# *Supporting Information*

## Polychlorinated Alkylation Annulation of *N*-arylacrylamide under Electrochemical Conditions

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# 1. General Information

Unless stated otherwise, all reactions were carried out under an air atmosphere. All solvents were purified and dried according to standard methods prior to use. All commercial reagents were used without additional purification. Flash chromatography was carried out with silica gel (200-300 mesh). $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded at 400/500/600 MHz and 100/125 MHz spectrometers in $CDCl_3$. Data are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets); coupling constants (*J*) are in Hertz (Hz). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources.

# 2. General Procedure for the Electrolysis

(1) General Procedure

A 10-mL three-necked round-bottomed flask was charged with the substrate (0.2 mmol), $C_6H_5N_2BF_4$ (5eq) and electrolyte (0.1 M) The flask was equipped with a rubber stopper, a reticulated vitreous carbon (RVC) anode (1 cm x 1 cm x 1 cm) and a platinum plate (1 cm x 1 cm) cathode and then flushed with air. The reaction device in small scale was given in Figure S1a. DCM (4 mL) and $H_2O$ (2 mL) were added. The constant current (10 mA) electrolysis was carried out at room temperature until complete consumption of the substrate (monitored by TLC or $^{1}H$ NMR). The phases were separated and the aqueous phase was extracted with DCM (3 x 20 mL). The combined organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.

(2) Scale up experiment

A 200-mL beaker-type cell was charged with the substrate (6 mmol, 1.05 g), $C_6H_5N_2BF_4$ (5eq) and electrolyte (0.1 M) The flask was equipped with a rubber stopper, a reticulated vitreous carbon (RVC) anode (2 cm x 2 cm x 1 cm) and a platinum plate (2 cm x 2 cm) cathode and then flushed with air. DCM (100 mL) and $H_2O$ (50 mL) were added. The constant current (200 mA) electrolysis was carried out at room temperature until complete consumption of the substrate (monitored by TLC or $^{1}H$ NMR). The phases were separated and the aqueous phase was extracted with DCM (3 x 80 mL). The combined organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.

In addition, we optimized the current size of part of the amplification experiment and found that the yield was 67% under the optimized conditions. The condition: RVC anode (2 cm x 2 cm x 1 cm), Pt cathode (2 cm x 2 cm), constant current = 100 mA, 1a (6 mmol), 2a (100 mL), $C_6H_4N_2BF_4$ (5 eq), $nBu_4NBr$ (0.1 M) and $H_2O$ (50 mL) in an undivided cell under air atmosphere at room temperature. The reaction device in large scale was shown in Figure S1b.

(3) The picture of reaction


Figure S1 (a) The reaction device in small scale; (b) The reaction device in large scale; (c) The reaction constant potential rectifier (DJS-292B).

## 3. CV curves of diazo salt mediator

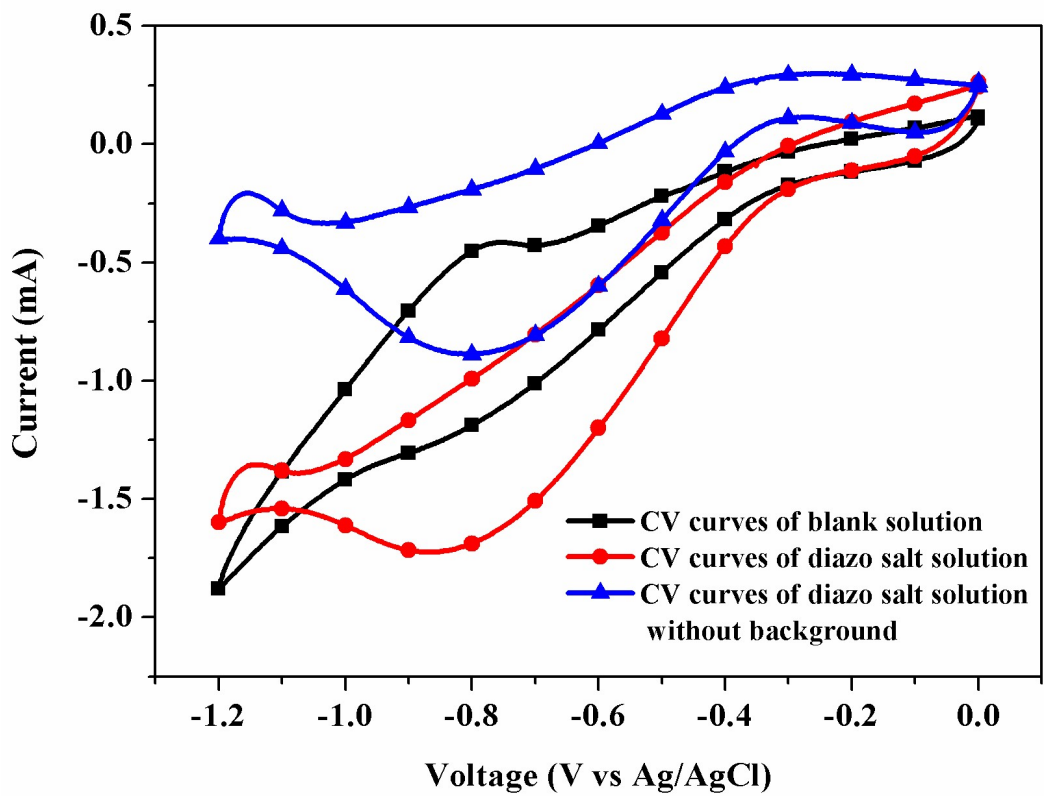
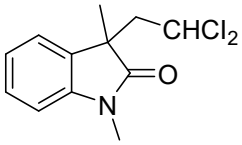



Figure S2 CV curves of $CH_2Cl_2$:$H_2O$ (4:2) containing 0.1 M $nBu_4NBr$ electrolyte solution (blank solution); CV curves of $CH_2Cl_2$:$H_2O$ (4:2) containing 0.1 M $nBu_4NBr$ electrolyte and 5 eq diazo salt solution (diazo salt solution); CV curves of $CH_2Cl_2$:$H_2O$ (4:2) containing 0.1 M $nBu_4NBr$ electrylyte and 5 eq diazo salt solution without background.

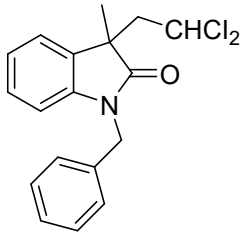
## 4. Characterization of Products



**3-(2,2-dichloroethyl)-1,3,7-trimethylindolin-2-one (3a)**

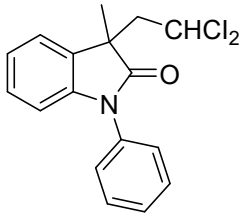
The reaction of **1a** (35.0 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3a** as yellow oil (43.5mg, 88%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.38 (m, 1H), 7.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.47 – 5.35 (m, 1H), 3.23 (s, 3H), 3.11 – 3.01 (m, 1H), 2.73 (dd, *J* = 14.9, 4.1 Hz, 1H), 1.42 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.0, 143.4, 131.0, 128.6, 122.6 (2C), 108.6, 69.6, 50.1, 47.7, 26.4, 24.7. The corresponding other spectral data of this compound can be seen in reference literature.[1]



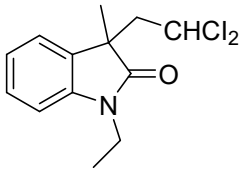

**1-benzyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one (3c)**

The reaction of **1c** (50.2 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3c** as yellow oil (39.3mg, 59%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 4.3 Hz, 4H), 7.23 – 7.17 (m, 3H), 7.07 (m, 1H), 6.82 – 6.76 (m, 1H), 5.45 (dd, *J* = 8.9, 4.4 Hz, 1H), 5.04 – 4.95 (m, 2H), 4.81 (d, *J* = 15.5 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.76 (dd, *J* = 14.9, 4.4 Hz, 1H), 1.45 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.1, 142.6, 135.7, 131.1, 129.3, 128.8, 128.5, 127.9, 127.4, 122.7, 109.7, 69.6, 49.9, 47.2, 44.1, 26.1. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**3-(2,2-dichloroethyl)-3-methyl-1-phenylindolin-2-one (3d)**

The reaction of **1d** (47.4 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3d** as yellow oil (42.6mg, 67%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1). **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 8.8, 6.7 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.29 – 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 6.87 (dd, *J* = 7.1, 3.5 Hz, 1H), 5.49 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.16 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.80 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.52 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.5, 143.4, 134.4, 130.7, 129.6, 128.2, 126.4, 123.2, 122.9, 122.6, 110.0, 69.9, 50.2, 47.3, 26.1. The corresponding other spectral data of this compound can be seen in reference literature.[1]

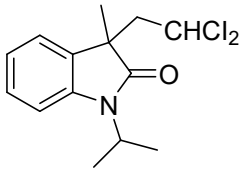


**3-(2,2-dichloroethyl)-1-ethyl-3-methylindolin-2-one (3e)**

The reaction of **1e** (37.4 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3e** as yellow oil (26.8mg, 49%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 7.12 – 7.06 (m, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.40 (dd, *J* = 9.2, 4.2 Hz, 1H), 3.85 (m, 1H), 3.69 (m, 1H), 3.10 – 3.02 (m, 1H), 2.71 (dd, *J* = 14.8, 4.2 Hz, 1H), 1.39 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.6, 142.5, 131.3, 128.6, 122.8, 122.5, 108.8, 69.7, 49.9, 47.1, 34.8, 25.8, 12.2.

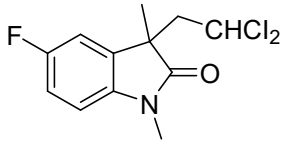
HRMS (ESI) m/z calcd for $C_{13}H_{15}Cl_2NONa^+$ $(M+Na)^+$ 294.0423, found 294.0424. The corresponding other spectral data of this compound can be seen in reference literature.[4]




**3-(2,2-dichloroethyl)-1-isopropyl-3-methylindolin-2-one (3f)**

The reaction of **1f** (47.4 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3f** as yellow oil (26.1mg, 46%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

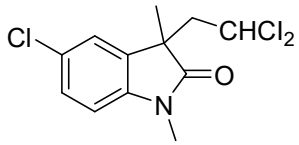
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 3.0 Hz, 1H), 7.05 (m, 3H), 5.40 (dd, *J* = 9.2, 4.2 Hz, 1H), 4.71 – 4.58 (m, 1H), 3.04 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.74 – 2.62 (m, 1H), 1.46 (dd, *J* = 7.1, 3.4 Hz, 8H), 1.37 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.0, 142.5, 134.3, 128.3, 122.9, 122.1, 110.4, 70.3, 50.0, 46.9, 43.7, 26.8, 19.3, 18.9. HRMS (ESI) m/z calcd for $C_{14}H_{17}Cl_2NONa^+$ $(M+Na)^+$ 308.0579, found 308.0575. The corresponding other spectral data of this compound can be seen in reference literature.[4]




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

The reaction of **1g** (38.6 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3g** as yellow oil (37.7mg, 68%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

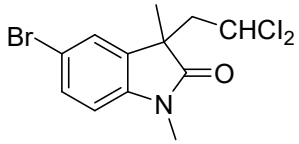
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.99 (dd, *J* = 7.7, 2.6 Hz, 1H), 6.82 (dd, *J* = 8.5, 4.1 Hz, 1H), 5.44 (dd, *J* = 8.9, 4.6 Hz, 1H), 3.22 (s, 3H), 3.07 – 3.01 (m, 1H), 2.71 (dd, *J* = 14.9, 4.6 Hz, 1H), 1.42 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.6, 159.9, 159.4, 139.2, 132.6, 132.1, 115.0, 114.8, 111.1, 110.8, 109.2, 109.1, 69.4, 49.9, 47.3, 46.8, 26.6, 25.0. The corresponding other spectral data of this compound can be seen in reference literature.[1]




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

The reaction of **1h** (41.9 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3h** as yellow oil (48.9mg, 84%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

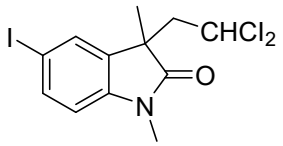
**$^1$H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.42 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.20 (s, 3H), 3.03 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.69 (dd, *J* = 14.9, 4.5 Hz, 1H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.6, 142.0, 132.9, 128.6, 128.2, 123.3, 109.6, 69.4, 49.9, 47.5, 26.6, 25.5. The corresponding other spectral data of this compound can be seen in reference literature.[1]




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

The reaction of **1i** (50.8 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3i** as yellow oil (43.6mg, 65%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

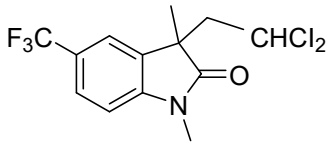
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 5.42 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.19 (s, 3H), 3.07 – 2.99 (m, 1H), 2.69 (dd, *J* = 14.9, 4.5 Hz, 1H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.6, 142.5, 132.5, 131.5, 125.9, 117.2, 110.1, 69.3, 49.9, 47.4, 26.6, 25.4. The corresponding other spectral data of this compound can be seen in reference literature.[2]




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

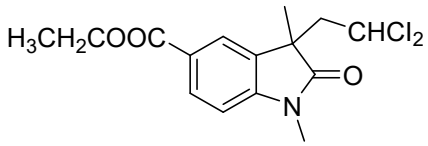
The reaction of **1j** (60.2 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3j** as yellow oil (52.0mg, 68%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 5.40 (dd, *J* = 9.1, 4.3 Hz, 1H), 3.18 (s, 3H), 3.06 – 2.99 (m, 1H), 2.68 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.4, 143.1, 137.5, 133.6, 131.5, 110.7, 85.2, 69.4, 49.9, 47.3, 26.6, 25.5. The corresponding other spectral data of this compound can be seen in reference literature.[2]




**3-(2,2-Dichloroethyl)-1,3-dimethyl-5-(trifluoromethyl) indolin-2-one (3k)**

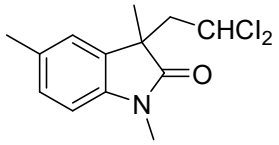
The reaction of **1k** (48.6 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3k** as yellow oil (49.8mg, 77%);The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1). **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.39 (dd, *J* = 8.9, 4.6 Hz, 1H), 3.25 (s, 3H), 3.08 – 3.03 (m, 1H), 2.75 (dd, *J* = 14.9, 4.6 Hz, 1H), 1.43 (s, 3H).**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.1, 146.3, 132.4, 129.7,127.7,126.8 126.5, 125.6, 125.3, 122.8, 119.8,119.3, 108.5, 69.2, 49.8, 47.2, 26.7, 25.5. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**ethyl 3-(3,3-2,2-dichloroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3l)**

The reaction of **1l** (49.4 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3l** as yellow oil (27.7mg, 42%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

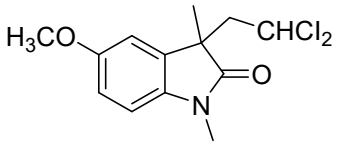
**$^1$H NMR** (400 MHz, Chloroform-d) δ 8.02 (dd, J = 8.2, 1.7 Hz, 1H), 7.80 (dd, J = 7.7, 1.6 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 5.32 (dd, J = 9.5, 4.1 Hz, 1H), 4.33 (m, 2H), 3.18 (s, 2H), 3.00 (dd, J = 14.9, 9.2 Hz, 1H), 2.71 (dd, J = 14.9, 4.3 Hz, 1H), 1.40 – 1.30 (m, 6H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.3, 166.3, 147.5, 131.3, 130.8, 125.0, 123.9, 108.1, 69.5, 61.1, 49.9, 47.0, 26.7, 25.5, 14.4. The corresponding other spectral data of this compound can be seen in reference literature.[3]




**3-(2,2-dichloroethyl)-1,3,5-trimethylindolin-2-one (3m)**

The reaction of **1m** (37.8 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3m** as yellow oil (47.2mg, 87%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

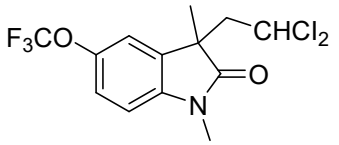
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.76 – 6.69 (m, 1H), 5.29 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.25 (s, 3H), 3.09 (dd, *J* = 15.4, 10.0 Hz, 1H), 2.96 (dd, *J* = 14.9, 3.9 Hz, 1H), 1.49 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.3, 141.1, 132.4, 131.0, 128.9, 123.5, 108.4, 69.7, 50.1, 47.3, 26.5, 25.5, 21.2. The corresponding other spectral data of this compound can be seen in reference literature.[1]




