

## Supporting Information

### Palladium-catalyzed allylic alkylation dearomatization of $\beta$ -naphthols and indoles with *gem*-difluorinated cyclopropanes

Zhiyuan Fu, Jianping Zhu, Songjin Guo,\* and Aijun Lin\*

State Key Laboratory of Natural Medicines and Department of Medicinal Chemistry, School of Pharmacy, China Pharmaceutical University, Nanjing 210009, P. R. China

E-mail: yd1029820332@163.com; ajlin@cpu.edu.cn

## Content

<b>1. General Information</b> .....	<b>2</b>
<b>2. Preparation of Starting Materials</b> .....	<b>2</b>
<b>3. Optimization of Reaction Conditions for the Synthesis of Products 3a and 5a</b> .....	<b>5</b>
<b>4. General Experimental Procedures</b> .....	<b>8</b>
<b>5. Further Functionalization of the Products</b> .....	<b>10</b>
<b>6. Optimization of Reaction Conditions for the Synthesis of Product 3q</b> .....	<b>13</b>
<b>7. Optimization of Reaction Conditions for the Synthesis of Product 3r</b> .....	<b>15</b>
<b>8. Optimization of the Asymmetric Reaction Conditions for Product 3a</b> .....	<b>17</b>
<b>9. Optimization of the Asymmetric Reaction Conditions for Product 5a</b> .....	<b>19</b>
<b>10. Characterization of the Products</b> .....	<b>21</b>
<b>11. X-ray Crystallography Data of 3l and 5a</b> .....	<b>46</b>
<b>12. References</b> .....	<b>48</b>
<b>13. NMR Copies of Substrates and Products</b> .....	<b>49</b>

## 1. General Information

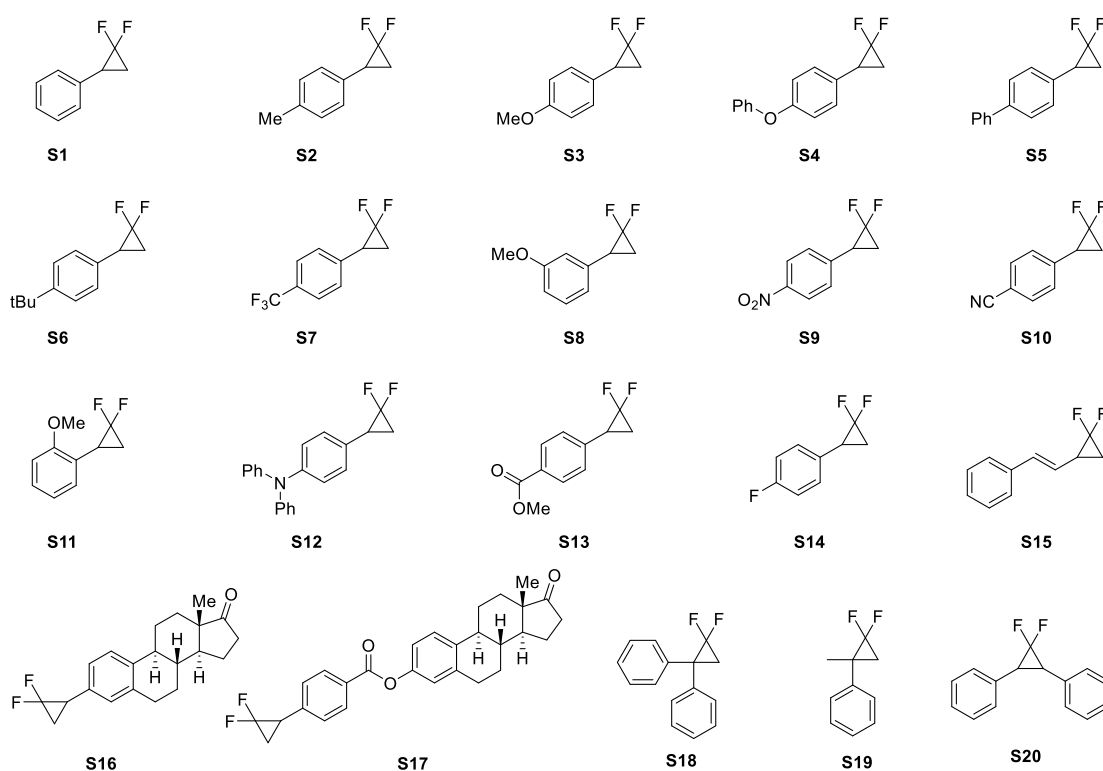
**Reagents and Solvents:** PE refers to petroleum ether b.p. 60–90 °C and EA refers to ethyl acetate. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

**Chromatography:** Flash column chromatography was carried out using commercially available 200–300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

**Data collection:**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using  $\text{CDCl}_3$  as solvent. Chemical shifts of  $^1\text{H}$  NMR were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta = 0.00$  ppm) with the solvent resonance as an internal standard ( $\text{CDCl}_3$ :  $\delta = 7.26$  ppm). Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of  $^{13}\text{C}$  NMR were reported in ppm with the solvent as the internal standard ( $\text{CDCl}_3$ :  $\delta = 77.16$  ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.

## 2. Preparation of Starting Materials

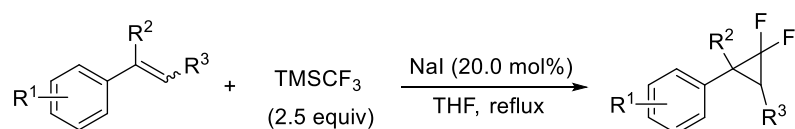
Table S1. Substituted *gem*-difluorinated cyclopropanes



## 2.1 General Procedure for the Synthesis of *gem*-Difluorinated Cyclopropanes

**S1-S20** were synthesized according to the reported procedures,<sup>1-5</sup> characterization of unreported *gem*-difluorinated cyclopropanes **S4**, **S8**, **S12**, **S13** are listed below.

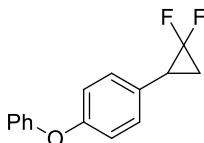
Substituted *gem*-difluorinated cyclopropanes were prepared according to the reported literature<sup>2</sup> as the following procedures:



To a 250 mL pressure tube charged with a tefloncoated stir bar was added anhydrous NaI (0.3 g, 2.0 mmol, 0.2 equiv), 50.0 mL of freshly distilled THF as solvent, and the corresponding alkene (10.0 mmol, 1.0 equiv) in that order under argon atmosphere. To this mixture was added TMSCF<sub>3</sub> (3.6 g, 25.0 mmol, 2.5 equiv). The reaction vessel was sealed and reflux in an oil bath for a period of 4 h. The reaction mixture was evaporated to dryness under reduced pressure to remove THF. The crude was extracted with ether (30.0 mL) and washed with water (20.0 mL), saturated Na<sub>2</sub>SO<sub>3</sub> solution (20.0 mL), saturated NaHCO<sub>3</sub> solution (20.0 mL), and water (20.0 mL), in that order. The ether layer was then collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The ether layer was evaporated under reduced pressure to obtain the crude products. The crude products were purified by flash chromatography on silica gel (PE/EA) to afford the desired products.

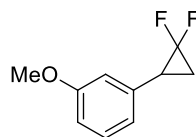
## 2.2 Characterization of the Substrates

### 1-(2,2-difluorocyclopropyl)-4-phenoxybenzene (**S4**)



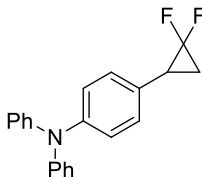
2.09 g, 85% yield, colorless oil,  $R_f = 0.3$  (PE = 100%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.29 (m, 2H), 7.20 – 7.15 (m, 2H), 7.12 – 7.07 (m, 1H), 7.02 – 6.93 (m, 4H), 2.77 – 2.66 (m, 1H), 1.85 – 1.73 (m, 1H), 1.62 – 1.51 (m, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  157.1, 156.5, 129.9, 129.5, 128.4, 123.4, 119.0, 118.9, 112.6 (dd,  $J = 286.8, 283.9$  Hz), 26.6 (t,  $J = 11.5$  Hz), 17.1 (t,  $J = 10.5$  Hz) ppm; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -126.02 (d,  $J = 153.8$  Hz), -142.23 (d,  $J = 153.8$  Hz) ppm; HRMS (ESI)  $m/z$ . Calcd for [C<sub>15</sub>H<sub>13</sub>F<sub>2</sub>O + H]<sup>+</sup> 247.0929, found 247.0919.

**1-(2,2-difluorocyclopropyl)-3-methoxybenzene (S8)**



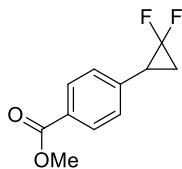
1.66 g, 90% yield, colorless oil,  $R_f = 0.3$  (PE = 100%),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.20 (m, 1H), 6.82 – 6.75 (m, 3H), 3.78 (s, 3H), 2.76 – 2.65 (m, 1H), 1.84 – 1.72 (m, 1H), 1.65 – 1.54 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 135.2, 129.5, 120.4 (t,  $J = 1.6$  Hz), 114.0 (t,  $J = 1.7$  Hz), 112.6 (dd,  $J = 286.7, 284.2$  Hz), 112.5, 55.2, 27.2 (t,  $J = 11.4$  Hz), 17.0 (t,  $J = 10.5$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.67 (d,  $J = 153.7$  Hz), -142.16 (d,  $J = 153.4$  Hz) ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{10}\text{H}_{11}\text{F}_2\text{O} + \text{H}]^+$  185.0772, found 185.0768.

**4-(2,2-difluorocyclopropyl)-N,N-diphenylaniline (S12)**



2.41 g, 75% yield, white solid,  $R_f = 0.75$  (PE/EA = 9:1), m.p. 65 – 66 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.20 (m, 4H), 7.10 – 7.05 (m, 6H), 7.05 – 7.02 (m, 2H), 7.02 – 6.97 (m, 2H), 2.74 – 2.63 (m, 1H), 1.84-1.72 (m, 1H), 1.62 – 1.49 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.7, 146.9, 129.3, 128.9 (t,  $J = 1.6$  Hz), 127.6, 124.3, 123.8, 122.9, 112.8 (dd,  $J = 287.0, 284.0$  Hz), 26.8 (t,  $J = 11.5$  Hz), 17.1 (t,  $J = 10.5$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.83 (d,  $J = 153.6$  Hz), -142.26 (d,  $J = 153.5$  Hz) ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{18}\text{F}_2\text{N} + \text{H}]^+$  322.1402, found 322.1402.

**methyl 4-(2,2-difluorocyclopropyl)benzoate (S13)**

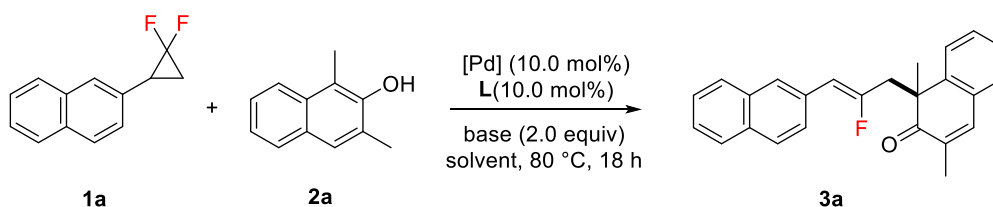


1.70 g, 80% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.98 (m, 2H), 7.30 – 7.26 (m, 2H), 3.91 (s, 3H), 2.84 – 2.73 (m, 1H), 1.95 – 1.83 (m, 1H), 1.74 – 1.63 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 139.0, 129.7, 129.0, 127.9 (t,  $J = 1.7$  Hz), 112.3 (dd,  $J = 287.6, 284.1$  Hz), 52.1, 27.3 (t,  $J = 11.5$  Hz), 17.5 (t,  $J = 10.5$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.54 (d,  $J = 154.4$  Hz), -142.18 (d,  $J = 154.1$  Hz) ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{11}\text{H}_{11}\text{F}_2\text{O}_2 + \text{H}]^+$  213.0722, found 213.0723.



### 3. Optimization of Reaction Conditions for the Synthesis of Products 3a and 5a

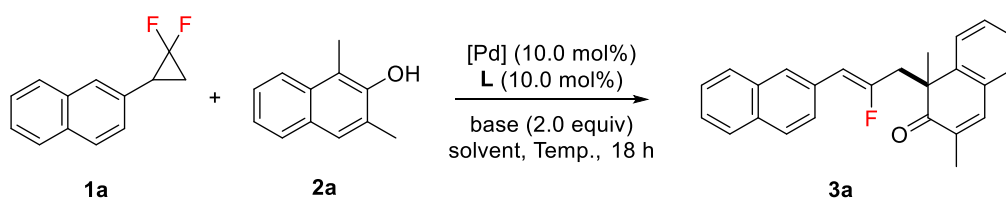
Table S2. Screening of base, catalysts and ligands<sup>a,b</sup>



entry	catalyst	ligand	base	solvent	yield
1	Pd(OTFA) <sub>2</sub>	XPhos	K <sub>3</sub> PO <sub>4</sub>	THF	37%
2	Pd(OTFA) <sub>2</sub>	XPhos	Cs <sub>2</sub> CO <sub>3</sub>	THF	51%
3	Pd(OTFA) <sub>2</sub>	XPhos	KHCO <sub>3</sub>	THF	15%
4	Pd(OTFA) <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	THF	86%
5	Pd(OTFA) <sub>2</sub>	XPhos	NaO <sup>t</sup> Bu	THF	74%
6	Pd(OTFA) <sub>2</sub>	XPhos	KO <sup>t</sup> Bu	THF	71%
7	PdCl <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	THF	trace
8	Pd(OAc) <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	THF	83%
9	Pd(PPh <sub>3</sub> ) <sub>4</sub>	XPhos	LiO <sup>t</sup> Bu	THF	80%
10	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	LiO <sup>t</sup> Bu	THF	85%
<b>11</b>	<b>[η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>PdCl]<sub>2</sub></b>	<b>XPhos</b>	<b>LiO<sup>t</sup>Bu</b>	<b>THF</b>	<b>92%</b>
12	[η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	Cy <sub>3</sub> P	LiO <sup>t</sup> Bu	THF	46%
13	[η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	PPh <sub>3</sub>	LiO <sup>t</sup> Bu	THF	<5%
14	[η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	SPhos	LiO <sup>t</sup> Bu	THF	58%
15	[η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	XantPhos	LiO <sup>t</sup> Bu	THF	37%
16	[η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	<sup>t</sup> Bu-XPhos	LiO <sup>t</sup> Bu	THF	15%
17	[η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	DavePhos	LiO <sup>t</sup> Bu	THF	40%

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Pd] (10.0 mol%), ligand (10.0 mol%), base (2.0 equiv.), solvent (2.0 mL), at 80 °C under Ar atmosphere for 18 h, sealed tube. <sup>b</sup>Isolated yield.

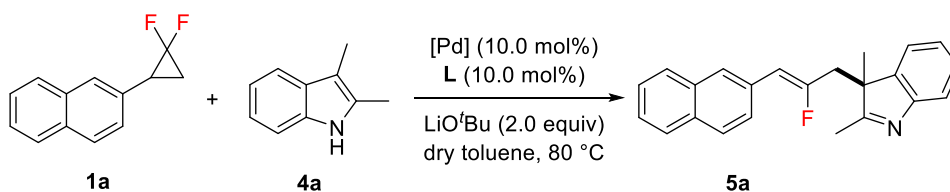
**Table S3. Screening of solvents and temperature<sup>a,b</sup>**



entry	catalyst	ligand	temperature	solvent	yield
1	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	80 °C	THF	92%
2	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	80 °C	mesitylene	90%
3	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	80 °C	toluene	87%
4	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	80 °C	CH <sub>3</sub> CN	33%
5	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	80 °C	1,4-dioxane	74%
6	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	60 °C	THF	67%
7	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	100 °C	THF	87%
8	–	XPhos	80 °C	THF	n.r.
9	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	–	80 °C	THF	n.r.

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol),  $[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$  (5.0 mol%), XPhos (10.0 mol%), LiO<sup>t</sup>Bu (2.0 equiv.), solvent (2.0 mL), under Ar atmosphere for 18 h, sealed tube. <sup>b</sup>Isolated yield. n.r. = no reaction.

**Table S4. Screening of catalysts<sup>a,b</sup>**

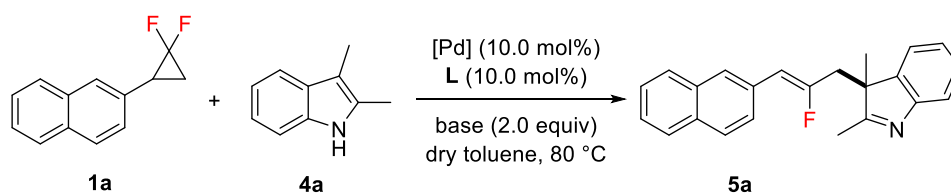


entry	catalyst	ligand	base	temperature	yield
1	Pd(OTFA) <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	44%
2	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	45%
3	Pd(OAc) <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	57%
4	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	43%
5	PdCl <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	n.r.
6	Pd(PP <sub>3</sub> ) <sub>4</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	46%
7	<b>Pd(XantPhos)Cl<sub>2</sub></b>	<b>XPhos</b>	<b>LiO<sup>t</sup>Bu</b>	<b>80 °C</b>	<b>80%</b>
8	Pd(dppf)Cl <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	40%
9 <sup>c</sup>	Pd(XantPhos)Cl <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	80 °C	55%

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **5a** (0.15 mmol), [Pd] (10.0 mol%), XPhos (10.0 mol%), LiO<sup>t</sup>Bu (2.0 equiv.), dry toluene (2.0 mL), at 80 °C under Ar atmosphere for 24 h, sealed tube. <sup>b</sup>Isolated yield.

<sup>c</sup>Pd(XantPhos)Cl<sub>2</sub> (5.0 mol%). n.r. = no reaction.

**Table S5. Screening of ligands, temperature and base<sup>a,b</sup>**



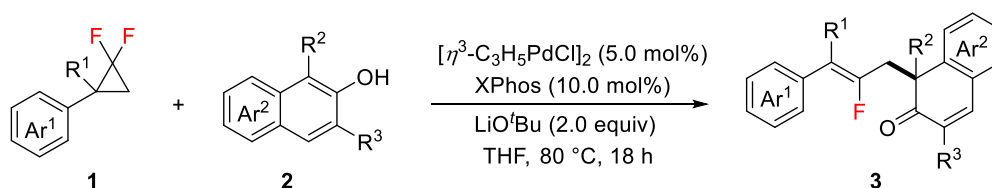
entry	catalyst	ligand	base	temperature	yield
1	Pd(XantPhos)Cl <sub>2</sub>	PPh <sub>3</sub>	LiO <sup>t</sup> Bu	80 °C	62%
2	Pd(XantPhos)Cl <sub>2</sub>	SPhos	LiO <sup>t</sup> Bu	80 °C	60%
3	Pd(XantPhos)Cl <sub>2</sub>	<sup>t</sup> Bu-XPhos	LiO <sup>t</sup> Bu	80 °C	10%
4	Pd(XantPhos)Cl <sub>2</sub>	DPPF	LiO <sup>t</sup> Bu	80 °C	51%
5	Pd(XantPhos)Cl <sub>2</sub>	DavePhos	LiO <sup>t</sup> Bu	80 °C	76%
6	Pd(XantPhos)Cl <sub>2</sub>	XantPhos	LiO <sup>t</sup> Bu	80 °C	44%
7	Pd(XantPhos)Cl <sub>2</sub>	-	LiO <sup>t</sup> Bu	80 °C	27%
8	Pd(XantPhos)Cl <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	100 °C	58%
9	Pd(XantPhos)Cl <sub>2</sub>	XPhos	LiO <sup>t</sup> Bu	60 °C	43%
10	Pd(XantPhos)Cl <sub>2</sub>	XPhos	Li <sub>2</sub> CO <sub>3</sub>	80 °C	n.r.
11	Pd(XantPhos)Cl <sub>2</sub>	XPhos	KO <sup>t</sup> Bu	80 °C	trace
12	Pd(XantPhos)Cl <sub>2</sub>	XPhos	K <sub>2</sub> CO <sub>3</sub>	80 °C	<5%
13	Pd(XantPhos)Cl <sub>2</sub>	XPhos	K <sub>3</sub> PO <sub>4</sub>	80 °C	45%
14	Pd(XantPhos)Cl <sub>2</sub>	XPhos	Cs <sub>2</sub> CO <sub>3</sub>	80 °C	43%

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **5a** (0.15 mmol), Pd(XantPhos)Cl<sub>2</sub> (10.0 mol%), ligand (10.0 mol%), base (2.0 equiv.), toluene (2.0 mL), at 80 °C under Ar atmosphere for 24 h, sealed tube.

<sup>b</sup>Isolated yield. n.r. = no reaction.

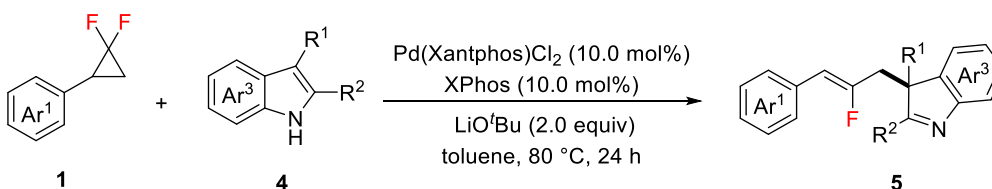
## 4. General Experimental Procedures

### 4.1 General Procedure for the Preparation of Compounds 3



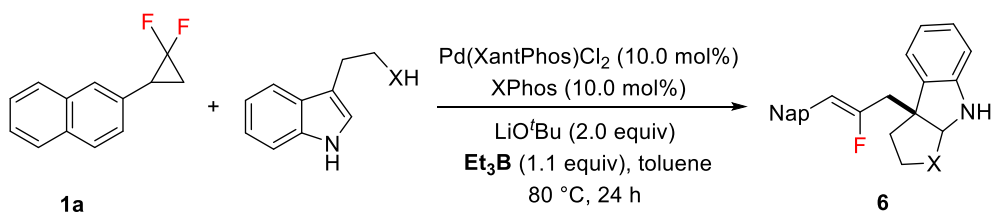
A sealed tube was charged with *gem*-difluorinated cyclopropanes **1** (0.2 mmol, 1.0 equiv),  $\beta$ -naphthols **2** (0.3 mmol, 1.5 equiv),  $[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$  (3.7 mg, 0.01 mmol, 5.0 mol%), XPhos (9.5 mg, 0.02 mmol, 10.0 mol%), LiO<sup>t</sup>Bu (32.0 mg, 0.4 mmol, 2.0 equiv), and THF (2.0 mL) under argon atmosphere. The reaction mixture was vigorously stirred at 80 °C (oil temperature) for 18 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of celite. The filtrate was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v/v* = 200:1 to 100:1) to afford dearomative products **3**.

### 4.2 General Procedure for the Preparation of Compounds 5



A sealed tube was charged with *gem*-difluorinated cyclopropanes **1** (0.2 mmol, 1.0 equiv), indoles **4** (0.3 mmol, 1.5 equiv), Pd(XantPhos)Cl<sub>2</sub> (15.1 mg, 0.02 mmol, 10.0 mol%), XPhos (9.5 mg, 0.02 mmol, 10.0 mol%), LiO<sup>t</sup>Bu (32.0 mg, 0.4 mmol, 2.0 equiv), and anhydrous toluene (2.0 mL) under argon atmosphere. The reaction mixture was vigorously stirred at 80 °C (oil temperature) for 24 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of celite. The filtrate was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v/v* = 20:1 to 5:1) to afford dearomative products **5**.

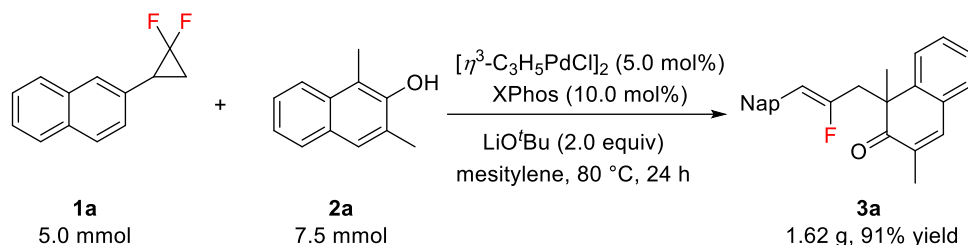
### 4.3 General Procedure for the Preparation of Compounds **6**



A sealed tube was charged with 2-(2,2-difluorocyclopropyl)naphthalene **1a** (40.8 mg, 0.2 mmol, 1.0 equiv), tryptophol or tryptamines (0.3 mmol, 1.5 equiv), Pd(XantPhos)Cl<sub>2</sub> (15.1 mg, 0.02 mmol, 10.0 mol%), XPhos (9.5 mg, 0.02 mmol, 10.0 mol%), LiO<sup>t</sup>Bu (32.0 mg, 0.4 mmol, 2.0 equiv), Et<sub>3</sub>B (0.22 mL, 1 mol/L in THF, 1.1 equiv), and anhydrous toluene (2.0 mL) under argon atmosphere. The reaction mixture was vigorously stirred at 80 °C (oil temperature) for 24 h. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel with PE/EA (*v/v* = 20:1 to 5:1) to afford the desired products **6**.

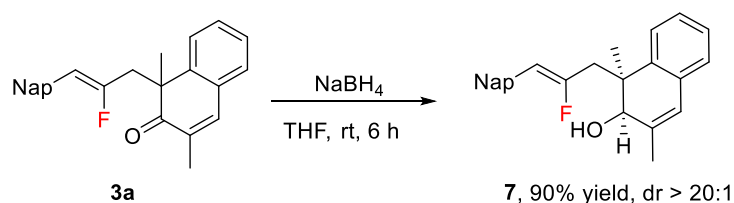
## 5. Further Functionalization of the Products

### 5.1 Scale-up (5.0 mmol) Experiment of 3a



A sealed tube was charged with 2-(2,2-difluorocyclopropyl)naphthalene **1a** (1.02 g, 5.0 mmol, 1.0 equiv),  $\beta$ -naphthol **2a** (1.29 g, 7.5 mmol, 1.5 equiv),  $[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$  (91.5 mg, 0.25 mmol, 5.0 mol%), XPhos (238.4 mg, 0.5 mmol, 10.0 mol%),  $\text{LiO}^t\text{Bu}$  (800.5 mg, 10.0 mmol, 2.0 equiv), and mesitylene (50.0 mL) under argon atmosphere. The reaction mixture was vigorously stirred at 80 °C (oil temperature) for 24 h. After cooling to room temperature, the reaction mixture was diluted with EA (30.0 mL) and filtered through a plug of celite. The filtrate was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v/v* = 200:1 to 100:1) to afford the product **3a**.

### 5.2 Synthetic Transformation of 3a to 7<sup>6-8</sup>



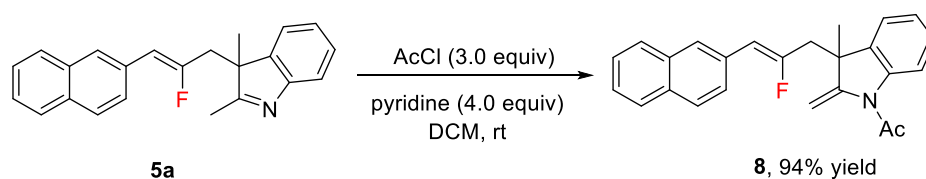
To a solution of **3a** (71.2 mg, 0.2 mmol) in anhydrous THF (2.0 mL),  $\text{NaBH}_4$  (9.8 mg, 0.24 mmol) was added. The reaction mixture was stirred at rt for 6 h. After the reaction was completed (monitored by TLC), the solvent was removed under reduced pressure. Then dr ratio was determined by  $^1\text{H}$  NMR of the crude reaction mixture. Then the residue was purified by silica gel column chromatography with PE/EA (*v/v* = 10:1, TLC:  $R_f$  = 0.4, PE/EA = 9:1) to afford the desired product **7** as a colorless oil. The relative configuration of **7** was confirmed by the NOE spectra.

#### (Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-1,3-dimethyl-1,2-dihydronaphthalen-2-ol (7)

64.5 mg, 90% yield, colorless oil,  $R_f$  = 0.4 (PE/EA = 9:1),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.86 (m, 1H), 7.79 – 7.75 (m, 3H), 7.62 (dd,  $J$  = 8.6, 1.7 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 – 7.13 (m, 2H), 7.08 – 7.02 (m, 1H),

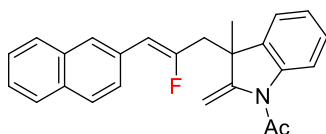
6.24 (q,  $J = 1.7$  Hz, 1H), 5.61 (d,  $J = 39.6$  Hz, 1H), 4.07 (d,  $J = 7.5$  Hz, 1H), 3.00 – 2.80 (m, 2H), 2.00 (d,  $J = 1.7$  Hz, 3H), 1.64 (d,  $J = 7.8$  Hz, 1H), 1.34 (d,  $J = 1.7$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6 (d,  $J = 267.6$  Hz), 139.7, 138.0, 133.5, 132.7, 132.3 (d,  $J = 1.7$  Hz), 131.4 (d,  $J = 2.7$  Hz), 128.0, 127.9, 127.6, 127.3 (d,  $J = 7.7$  Hz), 127.2, 127.0, 126.7 (d,  $J = 7.6$  Hz), 126.7, 126.1, 125.8, 125.1, 123.8, 109.9 (d,  $J = 8.6$  Hz), 75.6, 43.3 (d,  $J = 3.9$  Hz), 37.5 (d,  $J = 24.6$  Hz), 23.8 (d,  $J = 1.8$  Hz), 20.9 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -92.77 ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{24}\text{FO} + \text{Na}]^+$  381.1625, found 381.1628.

### 5.3 Synthetic Transformation of **5a** to **8**<sup>9</sup>



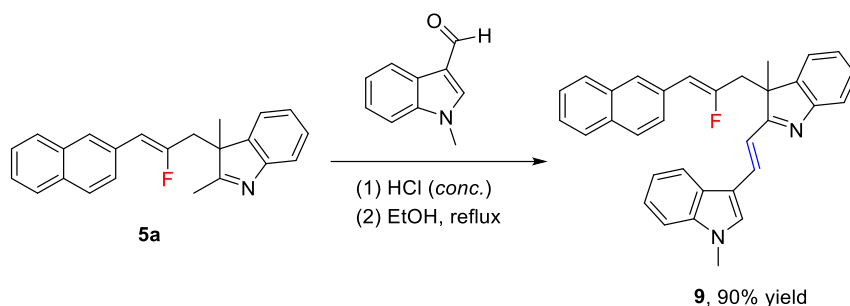
A sealed tube was charged with **5a** (65.8 mg, 0.2 mmol), pyridine (64  $\mu\text{L}$ , 0.8 mmol, 4.0 equiv) and the corresponding chloride (43  $\mu\text{L}$ , 0.6 mmol, 3.0 equiv) were added. The reaction mixture was stirred at room temperature until completion (monitored by TLC). Then saturated  $\text{NaHCO}_3$  (10.0 mL) was added, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (10.0 x 3 mL) and dried with  $\text{Na}_2\text{SO}_4$ . The mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography PE/EA ( $v/v = 50:1$  to  $10:1$ ) to afford the desired product **8**.

#### (*Z*)-3-(2-fluoro-3-(3-methoxyphenyl)allyl)-2,3-dimethyl-3H-indole (**8**)



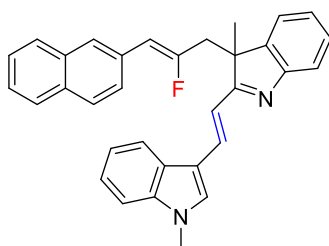
69.5 mg, 94% yield, yellow oil,  $R_f = 0.6$  (PE/EA = 6:1),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.1$  Hz, 1H), 7.76 – 7.70 (m, 4H), 7.49 (d,  $J = 8.6$  Hz, 1H), 7.44 – 7.37 (m, 2H), 7.27 – 7.19 (m, 2H), 7.10 (t,  $J = 7.4$  Hz, 1H), 5.38 (d,  $J = 38.6$  Hz, 1H), 5.19 (d,  $J = 2.4$  Hz, 1H), 4.90 (d,  $J = 2.3$  Hz, 1H), 2.60 (dd,  $J = 22.7, 3.5$  Hz, 2H), 2.43 (s, 3H), 1.55 (s, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 157.5 (d,  $J = 267.8$  Hz), 154.4, 141.7, 136.2, 133.4, 132.4, 130.8 (d,  $J = 2.7$  Hz), 128.2, 128.1, 128.0, 127.6, 127.4 (d,  $J = 7.4$  Hz), 126.5 (d,  $J = 7.6$  Hz), 126.2, 126.0, 124.4, 122.6, 116.8, 109.9 (d,  $J = 8.4$  Hz), 96.9, 47.6 (d,  $J = 3.6$  Hz), 46.8 (d,  $J = 24.6$  Hz), 25.6, 25.1 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.79 ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{22}\text{FNO} + \text{H}]^+$  372.1758, found 372.1762.

## 5.4 Synthetic Transformation of **5a** to **9**<sup>9</sup>



Concentrated hydrochloric acid (1.5 mL) was added dropwise into **5a** (60.2 mg, 0.2 mmol). The mixture was stirred at room temperature for 30 min. Then excess reagent was removed by rotary evaporation under reduced pressure to give the HCl salt. The HCl salt was then dissolved in anhydrous ethanol (10.0 mL) followed the addition of *N*-methyl indole-3-carbaldehyde (38.2 mg, 0.24 mmol, 1.2 equiv). The mixture was allowed to reflux for 4 h under argon atmosphere. The reaction was monitored by TLC until completion. Then the reaction mixture was cooled to room temperature and extracted with DCM (20.0 mL). The combined organic layer was washed with water and brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated to obtain a dark residue, which was further purified by flash column chromatography using PE/EA (*v/v* = 4:1) as the eluent to give the product **9**.

### 3-((*Z*)-2-fluoro-3-(naphthalen-2-yl)allyl)-3-methyl-2-((*E*)-2-(1-methyl-1*H*-indol-3-yl)vinyl)-3*H*-indole (**9**)

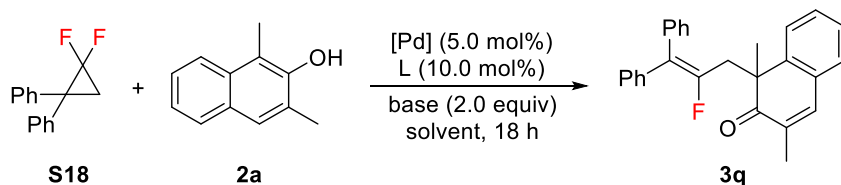


84.6 mg, 90% yield, yellow solid,  $R_f = 0.5$  (PE/EA = 2:1), m.p. 100 – 102 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 16.1 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.70 (m, 4H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.52 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.28 (m, 5H), 7.21 – 7.15 (m, 2H), 7.05 (d, *J* = 16.1 Hz, 1H), 5.50 (d, *J* = 38.7 Hz, 1H), 3.76 (s, 3H), 2.97 (dd, *J* = 21.5, 14.7 Hz, 1H), 2.77 (dd, *J* = 22.8, 14.7 Hz, 1H), 1.61 (s, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 182.6, 157.6 (d, *J* = 268.0 Hz), 154.8, 143.4, 138.1, 133.4, 132.4, 132.4, 132.0, 130.8 (d, *J* = 2.3 Hz), 128.3, 128.1, 127.9, 127.6, 127.5, 126.7 (d, *J* = 7.6 Hz), 126.2, 126.1, 126.0, 124.8, 122.9, 122.3, 121.2, 120.7, 120.1, 114.5, 113.7, 110.1, 109.7 (d, *J* = 7.9 Hz), 55.5 (d, *J* = 3.0 Hz), 41.1 (d, *J* = 25.1 Hz), 33.1, 22.4 ppm; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -95.06 ppm; HRMS (ESI) *m/z* Calcd for [C<sub>33</sub>H<sub>27</sub>FN<sub>2</sub> + H]<sup>+</sup> 471.2231, found 471.2226.



## 6. Optimization of Reaction Conditions for the Synthesis of Product 3q

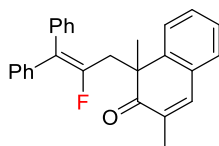
Table S6. Screening of reaction conditions<sup>a</sup>



entry	catalyst	ligand	base	temperature	solvent	yield <sup>b</sup>
1	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
2	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	XPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
3	$\text{Pd}(\text{OAc})_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
4	$\text{Pd}(\text{PP}_3)_4$	XPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
5	$\text{Pd}(\text{TFA})_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
6	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	$\text{PPh}_3$	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
7	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	SPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
8	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XantPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
9	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	<sup>t</sup> Bu-XPhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
10	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	DavePhos	LiO <sup>t</sup> Bu	80 °C	THF	n.d.
11	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	mesitylene	<5%
12	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	toluene	trace
13	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	1,4-dioxane	n.d.
14	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	DCE	n.d.
15	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	80 °C	$\text{CH}_3\text{CN}$	n.d.
16	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_2\text{CO}_3$	80 °C	mesitylene	18%
17	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_3\text{PO}_4$	80 °C	mesitylene	23%
18	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_2\text{HPO}_4$	80 °C	mesitylene	n.d.
19	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{Li}_2\text{CO}_3$	80 °C	mesitylene	n.d.
20	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{Cs}_2\text{CO}_3$	80 °C	mesitylene	12%
21 <sup>c</sup>	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_3\text{PO}_4$	80 °C	mesitylene	26%
22 <sup>d</sup>	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_3\text{PO}_4$	80 °C	mesitylene	29%
23	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_3\text{PO}_4$	100 °C	mesitylene	35%
24 <sup>c</sup>	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_3\text{PO}_4$	100 °C	mesitylene	32%

<sup>a</sup>Reaction conditions: **S18** (0.05 mmol), **2a** (0.075 mmol), catalyst (5.0 mol%), ligand (10.0 mol%), base (2.0 equiv.), solvent (0.5 mL), at 80 °C under Ar atmosphere for 18 h, sealed tube. <sup>b</sup>Isolated yield. <sup>c</sup>for 24 h. <sup>d</sup>for 36 h. n.d. = not detected.

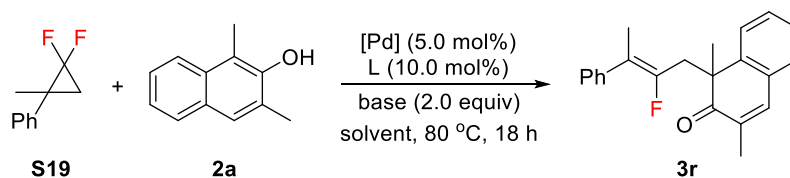
***1-(2-fluoro-3,3-diphenylallyl)-1,3-dimethylnaphthalen-2(1H)-one (3q)***



33.2 mg, 35% yield, colorless oil,  $R_f = 0.5$  (PE/EA=9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.25 (m, 6H), 7.25 – 7.17 (m, 1H), 7.16 – 7.05 (m, 3H), 7.00 – 6.89 (m, 3H), 6.82 – 6.73 (m, 2H), 3.39 (dd,  $J = 14.7, 5.6$  Hz, 1H), 2.94 (dd,  $J = 34.2, 14.7$  Hz, 1H), 2.02 (d,  $J = 1.4$  Hz, 3H), 1.35 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.5, 154.8 (d,  $J = 259.9$  Hz), 143.7, 141.2, 138.5 (d,  $J = 7.8$  Hz), 137.3, 132.1 (d,  $J = 1.5$  Hz), 130.4 (d,  $J = 3.0$  Hz), 130.0, 129.5, 129.4, 128.6, 128.5, 128.3, 127.8, 127.3, 127.0, 126.9, 122.5 (d,  $J = 15.2$  Hz), 49.8, 41.6 (d,  $J = 25.2$  Hz), 28.6, 16.2 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -103.7 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{27}\text{H}_{23}\text{FO} + \text{Na}]^+$  405.1625, found 405.1625.

## 7. Optimization of Reaction Conditions for the Synthesis of Product 3r

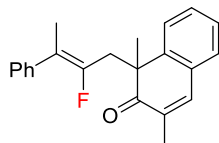
Table S7. Screening of reaction conditions<sup>a</sup>



entry	catalyst	ligand	base	solvent	yield <sup>b</sup>
1	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	THF	n.d.
2	$\text{Pd}_2(\text{dba})_3$ , $\text{CHCl}_3$	XPhos	LiO <sup>t</sup> Bu	THF	n.d.
3	$\text{Pd}(\text{OAc})_2$	XPhos	LiO <sup>t</sup> Bu	THF	n.d.
4	$\text{Pd}(\text{PP}_3)_4$	XPhos	LiO <sup>t</sup> Bu	THF	n.d.
5	$\text{Pd}(\text{TFA})_2$	XPhos	LiO <sup>t</sup> Bu	THF	n.d.
6	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	$\text{PPh}_3$	LiO <sup>t</sup> Bu	THF	n.d.
7	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	SPhos	LiO <sup>t</sup> Bu	THF	n.d.
8	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XantPhos	LiO <sup>t</sup> Bu	THF	n.d.
9	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	<sup>t</sup> Bu-XPhos	LiO <sup>t</sup> Bu	THF	n.d.
10	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	DavePhos	LiO <sup>t</sup> Bu	THF	n.d.
11	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	mesitylene	15%
12	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	toluene	19%
13	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	1,4-dioxane	n.d.
14	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	DCE	n.d.
15	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	$\text{CH}_3\text{CN}$	n.d.
16	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_2\text{CO}_3$	mesitylene	17%
17	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_3\text{PO}_4$	mesitylene	15%
18	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{K}_2\text{HPO}_4$	mesitylene	10%
19	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{Li}_2\text{CO}_3$	mesitylene	trace
20	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	$\text{Cs}_2\text{CO}_3$	mesitylene	8%
21 <sup>c</sup>	$[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$	XPhos	LiO <sup>t</sup> Bu	mesitylene	27%

<sup>a</sup>Reaction conditions: **S19** (0.05 mmol), **2a** (0.075 mmol), catalyst (5.0 mol%), ligand (10.0 mol%), base (2.0 equiv.), solvent (0.5 mL), at 80 °C under Ar atmosphere for 18 h, sealed tube. <sup>b</sup>Isolated yield. <sup>c</sup>at 100 °C. n.d. = not detected.

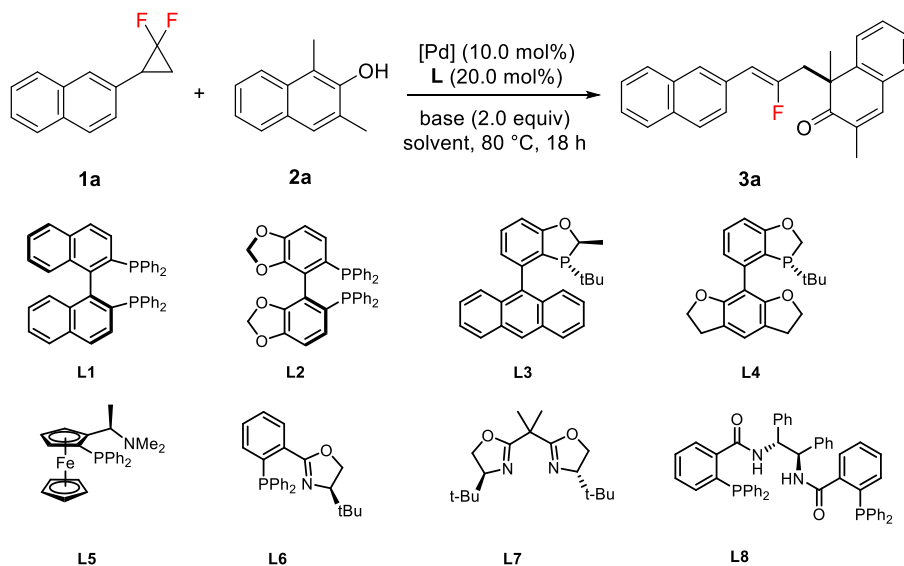
***1-(2-fluoro-3-phenylbut-2-en-1-yl)-1,3-dimethyl-4a,8a-dihydronaphthalen-2(1H)-one (3r)***



15.2 mg, 27% yield, colorless oil,  $R_f = 0.5$  (PE/EA=9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.42 (m, 1H), 7.36 – 7.30 (m, 1H), 7.29 – 7.27 (m, 1H), 7.26 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 7.17 – 7.15 (m, 1H), 7.04 – 7.00 (m, 2H), 3.12 (dd,  $J = 17.6, 14.6$  Hz, 1H), 2.89 (dd,  $J = 27.4, 14.5$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.59 – 1.58 (m, 6H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.9, 152.0 (d,  $J = 249.9$  Hz), 144.1, 141.4, 138.3, 132.4, 130.2, 128.6 (d,  $J = 6.2$  Hz), 128.0, 128.0, 127.9, 127.0, 126.7, 126.7, 115.3 (d,  $J = 14.2$  Hz), 50.2 (d,  $J = 2.4$  Hz), 42.6 (d,  $J = 27.1$  Hz), 25.9, 17.4 (d,  $J = 3.8$  Hz), 16.2 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -102.9 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{21}\text{FO} + \text{H}]^+$  321.1649, found 321.1649.

## 8. Optimization of the Asymmetric Reaction Conditions for Product 3a

Table S8. Preliminary Asymmetric Study<sup>a</sup>

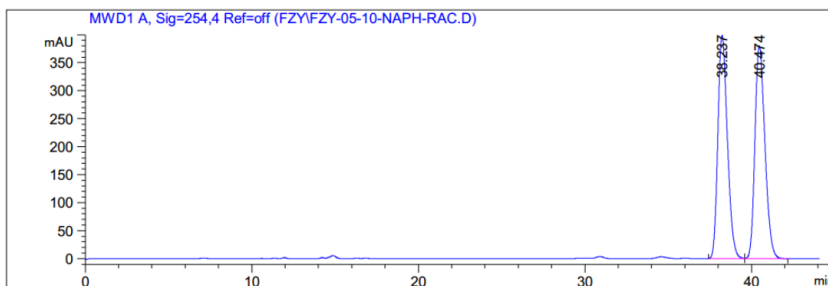


entry	catalyst	ligand	base	solvent	yield <sup>b</sup>	ee <sup>c</sup>
1	[ $\eta^3$ -C <sub>3</sub> H <sub>5</sub> PdCl] <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	THF	<5%	4%
2	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	THF	<5%	0
3	Pd(OAc) <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	THF	5%	4%
4	Pd(TFA) <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	THF	9%	16%
<b>5</b>	<b>Pd(TFA)<sub>2</sub></b>	<b>L1</b>	<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>THF</b>	<b>10%</b>	<b>24%</b>
6	Pd(TFA) <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	THF	n.d. <sup>d</sup>	/
7	Pd(TFA) <sub>2</sub>	<b>L1</b>	CsF	THF	<5%	10%
8	Pd(TFA) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	n.d.	/
9	Pd(TFA) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	mesitylene	5%	16%
10	Pd(TFA) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	DCE	<5%	10%
11 <sup>e</sup>	Pd(TFA) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	5%	16%
12	Pd(TFA) <sub>2</sub>	<b>L2</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	trace	/
13	Pd(TFA) <sub>2</sub>	<b>L3</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	<5%	4%
14	Pd(TFA) <sub>2</sub>	<b>L4</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	n.d.	/
15	Pd(TFA) <sub>2</sub>	<b>L5</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	n.d.	/
16	Pd(TFA) <sub>2</sub>	<b>L6</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	n.d.	/
17	Pd(TFA) <sub>2</sub>	<b>L7</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	n.d.	/
18	Pd(TFA) <sub>2</sub>	<b>L8</b>	Cs <sub>2</sub> CO <sub>3</sub>	THF	n.d.	/

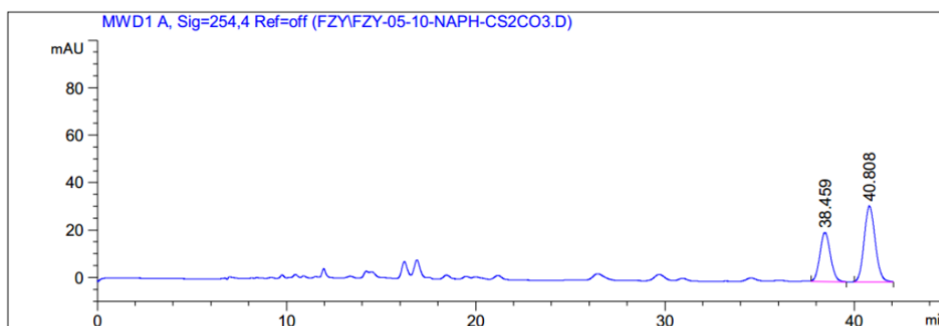
<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.075 mmol), [Pd] (10.0 mol%), **L** (20.0 mol%), base (2.0 equiv.), solvent (0.5 mL), at 80 °C under Ar atmosphere for 18 h, sealed tube. <sup>b</sup> Isolated yields.

<sup>c</sup> The ee values of the products were determined by chiral-phase HPLC analysis. <sup>d</sup> n.d.= not detected. <sup>e</sup> 100 °C.

**HPLC:** Daicel Chiralcel IC-3, n-hexane/isopropanol 98/2, flow rate = 0.5 mL/min,  
 uv-vis  $\lambda = 254 \text{ nm}$ ,  $t_{R1} = 38.5 \text{ min}$  (minor),  $t_{R2} = 40.8 \text{ min}$  (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.237	BV	0.6157	1.58650e4	399.12805	49.9634
2	40.474	VB	0.6471	1.58883e4	380.56332	50.0366
Totals :				3.17533e4	779.69138	

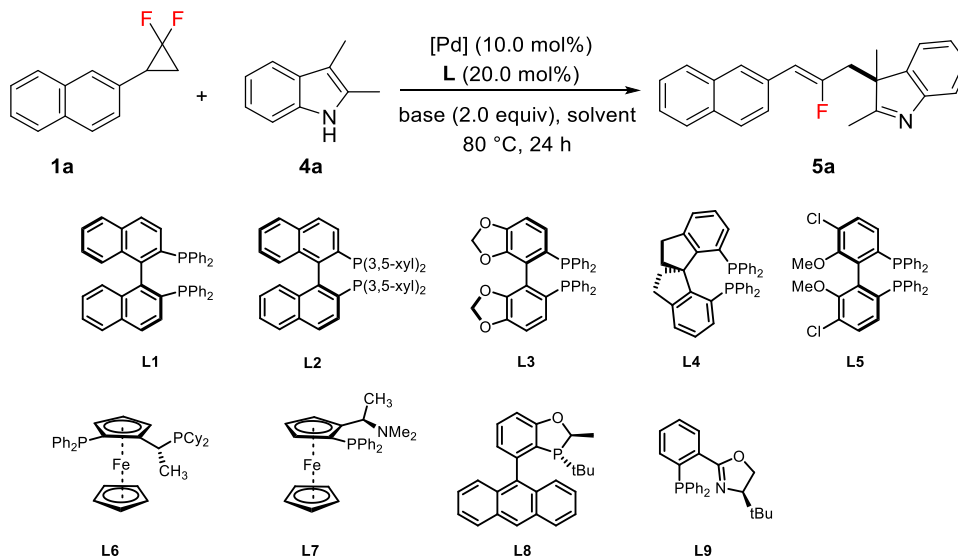


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.459	BB	0.6027	799.14227	20.68655	38.1369
2	40.808	BB	0.6337	1296.31445	31.92790	61.8631
Totals :				2095.45673	52.61445	

Supplementary Figure 1. HPLC Chromatographs of compound **3a**

## 9. Optimization of the Asymmetric Reaction Conditions for Product 5a

Table S9. Preliminary Asymmetric Study<sup>a</sup>



entry	catalyst	ligand	base	yield <sup>b</sup>	ee <sup>c</sup>
1	Pd(XantPhos)Cl <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	21%	4%
2	Pd(TFA) <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	13%	12%
3	Pd(OAc) <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	14%	4%
<b>4</b>	<b>PdCl<sub>2</sub></b>	<b>L1</b>	<b>LiO<sup>t</sup>Bu</b>	<b>19%</b>	<b>34%</b>
5	Pd(COD)Cl <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	18%	32%
6	Pd(dba) <sub>2</sub>	<b>L1</b>	LiO <sup>t</sup> Bu	5%	14%
7	PdCl <sub>2</sub>	<b>L2</b>	LiO <sup>t</sup> Bu	5%	-16%
8	PdCl <sub>2</sub>	<b>L3</b>	LiO <sup>t</sup> Bu	7%	-28%
9	PdCl <sub>2</sub>	<b>L4</b>	LiO <sup>t</sup> Bu	5%	6%
10	PdCl <sub>2</sub>	<b>L5</b>	LiO <sup>t</sup> Bu	5%	16%
11	PdCl <sub>2</sub>	<b>L6</b>	LiO <sup>t</sup> Bu	5%	28%
12	PdCl <sub>2</sub>	<b>L7</b>	LiO <sup>t</sup> Bu	7%	-10%
13	PdCl <sub>2</sub>	<b>L8</b>	LiO <sup>t</sup> Bu	6%	14%
14	PdCl <sub>2</sub>	<b>L9</b>	LiO <sup>t</sup> Bu	<5%	-8%
15	PdCl <sub>2</sub>	<b>L1</b>	Na <sub>2</sub> CO <sub>3</sub>	11%	14%
16	PdCl <sub>2</sub>	<b>L1</b>	LiOCH <sub>3</sub>	15%	26%
17	PdCl <sub>2</sub>	<b>L1</b>	DIPEA	trace	/

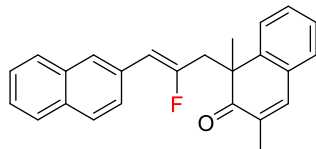
<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), **2a** (0.075 mmol), [Pd] (10.0 mol %), **L** (20.0 mol%), base (2.0 equiv.), solvent = toluene (0.5 mL), at 80 °C under Ar atmosphere for 24 h, sealed tube. <sup>b</sup> Isolated yields. <sup>c</sup> The ee values of the products were determined by chiral-phase HPLC analysis. <sup>d</sup> n.r. = no reaction.





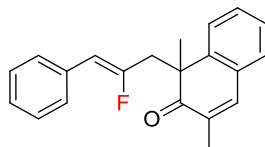
## 10. Characterization of the Products

### (Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3a)



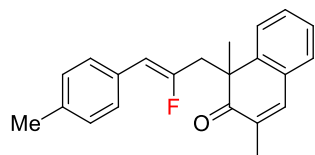
65.5 mg, 92% yield, white solid,  $R_f = 0.5$  (PE/EA = 9:1), m.p. 100 – 101 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.66 (m, 2H), 7.64 (d,  $J = 9.3$  Hz, 2H), 7.43 – 7.32 (m, 5H), 7.27 – 7.19 (m, 3H), 5.26 (d,  $J = 38.8$  Hz, 1H), 3.27 (dd,  $J = 16.9, 14.6$  Hz, 1H), 2.83 (dd,  $J = 22.8, 14.6$  Hz, 1H), 2.01 (d,  $J = 1.4$  Hz, 3H), 1.52 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 157.8 (d,  $J = 267.8$  Hz), 143.9, 141.8, 133.3, 132.3 (d,  $J = 1.7$  Hz), 130.8 (d,  $J = 2.7$  Hz), 130.0, 128.8 (d,  $J = 2.3$  Hz), 127.9, 127.7, 127.5, 127.3, 127.2, 127.1, 126.6, 126.5, 126.1, 125.8, 108.6 (d,  $J = 8.1$  Hz), 50.2 (d,  $J = 1.8$  Hz), 45.6 (d,  $J = 25.0$  Hz), 27.8, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.80 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{21}\text{FO} + \text{Na}]^+$  379.1469, found 379.1468.

### (Z)-1-(2-fluoro-3-phenylallyl)-1,3-dimethylnaphthalen-2(1H)-one (3b)



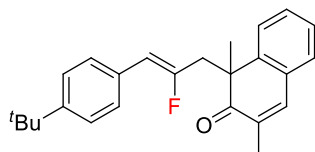
59.0 mg, 93% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.38 (m, 1H), 7.37 – 7.31 (m, 1H), 7.27 – 7.22 (m, 3H), 7.21 – 7.17 (m, 4H), 7.15 – 7.08 (m, 1H), 5.11 (d,  $J = 38.9$  Hz, 1H), 3.23 (dd,  $J = 16.4, 14.7$  Hz, 1H), 2.79 (dd,  $J = 22.8, 14.6$  Hz, 1H), 2.00 (d,  $J = 1.3$  Hz, 3H), 1.51 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 157.4 (d,  $J = 267.2$  Hz), 143.9, 141.8, 133.3 (d,  $J = 2.5$  Hz), 132.3, 130.0, 128.8 (d,  $J = 2.8$  Hz), 128.4, 128.3, 128.2, 127.1, 126.8 (d,  $J = 2.3$  Hz), 126.5, 108.5 (d,  $J = 8.3$  Hz), 50.1 (d,  $J = 1.7$  Hz), 45.5 (d,  $J = 25.1$  Hz), 27.8, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.98 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{19}\text{FO} + \text{Na}]^+$  329.1312, found 329.1317.

**(Z)-1-(2-fluoro-3-(p-tolyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3c)**



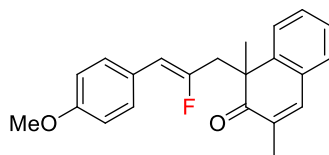
58.3 mg, 91% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.37 (m, 1H), 7.36 – 7.30 (m, 1H), 7.27 – 7.19 (m, 3H), 7.11 – 7.07 (m, 2H), 7.00 (d,  $J = 8.1$  Hz, 2H), 5.07 (d,  $J = 39.1$  Hz, 1H), 3.20 (dd,  $J = 16.7, 14.6$  Hz, 1H), 2.77 (dd,  $J = 22.9, 14.6$  Hz, 1H), 2.25 (s, 3H), 1.99 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 156.8 (d,  $J = 266.2$  Hz), 144.0, 141.7, 136.6 (d,  $J = 2.5$  Hz), 132.3, 130.5 (d,  $J = 2.4$  Hz), 130.0, 129.0, 128.8 (d,  $J = 2.5$  Hz), 128.3, 128.2, 127.0, 126.6, 108.3 (d,  $J = 8.4$  Hz), 50.2 (d,  $J = 1.9$  Hz), 45.6 (d,  $J = 25.3$  Hz), 27.7, 21.2, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.90 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{21}\text{FO} + \text{Na}]^+$  343.1469, found 343.1472.

**(Z)-1-(3-(4-(tert-butyl)phenyl)-2-fluoroallyl)-1,3-dimethylnaphthalen-2(1H)-one (3d)**



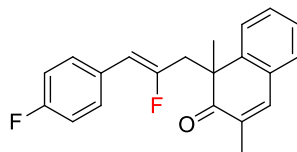
57.0 mg, 79% yield, colorless oil,  $R_f = 0.7$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.27 – 7.19 (m, 5H), 7.16 – 7.12 (m, 2H), 5.10 (d,  $J = 39.2$  Hz, 1H), 3.23 (dd,  $J = 16.1, 14.8$  Hz, 1H), 2.78 (dd,  $J = 23.2, 14.6$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H), 1.25 (s, 9H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 157.0 (d,  $J = 266.2$  Hz), 149.8 (d,  $J = 2.0$  Hz), 144.0, 141.7, 132.3, 130.5 (d,  $J = 2.3$  Hz), 130.0, 128.8 (d,  $J = 1.8$  Hz), 128.1, 128.0, 127.0, 126.6, 125.2, 108.2 (d,  $J = 8.5$  Hz), 50.1 (d,  $J = 1.9$  Hz), 45.4 (d,  $J = 25.2$  Hz), 34.5, 31.2, 27.9, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.78 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{27}\text{FO} + \text{Na}]^+$  385.1938, found 385.1939.

**(Z)-1-(2-fluoro-3-(4-methoxyphenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3e)**



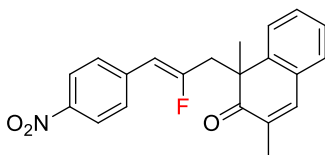
59.2 mg, 88% yield, colorless oil,  $R_f = 0.4$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.38 (m, 1H), 7.37 – 7.31 (m, 1H), 7.27 – 7.20 (m, 3H), 7.17 – 7.12 (m, 2H), 6.76 – 6.71 (m, 2H), 5.05 (d,  $J = 39.1$  Hz, 1H), 3.73 (s, 3H), 3.19 (dd,  $J = 17.0, 14.6$  Hz, 1H), 2.77 (dd,  $J = 22.8, 14.6$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.51 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.8, 158.3 (d,  $J = 2.8$  Hz), 156.0 (d,  $J = 264.6$  Hz), 144.0, 141.7, 132.3, 130.0, 129.6, 129.5, 128.8 (d,  $J = 2.8$  Hz), 127.0, 126.5, 126.0 (d,  $J = 2.3$  Hz), 113.7, 107.9 (d,  $J = 8.7$  Hz), 55.2, 50.2 (d,  $J = 1.9$  Hz), 45.6 (d,  $J = 25.4$  Hz), 27.6, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -100.79 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{21}\text{FO}_2 + \text{Na}]^+$  359.1418, found 359.1411.

**(Z)-1-(2-fluoro-3-(4-fluorophenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3f)**



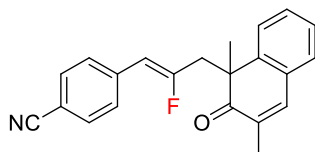
51.8 mg, 80% yield, yellow oil,  $R_f = 0.6$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.31 (m, 2H), 7.28 – 7.21 (m, 3H), 7.18 – 7.10 (m, 2H), 6.91 – 6.83 (m, 2H), 5.07 (d,  $J = 38.5$  Hz, 1H), 3.22 (dd,  $J = 16.8, 14.6$  Hz, 1H), 2.78 (dd,  $J = 22.7, 14.6$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 163.1, 163.1, 159.9, 159.8, 158.9, 158.9, 155.3, 155.3, 143.9, 141.8, 132.3, 130.0, 130.0, 129.9, 129.8, 129.4, 129.4, 129.4, 129.3, 128.8, 128.8, 127.7, 127.1, 126.5, 115.1 (d,  $J = 21.4$  Hz), 107.4 (d,  $J = 8.4$  Hz), 50.1 (d,  $J = 1.7$  Hz), 45.3 (d,  $J = 25.1$  Hz), 27.8, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.30 (d,  $J = 1.6$  Hz), -114.70 (d,  $J = 1.5$  Hz) ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{18}\text{F}_2\text{O} + \text{Na}]^+$  347.1218, found 347.1221.

**(Z)-1-(2-fluoro-3-(4-nitrophenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3g)**



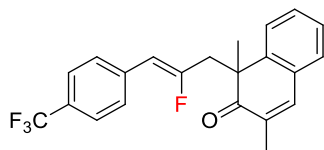
50.0 mg, 71% yield, yellow oil,  $R_f = 0.3$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 8.02 (m, 2H), 7.43 – 7.35 (m, 2H), 7.34 – 7.32 (m, 1H), 7.31 – 7.25 (m, 4H), 5.21 (d,  $J = 37.6$  Hz, 1H), 3.33 (dd,  $J = 16.4, 14.8$  Hz, 1H), 2.86 (dd,  $J = 22.5, 14.7$  Hz, 1H), 2.01 (d,  $J = 1.4$  Hz, 3H), 1.52 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.2, 160.7 (d,  $J = 274.0$  Hz), 146.1 (d,  $J = 2.8$  Hz), 143.5, 141.9, 139.8 (d,  $J = 2.6$  Hz), 132.2, 129.9, 129.0 (d,  $J = 4.4$  Hz), 128.8, 128.7, 127.3, 126.4, 123.6, 107.0 (d,  $J = 7.7$  Hz), 50.1 (d,  $J = 1.3$  Hz), 44.9 (d,  $J = 24.3$  Hz), 28.3, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -91.67 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{18}\text{FNO}_3 + \text{Na}]^+$  374.1163, found 374.1167.

**(Z)-4-(3-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-2-fluoroprop-1-en-1-yl)benzonitrile (3h)**



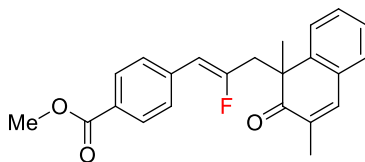
47.2 mg, 71% yield, yellow oil,  $R_f = 0.3$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.3$  Hz, 2H), 7.42 – 7.34 (m, 2H), 7.30 – 7.24 (m, 5H), 5.15 (d,  $J = 37.7$  Hz, 1H), 3.30 (t,  $J = 15.6$ , 1H), 2.84 (dd,  $J = 22.5, 14.7$  Hz, 1H), 2.01 (d,  $J = 1.5$  Hz, 3H), 1.51 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.3, 160.2 (d,  $J = 272.8$  Hz), 143.6, 141.9, 137.8 (d,  $J = 2.5$  Hz), 132.2, 132.0, 129.9, 128.9 (d,  $J = 4.2$  Hz), 128.7, 128.6, 127.2, 126.4, 119.0, 110.0 (d,  $J = 2.7$  Hz), 107.3 (d,  $J = 7.6$  Hz), 50.1 (d,  $J = 1.1$  Hz), 44.9 (d,  $J = 24.4$  Hz), 28.3, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -92.54 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{18}\text{FNO} + \text{H}]^+$  332.1445, found 332.1448.

**(Z)-1-(2-fluoro-3-(4-(trifluoromethyl)phenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3i)**



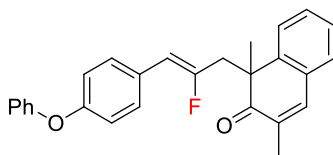
56.8 mg, 76% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.42 (m, 2H), 7.40 – 7.33 (m, 2H), 7.29 – 7.23f (m, 5H), 5.15 (d,  $J = 38.0$  Hz, 1H), 3.28 (dd,  $J = 16.6, 14.6$  Hz, 1H), 2.82 (dd,  $J = 22.8, 14.6$  Hz, 1H), 2.01 (d,  $J = 1.4$  Hz, 3H), 1.51 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.4, 159.2 (d,  $J = 270.7$  Hz), 143.7, 141.8, 136.8, 136.7, 136.7, 132.3, 130.0, 128.9, 128.9, 128.8, 128.7, 128.4, 128.3, 127.2, 126.4, 125.9, 125.1 (q,  $J = 3.9$  Hz), 122.3, 107.4 (d,  $J = 8.1$  Hz), 50.1 (d,  $J = 1.5$  Hz), 45.2 (d,  $J = 24.7$  Hz), 28.0, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.59, -94.80 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{18}\text{F}_4\text{O} + \text{H}]^+$  375.1367, found 375.1365.

**(Z)-methyl 4-(3-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-2-fluoroprop-1-en-1-yl)benzoate (3j)**



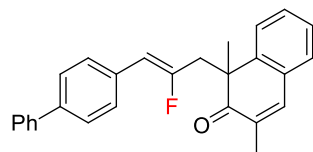
46.0 mg, 63% yield, yellow oil,  $R_f = 0.3$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.84 (m, 2H), 7.42 – 7.33 (m, 2H), 7.29 – 7.22 (m, 5H), 5.16 (d,  $J = 38.3$  Hz, 1H), 3.86 (s, 3H), 3.28 (dd,  $J = 16.4, 14.8$  Hz, 1H), 2.82 (dd,  $J = 22.6, 14.7$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.51 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.4, 166.8, 159.2 (d,  $J = 271.2$  Hz), 143.7, 141.8, 137.8 (d,  $J = 2.6$  Hz), 132.2, 129.9, 129.5, 128.9, 128.9, 128.1, 128.1 (d,  $J = 7.6$  Hz), 127.2, 126.4, 107.9 (d,  $J = 7.9$  Hz), 52.0, 50.1 (d,  $J = 1.5$  Hz), 45.2 (d,  $J = 24.7$  Hz), 28.0, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -94.12 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{21}\text{FO}_3 + \text{H}]^+$  365.1547, found 365.1554.

**(Z)-1-(2-fluoro-3-(4-phenoxyphenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3k)**



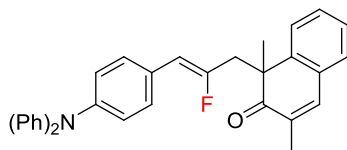
65.1 mg, 82% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 20:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 1H), 7.32 – 7.21 (m, 5H), 7.19 – 7.14 (m, 2H), 7.09 – 7.04 (m, 1H), 6.97 – 6.92 (m, 2H), 6.85 – 6.80 (m, 2H), 5.08 (d,  $J = 38.8$  Hz, 1H), 3.22 (dd,  $J = 16.7, 14.6$  Hz, 1H), 2.78 (dd,  $J = 22.8, 14.6$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 158.6 (d,  $J = 264.3$  Hz), 157.0, 156.0 (d,  $J = 2.9$  Hz), 144.0, 141.7, 132.3, 130.0, 129.8, 129.8, 129.7, 128.8 (d,  $J = 3.1$  Hz), 128.5 (d,  $J = 2.3$  Hz), 127.1, 126.5, 123.3, 119.0, 118.5, 107.7 (d,  $J = 8.6$  Hz), 50.2 (d,  $J = 1.7$  Hz), 45.4 (d,  $J = 25.2$  Hz), 27.8, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.50 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{27}\text{H}_{23}\text{FO}_2 + \text{Na}]^+$  421.1574, found 421.1578.

**(Z)-1-(3-([1,1'-biphenyl]-4-yl)-2-fluoroallyl)-1,3-dimethylnaphthalen-2(1H)-one (3l)**



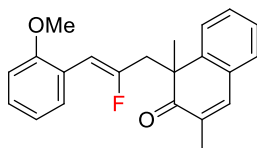
58.1 mg, 76% yield, white solid,  $R_f = 0.6$  (PE/EA = 9:1), m.p. 90 – 91 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.50 (m, 2H), 7.45 – 7.34 (m, 6H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 4H), 5.15 (d,  $J = 38.9$  Hz, 1H), 3.26 (dd,  $J = 16.6, 14.6$  Hz, 1H), 2.81 (dd,  $J = 22.9, 14.6$  Hz, 1H), 2.01 (d,  $J = 1.3$  Hz, 3H), 1.52 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 157.7 (d,  $J = 267.6$  Hz), 143.9, 141.8, 140.7, 139.5 (d,  $J = 2.5$  Hz), 132.4 (d,  $J = 2.5$  Hz), 132.3, 130.0, 128.9, 128.8 (d,  $J = 1.5$  Hz), 128.8, 128.7, 127.3, 127.1, 126.9, 126.5, 108.1 (d,  $J = 8.3$  Hz), 50.2 (d,  $J = 1.8$  Hz), 45.5 (d,  $J = 25.1$  Hz), 27.9, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.37 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{27}\text{H}_{23}\text{FO} + \text{Na}]^+$  405.1625, found 405.1630.

**(Z)-1-(3-(4-(diphenylamino)phenyl)-2-fluoroallyl)-1,3-dimethylnaphthalen-2(1H)-one (3m)**



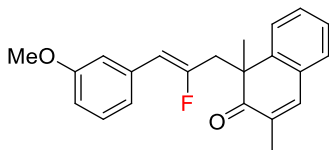
74.0 mg, 78% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.32 (m, 2H), 7.28 – 7.22 (m, 4H), 7.21 – 7.17 (m, 3H), 7.12 – 6.95 (m, 8H), 6.91 – 6.86 (m, 2H), 5.06 (d,  $J = 39.2$  Hz, 1H), 3.22 (dd,  $J = 16.5, 14.6$  Hz, 1H), 2.78 (dd,  $J = 22.9, 14.6$  Hz, 1H), 2.01 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.7, 156.5 (d,  $J = 265.6$  Hz), 147.5, 146.4 (d,  $J = 2.7$  Hz), 144.0, 141.7, 132.3, 130.0, 129.3, 129.2, 129.2, 128.8 (d,  $J = 2.8$  Hz), 127.5 (d,  $J = 2.6$  Hz), 127.0, 126.5, 124.4, 123.2, 122.9, 108.0 (d,  $J = 8.6$  Hz), 50.2 (d,  $J = 1.5$  Hz), 45.4 (d,  $J = 25.4$  Hz), 27.8, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.52 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{33}\text{H}_{28}\text{FNO} + \text{Na}]^+$  496.2047, found 496.2055.

**(Z)-1-(2-fluoro-3-(2-methoxyphenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3n)**



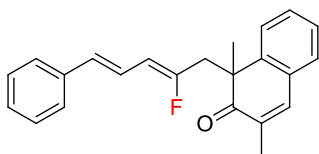
47.1 mg, 70% yield, pale yellow oil,  $R_f = 0.4$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.38 (m, 2H), 7.36 – 7.30 (m, 1H), 7.27 – 7.21 (m, 3H), 7.10 (td,  $J = 8.3, 1.7$  Hz, 1H), 6.82 – 6.72 (m, 2H), 5.52 (d,  $J = 40.0$  Hz, 1H), 3.70 (s, 3H), 3.24 (t,  $J = 15.0$  Hz, 1H), 2.81 (dd,  $J = 23.1, 14.6$  Hz, 1H), 2.01 (d,  $J = 1.3$  Hz, 3H), 1.51 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.8, 157.2 (d,  $J = 266.2$  Hz), 155.9, 144.0, 141.6, 132.3, 130.0, 129.8, 129.6, 128.8 (d,  $J = 8.0$  Hz), 128.0, 126.9, 126.6, 122.2 (d,  $J = 2.2$  Hz), 120.4, 110.4, 102.1 (d,  $J = 7.0$  Hz), 55.5, 50.1, 45.8 (d,  $J = 25.6$  Hz), 27.6, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -100.01 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{21}\text{FO}_2 + \text{Na}]^+$  359.1418, found 359.1420.

**(Z)-1-(2-fluoro-3-(3-methoxyphenyl)allyl)-1,3-dimethylnaphthalen-2(1H)-one (3o)**



53.8 mg, 80% yield, colorless oil,  $R_f = 0.6$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 7.13 – 7.08 (m, 1H), 6.78 – 6.75 (m, 2H), 6.70 – 6.66 (m, 1H), 5.08 (d,  $J = 38.6$  Hz, 1H), 3.71 (s, 3H), 3.23 (dd,  $J = 16.3, 14.7$  Hz, 1H), 2.78 (dd,  $J = 23.0, 14.6$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 159.4, 157.6 (d,  $J = 267.5$  Hz), 143.9, 141.8, 134.6 (d,  $J = 2.4$  Hz), 132.2, 130.0, 129.1, 128.8, 128.8, 127.1, 126.5, 121.0 (d,  $J = 6.9$  Hz), 113.8 (d,  $J = 7.9$  Hz), 112.5 (d,  $J = 2.1$  Hz), 108.4 (d,  $J = 8.0$  Hz), 55.1, 50.1 (d,  $J = 1.7$  Hz), 45.4 (d,  $J = 25.2$  Hz), 27.9, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.17 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{21}\text{FO}_2 + \text{Na}]^+$  359.1418, found 359.1420.

