

# Supporting Information

## Copper-Catalyzed Functionlization/Transformation of Styrenes with Polyhaloalkanes and Arenes Enables Heteroarene-Containing *gem*-Dihaloalkenes Synthesis

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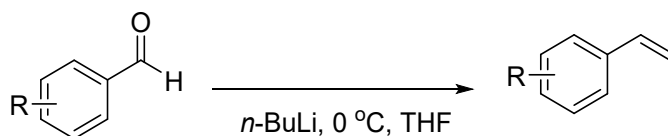
## (A) General Experimental Procedures

### (a) General information

The  $^1\text{H}$   $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded in  $\text{CDCl}_3$  solvent on an NMR spectrometer using TMS as internal standard. GC-MS data were recorded on SHIMADZU QP2020. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

### (b) Synthesis of Alkene.

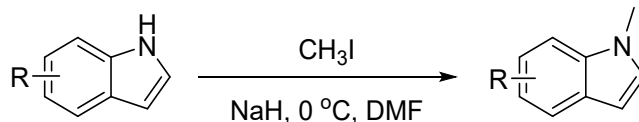
Alkene were synthesized according to the literature.



A solution of Aldehyde (5 mmol) and Methyltriphenylphosphonium bromide (5.5 mmol) in THF (8 mL) was cooled to  $0\text{ }^\circ\text{C}$  for about 30 min, then  $n\text{-BuLi}$  (7.5 mmol) was added. After stirring for 3 h at  $25\text{ }^\circ\text{C}$ . For the work-up, the mixture was treated with water (10 mL) and extracted with EtOAc ( $3\times 4$  mL). The combined organic phases were dried with  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum, and the residue was purified by column chromatography.

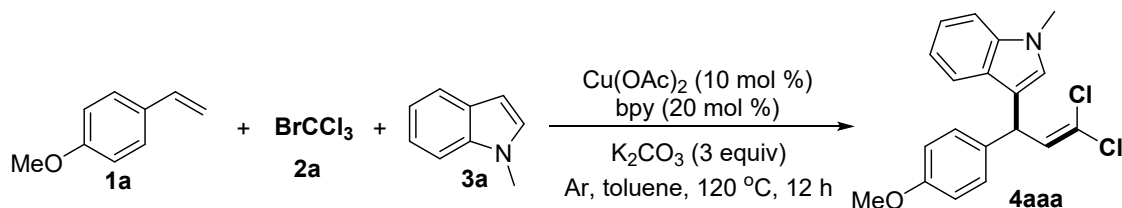
### (C) Synthesis of Methyl indole.

Methyl indole were synthesized according to the literature.



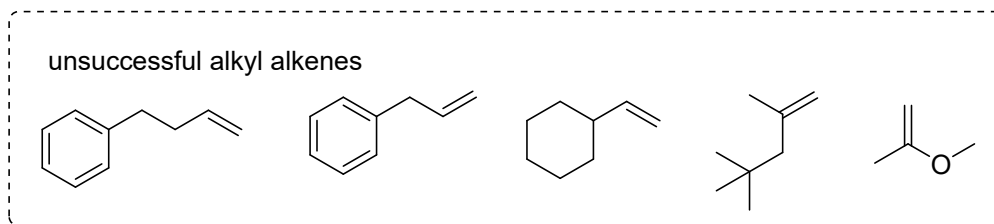
A solution of Indole (5 mmol) in DMF (8 mL) was cooled to  $0\text{ }^\circ\text{C}$ ,  $\text{NaH}$  (7.5 mmol) was added and stirring for 10 min at  $0\text{ }^\circ\text{C}$ , then  $\text{CH}_3\text{I}$  added and stirring for 30 min. For the work-up, the mixture was treated with water (10 mL) and extracted with EtOAc ( $3\times 4$  mL). The combined organic phases were dried with  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum, and the residue was purified by column chromatography.

### (c) General procedure



To a Schlenk tube were added 1-methoxy-4-vinylbenzene **1a** (0.2 mmol),  $\text{BrCCl}_3$  **2a** (3 equiv, 0.6 mmol), 1-methyl-1H-indole **3a** (2 equiv, 0.4 mmol),  $\text{Cu}(\text{OAc})_2$  (10 mol%, 0.02 mmol),  $\text{bpy}$  (20 mol%, 0.04 mmol),  $\text{K}_2\text{CO}_3$  (0.6 mmol, 3equiv; 82.8 mg), and toluene (2 mL). Then the mixture was stirred under argon atmosphere at 120 °C in oil bath for 12 h until consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford products.

Alkyl olefins are also not compatible with this reaction system, and we speculate that the alkyl radical or alkyl carbocation, which derived from alkyl olefins, are less stable than benzyl radicals and benzyl carbocation.



**Scheme S1. Unsuccessful alkyl alkenes.**

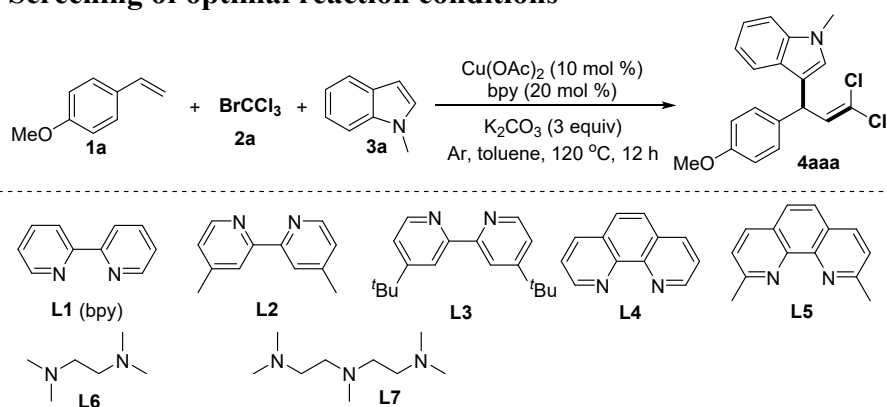
### (d) Experimental Procedure for the 1 mmol Scale.

To a Schlenk tube were added 1-methoxy-4-vinylbenzene **1a** (1 mmol; 134.1 mg),  $\text{BrCCl}_3$  **2a** (3 equiv, 0.6 mmol, 594.1 mg), 1-methyl-1H-indole **3a** (2 equiv, 2 mmol, 262.4 mg),  $\text{Cu}(\text{OAc})_2$  (20 mol%, 0.02 mmol; 18.7 mg),  $\text{bpy}$  (20 mol%, 0.04mmol; 31.1 mg),  $\text{K}_2\text{CO}_3$

(3 mmol, 3equiv; 415.2 mg), and toluene (10 mL). Then the mixture was stirred under argon atmosphere at 120 °C in oil bath for 12 h until consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA = 50: 1) to afford product **4aaa** in 80% yield (276.7 mg).

## (e) Screening of optimal reaction conditions

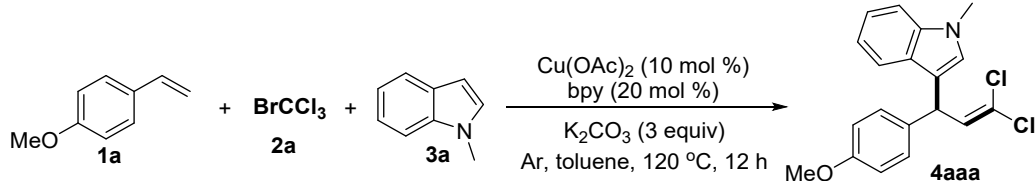
Table S1. Screening of optimal reaction conditions



Entry	Catalyst	Ligand	Solvent	temperature	Yield (%)
1	CuTc	<b>L1</b>	toluene	120 °C	68
2	$\text{Cu}(\text{MeCN})_4\text{PF}_6$	<b>L1</b>	toluene	120 °C	69
3	$\text{CuCl}_2$	<b>L1</b>	toluene	120 °C	45
<b>4</b>	<b><math>\text{Cu}(\text{OAc})_2</math></b>	<b>L1</b>	<b>toluene</b>	<b>120 °C</b>	<b>84</b>
5	CuI	<b>L1</b>	toluene	120 °C	63
6	CuBr	<b>L1</b>	toluene	120 °C	55
7	$\text{Cu}(\text{OTf})_2$	<b>L1</b>	toluene	120 °C	71
8	$\text{Cu}(\text{acac})_2$	<b>L1</b>	toluene	120 °C	56
9	$\text{Cu}_2\text{O}$	<b>L1</b>	toluene	120 °C	32
10	\	<b>L1</b>	toluene	120 °C	Trace
12	$\text{Cu}(\text{OAc})_2$	<b>L2</b>	toluene	120 °C	66
13	$\text{Cu}(\text{OAc})_2$	<b>L3</b>	toluene	120 °C	55
14	$\text{Cu}(\text{OAc})_2$	<b>L4</b>	toluene	120 °C	65
15	$\text{Cu}(\text{OAc})_2$	<b>L5</b>	toluene	120 °C	62
16	$\text{Cu}(\text{OAc})_2$	<b>L6</b>	toluene	120 °C	55
17	$\text{Cu}(\text{OAc})_2$	<b>L7</b>	toluene	120 °C	50
18	$\text{Cu}(\text{OAc})_2$	\	toluene	120 °C	Trace
19	$\text{Cu}(\text{OAc})_2$	<b>L1</b>	toluene	50 °C	27
20	$\text{Cu}(\text{OAc})_2$	<b>L1</b>	toluene	80 °C	35
21	$\text{Cu}(\text{OAc})_2$	<b>L1</b>	toluene	100 °C	43
22	$\text{Cu}(\text{OAc})_2$	<b>L1</b>	toluene	130 °C	67

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol, 3 equiv), **3a** (0.4 mmol, 2 equiv), Catalyst (0.02 mmol, 10 mol %), Ligand (0.04 mmol, 20 mol %) and base (0.6 mmol, 3 equiv) in solvent (2 mL), 120 °C, 12 h under argon atmosphere.

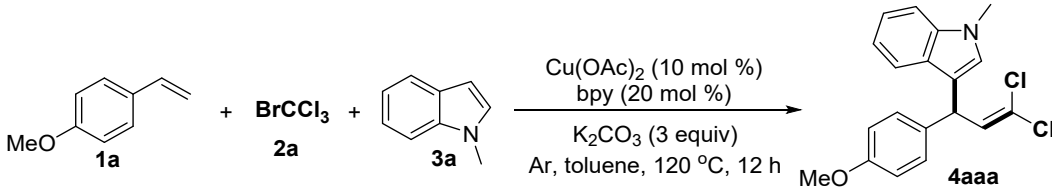
**Table S2. Screening of optimal reaction conditions for solvents.**



Entry	Catalyst	Ligand	Solvent	Yield (%)
1	Cu(OAc) <sub>2</sub>	bpy	MeCN	43
2	Cu(OAc) <sub>2</sub>	bpy	EtOH	37
3	Cu(OAc) <sub>2</sub>	bpy	1,4-dioxane	47
4	Cu(OAc) <sub>2</sub>	bpy	PhCl	42
<b>5</b>	<b>Cu(OAc)<sub>2</sub></b>	<b>bpy</b>	<b>PhMe</b>	<b>83</b>
6	Cu(OAc) <sub>2</sub>	bpy	Acetone	21
7	Cu(OAc) <sub>2</sub>	bpy	DMF	39
8	Cu(OAc) <sub>2</sub>	bpy	DMA	68
9	Cu(OAc) <sub>2</sub>	bpy	PhCF <sub>3</sub>	32
10	Cu(OAc) <sub>2</sub>	bpy	THF	55
11	Cu(OAc) <sub>2</sub>	bpy	DMSO	NR

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol, 3 equiv), **3a** (0.4 mmol, 2 equiv), Catalyst (0.02 mmol, 10 mol %), Ligand (0.04 mmol, 20 mol %) and base (0.6 mmol, 3 equiv) in solvent (2 mL), 120 °C, 12 h under argon atmosphere.

**Table S3. Screening of optimal reaction conditions for base.**



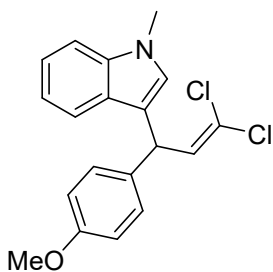
Entry	Base	Yield (%)
1	Without base	32
2	Na <sub>2</sub> CO <sub>3</sub>	67
3	Ag <sub>2</sub> CO <sub>3</sub>	55
4	K <sub>3</sub> PO <sub>4</sub>	63
5	NaOAc	51
6	2,6-Lutidine	66
7	Triethylamine	40

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol, 3 equiv), **3a** (0.4 mmol, 2 equiv), Catalyst (0.02 mmol, 10 mol %), Ligand (0.04 mmol, 20 mol %) and base (0.6 mmol, 3 equiv) in solvent (2 mL), 120 °C, 12 h under argon atmosphere.

°C, 12 h under argon atmosphere.

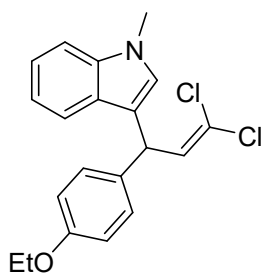
## (B) Analytical data

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aaa):



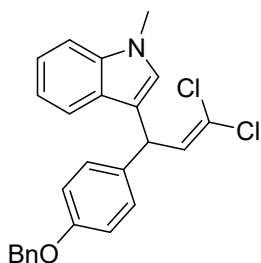
Following the general procedure A, product **4aaa** was obtained as a brown oil (58.0 mg, 84% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.18 (m, 1H), 7.16-7.08 (m, 4H), 6.98-6.91 (m, 1H), 6.79-6.72 (m, 2H), 6.70-6.65 (m, 1H), 6.27 (s, 1H), 5.21-5.09 (m, 1H), 3.69 (s, 3H), 3.63 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 136.4, 132.7, 131.2, 127.8, 125.8, 120.8, 118.7, 118.0, 114.3, 112.9, 108.3, 54.2, 41.6, 31.7; LRMS (EI, 70 eV)  $m/z$  (%): 347 ( $\text{M}^+ + 2$ , 24), 345 ( $\text{M}^+$ , 35), 310 (89), 207 (100), 179 (94); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{NO}$  346.0760; Found 346.0761.

### 3-(3,3-dichloro-1-(4-ethoxyphenyl)allyl)-1-methyl-1H-indole (4baa):



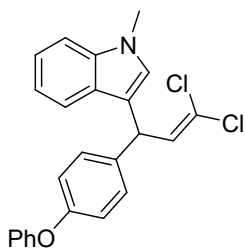
Following the general procedure A, product **4baa** was obtained as a brown oil (59.6 mg, 83% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 8.0$  Hz, 1H), 7.33 (d,  $J = 8.4$  Hz, 1H), 7.25 (m, 3H), 7.07 (m, 1H), 6.88 (d,  $J = 8.4$  Hz, 2H), 6.80 (s, 1H), 6.40 (d,  $J = 10.0$  Hz, 1H), 5.28 (d,  $J = 10.0$  Hz, 1H), 4.04 (m, 2H), 3.76 (s, 3H), 1.44 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.6, 132.4, 128.9, 126.9, 121.9, 119.8, 119.1, 115.4, 114.6, 109.4, 63.4, 42.7, 32.7, 14.9; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $\text{M}^+ + 2$ , 19), 359 ( $\text{M}^+$ , 29), 324 (100), 288 (31), 193 (92); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NO}$  360.0916; Found 360.0916.

### 3-(1-(4-(benzyloxy)phenyl)-3,3-dichloroallyl)-1-methyl-1H-indole (4caa):



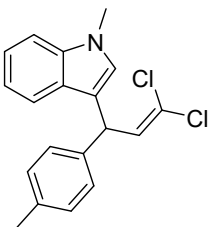
Following the general procedure A, product **4caa** was obtained as a brown oil (57.3 mg, 68% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.28 (m, 7H), 7.23-7.19 (m, 3H), 7.06-7.00 (m, 1H), 6.96-6.88 (m, 2H), 6.79-6.73 (m, 1H), 6.35 (s, 1H), 5.26-5.19 (m, 1H), 5.03 (s, 2H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 137.1, 134.1, 132.3, 128.9, 128.6, 128.0, 127.5, 126.9, 121.9, 119.8, 119.1, 115.3, 115.0, 109.4, 70.1, 42.7, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 423 ( $\text{M}^+ + 2$ , 6), 421 ( $\text{M}^+$ , 24), 340 (71), 304 (29), 209 (94); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{NO}$  422.1073; Found 422.1077.

### 3-(3,3-dichloro-1-(4-phenoxyphenyl)allyl)-1-methyl-1H-indole(4daa):



Following the general procedure A, product **4daa** was obtained as a brown oil (63.5 mg, 78% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 6.5$  Hz, 4H), 7.19-7.12 (m, 3H), 7.04-6.91 (m, 4H), 6.87 (d,  $J = 8.0$  Hz, 2H), 6.72 (s, 1H), 6.30 (d,  $J = 10.0$  Hz, 1H), 5.19 (d,  $J = 10.0$  Hz, 1H), 3.69 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 132.0, 129.7, 129.1, 126.8, 123.2, 122.0, 119.7, 119.2, 119.0, 118.9, 109.4, 42.8, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 409 ( $\text{M}^+ + 2$ , 23), 407 ( $\text{M}^+$ , 32), 372 (100), 336 (43), 241 (87); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NO}$  408.0916; Found 408.0906.

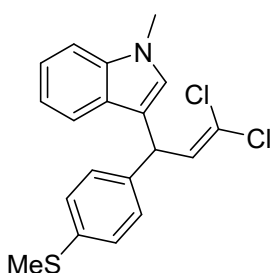
### 3-(3,3-dichloro-1-(p-tolyl)allyl)-1-methyl-1H-indole (4eaa):



Following the general procedure A, product **4eaa** was obtained as a brown oil (31.6 mg, 48% yield,  $R_f = 0.6$  (PE/EA = 80 : 1));  $^1\text{H}$  NMR (400

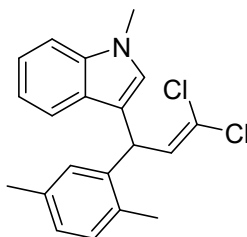
MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36 - 7.28 (m, 3H), 7.23 (m, 2H), 7.15 (m, 1H), 6.86 (s, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 5.39 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.8, 136.5, 132.4, 129.4, 127.9, 126.9, 126.9, 122.0, 119.8, 119.2, 115.3, 109.5, 43.2, 32.8, 21.2; LRMS (EI, 70 eV) *m/z* (%): 331 (M<sup>+2</sup>, 47), 329 (M<sup>+</sup>, 70), 294 (81), 207 (77), 147 (100); HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>18</sub>Cl<sub>2</sub>N 330.0811; Found 330.0807.

### 3-(3,3-dichloro-1-(4-(methylthio)phenyl)allyl)-1-methyl-1H-indole (4faa):



Following the general procedure A, product **4faa** was obtained as a brown oil (36.2 mg, 50% yield, *R<sub>f</sub>* = 0.6 (PE/EA = 30 : 1)); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (m, 2H), 7.25 (m, 5H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H), 2.49 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.6, 136.8, 131.9, 128.4, 126.9, 127.0, 122.0, 119.7, 119.2, 115.0, 109.4, 43.0, 32.8, 16.0; LRMS (EI, 70 eV) *m/z* (%): 363 (M<sup>+2</sup>, 34), 361 (M<sup>+</sup>, 45), 326 (87), 290 (44), 195 (100); HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>18</sub>Cl<sub>2</sub>NS 362.0532; Found 362.0534.

### 3-(3,3-dichloro-1-(2,5-dimethylphenyl)allyl)-1-methyl-1H-indole (4haa):

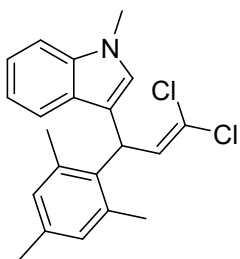


Following the general procedure A, product **4haa** was obtained as a brown oil (53.5 mg, 78% yield, *R<sub>f</sub>* = 0.6 (PE/EA = 80 : 1)); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.23-7.19 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 5H), 6.90 (d, *J* = 8.0 Hz, 3H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.33 (s, 3H), 3.46 (s, 3H), 2.90 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.6, 134.9, 134.5, 129.2, 128.6, 126.6, 126.4, 126.1, 118.7, 115.2, 50.8, 46.6, 29.2; LRMS (EI, 70 eV) *m/z* (%): 345 (M<sup>+2</sup>, 35), 343 (M<sup>+</sup>, 53), 308 (35), 238 (23), 177 (100); HRMS (ESI-



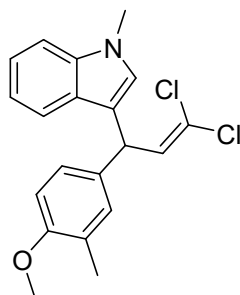
TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{20}Cl_2N$  344.0967; Found 344.0957.

**3-(3,3-dichloro-1-mesitylallyl)-1-methyl-1H-indole (4iaa):**

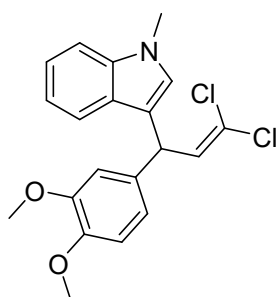


Following the general procedure A, product **4iaa** was obtained as a brown oil (64.2 mg, 90% yield,  $R_f = 0.6$  (PE/EA = 80 : 1));  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.30 (m, 2H), 7.22 (d,  $J = 7.6$  Hz, 1H), 7.06 (m, 1H), 6.90 (s, 2H), 6.62 (d,  $J = 8.8$  Hz, 1H), 6.50 (s, 1H), 5.61 (d,  $J = 8.8$  Hz, 1H), 3.71 (s, 3H), 2.32 (s, 3H), 2.30 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  136.8, 136.2, 134.6, 132.6, 130.0, 126.5, 121.7, 119.5, 119.0, 114.1, 109.3, 39.2, 32.7, 21.4, 20.8; LRMS (EI, 70 eV)  $m/z$  (%): 359 ( $M^{+2}$ , 53), 357 ( $M^+$ , 80), 322 (98), 245 (24), 191(100); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{21}H_{22}Cl_2N$  358.1124; Found 358.1124.

**3-(3,3-dichloro-1-(4-methoxy-3-methylphenyl)allyl)-1-methyl-1H-indole(4jaa):**



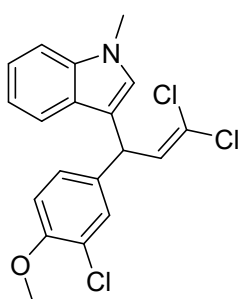
Following the general procedure A, product **4Jaa** was obtained as a brown oil (48.8 mg, 68% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 (d,  $J = 8.0$  Hz, 1H), 7.29 (d,  $J = 8.4$  Hz, 1H), 7.24-7.20 (m, 1H), 7.11-6.98 (m, 3H), 6.82-6.70 (m, 2H), 6.47-6.23 (m, 1H), 5.19 (d,  $J = 10.0$  Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.18 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  156.6, 137.4, 133.3, 132.5, 130.2, 126.8, 126.8, 126.0, 121.8, 120.0, 119.8, 119.1, 115.6, 109.9, 109.3, 55.4, 42.7, 32.7, 16.4; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $M^{+2}$ , 14), 359 ( $M^+$ , 21), 324 (69), 202 (38), 193(100); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{20}Cl_2NO$  360.0916; Found 360.0912.



**3-(3,3-dichloro-1-(3,4-dimethoxyphenyl)allyl)-1-methyl-1H-indole(4kaa):**

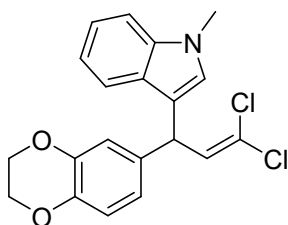
Following the general procedure A, product **4kaa** was obtained as a brown oil (52.5 mg, 70% yield,  $R_f = 0.5$  (PE/EA = 20 : 1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.32 (m, 1H), 7.31-7.28 (m, 1H), 7.27-7.18 (m, 2H), 7.04 (s, 1H), 6.87-6.75 (m, 3H), 6.36 (s, 1H), 5.28-5.2 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 147.9, 137.4, 134.2, 132.2, 126.9, 126.8, 121.9, 119.8, 119.7, 119.1, 115.3, 111.3, 111.2, 109.4, 55.9, 43.1, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 377 ( $\text{M}^{+2}$ , 18), 375 ( $\text{M}^+$ , 18), 340 (85), 304 (31), 209 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NO}_2$  376.0866; Found 376.0867.

**3-(3,3-dichloro-1-(4-methoxy-3-methylphenyl)allyl)-1-methyl-1H-indole(4laa):**



Following the general procedure A, product **4laa** was obtained as a brown oil (53.1 mg, 72% yield,  $R_f = 0.6$  (PE/EA = 20 : 1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.28 (m, 2H), 7.23 (d,  $J = 7.2$  Hz, 2H), 7.13 (dd,  $J = 8.0, 2.4$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 1H), 6.85 (d,  $J = 8.8$  Hz, 1H), 6.78 (s, 1H), 6.32 (d,  $J = 10.0$  Hz, 1H), 5.20 (d,  $J = 9.9$  Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 137.5, 134.9, 131.6, 129.6, 127.1, 126.8, 126.6, 122.6, 122.0, 120.9, 119.6, 119.3, 114.7, 112.1, 109.5, 56.2, 42.5, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 381 ( $\text{M}^{+2}$ , 45), 379 ( $\text{M}^+$ , 47), 344 (100), 284 (17), 213 (55); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{Cl}_3\text{NO}$  380.0370; Found 380.0371.

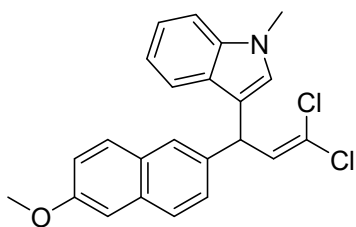
**3-(3,3-dichloro-1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)allyl)-1-methyl-1H-indole (4maa):**



Following the general procedure A, product **4maa** was obtained as a brown oil (59.7 mg, 80% yield,  $R_f = 0.5$  (PE/EA = 30 : 1);

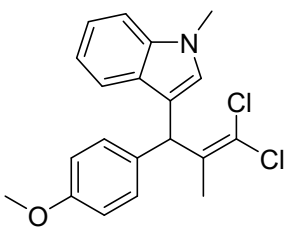
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.33 (m, 1H), 7.31-7.29 (m, 1H), 7.23-7.19 (m, 1H), 7.05 (s, 1H), 6.84-6.72 (m, 4H), 6.34 (d,  $J = 12.5$  Hz, 1H), 5.18 (d,  $J = 7.0$  Hz, 1H), 4.28-4.20 (m, 4H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 137.4, 135.0, 132.0, 126.7, 121.8, 120.8, 119.7, 119.1, 116.6, 115.1, 109.3, 64.4, 64.3, 42.7, 32.7; LRMS (EI, 70 eV)  $m/z$  (%): 375 ( $\text{M}^{+2}$ , 22), 373 ( $\text{M}^+$ , 33), 302 (47), 246 (14), 207 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{NO}_2$  374.0709; Found 374.0710.

### 3-(3,3-dichloro-1-(6-methoxynaphthalen-2-yl)allyl)-1-methyl-1H-indole (4naa):



Following the general procedure A, product **4naa** was obtained as a brown oil (59.4 mg, 63% yield,  $R_f = 0.5$  (PE/EA = 30 : 1));  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.66 (m, 3H), 7.38-7.29 (m, 3H), 7.25 (s, 1H), 7.13 (d,  $J = 9.6$  Hz, 2H), 7.01 (t,  $J = 7.6$  Hz, 1H), 6.79 (s, 1H), 6.45 (d,  $J = 10.0$  Hz, 1H), 5.41 (d,  $J = 10.0$  Hz, 1H), 3.91 (s, 3H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 137.4, 136.8, 133.6, 132.0, 129.3, 129.0, 127.2, 127.0, 126.9, 126.0, 121.9, 119.7, 119.2, 118.9, 115.2, 109.4, 105.6, 55.4, 43.4, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 397 ( $\text{M}^{+2}$ , 17), 395 ( $\text{M}^+$ , 26), 360 (49), 347 (27), 229 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{20}\text{Cl}_2\text{NO}$  396.0916; Found 396.0915.

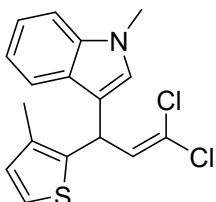
### 3-(3,3-dichloro-1-(4-methoxyphenyl)-2-methylallyl)-1-methyl-1H-indole (4oaa):



Following the general procedure A, product **4oaa** was obtained as a brown oil (58.9 mg, 82% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.67 (m, 1H), 7.25-7.15 (m, 4H), 7.05-7.0 (m, 1H), 6.9-6.8 (m, 2H), 6.68 (s, 1H), 5.74 (s, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 1.79 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 137.3, 136.7,

132.8, 129.5, 127.8, 127.5, 121.9, 119.9, 119.1, 114.5, 113.8, 109.3, 55.3, 45.9, 32.8, 18.2;  
LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $M^{+2}$ , 30), 359 ( $M^{+}$ , 45), 324 (35), 250 (100), 193 (47);  
HRMS (ESI-TOF)  $m/z$ :  $[M + H]^{+}$  Calcd for  $C_{20}H_{20}Cl_2NO$  360.0916; Found 360.0919.

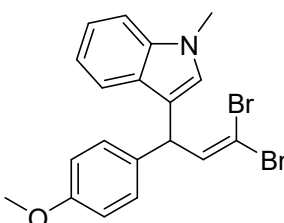
**3-(3,3-dichloro-1-(3-methylthiophen-2-yl)allyl)-1-methyl-1H-**



**indole (4paa):**

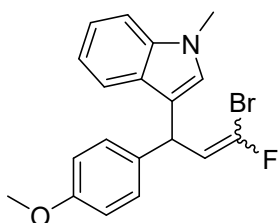
Following the general procedure A, product **4paa** was obtained as a brown oil (53.6 mg, 80% yield,  $R_f = 0.6$  (PE/EA = 30 : 1);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.48-7.41 (m, 1H), 7.32-7.28 (m, 1H), 7.24-7.20 (m, 1H), 7.13-7.04 (m, 2H), 6.87-6.83 (m, 1H), 6.80 (s, 1H), 6.33 (d,  $J = 11.0$  Hz, 1H), 5.52 (d,  $J = 10.0$  Hz, 1H), 3.75 (s, 3H), 2.24 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  137.4, 133.7, 131.6, 130.2, 126.7, 122.5, 122.1, 120.9, 119.5, 119.3, 115.0, 109.5, 37.3, 32.9, 14.1; LRMS (EI, 70 eV)  $m/z$  (%): 337 ( $M^{+2}$ , 19), 335 ( $M^{+}$ , 28), 300 (100), 264 (47), 202 (52); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^{+}$  Calcd for  $C_{17}H_{16}Cl_2NS$  336.0375; Found 336.0388

**3-(3,3-dibromo-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aca):**



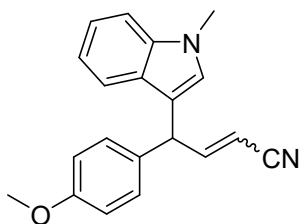
Following the general procedure A, product **4aca** was obtained as a brown oil (56.3 mg, 65% yield,  $R_f = 0.6$  (PE/EA = 60 : 1);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.31 (t,  $J = 8.4$  Hz, 2H), 7.25-7.20 (m, 3H), 7.04 (d,  $J = 7.6$  Hz, 1H), 6.89-6.81 (m, 3H), 6.78 (s, 1H), 5.14 (d,  $J = 12.0$  Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H).;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.5, 140.6, 137.4, 133.3, 128.9, 126.9, 126.7, 121.9, 119.8, 119.1, 114.8, 114.0, 109.4, 55.3, 46.0, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 435 ( $M^{+2}$ , 30), 433 ( $M^{+}$ , 15), 354 (51), 274 (71), 223 (100); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^{+}$  Calcd for  $C_{19}H_{18}Br_2NO$  433.9750; Found 433.9764.

### 3-(3-bromo-3-fluoro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4ada):



Following the general procedure A, product **4ada** was obtained as a brown oil (60.4 mg, 81% yield,  $E:Z = 1:1$ ;  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.17 (m, 2H), 7.12 (dq,  $J = 7.2, 2.8, 2.3$  Hz, 4H), 6.94 (t,  $J = 7.5$  Hz, 1H), 6.75 (d,  $J = 8.4$  Hz, 2H), 6.66 (s, 1H), 5.93 (dd,  $J = 12.8, 10.2$  Hz, 0.52H), 5.49 (dd,  $J = 30.0, 10.4$  Hz, 0.48H), 5.21 (d,  $J = 10.4$  Hz, 0.50H), 4.86 (dd,  $J = 10.3, 3.6$  Hz, 0.54H), 3.68 (s, 3H), 3.62 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 157.2, 136.4, 133.3, 127.7, 125.8, 125.7, 125.7, 125.6, 120.8, 118.7, 118.6, 118.0, 118.0, 114.9, 114.8, 114.7, 114.6, 112.9, 112.5, 112.3, 108.3, 76.2, 54.2, 40.3, 40.3, 37.8, 37.7, 31.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.52, -75.56. LRMS (EI, 70 eV)  $m/z$  (%): 375 ( $\text{M}^{+2}$ , 31), 373 ( $\text{M}^+$ , 32), 294 (100), 250(21), 163(81); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{BrFNO}$  374.0550; Found 374.0559.

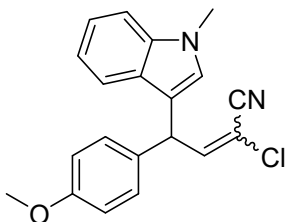
### 3-(3-bromo-3-fluoro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4afa):



Following the general procedure A, product **4afa** was obtained as a brown oil (36.2 mg, 60% yield,  $E:Z = 2.3:1$ ;  $R_f = 0.6$  (PE/EA = 10 : 1));  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.04 (m, 7H), 6.94-6.72 (m, 3H), 6.64 (s, 1H), 5.44 (d,  $J = 10.4$  Hz, 0.27H), 5.36 (d,  $J = 10.4$  Hz, 0.29H), 5.21 (dd,  $J = 16.4, 2.0$  Hz, 0.70H), 5.02 (d,  $J = 6.0$  Hz, 0.72H), 3.77 (d,  $J = 3.2$  Hz, 3H), 3.71 (d,  $J = 4.4$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8,

156.9, 155.7, 137.4, 132.0, 129.5, 129.0, 127.7, 127.0, 126.7, 122.2, 122.1, 119.8, 119.4, 119.4, 119.3, 117.8, 114.3, 114.0, 109.6, 109.5, 100.5, 98.0, 55.3, 45.4, 44.5, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 304 ( $M^{+2}$ , 3), 302 ( $M^+$ , 100), 287 (22), 193(23),144(25); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{19}N_2O$  303.1492; Found 303.1492.

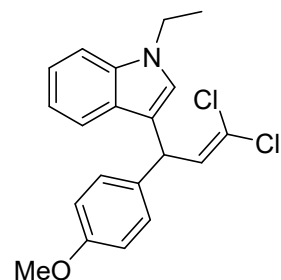
**2-chloro-4-(4-methoxyphenyl)-4-(1-methyl-1H-indol-3-yl)but-2-enitrile (4aga):**



Following the general procedure A, product **4aga** was obtained as a brown oil (40.3 mg, 60% yield,  $E:Z = 1:1$ ;  $R_f = 0.6$  (PE/EA = 10 : 1);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.30 (dd,  $J = 8.0, 2.4$  Hz, 2H),

7.25 -7.17 (m, 3H), 7.08-6.97 (m, 2H), 6.85 (d,  $J = 8.4$  Hz, 2H), 6.80 (s, 1H), 5.35 (d,  $J = 11.2$  Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.0, 150.2, 137.5, 132.0, 128.9, 127.1, 126.4, 122.3, 119.6, 114.4, 113.6, 109.6, 101.9, 55.4, 44.4; LRMS (EI, 70 eV)  $m/z$  (%):338 ( $M^{+2}$ , 7), 336 ( $M^+$ , 21), 301 (100), 193(40),170(51); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{18}ClN_2O$  337.1102; Found 337.1101.

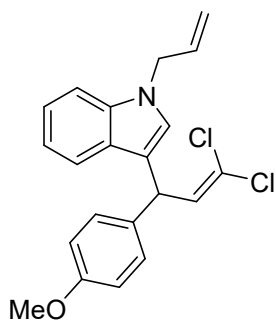
**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-ethyl-1H-indole(4aab):**



Following the general procedure A, product **4aab** was obtained as a brown oil (52.4 mg, 73% yield,  $R_f = 0.6$  (PE/EA = 50 : 1);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.36-7.28 (m, 2H), 7.25-7.18 (m, 3H), 7.02 (d,  $J = 3.5$  Hz, 1H), 6.91-6.81 (m, 3H), 6.34 (s, 1H), 5.22 (s, 1H), 4.26-4.06 (m, 2H), 3.79 (s, 3H), 1.43 (s, 3H);  $^{13}C$  NMR (126

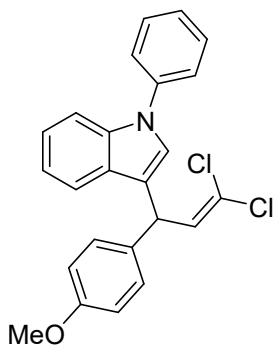
MHz,  $CDCl_3$ )  $\delta$  158.4, 132.3, 128.9, 125.1, 121.7, 119.9, 119.0, 114.0, 109.4, 55.3, 42.8, 15.5;LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $M^{+2}$ , 34), 357 ( $M^+$ , 51), 324 (100), 288 (55), 179 (92); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{20}Cl_2NO$  360.0916; Found 360.0920.

### 1-allyl-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1H-indole(4aac):



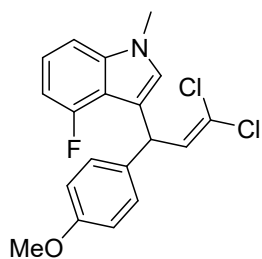
Following the general procedure A, product **4aac** was obtained as a brown oil (59.4 mg, 80% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 4.6$  Hz, 1H), 7.25-7.14 (m, 4H), 7.03 (d,  $J = 7.2$  Hz, 1H), 6.87-6.80 (m, 3H), 6.35 (d,  $J = 10.0$  Hz, 1H), 5.97 (ddd,  $J = 11.9, 10.2, 5.1$  Hz, 1H), 5.27 – 5.17 (m, 2H), 5.09 (dt,  $J = 17.0, 1.6$  Hz, 1H), 4.67 (dt,  $J = 5.6, 1.6$  Hz, 2H), 3.78 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 136.9, 133.8, 133.4, 132.3, 128.9, 127.0, 125.8, 121.9, 119.9, 119.3, 117.4, 115.8, 114.0, 109.8, 55.3, 48.8, 42.8; LRMS (EI, 70 eV)  $m/z$  (%): 373 ( $\text{M}^{+2}$ , 23), 371 ( $\text{M}^+$ , 34), 336 (100), 228 (21), 179 (98); HRMS (ESI-TOF)  $m/z$ : [ $\text{M} + \text{H}$ ] $^+$  Calcd for  $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{NO}$  372.0916; Found 372.0918.

