

Electronic Supplementary Information

Visible-Light-Induced Radical Cascade Reaction to Prepare Oxindoles via Alkyl Radical Addition to *N*-Arylacryl Amides

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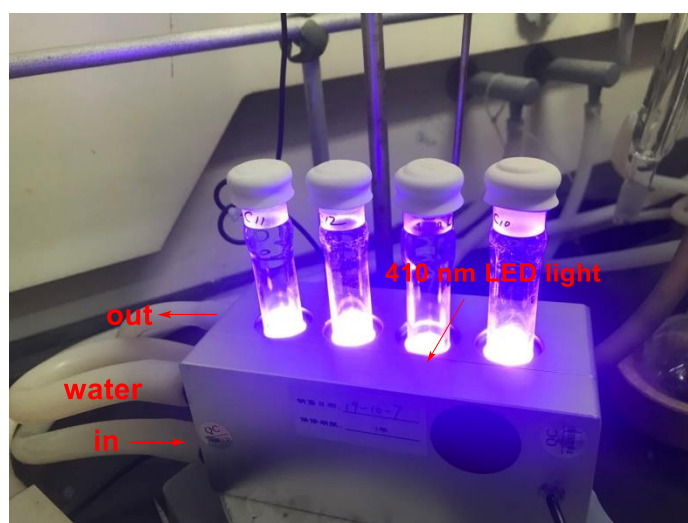
Supporting Information

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1. General information

Unless otherwise noted, all chemicals were purchased from commercial sources and used without further purification. All solvents for photophysical studies were used with anhydrous grade. Analytical TLC was performed on silica gel 60 F₂₅₄ pre-coated plates. NMR spectra were recorded on Bruker Ascend™ 400 MHz and 500 MHz NMR spectrometers with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in δ (ppm) relative to TMS. High resolution mass spectra were recorded using an Exactive Thermo Fisher Scientific mass spectrometer. Gas chromatography-mass spectrometry (GC-MS) analyses were carried out by an Agilent Technologies 7890A Network GC System. Irradiation was performed using 410 and 365 nm LEDs illumination instruments (3 W \times 4) under argon atmosphere.



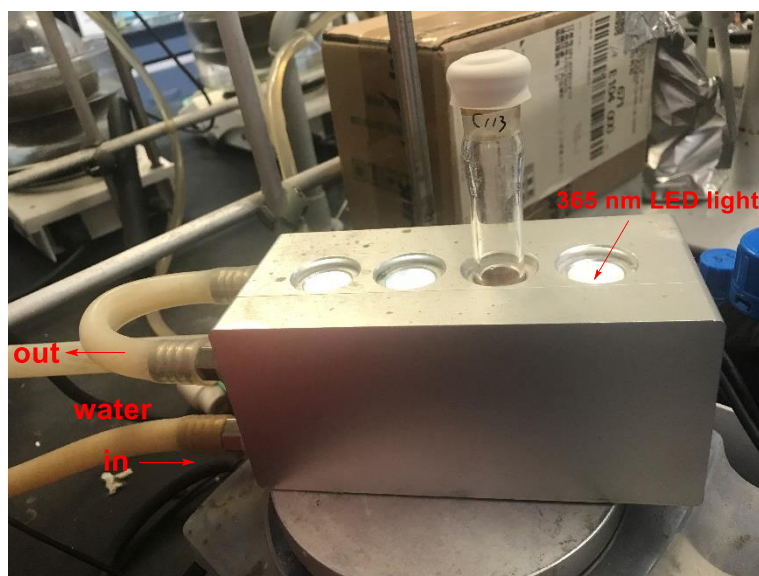
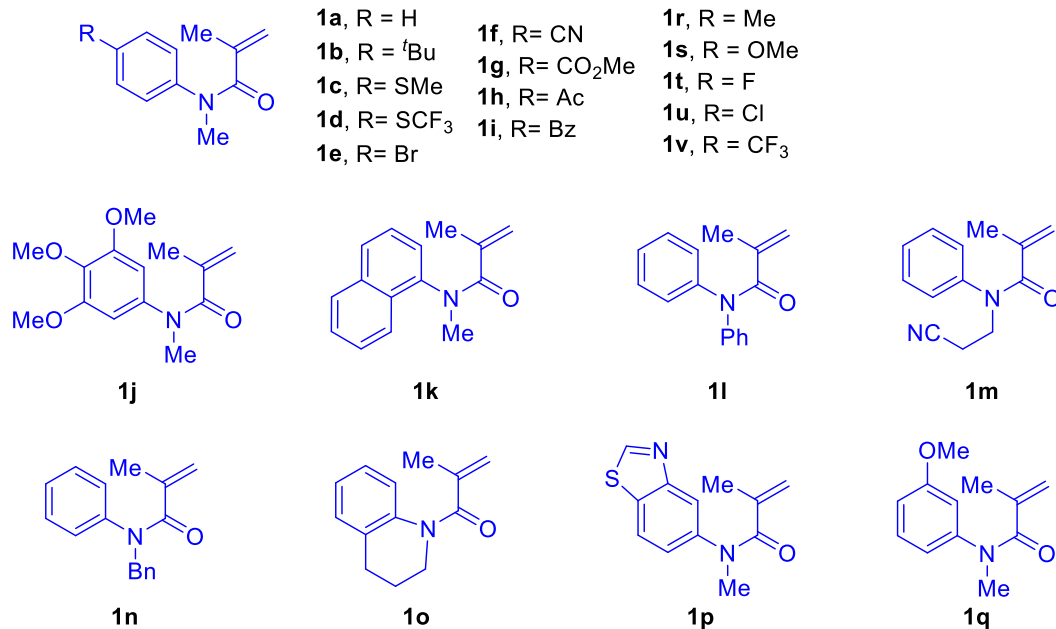
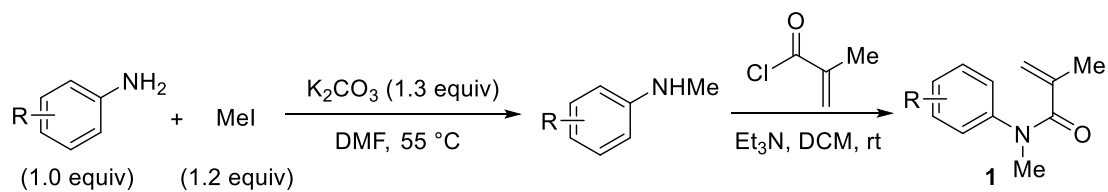


Fig. S1 Reaction setup (the setup was cooled by water)

2. General procedures for the preparation of substrates

Preparation of *N*-arylacrylamides.¹ Aniline (10 mmol), methyl iodide (12.0 mmol), potassium carbonate (13.0 mmol), and *N,N*-dimethylformamide (DMF, 25 mL) were added to a pressure vessel with a magnetic stirring bar. The vessel was then sealed and heated to 55 °C for 24 h. After being allowed to cool to room temperature, water was added into the mixture. The organic phase was collected, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The crude product of *N*-methyl substituted aniline, if containing *N,N*-dimethyl substituted aniline and/or unreacted aniline, was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent, or otherwise was directly used in the next step.

A round flask equipped with a magnetic stirring bar was charged with *N*-methyl substituted aniline (10 mmol) and trimethylamine (15.0 mmol), and dichloromethane (DCM, 50 mL). Methacryloyl chloride (15.0 mmol) in DCM solution was slowly added into the reaction at 0 °C. Then, the reaction mixture was stirred at room temperature overnight. After addition of water into the mixture, the organic phase was collected, and the aqueous layer was extracted with DCM. The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.



Scheme S1 Preparation of **1**

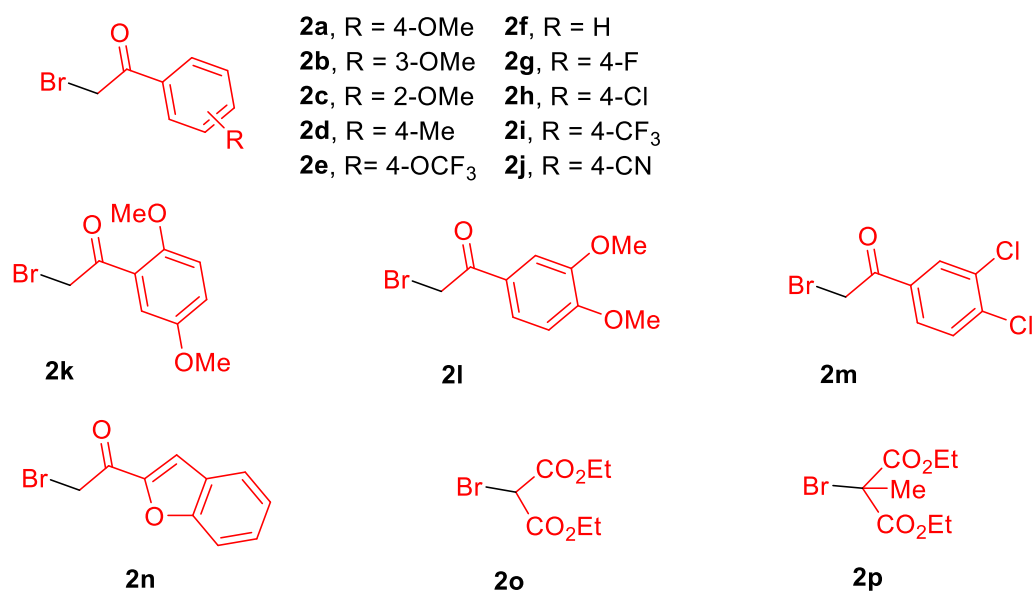
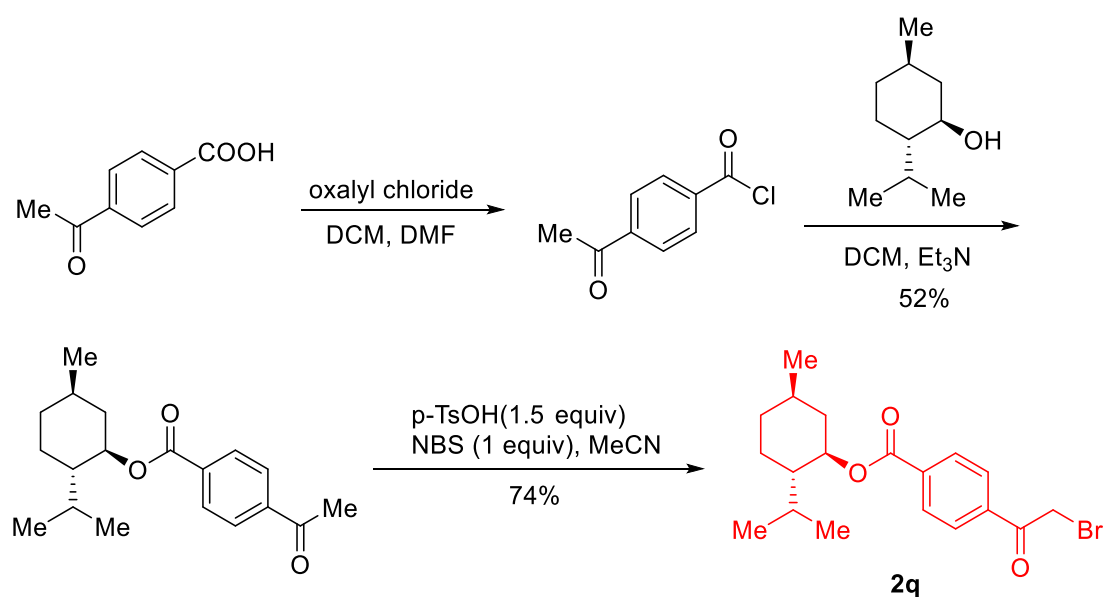


Fig. S2 Chemical structures of **2**

Preparation of 2q. 1) To a solution of 4-acetylbenzoic acid (3.283 g, 20.0 mmol) in DCM (100 mL) at room temperature was added oxalyl chloride (5.077 g, 40.0 mmol) dropwise, followed by a catalytic amount of DMF (3 drops). The reaction mixture was stirred for 12 h at room temperature. After concentration under vacuum to remove DCM and unreacted oxalyl chloride, the crude acid chloride was re-dissolved in DCM (20 mL) and used in the next step without further purification. 2) To a solution of (-)-menthol (468.8 mg, 3.00 mmol) and Et₃N (607.1 mg, 6.00 mmol) in DCM (20 mL) was added the solution of the acid chloride in DCM (4 mL) dropwise at 0 °C. The resulting reaction mixture was stirred at room temperature for 24 h. Afterwards, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. 52% yield (menthol 4-acetylbenzoate, 470.0 mg, yellow oil). 3) To a stirred solution of menthol 4-acetylbenzoate (370.0 mg, 1.224 mmol) in MeCN (30 mL) were added *p*-TsOH·H₂O (349.0 mg, 1.836 mmol, 1.5 eq.) and NBS (217.8 mg, 1.224 mmol, 1.0 eq.), and the mixture was stirred for 12 h at 85 °C. After being concentrated under reduced pressure, the residue was re-dissolved in EtOAc, washed with water, dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by silica-gel flash column chromatography with DCM/pentane (2:1). 74% yield (282.0 mg, white solid).

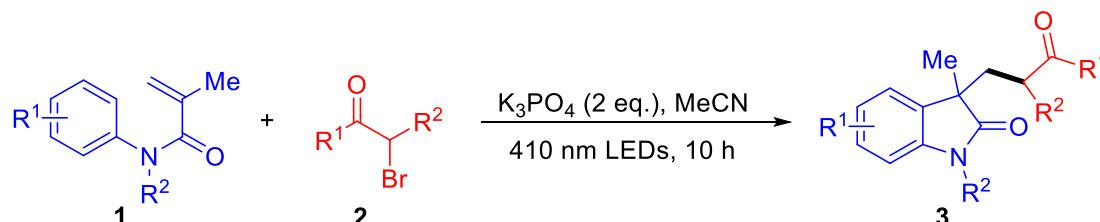


Scheme S2 Preparation of **2q**

3. General procedures for synthesis of oxindoles

Procedure A: To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1** (0.2 mmol, 1.0 equiv), alkyl bromide **2** (0.4 mmol, 2.0 equiv), K₃PO₄ (0.4 mmol, 2.0 equiv), and MeCN (4.0 mL). The

reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product **3** was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. For 1.0 mmol scale reaction, all reagents were scaled-up by ratio with 6.0 mL of MeCN were used as solvent.



Scheme S3 Preparation of **3**

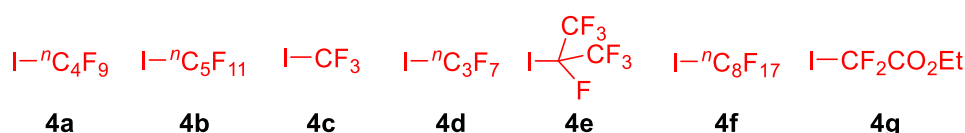
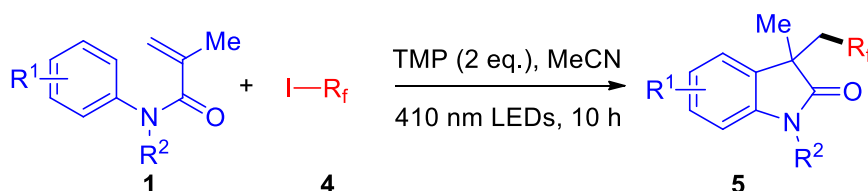


Fig. S3 Chemical structures of **4**

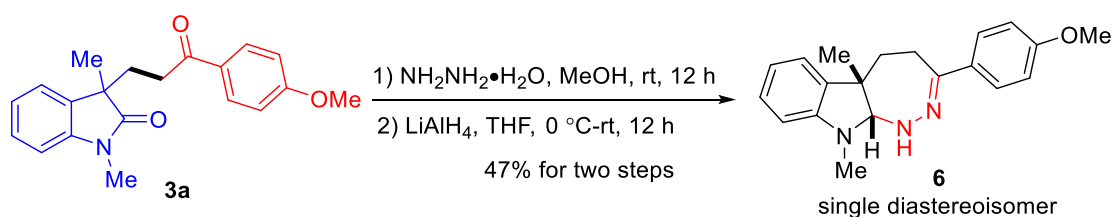
Procedure B: To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1** (0.2 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (TMP, 0.4 mmol, 2.0 equiv) and MeCN (2.0 mL). The reaction mixture was deaerated with argon for 15 min, followed by addition of alkyl iodide **4** (0.4 mmol, 2.0 equiv). The resulting mixture was irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was concentrated under reduced pressure by rotary evaporation. The desired product **5** was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. For 1.0 mmol scale reaction, all reagents were scaled-up by ratio with 6.0 mL of MeCN as solvent.



Scheme S4 Preparation of **5**

4. Preparation of 6

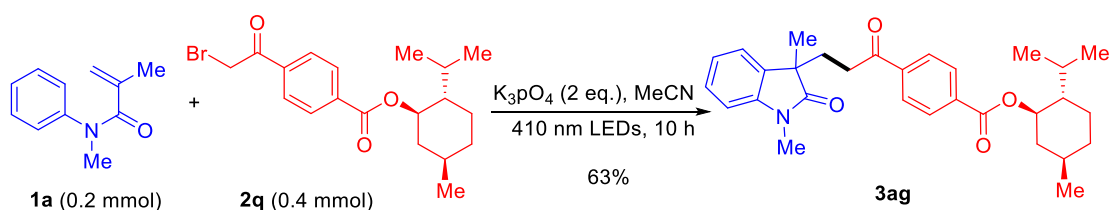
1) To a round bottom flask equipped with a magnetic stirring bar, the purified oxindole **3a** (97.0 mg, 0.30 mmol) and MeOH (4.0 mL) were added, followed by the addition of NH_2NH_2 (10.0 equiv., 80% w/w solution in water). After stirred at room temperature for 12 h, the resulting solution was concentrated, and the residue was extracted with ethyl acetate for 3 times. The combined organic fractions were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The concentrated residue was directly used without further purification. By addition of freshly-distilled THF (6 mL) through a syringe under argon, the resulting solution was cooled to 0 °C and LiAlH_4 (113.9 mg, 3.00 mmol, 10.0 equiv) was added portionwise over 10 min under argon. Then, the suspension was stirred for 12 h at room temperature and quenched by saturated NaOH solution at 0 °C. The reaction mixture was filtered to collect the filtrate and the residue was soaked by ethyl acetate. Afterwards, the filtrate was extracted with ethyl acetate and combined with the soaking fraction. The combined fractions were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent. 47% yield (45.3 mg, white solid).



Scheme S5 Preparation of 6

5. Preparation of 3ag

To a dried reaction tube equipped with magnetic stirring bar were added acrylamide **1a** (0.2 mmol, 1.0 equiv), **2q** (0.4 mmol, 2.0 equiv), K_3PO_4 (0.4 mmol, 2.0 equiv), and MeCN (4.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product **3ag** was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent (60.0 mg, 63% yield).



Scheme S6 Preparation of 3ag

6. Preparation of key intermediates 12 and 14 for the synthesis of core skeletons of physovenine, esermethole and physostigmine

Preparation of diethyl 2-[(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]malonate (3ah). To a dried reaction tube equipped with magnetic stirring bar were added acrylamide **1s** (41 mg, 0.20 mmol, 1.0 equiv), diethyl 2-bromomalonate **2o** (96 mg, 0.40 mmol, 2.0 equiv.), NaHCO₃ (34 mg, 0.40 mmol, 2.0 equiv.), and MeCN (4.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 24 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product **3ah** was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.

Preparation of 2-[(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]malonic acid (7). **3ah** (1.1 g, 3.03 mmol 1.0 equiv.) was added to a solution of KOH in EtOH (15% wt, 25 mL) and stirred at 95 °C for 3 h. Upon reaction completion checked by TLC, the reaction mixture was acidified with concentrated HCl to pH < 2. After evaporating most of ethanol under reduced pressure, the aqueous residue was extracted with DCM (50 mL × 6). The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation.

Preparation of 3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (8). A mixture of **7** (500 mg, 1.63 mmol, 1.0 equiv.) and Cu₂O (350 mg, 2.45 mmol, 1.5 equiv.) in 40 mL of MeCN was refluxed for 30 h. Then, the mixture was acidified with concentrated HCl to pH < 2 and concentrated under reduced pressure. The residue was extracted with DCM (50 mL × 3). The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica gel flash chromatography (DCM/MeOH = 20:1 v/v).

Preparation of 1,3-dioxoisindolin-2-yl 3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoate (9). To a mixture of **8** (100 mg, 0.38 mmol, 1.0 equiv.), *N,N*-dimethylpyridin-4-amine (DMAP, 5 mg, 0.04 mmol, 0.1 equiv.), and 2-hydroxyisindoline-1,3-dione (75 mg, 0.46 mmol, 1.2 equiv.) in 4 mL of anhydrous DCM was added diisopropylmethanediimine (58 mg, 0.46 mmol, 1.2 equiv.) at 0 °C under argon. The reaction mixture was stirred at room temperature under argon for 12 h. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1 v/v).

Preparation of 3-(3-iodopropyl)-5-methoxy-1,3-dimethylindolin-2-one (10).

A mixture of **9** (80 mg, 0.20 mmol, 1.0 equiv.), LiI (32 mg, 0.24 mmol, 1.2 equiv.) and PPh₃ (5 mg, 0.02 mmol, 0.1 equiv.) in 4 mL of anhydrous acetone was deaerated with argon for 15 min. Then, the mixture was irradiated under 456 nm light for 24 h with stirring at room temperature. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1 v/v).

Preparation of 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)ethyl acetate (11). A mixture of **10** (50 mg, 0.14 mmol, 1.0 equiv.) and NaOAc (46 mg, 0.56 mmol, 4.0 equiv.) in 10 mL of anhydrous DMF was stirred at 110 °C under argon for 12 h. Upon reaction completion checked by TLC, the mixture was diluted with water and extracted with ethyl acetate (50 mL × 3). The combined organic phase was washed with saturated brine and dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3:1 v/v).

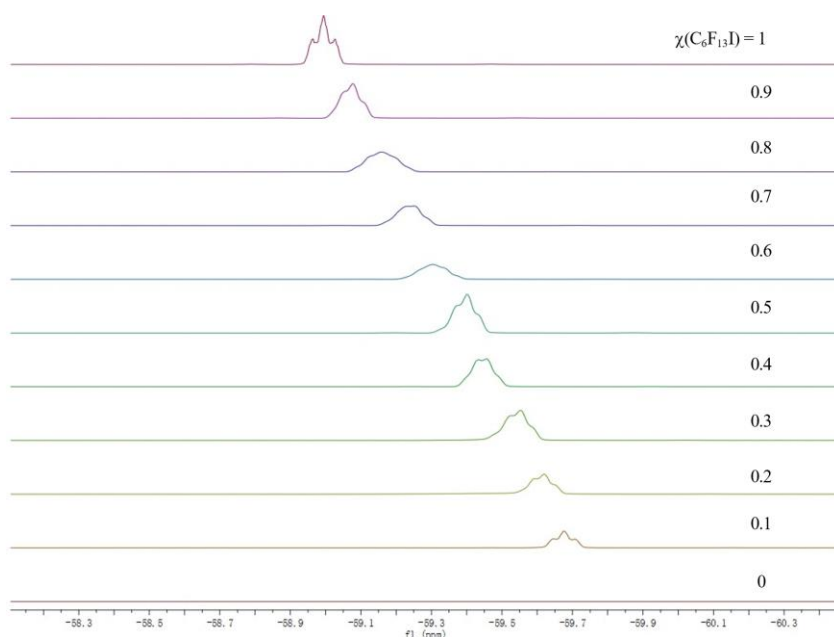
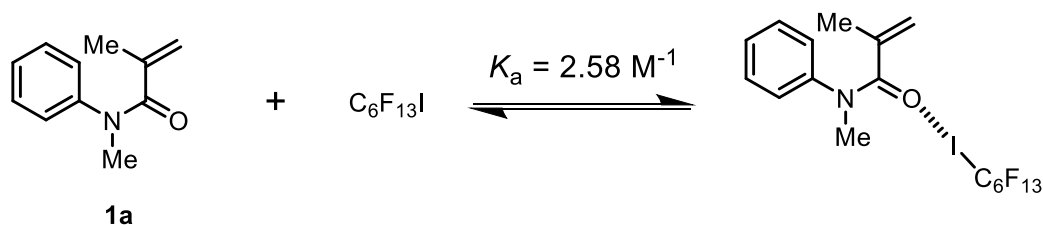
Preparation of 3-(2-hydroxyethyl)-5-methoxy-1,3-dimethylindolin-2-one (12). A mixture of **11** (50 mg, 0.18 mmol, 1.0 equiv.) and Na₂CO₃ (50 mg, 0.36 mmol, 2.0 equiv.) in 15 mL of EtOH was refluxed for 5 h. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure by rotary evaporation and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1:1 v/v).

Preparation of 3-(2-isocyanatoethyl)-5-methoxy-1,3-dimethylindolin-2-one (13). To a solution of **8** (85 mg, 0.32 mmol, 1.0 equiv.) and Et₃N (36 mg, 0.35 mmol, 1.1 equiv.) in 5 mL of anhydrous THF was added DPPA (101 mg, 0.36 mmol, 1.1 equiv.) at 0 °C under argon. Then, the mixture was stirred at room temperature for 24 h. After evaporation of THF under reduced pressure, the residue was re-dissolved in 12 mL of toluene and reflux for additional 24 h. Upon reaction completion checked by TLC, the mixture was concentrated under reduced pressure by rotary evaporation and the residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3:1 v/v).

Preparation of 3-(2-aminoethyl)-5-methoxy-1,3-dimethylindolin-2-one (14). A suspension of **13** (50 mg, 0.19 mmol, 1.0 equiv.) in a mixture of 12 M HCl / dioxane (6 mL, 1:1) was refluxed for 12 h. Upon reaction completion checked by TLC, the mixture was acidified with KOH (15%) to pH > 12 and extracted with DCM (50 mL × 3). The combined organic phase was washed with saturated brine and dried over MgSO₄, filtered, and concentrated under reduced pressure by rotary evaporation. The residue was purified by silica gel flash chromatography (DCM/MeOH = 10:1 v/v).

7. NMR titration experiments

(1) **Determination of the binding stoichiometry between *N*-arylacrylamide **1a** and $C_6F_{13}I$.** ^{19}F NMR spectra of ten samples of mixtures of **1a** and $C_6F_{13}I$ in $CDCl_3$ were recorded at room temperature. $PhCF_3$ ($\delta_{C-F} = -62.76$ ppm) was used as an internal standard. The total volume of the mixture was 0.5 mL, and the total amount of **1a** and $C_6F_{13}I$ was kept constant at 0.25 mmol (0.5 M), while the amount of $C_6F_{13}I$ was varied from 0 to 0.25 mmol (0–0.5 M). The molar ratios of $C_6F_{13}I/(C_6F_{13}I + \mathbf{1a})$ (i.e. $\chi(C_6F_{13}I)$) were increased from 0.0 to 1.0 with a step of 0.1. ^{19}F NMR spectrum for each sample was recorded and the chemical shifts differences ($\Delta\delta$) for $-CF_2I$ of $C_6F_{13}I$ were used to draw the Job plot. The stoichiometry was determined by plotting ratios of $[C_6F_{13}I] \times \Delta\delta$ against $\chi(C_6F_{13}I)$, which afforded a maximum at ratio $\chi(C_6F_{13}I) = 0.5$, suggesting a 1:1 complex ratio between **1a** and $C_6F_{13}I$.



$\chi(\text{C}_6\text{F}_{13}\text{I})$	$[\text{C}_6\text{F}_{13}\text{I}]$ (M)	δ (ppm)	$\Delta\delta$ (ppm)	$[\text{C}_6\text{F}_{13}\text{I}]*\Delta\delta$ (ppm)
0	0	0	0	0
0.1	0.05	59.6700	0.6813	0.0341
0.2	0.1	59.6141	0.6254	0.0625
0.3	0.15	59.5466	0.5579	0.0837
0.4	0.2	59.4377	0.4490	0.0898
0.5	0.25	59.3954	0.4067	0.1017
0.6	0.3	59.2990	0.3103	0.0931
0.7	0.35	59.2345	0.2458	0.0860
0.8	0.4	59.1536	0.1649	0.0660
0.9	0.45	59.0716	0.0829	0.0373
1	0.5	58.9887	0	0

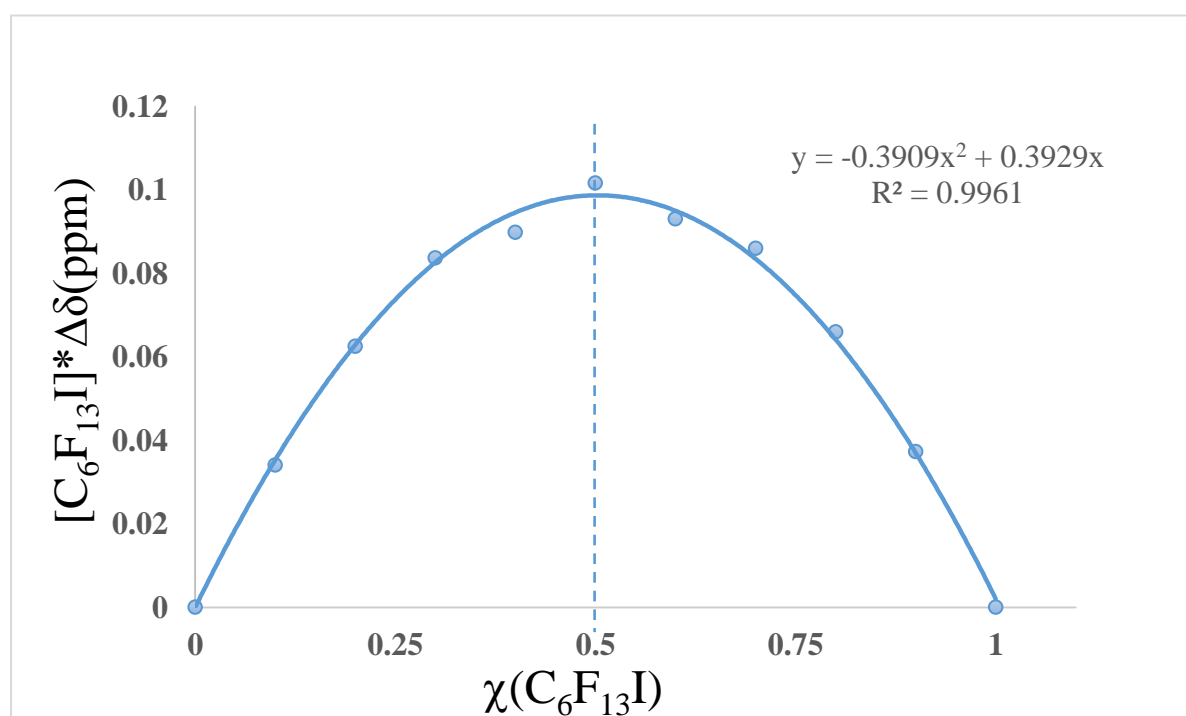
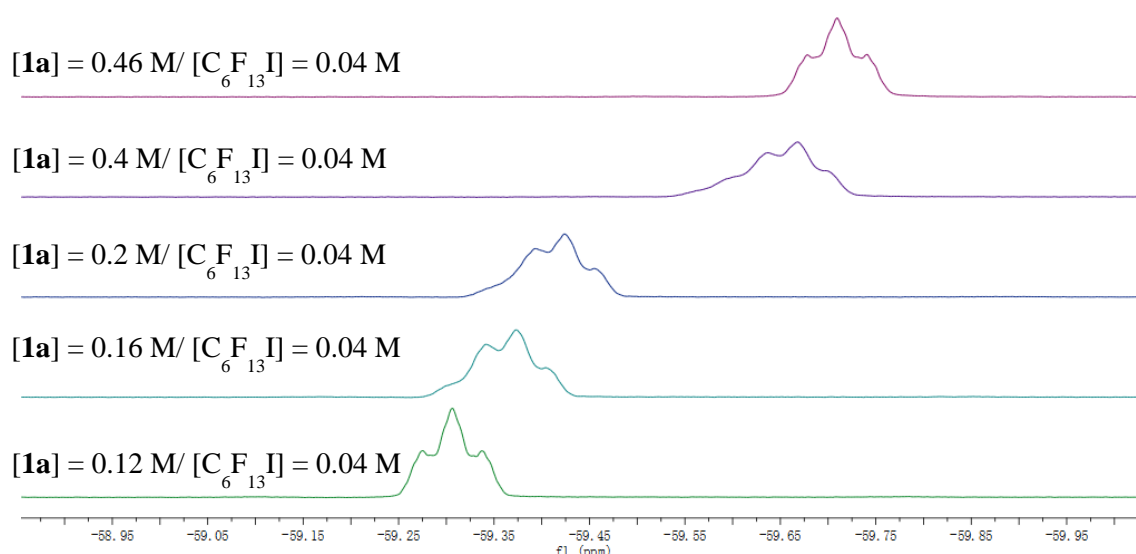


Fig. S4 Job plot for **1a** and $\text{C}_6\text{F}_{13}\text{I}$ in CDCl_3

(2) **Determination of the association constant (K_a).** ^{19}F NMR spectra of five samples of mixtures of $\text{C}_6\text{F}_{13}\text{I}$ and **1a** in CDCl_3 were recorded at room temperature. PhCF_3 ($\delta_{\text{C-F}} = -62.76$ ppm) was used as an internal standard. The total volume of the mixture was 0.5 mL, the amount of $\text{C}_6\text{F}_{13}\text{I}$ was kept constant at 0.02 mmol (0.04 M), while that of **1a** increased from 0.06 (0.12 M) to 0.23 mmol (0.46 M). ^{19}F NMR spectrum for each sample was recorded and the chemical shifts differences ($\Delta\delta$) for $-\text{CF}_2\text{I}$ were used to draw the plot. The association constant (K_a) of $\text{C}_6\text{F}_{13}\text{I}$ and **1a** was calculated by intercept/slope from the plot, which gives 2.58 M^{-1} .



[1a] (M)	1/ [1a] (M^{-1})	$\Delta\delta$ (ppm)	1/ $\Delta\delta$ (ppm)	Δ (ppm)
0.12	8.33	0.31	3.21	59.30
0.16	6.25	0.38	2.64	59.37
0.2	5	0.43	2.33	59.42
0.4	2.5	0.67	1.49	59.67
0.46	2.17	0.71	1.40	59.70

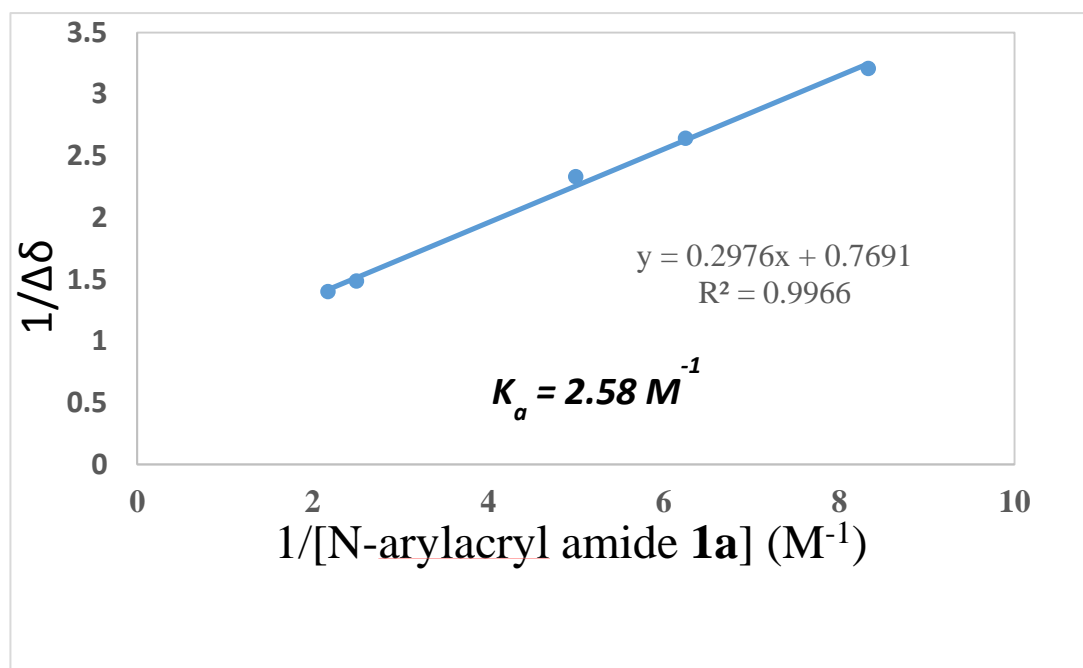
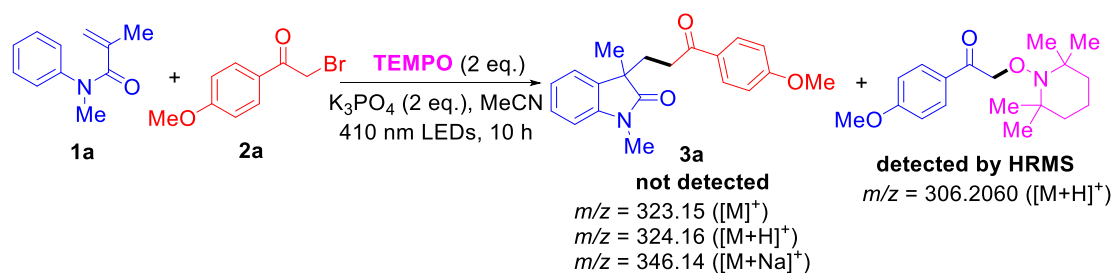
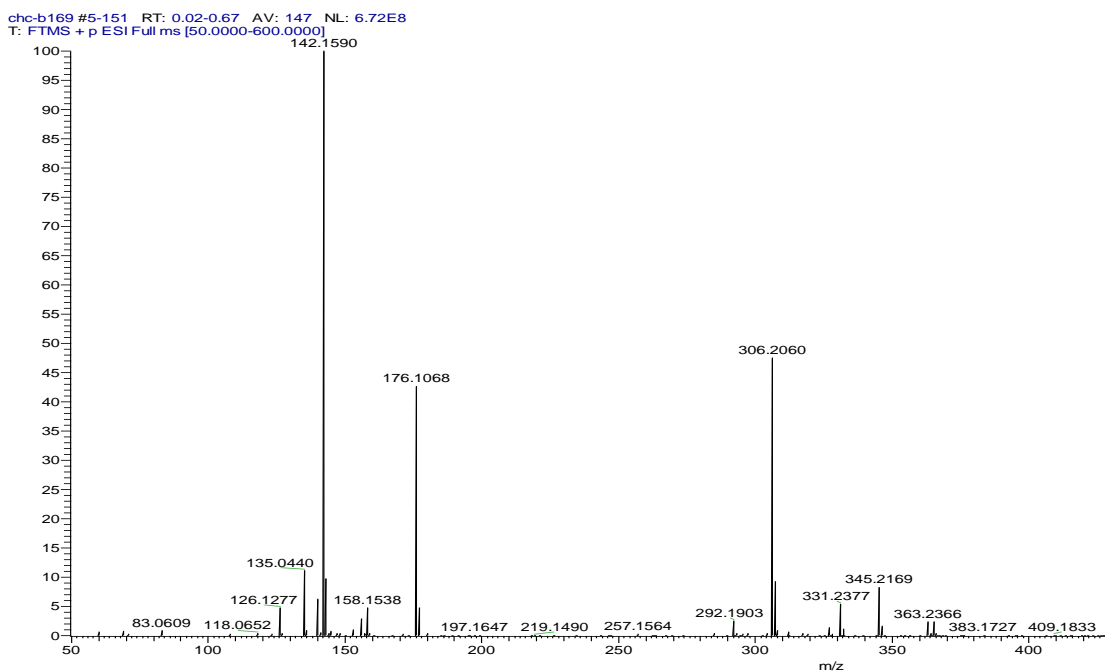


Fig. S5 Plot of $1/\Delta\delta$ against $1/[N\text{-arylacryl amide } \mathbf{1a}]$ in CDCl_3

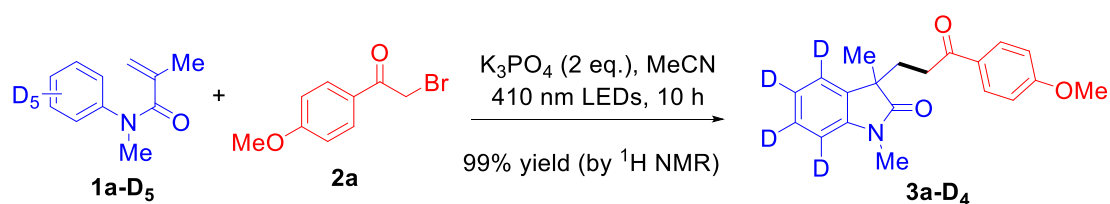
8. Control experiments

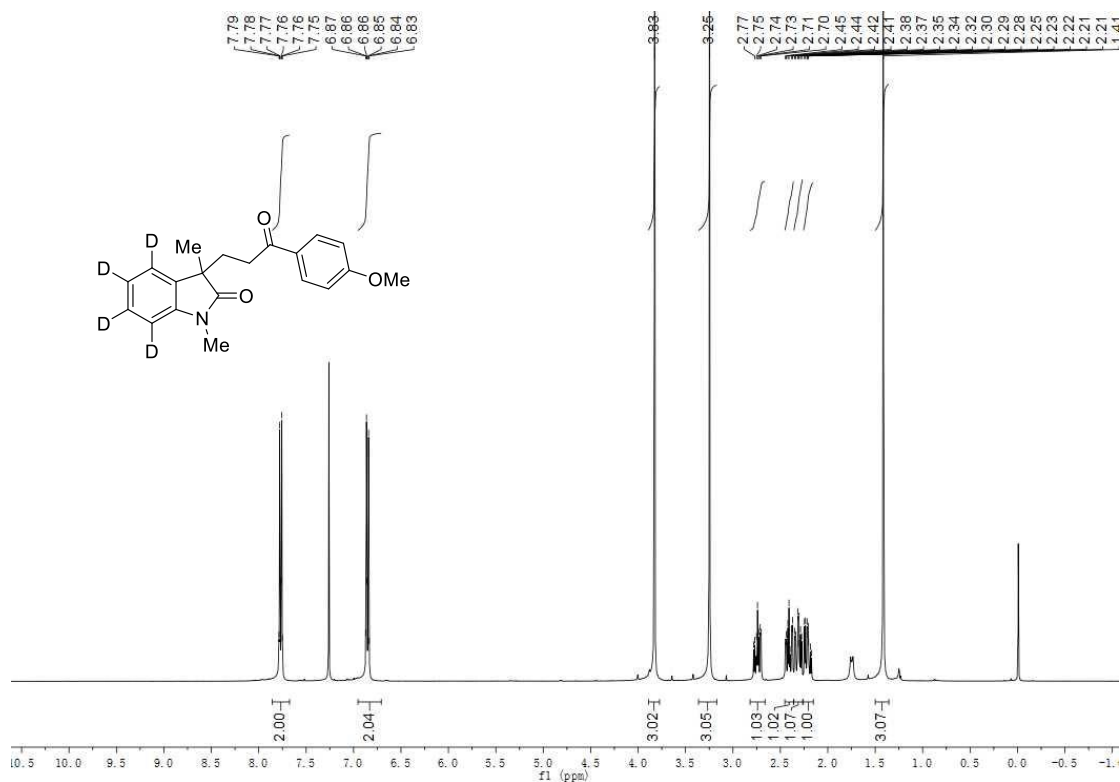
(1) To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1a** (0.2 mmol), alkyl bromide **2a** (0.4 mmol), K_3PO_4 (0.4 mmol), TEMPO (0.4 mmol), and MeCN (4.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was analysed by high resolution mass spectroscopy (HR MS).



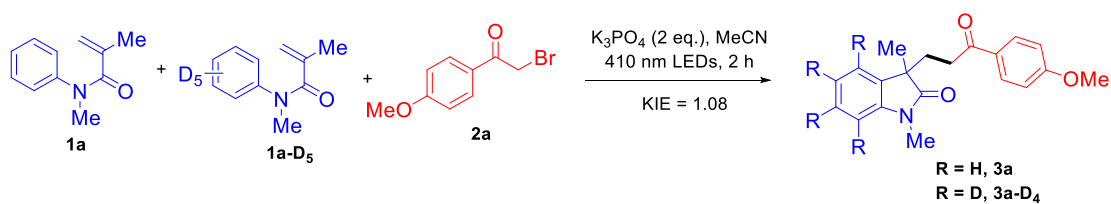


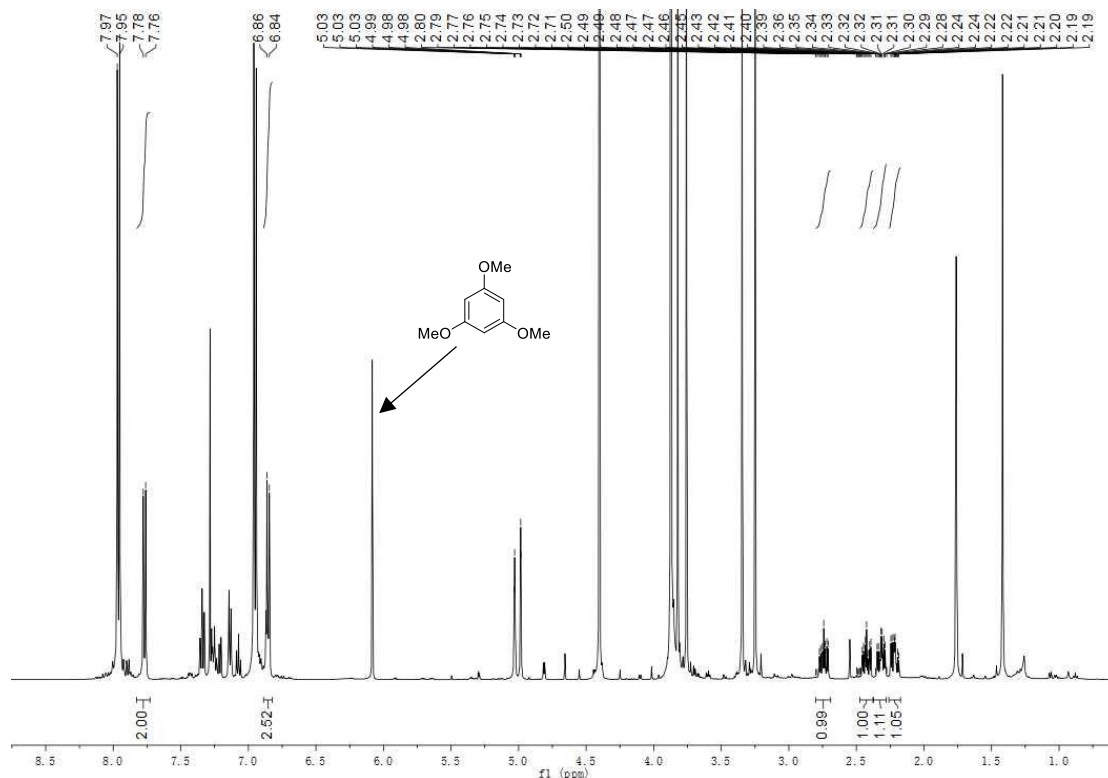
(2) To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1a-D₅** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), and K₃PO₄ (0.2 mmol), followed by 2 mL of MeCN. The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product **3a-D₄** was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.



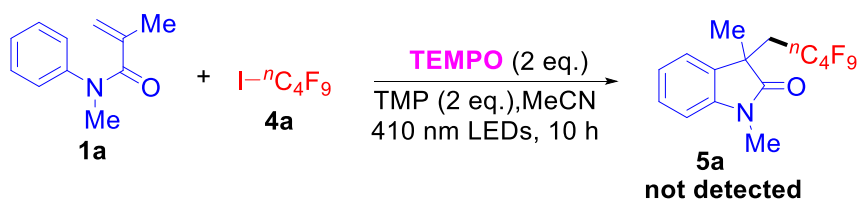


(3) To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1a** (0.1 mmol), **1a-D₅** (0.1 mmol), **2a** (0.4 mmol), K₃PO₄ (0.4 mmol), followed by 4 mL of MeCN. The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs. The ratio of crude product **3a** and **3a-D₄** was analysed by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The value of KIE is 1.08.

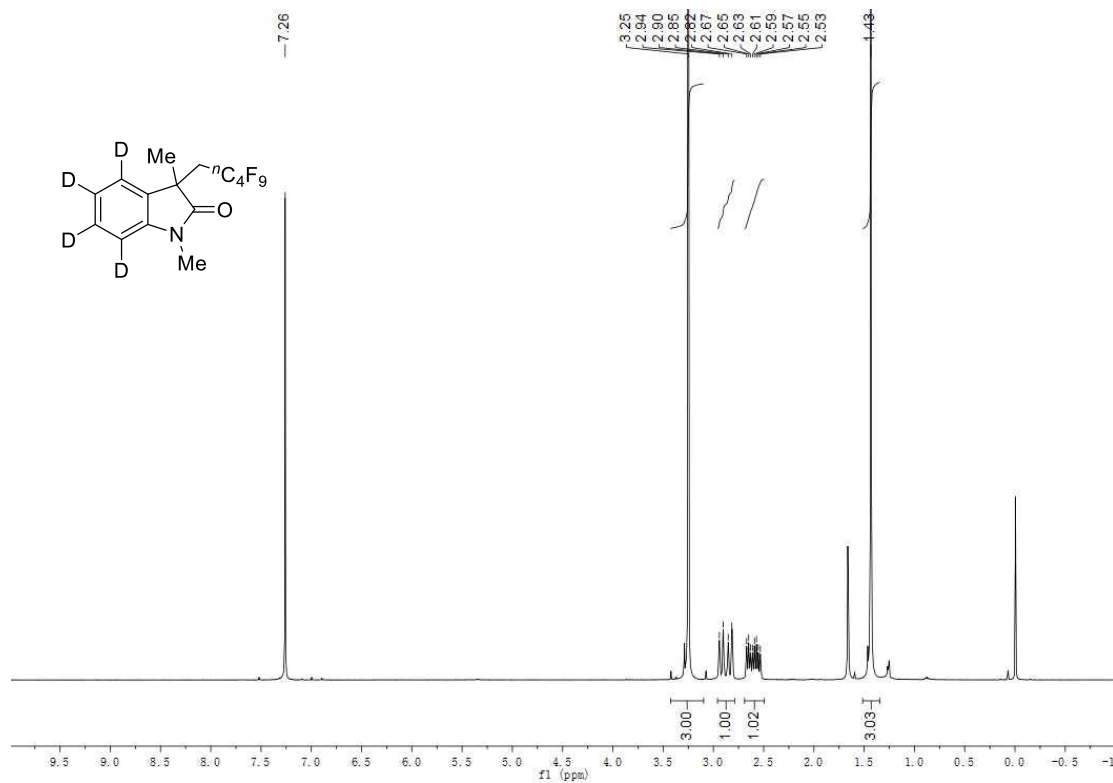
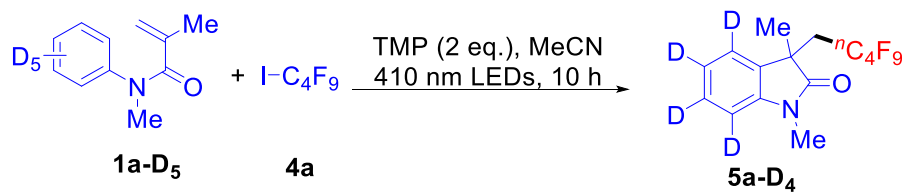




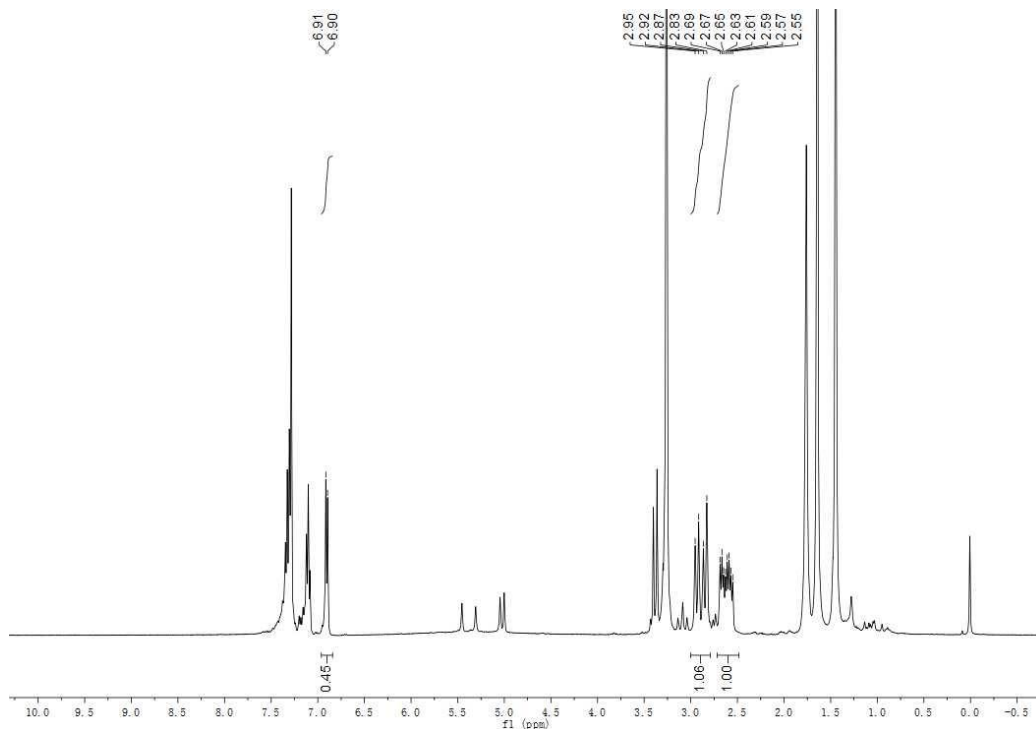
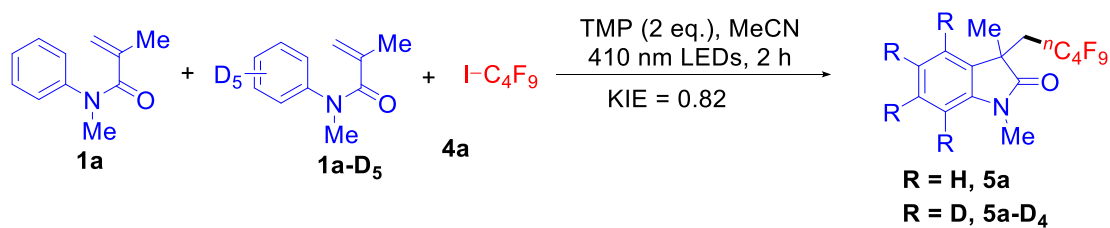
(4) To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1a** (0.1 mmol), alkyl iodide **4a** (0.2 mmol), TMP (0.2 mmol), TEMPO (0.2 mmol), and MeCN (1.0 mL). The reaction mixture was deaerated with argon for 15 min and irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was analysed by high resolution mass spectroscopy (HR MS).



(5) To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1a-D₅** (0.1 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (TMP, 0.2 mmol, 2.0 equiv) and MeCN (1.0 mL). The reaction mixture was deaerated with argon for 15 min, followed by addition of alkyl iodide **4a** (0.4 mmol, 2.0 equiv). The resulting mixture was irradiated by 410 nm LEDs for 10 h. After reaction, the mixture was filtered to remove the insoluble fraction. The filtrate was concentrated under reduced pressure by rotary evaporation. The desired product **5a-D₄** was obtained by silica-gel flash column chromatography using petroleum ether/ethyl acetate as the eluent.



(6) To a dried reaction tube equipped with magnetic stirring bar were added *N*-methyl-*N*-phenylmethacrylamide **1a** (0.1 mmol), **1a-D₅** (0.1 mmol), TMP (0.4 mmol), and 2 mL of MeCN. The reaction mixture was deaerated with argon for 15 min, followed by addition of alkyl iodide **4a** (0.4 mmol, 2.0 equiv). The resulting mixture was irradiated by 410 nm LEDs. The ratio of crude product **5a** and **5a-D₄** was analysed by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The value of KIE is 0.82.



9. Characterization of substrates and products

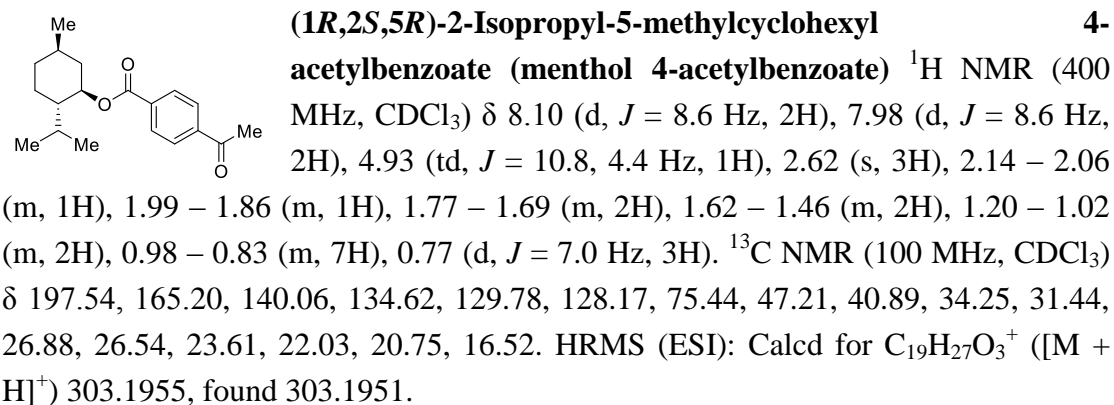
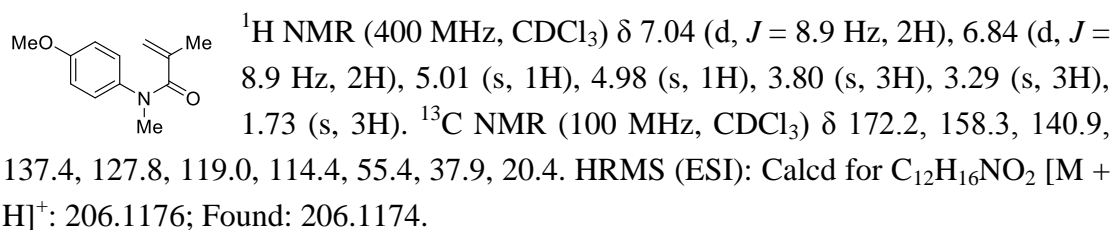
N-Methyl-*N*-[4-(methylthio)phenyl]methacrylamide (**1c**)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20 (d, $J = 8.6$ Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 5.04 (s, 1H), 4.99 (s, 1H), 3.28 (s, 3H), 2.45 (s, 3H), 1.73 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.0, 141.6, 140.6, 137.4, 127.0, 126.9, 119.4, 37.7, 20.3, 15.8. HRMS (ESI): Calcd for $\text{C}_{12}\text{H}_{16}\text{NOS}$ ($[\text{M} + \text{H}]^+$) 222.0947, found 222.0944.

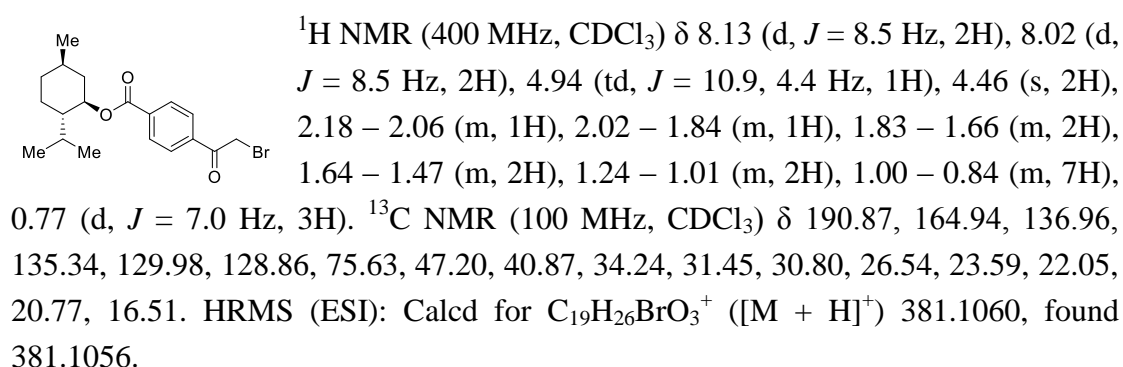
N-Methyl-*N*-{4-[(trifluoromethyl)thio]phenyl}methacrylamide (**1d**)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 5.07 – 5.06 (m, 1H), 4.97 – 4.96 (m, 1H), 3.33 (s, 3H), 1.77 (dd, $J = 1.7, 1.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.8, 147.1, 140.2, 137.2, 129.4 (q, $J = 308.2$ Hz), 127.0, 122.4 (q, $J = 2.1$ Hz), 120.1, 37.5, 20.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -42.85 (s). HRMS (ESI): Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{NOS}$ ($[\text{M} + \text{H}]^+$) 276.0664, found 276.0664.

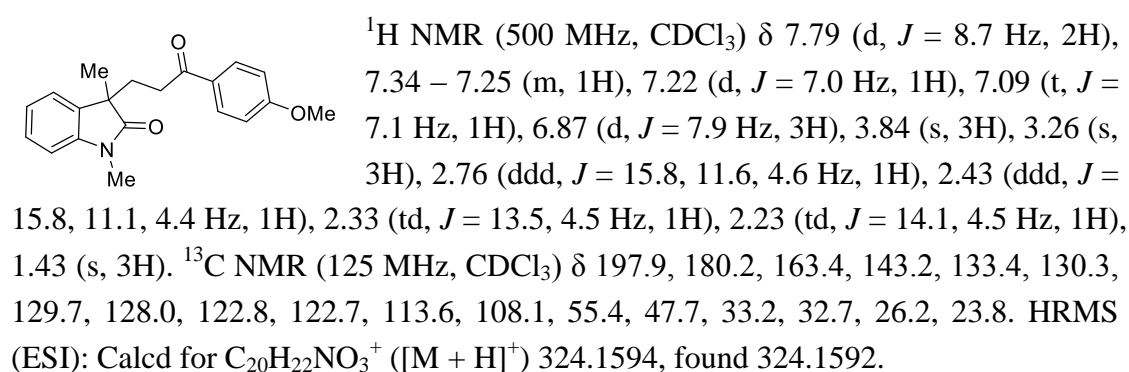
4-Methoxy-N-methyl-N-(3-methylbut-3-en-2-yl)aniline (1s)



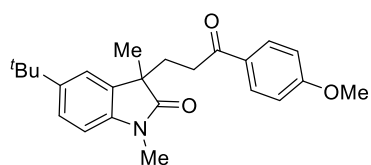
(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-(2-bromoacetyl)benzoate (2q)



3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3a)

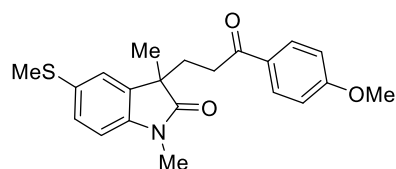


5-(*tert*-Butyl)-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one
(3b)



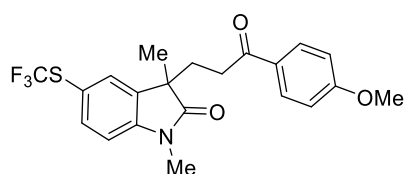
^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J=8.9$ Hz, 2H), 7.31 (dd, $J=8.1, 2.0$ Hz, 1H), 7.25 (d, $J=1.9$ Hz, 1H), 6.87 (d, $J=6.8$ Hz, 2H), 6.80 (d, $J=8.1$ Hz, 1H), 3.85 (s, 3H), 3.25 (s, 3H), 2.76 (ddd, $J=16.1, 11.1, 5.2$ Hz, 1H), 2.49 (ddd, $J=15.9, 10.7, 4.9$ Hz, 1H), 2.33 (ddd, $J=13.8, 10.7, 5.2$ Hz, 1H), 2.24 (ddd, $J=13.8, 11.1, 4.9$ Hz, 1H), 1.44 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 180.4, 163.4, 146.1, 140.8, 133.2, 130.3, 129.8, 124.6, 119.8, 113.6, 107.4, 55.4, 47.9, 34.6, 33.3, 32.8, 31.6, 26.2, 23.8. HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{30}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 380.2220, found 380.2217.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-5-(methylthio)indolin-2-one
(3c)



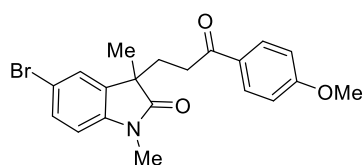
^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J=8.8$ Hz, 2H), 7.22 (dd, $J=8.1, 1.9$ Hz, 1H), 7.16 (d, $J=1.8$ Hz, 1H), 6.86 (d, $J=8.8$ Hz, 2H), 6.78 (d, $J=8.1$ Hz, 1H), 3.83 (s, 3H), 3.23 (s, 3H), 2.80 – 2.66 (m, 1H), 2.47 (s, 3H), 2.46 – 2.39 (m, 1H), 2.31 (ddd, $J=13.8, 11.0, 5.0$ Hz, 1H), 2.20 (ddd, $J=13.8, 11.2, 4.6$ Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.8, 179.9, 163.4, 141.4, 134.4, 131.8, 130.3, 129.7, 128.0, 123.2, 113.6, 108.5, 55.5, 47.8, 33.2, 32.7, 26.3, 23.8, 17.7. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$) 370.1471, found 370.1472.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-5-[(trifluoromethyl)thio]indolin-2-one
(3d)



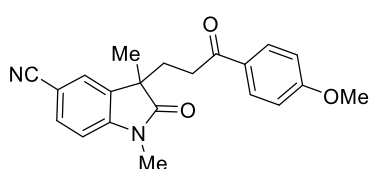
^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J=8.9$ Hz, 2H), 7.59 (dd, $J=8.1, 1.8$ Hz, 1H), 7.46 (d, $J=1.8$ Hz, 1H), 6.98 – 6.77 (m, 3H), 3.83 (s, 3H), 3.25 (s, 3H), 2.72 (ddd, $J=16.0, 10.8, 5.2$ Hz, 1H), 2.51 (ddd, $J=15.9, 10.8, 4.8$ Hz, 1H), 2.42 – 2.27 (m, 1H), 2.21 (ddd, $J=14.0, 11.0, 4.9$ Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.4, 180.0, 163.5, 145.8, 137.5, 134.9, 130.9, 130.3, 129.6, 129.5 (q, $J=306.2$ Hz), 117.3 (q, $J=2.0$ Hz), 113.7, 108.9, 55.5, 47.7, 33.0, 32.6, 26.4, 23.5. ^{19}F NMR (376 MHz, CDCl_3) δ -43.7 (s). HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{NO}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$) 424.1189, found 424.1190.

5-Bromo-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3e)



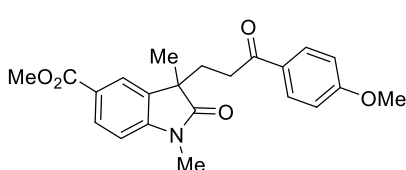
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.9$ Hz, 2H), 7.39 (dd, $J = 8.2, 2.0$ Hz, 1H), 7.31 (d, $J = 1.9$ Hz, 1H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.73 (d, $J = 8.2$ Hz, 1H), 3.84 (s, 3H), 3.23 (s, 3H), 2.74 (ddd, $J = 16.0, 11.2, 5.0$ Hz, 1H), 2.45 (ddd, $J = 15.9, 10.9, 4.7$ Hz, 1H), 2.32 (ddd, $J = 13.9, 10.9, 5.0$ Hz, 1H), 2.19 (ddd, $J = 13.8, 11.2, 4.7$ Hz, 1H), 1.41 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.7, 179.7, 163.6, 142.3, 135.7, 131.0, 130.4, 129.8, 126.2, 115.6, 113.8, 109.6, 55.6, 48.0, 33.2, 32.8, 26.4, 23.8. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{21}\text{BrNO}_3^+$ ($[\text{M} + \text{H}]^+$) 402.0699, found 402.0696.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3f)



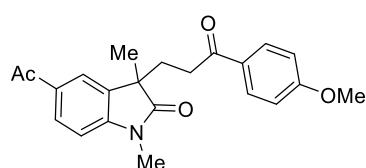
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.9$ Hz, 2H), 7.59 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.43 (d, $J = 1.4$ Hz, 1H), 6.89 (dd, $J = 13.4, 8.5$ Hz, 3H), 3.84 (s, 3H), 3.26 (s, 3H), 2.74 (ddd, $J = 16.0, 10.6, 5.3$ Hz, 1H), 2.49 (ddd, $J = 16.0, 10.3, 5.1$ Hz, 1H), 2.33 (ddd, $J = 14.1, 10.3, 5.3$ Hz, 1H), 2.22 (ddd, $J = 14.1, 10.6, 5.2$ Hz, 1H), 1.43 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.1, 179.9, 163.5, 147.0, 134.6, 133.5, 130.3, 129.5, 126.2, 119.1, 113.7, 108.5, 105.9, 55.5, 47.5, 32.9, 32.5, 26.5, 23.5. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) 349.1547, found 349.1543.

Methyl 3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-2-oxoindoline-5-carboxylate (3g)



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.87 (d, $J = 1.4$ Hz, 1H), 7.80 – 7.69 (m, 2H), 6.89 (d, $J = 8.2$ Hz, 1H), 6.88 – 6.83 (m, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 3.27 (s, 3H), 2.73 (ddd, $J = 15.8, 11.3, 4.8$ Hz, 1H), 2.45 (ddd, $J = 15.6, 11.0, 4.5$ Hz, 1H), 2.34 (ddd, $J = 13.8, 10.9, 4.8$ Hz, 1H), 2.23 (ddd, $J = 13.8, 11.3, 4.5$ Hz, 1H), 1.44 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.5, 180.5, 166.8, 163.4, 147.3, 133.5, 130.9, 130.3, 129.6, 124.7, 124.0, 113.6, 107.7, 55.4, 52.1, 47.5, 33.1, 32.6, 26.4, 23.7. HRMS (ESI): Calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_5^+$ ($[\text{M} + \text{H}]^+$) 382.1649, found 382.1650.

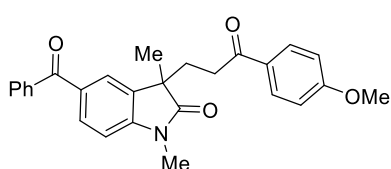
5-Acetyl-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3h)



$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.95 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.83 (d, $J = 1.5$ Hz, 1H), 7.78 – 7.74 (m, 2H), 6.91 (d, $J = 8.2$ Hz, 1H), 6.89 – 6.84 (m, 2H), 3.84 (s, 3H), 3.29 (s, 3H), 2.74 (ddd, $J = 16.1, 11.0, 5.1$ Hz,

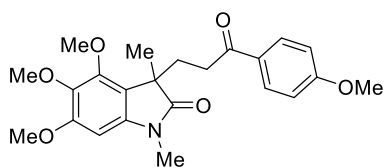
1H), 2.59 (s, 3H), 2.48 (ddd, $J = 16.0, 10.8, 4.9$ Hz, 1H), 2.36 (ddd, $J = 15.8, 10.8, 5.1$ Hz, 1H), 2.26 (ddd, $J = 14.0, 11.1, 4.8$ Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.5, 196.9, 180.6, 163.4, 147.5, 133.7, 132.3, 130.3, 130.1, 129.6, 122.8, 113.6, 107.6, 55.5, 47.5, 33.1, 32.6, 26.5, 26.5, 23.6. HRMS (ESI): Calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$) 366.1700, found 366.1697.

5-Benzoyl-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3i)



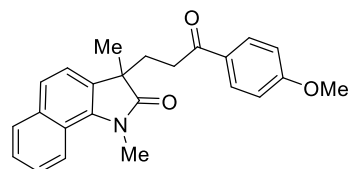
^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.75 (m, 6H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 6.91 (d, $J = 8.1$ Hz, 1H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.84 (s, 3H), 3.30 (s, 3H), 2.77 (ddd, $J = 16.0, 11.0, 5.0$ Hz, 1H), 2.56 (ddd, $J = 16.0, 10.5, 5.0$ Hz, 1H), 2.38 – 2.32 (m, 1H), 2.29 – 2.20 (m, 1H), 1.46 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.5, 195.7, 180.6, 163.5, 147.2, 138.1, 133.7, 132.2, 132.1, 130.3, 129.8, 129.6, 128.3, 124.7, 113.7, 107.4, 55.5, 47.6, 33.1, 32.6, 26.5, 23.6. HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$) 428.1856, found 428.1858.

4,5,6-Trimethoxy-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3j)



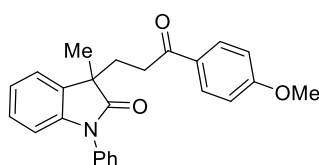
^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.76 (m, 2H), 6.91 – 6.83 (m, 2H), 6.21 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.20 (s, 3H), 2.67 (ddd, $J = 16.8, 11.1, 5.1$ Hz, 1H), 2.52 – 2.39 (m, 2H), 2.29 (ddd, $J = 13.0, 11.7, 5.1$ Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 180.7, 163.3, 154.2, 150.8, 139.3, 137.6, 130.3, 129.8, 115.6, 113.6, 89.5, 61.0, 60.8, 56.4, 55.4, 48.5, 33.7, 31.8, 26.3, 22.6. HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_6^+$ ($[\text{M} + \text{H}]^+$) 414.1911, found 414.1907.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-1,3-dimethyl-1,3-dihydro-2H-benzo[g]indol-2-one (3k)



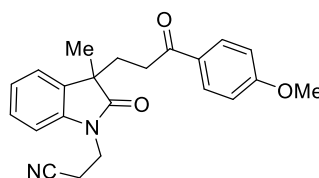
^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.67 (m, 3H), 7.59 – 7.50 (m, 2H), 7.50 – 7.42 (m, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 8.9$ Hz, 2H), 3.82 (s, 3H), 3.57 (s, 3H), 2.87 (ddd, $J = 16.1, 11.6, 4.9$ Hz, 1H), 2.76 (ddd, $J = 13.8, 11.4, 4.9$ Hz, 1H), 2.49 (ddd, $J = 15.7, 11.4, 4.1$ Hz, 1H), 2.40 (ddd, $J = 13.7, 11.6, 4.1$ Hz, 1H), 1.70 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.2, 173.0, 163.3, 137.5, 136.7, 133.4, 130.3, 129.7, 127.3, 126.4, 126.3, 122.8, 122.6, 119.7, 113.5, 108.5, 55.4, 47.1, 37.6, 34.5, 31.4, 29.8. HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 374.1751, found 374.1751.

