

## Practical Organic Solvent-free Cu(OAc)<sub>2</sub>/DMAP/TEMPO-Catalyzed aldehydes and imines formation from alcohols under air atmosphere

Mingyu Guan,<sup>a</sup> Chao Wang,<sup>a</sup> Jingyu Zhang<sup>\*b</sup> and Yingsheng Zhao<sup>\*a</sup>

<sup>a</sup>College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China.

<sup>b</sup>College of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, China.

### *Supplementary Information*

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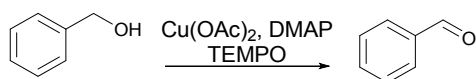
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**1. Reagents:** Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 300–400 mesh silica gel.

**2. Instruments:** NMR spectra were recorded on Bruker DRX–400 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br = broad singlet, m = multiplet.

### 3. Screening of reaction conditions<sup>a</sup>

**Table S1.** Screening of reaction conditions

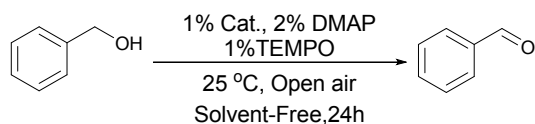


Entry	Cu(OAc) <sub>2</sub>	DMAP	TEMPO	Atmosphere	T(°C)	T(h)	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	1%	2%	1%	Open air	25	24	100	97
2	-	2%	1%	Open air	25	24	0	0
3	1%	-	1%	Open air	25	24	20	9
4	1%	2%	-	Open air	25	24	0	0
5	1%	2%	-	Open air	80	24	37	25
6	1%	2%	1%	O <sub>2</sub>	25	24	97	80
7	1%	2%	1%	Ar	25	24	21	9

<sup>a</sup> Reactions were carried out on a 1mmol scale; <sup>b</sup>, <sup>c</sup>Determined by GC using tridecane as an internal standard.

### 4. Screening of catalysts<sup>a</sup>

**Table S2.** Screening of catalysts



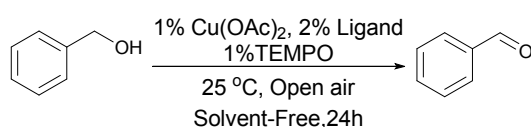
Entry	Cat.	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	Cu(OAc) <sub>2</sub>	100	97
2	Cu(acac) <sub>2</sub>	75	61

3	CuCl <sub>2</sub>	100	97
4	CuBr <sub>2</sub>	100	95
5	CuCl	100	96
6	CuBr	100	96
7	CuI	100	95
8	Fe(acac) <sub>2</sub>	0	0
9	FeCl <sub>3</sub>	0	0

<sup>a</sup> Reaction conditions: benzyl alcohol (1 mmol), Catalyst (1 mol%), DMAP (1 mol%), TEMPO (1 mol%), 25 °C, Solvent-free, Open air. <sup>b</sup> <sup>c</sup>Determined by GC using tridecane as an internal standard.

## 5. Screening of Ligands<sup>a</sup>

**Table S3.** Screening of ligands



Entry	Ligand	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	pyridine	64	43
2	2-methylpyridine	66	47
3	2,6-dimethylpyridine	70	51
5	2.2'-Bipyridine	45	21
6	1,10-Phenanthroline	98	78
7	DABCO	55	36
8	DBU	83	72
9	L-Proline	47	35
10	Picolinic acid	43	31
11	DMAP	100	97

<sup>a</sup> Reaction conditions: benzyl alcohol (1 mmol), Cu(OAc)<sub>2</sub> (1 mol%), Ligand (1 mol% or 2 mol%), TEMPO (1 mol%), 25 °C, Solvent-free, Open air. <sup>b</sup> <sup>c</sup>Determined by GC using tridecane as an internal standard.

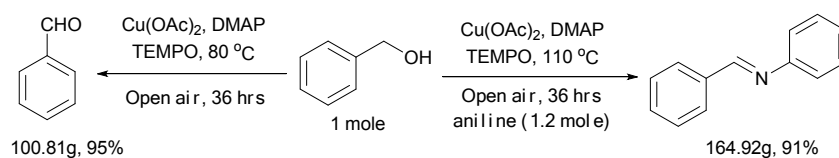
## 6. General procedures for synthesis of aldehydes

A mixture of alcohol (1 mmol, 1.0 eq),  $\text{Cu}(\text{OAc})_2$  (1.8 mg, 0.01 eq), DMAP (2.4 mg, 0.02 eq) and TEMPO (1.5 mg, 0.01 eq) in a 15 mL glass tube (under air atmosphere) was heated at  $x^\circ\text{C}$  for 24 hours. The reaction mixture was cooled to rt, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the aldehyde.

## 7. General procedures for synthesis of imines

A mixture of alcohol (1 mmol, 1.0 eq), amine (1.2 mmol, 1.2 eq),  $\text{Cu}(\text{OAc})_2$  (1.8 mg, 0.01 eq), DMAP (2.4 mg, 0.02 eq) and TEMPO (1.5 mg, 0.01 eq) in a 15 mL glass tube (under air atmosphere) was heated at  $110^\circ\text{C}$  for 24 hours. The reaction mixture was cooled to rt, and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give the imine. The silica gel column was leached by eluent (PE :  $\text{Et}_3\text{N}$  = 100:1) at first.

## 8. Mole-scale reaction

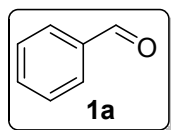


A mixture of benzyl alcohol (1 mol, 108.14g, 1.0 eq),  $\text{Cu}(\text{OAc})_2$  (900 mg, 0.005 eq), DMAP (1200 mg, 0.01 eq) and TEMPO (750 mg, 0.005 eq) in a 250 mL round-bottomed flask (under air atmosphere) was heated at  $80^\circ\text{C}$  for 36 hours. After the reaction was finished, the reaction mixture was extracted with n-pentane ( $5 \times 250$  mL). The combined n-pentane phase was concentrated in vacuo. The yield was determined by GC using tridecane as an internal standard and the residue was purified by vacuum distillation to afford benzaldehyde (87% isolated yield).

A mixture of benzyl alcohol (1 mol, 108.14g, 1.0 eq), aniline (1.2 mol, 111.76g, 1.2 eq),  $\text{Cu}(\text{OAc})_2$  (900 mg, 0.005 eq), DMAP (1200 mg, 0.01 eq) and TEMPO (750 mg, 0.005 eq) in a 500 mL round-bottomed flask (under air atmosphere) was heated at  $110^\circ\text{C}$  with a decantor for 36 hours before it was quenched by  $\text{NH}_4\text{Cl}$  (250 mL, sat. aq.). The layers were separated and the aqueous layer was extracted with EtOAc ( $3 \times 250$  mL). The combined ethyl acetate phase was concentrated in vacuo. The yield was determined by GC using tridecane as an internal standard and the residue was purified by recrystallization (ethyl acetate/ n-pentane, three times) to afford N-benzylideneaniline (80% isolated yield).

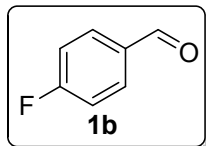
## 9. Characterization data of products

### Benzaldehyde(1a)



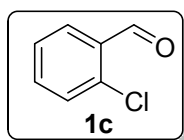
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.01 (s, 1H), 7.90 – 7.84 (m, 2H), 7.65 – 7.59 (m, 1H), 7.52 (dd,  $J$  = 7.9, 7.1 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.49, 136.47, 134.55, 129.82, 129.08. This compound was known.<sup>1</sup>

#### 4-Fluorobenzaldehyde(1b)



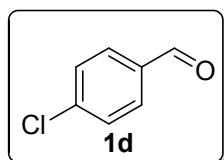
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.94 (s, 1H), 7.91 – 7.86 (m, 2H), 7.23 – 7.15 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.65, 167.90, 165.34, 133.07, 133.05, 132.92, 132.83, 132.38, 132.28, 116.55, 116.33, 115.85, 115.64.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -102.36. This compound was known.<sup>1</sup>

#### 2-Chlorobenzaldehyde(1c)



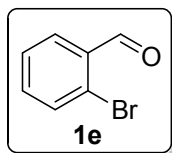
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.47 (s, 1H), 7.91 (dd,  $J$  = 7.7, 1.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.44 (dd,  $J$  = 8.1, 1.1 Hz, 1H), 7.40 – 7.36 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.96, 138.07, 135.26, 132.56, 130.73, 129.49, 127.41. This compound was known.<sup>1</sup>

#### 4-Chlorobenzaldehyde(1d)



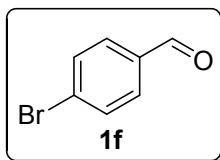
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.98 (s, 1H), 7.82 (d,  $J$  = 8.5 Hz, 2H), 7.51 (d,  $J$  = 8.4 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.98, 141.08, 134.83, 131.03, 129.58. This compound was known.<sup>1</sup>

#### 2-Bromobenzaldehyde(1e)



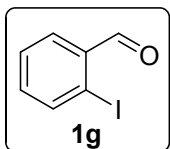
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.37 (s, 1H), 7.96 – 7.80 (m, 1H), 7.73 – 7.53 (m, 1H), 7.51 – 7.31 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.83, 135.37, 133.93, 133.54, 129.89, 127.95, 127.14. This compound was known.<sup>2</sup>

#### 4-Bromobenzaldehyde(1f)



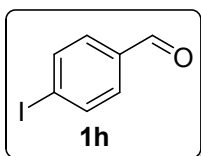
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.97 (s, 1H), 7.77 – 7.71 (m, 2H), 7.71 – 7.65 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.20, 135.20, 132.58, 131.10, 129.91. This compound was known.<sup>1</sup>

### 2-Iodobenzaldehyde(1g)



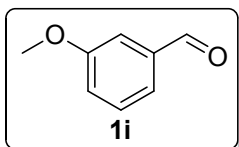
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.06 (s, 1H), 7.95 (dd,  $J$  = 7.9, 2.3 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.48 – 7.44 (m, 1H), 7.31 – 7.26 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 195.86, 140.75, 135.58, 135.22, 130.36, 128.83, 100.82. This compound was known.<sup>3</sup>

### 4-Iodobenzaldehyde(1h)



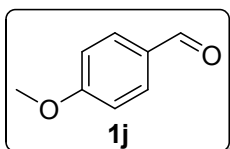
$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  = 9.97 (s, 1H), 8.05 – 7.98 (m, 2H), 7.70 – 7.64 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  = 192.69, 138.13, 135.37, 130.89, 103.56. This compound was known.<sup>4</sup>

### 3-Methoxybenzaldehyde(1i)



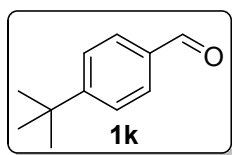
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.93 (s, 1H), 7.45 – 7.39 (m, 2H), 7.36 – 7.33 (m, 1H), 7.16 – 7.10 (m, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.15, 160.12, 137.78, 130.03, 123.49, 121.46, 112.07, 55.42. This compound was known.<sup>5</sup>

### 4-Methoxybenzaldehyde(1j)



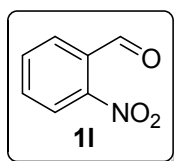
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.89 (s, 1H), 7.84 (d,  $J$  = 8.8 Hz, 2H), 7.01 (d,  $J$  = 8.7 Hz, 2H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.91, 164.67, 132.05, 129.99, 114.37, 55.64. This compound was known.<sup>1</sup>

#### 4-tert-Butylbenzaldehyde(1k)



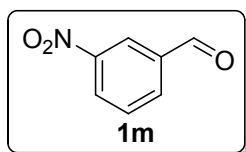
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.95 (s, 1H), 7.82 – 7.78 (m, 2H), 7.53 (dd,  $J$  = 8.5, 2.0 Hz, 2H), 1.34 – 1.32 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.04, 158.44, 134.12, 129.72, 126.02, 35.37, 31.09. This compound was known.<sup>6</sup>

#### 2-Nitrobenzaldehyde(1l)



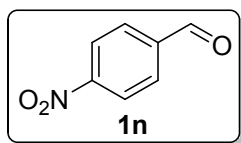
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.38 (s, 1H), 8.09 (dd,  $J$ =7.8, 1.4 Hz, 1H), 7.92 (dd,  $J$ =7.4, 1.7 Hz, 1H), 7.82 – 7.73 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 188.26, 149.62, 134.18, 133.81, 131.39, 129.69, 124.56. This compound was known.<sup>2</sup>

#### 3-Nitrobenzaldehyde(1m)



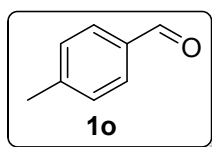
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.12 (s, 1H), 8.77 – 8.66 (m, 1H), 8.51 – 8.46 (m, 1H), 8.23 (dt,  $J$ =7.6, 1.3 Hz, 1H), 7.77 (t,  $J$ =7.9 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.86, 148.90, 137.51, 134.77, 130.52, 128.72, 124.60. This compound was known.<sup>7</sup>

#### 4-Nitrobenzaldehyde(1n)



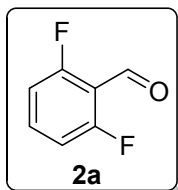
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.16 (s, 1H), 8.39 (d,  $J$ =8.6 Hz, 2H), 8.11 – 8.04 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.42, 151.27, 140.18, 130.62, 124.45. This compound was known.<sup>1</sup>

#### 4-Methylbenzaldehyde(1o)



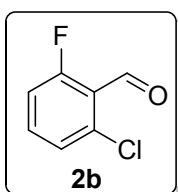
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.96 (s, 1H), 7.77 (d,  $J$ =7.9 Hz, 2H), 7.32 (d,  $J$ =7.8 Hz, 2H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.87, 145.42, 134.09, 129.72, 129.59, 21.76. This compound was known.<sup>1</sup>

### 2,6-Difluorobenzaldehyde(2a)



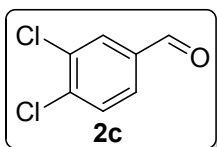
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.33 (s, 1H), 7.56 (m, 1H), 6.98 (t,  $J=8.6\text{Hz}$ , 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 184.67, 184.62, 184.58, 164.50, 164.44, 161.88, 161.83, 136.46, 136.34, 136.23, 114.30, 114.19, 114.09, 112.65, 112.60, 112.45, 112.40.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -114.85. This compound was known.<sup>17</sup>

### 2-Chloro-6-fluorobenzaldehyde(2b)



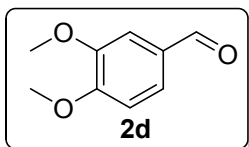
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.46 (s, 1H), 7.53 – 7.46 (m, 1H), 7.29 (d,  $J=8.3\text{ Hz}$ , 1H), 7.14 – 7.08 (m, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 186.79, 186.77, 164.46, 161.83, 136.97, 136.93, 135.30, 135.19, 126.78, 126.74, 121.75, 121.65, 115.74, 115.52.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -114.39. This compound was known.<sup>3</sup>

### 3,4-Dichlorobenzaldehyde(2c)



$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.95 (s, 1H), 7.96 (d,  $J=1.8\text{ Hz}$ , 1H), 7.72 (dd,  $J=8.2, 1.9\text{ Hz}$ , 1H), 7.63 (d,  $J=8.2\text{ Hz}$ , 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.81, 139.28, 135.95, 134.12, 131.45, 131.39, 128.53. This compound was known.<sup>8</sup>

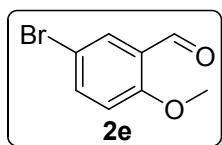
### 3,4-Dimethoxy-benzaldehyde(2d)



$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.81 (s, 1H), 7.42 (dd,  $J=8.2, 1.9\text{ Hz}$ , 1H), 7.37 (d,  $J=1.8\text{ Hz}$ , 1H), 6.95 (d,  $J=8.2\text{ Hz}$ , 1H), 3.93 (s, 3H), 3.90 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.96, 154.53, 149.66, 130.17, 126.92, 110.44, 108.98, 56.21, 56.03. This compound was known.<sup>1</sup>

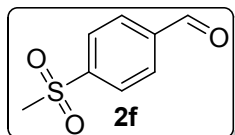
### 5-Bromo-2-methoxybenzaldehyde(2e)





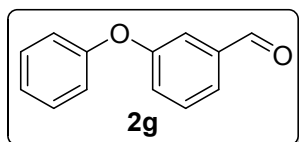
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.36 (s, 1H), 7.89 (d,  $J=2.6$  Hz, 1H), 7.61 (dd,  $J=8.9, 2.6$  Hz, 1H), 6.88 (d,  $J=8.9$  Hz, 1H), 3.91 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 188.45, 160.82, 138.38, 131.03, 126.09, 113.82, 113.49, 56.06. This compound was known.<sup>9</sup>

#### 4-Methylsulphonyl benzaldehyde(2f)



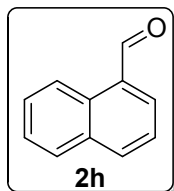
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  = 10.14 (s, 1H), 8.16 (s, 4H), 3.30 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.55, 145.31, 139.29, 130.23, 127.77, 43.15. This compound was known.<sup>10</sup>

#### 3-Phenoxy-benzaldehyde(2g)



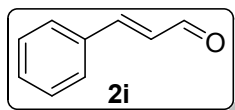
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.95 (s, 1H), 7.60 (d,  $J=7.5$  Hz, 1H), 7.52 – 7.45 (m, 2H), 7.38 (t,  $J=7.9$  Hz, 2H), 7.31 – 7.26 (m, 1H), 7.17 (t,  $J=7.4$  Hz, 1H), 7.05 (dd,  $J=8.6, 0.9$  Hz, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.65, 158.43, 156.25, 138.12, 130.49, 130.10, 124.75, 124.61, 124.24, 119.53, 118.16. This compound was known.<sup>11</sup>

#### 1-Naphthalenecarboxaldehyde(2h)



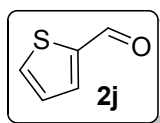
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.38 (s, 1H), 9.26 (d,  $J=8.6$  Hz, 1H), 8.07 (d,  $J=8.2$  Hz, 1H), 7.95 (dd,  $J=7.1, 1.3$  Hz, 1H), 7.90 (d,  $J=7.9$  Hz, 1H), 7.71 – 7.66 (m, 1H), 7.63 – 7.55 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.61, 136.73, 135.32, 133.74, 131.40, 130.54, 129.09, 128.52, 126.99, 124.90. This compound was known.<sup>1</sup>

#### 3-Phenyl-2-propenal(2i)



$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.69 (d,  $J=7.7$  Hz, 1H), 7.56 (d,  $J=1.8$  Hz, 1H), 7.54 (s, 1H), 7.49 – 7.38 (m, 4H), 6.70 (dd,  $J=16.0, 7.7$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.68, 152.77, 133.98, 131.26, 129.09, 128.55, 128.49. This compound was known.<sup>1</sup>

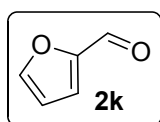
### 2-Thiophenecarboxaldehyde(2j)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.92 (s, 1H), 7.79 – 7.73 (m, 2H), 7.22 – 7.17 (dd,  $J=4.9, 3.8$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 183.12, 144.05, 136.48, 135.23, 128.41. This compound was known.<sup>1</sup>

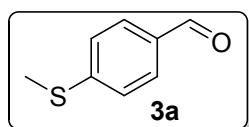
### 2-Furancarboxaldehyde(2k)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.67 (s, 1H), 7.71 (s, 1H), 7.30 – 7.25 (m, 1H), 6.65 – 6.57 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.99, 153.04, 148.20, 121.20, 112.69 This compound was known.<sup>1</sup>

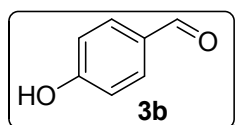
### 4-(Methylthio)benzaldehyde(3a)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.90 (s, 1H), 7.80 – 7.71 (m, 2H), 7.35 – 7.26 (m, 2H), 2.52 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.20, 147.90, 132.90, 129.95, 125.14, 14.63. This compound was known.<sup>12</sup>

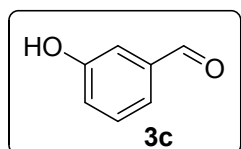
### 4-Hydroxybenzaldehyde(3b)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.83 (s, 1H), 7.89 – 7.75 (m, 2H), 7.47 (s, 1H), 7.07 – 6.92 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.04, 162.52, 132.90, 129.50, 116.30. This compound was known.<sup>13</sup>

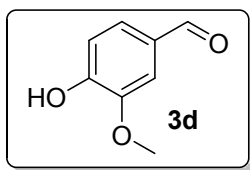
### 3-Hydroxybenzaldehyde(3c)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.92 (s, 1H), 7.51 – 7.34 (m, 3H), 7.19 (d,  $J=7.0$  Hz, 1H), 7.03 (s, 1H).

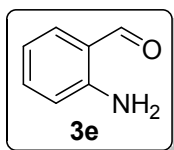
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.48, 156.85, 137.67, 130.56, 123.70, 122.66, 115.02. This compound was known.<sup>13</sup>

#### 4-Hydroxy-3-methoxybenzaldehyde(3d)



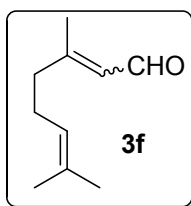
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.82 (s, 1H), 7.44 – 7.40 (m, 2H), 7.06 – 7.02 (m, 1H), 6.26 (s, 1H), 3.96 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.05, 151.82, 147.28, 130.02, 127.69, 114.52, 108.90, 56.26. This compound was known.<sup>14</sup>

#### 2-Aminobenzaldehyde(3e)



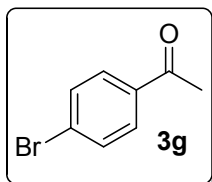
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.84 (s, 1H), 7.45 (d,  $J=7.8$  Hz, 1H), 7.32 – 7.24 (m, 1H), 6.72 (t,  $J=7.4$  Hz, 1H), 6.63 (d,  $J=8.3$  Hz, 1H), 6.15 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 194.05, 149.91, 135.68, 135.16, 118.74, 116.27, 116.00. This compound was known.<sup>3</sup>

#### 3,7-Dimethyl-2,6-octadienal(3f)



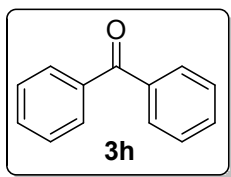
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.97 – 9.79 (m, 1H), 5.81 (dd,  $J=6.9, 1.1$  Hz, 1H), 5.08 – 4.98 (m, 1H), 2.53 (td,  $J=7.5, 1.5$  Hz, 1H), 2.16 (d,  $J=5.8$  Hz, 3H), 2.11 (d,  $J=2.1$  Hz, 2H), 1.92 (dd,  $J=2.2, 1.3$  Hz, 1H), 1.62 (s, 3H), 1.54 (d,  $J=6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.19, 190.67, 163.74, 133.60, 132.82, 128.62, 127.38, 122.58, 122.28, 40.57, 32.53, 27.01, 25.71, 25.60, 25.01, 17.67, 17.52. This compound was known.<sup>15</sup>

#### 4'-Bromoacetophenone(3g)



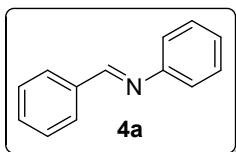
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.77 (d,  $J=8.6$  Hz, 2H), 7.56 (d,  $J=8.7$  Hz, 2H), 2.54 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 196.99, 135.83, 131.89, 129.86, 128.30, 26.56. This compound was known.<sup>1</sup>

#### Diphenylmethanone(3h)



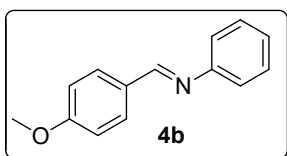
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.81 (d,  $J=7.9$  Hz, 4H), 7.60 (dd,  $J=10.9, 3.8$  Hz, 2H), 7.48 (t,  $J=7.6$  Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 196.88, 137.72, 132.54, 130.18, 128.40. This compound was known.<sup>1</sup>

#### N-Benzylideneaniline (4a)



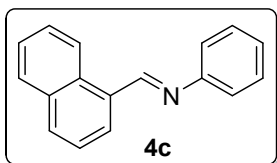
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.45 (s, 1H), 7.91 (dd,  $J=6.5, 3.1$  Hz, 2H), 7.51 – 7.44 (m, 3H), 7.40 (dd,  $J=10.6, 4.9$  Hz, 2H), 7.27 – 7.17 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.56, 152.20, 136.33, 131.51, 129.28, 128.94, 128.90, 126.07, 120.99. This compound was known.<sup>5</sup>

#### N-(4-methoxybenzylidene)aniline (4b)



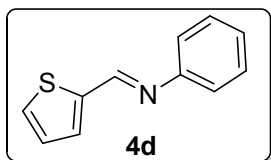
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.37 (s, 1H), 7.84 (d,  $J=8.7$  Hz, 2H), 7.37 (t,  $J=7.7$  Hz, 2H), 7.21 (d,  $J=8.2$  Hz, 2H), 7.18 (s, 1H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 162.36, 159.82, 152.48, 130.62, 129.38, 129.22, 125.67, 120.99, 114.30, 55.53. This compound was known.<sup>5</sup>

#### N-(naphthalen-1-ylmethylene)aniline(4c)



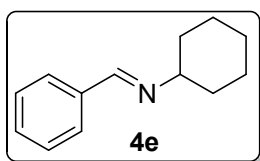
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.08 (s, 1H), 9.04 (d,  $J=8.5$  Hz, 1H), 8.08 (d,  $J=7.1$  Hz, 1H), 7.95 (d,  $J=8.2$  Hz, 1H), 7.90 (d,  $J=8.1$  Hz, 1H), 7.64 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.43 (t,  $J=7.8$  Hz, 2H), 7.27 (dd,  $J=16.2, 7.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.20, 152.79, 134.02, 132.05, 131.61, 131.57, 129.96, 129.33, 128.88, 127.59, 126.34, 126.05, 125.42, 124.35, 121.06. This compound was known.<sup>5</sup>

#### N-(Thiophen-2-ylmethylene)aniline(4d)



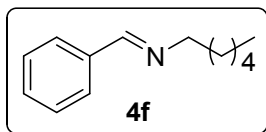
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.48 (s, 1H), 7.43 – 7.39 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 – 7.15 (m, 3H), 7.05 (dd,  $J$ =5.0, 3.7 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 152.97, 151.36, 142.79, 132.27, 130.28, 129.12, 127.74, 126.02, 120.99. This compound was known.<sup>5</sup>

#### **N-benzylidenecyclohexanamine (4e)**



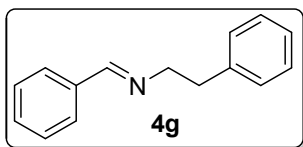
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.32 (s, 1H), 7.77 – 7.69 (m, 2H), 7.43 – 7.35 (m, 3H), 3.25 – 3.15 (m, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.54 (m, 5H), 1.44 – 1.21 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 158.72, 136.74, 130.43, 128.63, 128.17, 70.13, 34.49, 25.77, 24.94. This compound was known.<sup>5</sup>

#### **N-benzylidenehexan-1-amine (4f)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.27 (s, 1H), 7.79 – 7.67 (m, 2H), 7.47 – 7.35 (m, 3H), 3.61 (dd,  $J$ =7.0, 6.3 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.39 – 1.30 (m, 6H), 0.90 (t,  $J$ =6.8 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.81, 136.49, 130.53, 128.67, 128.12, 61.94, 31.79, 31.01, 27.16, 22.74, 14.19. This compound was known.<sup>16</sup>

