

## Visible-Light Induced and Copper-Catalyzed Oxidative Cyclization of Substituted o-Aminophenylacetylene for the Synthesis of Quinoline and Indole Derivatives

Quan Huang,<sup>a</sup> Mingming Zhao,<sup>a</sup> Yiqiang Yang,<sup>a</sup> Yan-Ning Niu,<sup>b</sup> Xiao-Feng Xia<sup>\*,a</sup>

<sup>a</sup>Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu, 214122, China. E-mail: [xiacf@jiangnan.edu.cn](mailto:xiacf@jiangnan.edu.cn)

<sup>b</sup>Department of Teaching and Research, Nanjing Forestry University, Huaian, Jiangsu, 223003, China. E-mail: [zjsnyn@163.com](mailto:zjsnyn@163.com)

| Table of Contents |                                                                                                 |         |
|-------------------|-------------------------------------------------------------------------------------------------|---------|
| I                 | General Remarks                                                                                 | S2      |
| II                | The UV-visible spectroscopy and Fluorescence quenching studies (Stern–Volmer Studies)           | S2-S8   |
| III               | Isotope labelling experiments                                                                   | S9      |
| IV                | A possible mechanism for the synthesis of 3-acylindole product                                  | S9-S10  |
| V                 | Preparation of Starting Materials 1, 3, 6                                                       | S10-S15 |
| VI                | General Procedure for the synthesis of products 2, 4, 5, 7.                                     | S15-S17 |
| VII               | Table S1. Screening of reaction conditions for the synthesis of 7a                              | S17     |
| VIII              | Date of products 2, 4, 5, 7.                                                                    | S18-S33 |
| IX                | <sup>1</sup> H NMR, <sup>13</sup> C NMR and <sup>19</sup> F NMR spectra of compound 2, 4, 5, 7. | S34-S87 |

**I. General Remarks.** Column chromatography was carried out on silica gel. Unless noted  $^1\text{H}$  NMR spectra were recorded on 400 MHz in  $\text{CDCl}_3$ ,  $^{13}\text{C}$  NMR spectra were recorded on 100 MHz in  $\text{CDCl}_3$ ,  $^{19}\text{F}$  NMR spectra were recorded on 376 MHz in  $\text{CDCl}_3$ . NMR spectra were recorded on an AVANCE III HD 400 MHz spectrometer. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in  $\text{cm}^{-1}$ . UV-Vis spectra were recorded on a TU-1950 UV spectrometer and are reported in 190-900 nm. The fluorescence emission intensities were recorded on a CARY Eclipse spsespectrofluorimeter. Melting points were determined on a microscopic apparatus and were uncorrected.

## II. The UV-visible spectroscopy and Fluorescence quenching studies (Stern–Volmer Studies)

### Preparation of the samples for UV-Vis spectra measurement

**1a** in DMF (0.0004 mol/L): **1a** (0.02mmol) was dissolved in DMF (50 mL).

CuCl in DMF (0.0008 mol/L): CuCl (0.04mmol) was dissolved in DMF (50 mL).

CuCl<sub>2</sub> in DMF (0.0004 mol/L): CuCl<sub>2</sub> (0.02mmol) was dissolved in DMF (50 mL).

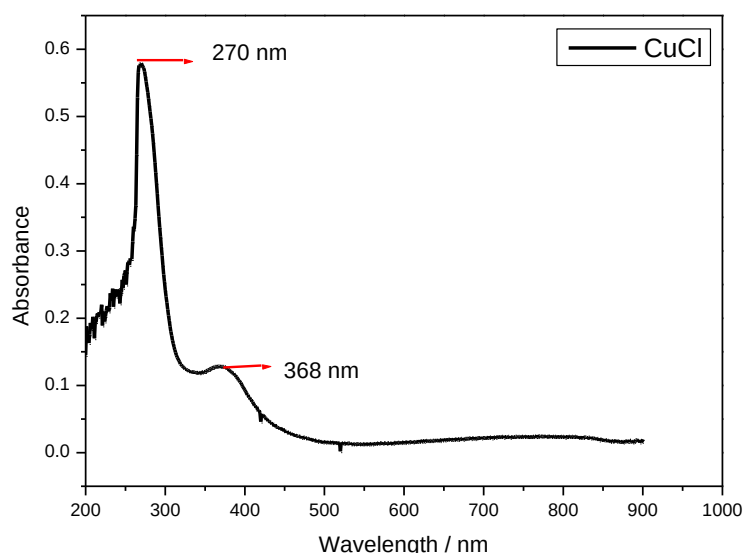
**1a** and CuCl in DMF (0.0004 mol/L): **1a** (0.02mmol) and CuCl (0.02mmol) was dissolved in DMF (50 mL).

**1a** and CuCl<sub>2</sub> in DMF (0.0004 mol/L): **1a** (0.02mmol) and CuCl<sub>2</sub> (0.02mmol) was dissolved in DMF (50 mL).

**6a** in DMF (0.00001 mol/L): **6a** (0.05mmol) was dissolved in DMF (50 mL). Take 0.1mL of the above solution in a volumetric flask and dilute to 10 mL.

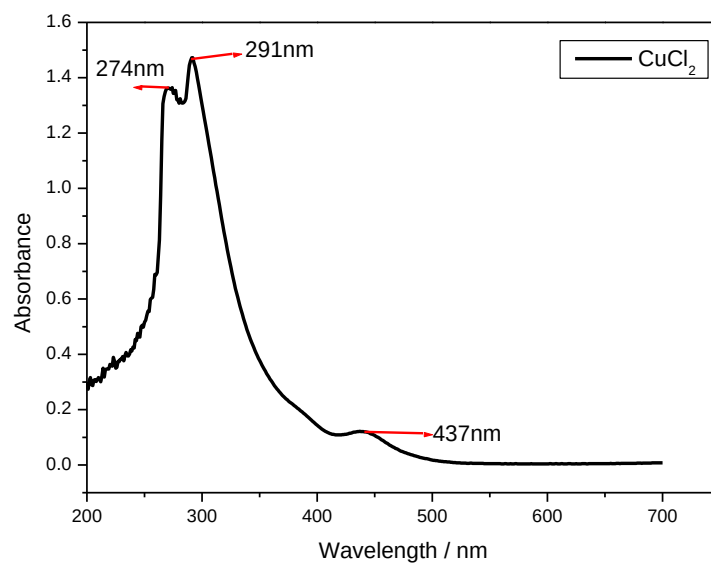
CuBr<sub>2</sub> in DMF (0.00001 mol/L): CuBr<sub>2</sub> (0.05mmol) was dissolved in DMF (50 mL). Take 0.1mL of the above solution in a volumetric flask and dilute to 10 mL.

CuBr<sub>2</sub> (0.00001 mol/L) and Phen(0.00002 mol/L) in DMF: CuBr<sub>2</sub> (0.05mmol) and Phen (0.1mmol) was dissolved in DMF (50 mL). Take 0.1mL of the above solution in a volumetric flask and dilute to 10 mL.



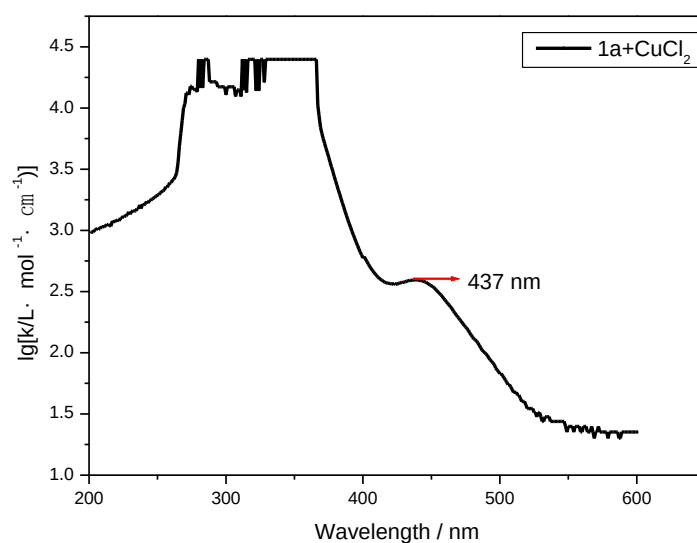
**Fig. S1** UV-vis absorption spectra of CuCl. The sample was prepared as a 0.0008 M solution in DMF and used freshly for the measurement.

CuCl has no absorption peak in the region of visible light.



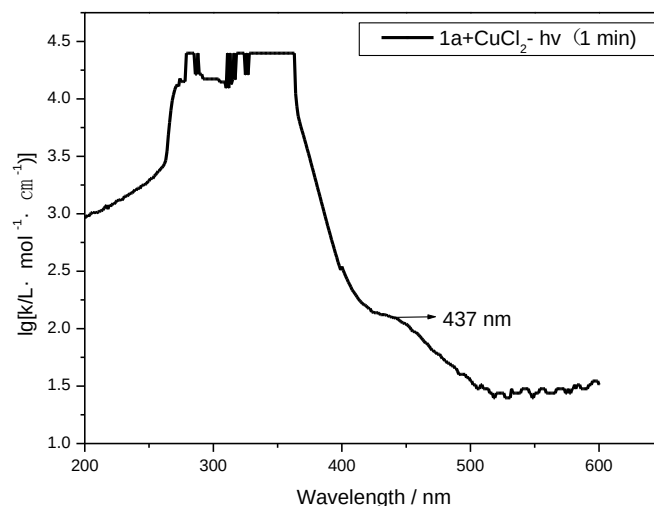
**Fig. S2** UV-vis absorption spectra of  $\text{CuCl}_2$ . The sample was prepared as a 0.0004 M solution in DMF and used freshly for the measurement.

After being excited by radiant energy, an electron transfers from the outer orbit of the ligand  $\text{Cl}^-$  to the central ion  $\text{Cu}^{2+}$  to generate a charge transfer absorption spectrum, which has a weak absorption peaks at 437 nm.



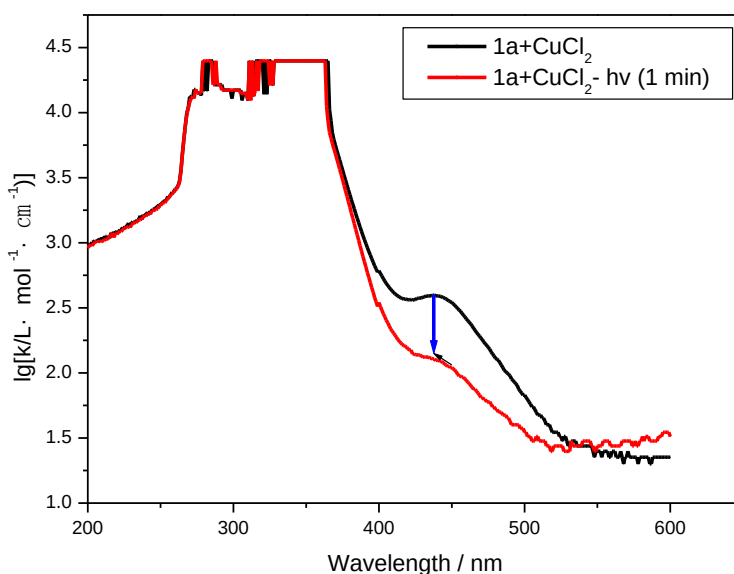
**Fig. S3** UV-vis absorption spectra of  $[1\mathbf{a} + \text{CuCl}_2]$ . The sample was prepared as a 0.0004 M solution in DMF and used freshly for the measurement.

$\text{CuCl}_2$  can coordinate with the substrate  $1\mathbf{a}$  to form a new complex, which affects the coordination field and makes ligand to metal charge transfer easier to be produced, thus enhanced the highest absorption peak at 437nm.



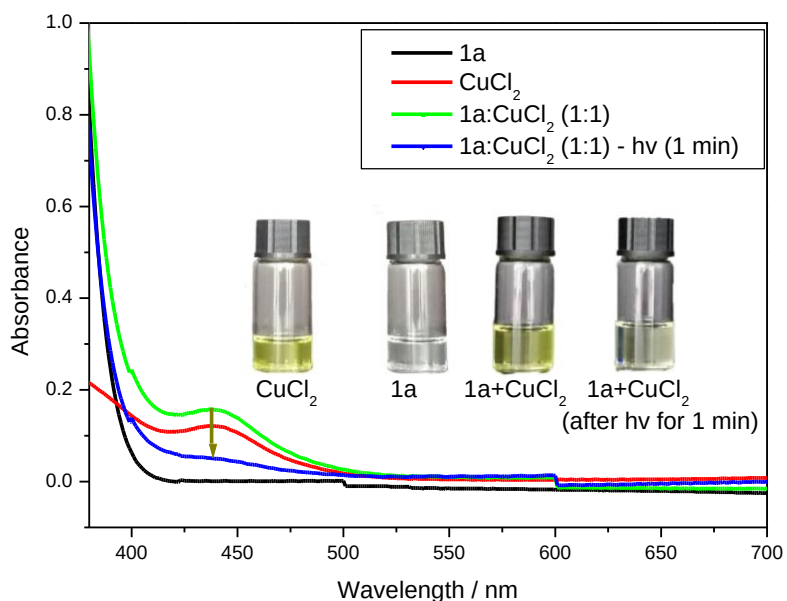
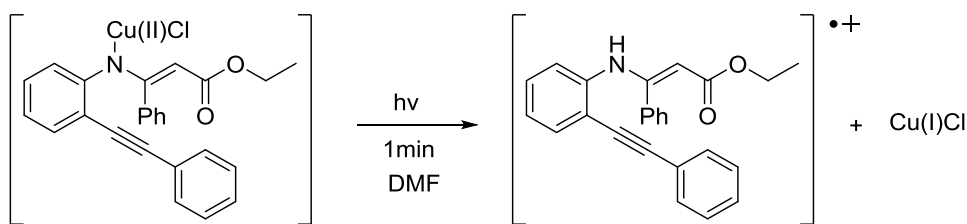
**Fig. S4** UV-vis absorption spectra of **[1a + CuCl<sub>2</sub>]** (after  $h\nu$  for 1 min). The samples were prepared as a 0.0004 M solution in DMF and used freshly for the measurement.

After 40 W blue LEDs irradiation for 1 min, a weak absorption peak at 437nm was observed.



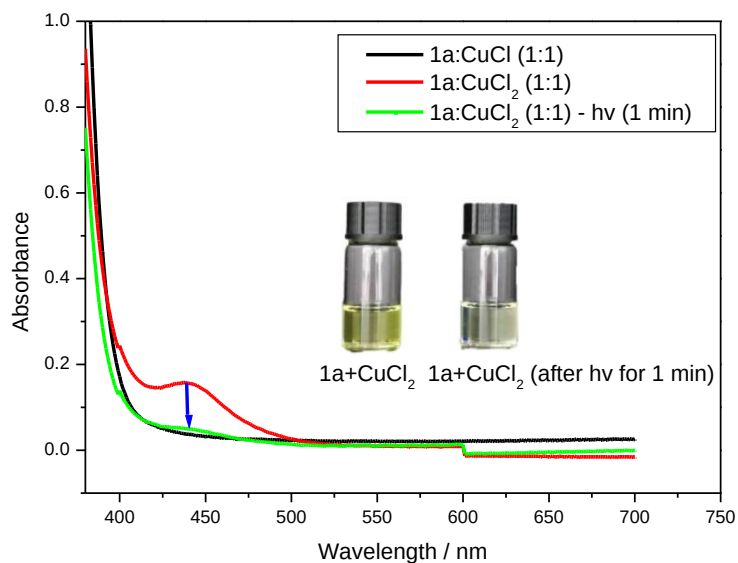
**Fig. S5** UV-vis absorption spectra between **[1a + CuCl<sub>2</sub>]** (0.0004 M) and **[1a + CuCl<sub>2</sub>]** (0.0004 M) (after  $h\nu$  for 1 min) in DMF were recorded in 1 cm path quartz cuvettes using UV/vis spectrometer.

After 40 W blue LEDs irradiation for 1 min, the absorption peak at 437 nm of the absorption spectrum becomes weaker. We think that a redox reaction may occur between the substrate **1a** and Cu(II)Cl.



**Fig. S6** UV-Vis spectra of the substrates **1a**, copper salts CuCl<sub>2</sub>, and [**1a** + CuCl<sub>2</sub>], [**1a** + CuCl<sub>2</sub>] (after  $h\nu$  for 1 min). All the samples were prepared as a 0.0004 M solution in DMF and used freshly for the measurement.

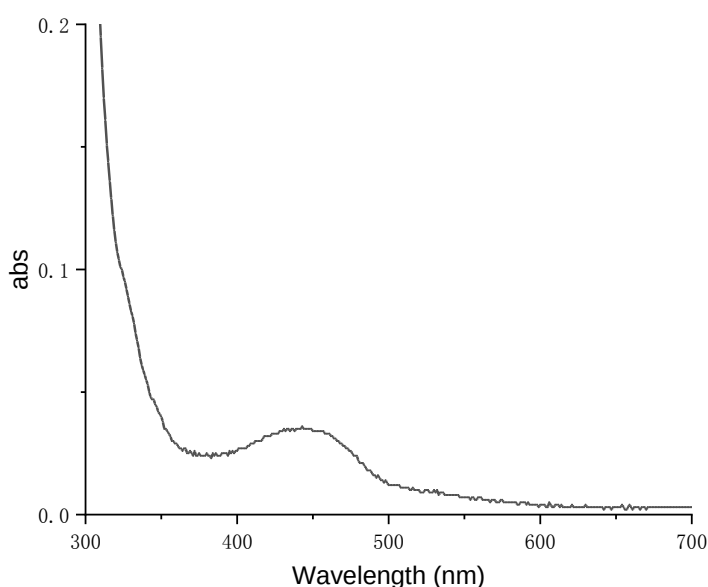
**1a** and CuCl<sub>2</sub> dissolved in DMF, the color of the reaction system is similar to that of CuCl<sub>2</sub>, and the absorption peak was enhanced. After 40 W blue LEDs irradiation for 1 min, the color of the reaction system changed and the absorption peak of the absorption spectrum became weaker.



**Fig. S7** UV-Vis spectra of the [1a + CuCl], [1a + CuCl<sub>2</sub>] and [1a + CuCl<sub>2</sub>] (after hν for 1 min). All the samples were prepared as a 0.0004 M solution in DMF and used freshly for the measurement.

After 40 W blue LEDs irradiation for 1 min, the color of the [1a + CuCl<sub>2</sub>] reaction system changed and the absorption peak of the absorption spectrum became weaker, the absorption spectrum curve is similar to that of [1a + CuCl].

For the emission quenching of CuBr<sub>2</sub> (0.01mM)/Phen (0.02mM) solution, the UV-visible spectroscopy indicated that the maximum absorption wavelength of CuBr<sub>2</sub>/Phen (1:2) solution was found to be 443 nm. The absorption was collected and the result was listed in **Figure S8**.

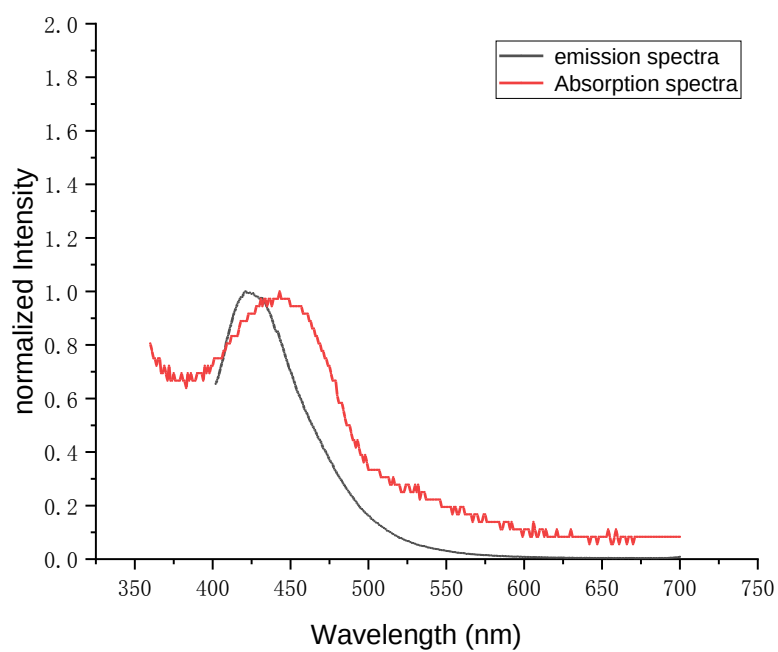


**Figure S8.** UV-vis spectrum of CuBr<sub>2</sub>/Phen(1:2)

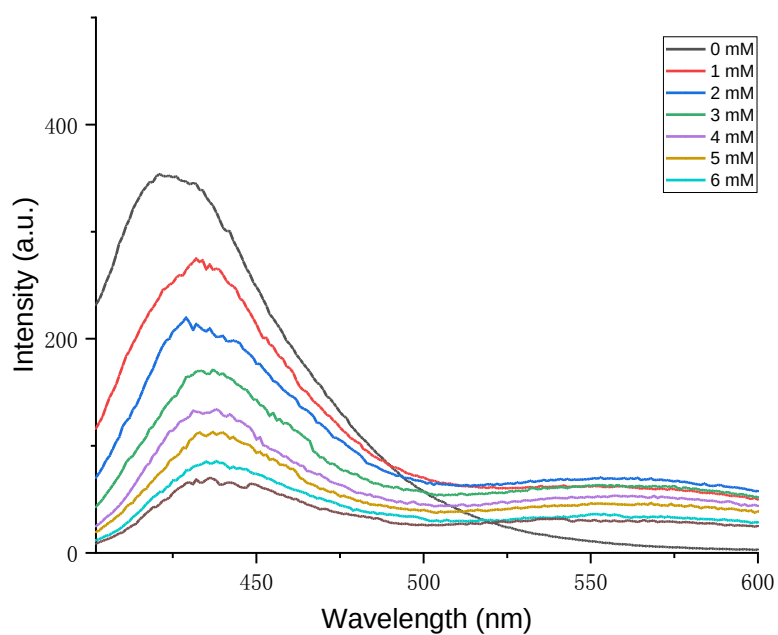
The samples were prepared by mixing by CuBr<sub>2</sub>/Phen (1:2) and varying concentrations of quencher **6a** in DMF in quartz cuvettes. For the emission quenching of CuBr<sub>2</sub> (0.01mM)/Phen (0.02mM) solution, the excitation wavelength was fixed at 370 nm, and the emission wavelength was measured at 422 nm (emission maximum). The concentration of **6a** solution is 0.1 mol/L in DMF. For each quenching experiment, different volume of **6a** solution was titrated to a 3 mL mixed solution of CuBr<sub>2</sub>/Phen. For the Plots were constructed according to the Stern-Volmer equation.

$$I_0/I = 1 + K_{sv}[Q] = 1 + k_q\tau_0[Q]$$

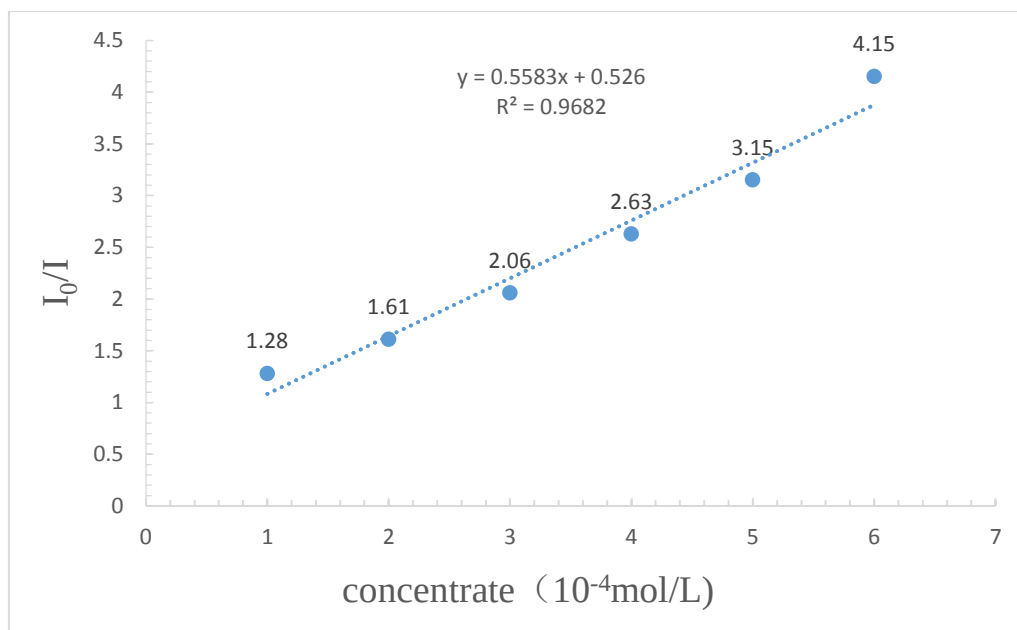
where **I**<sub>0</sub> and **I** are the fluorescence intensity in the absence and presence of quencher **Q**, **K**<sub>SV</sub> is the Stern-Volmer constant, **k**<sub>q</sub> is the bimolecular quenching constant, and [**Q**] is the concentration of quencher.



**Figure S9.** Absorption and emission spectra of CuBr<sub>2</sub>/Phen(1:2)

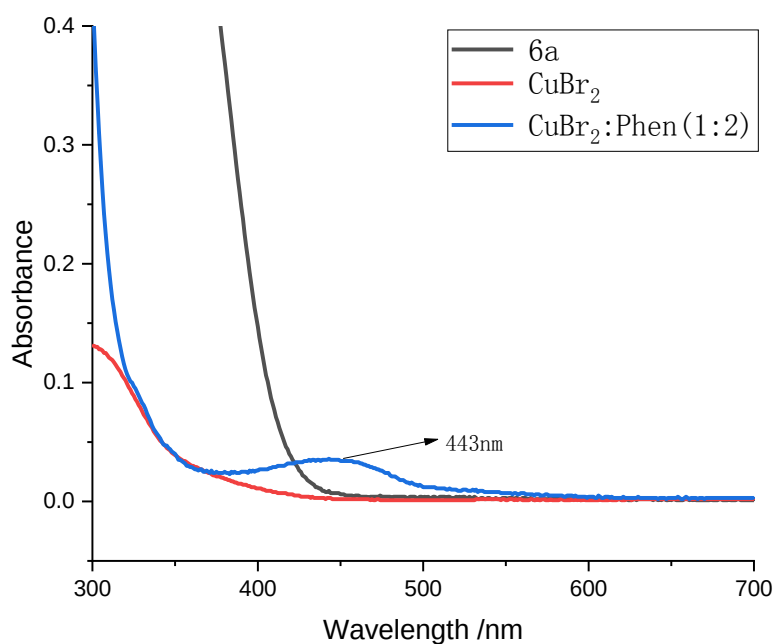


**Figure S10.** CuBr<sub>2</sub>/Phen (1:2) emission quenching by 6a.



**Figure S11.** Stern-Volmer emission quenching studies of  $\text{CuBr}_2/\text{Phen}$  and **6a**

When the concentration of **6a** was gradually increased, the emission intensity of excited  $\text{CuBr}_2/\text{Phen}(1:2)$  was found to be diminished. These results indicated that an energy transfer process should occur between excited  $\text{CuBr}_2/\text{Phen}(1:2)$  and **6a** in the presence of light.



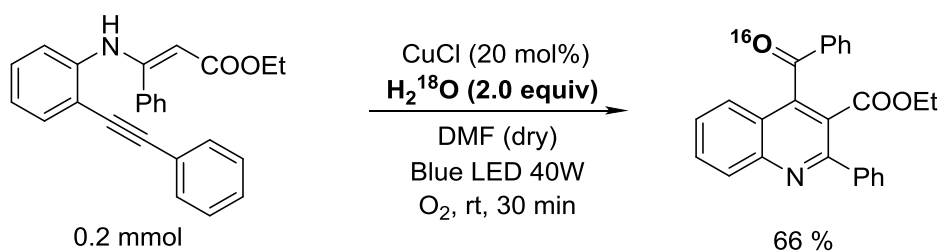
**Figure S12.** UV-vis spectrum of substrate **6a**,  $\text{CuBr}_2$ ,  $\text{CuBr}_2/\text{Phen}(1:2)$

Substrate **6a** and  $\text{CuBr}_2$  has no absorption peak in the region of visible light, the in-situ formed complex of  $\text{CuBr}_2$  and phen has an obvious absorption peak at 443 nm, which indicates that the energy of light can be absorbed by the complex of  $\text{Cu}(\text{Phen})\text{Br}_2$  in the reaction of substrate **6a** for the synthesis of indole.

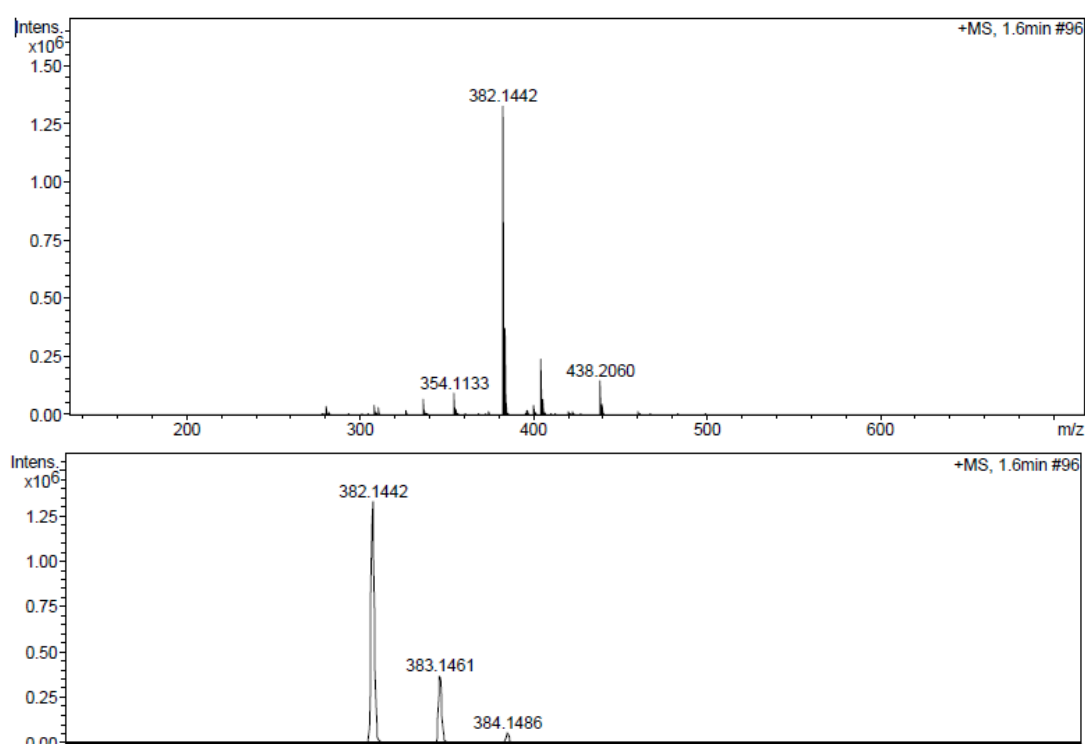


### III. Isotope labelling experiments:

Using 2.0 eq.  $\text{H}_2^{18}\text{O}$  under the standard condition:

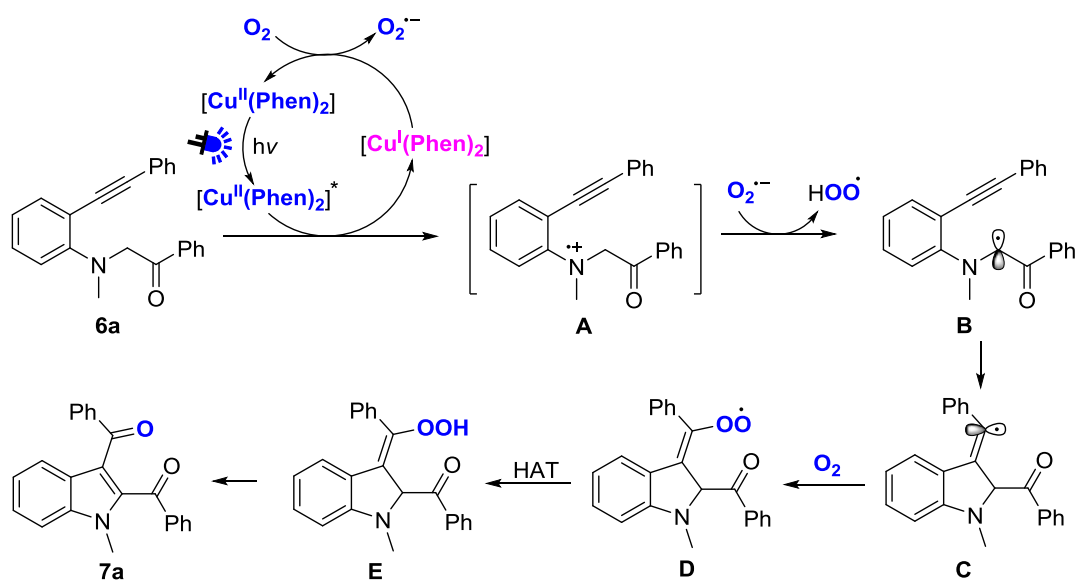


HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_1\text{O}_2^{18}\text{O}^+ (\text{M}+\text{H})^+$  384.1485, not found 384.1480, calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_1\text{O}_2^{16}\text{O}^+ (\text{M}+\text{H})^+$  382.1437, found 382.1442.

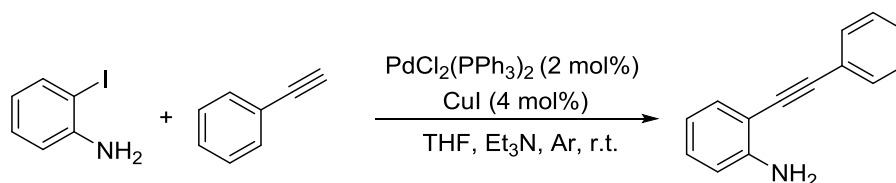


### IV. A possible mechanism for the synthesis of 3-acylindole product:

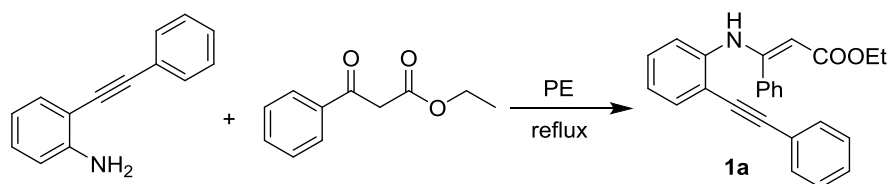
A plausible mechanism for the reaction is proposed. Initially,  $\text{Cu}^{\text{II}}$  complex is irradiated by visible light to reach its excited state, then the single electron transfer from **6a** to copper catalyst leads to  $\text{Cu}^{\text{I}}$  and intermediate **A**.  $\text{Cu}^{\text{I}}$  could be readily oxidized by molecular oxygen to form  $\text{Cu}^{\text{II}}$  and superoxide anion. Next, intermediate **A** and superoxide anion undergoes hydrogen atom transfer to produce the hydroperoxy radical and carbon radical intermediate **B**. The resulting **B** undergoes an intramolecular radical cyclization to give rise **C**, which is further captured by molecular  $\text{O}_2$  followed by hydrogen atom transfer (HAT) to form peroxide **E**. After removing one molecule of water, 3-acylindole **7a** is obtained.



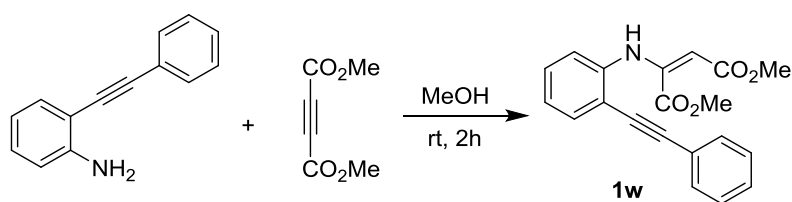
## V. Preparation of Starting Materials 1, 3, 6



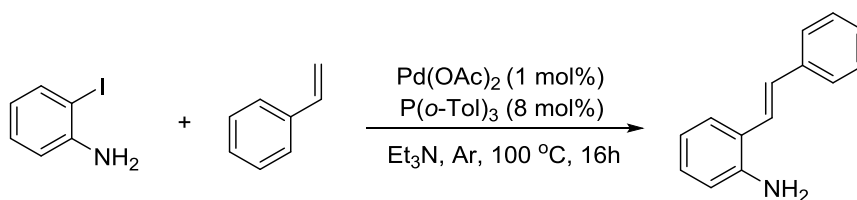
To a mixture of 2-iodoaniline (2.628 g, 12 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (168 mg, 2 mol%) and CuI (92 mg, 4 mol%) in THF (20 mL), were added ethynylbenzene (1.2 equiv, 1.47 g) and triethylamine (8.0 equiv, 0.97 g) under nitrogen atmosphere. The reaction was performed at room temperature for 4~16 h monitored by TLC analysis until the starting material was consumed. Saturated  $\text{NH}_4\text{Cl}$  solution was added to the mixture and extracted with ethyl acetate twice. The combined organic phase was washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . The concentrated residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent to get the product (2.2 g, 95 %).



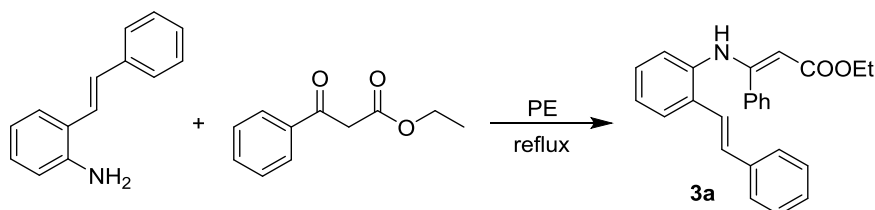
A mixture of ethyl 3-oxo-3-phenylpropanoate (1.73 mL, 10.00 mmol) and 2-(phenylethynyl)aniline (0.965 g, 5.00 mmol) in petroleum ether (40 mL) was heated under reflux for 10h to remove the resulting water. The resulting mixture was concentrated and the residue was taken up in DCM. The organic layer was washed with 5% HCl and water, dried over  $\text{MgSO}_4$  and concentrated. Purification of the crude product by flash column chromatography afforded the enamine (yield 60%). All the compounds **1a-1v** were synthesized according to the above method.



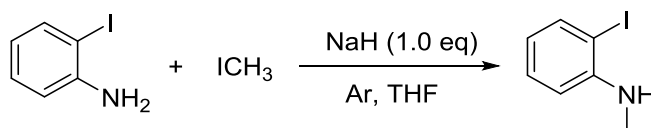
A solution of dimethyl acetylenedicarboxylate (337 mg, 2.37 mmol) and (2-ethynylphenyl)amine (253 mg, 2.16 mmol) in methanol (5 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate (20 mL), washed with water (3 × 5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 1:15 ethyl acetate–petroleum ether) to give **1w** (520 mg, 93%).



To a solution of 2-iodoaniline (2.7 g, 15.52 mmol, 1 equiv) in NEt<sub>3</sub> (15.0 mL, 1.0 M) were added Pd(OAc)<sub>2</sub> (34.8 mg, 0.155 mmol, 1 mol%), P(*o*-Tol)<sub>3</sub> (398.0 mg, 1.241 mmol, 8 mol%), and olefin (18.62 mmol, 1.2 equiv). After being stirred at 100 °C overnight, the reaction mixture was poured into water and then the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (three times). The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product.

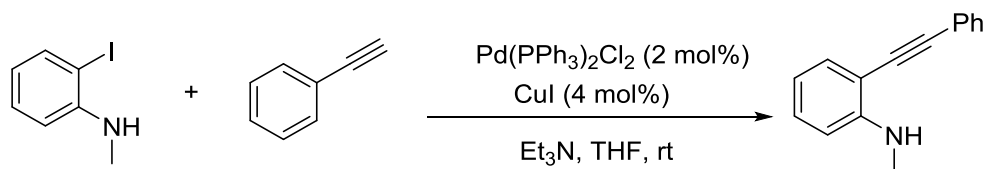


A mixture of ethyl 3-oxo-3-phenylpropanoate (1.73 mL, 10.00 mmol) and (E)-2-styrylaniline (0.965 g, 5.00 mmol) in petroleum ether (40 mL) was heated under reflux for 24 h to remove the resulting water. The resulting mixture was concentrated and the residue was taken up in DCM. The organic layer was washed with 5% HCl and water, dried over MgSO<sub>4</sub> and concentrated. Purification of the crude product by flash column chromatography afforded the enamine (yield 60%). All the compounds **3** were synthesized according to the above method.

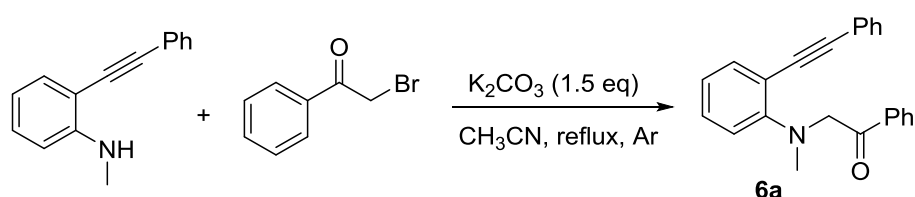


NaH (8.00 mmol, 1.00 equiv.) and THF (10 mL) were taken in an oven-dried flask under argon. *o*-Iodoaniline (8.0 mmol, 1.00 equiv.) was added to it at 0 °C and the mixture was stirred for 30 min. Iodomethane (12.00 mmol, 1.50 equiv.) was added

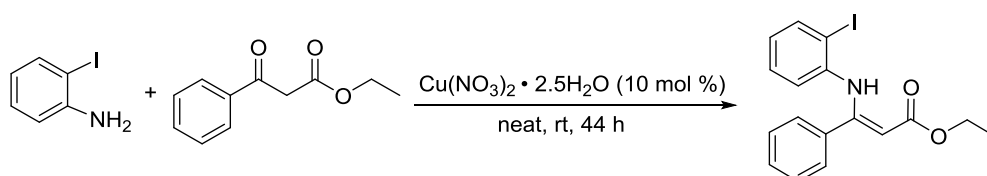
and the reaction mixture was warmed to room temperature and stirred overnight. After that, water was added and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The crude mixture was purified by flash column chromatography to afford o-(N-methylamino)-iodobenzene as an orange liquid in 92% yield.



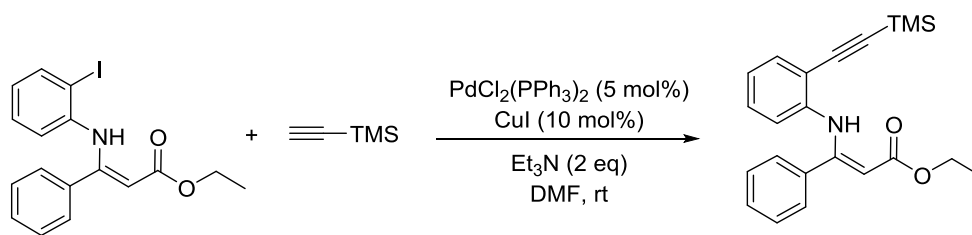
The Sonogashira cross-coupling reaction of 2-iodo-N-methylaniline and iodobenzene was carried out according to the reported procedure. 2-iodo-N-methylaniline (1.398 g, 6.00 mmol), iodobenzene (7.20 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.12 mmol),  $\text{CuI}$  (0.24 mmol), and  $\text{Et}_3\text{N}$  (6 mL) in THF (8 mL) were stirred for 15 h under nitrogen at room temperature. The reaction mixture was then quenched with water and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over  $\text{MgSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; hexane : ethyl acetate = 100 : 1) afforded the target product.



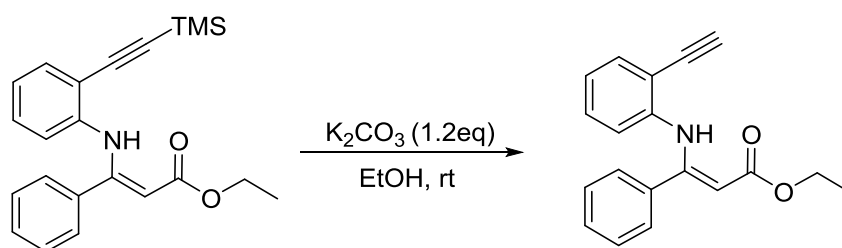
The corresponding 2-Br-phenylethanone (5.00 mmol), N-substituted aniline (5.00 mmol),  $\text{K}_2\text{CO}_3$  (7.50 mmol) were dissolved in  $\text{CH}_3\text{CN}$  (10 mL) and heated to reflux for 24 h under Ar atmosphere. The reaction was then filtered and concentrated in vacuo. The crude product was purified via flash chromatography with PE/EA as elute.



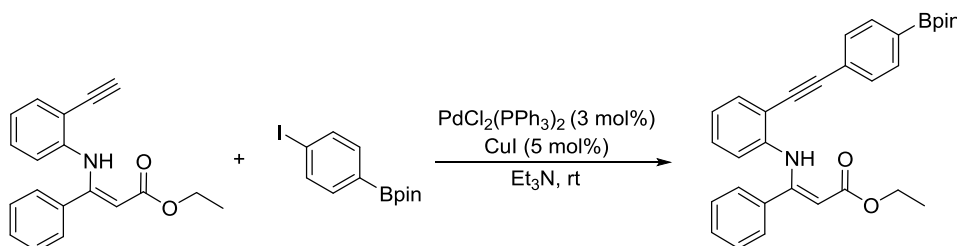
A mixture of 2-iodoaniline (1.12 g, 5.0 mmol), ethyl benzoylacetate (2.66 mL, 15.0 mmol) and  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (119 mg, 0.5 mmol) was stirred for 44 h at room temperature. The reaction mixture was quenched with water and organic materials were extracted twice with EtOAc. The combined extracts were washed with brine and dried over  $\text{NaSO}_4$ . After removal of the solvents, the resulting crude residue was purified by flash column chromatography (silica gel; PE : EA= 100:1) to afford (Z)-ethyl 3-(2-iodophenylamino)-3-phenylacrylate (1.53 g, 3.89 mmol) as a white solid in 72% yield.



A DMF solution (10 mL) of (Z)-ethyl 3-(2-iodophenylamino)-3-phenylacrylate (977.5 mg, 2.5 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (87.7 mg, 0.125 mmol), copper iodide (47.5, 0.25 mmol), triethylamine (0.9 mL, 5 mmol) and ethynyltrimethylsilane (294 mg, 3 mmol) was stirred overnight under nitrogen at room temperature. The reaction was quenched with saturated ammonium chloride solution and the aqueous layer extracted twice with EtOAc. The combined organic layers were washed with brine, dried over  $\text{NaSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE : EA= 30:1) afforded ethyl (Z)-3-phenyl-3-((2-((trimethylsilyl)ethynyl)phenyl)amino)acrylate as a yellow solid in 87% yield.

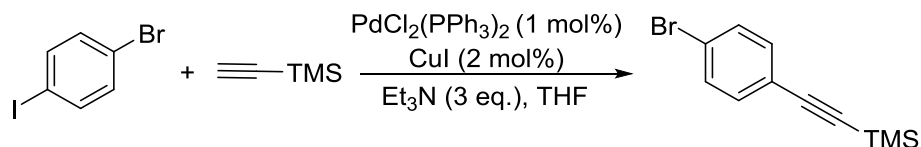


To a solution of ethyl (Z)-3-phenyl-3-((2-((trimethylsilyl)ethynyl)phenyl)amino)acrylate (844 mg, 2.3 mmol) in EtOH (10 mL) was added potassium carbonate (380 mg, 2.76 mmol). The resulting mixture was stirred for 4 h at room temperature. The solvent was then removed in vacuo. Water was then added and the aqueous layer extracted twice with EtOAc. The combined organic layers were washed with brine, dried over  $\text{NaSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE:EA=20:1) afforded ethyl (Z)-3-((2-ethynylphenyl)amino)-3-phenylacrylate as a white solid in 91% yield.

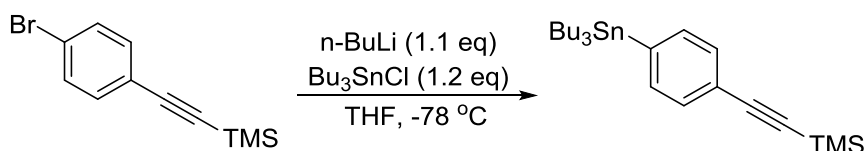


To a solution of 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 mmol, 396 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (21 mg, 0.03 mmol), copper iodide (9.5 mg, 0.05 mmol) in  $\text{Et}_3\text{N}$  (6 mL) was slowly added ethyl (Z)-3-((2-ethynylphenyl)amino)-3-phenylacrylate (1 mmol, 391 mg) in  $\text{Et}_3\text{N}$  (4 mL) under nitrogen at room temperature. After stirring overnight at room temperature, Water was then added and the aqueous layer extracted twice with EtOAc. The combined organic layers were washed with brine, dried over  $\text{NaSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE : EA= 40:1) afforded ethyl (Z)-3-phenyl-3-((2-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)phenyl)amino)-

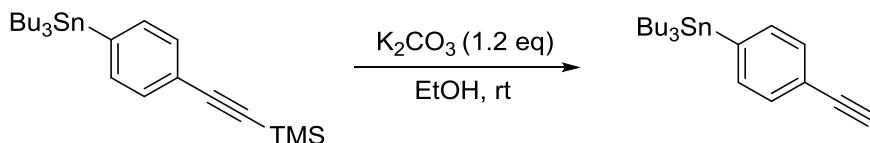
acrylate as a white solid in 62% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 10.86 (s, 1H), 7.85 – 7.69 (m, 4H), 7.47 – 7.42 (m, 1H), 7.40 – 7.28 (m, 5H), 6.87 – 6.79 (m, 2H), 6.23 – 6.15 (m, 1H), 5.06 (s, 1H), 4.24 (q,  $J = 7.1$  Hz, 2H), 1.35 (d,  $J = 10.3$  Hz, 15H). IR( $\text{cm}^{-1}$ ): 3059, 2976, 2925, 1662, 1617, 1592, 1550, 1492, 1455, 1392, 1359, 1322 1287, 1174, 1142, 1081, 1020, 9961, 858, 838, 802, 771, 751, 699.



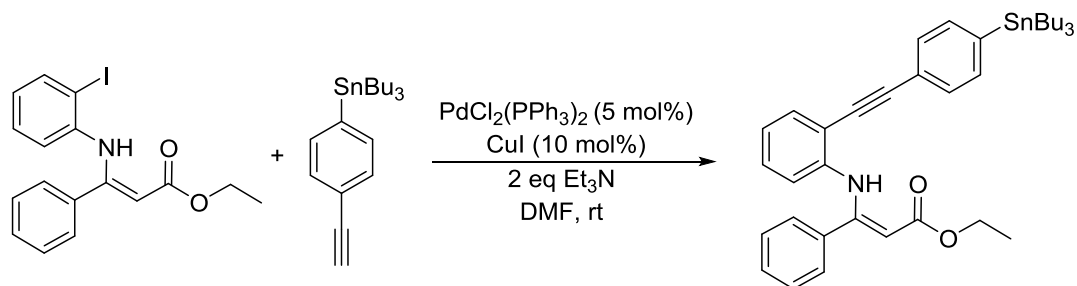
A THF solution (20 mL) of 1-bromo-4-iodobenzene (1.414g, 5mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (35mg, 0.05 mmol), copper iodide (19, 0.1 mmol), triethylamine (2.1 mL, 15 mmol) and ethynyltrimethylsilane (589mg, 6 mmol) was stirred overnight under nitrogen at room temperature. The reaction was quenched with saturated ammonium chloride solution and the aqueous layer extracted twice with EtOAc. The combined organic layers were washed with brine, dried over  $\text{NaSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE: EA= 200:1) afforded ((4-bromophenyl)ethynyl)trimethylsilane as a white solid in 92% yield.