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

The reaction of **1n** (41.0 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3n** as yellow oil (34.2mg, 62%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

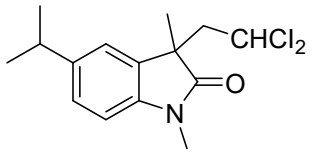
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 6.87 – 6.76 (m, 3H), 5.42 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.82 (s, 3H), 3.19 (s, 3H), 3.02 (dd, *J* = 9.7, 5.1 Hz, 1H), 2.68 (dd, *J* = 14.9, 4.2 Hz, 1H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.8, 156.2, 136.9, 132.5, 112.4, 110.5, 108.9, 69.6, 55.9, 50.1, 47.6, 26.6, 25.5. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**3-(2,2-dichloroethyl)-1,3-dimethyl-5- (trifluoromethoxy) indolin-2-one (3o)**

The reaction of **1o** (51.8 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3o** as yellow oil (58.4mg, 85%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

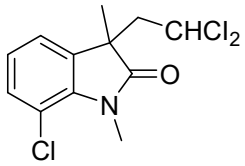
**$^1$H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.42 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.20 (s, 3H), 3.03 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.69 (dd, *J* = 14.9, 4.5 Hz, 1H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.7, 144.8, 142.0, 129.8, 127.7, 121.8, 116.9, 109.1, 69.2, 49.9, 47.5, 26.7, 25.4. The corresponding other spectral data of this compound can be seen in reference literature.[1]




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

The reaction of **1p** (43.4 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3p** as yellow oil (54.2mg, 90%); Purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1);

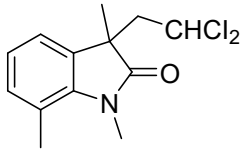
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.76 – 6.69 (m, 1H), 5.29 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.25 (s, 3H), 3.09 (dd, *J* = 15.4, 10.0 Hz, 1H), 2.96 (dd, *J* = 14.9, 3.9 Hz, 1H), 1.49 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.3, 147.5, 131.3, 130.8, 129.7, 123.9, 108.1, 69.5, 49.9, 47.0, 26.7, 25.5, 21.0, 14.4, 14.2. **HRMS** (ESI) m/z calcd for $C_{15}H_{19}Cl_2NONa^+$ $(M+Na)^+$ 322.0736, found 322.0735. **Molecular formula** $C_{15}H_{19}Cl_2NO$' requires C, 63.3; H, 4.3; N, 5.9%'.




**7-chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (3q)**

The reaction of **1q** (41.9 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3q** as yellow oil (14.8mg, 25%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

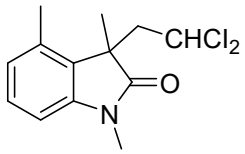
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.07 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.04 – 7.00 (m, 1H), 5.39 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.58 (s, 4H), 3.03 (dd, *J* = 14.8, 9.0 Hz, 1H), 2.68 (dd, *J* = 14.9, 4.5 Hz, 1H), 1.39 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.3, 139.3, 133.9, 130.9, 123.5, 121.2, 116.3, 69.4, 50.2, 47.0, 29.9, 25.8. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**3-(2,2-dichloroethyl)-1,3,7-trimethylindolin-2-one (3r)**

The reaction of **1r** (37.8 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3r** as yellow oil (47.5mg, 87%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

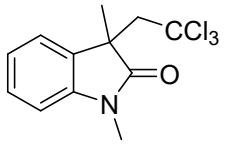
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.07 – 6.97 (m, 3H), 5.37 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.48 (s, 3H), 3.06 – 2.99 (m, 1H), 2.71 – 2.60 (m, 1H), 2.58 (s, 3H), 1.37 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.6, 141.1, 132.4, 131.7, 122.7, 120.5, 117.2, 69.8, 50.4, 46.5, 29.8, 25.8, 19.1. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**3-(2,2-dichloroethyl)-1,3,4-trimethylindolin-2-one (3t)**

The reaction of **1t** (37.8 mg, 0.2 mmol) and **2a** (192.0 mg, 1.0 mmol) gave **3t** as yellow oil (35.7mg, 66%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

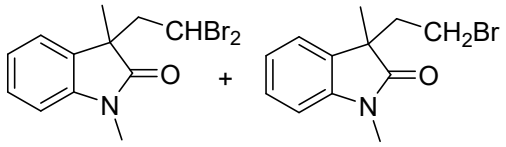
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.15 – 7.09 (m, 1H), 7.00 (d, *J* = 1.6 Hz, 1H), 6.75 (d, *J* = 3.4 Hz, 1H), 5.39 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.19 (s, 3H), 3.05 – 2.99 (m, 1H), 2.68 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.37 (s, 3H), 1.38 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.3, 141.4, 134.1, 132.5, 129.8, 128.9, 108.5, 69.7, 50.1, 47.4, 26.6, 25.5, 21.2. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**1,3-dimethyl-3-(3,3,3-triiodo-3λ$^6$-prop-2-yn-1-yl)indolin-2-one (3u)**

The reaction of **1a** (35.0 mg, 0.2 mmol) and **2b** (4ml) gave **3u** as yellow oil (58.2mg, 79%); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 3.74 – 3.65 (m, 1H), 3.34 (d, *J* = 15.3 Hz, 1H), 3.24 (s, 3H), 1.40 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 178.7, 143.3, 129.7, 128.5, 125.7, 122.1, 108.4, 96.1, 59.8, 48.0, 26.8, 26.6. The corresponding other spectral data of this compound can be seen in reference literature.[1]




**3-(2,2-Dibromoethyl)-1,3-dimethylindolin-2-one (3v) and 3-(2-Bromoethyl)-1,3-dimethylindolin-2-one (3w)**

The reaction of **1a** (35.0 mg, 0.2 mmol) and **2c** (4ml) gave **3v, 3w** as yellow oil (41.2mg, 67%, 2:1); The product was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 0.75H), 7.25 (d, *J* = 1.2 Hz, 0.29H), 7.19 (m, 1H), 7.14 – 7.08 (m, 1H), 6.89 – 6.84 (m, 1H), 5.30 (dd, *J* = 9.5, 4.3 Hz, 0.31H), 3.28 (dd, *J* = 15.1, 9.6 Hz, 0.29H), 3.22 (s, 2H), 3.21 (s, 1H), 3.10–2.93 (m, 2H), 2.52 (m, *J* = 13.6, 11.2, 5.9 Hz, 0.75H), 2.31 (m, *J* = 13.6, 11.3, 4.8 Hz, 0.78H), 1.39 (s, 2H), 1.38 (s, 1H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 179.6, 179.0, 143.1, 142.9, 132.4, 129.7, 128.8, 128.3, 122.6, 121.9, 108.8, 108.4, 51.5, 50.1, 48.6, 41.1, 40.5, 27.2, 26.5, 26.3, 25.5, 23.8. The corresponding other spectral data of this compound can be seen in reference literature.[1]

# 5. References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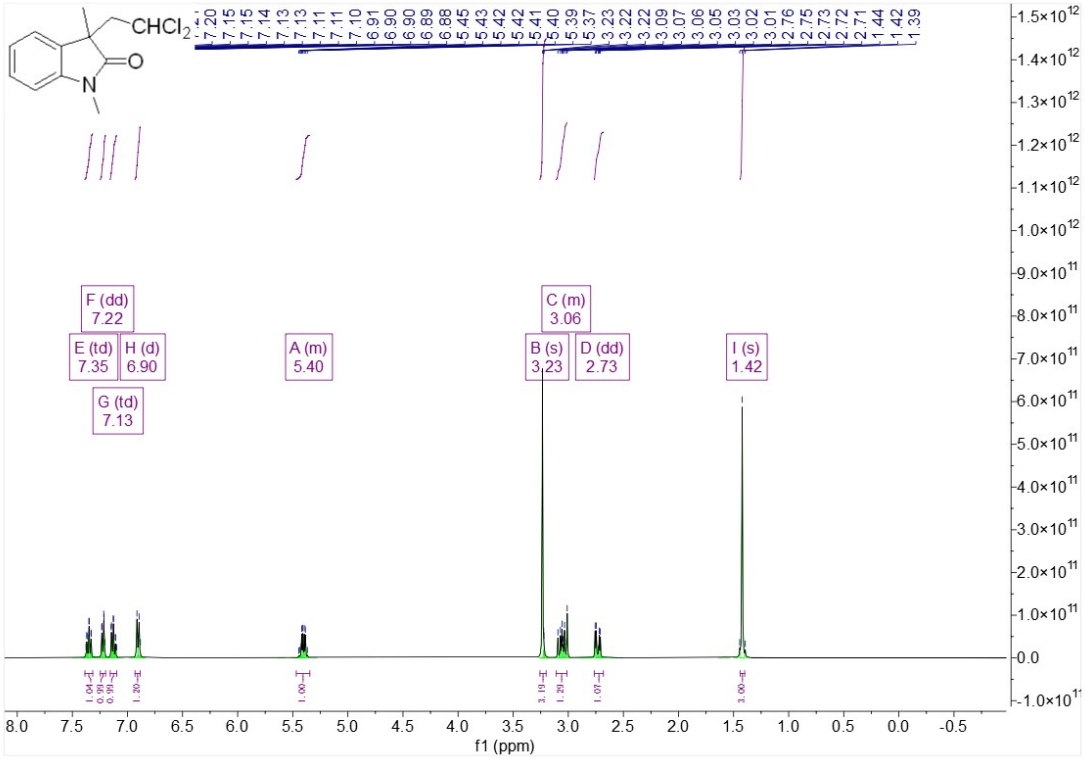
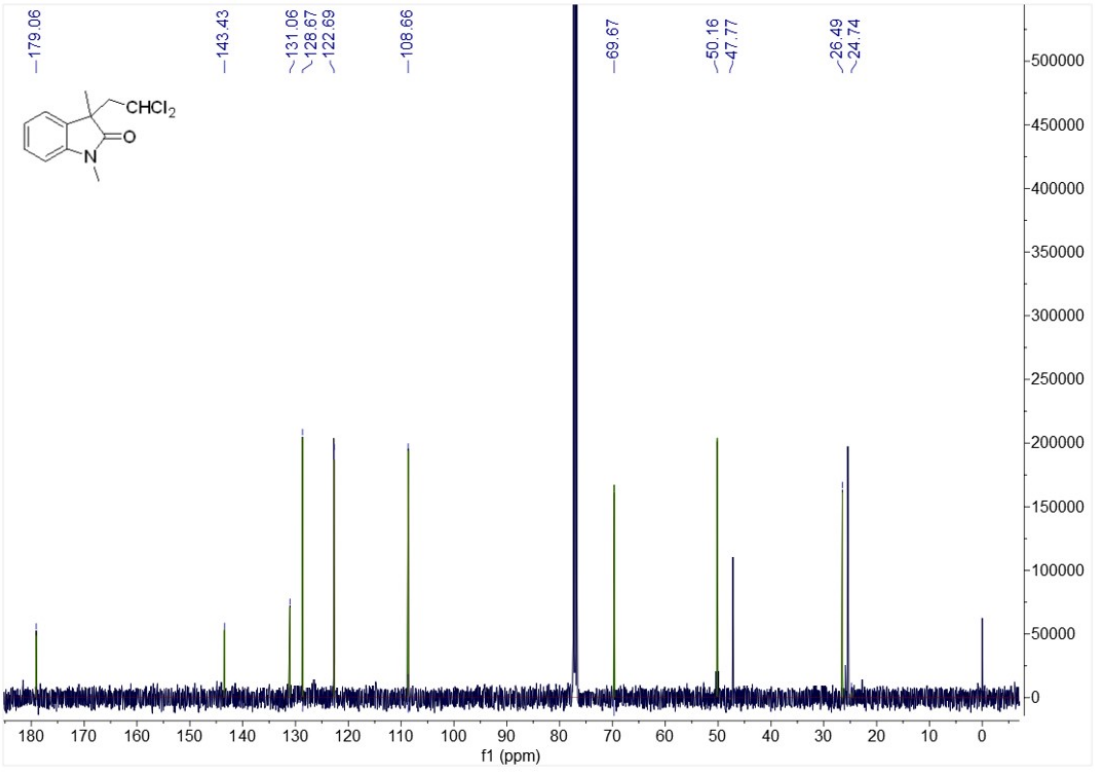
5 P. Xiong, H.-H. Xu, and H.-C. Xu, Metal- and Reagent-Free Intramolecular Oxidative Amination of Tri- and Tetrasubstituted Alkenes, J. Am. Chem. Soc., 2017, **139**, 2956.

# 6. NMR spectra

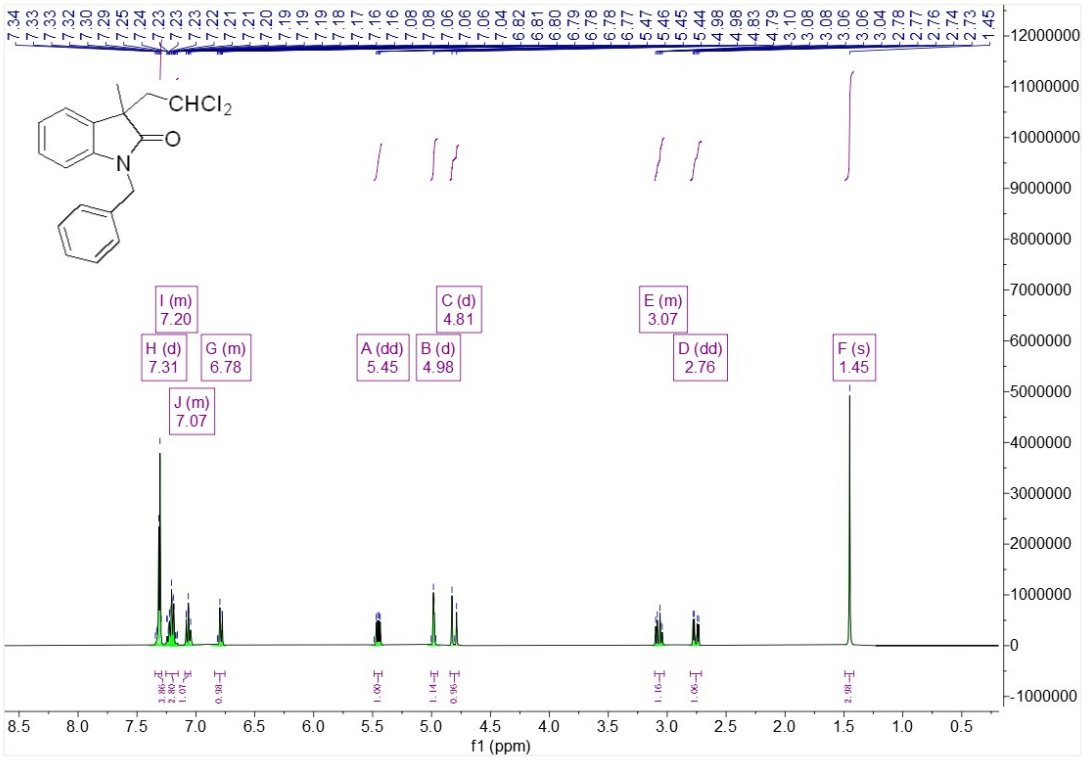
**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3a**