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-phenyl-1H-indole(4aad):



Following the general procedure A, product **4aad** was obtained as a brown oil (65,2mg, 80% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60-7.44 (m, 5H), 7.38 (d,  $J = 8.0$  Hz, 1H), 7.32 (tt,  $J = 6.0, 2.6$  Hz, 1H), 7.23 (dd,  $J = 16.0, 6.4$  Hz, 3H), 7.13-7.03 (m, 2H), 6.86 (d,  $J = 8.4$  Hz, 2H), 6.39 (d,  $J = 10.0$  Hz, 1H), 5.29 (d,  $J = 9.6$  Hz, 1H), 3.78 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 139.6, 136.6, 133.4, 132.0, 129.7, 129.0, 127.8, 126.5, 125.9, 124.3, 122.8, 120.3, 120.0, 118.0, 114.2, 110.7, 55.3, 42.8; LRMS (EI, 70 eV)  $m/z$  (%): 409 ( $\text{M}^{+2}$ , 20), 407 ( $\text{M}^+$ , 29), 372 (93), 336 (35), 179 (100); HRMS (ESI-TOF)  $m/z$ : [ $\text{M} + \text{H}$ ] $^+$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NO}$  408.0916; Found 408.0919.

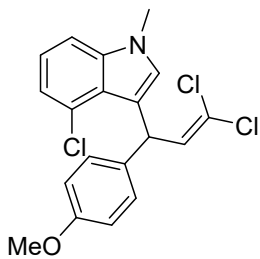
### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-4-fluoro-1-methyl-1H-indole (4aae):



Following the general procedure A, product **4aae** was obtained as a brown oil (56.6 mg, 78% yield,  $R_f = 0.6$  (PE/EA = 30 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.21 (m, 1H), 7.19-7.14 (m, 1H), 7.13-7.09 (m, 1H), 7.07-7.03 (m, 1H), 6.86-6.78 (m, 3H), 6.74-6.64 (m, 1H), 6.40 (s, 1H), 5.45-5.35 (m, 1H), 3.76 (s, 3H), 3.72 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 132.5, 128.6, 126.9, 113.8, 105.5, 55.2, 42.8, 33.1;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.02. HRMS (EI, 70 eV)  $m/z$  (%): 365 ( $\text{M}^{+2}$ , 9), 363 ( $\text{M}^+$ , 13), 328 (100), 292 (26), 179 (91); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{FNO}$  364.0666; Found 364.0666.

### 4-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-

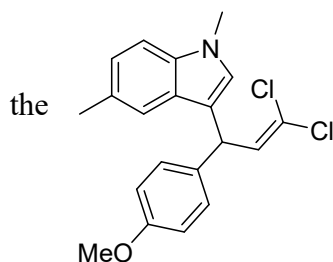
### 1H-indole (4aaf):



Following the general procedure A, product **4aaf** was obtained as a brown oil (60.1 mg, 80% yield,  $R_f = 0.6$  (PE/EA = 20 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.22 (m, 1H), 7.16-7.12 (m, 2H), 7.12-7.08 (m, 1H), 7.05-7.00 (m, 1H), 6.85-6.75 (m, 3H), 6.35 (s, 1H), 5.90-5.75 (m, 1H), 3.77 (s, 3H), 3.73 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 138.6, 135.3, 133.2, 128.8, 128.2, 122.4, 120.5, 113.8, 108.1, 55.2, 42.0, 33.1; LRMS (EI, 70 eV)  $m/z$  (%): 381 ( $\text{M}^{+2}$ , 9), 379 ( $\text{M}^+$ , 10), 344 (85), 308 (25), 179 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{Cl}_3\text{NO}$  380.0370; Found 380.0361.

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,5-dimethyl-1H-indole (4aag):

Following

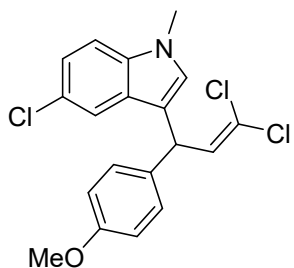


general procedure A, product **4aag** was



obtained as a brown oil (64.8 mg, 90% yield,  $R_f = 0.6$  (PE/EA = 50 : 1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (s, 1H), 7.18 (d,  $J = 8.0$  Hz, 2H), 7.11 (s, 1H), 7.04 (d,  $J = 8.4$  Hz, 1H), 6.84 (d,  $J = 8.3$  Hz, 2H), 6.72 (s, 1H), 6.34 (d,  $J = 10.0$  Hz, 1H), 5.20 (d,  $J = 10.0$  Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 135.9, 132.4, 128.8, 126.9, 123.5, 120.1, 119.3, 114.7, 114.0, 109.1, 55.3, 42.6, 32.8, 21.5 ; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $\text{M}^{+2}$ , 24), 359 ( $\text{M}^+$ , 36), 324 (84), 288 (40), 179 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NO}$  360.0916; Found 360.0918.

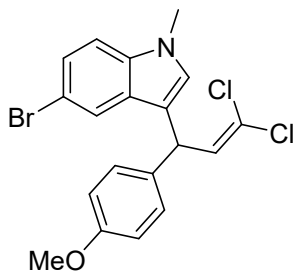
**5-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aah):**



Following the general procedure A, product **4aah** was obtained as a brown oil (59.1 mg, 78% yield,  $R_f = 0.6$  (PE/EA = 20 : 1);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (s, 1H), 7.21-7.11 (m, 4H), 6.90-

6.84 (m, 2H), 6.81-6.77 (m, 1H), 6.31 (s, 1H), 5.25-5.10 (m, 1H), 3.78 (s, 3H), 3.72 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 133.4, 131.9, 128.8, 128.1, 125.0, 122.2, 119.1, 114.1, 110.4, 55.3, 42.5, 33.0; LRMS (EI, 70 eV)  $m/z$  (%): 381( $\text{M}^{+2}$ , 10), 379 ( $\text{M}^+$ , 10), 344 (83), 308 (25), 179 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{Cl}_3\text{NO}$  380.0370; Found 380.0365.

**5-bromo-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aai):**

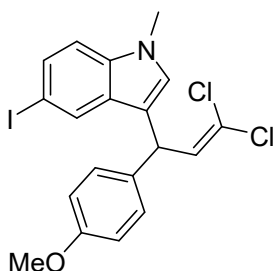


Following the general procedure A, product **4aai** was obtained as a brown oil (74.5 mg, 88% yield,  $R_f = 0.6$  (PE/EA = 20 : 1);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (s, 1H), 7.30-7.25 (m, 1H), 7.20-

7.10 (m, 3H), 6.88-6.82 (m, 2H), 6.80-6.76 (m, 1H), 6.32 (s, 1H), 5.25-5.12 (m, 1H), 3.78

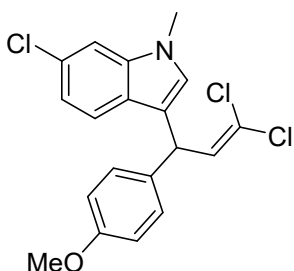
(s, 3H), 3.72 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  133.3, 131.9, 128.8, 127.9, 124.8, 122.2, 114.1, 110.9, 55.3, 42.4, 32.9; LRMS (EI, 70 eV)  $m/z$  (%): 425 ( $\text{M}^{+2}$ , 5), 423 ( $\text{M}^+$ , 3), 390 (69), 309 (48), 274 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{BrCl}_2\text{NO}$  423.9865; Found 423.9864.

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-5-iodo-1-methyl-1H-indole (4aaj):



Following the general procedure A, product **4aaj** was obtained as a brown oil (59.3 mg, 63% yield,  $R_f = 0.6$  (PE/EA = 20 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (s, 1H), 7.50-7.40 (m, 1H), 7.28-7.22 (m, 1H), 7.20-7.12 (m, 1H), 7.08-7.00 (m, 1H), 6.90-6.80 (m, 2H), 6.78-6.70 (m, 1H), 6.31 (s, 1H), 5.22-5.10 (m, 1H), 3.79 (s, 3H), 3.70 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 136.5, 133.4, 131.9, 130.3, 128.8, 128.4, 127.6, 114.8, 114.1, 111.4, 82.8, 55.3, 42.4, 32.9; LRMS (EI, 70 eV)  $m/z$  (%): 473 ( $\text{M}^{+2}$ , 19), 471 ( $\text{M}^+$ , 23), 436 (17), 309 (36), 274 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{INO}$  471.9726; Found 471.9719.

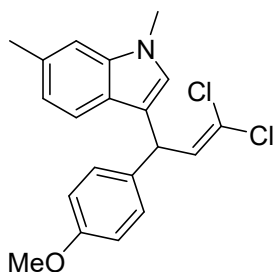
### 6-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aak):



Following the general procedure A, product **4aak** was obtained as a brown oil (37.9 mg, 50% yield,  $R_f = 0.6$  (PE/EA = 20 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.26 (m, 2H), 7.20-7.14 (m, 2H), 7.01-6.95 (m, 1H), 6.90-6.89 (m, 2H), 6.80-6.75 (m, 1H), 6.31 (s, 1H), 5.25-5.15 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 133.4, 131.9, 128.8, 128.1, 127.5, 125.3, 120.6, 120.5, 119.8, 115.7, 114.1, 109.4, 55.3, 42.6, 32.9; LRMS (EI, 70 eV)  $m/z$  (%): 381 ( $\text{M}^{+2}$ , 13), 379 ( $\text{M}^+$ , 13), 344 (100), 308 (28), 179 (98); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{17}\text{Cl}_3\text{NO}$  380.0370; Found

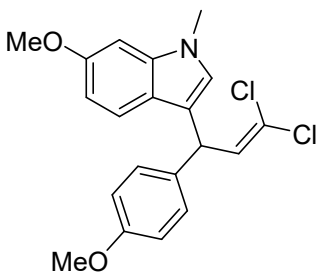
380.0363.

**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,6-dimethyl-1H-indole (4aal):**



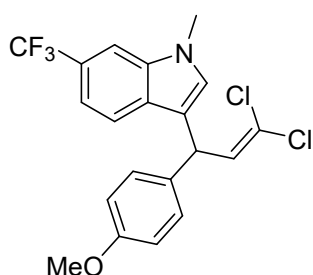
Following the general procedure A, product 4aal was obtained as a brown oil (42.3 mg, 59% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.17 (s, 3H), 7.12-7.06 (m, 1H), 6.90-6.81 (m, 3H), 6.71-6.66 (m, 1H), 6.34 (s, 1H), 5.40-5.10 (m, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.46 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 137.9, 133.9, 132.4, 131.8, 128.9, 126.3, 120.9, 119.4, 115.2, 114.0, 109.4, 55.3, 42.8, 32.7, 21.9; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $\text{M}^+ + 2$ , 33), 359 ( $\text{M}^+$ , 51), 324 (100), 288 (58), 264 (26); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NO}$  360.0916; Found 360.0918.

**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-6-methoxy-1-methyl-1H-indole (4aam):**



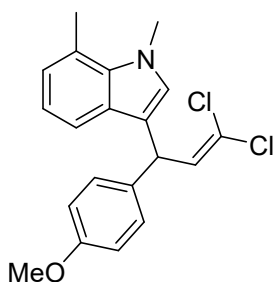
Following the general procedure A, product 4aam was obtained as a brown oil (30.1 mg, 40% yield,  $R_f = 0.6$  (PE/EA = 20 : 1));  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.12 (m, 3H), 6.90-6.80 (m, 2H), 6.73 (s, 1H), 6.69 (d,  $J = 8.0$  Hz, 1H), 6.66 (s, 1H), 6.32 (d,  $J = 11.0$  Hz, 1H), 5.18 (d,  $J = 10.5$  Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 156.5, 138.2, 133.8, 132.3, 128.9, 125.7, 121.1, 120.4, 120.2, 115.4, 114.0, 109.0, 93.0, 55.7, 55.3, 42.8, 32.8; LRMS (EI, 70 eV)  $m/z$  (%): 377 ( $\text{M}^+ + 2$ , 55), 375 ( $\text{M}^+$ , 85), 340 (100), 304 (60), 179 (62); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NO}_2$  376.0866; Found 376.0864.

**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-6-(trifluoromethyl)-1H-indole (4aan):**



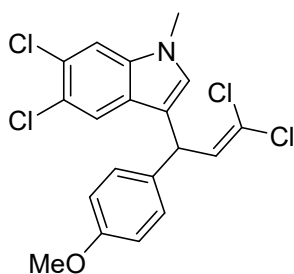
Following the general procedure A, product **4aan** was obtained as a brown oil (59.4 mg, 70% yield,  $R_f = 0.5$  (PE/EA = 20 : 1);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (s, 1H), 7.42-7.33 (m, 1H), 7.20-7.10 (m, 2H), 6.98-6.90 (m, 1H), 6.88-6.78 (m, 2H), 6.33 (s, 1H), 5.40-5.10 (m, 1H), 3.86-3.75 (m, 6H).;  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 133.3, 131.8, 129.4, 128.9, 128.8, 120.2, 115.8, 114.1, 107.0, 55.3, 42.5, 33.0;  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -60.56. LRMS (EI, 70 eV)  $m/z$  (%): 415 ( $\text{M}^{+2}$ , 8), 413 ( $\text{M}^+$ , 12), 378 (89), 342 (25), 179 (100); 377 ( $\text{M}^{+2}$ , 55), 375 (85), 340 (100), 304 (60), 179 (62); HRMS (ESI-TOF)  $m/z$ : [ $\text{M} + \text{H}$ ] $^+$  Calcd for  $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{F}_3\text{NO}$  414.0634; Found 414.0644.

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,7-dimethyl-1H-indolee (**4aao**):



Following the general procedure A, product **4aao** was obtained as a brown oil (64.6 mg, 90% yield,  $R_f = 0.6$  (PE/EA = 50 : 1);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.10 (m, 3H), 6.93-6.86 (m, 2H), 6.85-6.77 (m, 2H), 6.70-6.60 (m, 1H), 6.31 (s, 1H), 5.38-4.98 (m, 1H), 3.99 (s, 3H), 3.77 (s, 3H), 2.73 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 133.8, 132.3, 128.9, 128.5, 127.9, 124.6, 121.4, 119.5, 117.8, 115.0, 114.0, 55.3, 42.6, 36.7, 19.7; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $\text{M}^{+2}$ , 31), 359 ( $\text{M}^+$ , 47), 324 (80), 288 (62), 179 (100); HRMS (ESI-TOF)  $m/z$ : [ $\text{M} + \text{H}$ ] $^+$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{NO}$  360.0916; Found 360.0914.

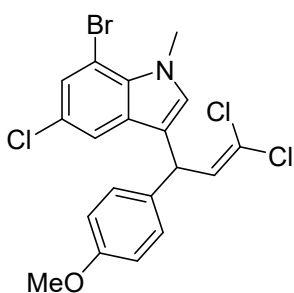
### 5,6-dichloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (**4aap**):



Following the general procedure A, product **4aap** was obtained as a brown oil (61.8 mg, 75% yield,  $R_f = 0.6$  (PE/EA = 50 : 1);  $^1\text{H NMR}$

NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (s, 1H), 7.32 (s, 1H), 7.24-7.08 (s, 2H), 6.93-6.82 (m, 2H), 6.80 (s, 1H), 6.28 (d, *J* = 8.5 Hz, 1H), 5.14 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.6, 133.1, 131.6, 128.7, 128.7, 126.3, 126.0, 123.3, 120.8, 120.7, 115.2, 114.2, 111.0, 55.3, 42.4, 33.0; LRMS (EI, 70 eV) *m/z* (%): 415 (M<sup>+</sup>+2, 14), 413 (M<sup>+</sup>, 11), 378 (54), 308 (15), 179 (100); HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>Cl<sub>4</sub>NO 413.9981; Found 413.9996

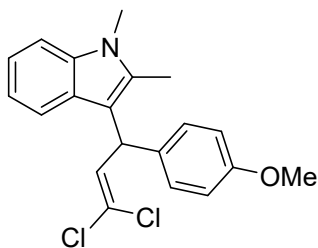
**7-bromo-5-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole**



**(4aaq):**

Following the general procedure A, product **4aaq** was obtained as a brown oil (29.2 mg, 32% yield, *R<sub>f</sub>* = 0.6 (PE/EA = 20 : 1)); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31 (s, 1H), 7.20-7.10 (m, 3H), 6.89-6.81 (m, 2H), 6.78-6.72 (m, 1H), 6.26 (s, 1H), 5.19-5.04 (m, 1H), 4.09 (s, 3H), 3.81 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.6, 132.9, 131.5, 131.1, 130.1, 128.7, 126.6, 125.0, 120.9, 118.4, 114.2, 104.1, 55.3, 42.2, 36.8; LRMS (EI, 70 eV) *m/z* (%): 459 (M<sup>+</sup>+2, 17), 457 (M<sup>+</sup>, 9), 424 (74), 308 (26), 179 (100); HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>BrCl<sub>3</sub>NO 457.9475; Found 457.9484.

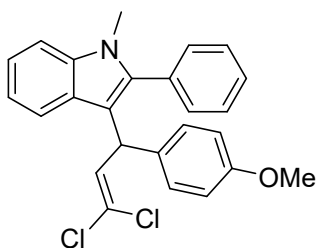
**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,2-dimethyl-1H-indole (4aar):**



Following the general procedure A, product **4aar** was obtained as a brown oil (56.0 mg, 78% yield, *R<sub>f</sub>* = 0.6 (PE/EA = 50 : 1)); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31-7.21 (m, 2H), 7.2-7.05 (m, 3H), 7.00-6.90 (m, 1H), 6.88-6.76 (m, 2H), 6.58-6.46 (s, 1H), 5.42-5.18 (s, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 2.39 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.2, 137.0, 134.0, 133.4, 131.7, 128.5, 126.2, 120.8, 120.4, 119.2, 119.0,

113.8, 110.5, 108.9, 55.3, 41.6, 29.7, 10.7; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $M^{+2}$ , 21), 359 ( $M^{+}$ , 35), 324 (83), 288 (45), 179 (100); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^{+}$  Calcd for  $C_{20}H_{20}Cl_2NO$  360.0916; Found 360.0914.

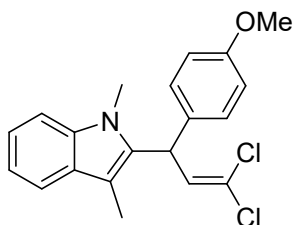
**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-2-phenyl-1H-indole(4aas):**



Following the general procedure A, product **4aas** was obtained as a brown oil (53.0 mg, 63% yield,  $R_f = 0.6$  (PE/EA = 80 : 1);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.40-7.24 (m, 5H), 7.15-6.95 (m, 5H), 6.75-6.60 (m, 2H), 6.46-6.29 (m, 1H),

5.14-4.92 (m, 1H), 3.64 (s, 3H), 3.49 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  158.2, 133.7, 131.6, 130.9, 128.5, 128.4, 121.9, 120.5, 120.2, 119.6, 113.8, 112.3, 109.7, 55.3, 41.9, 30.9; LRMS (EI, 70 eV)  $m/z$  (%): 423 ( $M^{+2}$ , 30), 421 ( $M^{+}$ , 46), 386 (100), 350 (64), 179 (53); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^{+}$  Calcd for  $C_{25}H_{22}Cl_2NO$  422.1073; Found 422.1071.

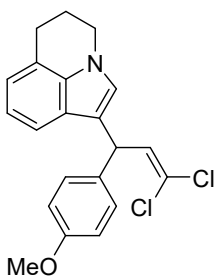
**2-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,3-dimethyl-1H-indole (4aat):**



Following the general procedure A, product **4aat** was obtained as a brown oil (22.3 mg, 31% yield,  $R_f = 0.6$  (PE/EA = 50 : 1);

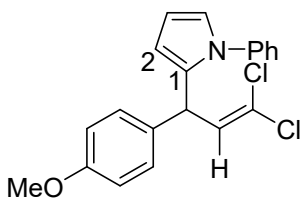
$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.58-7.38 (m, 1H), 7.19-7.12 (m, 3H), 7.00-6.88 (m, 2H), 6.81-6.66 (m, 2H), 6.42-6.19 (m, 1H), 5.47-5.27 (m, 1H), 3.71 (s, 3H), 3.41 (s, 3H), 2.21 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  134.2, 131.5, 129.3, 128.4, 128.1, 122.8, 121.6, 119.0, 118.6, 114.2, 108.8, 77.2, 55.3, 41.3, 30.7; LRMS (EI, 70 eV)  $m/z$  (%): 361 ( $M^{+2}$ , 50), 359 ( $M^{+}$ , 78), 324 (100), 288 (89), 179 (87); HRMS (ESI-TOF)  $m/z$ :  $[M + H]^{+}$  Calcd for  $C_{20}H_{20}Cl_2NO$  360.0916; Found 360.0916.

**1-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-5,6-dihydro-4H-**

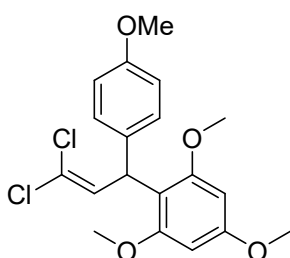


**pyrrolo[3,2,1-ij]quinoline(4aau):**

Following the general procedure A, product **4aau** was obtained as a brown oil (63.1 mg, 85% yield,  $R_f = 0.6$  (PE/EA = 50 : 1);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.11 (m, 2H), 7.06-6.99 (m, 1H), 6.88-6.80 (m, 2H), 6.78-6.73 (m, 2H), 6.72-6.67 (m, 1H), 6.29 (s, 1H), 5.13 (d,  $J = 8.5$  Hz, 1H), 4.06-3.93 (m, 2H), 3.70 (s, 3H), 2.93-2.83 (m, 2H), 2.19-2.07 (m, 2H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 132.9, 131.4, 127.8, 123.0, 120.8, 119.0, 118.4, 117.7, 116.2, 114.3, 112.9, 54.2, 42.9, 42.0, 23.6, 21.8; LRMS (EI, 70 eV)  $m/z$  (%): 373 ( $\text{M}^+ + 2$ , 4), 371 ( $\text{M}^+$ , 80), 356 (19), 265 (100), 91 (51); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{NO}$  372.0916; Found 372.0919.

**2-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-phenyl-1H-pyrrole (4aav):**

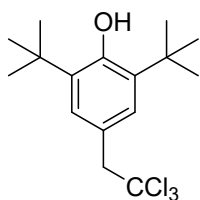
Following the general procedure A, product **4aaa** was obtained as a brown oil (49.3 mg, 68 % yield,  $R_f = 0.6$  (PE/EA = 50 : 1;  $\text{C}_1:\text{C}_2 = 6.1:1$ );  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.59-7.50 (m, 0.38H), 7.48-7.39 (m, 2.75H), 7.34-7.28 (m, 0.39H), 7.24-7.16 (m, 2.45H), 6.95-6.92 (m, 1.81H), 6.91-6.89 (m, 0.28H), 6.85-6.79 (m, 2.09H), 6.77-6.75 (m, 0.18H), 6.63-6.57 (m, 0.83H), 6.21-6.14 (s, 1H), 4.88 (d,  $J = 9.5$  Hz, 1H), 3.70 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  158.6, 158.5, 140.2, 139.7, 135.1, 134.0, 133.3, 132.9, 132.7, 130.1, 129.7, 129.0, 128.9, 128.2, 127.1, 126.8, 125.6, 123.2, 119.9, 119.5, 119.0, 118.50, 116.7, 114.4, 114.2, 110.6, 108.7, 108.5, 60.7, 55.5, 43.9, 42.9; LRMS (EI, 70 eV)  $m/z$  (%): 359 ( $\text{M}^+ + 2$ , 9), 357 ( $\text{M}^+$ , 14), 322 (100), 288 (5), 179 (15); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{NO}$  358.0760; Found 357.0762.

**2-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,3,5-trimethoxybenzene (4aaw):**

Following the general procedure A, product **4aaw** was obtained

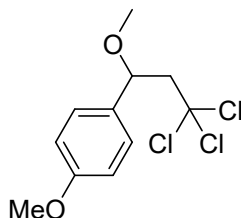
as a brown oil (23.4 mg, 31% yield,  $R_f = 0.6$  (PE/EA = 20 : 1);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.25 (m, 1H), 7.08-7.05 (m, 1H), 6.80-6.75 (m, 2H), 6.16 (d,  $J = 5.5$  Hz, 2H), 5.64-5.56 (m, 1H), 3.89 (s, 1H), 3.81 (s, 3H), 3.78-3.70 (m, 9H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 158.9, 134.5, 132.0, 127.9, 113.4, 91.4, 55.9, 55.3, 55.2, 39.2; LRMS (EI, 70 eV)  $m/z$  (%): 384 ( $\text{M}^{+2}$ , 7), 382 ( $\text{M}^+$ , 10), 347 (50), 311 (100), 179 (18); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{21}\text{Cl}_2\text{O}_4$  383.0811; Found 383.0831.

### 1,3-di-tert-butyl-5-methyl-2-(trichloromethoxy)benzene (5a):



Following the general procedure A, product **5a** was obtained as a brown oil (22.2 mg, 33% yield,  $R_f = 0.6$  (PE/EA = 100 : 1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (s, 1H), 7.22 (s, 1H), 5.27 (s, 1H), 3.83 (s, 2H), 1.45 (s, 18H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 135.4, 128.5, 124.2, 100.0, 59.9, 34.3, 30.3; LRMS (EI, 70 eV)  $m/z$  (%): 338 ( $\text{M}^{+2}$ , 5), 336 ( $\text{M}^+$ , 21), 321 (15), 285(15), 219(100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{24}\text{Cl}_3\text{O}$  337.0887; Found 337.0881.

### 1-methoxy-4-(3,3,3-trichloro-1-methoxypropyl)benzene(5b):

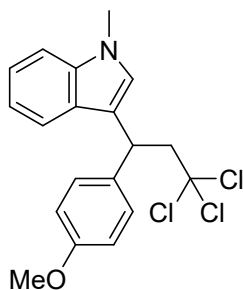


Following the general procedure A, product **5b** was obtained as a brown oil (37.1 mg, 66% yield  $R_f = 0.6$  (PE/EA = 100 : 1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.15 (m, 2H), 7.07 -6.42 (m, 2H), 4.60-4.50 (m, 1H), 3.81 (s, 3H), 3.37 -3.14 (m, 4H), 2.97 (dd,  $J = 15.2, 3.2$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 132.7, 127.9, 114.1, 80.7, 62.1, 56.4, 55.3; LRMS (EI, 70 eV)  $m/z$  (%): 284 ( $\text{M}^{+2}$ , 4), 282 ( $\text{M}^+$ , 4), 151 (100), 135 (21), 91 (7); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_{14}\text{Cl}_3\text{O}_2$  283.0054; Found



283.0053.

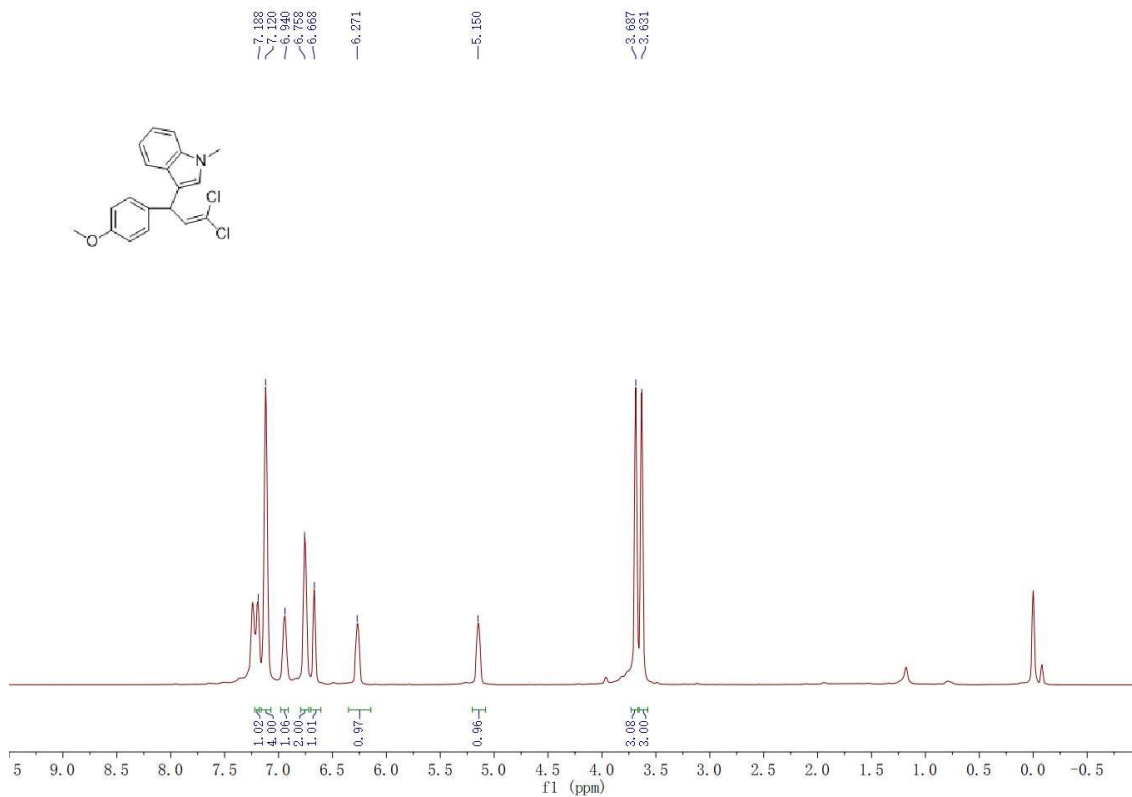
**1-methyl-3-(3,3,3-trichloro-1-(4-methoxyphenyl)propyl)-1H-indole(5c):**



Following the general procedure A , product **5c** was obtained as a brown oil (39.5 mg, 50% yield,  $R_f = 0.6$  (PE/EA = 50 : 1));  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.57 (m, 1H), 7.33-7.20 (m, 4H), 7.14-7.04 (m, 1H), 6.90-6.82 (m, 2H), 6.74 (m, 1H), 4.84-4.70 (m, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.65-3.45 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 137.3, 135.3, 129.2, 126.6, 121.9, 119.3, 119.1, 113.9, 109.4, 99.2, 60.1, 55.2, 40.4, 32.7; LRMS (EI, 70 eV)  $m/z$  (%): 383 ( $\text{M}^+ + 2$ , 6), 381 ( $\text{M}^+$ , 17), 344 (41), 308 (31), 179 (100); HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{19}\text{Cl}_3\text{NO}$  382.0527; Found 382.0524.

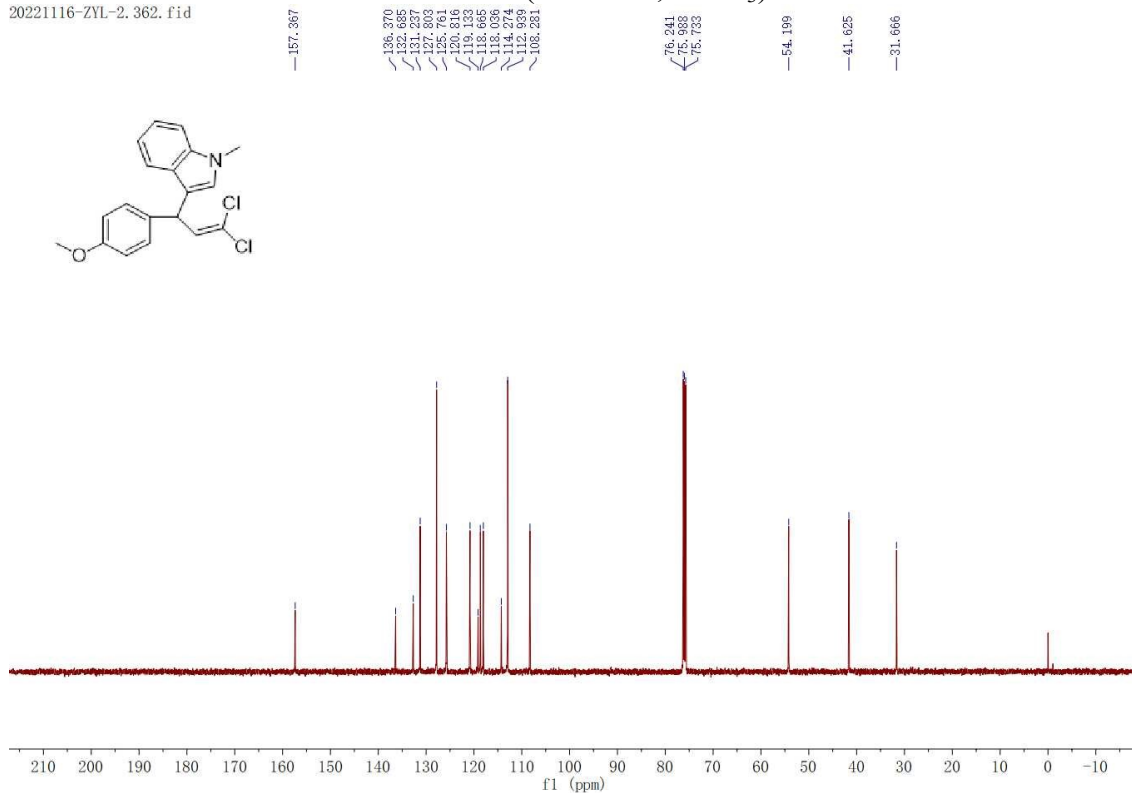
**(C) Spectra**

**3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aaa):**



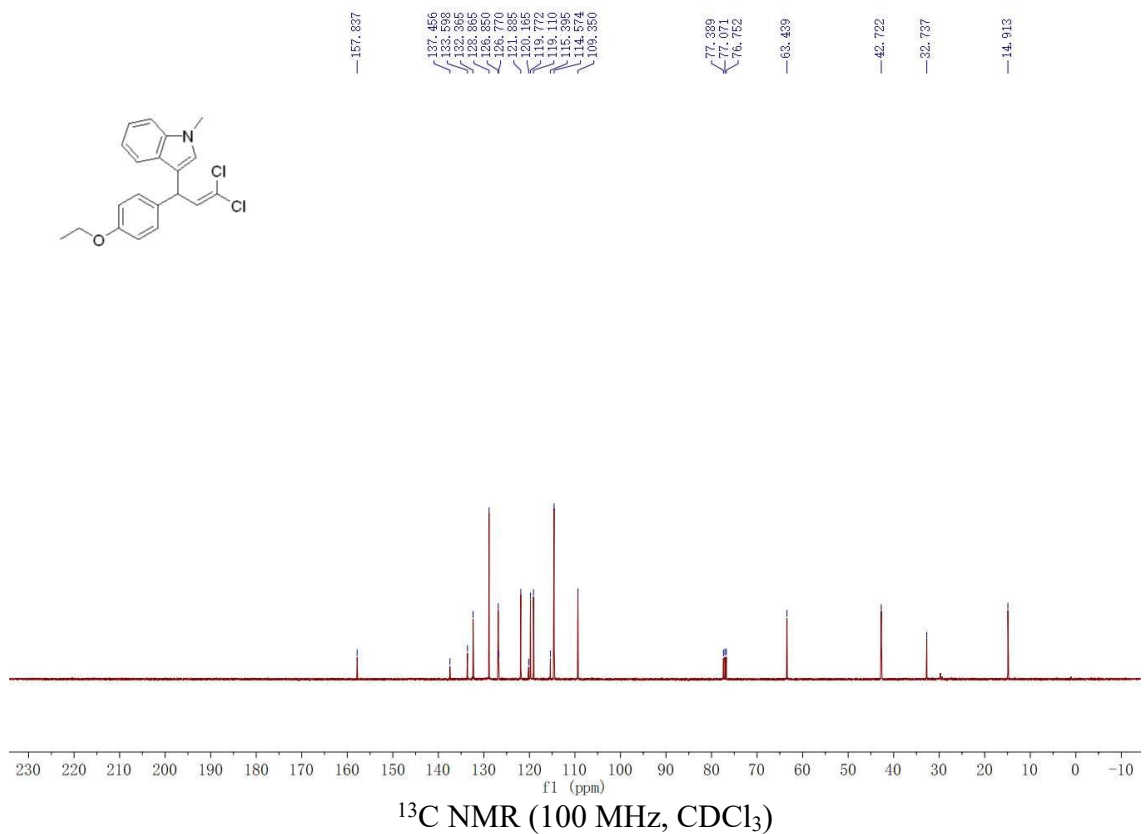
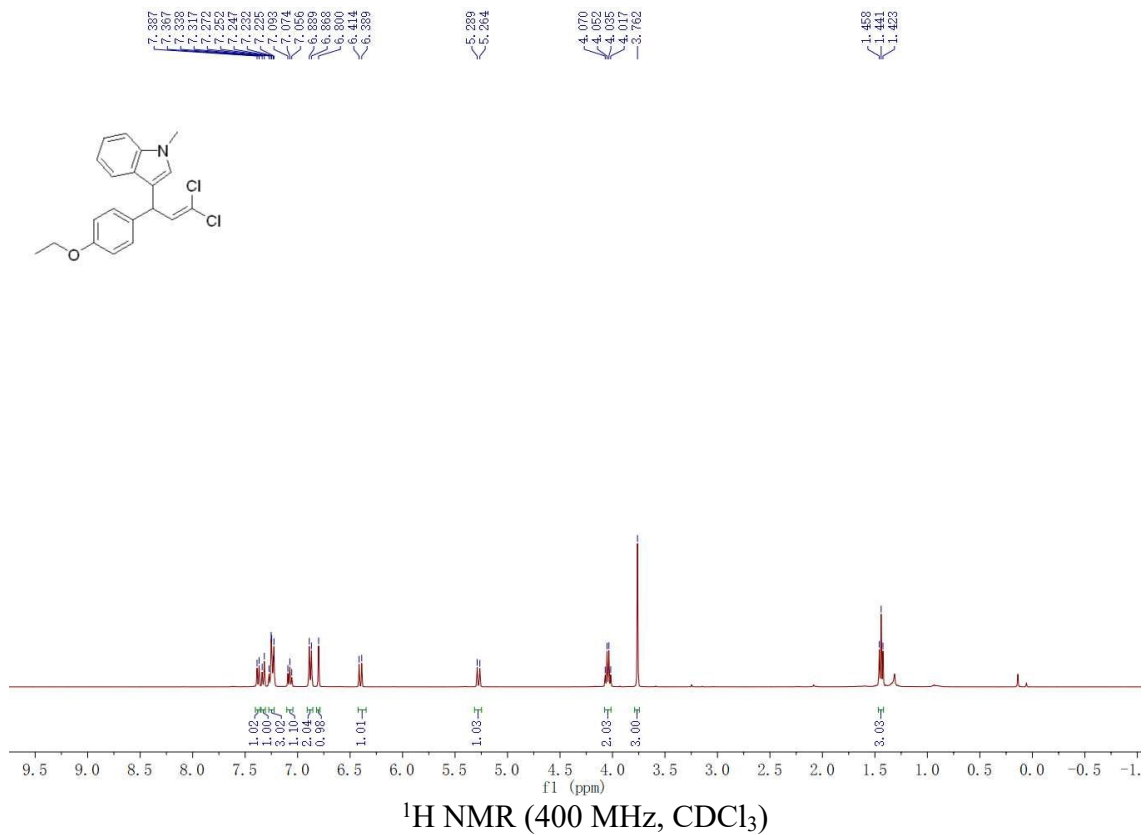
20221116-ZYL-2.362.fid