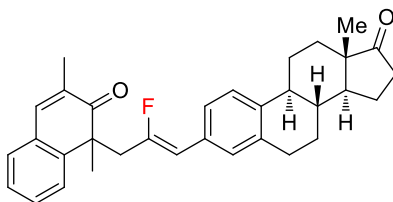
**1-((2Z,4E)-2-fluoro-5-phenylpenta-2,4-dien-1-yl)-1,3-dimethylnaphthalen-2(1H)-one (3p)**



43.8 mg, 66% yield, pale yellow oil,  $R_f = 0.4$  (PE/EA = 20:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.33 (m, 2H), 7.31 – 7.21 (m, 7H), 7.19 – 7.13 (m, 1H), 6.73 (dd,  $J = 15.9, 10.8$  Hz, 1H), 6.25 (d,  $J = 15.9$  Hz, 1H), 5.06 (dd,  $J = 34.8, 10.8$  Hz, 1H), 3.18 (dd,  $J = 16.7, 14.6$  Hz, 1H), 2.75 (dd,  $J = 22.7, 14.6$  Hz, 1H), 2.01 (d,  $J = 1.4$  Hz, 3H), 1.48 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 157.7 (d,  $J = 265.6$  Hz), 143.9, 141.8, 137.2, 132.2, 130.5 (d,  $J = 3.5$  Hz), 129.9, 128.9, 128.8, 128.6, 127.5, 127.1, 126.5, 126.3, 120.3 (d,  $J = 5.3$  Hz), 109.6 (d,  $J = 11.6$  Hz), 50.1 (d,  $J = 1.1$  Hz), 44.7 (d,  $J = 24.6$  Hz), 27.8, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.86 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{21}\text{FO} + \text{Na}]^+$  355.1469, found 355.1464.

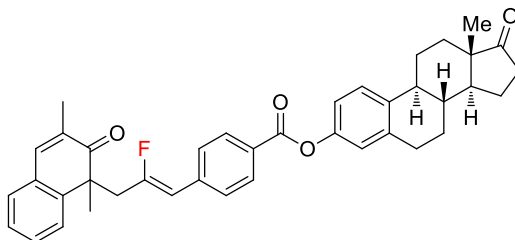


**(8R,9S,13S,14S)-3-((Z)-3-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-2-fluoroprop-1-en-1-yl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3t)**



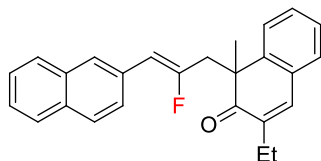
75.3 mg, 78% yield, colorless oil,  $R_f = 0.4$  (PE/EA = 4:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.30 (m, 2H), 7.27 – 7.21 (m, 3H), 7.13 (d,  $J = 8.1$  Hz, 1H), 7.02 – 6.96 (m, 2H), 5.08 (d,  $J = 39.2$  Hz, 1H), 3.24 (dd,  $J = 16.6, 14.6$  Hz, 1H), 2.85 – 2.73 (m, 3H), 2.49 (dd,  $J = 18.5, 8.4$  Hz, 1H), 2.39 – 2.33 (m, 1H), 2.22 – 2.05 (m, 2H), 2.03 – 1.98 (m, 4H), 1.95 – 1.91 (m, 1H), 1.65 – 1.52 (m, 3H), 1.50 (s, 3H), 1.46 – 1.26 (m, 4H), 0.87 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  220.9, 202.7, 157.1 (d,  $J = 266.9$  Hz), 143.9, 141.8, 138.5 (d,  $J = 2.0$  Hz), 136.3, 132.2, 130.9 (d,  $J = 2.4$  Hz), 130.0, 128.9 (d,  $J = 7.0$  Hz), 128.8, 128.8, 127.0, 126.5, 125.9 (d,  $J = 7.1$  Hz), 125.2, 108.1 (d,  $J = 8.4$  Hz), 50.5, 50.1, 48.0, 45.3 (d,  $J = 25.0$  Hz), 44.4, 38.1, 35.9, 31.6, 29.3, 27.9, 26.5, 25.6, 21.6, 16.1, 13.8 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.52 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{33}\text{H}_{35}\text{FO}_2 + \text{Na}]^+$  505.2513, found 505.2518.

**(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-((Z)-3-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-2-fluoroprop-1-en-1-yl)benzoate (3u)**



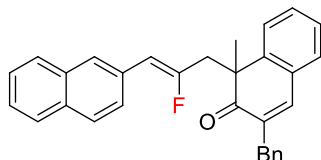
102.4 mg, 85% yield, white solid,  $R_f = 0.4$  (PE/EA = 2:1), m.p. = 113 – 114 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.98 (m, 2H), 7.44 – 7.34 (m, 2H), 7.32 – 7.24 (m, 6H), 6.95 – 6.89 (m, 2H), 5.20 (d,  $J = 38.2$  Hz, 1H), 3.29 (dd,  $J = 16.5, 14.7$  Hz, 1H), 2.94 – 2.78 (m, 3H), 2.55 – 2.38 (m, 2H), 2.34 – 2.25 (m, 1H), 2.20 – 2.09 (m, 1H), 2.05 – 1.93 (m, 6H), 1.64 – 1.40 (m, 9H), 0.91 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  220.8, 202.4, 165.1, 159.6 (d,  $J = 271.7$  Hz), 148.8, 143.7, 141.8, 138.5 (d,  $J = 2.6$  Hz), 138.1, 137.4, 132.3, 130.1, 130.0, 128.9, 128.9, 128.3, 128.2, 127.6 (d,  $J = 2.3$  Hz), 127.2, 126.5, 121.7, 118.9, 107.8 (d,  $J = 7.7$  Hz), 50.4, 50.1 (d,  $J = 1.4$  Hz), 48.0, 45.3 (d,  $J = 24.5$  Hz), 44.2, 38.0, 35.9, 31.6, 29.4, 28.1, 26.4, 25.8, 21.6, 16.0, 13.9 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -93.50 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{40}\text{H}_{39}\text{FO}_4 + \text{H}]^+$  603.2905, found 603.2919.

**(Z)-3-ethyl-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-1-methylnaphthalen-2(1H)-one**  
(3v)



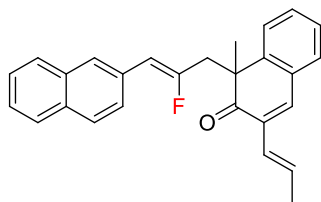
66.0 mg, 89% yield, colorless oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.66 (m, 2H), 7.66 – 7.59 (m, 2H), 7.44 – 7.31 (m, 5H), 7.27 – 7.22 (m, 2H), 7.18 (t, 1H), 5.25 (d,  $J = 38.9$  Hz, 1H), 3.27 (dd,  $J = 17.2, 14.6$  Hz, 1H), 2.82 (dd,  $J = 22.4, 14.6$  Hz, 1H), 2.54 – 2.33 (m, 2H), 1.52 (s, 3H), 1.12 (t,  $J = 7.4$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.3, 157.8 (d,  $J = 268.0$  Hz), 143.8, 140.3, 137.7, 133.3, 132.3, 130.9 (d,  $J = 2.4$  Hz), 130.1, 129.0, 128.9, 128.0, 127.7, 127.5, 127.2 (d,  $J = 7.4$  Hz), 127.1, 126.5 (d,  $J = 7.6$  Hz), 126.5, 126.1, 125.8, 108.7 (d,  $J = 8.0$  Hz), 50.3, 45.6 (d,  $J = 25.2$  Hz), 27.7, 22.6, 12.7 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.09 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{26}\text{H}_{23}\text{FO} + \text{Na}]^+$  393.1625, found 393.1629.

**(Z)-3-benzyl-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-1-methylnaphthalen-2(1H)-one**  
(3w)



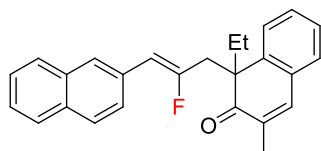
72.6 mg, 84% yield, pale yellow oil,  $R_f = 0.4$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.58 (m, 4H), 7.42 – 7.31 (m, 5H), 7.24 – 7.12 (m, 7H), 7.04 – 7.03 (m, 1H), 5.20 (d,  $J = 38.9$  Hz, 1H), 3.80 – 3.68 (m, 2H), 3.25 (dd,  $J = 17.7, 14.6$  Hz, 1H), 2.82 (dd,  $J = 21.8, 14.6$  Hz, 1H), 1.52 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  201.9, 157.7 (d,  $J = 267.9$  Hz), 144.0, 142.3, 139.2, 135.7, 133.4, 132.3 (d,  $J = 1.8$  Hz), 130.8 (d,  $J = 2.6$  Hz), 129.8, 129.3 (d,  $J = 10.9$  Hz), 129.3, 128.5, 128.0, 127.7, 127.5, 127.3 (d,  $J = 7.5$  Hz), 127.1, 126.6, 126.6, 126.5, 126.3, 126.1, 125.9, 108.7 (d,  $J = 8.0$  Hz), 50.5 (d,  $J = 1.7$  Hz), 45.6 (d,  $J = 25.1$  Hz), 35.4, 27.7 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.88 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{31}\text{H}_{25}\text{FO} - \text{H}]^-$  431.1816, found 431.1823.

**1-((Z)-2-fluoro-3-(naphthalen-2-yl)allyl)-1-methyl-3-((E)-prop-1-en-1-yl)naphthalen-2(1H)-one (3x)**



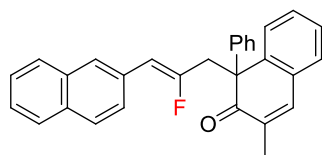
61.9 mg, 81% yield, yellow oil,  $R_f = 0.4$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.68 (m, 2H), 7.67 – 7.64 (m, 2H), 7.44 – 7.31 (m, 6H), 7.29 – 7.23 (m, 2H), 6.51 – 6.36 (m, 2H), 5.29 (d,  $J = 38.8$  Hz, 1H), 3.29 (dd,  $J = 16.7, 14.6$  Hz, 1H), 2.85 (dd,  $J = 22.8, 14.6$  Hz, 1H), 1.89 – 1.87 (m, 3H), 1.55 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  201.6, 157.6 (d,  $J = 267.8$  Hz), 143.7, 138.3, 133.3, 132.2 (d,  $J = 1.7$  Hz), 131.6, 130.8 (d,  $J = 2.5$  Hz), 130.1, 129.5 (d,  $J = 4.6$  Hz), 129.1, 127.9, 127.7, 127.5, 127.3, 127.2, 127.2, 126.5 (d,  $J = 7.7$  Hz), 126.5, 126.0, 125.8, 124.9, 108.8 (d,  $J = 8.1$  Hz), 50.9 (d,  $J = 1.7$  Hz), 45.3 (d,  $J = 25.2$  Hz), 27.3, 19.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.14 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{27}\text{H}_{23}\text{FO} + \text{Na}]^+$  405.1625, found 405.1631.

**(Z)-1-ethyl-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-3-methylnaphthalen-2(1H)-one (3y)**



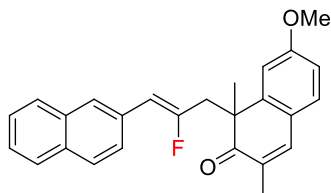
70.0 mg, 95% yield, pale yellow oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.66 (m, 2H), 7.64 – 7.60 (m, 2H), 7.40 – 7.32 (m, 5H), 7.27 – 7.19 (m, 3H), 5.25 (d,  $J = 38.9$  Hz, 1H), 3.28 (dd,  $J = 16.2, 14.4$  Hz, 1H), 2.80 (dd,  $J = 23.7, 14.4$  Hz, 1H), 2.34 – 2.23 (m, 1H), 1.99 (d,  $J = 1.3$  Hz, 3H), 1.95 – 1.84 (m, 1H), 0.50 (t, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.9, 157.8 (d,  $J = 267.9$  Hz), 142.4, 142.2, 133.5, 133.3, 132.2 (d,  $J = 1.8$  Hz), 131.6, 130.9 (d,  $J = 2.3$  Hz), 128.8, 128.7, 127.9, 127.7, 127.5, 127.2 (d,  $J = 7.5$  Hz), 127.0, 126.5 (d,  $J = 7.0$  Hz), 126.5, 126.0, 125.8, 108.4 (d,  $J = 8.0$  Hz), 55.0, 46.0 (d,  $J = 24.8$  Hz), 36.4, 15.9, 8.8 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.96 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{26}\text{H}_{23}\text{FO} + \text{Na}]^+$  393.1625, found 393.1633.

**(Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-3-methyl-1-phenylnaphthalen-2(1H)-one**  
**(3z)**



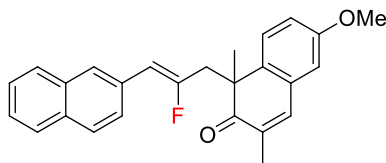
45.0 mg, 54% yield, white solid,  $R_f = 0.8$  (PE/EA = 9:1), m.p. = 126 – 127 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.68 (m, 2H), 7.66 – 7.61 (m, 2H), 7.40 – 7.33 (m, 3H), 7.32 – 7.21 (m, 7H), 7.15 – 7.09 (m, 3H), 5.36 (d,  $J = 38.9$  Hz, 1H), 4.13 (dd,  $J = 14.1, 13.1$  Hz, 1H), 3.23 (dd,  $J = 25.0, 14.1$  Hz, 1H), 1.97 (d,  $J = 1.3$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.4, 157.5 (d,  $J = 268.1$  Hz), 143.4, 143.1, 142.0, 133.3, 132.4, 132.3 (d,  $J = 1.6$  Hz), 131.0, 130.8 (d,  $J = 2.6$  Hz), 129.3, 128.9, 128.7, 128.7, 127.9, 127.7, 127.5 (d,  $J = 3.5$  Hz), 127.3, 127.2, 127.2, 126.5 (d,  $J = 7.4$  Hz), 126.1, 125.8, 109.2 (d,  $J = 8.2$  Hz), 58.0 (d,  $J = 1.7$  Hz), 43.5 (d,  $J = 24.3$  Hz), 16.2 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.55 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{30}\text{H}_{23}\text{FO} + \text{Na}]^+$  441.1625, found 441.1627.

**(Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-7-methoxy-1,3-dimethylnaphthalen-2(1H)-one**  
**(3aa)**



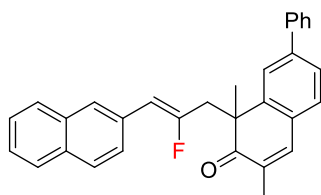
74.9 mg, 97% yield, pale yellow oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.64 (m, 4H), 7.42 – 7.34 (m, 3H), 7.21 – 7.15 (m, 2H), 6.97 (d,  $J = 2.5$  Hz, 1H), 6.78 (dd,  $J = 8.4, 2.5$  Hz, 1H), 5.30 (d,  $J = 38.9$  Hz, 1H), 3.81 (s, 3H), 3.27 (dd,  $J = 17.2, 14.7$  Hz, 1H), 2.81 (dd,  $J = 21.8, 14.6$  Hz, 1H), 1.98 (d,  $J = 1.3$  Hz, 3H), 1.52 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.5, 160.4, 157.8 (d,  $J = 268.0$  Hz), 146.1, 141.8, 133.3, 132.2 (d,  $J = 1.5$  Hz), 130.9 (d,  $J = 2.6$  Hz), 130.2, 129.7, 127.9, 127.7, 127.5, 127.2 (d,  $J = 7.4$  Hz), 126.5 (d,  $J = 7.4$  Hz), 126.0, 125.8, 123.4, 113.4, 111.7, 108.6 (d,  $J = 8.0$  Hz), 55.4, 50.3 (d,  $J = 1.4$  Hz), 45.5 (d,  $J = 25.1$  Hz), 28.1, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.17 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{26}\text{H}_{23}\text{FO}_2 - \text{H}]^-$  385.1609, found 385.1621.

**(Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-6-methoxy-1,3-dimethylnaphthalen-2(1H)-one (3ab)**



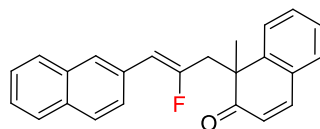
74.5 mg, 96% yield, pale yellow oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.68 (m, 2H), 7.67 – 7.64 (m, 2H), 7.42 – 7.34 (m, 3H), 7.31 (d,  $J = 8.6$  Hz, 1H), 7.18 (d,  $J = 1.5$  Hz, 1H), 6.90 (dd,  $J = 8.6, 2.7$  Hz, 1H), 6.73 (d,  $J = 2.7$  Hz, 1H), 5.27 (d,  $J = 38.9$  Hz, 1H), 3.78 (s, 3H), 3.24 (dd,  $J = 16.9, 14.5$  Hz, 1H), 2.79 (dd,  $J = 23.1, 14.5$  Hz, 1H), 2.00 (d,  $J = 1.4$  Hz, 3H), 1.50 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.0, 157.9 (d,  $J = 267.9$  Hz), 158.3, 141.7, 135.9, 133.3, 132.8, 132.2 (d,  $J = 1.7$  Hz), 131.0, 130.9 (d,  $J = 2.6$  Hz), 127.9, 127.7, 127.7, 127.5, 127.2 (d,  $J = 7.5$  Hz), 126.5 (d,  $J = 7.4$  Hz), 126.1, 125.8, 114.8, 113.3, 108.6 (d,  $J = 8.1$  Hz), 55.3, 49.7 (d,  $J = 1.7$  Hz), 45.7 (d,  $J = 24.9$  Hz), 27.9, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.23 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{26}\text{H}_{23}\text{FO}_2 + \text{Na}]^+$  409.1574, found 409.1581.

**(Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-1,3-dimethyl-7-phenylnaphthalen-2(1H)-one (3ac)**



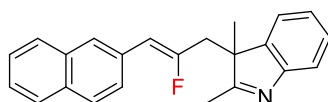
78.5 mg, 90% yield, pale yellow oil,  $R_f = 0.5$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.61 (m, 5H), 7.58 – 7.54 (m, 2H), 7.46 – 7.32 (m, 7H), 7.26 – 7.19 (m, 2H), 5.32 (d,  $J = 38.8$  Hz, 1H), 3.27 (dd,  $J = 17.9, 14.6$  Hz, 1H), 2.89 (dd,  $J = 22.4, 14.6$  Hz, 1H), 2.02 (d,  $J = 1.4$  Hz, 3H), 1.57 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 157.9 (d,  $J = 267.9$  Hz), 144.4, 141.7, 141.5, 140.7, 133.4, 132.3 (d,  $J = 1.7$  Hz), 132.2, 130.8 (d,  $J = 2.7$  Hz), 129.3, 129.1, 129.0, 128.0, 127.8, 127.8, 127.5, 127.4, 127.2, 126.5 (d,  $J = 7.4$  Hz), 126.1, 126.0, 125.9, 125.7, 109.0 (d,  $J = 8.0$  Hz), 50.5 (d,  $J = 2.0$  Hz), 45.6 (d,  $J = 25.0$  Hz), 27.7, 16.2 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.80 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{31}\text{H}_{25}\text{FO} + \text{Na}]^+$  455.1782, found 455.1784.

**(Z)-1-(2-fluoro-3-(naphthalen-2-yl)allyl)-1-methylnaphthalen-2(1H)-one (3ad)**



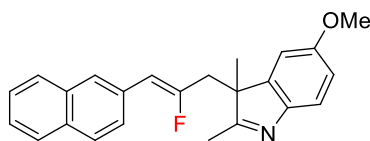
45.8 mg, 67% yield, yellow oil,  $R_f = 0.4$  (PE/EA = 9:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.67 (m, 3H), 7.66 – 7.63 (m, 3H), 7.47 – 7.35 (m, 6H), 7.32 – 7.23 (m, 2H), 6.22 (d,  $J = 9.8$  Hz, 1H), 5.30 (d,  $J = 39.0$  Hz, 1H), 3.32 (dd,  $J = 16.6, 14.8$  Hz, 1H), 2.86 (dd,  $J = 22.6, 14.7$  Hz, 1H), 1.53 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 157.6 (d,  $J = 267.7$  Hz), 145.4, 144.6, 133.3, 132.3 (d,  $J = 1.7$  Hz), 130.8 (d,  $J = 2.7$  Hz), 129.9 (d,  $J = 17.1$  Hz), 129.5, 128.0, 127.7, 127.5, 127.3, 127.2, 127.2, 126.9, 126.5 (d,  $J = 7.5$  Hz), 126.1, 125.8, 124.9, 108.8 (d,  $J = 8.0$  Hz), 50.5 (d,  $J = 1.7$  Hz), 45.0 (d,  $J = 25.1$  Hz), 28.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.32 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{24}\text{H}_{19}\text{FO} + \text{Na}]^+$  365.1312, found 365.1315.

**(Z)-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-2,3-dimethyl-3H-indole (5a)**



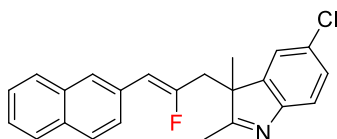
52.7 mg, 80% yield, yellow solid,  $R_f = 0.4$  (PE/EA = 2:1), m.p. 117 – 118 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.69 (m, 4H), 7.55 – 7.52 (m, 1H), 7.47 – 7.38 (m, 3H), 7.34 – 7.28 (m, 2H), 7.21 – 7.16 (m, 1H), 5.36 (d,  $J = 38.7$  Hz, 1H), 2.87 (dd,  $J = 22.5, 14.7$  Hz, 1H), 2.63 (dd,  $J = 20.4, 14.7$  Hz, 1H), 2.37 (s, 3H), 1.41 (d,  $J = 1.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.8, 157.1 (d,  $J = 267.3$  Hz), 154.2, 142.7, 133.3, 132.4 (d,  $J = 1.6$  Hz), 130.5 (d,  $J = 2.8$  Hz), 128.1, 128.0, 127.9, 127.5, 127.4 (d,  $J = 7.5$  Hz), 126.5 (d,  $J = 7.5$  Hz), 126.2, 126.0, 125.2, 122.3 (d,  $J = 1.0$  Hz), 120.2, 109.3 (d,  $J = 8.3$  Hz), 56.6 (d,  $J = 2.7$  Hz), 40.3 (d,  $J = 26.2$  Hz), 22.0, 16.0 (d,  $J = 1.7$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.13 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{20}\text{FN} + \text{H}]^+$  330.1653, found 330.1655.

**(Z)-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-5-methoxy-2,3-dimethyl-3H-indole (5b)**



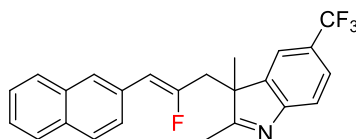
45.3 mg, 63% yield, yellow oil,  $R_f = 0.4$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.70 (m, 4H), 7.47 (dd,  $J = 8.6, 1.7$  Hz, 1H), 7.45 – 7.40 (m, 3H), 6.89 (d,  $J = 2.5$  Hz, 1H), 6.82 (dd,  $J = 8.4, 2.5$  Hz, 1H), 5.38 (d,  $J = 38.7$  Hz, 1H), 3.75 (s, 3H), 2.84 (dd,  $J = 22.0, 14.7$  Hz, 1H), 2.61 (dd,  $J = 20.6, 14.7$  Hz, 1H), 2.33 (s, 3H), 1.40 (d,  $J = 1.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  183.6, 157.9, 157.1 (d,  $J = 267.4$  Hz), 147.9, 144.3, 133.3, 132.4 (d,  $J = 1.4$  Hz), 130.5 (d,  $J = 2.8$  Hz), 128.0, 127.9, 127.5, 127.4 (d,  $J = 7.5$  Hz), 126.5 (d,  $J = 7.5$  Hz), 126.2, 126.0, 120.4, 112.7, 109.3 (d,  $J = 8.2$  Hz), 109.0 (d,  $J = 1.0$  Hz), 56.7 (d,  $J = 2.7$  Hz), 55.7, 40.3 (d,  $J = 26.2$  Hz), 22.2, 15.9 (d,  $J = 1.6$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.99 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{24}\text{H}_{22}\text{FNO} + \text{H}]^+$  360.1758, found 360.1763.

**(Z)-5-chloro-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-2,3-dimethyl-3H-indole (5c)**



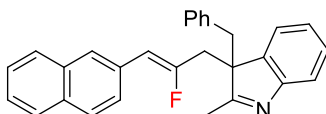
41.4 mg, 57% yield, yellow solid,  $R_f = 0.3$  (PE/EA = 2:1), m.p. 120 – 121 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.70 (m, 4H), 7.47 – 7.40 (m, 4H), 7.31 – 7.25 (m, 2H), 5.39 (d,  $J = 38.6$  Hz, 1H), 2.84 (dd,  $J = 23.2, 14.8$  Hz, 1H), 2.67 (dd,  $J = 19.3, 14.7$  Hz, 1H), 2.36 (s, 3H), 1.39 (d,  $J = 0.8$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  186.3, 156.5 (d,  $J = 267.0$  Hz), 152.8, 144.5, 133.3, 132.4 (d,  $J = 1.9$  Hz), 131.0, 130.3 (d,  $J = 2.7$  Hz), 128.3, 128.0, 128.0, 127.6, 127.5 (d,  $J = 7.7$  Hz), 126.4 (d,  $J = 7.4$  Hz), 126.2, 126.1, 122.8, 121.0, 109.6 (d,  $J = 8.3$  Hz), 57.1 (d,  $J = 2.3$  Hz), 40.2 (d,  $J = 25.9$  Hz), 22.0, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.79 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{19}\text{ClFN} + \text{H}]^+$  364.1263, found 364.1270.

**(Z)-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-2,3-dimethyl-5-(trifluoromethyl)-3H-indole (5d)**



40.5 mg, 51% yield, yellow oil,  $R_f = 0.3$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 – 7.70 (m, 4H), 7.60 – 7.58 (m, 3H), 7.45 – 7.39 (m, 3H), 5.38 (d,  $J = 38.5$  Hz, 1H), 2.90 (dd,  $J = 23.4, 14.7$  Hz, 1H), 2.70 (dd,  $J = 19.4, 14.7$  Hz, 1H), 2.42 (s, 3H), 1.44 (d,  $J = 0.8$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  189.0, 157.0, 156.4 (d,  $J = 267.0$  Hz), 143.3, 133.3, 132.5, 130.1 (d,  $J = 2.5$  Hz), 128.0, 128.0, 127.6, 127.5, 127.5, 127.1, 126.7, 126.4, 126.3, 126.2, 126.1, 125.9 (q,  $J = 3.9$  Hz), 122.8, 120.3, 119.4, 119.3, 109.8 (d,  $J = 8.4$  Hz), 57.1 (d,  $J = 2.3$  Hz), 40.3 (d,  $J = 26.3$  Hz), 21.8, 16.3 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.31, -98.04 ppm; **HRMS (ESI)  $m/z$**  Calcd for  $[\text{C}_{24}\text{H}_{19}\text{F}_4\text{N} + \text{H}]^+$  398.1526, found 398.1536.

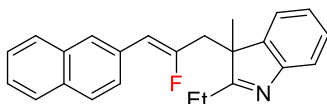
**(Z)-3-benzyl-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-2-methyl-3H-indole (5e)**



57.5 mg, 71% yield, yellow solid,  $R_f = 0.7$  (PE/EA = 2:1), m.p. 99 – 100 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.66 (m, 4H), 7.44 – 7.36 (m, 4H), 7.28 – 7.23 (m, 4H), 7.19 – 7.16 (m, 2H), 7.12 – 7.04 (m, 3H), 6.79 – 6.75 (m, 2H), 5.31 (d,  $J = 38.8$  Hz, 1H), 3.34 (d,  $J = 13.5$  Hz, 1H), 3.08 – 2.81 (m, 3H), 2.44 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  183.9, 156.6 (d,  $J = 267.1$  Hz), 154.9, 140.0, 135.3, 133.3, 132.4 (d,  $J = 1.7$  Hz), 130.4 (d,  $J = 2.7$  Hz), 129.5, 128.3, 128.0, 127.9, 127.8, 127.5, 127.4 (d,  $J = 7.5$  Hz), 127.0, 126.5 (d,  $J = 7.3$  Hz), 126.1, 126.0, 124.8, 123.3, 120.1, 109.4 (d,  $J = 8.4$  Hz), 61.8 (d,  $J = 2.8$  Hz), 42.1, 39.6 (d,  $J = 26.0$  Hz), 17.0 (d,  $J = 2.1$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.19 ppm; **HRMS (ESI)  $m/z$**  Calcd for  $[\text{C}_{29}\text{H}_{24}\text{FN} + \text{H}]^+$  406.1966, found 406.1970.

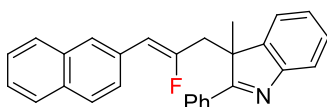


**(Z)-2-ethyl-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-3-methyl-3H-indole (5f)**



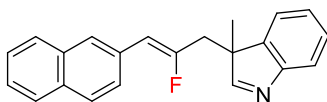
43.2 mg, 63% yield, yellow oil,  $R_f = 0.6$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.69 (m, 4H), 7.61 – 7.58 (m, 1H), 7.47 – 7.40 (m, 3H), 7.34 – 7.28 (m, 2H), 7.19 (td,  $J = 7.3, 1.1$  Hz, 1H), 5.34 (d,  $J = 38.7$  Hz, 1H), 2.89 (dd,  $J = 22.2, 14.7$  Hz, 1H), 2.76 – 2.56 (m, 3H), 1.43 (t, 3H), 1.42 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  189.9, 157.1 (d,  $J = 267.4$  Hz), 154.1, 142.7, 133.3, 132.4 (d,  $J = 1.7$  Hz), 130.5 (d,  $J = 2.7$  Hz), 128.1, 128.0, 127.9, 127.5, 127.4 (d,  $J = 7.4$  Hz), 126.5 (d,  $J = 7.5$  Hz), 126.2, 126.0, 125.1, 122.2 (d,  $J = 1.0$  Hz), 120.3, 109.3 (d,  $J = 8.3$  Hz), 56.7 (d,  $J = 2.8$  Hz), 40.4 (d,  $J = 25.9$  Hz), 22.5 (d,  $J = 1.2$  Hz), 22.2 (d,  $J = 1.1$  Hz), 10.5 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.12 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{22}\text{FN} + \text{H}]^+$  344.1809, found 344.1816.

**(Z)-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-3-methyl-2-phenyl-3H-indole (5g)**



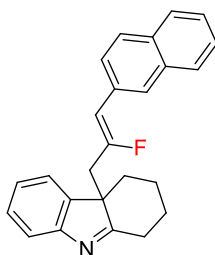
55.5 mg, 71% yield, yellow oil,  $R_f = 0.7$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 – 8.14 (m, 2H), 7.73 – 7.64 (m, 5H), 7.53 – 7.48 (m, 3H), 7.42 – 7.34 (m, 5H), 7.26 (td,  $J = 7.4, 1.1$  Hz, 1H), 5.23 (d,  $J = 38.6$  Hz, 1H), 3.17 (dd,  $J = 20.2, 14.8$  Hz, 1H), 2.91 (dd,  $J = 22.4, 14.8$  Hz, 1H), 1.74 (d,  $J = 1.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  181.5, 157.1 (d,  $J = 268.0$  Hz), 153.6, 144.4, 133.5, 133.3, 132.4, 130.7, 130.6 (d,  $J = 2.7$  Hz), 128.8, 128.4, 128.3, 128.0, 127.8, 127.5, 127.4, 127.3, 126.5 (d,  $J = 7.5$  Hz), 126.1, 125.9 (d,  $J = 2.7$  Hz), 122.1, 121.2, 109.4 (d,  $J = 8.0$  Hz), 56.7 (d,  $J = 2.8$  Hz), 41.6 (d,  $J = 25.7$  Hz), 23.6 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.49 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{28}\text{H}_{22}\text{FN} + \text{H}]^+$  392.1809, found 392.1810.

**(Z)-3-(2-fluoro-3-(naphthalen-2-yl)allyl)-3-methyl-3H-indole (5h)**



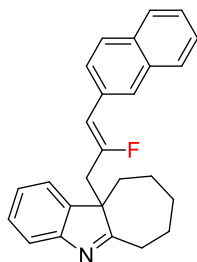
31.5 mg, 50% yield, yellow oil,  $R_f = 0.4$  (PE/EA = 6:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d,  $J = 2.5$  Hz, 1H), 7.87 – 7.86 (m, 1H), 7.81 – 7.77 (m, 3H), 7.68 – 7.58 (m, 2H), 7.49 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 – 7.29 (m, 1H), 5.65 (d,  $J = 38.5$  Hz, 1H), 2.83 – 2.59 (m, 2H), 1.47 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.1, 157.3 (d,  $J = 268.0$  Hz), 154.4, 142.8, 133.4, 132.5, 130.5 (d,  $J = 2.4$  Hz), 128.3, 128.1, 127.6, 127.5, 126.5, 126.4, 126.3, 126.1, 121.8, 121.5, 109.8 (d,  $J = 8.4$  Hz), 56.1 (d,  $J = 3.6$  Hz), 39.9 (d,  $J = 26.9$  Hz), 19.4 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.88 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{18}\text{FN} + \text{H}]^+$  316.1496, found 316.1495.

**(Z)-4a-(2-fluoro-3-(naphthalen-2-yl)allyl)-2,3,4,4a-tetrahydro-1H-carbazole (5i)**



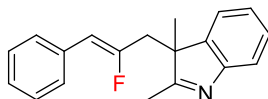
44.0 mg, 62% yield, yellow solid,  $R_f = 0.4$  (PE/EA = 2:1), m.p. 152 – 153 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.68 (m, 4H), 7.61 – 7.58 (m, 1H), 7.46 – 7.39 (m, 3H), 7.37 – 7.29 (m, 2H), 7.18 (td,  $J = 7.4, 1.1$  Hz, 1H), 5.33 (d,  $J = 38.8$  Hz, 1H), 3.03 – 2.90 (m, 2H), 2.75 – 2.61 (m, 2H), 2.56 – 2.48 (m, 1H), 2.26 – 2.20 (m, 1H), 1.94 – 1.70 (m, 2H), 1.55 – 1.39 (m, 1H), 1.26 – 1.14 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9, 157.3 (d,  $J = 267.5$  Hz), 154.9, 143.7, 133.3, 132.4 (d,  $J = 1.6$  Hz), 130.6 (d,  $J = 2.8$  Hz), 128.0, 128.0, 127.9, 127.5, 127.4 (d,  $J = 7.5$  Hz), 126.5 (d,  $J = 7.5$  Hz), 126.2, 125.9, 124.8, 122.4 (d,  $J = 1.8$  Hz), 120.5, 109.3 (d,  $J = 8.3$  Hz), 56.8 (d,  $J = 3.0$  Hz), 37.2, 36.9 (d,  $J = 26.0$  Hz), 30.2, 29.0, 21.3 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.19 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{22}\text{FN} + \text{H}]^+$  356.1809, found 356.1816.

**(Z)-10a-(2-fluoro-3-(naphthalen-2-yl)allyl)-6,7,8,9,10,10a-hexahydrocyclohepta[b]indole (5j)**



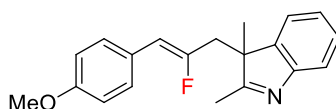
46.5 mg, 65% yield, yellow oil,  $R_f = 0.5$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 – 7.70 (m, 4H), 7.52 – 7.49 (m, 1H), 7.47 – 7.38 (m, 3H), 7.32 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 5.32 (d,  $J = 38.5$  Hz, 1H), 3.07 – 2.99 (m, 1H), 2.87 (dd,  $J = 22.3, 14.4$  Hz, 1H), 2.74 – 2.58 (m, 2H), 2.20 (dd,  $J = 14.2, 8.5$  Hz, 1H), 2.13 – 2.02 (m, 1H), 1.99 – 1.91 (m, 1H), 1.83 – 1.73 (m, 1H), 1.70 – 1.56 (m, 2H), 1.54 – 1.41 (m, 1H), 0.77 – 0.64 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  190.1, 157.1 (d,  $J = 267.5$  Hz), 154.8, 142.7, 133.3, 132.4 (d,  $J = 1.7$  Hz), 130.6 (d,  $J = 2.6$  Hz), 128.1, 128.0, 127.9, 127.5, 127.4 (d,  $J = 7.5$  Hz), 126.5 (d,  $J = 7.4$  Hz), 126.1, 125.9, 125.1, 122.3, 120.0, 109.5 (d,  $J = 8.4$  Hz), 61.2 (d,  $J = 3.3$  Hz), 40.9 (d,  $J = 26.0$  Hz), 34.6, 31.6, 30.5, 28.9, 24.6 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.25 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{26}\text{H}_{24}\text{FN} + \text{H}]^+$  370.1966, found 370.1977.

**(Z)-3-(2-fluoro-3-phenylallyl)-2,3-dimethyl-3H-indole (5k)**



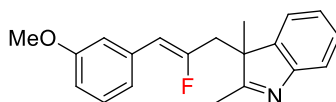
28.0 mg, 50% yield, yellow oil,  $R_f = 0.6$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8.3$  Hz, 1H), 7.33 – 7.22 (m, 6H), 7.17 (td,  $J = 7.1, 3.9$  Hz, 2H), 5.21 (d,  $J = 38.6$  Hz, 1H), 2.82 (dd,  $J = 22.4, 14.7$  Hz, 1H), 2.58 (dd,  $J = 20.4, 14.7$  Hz, 1H), 2.35 (s, 3H), 1.39 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.9, 156.8 (d,  $J = 266.9$  Hz), 154.2, 142.7, 133.1 (d,  $J = 2.4$  Hz), 128.6, 128.5, 128.2, 127.2 (d,  $J = 2.3$  Hz), 125.2, 122.3, 120.2, 109.3 (d,  $J = 8.4$  Hz), 56.7 (d,  $J = 2.4$  Hz), 40.2 (d,  $J = 26.1$  Hz), 22.1, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.60 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{19}\text{H}_{18}\text{FN} + \text{H}]^+$  280.1496, found 280.1500.

**(Z)-3-(2-fluoro-3-(4-methoxyphenyl)allyl)-2,3-dimethyl-3H-indole (5l)**



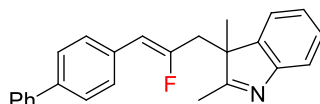
42.0 mg, 68% yield, yellow oil,  $R_f = 0.5$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.8$  Hz, 1H), 7.33 – 7.24 (m, 4H), 7.18 (t,  $J = 7.4$  Hz, 1H), 6.79 (d,  $J = 8.3$  Hz, 2H), 5.17 (d,  $J = 39.0$  Hz, 1H), 3.77 (s, 3H), 2.81 (dd,  $J = 22.5, 14.7$  Hz, 1H), 2.56 (dd,  $J = 20.7, 14.7$  Hz, 1H), 2.35 (s, 3H), 1.39 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  186.1, 158.6 (d,  $J = 2.6$  Hz), 155.5 (d,  $J = 264.1$  Hz), 154.1, 142.8, 129.8 (d,  $J = 7.4$  Hz), 128.1, 125.8 (d,  $J = 2.2$  Hz), 125.2, 122.4, 120.2, 113.8, 108.7 (d,  $J = 8.8$  Hz), 56.7 (d,  $J = 3.4$  Hz), 55.3, 40.2 (d,  $J = 26.3$  Hz), 22.1, 16.1 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -100.42 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{20}\text{FNO} + \text{H}]^+$  310.1602, found 310.1607.

**(Z)-3-(2-fluoro-3-(3-methoxyphenyl)allyl)-2,3-dimethyl-3H-indole (5m)**



39.5 mg, 65% yield, yellow oil,  $R_f = 0.5$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.9$  Hz, 1H), 7.33 – 7.25 (m, 2H), 7.21 – 7.14 (m, 2H), 6.88 – 6.86 (m, 2H), 6.74 (d,  $J = 8.4$  Hz, 1H), 5.19 (d,  $J = 38.4$  Hz, 1H), 3.75 (s, 3H), 2.82 (dd,  $J = 22.5, 14.6$  Hz, 1H), 2.58 (dd,  $J = 20.4, 14.6$  Hz, 1H), 2.35 (s, 3H), 1.39 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.8, 159.5, 156.9 (d,  $J = 267.5$  Hz), 154.1, 142.6, 134.3 (d,  $J = 2.3$  Hz), 129.3, 128.1, 125.2, 122.3, 121.1 (d,  $J = 7.0$  Hz), 120.1, 113.9 (d,  $J = 8.1$  Hz), 112.8, 109.2 (d,  $J = 7.8$  Hz), 56.6 (d,  $J = 2.5$  Hz), 55.2, 40.1 (d,  $J = 26.1$  Hz), 22.0, 16.0 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.79 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{20}\text{FNO} + \text{H}]^+$  310.1602, found 310.1607.

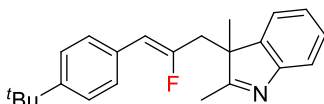
**(Z)-3-(3-([1,1'-biphenyl]-4-yl)-2-fluoroallyl)-2,3-dimethyl-3H-indole (5n)**



50.0 mg, 70% yield, yellow solid,  $R_f = 0.5$  (PE/EA = 2:1), m.p. 118 – 119 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.53 (m, 3H), 7.49 (d,  $J = 8.0$  Hz, 2H), 7.43 – 7.36 (m, 4H), 7.34 – 7.28 (m, 3H), 7.23 – 7.16 (m, 1H), 5.25 (d,  $J = 38.7$  Hz, 1H), 2.84 (dd,  $J = 22.5, 14.6$  Hz, 1H), 2.60 (dd,  $J = 20.4, 14.7$  Hz, 1H), 2.36 (s, 3H), 1.40 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.8, 157.0 (d,  $J = 267.4$  Hz), 154.2, 142.7,

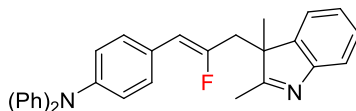
140.7, 139.9 (d,  $J = 1.9$  Hz), 132.1 (d,  $J = 2.5$  Hz), 128.9, 128.8, 128.1, 127.4, 127.1, 127.0, 125.2, 122.3, 120.2, 108.9 (d,  $J = 8.4$  Hz), 56.6, 40.2 (d,  $J = 26.0$  Hz), 22.0, 16.0 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.00 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{22}\text{FN} + \text{H}]^+$  356.1809, found 356.1814.

**(Z)-3-(3-(4-(tert-butyl)phenyl)-2-fluoroallyl)-2,3-dimethyl-3H-indole (5o)**



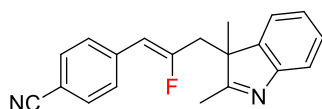
43.2 mg, 64% yield, yellow oil,  $R_f = 0.4$  (PE/EA = 4:1),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.7$  Hz, 1H), 7.32 – 7.24 (m, 6H), 7.17 (t,  $J = 7.4$  Hz, 1H), 5.21 (d,  $J = 39.0$  Hz, 1H), 2.81 (dd,  $J = 22.6, 14.6$  Hz, 1H), 2.57 (dd,  $J = 20.4, 14.6$  Hz, 1H), 2.34 (s, 3H), 1.39 (s, 3H), 1.28 (s, 9H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.9, 156.3 (d,  $J = 265.8$  Hz), 154.1, 150.2 (d,  $J = 1.9$  Hz), 142.7, 130.2 (d,  $J = 2.1$  Hz), 128.2 (d,  $J = 7.1$  Hz), 128.0, 125.3, 125.1, 122.3, 120.1, 109.0 (d,  $J = 8.6$  Hz), 56.6 (d,  $J = 2.2$  Hz), 40.1 (d,  $J = 26.3$  Hz), 34.6, 31.3, 22.0, 16.0 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.36 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{26}\text{FN} + \text{H}]^+$  336.2122, found 336.2124.

**(Z)-4-(3-(2,3-dimethyl-3H-indol-3-yl)-2-fluoroprop-1-en-1-yl)-N,N-diphenylaniline (5p)**



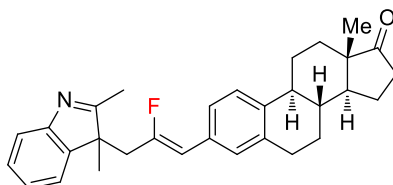
73.6 mg, 82% yield, yellow oil,  $R_f = 0.5$  (PE/EA = 2:1),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.2$  Hz, 1H), 7.30 (td,  $J = 6.7, 6.0, 1.6$  Hz, 2H), 7.22 – 7.15 (m, 6H), 7.07 – 7.04 (m, 4H), 7.02 – 6.92 (m, 4H), 5.16 (d,  $J = 39.1$  Hz, 1H), 2.82 (dd,  $J = 22.4, 14.7$  Hz, 1H), 2.58 (dd,  $J = 20.6, 14.7$  Hz, 1H), 2.35 (s, 3H), 1.39 (s, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.9, 155.8 (d,  $J = 265.8$  Hz), 154.0, 147.5, 146.7 (d,  $J = 2.1$  Hz), 142.8, 129.4, 129.3, 128.1, 127.1 (d,  $J = 2.0$  Hz), 125.2, 124.5, 123.3, 123.0, 122.3, 120.1, 108.8 (d,  $J = 8.3$  Hz), 56.7 (d,  $J = 2.6$  Hz), 40.1 (d,  $J = 26.1$  Hz), 22.0, 16.0 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.09 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{31}\text{H}_{27}\text{FN}_2 + \text{Na}]^+$  469.2050, found 469.2049.

**(Z)-4-(3-(2,3-dimethyl-3H-indol-3-yl)-2-fluoroprop-1-en-1-yl)benzotrile (5q)**



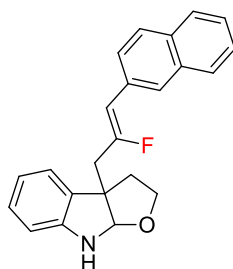
31.5 mg, 52% yield, yellow oil,  $R_f = 0.4$  (PE/EA = 2:1),  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.52 (m, 3H), 7.38 – 7.31 (m, 4H), 7.23 (td,  $J = 7.3, 1.1$  Hz, 1H), 5.22 (d,  $J = 37.6$  Hz, 1H), 2.92 (dd,  $J = 23.1, 14.8$  Hz, 1H), 2.72 (dd,  $J = 19.5, 14.7$  Hz, 1H), 2.39 (s, 3H), 1.44 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  185.4, 159.3 (d,  $J = 272.0$  Hz), 154.1, 142.2, 137.5 (d,  $J = 2.7$  Hz), 132.1, 128.8 (d,  $J = 7.9$  Hz), 128.3, 125.3, 122.0, 120.2, 118.9, 110.3 (d,  $J = 2.6$  Hz), 107.8 (d,  $J = 7.9$  Hz), 56.6, 40.2 (d,  $J = 25.5$  Hz), 22.2, 15.9 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -92.44 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{17}\text{FN}_2 + \text{H}]^+$  305.1449, found 305.1454.

**(8R,9S,13S,14S)-3-((Z)-3-(2,3-dimethyl-3H-indol-3-yl)-2-fluoroprop-1-en-1-yl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (5r)**



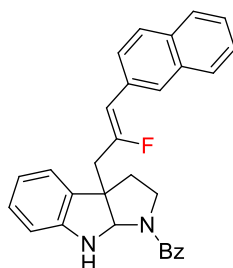
66.1 mg, 73% yield, yellow solid,  $R_f = 0.4$  (PE/EA = 2:1), m.p. 156 – 158 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 7.4$  Hz, 1H), 7.31 – 7.26 (m, 2H), 7.19 – 7.24 (m, 2H), 7.11 – 7.06 (m, 2H), 5.17 (d,  $J = 39.0$  Hz, 1H), 2.87 – 2.75 (m, 3H), 2.64 – 2.44 (m, 2H), 2.34 (s, 3H), 2.26 – 1.91 (m, 6H), 1.64 – 1.42 (m, 6H), 1.38 (s, 3H), 0.87 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  220.9, 185.9, 156.5 (d,  $J = 265.8$  Hz), 154.1, 142.7, 138.9, 136.5, 130.6 (d,  $J = 2.2$  Hz), 129.0 (d,  $J = 7.0$  Hz), 128.0, 126.0 (d,  $J = 7.0$  Hz), 125.4, 125.1, 122.3, 120.1, 108.9 (d,  $J = 8.5$  Hz), 56.6, 50.4, 48.0, 44.4, 40.1 (d,  $J = 25.9$  Hz), 38.1, 35.9, 31.6, 29.4, 26.5, 25.7, 22.1, 21.6, 16.0, 13.8 ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.15 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{31}\text{H}_{34}\text{FNO} + \text{H}]^+$  456.2697, found 456.2688.

**(Z)-3a-(2-fluoro-3-(naphthalen-2-yl)allyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (6a)**



55.2 mg, 80% yield, white solid,  $R_f = 0.5$  (PE/EA = 9:1), m.p. 141 – 142 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 1.7$  Hz, 1H), 7.81 – 7.75 (m, 3H), 7.58 (dd,  $J = 8.6, 1.7$  Hz, 1H), 7.48 – 7.40 (m, 2H), 7.12 – 7.04 (m, 2H), 6.73 (td,  $J = 7.5, 1.0$  Hz, 1H), 6.62 – 6.59 (m, 1H), 5.65 – 5.47 (m, 2H), 4.59 (s, 1H), 4.04 – 3.98 (m, 1H), 3.61 – 3.53 (m, 1H), 2.93 – 2.68 (m, 2H), 2.43 – 2.33 (m, 1H), 2.30 – 2.23 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2 (d,  $J = 267.2$  Hz), 149.4, 133.4, 132.4 (d,  $J = 1.7$  Hz), 131.0, 130.8 (d,  $J = 2.7$  Hz), 128.6, 128.0 (d,  $J = 5.9$  Hz), 127.6, 127.4 (d,  $J = 7.6$  Hz), 126.6 (d,  $J = 7.5$  Hz), 126.2, 126.0, 124.1, 119.0, 109.7 (d,  $J = 8.3$  Hz), 108.6, 97.8 (d,  $J = 2.2$  Hz), 67.7, 57.0 (d,  $J = 3.6$  Hz), 41.3, 41.0, 39.4 (d,  $J = 1.8$  Hz) ppm;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.38 ppm; **HRMS (ESI)**  $m/z$ . Calcd for  $[\text{C}_{23}\text{H}_{20}\text{FNO} + \text{H}]^+$  346.1602, found 346.1605.

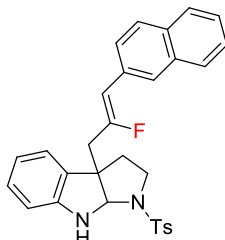
**(Z)-(3a-(2-fluoro-3-(naphthalen-2-yl)allyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-1(2H)-yl)(phenyl)methanone (6b)**



71.7 mg, 80% yield, white solid,  $R_f = 0.5$  (PE/EA = 2:1), m.p. 190 – 191 °C,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (s, 1H), 7.80 – 7.76 (m, 3H), 7.61 (dd,  $J = 8.6, 1.7$  Hz, 1H), 7.50 – 7.30 (m, 7H), 7.15 – 7.10 (m, 2H), 6.75 (t,  $J = 7.4$  Hz, 1H), 6.68 (d,  $J = 7.7$  Hz, 1H), 5.64 (s, 1H), 5.54 (d,  $J = 39.0$  Hz, 1H), 3.60 – 3.54 (m, 1H), 3.38 – 3.22 (m, 1H), 2.86 – 2.64 (m, 2H), 2.42 – 2.27 (m, 2H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 157.8 (d,  $J = 266.9$  Hz), 149.4, 136.1, 133.4, 132.4 (d,  $J = 1.2$  Hz), 130.7, 130.7, 130.1, 128.9, 128.2, 128.0, 127.9, 127.5, 127.4, 127.1, 126.5 (d,  $J = 7.5$  Hz), 126.1, 125.9, 123.7, 118.9, 110.0 (d,  $J = 8.1$  Hz), 109.5, 80.7, 55.2 (d,  $J = 4.0$  Hz), 49.3, 40.7

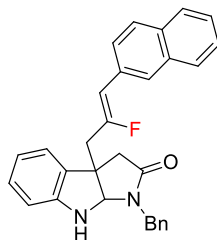
(d,  $J = 26.0$  Hz), 35.2 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.56 ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{30}\text{H}_{25}\text{FN}_2\text{O} + \text{H}]^+$  449.2024, found 449.2020.

**(Z)-3a-(2-fluoro-3-(naphthalen-2-yl)allyl)-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole (6c)**



80.7 mg, 81% yield, white solid,  $R_f = 0.5$  (PE/EA = 4:1), m.p. 151 – 152 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.84 (m, 4H), 7.75 – 7.71 (m, 2H), 7.60 – 7.50 (m, 3H), 7.18 (td,  $J = 7.6$ , 1.3 Hz, 1H), 7.12 – 7.09 (m, 3H), 6.82 (td,  $J = 7.4$ , 1.0 Hz, 1H), 6.75 (d,  $J = 7.8$  Hz, 1H), 5.57 (d,  $J = 39.1$  Hz, 1H), 5.35 (s, 1H), 3.53 – 3.46 (m, 1H), 3.27 – 3.18 (m, 1H), 2.70 (s, 1H), 2.62 (d,  $J = 2.2$  Hz, 1H), 2.29 – 2.23 (m, 1H), 2.20 (s, 3H), 2.12 – 2.02 (m, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6 (d,  $J = 267.1$  Hz), 148.7, 143.6, 135.7, 133.4, 132.5, 130.6 (d,  $J = 2.5$  Hz), 130.5, 129.8, 129.0, 128.1, 128.0, 127.6, 127.5 (d,  $J = 7.8$  Hz), 126.9, 126.5 (d,  $J = 7.7$  Hz), 126.4, 126.2, 123.3, 119.5, 110.3, 110.1, 82.5, 57.3 (d,  $J = 4.1$  Hz), 47.9, 40.3 (d,  $J = 25.1$  Hz), 34.8, 21.3 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.81 – -97.11 (m, 1F) ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{30}\text{H}_{27}\text{FN}_2\text{O}_2\text{S} + \text{H}]^+$  499.1850, found 499.18479.

**(Z)-1-benzyl-3a-(2-fluoro-3-(naphthalen-2-yl)allyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (6d)**



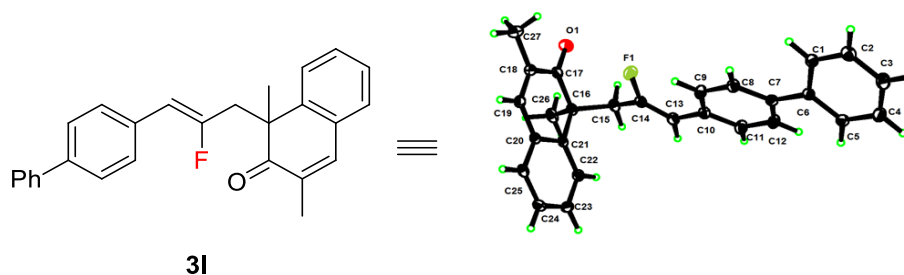
80.7 mg, 90% yield, white solid,  $R_f = 0.4$  (PE/EA = 4:1), m.p. 79 – 80 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 – 7.74 (d,  $J = 8.2$  Hz, 4H), 7.51 (dd,  $J = 8.6$ , 1.6 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.24 – 7.19 (m, 5H), 7.09 (dd,  $J = 11.1$ , 7.6 Hz, 2H), 6.81 (t,  $J = 7.4$  Hz, 1H), 6.55 (d,  $J = 7.8$  Hz, 1H), 5.47 (d,  $J = 39.2$  Hz, 1H), 5.13 (s, 1H), 4.81 (d,  $J = 15.2$  Hz, 1H), 4.27 (d,  $J = 15.2$  Hz, 1H), 3.09 – 2.88 (m, 2H), 2.77 – 2.58 (m, 2H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 157.2 (d,  $J = 266.6$  Hz), 147.3, 136.2, 133.6, 133.4, 132.5, 130.4 (d,  $J = 2.3$  Hz), 129.2, 128.9, 128.1, 127.9, 127.7, 127.6,



127.6, 126.5, 126.4, 126.3, 126.1, 124.0, 120.5, 111.2, 110.4 (d,  $J = 8.1$  Hz), 80.1 (d,  $J = 1.9$  Hz), 77.3, 50.2 (d,  $J = 3.4$  Hz), 43.8, 41.7 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.11 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{30}\text{H}_{25}\text{FN}_2\text{O} + \text{H}]^+$  449.2024, found 449.2022.

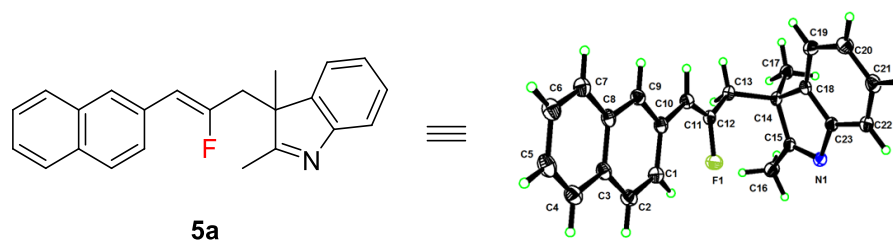
## 11. X-ray Crystallography Data of 3l and 5a

Procedure for recrystallization of compounds **3l** and **5a**: hexane was slowly added into the solution of target product in dichloromethane (with different concentration), then the dichloromethane was evaporated from the mixed solvent system at room temperature under dark and ventilated place, the crystals were obtained after a few days.



### Crystallographic Data of 3l

CCDC number	1974934
Bond precision	C-C = 0.0030 Å Wavelength = 0.71073
Cell	A = 9.3789(4) b = 9.7180(3) c = 22.5084(9) alpha = 90 beta = 100.325(2) gamma = 90
Temperature	170 K
Volume	2018.29(13)
Space group	P 1 21/c 1
Sum formula	C <sub>27</sub> H <sub>23</sub> F O
Mr	382.45
Dx, g cm <sup>-3</sup>	1.259
Z	4
Mu (mm <sup>-1</sup> )	0.081
F000	808.0
h,k,lmax	11, 12, 28
Nref	4068
Tmin, Tmax	0.638, 0.745
Correction method	# Reported T Limits: Tmin = 0.638 Tmax = 0.745
AbsCorr	MULTI-SCAN
Data completeness	0.983
Theta(max)	26.392
R(reflections)	0.0519( 2564)
wR2(reflections)	0.1435( 4068)
S	1.020



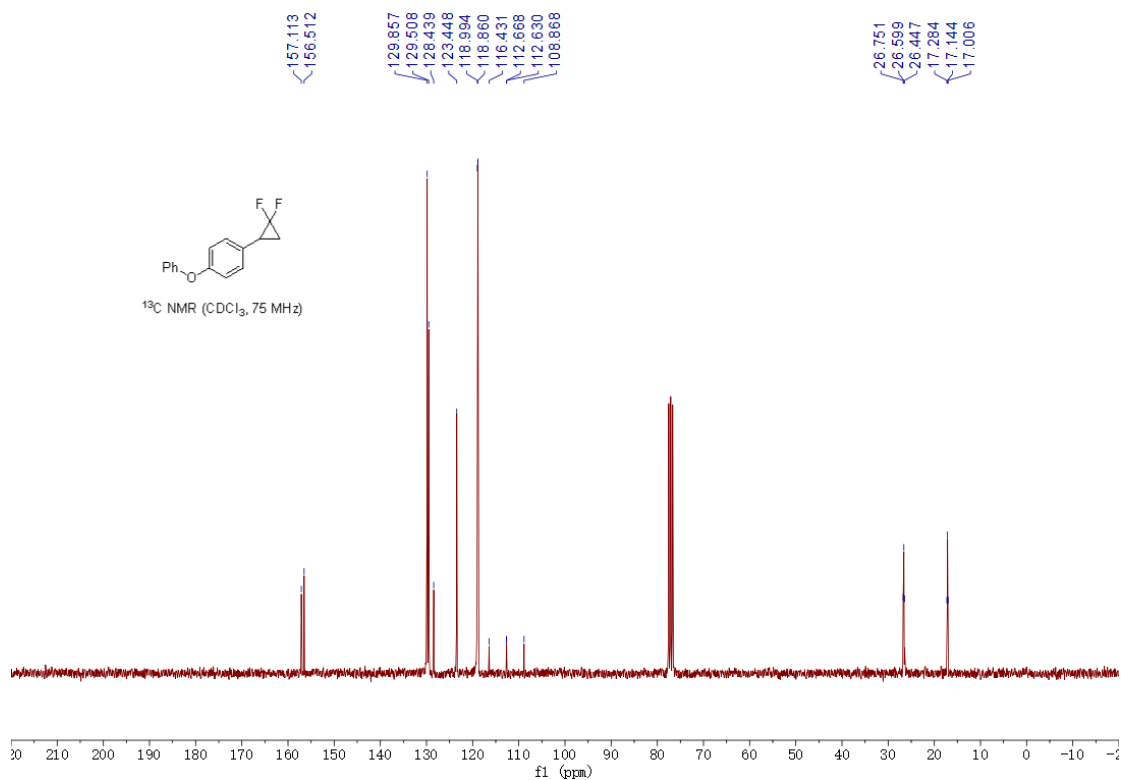
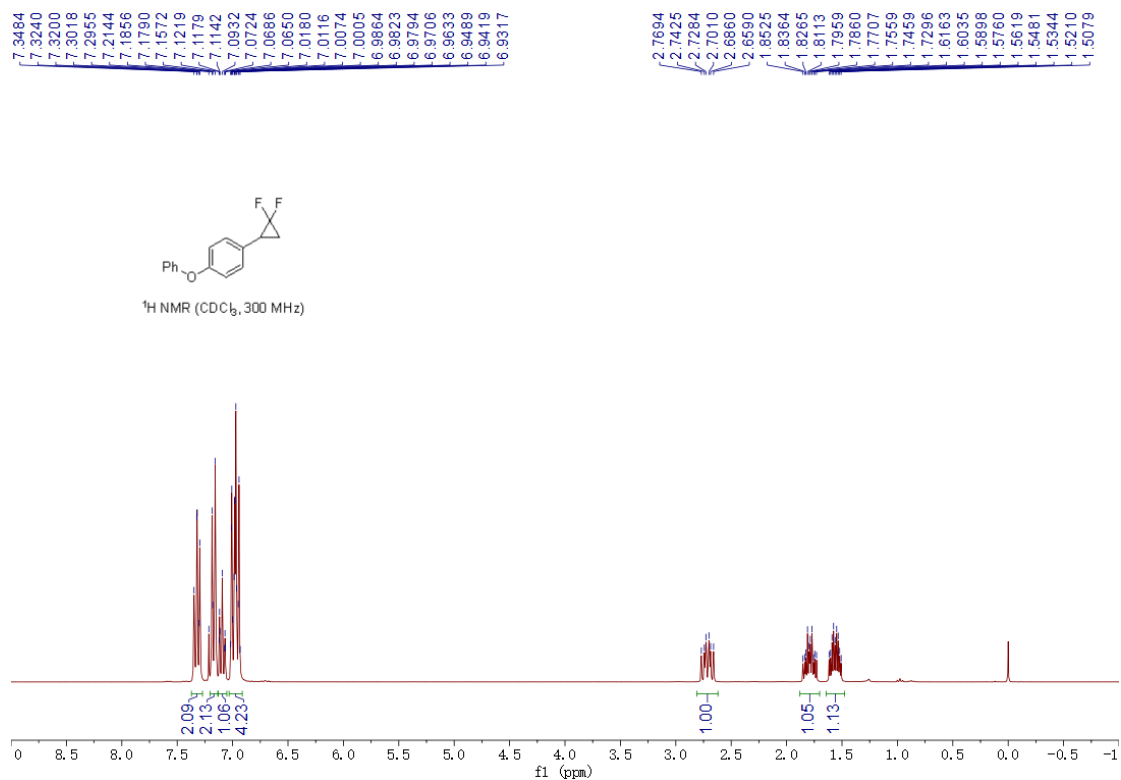
### Crystallographic Data of 5a

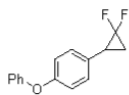
CCDC number	1974930
Bond precision	C-C = 0.0030 Å Wavelength = 0.71073
Cell	A = 23.0769(10) b = 6.4038(2) c = 24.0305(10) alpha=90 beta = 97.876(2) gamma = 90
Temperature	170 K
Volume	3517.7(2)
Space group	C 1 2/c 1
Sum formula	C <sub>23</sub> H <sub>20</sub> F N
Mr	329.40
D <sub>x</sub> , g cm <sup>-3</sup>	1.244
Z	8
Mu (mm <sup>-1</sup> )	0.079
F <sub>000</sub>	1392.0
h,k,l <sub>max</sub>	28,8,30
N <sub>ref</sub>	3570
T <sub>min</sub> , T <sub>max</sub>	0.684, 0.745
Correction method	# Reported T Limits: T <sub>min</sub> = 0.684 T <sub>max</sub> = 0.745
AbsCorr	MULTI-SCAN
Data completeness	0.993
Theta(max)	26.424
R(reflections)	0.0503( 2367)
wR <sub>2</sub> (reflections)	0.1235( 3570)
S	1.035

## 12. References

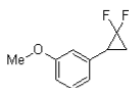
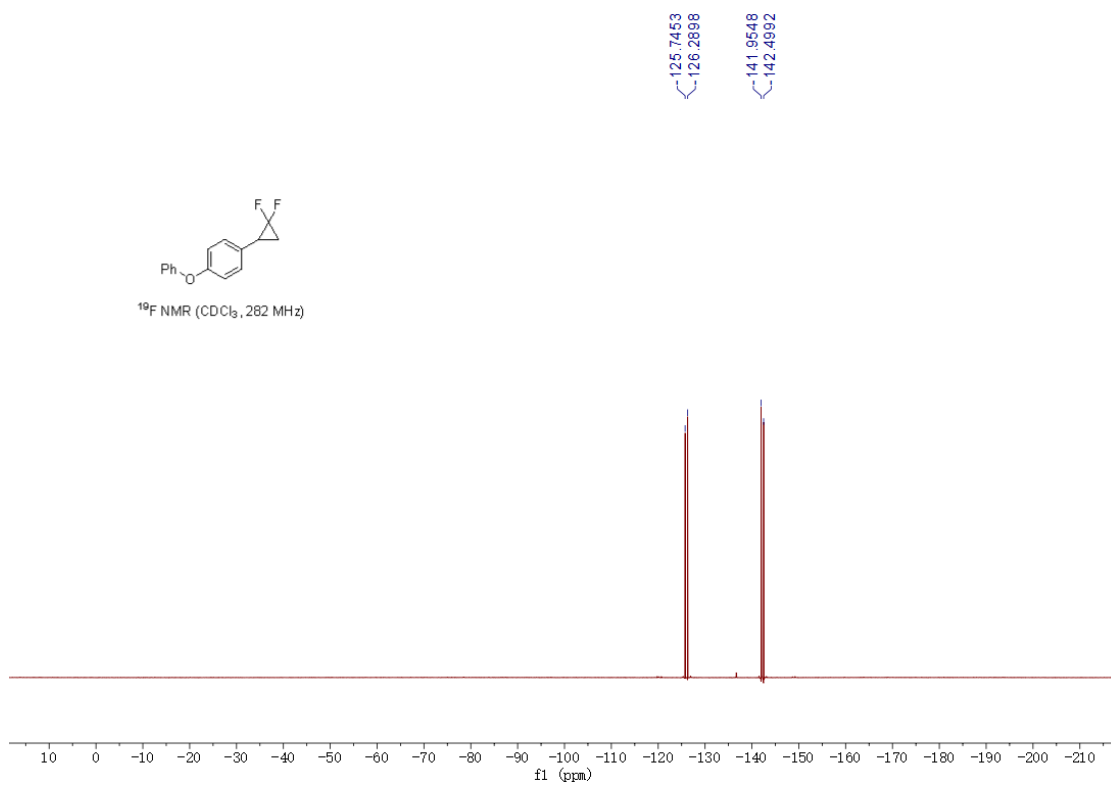
- (1) Wang, F.; Luo T.; Hu, J.; Wang, Y.; Krishnan, H. S.; Jog, P. V.; Ganesh, S. K.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7153–7157.
- (2) Xu, J.; Ahmed, E.-A.; Xiao, B.; Lu, Q.; Wang, Y.; Yu, C.; Fu, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 8231–8235.
- (3) Ahmed, E.-A. M. A.; Suliman, A. M. Y.; Gong, T.-J.; Fu, Y. *Org. Lett.* **2019**, *21*, 5645–5649.
- (4) Ahmed, E.-A. M. A.; Suliman, A. M. Y.; Gong, T.-J.; Fu, Y. *Org. Lett.* **2020**, *22*, 1414–1419.
- (5) Ni, J.; Nishonov, B.; Pardaev, A.; Zhang, A. *J. Org. Chem.* **2019**, *84*, 13646–13654.
- (6) Fang, X.; Zeng, Y.; Li, Q.; Wu, Z.; Yao, H.; Lin, A. *Org. Lett.* **2018**, *20*, 2530–2533.
- (7) Zhuo, C.-X.; You, S.-L. *Angew. Chem., Int. Ed.* **2013**, *52*, 10056–10059.
- (8) Tu, H.-F.; Zheng, C.; Xu, R.-Q.; Liu, X.-J.; You, S.-L. *Angew. Chem., Int. Ed.* **2017**, *56*, 3237–3241.
- (9) Fang, X.; Li, Q.; Shi, R.; Yao, H.; Lin, A. *Org. Lett.* **2018**, *20*, 6084–6088.

