

# Visible light-induced aerobic photooxidative cleavage of $C(sp^3)-C(sp^2)$ $\sigma$ -bonds of allylarenes

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## Supplementary Information

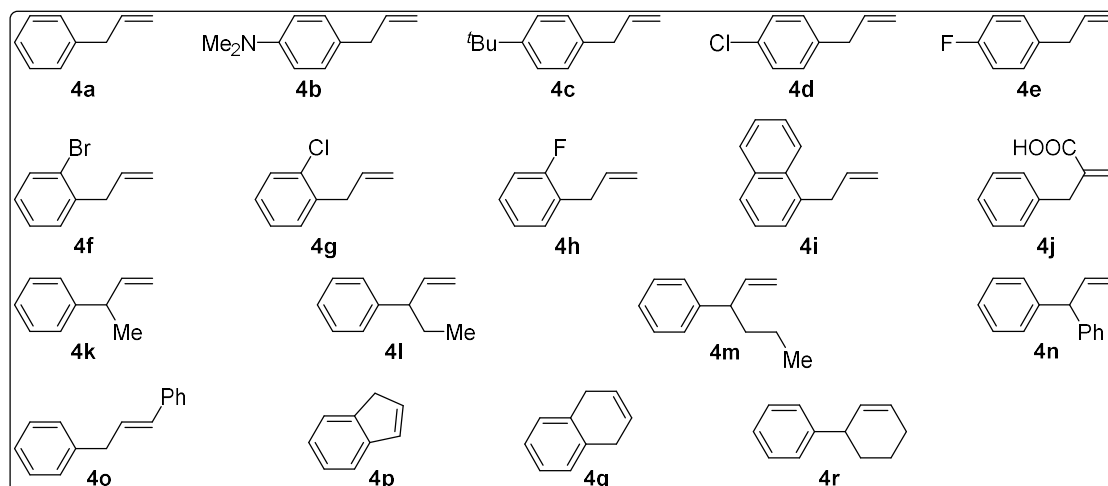
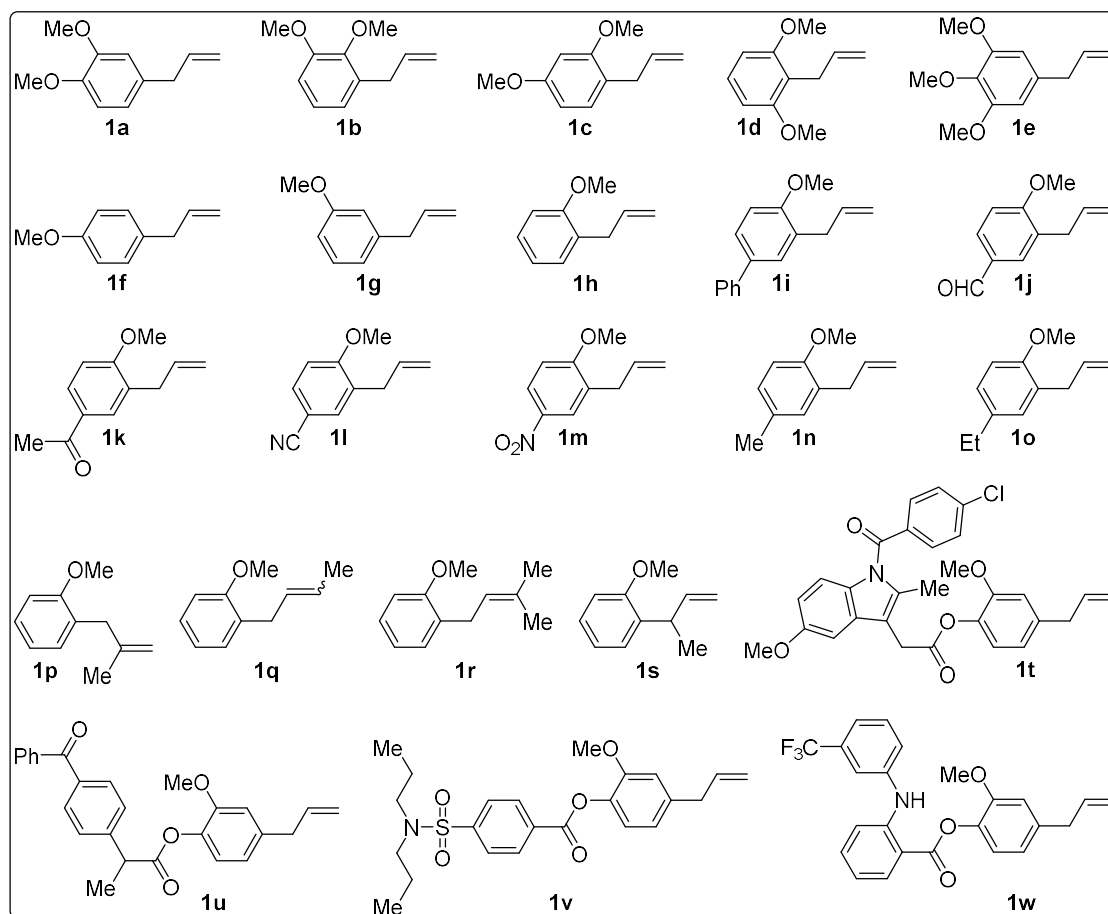
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## 1. General Information

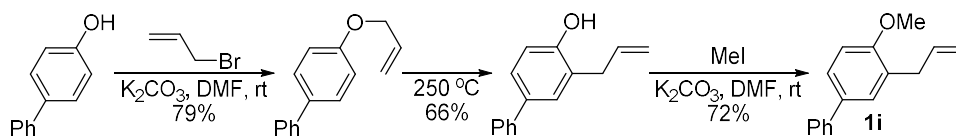
Unless otherwise stated, commercially available reagents including dry solvents were used without additional purification. Petroleum ether refers to the bp 60–90 °C petroleum fraction. Allylarenes which were not commercially available were prepared according to the literature.<sup>1</sup> The instrument for photocatalysis was a PR-PCR2-450nm instrument with no filters (Shenzhen Purui Material Technology Co., Ltd.). The reaction vessel was a Schlenk borosilicate tube. The distance from the light source to the irradiation Schlenk tube was approximately 20–30 mm. All reactions were studied in oven-dried Schlenk tubes irradiated by 36 W blue light (425–475 nm). Flash chromatography was performed using the indicated solvent system on standard grade silica gel (200–300 mesh). <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker 400 (400 MHz) or JEOL 500 (500 MHz) spectrometer. <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker 400 (100 MHz) or JEOL 500 (126 MHz) spectrometer. <sup>19</sup>F NMR spectra were recorded in CDCl<sub>3</sub> on a JEOL 500 (471 MHz) spectrometer. Chemical shifts were reported relative to CDCl<sub>3</sub> ( $\delta$  7.26 ppm) for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta$  77.16 ppm) for <sup>13</sup>C NMR. High-resolution mass spectra (HRMS) were recorded on a Q-Exactive Orbitrap mass spectrometer (Thermo). UV-vis absorption spectra were measured on a Shimadzu UV-2700 spectrophotometer. Melting points were uncorrected and measured on a micro melting point apparatus. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet.

## 2. Overview of Substrates Numbering



### 3. Experimental Section

#### 1) General Procedure for the Synthesis of Allylarenes **1i**–**1o** and **1s**<sup>1a</sup>

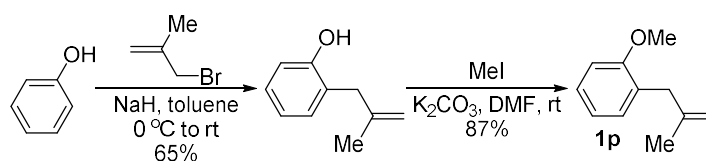


To a solution of 4-phenylphenol (2.55 g, 15 mmol) and allyl bromide (1.81 g, 15 mmol) in DMF (5 mL) was added  $K_2CO_3$  (2.49 g, 18 mmol). The resultant mixture was stirred at room temperature until 4-phenylphenol was consumed. Ethyl acetate (25 mL) and water (30 mL) were then added to the mixture. The aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layers were washed with water (20 mL) and brine (30 mL), dried over  $Na_2SO_4$  and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give the corresponding allyl aryl ether (2.49 g, 79%).

The corresponding allyl aryl ether (2.10 g, 10 mmol) was heated in a microwave reactor using a temperature-driven variable power setting. It was held constant at 250 °C for 30 min. After cooling to room temperature, the crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give the corresponding 2-allylphenol (1.39 g, 66%).

To a solution of the corresponding 2-allylphenol (1.26 g, 6.0 mmol) and MeI (1.02 g, 7.2 mmol) in DMF (5 mL) was added  $K_2CO_3$  (1.00 g, 7.2 mmol). The resultant mixture was stirred at room temperature until 2-allylphenol was consumed. Ethyl acetate (25 mL) and  $H_2O$  (30 mL) were then added to the mixture. The aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layers were washed with water (20 mL) and brine (30 mL), dried over  $Na_2SO_4$  and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give 3-allyl-4-methoxy-1,1'-biphenyl **1i** (0.97 g, 72%) as a white solid.

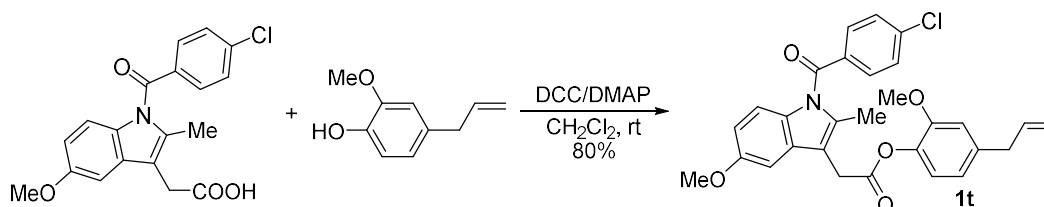
## 2) General Procedure for the Synthesis of Allylarenes **1p–1r**<sup>1b</sup>



To a solution of phenol (0.47 g, 5.0 mmol) and methallyl bromide (0.74 g, 5.5 mmol) in toluene (10 mL) was added NaH (60% in oil, 0.22 g, 5.5 mmol) in toluene (40 mL) at 0 °C. The resultant mixture was stirred at room temperature for 24 h and subsequently poured into water (20 mL). The mixture was extracted with ethyl acetate (20 mL) for three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give the corresponding 2-(2-methylallyl)phenol (0.48 g, 65%).

To a solution of the corresponding 2-(2-methylallyl)phenol (445 mg, 3.0 mmol) and MeI (511 mg, 3.6 mmol) in DMF (5 mL) was added K<sub>2</sub>CO<sub>3</sub> (498 mg, 3.6 mmol). The resultant mixture was stirred at room temperature until 2-(2-methylallyl)phenol was consumed. Ethyl acetate (25 mL) and H<sub>2</sub>O (30 mL) were then added to the mixture. The aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layers were washed with water (20 mL) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give 1-methoxy-2-(2-methylallyl)benzene **1p** (423 mg, 87%) as a colorless oil.

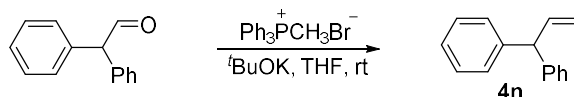
## 3) General Procedure for the Synthesis of Allylarenes **1t–1w**<sup>1c</sup>



To a solution of indomethacin (1.79 g, 5.0 mmol), eugenol (0.99 g, 6.0 mmol) and DCC (1.24 g, 6.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added DMAP (61 mg, 0.5 mmol). The resultant mixture was stirred at room temperature for 10 h. After removal of the

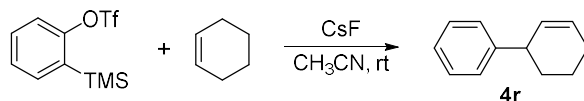
solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give 4-allyl-2-methoxyphenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl) acetate **1t** (202 mg, 80%) as a white solid.

#### 4) Procedure for the Synthesis of Allylarene **4n**<sup>1d</sup>



Methyltriphenylphosphonium bromide (1.78 g, 5.0 mmol) was added over a 10-min period to a mixture of *t*BuOK (616 mg, 5.5 mmol) and dry THF (20 mL) with stirring and under N<sub>2</sub>. After 1 h, a solution of 2,2-diphenylacetaldehyde (0.98 g, 5.0 mmol) in dry THF (10 mL) was added to the mixture over a 6-min period. The resultant mixture was stirred at room temperature for 20 h and subsequently poured into water (20 mL). The mixture was extracted with ethyl acetate (20 mL) for three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (50:1) to give prop-2-ene-1,1-diyldibenzene **4n** (0.61 g, 62%) as a yellowish solid.

#### 5) Procedure for the Synthesis of Allylarene **4r**<sup>1e</sup>

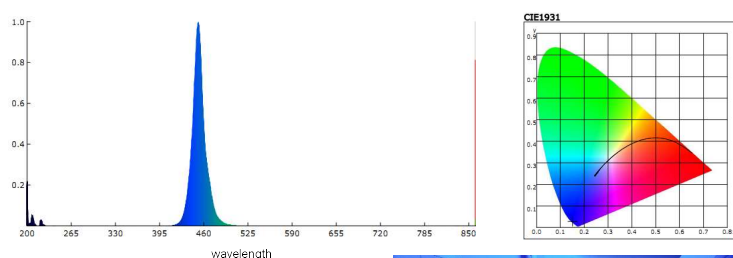


To a solution of 2-(trimethylsilyl)phenyl triflate (0.60 g, 2.0 mmol) and cyclohexene (0.66 g, 8.0 mmol) in CH<sub>3</sub>CN (10 mL) was added CsF (1.22 g, 8.0 mmol). The resultant mixture was stirred at room temperature for 12 h. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (30:1) to give 1,2,3,4-tetrahydro-1,1'-biphenyl **4r** (215 mg, 68%) as a colorless oil.

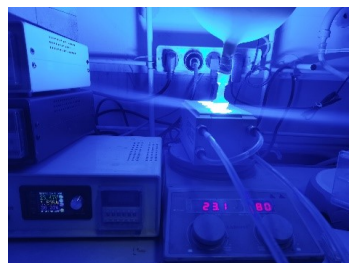
## 6) General Procedure for the C(sp<sup>3</sup>)-C(sp<sup>2</sup>) $\sigma$ -Bond Cleavage of Allylarenes



A mixture of 1,2-dimethoxy-4-allylbenzene **1a** (71 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol) in CH<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue light-emitting diodes (LEDs) with an emitting wavelength of 425–475 nm for 10 h (Figure S1). After removal of the solvent, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give 3,4-dimethoxybenzaldehyde **2a** (51 mg, 77%) as a white solid.

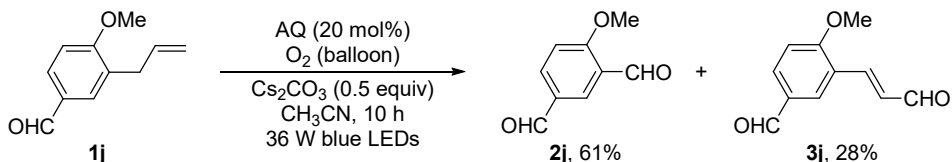


Manufacturer: PR-PCR2-450nm (China);  
The peak wavelength: 452.5 nm;  
Chromaticity coordinates:  $x = 0.1511$ ;  
 $y = 0.0273/u' = 0.1997$ ;  $v' = 0.0812$ ;  
CIE1931 X: 26541.652;  
CIE1931 Y: 4797.261;  
CIE1931 Z: 144361.125;  
Color rendering index: Ra = -65.4.



**Figure S1.** Experimental Apparatus and Pictures

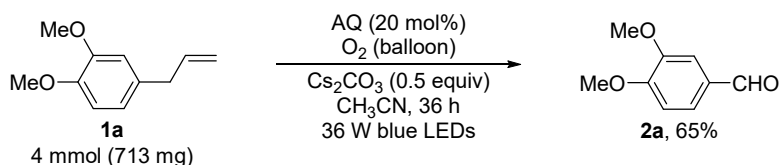
## 7) General Procedure for the Synthesis of (*E*)-Cinnamaldehydes



A mixture of 3-allyl-4-methoxybenzaldehyde **1j** (70 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol) in CH<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 10 h (Figure S1). After removal of the solvent,

the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give 4-methoxyisophthalaldehyde **2j** (40 mg, 61%) as a white solid and (*E*)-4-methoxy-3-(3-oxoprop-1-en-1-yl)benzaldehyde **3j** (21 mg, 28%) as a white solid.

## 8) Scale-Up Synthesis



A mixture of **1a** (713 mg, 4 mmol), AQ (166 mg, 0.8 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (652 mg, 2 mmol) in CH<sub>3</sub>CN (20 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 36 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give **2a** (432 mg, 65%).

## 9) Optimization of Reaction Conditions

**Table S1.** Optimization of reaction conditions<sup>a,b</sup>

Entry	Deviation from standard conditions	Yield (%) of <b>2a</b>	Yield (%) of <b>3a</b>
1	None	77	Trace
2	<b>PC2</b> instead of <b>PC1</b>	47	Trace

Reaction scheme showing the synthesis of **2a** and **3a** from **1a** under the following conditions: PC1 (20 mol%), O<sub>2</sub> (balloon), Cs<sub>2</sub>CO<sub>3</sub> (0.5 equiv), CH<sub>3</sub>CN, 10 h, blue LEDs. The reaction is labeled as "standard conditions".

Structures of PC1, PC2, PC3, PC4, and PC5 are shown below the reaction scheme. PC1, R = H (AQ); PC2, R = Cl; PC3, R = Br; PC4 and PC5 are other photocatalysts.

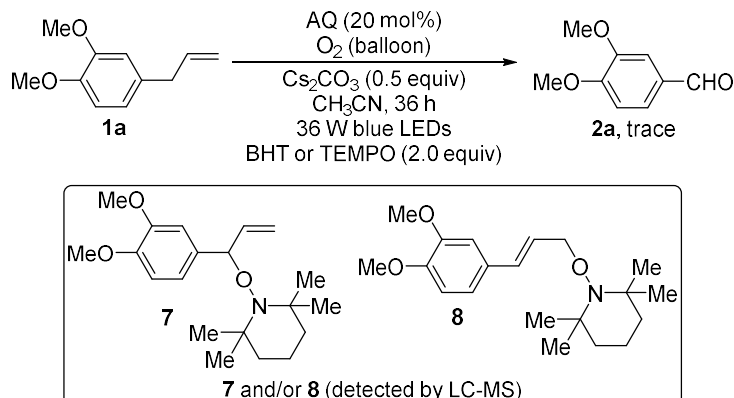


3	<b>PC3</b> instead of <b>PC1</b>	59	Trace
4	<b>PC4</b> instead of <b>PC1</b>	36	15
5	<b>PC5</b> instead of <b>PC1</b>	54	17
6	Rhodamine 6G instead of <b>PC1</b>	0	0
7	Eosin Y instead of <b>PC1</b>	0	0
8	30 mol% of <b>PC1</b>	73	Trace
9	10 mol% of <b>PC1</b>	46	Trace
10	24 W blue LEDs as light source	56	Trace
11	12 W blue LEDs as light source	39	Trace
12	K <sub>2</sub> CO <sub>3</sub> instead of Cs <sub>2</sub> CO <sub>3</sub>	55	Trace
13	Na <sub>2</sub> CO <sub>3</sub> instead of Cs <sub>2</sub> CO <sub>3</sub>	Trace	0
14	CsF instead of Cs <sub>2</sub> CO <sub>3</sub>	37	Trace
15	EtOAc instead of CH <sub>3</sub> CN	49	Trace
16	DCE instead of CH <sub>3</sub> CN	45	26
17	DMSO instead of CH <sub>3</sub> CN	Trace	0
18	THF instead of CH <sub>3</sub> CN	0	0
19	EtOH instead of CH <sub>3</sub> CN	Trace	0
20 <sup>c</sup>	No light	0	0
21	No PC	0	0
22	No base	Trace	0
23	Under N <sub>2</sub>	0	0
24	Under air	47	Trace
25	36 W white LEDs as light source	30	Trace
26	36 W red LEDs as light source	15	Trace
27	36 W yellow LEDs as light source	34	Trace
28	36 W green LEDs as light source	36	Trace

<sup>a</sup> Reaction conditions: **1a** (0.4 mmol), AQ (0.08 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.2 mmol), CH<sub>3</sub>CN (4.0 mL), O<sub>2</sub> (balloon), irradiation with 36 W blue LEDs (425–475 nm), 10 h. <sup>b</sup> Isolated yield based on **1a**. <sup>c</sup> The reaction was performed at 50 °C in the dark.

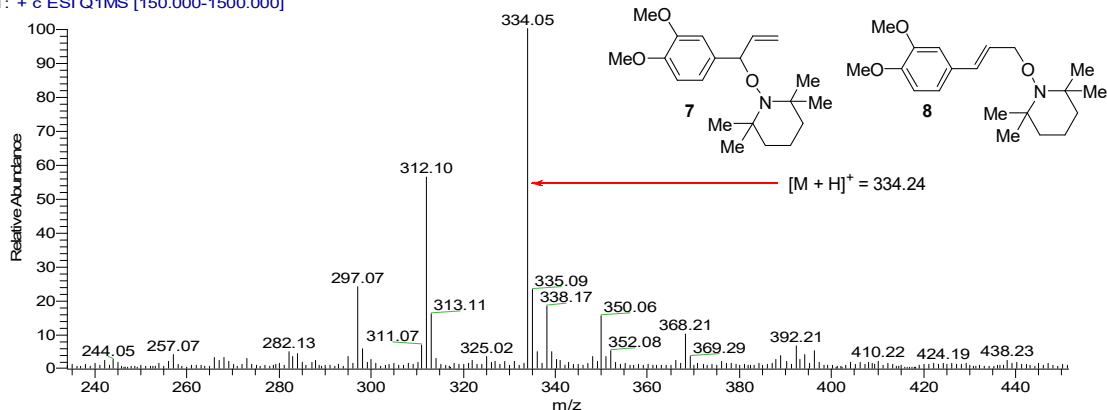
## 4. Mechanistic Studies

### 1) Radical Trapping Experiments

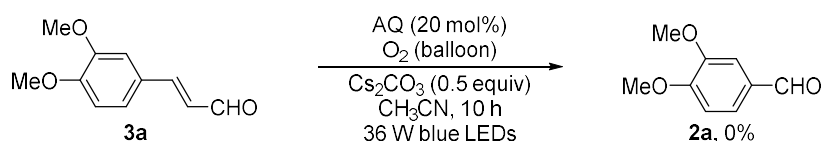


To a mixture of **1a** (71 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and  $\text{Cs}_2\text{CO}_3$  (65 mg, 0.2 mmol) in  $\text{CH}_3\text{CN}$  (4.0 mL) was added a radical scavenger BHT (176 mg, 0.8 mmol) or TEMPO (125 mg, 0.8 mmol). The resultant mixture was stirred an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 10 h. The reaction mixture was concentrated under reduced pressure. The desired reaction of **1a** was completely inhibited, and the TEMPO adducts **7** and/or **8** was observed by LC-MS spectra of the crude mixtures, suggesting that the reaction might be initiated by a delocalized allylic radical.

ZHAOXI #5 RT: 0.09 AV: 1 SB: 1 0.19 NL: 5.72E7  
T: + c ESI Q1MS [150.000-1500.000]

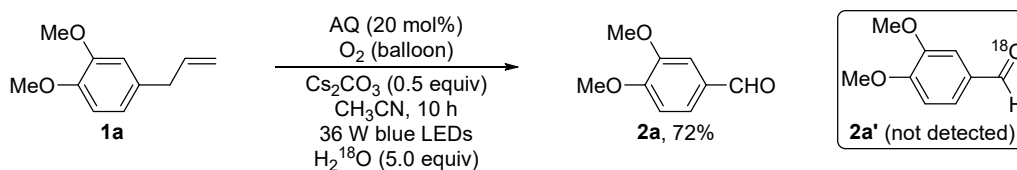


### 2) Investigation of Possible Intermediates

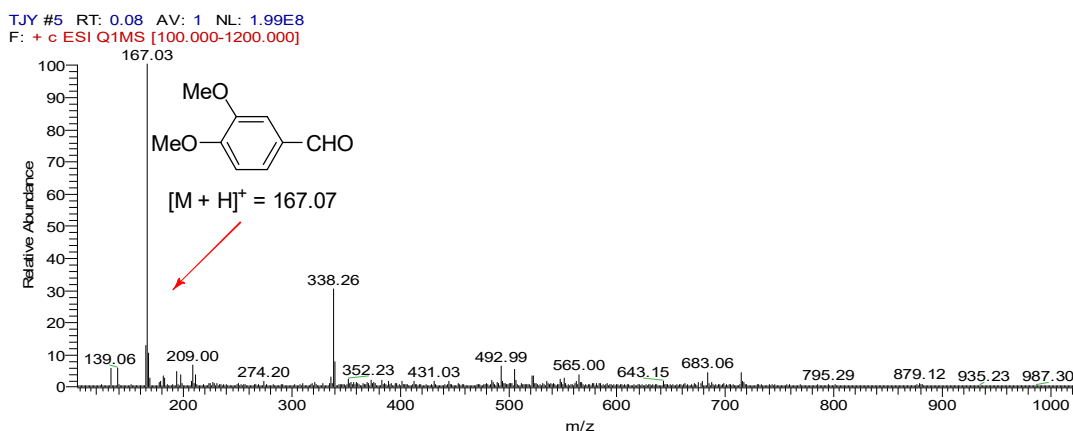


A mixture of (*E*)-3-(3,4-dimethoxyphenyl)acrylaldehyde **3a** (77 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol) in CH<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 10 h. The desired product **2a** was not detected by thin-layer chromatography (TLC), suggesting that (*E*)-cinnamaldehyde might not be an intermediate.

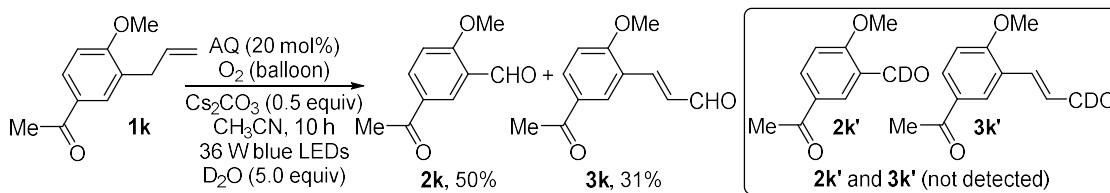
### 3) Isotope Labelling Experiments with H<sub>2</sub><sup>18</sup>O



A mixture of **1a** (71 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol), and <sup>18</sup>O-labelled water (40 mg, 2 mmol) in CH<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 10 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give **2a** (48 mg, 72%), while the <sup>18</sup>O-labelled product **2a'** was not observed by LC-MS spectra (see below). The results suggested that trace amounts of water in the solvent were not the oxygen source for products **2**, and oxygen atoms of aldehyde groups might be derived from O<sub>2</sub>.

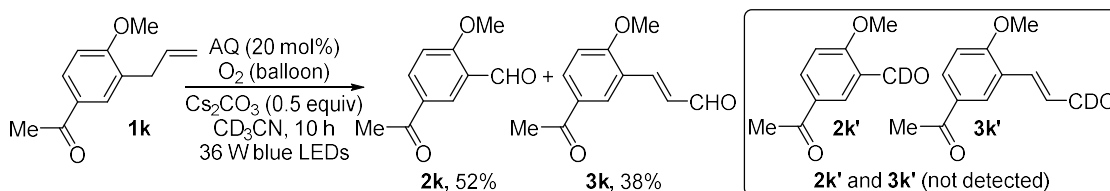


#### 4) Isotope Labelling Experiments with D<sub>2</sub>O



A mixture of 1-(3-allyl-4-methoxyphenyl)ethan-1-one **1k** (76 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol), and D<sub>2</sub>O (40 mg, 2 mmol) in CH<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 10 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give 5-acetyl-2-methoxybenzaldehyde **2k** (36 mg, 50%) and (*E*)-3-(5-acetyl-2-methoxyphenyl)acrylaldehyde **3k** (25 mg, 31%), while the deuterated products **2k'** and **3k'** were not detected by <sup>1</sup>H NMR spectra, suggesting that trace amounts of water in the solvent were not the proton source for aldehyde groups in **2** and **3**.

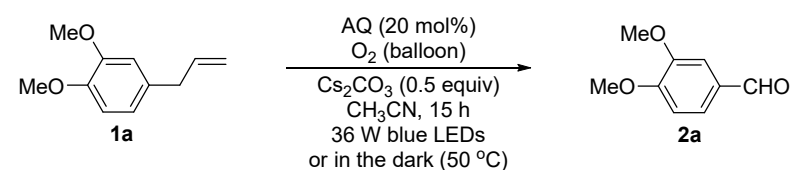
#### 5) Isotope Labelling Experiments with CD<sub>3</sub>CN



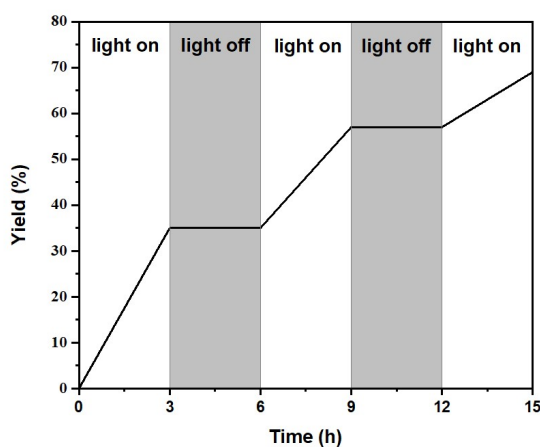
A mixture of **1k** (76 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol) in CD<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm for 10 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give **2k** (37 mg, 52%) and **3k** (31 mg, 38%), while the deuterated products **2k'** and **3k'** were not detected by <sup>1</sup>H NMR spectra, demonstrating that CH<sub>3</sub>CN was not the proton source for aldehyde groups in **2** and **3**. Thus, allylic hydrogen atoms on the sp<sup>3</sup> carbons of substrates **1** might serve as the proton source of aldehyde groups in **2** and **3**.

## 6) Light On–Off Experiment

To study the necessity of continuous irradiation with visible light for the progress of the reaction, we started a reaction with successive irradiation and black periods. A mixture of **1a** (71 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (65 mg, 0.2 mmol) in CH<sub>3</sub>CN (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 425–475 nm or in the dark (at 50 °C) for the corresponding time (Figure S2). Afterwards, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to determine the yields of **2a**. The grey boxes represent the periods in which the reaction vessels were covered (dark period). These results indicated that continuous irradiation was essential for the formation of the product, and a radical chain mechanism might not be the predominant process.



Entry	Time (h)	Yield of <b>2a</b> (%)
1	0	0
2	3	35
3	6	35
4	9	57
5	12	57
6	15	69



**Figure S2.** Light On–Off Experiments

## 7) Determination of Quantum Yield

### I. Determination of the light intensity at 450 nm

The instrument for photocatalysis is PR-PCR2-450nm with no filters. For convenience of calculations, the wavelength of the photoreactor was set at 450 nm. The photon flux of the PR-PCR2-450nm was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub>. A buffered solution of 1,10-phenanthroline was prepared by dissolving 50 mg of 1,10-phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>. Both solutions were stored in the dark. To determine the photon flux of the PR-PCR2-450nm, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 10.0 seconds at  $\lambda = 450$  nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A(510 \text{ nm})}{l \cdot \epsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and  $\epsilon$  is the molar absorptivity at 510 nm (11.100 L mol<sup>-1</sup> cm<sup>-1</sup>). The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} \quad (2)$$

Where  $\Phi$  is the quantum yield for the ferrioxalate actinometer (0.844 for a 0.15 M solution at  $\lambda = 450$  nm), t is the time (10.0 s), and f is the fraction of light absorbed at  $\lambda = 450$  nm (0.99979, vide infra). The photon flux was calculated (average of three experiments) to be  $5.51 \times 10^{-8}$  einstein s<sup>-1</sup>.

Sample calculation:

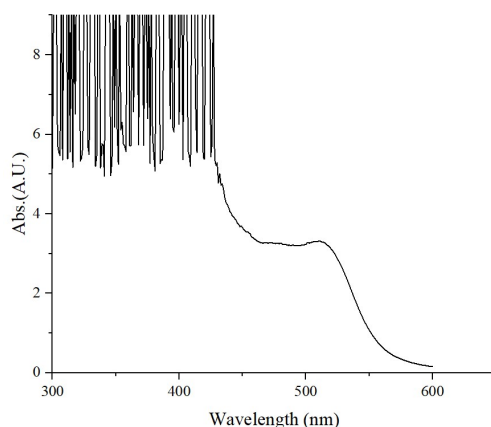
$$\text{mol Fe}^{2+} = \frac{0.00235 \text{ L} \times 2.195}{1.000 \text{ cm} \times 11,100 \text{ L mol}^{-1}\text{cm}^{-1}} = 4.65 \times 10^{-7} \text{ mol}$$

$$\text{photon flux} = \frac{4.65 \times 10^{-7} \text{ mol}}{0.844 \times 10 \times 0.99979} = 5.51 \times 10^{-8} \text{ einstein s}^{-1}$$

## II. Determination of fraction of light absorbed at 450 nm for the ferrioxalate solution

The absorbance of the above ferrioxalate solution at 450 nm was measured to be 3.655. The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 450 nm.

$$f = 1 - 10^{-A(450 \text{ nm})} \quad (3)$$



**Figure S3.** Absorbance of the Ferrioxalate Actinometer Solution

## III. Determination of the reaction quantum yield



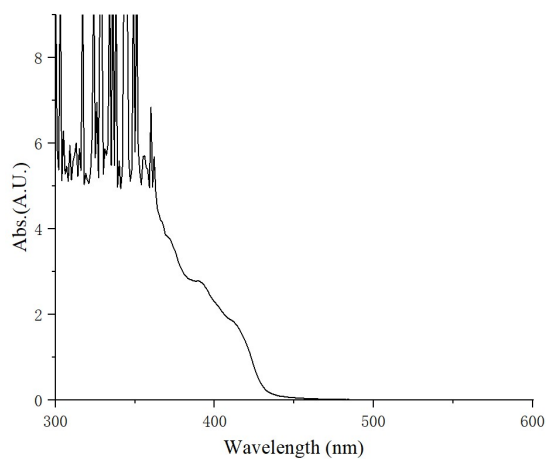
A mixture of **1a** (71 mg, 0.4 mmol), AQ (17 mg, 0.08 mmol), and  $\text{Cs}_2\text{CO}_3$  (65 mg, 0.2 mmol) in  $\text{CH}_3\text{CN}$  (4.0 mL) was stirred under an oxygen atmosphere (1 atm, with a balloon) irradiated by 36 W blue LEDs with an emitting wavelength of 450 nm for 3600 s. After irradiation, the solution was passed through a silica plug. The yield of **2a** was determined by  $^1\text{H}$  NMR spectra of crude reaction mixtures using  $\text{CH}_2\text{Br}_2$  as the internal standard. The quantum yield was determined using eq 4. The reaction quantum

yield ( $\Phi$ ) was thus determined to be  $0.514 < 1$ , suggesting that a radical chain mechanism might not be the predominant process.

$$\Phi = \frac{\text{mol Product}}{\text{photon flux} \times t \times f} \quad (4)$$

#### IV. Absorbance of anthraquinone

The absorbance of anthraquinone in DCE was measured at the reaction concentration of  $2.0 \times 10^{-2}$  M. The absorbance at 450 nm for a  $2.0 \times 10^{-2}$  M solution is 0.095, indicating that the fraction of light absorbance is 0.196.