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

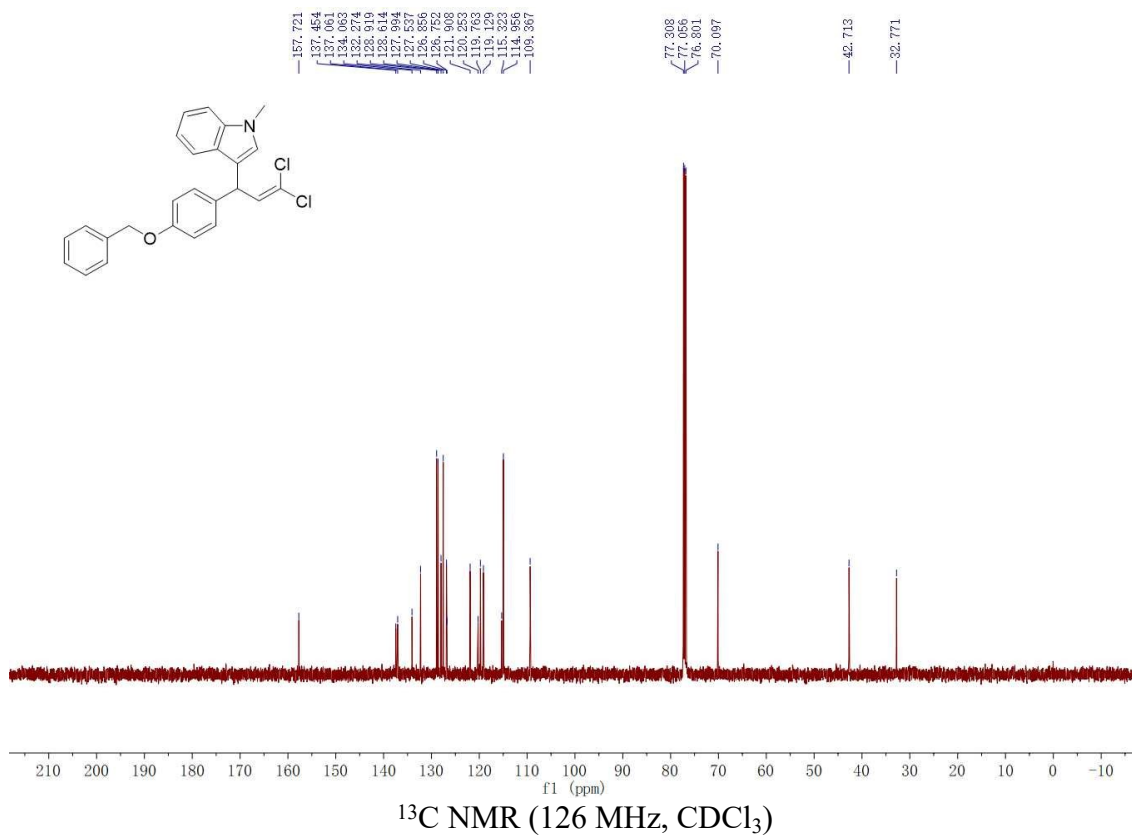
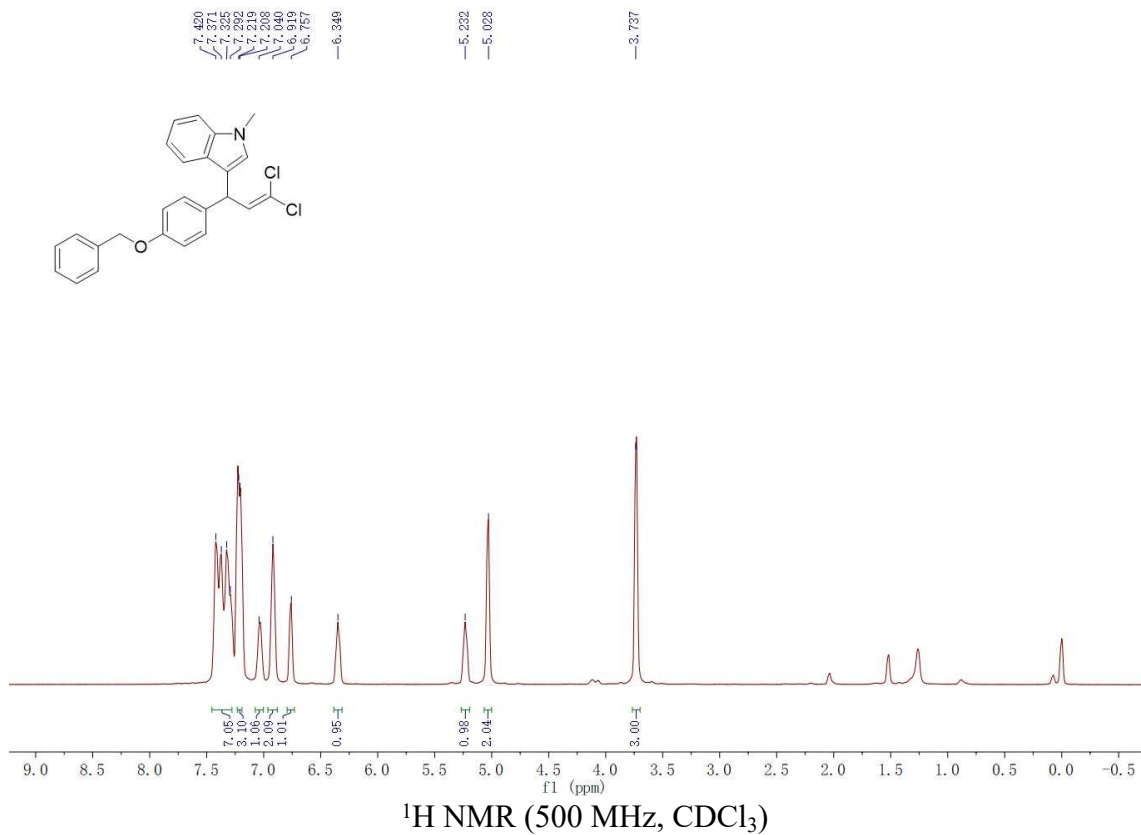


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

**3-(3-dichloro-1-(4-ethoxyphenyl)allyl)-1-methyl-1H-indole (4baa):**

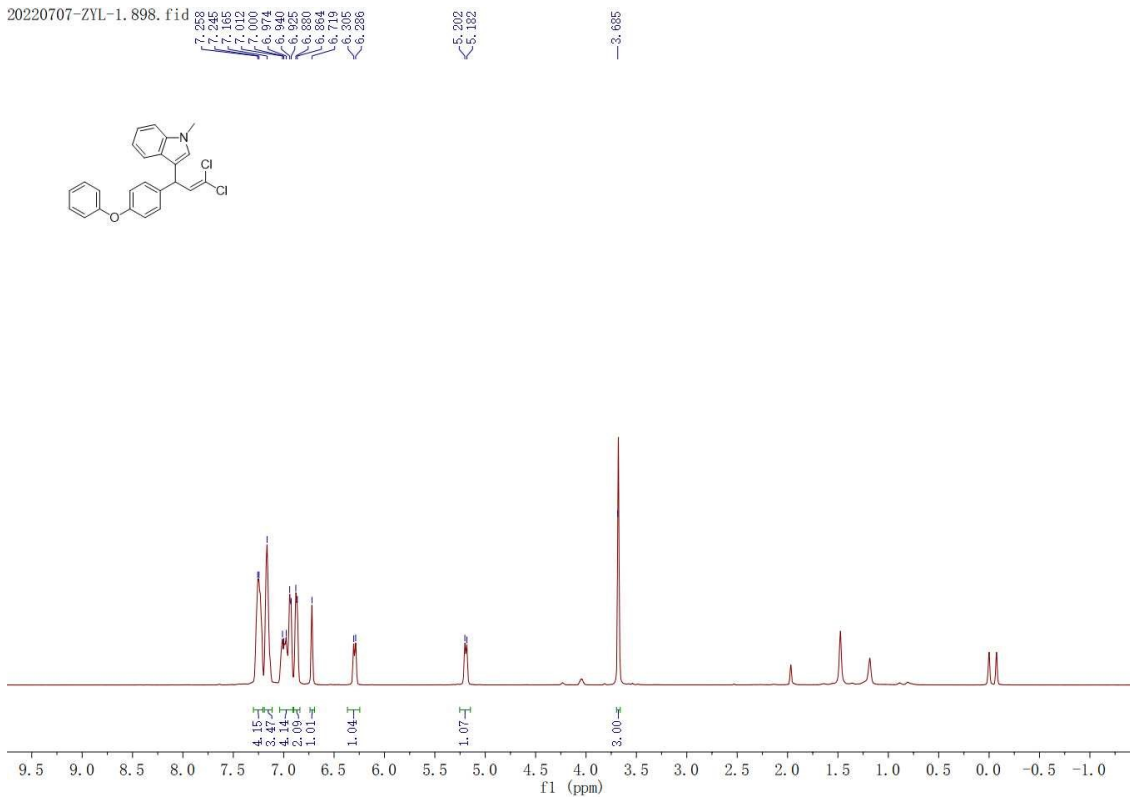


**3-(1-(4-(benzyloxy)phenyl)-3,3-dichloroallyl)-1-methyl-1H-indole (4caa):**



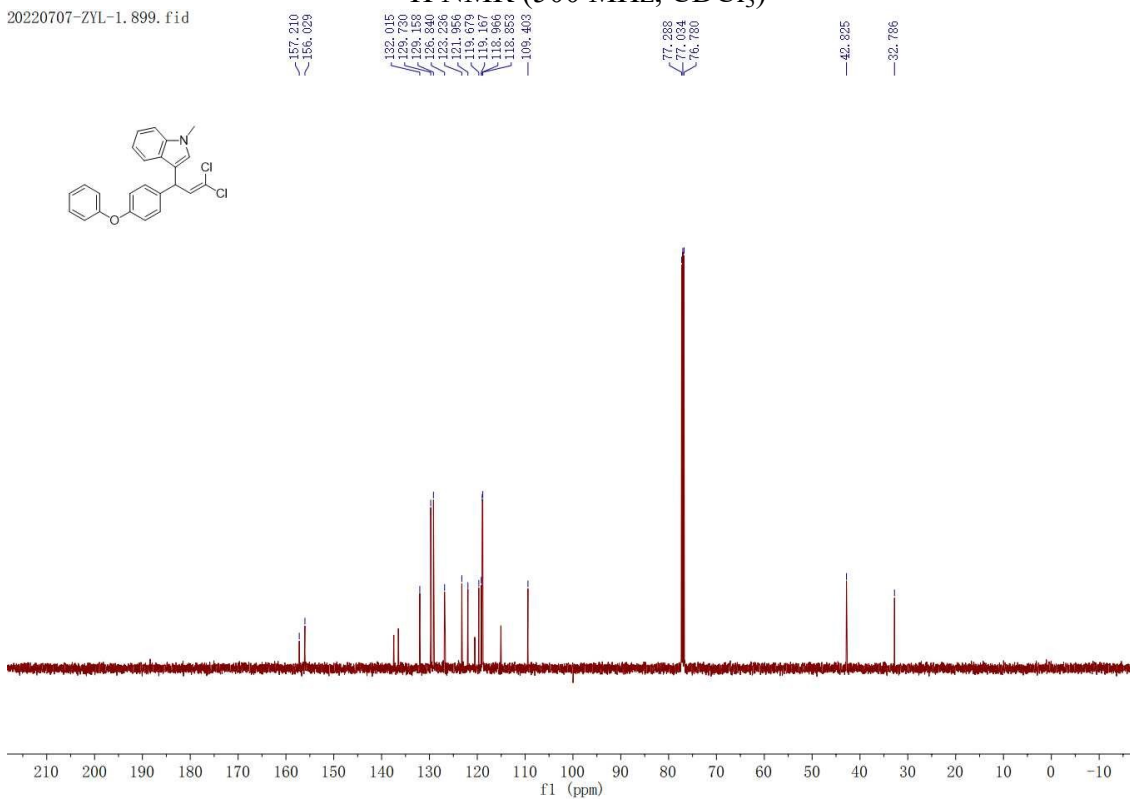
**3-(3,3-dichloro-1-(4-phenoxyphenyl)allyl)-1-methyl-1H-indole (4daa):**

20220707-ZYL-1.898.fid



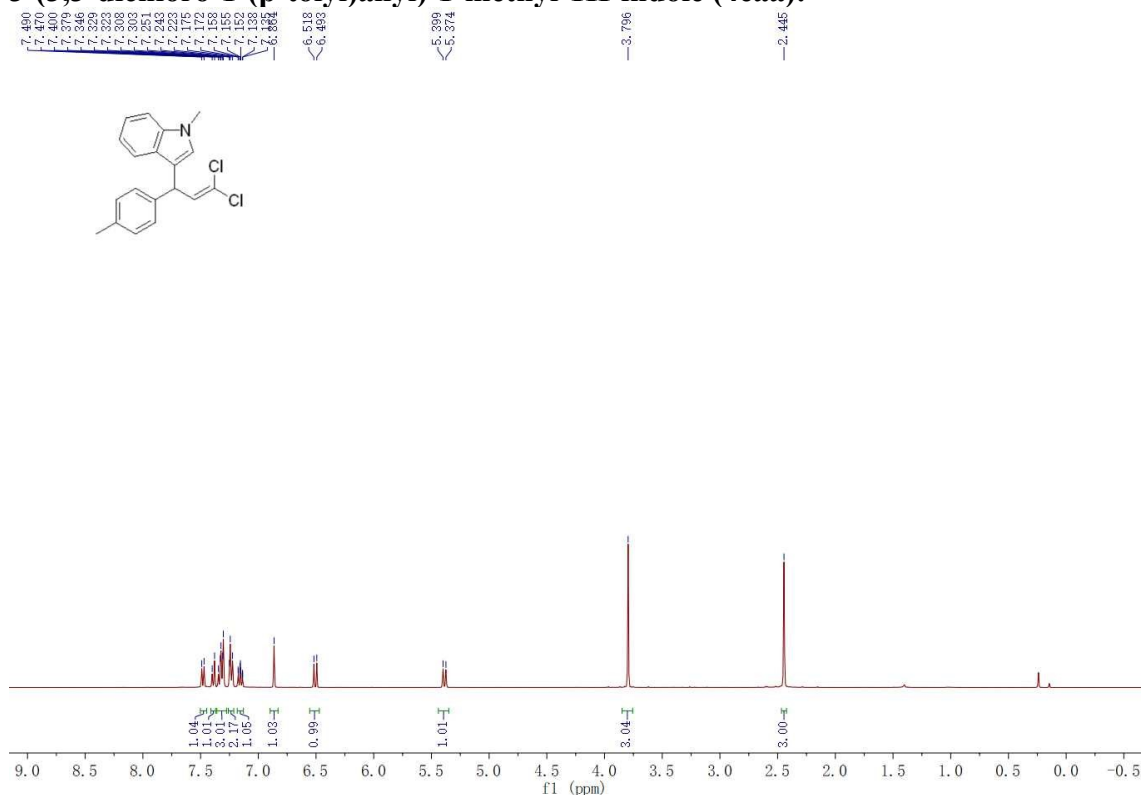
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

20220707-ZYL-1.899.fid



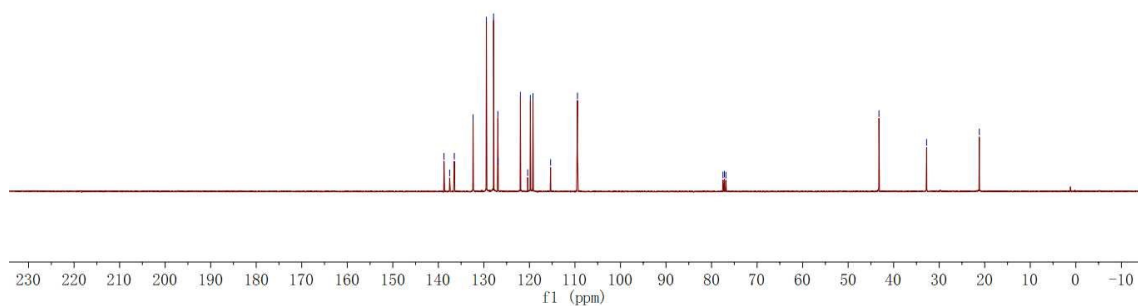
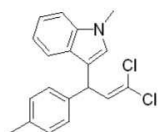
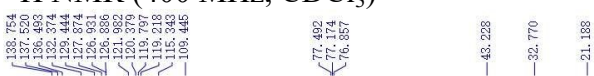
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

**3-(3,3-dichloro-1-(p-tolyl)allyl)-1-methyl-1H-indole (4eaa):**



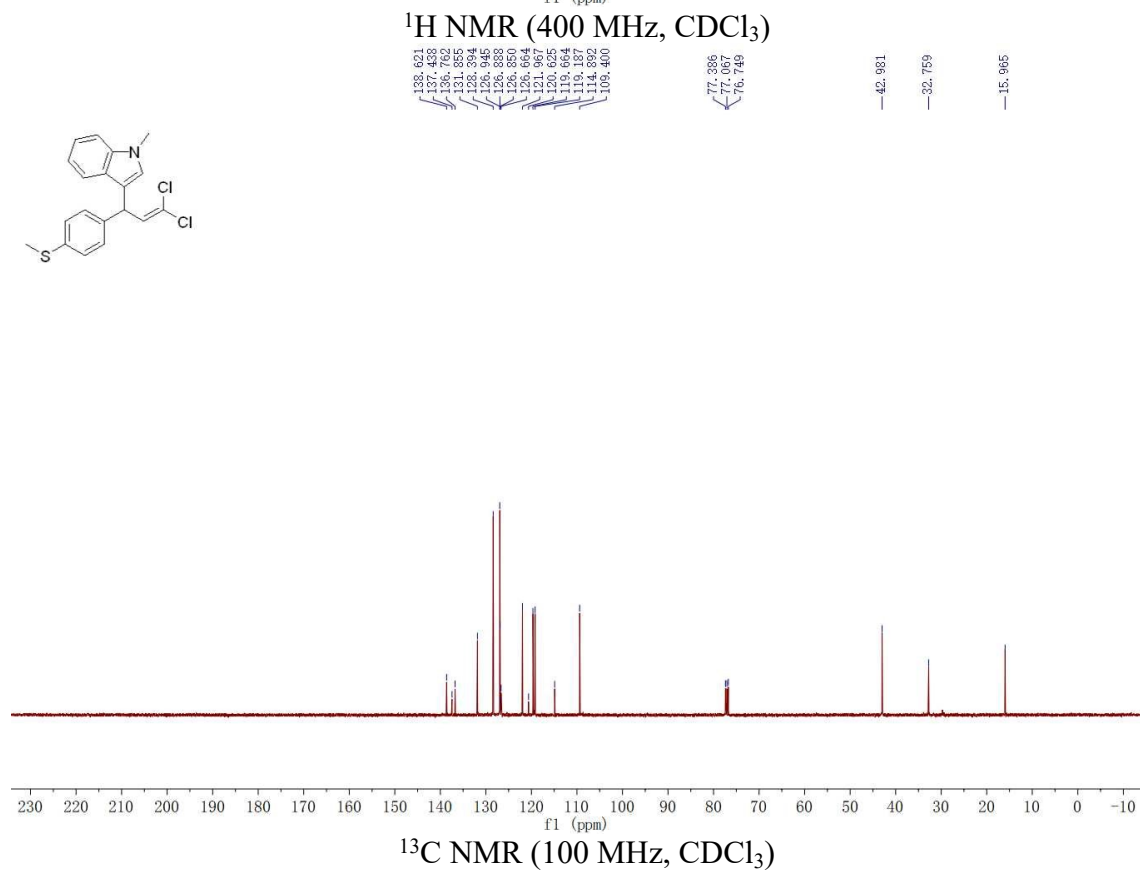
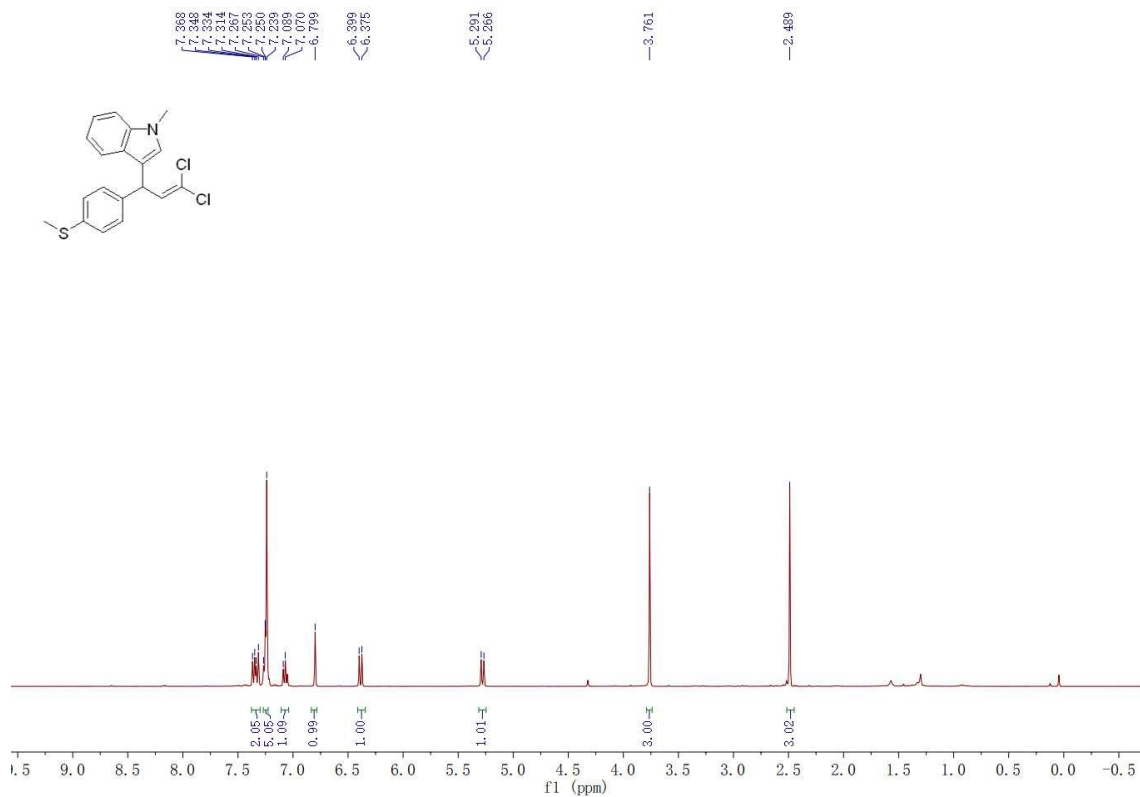
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

2-1-C  
Gradient Shimming



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

**3-(3,3-dichloro-1-(4-(methylthio)phenyl)allyl)-1-methyl-1H-indole (4faa):**



**3-(3,3-dichloro-1-(2,5-dimethylphenyl)allyl)-1-methyl-1H-indole (4haa):**

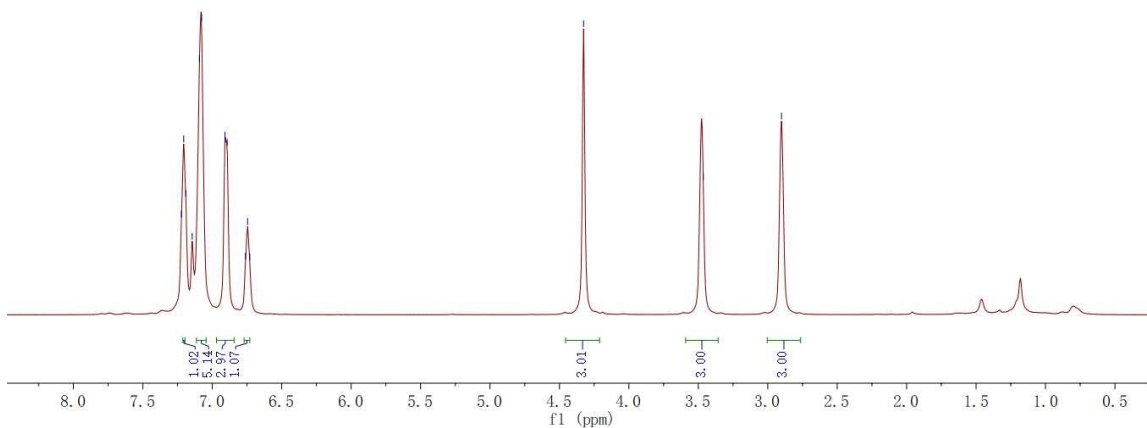
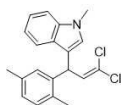
20220607-ZYL-1. 223

7.228  
7.206  
7.191  
7.155  
7.077  
6.908  
6.892  
6.761  
6.746  
6.730

4.326

3.464

2.901



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

20220607-ZYL-1. 223. fid

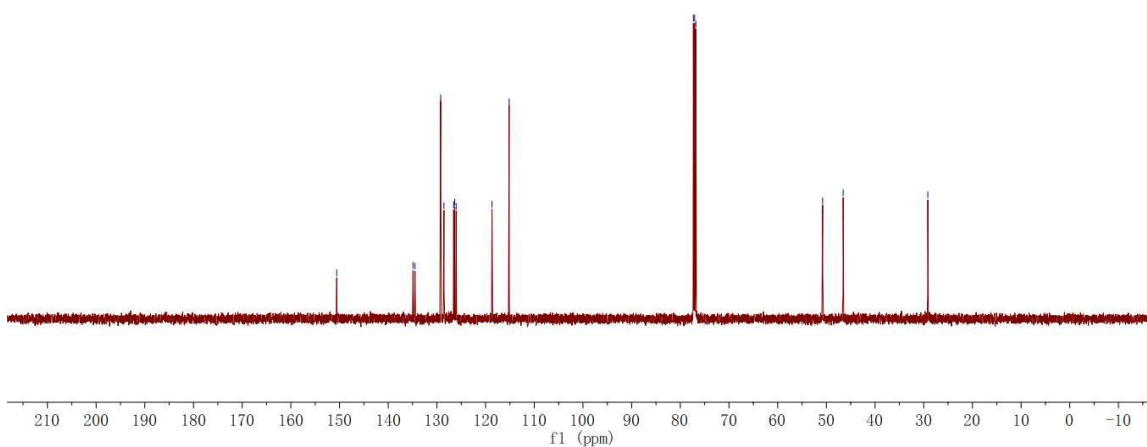
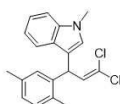
150.579

134.503  
134.493  
129.227  
128.547  
126.564  
126.552  
126.050  
118.888  
115.167

77.318  
77.085  
76.809

50.765  
46.554

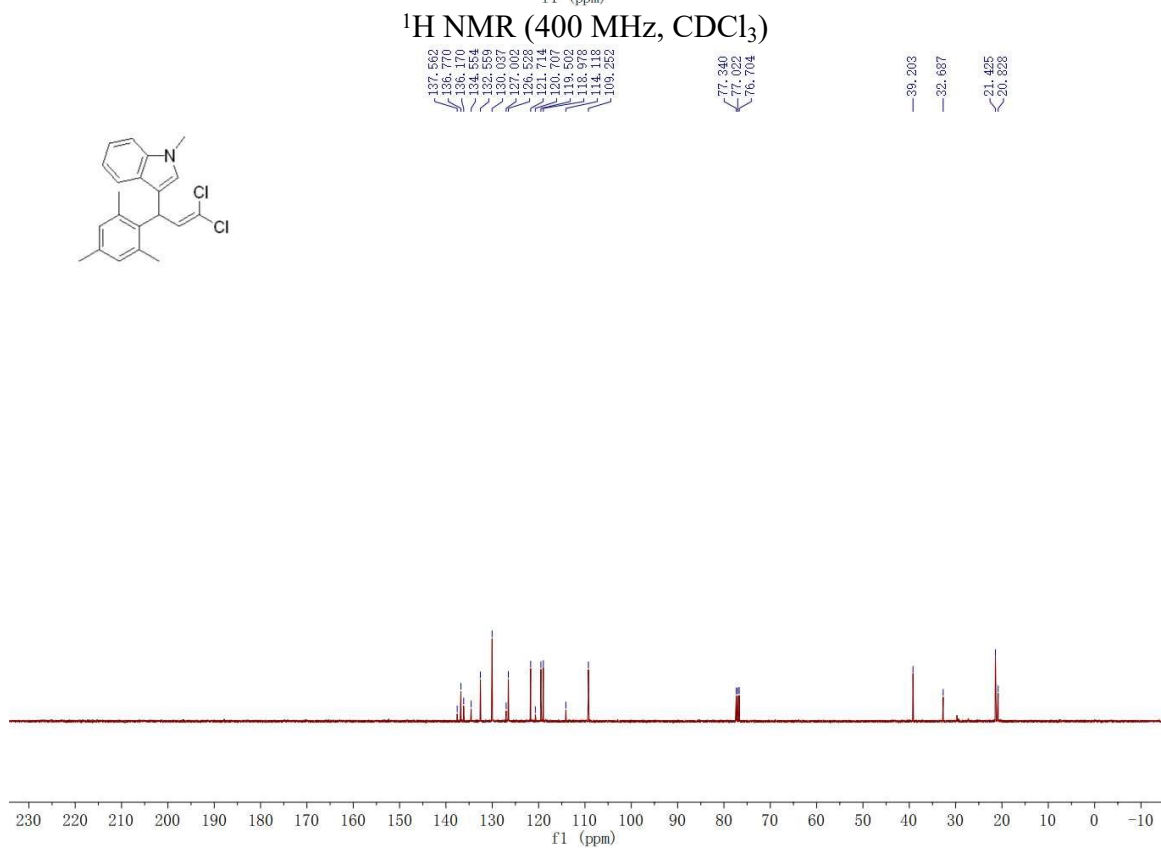
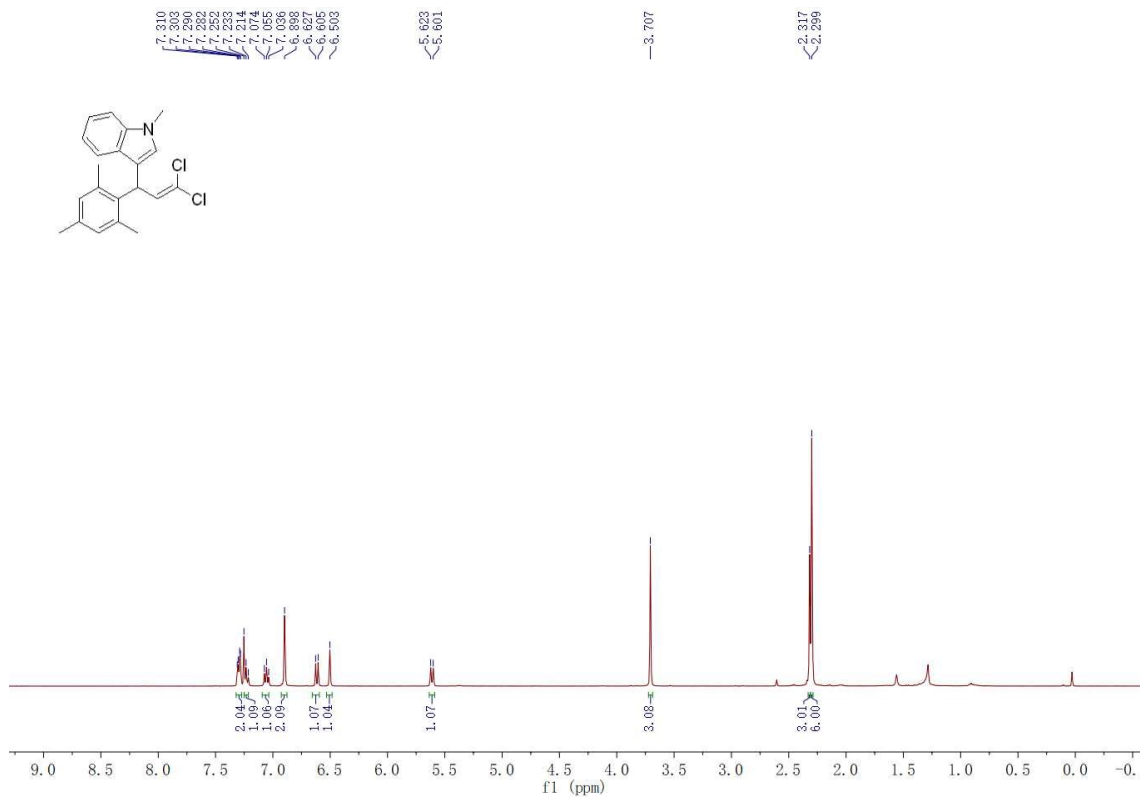
29.158



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

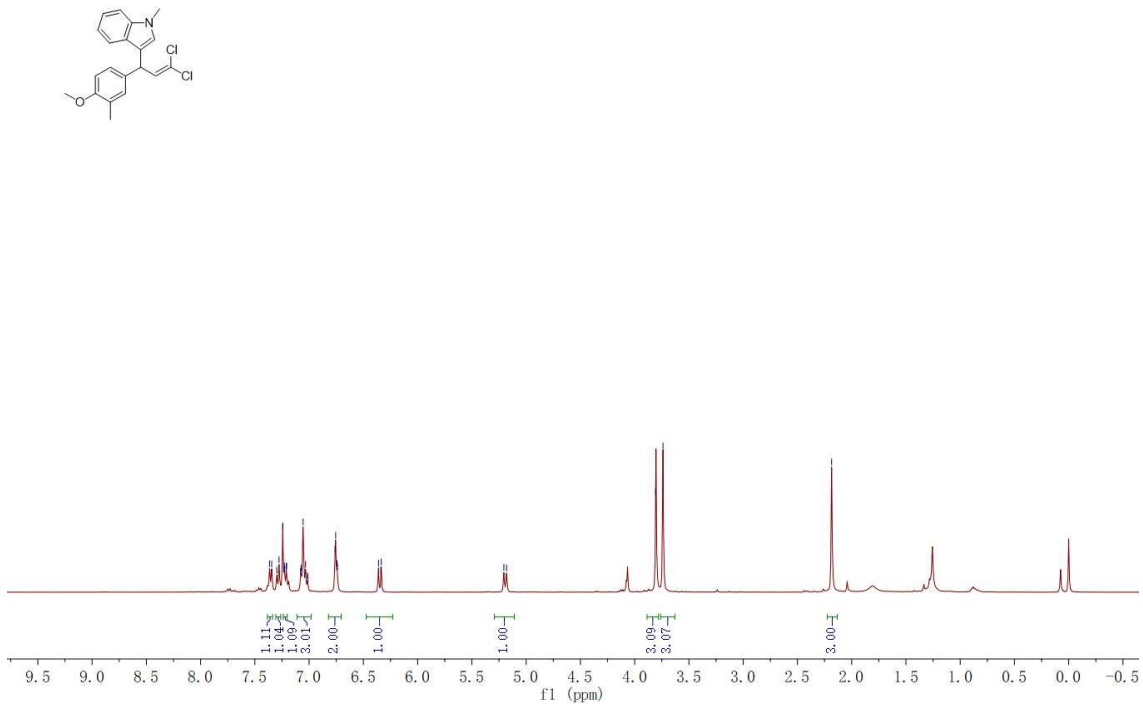
**3-(3,3-dichloro-1-mesitylallyl)-1-methyl-1H-indole (4iaa):**





