Supporting Information

Heat- or light-induced acylarylation of unactivated alkenes towards 3-(α-acyl) indolines

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I. General considerations

Unless otherwise stated, commercially available chemicals were used without treatment. Solvents were degassed by bubbling Ar for 30 minutes before use. Reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography over 300-400 mesh silica gel under a positive pressure of air. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer using TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). Gas chromatography-mass spectrometry (GC-MS) analyses were performed on an Agilent 7890A gas chromatograph interfaced to a 5975C mass selective detector in electron impact ionization mode. Substrates **1** were prepared from anilides and allyl bromides and are known compounds.[1] The photoreactors used in this research were bought from GeAo Chem (Figure S1, containing 24 small blue LEDs, 1 W for every LED, and every reaction tube is irradiated by 6 LEDs).

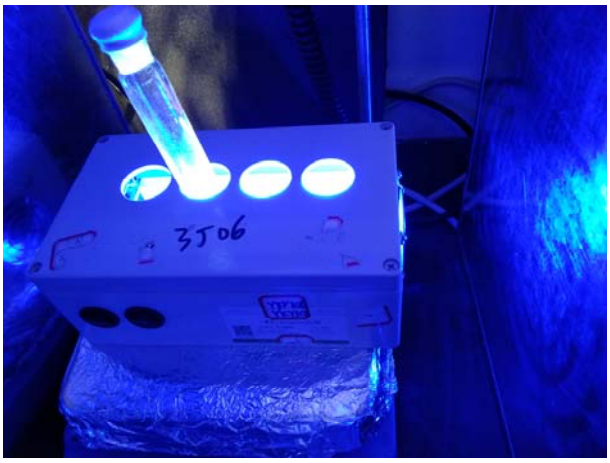
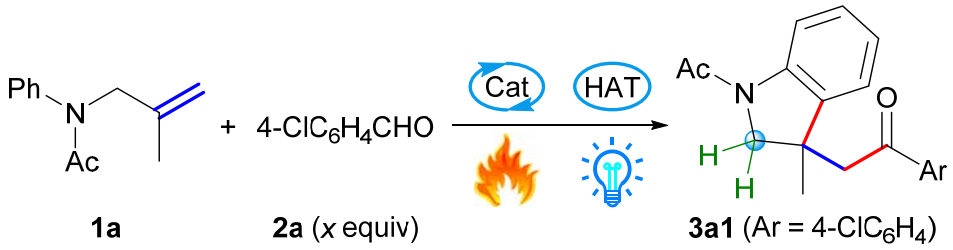


Figure S1 Photochemical setup

1 D. Liang, Q. Dong, P. Xu, Y. Dong, W. Li and Y. Ma, *J. Org. Chem.*, 2018, **83**, 11978−11986.

II. Detailed optimization of reaction conditions

Table S1 Optimization of reaction conditions[a]



1a **2a** (*x* equiv) **3a1** (Ar = 4-ClC$_6$H$_4$)

entry	*x*	catalyst (mol%)	oxidant (equiv)	PC[b] (mol%)	solvent	*T* (°C)	*t* (h)	yield (%)
1	**3**	**$FeCl_2$ (5)**	**DTBP (4)**	**–**	**PhCl**	**120**	**6**	**87**
2	3	–	DTBP (4)	–	PhCl	120	6	68
3	3	$Fe(OAc)_2$ (5)	DTBP (4)	–	PhCl	120	6	57
4	3	$FeSO_4$ (5)	DTBP (4)	–	PhCl	120	6	69
5	3	$FeCl_3$ (5)	DTBP (4)	–	PhCl	120	6	57
6	3	$Fe(NO_3)_3$ (5)	DTBP (4)	–	PhCl	120	6	51
7	3	$Fe_2(SO_4)_3$ (5)	DTBP (4)	–	PhCl	120	6	67
8	3	CuI (5)	DTBP (4)	–	PhCl	120	6	41
9	3	$Cu(OAc)_2$ (5)	DTBP (4)	–	PhCl	120	6	trace
10	3	$AgNO_3$ (5)	DTBP (4)	–	PhCl	120	6	18
11	3	$NiCl_2$ (5)	DTBP (4)	–	PhCl	120	6	26
12	3	$CoCl_2$ (5)	DTBP (4)	–	PhCl	120	6	0
13	3	$MnCl_2$ (5)	DTBP (4)	–	PhCl	120	6	61
14	3	TBAI (5)	DTBP (4)	–	PhCl	120	6	32
15	3	$FeCl_2$ (5)	TBHP[c] (4)	–	PhCl	120	6	55
16	3	$FeCl_2$ (5)	TBHP[d] (4)	–	PhCl	120	6	53
17	3	$FeCl_2$ (5)	DCP (4)	–	PhCl	120	6	71
18	3	$FeCl_2$ (5)	BPO (4)	–	PhCl	120	6	trace
19	3	$FeCl_2$ (5)	TBPB (4)	–	PhCl	120	6	61
20	3	$FeCl_2$ (5)	$K_2S_2O_8$ (4)	–	PhCl	120	6	trace
21	3	$FeCl_2$ (5)	Oxone (4)	–	PhCl	120	6	0
22	3	$FeCl_2$ (5)	*m*CPBA (4)	–	PhCl	120	6	0
23	3	$FeCl_2$ (5)	I_2O_5 (4)	–	PhCl	120	6	0

24	3	$FeCl_2$ (5)	DTBP (4)	–	toluene	120	6	39
25	3	$FeCl_2$ (5)	DTBP (4)	–	DCE	120	6	11
26	3	$FeCl_2$ (5)	DTBP (4)	–	EtOAc	120	6	25
27	3	$FeCl_2$ (5)	DTBP (4)	–	CH_3CN	120	6	0
28	3	$FeCl_2$ (5)	DTBP (4)	–	CH_3NO_2	120	6	0
29	3	$FeCl_2$ (5)	DTBP (4)	–	THF	120	6	17
30	3	$FeCl_2$ (5)	DTBP (4)	–	DMF	120	6	18
31	3	$FeCl_2$ (5)	DTBP (4)	–	DMSO	120	6	0
32	3	$FeCl_2$ (5)	DTBP (4)	–	PhCl	80	6	16
33	2	$FeCl_2$ (5)	DTBP (4)	–	PhCl	120	6	66
34	3	$FeCl_2$ (5)	DTBP (3)	–	PhCl	120	6	78
35	3	$FeCl_2$ (2)	DTBP (4)	–	PhCl	120	6	70
36	3	$FeCl_2$ (5)	DTBP (4)	–	PhCl	120	3	55
37[e]	3	$FeCl_2$ (5)	DTBP (4)	–	PhCl	120	6	45
38	3	$FeCl_2$ (5)	DTBP (4)	*fac*-Ir(ppy)$_3$ (1)	PhCl	rt	12	52
39[f]	3	$FeCl_2$ (5)	DTBP (4)	*fac*-Ir(ppy)$_3$ (1)	PhCl	rt	12	35
40	3	$FeCl_2$ (5)	DTBP (4)	$Ru(bpy)_3Cl_2$ (1)	PhCl	rt	12	nr
41	3	$FeCl_2$ (5)	DTBP (4)	Mes-Acr$^+ClO_4^-$ (1)	PhCl	rt	12	trace
42	3	$FeCl_2$ (5)	DTBP (4)	**4CzIPN** (1)	PhCl	rt	12	62
43	3	$FeCl_2$ (5)	DTBP (4)	Eosin Y (5)	PhCl	rt	12	nr
44	3	$FeCl_2$ (5)	DTBP (4)	Rose Bengal (5)	PhCl	rt	12	nr
45	3	$FeCl_2$ (5)	DTBP (4)	Rhodamine B (5)	PhCl	rt	12	trace
46	3	$FeCl_2$ (5)	DTBP (4)	AQN-2-CO_2H (5)	PhCl	rt	12	nr
47	3	$FeCl_2$ (5)	DTBP (4)	4CzIPN (1)	DCE	rt	12	52
48	3	$FeCl_2$ (5)	DTBP (4)	4CzIPN (1)	CH_3CN	rt	12	30
49	3	$FeCl_2$ (5)	DTBP (4)	4CzIPN (1)	DMSO	rt	12	nr
50	3	$FeCl_2$ (5)	TBHP[c] (4)	4CzIPN (1)	PhCl	rt	12	trace
51	3	$FeCl_2$ (5)	TBHP[d] (4)	4CzIPN (1)	PhCl	rt	12	trace
52	3	$FeCl_2$ (5)	DCP (4)	4CzIPN (1)	PhCl	rt	12	56
53	3	$FeCl_2$ (5)	BPO (4)	4CzIPN (1)	PhCl	rt	12	trace
54	3	$FeCl_2$ (5)	TBPB (4)	4CzIPN (1)	PhCl	rt	12	44
55	3	$FeCl_2$ (5)	$K_2S_2O_8$ (4)	4CzIPN (1)	PhCl	rt	12	nr
56	3	–	DTBP (4)	4CzIPN (1)	PhCl	rt	12	51
57	3	$FeCl_2$ (5)	DTBP (4)	4CzIPN (2)	PhCl	rt	12	53
58	**3**	**$FeCl_2$ (5)**	**DTBP (4)**	**4CzIPN (1)**	**PhCl**	**rt**	**24**	**70**

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3.0 equiv), catalyst (5 mol%), oxidant (4.0 equiv), solvent (2.0 mL), Ar. [b] 6 W Blue LEDs were used to excite the PCs. [c] 70% aqueous. [d] 5.0–6.0 mol/L in decane. [e] The reaction tube was sealed without degassing. [f] 2,6-Lutidine (1.0 equiv) was added.

III. Experimental procedures

1. General procedure for the heat-induced reactions

A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with *N*-allyl aniline (0.5 mmol), aldehyde (1.5 mmol), $FeCl_2$ (0.025 mmol, 3 mg), and DTBP (2.0 mmol, 292 mg) under argon, followed by the addition of degassed chlorobenzene (2.0 mL). A strictly oxygen-free environment is necessary. The mixture was stirred at 120 °C for 6 h, then it was quenched with saturated aqueous $Na_2S_2O_3$ (1.0 mL), aqueous NaOH (0.1 M, 1.0 mL) and water (5 mL), and extracted with CH_2Cl_2 (10.0 mL) three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v).

2. General procedure for the photoredox reactions

A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with *N*-allyl anilines (0.5 mmol), aldehyde (1.5 mmol), $FeCl_2$ (0.025 mmol, 3 mg), 4CzIPN (0.005 mmol, 4 mg) and DTBP (2.0 mmol, 292 mg) under argon, followed by the addition of degassed chlorobenzene (2.0 mL). A strictly oxygen-free environment is necessary. The mixture was stirred at room temperature under blue LED irradiation for 24 h, then it was quenched with aqueous NaOH (0.1 M, 1.0 mL) and water (5 mL), and extracted with CH_2Cl_2 (10.0 mL) three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v).

3. Gram-scale reactions

By heating: A 35-mL Schlenk tube, equipped with a magnetic stirring bar, was

charged sequentially with *N*-(2-methylallyl) acetanilide **1a** (6.0 mmol, 1135 mg), 4-chlorobenzaldehyde **2a** (18.0 mmol, 2530 mg), $FeCl_2$ (0.3 mmol, 38 mg) and DTBP (24.0 mmol, 3510 mg) under argon, followed by the addition of degassed chlorobenzene (24.0 mL). The mixture was stirred at 120 °C for 6 h, then it was quenched with saturated aqueous $Na_2S_2O_3$ (10.0 mL), aqueous NaOH (0.1 M, 10.0 mL) and water (50 mL), and extracted with CH_2Cl_2 (100.0 mL) three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v).

By irradiation: A 35-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with *N*-(2-methylallyl) acetanilide **1a** (6.0 mmol, 1135 mg), 4-chlorobenzaldehyde **2a** (18.0 mmol, 2530 mg), $FeCl_2$ (0.3 mmol, 38 mg), 4CzIPN (0.06 mmol, 47 mg) and DTBP (24.0 mmol, 3510 mg) under argon, followed by the addition of degassed chlorobenzene (24.0 mL). The mixture was stirred at room temperature under 6 W blue LED irradiation for 24 h (see Figure S2), then it was quenched with aqueous NaOH (0.1 M, 10.0 mL) and water (50 mL), and extracted with CH_2Cl_2 (100.0 mL) three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v).

Figure S2 Setup for photochemical gram-scale synthesis

IV. Mechanistic investigations

1. KIE experiments

Heat-induced: A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with *N*-(2-methylallyl) acetanilide **1a** (0.25 mmol, 47 mg), *N*-(2-methylallyl)-*N*-(phenyl-d_5)acetamide **1a-d_5** (0.25 mmol, 49 mg), 4-chlorobenzaldehyde **2a** (1.5 mmol, 211 mg), $FeCl_2$ (0.025 mmol, 3 mg), and DTBP (2.0 mmol, 292 mg) under argon, followed by the addition of degassed chlorobenzene (2.0 mL). The mixture was stirred at 120 °C for 6 h, then it was quenched with saturated aqueous $Na_2S_2O_3$ (1.0 mL), aqueous NaOH (0.1 M, 1.0 mL) and water (5.0 mL), and extracted with CH_2Cl_2 (10.0 mL) three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v), and the isolated pure product was subjected to ^{1}H NMR analysis (Figure S3).

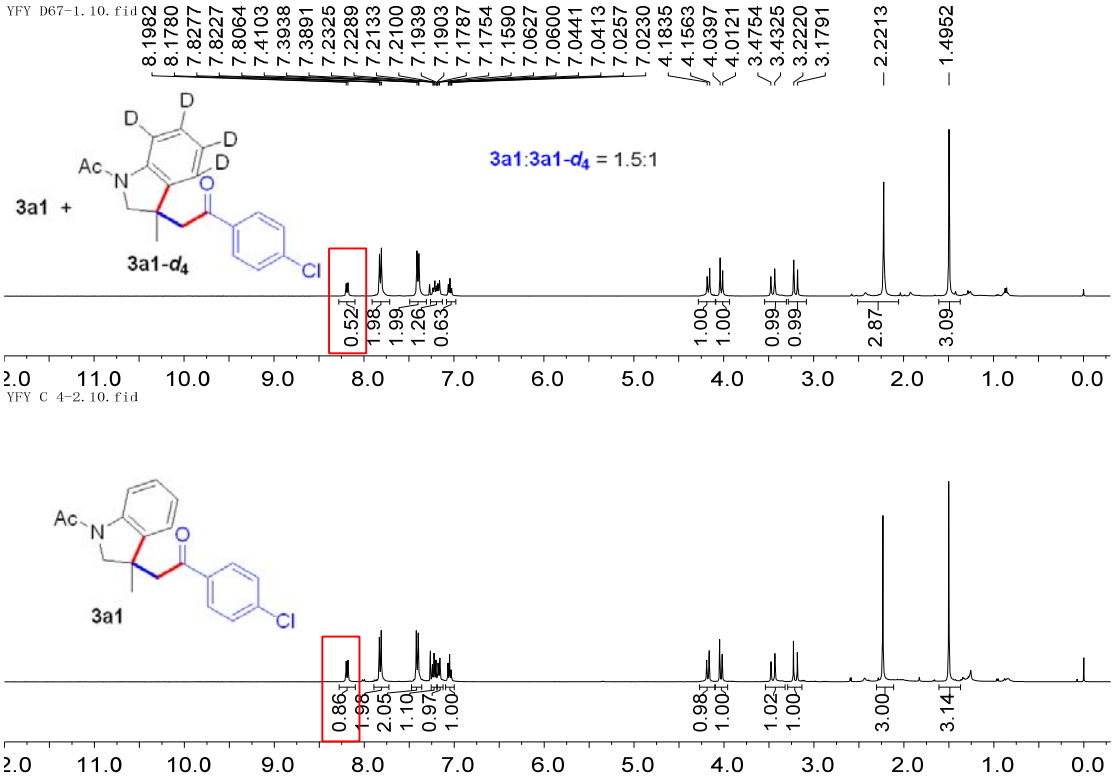


Figure S3 ^{1}H NMR analysis of the KIE experiment under the heating conditions

Photoredox catalysis: A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with *N*-(2-methylallyl) acetanilide **1a** (0.25 mmol, 47 mg), *N*-(2-methylallyl)-*N*-(phenyl-d_5)acetamide **1a-*d*$_5$** (0.25 mmol, 49 mg), 4-chlorobenzaldehyde **2a** (1.5 mmol, 211 mg), $FeCl_2$ (0.025 mmol, 3 mg), 4CzIPN (0.005 mmol, 4 mg)) and DTBP (2.0 mmol, 292 mg) under argon, followed by the addition of degassed chlorobenzene (2.0 mL). The mixture was stirred at room temperature under blue LED irradiation for 24 h, then it was quenched with aqueous NaOH (0.1 M, 1.0 mL) and water (5.0 mL), and extracted with CH_2Cl_2 (10.0 mL) three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v), and the isolated pure product was subjected to ^{1}H NMR analysis (Figure S4).

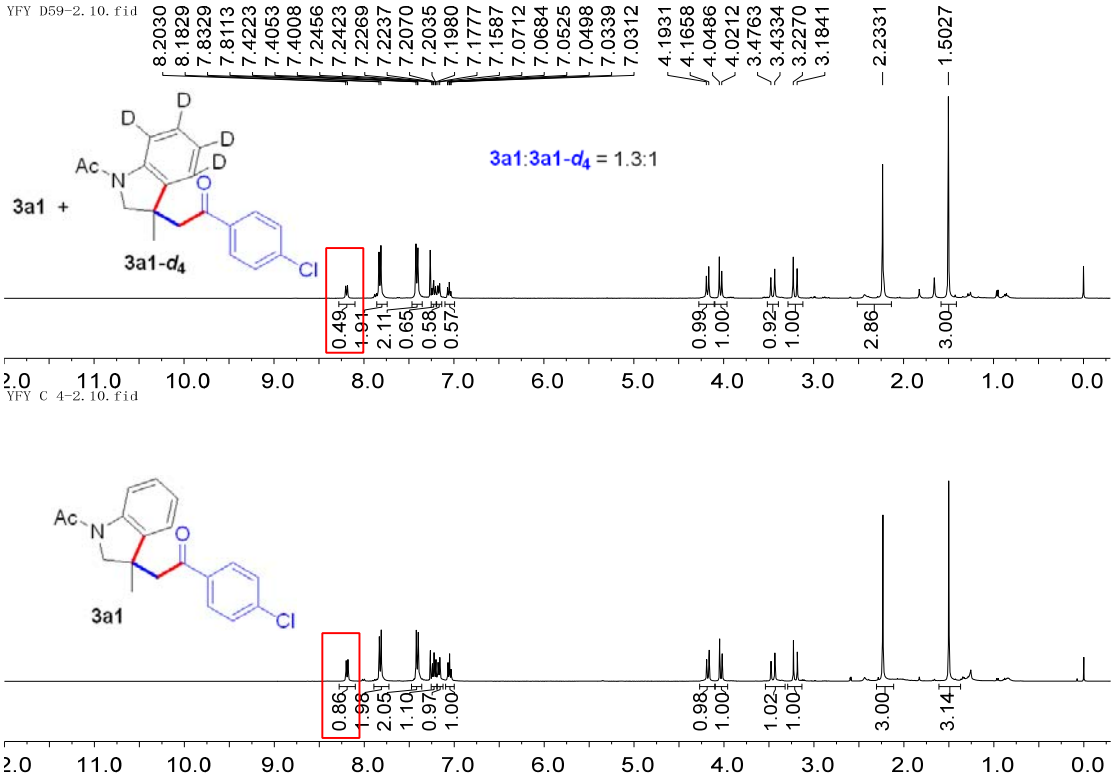


Figure S4 ^{1}H NMR analysis of the KIE experiment under the photoredox conditions

2. Light on-off experiments

Table S2 Light on-off experiments

Time (h)	2	4	6	8	10	12
Yield[a] (%)	5.56	8.57	36.88	39.62	61.44	73.89

[a] The yields of **3a1** were determined by GC-MS analysis using biphenyl as the internal standard.

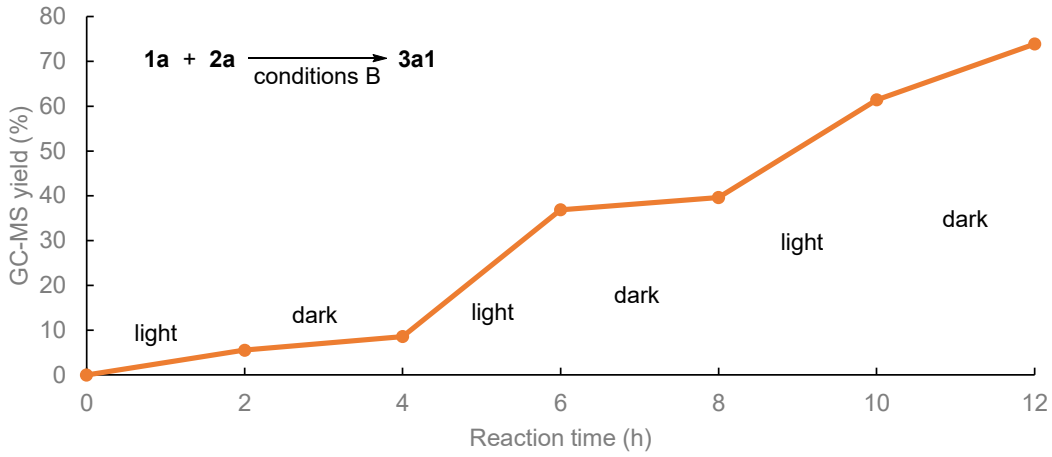
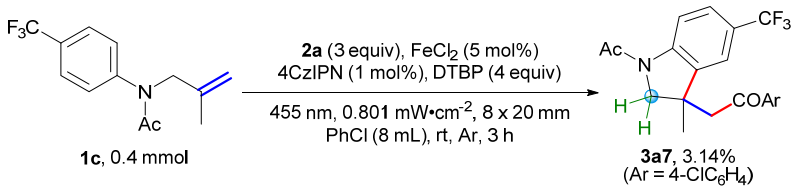


Figure S5 Light on-off experiments

3. Quantum yield measurements



A quartz cuvette (10 × 30 × 45 mm), equipped with a magnetic stirring bar, was charged under argon sequentially with *N*-(2-methylallyl)-*N*-(4-(trifluoromethyl)phenyl)acetamide **1c** (0.4 mmol, 103 mg), 4-chlorobenzaldehyde **2a** (1.2 mmol, 169 mg), $FeCl_2$ (0.02 mmol, 3 mg), 4CzIPN (0.004 mmol, 3 mg) and DTBP (1.6 mmol, 234 mg), followed by the addition of degassed chlorobenzene (8.0 mL). The mixture was irradiated (λ = 455 nm, slit width = 8.0 mm, slit height 2.0 mm with the light intensity of 0.801 mW·cm^{-2}) for 10800 s. The set up used fot this chemical actinometry is shown in Figure S6, and the light

intensity was measured in the PAR-range (Photosynthetic active radiation, 400–700 nm) using a PAR sensor (FZ-A, Photoelectric Instrument Factory of Beijing Normal University).

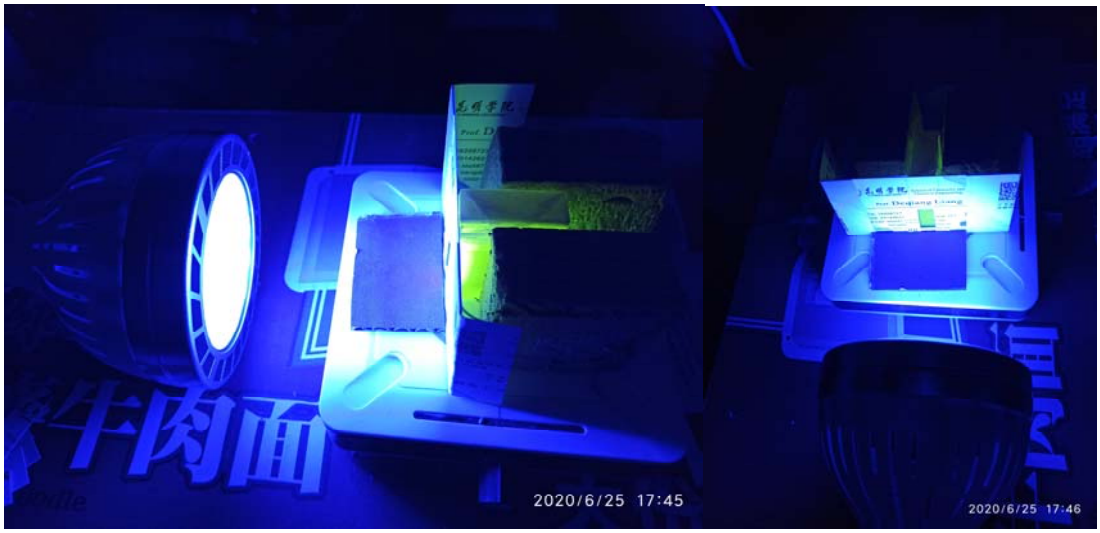


Figure S6 Set up for the chemical actinometry

After irradiation, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (1.0 mL), aqueous NaOH (0.1 M, 1.0 mL) and water (5.0 mL), and extracted with CH_2Cl_2 (10.0 mL) three times in a dark room under red light conditions. At last, the yield of product formed was determined by ^{19}F NMR based on a trifluorotoluene standard.

The fraction of photons absorbed by the reaction solution was recorded using a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu, Japan) in a 1 cm quartz cell (Figure S7).

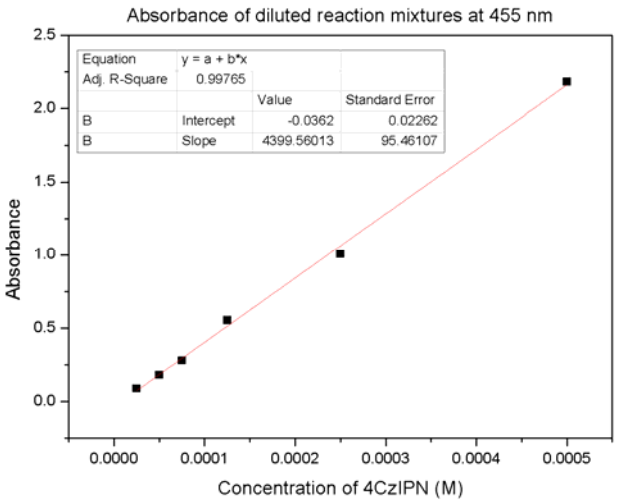


Figure S7 Absorbance of diluted reaction mixtures at 455 nm

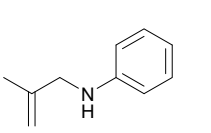
The quantum yield was determined as follows.

ϕ = Mole number for product/Mole number for absorption of photons = 0.240

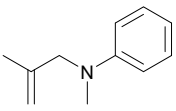
$$\phi = \frac{n_{3a7}N_A/t}{fP\lambda/hc}$$

n_{3a7}: the mole number of the product **3a7**; t: reaction time (t = 10800 s); N_A: 6.02 × 10^{23}/mol; f: 1-10^{-A} (455 nm, A = 2.1844); P: P = E × S (E: illumination intensity, E = 0.000801 W/cm^2; S: the area that irradiated, S = 1.60 cm^2); λ: wavelength (λ = 4.55×10^{-7} m); h: planck constant (h = 6.626 × 10^{-34} J*s); c: velocity of light (c = 3 × 108 m/s).

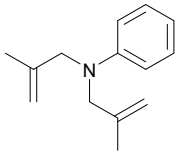
VI. Unsuccessful substrates



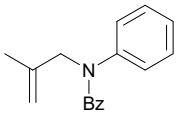
with **2a**, complex



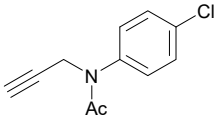
with **2a**, complex



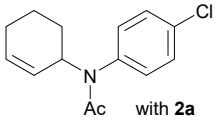
with **2a**, complex



with **2a**, complex

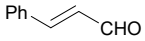


with **2a**, complex



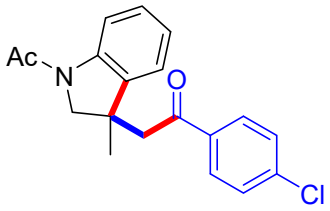
with **2a**

Conditions A: 22%
Conditions B: 15%
one unidentified isomer

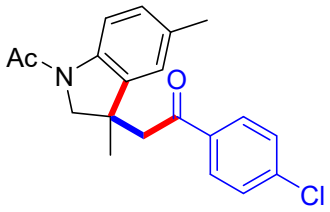


with **1a**, complex

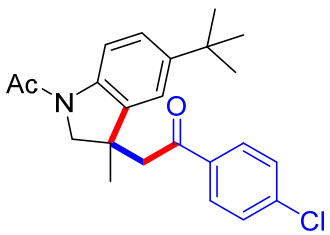
VI. Spectral Data of Products



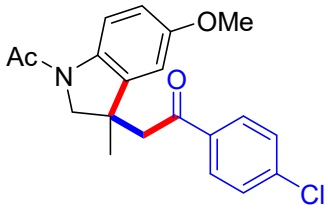
3a1, 2-(1-acetyl-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.24–7.20 (m, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.05 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 4.18 (d, J = 11.0 Hz, 1H), 4.03 (d, J = 11.0 Hz, 1H), 3.46 (d, J = 17.2 Hz, 1H), 3.21 (d, J = 17.2 Hz, 1H), 2.23 (s, 3H), 1.50 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.0, 168.9, 141.6, 139.9, 138.9, 135.4, 129.4, 129.0, 128.4, 123.8, 122.0, 117.2, 61.2, 48.2, 42.2, 26.3, 24.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{19}ClNO_2^+$ ([M+H]$^+$) 328.1099. Found 328.1093.



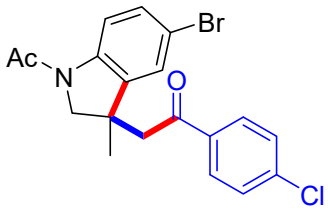
3a2, 2-(1-acetyl-3,5-dimethylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.1 Hz, 1H), 6.95 (s, 1H), 4.16 (d, J = 11.0 Hz, 1H), 4.02 (d, J = 11.0 Hz, 1H), 3.45 (d, J = 17.2 Hz, 1H), 3.18 (d, J = 17.2 Hz, 1H), 2.32 (s, 3H), 2.21 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.1, 168.5, 139.9, 139.3, 139.0, 135.4, 133.4, 129.4, 128.9, 128.8, 122.7, 116.9, 61.4, 48.2, 42.2, 26.2, 24.2, 21.1; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_2^+$ ([M+H]$^+$) 342.1255. Found 342.1258.



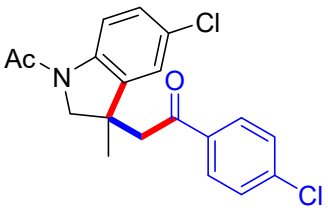
3a3, 2-(1-acetyl-5-(*tert*-butyl)-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.23 (dd, J = 8.5, 2.0 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 4.17 (d, J = 10.9 Hz, 1H), 4.00 (d, J = 10.8 Hz, 1H), 3.41 (d, J = 16.5 Hz, 1H), 3.18 (d, J = 16.5 Hz, 1H), 2.22 (s, 3H), 1.52 (s, 3H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.3, 168.5, 147.0, 139.8, 139.3, 138.2, 135.5, 129.4, 128.9, 125.3, 118.7, 116.6, 61.5, 48.3, 42.6, 34.6, 31.5, 26.0, 24.1; HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_2^+$ ([M+H]$^+$) 384.1725. Found 384.1726.



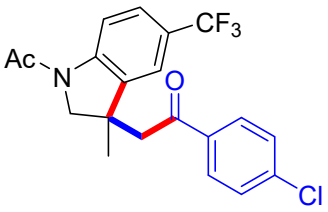
3a4, 2-(1-acetyl-5-methoxy-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, colorless semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 6.74 (dd, J = 8.7, 2.6 Hz, 1H), 6.71 (d, J = 2.6 Hz, 1H), 4.17 (d, J = 11.0 Hz, 1H), 4.02 (d, J = 10.9 Hz, 1H), 3.79 (s, 3H), 3.43 (d, J = 17.2 Hz, 1H), 3.20 (d, J = 17.2 Hz, 1H), 2.21 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.9, 168.1, 156.5, 140.5, 139.9, 135.39, 135.38, 129.4, 129.0, 117.9, 112.2, 108.9, 61.4, 55.7, 48.0, 42.3, 26.1, 24.0; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_3^+$ ([M+H]$^+$) 358.1204. Found 358.1207.



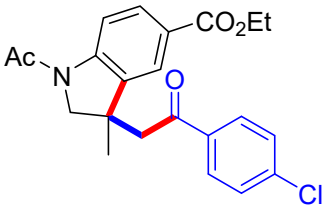
3a5, 2-(1-acetyl-5-bromo-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.32 (dd, J = 8.6, 2.1 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 4.18 (d, J = 11.0 Hz, 1H), 4.05 (d, J = 11.0 Hz, 1H), 3.44 (d, J = 17.3 Hz, 1H), 3.21 (d, J = 17.4 Hz, 1H), 2.22 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.6, 169.0, 141.2, 140.8, 140.1, 135.2, 131.2, 129.4, 129.1, 125.4, 118.7, 116.1, 61.3, 48.0, 42.2, 26.5, 24.2; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}BrClNO_2^+$ ([M+H]$^+$) 406.0204. Found 406.0202.



3a6, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.18 (dd, J = 8.7, 2.2 Hz, 1H), 7.12 (d, J = 2.2 Hz, 1H), 4.19 (d, J = 11.0 Hz, 1H), 4.06 (d, J = 11.0 Hz, 1H), 3.44 (d, J = 17.4 Hz, 1H), 3.22 (d, J = 17.4 Hz, 1H), 2.23 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.6, 168.9, 140.8, 140.3, 140.1, 135.2, 129.4, 129.0, 128.6, 128.3, 122.4, 118.2, 61.3, 48.0, 42.2, 26.4, 24.1; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}Cl_2NO_2^+$ ([M+H]$^+$) 362.0709. Found 362.0707.

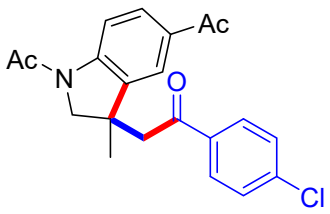


3a7, 2-(1-acetyl-3-methyl-5-(trifluoromethyl)indolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.38 (s, 1H), 4.24 (d, J = 11.0 Hz, 1H), 4.11 (d, J = 11.0 Hz, 1H), 3.48 (d, J = 17.3 Hz, 1H), 3.25 (d, J = 17.3 Hz, 1H), 2.26 (s, 3H), 1.52 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.5, 169.4, 144.5, 140.2, 139.4, 135.1, 129.4, 129.1, 126.08 (q, $^{3}J_{(C–F)}$ = 3.5 Hz), 126.06 (q, $^{2}J_{(C–F)}$ = 32.6 Hz), 125.6, 124.3 (q, $^{1}J_{(C–F)}$ = 270.0 Hz), 119.20 (q, $^{3}J_{(C–F)}$ = 3.4 Hz), 116.9, 61.4, 48.0, 42.2, 26.6, 24.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ = –61.53 (s, 3F); HRMS (ESI-TOF) Calcd for $C_{20}H_{18}ClF_3NO_2^+$ ([M+H]$^+$) 396.0973. Found 396.0965.

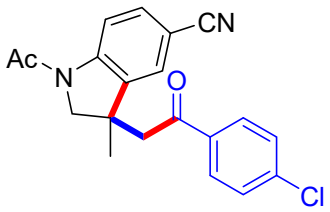


3a8, ethyl 1-acetyl-3-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylindoline-5-carboxylate, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, J = 8.5 Hz, 1H), 7.95 (dd, J =

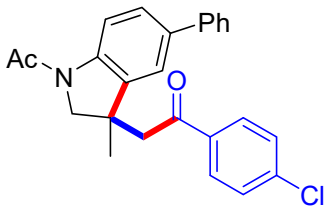
8.5, 1.8 Hz, 1H), 7.87–7.84 (m, 3H), 7.43 (d, J = 8.6 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 4.24 (d, J = 11.1 Hz, 1H), 4.12 (d, J = 11.0 Hz, 1H), 3.55 (d, J = 17.5 Hz, 1H), 3.24 (d, J = 17.5 Hz, 1H), 2.26 (s, 3H), 1.51 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.7, 169.5, 166.3, 145.5, 140.1, 139.2, 135.2, 130.8, 129.4, 129.0, 125.8, 123.6, 116.4, 61.6, 61.0, 48.1, 41.9, 26.8, 24.4, 14.4; HRMS (ESI-TOF) Calcd for $C_{22}H_{23}ClNO_4^+$ ($[M+H]^+$) 400.1310. Found 400.1311.



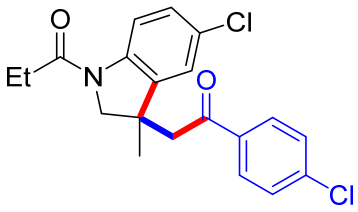
3a9, 1,1'-(3-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylindoline-1,5-diyl)bis(ethan-1-one), pale yellow solid: mp 118–119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, J = 8.4 Hz, 1H), 7.86–7.83 (m, 4H), 7.43 (d, J = 8.6 Hz, 2H), 4.24 (d, J = 11.0 Hz, 1H), 4.12 (d, J = 11.0 Hz, 1H), 3.56 (d, J = 17.5 Hz, 1H), 3.24 (d, J = 17.5 Hz, 1H), 2.59 (s, 3H), 2.28 (s, 3H), 1.50 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.0, 196.7, 169.5, 145.7, 140.1, 139.7, 135.2, 133.0, 130.6, 129.4, 129.0, 121.9, 116.2, 61.6, 48.0, 41.9, 26.9, 26.5, 24.4; HRMS (ESI-TOF) Calcd for $C_{21}H_{21}ClNO_3^+$ ($[M+H]^+$) 370.1204. Found 370.1216.



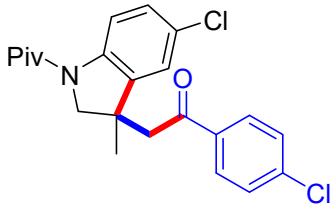
3a10, 1-acetyl-3-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylindoline-5-carbonitrile, pale yellow solid: mp 134–135 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.28 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.53 (dd, J = 8.4, 1.7 Hz, 1H), 7.46–7.43 (m, 3H), 4.24 (d, J = 11.0 Hz, 1H), 4.11 (d, J = 11.0 Hz, 1H), 3.50 (d, J = 17.6 Hz, 1H), 3.27 (d, J = 17.6 Hz, 1H), 2.27 (s, 3H), 1.51 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.2, 169.6, 145.4, 140.3, 140.0, 135.0, 133.3, 129.3, 129.1, 126.0, 119.2, 117.3, 106.5, 61.4, 47.8, 42.0, 26.9, 24.4; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}ClN_2O_2^+$ ($[M+H]^+$) 353.1051. Found 353.1048.



3a11, 2-(1-acetyl-3-methyl-5-phenylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow solid: mp 187–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.56–7.53 (m, 2H), 7.47–7.39 (m, 5H), 7.35–7.31 (m, 2H), 4.23 (d, J = 10.9 Hz, 1H), 4.08 (d, J = 10.9 Hz, 1H), 3.50 (d, J = 17.1 Hz, 1H), 3.26 (d, J = 17.1 Hz, 1H), 2.26 (s, 3H), 1.56 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.0, 168.9, 141.1, 140.9, 140.0, 139.5, 137.1, 135.4, 129.4, 129.0, 128.8, 127.4, 127.1, 126.9, 120.8, 117.4, 61.5, 48.3, 42.4, 26.3, 24.3; HRMS (ESI-TOF) Calcd for $C_{25}H_{23}ClNO_2^+$ ([M+H]$^+$) 404.1412. Found 404.1406.