3-[3-(4-Methoxyphenyl)-3-oxopropyl]-3-methyl-1-phenylindolin-2-one (3l)



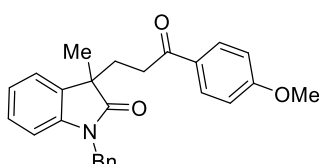
^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.8$ Hz, 2H), 7.55 (dd, $J = 8.5, 7.1$ Hz, 2H), 7.48 – 7.37 (m, 3H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.20 (t, $J = 7.7$ Hz, 1H), 7.11 (t, $J = 7.4$ Hz, 1H), 6.86 (dd, $J = 8.4, 3.1$ Hz, 3H), 3.83 (s, 3H), 2.91 (ddd, $J = 16.1, 11.3, 5.0$ Hz, 1H), 2.57 (ddd, $J = 15.8, 11.0, 4.6$ Hz, 1H), 2.42 (ddd, $J = 16.0, 11.3, 5.0$ Hz, 1H), 2.31 (ddd, $J = 13.8, 11.5, 4.6$ Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.8, 179.7, 163.4, 143.0, 134.5, 133.3, 130.3, 129.7, 129.7, 128.1, 128.0, 126.5, 123.3, 123.1, 113.7, 109.4, 55.5, 47.8, 33.3, 33.3, 24.0. HRMS (ESI): Calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 386.1751, found 386.1745.

3-{3-[3-(4-Methoxyphenyl)-3-oxopropyl]-3-methyl-2-oxoindolin-1-yl}propanenitrile (3m)



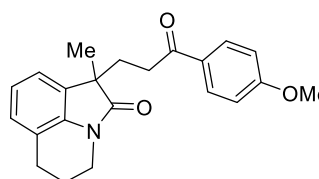
^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.74 (m, 2H), 7.37 – 7.19 (m, 2H), 7.13 (td, $J = 7.5, 1.0$ Hz, 1H), 6.95 (d, $J = 7.8$ Hz, 1H), 6.91 – 6.82 (m, 2H), 4.15 (dt, $J = 14.2, 6.6$ Hz, 1H), 4.00 (dt, $J = 14.1, 6.8$ Hz, 1H), 3.84 (s, 3H), 2.99 – 2.73 (m, 3H), 2.46 (ddd, $J = 16.0, 10.6, 4.7$ Hz, 1H), 2.40 – 2.22 (m, 2H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 180.4, 163.4, 141.2, 133.3, 130.3, 129.7, 128.2, 123.4, 123.3, 117.2, 113.6, 108.0, 55.4, 47.6, 35.9, 33.2, 32.6, 24.1, 16.4. HRMS (ESI): Calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) 363.1703, found 363.1703.

1-Benzyl-3-[3-(4-methoxyphenyl)-3-oxopropyl]-3-methylindolin-2-one (3n)



^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.61 (m, 2H), 7.43 – 7.29 (m, 5H), 7.25 – 7.16 (m, 2H), 7.05 (td, $J = 7.5, 1.0$ Hz, 1H), 6.89 – 6.80 (m, 3H), 5.11 (d, $J = 15.4$ Hz, 1H), 4.84 (d, $J = 15.4$ Hz, 1H), 3.86 (s, 3H), 2.88 – 2.65 (m, 1H), 2.49 – 2.18 (m, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 180.4, 163.4, 142.3, 136.3, 133.4, 130.2, 129.7, 128.9, 128.0, 127.7, 127.6, 122.9, 122.8, 113.6, 109.0, 55.4, 47.7, 43.7, 33.3, 32.7, 24.0. HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 400.1907, found 400.1909.

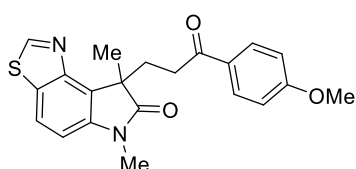
1-[3-(4-Methoxyphenyl)-3-oxopropyl]-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-2(1H)-one (3o)



^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.74 (m, 2H), 7.02 (dd, $J = 9.9, 7.1$ Hz, 2H), 6.98 – 6.92 (m, 1H), 6.90 – 6.83 (m, 2H), 3.83 (s, 3H), 3.74 (t, $J = 5.9$ Hz, 2H), 2.86 – 2.72 (m, 3H), 2.48 (ddd, $J = 15.9, 10.8, 4.9$ Hz, 1H), 2.35 – 2.15 (m, 2H), 2.07 – 1.96 (m, 2H), 1.42 (s, 3H). ^{13}C NMR

(100 MHz, CDCl₃) δ 198.0, 179.1, 163.4, 138.9, 132.0, 130.3, 129.8, 126.8, 122.2, 120.6, 120.1, 113.6, 55.4, 49.1, 38.8, 33.4, 32.7, 24.6, 23.5, 21.4. HRMS (ESI): Calcd for C₂₂H₂₄NO₃⁺ ([M + H]⁺) 350.1751, found 350.1752.

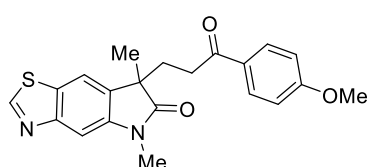
8-[3-(4-Methoxyphenyl)-3-oxopropyl]-6,8-dimethyl-6,8-dihydro-7H-thiazolo[4,5-e]indol-7-one (3p)



¹H NMR (500 MHz, CDCl₃) δ 9.03 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.63 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.88 – 6.72 (m, 2H), 3.82 (s, 3H), 3.33 (s, 3H), 2.84 – 2.64 (m, 2H), 2.55 – 2.45 (m, 2H), 1.67 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.9, 180.3, 163.2, 156.2, 149.0, 142.0, 130.3, 129.8, 129.0, 125.7, 121.4, 113.5, 107.2, 55.4, 49.2, 33.9, 32.2, 26.7, 22.7. HRMS (ESI): Calcd for C₂₁H₂₁N₂O₃S⁺ ([M + H]⁺) 381.1267, found 381.1267.

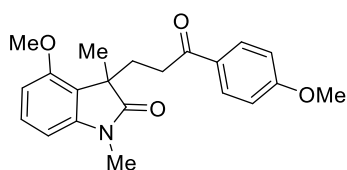
7-[3-(4-Methoxyphenyl)-3-oxopropyl]-5,7-dimethyl-5,7-dihydro-6H-thiazolo[5,4-f]indol-6-one (3p')



¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 7.80 – 7.68 (m, 3H), 7.55 (s, 1H), 6.86 – 6.80 (m, 2H), 3.83 (s, 3H), 3.35 (s, 3H), 2.95 – 2.61 (m, 1H), 2.46 – 2.36 (m, 2H), 2.30 (td, *J* = 10.6, 1.6 Hz, 1H), 1.49 (s, 3H). ¹³C NMR

(125 MHz, CDCl₃) δ 197.7, 179.7, 163.4, 154.3, 153.2, 142.7, 133.2, 130.2, 129.6, 128.1, 116.2, 113.6, 102.5, 55.4, 47.7, 33.1, 33.1, 26.6, 24.4. HRMS (ESI): Calcd for C₂₁H₂₁N₂O₃S⁺ ([M + H]⁺) 381.1267, found 381.1267.

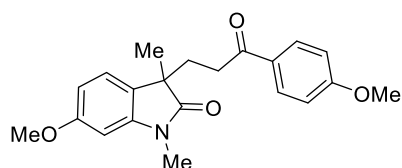
4-Methoxy-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3q)



¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.75 (m, 2H), 7.26 (t, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.24 (s, 3H), 2.73 – 2.61 (m, 1H), 2.57 – 2.40

(m, 2H), 2.31 (ddd, *J* = 12.7, 11.1, 4.7 Hz, 1H), 1.50 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 198.3, 180.6, 163.3, 156.1, 144.4, 130.4, 129.8, 129.2, 118.5, 113.5, 105.9, 101.4, 55.4, 55.4, 48.4, 33.9, 30.7, 26.4, 21.6. HRMS (ESI): Calcd for C₂₁H₂₄NO₄⁺ ([M + H]⁺) 354.1700, found 354.1700.

6-Methoxy-3-[3-(4-methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3q')

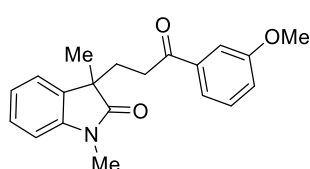


¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.59 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.25 (s, 3H),

2.73 (ddd, *J* = 16.2, 11.3, 5.0 Hz, 1H), 2.44 (ddd, *J* = 15.9, 11.0, 4.7 Hz, 1H), 2.31

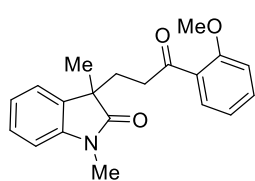
(ddd, $J = 13.7, 10.9, 5.0$ Hz, 1H), 2.21 (ddd, $J = 13.8, 11.3, 4.7$ Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.0, 180.9, 163.4, 160.1, 144.4, 130.3, 129.8, 125.3, 123.3, 113.6, 106.4, 96.2, 55.5, 55.5, 47.3, 33.3, 32.9, 26.3, 24.1. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$) 354.1700, found 354.1700.

3-[3-(3-Methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3r)



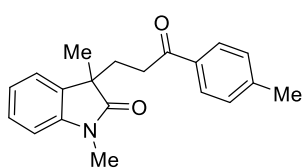
^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.12 – 7.04 (m, 2H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.84 (s, 3H), 3.27 (s, 3H), 2.79 (ddd, $J = 16.3, 11.3, 5.0$ Hz, 1H), 2.49 (ddd, $J = 16.2, 11.0, 4.6$ Hz, 1H), 2.35 (ddd, $J = 13.9, 10.9, 5.0$ Hz, 1H), 2.25 (ddd, $J = 13.8, 11.2, 4.6$ Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 199.2, 180.2, 159.7, 143.2, 138.0, 133.4, 129.5, 128.1, 122.8, 122.7, 120.7, 119.4, 112.3, 108.1, 55.4, 47.6, 33.7, 32.5, 26.3, 23.9. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 324.1594, found 324.1592.

3-[3-(2-Methoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3s)



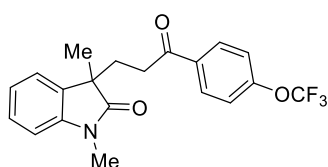
^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.41 (ddd, $J = 8.3, 7.3, 1.8$ Hz, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.09 (td, $J = 7.5, 1.0$ Hz, 1H), 6.95 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (dd, $J = 13.1, 8.1$ Hz, 2H), 3.77 (s, 3H), 3.24 (s, 3H), 2.80 (ddd, $J = 16.6, 11.3, 5.2$ Hz, 1H), 2.51 (ddd, $J = 16.8, 10.9, 4.8$ Hz, 1H), 2.37 – 2.13 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 201.9, 180.4, 158.4, 143.4, 133.8, 133.4, 130.2, 128.3, 128.0, 122.9, 122.7, 120.7, 111.6, 108.0, 55.4, 47.8, 38.9, 32.9, 26.2, 23.5. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 324.1594, found 324.1591.

1,3-Dimethyl-3-(3-oxo-3-(*p*-tolyl)propyl)indolin-2-one (3t)²



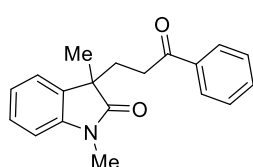
^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.2$ Hz, 2H), 7.27 (td, $J = 7.7, 1.2$ Hz, 1H), 7.24 – 7.15 (m, 3H), 7.07 (td, $J = 7.5, 0.8$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.77 (ddd, $J = 16.2, 11.3, 5.0$ Hz, 1H), 2.46 (ddd, $J = 16.0, 11.0, 4.6$ Hz, 1H), 2.37 (s, 3H), 2.36 – 2.28 (m, 1H), 2.22 (ddd, $J = 13.8, 11.3, 4.6$ Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 180.2, 143.7, 143.2, 134.2, 133.5, 129.2, 128.1, 128.0, 122.8, 122.7, 108.1, 47.7, 33.5, 32.6, 26.2, 23.8, 21.6. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_2^+$ ($[\text{M} + \text{H}]^+$) 308.1645, found 308.1643.

1,3-Dimethyl-3-[3-oxo-3-[4-(trifluoromethoxy)phenyl]propyl]indolin-2-one (3u)



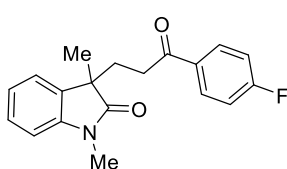
^1H NMR (500 MHz, CDCl_3) δ 7.91 – 7.79 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.17 (m, 3H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.77 (ddd, $J = 16.3, 11.1, 5.0$ Hz, 1H), 2.58 – 2.40 (m, 1H), 2.34 (ddd, $J = 13.9, 10.8, 5.0$ Hz, 1H), 2.23 (ddd, $J = 14.0, 11.1, 4.7$ Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.8, 180.1, 152.5, 143.1, 134.8, 133.3, 130.0, 128.2, 122.9, 122.7, 120.3, 120.2 (q, $J = 257.5$ Hz), 108.2, 47.6, 33.6, 32.4, 26.3, 23.8. ^{19}F NMR (376 MHz, CDCl_3) δ –57.64 (s). HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 378.1312, found 378.1310.

1,3-Dimethyl-3-(3-oxo-3-phenylpropyl)indolin-2-one (3v)²



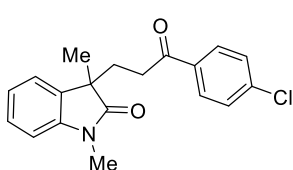
^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.75 (m, 2H), 7.60 – 7.48 (m, 1H), 7.47 – 7.35 (m, 2H), 7.29 (td, $J = 7.7, 1.2$ Hz, 1H), 7.23 (d, $J = 7.3$ Hz, 1H), 7.09 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.27 (s, 3H), 2.82 (ddd, $J = 16.3, 11.2, 5.0$ Hz, 1H), 2.51 (ddd, $J = 16.5, 10.9, 4.7$ Hz, 1H), 2.36 (ddd, $J = 13.8, 10.9, 5.0$ Hz, 1H), 2.25 (ddd, $J = 13.9, 11.2, 4.7$ Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 180.2, 143.2, 136.7, 133.4, 133.0, 128.5, 128.1, 128.0, 122.8, 122.7, 108.1, 47.6, 33.6, 32.5, 26.2, 23.8. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ ($[\text{M} + \text{H}]^+$): 294.1489, found 294.1485.

3-[3-(4-Fluorophenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3w)



^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.73 (m, 2H), 7.28 (td, $J = 7.7, 1.3$ Hz, 1H), 7.25 – 7.16 (m, 1H), 7.15 – 6.99 (m, 3H), 6.86 (d, $J = 7.7$ Hz, 1H), 3.25 (s, 3H), 2.76 (ddd, $J = 16.2, 11.2, 5.0$ Hz, 1H), 2.47 (ddd, $J = 16.3, 10.8, 4.7$ Hz, 1H), 2.33 (ddd, $J = 13.8, 10.8, 5.0$ Hz, 1H), 2.22 (ddd, $J = 13.8, 11.2, 4.7$ Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 180.3, 167.0, 164.5, 143.3, 133.5, 133.2 (d, $J = 3.0$ Hz), 130.8, 129.5 (d, $J = 250.9$ Hz), 122.9 (d, $J = 10.7$ Hz), 115.7 (d, $J = 21.7$ Hz), 108.2, 47.7, 33.6, 32.6, 26.4, 23.9. ^{19}F NMR (376 MHz, CDCl_3) δ –105.39 (tt, $J = 8.6, 5.4$ Hz). HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{19}\text{FNO}_2^+$ ($[\text{M} + \text{H}]^+$) 312.1394, found 312.1391.

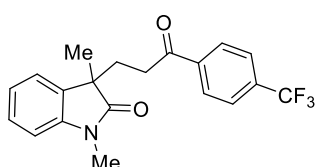
3-[3-(4-Chlorophenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3x)²



^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.71 (m, 2H), 7.40 – 7.35 (m, 2H), 7.30 (td, $J = 7.7, 1.2$ Hz, 1H), 7.22 (d, $J = 7.3$ Hz, 1H), 7.09 (td, $J = 7.5, 0.9$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.27 (s, 3H), 2.77 (ddd, $J = 16.3, 11.1, 5.1$ Hz, 1H), 2.50 (ddd, $J = 16.4, 10.7, 4.8$ Hz, 1H), 2.34 (ddd, $J = 13.9, 10.8, 5.0$ Hz, 1H), 2.23

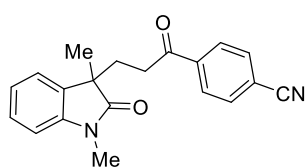
(ddd, $J = 13.9, 11.1, 4.8$ Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 180.1, 143.1, 139.4, 134.9, 133.3, 129.4, 128.8, 128.1, 122.8, 122.7, 108.1, 47.6, 33.6, 32.4, 26.3, 23.8. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{19}\text{ClNO}_2^+$ ($[\text{M} + \text{H}]^+$) 328.1099, found 328.1097.

1,3-Dimethyl-3-{3-oxo-3-[4-(trifluoromethyl)phenyl]propyl}indolin-2-one (3y)



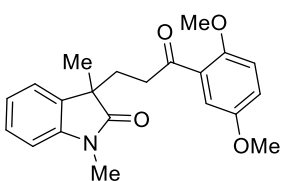
^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.1$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 2H), 7.30 (td, $J = 7.7, 1.2$ Hz, 1H), 7.22 (d, $J = 6.8$ Hz, 1H), 7.10 (td, $J = 7.5, 0.8$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.27 (s, 3H), 2.82 (ddd, $J = 16.3, 10.9, 5.1$ Hz, 1H), 2.66 – 2.46 (m, 1H), 2.42 – 2.31 (m, 1H), 2.30 – 2.20 (m, 1H), 1.45 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.4, 180.1, 143.1, 139.3, 134.3 (q, $J = 32.7$ Hz), 133.2, 128.3, 128.2, 125.6 (q, $J = 3.7$ Hz), 123.6 (q, $J = 272.6$ Hz), 122.9, 122.7, 108.2, 47.5, 33.9, 32.2, 26.3, 23.8. ^{19}F NMR (376 MHz, CDCl_3) δ -63.1 (s). HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_2^+$ ($[\text{M} + \text{H}]^+$) 362.1362, found 362.1359.

4-[3-(1,3-Dimethyl-2-oxoindolin-3-yl)propanoyl]benzonitrile (3z)²



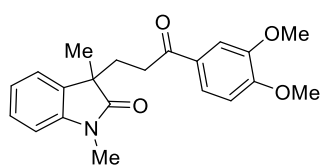
^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.79 (m, 2H), 7.73 – 7.66 (m, 2H), 7.33 – 7.25 (m, 1H), 7.20 (dd, $J = 7.4, 0.7$ Hz, 1H), 7.08 (td, $J = 7.5, 1.0$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.79 (ddd, $J = 16.8, 10.8, 5.1$ Hz, 1H), 2.56 (ddd, $J = 16.8, 10.5, 4.9$ Hz, 1H), 2.34 (ddd, $J = 13.9, 10.5, 5.2$ Hz, 1H), 2.23 (ddd, $J = 13.9, 10.8, 4.9$ Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 180.0, 143.1, 139.6, 133.2, 132.4, 128.4, 128.2, 122.9, 122.7, 117.9, 116.3, 108.2, 47.5, 33.9, 32.1, 26.3, 23.8. HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_2^+$ ($[\text{M} + \text{H}]^+$) 319.1441, found 319.1440.

3-[3-(2,5-Dimethoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3aa)



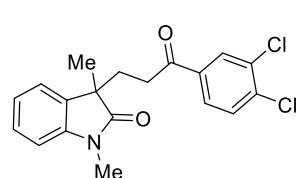
^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.13 – 7.06 (m, 2H), 6.97 (dd, $J = 9.0, 3.2$ Hz, 1H), 6.85 (dd, $J = 14.4, 8.4$ Hz, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.24 (s, 3H), 2.83 – 2.77 (m, 1H), 2.56 – 2.49 (m, 1H), 2.30 – 2.17 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 201.3, 180.3, 153.4, 152.9, 143.3, 133.6, 128.3, 127.9, 122.9, 122.6, 119.9, 113.7, 113.1, 107.8, 55.9, 55.8, 47.7, 38.8, 32.8, 26.1, 23.3. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$) 354.1700, found 354.1697.

3-[3-(3,4-Dimethoxyphenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3ab)



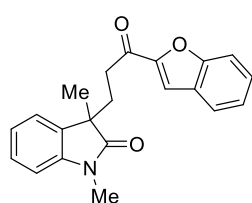
^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.36 (m, 2H), 7.26 (td, $J = 7.7, 1.2$ Hz, 1H), 7.23 – 7.18 (m, 1H), 7.07 (td, $J = 7.5, 0.8$ Hz, 1H), 6.82 (dd, $J = 15.5, 7.9$ Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.24 (s, 3H), 2.75 (ddd, $J = 15.8, 11.3, 4.8$ Hz, 1H), 2.43 (ddd, $J = 15.5, 11.0, 4.6$ Hz, 1H), 2.32 (ddd, $J = 13.8, 11.0, 4.8$ Hz, 1H), 2.20 (ddd, $J = 13.7, 11.3, 4.6$ Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 180.2, 153.2, 148.9, 143.2, 133.4, 129.9, 128.0, 122.8, 122.8, 122.7, 110.1, 109.9, 108.1, 56.0, 56.0, 47.7, 33.2, 33.0, 26.2, 23.8. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$) 354.1700, found 354.1698.

3-[3-(3,4-Dichlorophenyl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3ac)



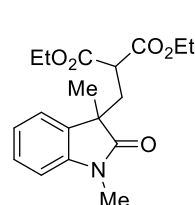
^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 2.0$ Hz, 1H), 7.62 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.48 (d, $J = 8.3$ Hz, 1H), 7.30 (td, $J = 7.7, 1.3$ Hz, 1H), 7.21 (ddd, $J = 7.4, 1.3, 0.6$ Hz, 1H), 7.09 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.27 (s, 3H), 2.74 (ddd, $J = 16.6, 10.7, 5.2$ Hz, 1H), 2.52 (ddd, $J = 16.7, 10.3, 5.0$ Hz, 1H), 2.34 (ddd, $J = 13.9, 10.4, 5.3$ Hz, 1H), 2.24 (ddd, $J = 13.9, 10.7, 5.0$ Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 180.1, 143.1, 137.5, 136.2, 133.2, 133.2, 130.6, 130.0, 128.2, 127.1, 122.9, 122.8, 108.2, 47.5, 33.6, 32.2, 26.3, 23.9. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{NO}_2^+$ ($[\text{M} + \text{H}]^+$) 362.0709, found 362.0708.

3-[3-(Benzofuran-2-yl)-3-oxopropyl]-1,3-dimethylindolin-2-one (3ad)



^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.6$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.48 – 7.41 (m, 1H), 7.36 (d, $J = 0.8$ Hz, 1H), 7.32 – 7.20 (m, 3H), 7.08 (td, $J = 7.5, 1.0$ Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 3.27 (s, 3H), 2.77 (ddd, $J = 16.1, 10.7, 5.4$ Hz, 1H), 2.53 (ddd, $J = 16.1, 10.2, 5.4$ Hz, 1H), 2.45 – 2.22 (m, 2H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.3, 180.1, 155.5, 152.1, 143.2, 133.1, 128.2, 128.1, 127.0, 123.9, 123.3, 122.9, 122.8, 112.9, 112.4, 108.1, 47.7, 34.0, 32.3, 26.3, 23.8. HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_3$ ($[\text{M} + \text{H}]^+$) 334.1438, found 334.1429.

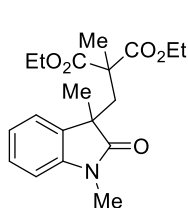
Diethyl 2-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]malonate (3ae)³



^1H NMR (400 MHz, CDCl_3) δ 7.25 (td, $J = 7.7, 1.2$ Hz, 1H), 7.18 – 7.12 (m, 1H), 7.03 (td, $J = 7.5, 0.8$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.82 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.65 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.20 (s, 3H), 3.01 (dd, $J = 8.1, 5.4$ Hz, 1H), 2.63 – 2.40 (m, 2H), 1.37 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.2$

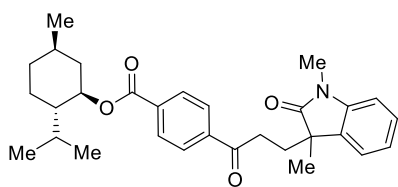
Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 179.3, 168.9, 168.8, 143.4, 132.0, 128.3, 123.5, 122.4, 108.1, 61.6, 61.4, 48.7, 47.1, 35.8, 26.2, 24.5, 14.0, 13.8. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_5$ ($[\text{M} + \text{H}]^+$) 334.1649, found 334.1637.

Diethyl 2-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]-2-methylmalonate (3af)⁴



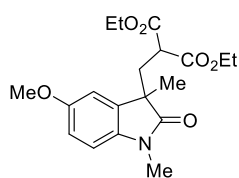
^1H NMR (400 MHz, CDCl_3) δ 7.26 (td, $J = 7.7, 1.2$ Hz, 1H), 7.09 (d, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 7.9$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 4.17 – 4.06 (m, 2H), 3.78 (q, $J = 7.1$ Hz, 2H), 3.21 (s, 3H), 2.75 (d, $J = 2.3$ Hz, 2H), 1.35 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H), 1.09 (t, $J = 7.1$ Hz, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 179.9, 172.0, 171.2, 143.2, 131.8, 128.1, 124.0, 121.9, 108.2, 61.5, 61.0, 52.9, 46.2, 41.1, 27.9, 26.3, 18.8, 13.9, 13.6. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_5$ ($[\text{M} + \text{H}]^+$) 348.1805, found 348.1795.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(3-(1,3-dimethyl-2-oxoindolin-3-yl)propanoyl)benzoate (3ag)



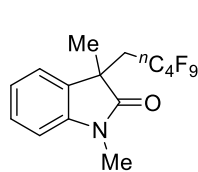
^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 4.93 (td, $J = 10.8, 4.3$ Hz, 1H), 3.26 (s, 3H), 2.91 – 2.69 (m, 1H), 2.65 – 2.44 (m, 1H), 2.41 – 2.30 (m, 1H), 2.30 – 2.19 (m, 1H), 2.18 – 2.08 (m, 1H), 1.99 – 1.85 (m, 1H), 1.79 – 1.69 (m, 2H), 1.65 – 1.50 (m, 2H), 1.43 (s, 3H), 1.21 – 1.04 (m, 2H), 1.00 – 0.86 (m, 7H), 0.78 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.83 (d, $J = 3.7$ Hz), 180.08, 165.19, 143.14, 139.65 (d, $J = 0.8$ Hz), 134.47, 133.25, 129.69, 128.15, 127.85, 122.83, 122.71, 108.17, 75.42, 47.55, 47.20, 40.87, 34.24, 33.97, 32.30 (d, $J = 3.9$ Hz), 31.44, 26.53, 26.26, 23.81 (d, $J = 2.3$ Hz), 23.62, 22.04, 20.75, 16.53 (d, $J = 1.4$ Hz). HRMS (ESI): Calcd for $\text{C}_{30}\text{H}_{38}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$) 476.2795, found 476.2788.

Diethyl 2-((5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl)malonate (3ah)



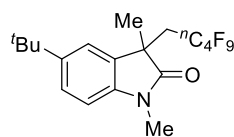
^1H NMR (400 MHz, CDCl_3) δ 6.81 – 6.77 (m, 2H), 6.74 (d, $J = 8.0$ Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.93 – 3.81 (m, 1H), 3.79 (s, 3H), 3.73 (m, 1H), 3.19 (s, 3H), 3.03 (dd, $J = 8.0, 5.5$ Hz, 1H), 2.57 (dd, $J = 14.3, 5.5$ Hz, 1H), 2.48 (dd, $J = 14.3, 8.0$ Hz, 1H), 1.38 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.09 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.00, 168.93, 168.81, 155.98, 136.90, 133.40, 112.65, 110.80, 108.46, 61.63, 61.39, 55.83, 48.68, 47.54, 35.86, 26.30, 24.43, 13.95, 13.78. HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_6^+$ ($[\text{M} + \text{H}]^+$) 364.1755, found 364.1750.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5a)^{5,6}



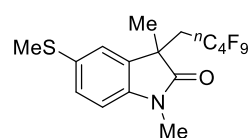
¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.20 (m, 2H), 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.88 (dd, *J* = 35.2, 15.3 Hz, 1H), 2.60 (ddd, *J* = 31.0, 15.4, 8.1 Hz, 1H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.6, 142.8, 131.3, 128.5, 123.6, 123.5, 122.6, 108.5, 44.2 (d, *J* = 2.1 Hz), 36.9 (t, *J* = 20.4 Hz), 26.5, 25.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (tt, *J* = 9.7, 2.7 Hz, 3F), -108.0 – -109.7 (m, 1F), -113.8 – -115.6 (m, 1F), -124.1 – -125.0 (m, 2F), -125.2 – -126.8 (m, 2F). HRMS (ESI): Calcd for C₁₅H₁₃F₉NO⁺ [M + H]⁺: 394.0848; Found: 394.0843.

5-(*tert*-Butyl)-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5b)



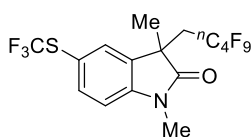
¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.32 (m, 2H), 6.81 (d, *J* = 8.6 Hz, 1H), 3.23 (s, 3H), 2.87 (dd, *J* = 35.6, 14.8 Hz, 1H), 2.61 (ddd, *J* = 30.7, 15.4, 8.4 Hz, 1H), 1.44 (s, 3H), 1.32 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 145.9, 140.4, 130.9, 124.9, 121.0, 120.9, 107.8, 44.5 (d, *J* = 2.3 Hz), 36.7 (t, *J* = 20.2 Hz), 34.6, 31.5, 26.5, 25.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (t, *J* = 10.0 Hz, 3F), -107.8 – -110.7 (m, 1F), -113.7 – -115.8 (m, 1F), -124.6 – -124.7 (m, 2F), -125.7 – -126.2 (m, 2F). HRMS (ESI): Calcd for C₁₉H₂₁F₉NO⁺ ([M + H]⁺) 450.1474, found 450.1475.

1,3-Dimethyl-5-(methylthio)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5c)



¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.18 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.24 (s, 3H), 2.89 (dd, *J* = 35.2, 15.3 Hz, 1H), 2.59 (ddd, *J* = 30.9, 15.4, 8.0 Hz, 1H), 2.48 (s, 3H), 1.43 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.2, 141.2, 132.2, 131.7, 128.8, 124.4, 109.0, 44.3 (d, *J* = 2.1 Hz), 36.9 (t, *J* = 20.3 Hz), 26.6, 25.9, 18.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -79.8 – -83.9 (m, 3F), -106.2 – -110.5 (m, 1F), -111.6 – -116.8 (m, 1F), -123.8 – -125.2 (m, 2F), -125.2 – -126.7 (m, 2F). HRMS (ESI): Calcd for C₁₆H₁₅F₉NOS⁺ ([M + H]⁺) 440.0725, found 440.0721.

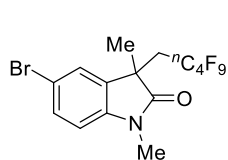
1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-((trifluoromethyl)thio)indolin-2-one (5d)



¹H NMR (500 MHz, CDCl₃) δ 7.64 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.55 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 3.26 (s, 3H), 2.91 (dd, *J* = 34.6, 15.3 Hz, 1H), 2.62 (ddd, *J* = 30.6, 15.5, 8.1 Hz, 1H), 1.46 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.4, 145.5, 137.9, 132.5, 131.9, 129.5 (q, *J* = 308.4 Hz), 117.4 (d, *J* = 2.3 Hz), 109.4, 44.1 (d, *J* = 2.3 Hz), 37.0 (t, *J* = 20.4 Hz), 26.7, 25.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -44.0 (s, 3F),

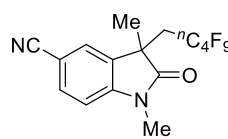
-81.1 (tt, $J = 9.7, 2.7$ Hz, 3F), -106.5 – -110.5 (m, 1F), -112.5 – -116.1 (m, 1F), -123.0 – -125.3 (m, 2F), -125.1 – -129.5 (m, 2F). HRMS (ESI): Calcd for $C_{16}H_{12}F_{12}NOS^+$ ($[M + H]^+$) 494.0442, found 494.0440.

5-Bromo-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5e)



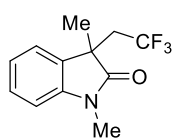
1H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.39 (s, 1H), 6.77 (d, $J = 8.3$ Hz, 1H), 3.22 (s, 3H), 2.88 (dd, $J = 35.2, 15.4$ Hz, 1H), 2.57 (ddd, $J = 29.2, 14.7, 7.2$ Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 141.9, 133.3, 131.4, 126.8, 115.3, 110.0, 44.3 (d, $J = 2.3$ Hz), 36.9 (t, $J = 20.4$ Hz), 26.6, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.10 (tt, $J = 9.7, 2.4$ Hz, 3F), -104.01 – -110.49 (m, 1F), -112.52 – -16.77 (m, 1F), -123.04 – -125.48 (m, 2F), -124.86 – -127.09 (m, 2F). HRMS (ESI): Calcd for $C_{15}H_{12}BrF_9NO^+$ ($[M + H]^+$) 471.9953, found 471.9957.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-carbonitrile (5f)



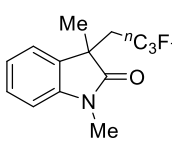
1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.54 (s, 1H), 6.97 (d, $J = 8.2$ Hz, 1H), 3.27 (s, 3H), 2.92 (dd, $J = 34.5, 14.9$ Hz, 1H), 2.63 (ddd, $J = 30.5, 15.5, 8.0$ Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 146.7, 133.9, 132.3, 127.0, 119.0, 109.1, 106.0, 43.9 (d, $J = 2.4$ Hz), 36.9 (t, $J = 20.3$ Hz), 26.7, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (tt, $J = 9.7, 2.6$ Hz, 3F), -107.7 – -109.2 (m, 1F), -113.5 – -115.1 (m, 1F), -124.3 – -125.5 (m, 2F), -125.5 – -126.5 (m, 2F). HRMS (ESI): Calcd for $C_{16}H_{12}F_9N_2O^+$ ($[M + H]^+$) 419.0800, found 419.0803.

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5g)⁷



1H NMR (500 MHz, $CDCl_3$) δ 7.34 (td, $J = 7.7, 1.2$ Hz, 1H), 7.31 – 7.27 (m, 1H), 7.11 (td, $J = 7.6, 0.9$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 3.26 (s, 3H), 2.84 (dq, $J = 15.1, 10.7$ Hz, 1H), 2.67 (dq, $J = 15.1, 10.4$ Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.5, 142.9, 131.0, 128.5, 125.2 (q, $J = 278.1$ Hz), 123.6, 122.7, 108.5, 44.4 (d, $J = 2.1$ Hz), 40.6 (q, $J = 28.3$ Hz), 26.4, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.95 (t, $J = 10.6$ Hz). HRMS (ESI): Calcd for $C_{12}H_{13}F_3NO^+$ ($[M + H]^+$) 244.0944, found 244.0939.

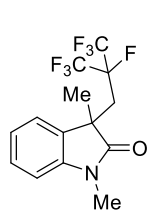
3-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3-dimethylindolin-2-one (5h)⁶



1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 7.10 (td, $J = 7.6, 0.9$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.84 (d, $J = 15.4$ Hz, 1H), 2.71 – 2.52 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 142.8, 131.3, 128.5, 123.6, 123.6, 122.6, 108.5, 44.2 (d, $J = 2.1$ Hz), 36.7 (t, $J = 20.2$ Hz), 26.5, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ

-80.30 (t, $J = 9.8$ Hz, 3F), -107.56 – -110.28 (m, 1F), -112.72 – -117.26 (m, 1F), -126.88 – -128.90 (m, 2F). HRMS (ESI): Calcd for $C_{14}H_{13}F_7NO^+$ ($[M + H]^+$) 344.0880, found 344.0875.

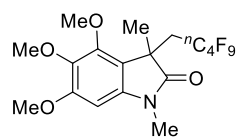
1,3-Dimethyl-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)indolin-2-one (5i)



1H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, $J = 7.7, 1.2$ Hz, 1H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.07 (td, $J = 7.6, 1.0$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.23 (s, 3H), 2.86 (t, $J = 16.7$ Hz, 1H), 2.67 (t, $J = 15.3$ Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 142.8, 131.1, 128.4, 123.6, 122.4, 108.3, 45.4 (d, $J = 3.8$ Hz), 34.0, 33.9 (d, $J = 18.6$ Hz), 27.7, 26.4.

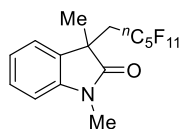
^{19}F NMR (376 MHz, $CDCl_3$) δ -77.30 (d, $J = 7.1$ Hz, 6F), -186.34 (ddd, $J = 24.2, 14.5, 7.2$ Hz, 1F). HRMS (ESI): Calcd for $C_{14}H_{13}F_7NO^+$ ($[M + H]^+$) 344.0880, found 344.0876.

4,5,6-Trimethoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5j)



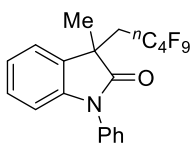
1H NMR (400 MHz, $CDCl_3$) δ 6.23 (s, 1H), 4.00 (s, 3H), 3.90 (s, 3H), 3.78 (s, 3H), 3.19 (s, 3H), 2.94 – 2.72 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 154.8, 150.8, 138.8, 137.2, 113.5, 89.4, 61.0, 60.5, 56.3, 43.9 (d, $J = 2.4$ Hz), 35.9 (t, $J = 19.8$ Hz), 26.5, 24.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 – -82.2 (m, 3F), -110.8 – -113.4 (m, 1F), -114.8 – -117.1 (m, 1F), -124.1 – -125.1 (m, 2F), -125.9 – -126.1 (m, 2F). HRMS (ESI): Calcd for $C_{18}H_{19}F_9NO_4^+$ ($[M + H]^+$) 484.1165, found 484.1167.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)indolin-2-one (5k)



1H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, $J = 8.1$ Hz, 1H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.89 (dd, $J = 35.2, 15.3$ Hz, 1H), 2.61 (ddd, $J = 31.0, 15.4, 7.9$ Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.7, 108.5, 44.2 (d, $J = 2.2$ Hz), 37.0 (t, $J = 20.3$ Hz), 26.5, 25.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.88 (tt, $J = 9.9, 2.2$ Hz, 3F), -107.88 – -109.33 (m, 1F), -113.63 – -115.62 (m, 1F), -122.13 – -122.98 (m, 2F), -123.92 (t, $J = 14.9$ Hz, 2F), -125.57 – -126.82 (m, 2F). HRMS (ESI): Calcd for $C_{16}H_{13}F_{11}NO^+$ ($[M + H]^+$) 444.0816, found 444.0810.

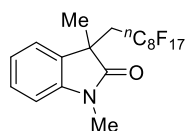
3-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-phenylindolin-2-one (5l)



1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.51 – 7.42 (m, 3H), 7.37 (d, $J = 7.4$ Hz, 1H), 7.31 – 7.24 (m, 1H), 7.16 (td, $J = 7.5, 0.8$ Hz, 1H), 6.93 – 6.85 (m, 1H), 3.05 (dd, $J = 35.1, 15.2$ Hz, 1H), 2.71 (ddd, $J = 30.8, 15.4, 8.1$ Hz, 1H), 1.59 (s, 3H). ^{13}C NMR (100

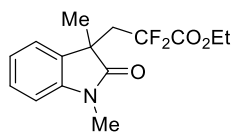
MHz, CDCl₃) δ 178.1, 142.9, 134.3, 131.0, 129.7, 128.4, 128.3, 126.6, 123.80 (d, J = 2.1 Hz), 123.1, 109.8, 44.3 (d, J = 1.8 Hz), 37.4 (t, J = 20.3 Hz), 26.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.09 (tt, J = 9.8, 3.1 Hz, 3F), -105.96 – -110.63 (m, 1F), -112.72 – -118.02 (m, 1F), -124.04 – -125.13 (m, 2F), -125.38 – -126.46 (m, 2F). HRMS (ESI): Calcd for C₂₀H₁₅F₉NO⁺ ([M + H]⁺) 456.1004, found 456.1000.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1,3-dimethylindolin-2-one (5m)⁶



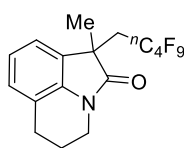
¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.24 (m, 2H), 7.18 – 7.04 (m, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 2.91 (dd, J = 35.0, 15.2 Hz, 1H), 2.63 (ddd, J = 31.0, 15.4, 8.1 Hz, 1H), 1.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.6, 142.8, 131.3, 128.5, 123.6, 122.6, 108.5, 44.2, 37.0 (t, J = 20.3 Hz), 26.4, 25.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.88 (dt, J = 20.0, 9.8 Hz, 3F), -107.98 – -109.70 (m, 1F), -113.47 – -115.26 (m, 1F), -121.58 (s, 2F), -122.01 (s, 4F), -122.80 (s, 2F), -123.69 (s, 2F), -126.21 (s, 2F). HRMS (ESI): Calcd for C₁₉H₁₃F₁₇NO⁺ ([M + H]⁺) 594.0720, found 594.0715.

Ethyl 3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate (5n)⁸



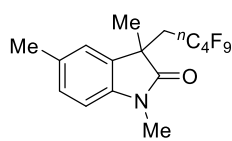
¹H NMR (500 MHz, CDCl₃) δ 7.28 (td, J = 7.7, 1.2 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.08 – 7.00 (m, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.02 (dq, J = 10.7, 7.2 Hz, 1H), 3.92 (dq, J = 10.7, 7.2 Hz, 1H), 3.22 (s, 3H), 2.93 – 2.65 (m, 2H), 1.39 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.8, 163.5 (t, J = 32.2 Hz), 143.4, 130.8, 128.5, 123.8, 122.2, 114.6 (dd, J = 255.4, 248.8 Hz), 108.4, 62.9, 44.4 (d, J = 6.2 Hz), 41.2 (dd, J = 24.5, 22.3 Hz), 26.4, 25.5, 13.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -98.7 (dt, J = 267.4, 12.7 Hz, 1F), -106.2 (ddd, J = 267.3, 21.5, 15.3 Hz, 1F). HRMS (ESI): Calcd for C₁₅H₁₈F₂NO₃⁺ ([M + H]⁺) 298.1249, found 298.1244.

1-Methyl-1-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (5o)



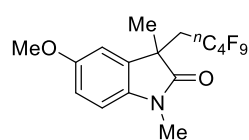
¹H NMR (400 MHz, CDCl₃) δ 7.12 (d, J = 7.4 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 4.03 – 3.62 (m, 2H), 3.00 – 2.71 (m, 3H), 2.59 (ddd, J = 31.2, 15.4, 8.2 Hz, 1H), 2.05 – 2.02 (m, 2H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 138.6, 129.9, 127.3, 122.1, 121.5 (t, J = 2.4 Hz), 120.6, 45.5 (d, J = 2.1 Hz), 39.1, 36.8 (t, J = 20.7 Hz), 25.4, 24.6, 21.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.08 (tt, J = 10.2, 3.1 Hz, 3F), -108.19 – -109.42 (m, 1F), -113.72 – -115.53 (m, 1F), -124.24 – -124.89 (m, 2F), -125.63 – -126.13 (m, 2F). HRMS (ESI): Calcd for C₁₇H₁₅F₉NO⁺ ([M + H]⁺) 420.1004; Found: 420.0997.

1,3,5-Trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5p)⁹



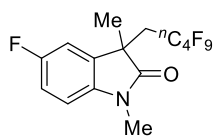
¹H NMR (500 MHz, CDCl₃) δ 7.15 – 7.05 (m, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 3.23 (s, 3H), 2.86 (dd, *J* = 35.3, 15.3 Hz, 1H), 2.57 (ddd, *J* = 31.1, 15.4, 7.9 Hz, 1H), 2.36 (s, 3H), 1.42 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.5, 140.4, 132.2, 131.3, 128.8, 124.4, 108.2, 44.3 (d, *J* = 2.1 Hz), 36.9 (t, *J* = 19.9 Hz), 26.5, 26.0, 21.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (tt, *J* = 9.5, 2.7 Hz, 3F), -108.3 – -109.4 (m, 1F), -112.7 – -119.0 (m, 1F), -124.3 – -124.8 (m, 2F), -125.5 – -126.3 (m, 2F). HRMS (ESI): Calcd for C₁₆H₁₅F₉NO⁺ ([M + H]⁺) 408.1004, found 408.1006.

5-Methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5q)⁹



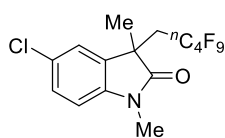
¹H NMR (500 MHz, CDCl₃) δ 6.89 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.22 (s, 3H), 2.87 (dd, *J* = 35.3, 15.3 Hz, 1H), 2.57 (ddd, *J* = 31.1, 15.4, 7.8 Hz, 1H), 1.42 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.2, 156.0, 136.3, 132.7, 112.5, 111.3, 108.8, 55.8, 44.6, 36.9 (t, *J* = 20.4 Hz), 26.6, 25.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (tt, *J* = 10.2, 2.8 Hz, 3F), -108.3 – -108.5 (m, 1F), -114.0 – -115.4 (m, 1F), -124.5 – -124.7 (m, 2F), -125.7 – -126.1 (m, 2F). HRMS (ESI): Calcd for C₁₆H₁₅F₉NO₂⁺ ([M + H]⁺) 424.0954, found 424.0956.

5-Fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5r)⁹



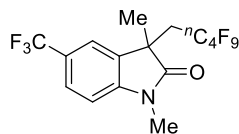
¹H NMR (400 MHz, CDCl₃) δ 7.14 – 6.95 (m, 2H), 6.83 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.25 (s, 3H), 2.90 (dd, *J* = 34.6, 16.0 Hz, 1H), 2.60 (ddd, *J* = 30.9, 15.5, 8.0 Hz, 1H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.2, 159.3 (d, *J* = 240.7 Hz), 138.7 (d, *J* = 2.1 Hz), 132.9 (d, *J* = 8.0 Hz), 114.8 (d, *J* = 23.5 Hz), 111.8 (d, *J* = 25.2 Hz), 109.0 (d, *J* = 8.2 Hz), 44.6, 36.9 (t, *J* = 20.4 Hz), 26.6, 25.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -79.90 – -82.22 (m, 3F), -105.96 – -109.97 (m, 1F), -114.65 (ddt, *J* = 271.3, 28.4, 12.8 Hz, 1F), -120.49 (tt, *J* = 8.2, 3.4 Hz, 1F), -123.74 – -125.48 (m, 2F), -125.16 – -127.17 (m, 2F). HRMS (ESI): Calcd for C₁₅H₁₂F₁₀NO⁺ ([M + H]⁺) 412.0754, found 412.0750.

5-Chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (5s)⁹



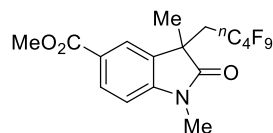
¹H NMR (400 MHz, CDCl₃) δ 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.26 (s, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.24 (s, 3H), 2.89 (dd, *J* = 36.1, 15.4 Hz, 1H), 2.58 (ddd, *J* = 30.8, 15.5, 8.0 Hz, 1H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 141.4, 132.9, 128.6, 128.1, 124.1, 109.5, 44.4 (d, *J* = 2.2 Hz), 36.9 (t, *J* = 20.3 Hz), 26.6, 25.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (tt, *J* = 9.7, 2.6 Hz, 3F), -105.11 – -111.18 (m, 1F), -112.71 – -118.99 (m, 1F), -122.82 – -125.27 (m, 2F), -125.27 – -128.19 (m, 2F). HRMS (ESI): Calcd for C₁₅H₁₂ClF₉NO⁺ ([M + H]⁺) 428.0458, found 428.0461.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (5t)⁹



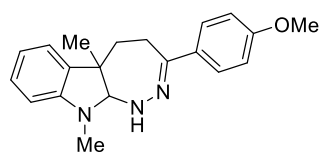
¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 9.0 Hz, 1H), 7.51 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.28 (s, 3H), 2.93 (dd, *J* = 35.0, 15.4 Hz, 1H), 2.63 (ddd, *J* = 30.5, 15.5, 8.0 Hz, 1H), 1.46 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.5, 145.8, 131.8, 126.4 (q, *J* = 4.0 Hz), 125.0 (q, *J* = 32.7 Hz), 124.3 (q, *J* = 271.4 Hz), 120.8 – 120.6 (m), 108.4, 44.1 (d, *J* = 2.3 Hz), 37.0 (t, *J* = 20.3 Hz), 26.7, 25.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.5 (s, 3F), -81.1 (tt, *J* = 9.7, 2.6 Hz, 3F), -107.9 – -109.6 (m, 1F), -113.8 – -116.0 (m, 1F), -124.2 – -124.7 (m, 2F), -125.6 – -126.3 (m, 2F). HRMS (ESI): Calcd for C₁₆H₁₂F₁₂NO⁺ ([M + H]⁺) 462.0722, found 462.07118.

Methyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindoline-5-carboxylate (5u)¹⁰



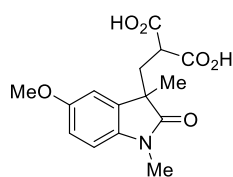
¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.98 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.94 (s, 3H), 3.30 (s, 3H), 2.93 (d, *J* = 35.0 Hz, 1H), 2.67 (ddd, *J* = 30.6, 15.4, 8.0 Hz, 1H), 1.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 166.7, 146.9, 131.2, 124.8, 124.8, 124.7, 108.1, 52.1, 43.9, 37.00 (t, *J* = 20.0 Hz), 26.7, 25.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (tt, *J* = 9.7, 2.5 Hz, 3F), -107.4 – -109.8 (m, 1F), -112.5 – -116.8 (m, 1F), -123.0 – -125.5 (m, 2F), -124.7 – -128.4 (m, 2F). HRMS (ESI): Calcd for C₁₇H₁₅F₉NO₃⁺ ([M + H]⁺) 452.0903, found 452.0900.

3-(4-Methoxyphenyl)-5a,10-dimethyl-1,4,5,5a,10,10a-hexahydro-[1,2]diazepino[3,4-*b*]indole (6)



¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.47 (m, 2H), 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.13 (d, *J* = 4.5 Hz, 1H), 4.28 (d, *J* = 4.5 Hz, 1H), 3.83 (s, 3H), 2.71 (s, 3H), 2.68 – 2.40 (m, 3H), 1.77 – 1.58 (m, 1H), 1.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.53, 151.28, 150.04, 134.80, 133.10, 128.29, 127.08, 121.79, 117.87, 113.38, 106.79, 92.74, 55.33, 45.97, 35.96, 31.65, 29.02, 26.07. HRMS (ESI): Calcd for C₂₀H₂₄N₃O⁺ ([M + H]⁺) 322.1914, found 322.1907.

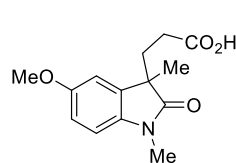
2-((5-Methoxy-1,3-dimethyl-2-oxindolin-3-yl)methyl)malonic acid (7)



¹H NMR (400 MHz, MeOH-*d*₄) δ 6.96 – 6.90 (m, 2H), 6.90 – 6.85 (m, 1H), 3.79 (s, 3H), 3.37 (s, 1H), 3.19 (s, 3H), 2.49 (s, 2H), 1.37 (s, 3H). ¹³C NMR (101 MHz, MeOH-*d*₄) δ 180.04, 170.95, 156.53, 136.45, 133.26, 112.86, 110.30, 108.90, 54.84, 48.50, 47.70, 35.87, 25.21, 23.14. HRMS (ESI): Calcd for C₁₅H₁₈NO₆⁺

$([M + H]^+)$ 308.1129, found 308.1126.

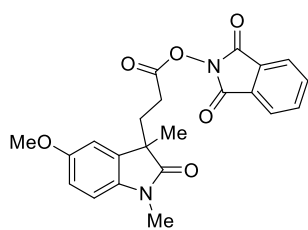
3-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (8)³



¹H NMR (500 MHz, DCM-*d*₂) δ 6.84 (m, 2H), 6.81 (d, *J* = 9.1 Hz, 1H), 3.81 (s, 3H), 3.19 (s, 3H), 2.27 – 2.14 (m, 1H), 2.14 – 2.03 (m, 2H), 2.01 – 1.88 (m, 1H), 1.38 (s, 3H). ¹³C NMR (126 MHz, DCM-*d*₂) δ 179.30, 176.78, 156.21, 136.82, 134.21, 112.19, 110.10, 108.44, 55.69, 47.82, 32.72, 29.04, 26.05, 23.38. HRMS (ESI): Calcd for C₁₄H₁₈NO₄⁺ ($[M + H]^+$) 264.1230, found 264.1232.

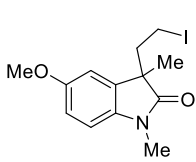
1,3-Dioxoisindolin-2-yl

3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanoate (9)



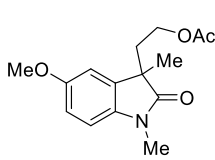
¹H NMR (400 MHz, DCM-*d*₂) δ 7.92 – 7.87 (m, 2H), 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.88 (dd, *J* = 7.0, 2.4 Hz, 2H), 6.85 (d, *J* = 9.3 Hz, 1H), 3.84 (s, 3H), 3.23 (s, 3H), 2.53 – 2.41 (m, 1H), 2.40 – 2.27 (m, 2H), 2.25 – 2.12 (m, 1H), 1.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 179.07, 168.88, 161.78, 156.41, 136.60, 134.76, 133.85, 128.88, 123.99, 112.50, 110.28, 108.65, 55.83, 47.80, 32.53, 26.48, 26.37, 23.43. HRMS (ESI): Calcd for C₂₂H₂₁N₂O₆⁺ ($[M + H]^+$) 409.1394, found 409.1400.

3-(2-Iodoethyl)-5-methoxy-1,3-dimethylindolin-2-one (10)



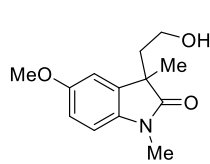
¹H NMR (500 MHz, DCM-*d*₂) δ 6.83 (d, *J* = 7.6 Hz, 2H), 6.80 – 6.76 (m, 1H), 3.80 (s, 3H), 3.16 (s, 3H), 2.84 (ddd, *J* = 12.6, 9.3, 5.2 Hz, 1H), 2.74 (ddd, *J* = 12.3, 9.3, 4.5 Hz, 1H), 2.50 (td, *J* = 12.9, 5.2 Hz, 1H), 2.33 (td, *J* = 13.0, 4.5 Hz, 1H), 1.34 (s, 3H). ¹³C NMR (126 MHz, DCM-*d*₂) δ 178.49, 156.21, 136.92, 133.61, 112.13, 110.13, 108.46, 55.72, 50.44, 42.76, 26.08, 23.20, -1.69. HRMS (ESI): Calcd for C₁₃H₁₇INO₂⁺ ($[M + H]^+$) 346.0298, found 346.0301.

2-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)ethyl acetate (11)



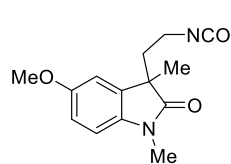
¹H NMR (500 MHz, DCM-*d*₂) δ 6.84 (dd, *J* = 6.4, 2.5 Hz, 2H), 6.80 (d, *J* = 9.1 Hz, 1H), 3.89 (ddd, *J* = 11.8, 7.0, 5.3 Hz, 1H), 3.82 (s, 3H), 3.68 (dt, *J* = 11.2, 7.2 Hz, 1H), 3.19 (s, 3H), 2.31 (dt, *J* = 14.4, 7.4 Hz, 1H), 2.08 (dt, *J* = 12.2, 6.8 Hz, 1H), 1.85 (s, 3H), 1.37 (s, 3H). ¹³C NMR (126 MHz, DCM-*d*₂) δ 179.32, 170.34, 156.06, 136.87, 134.29, 111.90, 110.29, 108.31, 60.73, 55.71, 46.73, 36.27, 26.05, 24.41, 20.40. HRMS (ESI): Calcd for C₁₅H₁₉NO₄Na⁺ ($[M + Na]^+$) 300.1206, found 300.1206.

3-(2-Hydroxyethyl)-5-methoxy-1,3-dimethylindolin-2-one (12)



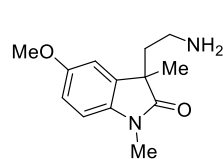
^1H NMR (500 MHz, $\text{DCM-}d_2$) δ 6.83 (m, 2H), 6.81 (d, $J = 9.4$ Hz, 1H), 3.82 (s, 3H), 3.65 (s, 1H), 3.45 (dq, $J = 12.5, 6.4$ Hz, 1H), 3.20 (s, 3H), 2.41 (s, 1H), 2.11 (m, 1H), 1.96 (m, 1H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $\text{DCM-}d_2$) δ 180.94, 156.22, 136.49, 135.65, 111.83, 110.07, 108.46, 59.14, 55.70, 47.28, 40.04, 26.18, 23.27. HRMS (ESI): Calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_3^+$ ($[\text{M} + \text{H}]^+$) 236.1281, found 236.1282.

3-(2-Isocyanatoethyl)-5-methoxy-1,3-dimethylindolin-2-one (13)



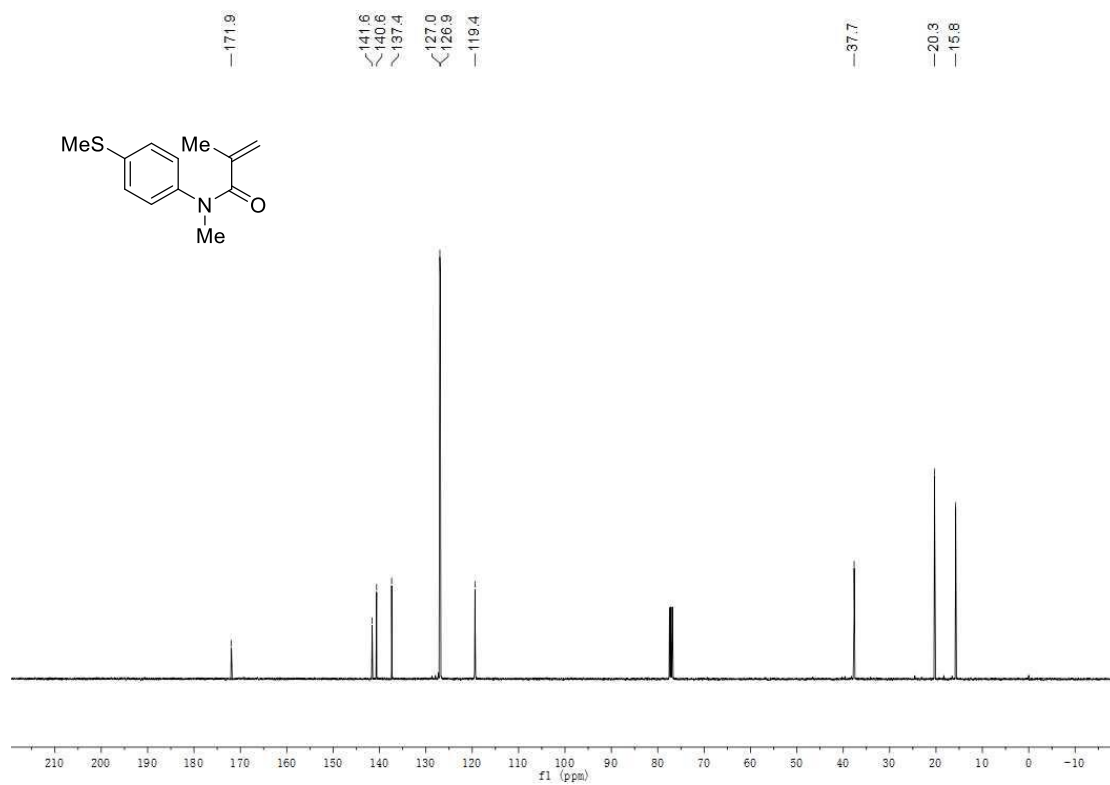
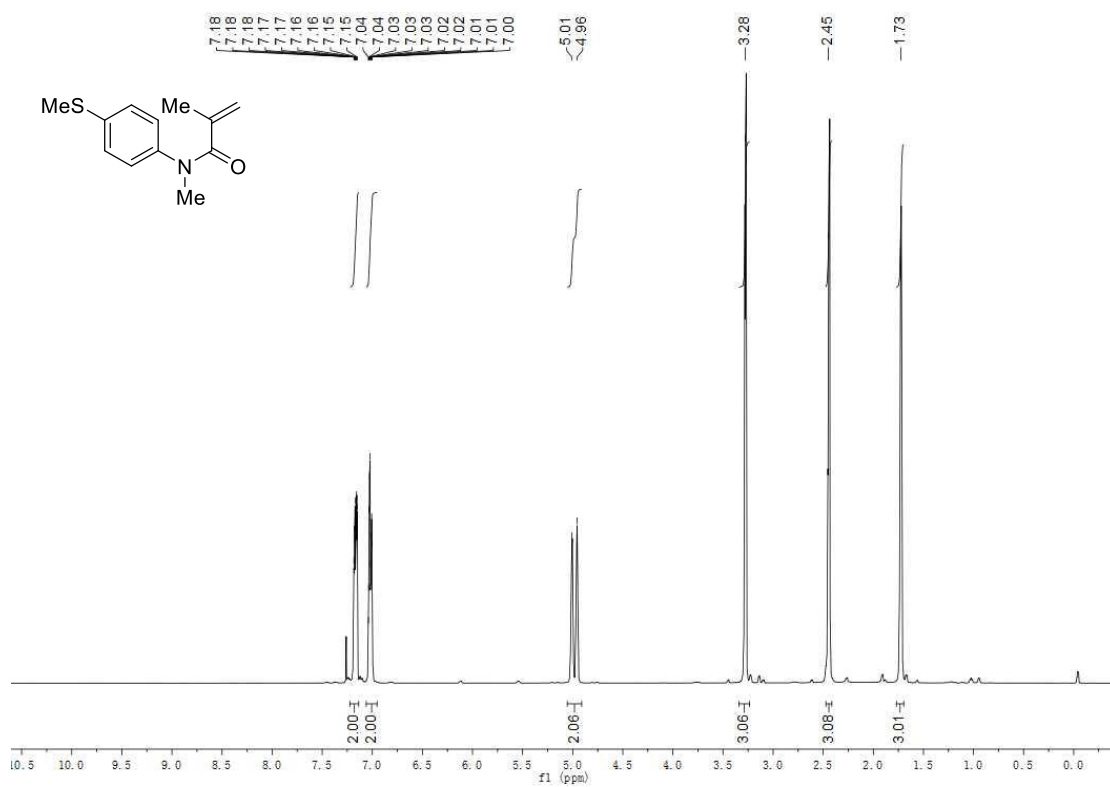
^1H NMR (500 MHz, CDCl_3) δ 6.81 (dd, $J = 10.4, 2.2$ Hz, 2H), 6.77 (d, $J = 8.2$ Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 3.05 (q, $J = 6.6, 5.7$ Hz, 2H), 2.13 (dt, $J = 13.7, 6.8$ Hz, 1H), 1.97 (dt, $J = 14.0, 7.0$ Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.05, 156.43, 156.08, 136.32, 134.57, 112.25, 110.21, 108.74, 55.84, 47.45, 37.45, 36.93, 26.39, 23.95. HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) 261.1234, found 261.1232.

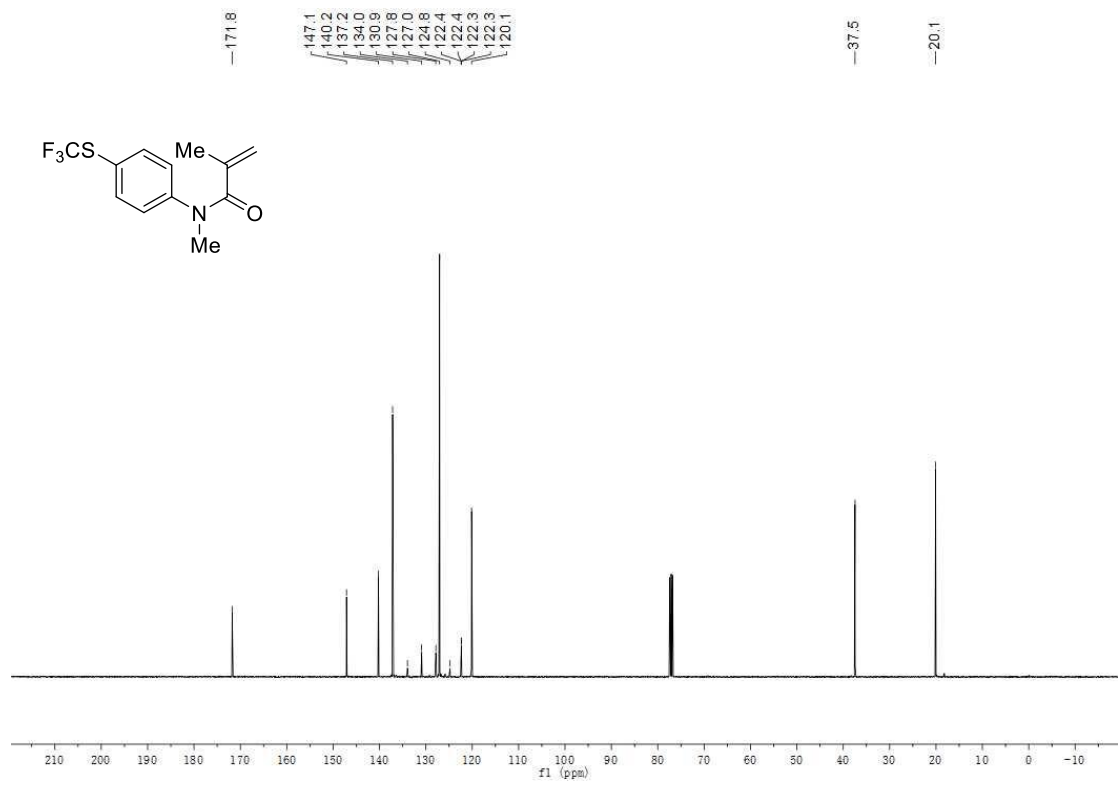
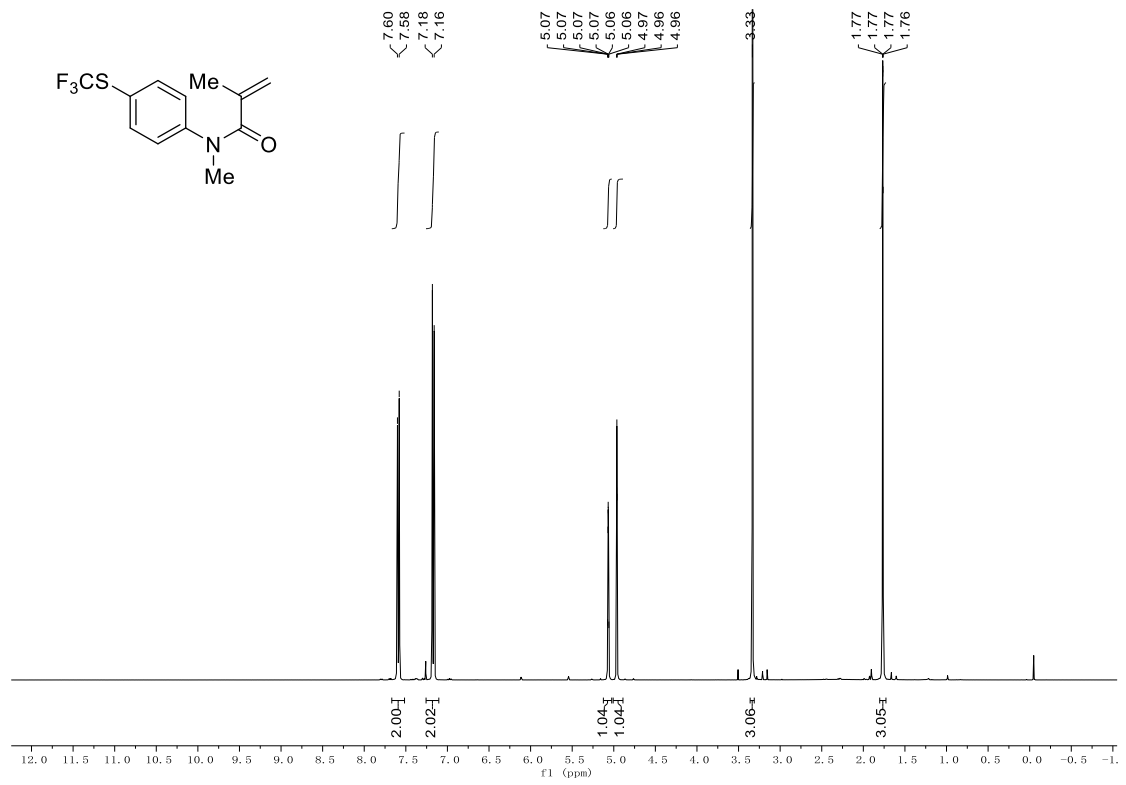
3-(2-Aminoethyl)-5-methoxy-1,3-dimethylindolin-2-one (14)

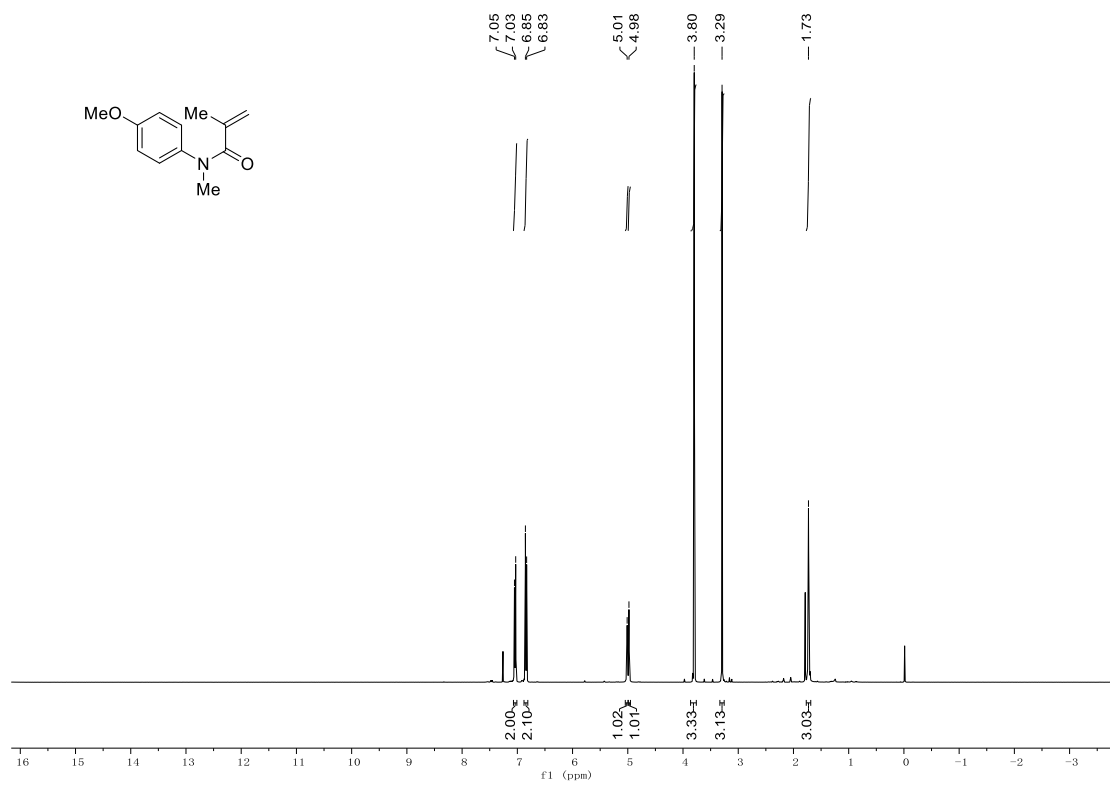
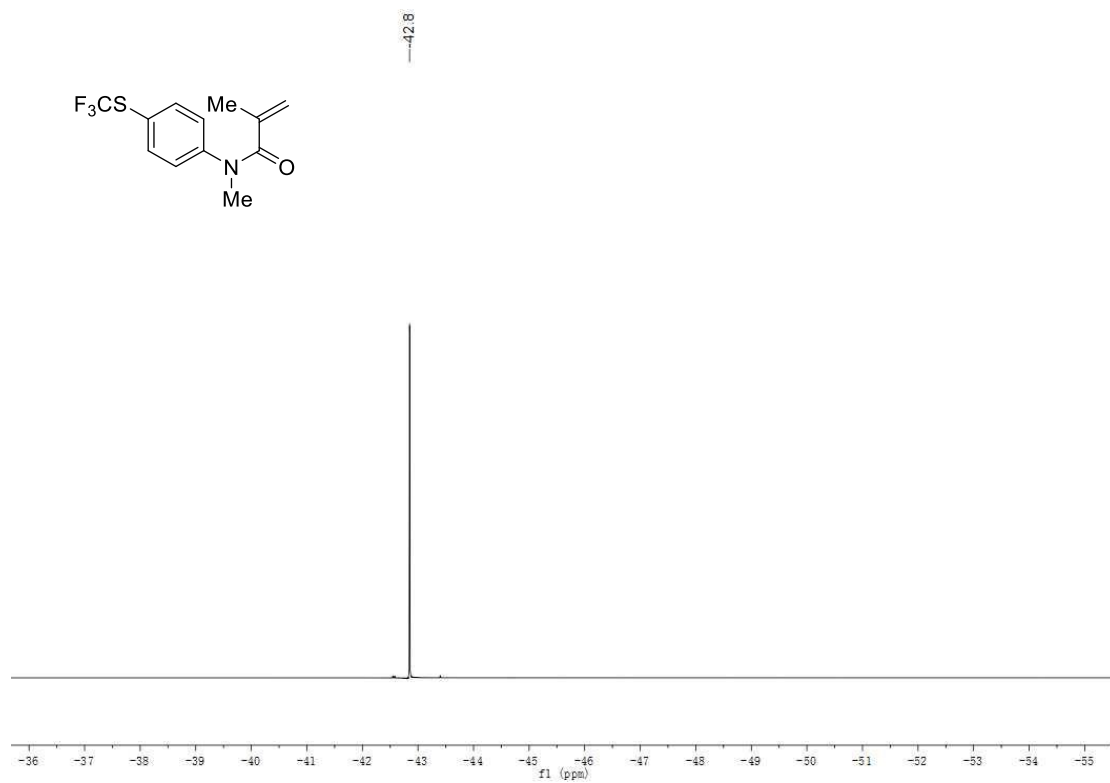


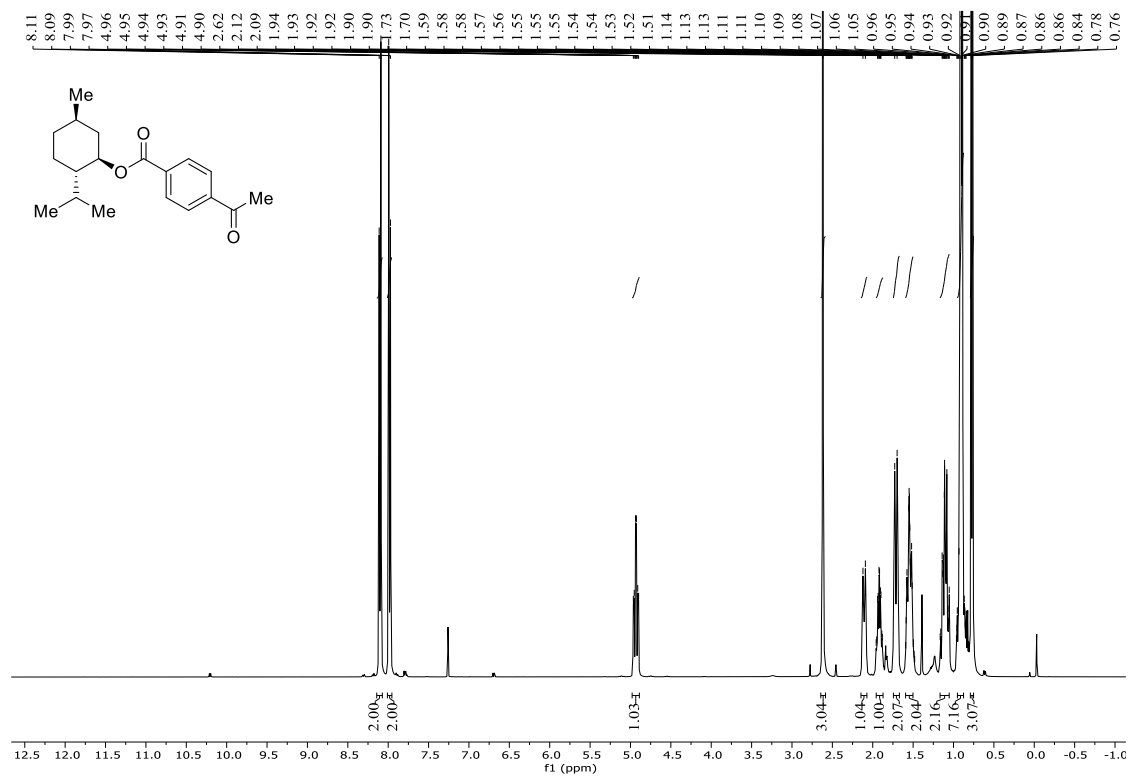
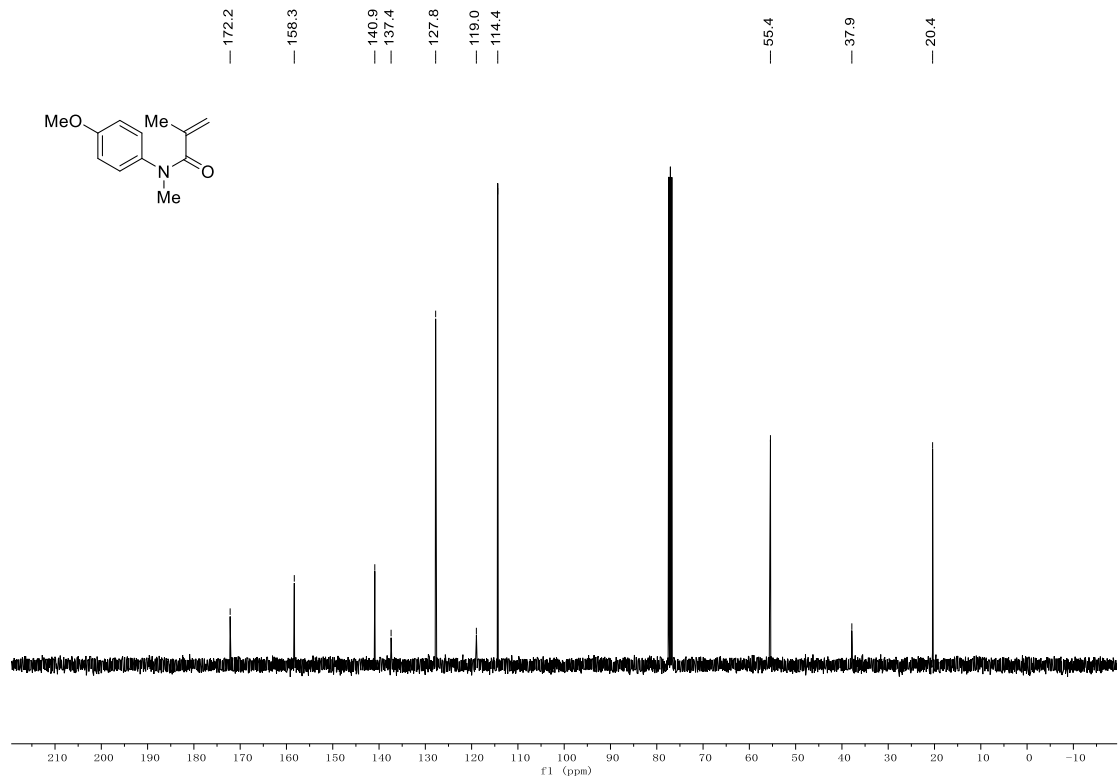
^1H NMR (400 MHz, CDCl_3) δ 6.83 – 6.76 (m, 2H), 6.74 (d, $J = 8.2$ Hz, 1H), 3.80 (s, 3H), 3.18 (s, 3H), 2.39 (m, 1H), 2.30 (m, 1H), 2.07 (ddd, $J = 13.2, 10.0, 5.8$ Hz, 1H), 1.90 (ddd, $J = 13.2, 10.1, 5.1$ Hz, 1H), 1.36 (s, 2H), 1.35 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.19, 156.08, 136.64, 135.11, 111.75, 110.21, 108.28, 55.78, 47.68, 42.14, 38.10, 26.25, 24.27. MS on Bruker Q-Tof (ESI): Calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_2^+$ ($[\text{M} + \text{H}]^+$) 235.1441, found 235.1441.