### 13. NMR Copies of Substrates and Products

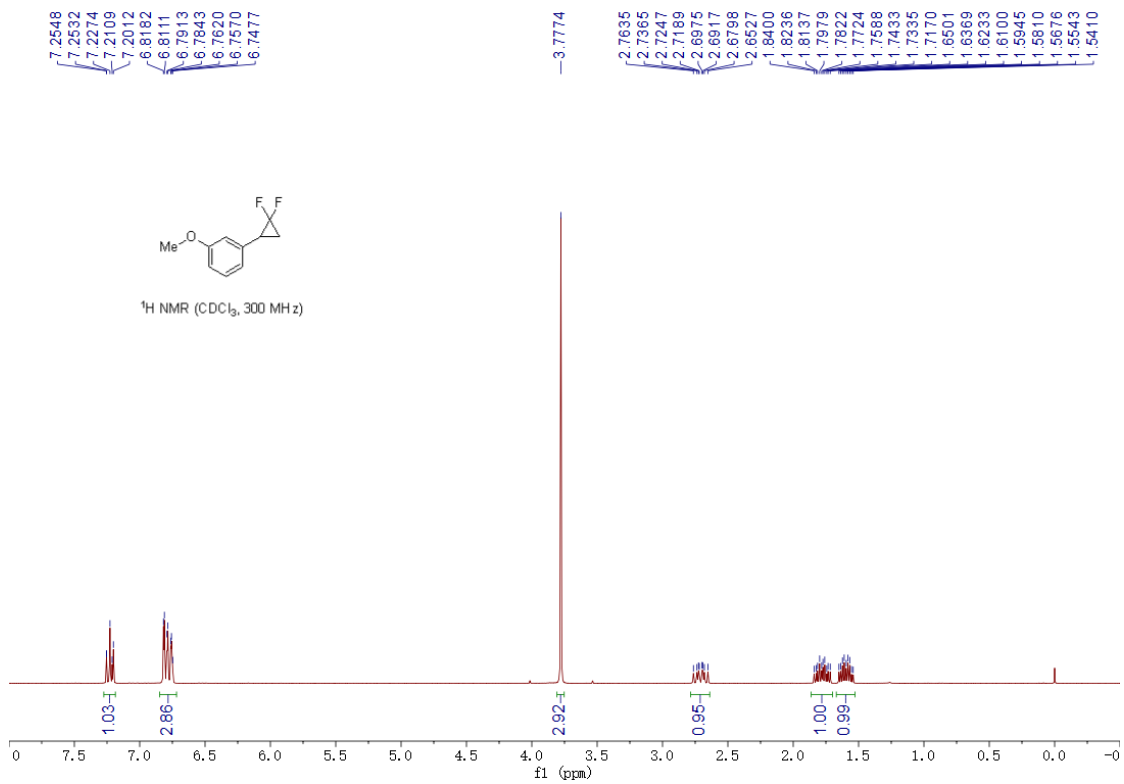


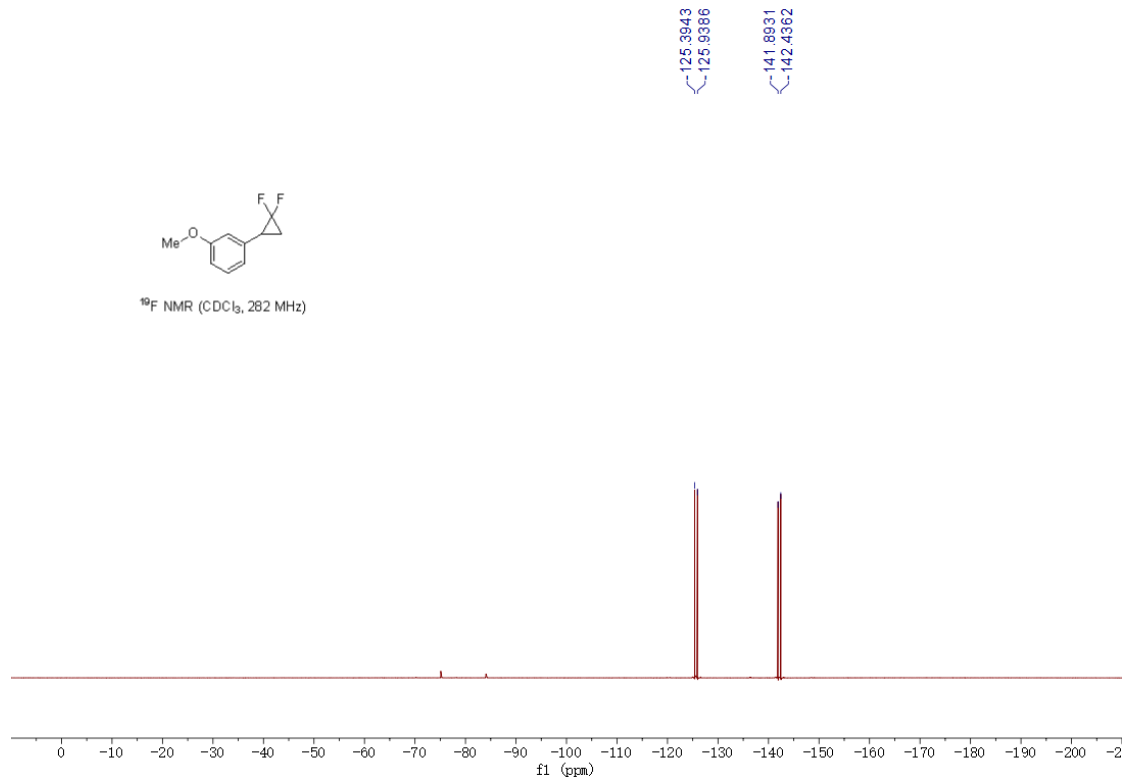
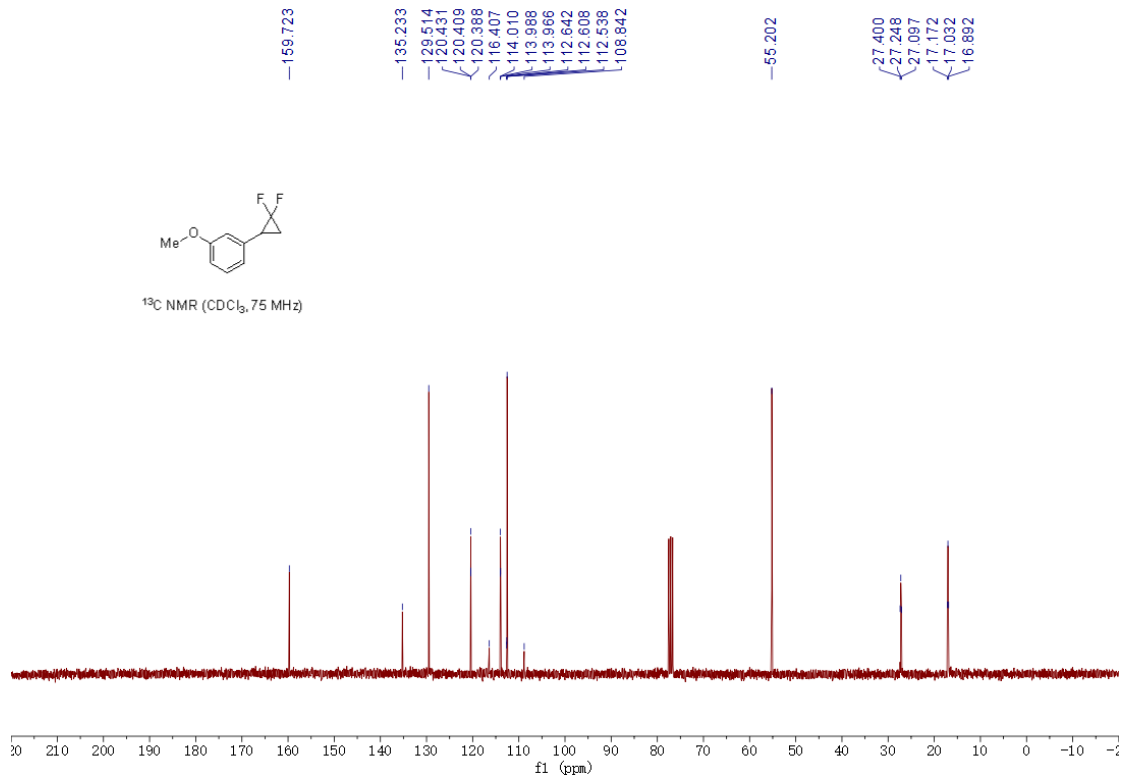


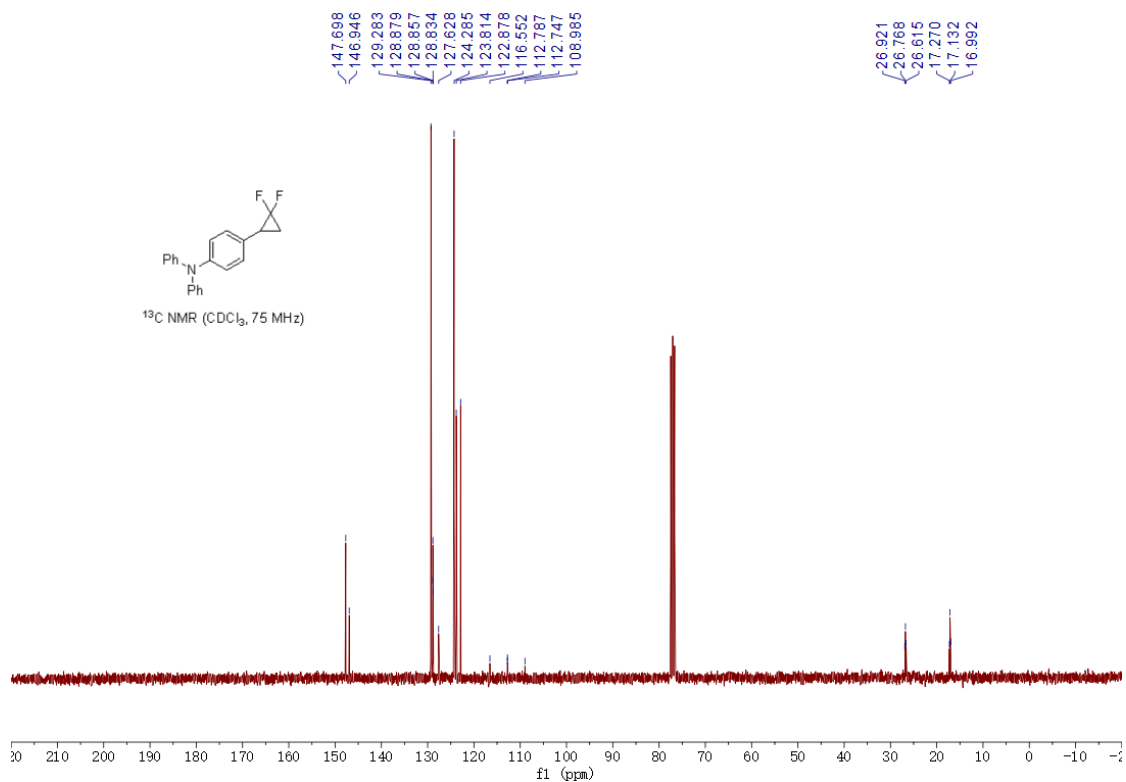
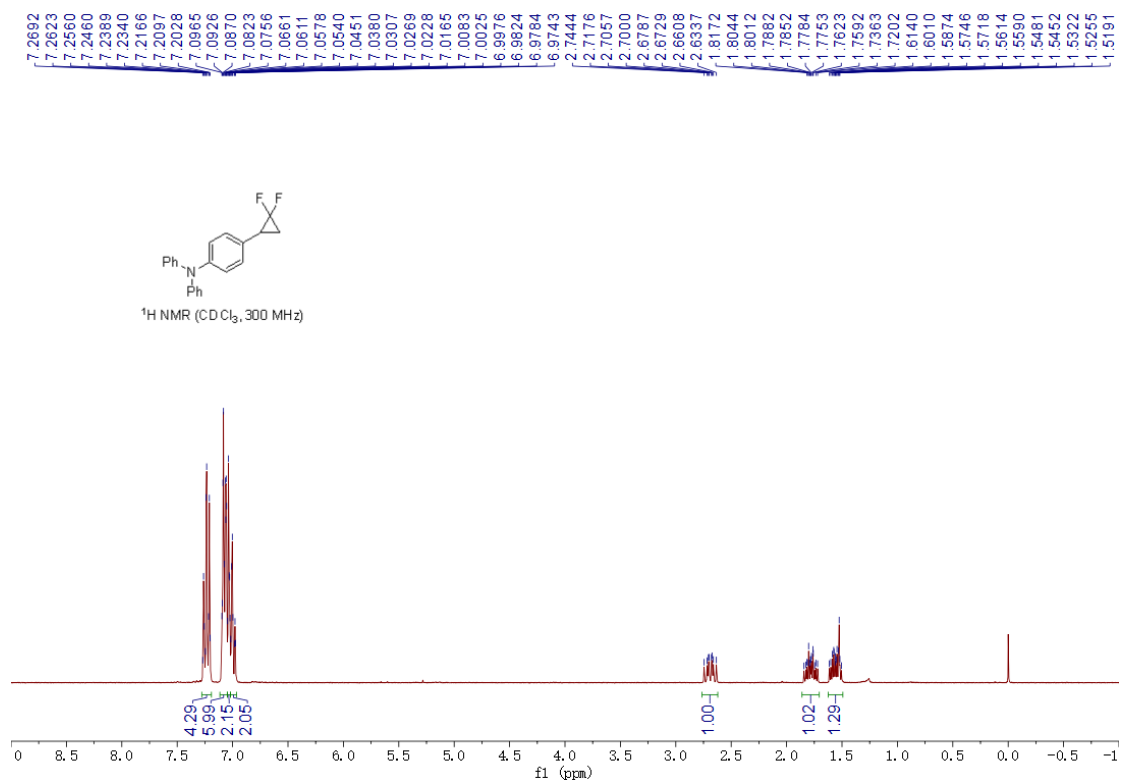
<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)



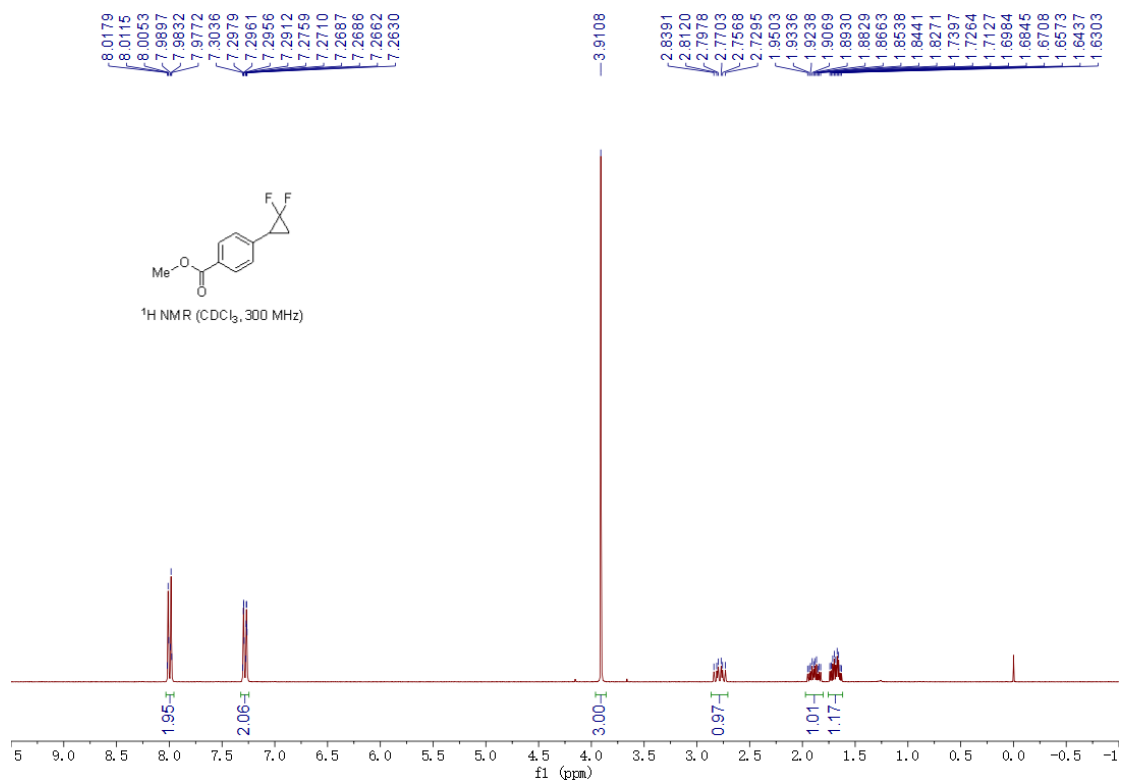
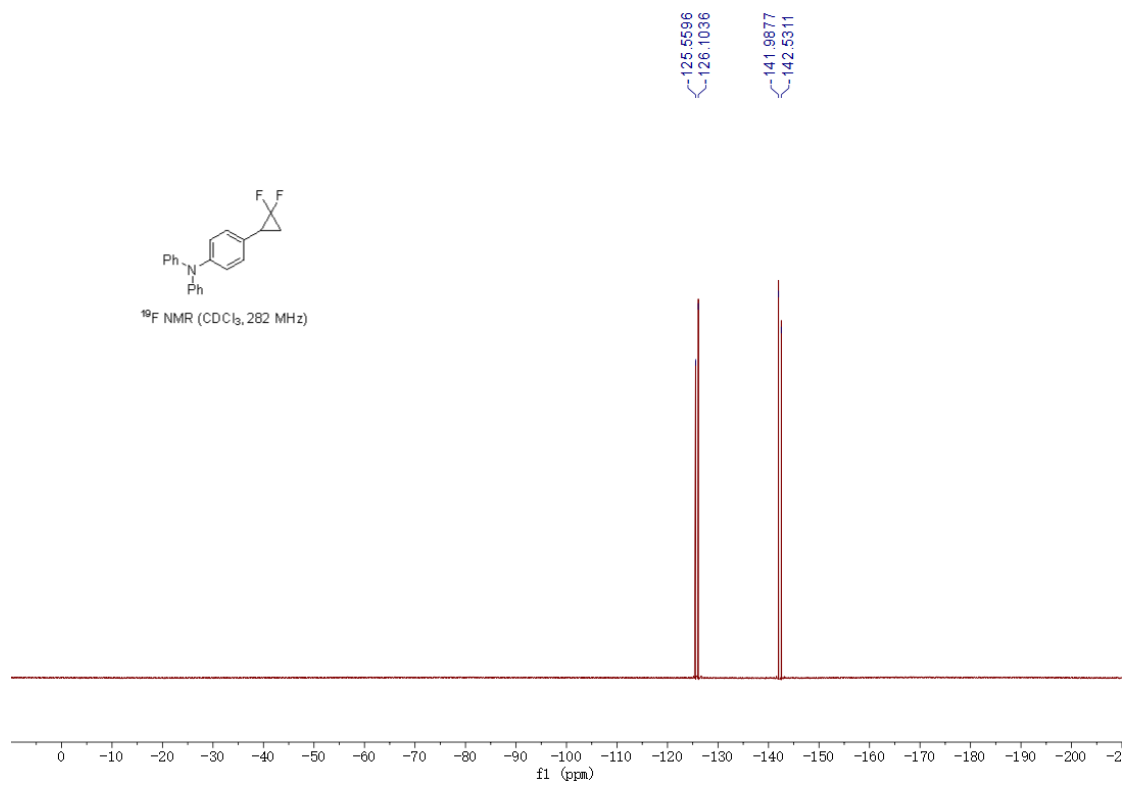
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

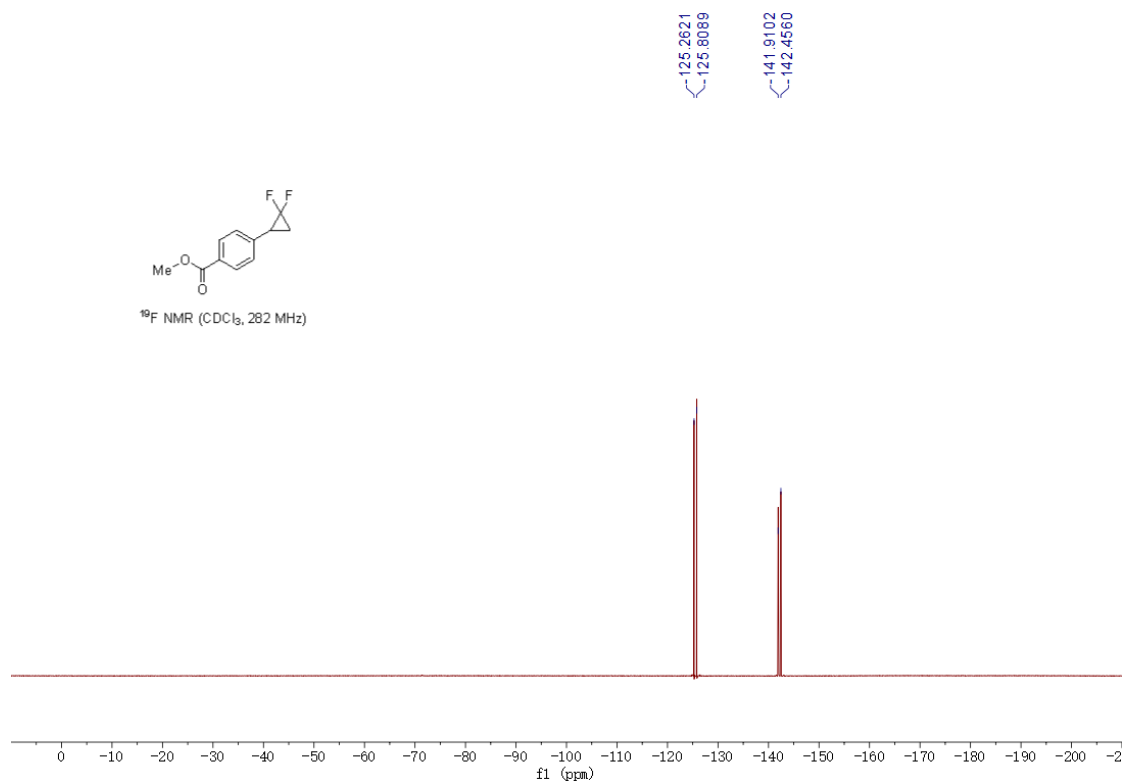
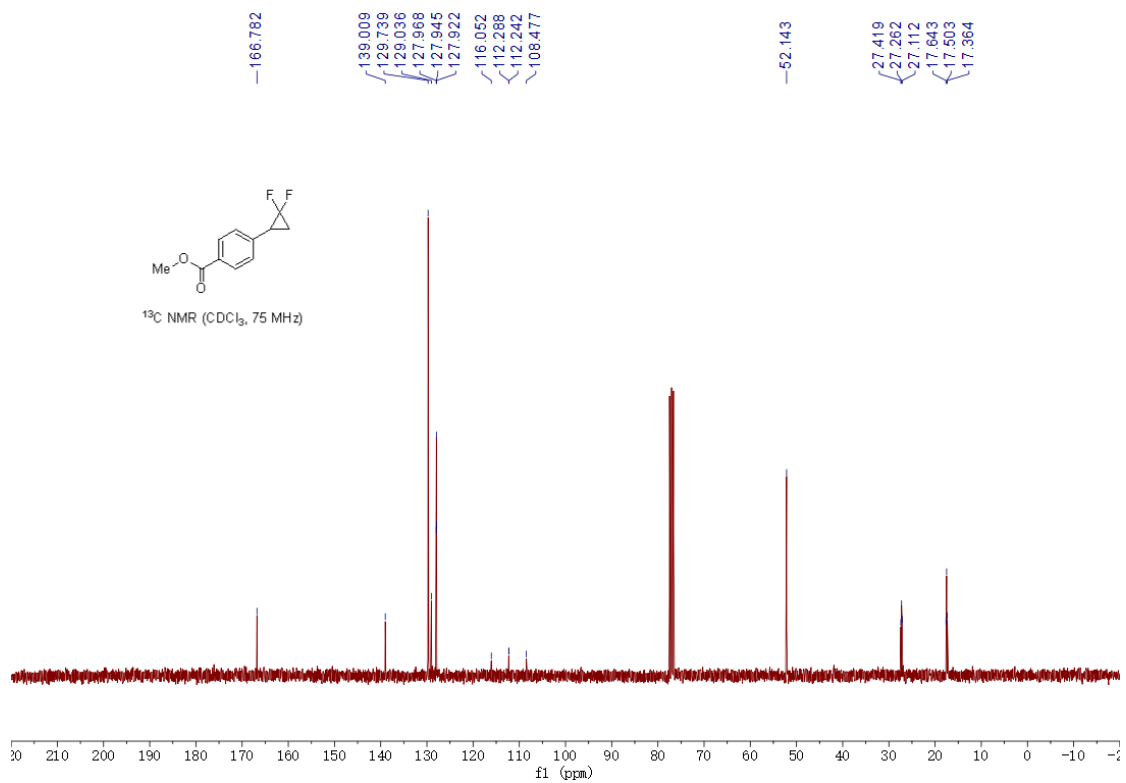


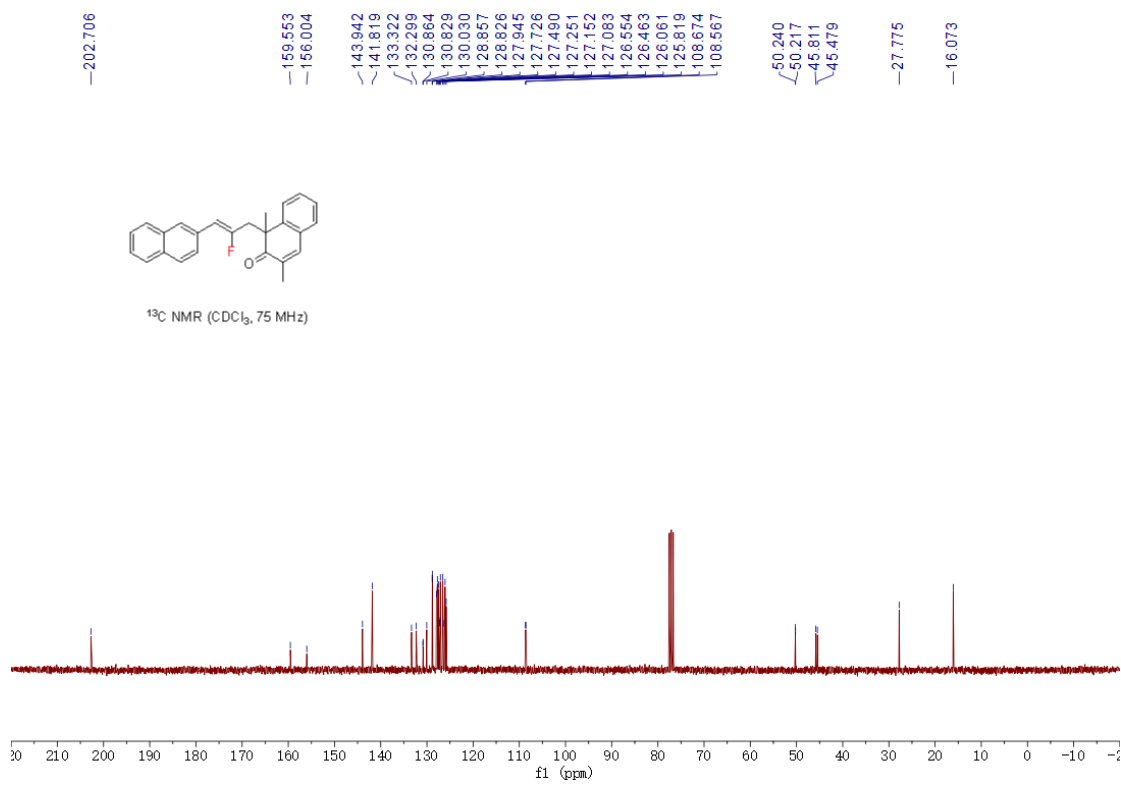
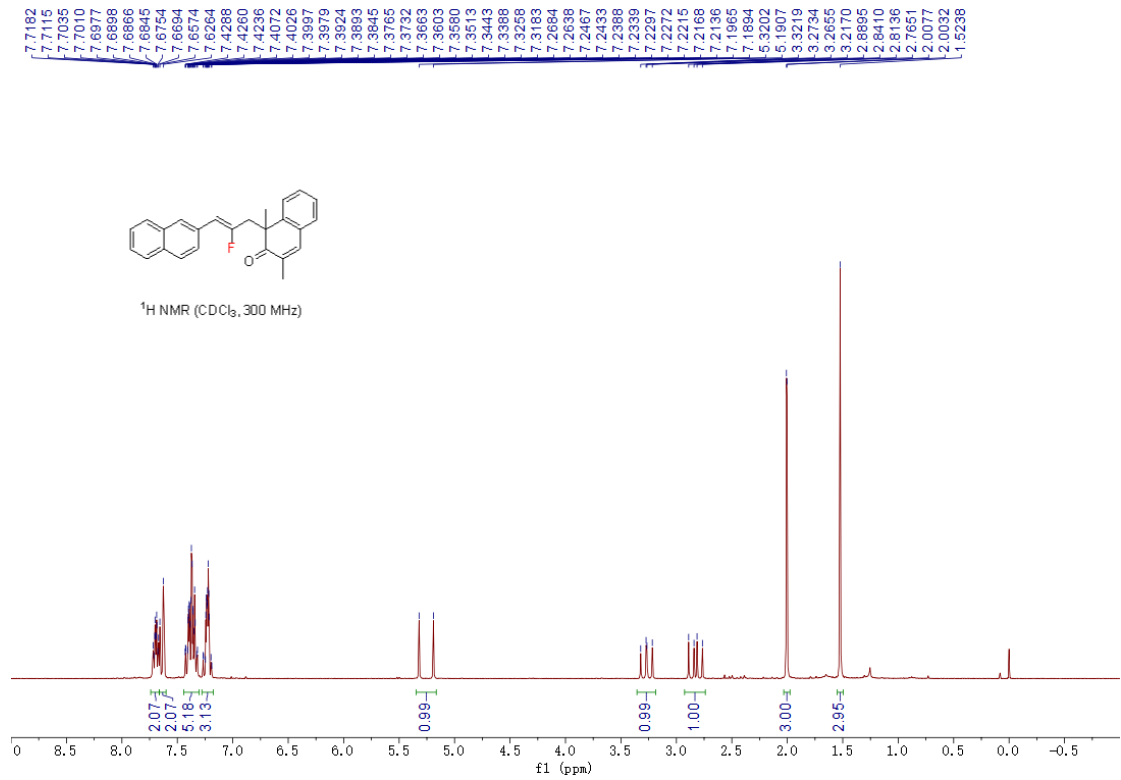


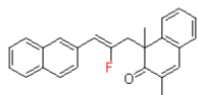




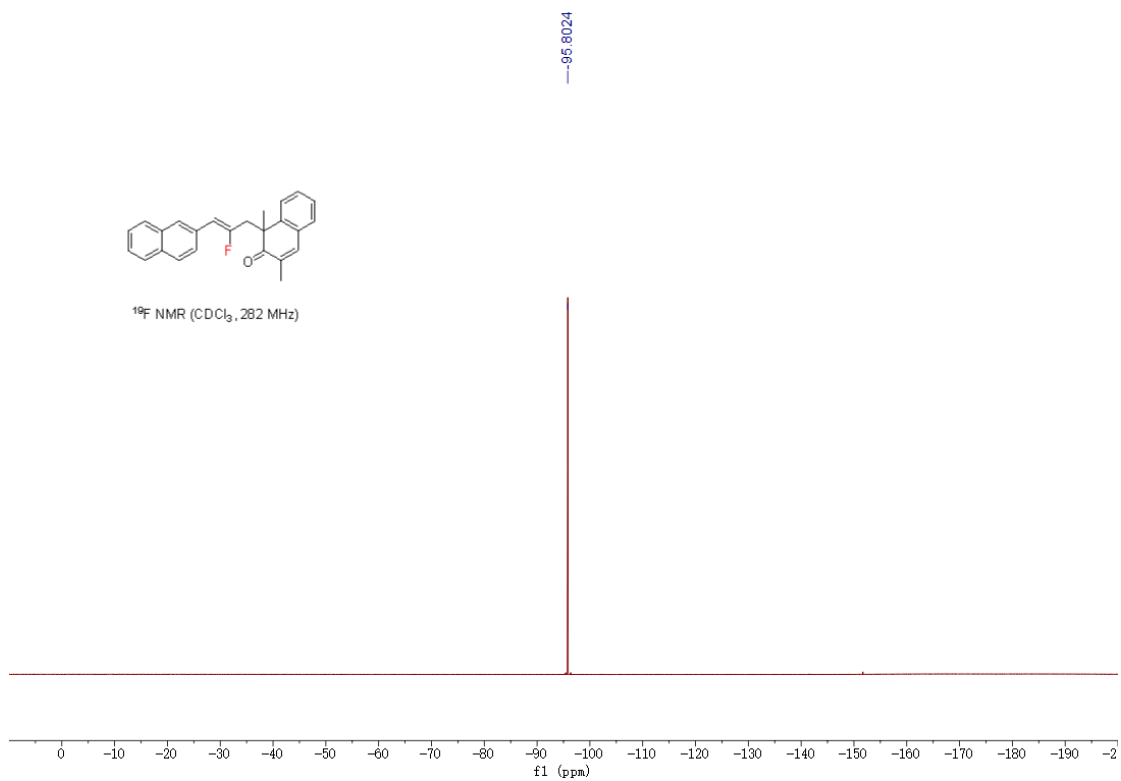




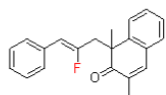




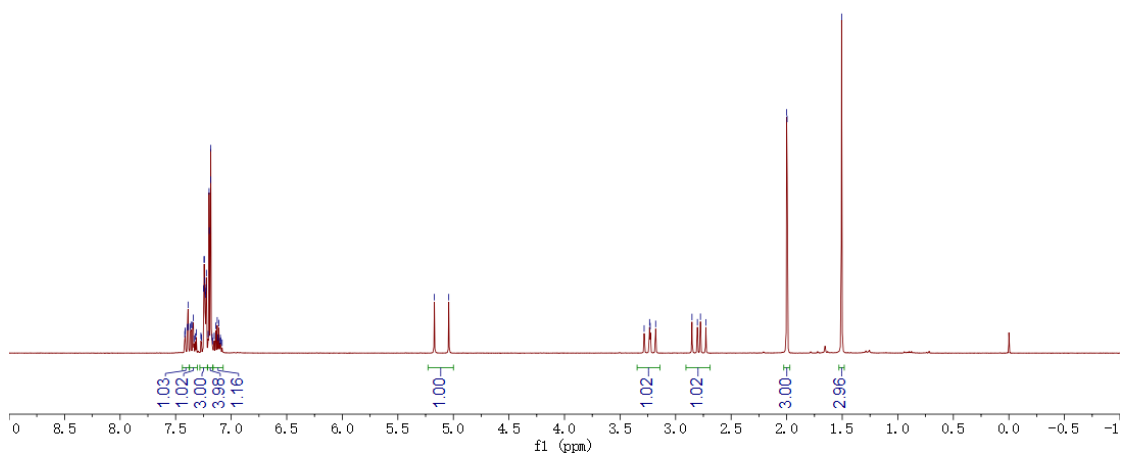
$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)

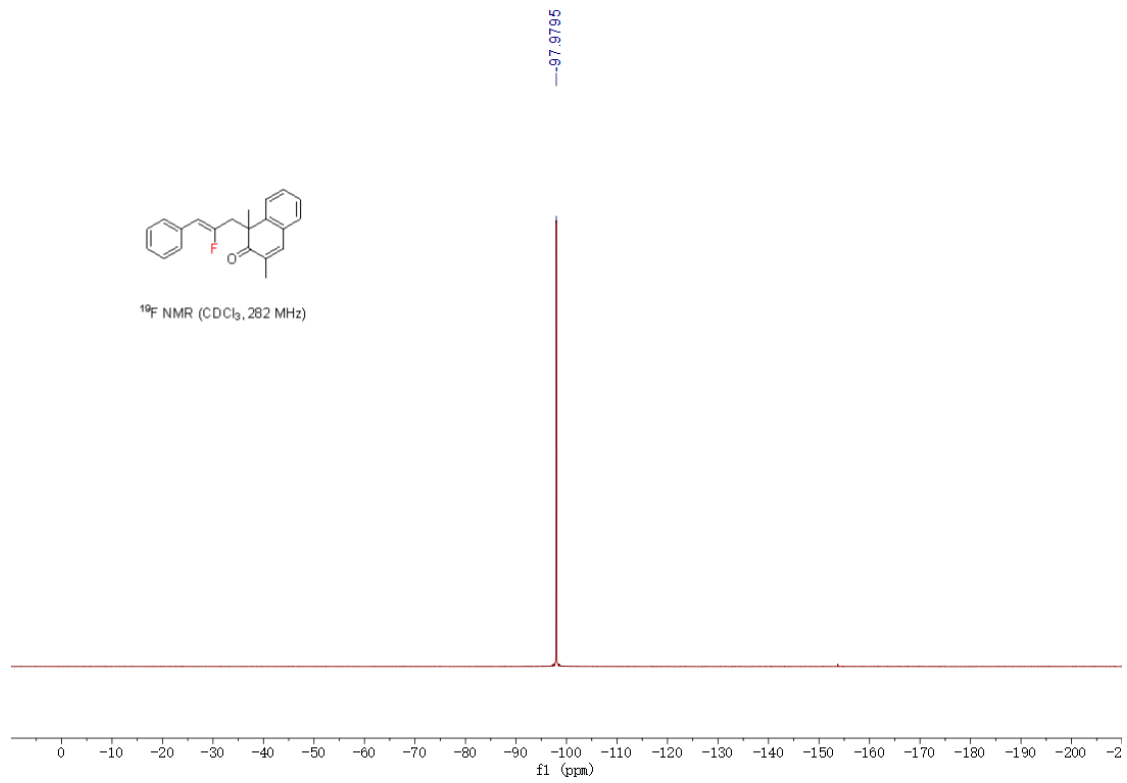
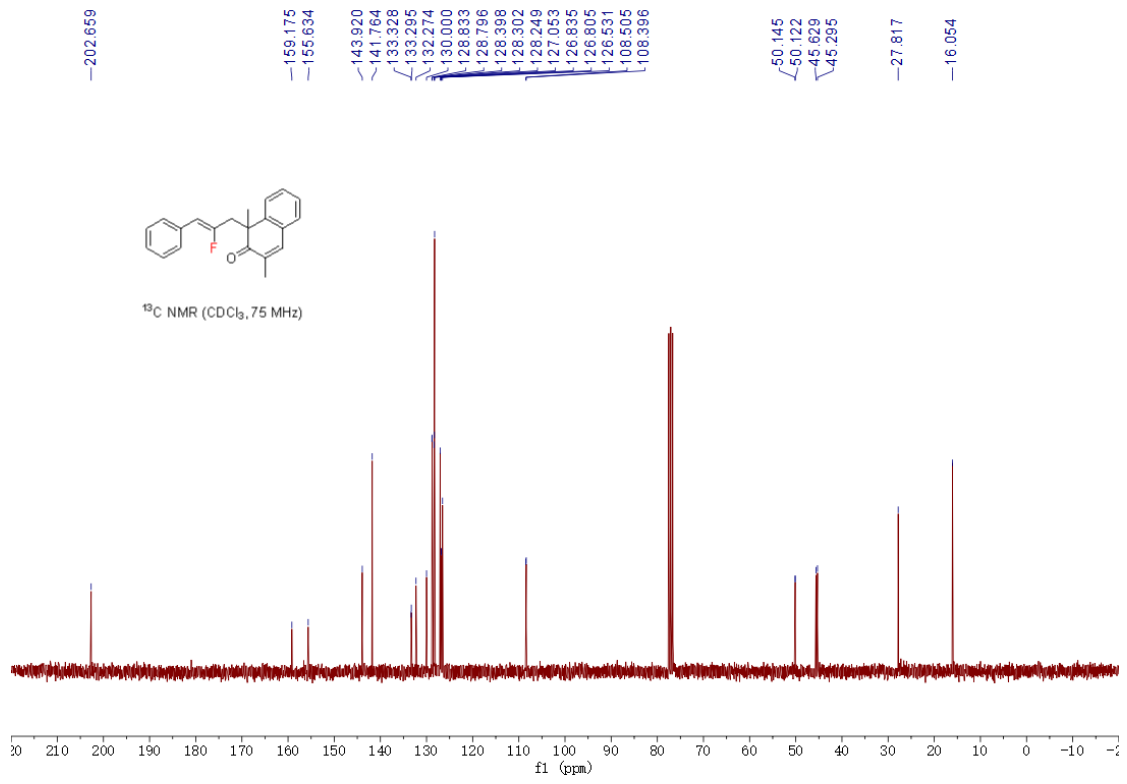


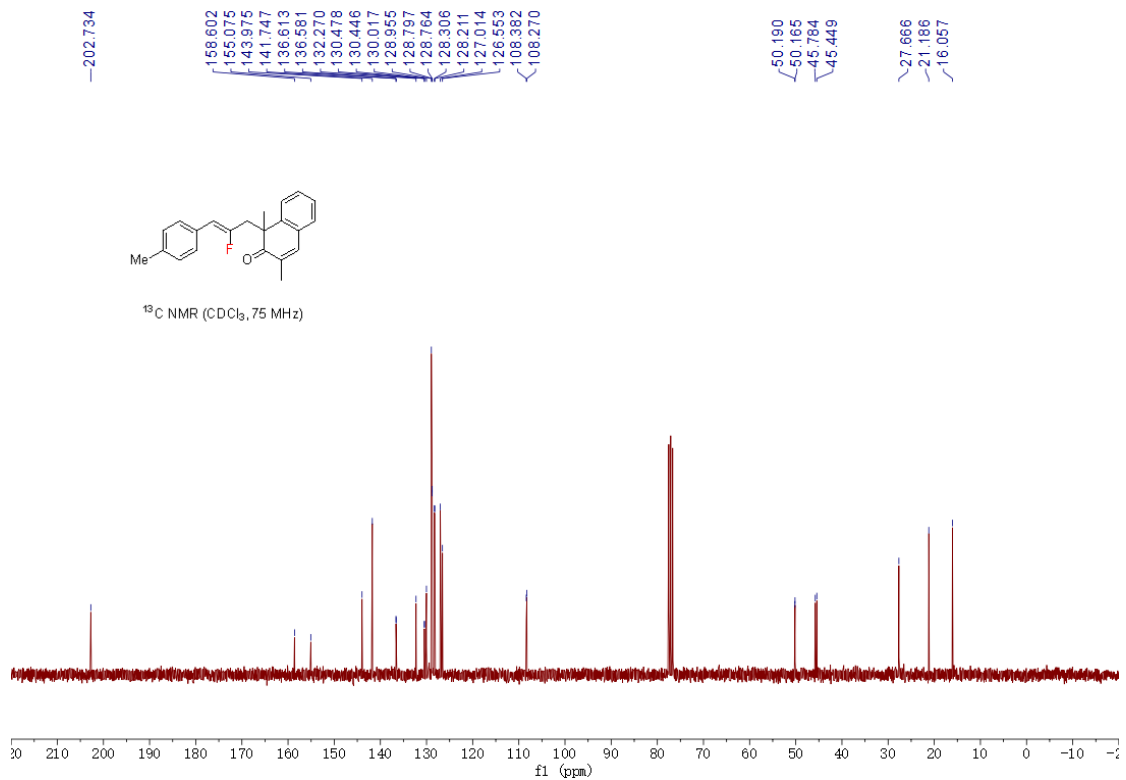
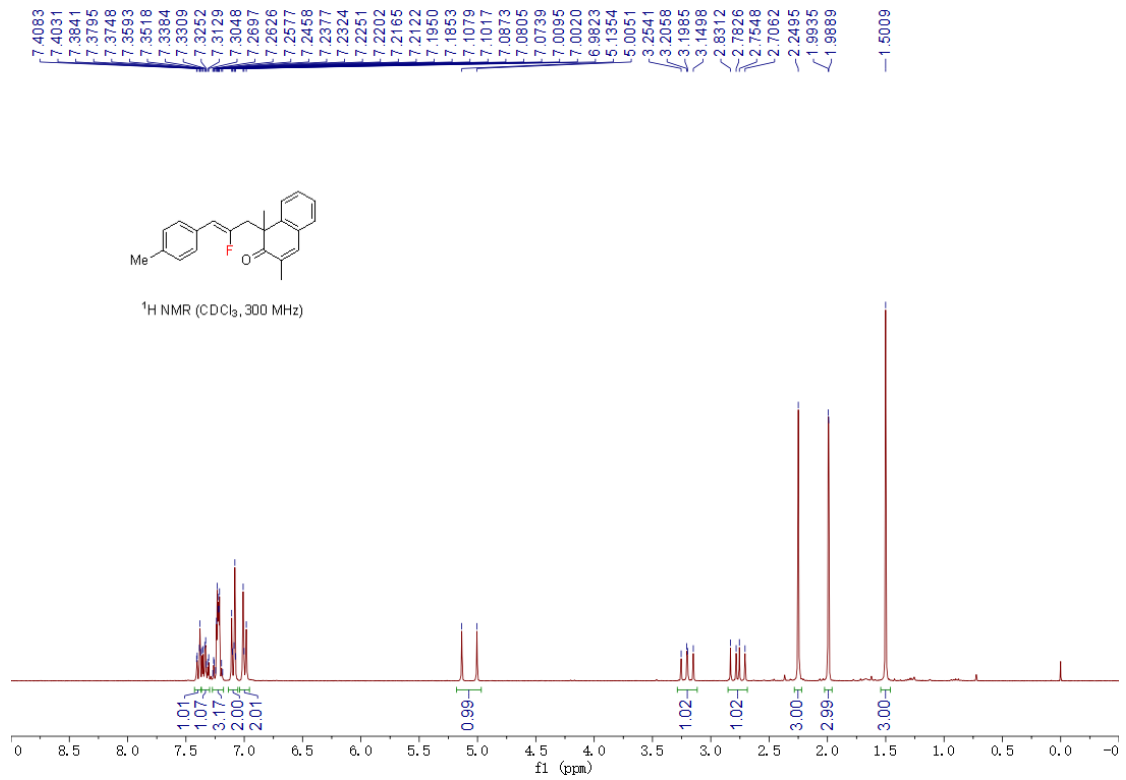
7.4179  
7.4154  
7.4130  
7.3939  
7.3881  
7.3848  
7.3689  
7.3610  
7.3484  
7.3405  
7.3231  
7.3144  
7.2730  
7.2479  
7.2432  
7.2379  
7.2336  
7.2316  
7.2266  
7.2231  
7.2076  
7.1993  
7.1970  
7.1856  
7.1835  
7.1713  
7.1528  
7.1369  
7.1256  
7.1109  
6.1713  
6.0418  
3.2832  
3.2340  
3.2283  
3.1794  
2.8038  
2.7763  
2.7277  
2.0007  
1.9962  
-1.5057

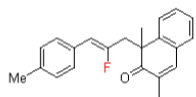


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)

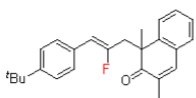
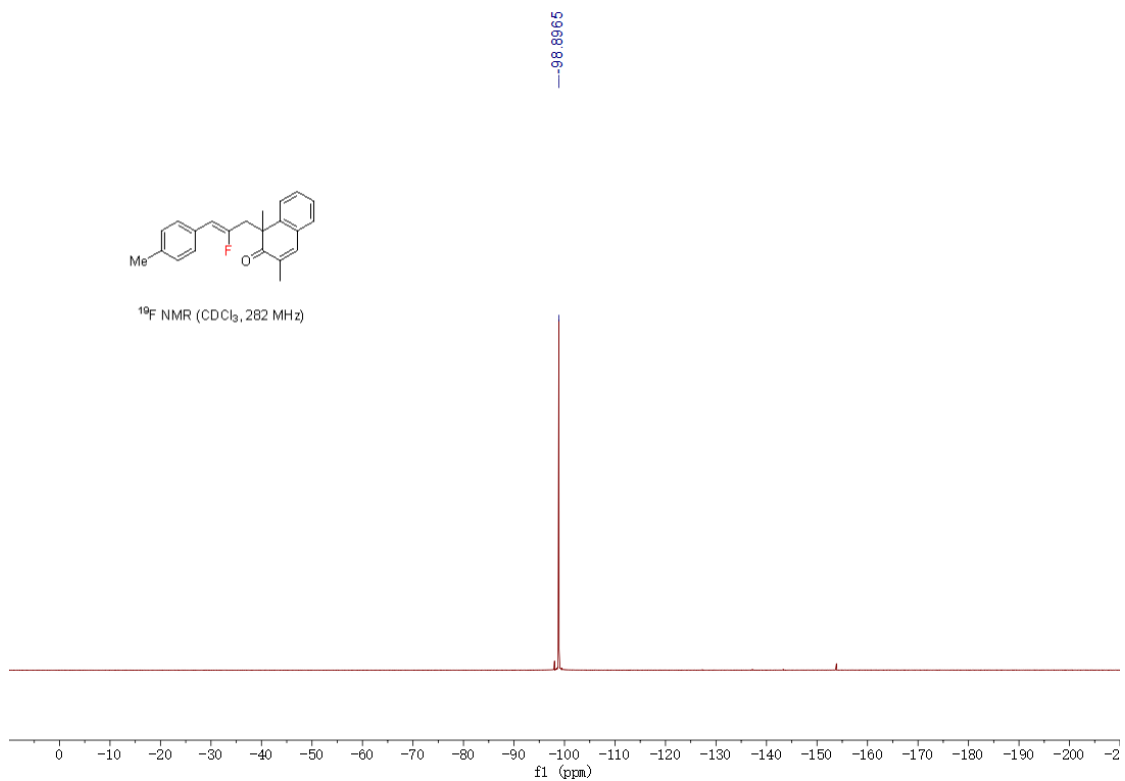




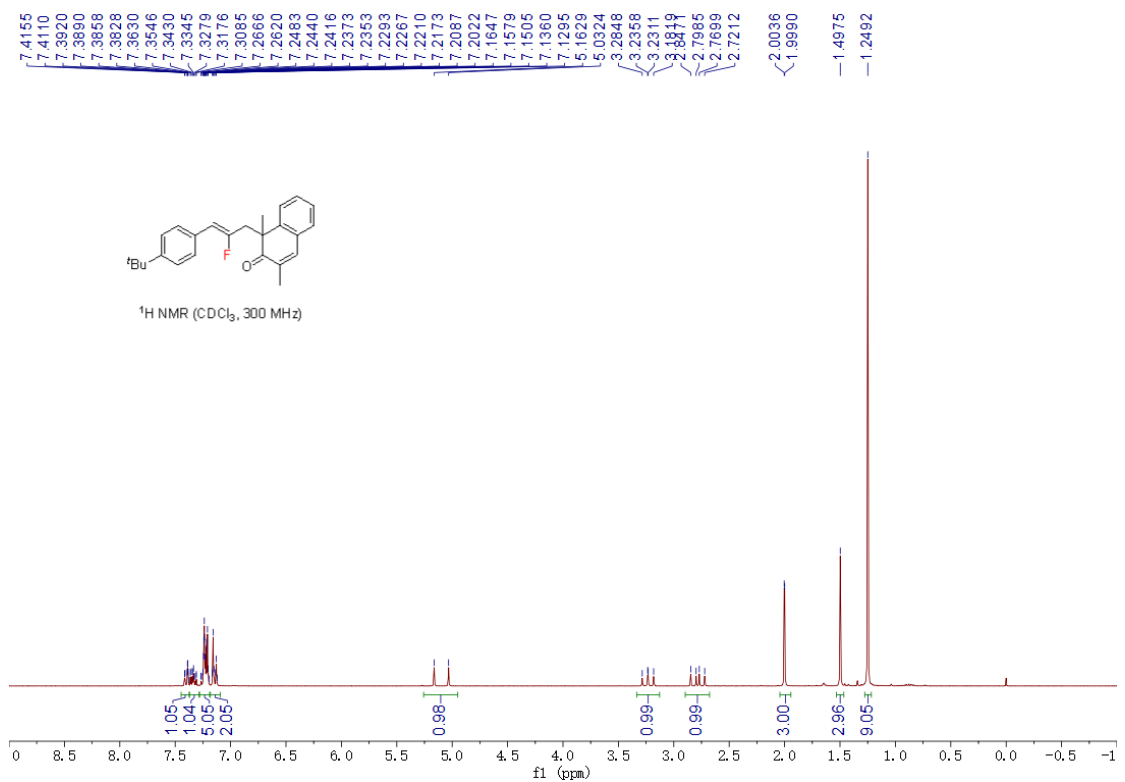


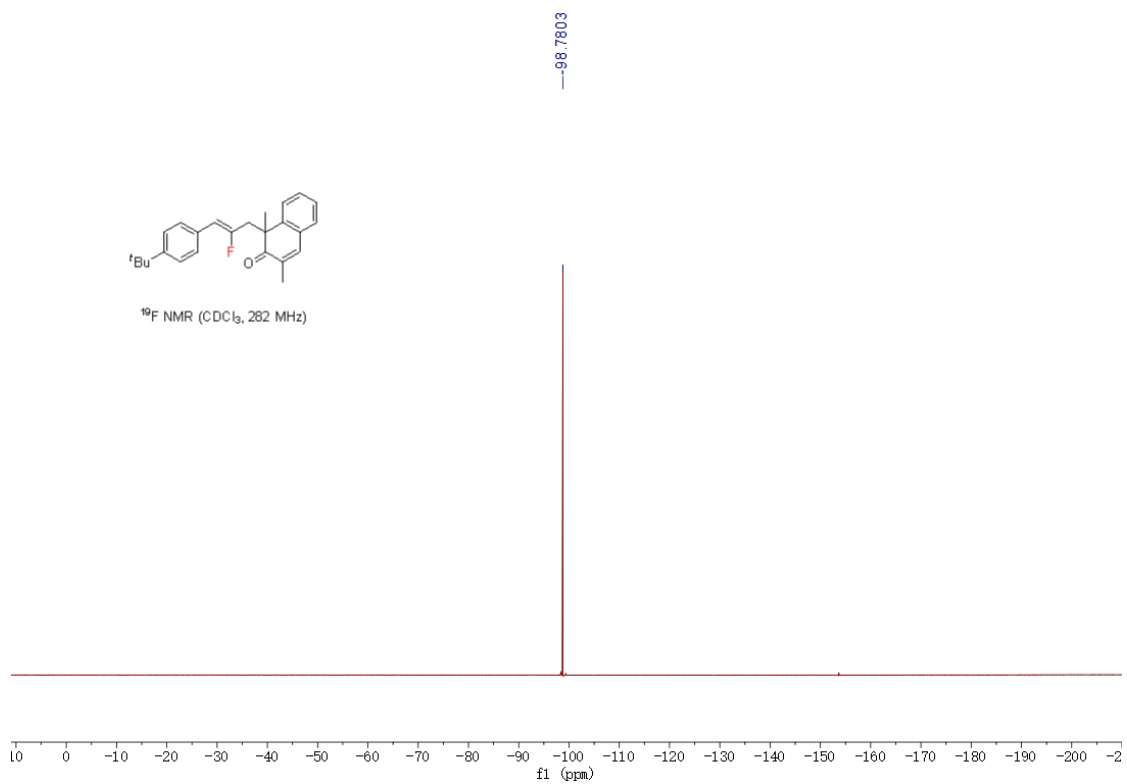
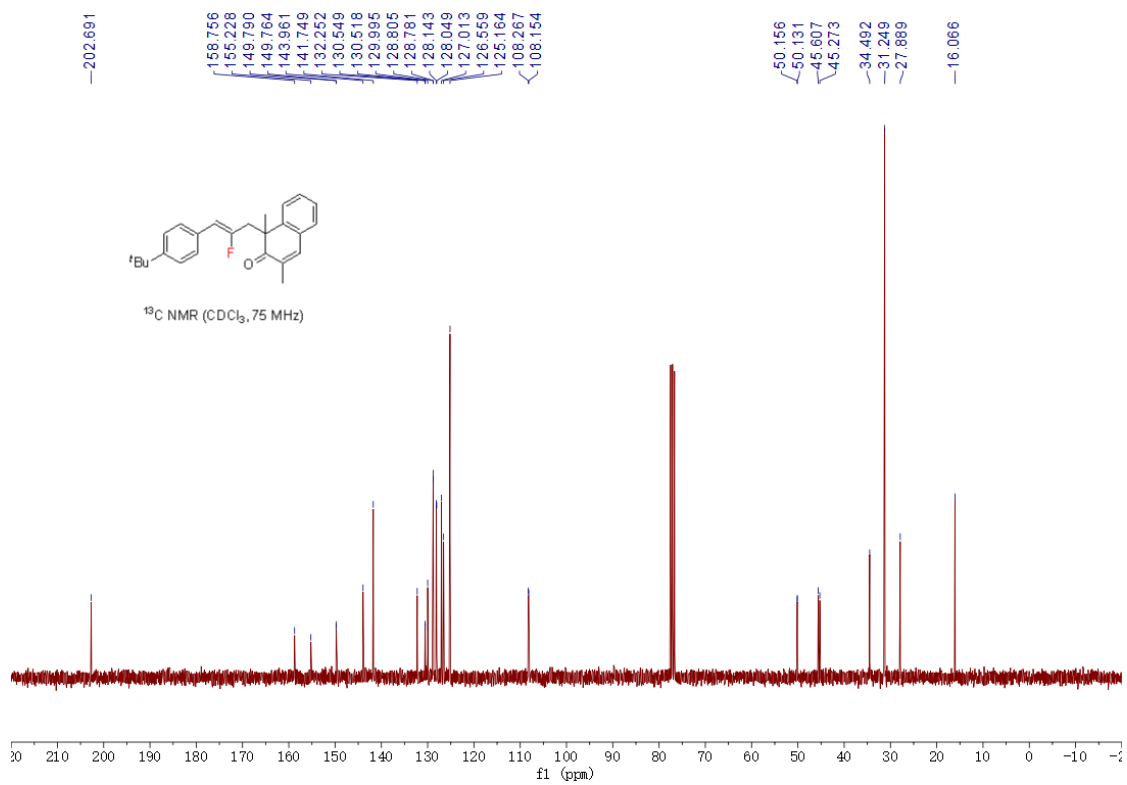


$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)

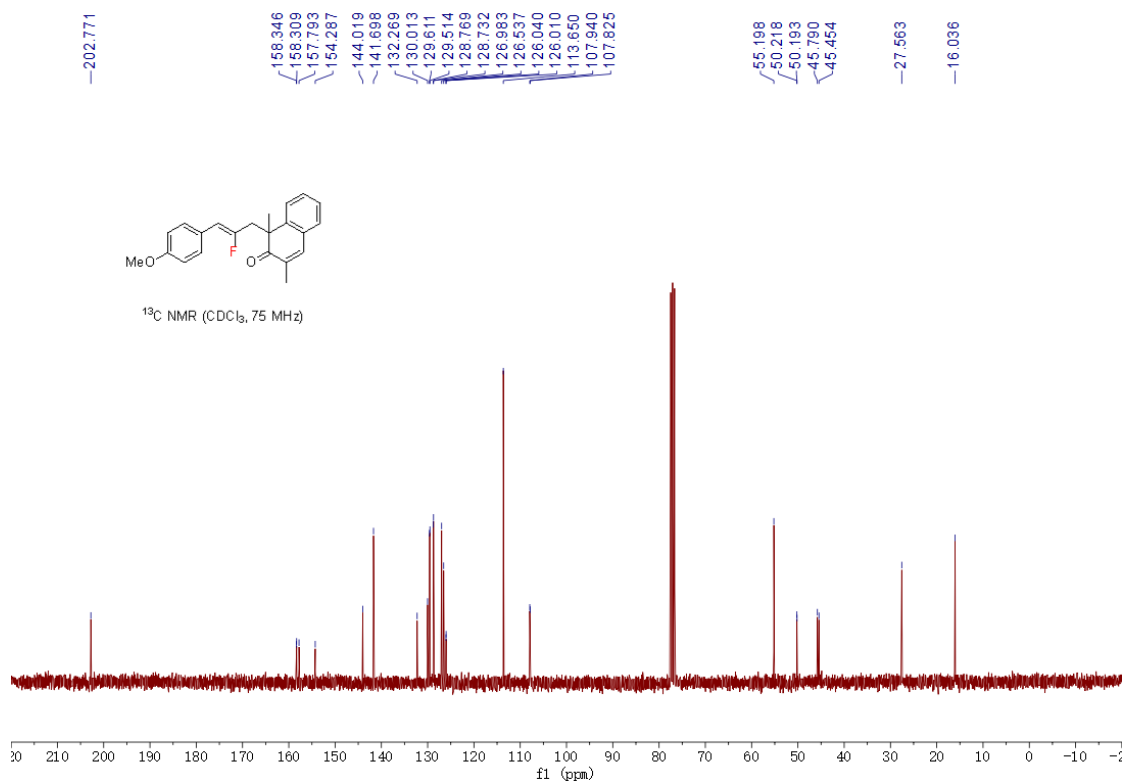
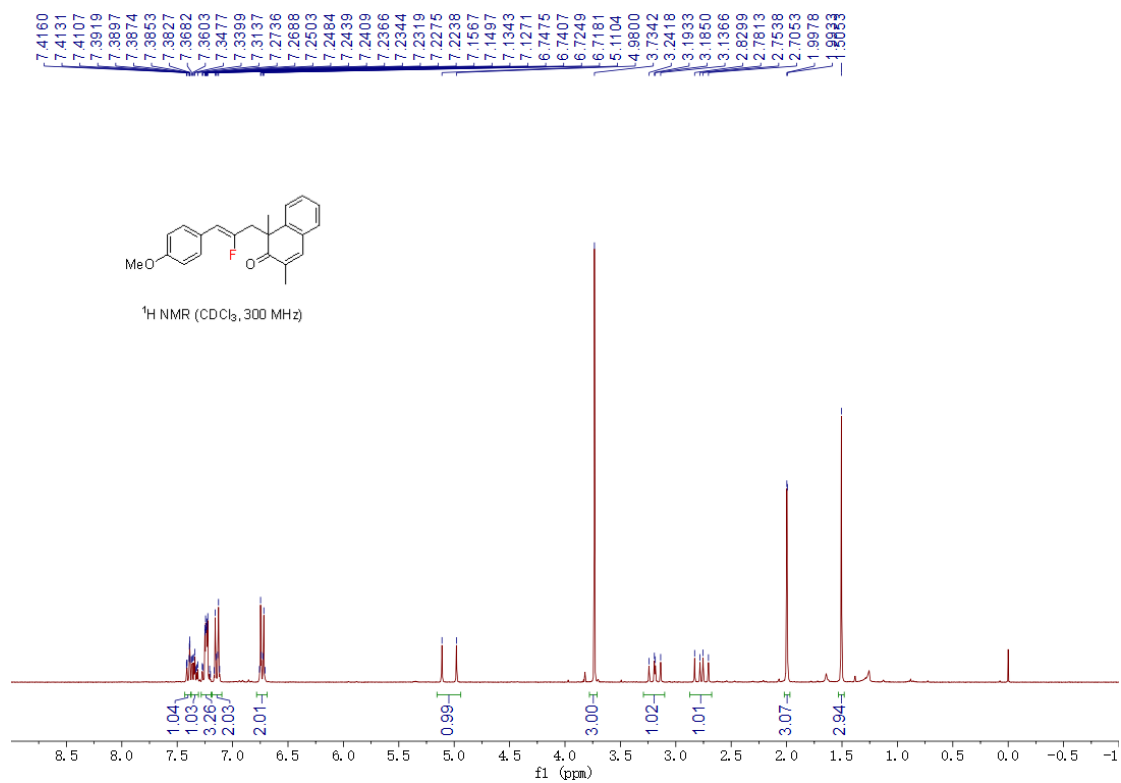


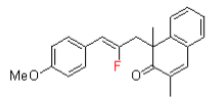
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)



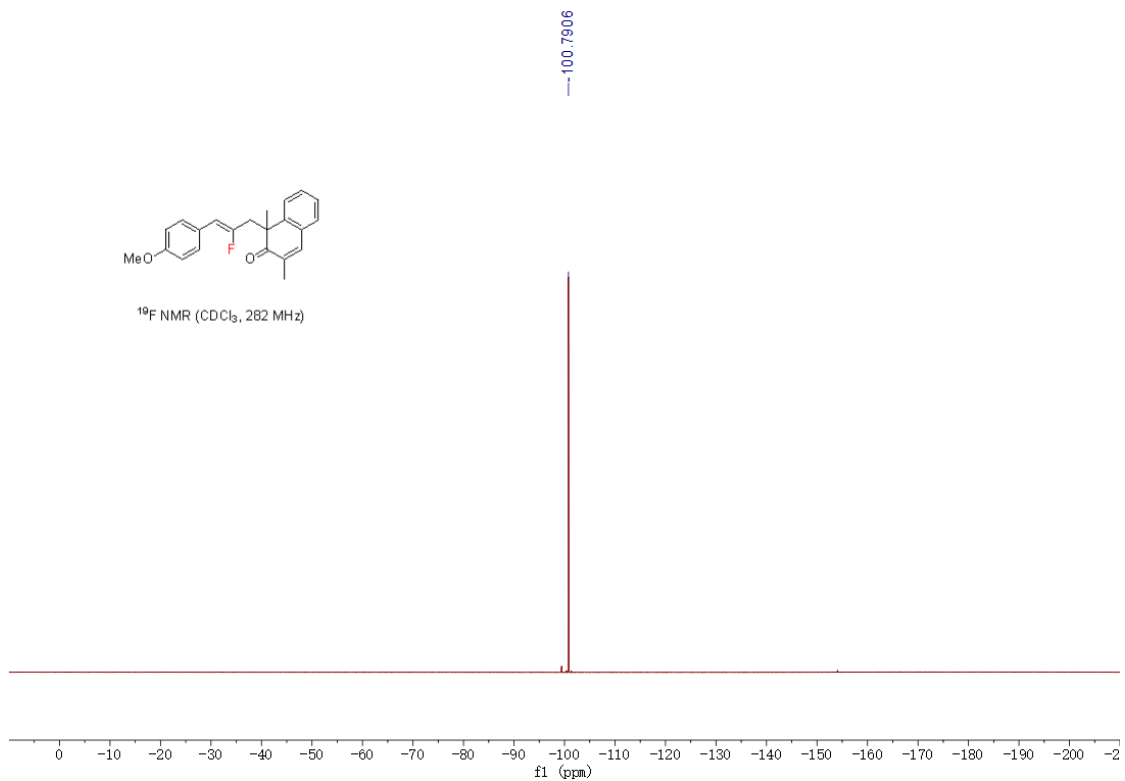




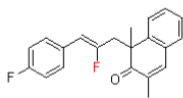




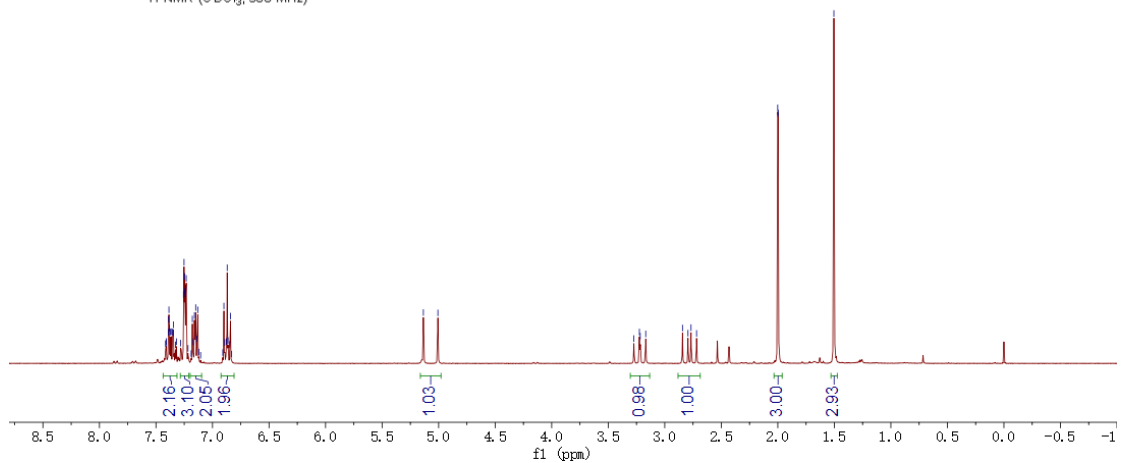
<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)

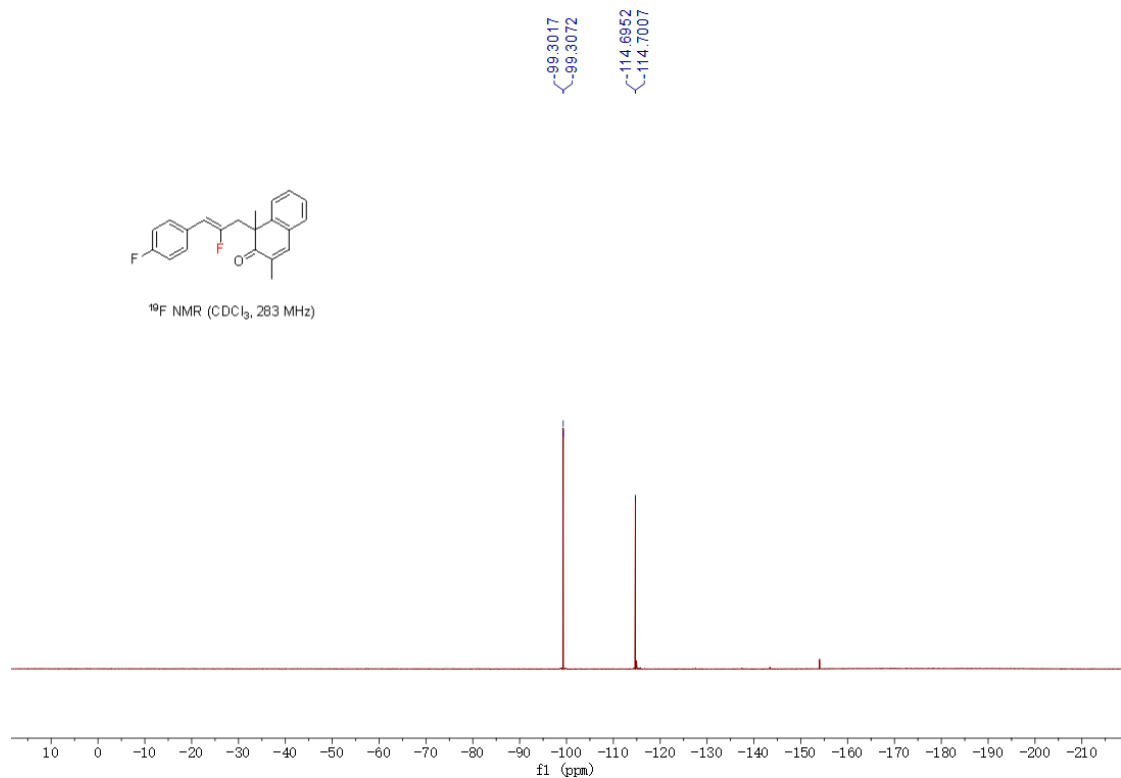
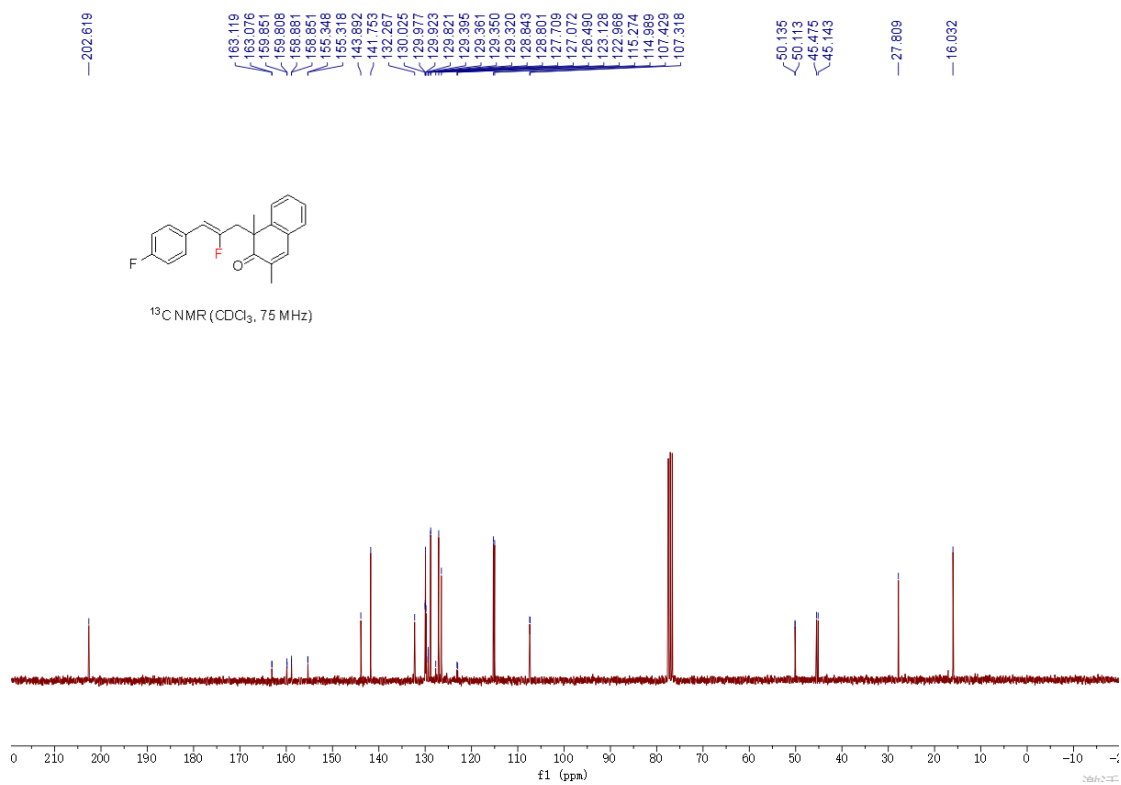


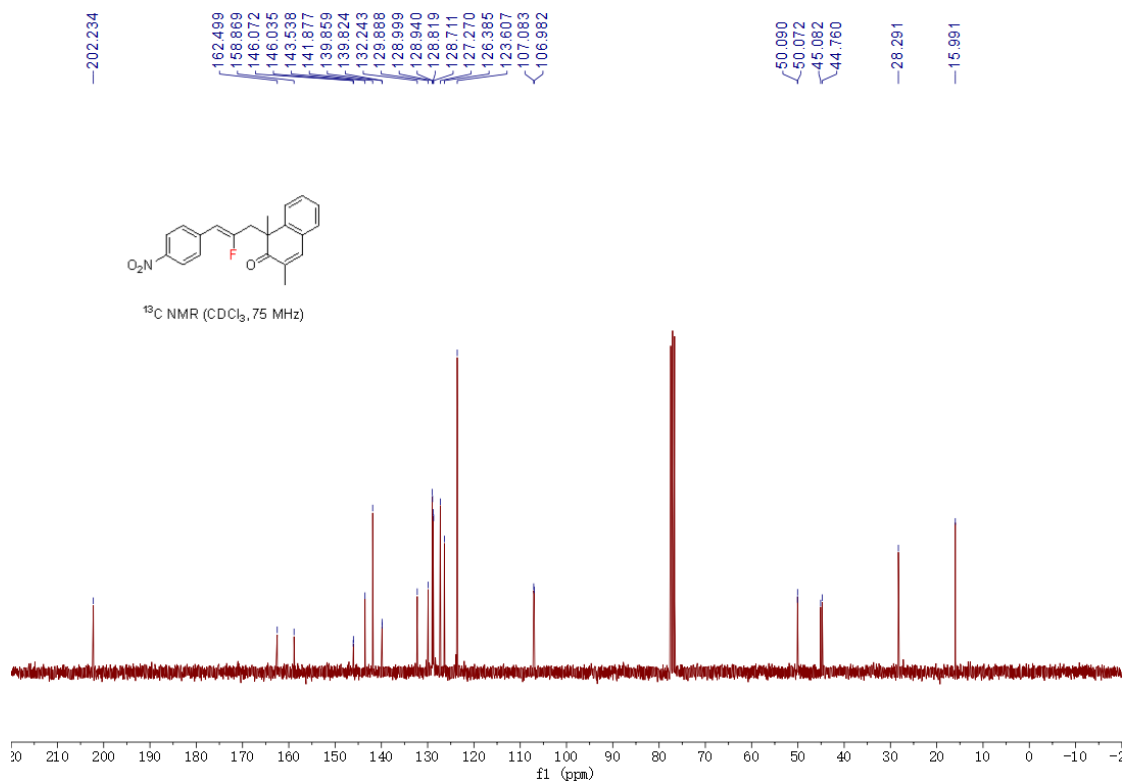
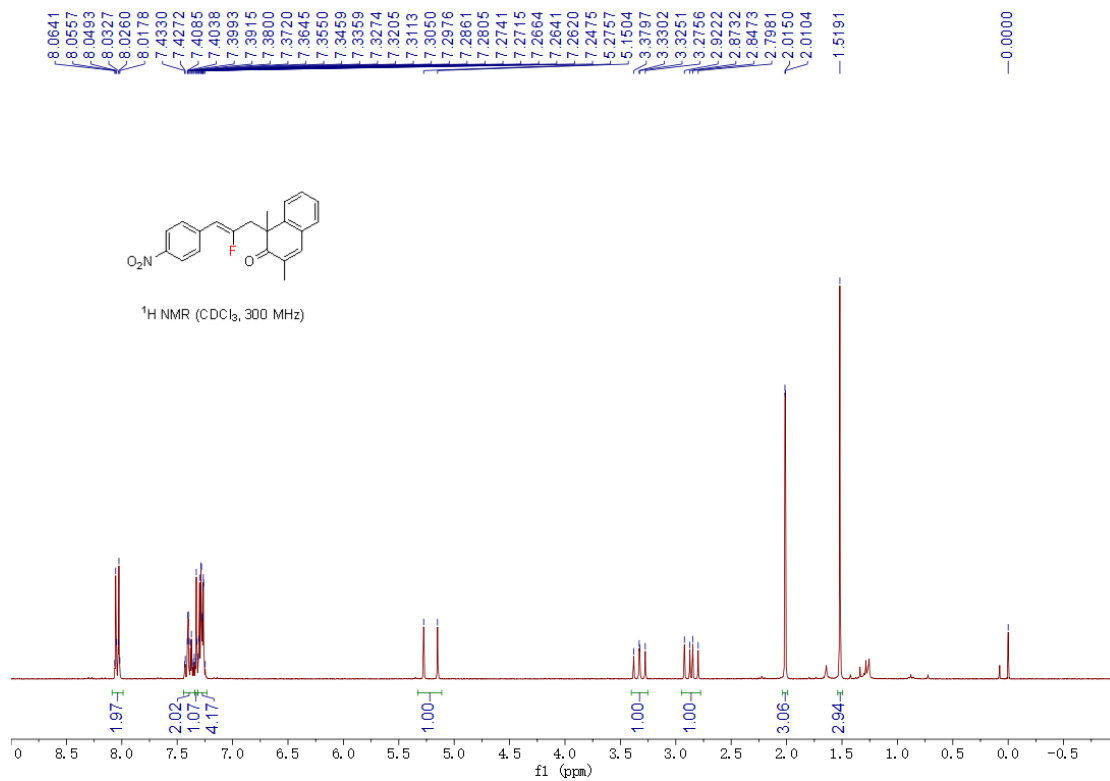
7.4142  
7.4115  
7.4092  
7.3905  
7.3882  
7.3853  
7.3820  
7.3737  
7.3658  
7.3536  
7.3456  
7.3281  
7.3195  
7.2819  
7.2568  
7.2517  
7.2473  
7.2431  
7.2406  
7.2361  
7.2322  
7.2169  
7.1883  
7.1783  
7.1710  
7.1599  
7.1487  
7.1380  
7.1305  
7.1208  
7.1051  
6.9089  
6.8991  
6.8919  
6.8768  
6.8689  
6.8629  
6.8477  
6.8407  
6.8306  
5.1349  
5.0066  
3.2730  
3.2244  
3.2169  
3.1683  
2.8431  
2.7943  
2.7674  
2.7186  
2.0009  
1.9963  
1.5040