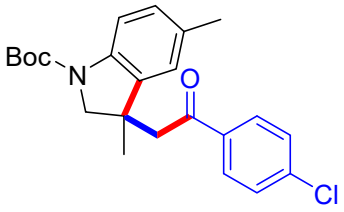


3b1, 1-(5-chloro-3-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylindolin-1-yl)propan-1-one, white solid: mp 168–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.18 (ddd, J = 8.6, 2.2, 0.7 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 4.18 (d, J = 11.0 Hz, 1H), 4.05 (d, J = 11.0 Hz, 1H), 3.44 (d, J = 17.4 Hz, 1H), 3.20 (d, J = 17.4 Hz, 1H), 2.54–2.38 (m, 2H), 1.48 (s, 3H), 1.22 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.6, 172.2, 140.7, 140.5, 140.1, 135.2, 129.4, 129.0, 128.4, 128.3, 122.4, 118.1, 60.4, 47.9, 42.2, 29.1, 26.4, 8.6; HRMS (ESI-TOF) Calcd for $C_{20}H_{20}Cl_2NO_2^+$ ([M+H]$^+$) 376.0866. Found 376.0865.

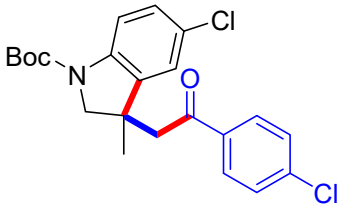


3b2, 1-(5-chloro-3-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylindolin-1-yl)-2,2-dimethylpropan-1-one, colorless crystal: mp 167–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.7 Hz, 1H), 7.85 (ddd, J = 8.7, 2.5, 2.0 Hz, 2H), 7.44 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.19 (dd,

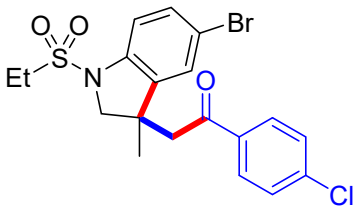
J = 8.7, 2.3 Hz, 1H), 7.12 (d, J = 2.2 Hz, 1H), 4.43 (d, J = 10.8 Hz, 1H), 4.23 (d, J = 10.8 Hz, 1H), 3.44 (d, J = 17.3 Hz, 1H), 3.08 (d, J = 17.3 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.8, 176.8, 142.1, 140.6, 140.1, 135.3, 129.4, 129.1, 128.7, 128.0, 122.1, 119.7, 61.4, 46.6, 43.0, 40.2, 27.6, 24.4; HRMS (ESI-TOF) Calcd for $C_{22}H_{24}Cl_2NO_2^+$ ($[M+H]^+$) 404.1179. Found 404.1186.



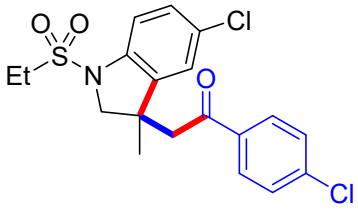
3c1, *tert*-butyl 3-(2-(4-chlorophenyl)-2-oxoethyl)-3,5-dimethylindoline-1-carboxylate, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.3 Hz, 2H), 7.65 (brs, 1H), 7.29 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.82 (s, 1H), 3.94 (d, J = 11.8 Hz, 1H), 3.81 (d, J = 11.7 Hz, 1H), 3.30 (d, J = 17.0 Hz, 1H), 3.07 (d, J = 16.9 Hz, 1H), 2.20 (s, 3H), 1.46 (s, 9H), 1.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 195.8 (br), 151.5, 138.5, 137.5 (br), 134.7, 130.7, 128.3, 127.8, 127.6, 122.0 (br), 113.6, 79.5 (br), 59.3, 47.2, 40.4 (br), 27.4, 25.1, 19.9; HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_3^+$ ($[M+H]^+$) 400.1674. Found 400.1677.



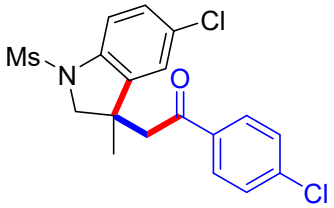
3c2, *tert*-butyl 5-chloro-3-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylindoline-1-carboxylate, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.6 Hz, 3H), 7.41 (d, J = 8.6 Hz, 2H), 7.14 (dd, J = 8.6, 2.2 Hz, 1H), 7.07 (d, J = 2.2 Hz, 1H), 4.05 (d, J = 11.8 Hz, 1H), 3.93 (d, J = 11.7 Hz, 1H), 3.38 (d, J = 17.3 Hz, 1H), 3.20 (d, J = 17.3 Hz, 1H), 1.55 (s, 9H), 1.47 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.3 (br), 152.3, 140.4 (br), 139.8, 135.4, 129.3, 128.9, 128.0, 127.2, 122.7 (br), 115.8, 81.2 (br), 60.3, 48.1, 41.4 (br), 28.4, 26.4; HRMS (ESI-TOF) Calcd for $C_{22}H_{24}Cl_2NO_3^+$ ($[M+H]^+$) 420.1128. Found 420.1141.



3d1, 2-(5-bromo-1-(ethylsulfonyl)-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.43 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.33–7.26 (m, 2H), 7.23 (d, J = 1.7 Hz, 1H), 4.13 (d, J = 10.5 Hz, 1H), 3.96 (d, J = 10.5 Hz, 1H), 3.43 (d, J = 17.6 Hz, 1H), 3.27 (d, J = 17.6 Hz, 1H), 3.18 (q, J = 7.4 Hz, 2H), 1.49 (s, 3H), 1.43 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 195.9, 140.6, 140.5, 140.1, 135.2, 131.3, 129.4, 129.0, 126.2, 115.6, 114.8, 62.1, 47.2, 44.3, 42.1, 26.8, 7.8; HRMS (ESI-TOF) Calcd for $C_{19}H_{20}BrClNO_3S^+$ ([M+H]$^+$) 456.0030. Found 456.0030.

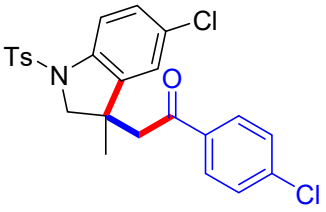


3d2, 2-(5-chloro-1-(ethylsulfonyl)-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.36 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.25 (d, J = 8.6 Hz, 1H), 7.08 (dd, J = 8.6, 2.2 Hz, 1H), 7.02 (d, J = 2.1 Hz, 1H), 4.06 (d, J = 10.5 Hz, 1H), 3.90 (d, J = 10.5 Hz, 1H), 3.36 (d, J = 17.6 Hz, 1H), 3.21 (d, J = 17.7 Hz, 1H), 3.11 (q, J = 7.4 Hz, 2H), 1.42 (s, 3H), 1.36 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 195.9, 140.2, 140.0, 140.0, 135.2, 129.3, 129.0, 128.3, 128.3, 123.3, 114.3, 62.2, 47.1, 44.3, 42.1, 26.7, 7.7; HRMS (ESI-TOF) Calcd for $C_{19}H_{20}Cl_2NO_3S^+$ ([M+H]$^+$) 412.0535. Found 412.0534.

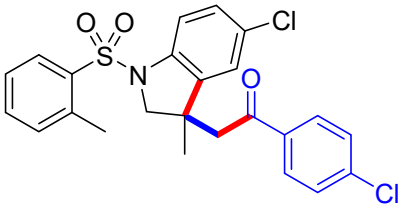


3e1, 2-(5-chloro-3-methyl-1-(methylsulfonyl)indolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, white solid: mp 143–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.43 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.36 (d, J = 8.6 Hz, 1H), 7.18 (dd, J

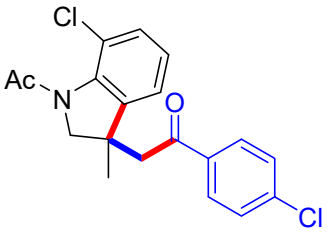
= 8.6, 2.2 Hz, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 4.10 (d, *J* = 10.5 Hz, 1H), 3.91 (d, *J* = 10.5 Hz, 1H), 3.44 (d, *J* = 17.8 Hz, 1H), 3.31 (d, *J* = 17.8 Hz, 1H), 2.98 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 195.8, 140.4, 140.0, 139.8, 135.0, 129.3, 129.0, 128.7, 128.4, 123.3, 114.3, 62.1, 47.0, 41.9, 34.8, 27.0; HRMS (ESI-TOF) Calcd for $C_{18}H_{18}Cl_2NO_3S^+$ ($[M+H]^+$) 398.0379. Found 398.0377.



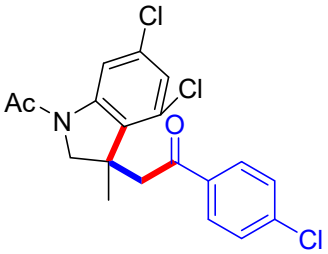
3e2, 2-(5-chloro-3-methyl-1-tosylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, white solid: mp 166–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (ddd, *J* = 8.6, 2.5, 2.0 Hz, 2H), 7.66 (ddd, *J* = 8.3, 2.1, 1.9 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.41 (ddd, *J* = 8.6, 2.5, 2.0 Hz, 2H), 7.20 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 2.2 Hz, 1H), 4.08 (d, *J* = 11.4 Hz, 1H), 3.87 (d, *J* = 11.4 Hz, 1H), 3.18 (d, *J* = 17.6 Hz, 1H), 2.64 (d, *J* = 17.7 Hz, 1H), 2.29 (s, 3H), 1.27 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 195.7, 144.3, 141.3, 139.9, 139.5, 135.1, 134.0, 129.8, 129.3, 129.05, 128.95, 128.4, 127.2, 123.3, 116.2, 61.6, 47.5, 42.2, 25.2, 21.5; HRMS (ESI-TOF) Calcd for $C_{24}H_{22}Cl_2NO_3S^+$ ($[M+H]^+$) 474.0692. Found 474.0694.



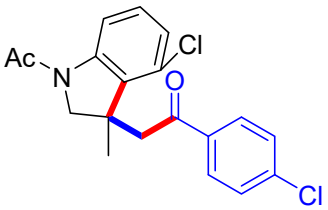
3e3, 2-(5-chloro-3-methyl-1-(o-tolylsulfonyl)indolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, white crystal: mp 166–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.77 (ddd, *J* = 8.7, 2.5, 2.0 Hz, 2H), 7.44–7.39 (m, 3H), 7.37 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.29–7.24 (m, 2H), 7.15 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 4.08 (d, *J* = 11.1 Hz, 1H), 3.91 (d, *J* = 11.1 Hz, 1H), 3.31 (d, *J* = 17.7 Hz, 1H), 2.95 (d, *J* = 17.6 Hz, 1H), 2.59 (s, 3H), 1.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 195.8, 141.0, 140.1, 140.0, 138.1, 137.0, 135.1, 133.2, 133.0, 129.5, 129.3, 129.0, 128.7, 128.3, 126.4, 123.3, 116.0, 61.5, 47.3, 42.4, 25.5, 21.0; HRMS (ESI-TOF) Calcd for $C_{24}H_{22}Cl_2NO_3S^+$ ($[M+H]^+$) 474.0692. Found 474.0691.



3f, 2-(1-acetyl-7-chloro-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, white semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.25 (dd, J = 7.7, 1.6 Hz, 1H), 7.13–7.06 (m, 2H), 4.29 (d, J = 11.2 Hz, 1H), 4.07 (d, J = 11.2 Hz, 1H), 3.40 (d, J = 16.9 Hz, 1H), 3.05 (d, J = 16.9 Hz, 1H), 2.31 (s, 3H), 1.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.6, 144.7, 140.0, 139.6, 135.4, 129.7, 129.4, 129.0, 126.4, 124.6, 120.8, 62.9, 45.8, 44.2, 23.7, 23.6; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}Cl_2NO_2^+$ ([M+H]$^+$) 362.0709. Found 362.0716.

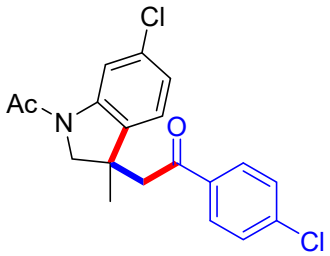


3g, 2-(1-acetyl-4,6-dichloro-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, white semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, J = 1.9 Hz, 1H), 7.85 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.43 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 6.97 (d, J = 1.9 Hz, 1H), 4.24 (d, J = 10.7 Hz, 1H), 4.01 (d, J = 10.8 Hz, 1H), 3.80 (d, J = 17.6 Hz, 1H), 3.52 (d, J = 17.5 Hz, 1H), 2.23 (s, 3H), 1.60 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.7, 169.1, 144.4, 140.0, 135.2, 134.7, 132.7, 129.8, 129.3, 129.0, 124.7, 116.1, 61.9, 45.3, 43.4, 24.9, 24.4; HRMS (ESI-TOF) Calcd for $C_{19}H_{17}Cl_3NO_2^+$ ([M+H]$^+$) 396.0319. Found 396.0317.

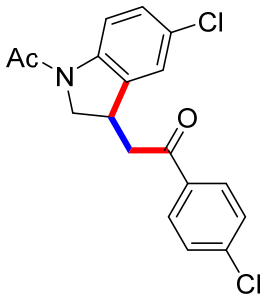


3h, 2-(1-acetyl-4-chloro-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.14 (dd, J = 8.1, 8.1 Hz, 1H), 6.96 (dd, J = 8.0, 1.0

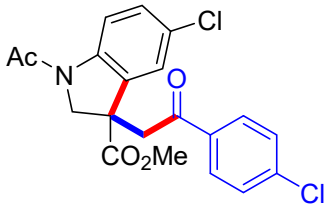
Hz, 1H), 4.24 (d, J = 10.8 Hz, 1H), 4.00 (d, J = 10.8 Hz, 1H), 3.86 (d, J = 17.3 Hz, 1H), 3.49 (d, J = 17.3 Hz, 1H), 2.23 (s, 3H), 1.63 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.1, 168.9, 143.9, 139.9, 135.3, 134.0, 129.65, 129.58, 129.4, 129.0, 125.2, 115.7, 61.5, 45.4, 43.7, 24.8, 24.4; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}Cl_2NO_2^+$ ($[M+H]^+$) 362.0709. Found 362.0710.



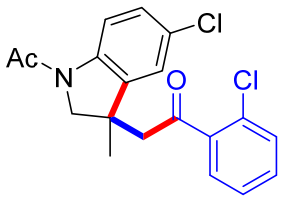
3h', 2-(1-acetyl-6-chloro-3-methylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, J = 1.9 Hz, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 1H), 7.02 (dd, J = 8.0, 1.9 Hz, 1H), 4.19 (d, J = 10.9 Hz, 1H), 4.05 (d, J = 10.9 Hz, 1H), 3.43 (d, J = 17.3 Hz, 1H), 3.20 (d, J = 17.4 Hz, 1H), 2.23 (s, 3H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.7, 169.0, 142.6, 140.1, 137.3, 135.3, 133.9, 129.3, 129.0, 123.7, 122.8, 117.4, 61.5, 48.0, 41.9, 26.5, 24.2; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}Cl_2NO_2^+$ ($[M+H]^+$) 362.0709. Found 362.0712.



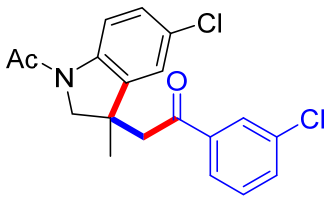
3i1, 2-(1-acetyl-5-chloroindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one, white crystal: mp 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.20 (ddd, J = 8.6, 2.2, 0.7 Hz, 1H), 7.16 (s, 1H), 4.48 (dd, J = 11.0, 9.5 Hz, 1H), 4.01 (tq, J = 9.8, 4.7, 4.2 Hz, 1H), 3.68 (dd, J = 10.9, 5.9 Hz, 1H), 3.52 (dd, J = 18.3, 3.8 Hz, 1H), 3.25 (dd, J = 18.3, 10.2 Hz, 1H), 2.21 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.6, 168.8, 141.4, 140.3, 135.4, 134.5, 129.4, 129.2, 128.6, 128.3, 123.9, 118.1, 55.8, 44.8, 35.5, 24.1; HRMS (ESI-TOF) Calcd for $C_{18}H_{16}Cl_2NO_2^+$ ($[M+H]^+$) 348.0553. Found 348.0552.



3i2, methyl 1-acetyl-5-chloro-3-(2-(4-chlorophenyl)-2-oxoethyl)indoline-3-carboxylate, pale yellow crystal: mp 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, J = 8.4 Hz, 1H), 7.91 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.47 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.29–7.26 (m, 2H), 5.12 (d, J = 11.5 Hz, 1H), 4.16 (d, J = 18.3 Hz, 1H), 3.84 (d, J = 11.5 Hz, 1H), 3.75 (s, 3H), 3.39 (d, J = 18.3 Hz, 1H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 195.9, 171.9, 168.7, 141.1, 140.6, 133.9, 132.9, 129.8, 129.6, 129.2, 128.7, 123.6, 118.4, 58.1, 53.4, 51.6, 48.5, 24.2; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}Cl_2NO_4^+$ ([M+H]$^+$) 406.0607. Found 406.0609.

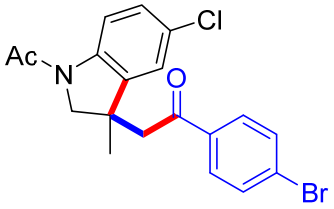


3j, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(2-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.42–7.36 (m, 2H), 7.33–7.28 (m, 2H), 7.15 (dd, J = 8.6, 2.2 Hz, 1H), 7.05 (d, J = 2.2 Hz, 1H), 4.26 (d, J = 11.0 Hz, 1H), 4.05 (d, J = 11.0 Hz, 1H), 3.42 (d, J = 17.3 Hz, 1H), 3.27 (d, J = 17.3 Hz, 1H), 2.25 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 201.4, 169.0, 140.4, 140.3, 139.3, 132.1, 130.6, 128.64, 128.56, 128.3, 127.1, 122.5, 118.2, 61.3, 52.3, 42.6, 26.6, 24.2; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}Cl_2NO_2^+$ ([M+H]$^+$) 362.0709. Found 362.0710.

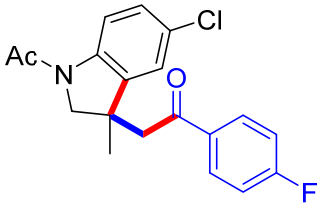


3k, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(3-chlorophenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.87 (dd, J = 2.0, 2.0 Hz, 1H), 7.78 (ddd, J = 7.8, 1.4, 1.4 Hz, 1H), 7.55 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.41 (dd, J = 7.9, 7.9 Hz, 1H), 7.18 (dd, J = 8.6, 2.2 Hz, 1H), 7.13 (d, J = 2.2 Hz, 1H),

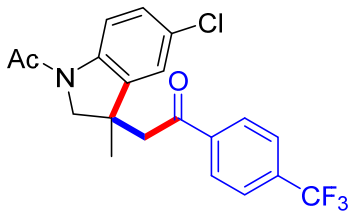
4.18 (d, J = 11.0 Hz, 1H), 4.06 (d, J = 11.0 Hz, 1H), 3.44 (d, J = 17.5 Hz, 1H), 3.23 (d, J = 17.4 Hz, 1H), 2.23 (s, 3H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.5, 168.9, 140.7, 140.3, 138.4, 135.2, 133.5, 130.1, 128.7, 128.3, 128.1, 126.0, 122.5, 118.2, 61.3, 48.1, 42.2, 26.4, 24.1; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}Cl_2NO_2^+$ ($[M+H]^+$) 362.0709. Found 362.0722.



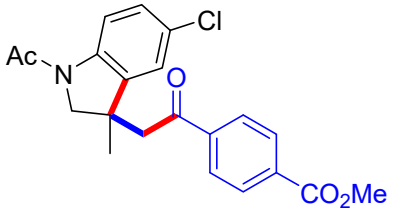
3l1, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(4-bromophenyl)ethan-1-one, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.18 (dd, J = 8.7, 2.2 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 4.19 (d, J = 10.9 Hz, 1H), 4.06 (d, J = 11.0 Hz, 1H), 3.43 (d, J = 17.4 Hz, 1H), 3.21 (d, J = 17.4 Hz, 1H), 2.23 (s, 3H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.7, 168.9, 140.8, 140.3, 135.6, 132.0, 129.4, 128.9, 128.6, 128.3, 122.4, 118.2, 61.3, 47.9, 42.2, 26.4, 24.2; HRMS (ESI-TOF) Calcd for $C_{19}H_{18}BrClNO_2^+$ ($[M+H]^+$) 406.0204. Found 406.0208.



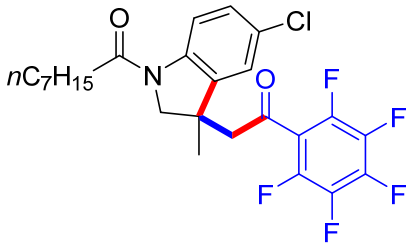
3l2, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(4-fluorophenyl)ethan-1-one, yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.95–7.92 (m, 2H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 7.15 – 7.10 (m, 3H), 4.20 (d, J = 11.0 Hz, 1H), 4.06 (d, J = 11.0 Hz, 1H), 3.45 (d, J = 17.3 Hz, 1H), 3.22 (d, J = 17.3 Hz, 1H), 2.23 (s, 3H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.2, 168.9, 166.0 (d, $^1J_{(C–F)}$ = 255.9 Hz), 140.9, 140.3, 133.4 (d, $^4J_{(C–F)}$ = 3.0 Hz), 130.7 (d, $^3J_{(C–F)}$ = 9.5 Hz), 128.6, 128.2, 122.5, 118.2, 115.9 (d, $^2J_{(C–F)}$ = 21.8 Hz), 61.4, 47.9, 42.2, 26.4, 24.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = –104.12 to –104.19 (m, 1F); HRMS (ESI-TOF) Calcd for $C_{19}H_{18}ClFNO_2^+$ ($[M+H]^+$) 346.1005. Found 346.1001.



3l3, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 7.12 (d, J = 2.2 Hz, 1H), 4.19 (d, J = 10.9 Hz, 1H), 4.07 (d, J = 11.0 Hz, 1H), 3.49 (d, J = 17.5 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 2.23 (s, 3H), 1.51 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.9, 168.9, 140.5, 140.3, 139.4, 134.8 (q, $^{2}J_{(C–F)}$ = 32.8 Hz), 128.7, 128.33, 128.31, 125.8 (q, $^{3}J_{(C–F)}$ = 3.7 Hz), 123.4473 (q, $^{1}J_{(C–F)}$ = 271.2 Hz), 124.8, 122.4, 122.1, 119.4, 118.2, 61.3, 48.4, 42.2, 26.4, 24.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = –63.20 (s, 3F); HRMS (ESI-TOF) Calcd for $C_{20}H_{18}ClF_3NO_2^+$ ([M+H]$^+$) 396.0973. Found 396.0970.

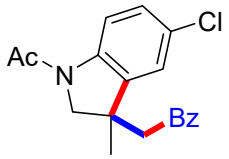


3l4, methyl 4-(2-(1-acetyl-5-chloro-3-methylindolin-3-yl)acetyl)benzoate, white semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15–8.10 (m, 3H), 7.95 (d, J = 8.1 Hz, 2H), 7.18 (dd, J = 8.6, 2.2 Hz, 1H), 7.13 (d, J = 2.2 Hz, 1H), 4.19 (d, J = 10.9 Hz, 1H), 4.08 (d, J = 10.9 Hz, 1H), 3.95 (s, 3H), 3.51 (d, J = 17.5 Hz, 1H), 3.28 (d, J = 17.5 Hz, 1H), 2.23 (s, 3H), 1.50 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.3, 168.8, 166.0, 140.7, 140.3, 140.0, 134.3, 129.9, 128.6, 128.3, 127.9, 122.5, 118.2, 61.3, 52.5, 48.4, 42.2, 26.4, 24.1; HRMS (ESI-TOF) Calcd for $C_{21}H_{21}ClNO_4^+$ ([M+H]$^+$) 386.1154. Found 386.1152.

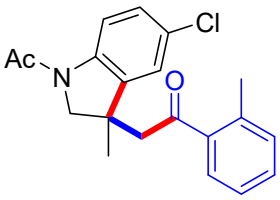


3m, 1-(5-chloro-3-methyl-3-(2-oxo-2-(perfluorophenyl)ethyl)indolin-1-yl)octan-1-one,

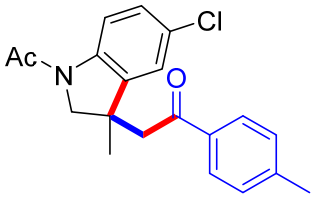
yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 8.7 Hz, 1H), 7.16 (dd, J = 8.7, 2.2 Hz, 1H), 7.05 (d, J = 2.2 Hz, 1H), 4.18 (d, J = 11.0 Hz, 1H), 4.01 (d, J = 11.1 Hz, 1H), 3.29–3.18 (m, 2H), 2.43 (t, J = 7.5 Hz, 2H), 1.73 (p, J = 7.5 Hz, 2H), 1.50 (s, 3H), 1.44–1.27 (m, 8H), 0.91–0.87 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 192.2, 171.6, 140.6, 139.2, 128.5, 122.3, 118.2, 60.2, 54.6, 42.6, 35.9, 31.7, 29.3, 29.1, 26.5, 24.5, 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = –140.77 to –140.86 (m, 2F), –148.12 to –148.23 (m, 1F), –159.29 to –159.45 (m, 2F); HRMS (ESI-TOF) Calcd for $C_{25}H_{26}ClF_5NO_2^+$ ([M+H]$^+$) 502.1567. Found 502.1566.



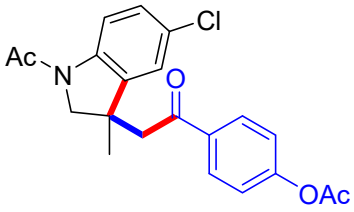
3n, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-phenylethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 7.2 Hz, 2H), 7.59 (dd, J = 7.4, 7.4 Hz, 1H), 7.47 (dd, J = 7.6, 7.6 Hz, 2H), 7.18 (dd, J = 8.6, 2.2 Hz, 1H), 7.13 (d, J = 2.2 Hz, 1H), 4.20 (d, J = 11.0 Hz, 1H), 4.08 (d, J = 11.0 Hz, 1H), 3.50 (d, J = 17.4 Hz, 1H), 3.24 (d, J = 17.4 Hz, 1H), 2.22 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.8, 168.9, 141.1, 140.3, 136.9, 133.6, 128.7, 128.6, 128.2, 128.0, 122.5, 118.1, 61.4, 47.9, 42.2, 26.5, 24.2; HRMS (ESI-TOF) Calcd for $C_{19}H_{19}ClNO_2^+$ ([M+H]$^+$) 328.1099. Found 328.1096.



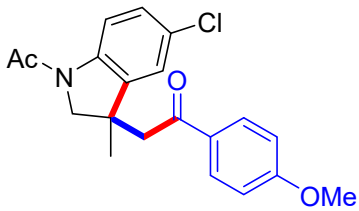
3o, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(*o*-tolyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 7.1 Hz, 1H), 7.39 (dd, J = 7.3, 7.3 Hz, 1H), 7.28–7.24 (m, 2H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 7.07 (d, J = 2.2 Hz, 1H), 4.25 (d, J = 11.0 Hz, 1H), 4.08 (d, J = 11.0 Hz, 1H), 3.39 (d, J = 17.1 Hz, 1H), 3.21 (d, J = 17.1 Hz, 1H), 2.46 (s, 3H), 2.23 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 168.9, 140.9, 140.3, 138.1, 137.8, 132.2, 131.8, 128.6, 128.4, 128.2, 125.8, 122.5, 118.1, 61.4, 50.7, 42.5, 26.6, 24.2, 21.3; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_2^+$ ([M+H]$^+$) 342.1255. Found 342.1261.



3p1, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(*p*-tolyl)ethan-1-one, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 8.6, 2.2 Hz, 1H), 7.13 (d, J = 2.2 Hz, 1H), 4.21 (d, J = 11.0 Hz, 1H), 4.07 (d, J = 11.0 Hz, 1H), 3.48 (d, J = 17.4 Hz, 1H), 3.20 (d, J = 17.3 Hz, 1H), 2.42 (s, 3H), 2.22 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.4, 168.9, 144.5, 141.2, 140.3, 134.5, 129.4, 128.5, 128.12, 128.08, 122.5, 118.1, 61.5, 47.7, 42.2, 26.5, 24.2, 21.7; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_2^+$ ([M+H]$^+$) 342.1255. Found 342.1257.

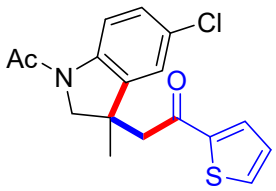


3p2, 4-(2-(1-acetyl-5-chloro-3-methylindolin-3-yl)acetyl)phenyl acetate, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 2H), 7.21–7.17 (m, 3H), 7.12 (d, J = 2.2 Hz, 1H), 4.19 (d, J = 11.0 Hz, 1H), 4.07 (d, J = 11.0 Hz, 1H), 3.47 (d, J = 17.4 Hz, 1H), 3.22 (d, J = 17.4 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 196.5, 168.9, 168.7, 154.7, 141.0, 140.3, 134.5, 129.6, 128.6, 128.2, 122.4, 122.0, 118.2, 61.4, 47.9, 42.2, 26.4, 24.2, 21.2; HRMS (ESI-TOF) Calcd for $C_{21}H_{21}ClNO_4^+$ ([M+H]$^+$) 386.1154. Found 386.1152.

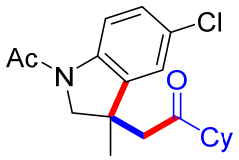


3p3, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(4-methoxyphenyl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.9 Hz, 2H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 7.13 (d, J = 2.2 Hz, 1H), 6.92 (d, J = 8.9 Hz, 2H), 4.22 (d, J = 11.0 Hz, 1H), 4.06 (d, J = 11.0 Hz, 1H), 3.87 (s, 3H), 3.45 (d, J

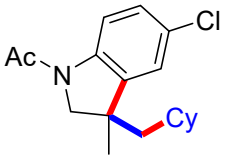
= 17.1 Hz, 1H), 3.17 (d, J = 17.2 Hz, 1H), 2.22 (s, 3H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.2, 169.0, 163.8, 141.3, 140.3, 130.3, 130.1, 128.5, 128.1, 122.5, 118.1, 113.9, 61.5, 55.5, 47.5, 42.3, 26.5, 24.2; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_3^+$ ($[M+H]^+$) 358.1204. Found 358.1204.



3q, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-(thiophen-2-yl)ethan-1-one, yellow solid: mp 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.67–7.66 (m, 2H), 7.18 (dd, J = 8.6, 2.2 Hz, 1H), 7.14–7.12 (m, 2H), 4.29 (d, J = 11.0 Hz, 1H), 4.00 (d, J = 11.0 Hz, 1H), 3.38 (d, J = 16.6 Hz, 1H), 3.14 (d, J = 16.6 Hz, 1H), 2.23 (s, 3H), 1.49 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 190.7, 168.9, 144.4, 140.7, 140.3, 134.5, 132.4, 128.6, 128.33, 128.26, 122.5, 118.2, 61.3, 48.5, 42.5, 26.3, 24.1; HRMS (ESI-TOF) Calcd for $C_{17}H_{17}ClNO_2S^+$ ($[M+H]^+$) 334.0663. Found 334.0661.

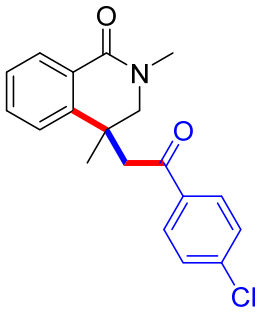


3r, 2-(1-acetyl-5-chloro-3-methylindolin-3-yl)-1-cyclohexylethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 8.6 Hz, 1H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 7.06 (d, J = 2.2 Hz, 1H), 4.09 (d, J = 11.0 Hz, 1H), 3.98 (d, J = 10.9 Hz, 1H), 2.94 (d, J = 17.5 Hz, 1H), 2.72 (d, J = 17.5 Hz, 1H), 2.29–2.21 (m, 4H), 1.92–1.74 (m, 4H), 1.37–1.16 (m, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 212.1, 168.9, 141.0, 140.2, 128.5, 128.1, 122.3, 118.1, 61.5, 51.6, 50.0, 41.9, 28.3, 28.2, 26.3, 25.7, 25.6, 25.5, 24.1; HRMS (ESI-TOF) Calcd for $C_{19}H_{25}ClNO_2^+$ ($[M+H]^+$) 334.1568. Found 334.1569.

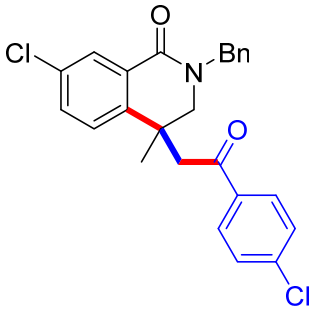


3r', 1-(5-chloro-3-(cyclohexylmethyl)-3-methylindolin-1-yl)ethan-1-one, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, J = 8.6 Hz, 1H), 7.15 (dd, J = 8.6, 2.2

Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 3.92 (d, J = 10.2 Hz, 1H), 3.71 (d, J = 10.2 Hz, 1H), 2.21 (s, 3H), 1.67–0.84 (m, 16H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 168.7, 142.2, 140.4, 128.5, 127.6, 122.7, 117.9, 61.9, 48.4, 43.8, 35.4, 34.7, 34.6, 27.8, 26.32, 26.26, 26.1, 24.2; HRMS (ESI-TOF) Calcd for $C_{18}H_{25}ClNO^+$ ($[M+H]^+$) 306.1619. Found 306.1622.

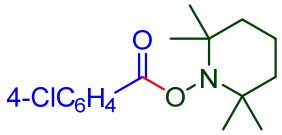


4a, 4-(2-(4-chlorophenyl)-2-oxoethyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2*H*)-one, white semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (dd, J = 7.7, 1.5 Hz, 1H), 7.68 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.43 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 7.36–7.32 (m, 3H), 7.27 (dd, J = 7.8, 1.2 Hz, 1H), 3.67 (d, J = 12.7 Hz, 1H), 3.54 (d, J = 12.7 Hz, 1H), 3.24 (d, J = 15.3 Hz, 1H), 3.12 (d, J = 9.0 Hz, 4H), 1.54 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.3, 164.5, 144.9, 139.7, 135.8, 132.1, 129.4, 128.9, 128.8, 128.2, 127.3, 123.8, 57.2, 45.6, 37.3, 35.1, 22.5; HRMS (ESI-TOF) Calcd for $C_{19}H_{19}ClNO_2^+$ ($[M+H]^+$) 328.1099. Found 328.1097.

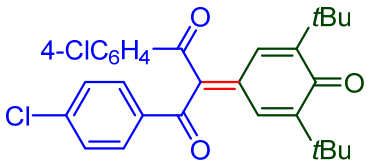


4b, 2-benzyl-7-chloro-4-(2-(4-chlorophenyl)-2-oxoethyl)-4-methyl-3,4-dihydroisoquinolin-1(2*H*)-one, yellow solid: mp 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 2.4 Hz, 1H), 7.55 (ddd, J = 8.6, 2.5, 2.0 Hz, 2H), 7.40 (dd, J = 8.3, 2.3 Hz, 1H), 7.33 (d, J = 8.5 Hz, 4H), 7.26–7.22 (m, 3H), 7.20–7.16 (m, 1H), 4.88 (d, J = 14.3 Hz, 1H), 4.57 (d, J = 14.3 Hz, 1H), 3.67 (d, J = 12.8 Hz, 1H), 3.43 (d, J = 12.8 Hz, 1H), 3.07 (d, J = 16.7 Hz, 1H), 2.88 (d, J = 16.7 Hz, 1H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.1, 163.0, 143.2, 139.7, 136.7, 135.3, 133.6, 132.0, 129.8, 129.3, 128.9, 128.8, 128.74, 128.71, 127.7, 126.2, 54.6, 50.6, 45.1, 36.4, 22.1; HRMS (ESI-TOF)

Calcd for $C_{25}H_{22}Cl_2NO_2^+$ ([M+H]$^+$) 438.1022. Found 438.1033.



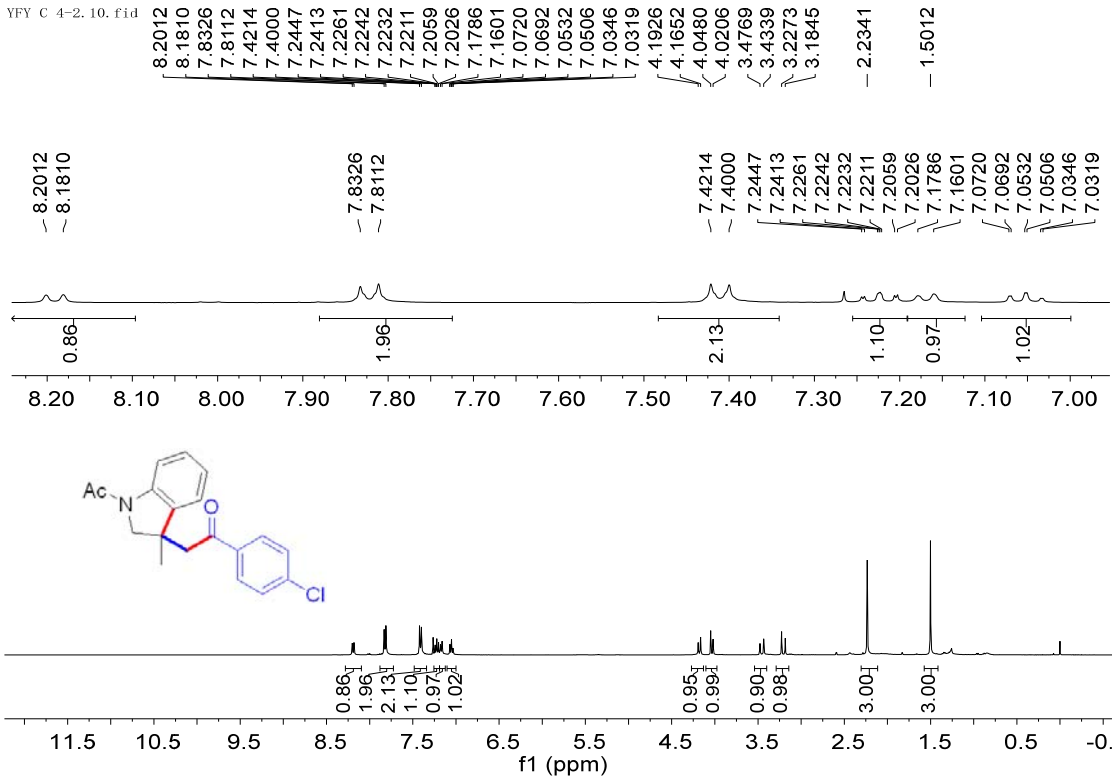
5a, 2,2,6,6-tetramethylpiperidin-1-yl 4-chlorobenzoate, greenish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (ddd, J = 8.6, 2.4, 2.0 Hz, 2H), 7.44 (ddd, J = 8.6, 2.4, 2.0 Hz, 2H), 1.81–1.58 (m, 5H), 1.49–1.42 (m, 1H), 1.26 (s, 6H), 1.11 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.5, 139.3, 130.9, 128.8, 128.0, 60.4, 39.0, 31.9, 20.8, 16.9; HRMS (ESI-TOF) Calcd for $C_{16}H_{23}ClNO_2^+$ ([M+H]$^+$) 296.1412. Found 296.1410.



