**SUPPORTING INFORMATION**

# Visible light promoted carbochloromethylation of activated alkenes: alkylation and cyclization

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### 1.1 General information

Chemicals and anhydrous solvents were purchased from commercial suppliers. Deoxygenation of chloroform (TCM), dichloromethane DCM, bromoform (TBM) under argon flow, green LED light bar (1 M, 9 W) was purchased from Inwares Pte Ltd (Singapore). $^{1}$H NMR and $^{13}$C NMR spectra were recorded on Bruker AV-III400 (400 MHZ) or MX 500 (500 MHz) spectrometer. All high-resolution mass spectrometry (HRMS) were obtained on the Finnigan /MAT 95XL-T spectrometer. All GC analyses were performed on Aglilent 7820A & 5977E GC-MS.

For raw material preparation, methyl acrylate, ethyl acrylate and (vinylsulfonyl) benzene were purchased from sigma reagent company. Other acrylates were synthesized according to the literature method [1-4]. Ethyl 2-(bromomethyl)acrylate were synthesized in two steps through acrylate (1.21). We listed butyl acrylate as the synthesis representative of acrylate compounds, ethyl 2-(bromomethyl)acrylate as an example of classical substrate synthesis in SI (1.2). N-substituted acrylamide is synthesized by amine compounds and acryloyl chloride [5].

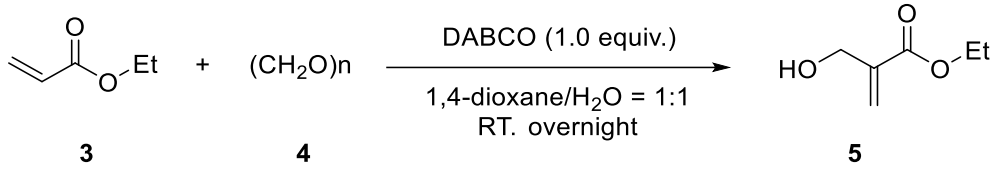
### 1.2. Experimental details and characterization data for representative products.


**1** **2** **3**

**Scheme 1.** Preparation of acrylate

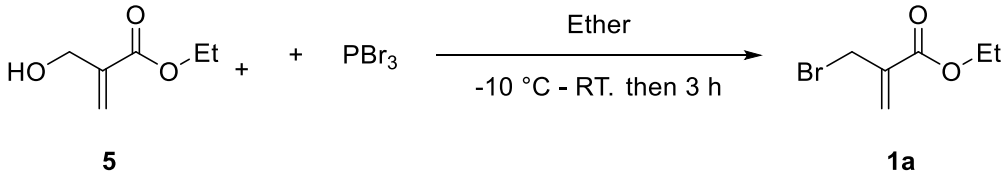
A mixture of alcohol or phenol **2** (3 mmol) under argon atmosphere and $Et_3N$ (4.5 mmol) in anhydrous DCM (10 mL) was cooled to 0 ℃ in an ice-water bath, and acryloyl chloride **1** (3.6 mmol) was slowly added dropwise. The mixture was slowly warmed and stirred overnight. TCL (PE: EtOAc = 10: 1) detection, the organic phase was washed with 1 M HCl (3 x 25 mL) and brine (25 mL). The combined organic phase was then dried with $Na_2SO_4$ and filtered. The filtrate was concentrated under vacuum. The residue was chromatographed on silica gel (PE: EtOAc = 30: 1) to give the desired product **3** (85-95% yield) (**Scheme 1**). Butyl acrylate. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, *J* =18.0 Hz, 1H), δ 6.11 (dd, *J* =17.2, 10.0 Hz, 1H), 5.84-5.77 (m, 2H), 5.06-4.98 (m, 2H), 4.16 (t, *J* =6.4 Hz, 2H), 2.17-2.11 (m, 2H), 1.80-1.73 (m, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz) 166.2, 137.4, 130.5, 128.5, 115.2, 63.9, 30.0, 27.7. The data obtained is consistent with the literature.

### 1.2.1 Representative method for preparation of acrylates




**Scheme 2.** Preparation of 2-(hydroxymethyl) acrylate

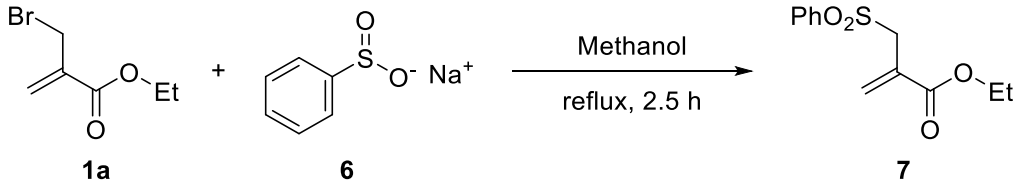
Ethyl acrylate **3** (109 mL, 1.0 mol) was dropwisely added to paraformaldehyde **4** (33.0 g, 1.1 mol) DABCO (11.3 g, 0.1 mol) in THF: water (100: 100 mL) mixed solution, and the reaction mixture was stirred at room temperature for 36 h. Sodium chloride (35 g) and ether (100 mL) were added to the reaction mixture. Most of the organic phase was separated, and the aqueous phase was extracted three times with ether. The combined organic layer was washed with saturated brine, dried and concentrated. The yield of ethyl 2-(hydroxymethyl)acrylate **5** obtained using column chromatography was 70% (PE: EtOAc = 30: 1) ( **Scheme 2**).




**Scheme 3.** Preparation of 2-(bromomethyl) acrylate

Ethyl 2-(bromomethyl)acrylate **1a** ( **Scheme 3**). To a solution of ethyl 2-(hydroxymethyl) acrylate **5** (3.01 g, 3.0 mmol) in anhydrous ether (20 mL) was slowly added phosphorus (III) bromide (0.76 mL, 8.0 mmol) at -10 ℃. At the end of the dropwise addition, the temperature was slowly raised to room temperature. After 3 hours of reaction, water (10 mL) was added to quench the mixture, and the mixture was extracted with ether (3 × 50 mL). The organic phase was washed with saturated sodium chloride solution (50 mL), dried and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE: EtOAc = 50: 1) to give ethyl 2-(bromomethyl) acrylate as a colorless oil (3.99 g, 89% yield) TLC Rf = 0.55 (EtOAc/hexanes = 1/10). Ethyl 2-(bromomethyl)acrylate $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 1H ), 5.95 (s, 1H) 4.27 (q, $J$ = 7.2 Hz, 2H), 4.19 (s, 2H), 1.33 (t, $J$ =7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.8, 137.6, 128.9, 61.3, 29.4, 14.1.

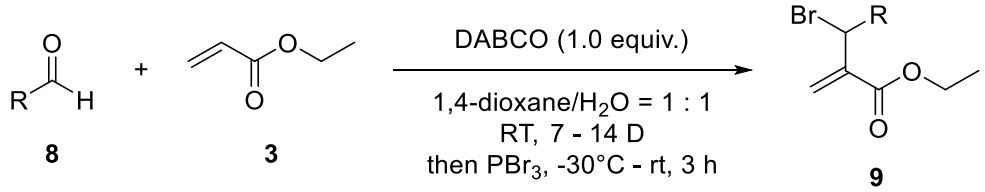
Ethyl 2-((phenylsulfonyl) methyl) acrylate



**Scheme 4.** Preparation of 2-((phenylsulfonyl)methyl) acrylate

To a solution of ethyl 2-(bromomethyl) acrylate **1a** (1.99 g, 10.4 mmol) in anhydrous methanol (25 mL) was added sodium phenylsulfinate **6** (2.50 g, 15.2 mmol). After refluxing for 2.5 h, the mixture was concentrated under reduced pressure, and the residue was dissolved with EtOAc and washed with brine, and the organic layer was dried over $Na_2SO_4$. The filtrate was distilled under reduced pressure and purified by chromatography to obtain ethyl 2-((Phenylsulfonyl) methyl) acrylate as a thick oil **7** (1.94 g, 74% yield) (**Scheme 4**). Ethyl 2-(bromomethyl) acrylate. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 6.51 (s, 1H), 5.92 (s, 1H), 4.17(s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.7, 138.4, 133.9, 133.3, 129.1, 129.0, 128.8, 61.5, 57.5, 14.0.

The synthesis of all the MBH alcohols was carried out according to the following reported procedure. Benzaldehyde (5 mmol), methyl acrylate (2.5 equiv.) and DABCO (1.0 equiv.) were taken in a 25 mL oven dried round bottom flask and sealed with a rubber septum. The resultant reaction mixture was stirred at room temperature under solvent free condition for 7-14 days. The progress of the reaction was monitored by TLC. After completion，the mixture was admixed with ethyl acetate (30 mL) and washed successively with saturated solution of sodium bicarbonate (2 x 5 mL) and brine solution (2 x 5 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated in vacuum. The crude product thus obtained was purified using column chromatography with hexane and EtOAc as eluent to afford the desired MBH alcohols in quantitative yield.

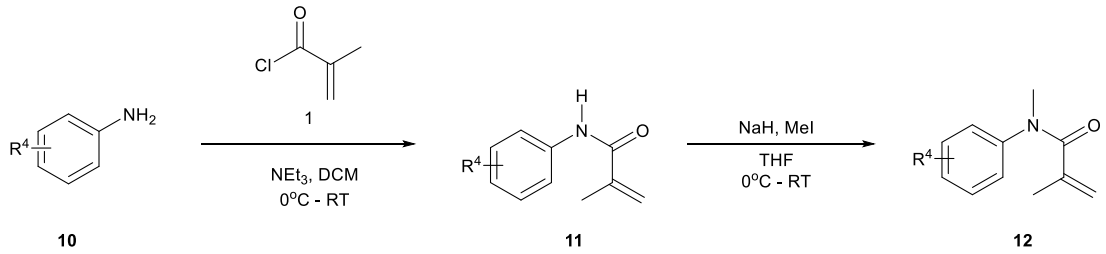



**Scheme 5.** Preparation of ethyl 3-bromo-2-methylenebutanoate/ethyl (E)-2-(bromomethyl)-3-phenylacrylate

To a stirred solution of hydroxyl acrylate (1 equiv.) in dry diethyl ether (0.25 M), phosphorous tribromide (4.0 equiv.) was slowly added at -30 ℃ and the mixture left stirring at room temperature for an additional hour. The mixture was then re-cooled to -10 ℃ and quenched by slow addition of water until bubbling ceased. The organic layer was separated and the aqueous layer extracted with a 1:1 mixture of diethyl ether/hexanes (3 x 30 mL). The combined organic layer was dried with $Na_2SO_4$ and filtered. After evaporation of the volatiles, The crude product was purified by column chromatography on silica gel (PE: EtOAc = 50: 1) to give ethyl 3-bromo-2-methylenebutanoate as a

colorless oil ( **Scheme 5**).

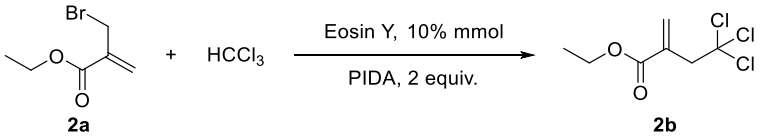
1.2.2 Preparation of cyclized substrates




**Scheme 6.** Preparation of *N*-substituted acrylamide

Aminobenzene **10** (10.0 mmol, 1.0 equiv.) was dissolved in DCM (30 mL) under nitrogen. $NEt_3$ (12.0 mmol, 1.2 equiv.) was added to the reaction flask at 0 ℃. Acryloyl chloride (12.0 mmol, 1.2 equiv.) was added slowly to the mixture and the reaction was monitored by TLC. After completion of the reaction, aqueous $NaHCO_3$ (25 mL) was added. The crude product was extracted with DCM (3 x 50 mL). The combined organic layer was washed with 1M HCl (3 x 20 mL) and brine (3 x 20 mL) and dried over $Na_2SO_4$. Solvent was removed in vacuo. The crude product was purified by flash column chromatography. Purified amide **11** (8.0 mmol, 1.0 equiv.) was dissolved in THF (50 mL) at 0 ℃. NaH (10.4 mmol, 1.3 equiv.) was in three portions and the mixture was stirred for further 15 min. $CH_3I$ (32.0 mmol, 4.0 equiv.) was added slowly and the reaction mixture was stirred until completion as monitored by TLC. THF was removed in vacuo. Water (30 mL) was added to the mixture and the crude product was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine (3 x 20 mL) and dried over $Na_2SO_4$. Solvent was removed in vacuo. The crude product **12** was purified by flash column chromatography ( **Scheme 6**) **S5**.

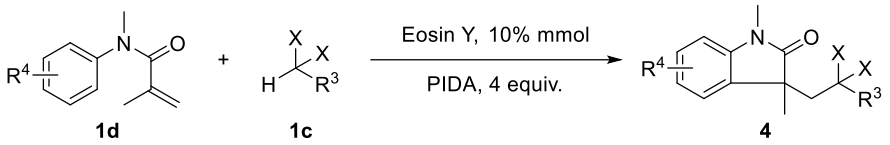
**Representative procedure for trichloromethylation of polar olefins**




**Scheme 7.** Synthesis of 4,4,4-trichloro-2-methylene butyrate

2 equiv. PIDA (128 mg) and 5% Eosin Y (6 mg) were added to the dried Schlinker tube in the glove box, then added ethyl 2-(bromomethyl) acrylate (38.2 mg) chloroform (0.5 mL), benzotrifluoride solution (1.5 mL). The reaction tube was removed from the glove box, stirred under green light at room temperature for 60 h, detected by TLC, the solvent was removed under reduced pressure, and the

column chromatography gave the target product (HEX: EA = 100: 1) (**Scheme 7**).




**Scheme 8.** Synthesis of 1,3-dimethyl-3 - (2,2,2-trichloroethyl) indole-2-one

**Representative procedure for cyclization of trichloromethyl**

4 equiv. PIDA (256 mg) and 10% Eosin Y (12 mg) were added to the dried Schlinker tube in the glove box, then added *N*-methyl-*N*-phenylmethacrylamide (35 mg) chloroform (0.5 mL), benzotrifluoride solution (1.5 mL). The reaction tube was removed from the glove box, stirred under blue light at room temperature for 48 h, detected by TLC, the solvent was removed under reduced pressure, and the column chromatography gave the target product. (HEX: EA = 5: 1) (**Scheme 8**).

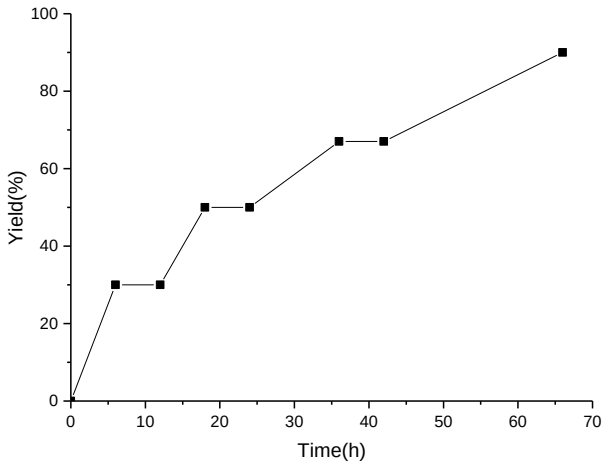
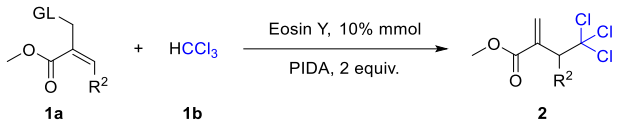



**Figure 1.** Light on/off experiments over time

To examine the impact of light, we conducted experiments under alternating periods of irradiation and darkness. These resulted in a total interruption of the reaction progress in the absence of light and recuperation of reactivity on further illumination, which allows precise temporal control over the entire reaction period. These results demonstrate that light is a necessary component of the reaction. Even though they do not definitively rule out a radical-chain process, the data shows that any chain-propagation process must be short-lived (**Figure 1**).

**Condition experiments**

**Table 1.** Condition optimization



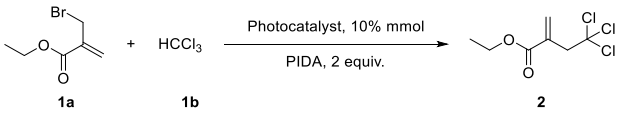

| Entry | Solvent (1.5 mL) | Oxygenant | Yield [%] |
|---|---|---|---|
| 1[b] | $PhCF_3$ | PIDA (2 equiv.) | NR |
| 2[c] | $PhCF_3$ | PIDA (2 equiv.) | < 10 |
| 3 | $PhCF_3$ | PIDA (2 equiv.) | 67 |
| 4[d] | $PhCF_3$ | PIDA (2 equiv.) | 85 |
| 5[e] | $PhCF_3$ | PIDA (2 equiv.) | 52 |
| 6 | $PhCF_3$ | PIDA (3 equiv.) | 60 |
| 7 | $PhCF_3$ | PIFA (2 equiv.) | 33 |
| 8 | $PhCF_3$ | DDQ (2 equiv.) | NR |
| 9 | $PhCF_3$ | OXONE (2 equiv.) | Trace |
| 10 | MeCN | PIDA (2 equiv.) | Trace |
| 11 | $PhCH_3$ | PIDA (2 equiv.) | 19 |
| 12 | PhF | PIDA (2 equiv.) | 48 |
| 13 | PhCl | PIDA (2 equiv.) | 50 |
| 14 | $PhCF_3$ | PIDA (1.5 equiv.) | 49 |
| 15 | $PhCF_3$ | PIDA (2.5 equiv.) | 69 |
| 16[f] | $PhCF_3$ | PIDA (2 equiv.) | 90 |

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1 equiv.), **1b** (0.5 mL), $R^2$ = H, LG = Br, 24 h; [b] $R^2$ = H, LG = H, 24 h; [c] $R^2$ = H, LG = Cl, 24 h; [d] $R^2$ = H, LG = I, 24 h; [e] $R^2$ = H, LG = $SO_2Ph$, 24 h; 5 W Green Light, rt, isolated yields.

We commenced our investigation by using the readily available 2-methacrylate as substrate, 10 mol% Eosin Y as the photocatalyst and PIDA as the oxidant. Initial reaction optimization focused on the trichloromethylation reaction of $HCCl_3$. when X = H, trichloromethyl radical can't add with olefins. Through the screening of the leaving groups, the conversion of 2-(bromomethyl) acrylate was 67% (Entries 1-5). Finally, methyl 4,4,4-trichloro-2-methylene butyrate was obtained, and the yield was increased to 90% after 60 hours (Table 1, Entry 16). Alternative of PIDA such as PIFA, OXONE or other oxidants, the yield of the reaction decreased (Entries 7-9). Through screening of solvents, $PhCF_3$ was optimal (Entries 10-13). (**Table 1**).

## Mechanistic Studies

**Table 2.** Selection of photocatalyst




| Entry | t/h | Photocatalyst | Yield [%] |
|---|---|---|---|
| 1 | 48 | Mes-Acr | 46 |
| 2 | 48 | 4-CzIPN | 36 |
| 3 | 48 | $Ru(bpy)_3$ | 44 |
| 4 | 48 | $Ir(dF.CF_3ppy)_2(dtbpy)_3$ | 56 |
| 5 | 48 | $Ir(ppy)_2(dtbpy)$ | 52 |
| 6 | 48 | $Ir(ppy)_3$ | 22 |

Photocatalysts are considered, while Mes-Acr has a yield of 46% (Entry 1). Both 4-CzIPN and $Ru(bpy)_3$ achieve 36% and 44% yields, respectively (Entries 2-3). The catalytic system for $Ir(dF.CF_3ppy)_2(dtbpy)_3$, $Ir(ppy)_2(dtbpy)$ and $Ir(ppy)_3$ achieved 56%, 52% and 22% yields, respectively (Entries 4-6) (**Table 2**).

**Radical-trapping experiment with TEMPO:** TEMPO (31.3 mg, 0.20 mmol, 1.0 equiv.) and Eosin Y (13.2 mg, 0.02 mmol, 10 mol%) were added to a 10 mL sealed tube with a magnetic stirring rod. The resulting mixture was sealed with septum and degassed via vacuum evacuation andsubsequent backfill with argon for three times. Then anhydrous chloroform (5.0 mL) and ethyl 2-(bromomethyl) acrylate (38.4 mg, 0.20 mmol, 1.0 equiv.) were added, and the mixture was cooled to 0 ℃ and bubbled with argon balloon for 20 min. After that, the reaction was carried out under green LED (1 m, 9 w) and irradiated at 25 ℃ for 24 h. The solvent was removed by reducing pressure on a rotary evaporator. The required product was not found, but TEMPO-$CCl_3$ was detected by GC-MS.

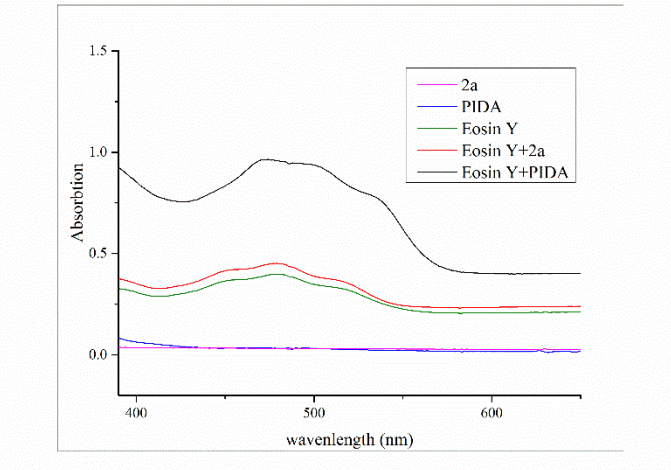


**Figure 2.** UV absorption. Test conditions: substrate **2a** (0.01 mmol/mL), PIDA (0.01 mmol/mL), Eosin Y (0.01 mmol/mL), **2a** + Eosin Y (0.005 mmol/mL), PIDA + Eosin Y (0.005 mmol/mL).

The mechanism needs further study. Considering that this is a photo-induced reaction system, We found that the UV-Vis absorption spectra of **2a** and PIDA are not obvious 380-680 nm, while Eosin Y shows strong absorption, which indicates that Eosin Y is excited by green-light absorption. In addition, after the addition of PIDA, the absorption spectrum of Eosin Y changed obviously, indicating that Eosin Y only interacted with PIDA directly, but not with substrate **2a**. Of course, it also implied a single-electron-transfer (SET) took places between Eosin Y and PIDA (**Figure 2**).

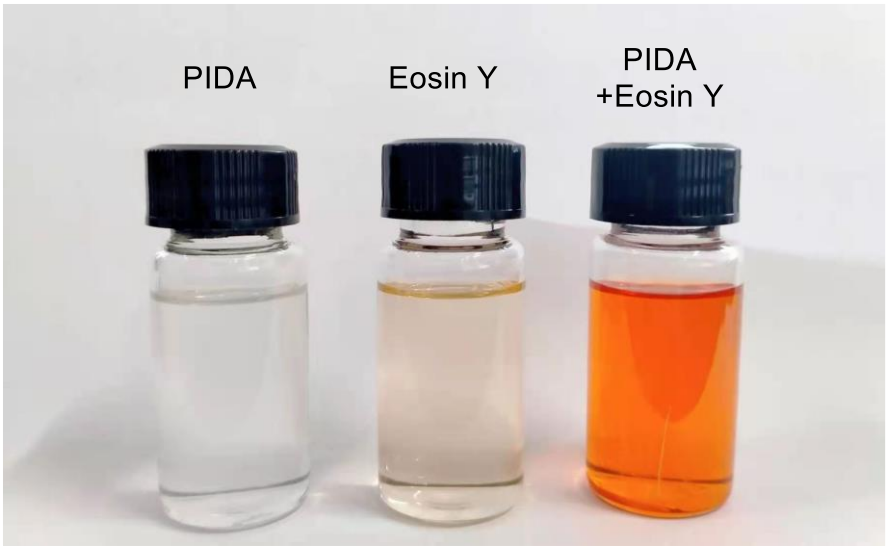



**Figure 3** Observable light absorption

PIDA (0.01 mmol/mL), Eosin Y (0.01 mmol/mL), PIDA + Eosin Y (0.005 mmol/mL) (**Figure 3**).

It can be observed that when PIDA is added to Eosin Y solution, the color of the solution is deepened.

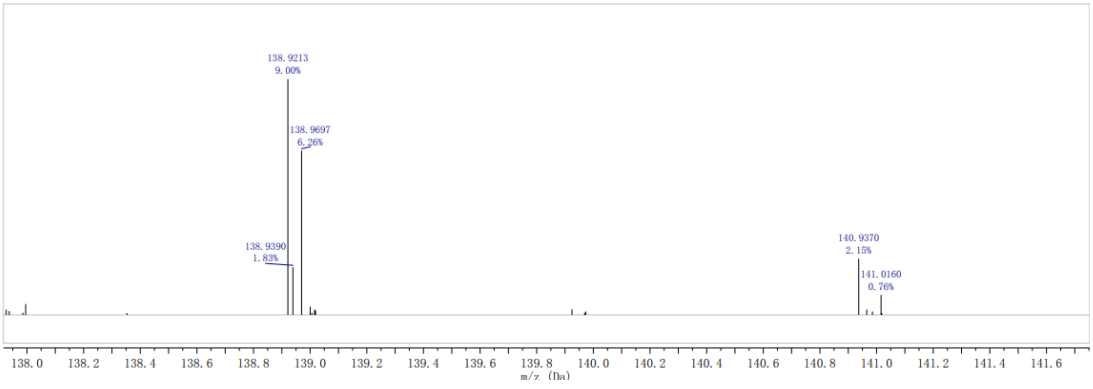



**Figure 4.** High resolution mass spectrometry of BrOAc

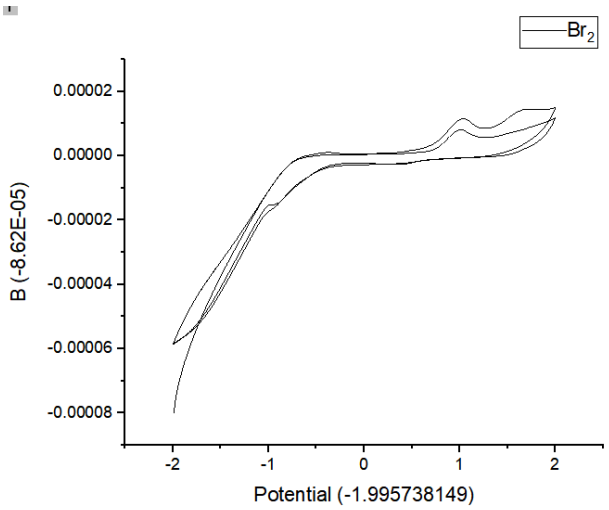



**Figure 5.** Cyclic voltammetry extraction of $HCCl_3$+$Br_2$,

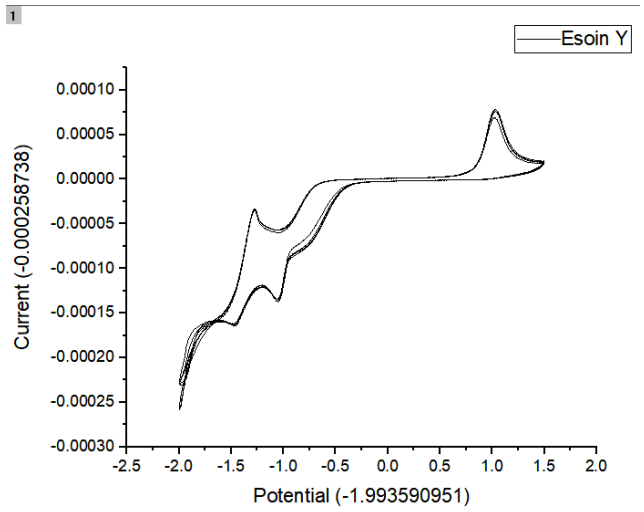



**Figure 6.** Cyclic voltammetry extraction of $HCCl_3$+Esoin Y.

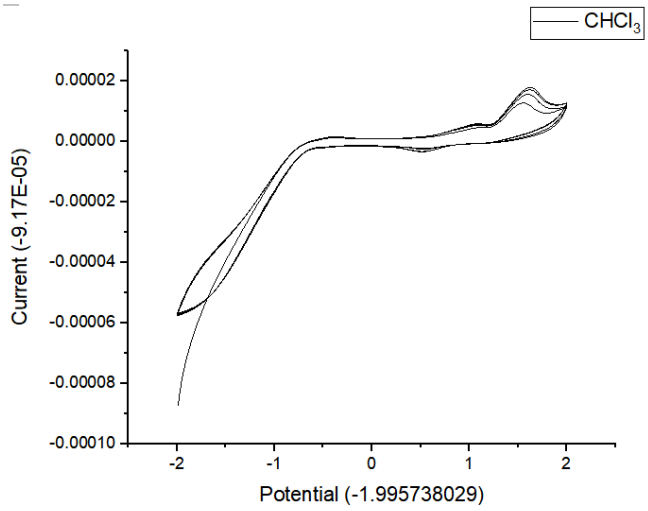


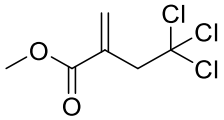

**Figure 7.** Cyclic voltammetry extraction of $HCCl_3$.

In comparison with figures 4-7, we excluded the process of bromine radical driving the whole

reaction, and further proved the process of Eosin Y activating chloroform to produce trichloromethyl radical.