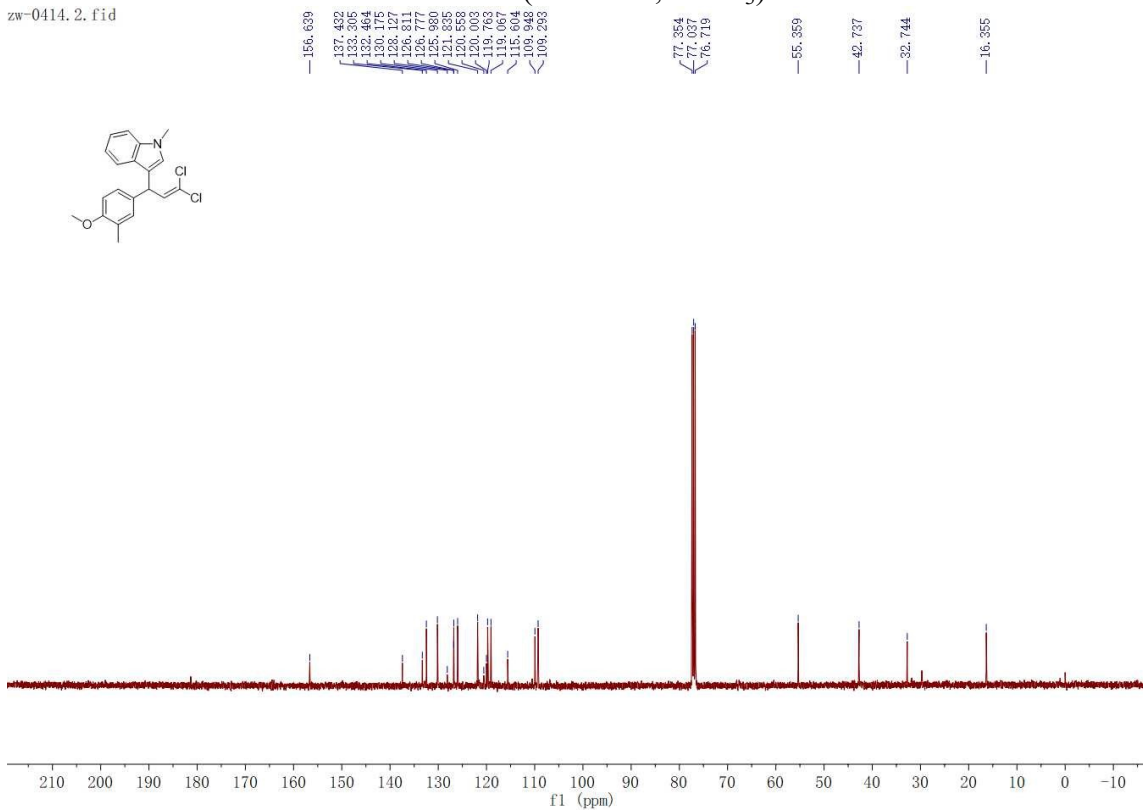
**3-(3,3-dichloro-1-(4-methoxy-3-methylphenyl)allyl)-1-methyl-1H-indole (4jaa):**

zw-0414.1.f1



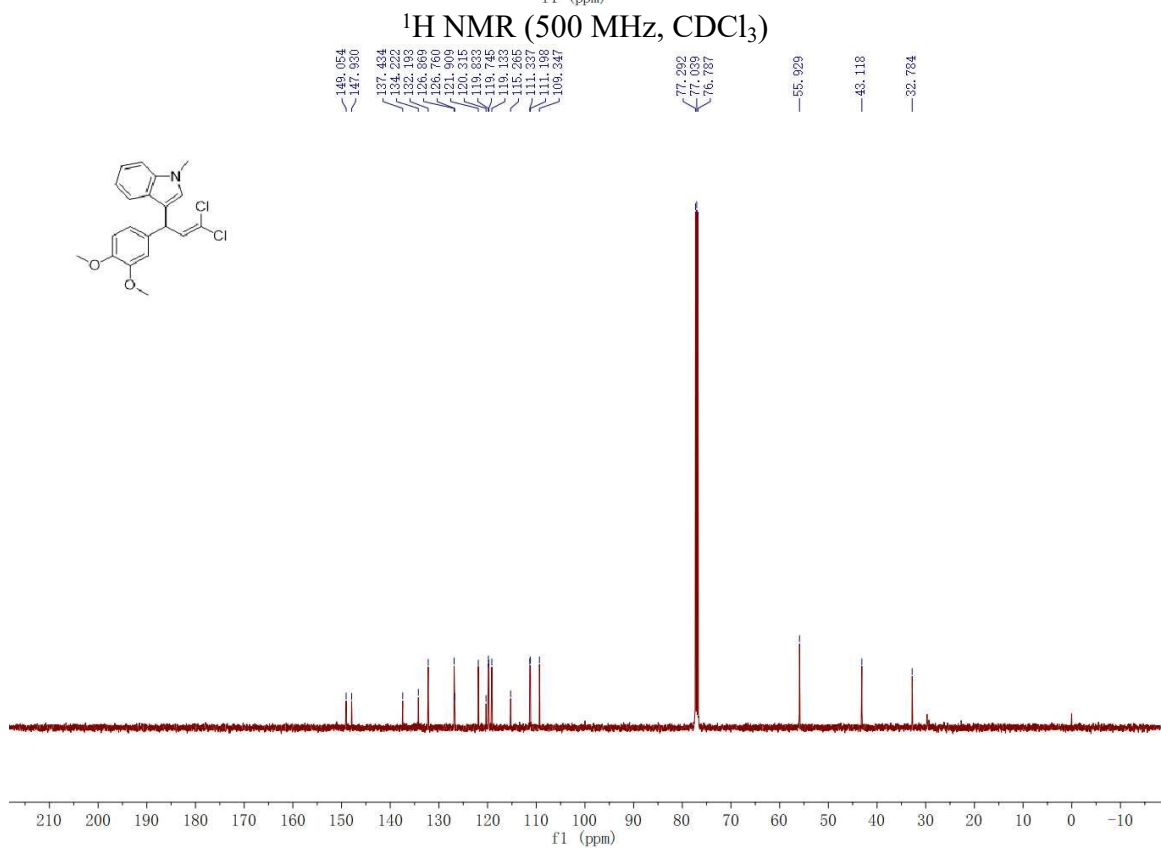
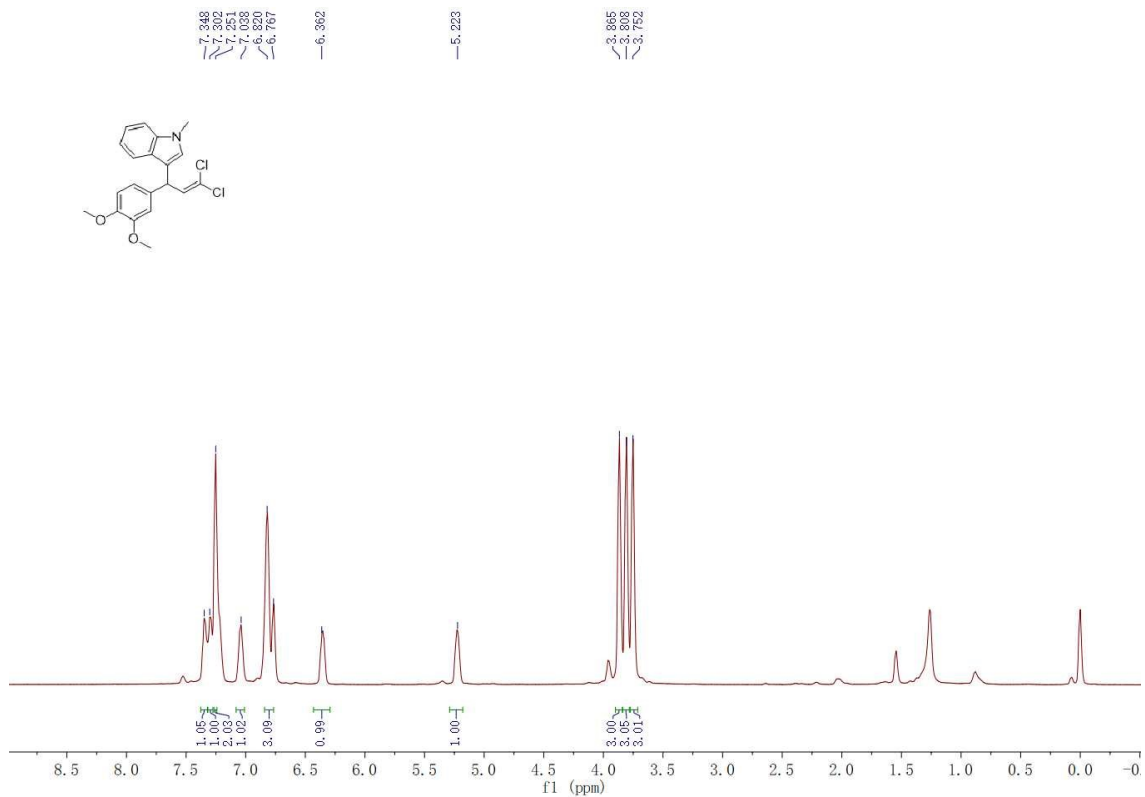
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

zw-0414.2.f1d

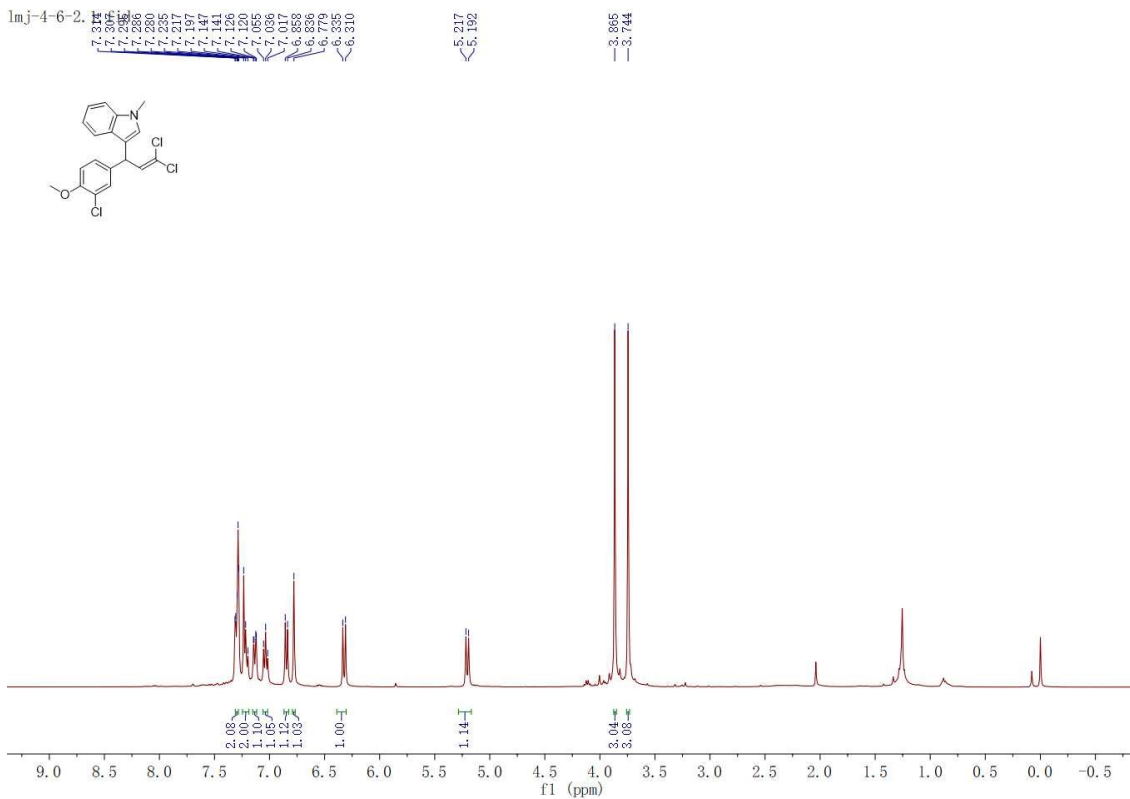


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**3-(3,3-dichloro-1-(3,4-dimethoxyphenyl)allyl)-1-methyl-1H-indole (4kaa):**

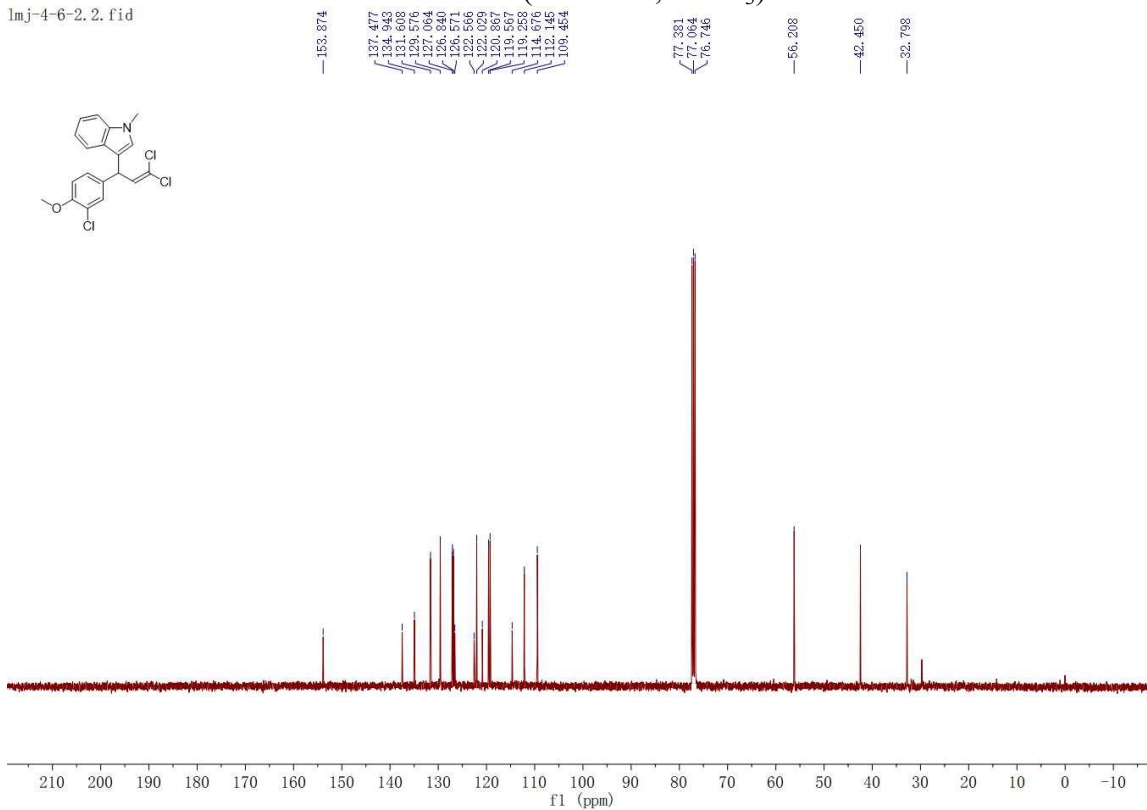


**3-(3,3-dichloro-1-(3-chloro-4-methoxyphenyl)allyl)-1-methyl-1H-indole (4laa):**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

lmj-4-6-2.2.fid



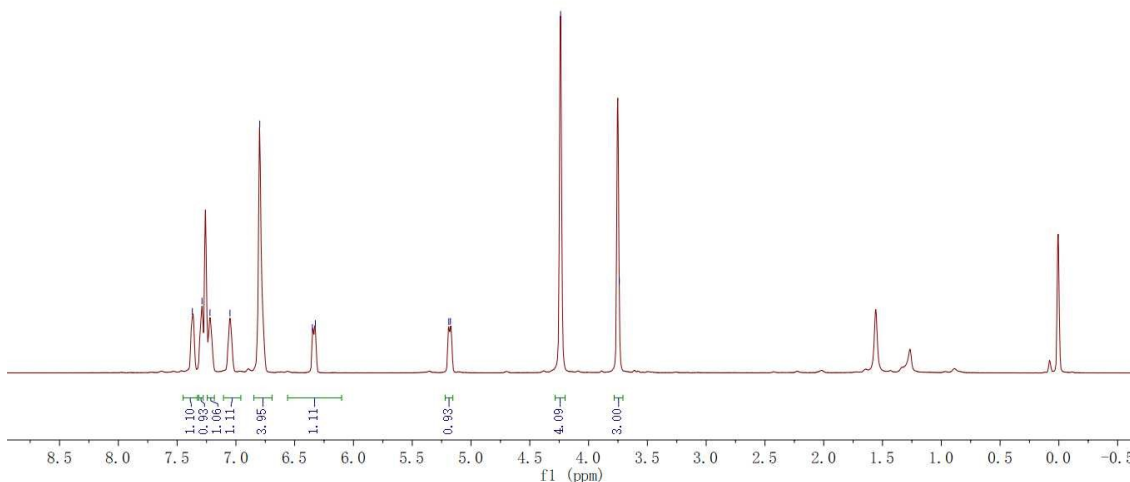
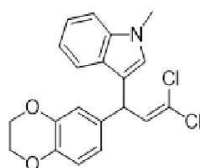
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

**3-(3,3-dichloro-1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)allyl)-1-methyl-1H-indole**

**(4maa):**

20220923-ZYL-2.143.fid

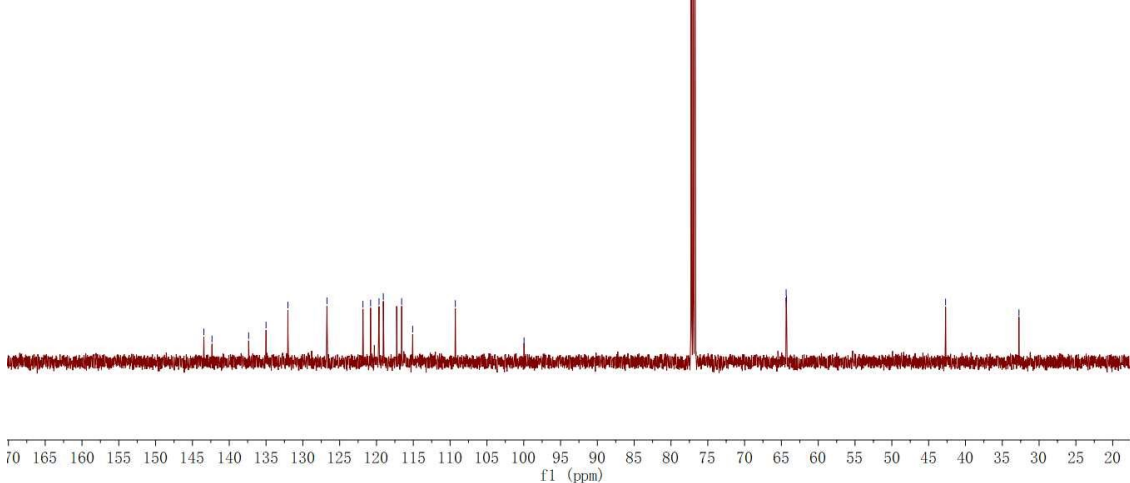
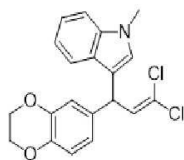
7.370  
7.288  
7.060  
7.050  
6.797  
6.349  
6.324  
5.189  
5.179  
4.238  
3.739



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

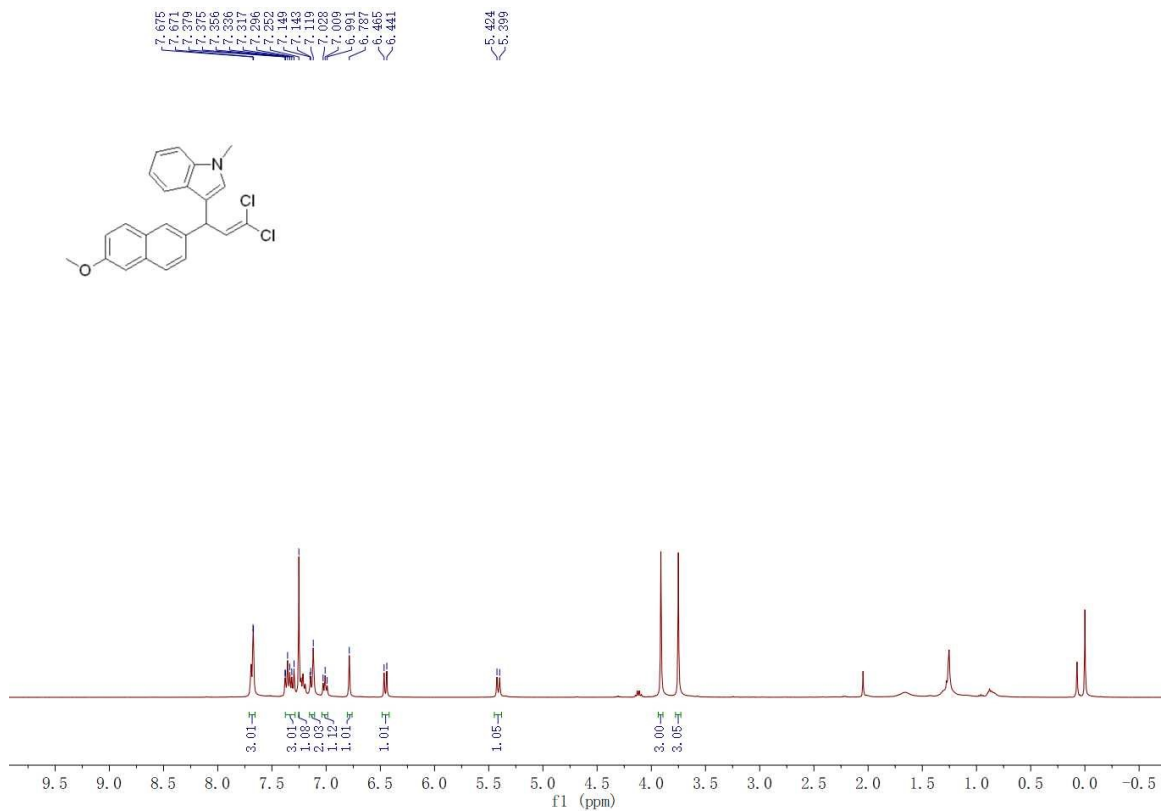
20220923-ZYL-2.144.fid

142.44  
142.346  
137.384  
135.003  
132.031  
126.725  
121.839  
120.800  
118.657  
118.072  
115.527  
115.032  
109.295  
99.960  
77.954  
76.999  
76.746  
64.357  
64.306  
42.700  
32.733

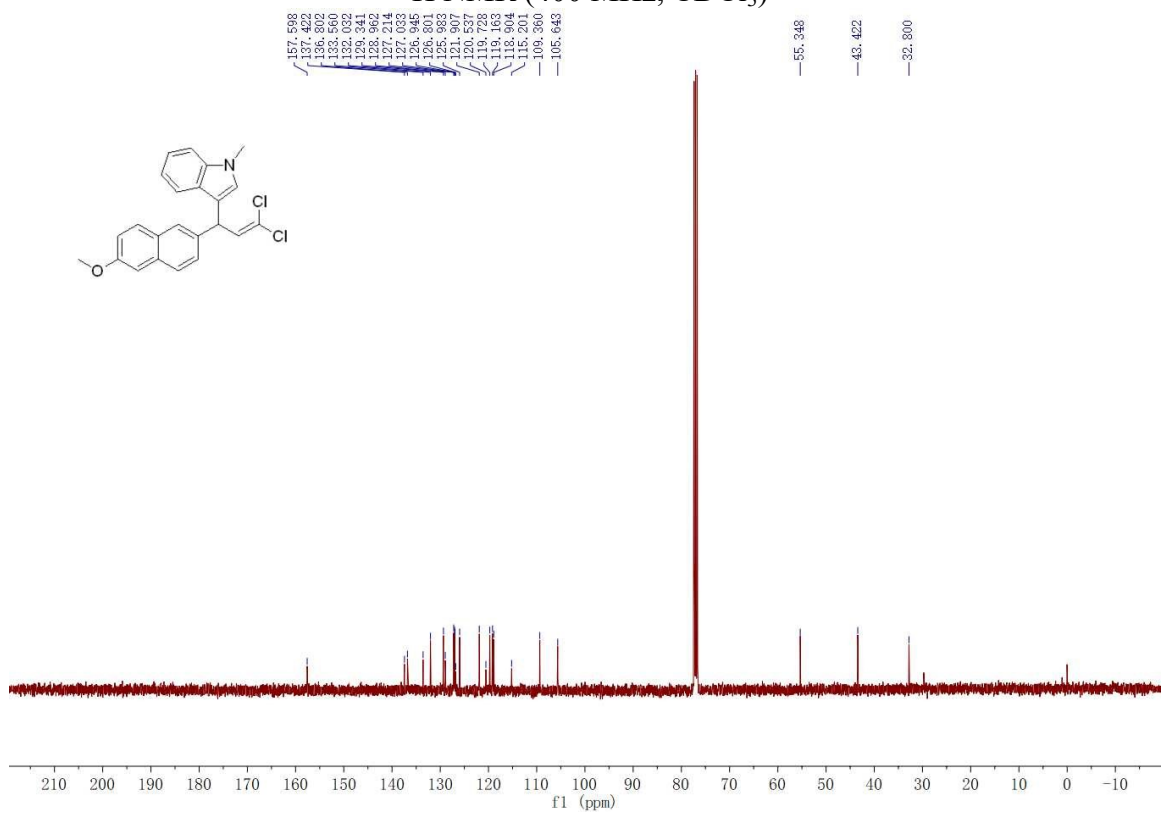


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

**3-(3,3-dichloro-1-(6-methoxynaphthalen-2-yl)allyl)-1-methyl-1H-indole (4oaa):**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



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

**3-(3,3-dichloro-1-(4-methoxyphenyl)-2-methylallyl)-1-methyl-1H-indole (4paa):**

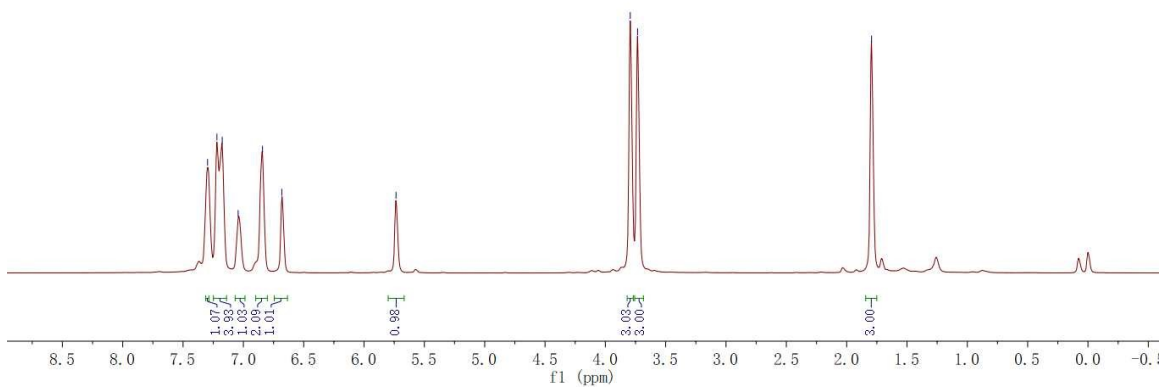
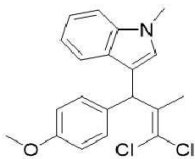
2022-12-2-ZYL. 65. fid

7.297  
7.219  
7.175  
7.063  
6.681

5.735

3.794  
3.733

1.794



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

2022-12-2-ZYL. 66. fid

158.409

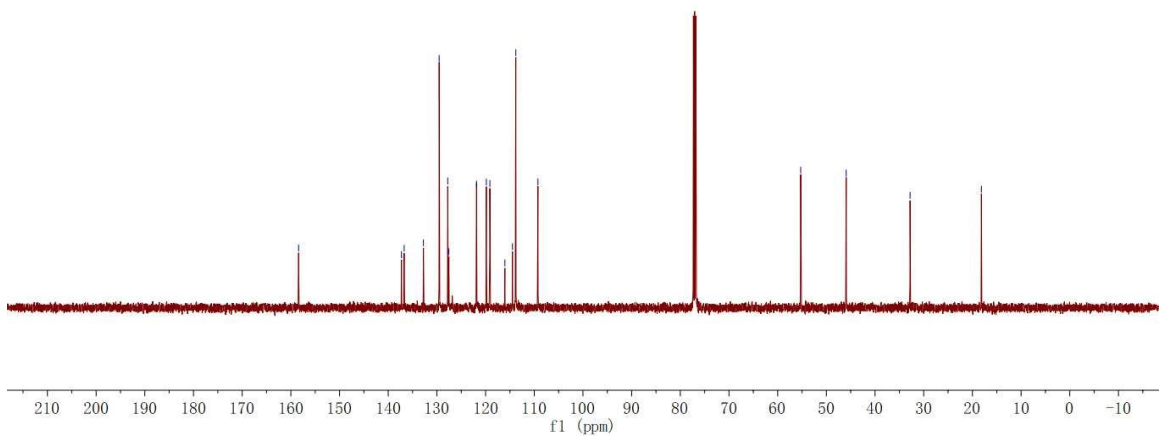
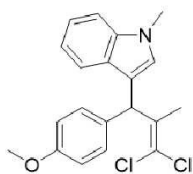
137.279  
136.717  
132.769  
129.537  
127.544  
121.857  
119.846  
119.118  
116.938  
114.303  
113.248  
108.249

55.272

45.924

32.808

18.157



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

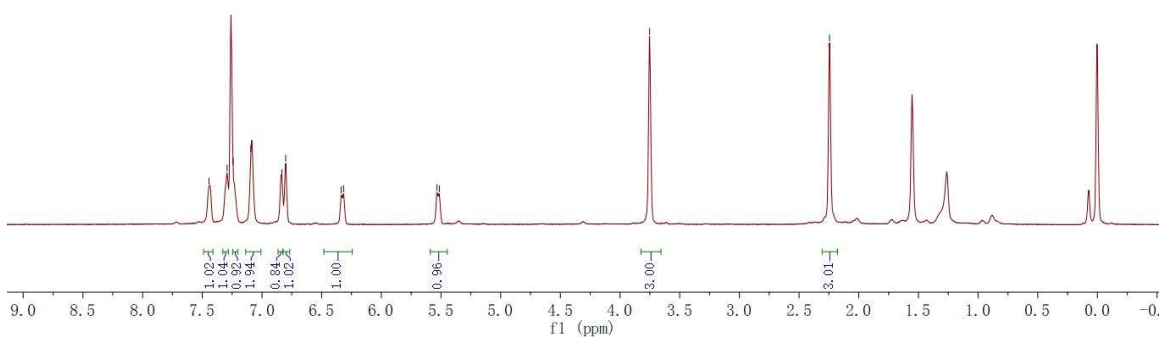
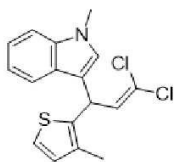
**3-(3,3-dichloro-1-(3-methylthiophen-2-yl)allyl)-1-methyl-1H-indole (4paa):**

20220923-ZYL-1.142.fid

7.444  
7.292  
7.282  
7.094  
6.833  
6.802  
6.336  
6.316  
5.534  
5.514

3.752

2.246



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

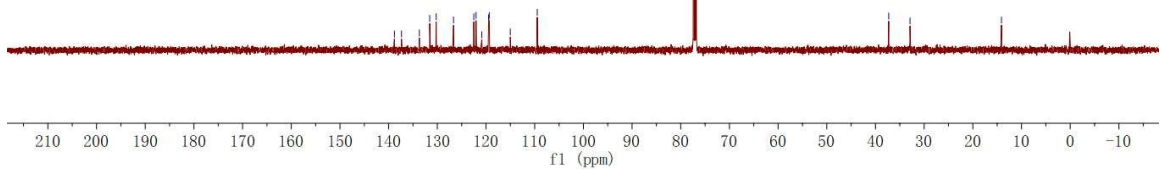
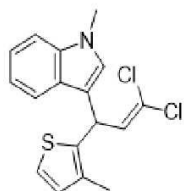
20220923-ZYL-1.143.fid

138.807  
137.361  
133.691  
133.691  
133.237  
126.670  
122.508  
122.508  
120.571  
118.524  
115.009  
109.476

77.957  
77.102  
76.849

37.282  
32.905

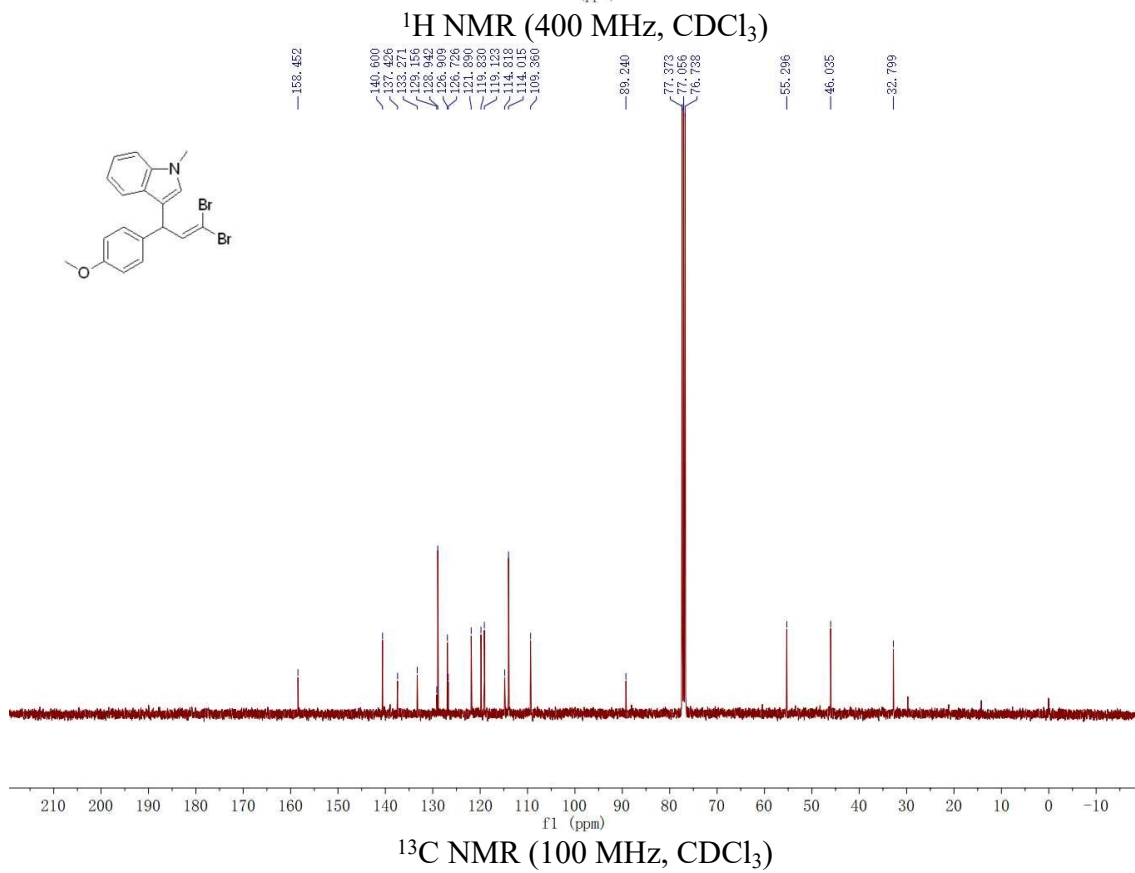
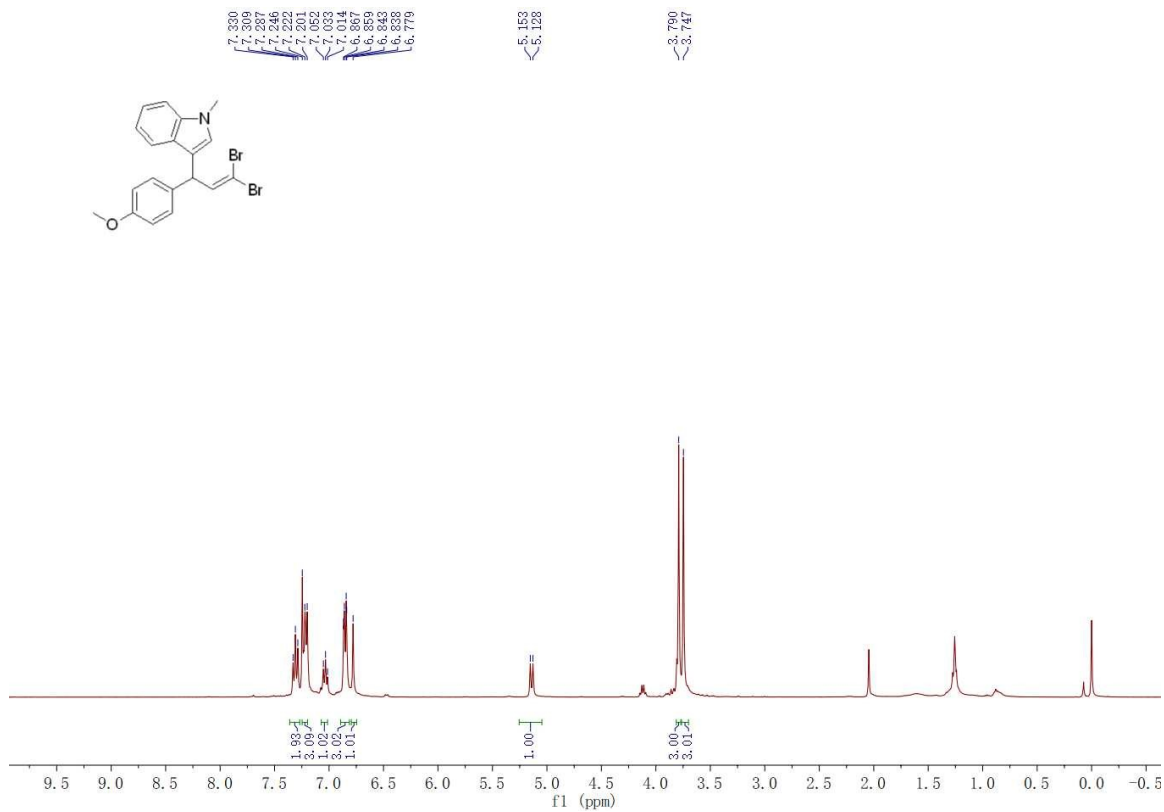
14.118



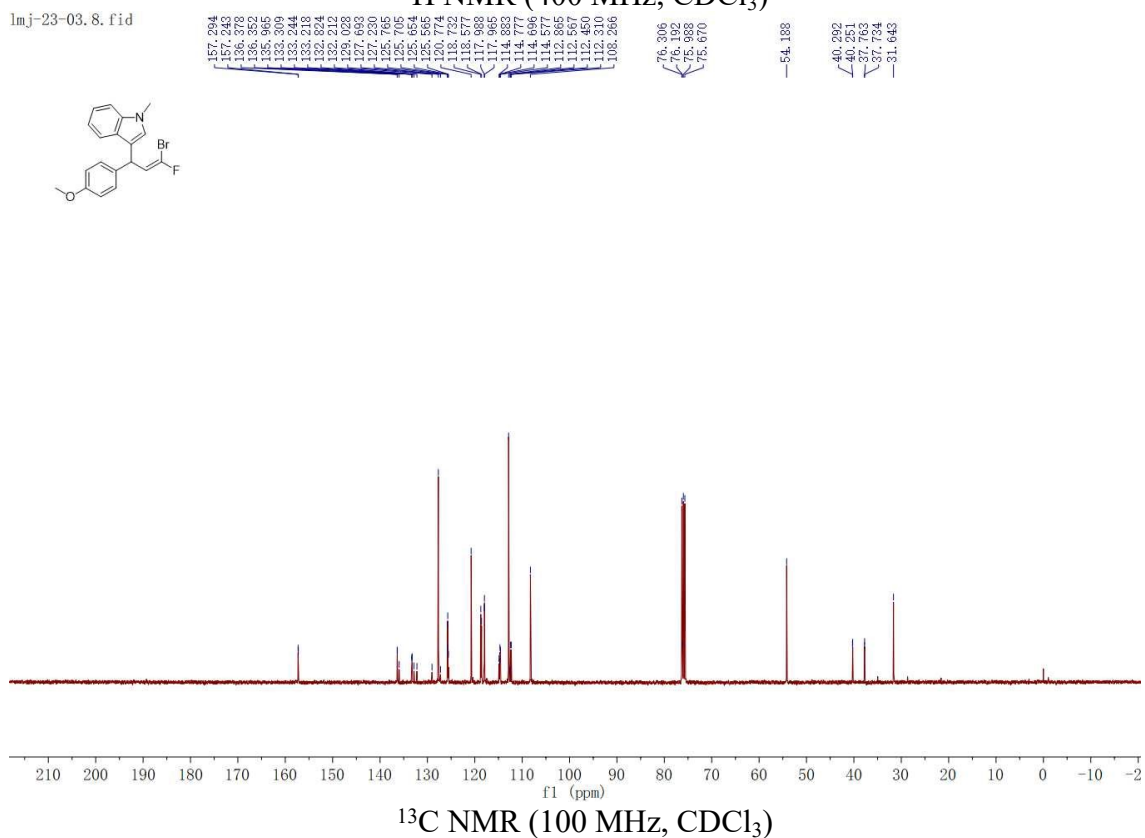
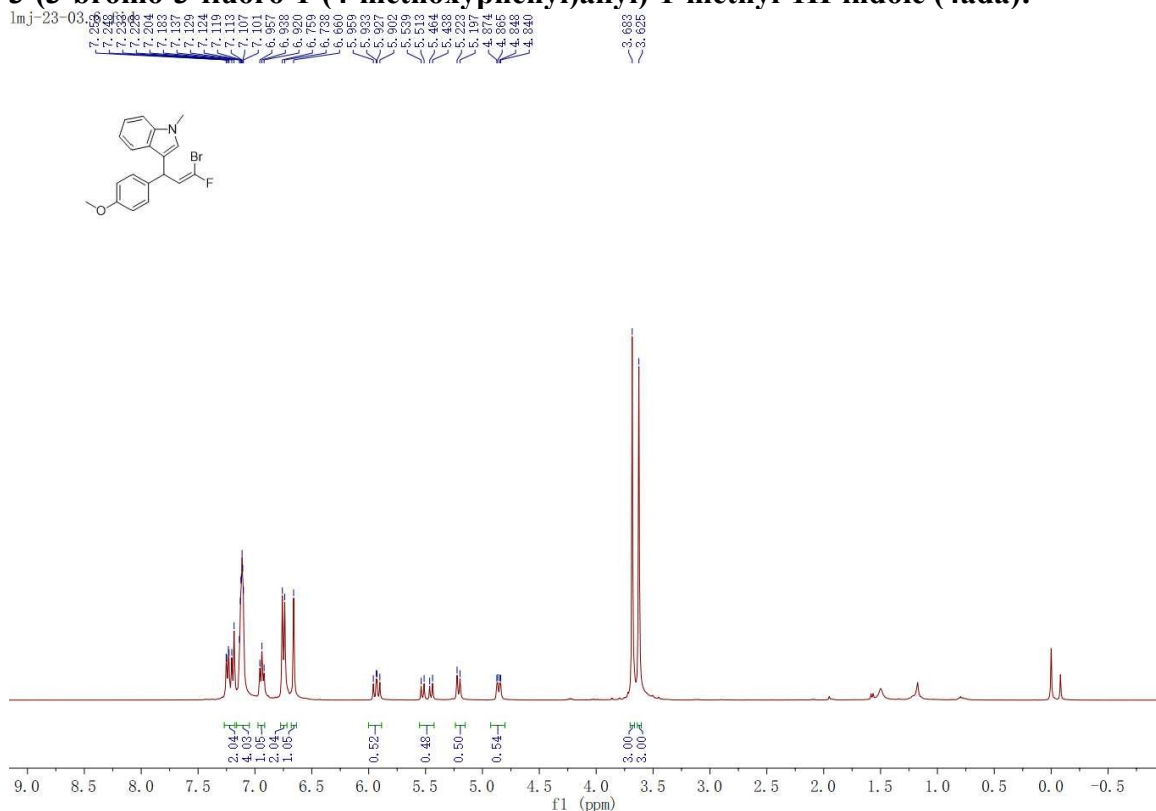
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

