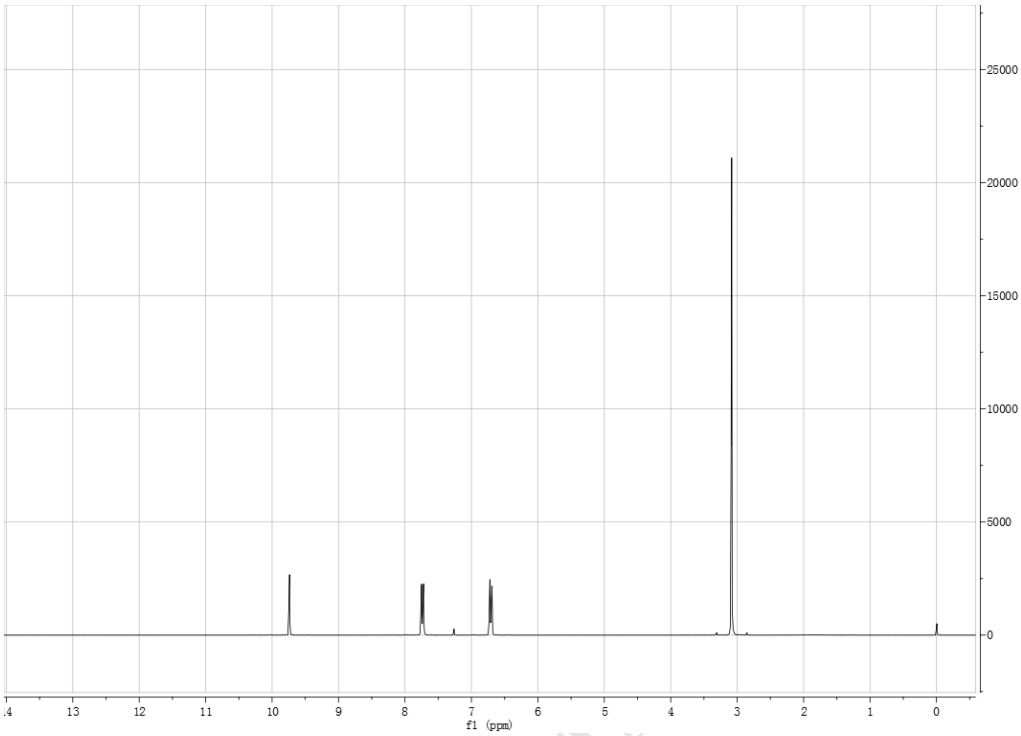
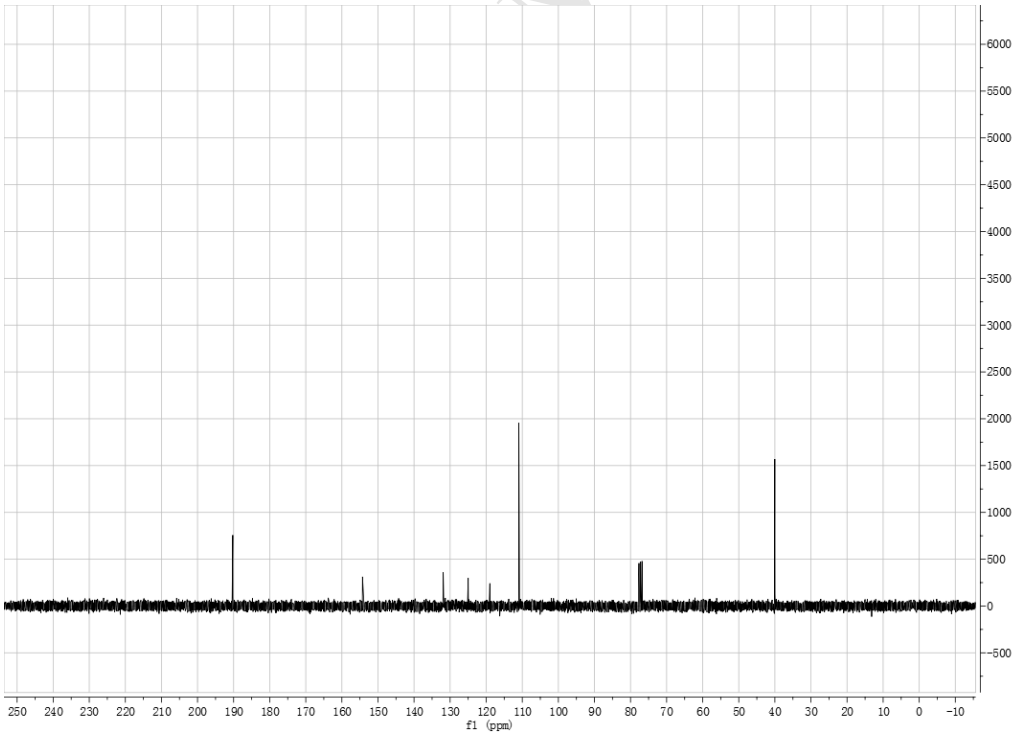