Into a 100 mL round bottom flask containing a solution of ((4-bromophenyl)ethynyl)trimethylsilane (1.16 g, 4.6 mmol) in THF (10 mL),  $n\text{-BuLi}$  (2.2 mL, 5.5 mmol) was added dropwise at  $-78^\circ\text{C}$  from an attached addition funnel. The reaction mixture was stirred for 45 min before adding dropwise tri- $n$ -butyltin chloride (1.5 mL, 5.2 mmol). The resulting mixture was stirred for 7h at room temperature, then quenched with water, extracted with EtOAc and dried over  $\text{NaSO}_4$ . Purification of the crude product by flash column chromatography (silica gel; PE) afforded trimethyl((4-(tributylstannyl)phenyl)ethynyl)silane as a clear liquid in 82% yield.

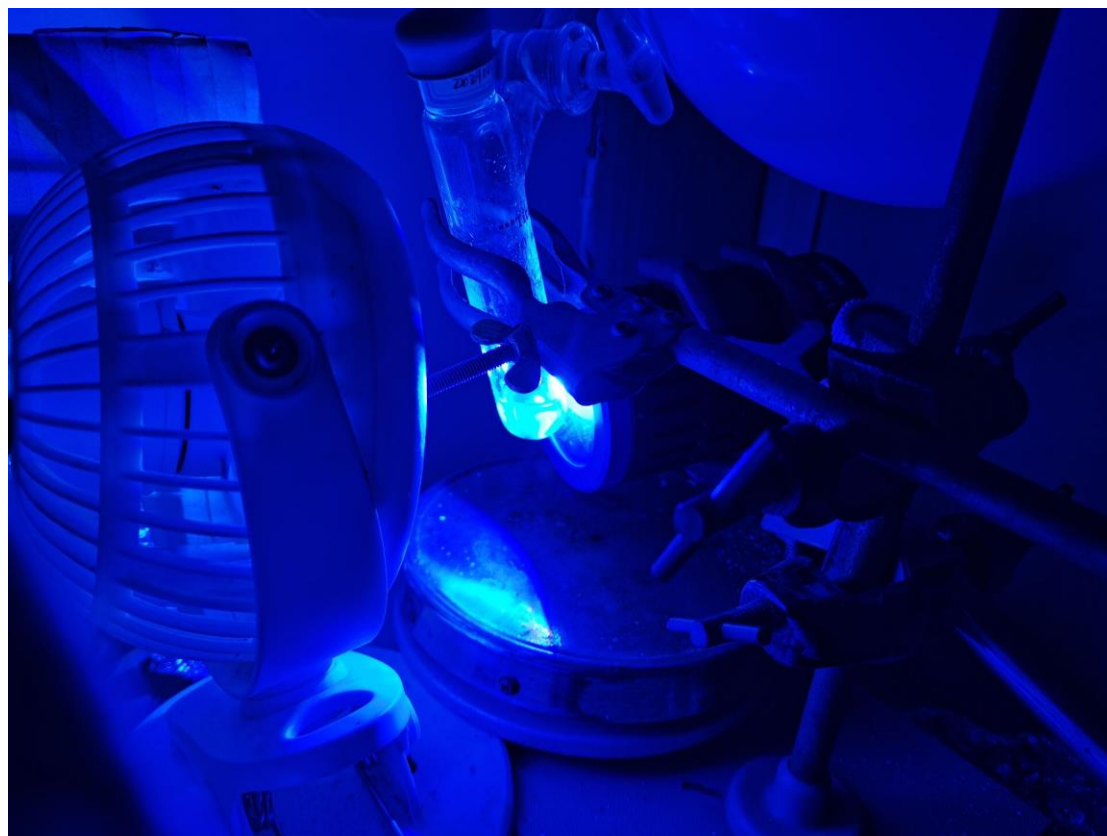


To a solution of trimethyl((4-(tributylstannyl)phenyl)ethynyl)silane (1.7 mg, 3.8 mmol) in EtOH (10 mL) was added potassium carbonate (629 mg, 4.56 mmol). The resulting mixture was stirred for 4h at room temperature. The solvent was then removed in vacuo. Water was then added and the aqueous layer extracted twice with EtOAc. The combined organic layers were washed with brine, dried over  $\text{NaSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE) afforded tributyl(4-ethynylphenyl)stannane as a clear liquid in 90% yield.

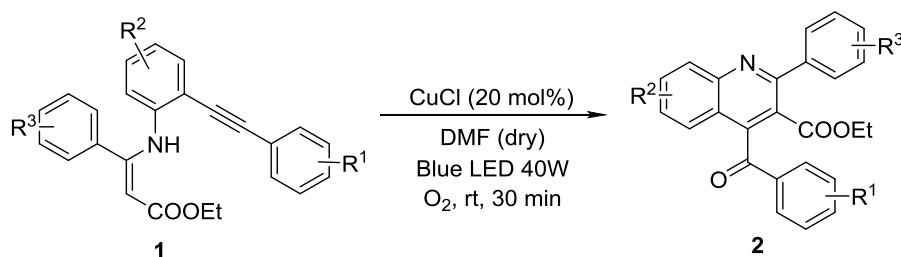


A DMF solution (6 mL) of (Z)-ethyl 3-(2-iodophenylamino)-3-phenylacrylate (391 mg, 1 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (35 mg, 0.05 mmol), copper iodide (19 mg, 0.1 mmol), triethylamine (0.3 mL, 3 mmol) and tributyl(4-ethynylphenyl)stannane (468 mg, 1.2 mmol) was stirred overnight at room temperature in Argon. The reaction was quenched with saturated ammonium chloride solution and the aqueous layer extracted twice with EtOAc. The combined organic layers were washed with brine, dried over  $\text{NaSO}_4$  and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE:EA = 30:1) afforded ethyl (Z)-3-phenyl-3-((2-((4-(tributylstannyl)phenyl)ethynyl)phenyl)amino)acrylate as a yellow solid in 71% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 10.76 (s, 1H), 7.65 (d,  $J$  = 8.1 Hz, 2H), 7.53 – 7.42 (m, 3H), 7.39 – 7.33 (m, 3H), 7.31 (d,  $J$  = 4.3 Hz, 2H), 6.87 – 6.79 (m, 2H), 6.21 (d,  $J$  = 7.1 Hz, 1H), 5.06 (s, 1H), 4.25 (q,  $J$  = 7.2 Hz, 2H), 1.60 – 1.50 (m, 6H), 1.35 (dt,  $J$  = 14.3, 7.3 Hz, 9H), 1.16 – 0.99 (m, 6H), 0.89 (t,  $J$  = 7.3 Hz, 9H). IR ( $\text{cm}^{-1}$ ): 3059, 2954, 2925, 2869, 2851, 1663, 1616, 1575, 1510, 1455, 1375, 1360, 1348, 1291, 1234, 1176, 1107, 1064, 1006, 969, 923, 835, 794, 768, 749, 706, 697, 634, 616.

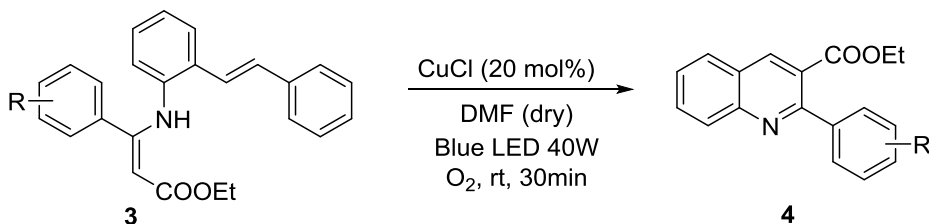
## VI. General Procedure for the synthesis of product 2, 4, 5, 7



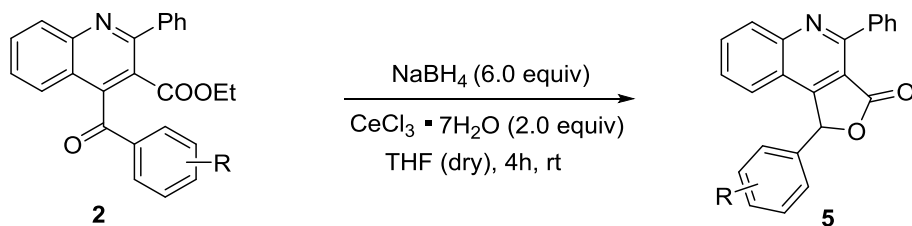
## The device of the reaction



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, ethyl (E)-3-phenyl-3-((2-(phenylethynyl)phenyl)amino)acrylate **1a** (0.2 mmol), CuCl (0.040 mmol). The flask was evacuated and backfilled with O<sub>2</sub> for 3 times. Then DMF (4.0 mL) was added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W,  $\lambda = 427$  nm). The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (8:1)).



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, ethyl (E)-3-phenyl-3-((E)-styryl)phenylamino)acrylate **2a** (0.2 mmol), CuCl (0.040 mmol). The flask was evacuated and backfilled with O<sub>2</sub> for 3 times. Then DMF (4.0 mL) was added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W,  $\lambda = 427$  nm). The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (10:1)).



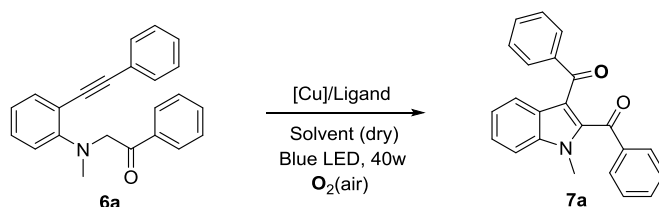


Ethyl 4-benzoyl-2-phenylquinoline-3-carboxylate **2** (0.30 mmol),  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (2.0 equiv, 0.60 mmol) was dissolved in dry THF (6.0 mL) and then  $\text{NaBH}_4$  (6.0 equiv, 1.80 mmol) was added at  $0^\circ\text{C}$ . The reaction mixture was then stirred at room temperature. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 4:1) furnished the product **5**.



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 2-(methyl(2-(phenylethynyl)phenyl)amino)-1-phenylethan-1-one **6** (0.2 mmol),  $\text{CuBr}_2$  (0.020 mmol), Phen (0.040 mmol), DMF (4.0 mL). The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W,  $\lambda = 427\text{nm}$ ) in air. The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. Purification of the crude product by flash column chromatography afforded the product **7** (petroleum ether/ethyl acetate as eluent (8:1)).

**VII.** Table S1. Screening of reaction conditions <sup>a</sup>

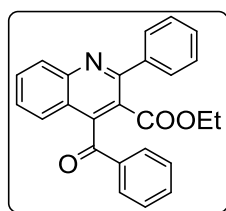


| Entry | Ligand                            | Catalyst                             | Solvent | Time(h) | Yield(%) <sup>b</sup> |
|-------|-----------------------------------|--------------------------------------|---------|---------|-----------------------|
| 1     | bipy                              | $\text{CuCl}$ (20 mmol%)             | DMF     | 17      | 61                    |
| 2     | phen                              | $\text{CuCl}$ (20 mmol%)             | DMF     | 24      | 67                    |
| 3     | dmp                               | $\text{CuCl}$ (20 mmol%)             | DMF     | 24      | 41                    |
| 4     | 4,4'-Di-tert-butyl-2,2'-bipyridyl | $\text{CuCl}$ (20 mmol%)             | DMF     | 24      | 59                    |
| 5     | 6,6'-Dimethyl-2,2'-bipyridyl      | $\text{CuCl}$ (20 mmol%)             | DMF     | 23      | <5                    |
| 6     | Phen                              | $\text{CuBr}$ (20 mmol%)             | DMF     | 19      | 79                    |
| 7     | Phen                              | $\text{CuBr}_2$ (20 mmol%)           | DMF     | 20      | 85                    |
| 8     | Phen                              | $\text{CuCl}_2$ (20 mmol%)           | DMF     | 20      | 53                    |
| 9     | Phen                              | $\text{Cu}(\text{OAc})_2$ (20 mmol%) | DMF     | 20      | 27                    |

|                    |      |                              |                    |    |           |
|--------------------|------|------------------------------|--------------------|----|-----------|
| 10                 | Phen | CuBr <sub>2</sub> (20 mmol%) | CH <sub>3</sub> CN | 10 | 41        |
| 11                 | Phen | CuBr <sub>2</sub> (20 mmol%) | THF                | 15 | 45        |
| 12                 | Phen | CuBr <sub>2</sub> (20 mmol%) | DCE                | 10 | 50        |
| 13 <sup>c</sup>    | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 12 | 82        |
| 14 <sup>c, d</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | <b>80</b> |
| 15 <sup>c, e</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 15 | <5        |
| 16 <sup>c, f</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 15 | 65        |
| 17 <sup>c, g</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 30 | 44        |
| 18 <sup>c, h</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | 84        |
| 19 <sup>c, i</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | –         |
| 20 <sup>c, j</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | –         |
| 21 <sup>c, k</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | 62        |
| 22 <sup>c, l</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | 53        |
| 23 <sup>c, m</sup> | Phen | CuBr <sub>2</sub> (10 mmol%) | DMF                | 10 | 50        |

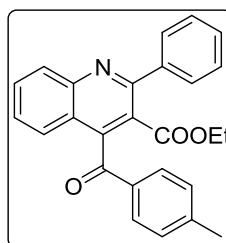
<sup>a</sup> Reaction conditions: **6a** (0.1 mmol), Cu catalyst (20 mmol%), Ligand (20 mmol%), solvent (2.0 mL), r.t., under O<sub>2</sub> atmosphere, Kessil A 160WE TUNA BLUE 40W ( $\lambda$  = 427 nm) was used. <sup>b</sup> Isolated yield. <sup>c</sup> 10 mol% Cu catalyst was used. <sup>d</sup> in air. <sup>e</sup> Under argon atmosphere. <sup>f</sup> 10 mol% phen was used. <sup>g</sup> household 30W blue LED was used. <sup>h</sup> white light. <sup>i</sup> without light at rt. <sup>j</sup> without light at 60 °C. <sup>k</sup> 2 eq. Na<sub>2</sub>CO<sub>3</sub> was added. <sup>l</sup> 2 eq. Et<sub>3</sub>N was added. <sup>m</sup> 2 eq. DABCO was added.

### VIII. Date of products 2, 4, 5, 7



**2a**

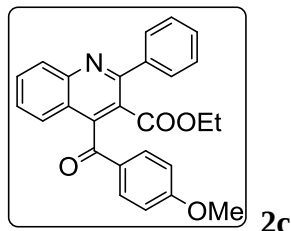
ethyl 4-benzoyl-2-phenylquinoline-3-carboxylate, 68%, 52 mg, M.P.= 124-126 °C, yellow solid. CAS: 1373169-66-4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.25 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.79 (m, 3H), 7.73 – 7.69 (m, 2H), 7.67 – 7.59 (m, 2H), 7.53 – 7.44 (m, 6H), 3.87 (q, *J* = 7.1 Hz, 2H), 0.81 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 195.51, 166.93, 157.28, 148.00, 146.93, 140.12, 136.47, 134.27, 131.53, 130.02, 129.61, 128.93, 128.84, 128.53, 128.38, 127.87, 125.71, 123.40, 123.00, 61.81, 13.11. IR(cm<sup>-1</sup>): 3059, 2980, 1721, 1674, 1612, 1595, 1569, 1551, 1492, 1400, 1372, 1348, 1295, 1233, 1176, 1107, 1062, 1023, 969, 921, 849, 800, 769, 738, 704, 631.



**2b**

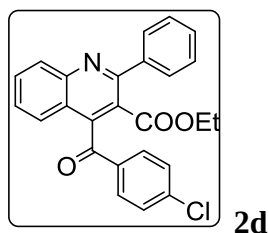
ethyl 4-(4-methylbenzoyl)-2-phenylquinoline-3-carboxylate, 57%, 45 mg, M.P.= 134-136 °C, yellow solid. CAS: 1374309-36-0. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.24 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.68 (m, 5H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.28 – 7.24 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>): 195.07, 166.97, 157.27, 147.99, 147.12, 145.45, 140.18, 134.15, 131.45, 129.99, 129.79, 129.57, 128.90, 128.54, 128.38, 127.78, 123.38, 123.07, 61.77, 21.83, 13.15. IR(cm<sup>-1</sup>): 3059, 2980, 1723, 1671, 1603, 1570, 1551, 1490, 1455, 1401, 1372, 1347, 1310, 1296, 1234, 1178, 1137, 1106, 1064, 1016, 969, 913, 832, 797, 769, 746, 728, 704, 644, 607.

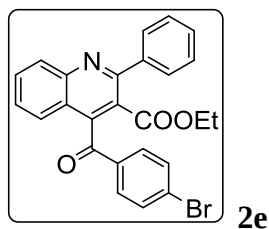


ethyl 4-(4-methoxybenzoyl)-2-phenylquinoline-3-carboxylate, 74%, 61mg, M.P.= 152-154 °C, yellow solid. CAS: 1374309-40-6. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.24 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.76 (m, 3H), 7.74 – 7.65 (m, 3H), 7.49 (dd, *J* = 16.1, 7.6 Hz, 4H), 6.93 (d, *J* = 9.1 Hz, 2H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 193.76, 167.01, 164.42, 157.15, 147.93, 147.02, 140.10, 131.39, 129.91, 129.68, 128.87, 128.49, 128.35, 127.73, 125.79, 123.38, 123.03, 114.07, 61.74, 55.51, 13.15.

IR(cm<sup>-1</sup>): 3060, 2980, 2840, 1723, 1666, 1596, 1572, 1551, 1509, 1491, 1456, 1443, 1422, 1400, 1372, 1347, 1296, 1263, 1244, 1169, 1138, 1107, 1064, 1024, 968, 923, 841, 811, 770, 754, 704, 669, 636, 609.

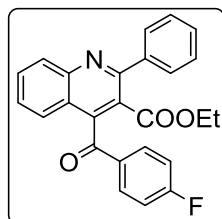


ethyl 4-(4-chlorobenzoyl)-2-phenylquinoline-3-carboxylate, 70%, 58 mg, M.P.= 165-167 °C, yellow solid. CAS: 1373169-81-3. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.26 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.70 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.55 – 7.42 (m, 6H), 3.90 (q, *J* = 7.1 Hz, 2H), 0.83 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 194.40, 166.93, 157.35, 148.03, 146.46, 140.89, 140.06, 134.92, 131.66, 130.92, 130.12, 129.28, 128.99, 128.52, 128.41, 128.01, 125.50, 123.38, 122.82, 61.92, 13.16. IR(cm<sup>-1</sup>): 3060, 2979, 1720, 1675, 1585, 1570, 1551, 1490, 1456, 1399, 1371, 1348, 1295, 1235, 1173, 1106, 1090, 1063, 1013, 970, 922, 839, 798, 767, 753, 736, 718, 702, 637.



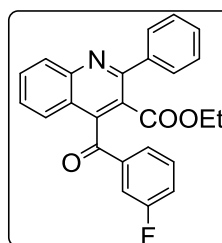
ethyl 4-(4-bromobenzoyl)-2-phenylquinoline-3-carboxylate, 68%, 63 mg, M.P.= 161-163 °C, yellow solid. CAS: 1374309-39-3. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.26 (d, *J* =

8.5 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.82 (t,  $J = 7.7$  Hz, 1H), 7.70 (d,  $J = 7.8$  Hz, 2H), 7.62 (d,  $J = 8.1$  Hz, 1H), 7.55 – 7.45 (m, 4H), 7.15 (t,  $J = 8.6$  Hz, 2H), 3.90 (q,  $J = 7.1$  Hz, 2H), 0.83 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 193.94, 166.96, 165.07, 157.29, 148.02, 146.54, 140.05, 133.07, 132.41, 132.32, 131.61, 130.09, 128.98, 128.51, 128.40, 127.97, 125.54, 123.39, 122.83, 116.27, 116.05, 61.87, 13.15. IR( $\text{cm}^{-1}$ ): 3060, 2980, 1719, 1675, 1612, 1584, 1568, 1550, 1481, 1456, 1443, 1397, 1371, 1348, 1294, 1235, 1174, 1133, 1106, 1070, 1010, 969, 923, 837, 796, 768, 751, 732, 710, 699, 635, 616.



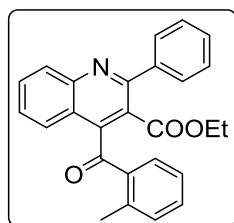
**2f**

ethyl 4-(4-fluorobenzoyl)-2-phenylquinoline-3-carboxylate, 66%, 53 mg, M.P.= 169-171 °C, yellow solid. CAS: 2114957-68-3.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.26 (d,  $J = 8.4$  Hz, 1H), 7.94 – 7.86 (m, 2H), 7.82 (t,  $J = 8.4$  Hz, 1H), 7.70 (dd,  $J = 7.5$ , 2.0 Hz, 2H), 7.63 (d,  $J = 9.1$  Hz, 1H), 7.55 – 7.45 (m, 4H), 7.15 (t,  $J = 8.7$  Hz, 2H), 3.90 (q,  $J = 7.2$  Hz, 2H), 0.83 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 193.96, 167.64 ( $J = 256.0$  Hz), 166.97, 165.08, 157.31, 148.03, 146.55, 140.06, 133.10 ( $J = 3.0$  Hz), 133.07, 132.43 ( $J = 10.0$  Hz), 132.33, 131.62, 130.11, 128.99, 128.52, 128.42, 127.98, 125.55, 123.39, 122.84, 116.29 ( $J = 22.0$  Hz), 116.07, 61.89, 13.16.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -102.42. IR( $\text{cm}^{-1}$ ): 3061, 2926, 1721, 1676, 1595, 1551, 1505, 1491, 1454, 1411, 1372, 1347, 1297, 1233, 1153, 1106, 1063, 1013, 970, 923, 843, 768, 752, 730, 704, 631, 602.



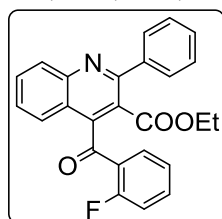
**2g**

ethyl 4-(3-fluorobenzoyl)-2-phenylquinoline-3-carboxylate, 65%, 62 mg, M.P.= 114-116 °C, yellow solid. CAS: 2114957-69-4.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.26 (d,  $J = 8.5$  Hz, 1H), 7.81 (d,  $J = 8.3$  Hz, 1H), 7.70 (dd,  $J = 7.5$ , 1.9 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.58 – 7.40 (m, 6H), 7.32 (td,  $J = 8.1$ , 2.2 Hz, 1H), 3.90 (q,  $J = 7.1$  Hz, 2H), 0.82 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 194.41, 194.38, 166.86, 164.06 ( $J = 248.0$  Hz), 161.58, 157.34, 148.01, 146.42, 140.04, 138.55 ( $J = 6.0$  Hz), 138.49, 131.67, 130.66 ( $J = 7.0$  Hz), 130.59, 130.09, 128.96, 128.51, 128.38, 128.03, 125.70, 125.68, 125.45, 122.79, 121.44 ( $J = 21.0$  Hz), 121.22, 115.79 ( $J = 22.0$  Hz), 115.57, 61.89, 13.11.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -110.95. IR( $\text{cm}^{-1}$ ): 3063, 2981, 1720, 1679, 1610, 1588, 1570, 1551, 1483, 1444, 1400, 1372, 1348, 1297, 1255, 1235, 1171, 1134, 1107, 1076, 1060, 1015, 1001, 987, 911, 892, 879, 846, 782, 730, 704, 674, 646, 604.



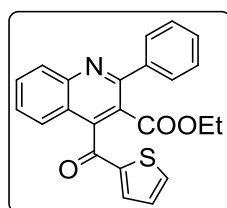
**2h**

ethyl 4-(2-methylbenzoyl)-2-phenylquinoline-3-carboxylate, 76%, 60 mg, M.P.= 133-135 °C, yellow solid. CAS: 373169-83-5.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.24 (d,  $J$  = 8.4 Hz, 1H), 7.80 (ddd,  $J$  = 8.4, 6.9, 1.3 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.52 (t,  $J$  = 7.7 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.38 – 7.31 (m, 2H), 7.13 (t,  $J$  = 7.3 Hz, 1H), 3.79 (q,  $J$  = 7.1 Hz, 2H), 2.79 (s, 3H), 0.75 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 196.96, 167.24, 157.03, 148.06, 147.80, 140.71, 140.10, 135.42, 133.02, 132.86, 132.20, 131.33, 129.97, 128.87, 128.47, 128.35, 127.90, 125.74, 125.60, 123.06, 61.64, 21.85, 13.10. IR( $\text{cm}^{-1}$ ): 3060, 2980, 1719, 1672, 1612, 1599, 1569, 1551, 1486, 1456, 1399, 1371, 1346, 1298, 1233, 1164, 1141, 1107, 1075, 1057, 1015, 966, 912, 870, 848, 829, 768, 739, 705, 671, 633, 603.



**2i**

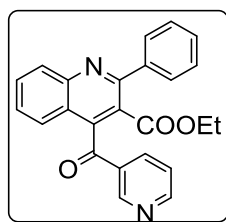
ethyl 4-(2-fluorobenzoyl)-2-phenylquinoline-3-carboxylate, 68%, 54 mg, oil. CAS: 2114957-70-7.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.24 (d,  $J$  = 8.5 Hz, 1H), 8.00 (t,  $J$  = 7.6 Hz, 1H), 7.81 (t,  $J$  = 8.4 Hz, 1H), 7.72 – 7.65 (m, 3H), 7.63 – 7.56 (m, 1H), 7.54 – 7.44 (m, 4H), 7.33 – 7.25 (m, 1H), 7.12 – 7.05 (m, 1H), 3.90 (q,  $J$  = 7.1 Hz, 2H), 0.82 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 192.13, 167.03, 163.40 ( $J$  = 259.0 Hz), 160.81, 157.47, 148.66, 148.07, 140.26, 136.19 ( $J$  = 9.0 Hz), 136.10, 131.45, 131.17, 130.03, 128.79, 128.48, 128.29, 127.84, 125.35 ( $J$  = 9.0 Hz), 125.26, 124.96, 124.59, 124.55, 122.31, 117.10 ( $J$  = 22.0 Hz), 116.88, 61.76, 13.10.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -108.53. IR( $\text{cm}^{-1}$ ): 3061, 2981, 1718, 1672, 1607, 1571, 1551, 1480, 1455, 1400, 1372, 1348, 1297, 1270, 1234, 1161, 1138, 1105, 1059, 1026, 1015, 969, 922, 869, 849, 837, 791, 768, 752, 733, 704, 654, 627, 618.



**2j**

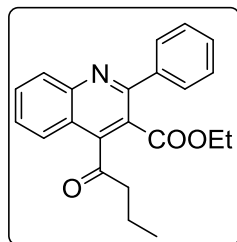
ethyl 2-phenyl-4-(thiophene-2-carbonyl)quinoline-3-carboxylate, 60%, 46 mg, M.P.= 96-98 °C, yellow solid. CAS: 1374309-44-0.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.24 (d,  $J$  = 8.3 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.72 (d,  $J$  = 2.2 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.43 (m, 3H), 7.32 (d,  $J$  = 3.8 Hz, 1H), 7.09 – 7.03 (m, 1H), 3.94 (s, 2H), 0.90 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 187.05, 166.85, 157.14, 148.05, 145.80, 143.72, 139.97, 136.09, 136.03, 131.55, 129.93, 128.96, 128.49, 128.39, 127.95, 125.64, 123.27, 122.69, 61.92, 13.18. IR( $\text{cm}^{-1}$ ): 3061, 2980, 1724, 1649,

1612, 1569, 1551, 1514, 1490, 1454, 1409, 1372, 1351, 1296, 1245, 1233, 1161, 1137, 1106, 1063, 1041, 1014, 921, 859, 843, 769, 737, 704, 677, 649, 612.



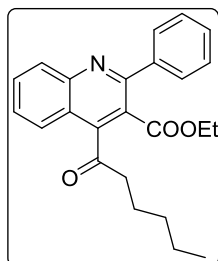
**2k**

ethyl 4-nicotinoyl-2-phenylquinoline-3-carboxylate, 69%, 53 mg, M.P.= 144-146 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 9.01 (d,  $J = 1.7$  Hz, 1H), 8.83 (dd,  $J = 4.8$ , 1.6 Hz, 1H), 8.28 (d,  $J = 8.5$  Hz, 1H), 8.18 (d,  $J = 8.0$  Hz, 1H), 7.84 (t,  $J = 7.7$  Hz, 1H), 7.70 (dd,  $J = 7.5$ , 2.0 Hz, 2H), 7.61 (d,  $J = 7.7$  Hz, 1H), 7.56 – 7.51 (m, 1H), 7.51 – 7.43 (m, 4H), 3.90 (q,  $J = 7.1$  Hz, 2H), 0.81 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 194.63, 166.85, 157.39, 154.30, 150.89, 148.05, 145.83, 139.97, 136.38, 131.98, 131.77, 130.18, 128.97, 128.46, 128.37, 128.17, 125.21, 123.73, 123.30, 122.53, 61.94, 13.09. IR( $\text{cm}^{-1}$ ): 3058, 2980, 1718, 1679, 1612, 1583, 1569, 1551, 1491, 1455, 1443, 1417, 1400, 1372, 1348, 1296, 1235, 1194, 1162, 1107, 1068, 1022, 968, 922, 850, 826, 792, 768, 748, 722, 699, 662, 633, 617; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_3^+$  ( $\text{M}+\text{H}$ ) $^+$  382.1395, found 383.1390.



**2l**

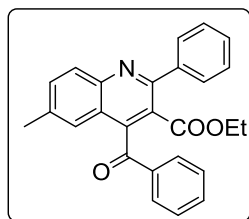
ethyl 4-butyryl-2-phenylquinoline-3-carboxylate, 48%, 33 mg, Oil. CAS: 2114957-73-0.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.21 (d,  $J = 8.3$  Hz, 1H), 7.82 (ddd,  $J = 8.4$ , 6.9, 1.4 Hz, 1H), 7.71 (d,  $J = 8.4$  Hz, 1H), 7.67 – 7.57 (m, 3H), 7.50 – 7.43 (m, 3H), 4.10 (q,  $J = 7.1$  Hz, 2H), 2.97 (t,  $J = 7.4$  Hz, 2H), 1.88 (q,  $J = 7.4$  Hz, 2H), 1.07 (t,  $J = 7.4$  Hz, 3H), 0.97 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 205.63, 167.42, 157.37, 149.27, 148.03, 140.35, 131.46, 130.16, 128.82, 128.36, 128.34, 127.91, 124.70, 121.68, 121.49, 61.96, 46.83, 16.70, 13.67, 13.34. IR( $\text{cm}^{-1}$ ): 3060, 2963, 1716, 1612, 1569, 1551, 1491, 1456, 1444, 1400, 1376, 1346, 1293, 1235, 1168, 1147, 1107, 1078, 1031, 1016, 922, 865, 838, 768, 703, 636.



**2m**

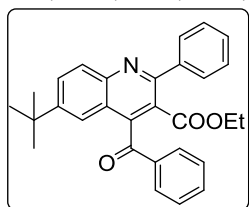
ethyl 4-hexanoyl-2-phenylquinoline-3-carboxylate, 43%, 32 mg, oil. CAS: 2307775-99-9.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.21 (d,  $J = 8.2$  Hz, 1H), 7.83 (ddd,  $J = 8.4$ , 6.8, 1.4 Hz, 1H), 7.71 (d,  $J = 8.4$  Hz, 1H), 7.68 – 7.59 (m, 3H), 7.50 – 7.43 (m, 3H), 4.10 (q,  $J = 7.1$  Hz, 2H), 3.02 – 2.93 (m, 2H), 1.85 (p,  $J = 7.5$  Hz, 2H), 1.41 (tt,  $J = 7.6$ , 4.2 Hz, 4H), 0.95 (dt,  $J = 14.3$ , 7.2 Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 205.78, 167.45,

157.41, 149.36, 148.07, 140.39, 131.48, 130.20, 128.84, 128.40, 128.37, 127.93, 124.75, 121.72, 61.99, 44.98, 31.23, 22.89, 22.46, 13.91. IR( $\text{cm}^{-1}$ ): 3060, 2955, 1717, 1612, 1569, 1551, 1491, 1456, 1399, 1375, 1347, 1293, 1235, 1164, 1145, 1107, 1016, 922, 855, 767, 701, 637.



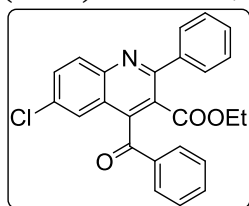
**2n**

ethyl 4-benzoyl-6-methyl-2-phenylquinoline-3-carboxylate, 71%, 56 mg, M.P.= 114-116 °C. CAS: 1373169-79-9.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.05 (d,  $J$  = 8.6 Hz, 1H), 7.77 (d,  $J$  = 7.5 Hz, 2H), 7.61 (d,  $J$  = 6.2 Hz, 2H), 7.53 (dd,  $J$  = 14.8, 7.5 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.32 (s, 1H), 3.75 (q,  $J$  = 7.1 Hz, 2H), 2.34 (s, 3H), 0.70 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 195.65, 167.00, 146.68, 146.10, 140.18, 138.14, 136.44, 134.18, 133.91, 129.62, 129.56, 128.79, 128.75, 128.49, 128.31, 124.29, 123.17, 122.98, 61.69, 21.72, 13.07. IR( $\text{cm}^{-1}$ ): 3058, 2980, 1721, 1675, 1622, 1580, 1552, 1494, 1448, 1402, 1372, 1347, 1292, 1277, 1235, 1175, 1108, 1061, 1023, 950, 912, 856, 828, 805, 791, 774, 708, 697, 628.



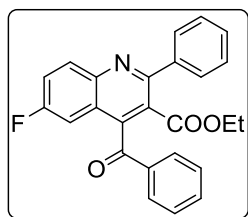
**2o**

ethyl 4-benzoyl-6-(tert-butyl)-2-phenylquinoline-3-carboxylate, 63%, 55 mg, oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.19 (d,  $J$  = 9.0 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.69 (d,  $J$  = 9.2 Hz, 2H), 7.59 (s, 1H), 7.53 (d,  $J$  = 1.9 Hz, 1H), 7.50 – 7.42 (m, 5H), 3.86 (q,  $J$  = 7.1 Hz, 2H), 1.26 (s, 9H), 0.81 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 195.91, 167.15, 156.56, 150.85, 146.67, 146.60, 140.24, 136.67, 134.10, 130.56, 129.54, 129.45, 128.75, 128.73, 128.49, 128.32, 122.68, 120.52, 61.71, 35.05, 30.82, 13.10. IR( $\text{cm}^{-1}$ ): 3060, 2962, 1721, 1675, 1618, 1595, 1580, 1551, 1496, 1448, 1402, 1363, 1348, 1297, 1263, 1236, 1199, 1177, 1106, 1075, 1058, 1023, 974, 948, 914, 839, 801, 771, 756, 710, 697, 653, 629, 604. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{29}\text{H}_{28}\text{N}_1\text{O}_3^+$ , ( $\text{M}+\text{H}$ ) $^+$  438.2069, found 438.2064.



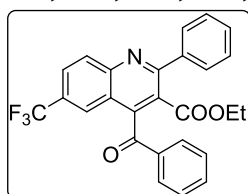
**2p**

ethyl 4-benzoyl-6-chloro-2-phenylquinoline-3-carboxylate, 68%, 57 mg, M.P.= 142-144 °C, yellow solid. CAS: 1373169-77-7.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.19 (d,  $J$  = 9.0 Hz, 1H), 7.85 (d,  $J$  = 7.4 Hz, 2H), 7.77 – 7.68 (m, 3H), 7.66 – 7.60 (m, 2H), 7.51 – 7.45 (m, 5H), 3.84 (q,  $J$  = 7.1 Hz, 2H), 0.80 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 194.69, 166.60, 146.41, 139.65, 136.07, 134.52, 133.86, 132.51, 131.53, 129.61, 129.14, 128.92, 128.48, 128.42, 124.38, 124.18, 123.59, 61.94, 13.07. IR( $\text{cm}^{-1}$ ): 3060, 2981, 1723, 1675, 1595, 1580, 1548, 1479, 1449, 1427, 1397, 1368, 1345, 1278, 1236, 1177, 1107, 1088, 1058, 1023, 1000, 973, 944, 930, 866, 834, 733, 701, 694, 646, 623.



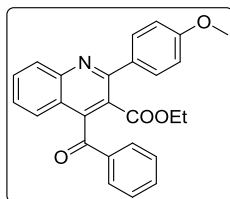
**2q**

ethyl 4-benzoyl-6-fluoro-2-phenylquinoline-3-carboxylate, 58%, 46 mg, M.P.= 108-110 °C, yellow solid. CAS: 2114957-71-8.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.26 (dd,  $J$  = 9.3, 5.4 Hz, 1H), 7.85 (d,  $J$  = 7.3 Hz, 2H), 7.70 (dd,  $J$  = 7.4, 2.1 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.52 – 7.44 (m, 5H), 7.28 (dd,  $J$  = 9.3, 2.8 Hz, 1H), 3.86 (q,  $J$  = 7.1 Hz, 2H), 0.81 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 194.88, 166.74, 162.22 ( $J$  = 249.0 Hz), 159.73, 146.16, 145.20, 139.76, 136.10, 134.49, 132.63 ( $J$  = 9.0 Hz), 132.54, 129.63, 129.03, 128.93, 128.48, 128.43, 124.20, 123.71 ( $J$  = 10.0 Hz), 123.61, 122.06, 121.80, 109.31 ( $J$  = 23.0 Hz), 109.08, 61.94.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -109.67. IR( $\text{cm}^{-1}$ ): 3060, 2981, 1723, 1675, 1625, 1595, 1581, 1553, 1493, 1449, 1402, 1373, 1347, 1290, 1235, 1186, 1106, 1075, 1058, 1023, 1000, 986, 960, 912, 837, 807, 794, 761, 729, 698, 629.



**2r**

ethyl 4-benzoyl-2-phenyl-6-(trifluoromethyl)quinoline-3-carboxylate, 51%, 46 mg, M.P.= 134-136 °C, yellow solid. CAS: 2307775-98-8.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.37 (d,  $J$  = 8.6 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.84 (d,  $J$  = 7.3 Hz, 2H), 7.73 (dd,  $J$  = 6.7, 3.0 Hz, 2H), 7.65 (t,  $J$  = 7.4 Hz, 1H), 7.50 (dd,  $J$  = 6.9, 2.5 Hz, 5H), 3.84 (q,  $J$  = 7.1 Hz, 2H), 0.82 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 194.43, 166.45, 159.27, 148.91, 139.46, 136.05, 134.70, 131.32, 129.79 ( $J$  = 33.0 Hz), 129.65, 129.49, 129.46, 129.00, 128.57, 128.54, 127.23 ( $J$  = 3.0 Hz), 127.20, 124.68 ( $J$  = 252.0 Hz), 123.60 ( $J$  = 5.0 Hz), 123.55, 122.16, 62.11, 13.10.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -62.56. IR( $\text{cm}^{-1}$ ): 3061, 2981, 1724, 1675, 1630, 1595, 1579, 1556, 1447, 1403, 1376, 1349, 1319, 1297, 1279, 1237, 1171, 1129, 1076, 1056, 1023, 973, 944, 894, 842, 824, 803, 773, 735, 708, 696, 642, 628, 609.

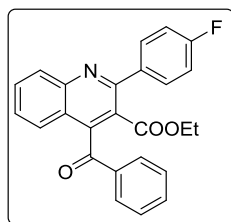


**2s**

ethyl 4-benzoyl-2-(4-methoxyphenyl)quinoline-3-carboxylate, 66%, 54 mg, M.P.= 146-148 °C, yellow solid. CAS: 1373169-70-0.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.22 (d,  $J$  = 8.4 Hz, 1H), 7.86 (d,  $J$  = 7.3 Hz, 2H), 7.78 (ddd,  $J$  = 8.4, 6.9, 1.3 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.65 – 7.57 (m, 2H), 7.50 – 7.42 (m, 3H), 7.00 (d,  $J$  = 8.8 Hz, 2H), 3.90 (q,  $J$  = 7.1 Hz, 2H), 3.86 (s, 3H), 0.87 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 195.52, 167.17, 160.41, 148.02, 136.45, 134.22, 132.48, 131.38, 130.02, 129.87, 129.61, 128.80, 127.55, 125.63, 123.24, 122.74, 113.86, 61.77, 55.32, 13.22. IR( $\text{cm}^{-1}$ ): 3060, 2979, 2935, 1720, 1674, 1608, 1578, 1549, 1515, 1490, 1449, 1418,

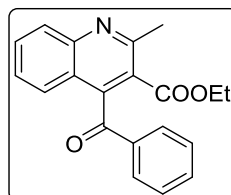


1399, 1371, 1348, 1293, 1250, 1235, 1176, 1106, 1062, 1029, 968, 912, 854, 836, 798, 764, 707, 686, 674, 646, 619.



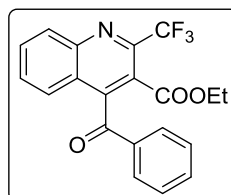
**2t**

ethyl 4-benzoyl-2-(4-fluorophenyl)quinoline-3-carboxylate, 57%, 45 mg, M.P.= 157-159 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.23 (d,  $J = 8.4$  Hz, 1H), 7.89 – 7.78 (m, 3H), 7.74 – 7.67 (m, 2H), 7.67 – 7.59 (m, 2H), 7.49 (dt,  $J = 15.7, 7.4$  Hz, 3H), 7.17 (t,  $J = 8.7$  Hz, 2H), 3.89 (q,  $J = 7.1$  Hz, 2H), 0.85 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 195.34, 166.81, 164.59 ( $J = 248.0$  Hz), 162.11, 147.97, 147.07, 136.42, 134.31, 131.65, 130.54 ( $J = 8.0$  Hz), 130.46, 129.95, 129.59, 128.86, 127.98, 125.73, 123.18, 123.01, 115.52 ( $J = 21.0$  Hz), 115.31, 61.90, 13.17.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -112.43. IR( $\text{cm}^{-1}$ ): 3063, 2981, 1722, 1675, 1596, 1578, 1552, 1492, 1449, 1398, 1372, 1348, 1298, 1276, 1158, 1138, 1105, 1061, 1014, 970, 912, 857, 806, 763, 744, 728, 706, 686, 646, 618. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{19}\text{F}_1\text{N}_1\text{O}_3^+$ , ( $\text{M}+\text{H}$ ) $^+$  400.1349, found 400.1343.



**2u**

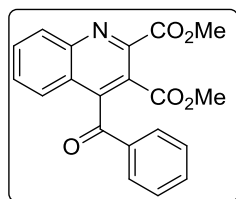
ethyl 4-benzoyl-2-methylquinoline-3-carboxylate, 62%, 40 mg, M.P.= 103-105 °C, yellow solid. CAS: 1373169-72-2.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.10 (d,  $J = 8.4$  Hz, 1H), 7.84 – 7.72 (m, 3H), 7.64 – 7.54 (m, 2H), 7.49 – 7.41 (m, 3H), 4.09 (q,  $J = 7.2$  Hz, 2H), 2.96 (s, 3H), 1.02 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 195.44, 166.16, 157.04, 148.05, 147.22, 136.64, 134.03, 131.51, 129.35, 129.04, 128.80, 127.16, 125.89, 122.91, 122.47, 61.88, 25.17, 13.27. IR( $\text{cm}^{-1}$ ): 3061, 2981, 1727, 1676, 1612, 1595, 1560, 1493, 1449, 1404, 1376, 1340, 1289, 1239, 1210, 1177, 1159, 1128, 1079, 1040, 1021, 918, 867, 793, 762, 705, 688, 669, 642, 623.



**2v**

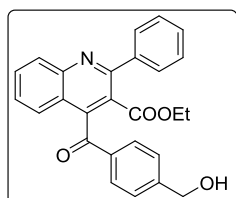
ethyl 4-benzoyl-2-(trifluoromethyl)quinoline-3-carboxylate, 65.7%, 49mg, M.P.=109-111 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.32 (d,  $J = 8.5$  Hz, 1H), 7.91 (ddd,  $J = 8.4, 6.5, 1.7$  Hz, 1H), 7.80 (d,  $J = 7.3$  Hz, 2H), 7.71 – 7.62 (m, 3H), 7.49 (t,  $J = 7.9$  Hz, 2H), 4.15 (q,  $J = 7.2$  Hz, 2H), 1.11 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 194.20, 164.52, 147.93, 146.69, 144.51 ( $J = 35.0$  Hz), 144.16, 136.14, 134.65, 132.35, 130.58, 130.20, 129.71, 128.98, 125.84, 125.08, 124.83, 122.33 ( $J = 274.0$  Hz), 119.59, 121.93, 116.84, 62.73, 13.32.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -63.71. IR( $\text{cm}^{-1}$ ): 3065, 2984, 1737, 1676, 1614, 1596, 1580, 1568, 1496, 1450, 1412, 1374, 1330, 1306, 1255, 1236, 1181, 1148, 1125, 1064, 1014, 978, 922, 863, 820, 799, 765,

715, 697, 686, 636. HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{15}F_3N_1O_3^+$ ,  $(M+H)^+$  374.1004, found 374.0999.



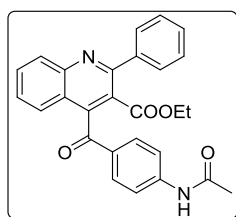
**2w**

dimethyl 4-benzoylquinoline-2,3-dicarboxylate, 78%, 55 mg, M.P.= 80-82 °C, yellow solid. CAS: 1373169-75-5.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.31 (dt,  $J$  = 8.5, 0.9 Hz, 1H), 7.88 (ddd,  $J$  = 8.4, 6.8, 1.5 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.69 – 7.58 (m, 3H), 7.49 – 7.44 (m, 2H), 4.06 (s, 3H), 3.66 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 194.44, 166.21, 165.06, 149.12, 148.04, 147.48, 136.17, 134.32, 132.34, 130.36, 129.56, 129.23, 128.88, 125.99, 124.46, 121.05, 53.31, 52.76. IR( $cm^{-1}$ ): 3063, 2952, 1732, 1676, 1612, 1595, 1580, 1496, 1449, 1397, 1372, 1313, 1248, 1199, 1172, 1154, 1128, 1072, 1028, 1014, 982, 913, 861, 805, 785, 729, 702, 637.



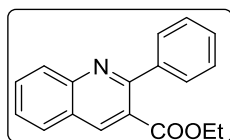
**2x**

ethyl 4-(4-(hydroxymethyl)benzoyl)-2-phenylquinoline-3-carboxylate, 55%, 54.7mg, M.P.= 61-63 °C, yellow solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.25 (d,  $J$  = 8.6 Hz, 1H), 7.85 – 7.77 (m, 3H), 7.73 – 7.65 (m, 2H), 7.62 (d,  $J$  = 8.4 Hz, 1H), 7.51 – 7.40 (m, 6H), 4.71 (d,  $J$  = 7.3 Hz, 2H), 3.93 – 3.81 (m, 2H), 0.81 (t,  $J$  = 7.2 Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 195.13, 166.92, 157.30, 147.93, 147.91, 147.04, 140.05, 135.57, 131.56, 129.88, 129.84, 128.93, 128.51, 128.36, 127.87, 126.70, 125.69, 123.39, 122.99, 64.19, 61.81, 13.11. IR( $cm^{-1}$ ): 3391, 3060, 2981, 2925, 1721, 1669, 1605, 1571, 1551, 1491, 1413, 1348, 1296, 1236, 1173, 1108, 1063, 1014, 971, 913, 832, 769, 746, 730, 704, 648, 616. HRMS (ESI)  $m/z$  calcd for  $C_{26}H_{22}NO_4^+$ ,  $(M+H)^+$  412.1543, found 412.1539.



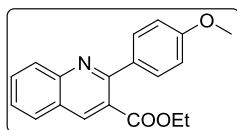
**2y**

ethyl 4-(4-acetamidobenzoyl)-2-phenylquinoline-3-carboxylate, 65%, 57.2mg, oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.44 (s, 1H), 8.22 (d,  $J$  = 9.4 Hz, 1H), 7.82 – 7.75 (m, 3H), 7.71 – 7.67 (m, 2H), 7.66 – 7.60 (m, 3H), 7.52 – 7.44 (m, 4H), 3.89 (q,  $J$  = 7.1 Hz, 2H), 2.13 (s, 3H), 0.83 (t,  $J$  = 7.2 Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 194.10, 168.84, 167.20, 157.24, 147.97, 146.94, 143.63, 140.06, 131.95, 131.60, 131.12, 129.93, 128.99, 128.51, 128.41, 127.91, 125.76, 123.38, 122.99, 118.96, 61.91, 24.61, 13.16. IR( $cm^{-1}$ ): 3320, 3055, 2927, 1721, 1704, 1663, 1588, 1550, 1527, 1490, 1409, 1371, 1348, 1310, 1234, 1174, 1106, 1014, 971, 860, 793, 706, 662, 636. HRMS (ESI)  $m/z$  calcd for  $C_{27}H_{23}N_2O_4^+$ ,  $(M+H)^+$  439.1652, found 439.1636.



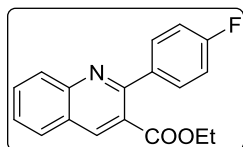
**4a**

ethyl 2-phenylquinoline-3-carboxylate, ethyl 2-phenylquinoline-3-carboxylate, 50%, 28 mg, oil. CAS: 30160-12-4.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.65 (s, 1H), 8.19 (d,  $J = 9.0$  Hz, 1H), 7.92 (d,  $J = 8.2$  Hz, 1H), 7.81 (ddd,  $J = 8.4, 6.9, 1.4$  Hz, 1H), 7.67 – 7.57 (m, 3H), 7.50 – 7.42 (m, 3H), 4.19 (q,  $J = 7.1$  Hz, 2H), 1.08 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 167.97, 158.11, 148.33, 140.74, 139.03, 131.50, 129.50, 128.52, 128.19, 128.15, 127.19, 125.81, 125.48, 61.50, 13.65. IR( $\text{cm}^{-1}$ ): 3058, 2979, 1721, 1618, 1594, 1554, 1485, 1455, 1443, 1419, 1372, 1323, 1291, 1266, 1247, 1229, 1199, 1179, 1145, 1130, 1098, 1034, 1019, 926, 861, 836, 803, 770, 715, 698, 626, 617.



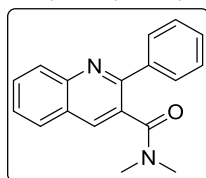
**4b**

ethyl 2-(4-methoxyphenyl)quinoline-3-carboxylate, 52%, 32 mg, oil. CAS: 187679-23-8.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.59 (s, 1H), 8.16 (d,  $J = 8.5$  Hz, 1H), 7.89 (d,  $J = 8.1$  Hz, 1H), 7.79 (t,  $J = 8.4$  Hz, 1H), 7.64 – 7.54 (m, 3H), 7.04 – 6.97 (m, 2H), 4.24 (q,  $J = 7.1$  Hz, 2H), 3.87 (s, 3H), 1.16 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 168.24, 160.12, 157.45, 148.33, 138.85, 133.05, 131.37, 130.02, 129.34, 128.10, 126.91, 125.57, 125.39, 113.64, 61.50, 55.32, 13.83. IR( $\text{cm}^{-1}$ ): 3056, 2978, 1722, 1608, 1594, 1578, 1554, 1515, 1486, 1454, 1421, 1372, 1322, 1298, 1248, 1230, 1199, 1175, 1145, 1130, 1095, 1034, 992, 845, 797, 757, 739, 652, 618.