#### **N-benzylidene-2-phenylethanamine (4g)**



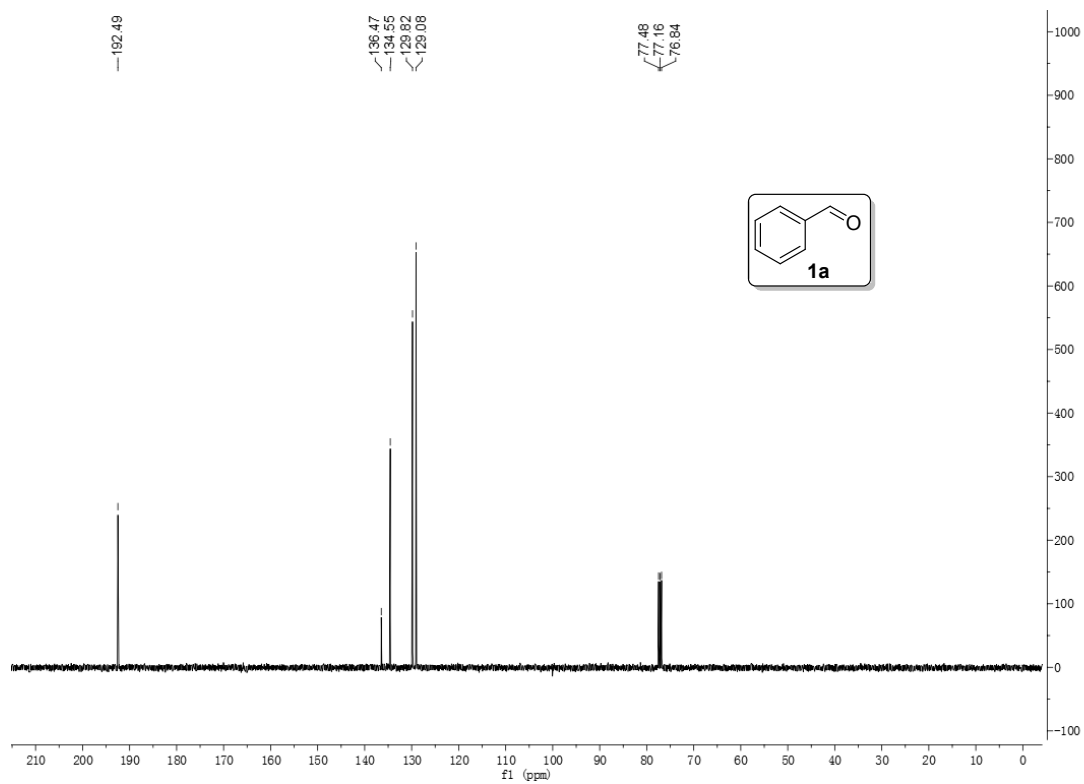
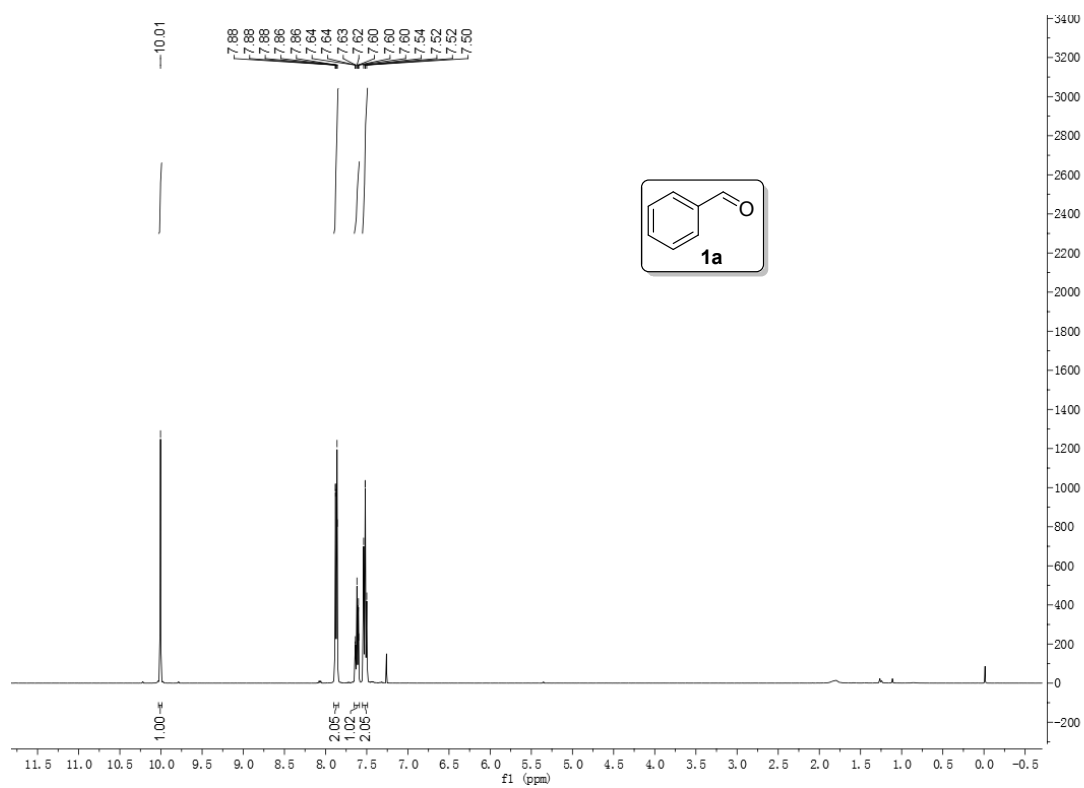
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.17 (s, 1H), 7.71 (dd,  $J$ =6.2, 3.3 Hz, 2H), 7.41 (dd,  $J$ =4.4, 2.5 Hz, 3H), 7.31 – 7.18 (m, 5H), 3.87 (t,  $J$ =7.5 Hz, 2H), 3.02 (t,  $J$ =7.5 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 161.61, 139.99, 136.24, 130.67, 129.11, 128.66, 128.42, 128.14, 126.19, 63.25, 37.60. This compound was known.<sup>5</sup>

## 10. References

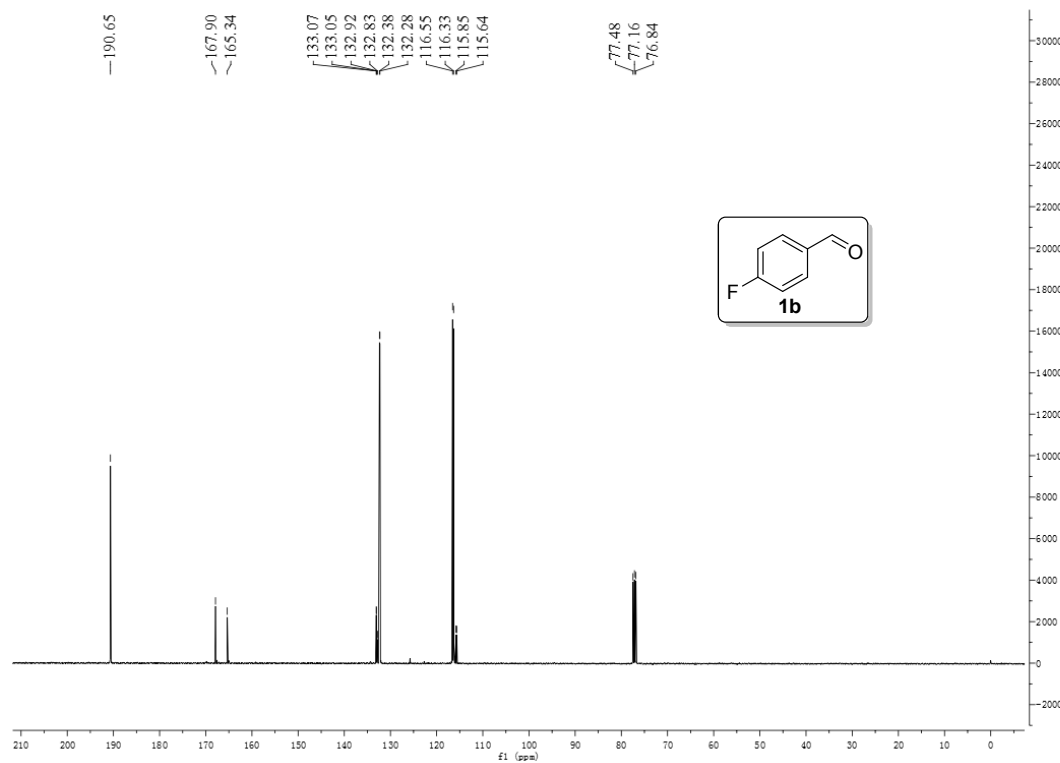
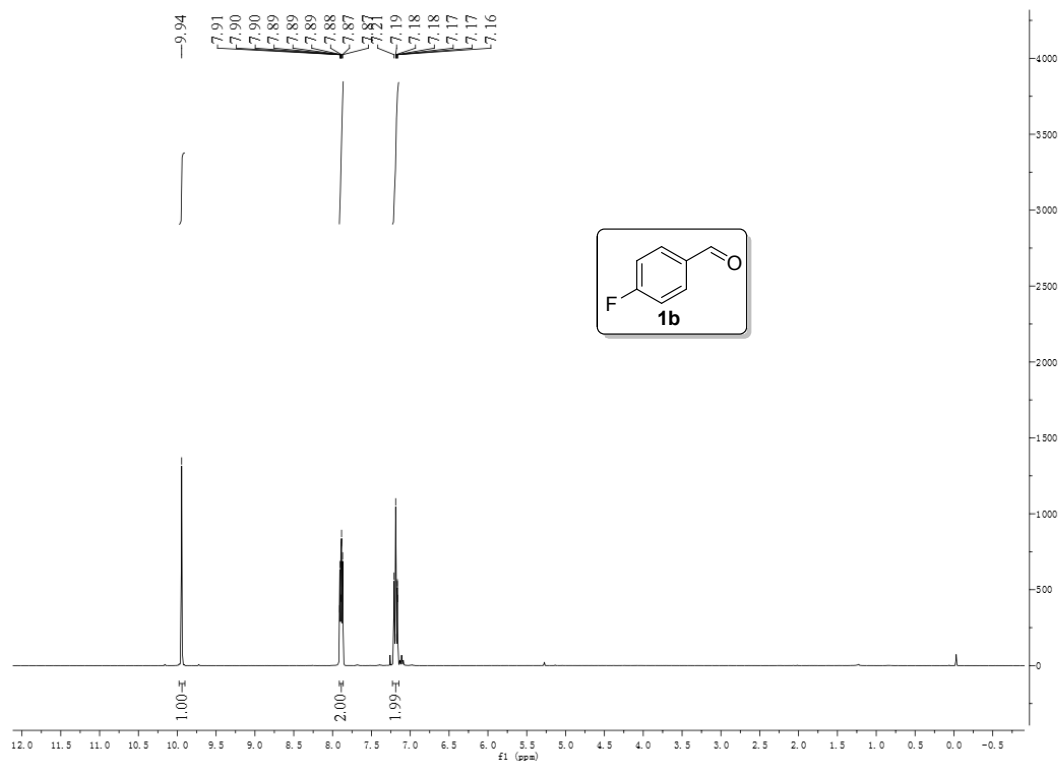
- 1 G. F. Zhang, X. W. Han, Y. X. Luan, Y. Wang, X. Wen and C. R. Ding, *Chem. Commun.*, 2013, **49**, 7908.
- 2 X. L. Liu, Q. Q. Xia, Y. J. Zhang, C. Y. Chen and W. Z. Chen, *J. Org. Chem.*, 2013, **78**, 8531.
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- 17 H. Sun and S. G. DiMagno, *Angew. Chem., Int. Ed.*, 2006, **45**, 2720.

## 11. NMR Spectra of products

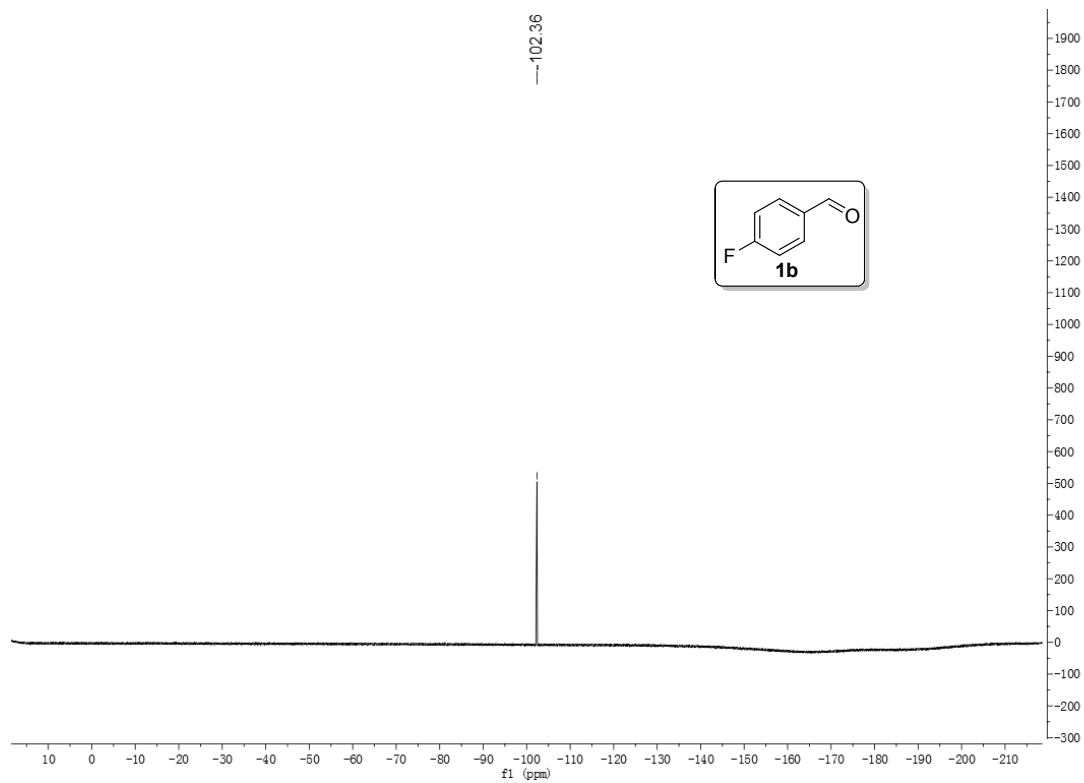
### Benzaldehyde(1a)



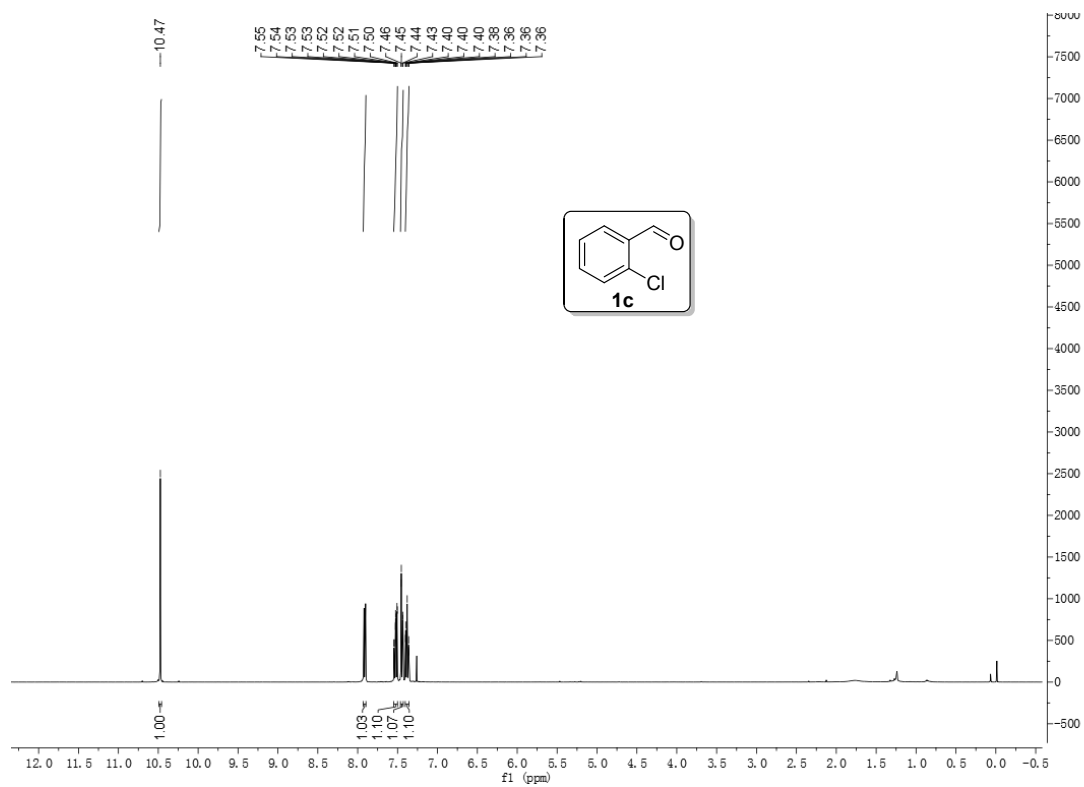
# 4-Fluorobenzaldehyde(1b)

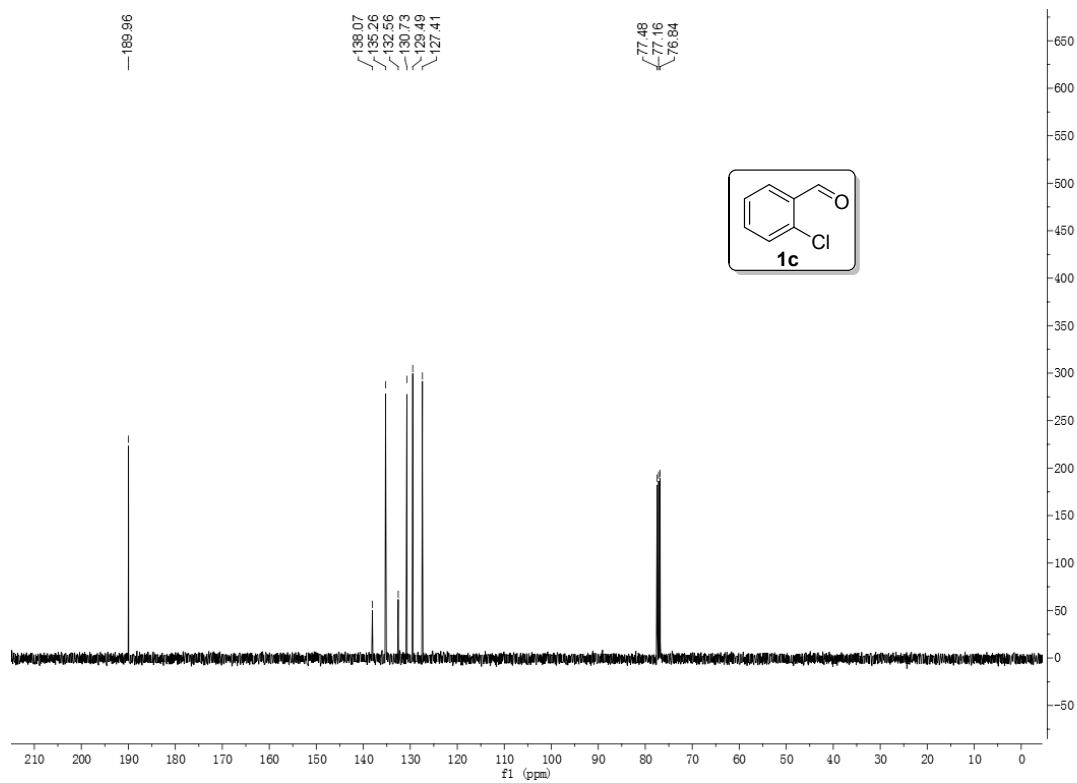




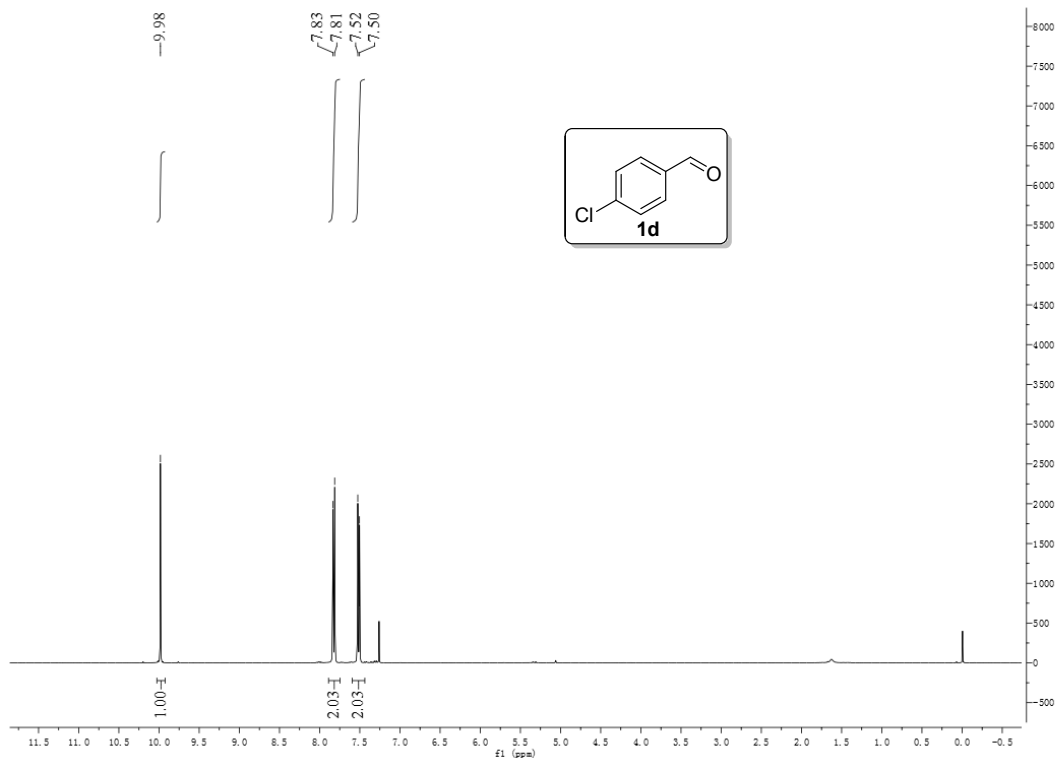


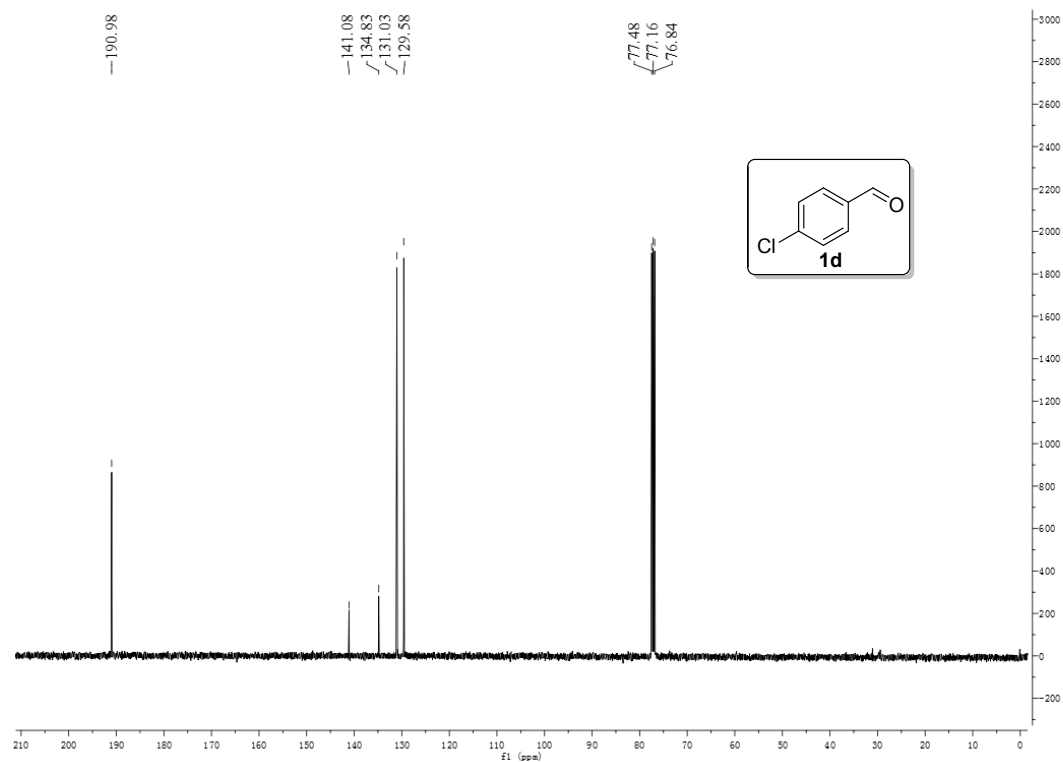
### 3-Chlorobenzaldehyde(1c)



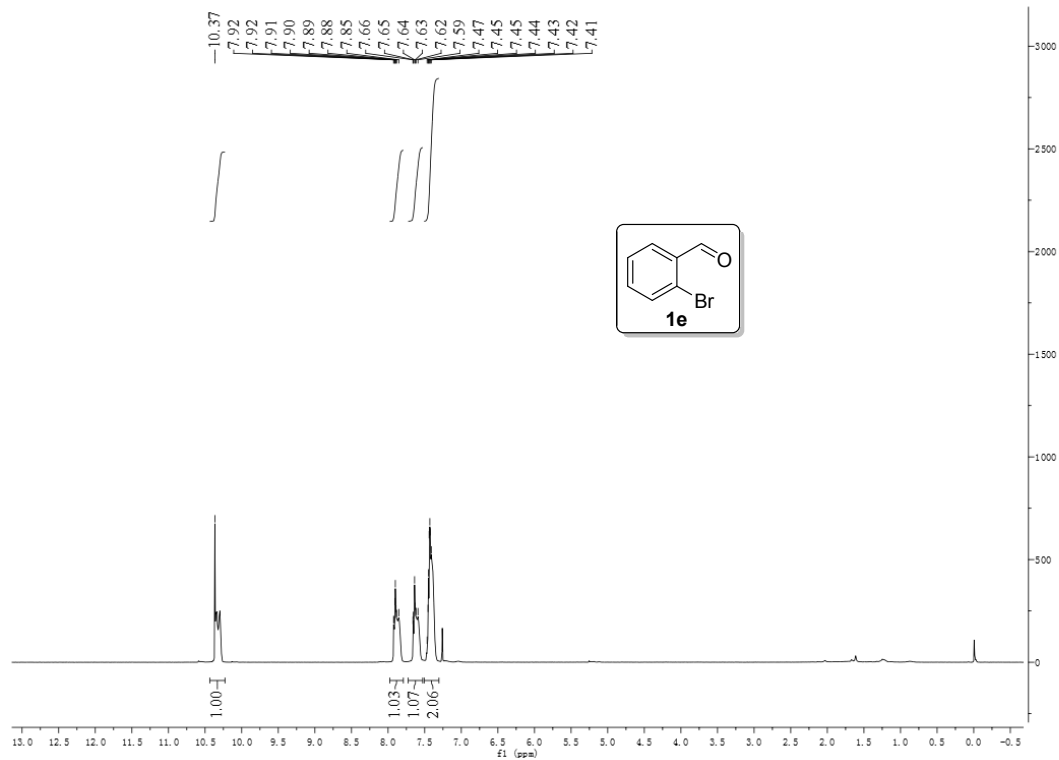


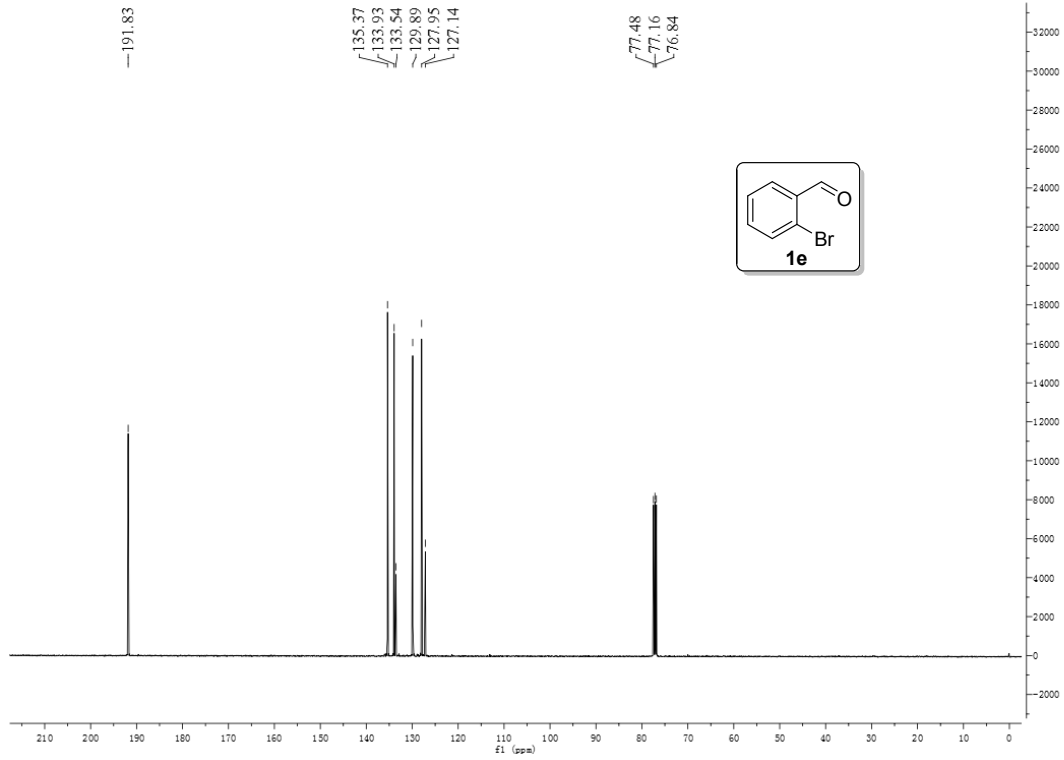
#### 4-Chlorobenzaldehyde(1d)