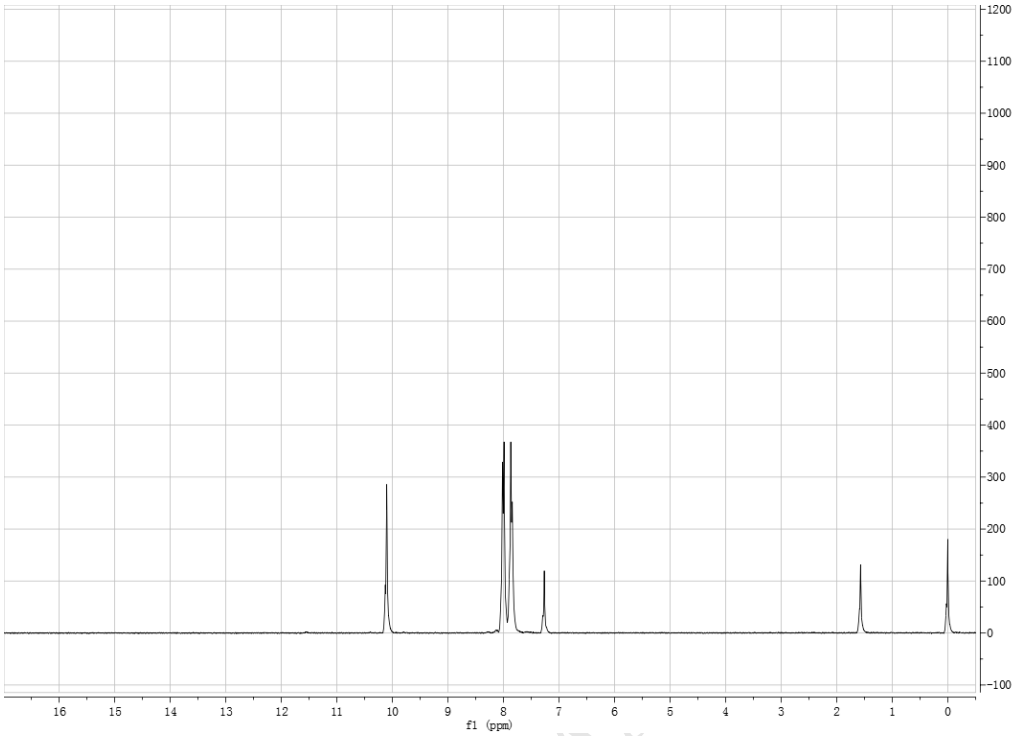


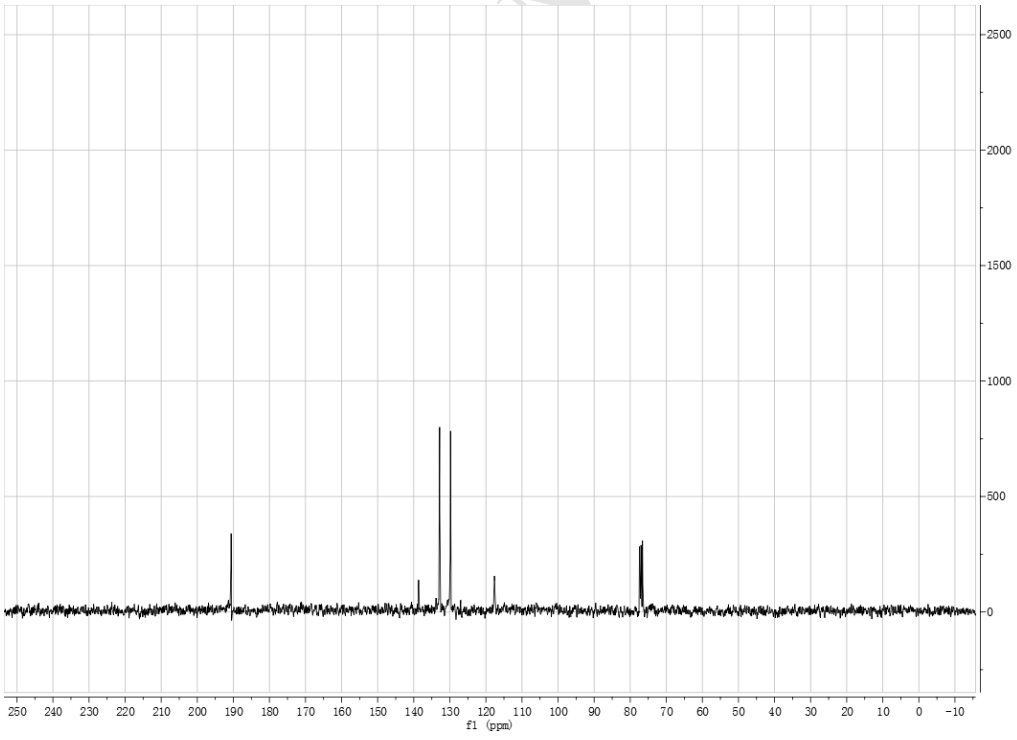
4-Dimethylaminobenzaldehyde (**4c**)



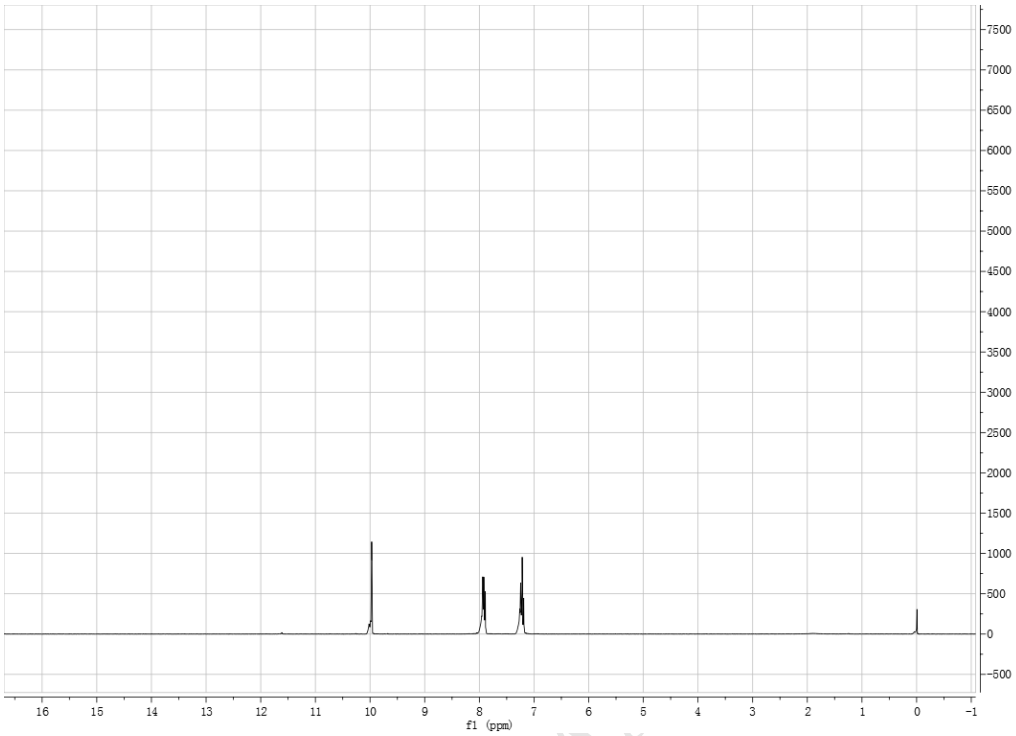


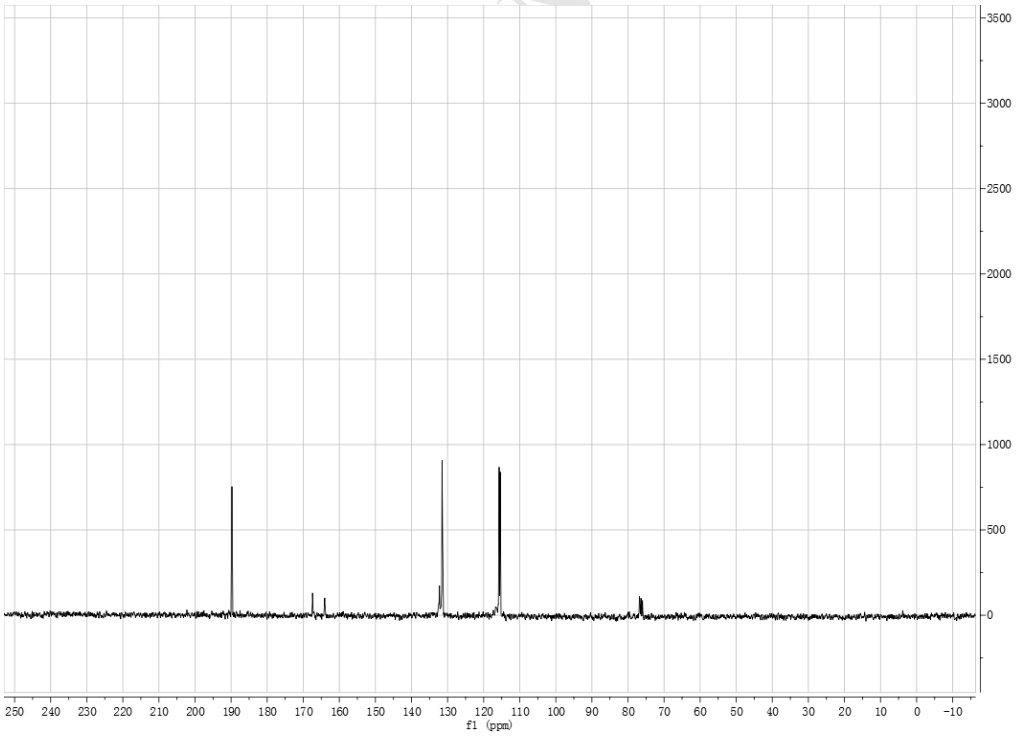
4-Formylbenzonitrile (**4d**)