**4c**

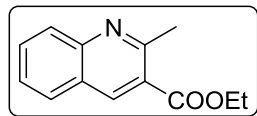
ethyl 2-(4-fluorophenyl)quinoline-3-carboxylate, 58%, 34 mg, M.P. = 82–84 °C, yellow solid. CAS: 1000388-89-5.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.66 (s, 1H), 8.16 (d,  $J = 8.5$  Hz, 1H), 7.92 (d,  $J = 8.1$  Hz, 1H), 7.82 (ddd,  $J = 8.4, 7.0, 1.4$  Hz, 1H), 7.67 – 7.57 (m, 3H), 7.17 (t,  $J = 8.7$  Hz, 2H), 4.23 (q,  $J = 7.1$  Hz, 2H), 1.14 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 167.70, 164.36 ( $J = 247.0$  Hz), 161.89, 156.98, 148.27, 139.27, 136.81, 136.78, 131.66, 130.50 ( $J = 8.0$  Hz), 130.42, 129.40, 128.20, 127.30, 125.80, 125.15, 115.22 ( $J = 21.0$  Hz), 115.01, 61.57, 13.76.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -113.24. IR( $\text{cm}^{-1}$ ): 3059, 2981, 1722, 1618, 1600, 1556, 1511, 1486, 1454, 1421, 1372, 1321, 1289, 1265, 1228, 1199, 1157, 1130, 1096, 1024, 995, 959, 929, 906, 850, 796, 757, 736, 651, 617.



**4d**

ethyl 2-methylquinoline-3-carboxylate, 30%, 17 mg, oil. CAS: 1398743-16-2.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.27 (d,  $J = 0.9$  Hz, 1H), 8.19 (dt,  $J = 8.6, 0.9$  Hz, 1H), 7.86 (ddd,  $J = 7.7, 5.3, 1.5$  Hz, 3H), 7.78 (ddd,  $J = 8.5, 6.9, 1.5$  Hz, 1H), 7.58 (ddd,  $J = 8.1, 6.9, 1.2$  Hz, 1H), 7.51 – 7.44 (m, 3H), 2.94 (s, 3H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 169.94, 155.27, 147.99, 139.41, 136.03, 130.51, 129.79, 129.52,

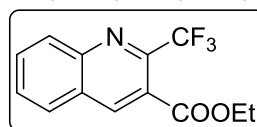
129.17, 128.71, 128.48, 127.67, 127.09, 126.33, 38.05, 34.82. IR( $\text{cm}^{-1}$ ): 3057, 2925, 1726, 1594, 1556, 1484, 1394, 1267, 1182, 1141, 1130, 1076, 1032, 1003, 929, 872, 773, 697, 677, 625, 616.



**4e**

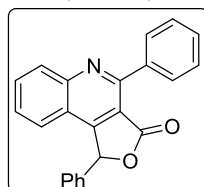
ethyl 2-methylquinoline-3-carboxylate, 65%, 28 mg, oil. CAS: 15785-08-7.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.71 (s, 1H), 8.03 (dd,  $J = 8.5, 1.0$  Hz, 1H), 7.84 (dd,  $J = 8.1, 1.4$  Hz, 1H), 7.76 (ddd,  $J = 8.4, 6.9, 1.5$  Hz, 1H), 7.52 (ddd,  $J = 8.1, 6.9, 1.1$  Hz, 1H), 4.44 (q,  $J = 7.1$  Hz, 2H), 2.99 (s, 3H), 1.45 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 166.39, 158.33, 148.49, 139.74, 131.51, 128.41, 128.34, 126.37, 125.62, 123.79, 61.26, 25.58, 14.22. IR( $\text{cm}^{-1}$ ): 3049, 2968, 1716, 1620, 1594, 1561, 1491, 1423, 1392, 1376, 1316, 1277, 1241, 1214, 1201, 1136, 1065, 1017, 932, 908, 870, 784, 774, 748, 654, 628.



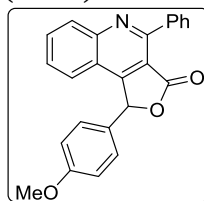
**4f**

ethyl 2-(trifluoromethyl)quinoline-3-carboxylate, 57%, 31 mg, M.P.= 65-67 °C, yellow solid. CAS: 1260890-78-5.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.59 (s, 1H), 8.15 (dd,  $J = 8.7, 1.2$  Hz, 1H), 7.91 – 7.77 (m, 2H), 7.64 (ddd,  $J = 8.1, 6.9, 1.2$  Hz, 1H), 4.39 (q,  $J = 7.1$  Hz, 2H), 1.36 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 165.48, 146.82, 145.15, 144.80 ( $J = 35.0$  Hz), 144.45, 144.10, 140.07, 132.33, 130.03 ( $J = 48.0$  Hz), 129.52, 128.14, 127.41, 125.21 ( $J = 274.0$  Hz), 123.99, 122.47, 119.73, 116.99, 62.44, 13.91.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -63.85. IR( $\text{cm}^{-1}$ ): 3065, 2962, 1733, 1618, 1564, 1494, 1457, 1433, 1391, 1303, 1285, 1231, 1205, 1180, 1138, 1114, 1076, 1031, 972, 940, 873, 799, 775, 762, 746, 640.



**5a**

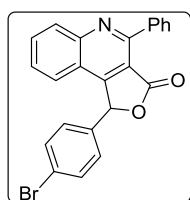
1,4-diphenylfuro[3,4-c]quinolin-3(1H)-one, 74%, 50 mg, M.P.= 80-82 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.31 (dd,  $J = 8.6, 1.1$  Hz, 1H), 8.11 – 8.01 (m, 2H), 7.86 (ddd,  $J = 8.5, 6.8, 1.5$  Hz, 1H), 7.62 – 7.47 (m, 5H), 7.45 – 7.36 (m, 3H), 7.35 – 7.28 (m, 2H), 6.72 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 168.18, 159.34, 156.96, 149.73, 136.34, 135.03, 132.77, 130.64, 130.12, 130.08, 129.96, 129.33, 128.27, 128.10, 127.92, 124.03, 121.03, 116.91, 81.24. IR( $\text{cm}^{-1}$ ): 3061, 2925, 1770, 1619, 1593, 1553, 1510, 1495, 1455, 1417, 1359, 1291, 1196, 1180, 1132, 1083, 1056, 1002, 968, 906, 847, 770, 696, 638, 601. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{16}\text{N}_1\text{O}_2^+$ , ( $\text{M}+\text{H}$ ) $^+$  338.1181, found 338.1176.



**5b**

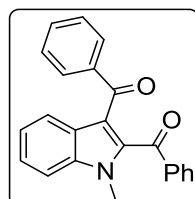
1-(4-methoxyphenyl)-4-phenylfuro[3,4-c]quinolin-3(1H)-one, 78%, 57 mg, M.P.= 175-177 °C, yellow solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.30 (dt,  $J = 8.5, 0.9$  Hz, 1H), 8.11 – 8.00 (m, 2H), 7.85 (ddd,  $J = 8.4, 6.8, 1.6$  Hz, 1H), 7.60 – 7.46 (m, 5H), 7.23 (d,  $J = 8.7$  Hz, 2H), 6.91 (d,  $J = 8.8$  Hz, 2H), 6.68 (s, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 168.21, 160.80, 159.42, 156.94, 149.72, 136.39, 132.70, 130.61, 130.12, 129.93, 129.73, 128.09, 127.86, 126.99, 124.15, 121.09, 117.06, 114.66, 80.99, 55.32. IR( $\text{cm}^{-1}$ ): 3059, 2911, 1763, 1619, 1556, 1513, 1456, 1417, 1361, 1251, 1196, 1180, 1141, 1076, 1028, 1002, 873, 772, 760, 697, 631. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{18}\text{NO}_3^+$ ,  $(\text{M}+\text{H})^+$  368.1281, found 368.1285.



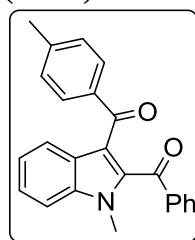
**5c**

1-(4-bromophenyl)-4-phenylfuro[3,4-c]quinolin-3(1H)-one, 68%, 56mg, M.P. > 200 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.31 (dd,  $J = 8.5, 1.0$  Hz, 1H), 8.03 (d,  $J = 7.5, 2.1$  Hz, 2H), 7.87 (ddd,  $J = 8.5, 4.9, 3.5$  Hz, 1H), 7.58 – 7.51 (m, 7H), 7.22 – 7.17 (m, 2H), 6.67 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 158.77, 156.98, 149.77, 136.21, 134.07, 132.94, 132.60, 130.77, 130.11, 130.05, 129.90, 128.13, 128.11, 124.41, 123.83, 120.83, 116.86, 80.34. IR( $\text{cm}^{-1}$ ): 3061, 2917, 1770, 1620, 1593, 1556, 1509, 1489, 1407, 1356, 1196, 1141, 1075, 1054, 1004, 954, 904, 848, 829, 801, 771, 696, 641, 606. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{15}\text{BrNO}_2^+$ ,  $(\text{M}+\text{H})^+$  416.0281, found 416.0276.



**7a**

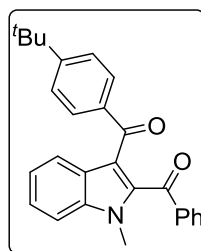
(1-methyl-1H-indole-2,3-diyl)bis(phenylmethanone), 80%, 27.2mg, M.P. = 143–145 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.98 (d,  $J = 8.1$  Hz, 1H), 7.53 – 7.41 (m, 5H), 7.39 – 7.31 (m, 4H), 7.19 (dt,  $J = 11.9, 7.8$  Hz, 4H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 192.03, 190.11, 140.98, 139.18, 138.91, 137.84, 133.21, 131.73, 129.17, 128.77, 128.28, 127.98, 125.99, 125.27, 123.00, 122.46, 119.22, 110.35, 31.65. IR( $\text{cm}^{-1}$ ): 3056, 1636, 1586, 1576, 1498, 1464, 1447, 1393, 1373, 1335, 1314, 1255, 1227, 1176, 1164, 1130, 1075, 1042, 1022, 1000, 950, 924, 875, 830, 788, 749, 731, 713, 692, 669, 634. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}_2^+$ ,  $(\text{M}+\text{H})^+$  340.1338, found 340.1332.



**7b**

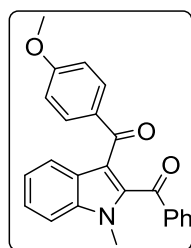
(2-benzoyl-1-methyl-1H-indol-3-yl)(p-tolyl)methanone, 82%, 28.9mg, M.P. = 148–150 °C, yellow solid, CAS: 1276042-14-8.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.95 (d,  $J = 8.1$  Hz, 1H), 7.51 – 7.43 (m, 4H), 7.42 – 7.38 (m, 1H), 7.30 (dd,  $J = 11.6, 8.1$  Hz, 3H), 7.20 (t,  $J = 7.8$  Hz, 2H), 6.98 (d,  $J = 7.9$  Hz, 2H), 3.91 (s, 3H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 190.10, 142.41, 138.99, 138.89, 138.33, 137.83, 133.12, 129.13, 128.97, 128.63, 128.13, 125.94, 125.16, 122.79, 122.44, 119.56, 110.29, 31.58, 21.47. IR( $\text{cm}^{-1}$ ): 3055, 1648, 1635, 1605, 1571, 1497, 1464, 1448, 1392, 1373, 1334, 1308, 1254, 1229, 1209, 1178, 1163, 1146, 1129, 1115, 1074, 1041, 1000, 960, 923, 881, 845, 825, 789, 751, 726, 691, 647, 617.



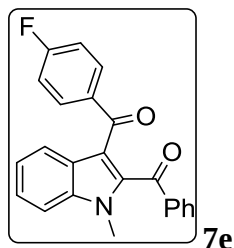
**7c**

(2-benzoyl-1-methyl-1H-indol-3-yl)(4-(tert-butyl)phenyl)methanone, 73%, 57.6mg, M.P. = 79–81 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.07 (d,  $J = 8.2$  Hz, 1H), 7.52 – 7.42 (m, 2H), 7.38 (d,  $J = 8.1$  Hz, 3H), 7.33 (t,  $J = 7.4$  Hz, 1H), 7.25 (d,  $J = 8.6$  Hz, 2H), 7.16 (dt,  $J = 7.7, 3.6$  Hz, 4H), 3.92 (s, 3H), 1.30 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 191.79, 190.13, 155.25, 139.16, 138.97, 138.61, 137.89, 132.98, 129.01, 128.66, 128.13, 126.08, 125.29, 124.86, 122.93, 122.61, 119.55, 110.27, 34.89, 31.63, 31.07. IR( $\text{cm}^{-1}$ ): 3056, 2961, 1651, 1635, 1603, 1496, 1436, 1448, 1391, 1374, 1257, 1230, 1176, 1165, 1106, 1075, 1043, 1013, 1000, 960, 924, 883, 835, 779, 748, 729, 705, 690, 625. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{26}\text{NO}_2^+$ ,  $(\text{M}+\text{H})^+$  396.1964, found 396.1958.

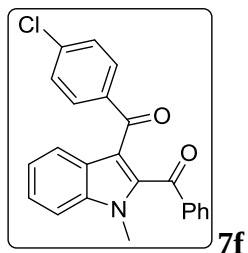


**7d**

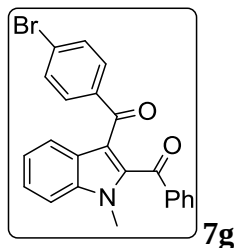
(2-benzoyl-1-methyl-1H-indol-3-yl)(4-methoxyphenyl)methanone, 73%, 26.6mg, M.P. = 136–138 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.95 (d,  $J = 8.1$  Hz, 1H), 7.52 – 7.48 (m, 3H), 7.47 – 7.40 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 7.22 (t,  $J = 7.8$  Hz, 2H), 6.68 (d,  $J = 8.8$  Hz, 2H), 3.93 (s, 3H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 190.10, 162.68, 139.00, 138.53, 137.88, 133.94, 133.12, 131.08, 129.07, 128.20, 125.95, 125.24, 122.71, 122.42, 119.89, 113.25, 110.31, 55.39, 31.62. IR( $\text{cm}^{-1}$ ): 3056, 1648, 1635, 1598, 1572, 1498, 1464, 1417, 1392, 1372, 1334, 1314, 1256, 1231, 1174, 1161, 1129, 1111, 1075, 1042, 1025, 959, 923, 881, 837, 791, 779, 728, 704, 614. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}_3^+$ ,  $(\text{M}+\text{H})^+$  370.1443, found 370.1438.



(2-benzoyl-1-methyl-1H-indol-3-yl)(4-fluorophenyl)methanone, 84%, 30mg, M.P. = 136-138 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.98 (d,  $J$  = 8.1 Hz, 1H), 7.53 – 7.42 (m, 5H), 7.40 – 7.32 (m, 3H), 7.26 – 7.22 (m, 2H), 6.86 (t,  $J$  = 8.7 Hz, 2H), 3.93 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 190.50, 189.98, 166.12 ( $J$  = 252.0 Hz), 163.60, 139.03, 138.89, 137.86, 137.38, 137.35, 133.38, 131.23 ( $J$  = 9.0 Hz), 131.14, 129.17, 128.35, 125.92, 125.41, 123.10, 122.36, 119.02, 115.17 ( $J$  = 21.0 Hz), 114.96, 110.41, 31.69.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -106.91. IR( $\text{cm}^{-1}$ ): 3060, 1650, 1635, 1597, 1496, 1465, 1448, 1391, 1373, 1314, 1229, 1171, 1153, 1130, 1095, 1075, 1040, 1012, 1000, 960, 924, 882, 840, 801, 778, 751, 727, 691, 627, 613. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{FNO}_2^+$ , ( $\text{M}+\text{H}$ ) $^+$  358.1243, found 358.1238.

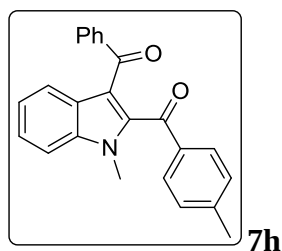


(2-benzoyl-1-methyl-1H-indol-3-yl)(4-chlorophenyl)methanone, 81%, 58mg, M.P. = 138-140 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.98 (d,  $J$  = 8.1 Hz, 1H), 7.53 – 7.41 (m, 5H), 7.37 – 7.20 (m, 5H), 7.19 – 7.10 (m, 2H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 190.55, 189.91, 139.28, 139.26, 138.80, 138.00, 137.81, 133.38, 130.03, 129.16, 128.29, 128.20, 125.83, 125.36, 123.13, 122.33, 118.72, 110.39, 31.65. IR ( $\text{cm}^{-1}$ ): 3056, 2946, 1649, 1589, 1498, 1483, 1465, 1448, 1391, 1373, 1350, 1334, 1256, 1226, 1175, 1163, 1129, 1085, 1041, 960, 923, 880, 833, 776, 751, 726, 692, 679, 647, 633. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{ClNO}_2^+$ , ( $\text{M}+\text{H}$ ) $^+$  374.0948, found 374.0942.

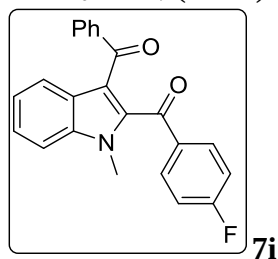


(2-benzoyl-1-methyl-1H-indol-3-yl)(4-bromophenyl)methanone, 83%, 34.7mg, M.P. = 132-134 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.99 (dt,  $J$  = 8.1, 1.0 Hz, 1H), 7.52 – 7.43 (m, 5H), 7.33 (dd,  $J$  = 16.3, 8.2 Hz, 3H), 7.27 – 7.20 (m, 4H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 190.75, 189.98, 139.74, 139.37, 138.84, 137.84, 133.43, 131.22, 130.19, 129.21, 128.33, 126.66, 125.87, 125.41, 123.21, 122.39, 118.70, 110.41, 31.69. IR( $\text{cm}^{-1}$ ): 3056, 1648, 1635, 1595, 1583, 1498, 1464, 1448,

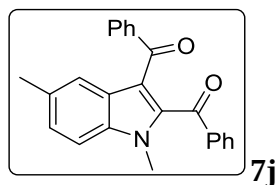
1397, 1334, 1314, 1254, 1225, 1175, 1163, 1130, 1107, 1068, 1040, 1009, 960, 922, 880, 830, 811, 775, 751, 726, 691, 676, 633. HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{17}BrNO_2^+$ ,  $(M+H)^+$  418.0443, found 418.0437.



(3-benzoyl-1-methyl-1H-indol-2-yl)(p-tolyl)methanone, 80%, 56.7mg, M.P. = 139-141 °C, yellow solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.94 (d,  $J$  = 8.1 Hz, 1H), 7.51 – 7.33 (m, 7H), 7.30 (t,  $J$  = 6.9 Hz, 1H), 7.18 (t,  $J$  = 7.8 Hz, 2H), 7.00 (d,  $J$  = 7.8 Hz, 2H), 3.88 (s, 3H), 2.32 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 191.92, 189.66, 144.29, 140.87, 139.66, 137.69, 136.31, 131.64, 129.30, 128.96, 128.73, 127.82, 125.93, 124.98, 122.82, 122.32, 118.79, 110.27, 31.52, 21.58. IR( $cm^{-1}$ ): 3055, 2946, 1647, 1603, 1575, 1497, 1392, 1373, 1335, 1257, 1227, 1179, 1163, 1146, 1129, 1116, 1042, 1022, 962, 923, 875, 839, 794, 742, 701, 675, 647, 614. HRMS (ESI)  $m/z$  calcd for  $C_{24}H_{20}NO_2^+$ ,  $(M+H)^+$  354.1494, found 354.1489.



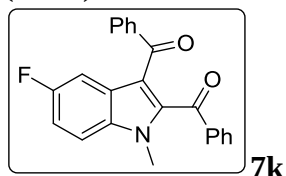
(3-benzoyl-1-methyl-1H-indol-2-yl)(4-fluorophenyl)methanone, 79%, 56.7mg, M.P. = 125-127 °C, yellow solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.96 (d,  $J$  = 8.1 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.47 – 7.42 (m, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.28 (m, 1H), 7.21 (t,  $J$  = 7.8 Hz, 2H), 6.92 – 6.83 (m, 2H), 3.90 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 191.80, 188.41, 166.92 ( $J$  = 255 Hz), 164.37, 140.85, 138.76, 137.83, 135.41 ( $J$  = 3 Hz), 135.38, 131.85, 131.77, 131.67, 128.72, 128.00, 125.89, 125.34, 123.02, 122.41, 119.18, 115.55 ( $J$  = 22 Hz), 115.33, 110.34, 31.57.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ ): -103.98. IR( $cm^{-1}$ ): 3057, 2924, 1652, 1596, 1577, 1497, 1465, 1408, 1392, 1373, 1295, 1252, 1229, 1164, 1154, 1075, 1041, 1022, 962, 924, 875, 849, 745, 721, 703, 675, 637, 613. HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{17}FNO_2^+$ ,  $(M+H)^+$  358.1243, found 358.1238.



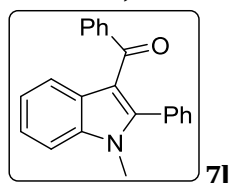
(1,5-dimethyl-1H-indole-2,3-diyl)bis(phenylmethanone), 80%, 56.2mg, M.P. = 124-126 °C, yellow solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.82 (s, 1H), 7.40 (t,  $J$  = 7.2 Hz, 3H), 7.37 – 7.29 (m, 4H), 7.29 – 7.24 (m, 1H), 7.16 (dt,  $J$  = 11.2, 7.8 Hz, 4H), 3.88 (s, 3H), 2.47 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 192.09, 189.98, 141.09, 139.03, 138.93, 136.33, 133.00, 132.68, 131.56, 129.08, 128.67, 128.14, 127.85, 127.11,



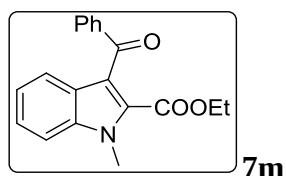
126.21, 121.71, 118.79, 109.98, 31.60, 21.47. IR( $\text{cm}^{-1}$ ): 3056, 2921, 1652, 1639, 1596, 1577, 1500, 1477, 1447, 1394, 1313, 1254, 1229, 1195, 1179, 1132, 1076, 1039, 1022, 962, 944, 795, 737, 701, 664, 625. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}_2^+$ ,  $(\text{M}+\text{H})^+$  354.1494, found 354.1489.



(5-fluoro-1-methyl-1H-indole-2,3-diyl)bis(phenylmethanone), 83%, 59.8mg, M.P. = 125-127 °C, yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.68 – 7.62 (m, 1H), 7.47 – 7.39 (m, 4H), 7.39 – 7.31 (m, 3H), 7.24 – 7.14 (m, 5H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 191.59, 189.74, 160.83 ( $J = 238$  Hz), 158.45, 140.71, 140.51, 138.56, 134.32, 133.33, 131.76, 129.07, 128.61, 128.28, 128.00, 126.50, 126.39, 118.72 ( $J = 5$  Hz), 118.67, 114.18 ( $J = 27$  Hz), 113.91, 111.46, 111.36, 107.38, 107.13, 31.80.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): -119.52. IR( $\text{cm}^{-1}$ ): 3057, 2948, 1650, 1595, 1577, 1502, 1397, 1309, 1297, 1243, 1174, 1135, 1035, 1020, 999, 979, 949, 862, 848, 809, 794, 739, 701, 647, 638, 615, 605. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{FNO}_2^+$ ,  $(\text{M}+\text{H})^+$  358.1243, found 358.1238.

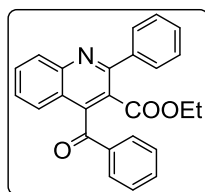


(1-methyl-2-phenyl-1H-indol-3-yl)(phenyl)methanone, 54%, 34mg, M.P. = 112-114 °C, yellow solid, CAS: 26821-93-2.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.01 (d,  $J = 7.7$  Hz, 1H), 7.51 (d,  $J = 6.8$  Hz, 2H), 7.42 (d,  $J = 8.2$  Hz, 1H), 7.35 (t,  $J = 6.9$  Hz, 1H), 7.29 (d,  $J = 6.8$  Hz, 1H), 7.23 (s, 6H), 7.11 (t,  $J = 7.6$  Hz, 2H), 3.67 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 192.84, 146.32, 140.09, 137.17, 130.91, 130.84, 130.71, 129.15, 128.66, 127.97, 127.57, 127.48, 123.21, 122.26, 121.82, 114.65, 109.74, 31.22. IR( $\text{cm}^{-1}$ ): 3054, 2924, 1619, 1575, 1466, 1444, 1393, 1213, 1173, 1157, 1128, 1065, 1037, 1023, 927, 882, 746, 723, 697, 661.

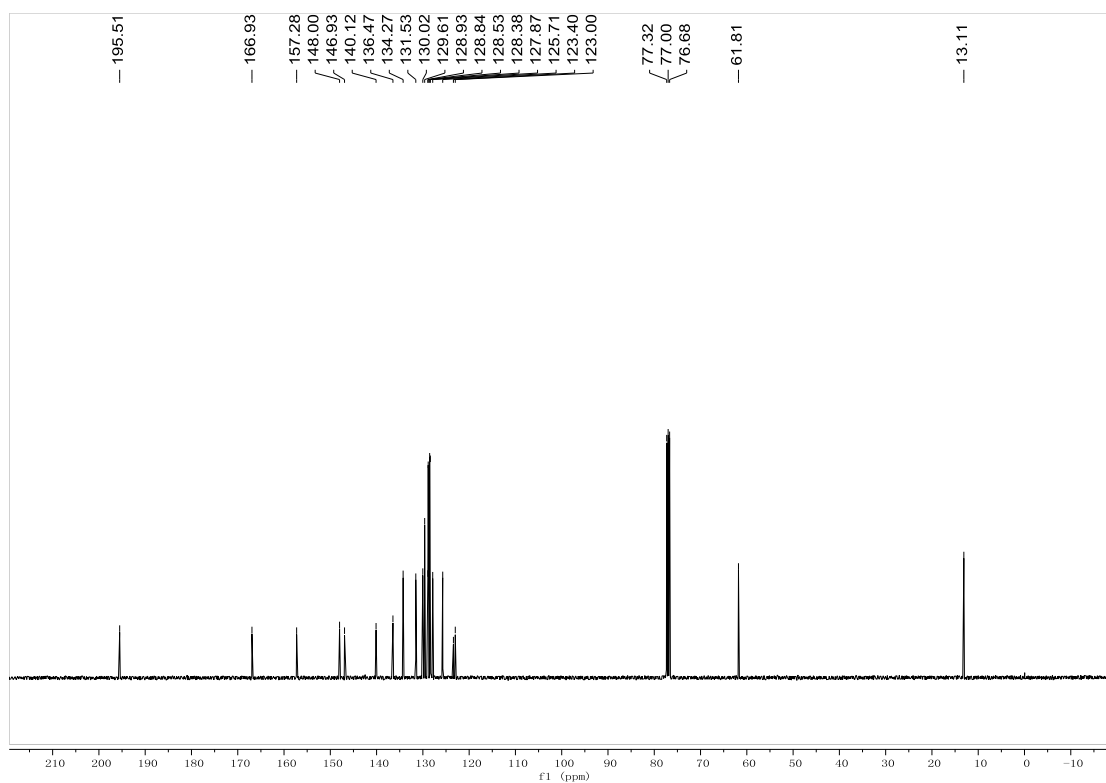
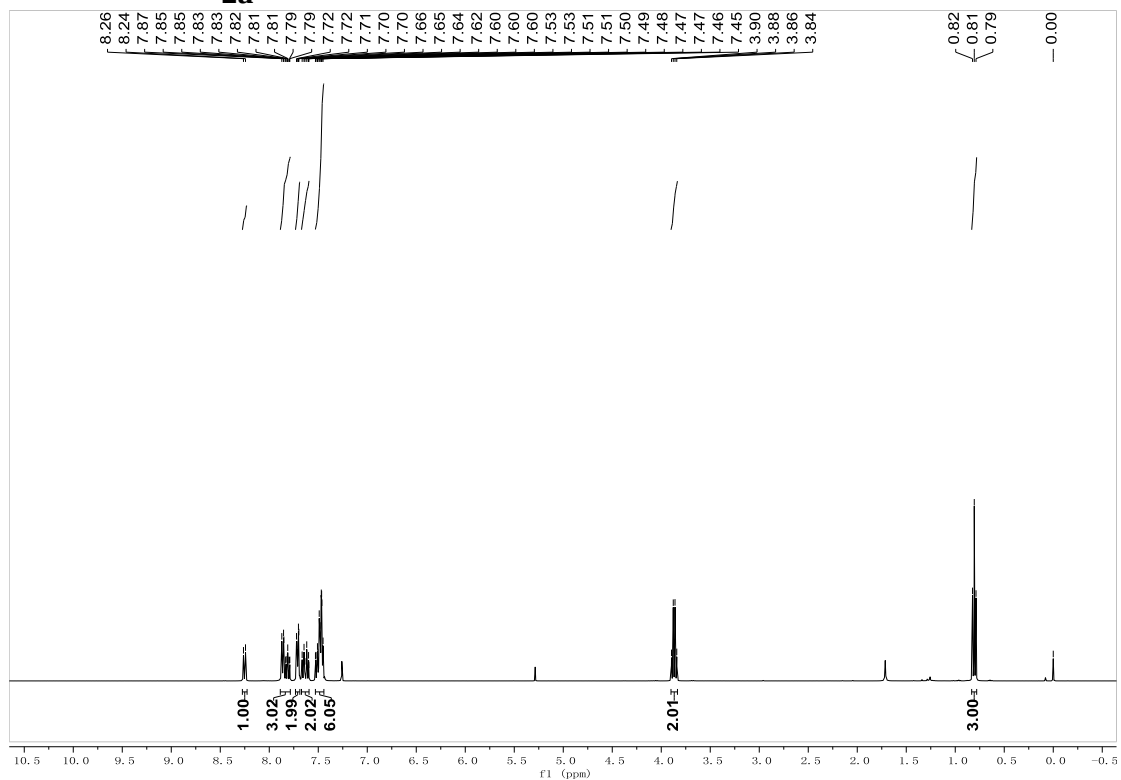


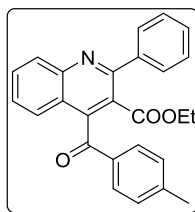
ethyl 3-benzoyl-1-methyl-1H-indole-2-carboxylate, 26%, 15mg, oil, CAS: 64269-36-9.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.88 – 7.81 (m, 2H), 7.79 (d,  $J = 8.1$  Hz, 1H), 7.53 (t,  $J = 7.3$  Hz, 1H), 7.42 (q,  $J = 8.2$  Hz, 4H), 7.22 (d,  $J = 8.1$  Hz, 1H), 4.06 (s, 3H), 3.85 (q,  $J = 7.1$  Hz, 2H), 0.87 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 192.63, 161.66, 139.87, 138.09, 132.48, 129.13, 128.39, 125.53, 122.33, 122.04, 110.31, 61.37, 30.89, 13.29. IR( $\text{cm}^{-1}$ ): 3060, 2979, 1742, 1672, 1593, 1496, 1448, 1383, 1223, 1127, 1091, 1028, 1010, 917, 863, 757, 691.

**$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra of compound 2, 4, 5, 7.**

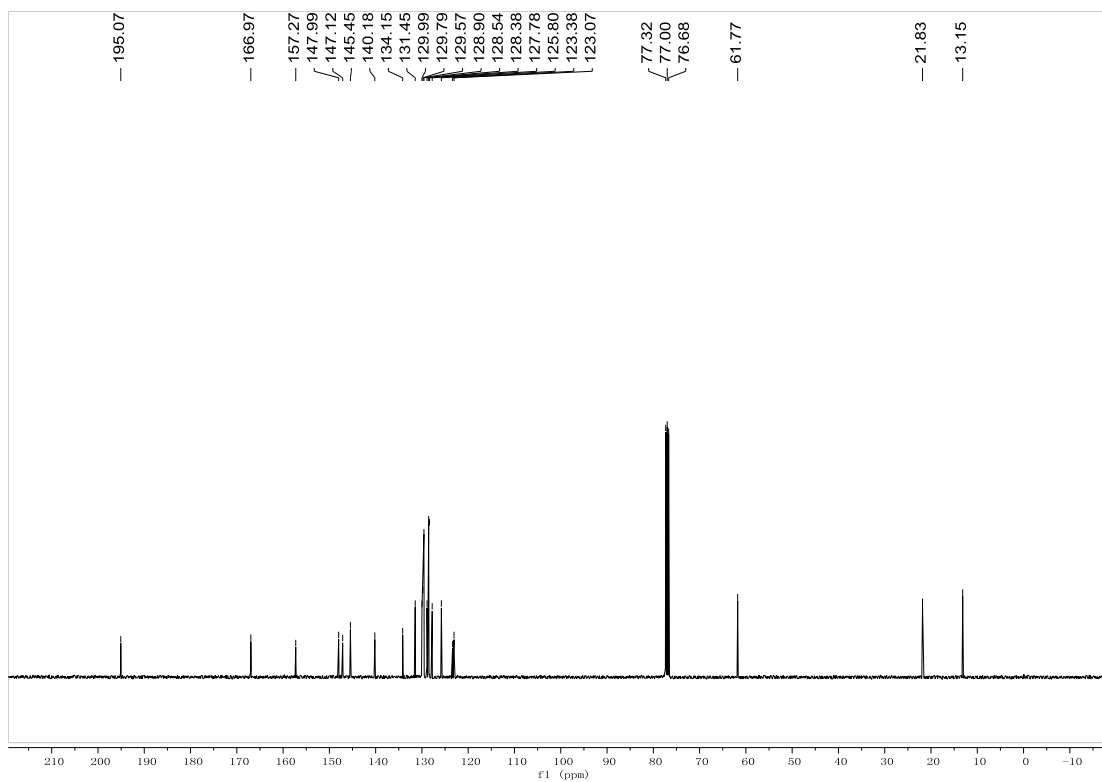
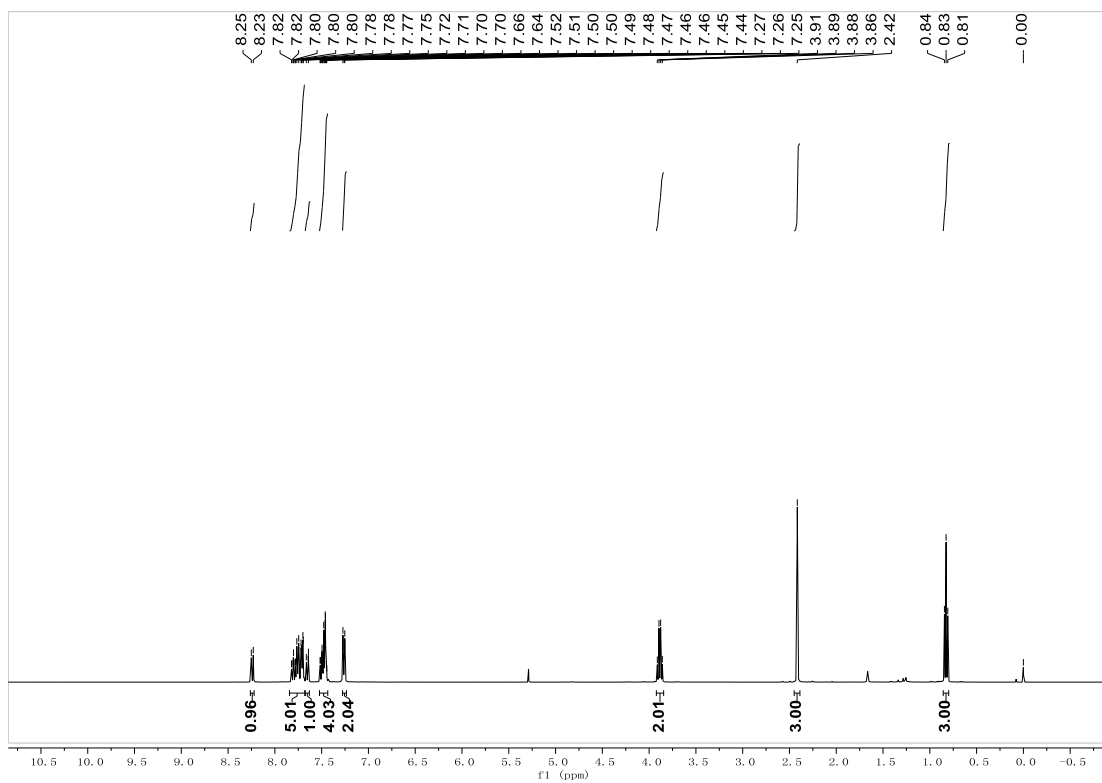


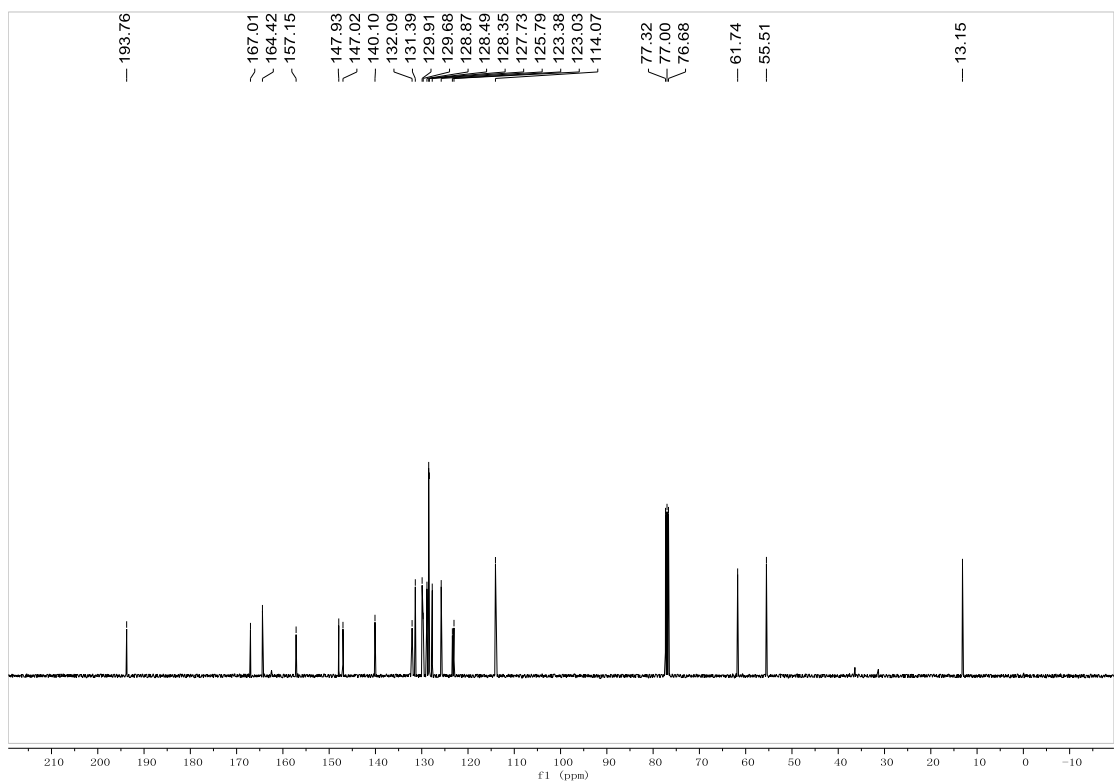
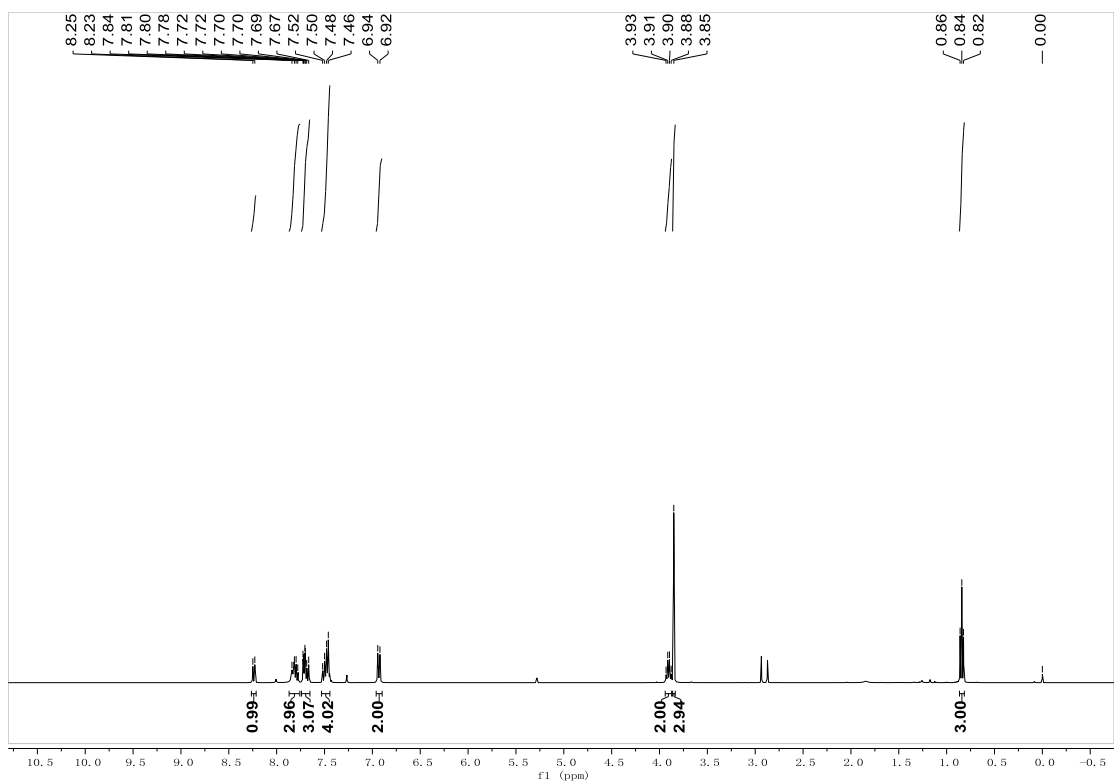
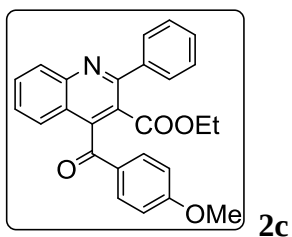
**2a**

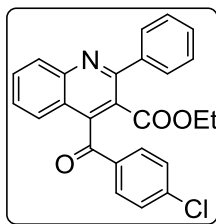




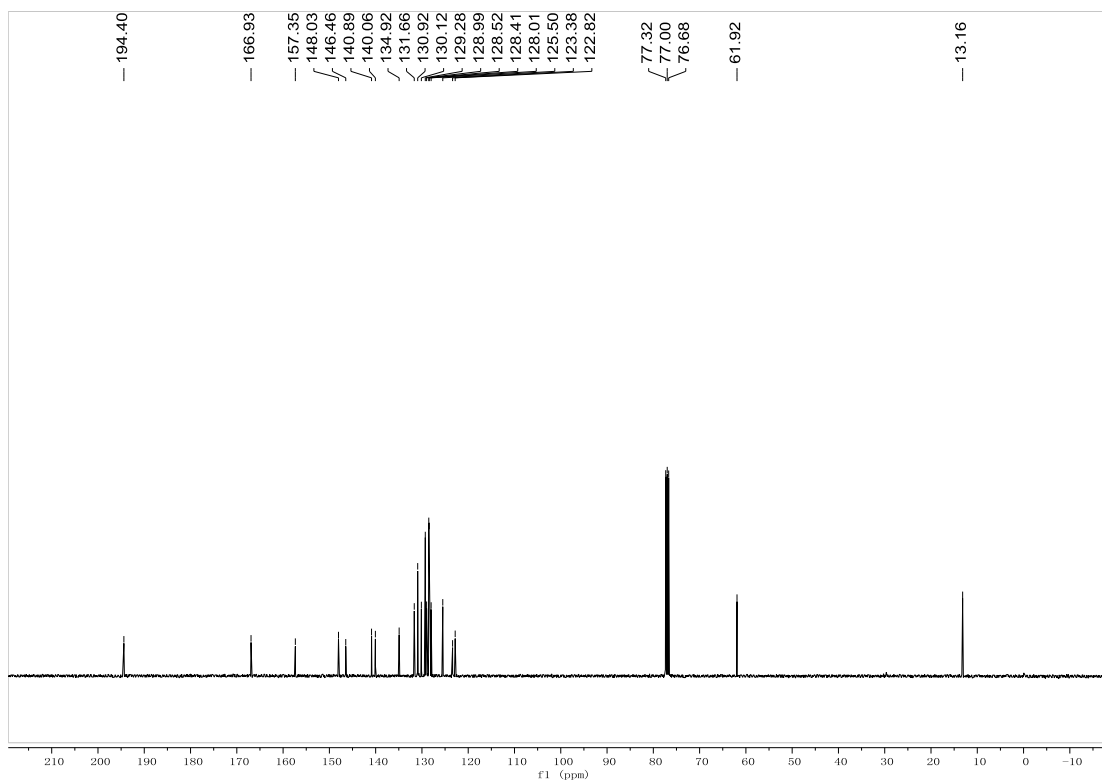
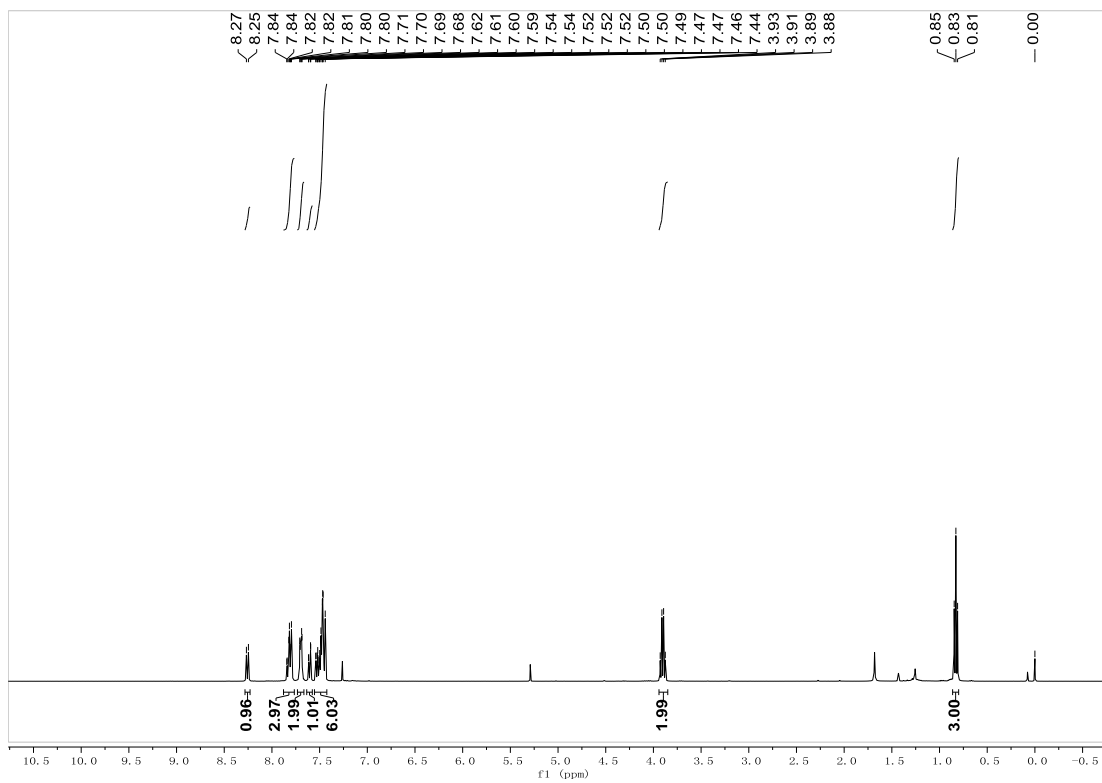
**2b**

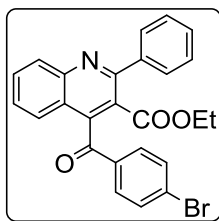




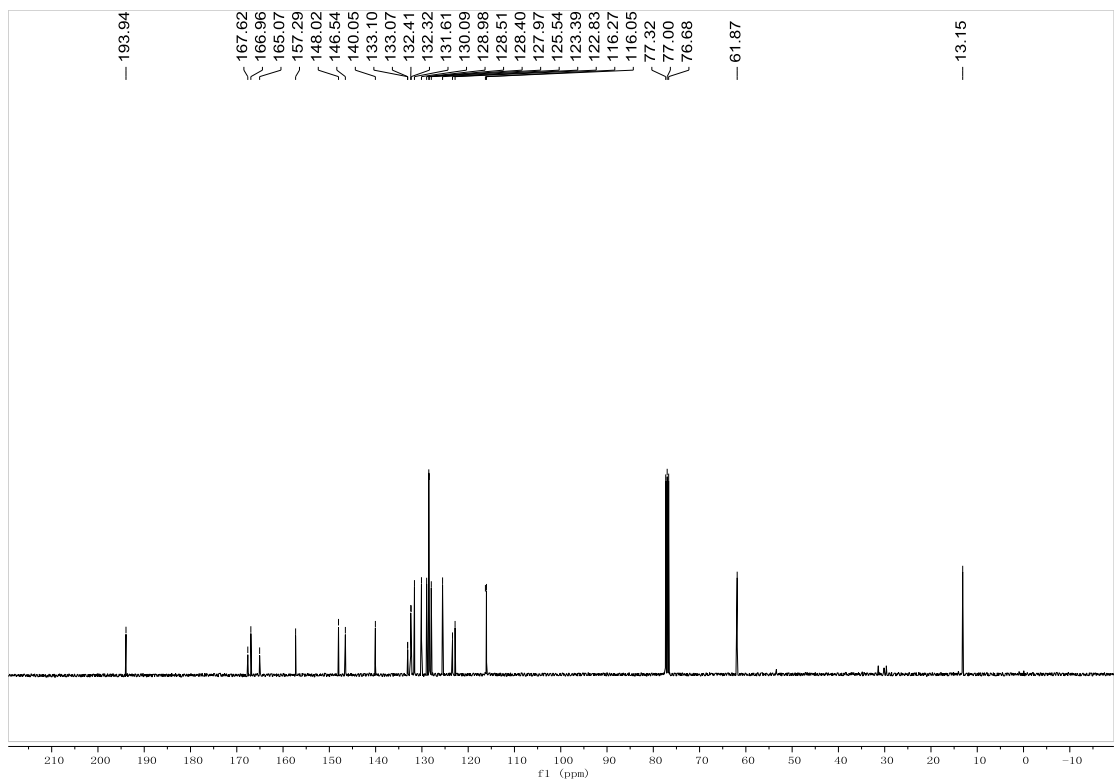
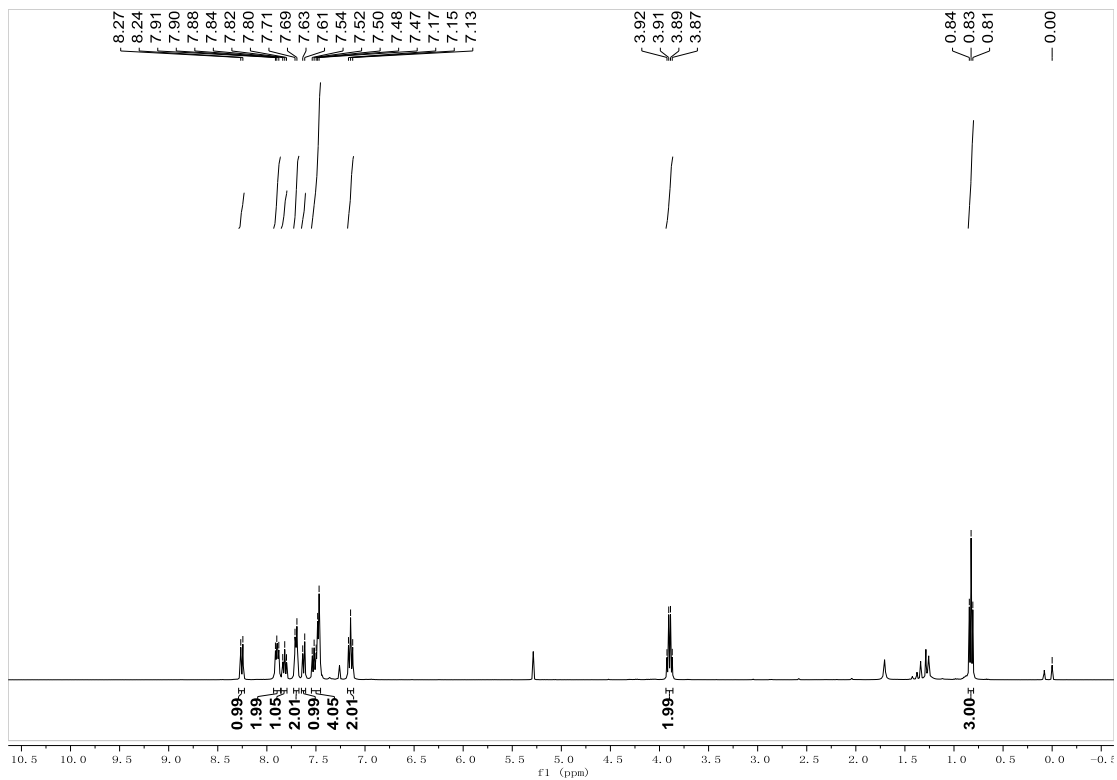