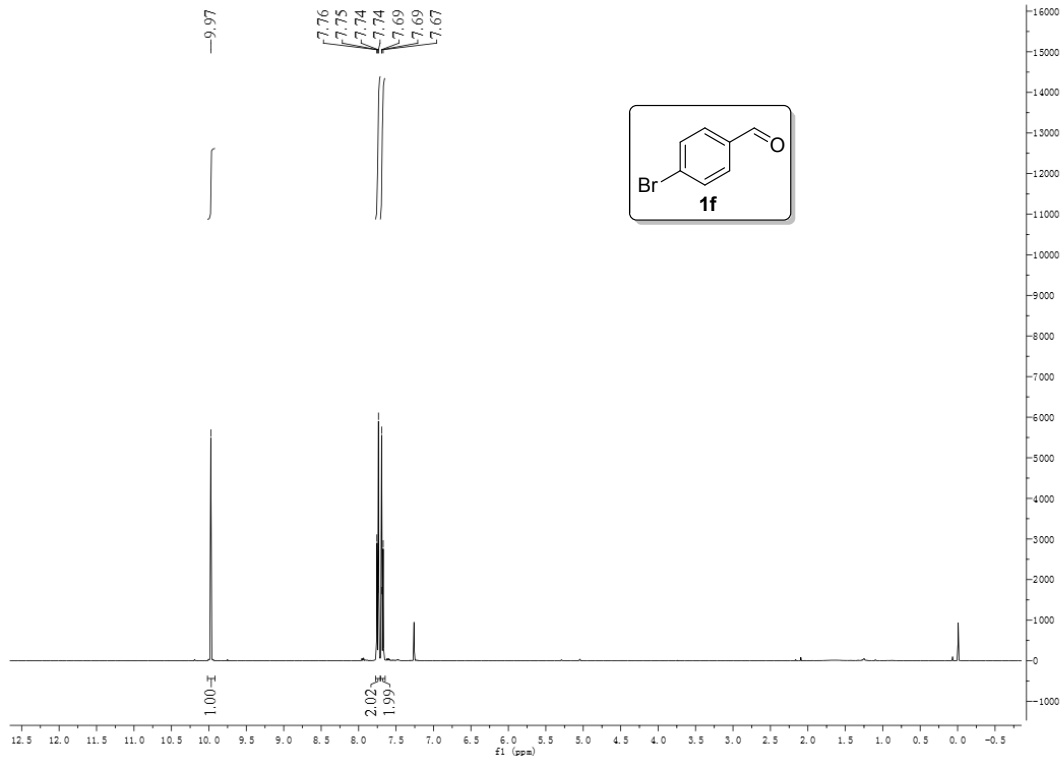


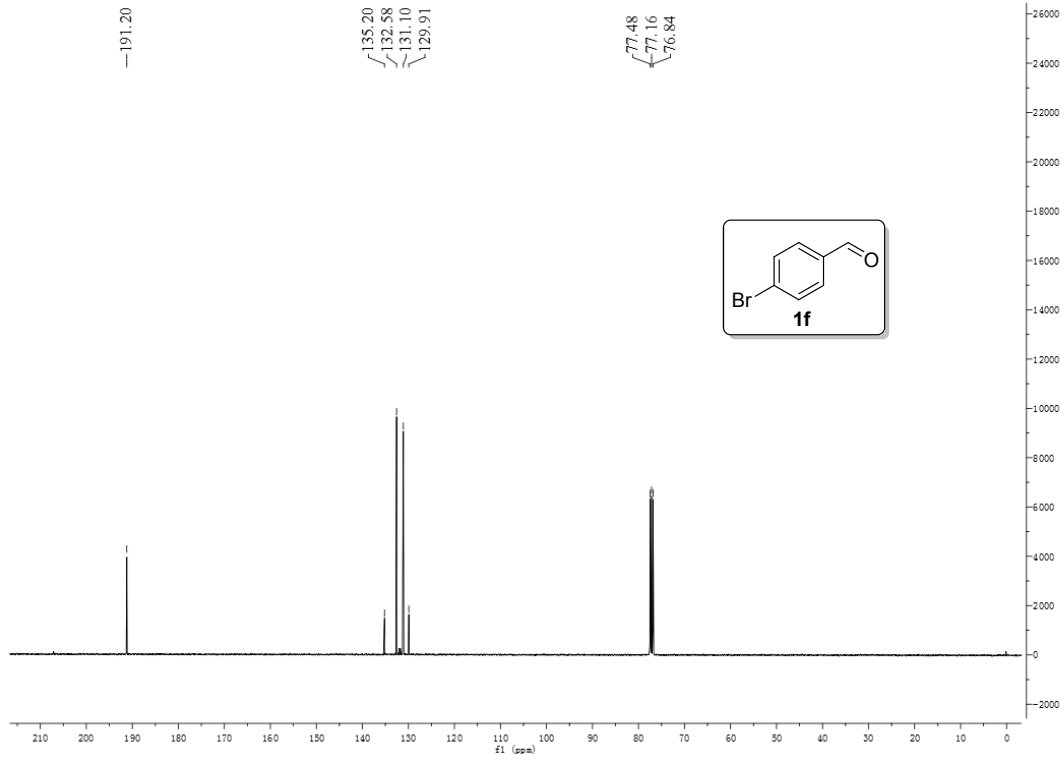
### 2-Bromobenzaldehyde(1e)



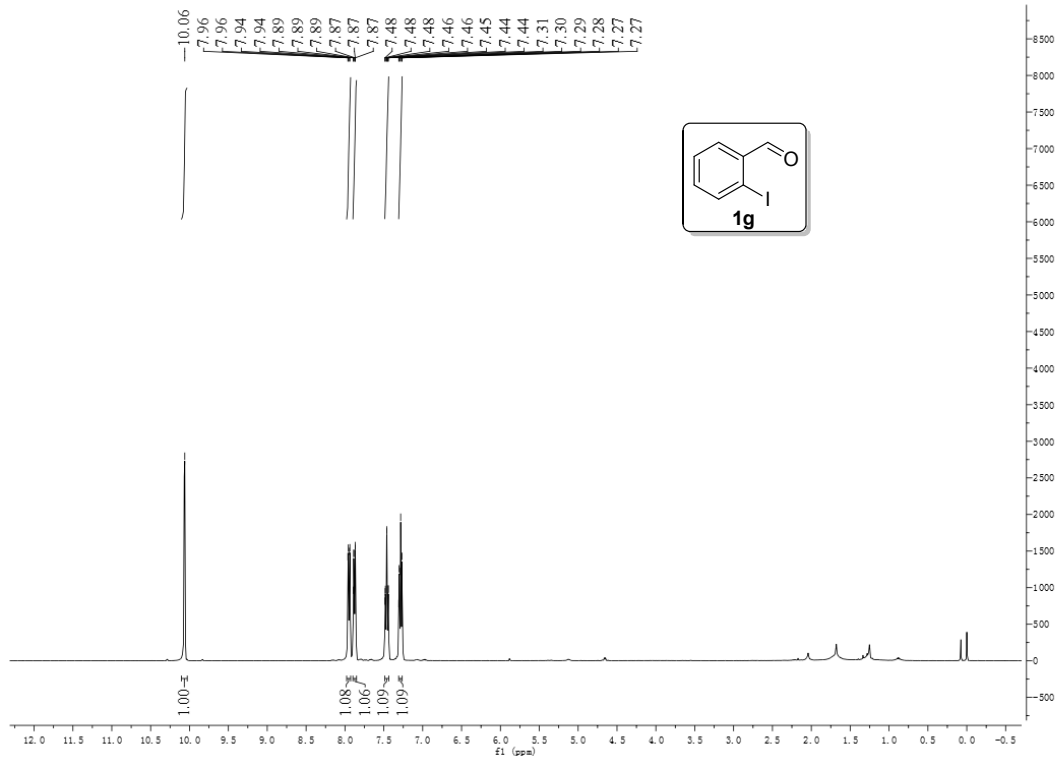


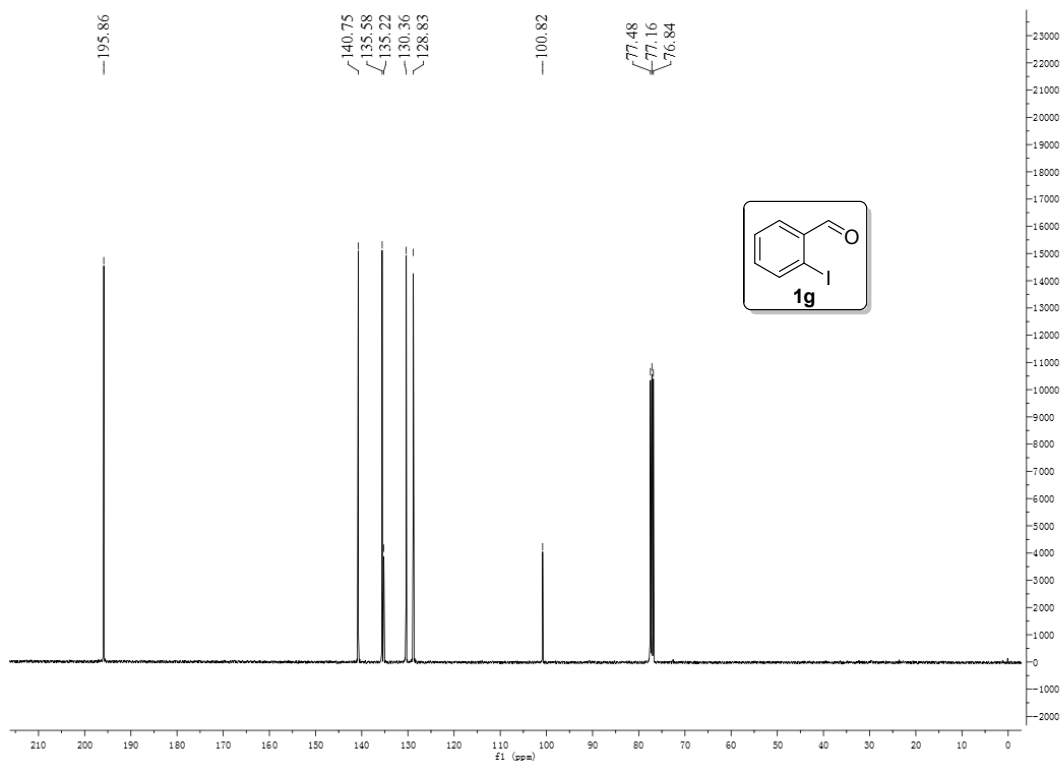
**4-Bromobenzaldehyde(1f)**



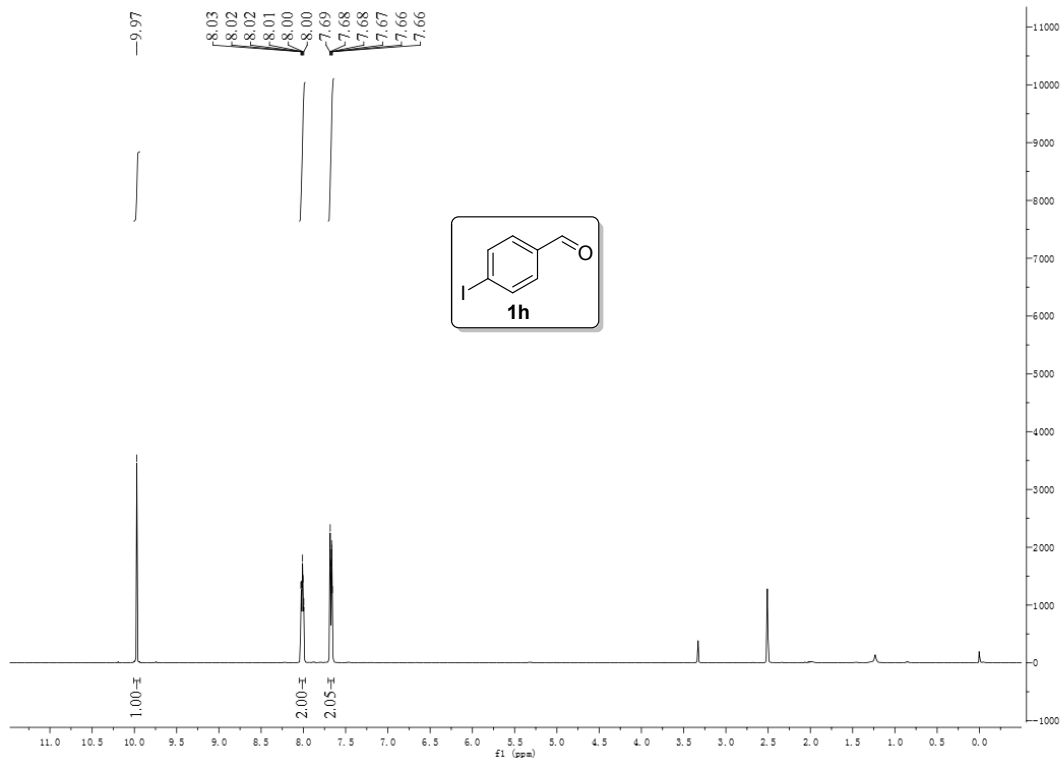


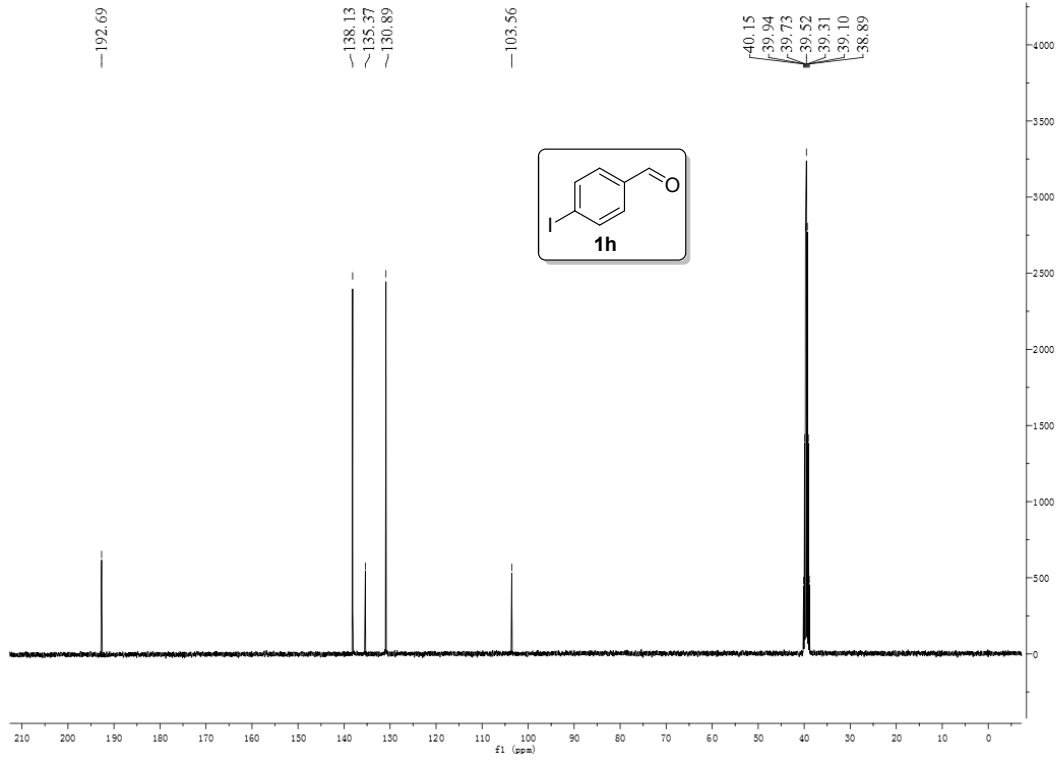
### 2-Iodobenzaldehyde(1g)



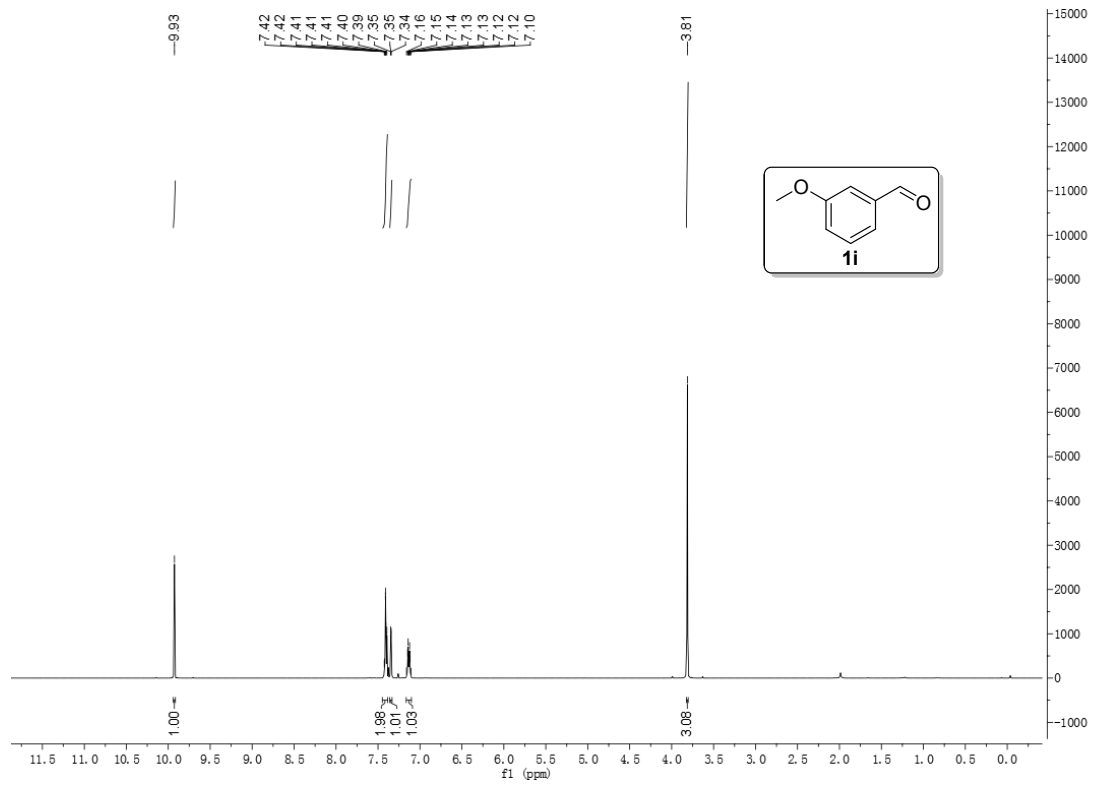


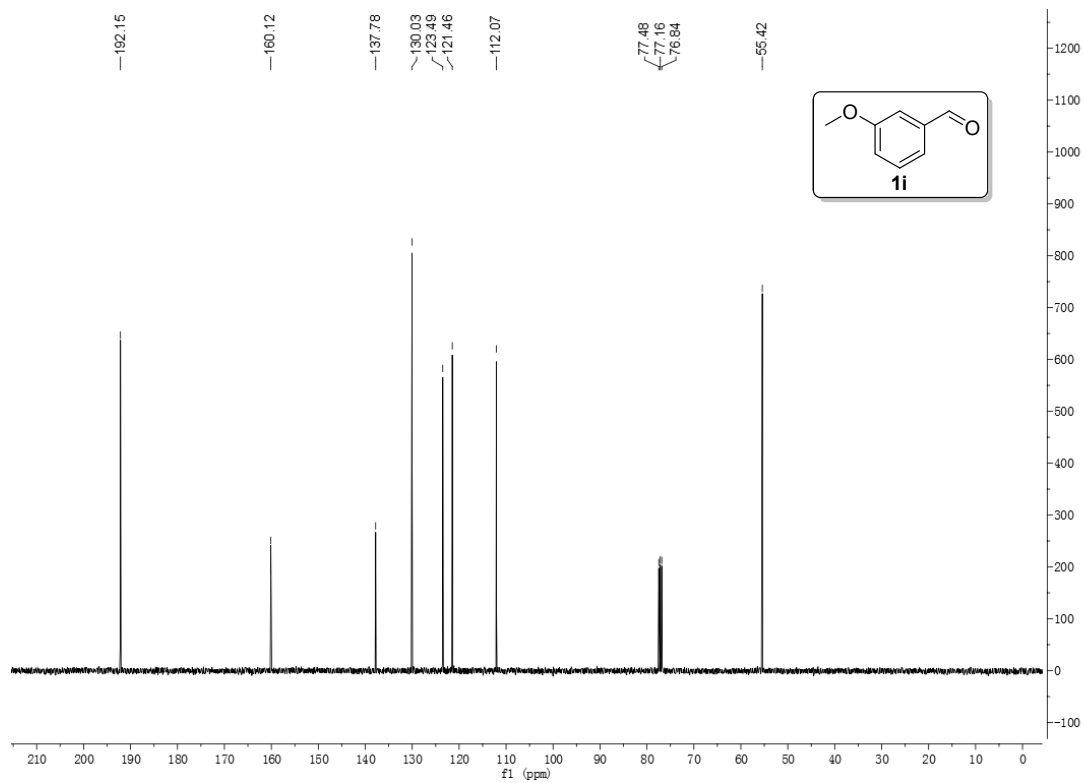
### 4-Iodobenzaldehyde(1h)



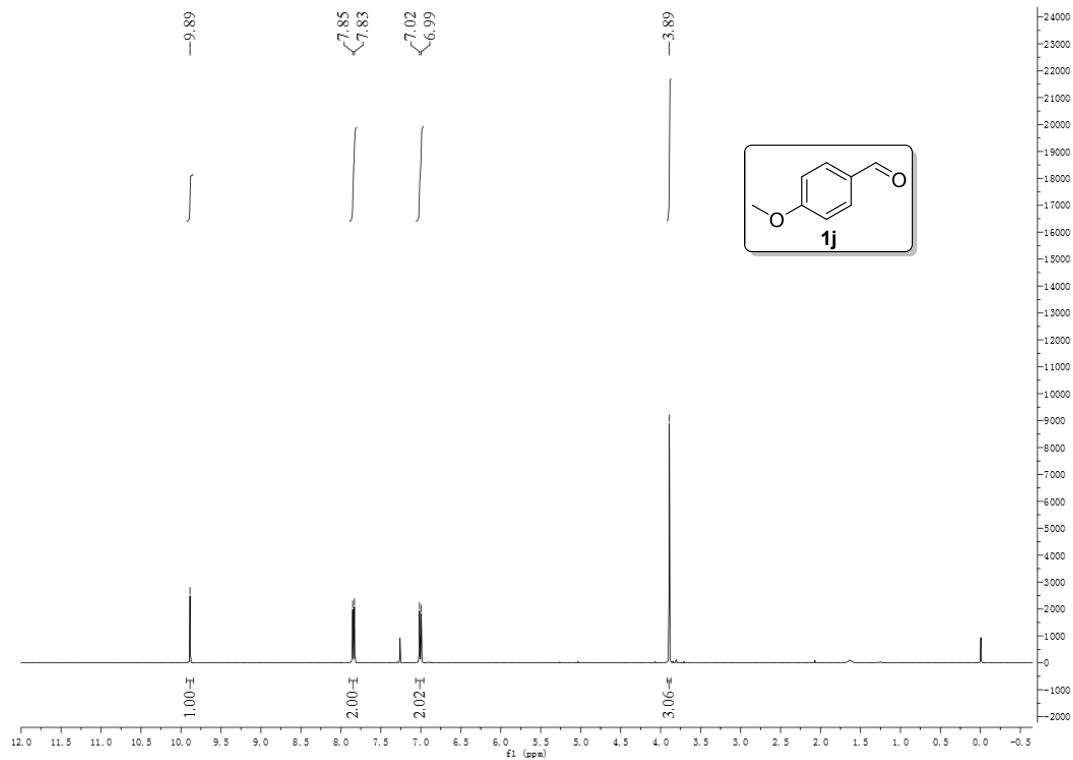


**3-Methoxybenzaldehyde(1i)**

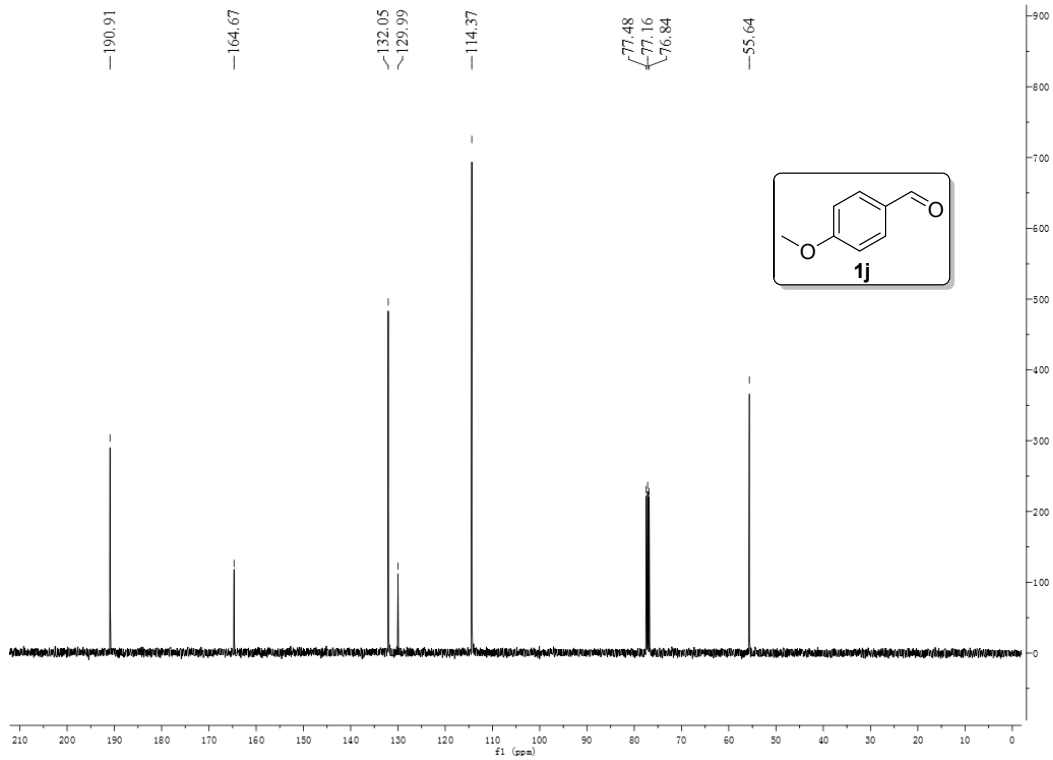




#### 4-Methoxybenzaldehyde(1j)

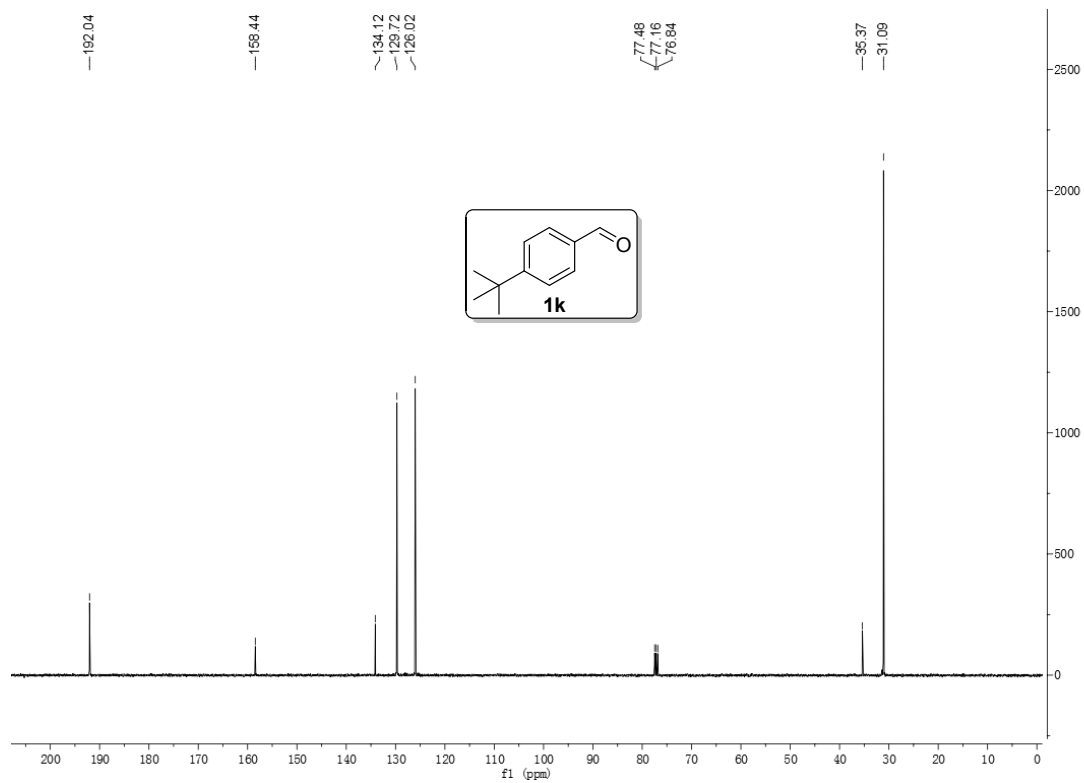




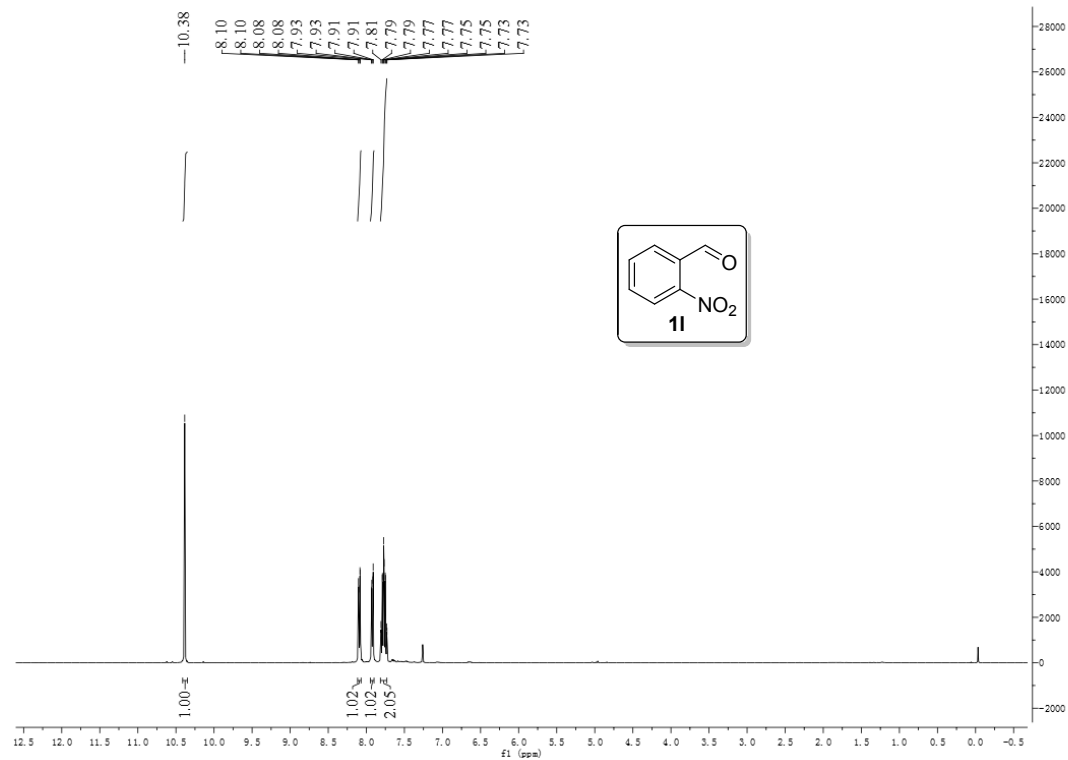


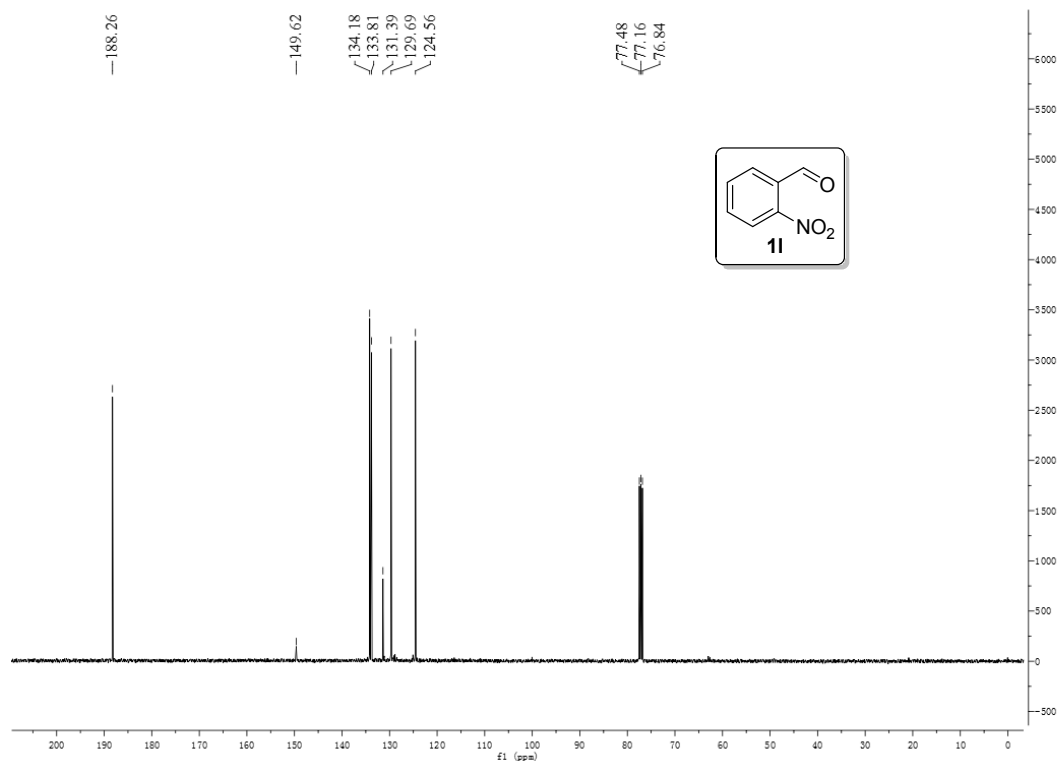
### 4-tert-Butylbenzaldehyde(1k)