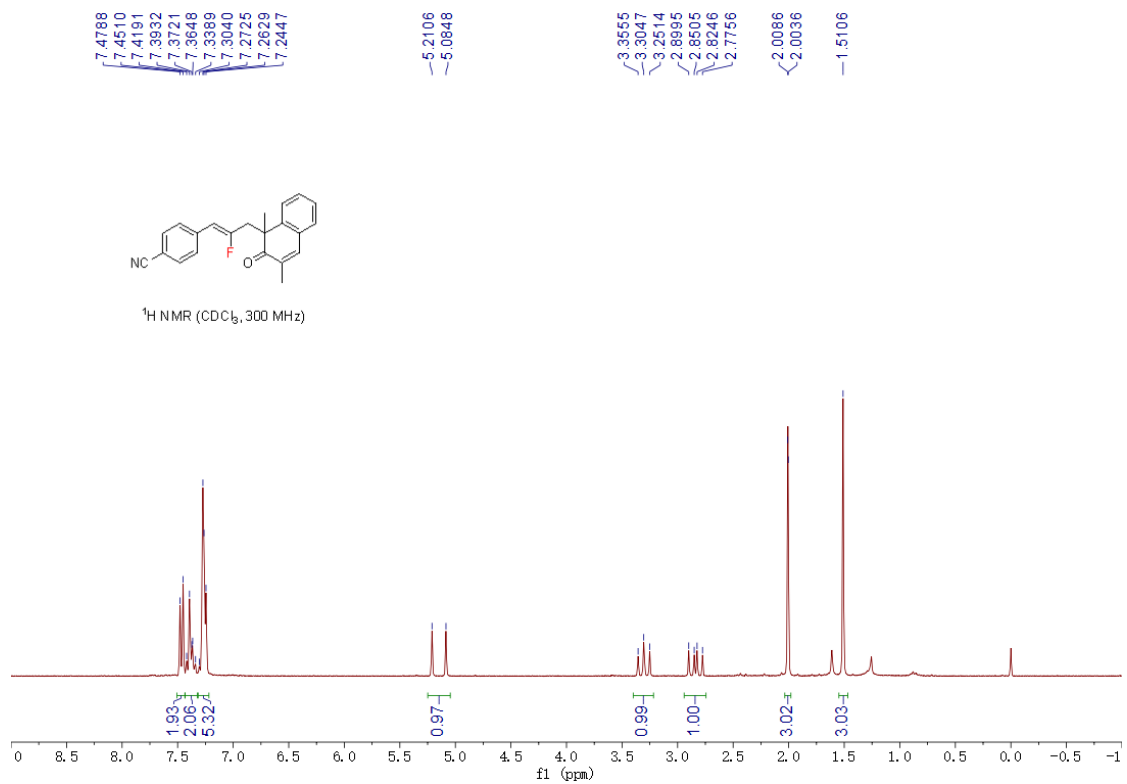
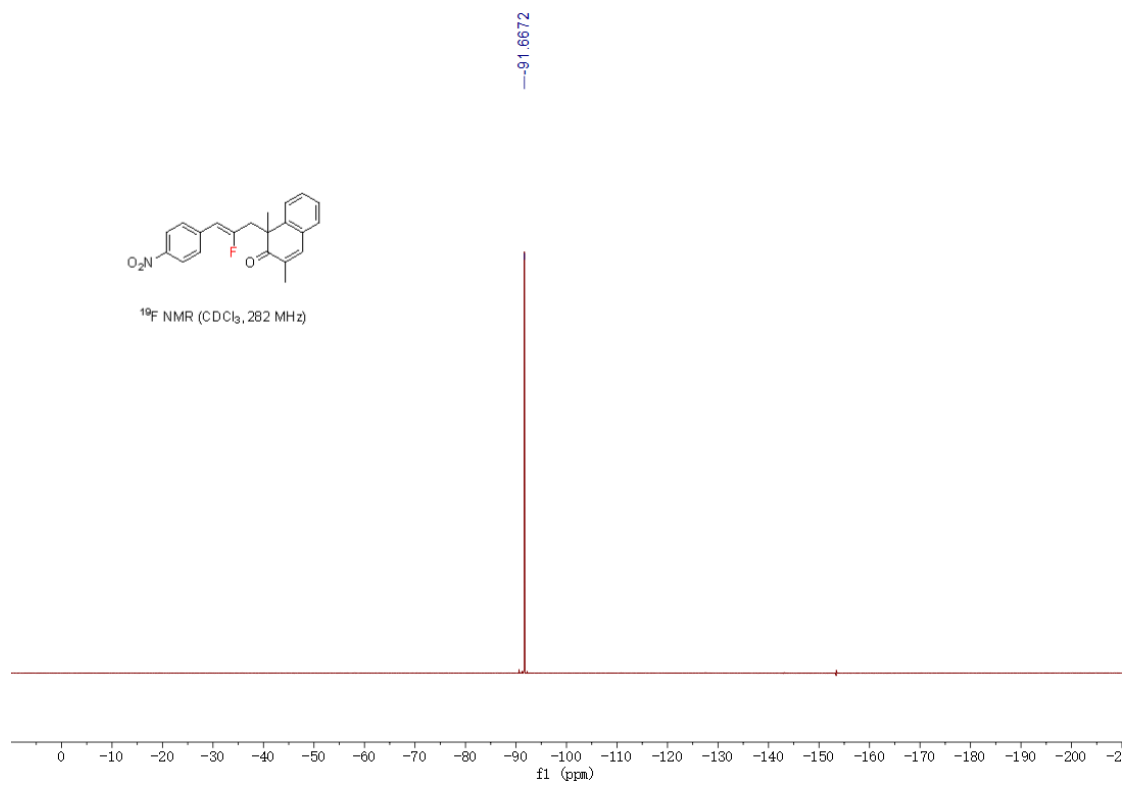


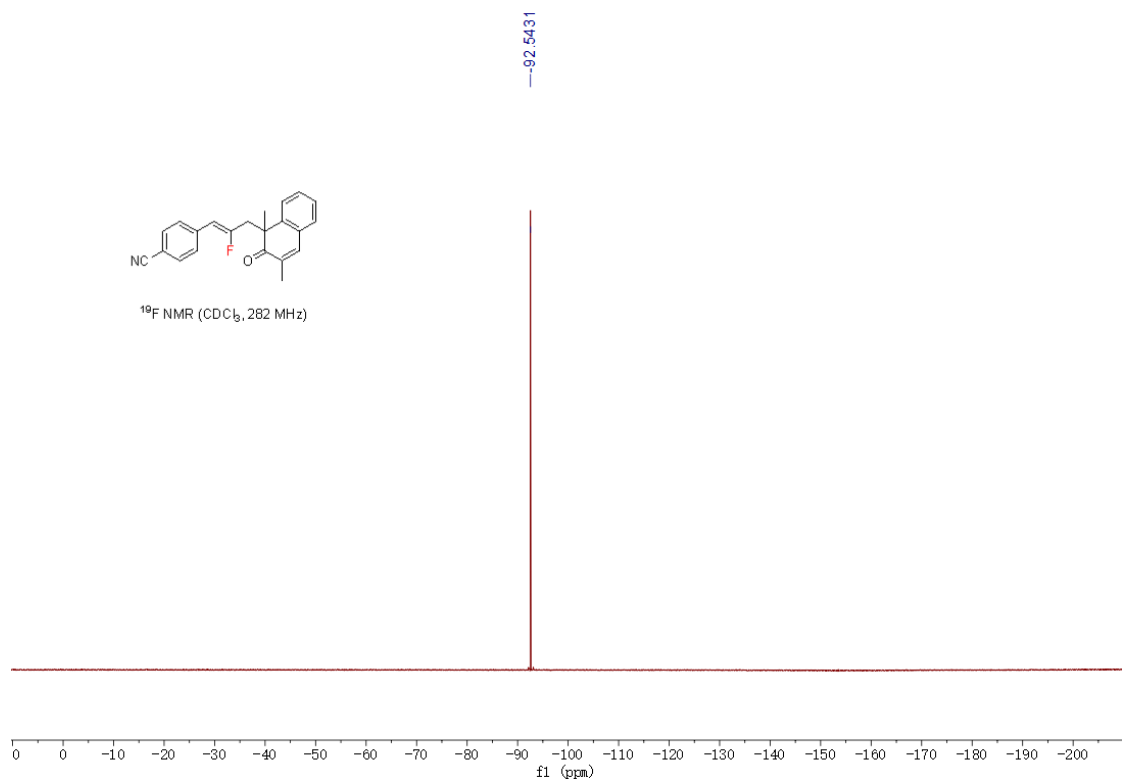
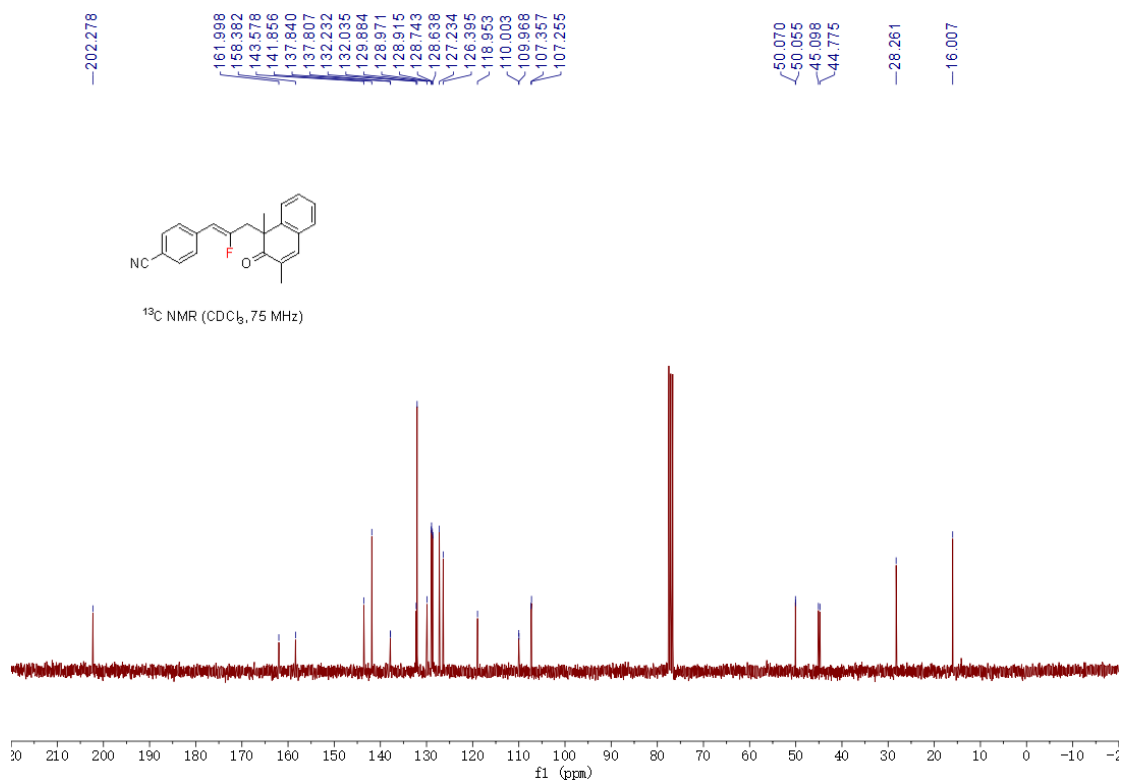
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

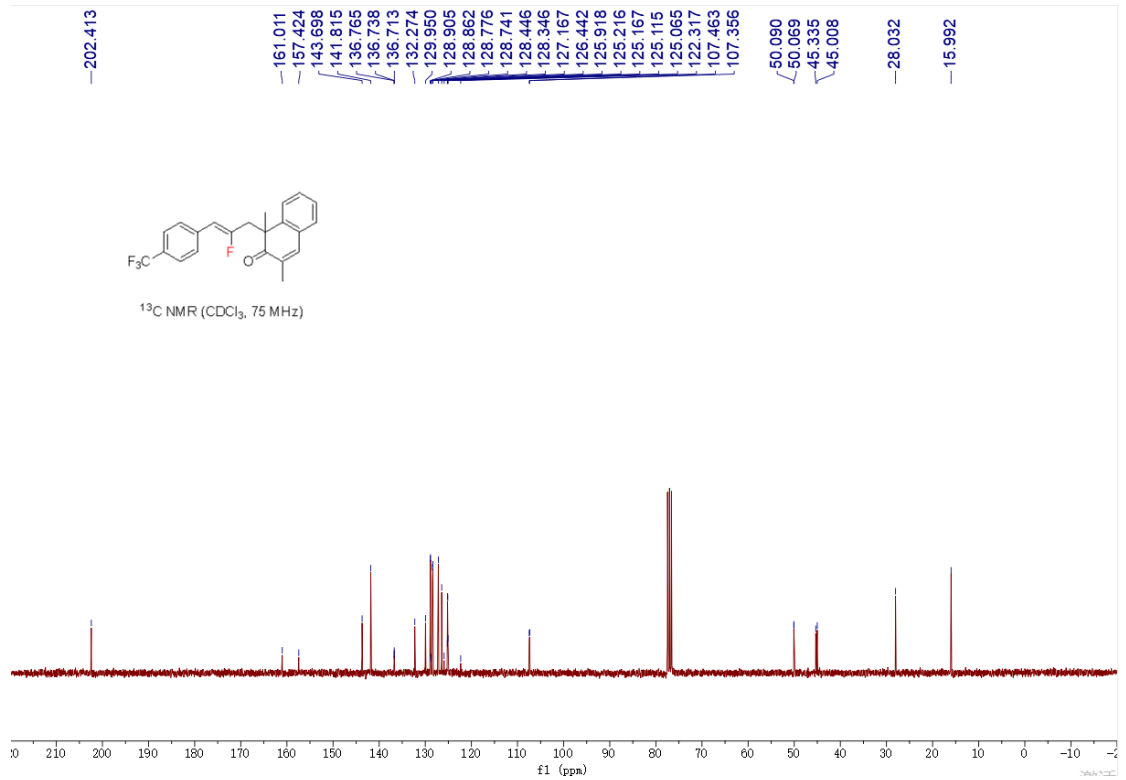
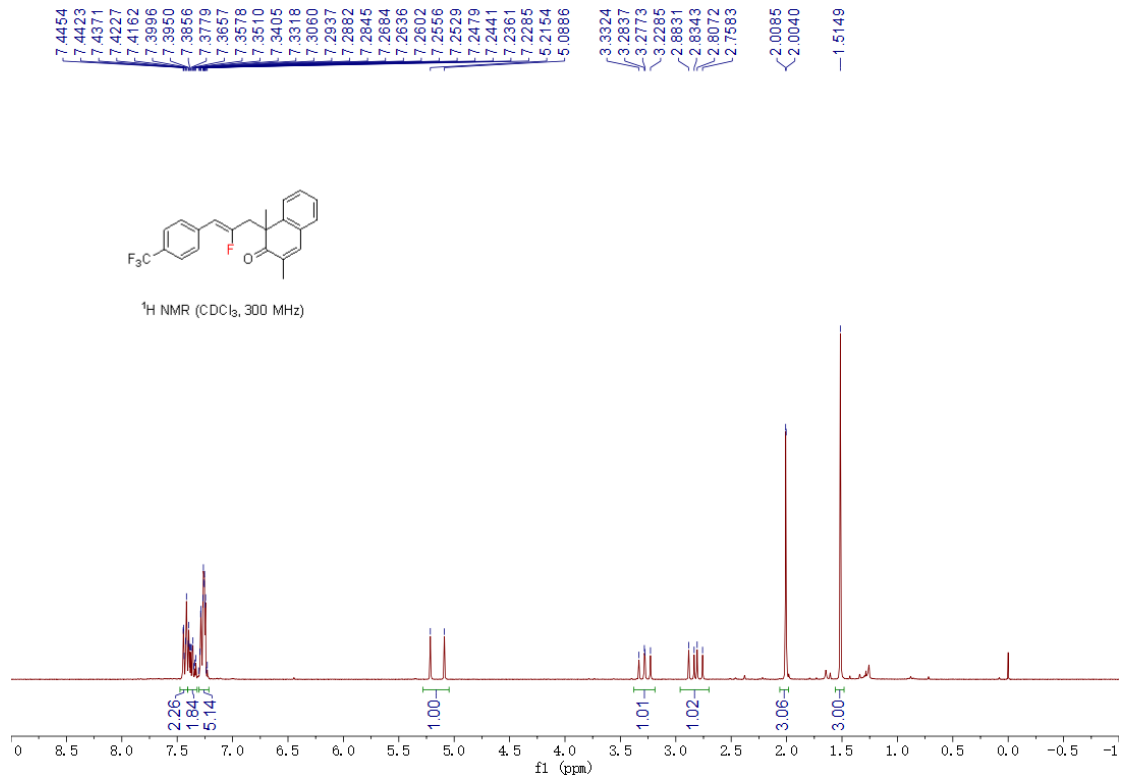


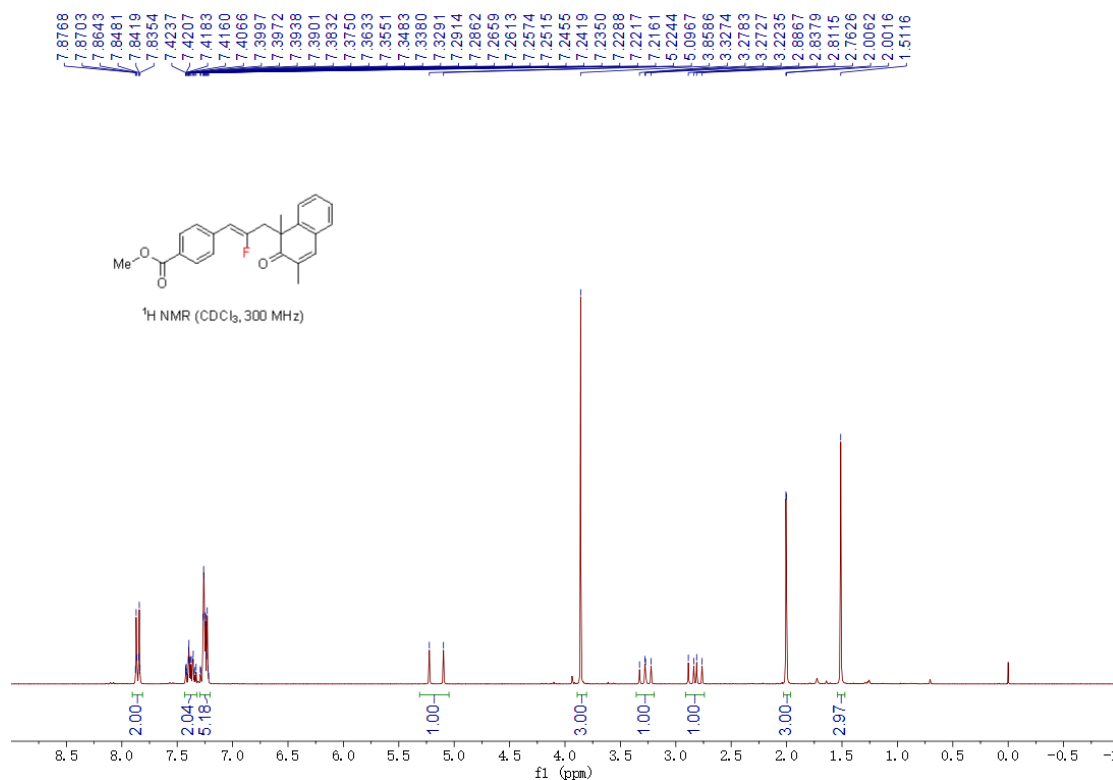
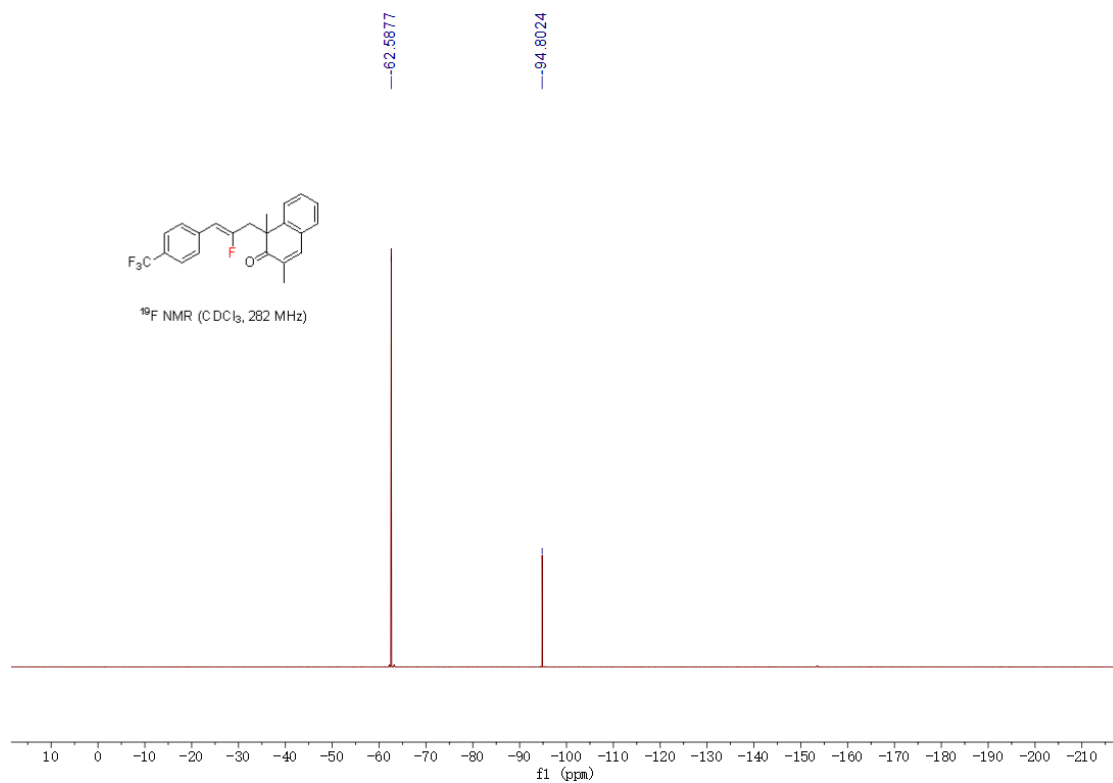




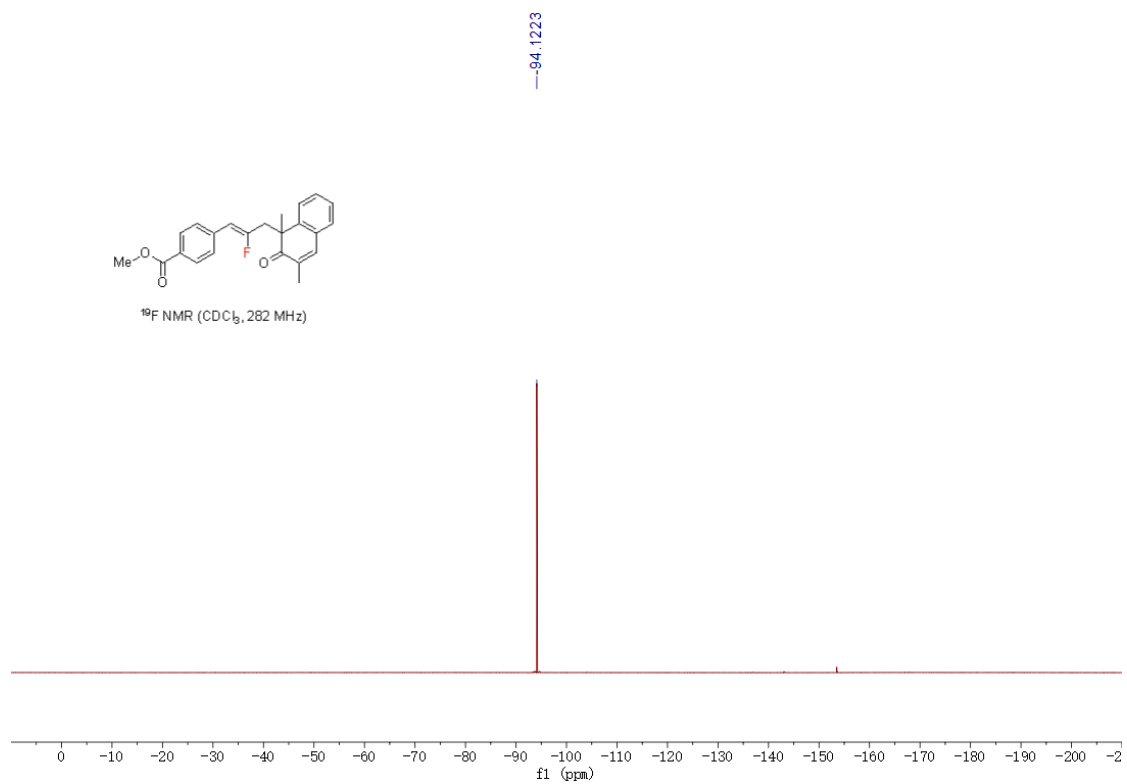
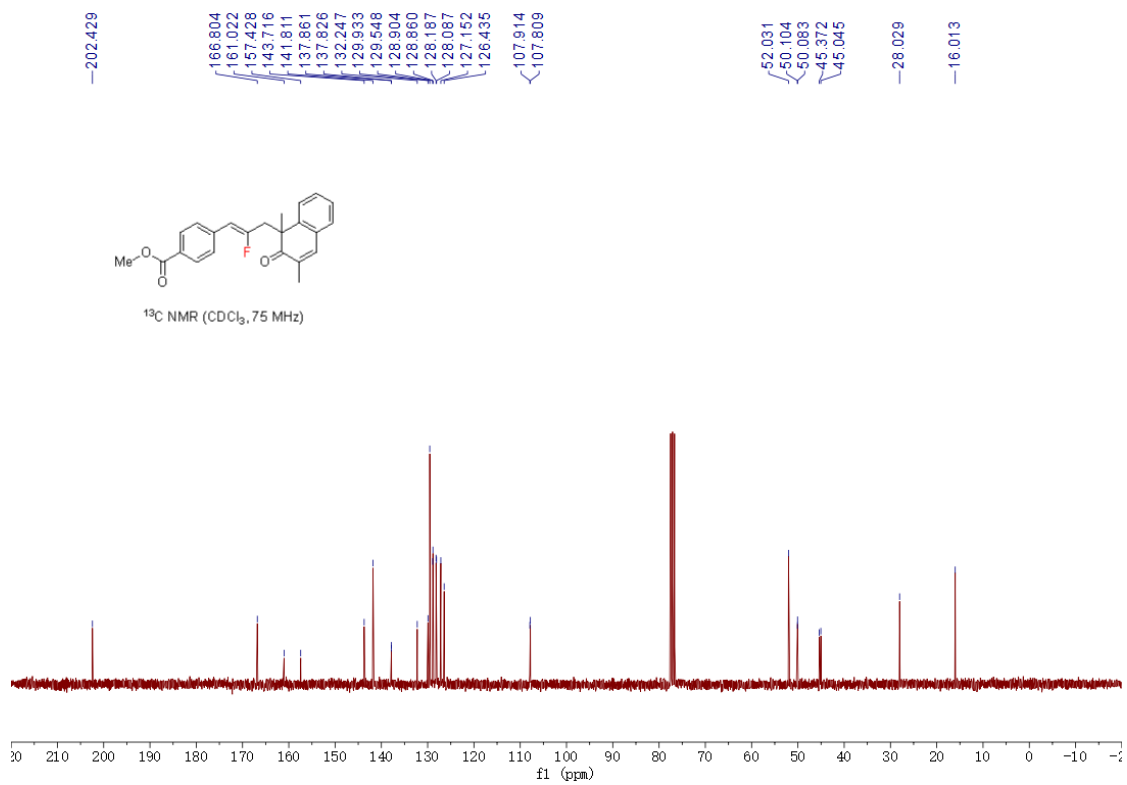


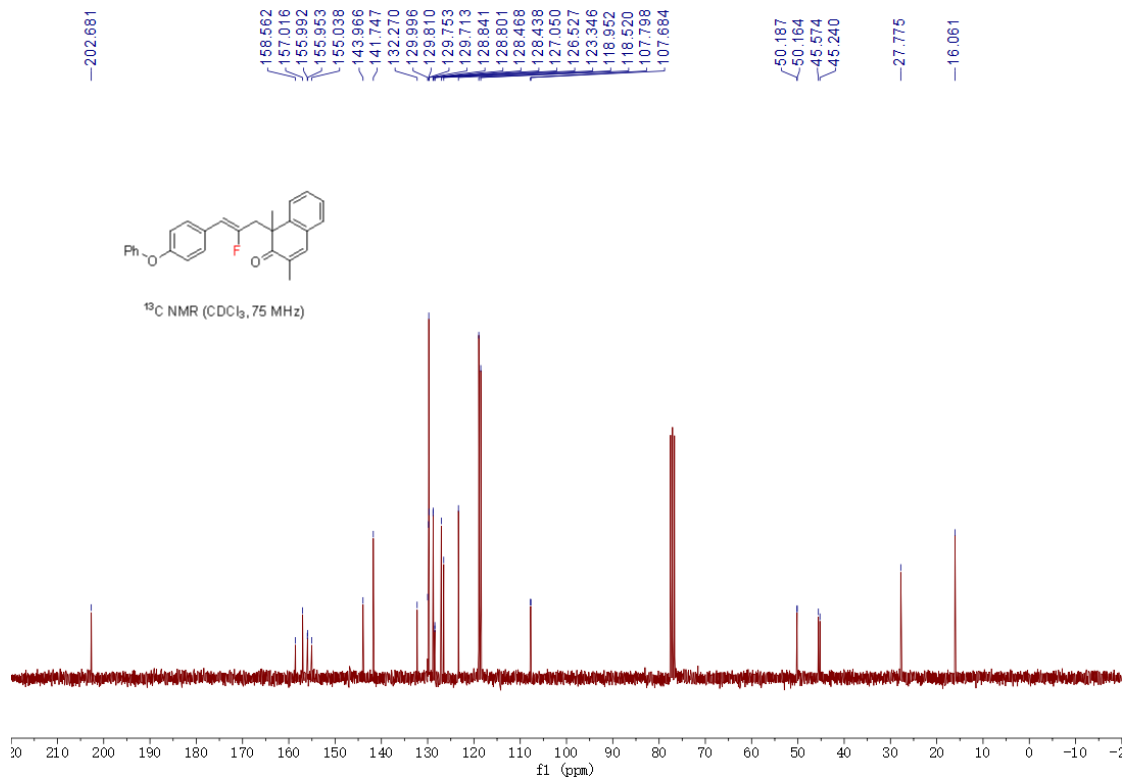
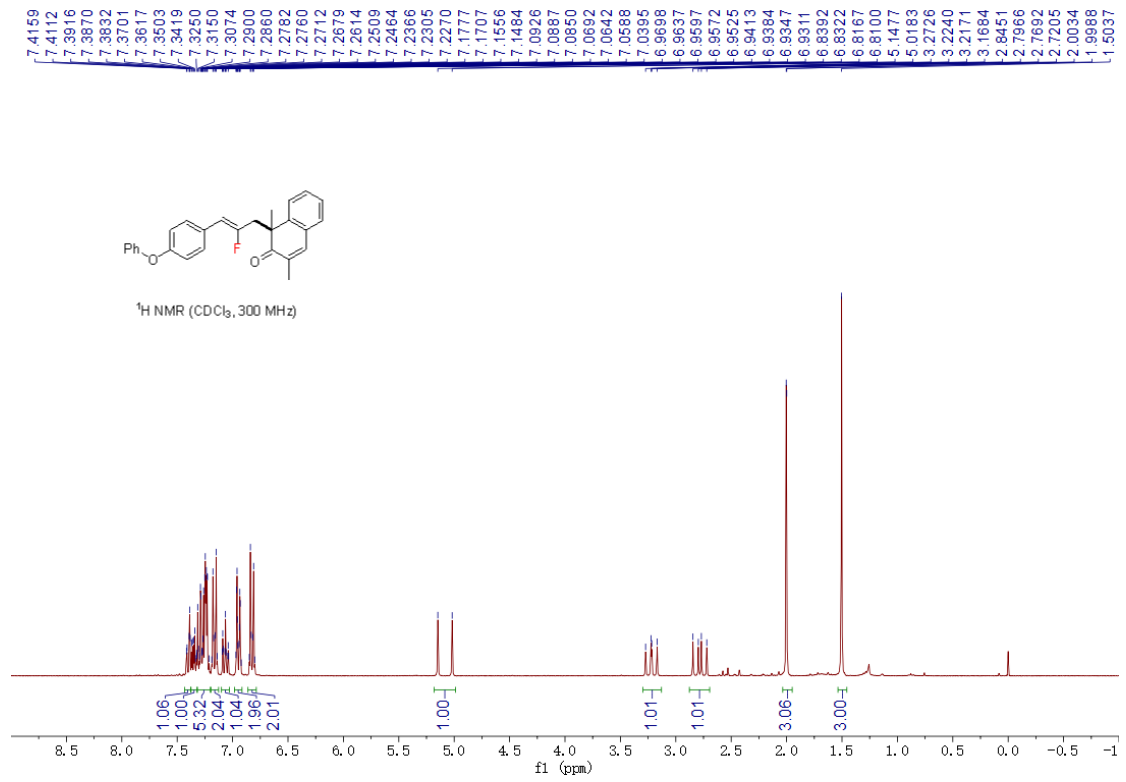


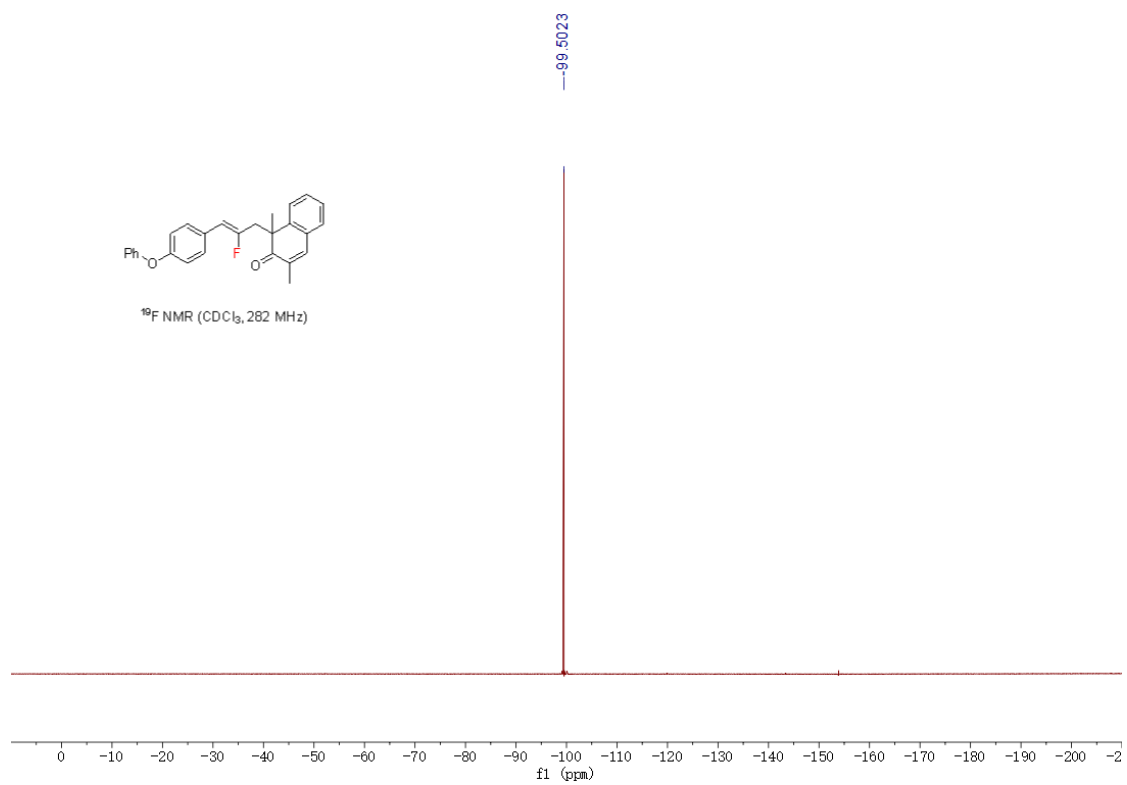




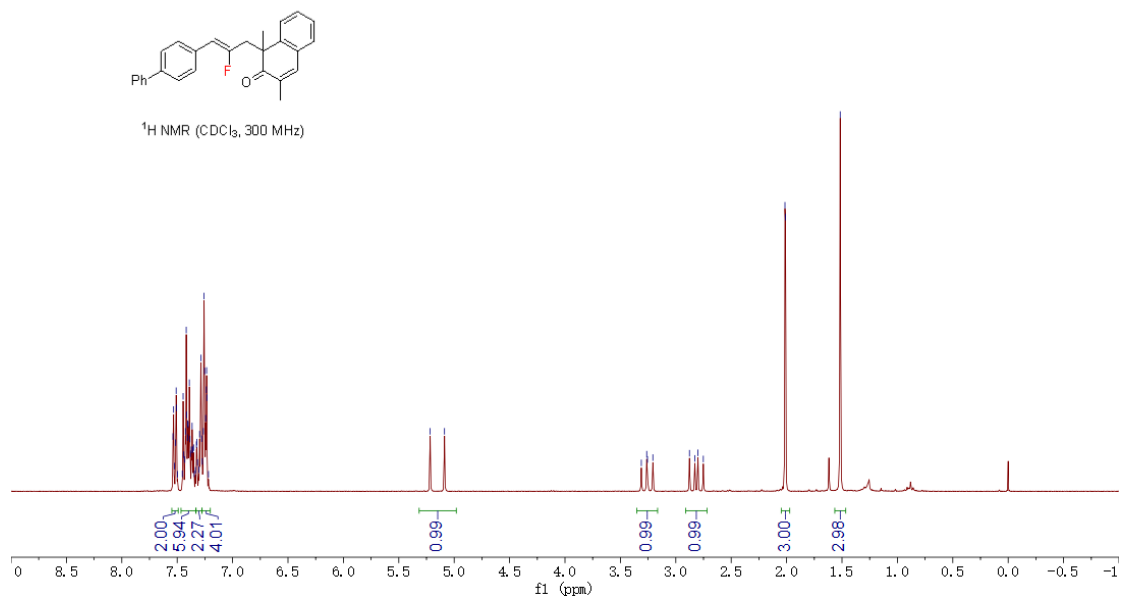


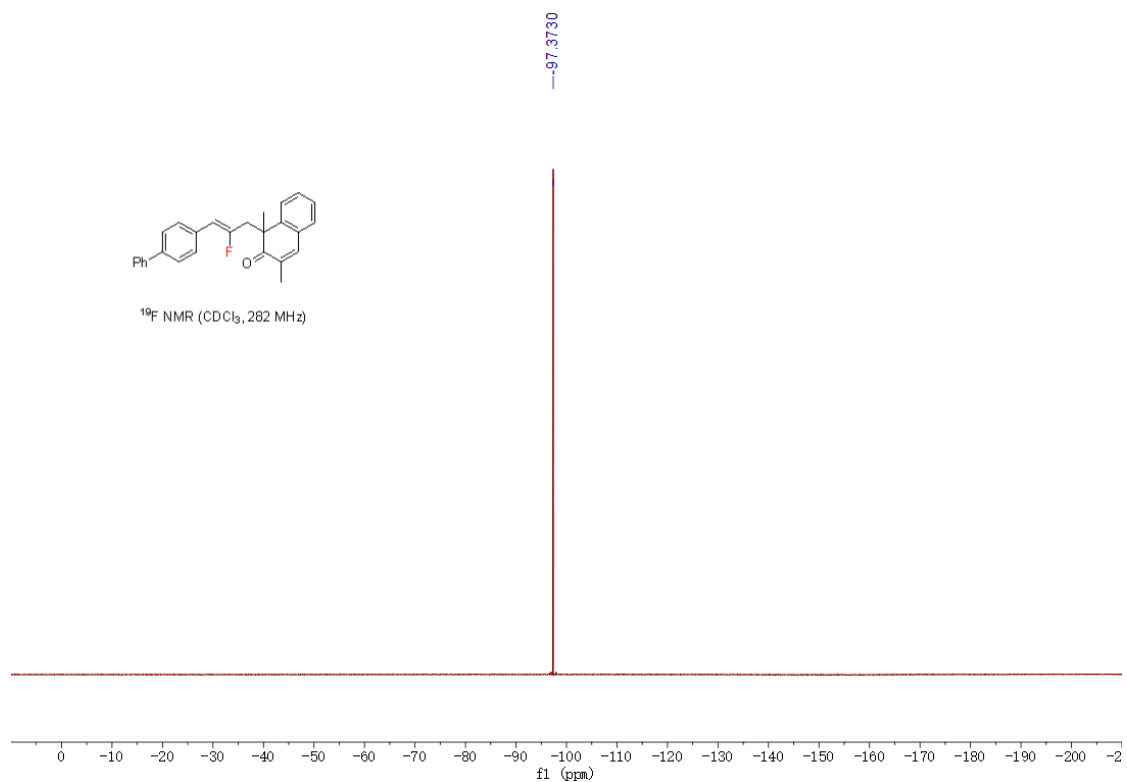
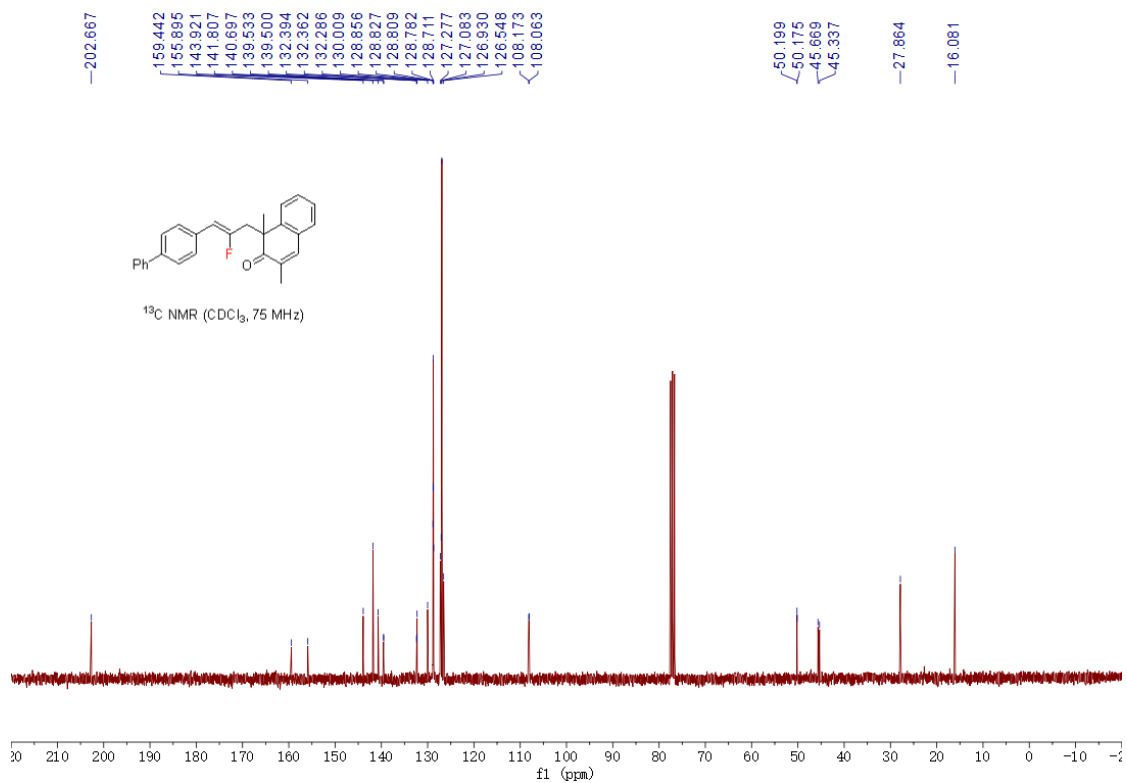




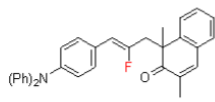


7.5379  
 7.5325  
 7.5258  
 7.5143  
 7.5092  
 7.5055  
 7.4980  
 7.4538  
 7.4465  
 7.4403  
 7.4315  
 7.4255  
 7.4184  
 7.4140  
 7.4076  
 7.4043  
 7.4014  
 7.3803  
 7.3850  
 7.3806  
 7.3725  
 7.3654  
 7.3600  
 7.3522  
 7.3456  
 7.3351  
 7.3263  
 7.3218  
 7.3173  
 7.3053  
 7.2979  
 7.2861  
 7.2786  
 7.2734  
 7.2641  
 7.2578  
 7.2527  
 7.2430  
 7.2367  
 7.2346  
 7.2325  
 7.2179  
 5.2170  
 5.0875  
 3.3111  
 3.2624  
 3.2555  
 3.2071  
 2.8766  
 2.8280  
 2.8003  
 2.7517  
 2.0147  
 2.0102  
 1.5160

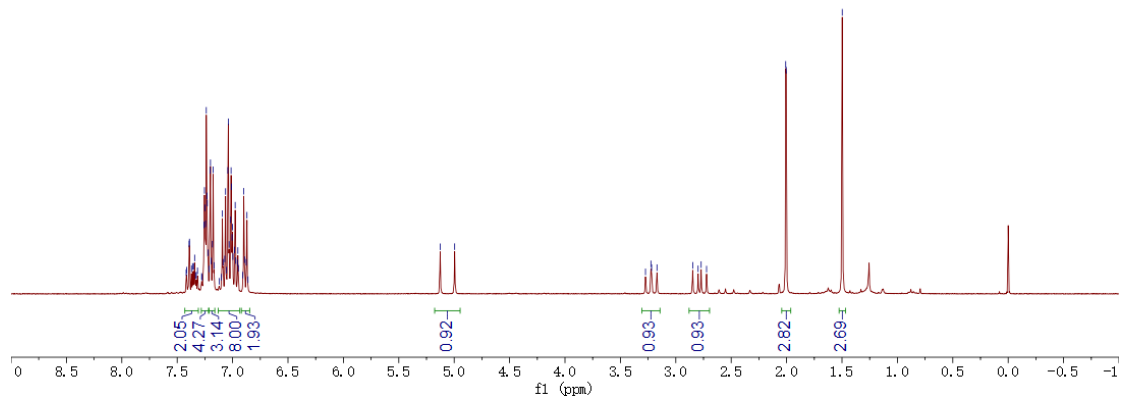




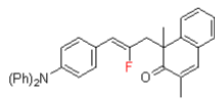
7.4188  
7.4144  
7.3921  
7.3892  
7.3709  
7.3614  
7.3523  
7.3426  
7.3165  
7.2579  
7.2538  
7.2486  
7.2437  
7.2374  
7.2319  
7.2279  
7.2211  
7.2118  
7.2041  
7.1996  
7.1931  
7.1822  
7.1756  
7.1681  
7.0927  
7.0860  
7.0706  
7.0637  
7.0548  
7.0428  
7.0383  
7.0315  
7.0172  
7.0137  
7.0100  
7.0047  
7.0009  
6.9967  
6.9920  
6.9765  
6.9714  
6.9563  
6.9523  
6.9484  
6.8993  
6.8924  
6.8767  
6.8704  
5.1263  
4.9858  
3.2735  
3.2246  
3.2183  
3.1698  
2.8473  
2.7986  
2.7712  
2.7224  
2.0079  
2.0034  
1.4978



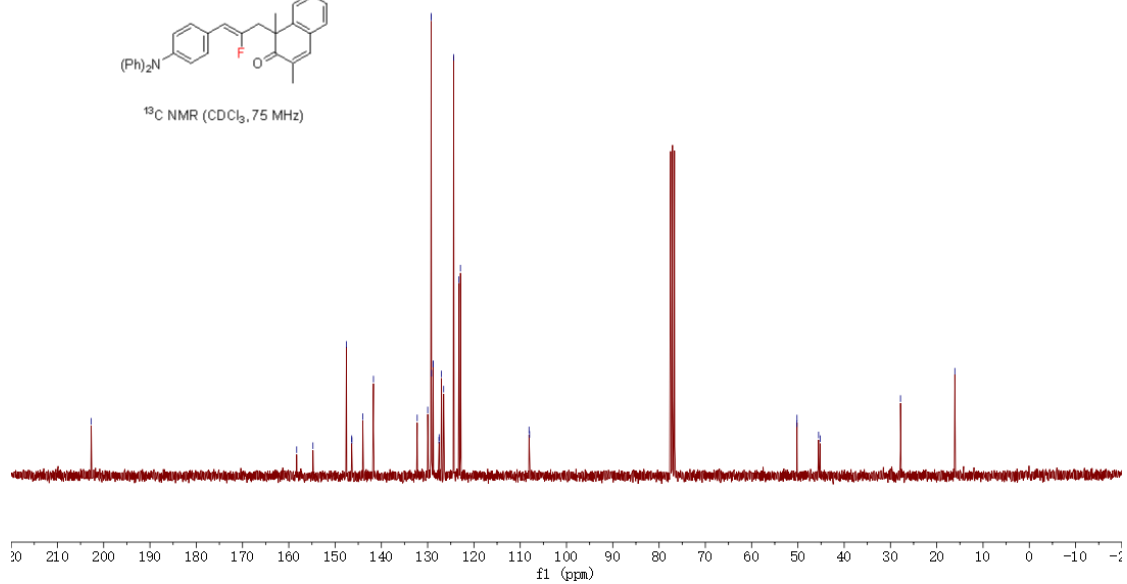
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

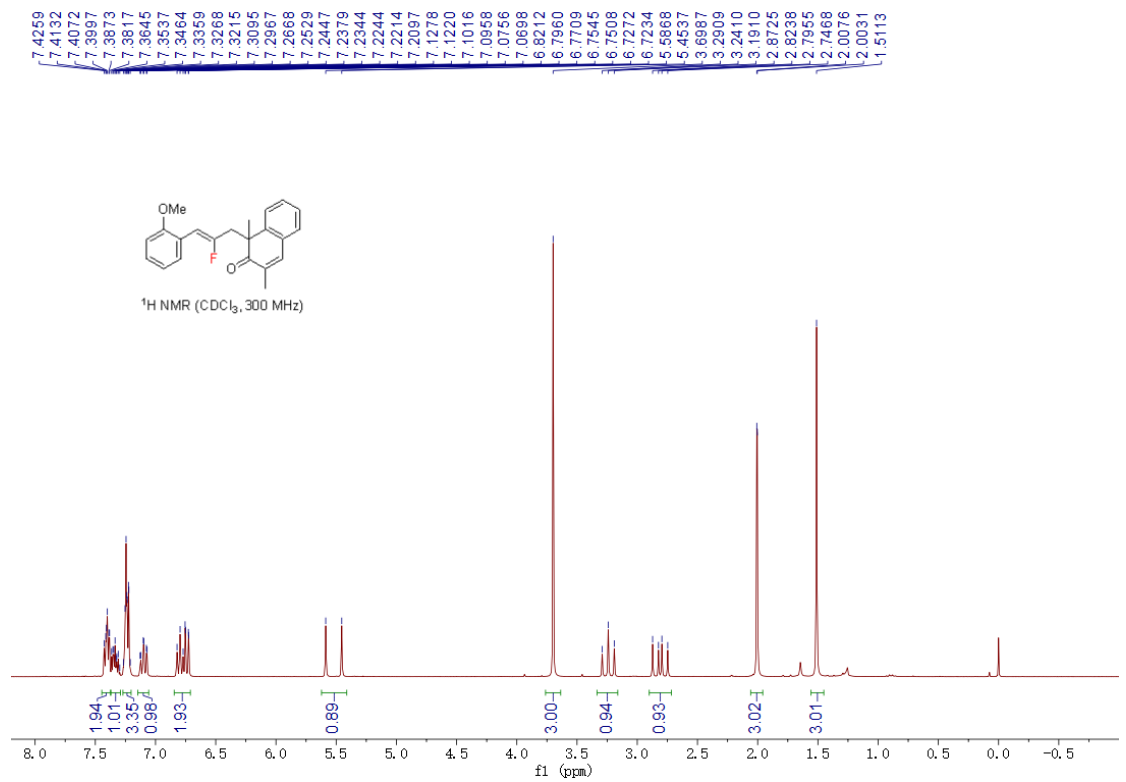
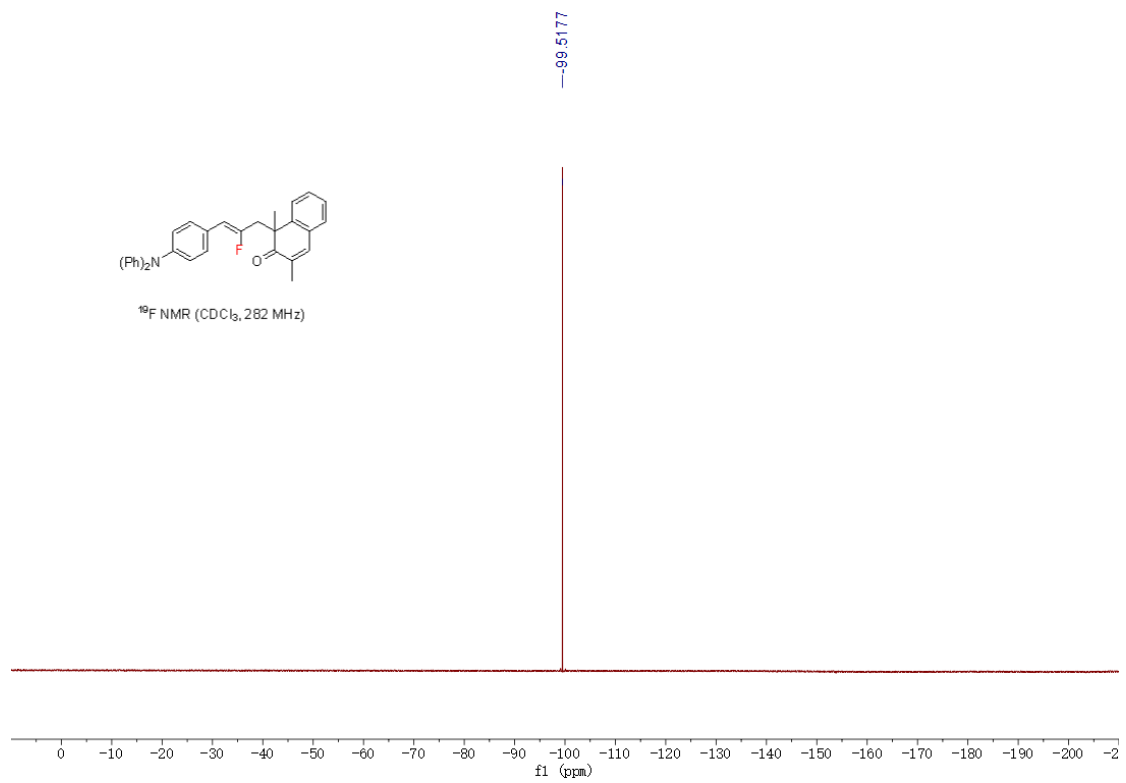


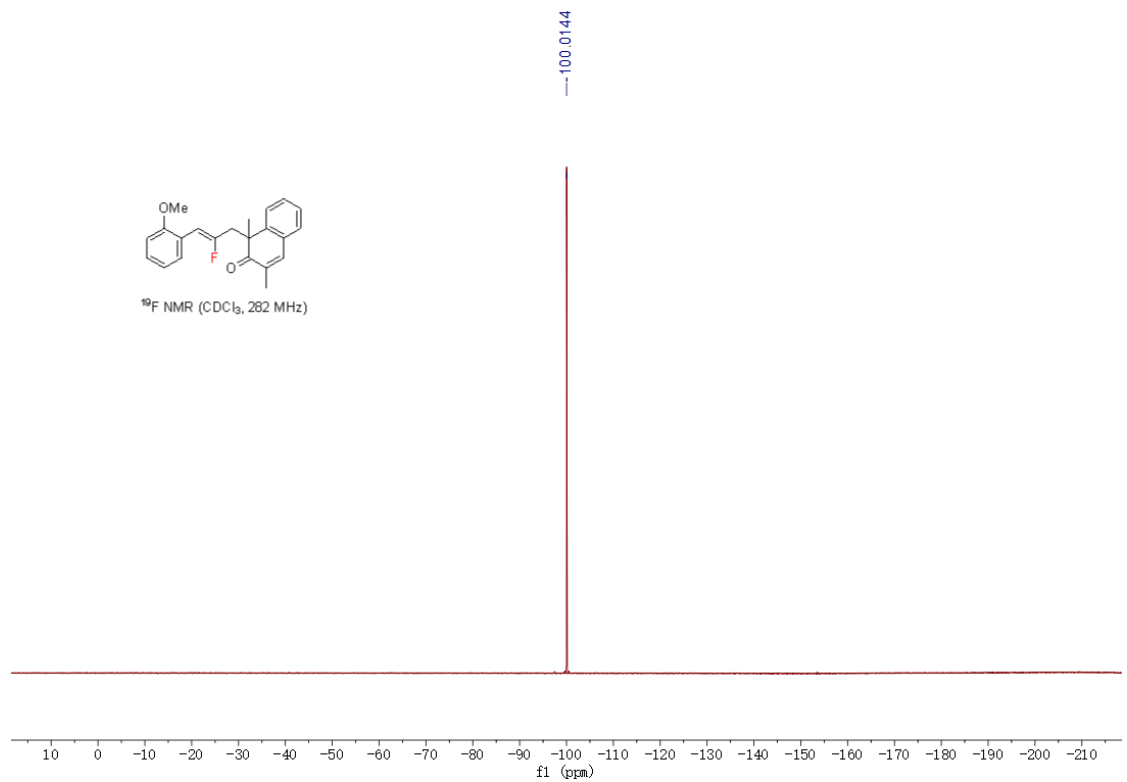
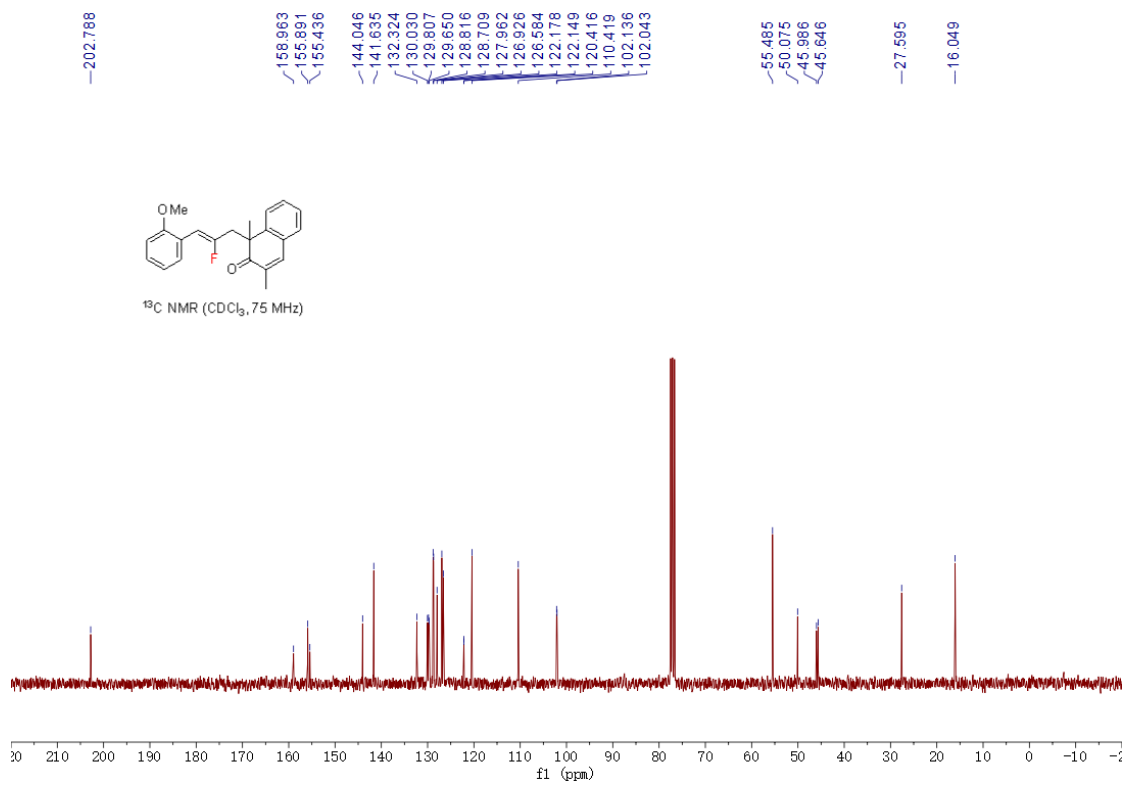
202.693  
158.288  
154.778  
147.547  
146.405  
146.369  
144.017  
141.709  
132.254  
129.984  
129.244  
129.169  
128.834  
128.797  
127.551  
127.516  
127.021  
126.537  
124.381  
123.237  
122.915  
108.099  
107.984  
50.215  
50.195  
45.533  
45.196  
27.835  
16.094

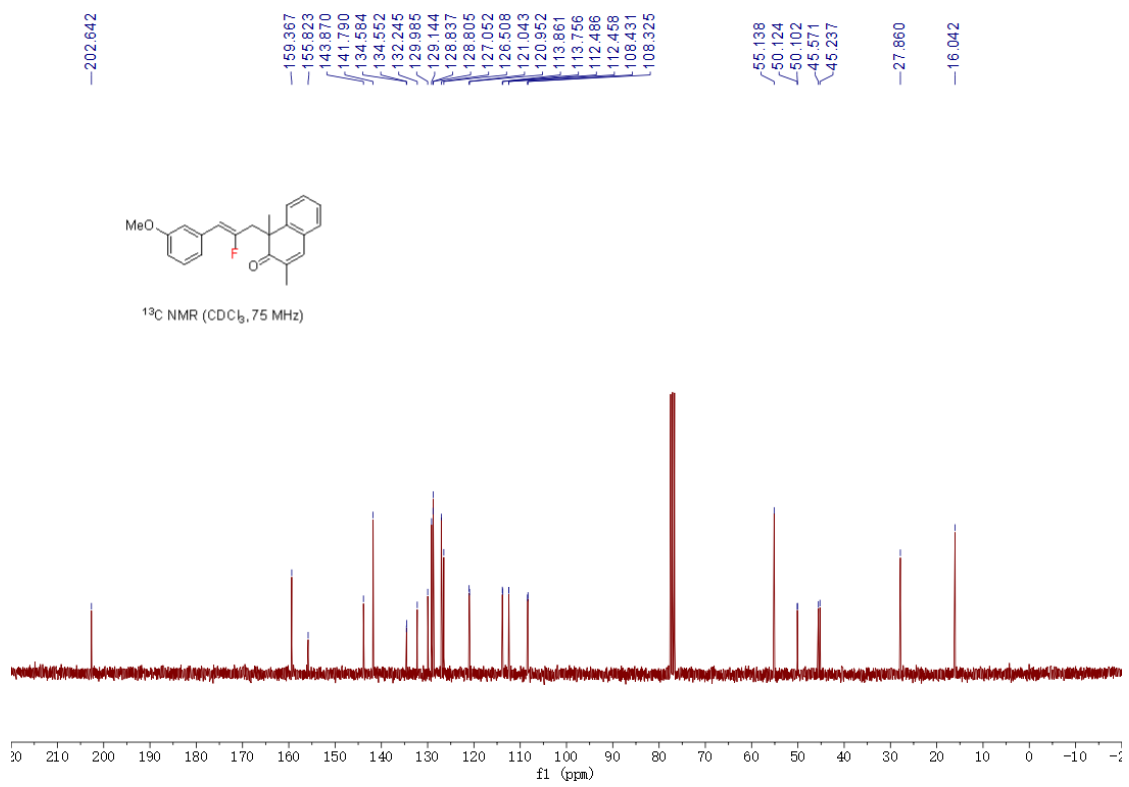
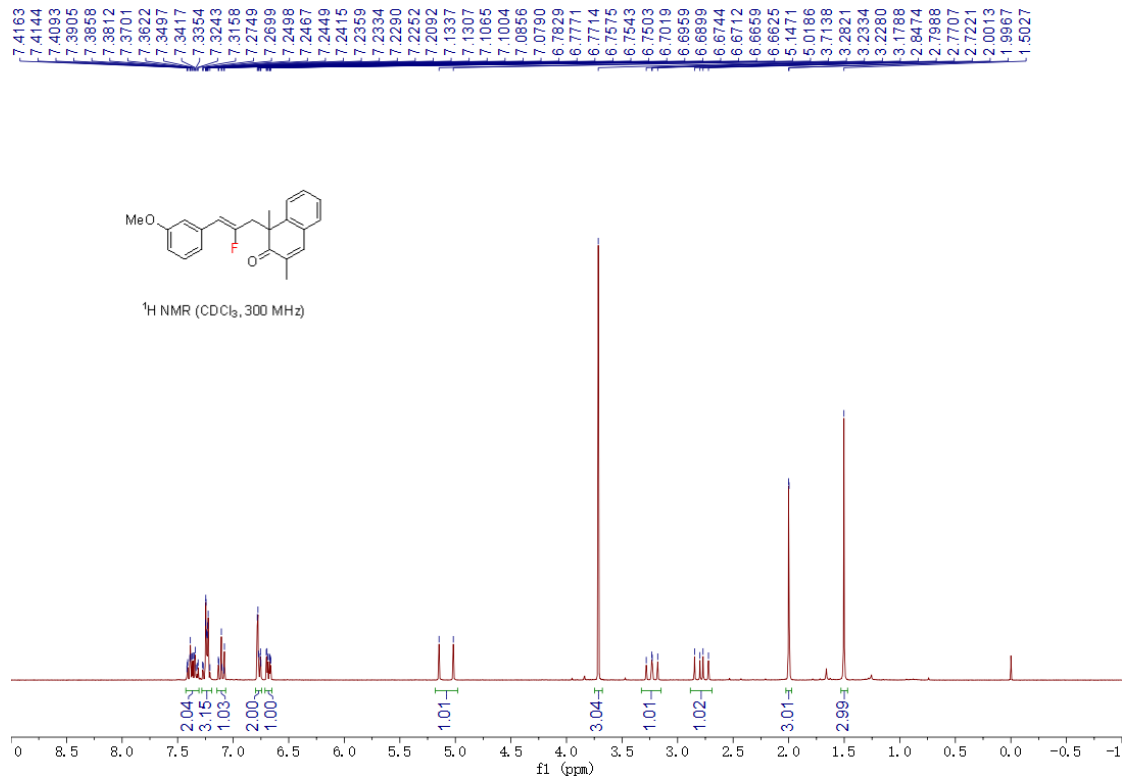


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

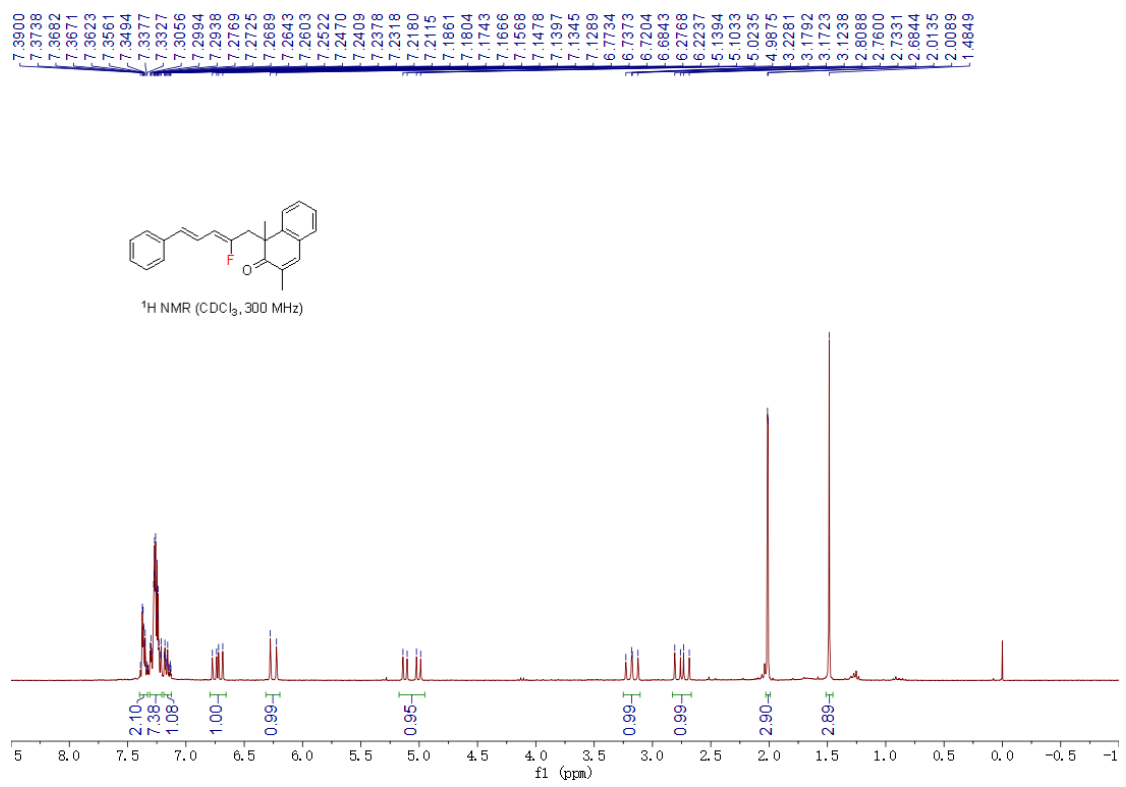
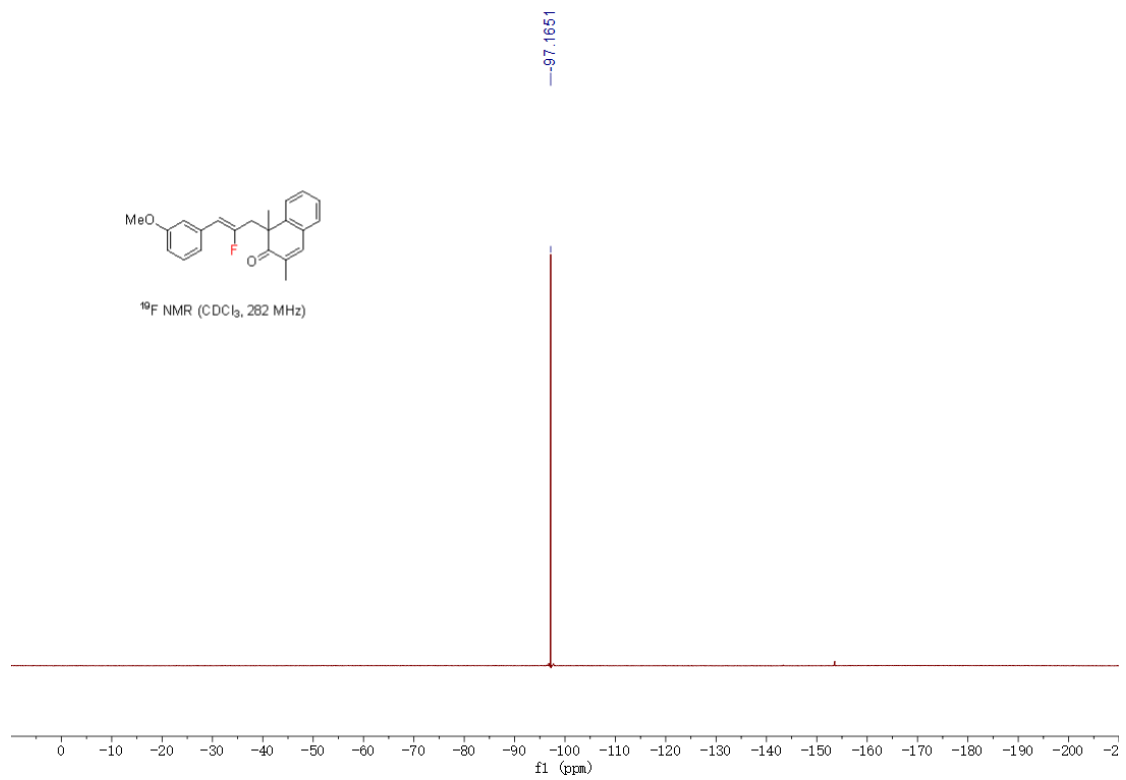


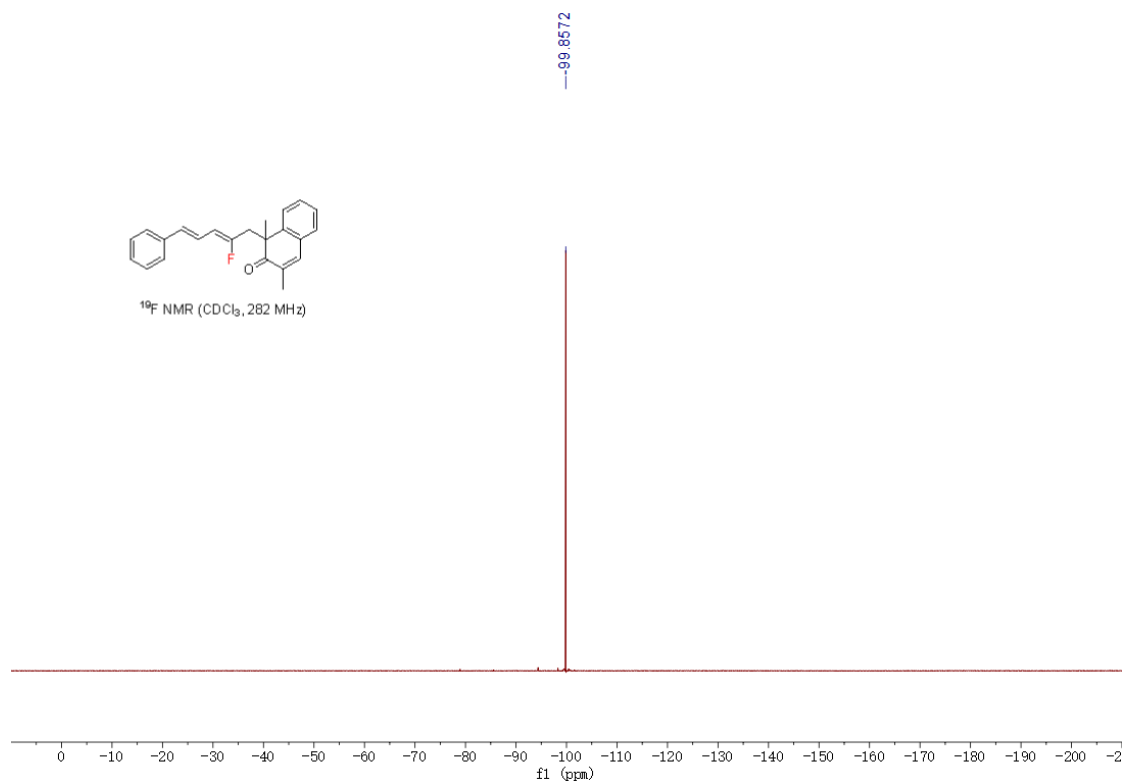
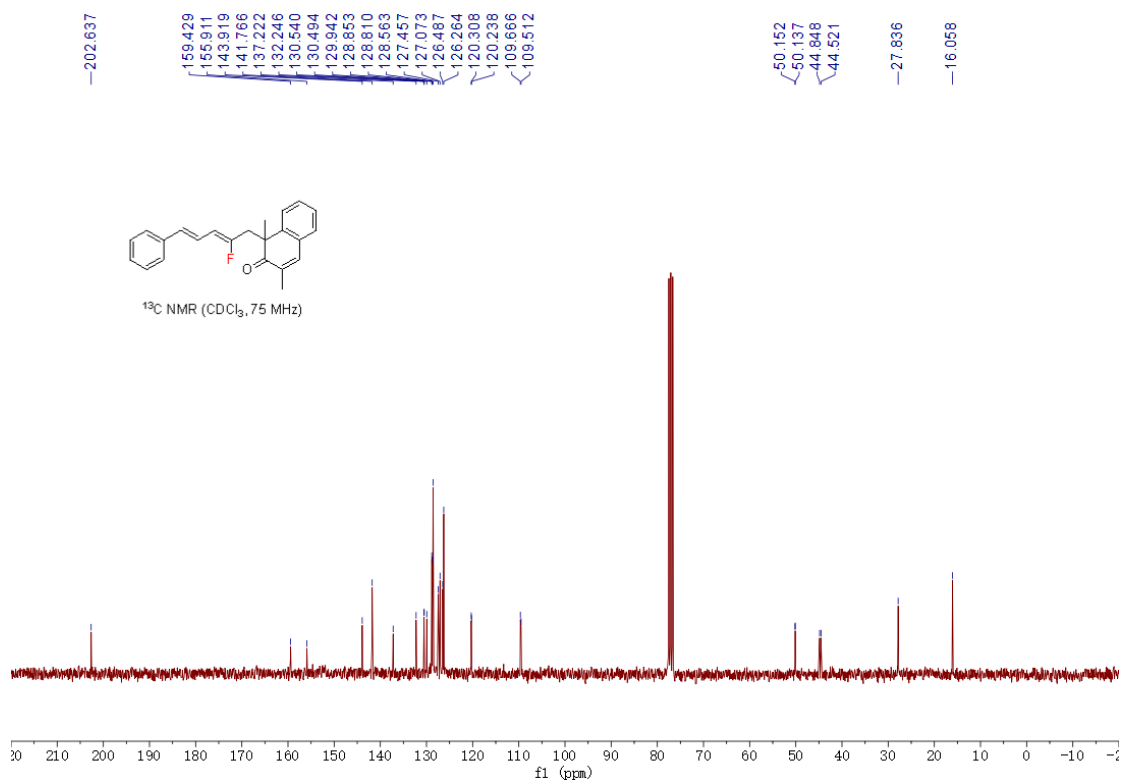