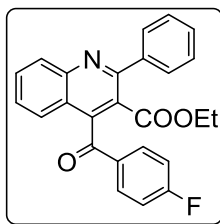
**2d**



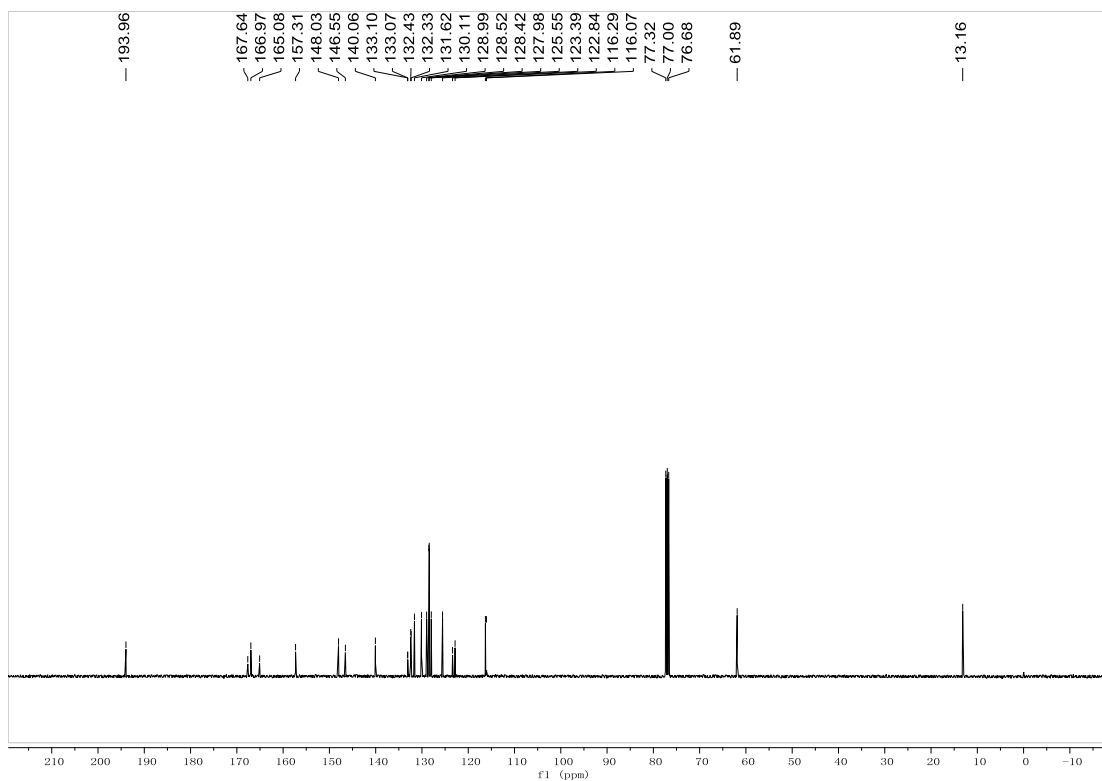
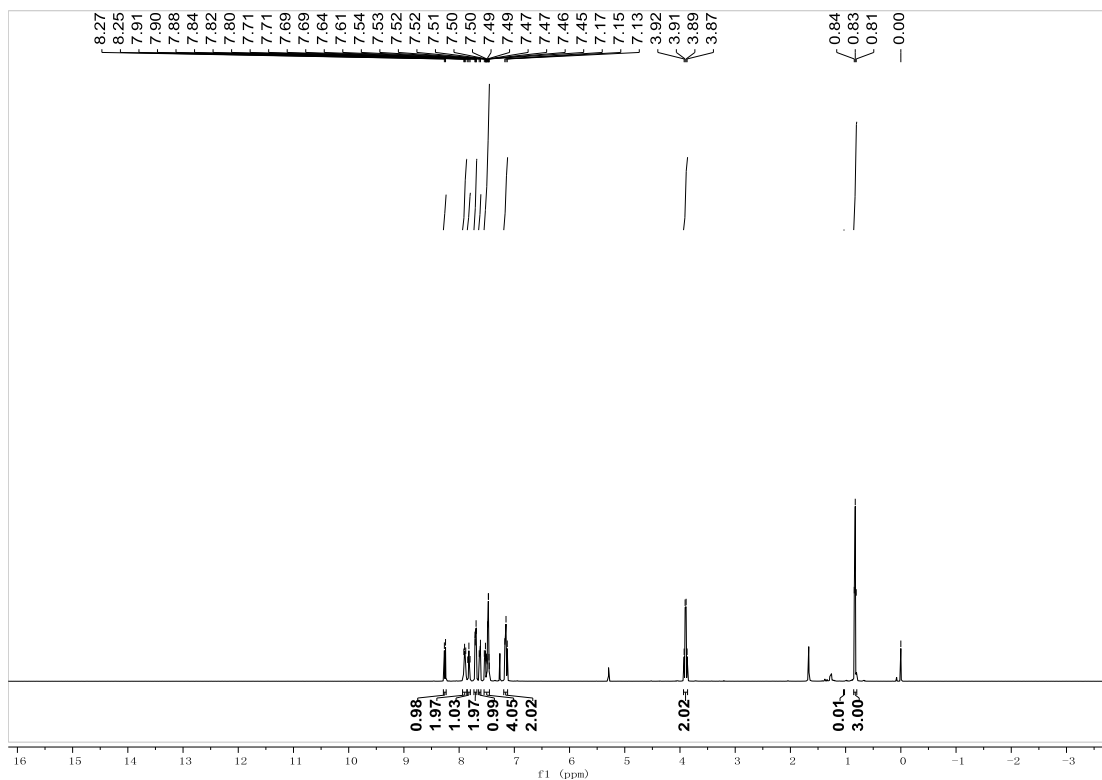


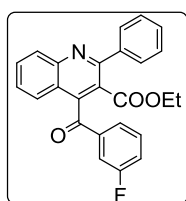
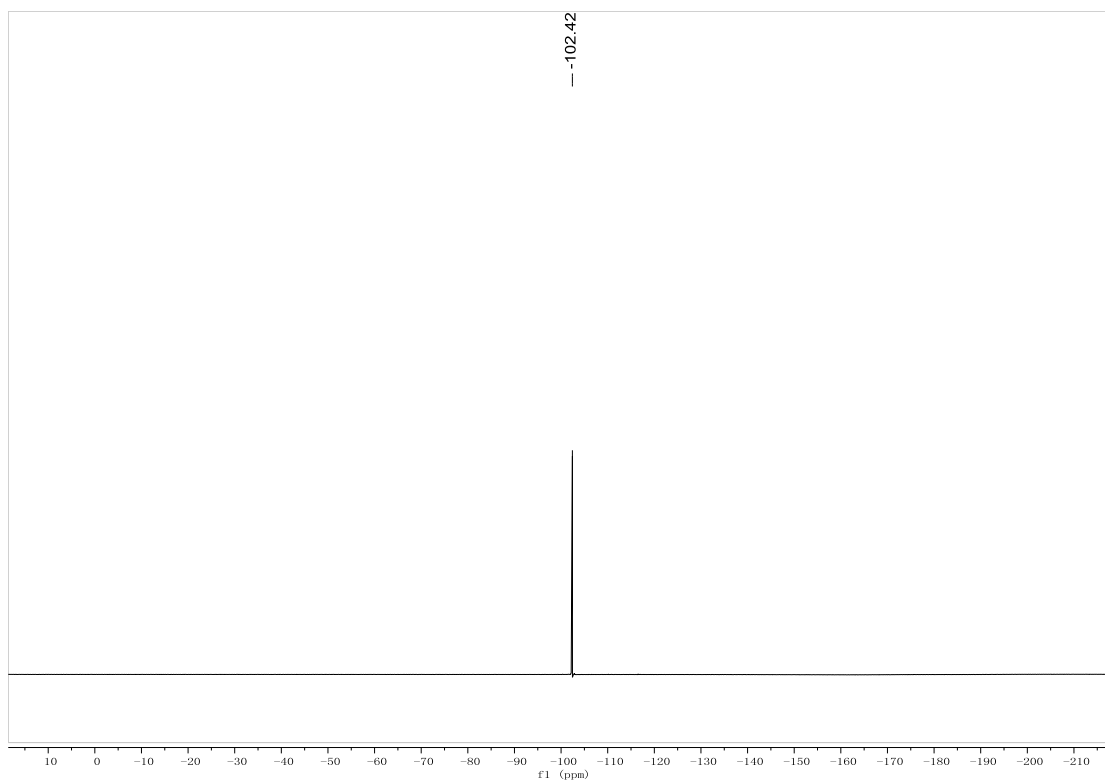
**2e**



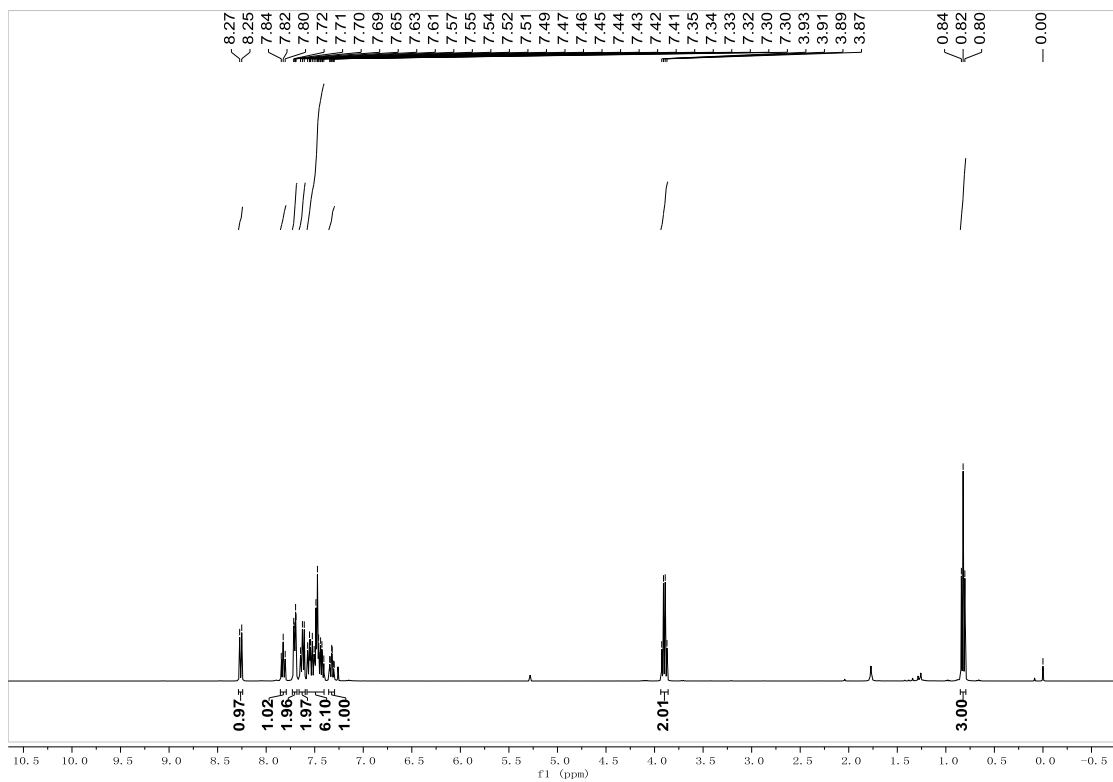


**2f**

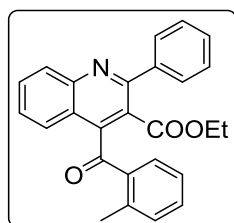
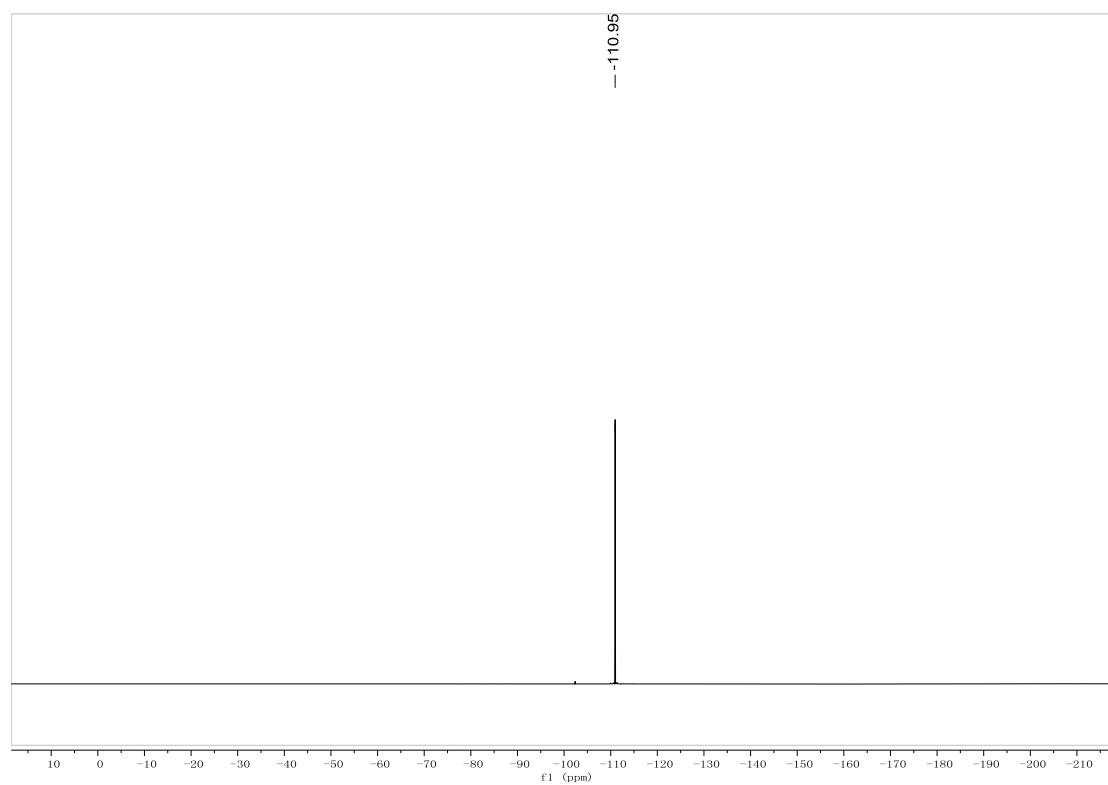
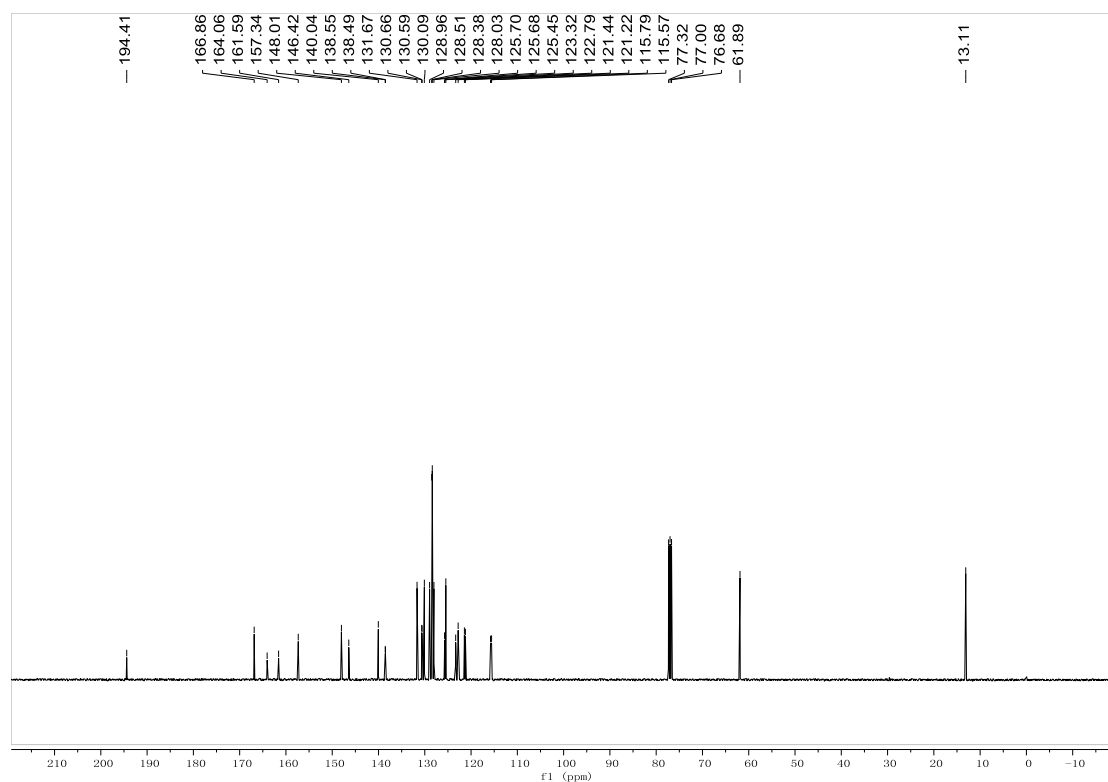




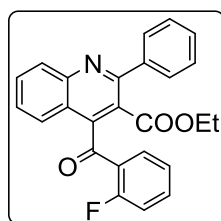
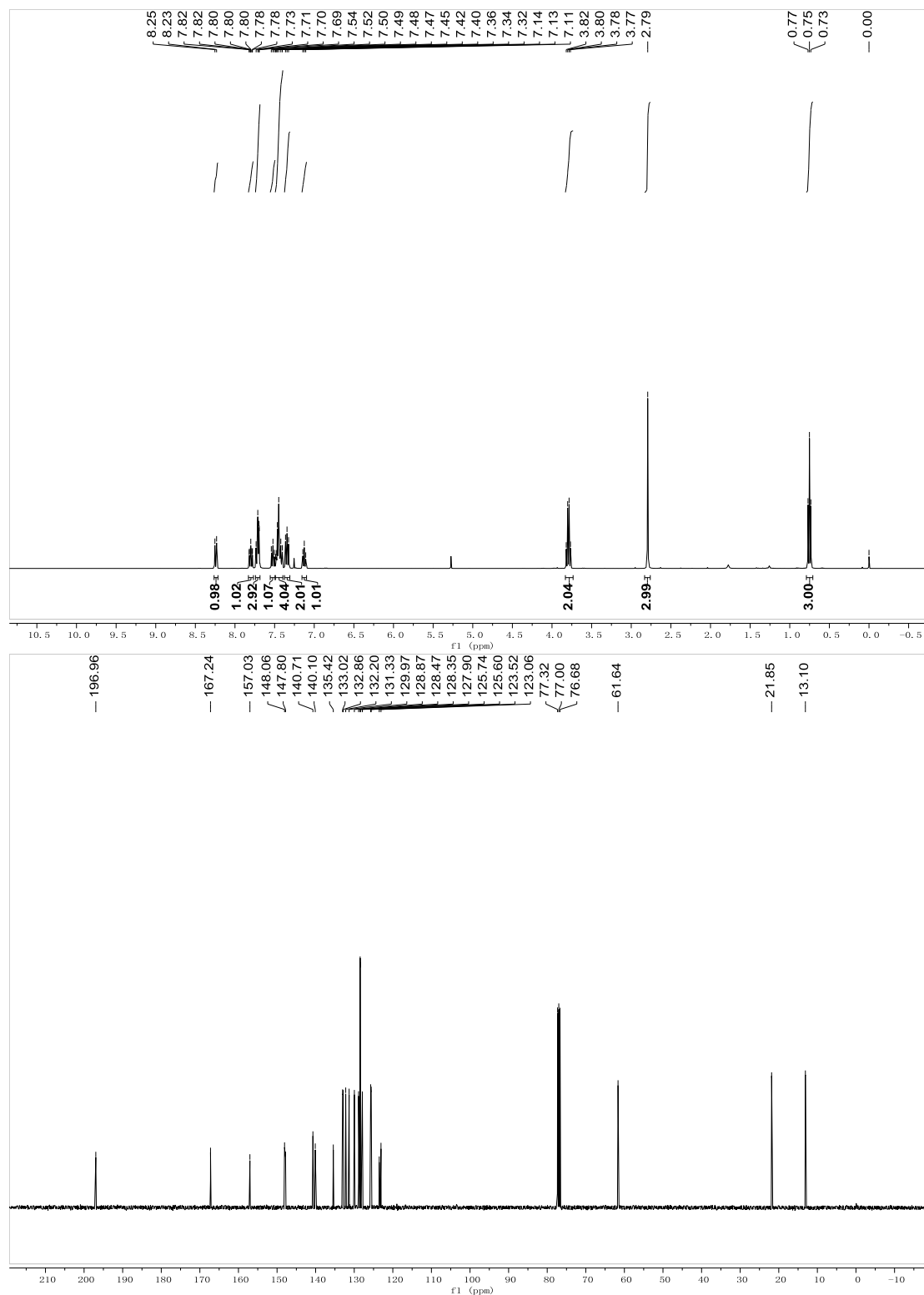
**2g**



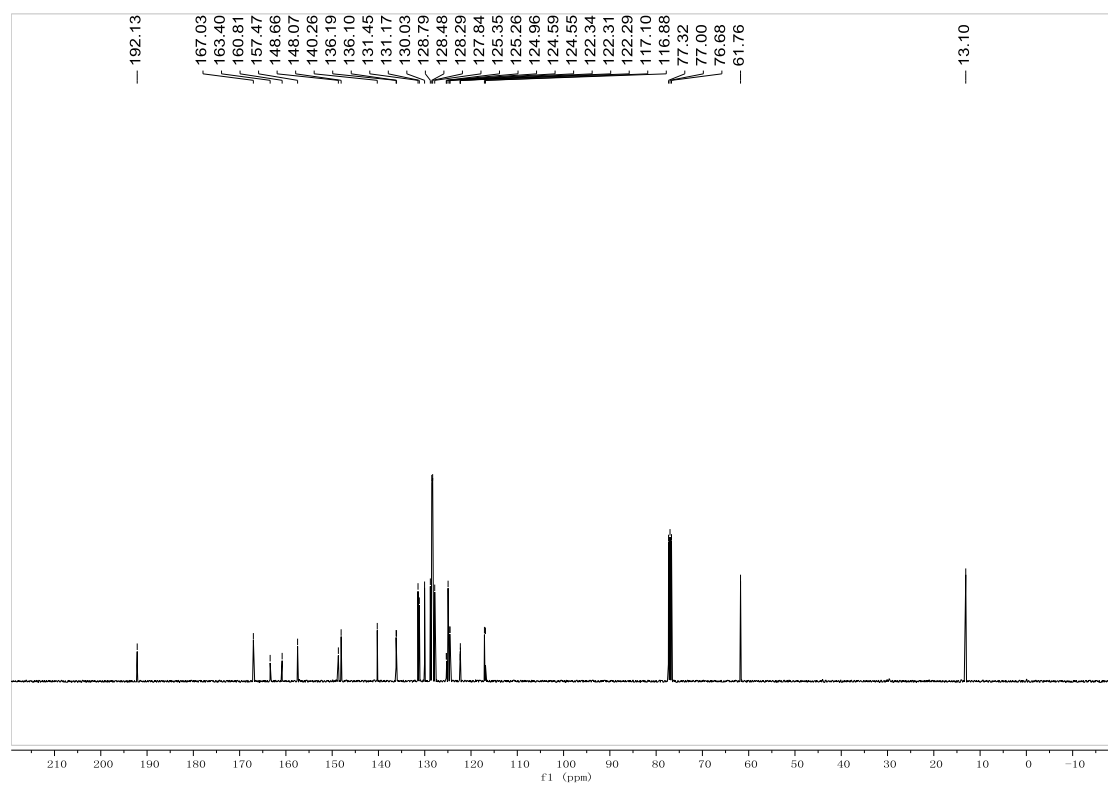
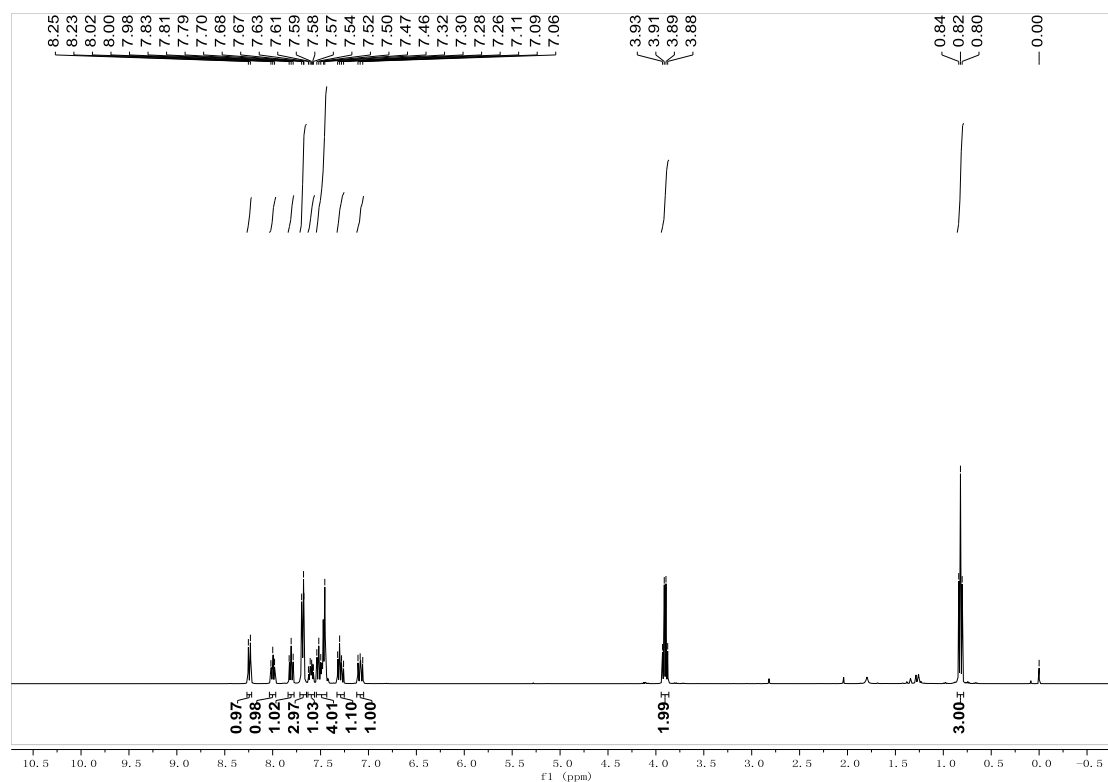


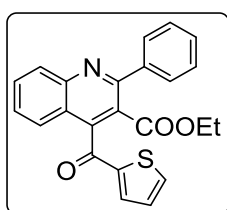
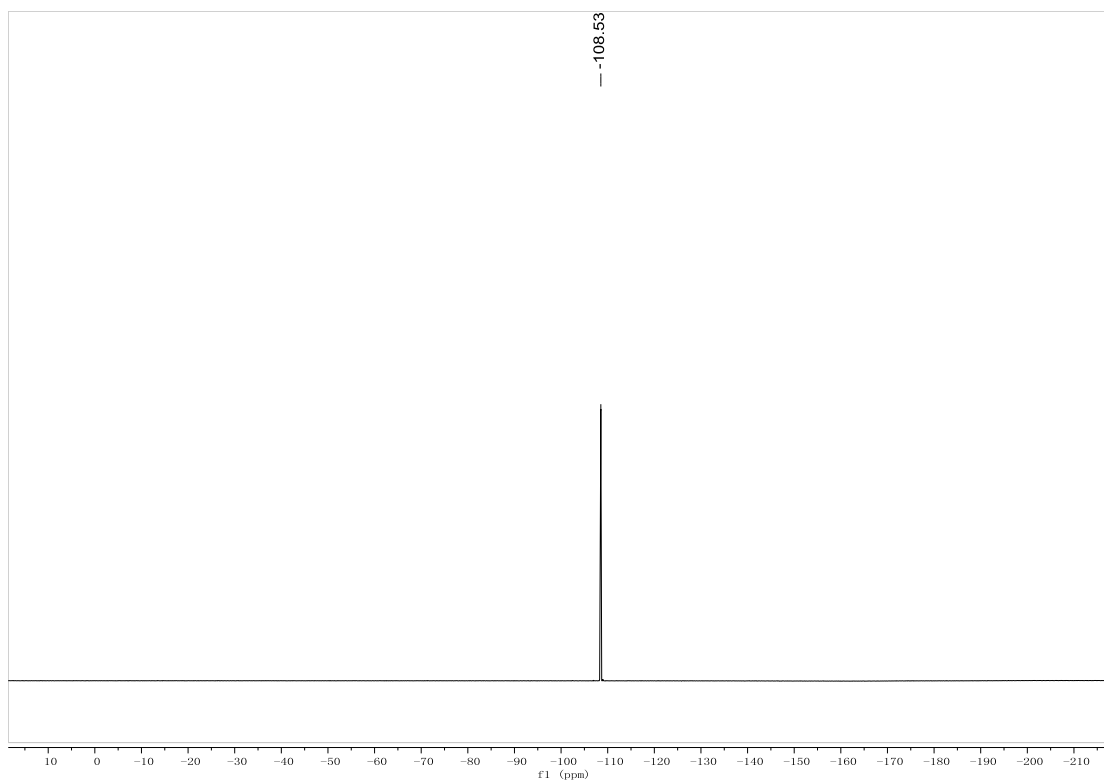


**2h**

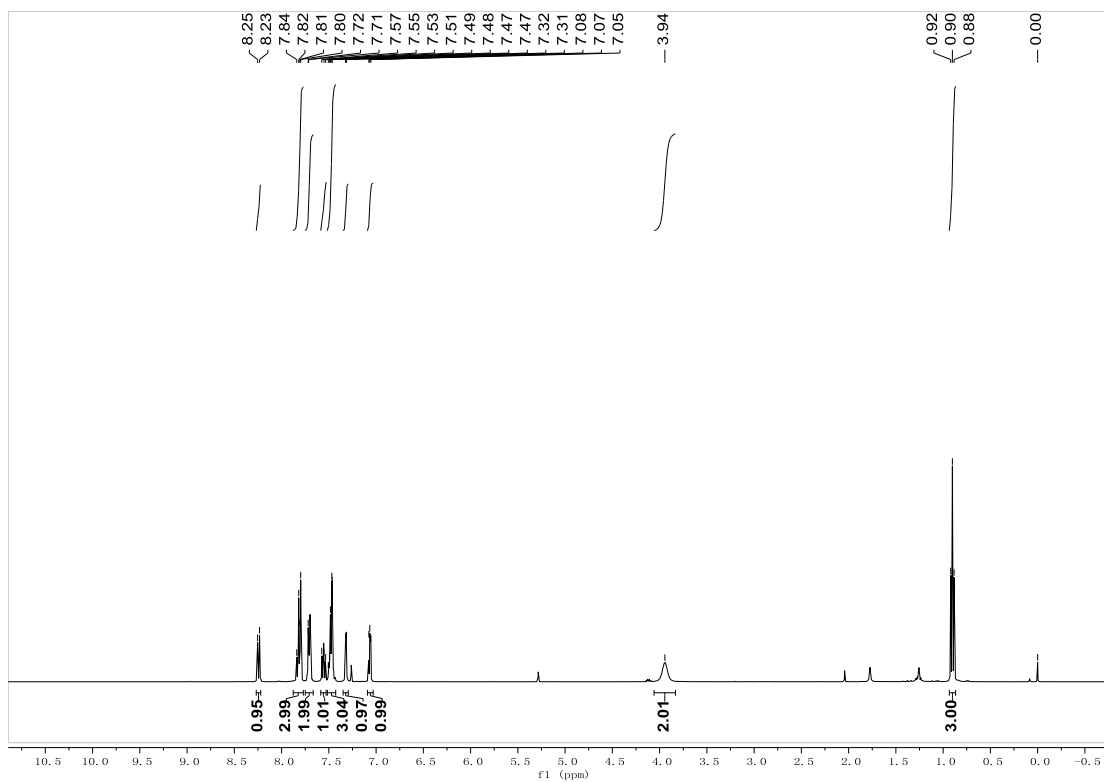


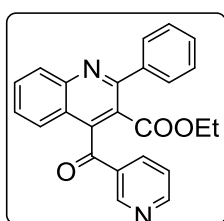
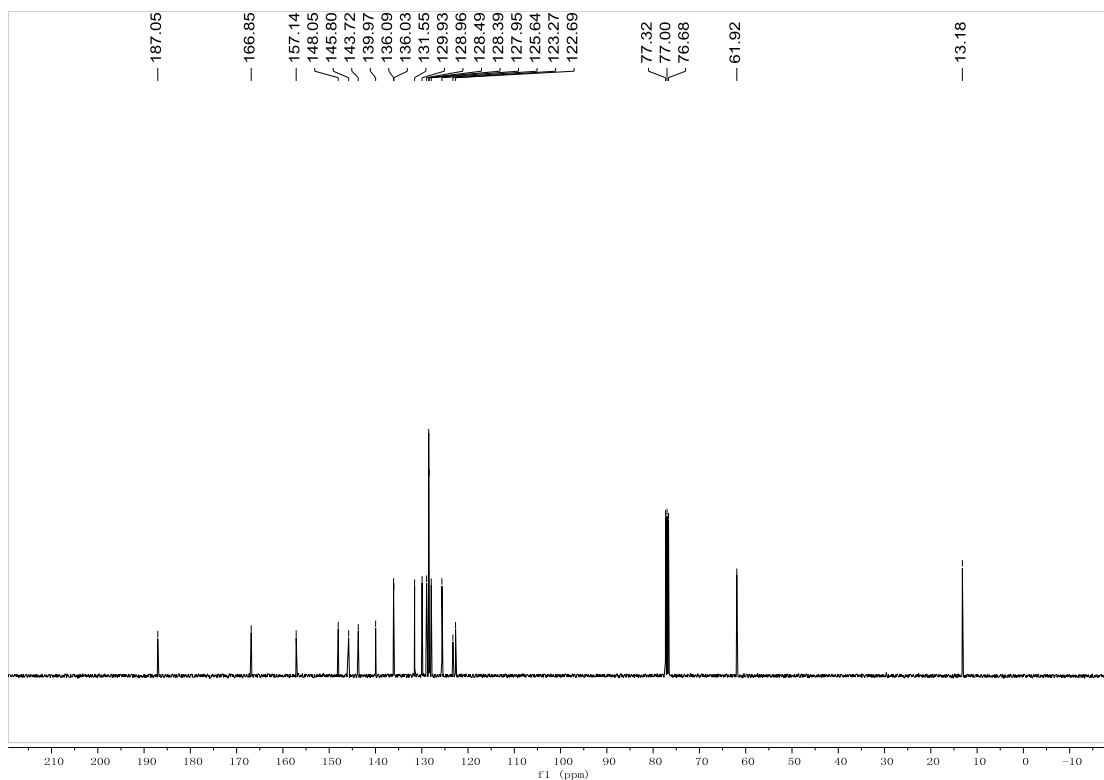
**2i**



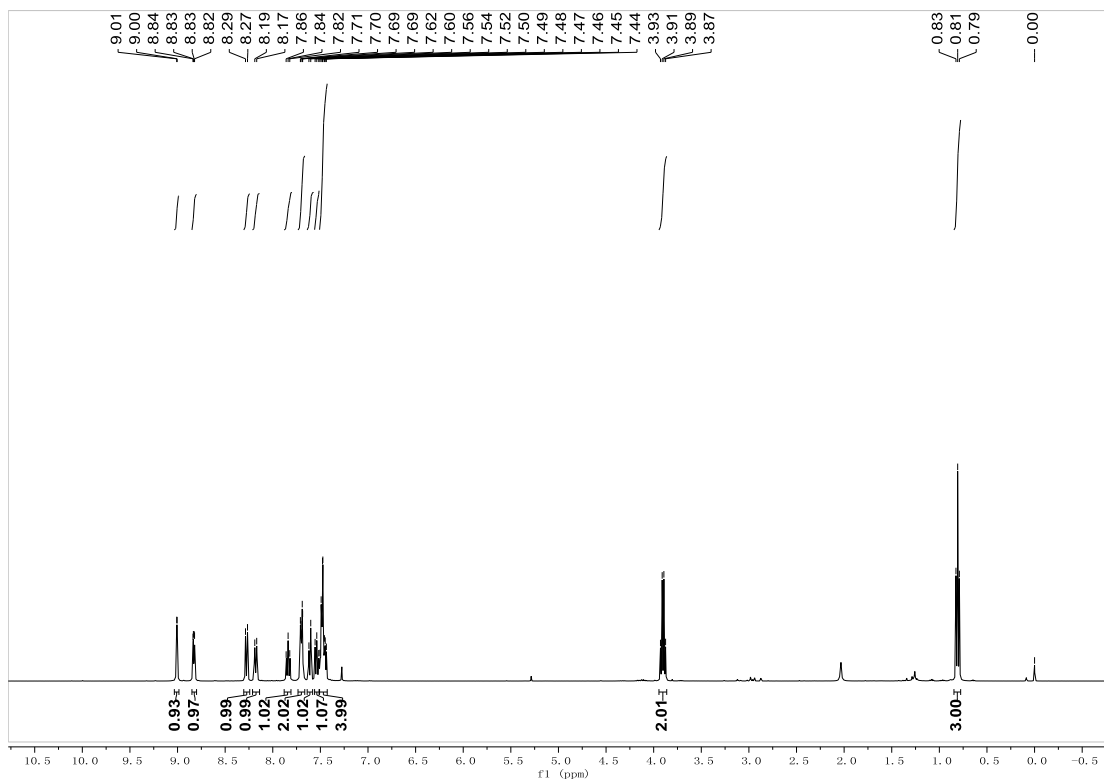


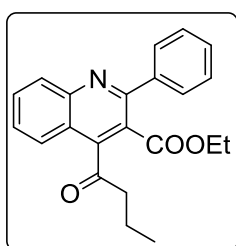
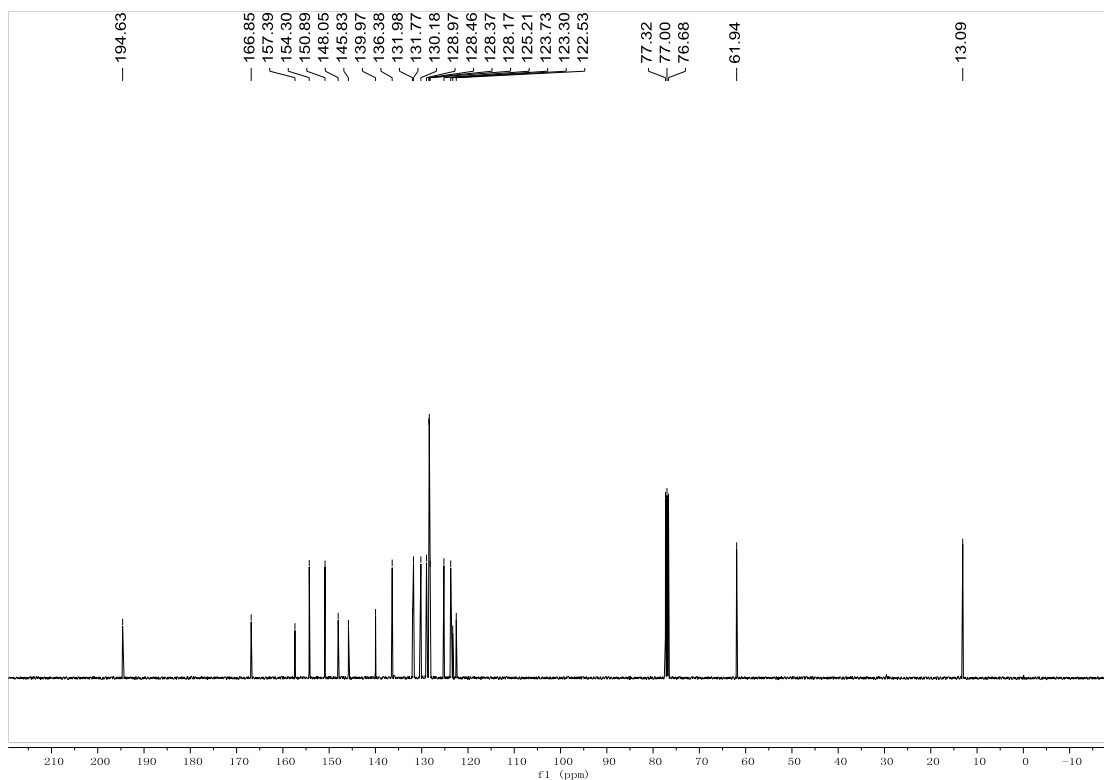
2j



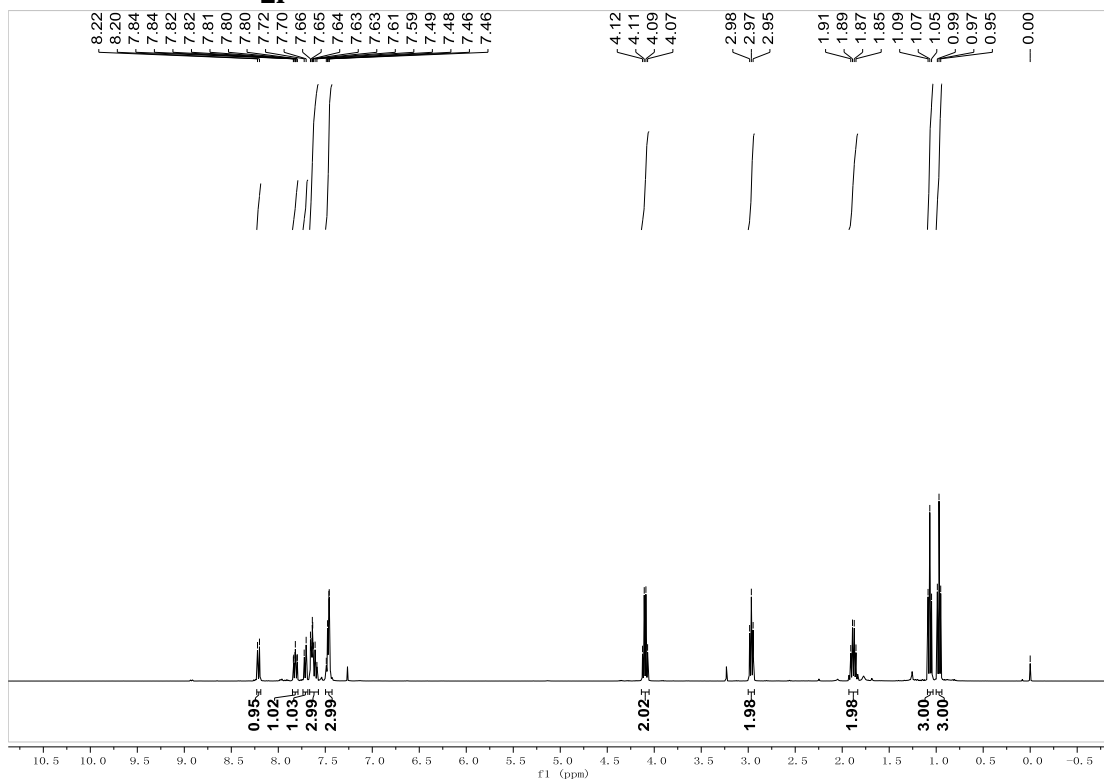


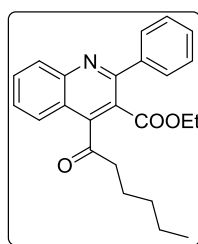
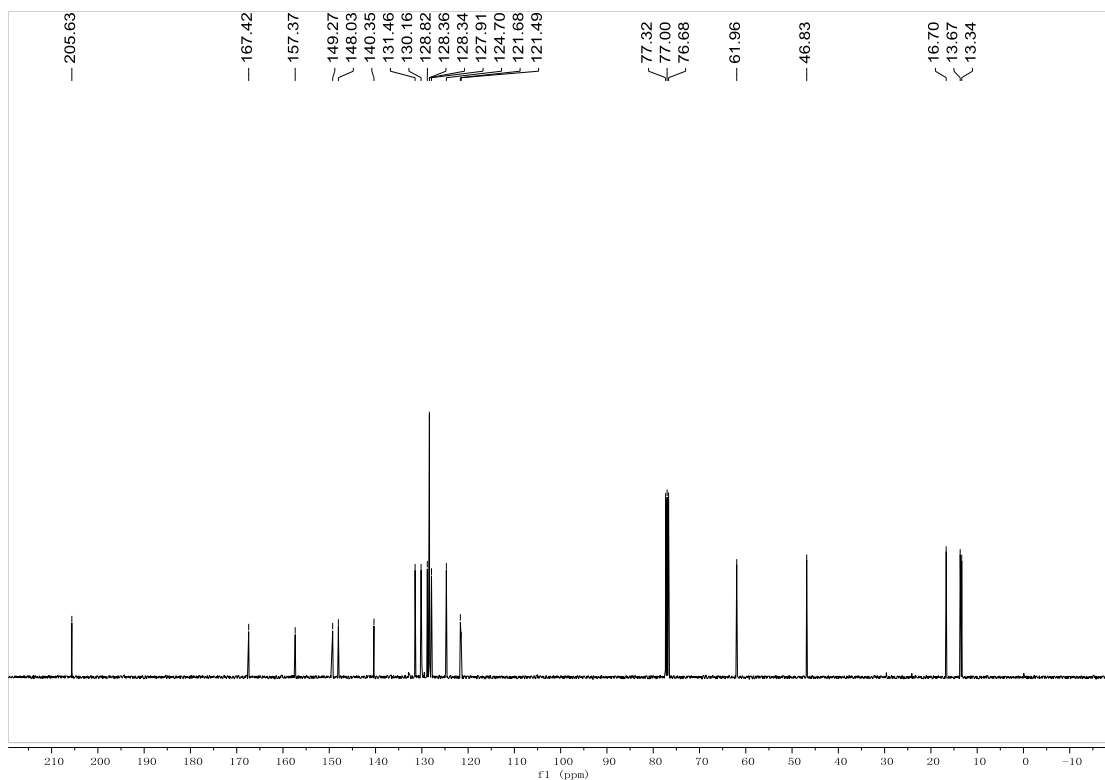
**2k**