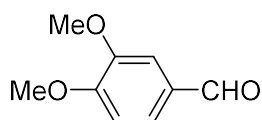
**Figure S4.** Absorbance of Anthraquinone



## 5. Analytic Data for Products

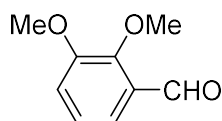
The characterization data of known compounds **2a–2m**, **2s**, **3a**, **5a–5i**, **5k–5n**, **6e**, and **6h** was in full agreement with previously reported data.<sup>2–15</sup>

### 3,4-Dimethoxybenzaldehyde (**2a**)<sup>2</sup>



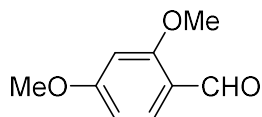
**2a** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (51 mg, 77%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.85 (s, 1H), 7.46 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.1, 154.6, 149.8, 130.3, 127.0, 110.5, 109.1, 56.3, 56.2.

### 2,3-Dimethoxybenzaldehyde (**2b**)<sup>3</sup>



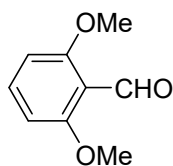
**2b** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (46 mg, 69%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.41 (s, 1H), 7.39 (dd, *J* = 7.1, 2.4 Hz, 1H), 7.16–7.08 (m, 2H), 3.97 (s, 3H), 3.89 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.3, 153.1, 152.7, 129.9, 124.3, 119.2, 118.2, 62.4, 56.1.

### 2,4-Dimethoxybenzaldehyde (**2c**)<sup>3</sup>



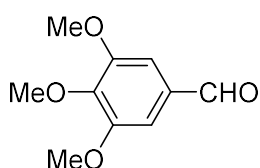
**2c** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (49 mg, 74%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.27 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 6.53 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 188.4, 166.3, 163.7, 130.8, 119.1, 105.9, 98.0, 55.72, 55.70.

### 2,6-Dimethoxybenzaldehyde (2d)<sup>4</sup>



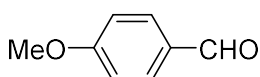
**2d** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (47 mg, 71%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.49 (s, 1H), 7.43 (dd, *J* = 8.5, 8.4 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 189.6, 162.3, 136.1, 114.4, 104.0, 56.2.

### 3,4,5-Trimethoxybenzaldehyde (2e)<sup>3</sup>



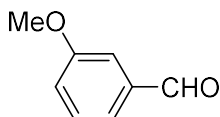
**2e** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (55 mg, 70%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.86 (s, 1H), 7.13 (s, 2H), 3.94 (s, 3H), 3.93 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.2, 153.8, 143.8, 131.9, 106.9, 61.1, 56.4.

### 4-Methoxybenzaldehyde (2f)<sup>2</sup>



**2f** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (42 mg, 77%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.88 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 191.0, 164.7, 132.1, 130.0, 114.4, 55.7.

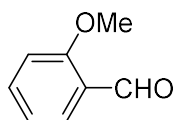
### 3-Methoxybenzaldehyde (2g)<sup>3</sup>



**2g** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (36 mg, 67%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.93 (s, 1H), 7.46–7.37 (m, 2H), 7.38–7.33 (m, 1H), 7.17–7.10 (m, 1H), 3.82 (s, 3H);

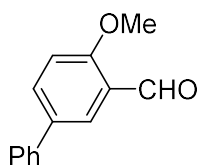
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 160.2, 137.8, 130.1, 123.5, 121.5, 112.1, 55.5.

#### 2-Methoxybenzaldehyde (**2h**)<sup>2</sup>



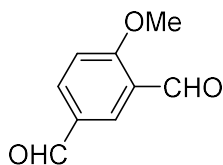
**2h** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (from **1h**: 41 mg, 75%; from **1p**: 38 mg, 70%; from **1q**: 34 mg, 63%; from **1r**: 33 mg, 61%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.45 (s, 1H), 7.83–7.78 (m, 1H), 7.57–7.48 (m, 1H), 7.04–6.92 (m, 2H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.9, 161.9, 136.0, 128.6, 124.9, 120.7, 111.7, 54.2.

#### 4-Methoxy-[1,1'-biphenyl]-3-carbaldehyde (**2i**)<sup>5</sup>



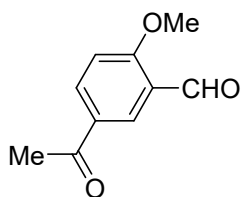
**2i** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a colorless oil (37 mg, 44%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.52 (s, 1H), 8.08 (d,  $J = 2.5$  Hz, 1H), 7.80 (dd,  $J = 8.7, 2.5$  Hz, 1H), 7.60–7.56 (m, 2H), 7.46–7.41 (m, 2H), 7.37–7.31 (m, 1H), 7.08 (d,  $J = 8.7$  Hz, 1H), 3.98 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.9, 161.4, 139.6, 134.5, 134.0, 129.0, 127.4, 127.0, 126.8, 125.1, 112.3, 56.0.

#### 4-Methoxyisophthalaldehyde (**2j**)<sup>6</sup>



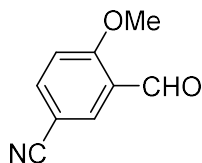
**2j** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as a white solid (from **1j**: 40 mg, 61%; from **1n**: 44 mg, 67%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.48 (s, 1H), 9.95 (s, 1H), 8.33 (d,  $J = 2.2$  Hz, 1H), 8.13 (dd,  $J = 8.7, 2.2$  Hz, 1H), 7.15 (d,  $J = 8.7$  Hz, 1H), 4.05 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.3, 188.8, 166.0, 135.8, 132.2, 129.8, 125.0, 112.5, 56.5.

### 5-Acetyl-2-methoxybenzaldehyde (**2k**)<sup>7</sup>



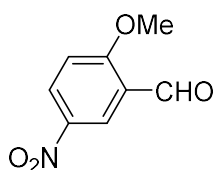
**2k** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (from **1k**: 37 mg, 52%; from **1o**: 45 mg, 63%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.47 (s, 1H), 8.40 (d, *J* = 2.4 Hz, 1H), 8.23 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 4.02 (s, 3H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.4, 189.1, 165.1, 135.9, 130.3, 129.8, 124.3, 112.1, 56.3, 26.6.

### 3-Formyl-4-methoxybenzonitrile (**2l**)<sup>7</sup>



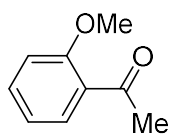
**2l** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (32 mg, 50%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.41 (s, 1H), 8.10 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 4.02 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.7, 164.3, 139.1, 133.1, 125.3, 118.1, 112.9, 104.9, 56.4.

### 2-Methoxy-5-nitrobenzaldehyde (**2m**)<sup>8</sup>



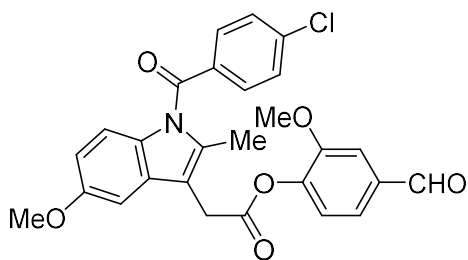
**2m** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a yellowish solid (33 mg, 46%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.44 (s, 1H), 8.68 (d, *J* = 2.9 Hz, 1H), 8.43 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.13 (d, *J* = 9.2 Hz, 1H), 4.08 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.7, 165.7, 141.8, 130.8, 124.8(2C), 112.4, 56.9.

### 1-(2-Methoxyphenyl)ethan-1-one (2s)<sup>9</sup>



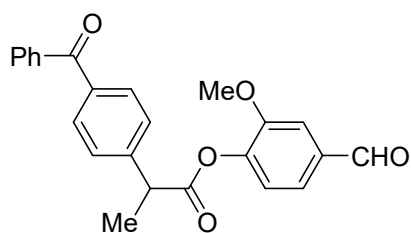
**2s** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (9:1) as a colorless oil (46 mg, 77%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.48–7.42 (m, 1H), 7.00–6.94 (m, 2H), 3.90 (s, 3H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 159.0, 133.8, 130.4, 128.4, 120.6, 111.7, 55.6, 31.9.

### 4-Mormyl-2-methoxyphenyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (2t)



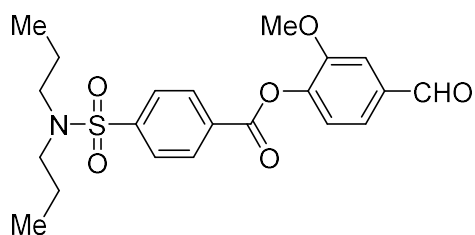
**2t** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as a white solid (112 mg, 57%): mp 124–126 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.93 (s, 1H), 7.74–7.63 (m, 2H), 7.52–7.43 (m, 4H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.95 (s, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.1, 168.4(2C), 156.2, 152.0, 145.1, 139.5, 136.5, 135.4, 134.0, 131.3, 131.0, 130.7, 129.3, 124.8, 123.4, 115.1, 112.0, 111.7, 111.0, 101.7, 56.1, 55.9, 30.1, 13.5; HRMS (ESI-Orbitrap) *m/z* [M + H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>23</sub>ClNO<sub>6</sub> 492.1208, found 492.1203.

#### 4-Formyl-2-methoxyphenyl 2-(4-benzoylphenyl)propanoate (2u)



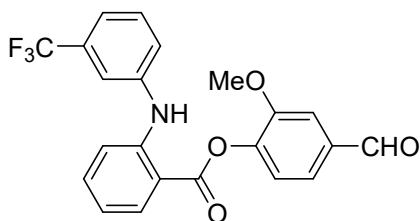
**2u** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as a colorless oil (101 mg, 65%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.92 (s, 1H), 7.91–7.88 (m, 1H), 7.84–7.78 (m, 2H), 7.74–7.70 (m, 1H), 7.68–7.64 (m, 1H), 7.62–7.55 (m, 1H), 7.52–7.41 (m, 5H), 7.14 (d,  $J = 8.4$  Hz, 1H), 4.11 (q,  $J = 7.2$  Hz, 1H), 3.76 (s, 3H), 1.68 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.6, 191.1, 171.6, 152.1, 145.1, 140.3, 138.1, 137.6, 135.4, 132.7, 131.9, 130.2, 129.5, 129.4, 128.7, 128.5, 124.8, 123.3, 110.9, 56.0, 45.4, 18.7; HRMS (ESI-Orbitrap)  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_5$  389.1384, found 389.1384.

#### 4-Formyl-2-methoxyphenyl 4-(*N,N*-dipropylsulfamoyl)benzoate (2v)



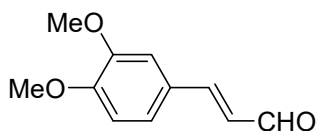
**2v** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as a white solid (102 mg, 61%): mp 82–84 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.96 (s, 1H), 8.31 (d,  $J = 8.4$  Hz, 2H), 7.93 (d,  $J = 8.5$  Hz, 2H), 7.54–7.51 (m, 2H), 7.34 (d,  $J = 7.8$  Hz, 1H), 3.88 (s, 3H), 3.11 (t,  $J = 6.0$  Hz, 4H), 1.58–1.52 (m, 4H), 0.87 (t,  $J = 7.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 163.0, 152.1, 145.2, 144.8, 135.6, 132.2, 131.1, 127.3, 124.8, 123.5, 111.1, 56.3, 50.1, 22.1, 11.3; HRMS (ESI-Orbitrap)  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{26}\text{NO}_6\text{S}$  420.1475, found 420.1466.

#### 4-Formyl-2-methoxyphenyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (**2w**)



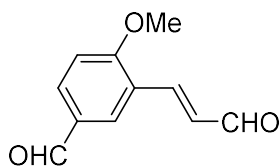
**2w** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (12:1) as a yellow oil (111 mg, 67%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.98 (s, 1H), 9.44 (s, 1H), 8.27 (dd,  $J = 8.1, 1.6$  Hz, 1H), 7.57 (d,  $J = 1.8$  Hz, 1H), 7.54 (dd,  $J = 7.9, 1.8$  Hz, 1H), 7.51–7.39 (m, 4H), 7.38–7.31 (m, 3H), 6.94–6.90 (m, 1H), 3.92 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 166.2, 152.3, 147.7, 144.9, 141.2, 135.4, 132.6, 131.9 (q,  $J = 32.8$  Hz), 130.1, 124.9(2C), 124.8, 124.0 (d,  $J = 273$  Hz), 123.8, 120.0 (d,  $J = 3.7$  Hz), 118.5, 118.3 (d,  $J = 3.7$  Hz), 114.3, 111.2, 110.9, 56.2;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6; HRMS (ESI-Orbitrap)  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{17}\text{F}_3\text{NO}_4$  416.1104, found 416.1095.

#### (*E*)-3-(3,4-Dimethoxyphenyl)acrylaldehyde (**3a**)<sup>10</sup>



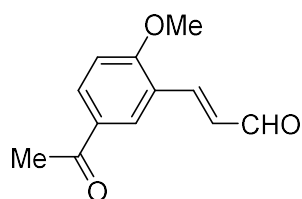
**3a** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a yellowish solid (Table 1, entry 16: 20 mg, 26%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.65 (d,  $J = 7.7$  Hz, 1H), 7.41 (d,  $J = 15.8$  Hz, 1H), 7.16 (dd,  $J = 8.3, 2.0$  Hz, 1H), 7.07 (d,  $J = 2.0$  Hz, 1H), 6.90 (d,  $J = 8.3$  Hz, 1H), 6.61 (dd,  $J = 15.8, 7.7$  Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.8, 153.0, 152.1, 149.4, 127.1, 126.8, 123.6, 111.2, 109.9, 56.2, 56.0.

#### (*E*)-4-Methoxy-3-(3-oxoprop-1-en-1-yl)benzaldehyde (**3j**)



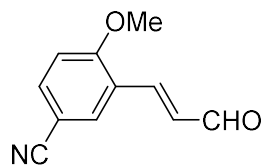
**3j** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as a white solid (from **1i**: 21 mg, 28%; from **1n**: 11 mg, 15%): mp 101–103 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.93 (s, 1H), 9.73 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.81 (d, *J* = 16.1 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.88 (dd, *J* = 16.1, 7.7 Hz, 1H), 4.02 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 194.2, 190.4, 162.7, 146.5, 134.2, 130.9, 130.6, 130.0, 123.9, 111.7, 56.4; HRMS (ESI-Orbitrap) *m/z* [M + H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>11</sub>O<sub>3</sub> 191.0703, found 191.0702.

**(E)-3-(5-Acetyl-2-methoxyphenyl)acrylaldehyde (3k)**



**3k** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (from **1k**: 31 mg, 38%; from **1o**: 15 mg, 18%): mp 96–98 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.71 (d, *J* = 7.7 Hz, 1H), 8.16 (d, *J* = 2.3 Hz, 1H), 8.04 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.79 (d, *J* = 16.1 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.87 (dd, *J* = 16.1, 7.8 Hz, 1H), 4.00 (s, 3H), 2.59 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 196.4, 194.4, 161.8, 147.2, 133.1, 130.5, 130.4, 129.8, 123.1, 111.2, 56.2, 26.5; HRMS (ESI-Orbitrap) *m/z* [M + H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>13</sub>O<sub>3</sub> 205.0859, found 205.0857.

**(E)-4-Methoxy-3-(3-oxoprop-1-en-1-yl)benzonitrile (3l)**

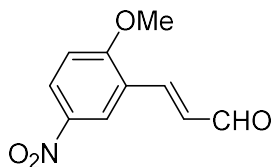


**3l** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a white solid (25 mg, 34%): mp 132–134 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.76–7.67 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.80 (dd, *J* = 16.1, 7.6 Hz, 1H), 3.99 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 194.0, 161.1, 145.3, 136.1, 132.9, 131.1, 124.4, 118.4, 112.2,



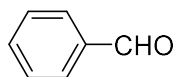
104.9, 56.3; HRMS (ESI-Orbitrap)  $m/z$   $[M + H]^+$  calcd for  $C_{11}H_{10}NO_2$  188.0706, found 188.0705.

**(E)-3-(2-Methoxy-5-nitrophenyl)acrylaldehyde (3m)**



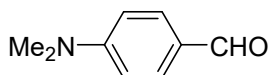
**3m** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a yellowish solid (22 mg, 27%): mp 123–125 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.74 (d,  $J = 7.6$  Hz, 1H), 8.44 (d,  $J = 2.8$  Hz, 1H), 8.31 (dd,  $J = 9.2, 2.7$  Hz, 1H), 7.76 (d,  $J = 16.1$  Hz, 1H), 7.05 (d,  $J = 9.1$  Hz, 1H), 6.87 (dd,  $J = 16.2, 7.6$  Hz, 1H), 4.05 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  193.8, 162.5, 145.2, 141.7, 131.4, 127.8, 124.6, 123.8, 111.4, 56.8; HRMS (ESI-Orbitrap)  $m/z$   $[M + H]^+$  calcd for  $C_{10}H_{10}NO_4$  208.0604, found 208.0602.

**Benzaldehyde (5a)**<sup>3</sup>



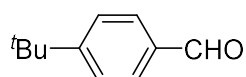
**5a** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as a colorless oil (from **4a**: 31 mg, 73%; from **4j**: 28 mg, 66%):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.00 (s, 1H), 7.88–7.85 (m, 2H), 7.65–7.58 (m, 1H), 7.53–7.49 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  192.5, 136.5, 134.5, 129.8, 129.1.

**4-(Dimethylamino)benzaldehyde (5b)**<sup>11</sup>



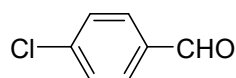
**5b** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as a yellow solid (36 mg, 61%):  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.71 (s, 1H), 7.71 (d,  $J = 8.8$  Hz, 2H), 6.67 (d,  $J = 7.2$  Hz, 2H), 3.05 (s, 6H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  190.5, 154.4, 132.1, 125.2, 111.1, 40.2.

#### 4-(*Tert*-butyl)benzaldehyde (**5c**)<sup>3</sup>



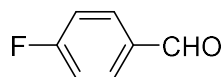
**5c** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a yellow oil (45 mg, 70%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 1.34 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 192.3, 158.6, 134.1, 129.8, 126.1, 35.5, 31.2.

#### 4-Chlorobenzaldehyde (**5d**)<sup>2</sup>



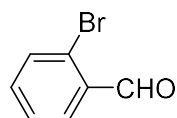
**5d** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (30 mg, 54%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.0, 141.1, 134.8, 131.0, 129.6.

#### 4-Fluorobenzaldehyde (**5e**)<sup>2</sup>



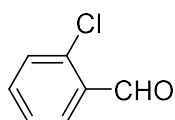
**5e** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (26 mg, 53%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.96 (s, 1H), 7.93–7.89 (m, 2H), 7.24–7.17 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 190.7, 166.7 (d, *J* = 257 Hz), 133.1 (d, *J* = 3.8 Hz), 132.4 (d, *J* = 10.1 Hz), 116.5 (d, *J* = 21.4 Hz); <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -102.

#### 2-Bromobenzaldehyde (**5f**)<sup>12</sup>



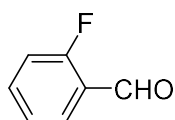
**5f** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (44 mg, 60%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.37 (s, 1H), 7.93–7.90 (m, 1H), 7.66–7.64 (m, 1H), 7.47–7.43 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 192.1, 135.5, 134.0, 133.6, 130.0, 128.1, 127.3.

### 2-Chlorobenzaldehyde (**5g**)<sup>13</sup>



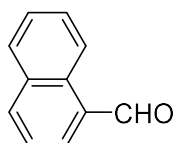
**5g** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (31 mg, 56%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.48 (s, 1H), 7.94–7.90 (m, 1H), 7.55–7.51 (m, 1H), 7.47–7.44 (m, 1H), 7.41–7.36 (m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 190.0, 138.1, 135.3, 132.6, 130.8, 129.5, 127.4.

### 2-Fluorobenzaldehyde (**5h**)<sup>13</sup>



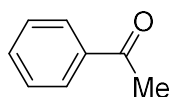
**5h** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (26 mg, 52%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.35 (s, 1H), 7.88–7.82 (m, 1H), 7.63–7.55 (m, 1H), 7.29–7.21 (m, 1H), 7.20–7.11 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.3 (d, *J* = 6.7 Hz), 164.8 (d, *J* = 257 Hz), 136.5 (d, *J* = 10.0 Hz), 128.8 (d, *J* = 1.9 Hz), 124.7 (d, *J* = 3.7 Hz), 124.3 (d, *J* = 7.9 Hz), 116.6 (d, *J* = 21.0 Hz); <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -122.

### 1-Naphthaldehyde (**5i**)<sup>12</sup>



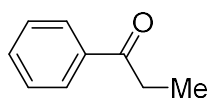
**5i** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (41 mg, 66%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.39 (s, 1H), 9.26 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.99–7.95 (m, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.74–7.66 (m, 1H), 7.65–7.56 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.7, 136.8, 135.4, 133.8, 131.5, 130.6, 129.2, 128.6, 127.1, 125.0(2C).

### Acetophenone (5k)<sup>9</sup>



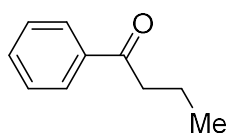
**5k** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (35 mg, 73%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98–7.94 (m, 2H), 7.59–7.54 (m, 1H), 7.49–7.44 (m, 2H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.3, 137.3, 133.2, 128.7, 128.4, 26.8.

### Propiophenone (5l)<sup>14</sup>



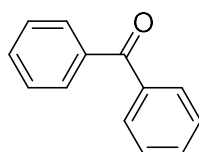
**5l** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (39 mg, 72%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98–7.95 (m, 2H), 7.57–7.53 (m, 1H), 7.48–7.43 (m, 2H), 3.01 (q, *J* = 7.3 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 201.0, 137.0, 133.0, 128.7, 128.1, 31.9, 8.4.

### 1-Phenylbutan-1-one (5m)<sup>14</sup>



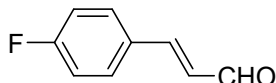
**5m** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (44 mg, 75%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98–7.95 (m, 2H), 7.57–7.53 (m, 1H), 7.48–7.43 (m, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 1.82–1.73 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 200.6, 137.2, 133.0, 128.7, 128.2, 40.7, 17.9, 14.0.

### Benzophenone (5n)<sup>3</sup>



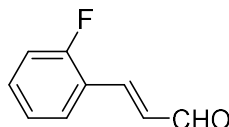
**5n** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a white solid (41 mg, 84%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82–7.79 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.47 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.9, 137.7, 132.6, 130.2, 128.4.

**(E)-3-(4-Fluorophenyl)acrylaldehyde (6e)**<sup>15</sup>



**6e** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (12 mg, 20%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69 (d,  $J = 7.6$  Hz, 1H), 7.59–7.55 (m, 2H), 7.45 (d,  $J = 16.0$  Hz, 1H), 7.13 (dd,  $J = 8.6, 8.5$  Hz, 2H), 6.65 (dd,  $J = 15.9, 7.7$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.7, 164.6 (d,  $J = 253$  Hz), 151.6, 130.7 (d,  $J = 8.8$  Hz), 130.4, 128.5 (d,  $J = 1.9$  Hz), 116.5 (d,  $J = 21.4$  Hz);  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.

**(E)-3-(2-Fluorophenyl)acrylaldehyde (6h)**<sup>16</sup>



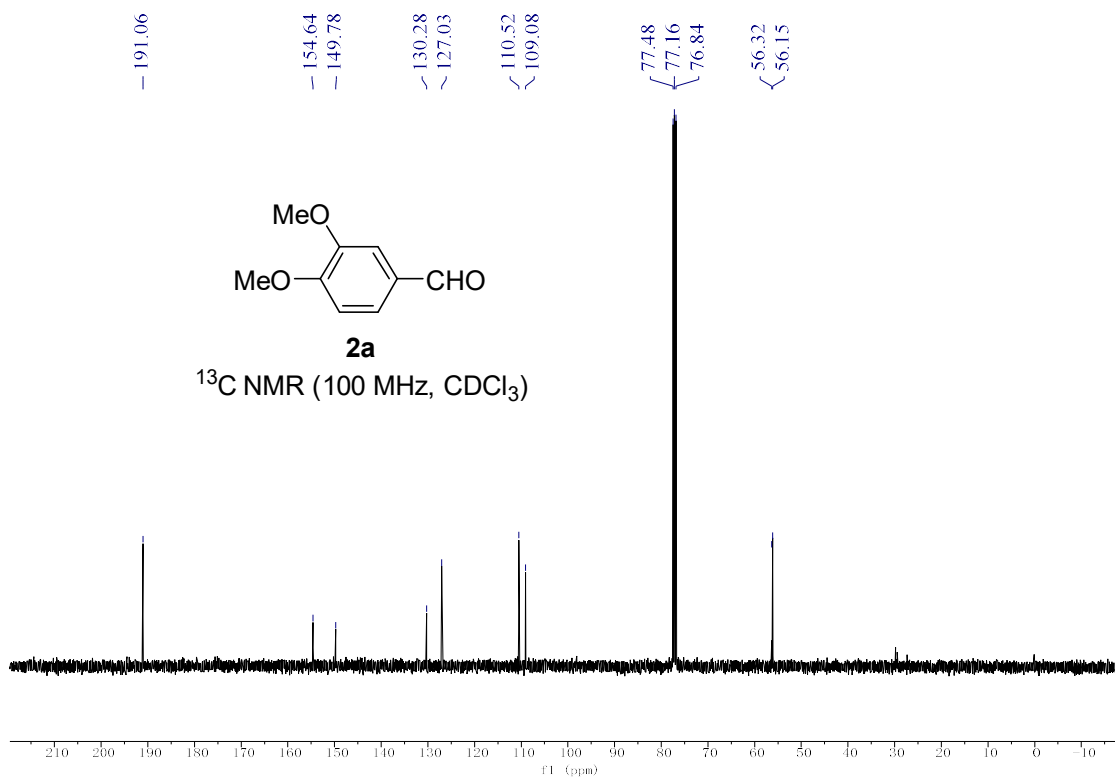
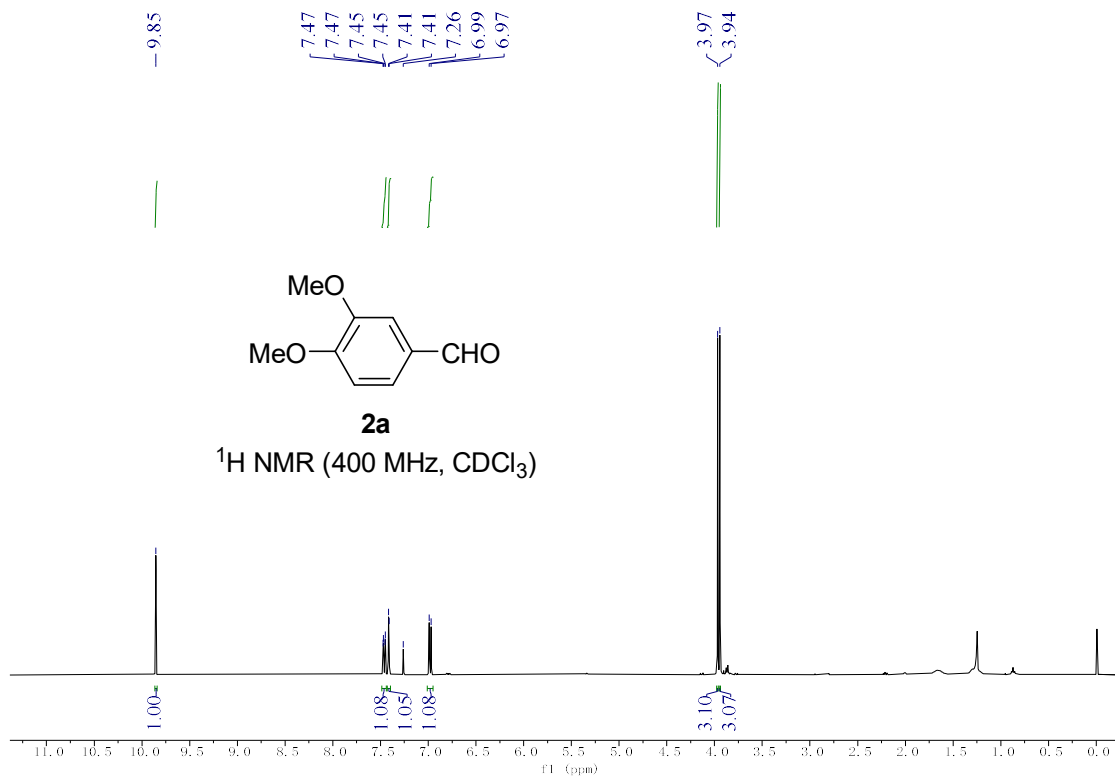
**6h** was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as a colorless oil (15 mg, 25%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.70 (d,  $J = 7.7$  Hz, 1H), 7.64 (d,  $J = 16.2$  Hz, 1H), 7.60–7.56 (m, 1H), 7.45–7.39 (m, 1H), 7.22–7.18 (m, 1H), 7.15–7.10 (m, 1H), 6.78 (dd,  $J = 16.2, 7.7$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.9, 161.3 (d,  $J = 255$  Hz), 144.9 (d,  $J = 3.8$  Hz), 133.0 (d,  $J = 8.8$  Hz), 130.6 (d,  $J = 5.0$  Hz), 128.9 (d,  $J = 2.5$  Hz), 124.8 (d,  $J = 3.8$  Hz), 122.3 (d,  $J = 11.3$  Hz), 116.4 (d,  $J = 21.4$  Hz);  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.