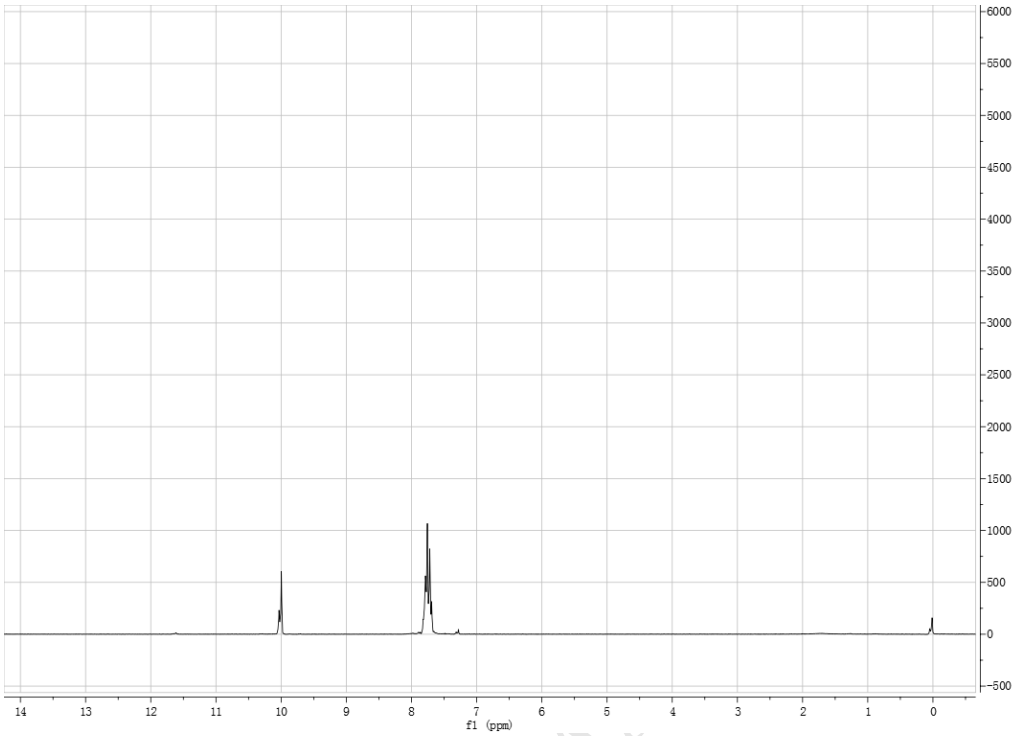


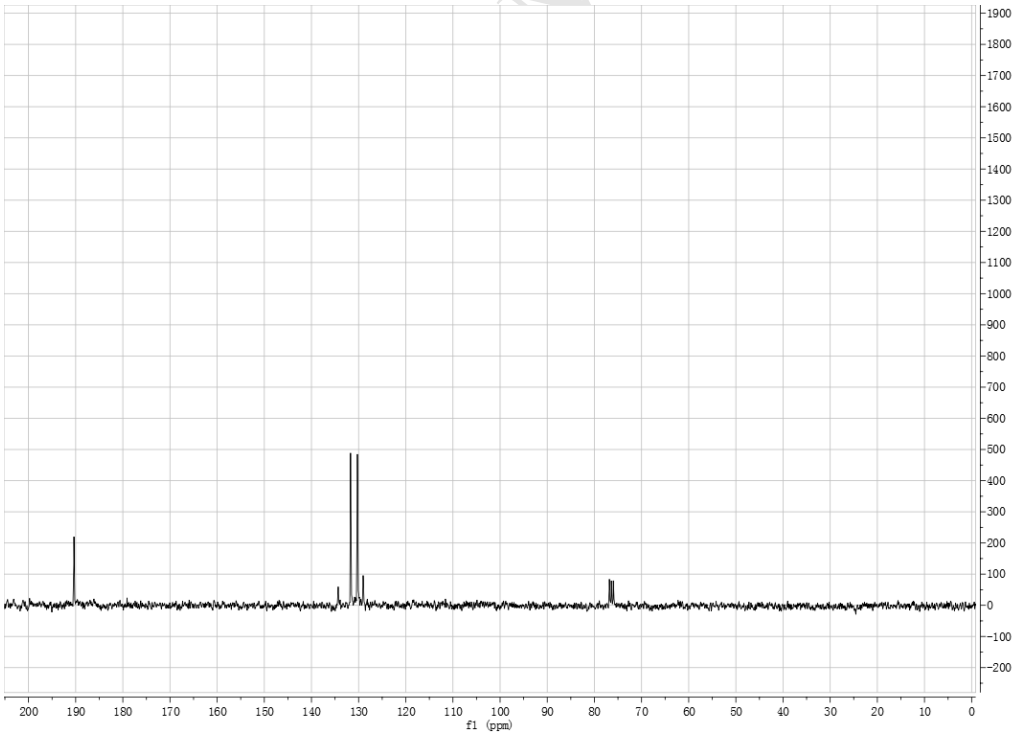
3-Fluorobenzaldehyde (**4e**)