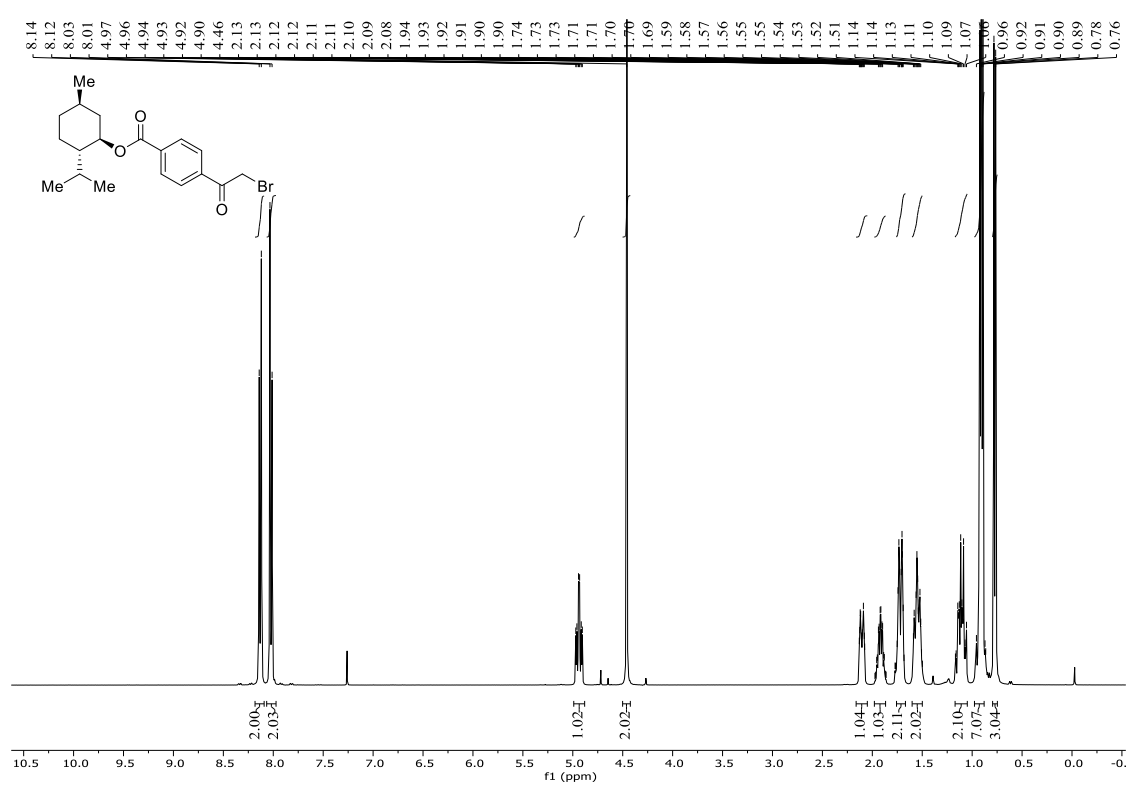
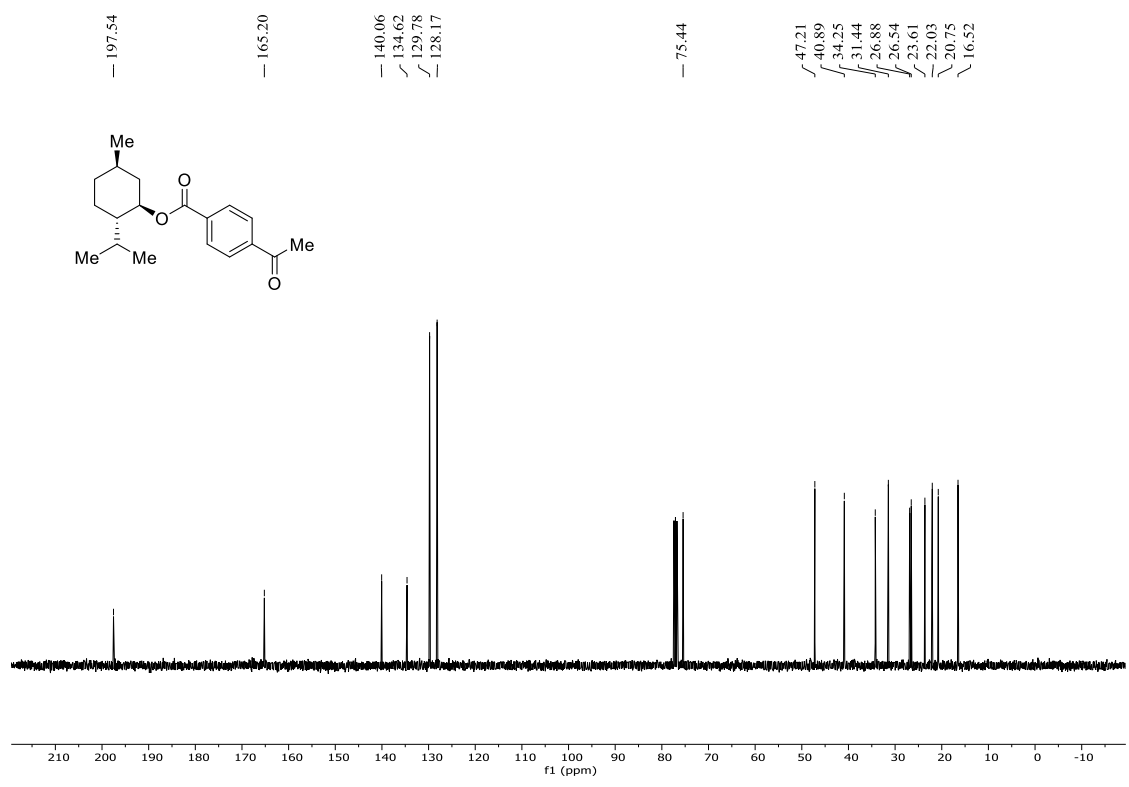
10. Copies of NMR Spectra

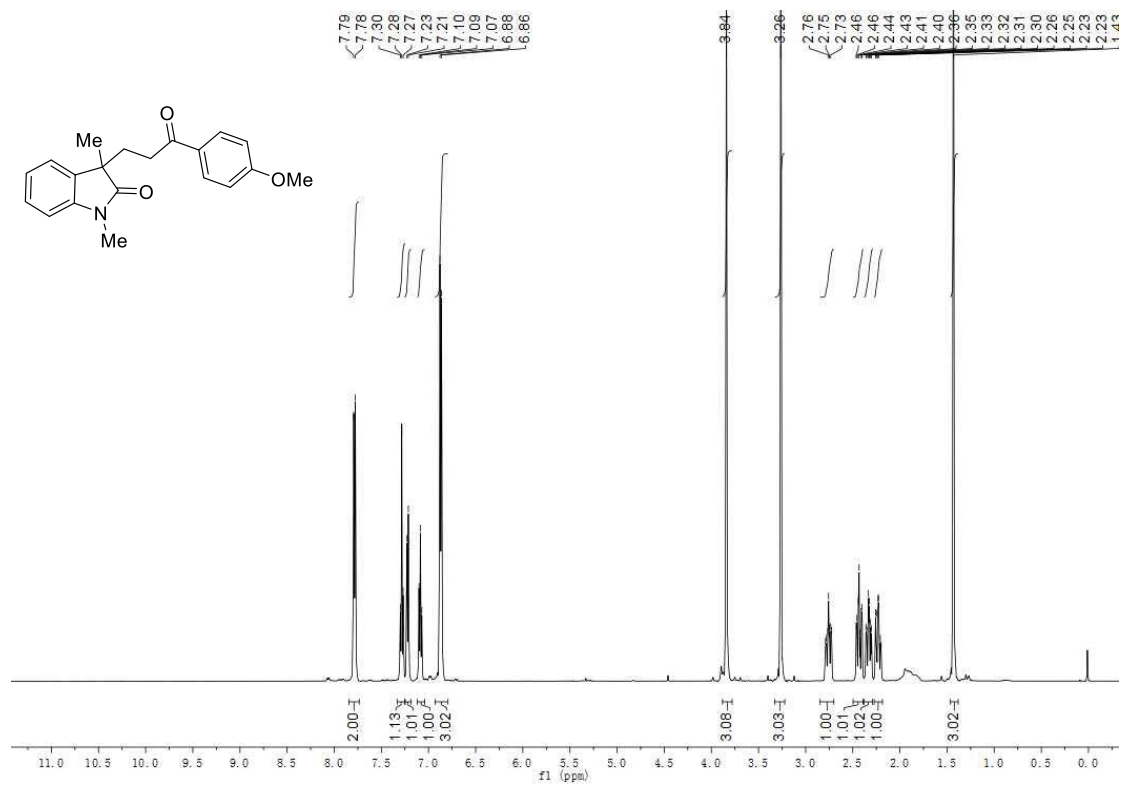
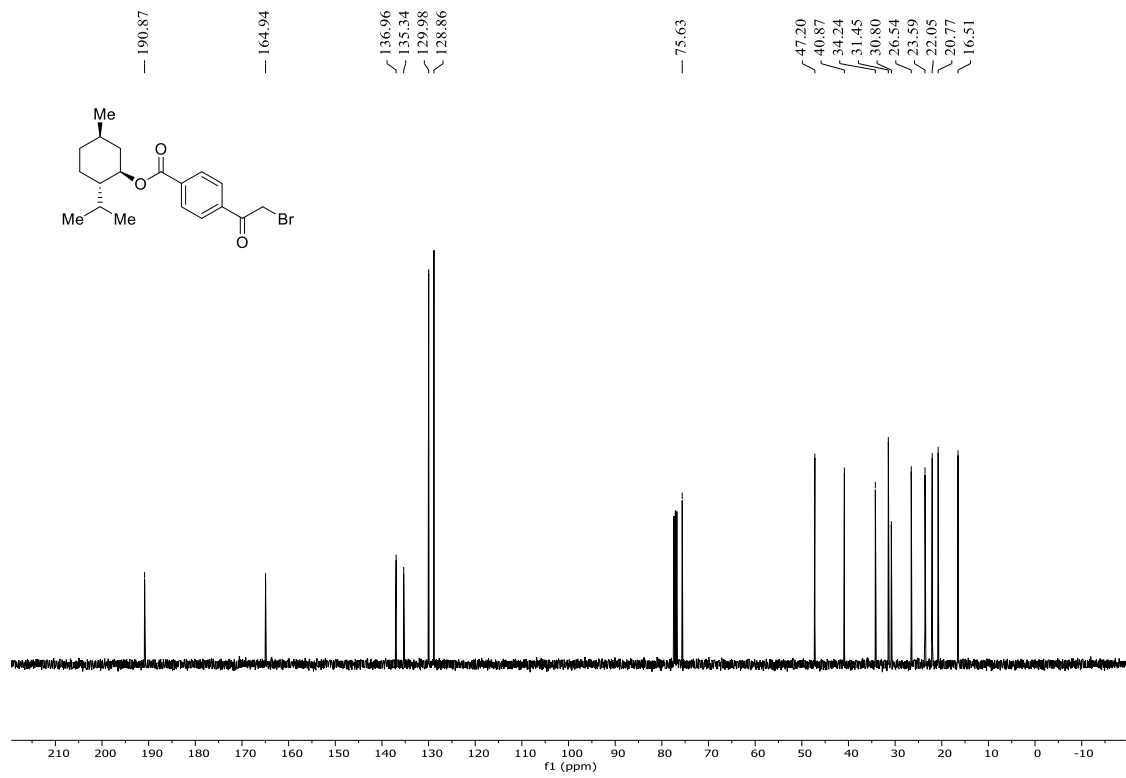


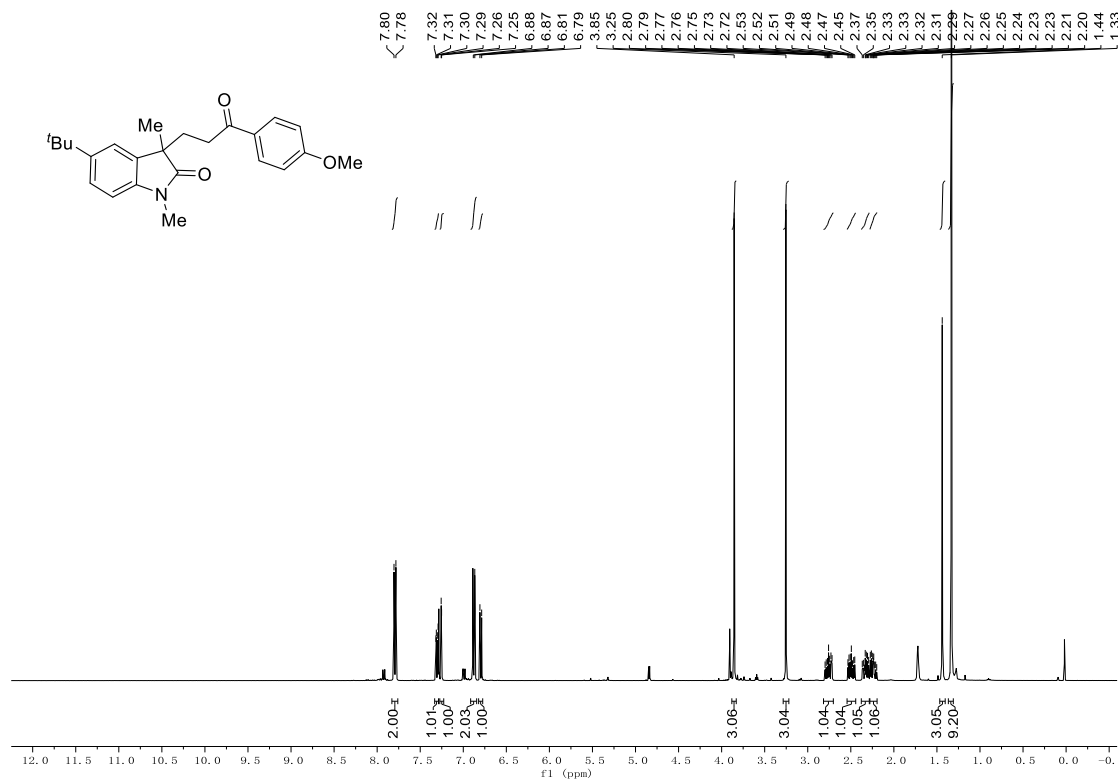
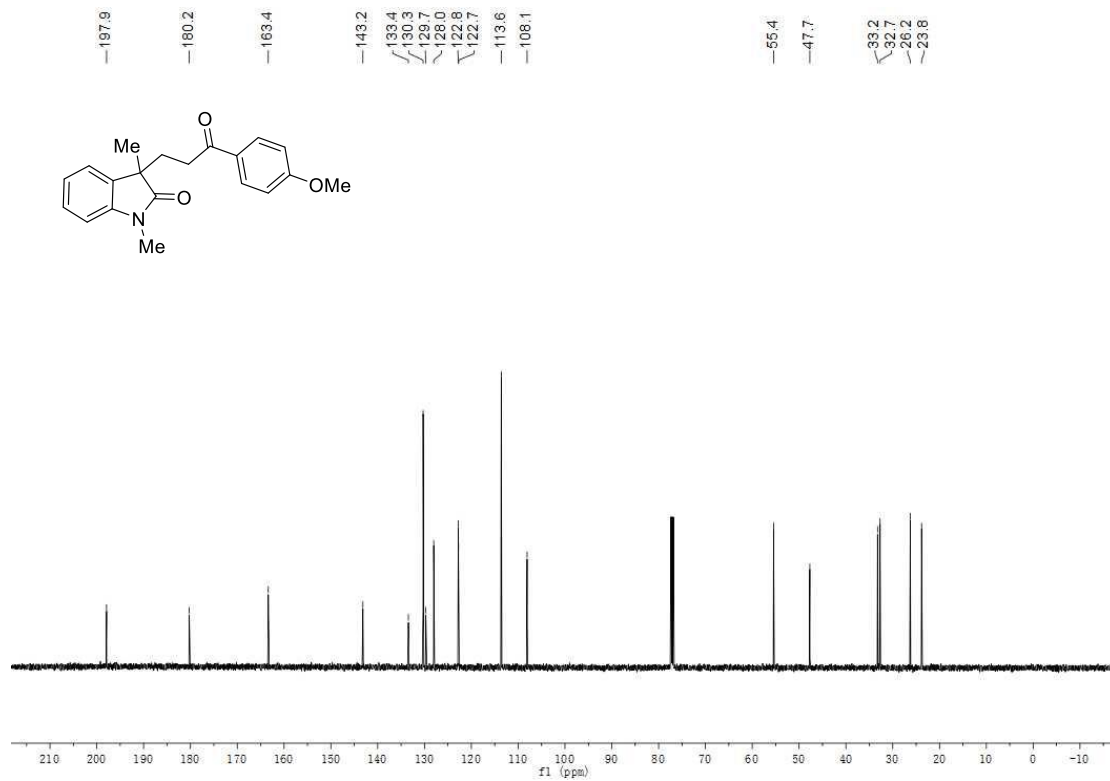


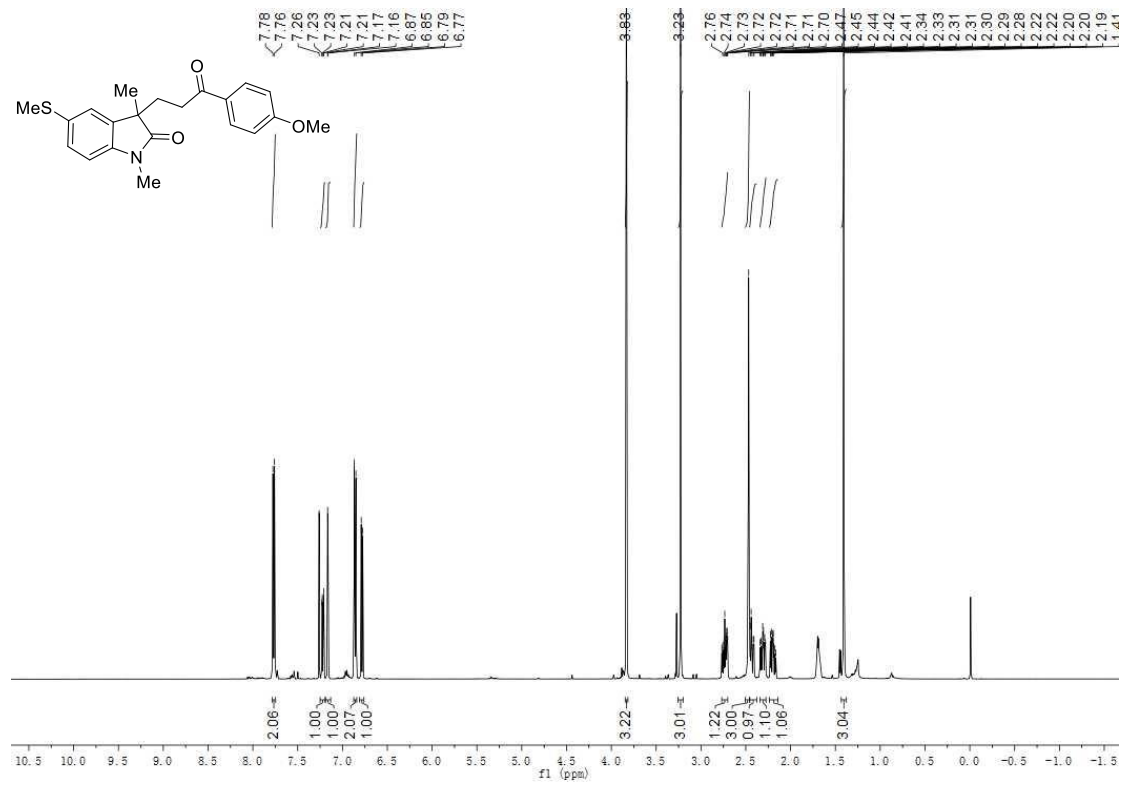
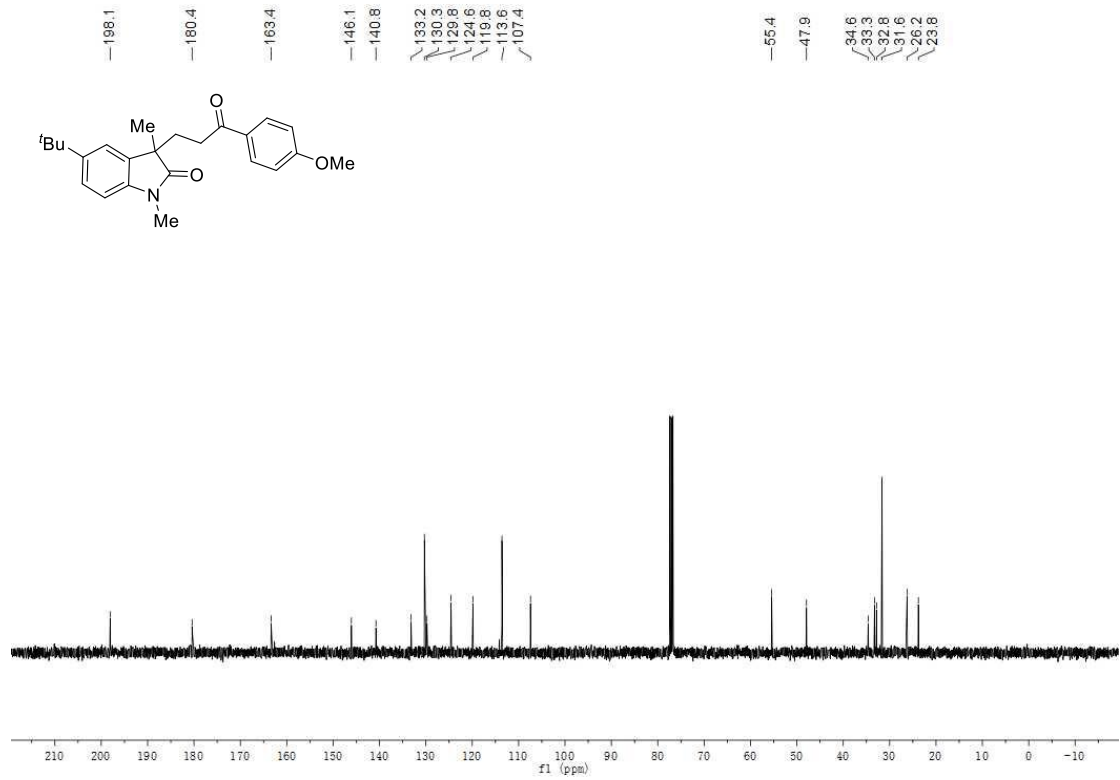


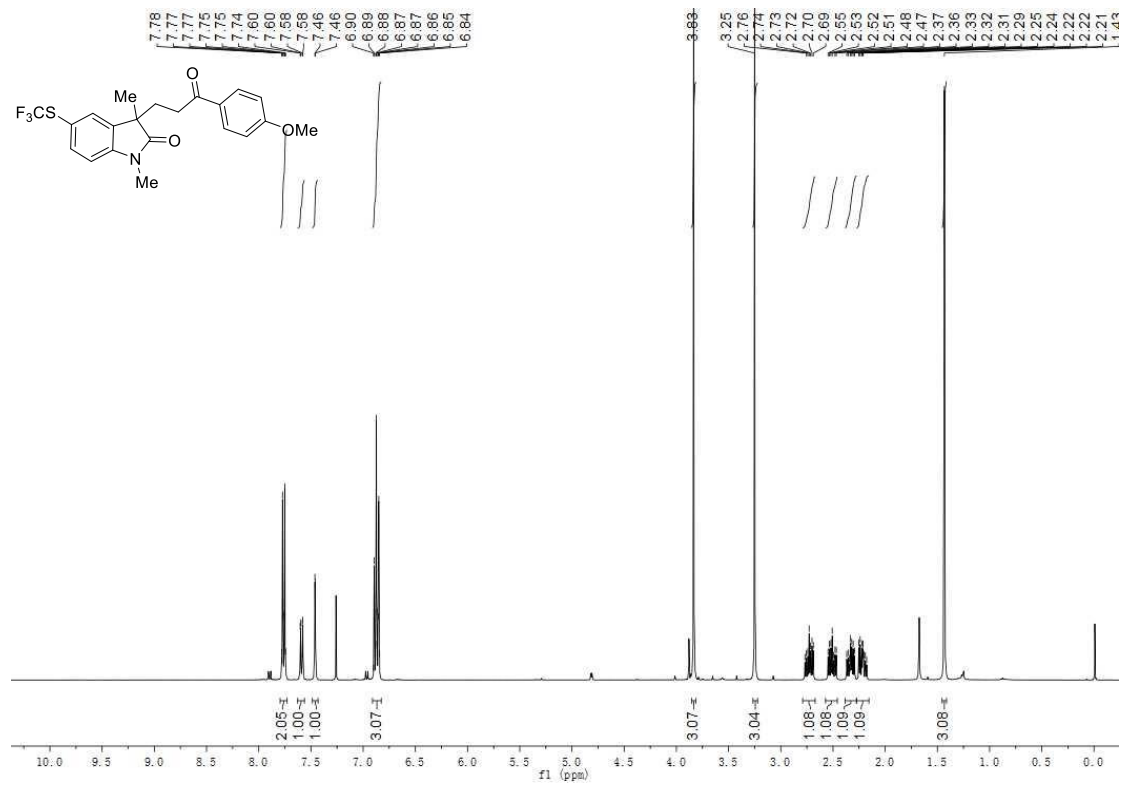
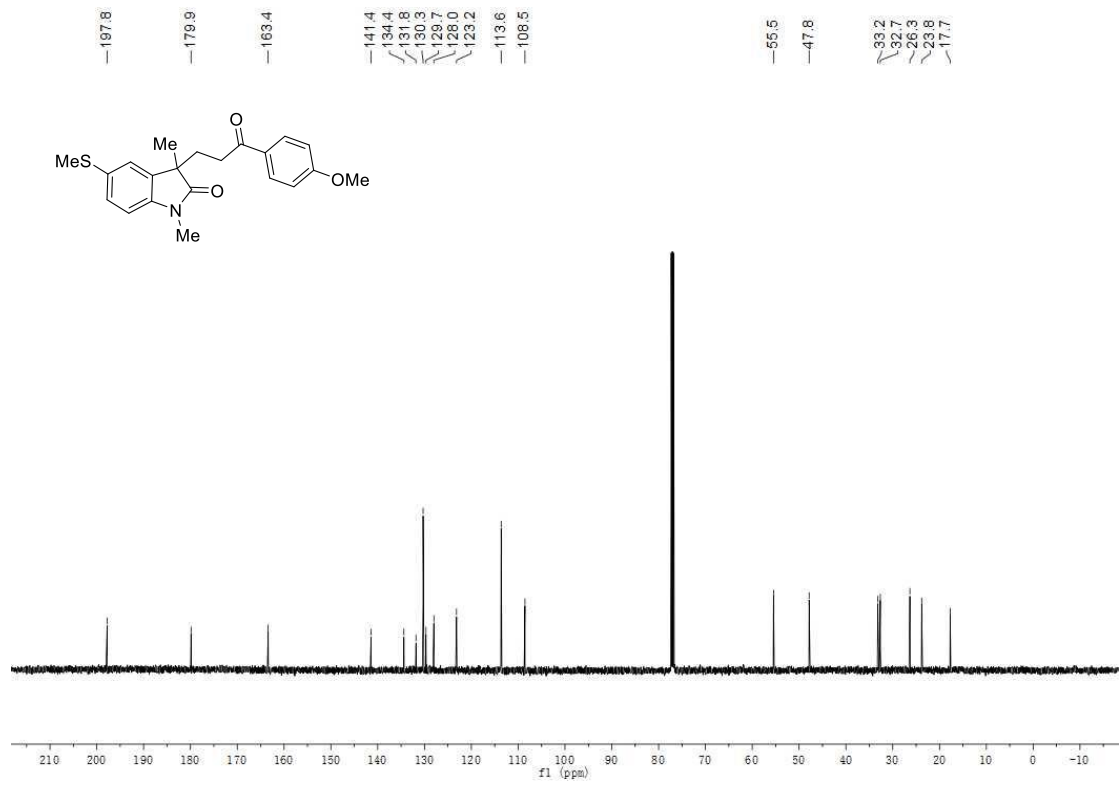


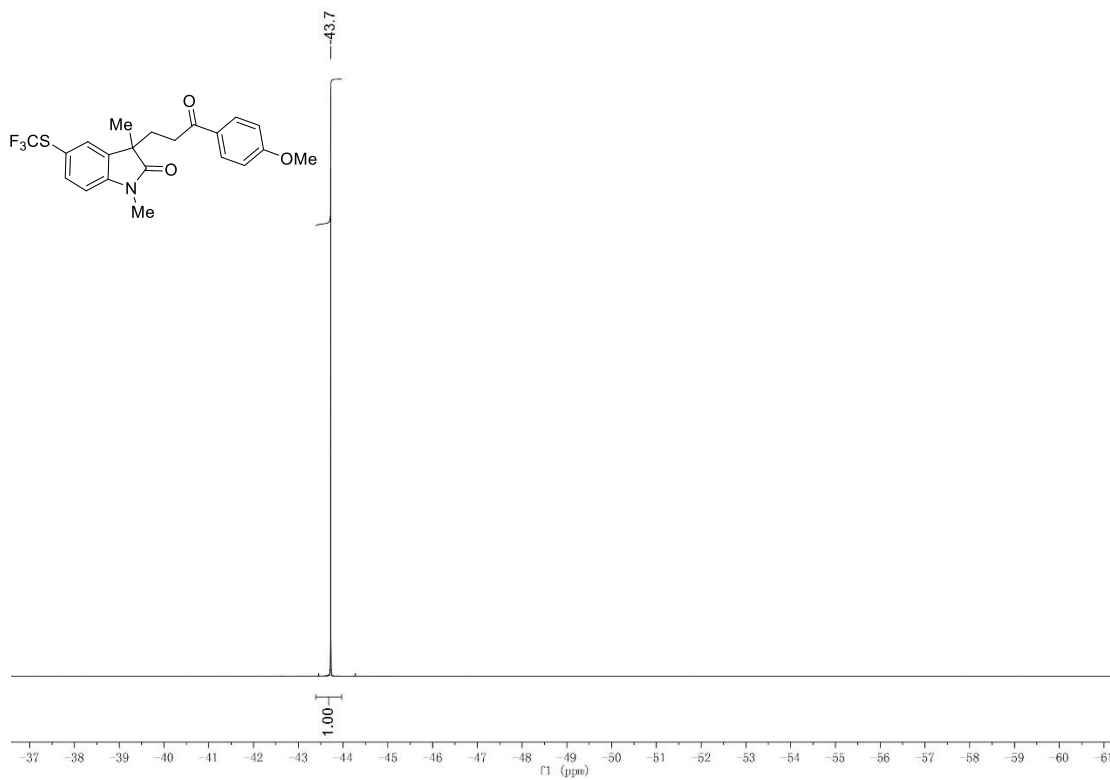
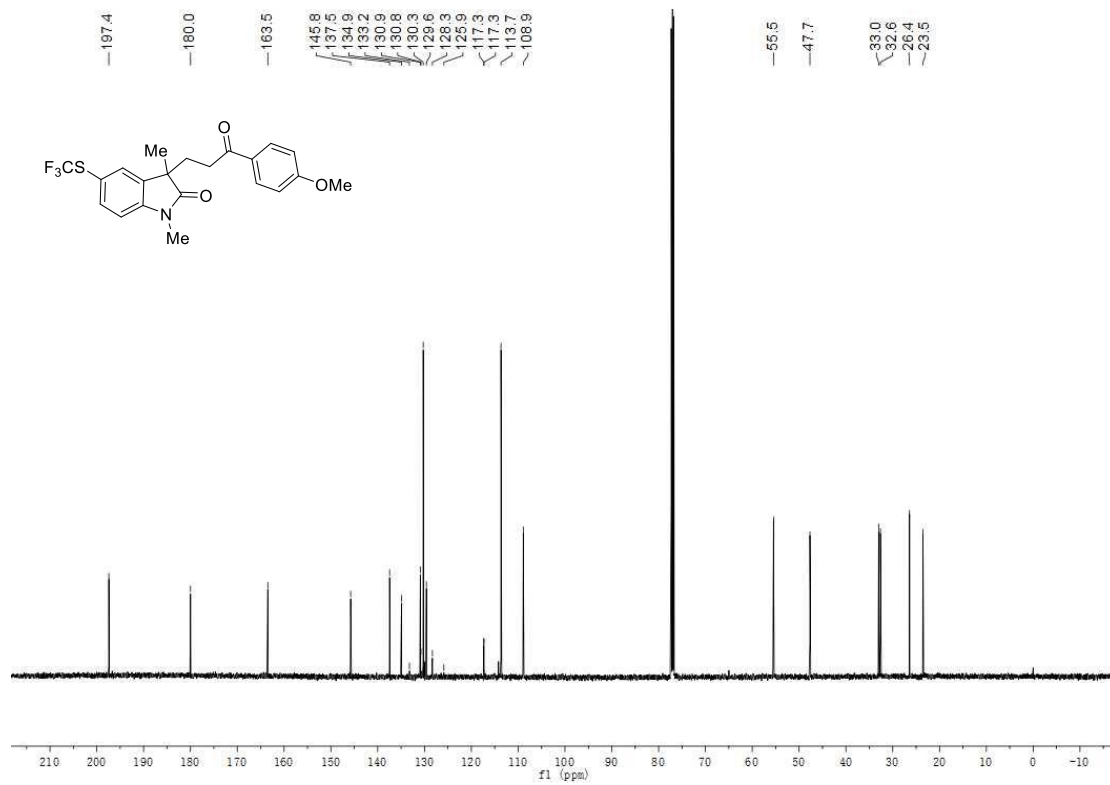


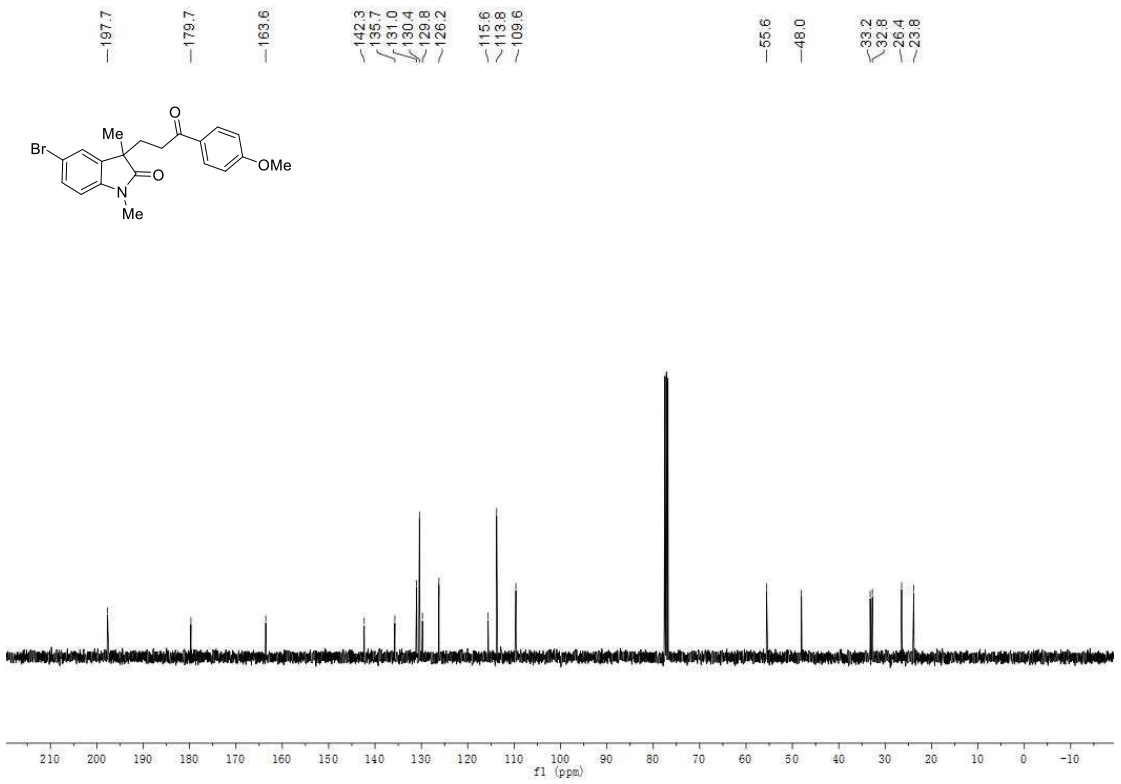
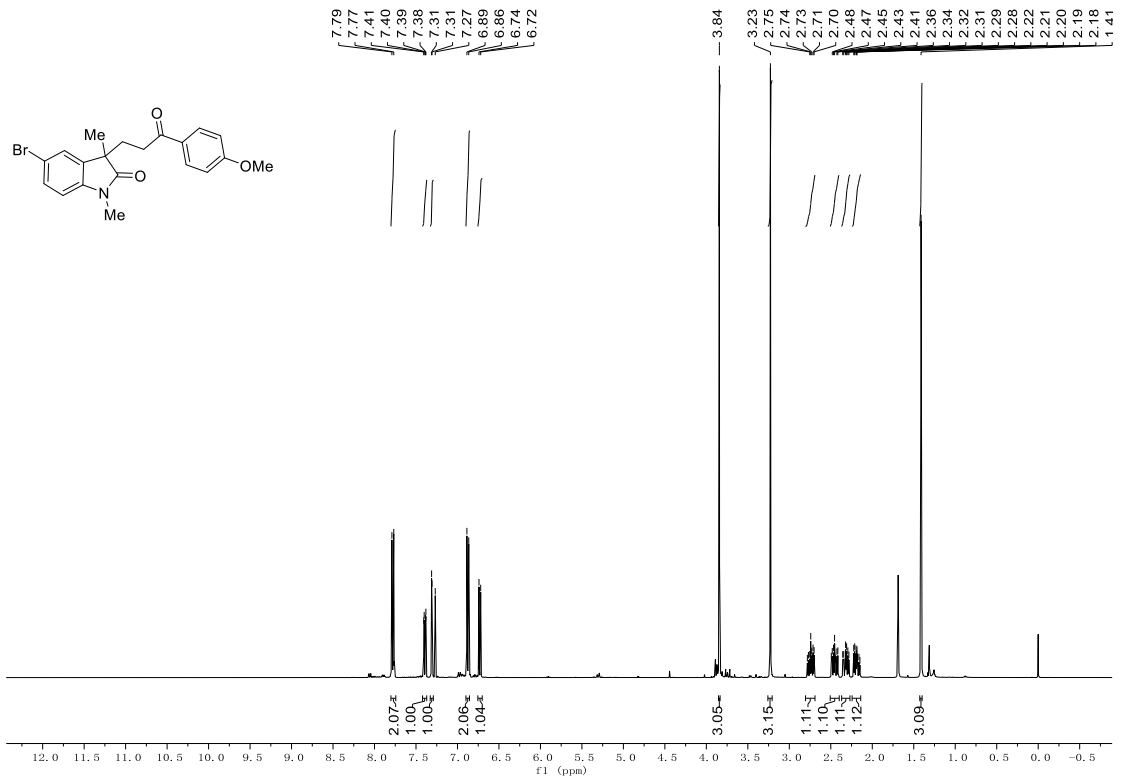


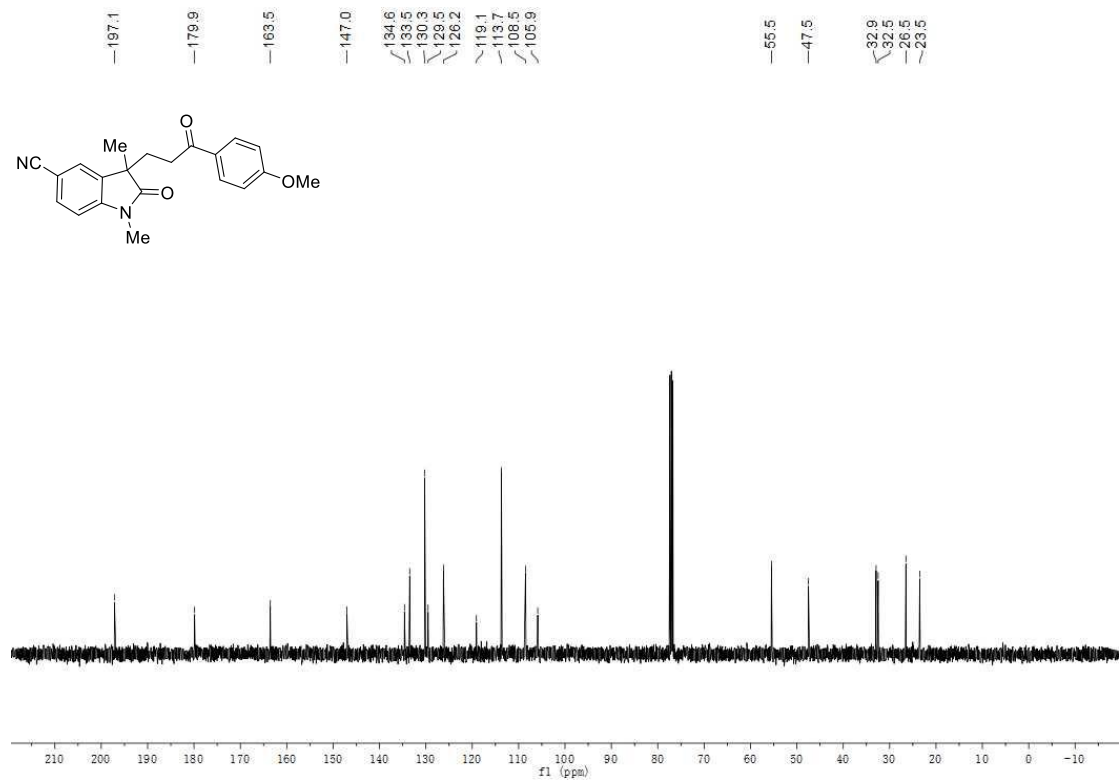
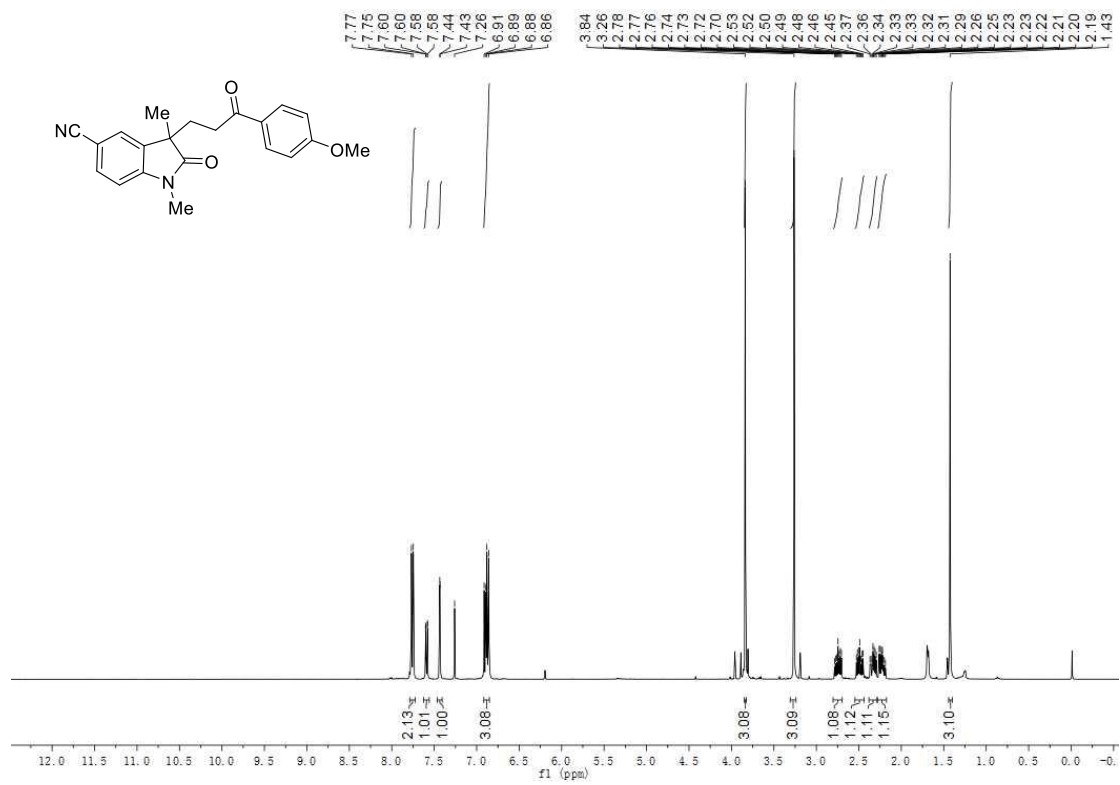


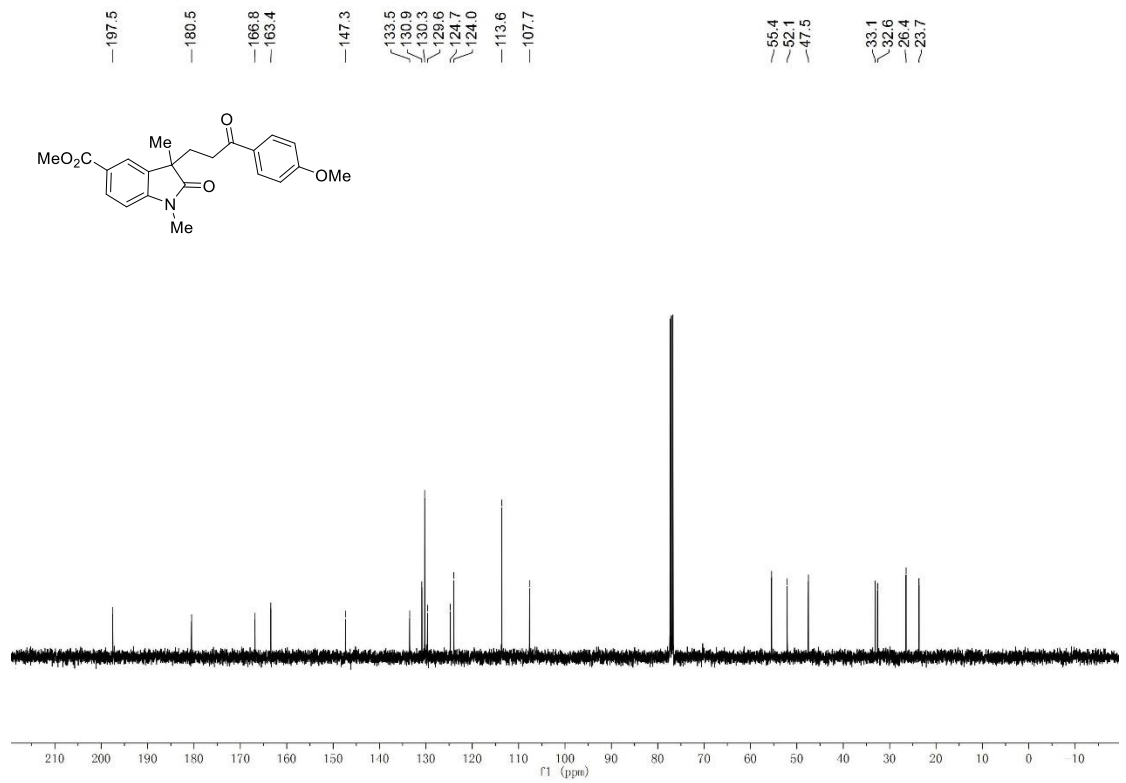
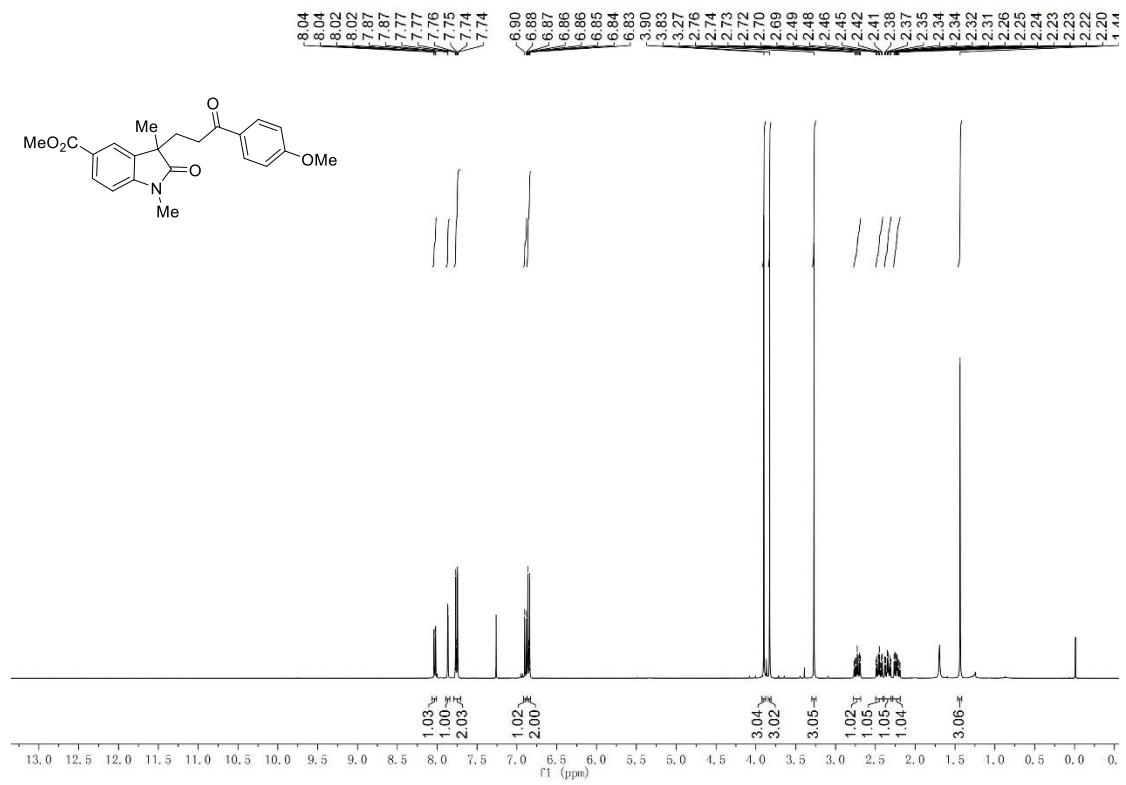


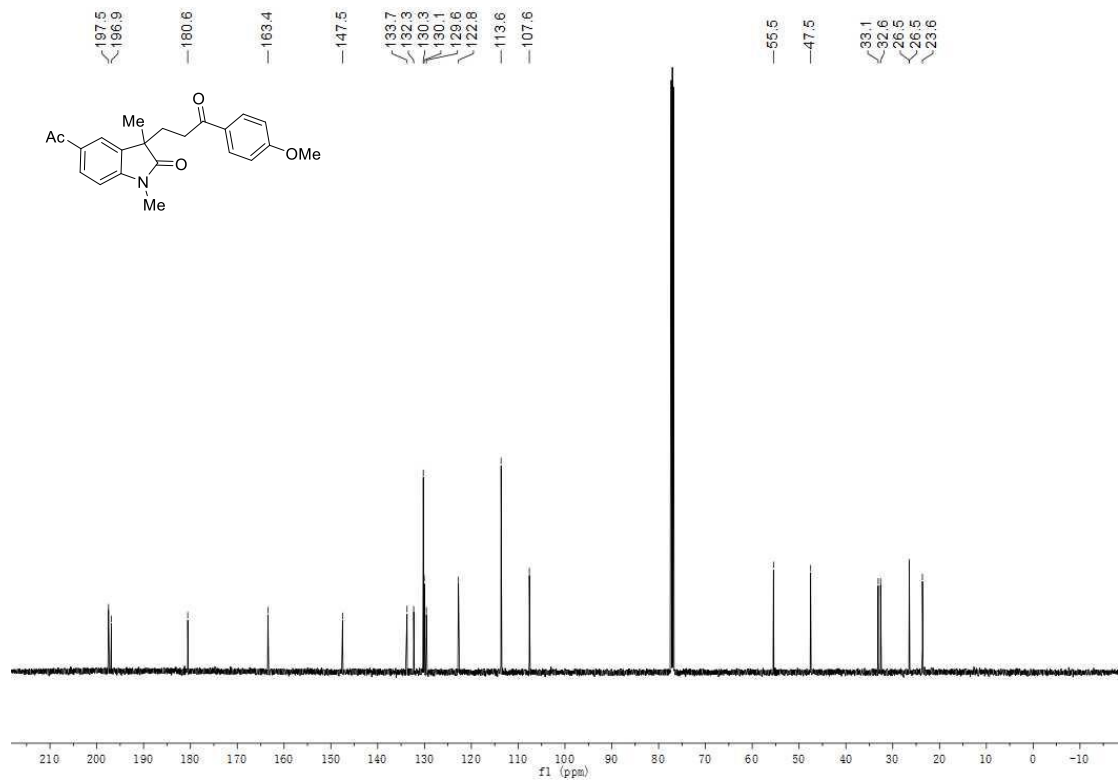
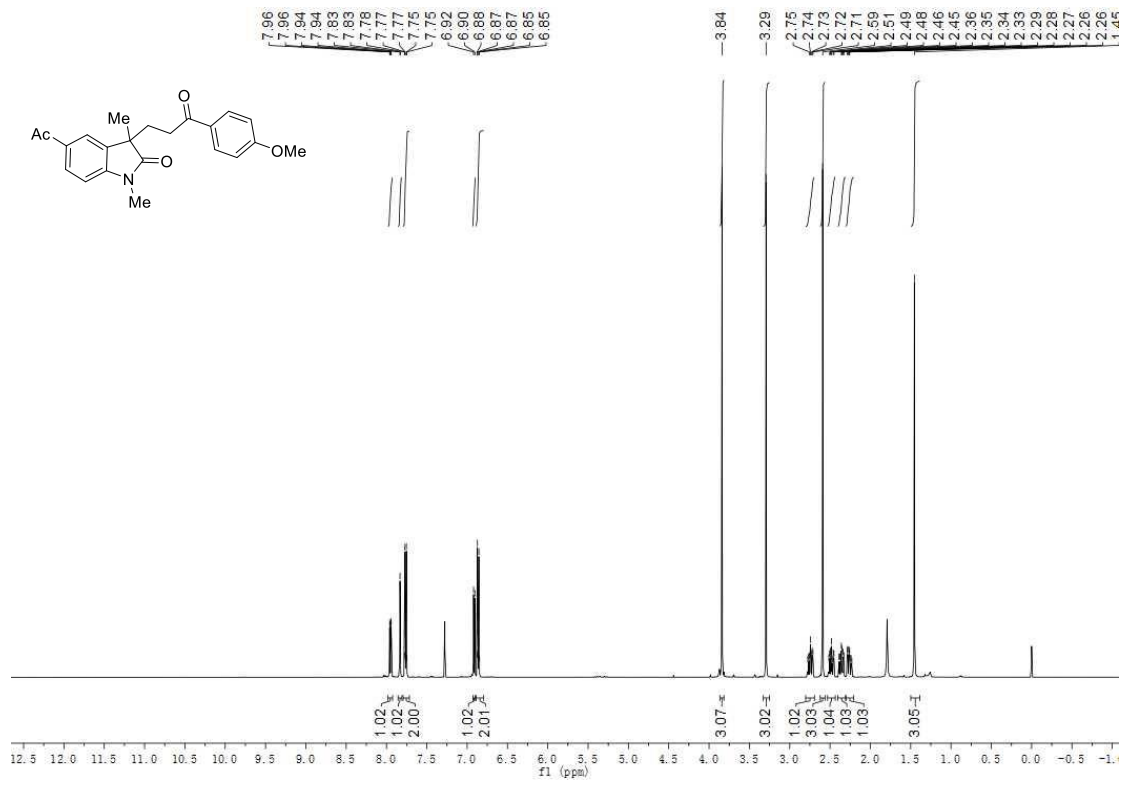


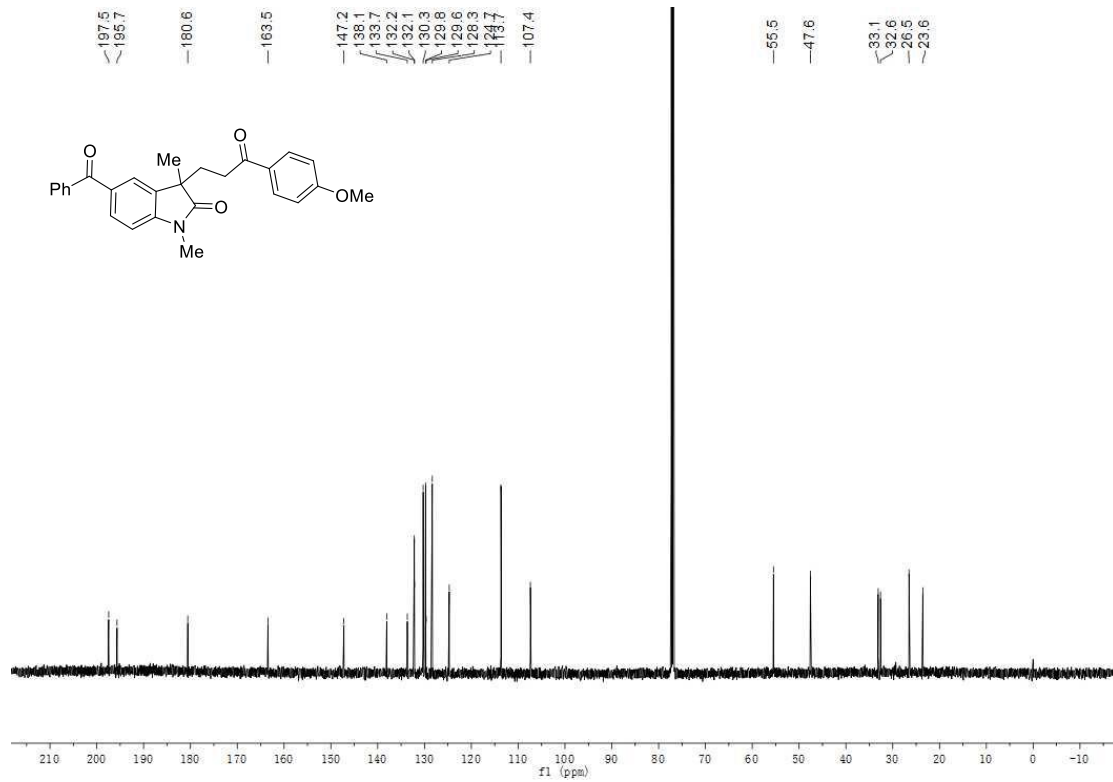
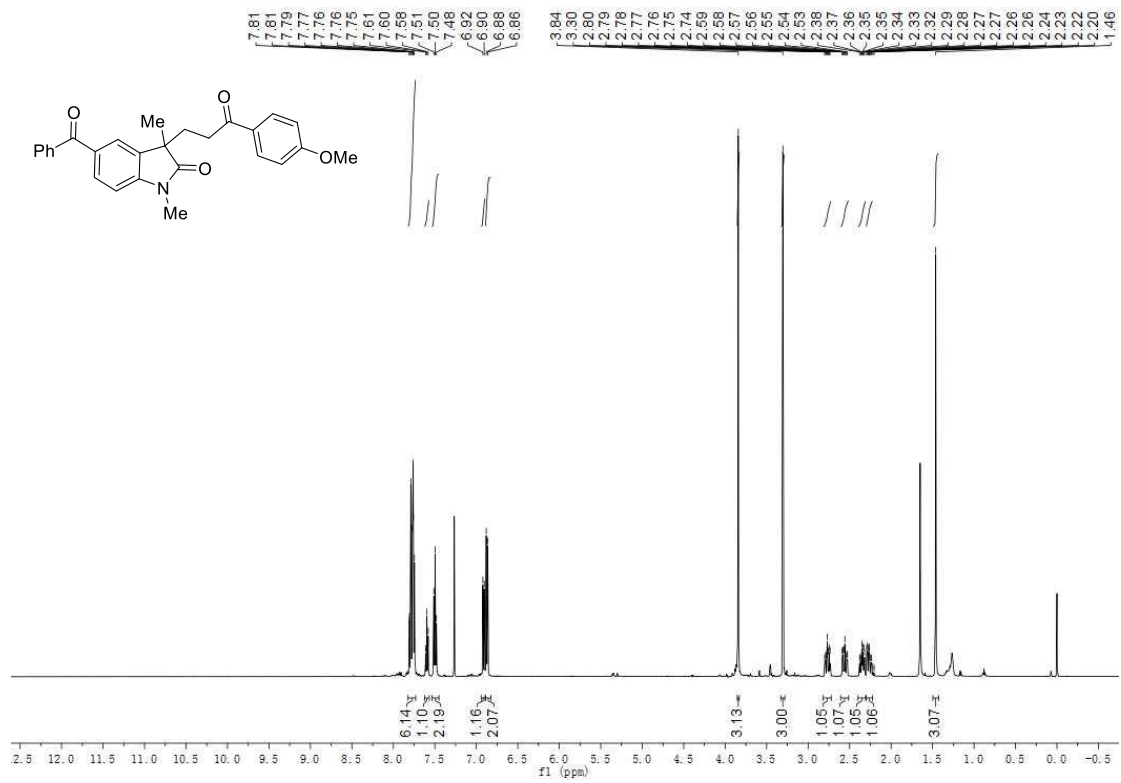


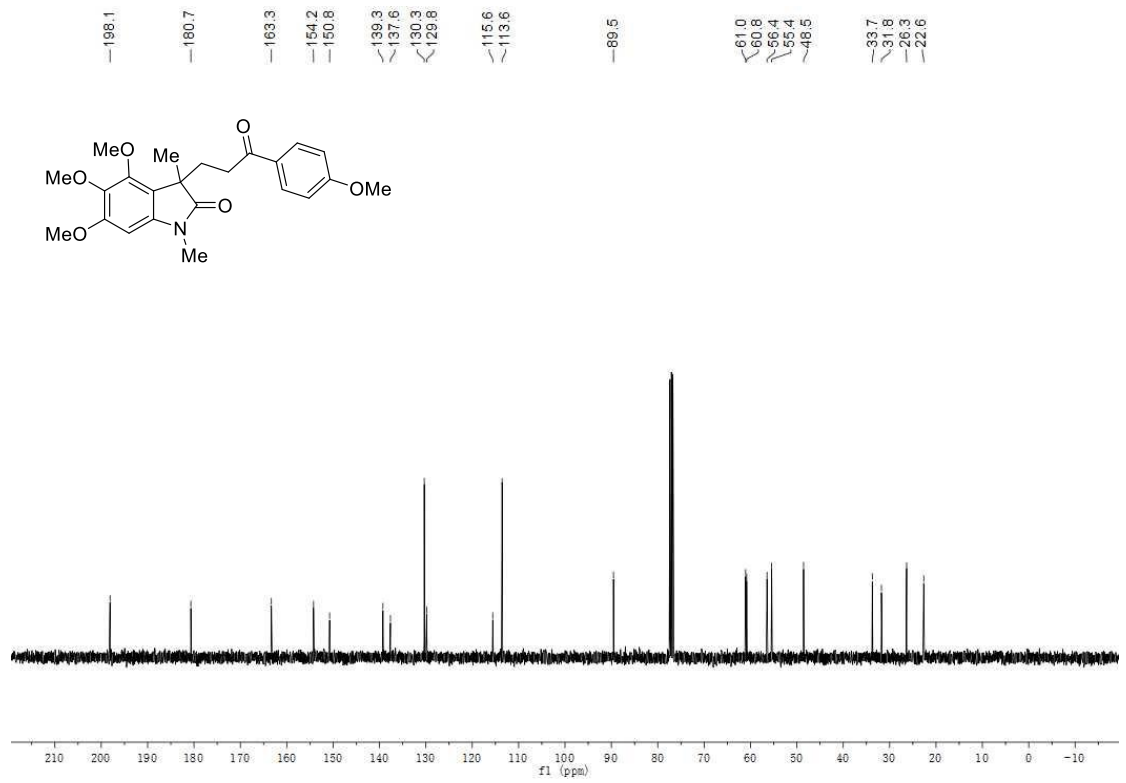
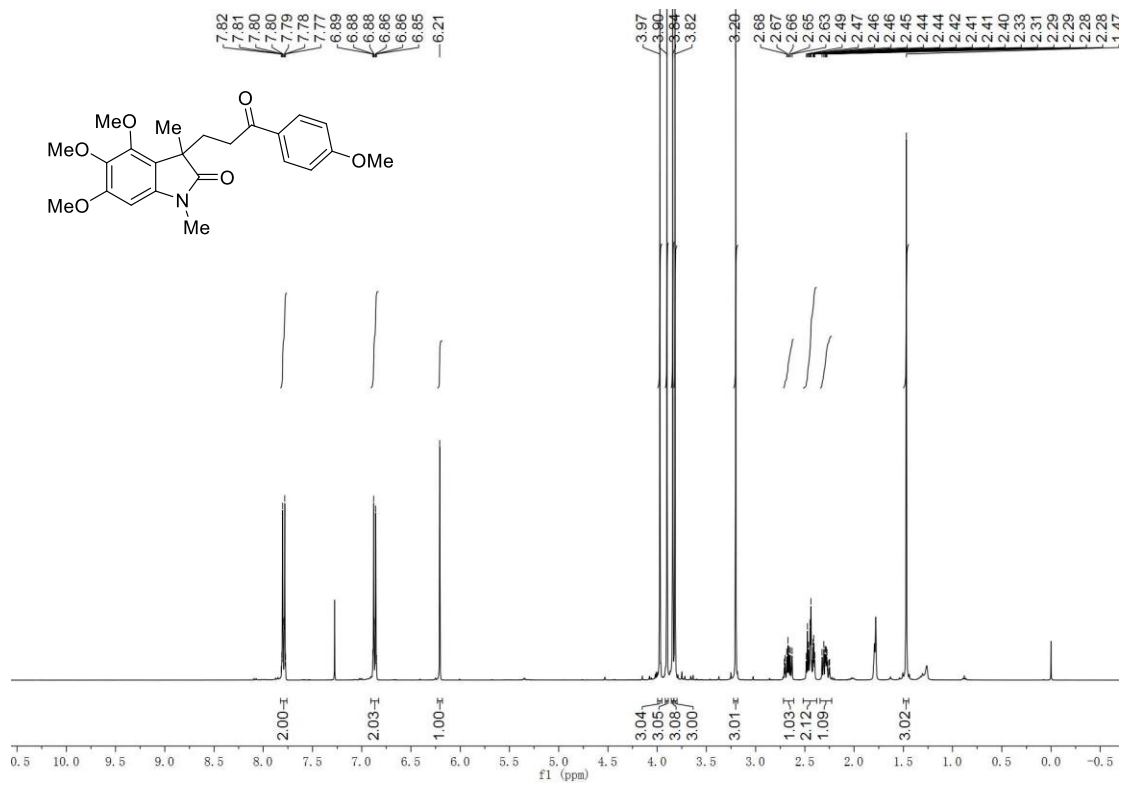