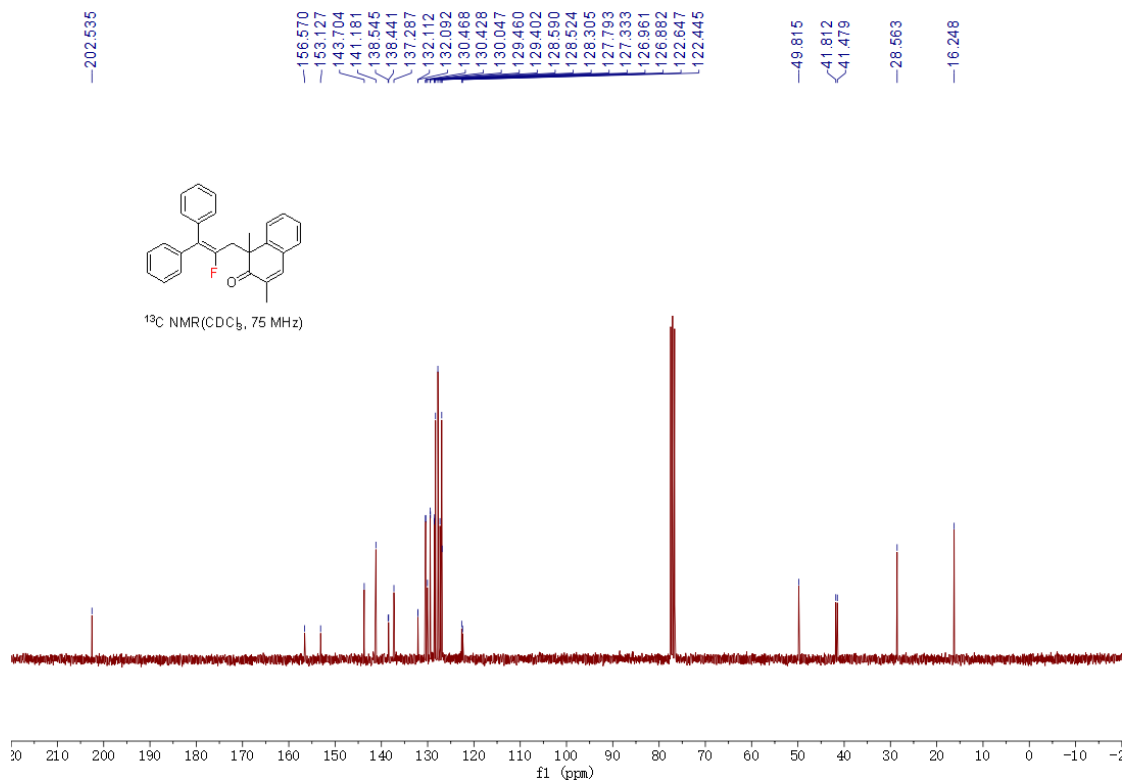
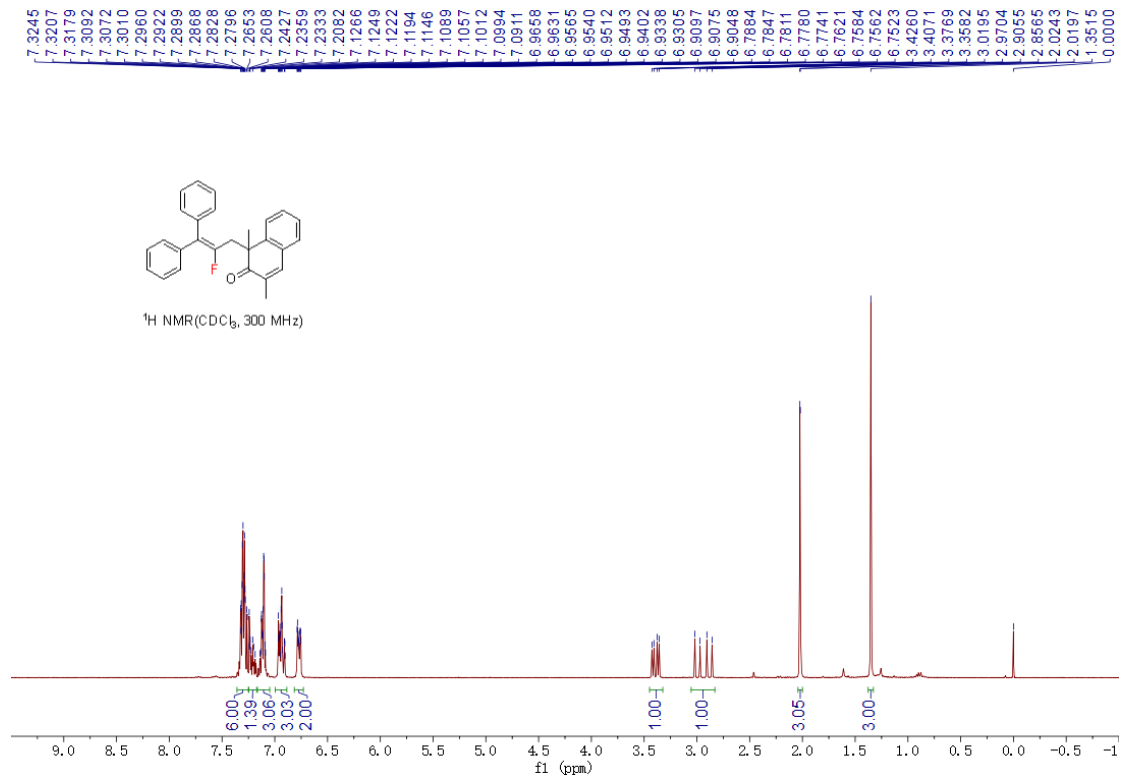


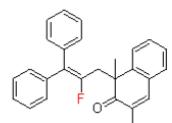




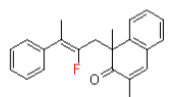
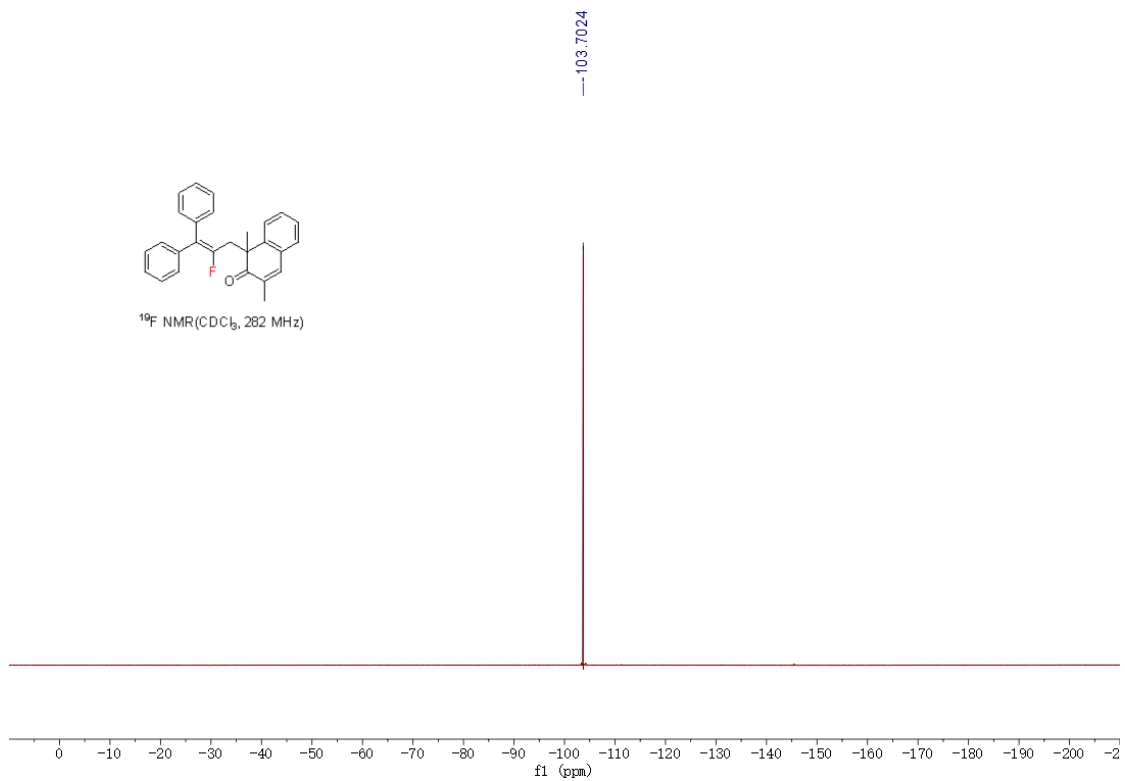




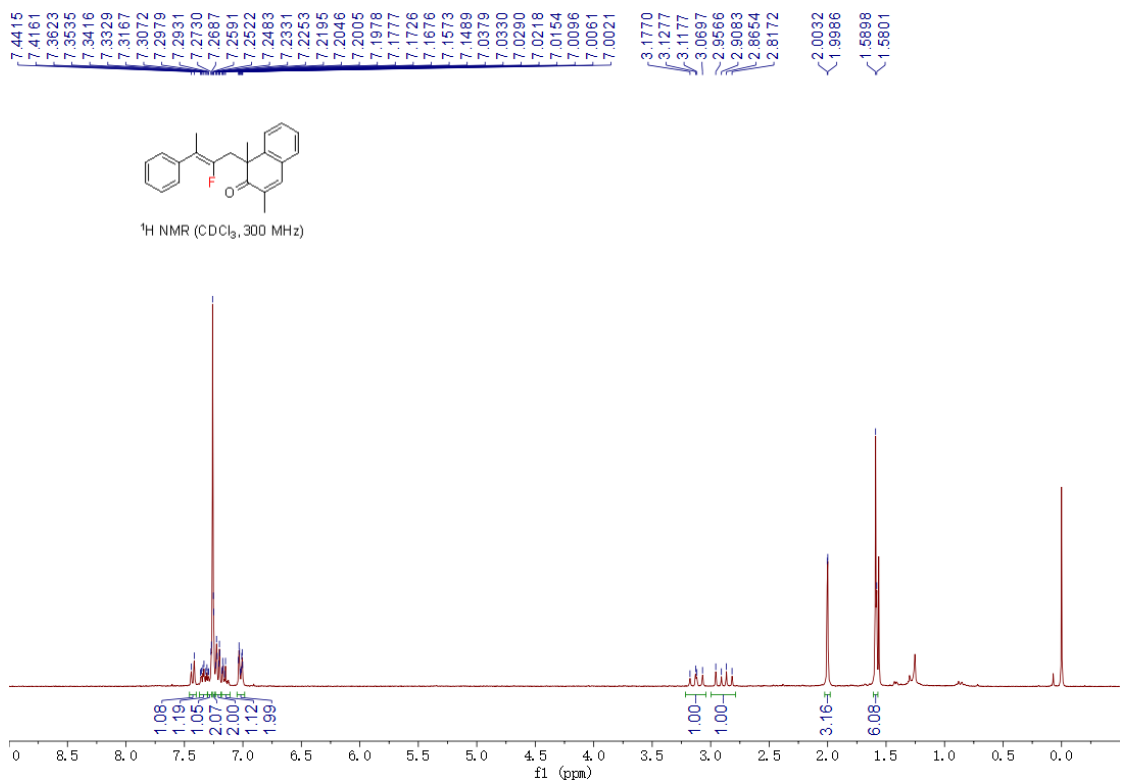


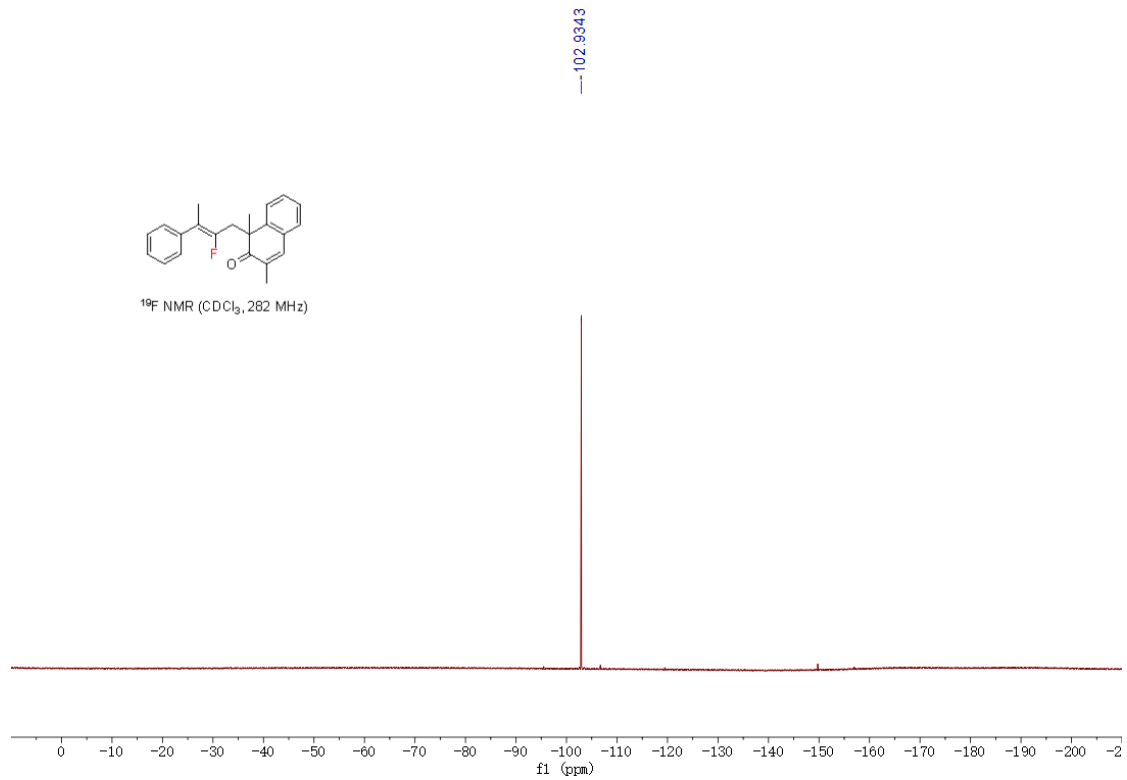
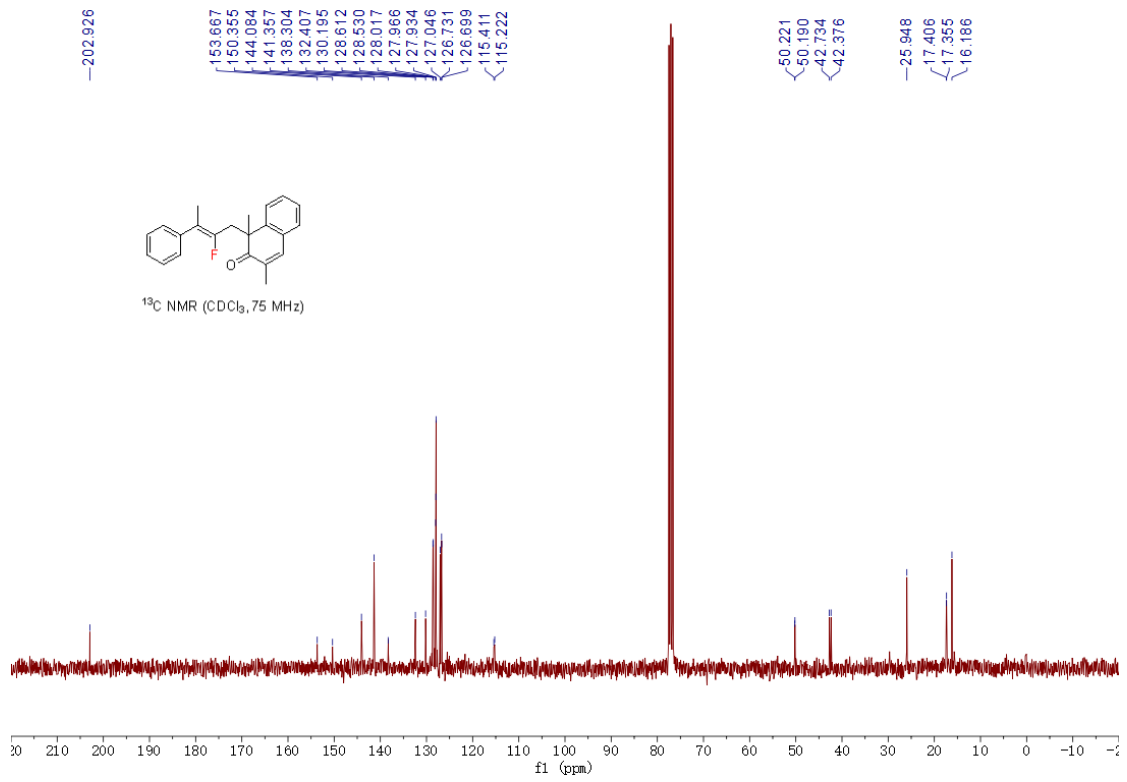


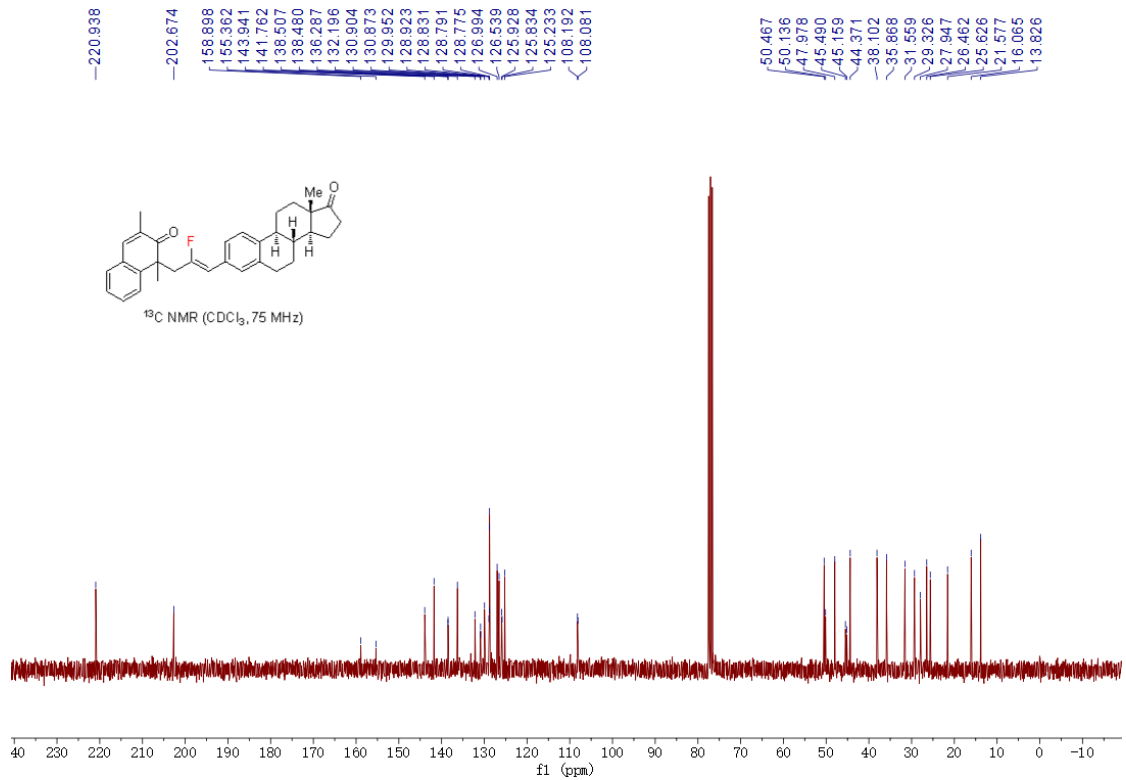
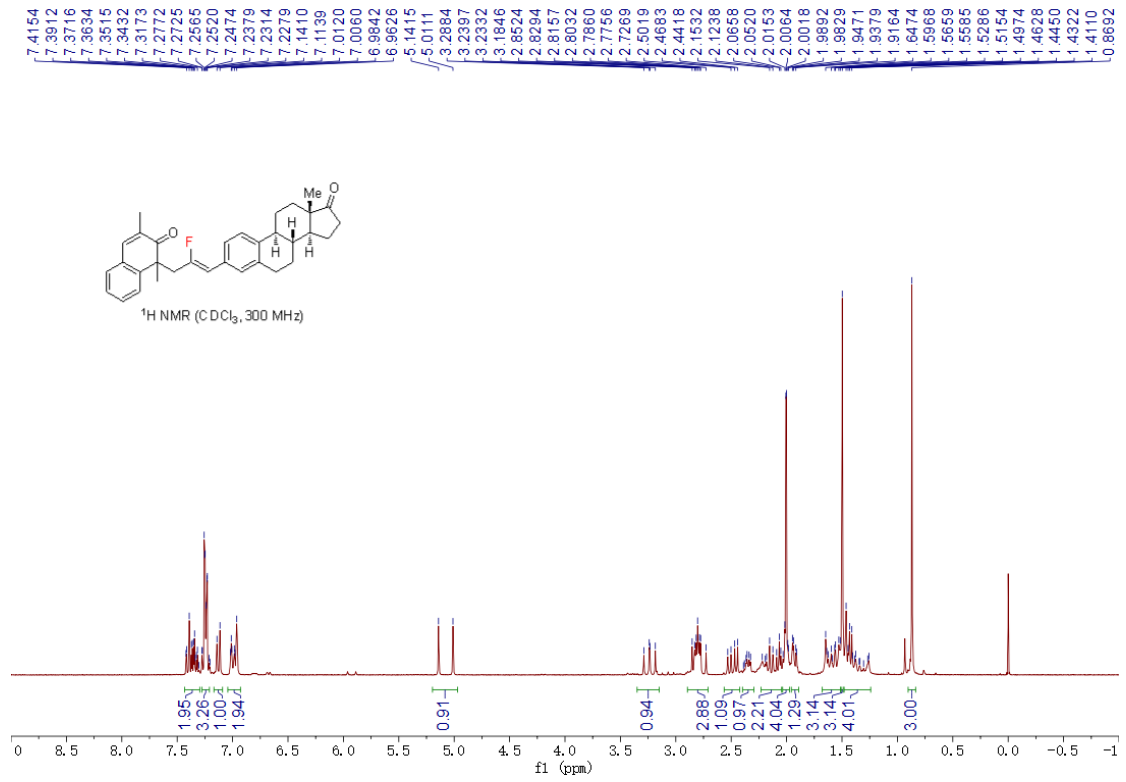
<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)

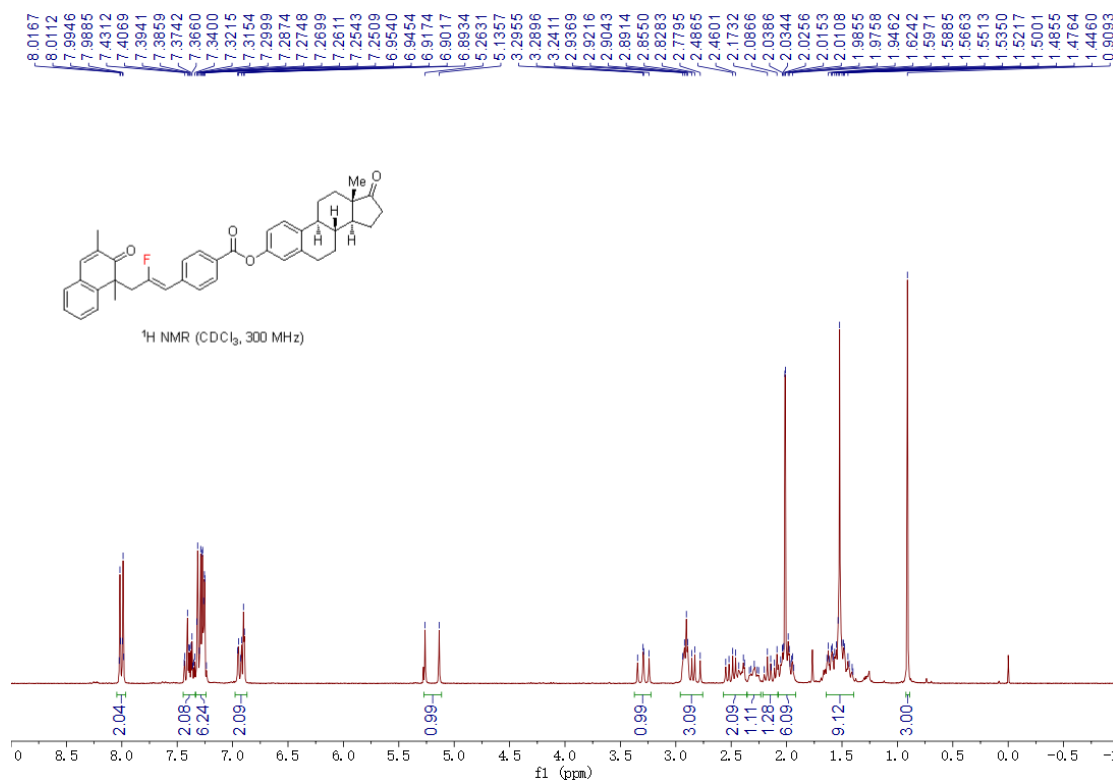
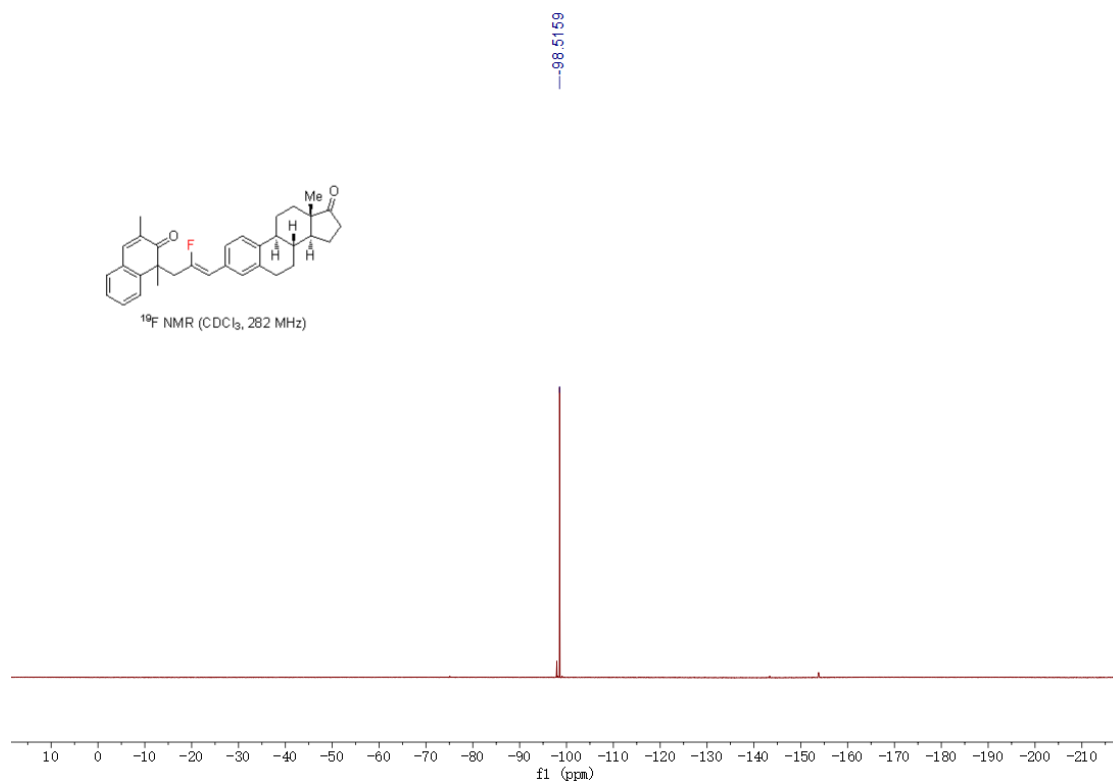


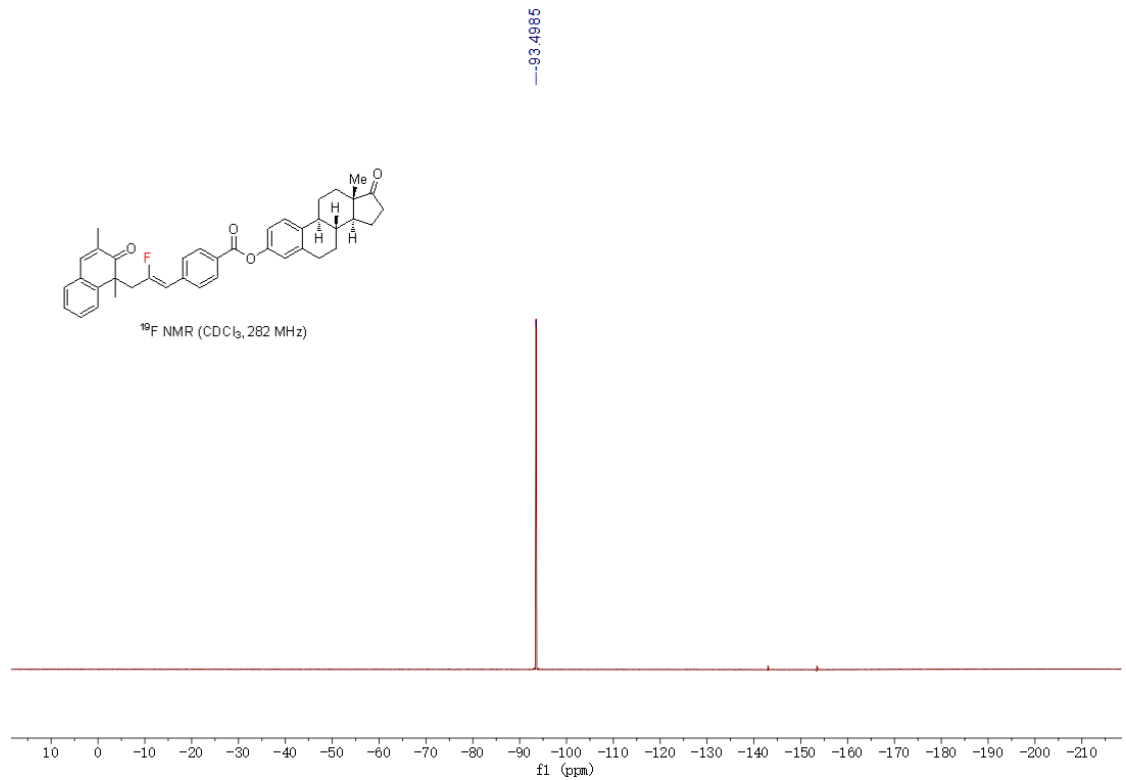
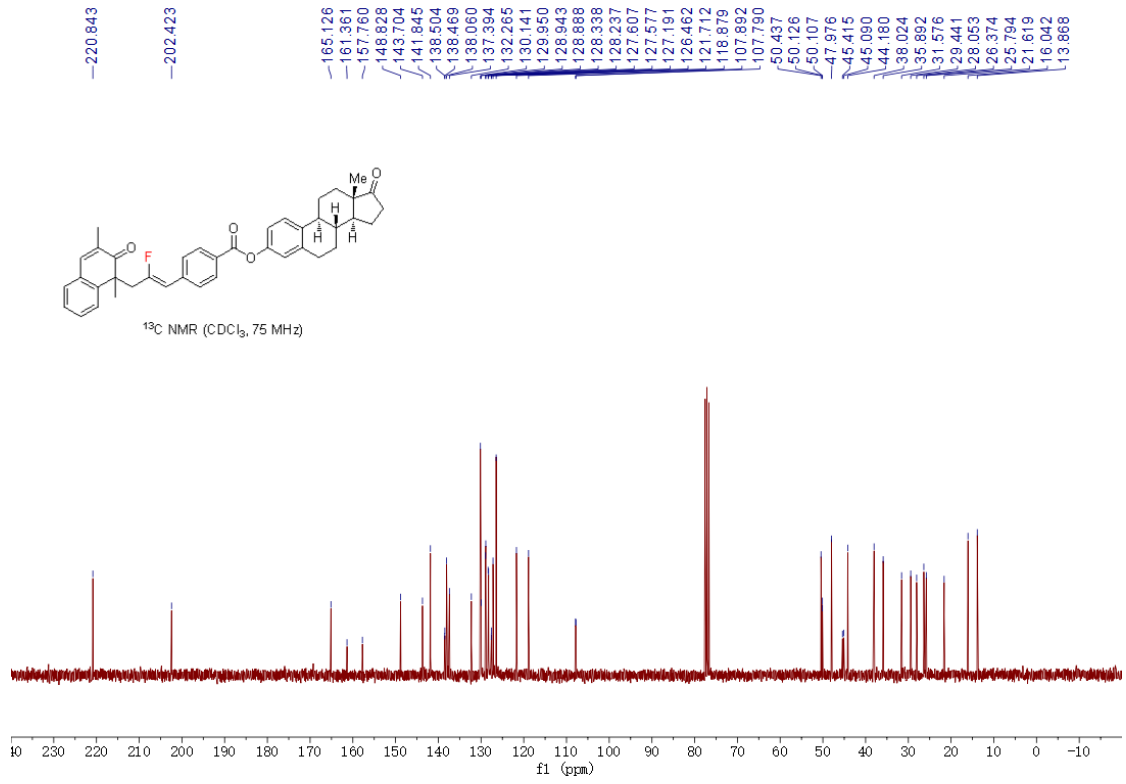
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



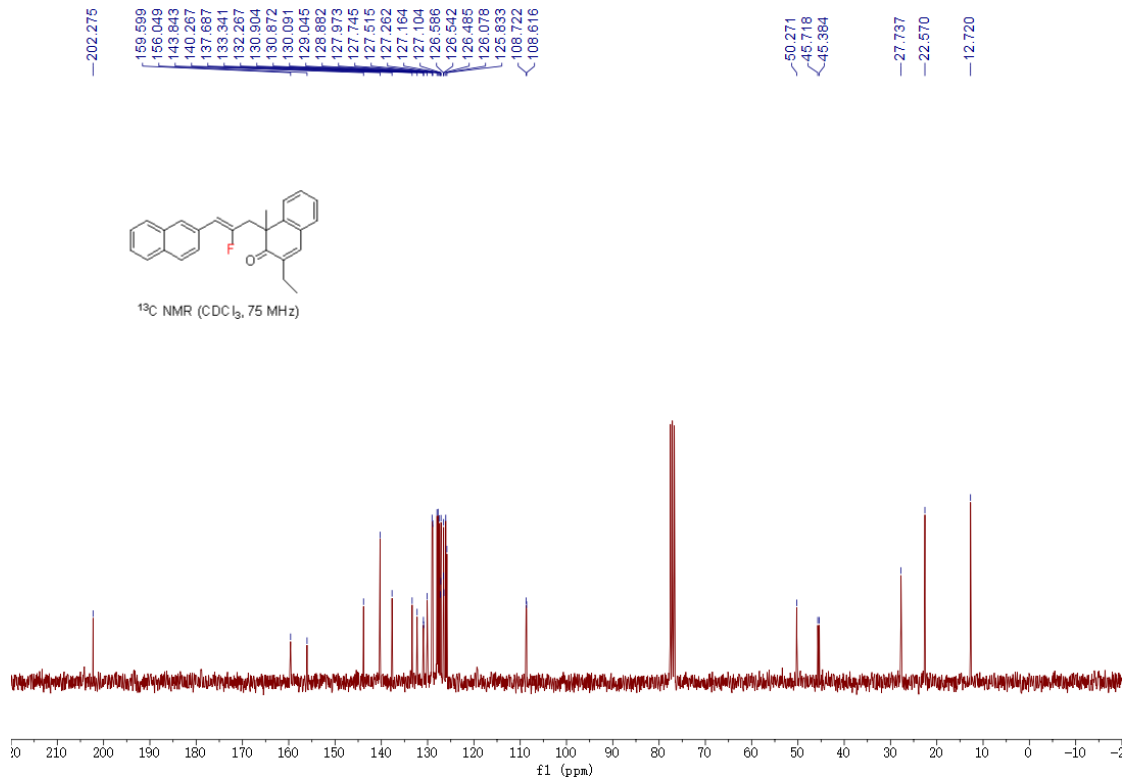
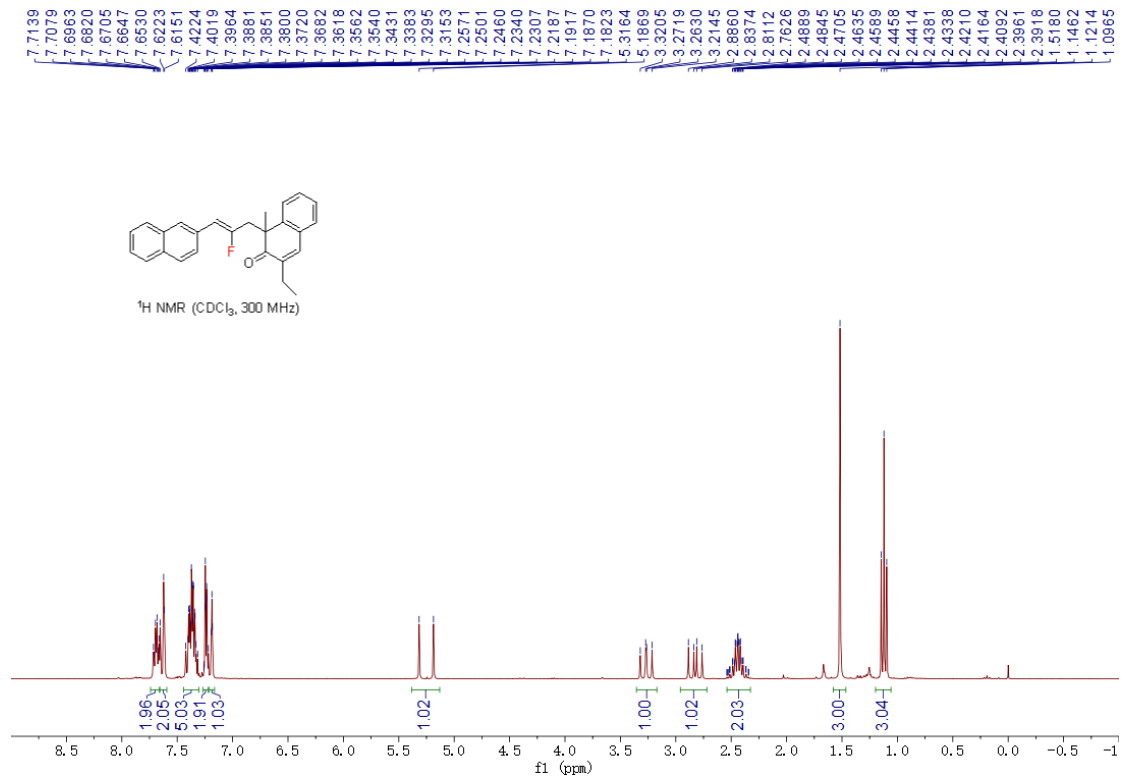


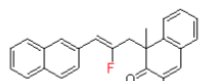




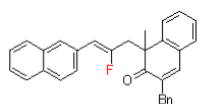
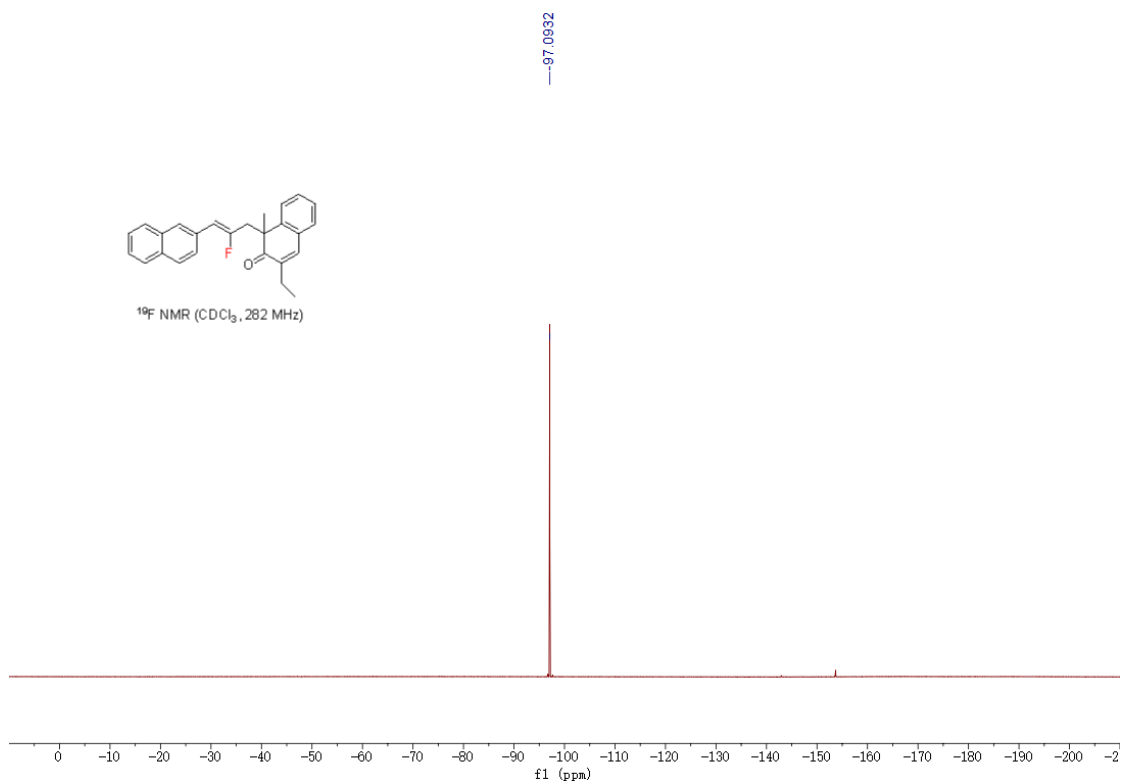




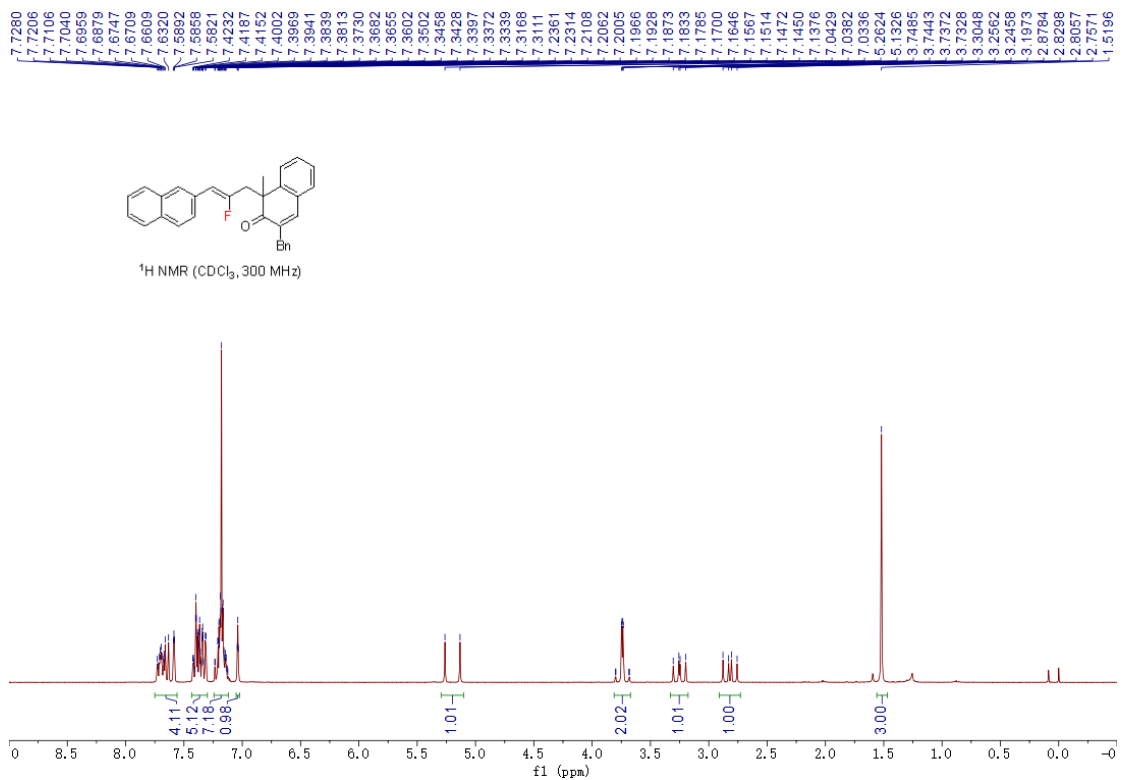


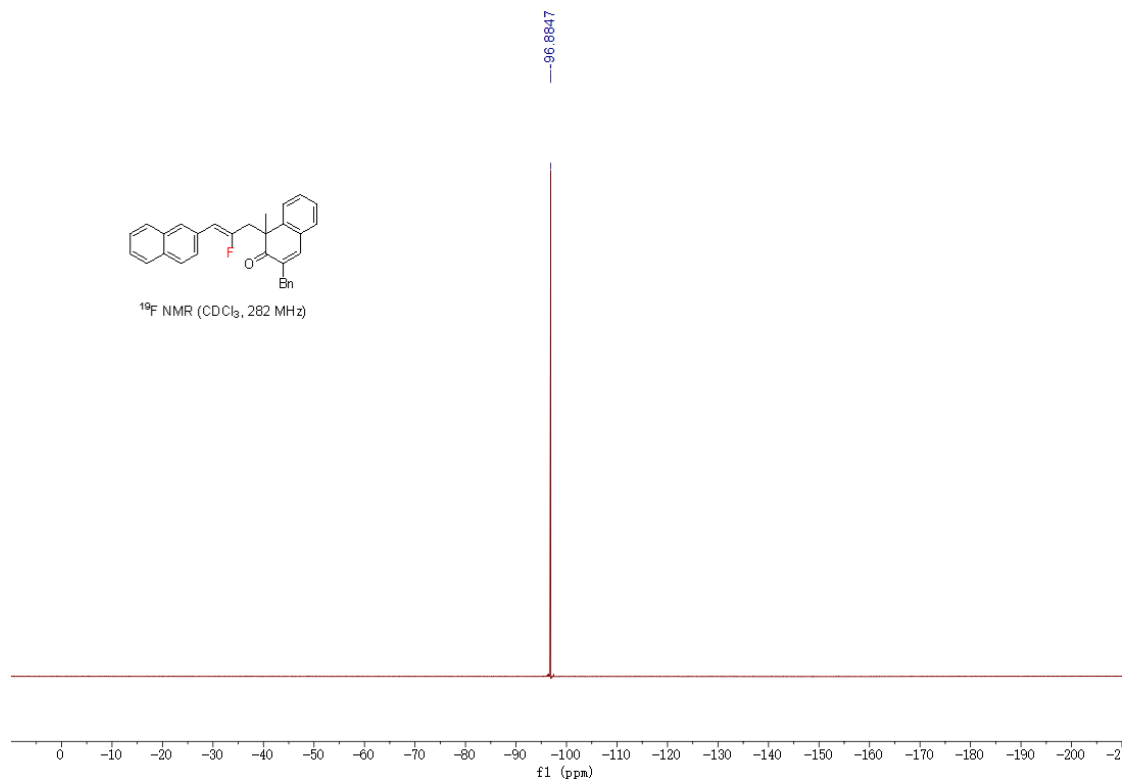
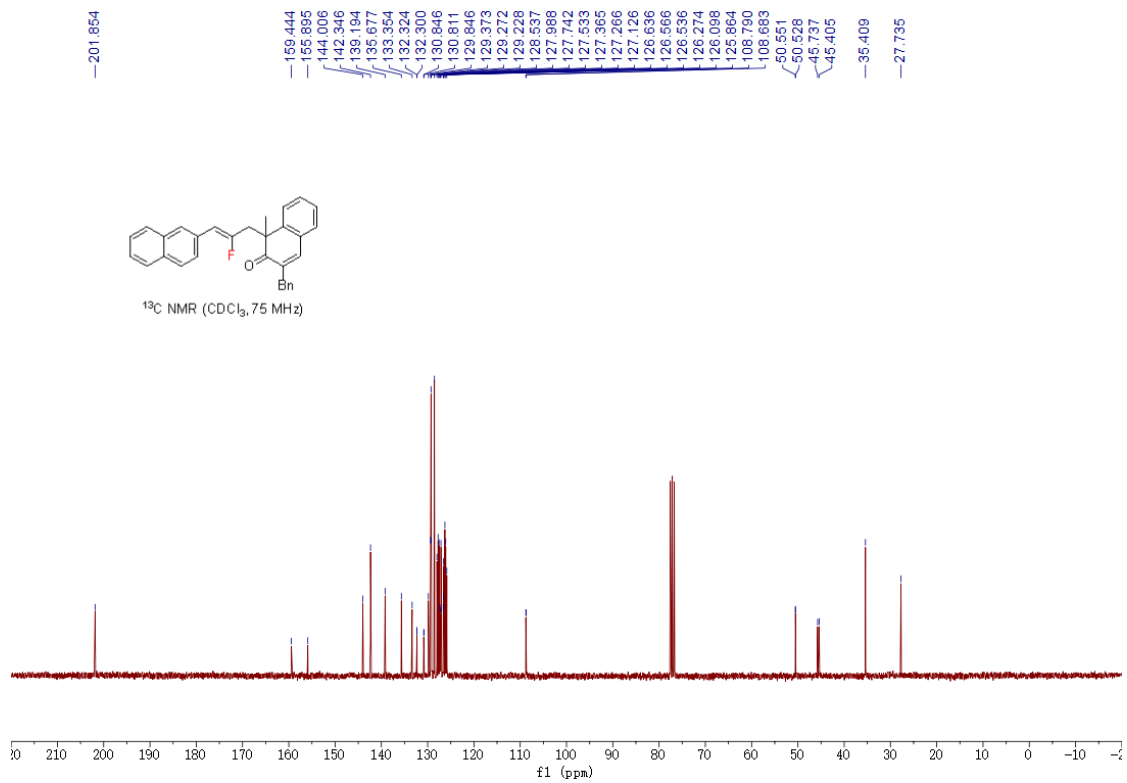


<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)

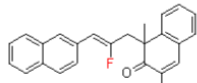


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

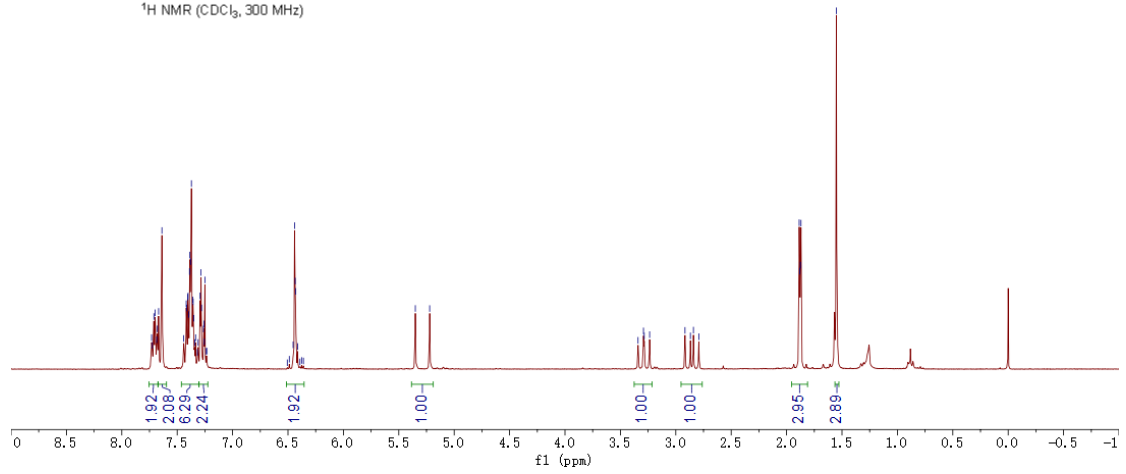




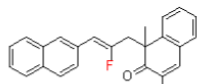
7.7311  
7.7242  
7.7104  
7.7000  
7.6848  
7.6789  
7.6677  
7.6579  
7.6414  
7.4184  
7.4136  
7.4045  
7.4017  
7.3863  
7.3866  
7.3684  
7.3784  
7.3716  
7.3597  
7.3560  
7.3508  
7.3409  
7.3338  
7.3178  
7.3109  
7.2929  
7.2849  
7.2801  
7.2632  
7.2588  
7.2550  
7.2501  
7.2379  
7.2332  
6.5064  
6.4882  
6.4536  
6.4409  
6.4351  
6.4299  
6.4134  
6.3921  
6.3770  
6.3607  
5.3508  
5.2214  
3.3407  
3.2918  
3.2849  
3.2362  
2.8169  
2.8681  
2.8408  
2.7821  
1.8663  
1.8618  
1.8754  
1.8700  
1.5509



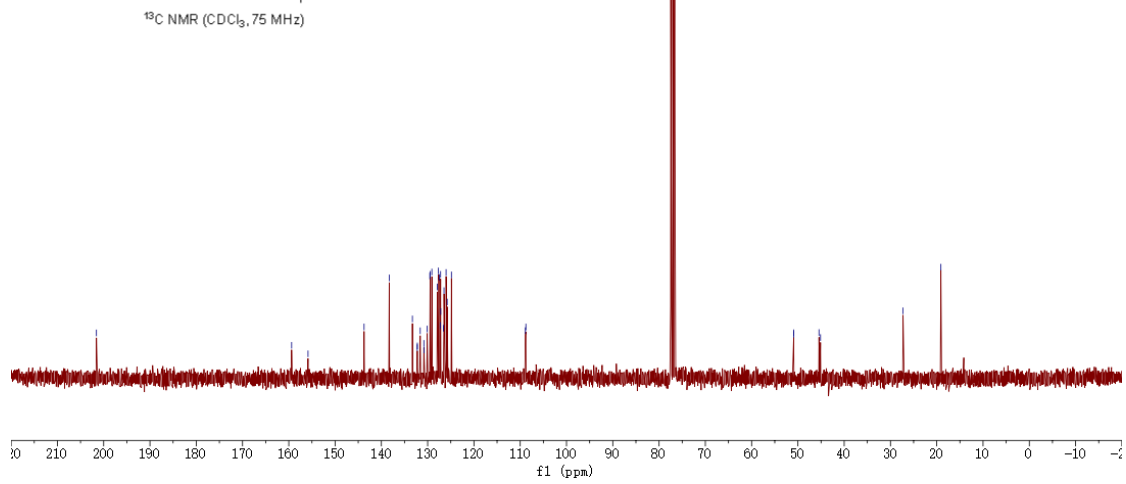
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

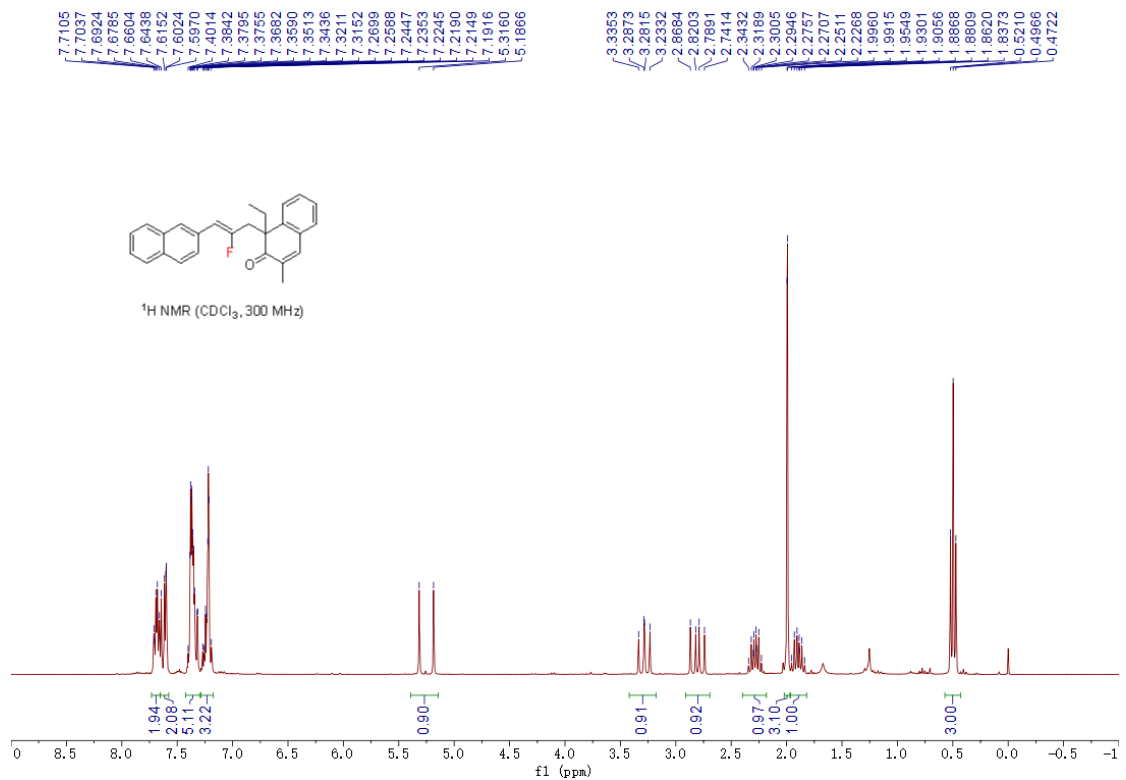
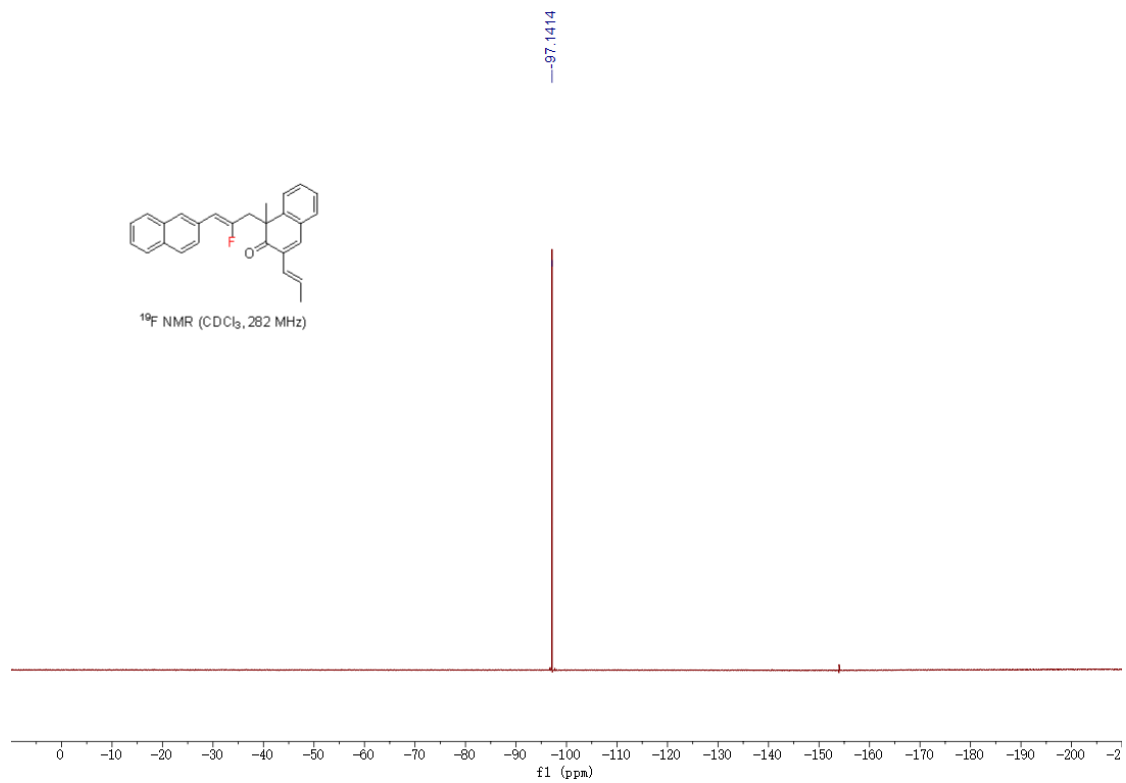


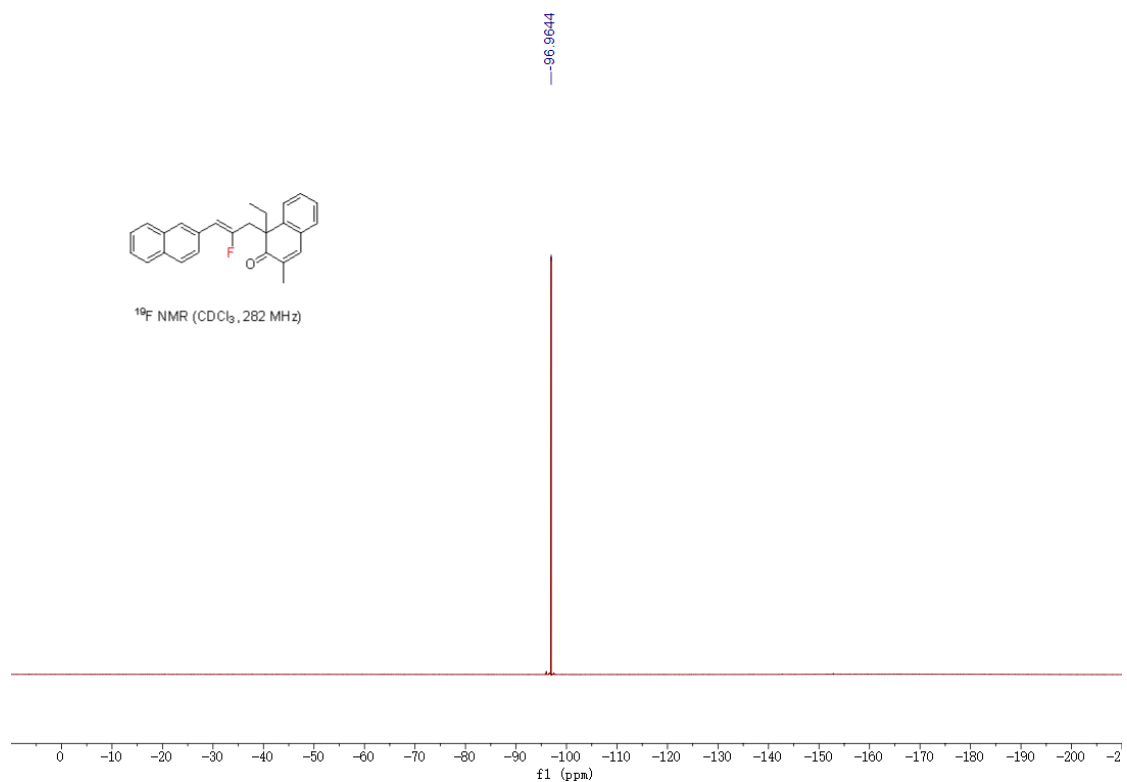
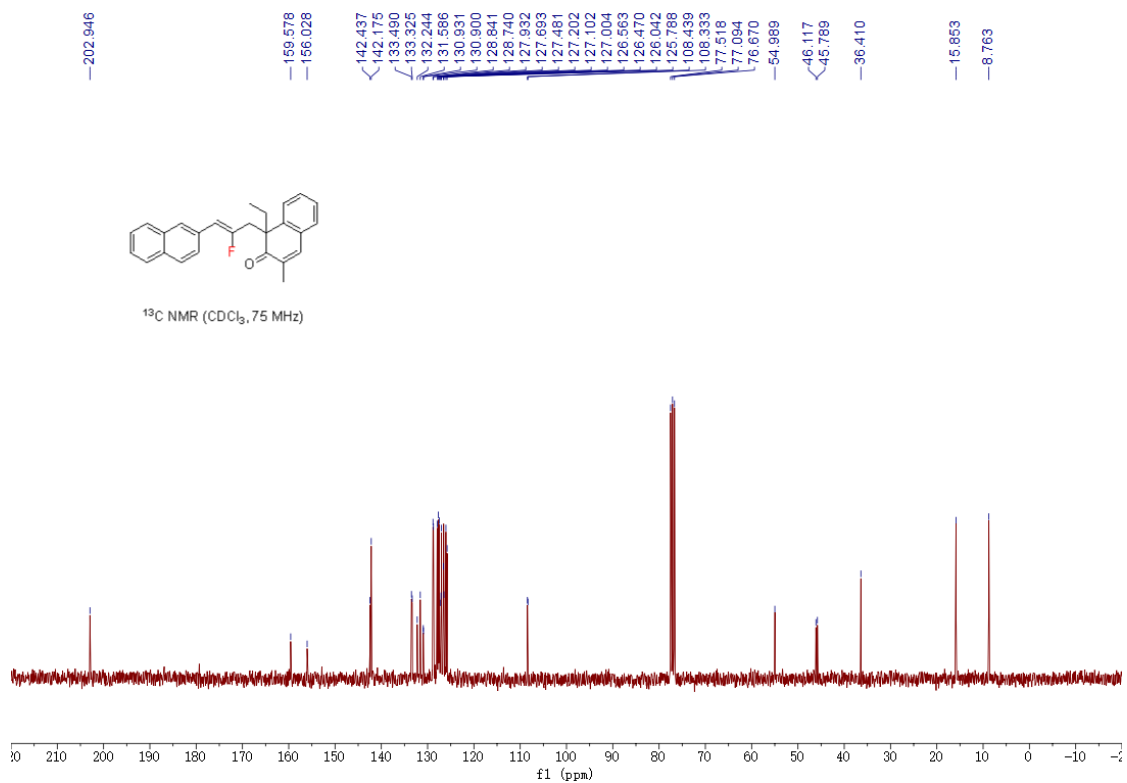
201.564  
159.391  
155.843  
143.734  
138.298  
133.295  
132.252  
132.229  
131.603  
130.819  
130.786  
130.110  
129.530  
128.469  
128.469  
127.926  
127.665  
127.451  
127.276  
127.202  
127.177  
126.584  
126.465  
126.018  
125.780  
124.864  
108.885  
108.778  
77.468  
77.045  
76.621  
50.935  
50.913  
45.450  
45.116  
27.286  
19.110



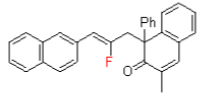
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



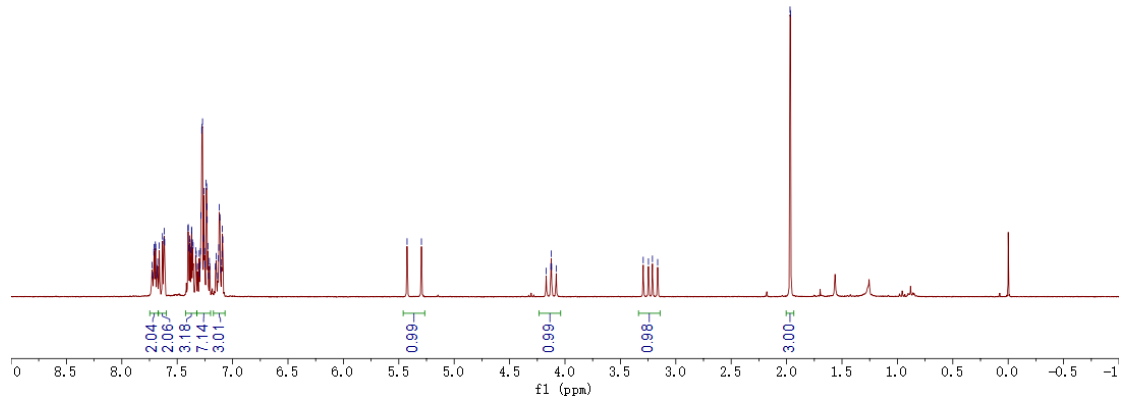




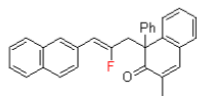
7.7278  
7.7111  
7.7075  
7.6973  
7.6938  
7.6804  
7.6759  
7.6618  
7.6331  
7.6208  
7.6132  
7.6023  
7.3998  
7.3942  
7.3871  
7.3835  
7.3764  
7.3703  
7.3685  
7.3620  
7.3560  
7.3333  
7.3276  
7.3162  
7.3012  
7.2960  
7.2930  
7.2900  
7.2861  
7.2786  
7.2764  
7.2713  
7.2624  
7.2590  
7.2527  
7.2478  
7.2388  
7.2340  
7.2315  
7.2288  
7.2232  
7.2092  
7.2060  
7.1547  
7.1482  
7.1279  
7.1246  
7.1209  
7.1142  
7.1069  
7.0998  
7.0931  
7.0882  
5.4362  
5.2657  
4.1697  
4.1277  
4.1243  
4.1210  
4.0793  
3.2468  
3.2107  
3.1637  
1.9690  
1.9646



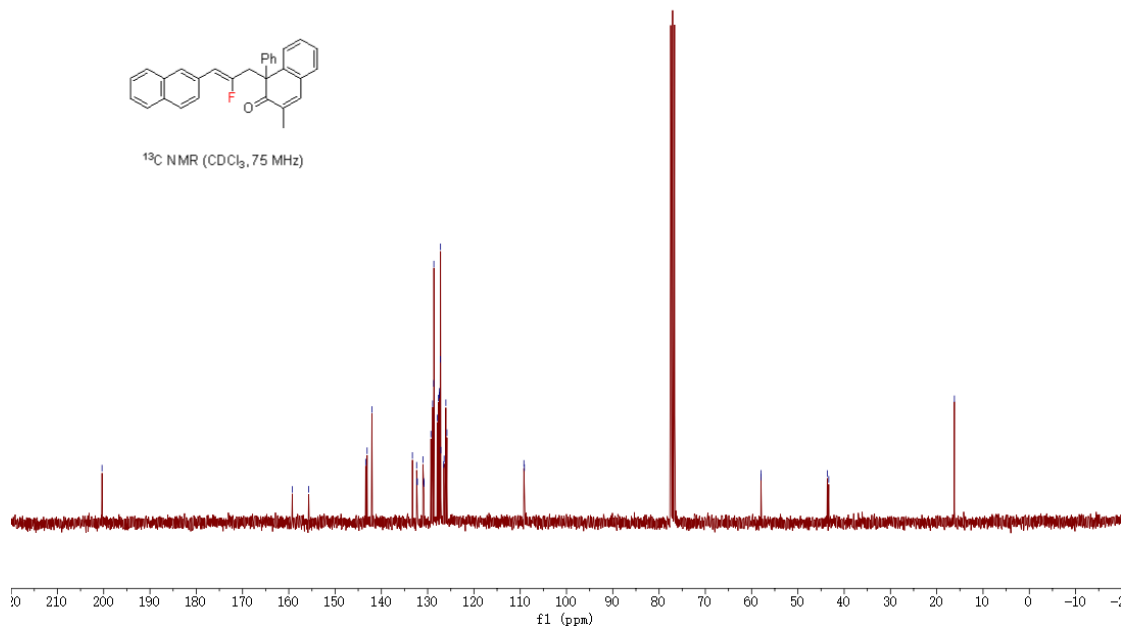
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