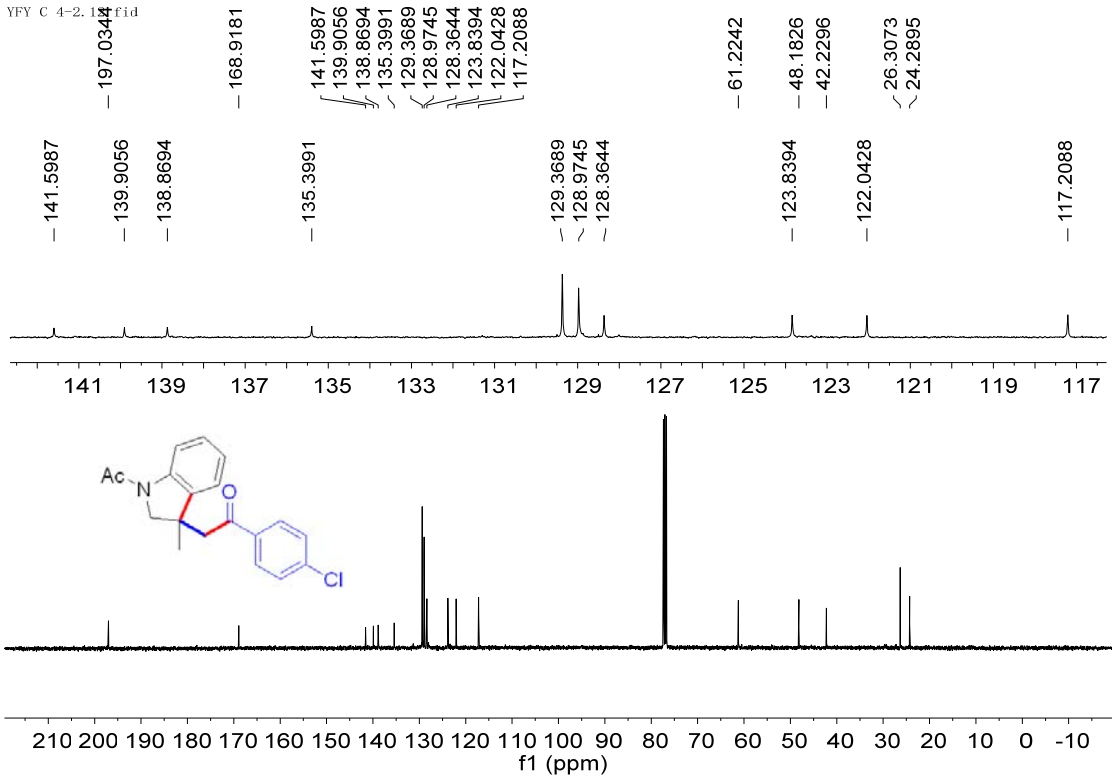
5b, 1,3-bis(4-chlorophenyl)-2-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)propane-1,3-dione, yellow solid: mp 171–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (ddd, J = 8.6, 2.4, 2.0 Hz, 4H), 7.48 (ddd, J = 8.6, 2.4, 2.0 Hz, 4H), 6.86 (s, 2H), 1.16 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 192.4, 185.8, 151.6, 145.9, 141.4, 135.3, 134.9, 131.7, 129.4, 127.9, 35.7, 29.3; HRMS (ESI-TOF) Calcd for $C_{29}H_{29}Cl_2O_3^+$ ([M+H]$^+$) 495.1488. Found 495.1492.

VII. Copies of ^{1}H, ^{19}F, ^{13}C and DEPT NMR Spectra

3a1, ^{1}H NMR



^{13}C NMR



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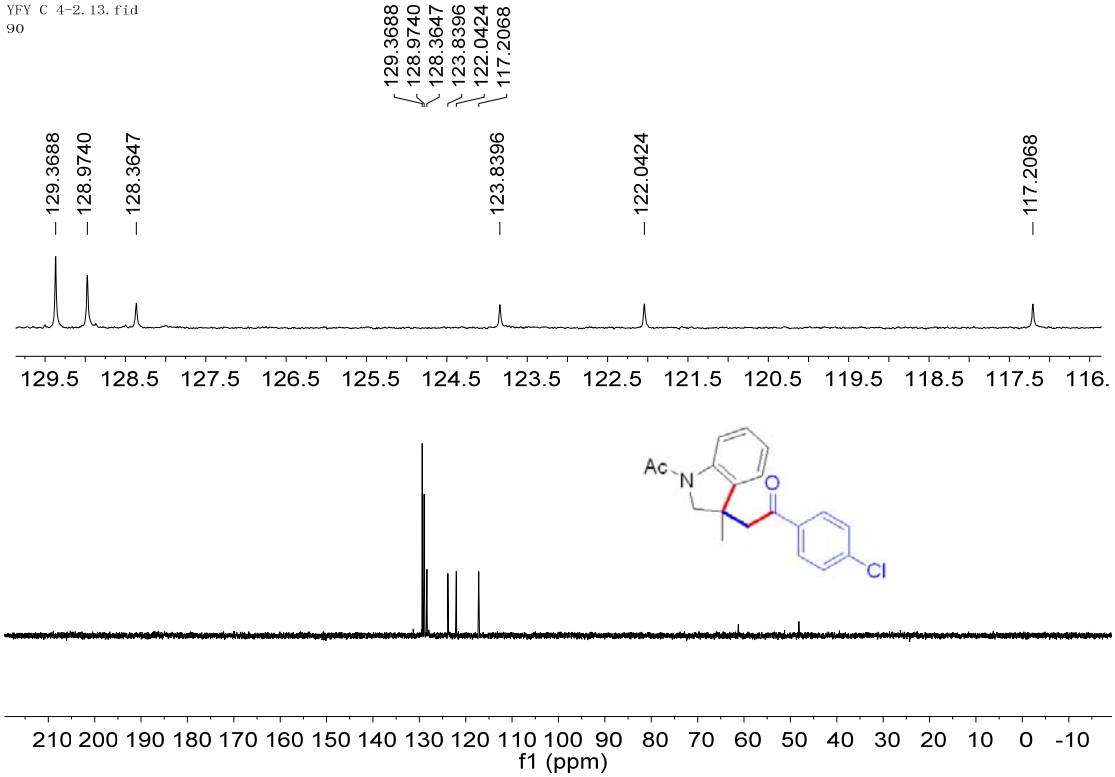

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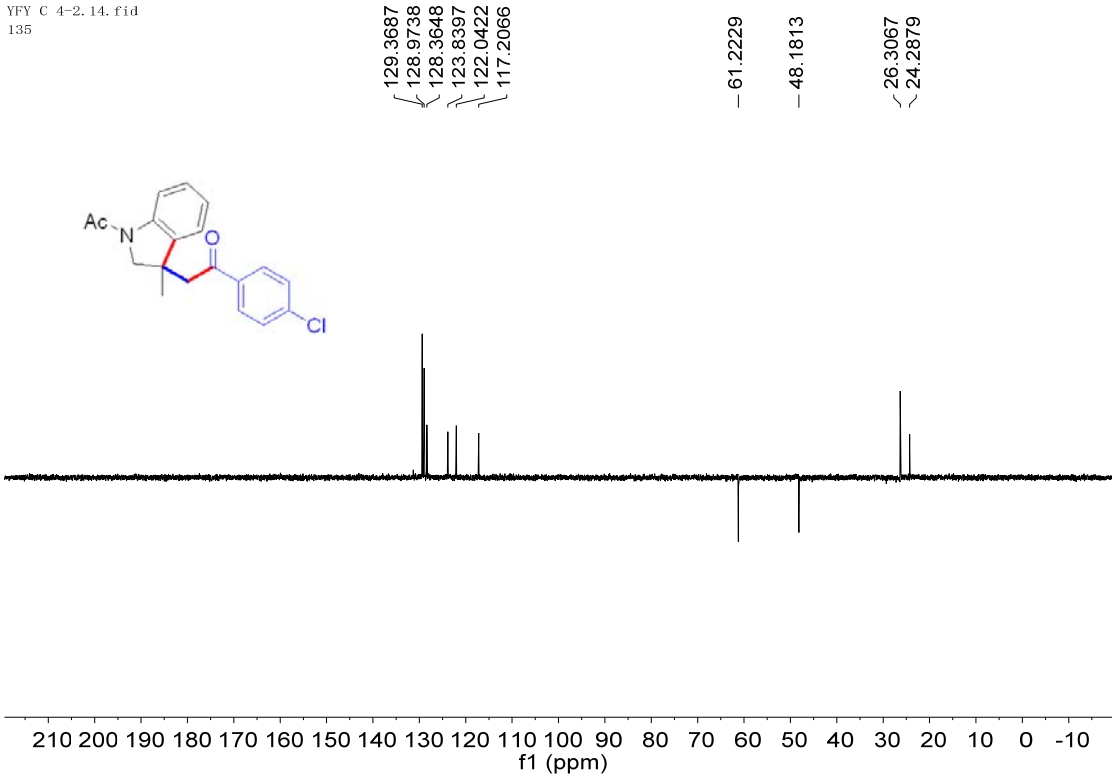
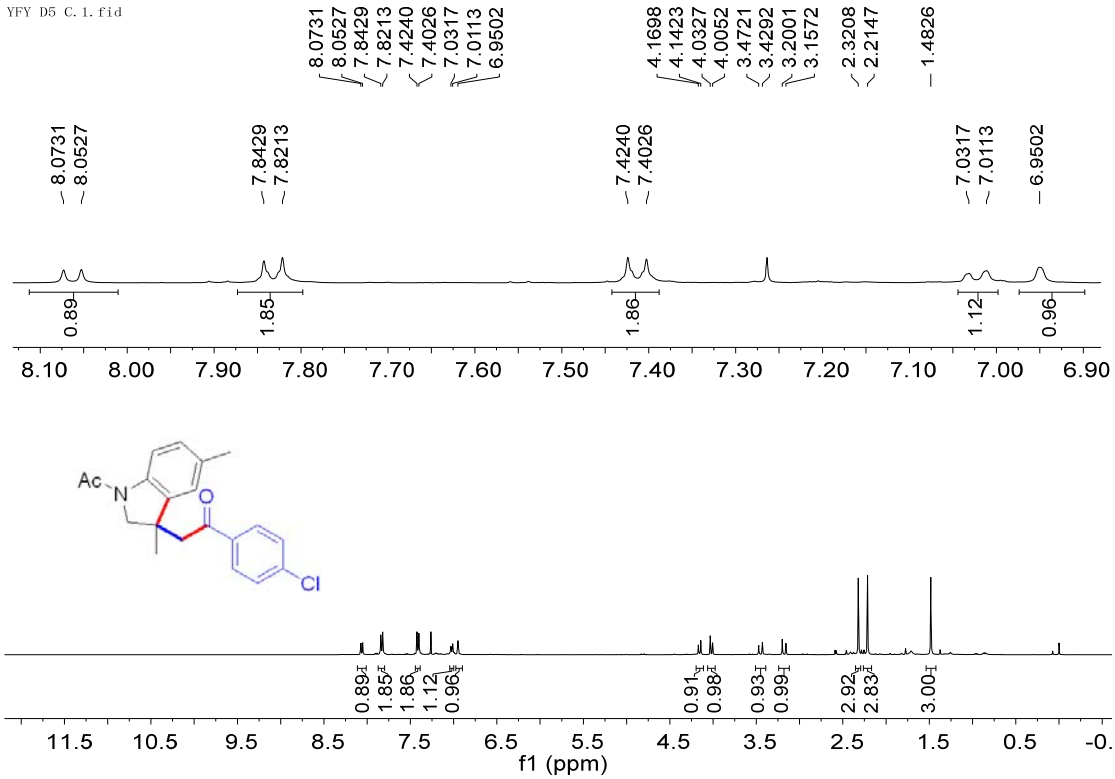
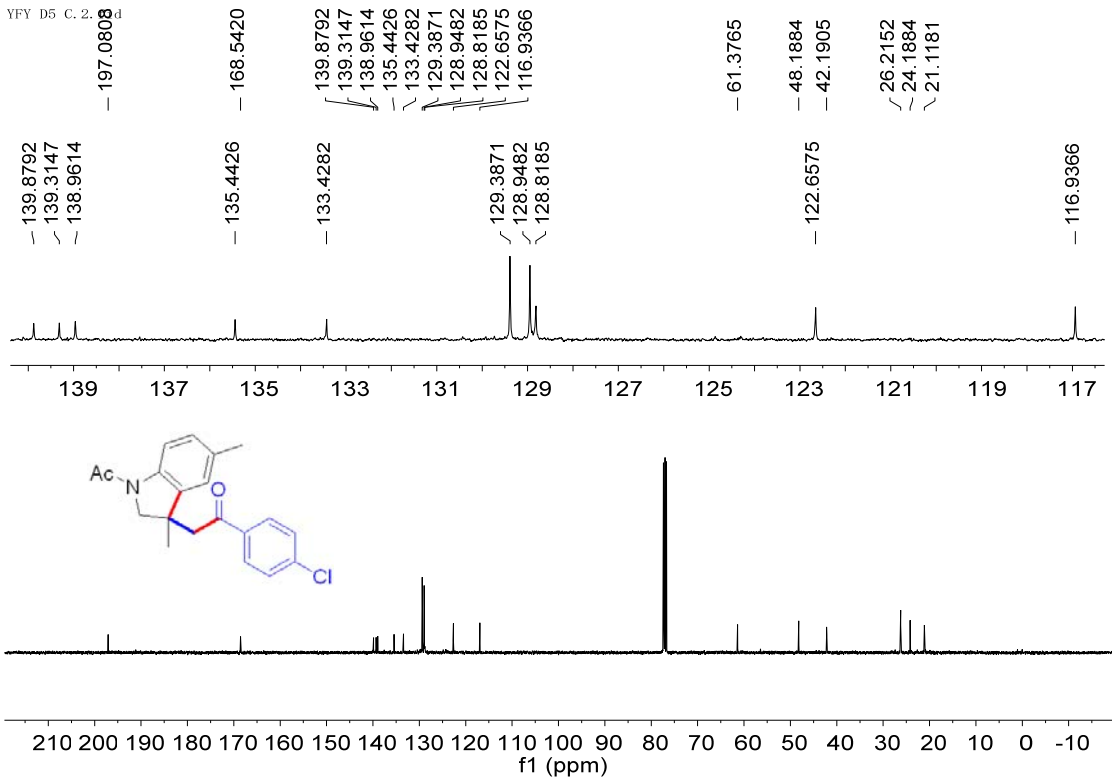


3a2, ^{1}H NMR



^{13}C NMR



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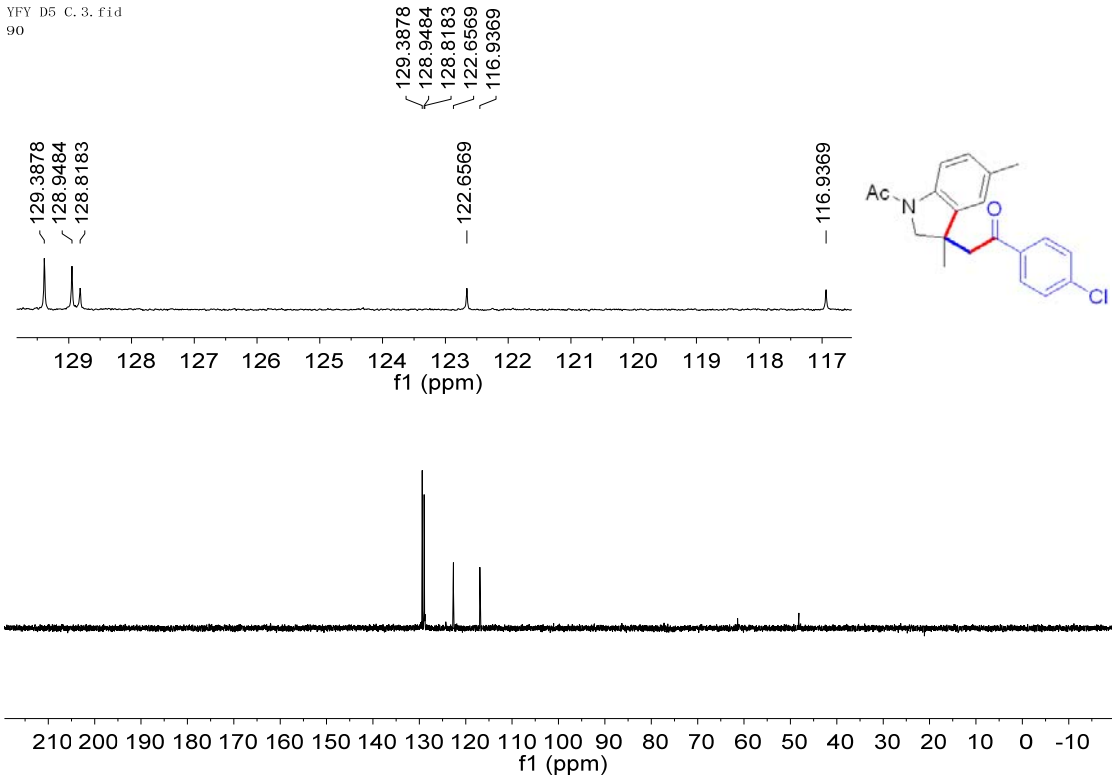

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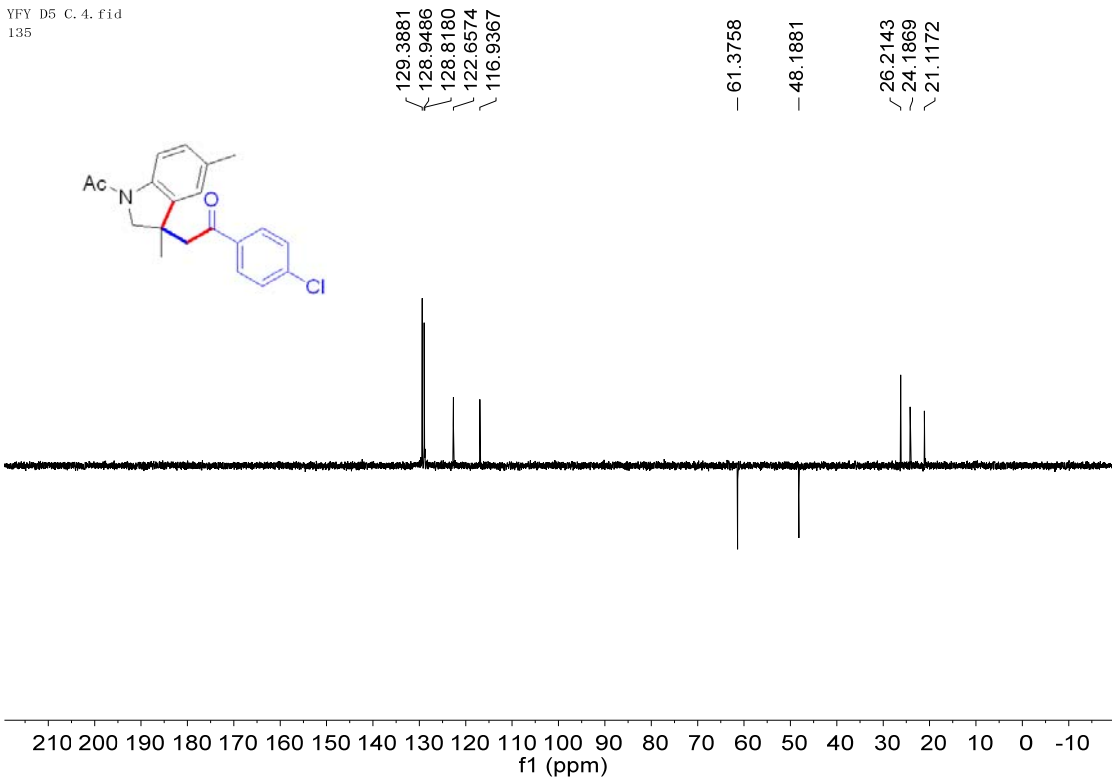
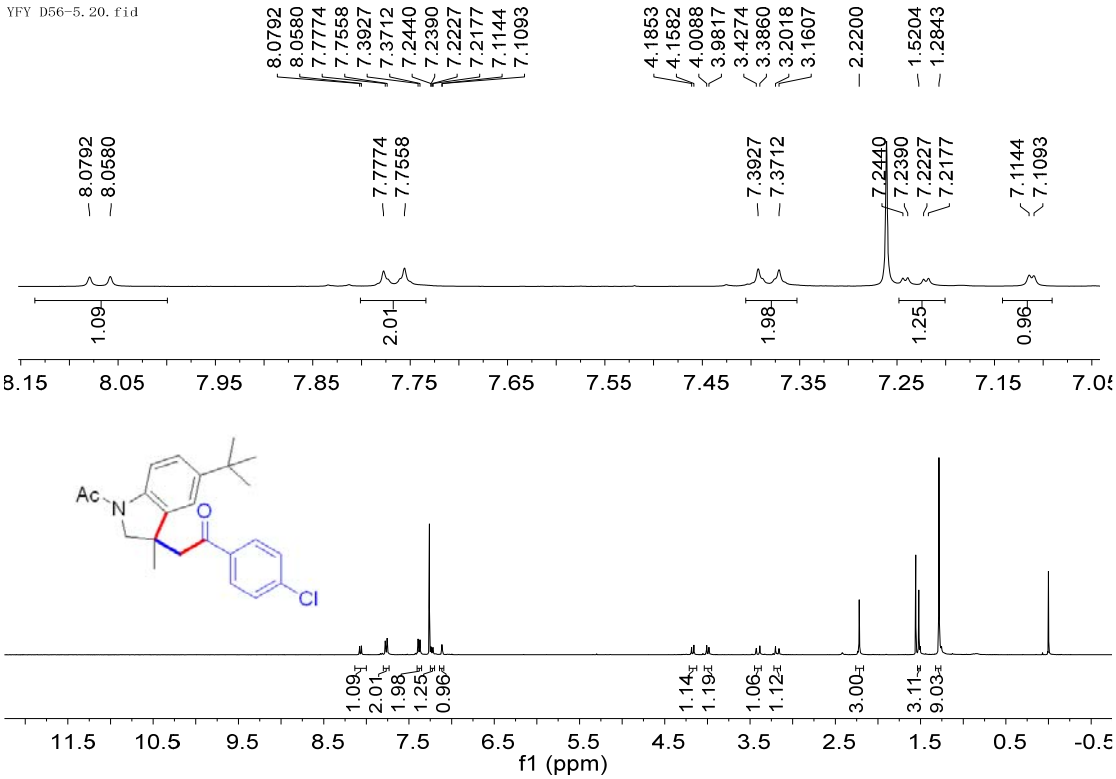
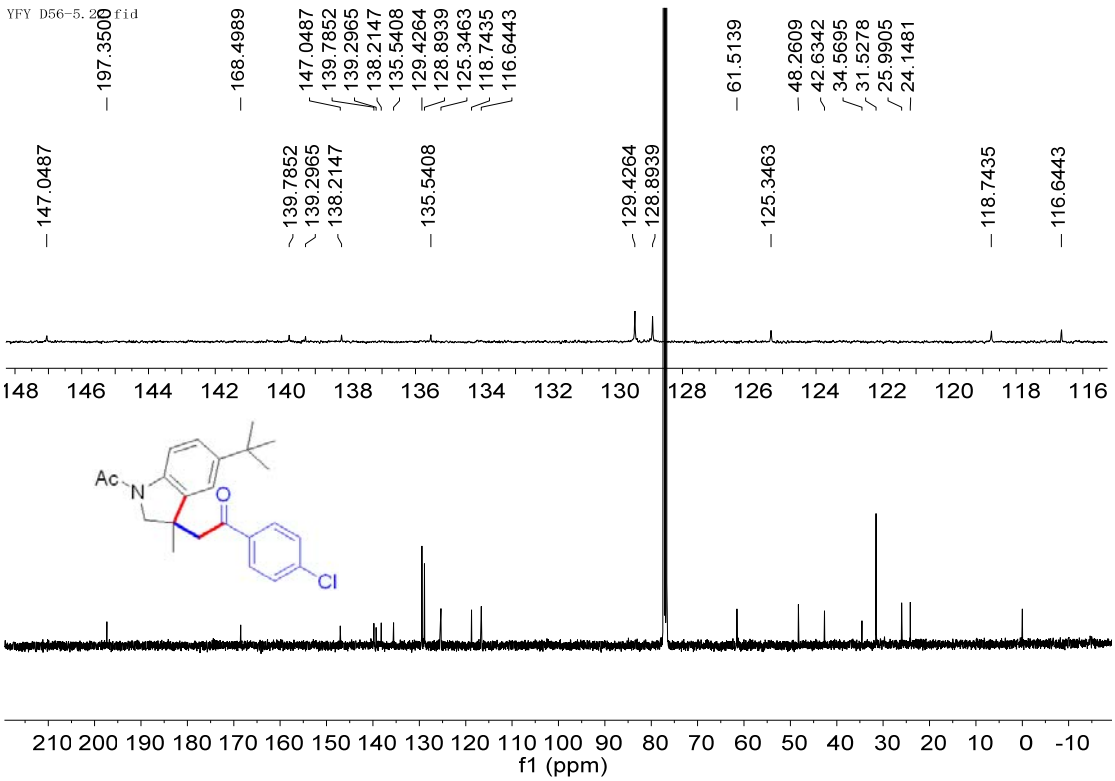


3a3, ^{1}H NMR



^{13}C NMR



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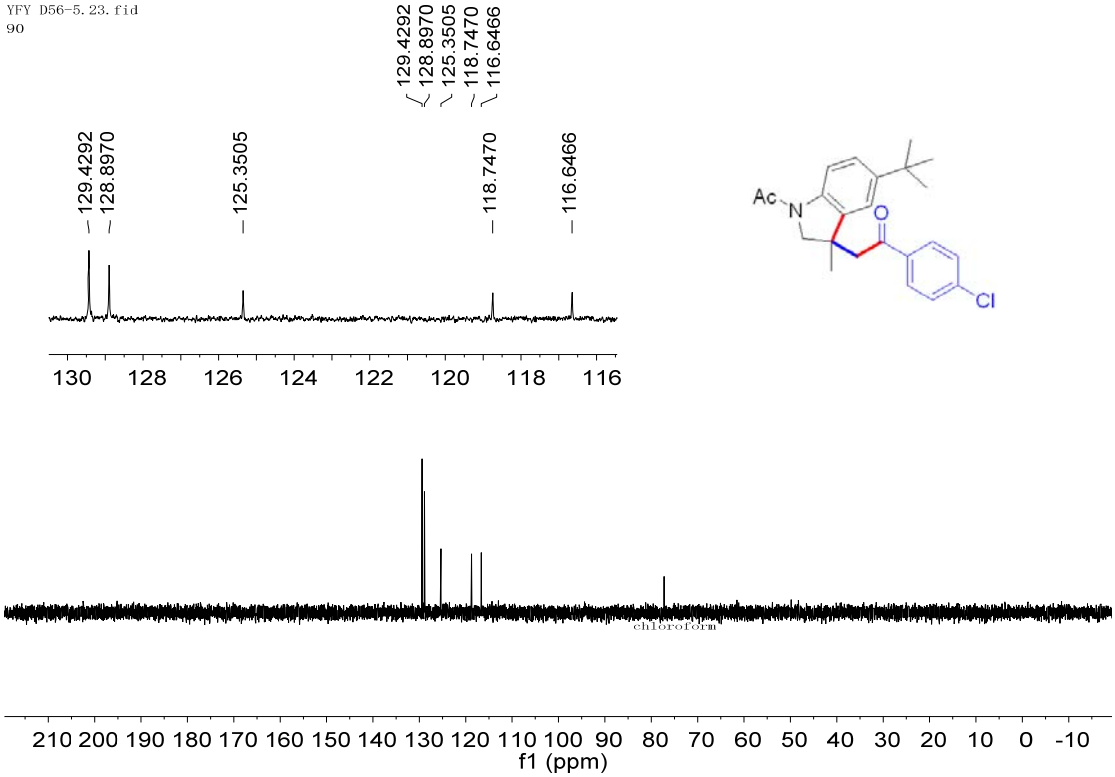

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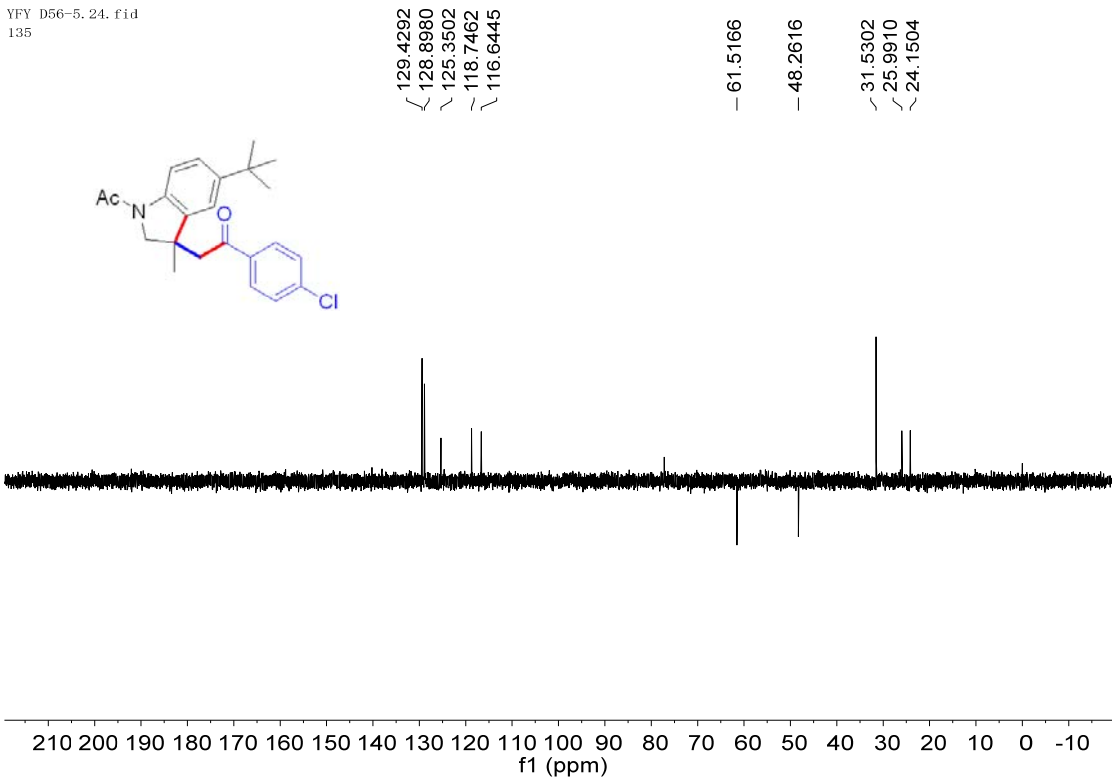
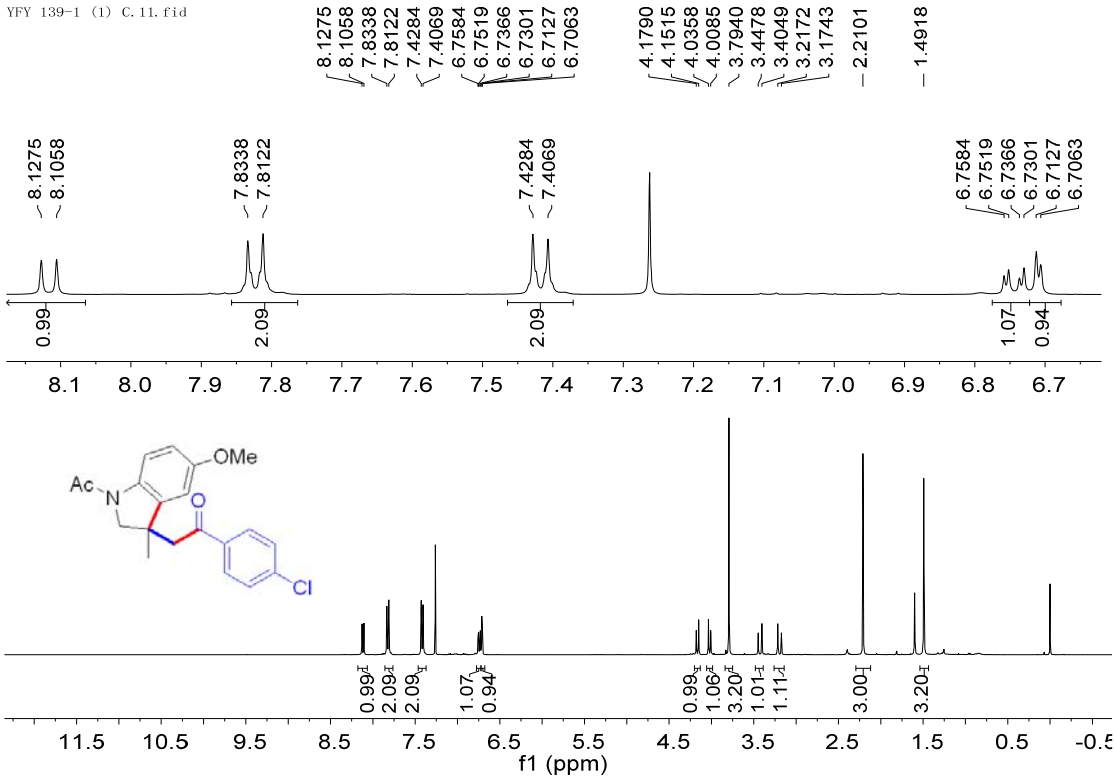
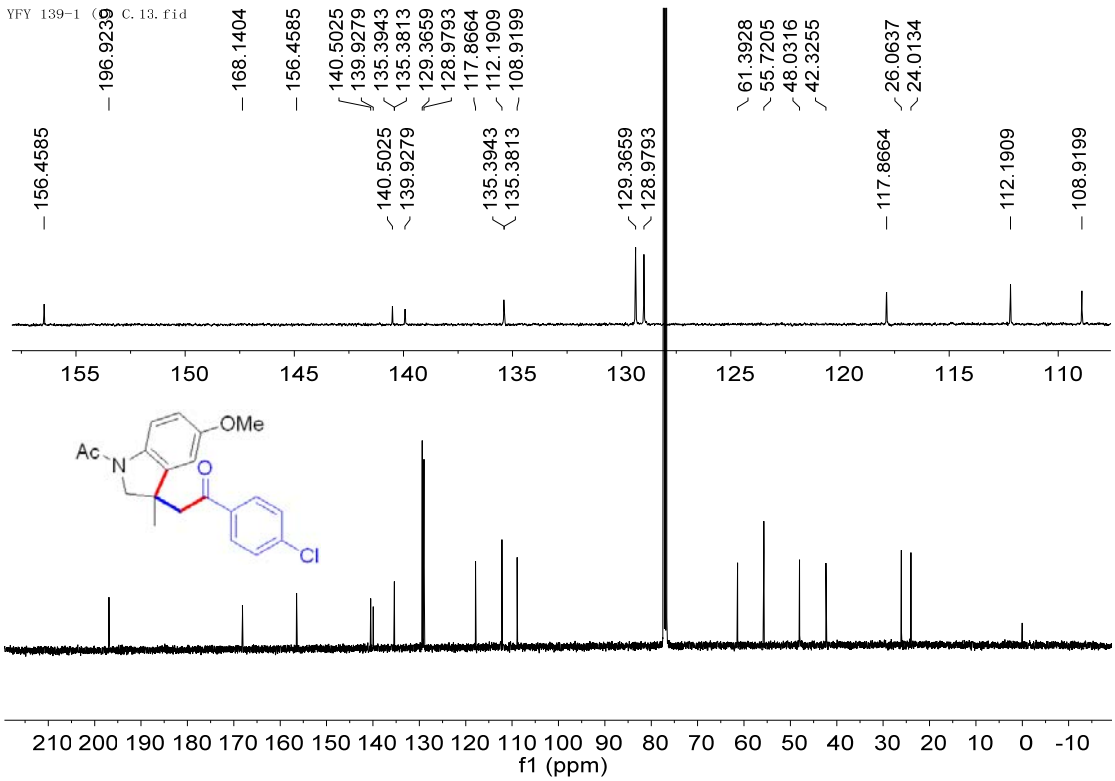


3a4, ^{1}H NMR



^{13}C NMR



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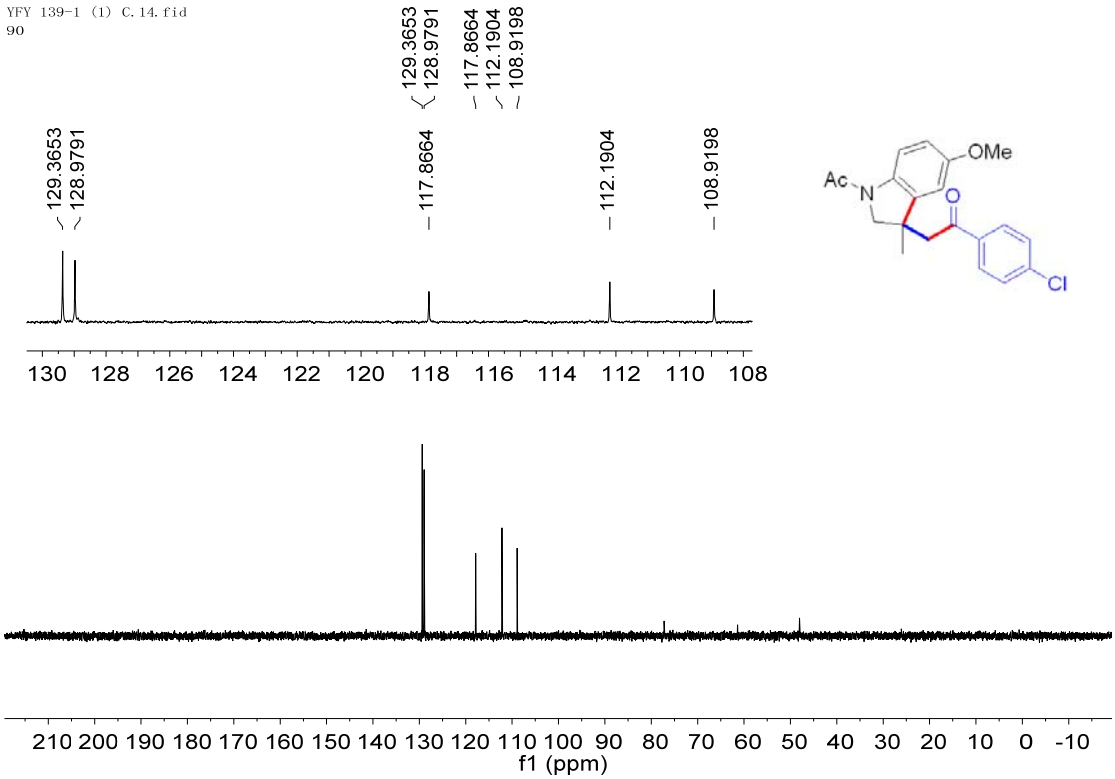