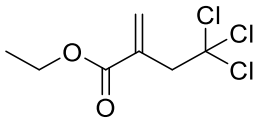
**Experimental details and characterization data for products**

**Methyl 4,4,4-trichloro-2-methylenebutanoate(2a)**



According to the general procedure. Colourless liquid (19 mg, 90%)

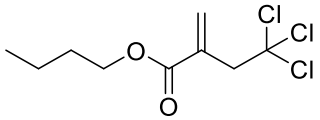
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 0.8 Hz, 1H), 5.97 (d, *J* = 1.2 Hz, 1H), 3.74 (s, 3H), 3.70 (d, *J* = 0.8 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.7, 133.5, 132.7, 129.2, 54.1, 52.4. HRMS (APCI) calcd for $C_6H_7Cl_3O_2$ $[M + H]^+$, 216.9584 found 216.9585.



**Ethyl 4,4,4-trichloro-2-methylenebutanoate(2b)**

According to the general procedure. Colourless liquid (21 mg, 92%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 1.2 Hz, 1H), 6.02 (d, *J* = 0.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.77 (d, *J* = 1.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.3, 133.8, 132.4, 61.4, 54.0, 29.7, 14.1. HRMS (APCI) calcd for $C_7H_9Cl_3O_2$ $[M + H]^+$, 230.9741 found 230.9738.

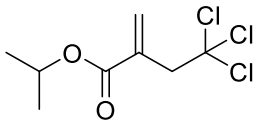


**Butyl 4,4,4-trichloro-2-methylenebutanoate(2c)**

According to the general procedure. Colourless liquid (23 mg, 90%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, *J* = 0.8 Hz, 1H), 6.02 (d, *J* = 0.8 Hz, 1H), 4.21 (t, *J* = 6.8 Hz, 2H), 3.77 (d, *J* = 0.8 Hz, 2H), 1.42 (m, 2H), 1.91 (m, 2H). 0.95 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.4, 133.8, 132.4, 97.9, 65.3, 54.1, 30.6, 19.2, 13.7.

HRMS (APCI) calcd for $C_9H_{13}Cl_3O_2$$[M + H]^+$, 259.0054 found 259.0056.

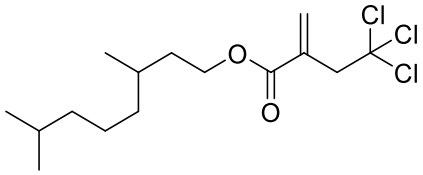


**Isopropyl 4,4,4-trichloro-2-methylenebutanoate(2d)**

According to the general procedure. Colourless liquid (18 mg, 74%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, *J* = 1.2 Hz, 1H), 5.98 (d, *J* = 1.2 Hz, 1H), 5.11 (p, *J* = 6.2 Hz, 1H), 3.76 (d, *J* = 0.8 Hz, 2H), 1.30 (d, *J* = 6.0 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8, 134.1, 132.1, 69.0, 54.1, 29.7, 21.72.

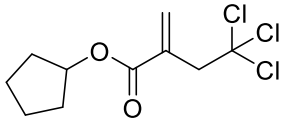
HRMS (APCI) calcd for $C_8H_{11}Cl_3O_2$ $[M + H]^+$, 244.9897 found 244.9895.



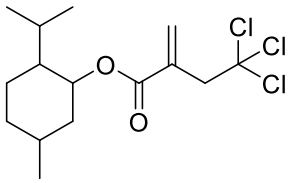
**3,7-Dimethyloctyl 4,4,4-trichloro-2-methylenebutanoate(2e)**

According to the general procedure. Colourless liquid (27 mg, 80%)

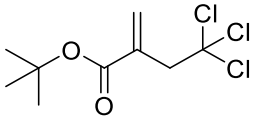
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 0.8 Hz, 1H), 6.01 (d, *J* = 0.8 Hz, 1H), 4.71 – 4.08 (m, 2H), 3.77 (d, *J* = 0.8 Hz, 2H), 1.76 – 1.68 (m, 1H), 1.54 – 1.45 (m, 2H), 1.33 – 1.23 (m, 4H), 1.15 (m, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.9, 136.1, 130.2, 63.8, 48.5, 43.1, 39.2, 37.1, 35.5, 30.0, 28.0, 24.7, 22.7, 19.6.
HRMS (APCI) calcd for $C_{15}H_{25}Cl_3O_2$ $[M + H]^+$, 343.0993 found 343.0987.



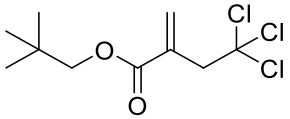

**Cyclopentyl 4,4,4-trichloro-2-methylenebutanoate(2f)**
According to the general procedure. Colourless liquid (24 mg, 87%)
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.51 (d, *J* = 1.0 Hz, 1H), 5.98 (d, *J* = 0.9 Hz, 1H), 5.46 – 5.16 (m, 1H), 3.75 (d, *J* = 0.8 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.79 – 1.71 (m, 4H), 1.61 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.0, 134.1, 132.1, 78.3, 54.1, 32.6, 23.8.
HRMS (APCI) calcd for $C_{10}H_{13}Cl_3O_2$ $[M + H]^+$, 271.0054 found 271.0056.



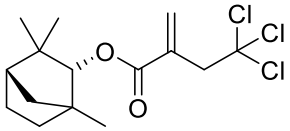

**5-Isopropyl-2-methylcyclohexyl 4,4,4-trichloro-2-methylenebutanoate(2g)**
According to the general procedure. Colourless liquid (26 mg, 75%)
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.44 (d, *J* = 0.8 Hz, 1H), 5.92 (d, *J* = 0.8 Hz, 1H), 4.93 – 4.58 (m, 1H), 4.04 – 3.56 (m, 2H), 2.00 – 1.90 (m, 1H), 1.82 (m, 1H), 1.68 – 1.56 (m, 2H), 1.41 (m, 2H), 1.06 – 0.93 (m, 2H), 0.83 (dd, *J* = 6.8, 5.6 Hz, 7H), 0.68 (d, *J* = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.9, 134.2, 131.8, 75.4, 54.1, 47.1, 40.6, 34.22, 31.4, 26.3, 23.5, 22.0, 20.7, 16.3.
HRMS (APCI) calcd for $C_{15}H_{23}Cl_3O_2$ $[M + H]^+$, 341.0836 found 341.08355.




**Tert-butyl 4,4,4-trichloro-2-methylenebutanoate(2h)**
According to the general procedure. Colourless liquid (22 mg, 85%)
$^1$H NMR (300 MHz, $CDCl_3$) δ 6.46 (d, *J* = 1.2 Hz, 1H), 5.93 (d, *J* = 1.5 Hz, 1H), 3.73 (s, 2H), 1.51 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.4, 135.1, 131.5, 81.5, 54.1, 31.0, 27.9.
HRMS (APCI) calcd for $C_9H_{13}Cl_3O_2$ $[M + H]^+$, 259.0054 found 259.0056.




**Neopentyl 4,4,4-trichloro-2-methylenebutanoate(2i)**
According to the general procedure. Colourless liquid (22 mg, 82%)
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.58 (d, *J* = 1.2 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 3.90 (s, 2H), 3.79 (d, *J* = 0.8 Hz, 2H), 0.98 (s, 9H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.3, 133.7, 132.3, 97.9, 74.7, 54.0, 31.5, 26.5.
HRMS (APCI) calcd for $C_{10}H_{15}Cl_3O_2$ $[M + H]^+$ 273.0210, found 273.0212.

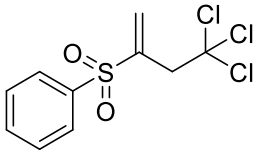


**(5S)-1,7,7-Trimethylbicyclo[3.1.1]heptan-6-yl 4,4,4-trichloro-2-methylenebutanoate (2j)**

According to the general procedure. Colourless liquid (27 mg, 81%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 1.2 Hz, 1H), 6.00 (d, *J* = 0.8 Hz, 1H), 4.77 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.76 (d, *J* = 0.8 Hz, 2H), 1.90 – 1.67 (m, 3H), 1.57 (s, 2H), 1.23 – 1.08 (m, 2H), 1.03 (s, 3H), 0.87 (d, *J* = 6.1 Hz, 6H).$^{13}$C NMR (75 MHz, $CDCl_3$) δ 165.8, 134.1, 131.8, 98.0, 82.2, 53.9, 49.0, 47.0, 45.0, 38.7, 33.7, 30.9, 27.0, 20.1, 20.0, 11.6.

HRMS (APCI) calcd for $C_{15}H_{21}Cl_3O_2$ $[M + H]^+$ 339.0680, found 339.0682.

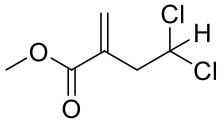


**((4,4,4-Trichlorobut-1-en-2-yl)sulfonyl)benzene(2k)**

According to the general procedure. Colourless liquid (24 mg, 81%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.59 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz,2H), 6.77 – 6.69 (t, *J* = 0.8 Hz,1H), 6.51 (d, *J* = 1.6 Hz, 1H), 3.67 (d, *J* = 0.8 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.0, 138.2, 134.0, 129.4, 129.1, 128.5, 51.6, 29.7.

HRMS (APCI) calcd for $C_{10}H_9Cl_3O_2S$ $[M + H]^+$ 298.9462, found 298.9465



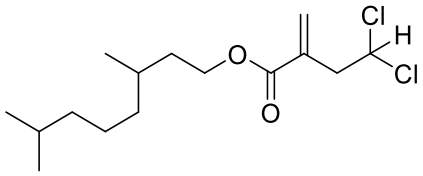
**Methyl 4,4-dichloro-2-methylenebutanoate(3a)**

According to the general procedure. Colourless liquid (11 mg, 64%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, *J* = 1.2 Hz, 1H), 5.98 (t, *J* = 6.8 Hz, 1H), 5.81 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 3.17 (dd, *J* = 6.8, 1.2 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.4, 134.3, 130.8, 71.0, 52.2, 46.7.

HRMS (APCI) calcd for $C_6H_8Cl_2O_2$ $[M + H]^+$ 182.9974, found 182.9970

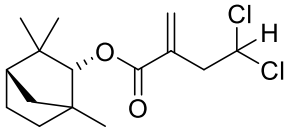
**3,7-Dimethyloctyl 4,4-dichloro-2-methylenebutanoate(3b)**



According to the general procedure. Colourless liquid (17 mg, 55%)

$^1$H NMR (300 MHz, $CDCl_3$) δ 6.42 (d, *J* = 2.4 Hz, 1H), δ 6.30 (d, *J* = 7.2 Hz, 1H), δ 5.83 (d, *J* = 2.1 Hz, 1H), 4.26 – 4.25 (m, 2H), 3.20 - 3.23 (dd, *J* = 6.9, 2.7 Hz, 2H), 1.76 (m, 1H), 1.57 (s, 2H), 1.38 – 1.27 (m, 4H), 1.21 (m, 3H), 0.96 (d, *J* = 2.4 Hz, 3H), 0.90 (d, *J* = 2.4 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.0, 134.6, 130.5, 71.1, 63.8, 46.8, 39.2, 37.1, 35.4, 29.9, 27.9, 24.6, 22.6, 19.5.

HRMS (APCI) calcd for $C_{15}H_{26}Cl_2O_2$ $[M + H]^+$ 309.1383, found 309.1387

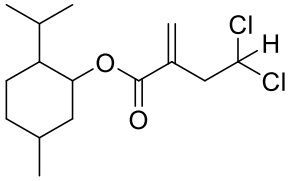


**(5S)-1,7,7-Trimethylbicyclo[3.1.1]heptan-6-yl 4,4-dichloro-2-methylenebutanoate(3c)**

According to the general procedure. Colourless liquid (18 mg, 59%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, *J* = 6.0 Hz, 1H), 5.98 (t, *J* = 6.6 Hz, 1H), 5.77 (q, *J* = 1.2 Hz, 1H), 4.77 – 4.63 (m, 1H), 3.16 (dd, *J* = 6.8, 1.2 Hz, 2H), 1.85 – 1.72 (m, 3H), 1.61 – 1.53 (m, 2H), 1.17 – 1.08 (m, 2H), 1.01 (s, 3H), 0.86 (d, *J* = 1.6 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.5, 134.9, 130.2, 82.0, 71.1, 49.0, 47.0, 46.8, 45.0, 38.8, 33.7, 30.9, 27.0, 20.1, 19.9, 11.6.

HRMS (APCI) calcd for $C_{15}H_{22}Cl_2O_2$ $[M + H]^+$ 305.1070, found 305.1072

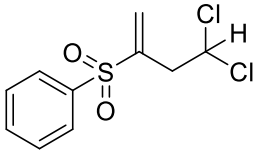


**5-Isopropyl-2-methylcyclohexyl 4,4-dichloro-2-methylenebutanoate(3d)**

According to the general procedure. Colourless liquid (18 mg, 62%)

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.35 (d, *J* = 1.2 Hz, 1H), 5.99 (t, *J* = 6.8 Hz, 1H), 5.77 (d, *J* = 1.2 Hz, 1H), 4.76 (td, *J* = 11.0, 4.5 Hz, 1H), 3.17 (dd, *J* = 5.5, 1.2 Hz, 2H), 2.10 – 1.96 (m, 1H), 1.84 (td, *J* = 7.0, 2.5 Hz, 1H), 1.70 (dt, *J* = 12.5, 3.0 Hz, 2H), 1.47 – 1.43 (m, 2H), 1.10 – 1.01 (m, 2H), 0.92-0.91 (dd, *J* = 9.0, 6.5 Hz, 7H), 0.77 (d, *J* = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.5, 135.0, 130.0, 75.2, 71.2, 47.2, 46.4, 40.8, 34.2, 31.4, 26.5, 23.5, 22.0, 20.7, 16.4.

HRMS (APCI) calcd for $C_{15}H_{24}Cl_2O_2$ $[M + H]^+$ 307.1226, found 307.1222



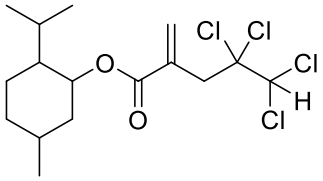
**((4,4-Dichlorobut-1-en-2-yl)sulfonyl)benzene(3e)**

According to the general procedure. Colourless liquid (29 mg, 73%)

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 2H), 7.67 – 7.62 (m, 1H), 7.57-7.60 (dd, *J* = 8.5, 7.0 Hz, 2H), 6.54-6.53 (d, *J* = 1.0 Hz, 1H), 6.03 (d, *J* = 1.0 Hz, 1H), 5.92-5.94 (t, *J* = 6.5 Hz, 1H), 3.10 (dd, *J* = 6.5, 1.0 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.4, 138.0, 134.1, 129.6, 129.5, 128.3, 69.7, 44.2.

HRMS (APCI) calcd for $C_{10}H_{10}Cl_2O_2S$ $[M + H]^+$ 264.9851, found 264.9854

**5-Isopropyl-2-methylcyclohexyl 4,4,6,6-tetrachloro-2-methylenehexanoate(3f)**



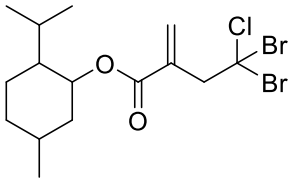
According to the general procedure. Colourless liquid (27 mg, 66%).

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.46 (d, *J* = 1.0 Hz, 1H), 6.00 (s, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 4.78 (td, *J* = 11.0, 4.5 Hz, 1H), 3.58 – 3.37 (m, 2H), 2.06 – 1.97 (m, 1H), 1.91 (td, *J* = 7.0, 2.5 Hz, 1H), 1.70

(dt, *J* = 12.5, 2.5 Hz, 2H), 1.48 – 1.43 (m, 2H), 1.15 – 0.97 (m, 2H), 0.90 (t, *J* = 6.8 Hz, 7H), 0.75 (d, *J* = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.2, 134.3, 130.8, 92.5, 78.2, 75.4, 47.1, 40.6, 34.2, 31.4, 26.3, 23.4, 22.0, 20.7, 16.3.

HRMS (APCI) calcd for $C_{16}H_{25}Cl_4O_2$ $[M + H]^+$ 389.0603, found 389.0605

**5-Isopropyl-2-methylcyclohexyl 4,4-dibromo-4-chloro-2-methylenebutanoate(3g)**

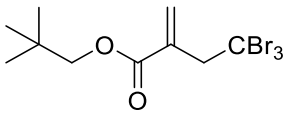



According to the general procedure. Colourless liquid (29 mg, 68%)

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.52 (d, *J* = 1.0 Hz, 1H), 6.02 (d, *J* = 1.0 Hz, 1H), 4.80 (td, *J* = 11.0, 4.5 Hz, 1H), 4.25 – 3.62 (m, 2H), 2.02 (dtd, *J* = 12.0, 4.0, 1.5 Hz, 1H), 1.90 (m, 1H), 1.74 – 1.65 (m, 2H), 1.53 – 1.47 (m, 2H), 1.16 – 1.02 (m, 2H), 0.90 (t, *J* = 6.5 Hz, 7H), 0.75 (d, *J* = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.9, 134.8, 131.7, 75.4, 55.5, 47.1, 40.6, 34.2, 31.4, 26.3, 23.4, 22.0, 20.7, 16.3.

HRMS (APCI) calcd for $C_{15}H_{23}Br_2ClO_2$ $[M + H]^+$ 428.9826, found 428.9822

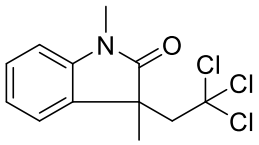
**Neopentyl 4,4,4-tribromo-2-methylenebutanoate(3h)**




According to the general procedure. Colourless liquid (21 mg, 53%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.62 (d, *J* = 0.8 Hz, 1H), 6.13 (d, *J* = 1.2 Hz, 1H), 4.15 (d, *J* = 0.8 Hz, 2H), 3.91 (s, 2H), 0.99 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.4, 135.9, 131.8, 74.8, 57.9, 39.2, 31.6, 26.6.

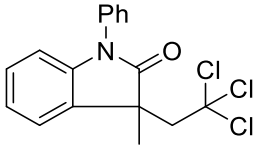
HRMS (APCI) calcd for $C_{10}H_{15}Br_3O_2$ $[M + H]^+$ 404.8695, found 404.8691.




**1,3-Dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one(4b)**

According to the general procedure. White solid (20 mg, 69%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.16 (m, 2H), 7.16 – 6.94 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.70 (d, *J* = 15.3 Hz, 1H), 3.34 (d, *J* = 15.3 Hz, 1H), 3.24 (s, 3H), 1.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.5, 143.2, 129.5, 128.5, 125.6, 122.0, 108.4, 96.1, 59.8, 47.9, 26.8, 26.5. HRMS (ESI) calcd for $C_{12}H_{13}Cl_3NO$ $[M + H]^+$: 292.0057, found: 292.0057.

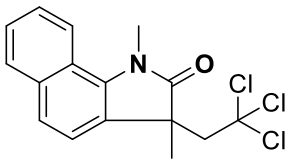



**3-Methyl-1-phenyl-3-(2,2,2-trichloroethyl)indolin-2-one(4c)**

According to the general procedure. White solid (27 mg, 76%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 4H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 6.0 Hz, 1H), 6.91 – 6.81 (m, 1H), 3.79 (d, *J* = 15.3 Hz, 1H), 3.42 (d, *J* = 15.7 Hz, 1H),

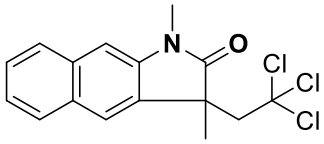
1.52 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 177.9, 143.2, 134.5, 129.6, 129.3, 128.4, 128.1, 126.2, 125.9, 122.4, 109.8, 96.2, 60.1, 48.1, 27.4. HRMS (ESI) calcd for $C_{17}H_{15}Cl_3NO$ $[M + H]^+$: 354.0214, found: 354.0214.



**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-1,3-dihydro-2H-benzo[g]indol-2-one(4d)**

According to the general procedure. White solid (28 mg, 82%)

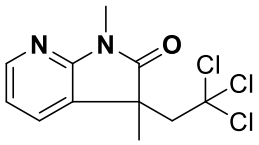
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.57 – 7.46 (m, 3H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.01 – 6.89 (m, 1H), 4.11 (d, *J* = 15.1 Hz, 1H), 3.53 (s, 3H), 3.34 (d, *J* = 15.0 Hz, 1H), 1.85 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 171.5, 136.3, 133.8, 133.4, 126.9, 126.4, 126.4, 125.0, 122.8, 120.0, 108.6, 96.7, 65.1, 46.9, 33.6, 30.0. HRMS (ESI) calcd for $C_{16}H_{14}Cl_3NNaO$ $[M + Na]^+$: 364.0033, found: 364.0032.



**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-1,3-dihydro-2H-benzo[f]indol-2-one(4e)**

According to the general procedure. White solid (27 mg, 79%)

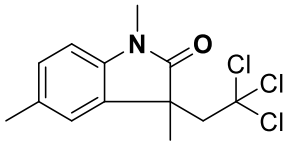
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 16.8, 8.4 Hz, 3H), 7.59 – 7.49 (m, 1H), 7.40 – 7.29 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 4.00 – 3.66 (m, 2H), 3.35 (s, 3H), 1.62 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 179.7, 140.9, 130.875, 130.3, 130.1, 129.6, 126.9, 123.5, 123.2, 121.6, 109.7, 96.0, 60.2, 49.2, 26.8, 25.6. HRMS (ESI) calcd for $C_{16}H_{15}Cl_3NO$ $[M + H]^+$: 342.0214, found: 342.0212.



**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-1,3-dihydro-2H-pyrrolo[2,3-b]pyridin-2-one(4f)**

According to the general procedure. White solid (22 mg, 75%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.07 (m, 1H), 7.68 – 7.48 (m, 1H), 6.96 (dd, *J* = 7.3, 5.2 Hz, 1H), 3.79 – 3.33 (m, 2H), 3.30 (s, 3H), 1.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.3, 156.5, 147.5, 133.2, 124.0, 117.6, 95.8, 59.4, 47.58, 26.4, 25.7. HRMS (ESI) calcd for $C_{11}H_{12}Cl_3N_2O$ $[M + H]^+$: 294.5795, found: 294.5792.

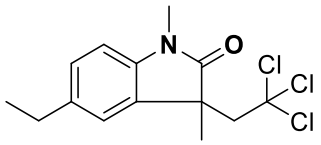


**1,3,5-Trimethyl-3-(2,2,2-trichloroethyl)indolin-2-one(4g)**

According to the general procedure. White solid (24 mg, 78%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 3.49 (dd, *J* = 146.6, 15.3 Hz, 2H), 3.21 (s, 3H), 2.33 (s, 3H), 1.37 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.5, 140.9, 131.4, 129.6, 128.7, 126.4, 108.1, 96.2, 59.8, 48.0, 26.9, 26.6, 21.1. HRMS (ESI) calcd

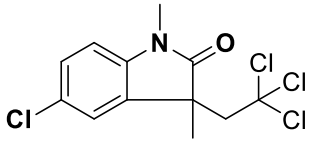
for $C_{13}H_{15}Cl_3NO$ $[M + H]^+$: 306.0214, found: 306.0216.



**5-Ethyl-1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one(4h)**

According to the general procedure. White solid (23 mg, 72%)

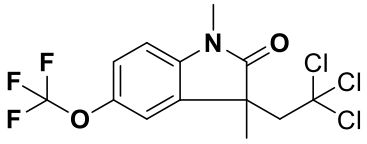
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.16 – 7.06 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 3.50 (dd, *J* = 143.7, 15.3 Hz, 2H), 3.21 (s, 3H), 2.62 (qd, *J* = 7.6, 1.9 Hz, 2H), 1.38 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.6, 141.1, 138.1, 129.4, 127.6, 125.3, 108.1, 96.2, 59.8, 48.0, 28.6, 26.8, 26.6, 16.1. HRMS (ESI) calcd for $C_{14}H_{17}Cl_3NO$ $[M + H]^+$: 320.0370, found: 320.0368.



**5-Chloro-1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one(4i)**

According to the general procedure. White solid (28 mg, 86%)

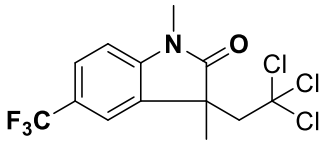
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.2 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.51 (dd, *J* = 147.3, 15.3 Hz, 2H), 3.23 (s, 3H), 1.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.0, 141.8, 131.3, 128.4, 127.4, 126.0, 109.3, 95.8, 59.7, 48.1, 26.7, 26.7. HRMS (ESI) calcd for $C_{12}H_{12}Cl_4NO$ $[M + H]^+$: 325.9668, found: 325.9667.



**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-5-(trifluoromethoxy)indolin-2-one(4j)**

According to the general procedure. White solid (19 mg, 51%)

1H-NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 6.66 (d, J = 8.1 Hz, 1H), 3.67 (m, 2H), 3.20 (s, 3H), 1.38 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.32, 144.25 (d, *J* = 2.2 Hz), 141.9, 130.9, 121.8, 119.8, 108.8, 95.8, 59.7, 48.2, 26.7, 26.6. $^{19}$F NMR (150 MHz, $CDCl_3$) δ -58.83. HRMS (ESI). calcd for $C_{13}H_{12}Cl_3F_3NO_2$ $[M + H]^+$: 375.9886, found: 375.9880.

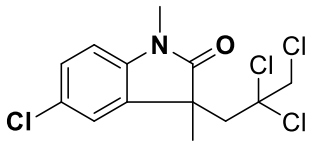


**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-5-(trifluoromethyl)indolin-2-one(4k)**

According to the general procedure. Yellow solid (30 mg, 84%)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.72 (d, J = 15.4 Hz, 1H), 3.37 (d, J = 15.4 Hz, 1H),, 3.27 (s, 3H), 1.42 (s, 3H).

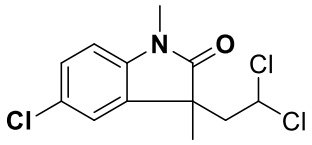
$^{13}$C-NMR (150 MHz, $CDCl_3$) δ 178.6, 146.7, 130.1, 126.2 (d, J = 4.0 Hz), 124.6 (q, J = 32.8 Hz), 124.2 (q, J = 271.8 Hz), 122.9 (d, J = 3.6 Hz), 108.2, 95.7, 59.7, 47.9, 26.8, 26.6. $^{19}$F NMR (150 MHz, $CDCl_3$) δ -61.87. HRMS (ESI) calcd for $C_{13}H_{12}Cl_3F_3NO$ $[M + H]^+$: 359.9937, found: 359.9940.



**5-Chloro-1,3-dimethyl-3-(2,2,3-trichloropropyl)indolin-2-one(4l)**

According to the general procedure. White solid (18 mg, 53%)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.1 Hz, 1H), 7.33 – 7.28 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.82 (d, *J* = 12.1 Hz, 1H), 3.52 (d, *J* = 12.0 Hz, 1H), 3.21 (s, 3H), 3.01 (d, *J* = 15.4 Hz, 2H), 1.37 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.7, 141.8, 132.1, 128.6, 127.6, 125.0, 109.3, 87.4, 54.8, 49.1, 47.4, 27.0, 26.7. HRMS (ESI) calcd for $C_{13}H_{14}Cl_4NO$ $[M + H]^+$: 339.9824, found: 339.9824.



**5-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one(4m)**

According to the general procedure. White solid (14 mg, 48%)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.44 (dd, *J* = 8.8, 4.6 Hz, 1H), 3.19 (s, 3H), 3.11 – 2.57 (m, 2H), 1.40 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 178.4, 142.0, 132.9, 128.6, 128.1, 123.2, 109.5, 69.3, 49.9, 47.4, 26.6, 25.4. HRMS (ESI) calcd for $C_{12}H_{13}Cl_3NO$ $[M + H]^+$: 292.0057, found: 292.0057.

Reference

[1] a) Q. Xiao, Q. J. He, J. C. Li, J. Wang, *Org. Lett*. **2015**, *17*, 6090-6093. b) X. X. Qi, F. Yu, P. H. Chen, G. S. Liu, *Chinese J. Catal.* **2017**, *56*, 12692-12696; c) A. Fürstner, O. R. Thiel, L. Ackermann, H. J. Schanz, S. P. Nolan, *J. Org. Chem*. **2000**, *65*, 2204-2207; d) D. L. Musso, G. F. Orr, F, R. Cochran. J. L. Kelley, J. L. Selph, G. C. Rigdon, B. R. Cooper, M. L. Jones, *J. Med. Chem*. **2003**, *46*, 409-416.