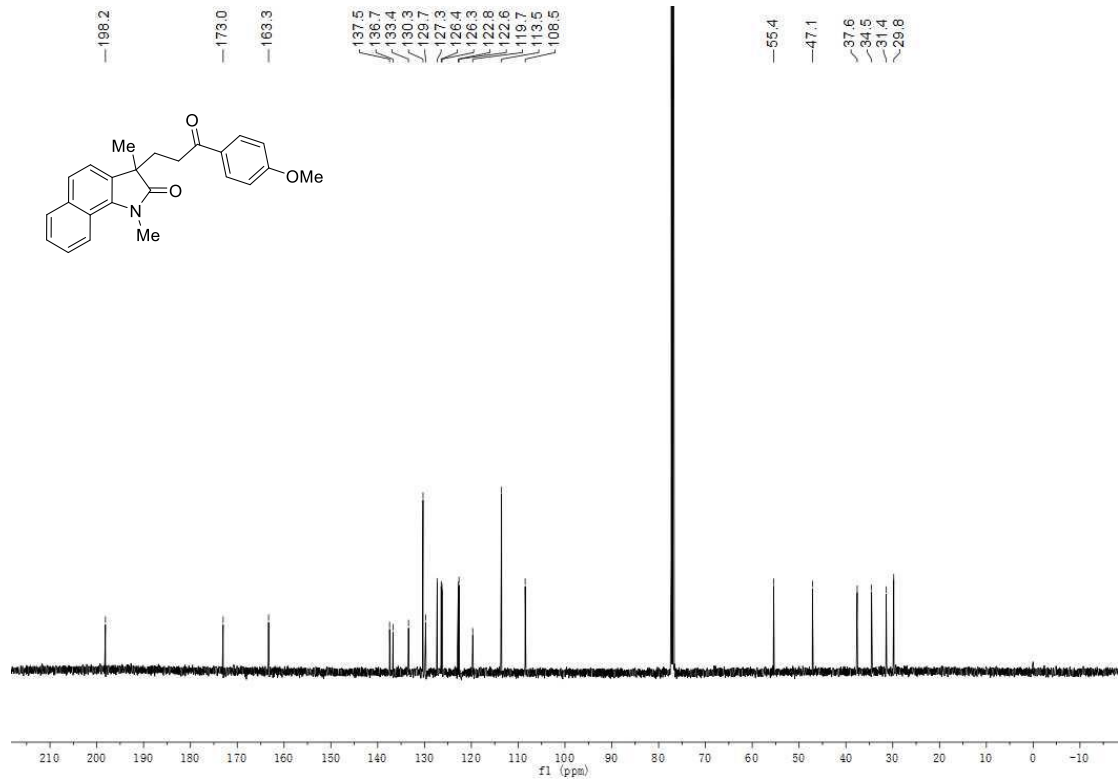
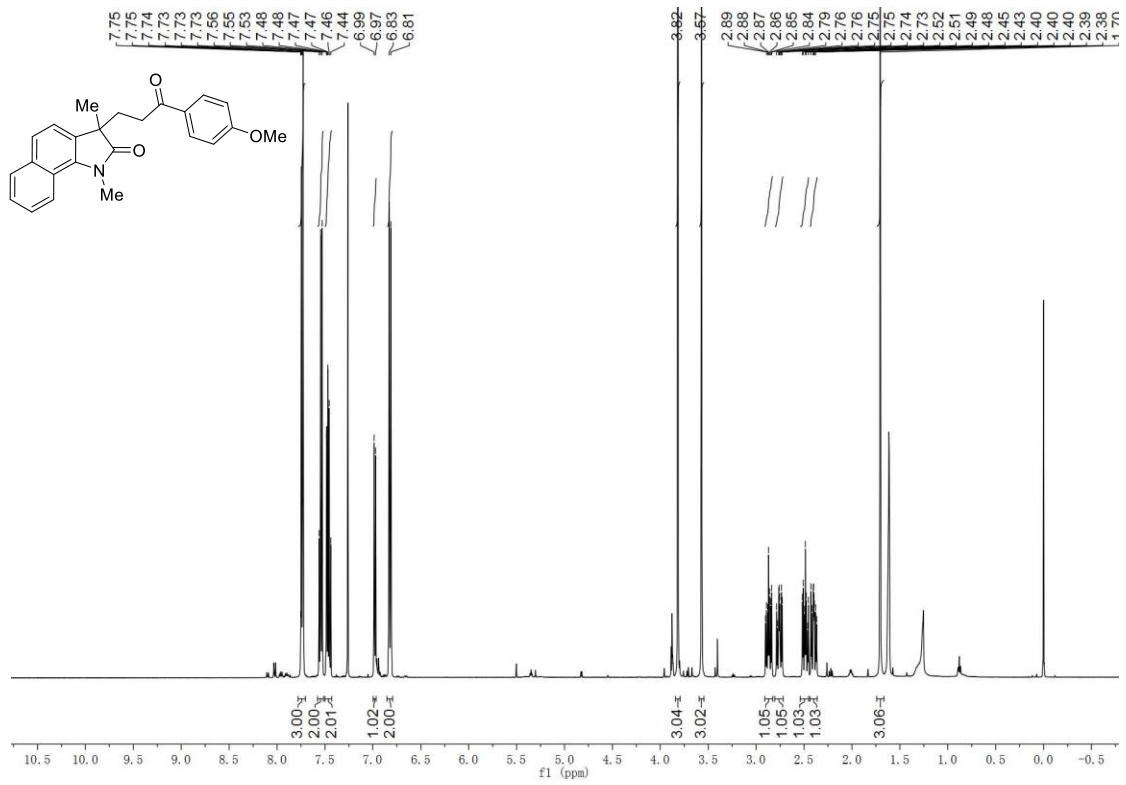


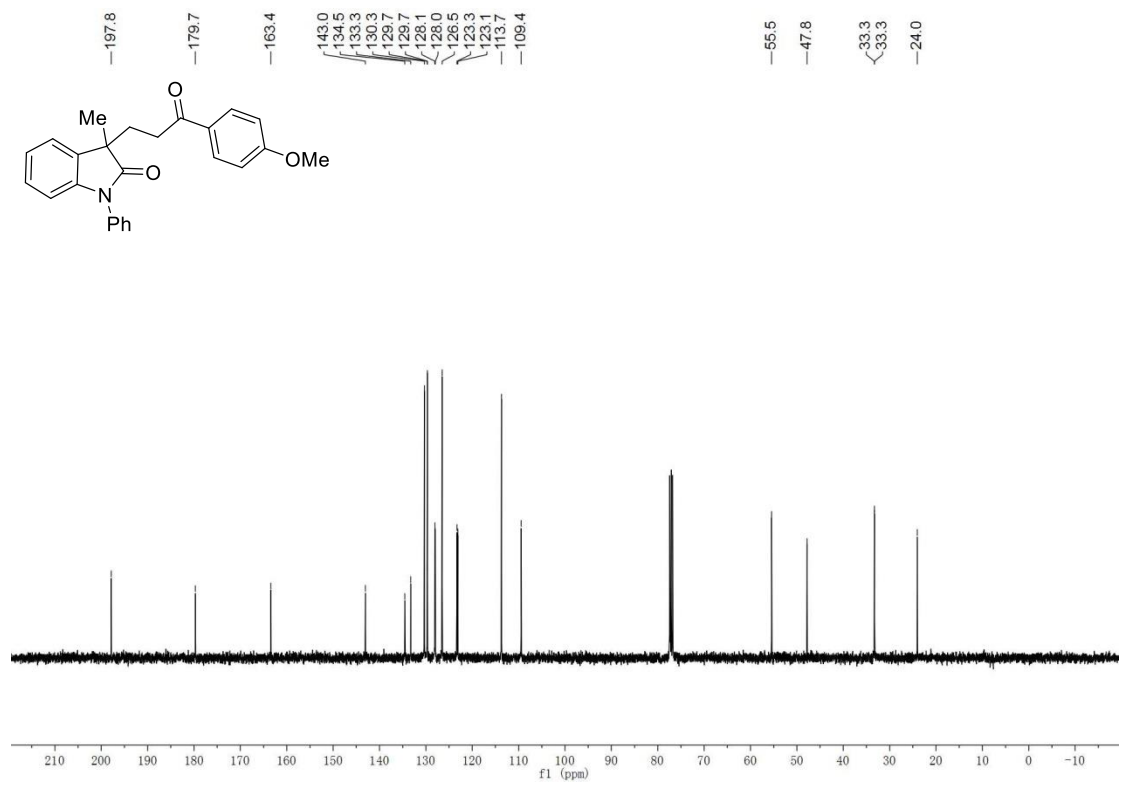
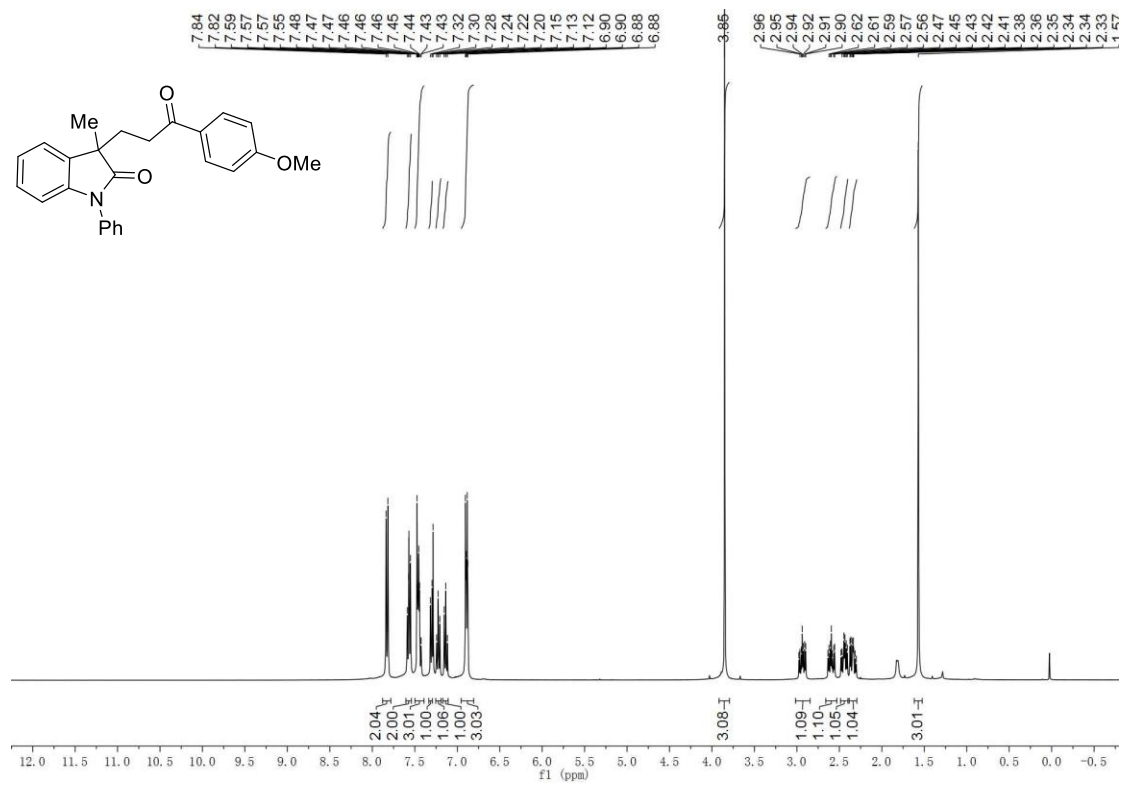


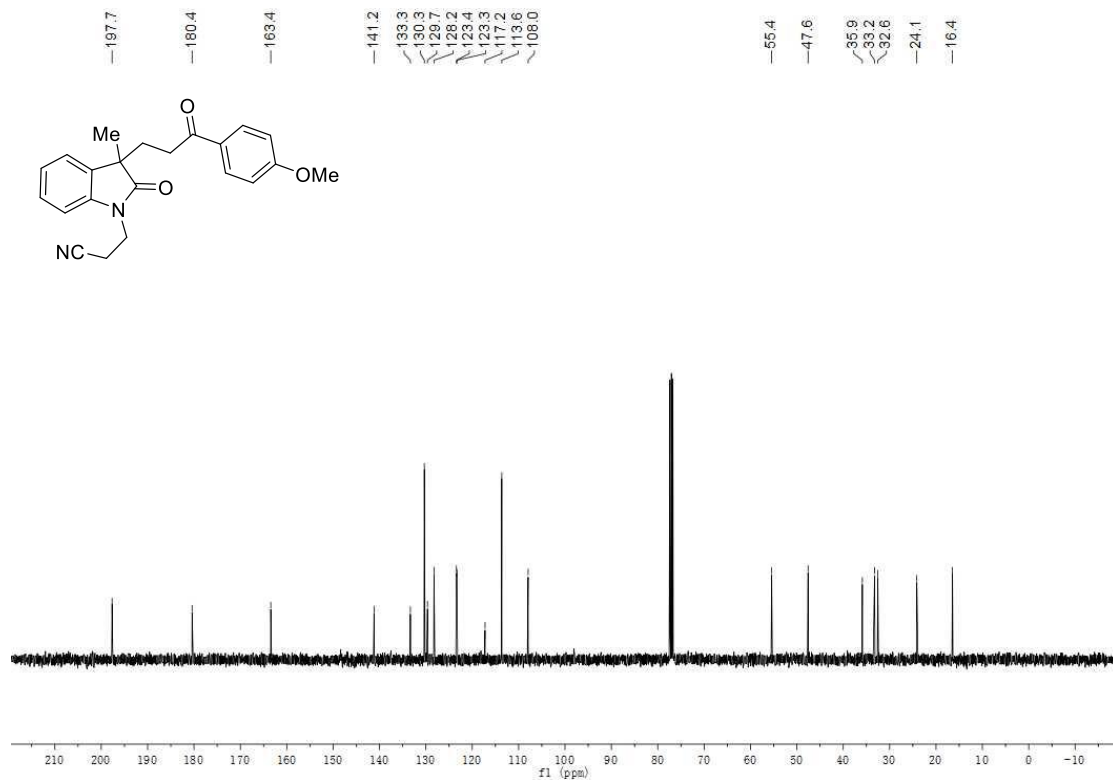
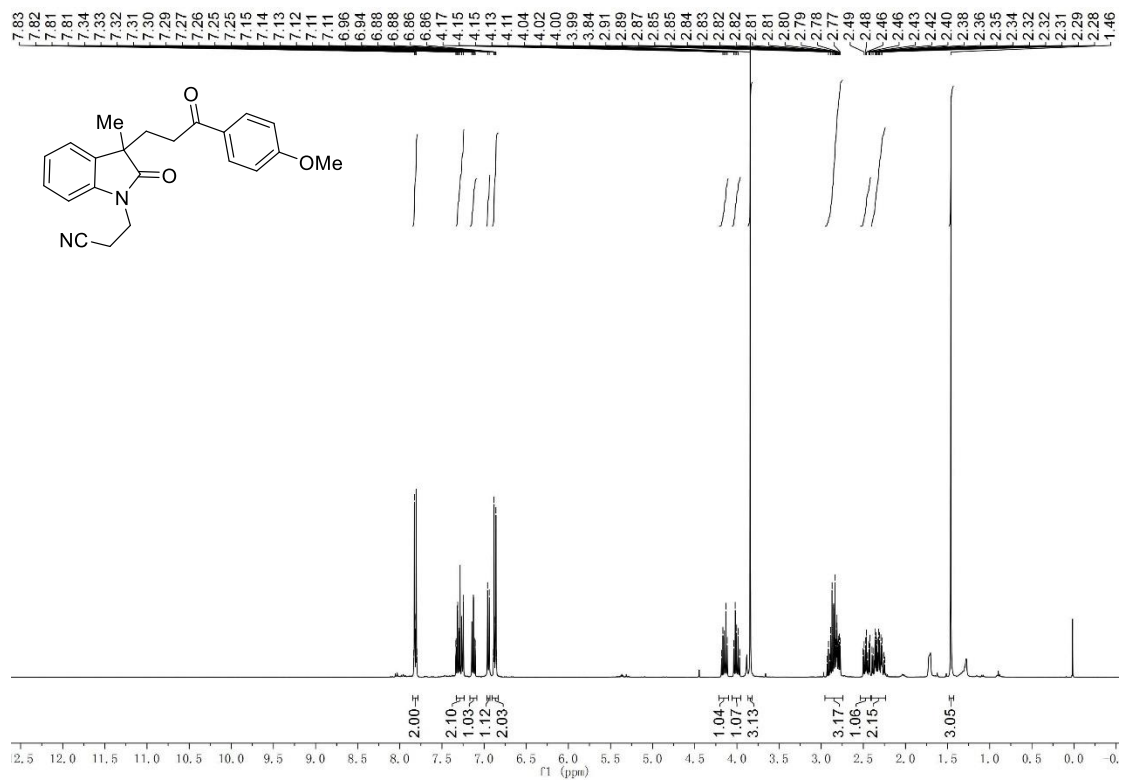


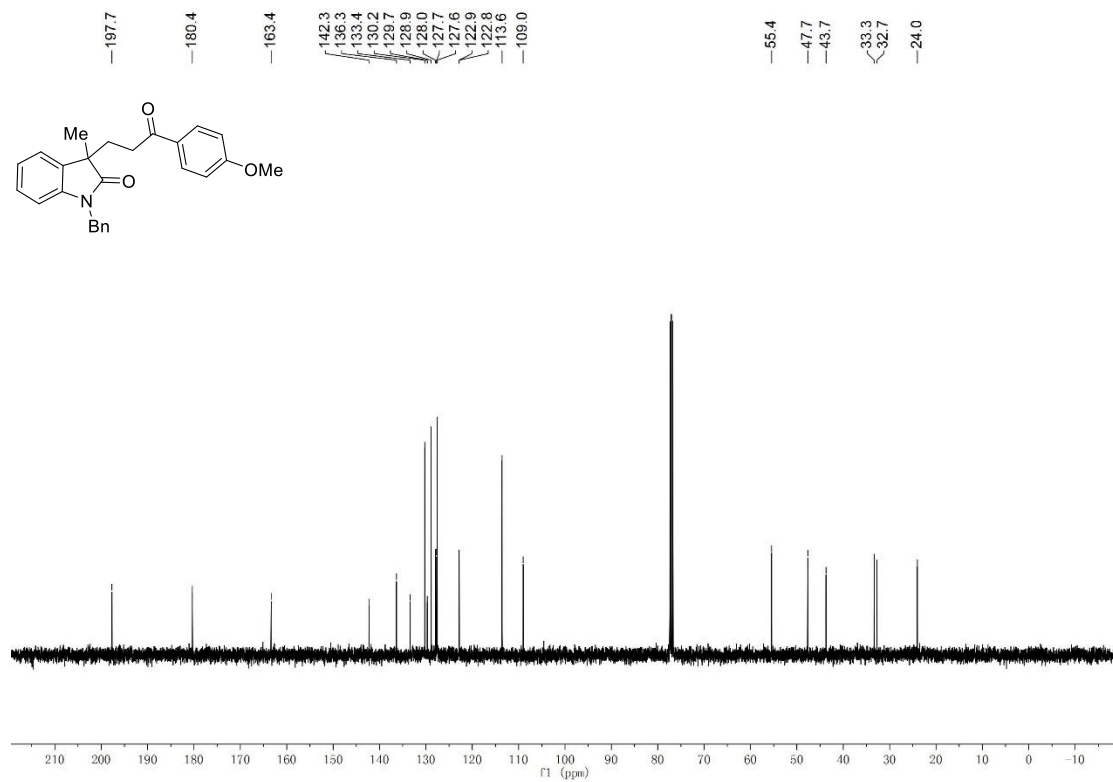
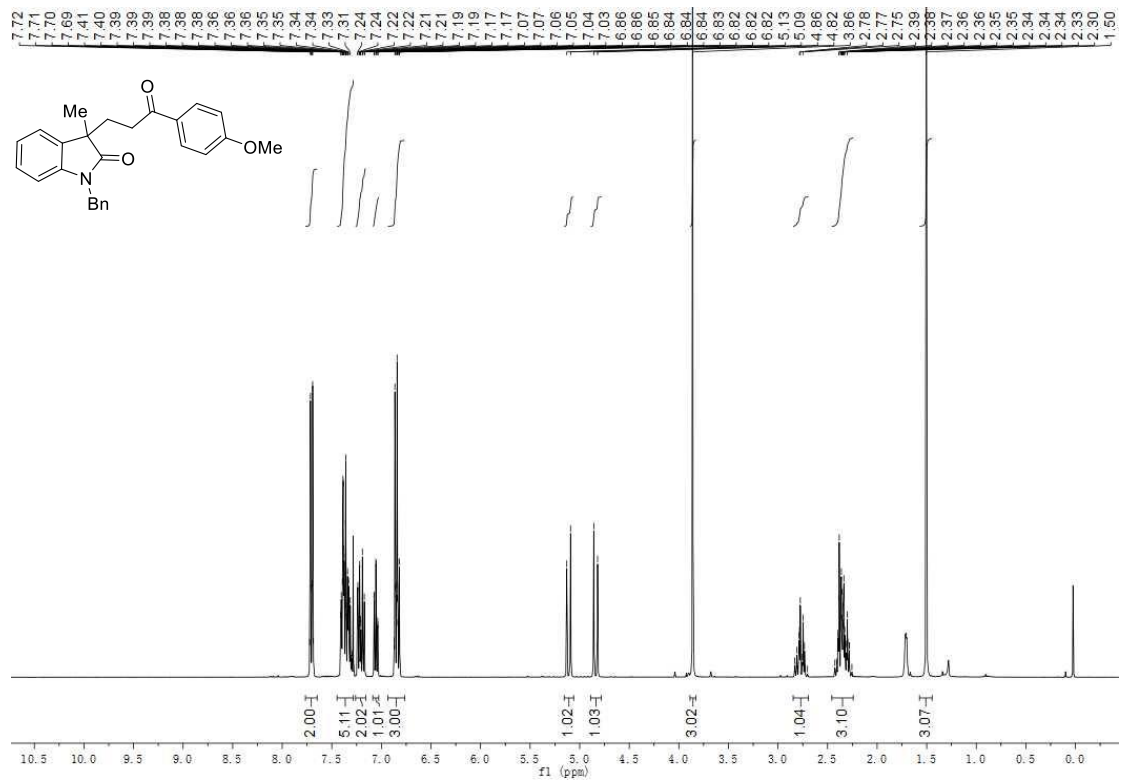


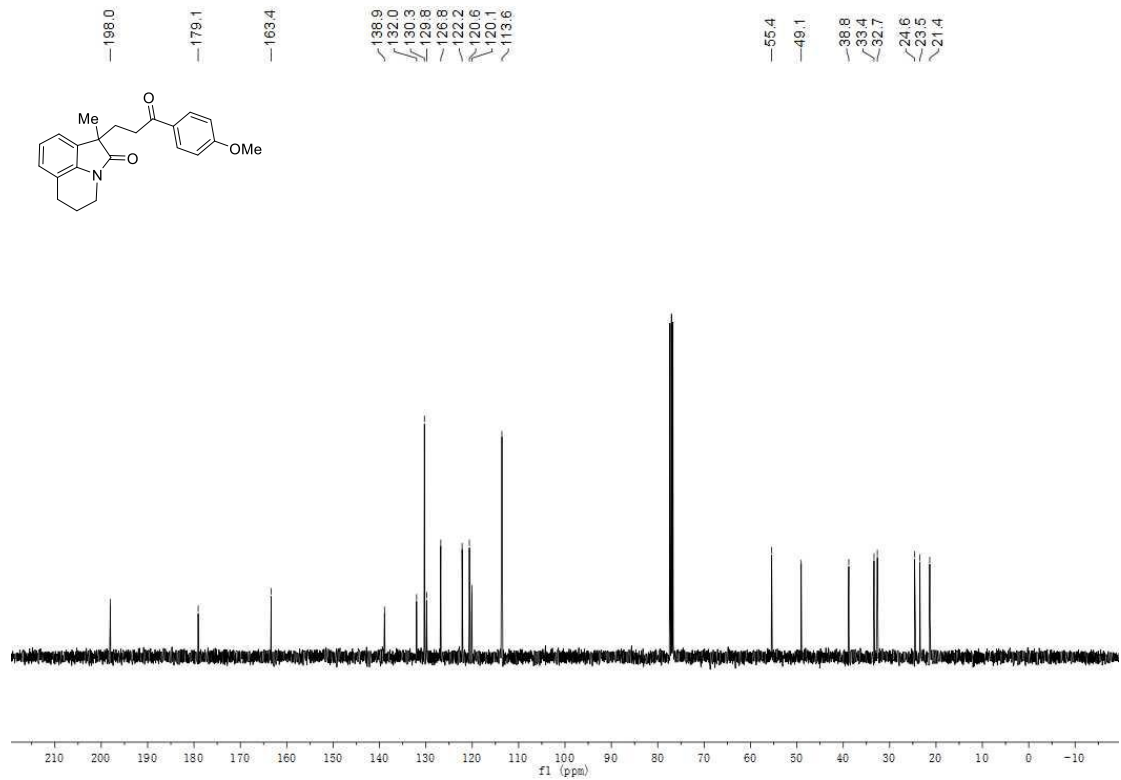
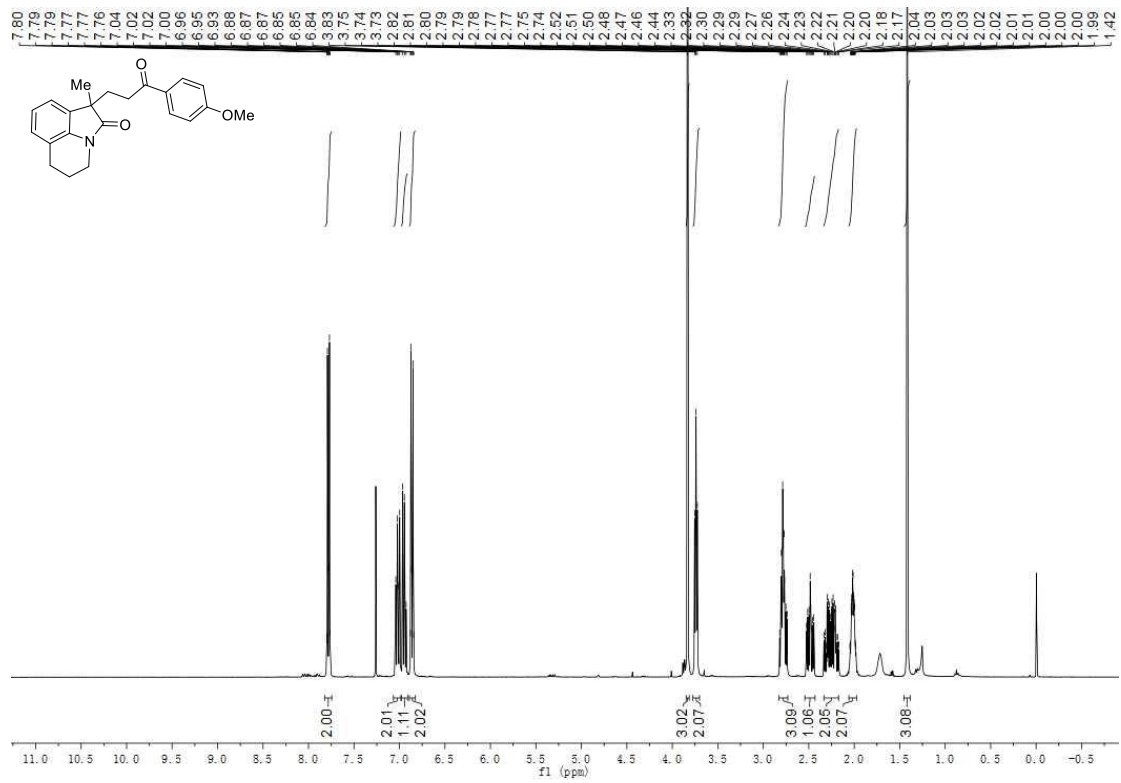


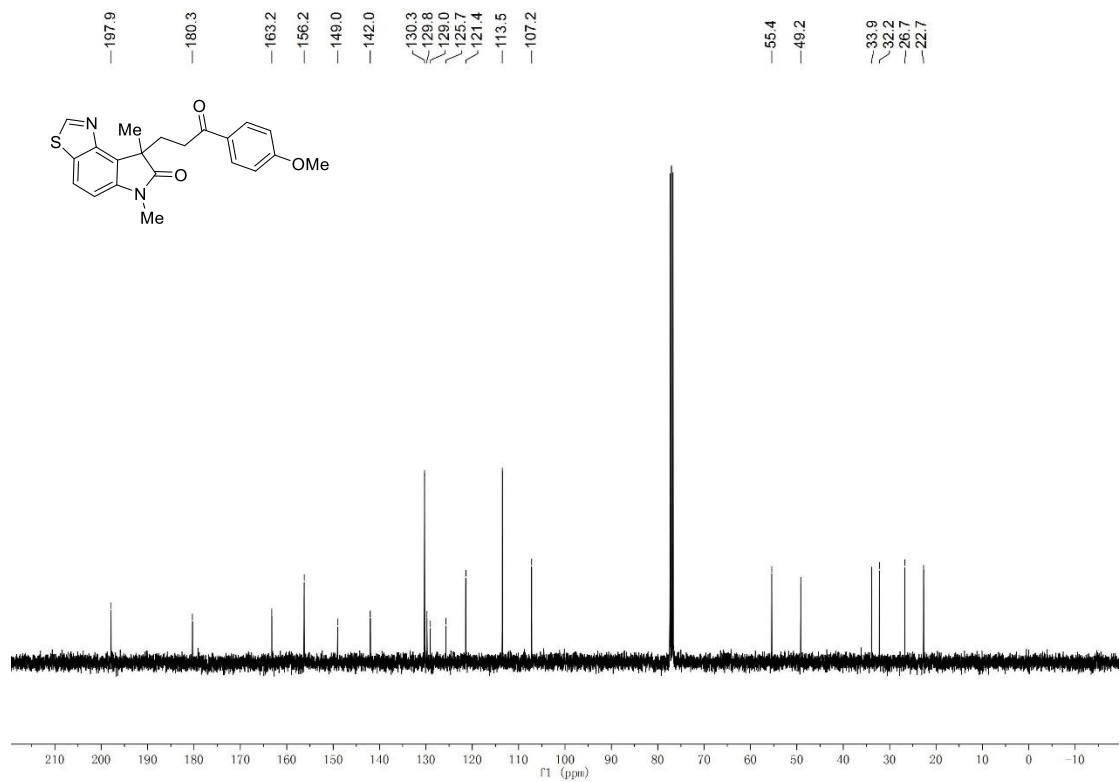
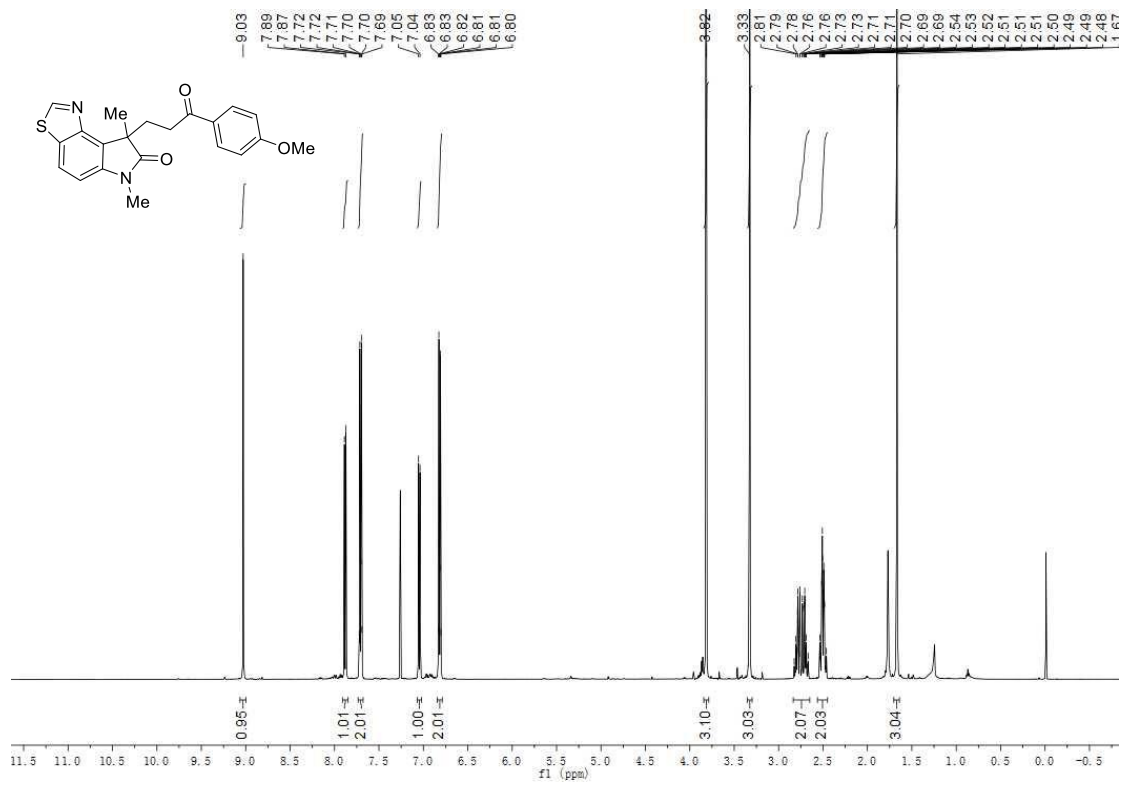


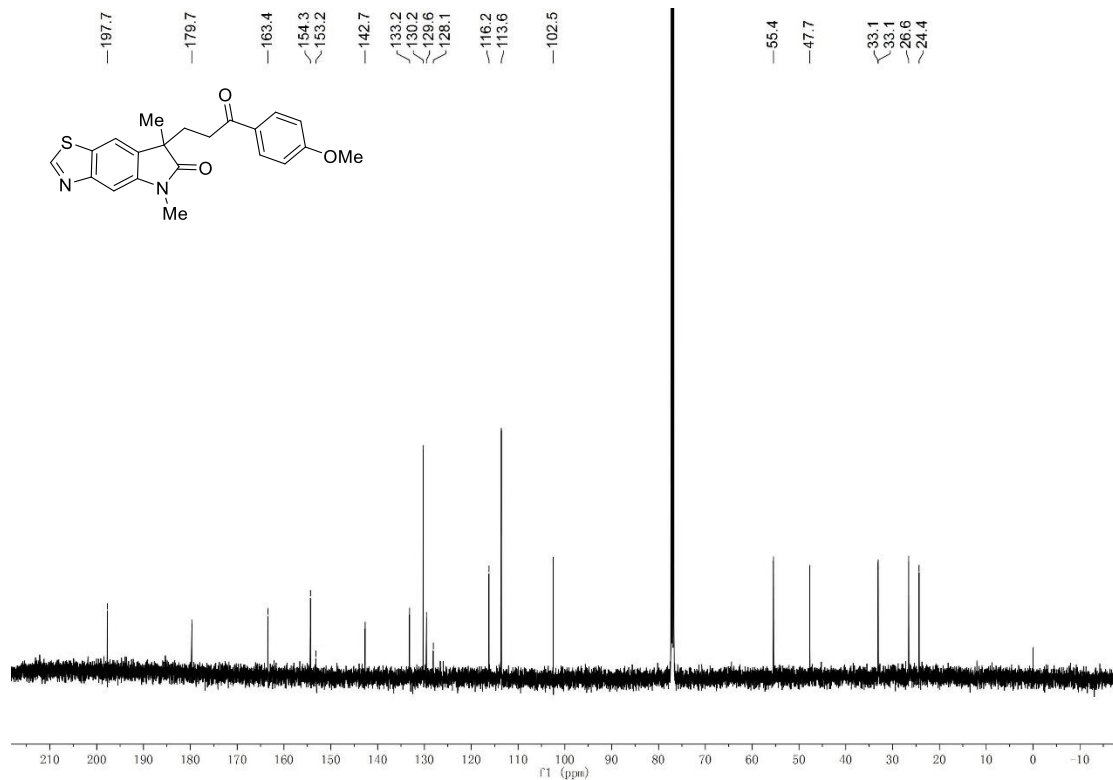
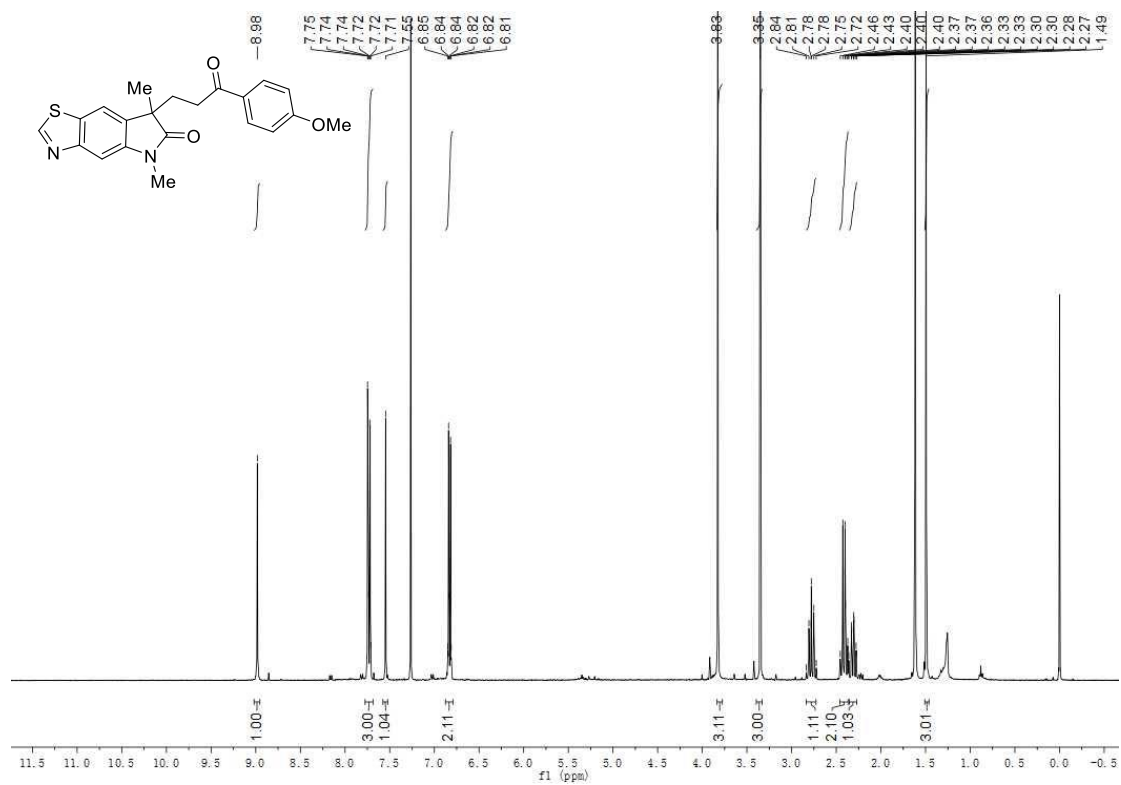


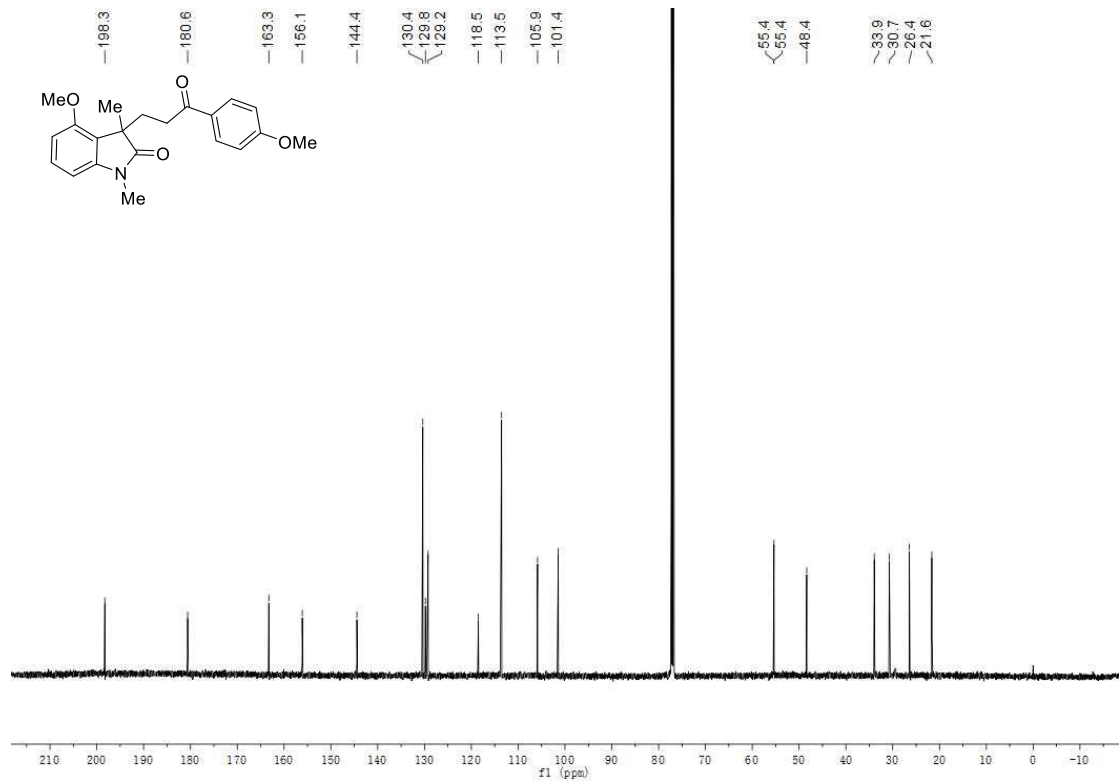
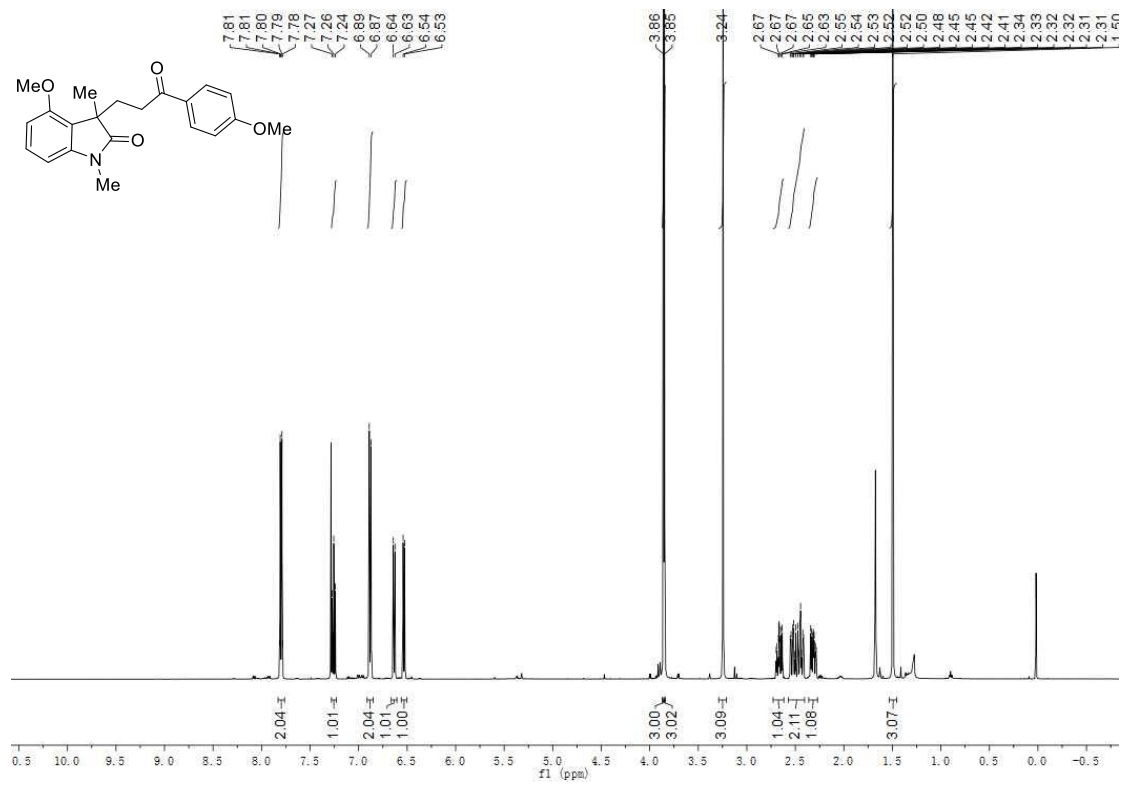


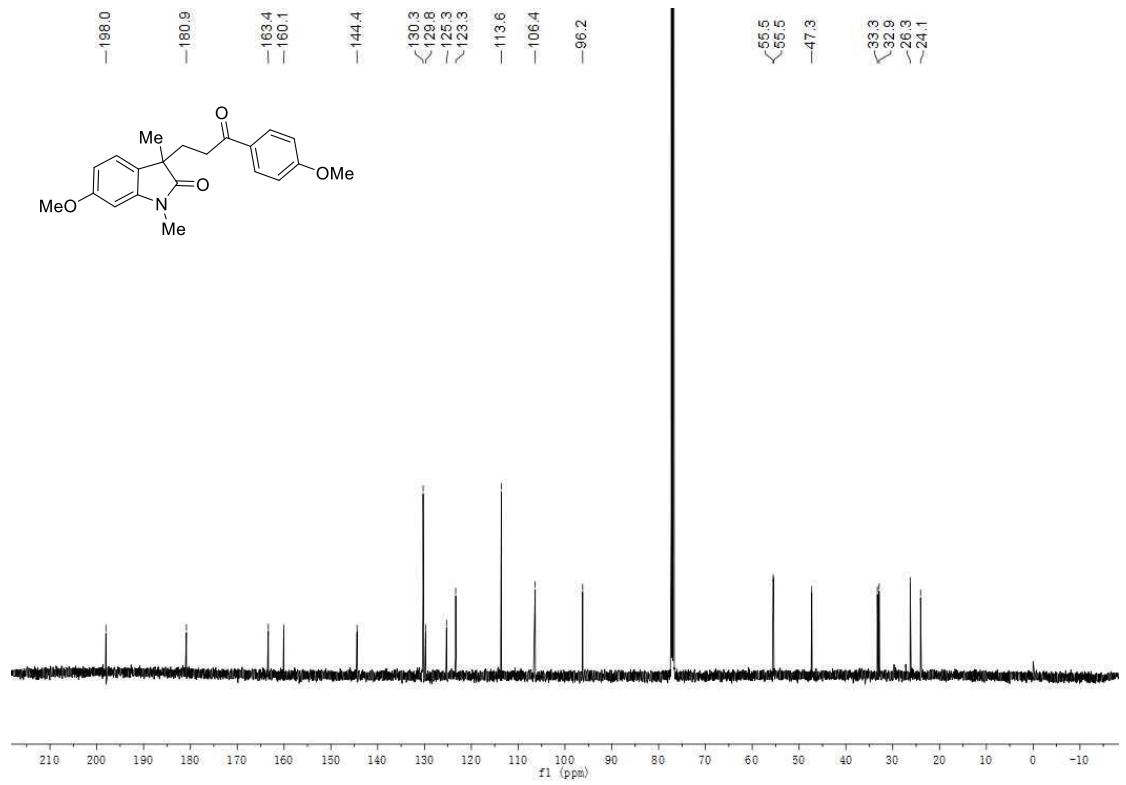
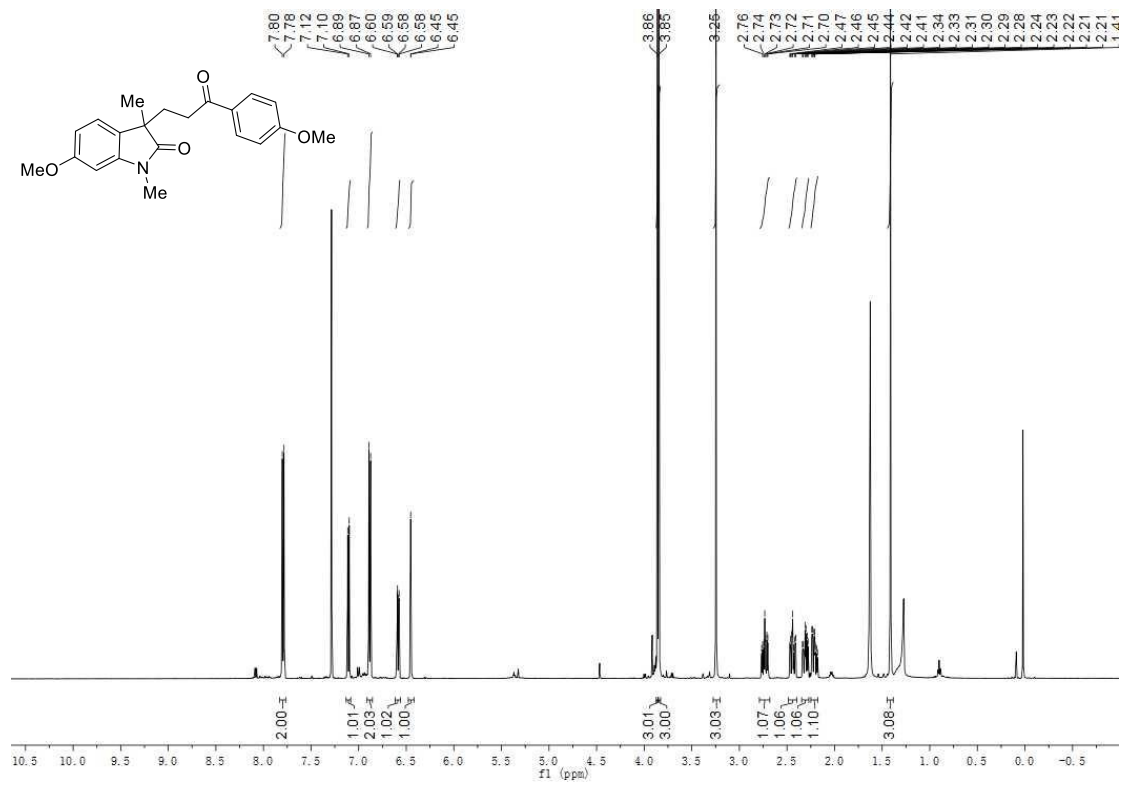


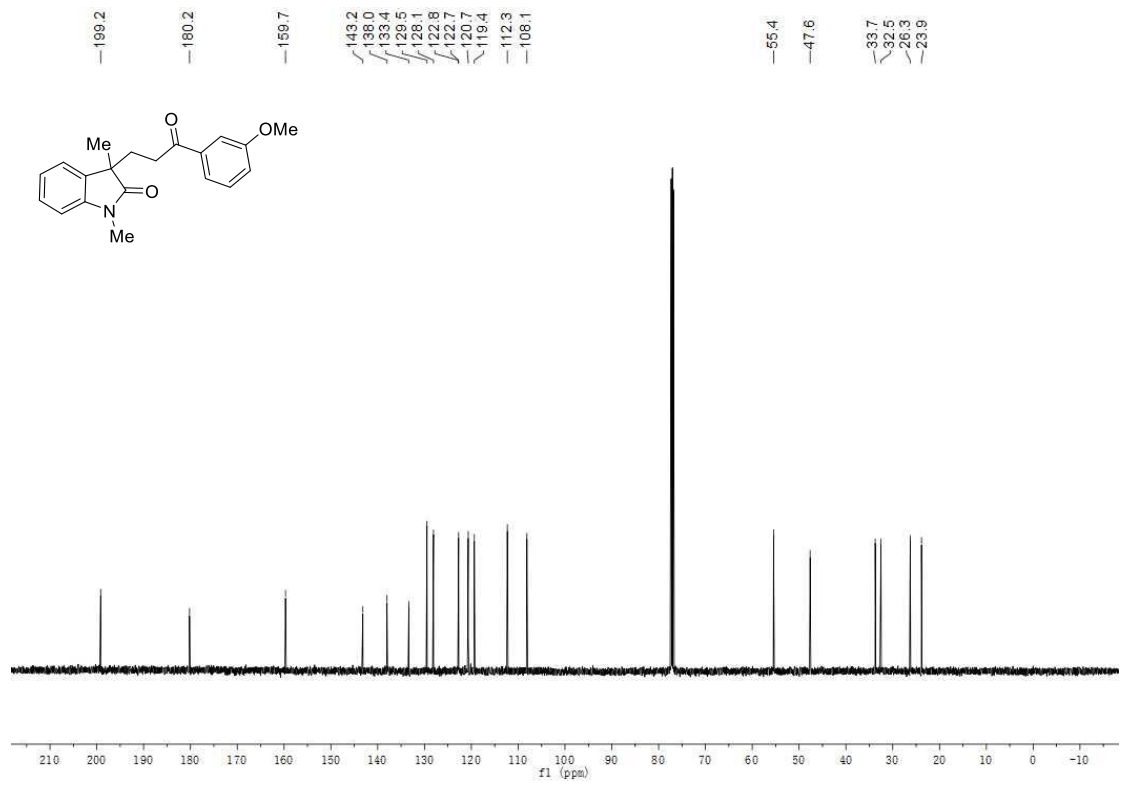
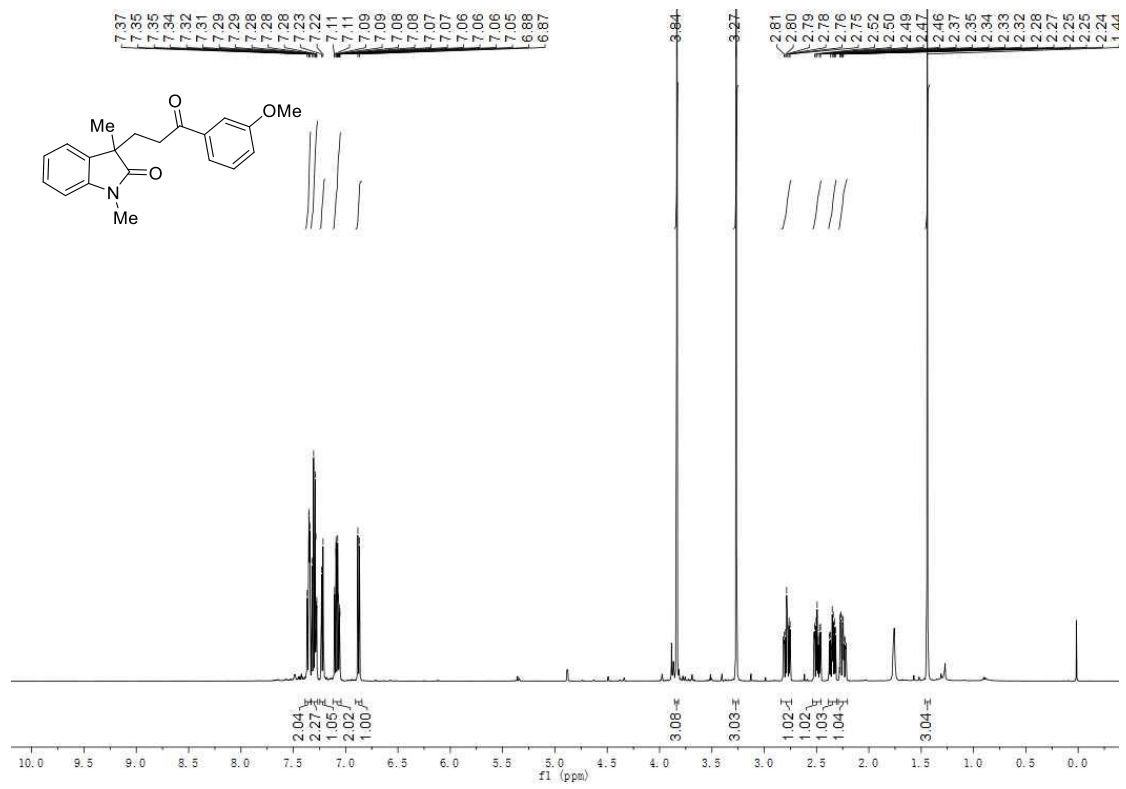


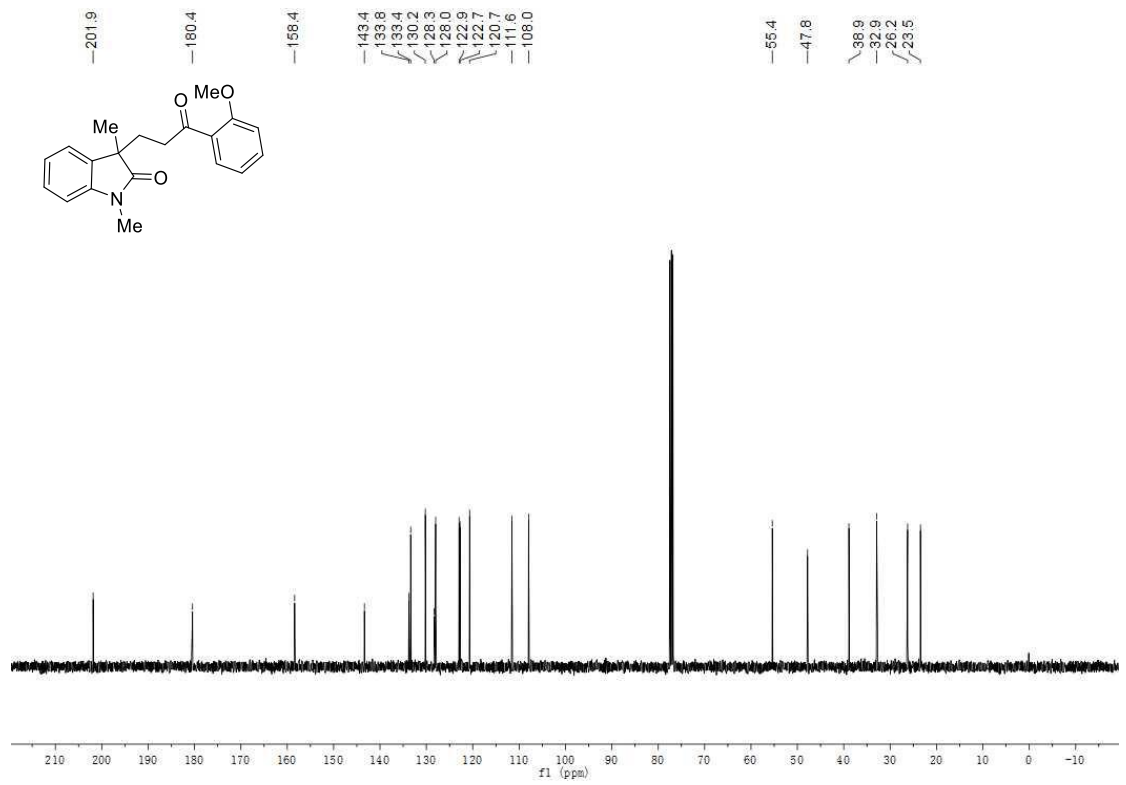
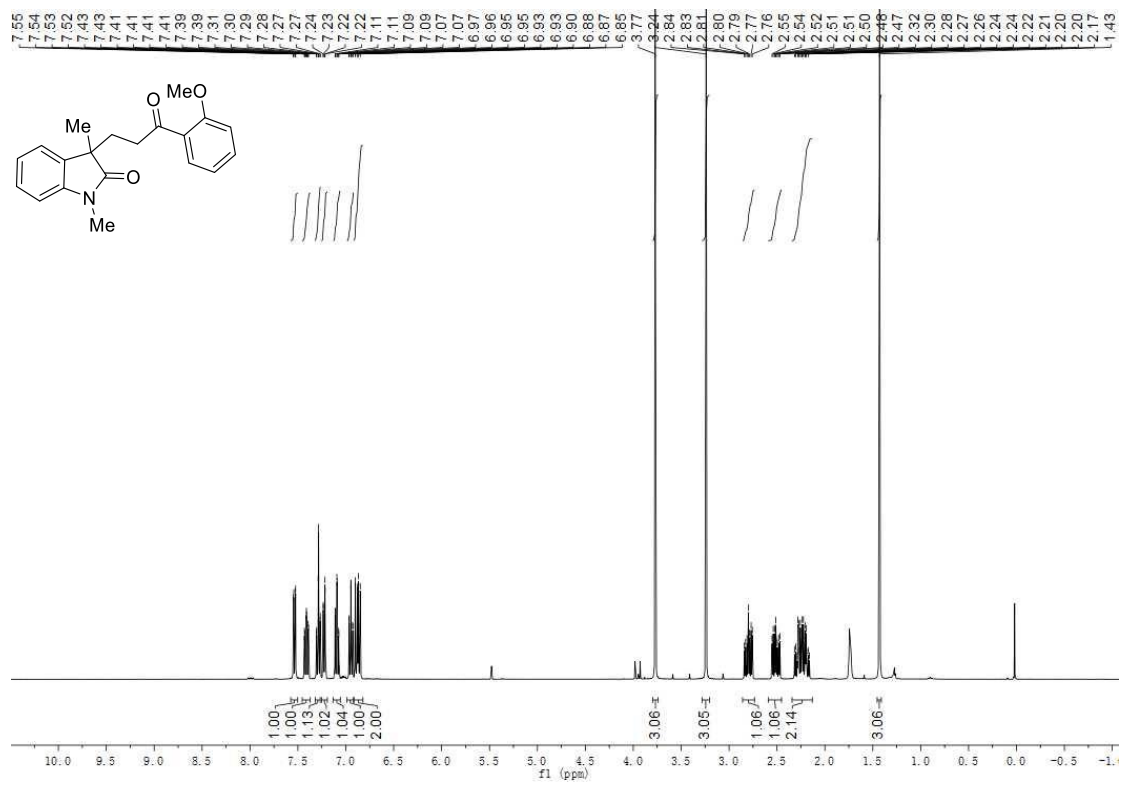


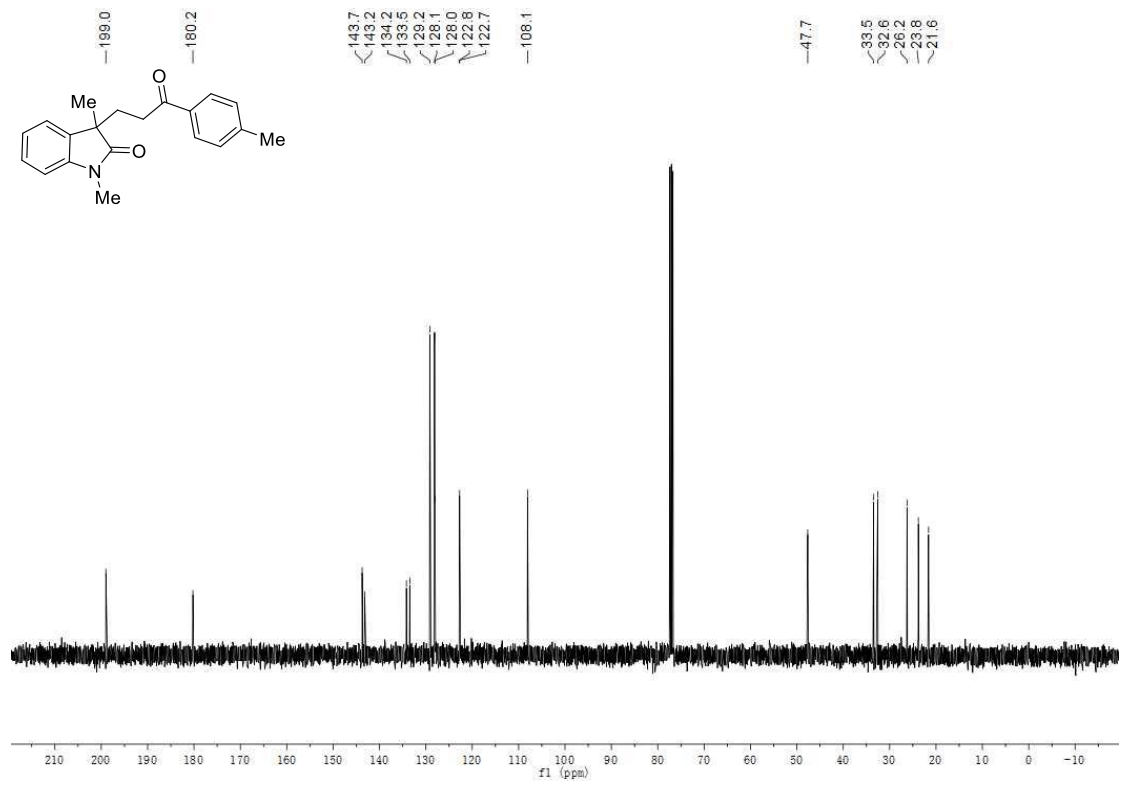
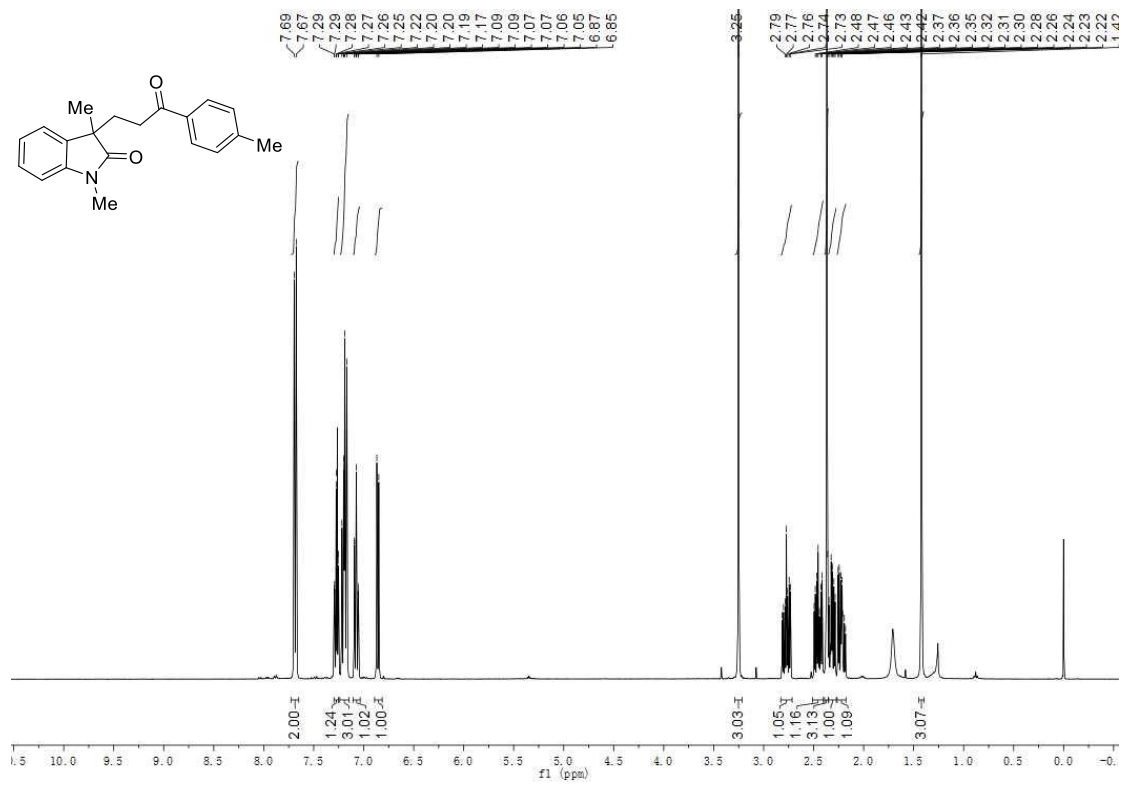


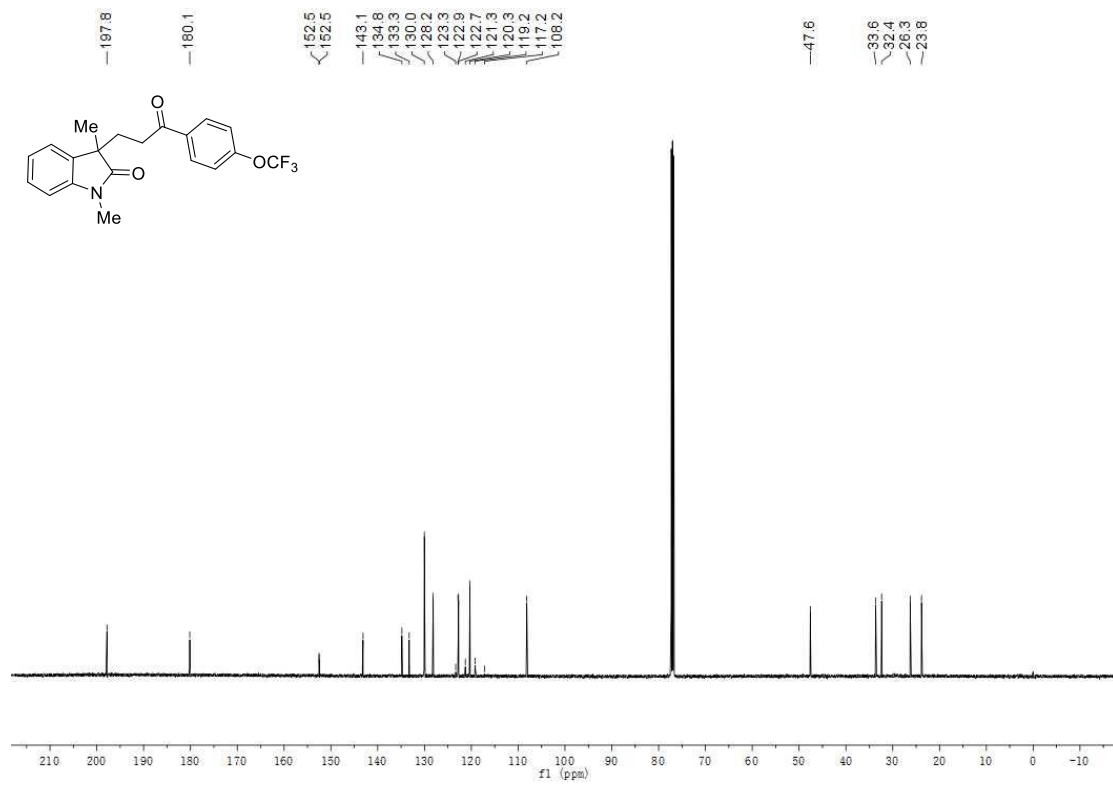
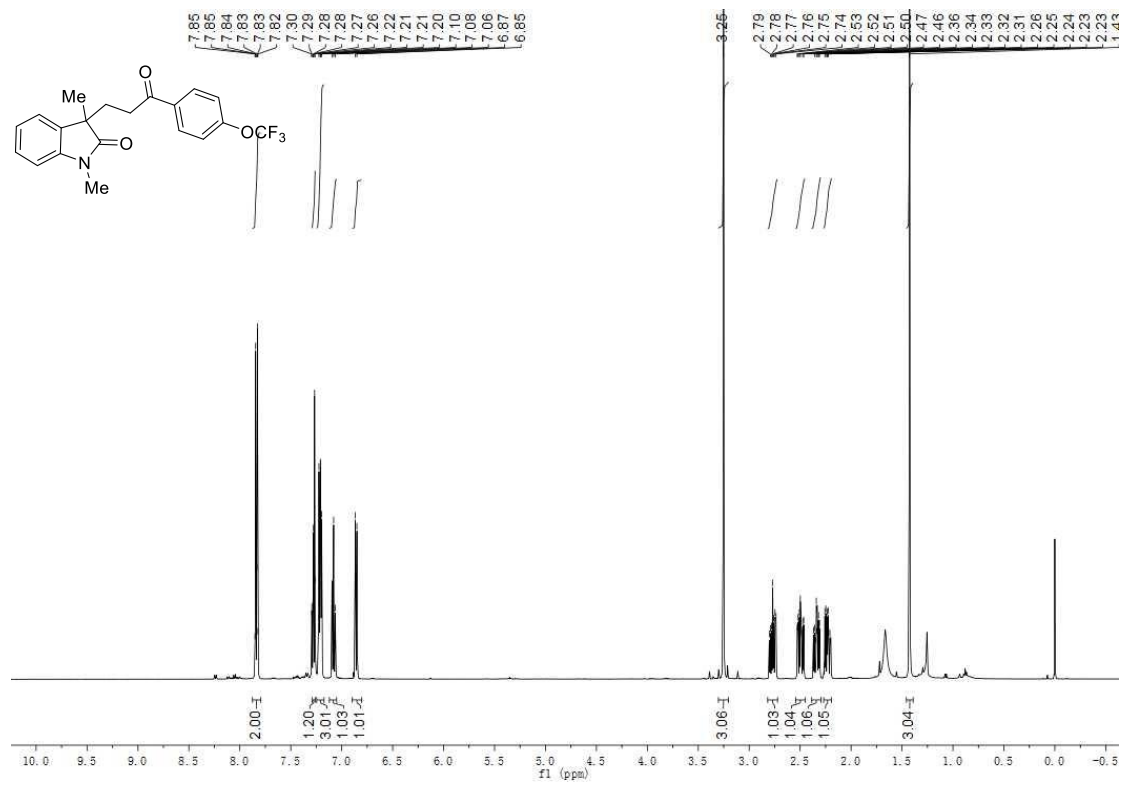