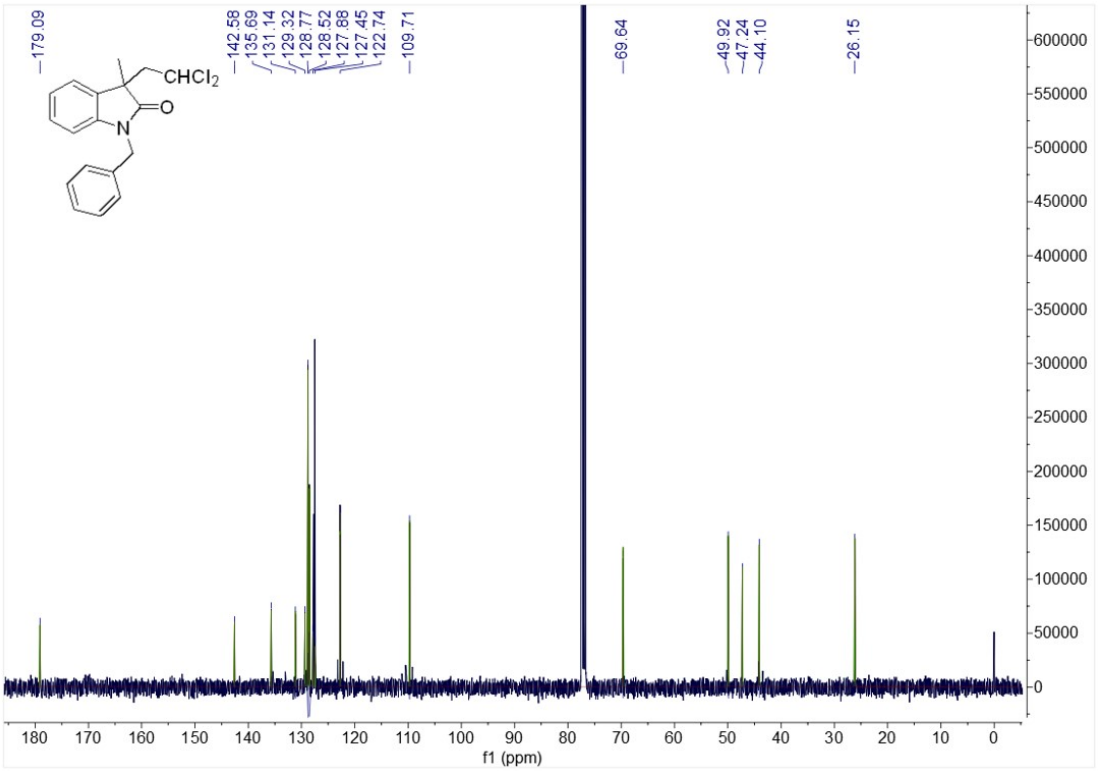

**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3a**



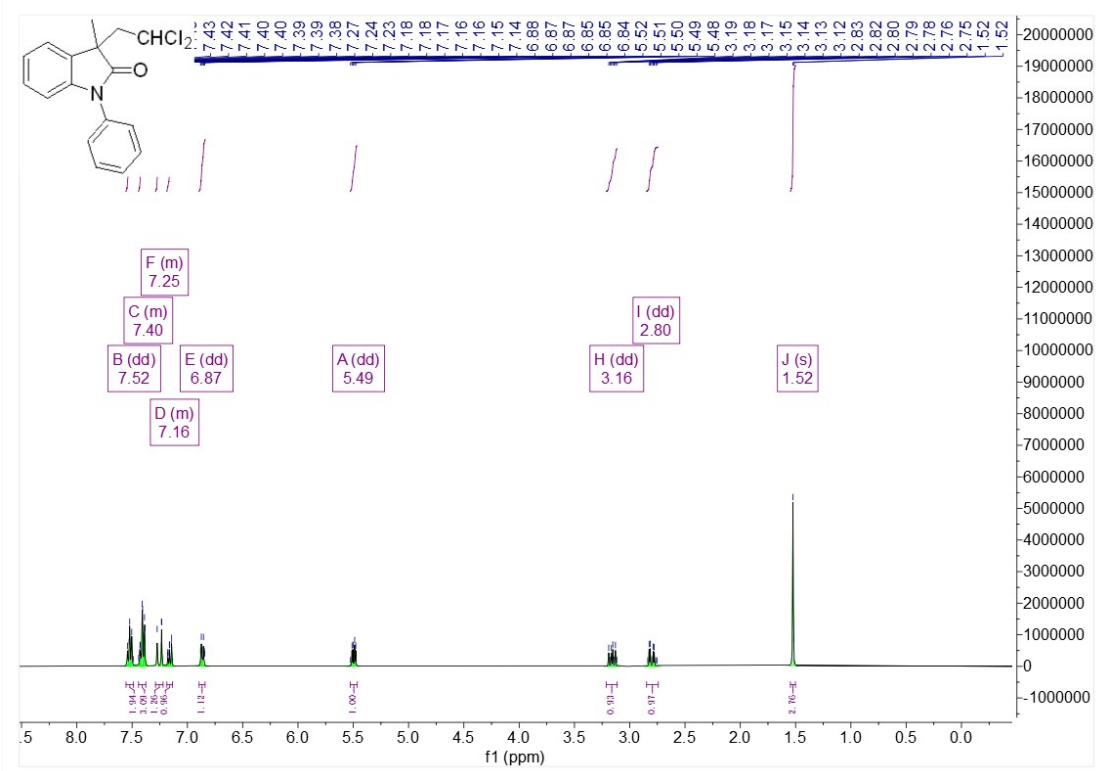

**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3c**



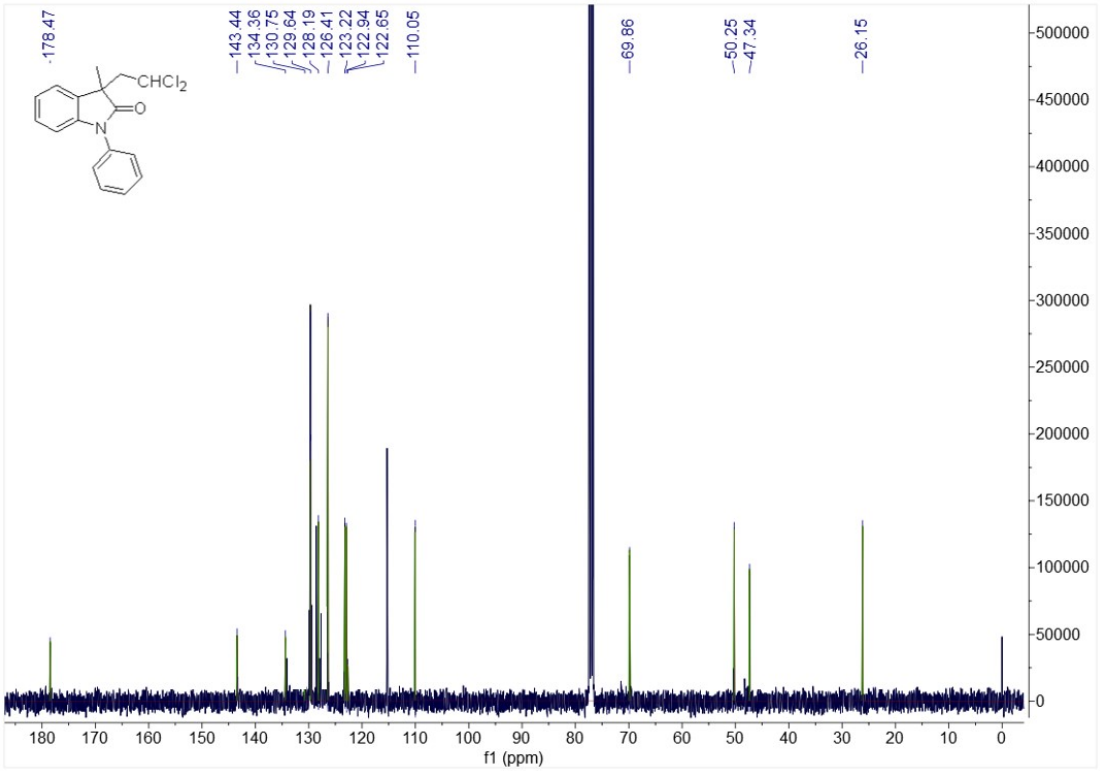

**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3c**




**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3d**




**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3d**

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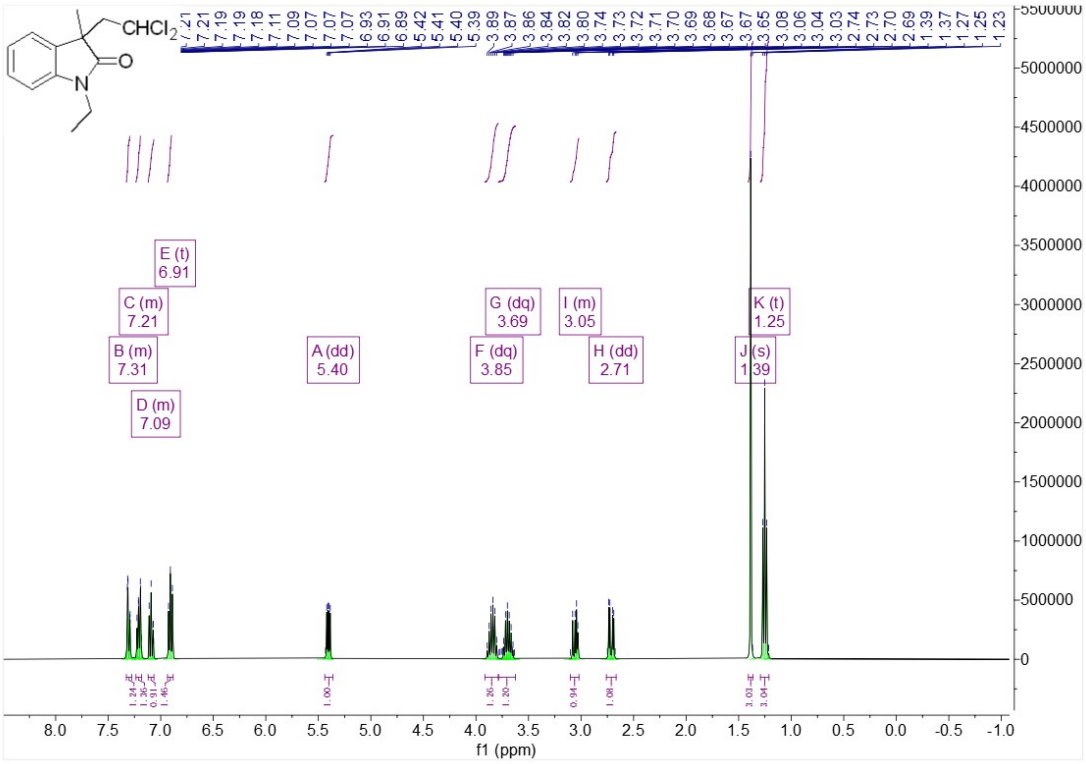
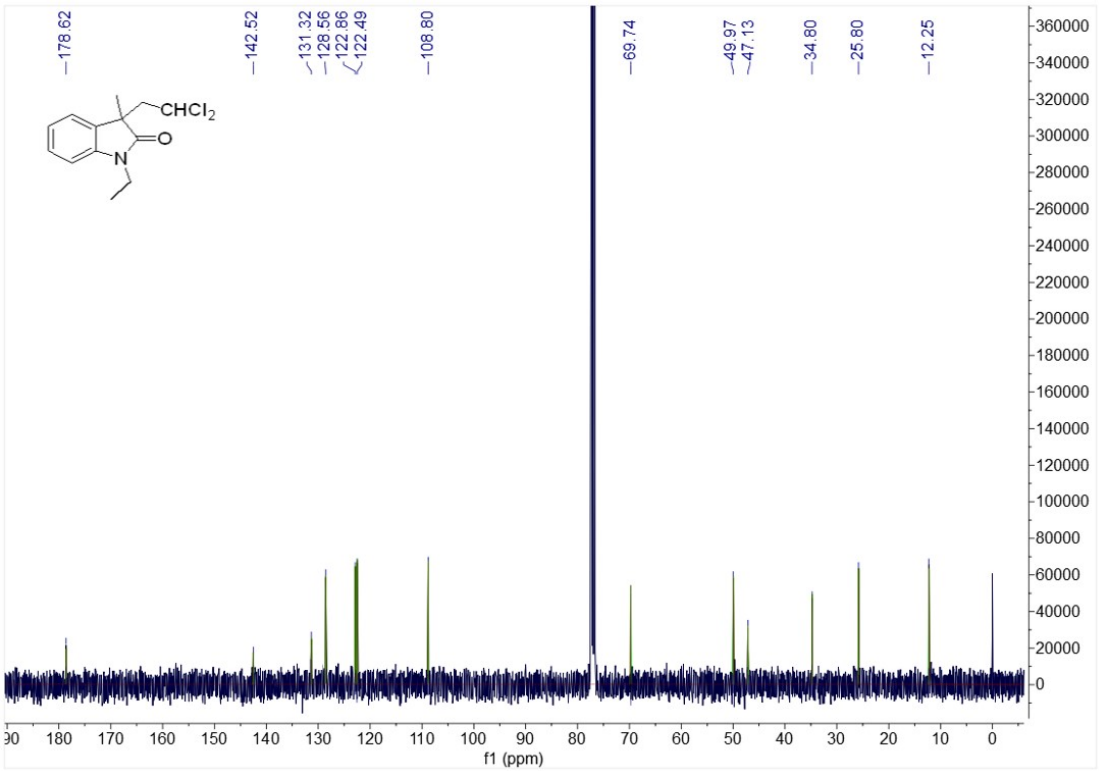
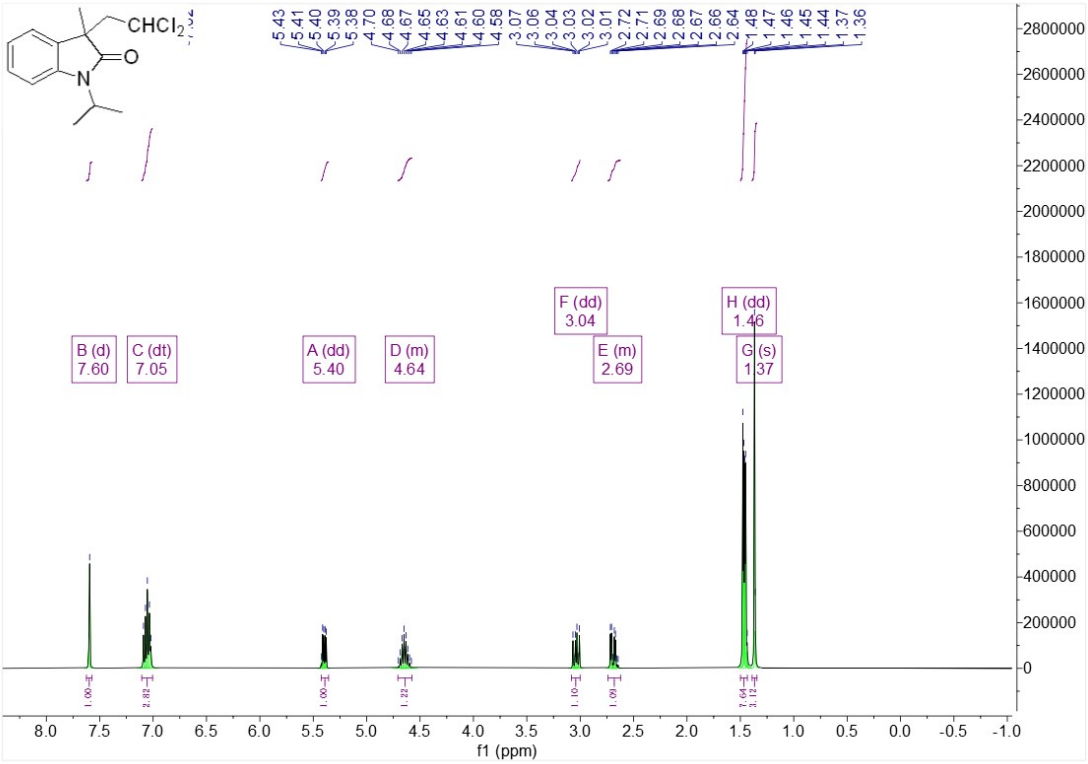