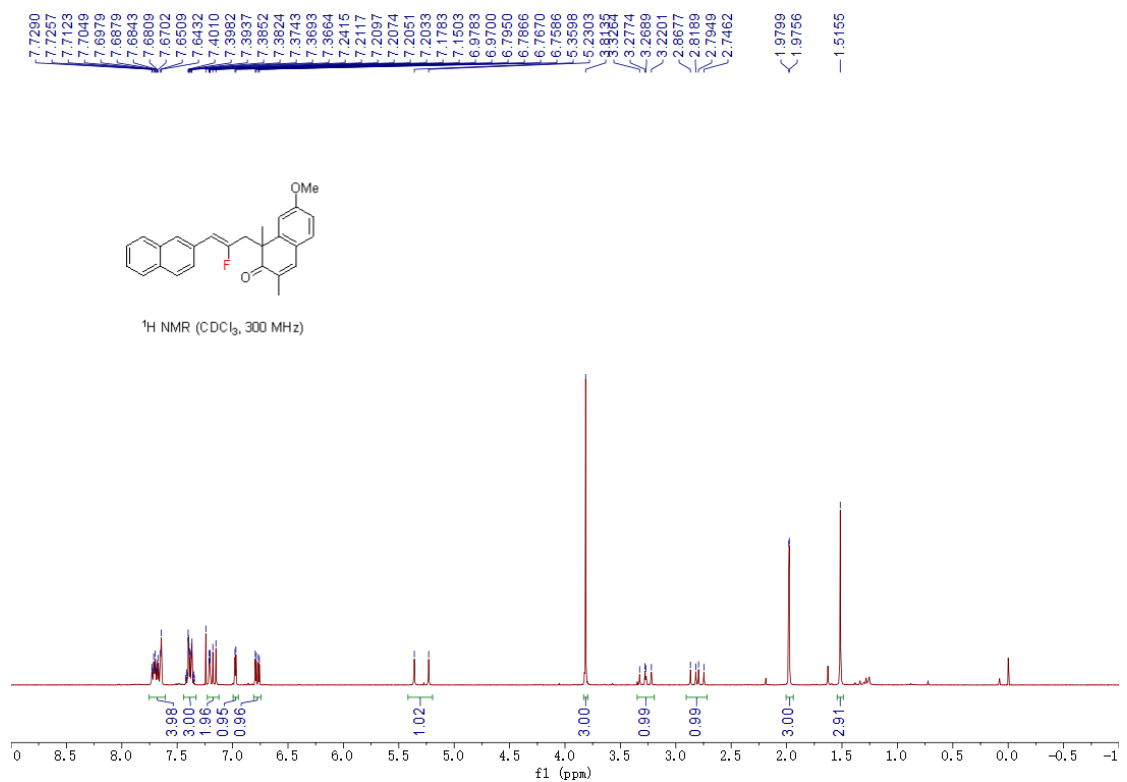
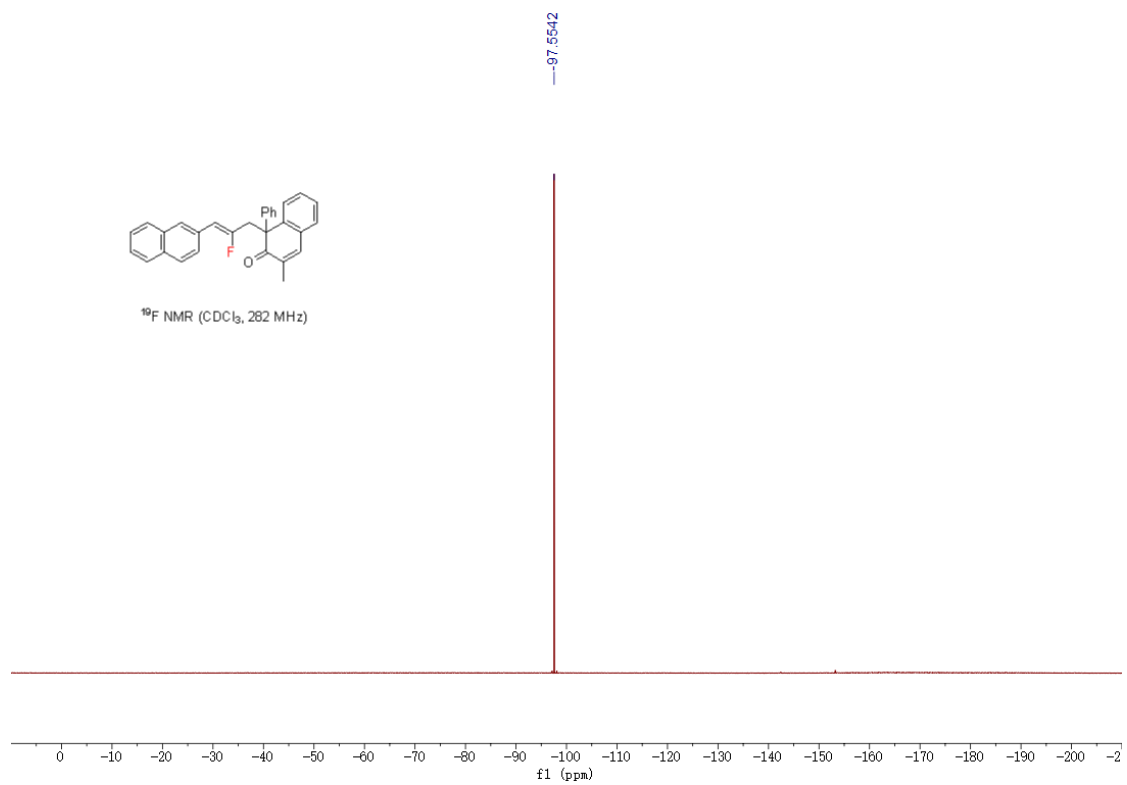


200.355  
159.250  
155.697  
143.388  
143.076  
142.042  
133.293  
132.376  
132.265  
132.243  
131.024  
130.834  
130.800  
129.296  
128.912  
128.667  
128.660  
127.941  
127.710  
127.480  
127.434  
127.251  
127.210  
127.157  
126.536  
126.436  
126.061  
125.830  
109.208  
109.089  
57.986  
43.657  
43.336  
16.190

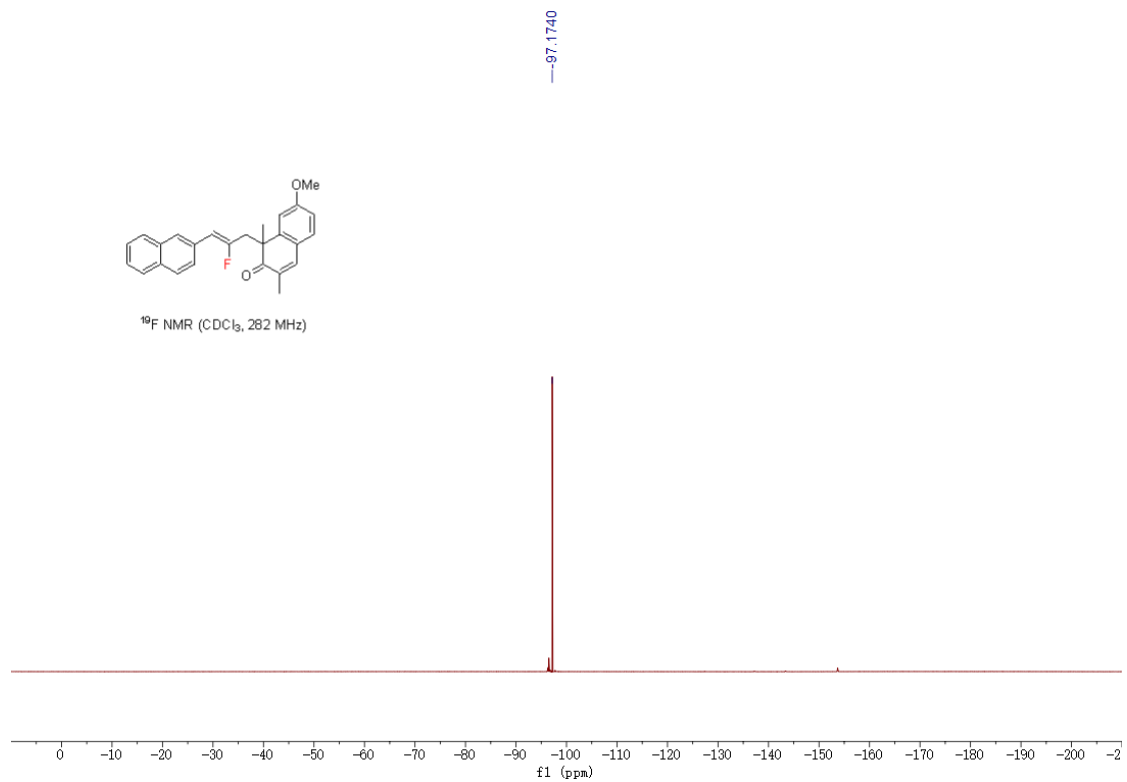
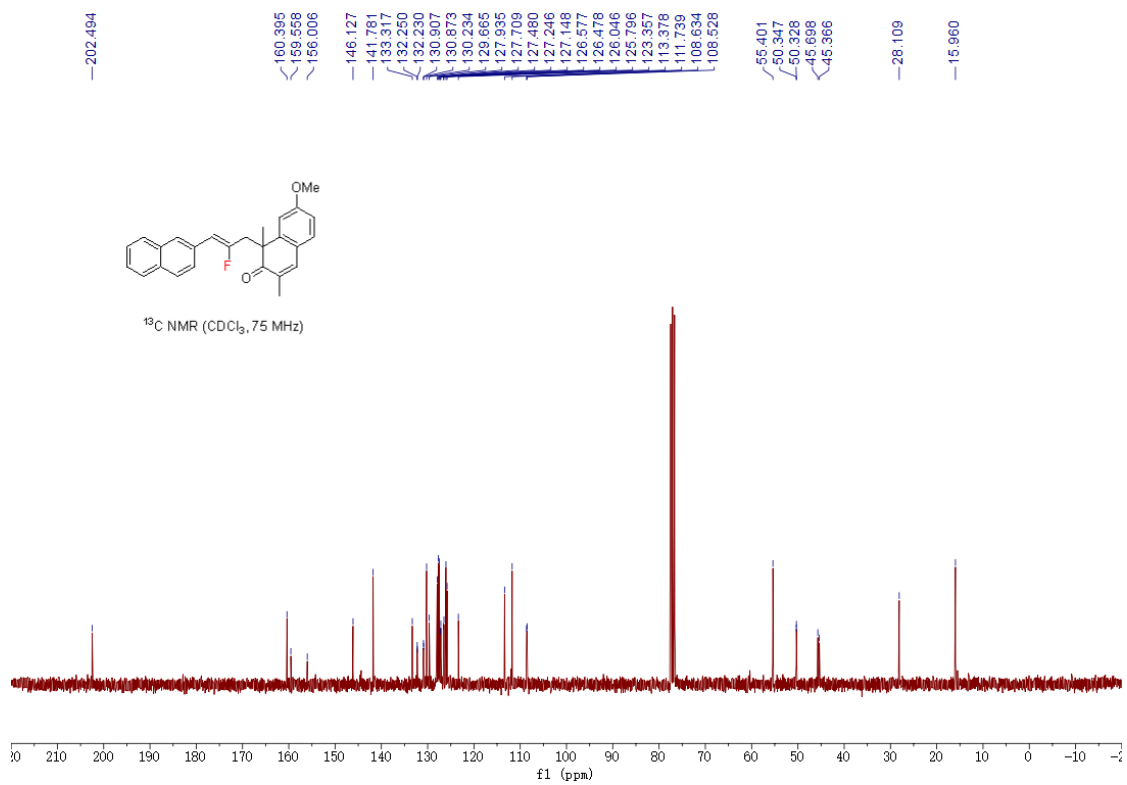


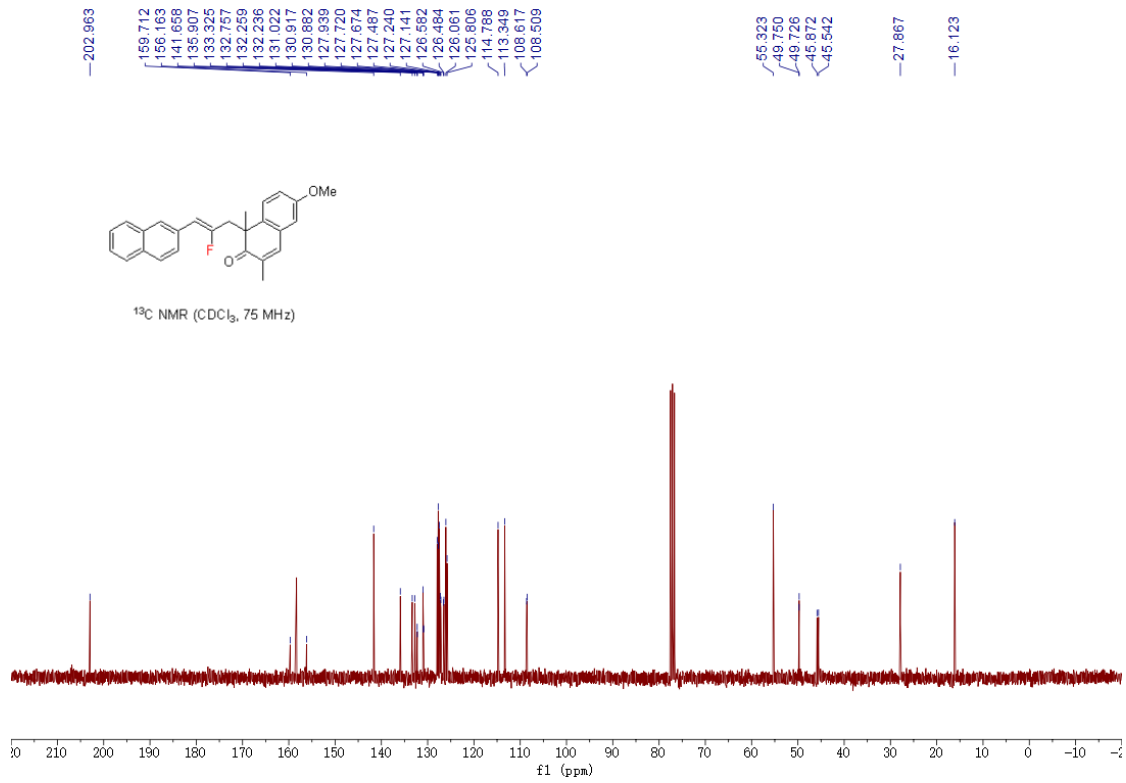
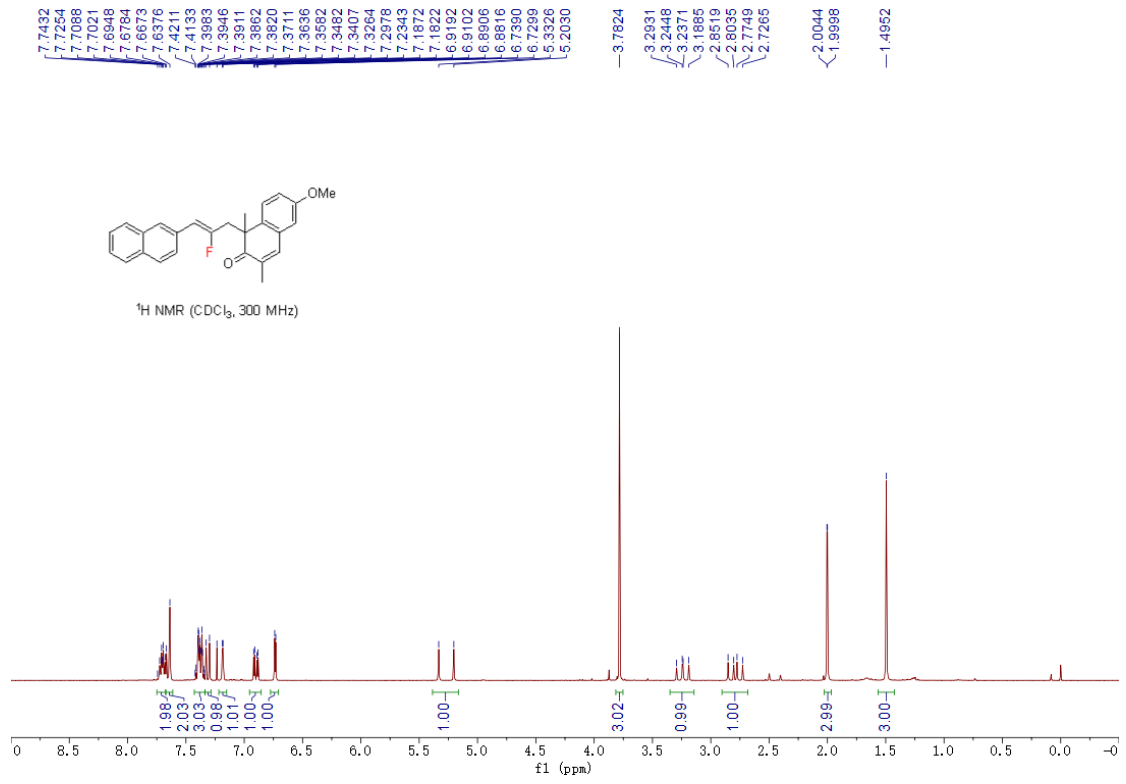
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

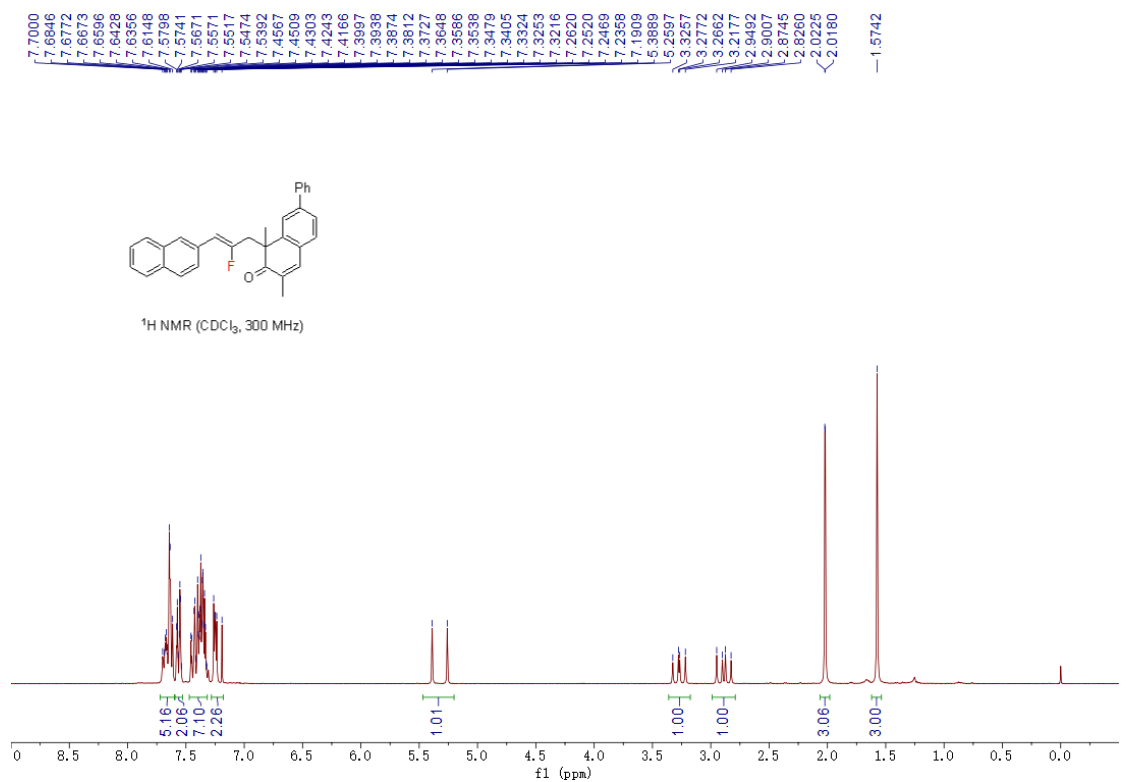
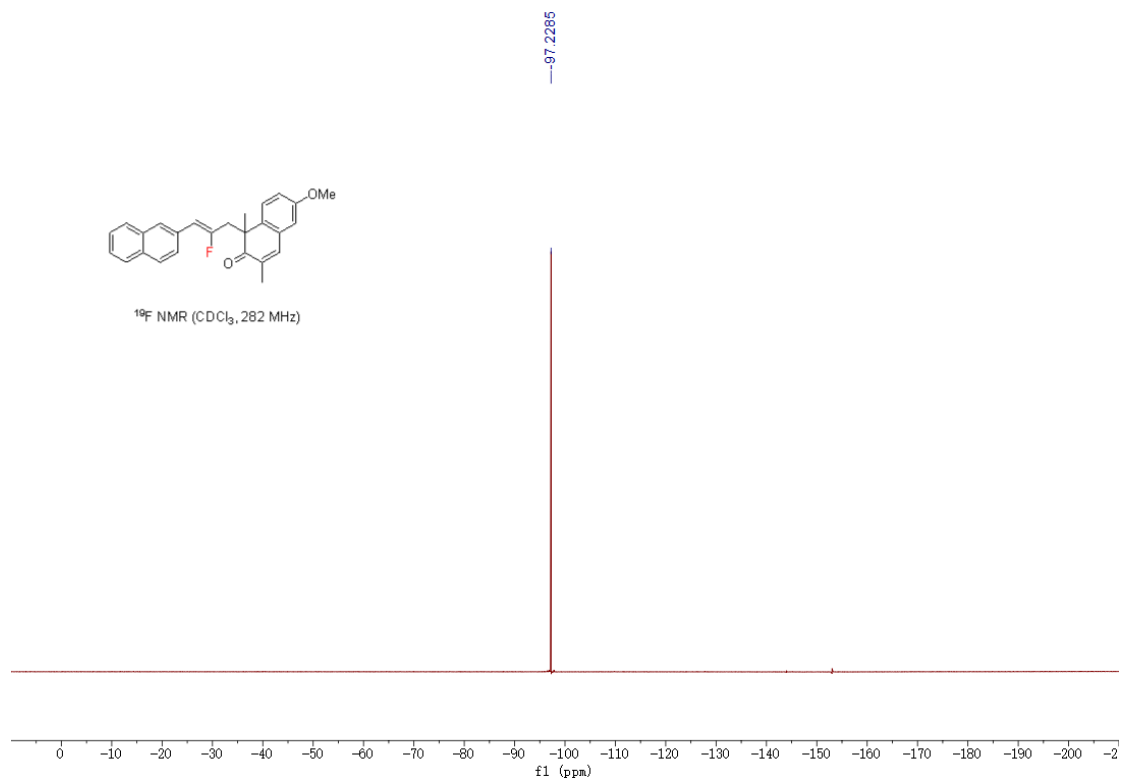


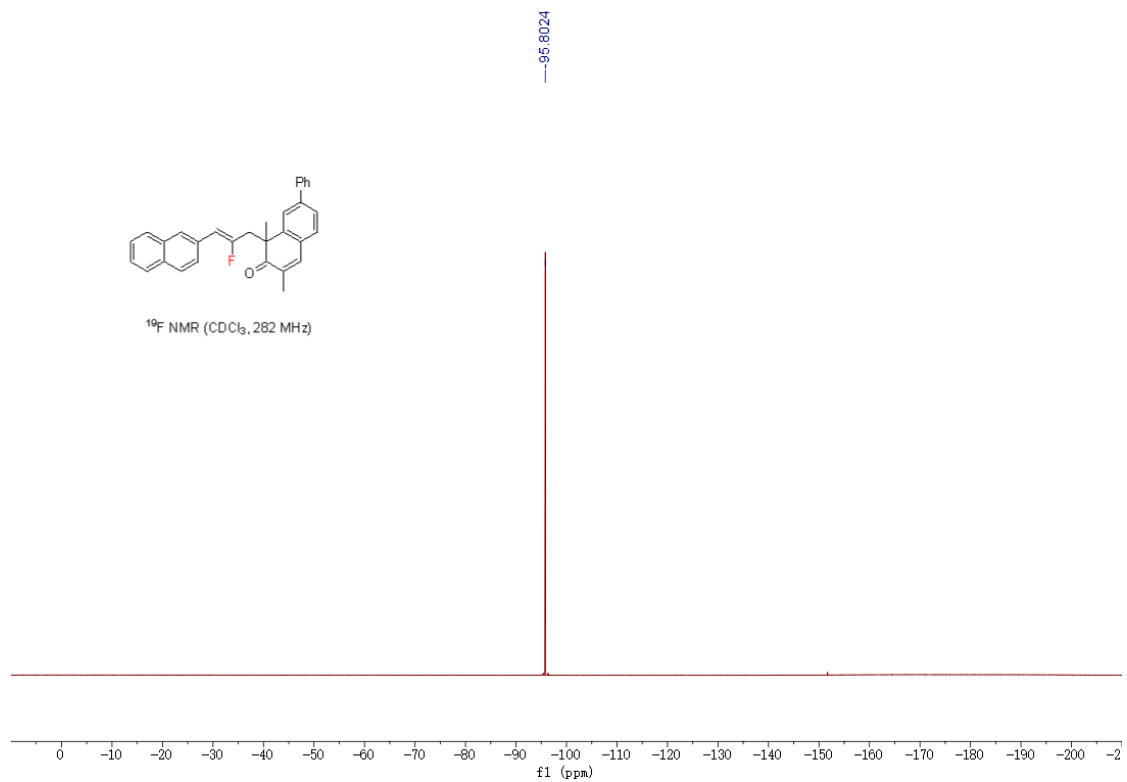
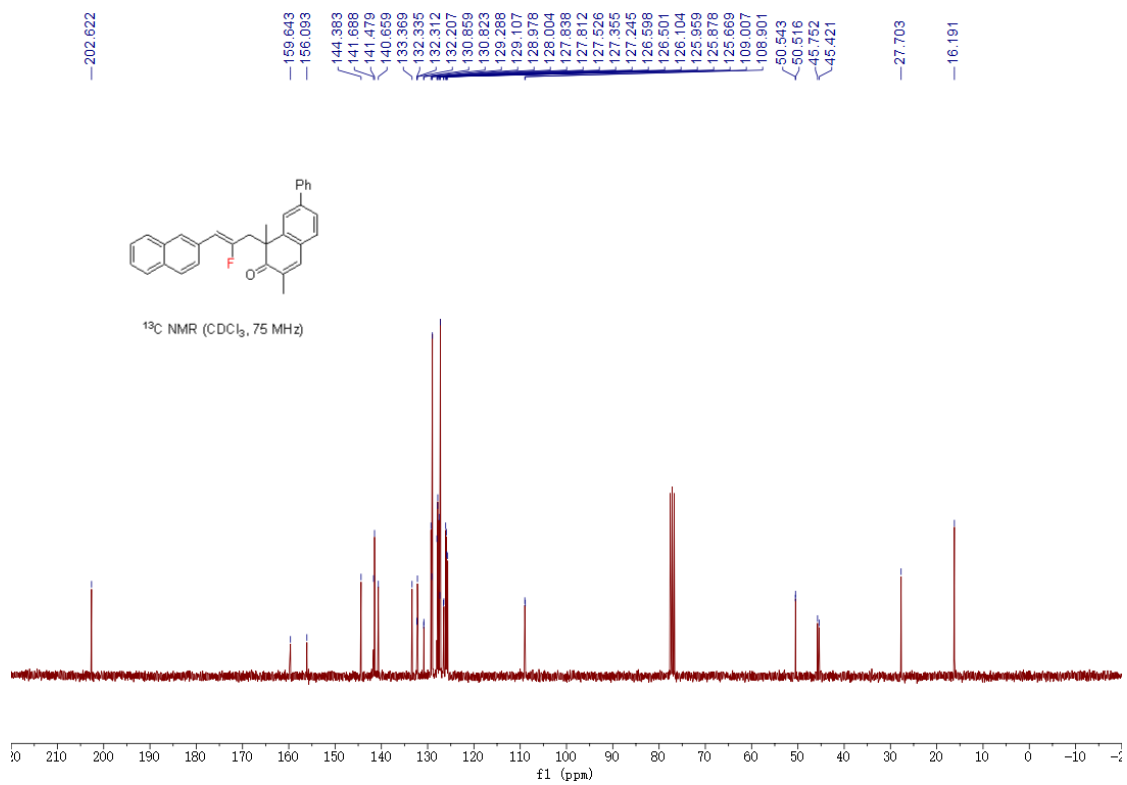




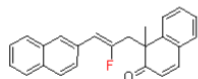




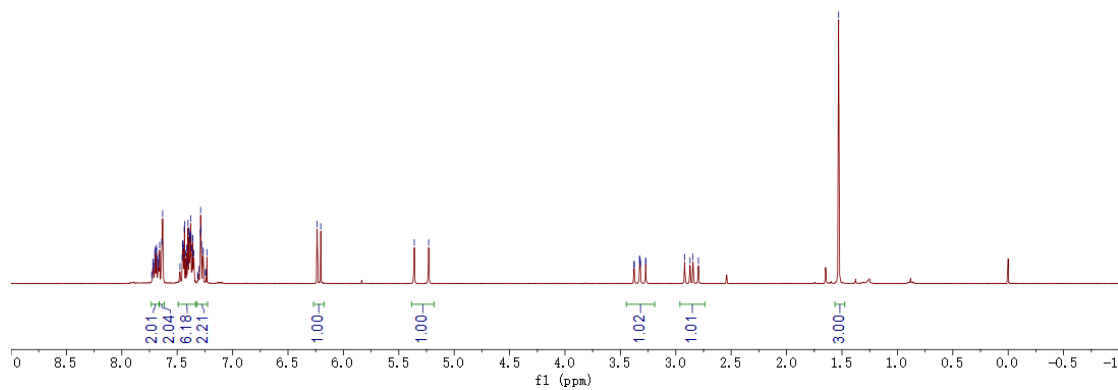




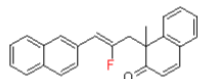
7.7295  
7.7252  
7.7199  
7.7167  
7.7124  
7.7045  
7.7025  
7.6987  
7.6885  
7.6851  
7.6833  
7.6746  
7.6671  
7.6584  
7.6393  
7.6315  
7.4749  
7.4544  
7.4522  
7.4496  
7.4466  
7.4419  
7.4389  
7.4385  
7.4232  
7.4143  
7.4084  
7.4022  
7.3945  
7.3918  
7.3863  
7.3835  
7.3789  
7.3756  
7.3684  
7.3624  
7.3606  
7.3549  
7.3493  
7.3129  
7.3058  
7.2911  
7.2888  
7.2844  
7.2804  
7.2703  
7.2649  
7.2451  
7.2398  
7.2319  
6.2369  
6.2042  
5.3602  
5.2302  
3.3767  
3.3766  
3.3276  
3.3257  
3.3212  
3.3190  
3.2726  
3.2703  
2.9201  
2.8712  
2.8450  
2.7961  
1.5307



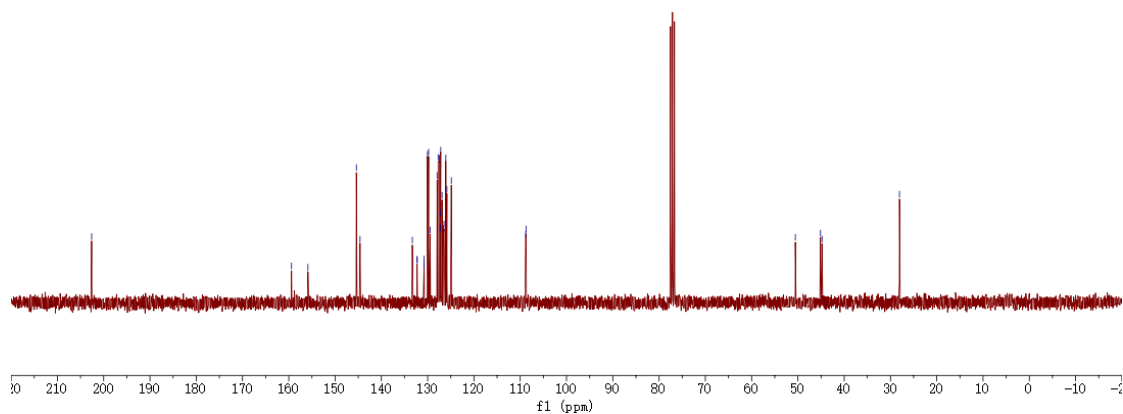
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

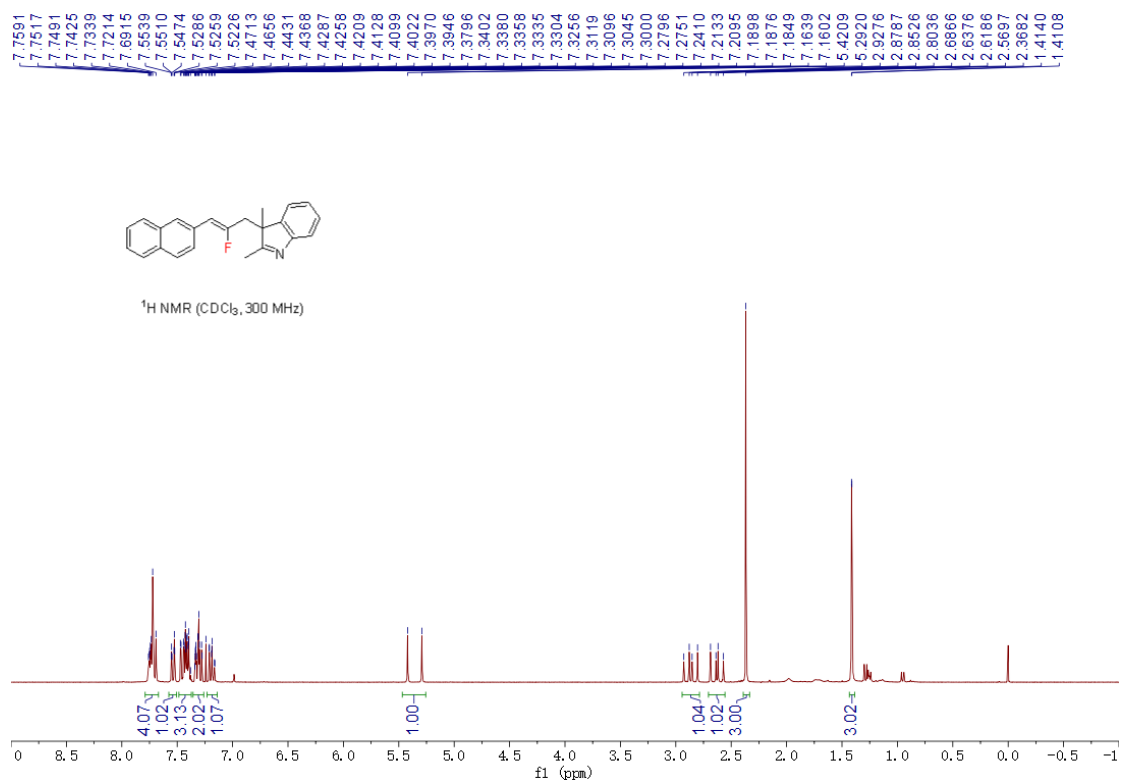
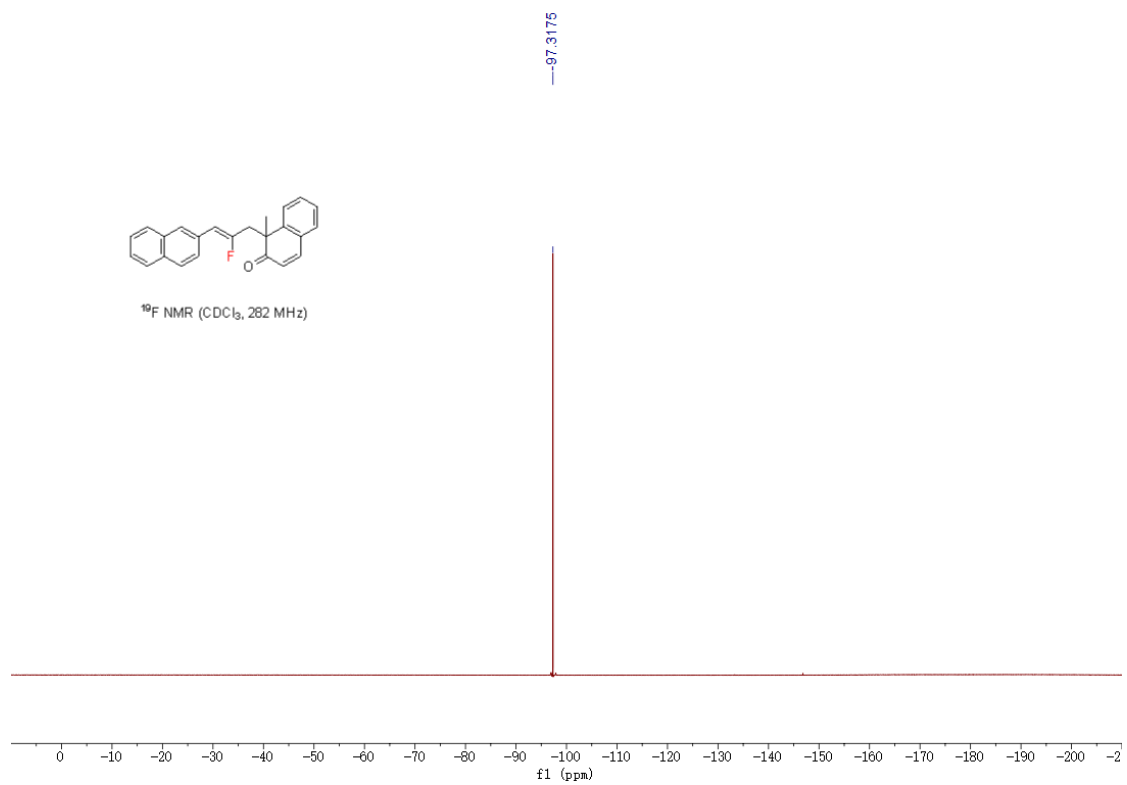


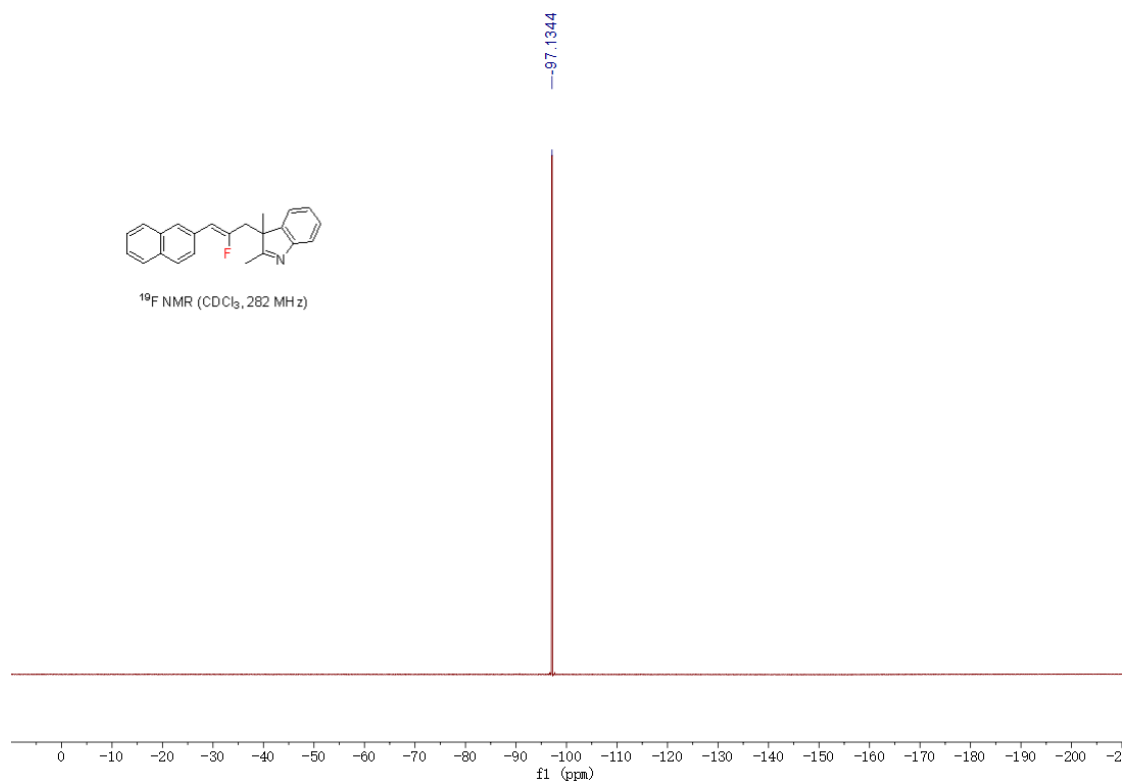
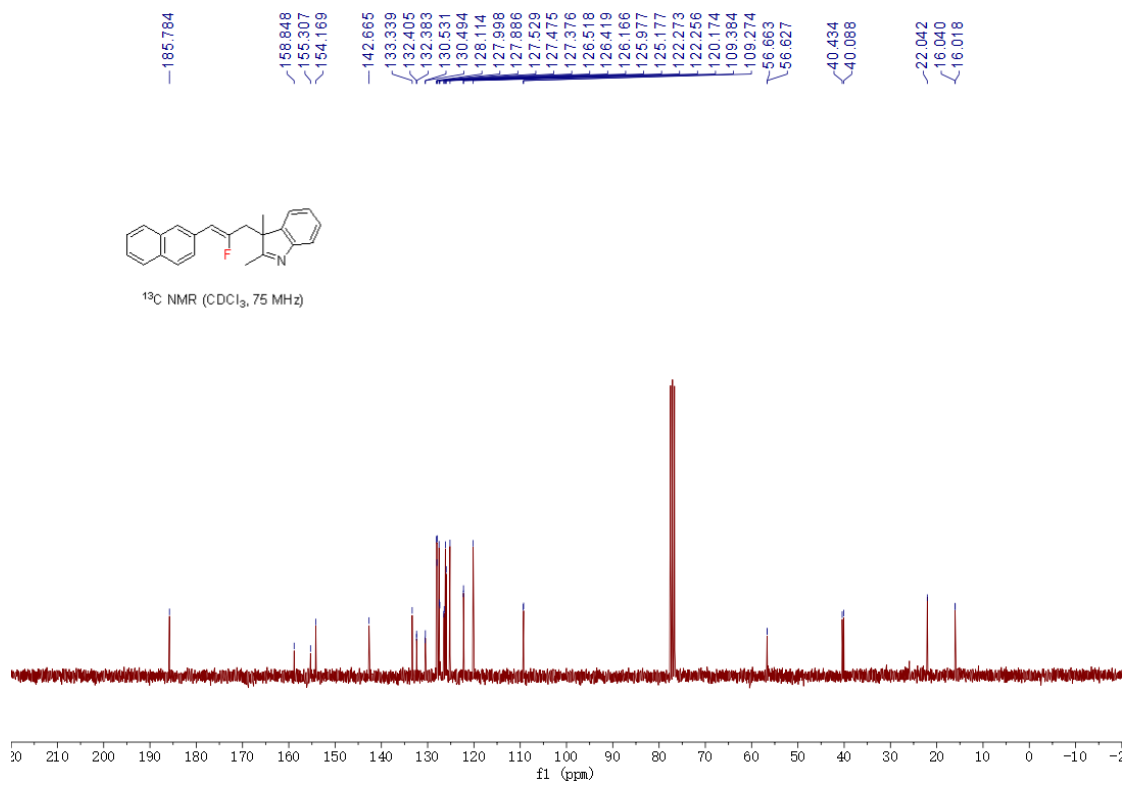
—202.602  
—159.412  
—156.865  
—145.401  
—144.607  
—133.313  
—132.281  
—132.259  
—130.801  
—130.765  
—130.024  
—129.797  
—129.457  
—127.951  
—127.734  
—127.487  
—127.307  
—127.205  
—127.177  
—126.887  
—126.560  
—126.480  
—126.073  
—125.842  
—124.866  
—108.899  
—108.732  
—50.559  
—45.122  
—44.790  
—28.055

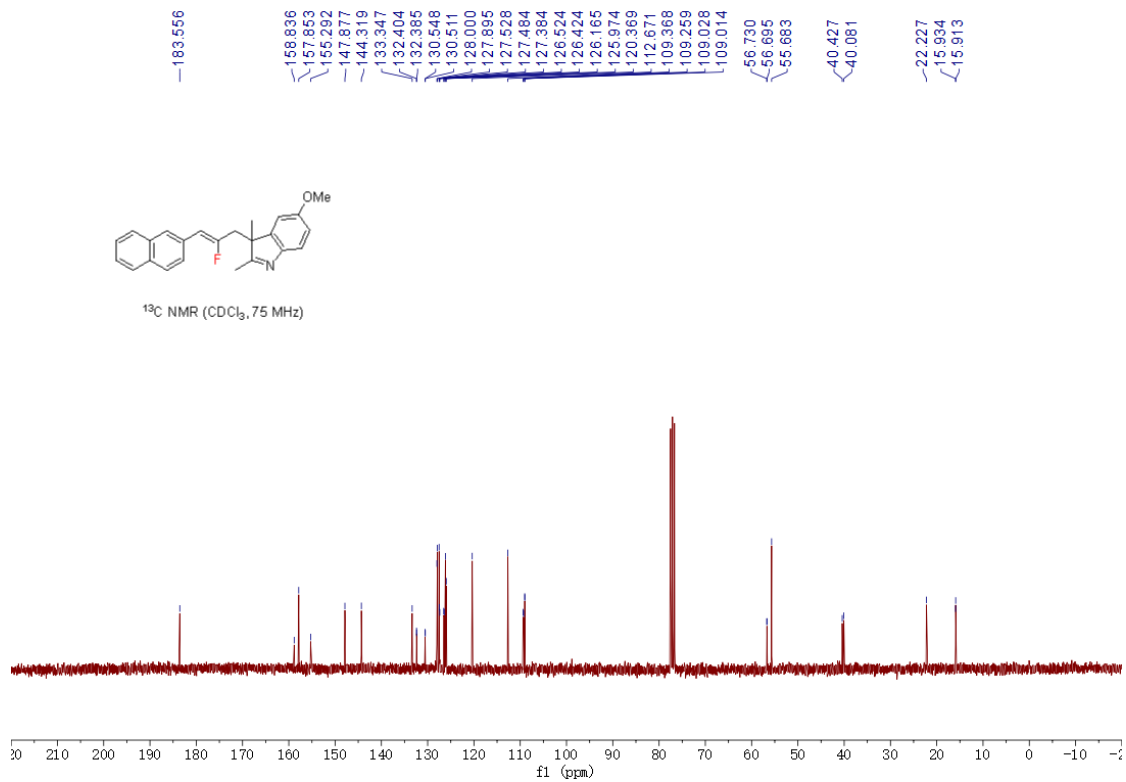
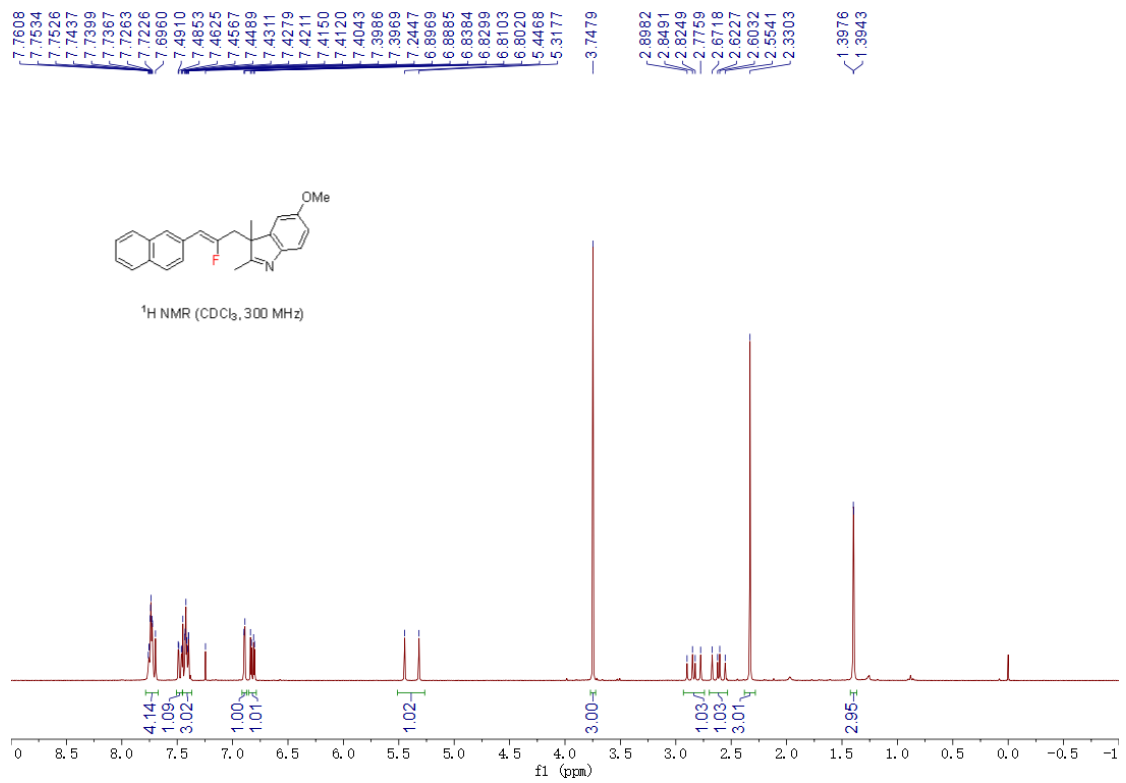


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

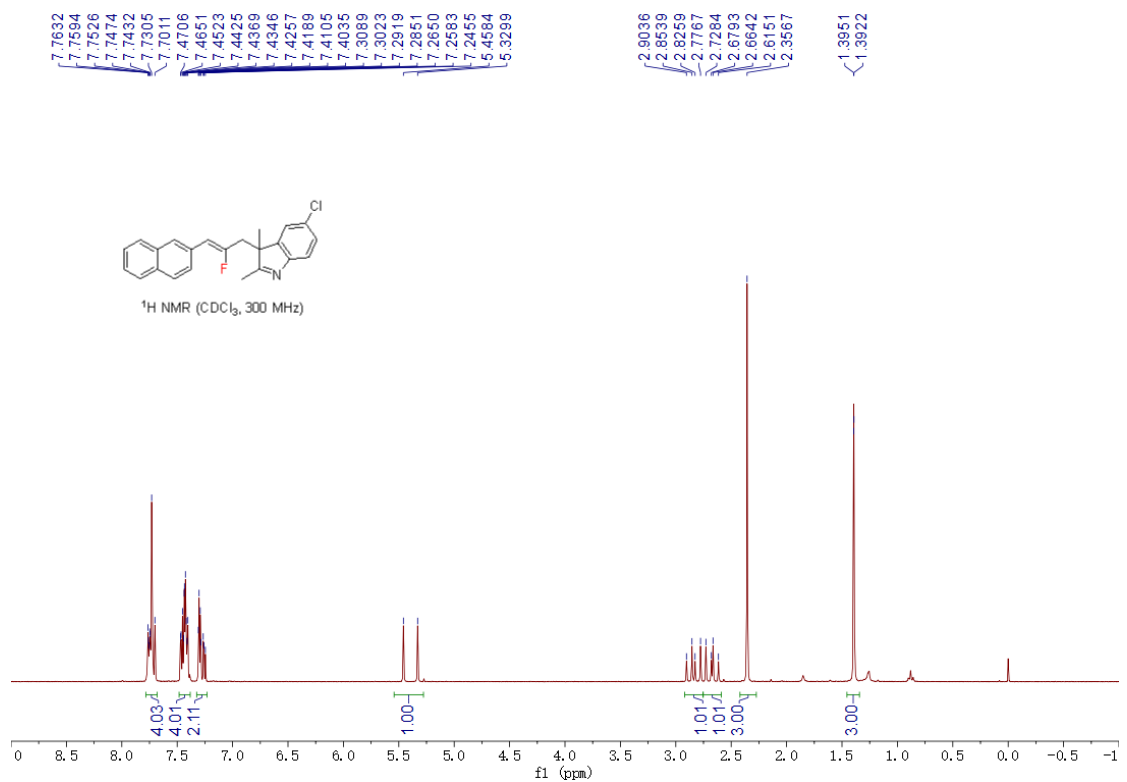
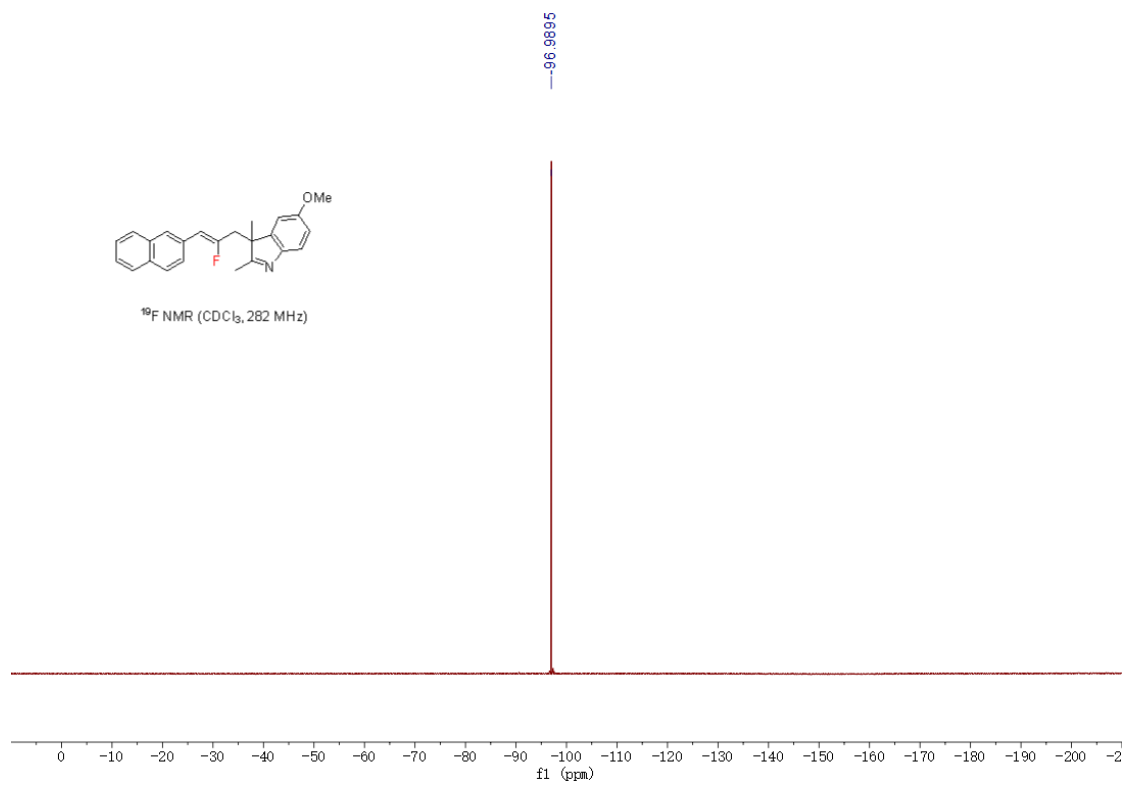


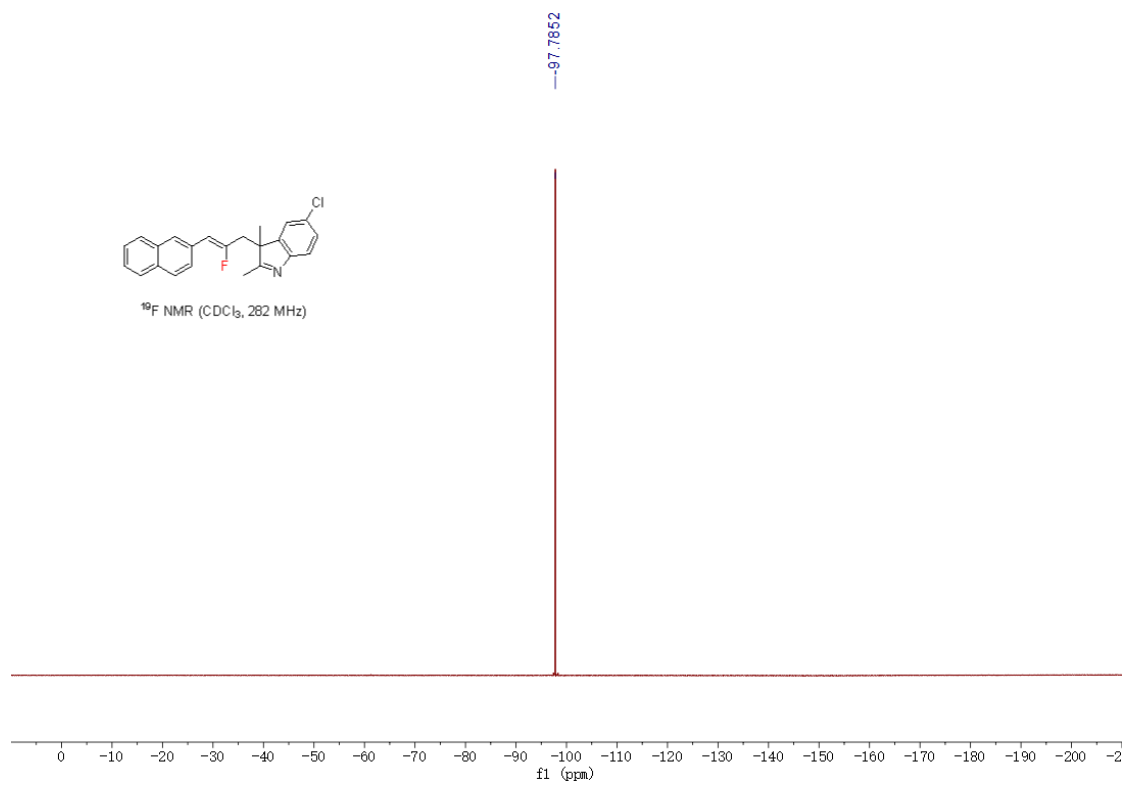
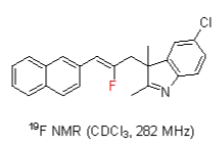
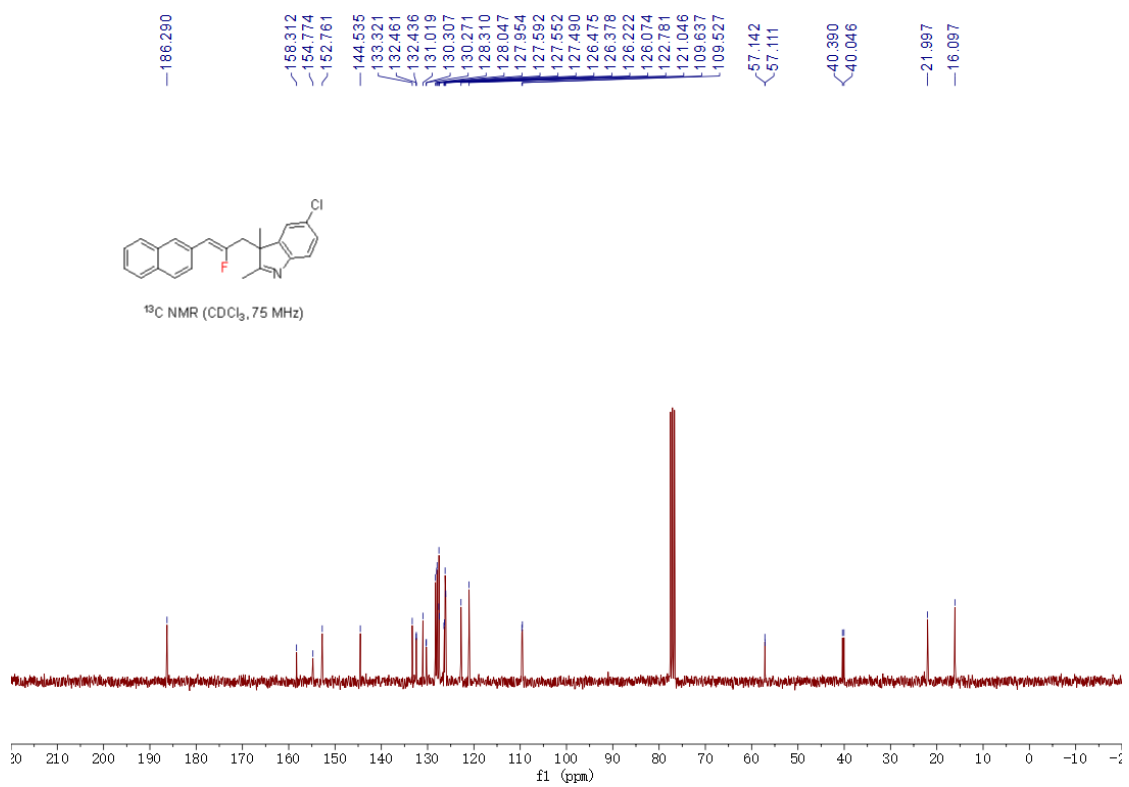
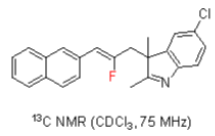


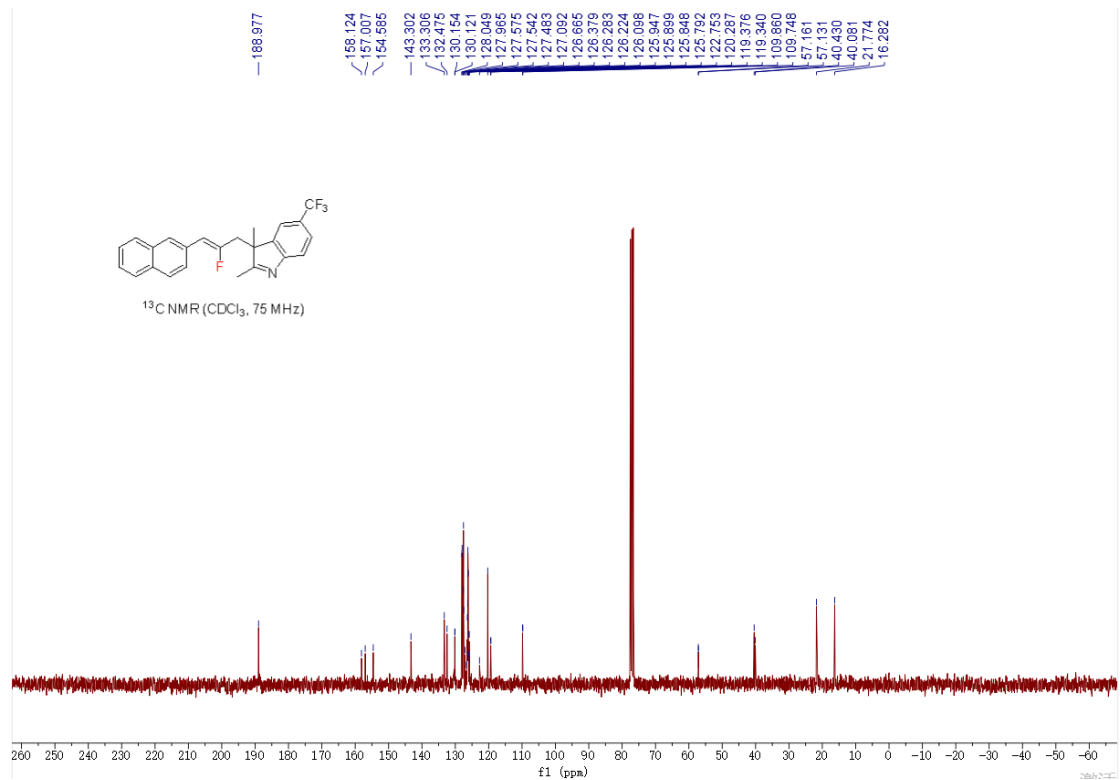
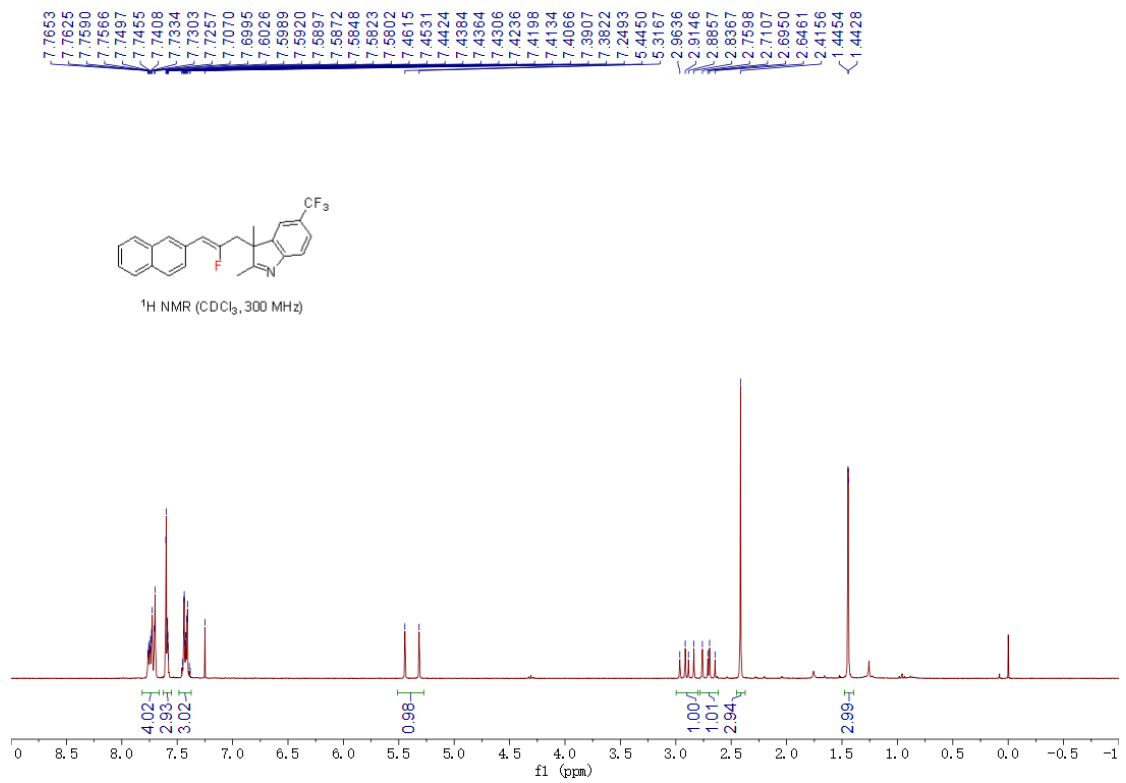


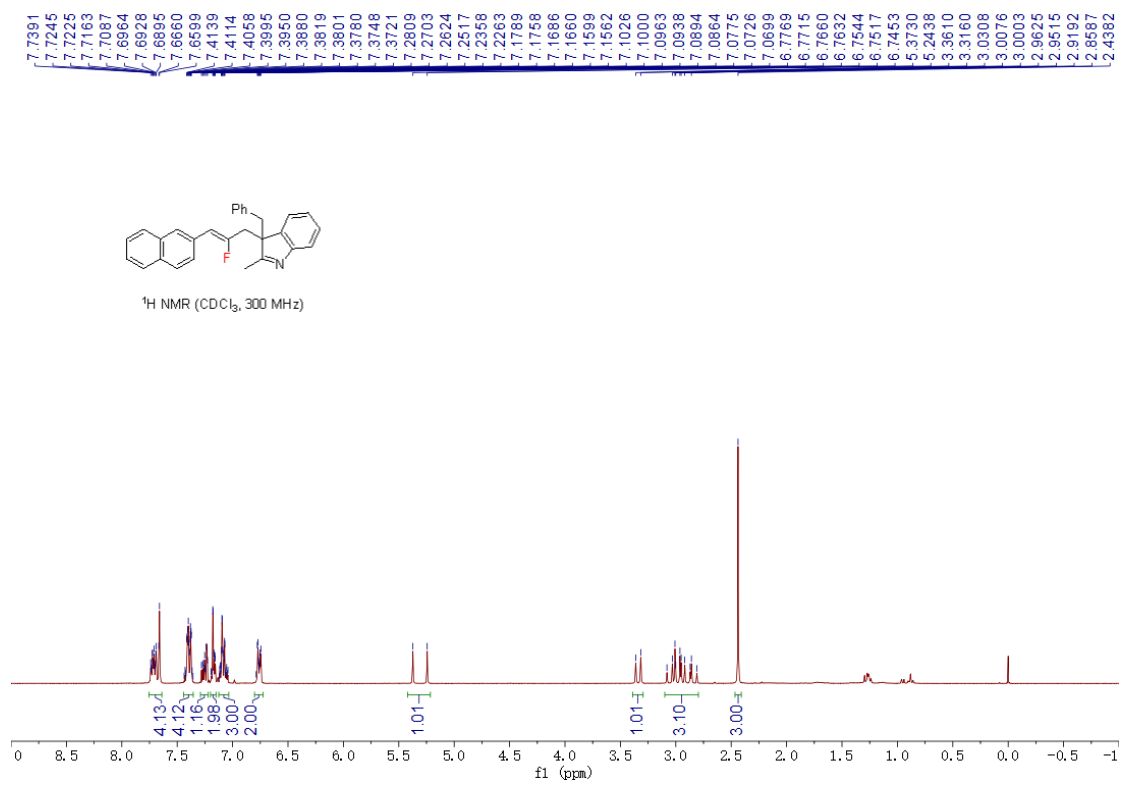
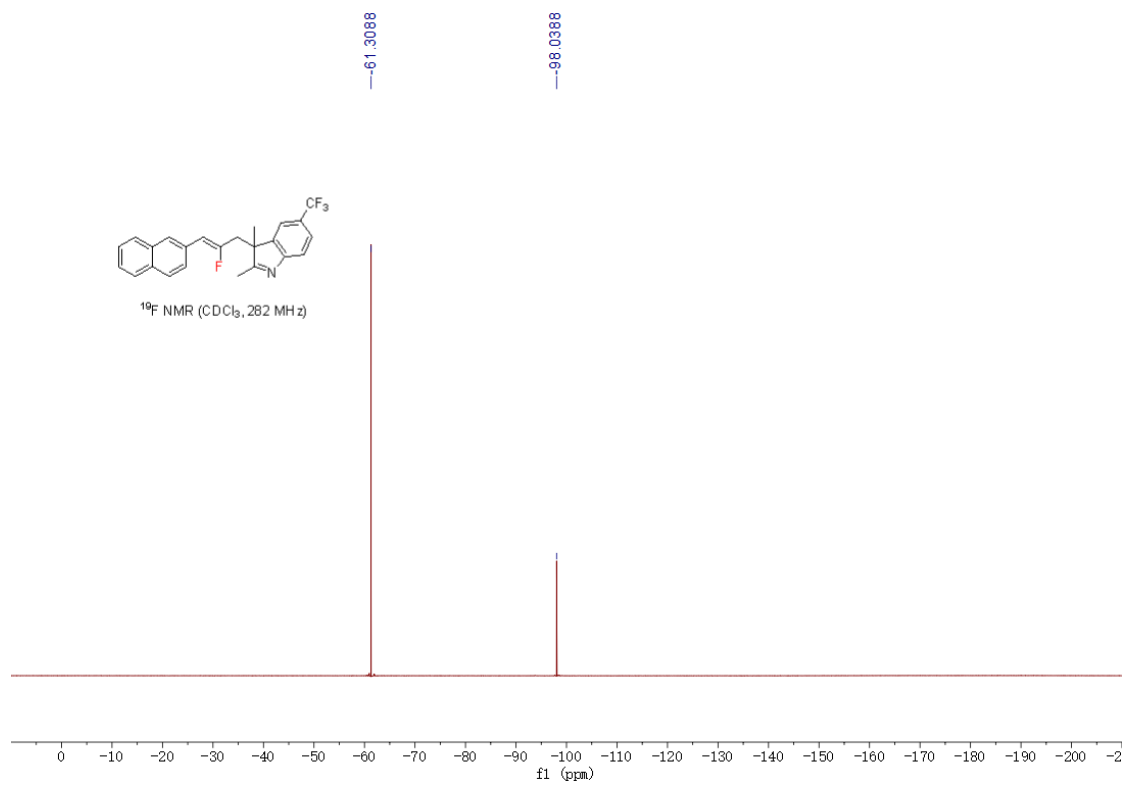


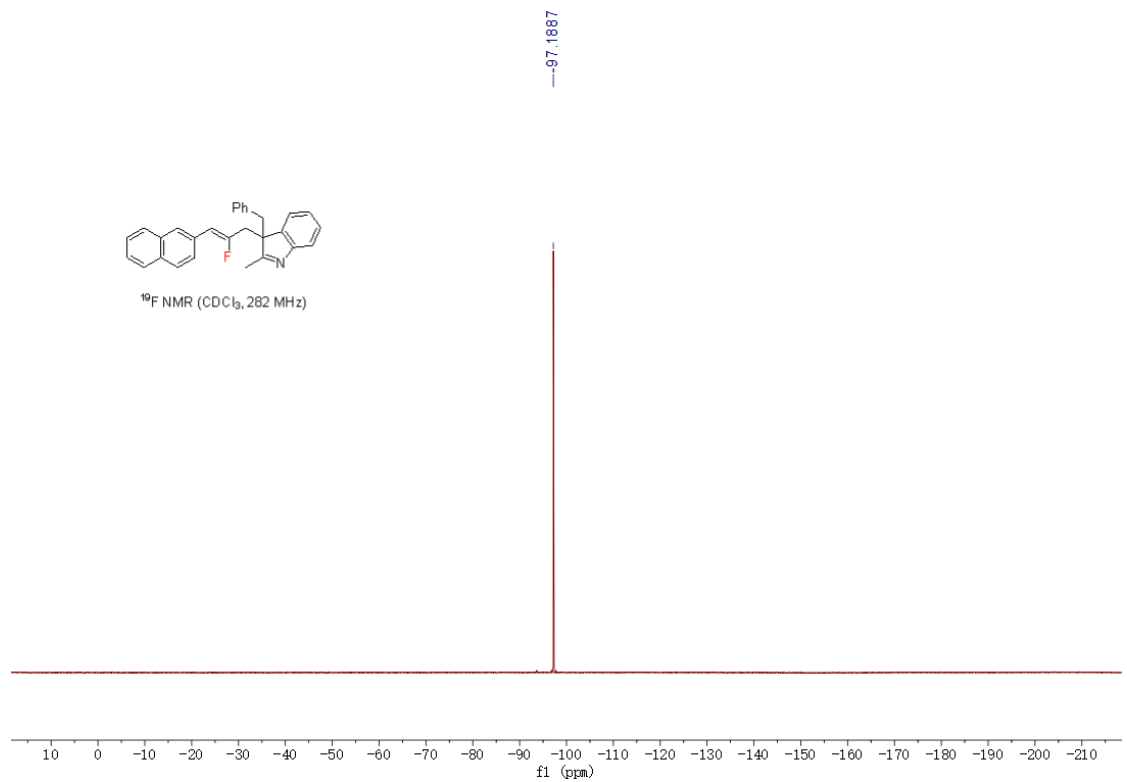
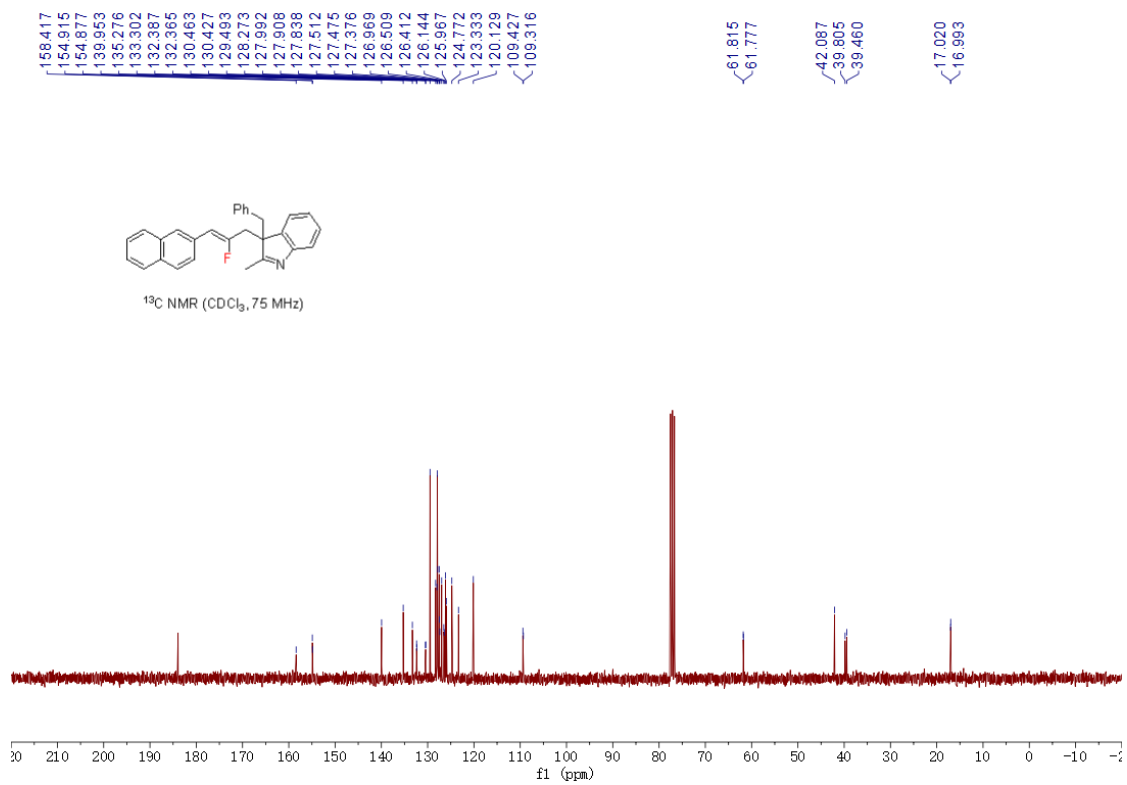