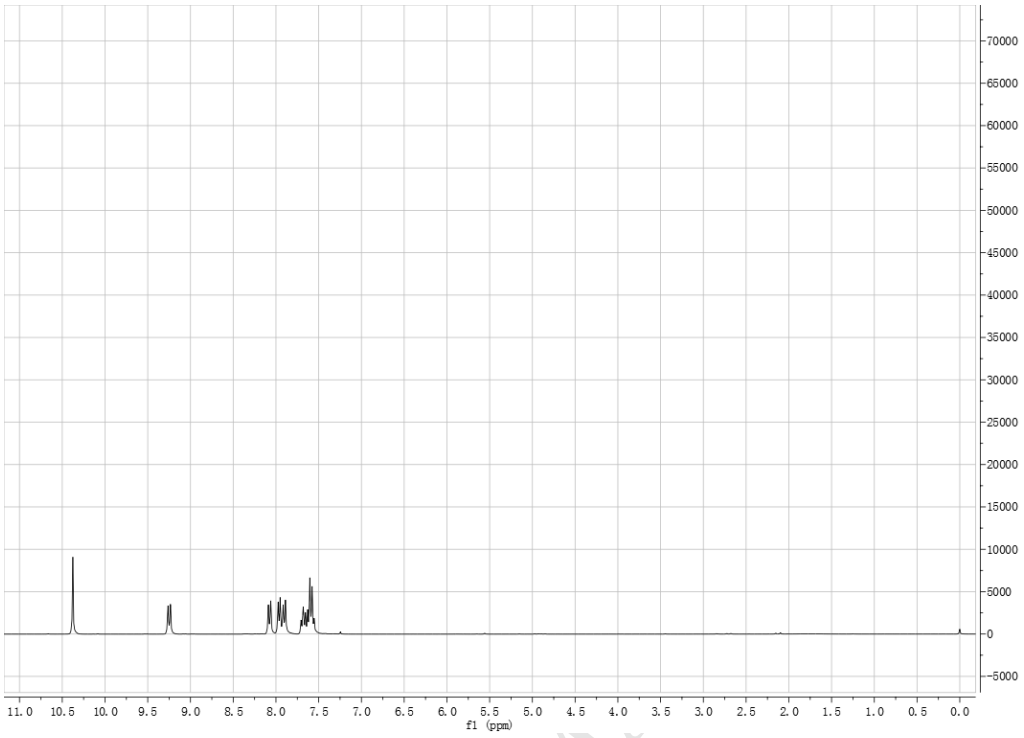


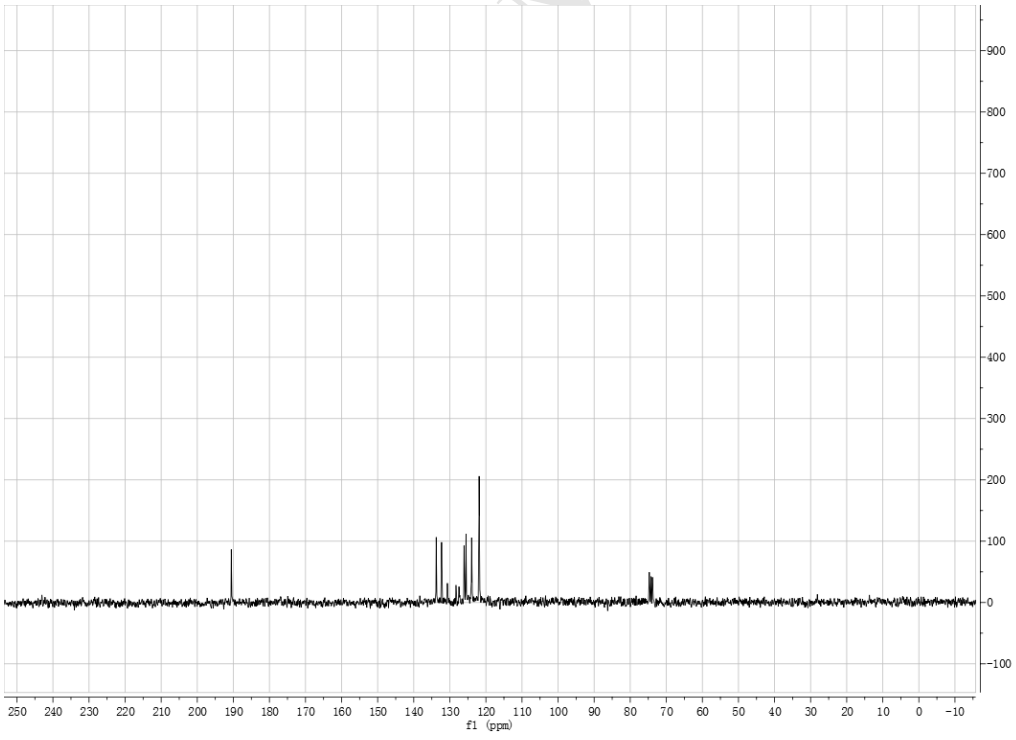
4-bromobenzaldehyde (**4f**)