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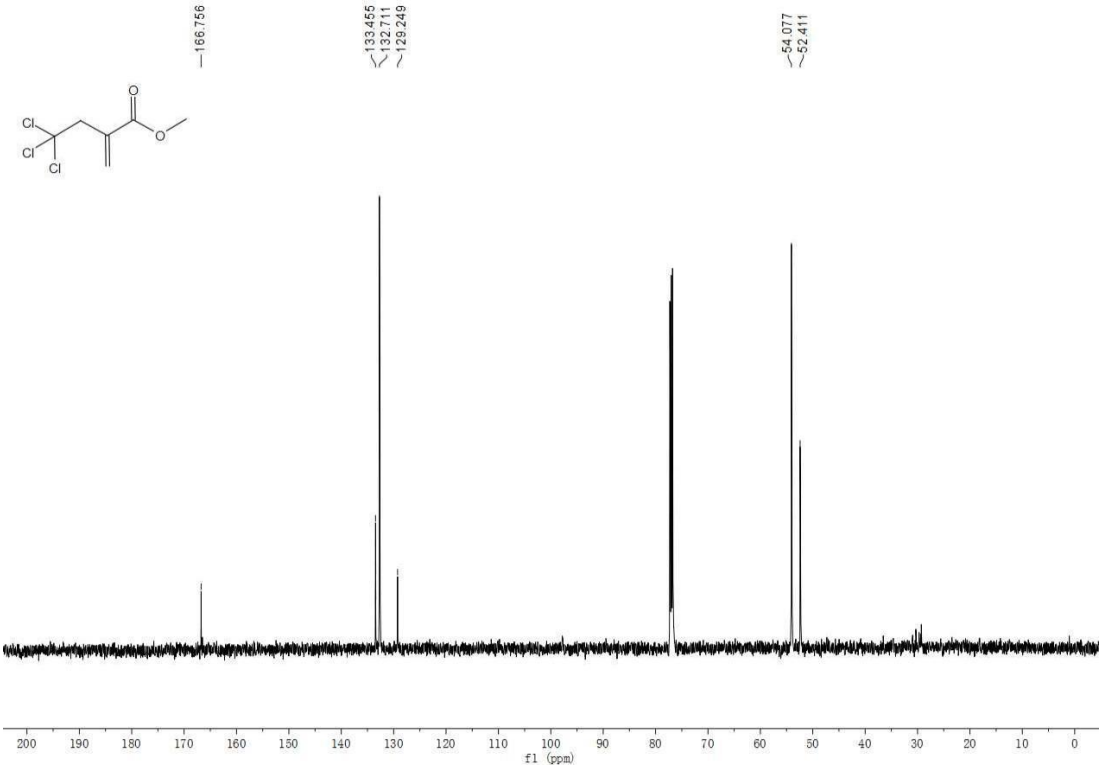
[5] a) J. Jia, M. G. Steinmetz, R. Shukla, R. Rathore, *J. Org. Chem*. **2008**, *73*, 8867-8879; b) T. Nishio, H. Asai, T. Miyazaki, *Hel. Chim. Act*., **2005** , *88*, 35-41; c) T. Wu, X. Mu, G. Liu, *Angew. Chem., Int. Ed*. **2011**, *50*, 12578-12581; *Angew. Chem*. **2011**, *123*, 12786-12789. C. W. Chan, P. Y. Lee, Z. Y. Zhou, W. Y. Yu, *Tetrahedron Letters*, **2015**, *56*, 2559-2563.