**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3e**




**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3f**

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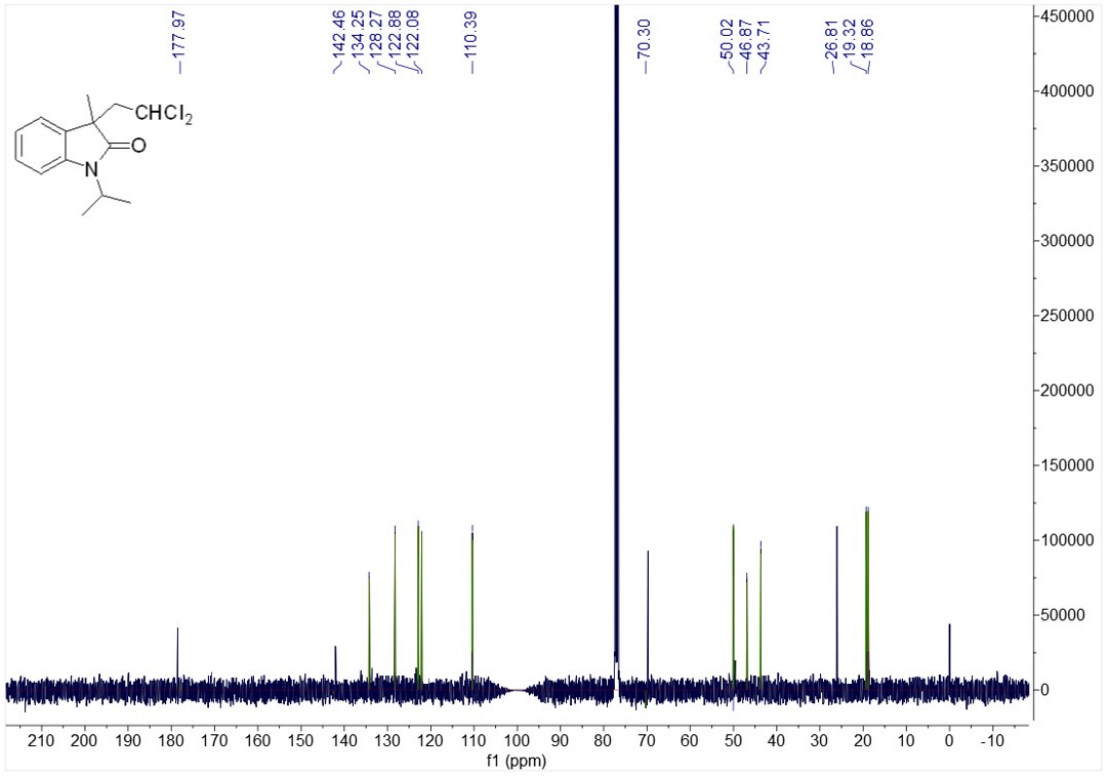
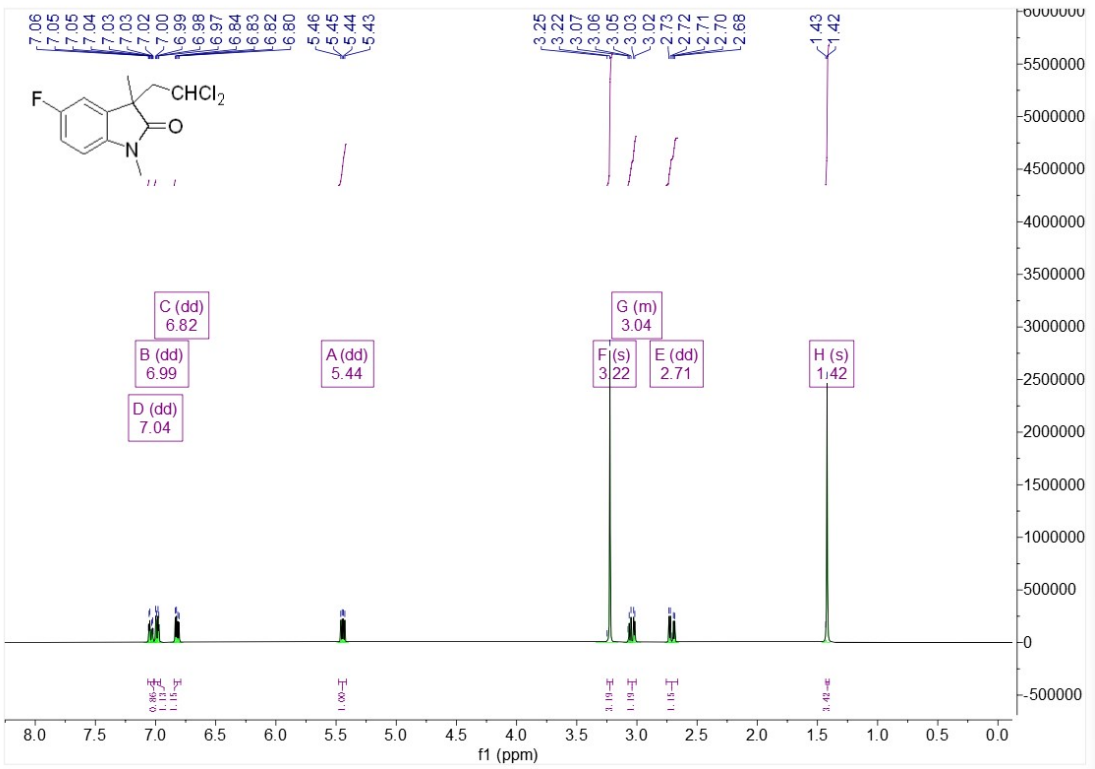



**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3g**

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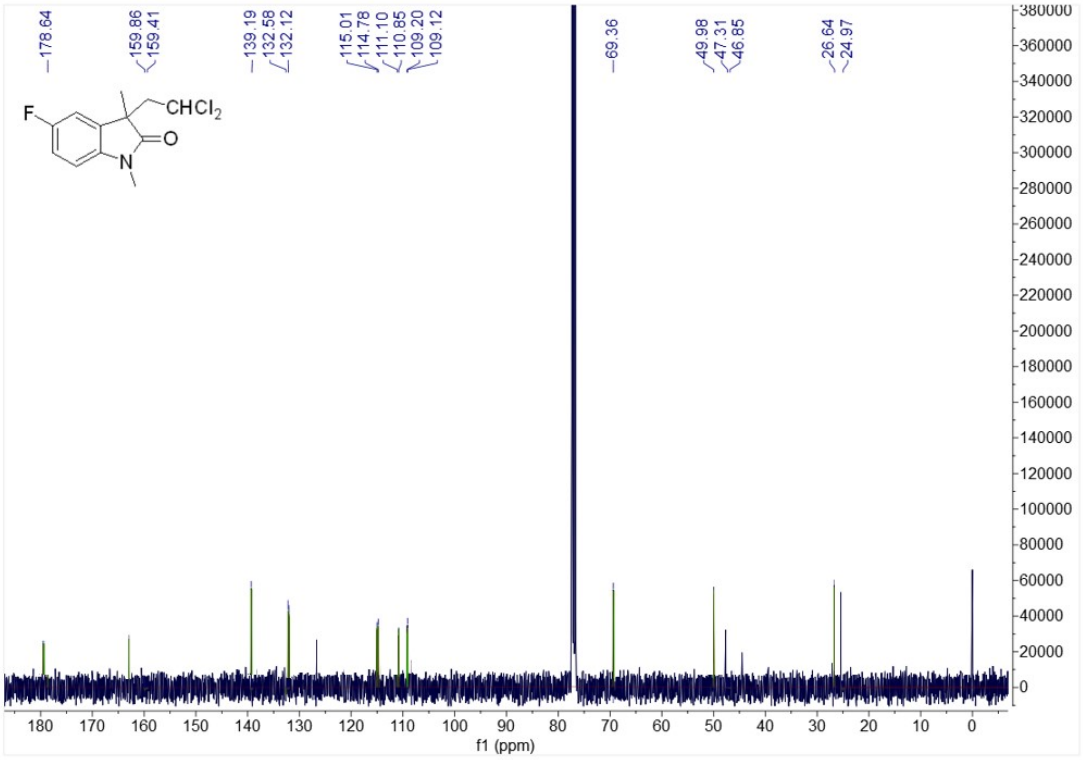
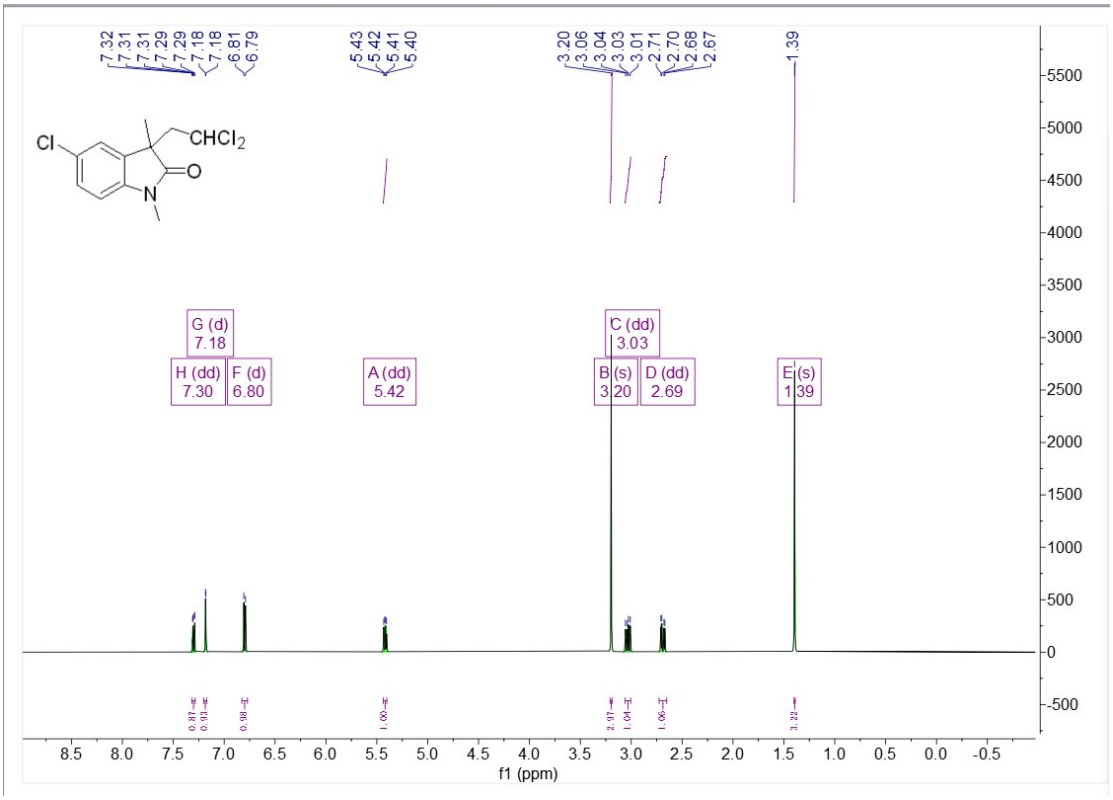



**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3h**

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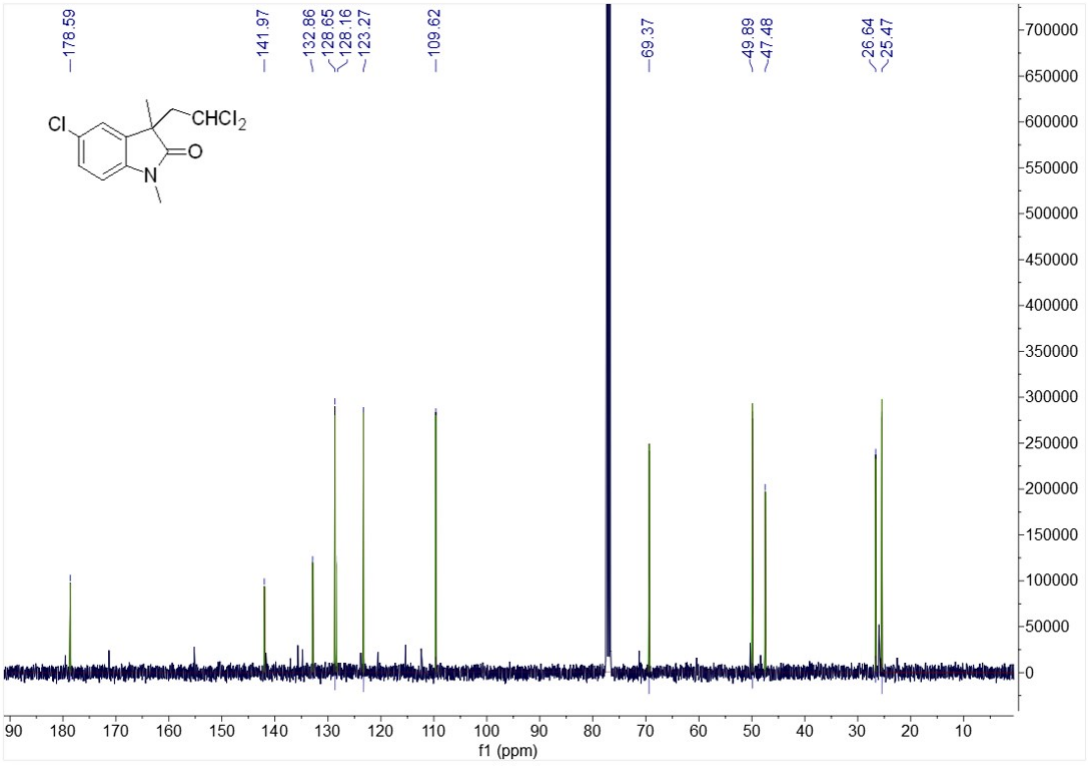
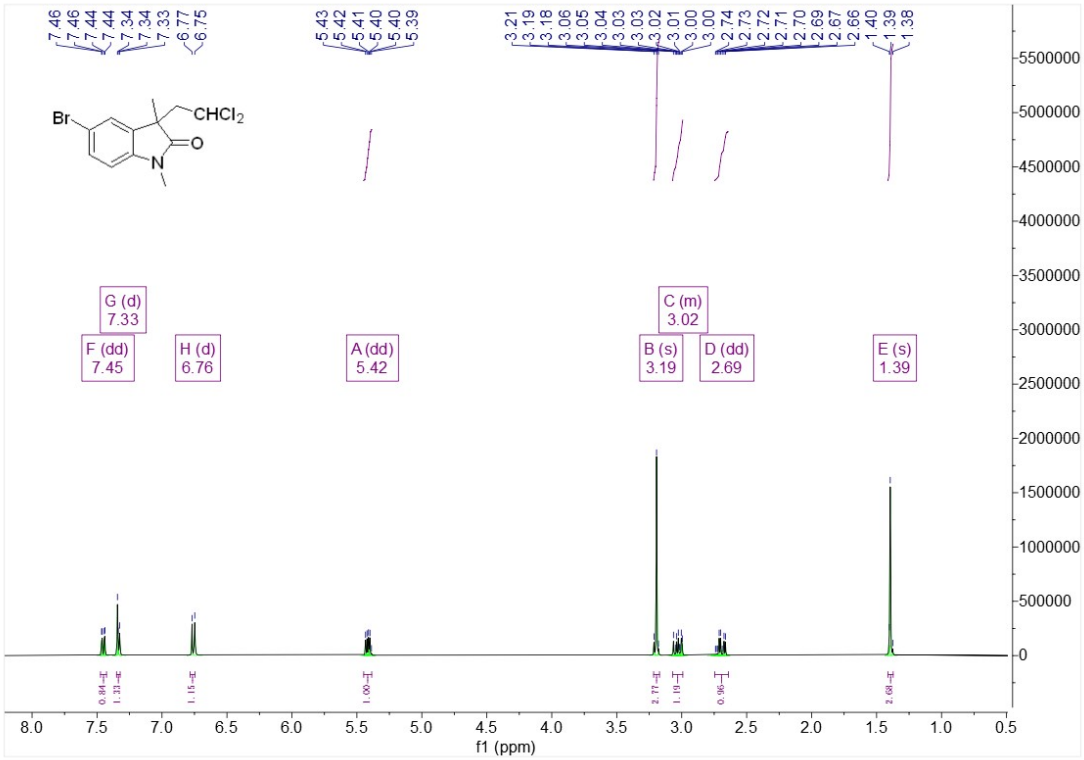