**3-(3,3-dibromo-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aca):**

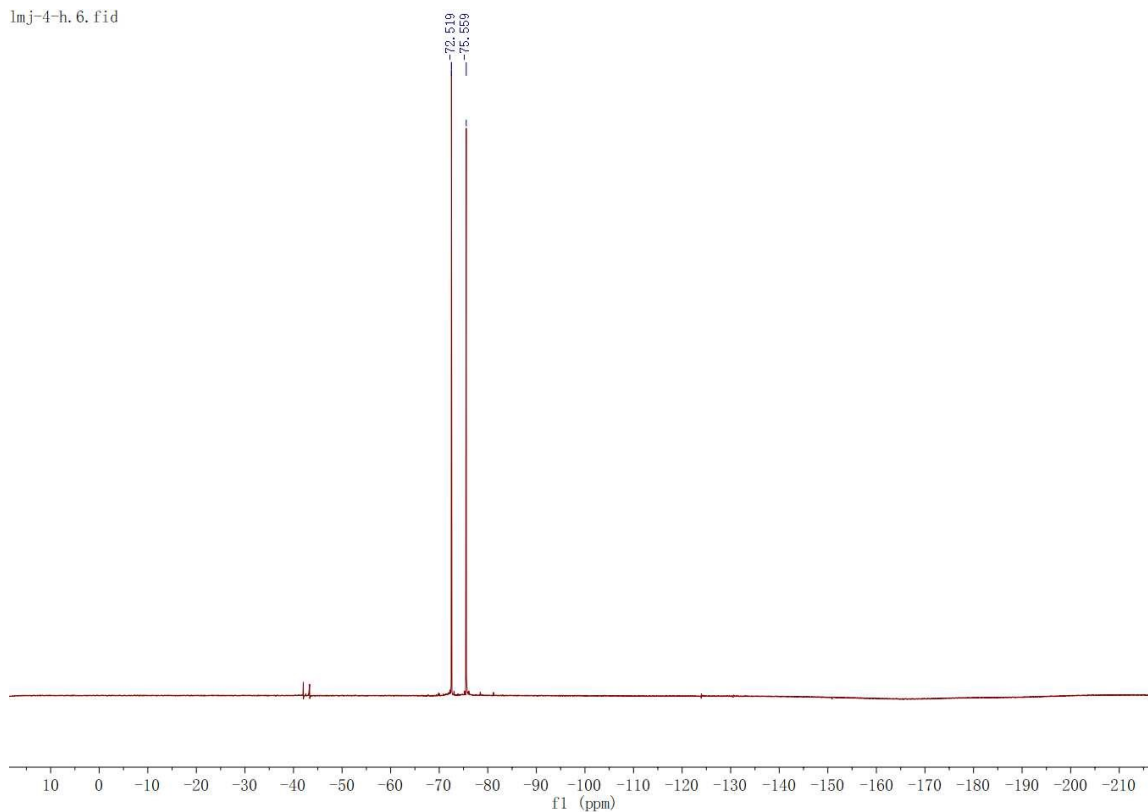




**3-(3-bromo-3-fluoro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4ada):**

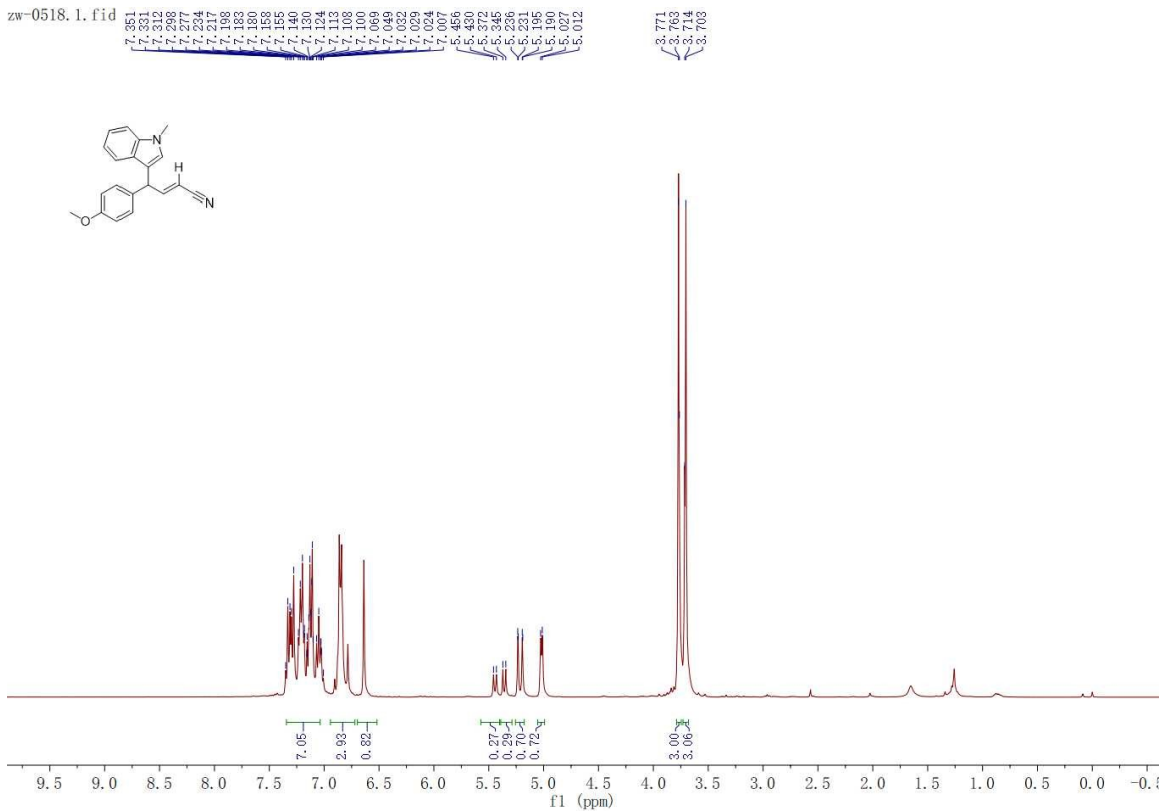


lmj-4-h. 6. fid

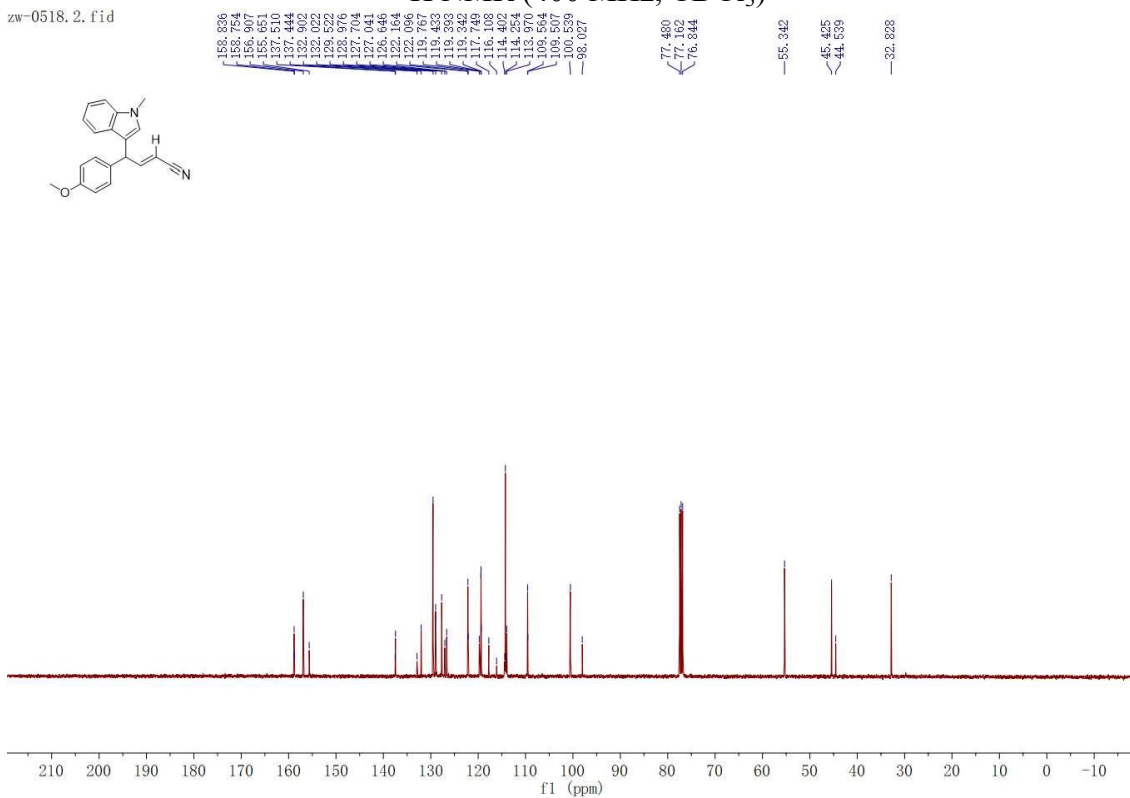


$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )

**3-(3-bromo-3-fluoro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4afa):**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

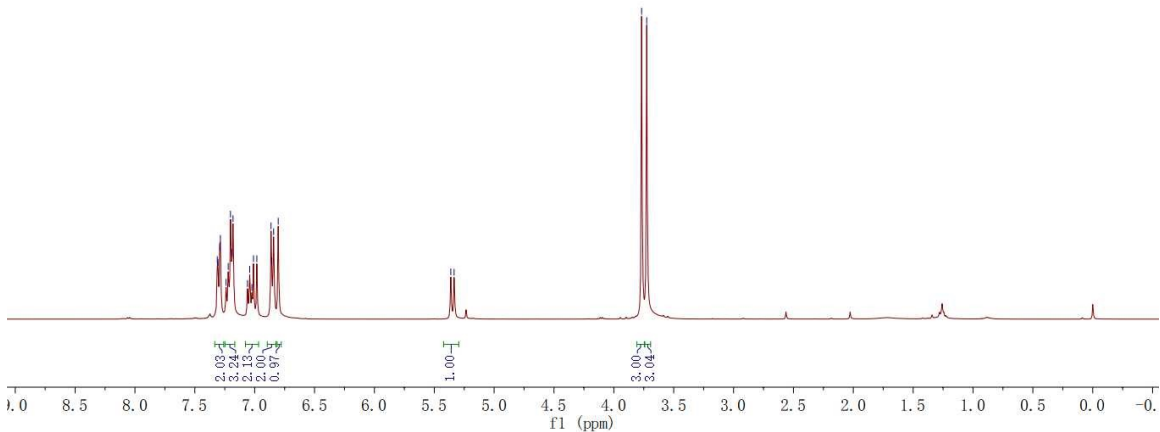
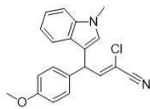
**2-chloro-4-(4-methoxyphenyl)-4-(1-methyl-1H-indol-3-yl)but-2-enitrile (4aga):**

zw-5-08-1.6.fid

7.318  
7.307  
7.288  
7.286  
7.284  
7.272  
7.191  
7.181  
7.060  
7.062  
7.050  
6.982  
6.863  
6.858  
6.842  
6.804

5.382  
5.354

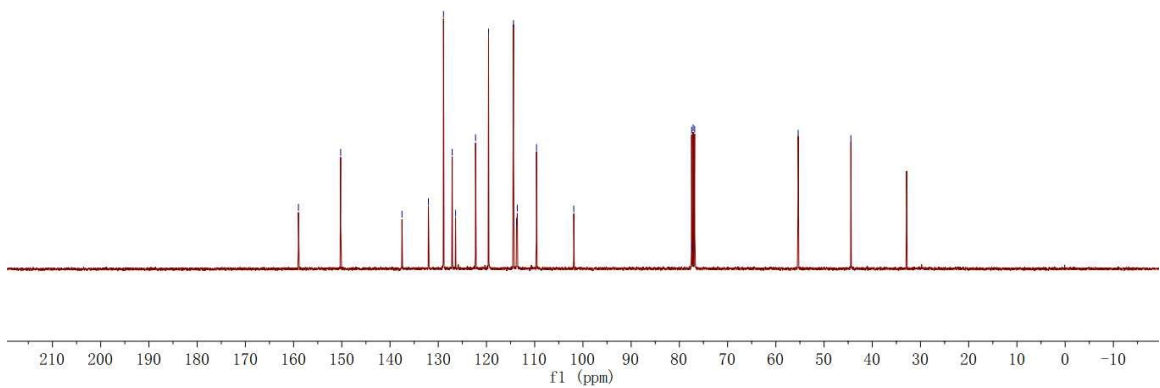
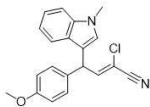
3.788  
3.725



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

zw-5-08-1.8.fid

158.996  
150.239  
137.521  
132.041  
128.516  
127.408  
122.269  
119.571  
114.401  
113.774  
113.605  
109.028  
101.900  
77.464  
77.349  
77.146  
76.829  
55.363  
44.431



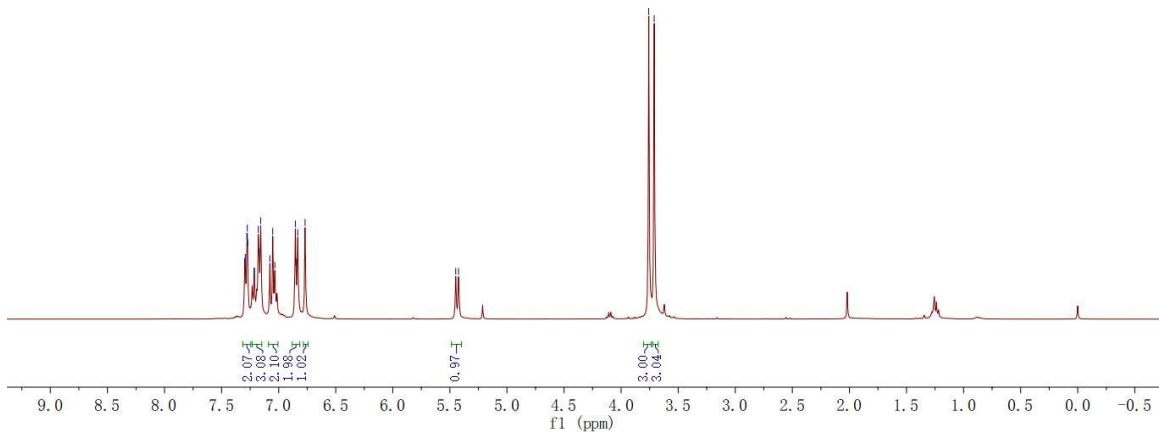
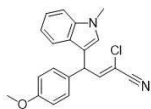
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

zw-5-08-2.9.fid

7.298  
7.292  
7.279  
7.275  
7.272  
7.259  
7.219  
7.171  
7.157  
7.077  
7.052  
6.984  
6.846  
6.833  
6.769

5.449  
5.424

3.758  
3.710



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

zw-5-08-2.11.fid

158.989

149.144

137.532

131.752

129.030

127.091

126.559

122.287

118.465

114.417

109.661

102.909

77.509

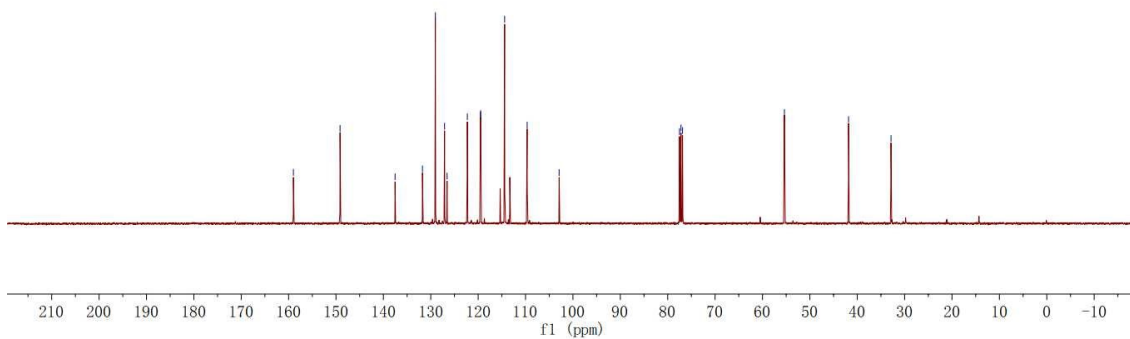
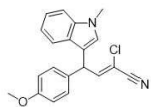
77.323

76.873

55.370

41.835

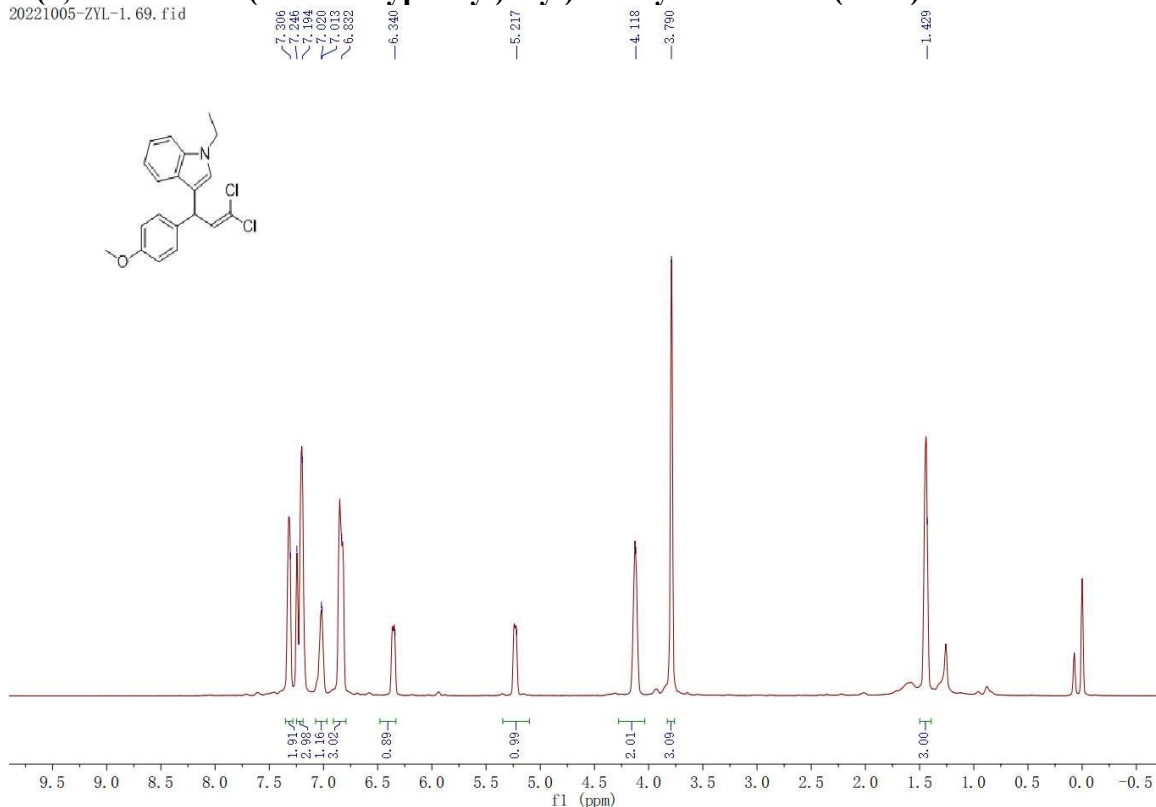
32.877



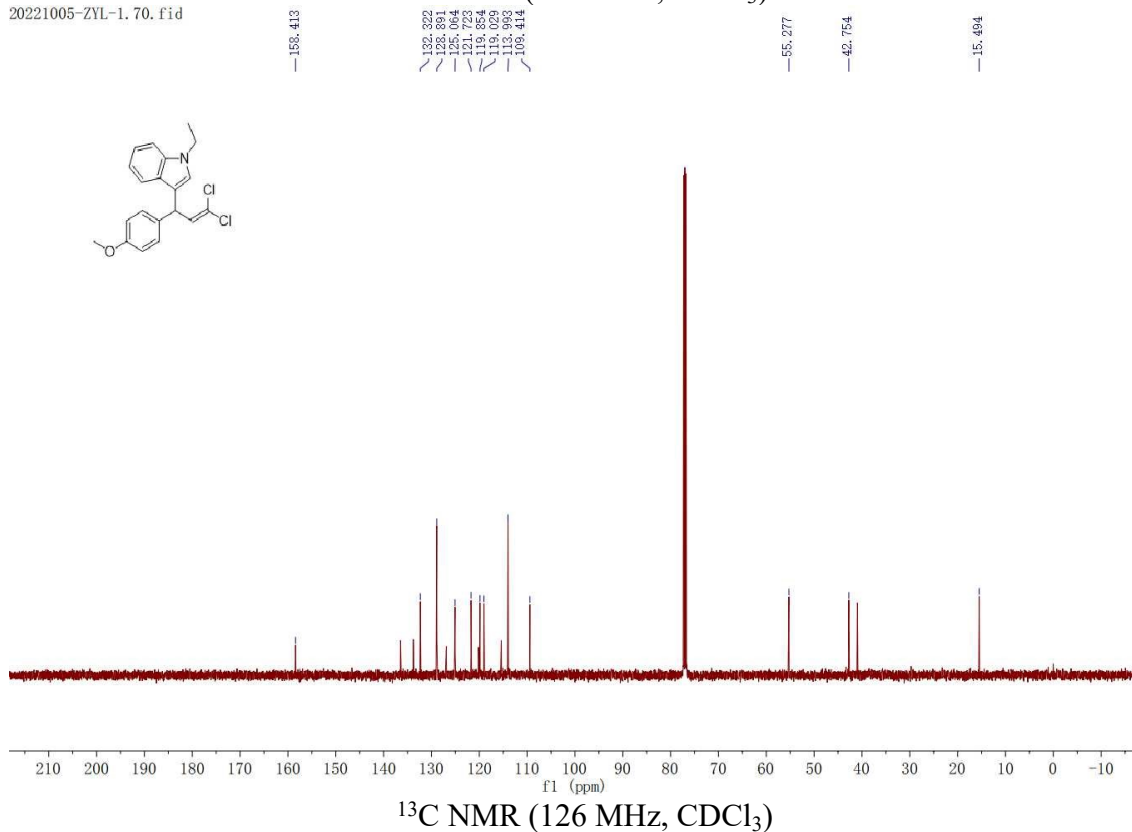
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-ethyl-1H-indole (4aab):

20221005-ZYL-1.69.fid

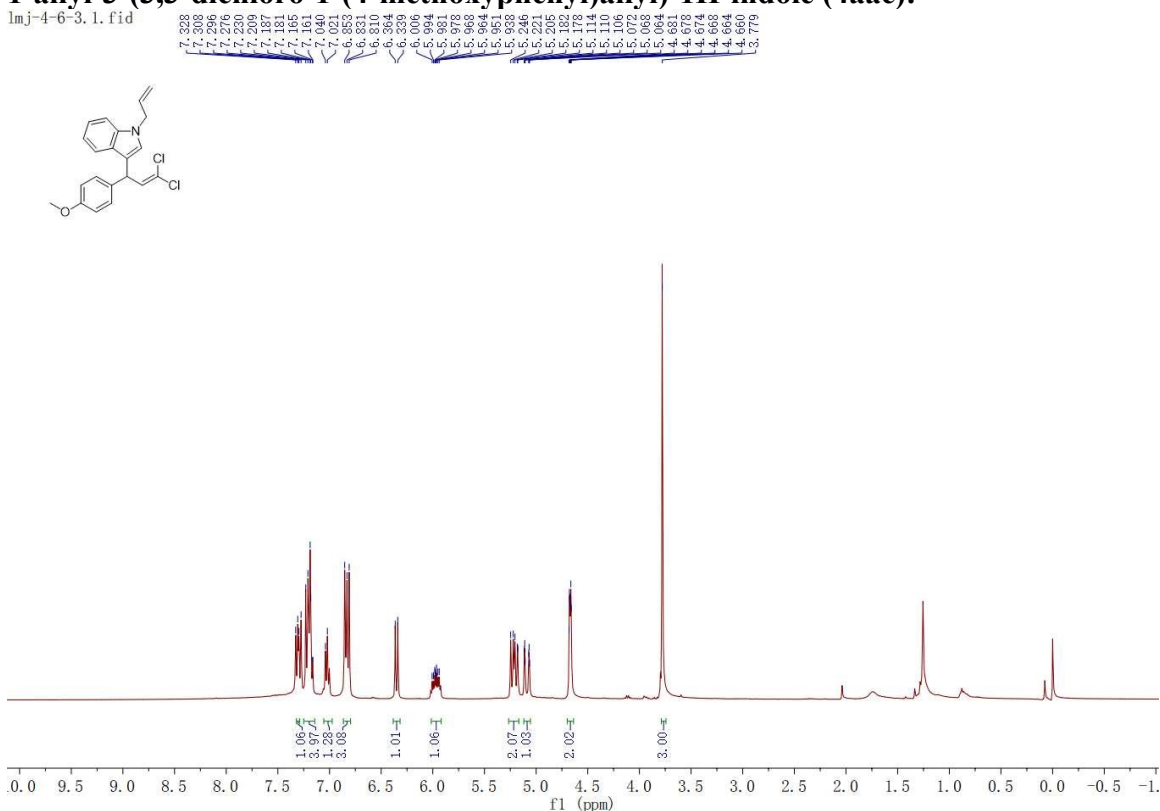


20221005-ZYL-1.70.fid

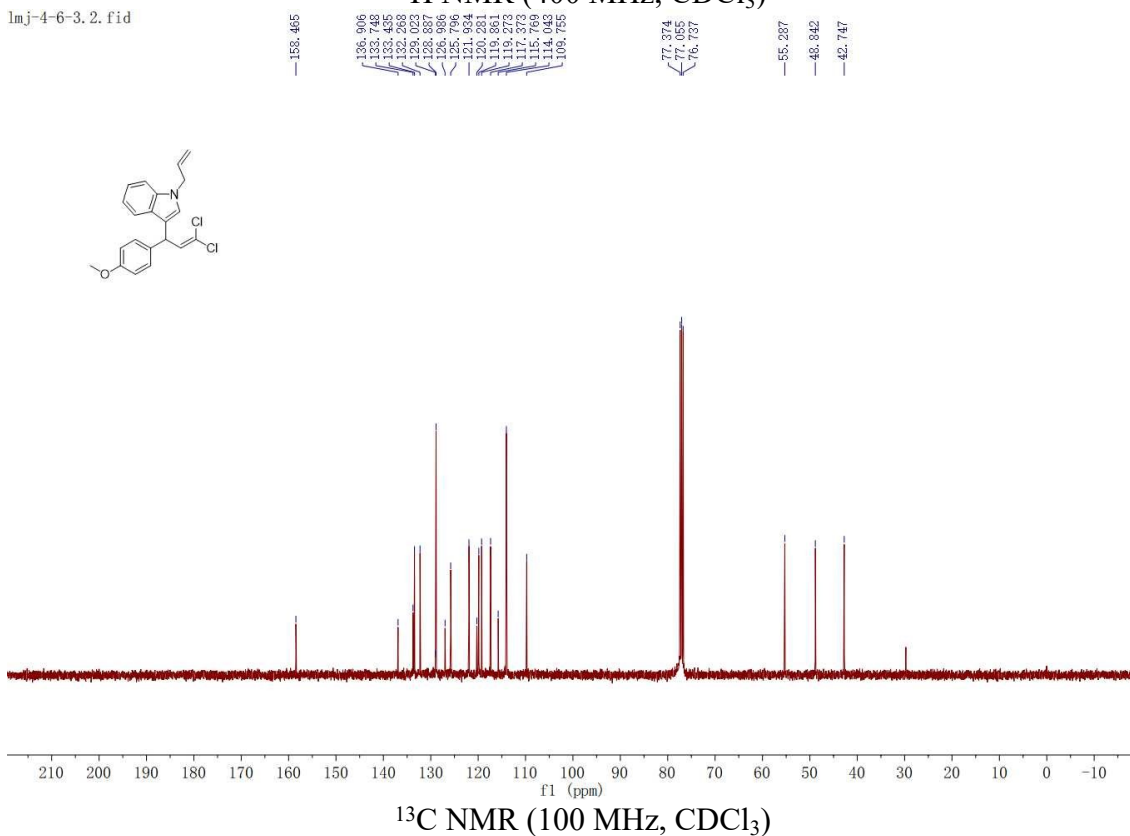


# 1-allyl-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1H-indole (4aac):

lmj-4-6-3.1.fid

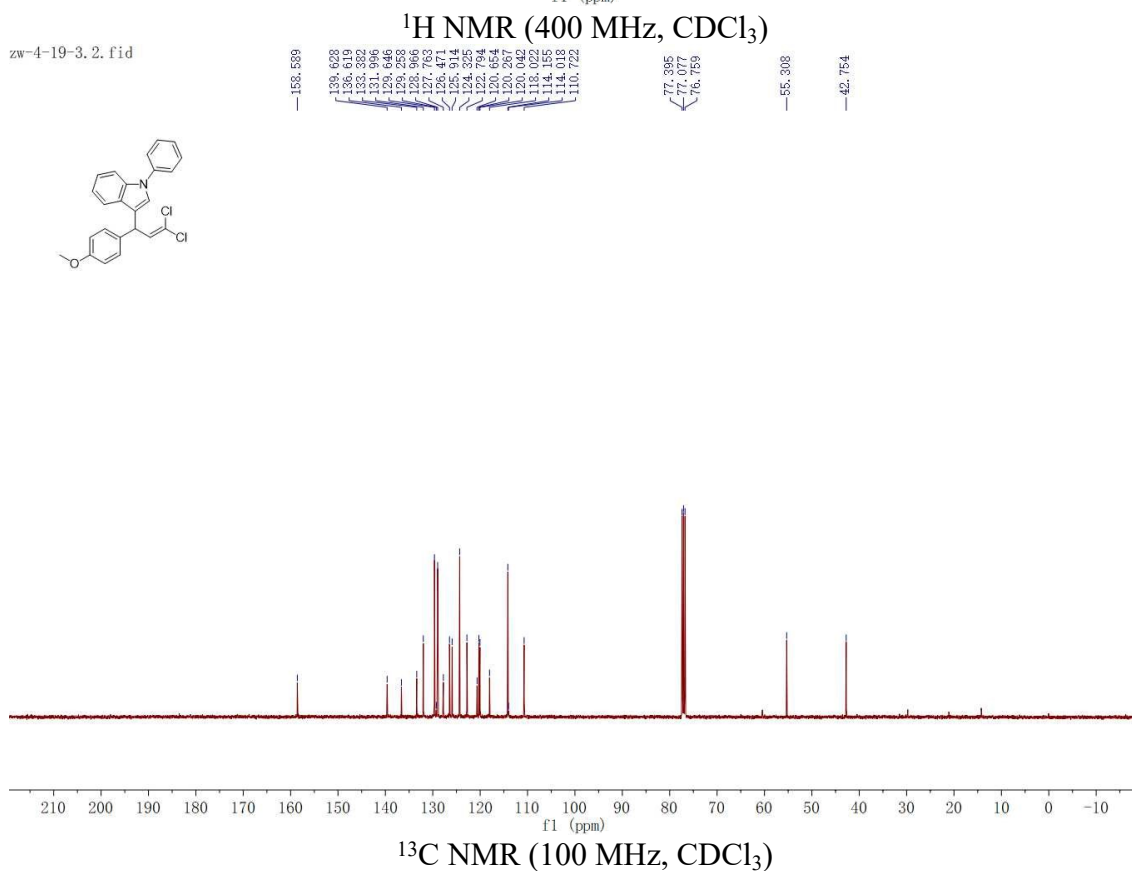
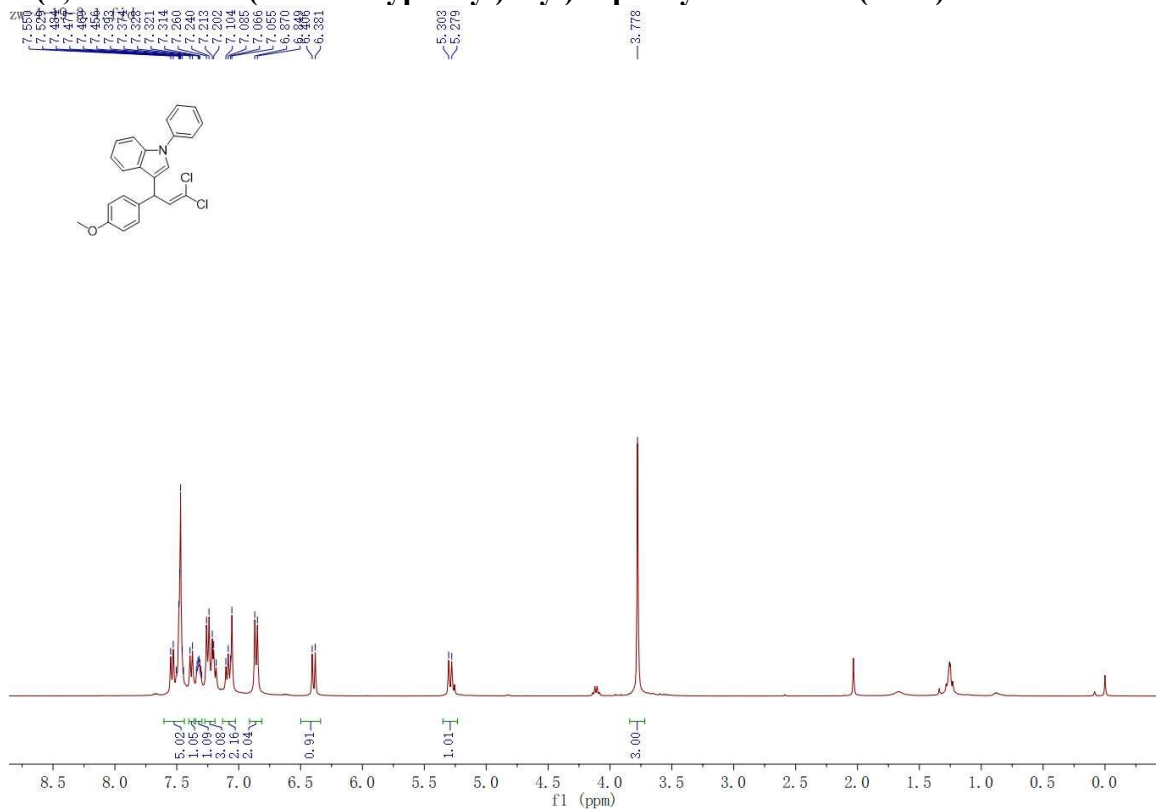


lmj-4-6-3.2.fid



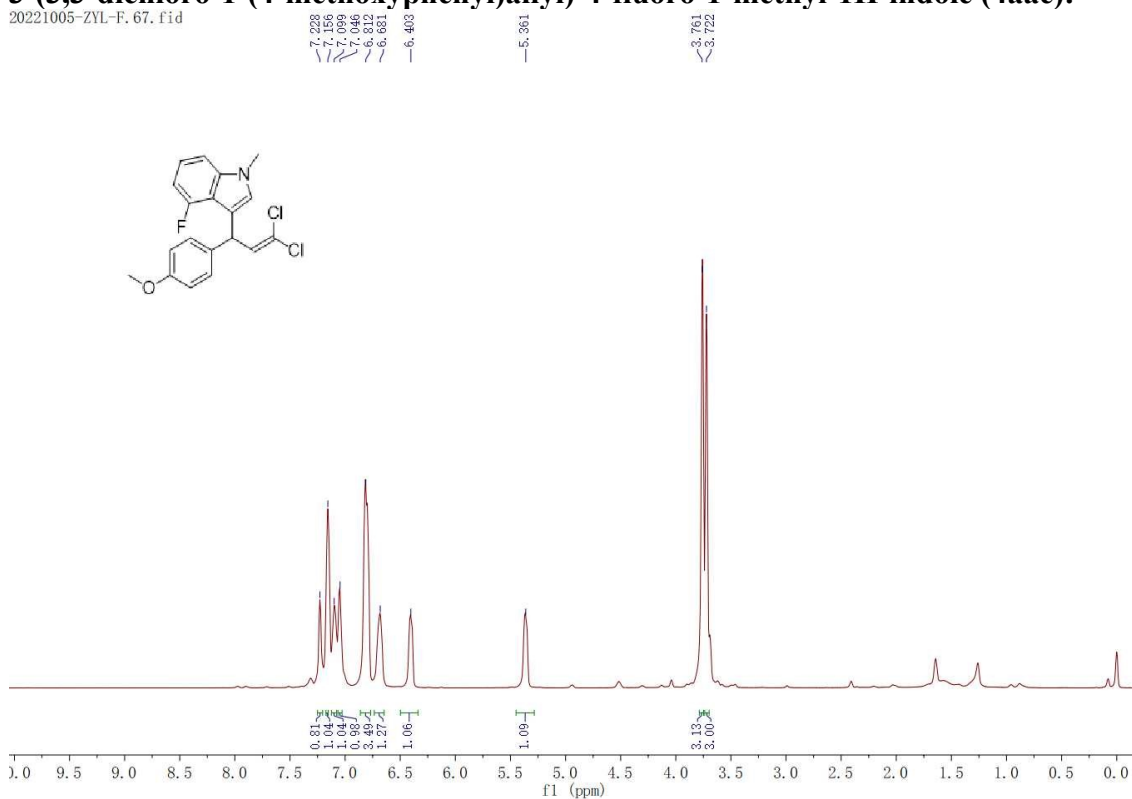


### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-phenyl-1H-indole (4aad):