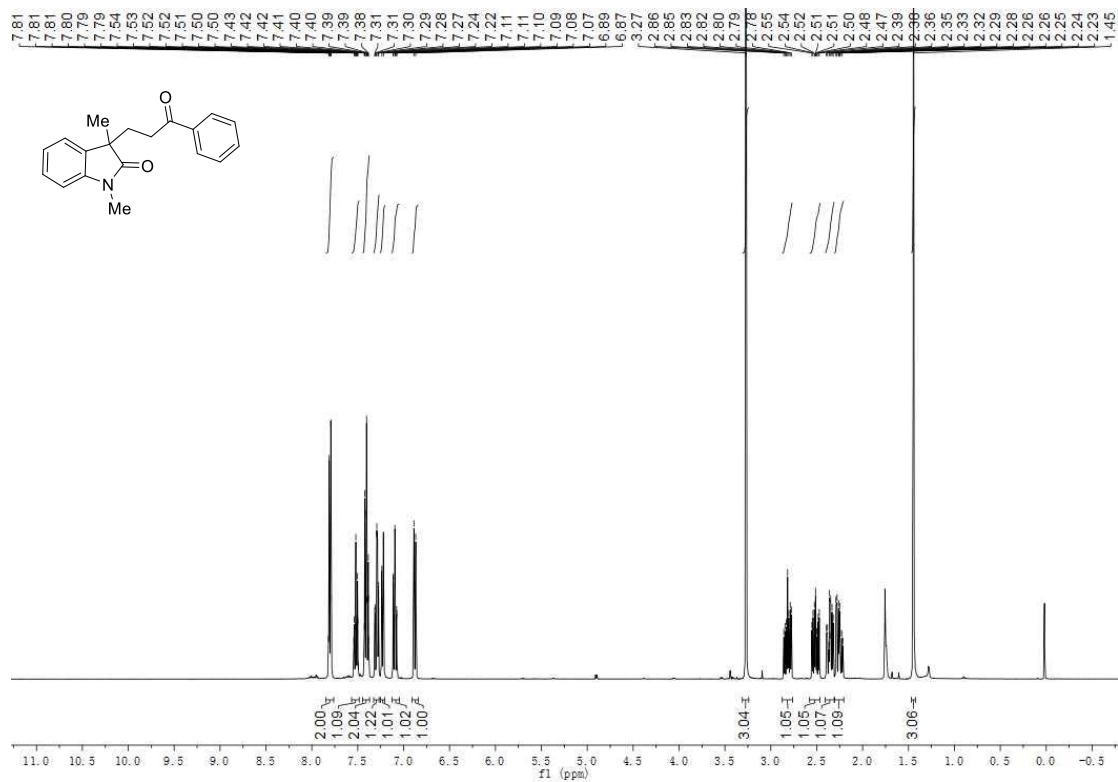
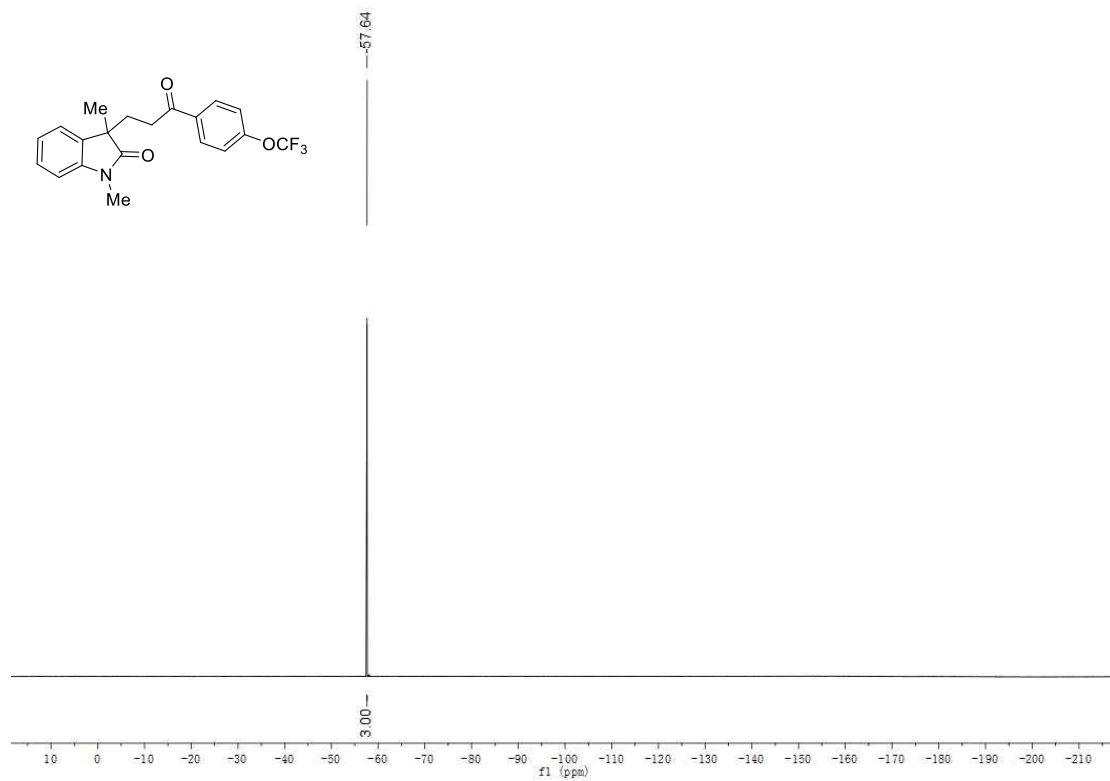


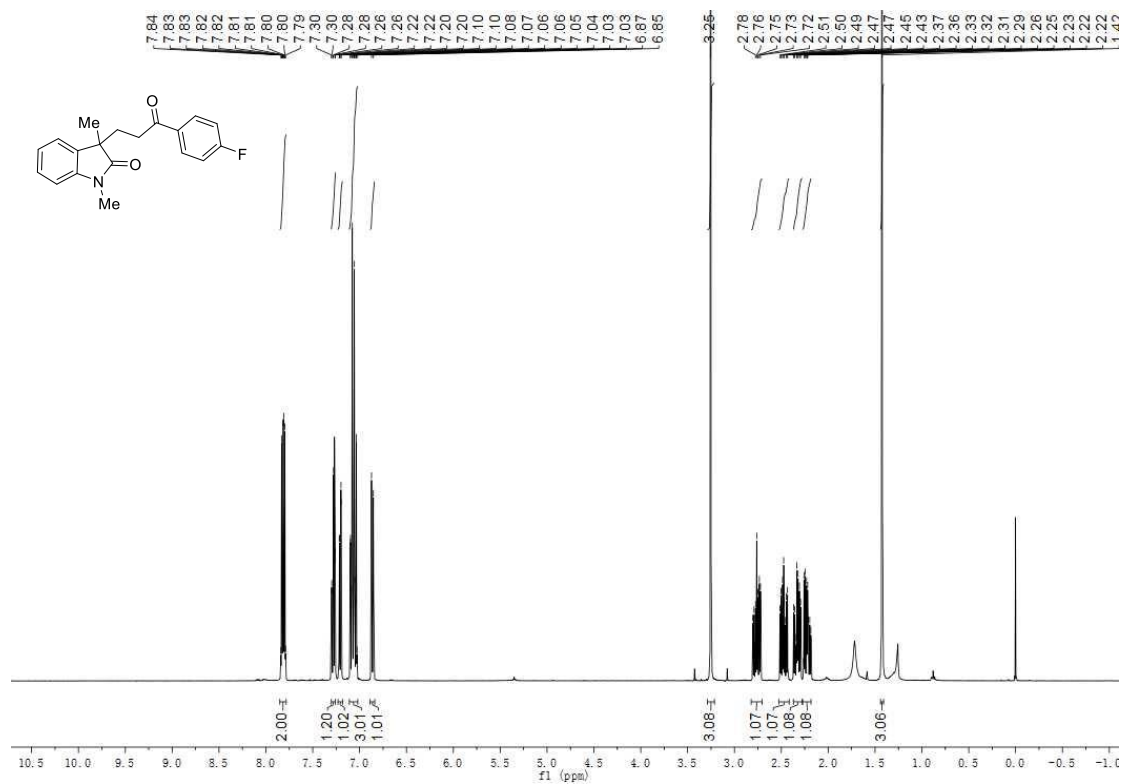
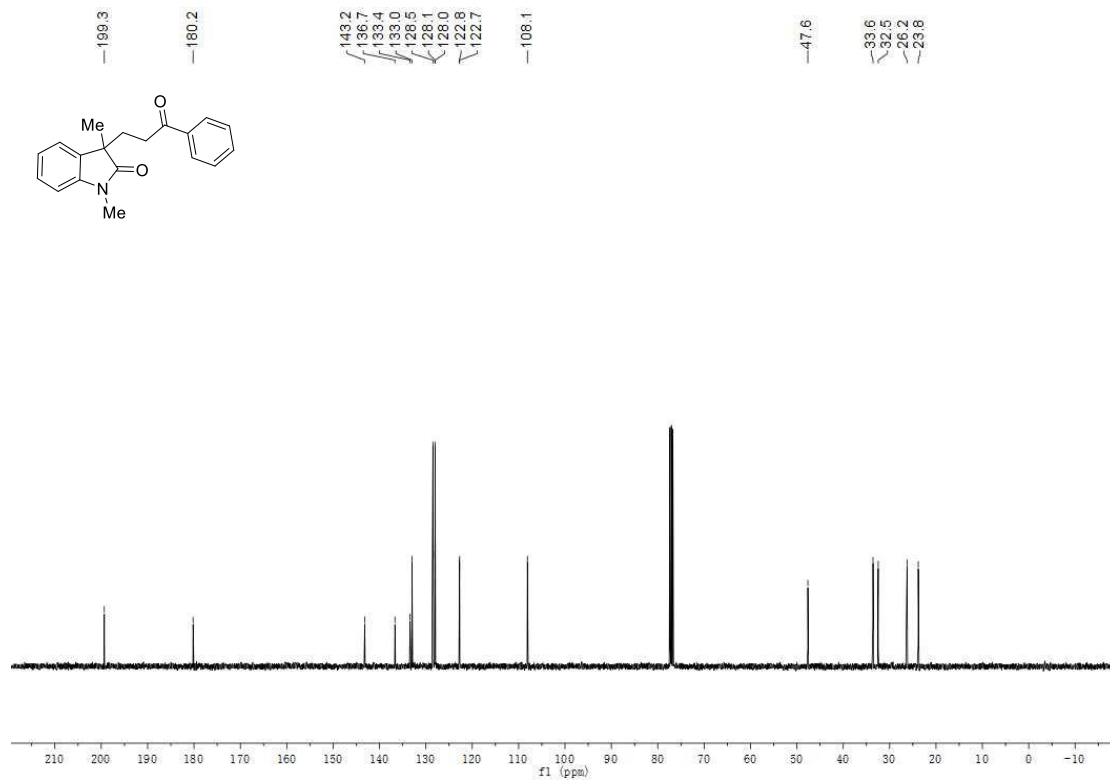


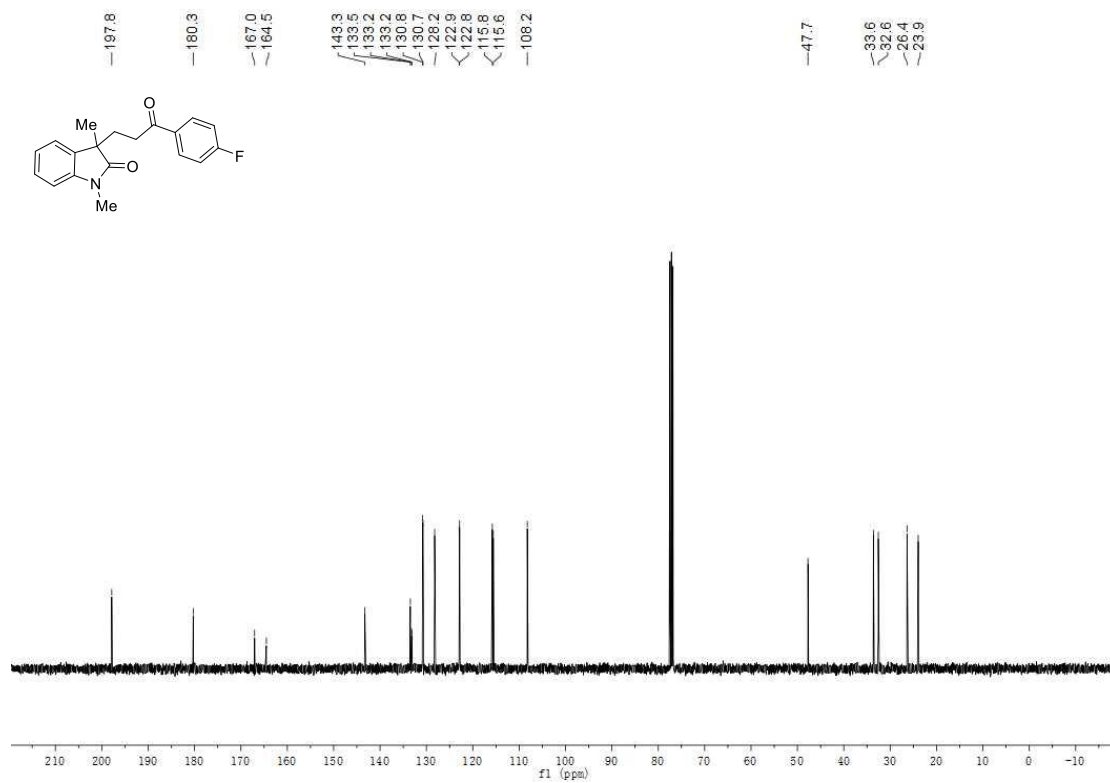


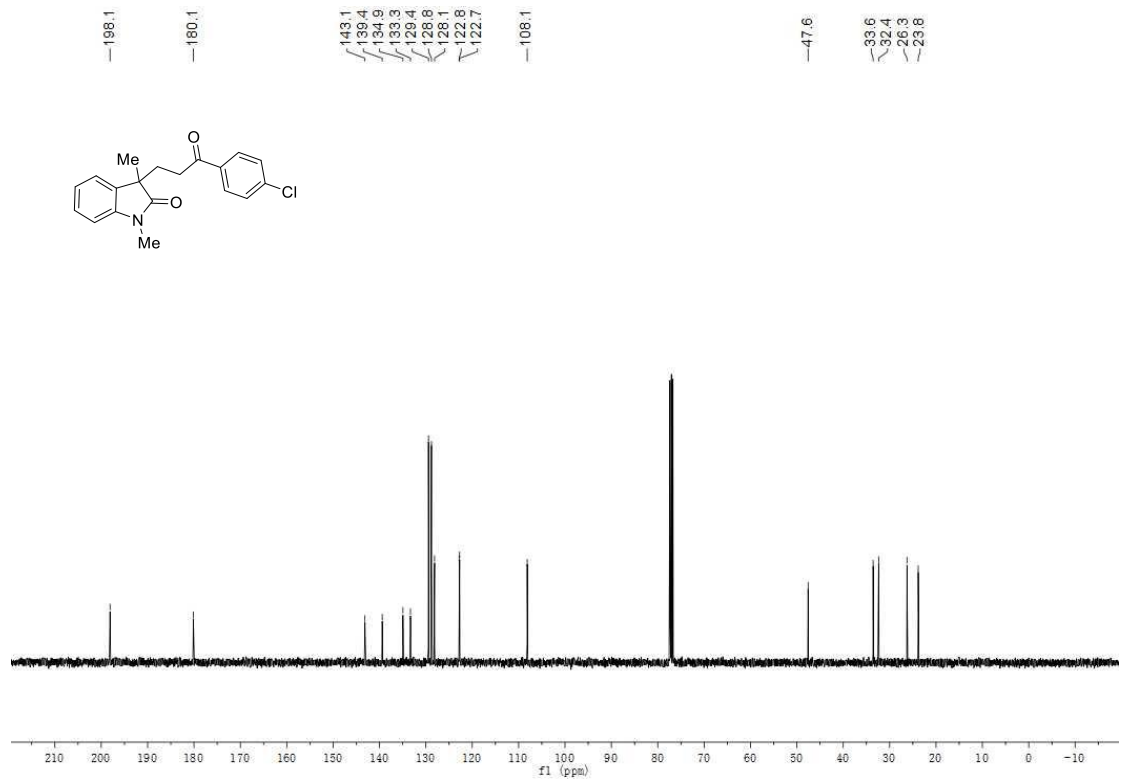
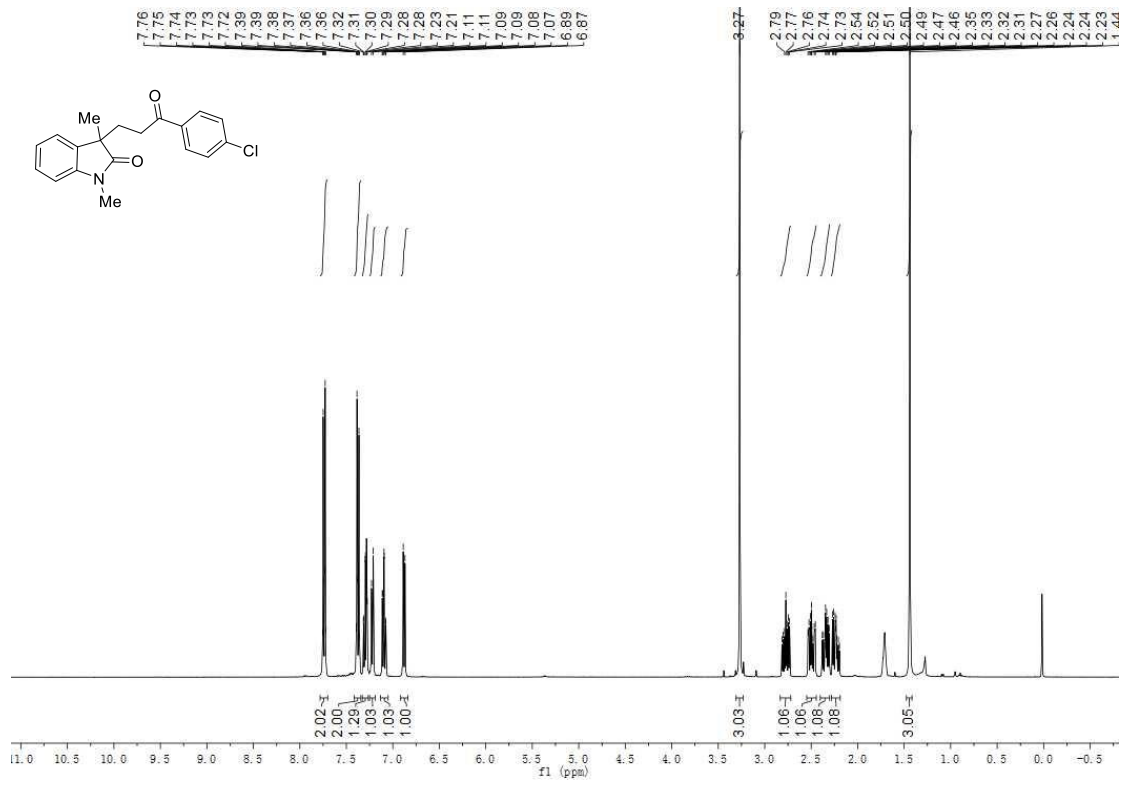


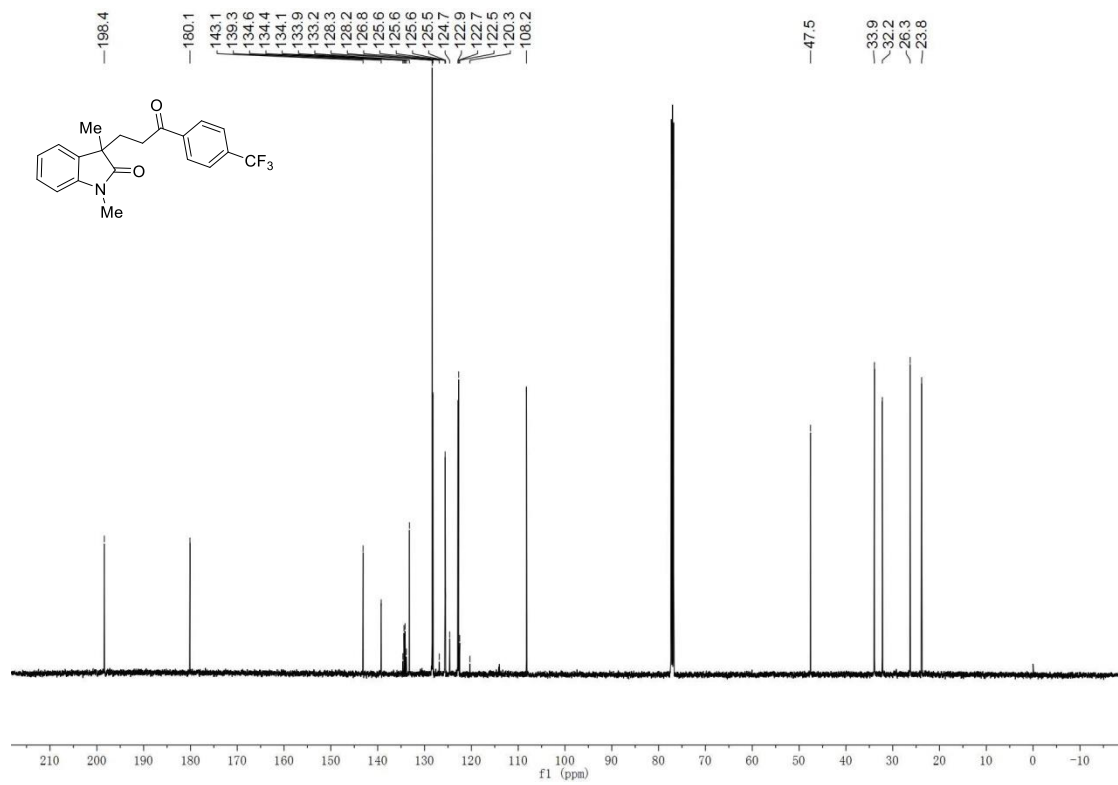
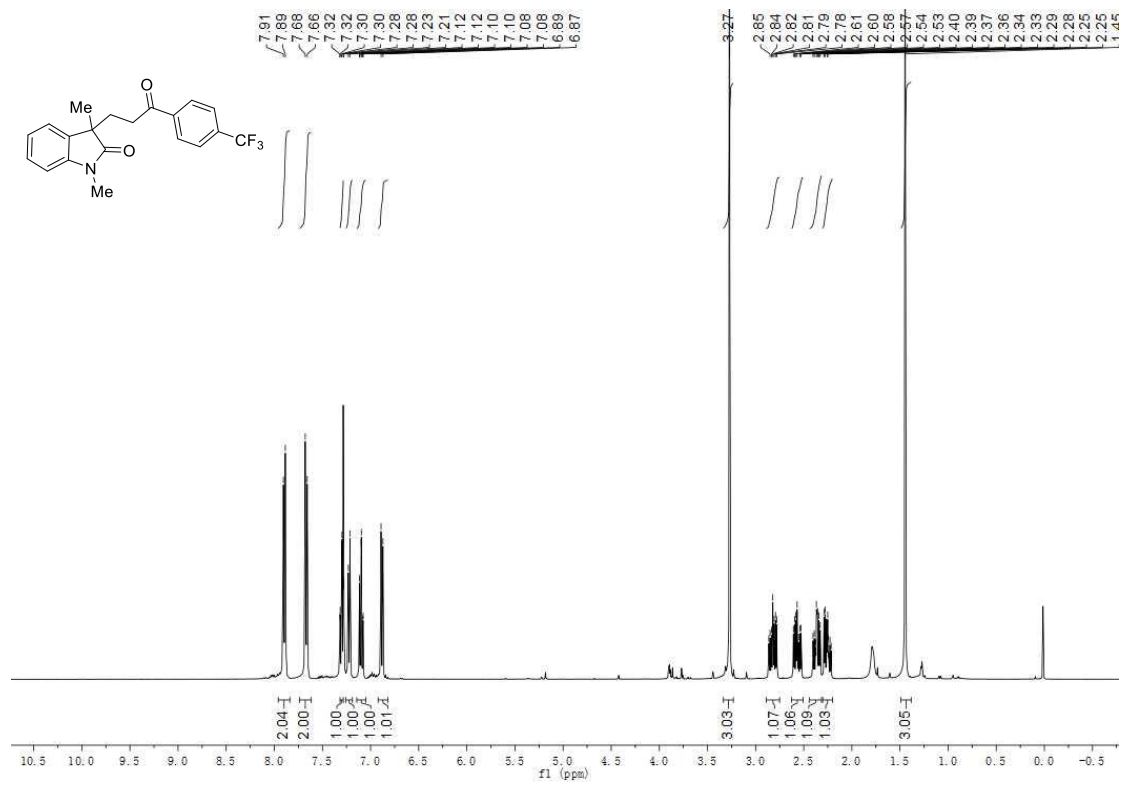


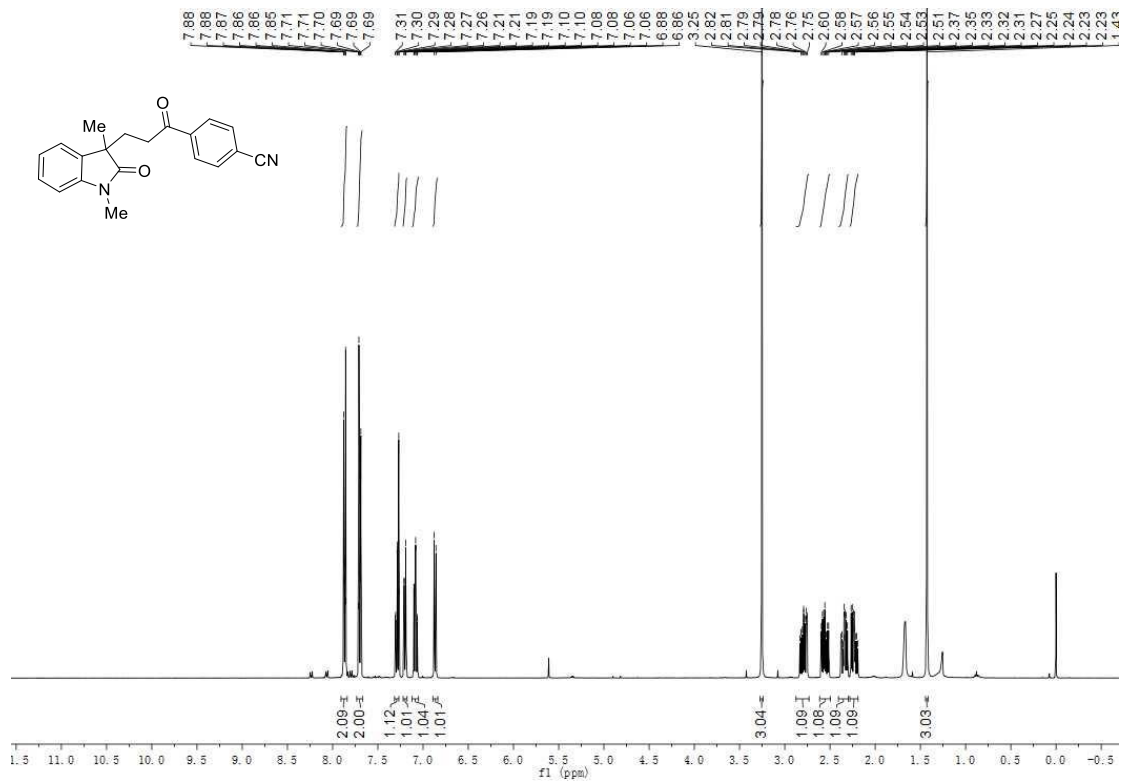
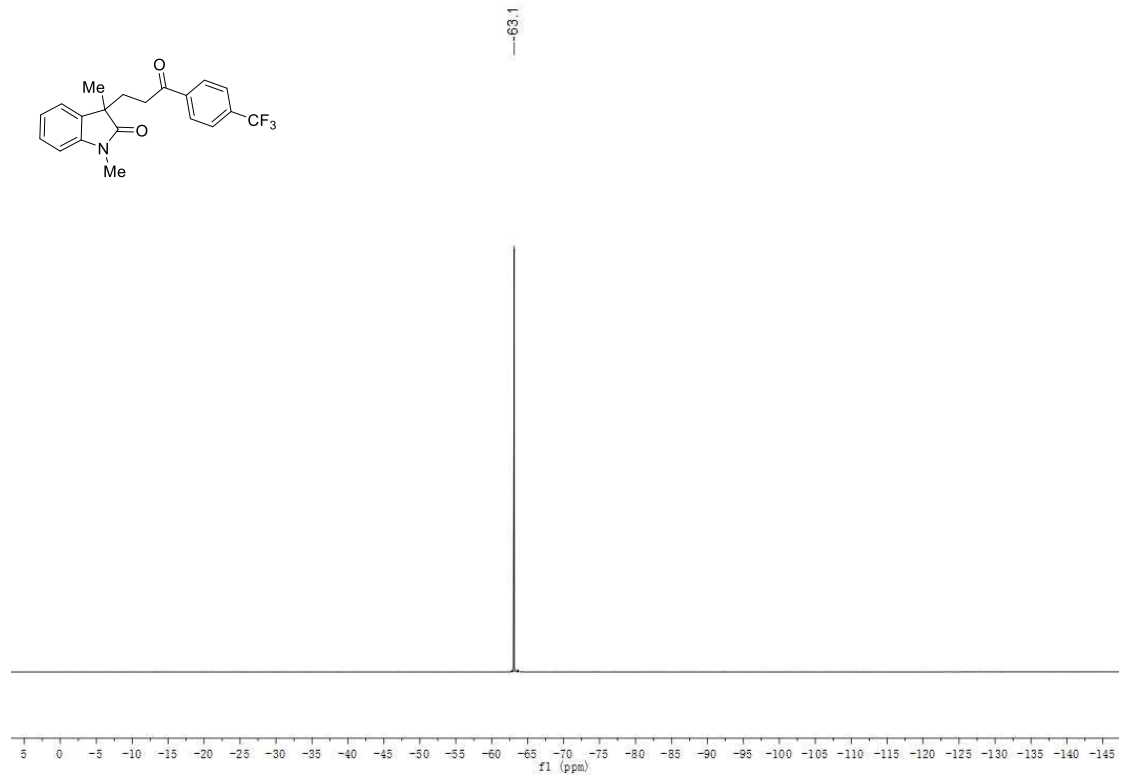


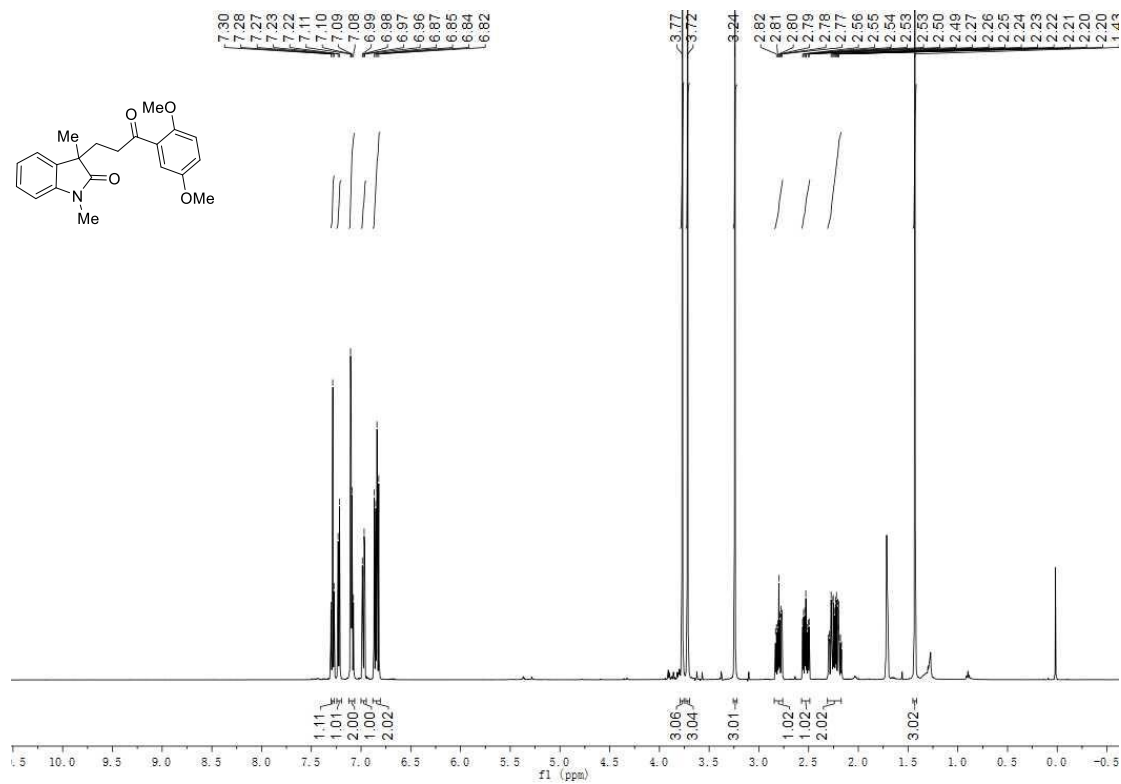
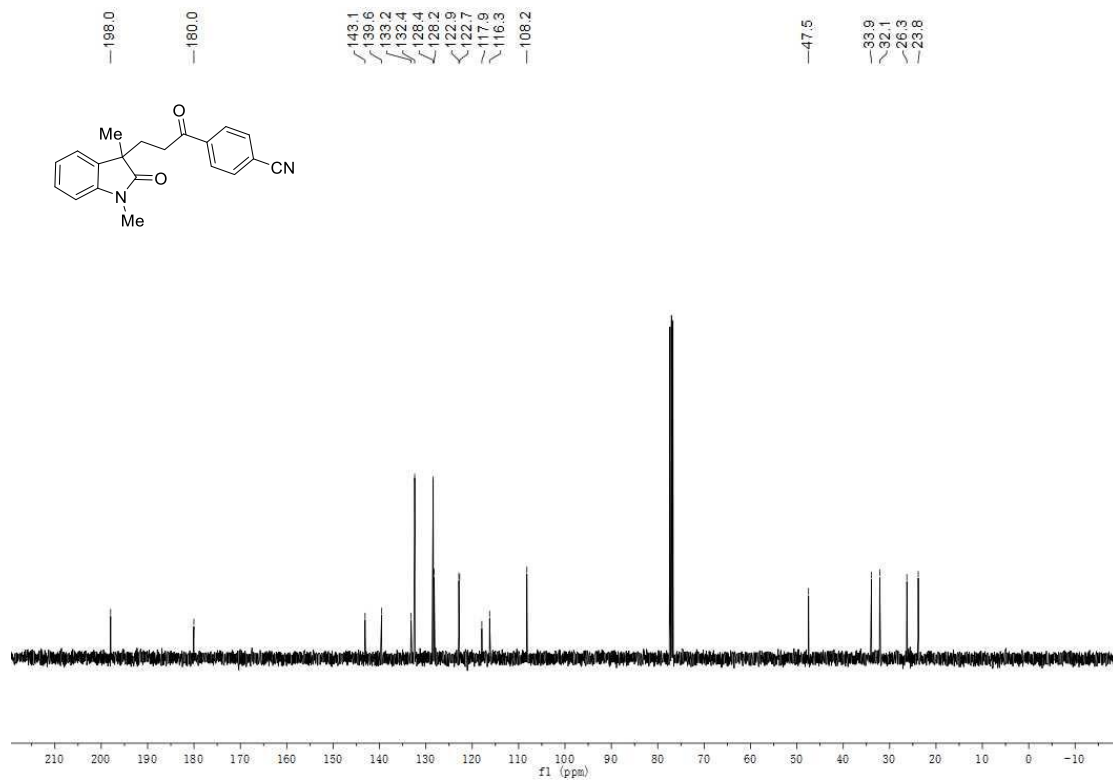


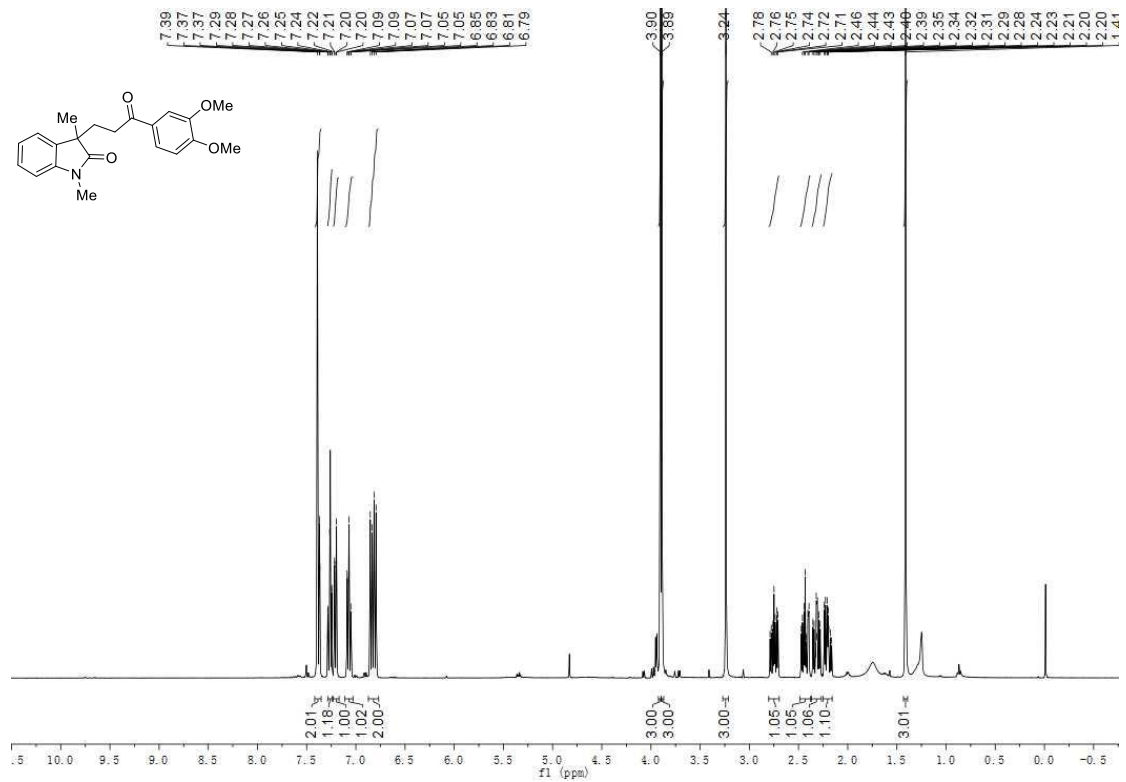
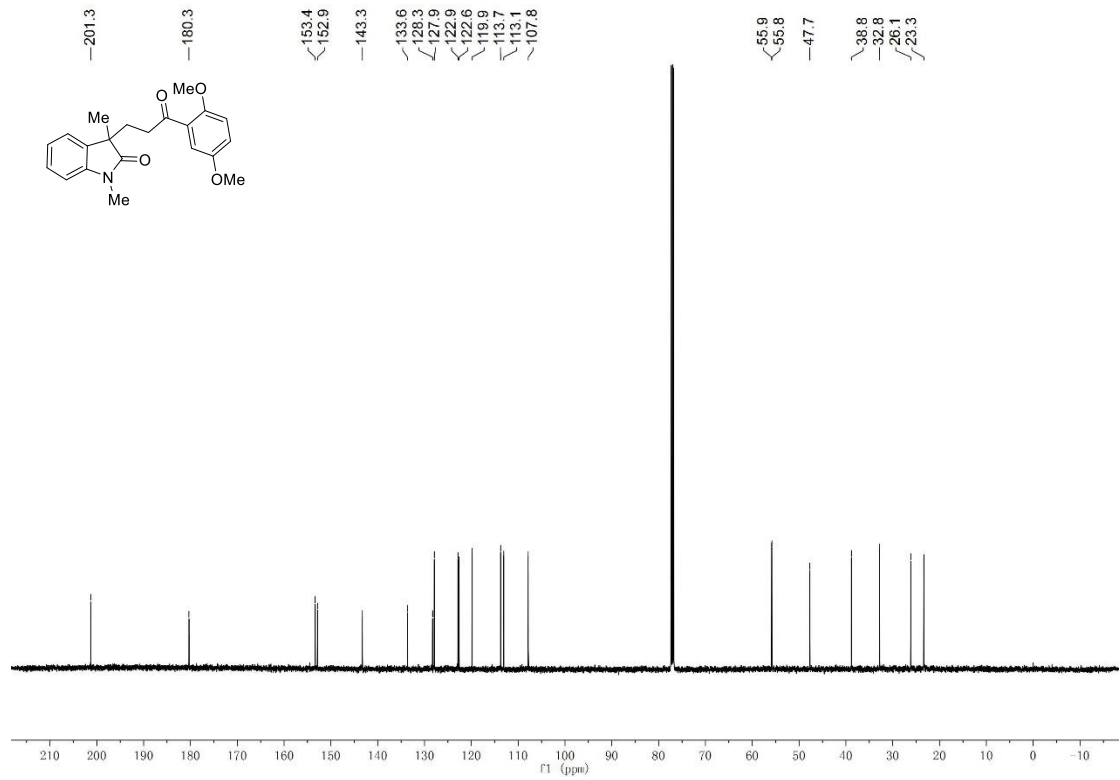


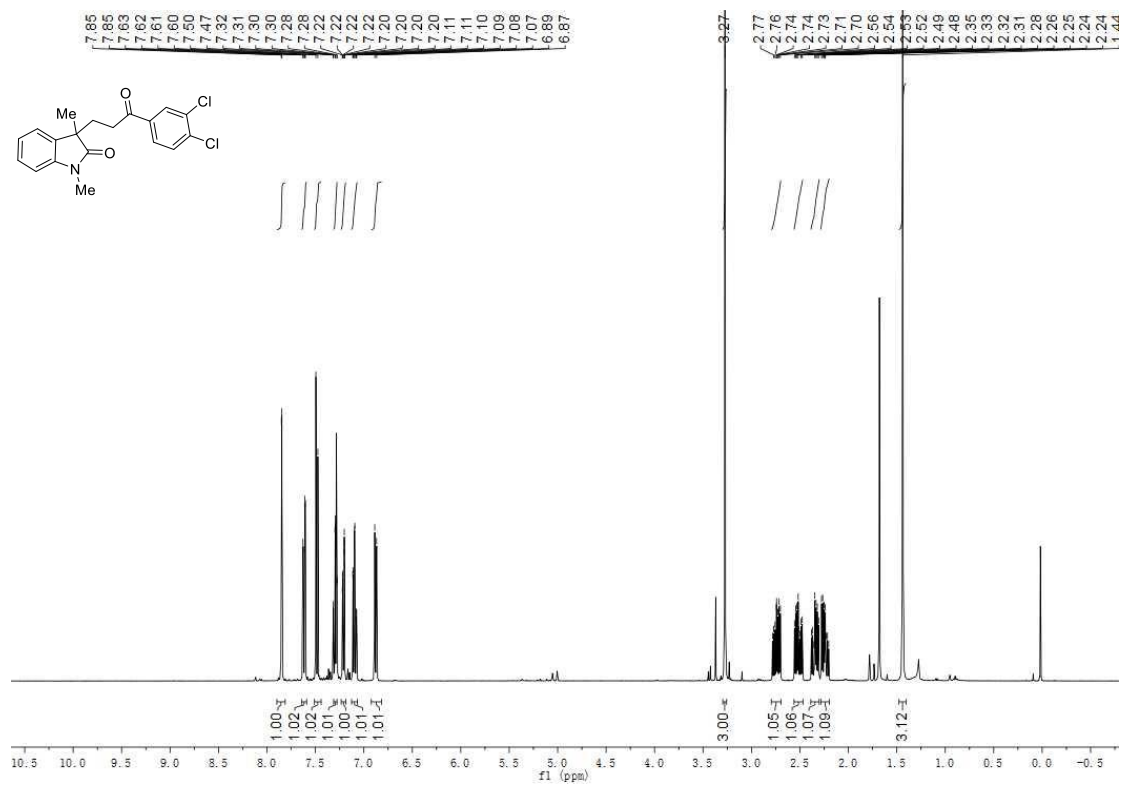
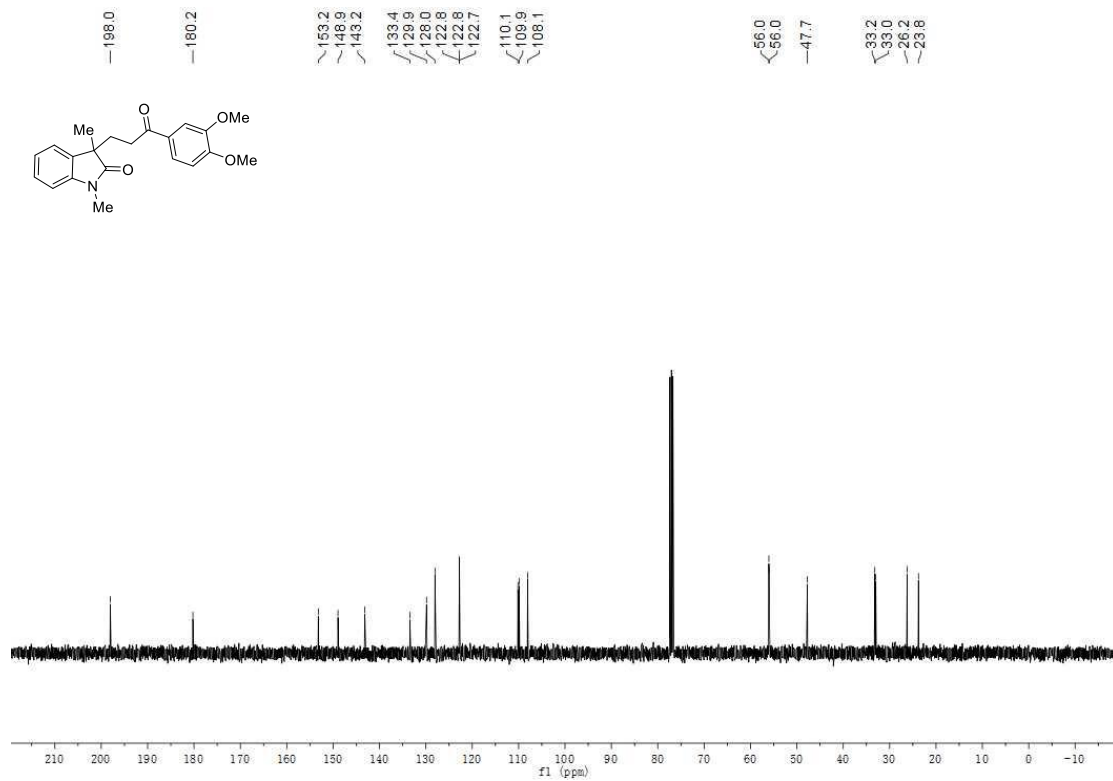


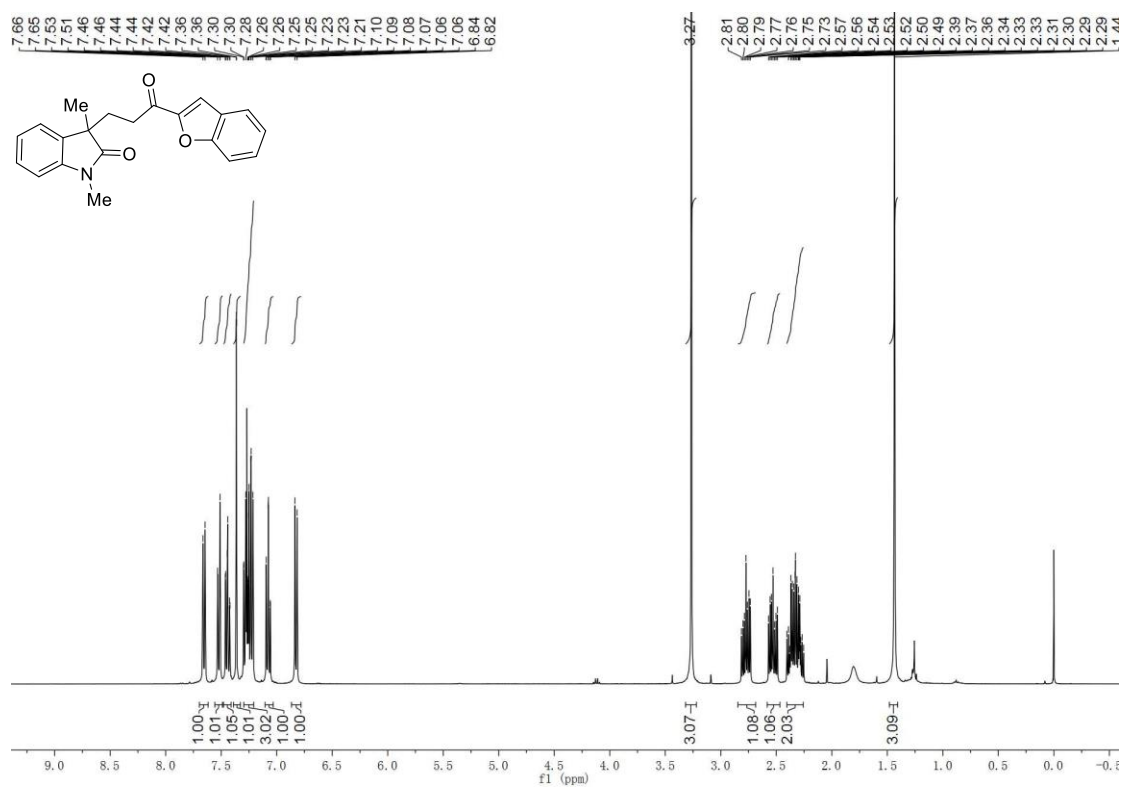
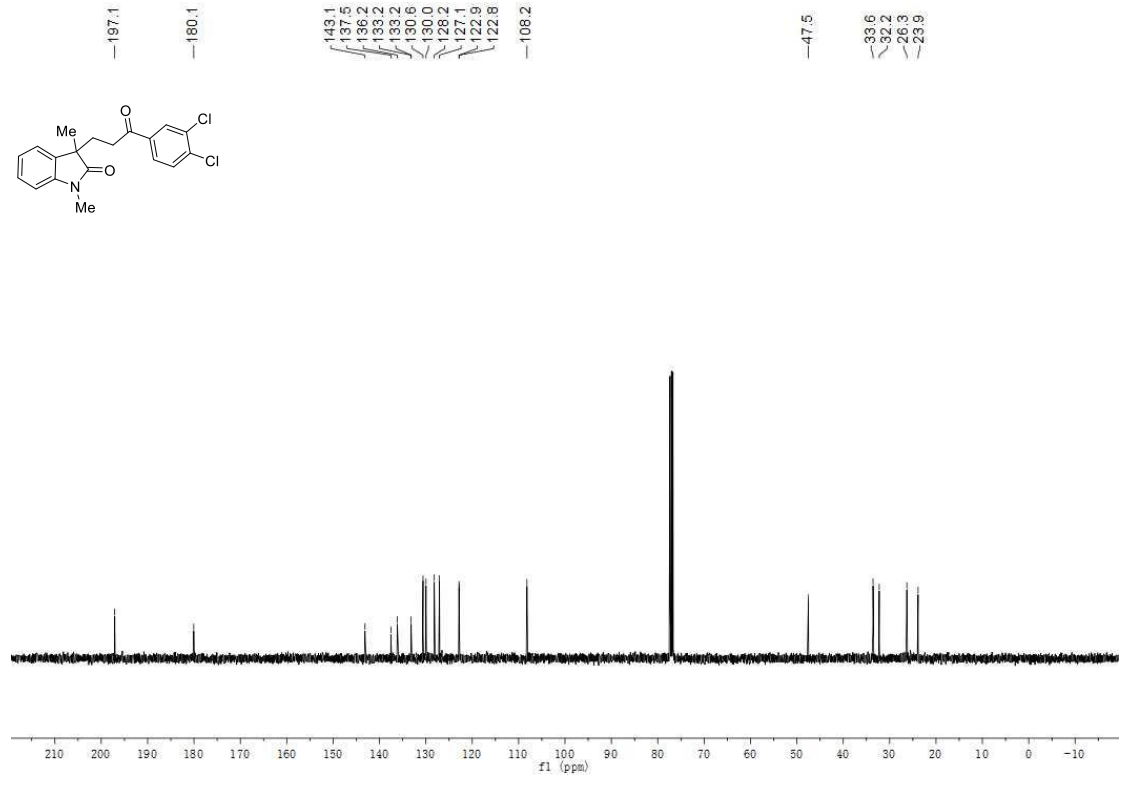


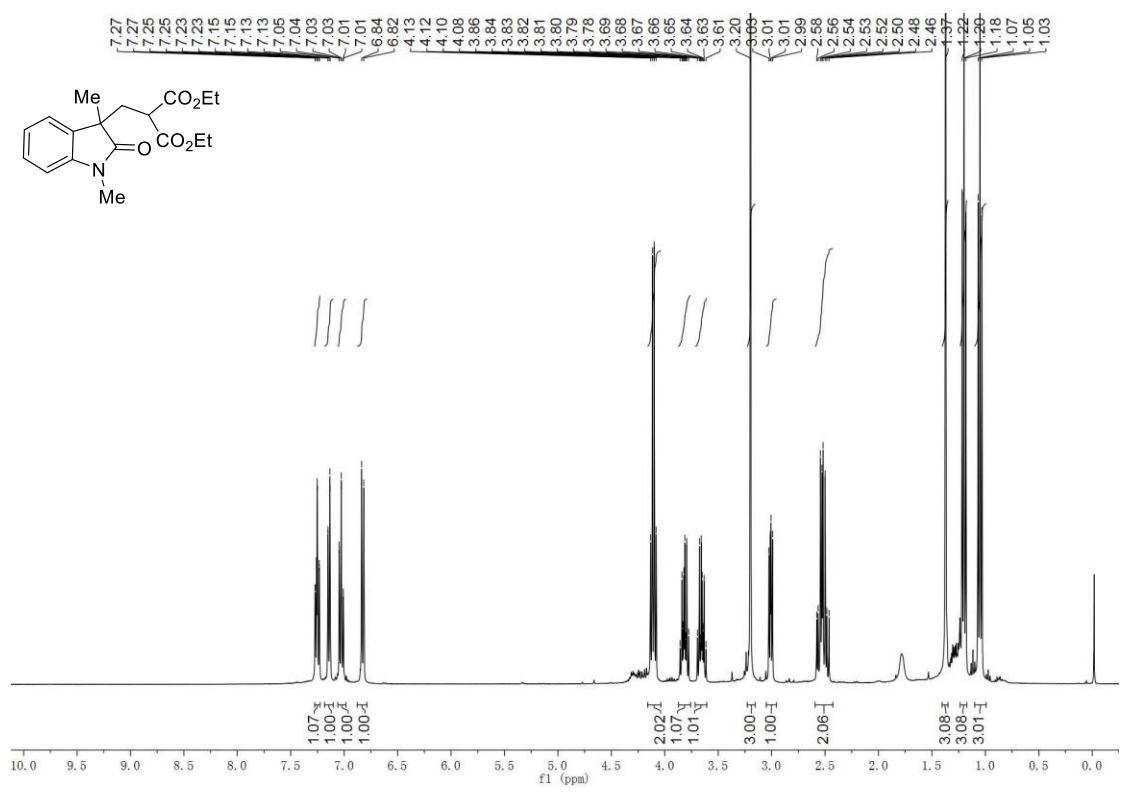
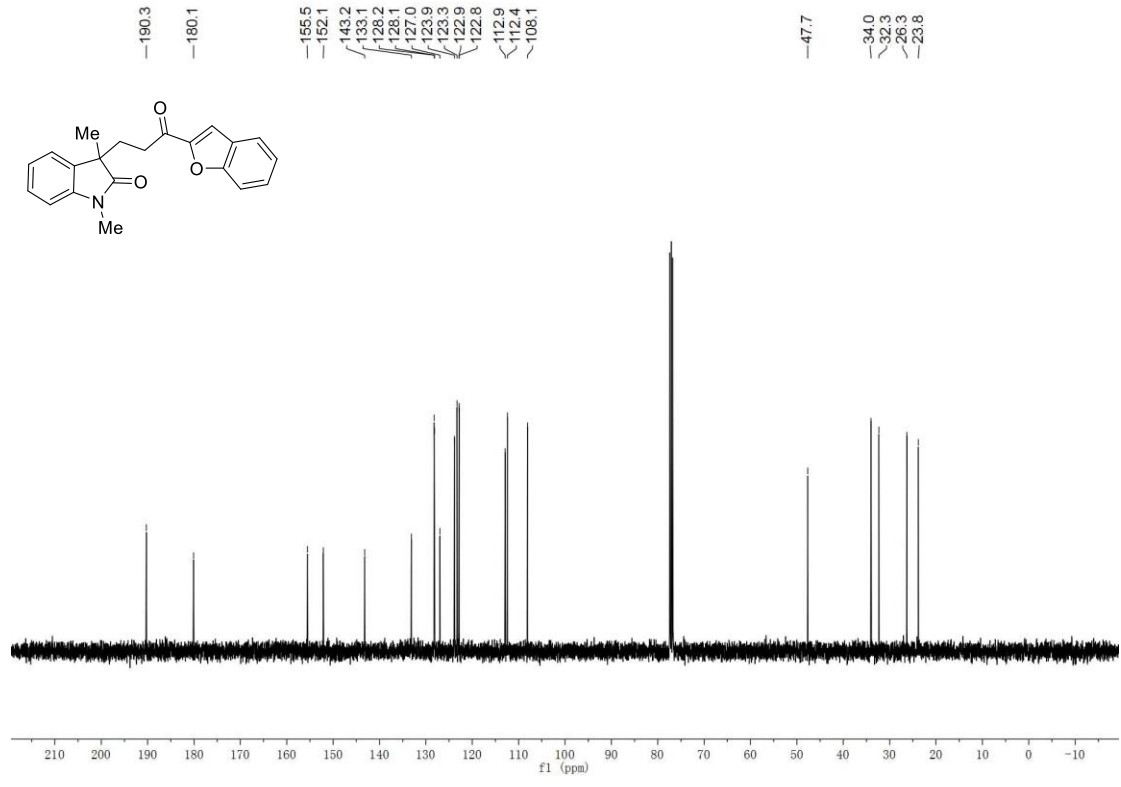


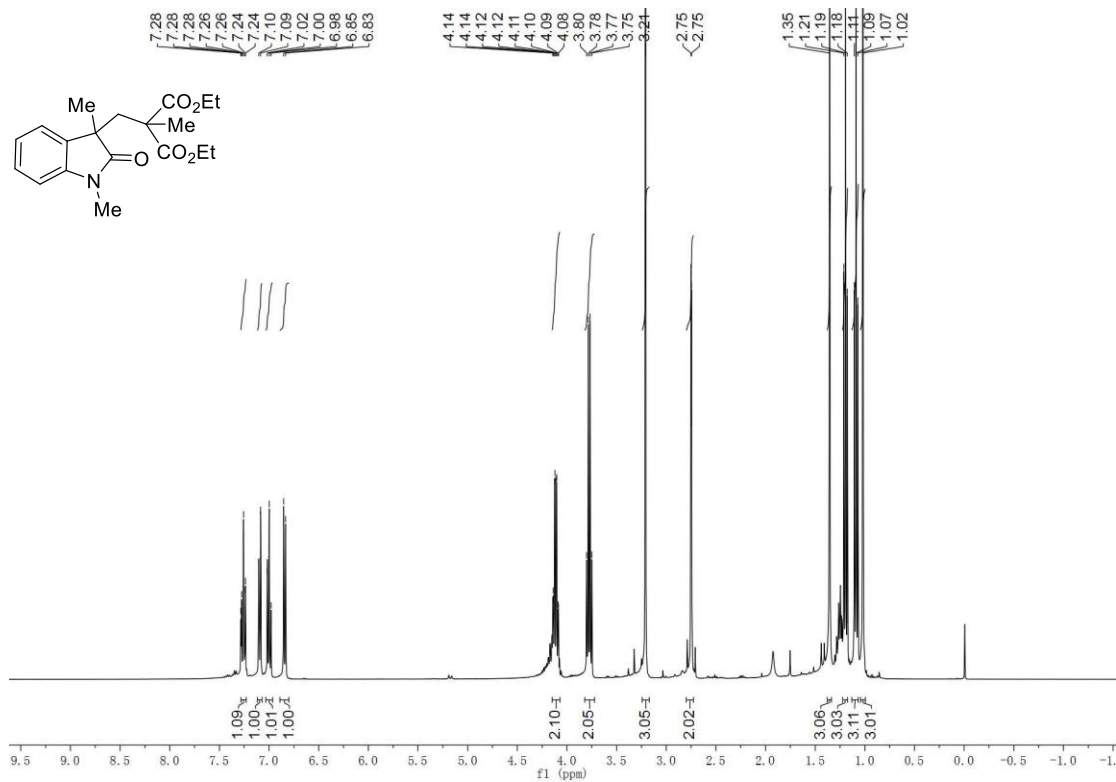
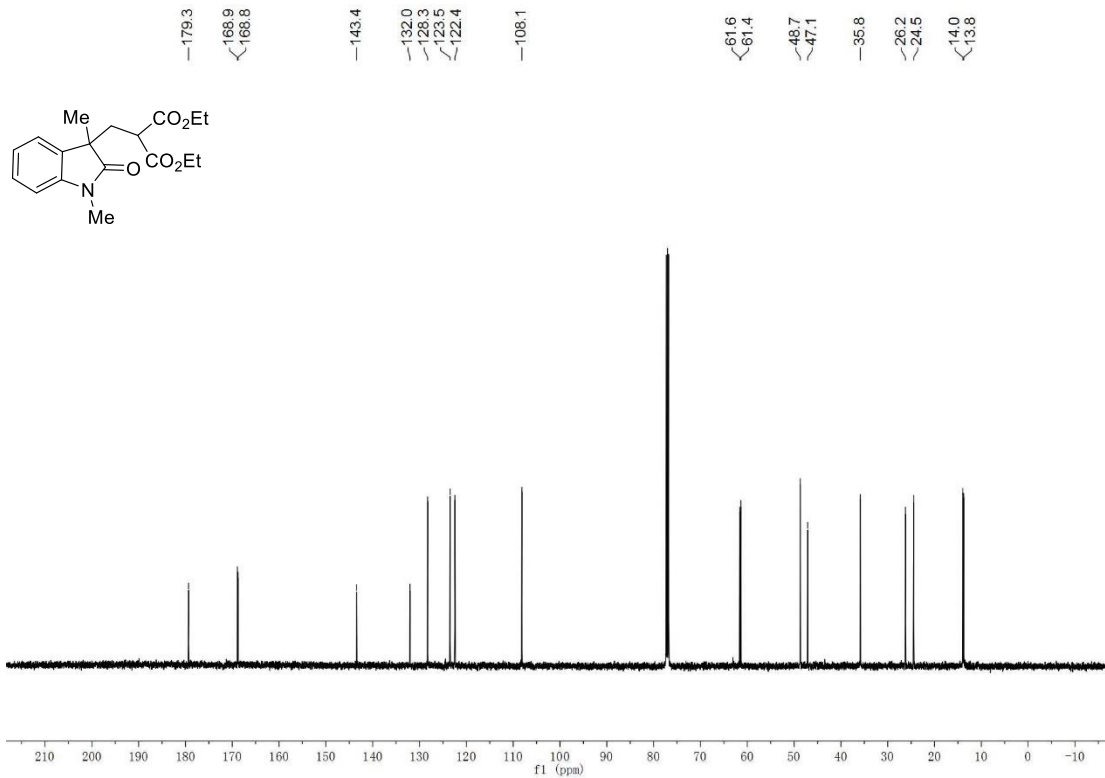


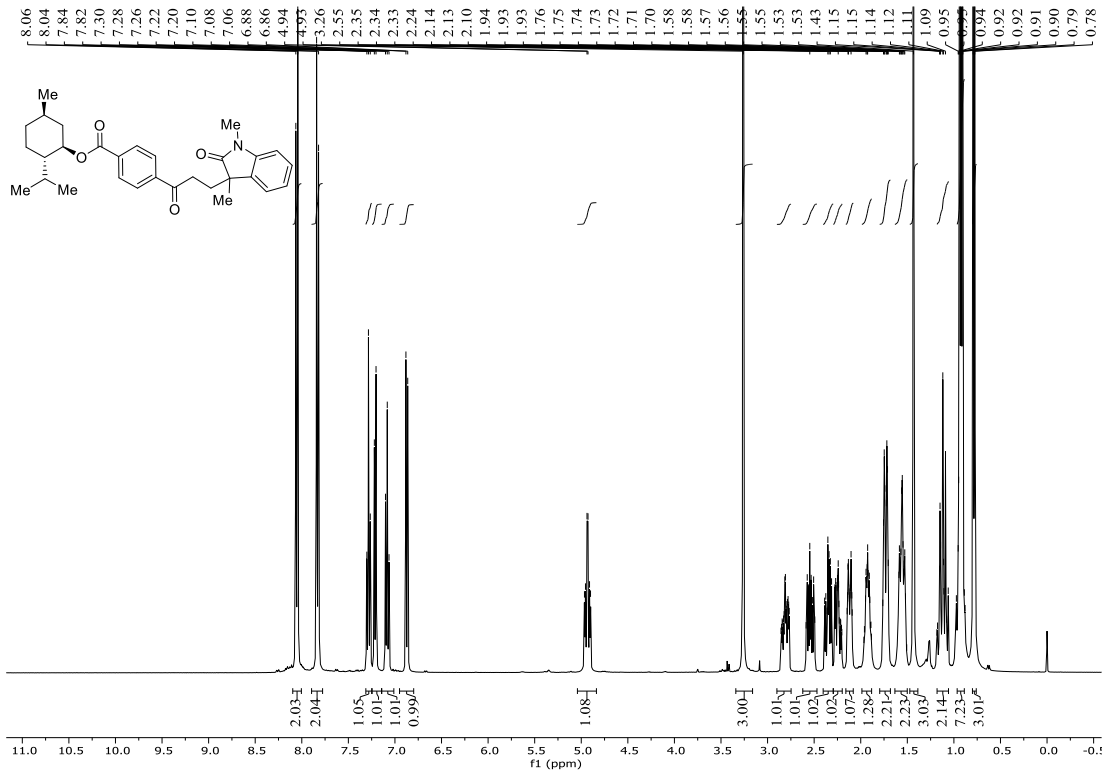
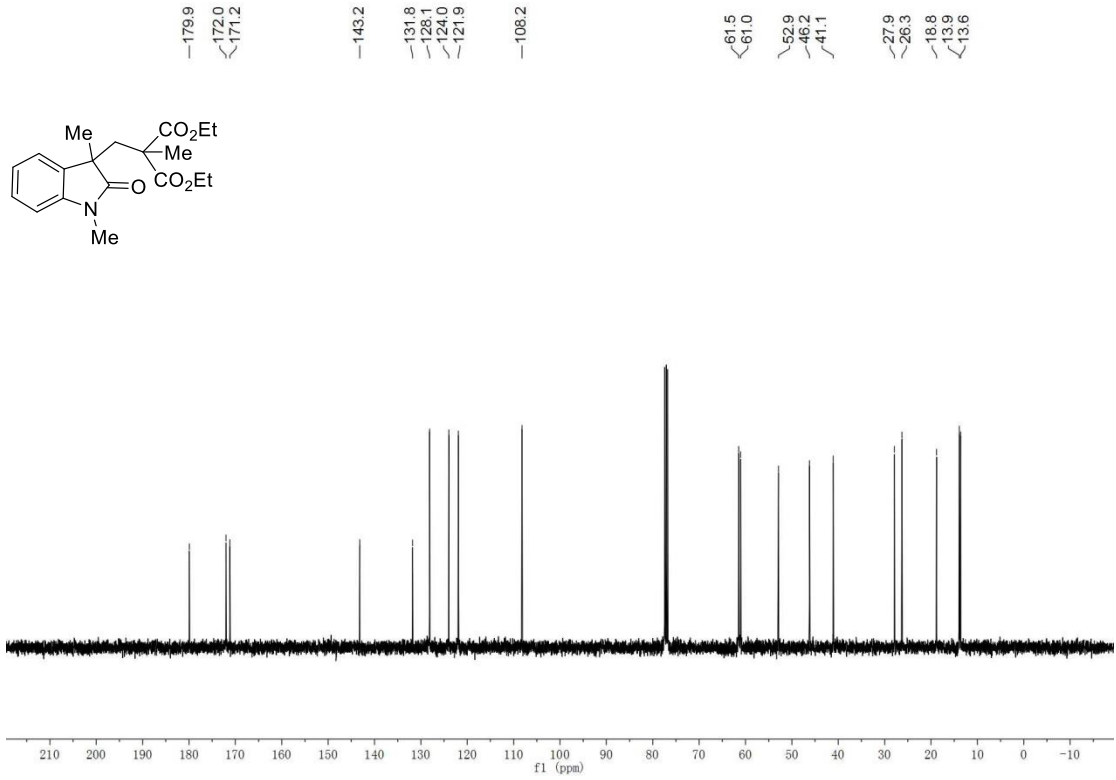


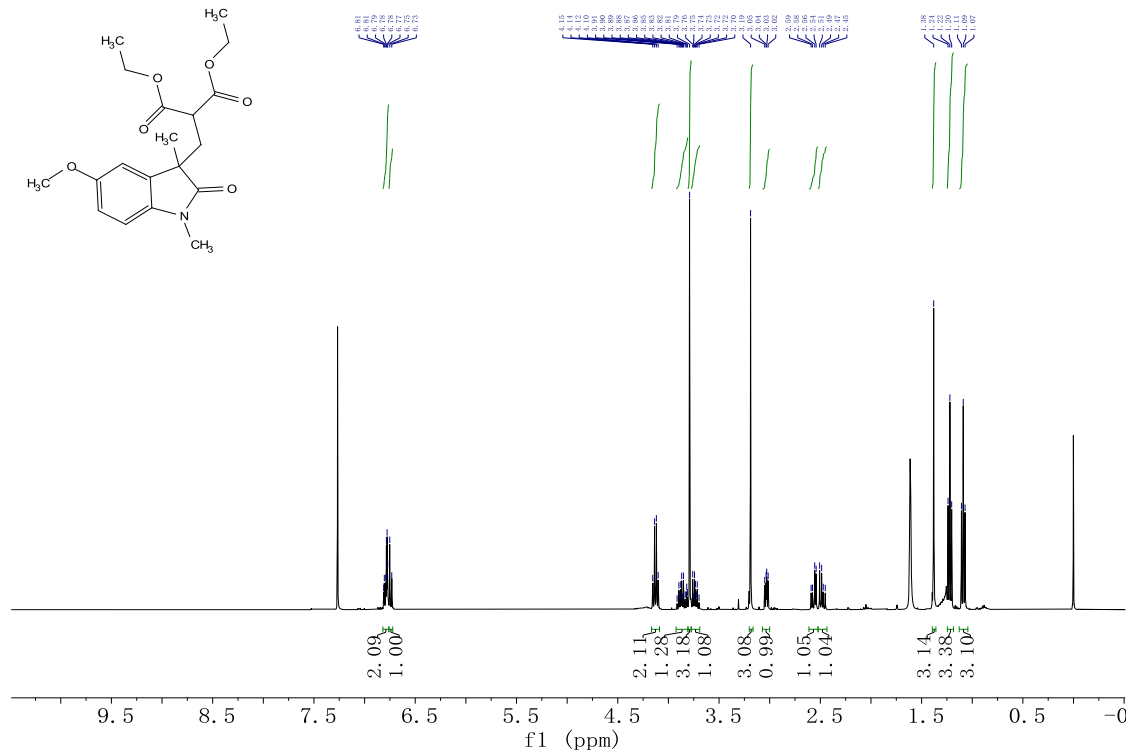
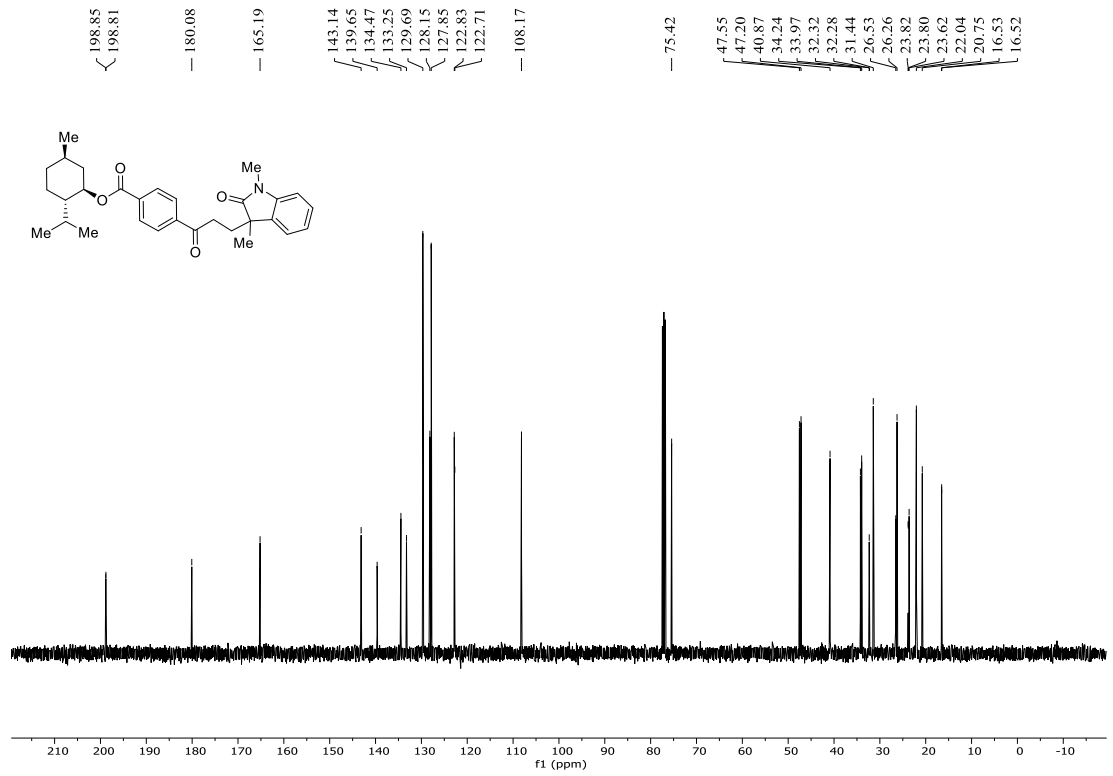