$^{1}H$, $^{13}C$ NMR Spectra of Products

## Methyl 4,4,4-trichloro-2-methylenebutanoate

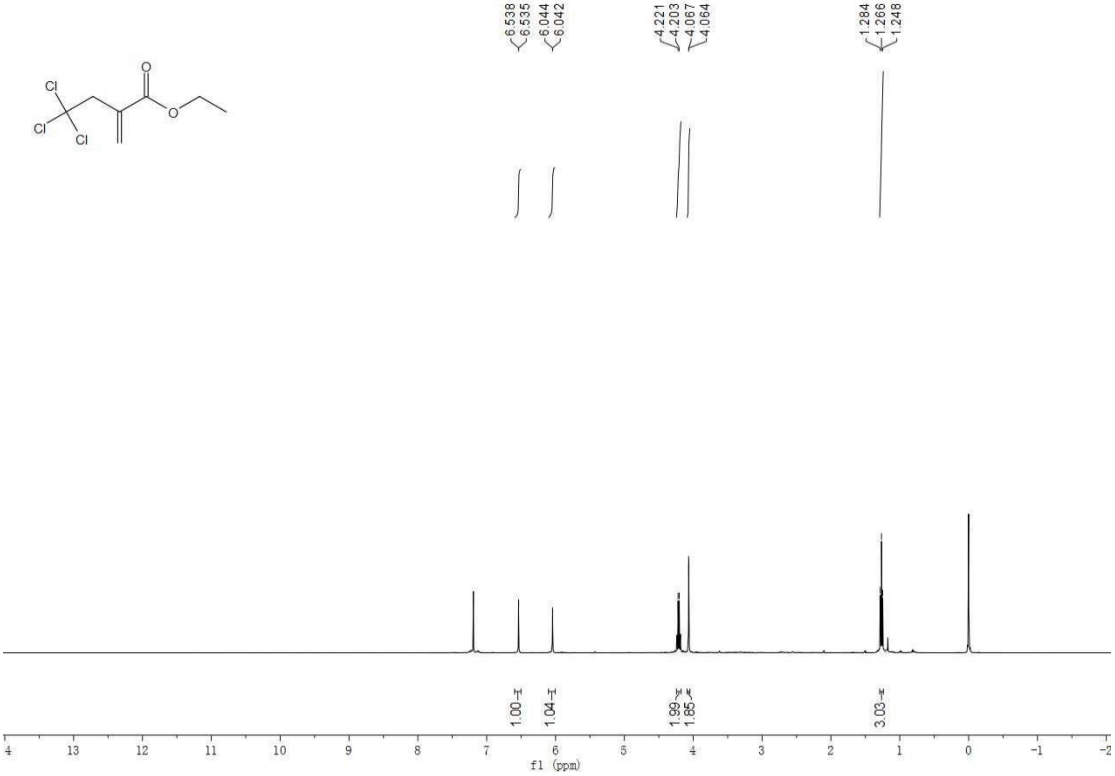
### Compound 2a $CDCl_3$ 500 MHz


### Compound 2a $CDCl_3$ 126 MHz

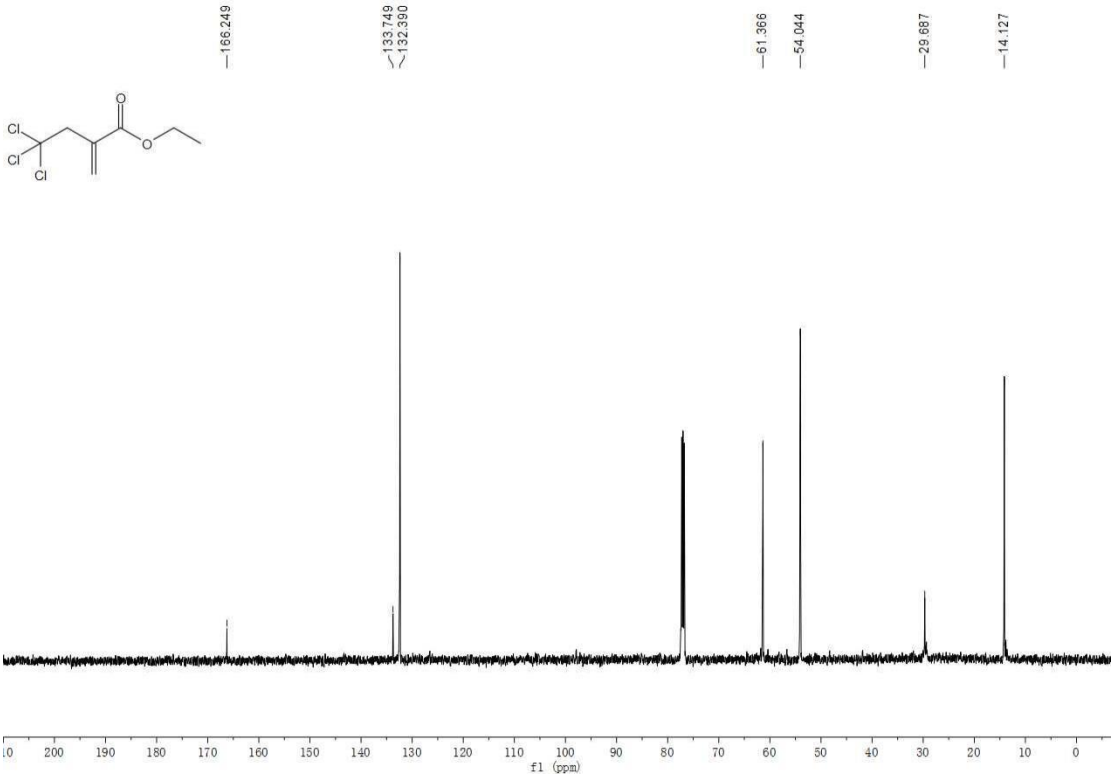


**Ethyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2b $CDCl_3$ 500 MHz**

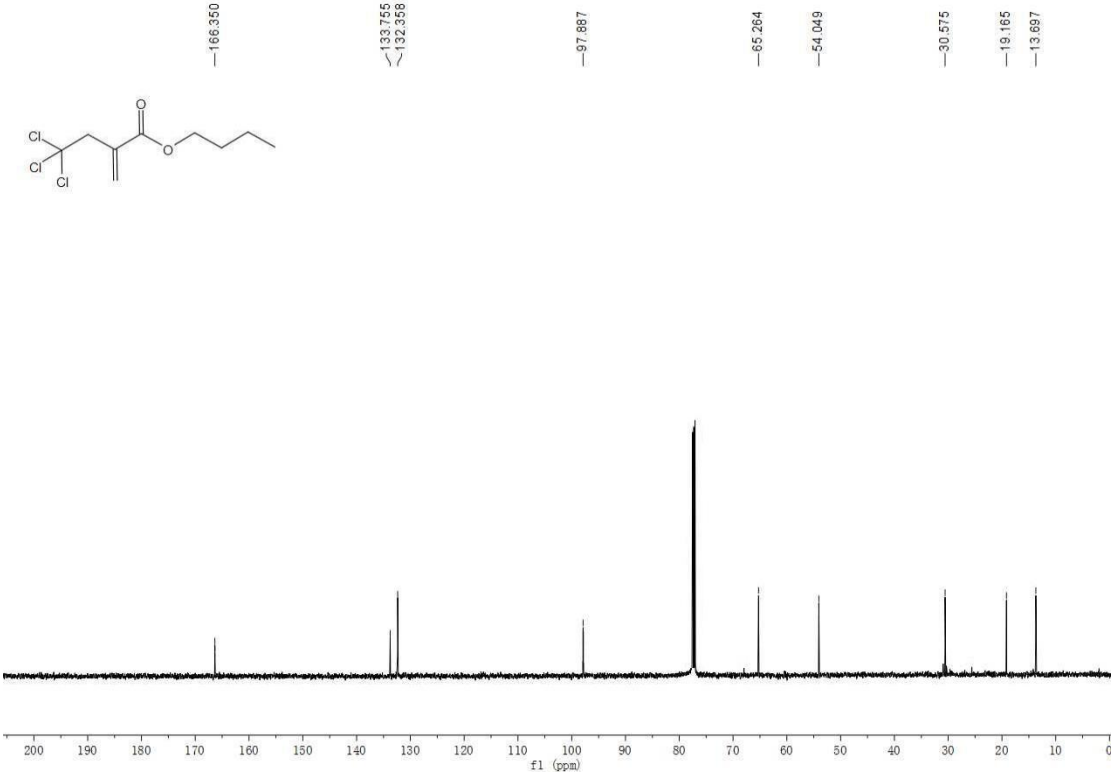



**Compound 2b $CDCl_3$ 126 MHz**

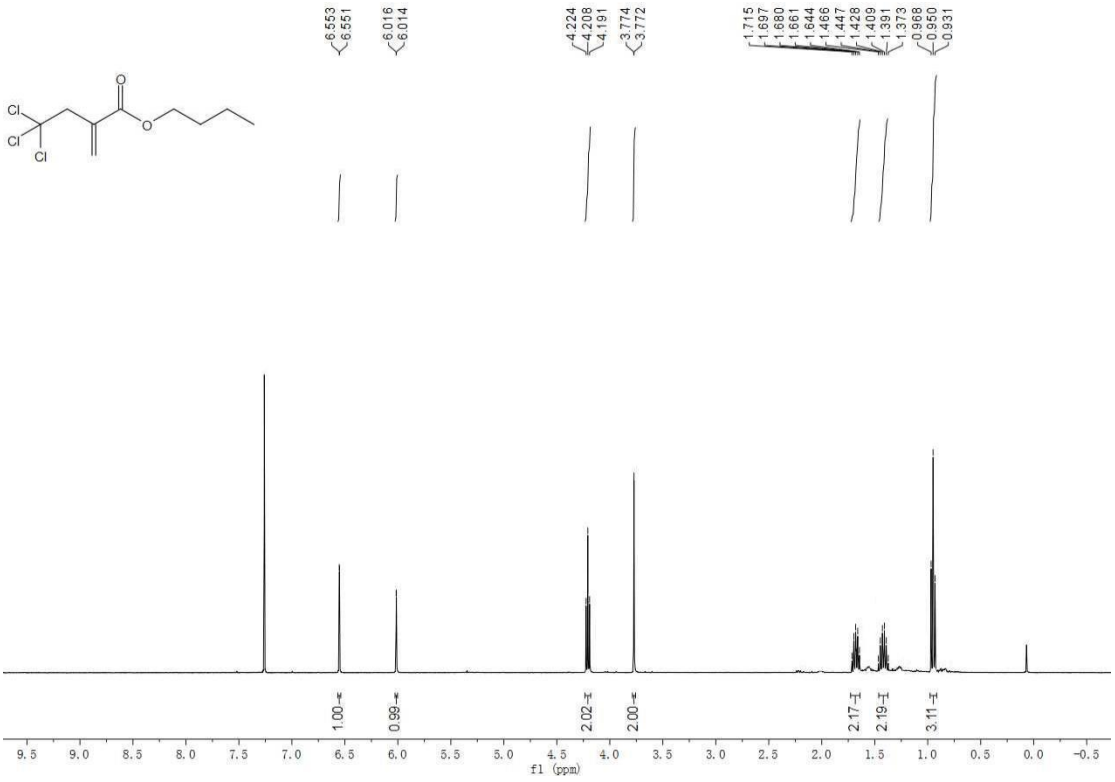


**Butyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2c $CDCl_3$ 500 MHz**

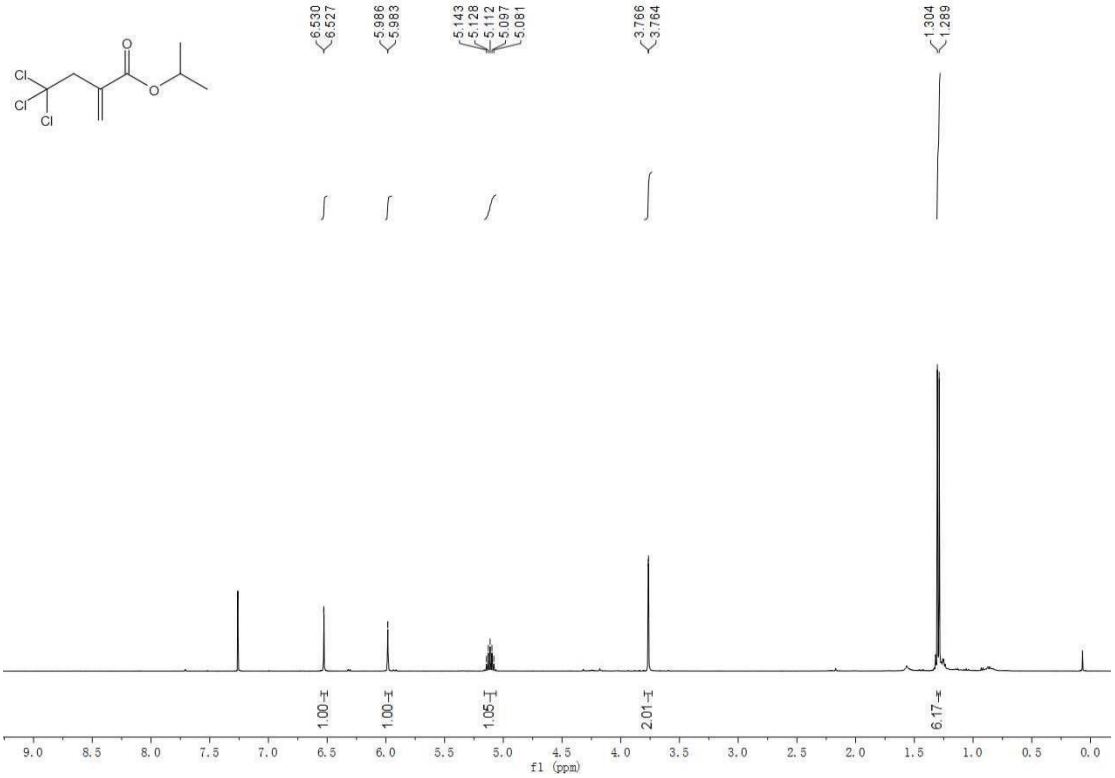



**Compound 2c $CDCl_3$ 75 MHz**

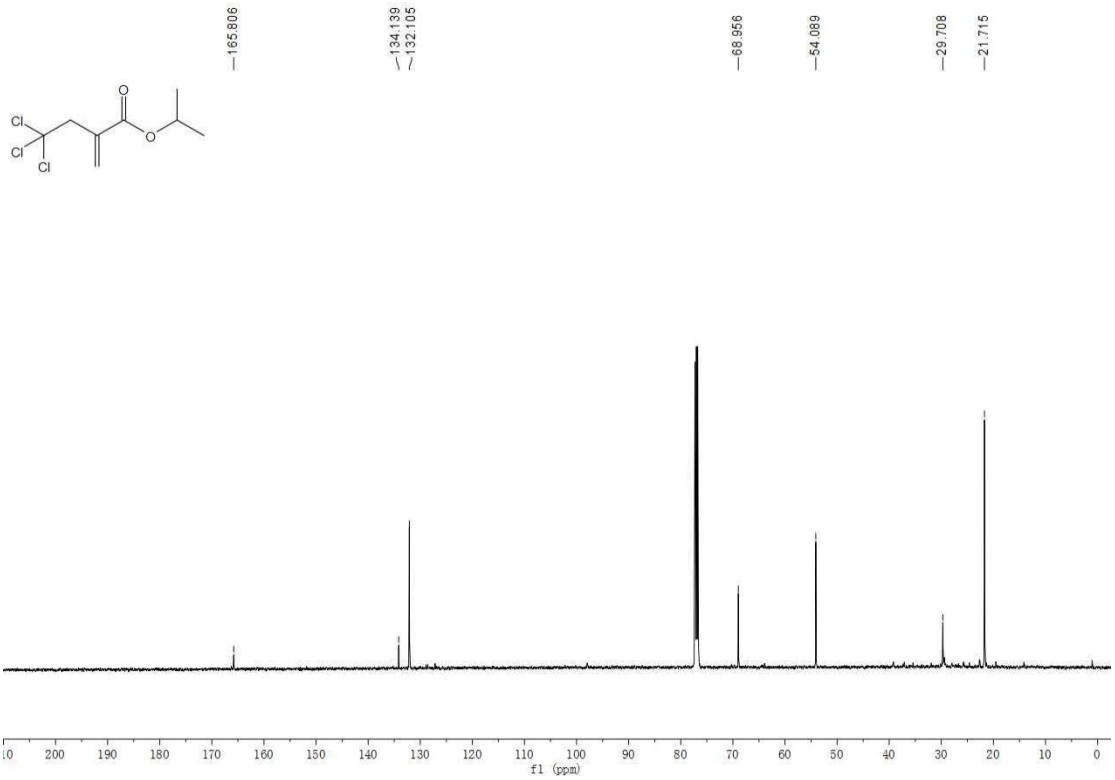


**Isopropyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2d $CDCl_3$ 500 MHz**

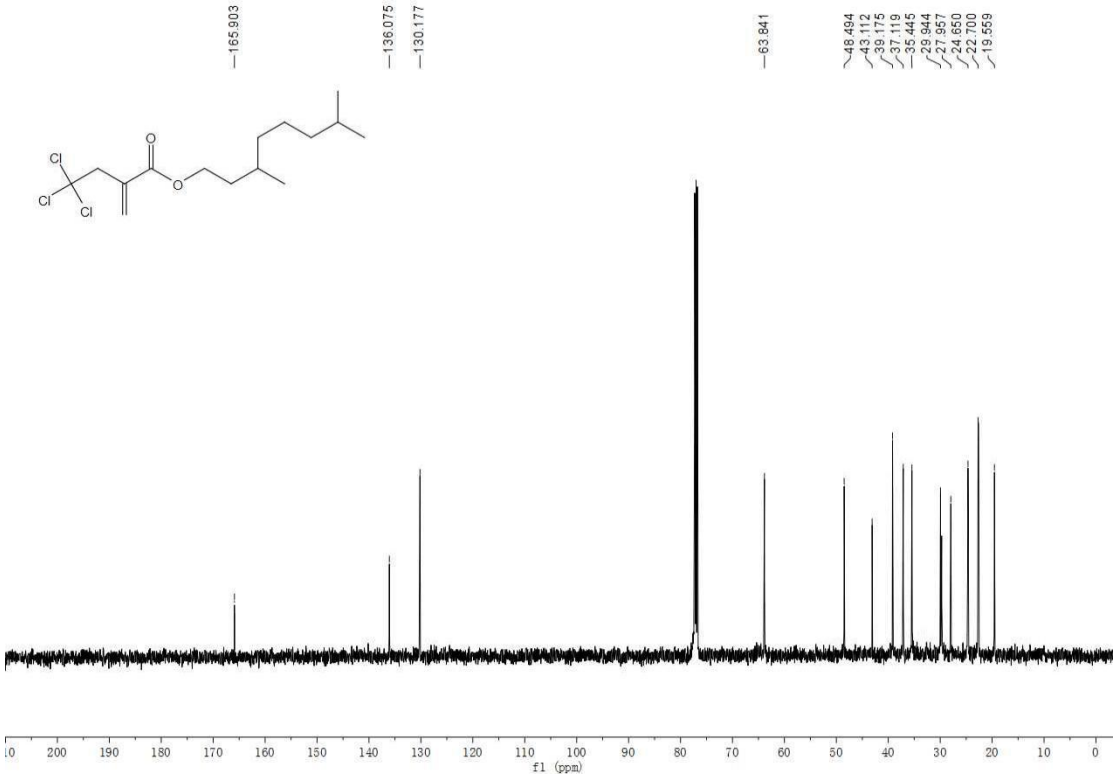



**Compound 2d $CDCl_3$ 126 MHz**

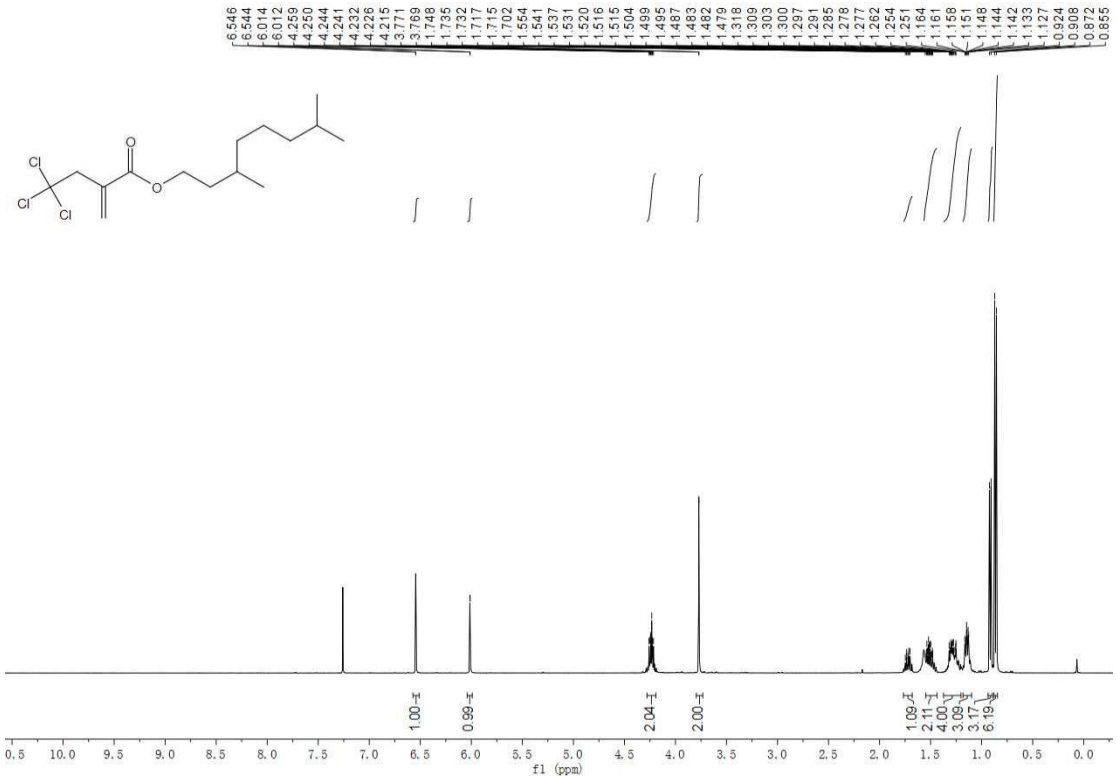


**3,7-Dimethyloctyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2e $CDCl_3$ 500 MHz**

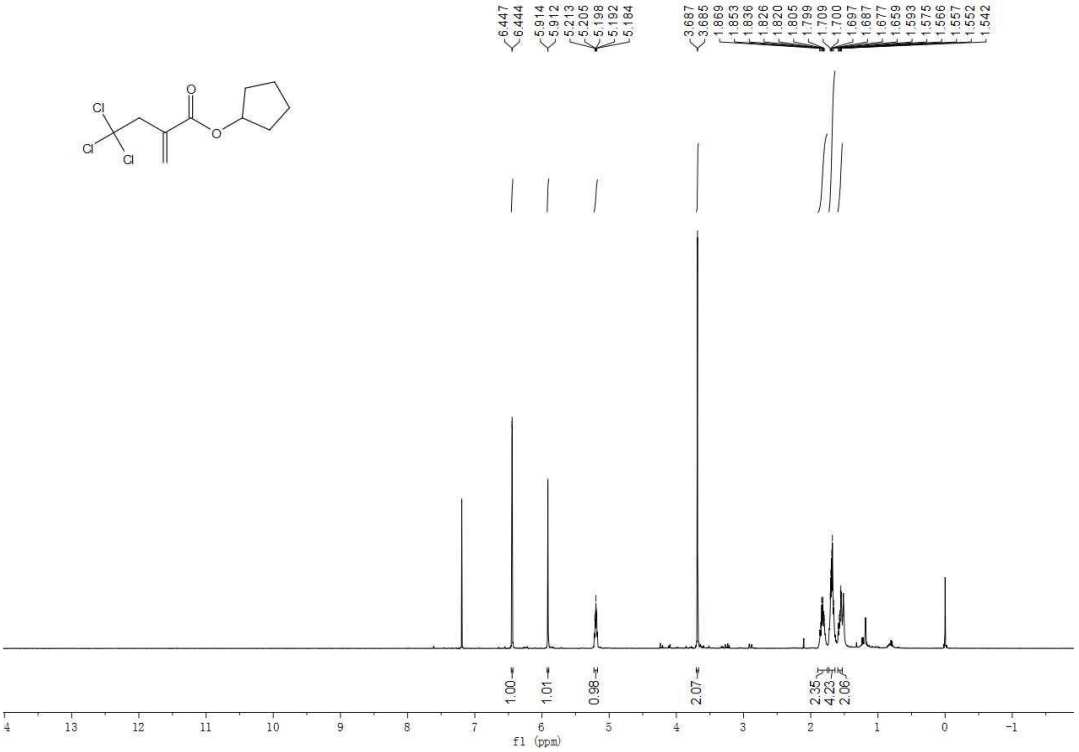



**Compound 2e $CDCl_3$ 126 MHz**

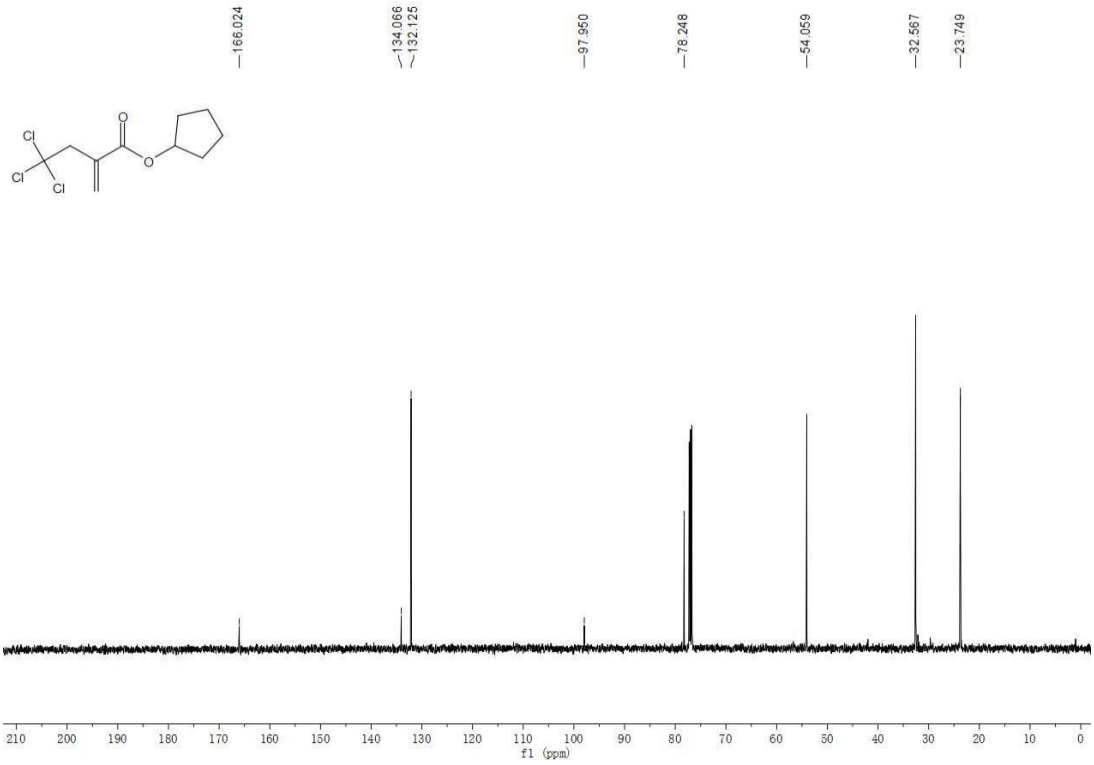


**Cyclopentyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2f $CDCl_3$ 500 MHz**

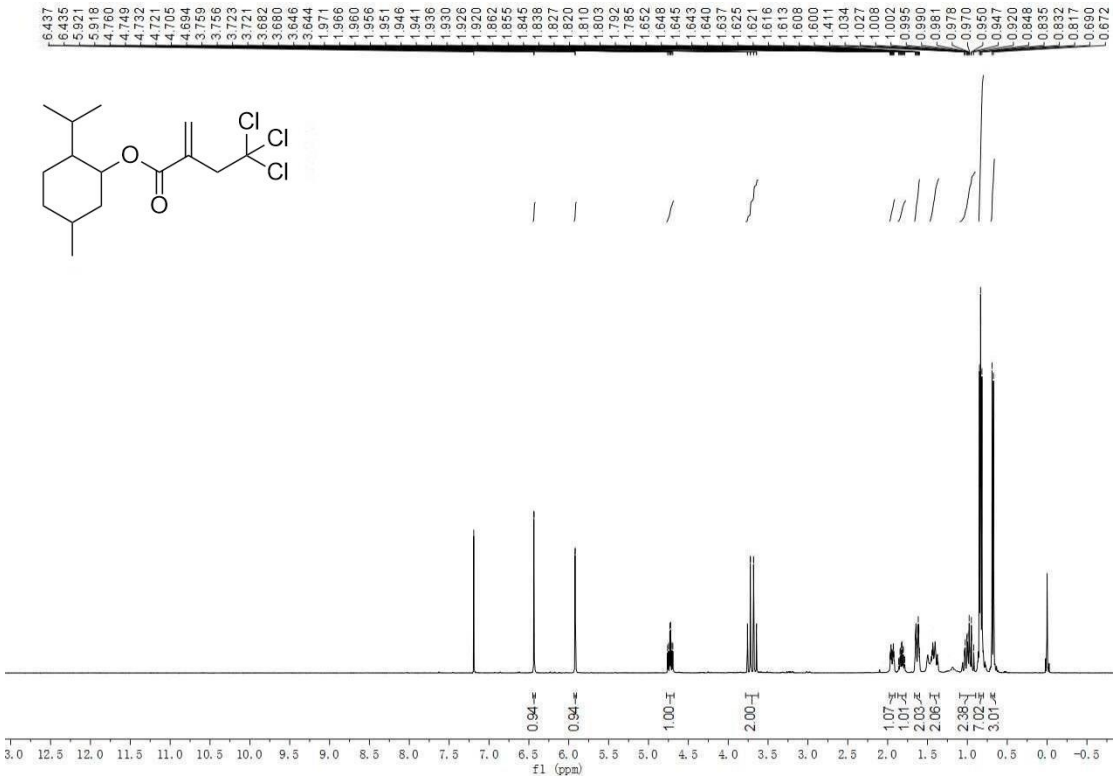



**Compound 2f $CDCl_3$ 126 MHz**

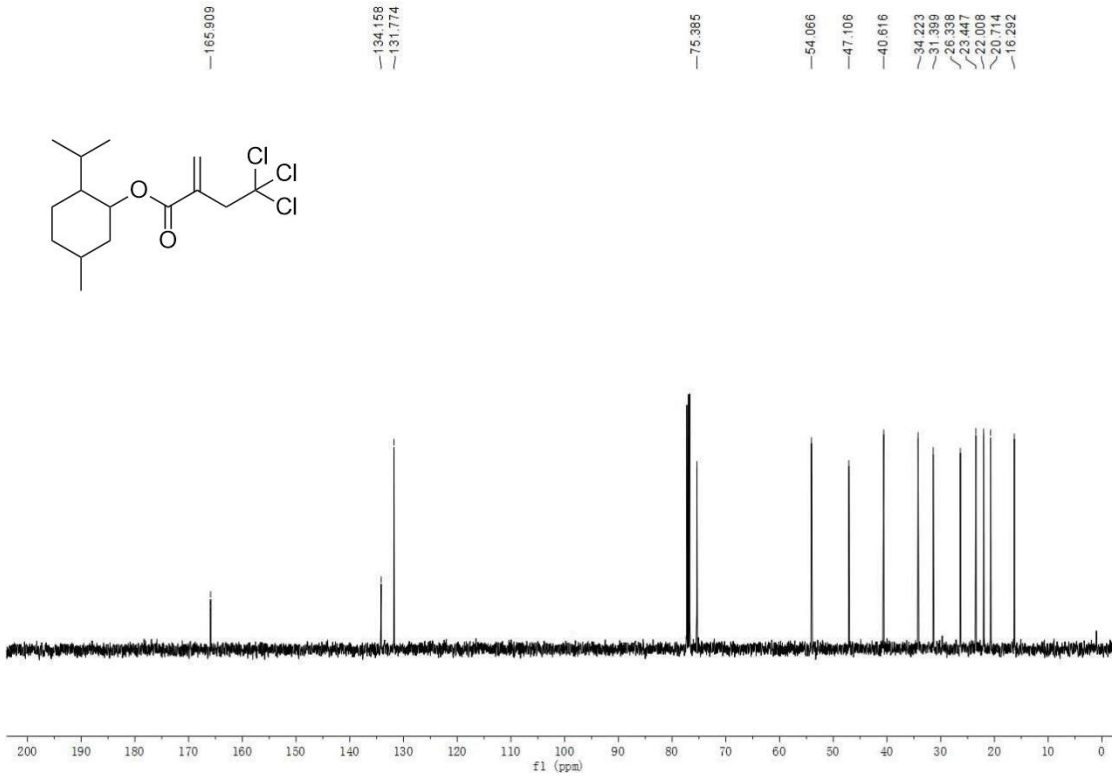


## 5-Isopropyl-2-methylcyclohexyl 4,4,4-trichloro-2-methylenebutanoate

## Compound 2g $CDCl_3$ 500 MHz

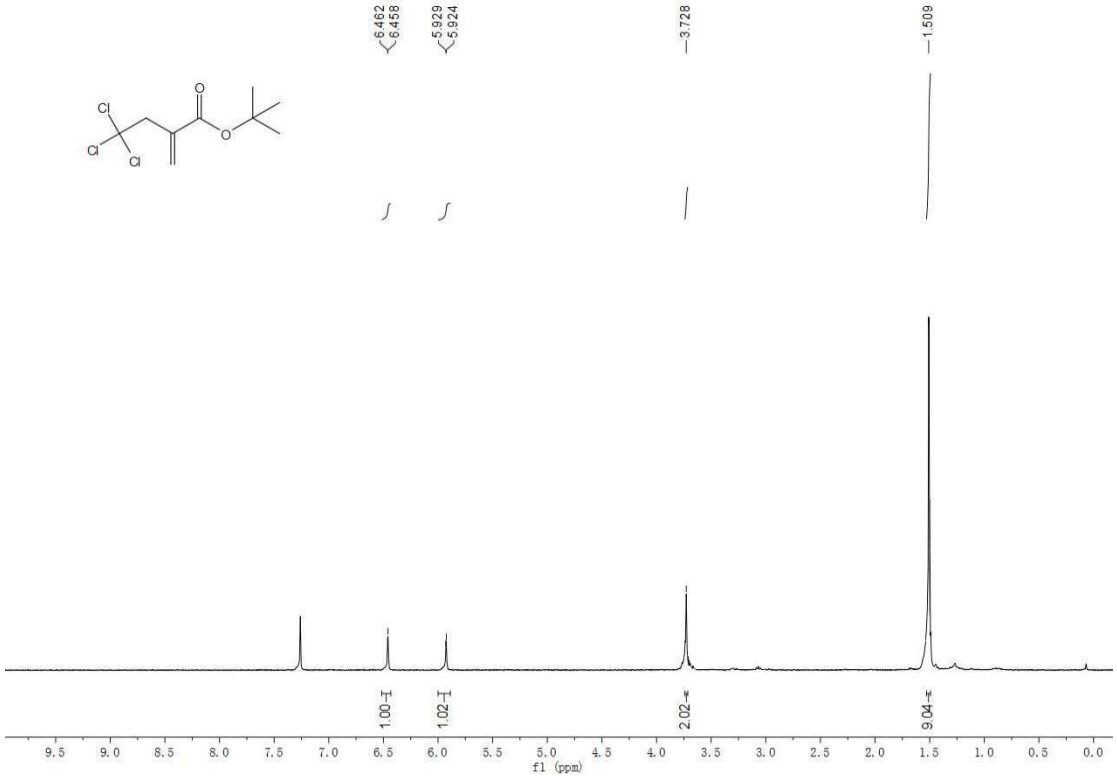