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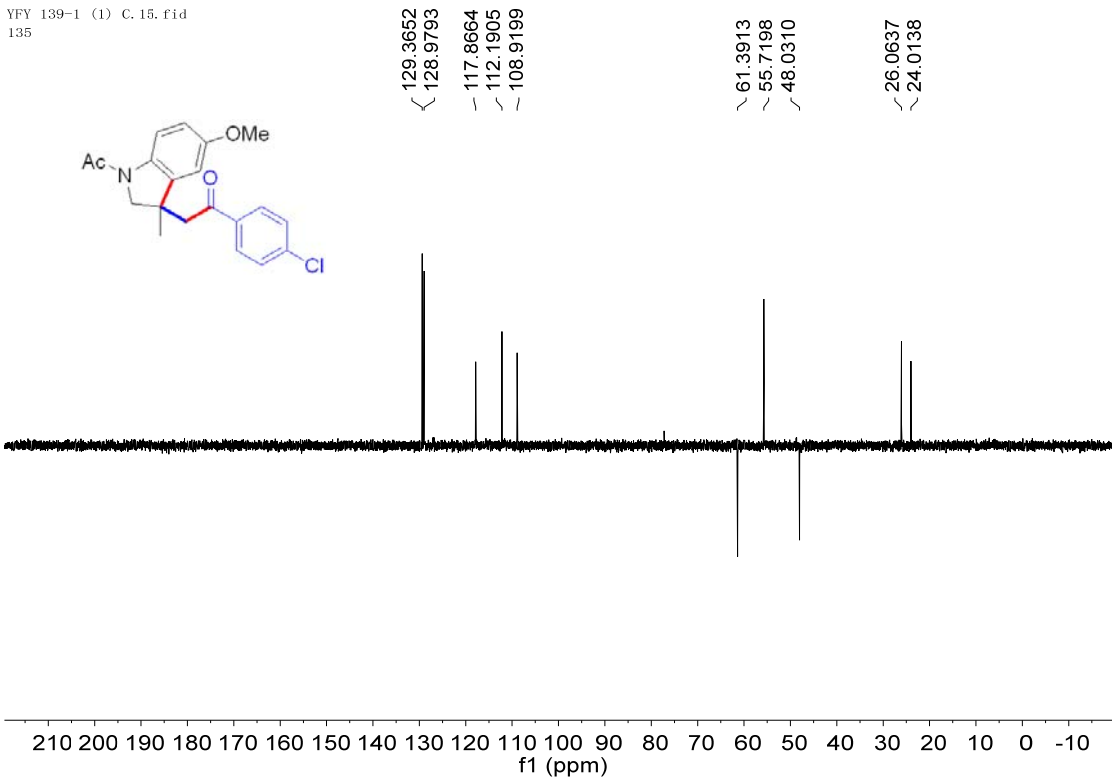
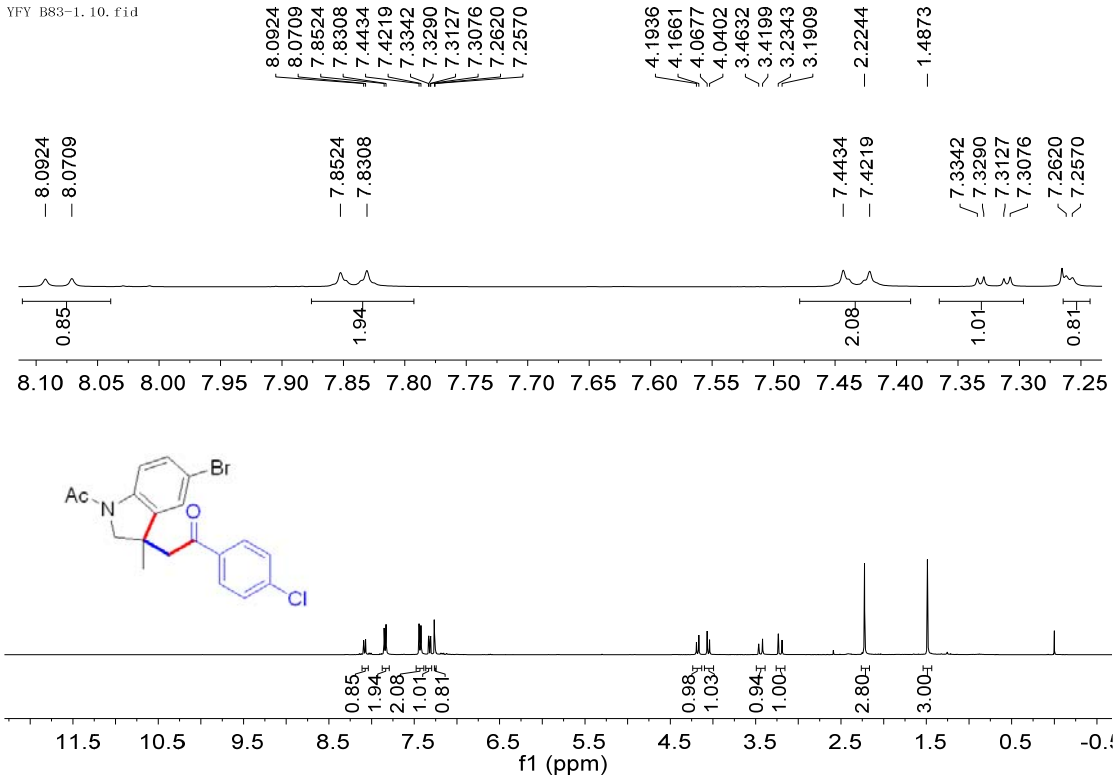
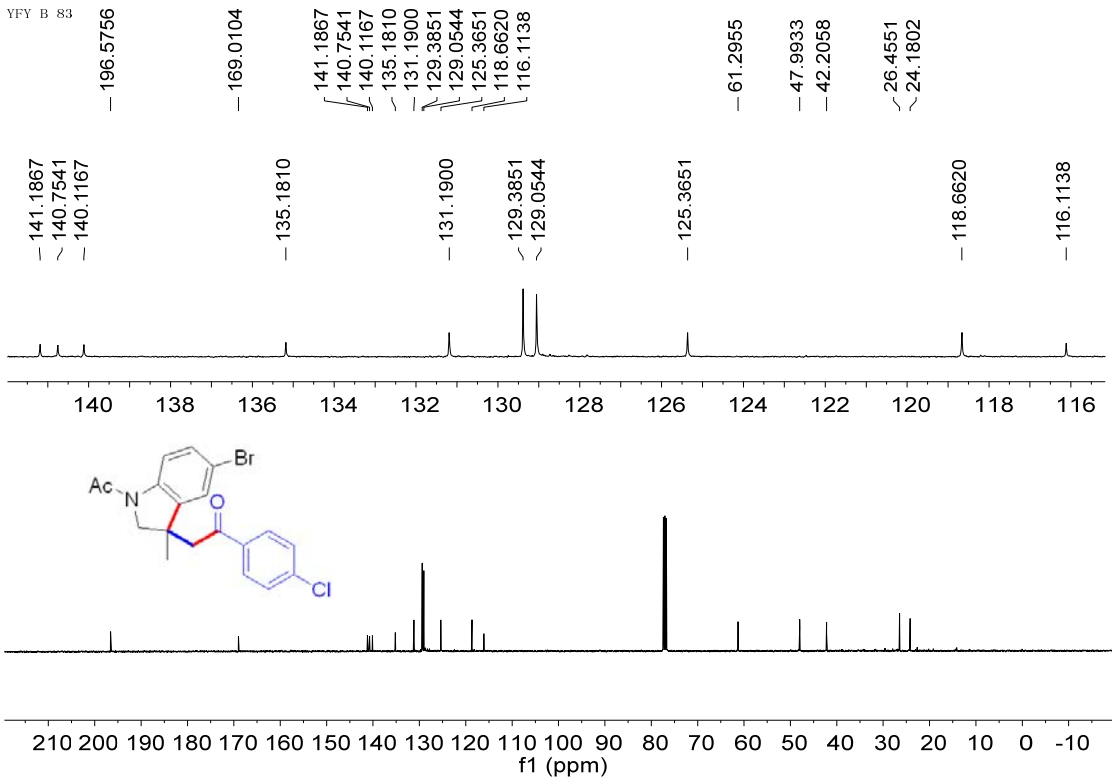


3a5, ^{1}H NMR



^{13}C NMR



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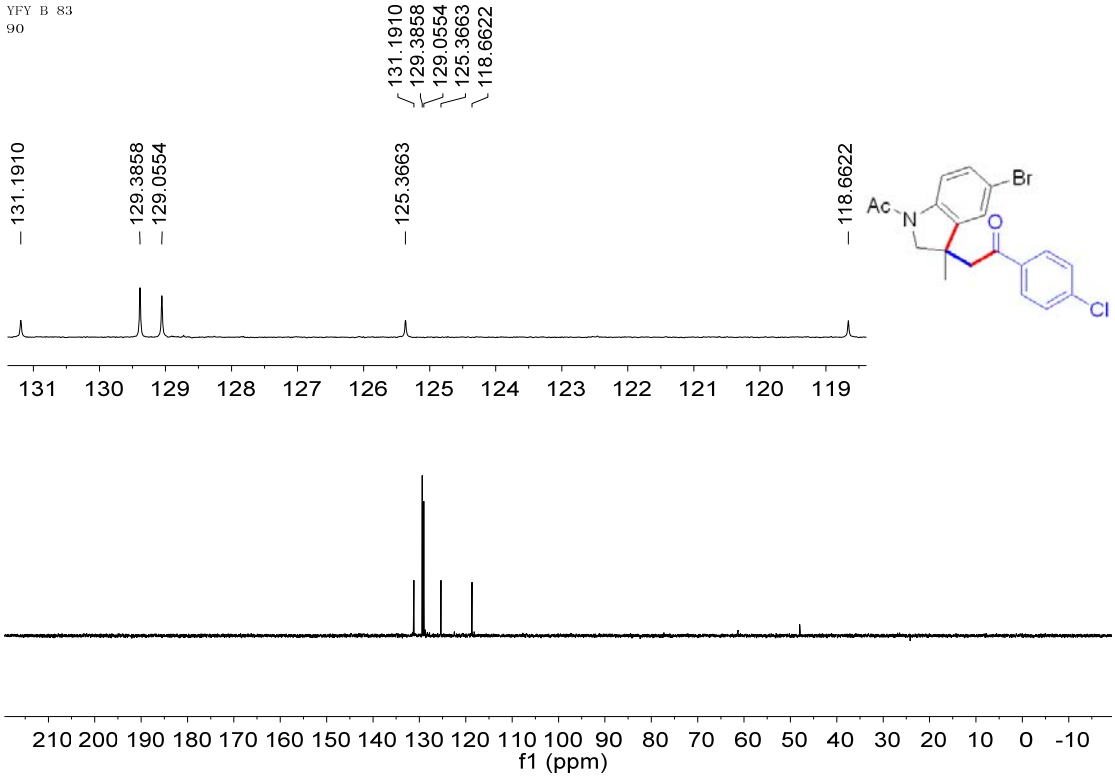

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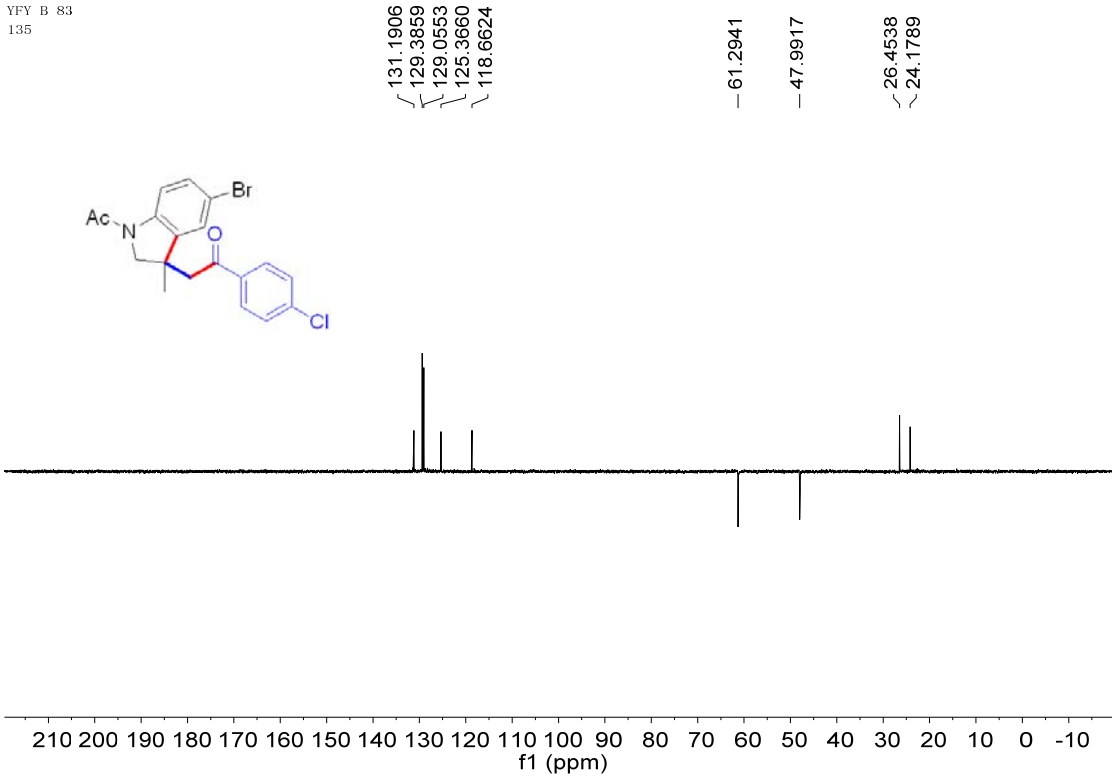
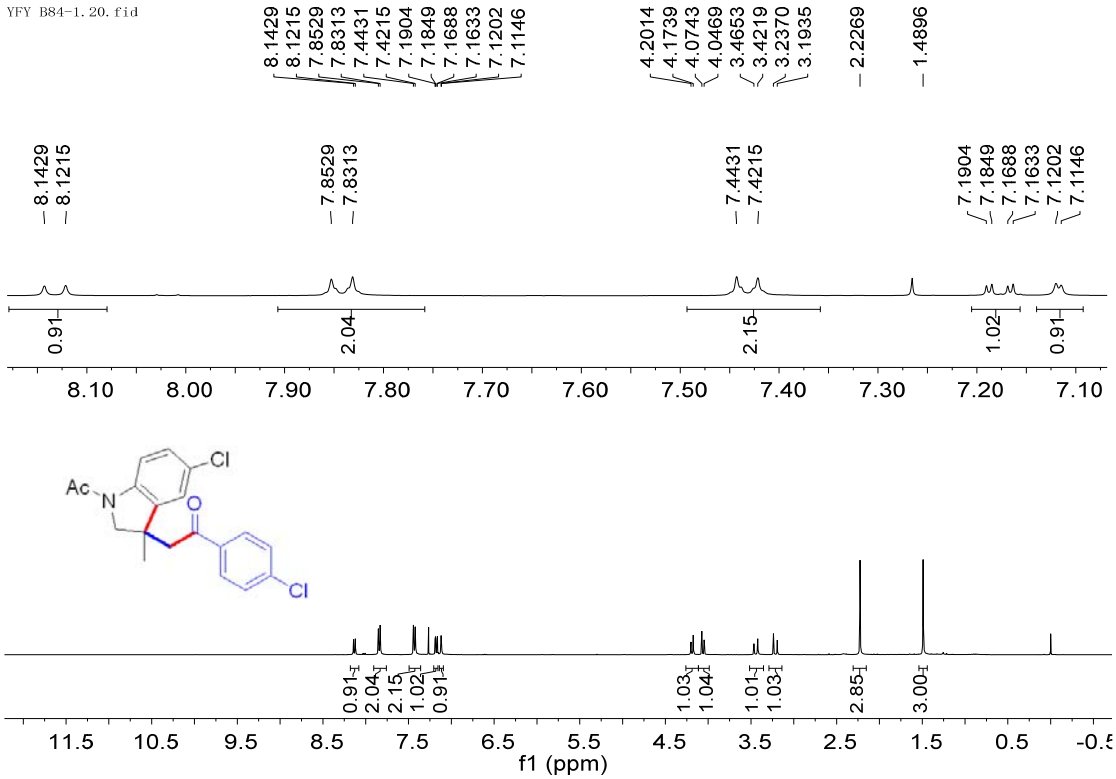
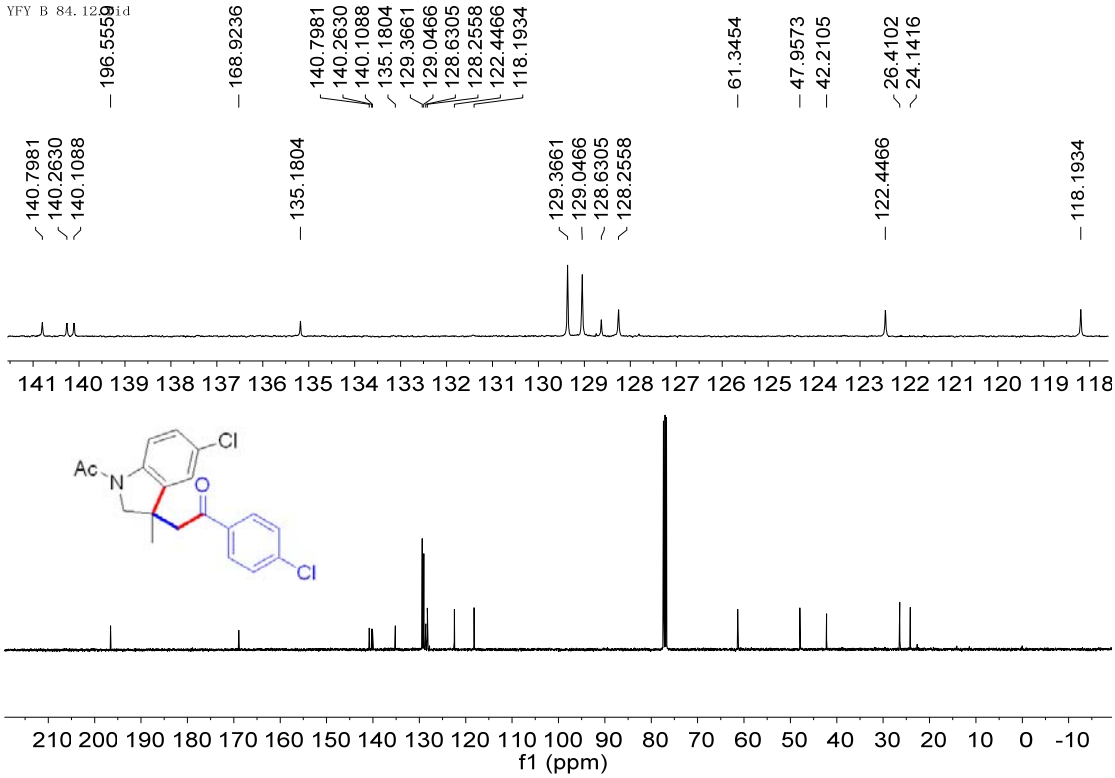


3a6, ^{1}H NMR



^{13}C NMR



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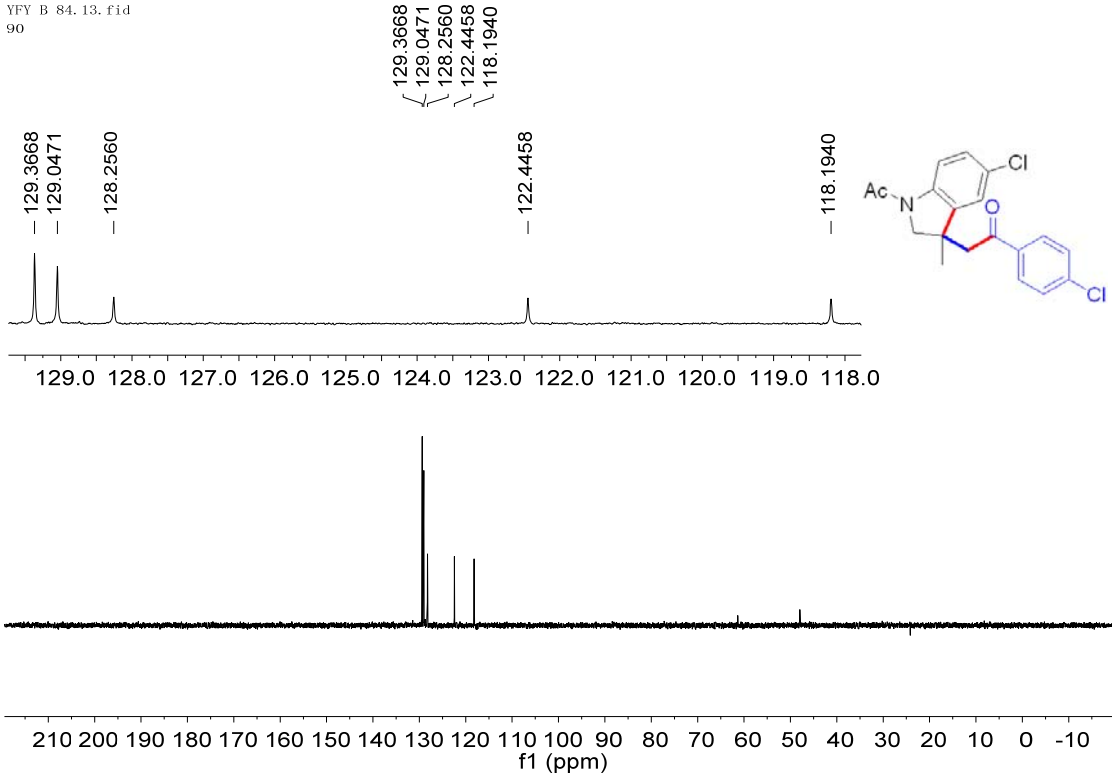

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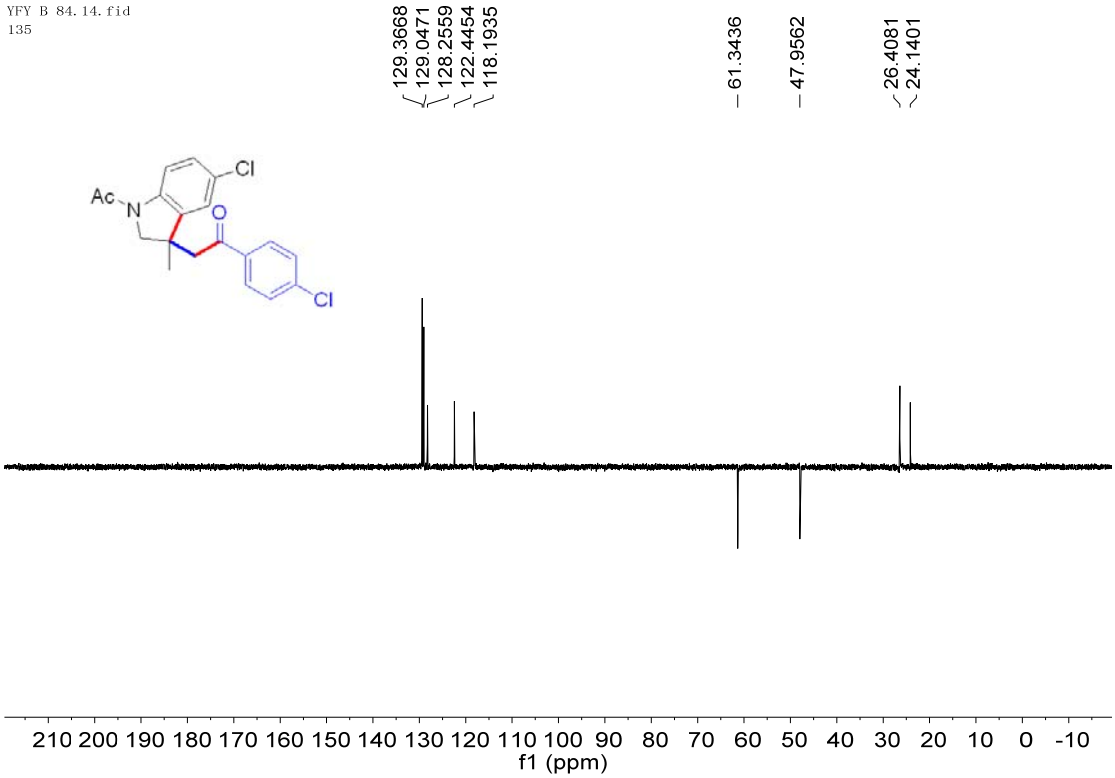
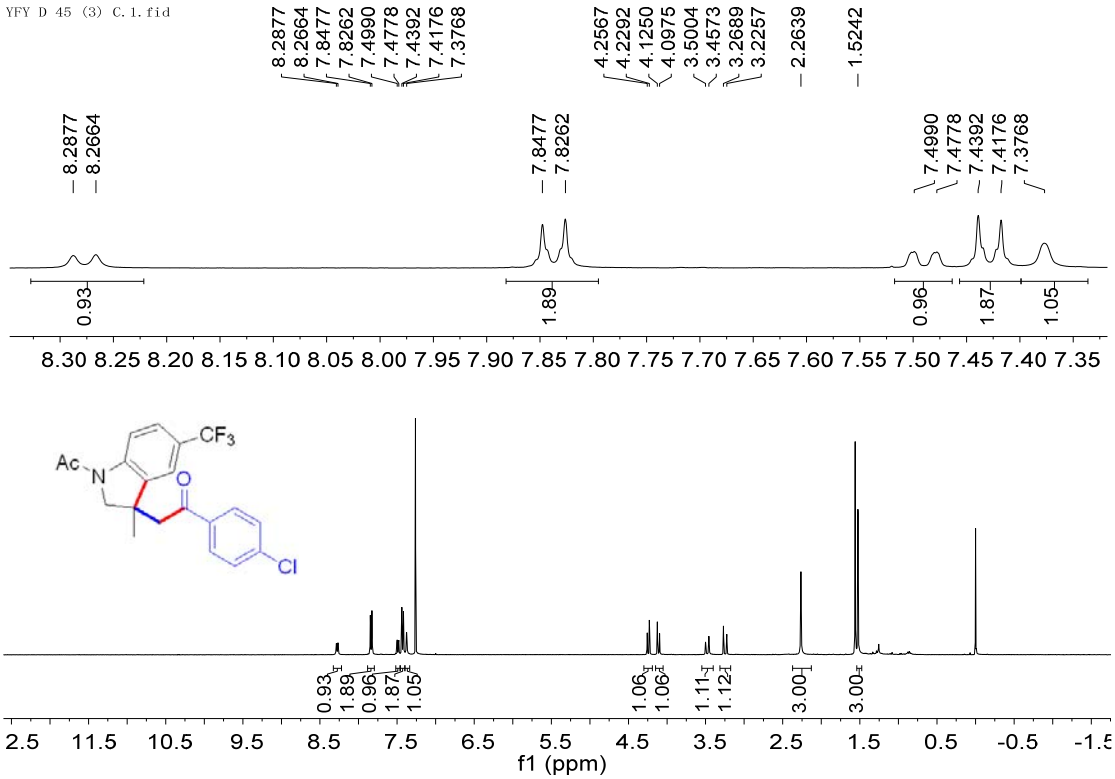
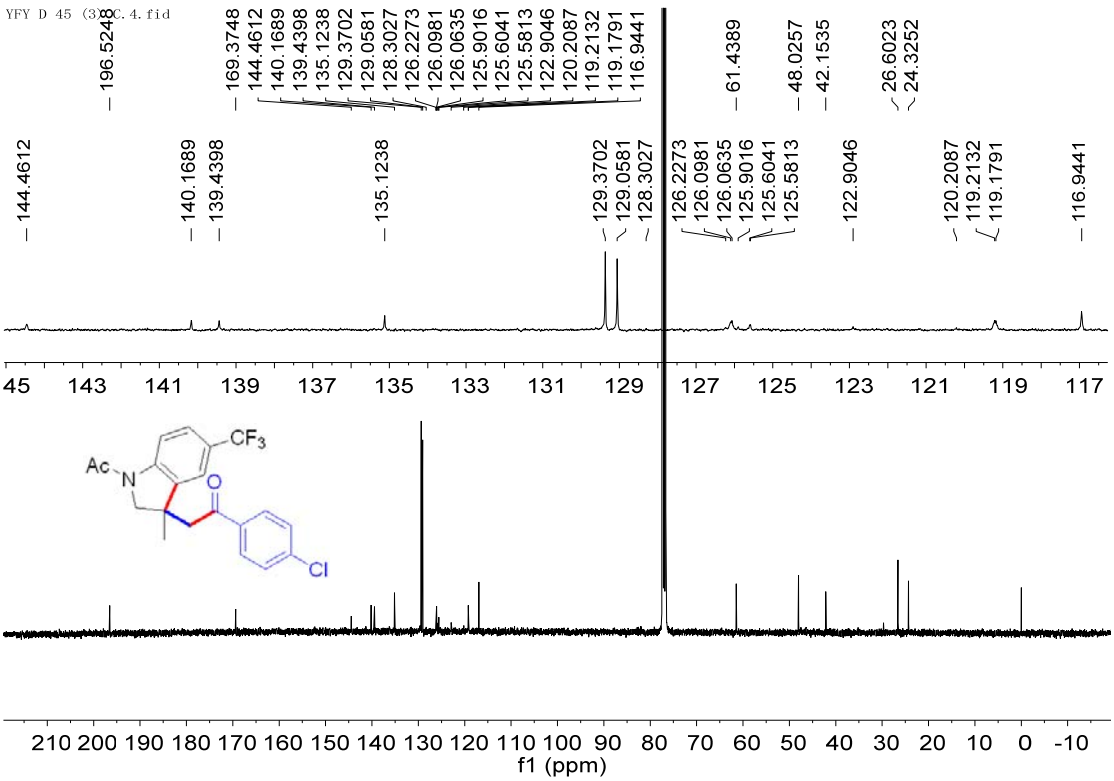


3a7, ^{1}H NMR



^{13}C NMR



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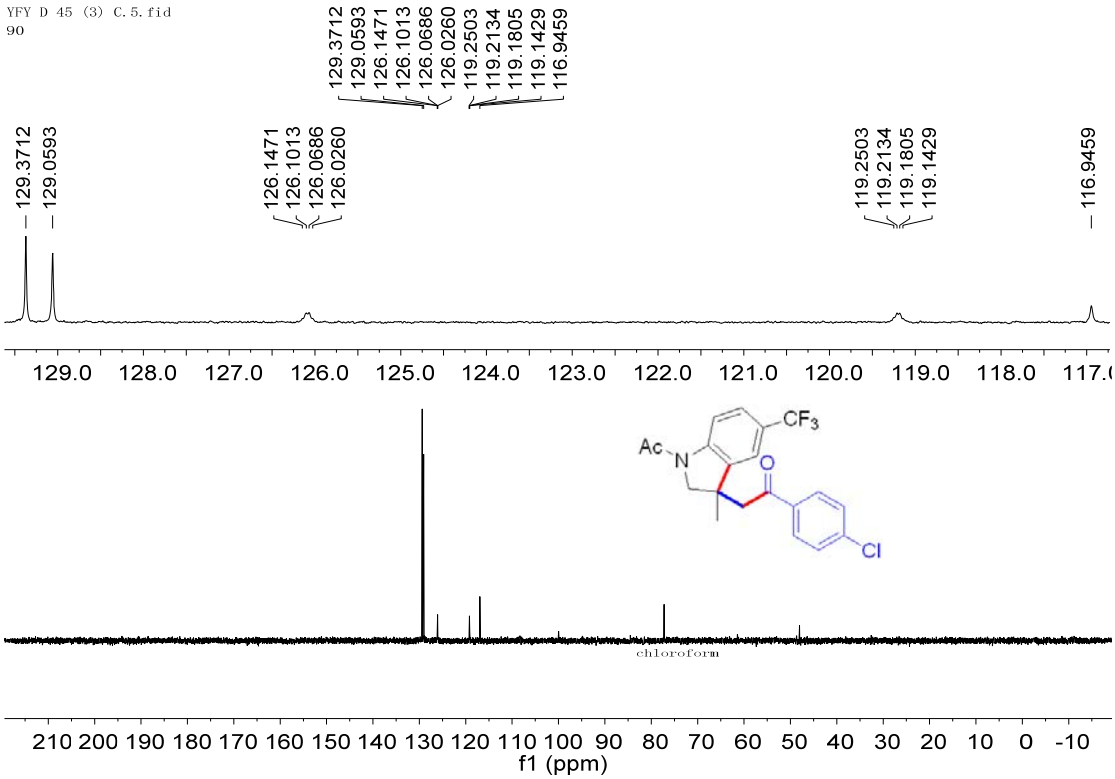

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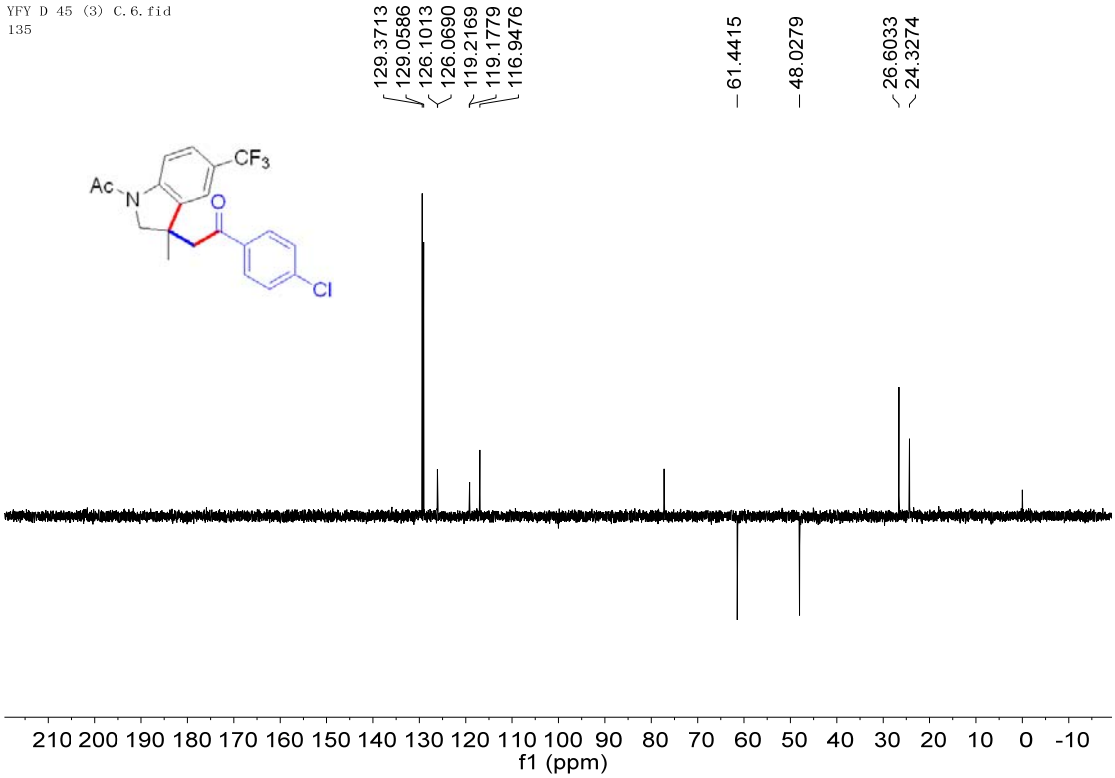
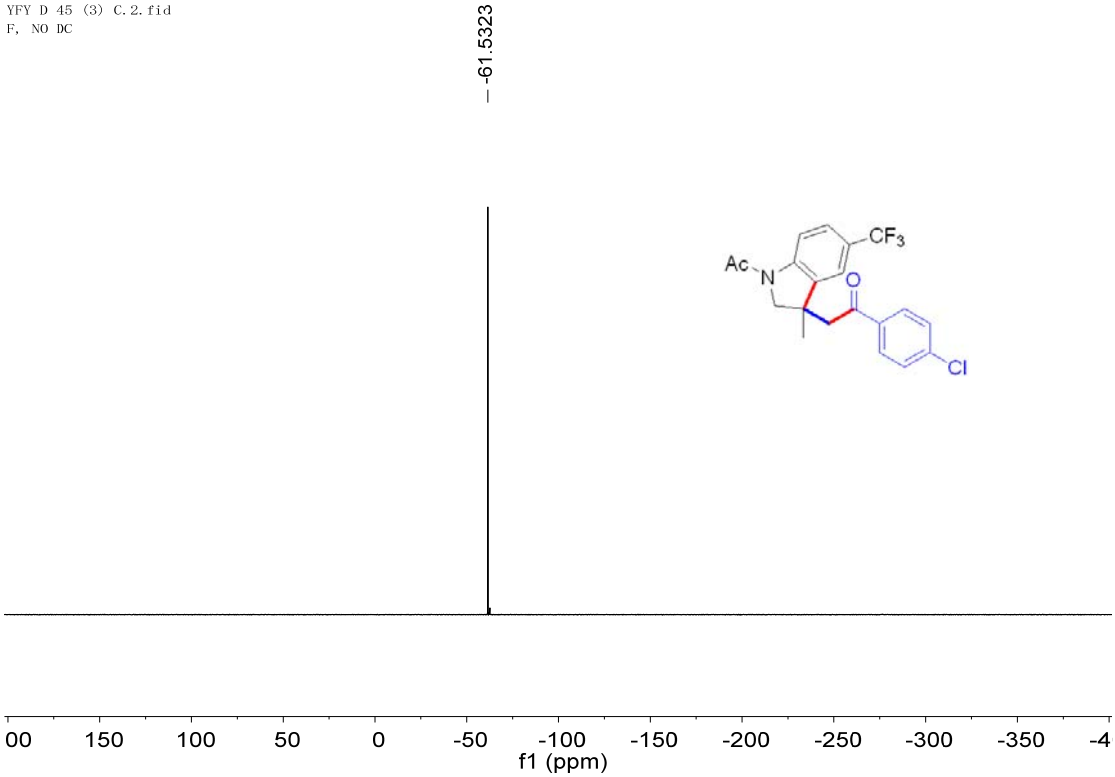
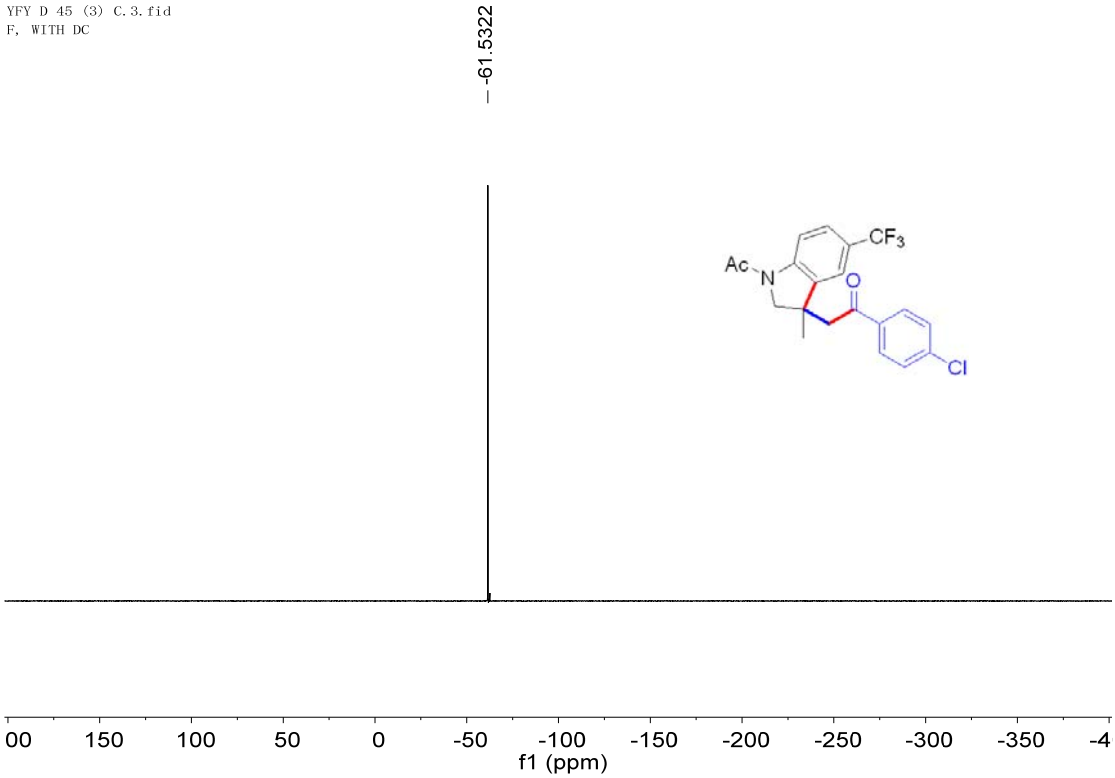