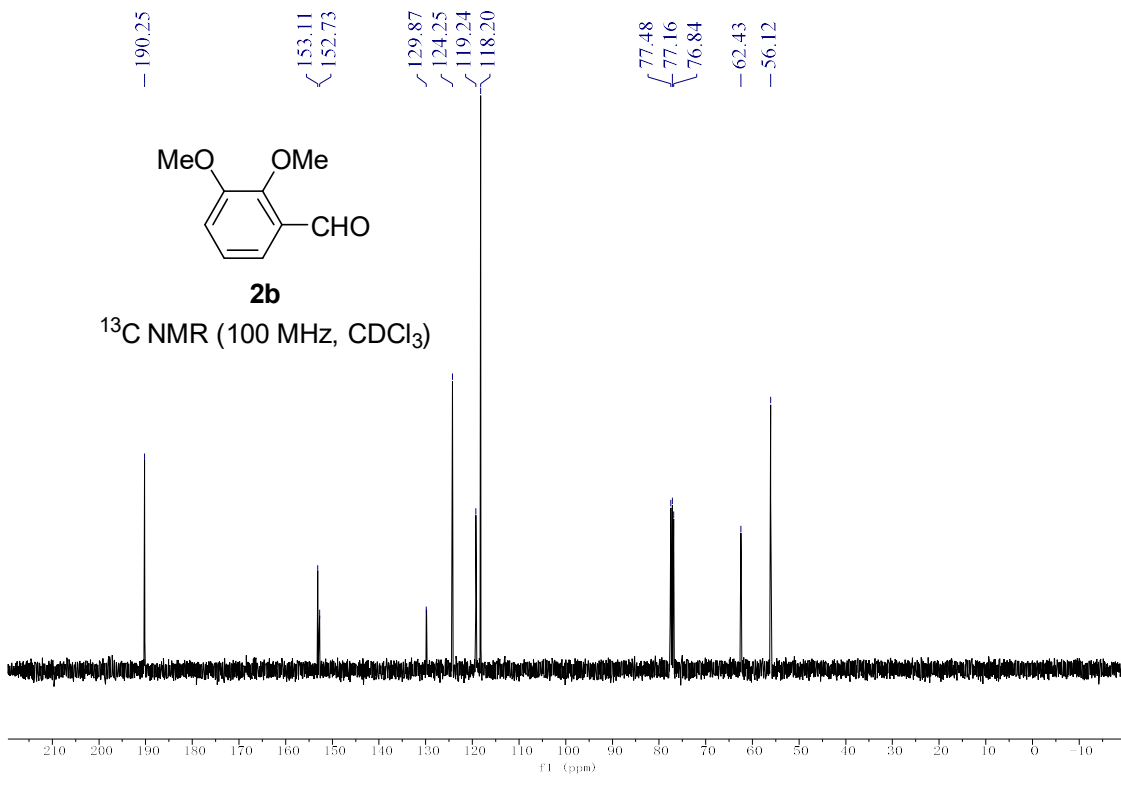
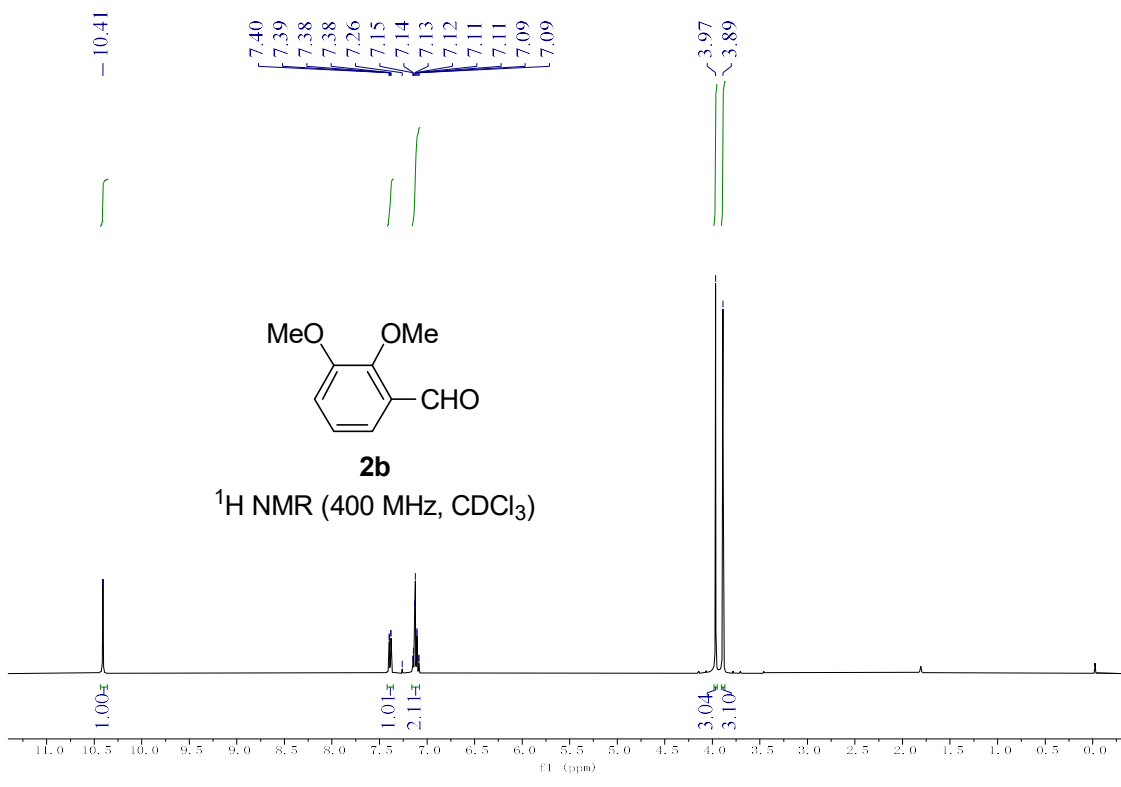
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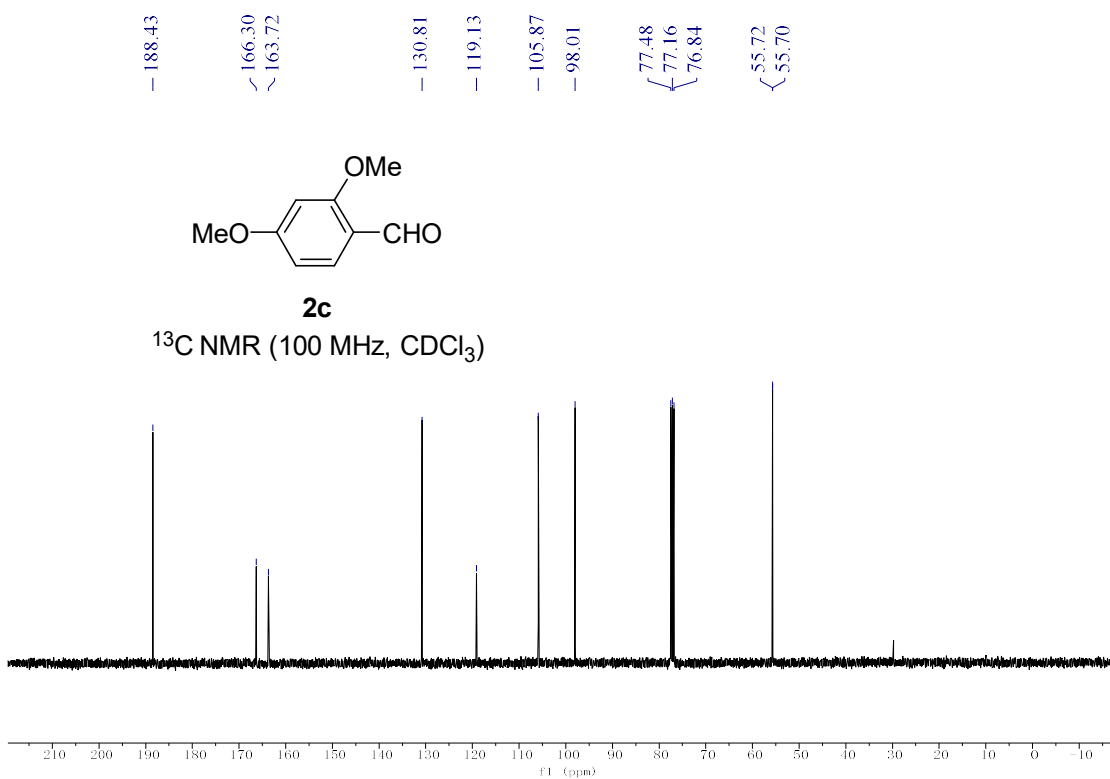
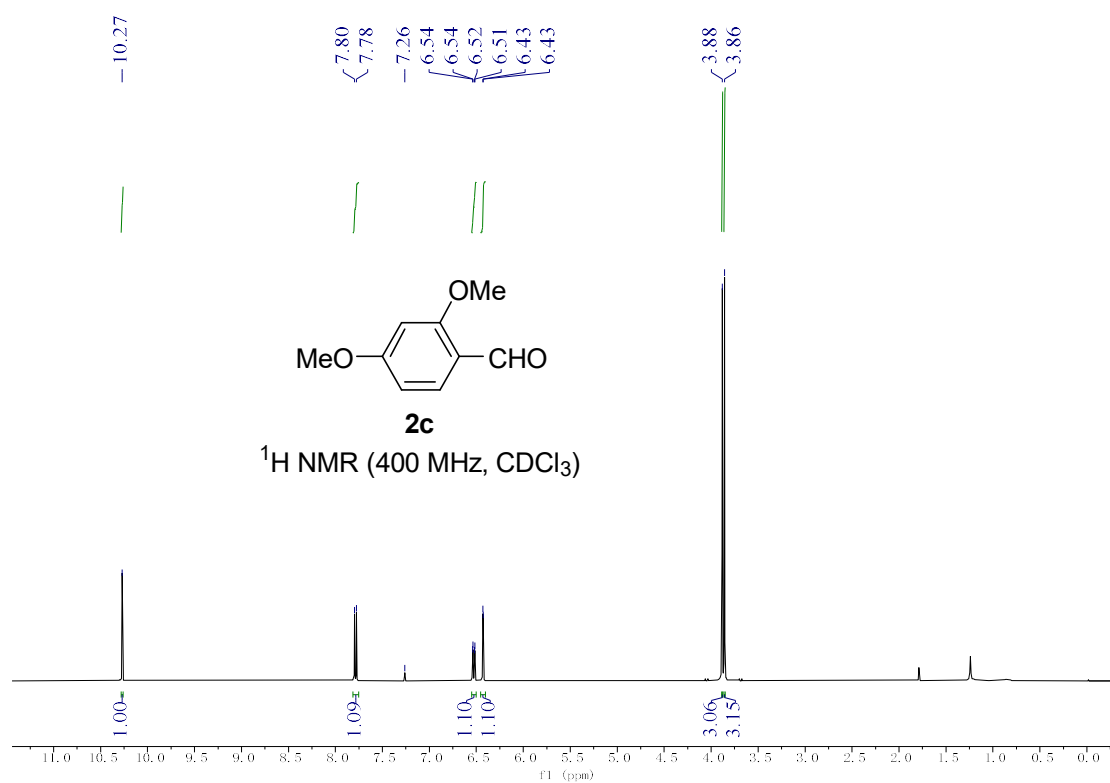
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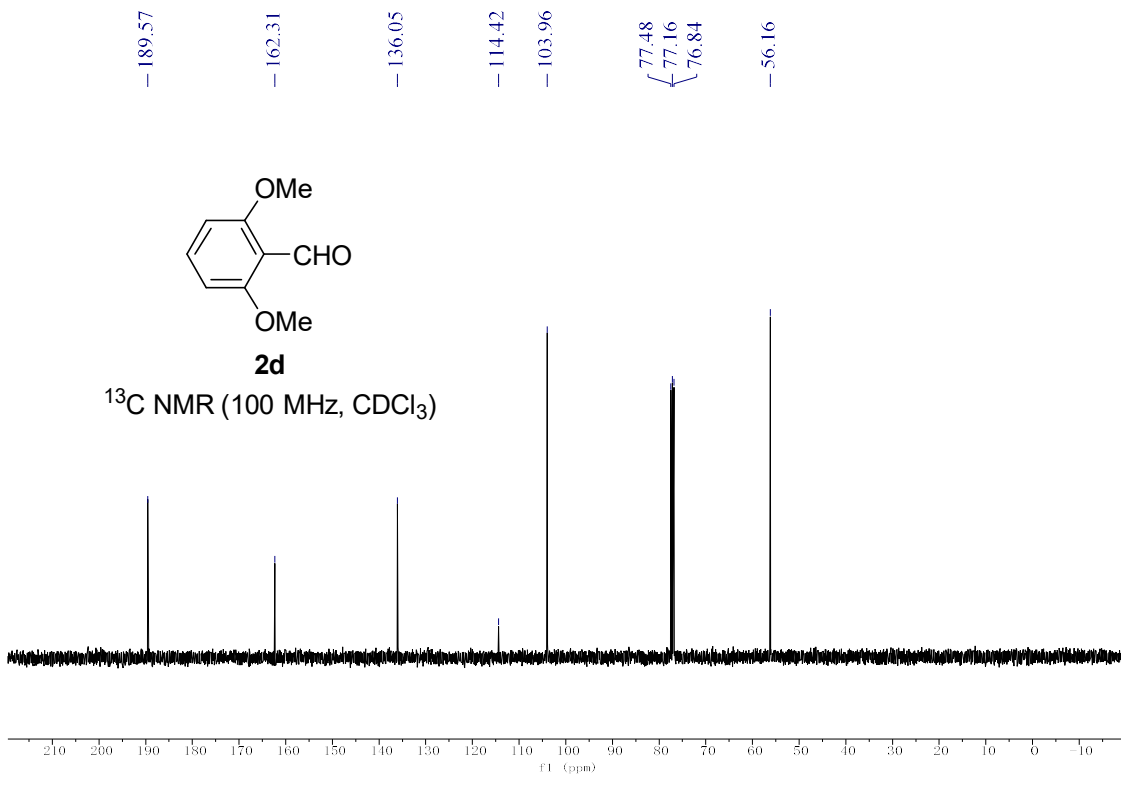
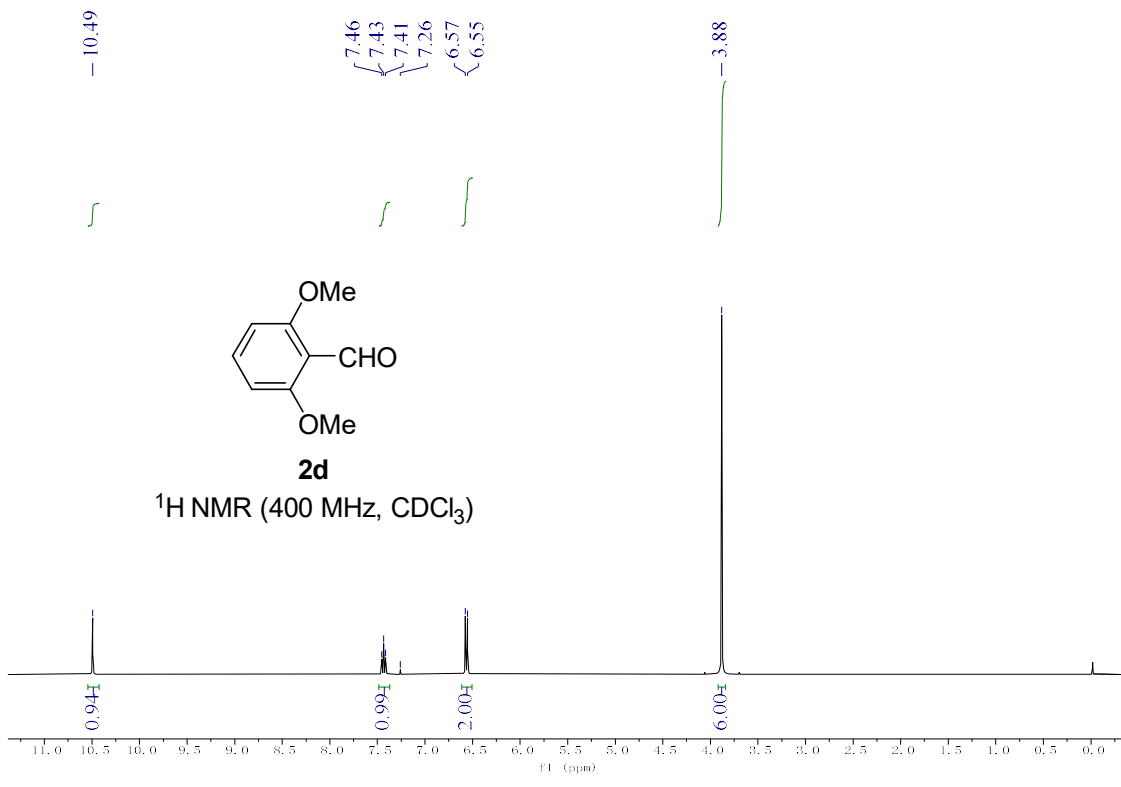
## 6. NMR Spectra for Products

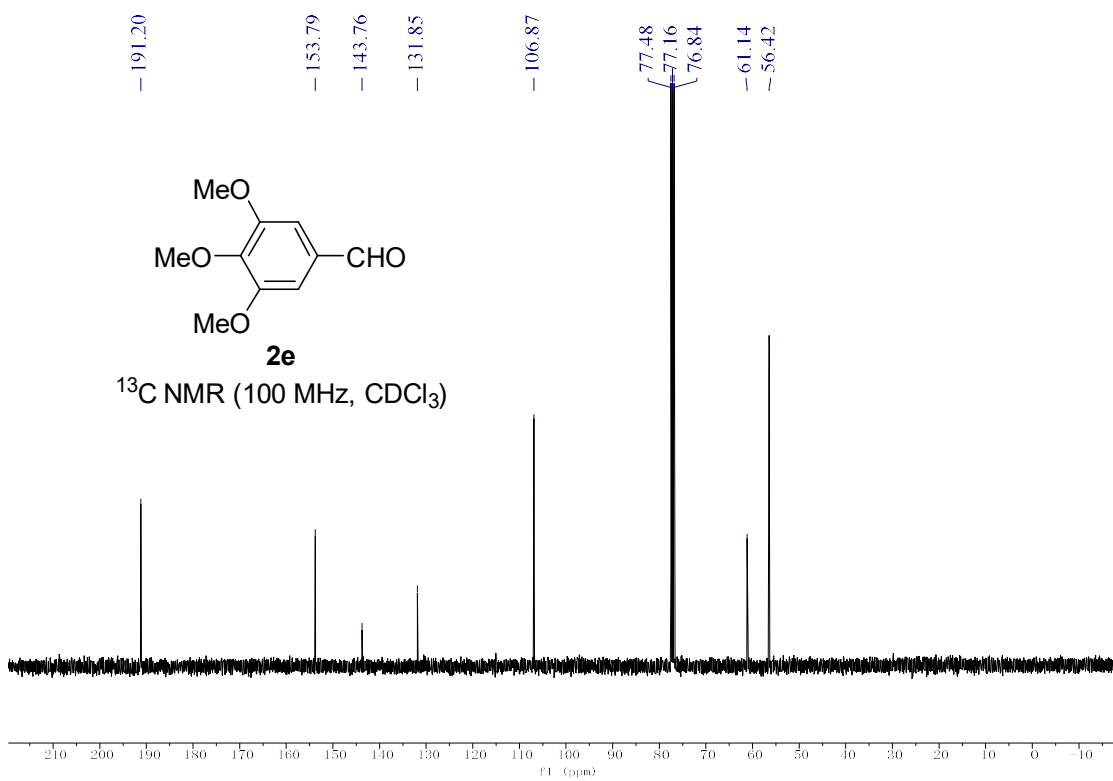
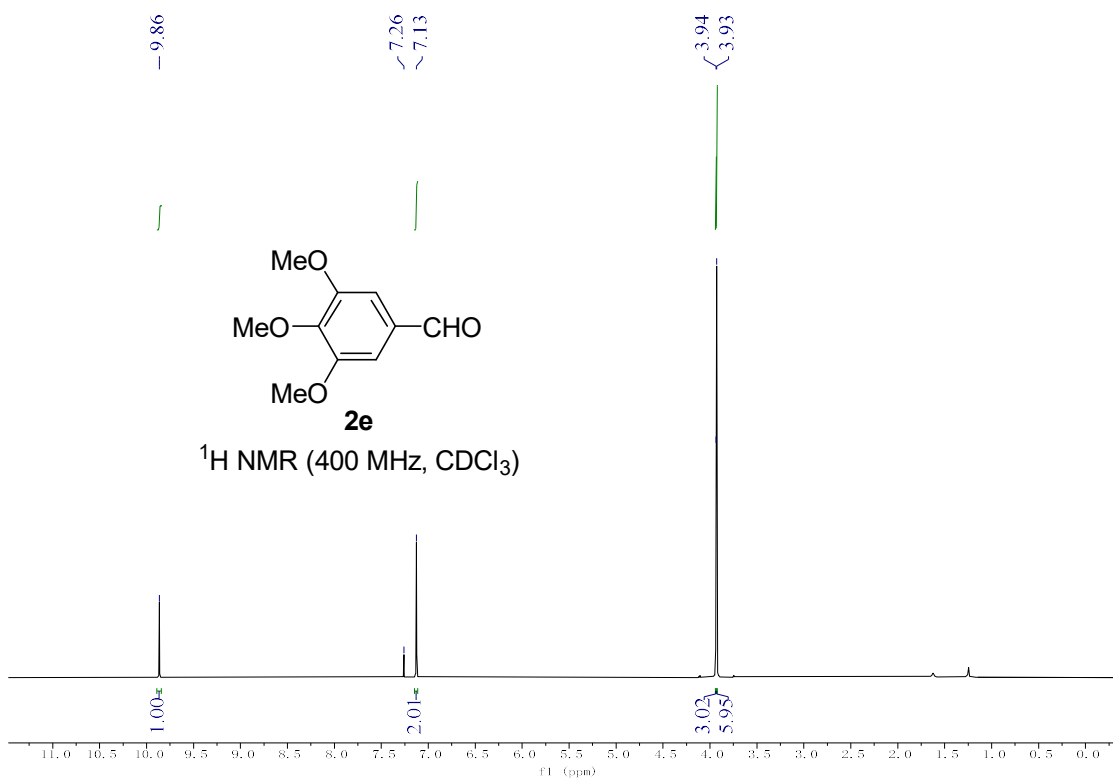


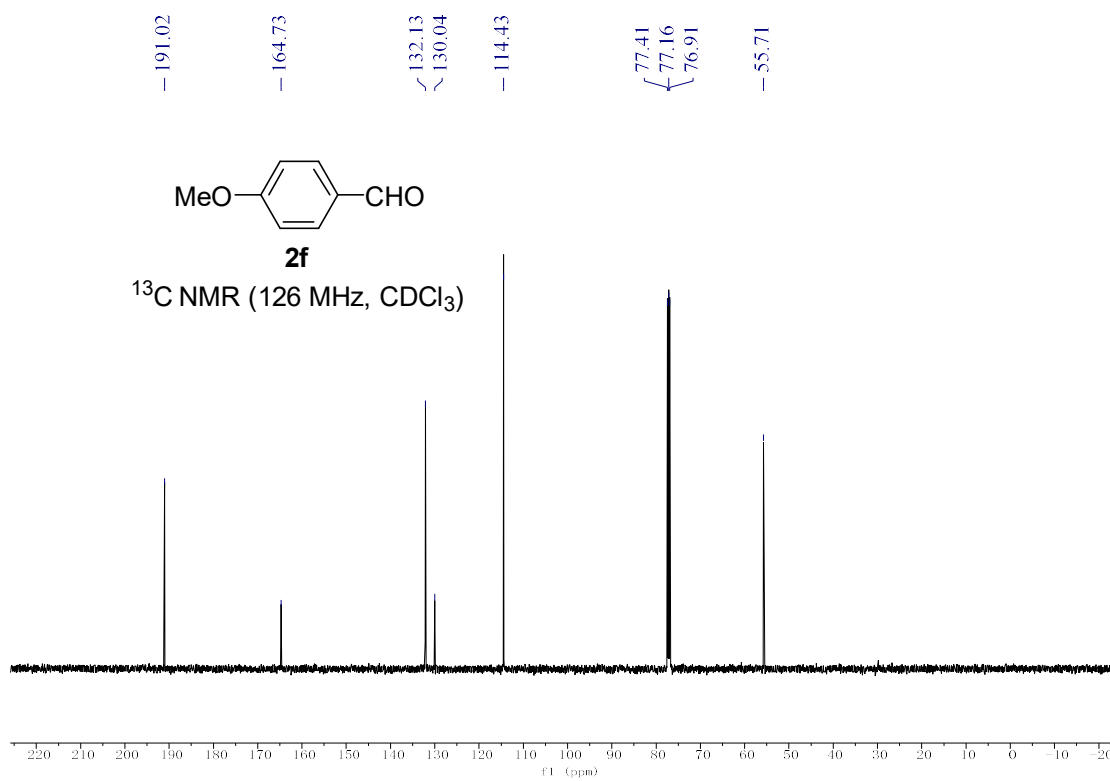
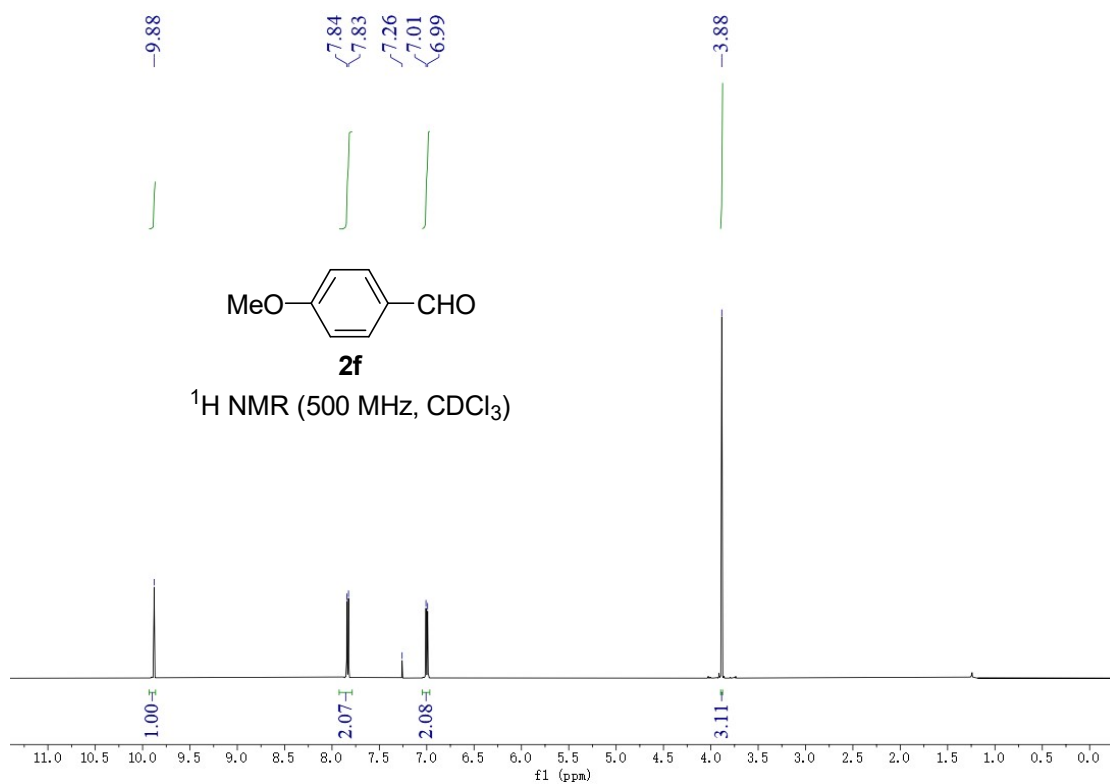


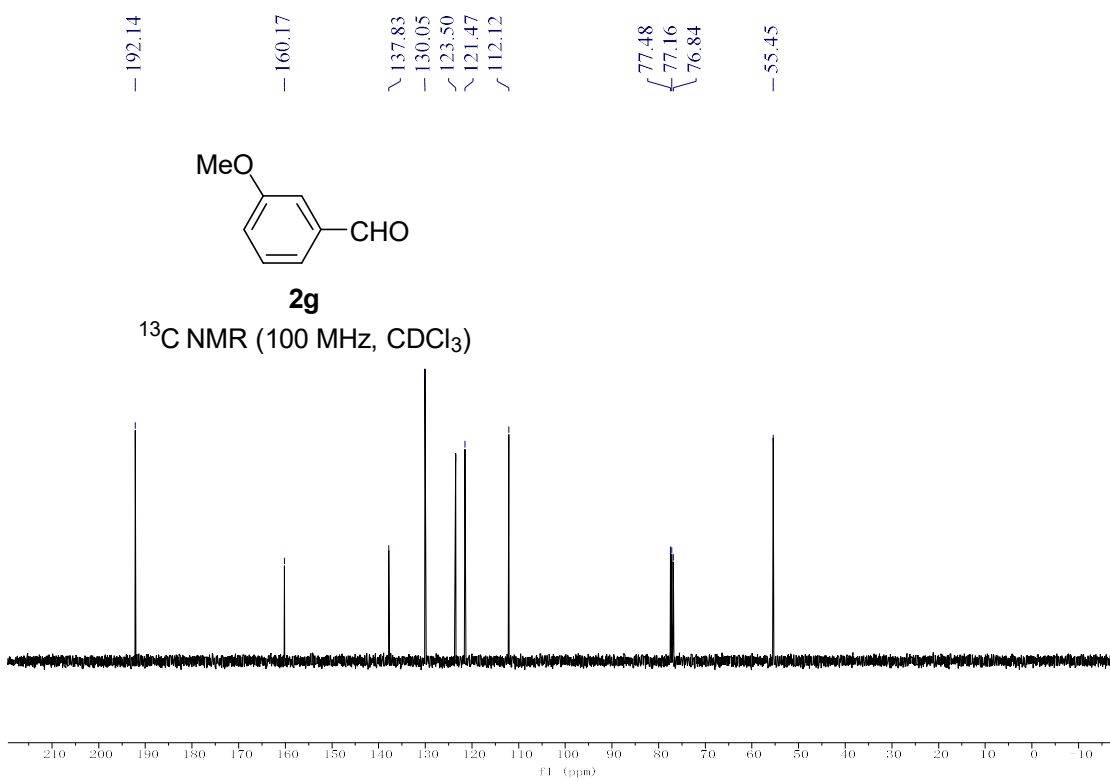
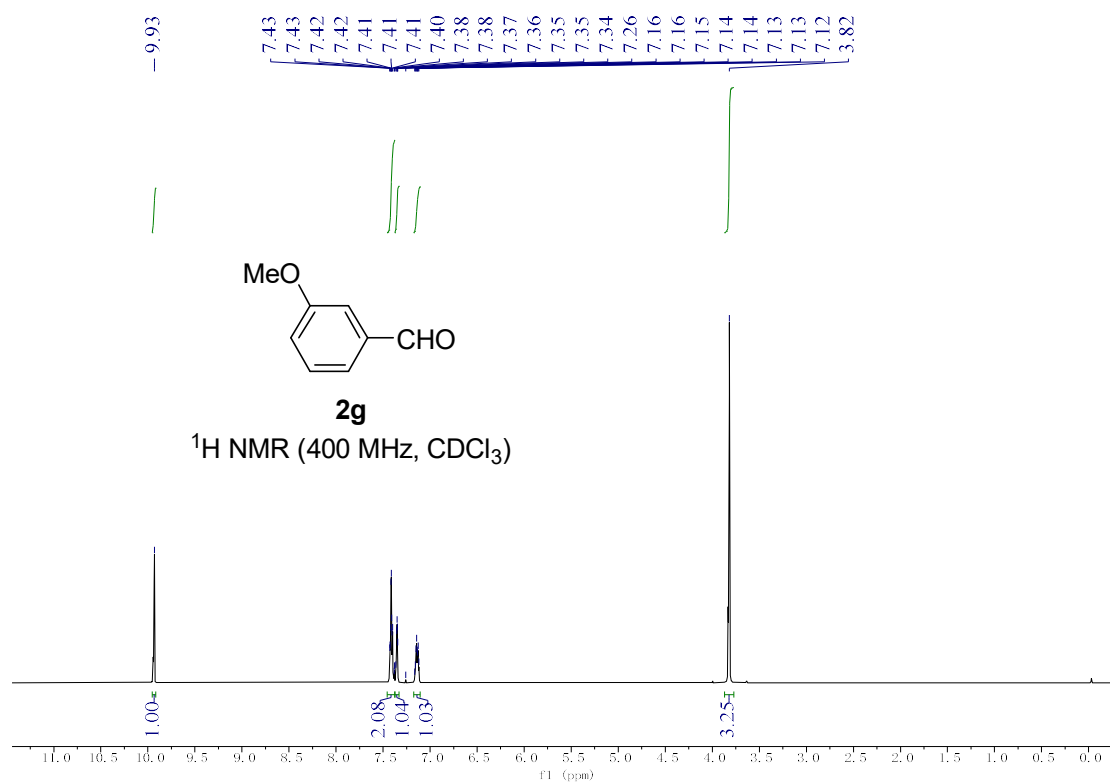


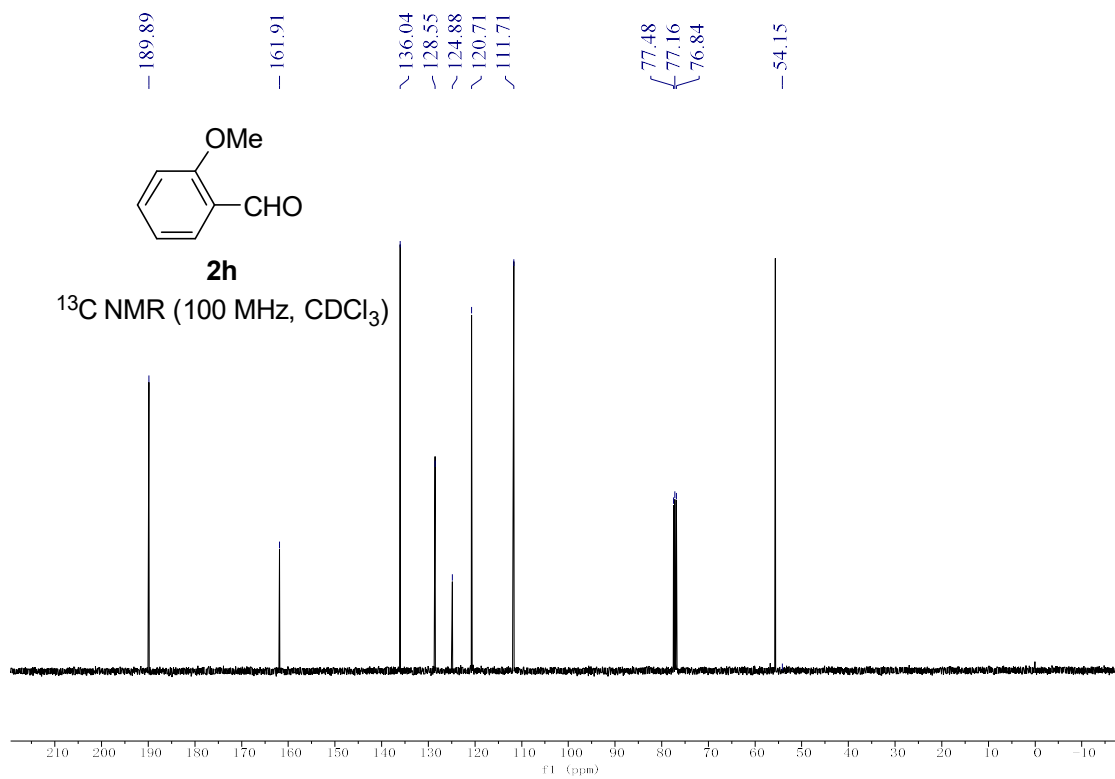
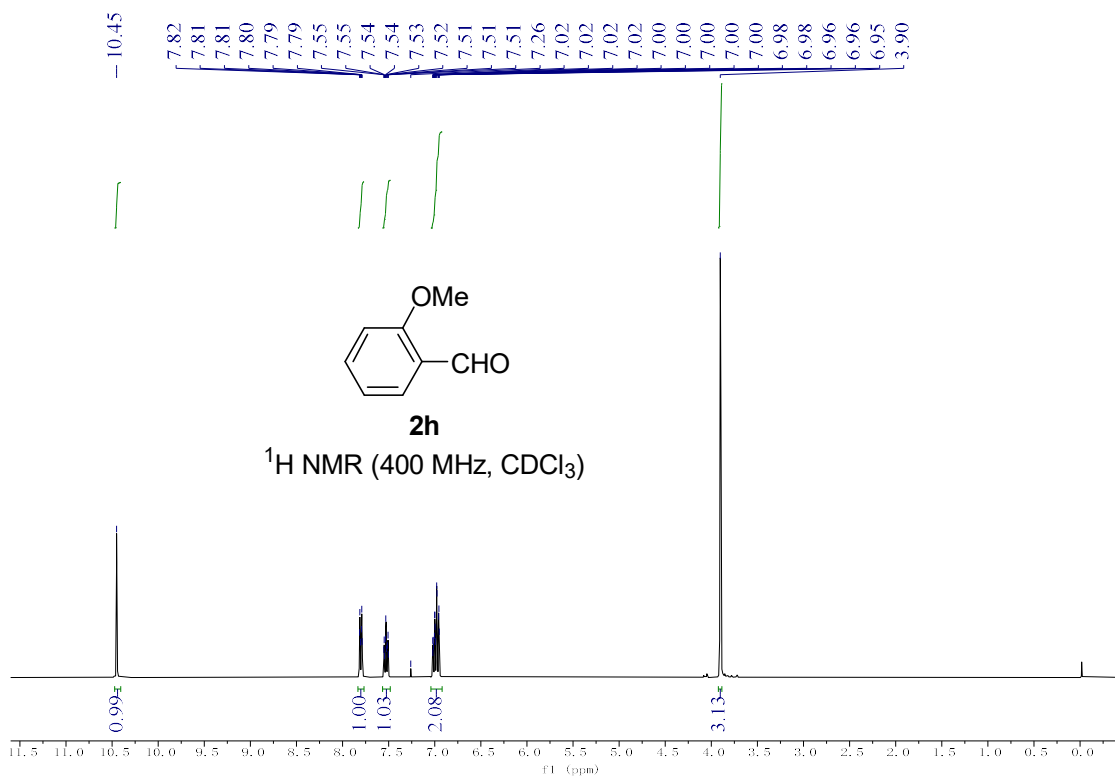