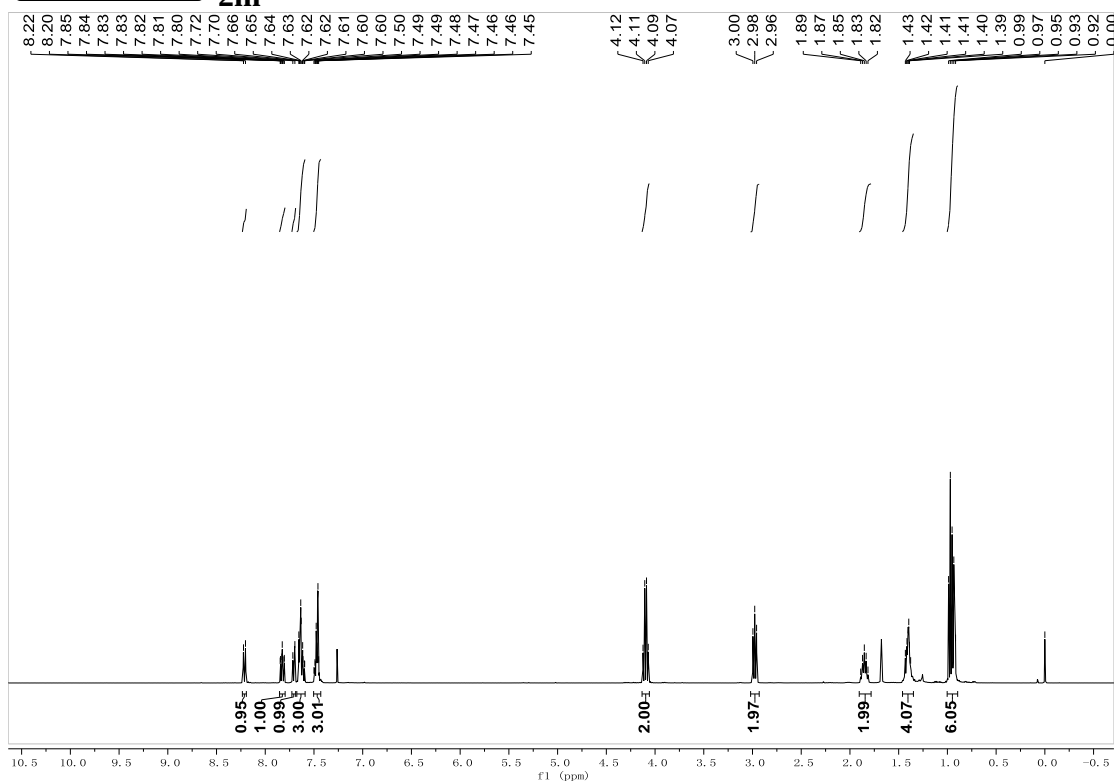


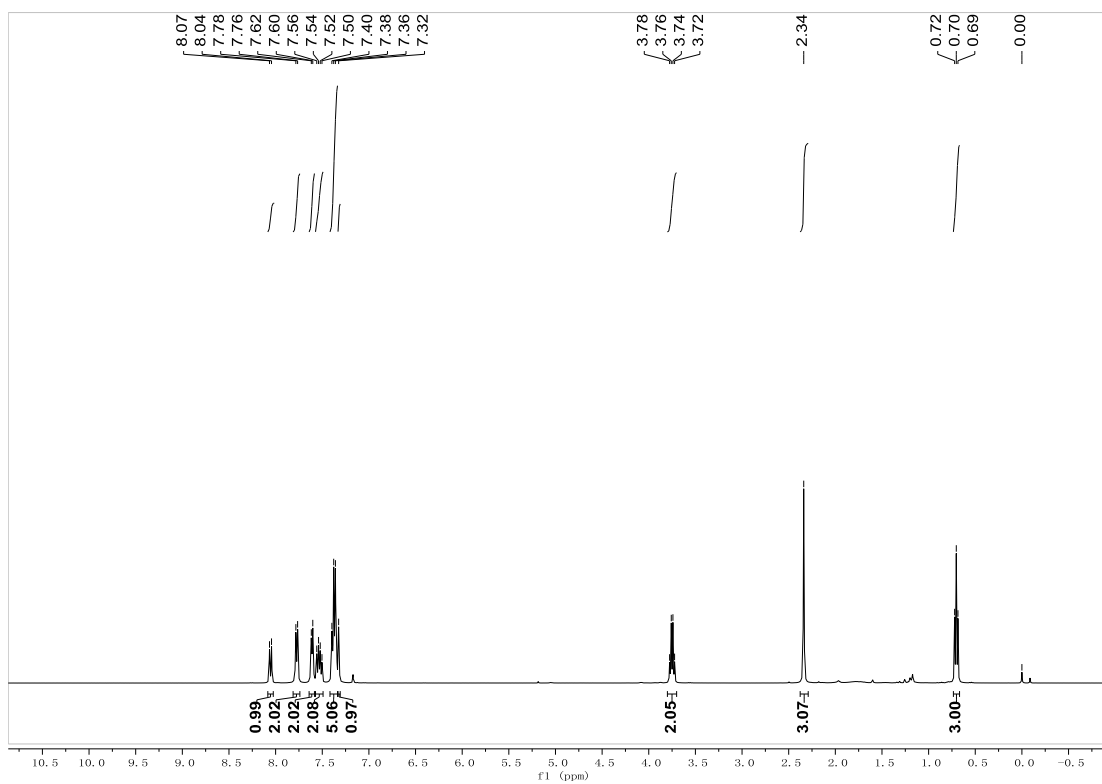
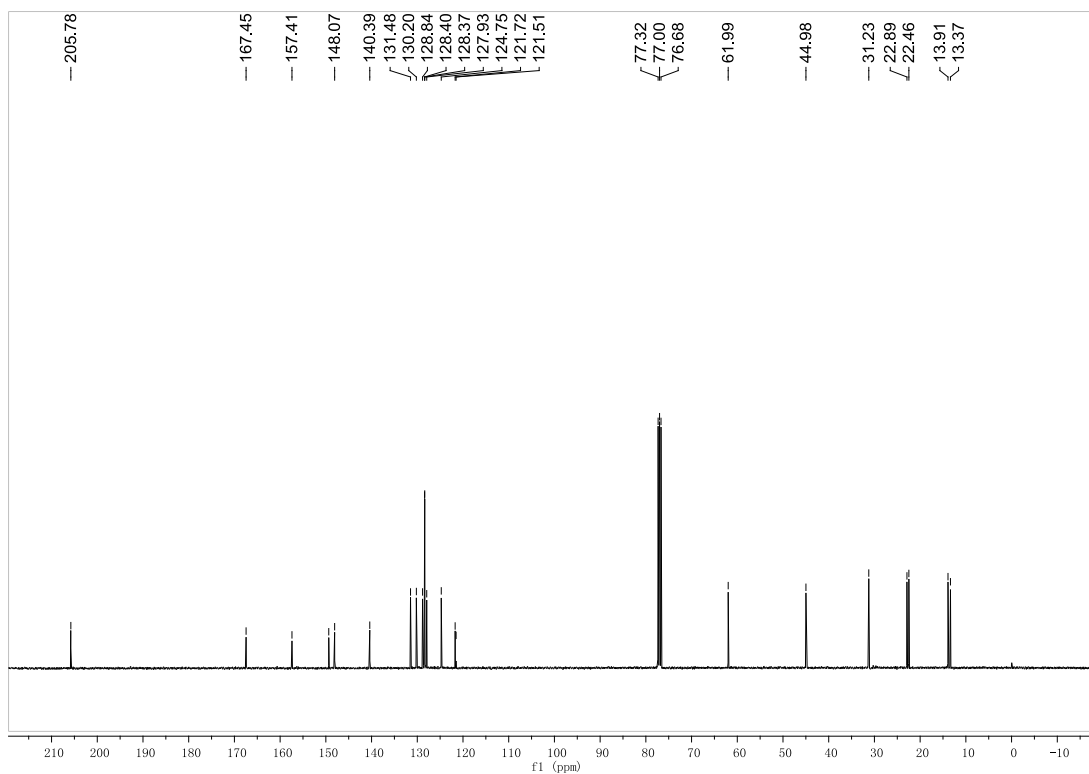
**21**



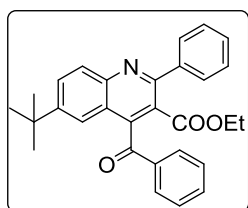
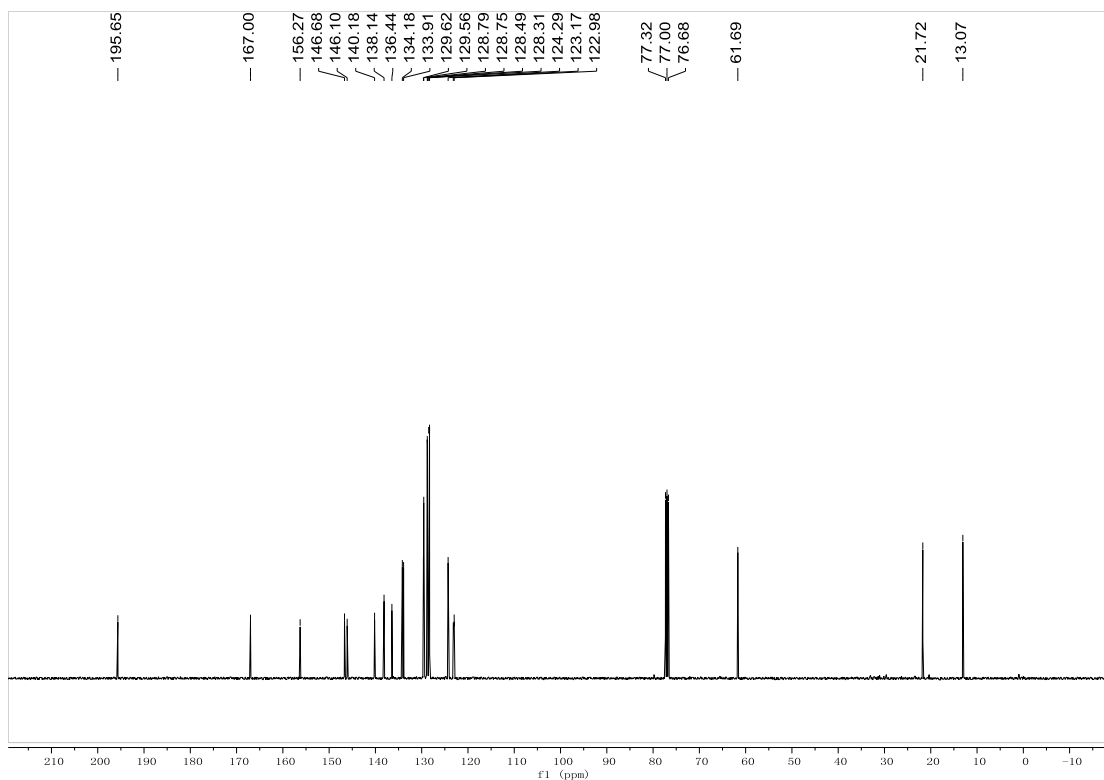


**2m**

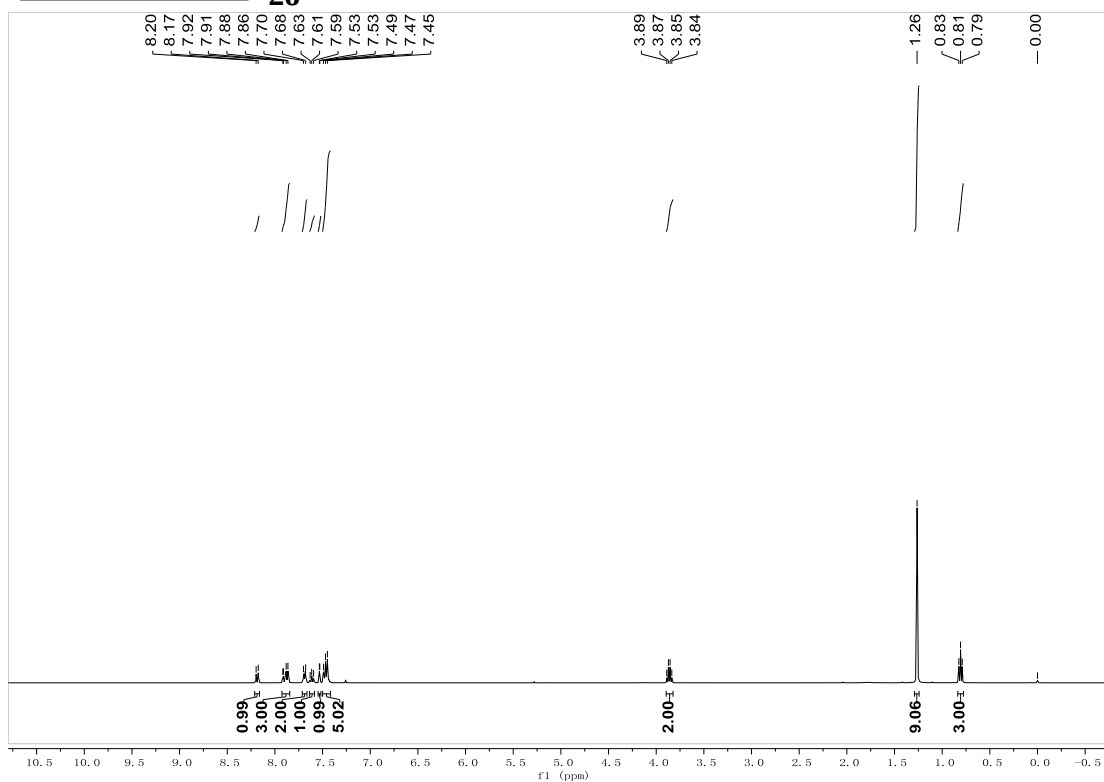


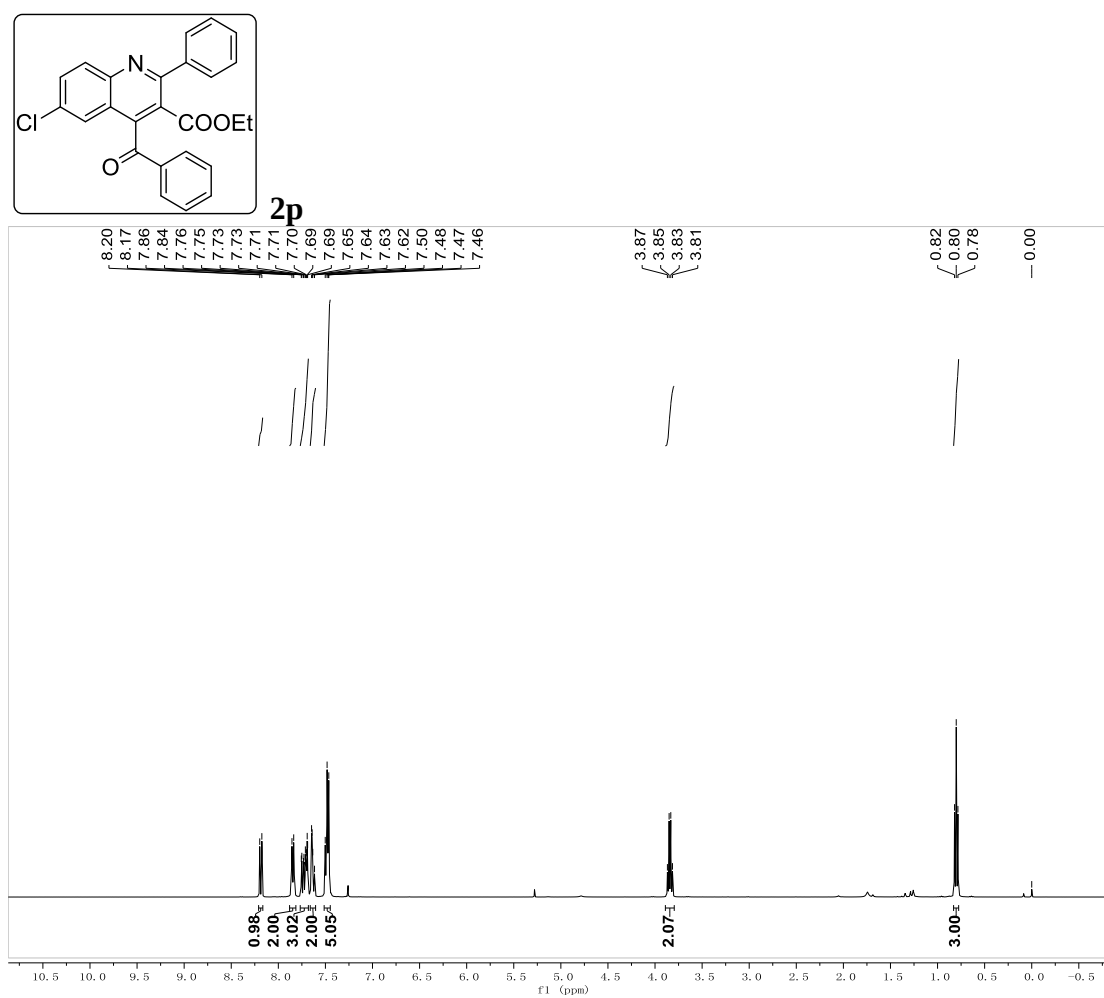
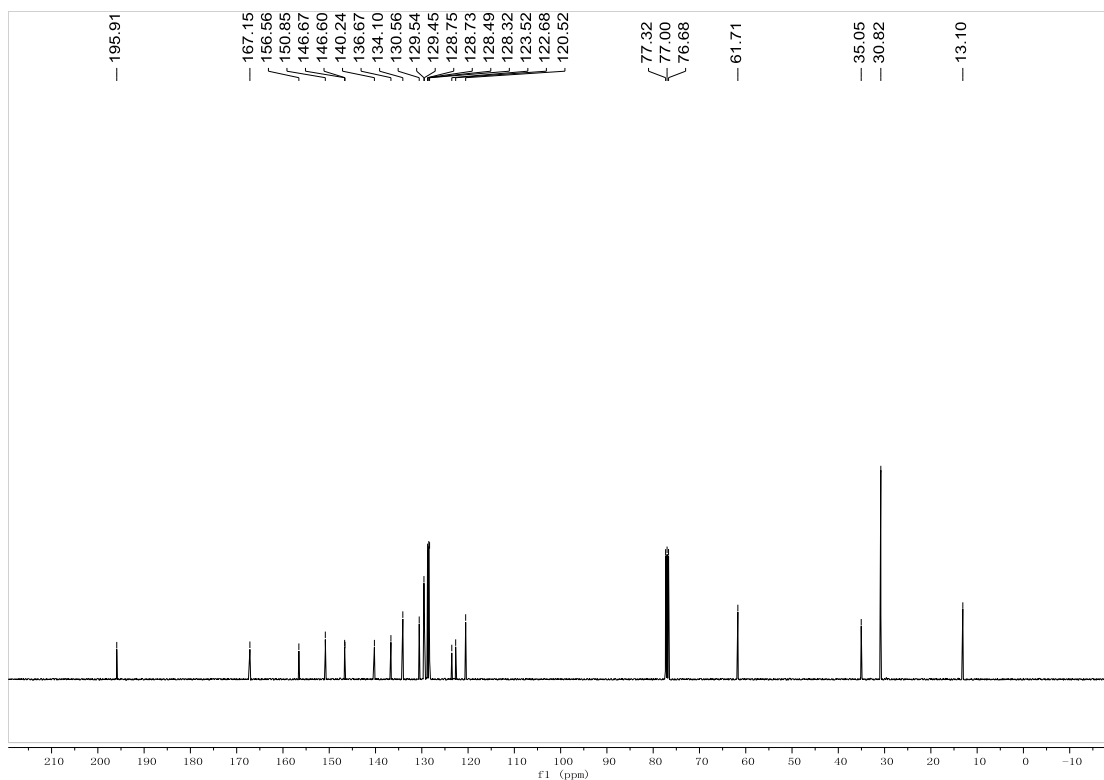


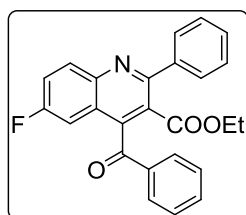
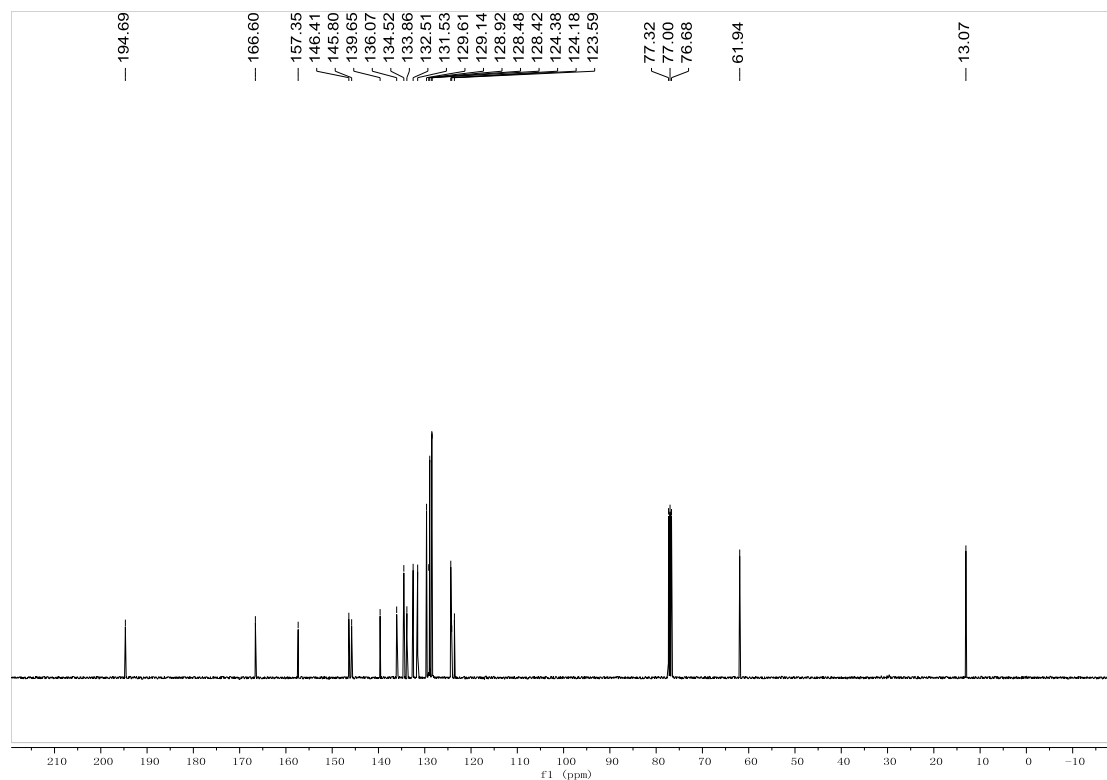




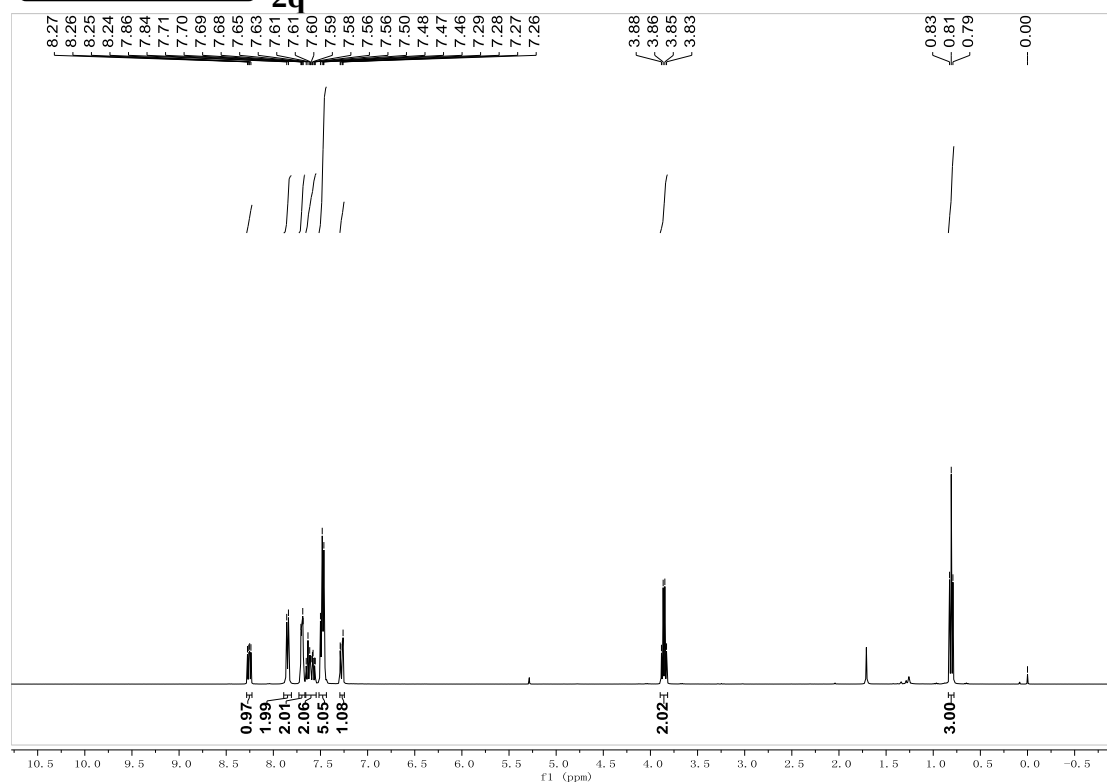
**20**

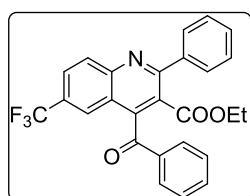
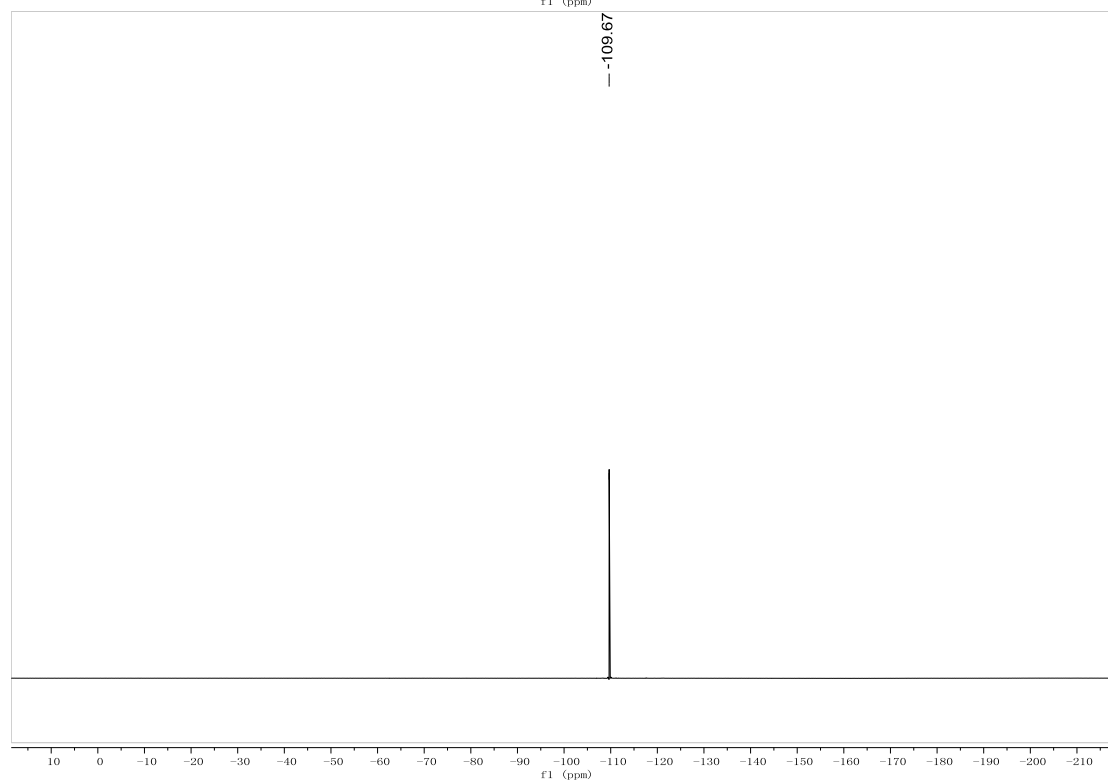
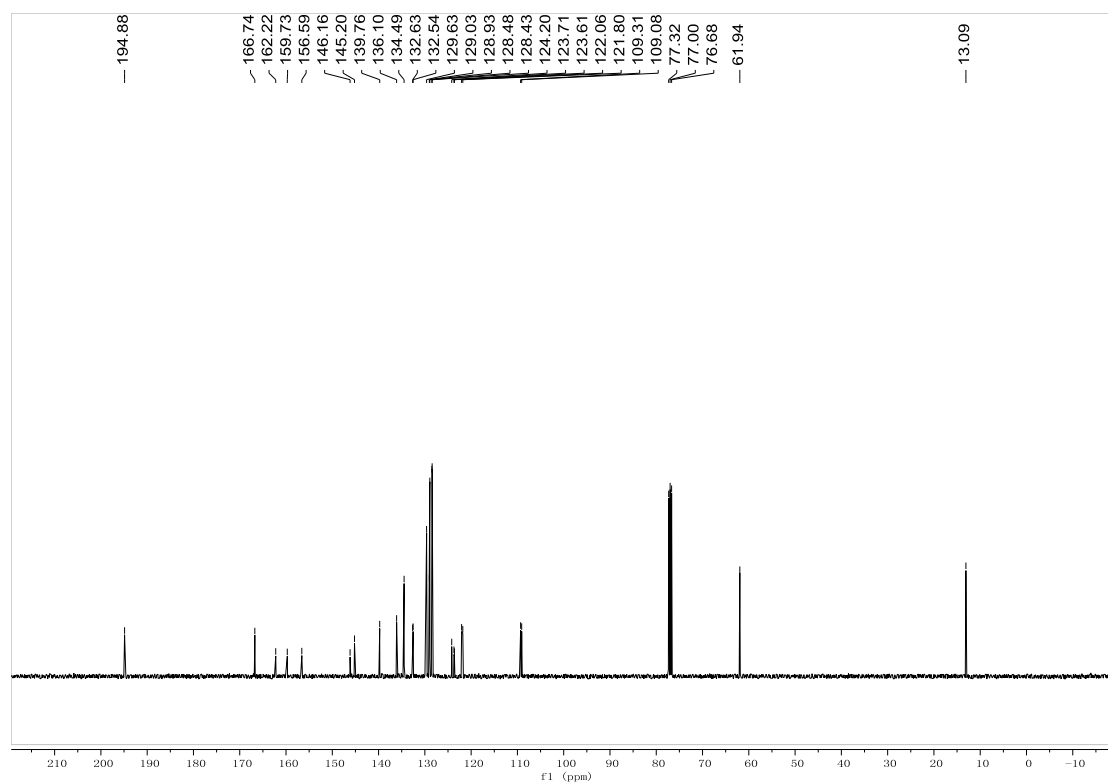




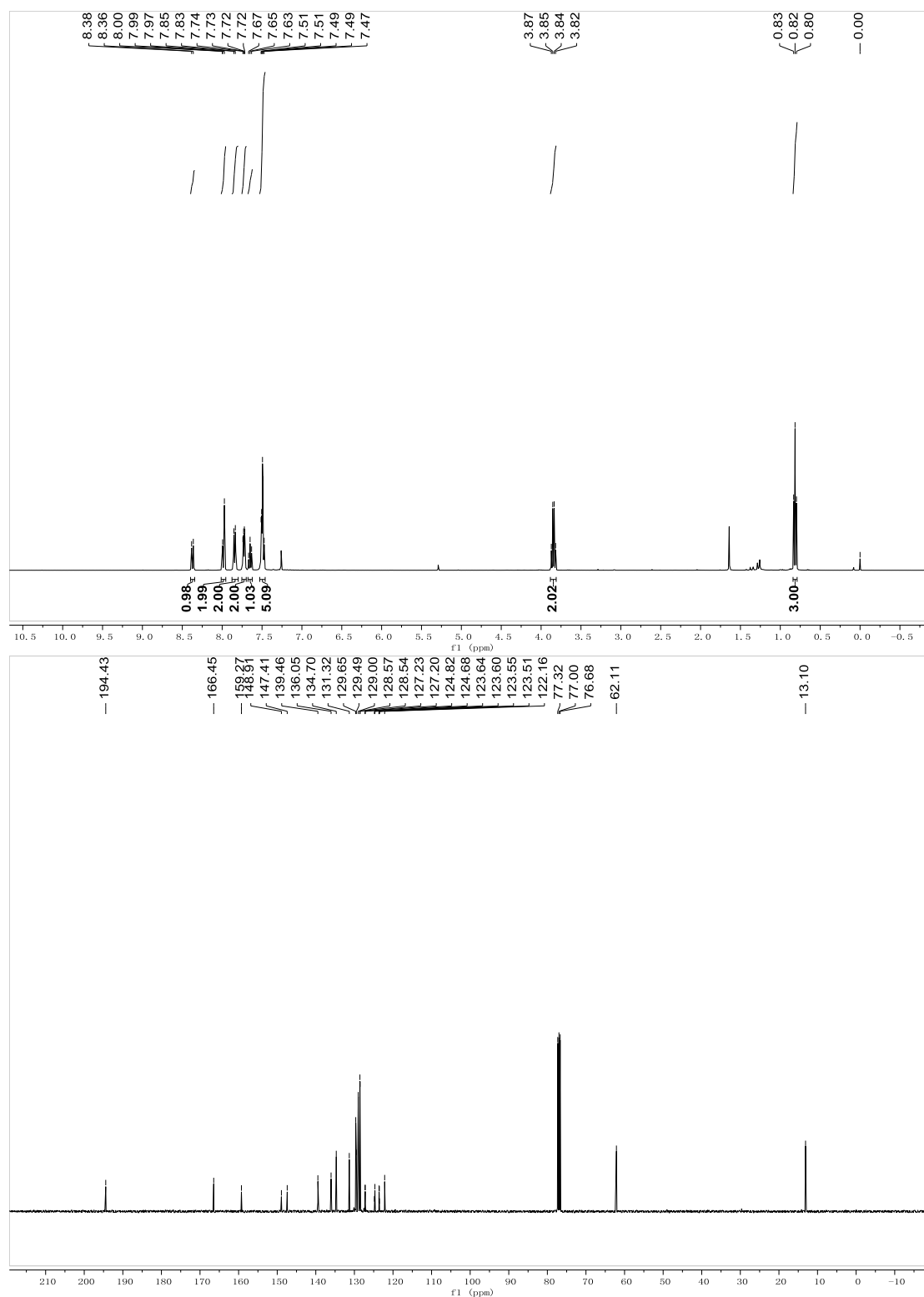


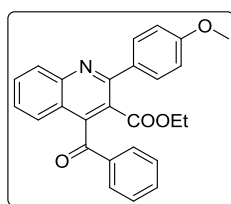
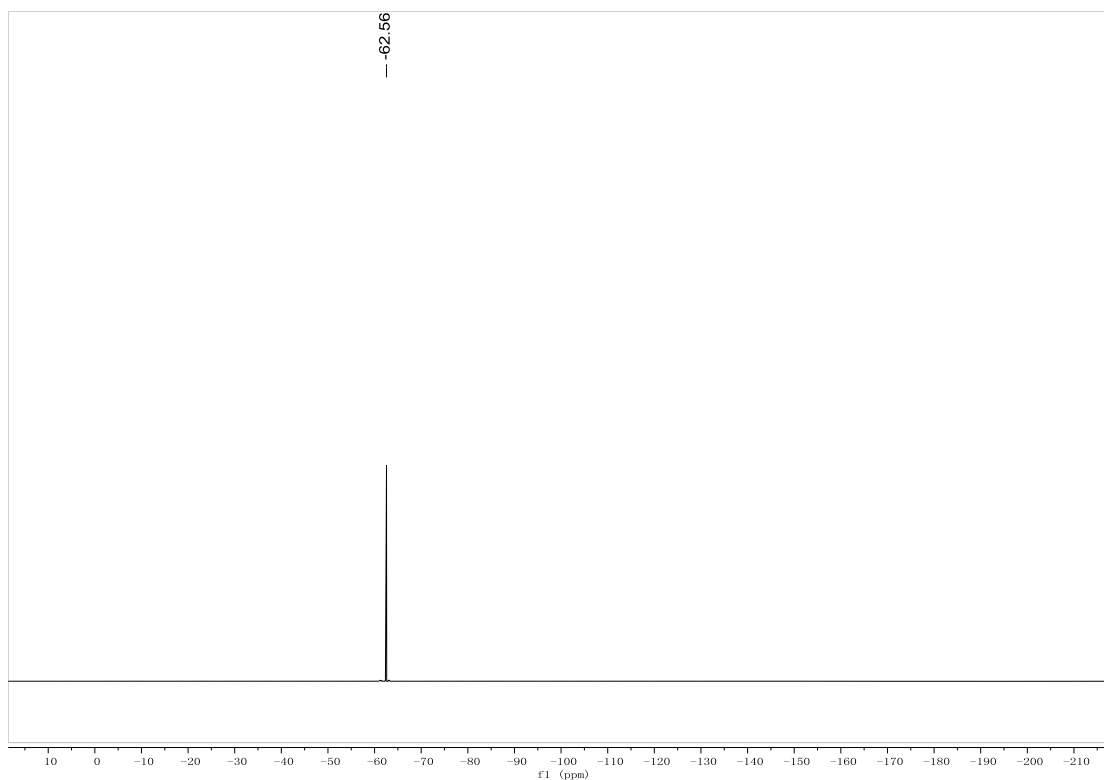
**2q**



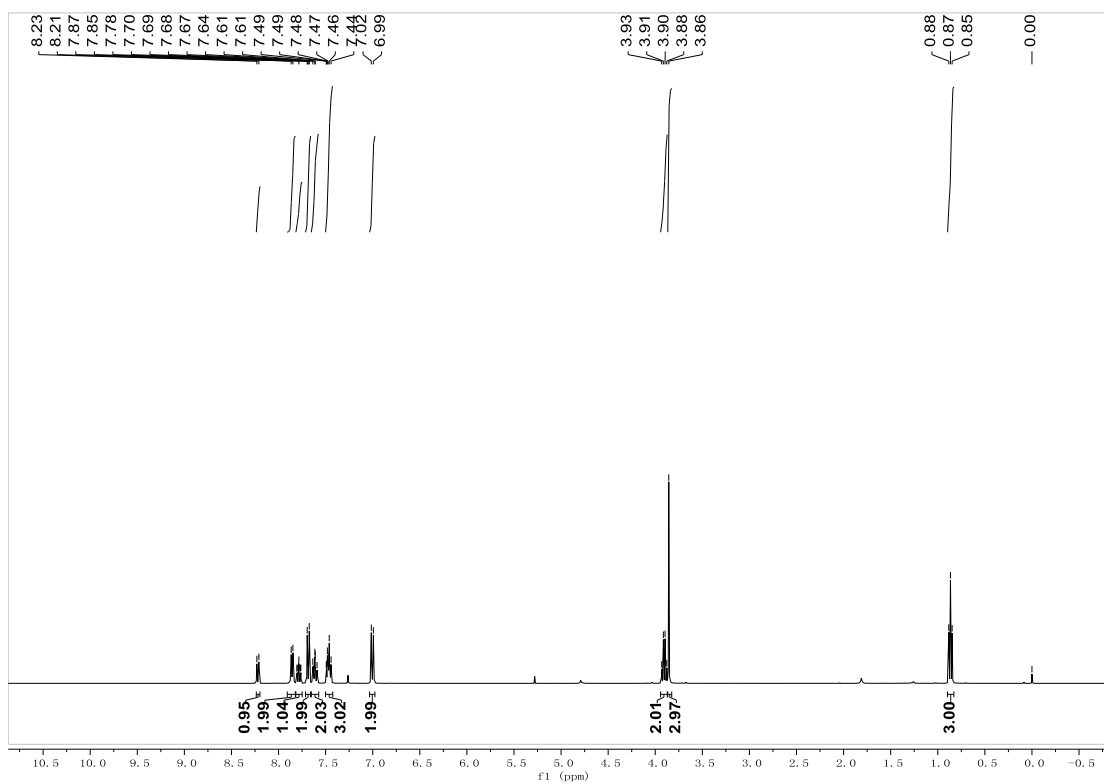


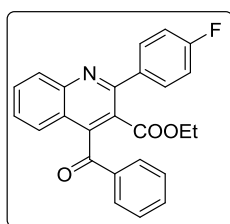
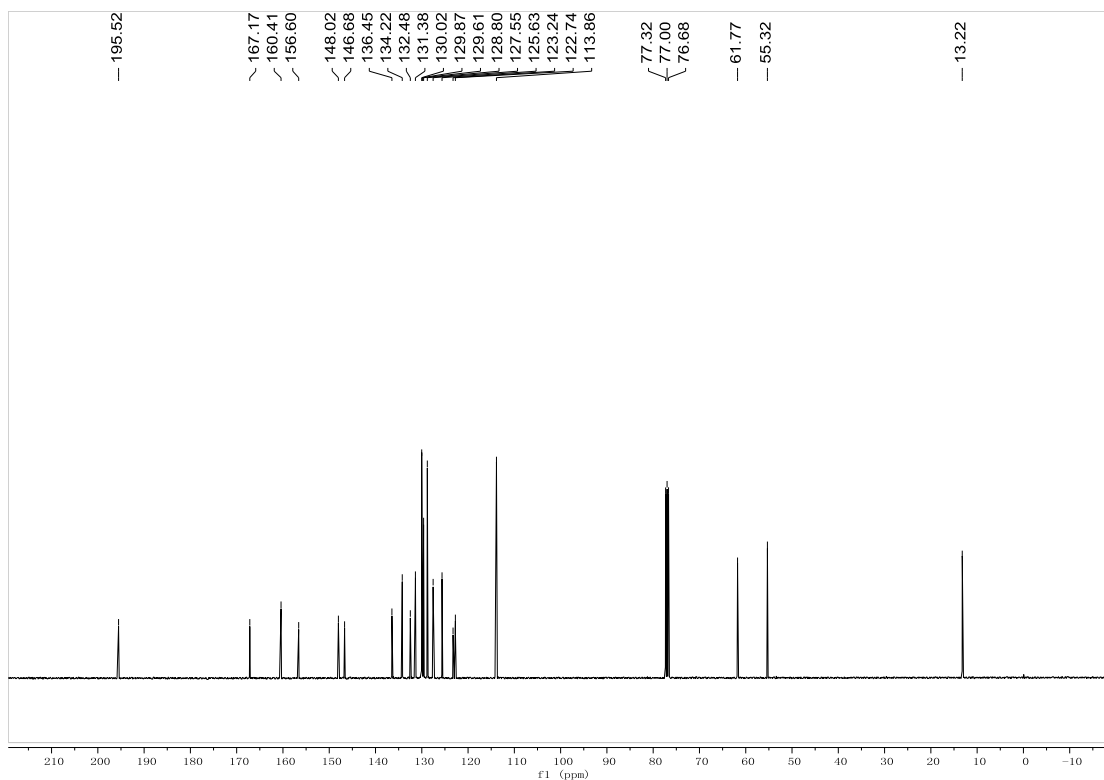
**2r**



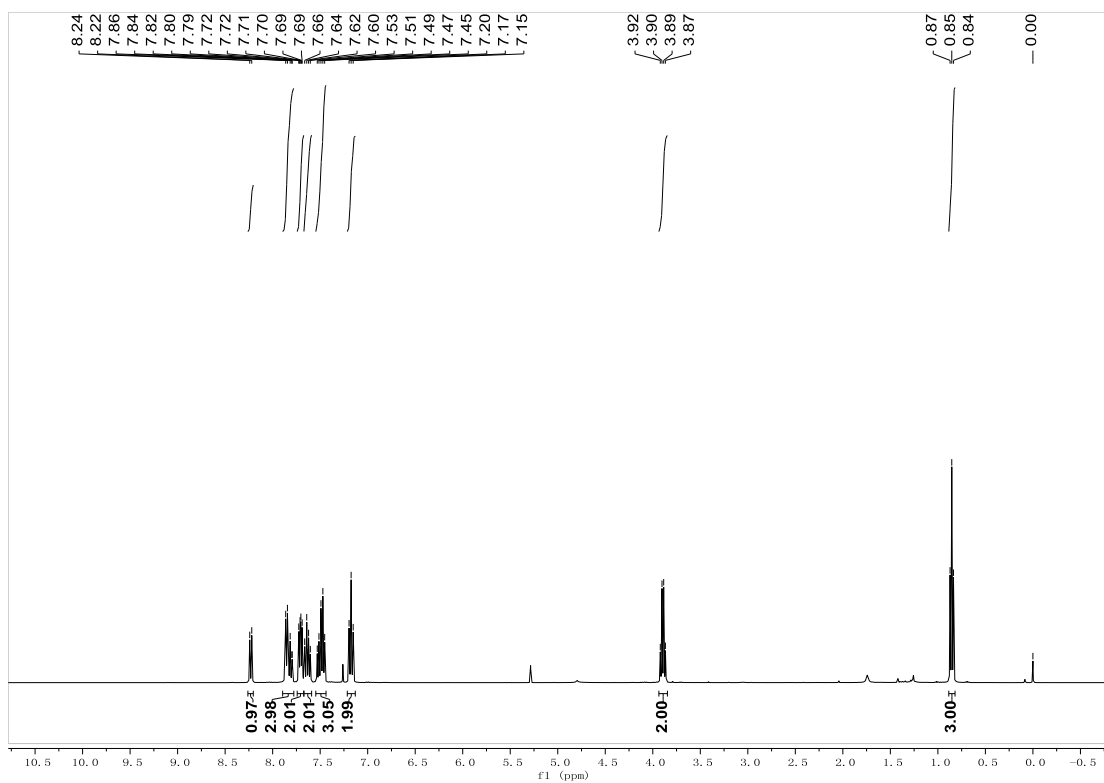


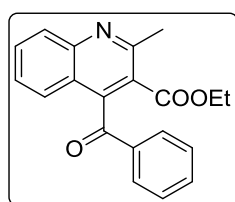
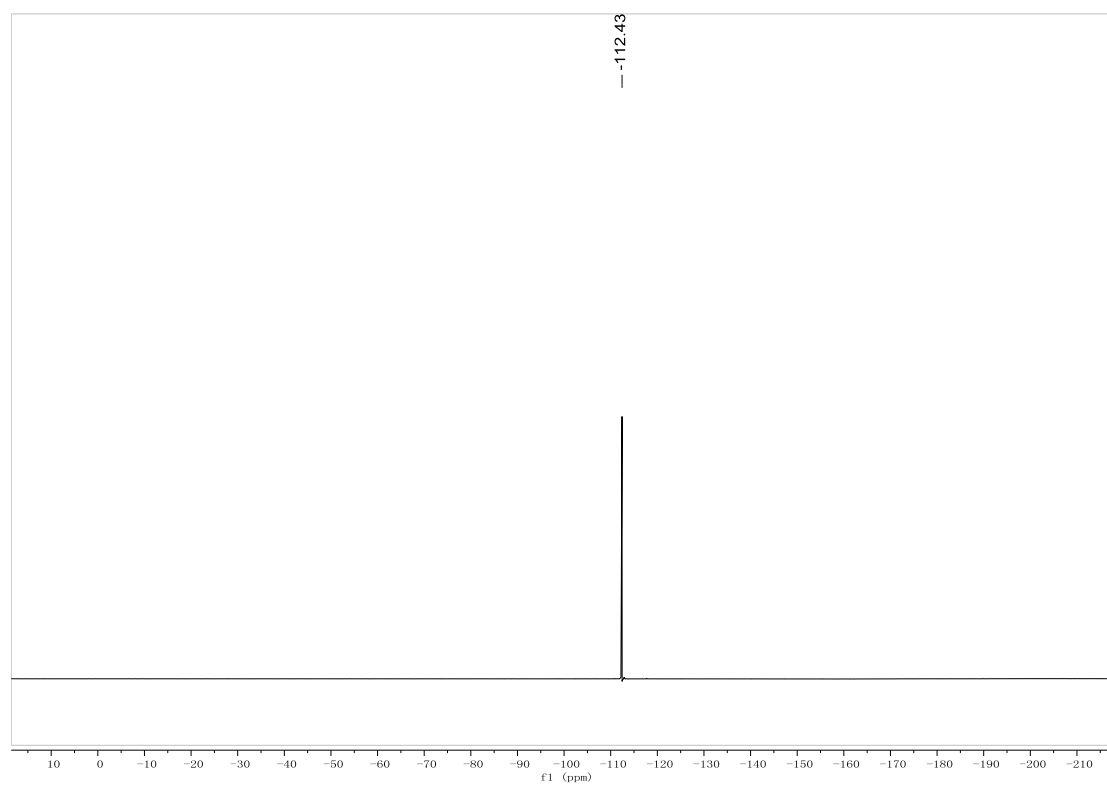
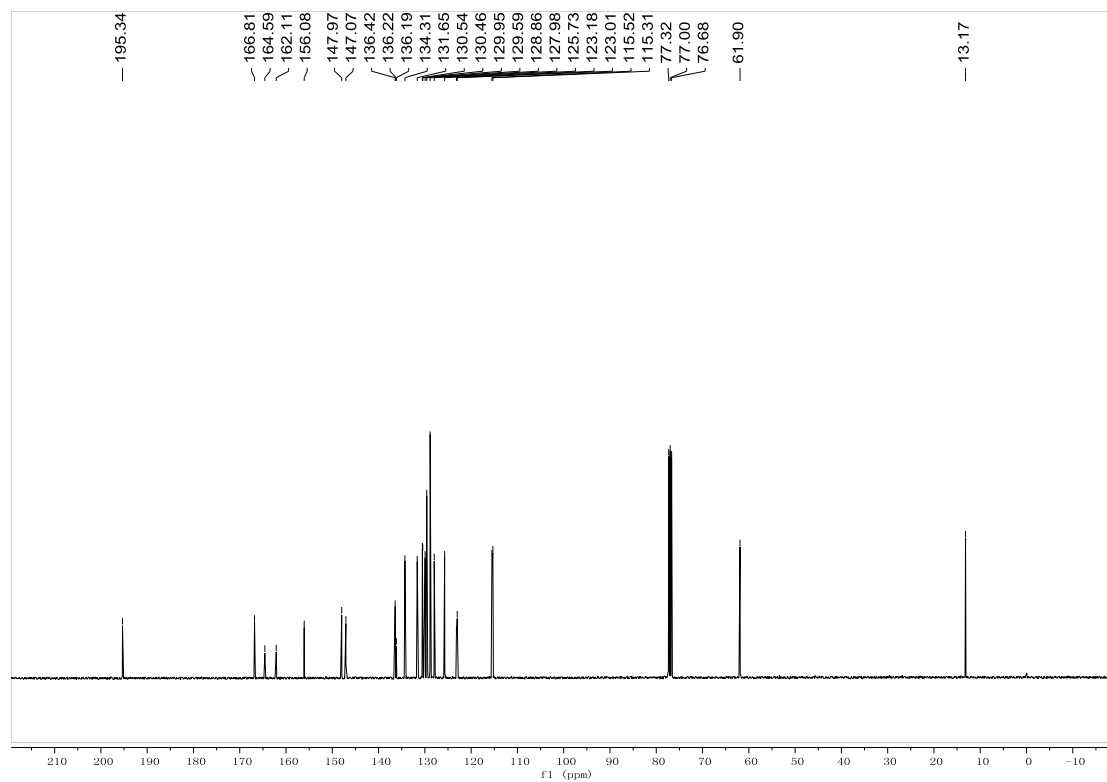
2s





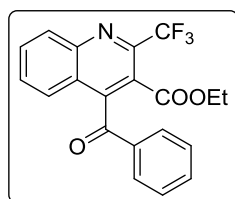
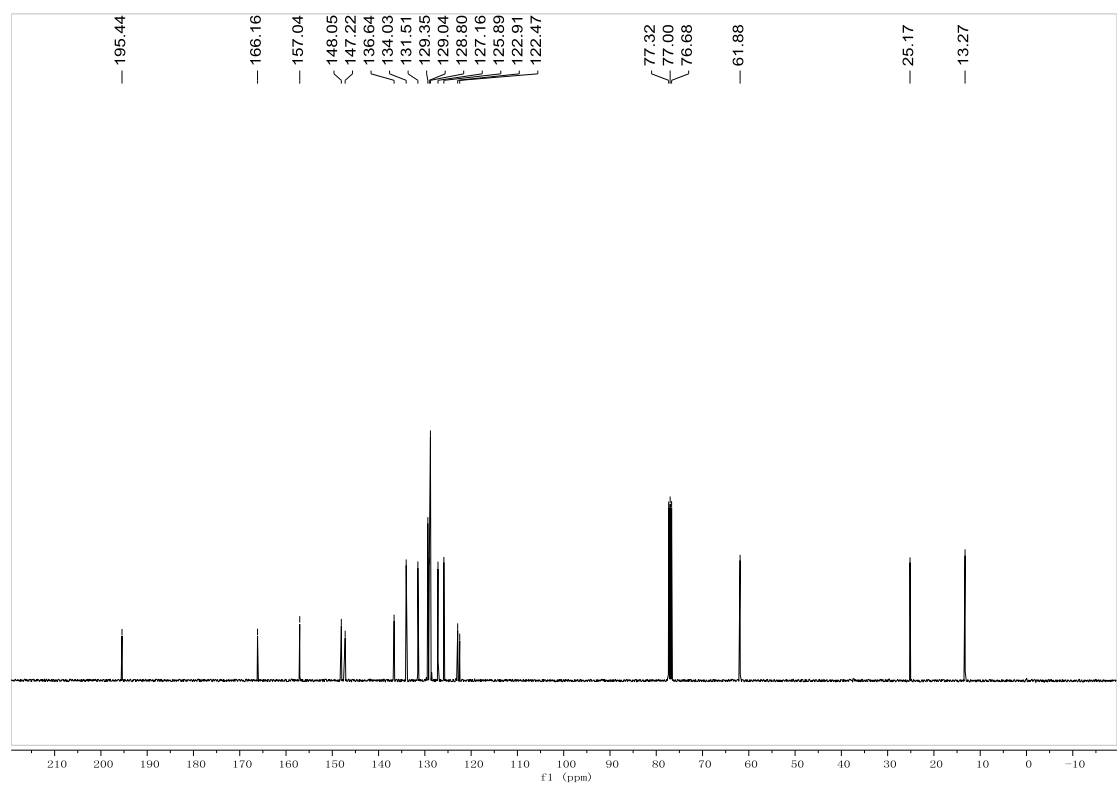
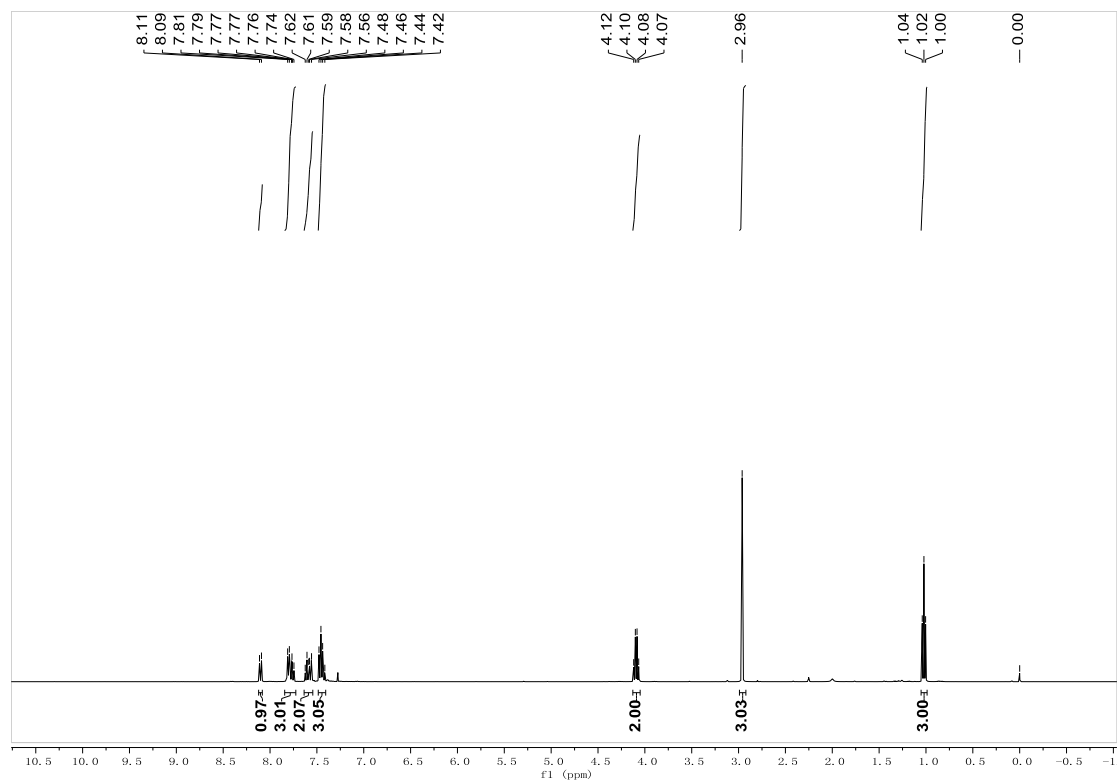
**2t**