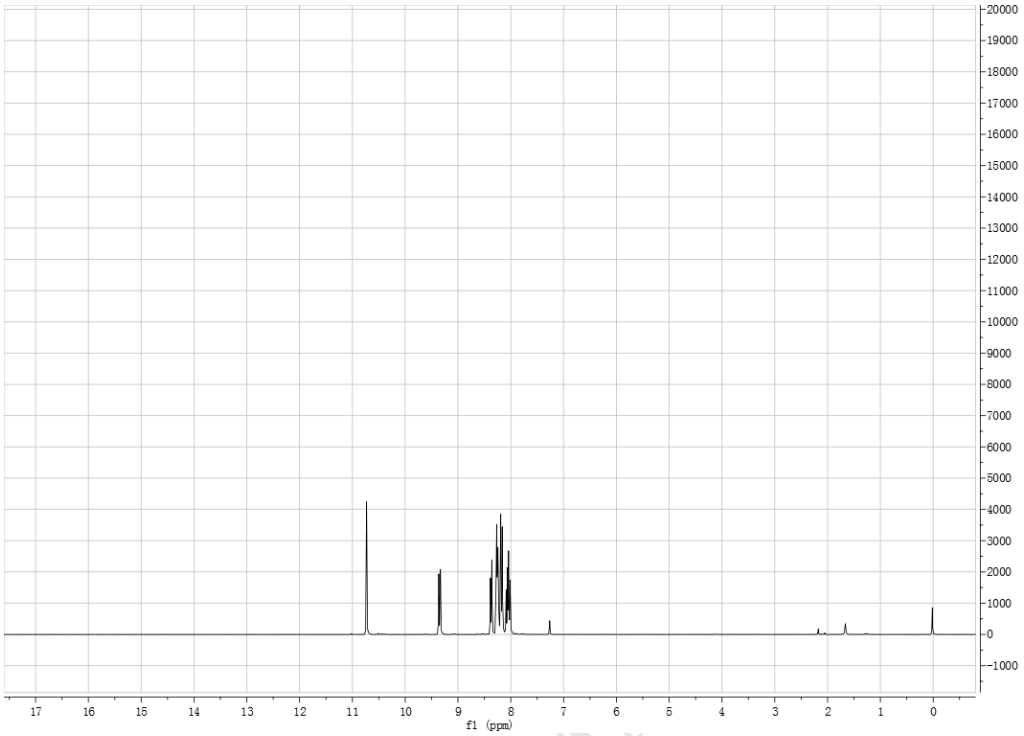


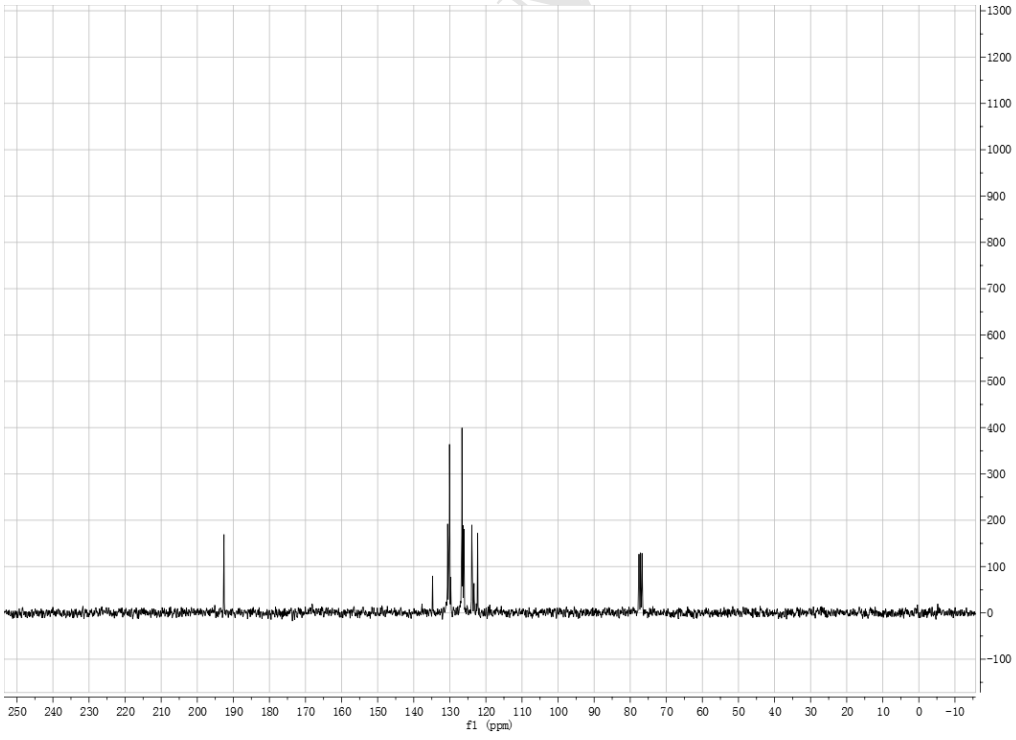
2-Naphthaldehyde (**4g**)



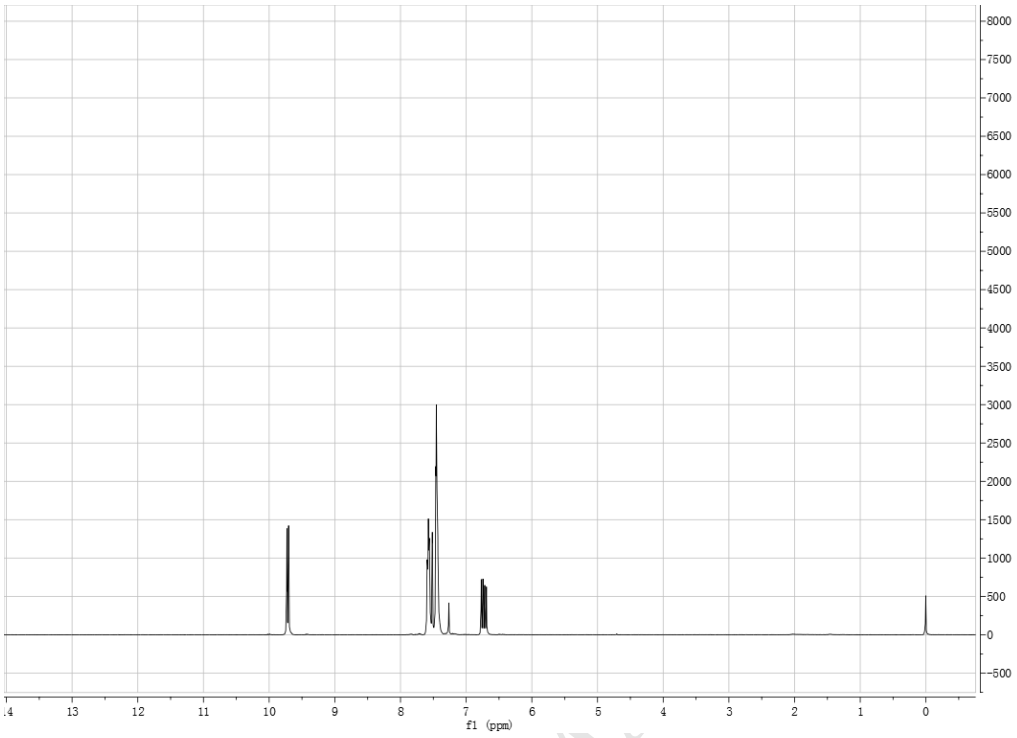


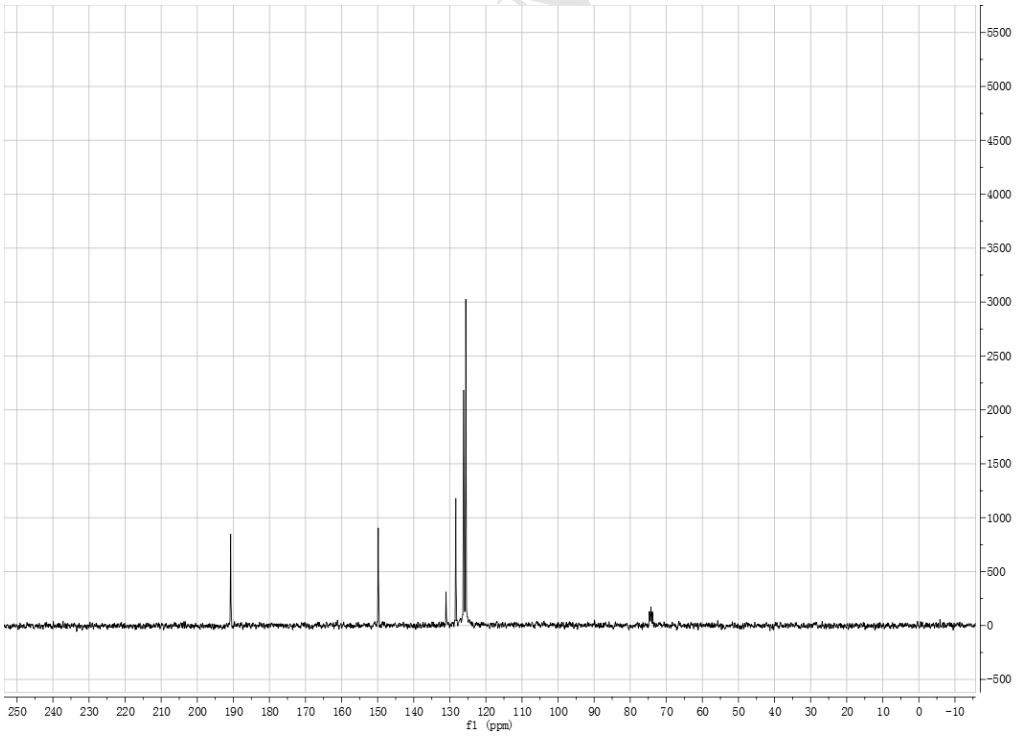
1-Pyrenecarboxaldehyde (**4h**)