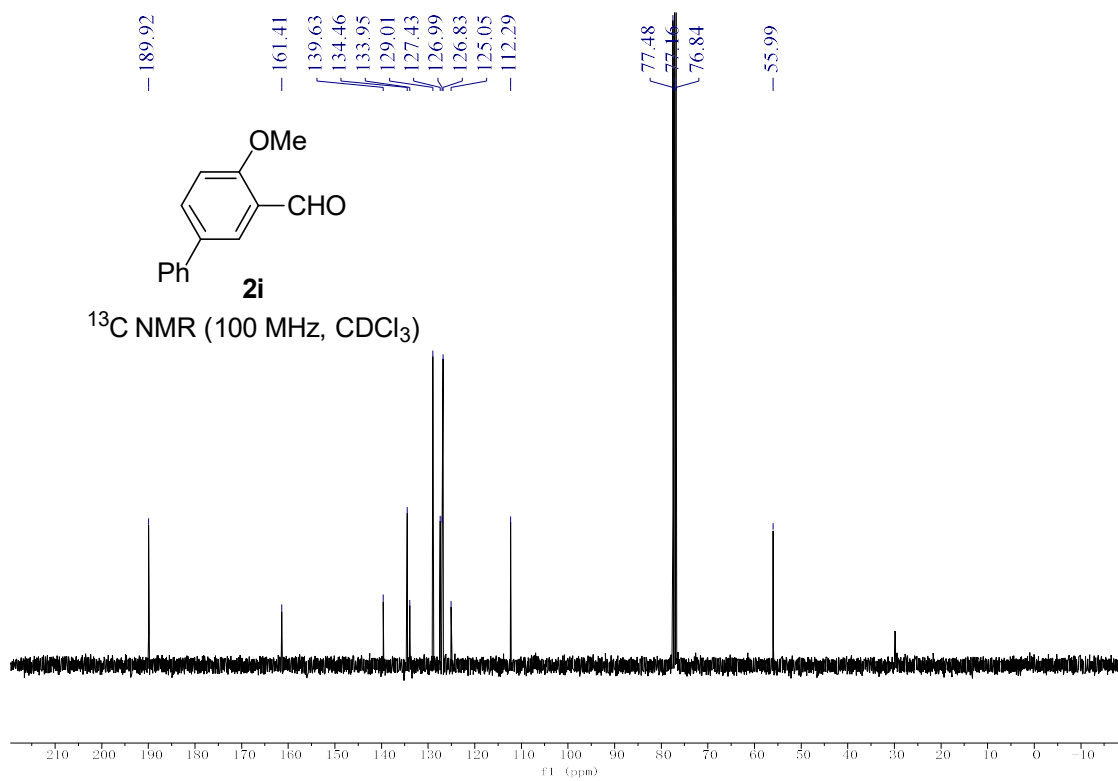
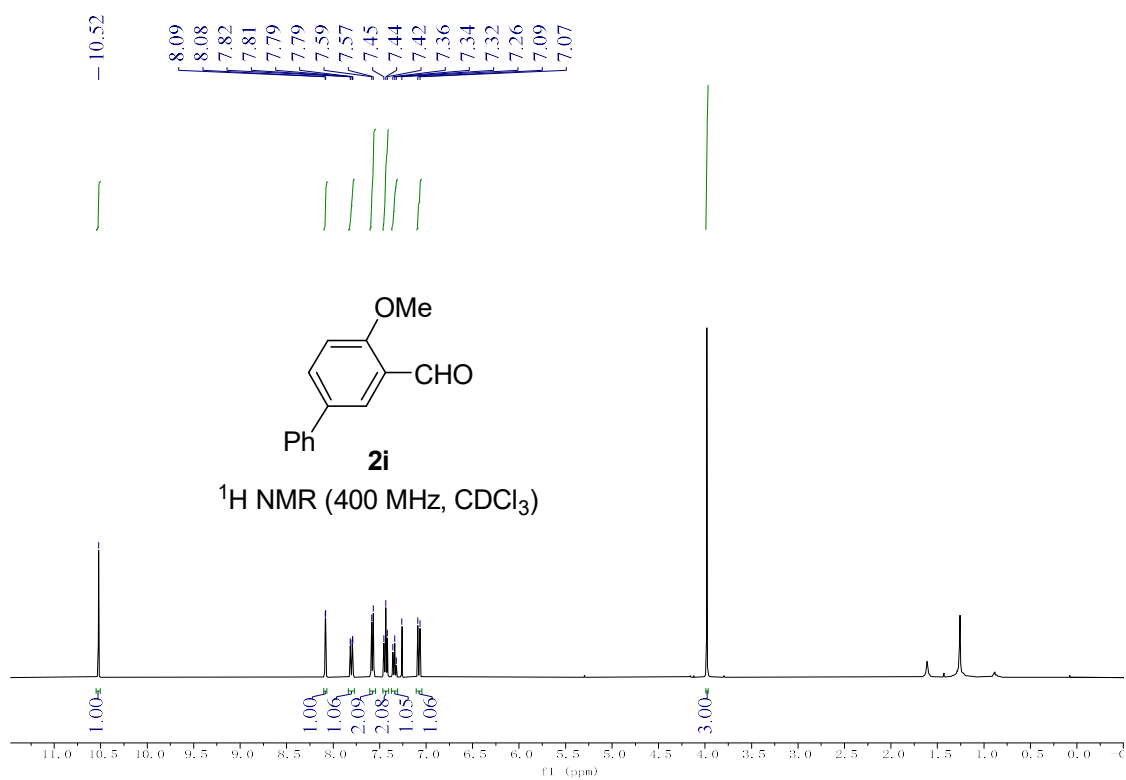


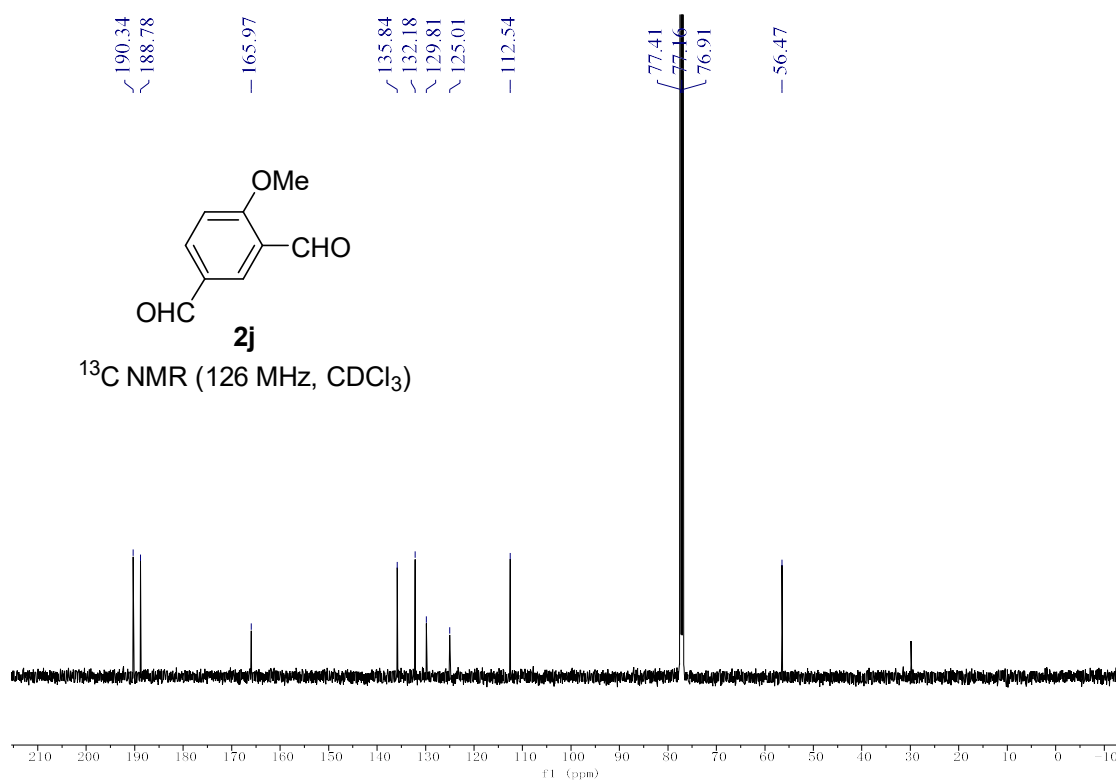
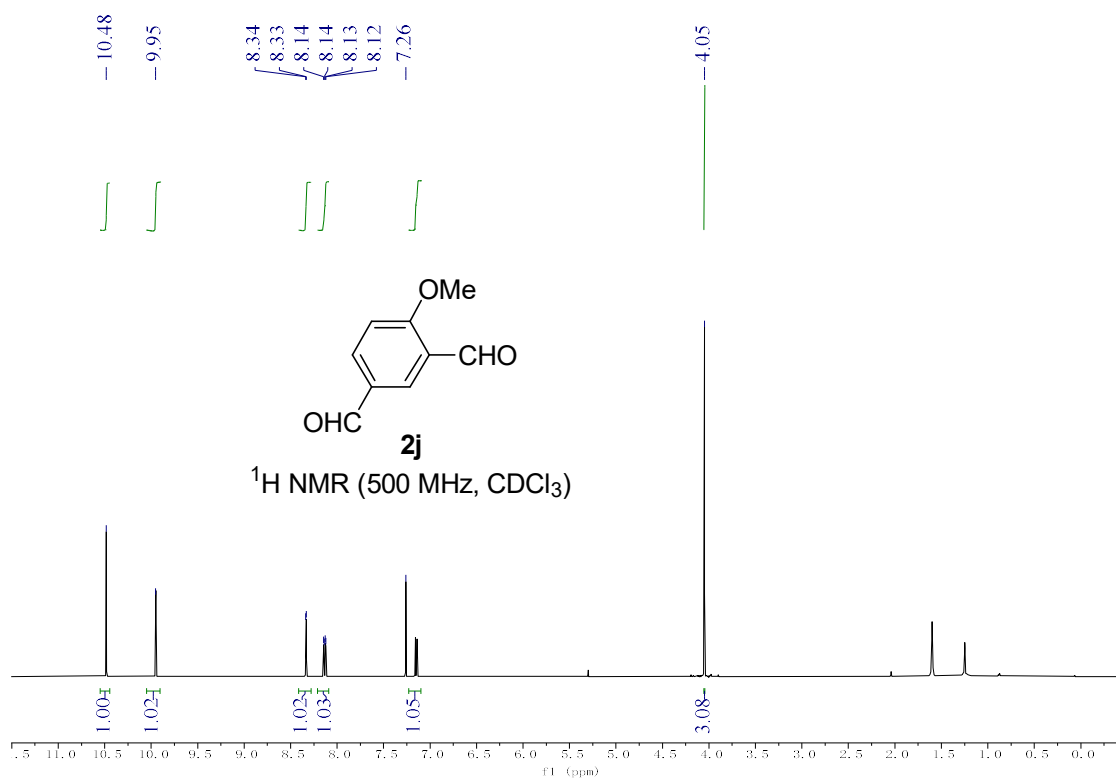




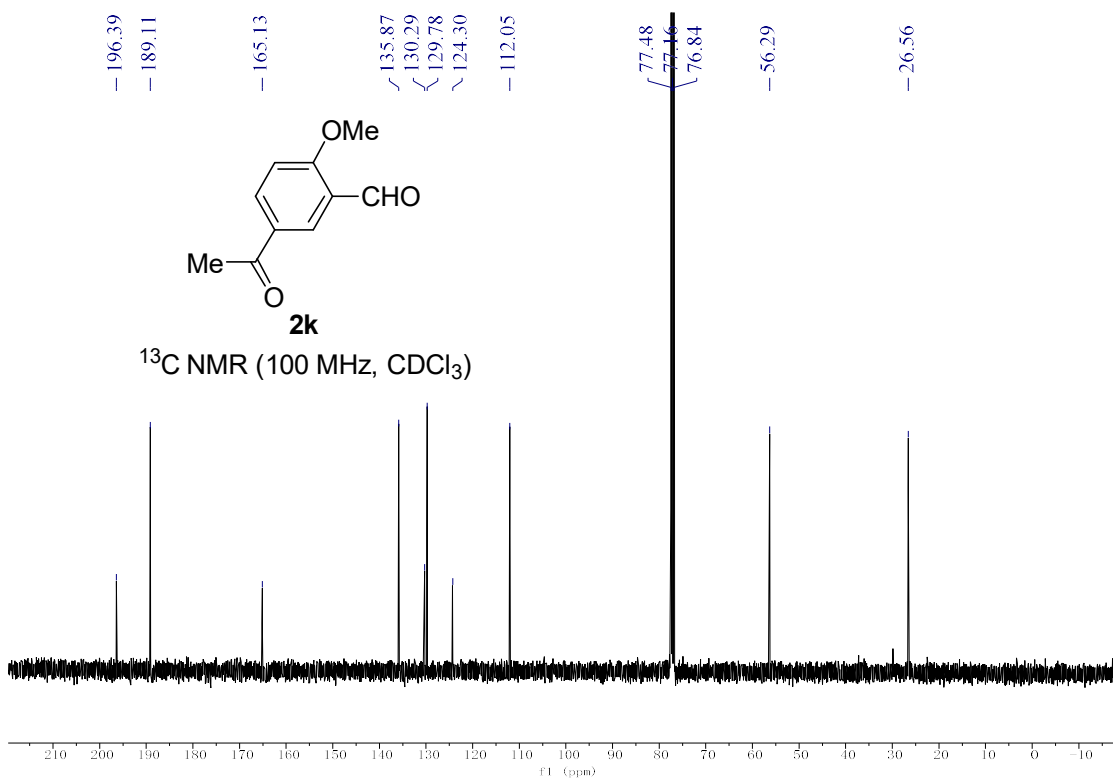
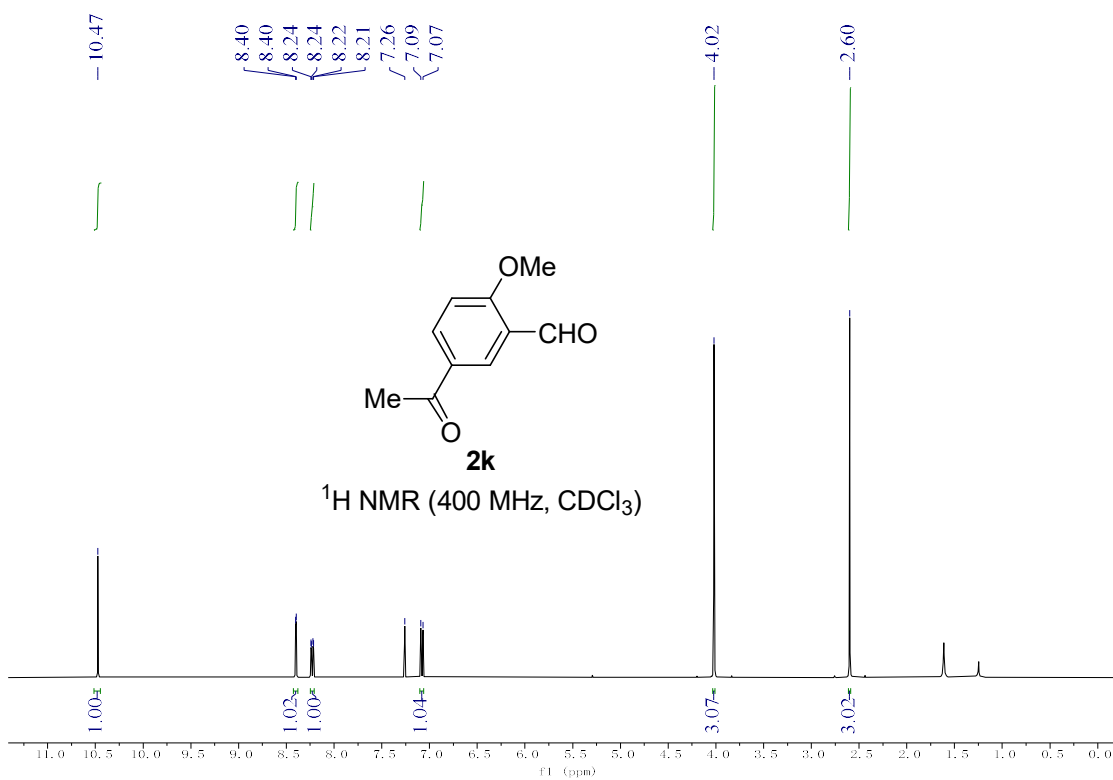


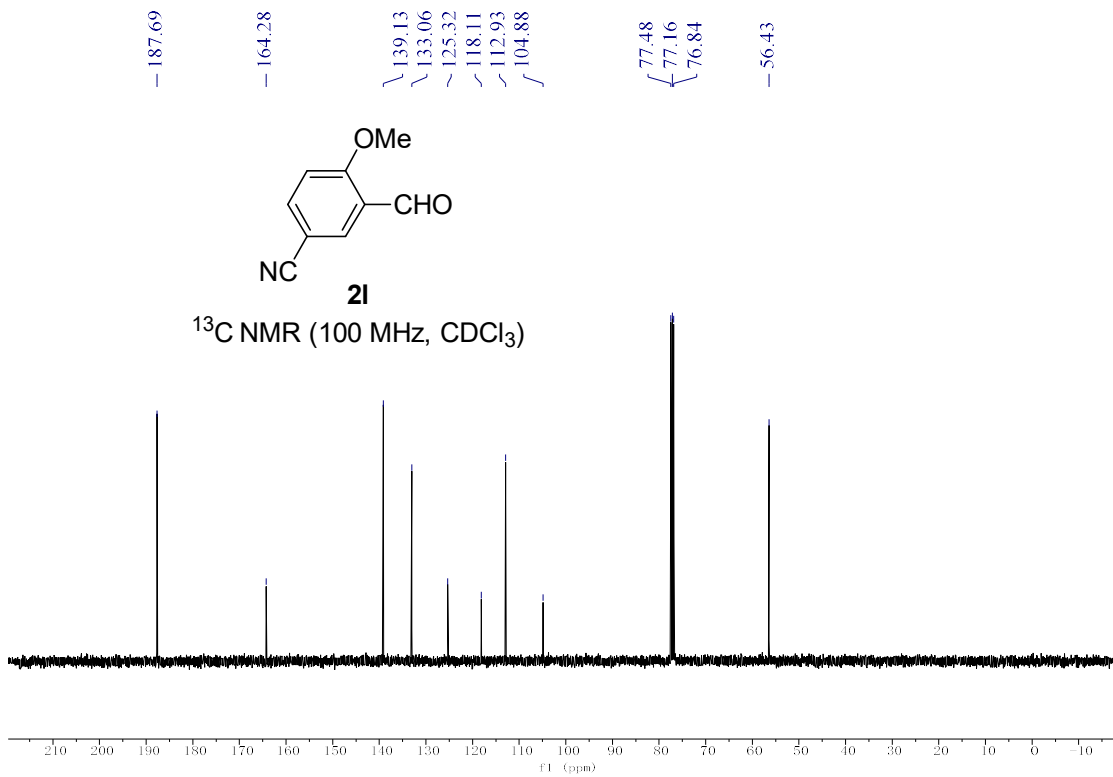
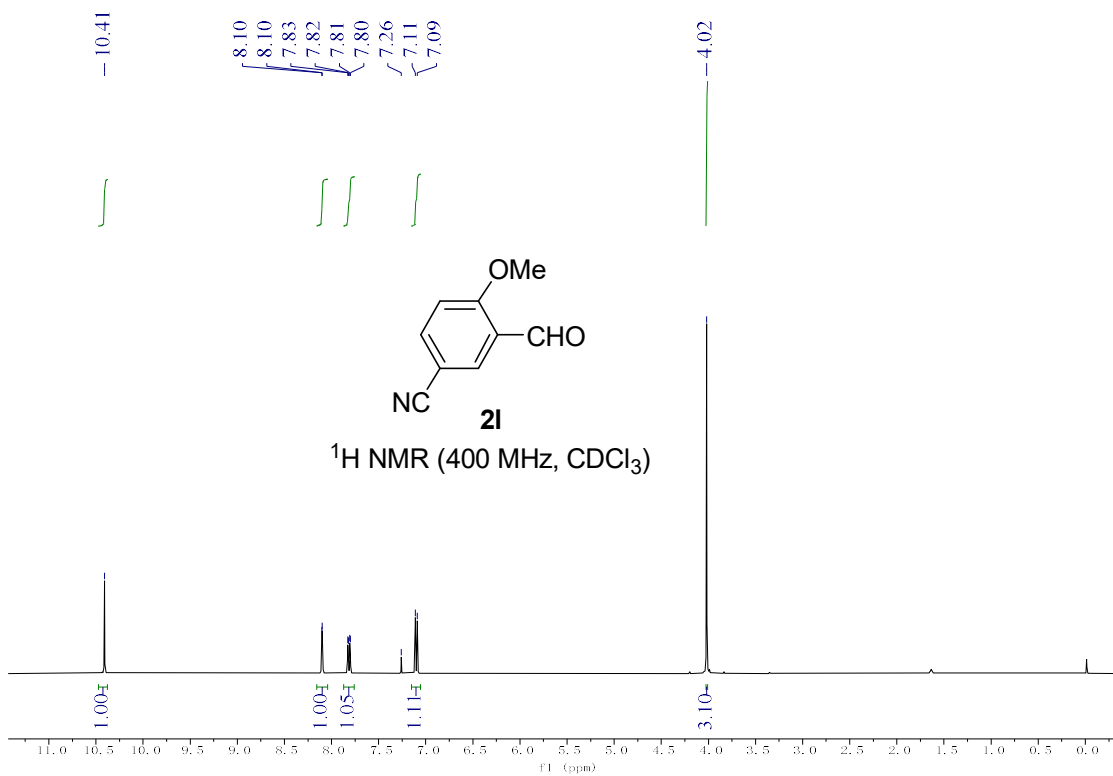


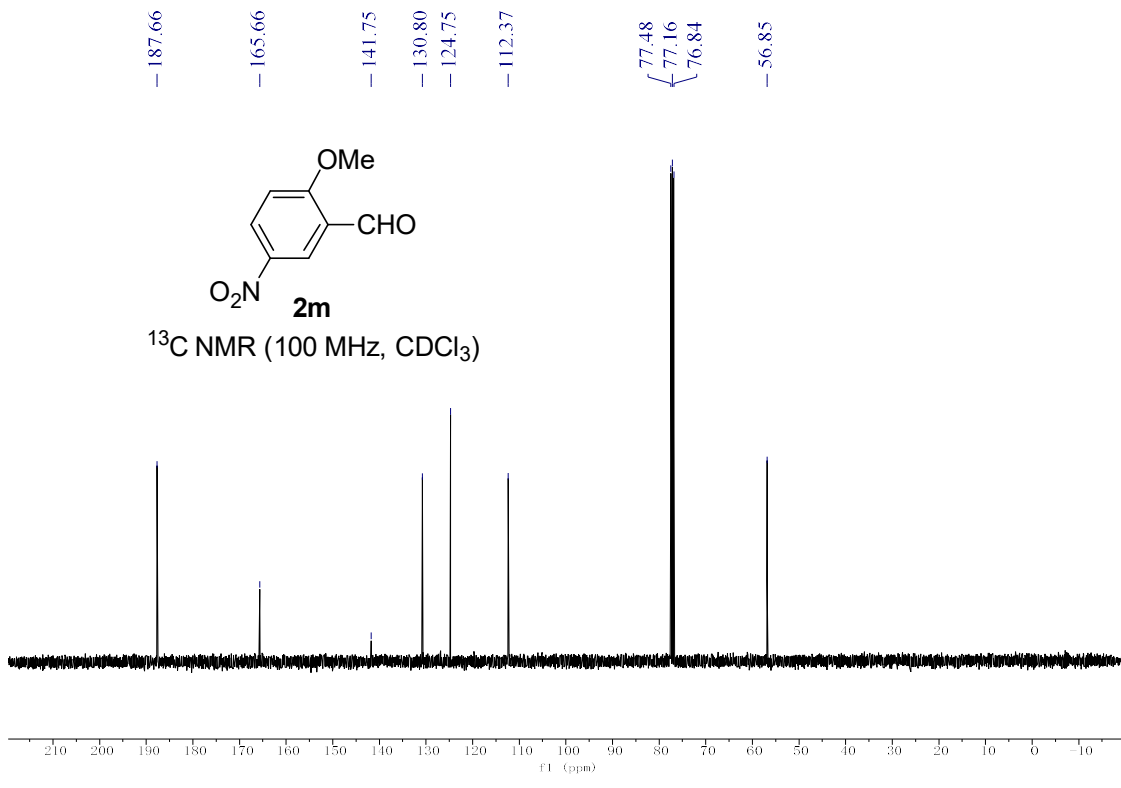
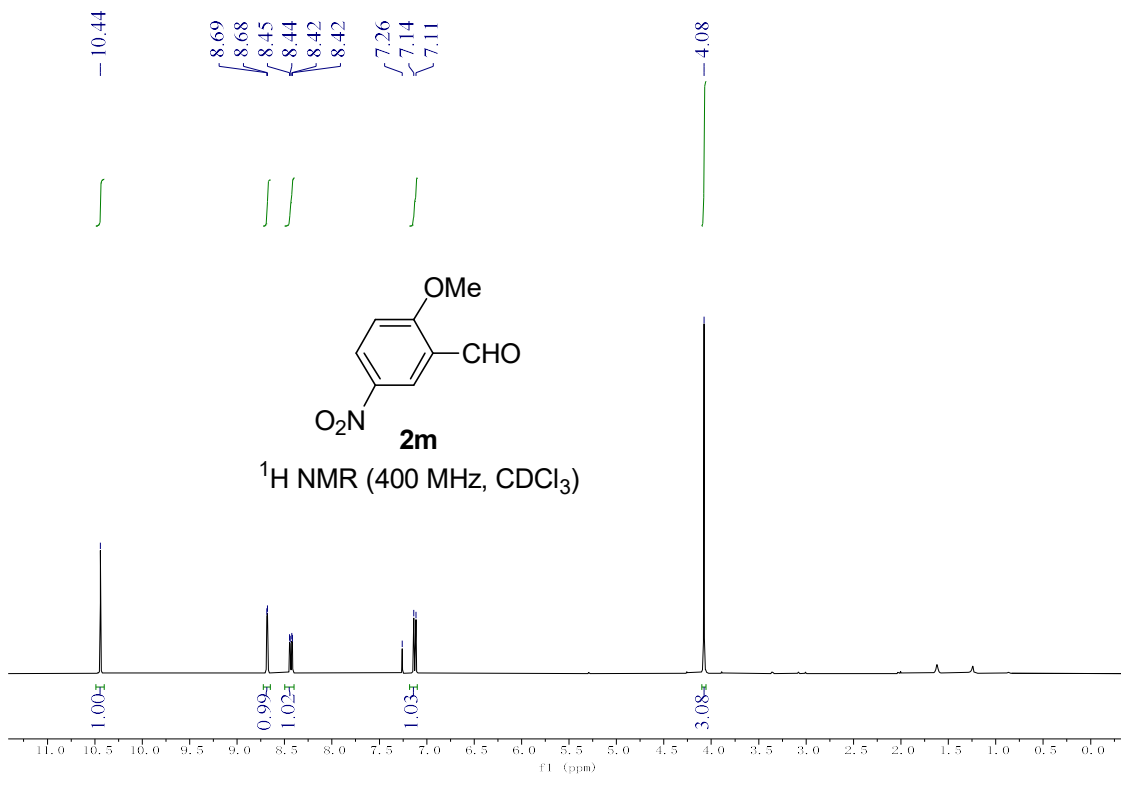


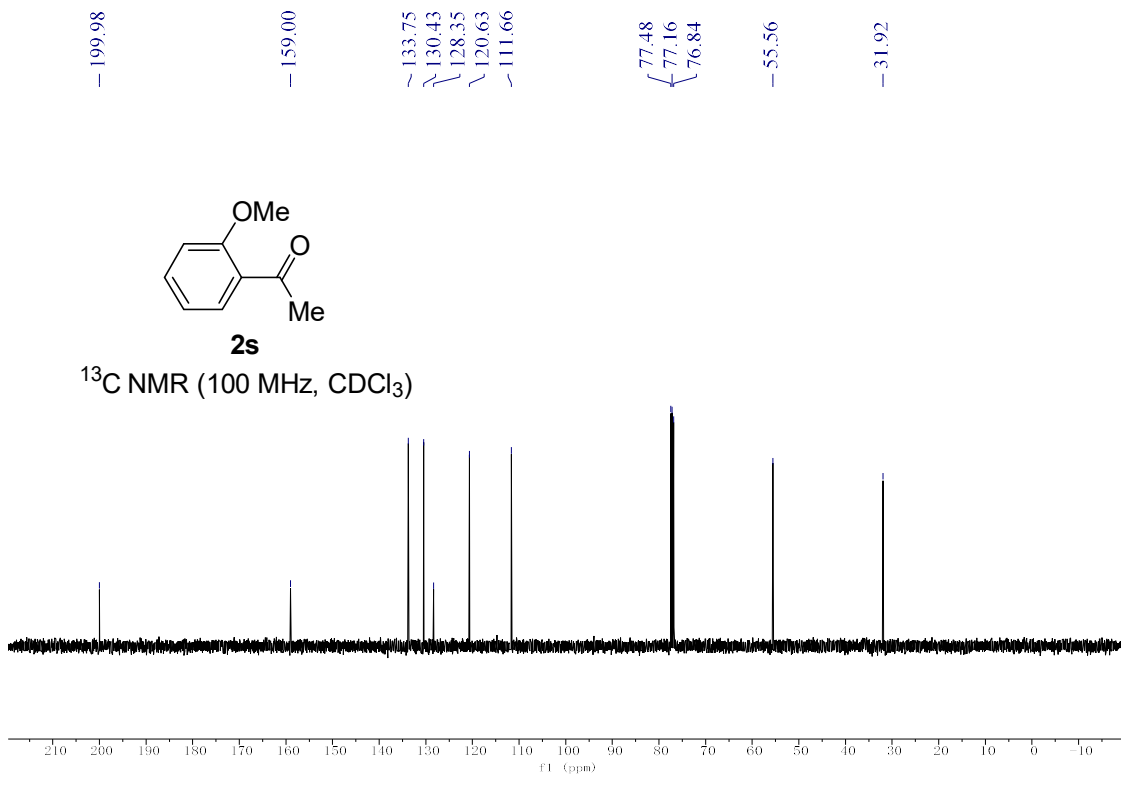
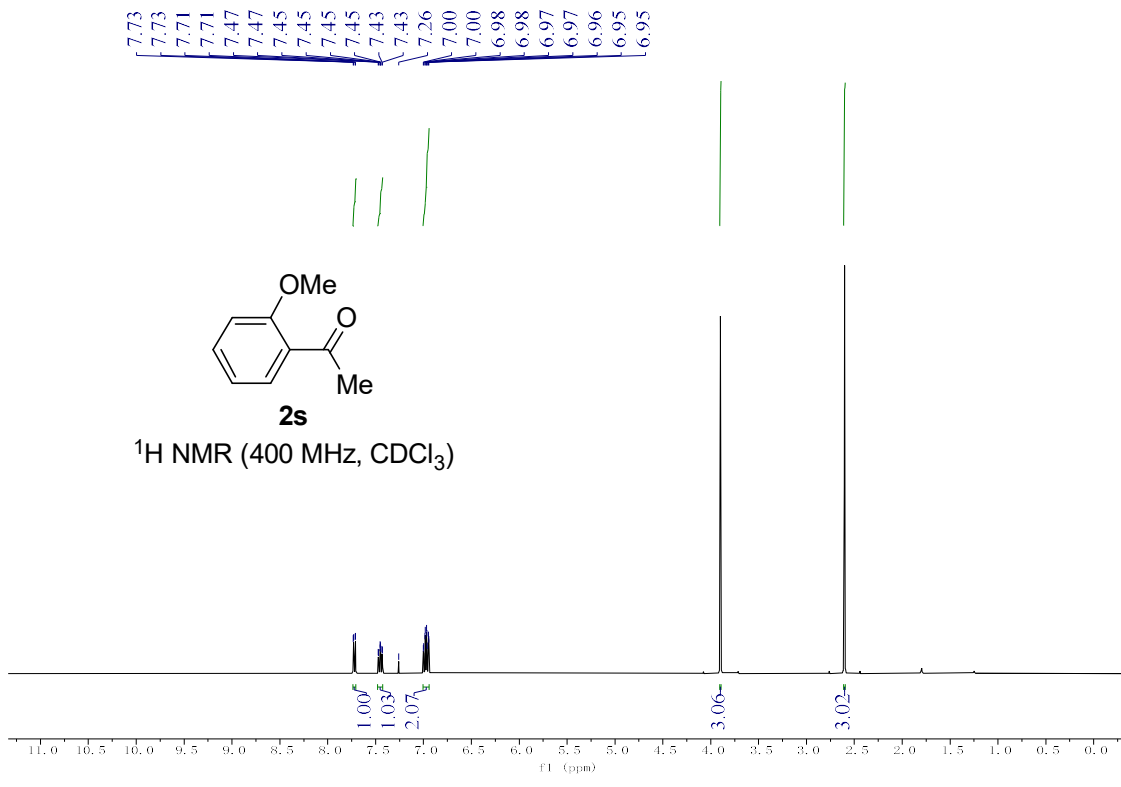