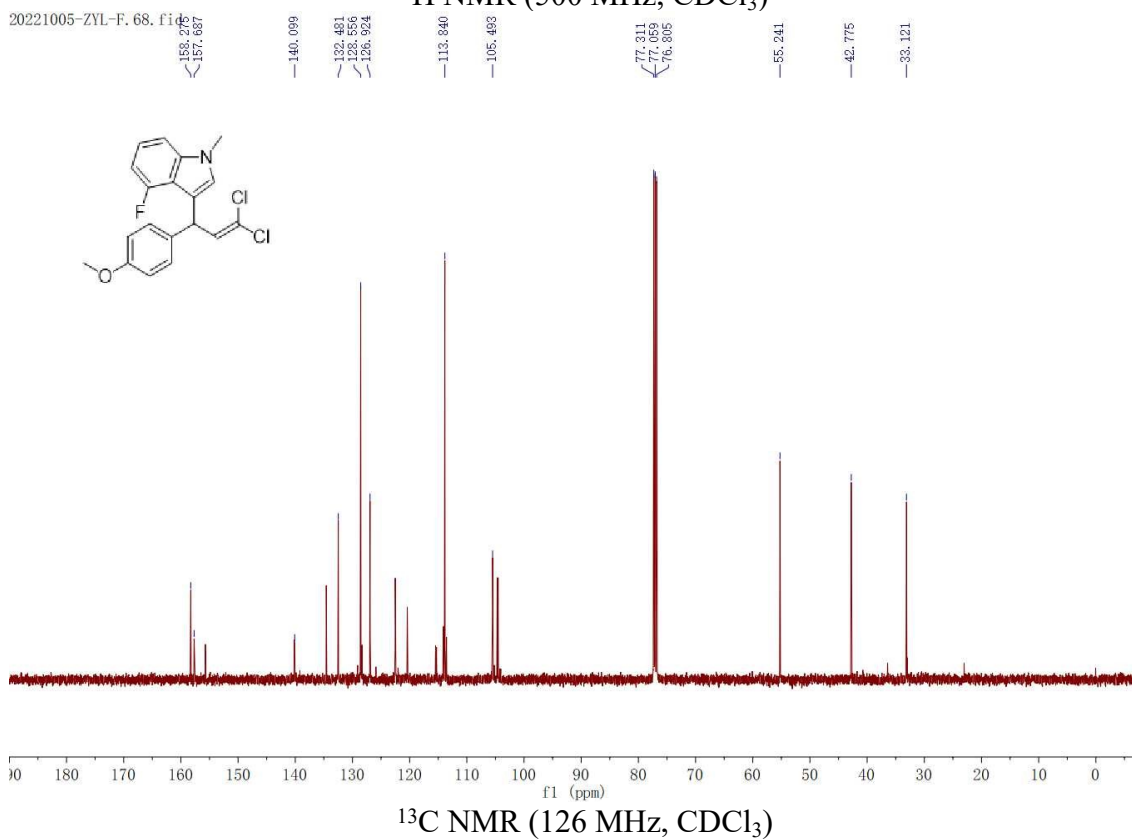


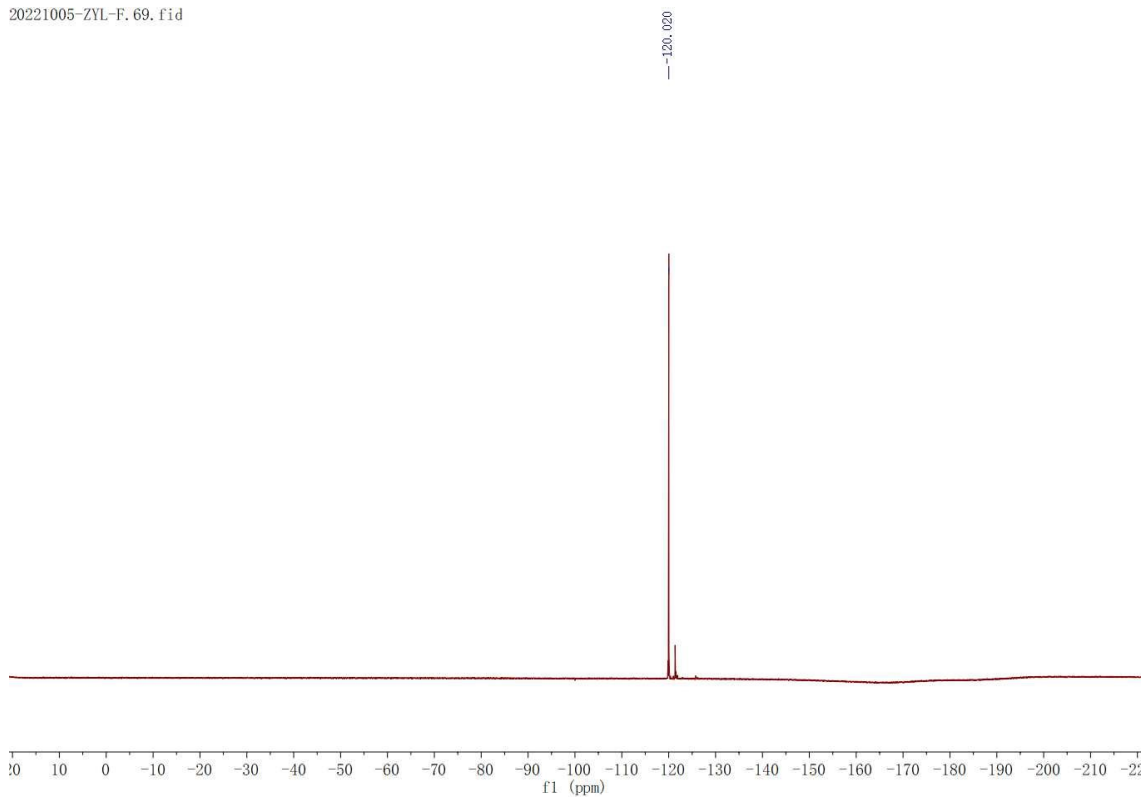
### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-4-fluoro-1-methyl-1H-indole (4aae):

20221005-ZYL-F. 67. fid



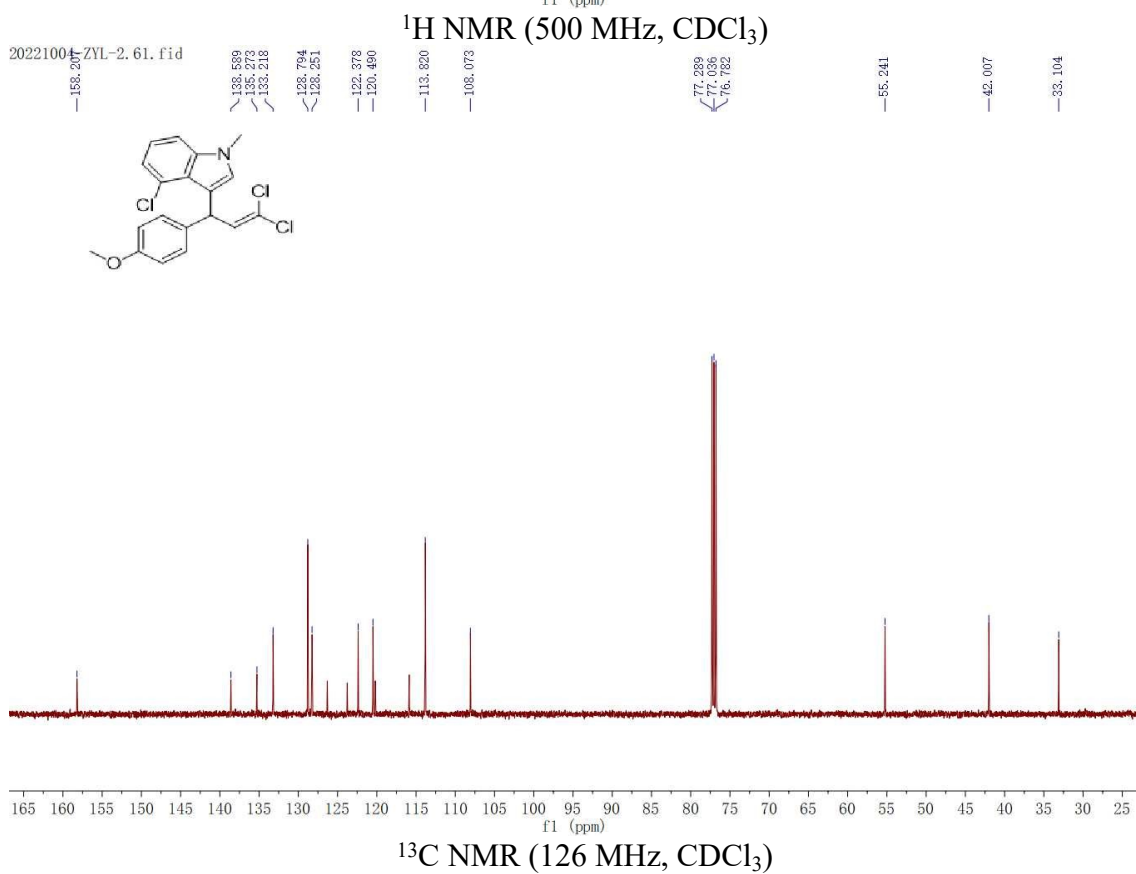
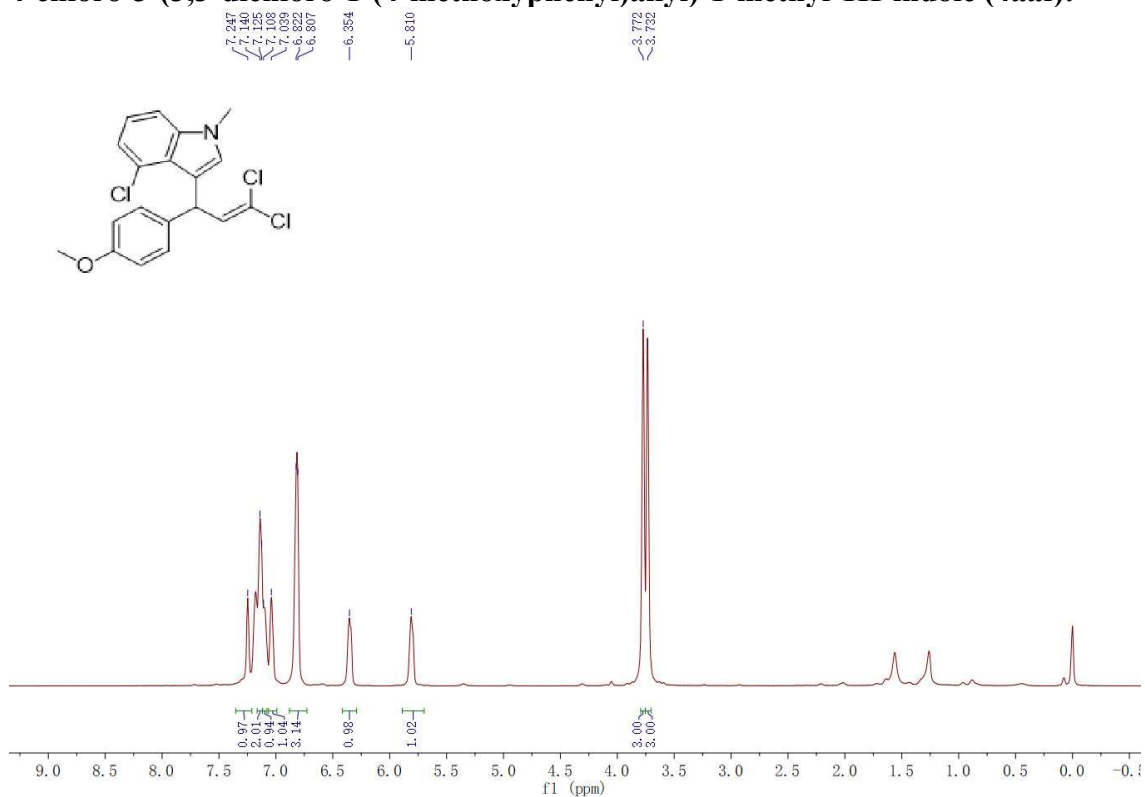
20221005-ZYL-F. 68. fid





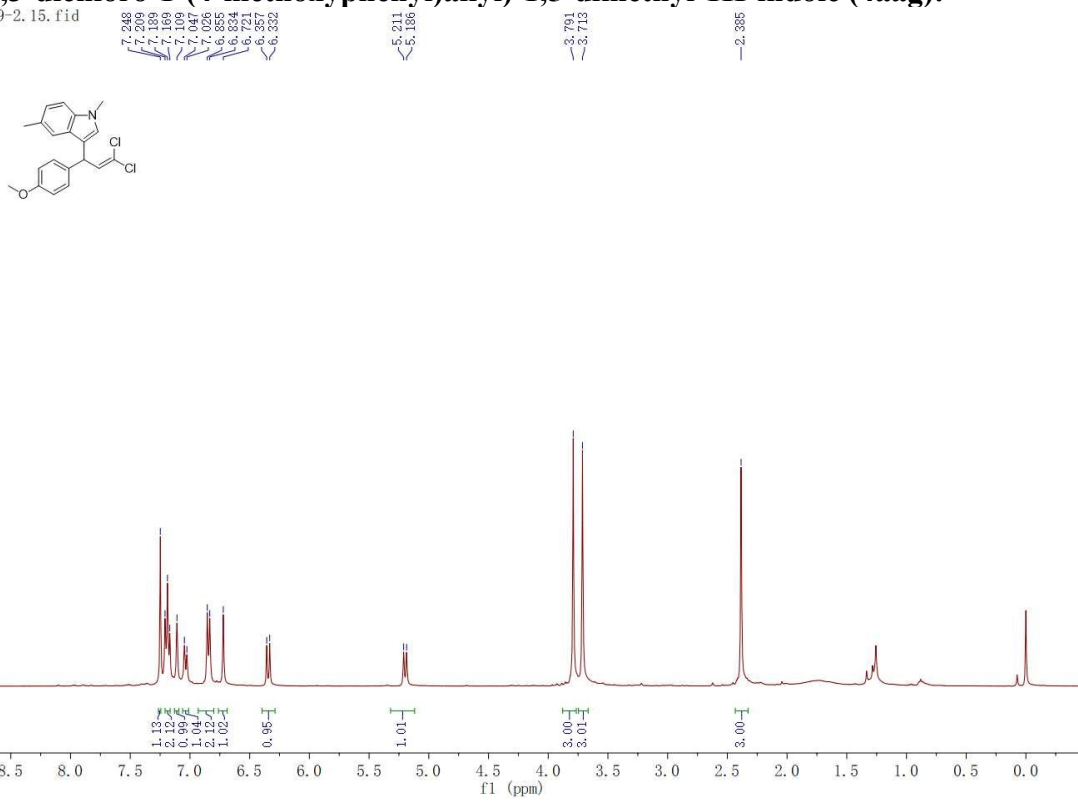
$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )

**4-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aaf):**

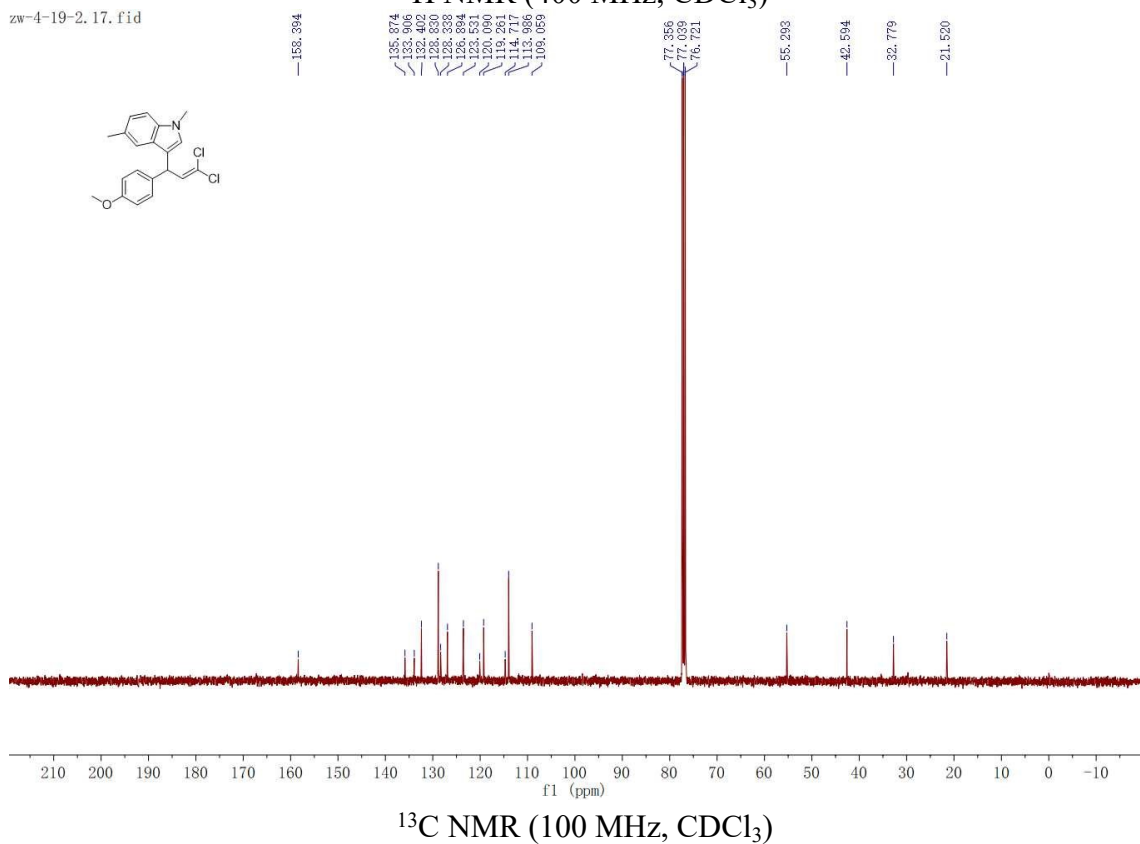


### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,5-dimethyl-1H-indole (4aag):

zw-4-19-2.15.fid



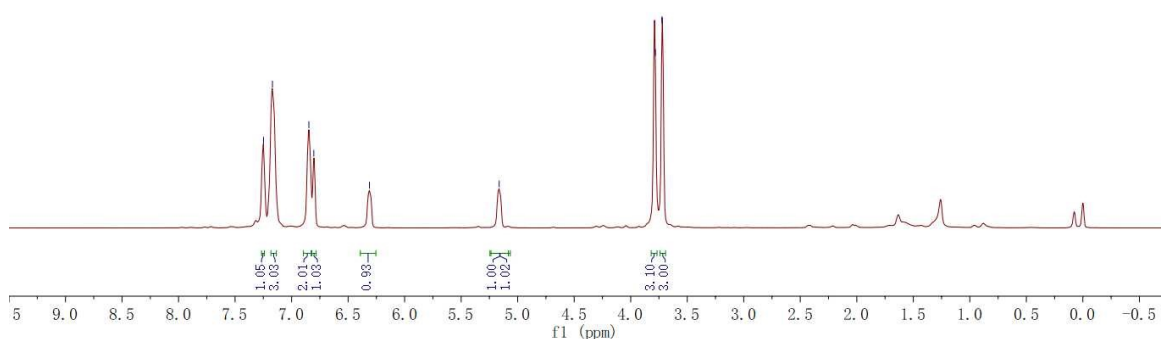
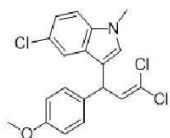
zw-4-19-2.17.fid



# 5-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aah):

20221004-ZYL-1.59.fid

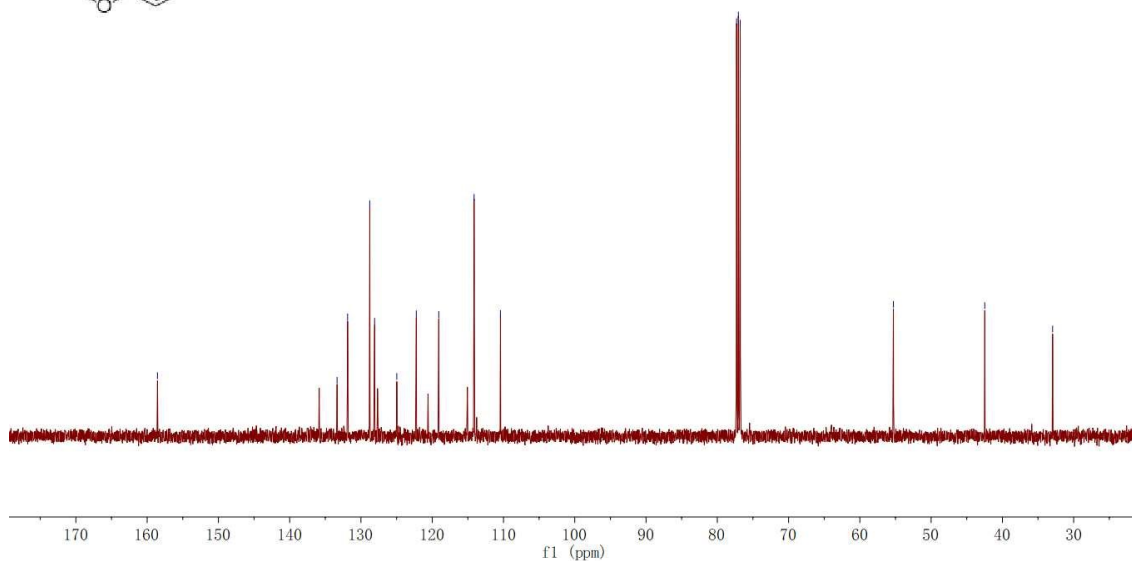
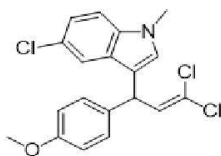
7.248  
7.169  
6.847  
6.803  
6.311  
5.164  
3.782  
3.724



## <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

20221004-ZYL-1.60.fid

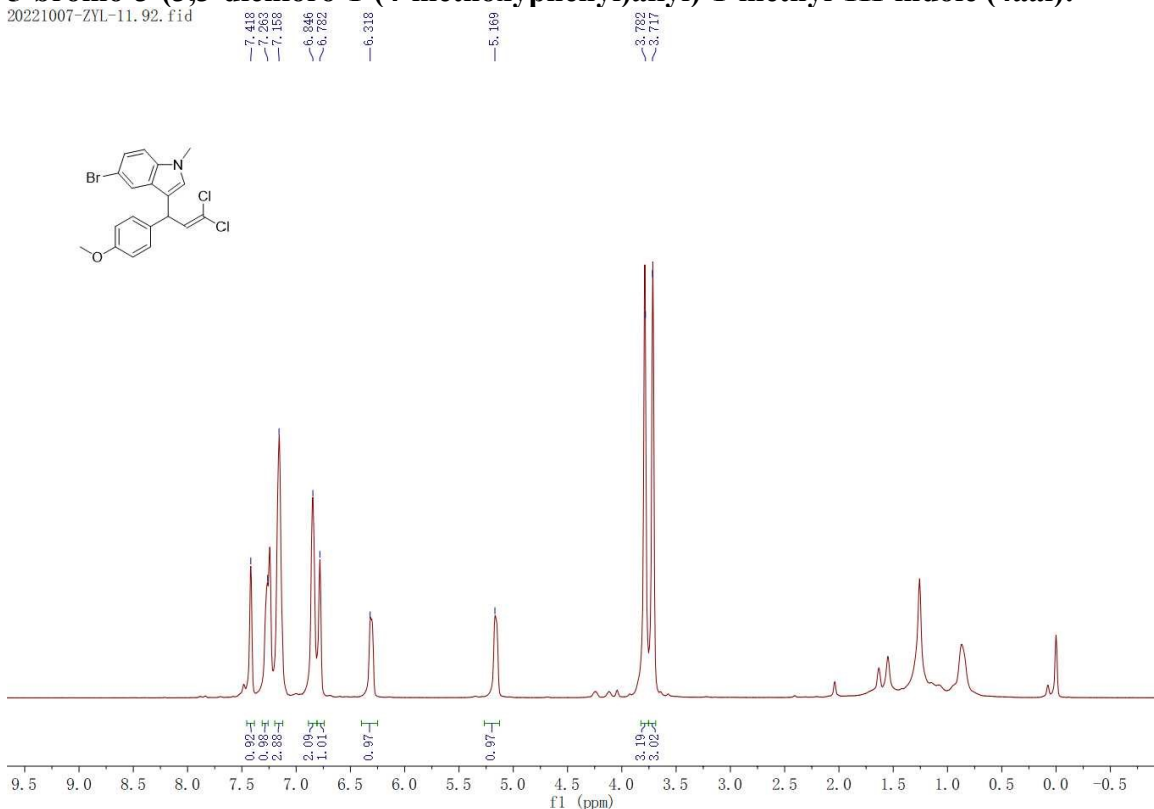
168.581  
139.951  
131.875  
128.766  
128.086  
124.973  
122.237  
119.061  
114.127  
110.430  
77.298  
77.044  
76.791  
55.296  
42.472  
32.959



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

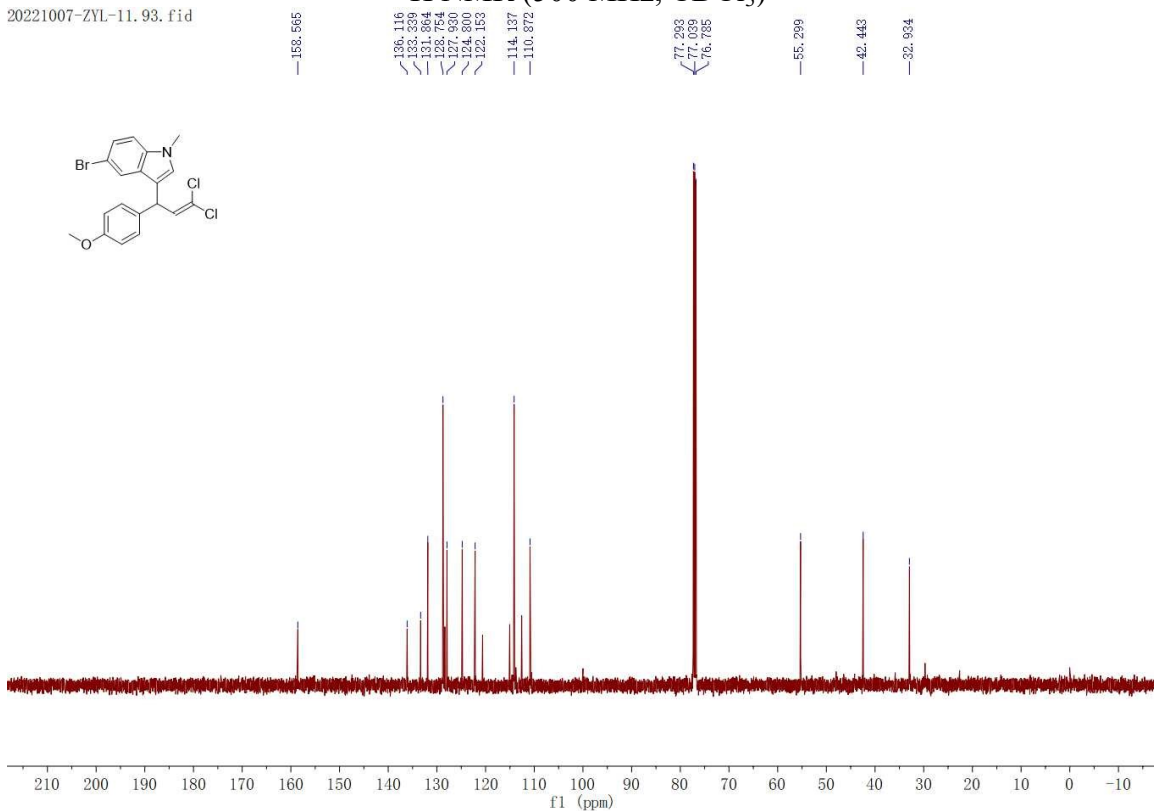
**5-bromo-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aai):**

20221007-ZYL-11.92.fid



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**

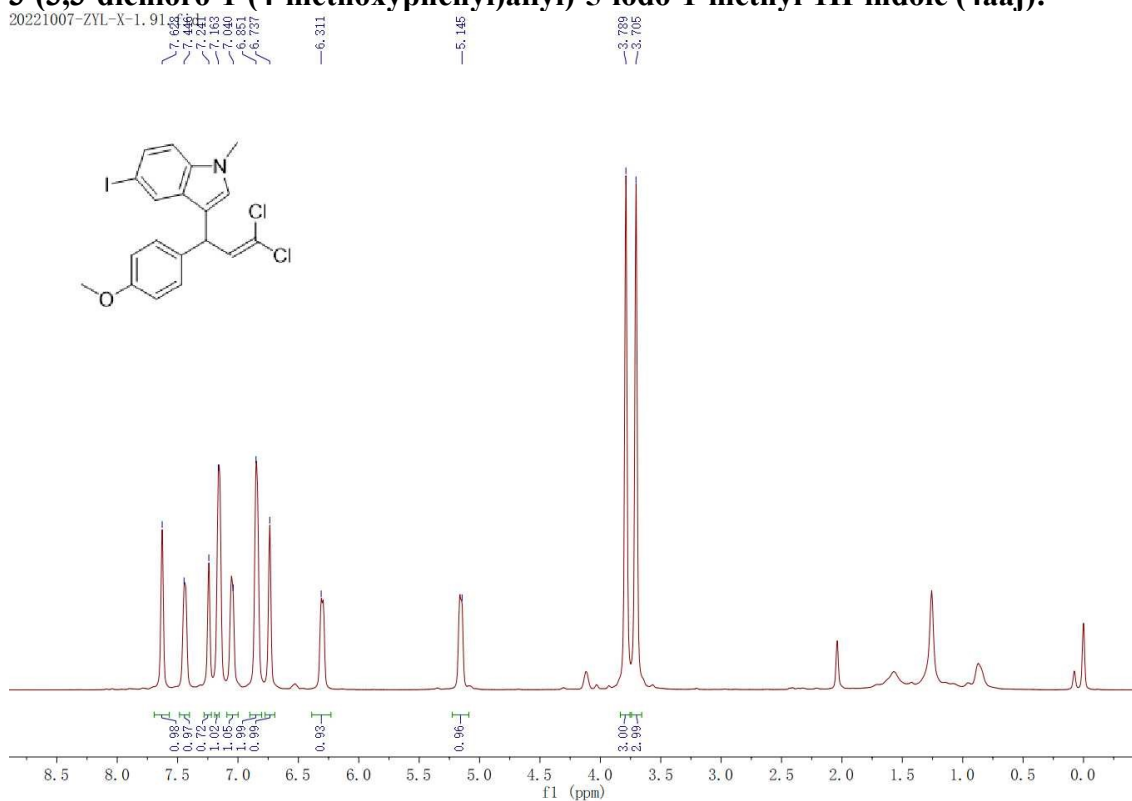
20221007-ZYL-11.93.fid



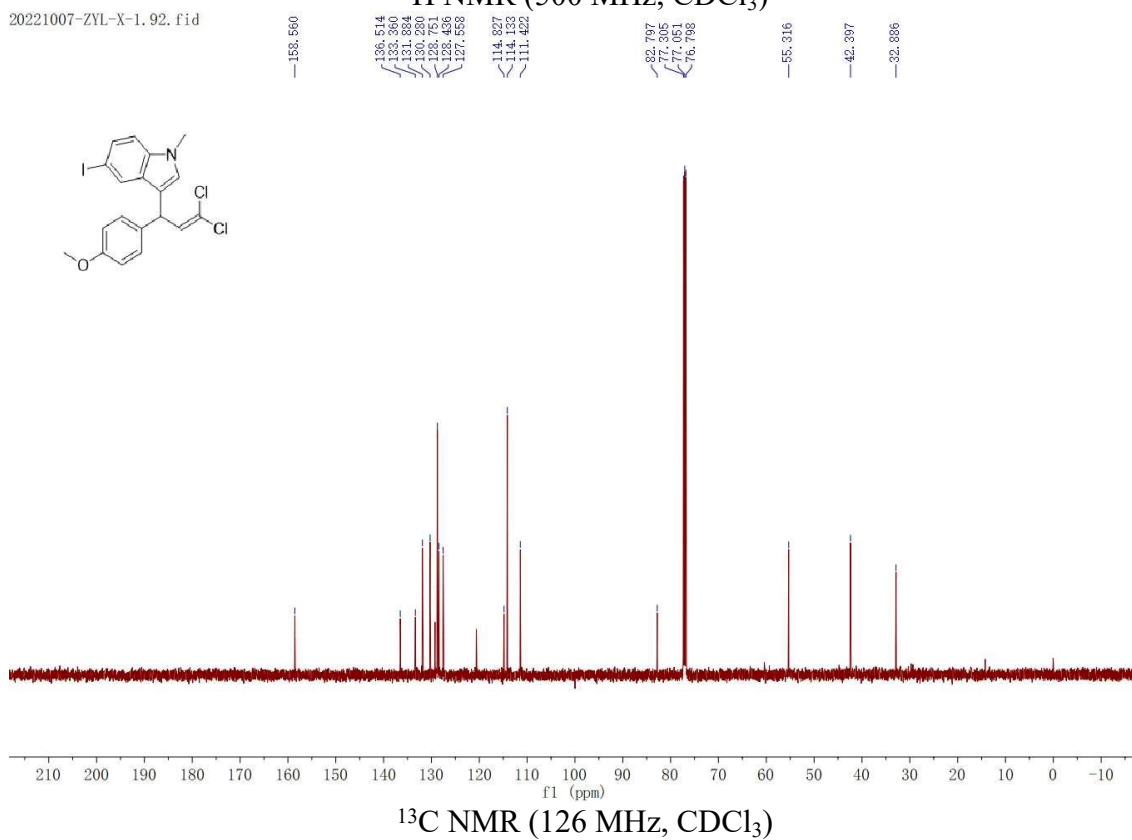
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-5-iodo-1-methyl-1H-indole (4aaj):

20221007-ZYL-X-1.91



20221007-ZYL-X-1.92.fid

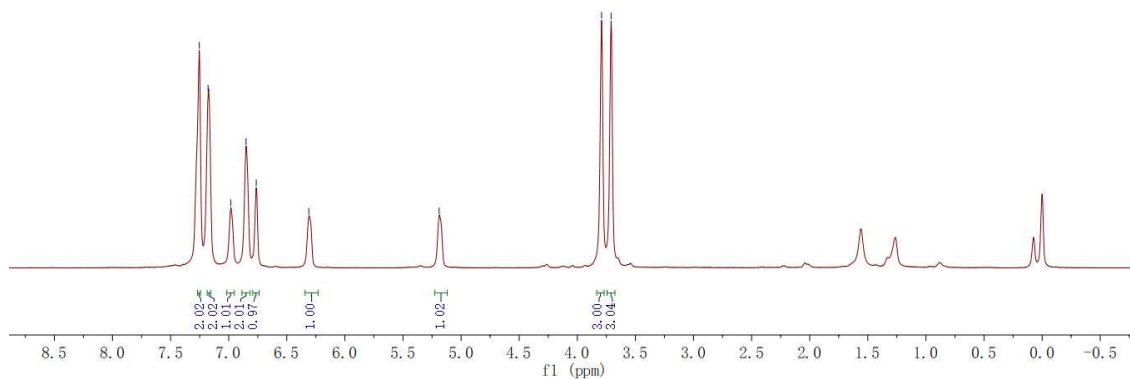
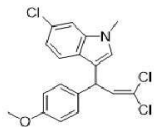




# 6-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aak):

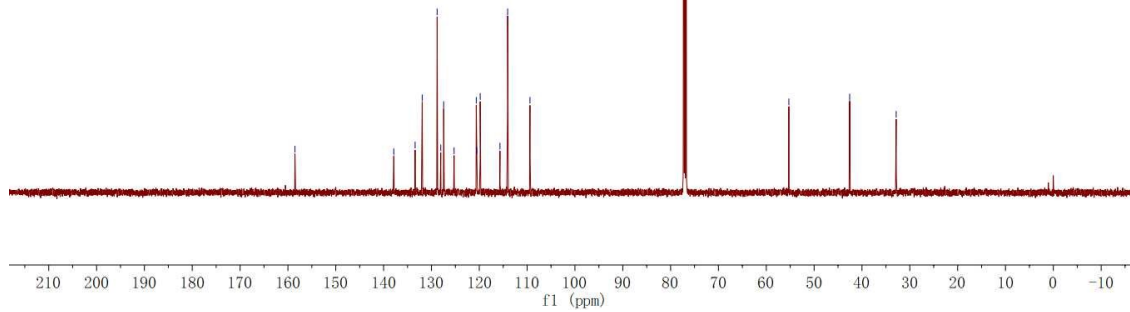
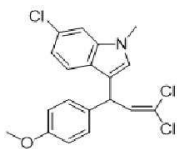
20221028-ZYL. 68. fid

7.253  
7.178  
6.982  
6.851  
6.763  
6.311  
5.189  
3.791  
3.709



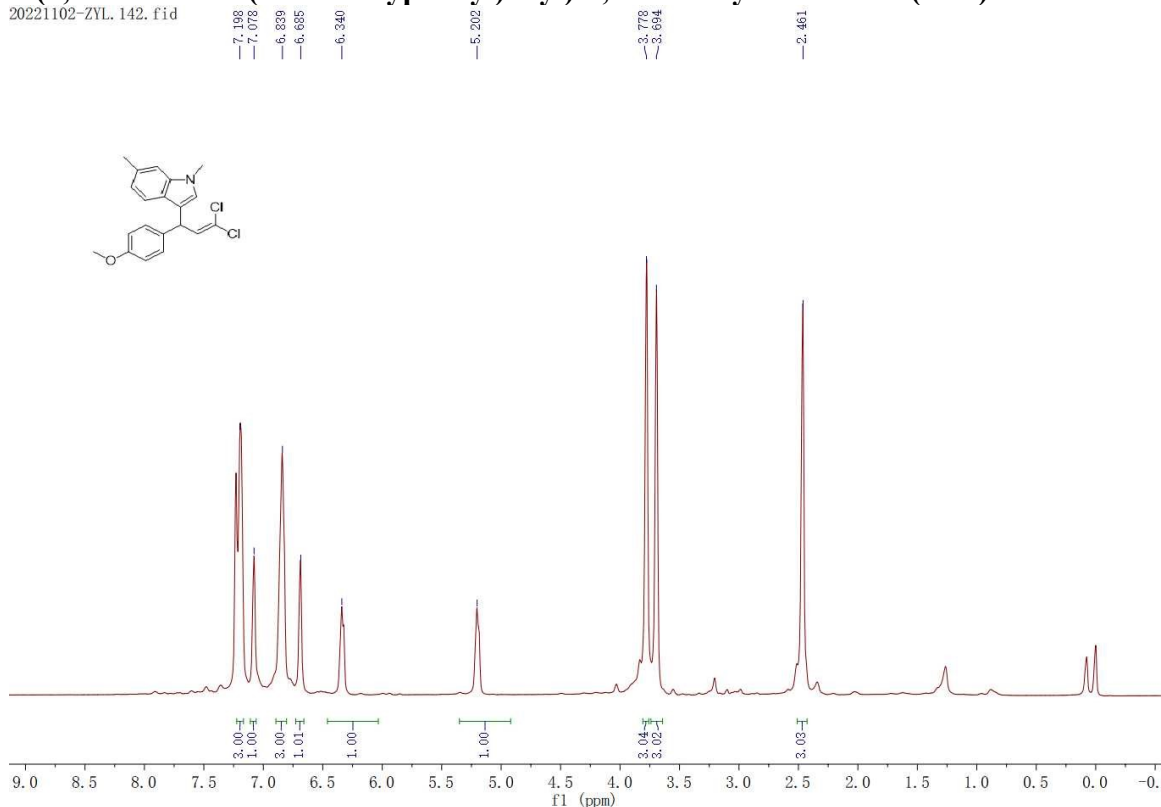
20221028-ZYL. 69. fid

158.527  
137.872  
137.852  
131.832  
128.811  
128.048  
127.444  
126.286  
120.531  
120.510  
119.810  
115.673  
114.071  
109.402  
77.278  
77.024  
76.770  
55.282  
42.573  
32.849