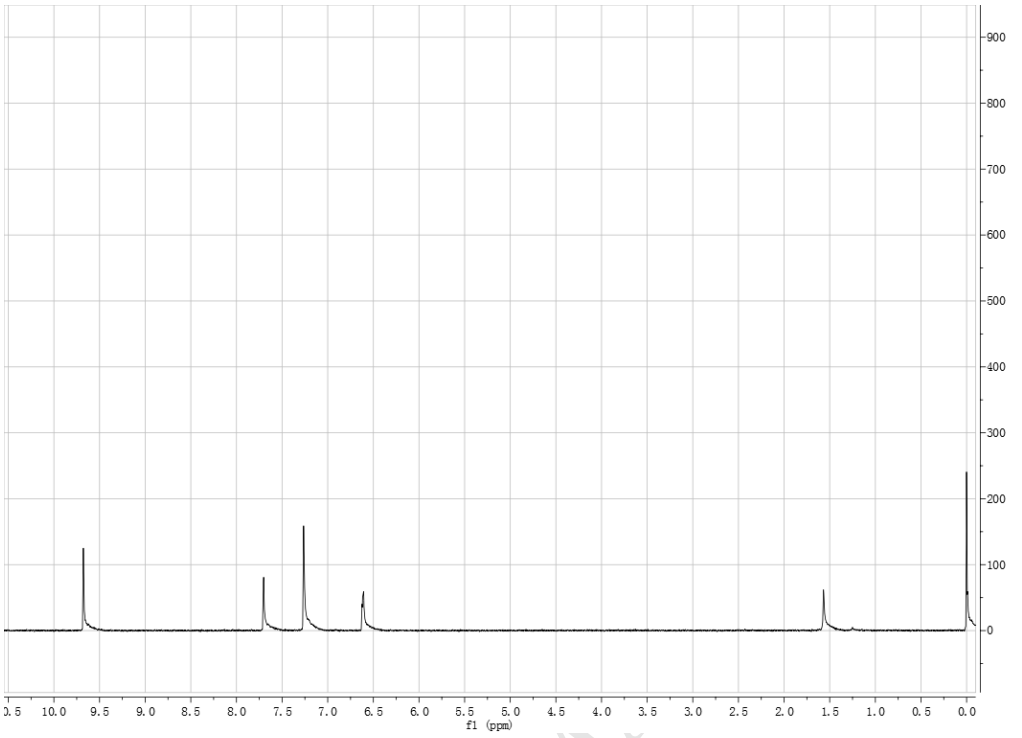


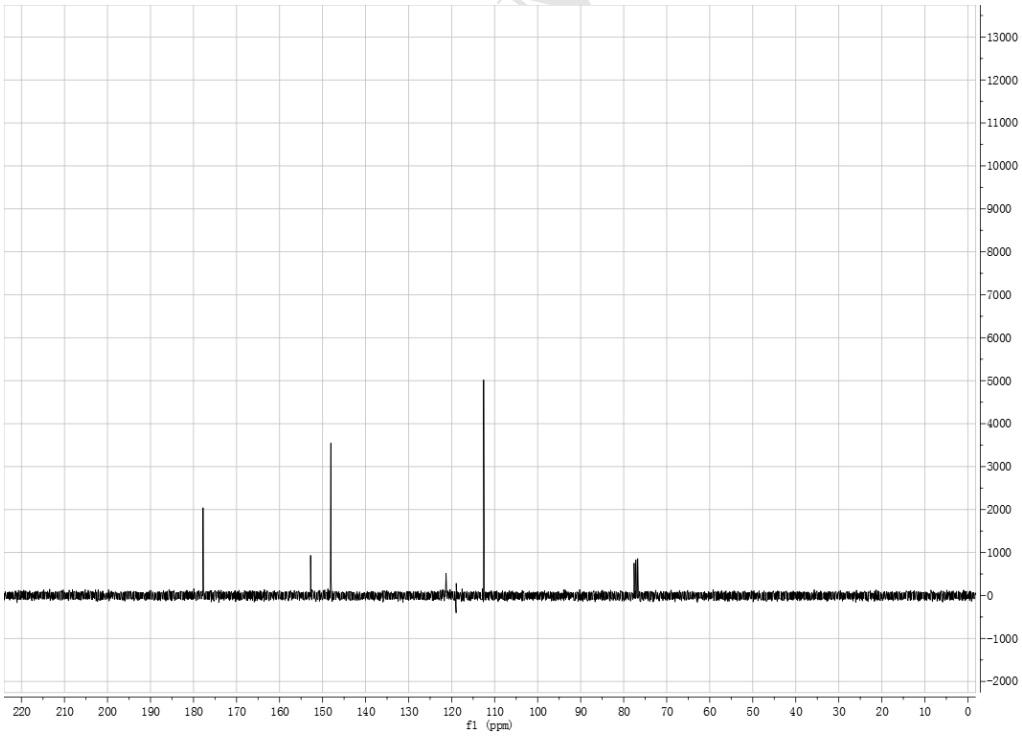
Phenylacrolein (**4i**)