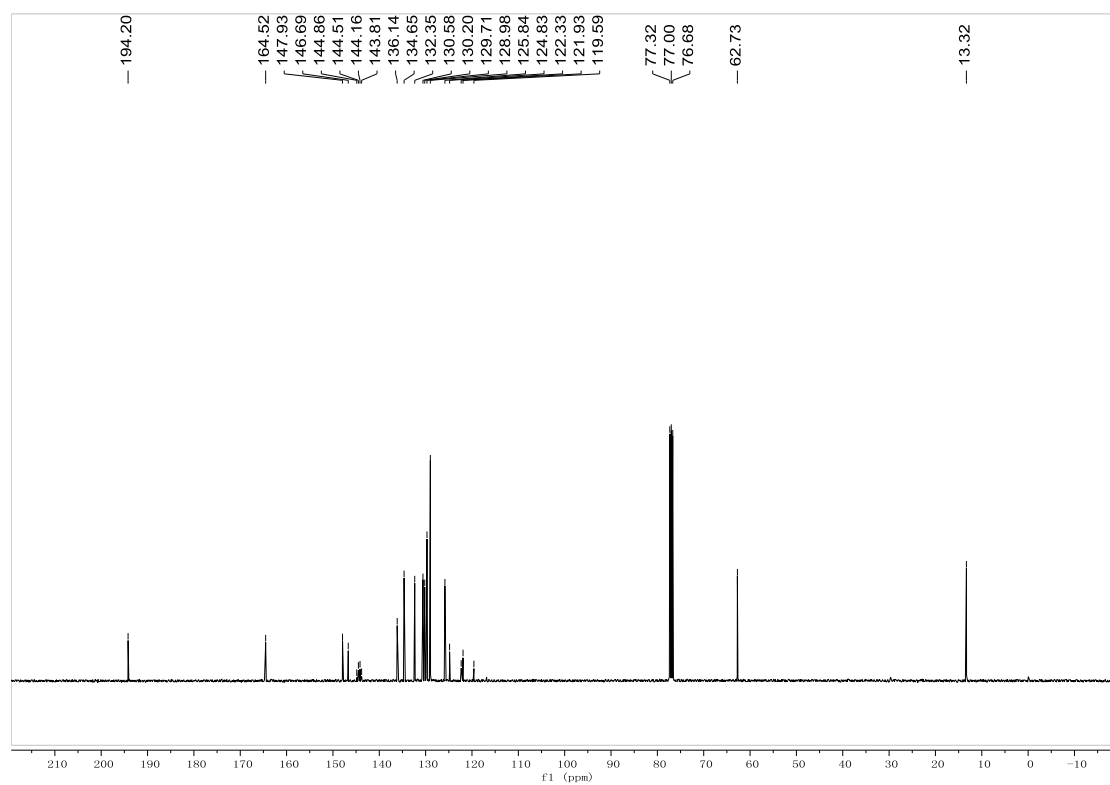
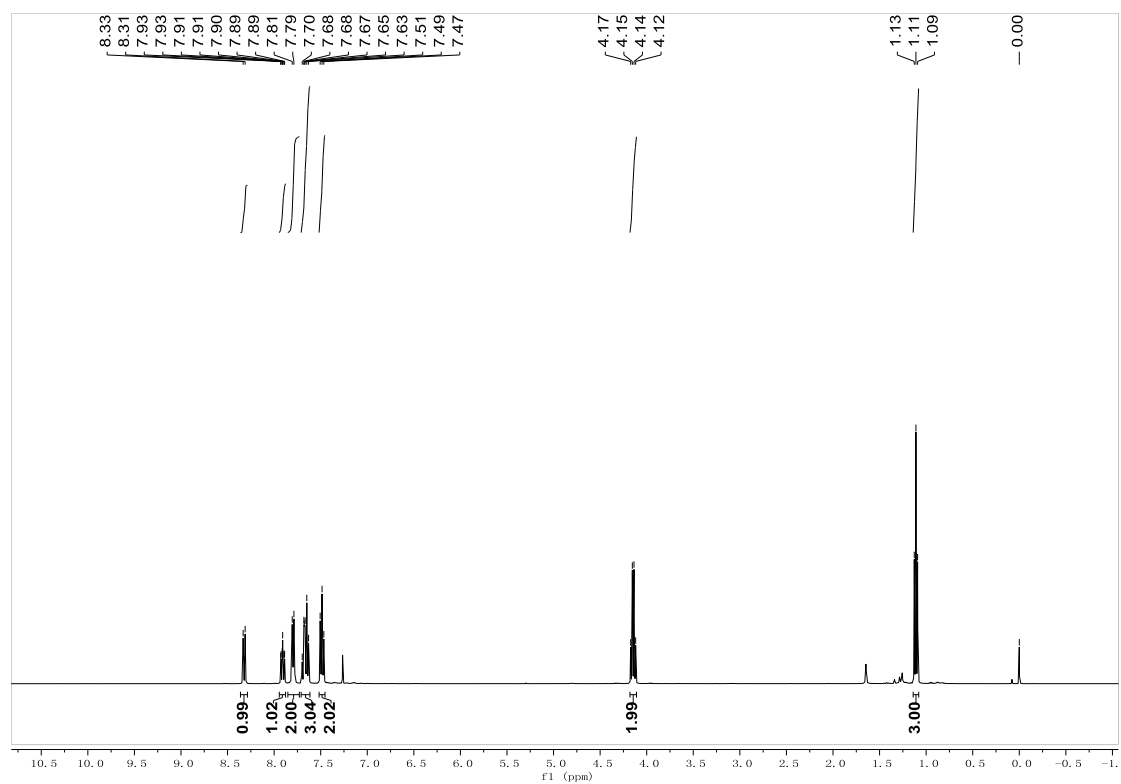


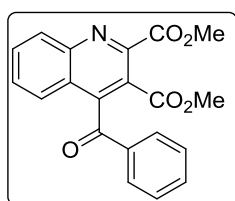
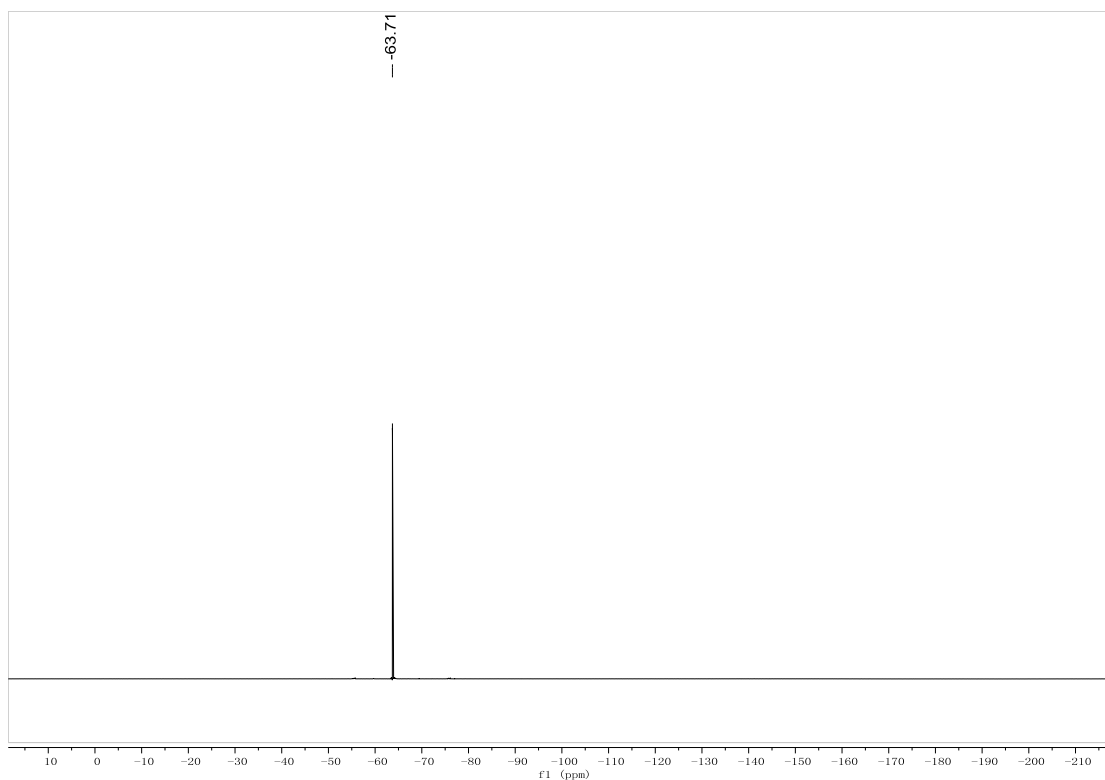
**2u**



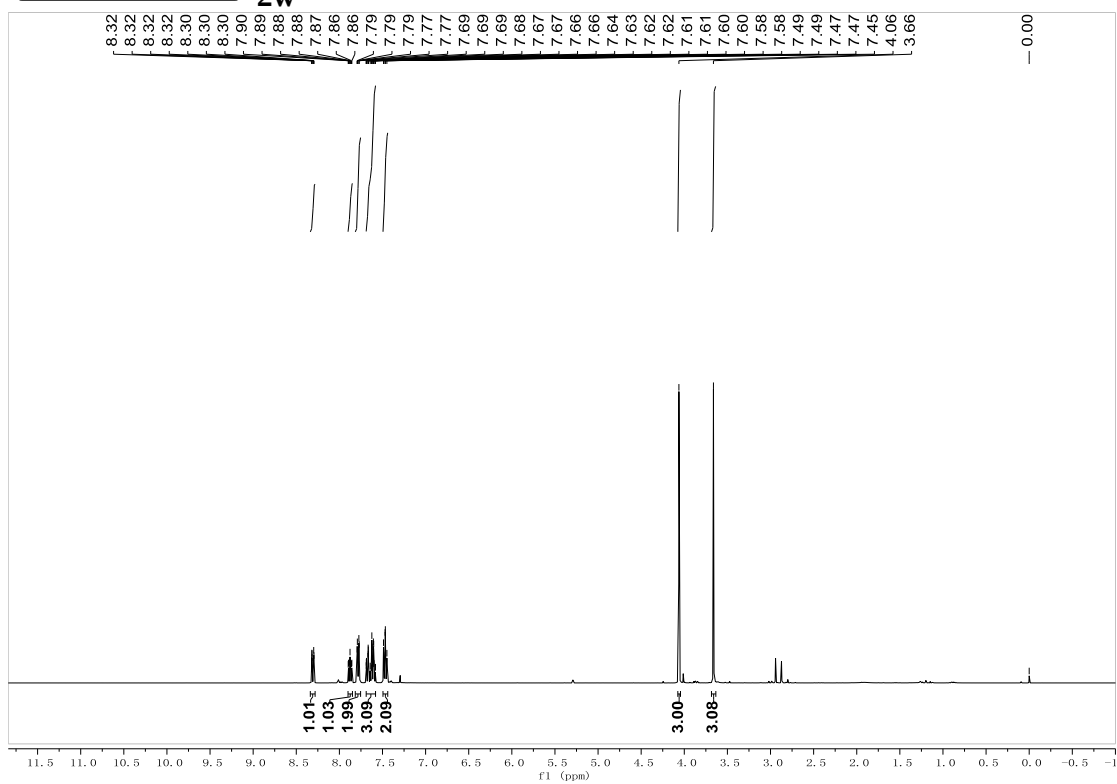


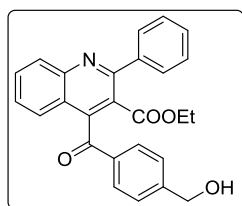
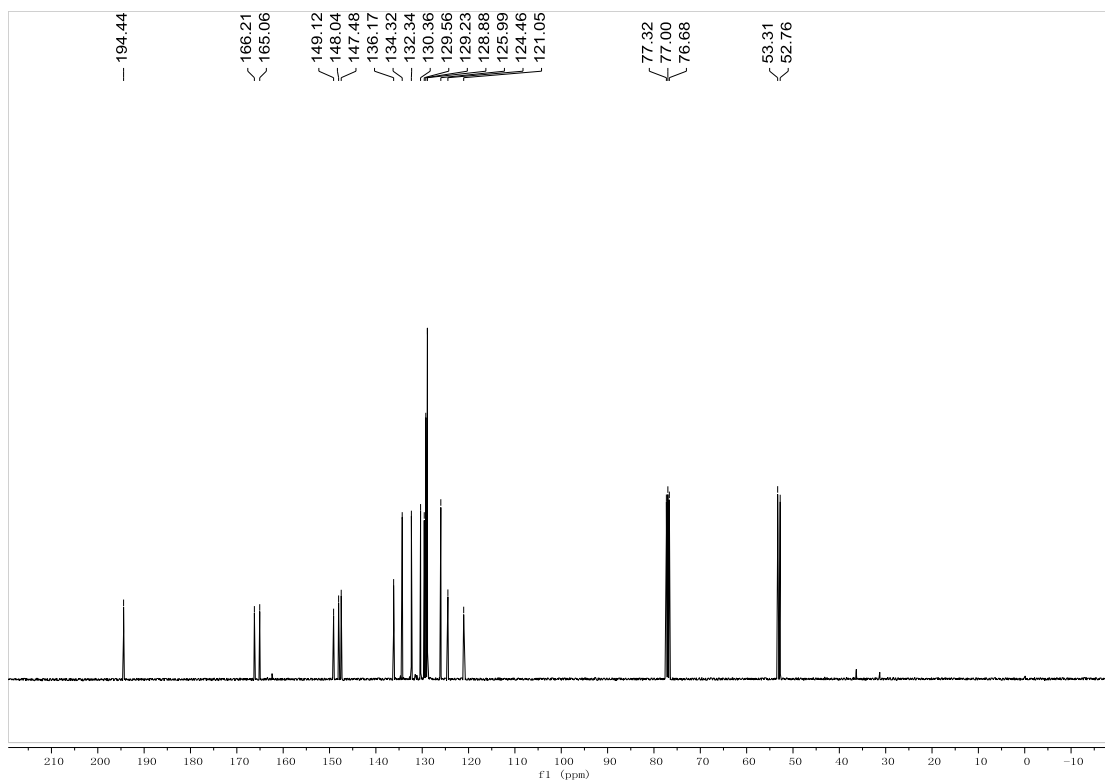
**2v**



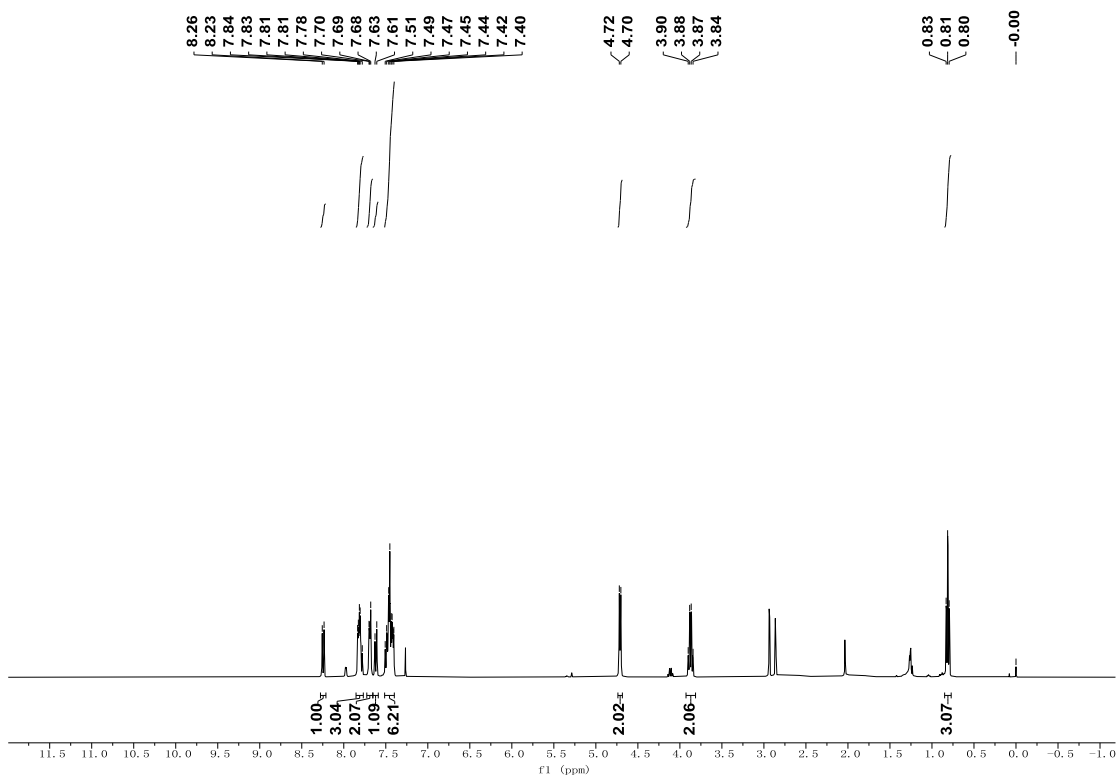


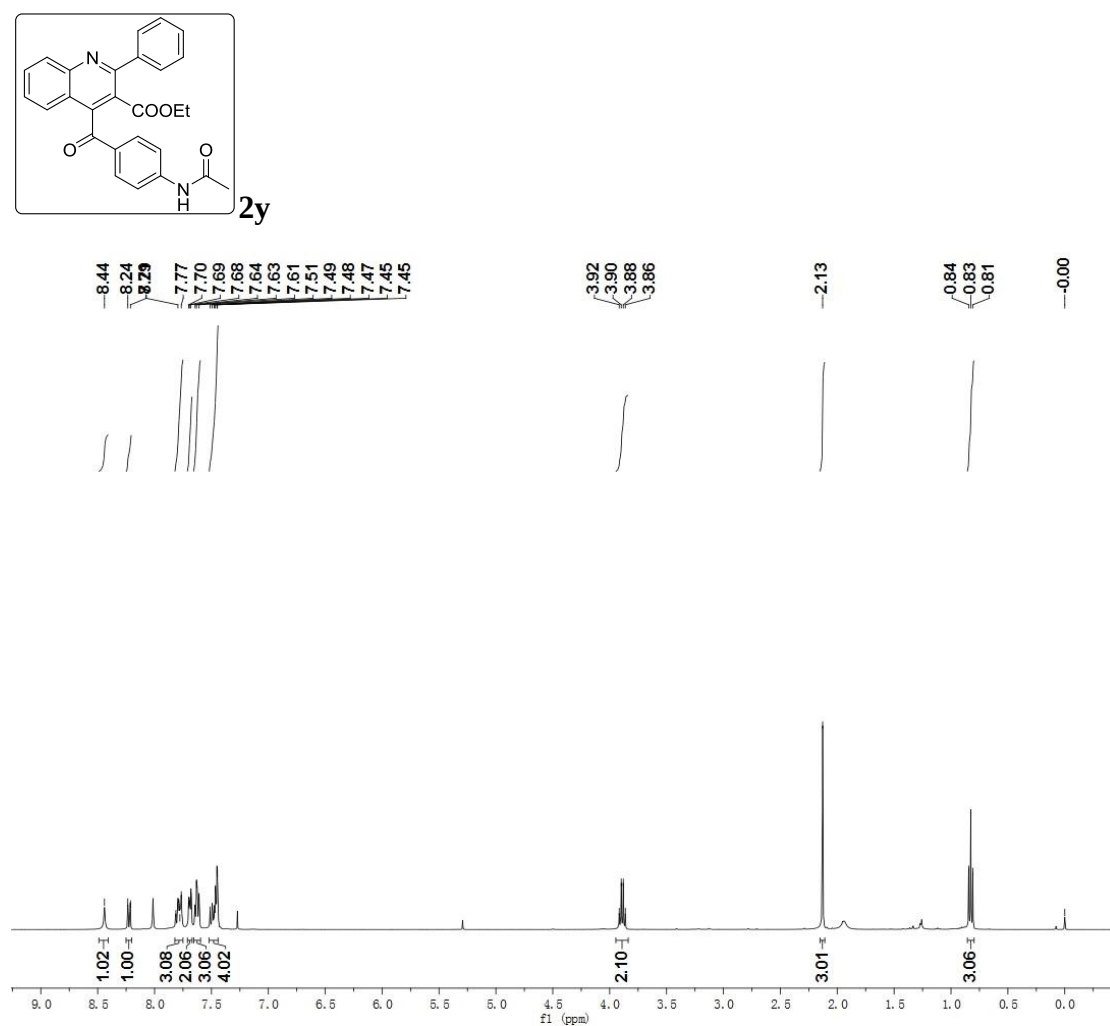
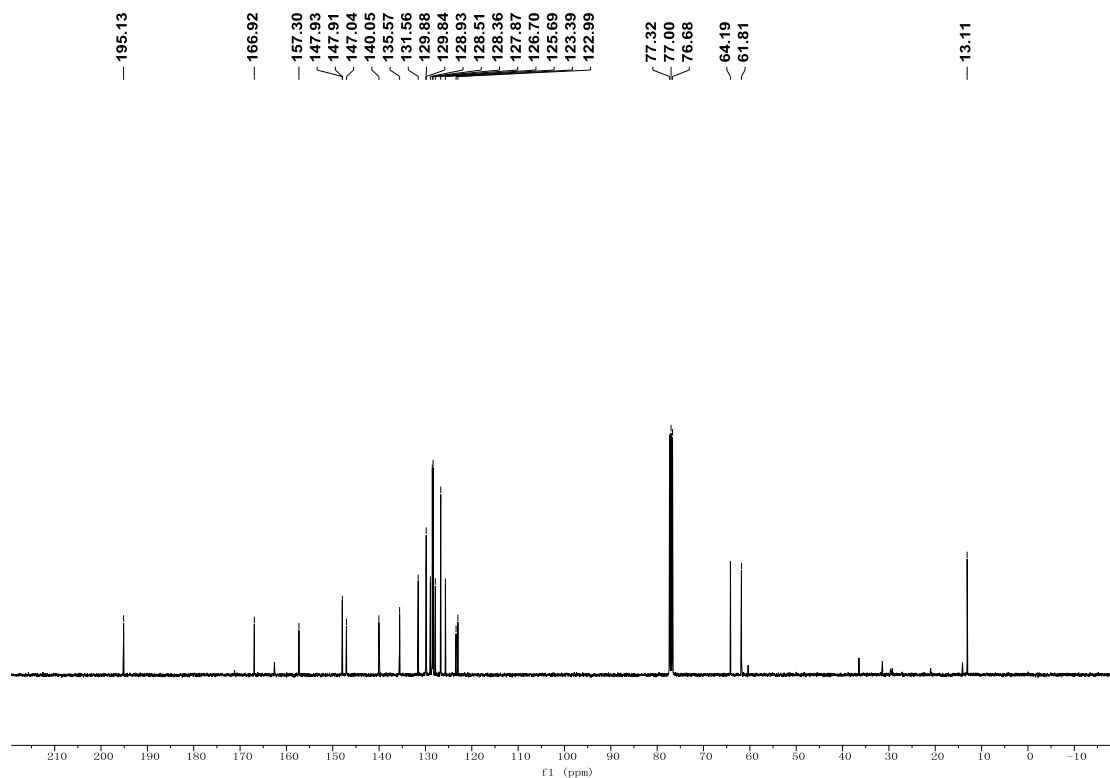
**2w**

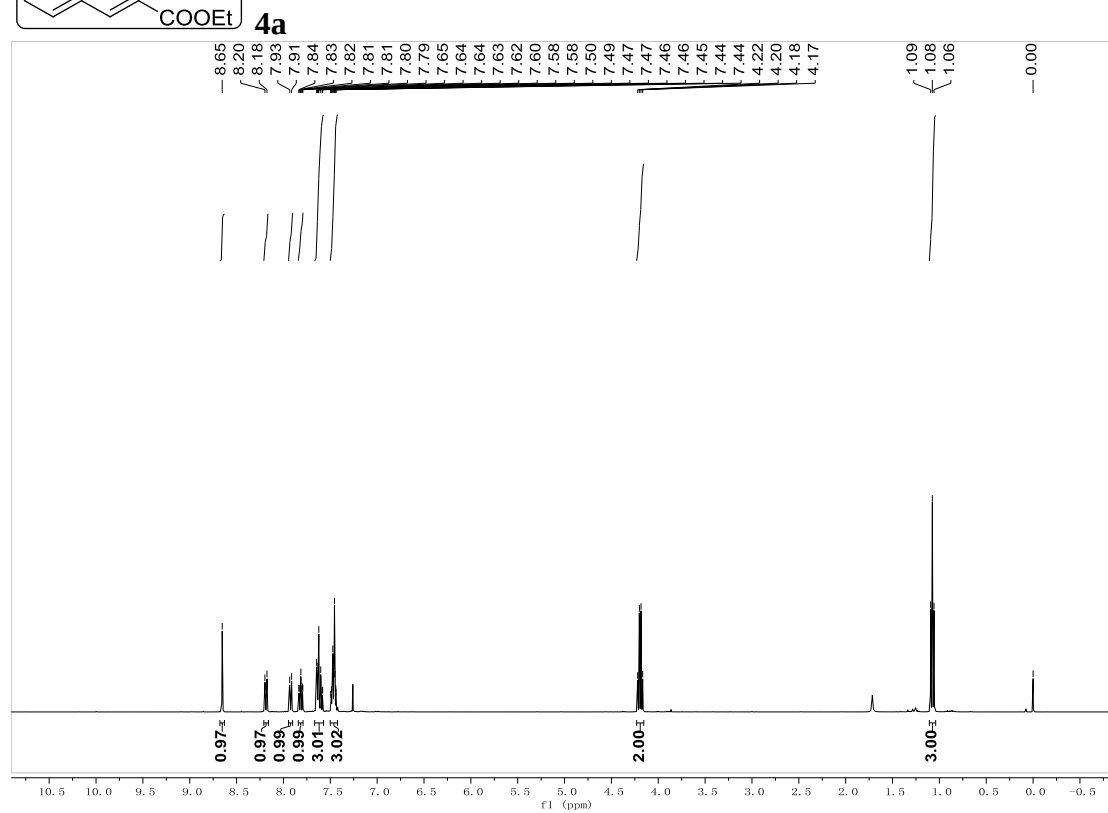
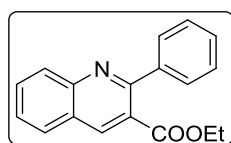
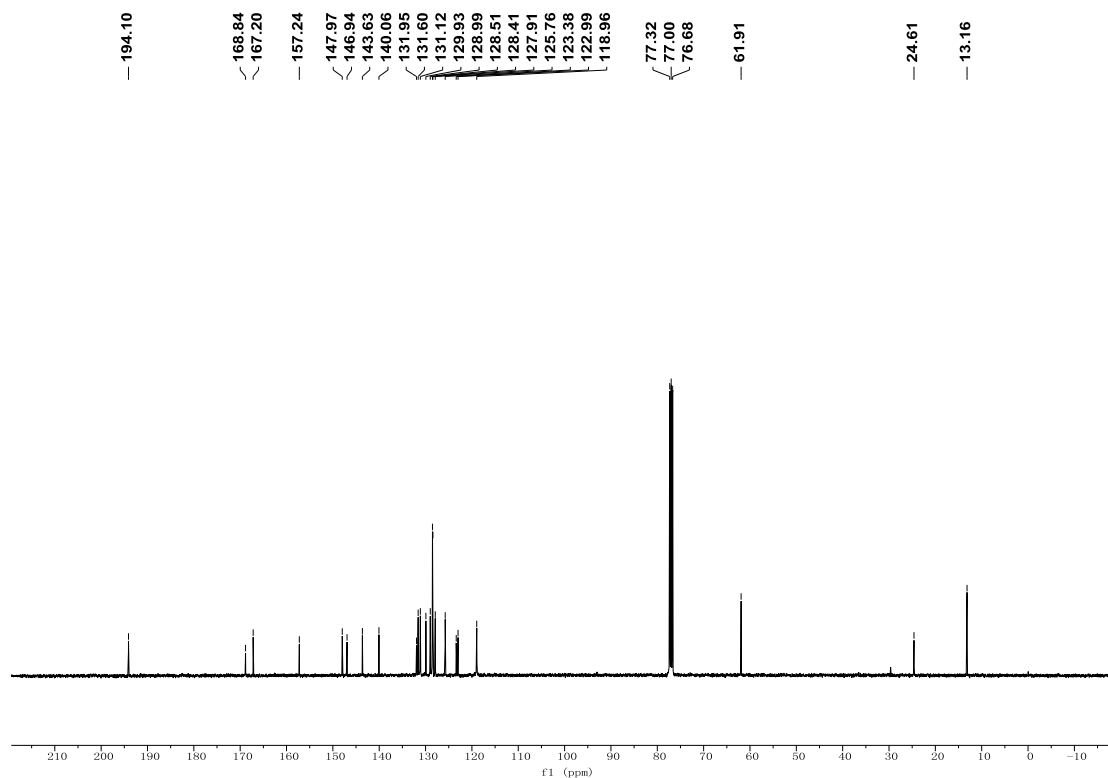


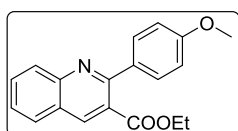
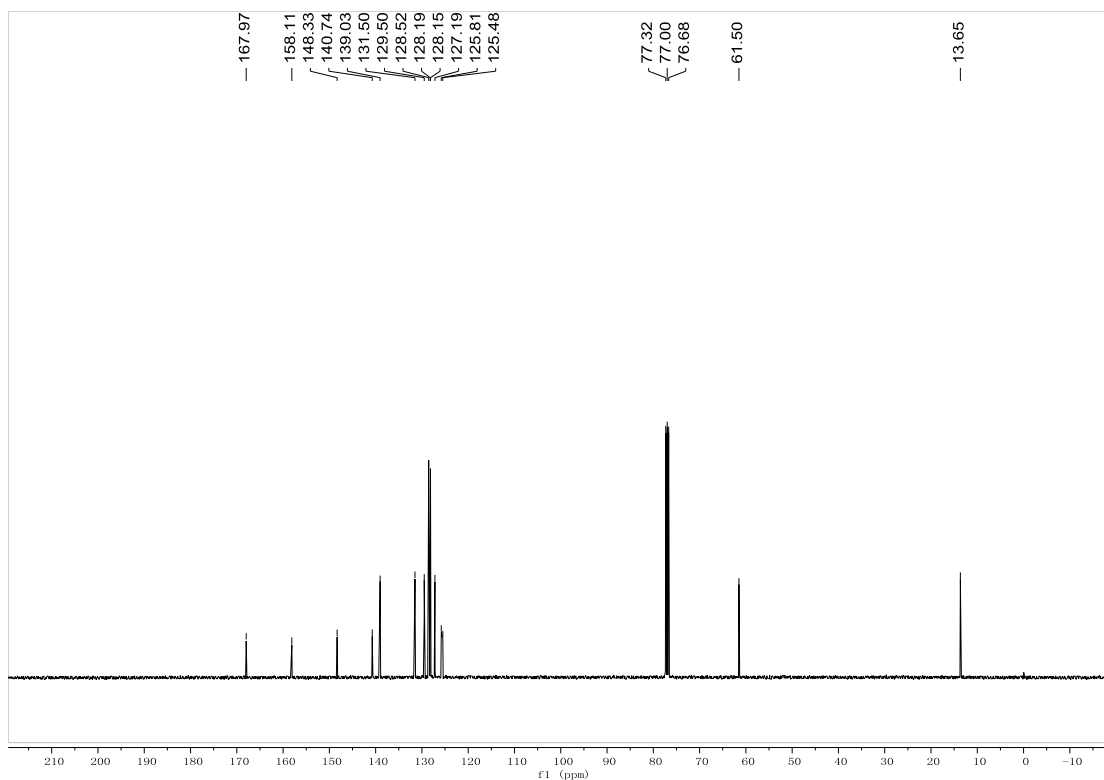


**2x**

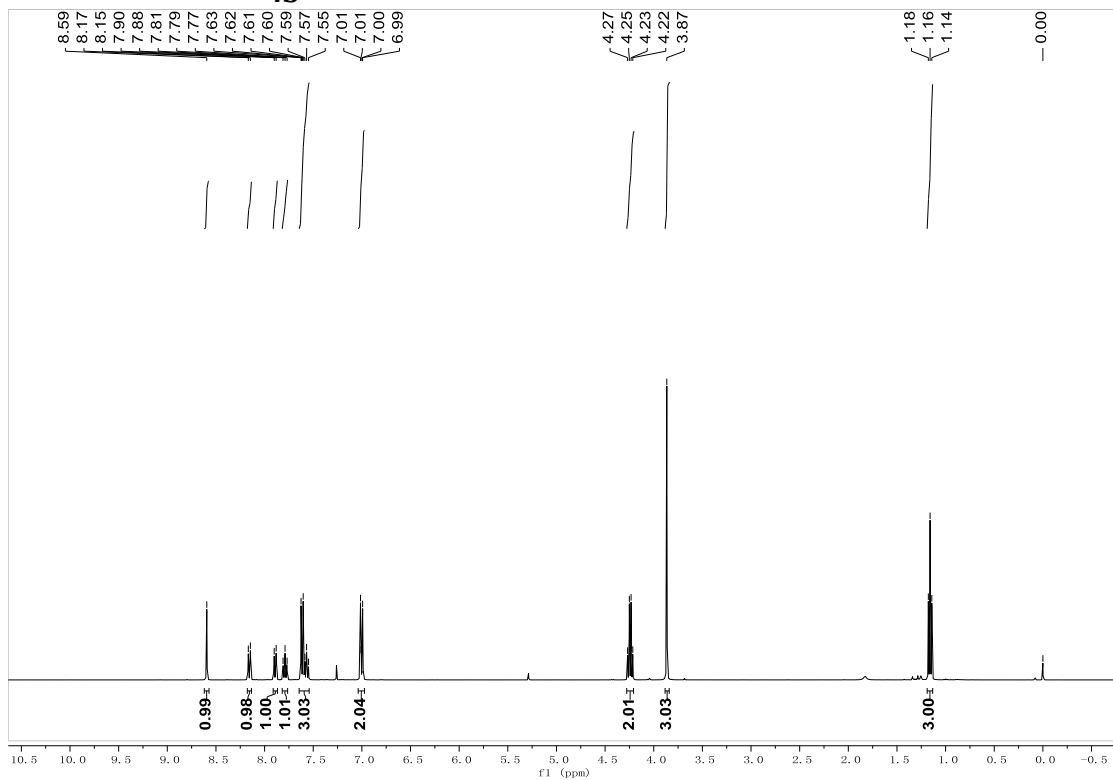


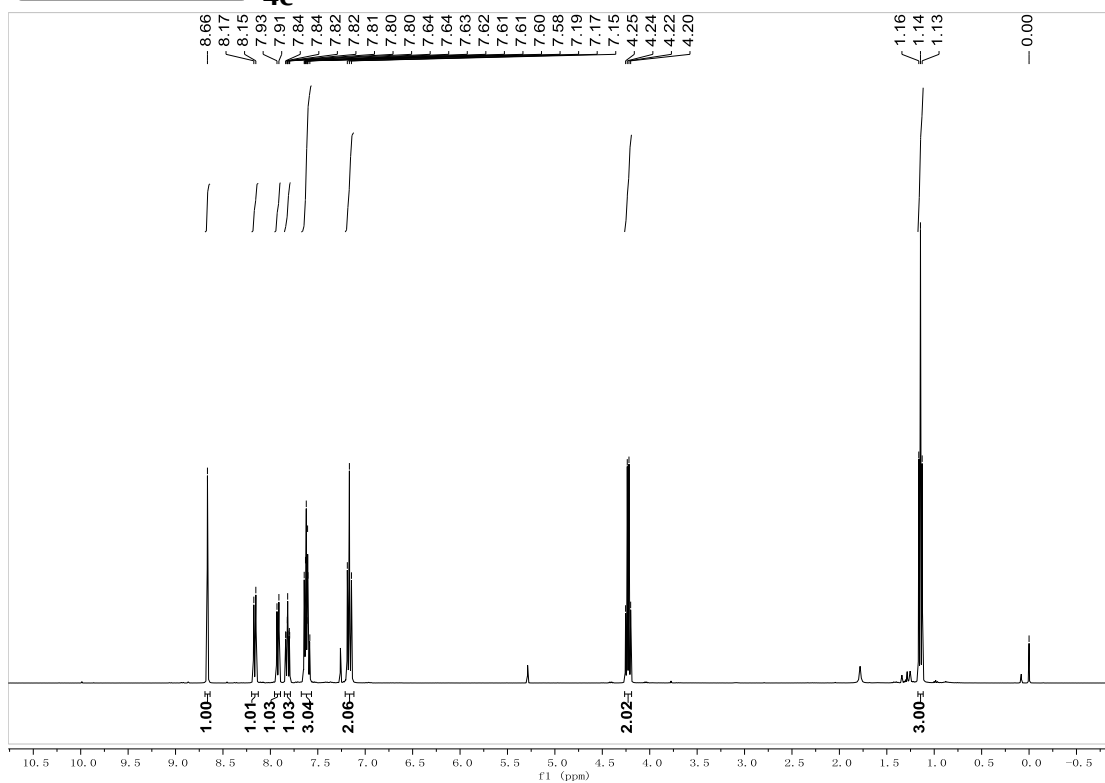
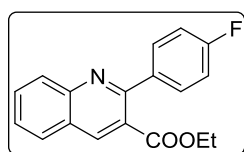
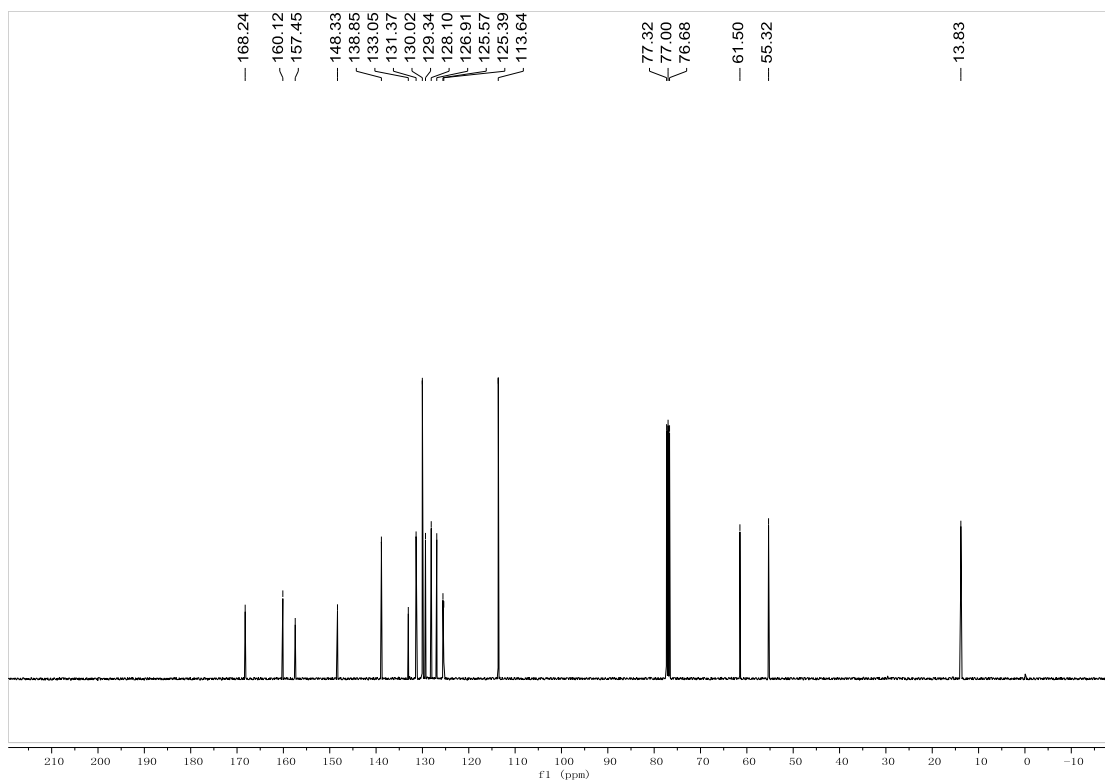




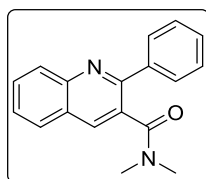
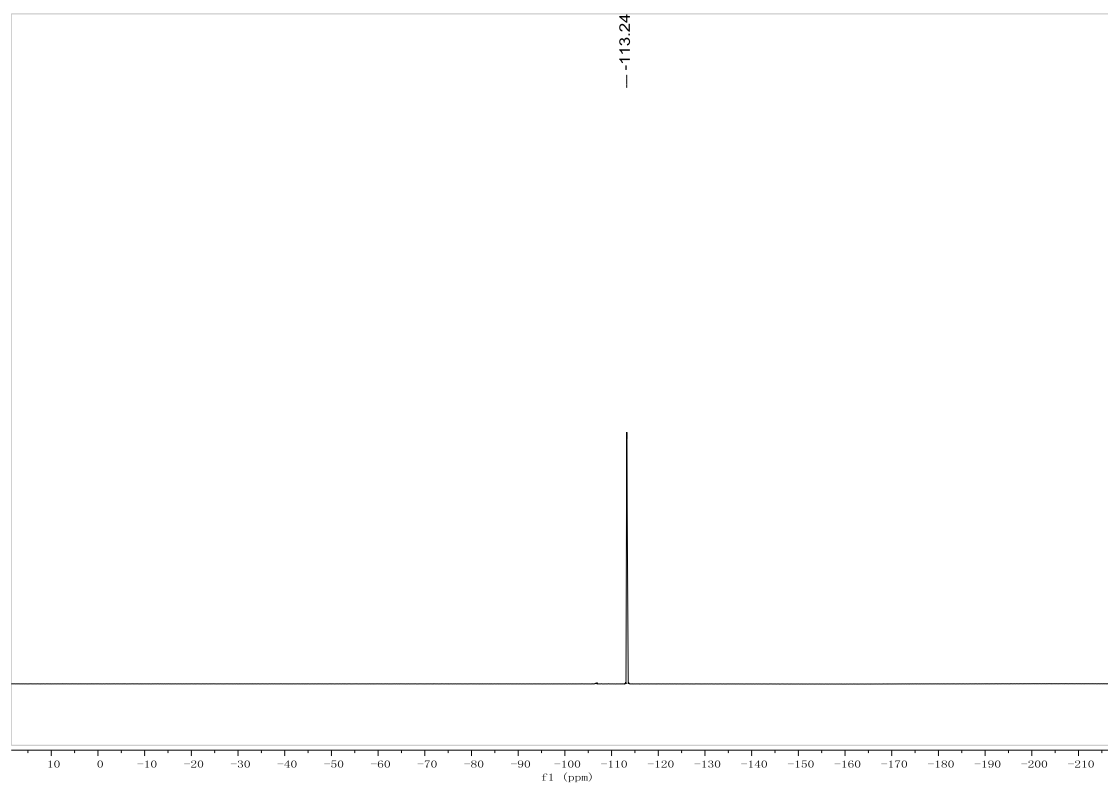
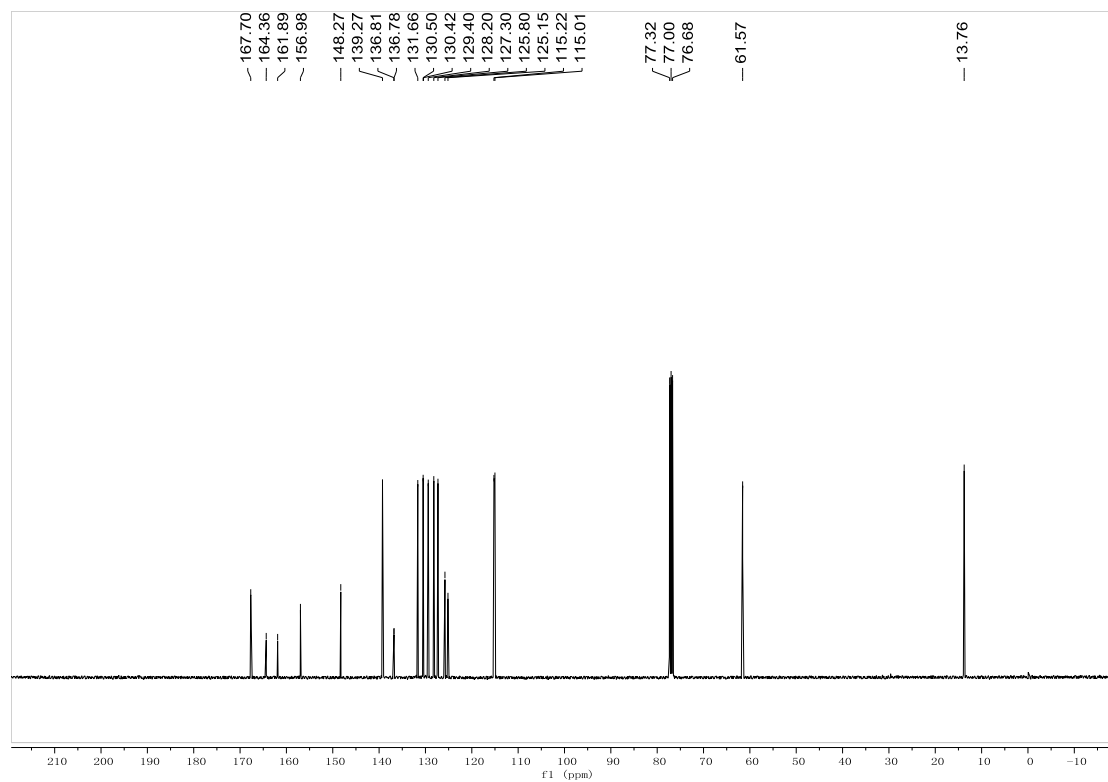


**4b**

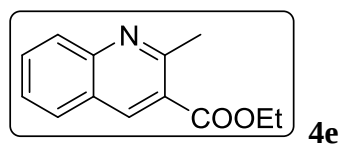
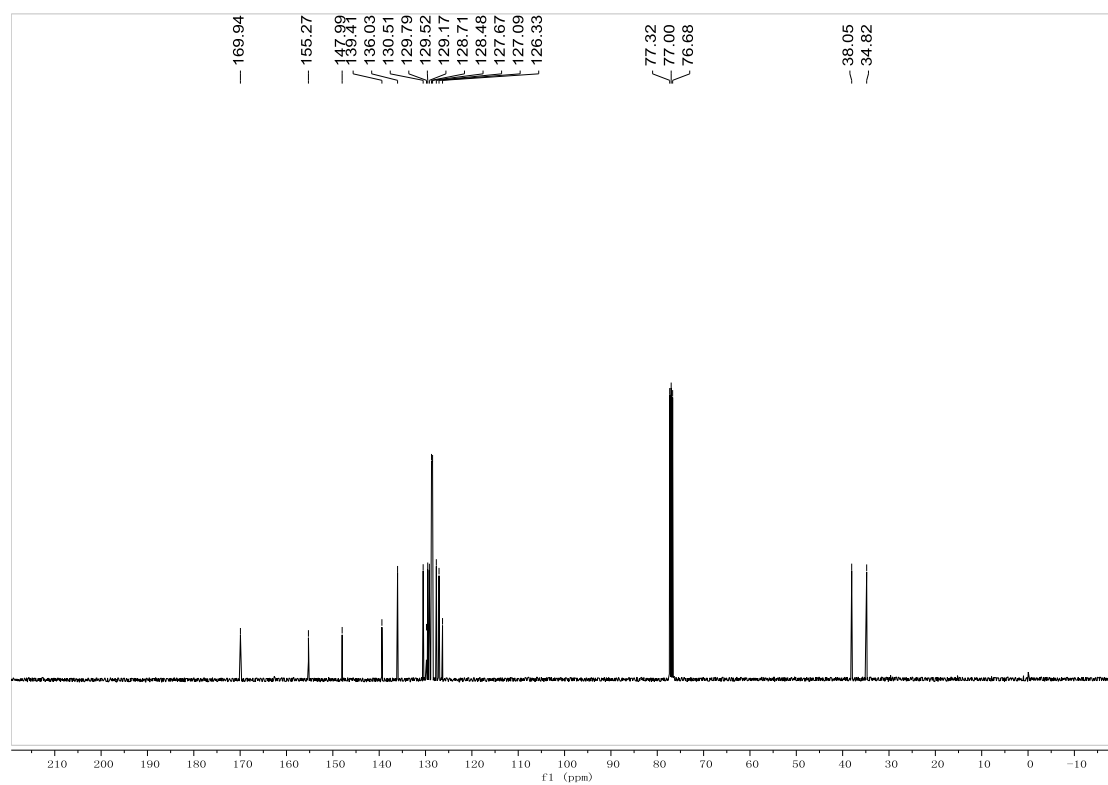
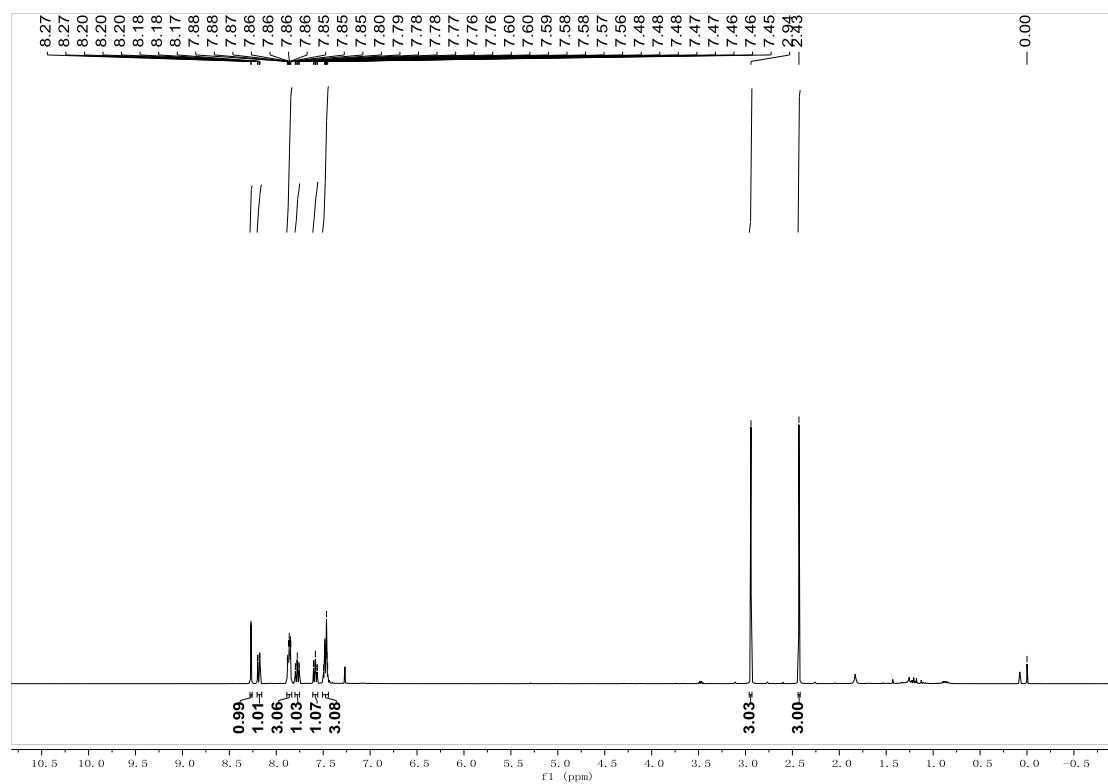