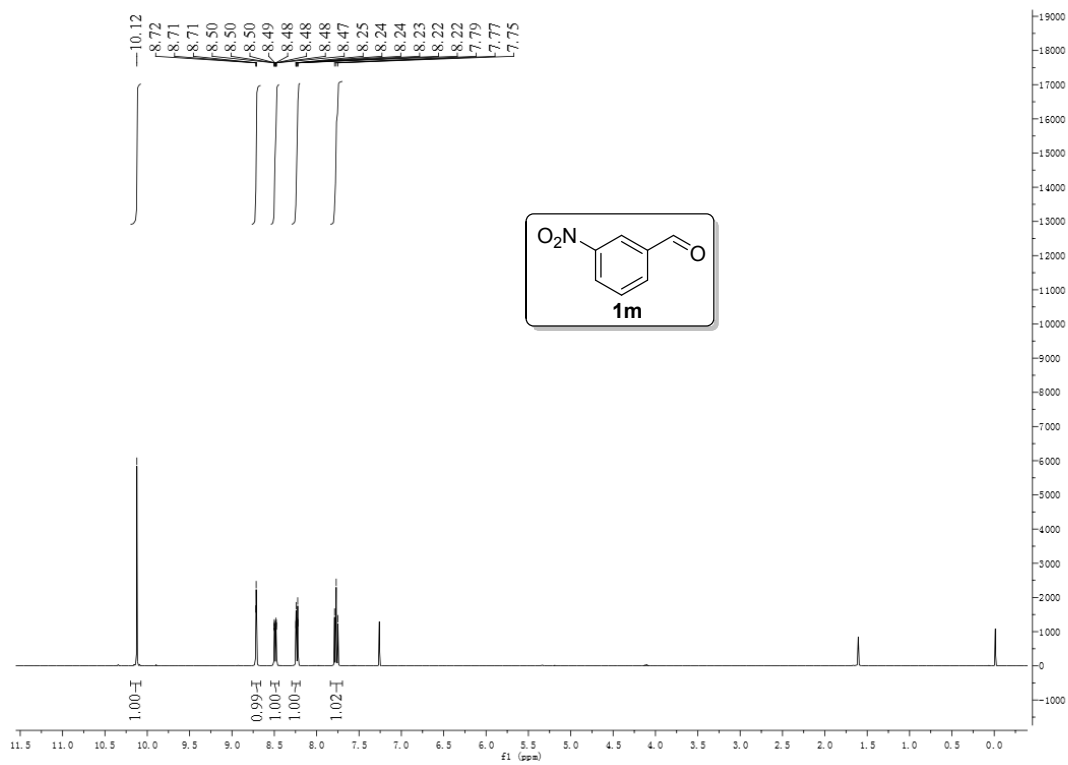


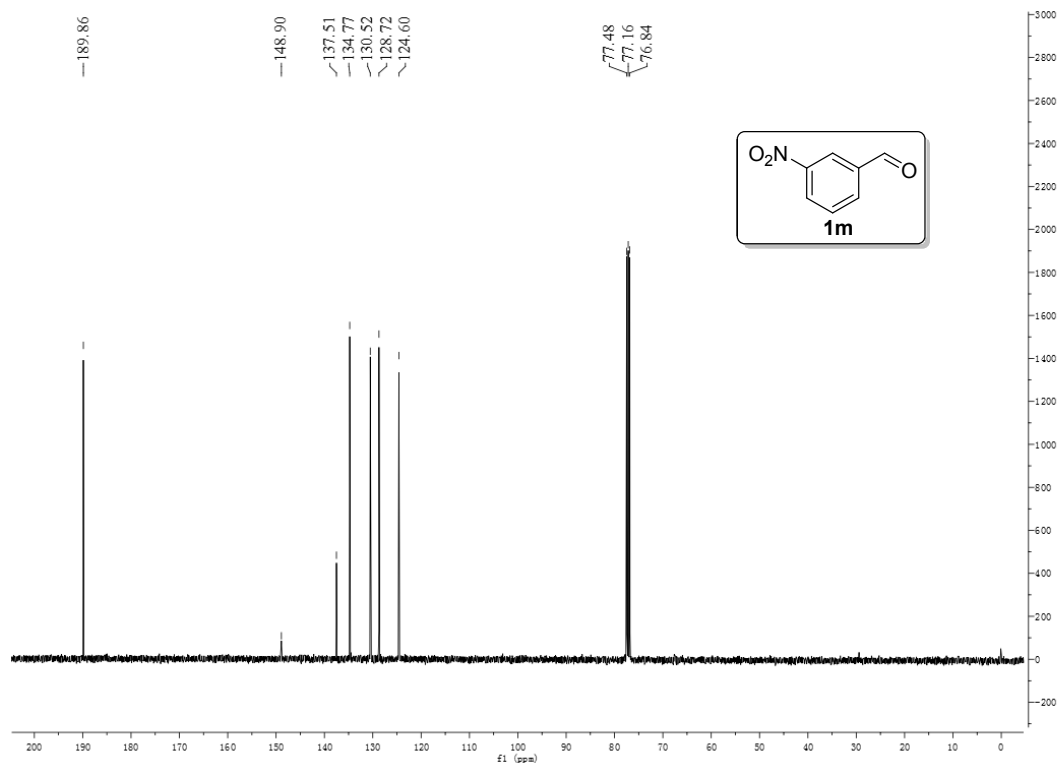
### 2-Nitrobenzaldehyde(1l)



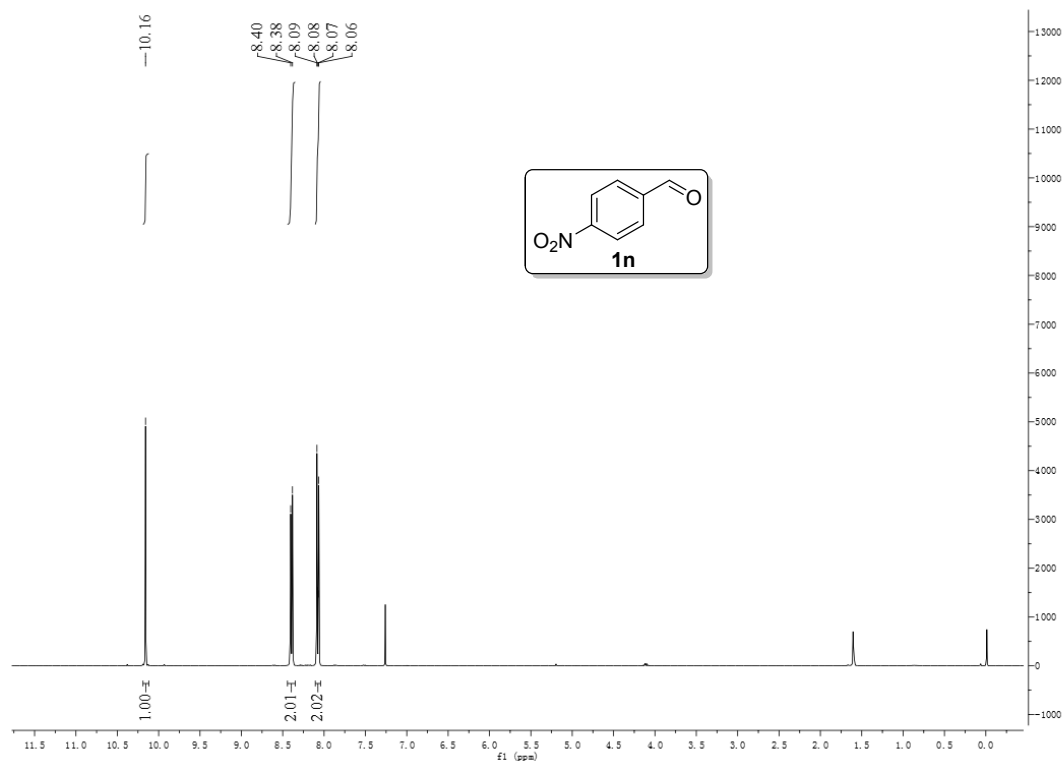


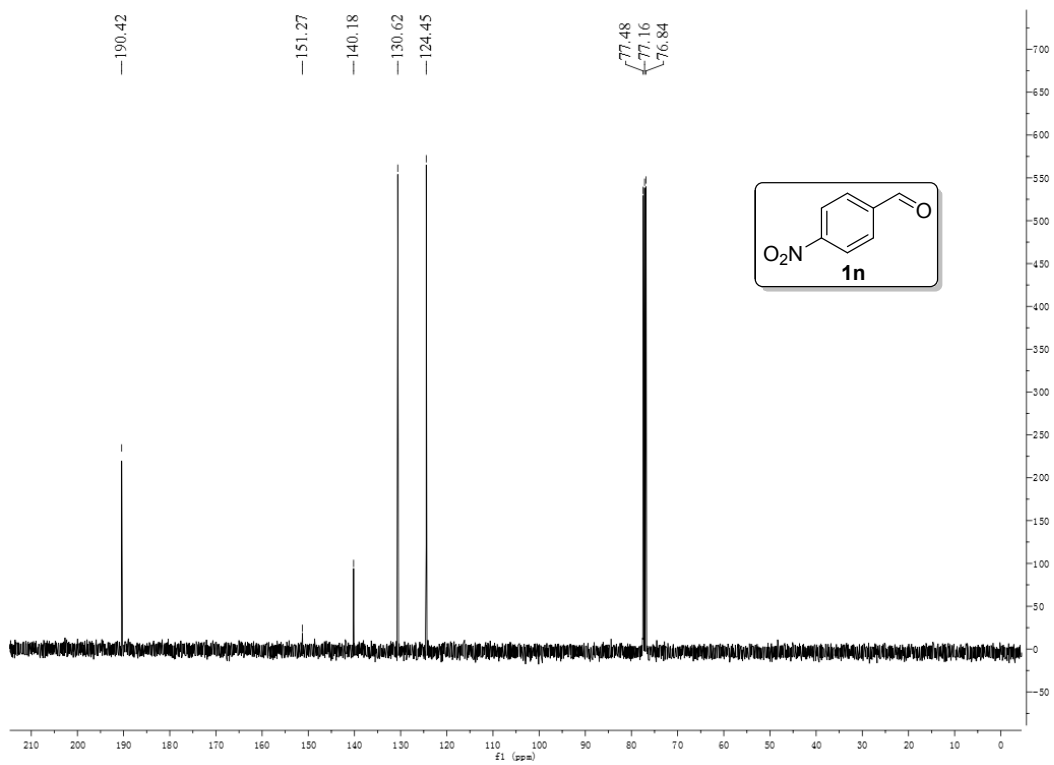
### 3-Nitrobenzaldehyde(1m)



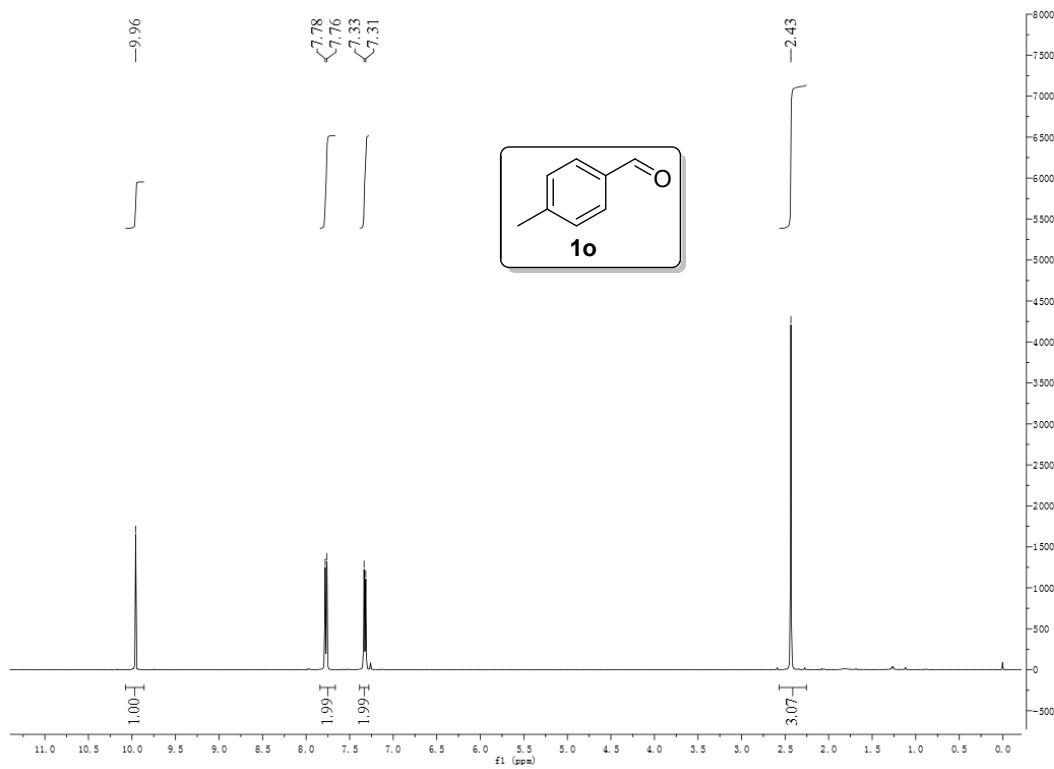


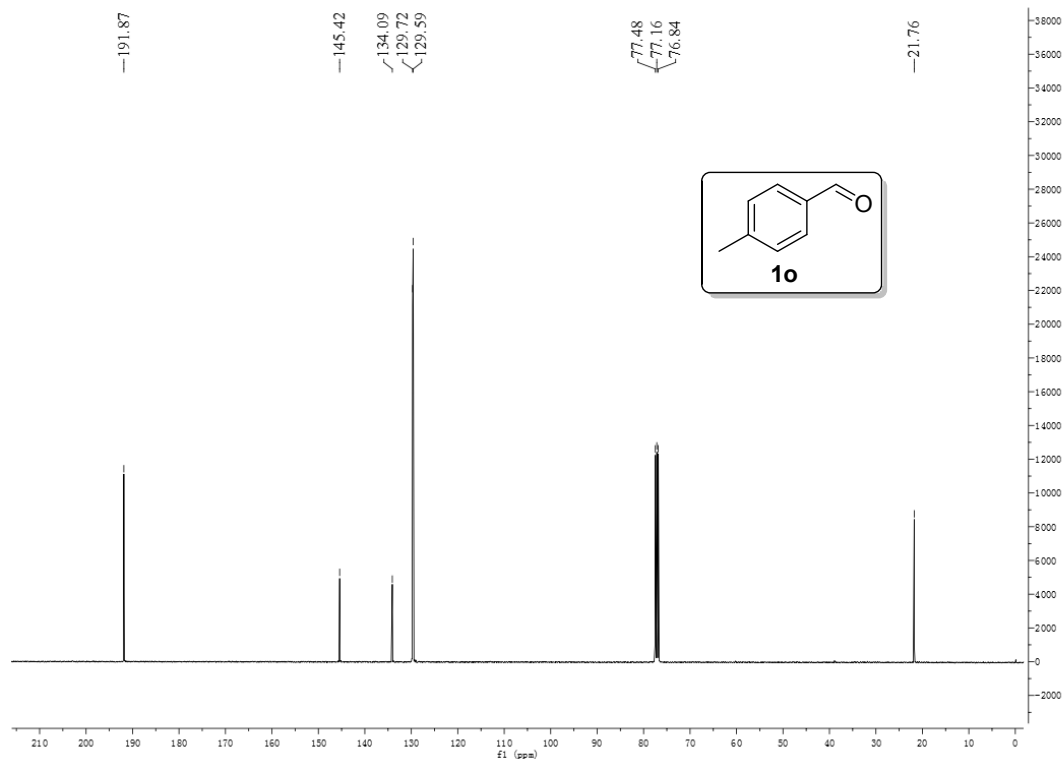
### 4-Nitrobenzaldehyde(1n)



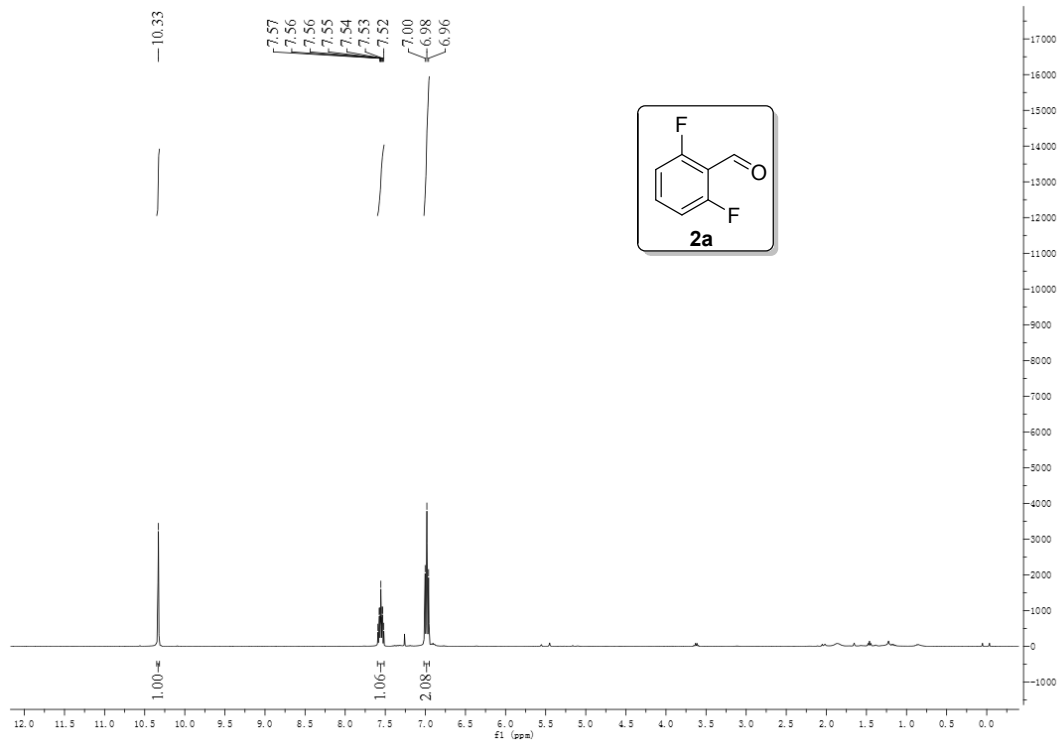


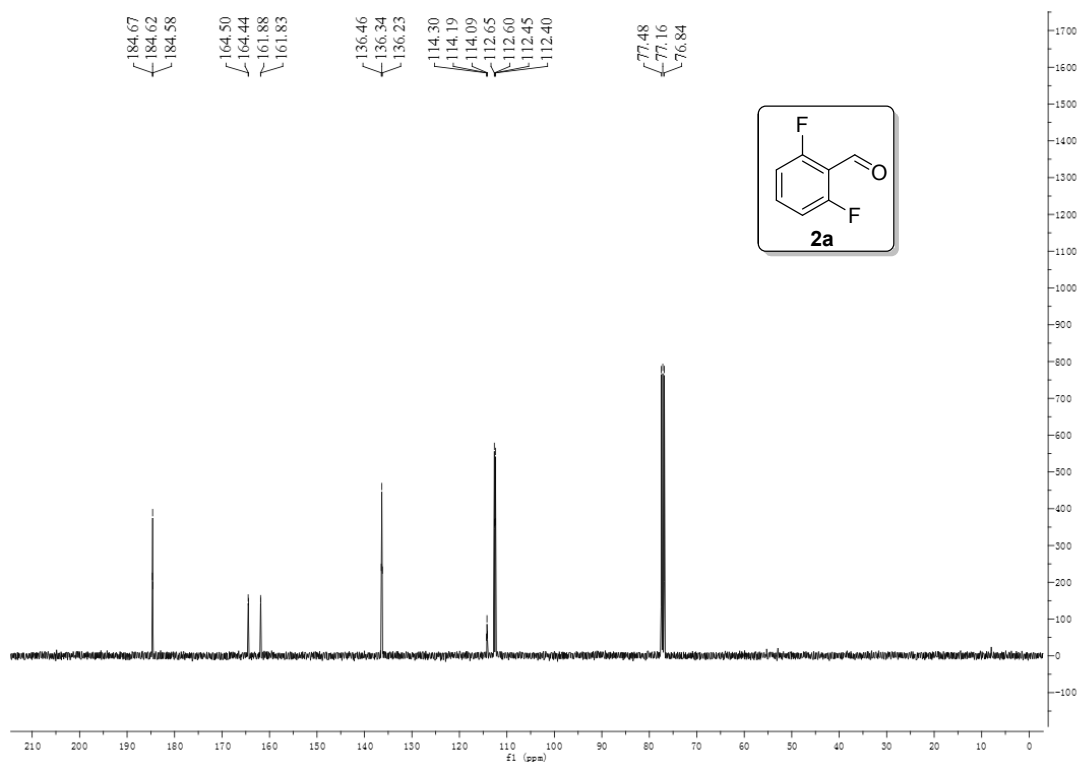
### 4-Methylbenzaldehyde(**1o**)



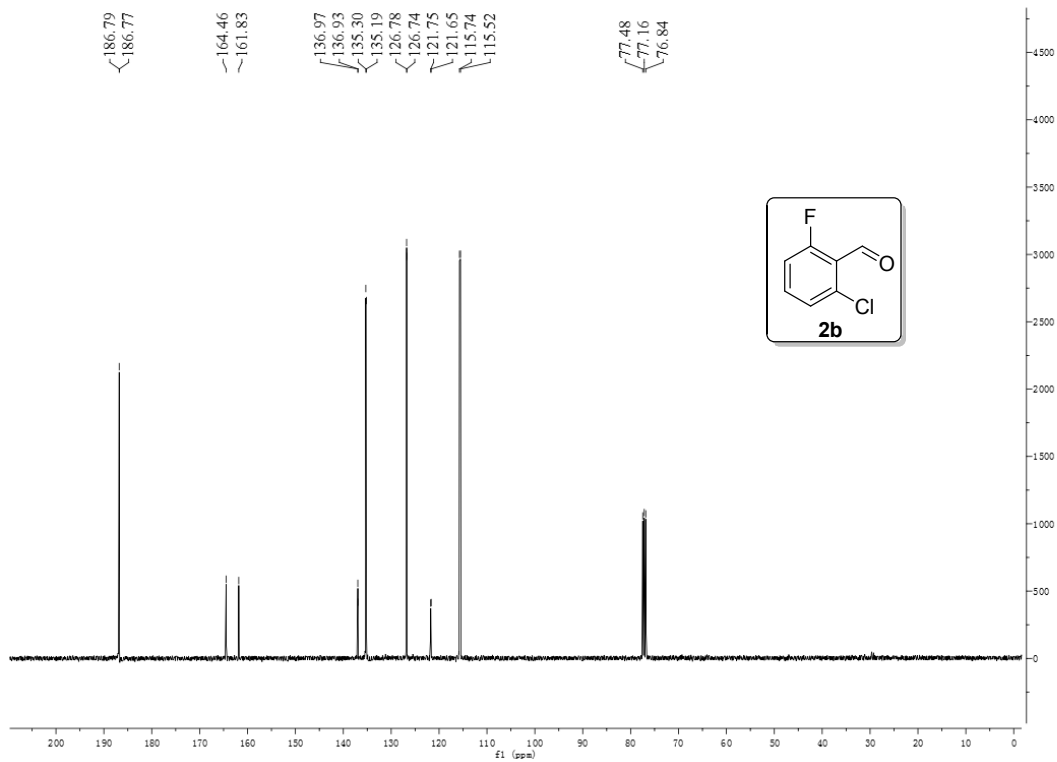
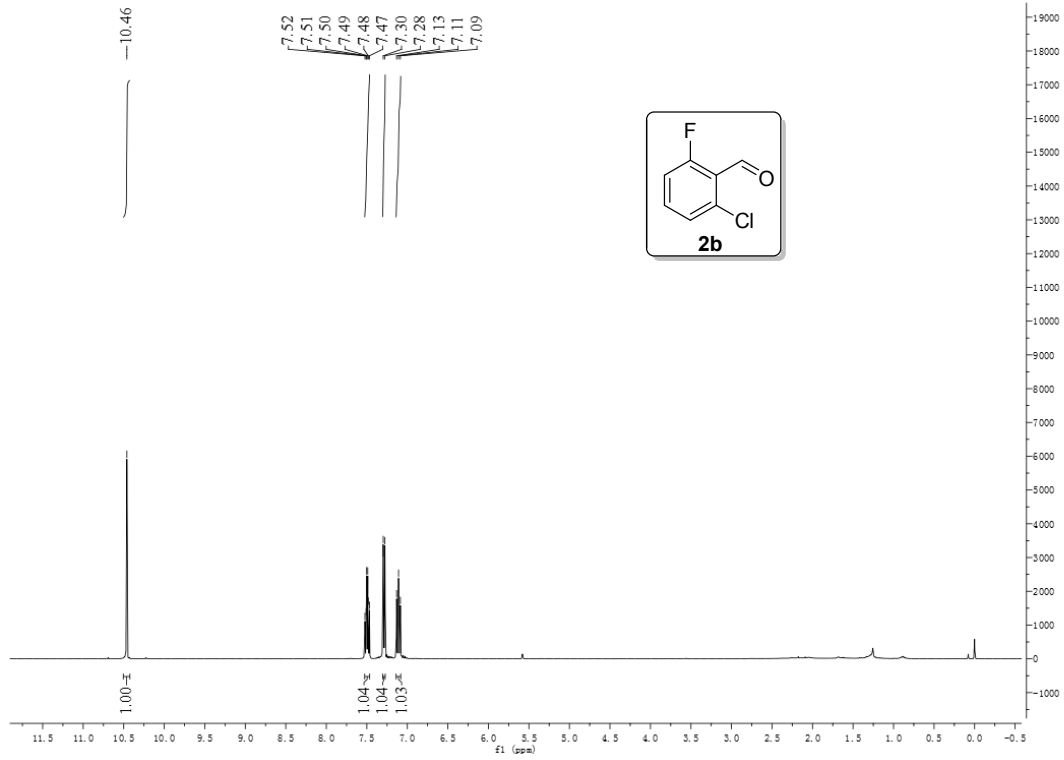