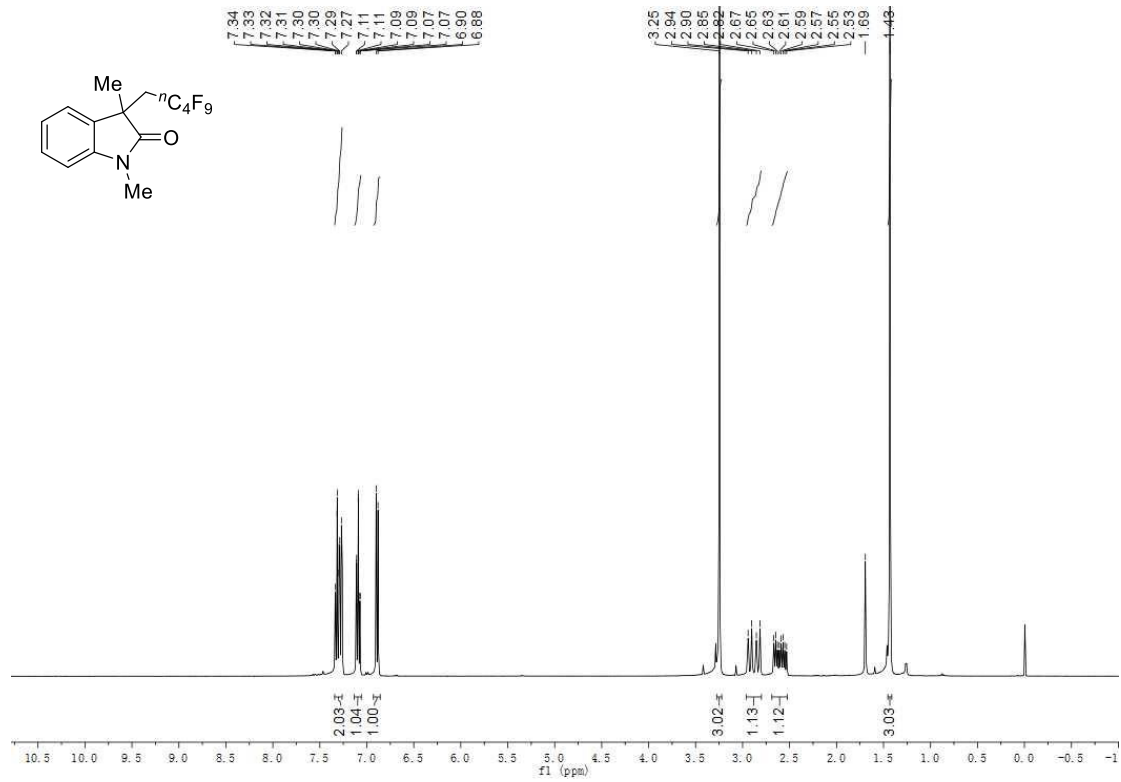
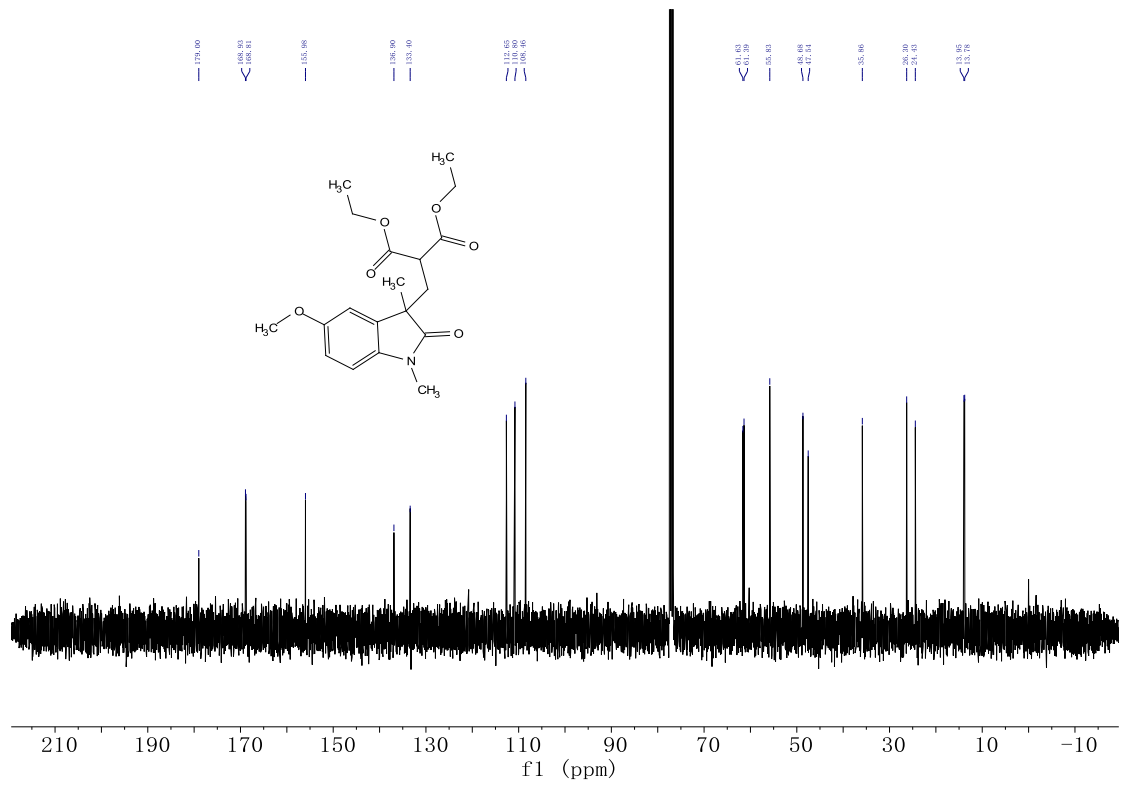


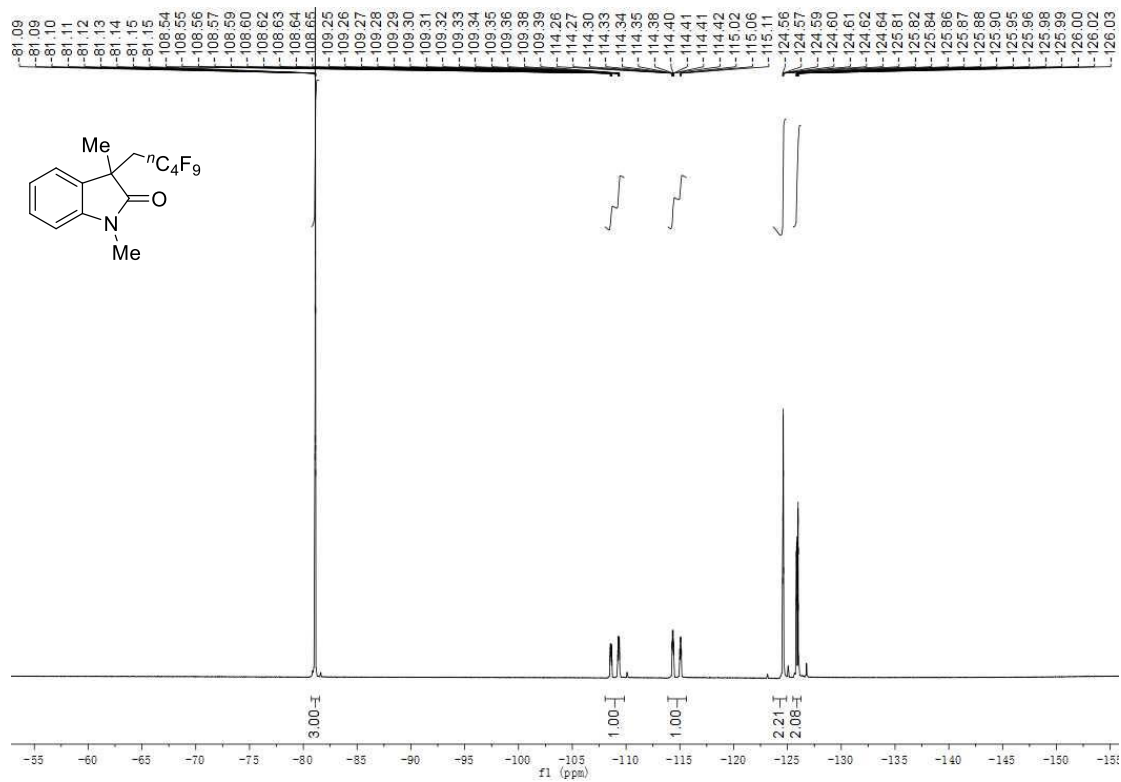
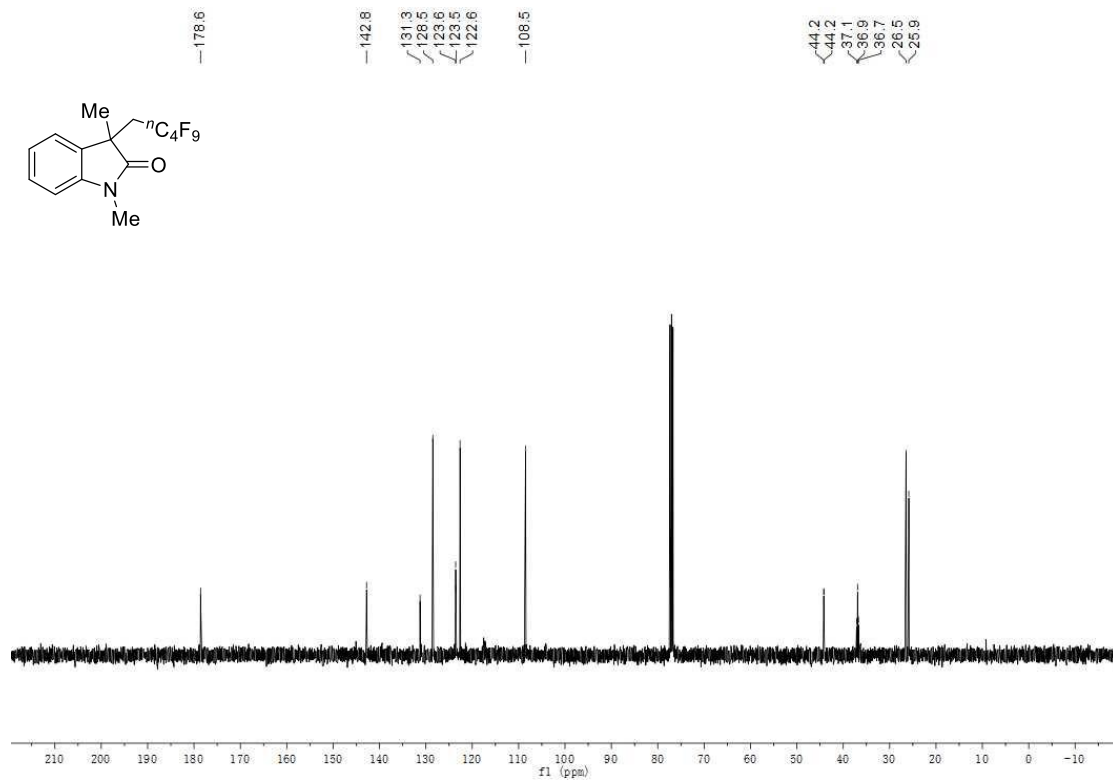


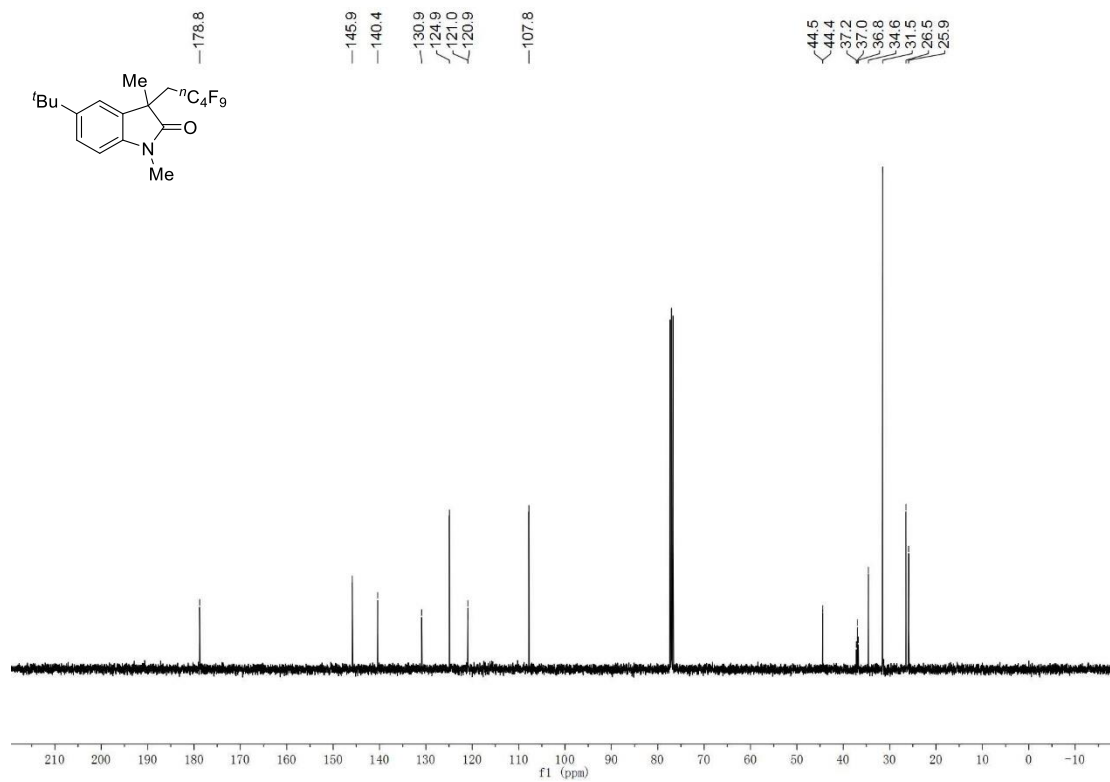
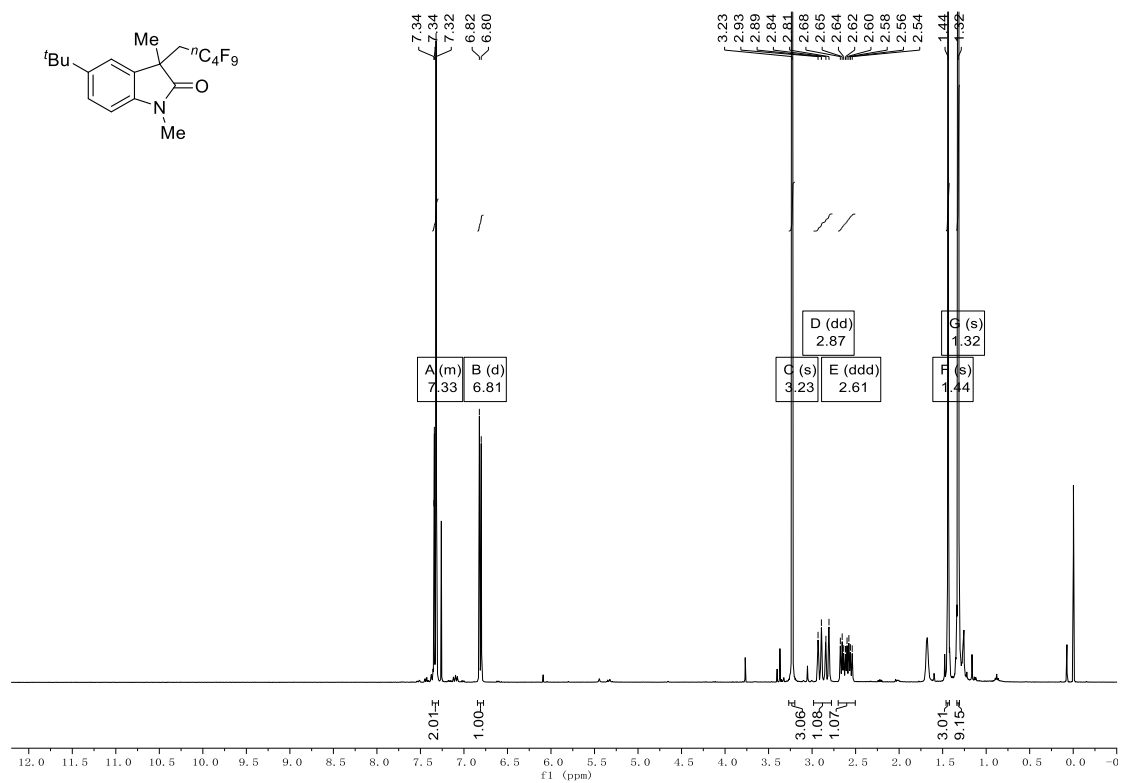


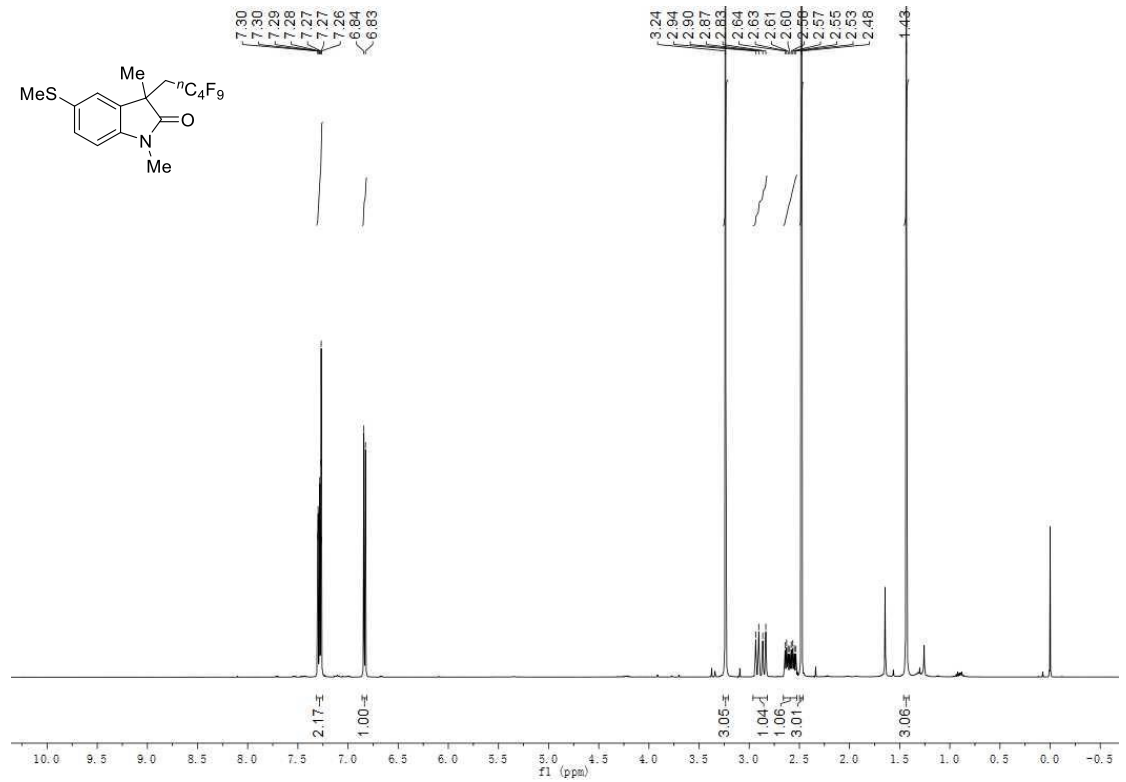
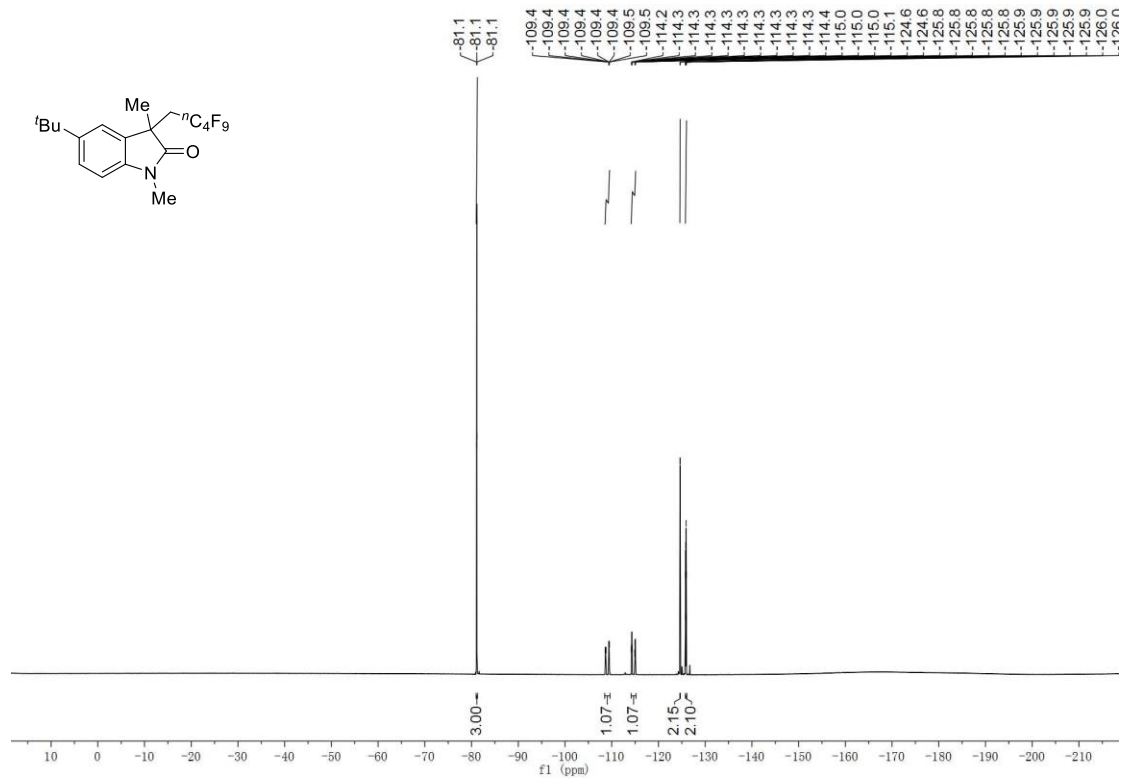


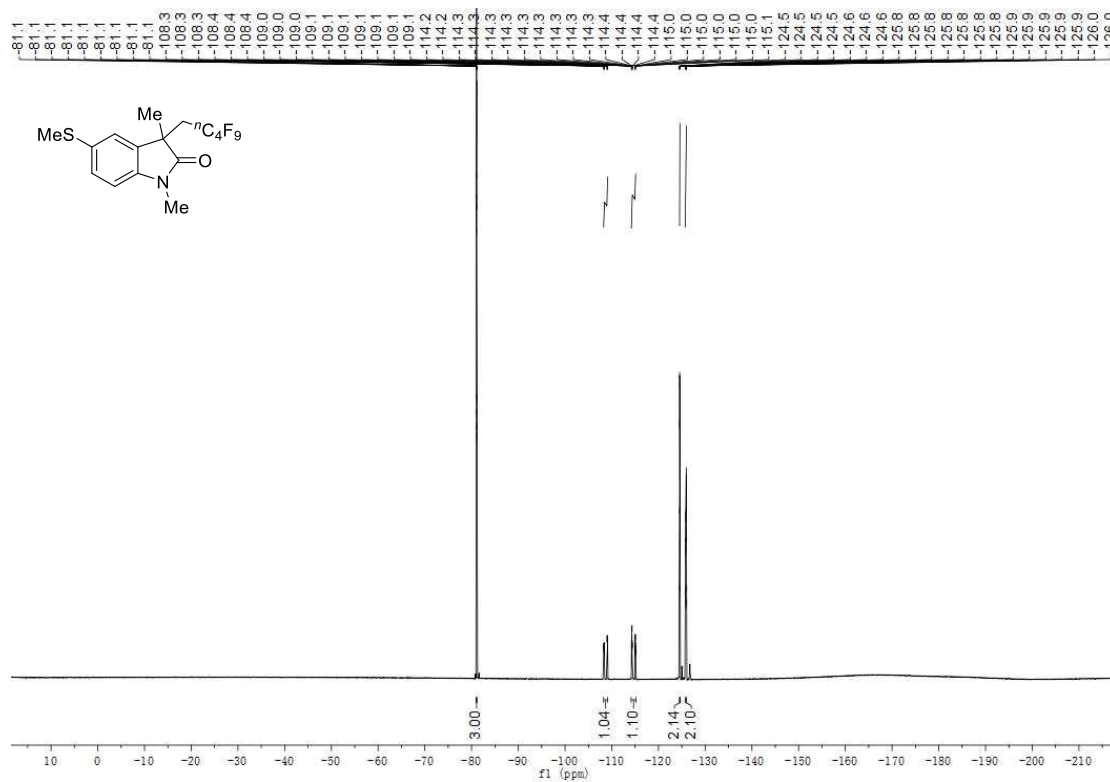
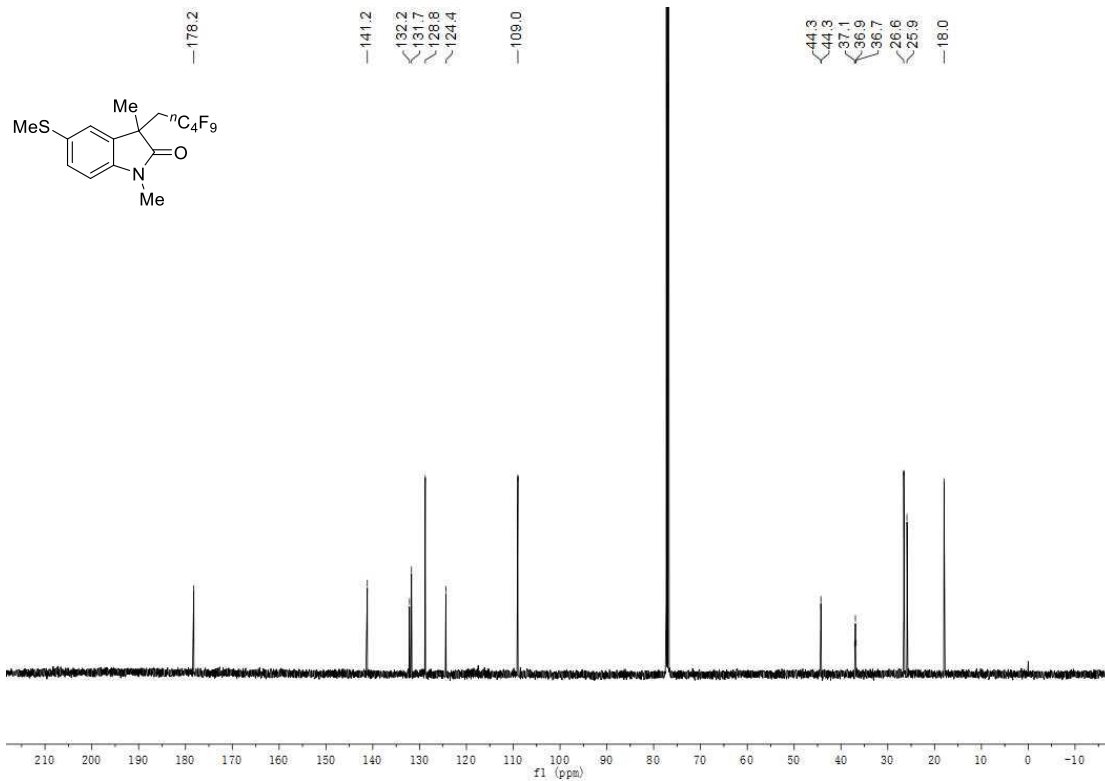


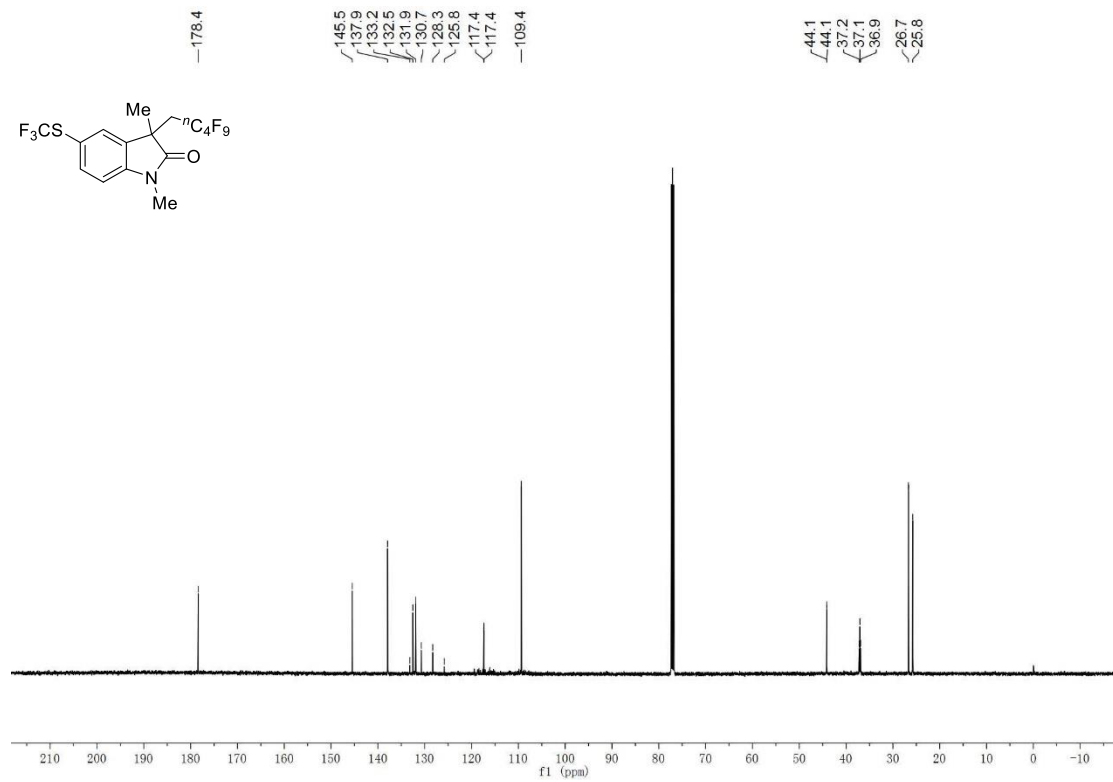
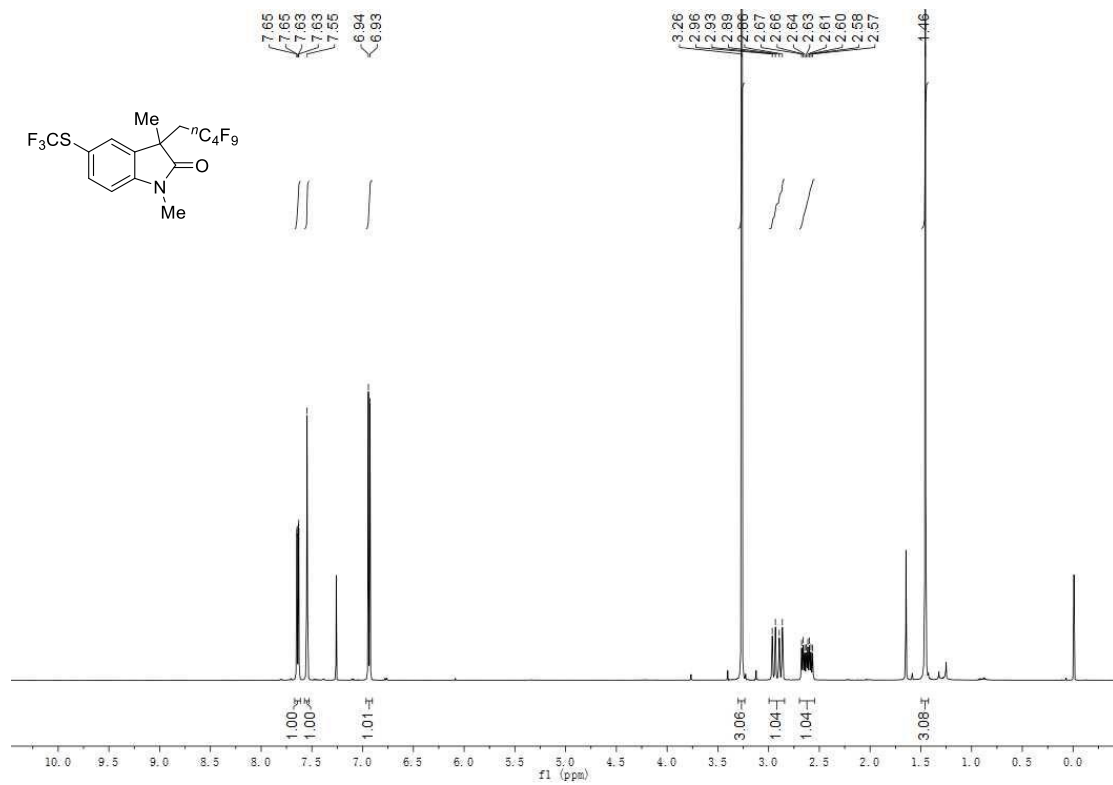


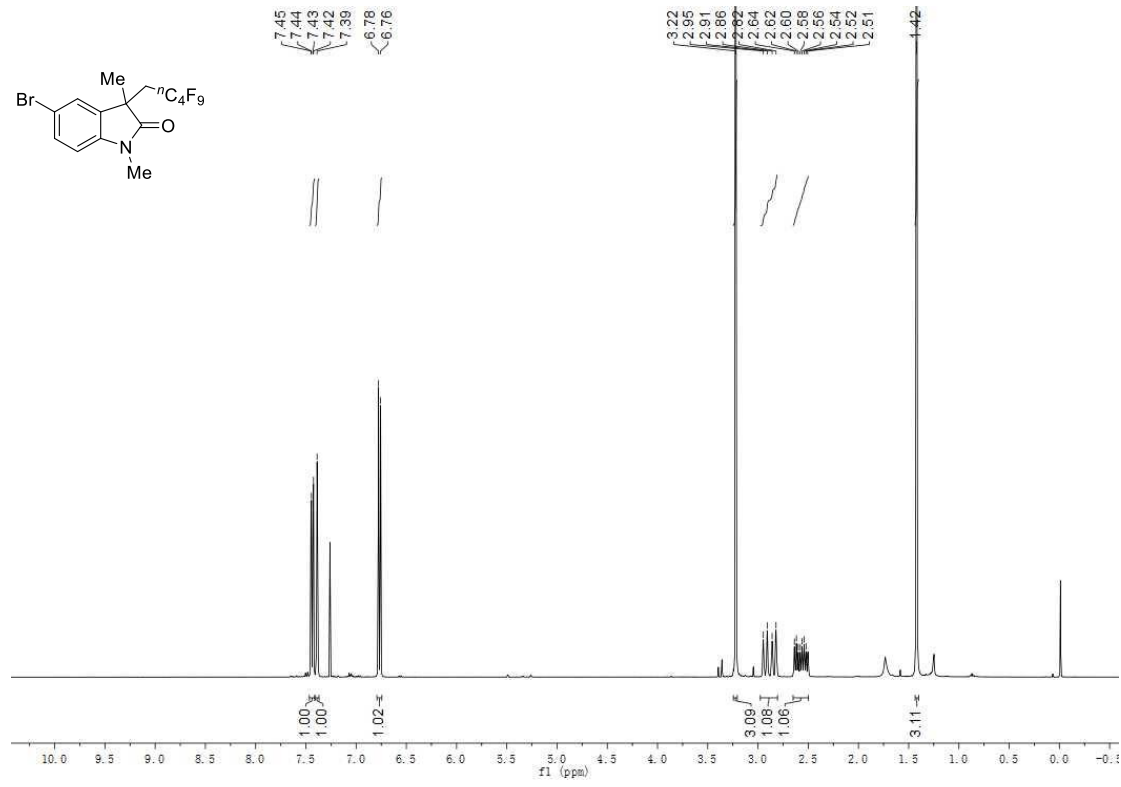
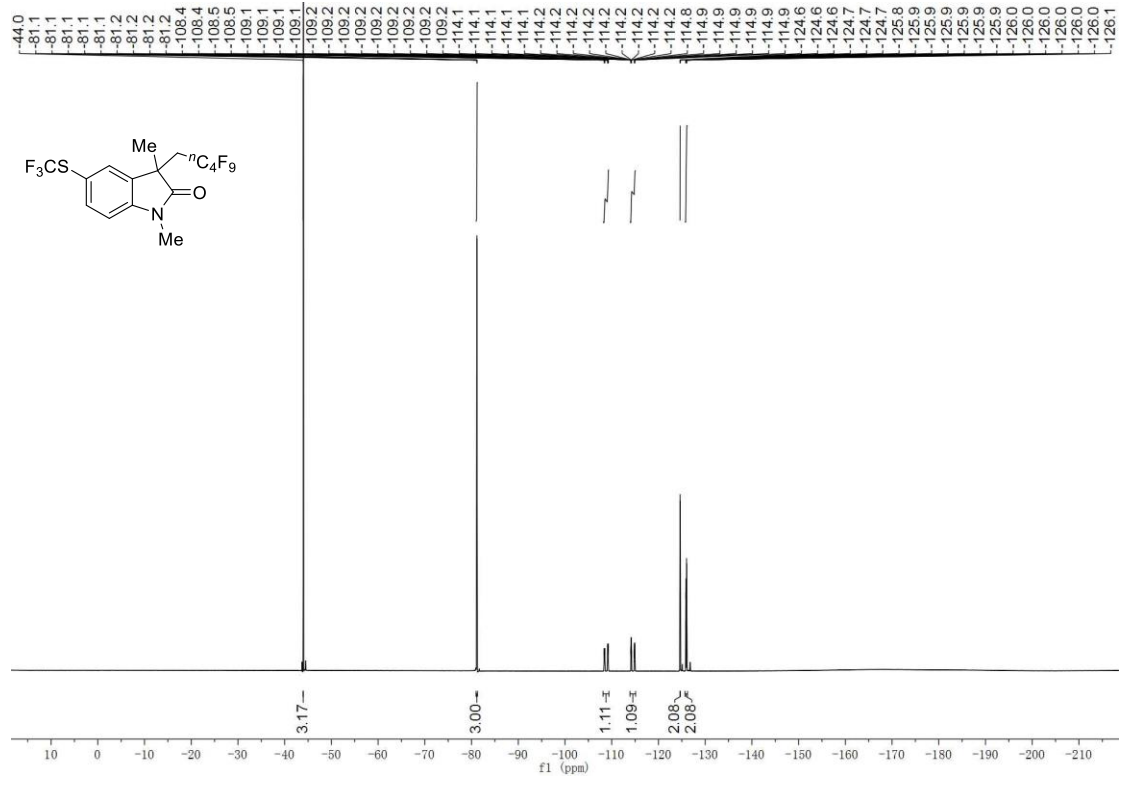


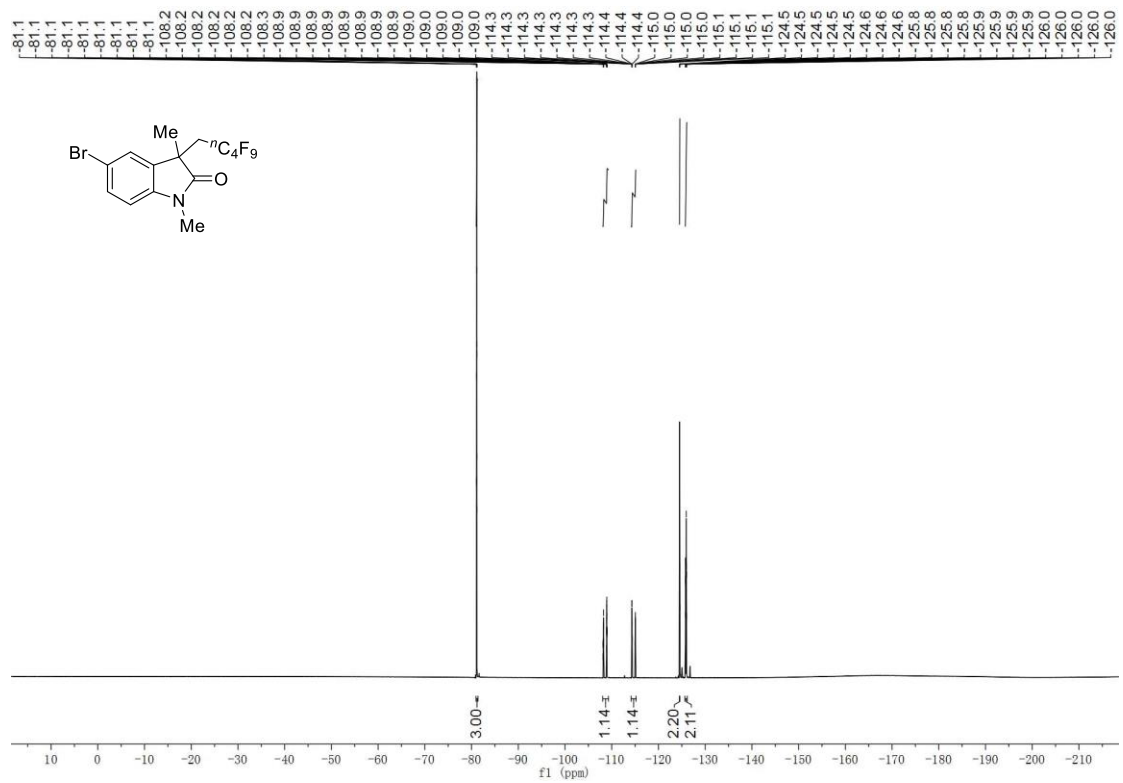
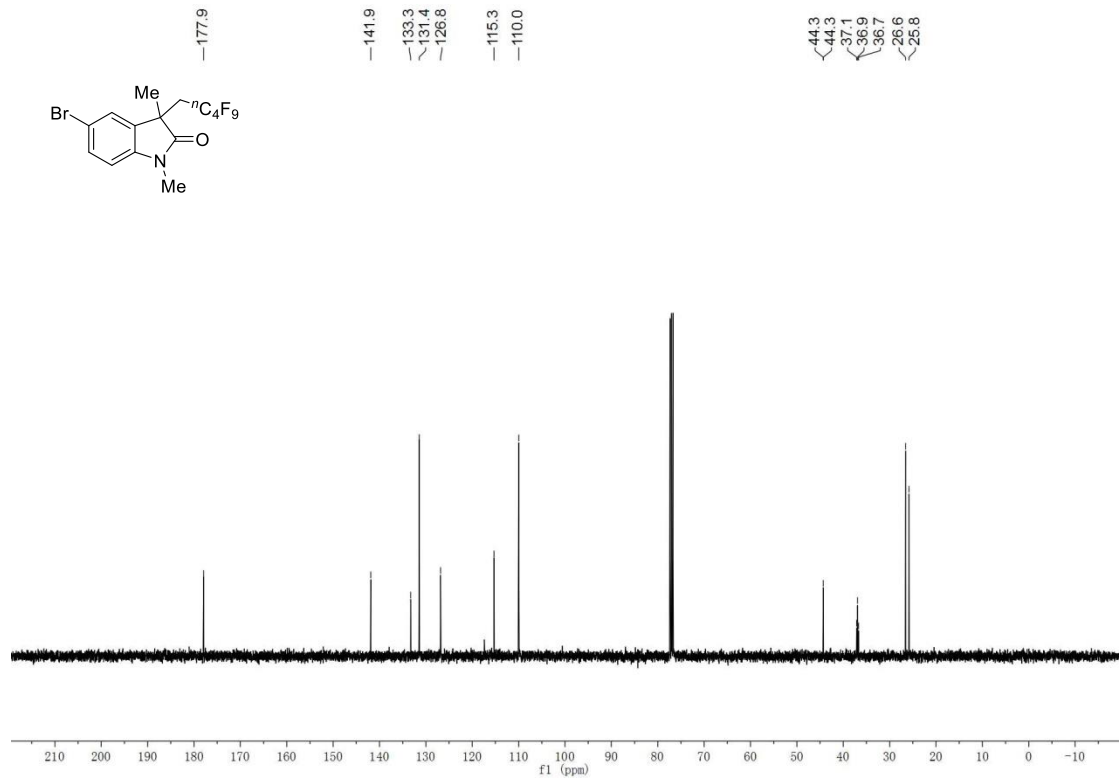


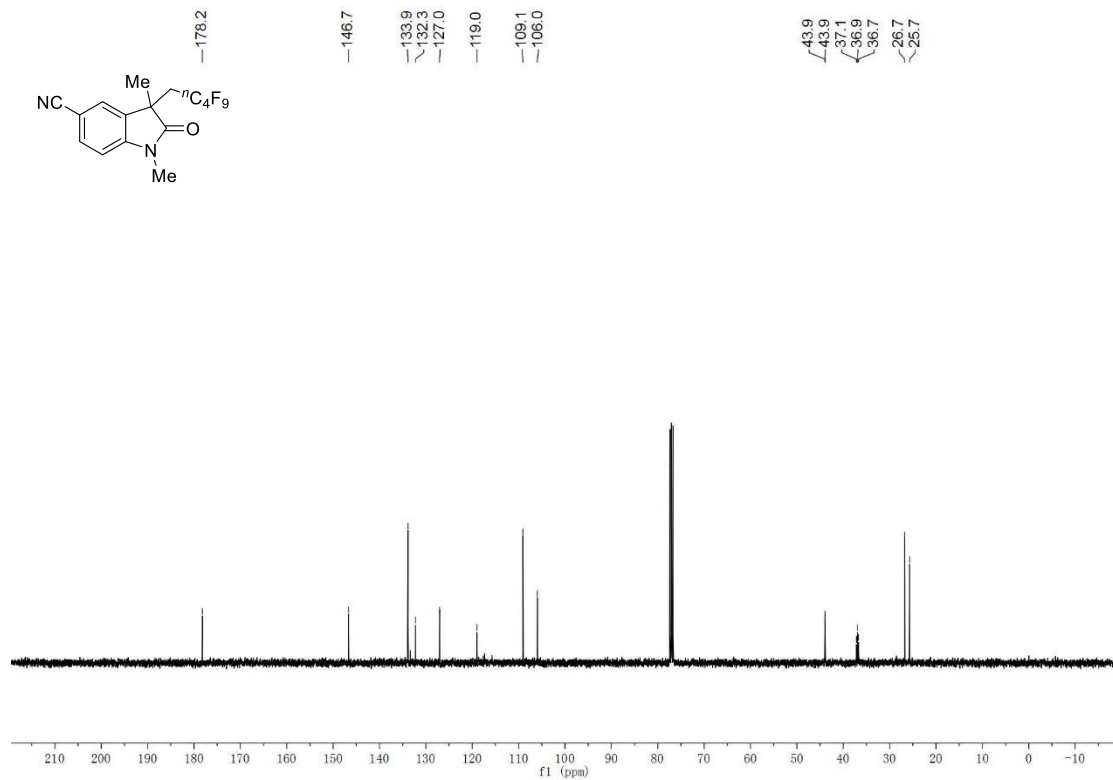
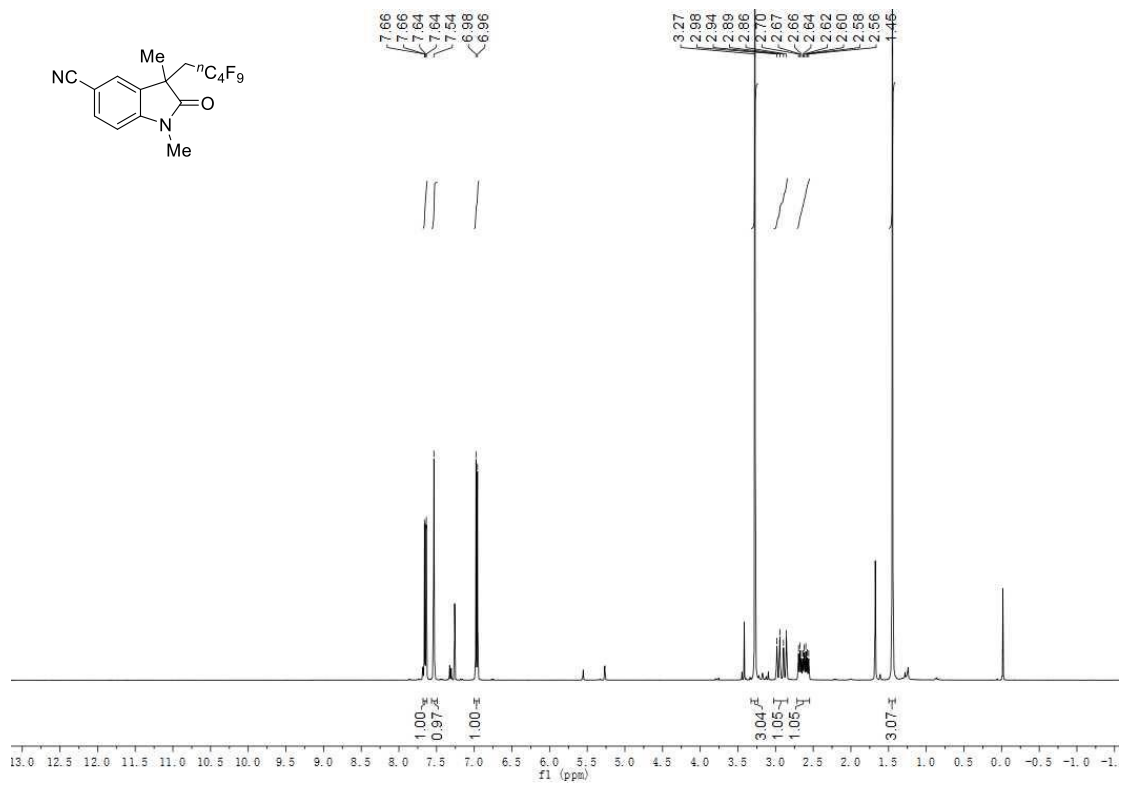


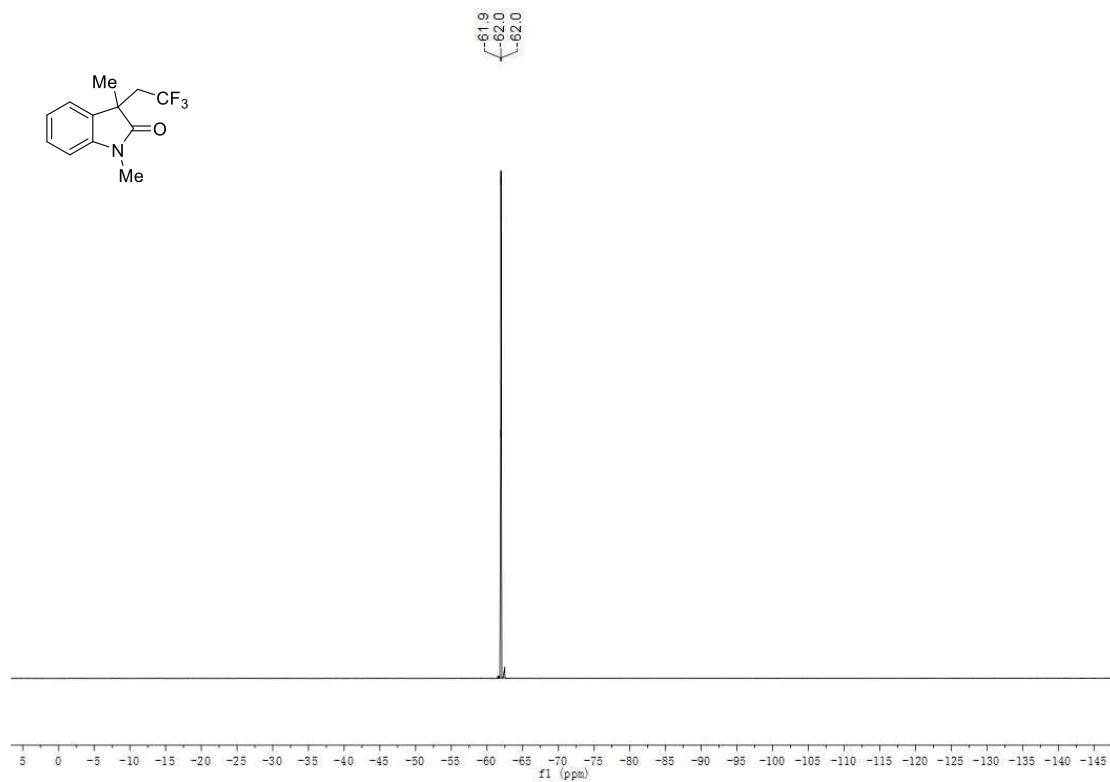
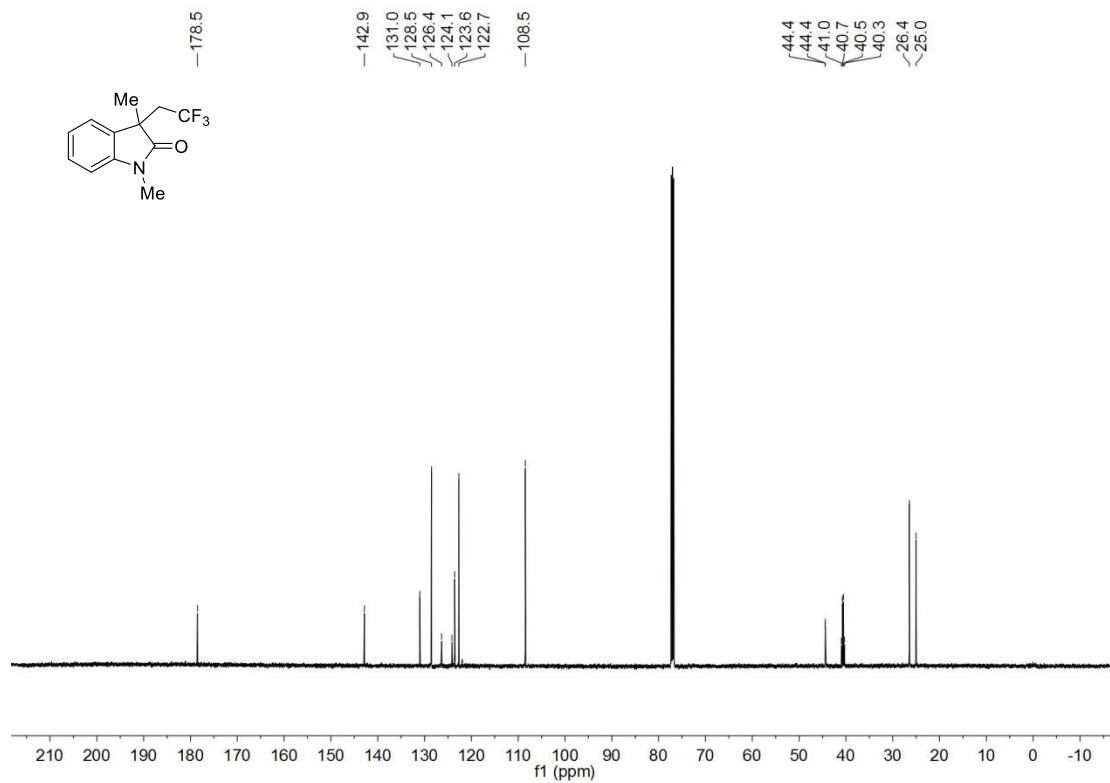


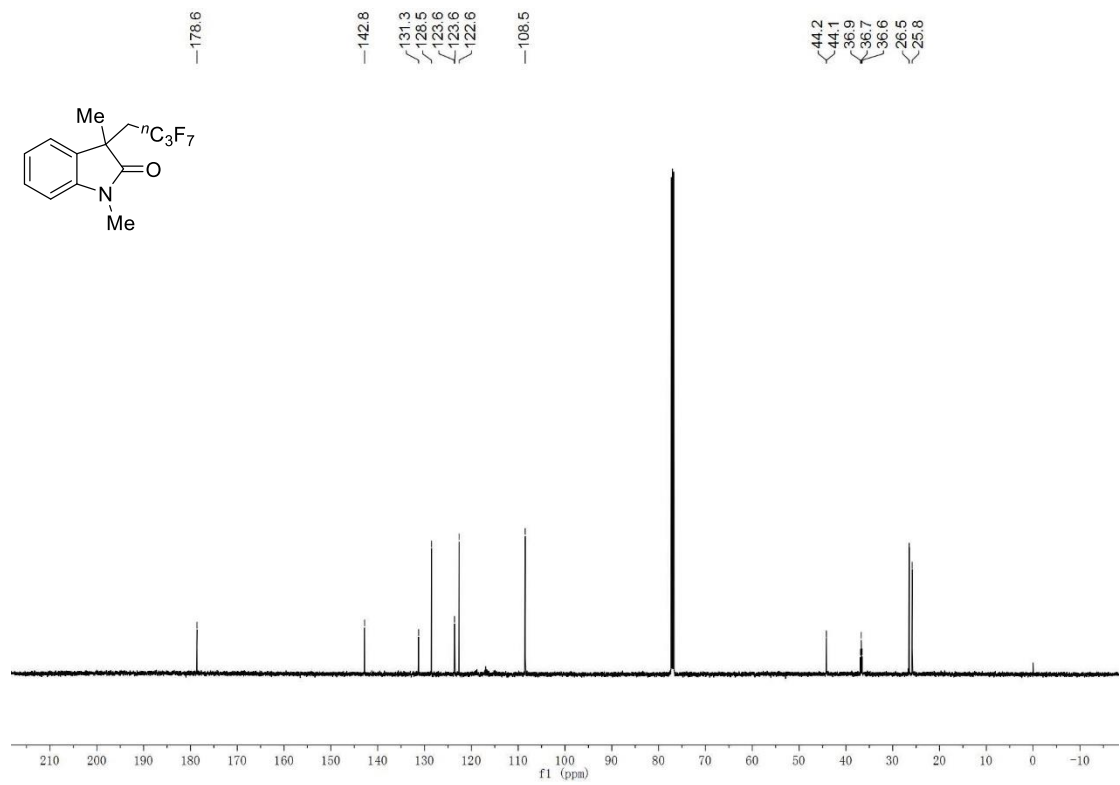
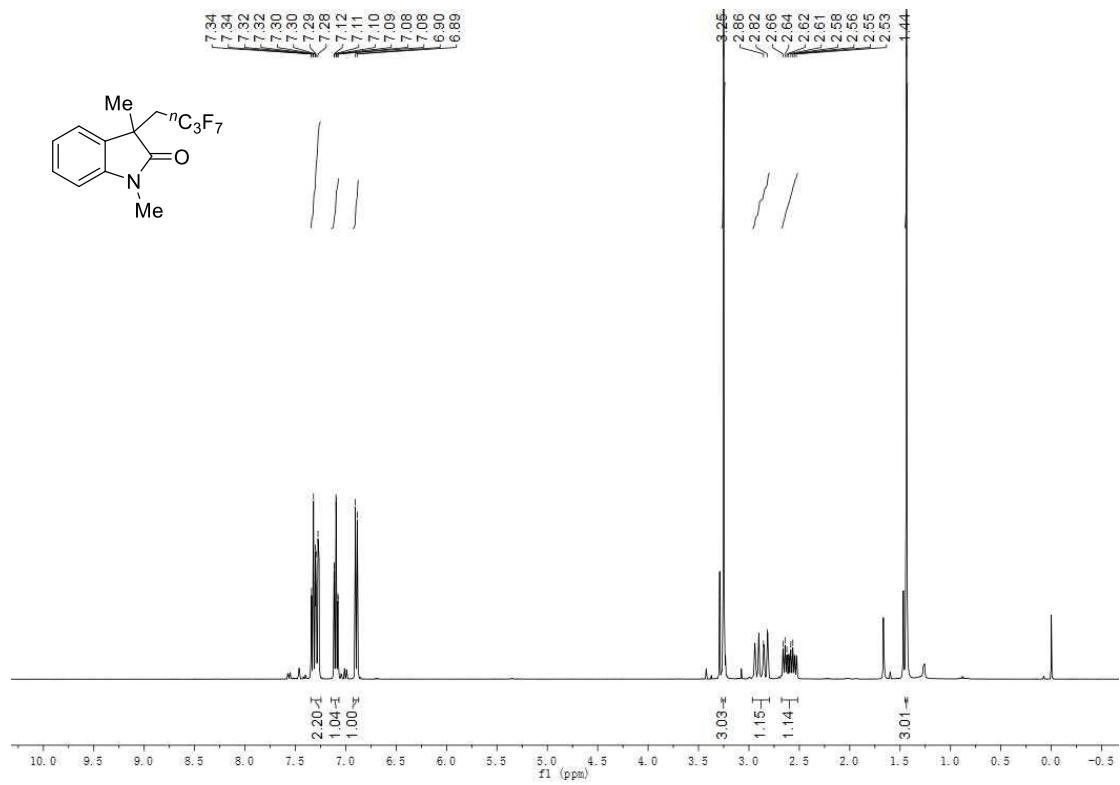


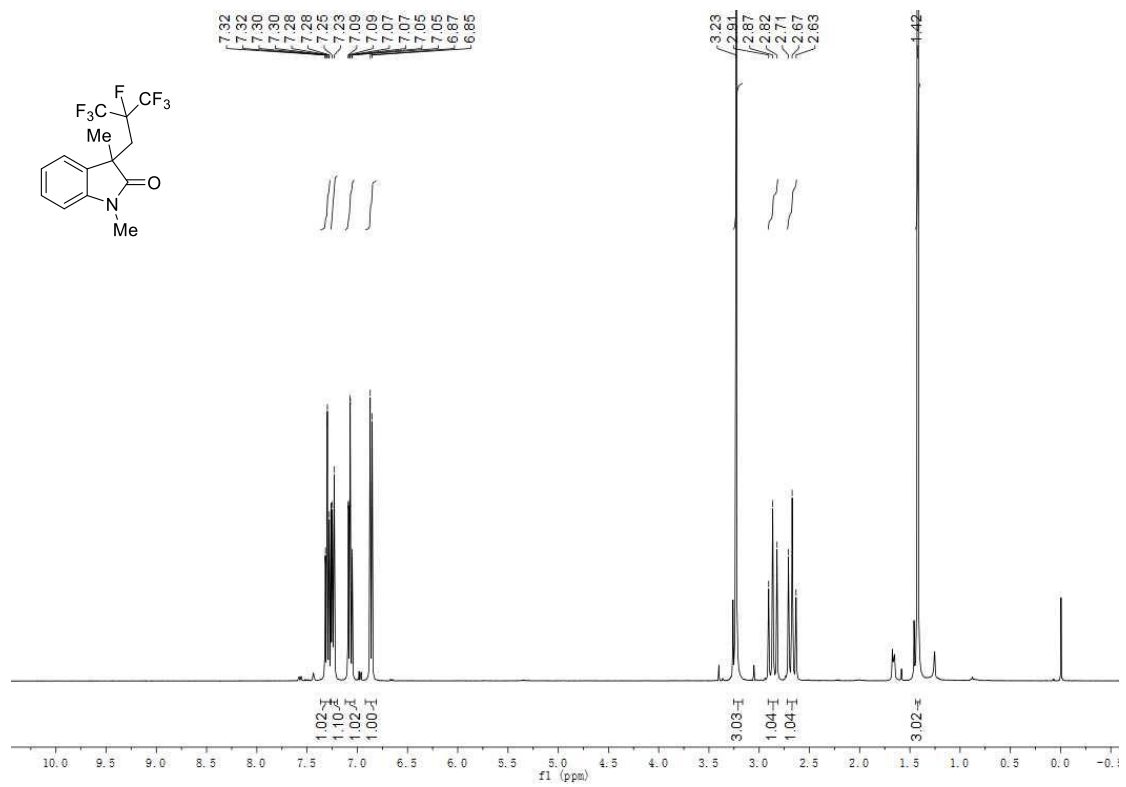
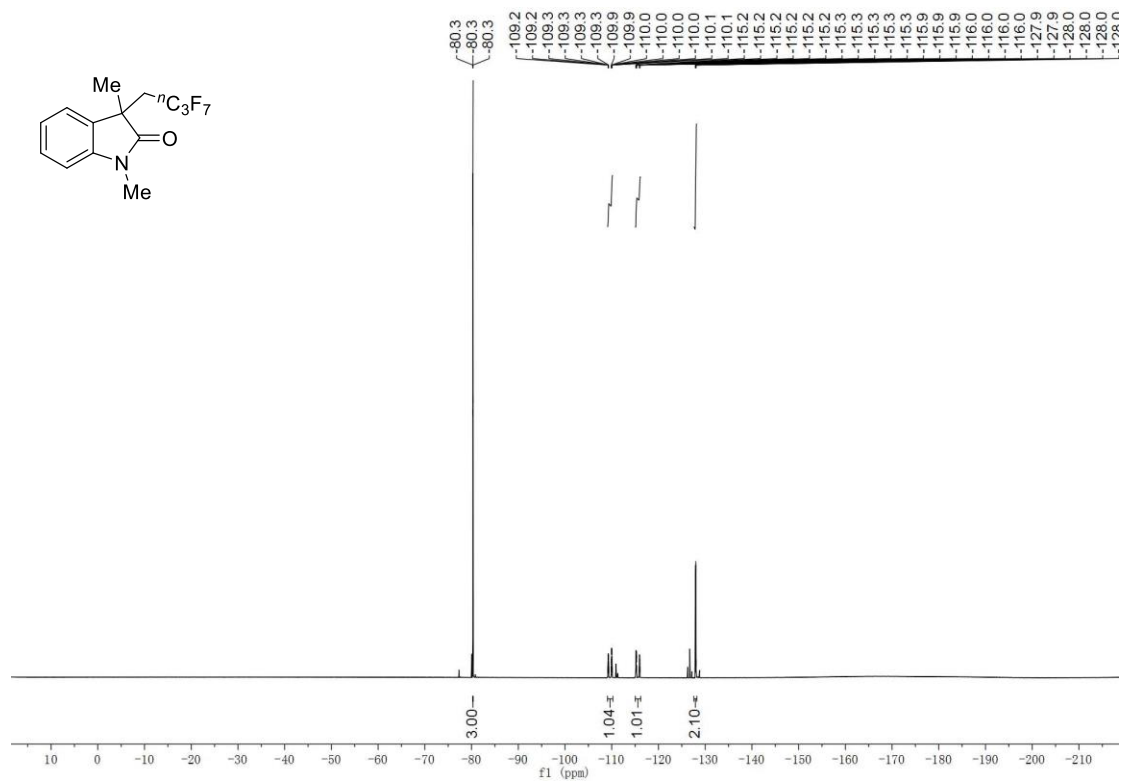


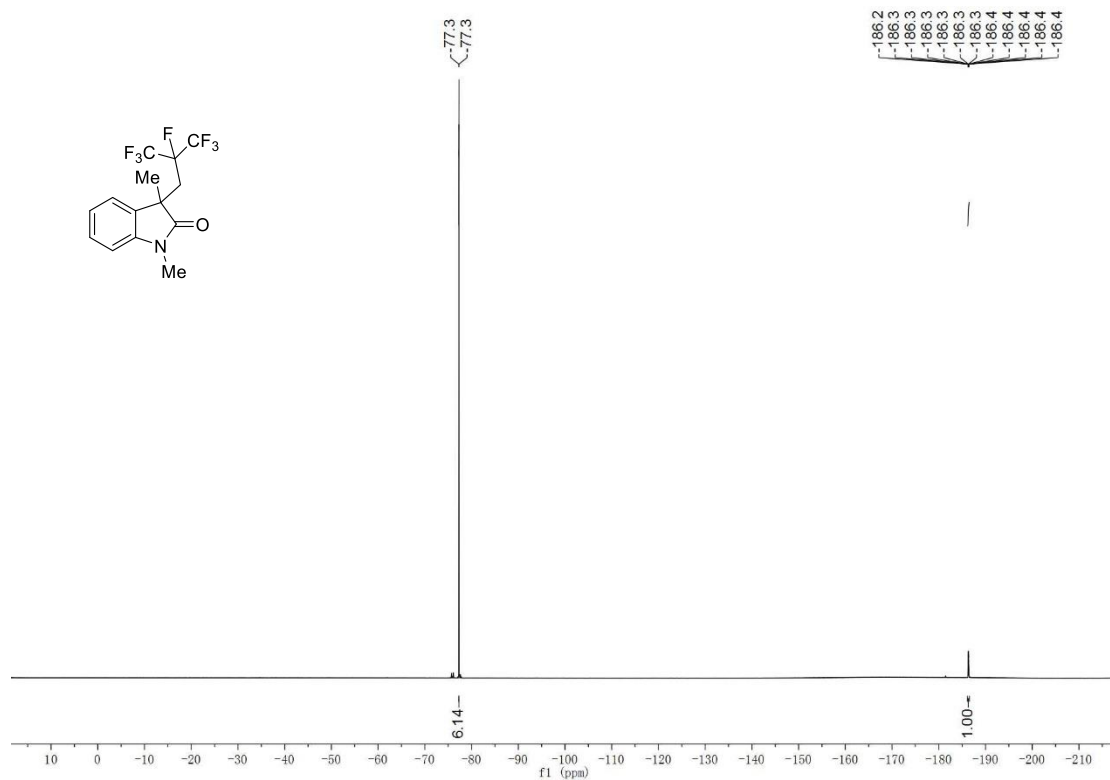
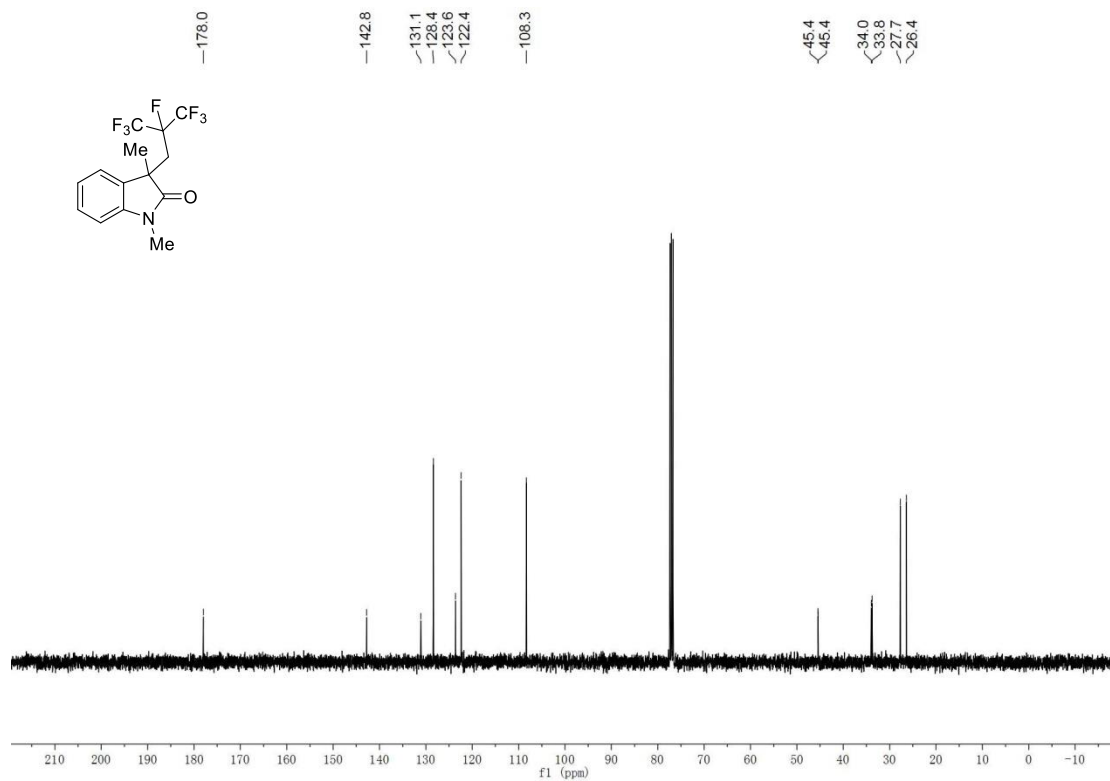