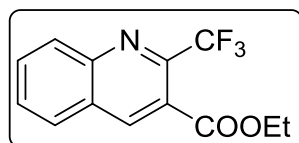
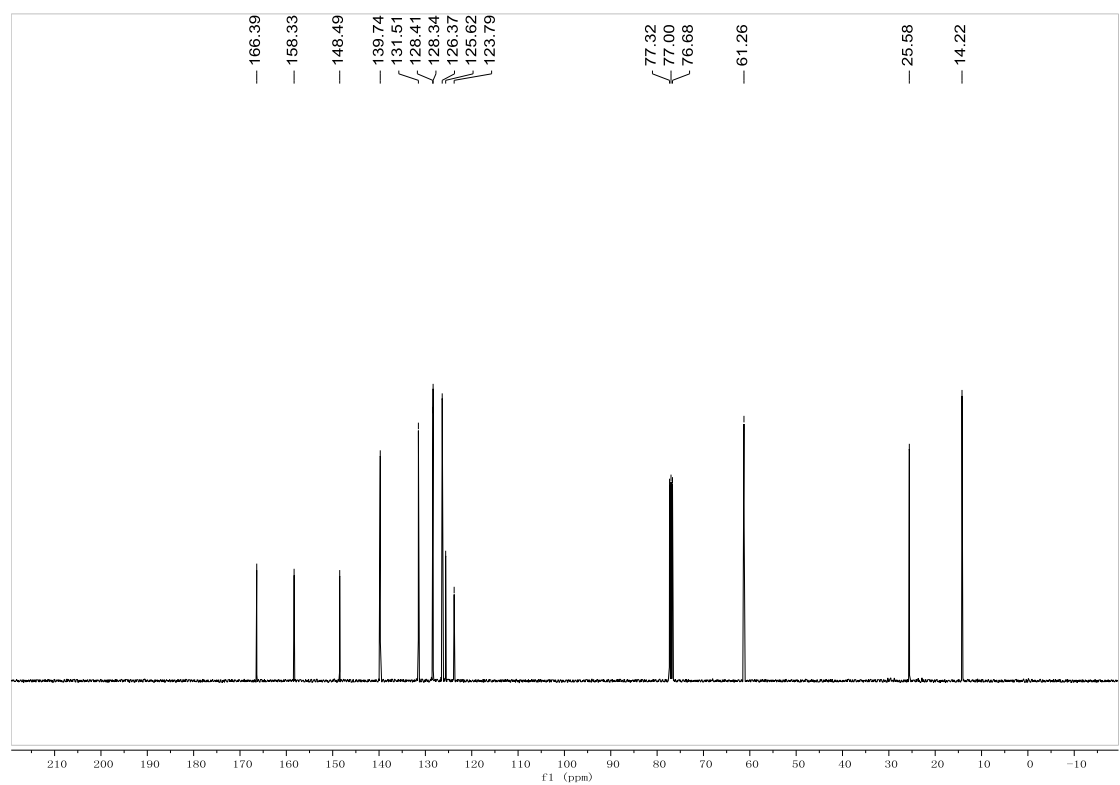
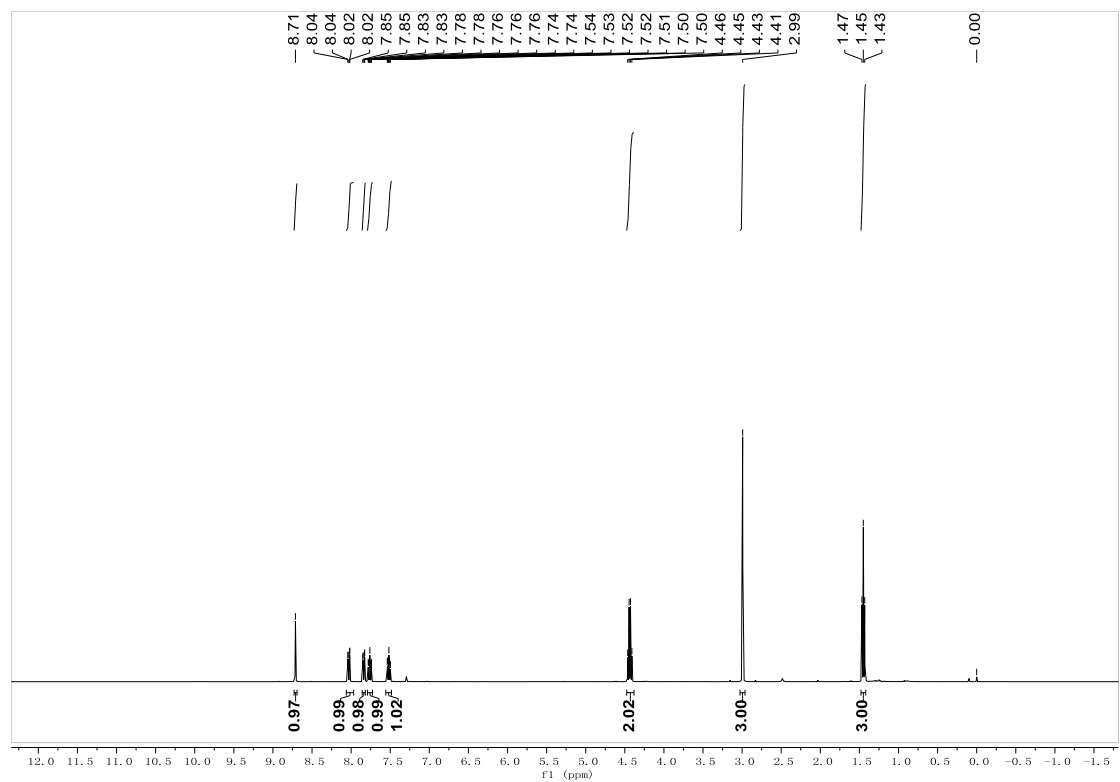




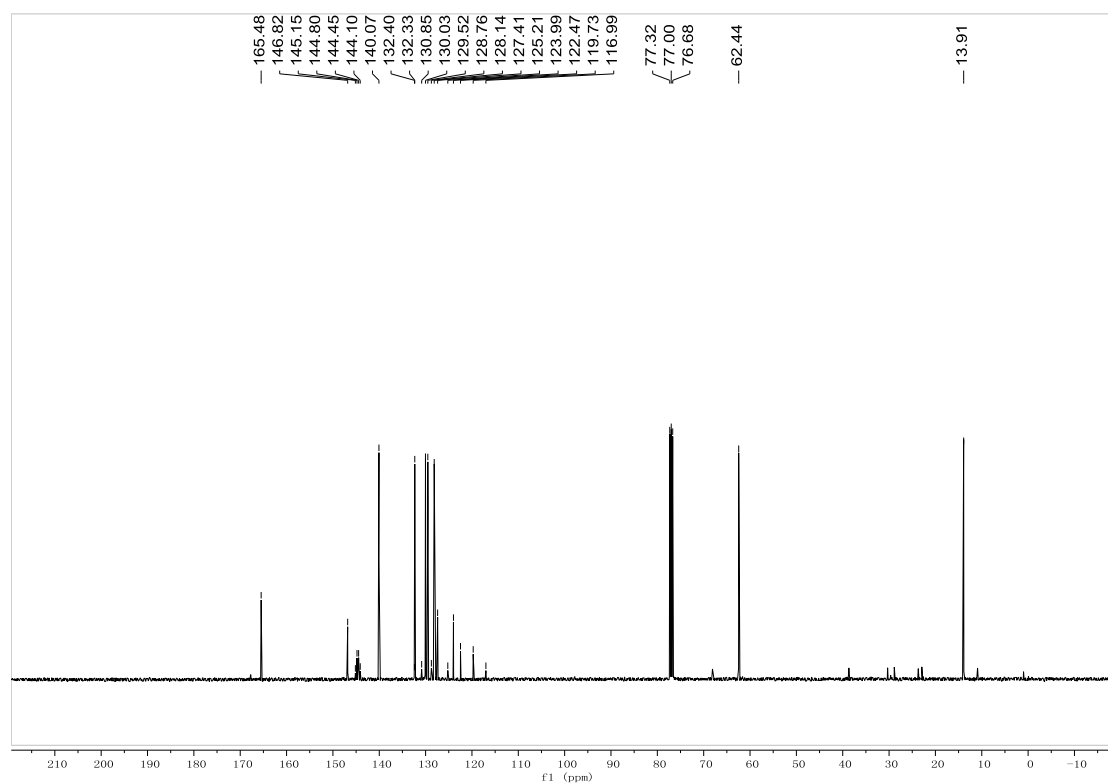
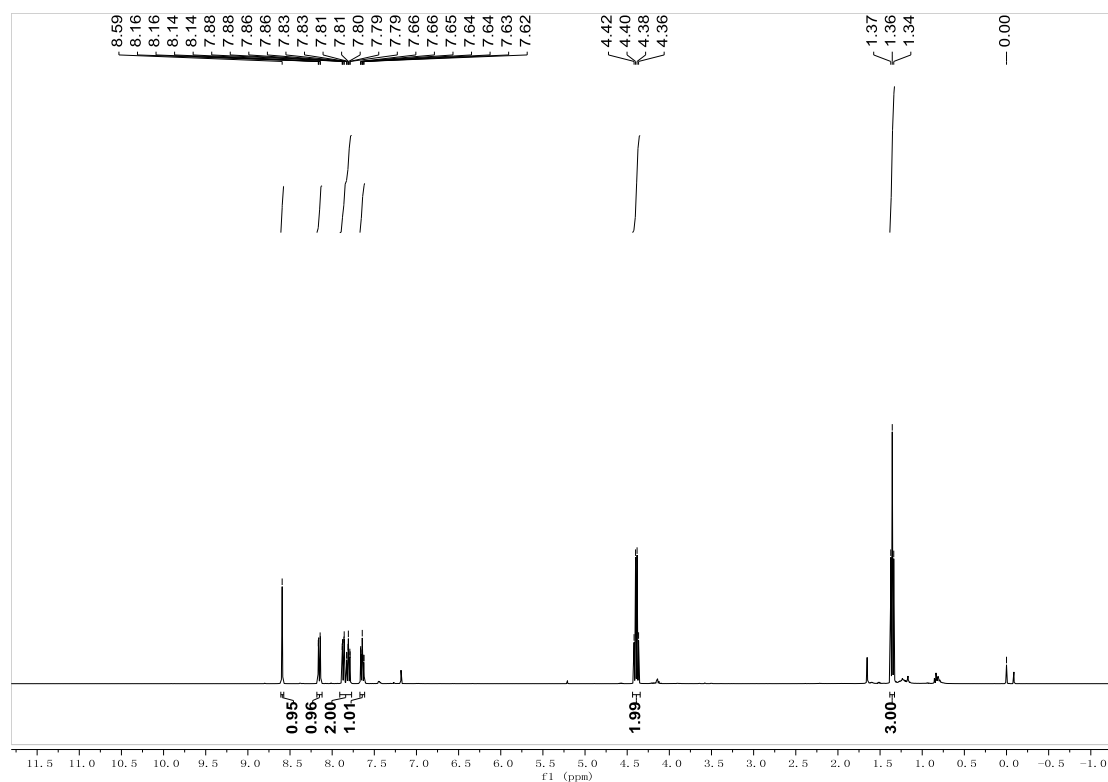


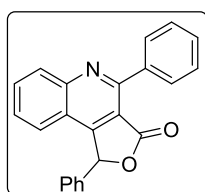
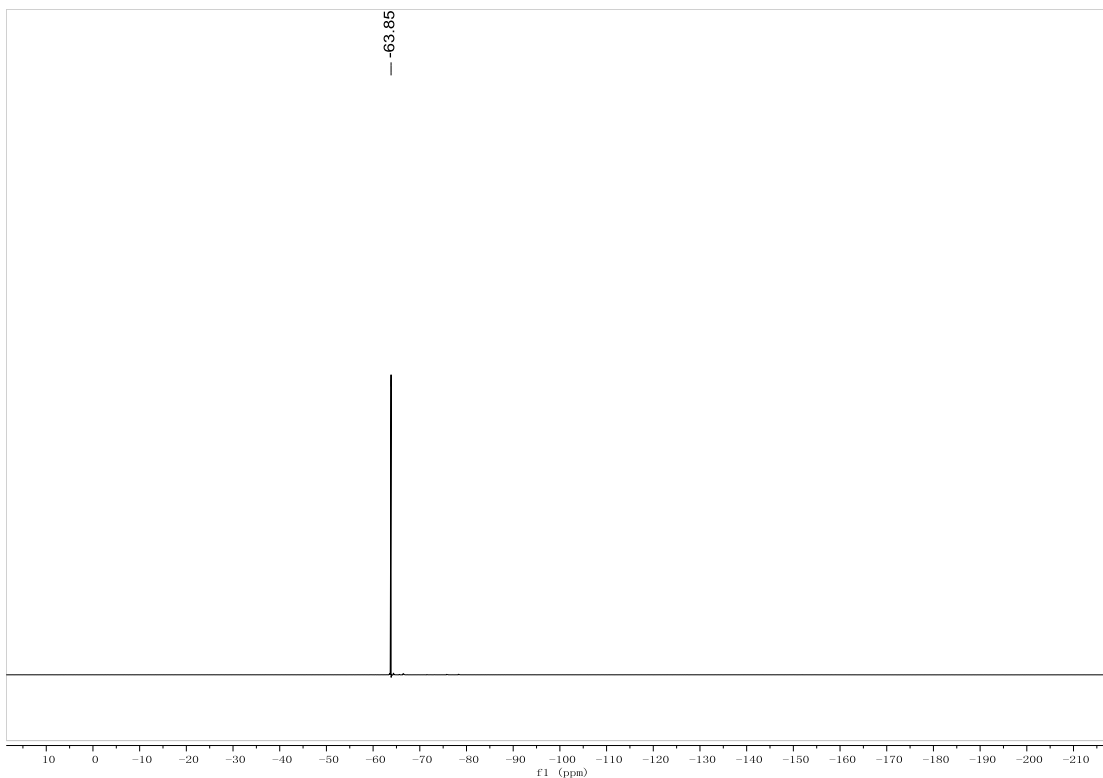
**4d**



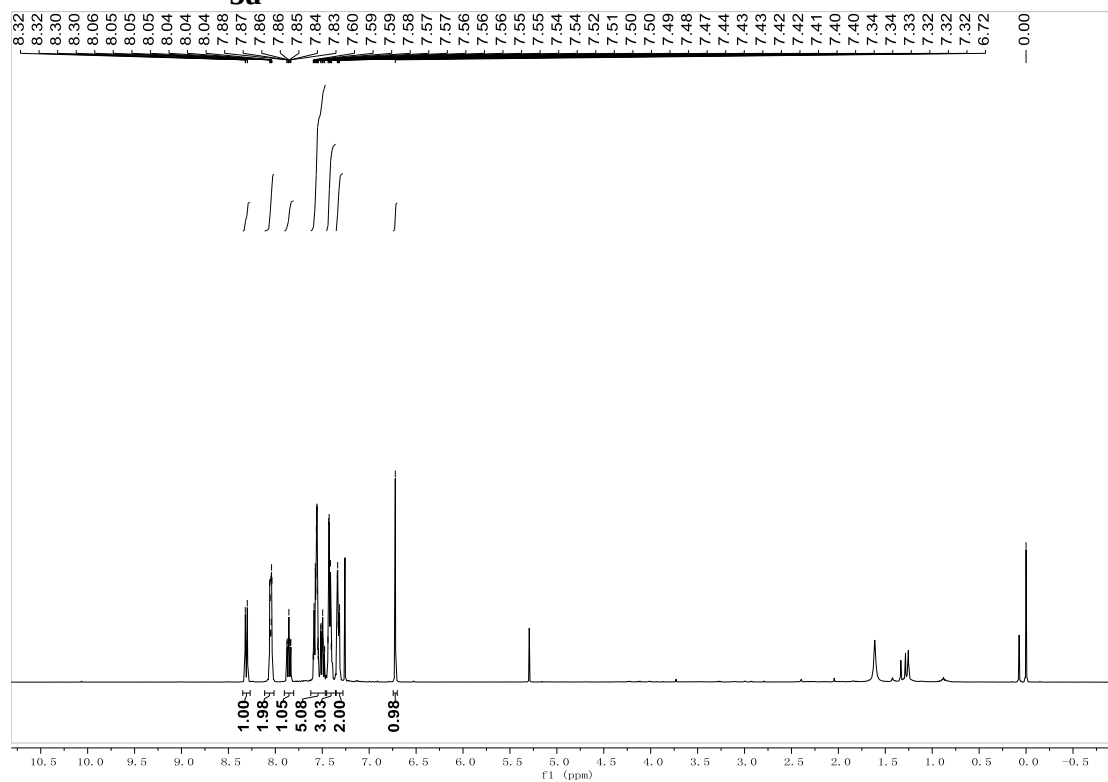


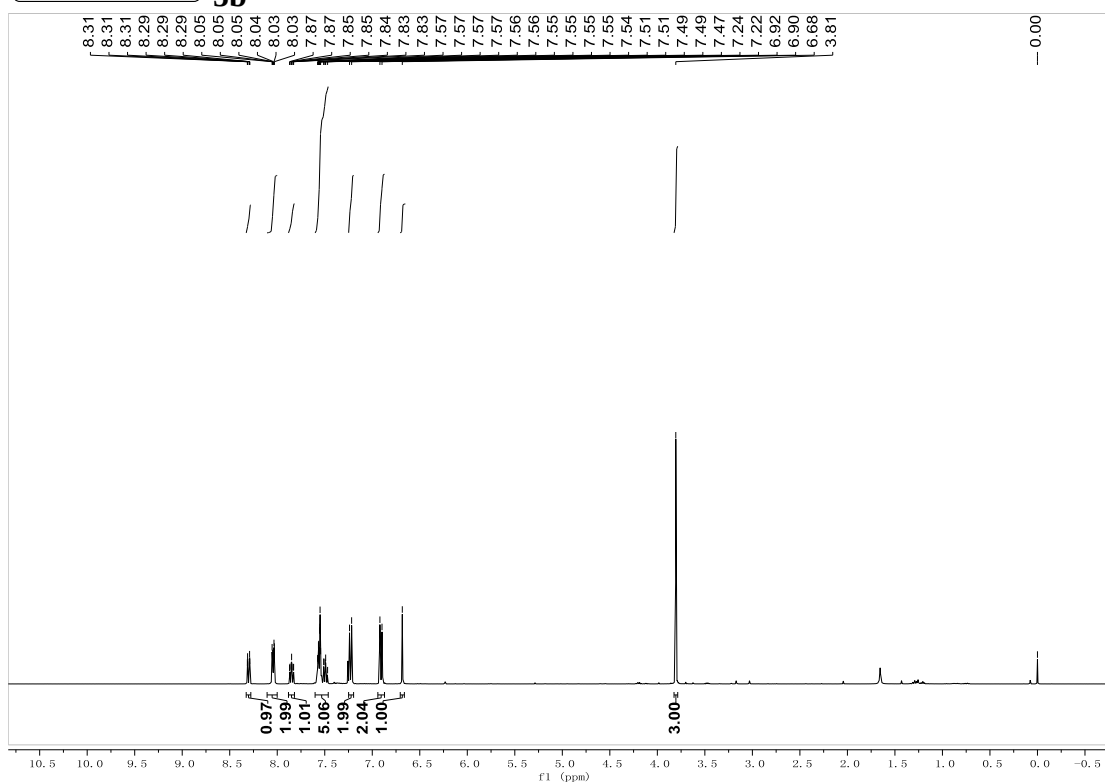
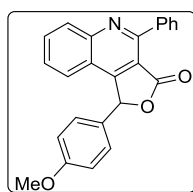
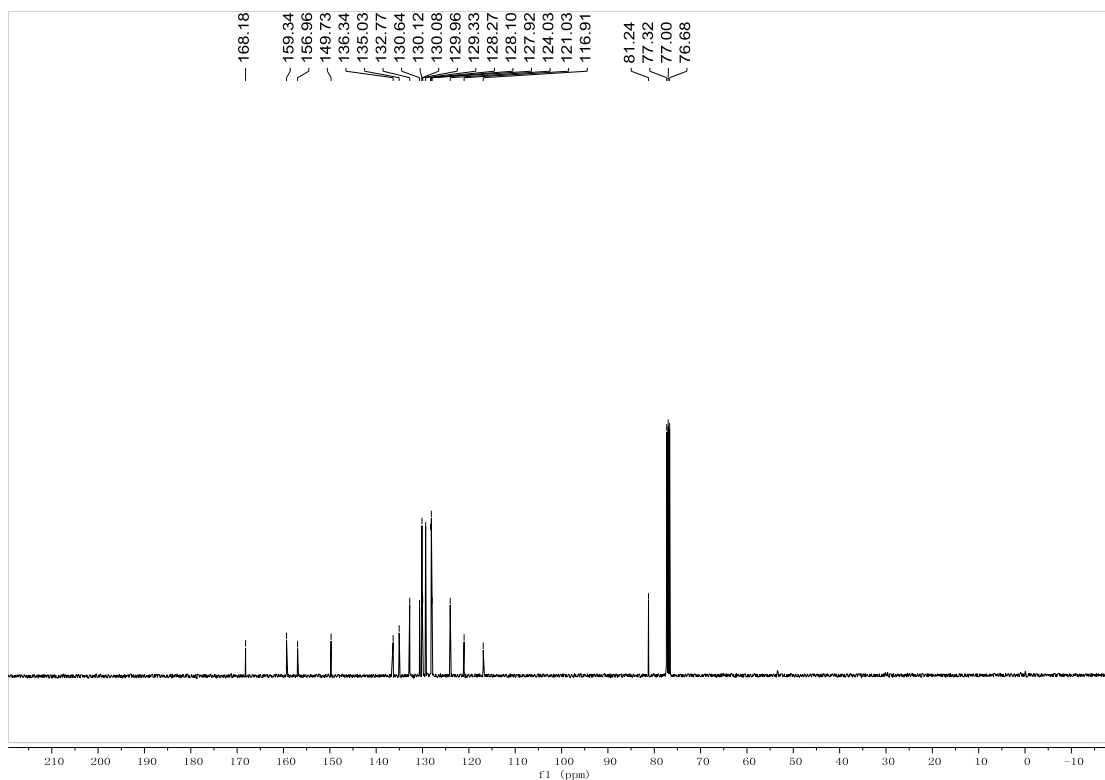
**4f**

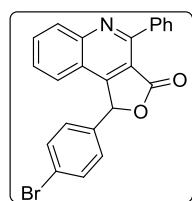
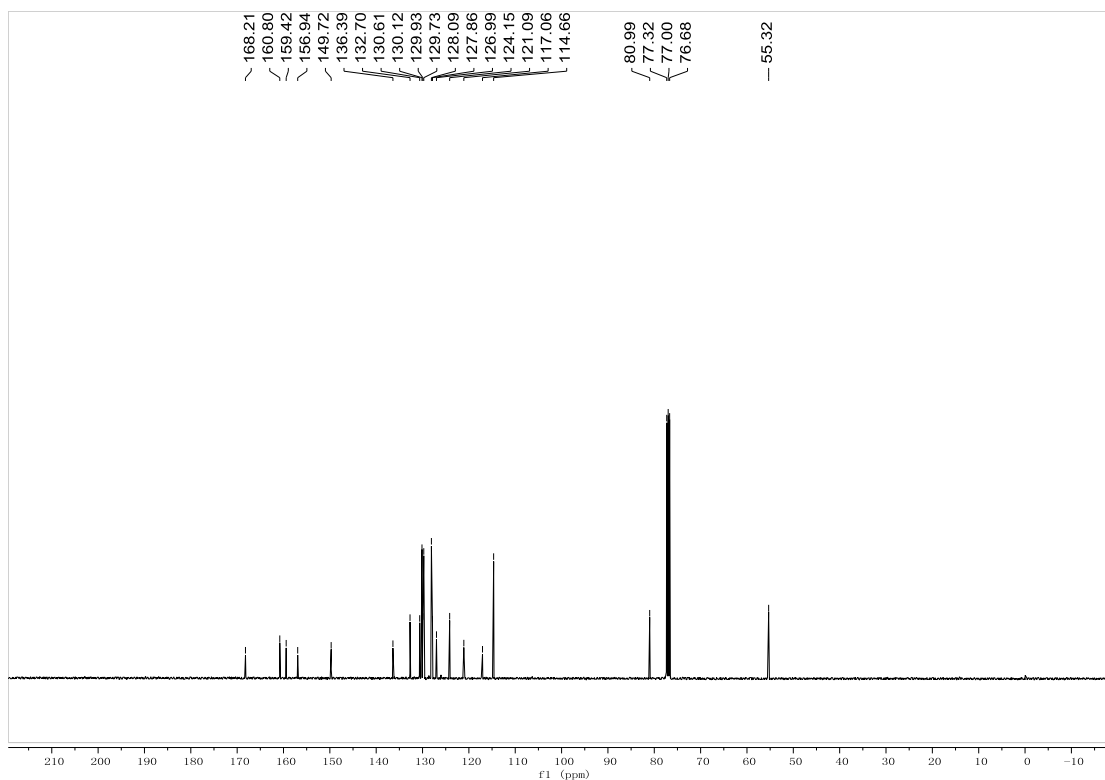




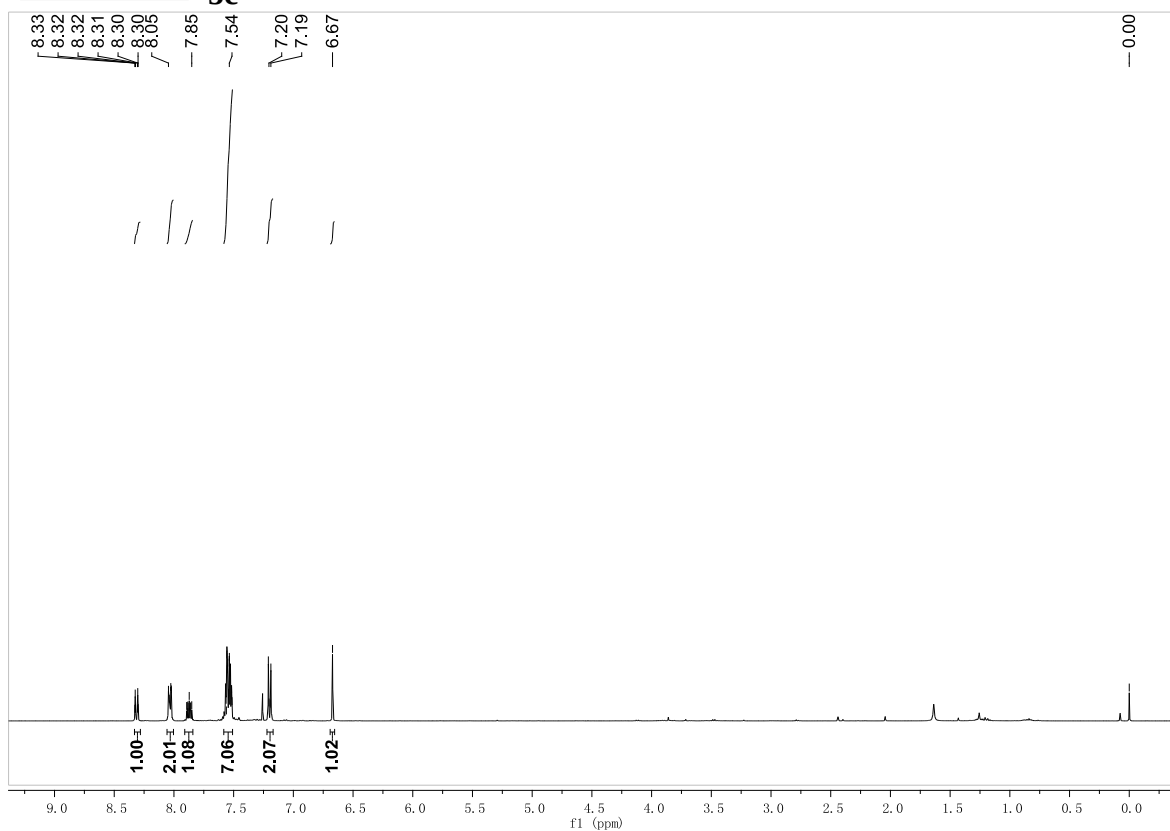
**5a**

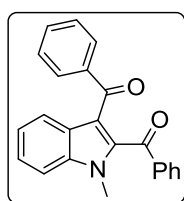
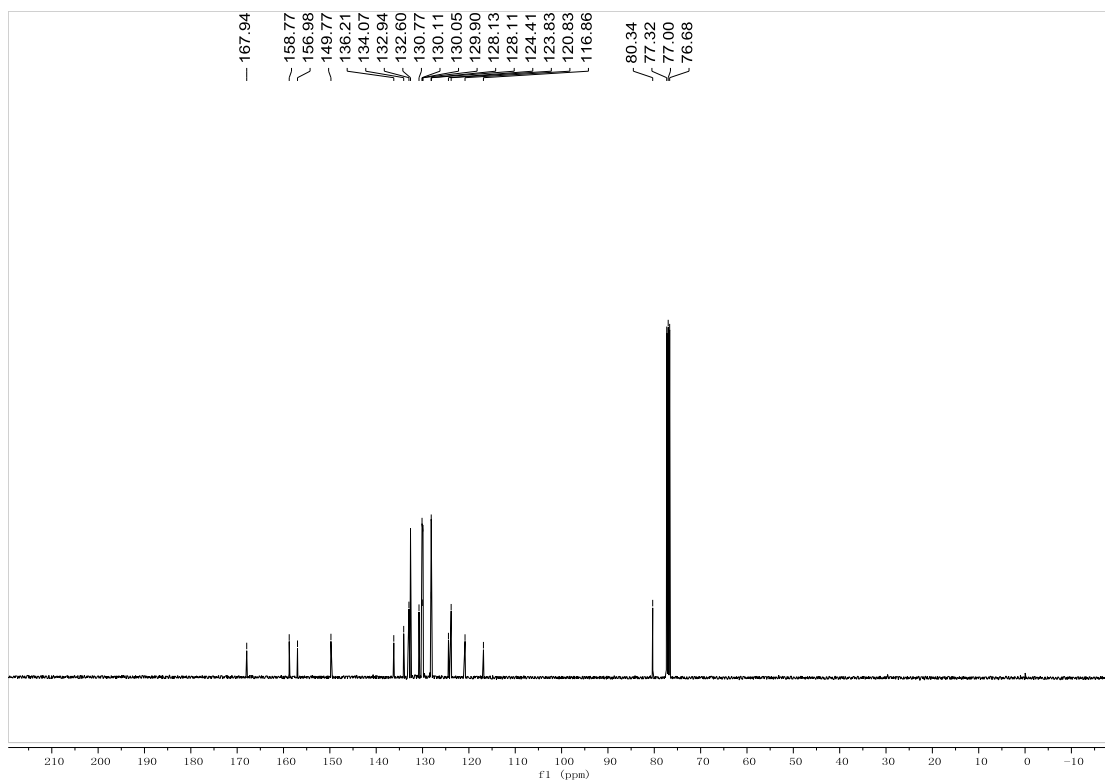




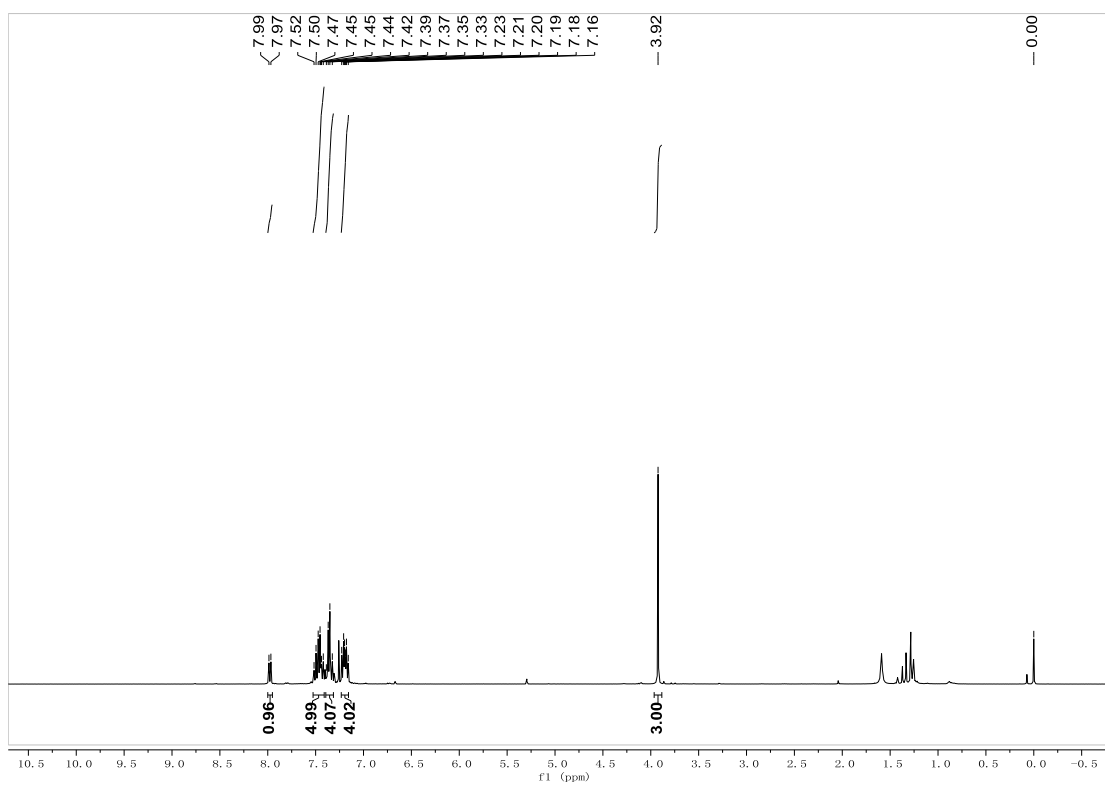


**5c**

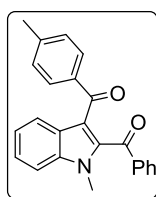
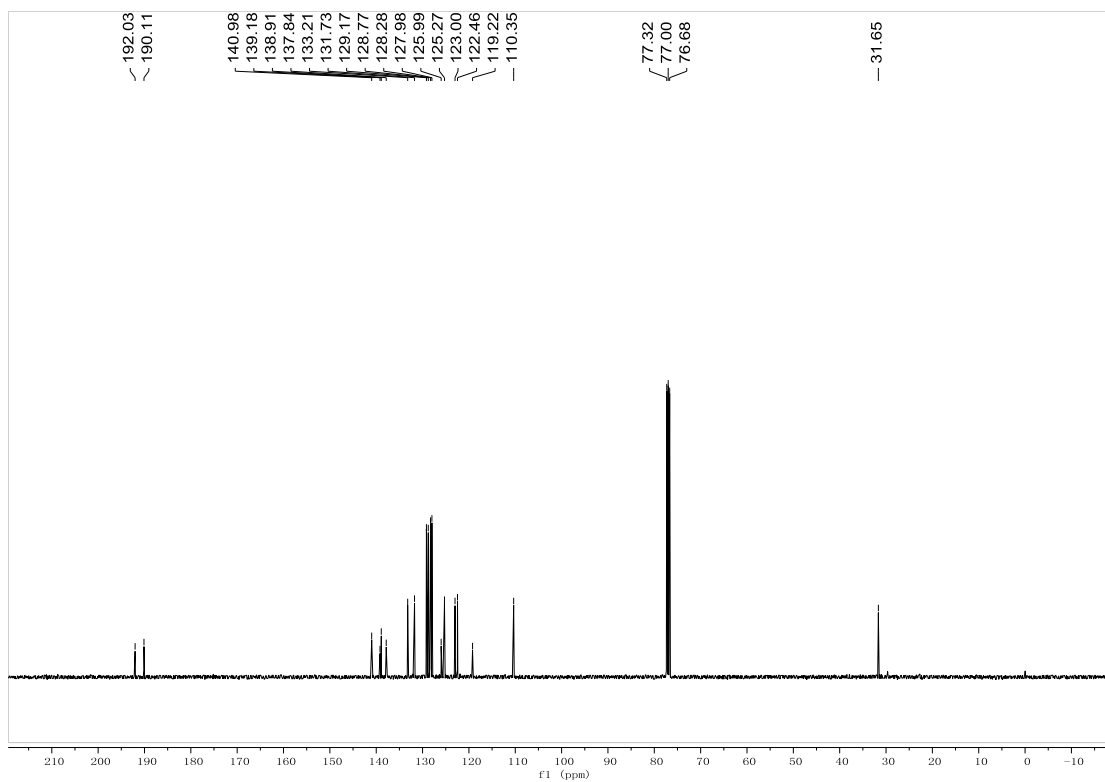




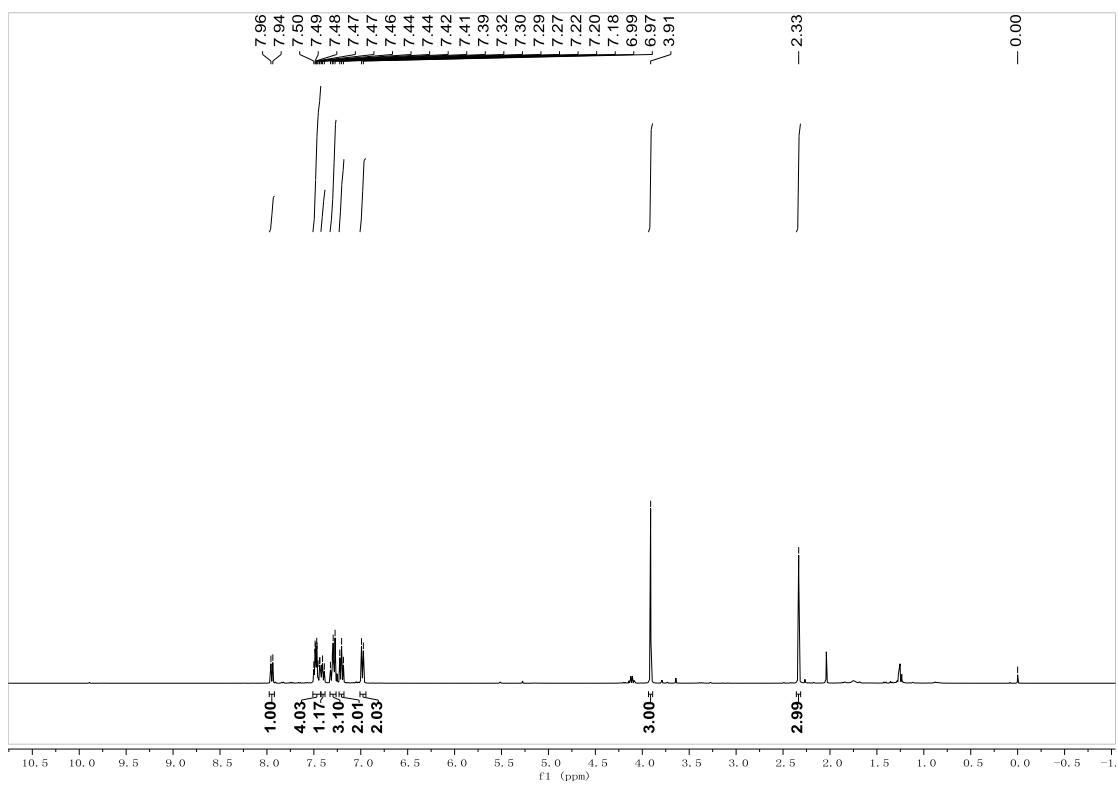
**7a**

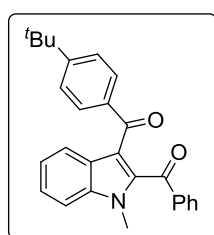
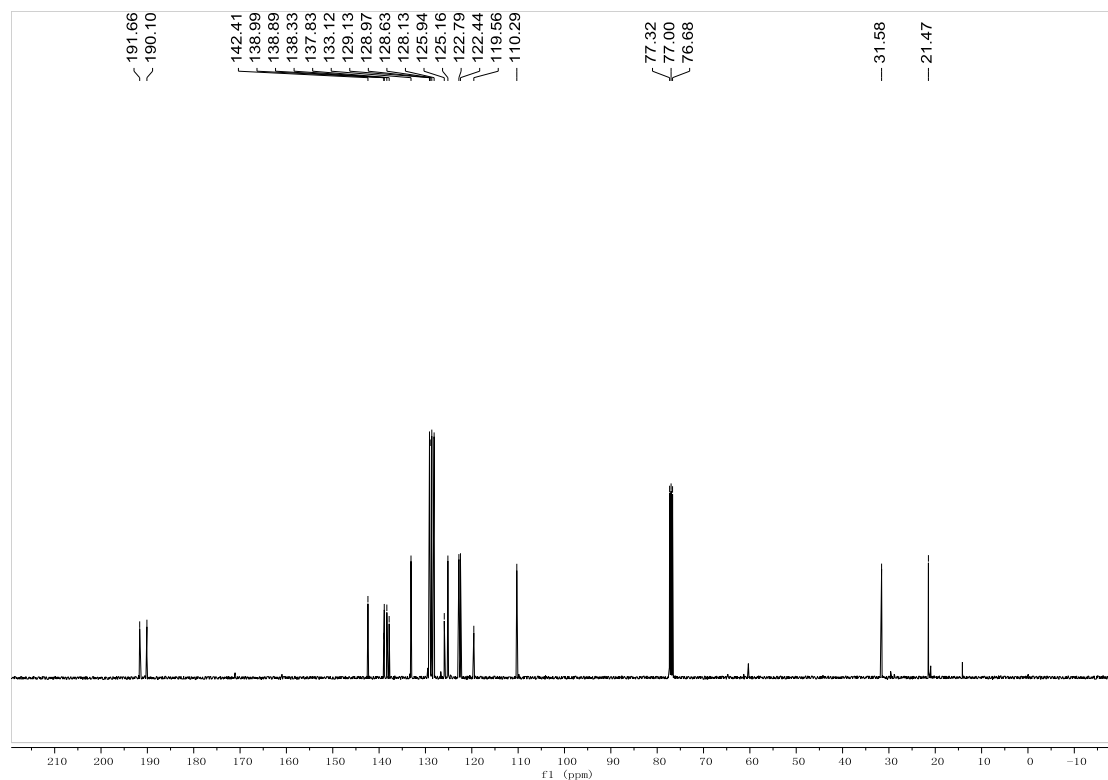




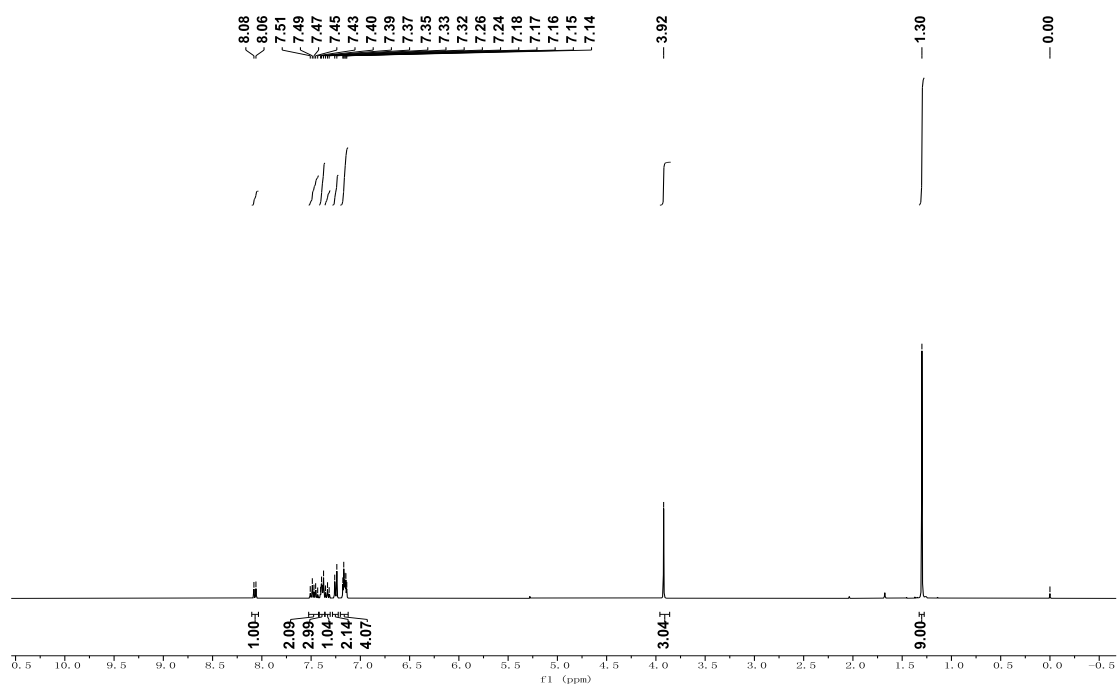


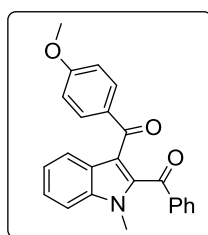
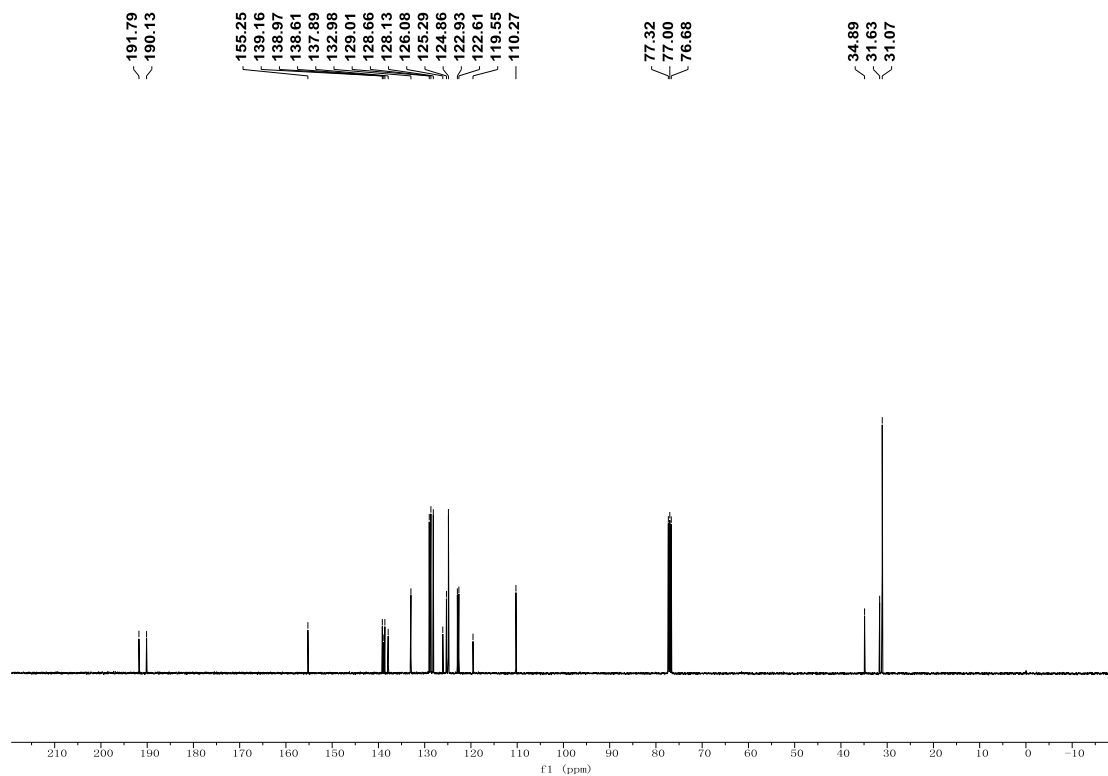
**7b**