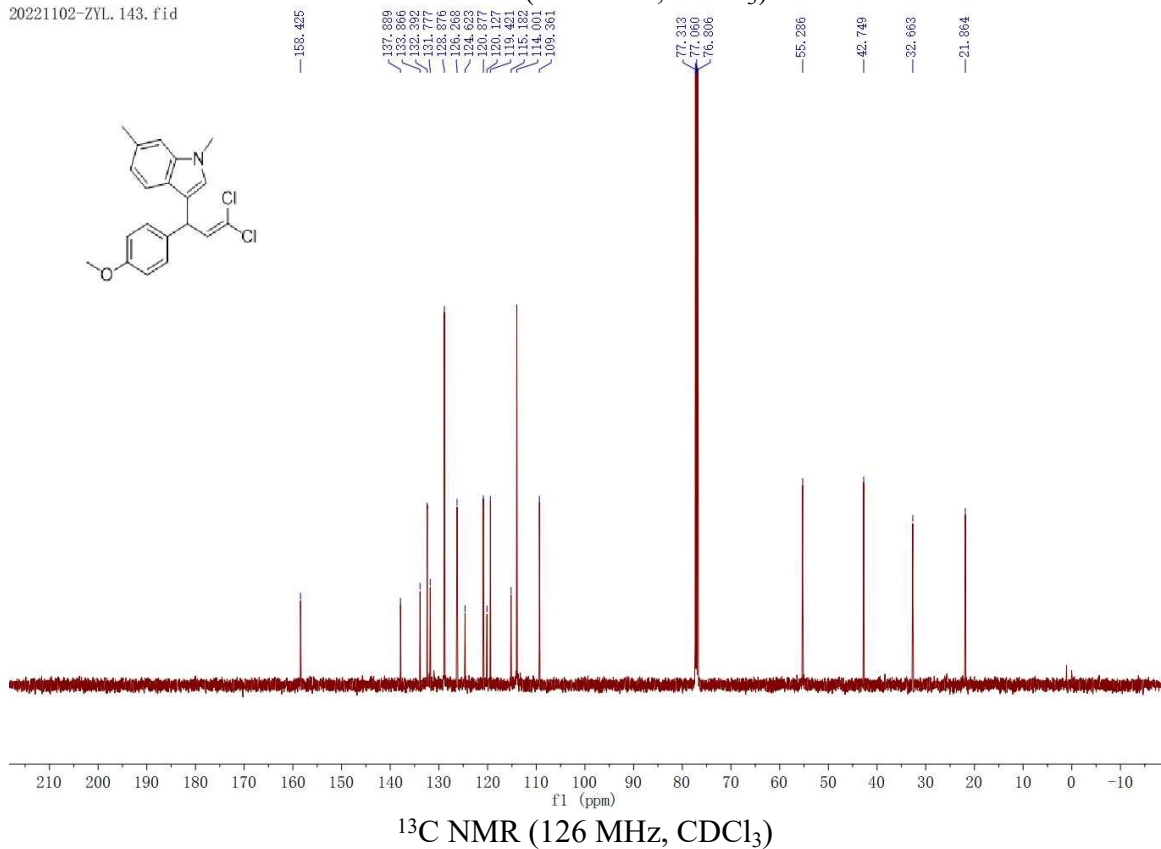


### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,6-dimethyl-1H-indole (4aal):

20221102-ZYL.142.fid

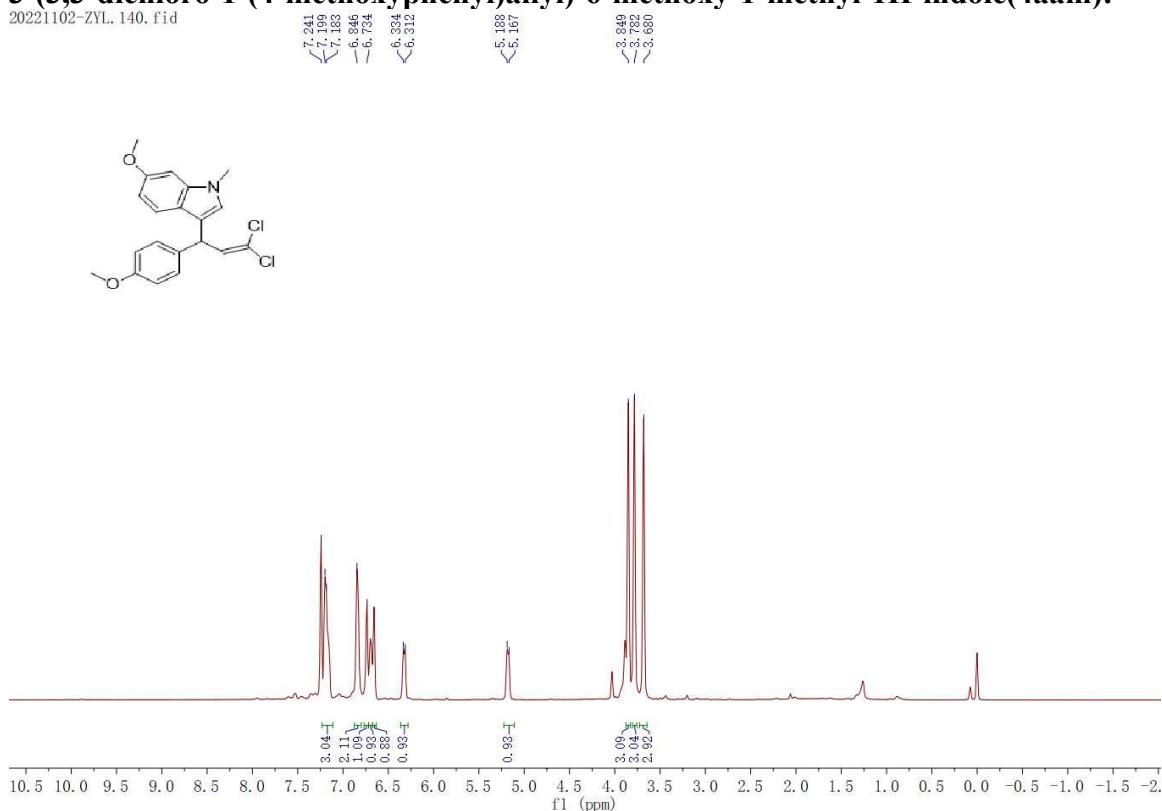


20221102-ZYL.143.fid

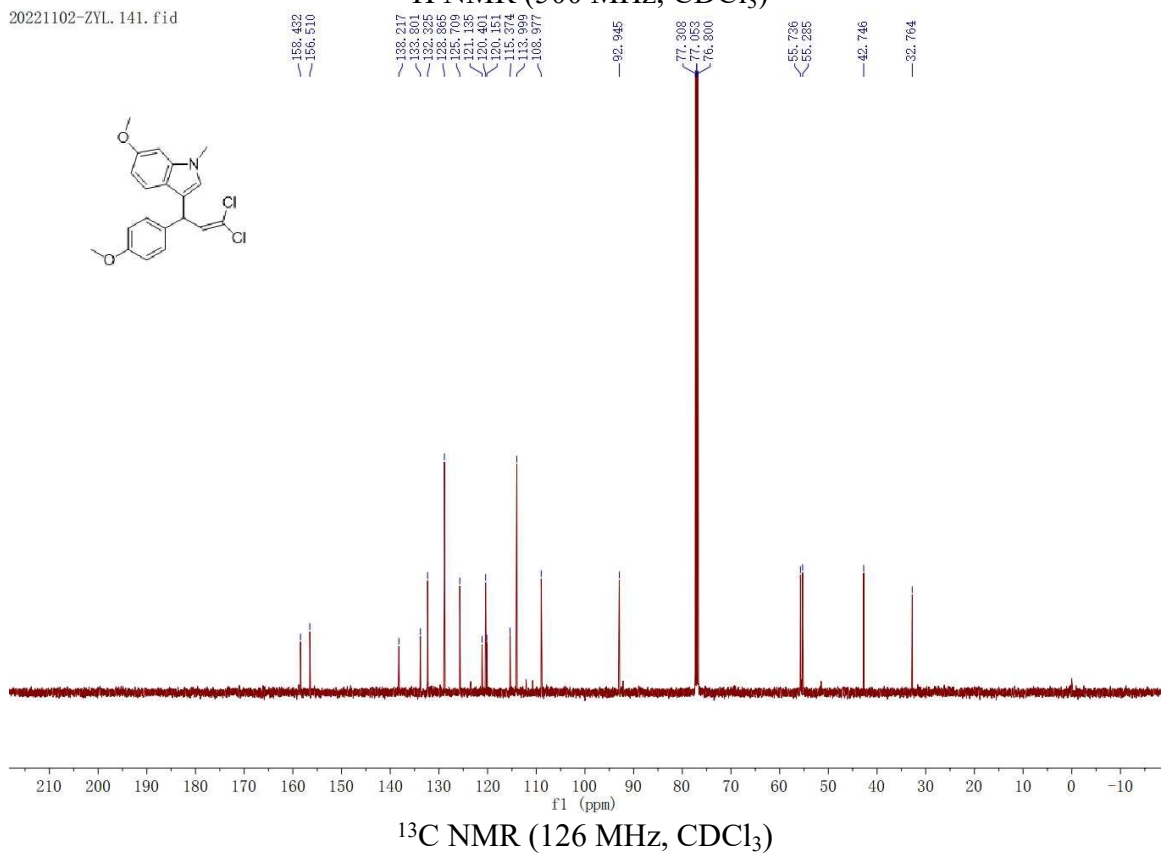


### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-6-methoxy-1-methyl-1H-indole(4aam):

20221102-ZYL 140. fid

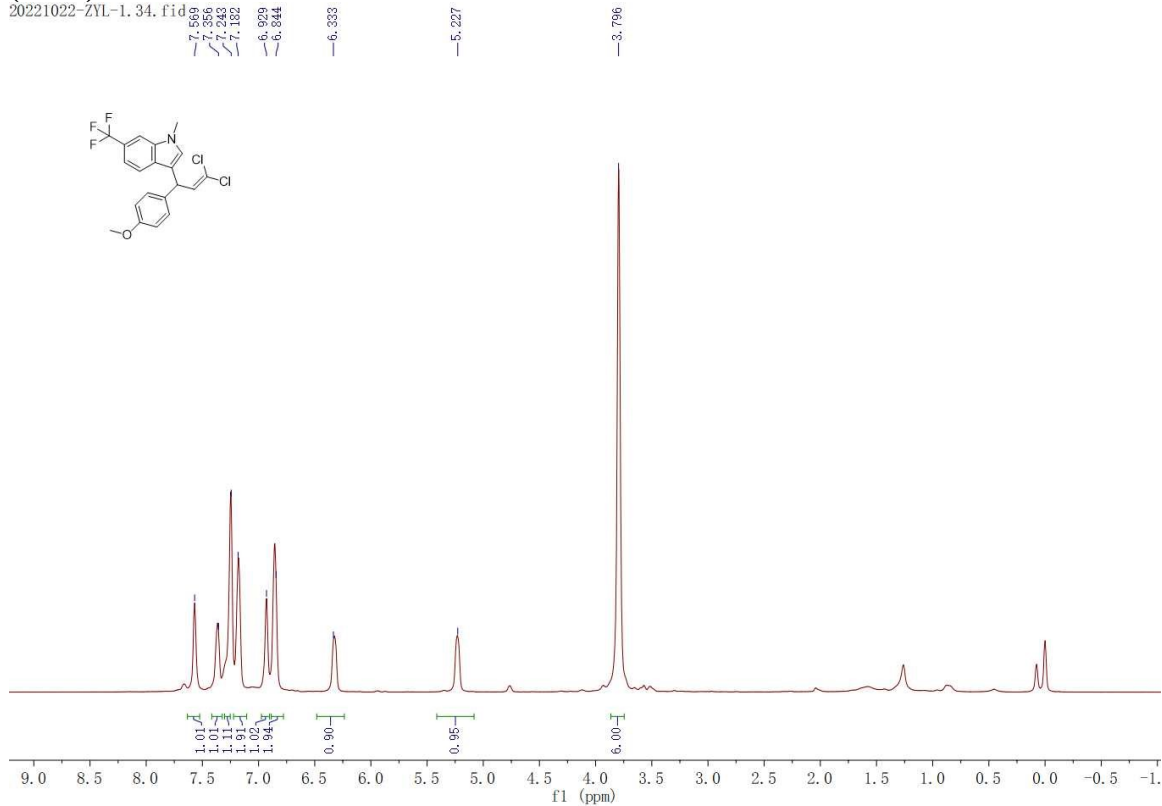


20221102-ZYL 141. fid

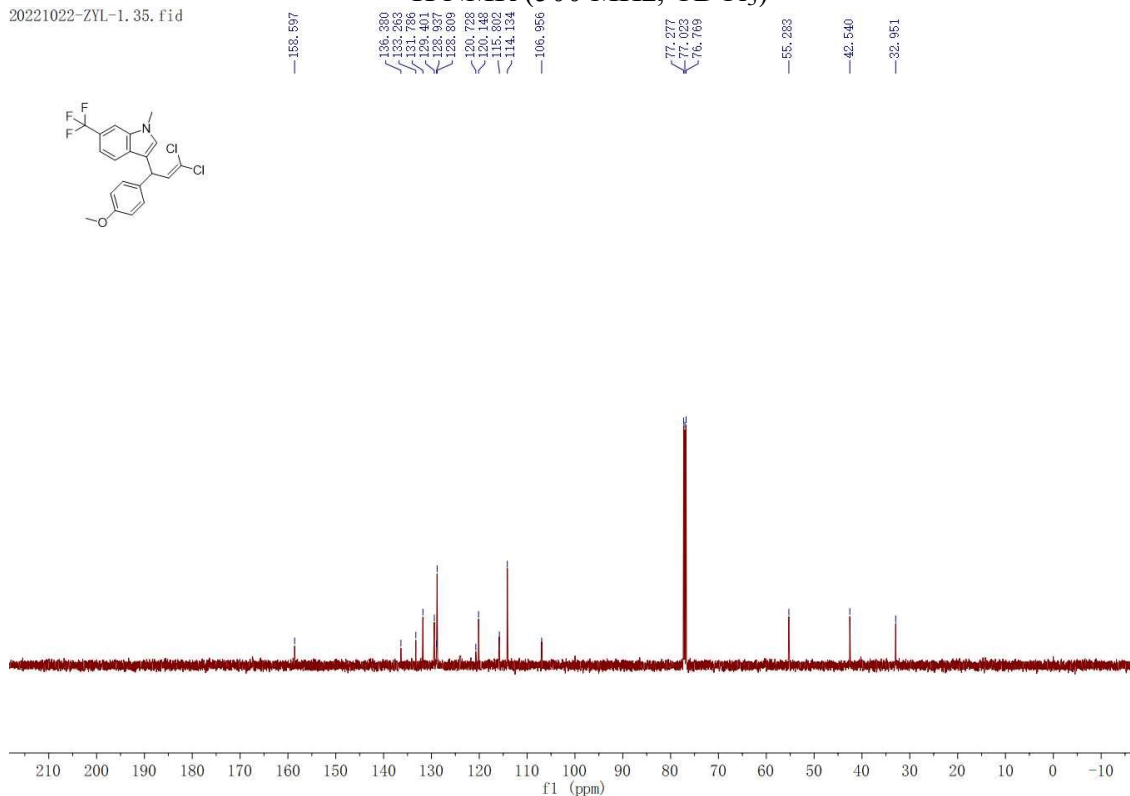


### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-6-(trifluoromethyl)-1H-indole (4aan):

20221022-ZYL-1.34. fid

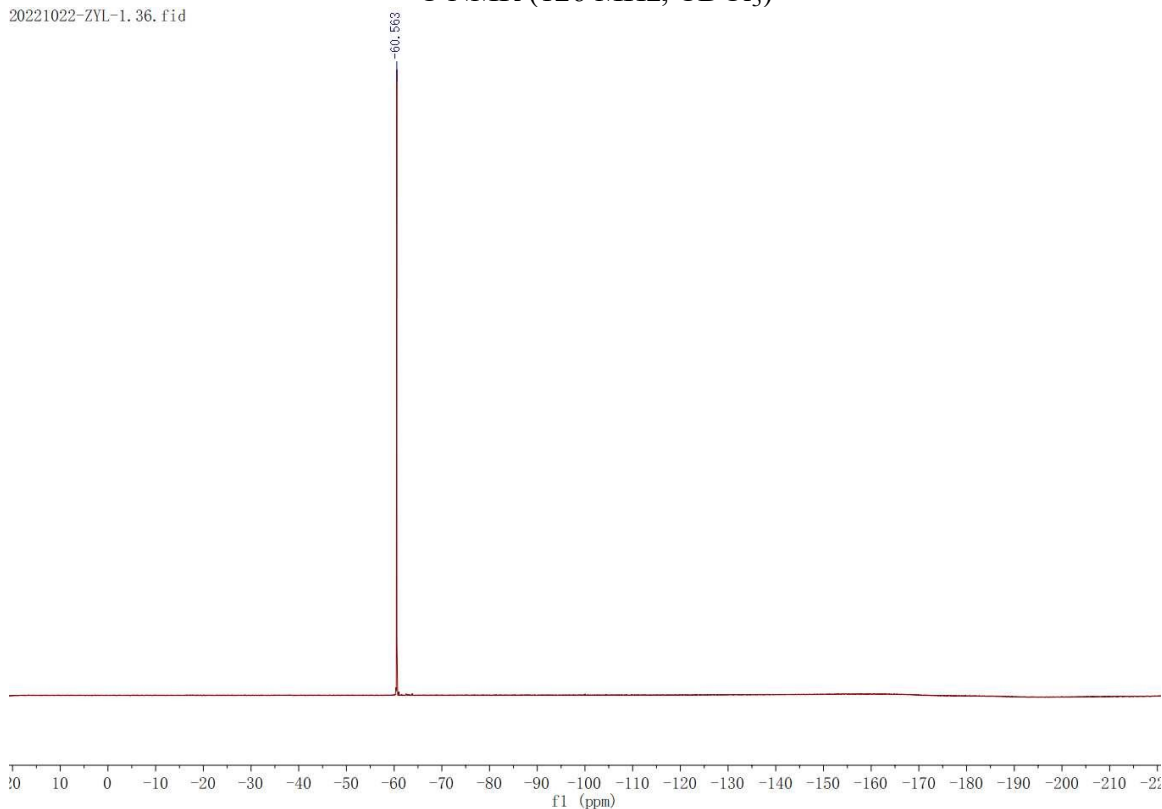


20221022-ZYL-1.35. fid



20221022-ZYL-1.36.fid

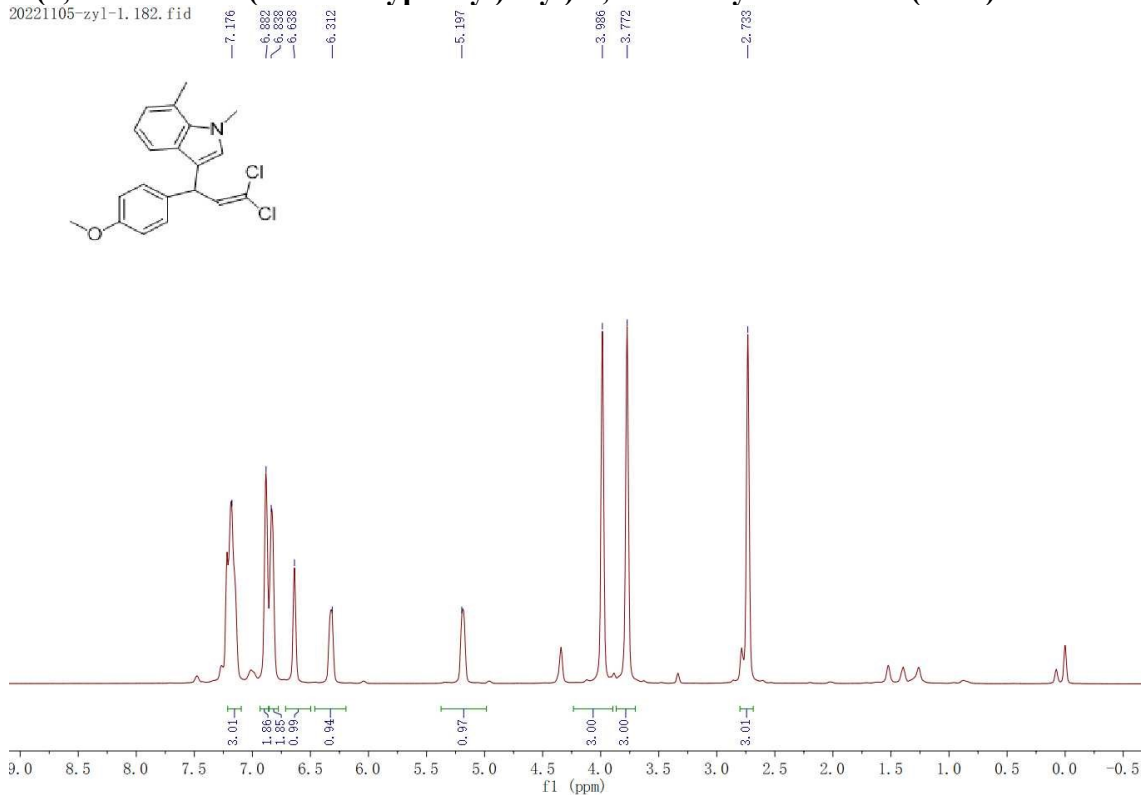
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )



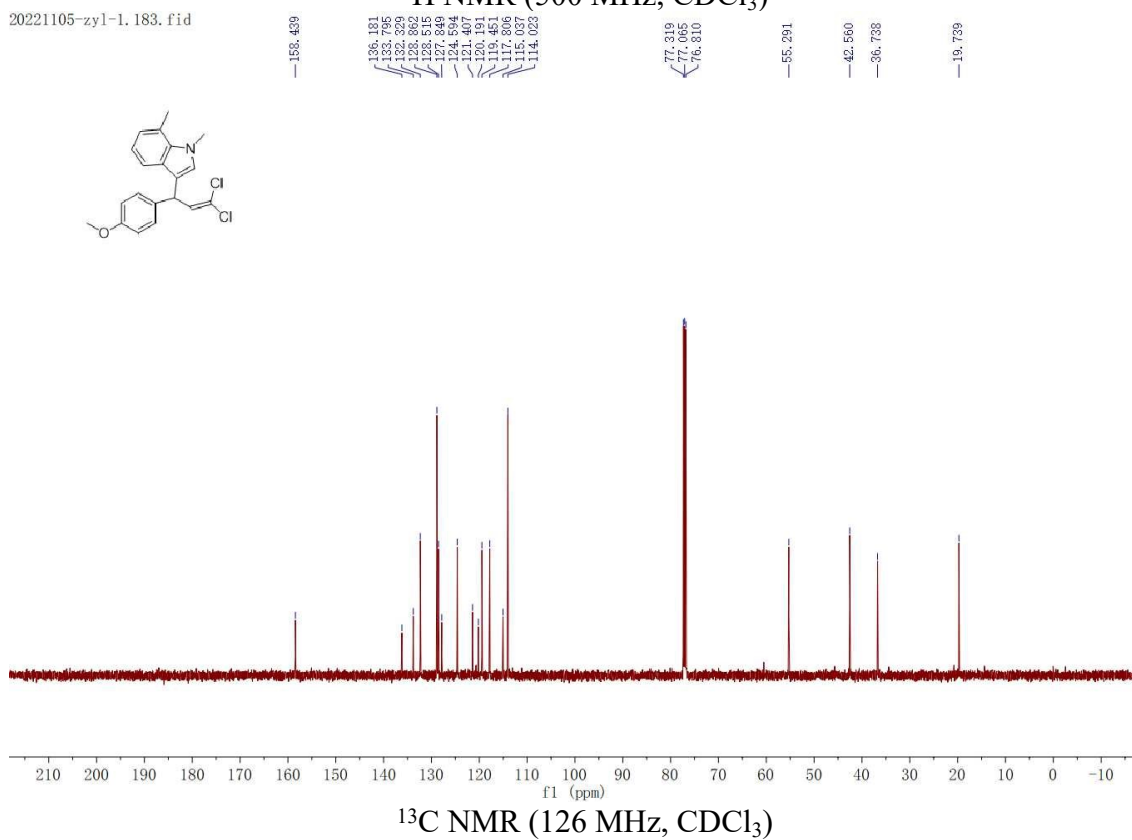
$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )

### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,7-dimethyl-1H-indole (4aao):

20221105-zyl-1.182.fid



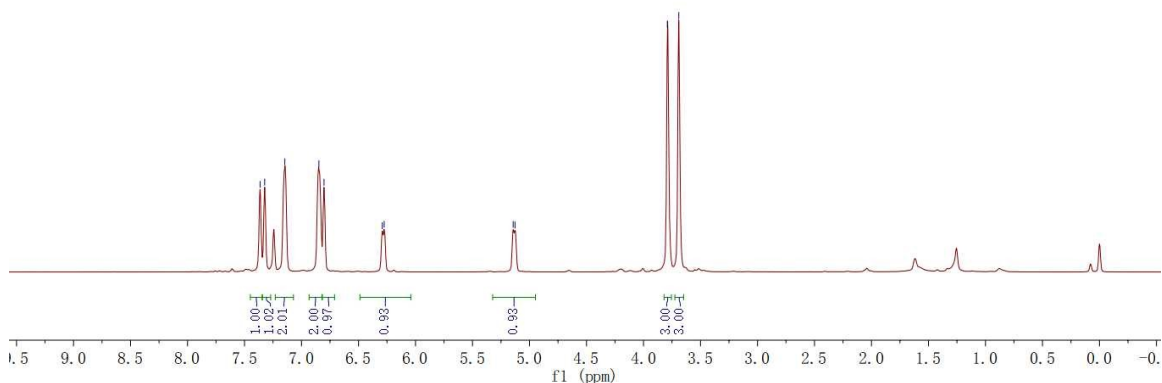
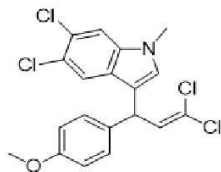
20221105-zyl-1.183.fid



**5,6-dichloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole (4aap):**

20220916-ZYL-2Cl.35.fid

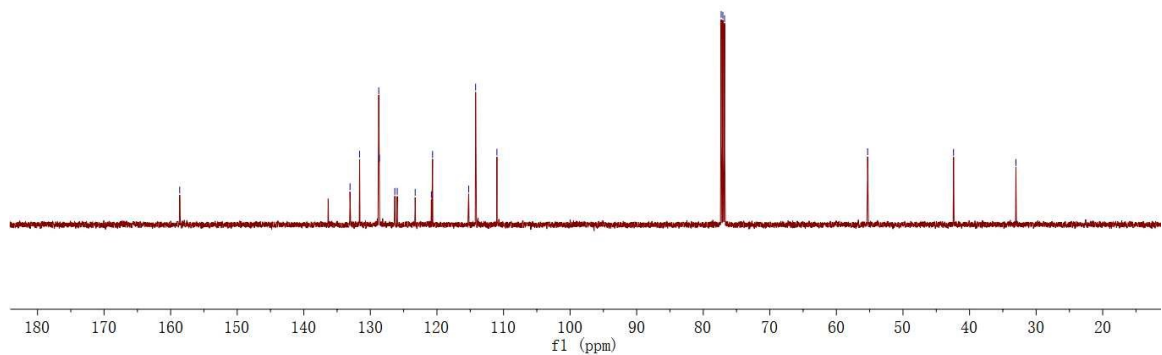
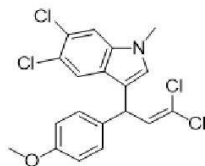
7.363  
7.323  
7.146  
6.847  
6.802  
6.292  
6.275  
5.149  
5.127  
3.791  
3.690



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

20220916-ZYL-2Cl.36.fid

158.644  
133.056  
131.613  
128.649  
128.629  
125.929  
125.962  
123.270  
120.838  
120.659  
115.232  
114.191  
110.989  
77.307  
77.054  
76.800  
55.306  
42.406  
33.035

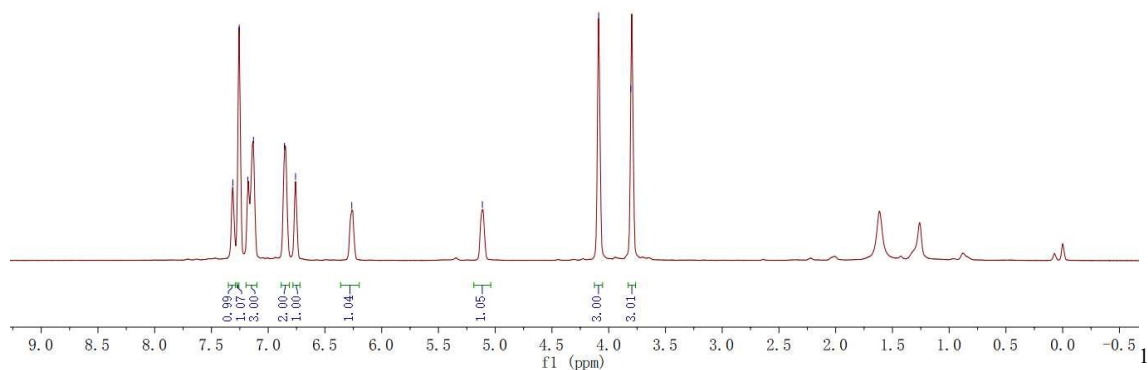
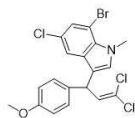


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

**7-bromo-5-chloro-3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-1H-indole  
(4aaq):**

20111112-zyl-2.327.fid

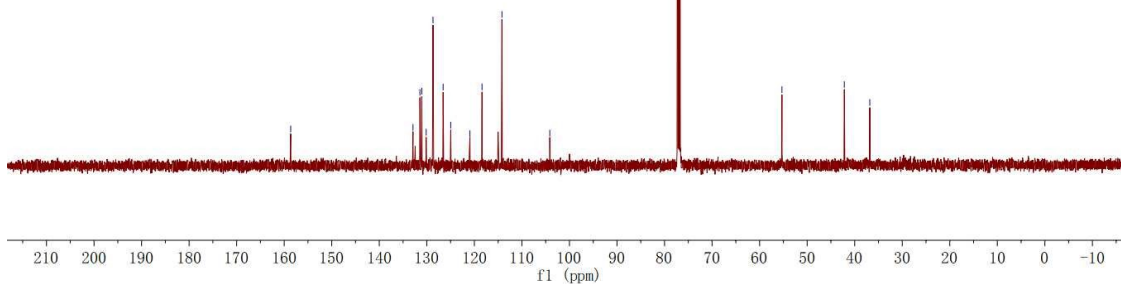
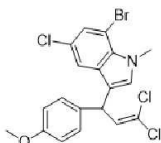
7.311  
7.255  
7.179  
7.130  
6.857  
6.759  
6.264  
5.113  
4.088  
3.806



**H NMR (500 MHz, CDCl<sub>3</sub>)**

20111112-zyl-2.328.fid

158.632  
132.910  
131.461  
131.146  
130.146  
128.699  
126.573  
124.872  
120.595  
118.198  
114.198  
104.136  
77.280  
77.026  
76.773  
55.303  
42.183  
36.825

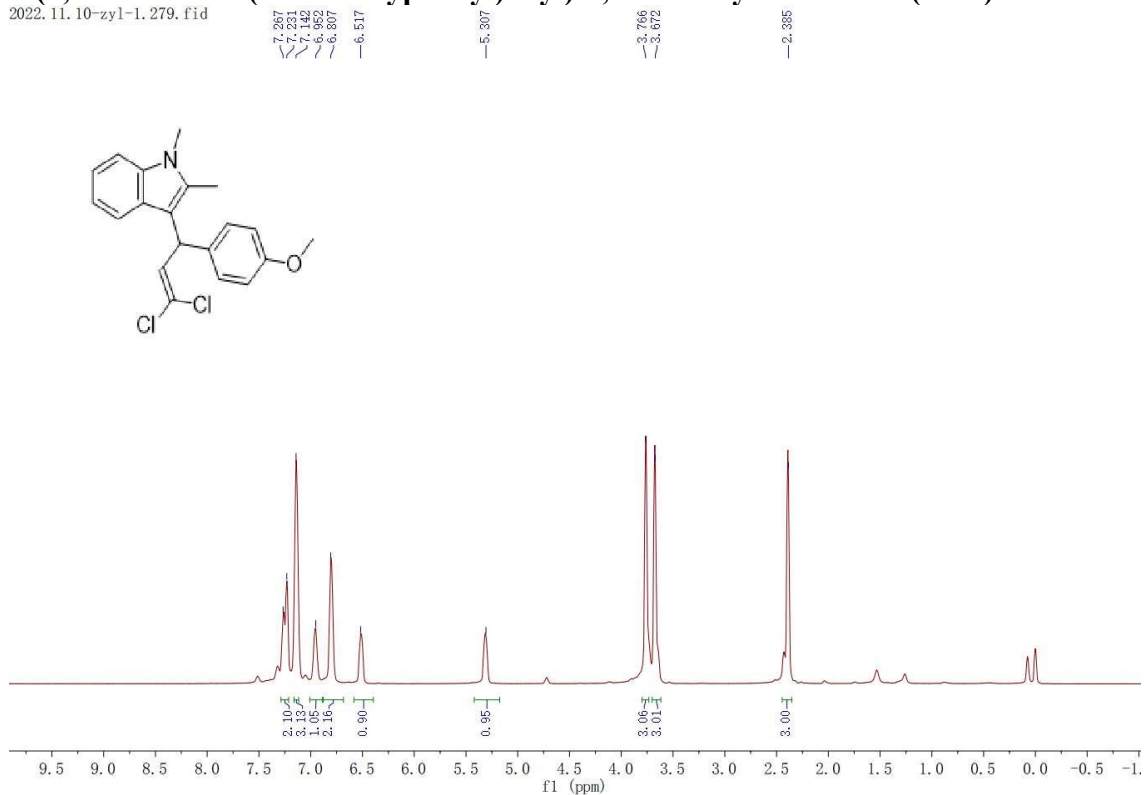


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**

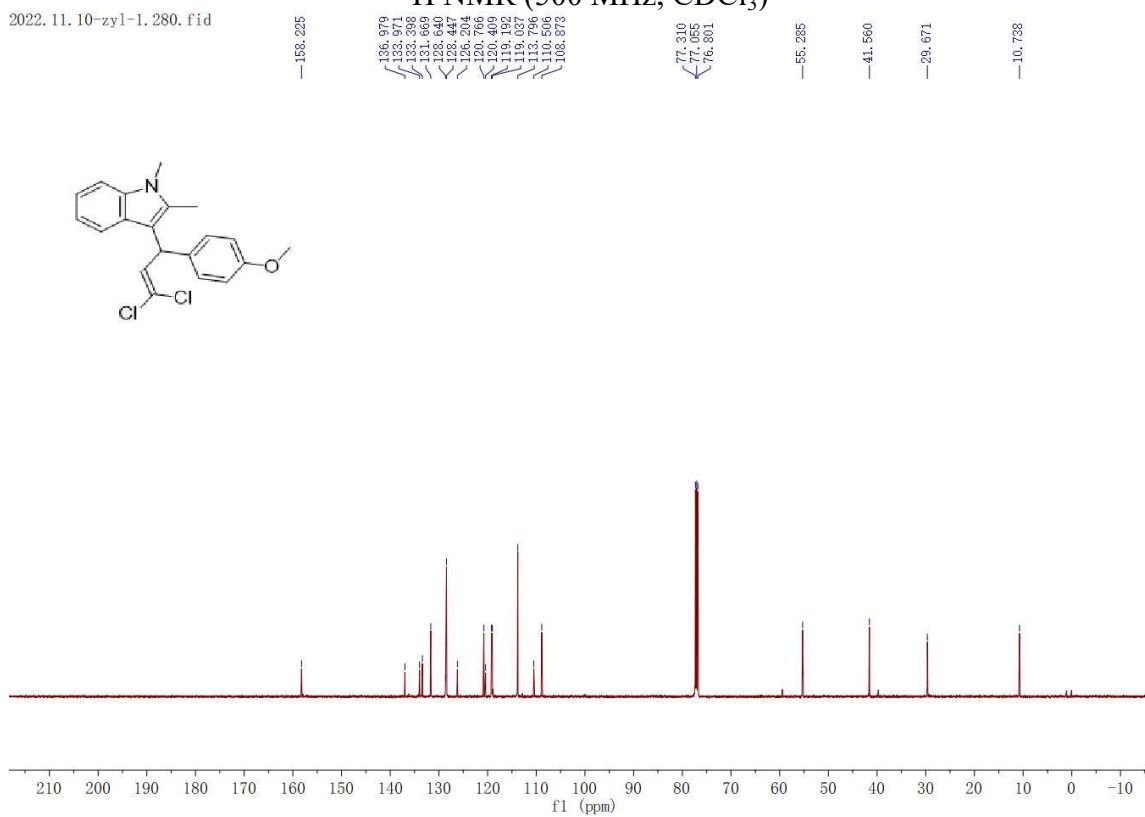


### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,2-dimethyl-1H-indole (4aar):

2022.11.10-zyl-1.279.fid



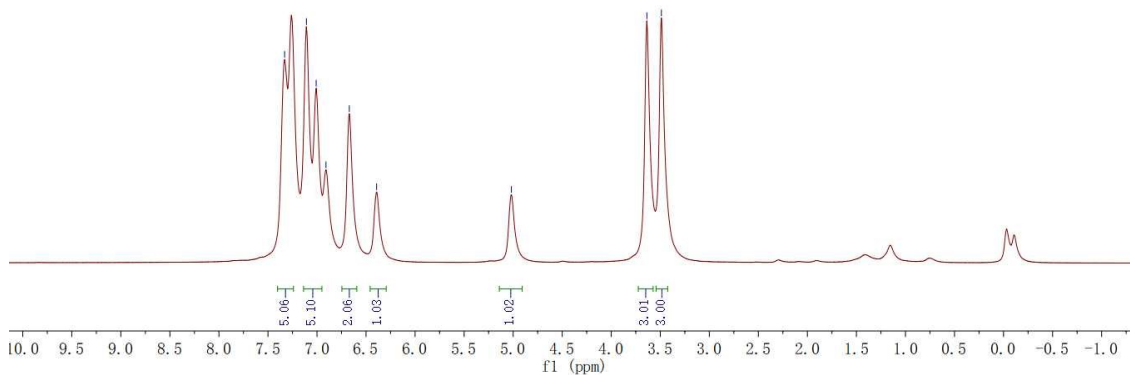
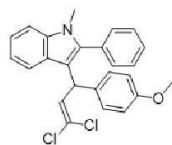
2022.11.10-zyl-1.280.fid



### 3-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-methyl-2-phenyl-1H-indole(4aas):

20221105-zyl-3.186.fid

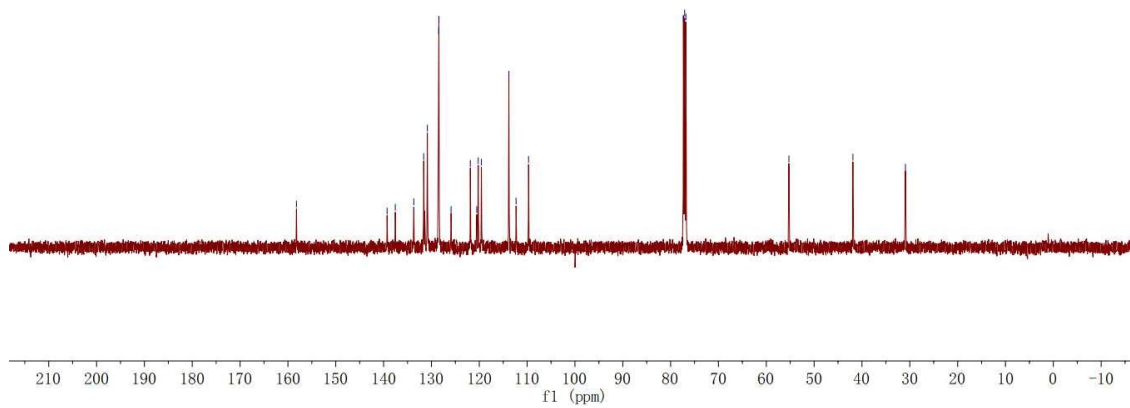
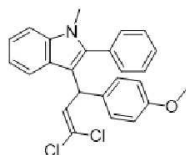
7.330  
7.108  
7.009  
6.671  
6.392  
5.018  
3.636  
3.489