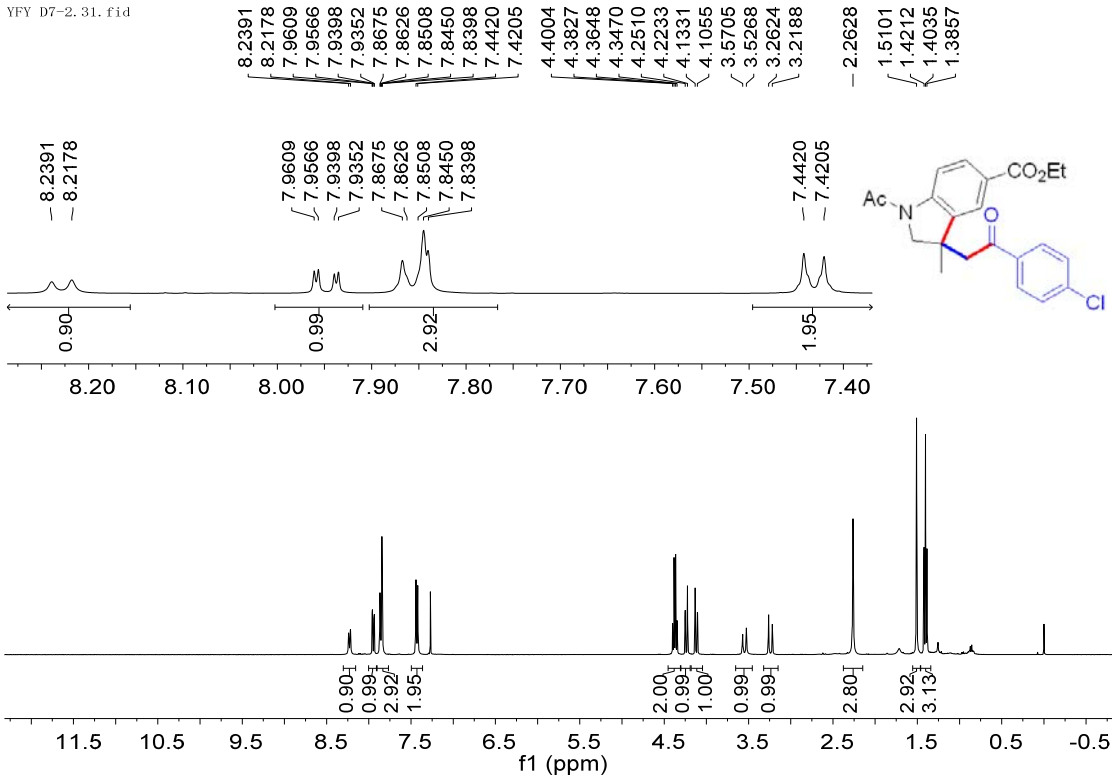
^{19}F NMR, no decoupling



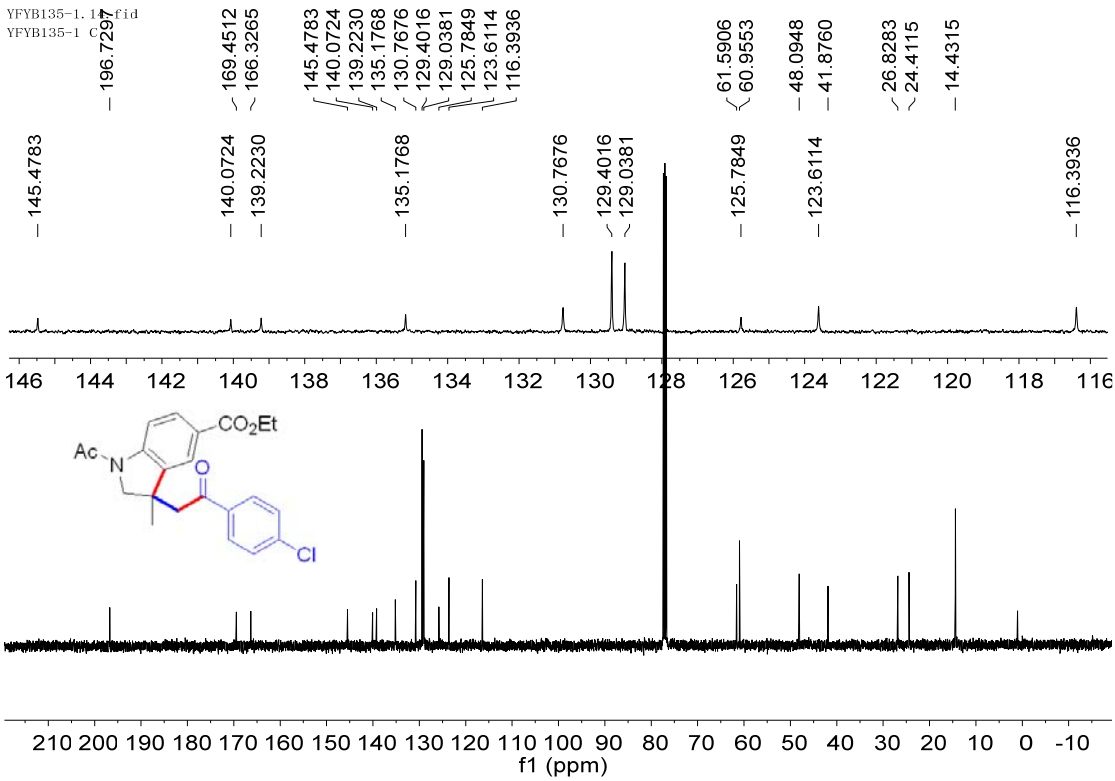
^{19}F NMR, with pulse decoupling



3a8, ^{1}H NMR



^{13}C NMR



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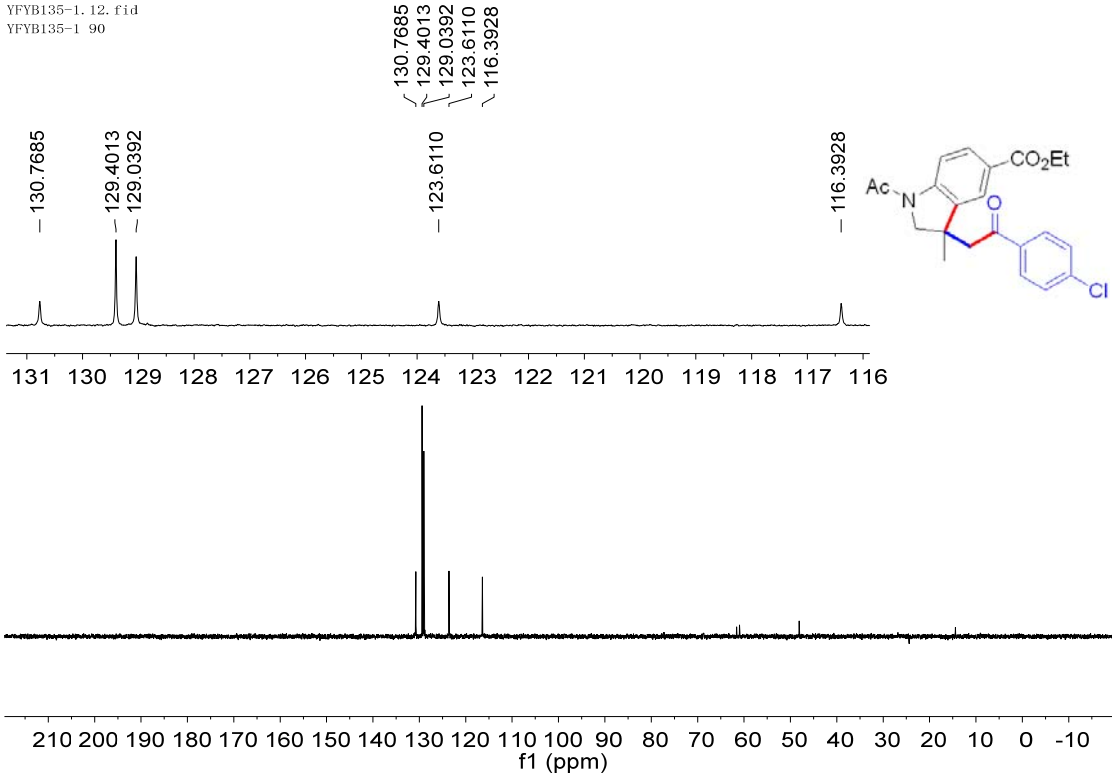

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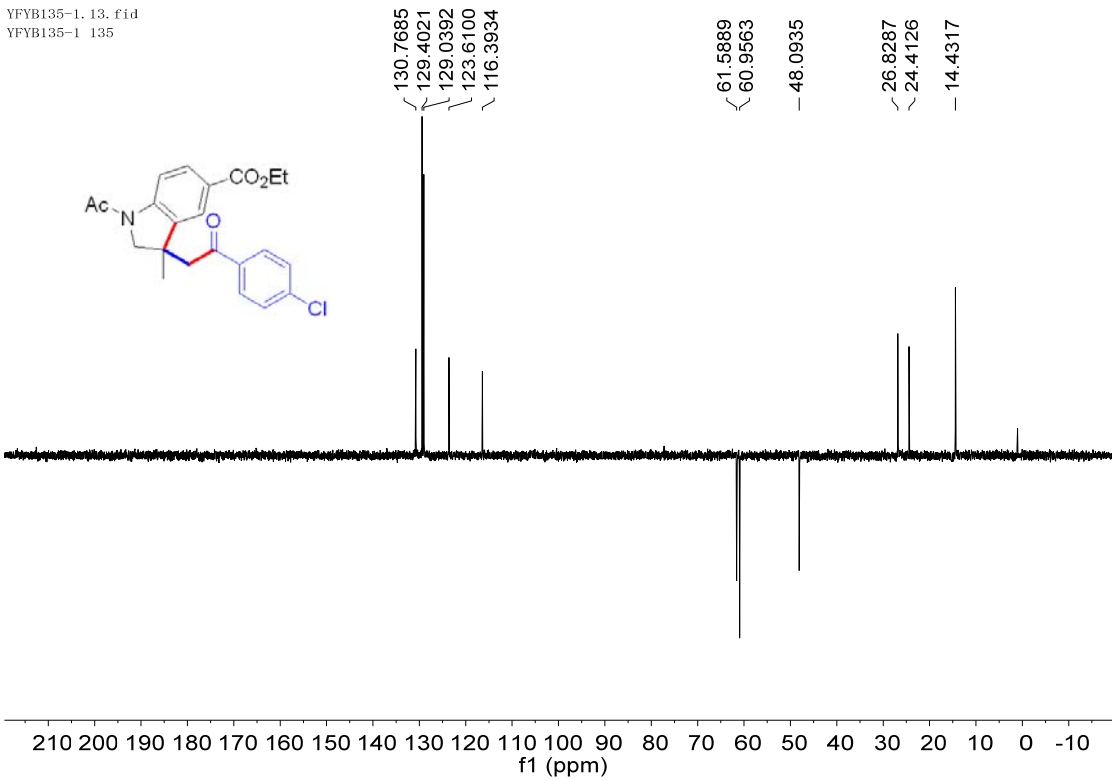
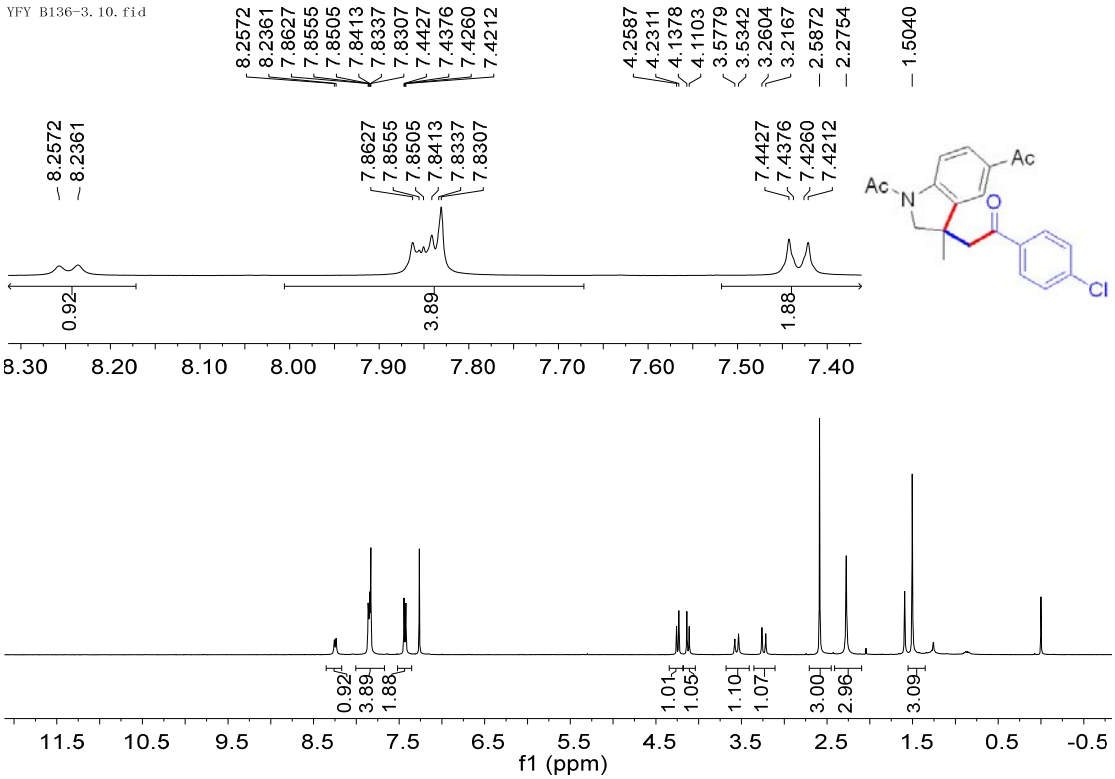
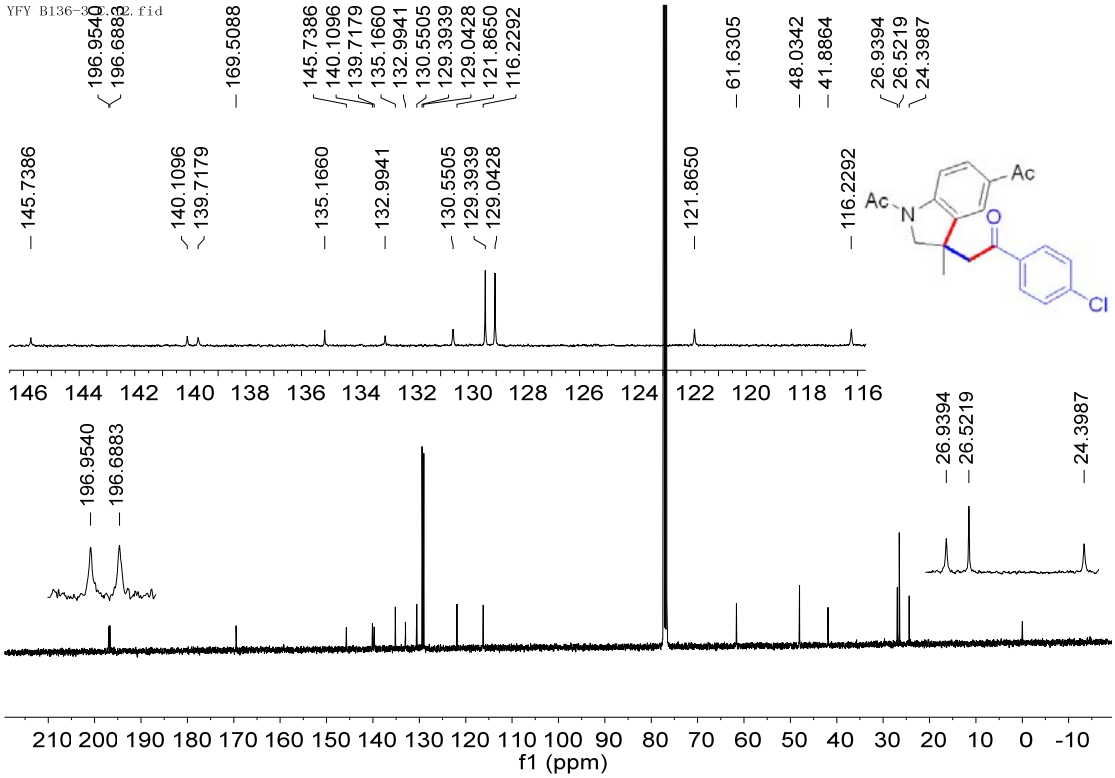


3a9, ^{1}H NMR



^{13}C NMR



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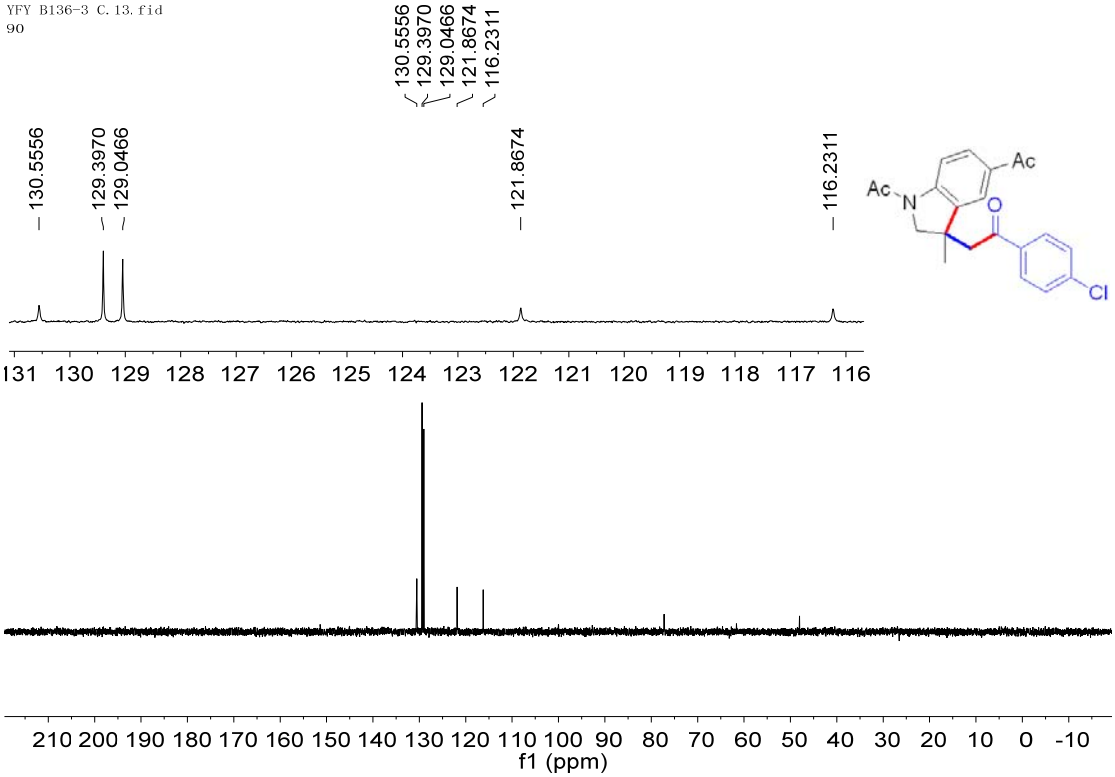

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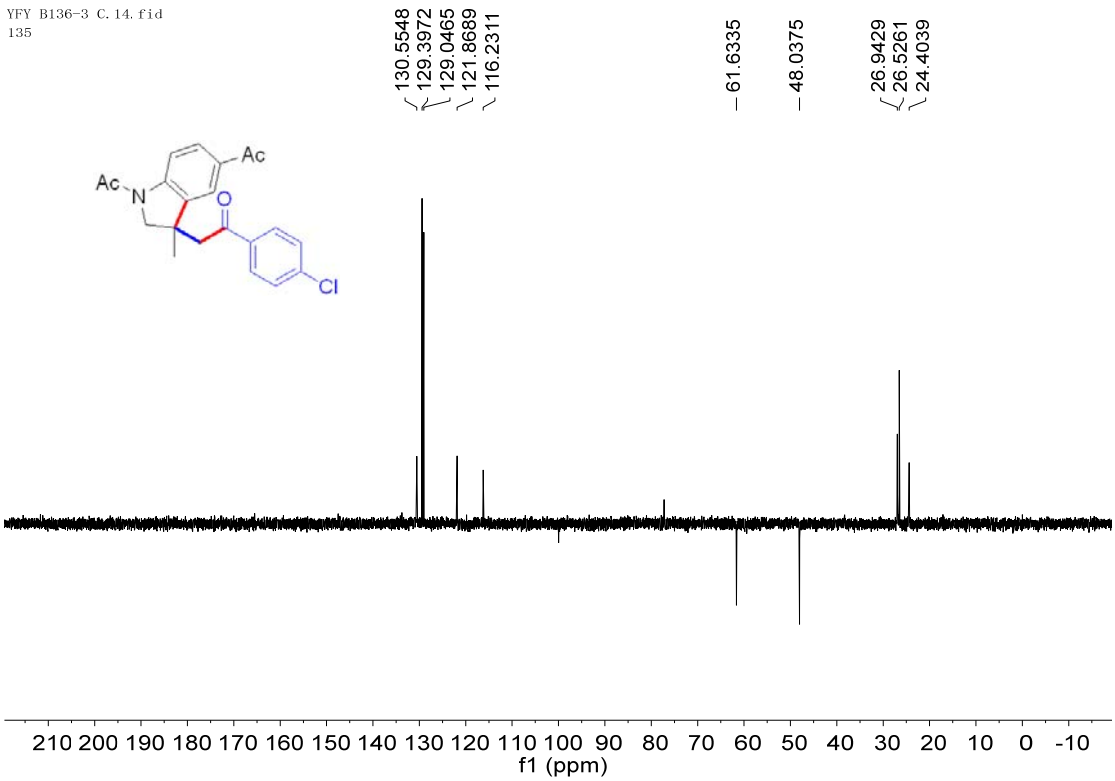
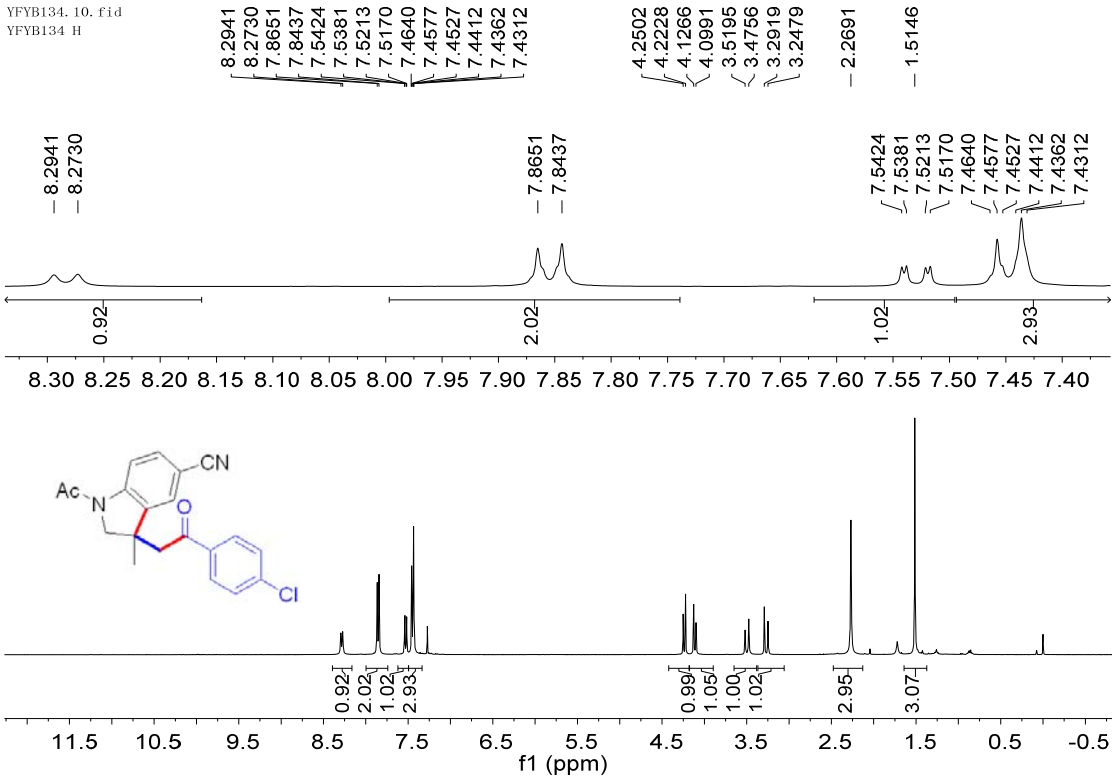
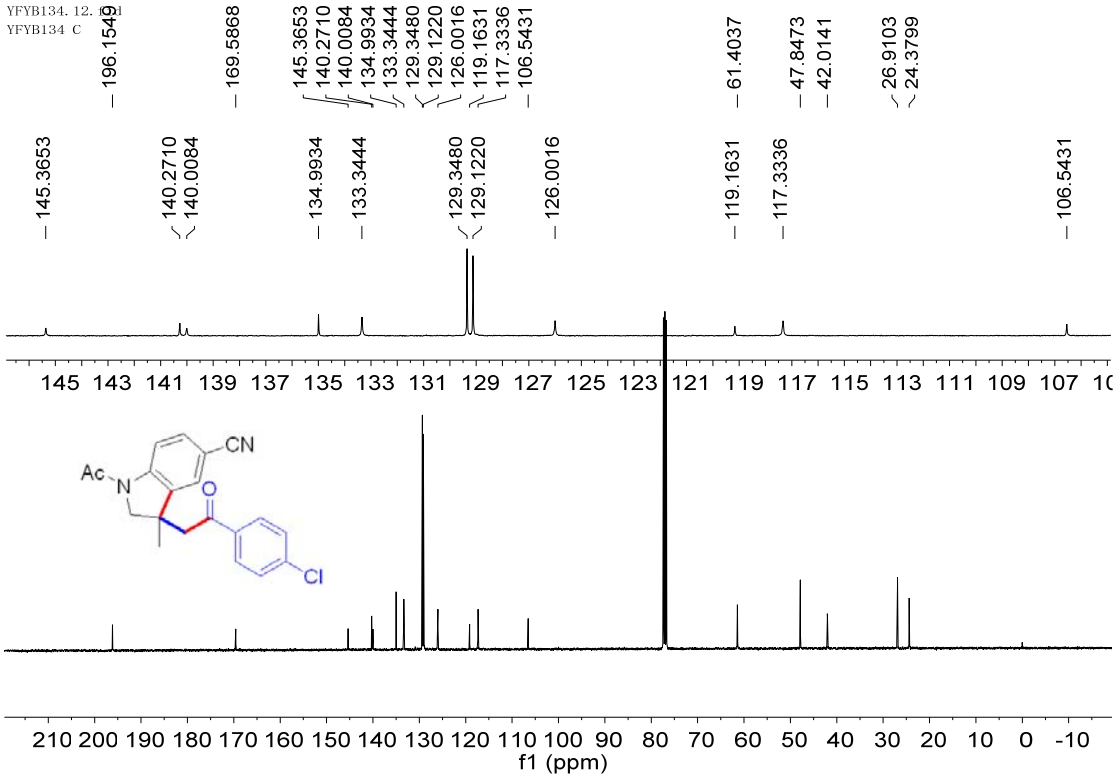


3a10, ^{1}H NMR



^{13}C NMR



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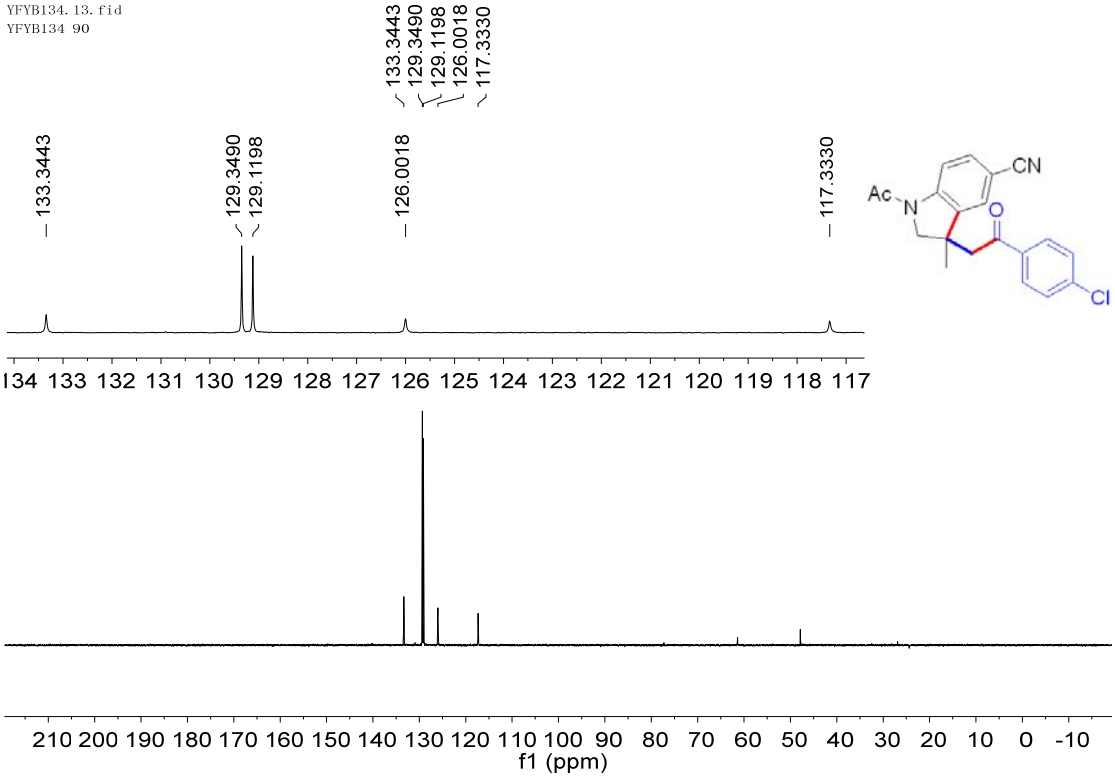

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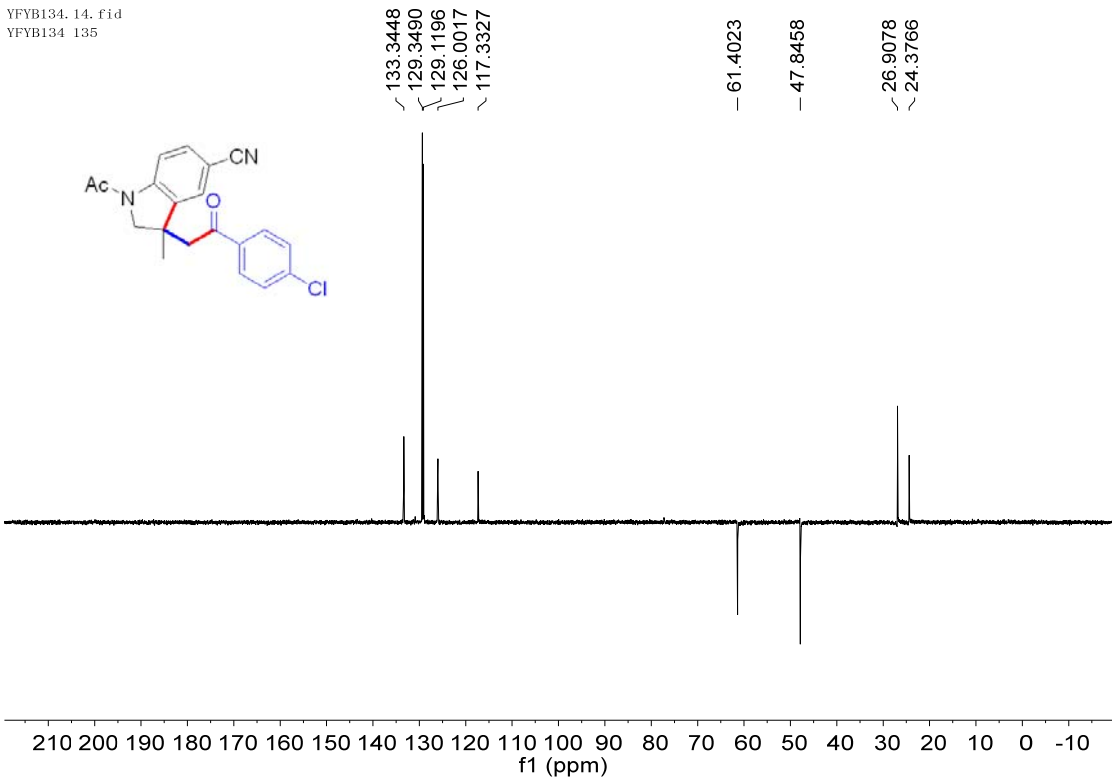
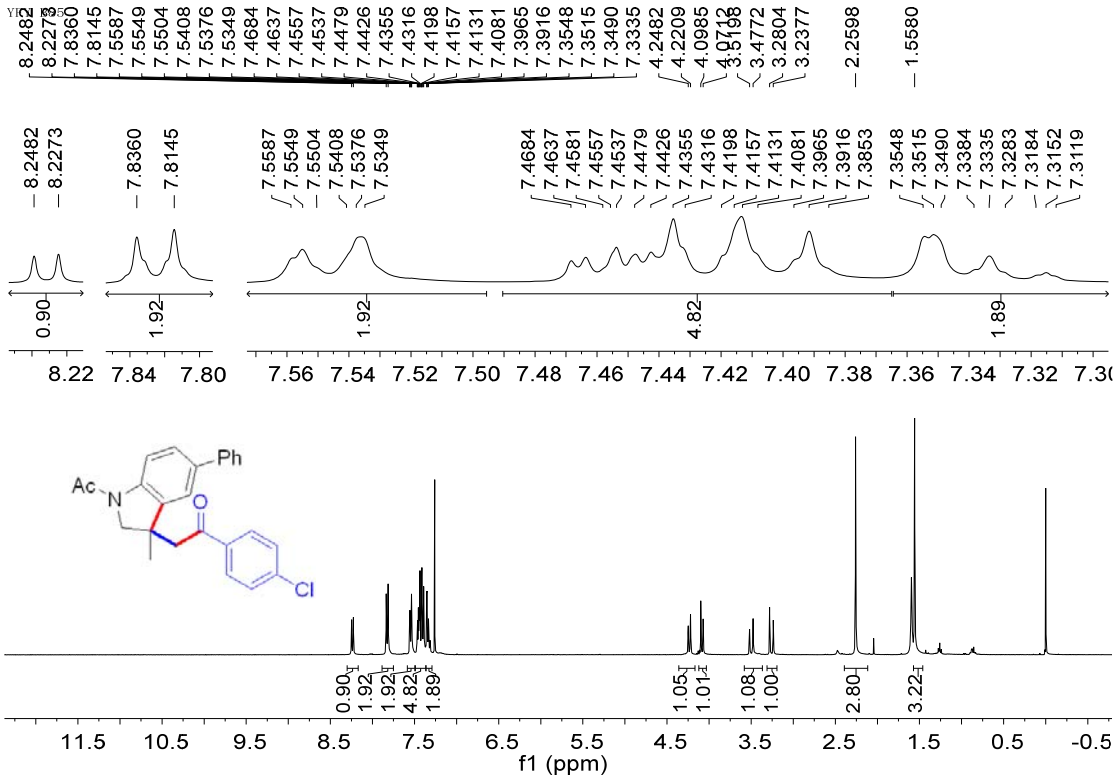
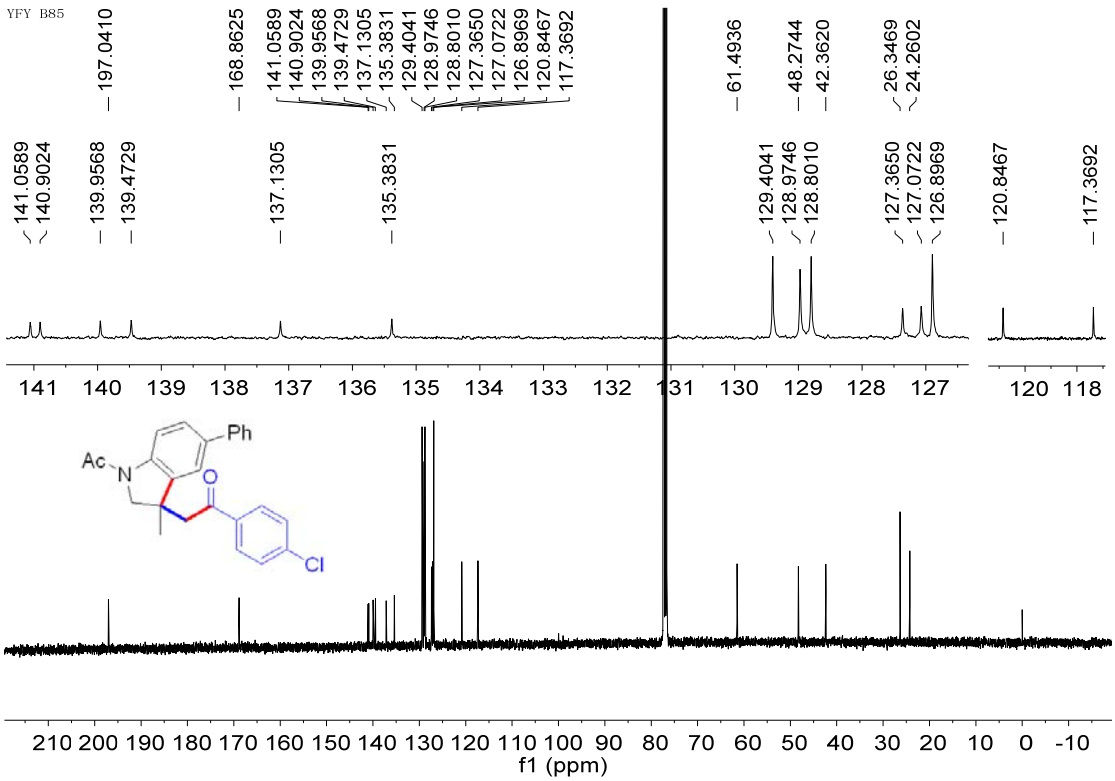


3a11, ^{1}H NMR



^{13}C NMR



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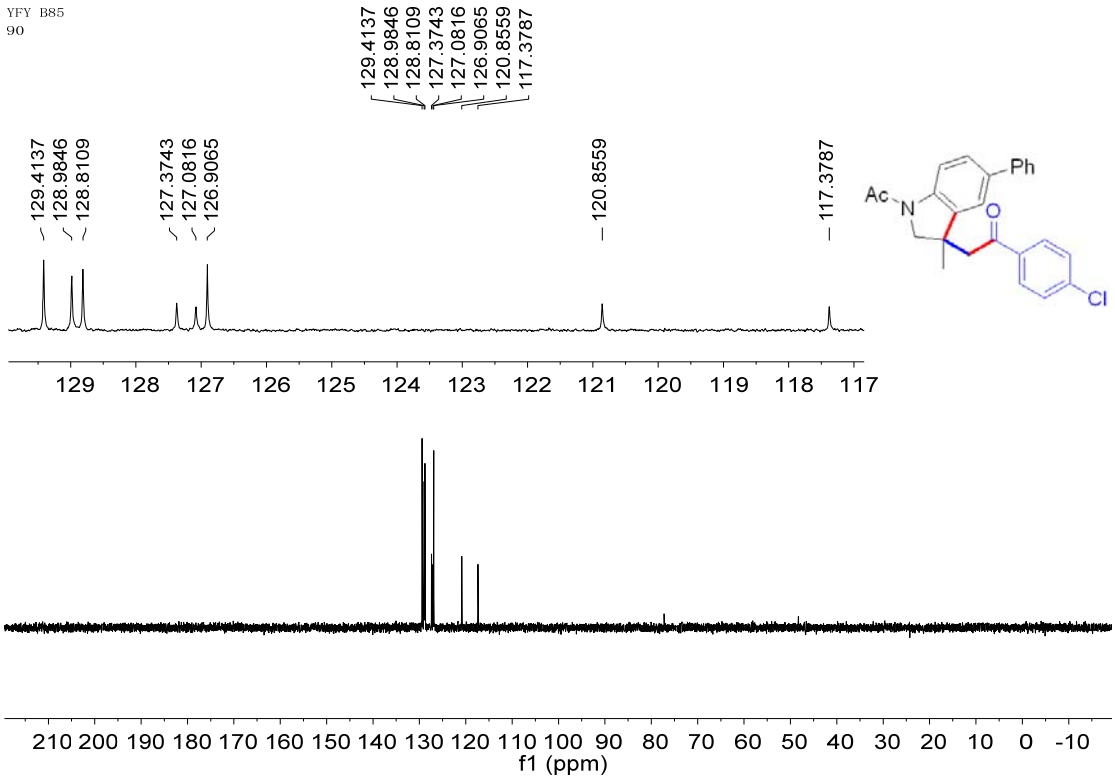