**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3i**

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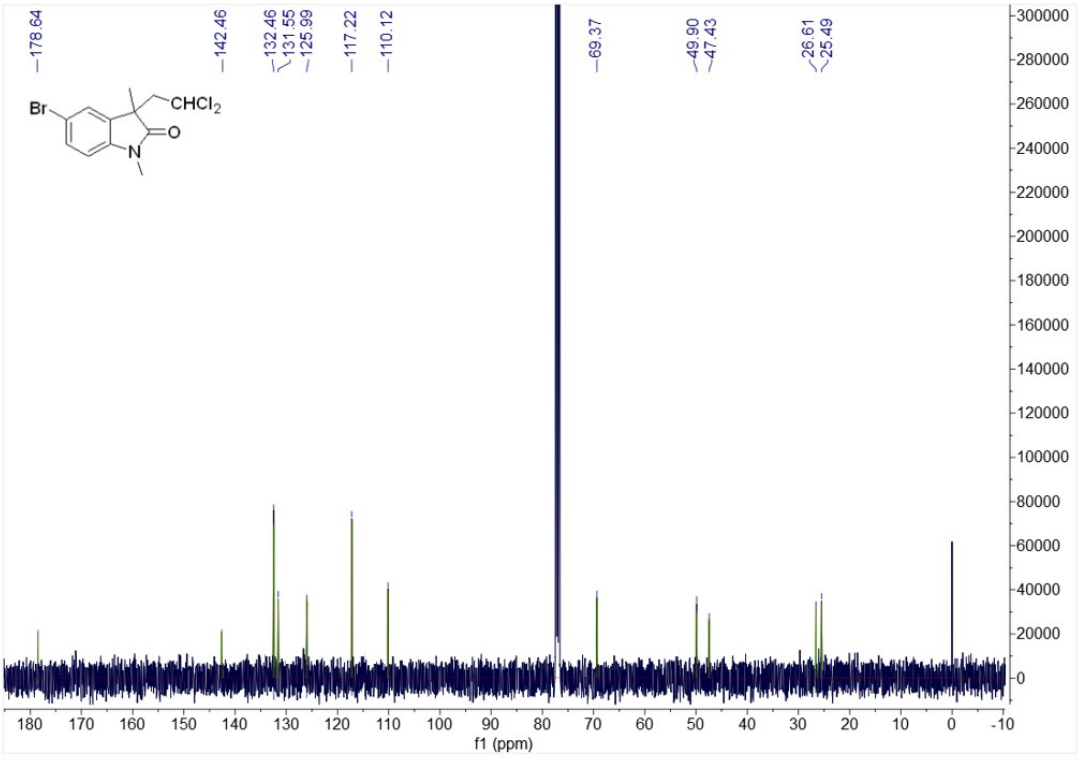


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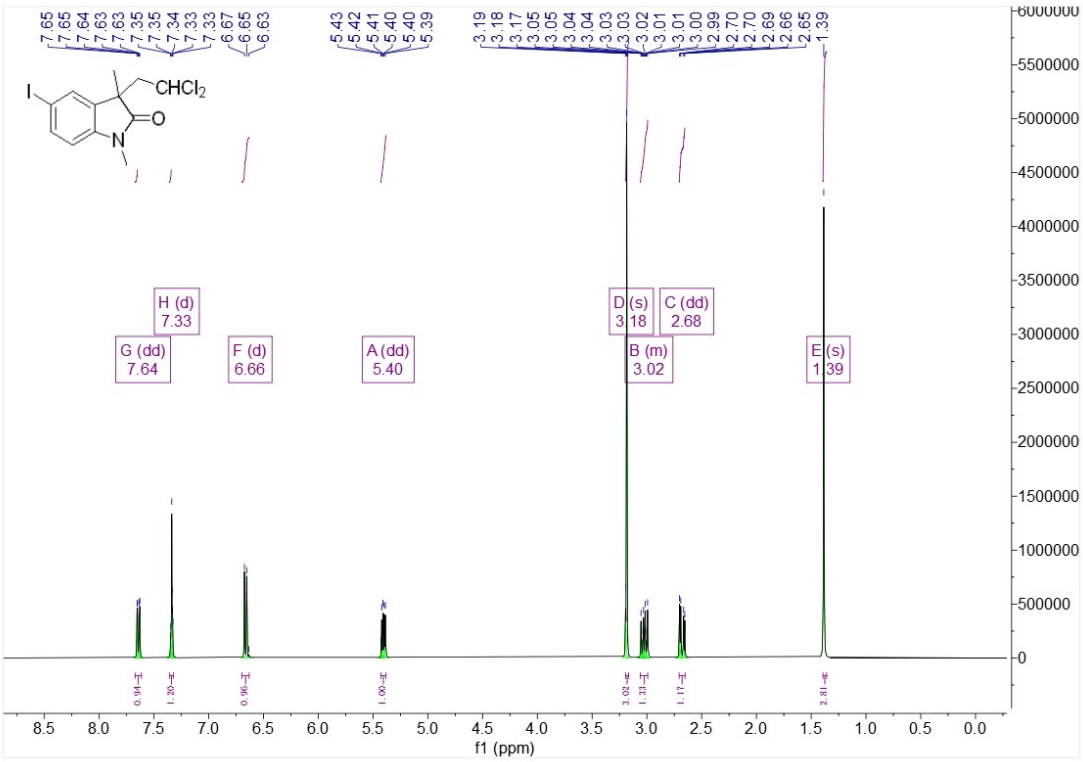


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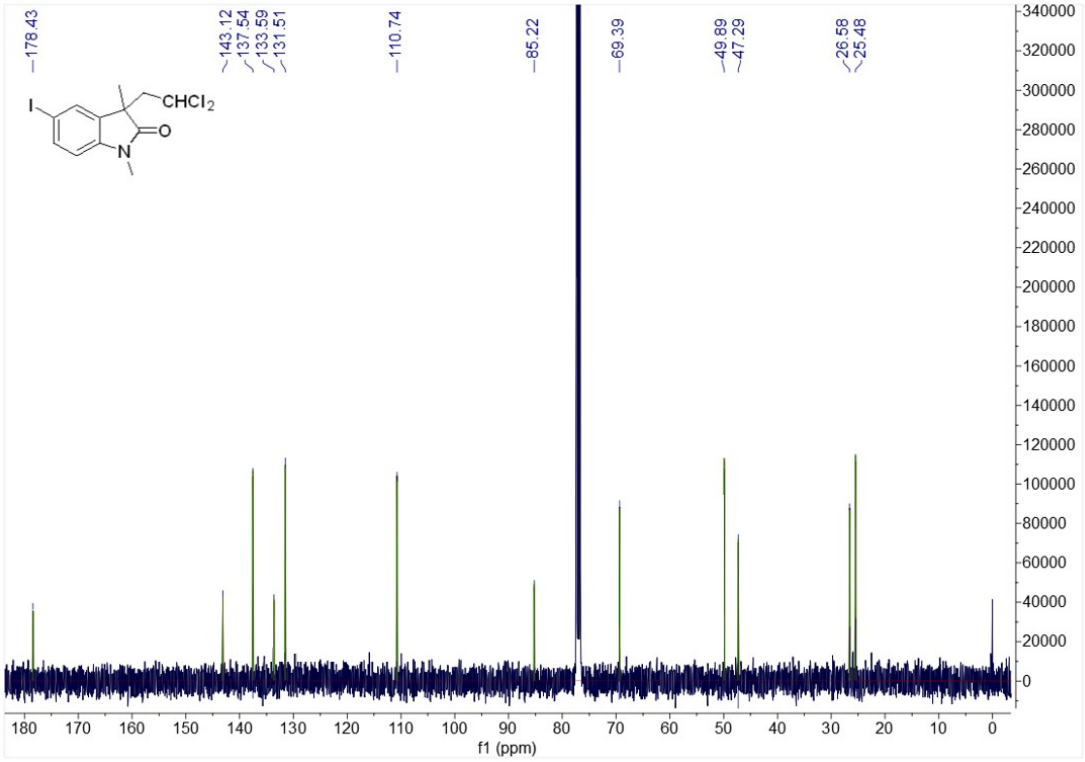


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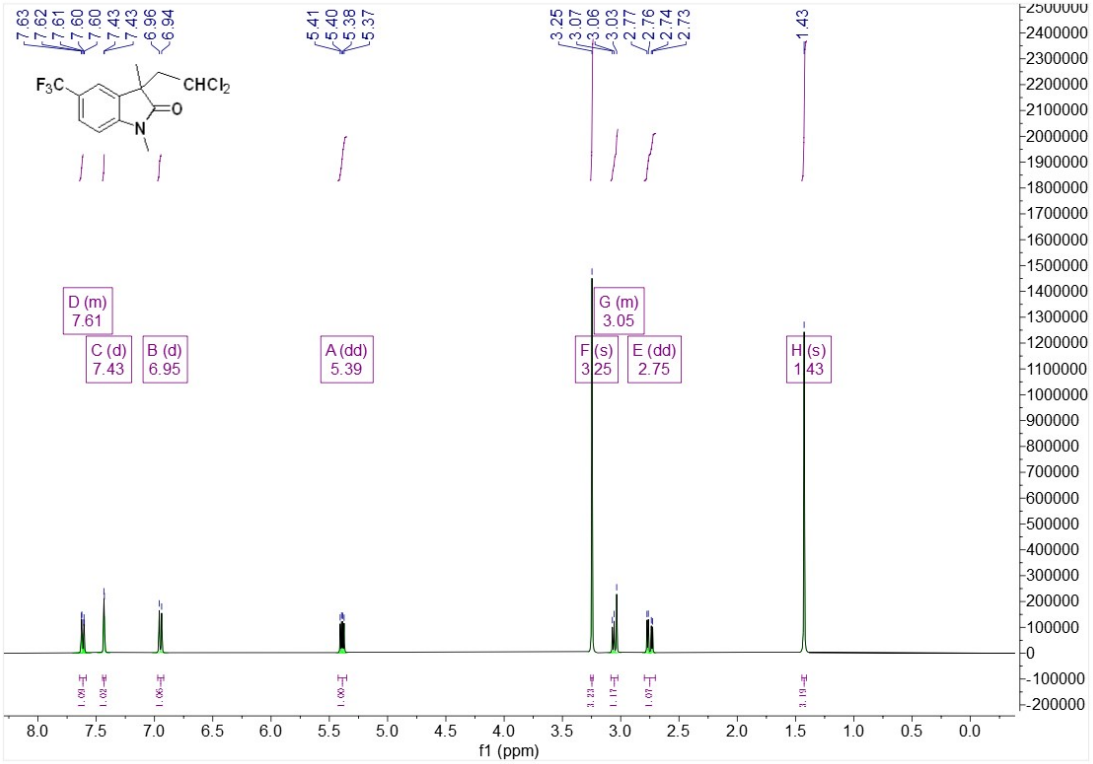


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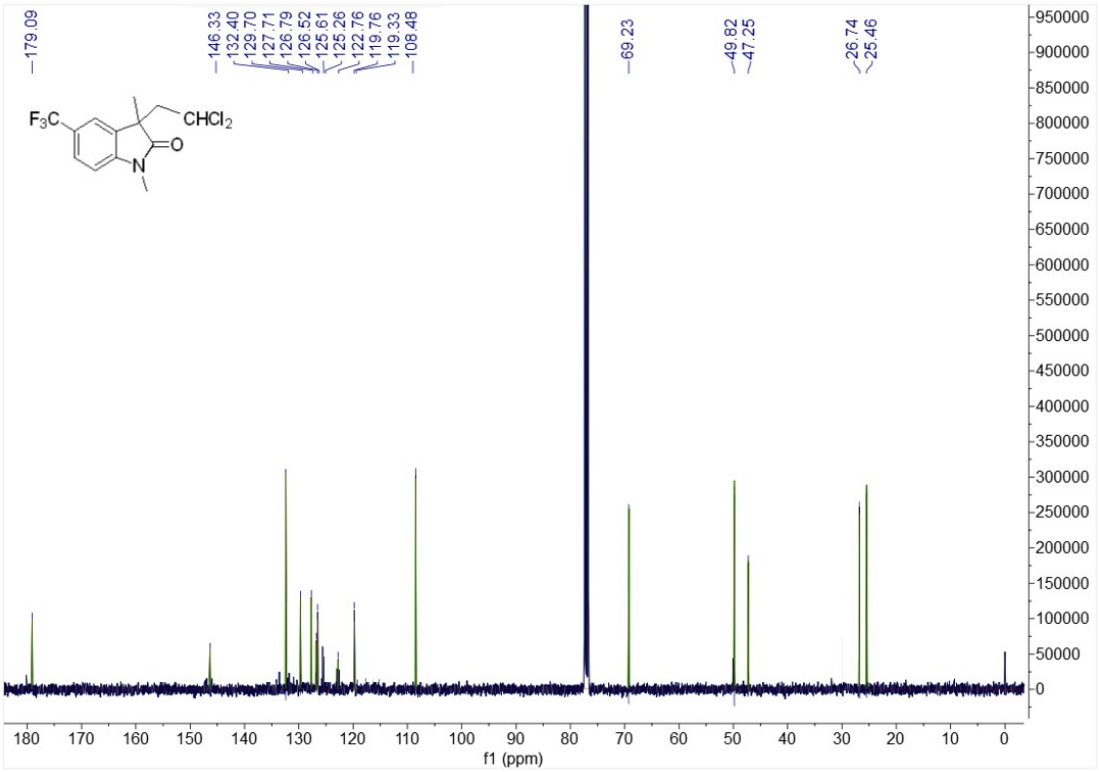


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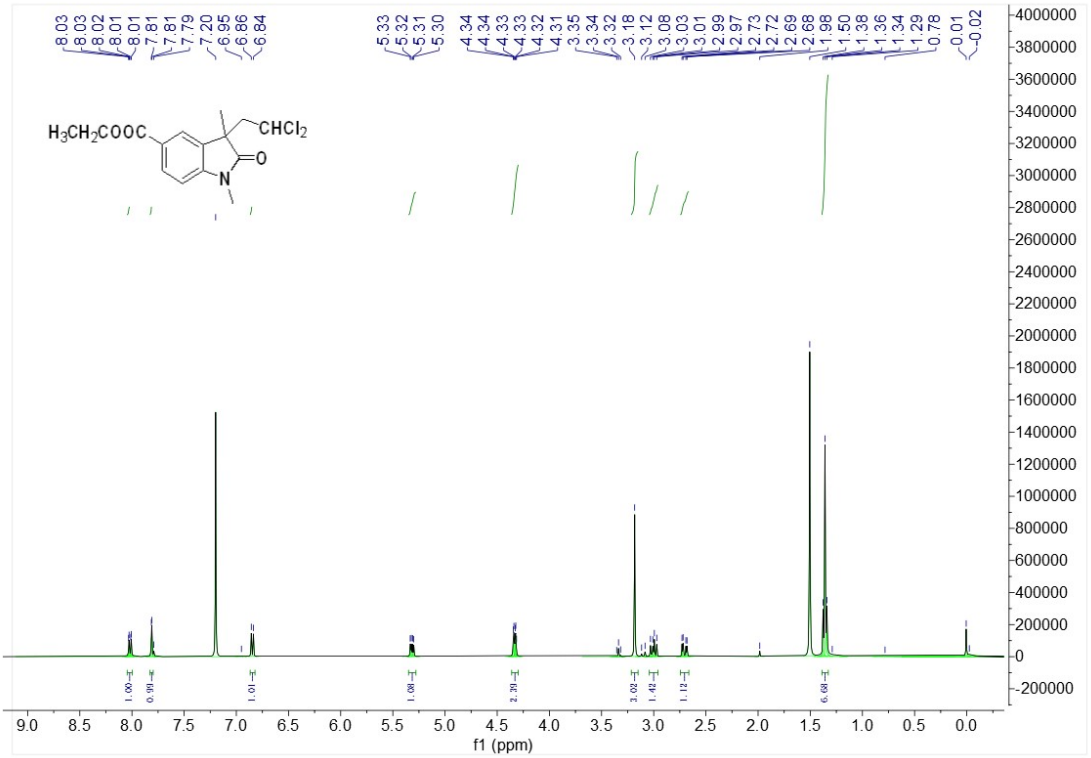