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

20221105-zyl-3.187.fid

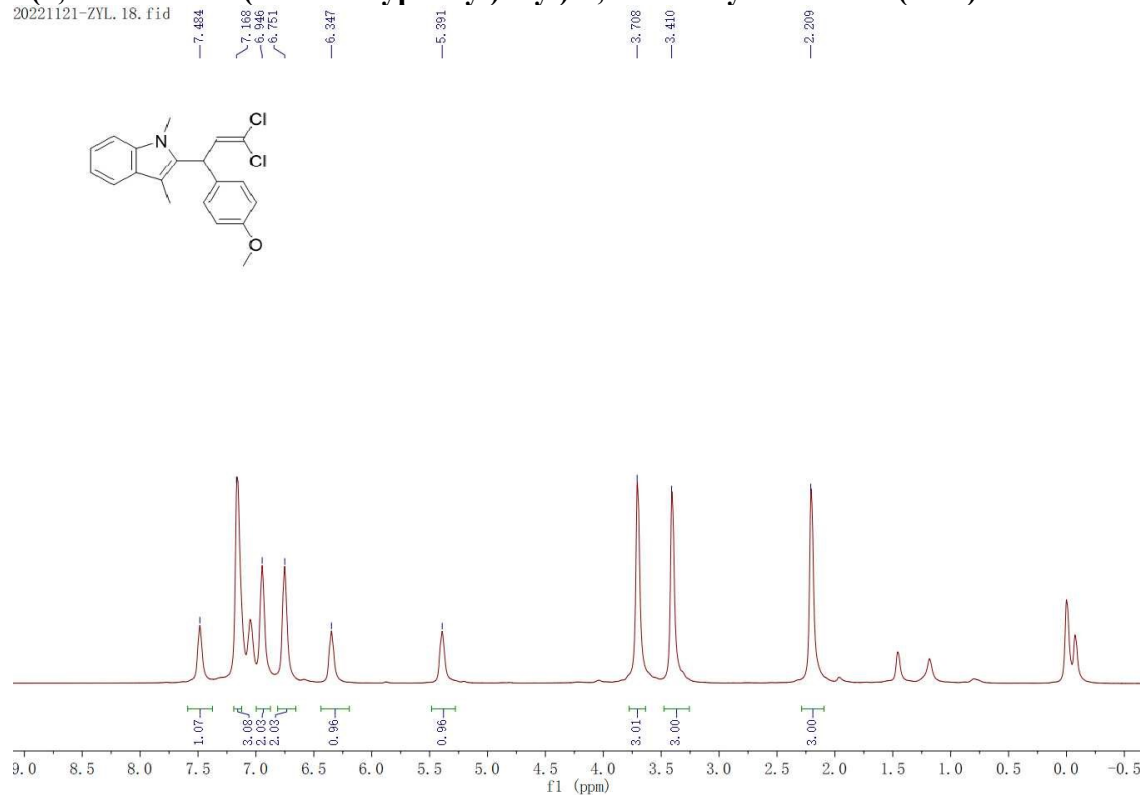
158.213  
139.274  
137.553  
133.685  
131.617  
130.354  
128.453  
125.837  
121.872  
120.527  
120.217  
119.535  
112.313  
109.698  
77.315  
77.007  
76.812  
55.277  
41.892  
30.913



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

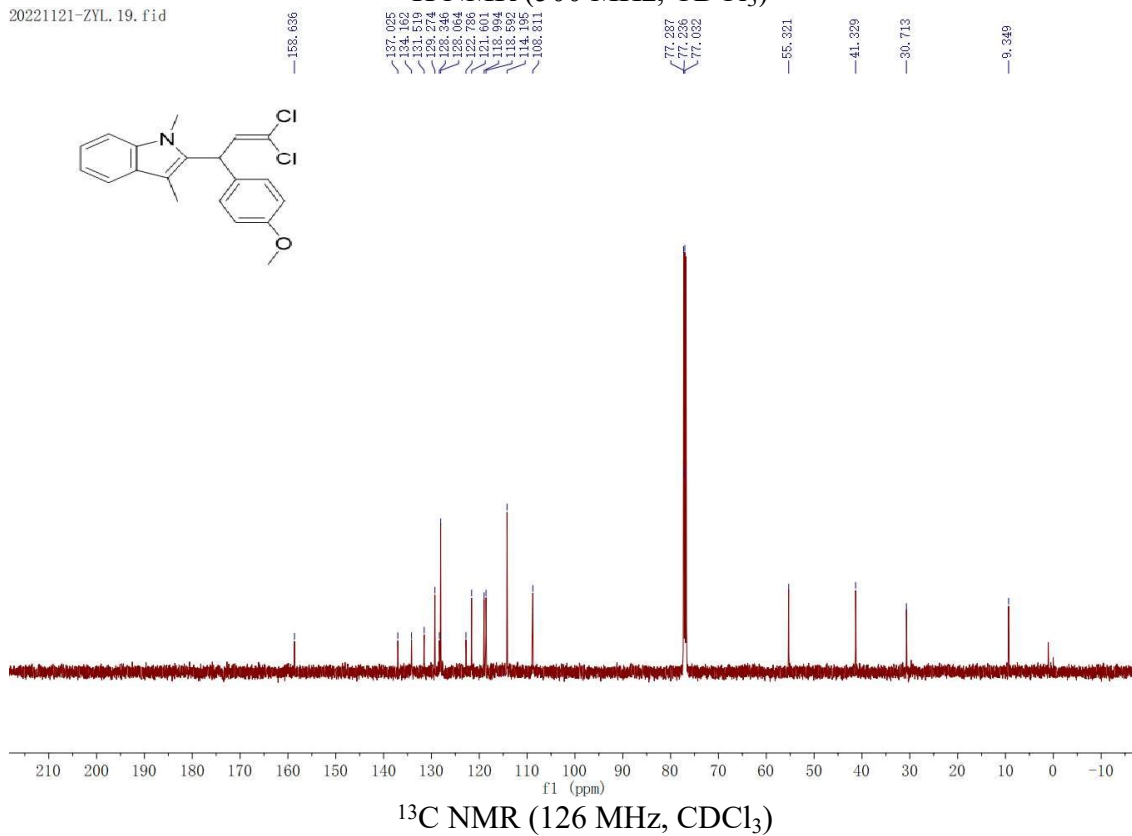
### 2-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,3-dimethyl-1H-indole(4aat):

20221121-ZYL. 18. fid



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

20221121-ZYL. 19. fid

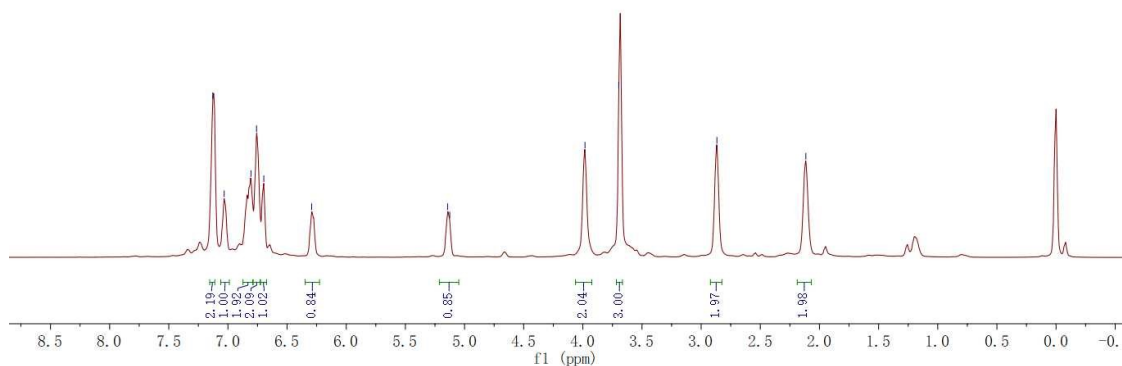
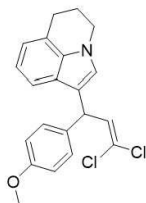


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

**1-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-5,6-dihydro-4H-pyrrolo[3,2-*ij*]quinoline(4aau):**

2022-12-3-ZYL-2.68.fid

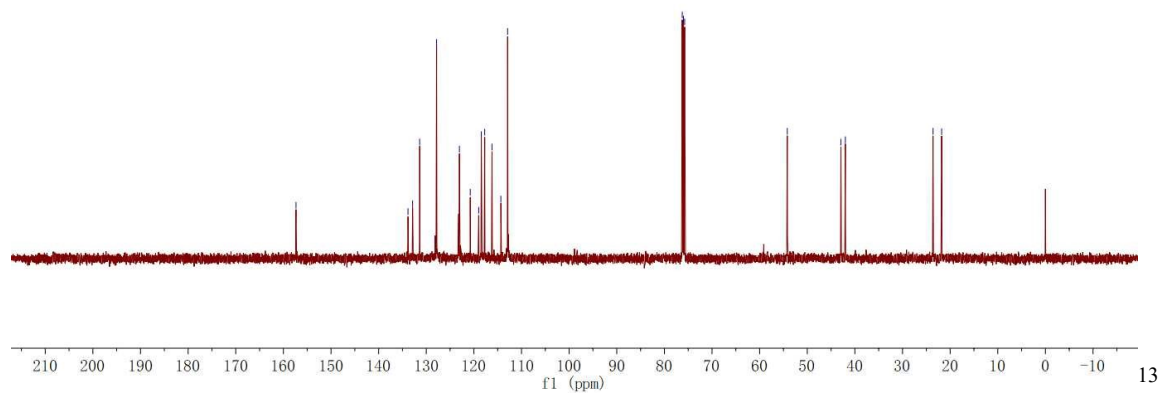
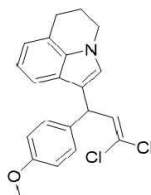
7.128  
7.032  
6.805  
6.758  
6.697  
6.292  
5.142  
5.125  
3.982  
3.697  
2.867  
2.115



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

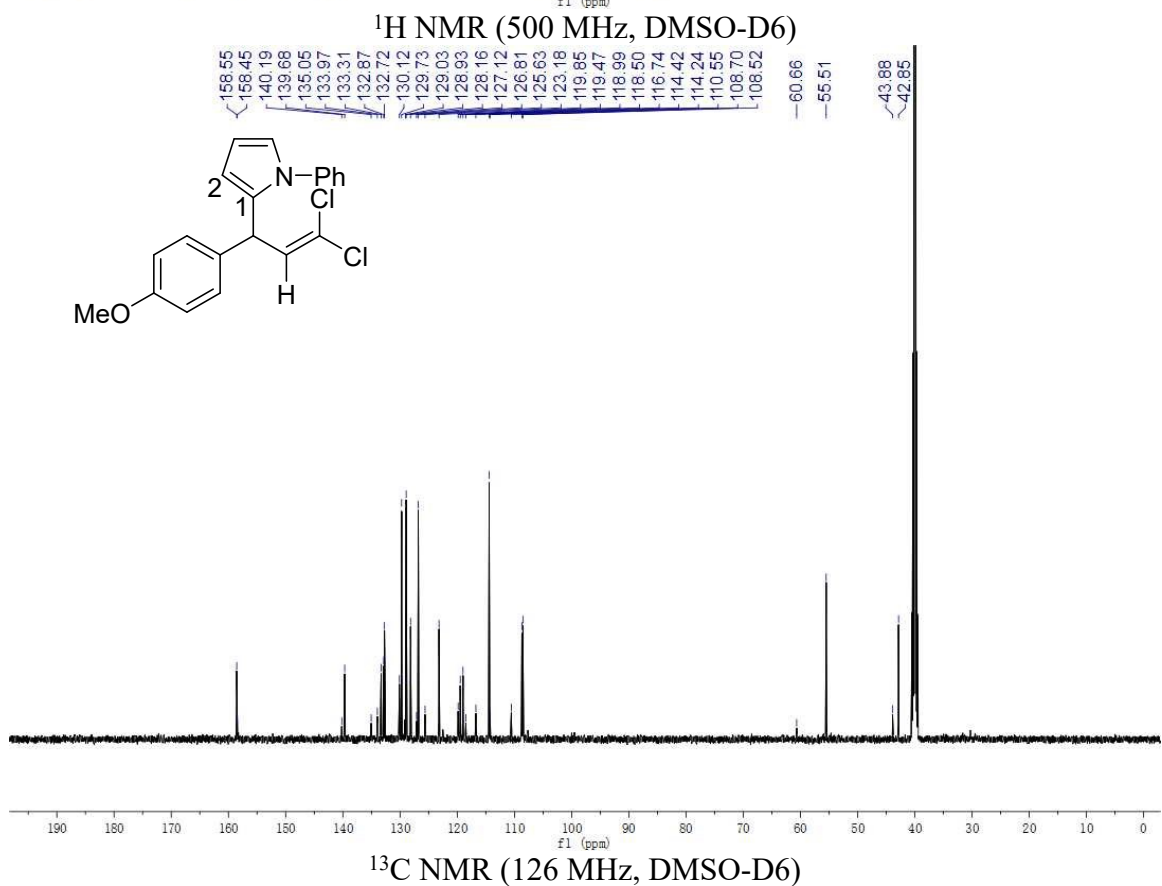
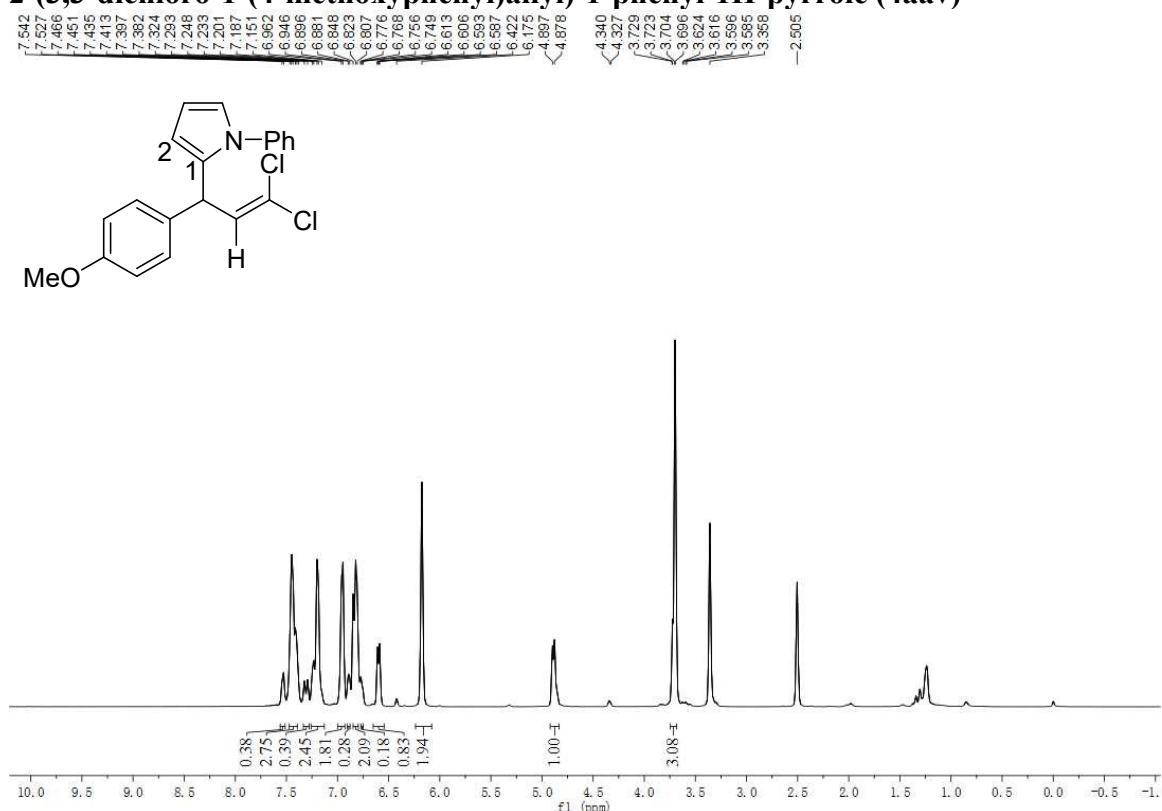
2022-12-3-ZYL-2.69.fid

157.349  
133.836  
132.868  
127.824  
127.824  
123.039  
120.760  
118.897  
118.442  
116.153  
114.837  
112.916  
76.260  
75.744  
54.200  
42.929  
42.002  
23.599  
21.785



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

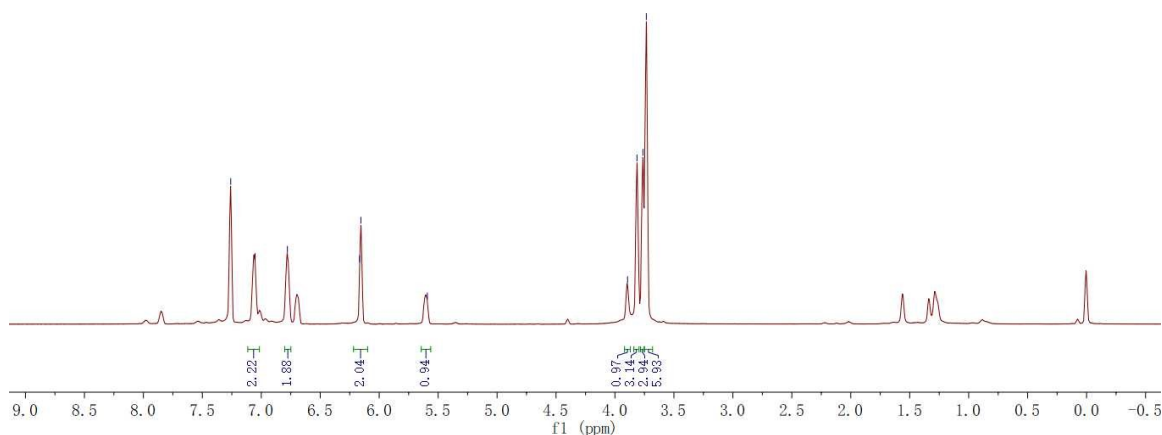
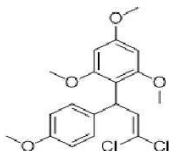
**2-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1-phenyl-1H-pyrrole (4aav)**



# 2-(3,3-dichloro-1-(4-methoxyphenyl)allyl)-1,3,5-trimethoxybenzene (4aaw):

20221104-ZYL.158.fid

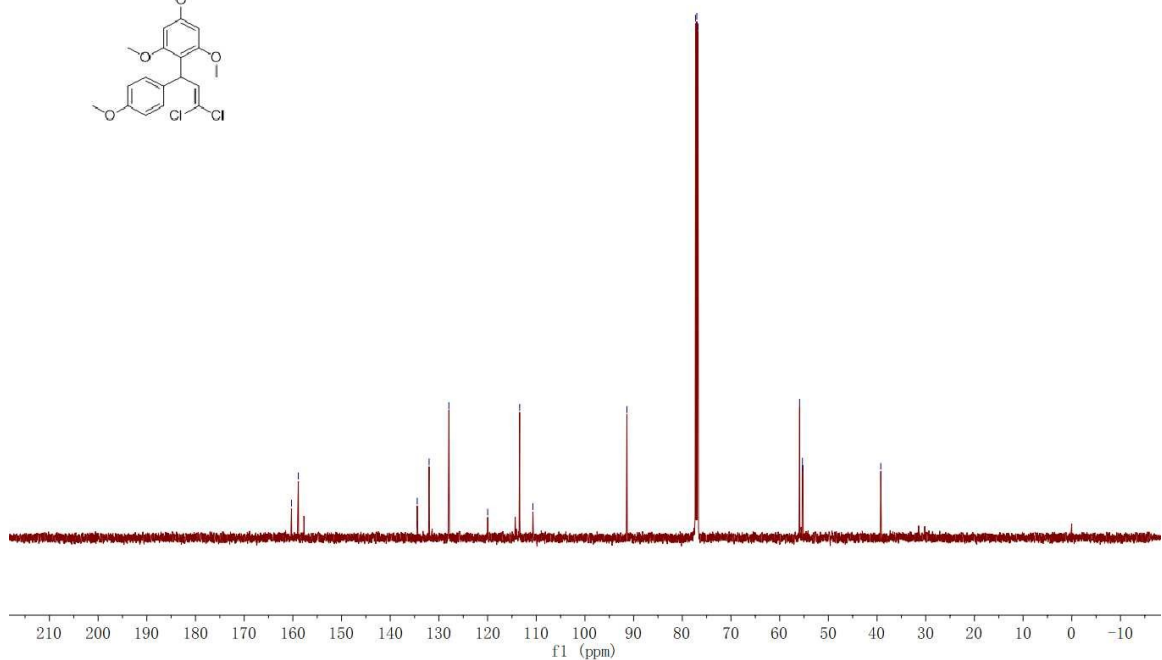
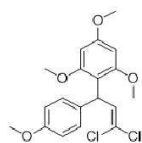
7.259  
7.052  
6.778  
6.166  
6.155  
5.992  
3.993  
3.813  
3.763  
3.734



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

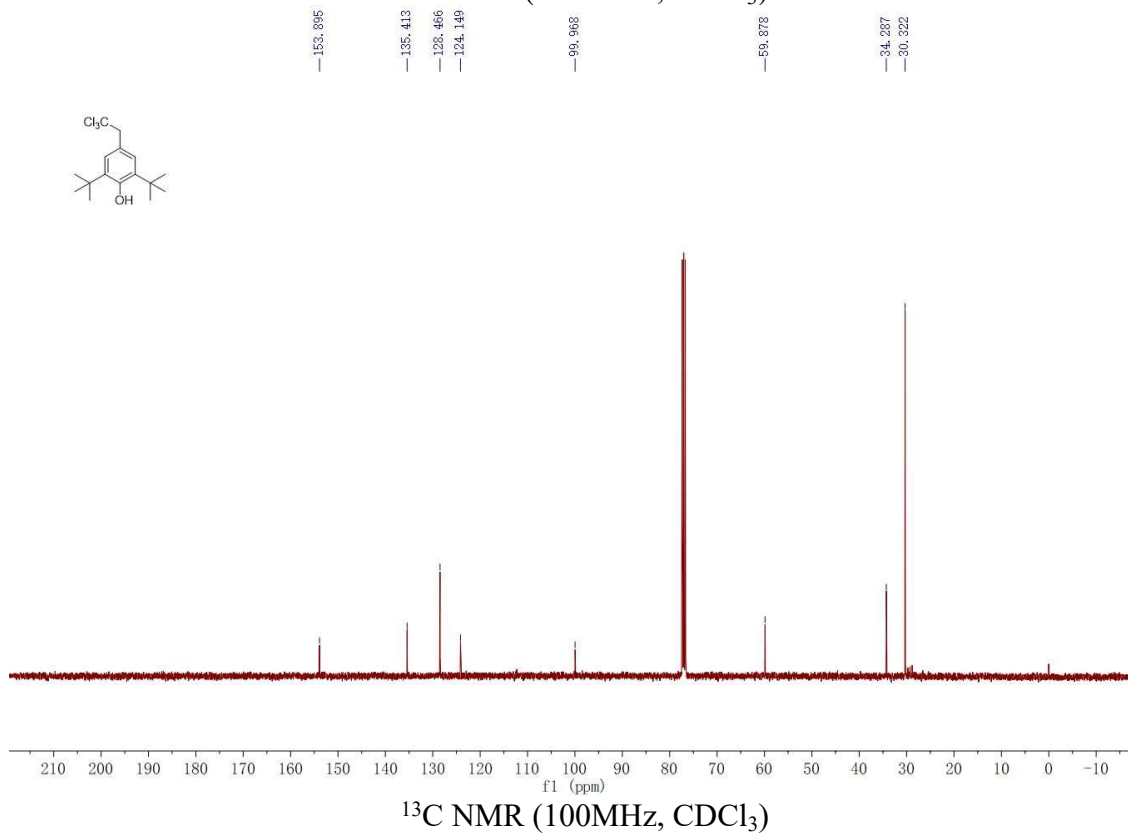
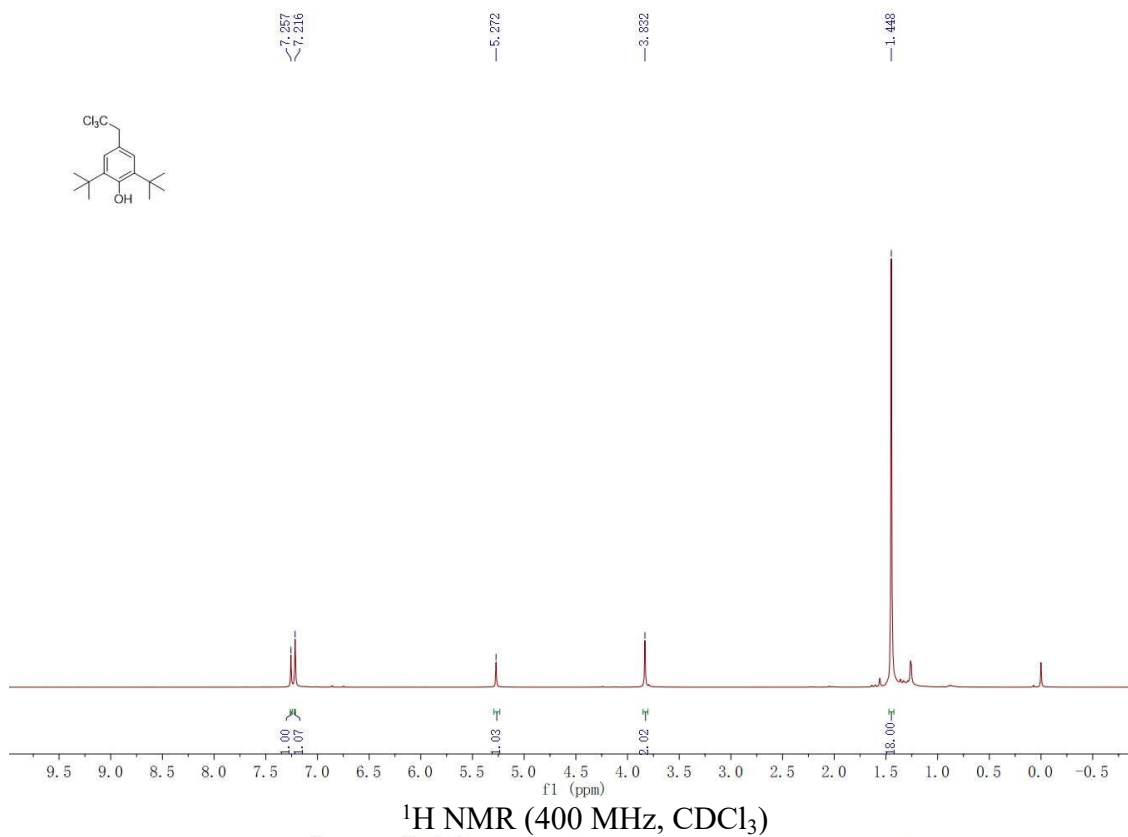
20221104-ZYL.159.fid

160.287  
158.875  
134.453  
132.016  
127.943  
119.976  
113.411  
110.633  
91.381  
77.976  
77.025  
76.771  
55.910  
55.326  
55.227  
39.229



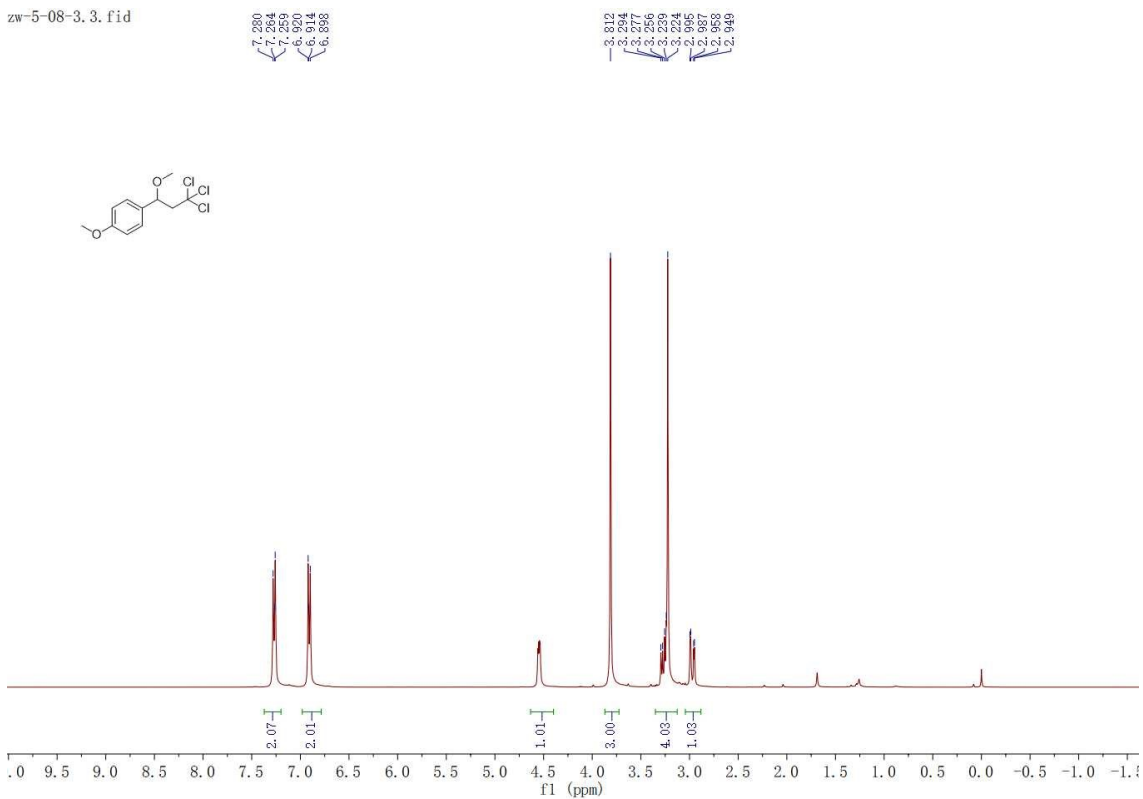
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

### 1,3-di-tert-butyl-5-methyl-2-(trichloromethoxy)benzene (5a):

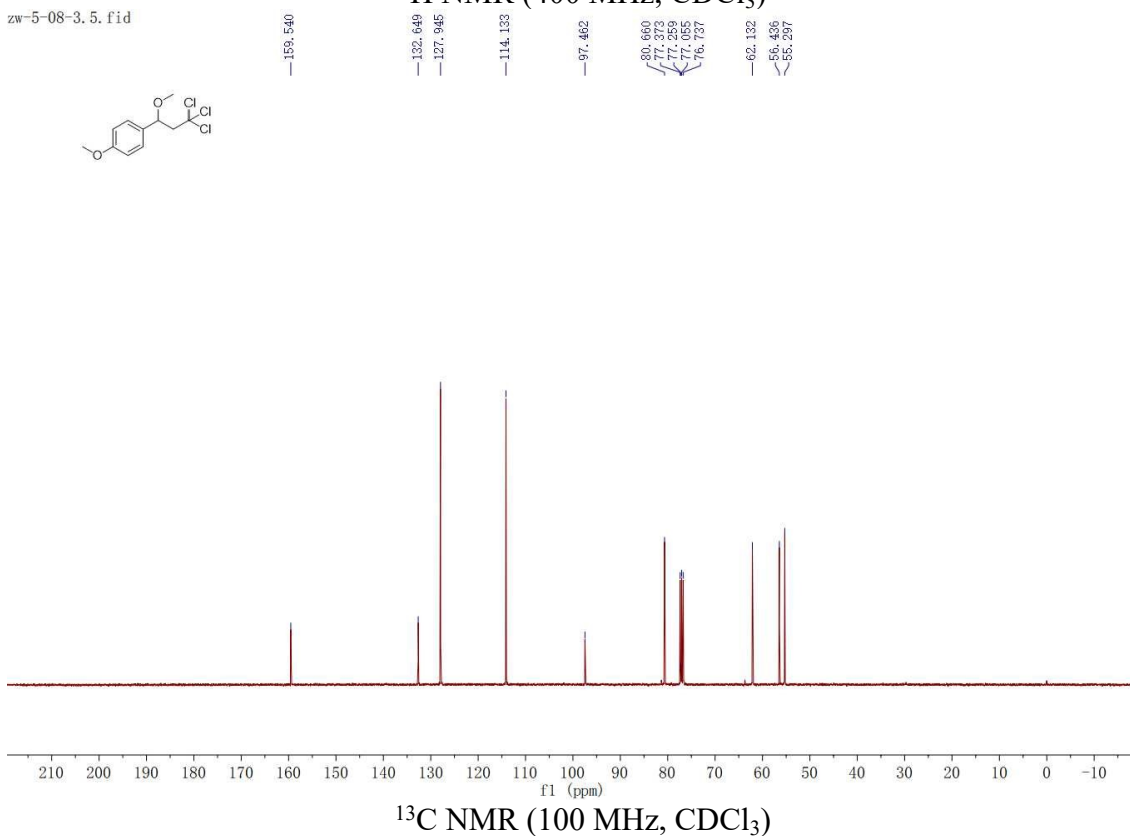


# 1-methoxy-4-(3,3,3-trichloro-1-methoxypropyl)benzene(5b):

zw-5-08-3.3.fid



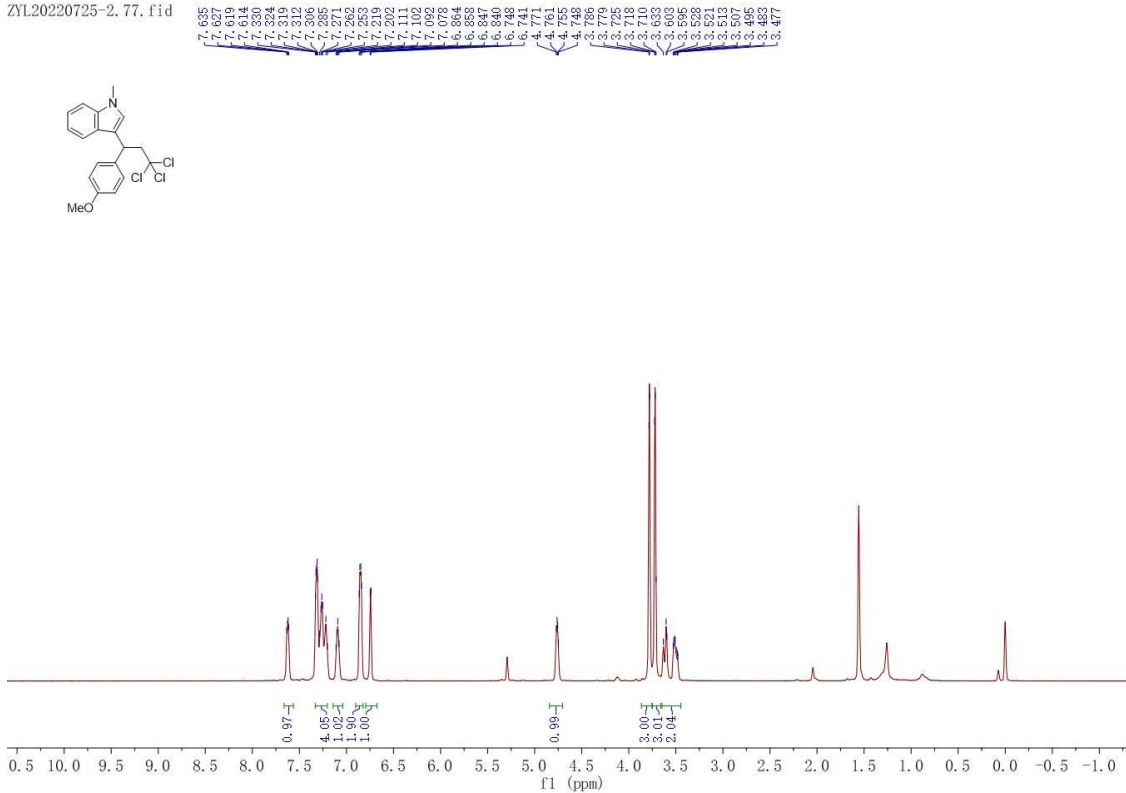
zw-5-08-3.5.fid





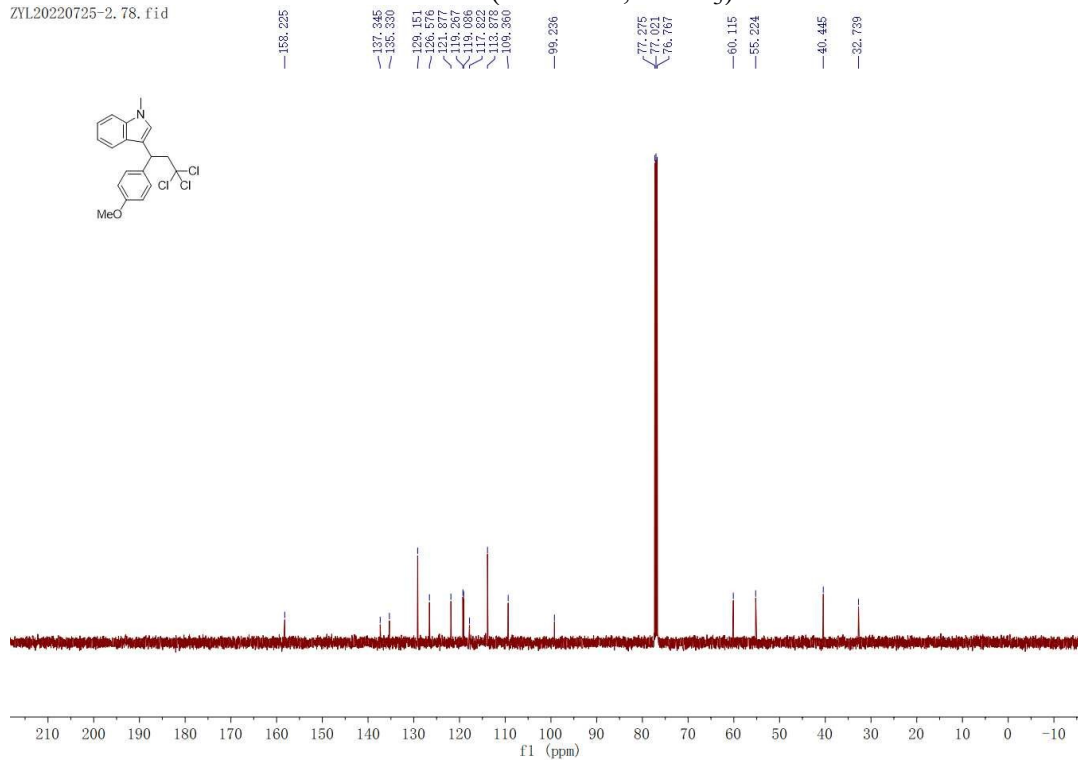
# 1-methyl-3-(3,3,3-trichloro-1-(4-methoxyphenyl)propyl)-1H-indole(5c):

ZYL20220725-2.77.fid



## <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

ZYL20220725-2.78.fid



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