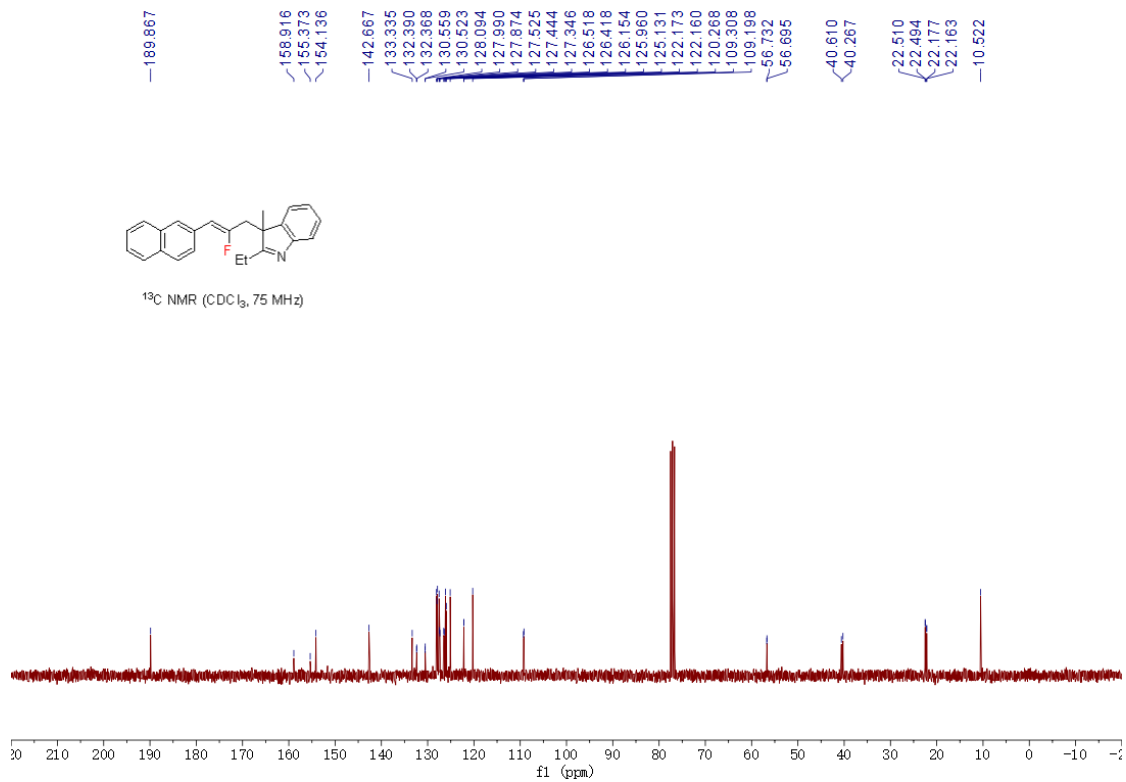
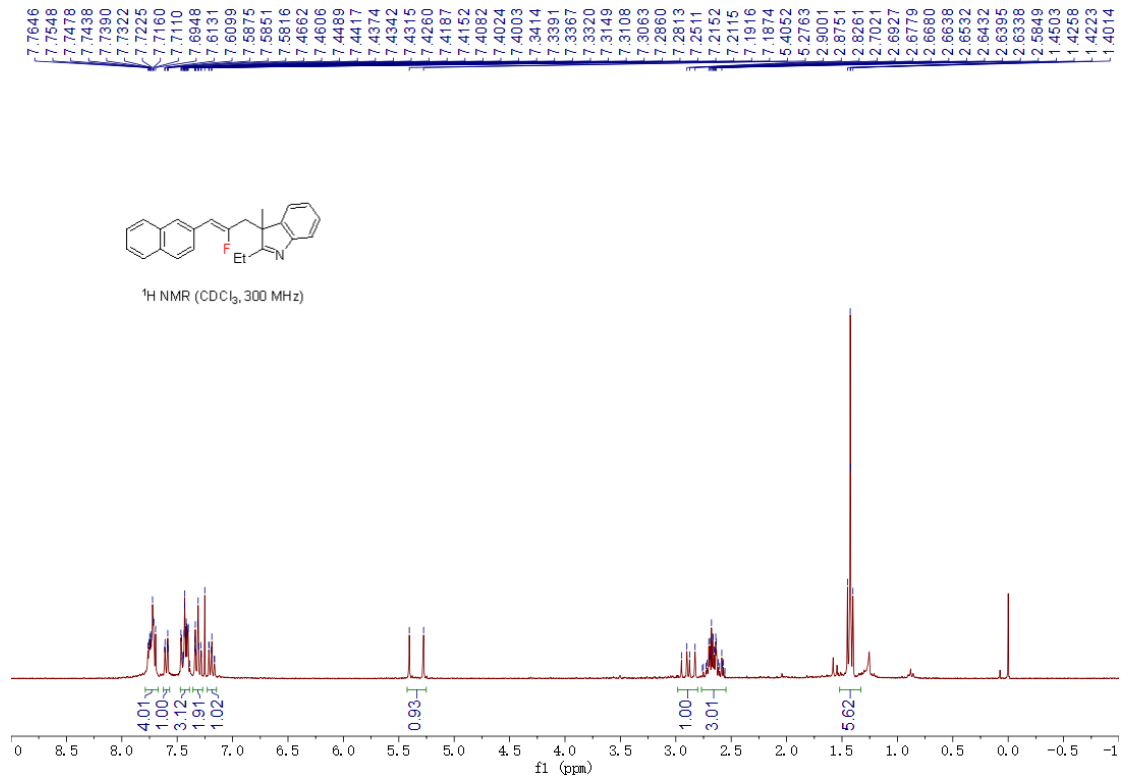


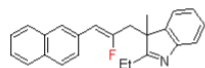




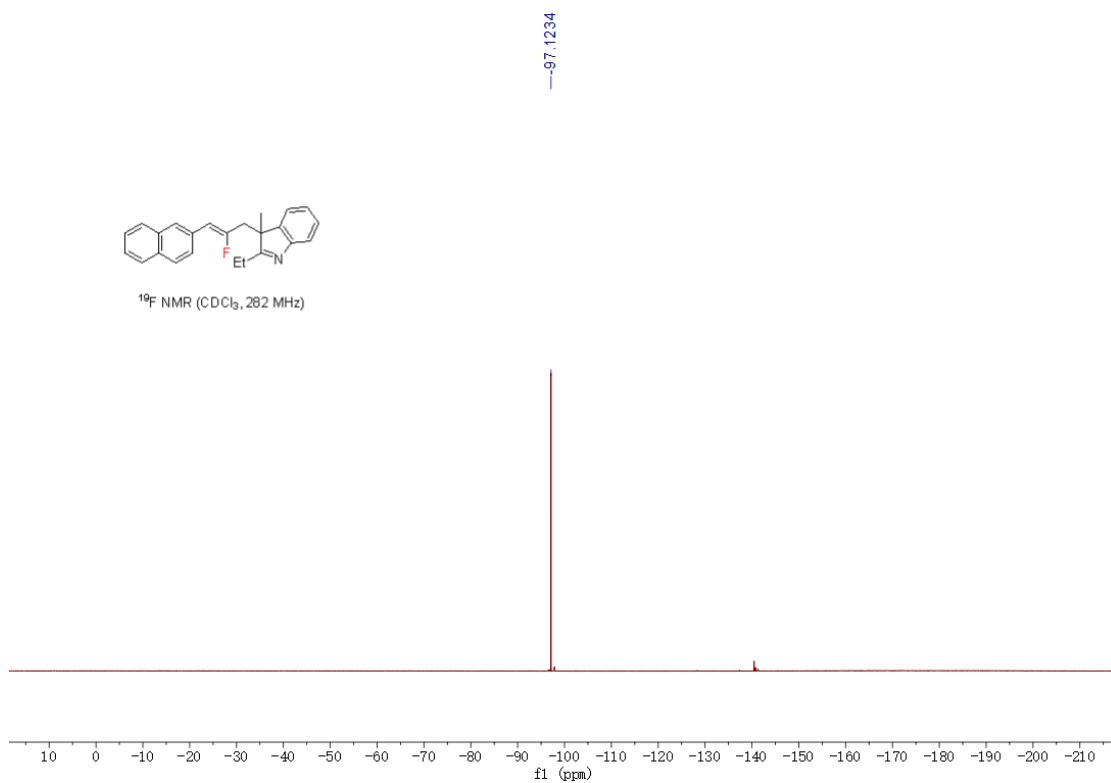




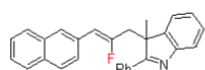




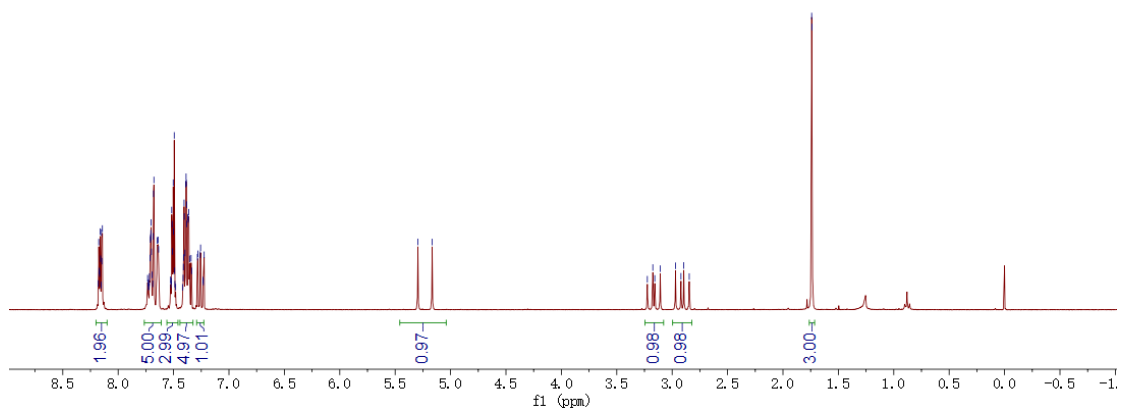
<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)

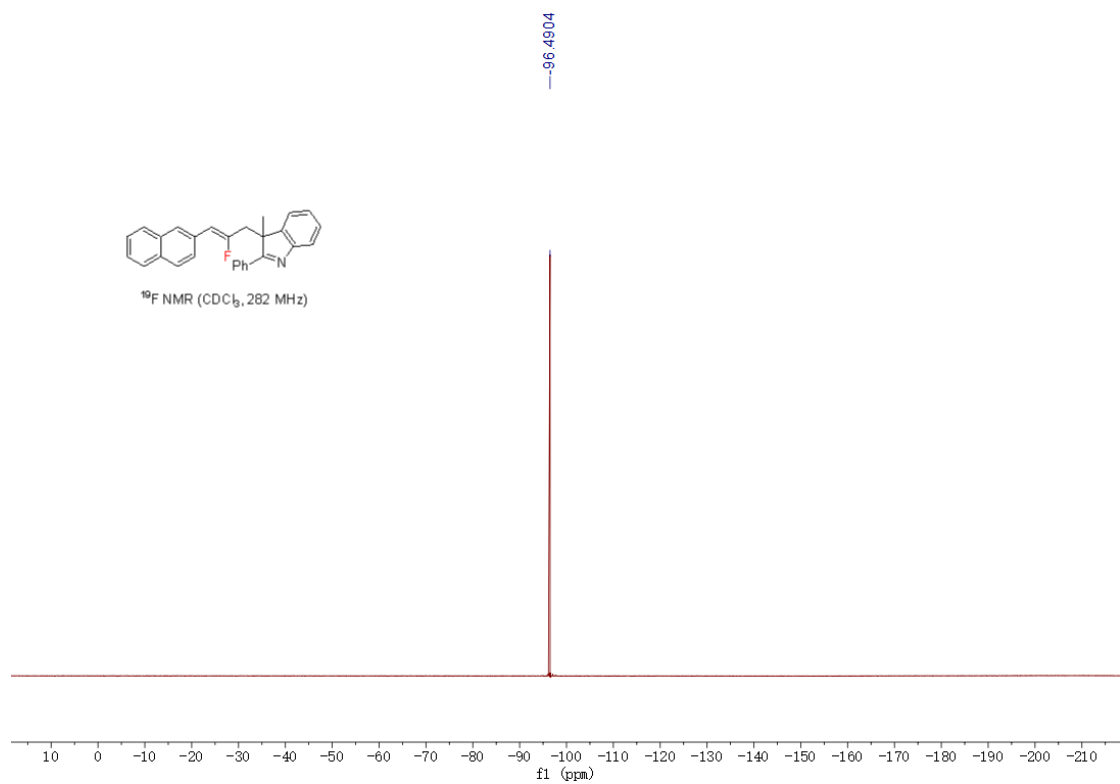
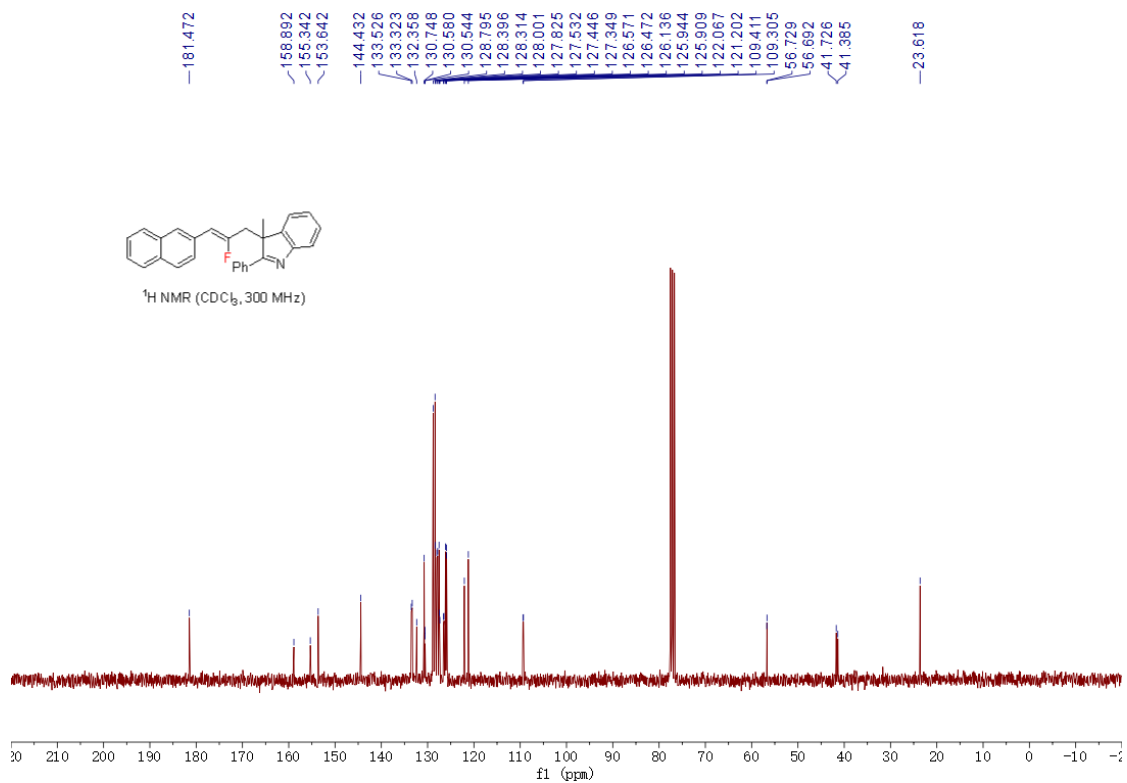


8.1752  
8.1716  
8.1677  
8.1628  
8.1586  
8.1504  
8.1477  
8.1424  
7.7175  
7.7125  
7.7087  
7.7055  
7.7050  
7.7026  
7.7001  
7.6948  
7.6833  
7.6804  
7.6775  
7.6488  
7.6401  
7.6351  
7.5166  
7.5131  
7.5094  
7.5032  
7.5003  
7.4939  
7.4903  
7.4135  
7.4112  
7.4088  
7.4051  
7.4032  
7.3967  
7.3904  
7.3870  
7.3846  
7.3825  
7.3801  
7.3726  
7.3668  
7.3621  
7.3557  
7.3416  
7.3369  
7.2845  
7.2806  
7.2599  
7.2562  
7.2237  
5.2946  
5.1661  
3.1747  
3.1076  
2.9699  
2.9205  
2.8951  
2.8458  
-1.7410  
-1.7377

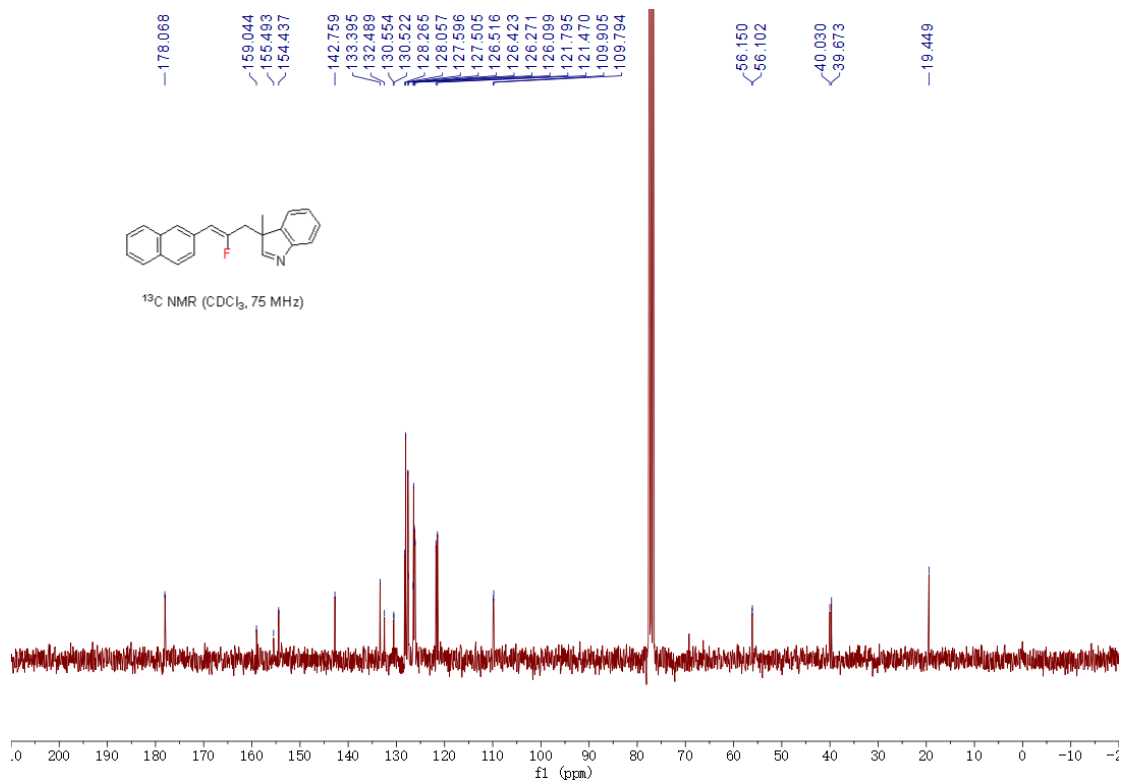
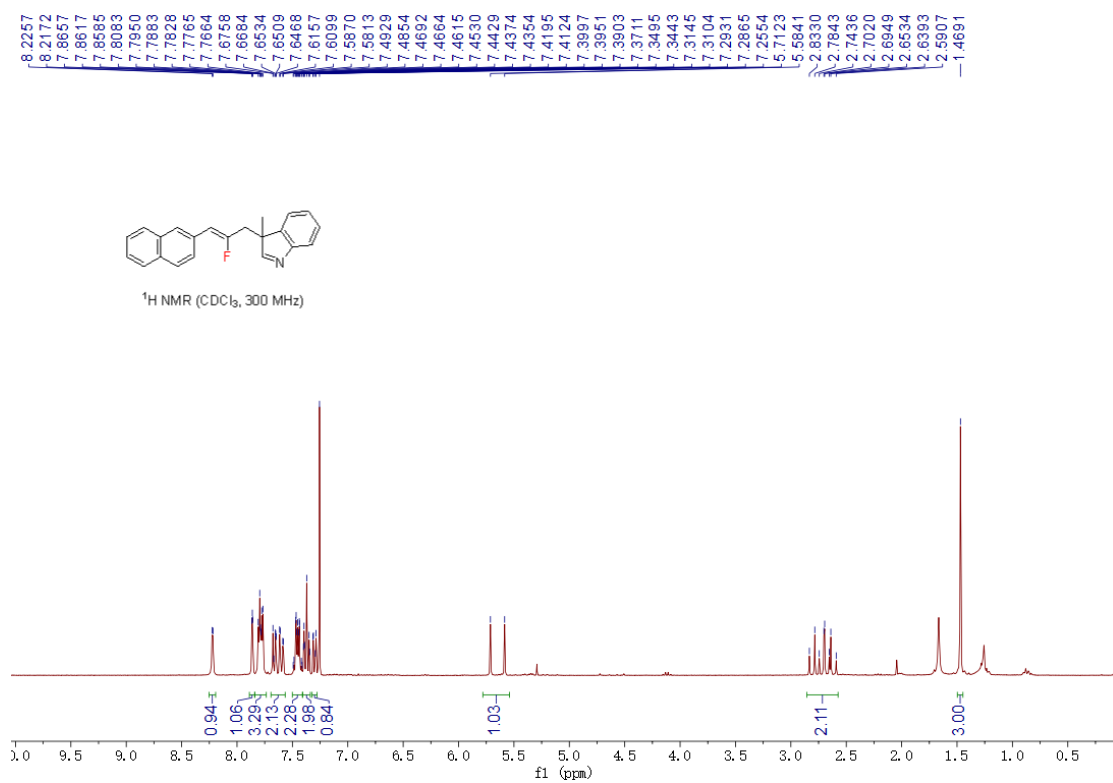


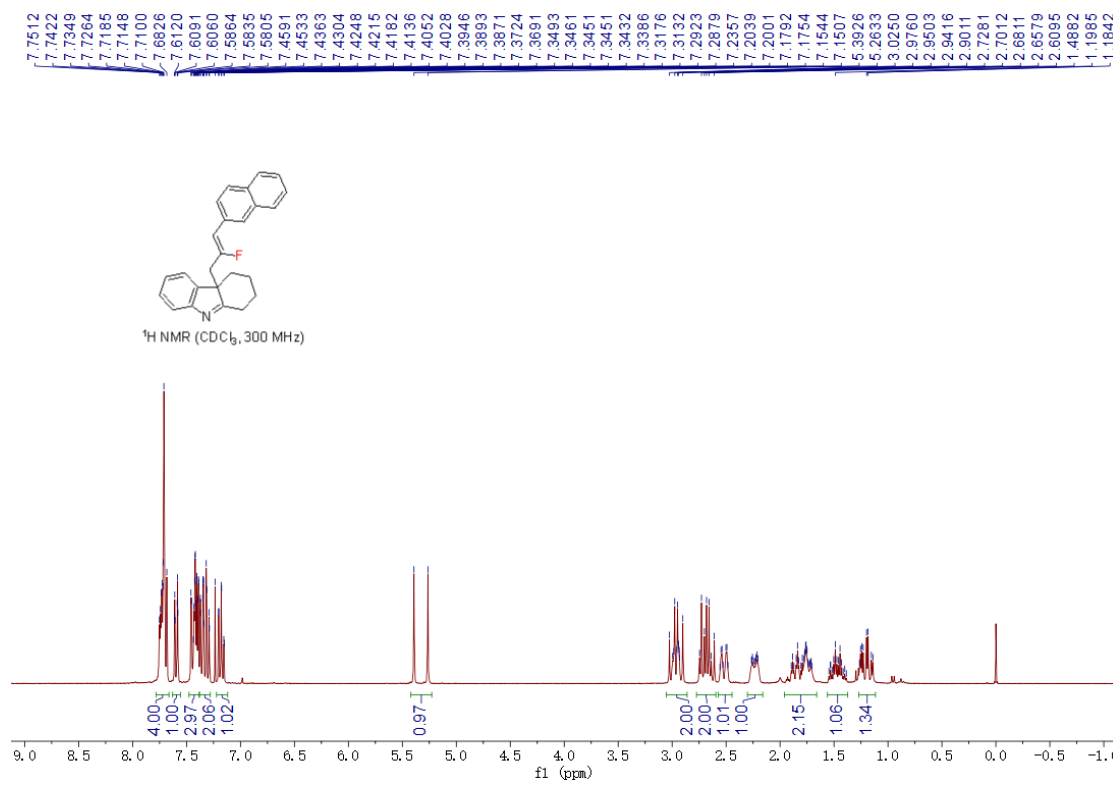
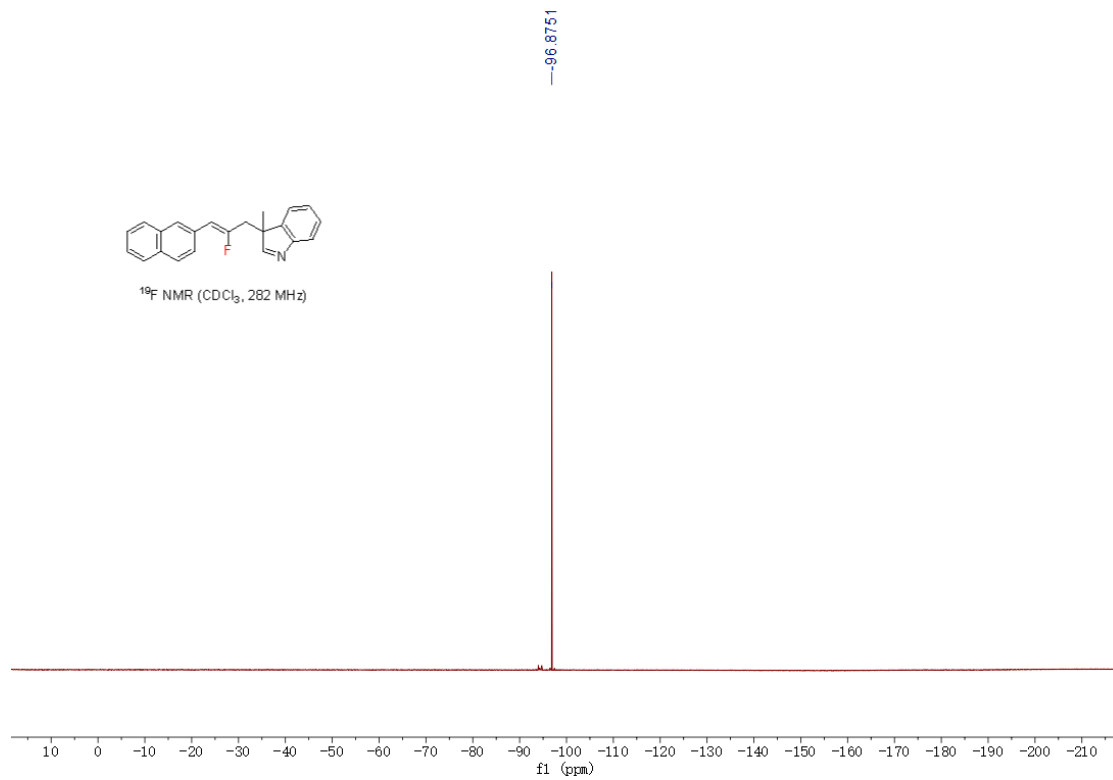
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

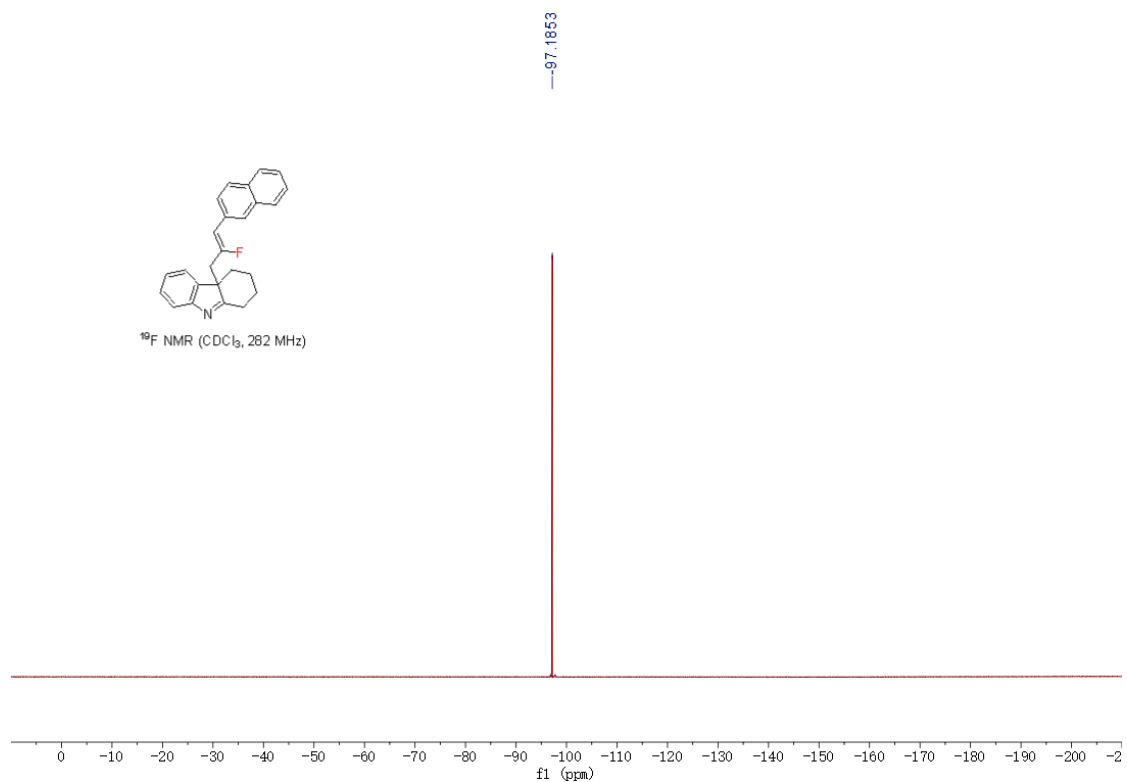
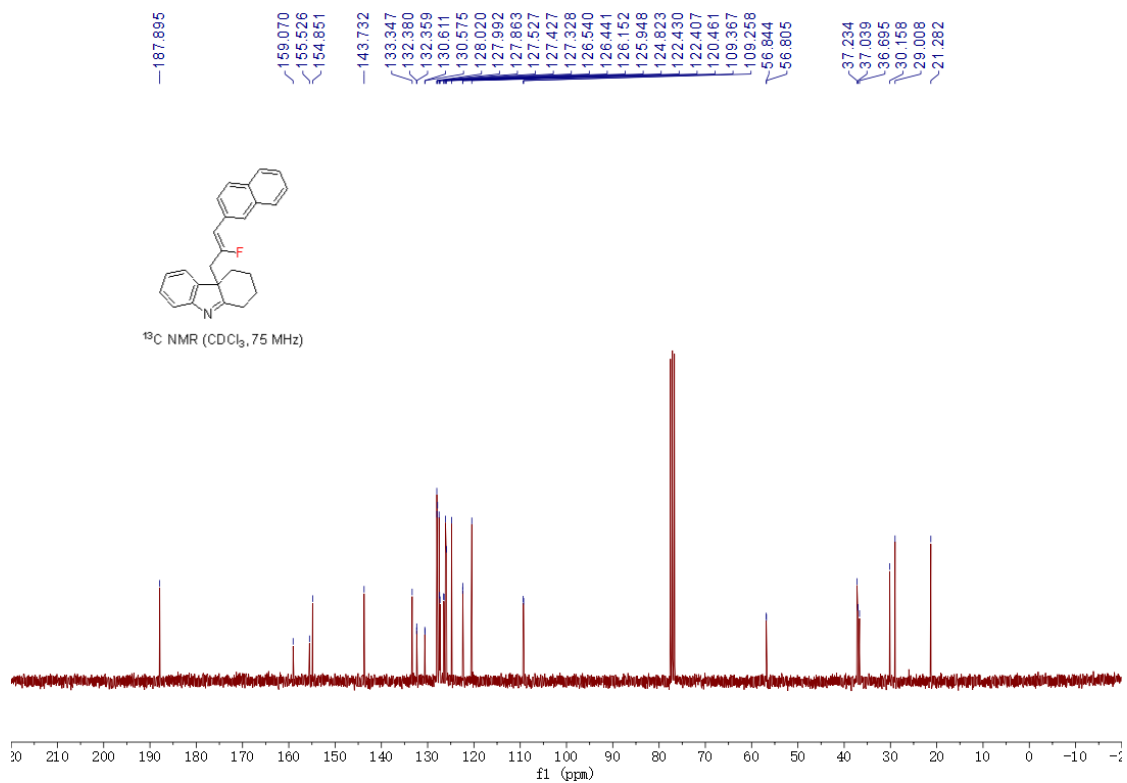


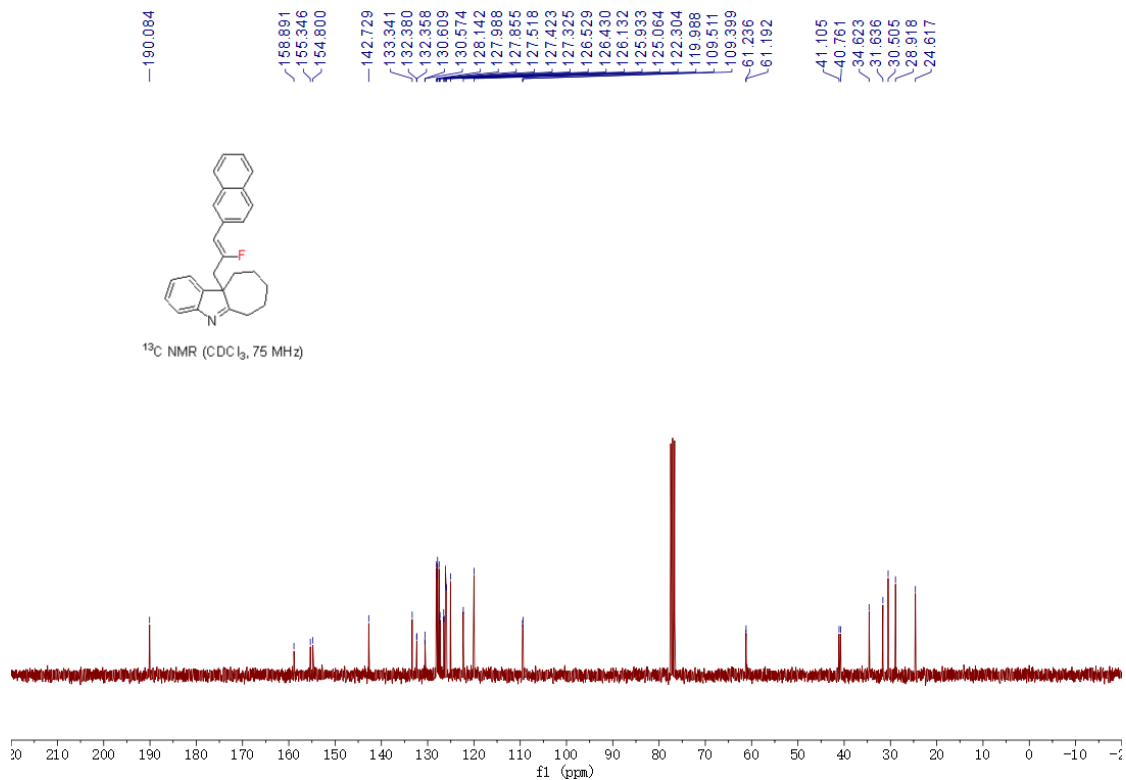
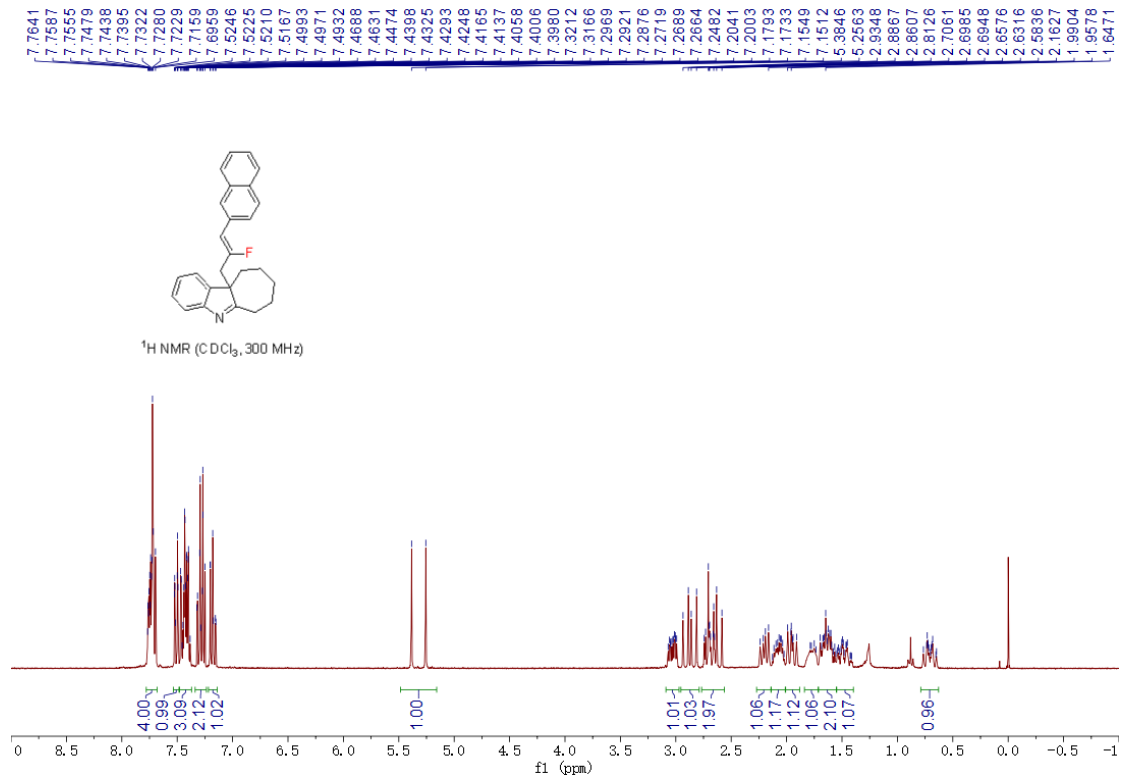


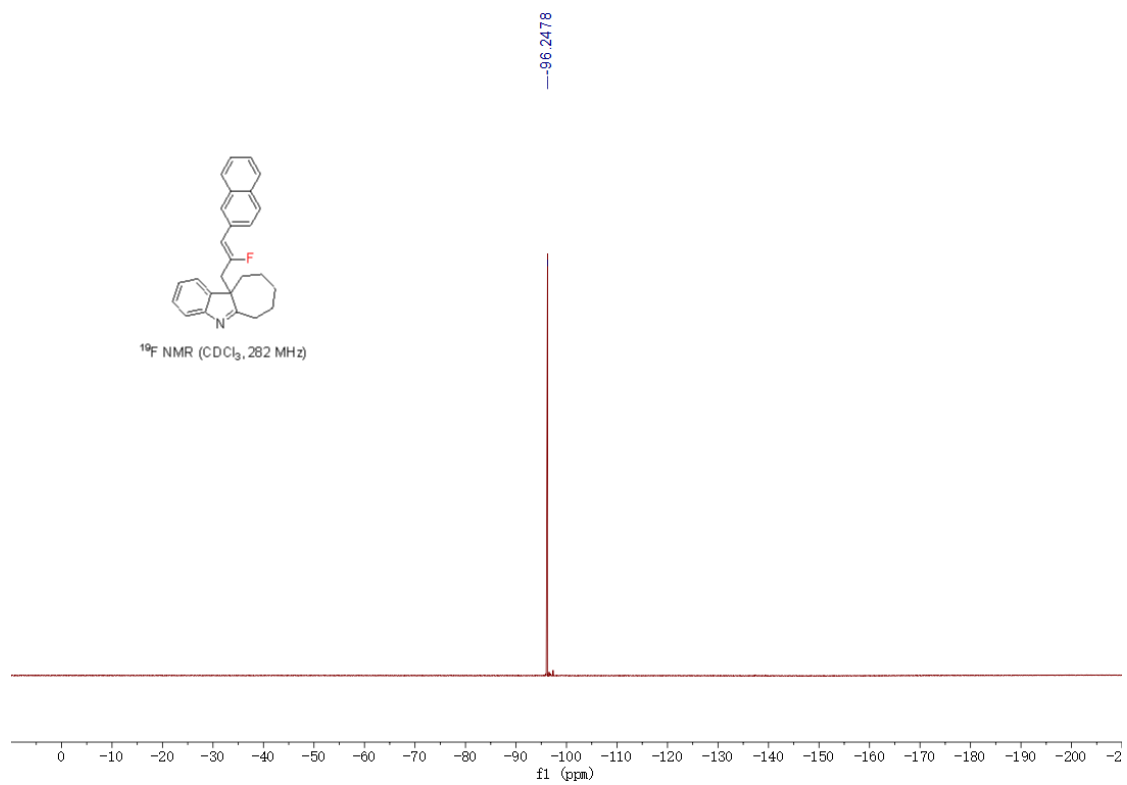




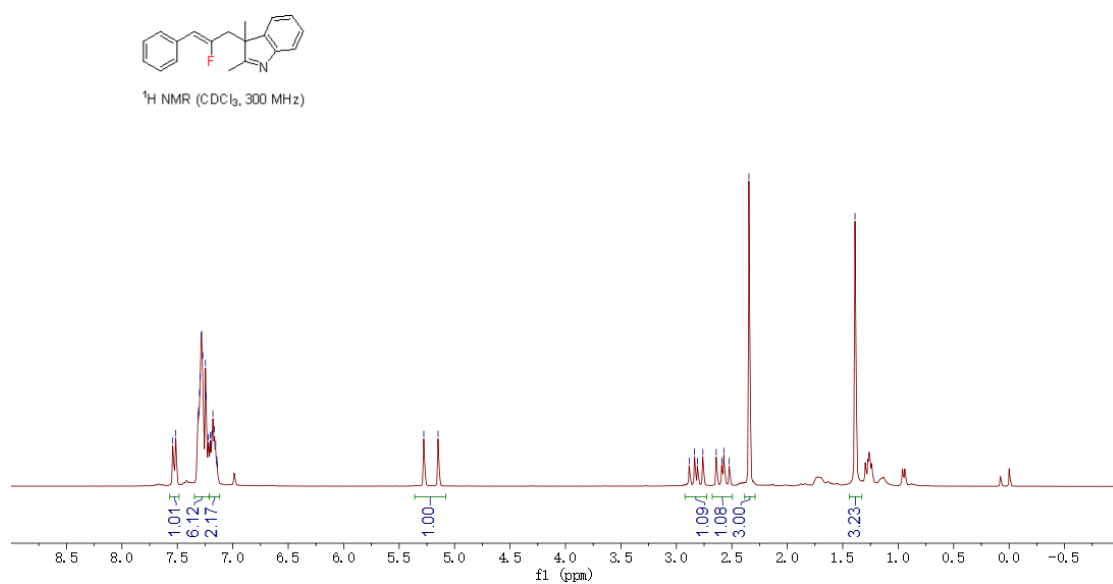


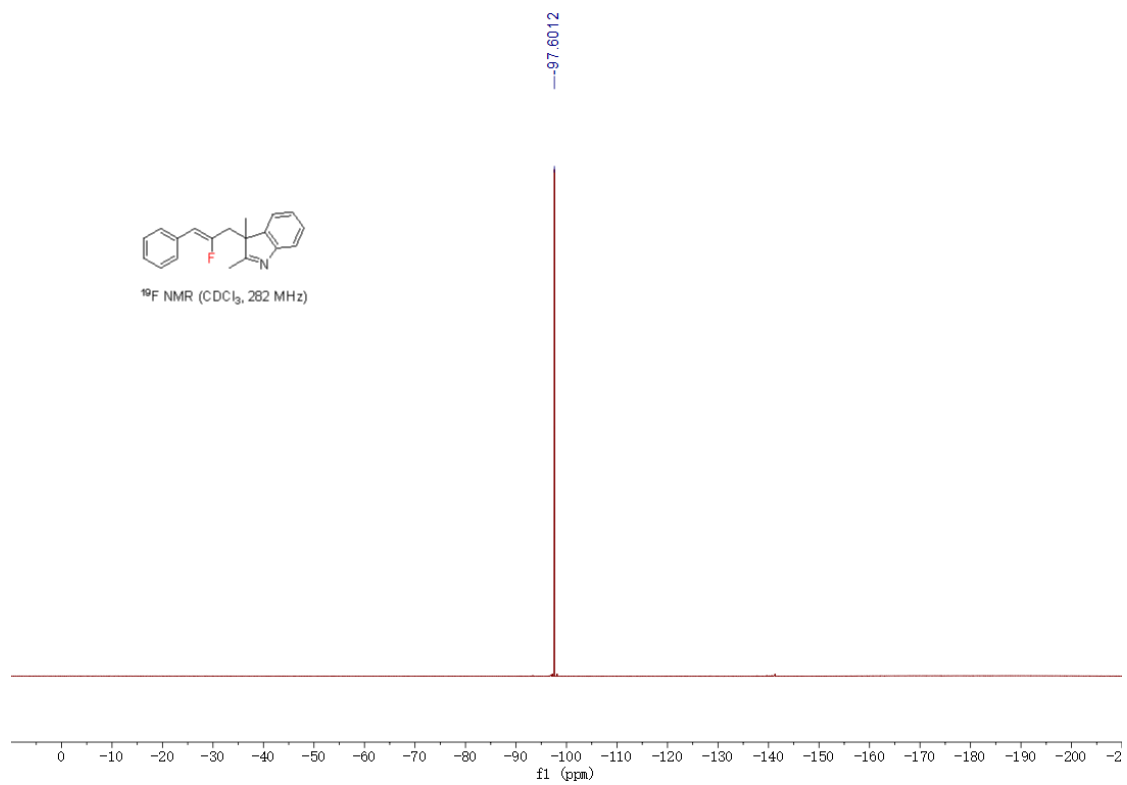
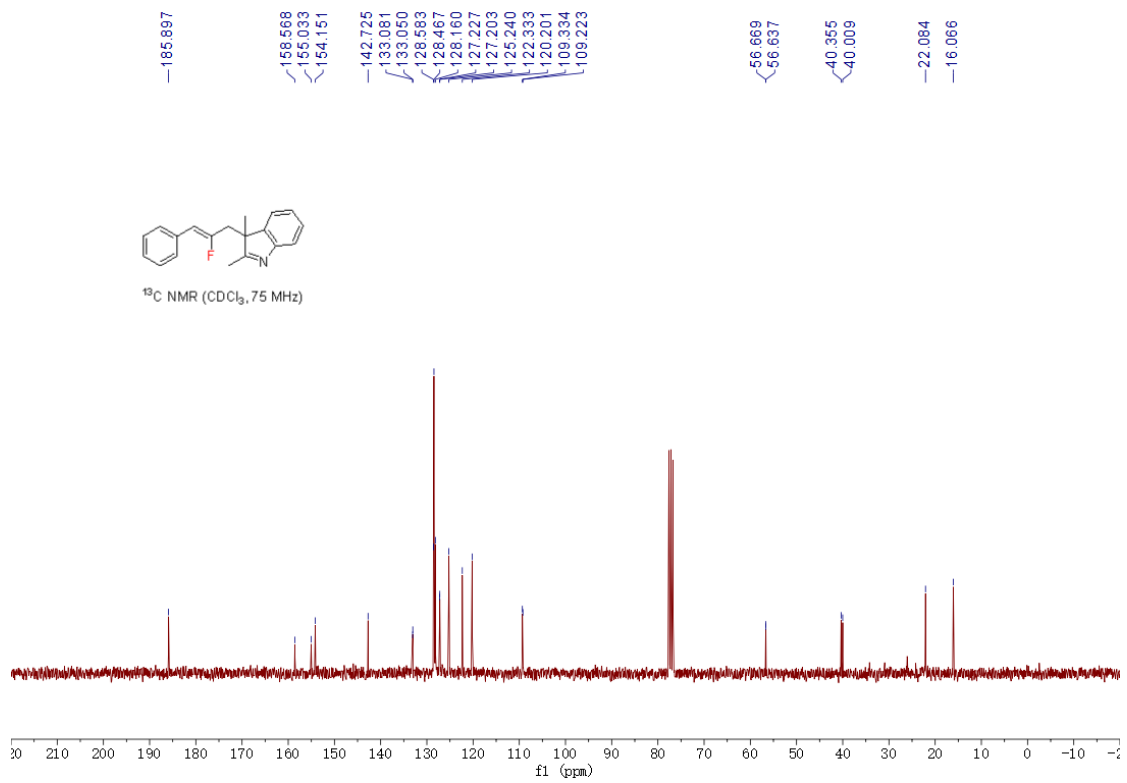


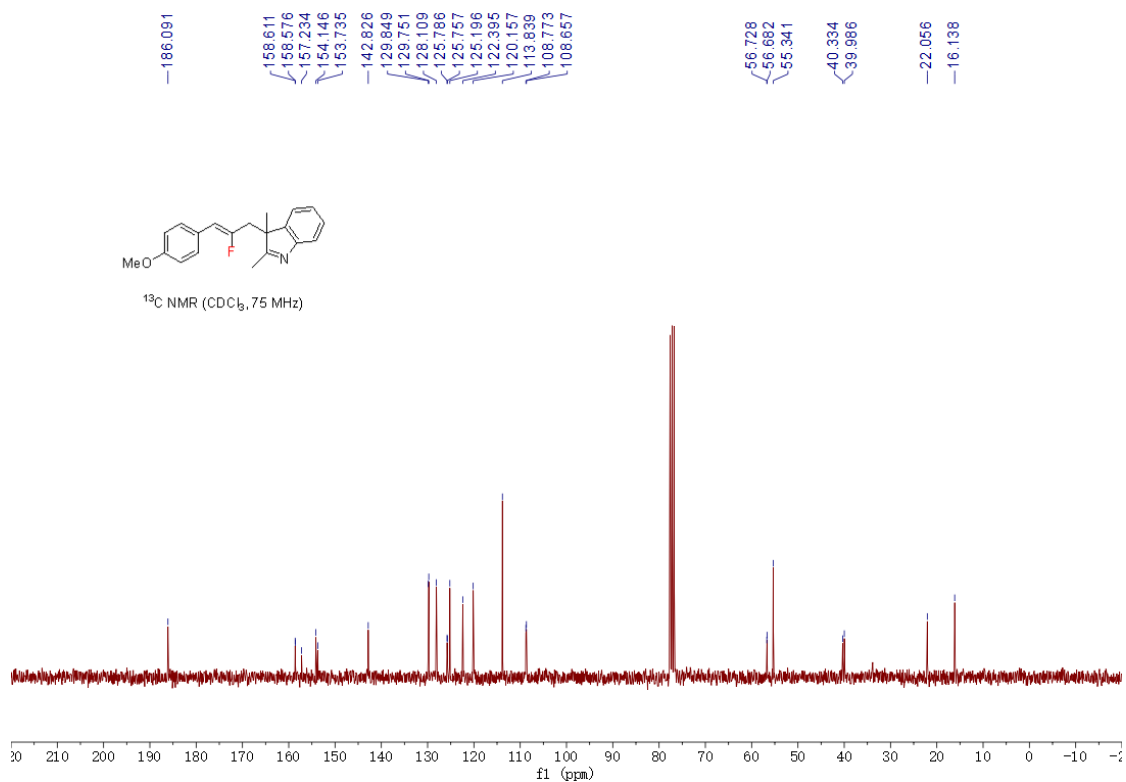
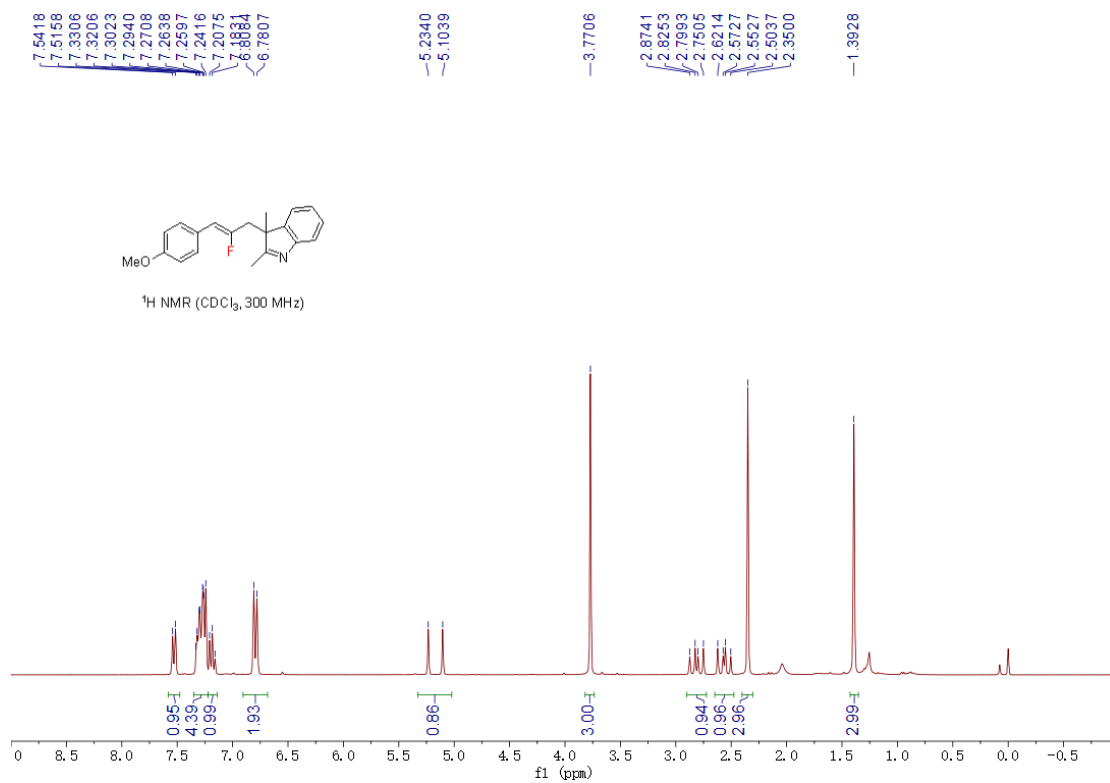


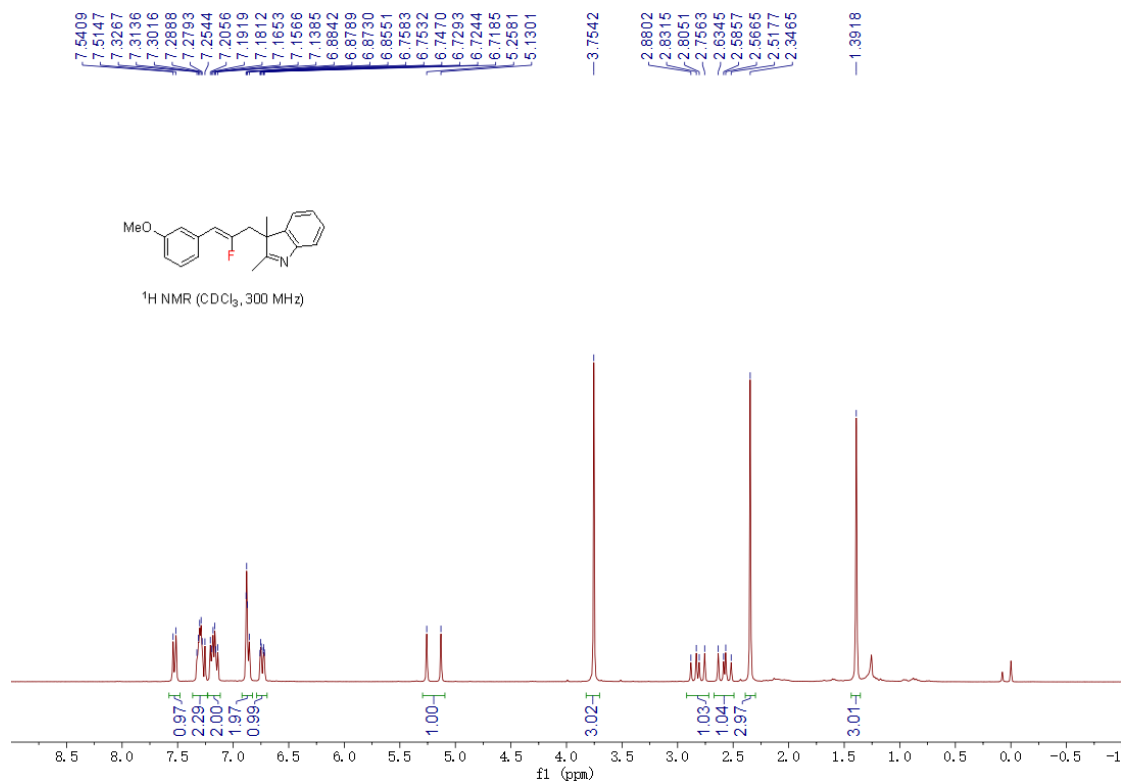
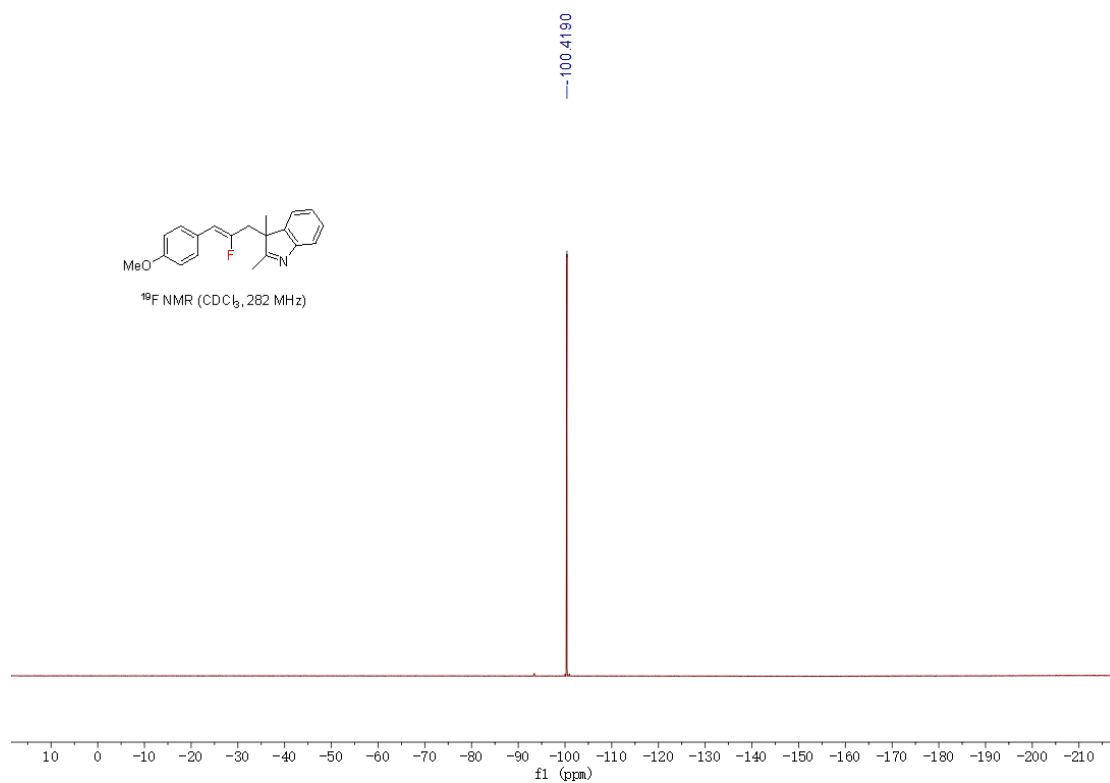


7.5420  
 7.5143  
 7.3149  
 7.3084  
 7.3000  
 7.2952  
 7.2863  
 7.2807  
 7.2709  
 7.2465  
 7.2405  
 7.2203  
 7.2042  
 7.1956  
 7.1899  
 7.1796  
 7.1650  
 7.1542  
 7.1433  
 7.1365  
 -5.2778  
 -5.1492  
 2.8846  
 2.8366  
 2.8100  
 2.7612  
 2.6406  
 2.5911  
 2.5722  
 2.5238  
 2.3461  
 -1.3891



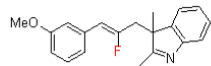




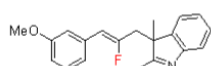
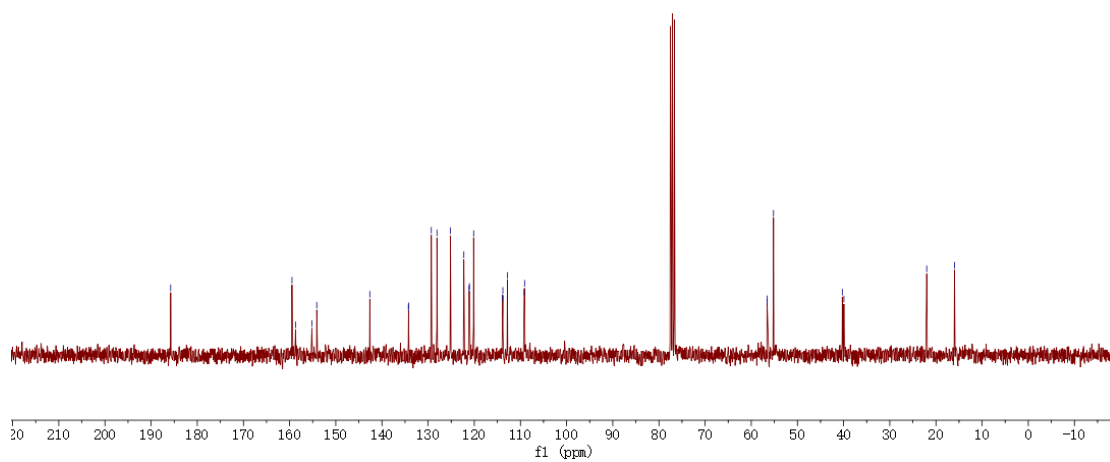




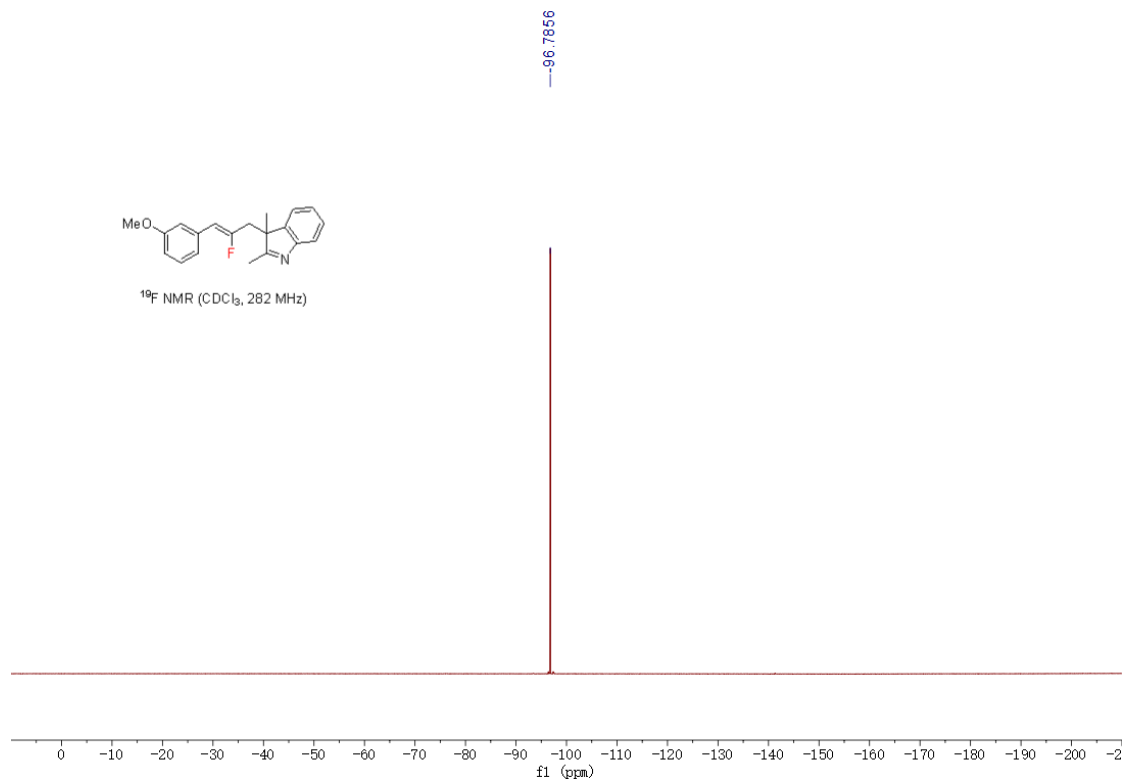
185.763  
 159.487  
 158.715  
 155.171  
 154.122  
 142.631  
 134.271  
 134.240  
 129.308  
 128.088  
 122.264  
 121.144  
 121.051  
 120.142  
 113.917  
 113.810  
 112.835  
 109.208  
 109.104  
 56.570  
 56.537  
 55.186  
 40.281  
 39.935  
 22.001  
 15.988

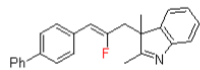
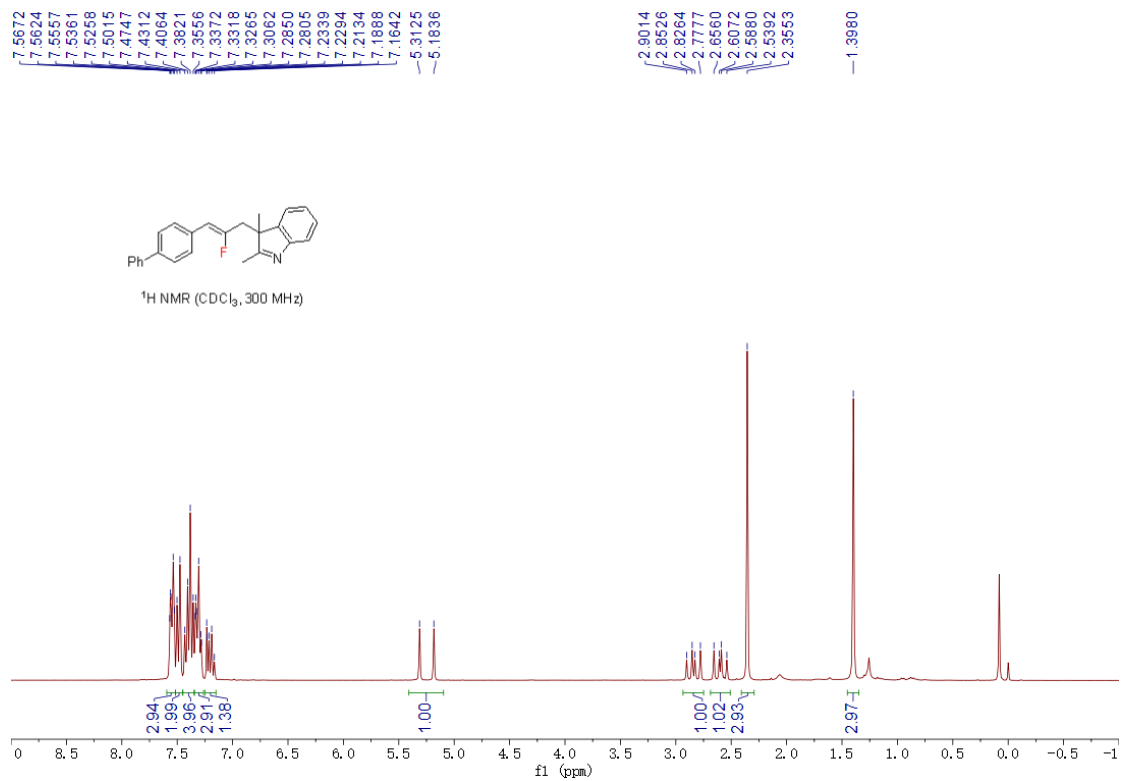


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

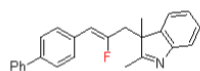
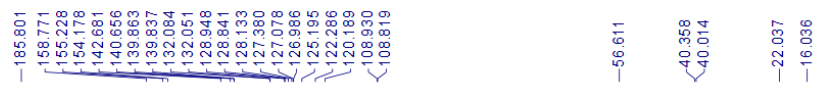


<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)

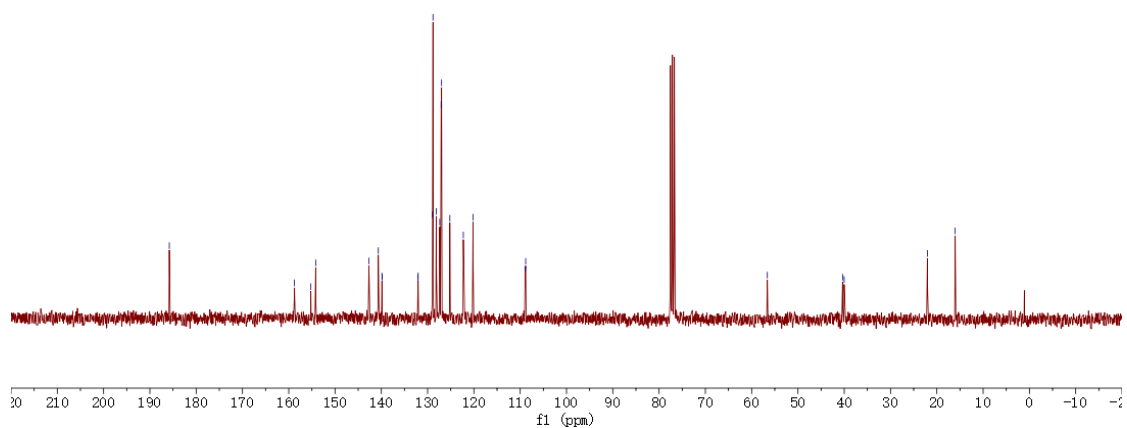


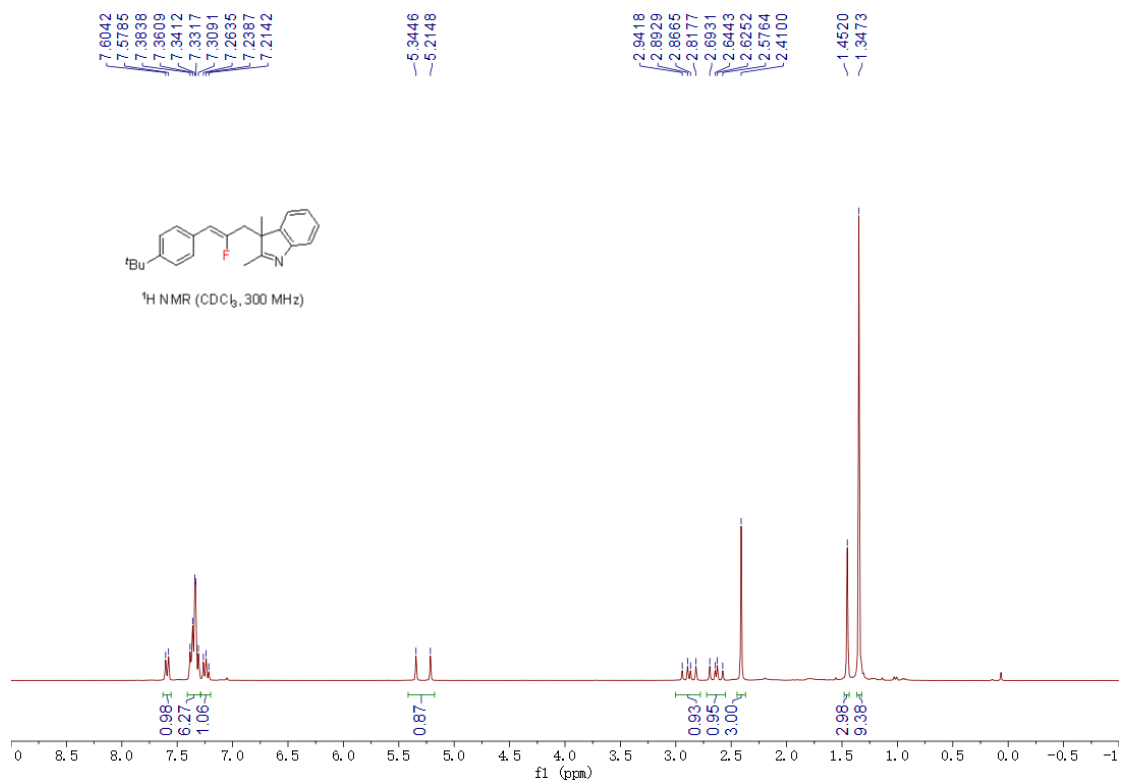
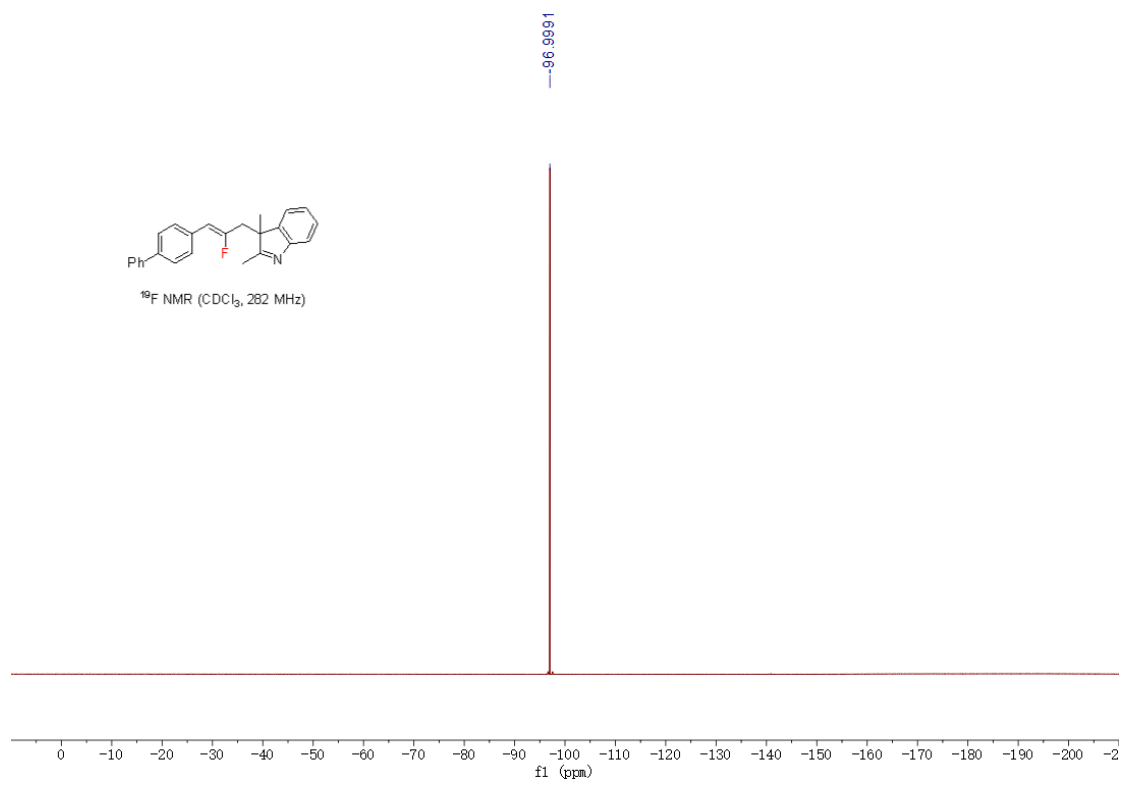