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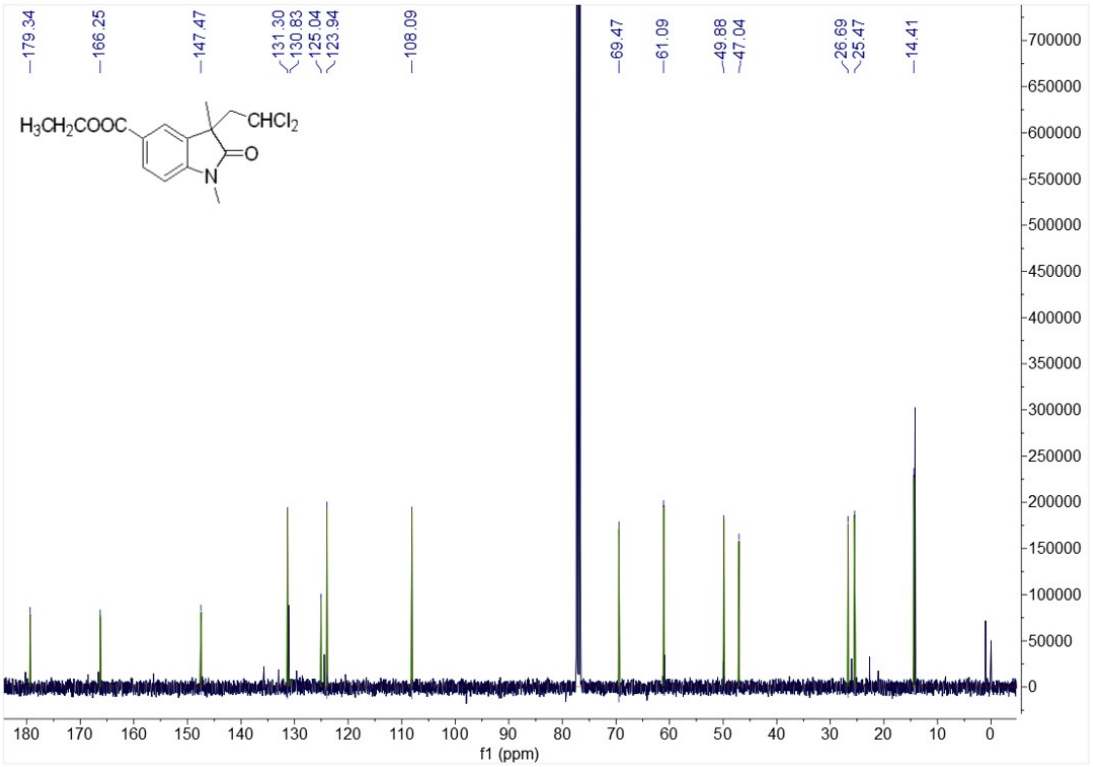


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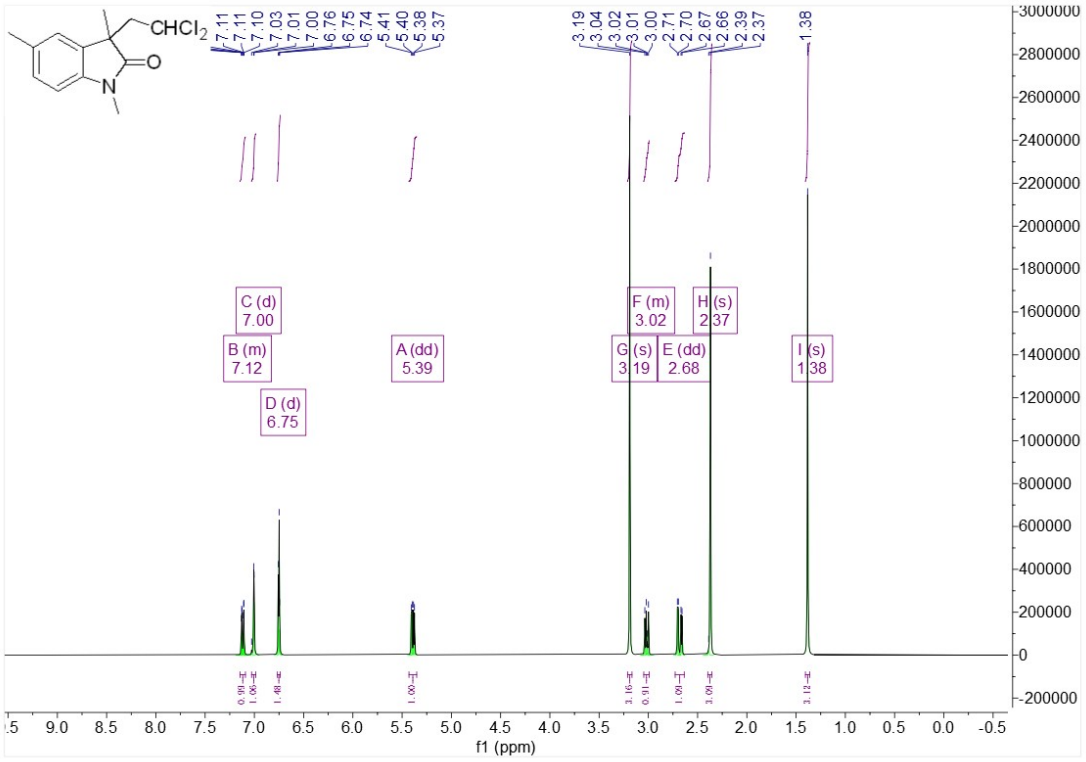


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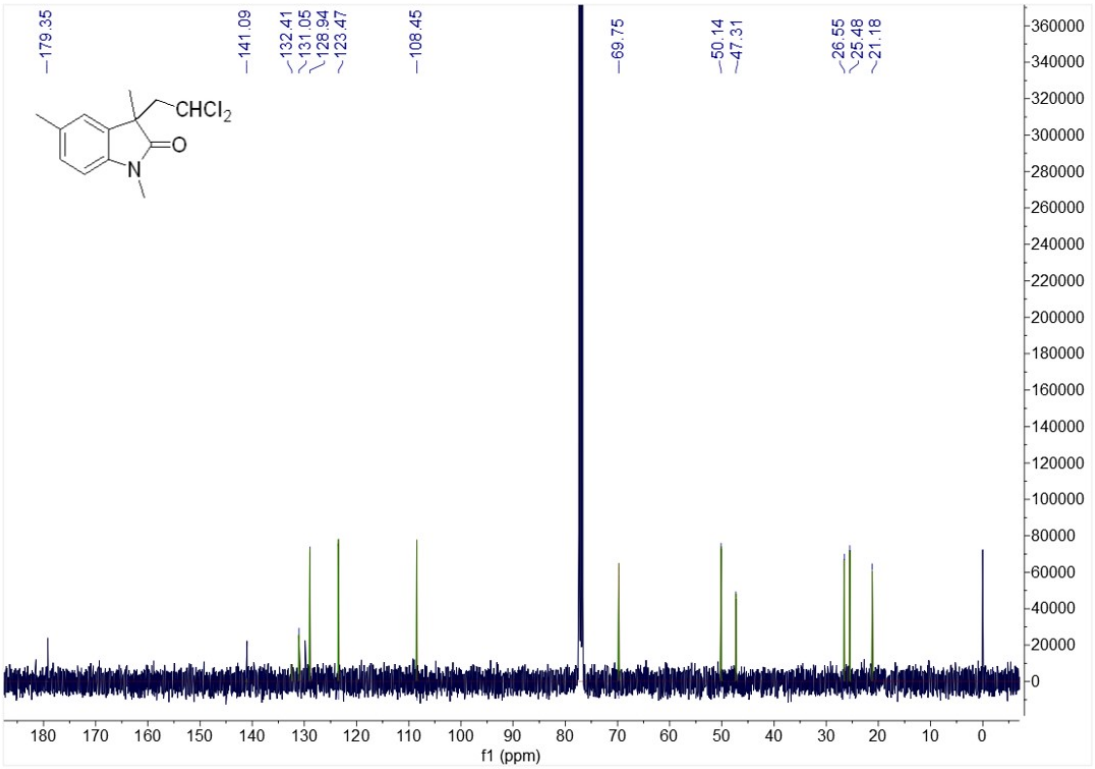


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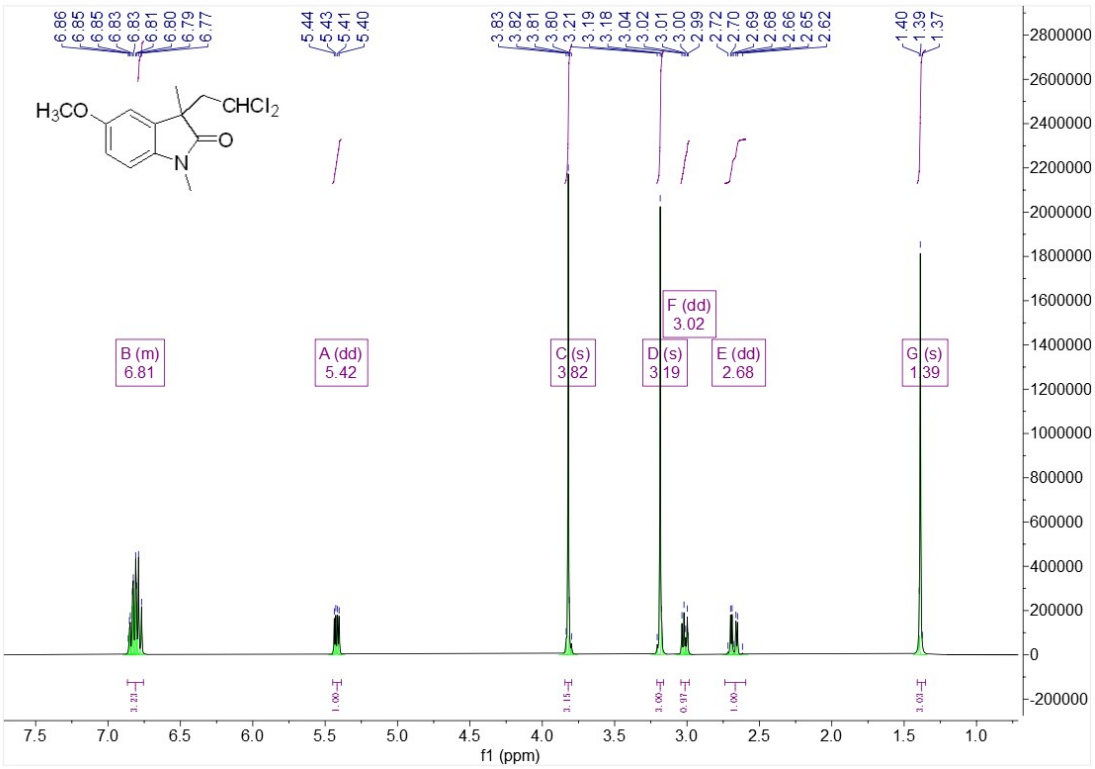


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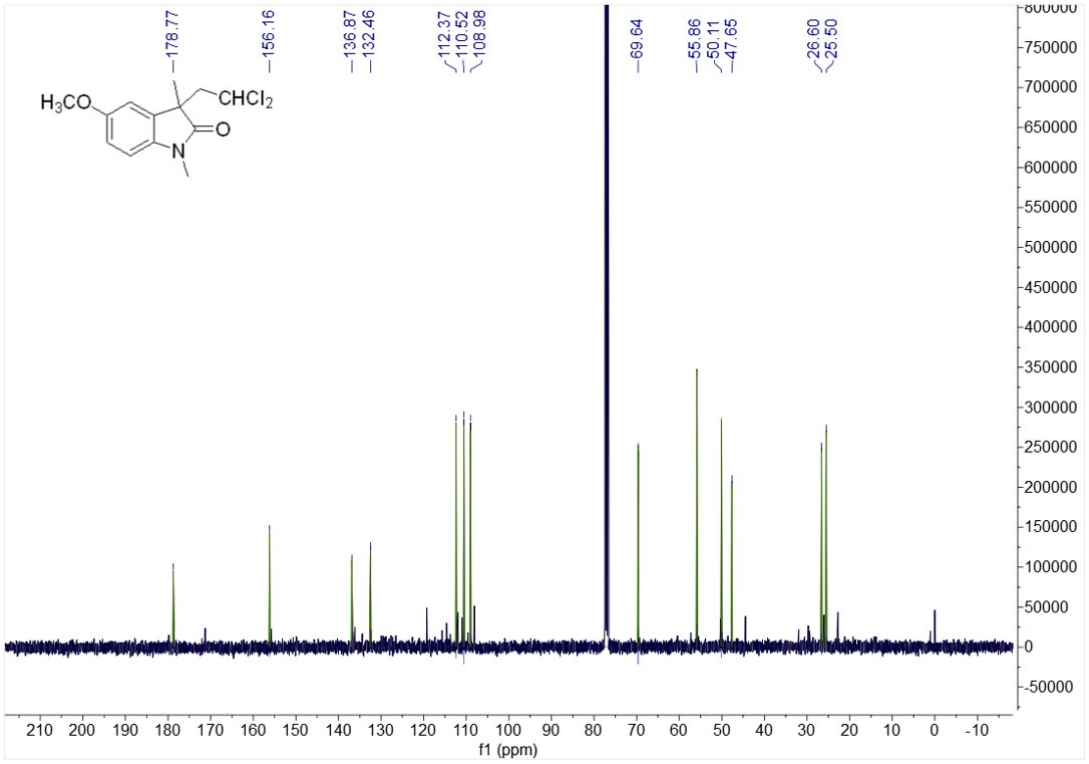


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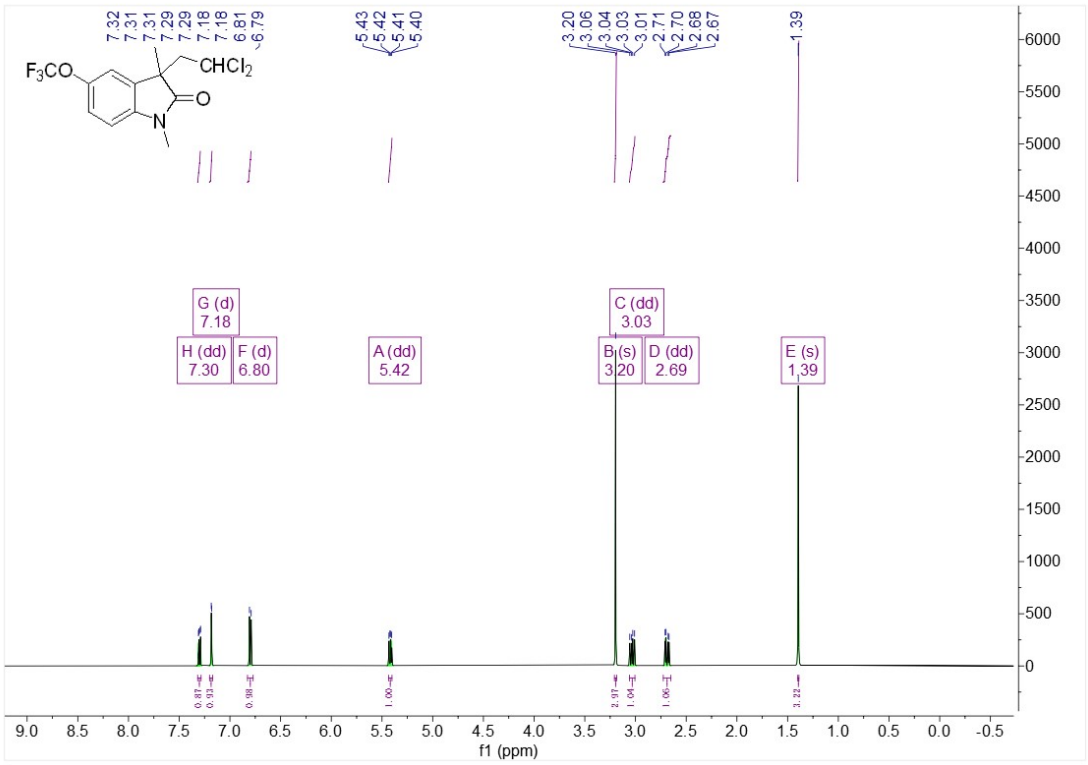