### 2,6-Difluorobenzaldehyde(2a)

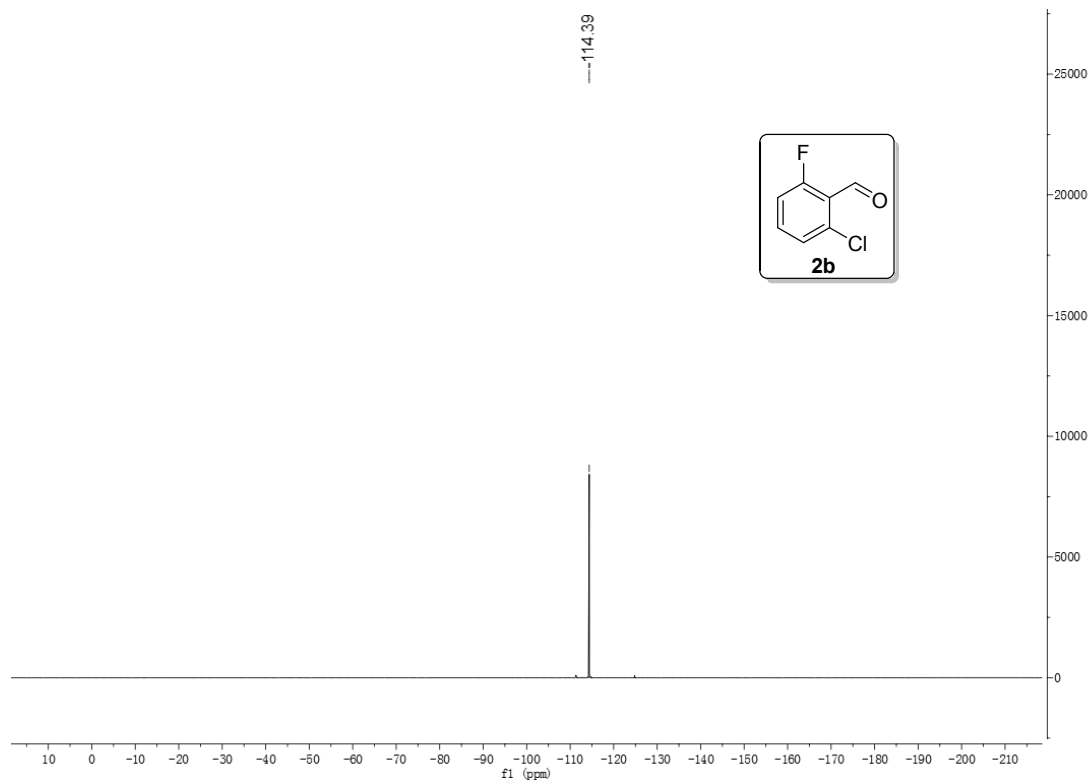




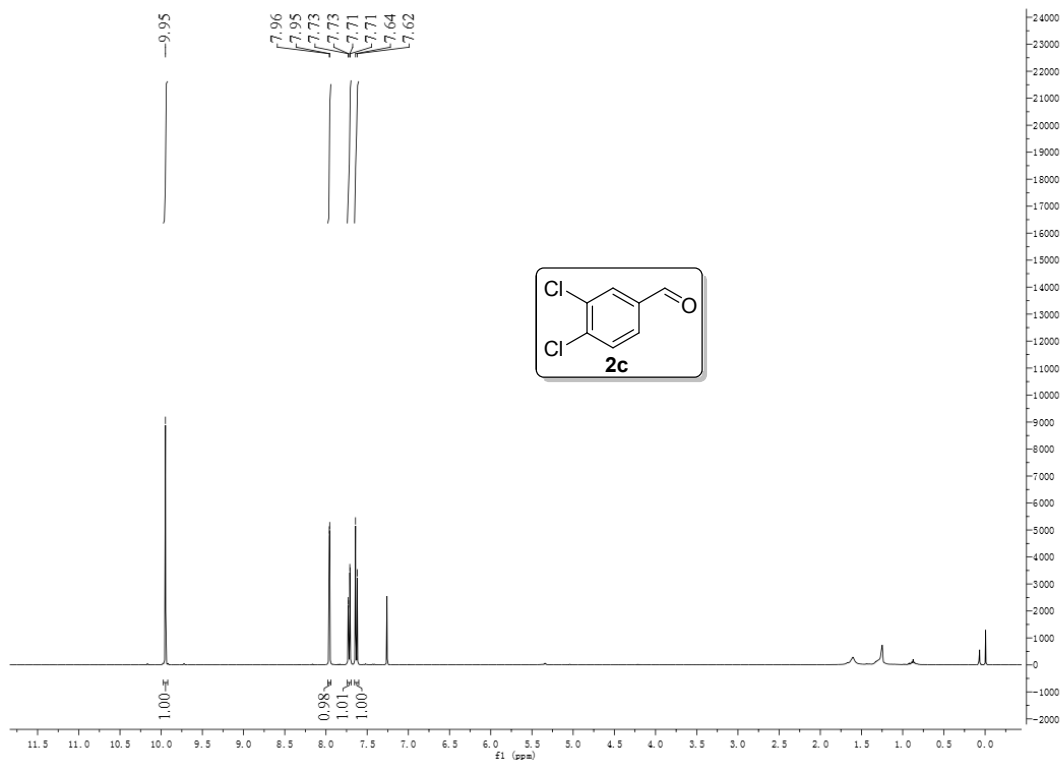
2-Chloro-6-fluorobenzaldehyde(2b)

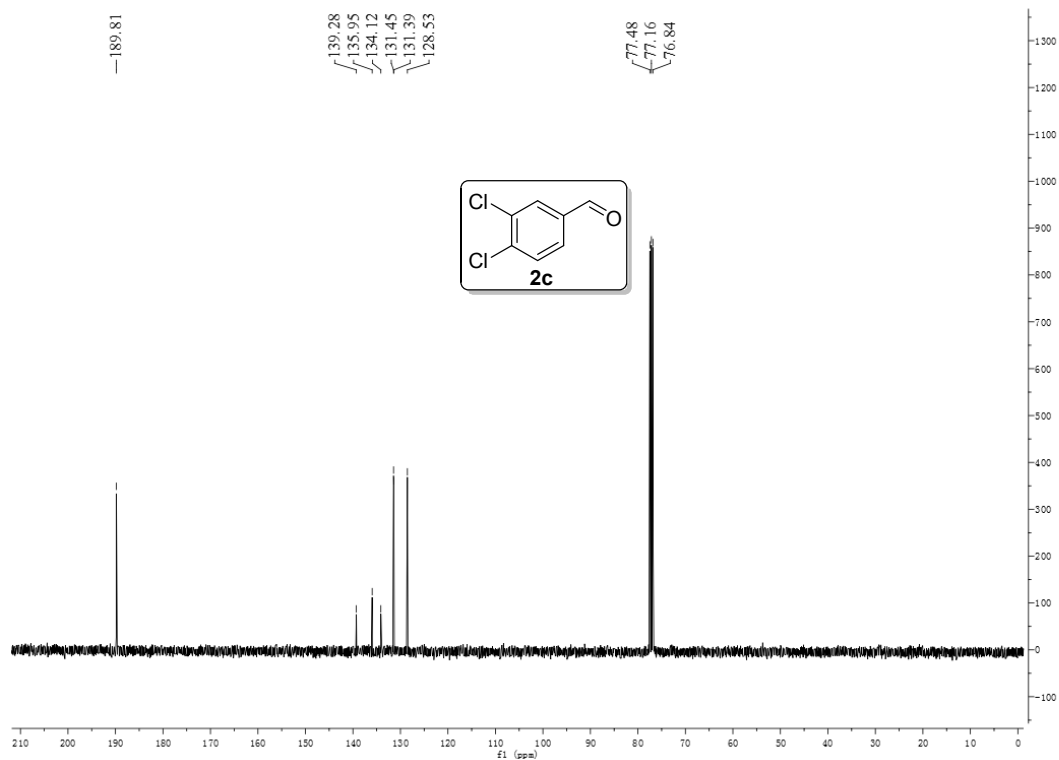




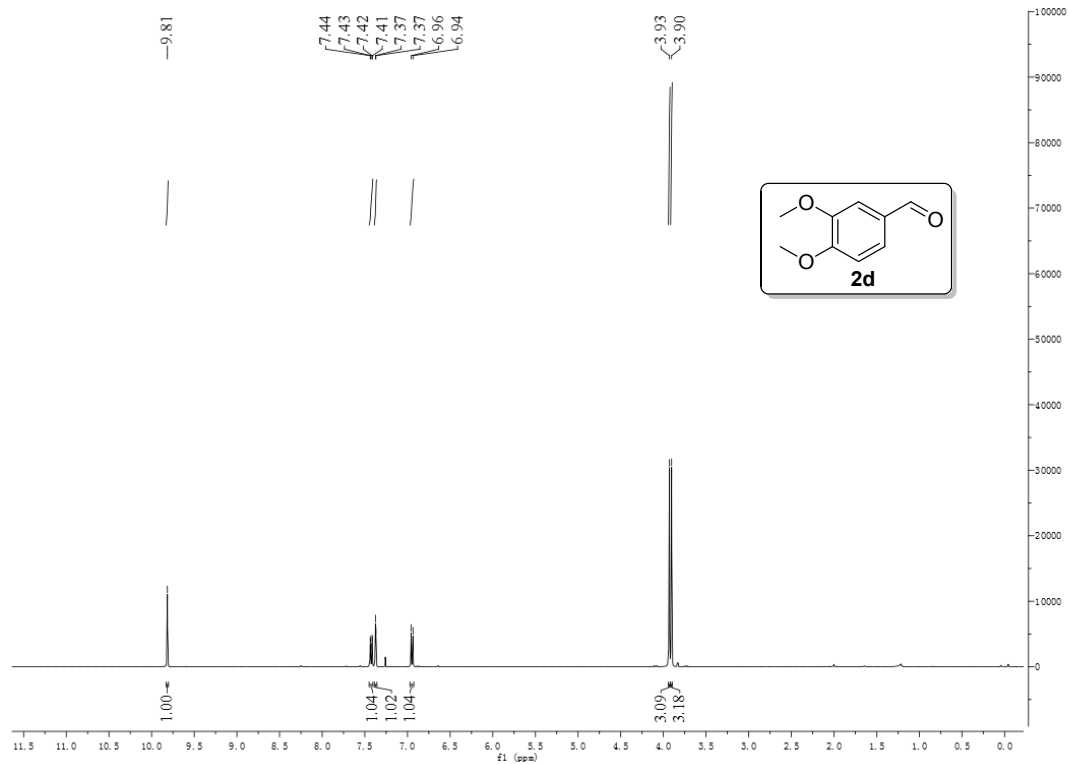


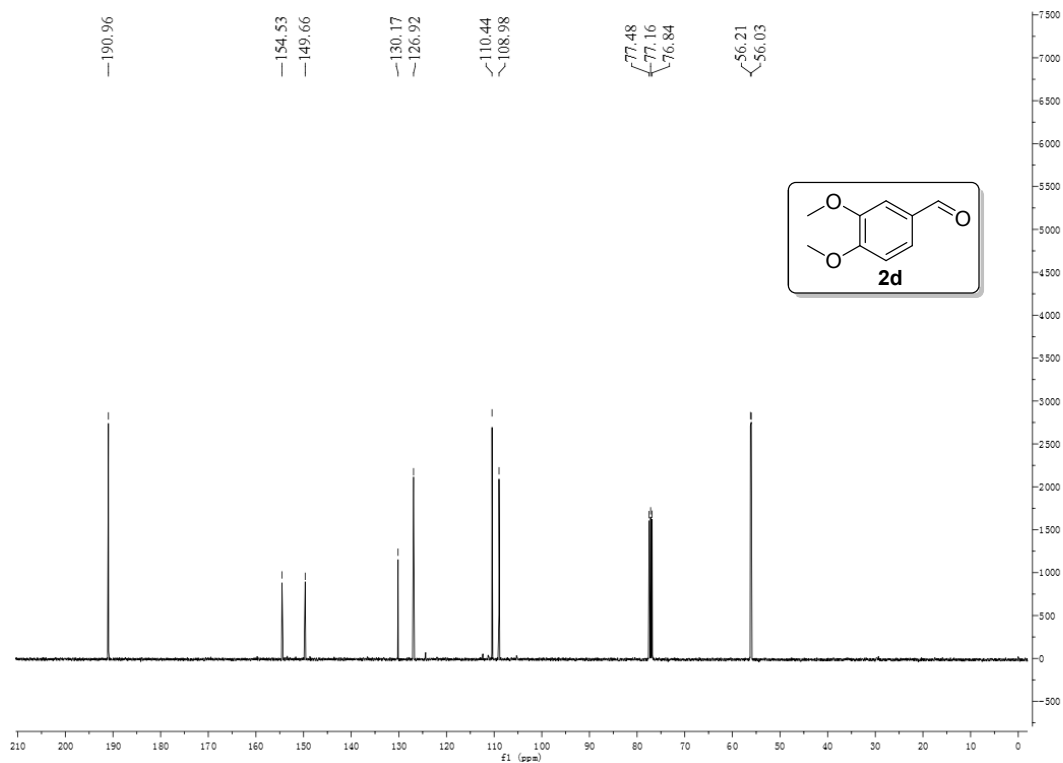
### 3,4-Dichlorobenzaldehyde(2c)



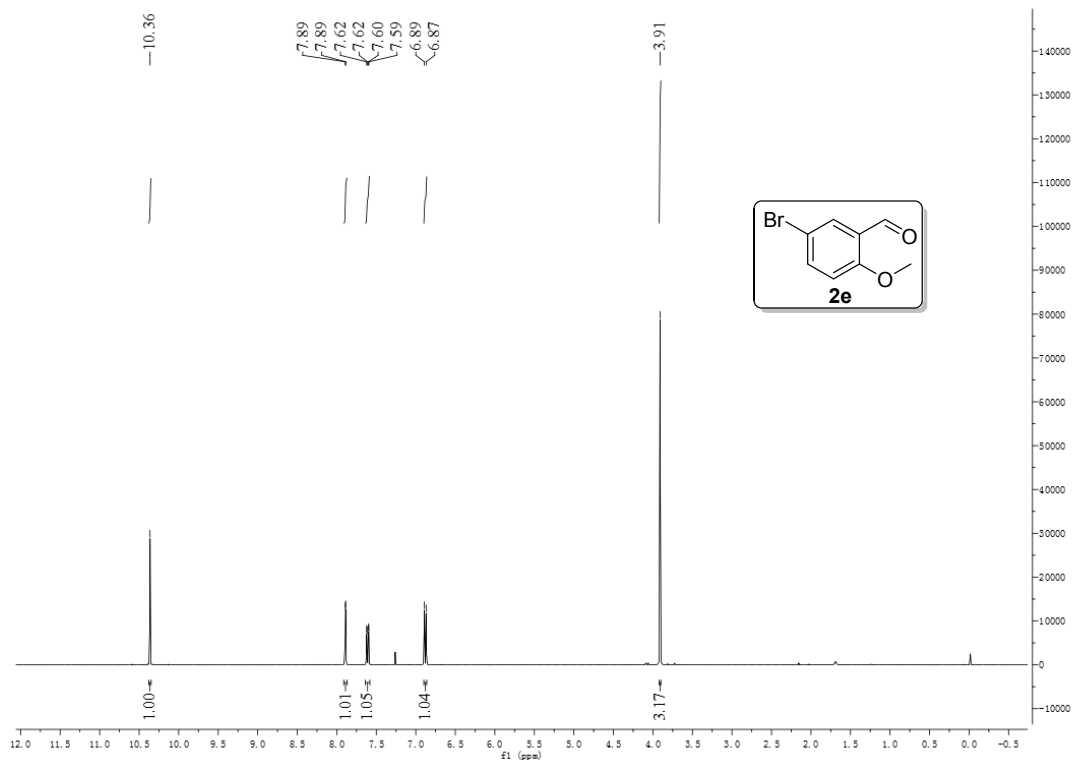


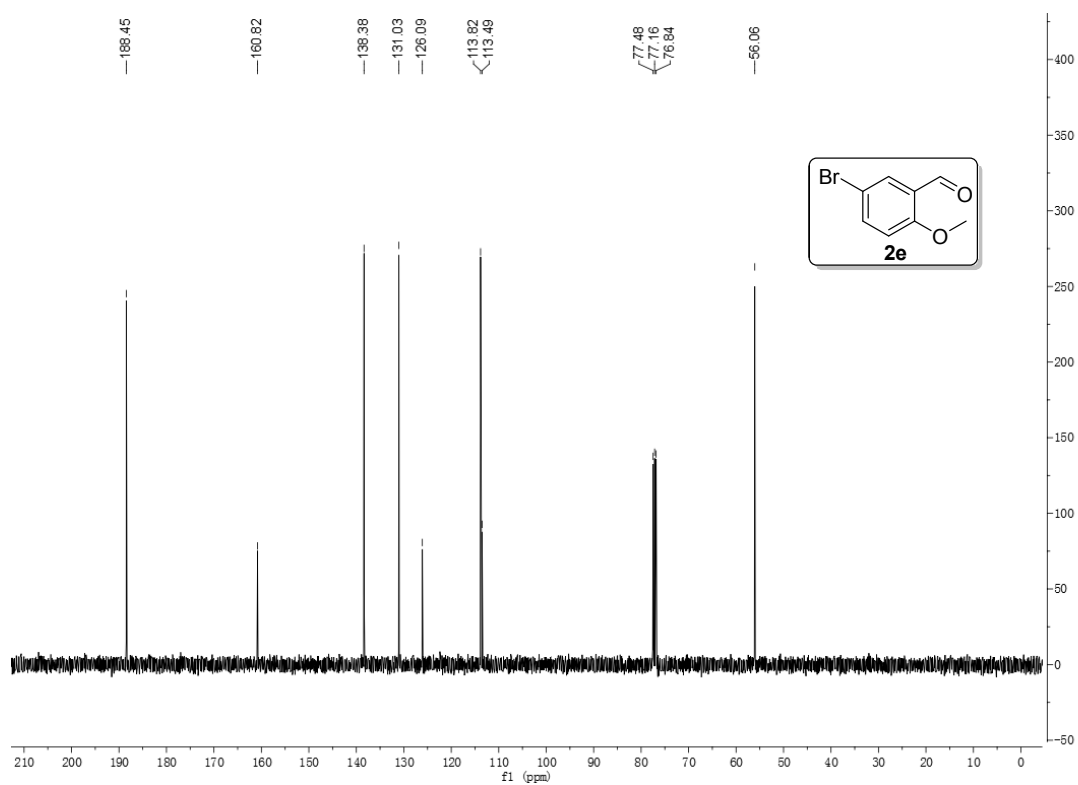
### 3,4-Dimethoxy-benzaldehyde(2d)



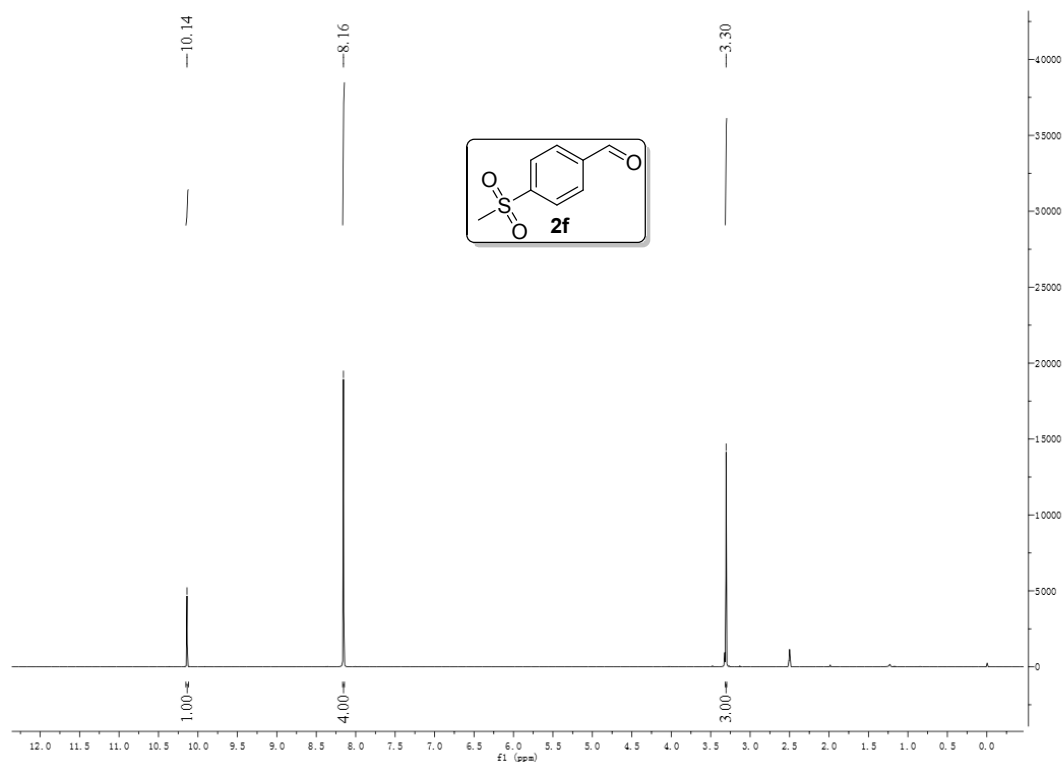


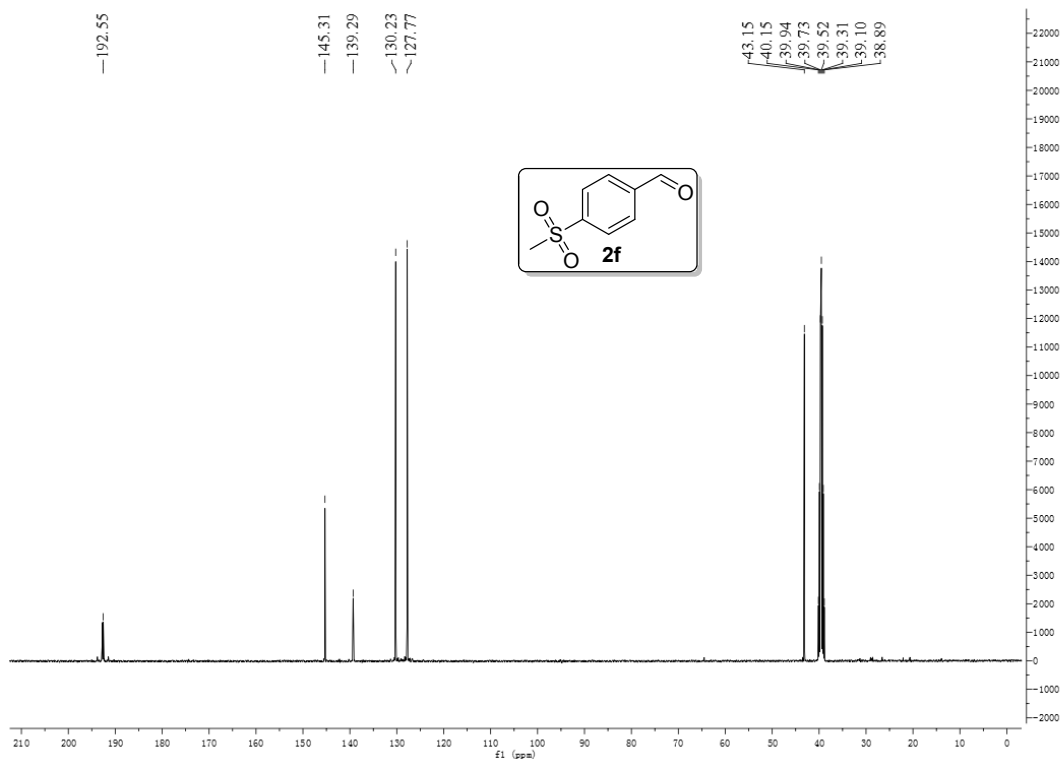
### 5-Bromo-2-methoxybenzaldehyde(2e)



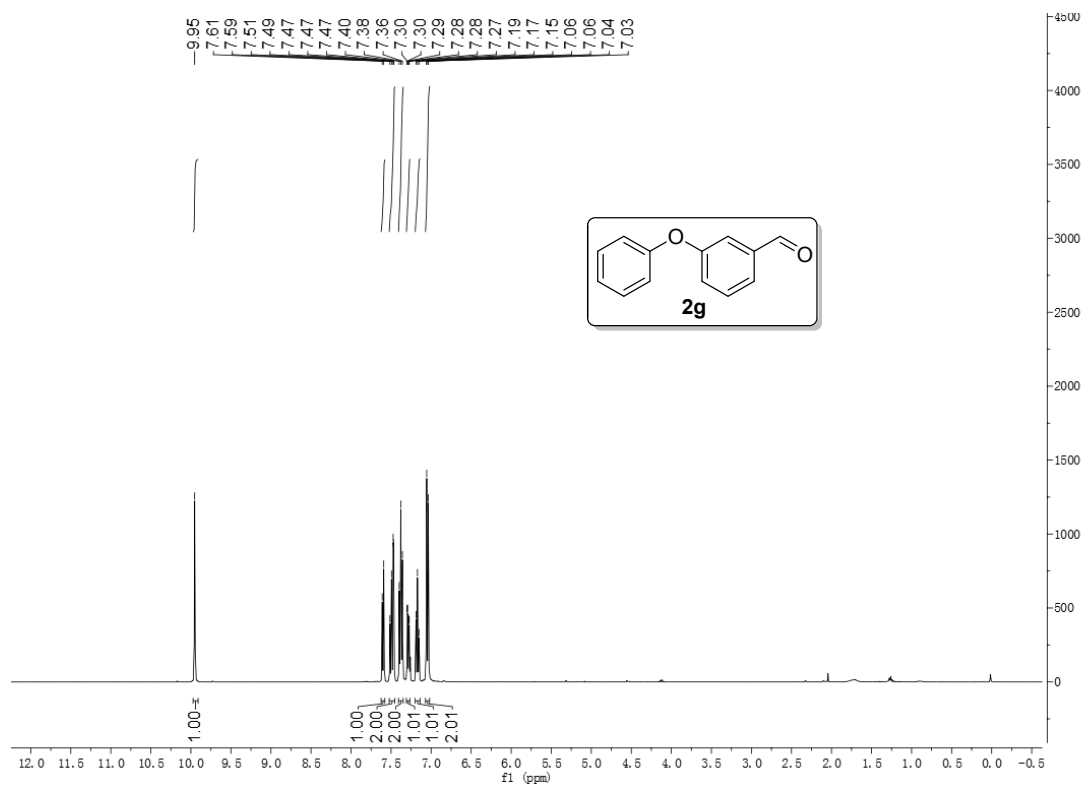


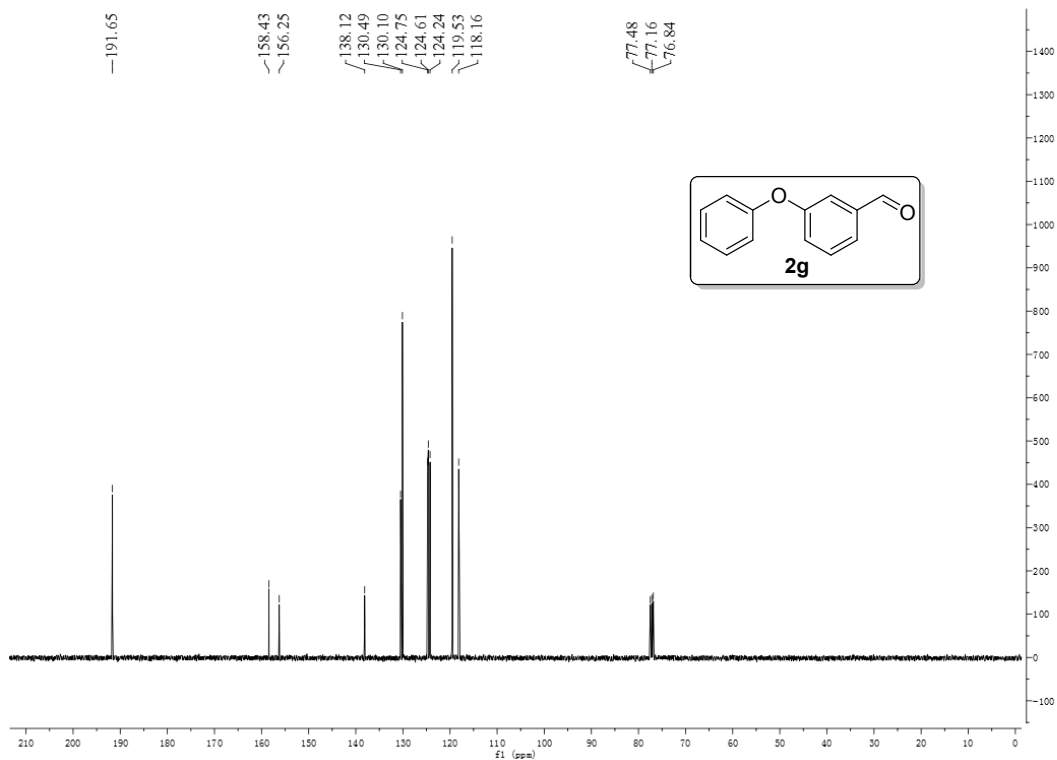
#### 4-Methylsulphonyl benzaldehyde(2f)