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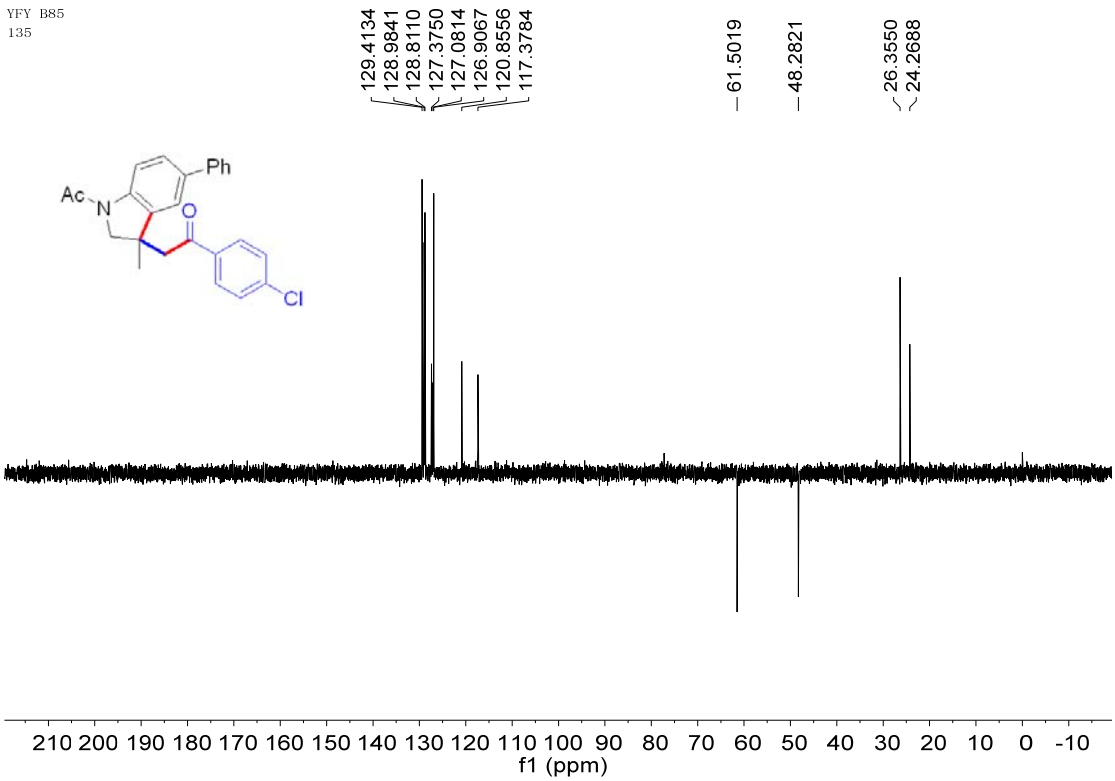
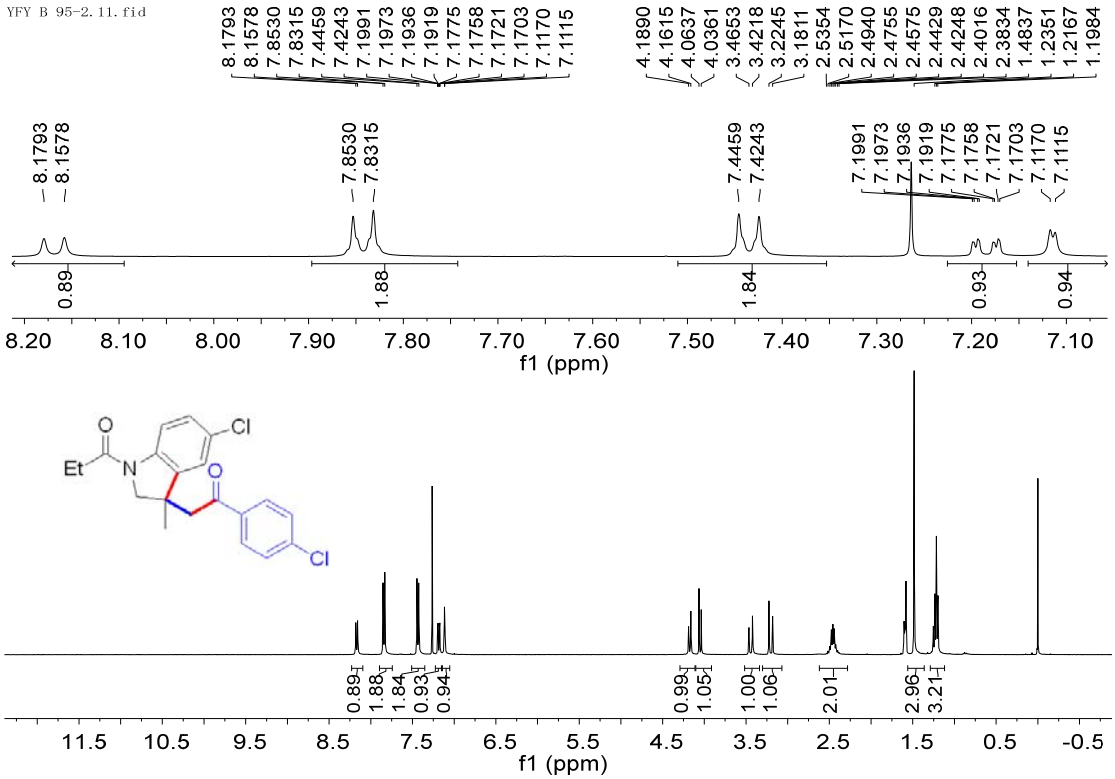
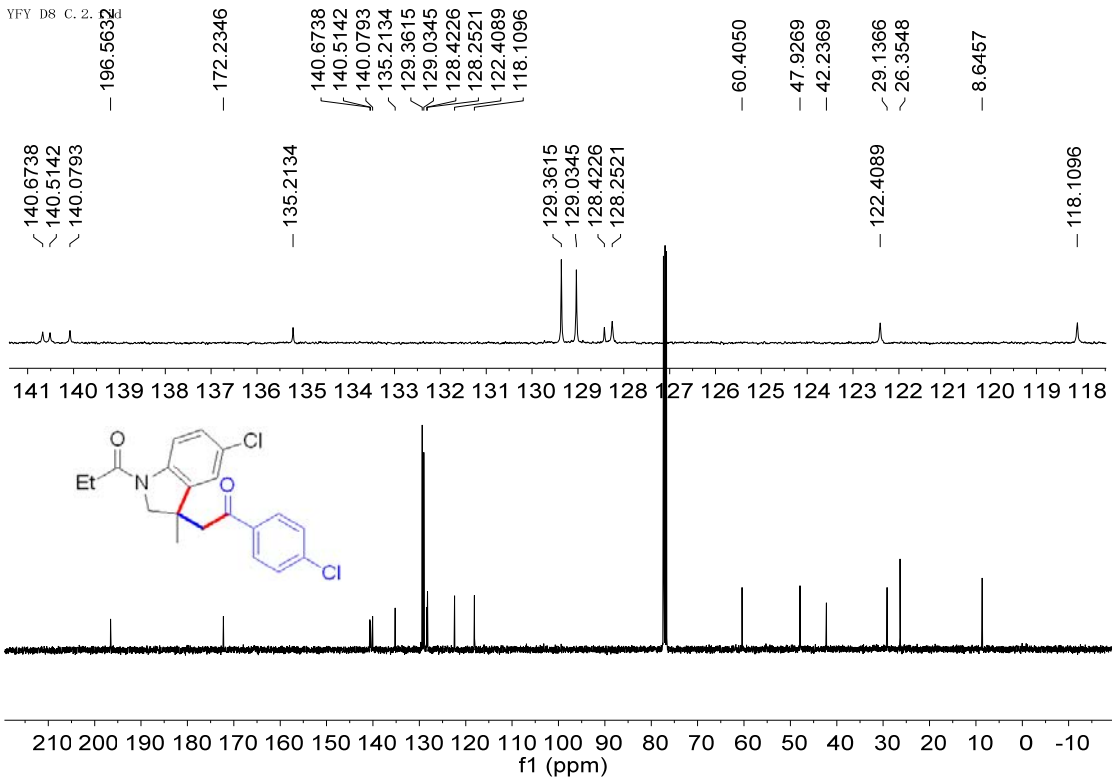


3b1, ^{1}H NMR



^{13}C NMR



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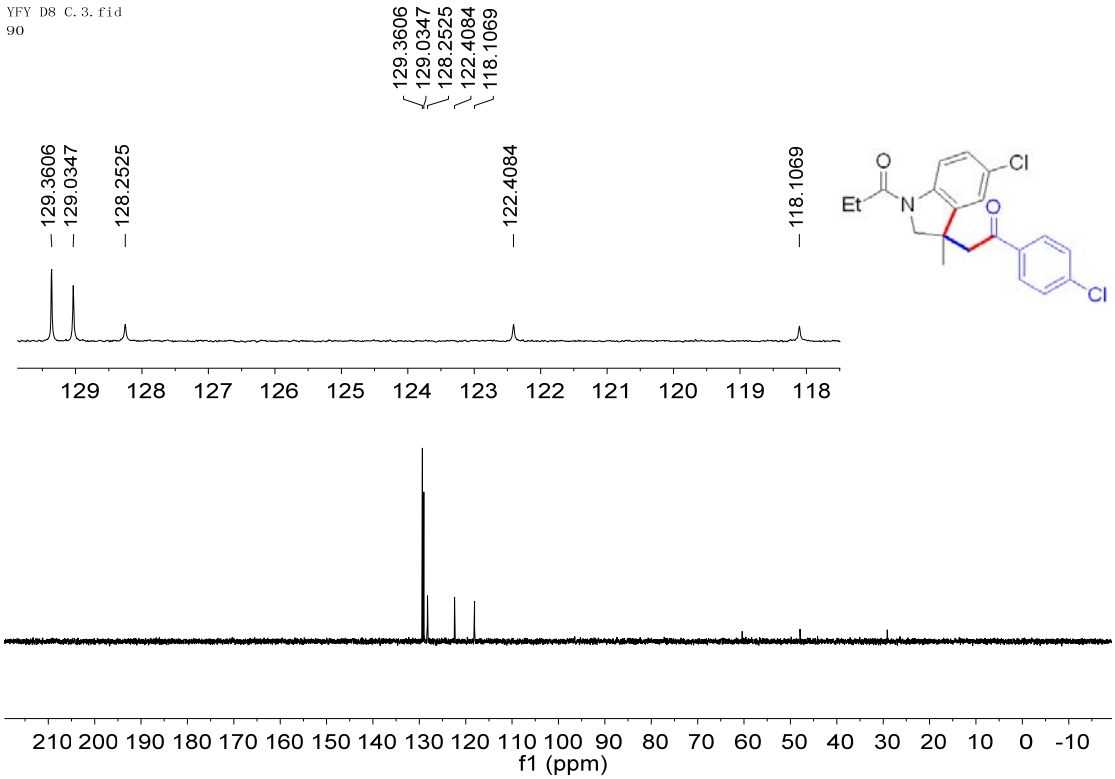

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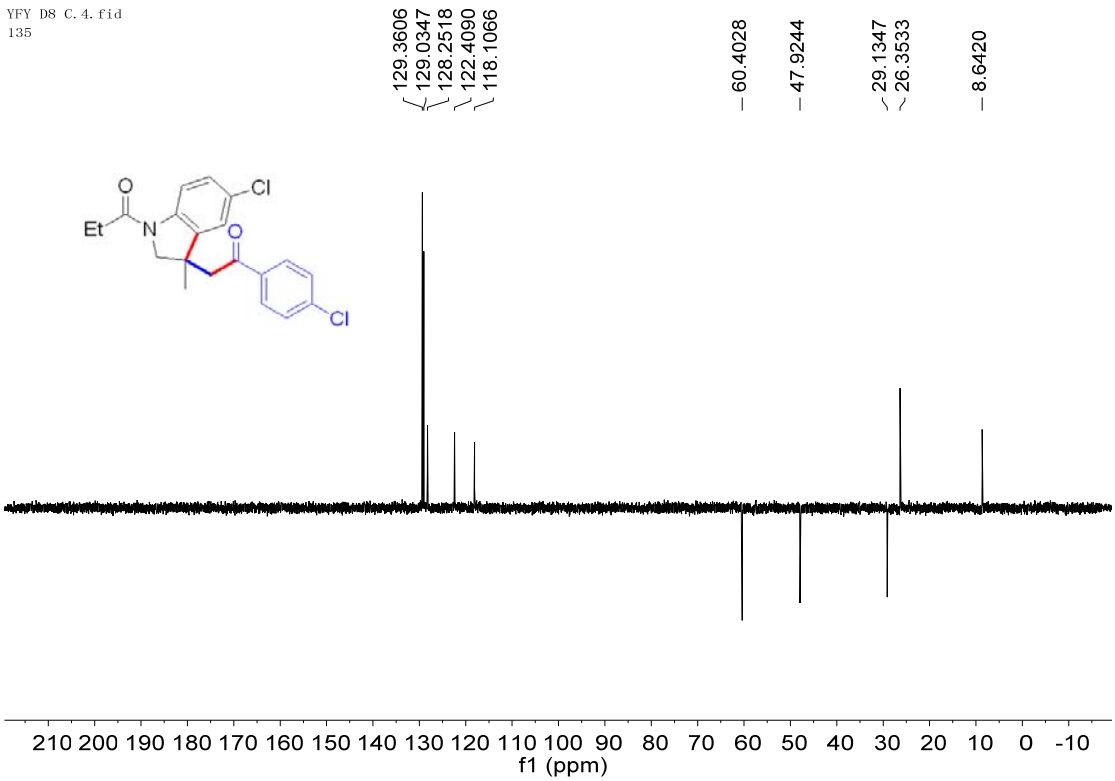
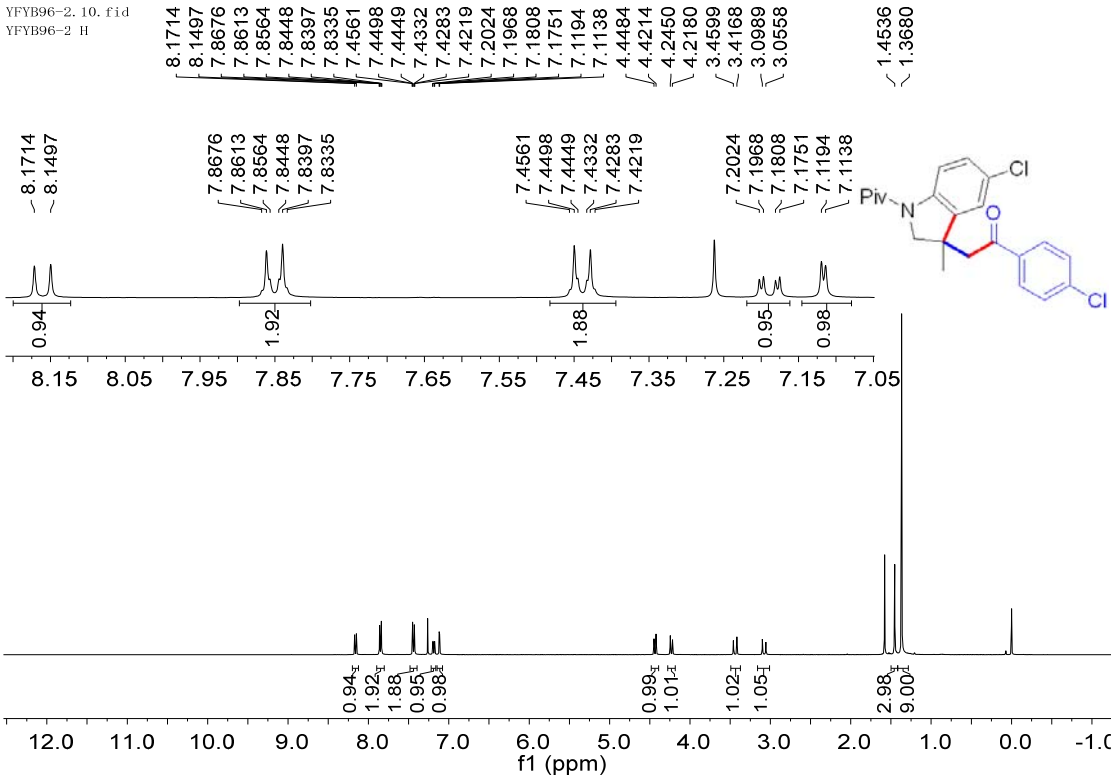
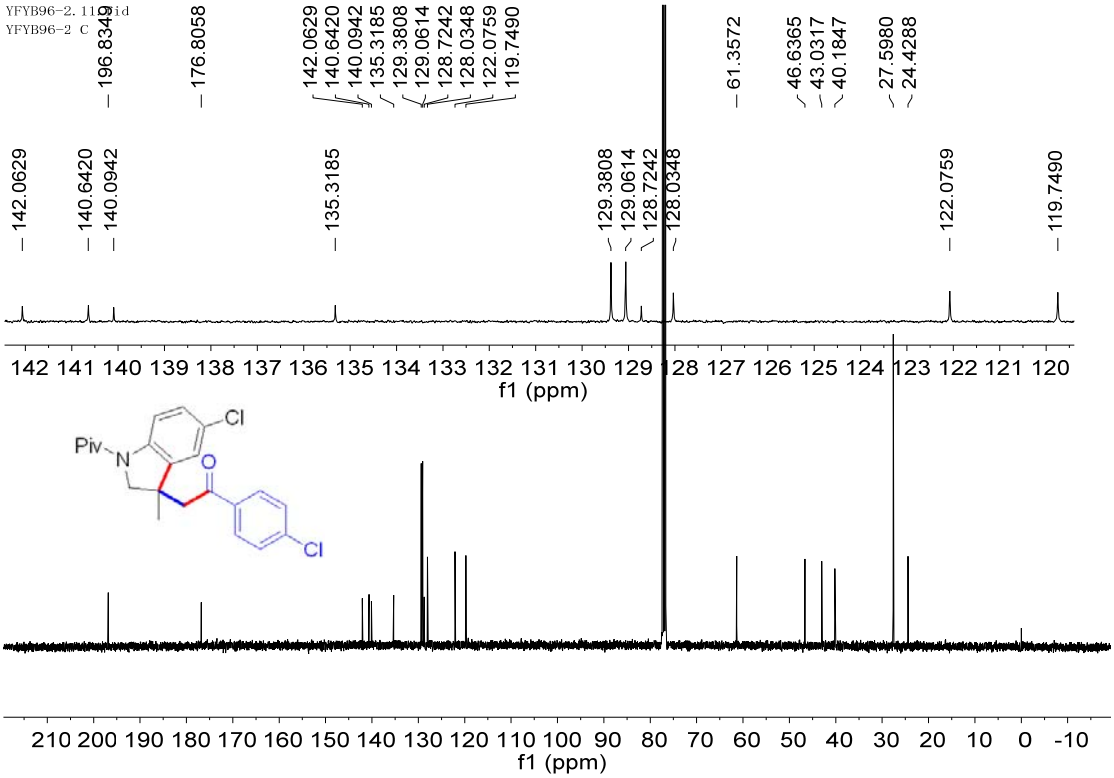


3b2, ^{1}H NMR



^{13}C NMR



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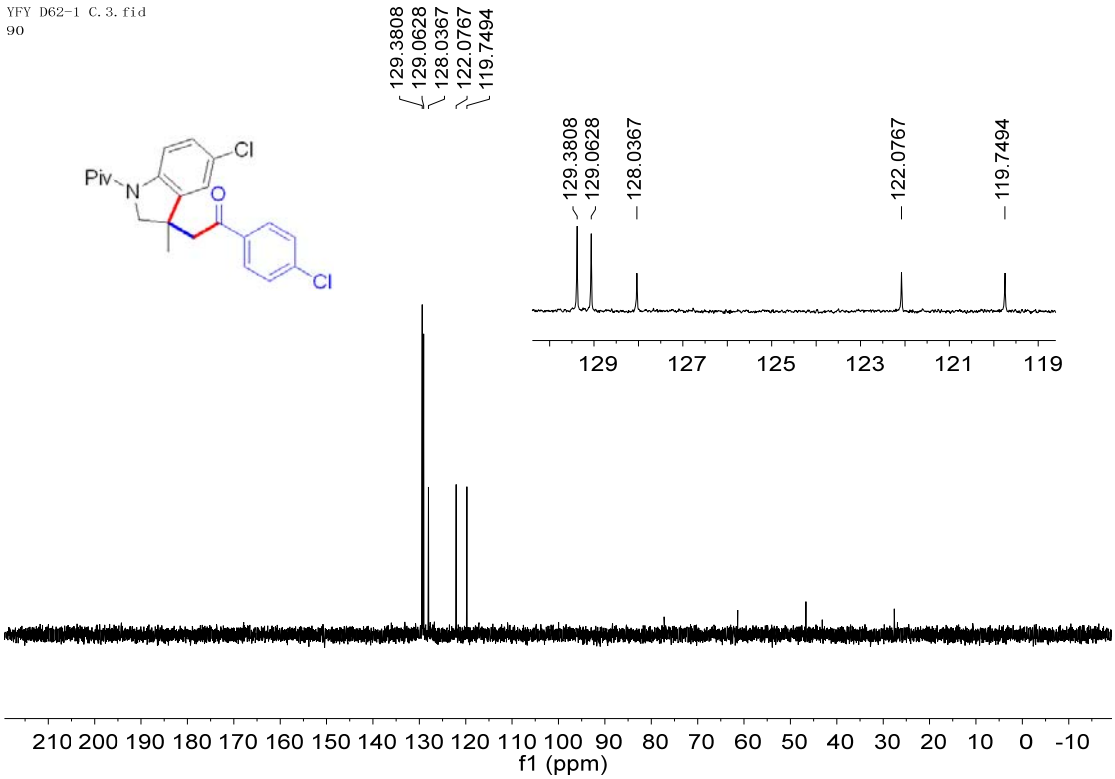

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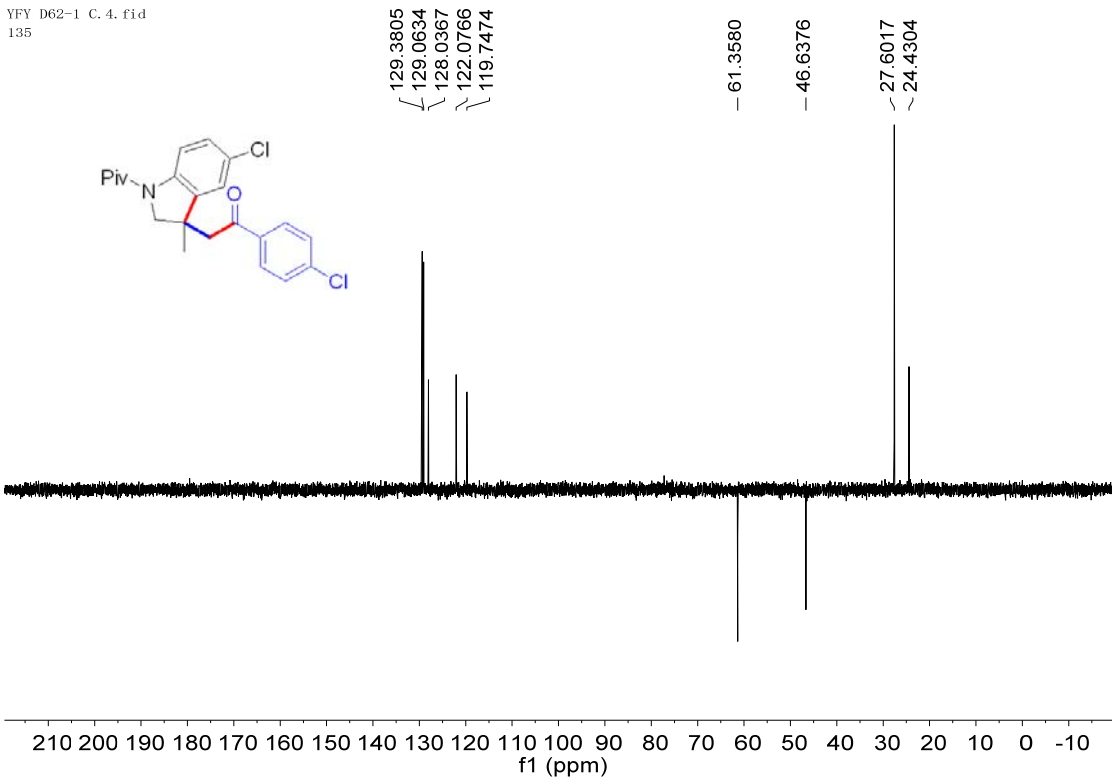
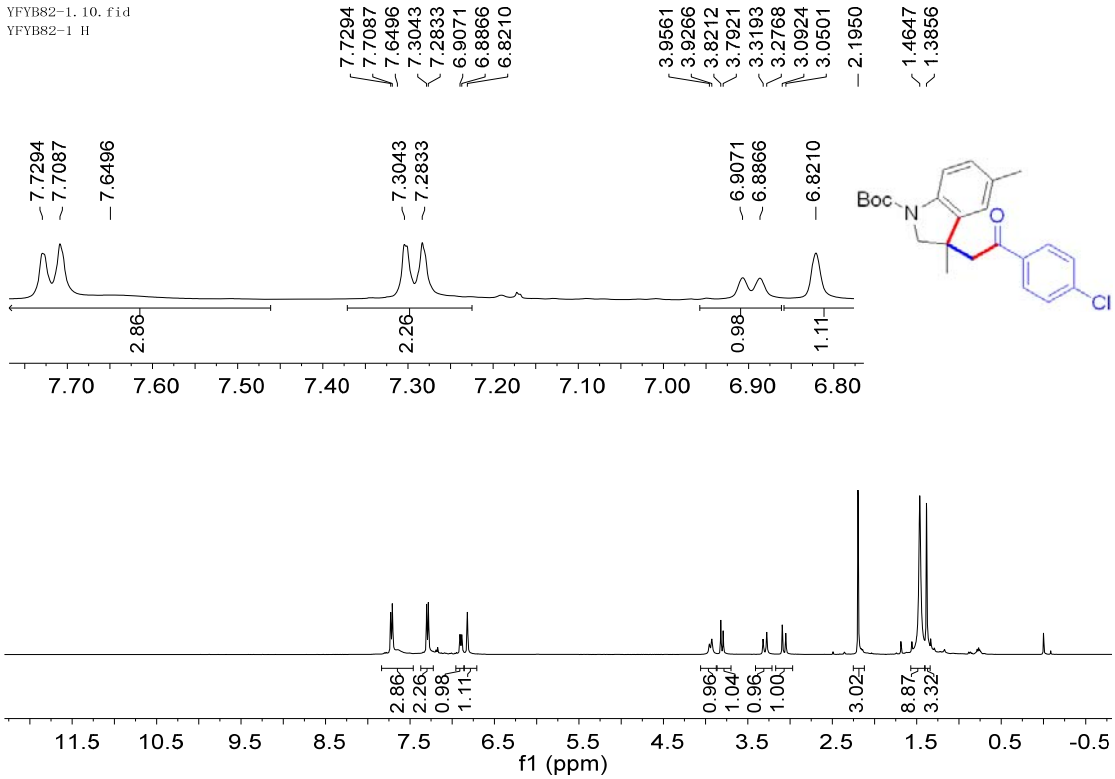
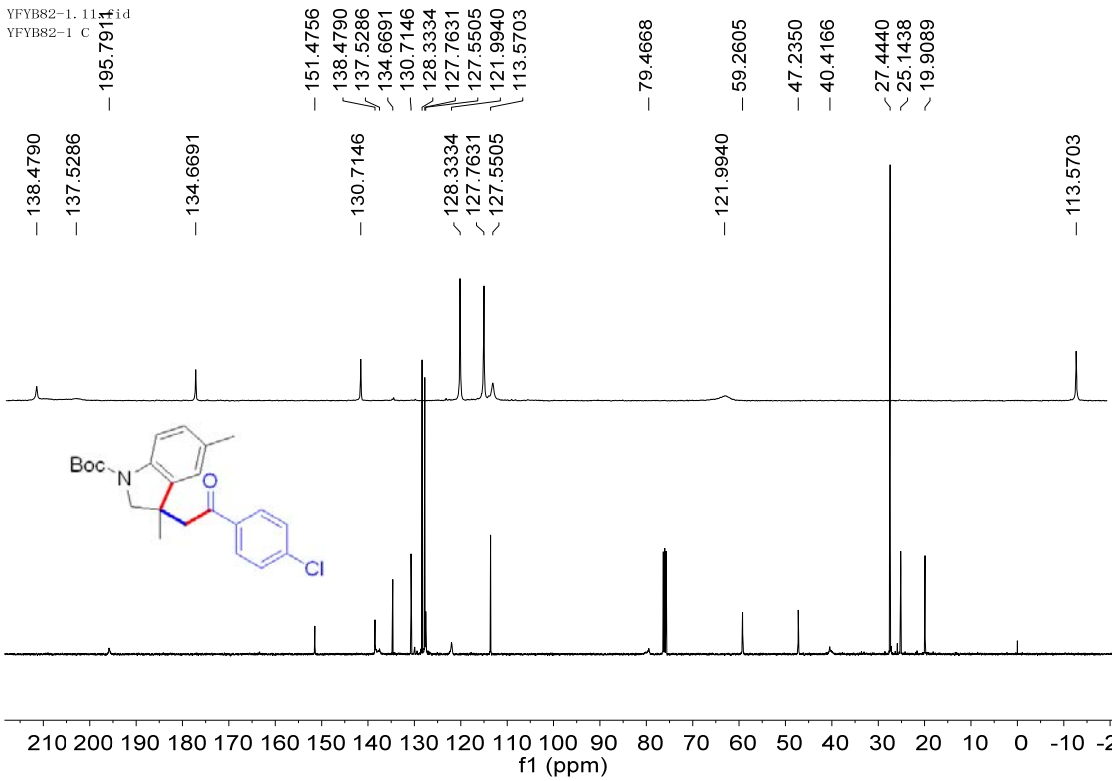


3c1, ^{1}H NMR



^{13}C NMR



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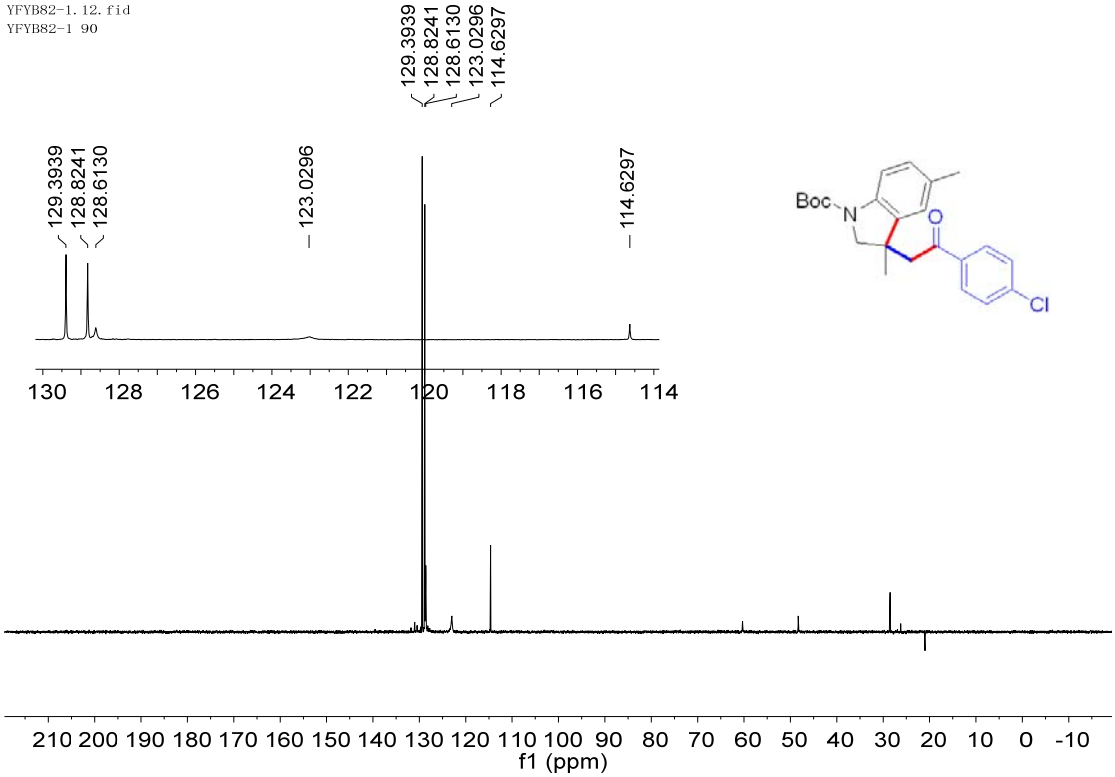

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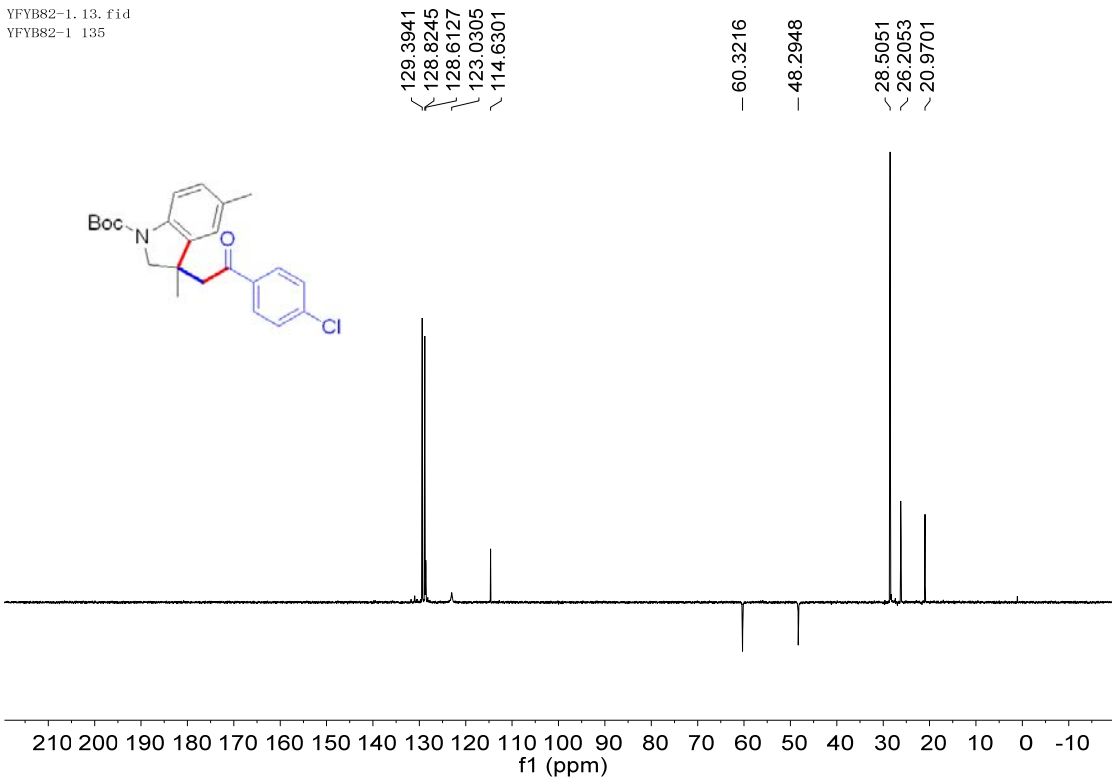
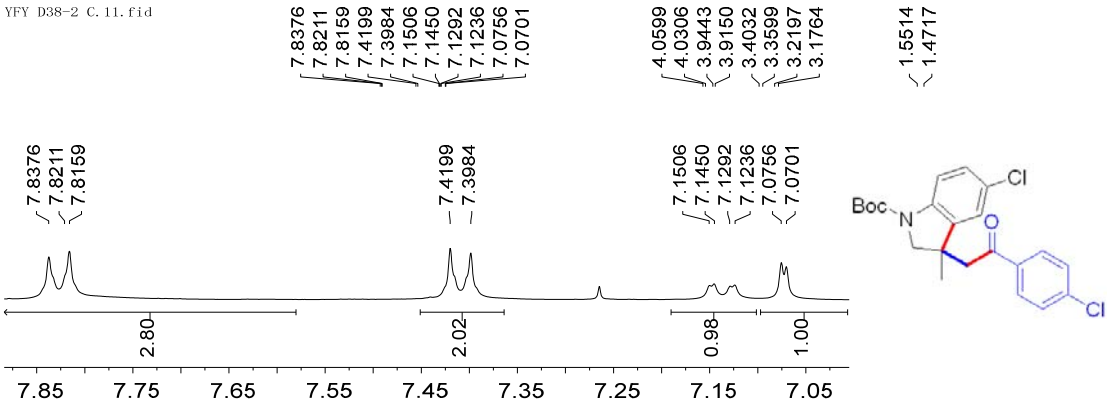
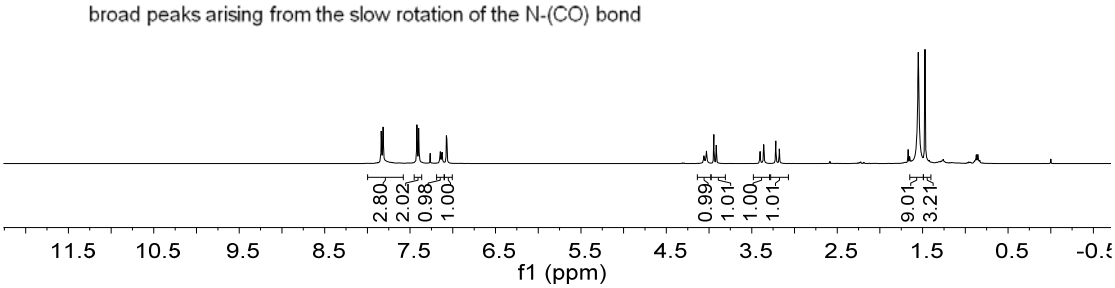
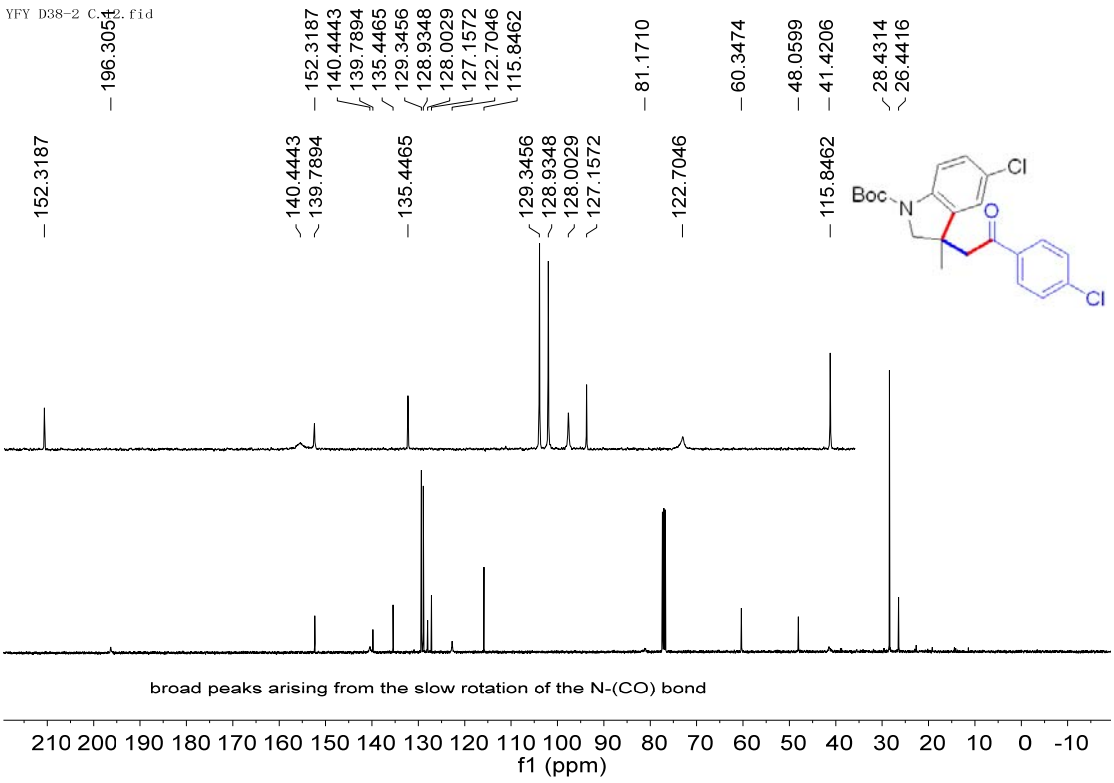