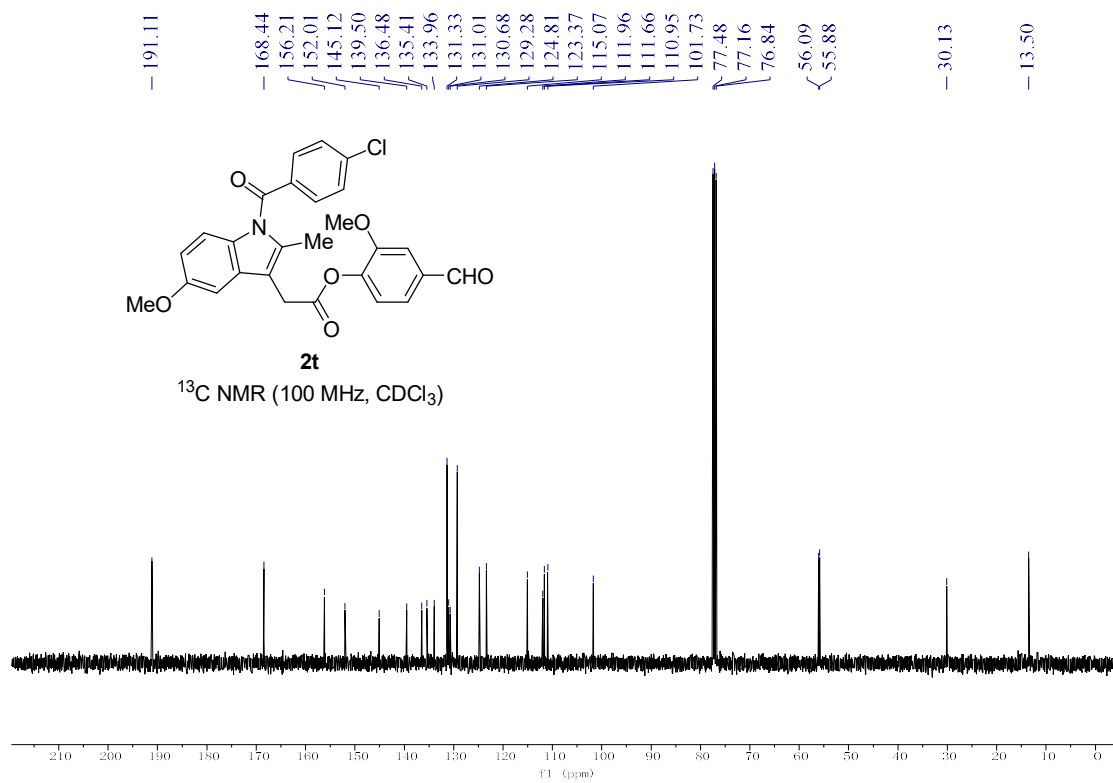
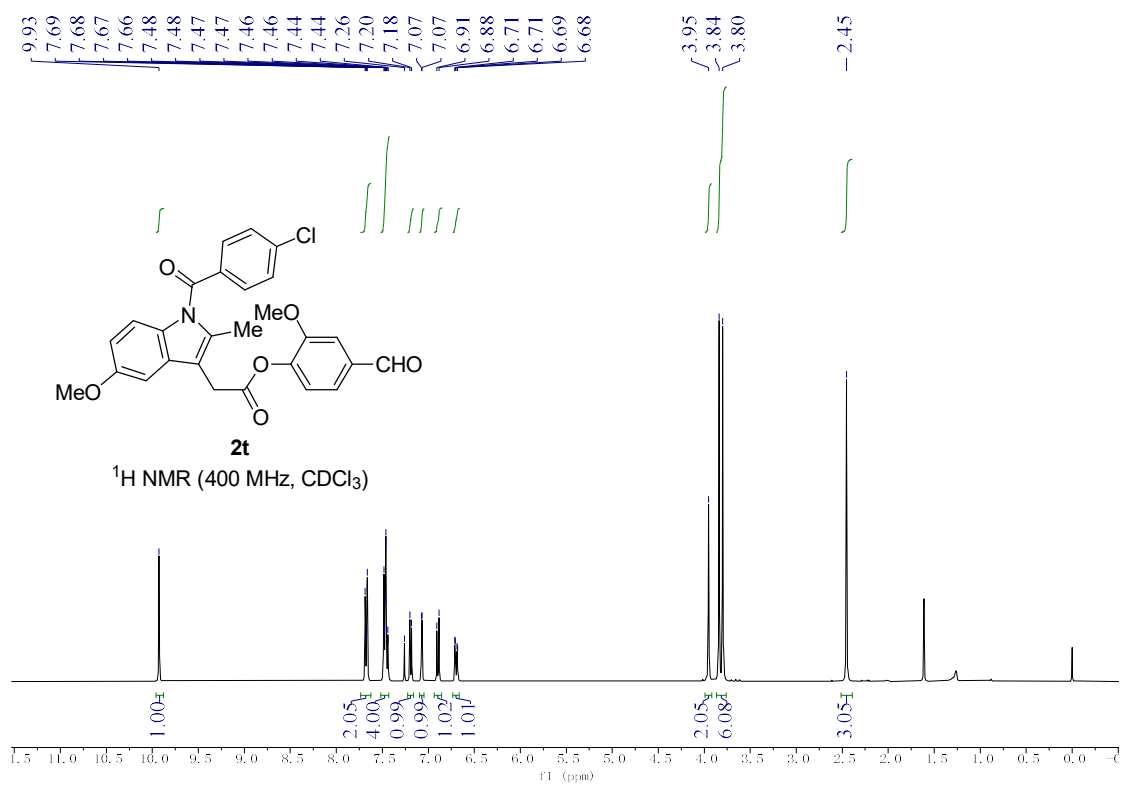


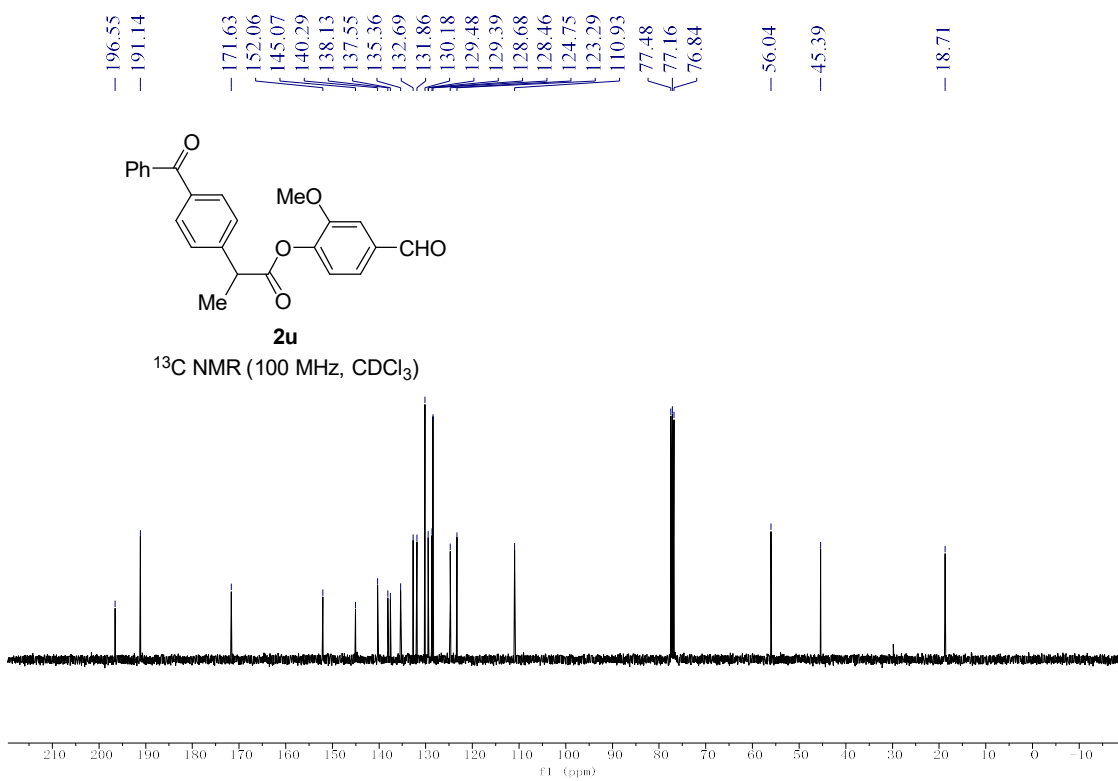
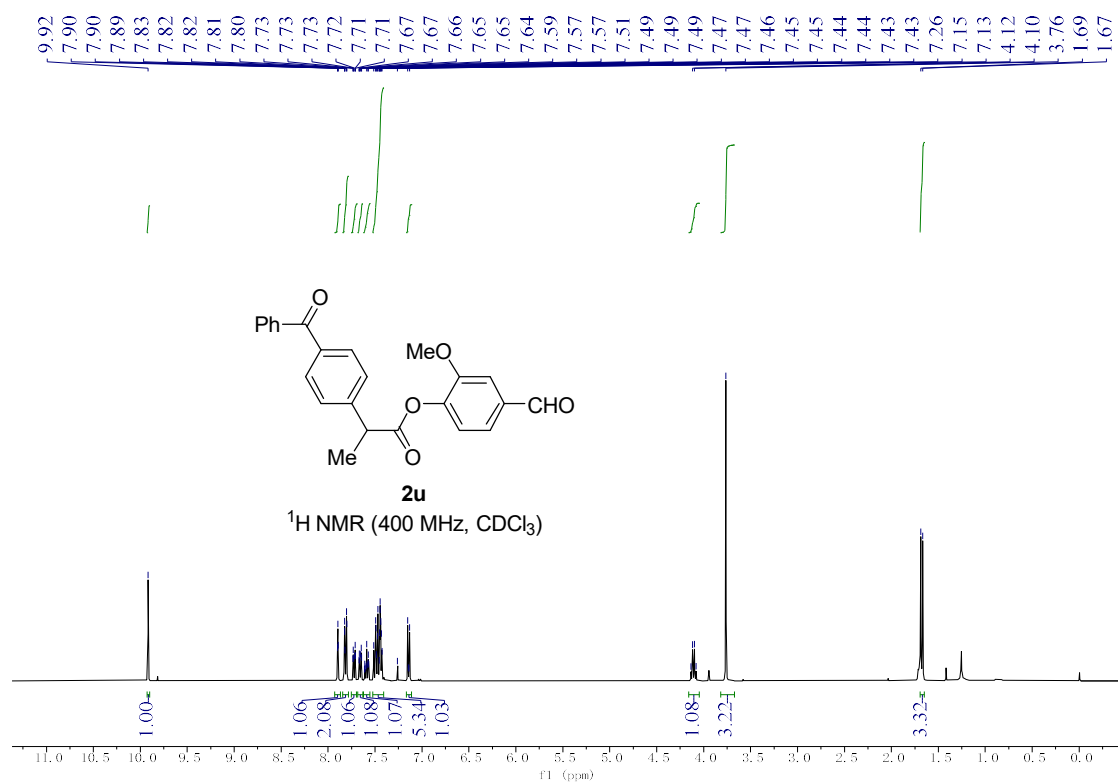


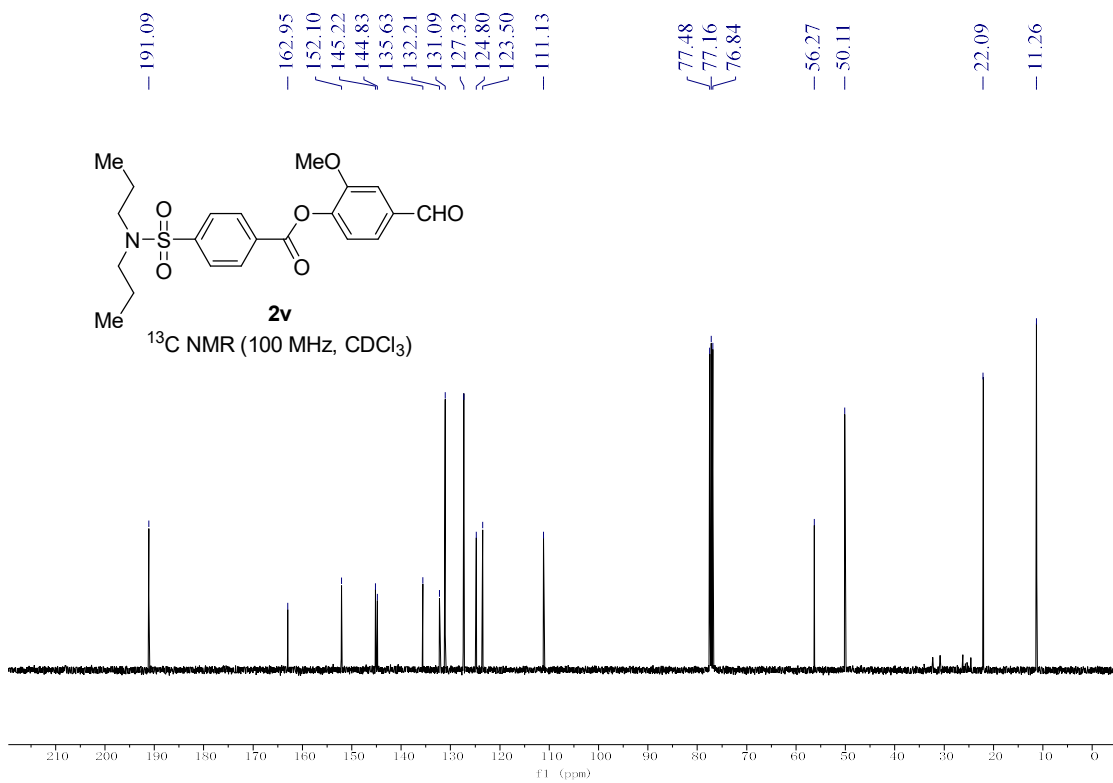
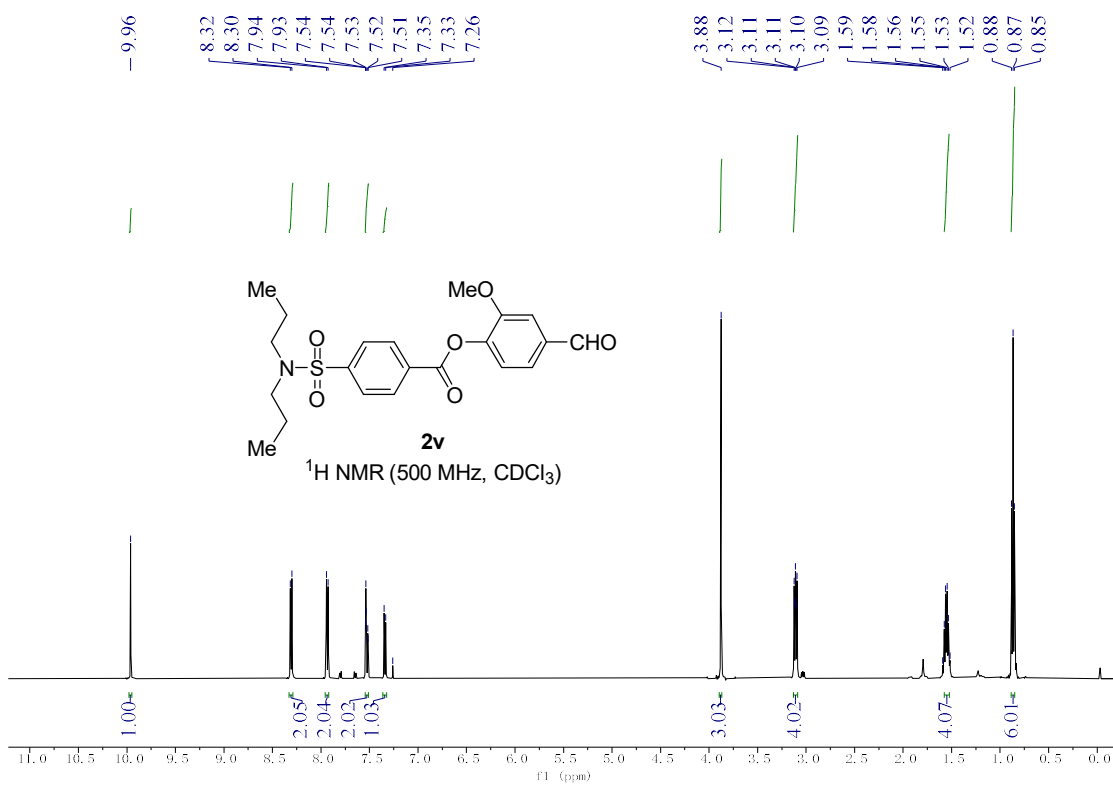


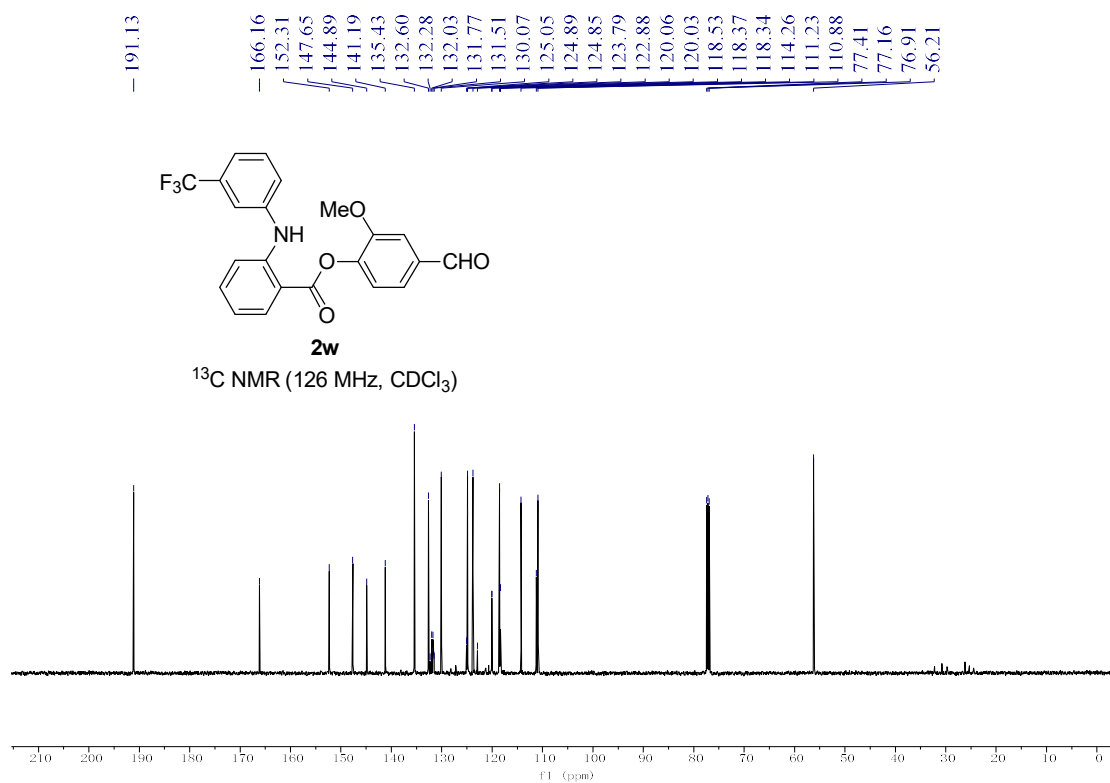
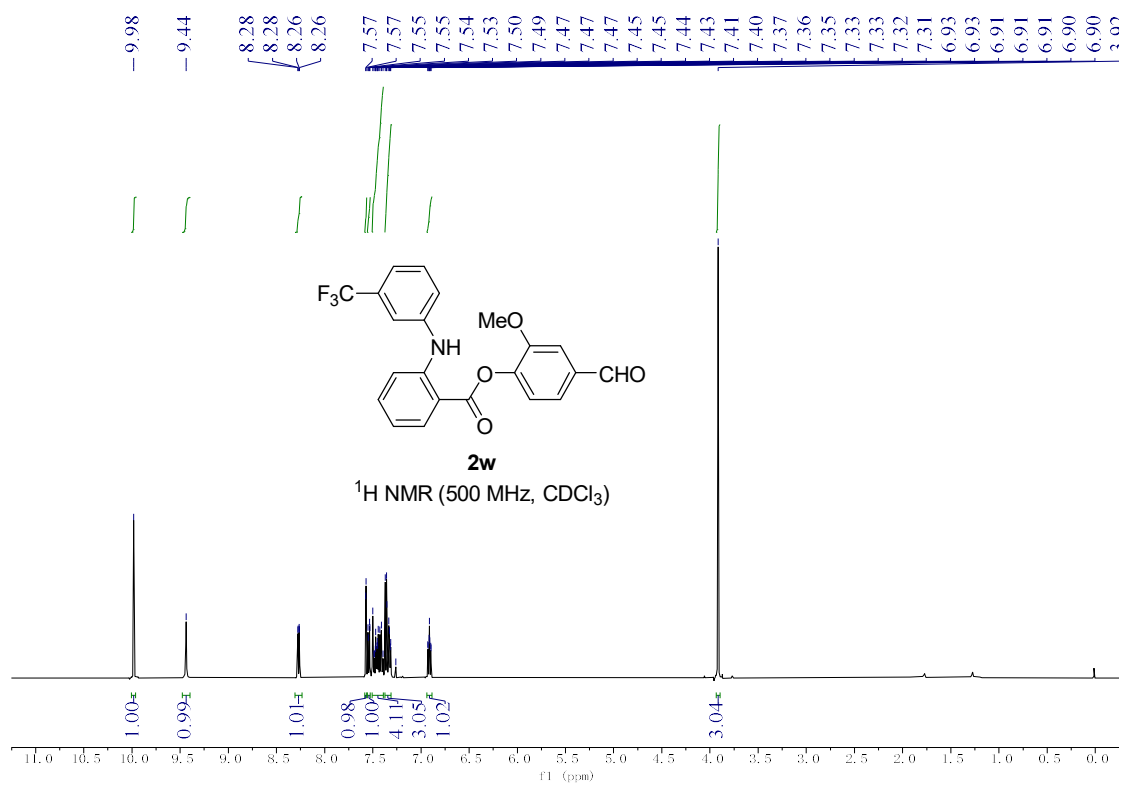




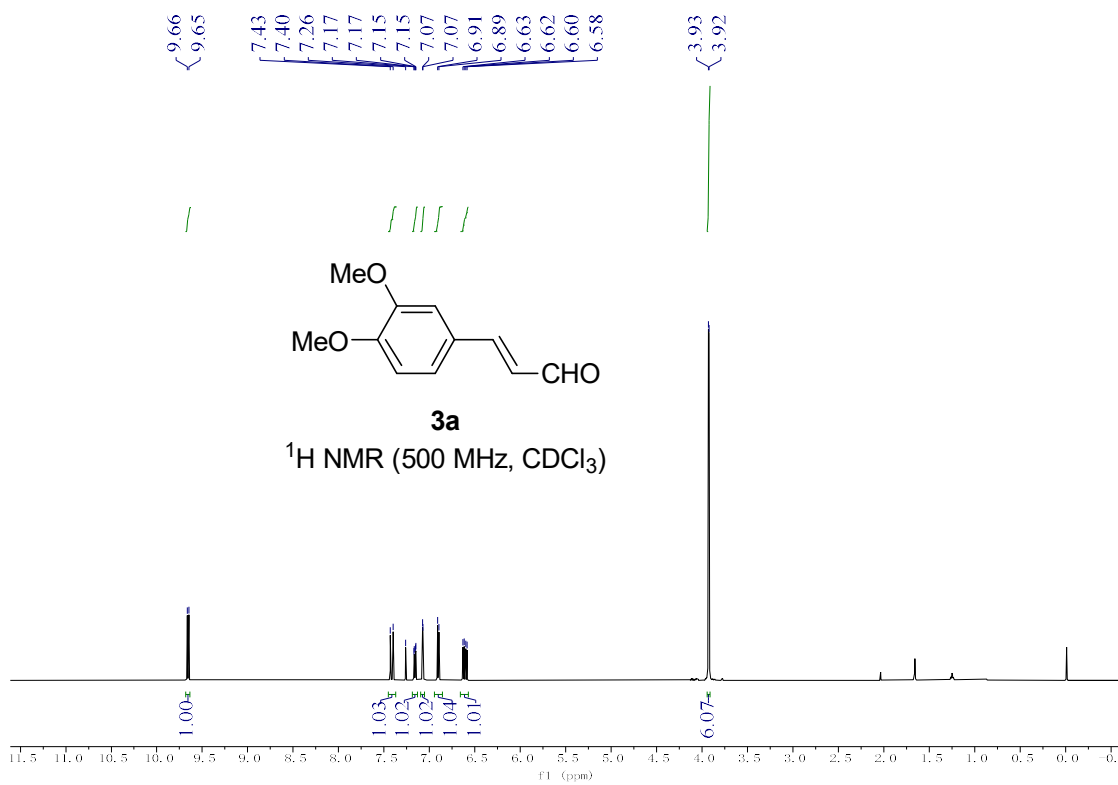
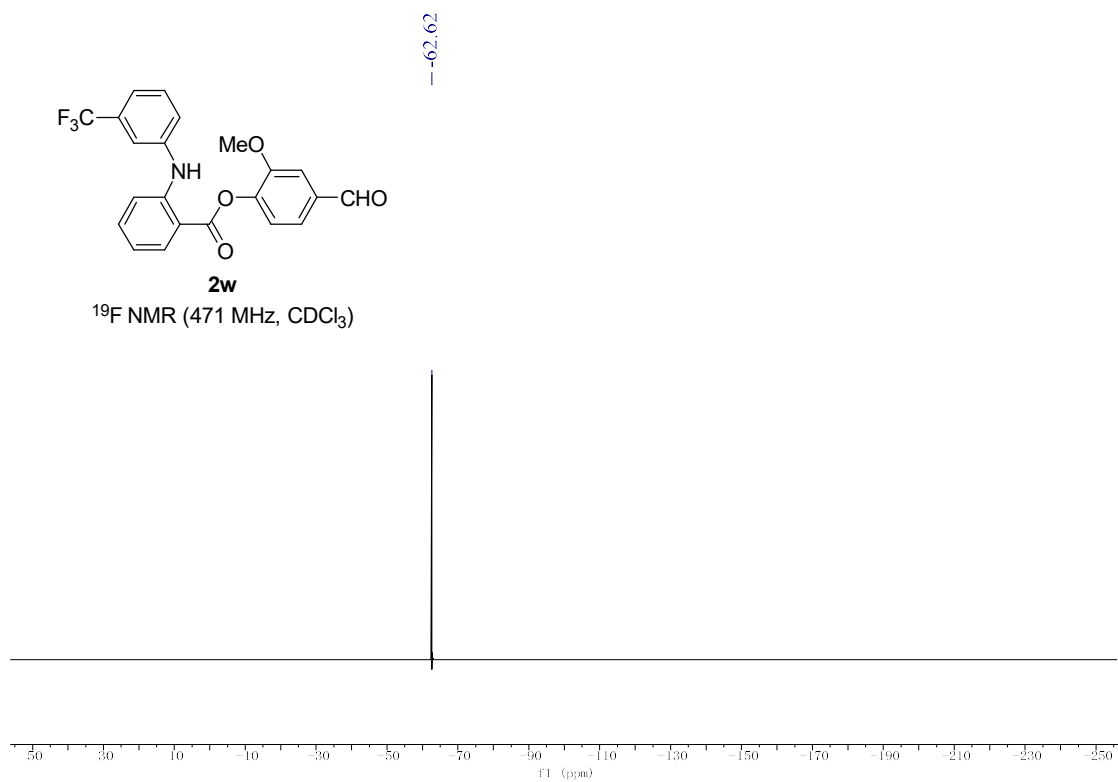


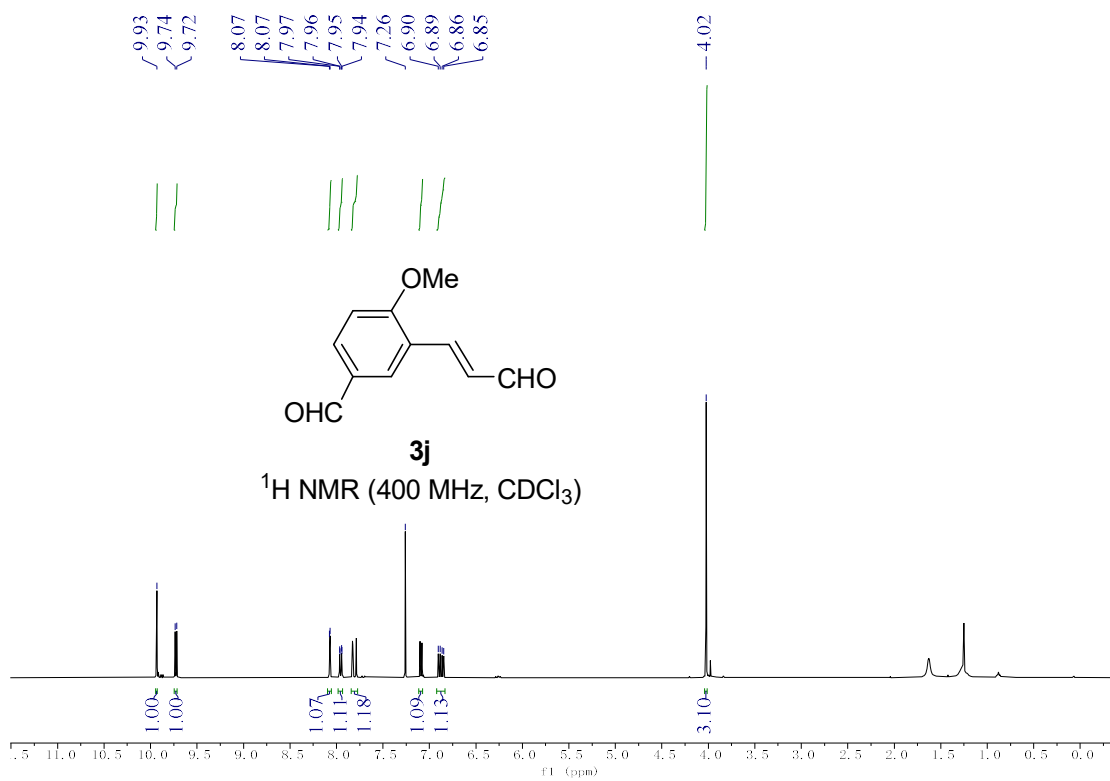
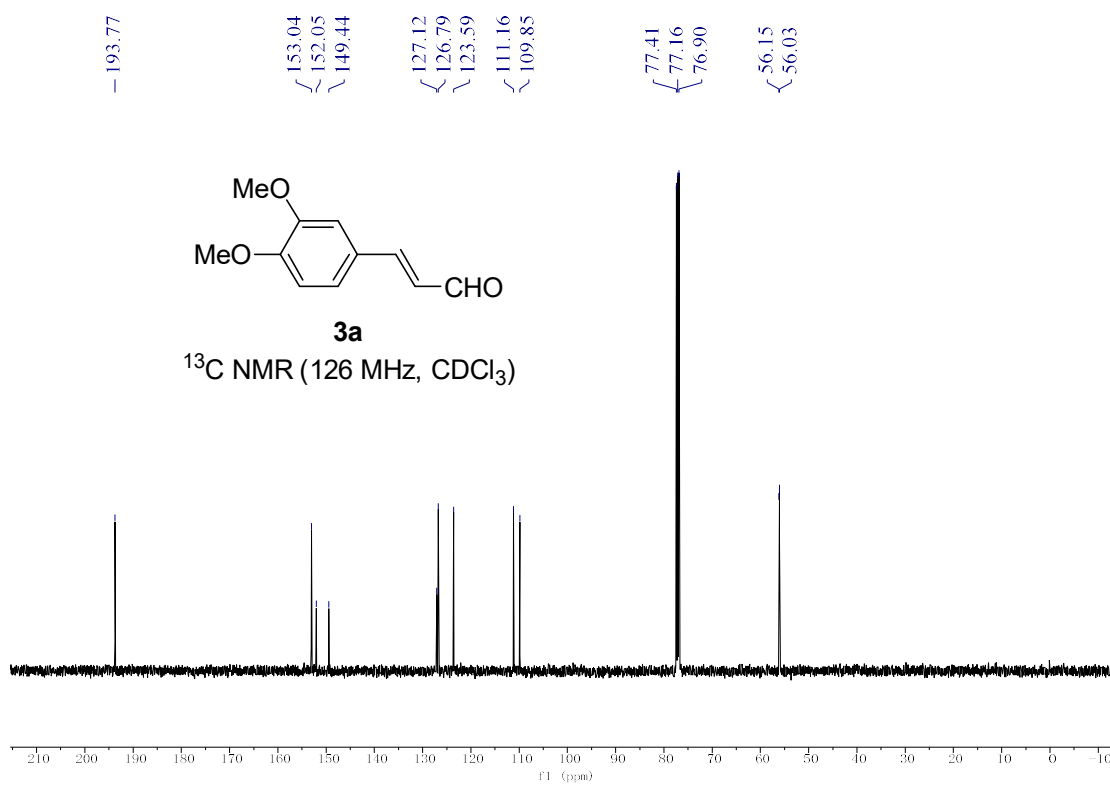


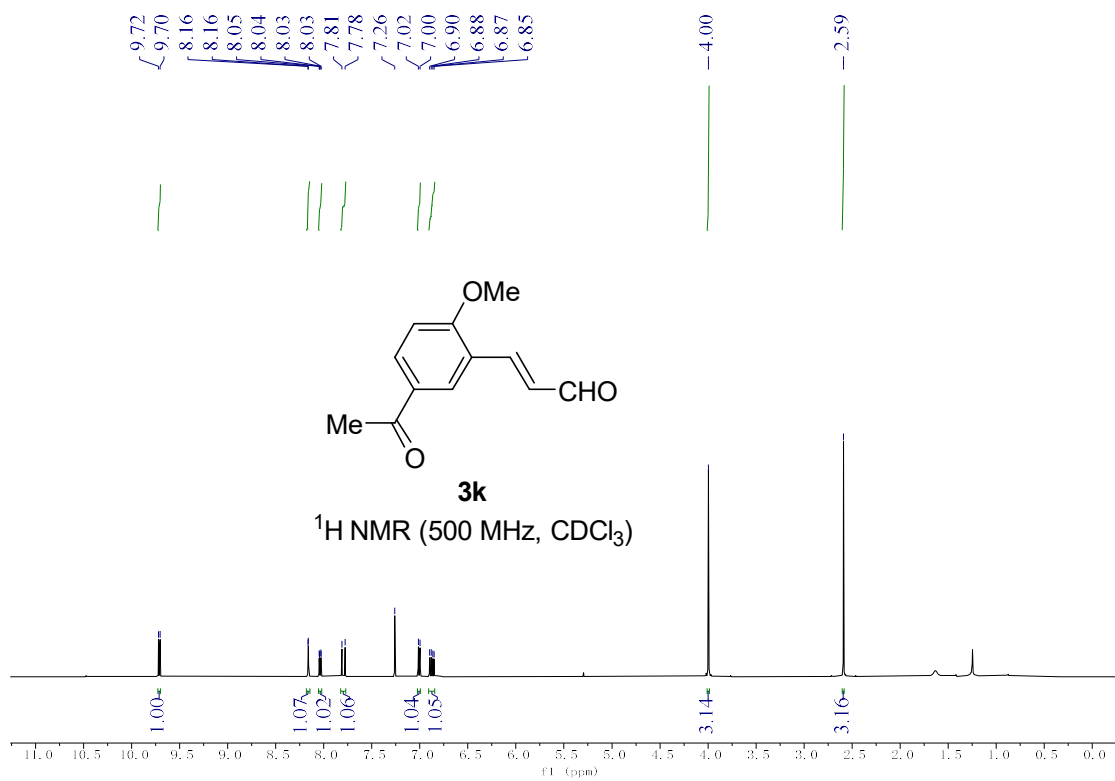
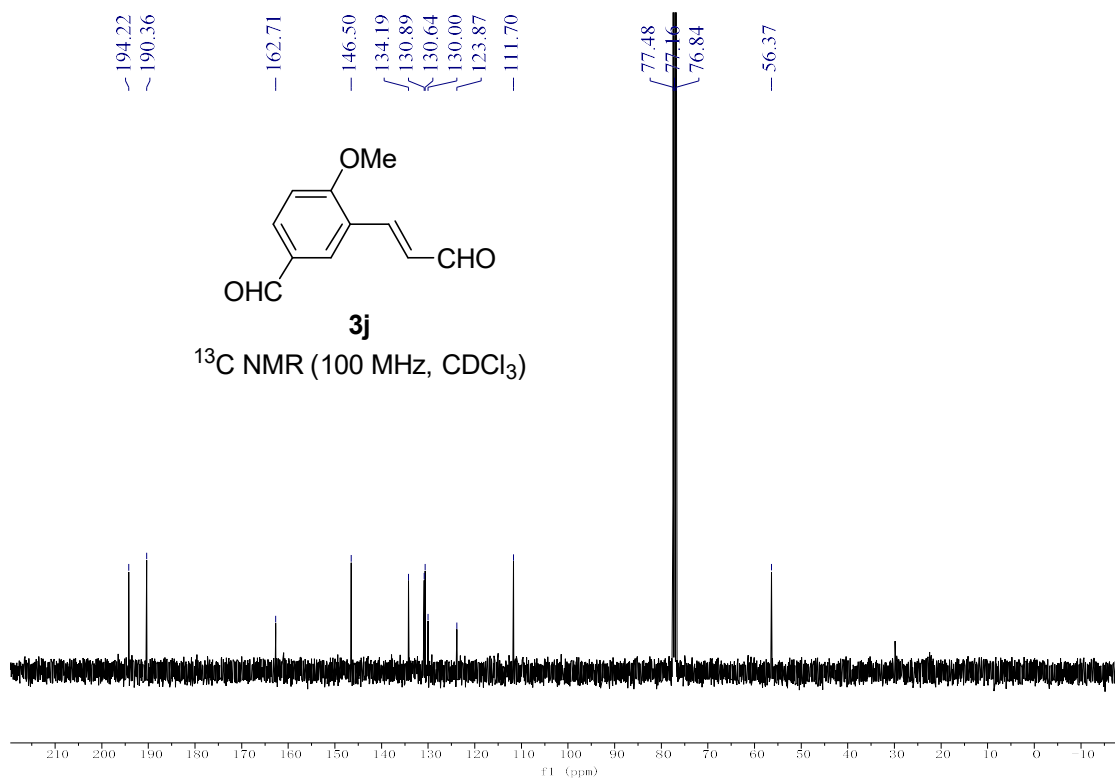