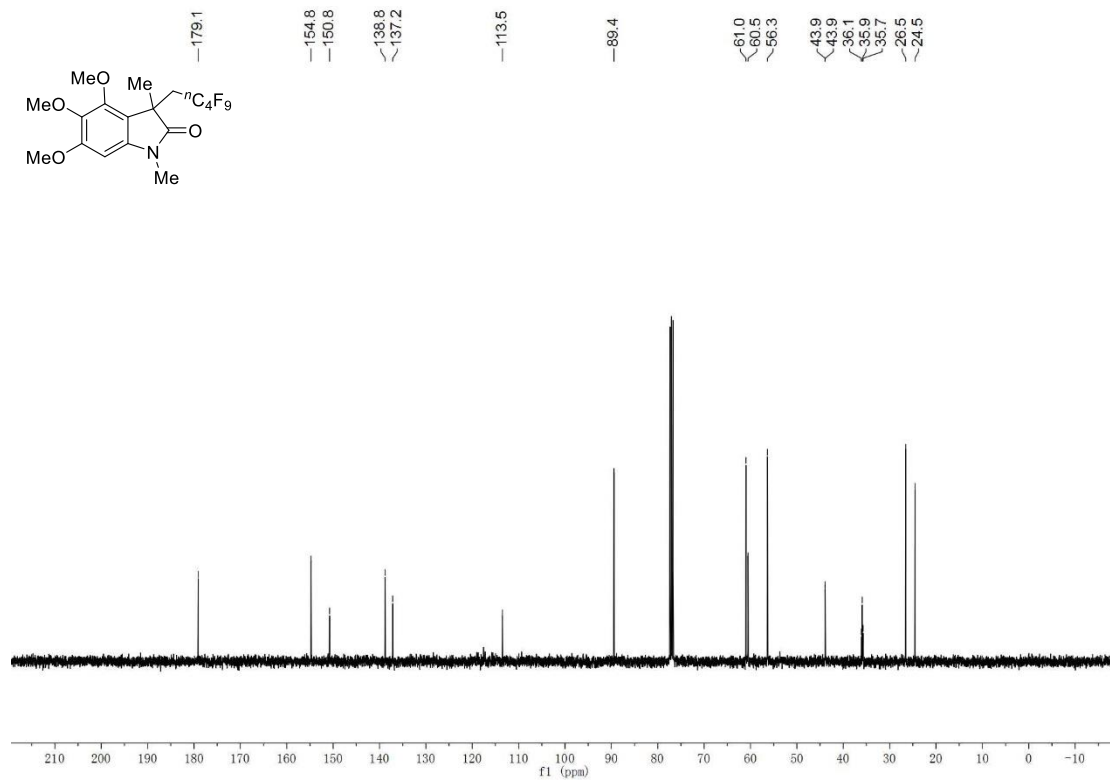
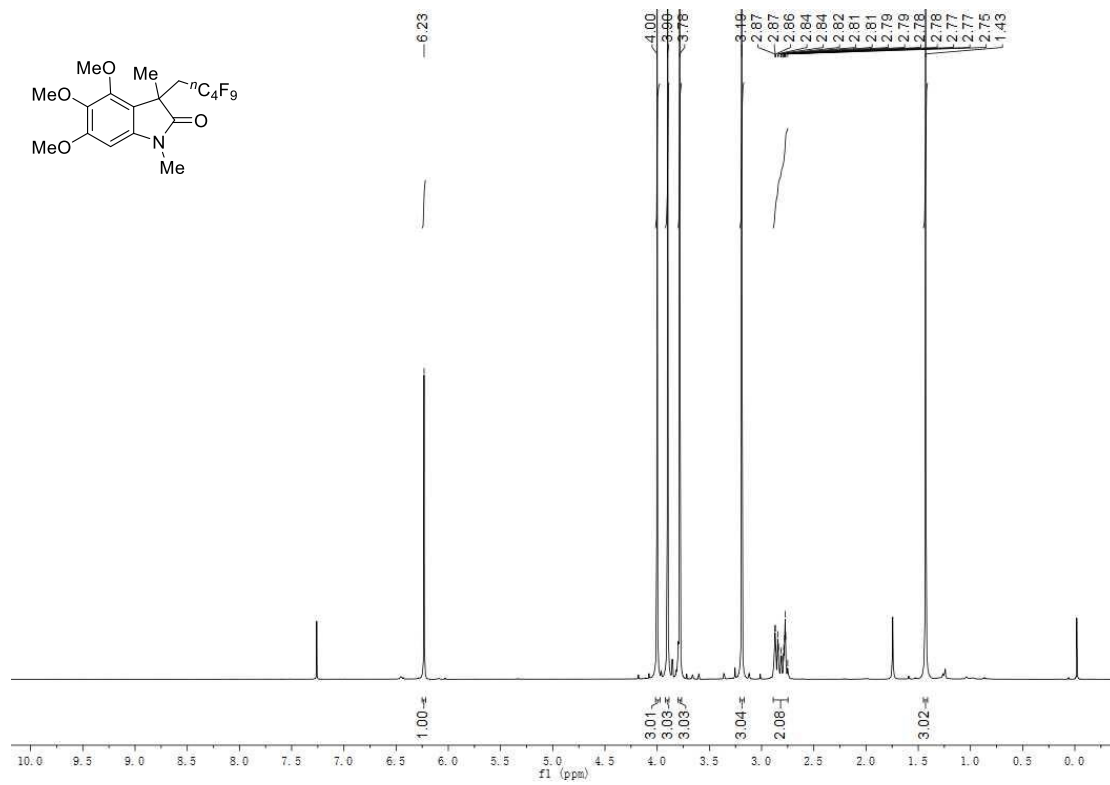


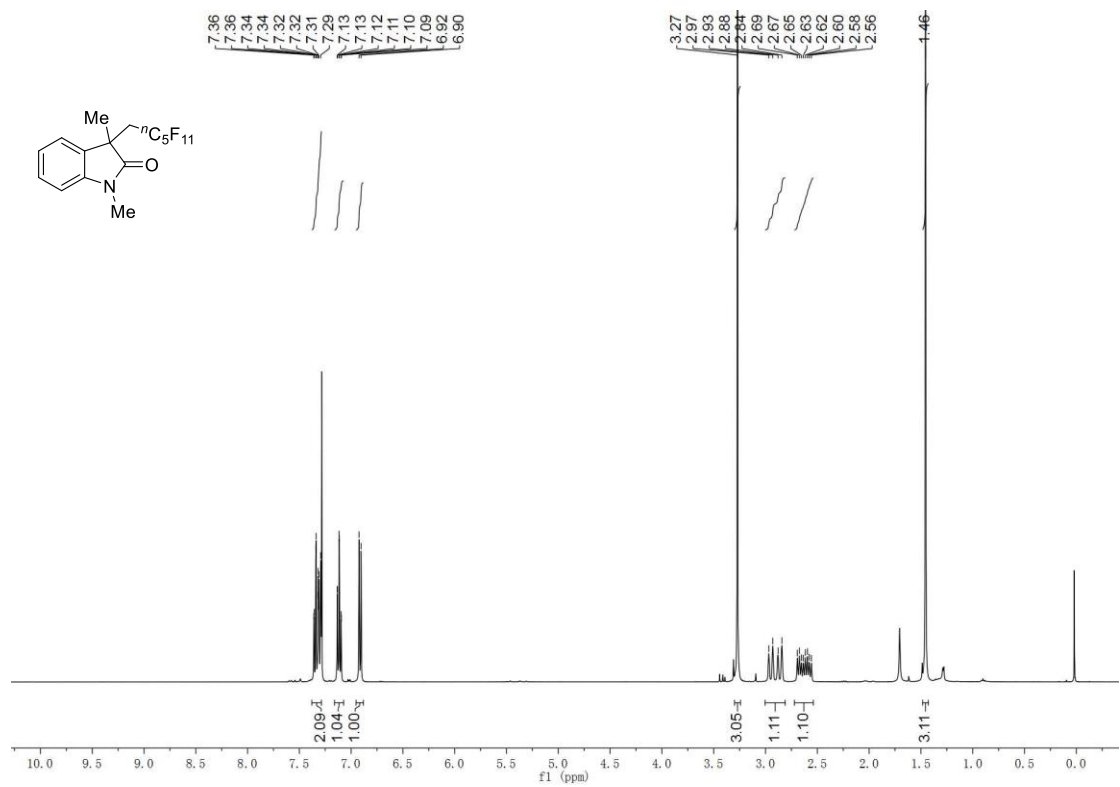
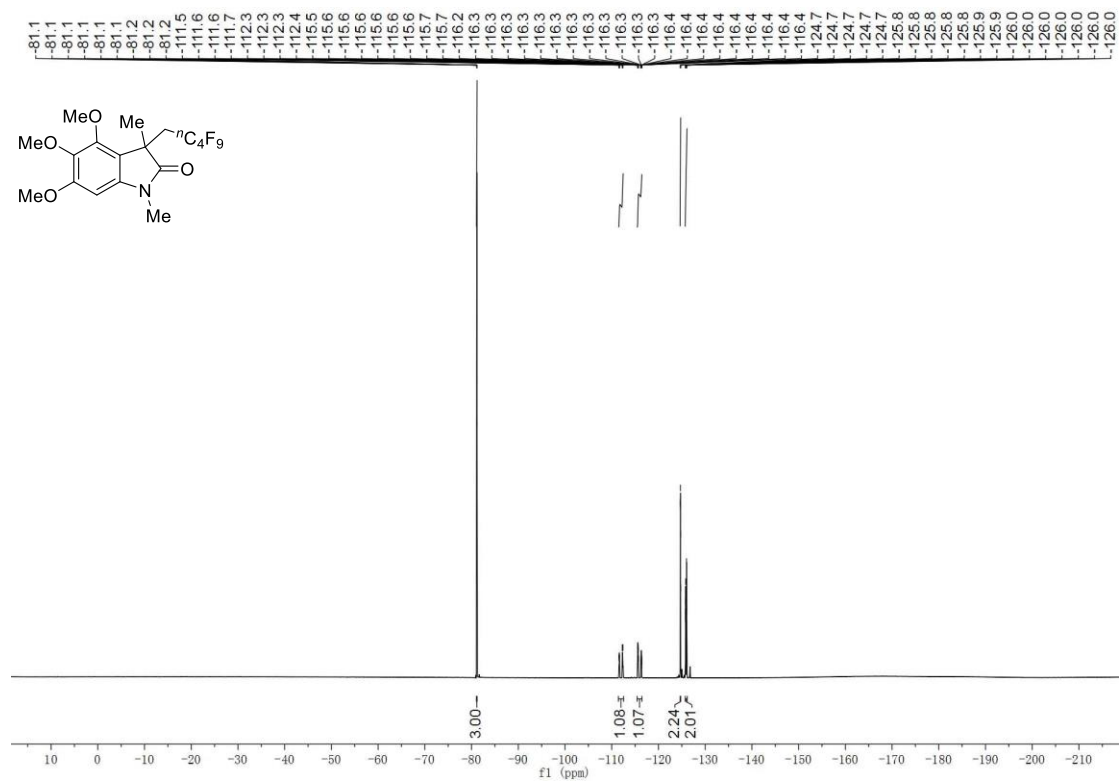


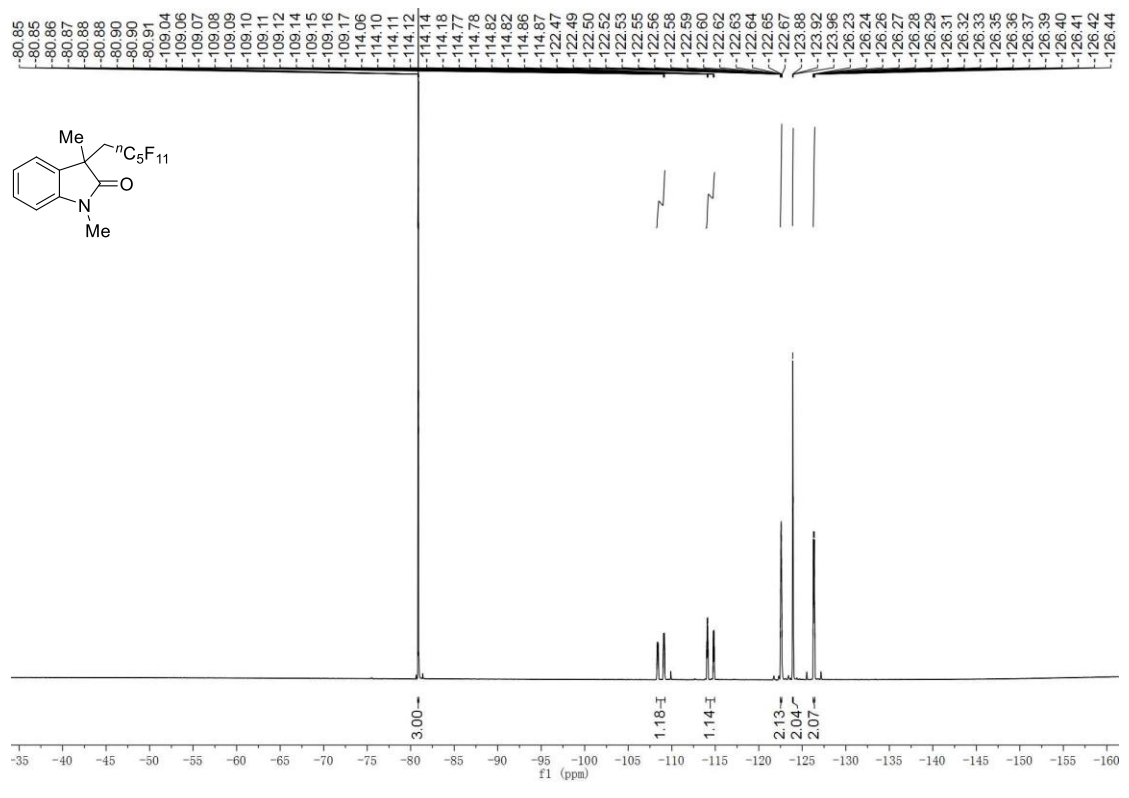
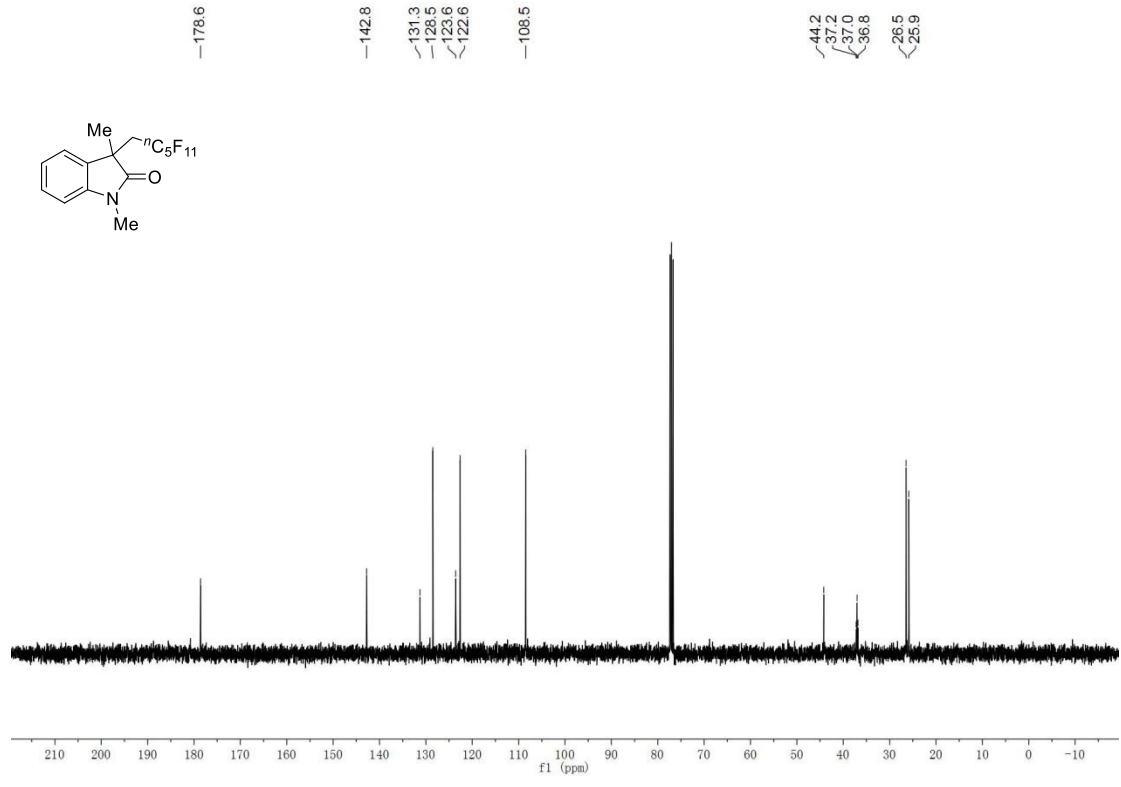


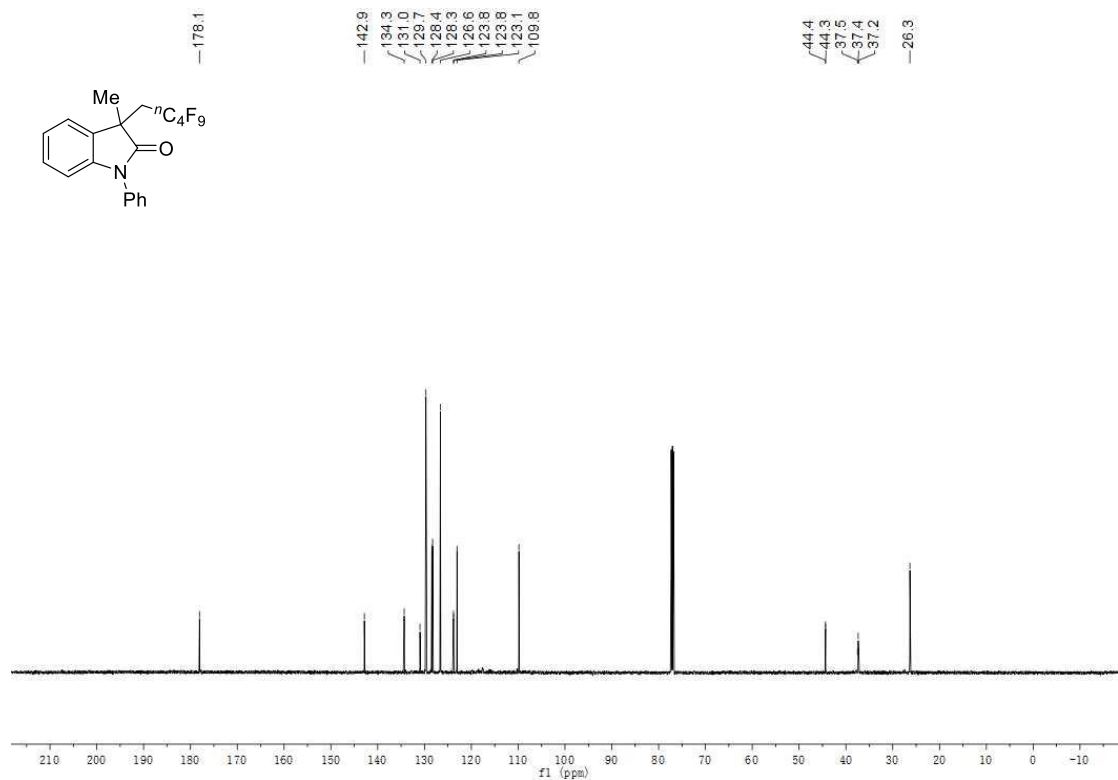
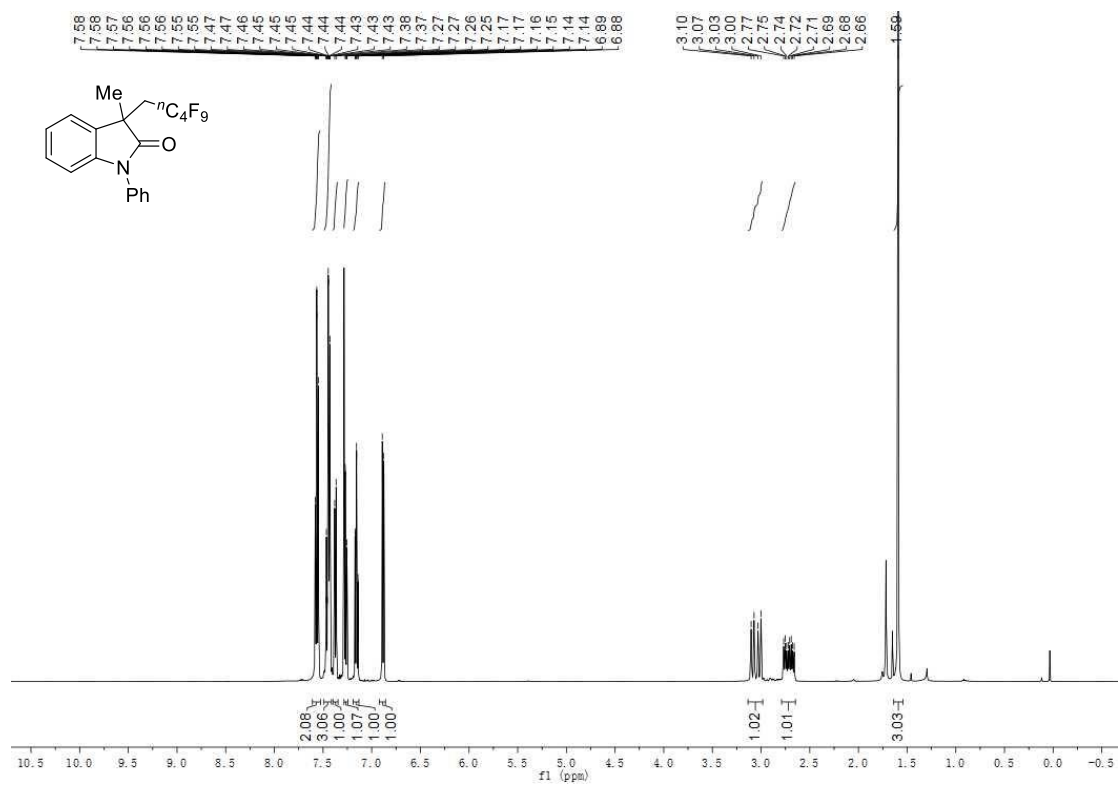


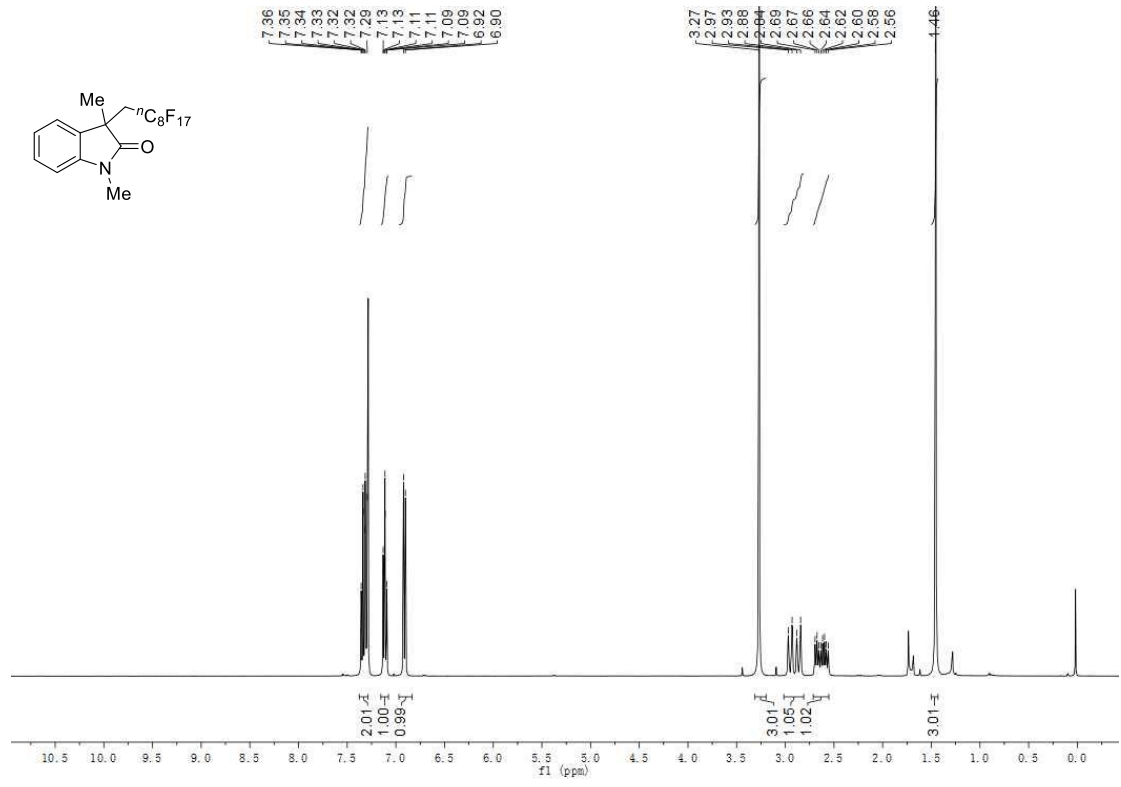
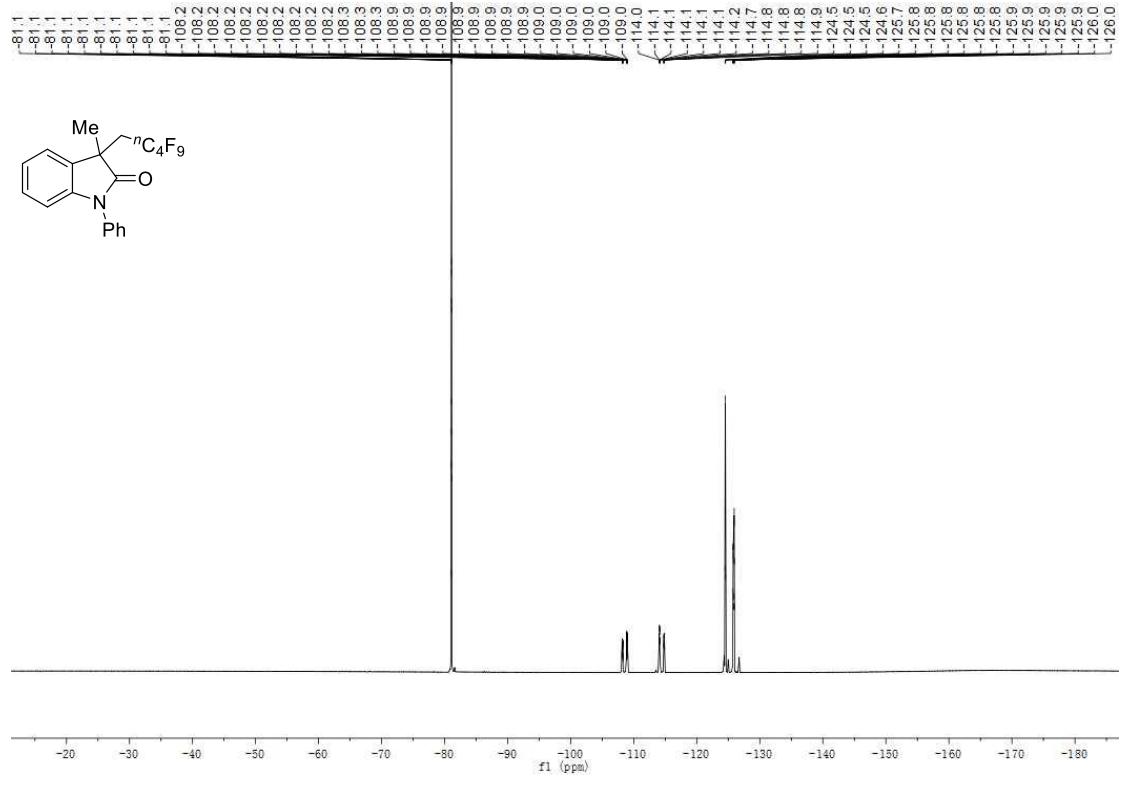


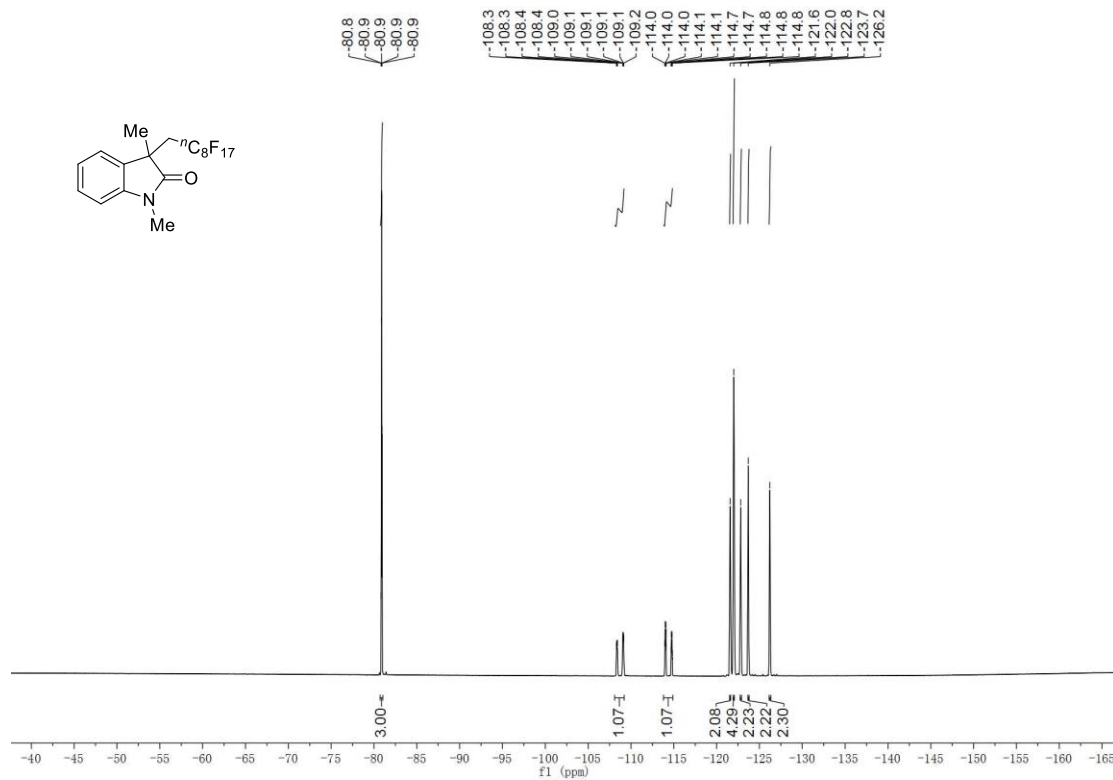
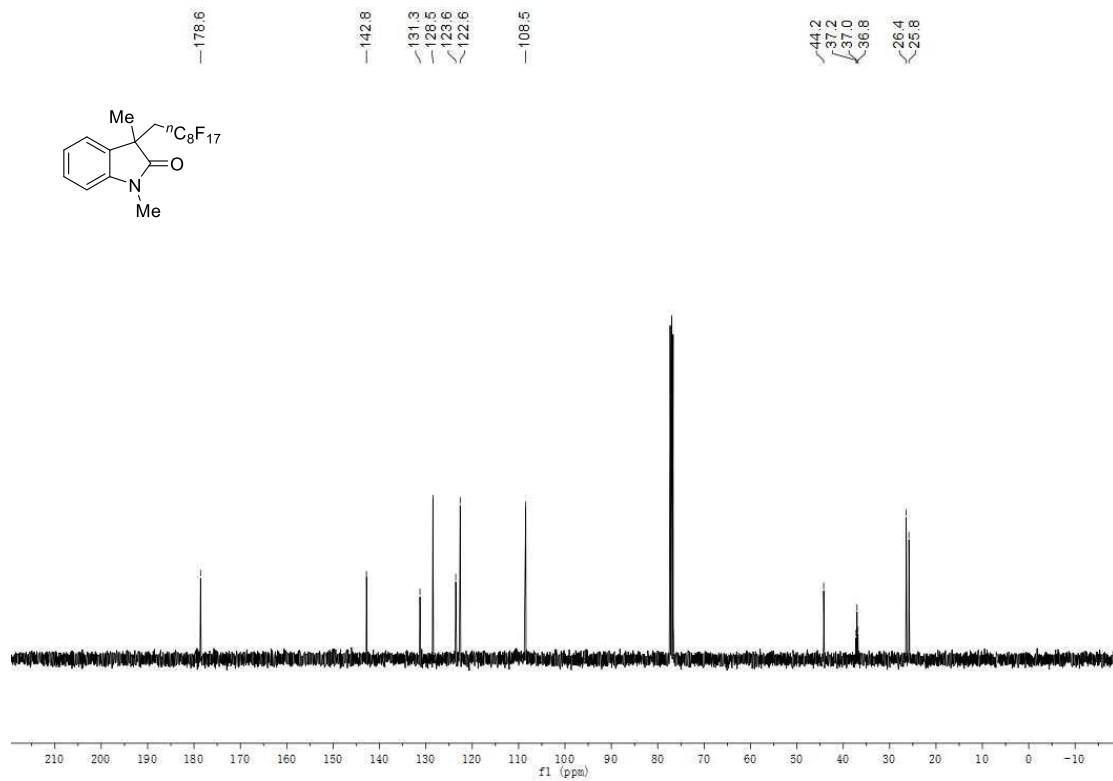


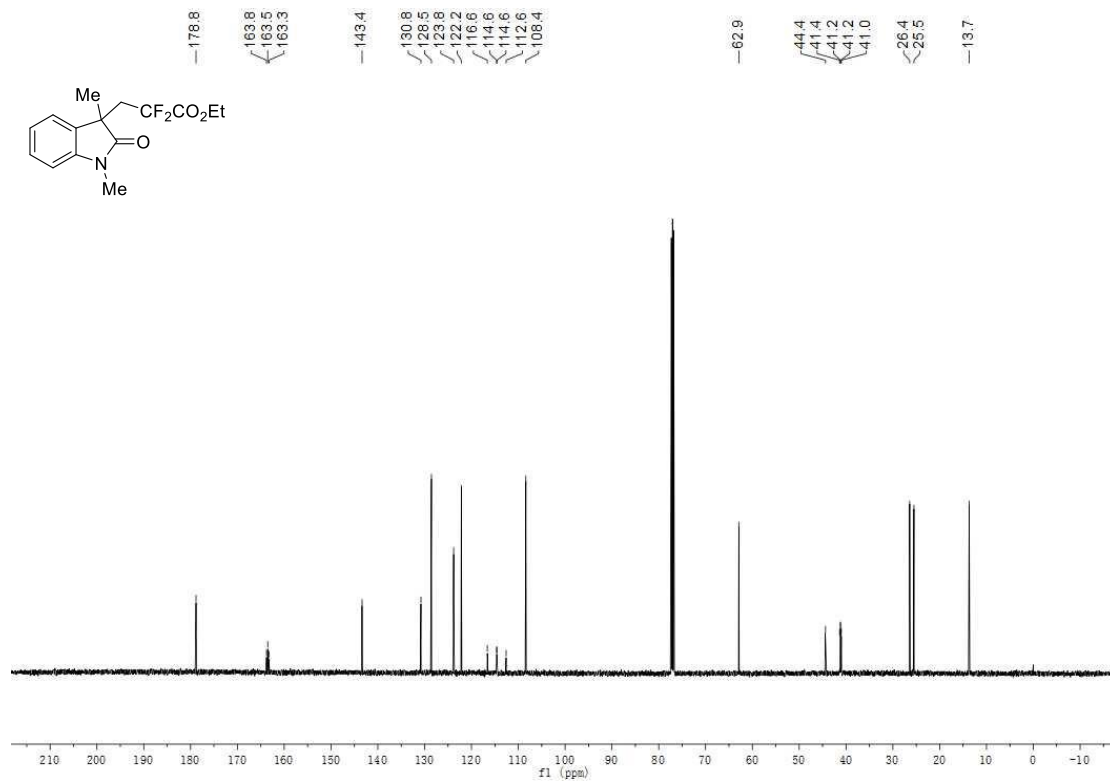
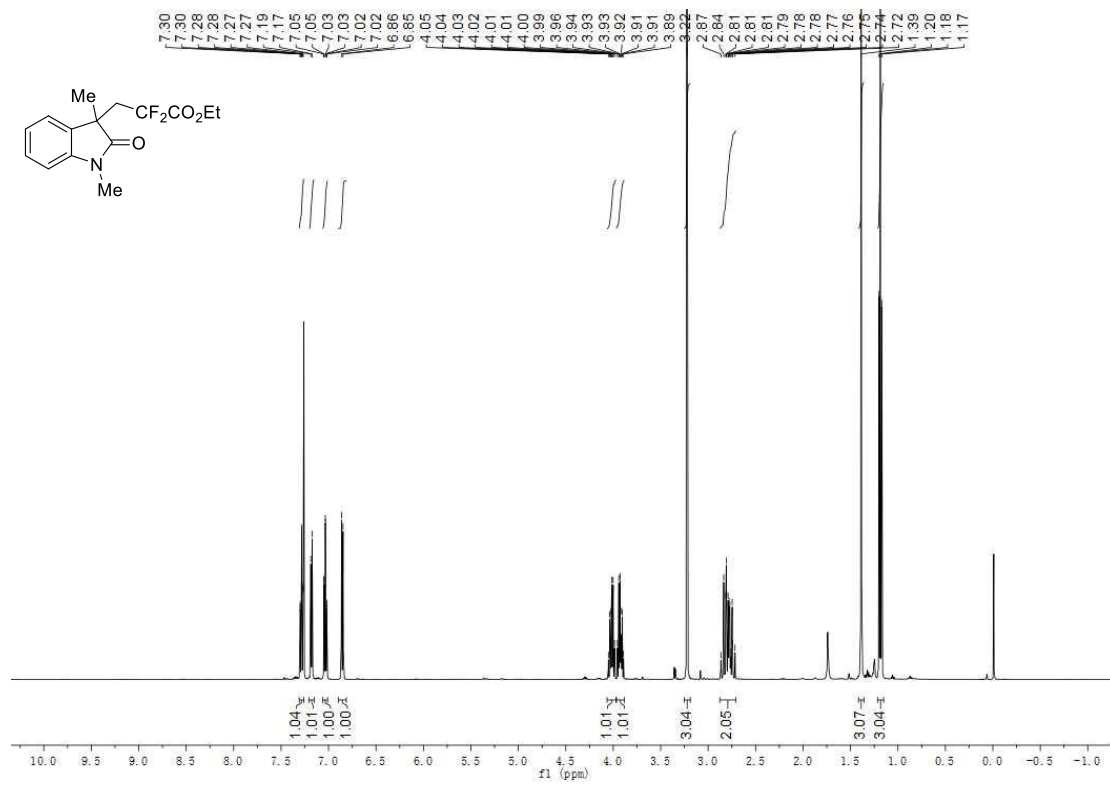


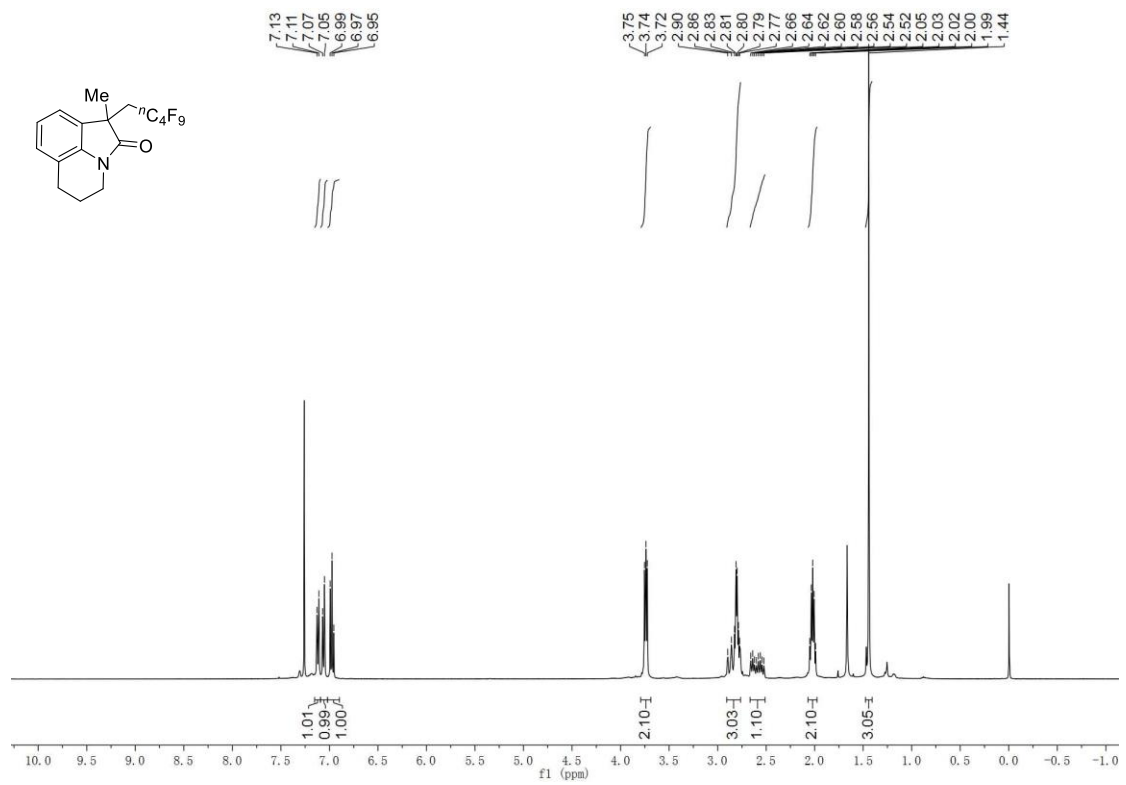
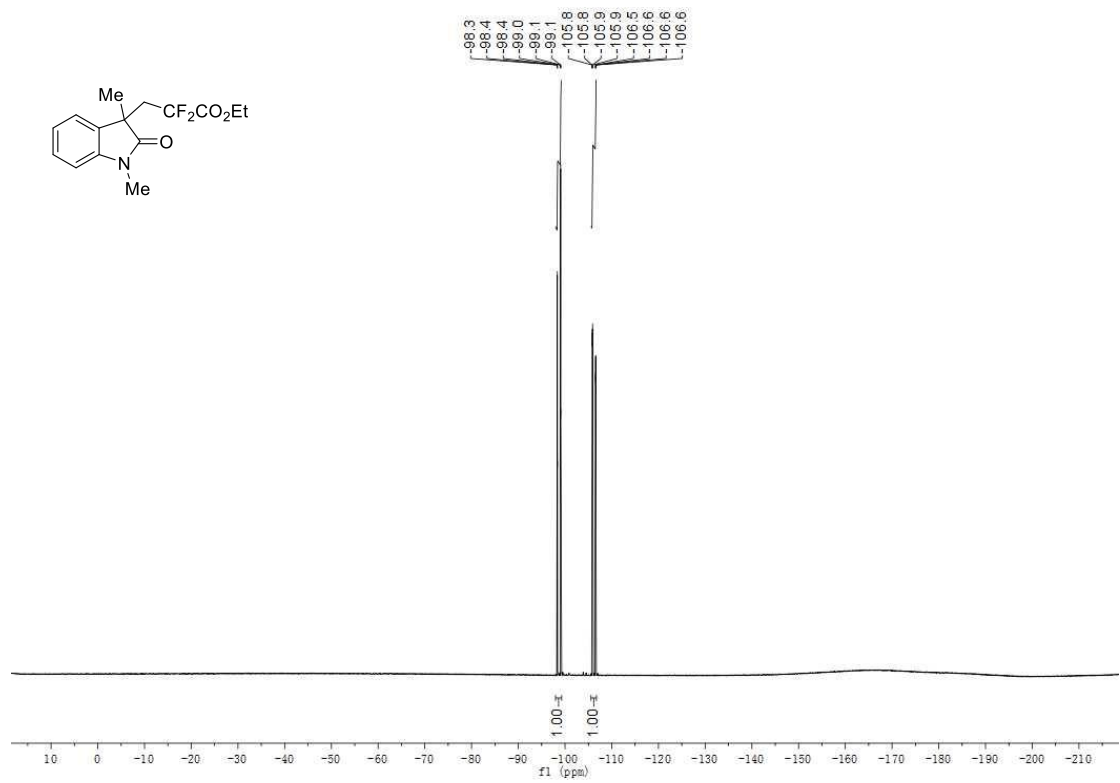


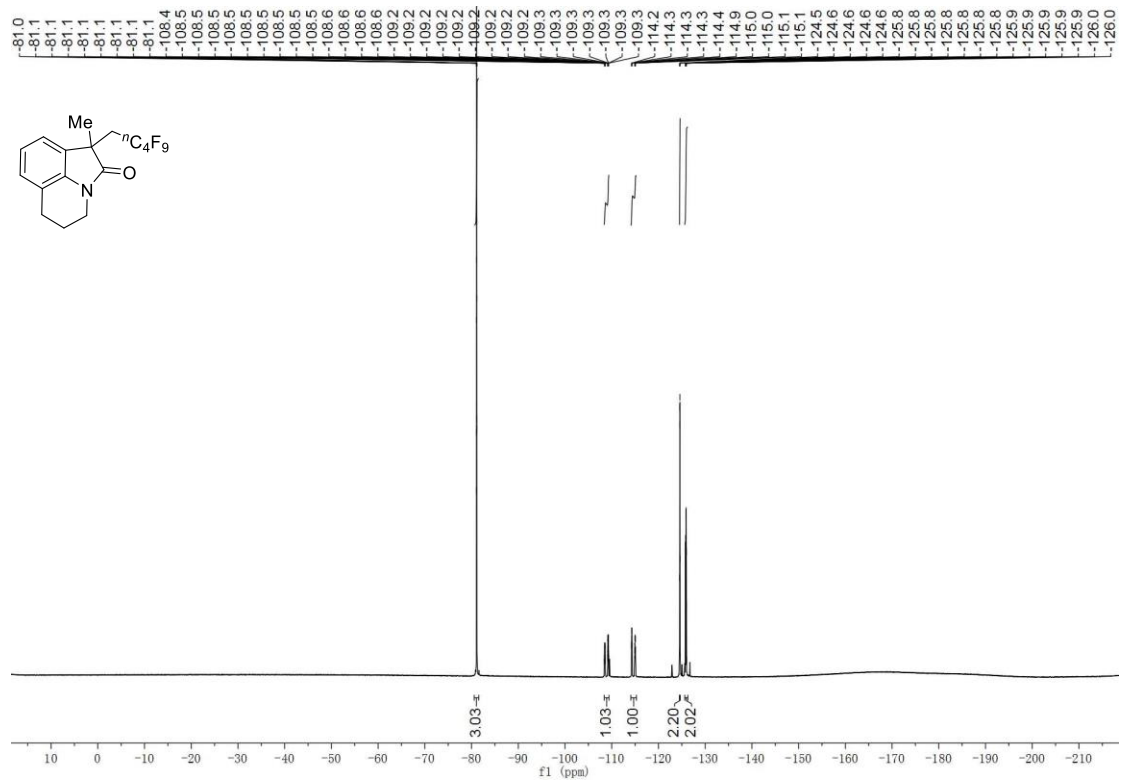
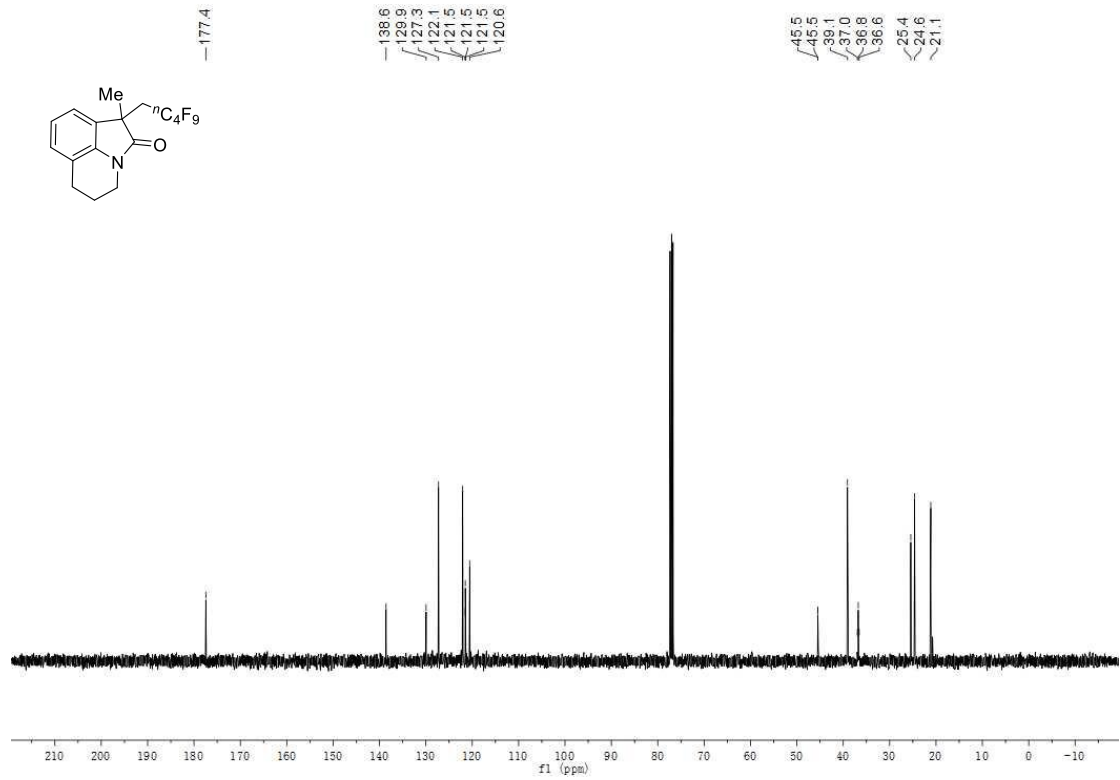


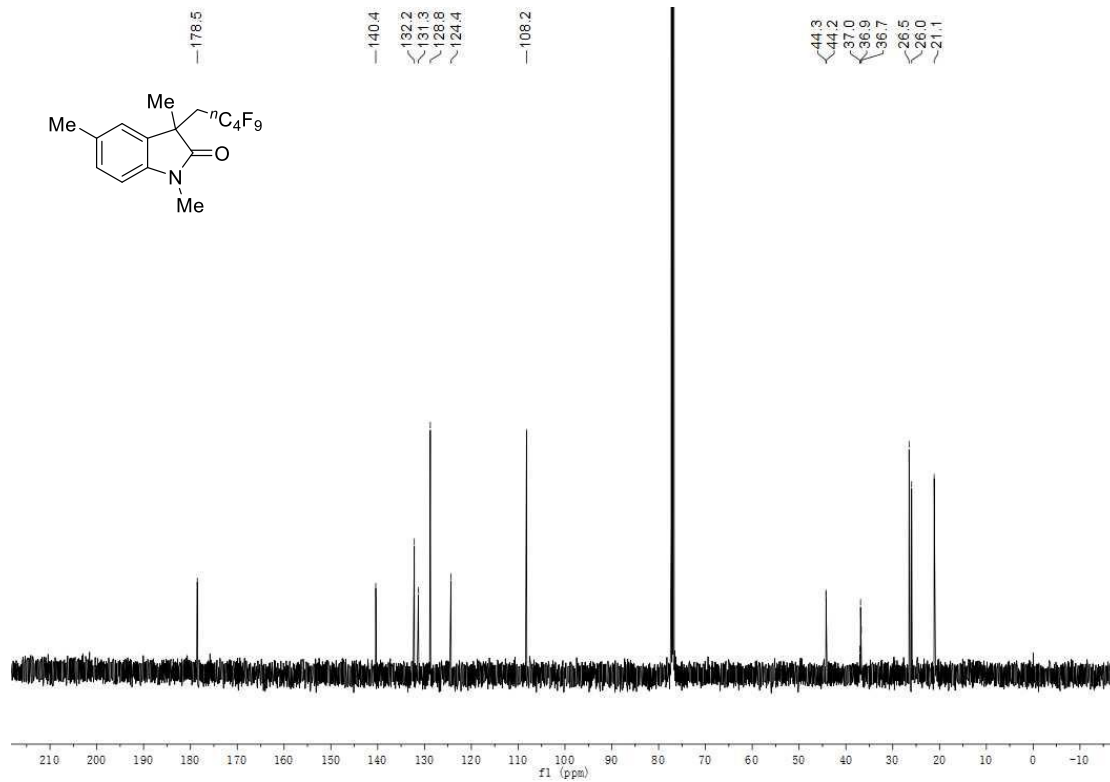
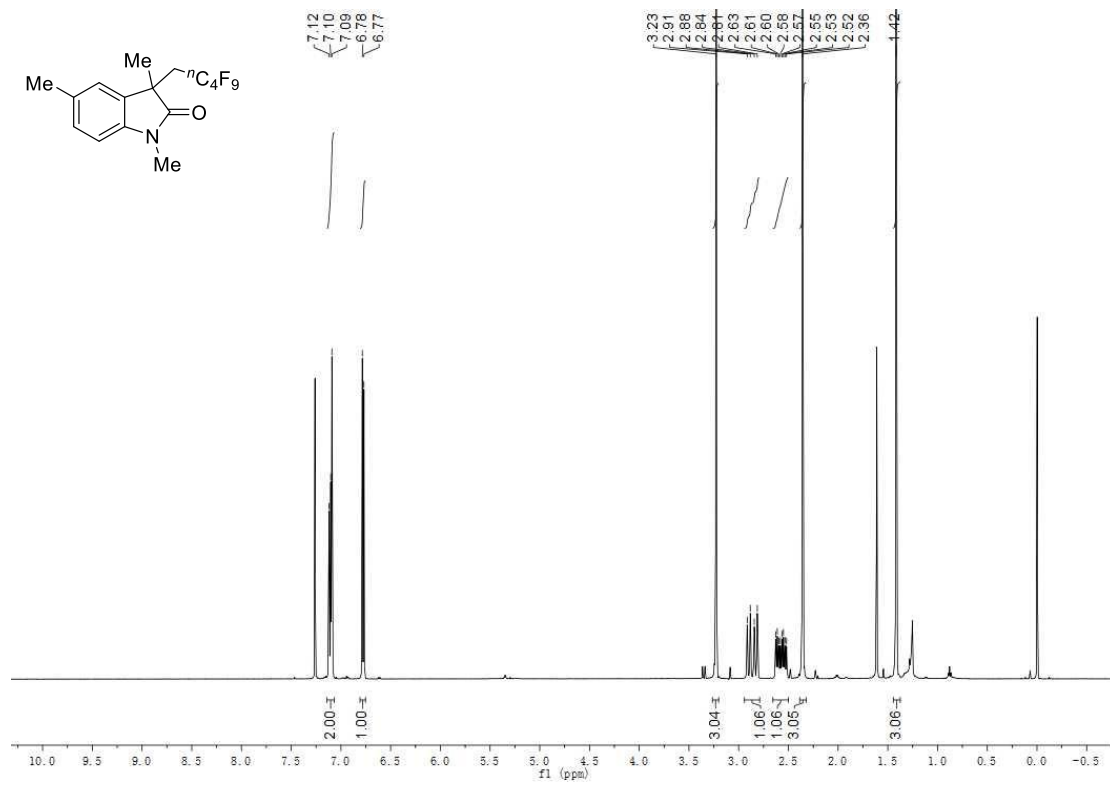


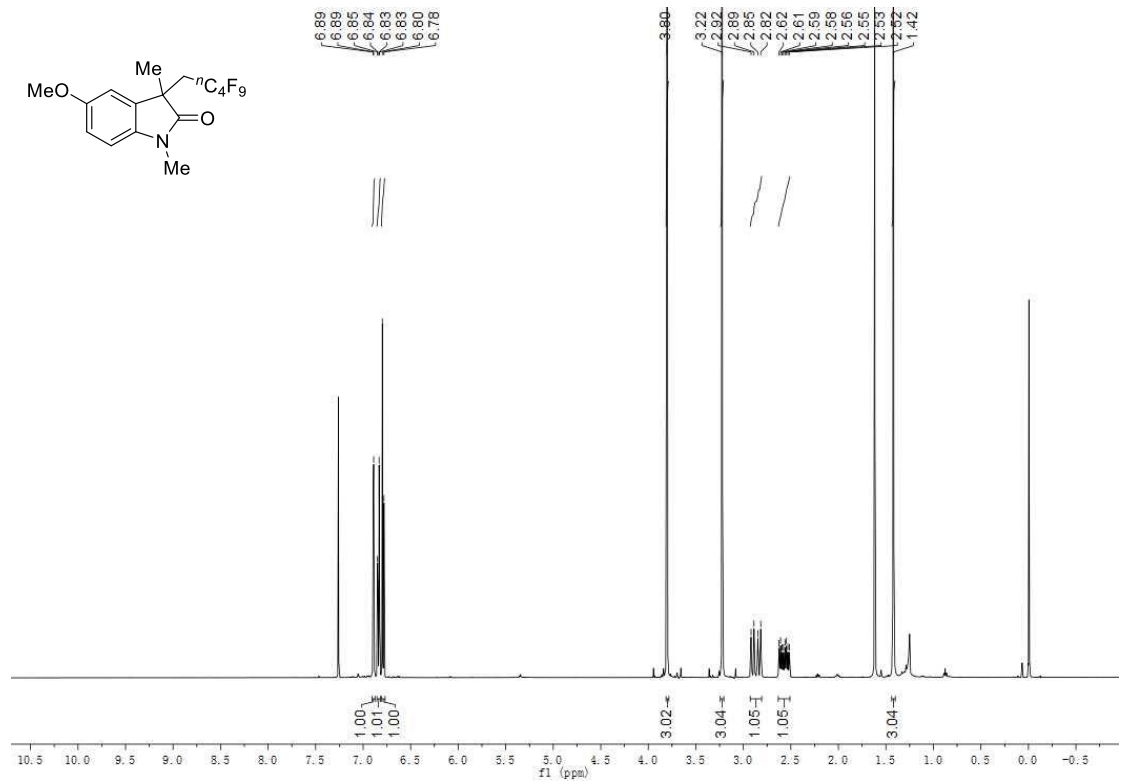
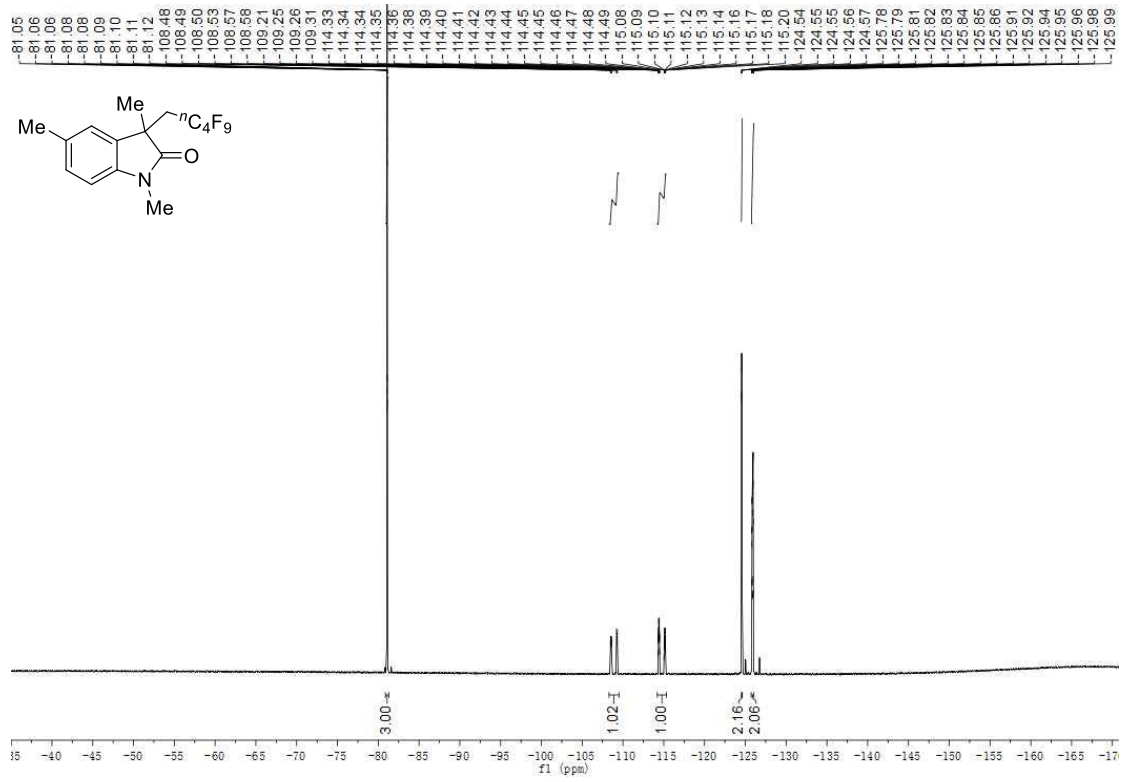


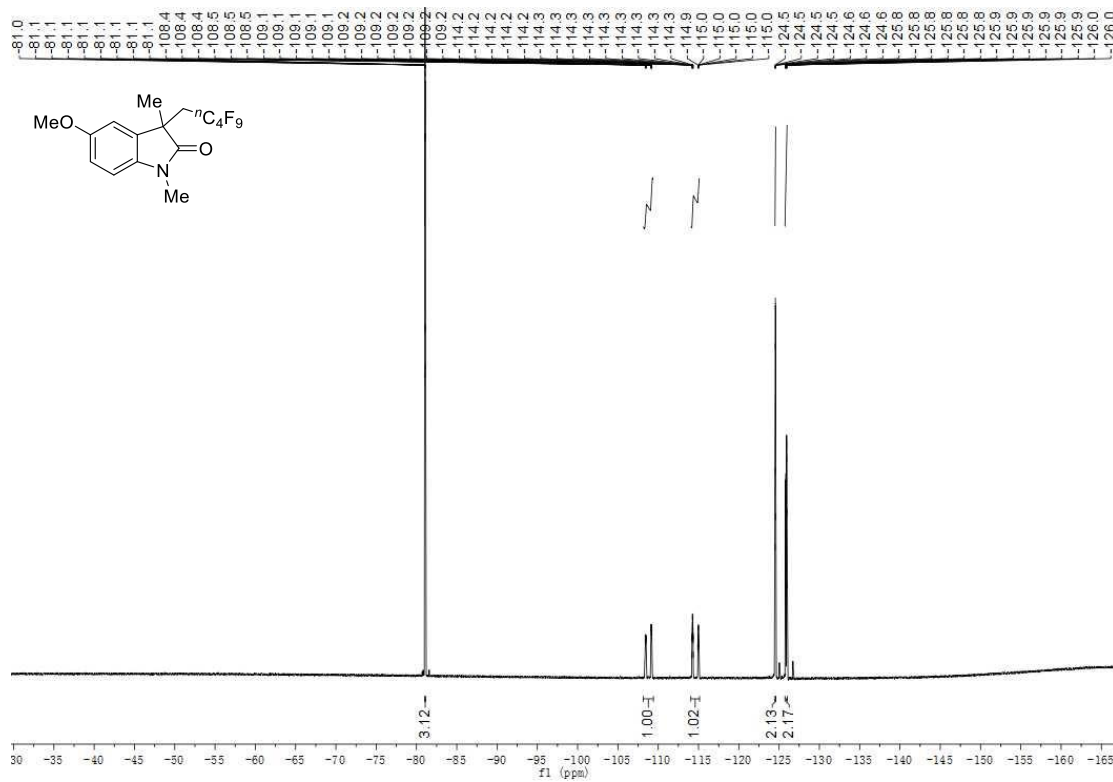
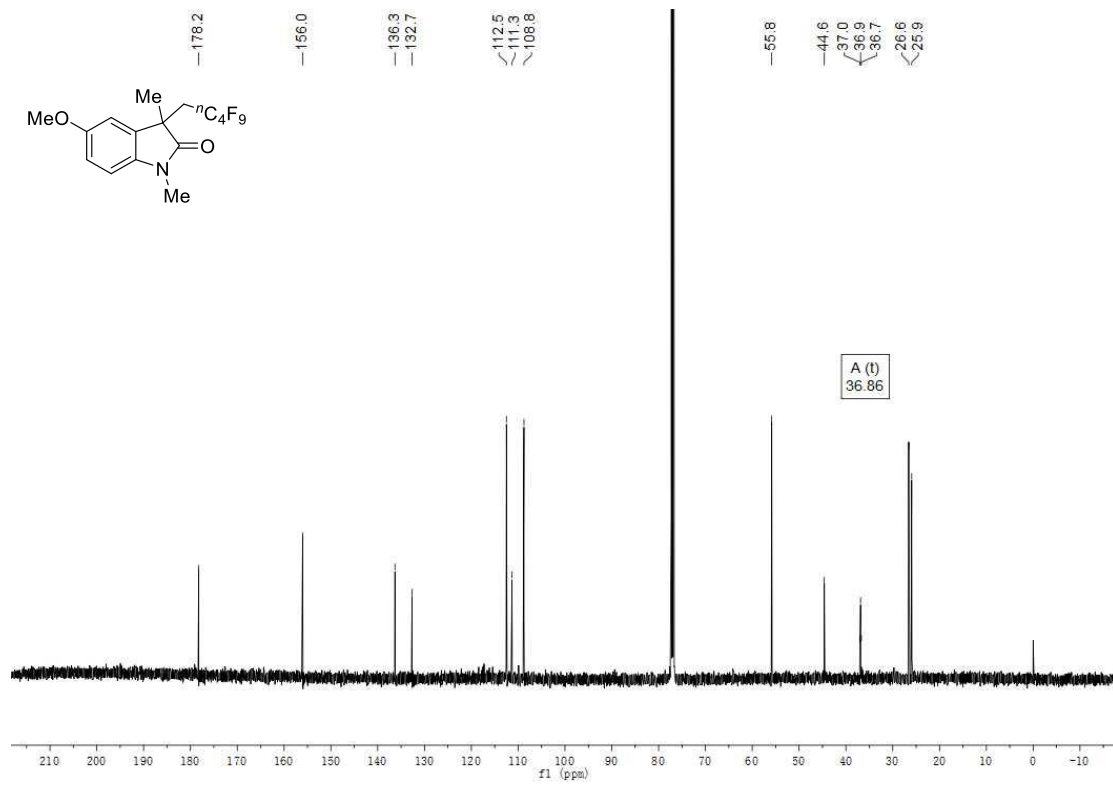


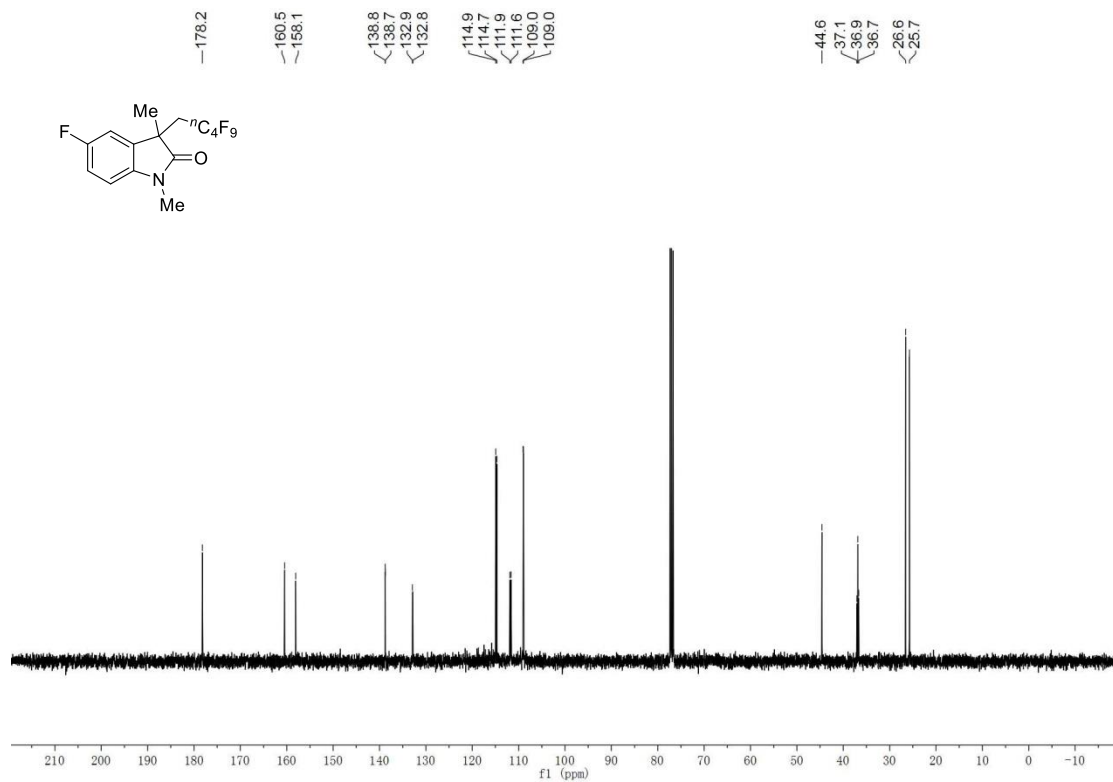
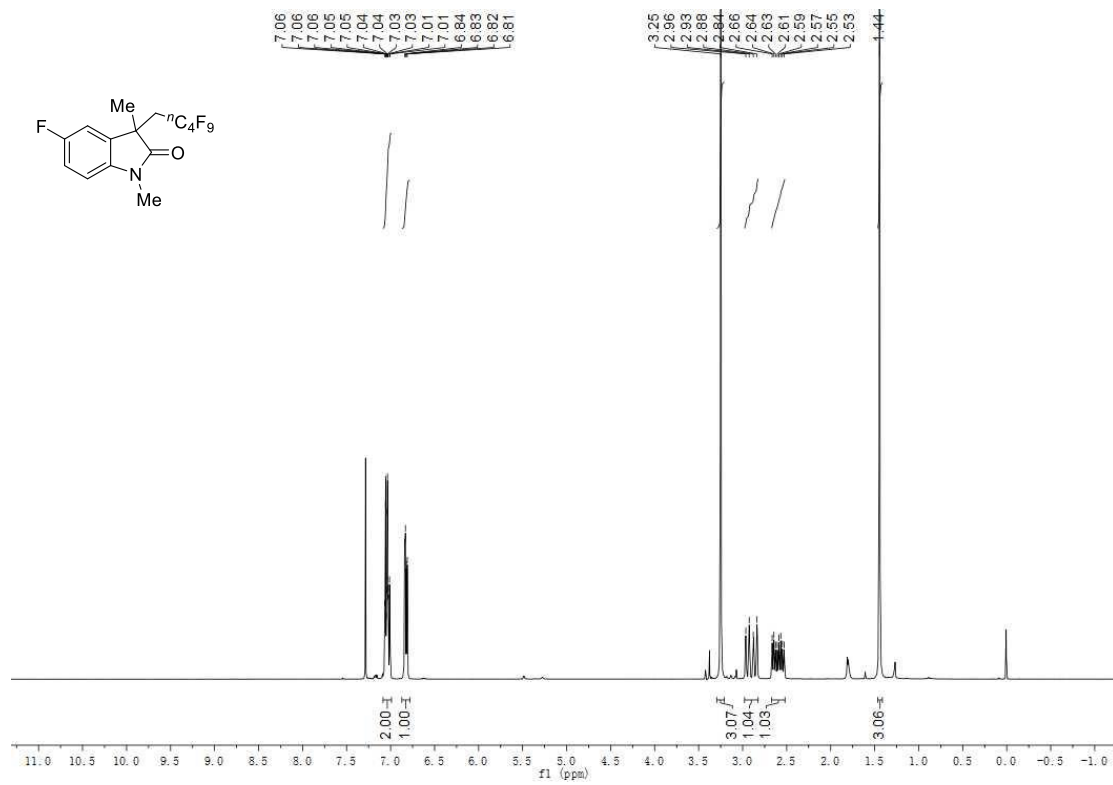


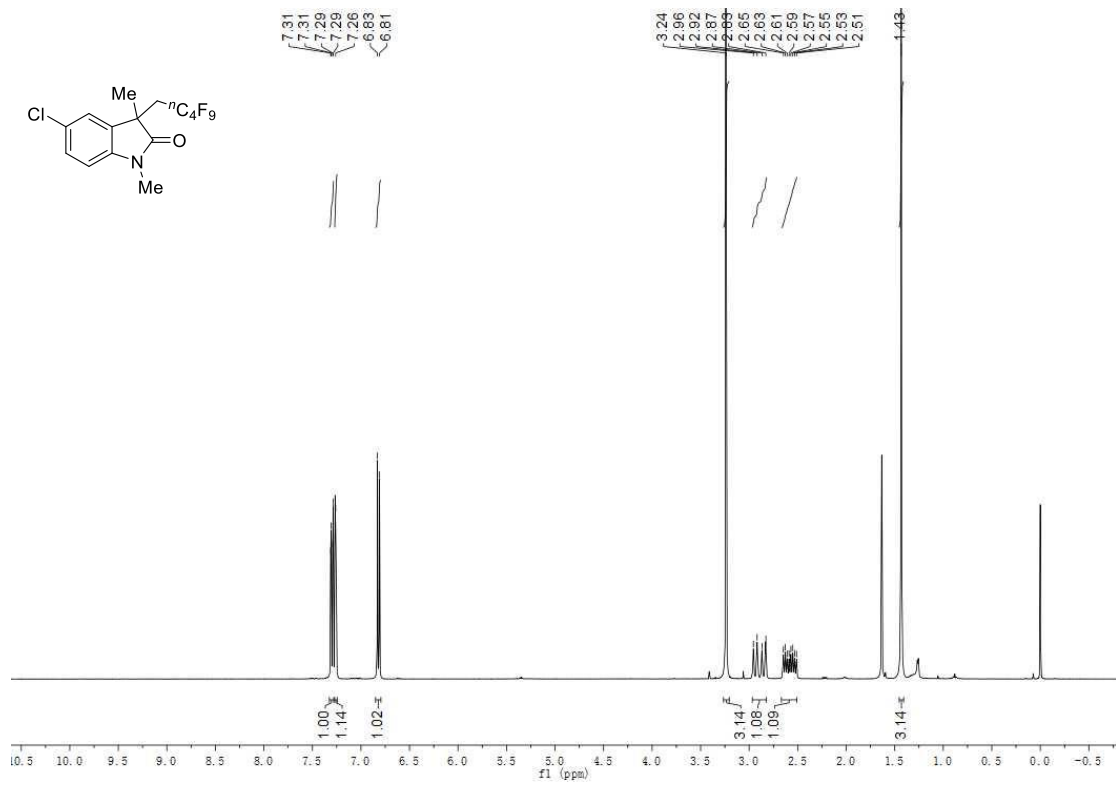
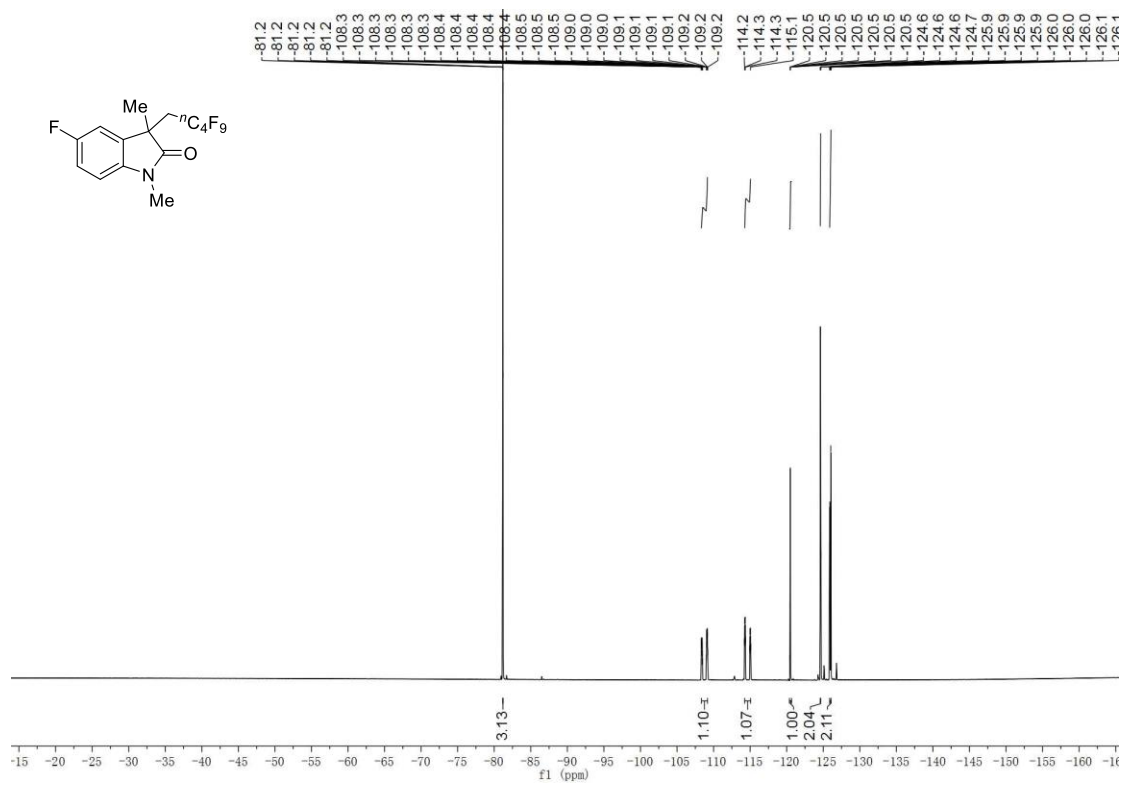