3c2, ^{1}H NMR





^{13}C NMR



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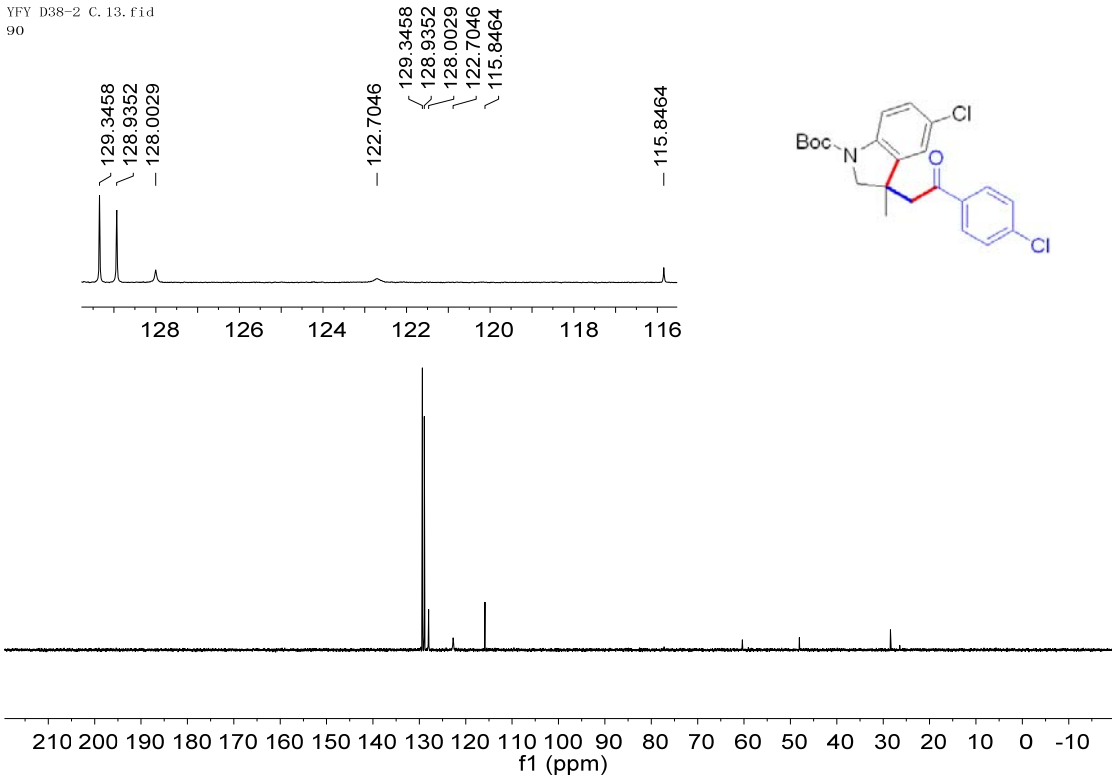

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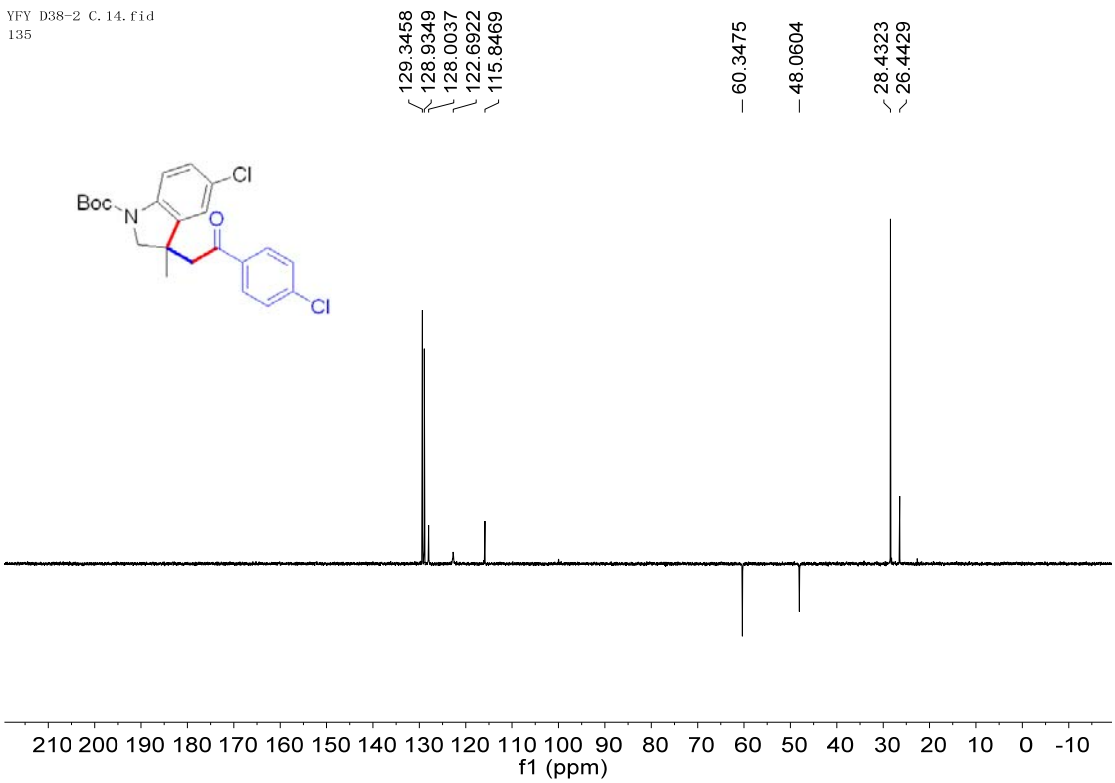

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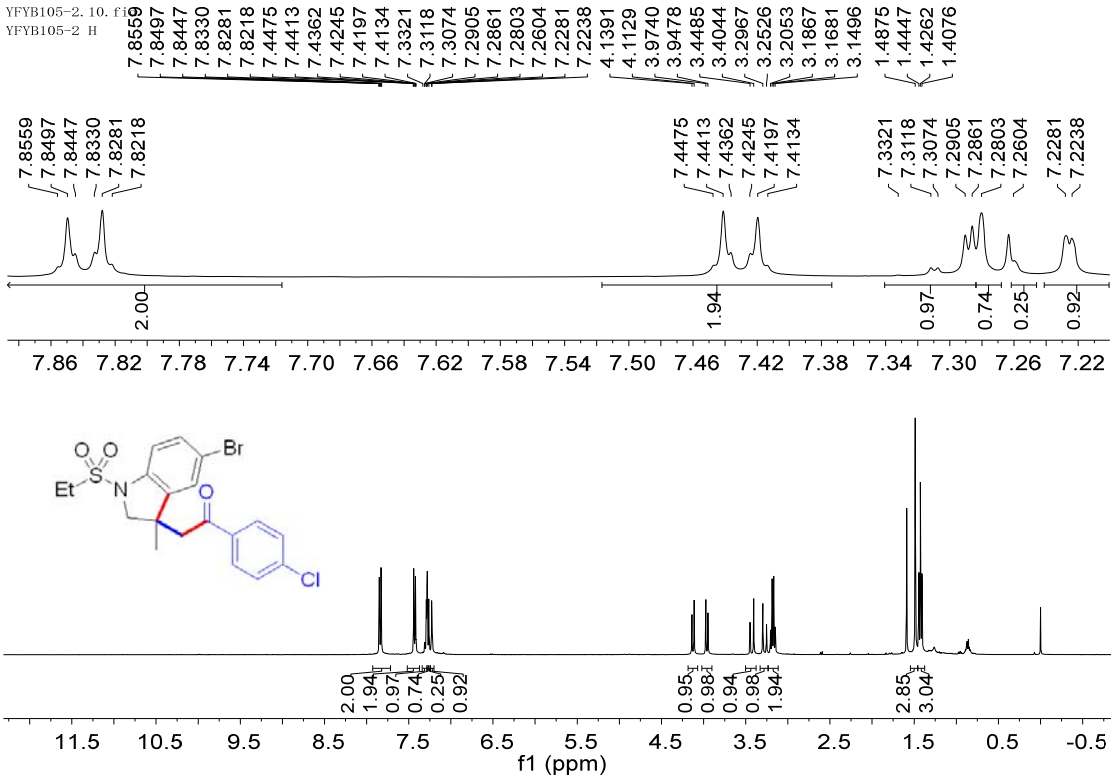

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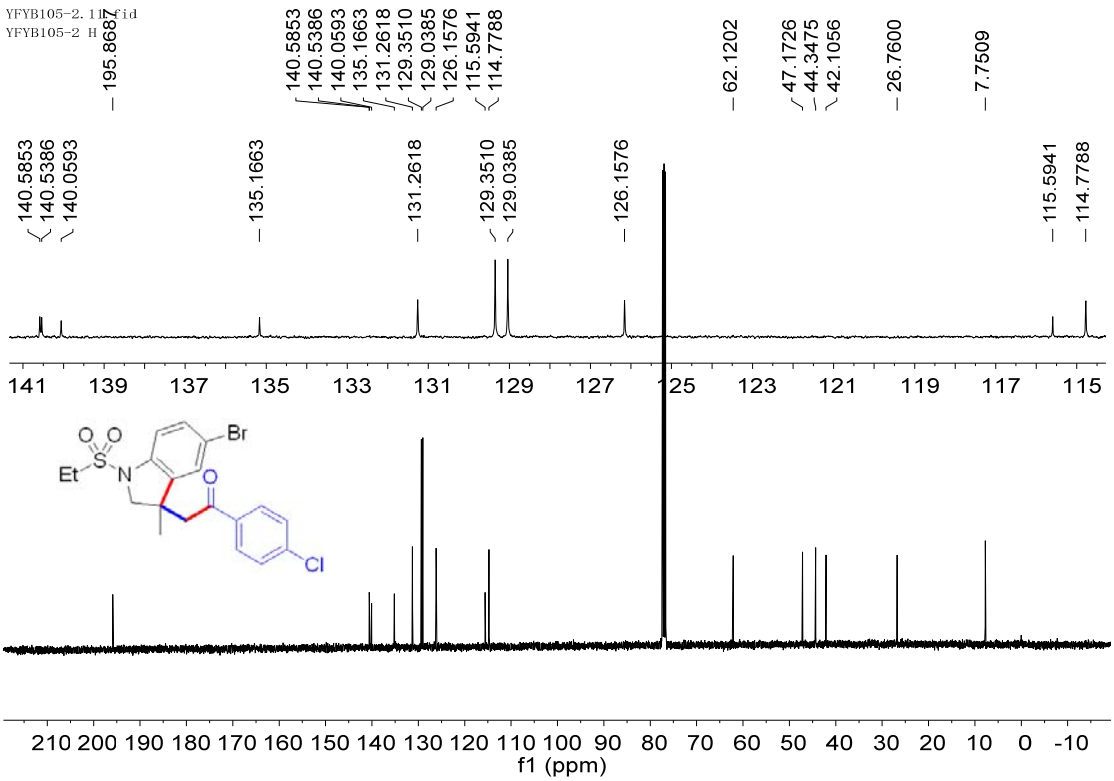

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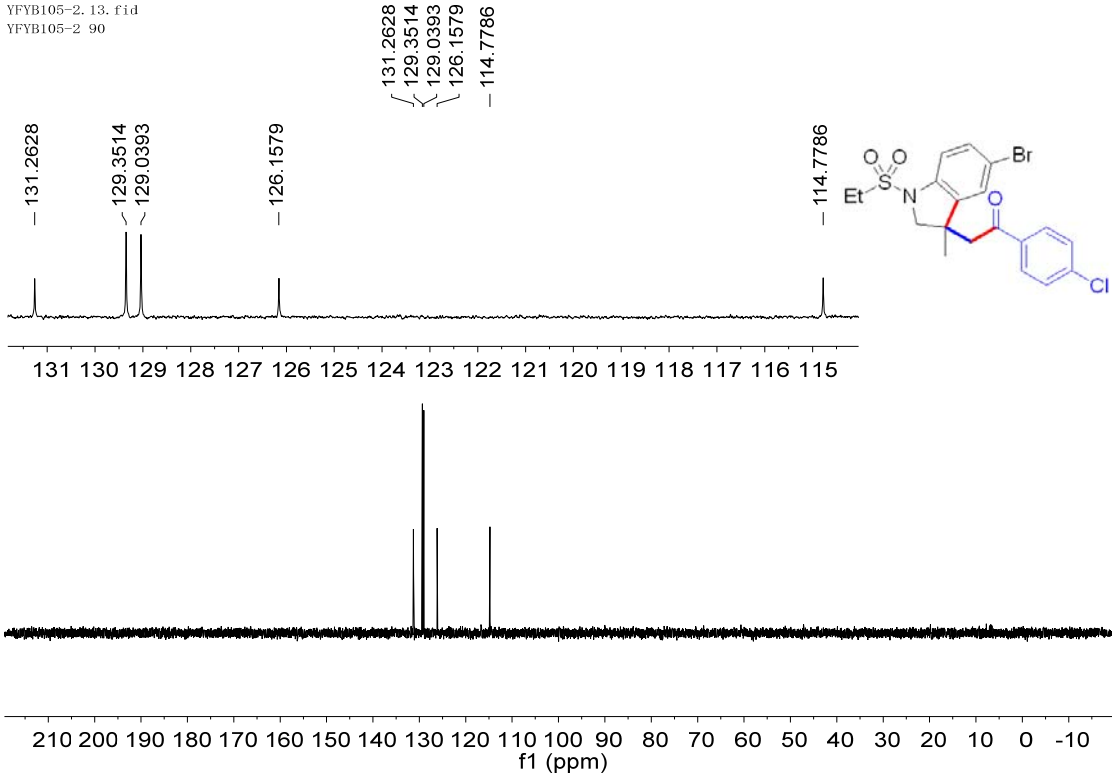

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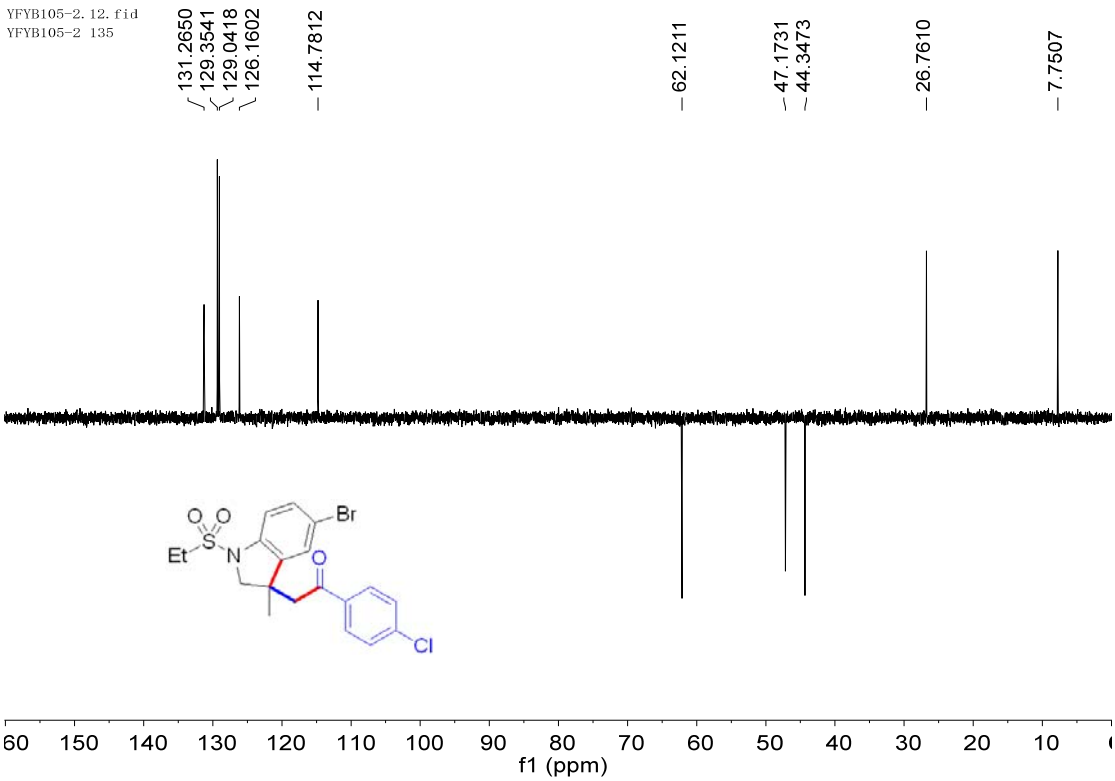

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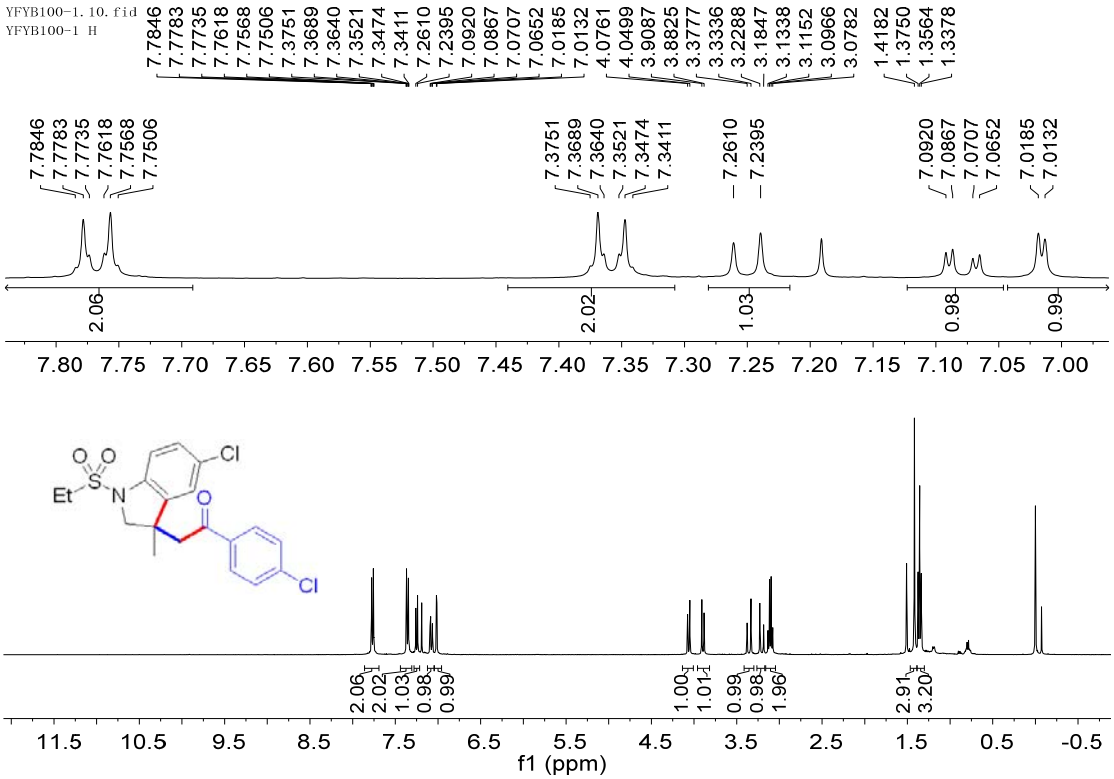

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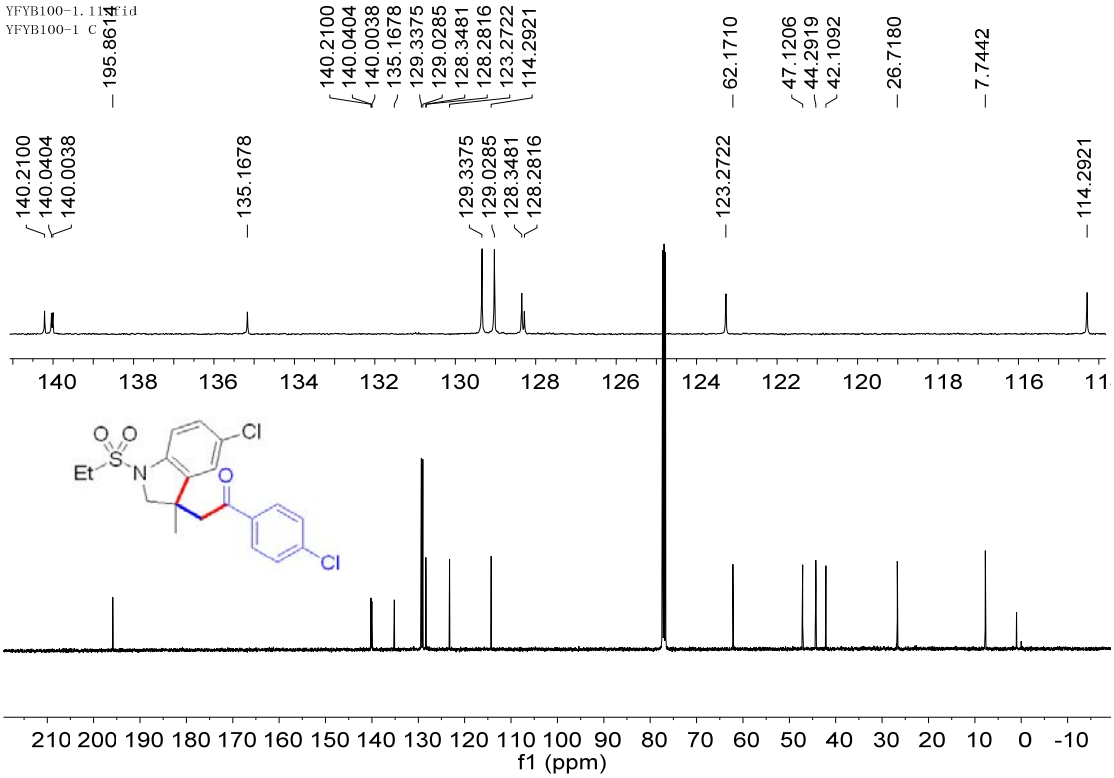

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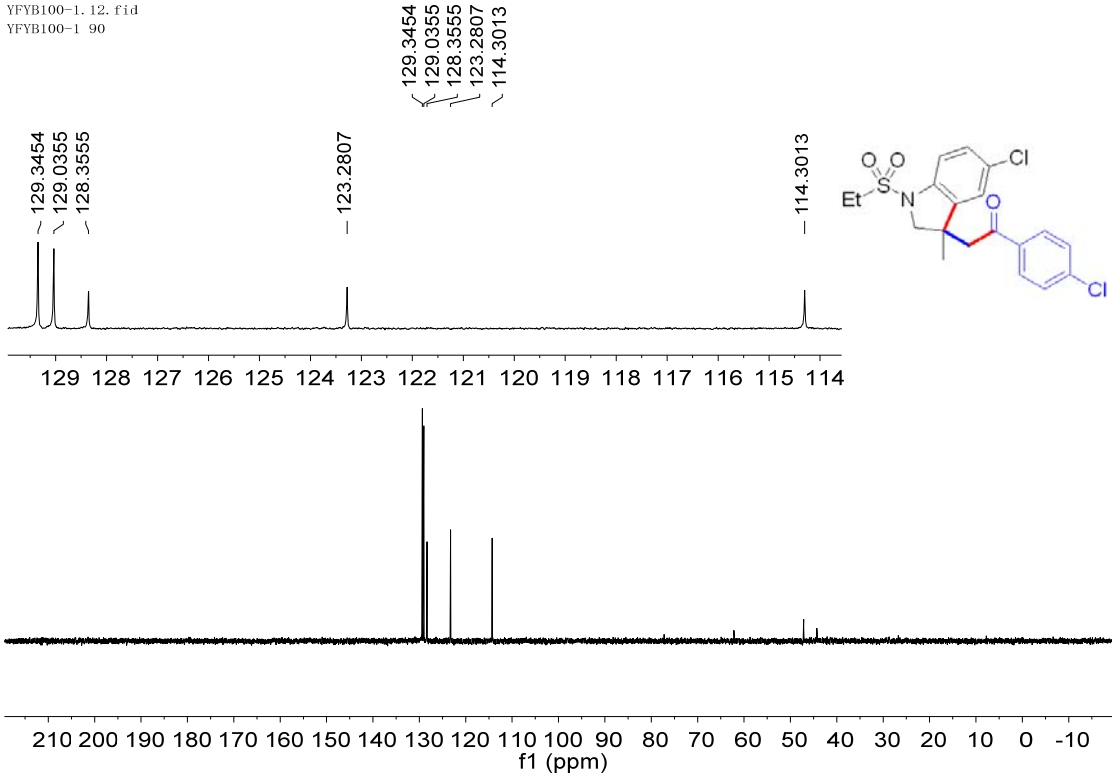

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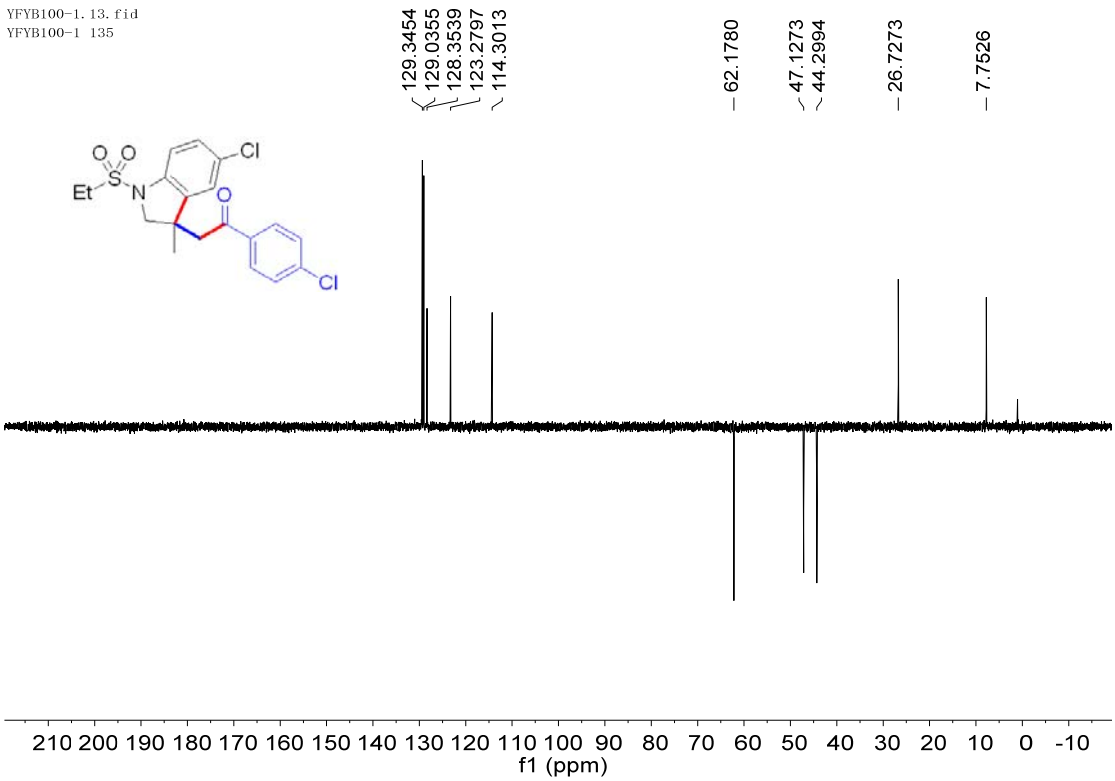

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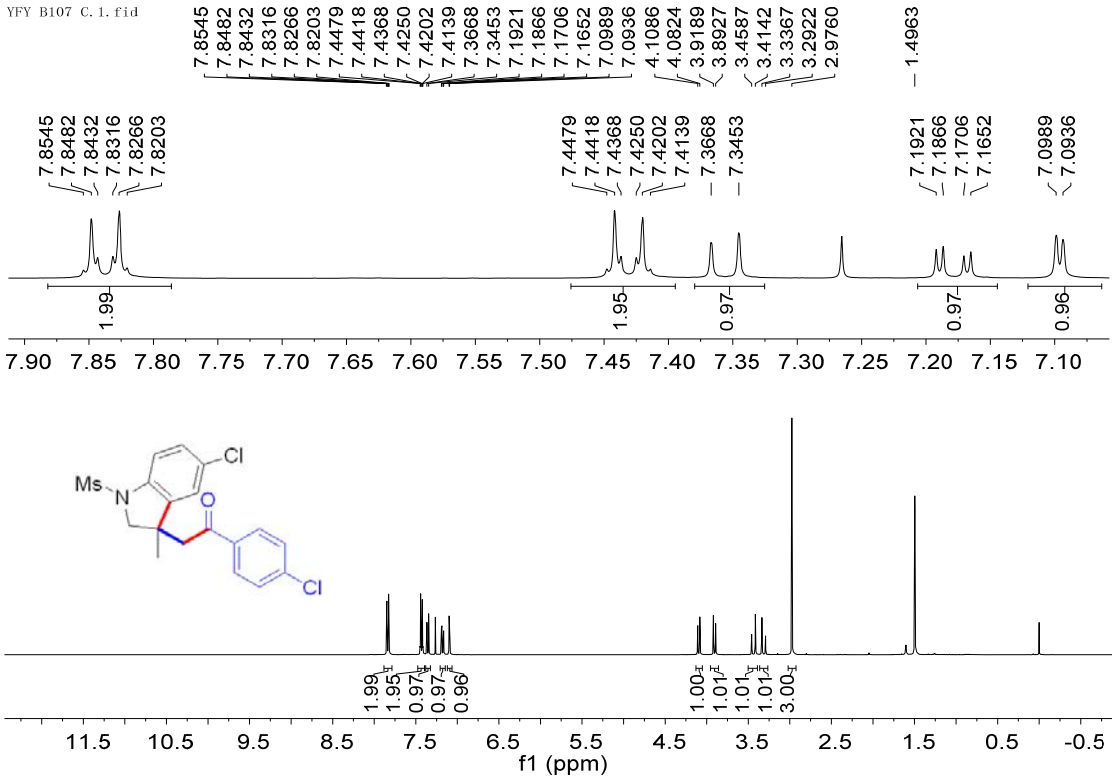

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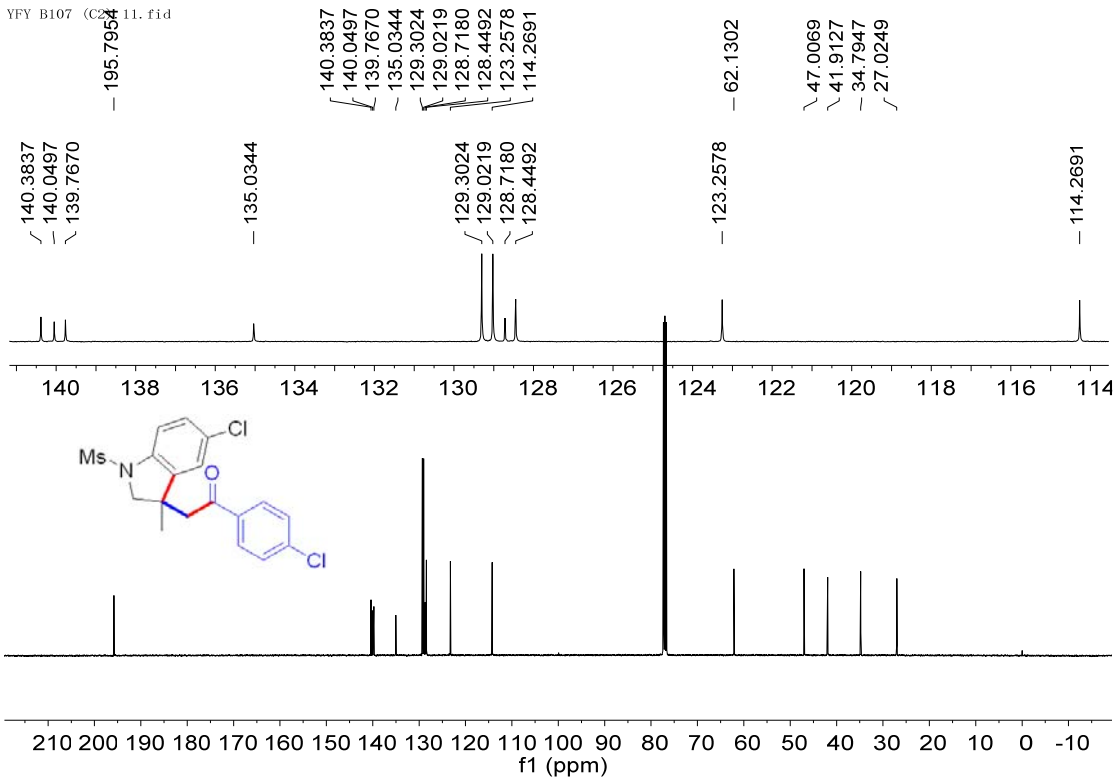

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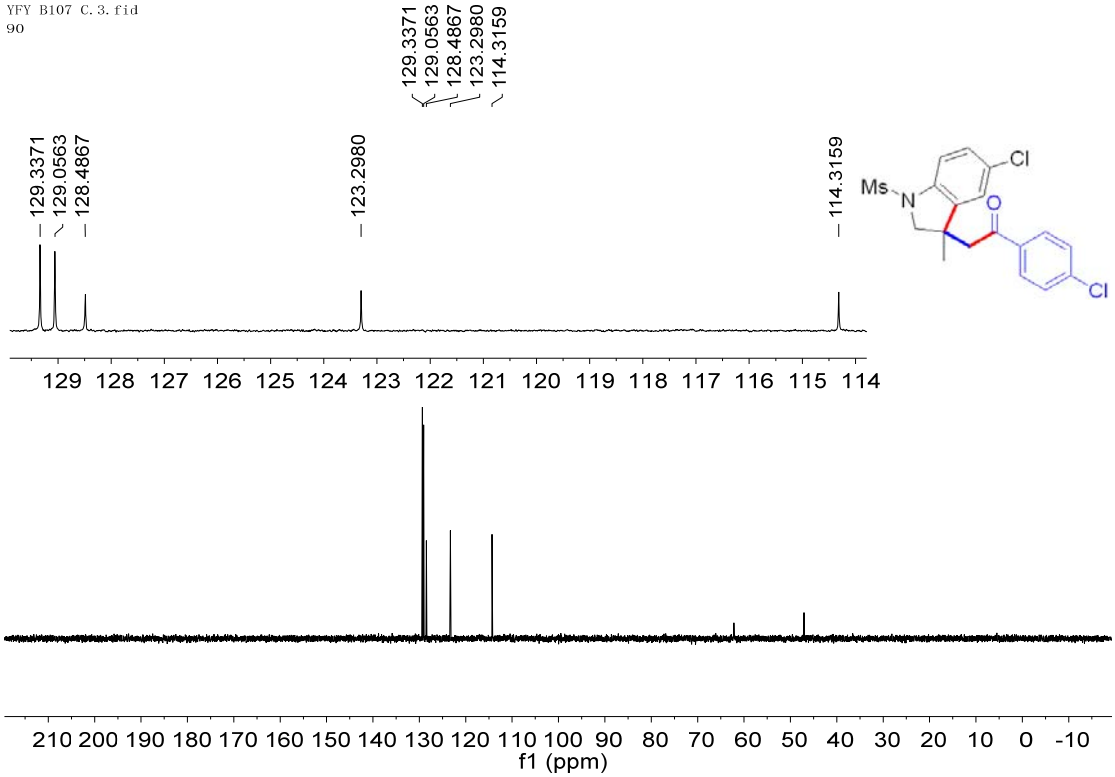

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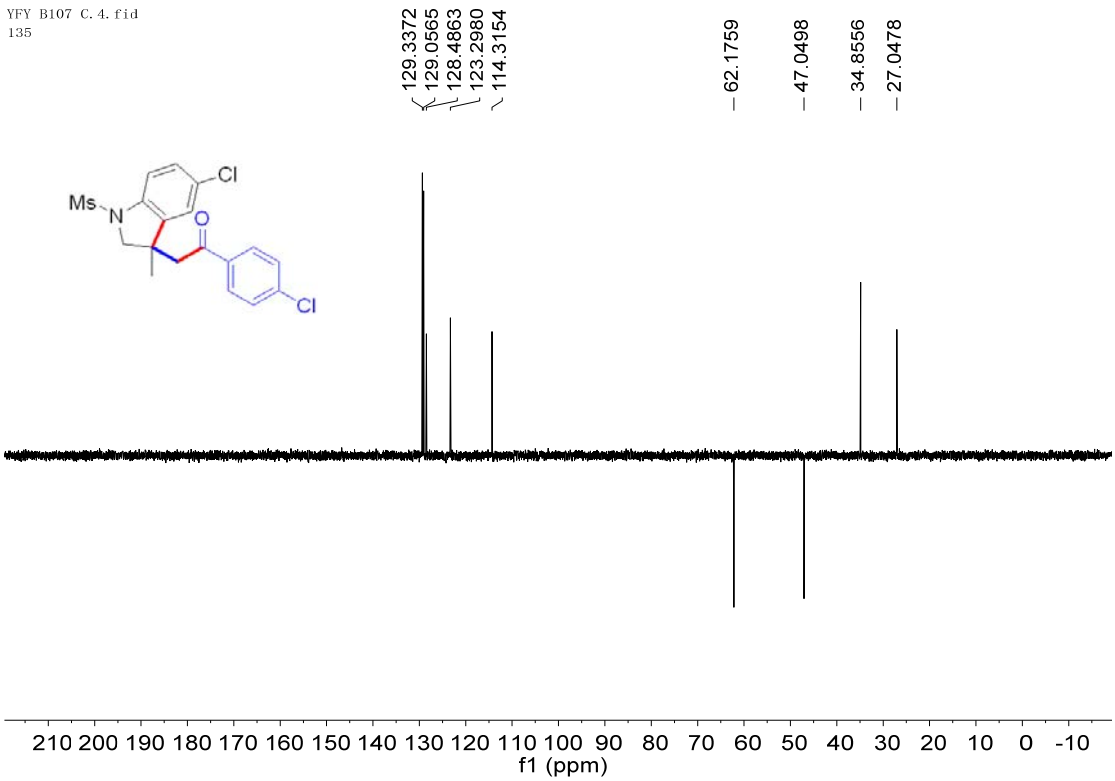
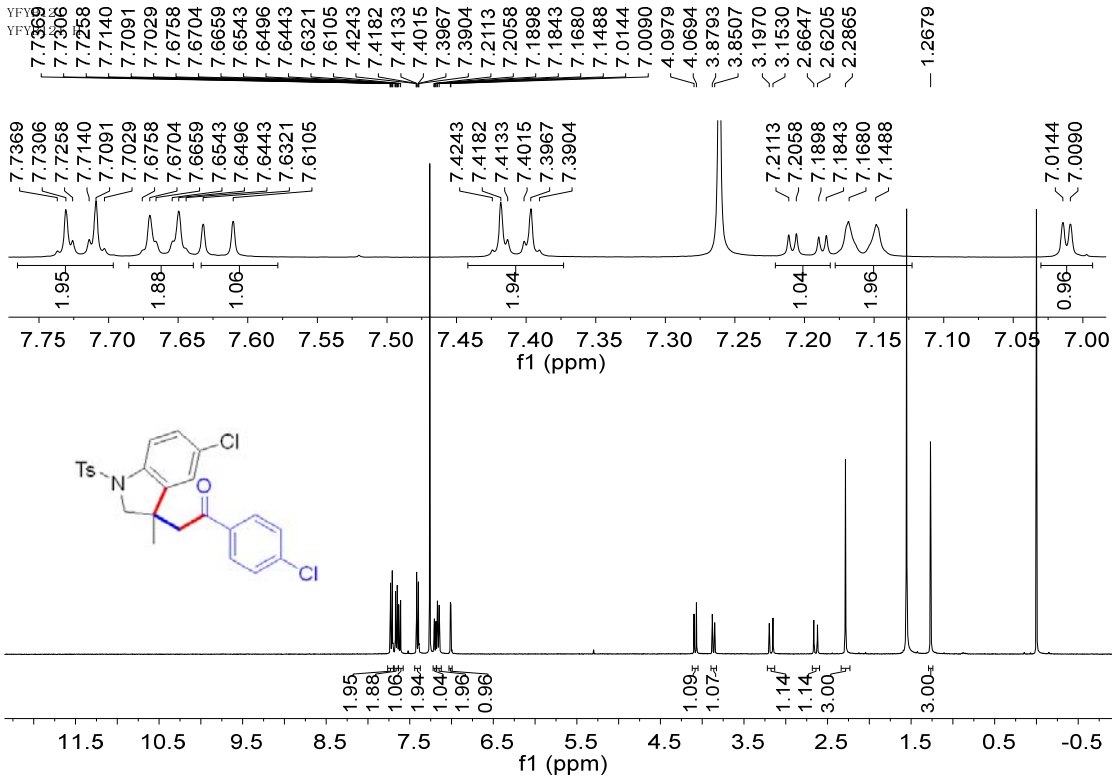