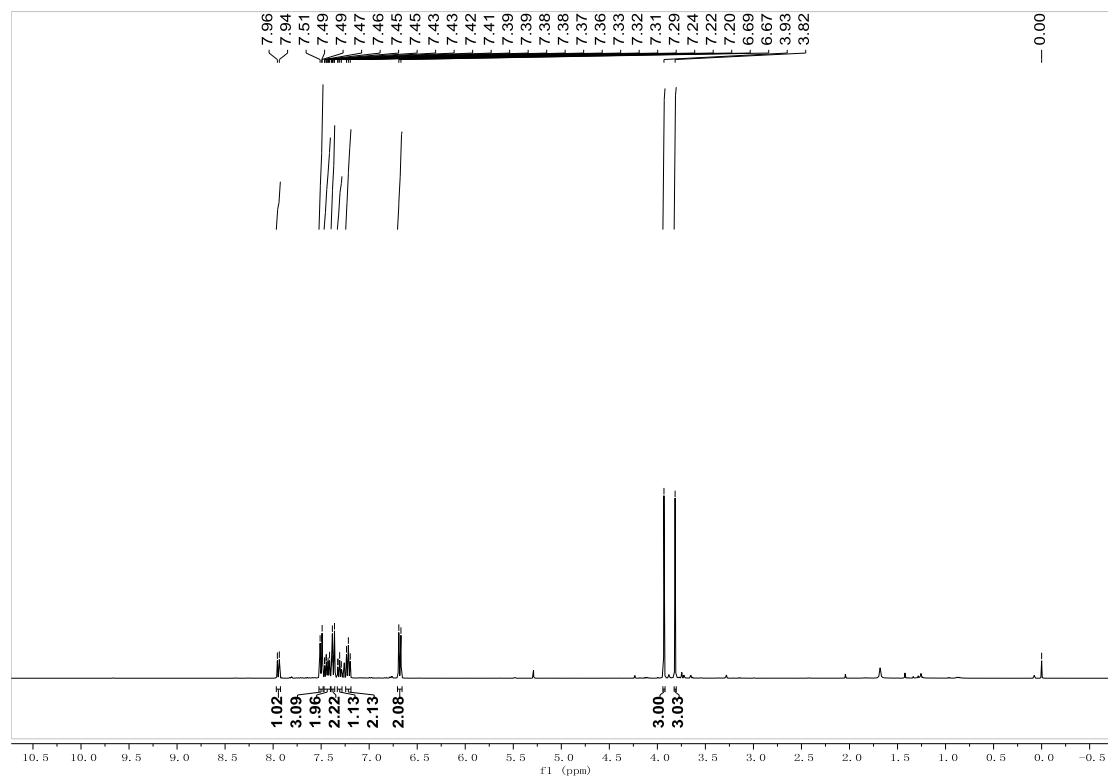


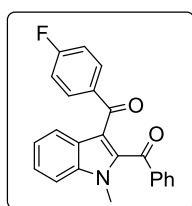
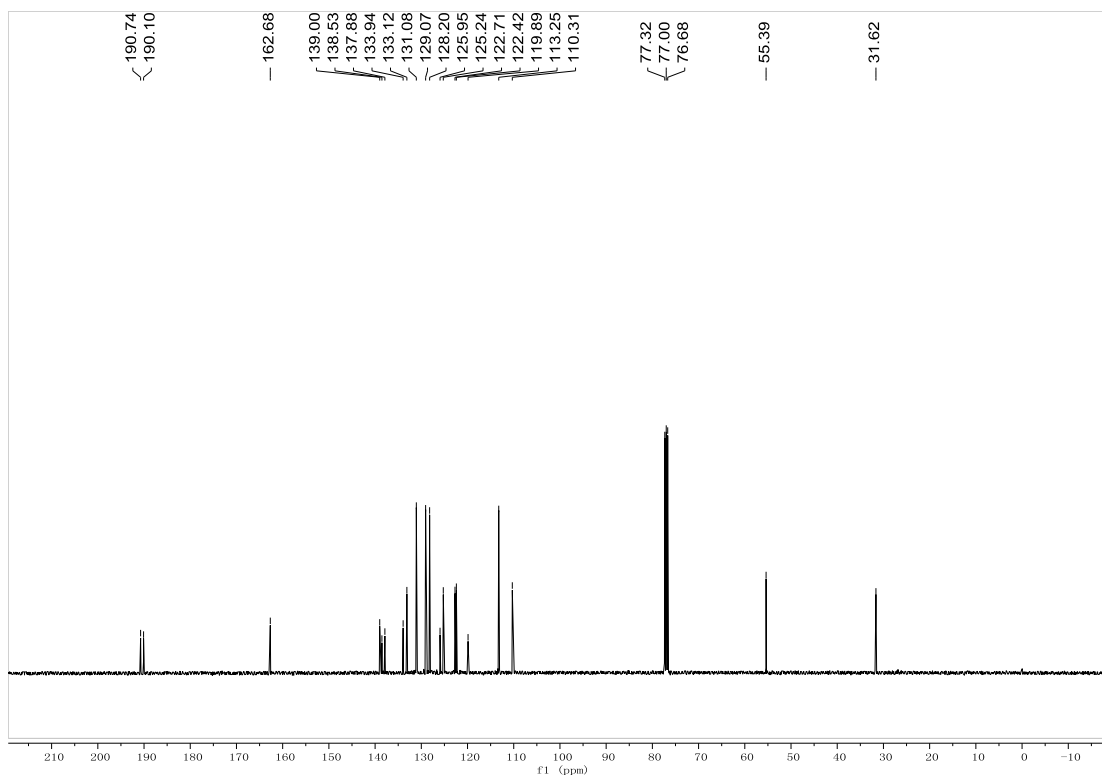
**7c**



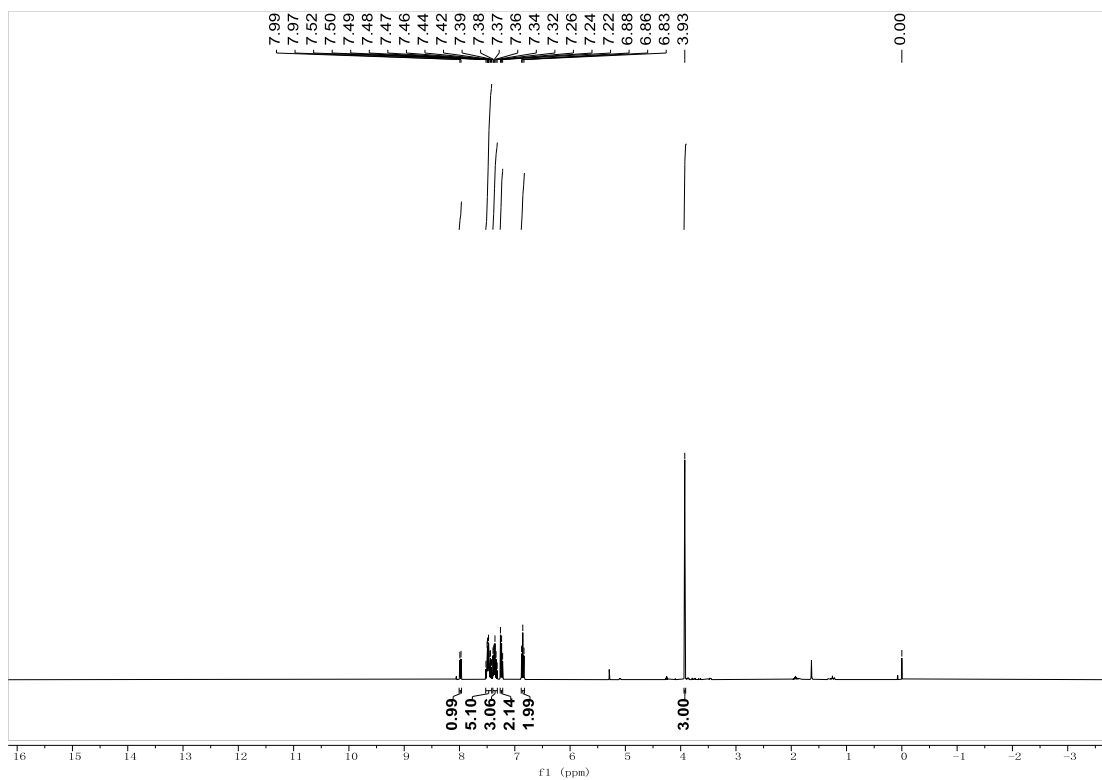


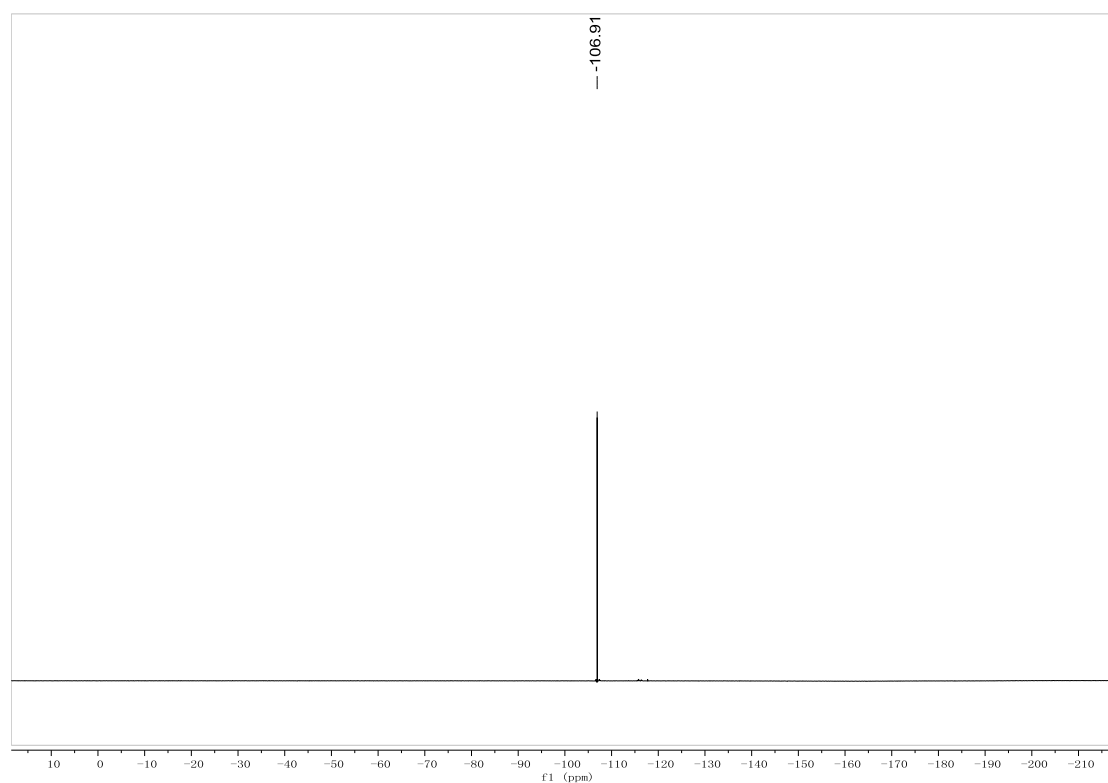
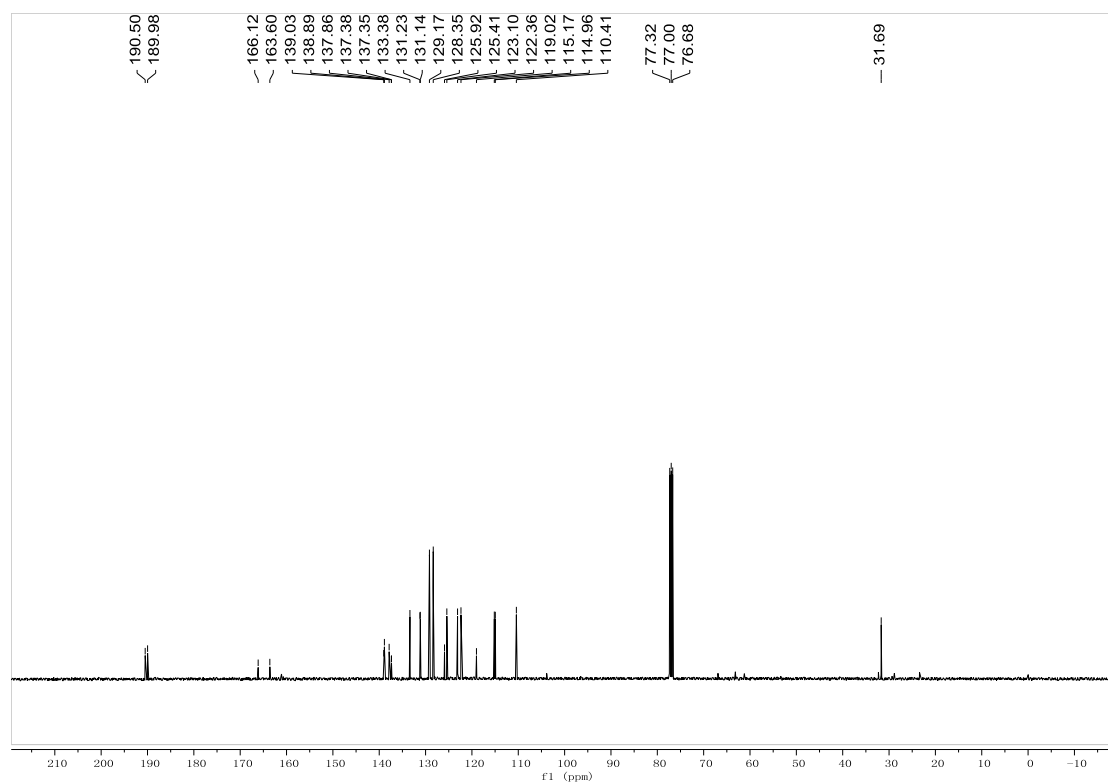
**7d**

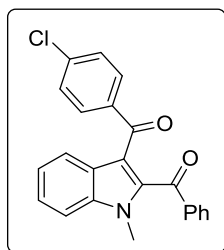




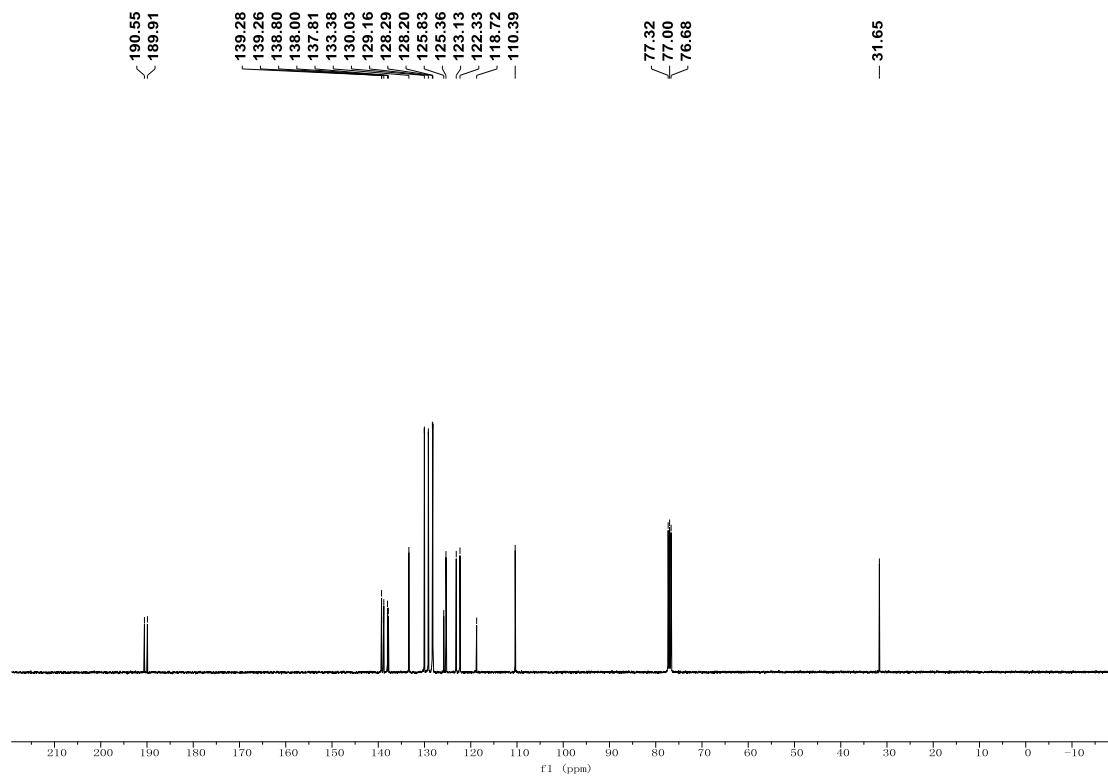
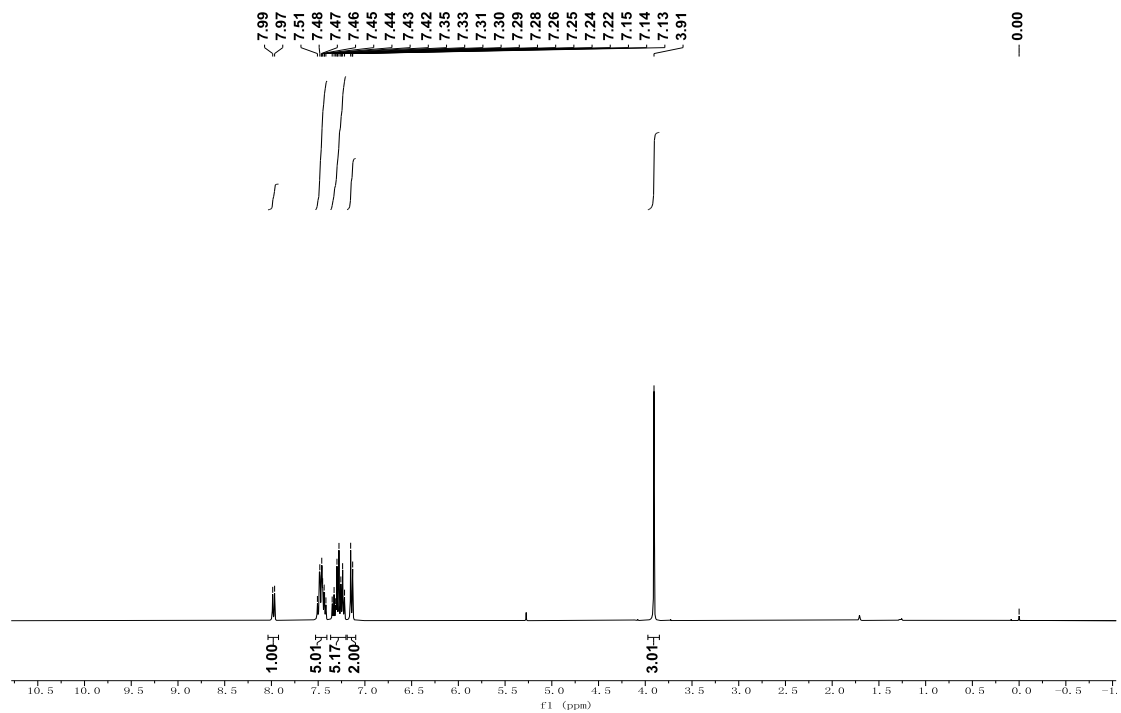
**7e**

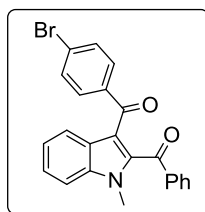




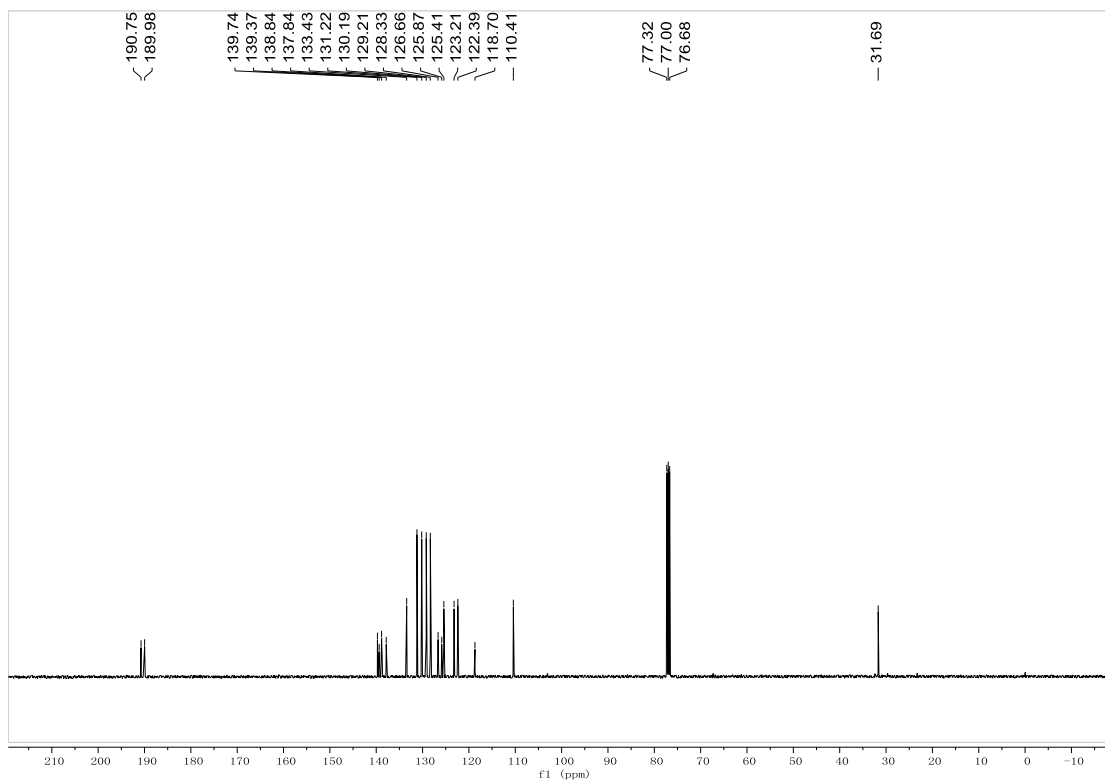
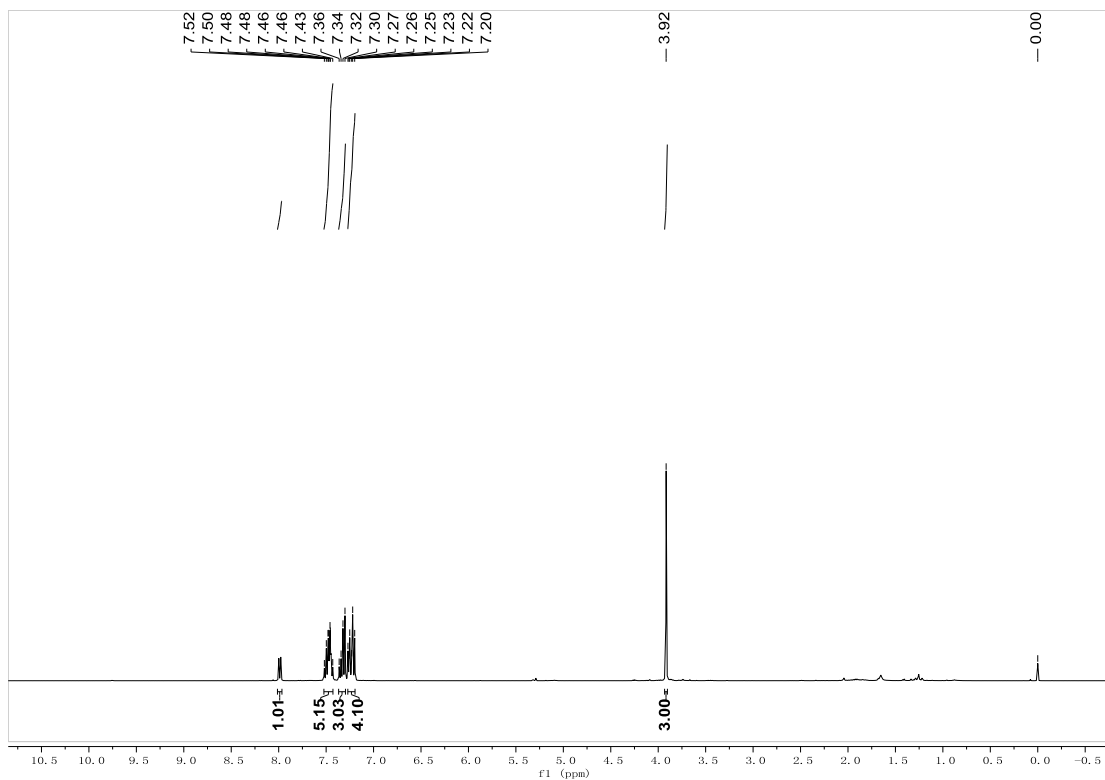


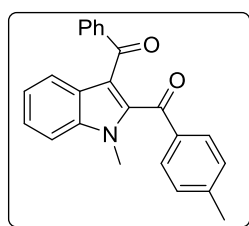
**7f**



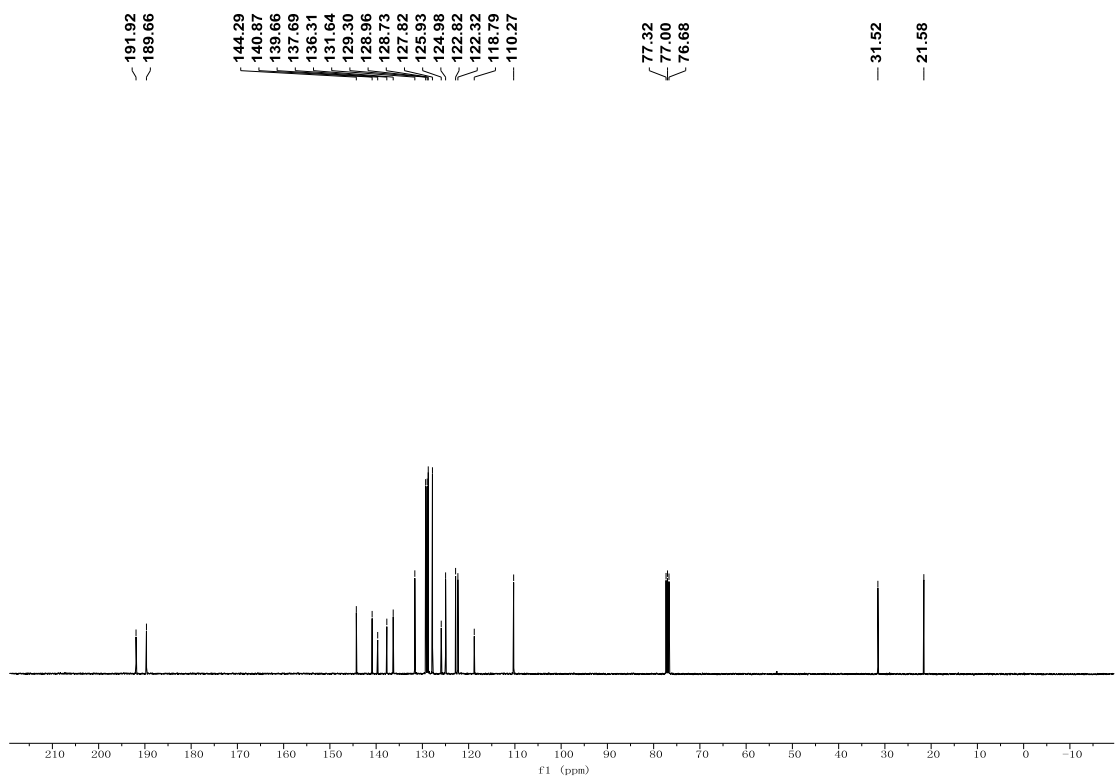
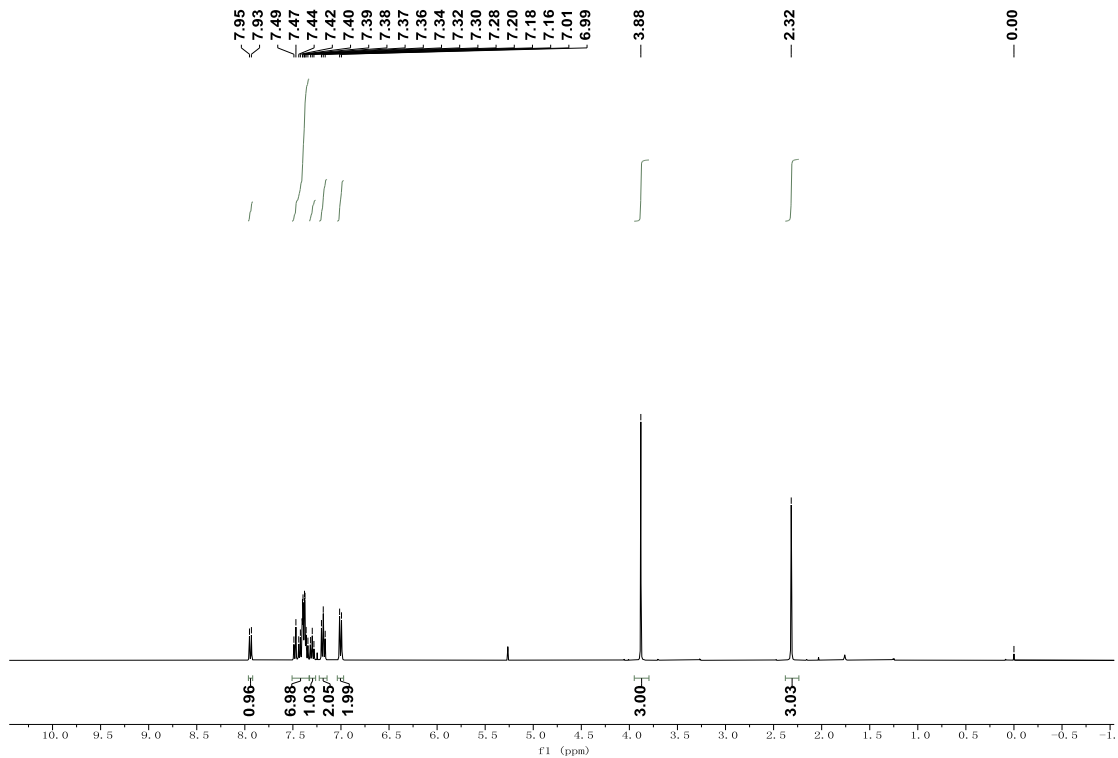


**7g**

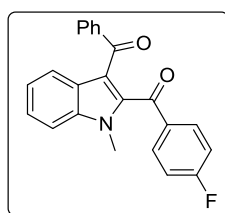




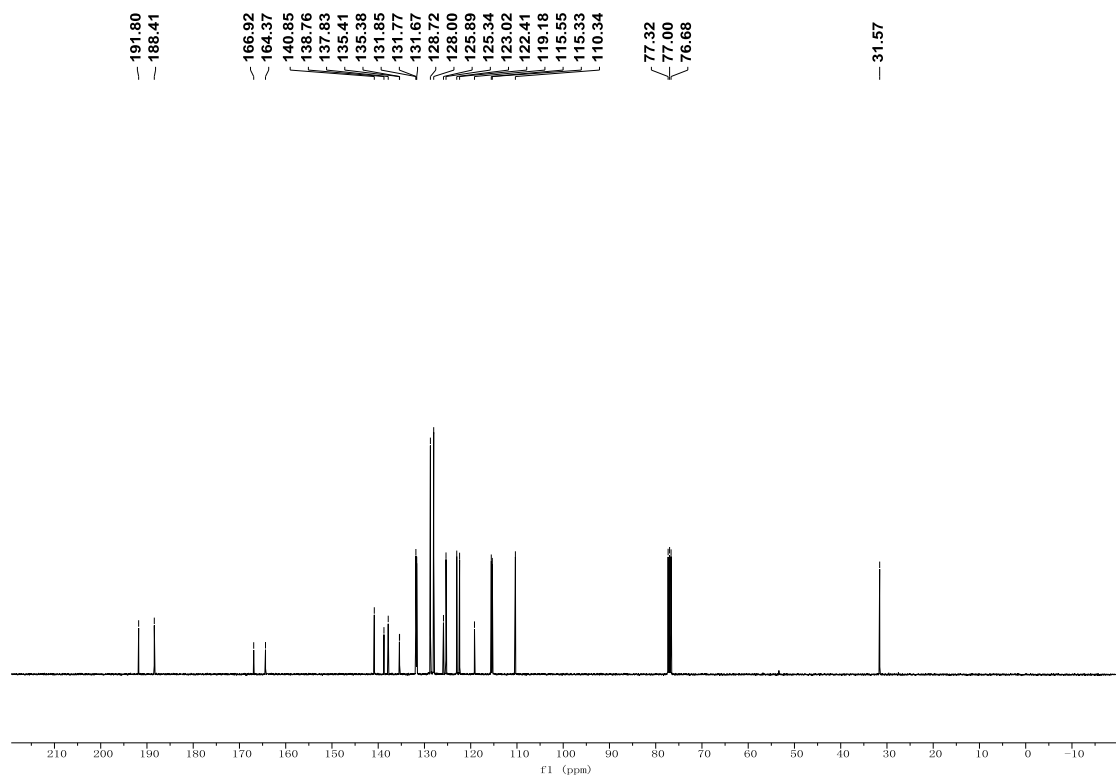
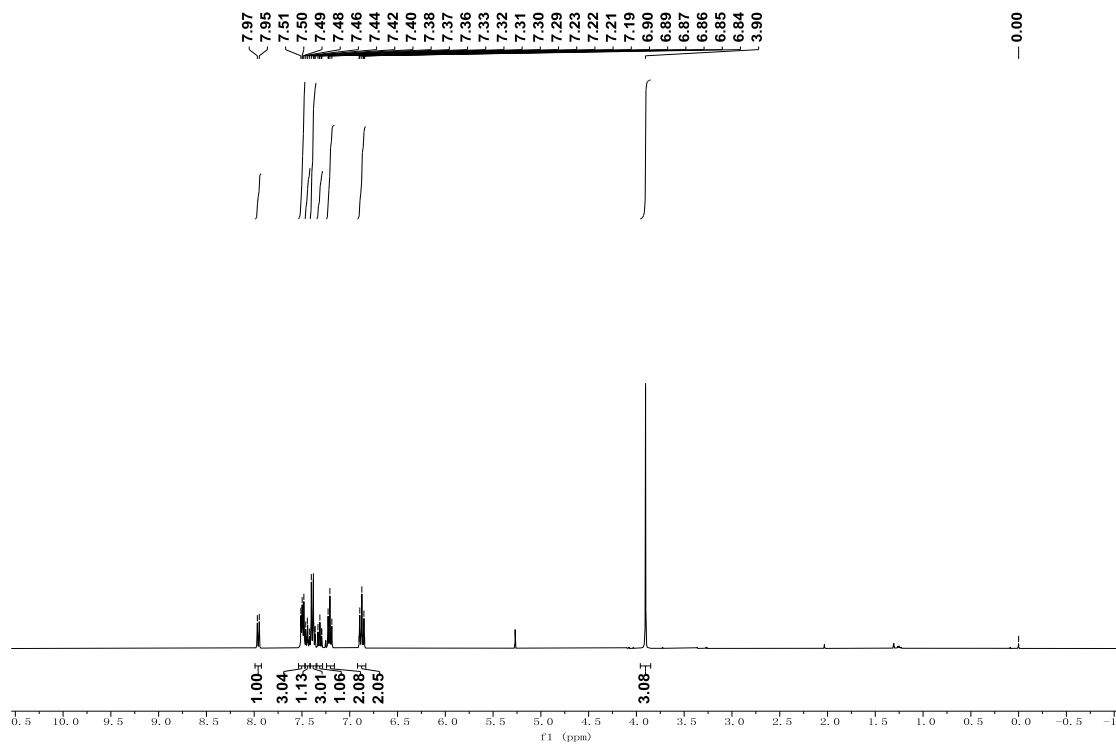
**7h**

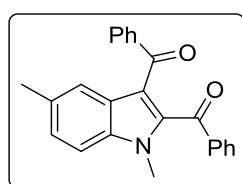
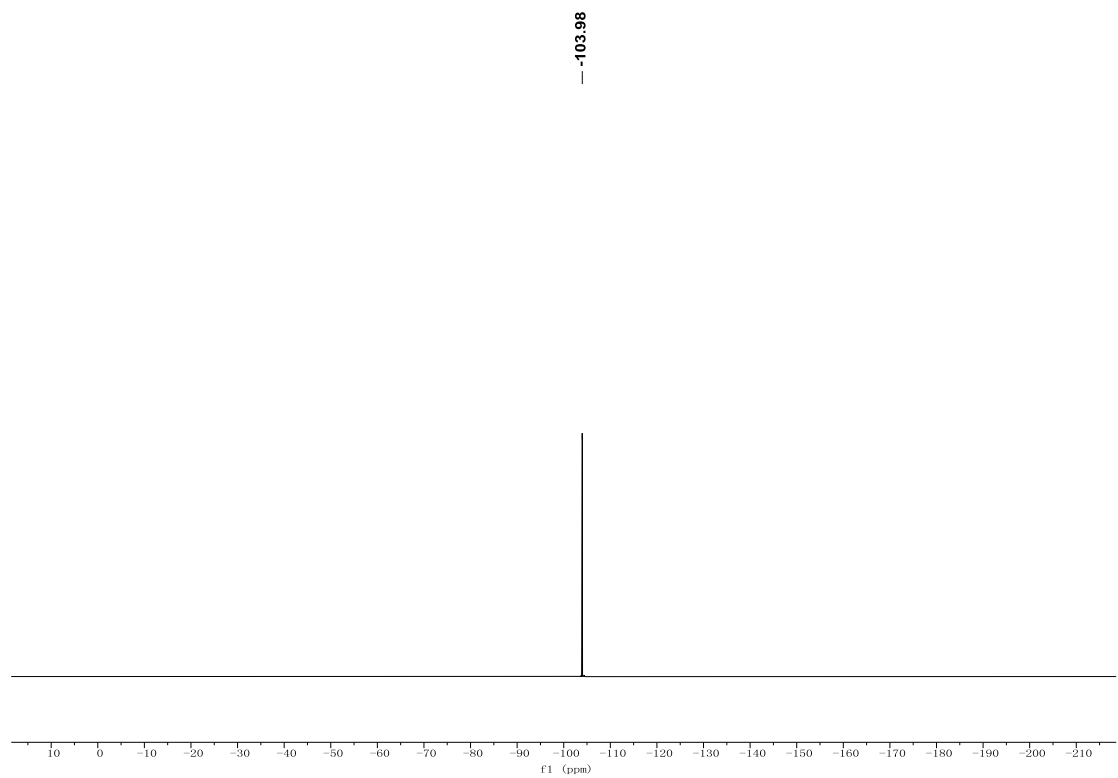




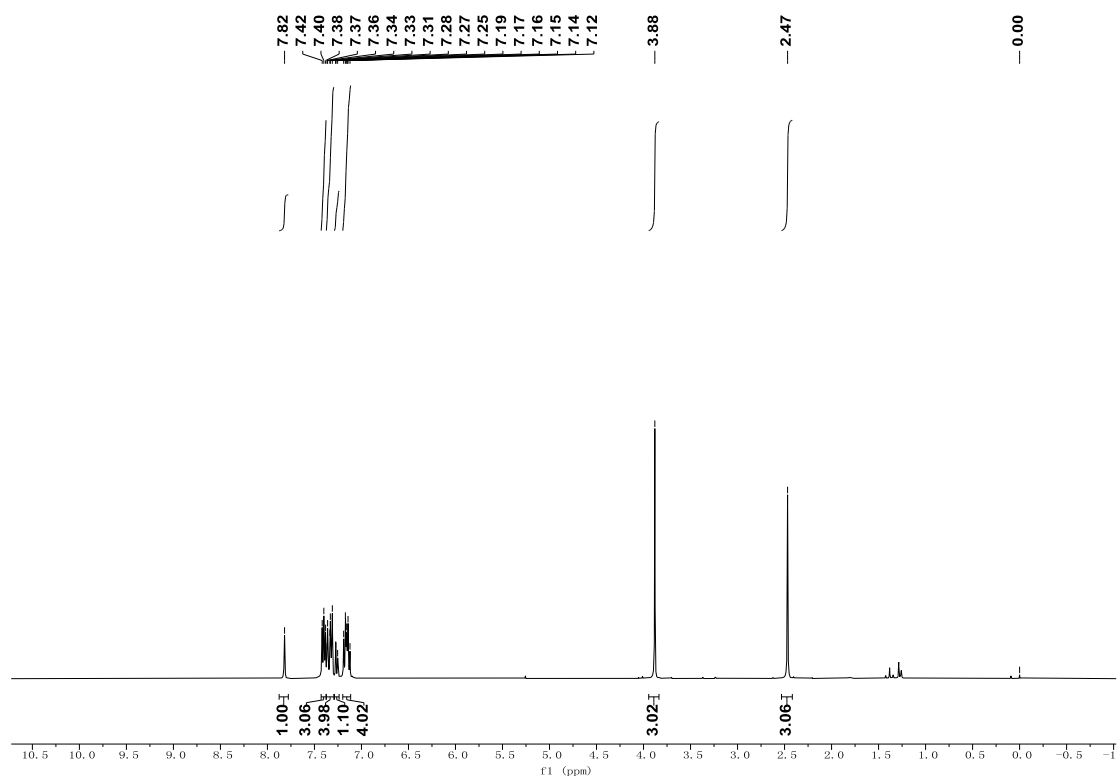


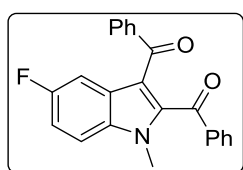
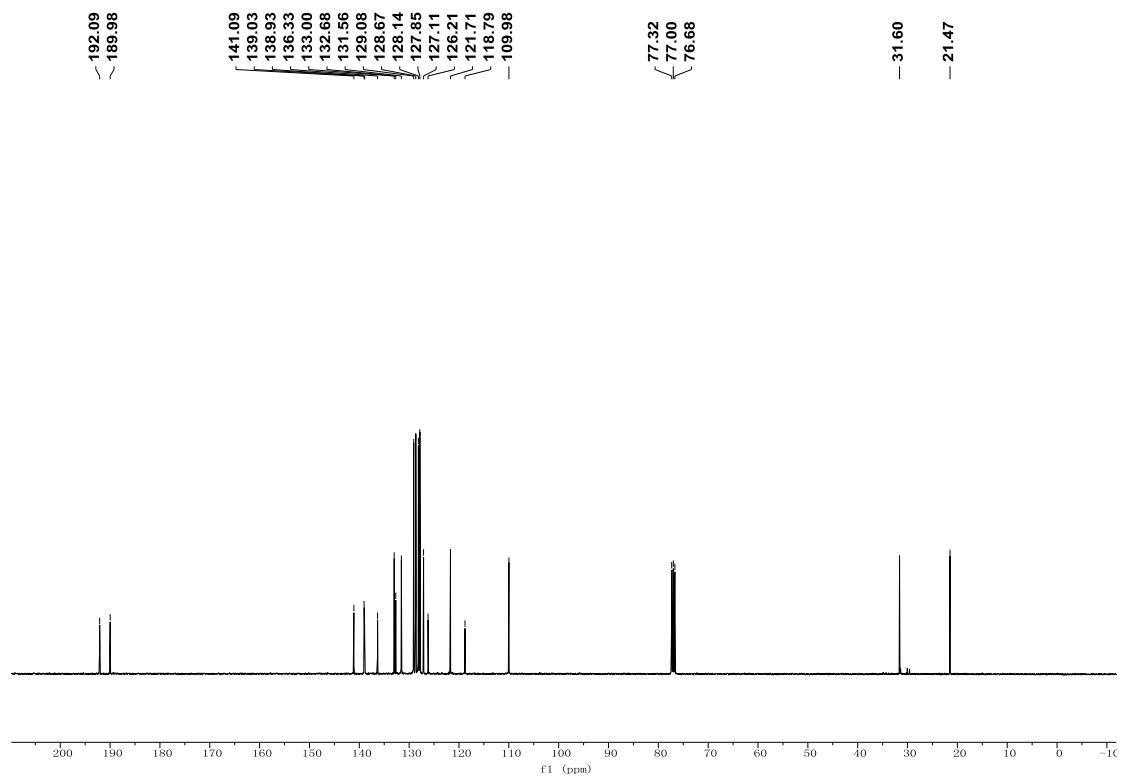
**7i**



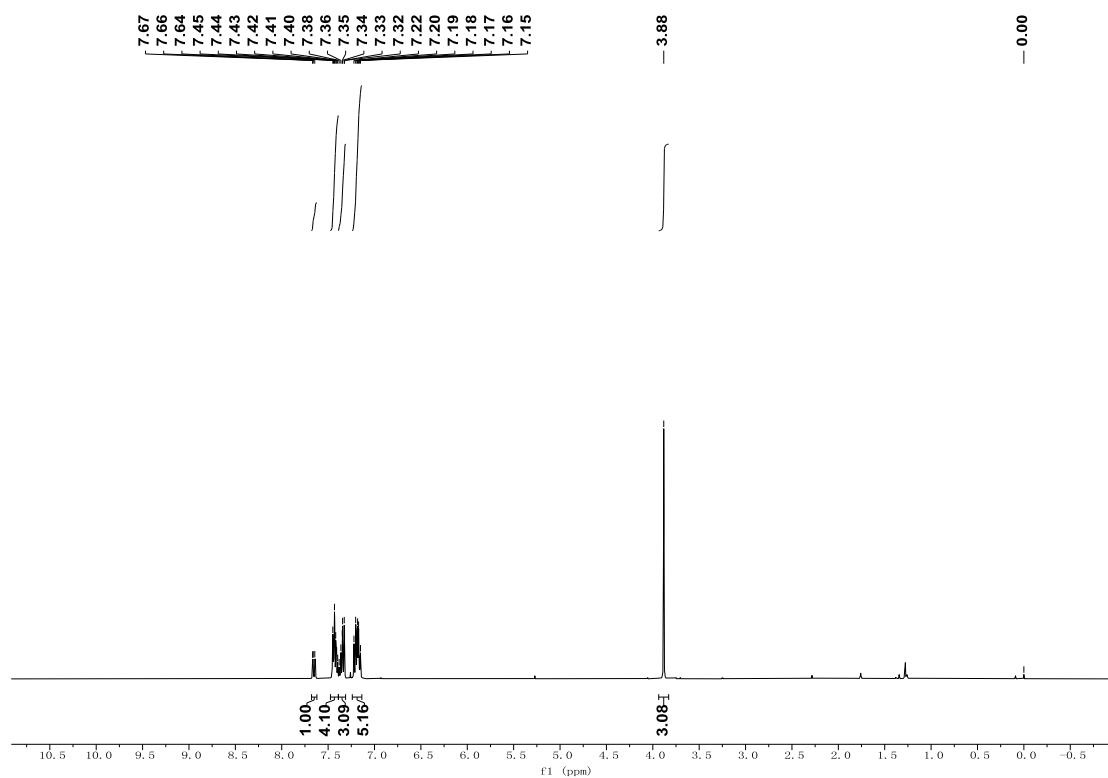


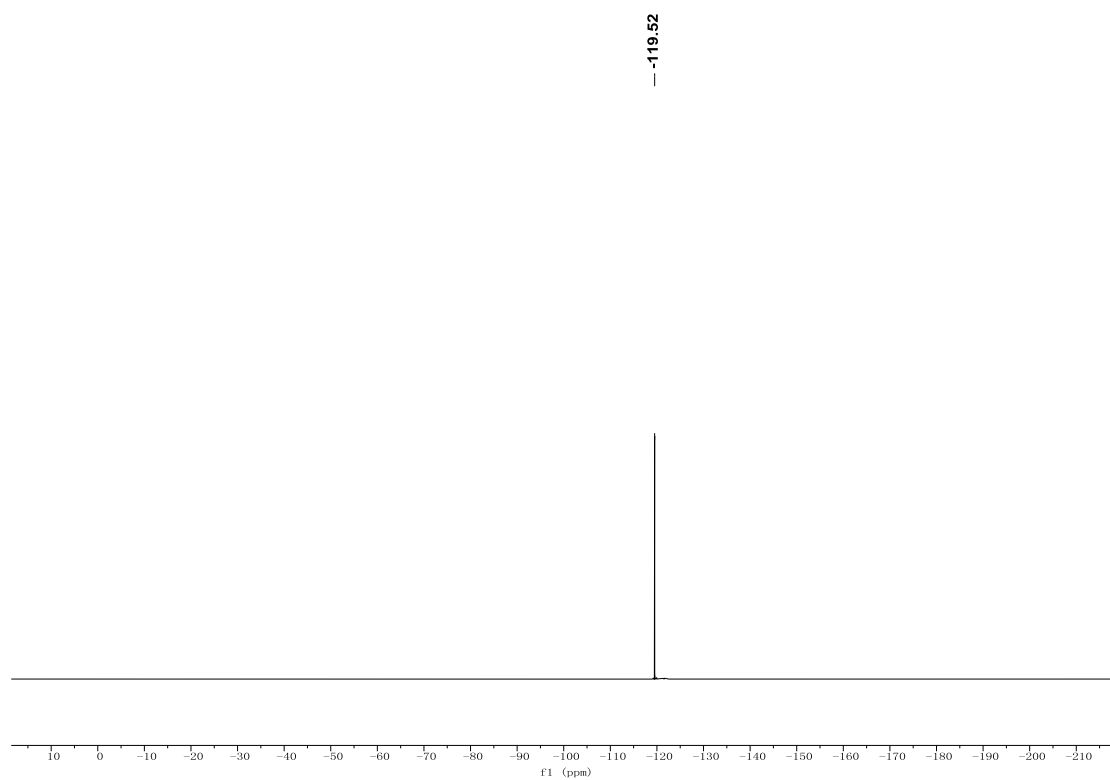
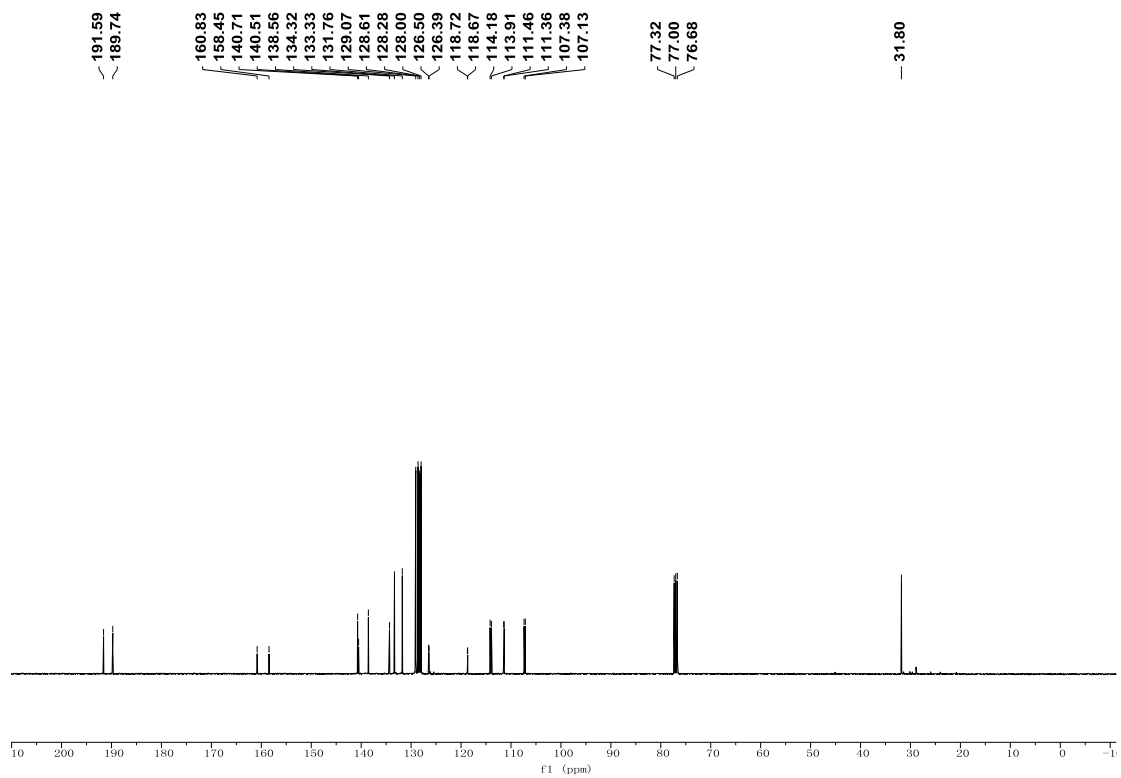
7j

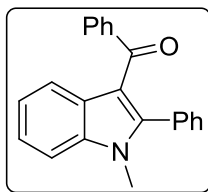




**7k**







71