## Compound 2g $CDCl_3$ 126 MHz

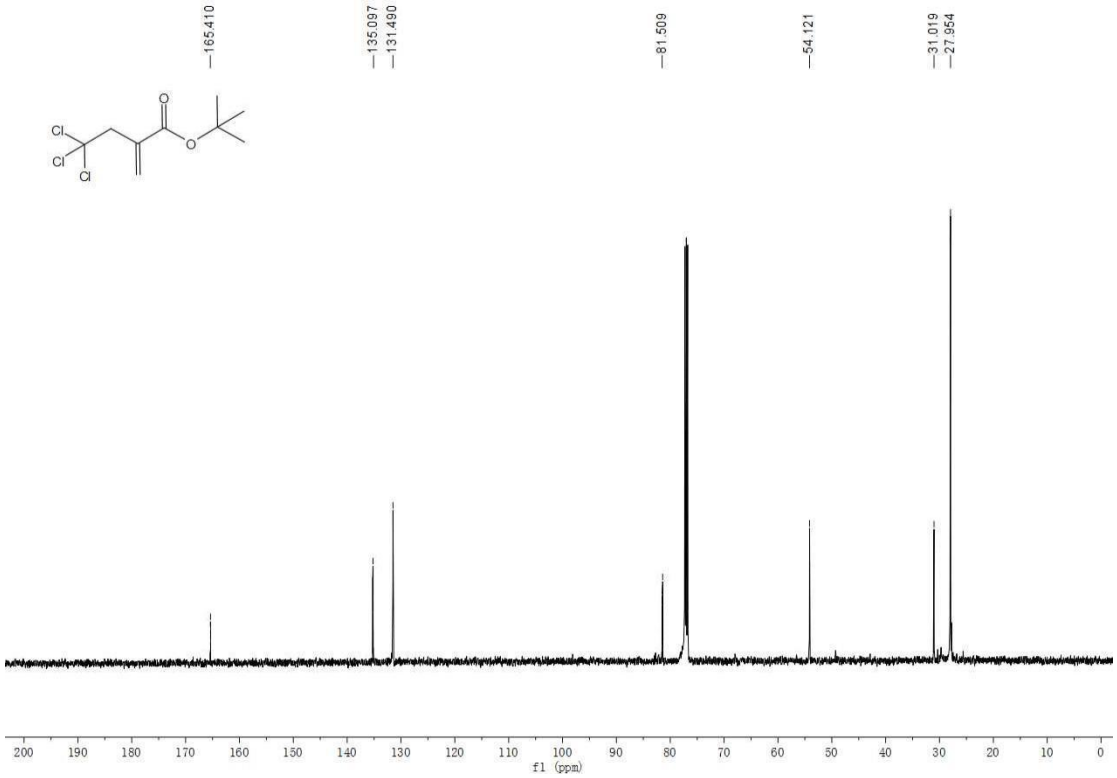


**Tert-butyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2h $CDCl_3$ 500 MHz**

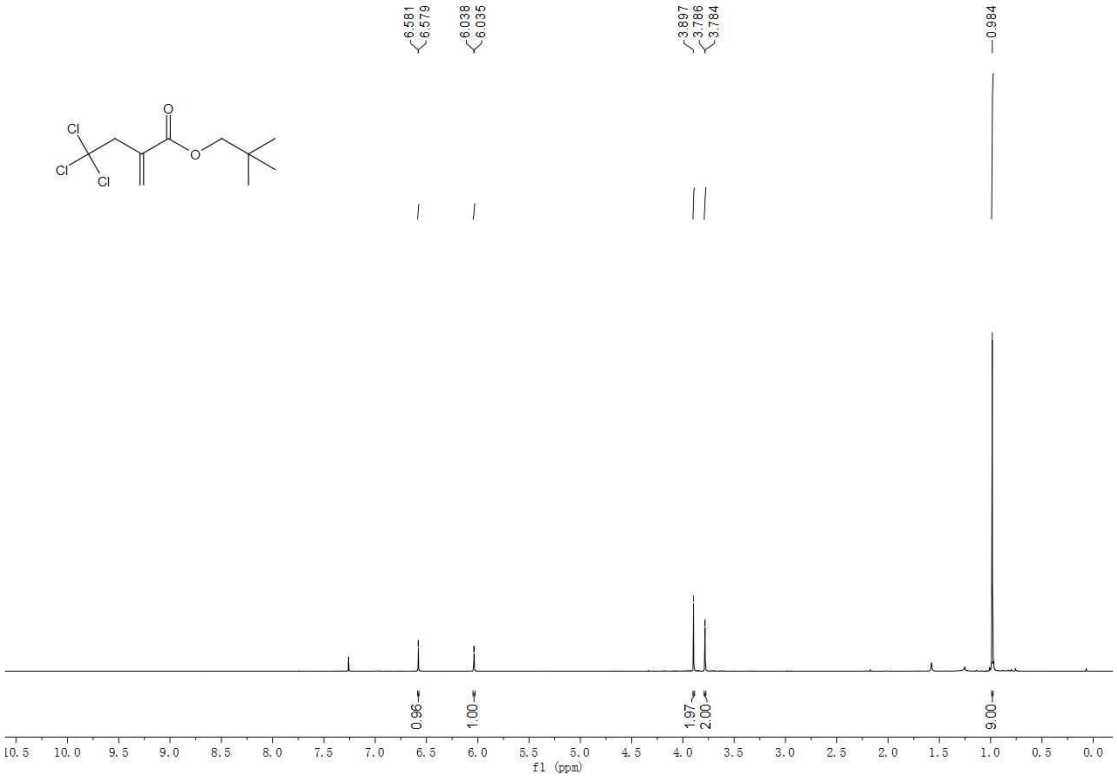



**Compound 2h $CDCl_3$ 126 MHz**

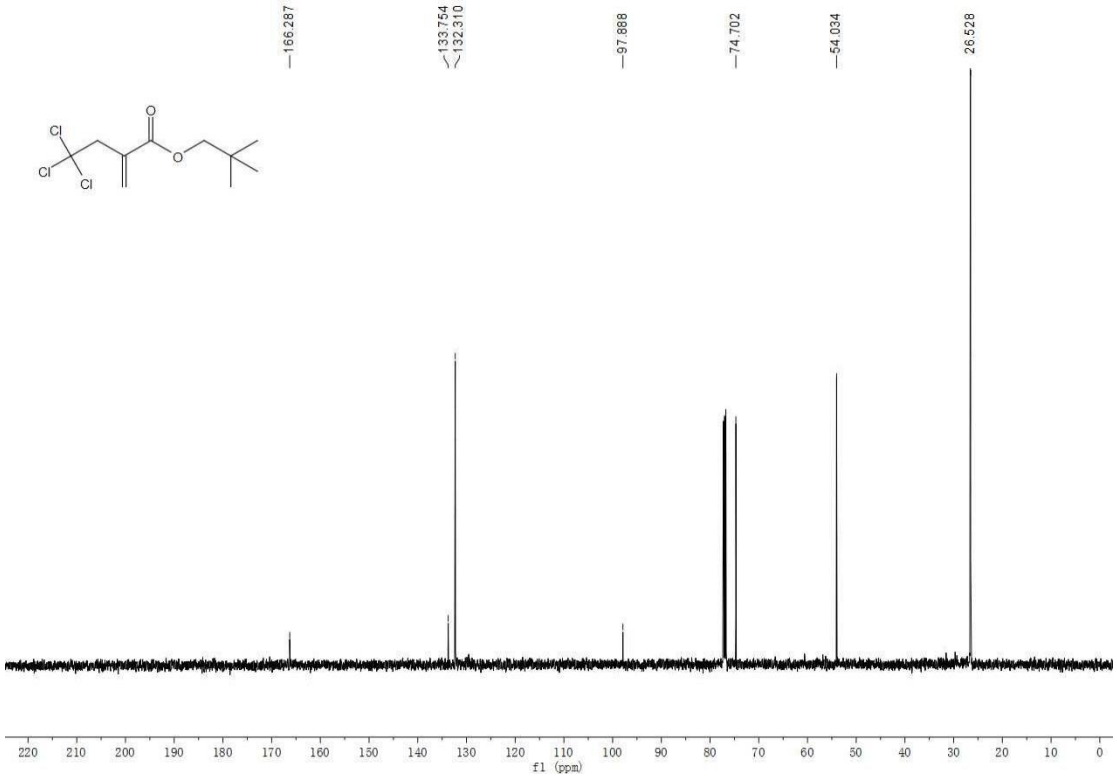


**Neopentyl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2i $CDCl_3$ 500 MHz**

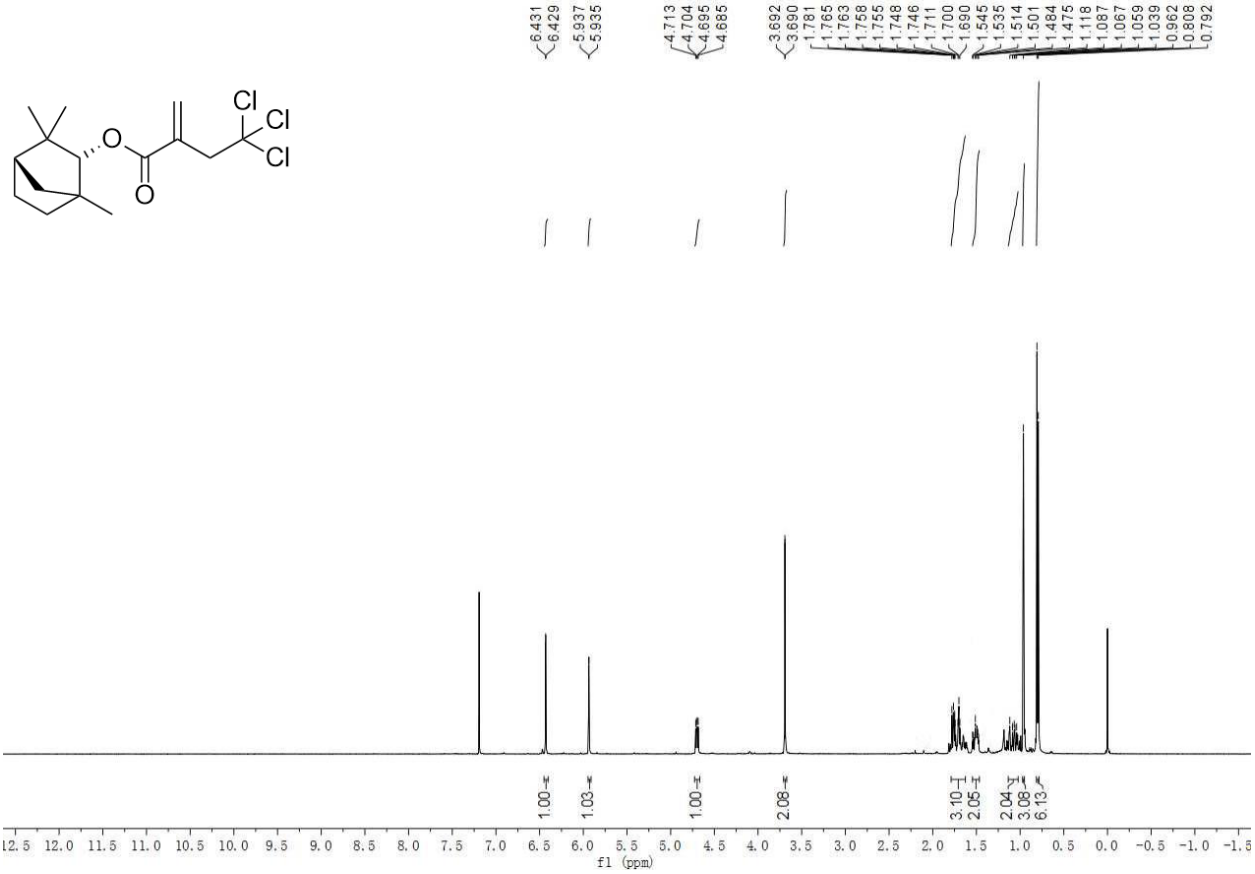



**Compound 2i $CDCl_3$ 126 MHz**

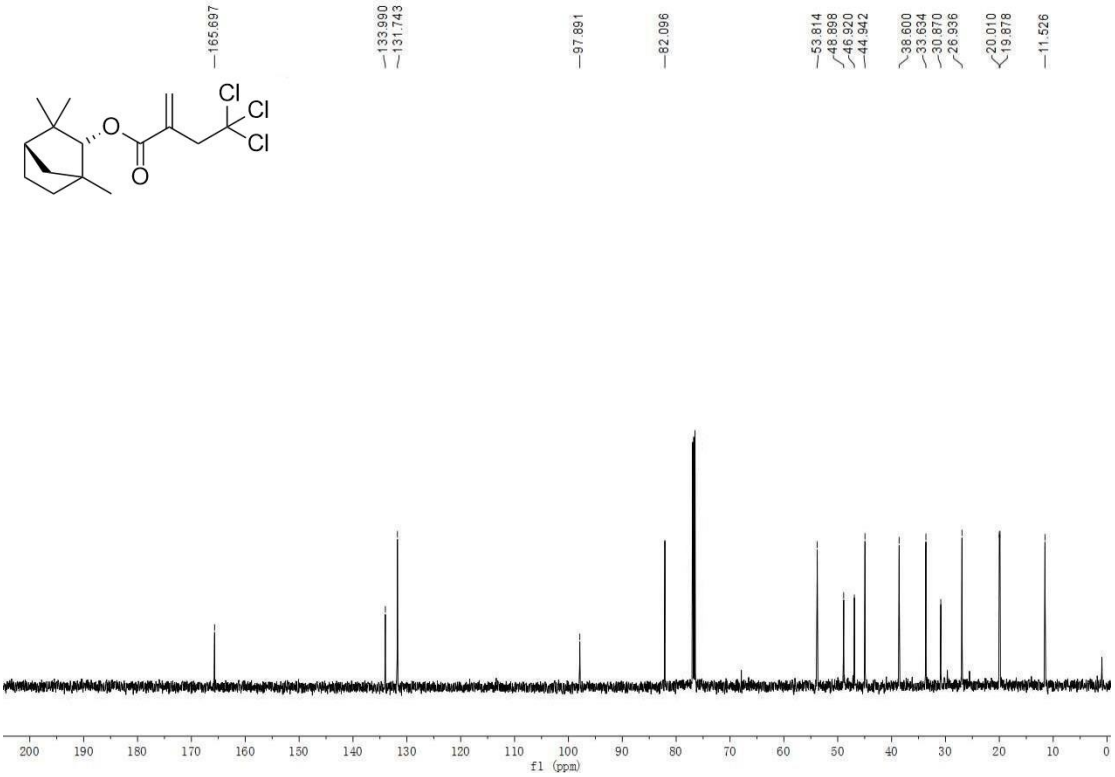


**(5S)-1,7,7-Trimethylbicyclo[3.1.1]heptan-6-yl 4,4,4-trichloro-2-methylenebutanoate**

**Compound 2j $CDCl_3$ 500 MHz**

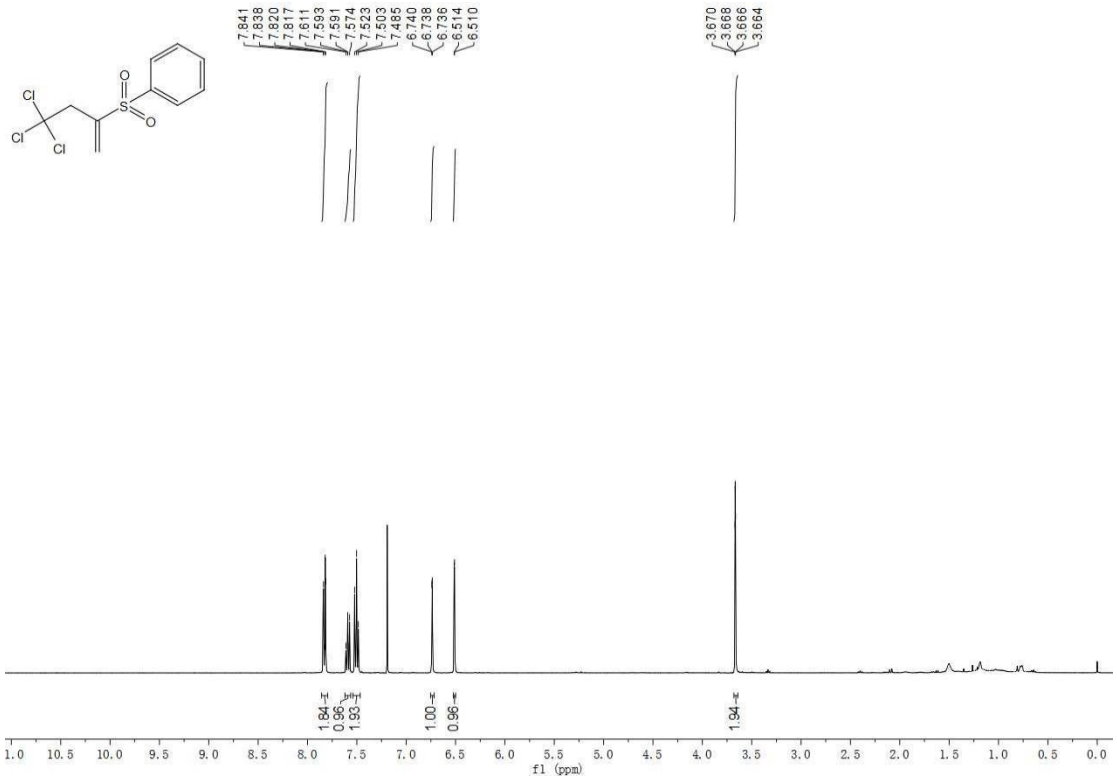



**Compound 2j $CDCl_3$ 75 MHz**

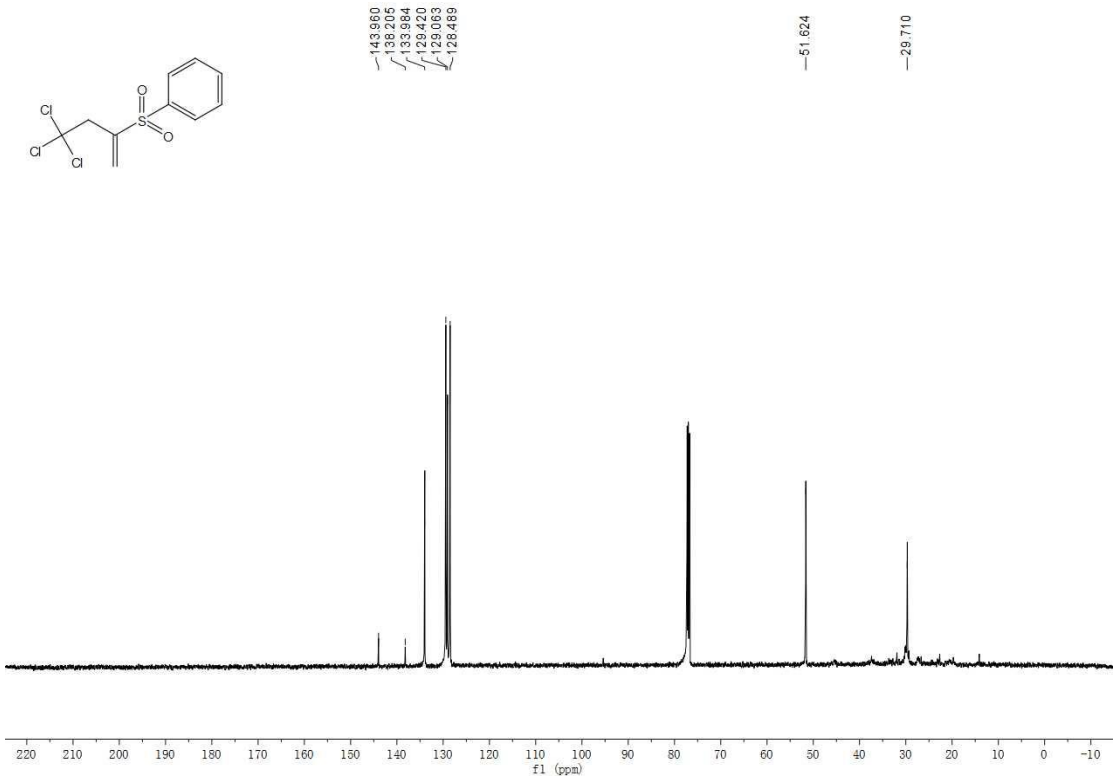


## ((4,4,4-Trichlorobut-1-en-2-yl)sulfonyl)benzene

## Compound 2m $CDCl_3$ 500 MHz

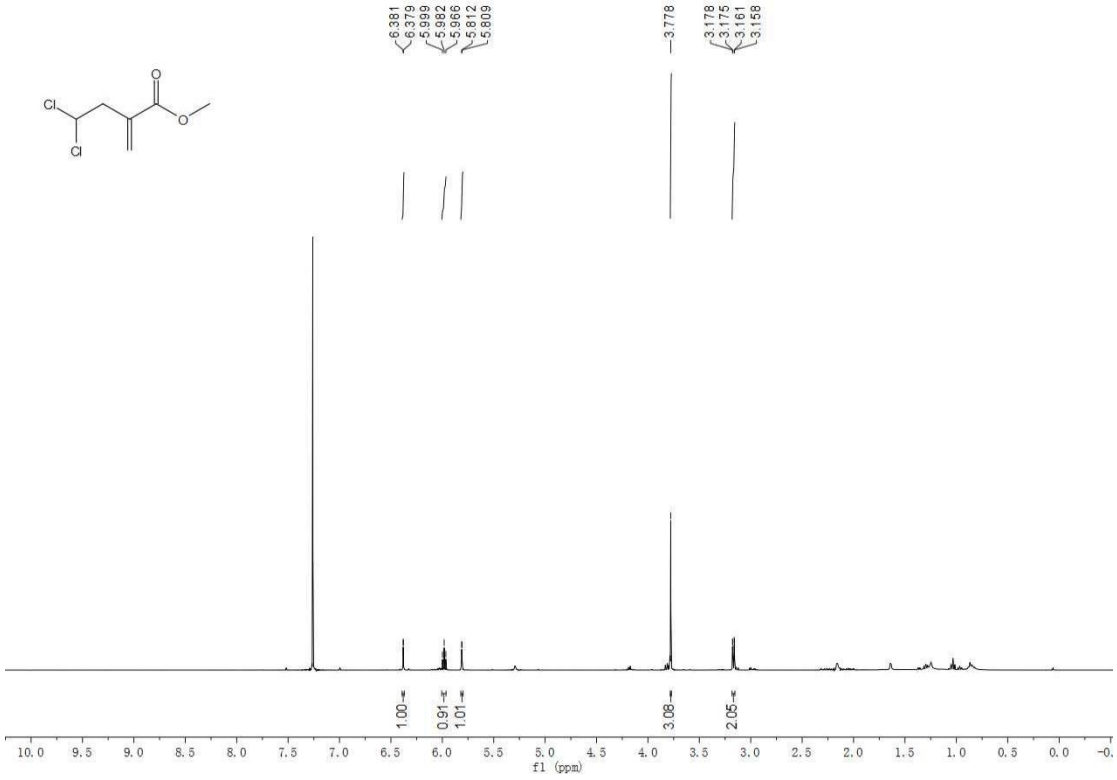



## Compound 2m $CDCl_3$ 126 MHz

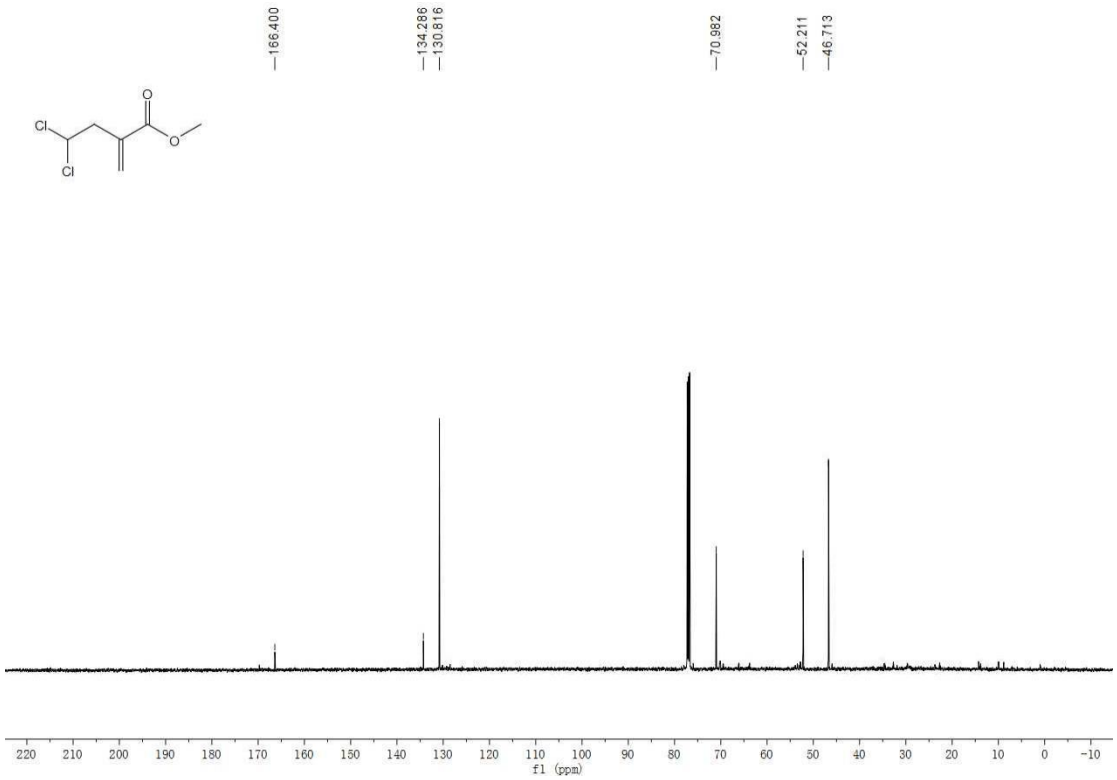


**Methyl 4,4-dichloro-2-methylenebutanoate**

**Compound 3a $CDCl_3$ 500 MHz**

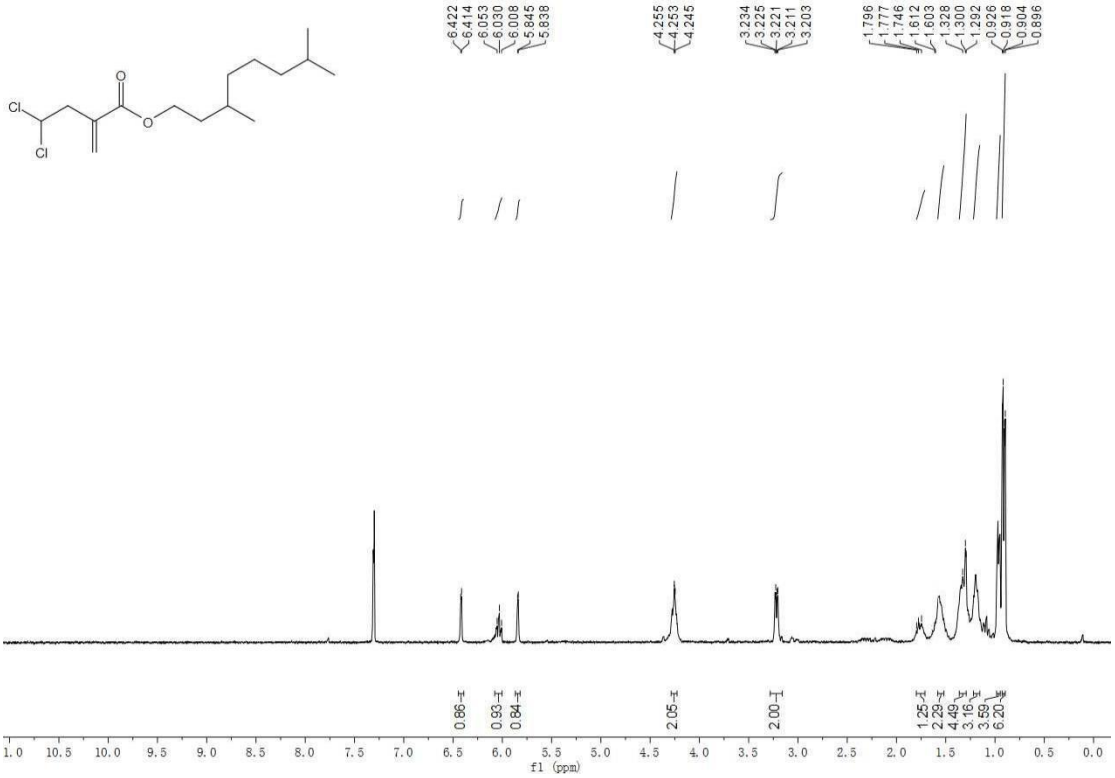



**Compound 3a $CDCl_3$ 126 MHz**

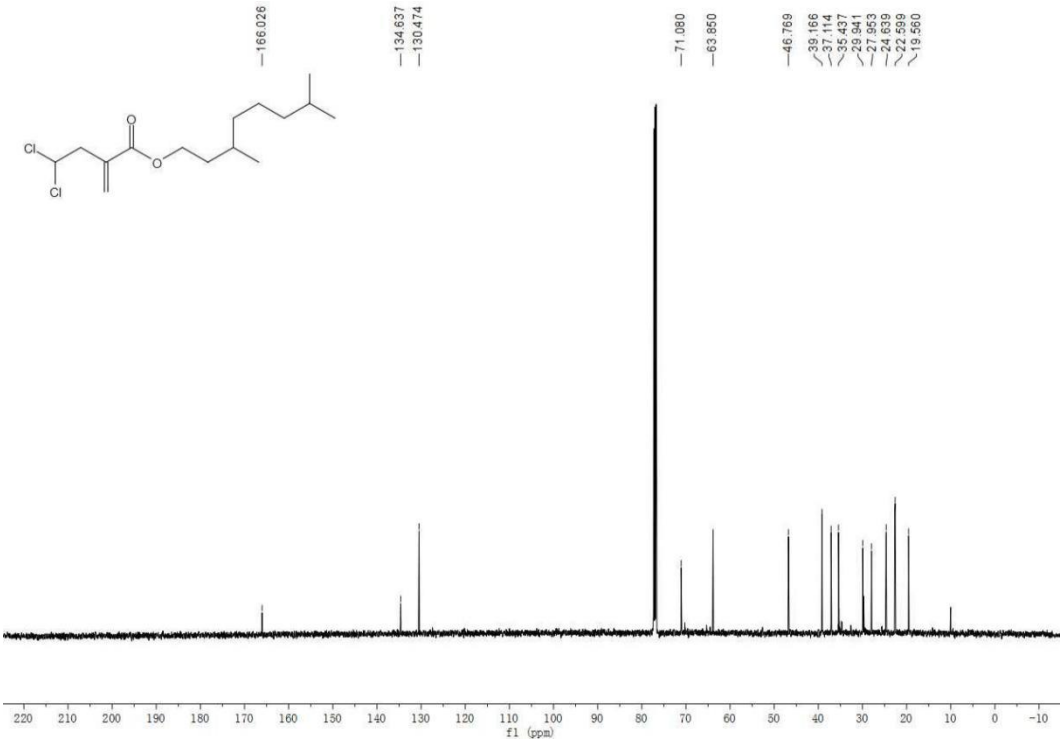


## 3,7-Dimethyloctyl 4,4-dichloro-2-methylenebutanoate

## Compound 3b $CDCl_3$ 500 MHz

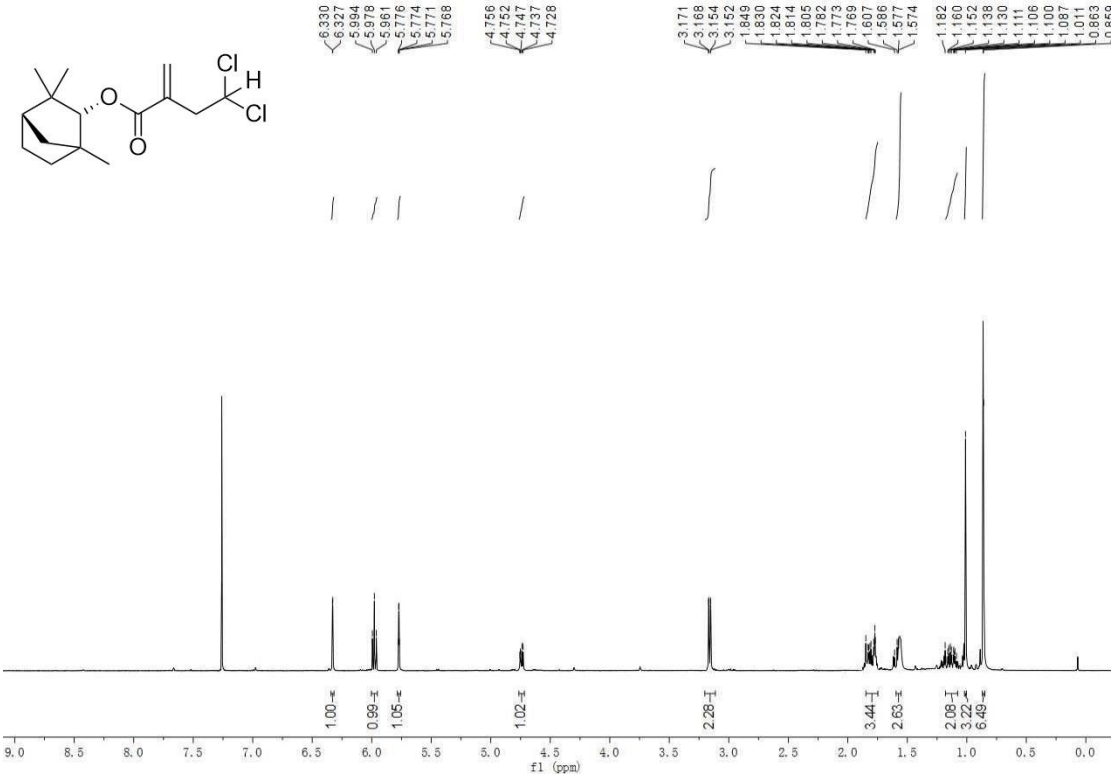



## Compound 3b $CDCl_3$ 126 MHz

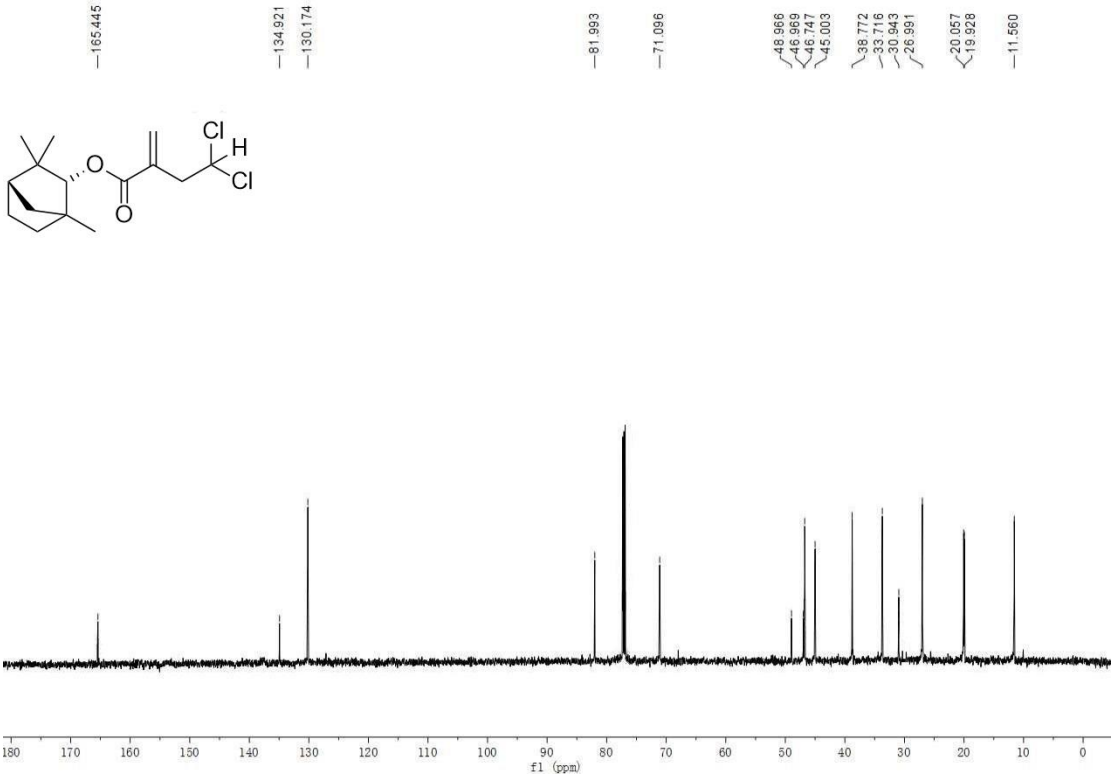