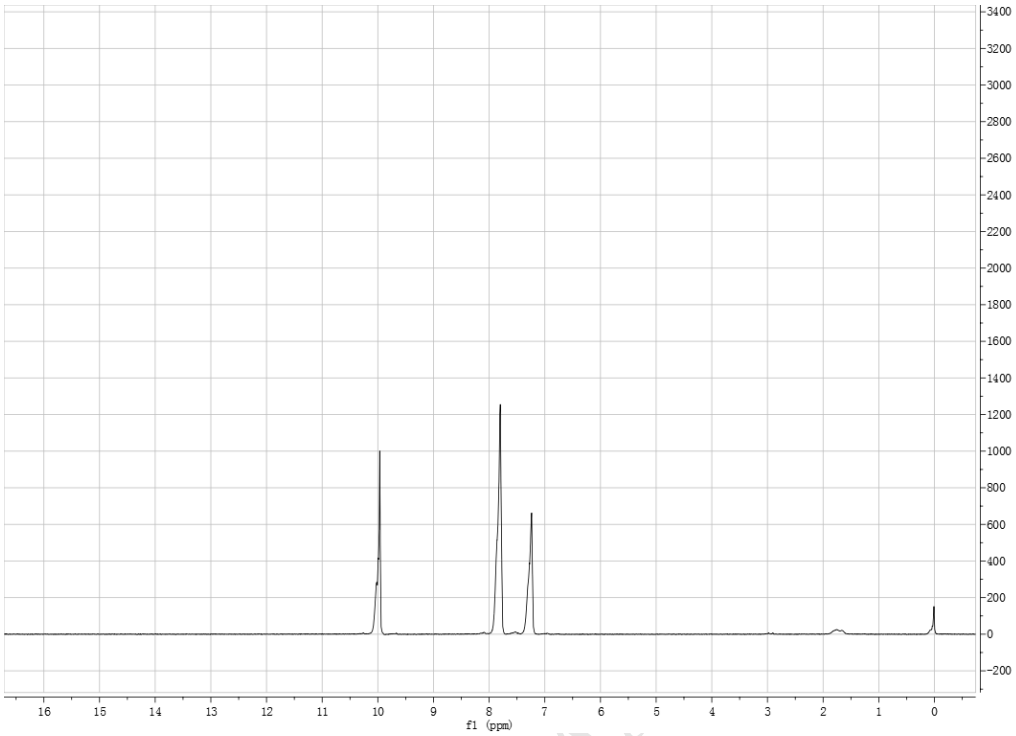


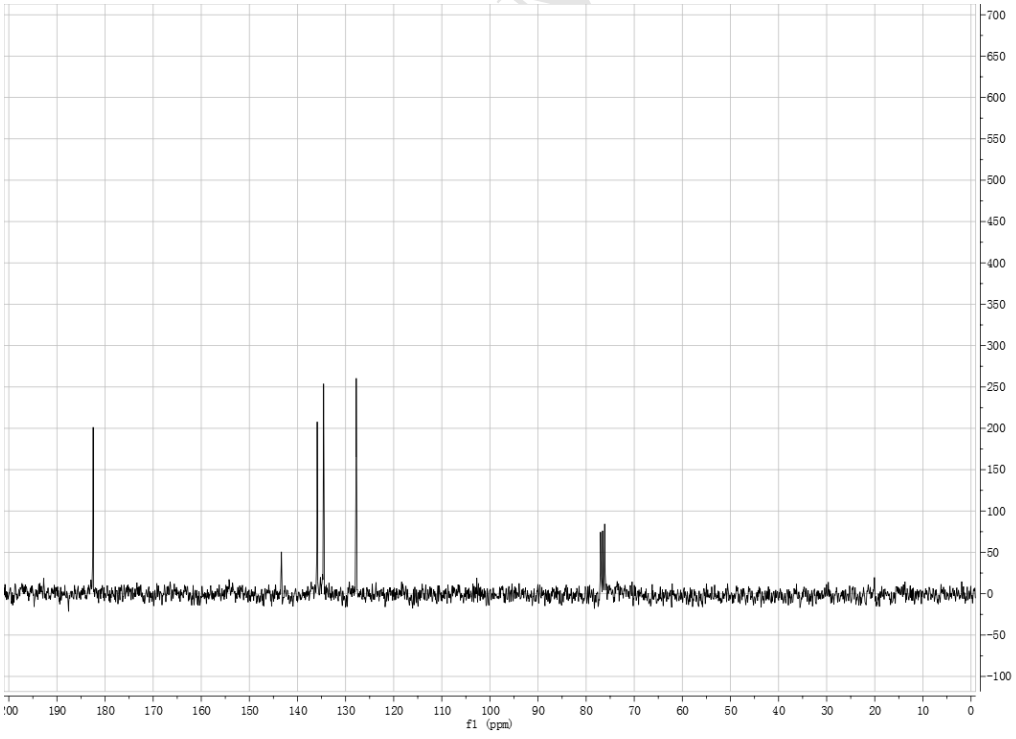
2-Furfural (**4j**)