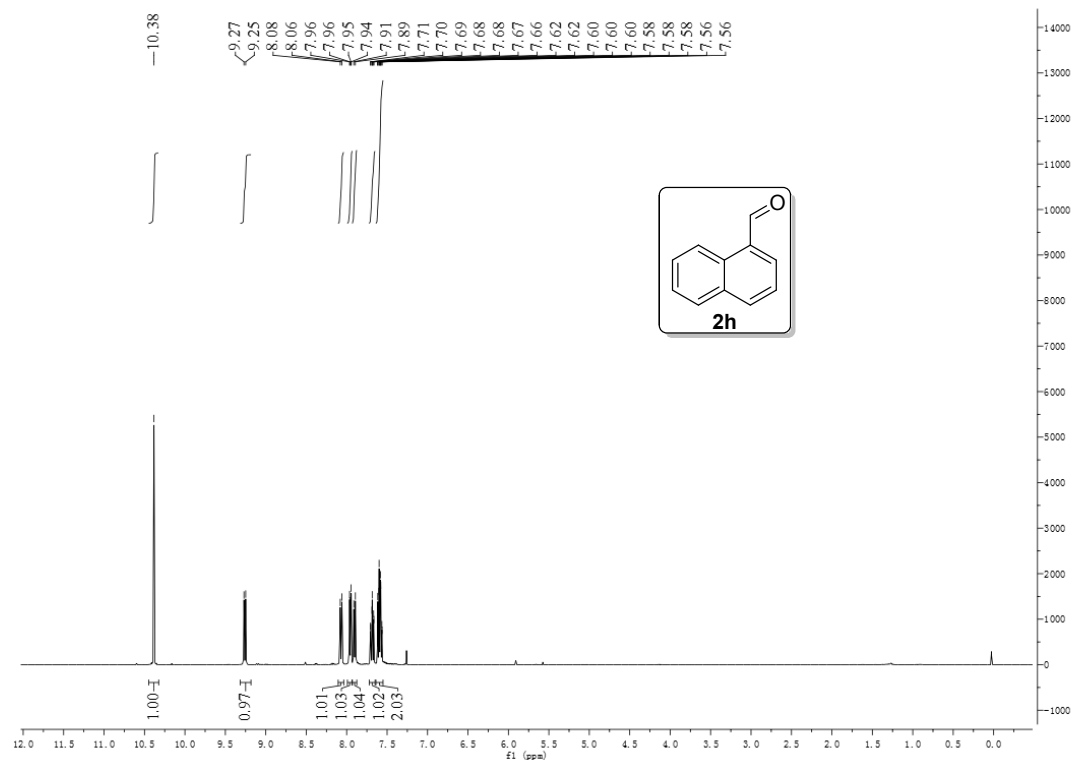


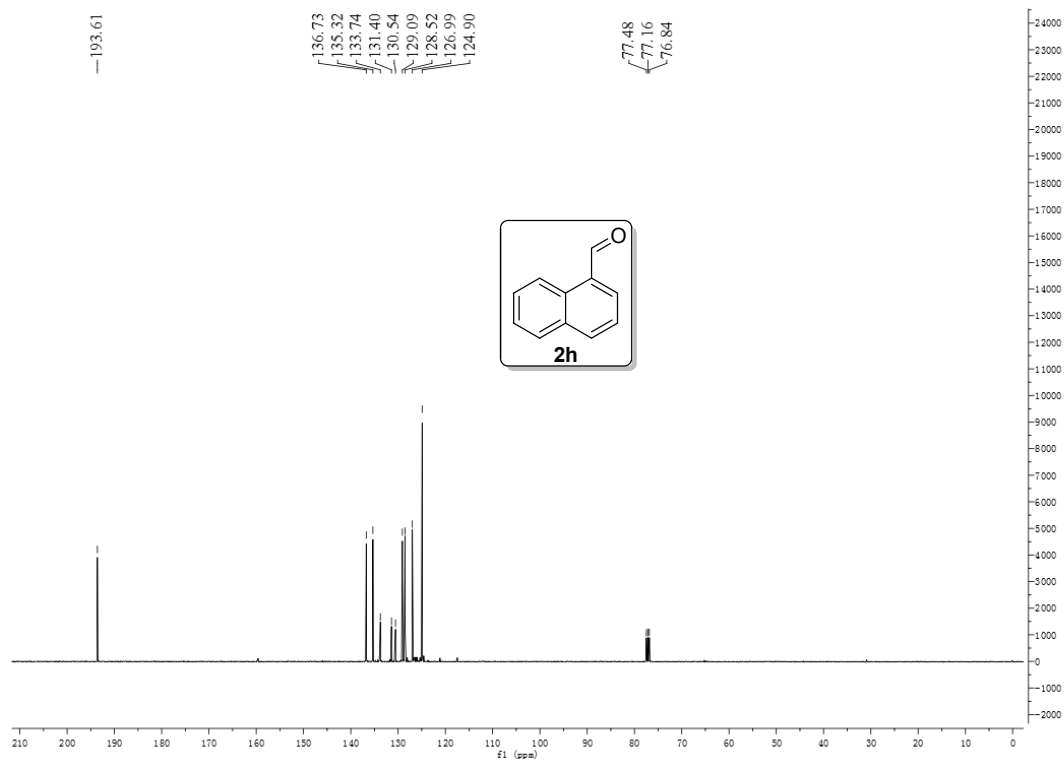
### 3-Phenoxy-benzaldehyde(2g)



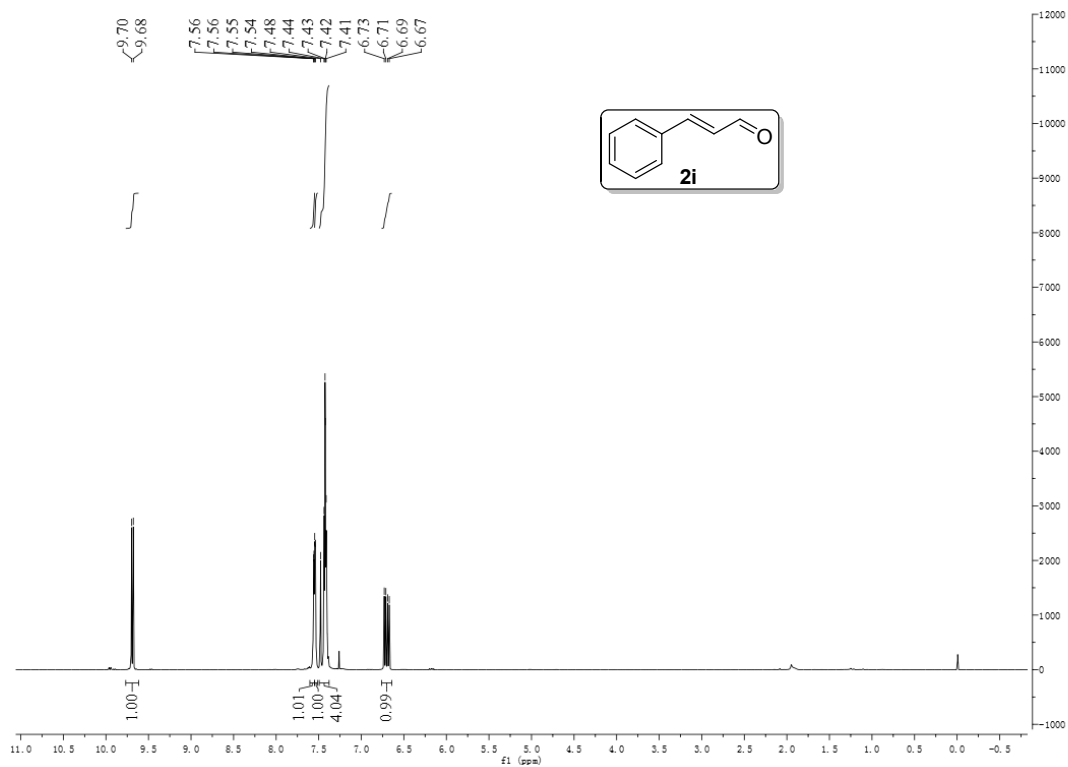


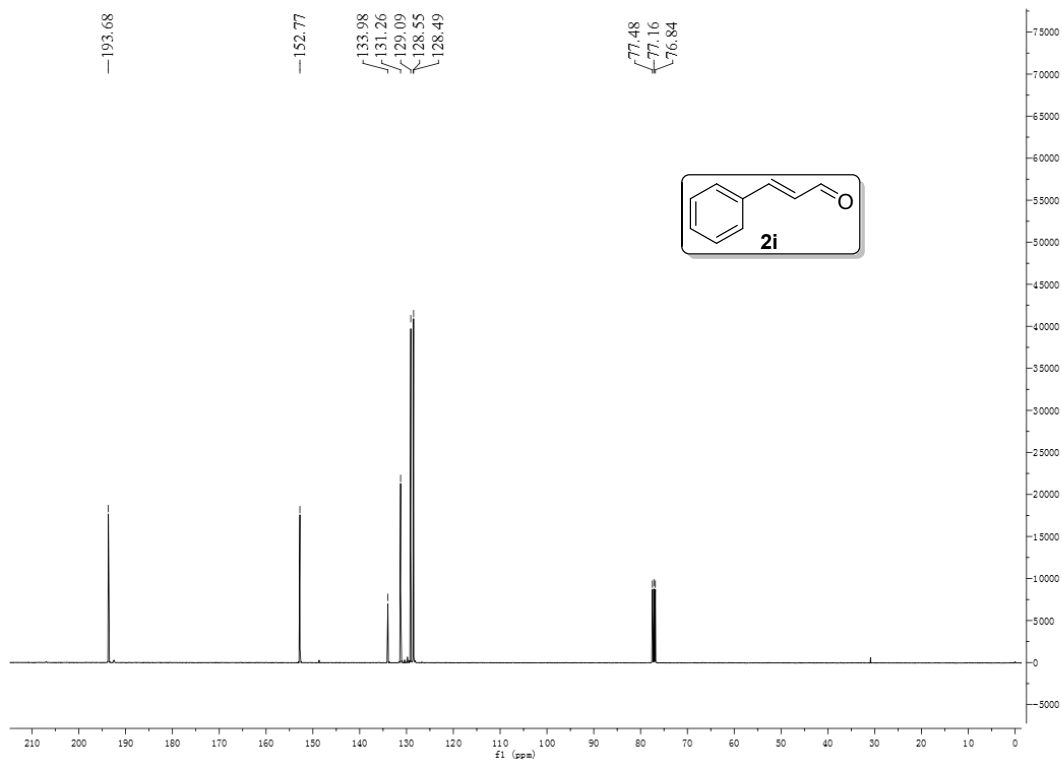
### 1-Naphthalenecarboxaldehyde(2h)



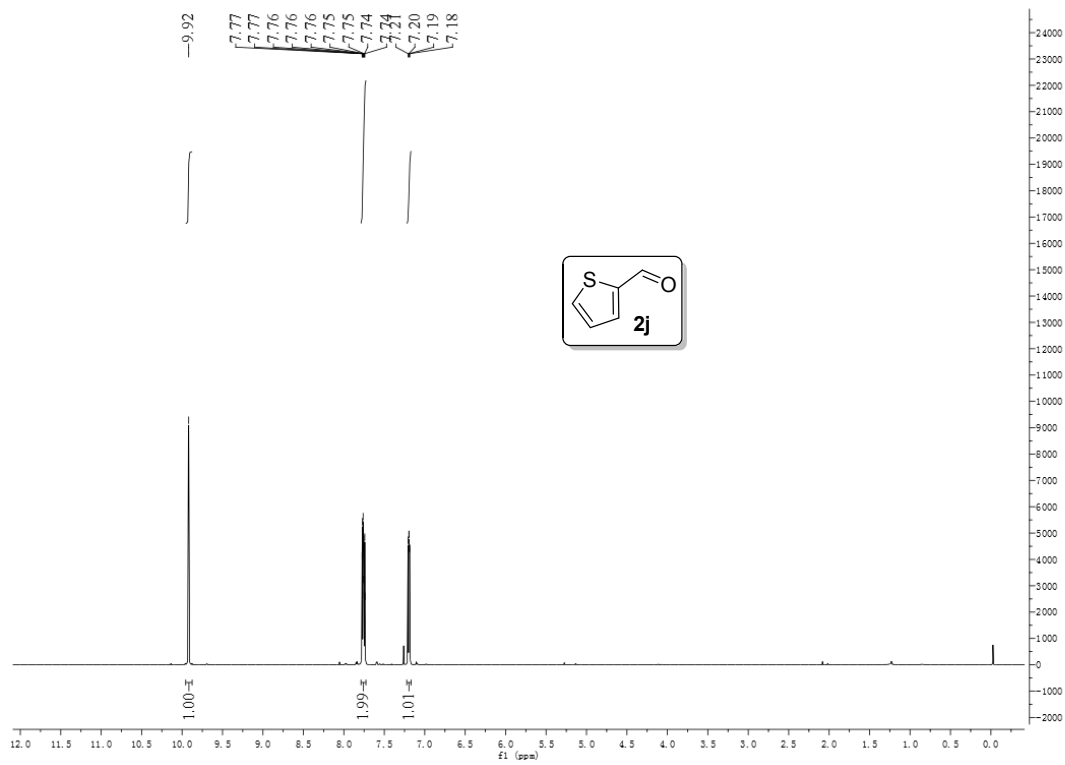


### 3-Phenyl-2-propenal(2i)

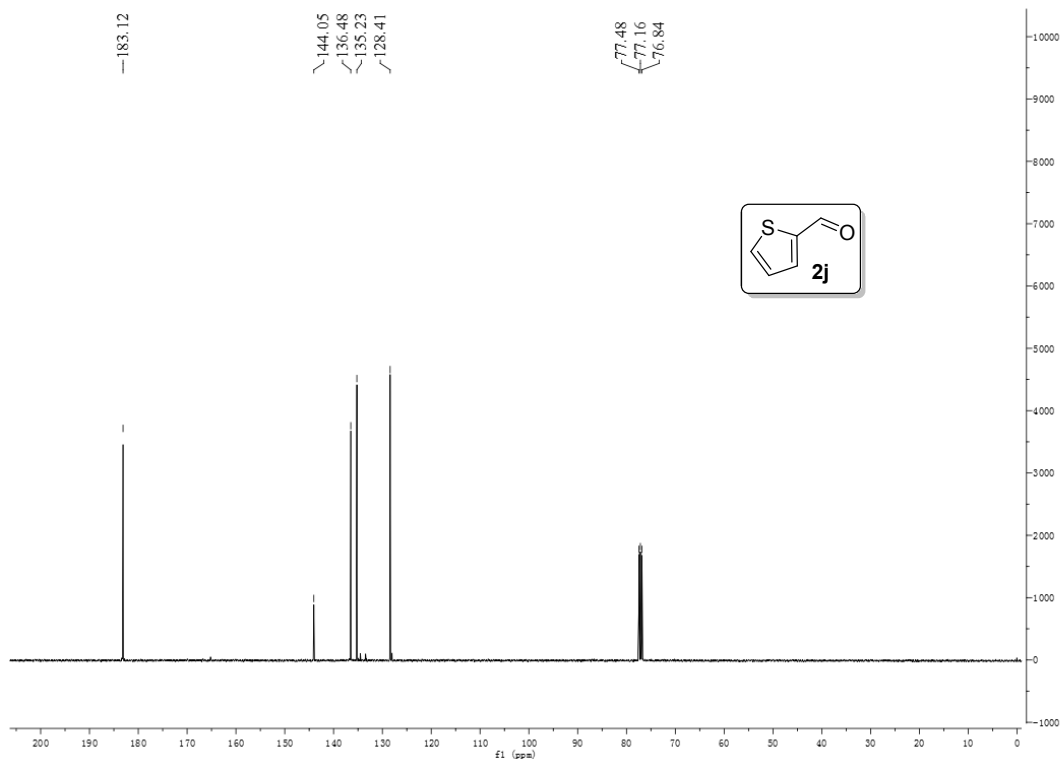




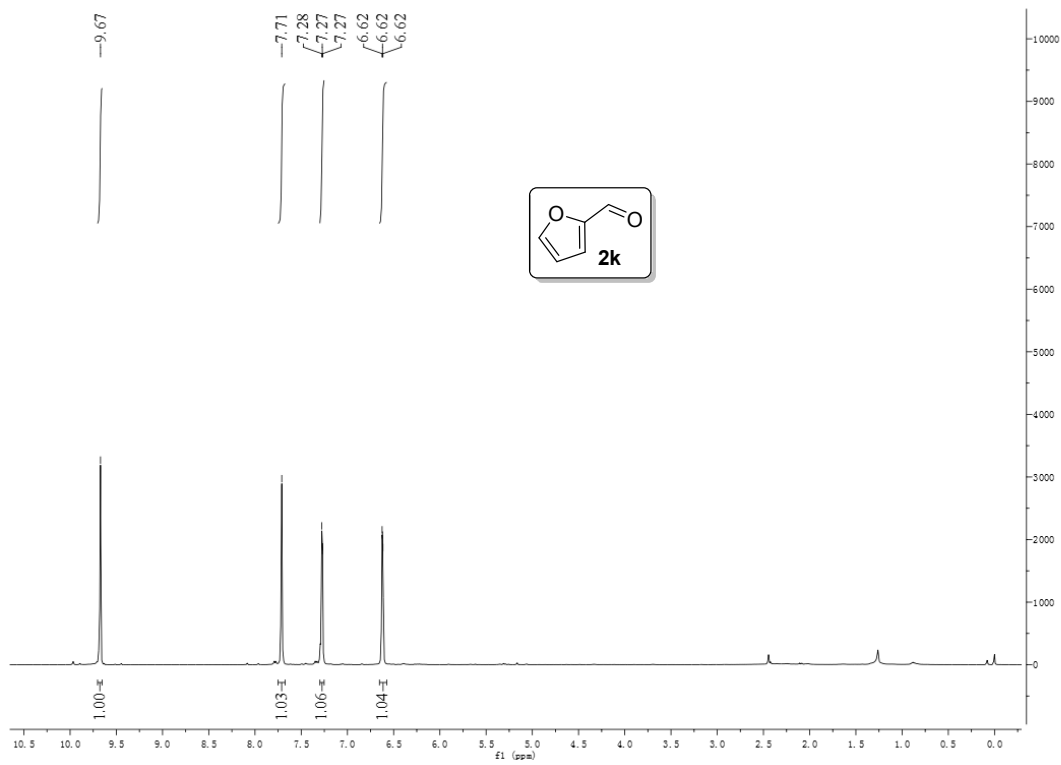
### 2-Thiophenecarboxaldehyde(2j)

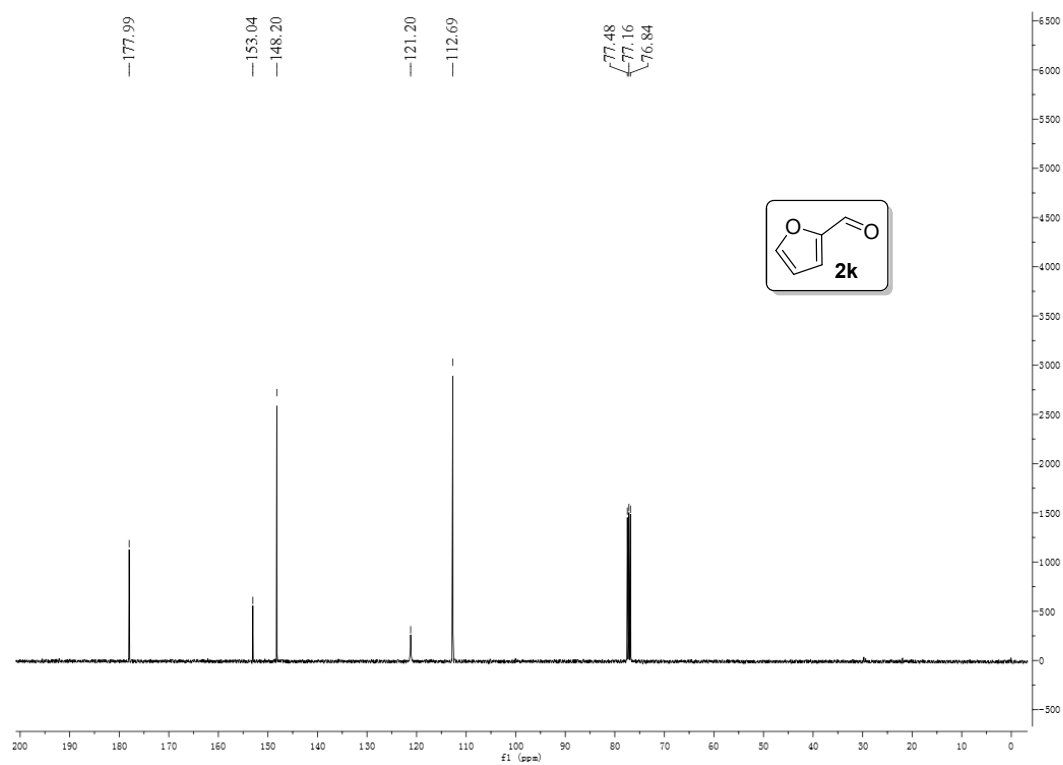




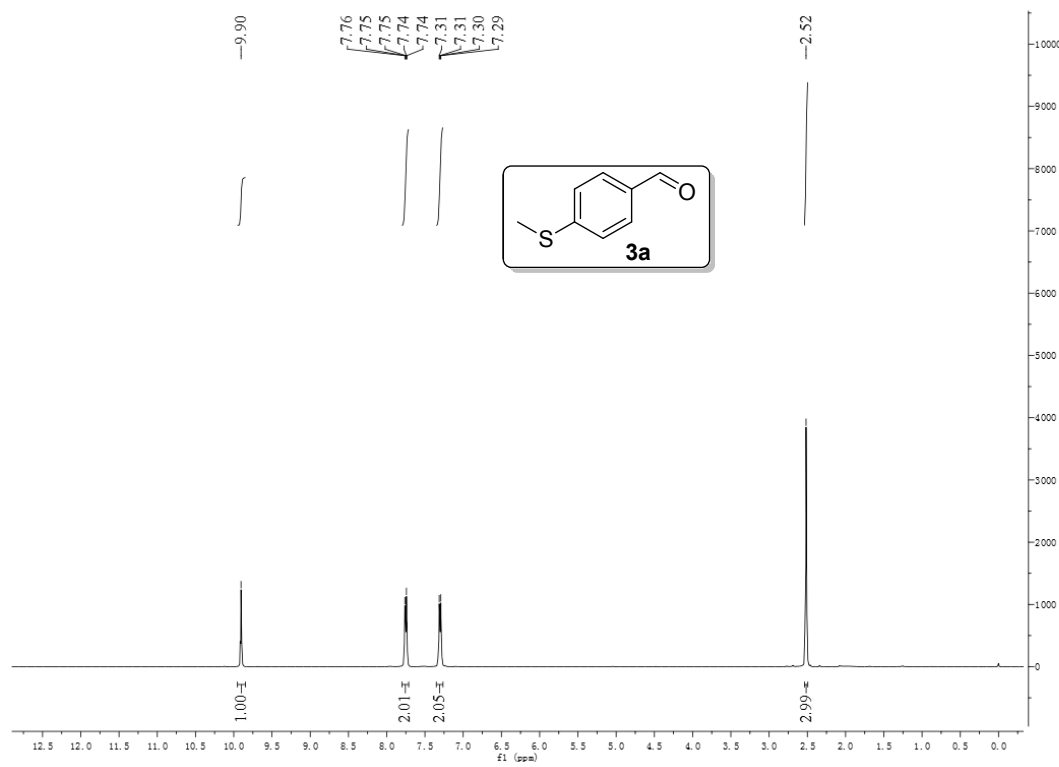


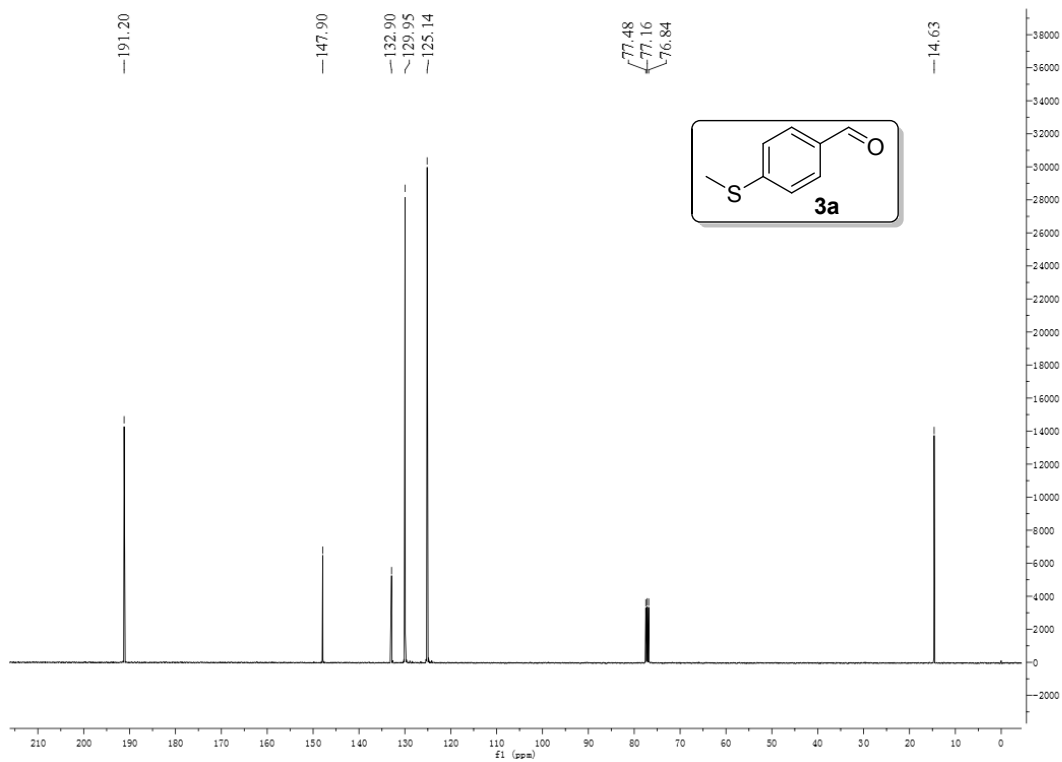
### 2-Furancarboxaldehyde(2k)



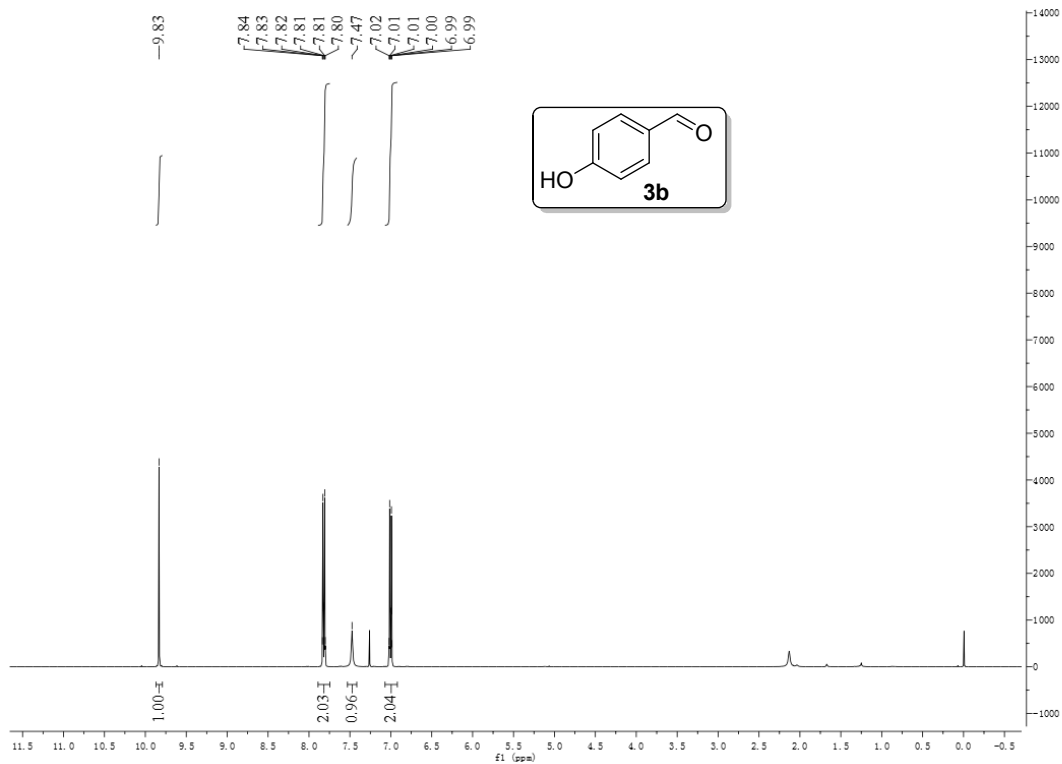


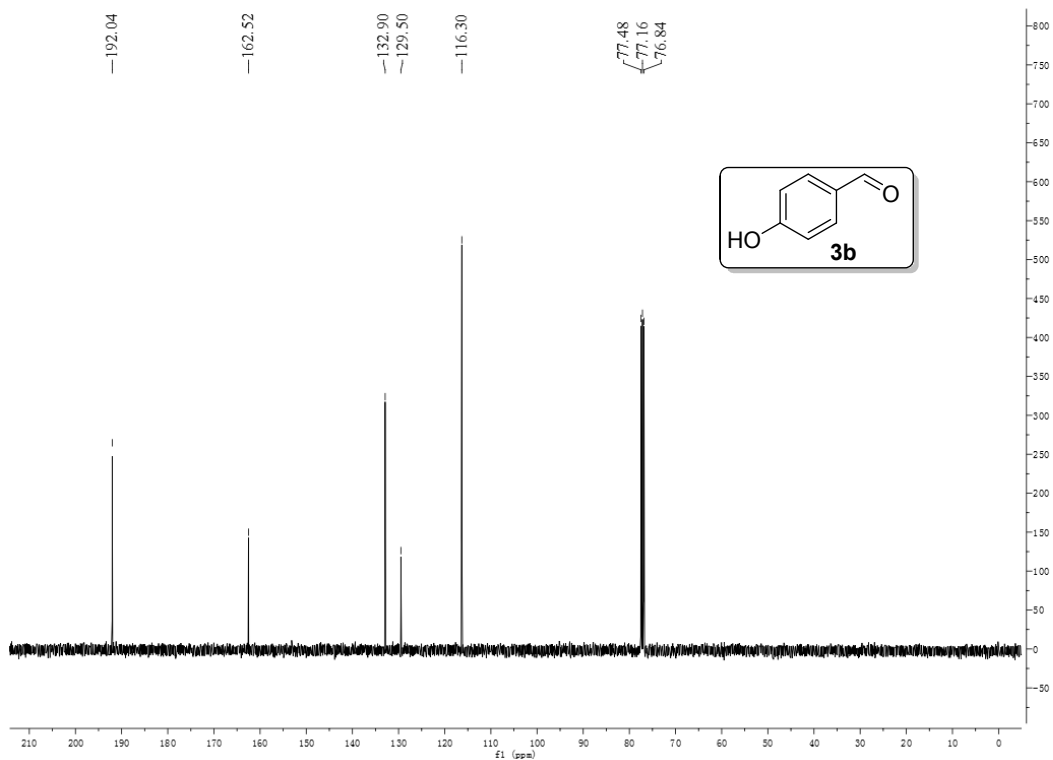
4-(Methylthio)benzaldehyde(3a)