**(5S)-1,7,7-Trimethylbicyclo[3.1.1]heptan-6-yl 4,4-dichloro-2-methylenebutanoate**

**Compound 3c $CDCl_3$ 500 MHz**

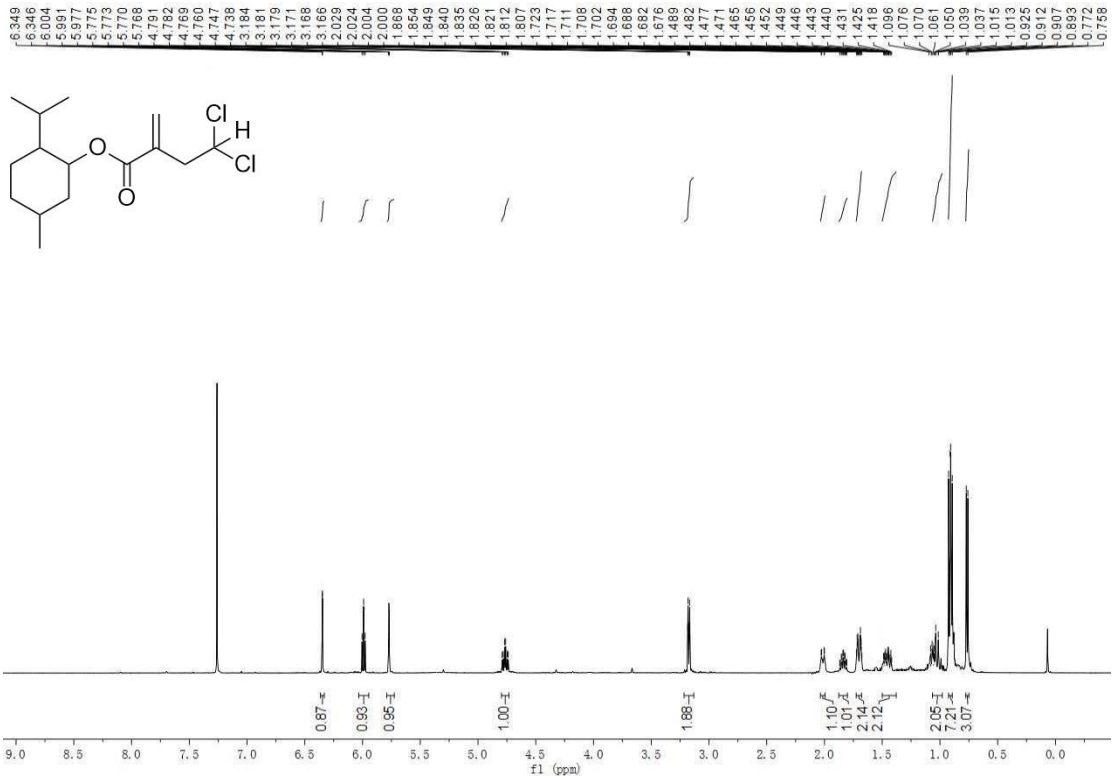



**Compound 3c $CDCl_3$ 126 MHz**

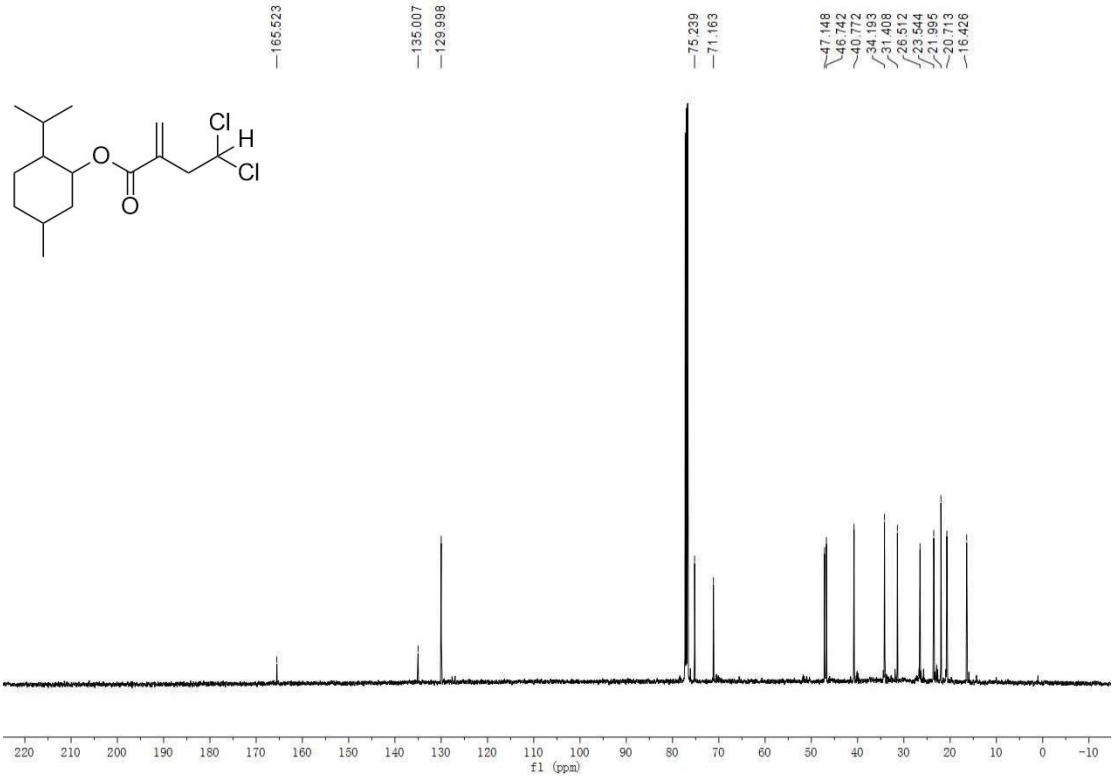


## 5-Isopropyl-2-methylcyclohexyl 4,4-dichloro-2-methylenebutanoate

## Compound 3d $CDCl_3$ 500 MHz

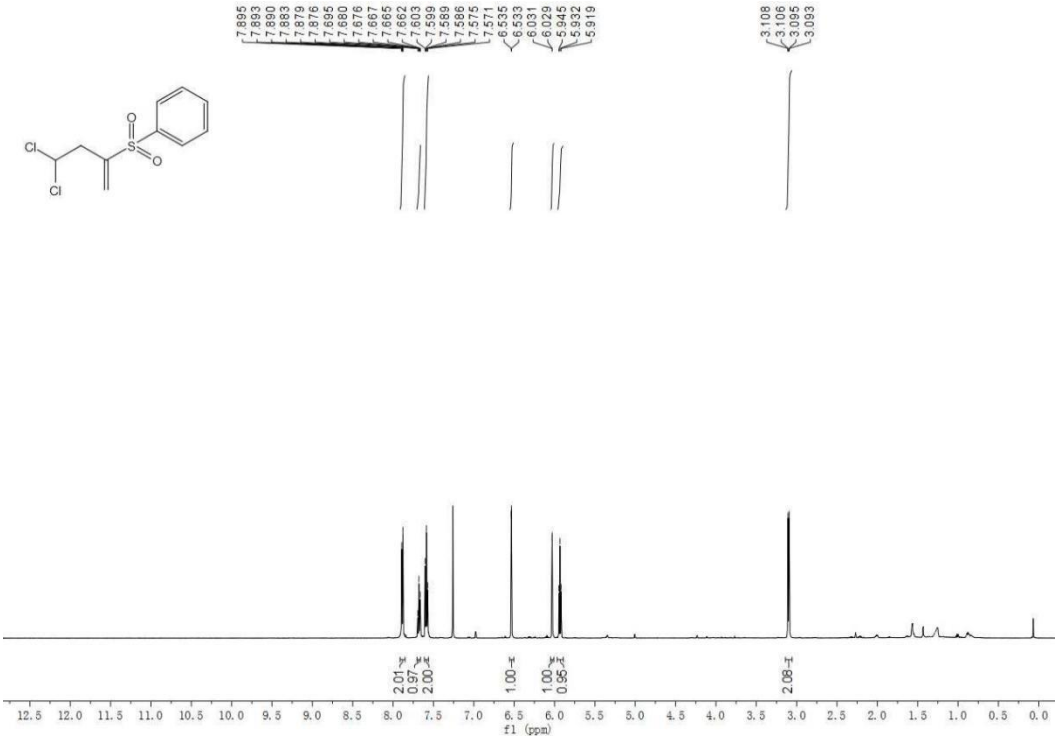



## Compound 3d $CDCl_3$ 126 MHz

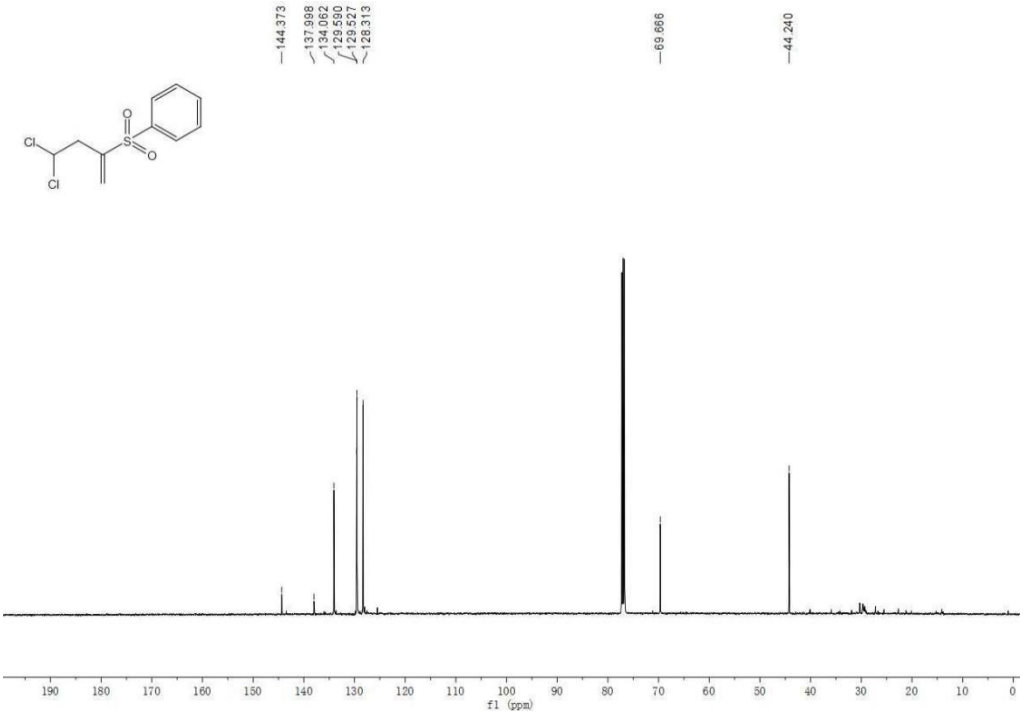


**((4,4-Dichlorobut-1-en-2-yl)sulfonyl)benzene**

**Compound 3e $CDCl_3$ 500 MHz**

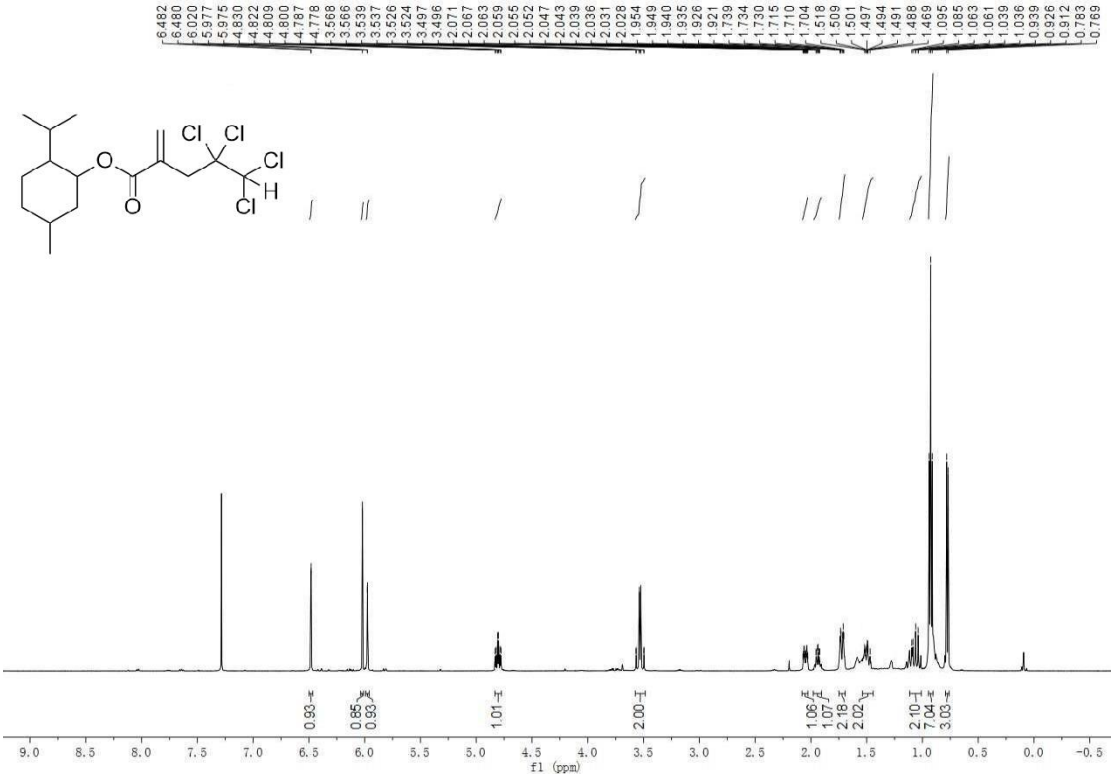



**Compound 3e $CDCl_3$ 126 MHz**

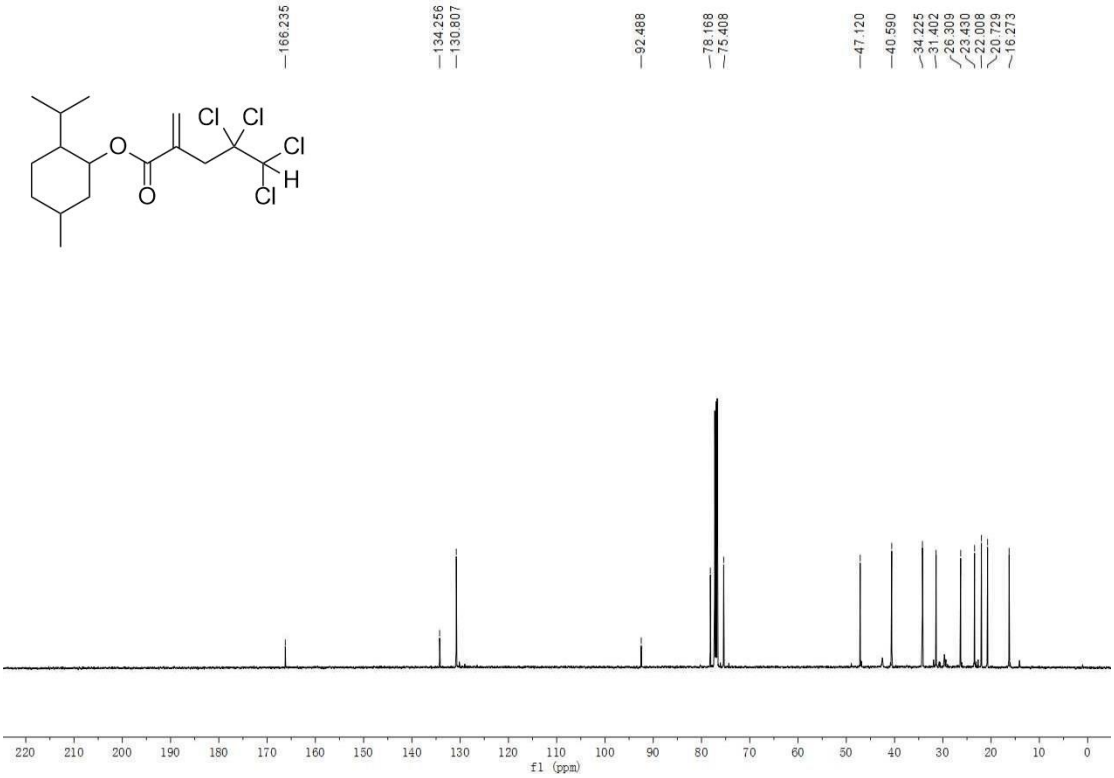


**5-Isopropyl-2-methylcyclohexyl 4,4,6,6-tetrachloro-2-methylenehexanoate**

**Compound 3f $CDCl_3$ 500 MHz**

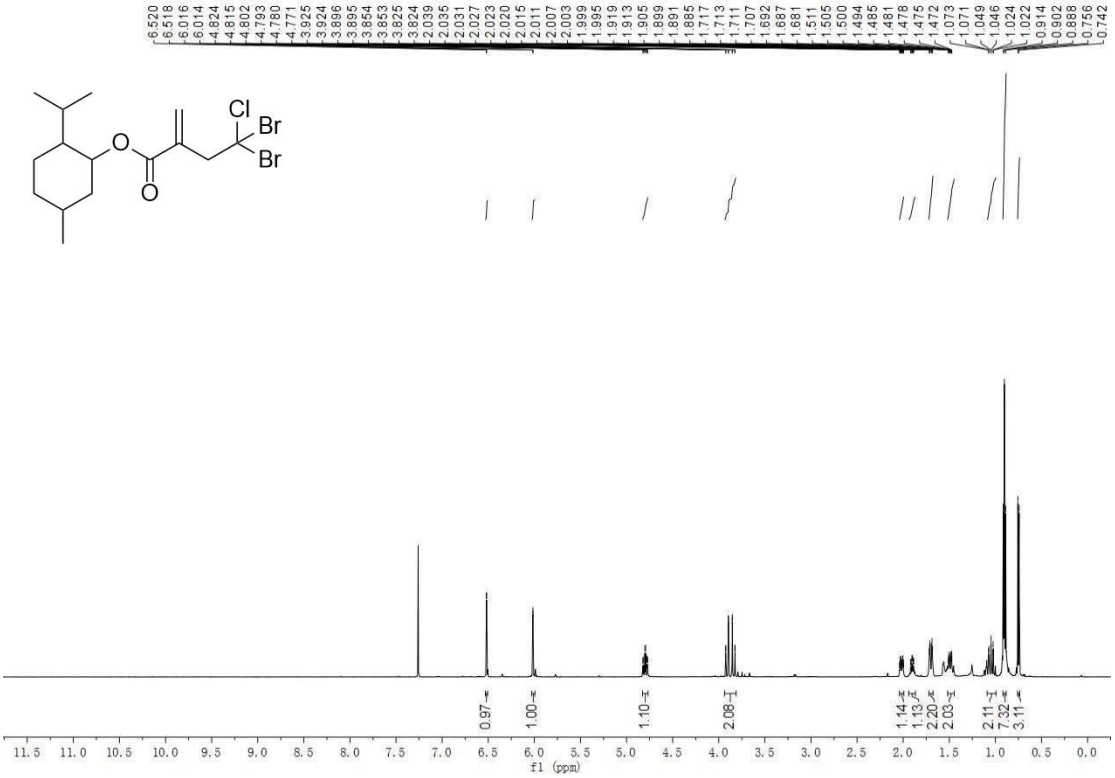



**Compound 3f $CDCl_3$ 126 MHz**

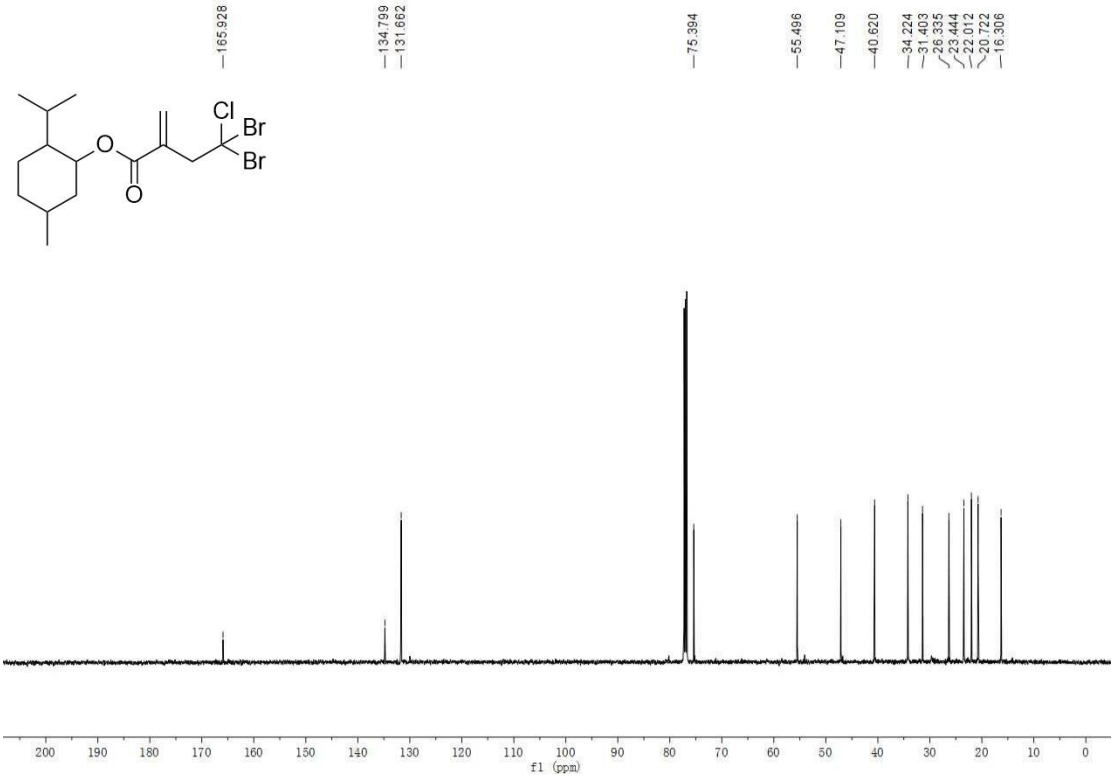


**5-Isopropyl-2-methylcyclohexyl 4,4-dibromo-4-chloro-2-methylenebutanoate**

**Compound 3g $CDCl_3$ 500 MHz**

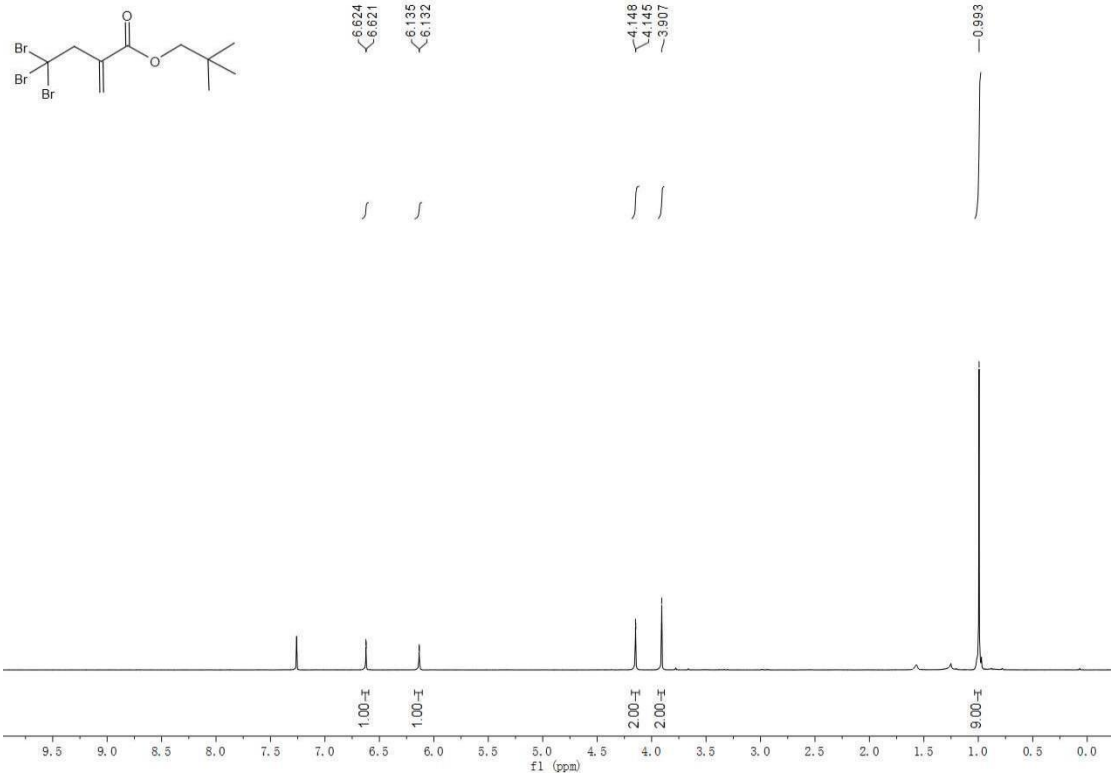



**Compound 3g $CDCl_3$ 126 MHz**

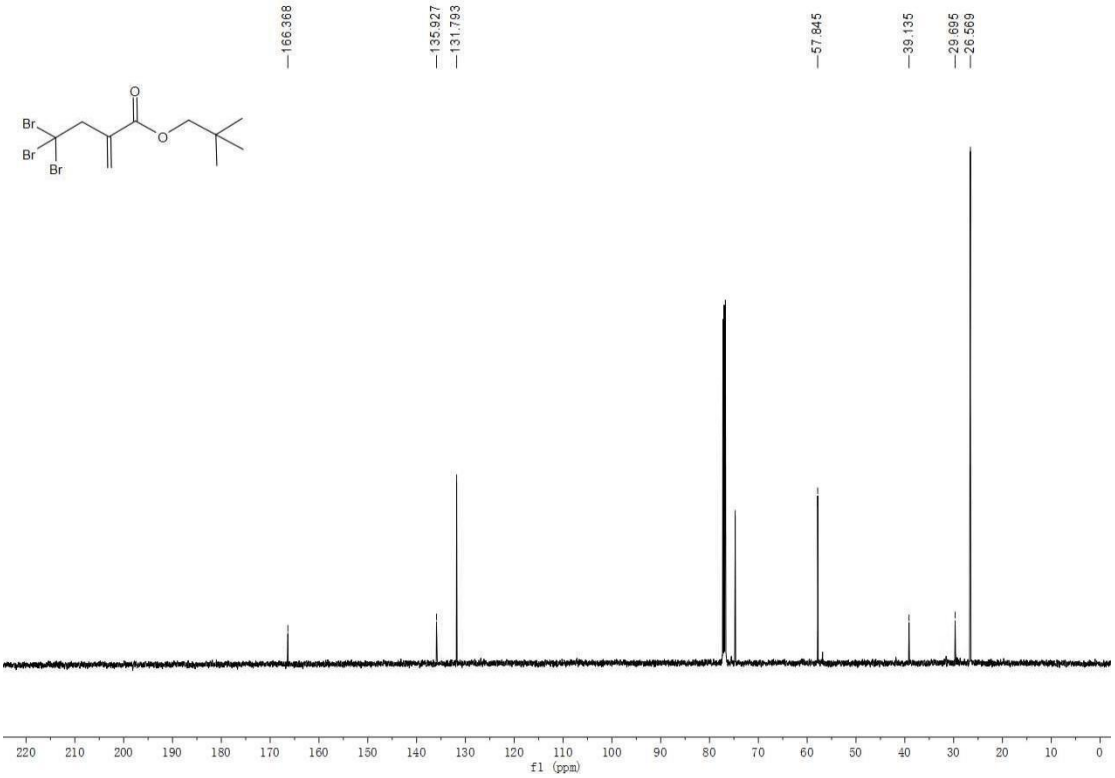


**Neopentyl 4,4,4-tribromo-2-methylenebutanoate**

**Compound 3h $CDCl_3$ 500 MHz**

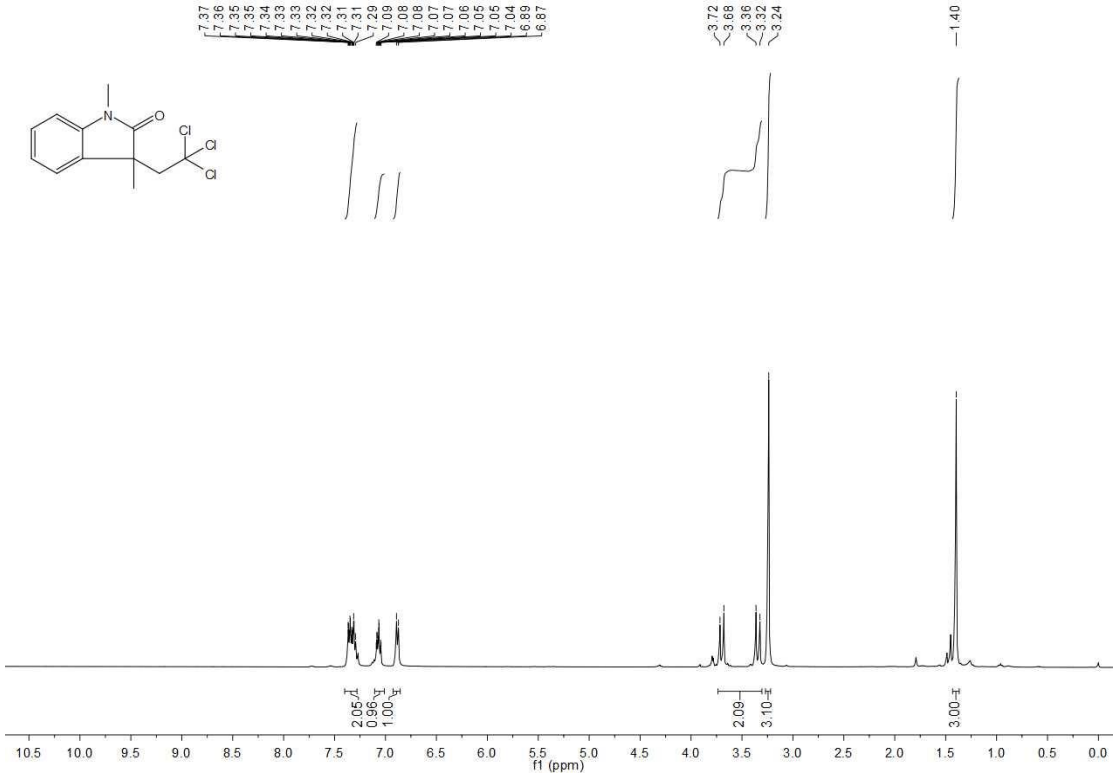



**Compound 3h $CDCl_3$ 126 MHz**

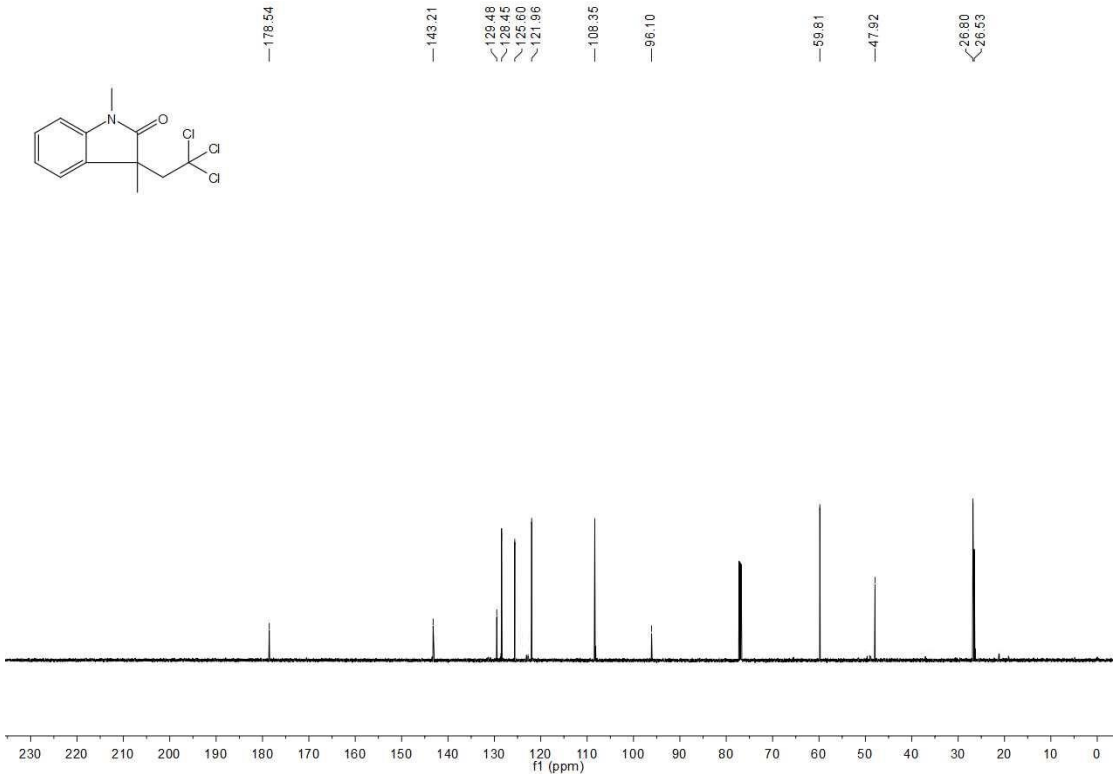