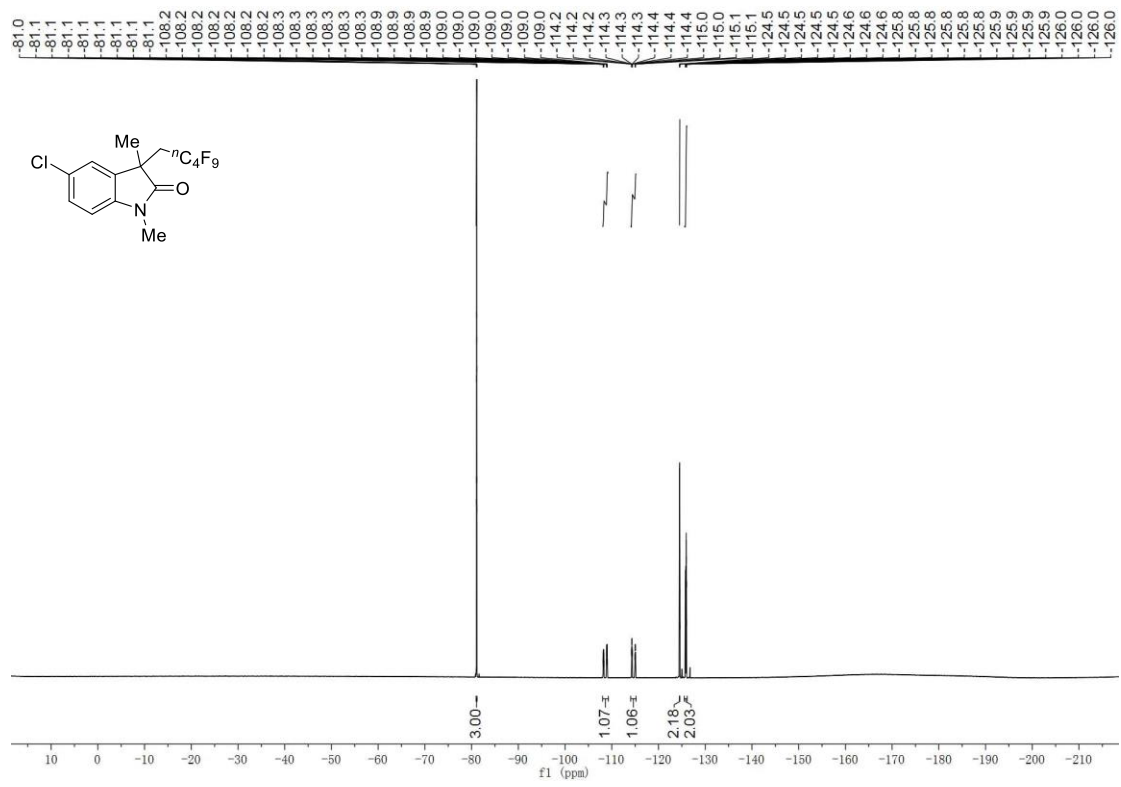
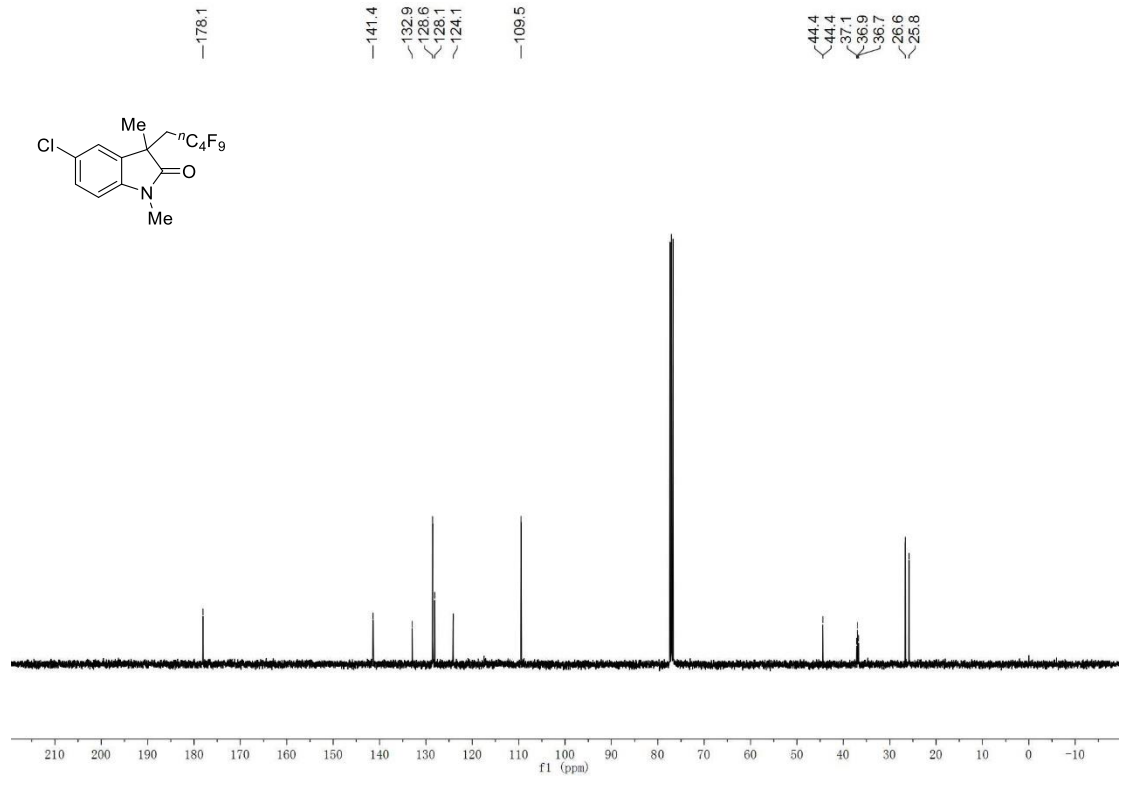


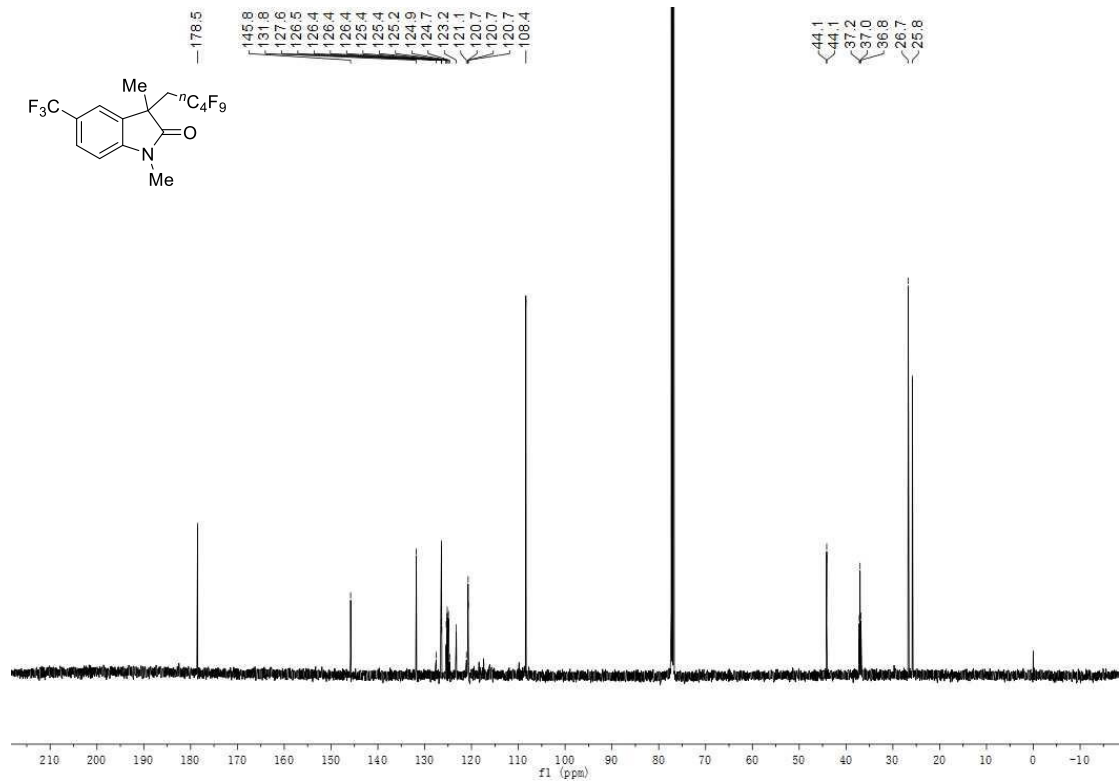
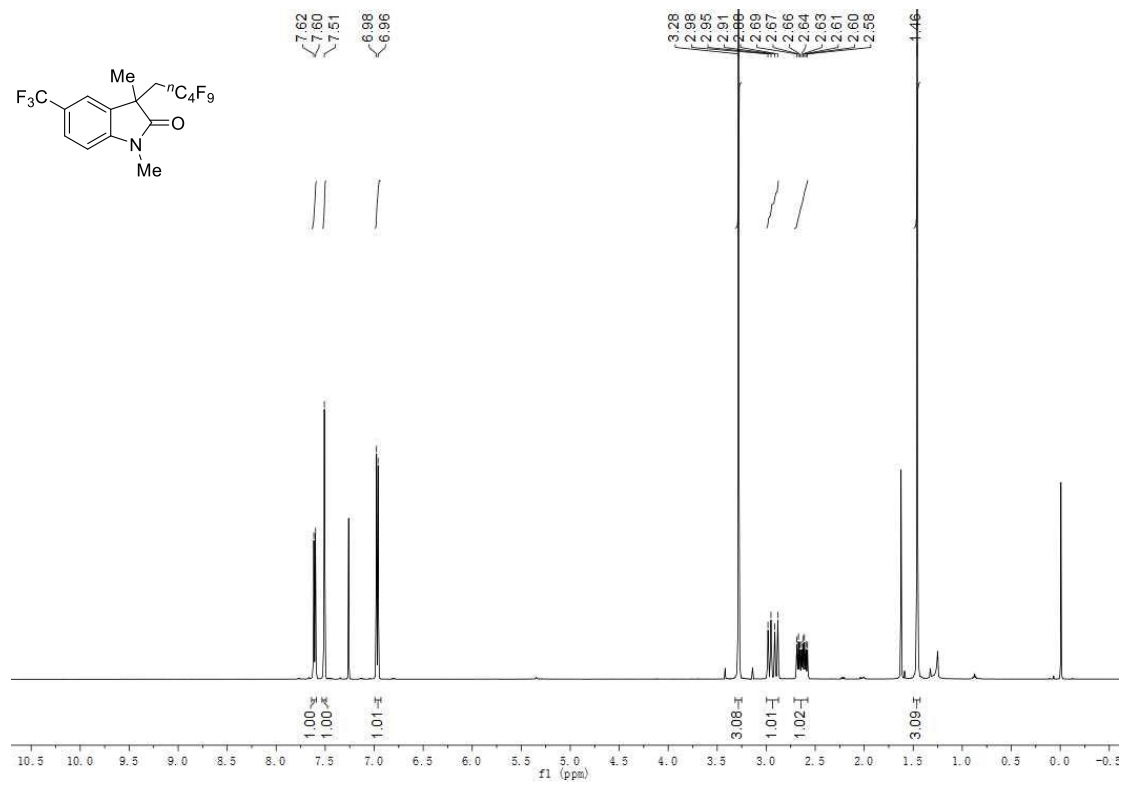


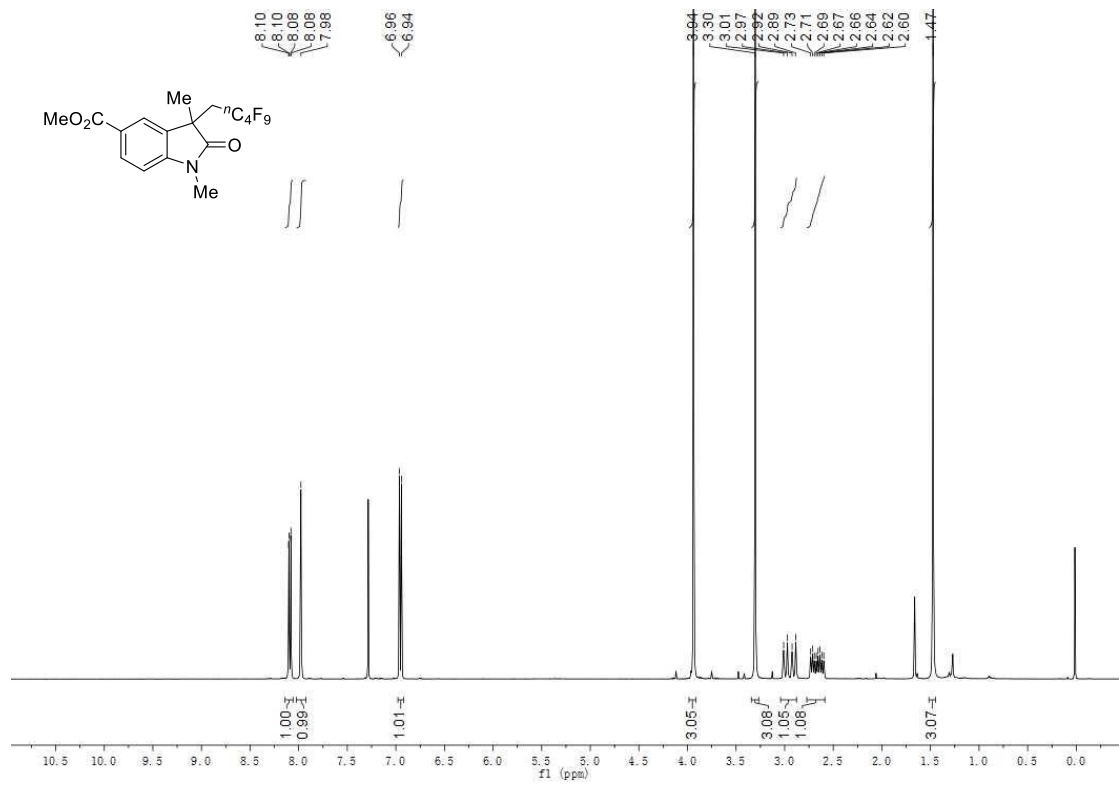
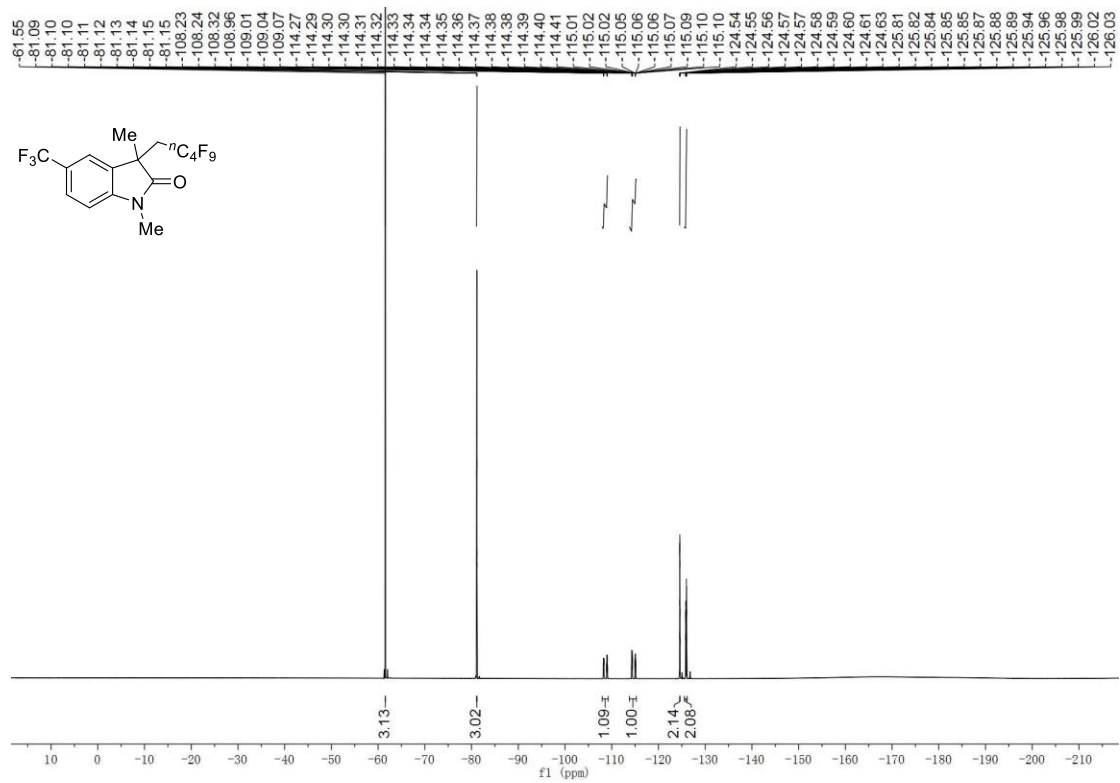


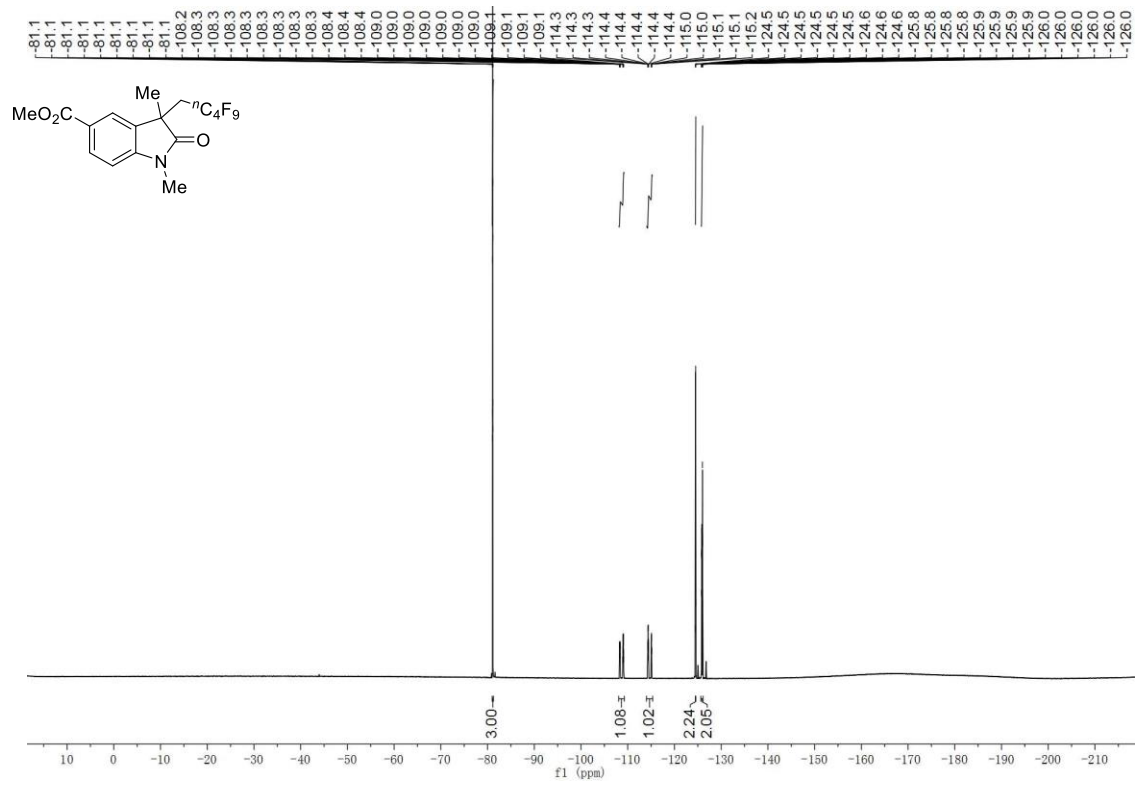
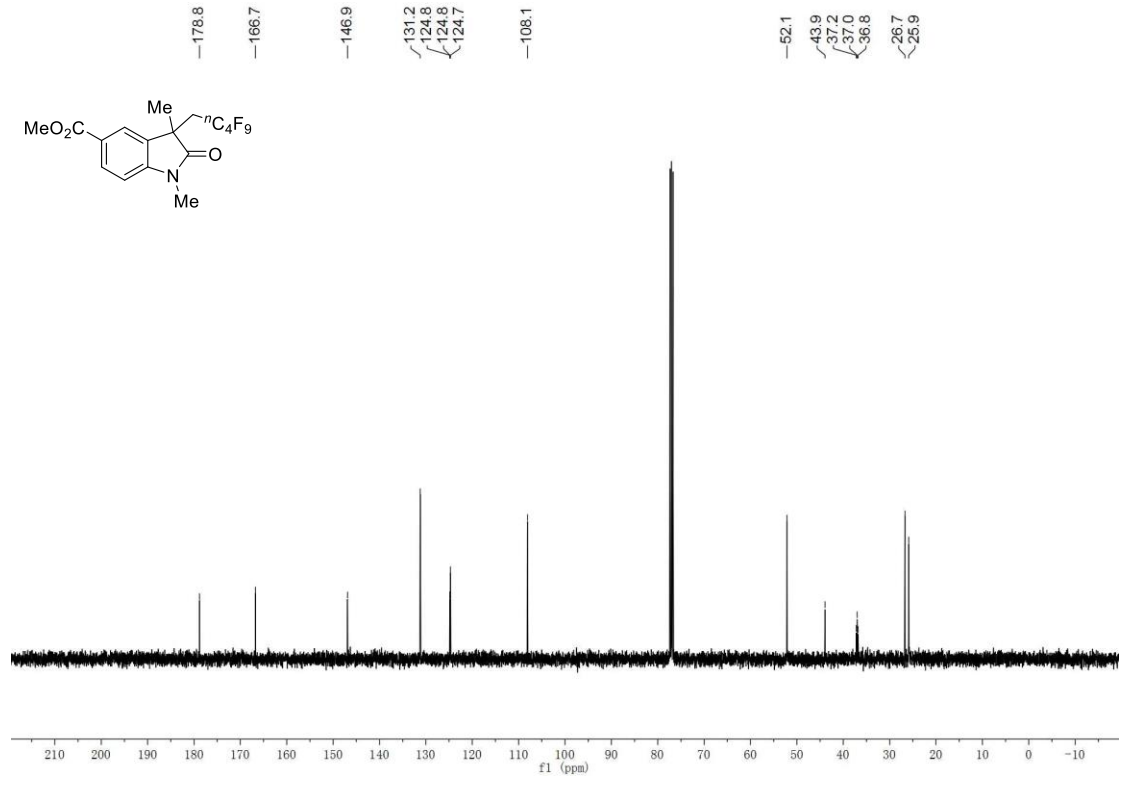


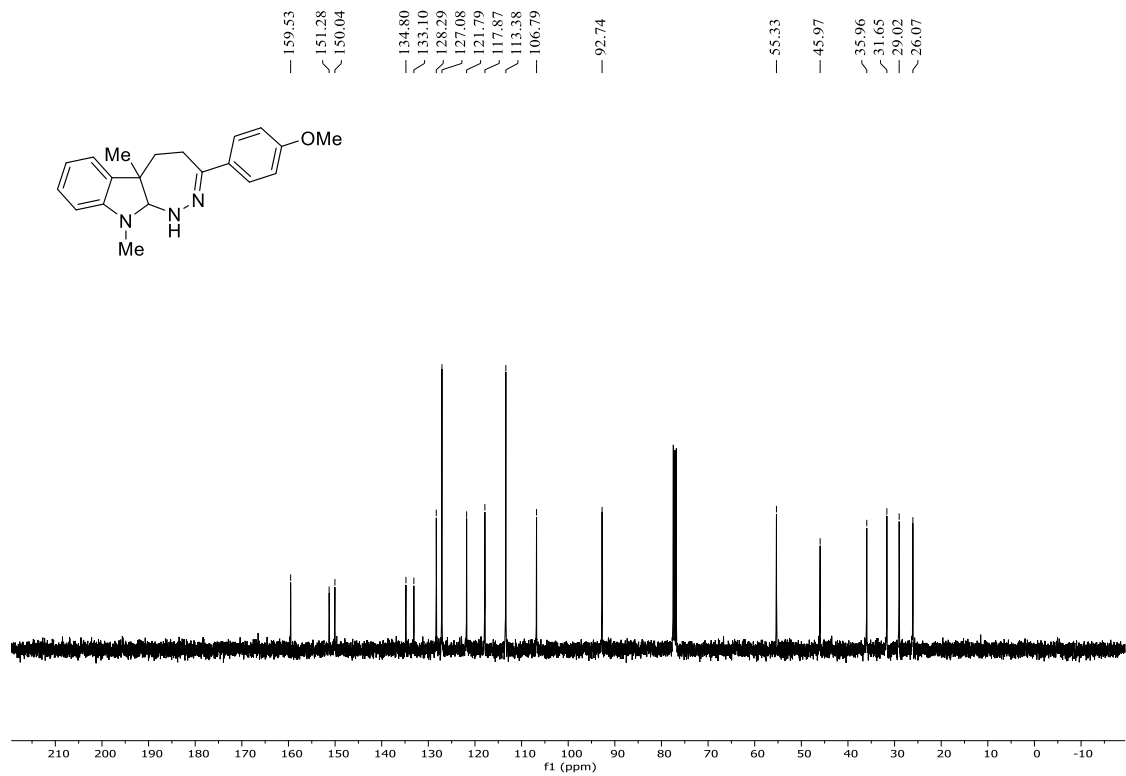
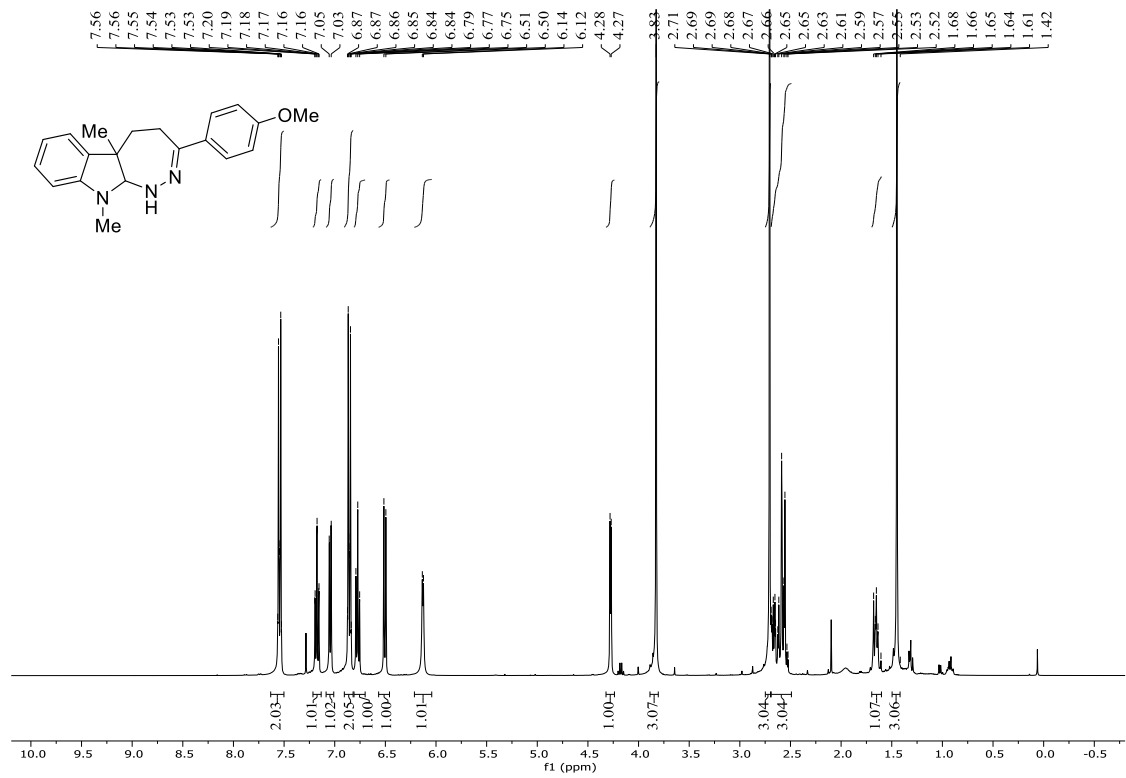


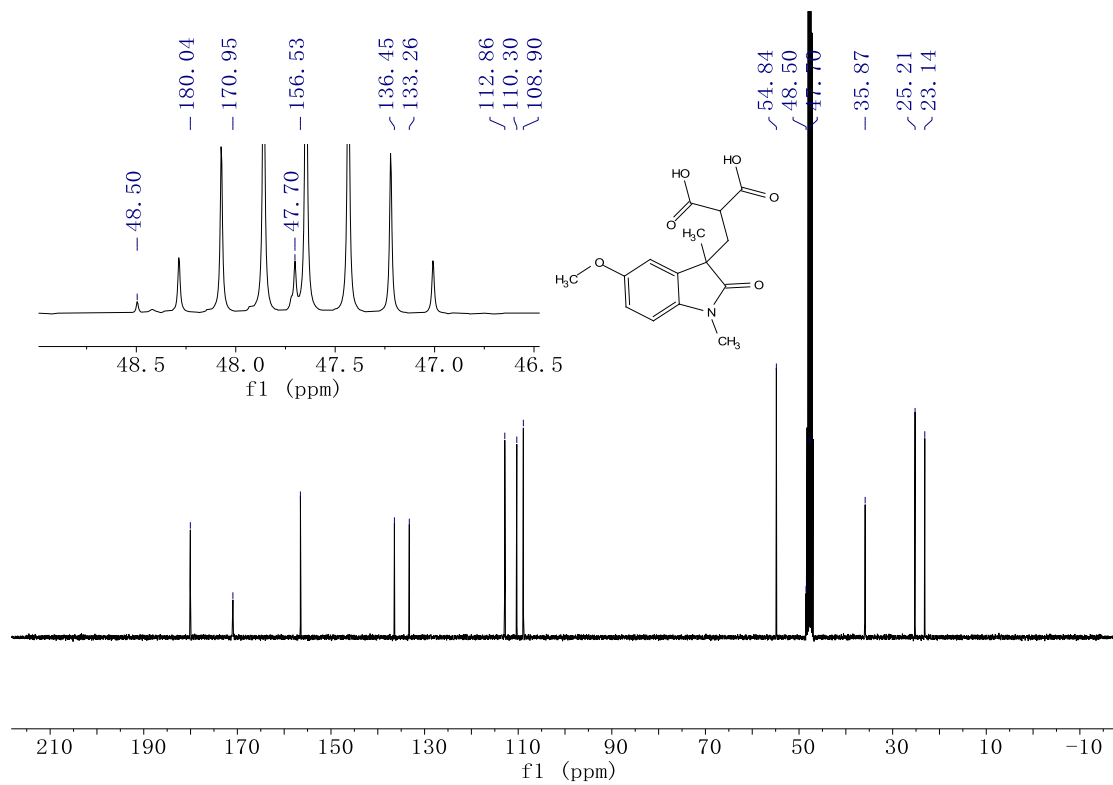
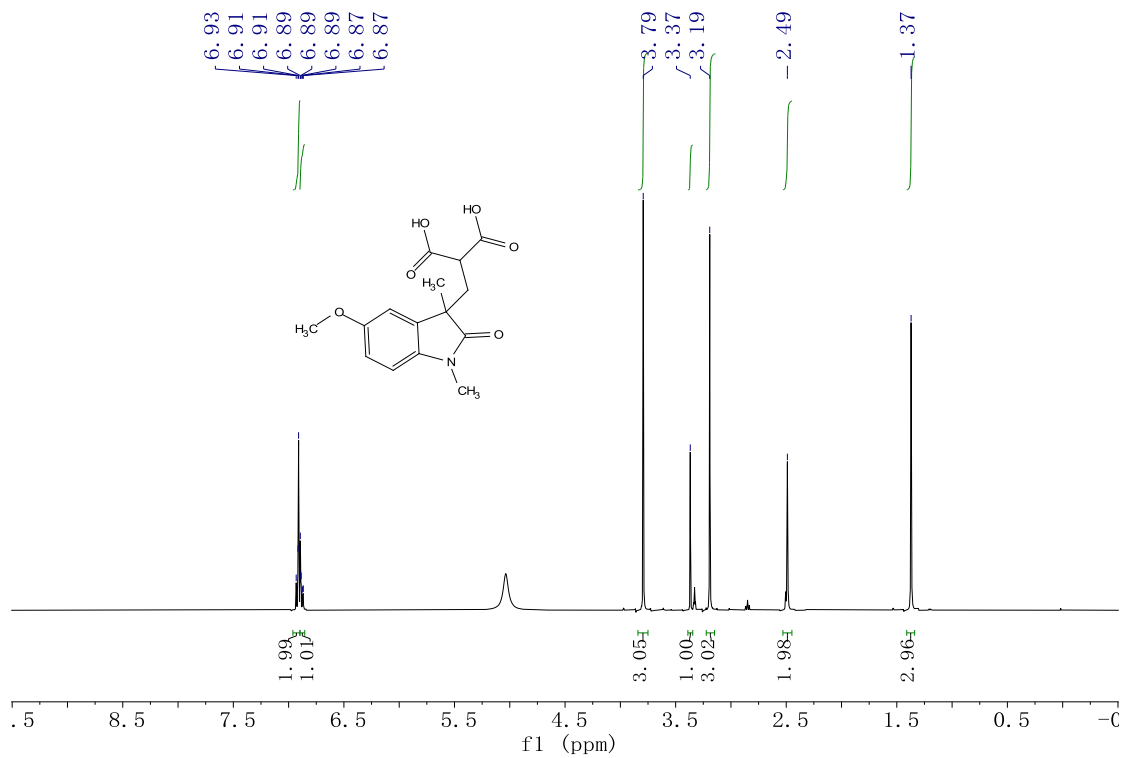


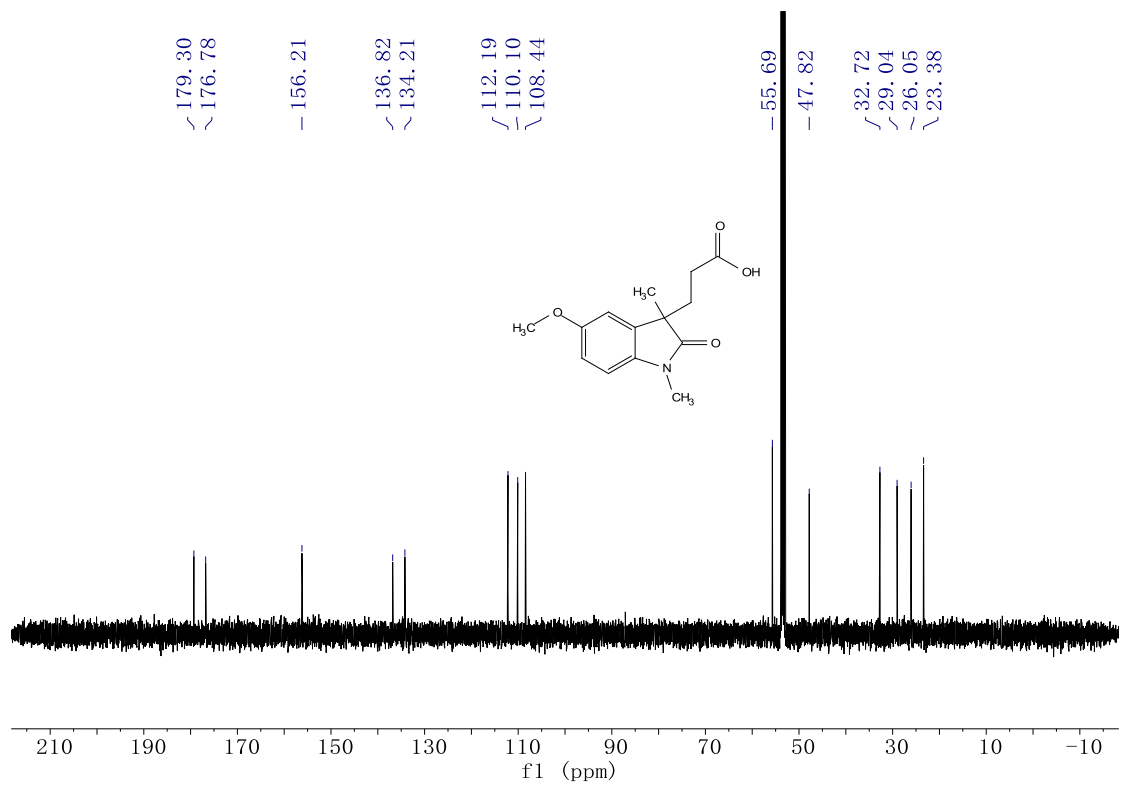
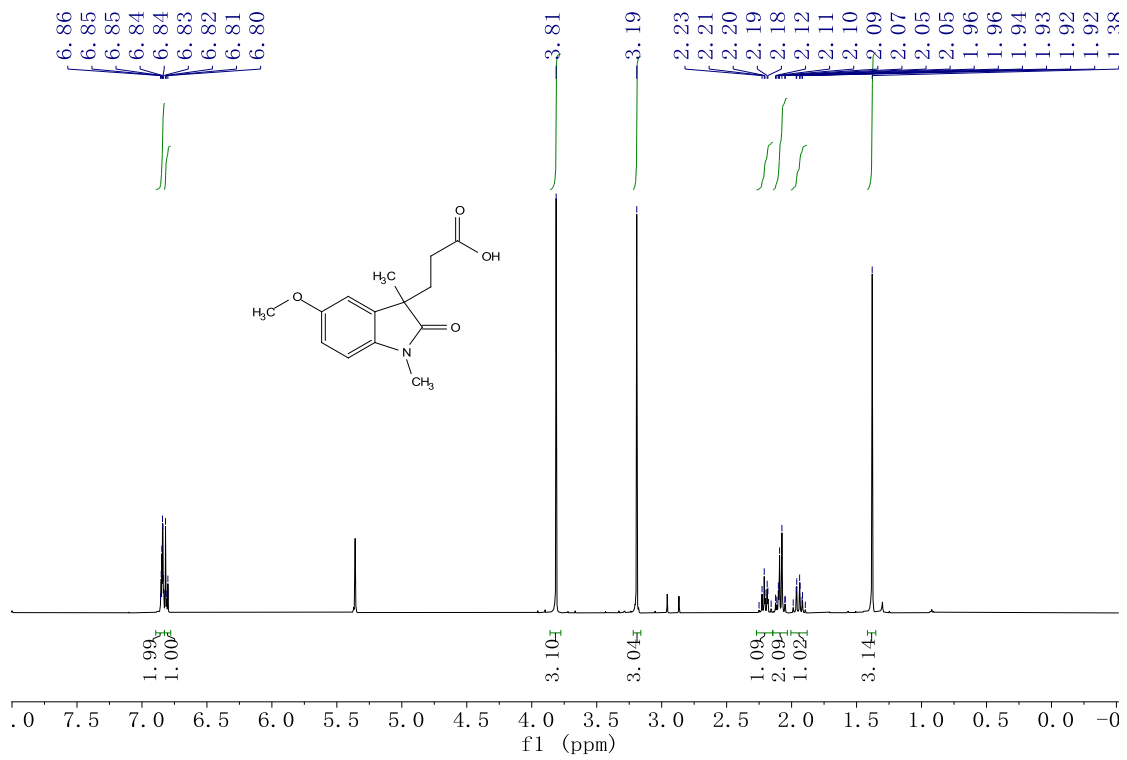


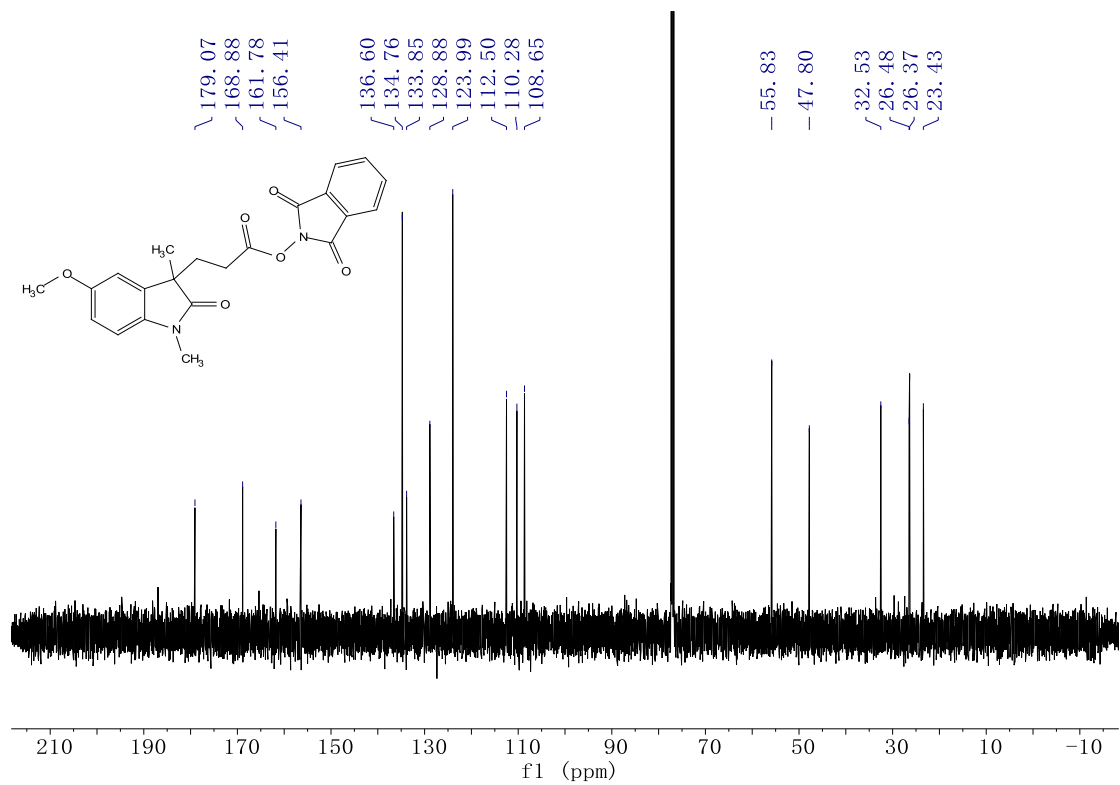
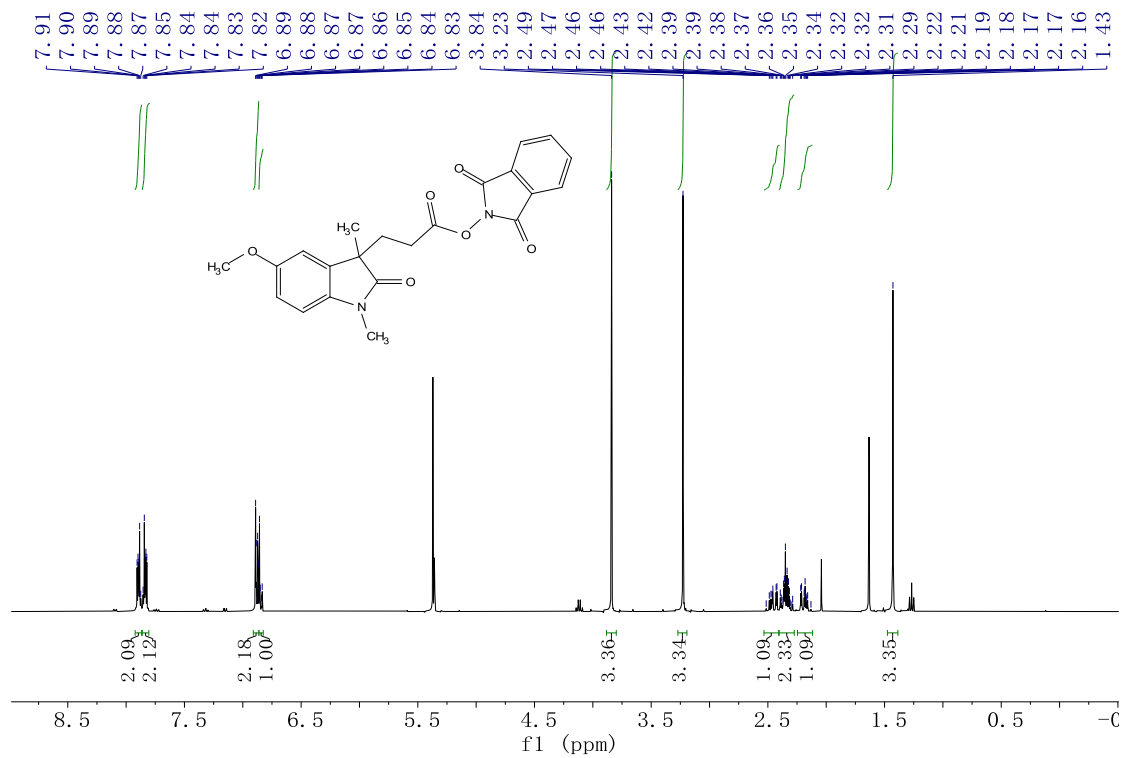


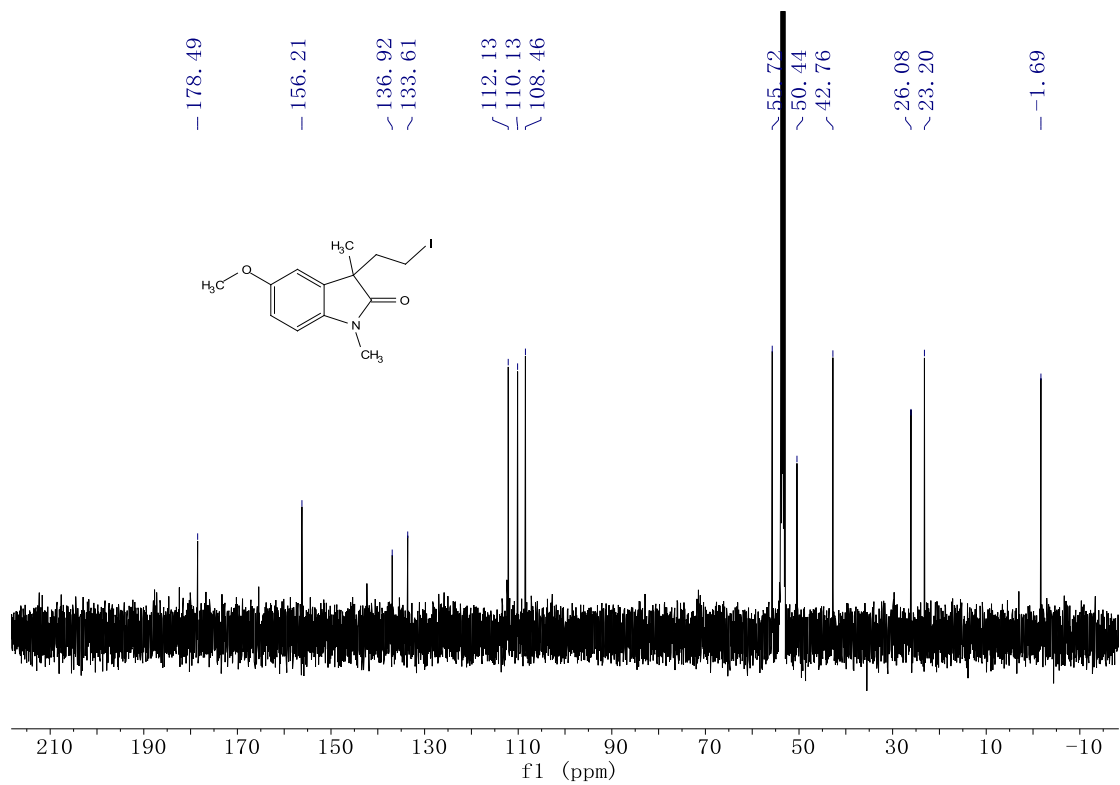
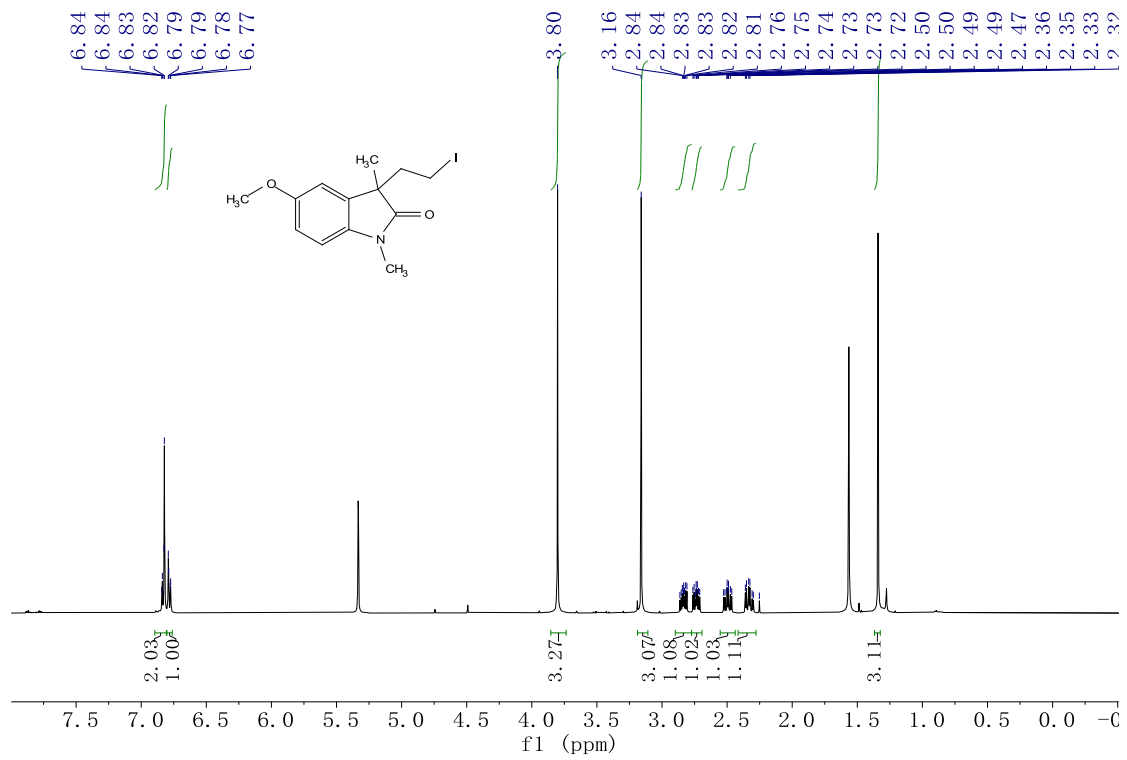


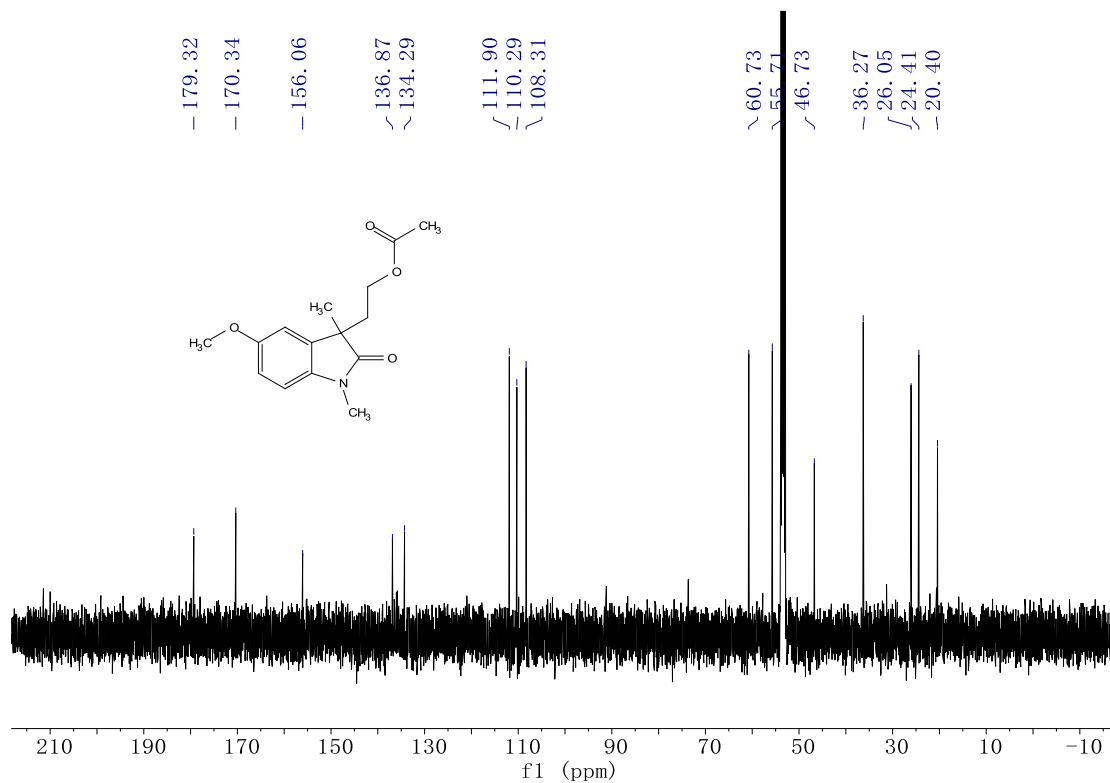
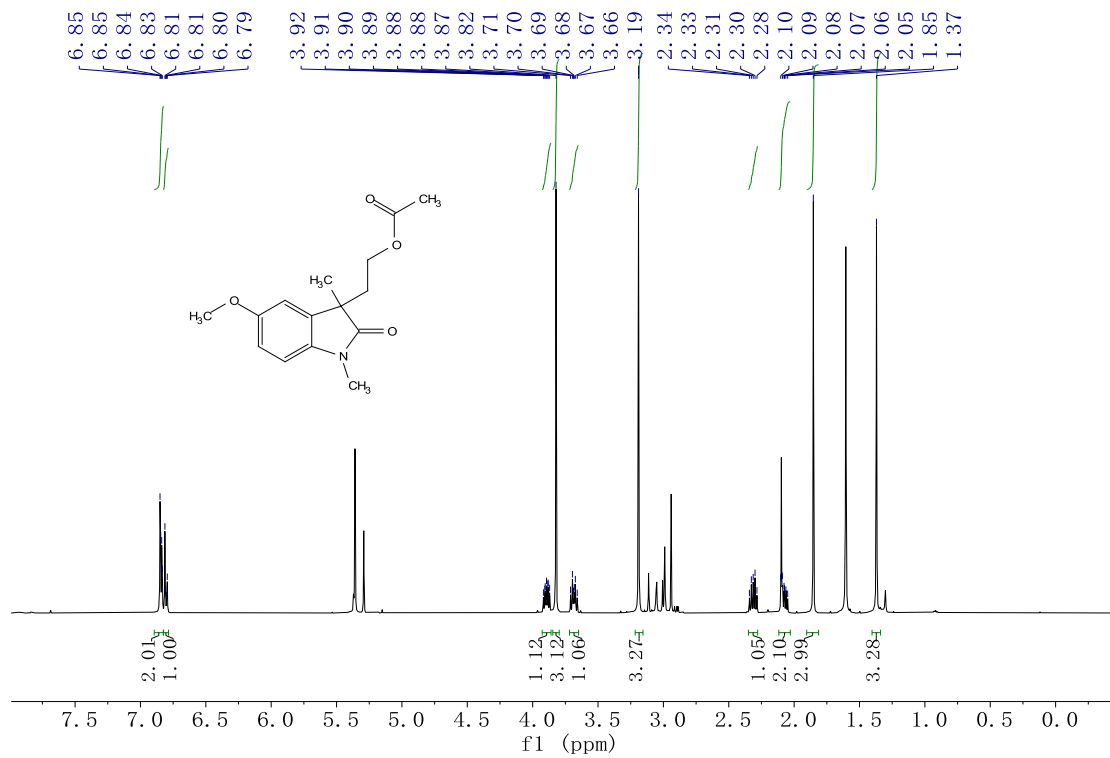


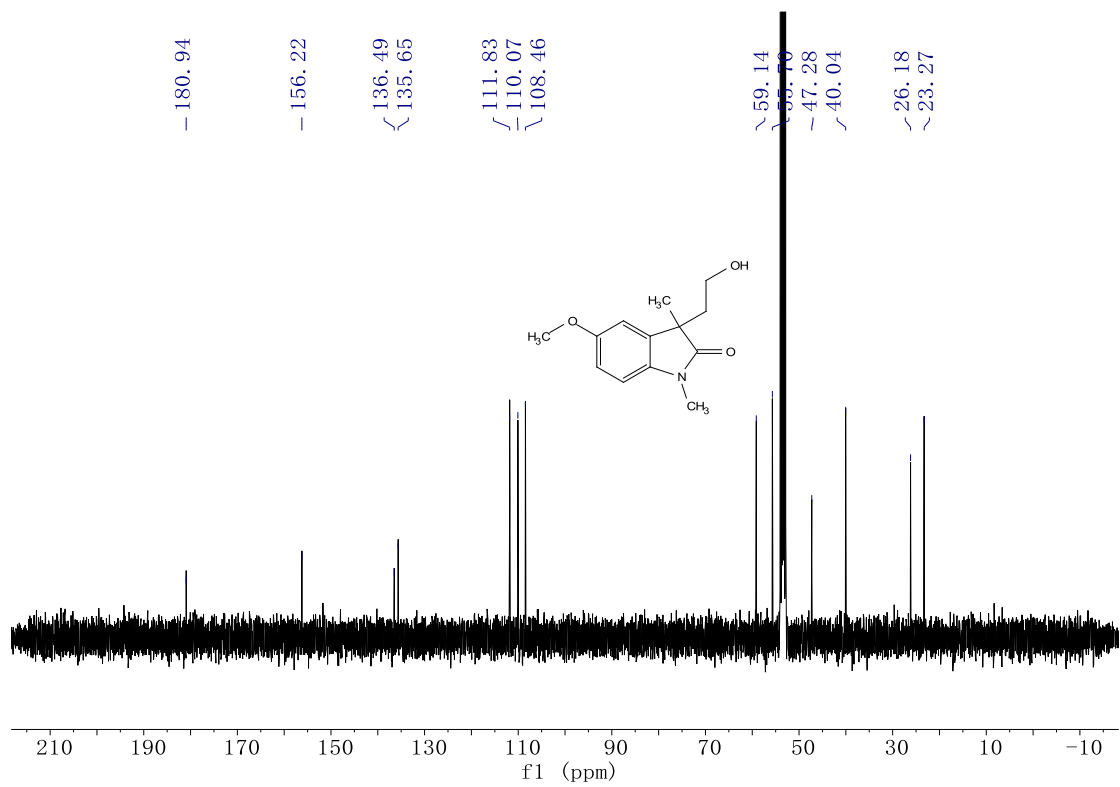
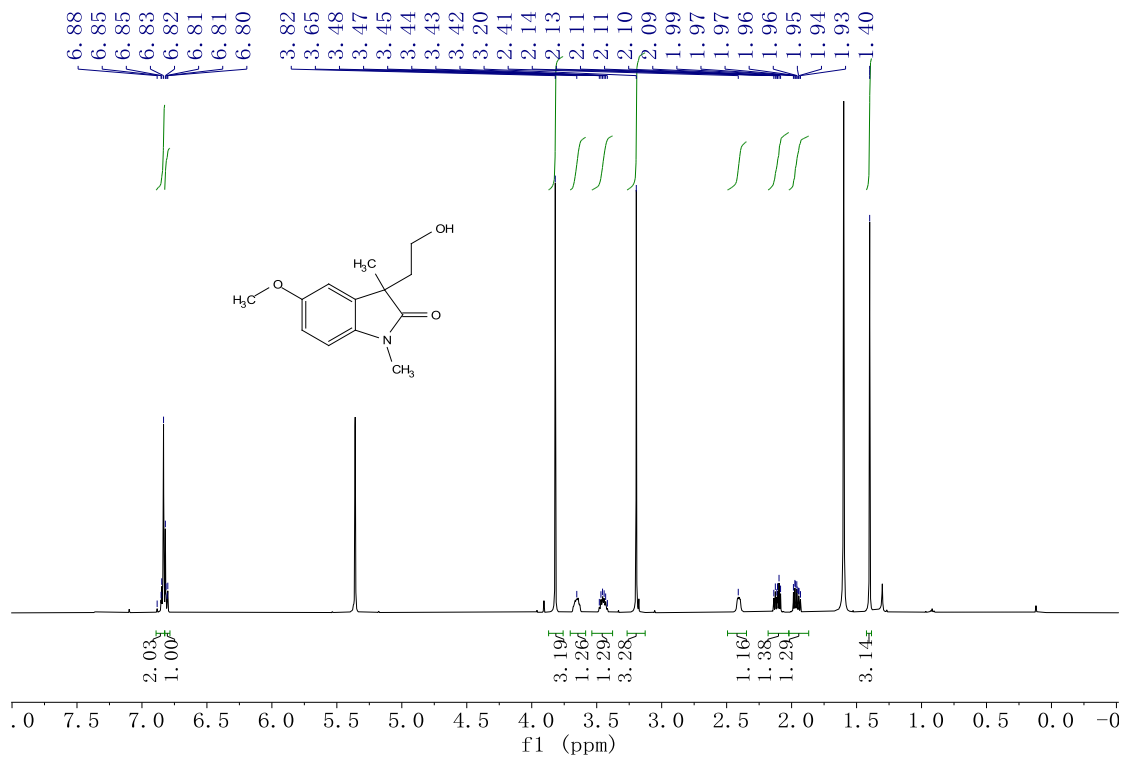


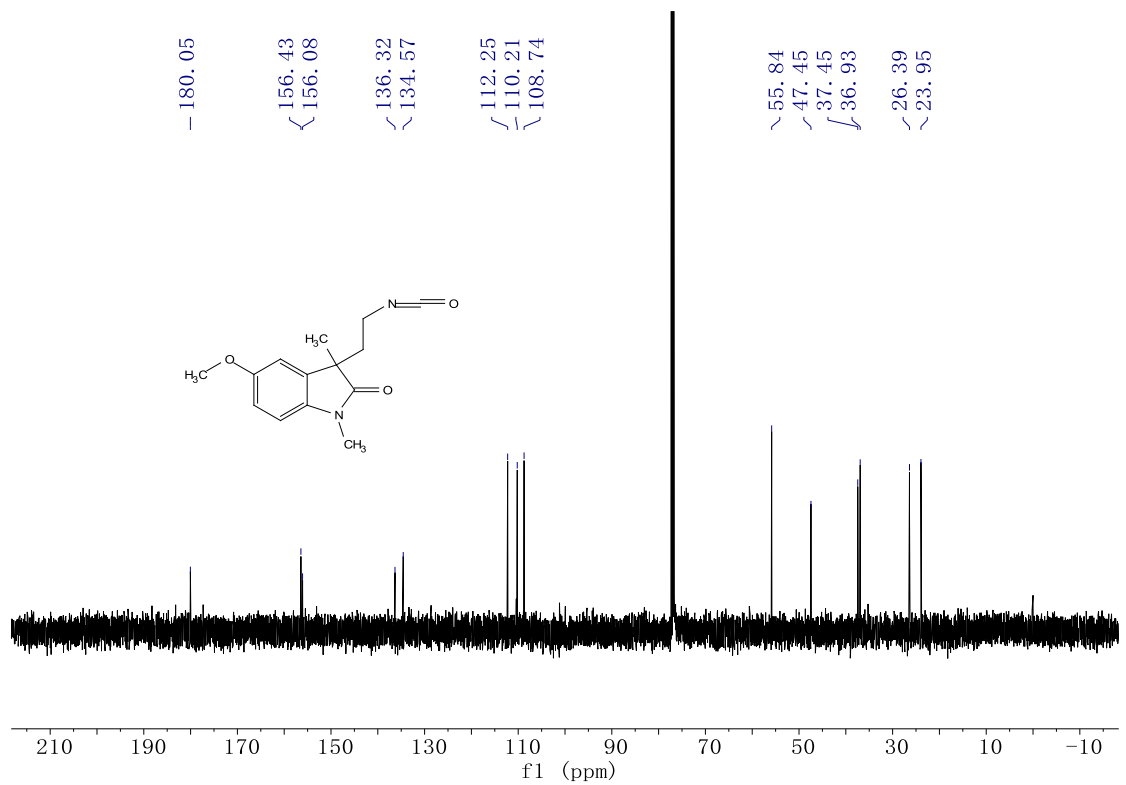
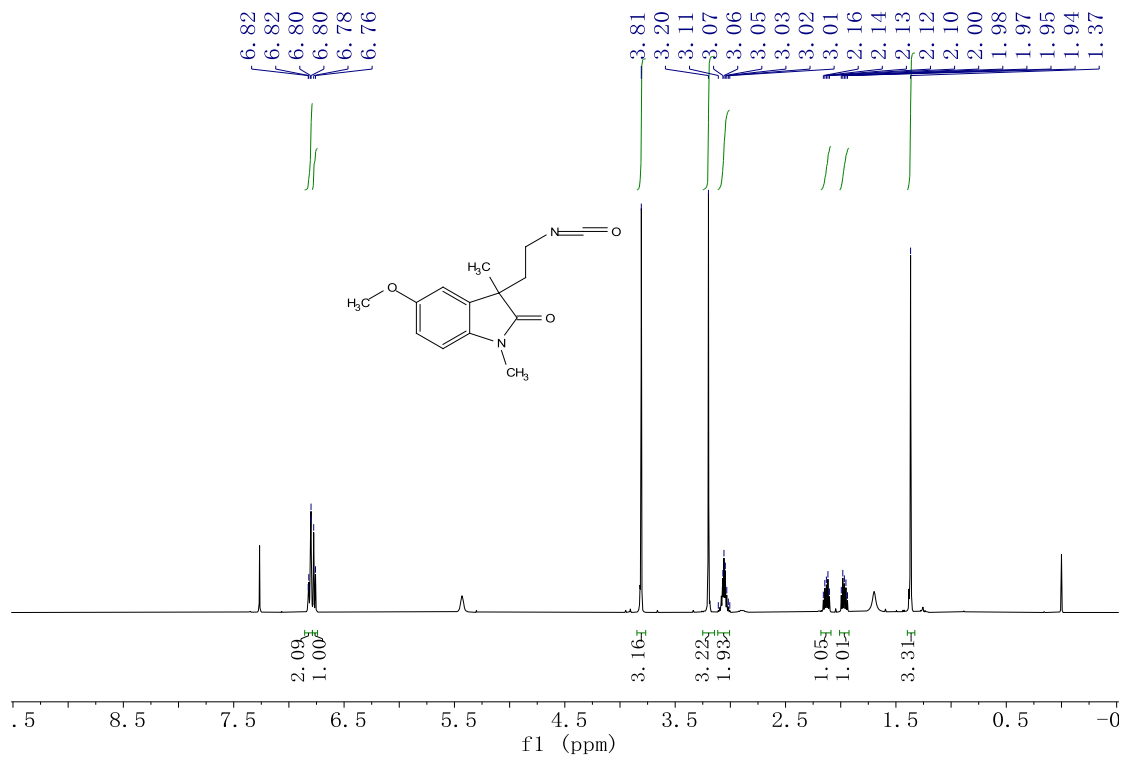


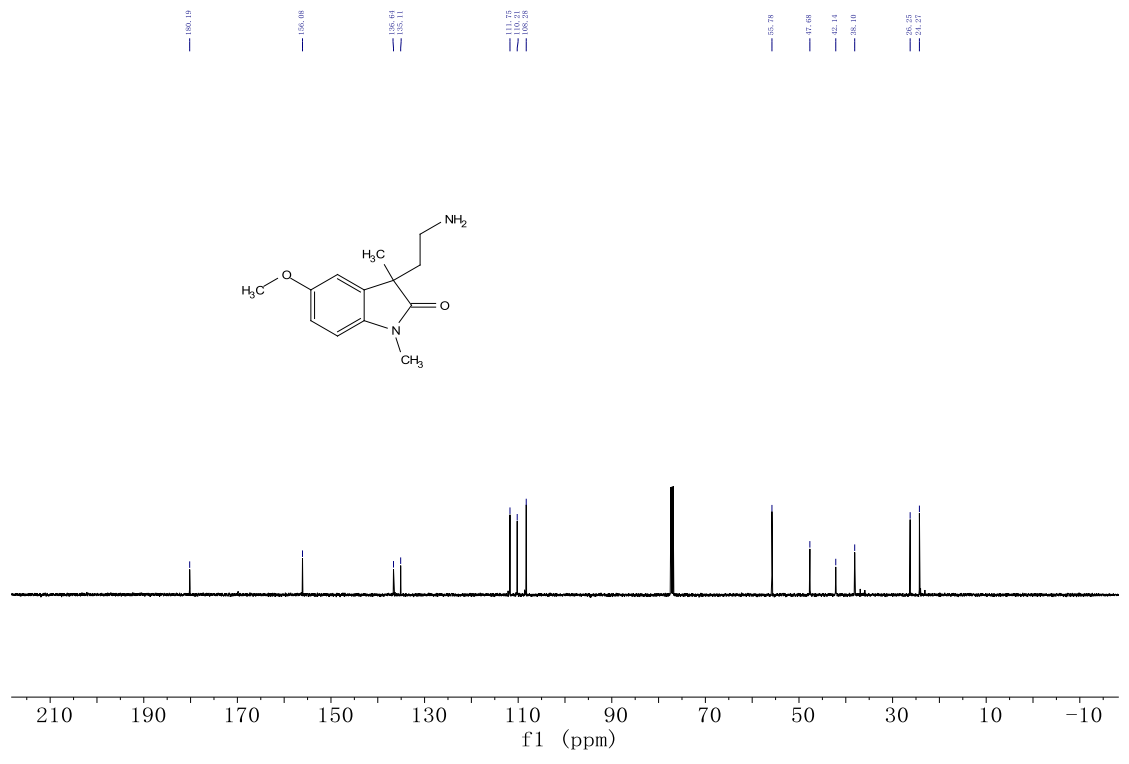
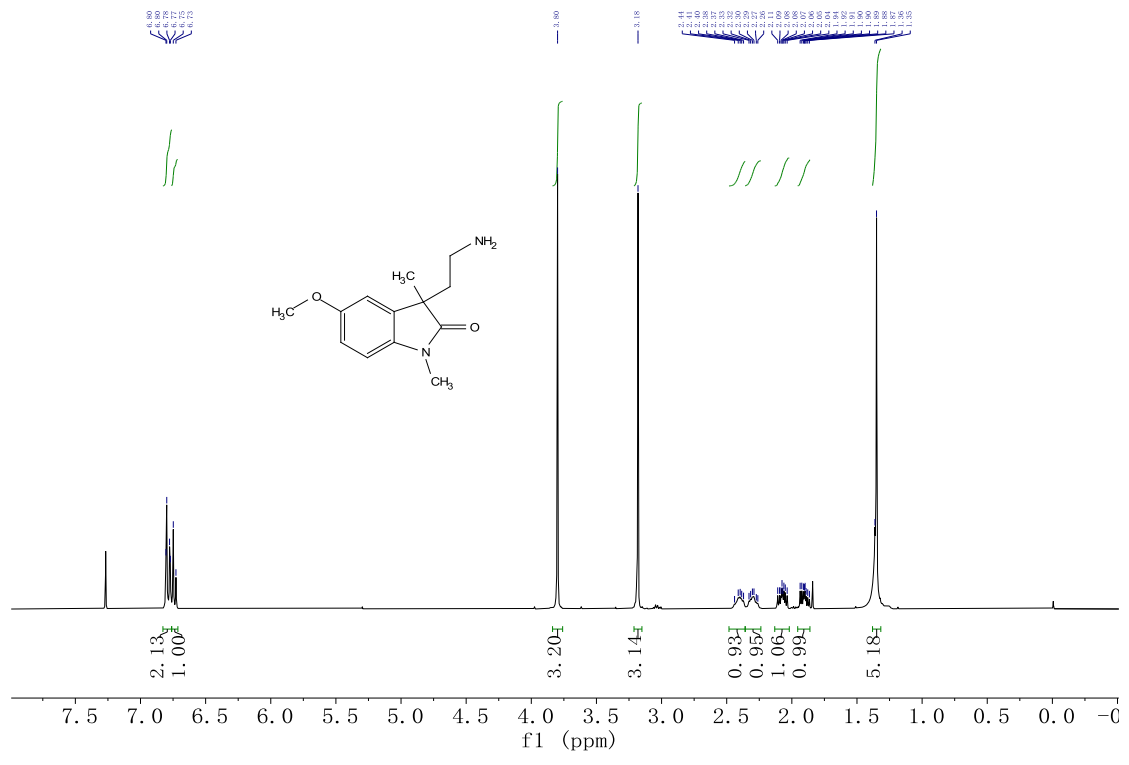












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