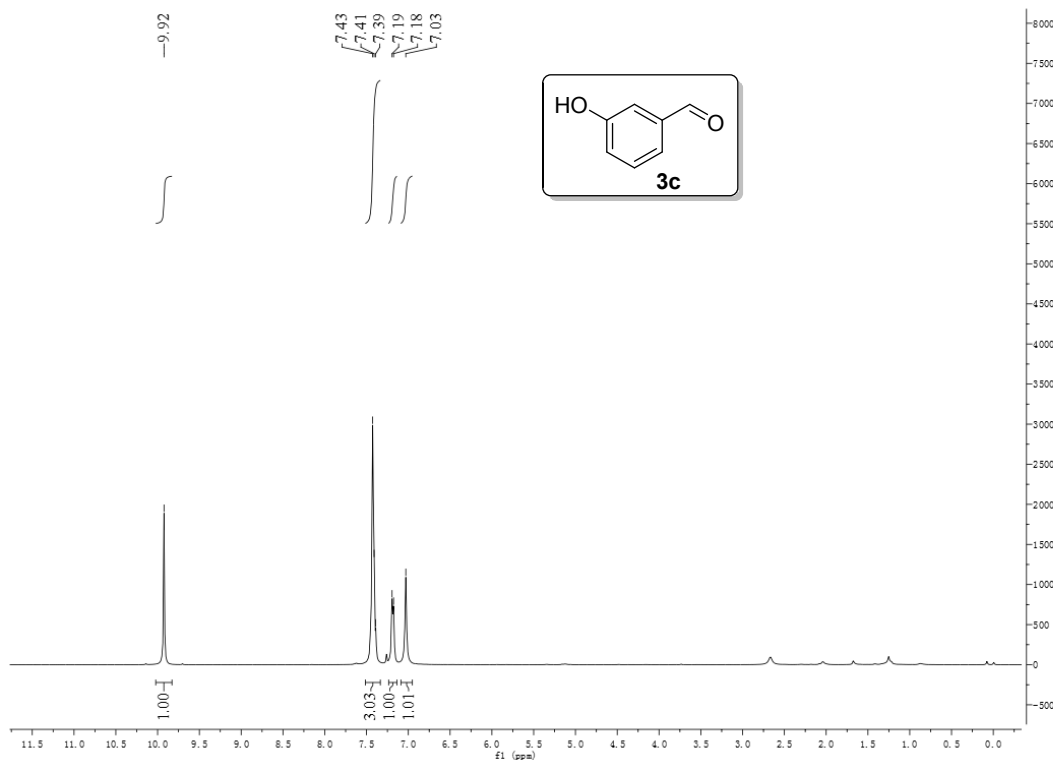


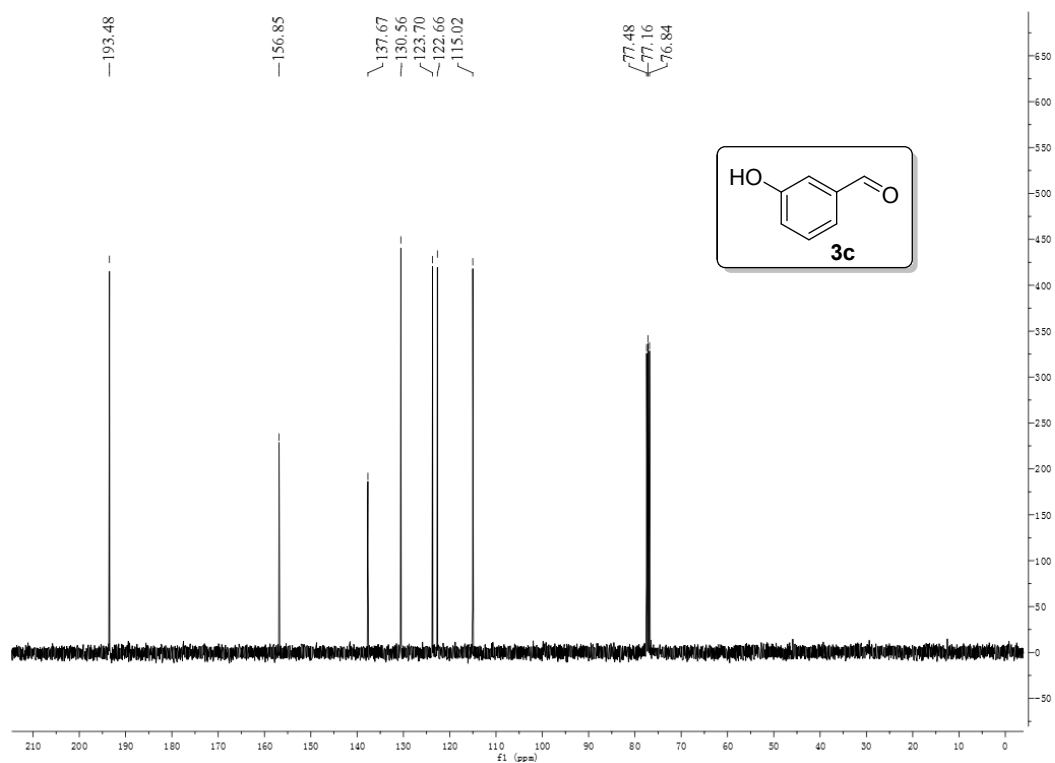
### 4-Hydroxybenzaldehyde(3b)



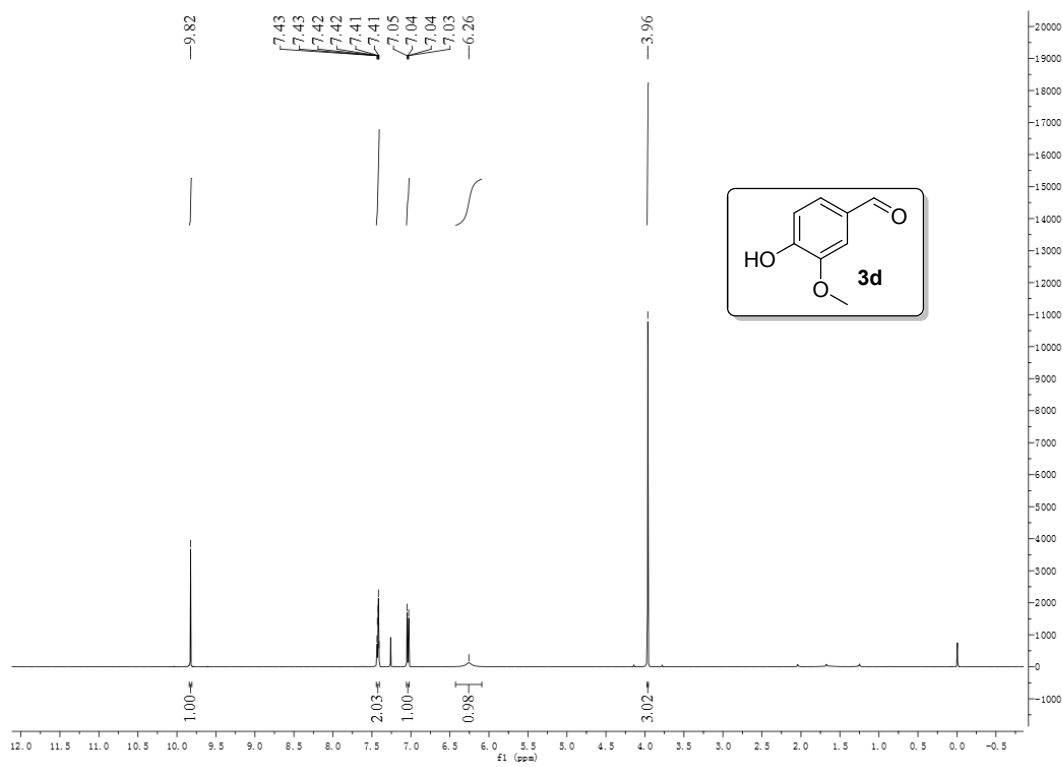


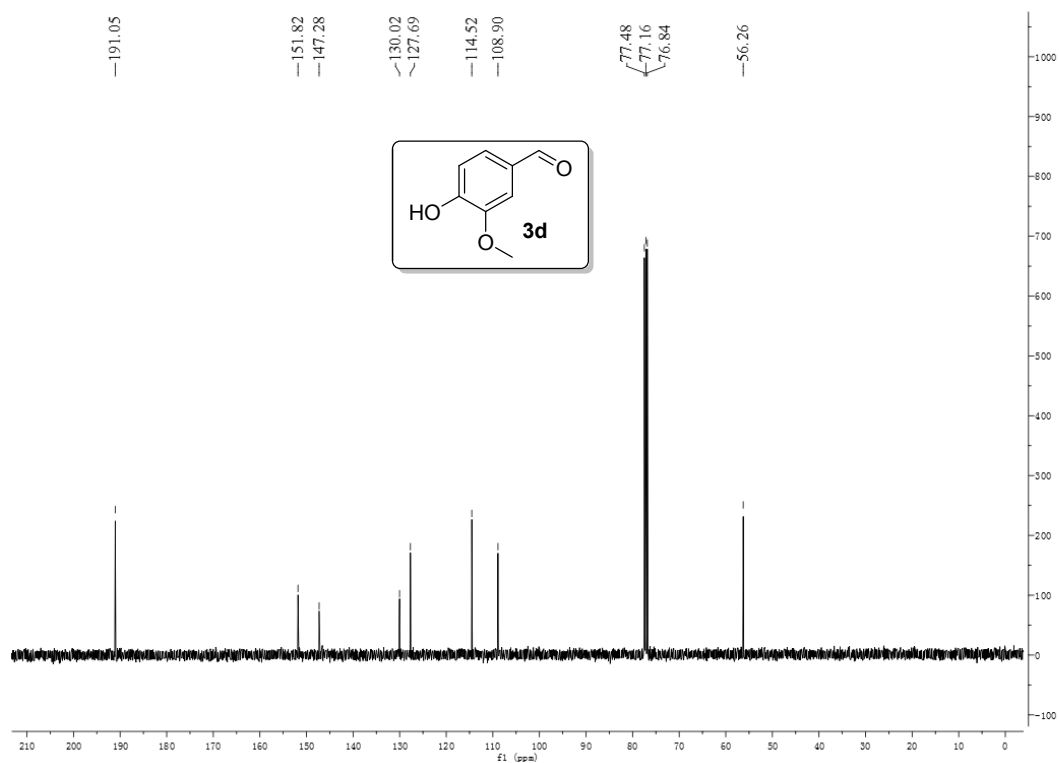
### 3-Hydroxybenzaldehyde(3c)



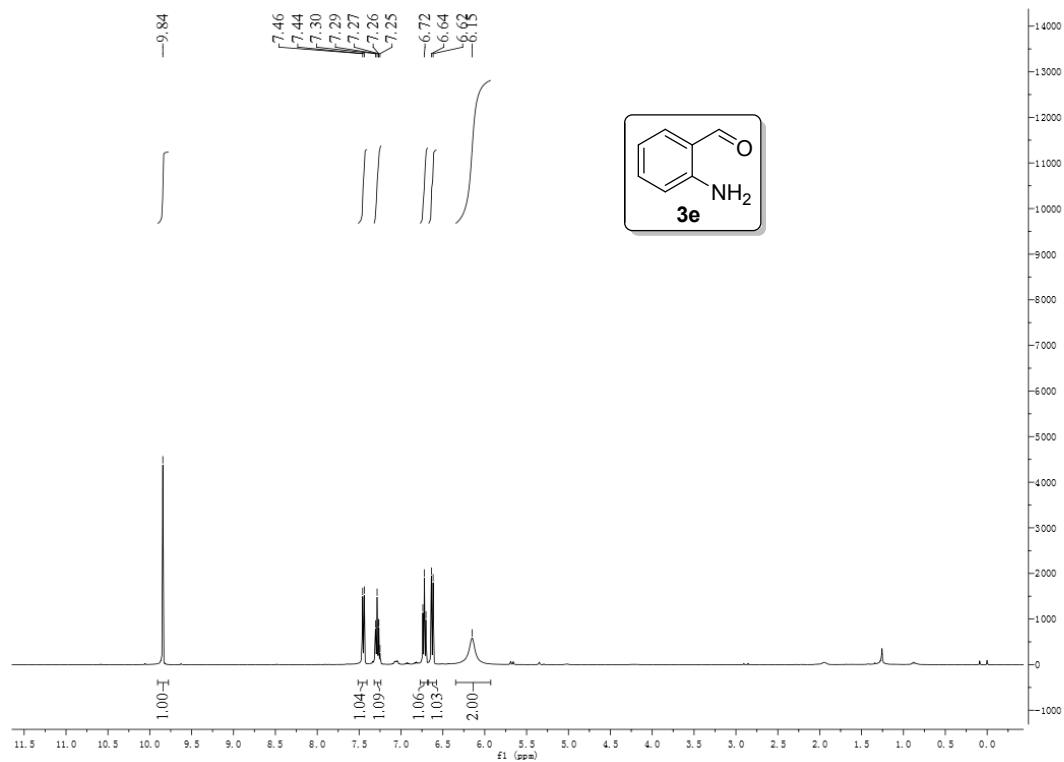


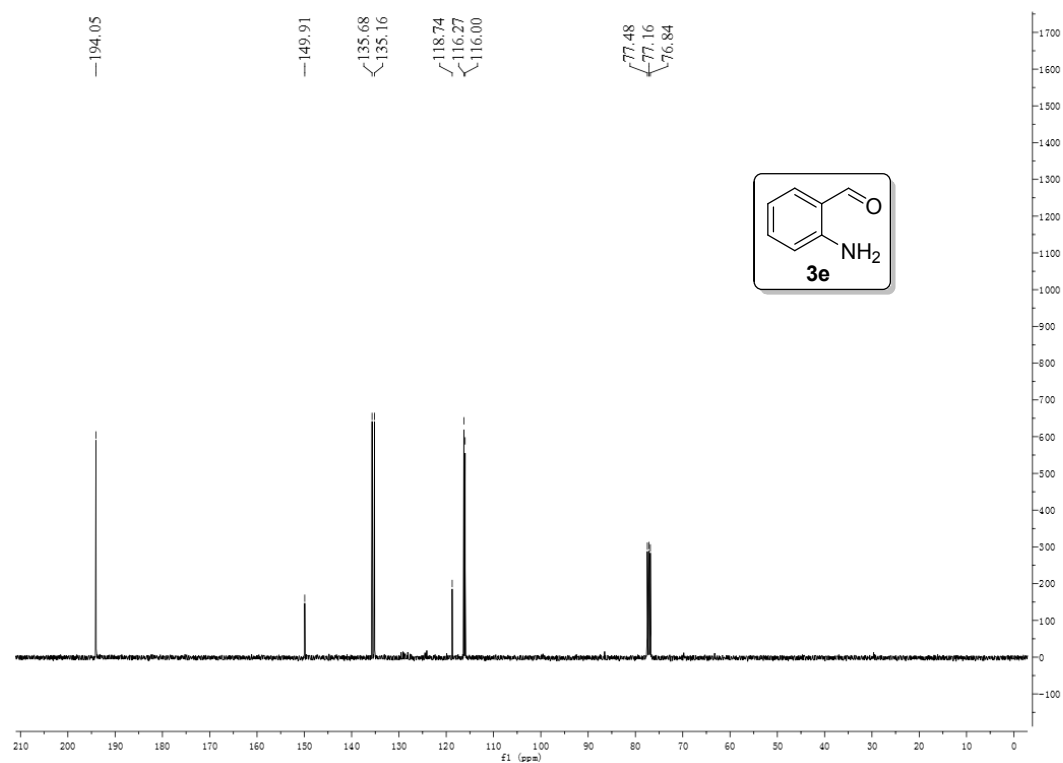
#### 4-Hydroxy-3-methoxybenzaldehyde(**3d**)



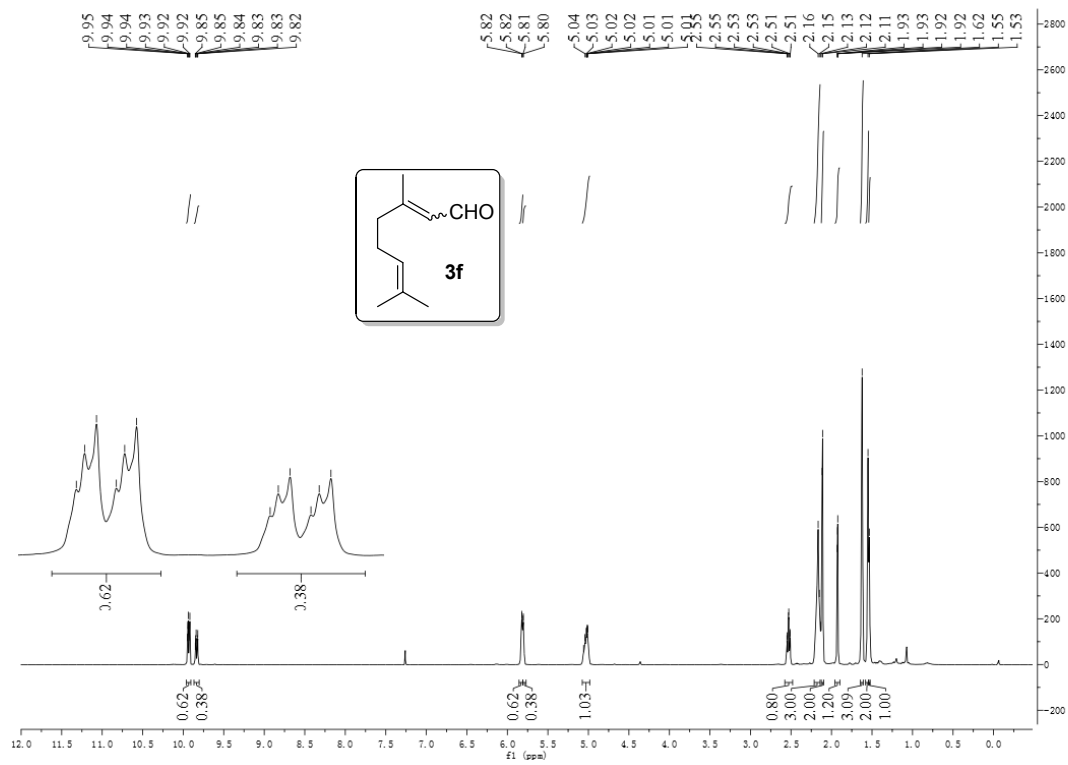


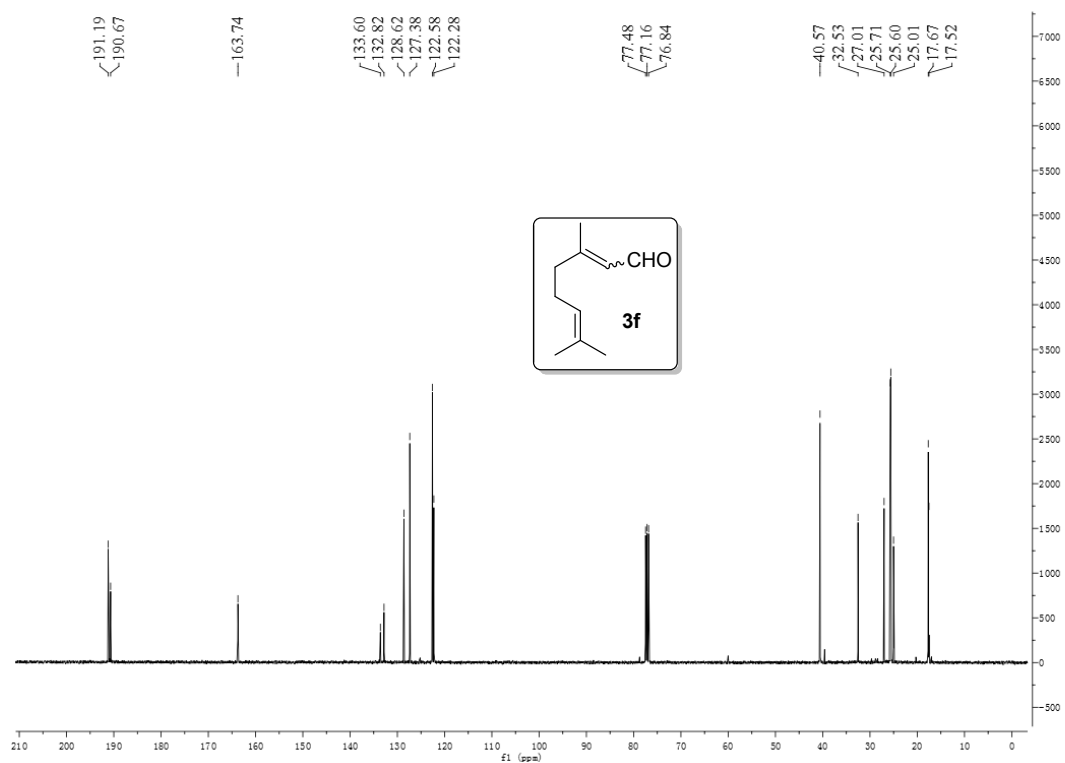
### 2-Aminobenzaldehyde(3e)



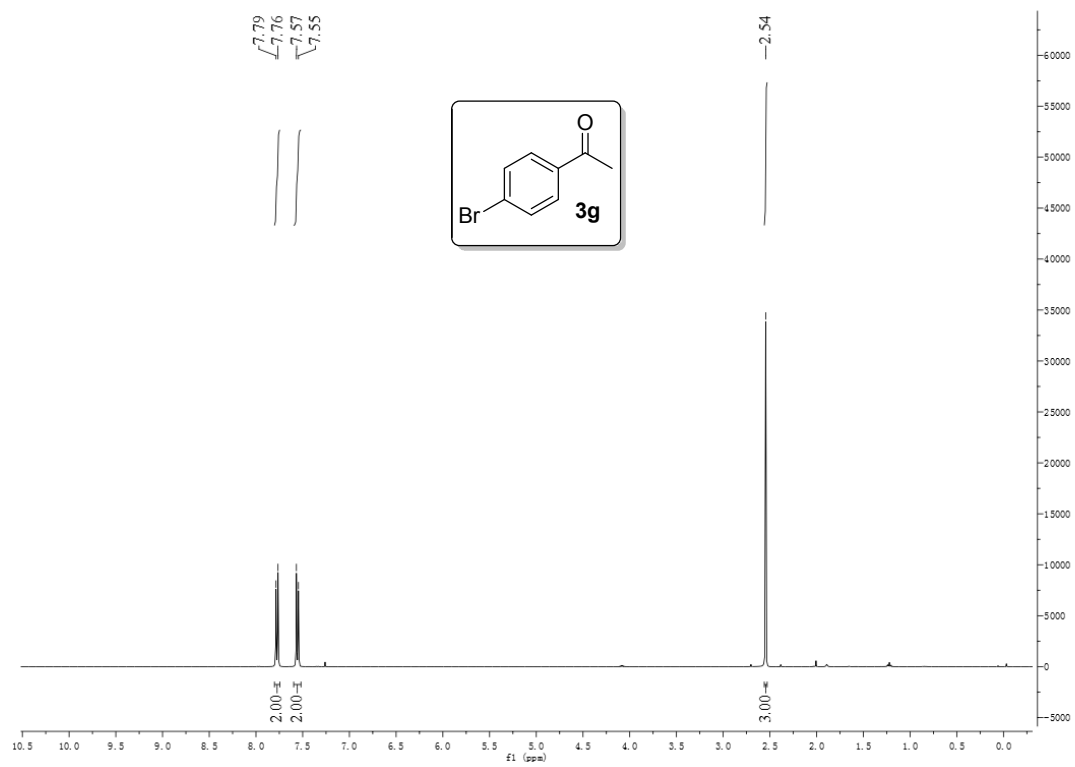


### 3,7-Dimethyl-2,6-octadienal (**3f**)





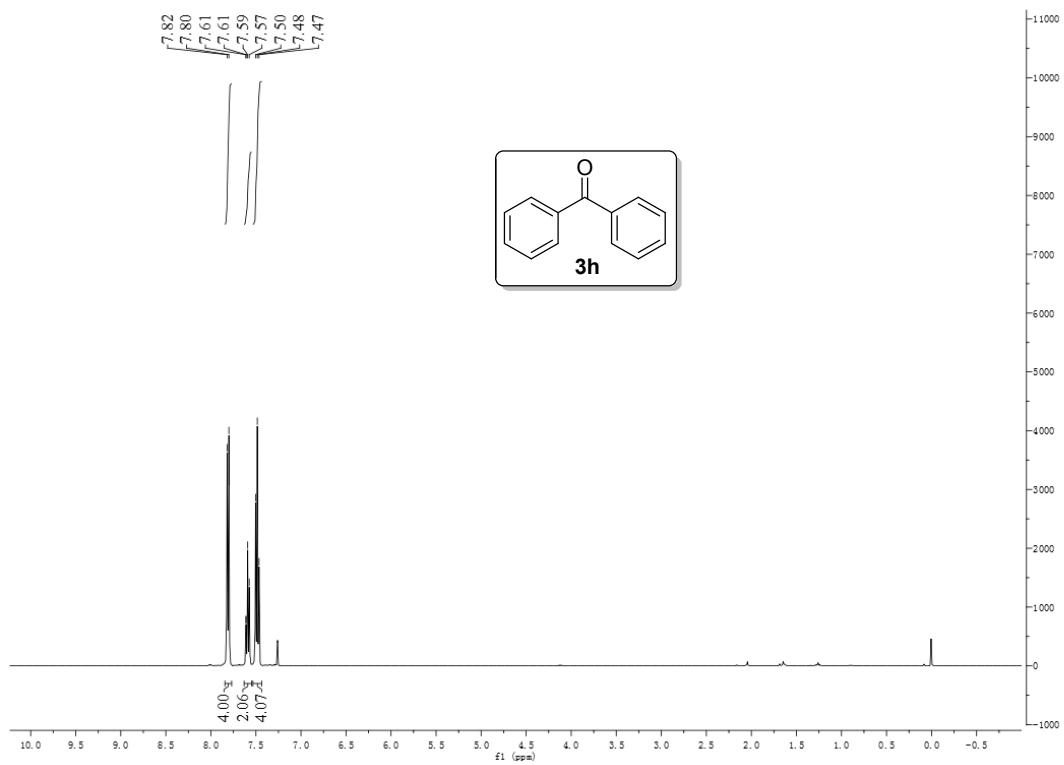
### 4'-Bromoacetophenone(3g)