## 1,3-Dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one

## Compound 4b, $CDCl_3$, 400 MHz

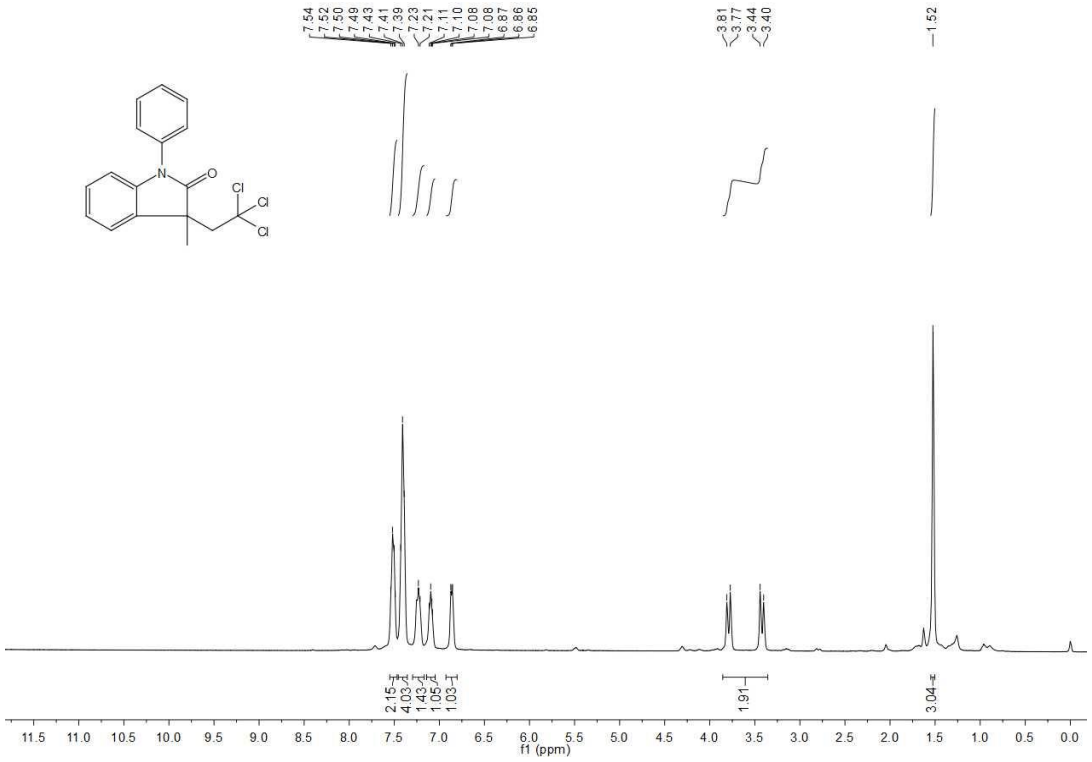



## Compound 4b, $CDCl_3$, 150 MHz

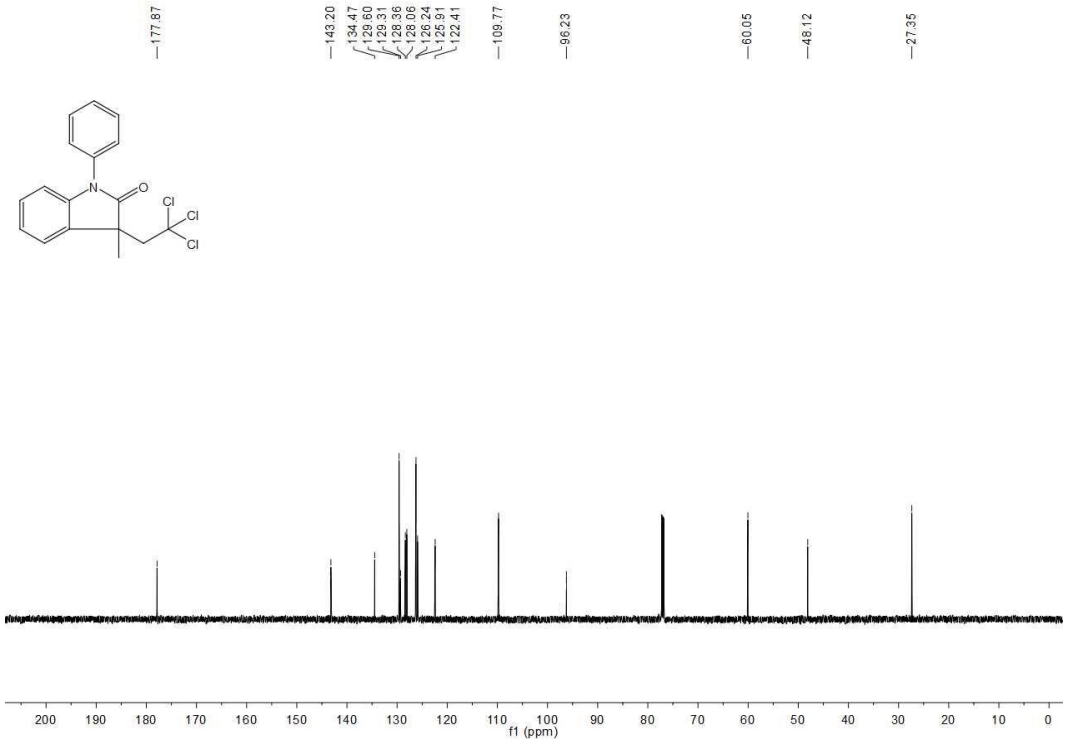


**3-Methyl-1-phenyl-3-(2,2,2-trichloroethyl)indolin-2-one**

**Compound 4c, $CDCl_3$, 400 MHz**

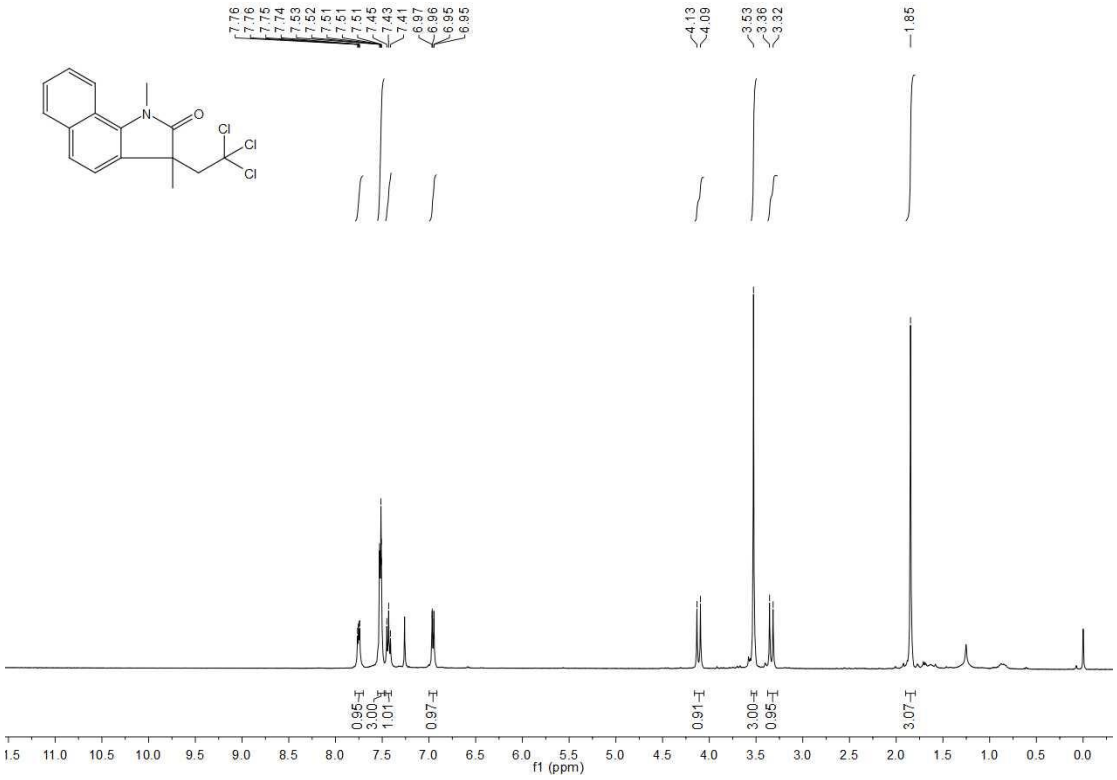



**Compound 4c, $CDCl_3$, 150 MHz**

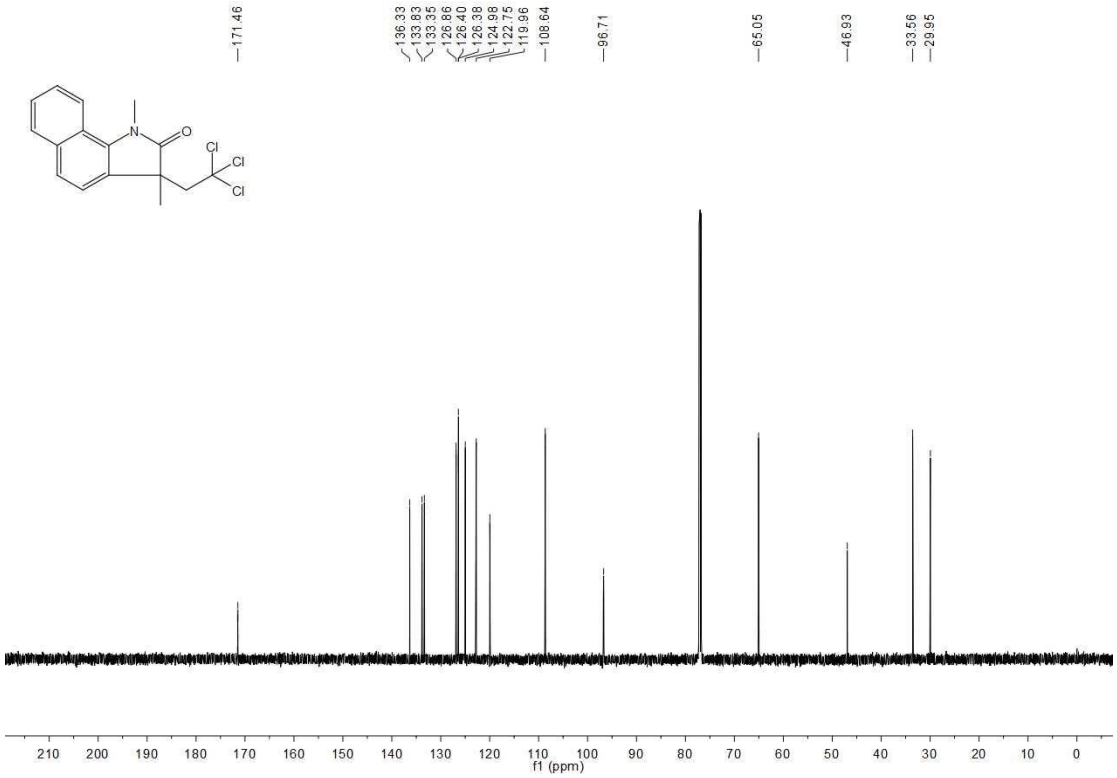


**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-1,3-dihydro-2H-benzo[g]indol-2-one**

**Compound 4d, $CDCl_3$, 400 MHz**

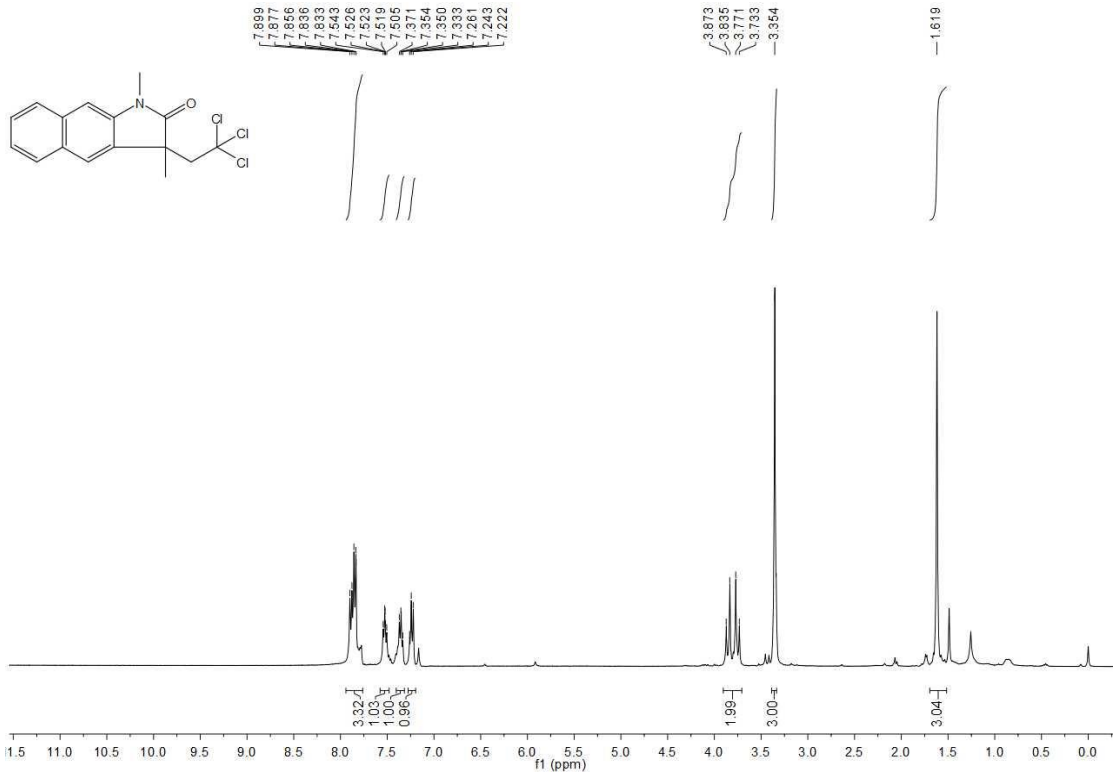



**Compound 4d, $CDCl_3$, 150 MHz**

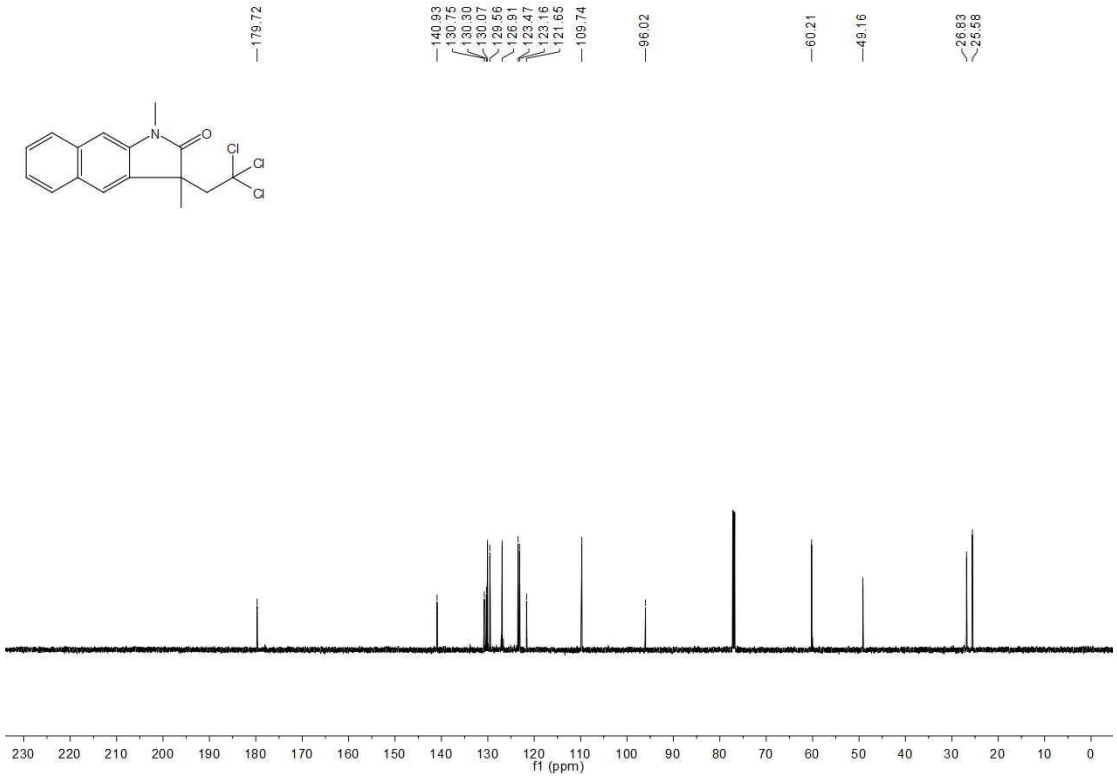


**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-1,3-dihydro-2H-benzo[f]indol-2-one**

**Compound 4e, $CDCl_3$, 400 MHz**

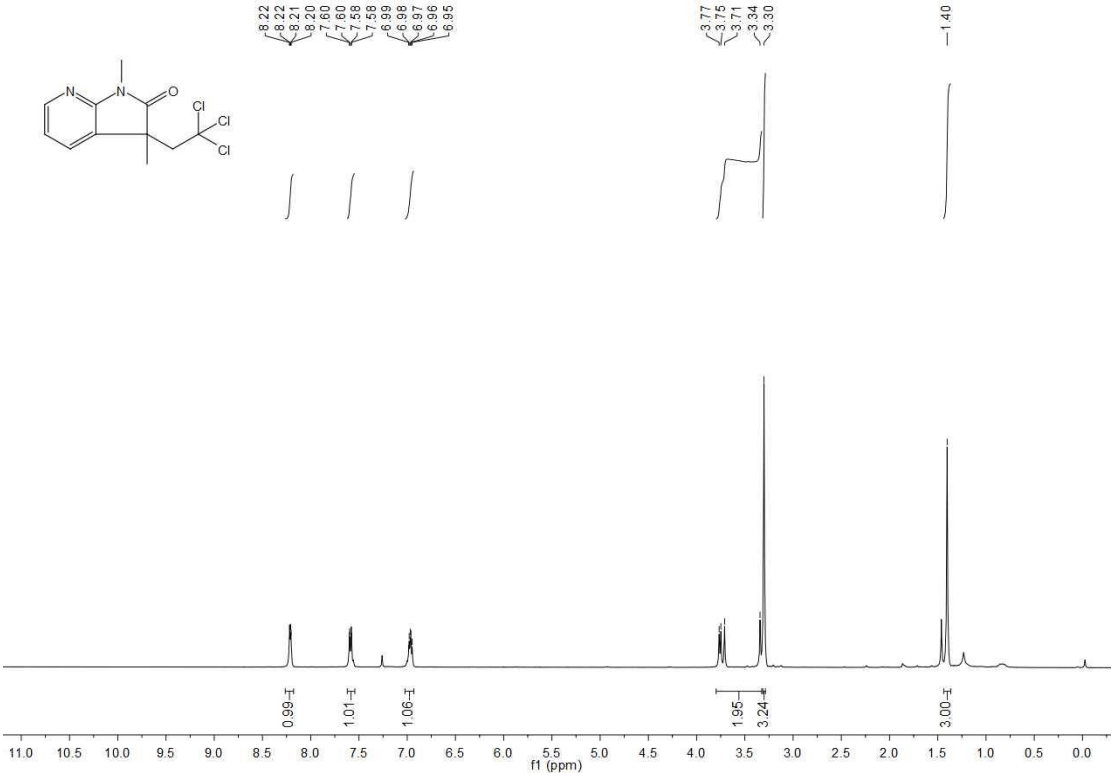



**Compound 4e, $CDCl_3$, 150 MHz**

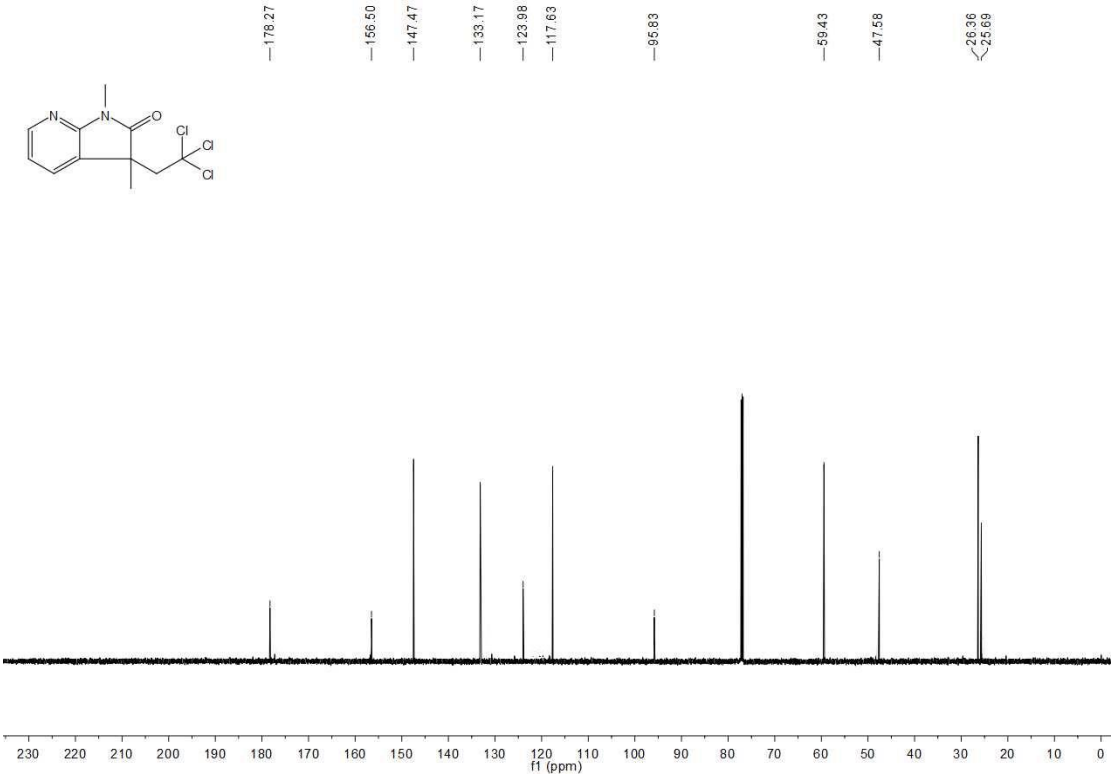


**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-1,3-dihydro-2H-pyrrolo[2,3-b]pyridin-2-one**

**Compound 4f, $CDCl_3$, 400 MHz**

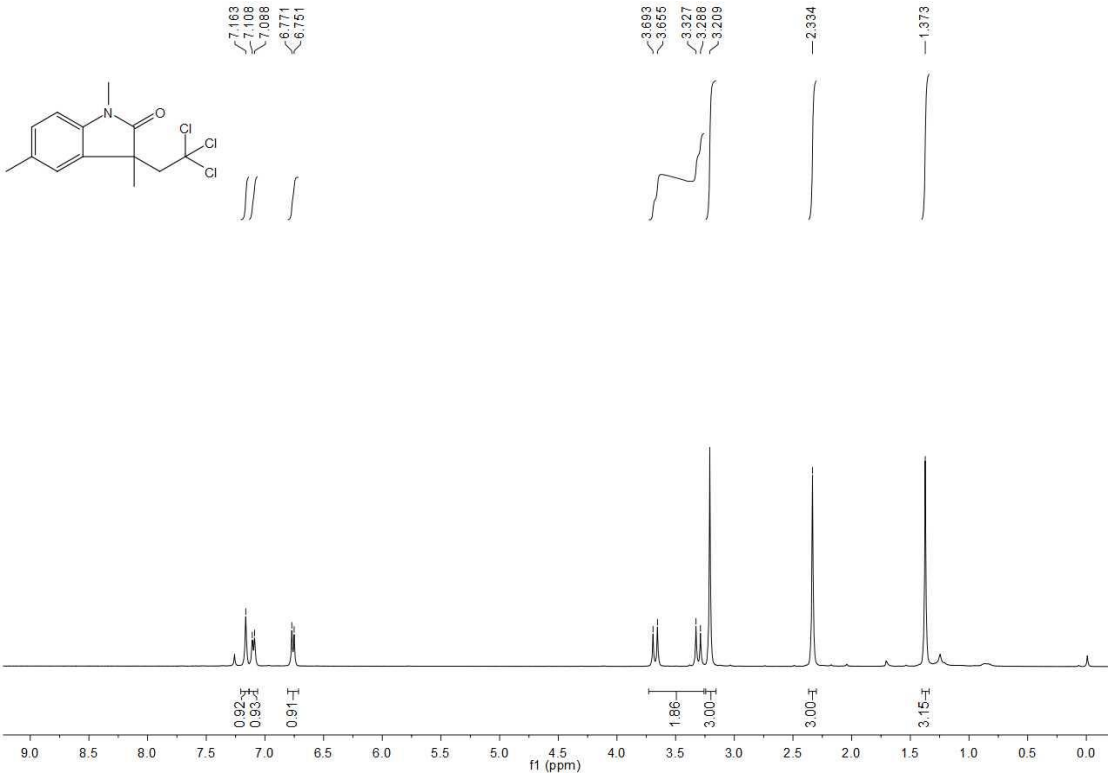



**Compound 4f, $CDCl_3$, 150 MHz**

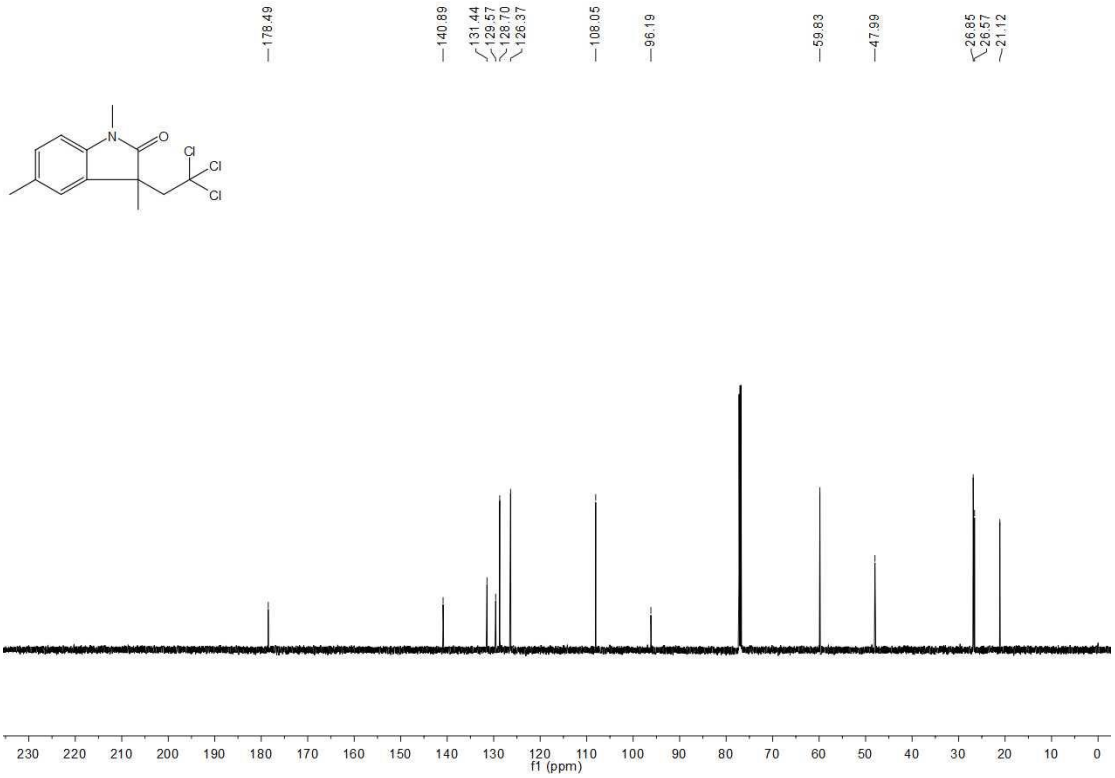


## 1,3,5-Trimethyl-3-(2,2,2-trichloroethyl)indolin-2-one

## Compound 4g, $CDCl_3$, 400 MHz



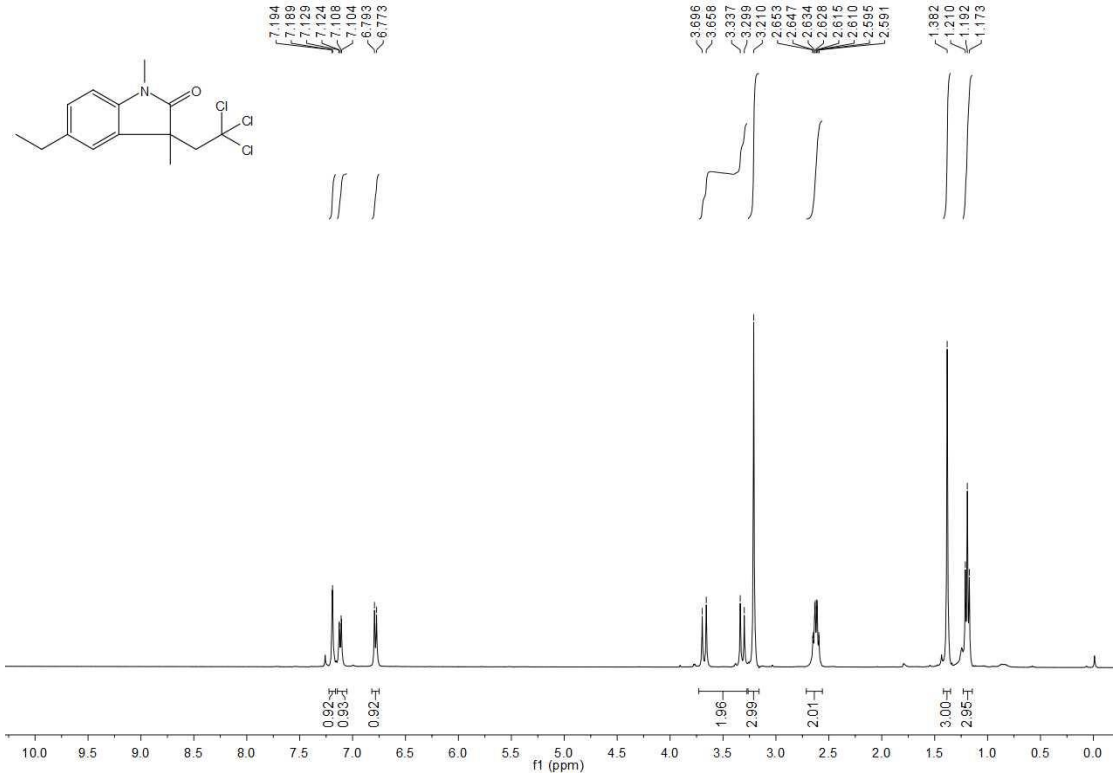

## Compound 4g, $CDCl_3$, 150 MHz



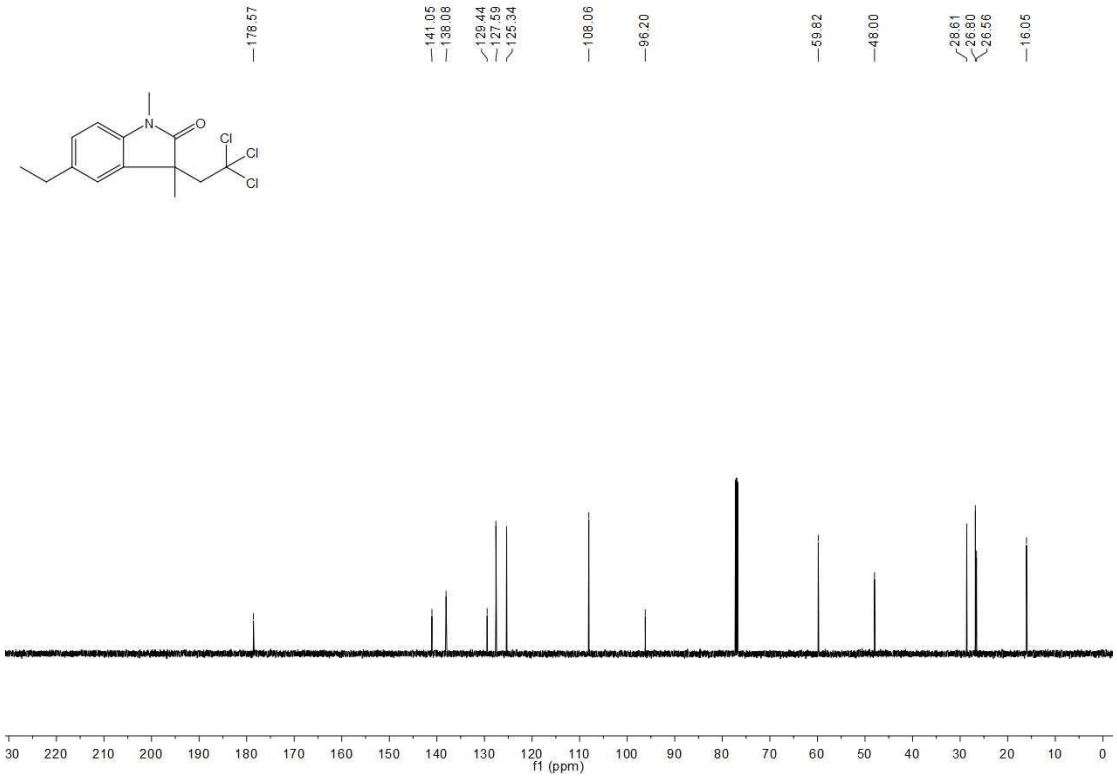

[redacted]