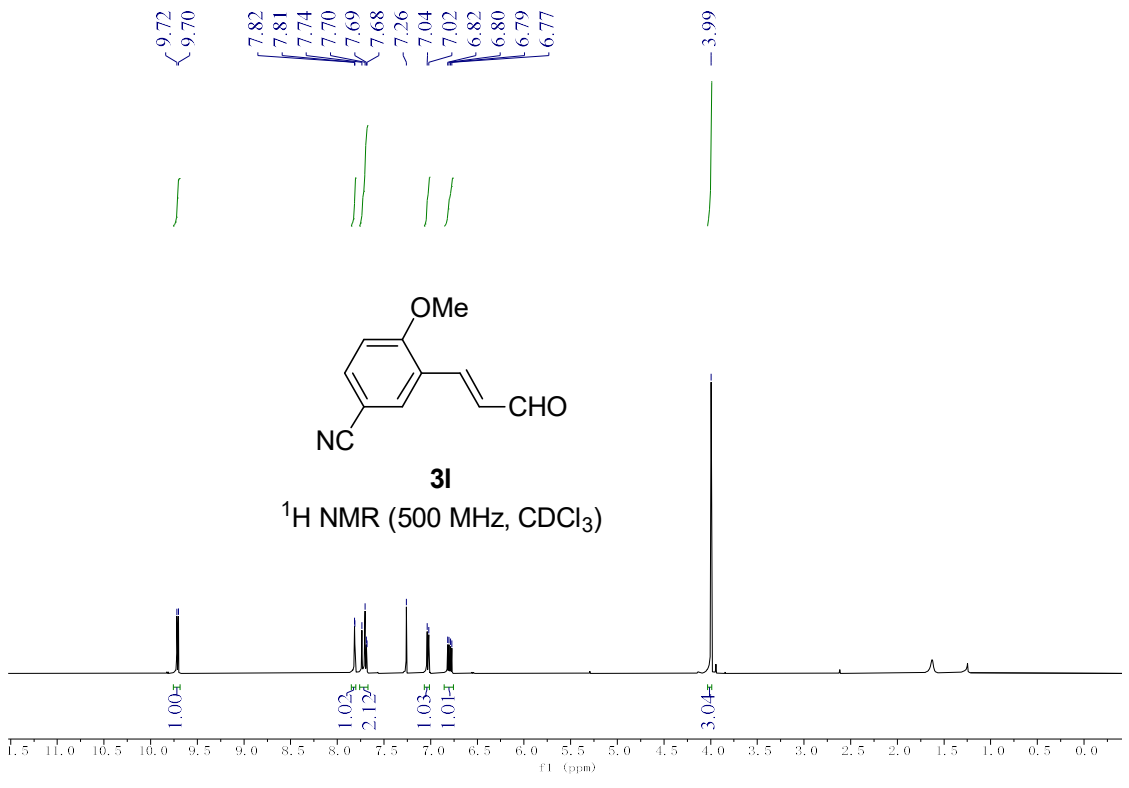
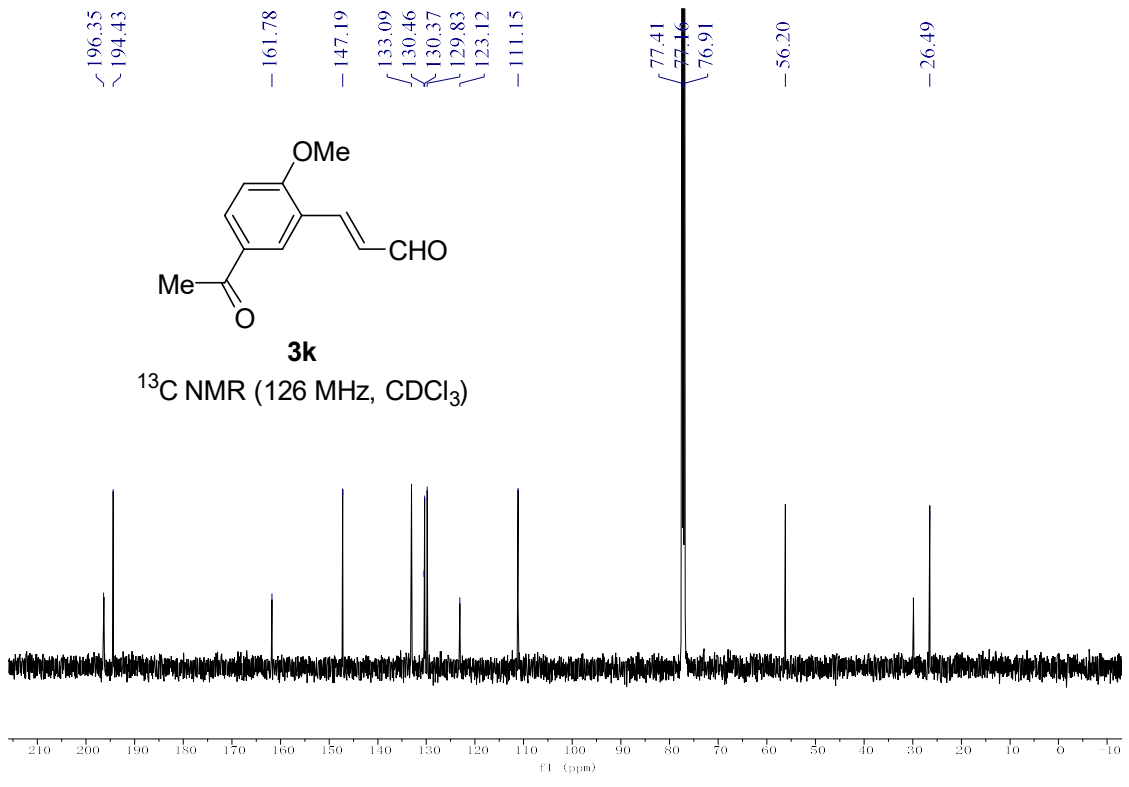


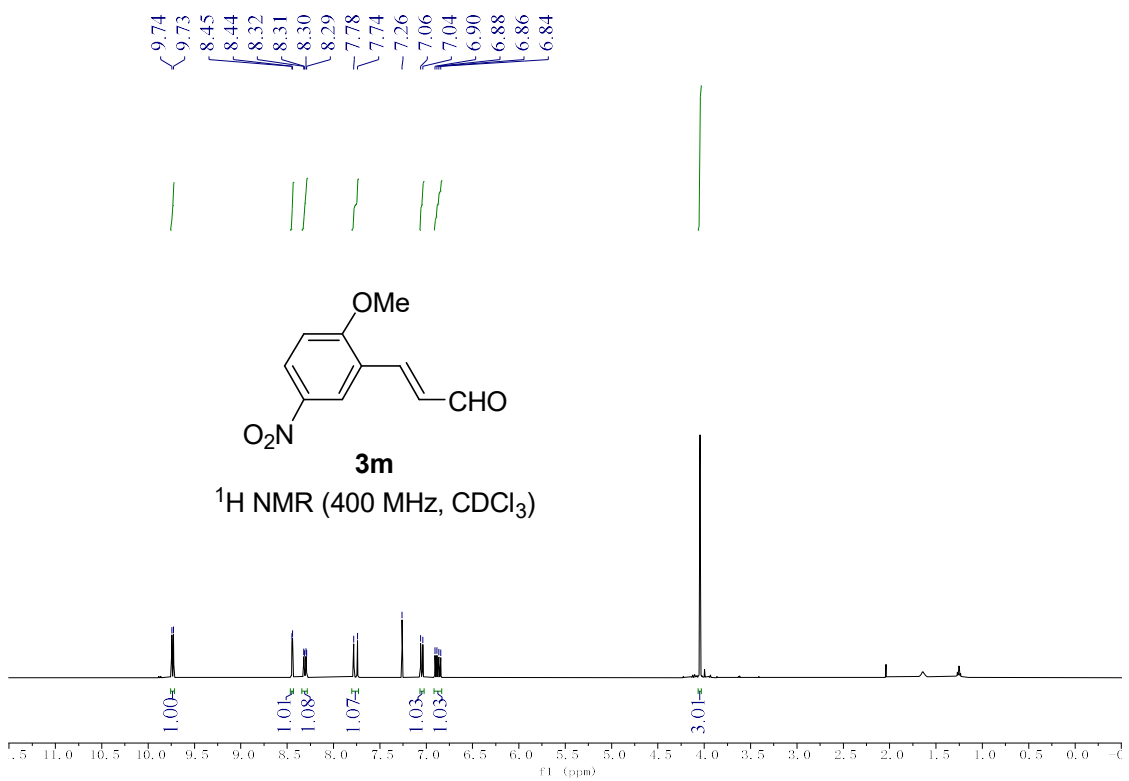
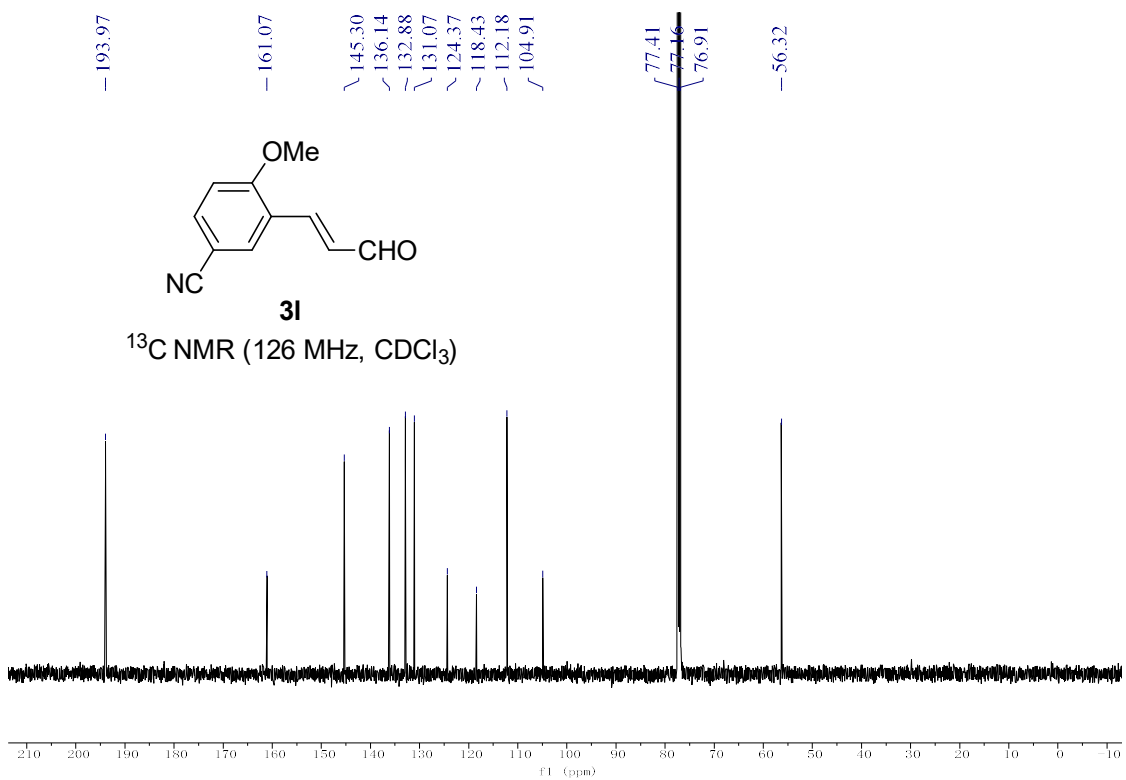


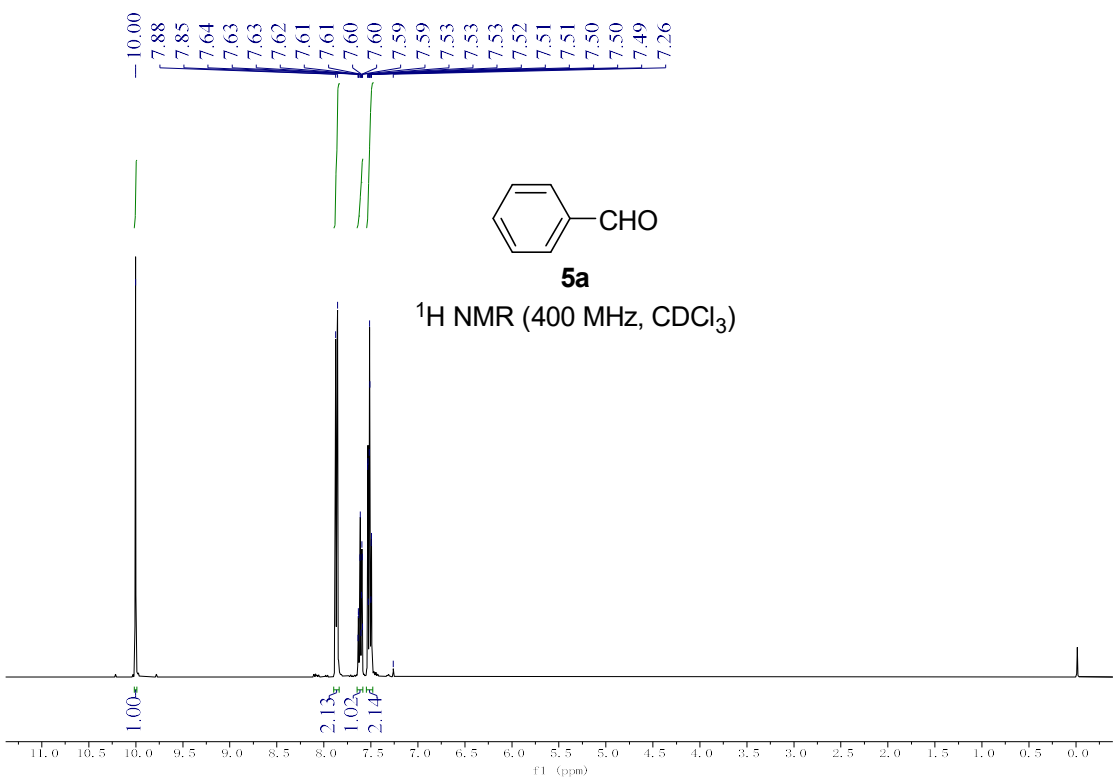
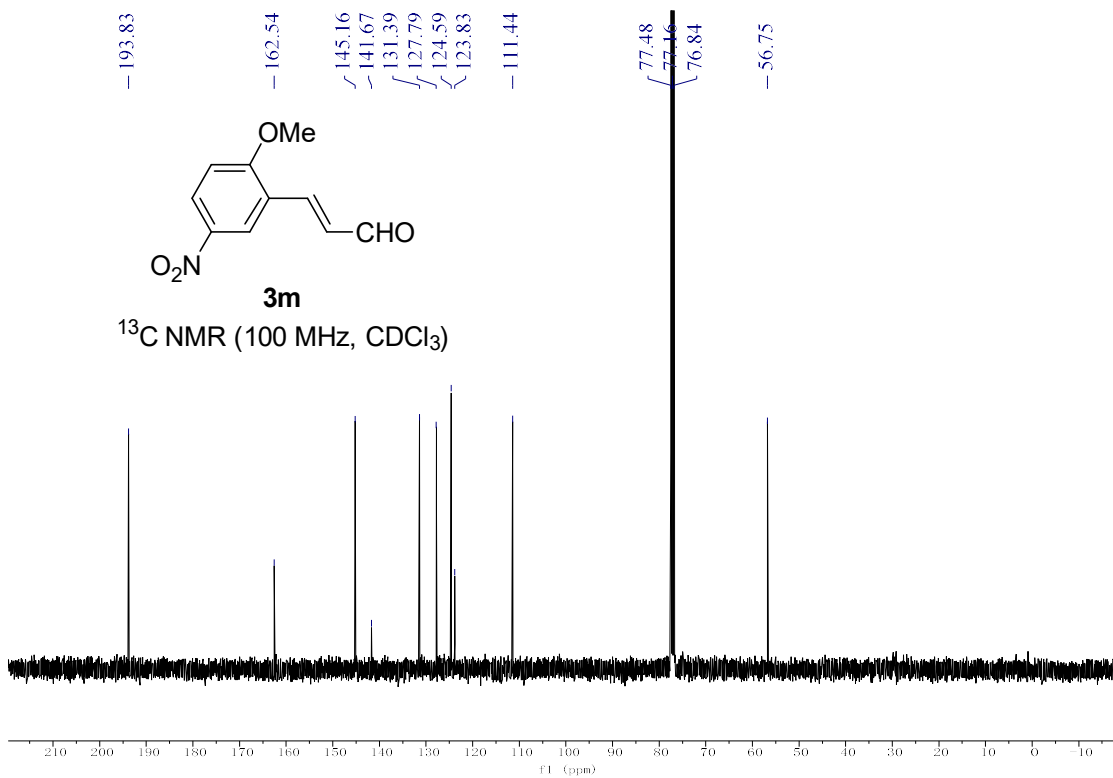


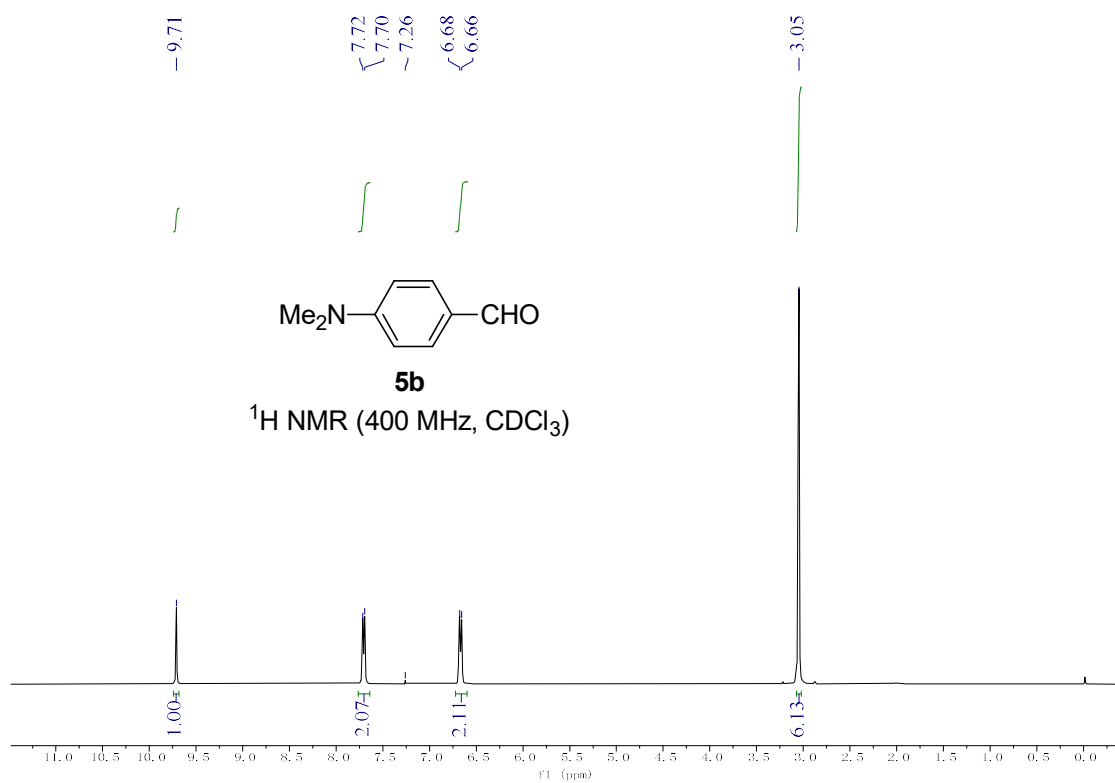
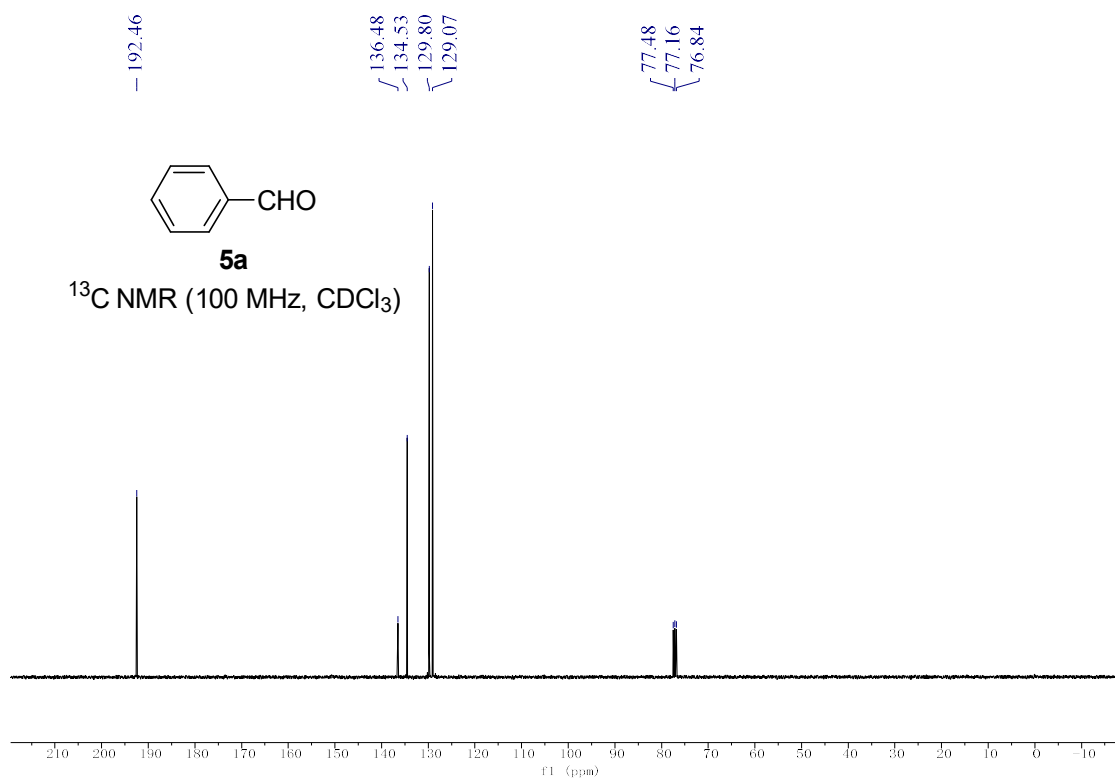


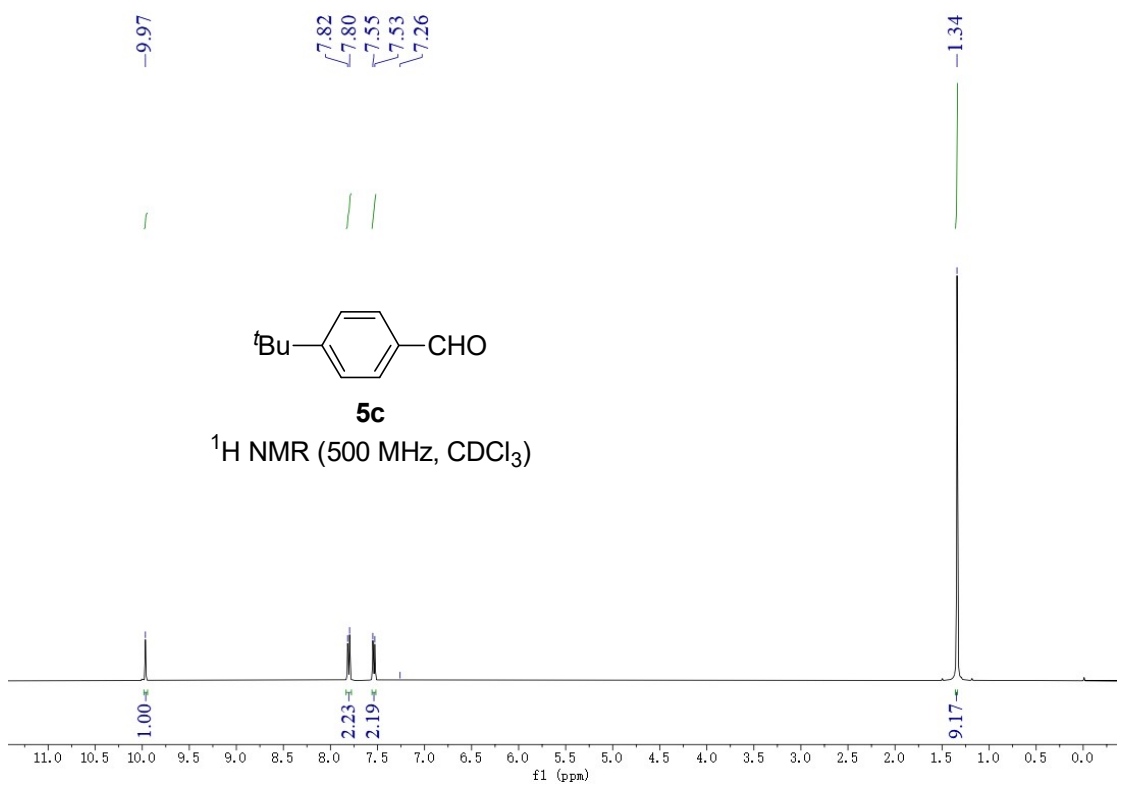
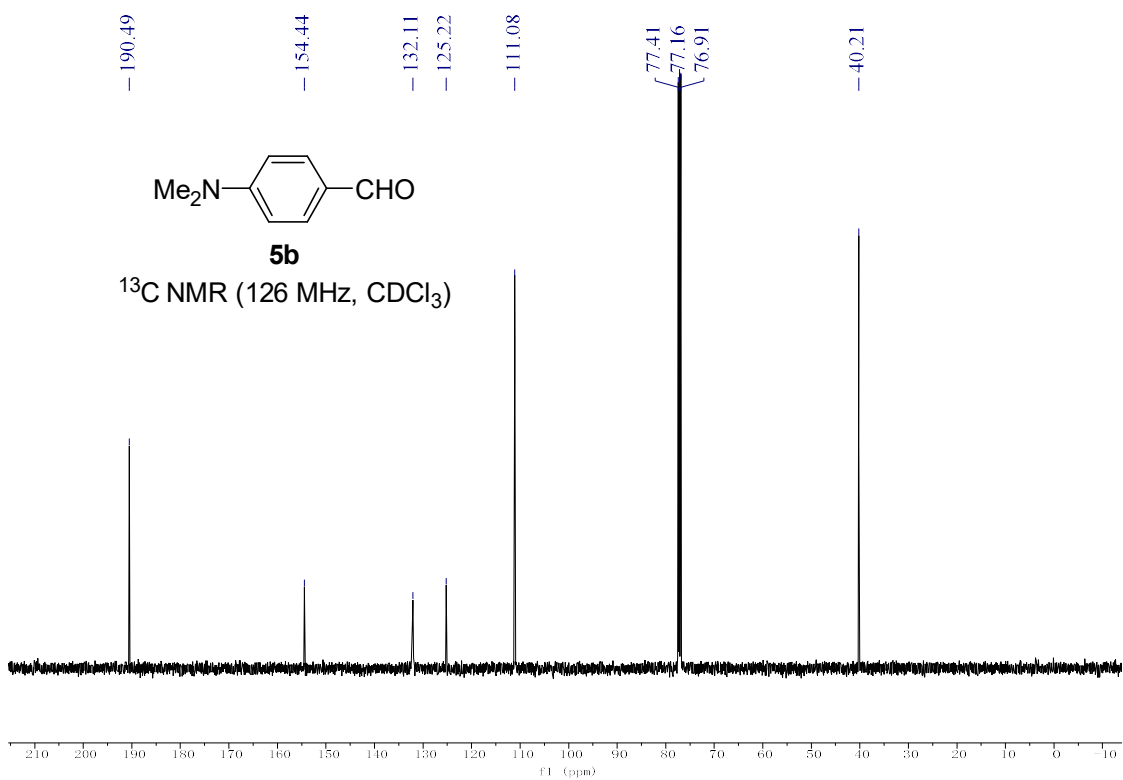




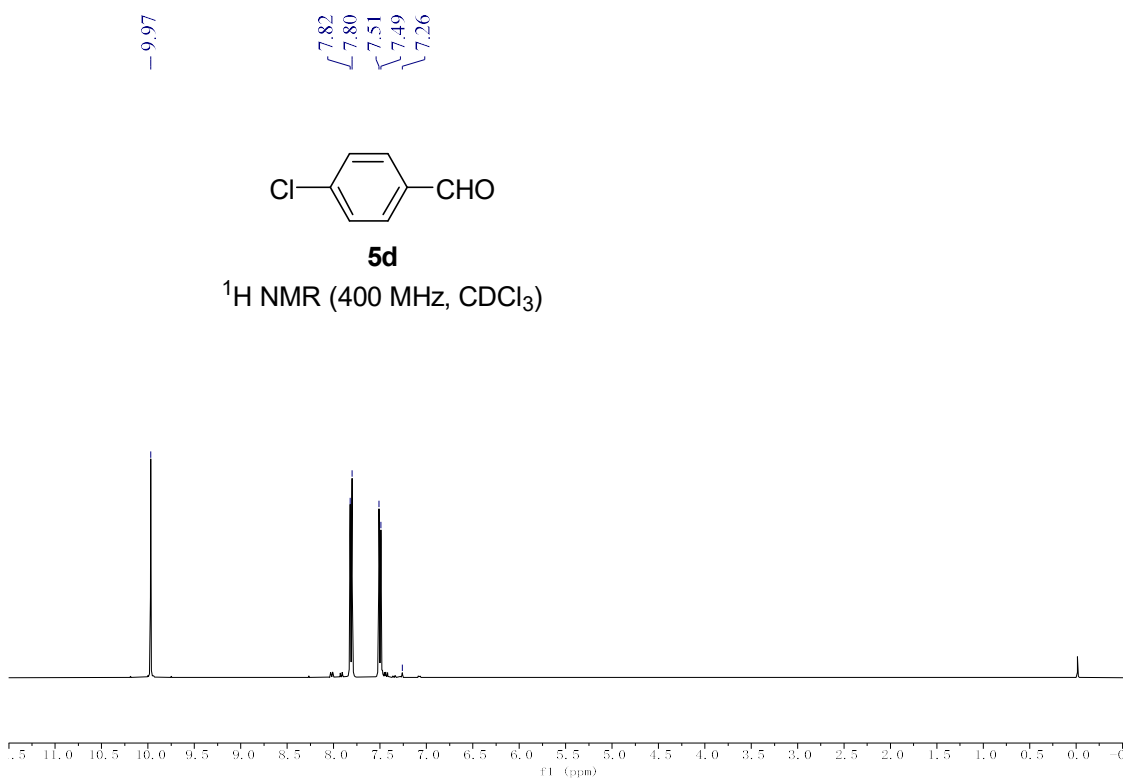
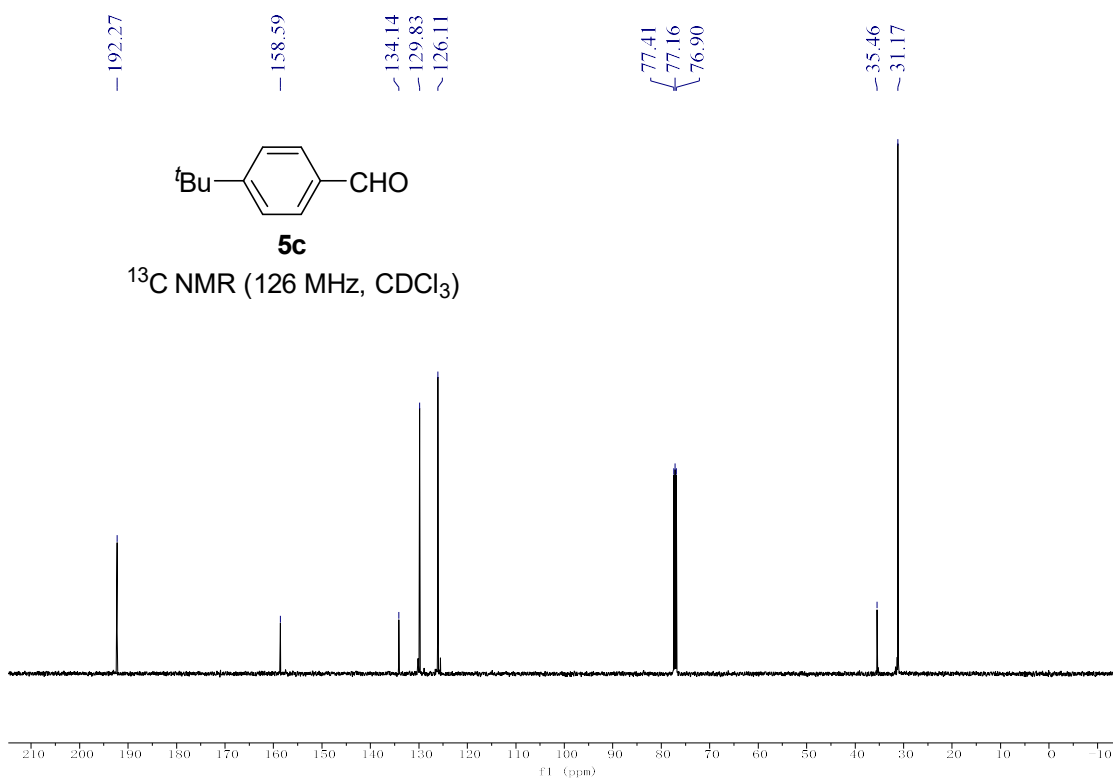