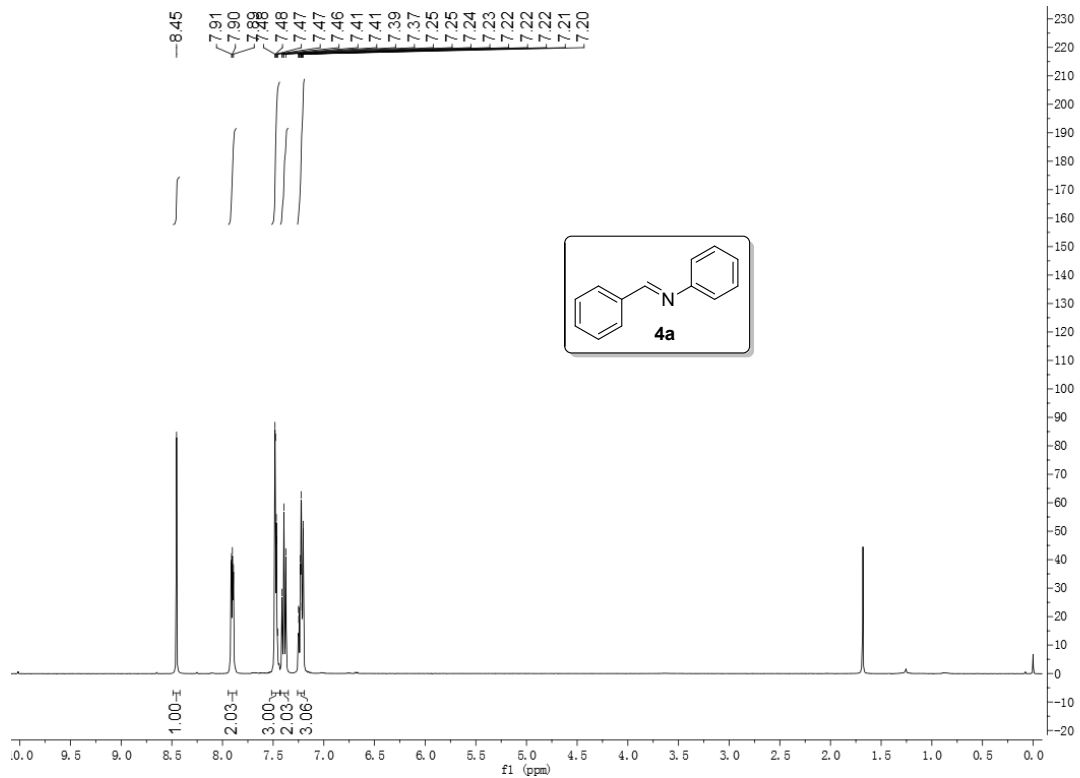


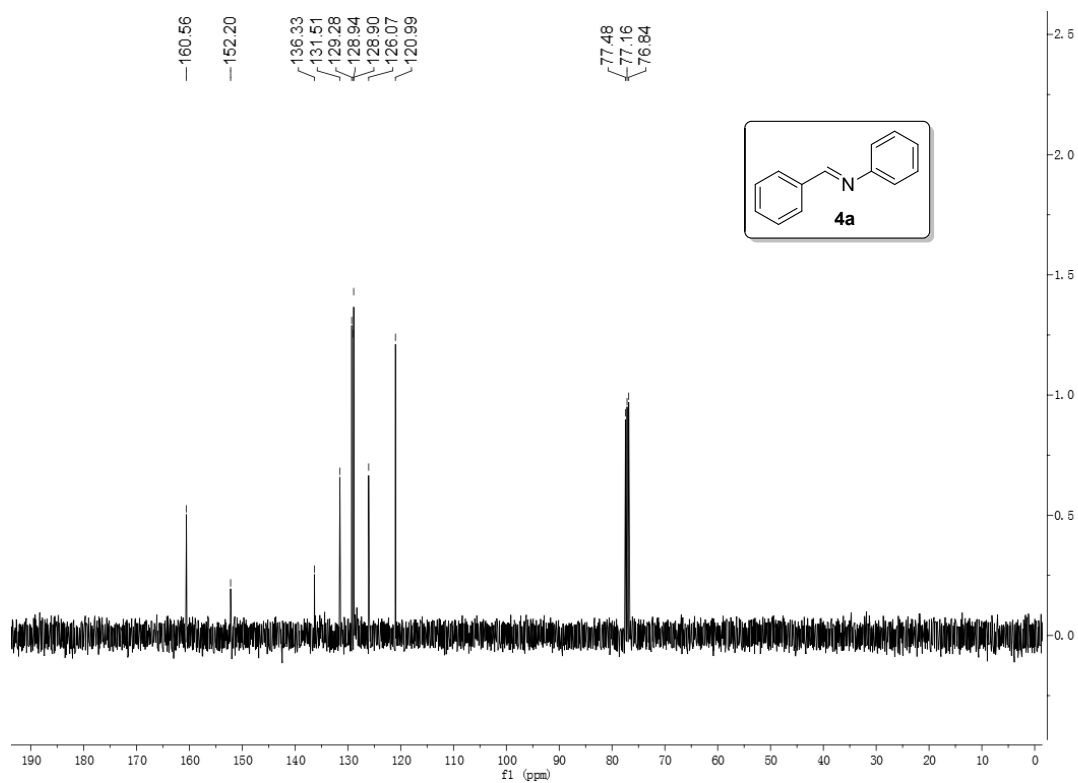
### Diphenylmethanone(3h)



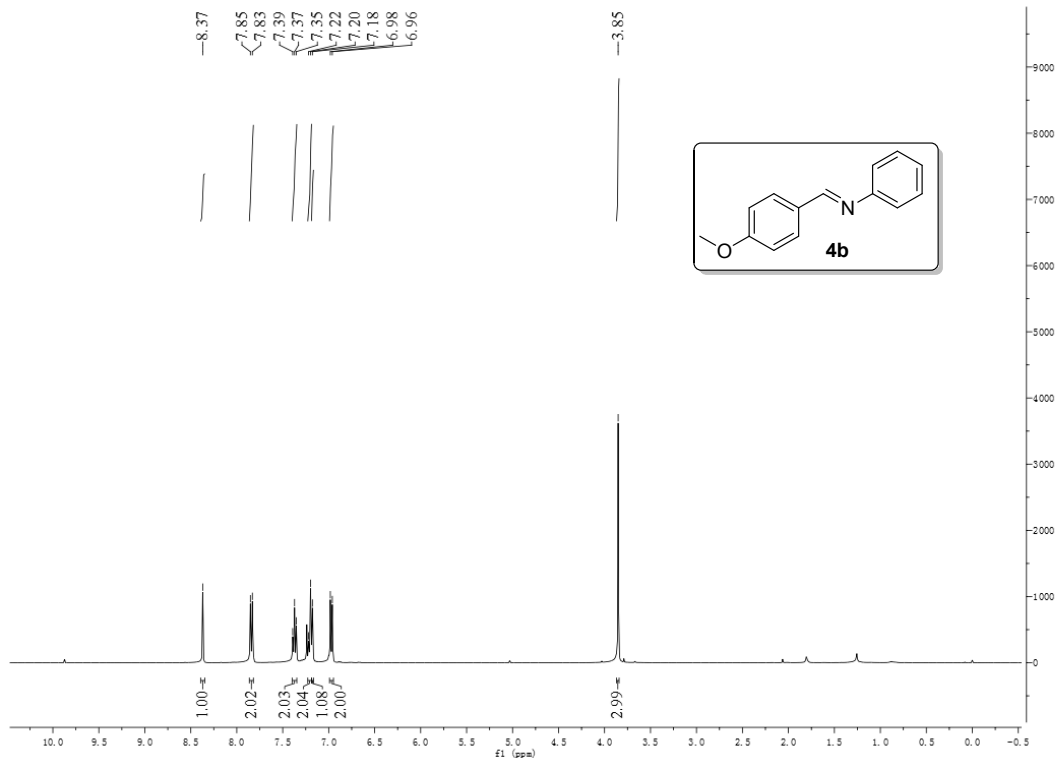


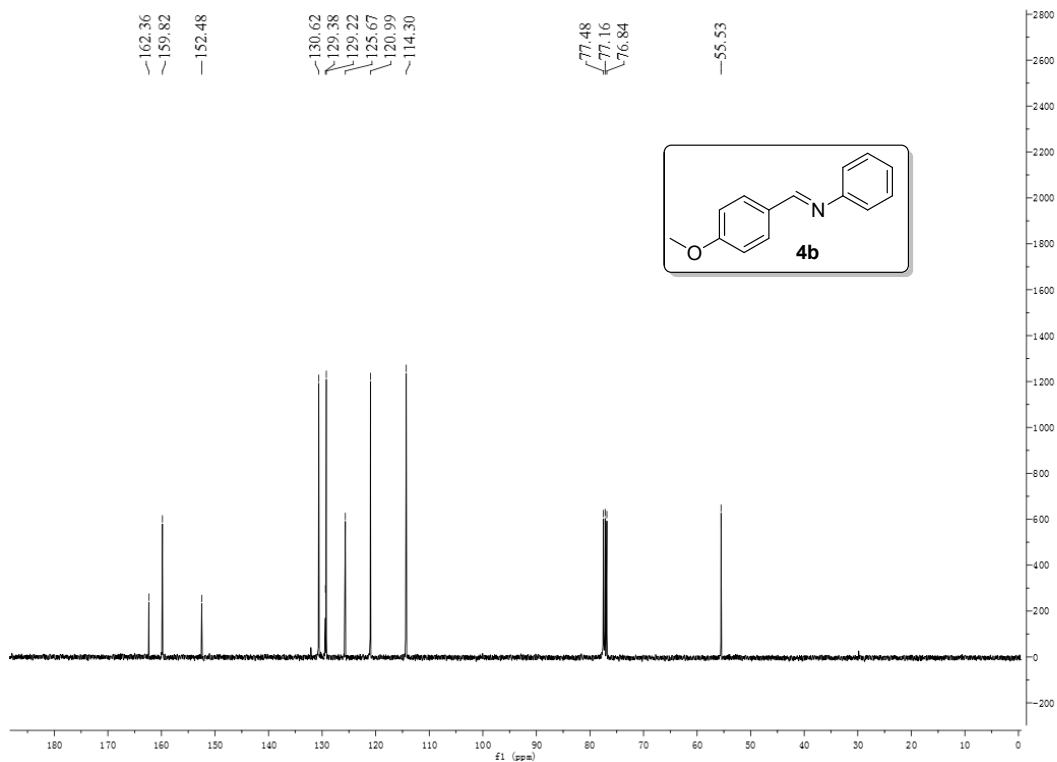
**N-Benzylideneaniline (4a)**



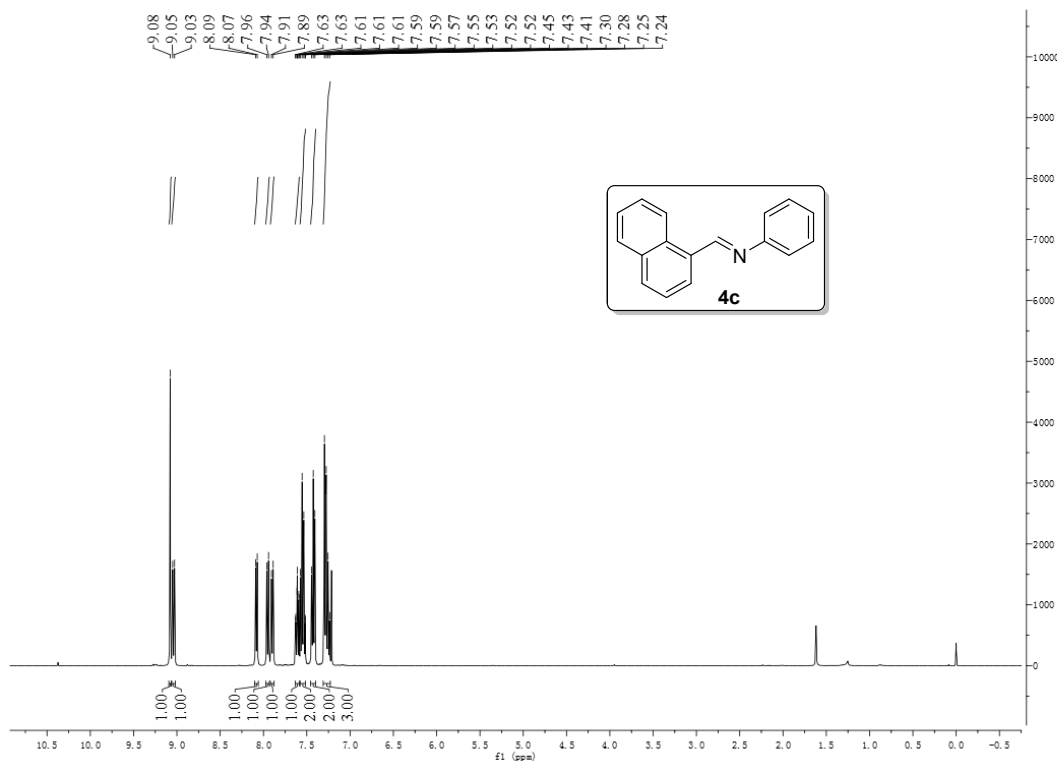


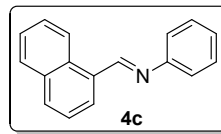
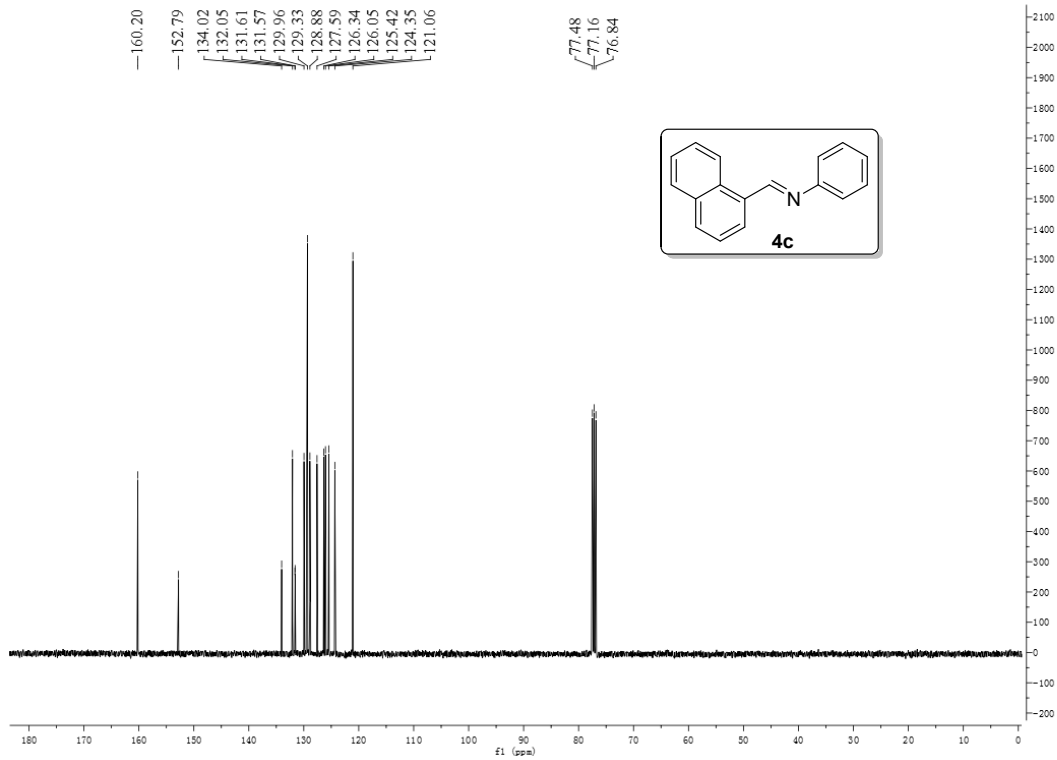
***N*-(4-methoxybenzylidene)aniline(4b)**



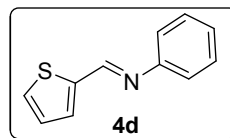
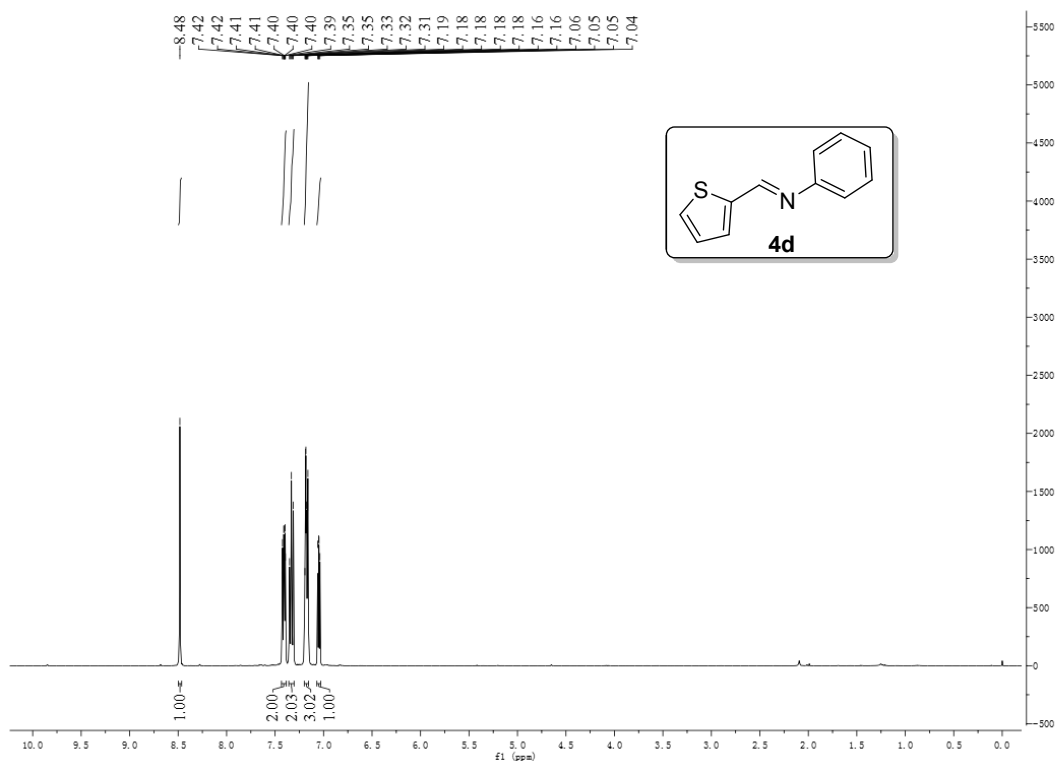


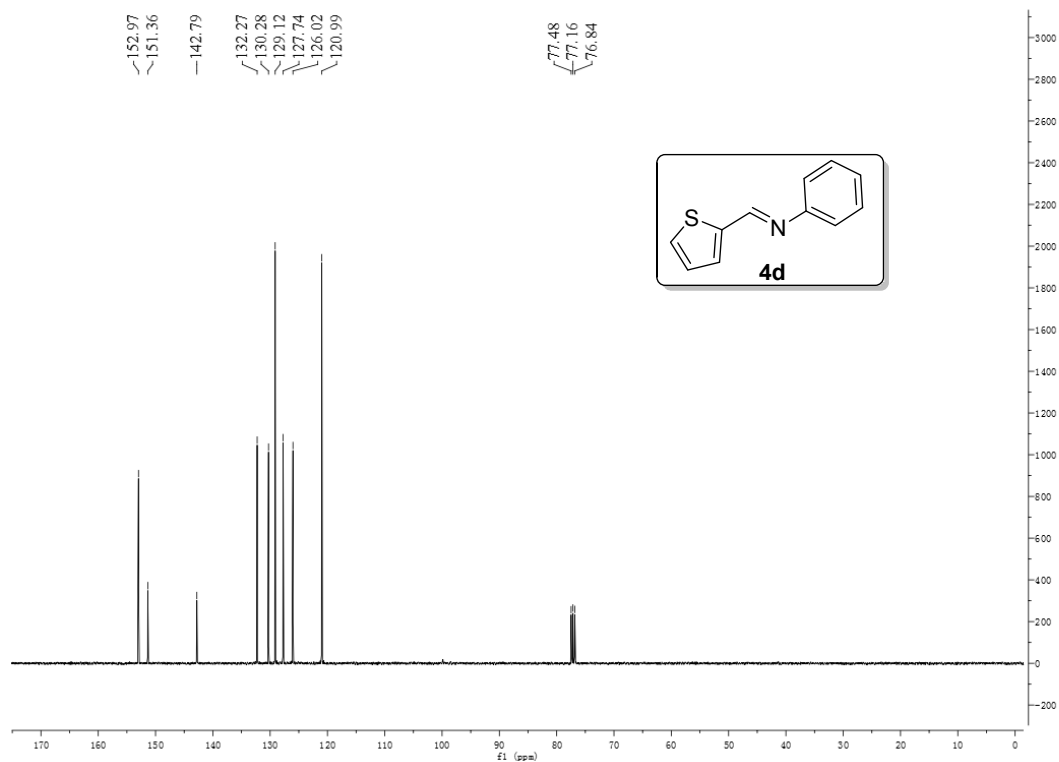
***N*-(naphthalen-1-ylmethylene)aniline(4c)**



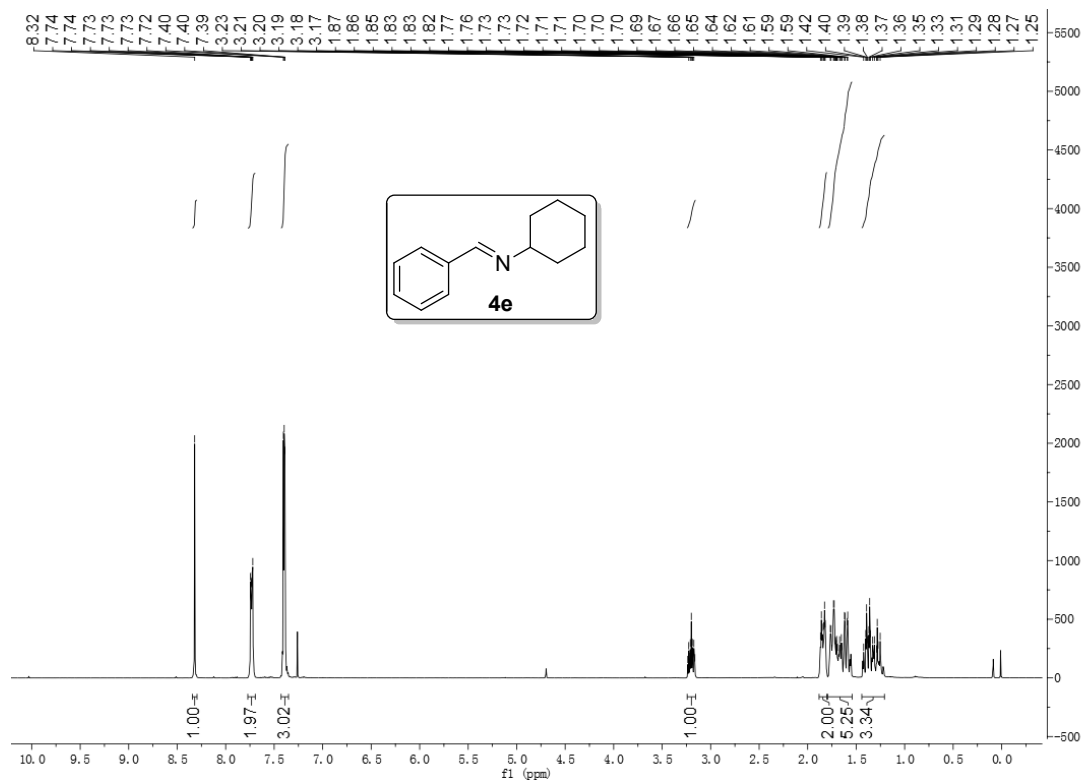


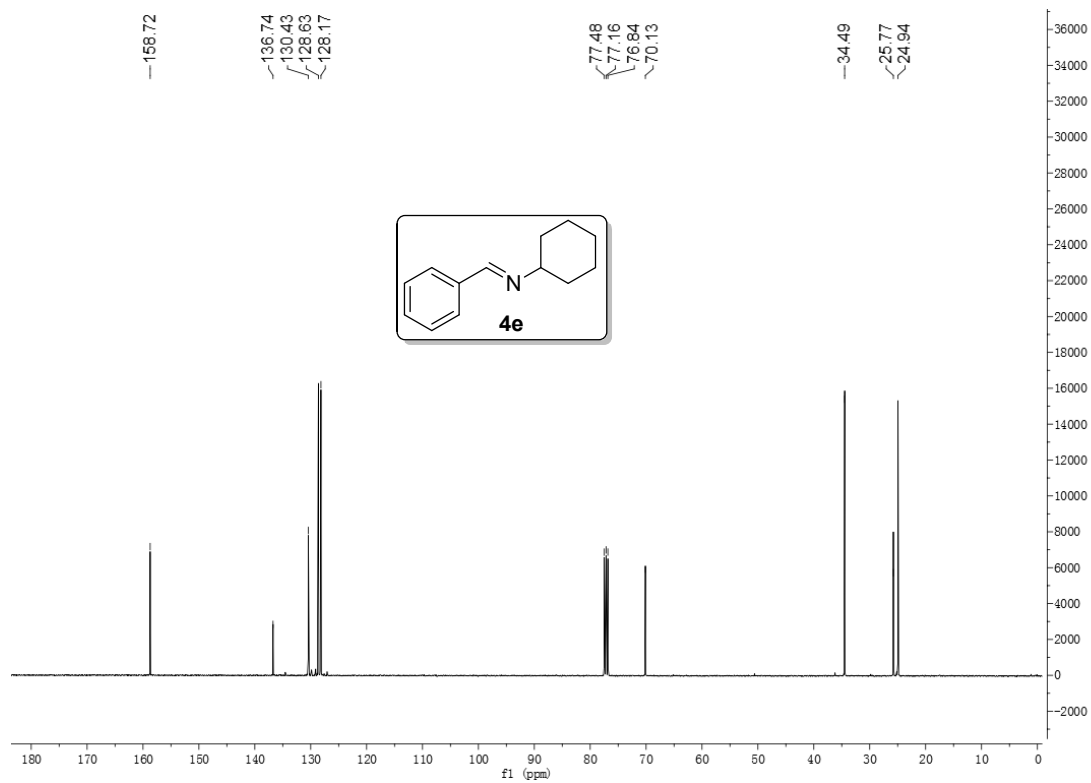
***N*-(Thiophen-2-ylmethylene)aniline(4d)**



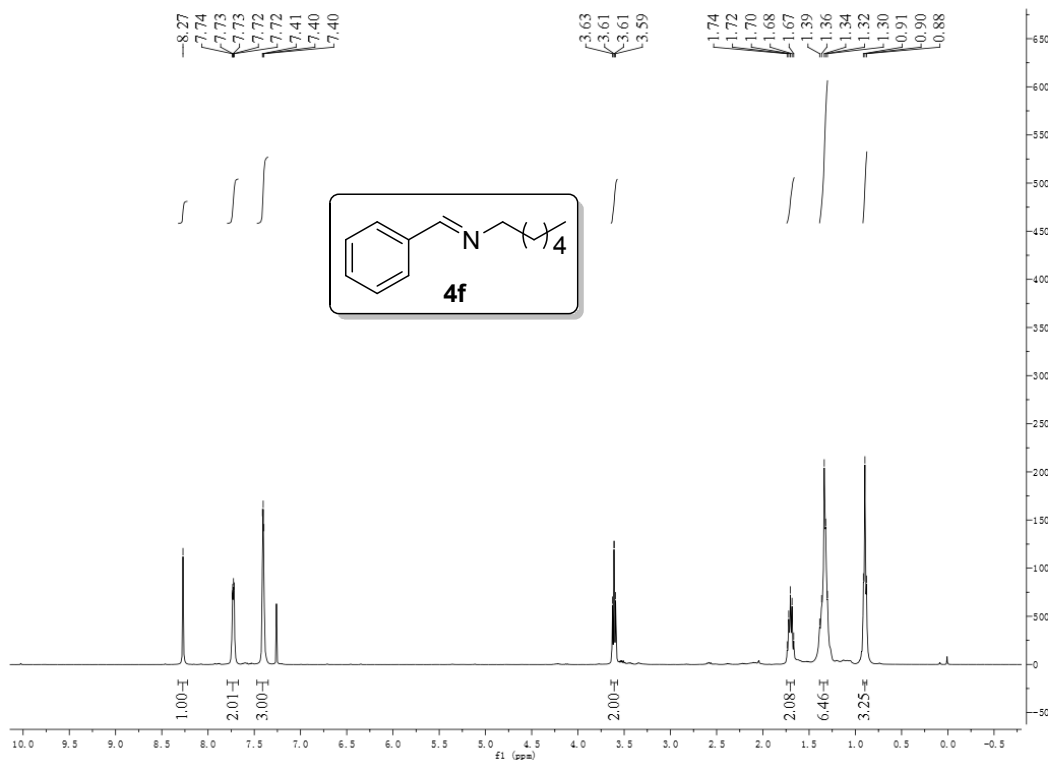


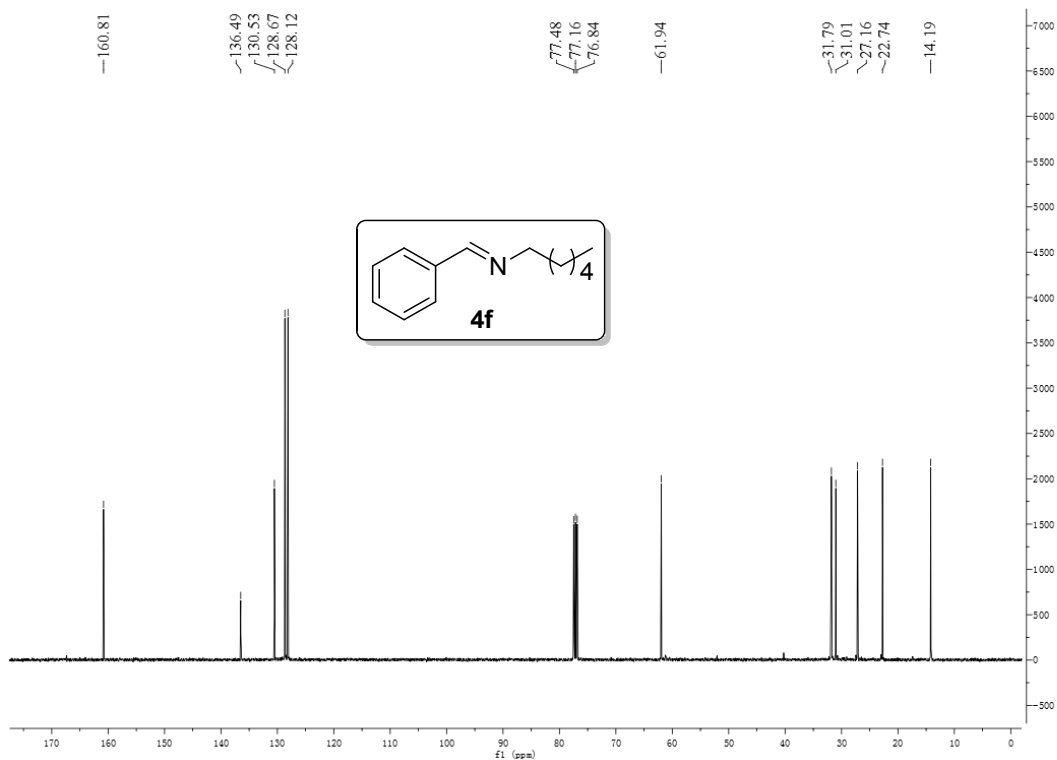
***N*-benzylidenecyclohexanamine(4e)**





**N-benzylidenehexan-1-amine (4f)**





***N*-benzylidene-2-phenylethanamine(4g)**