**5-Ethyl-1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one**

**Compound 4h, $CDCl_3$, 400 MHz**



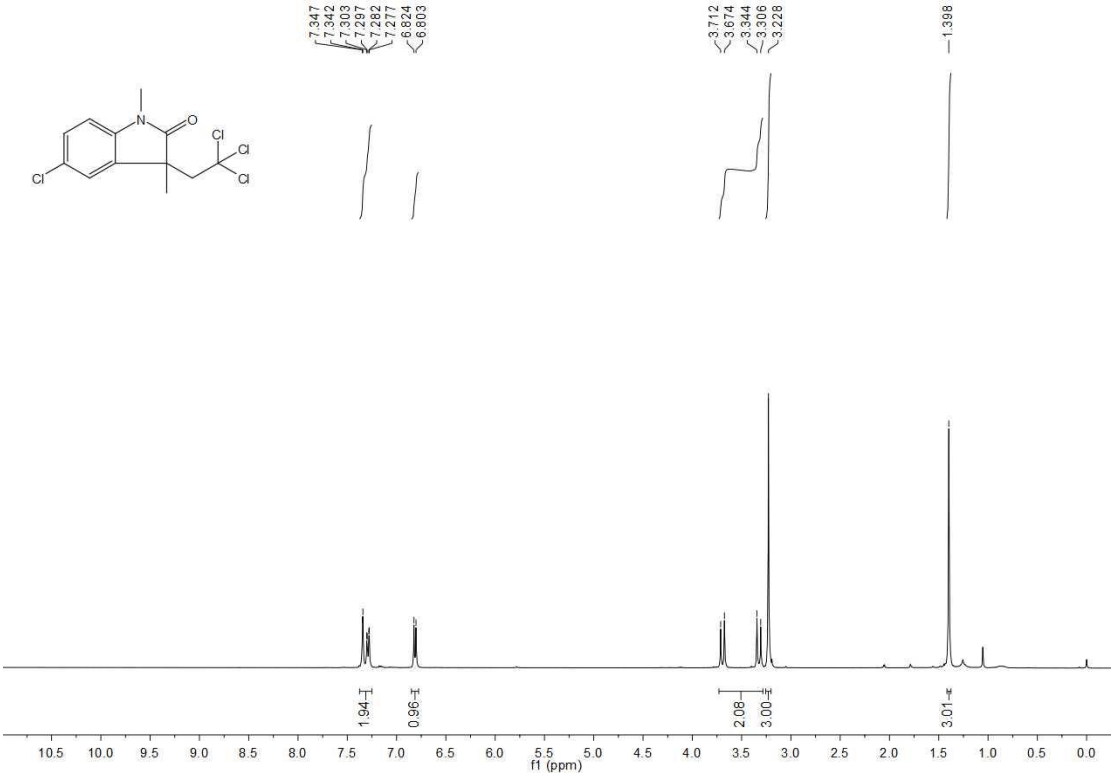

**Compound 4h, $CDCl_3$, 150 MHz**



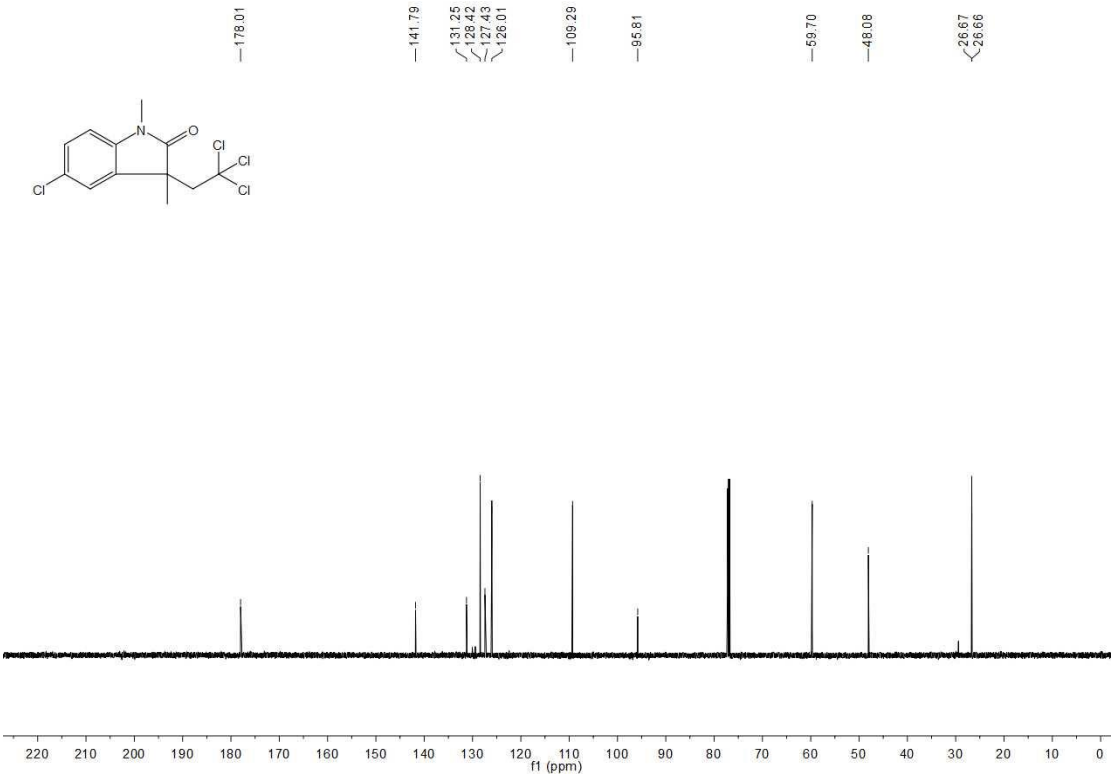

[redacted]

**5-Chloro-1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one**

**Compound 4i, $CDCl_3$, 400 MHz**



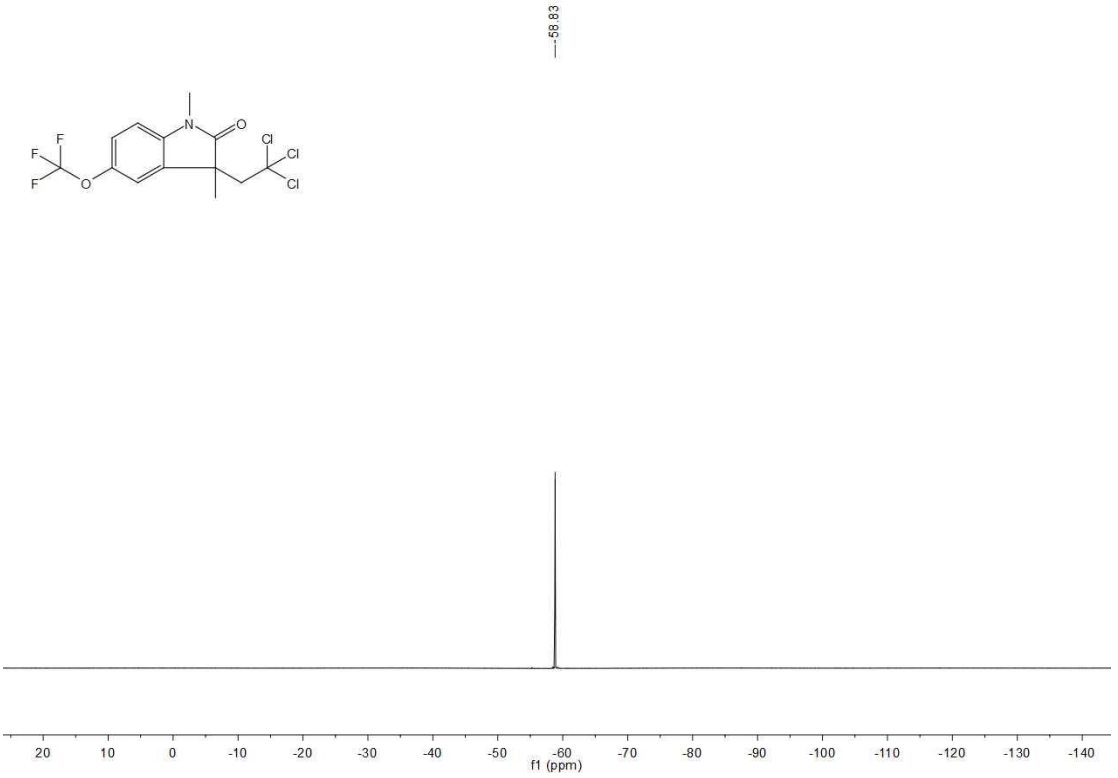

**Compound 4i, $CDCl_3$, 150 MHz**



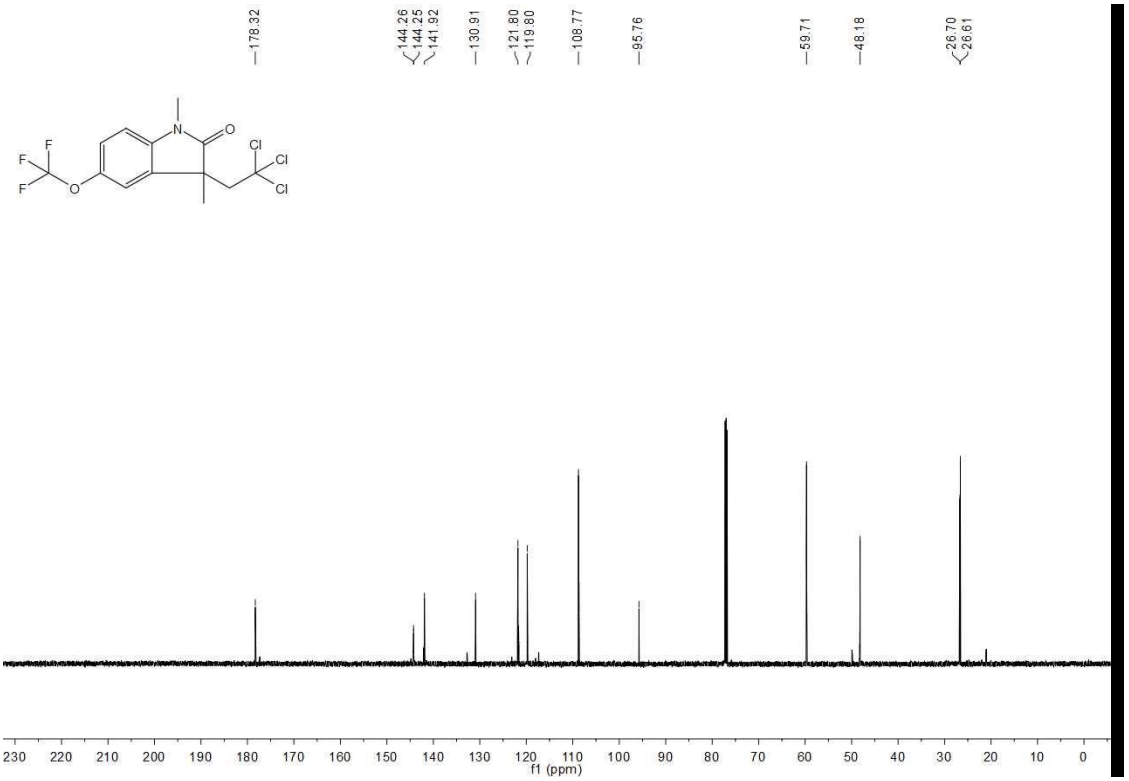

[redacted]

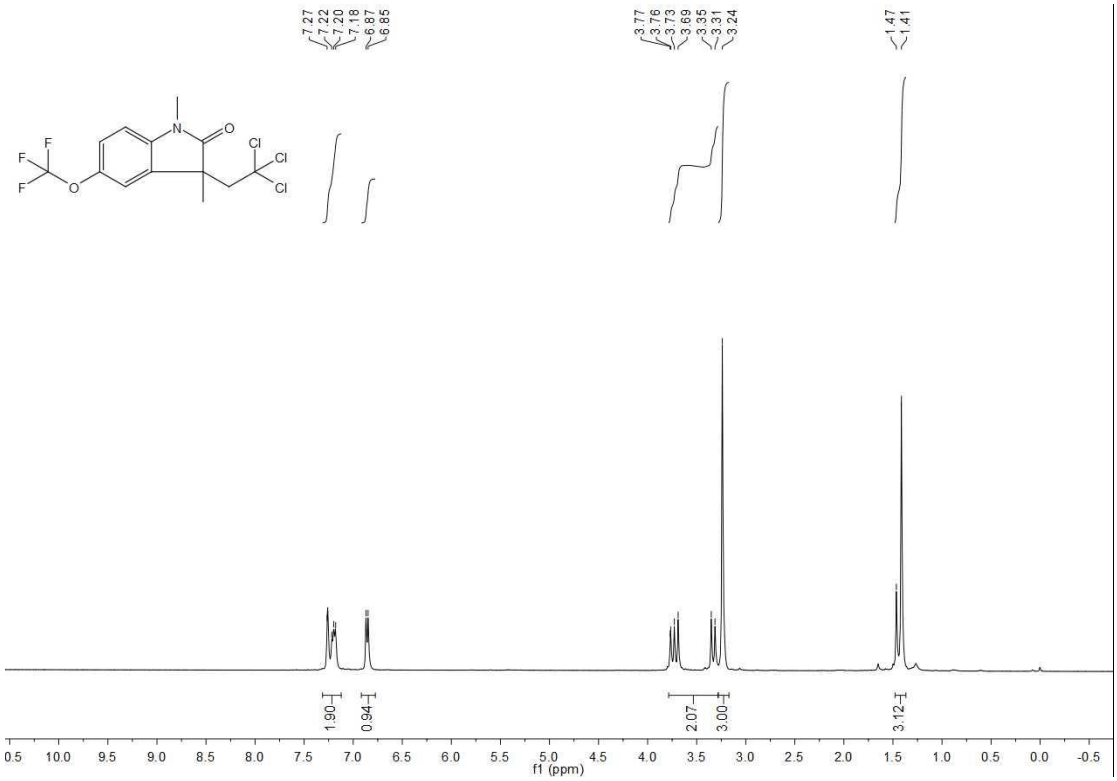
**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-5-(trifluoromethoxy)indolin-2-one**

**Compound 4j, $CDCl_3$, 400 MHz**



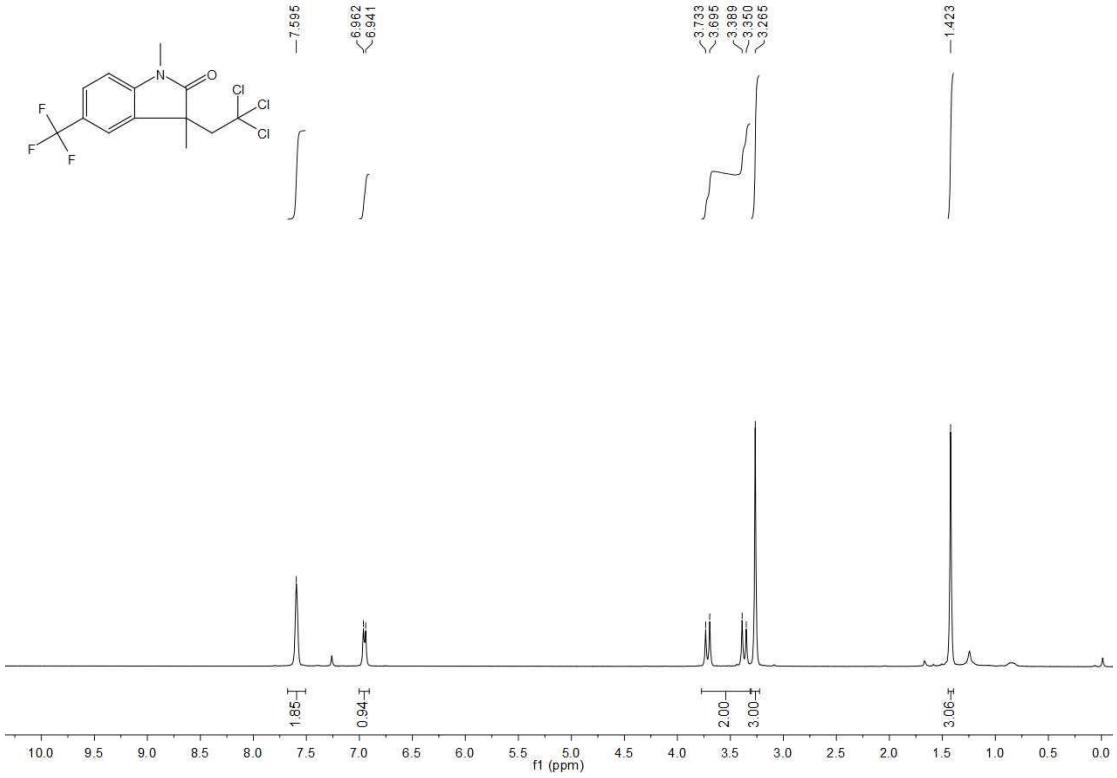

**Compound 4j, $CDCl_3$, 150 MHz**



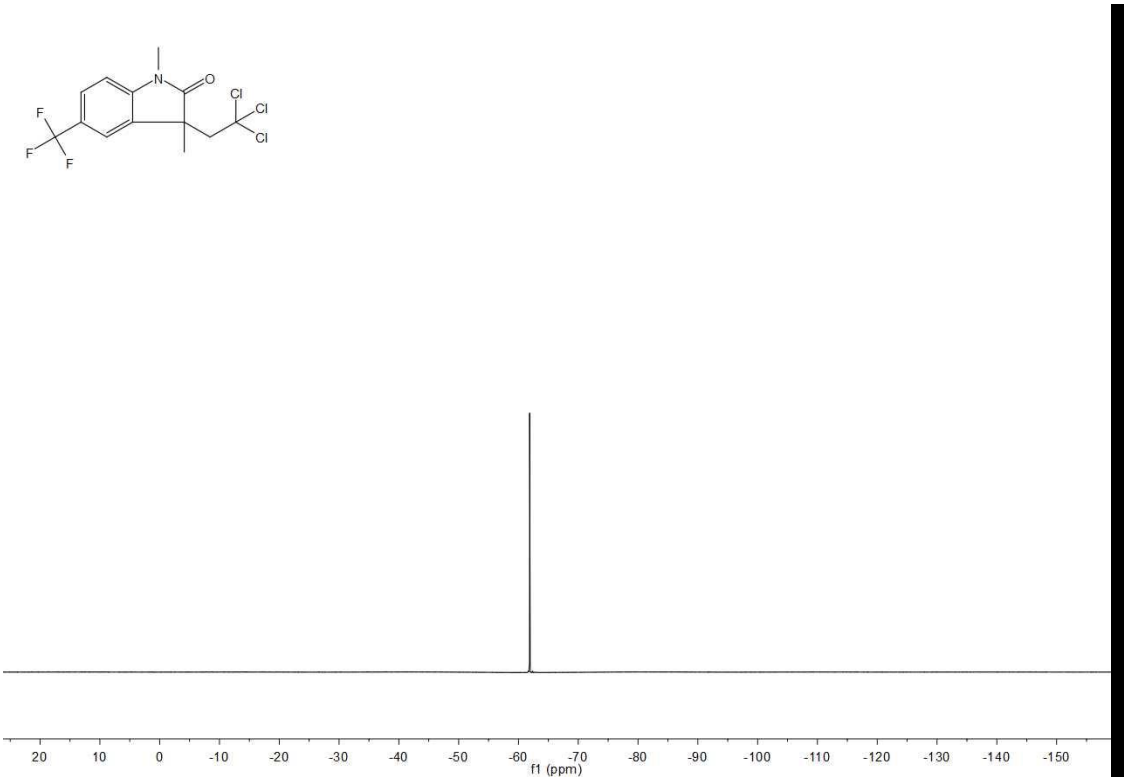


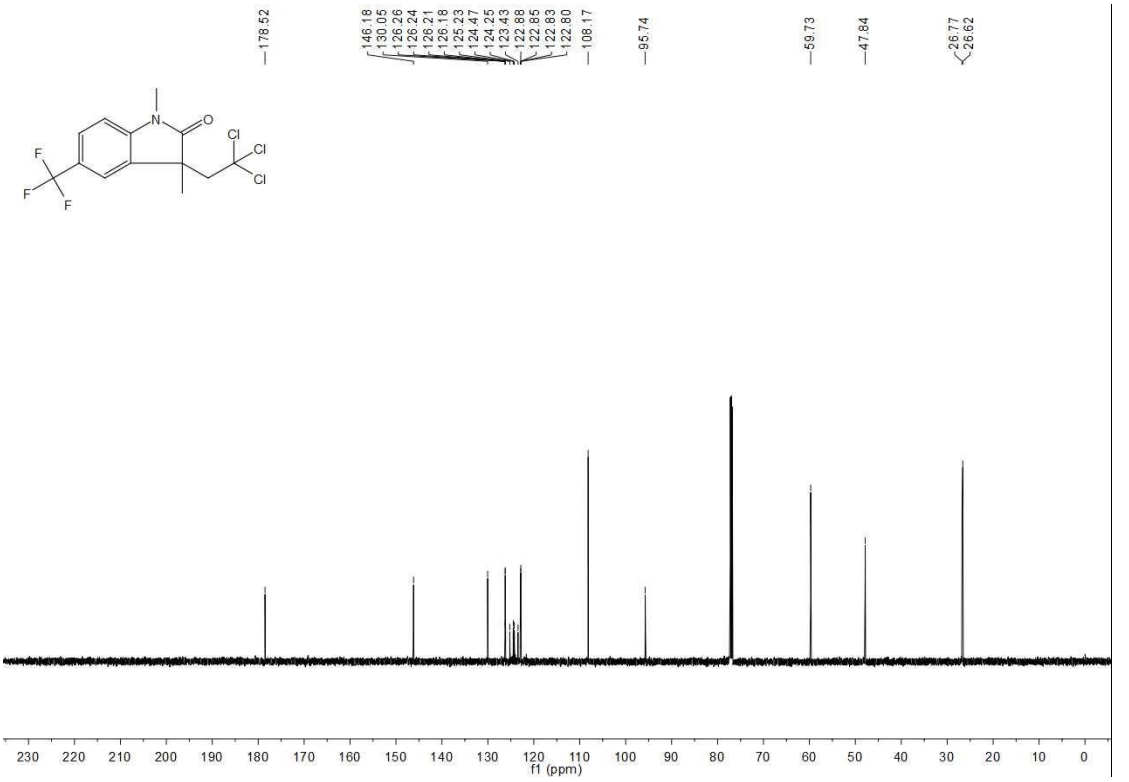

**1,3-Dimethyl-3-(2,2,2-trichloroethyl)-5-(trifluoromethyl)indolin-2-one**

**Compound 4k, $CDCl_3$, 400 MHz**



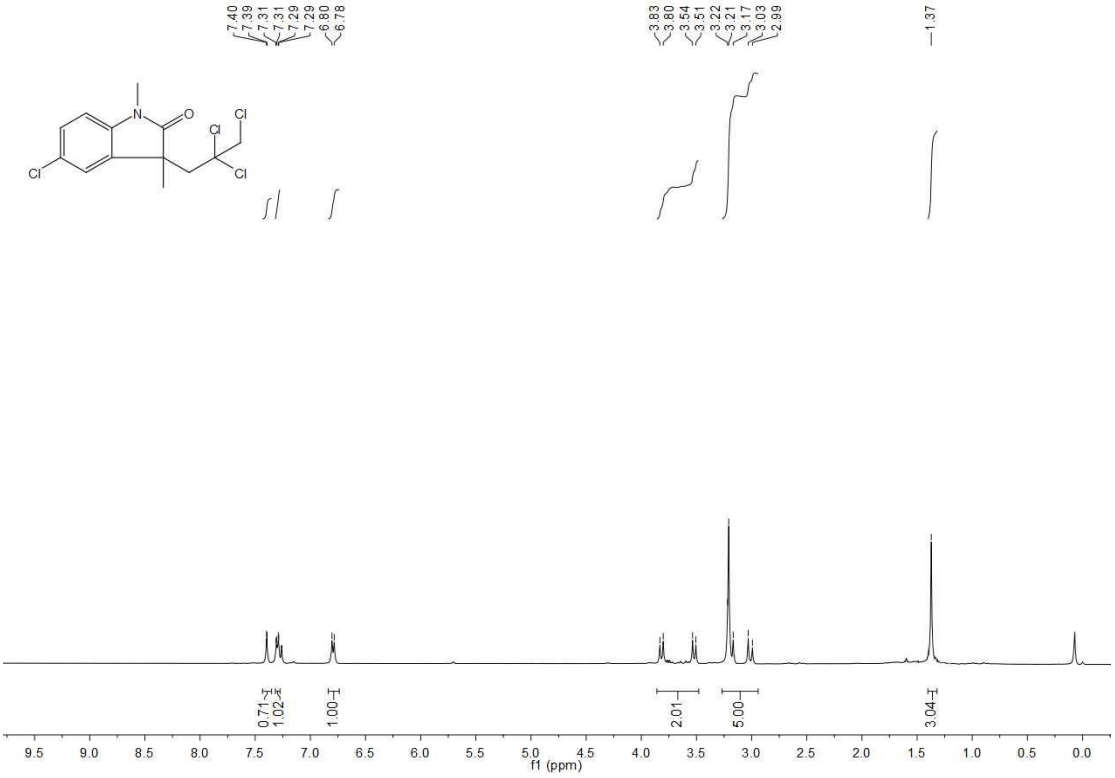

**Compound 4k, $CDCl_3$, 150 MHz**


F
F
F
N
O
Cl
Cl
Cl
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

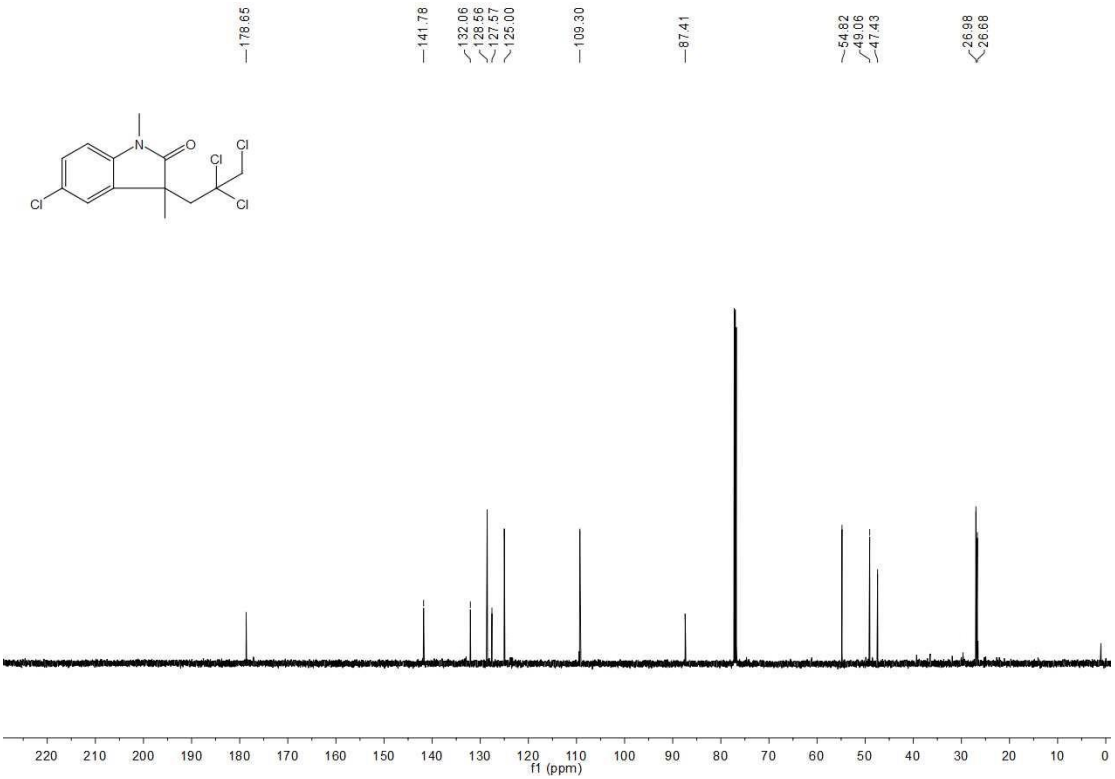

178.52
146.18
130.05
126.26
126.24
126.21
126.18
125.23
124.47
124.25
123.43
122.88
122.85
122.83
122.80
108.17
95.74
59.73
47.84
26.77
26.62
F
F
F
N
O
Cl
Cl
Cl
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**5-Chloro-1,3-dimethyl-3-(2,2,3-trichloropropyl)indolin-2-one**

**Compound 4l, $CDCl_3$, 400 MHz**

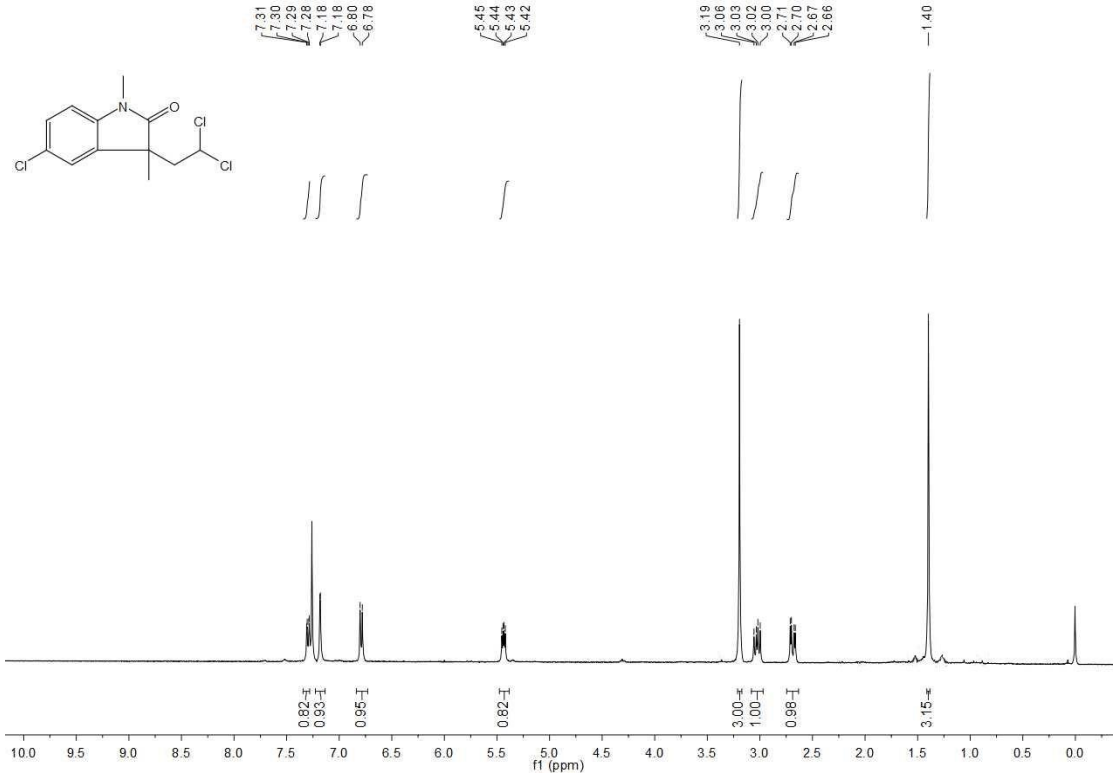



**Compound 4l, $CDCl_3$, 150 MHz**



**5-Chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one**

**Compound 4m, $CDCl_3$, 400 MHz**




**Compound 4m, $CDCl_3$, 150 MHz**