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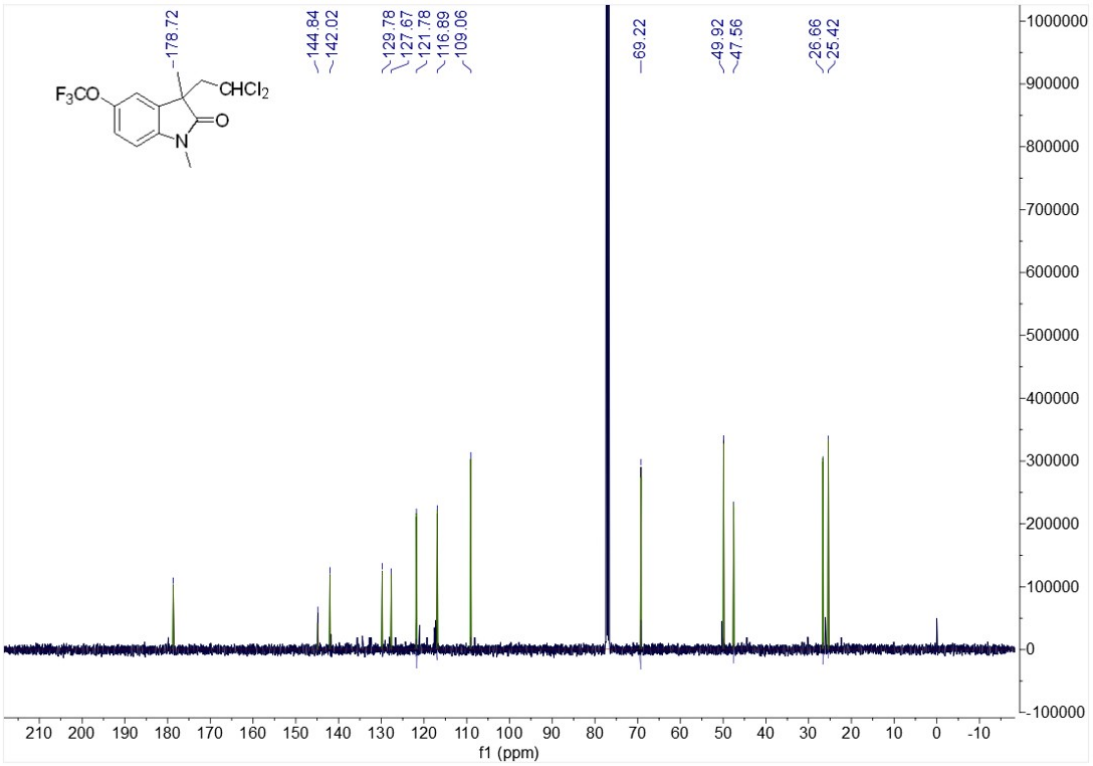
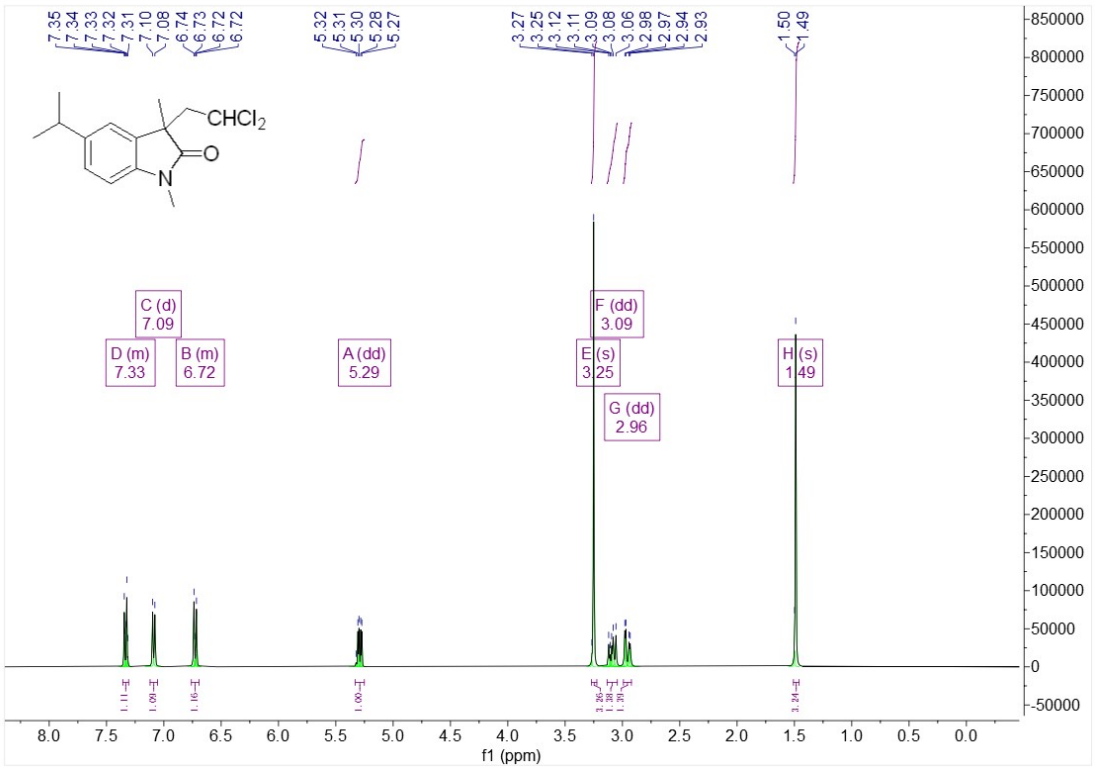
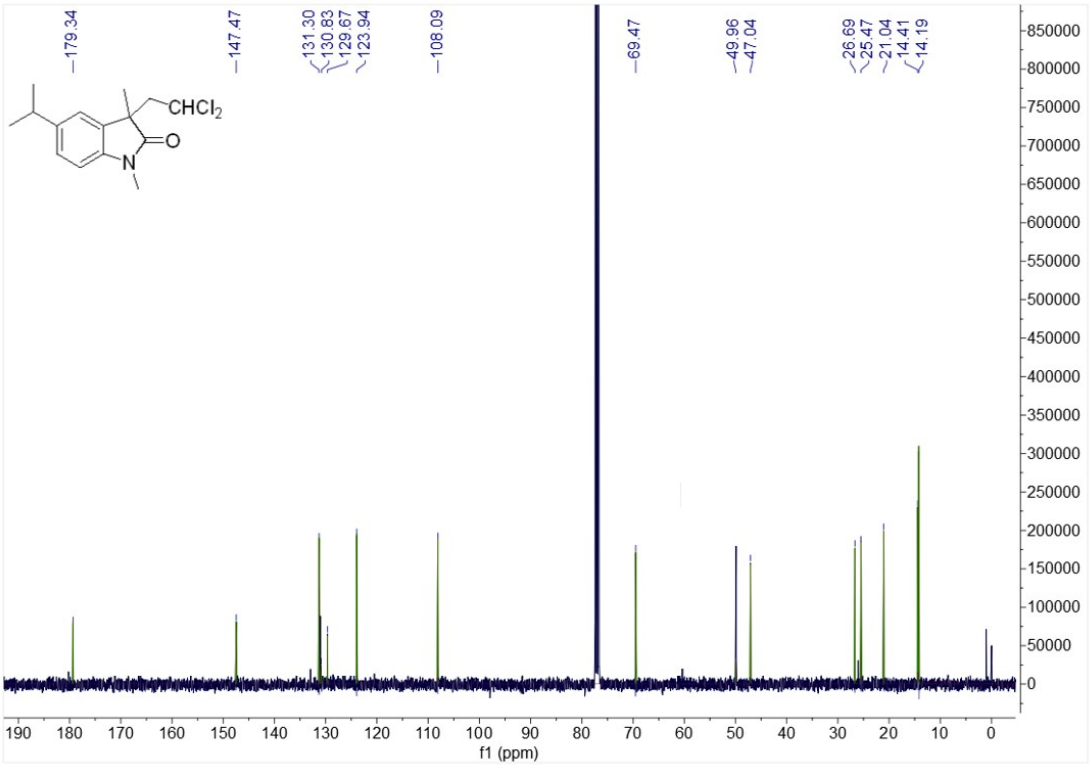