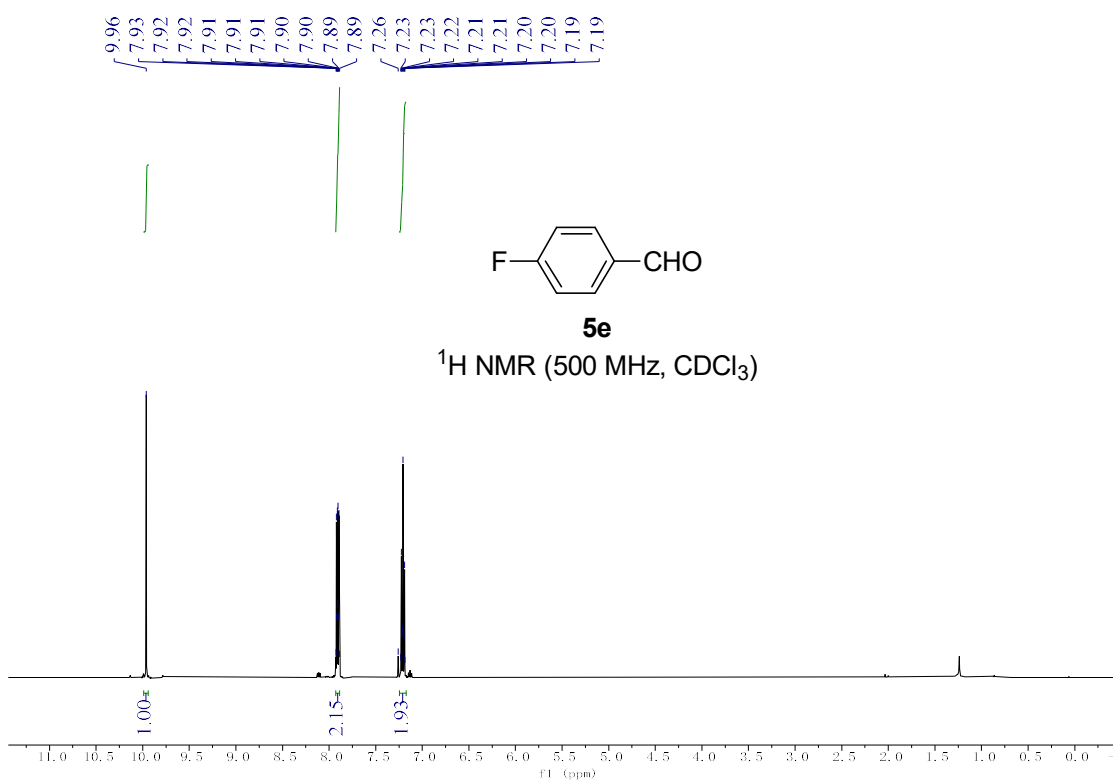
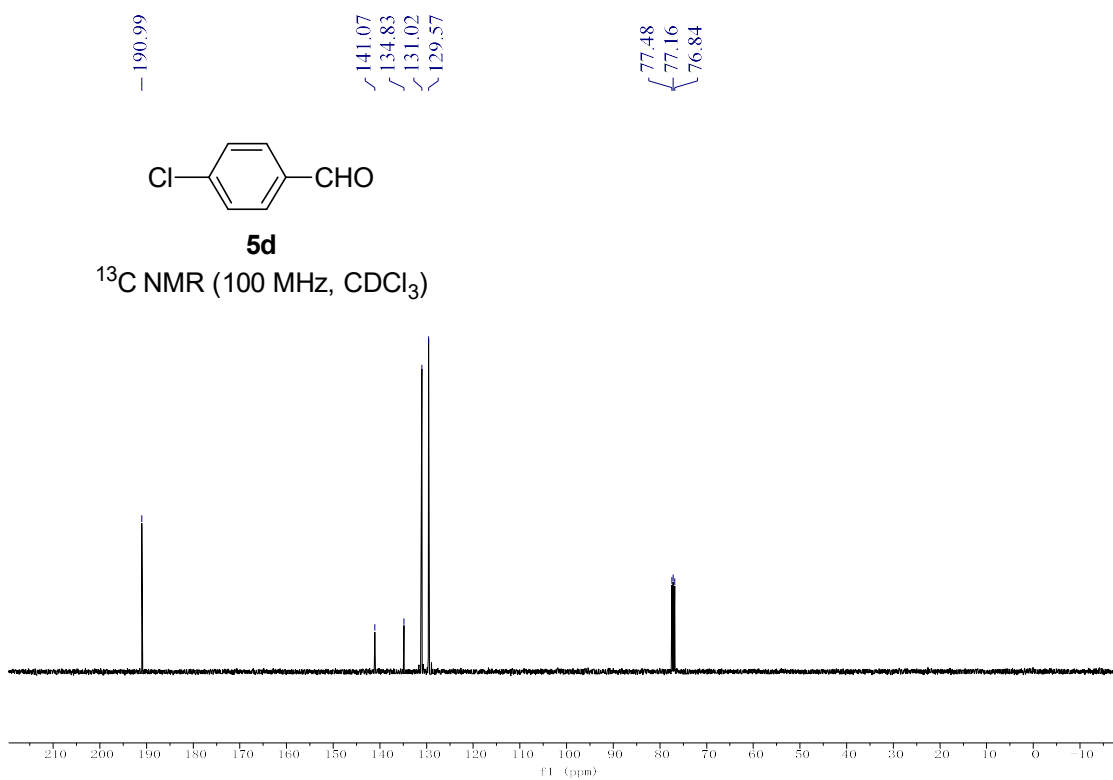




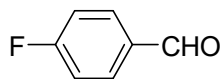






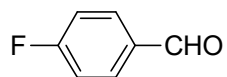
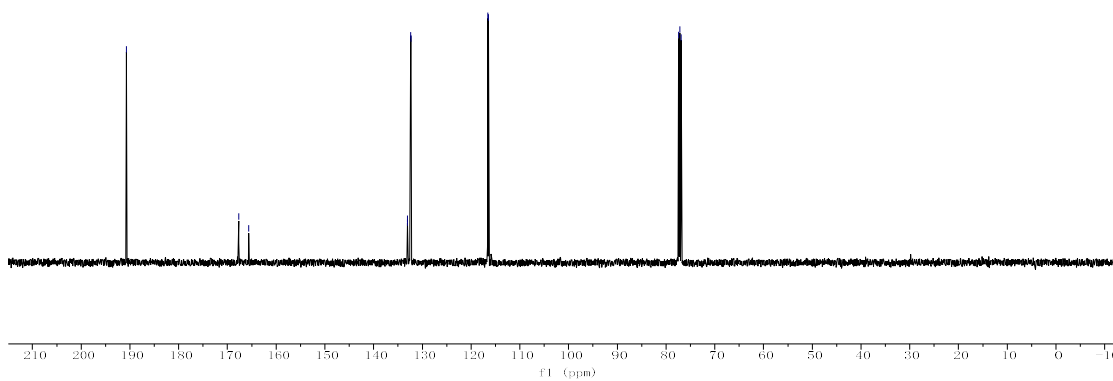


190.72  
167.69  
165.65  
133.08  
133.05  
132.43  
132.35  
116.59  
116.42  
77.42  
77.16  
76.91



**5e**

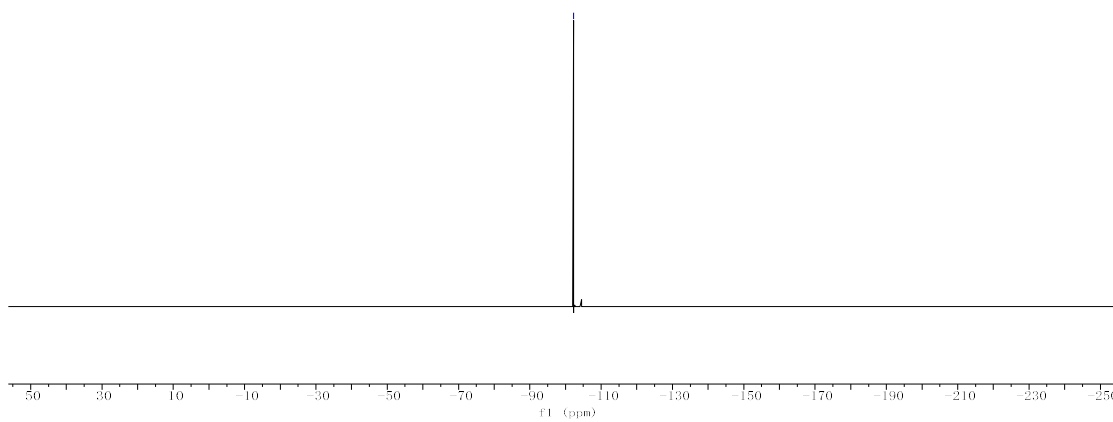
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

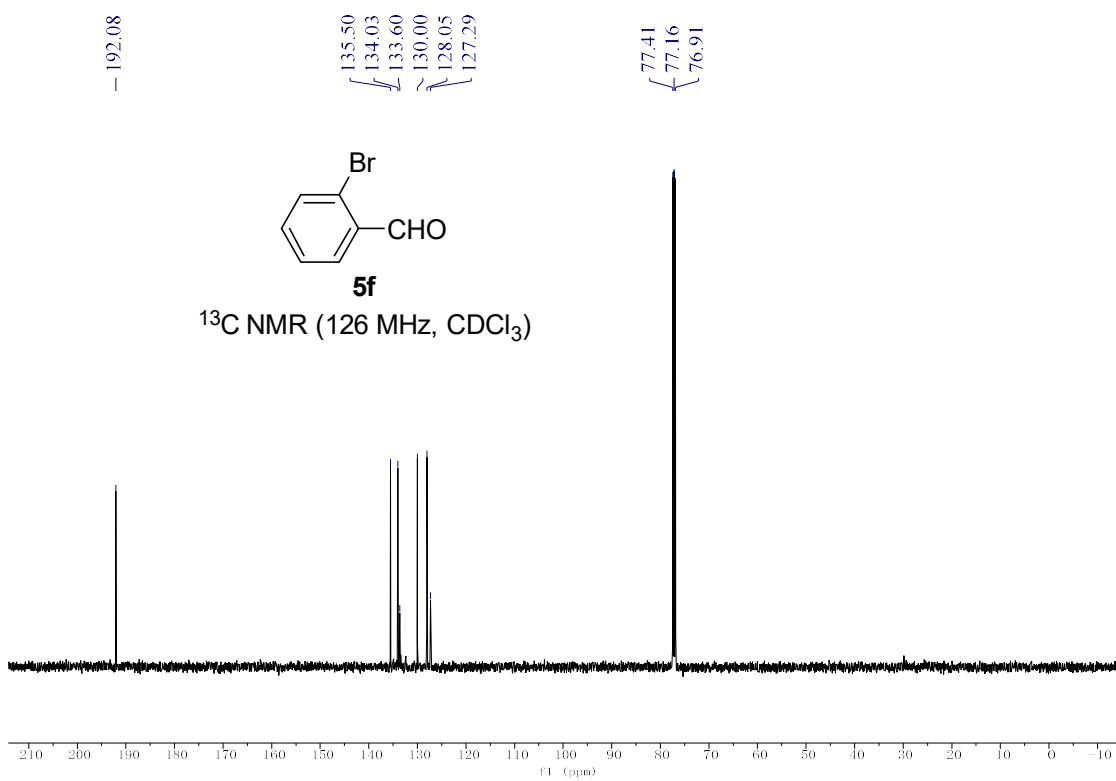
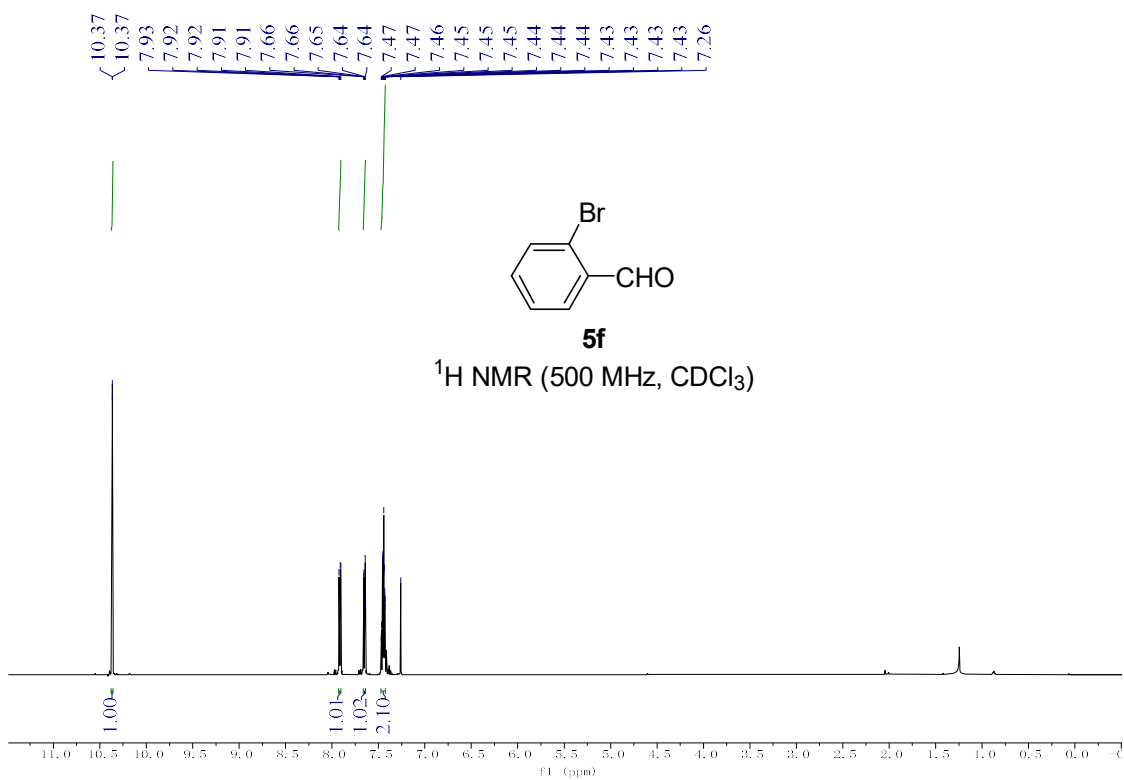


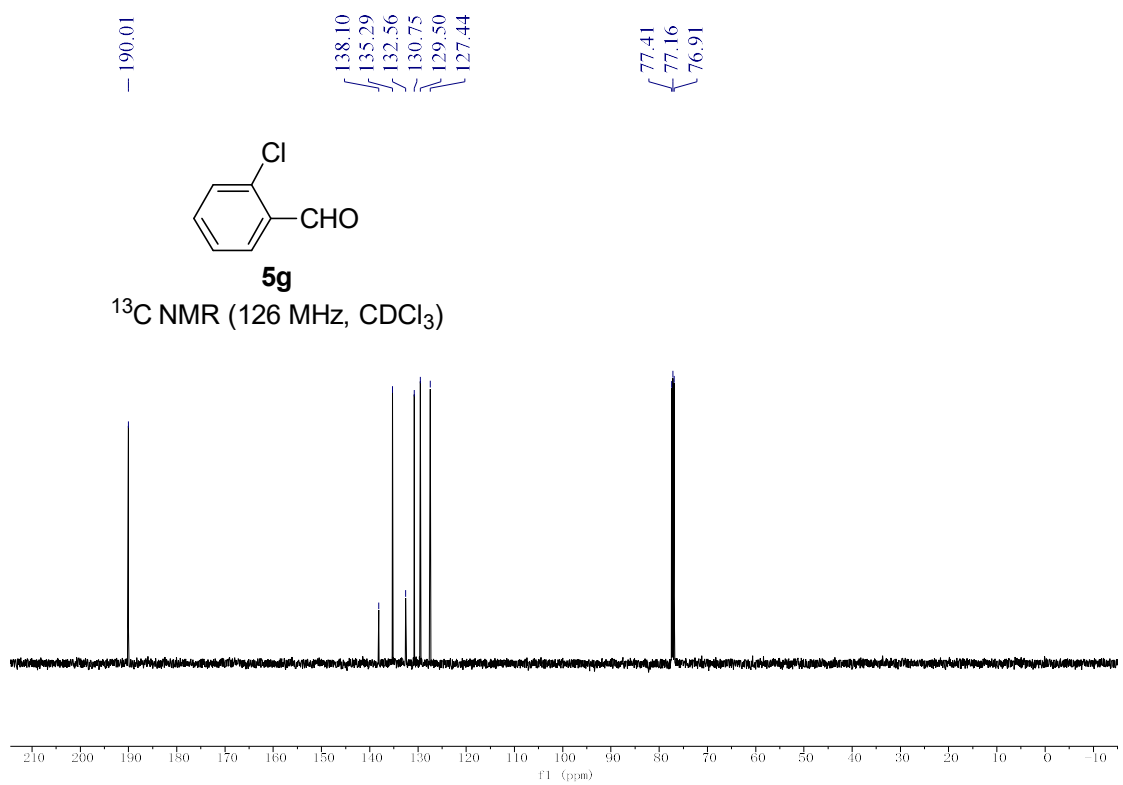
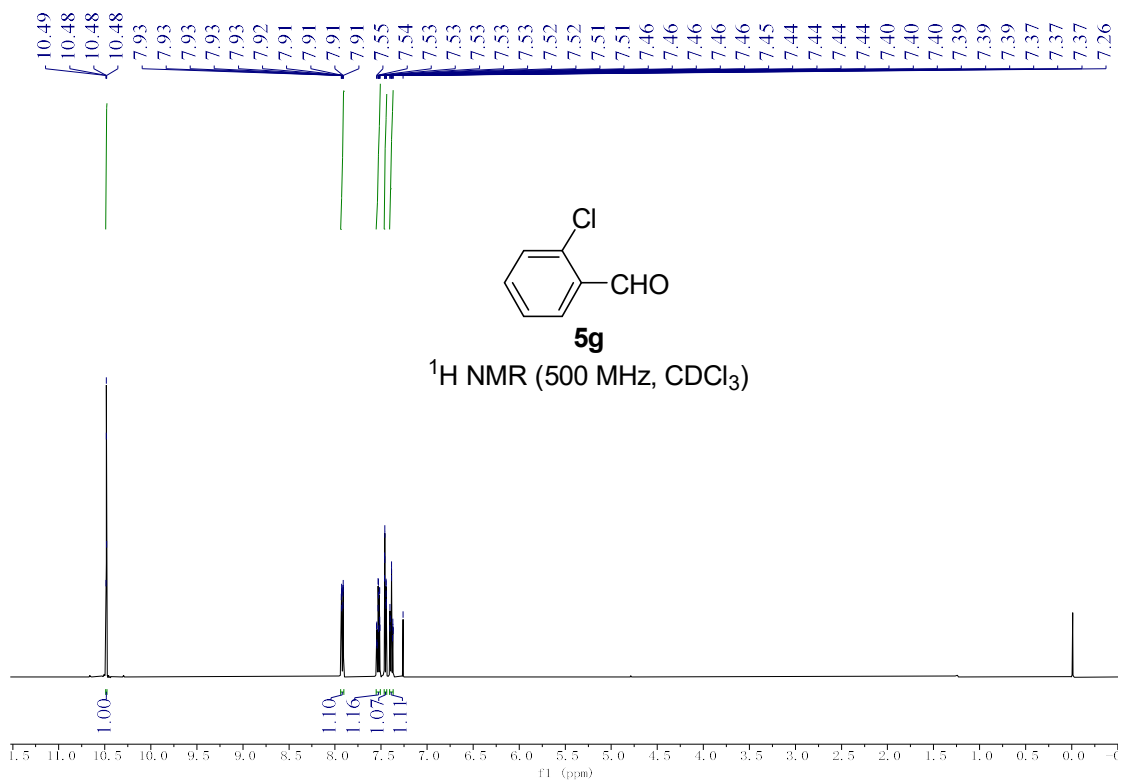
**5e**

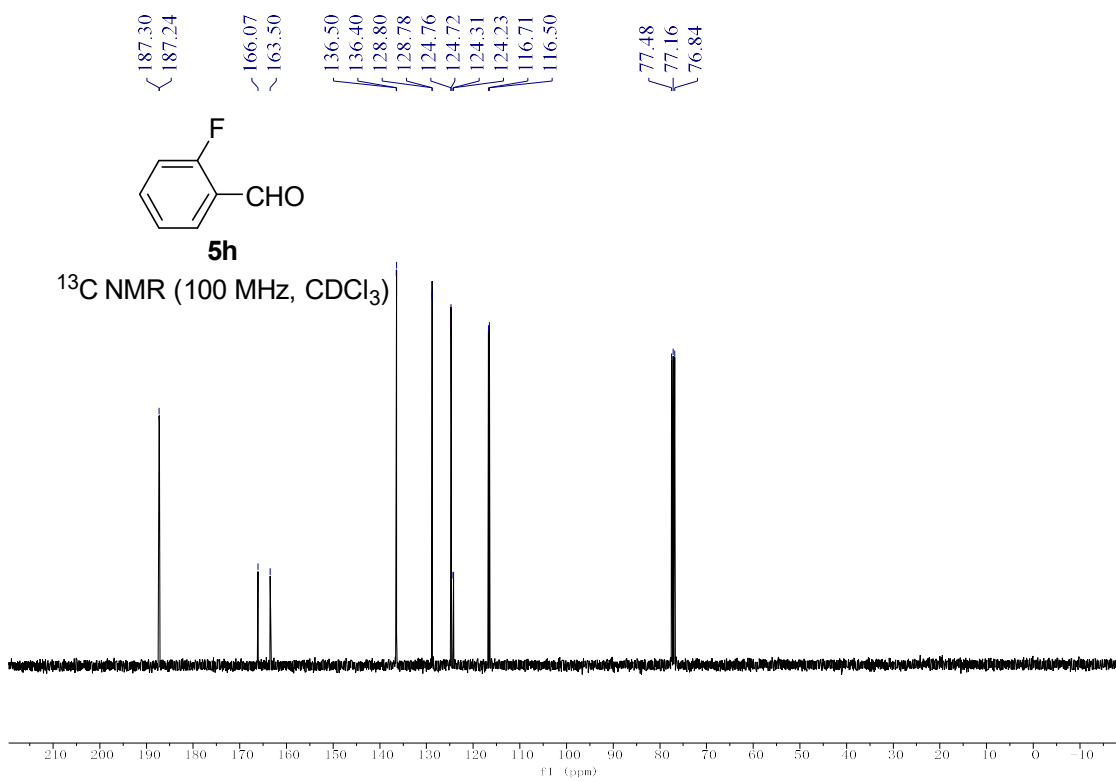
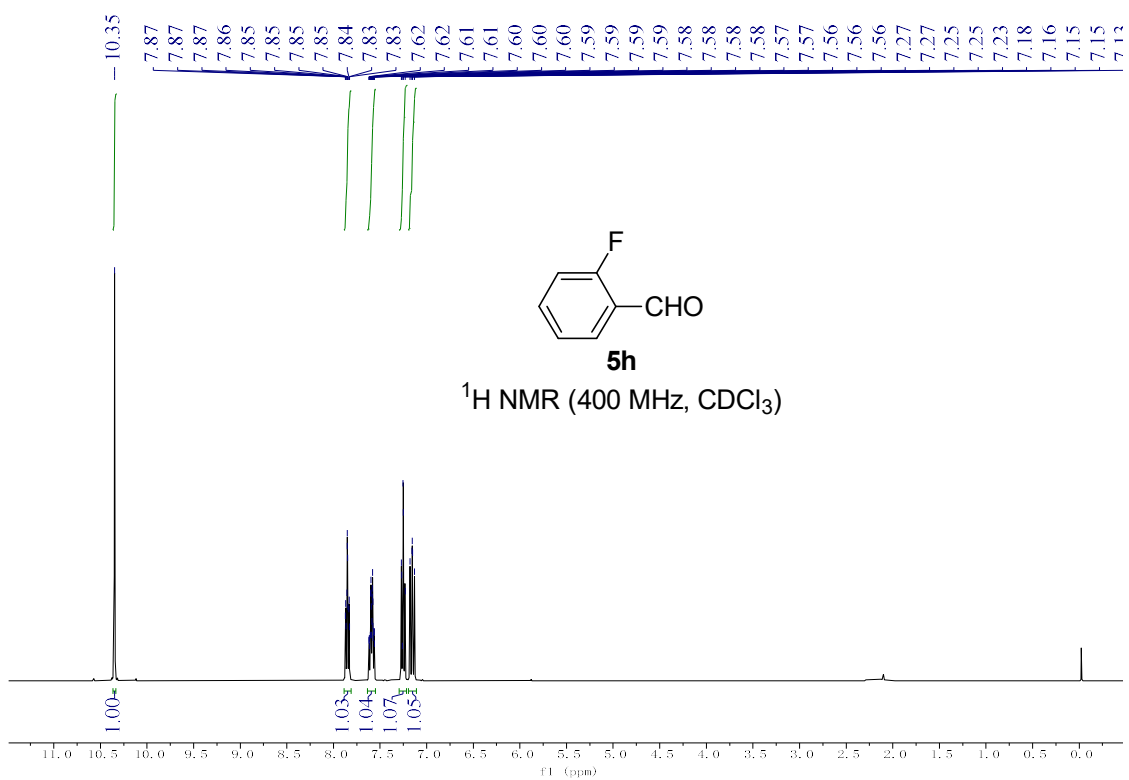
<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)

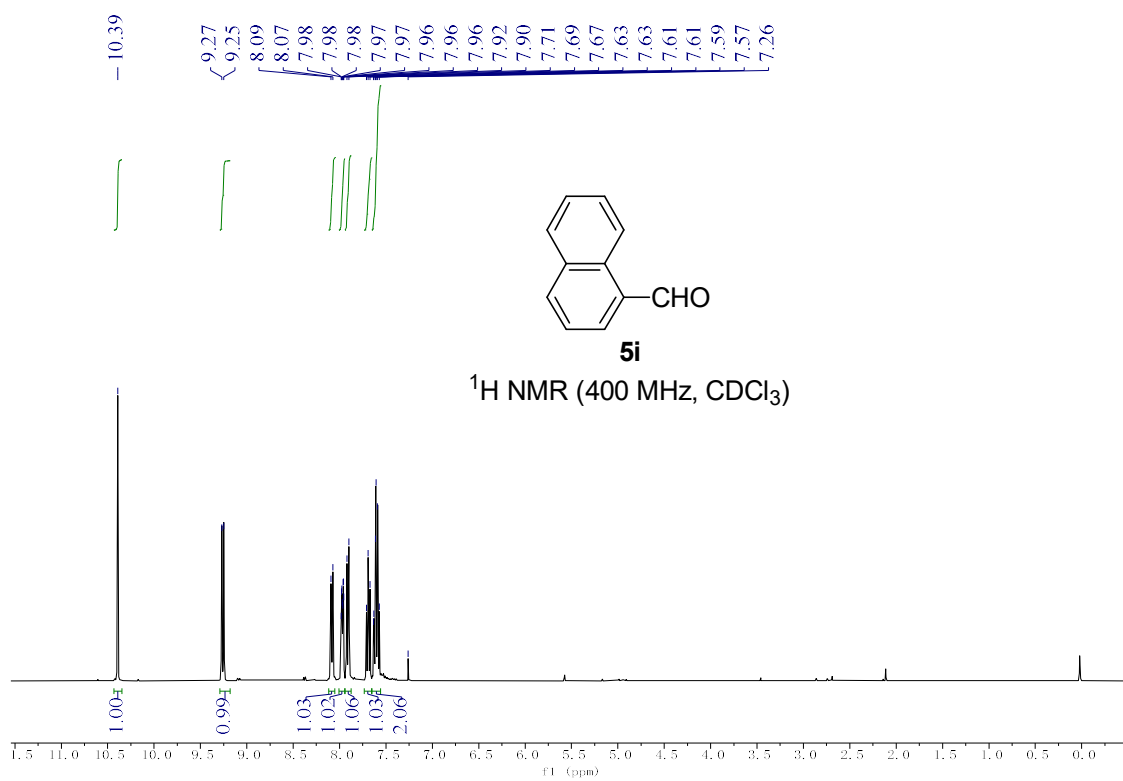
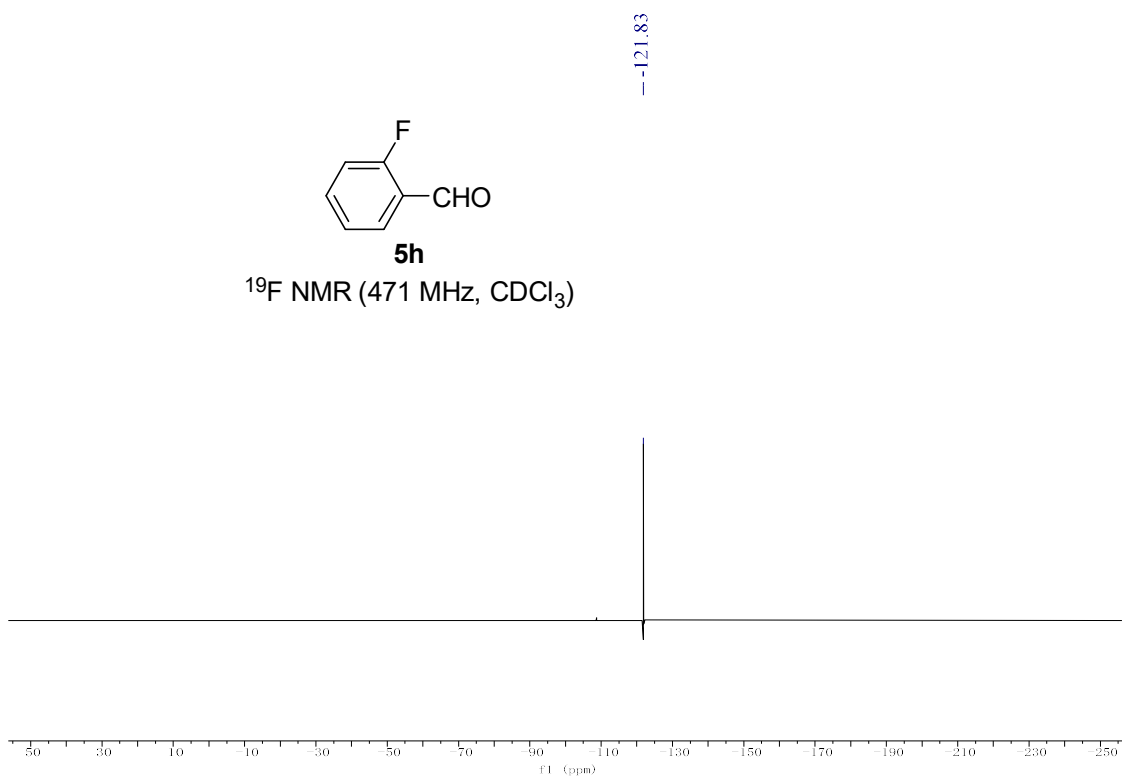
-102.23

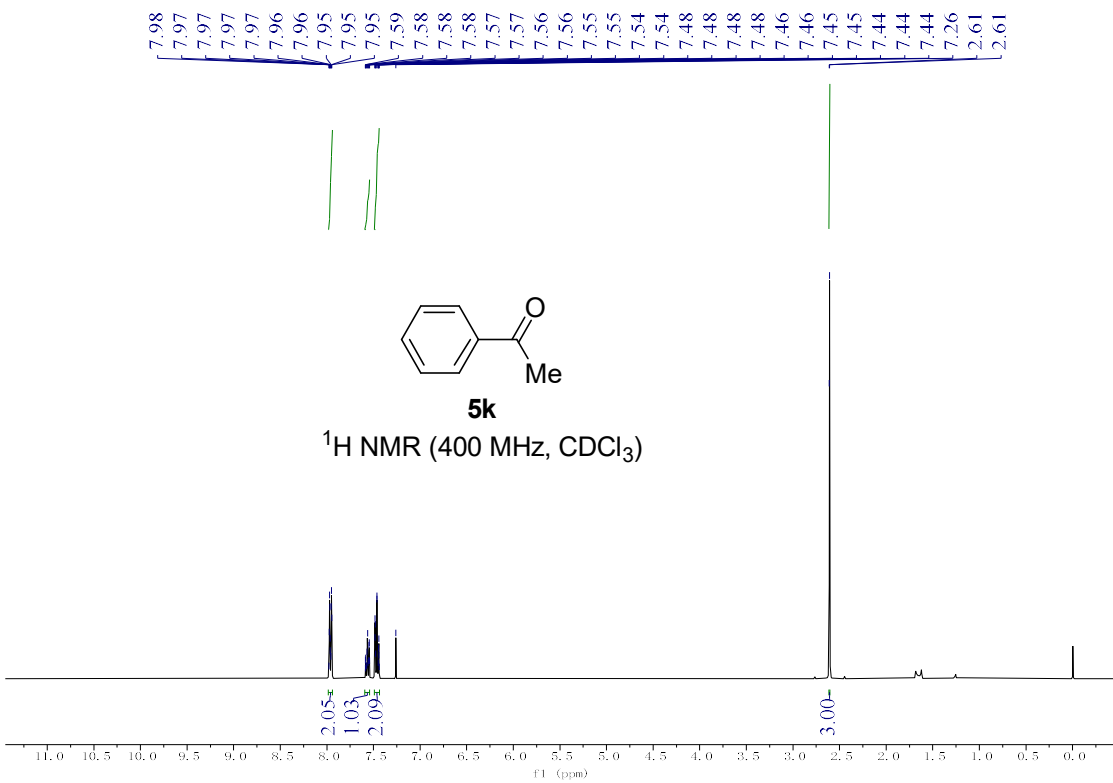
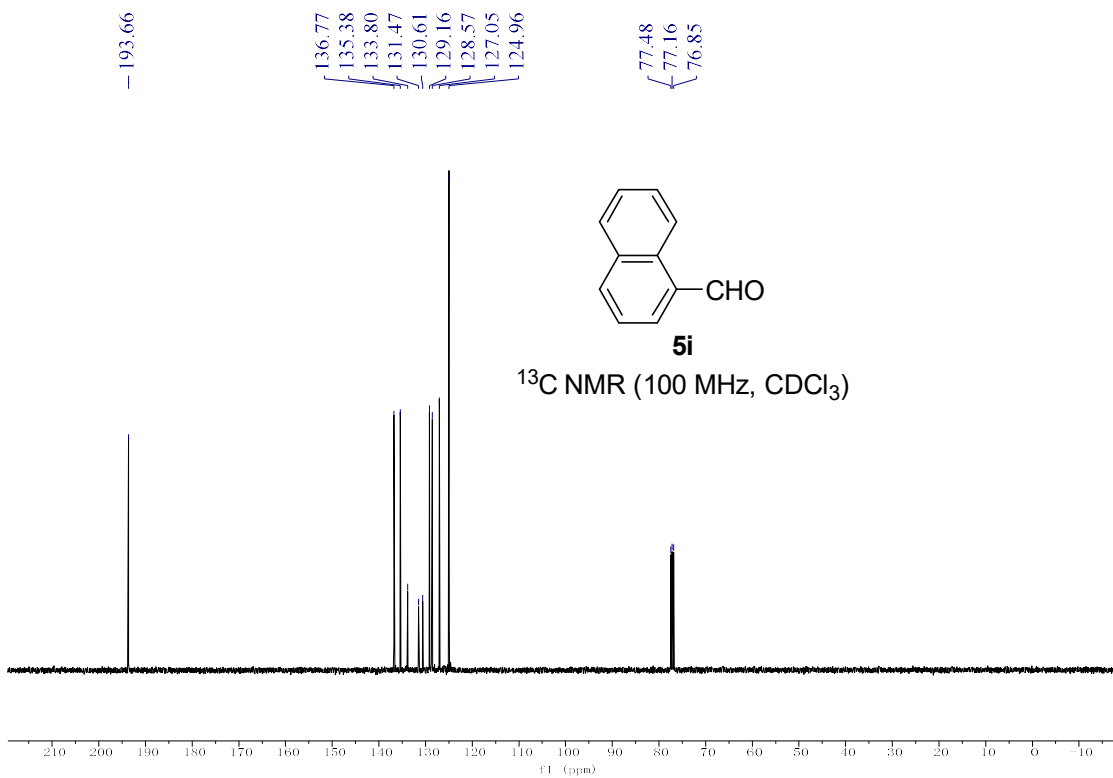