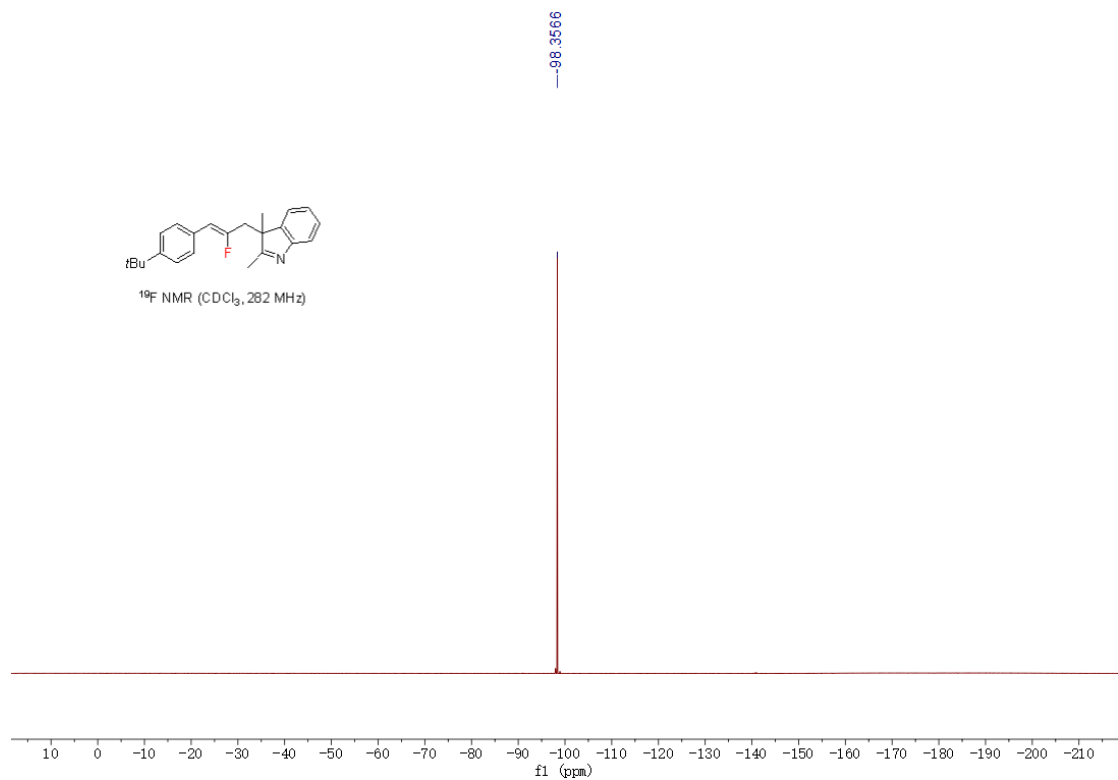
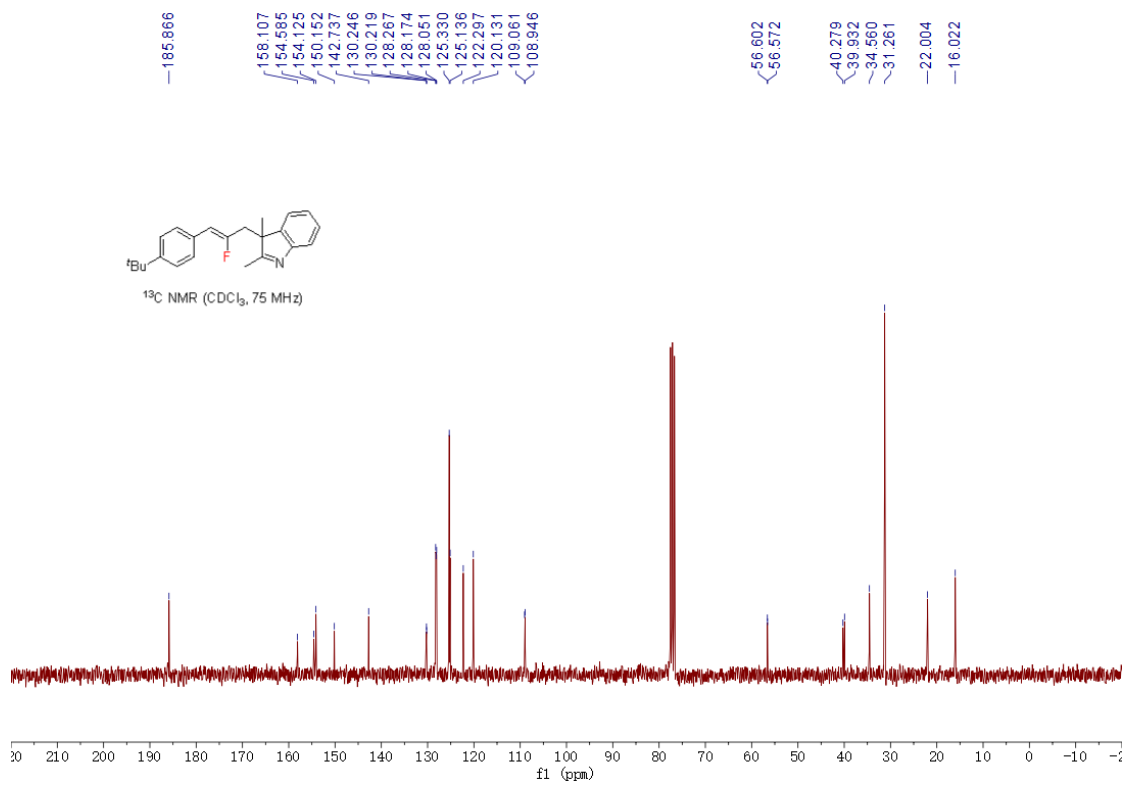
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

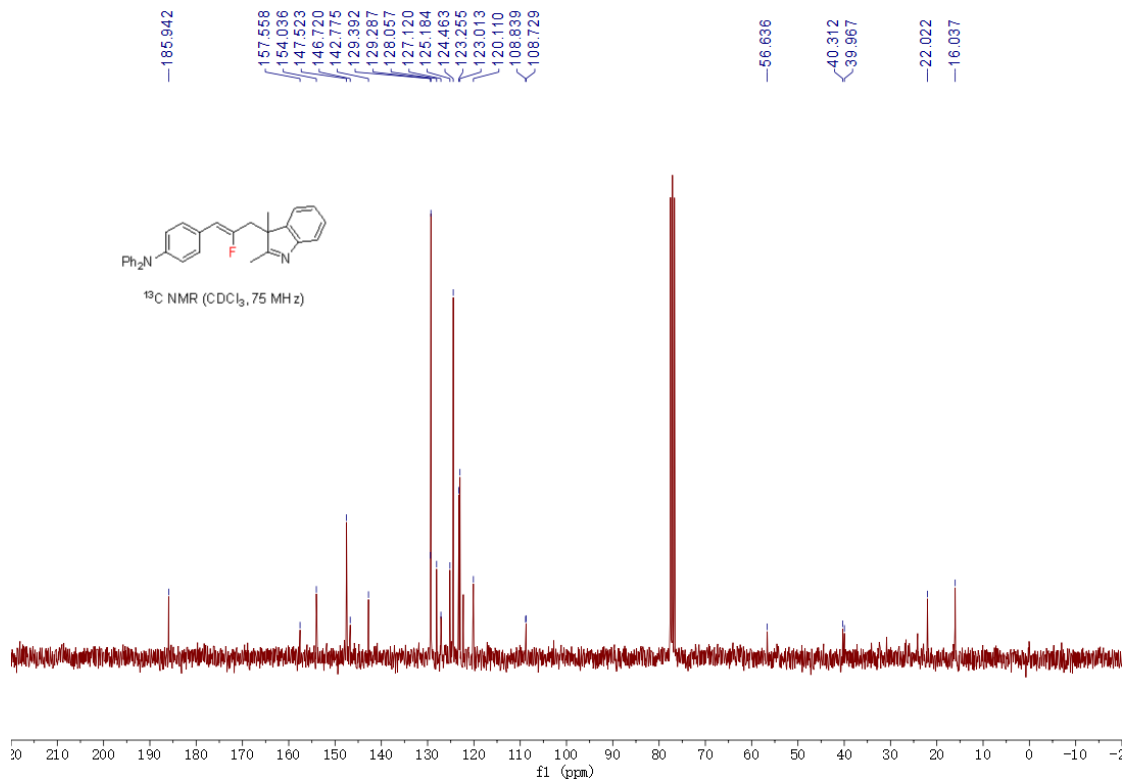
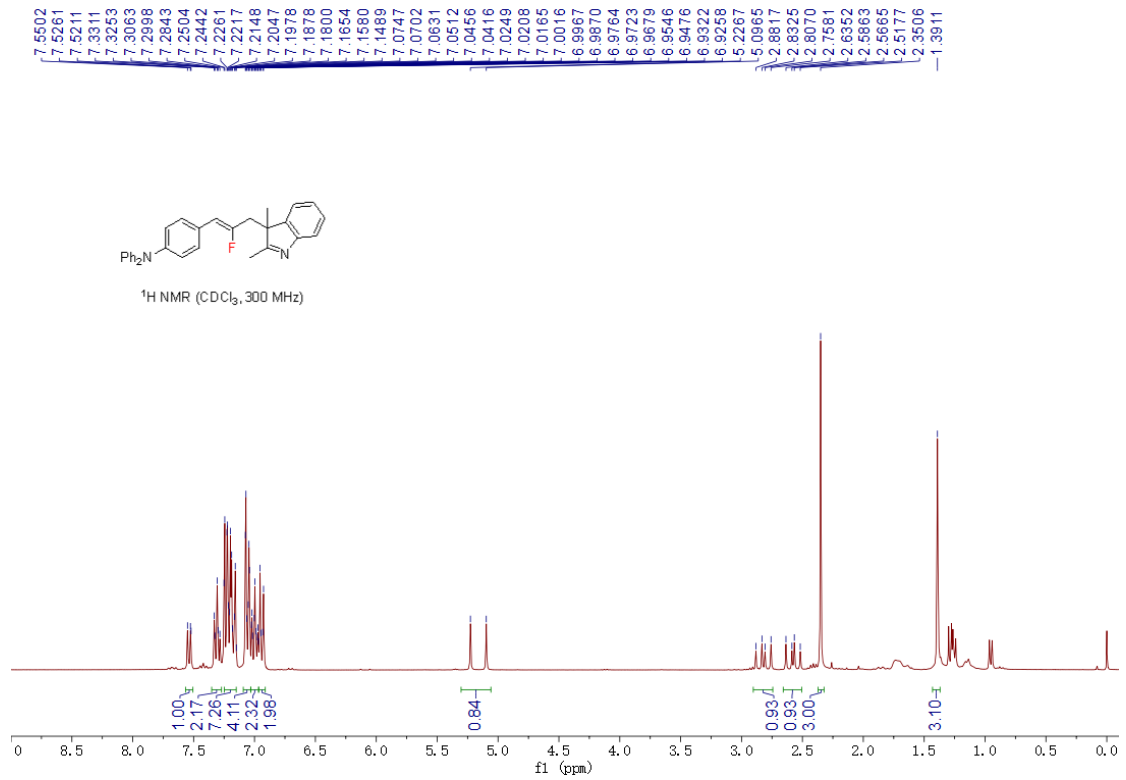


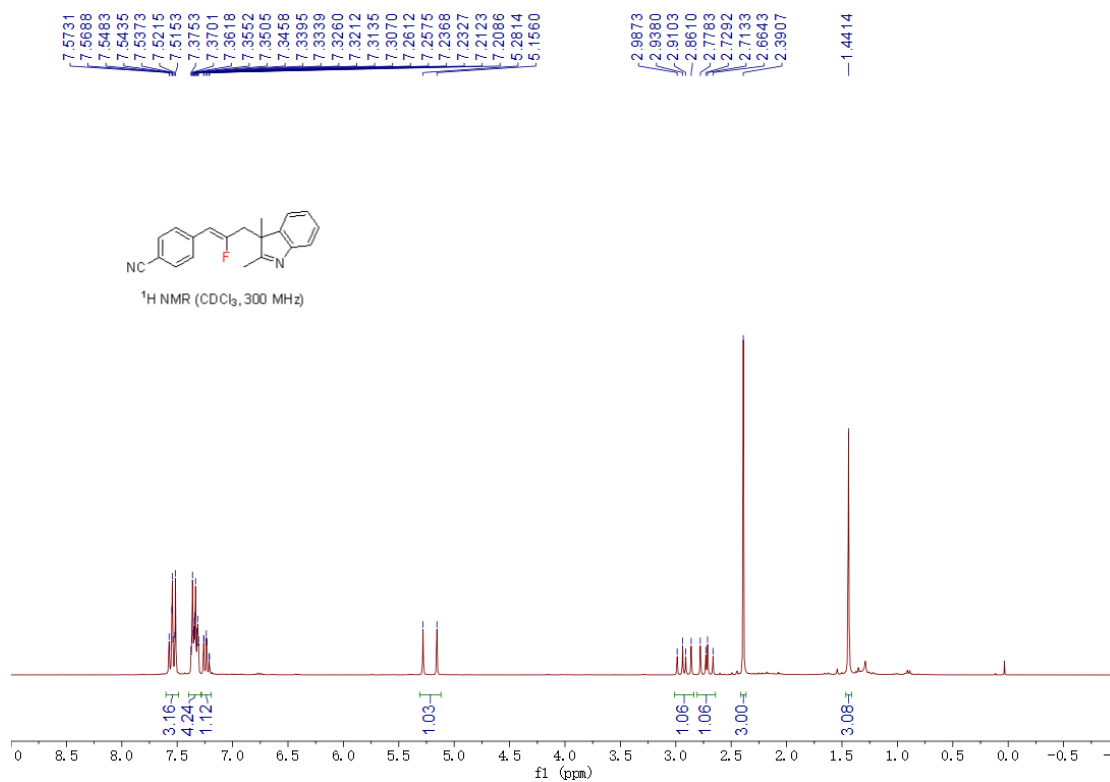
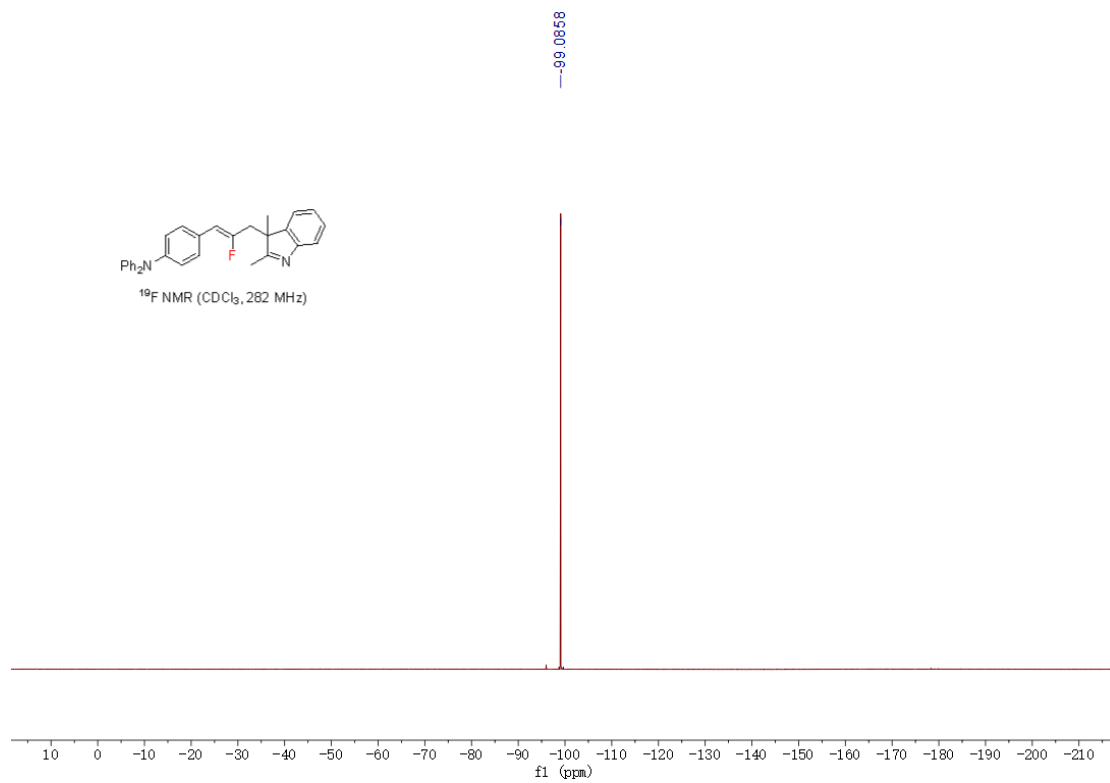
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

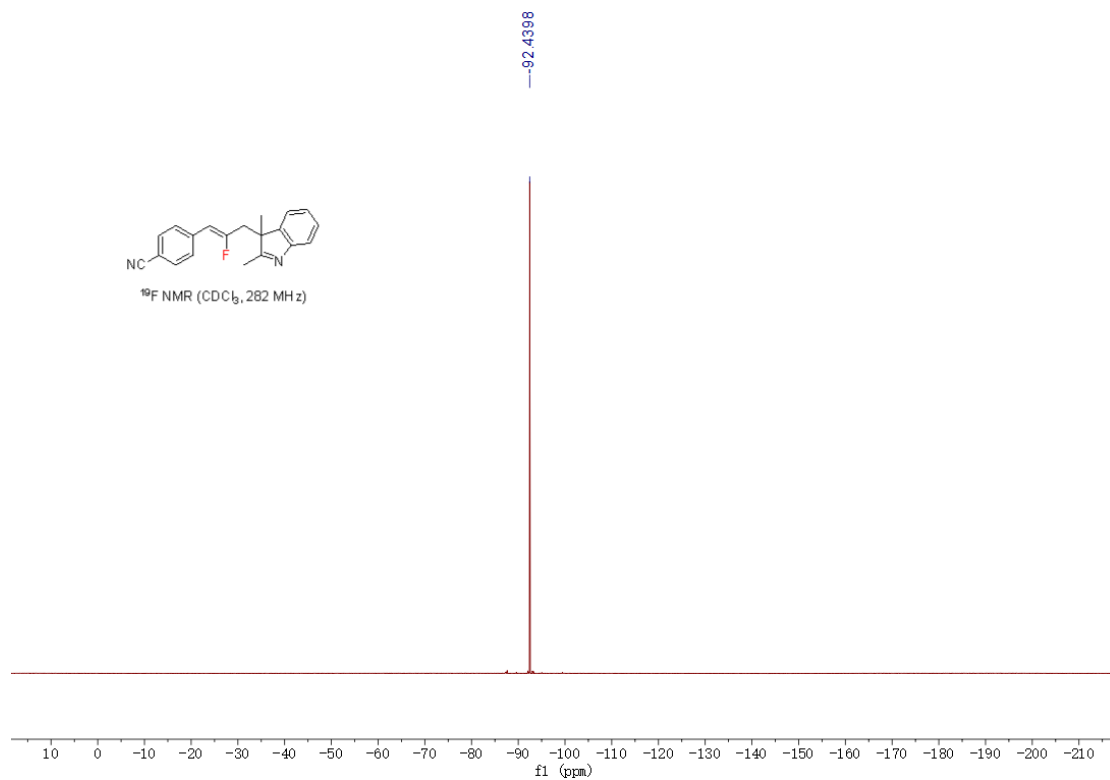
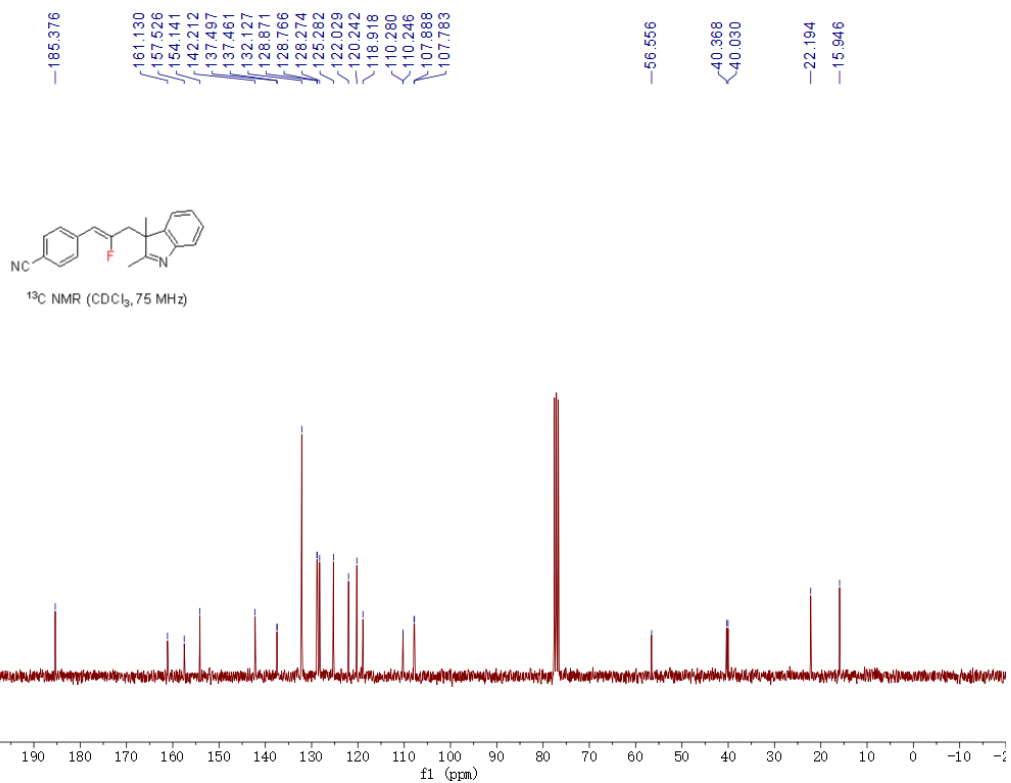


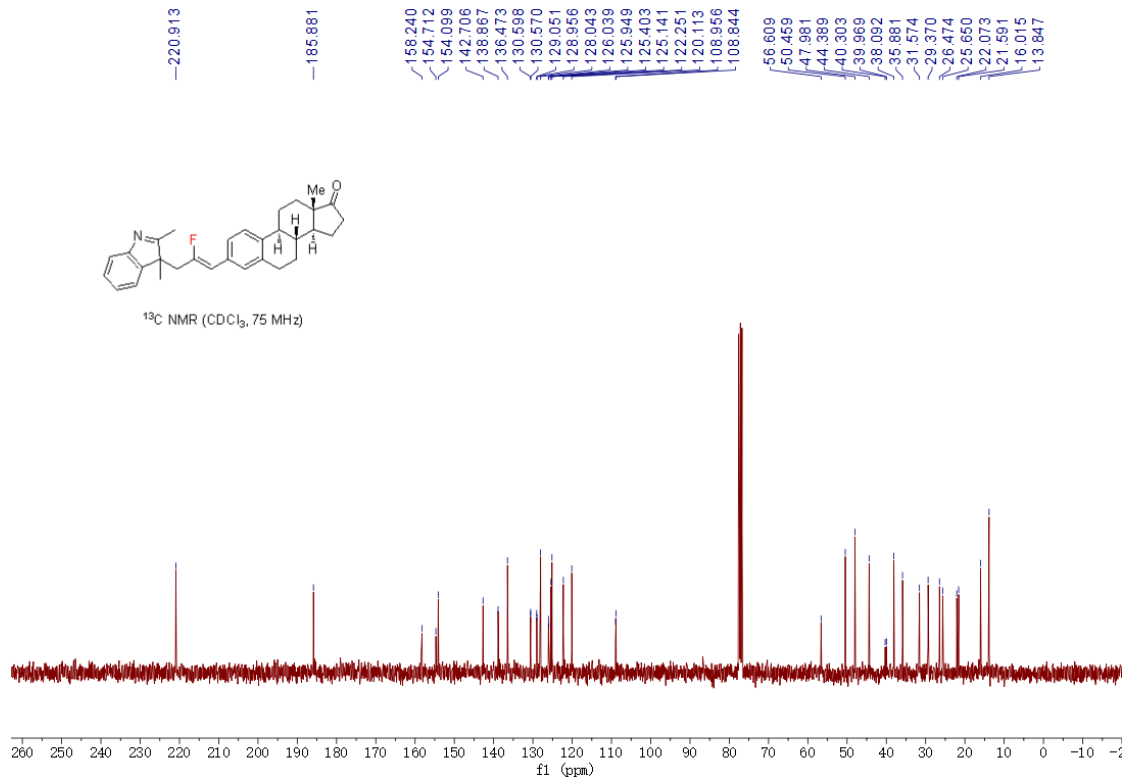
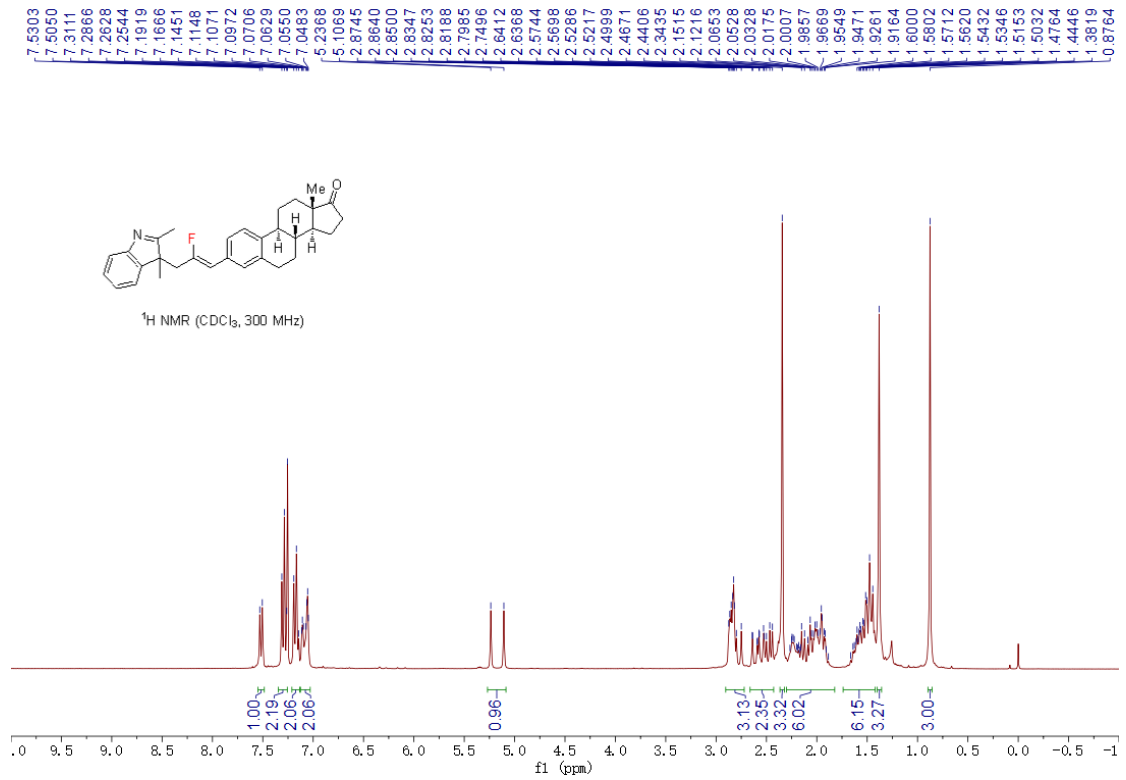




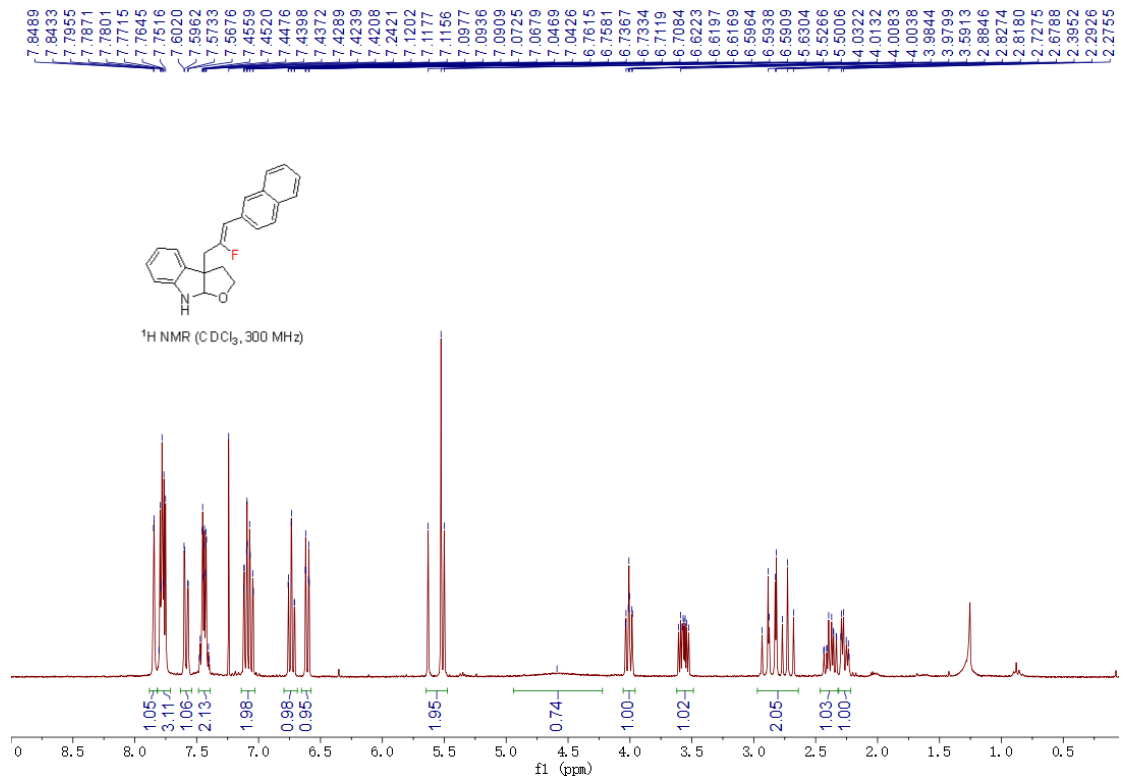
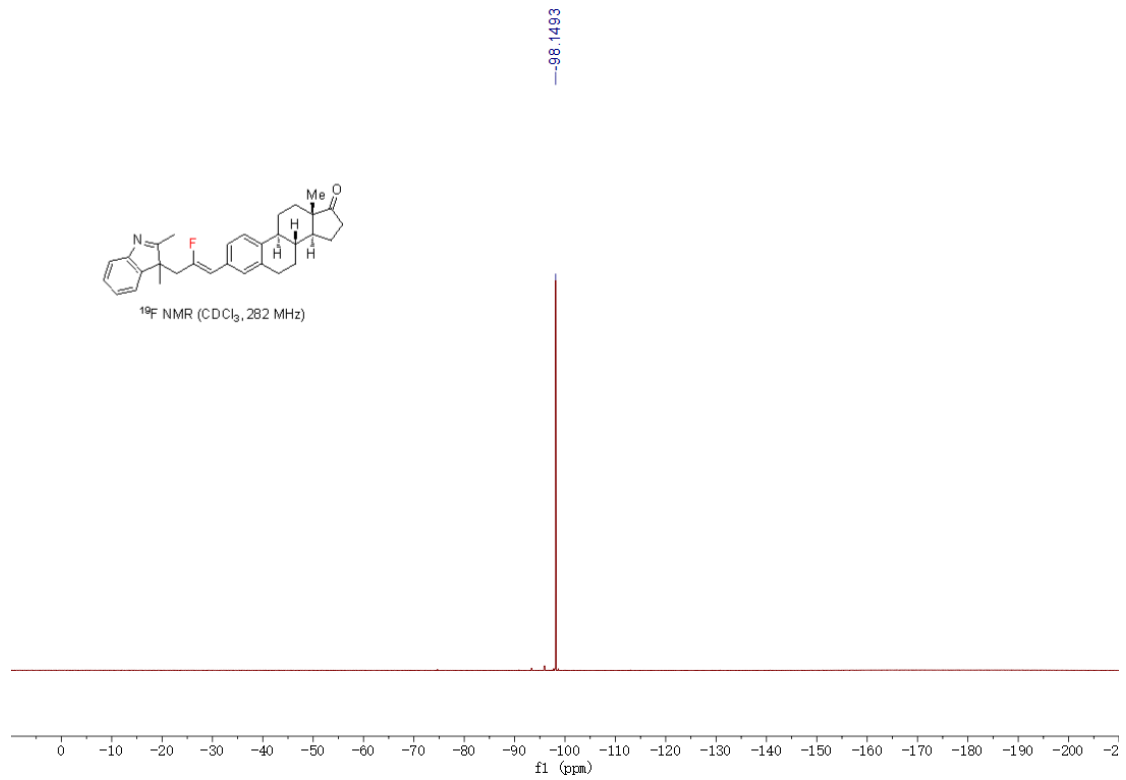


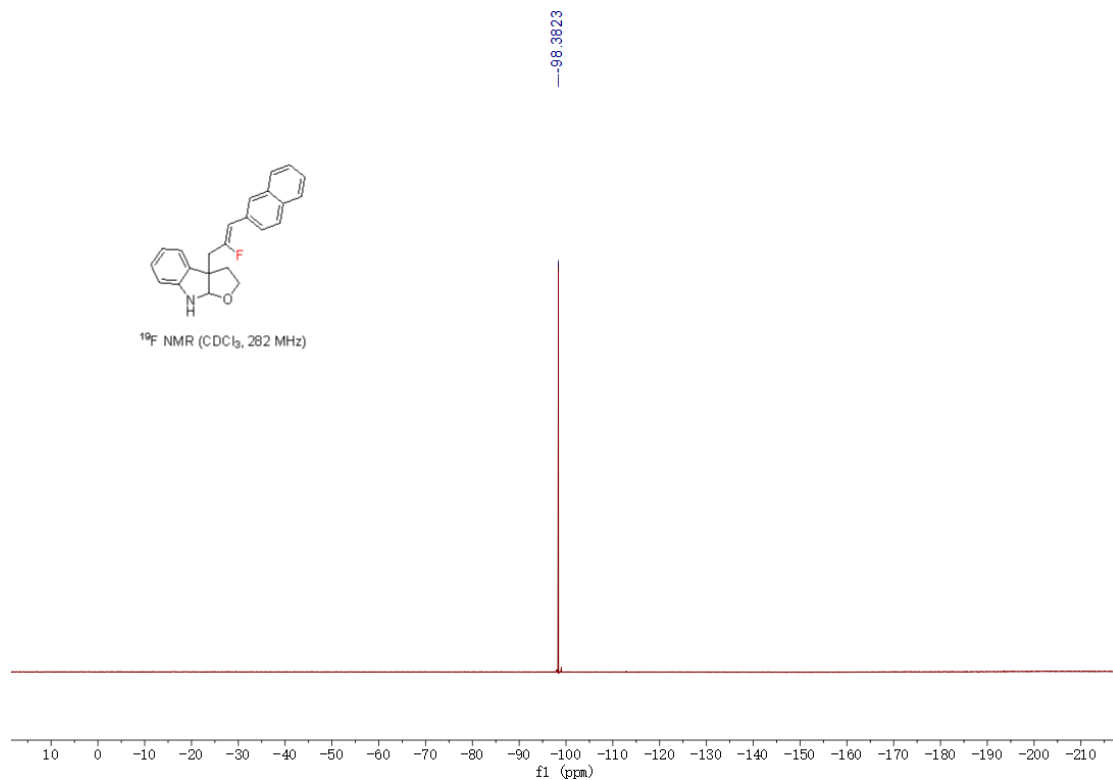
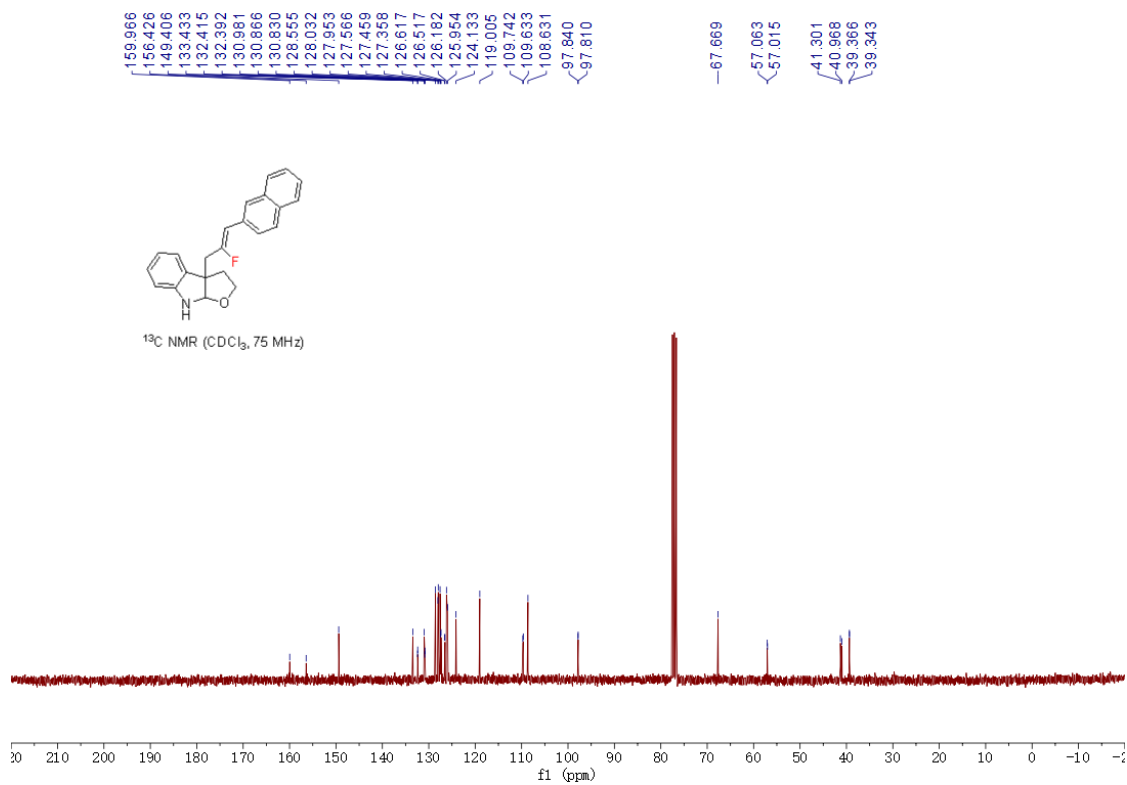


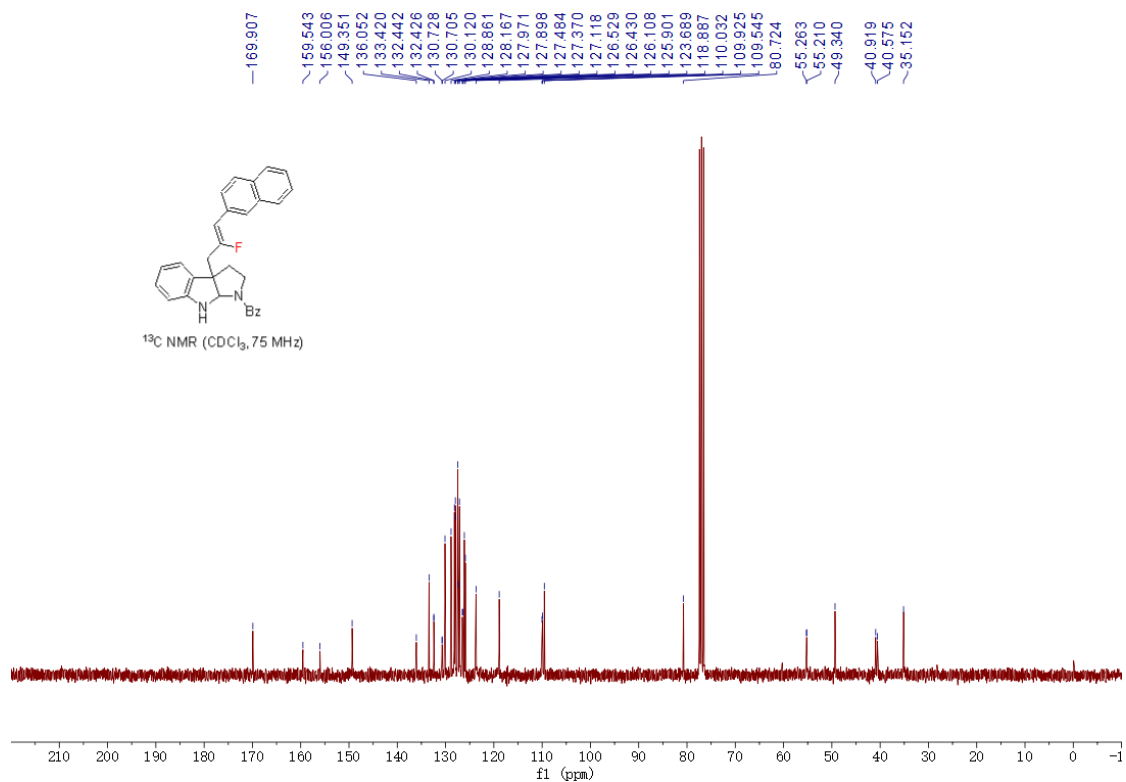
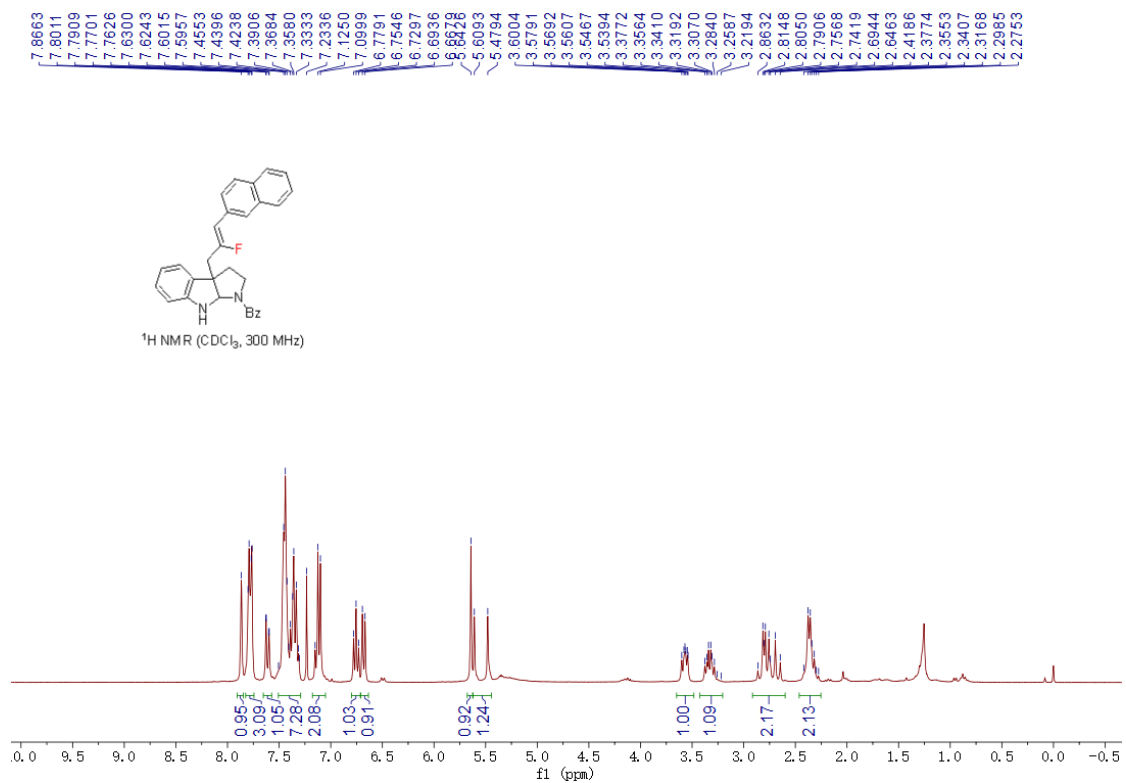


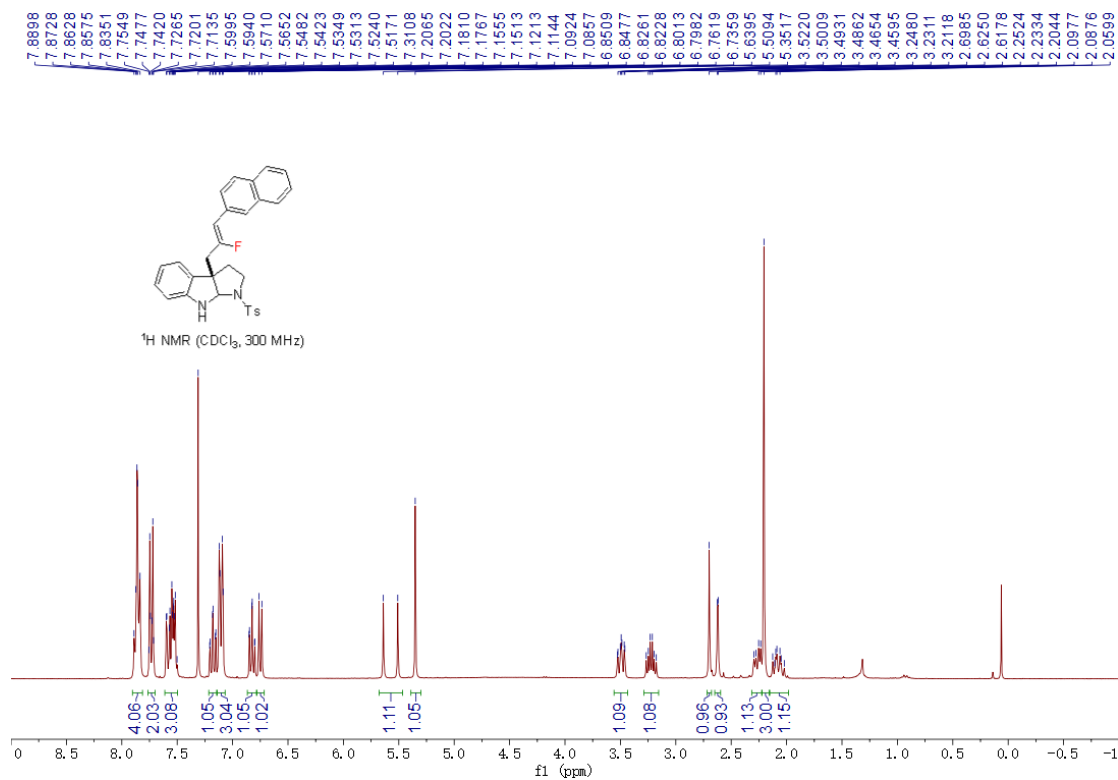
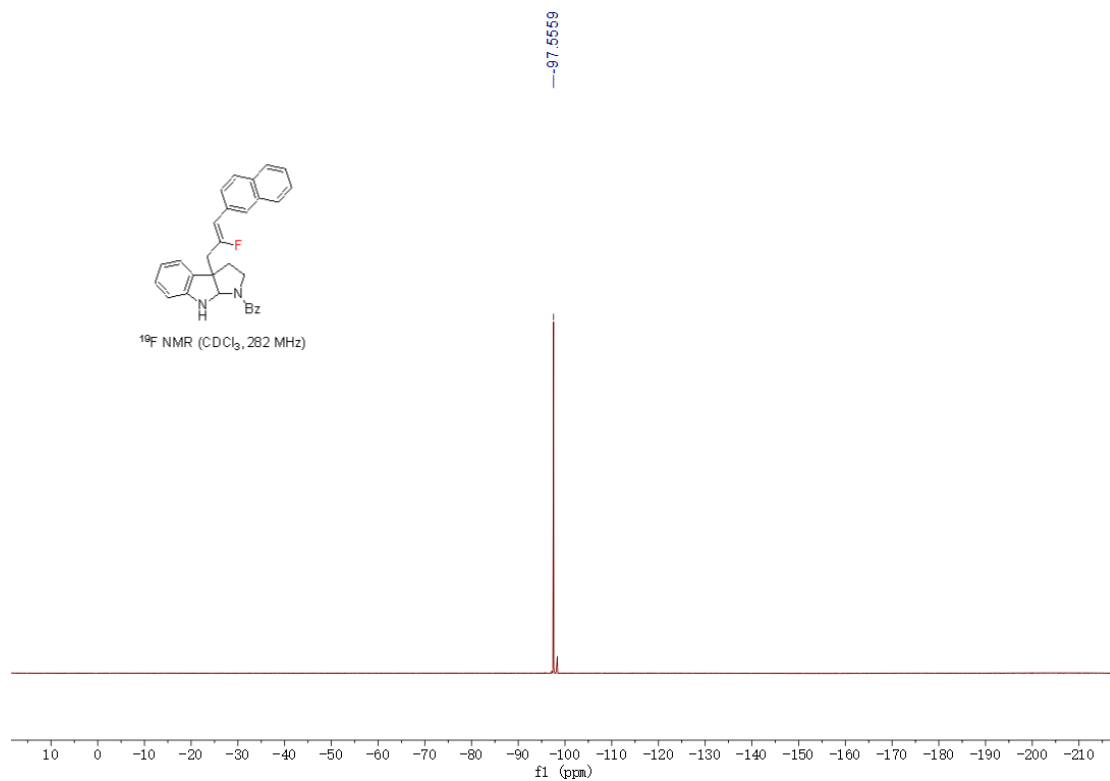


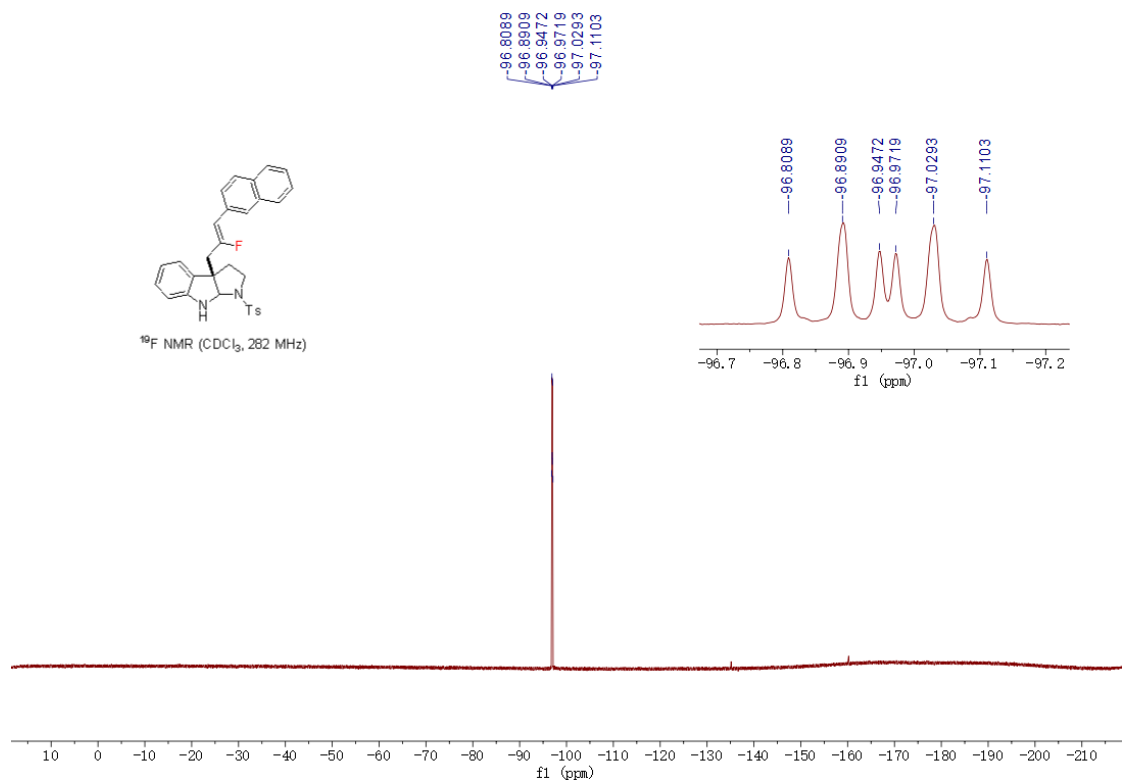
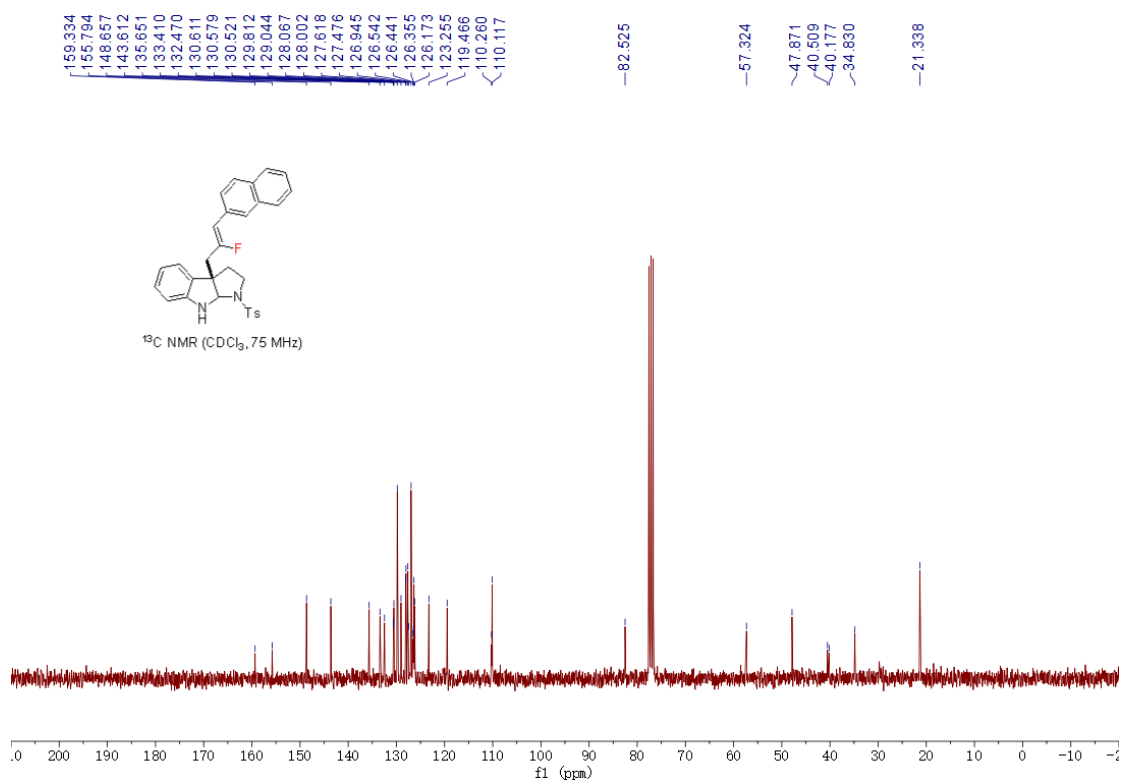


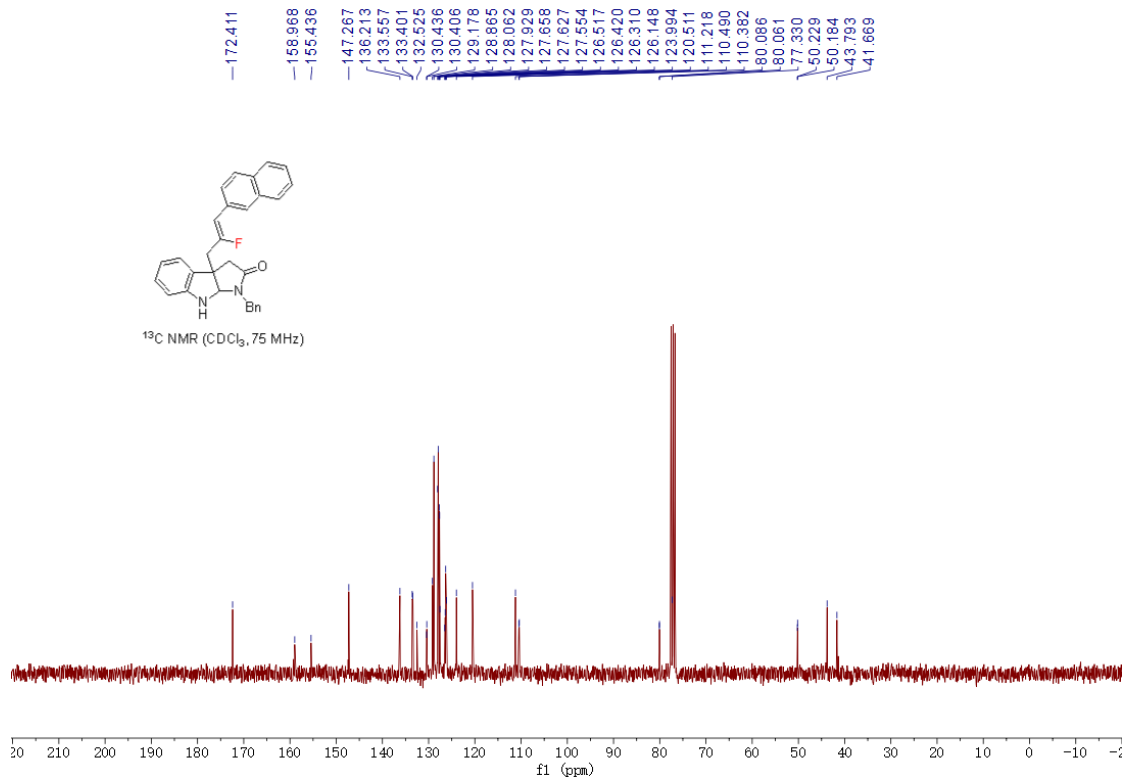
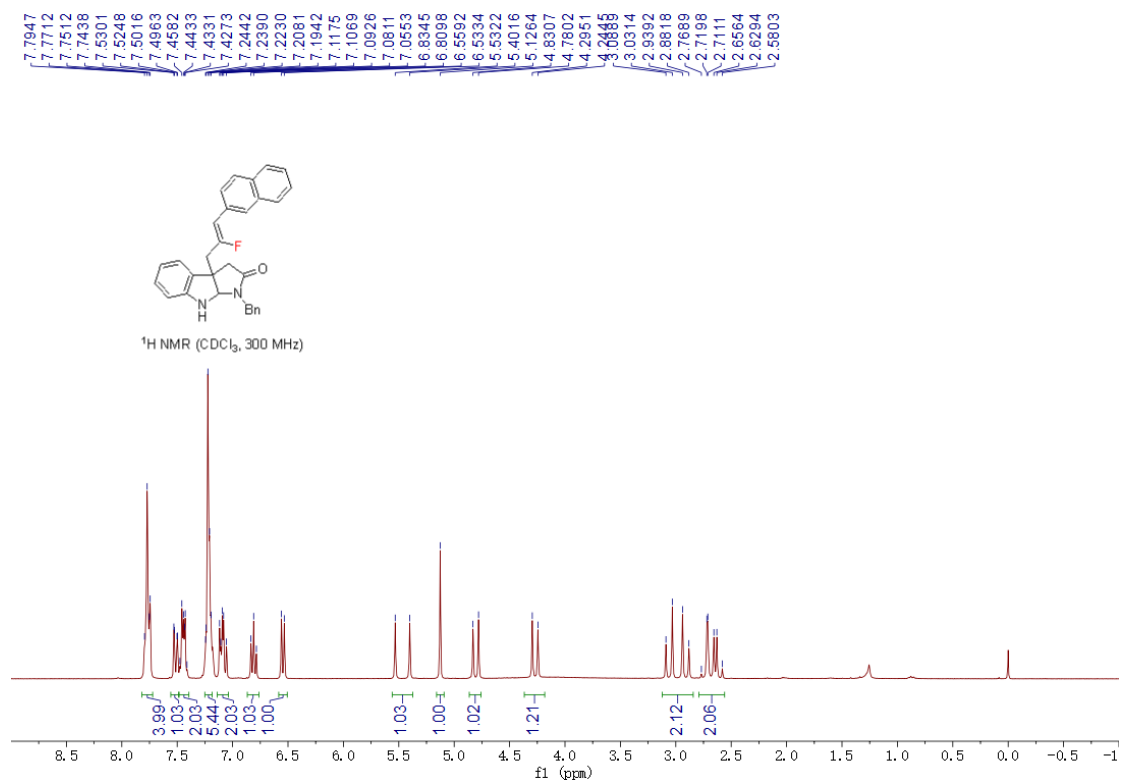


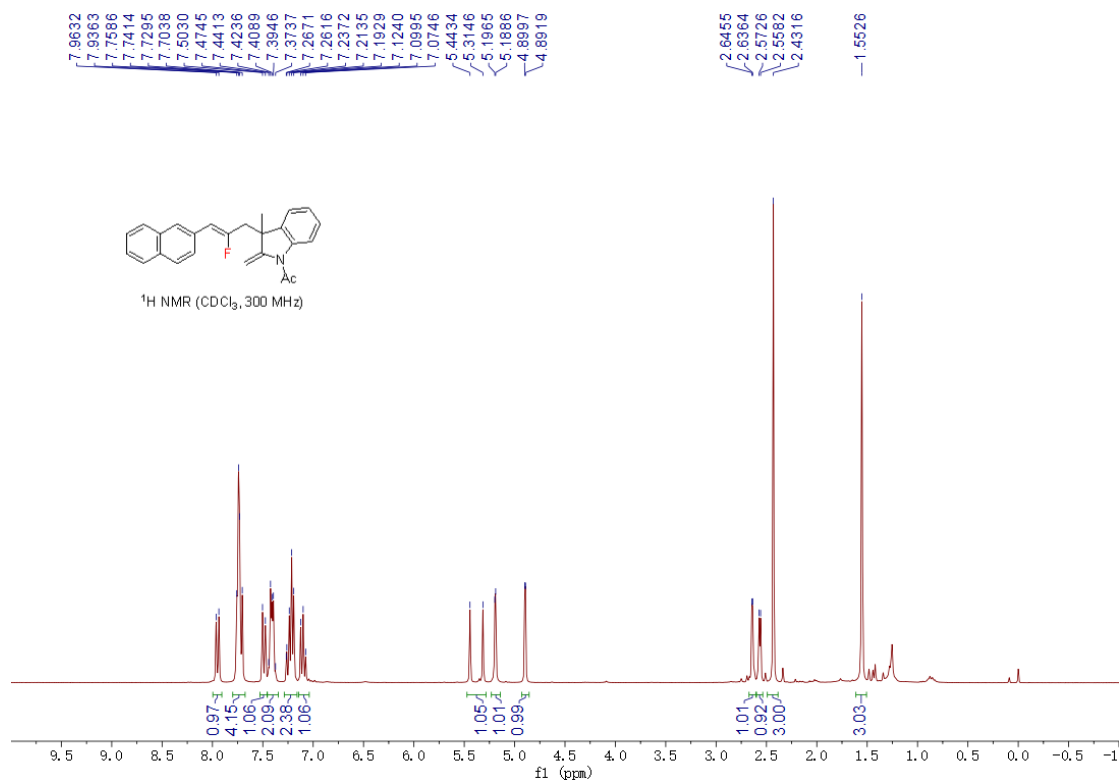
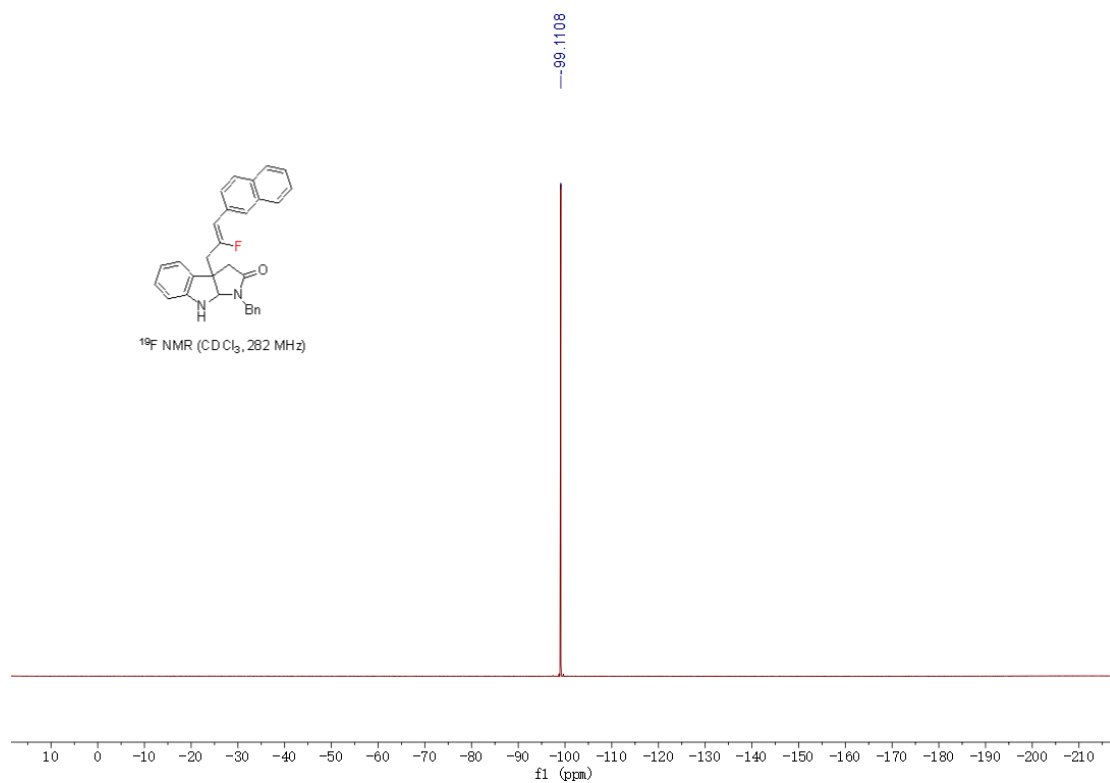








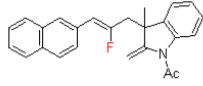




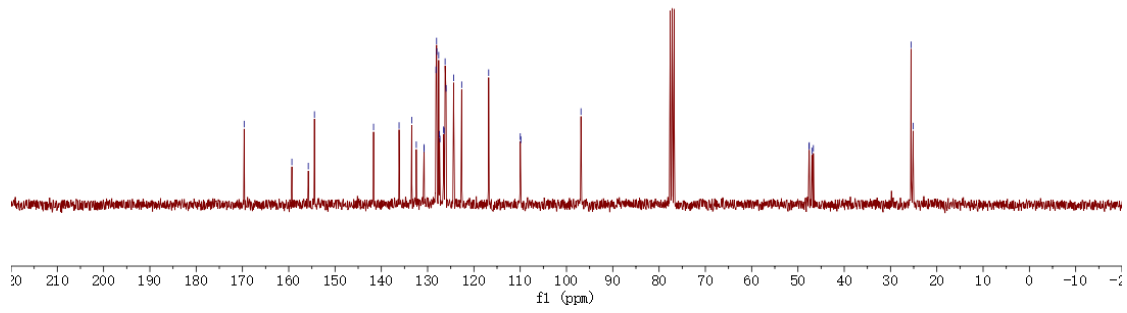
169.634  
 159.324  
 155.775  
 154.446  
 141.680  
 136.167  
 133.436  
 132.444  
 130.783  
 130.747  
 128.196  
 128.063  
 128.012  
 127.607  
 127.433  
 127.334  
 126.538  
 126.438  
 126.225  
 126.010  
 124.377  
 122.644  
 116.810  
 109.981  
 109.870  
 96.872

47.605  
 47.557  
 46.989  
 46.663

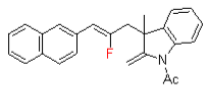
25.577  
 25.124



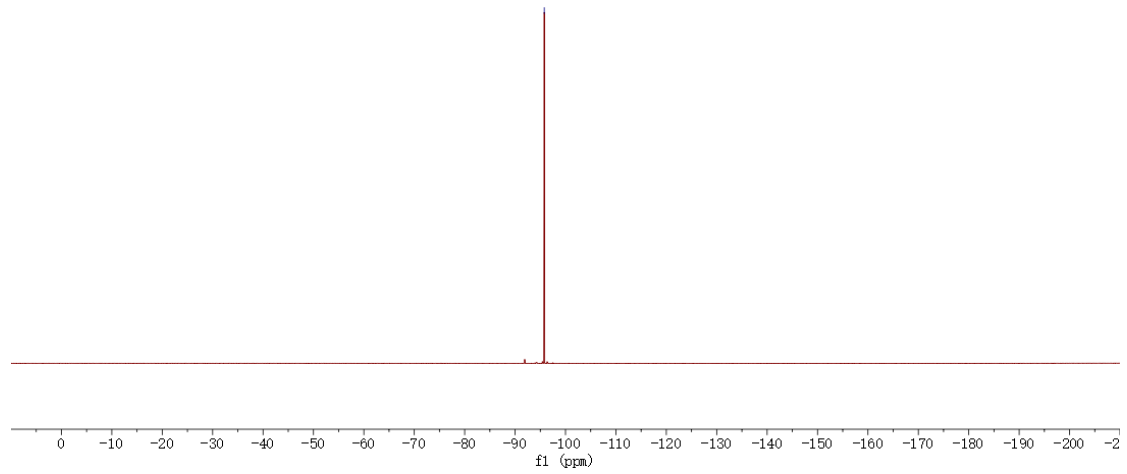
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



-95.7871

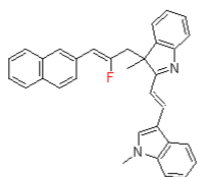


<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)

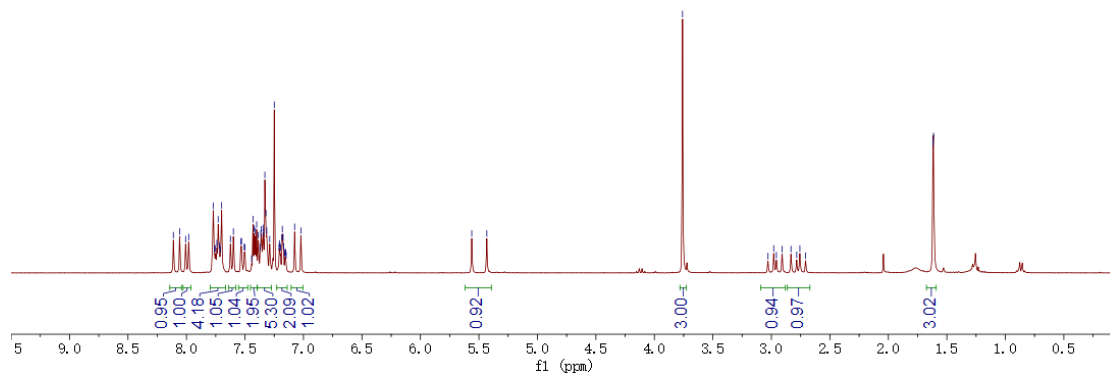




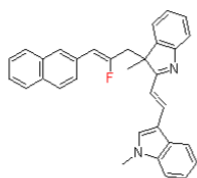
8.1122  
8.0585  
8.0074  
7.9811  
7.7715  
7.7590  
7.7510  
7.7401  
7.7289  
7.7196  
7.7110  
7.6894  
7.6244  
7.5990  
7.5350  
7.5294  
7.5060  
7.5005  
7.4431  
7.4317  
7.4208  
7.4108  
7.4000  
7.3858  
7.3701  
7.3647  
7.3602  
7.3450  
7.3409  
7.3298  
7.3208  
7.3141  
7.2888  
7.2494  
7.2091  
7.2056  
7.2012  
7.1961  
7.1845  
7.1804  
7.1743  
7.1697  
7.1597  
7.1562  
7.1524  
7.1475  
7.0755  
7.0219  
5.5614  
5.4325  
3.7594  
3.0290  
2.9801  
2.9573  
2.9084  
2.8325  
2.7835  
2.7565  
2.7076  
1.6184  
1.6139



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



182.637  
159.403  
155.849  
154.813  
143.411  
138.127  
133.427  
132.424  
132.351  
132.032  
130.830  
130.798  
128.328  
128.083  
127.928  
127.577  
127.462  
126.718  
126.617  
126.172  
126.090  
125.975  
124.817  
122.947  
122.280  
121.157  
120.687  
120.142  
114.480  
113.661  
110.057  
109.759  
109.654  
55.494  
41.291  
40.956  
33.102  
22.429



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