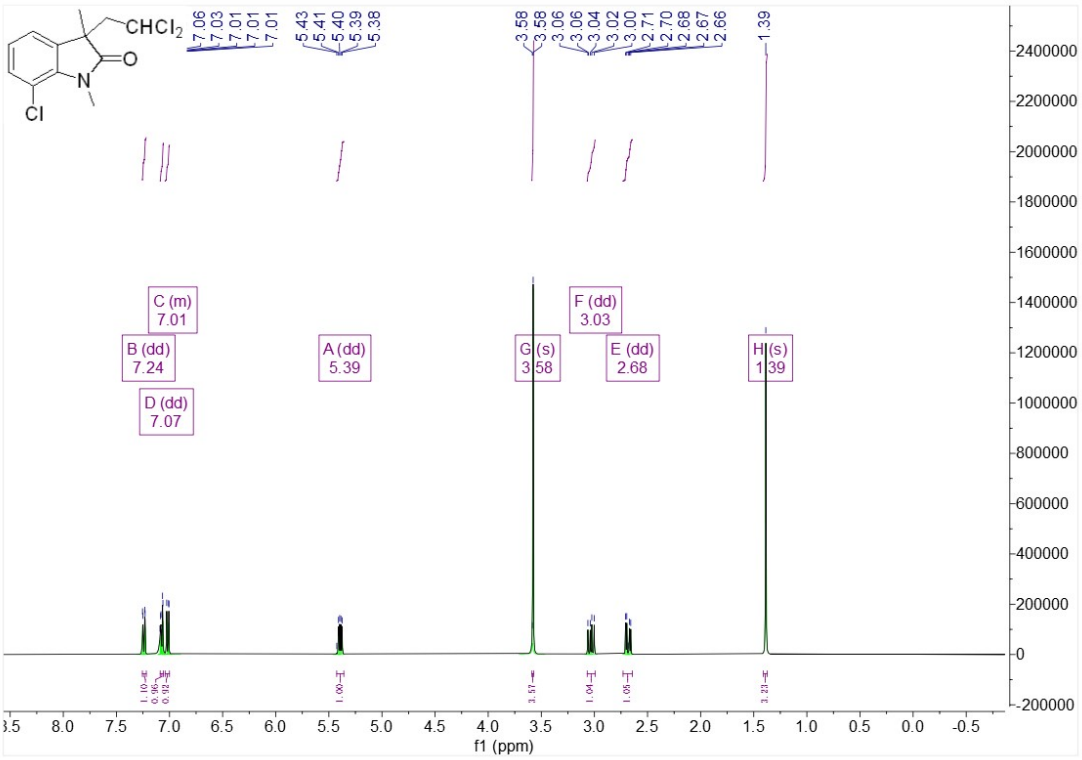

**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3p**



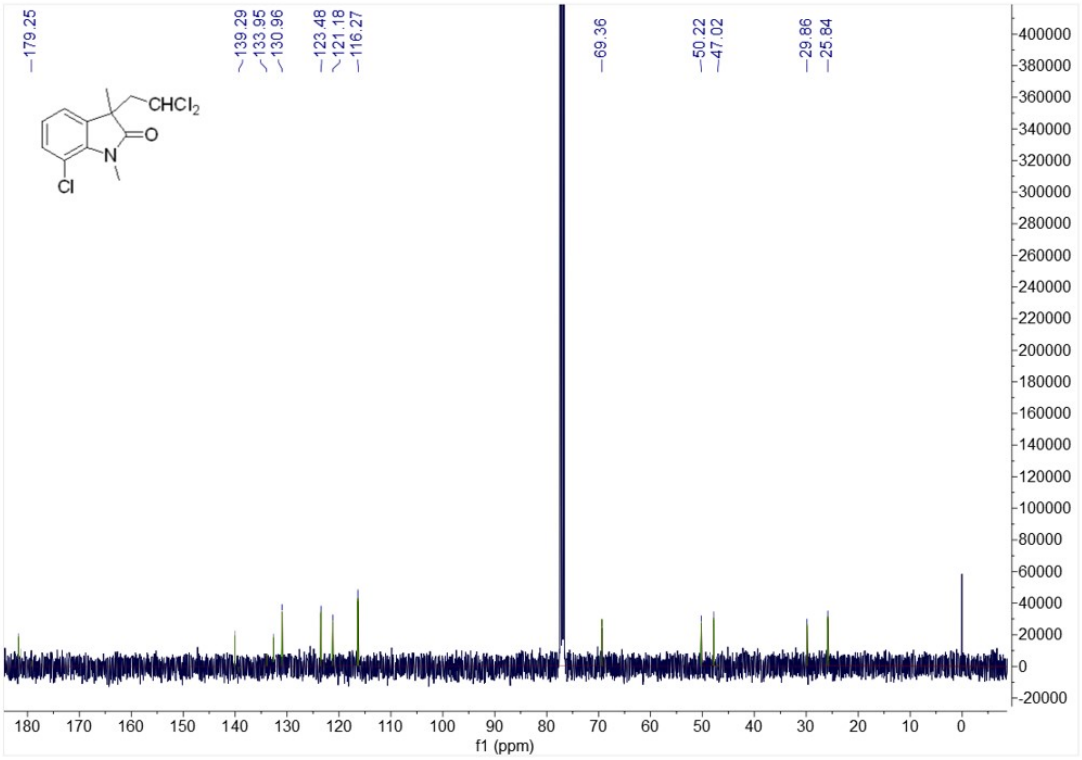

**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3p**



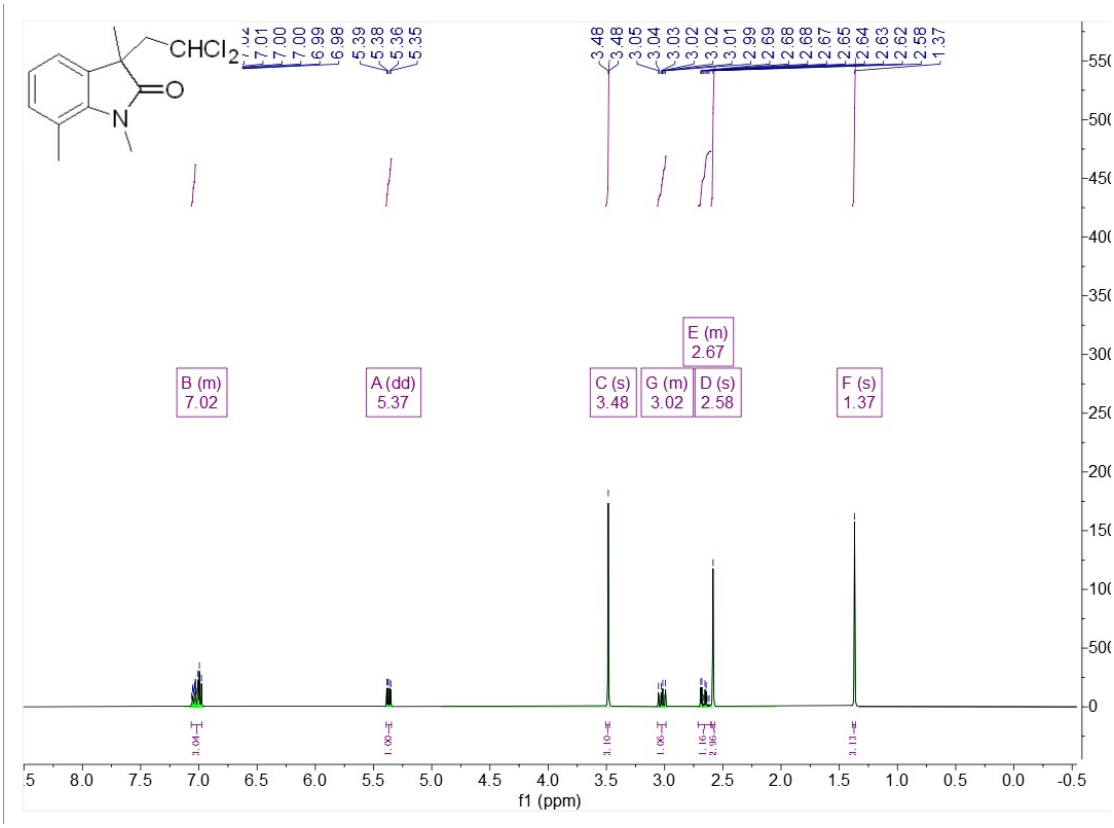

**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3q**



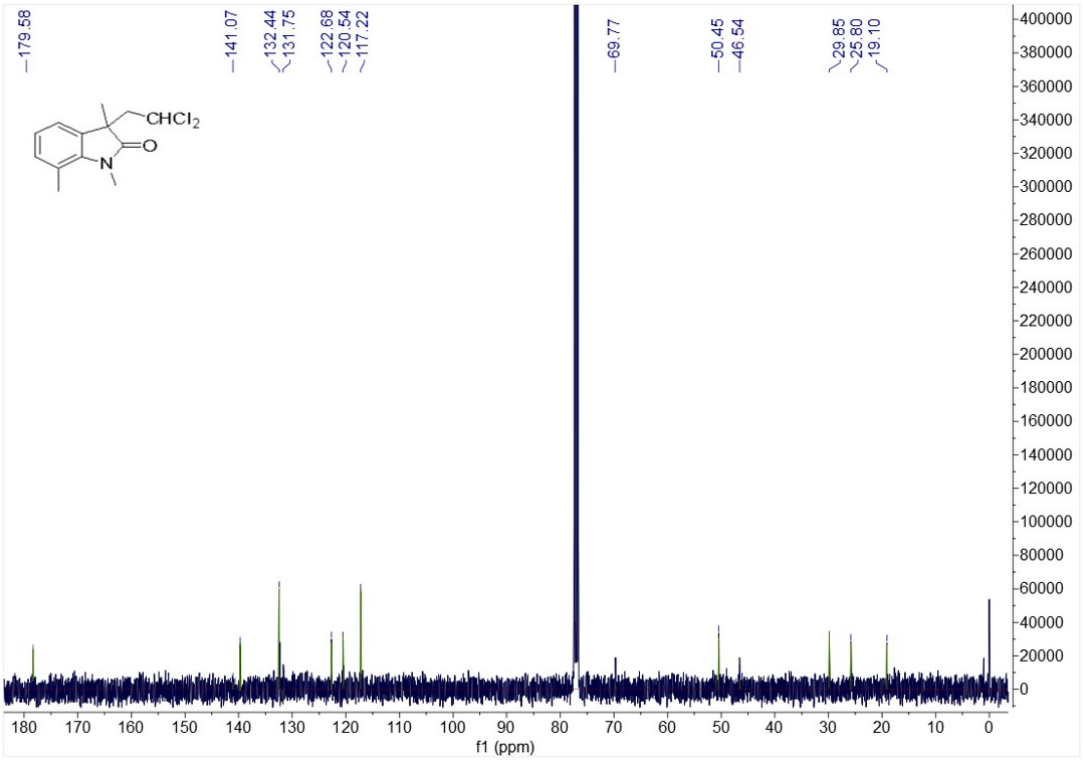

**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3q**



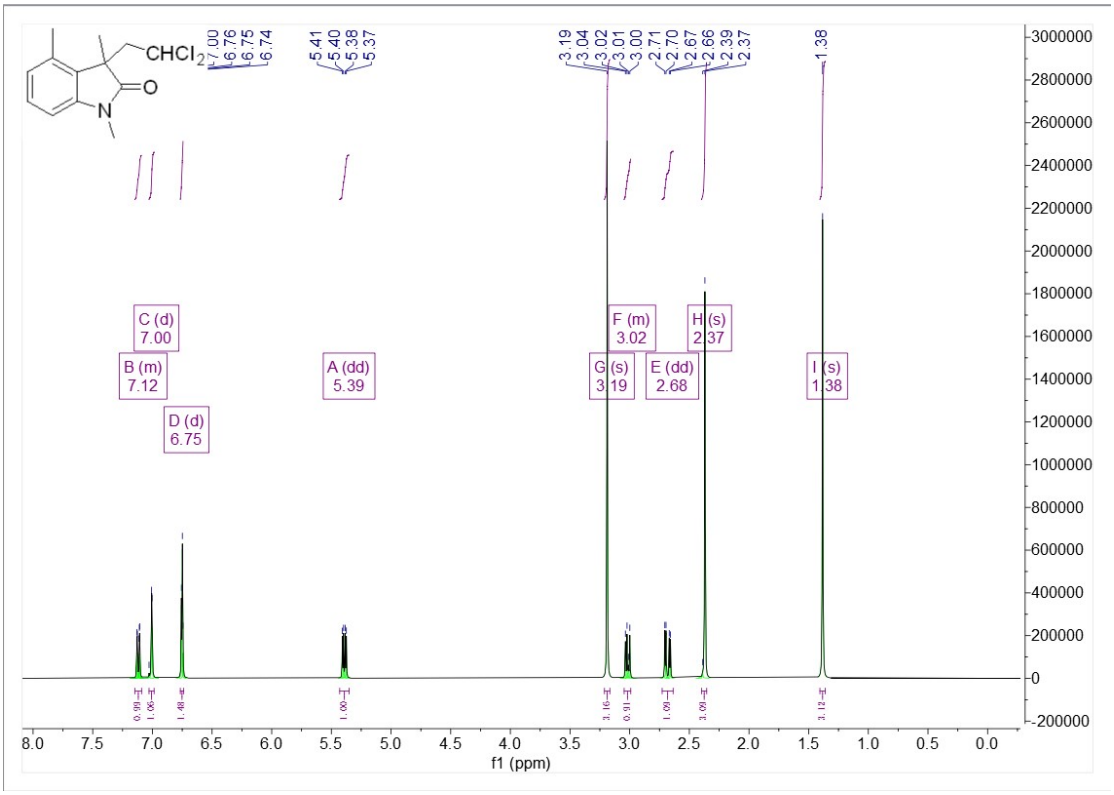

**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3r**



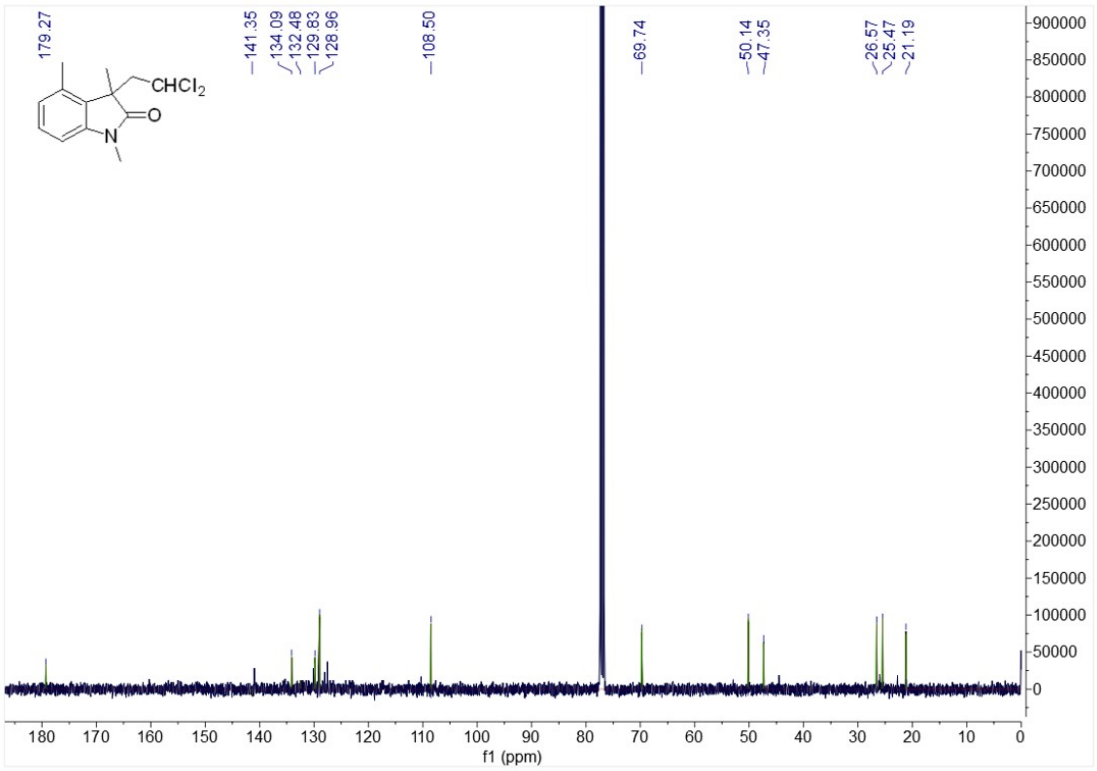

**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3r**



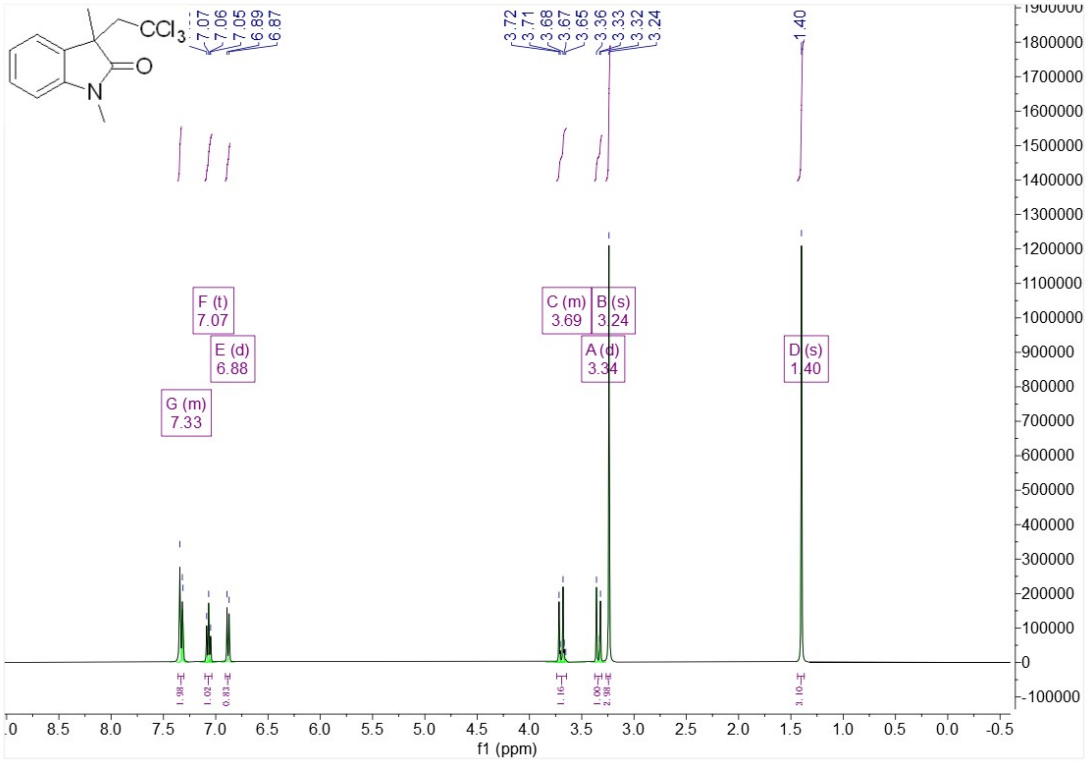

**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3s**



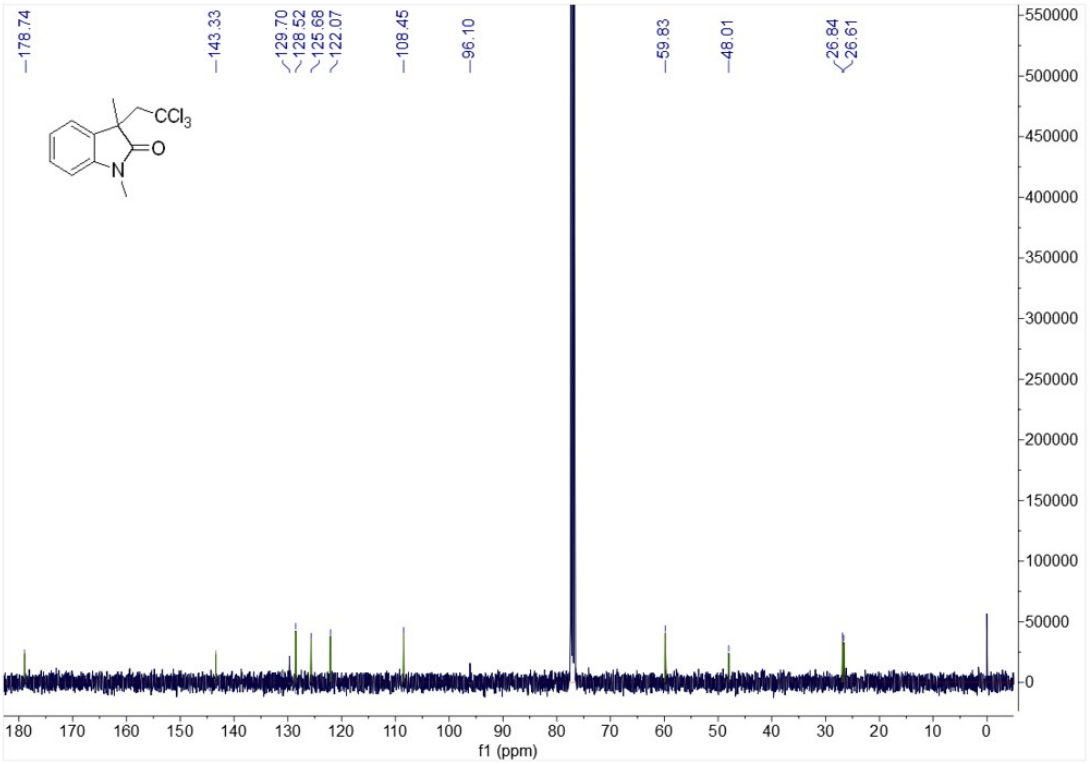

**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3s**



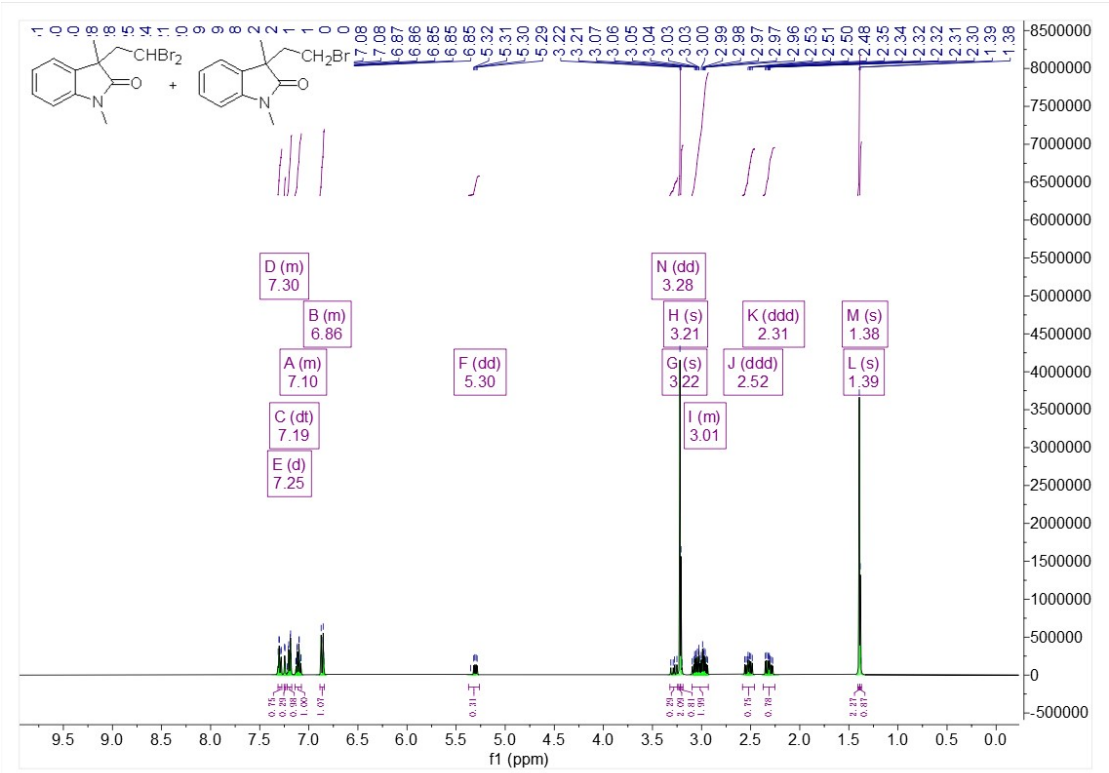

**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3t**




**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3t**




**$^{1}$H NMR-spectrum (400MHz, $CDCl_3$) of 3v，3w**




**$^{13}$C NMR-spectrum (101MHz, $CDCl_3$) of 3v,3w**