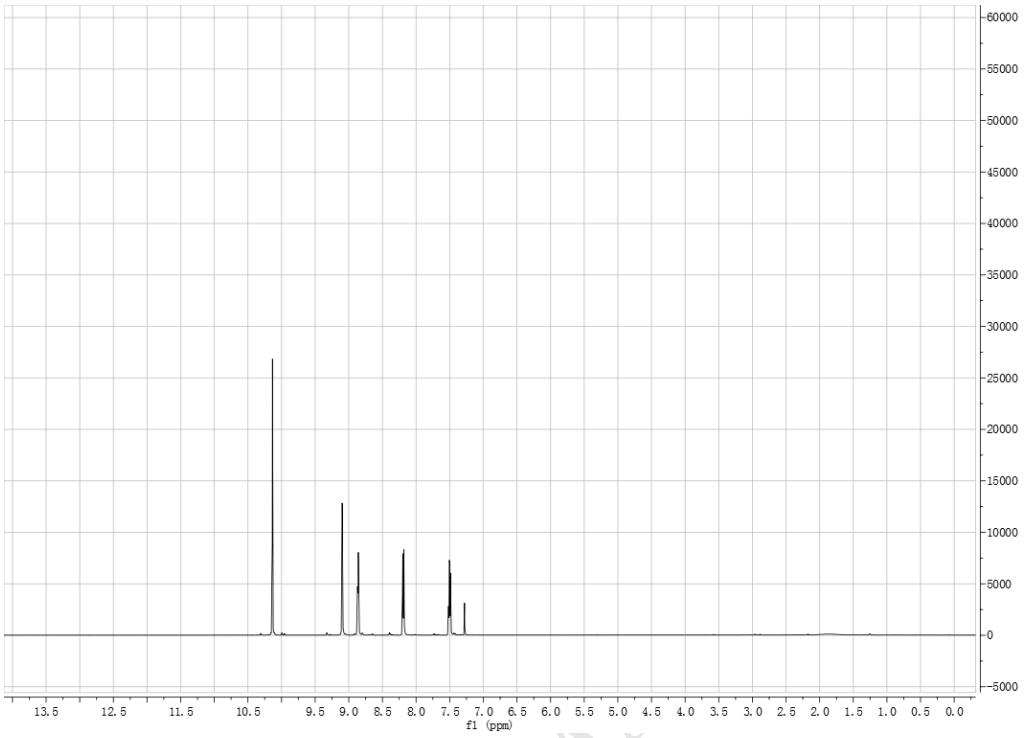


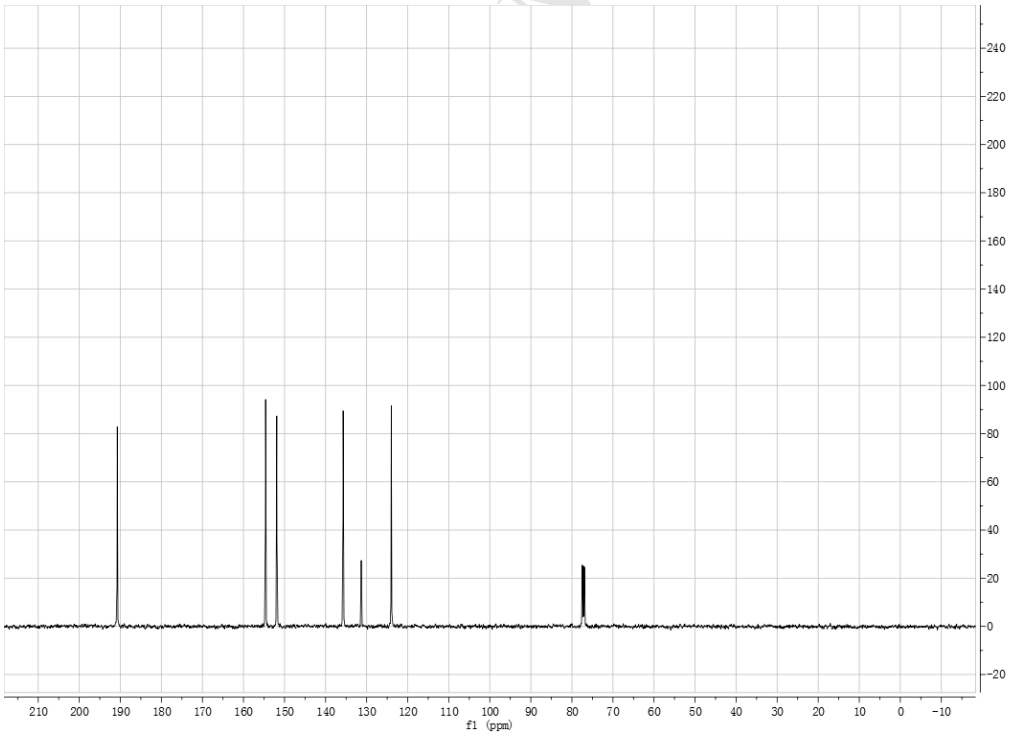
2-Thenaldehyde (**4k**)



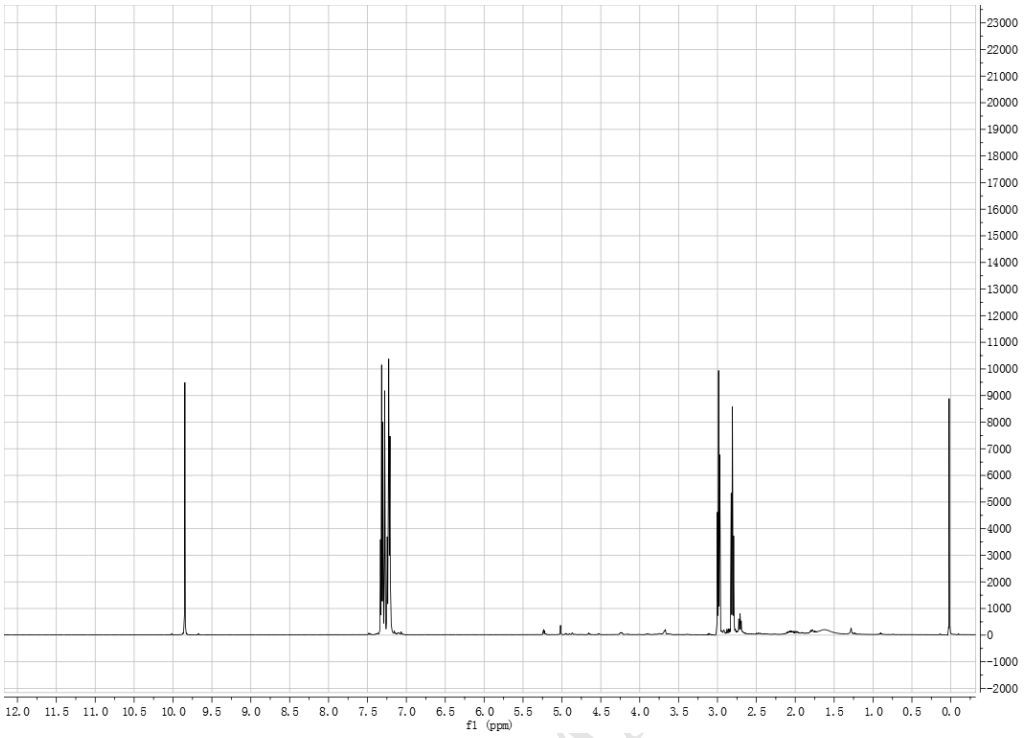


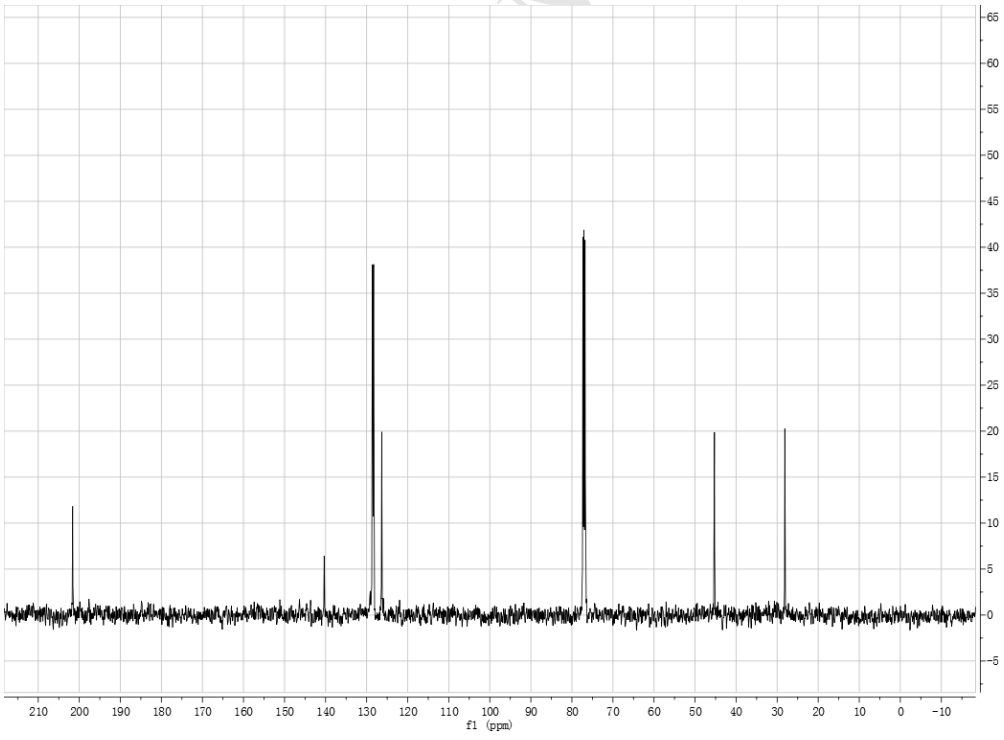
3-Pyridinecarboxaldehyde (**4l**)





3-Phenylpropanal (**4m**)





Octanal (**5n**)