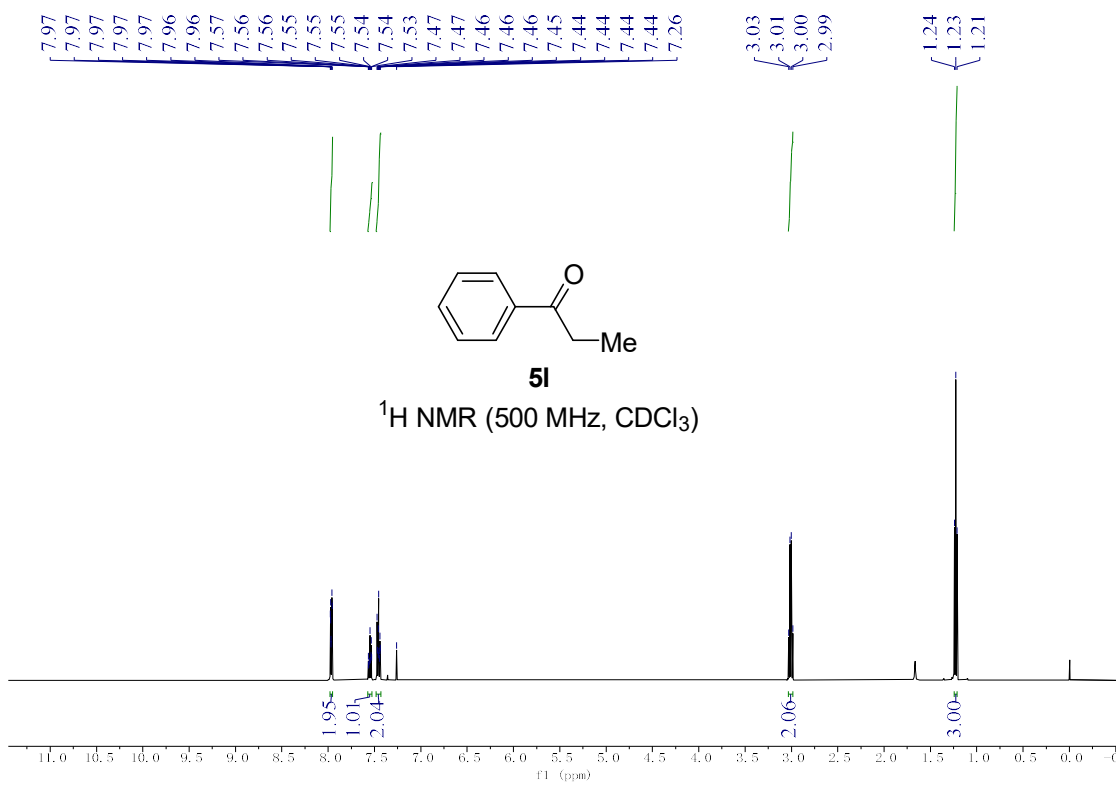
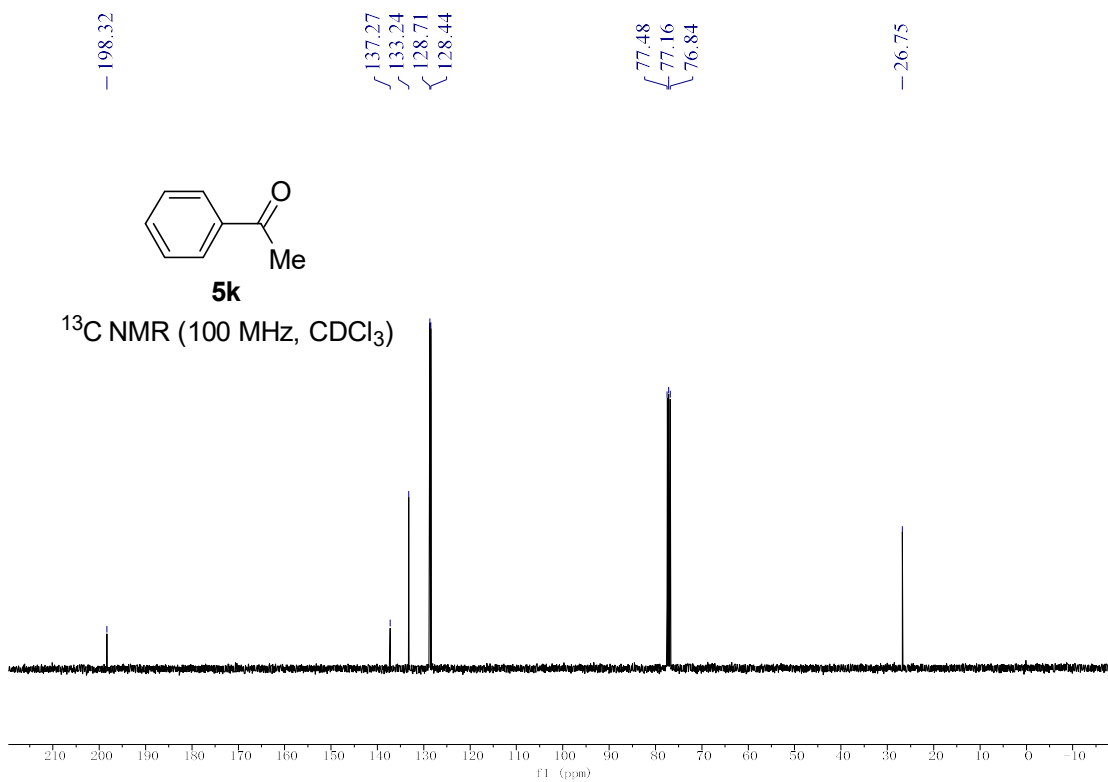


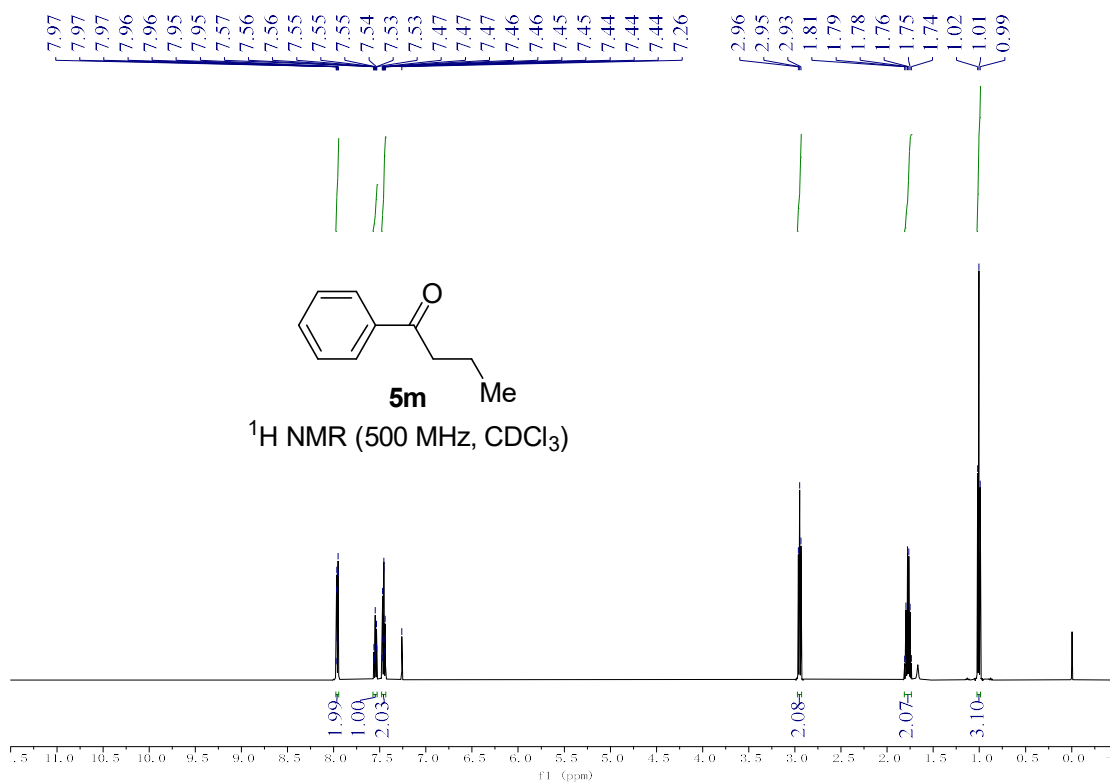
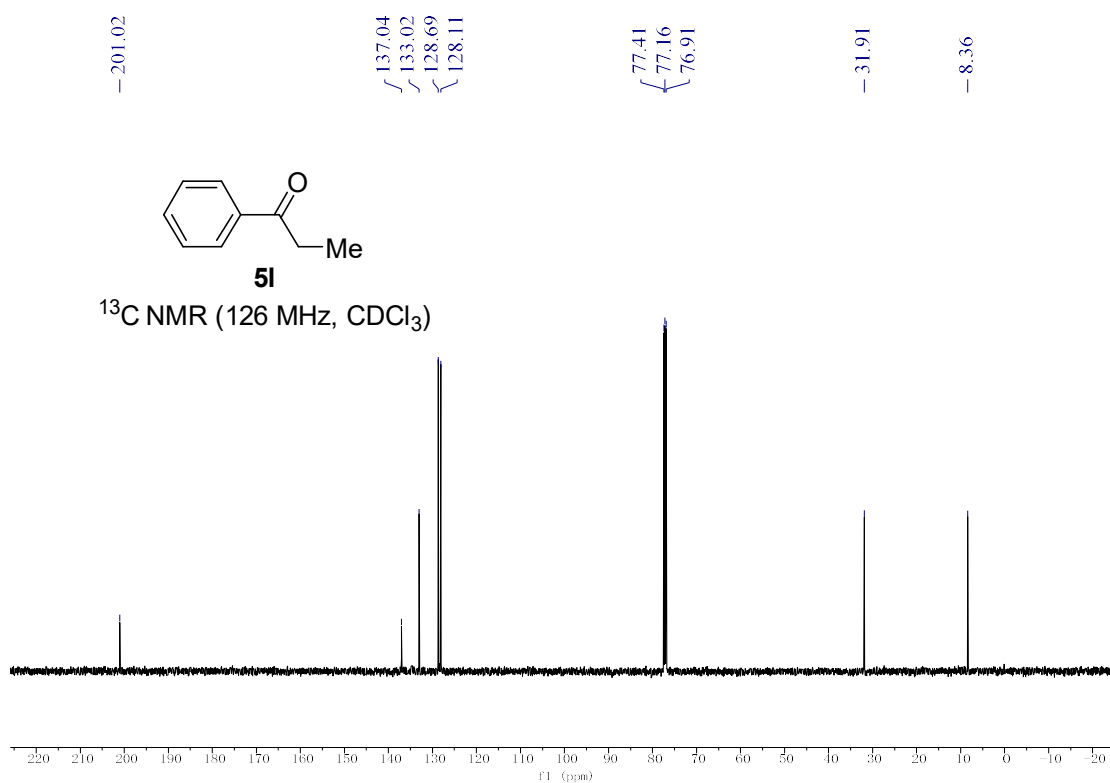


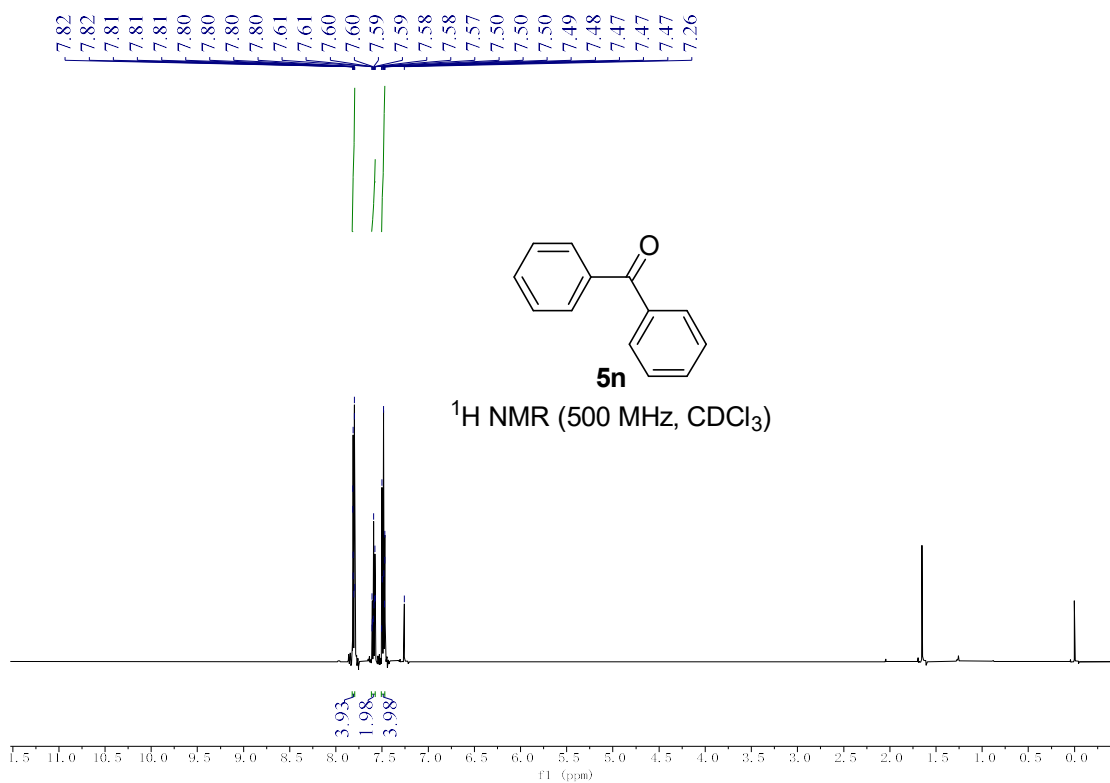
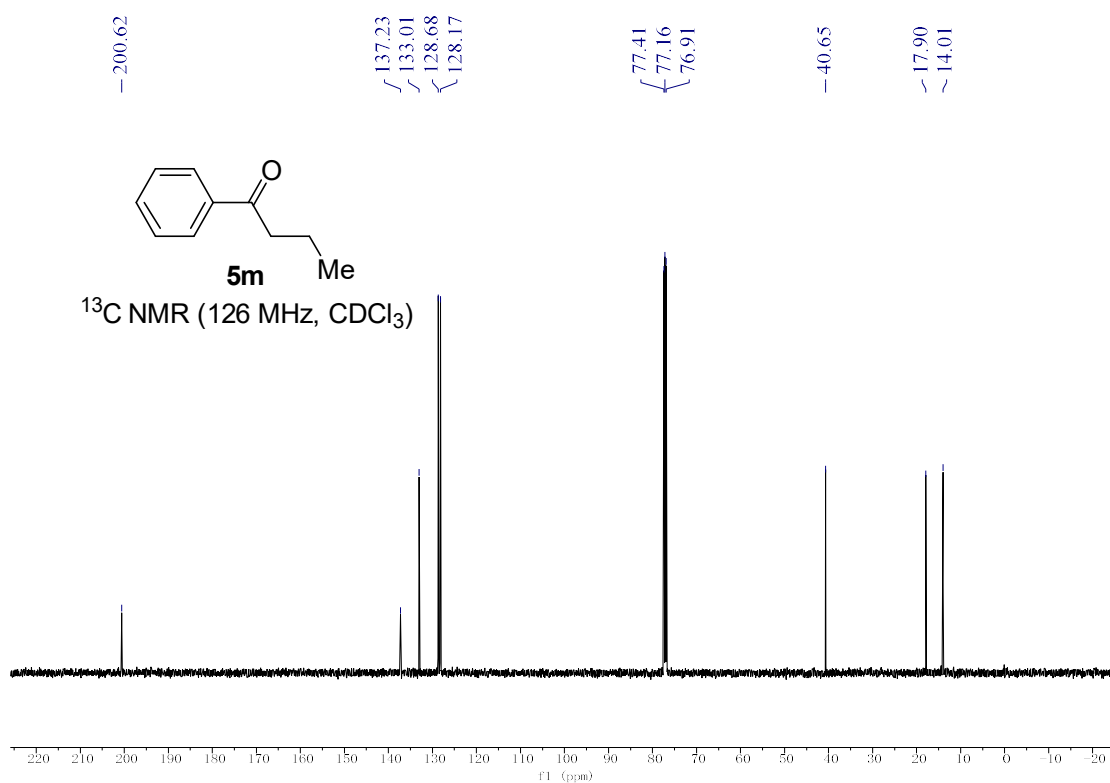


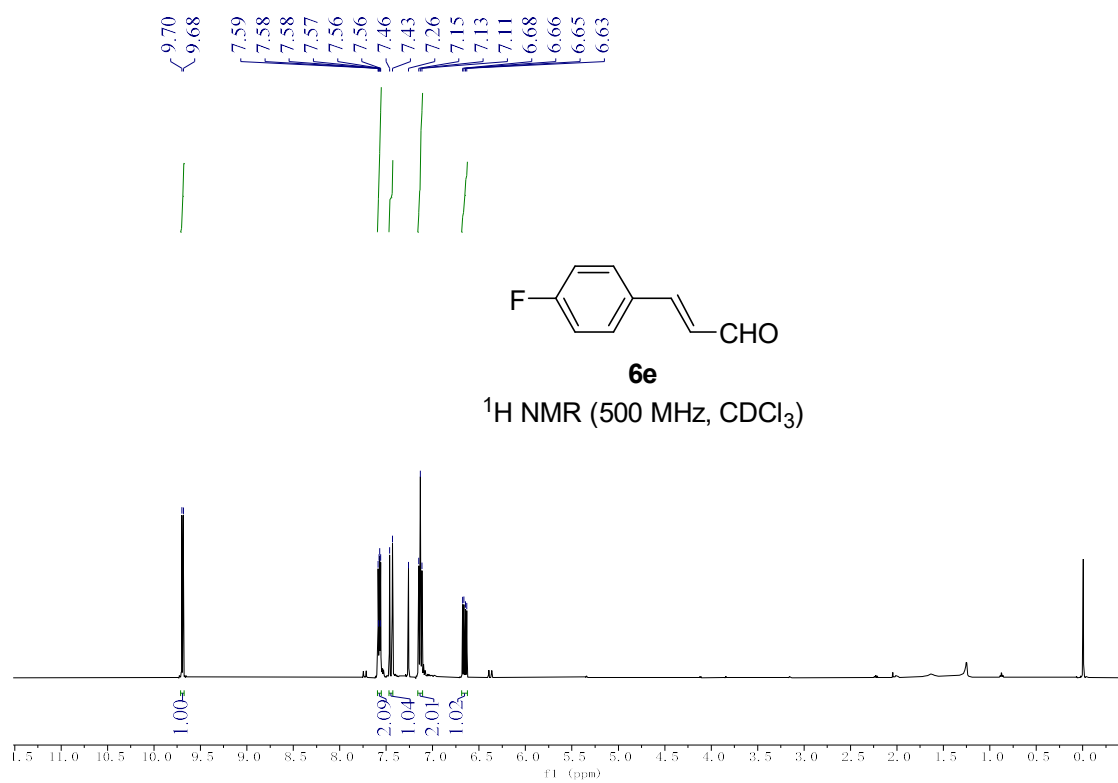
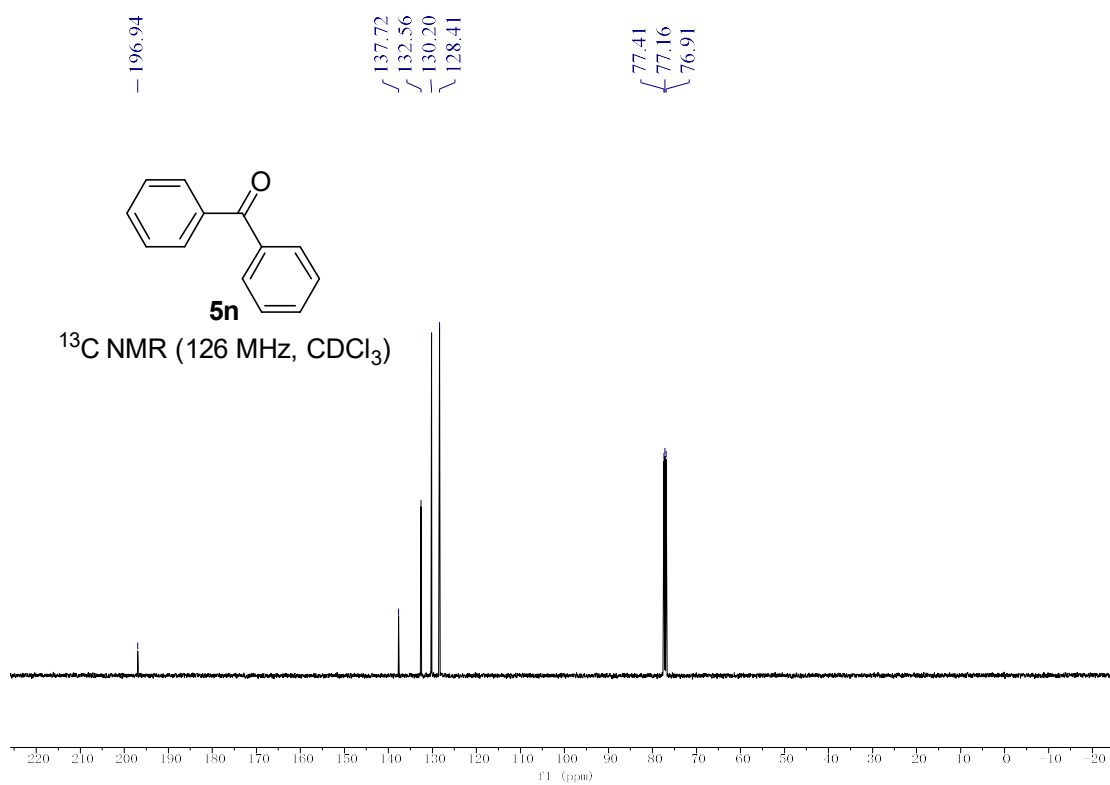


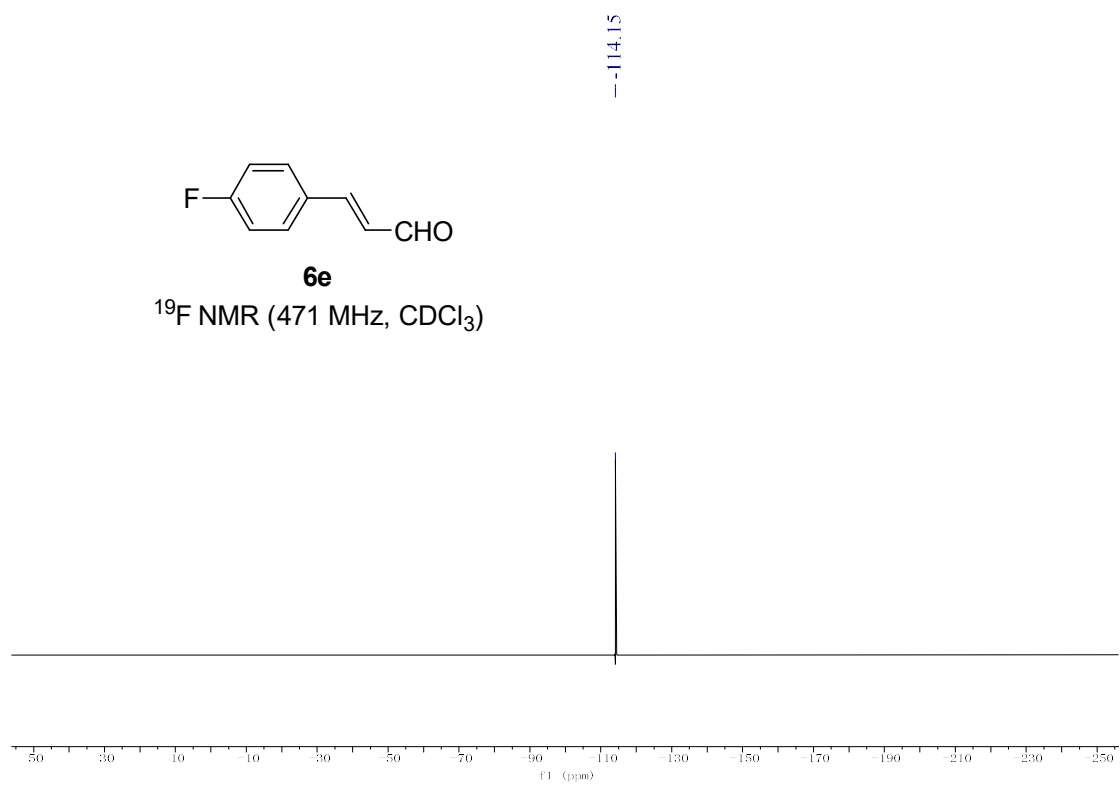
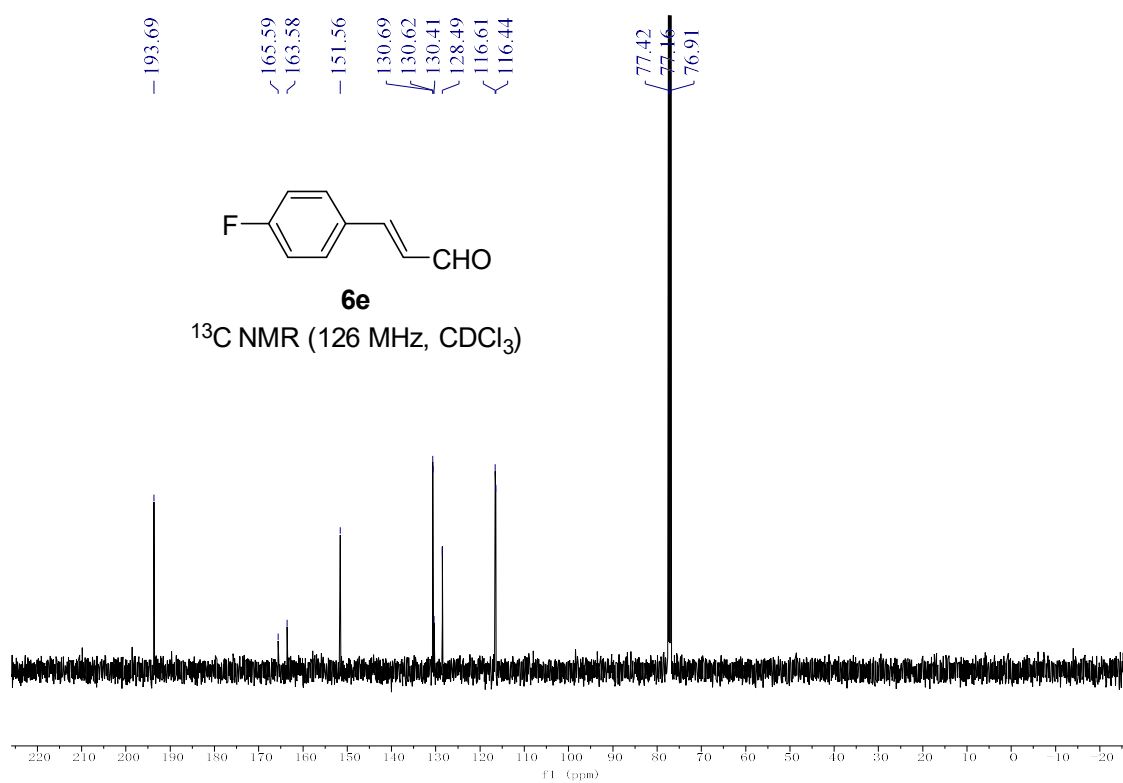


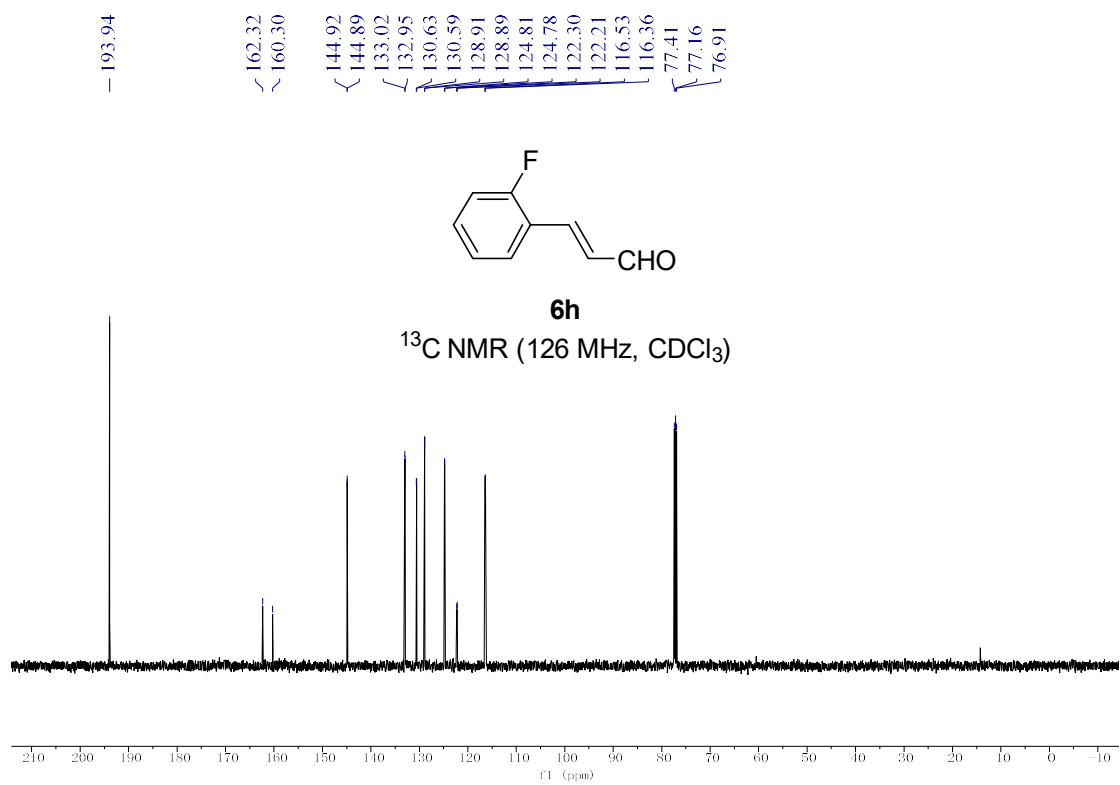
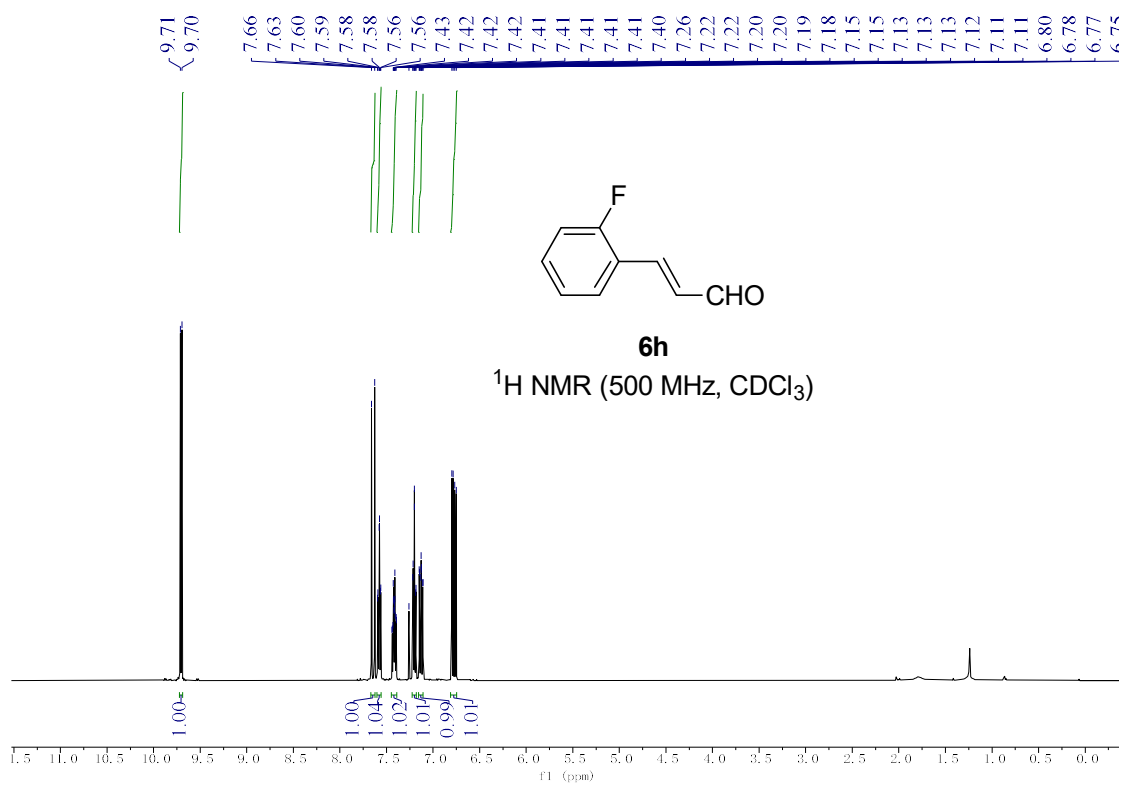


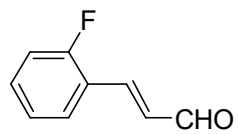












**6h**

<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)

-107.55