3e2, ^{1}H NMR



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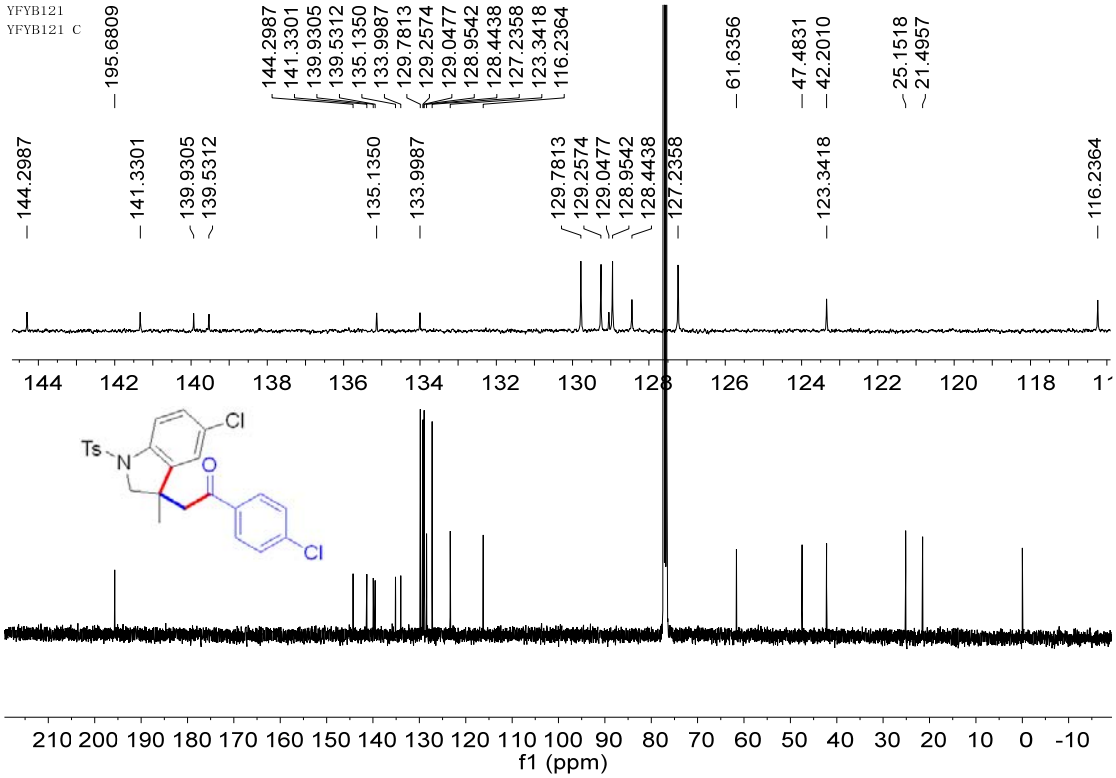

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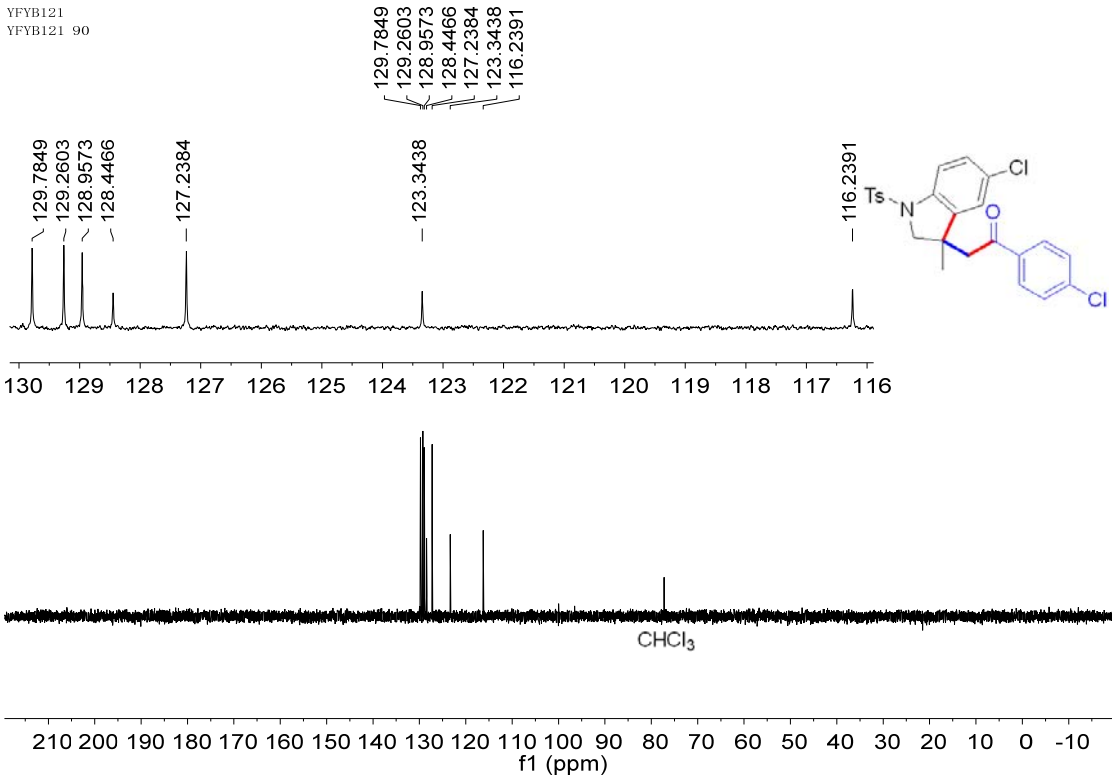

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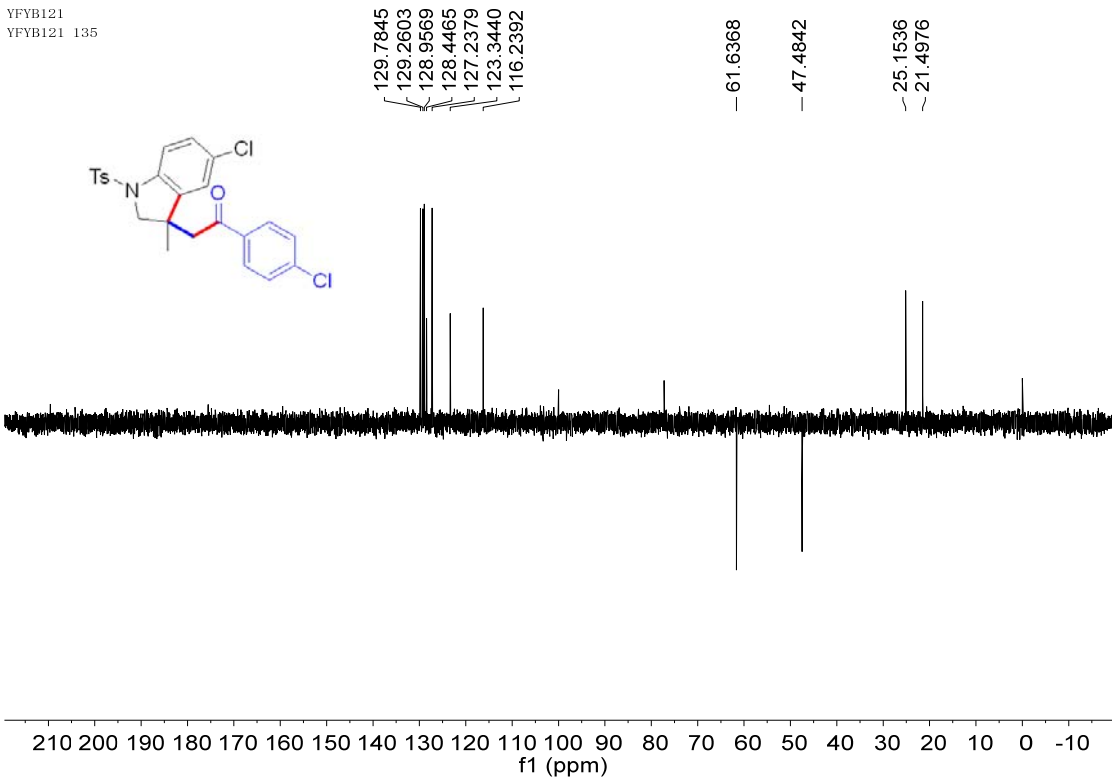

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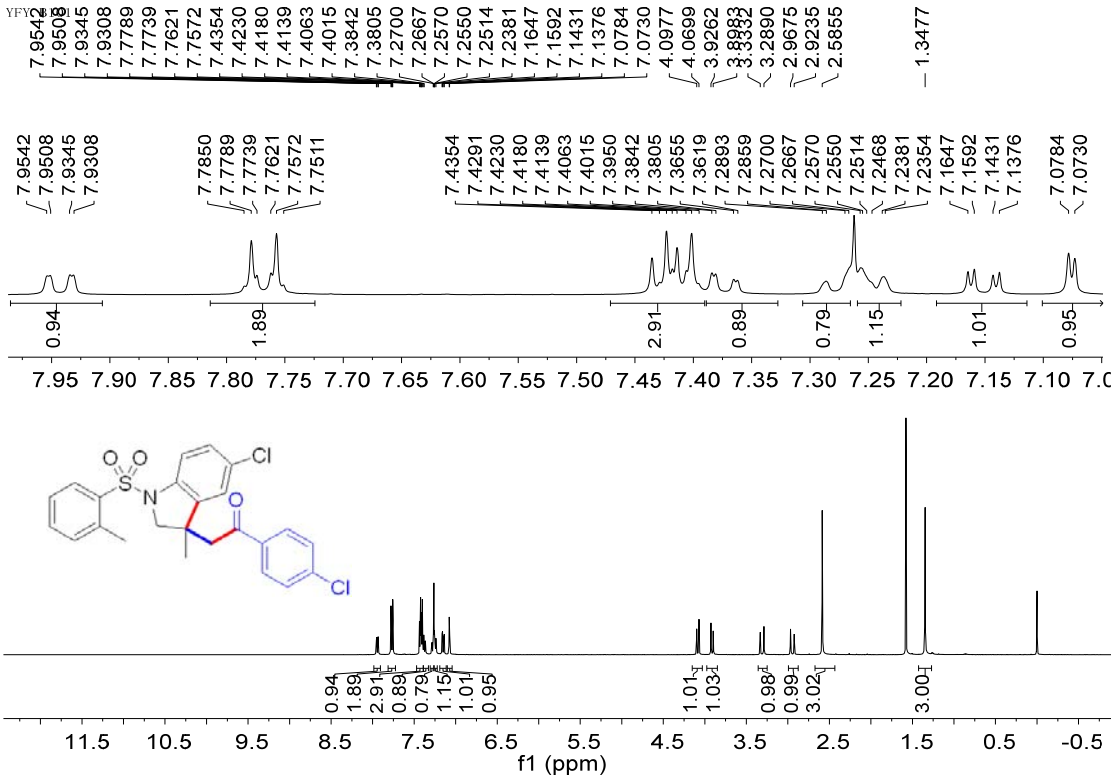

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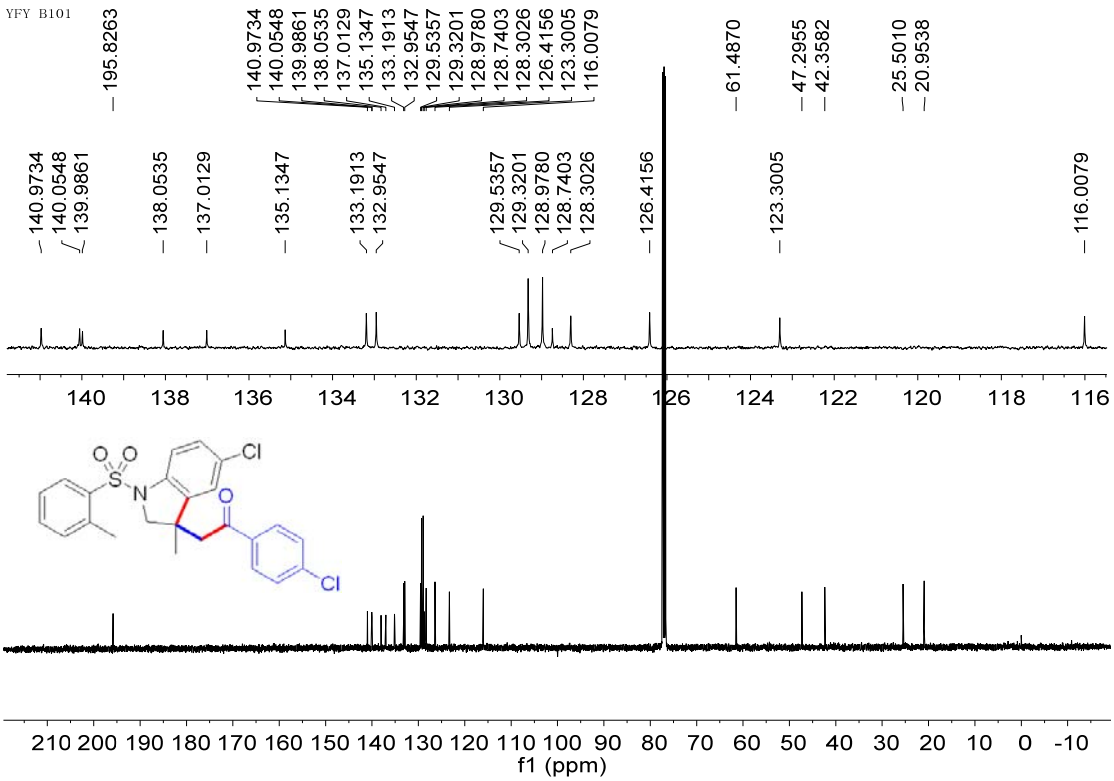

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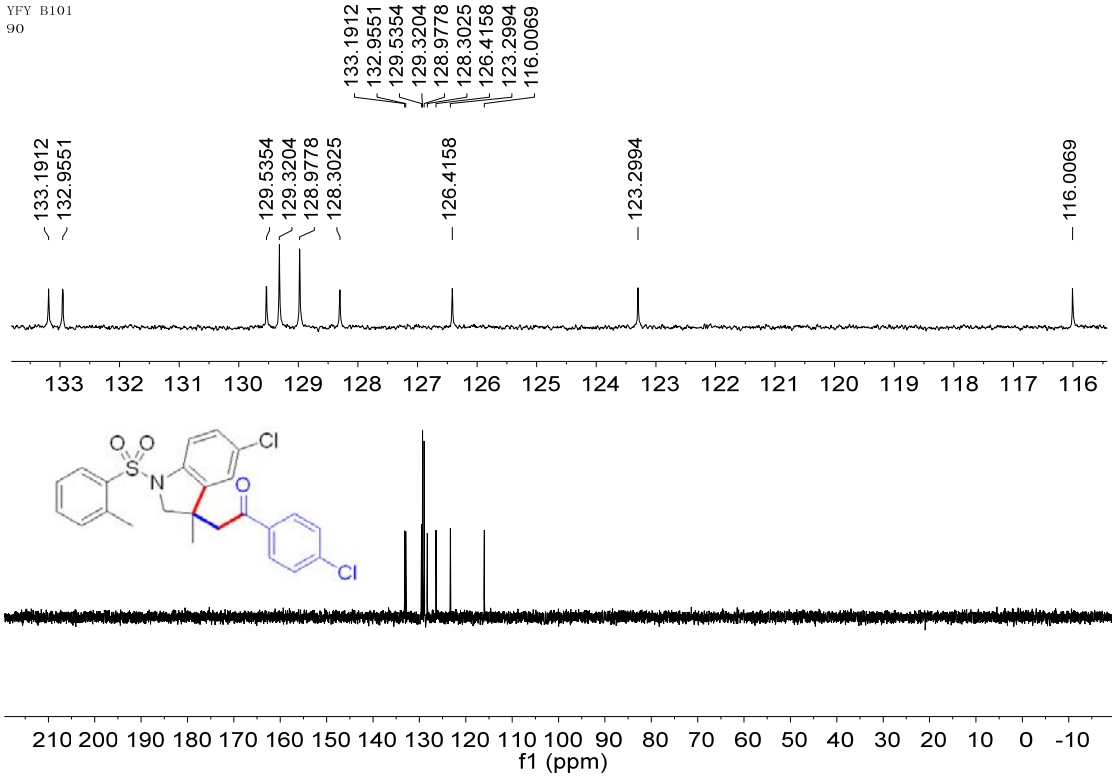

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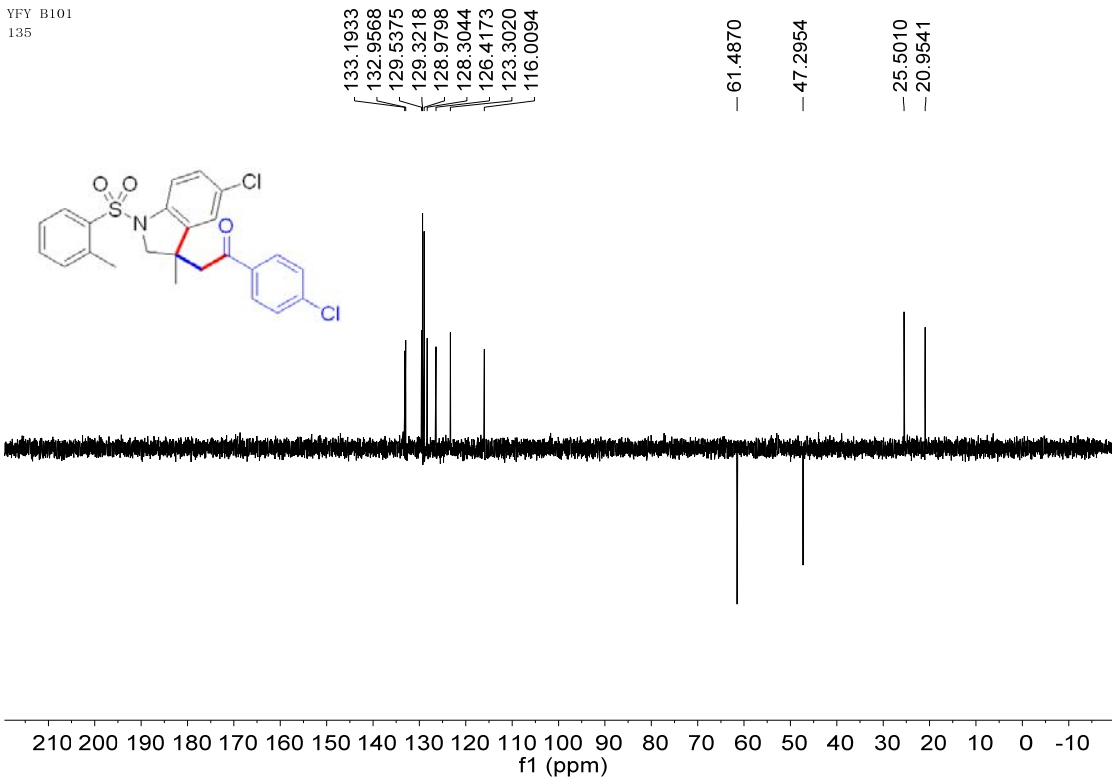
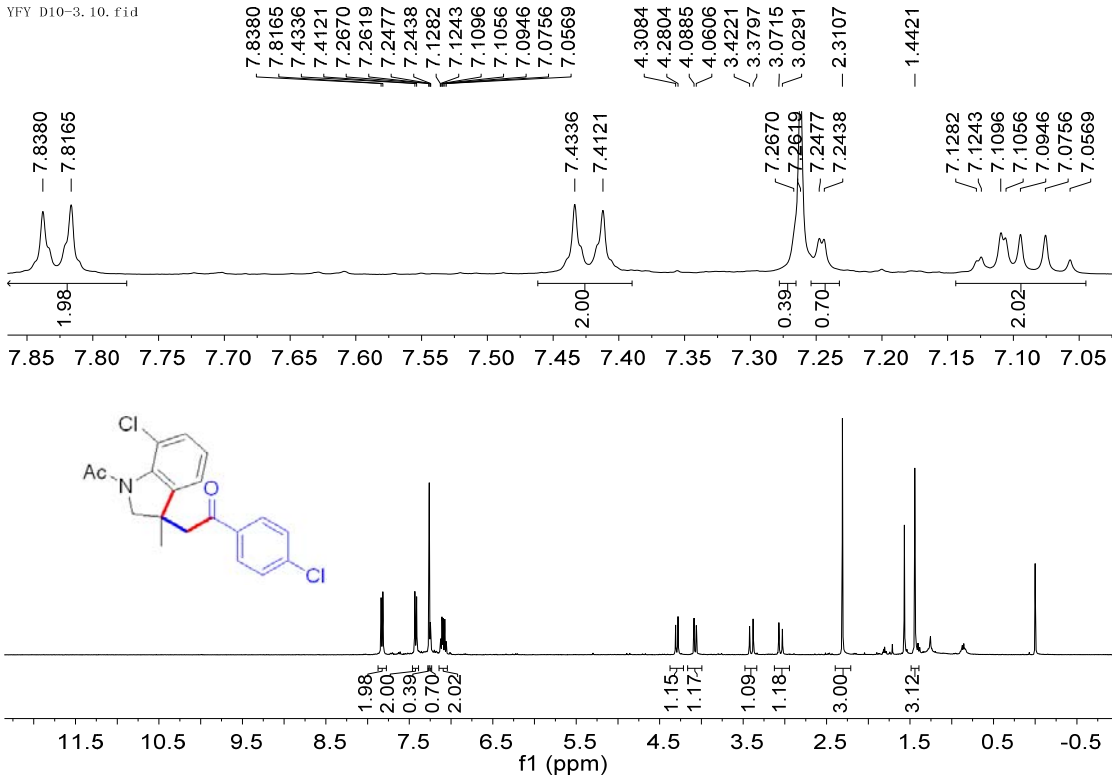
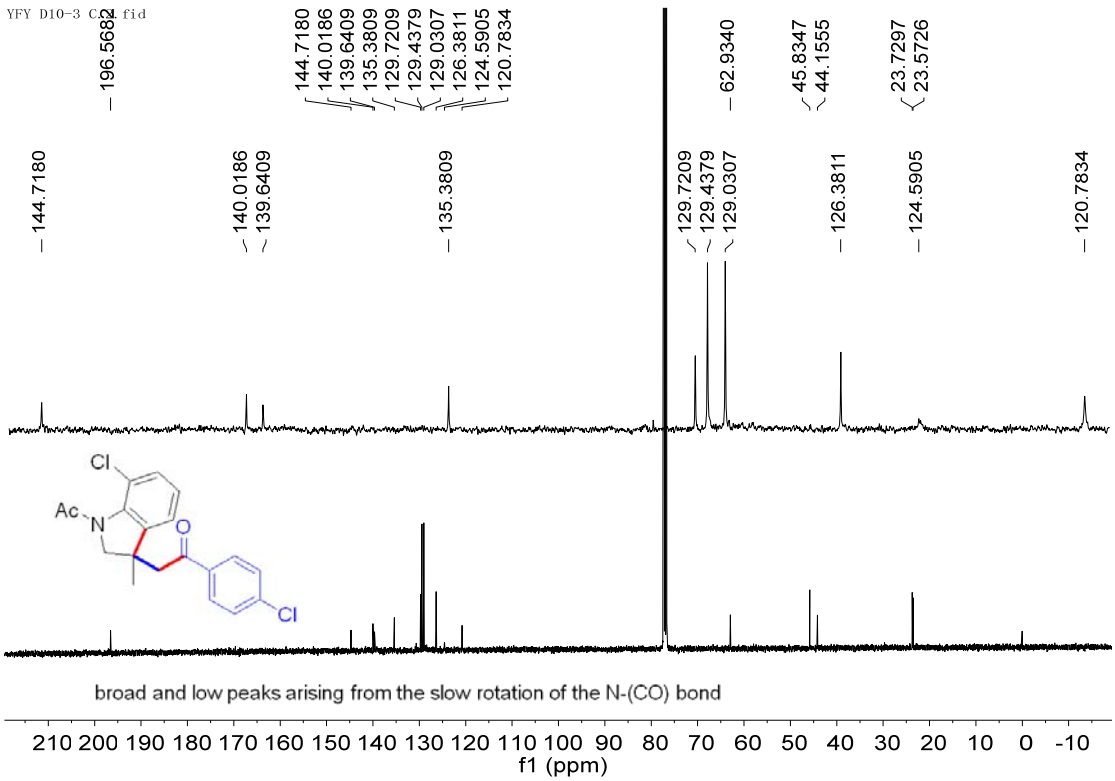


3f, ^{1}H NMR



^{13}C NMR



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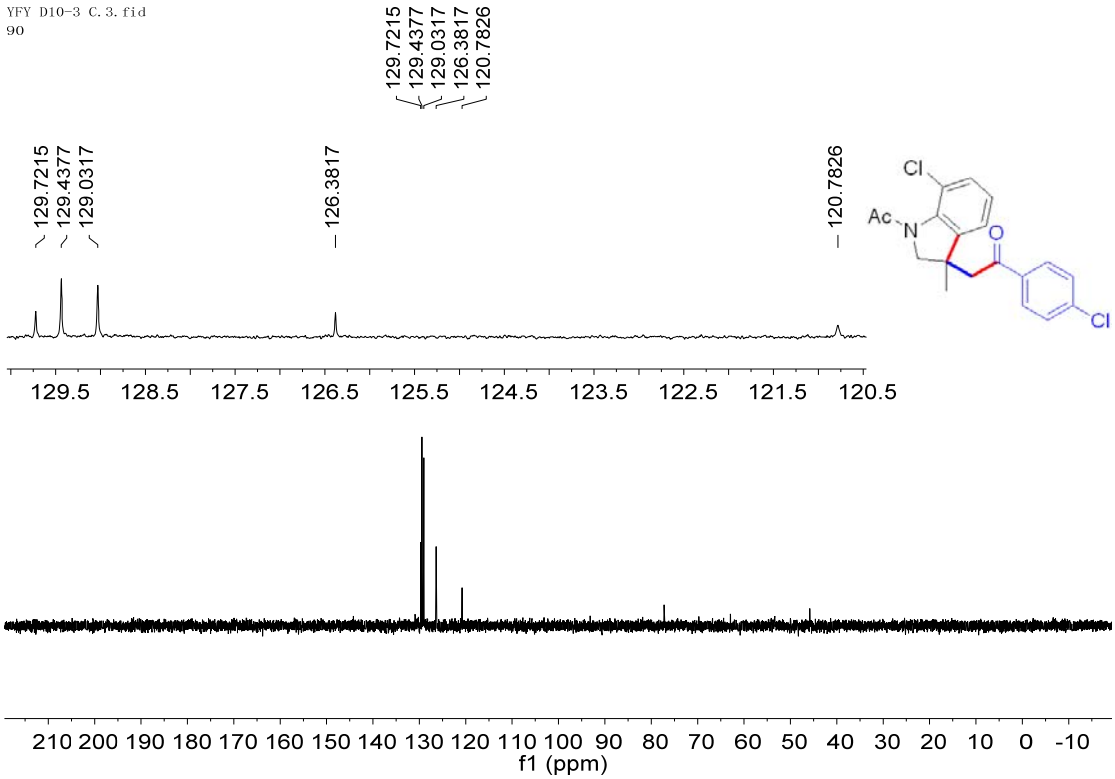

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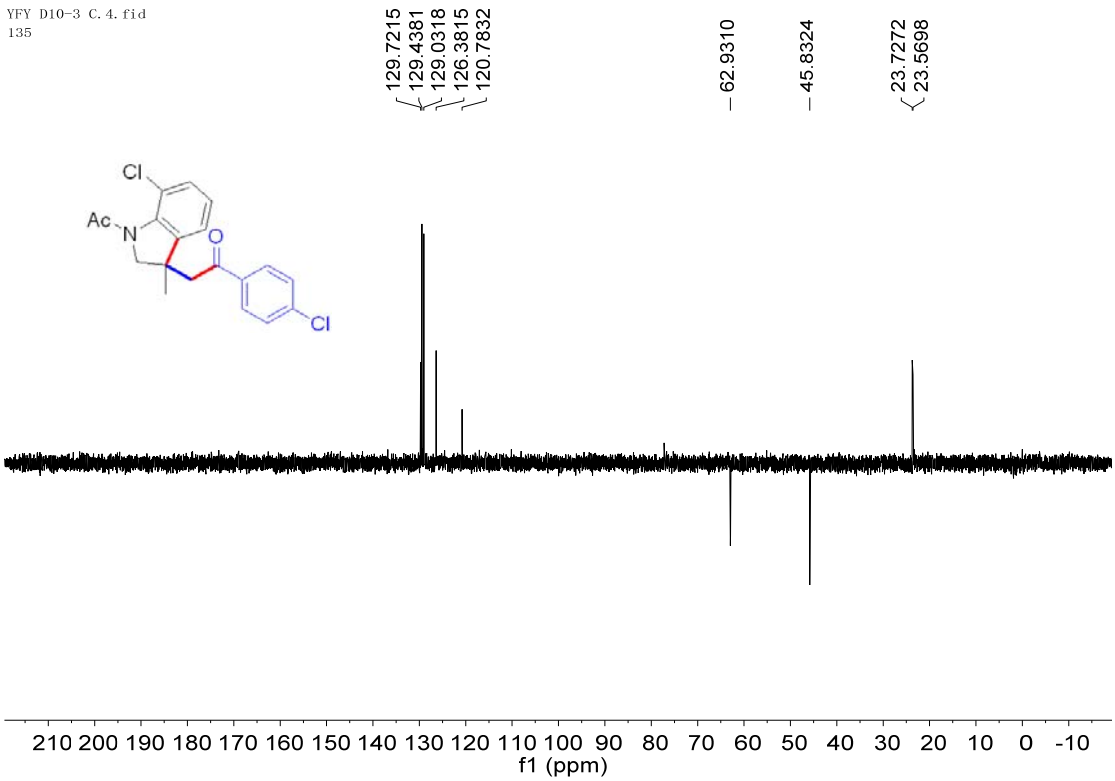
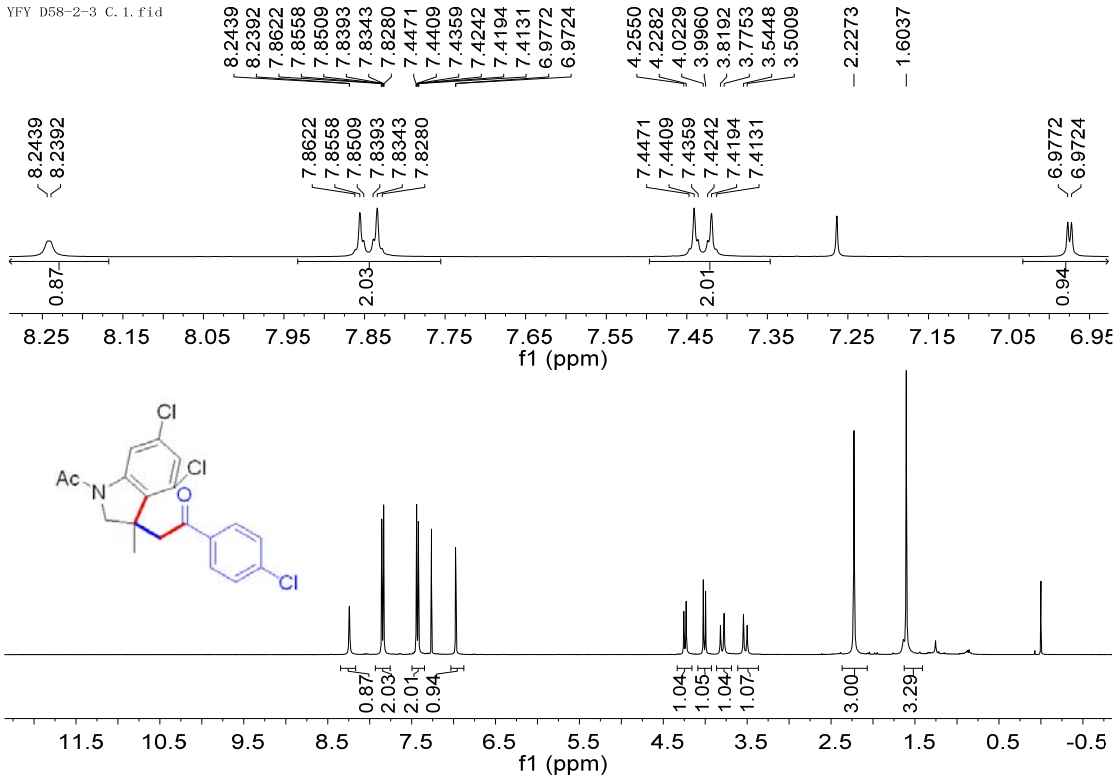
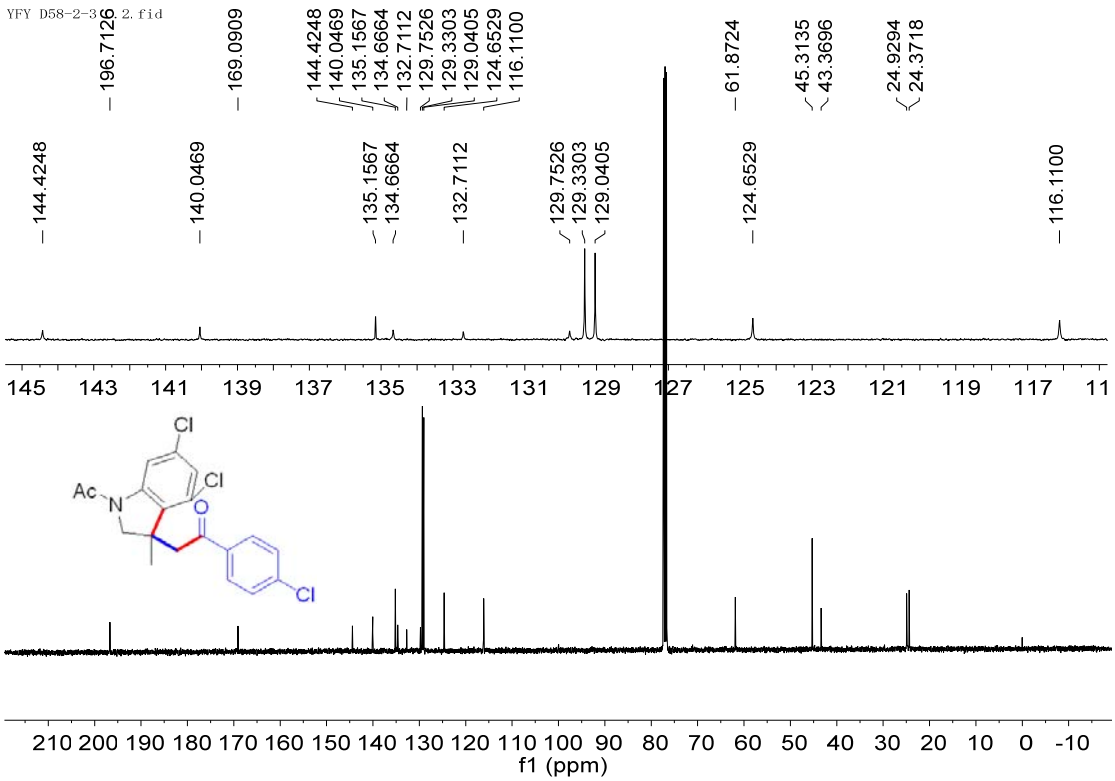


3g, ^{1}H NMR



^{13}C NMR



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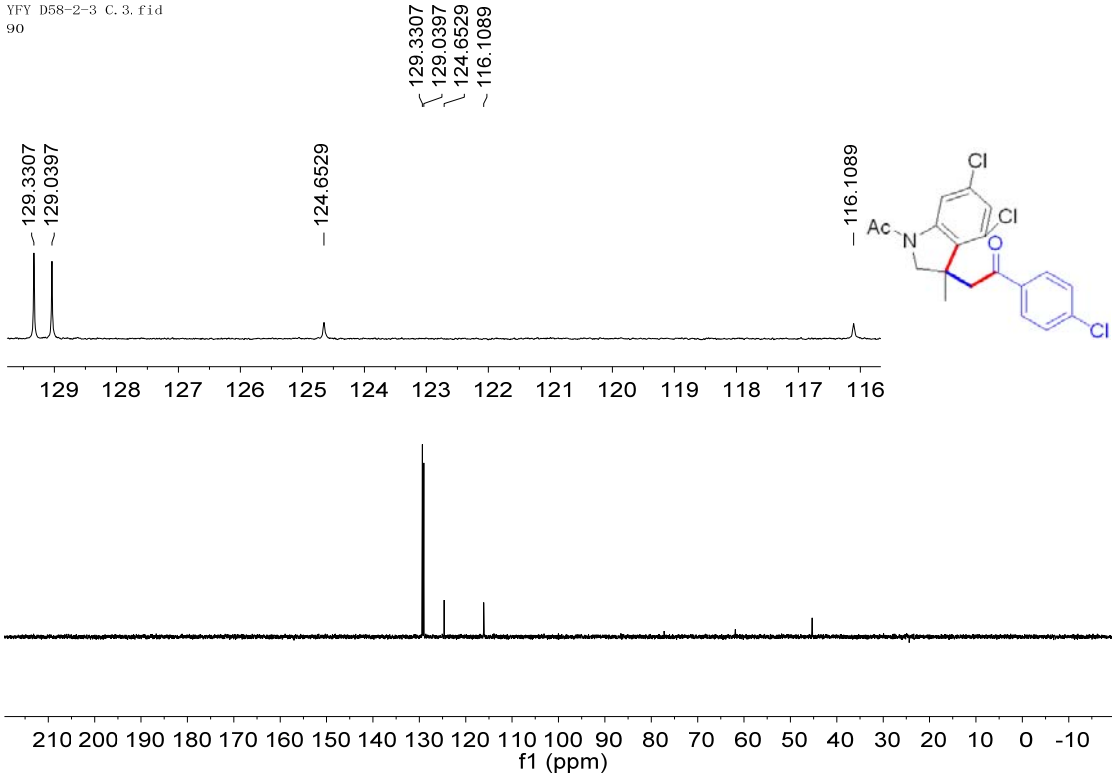

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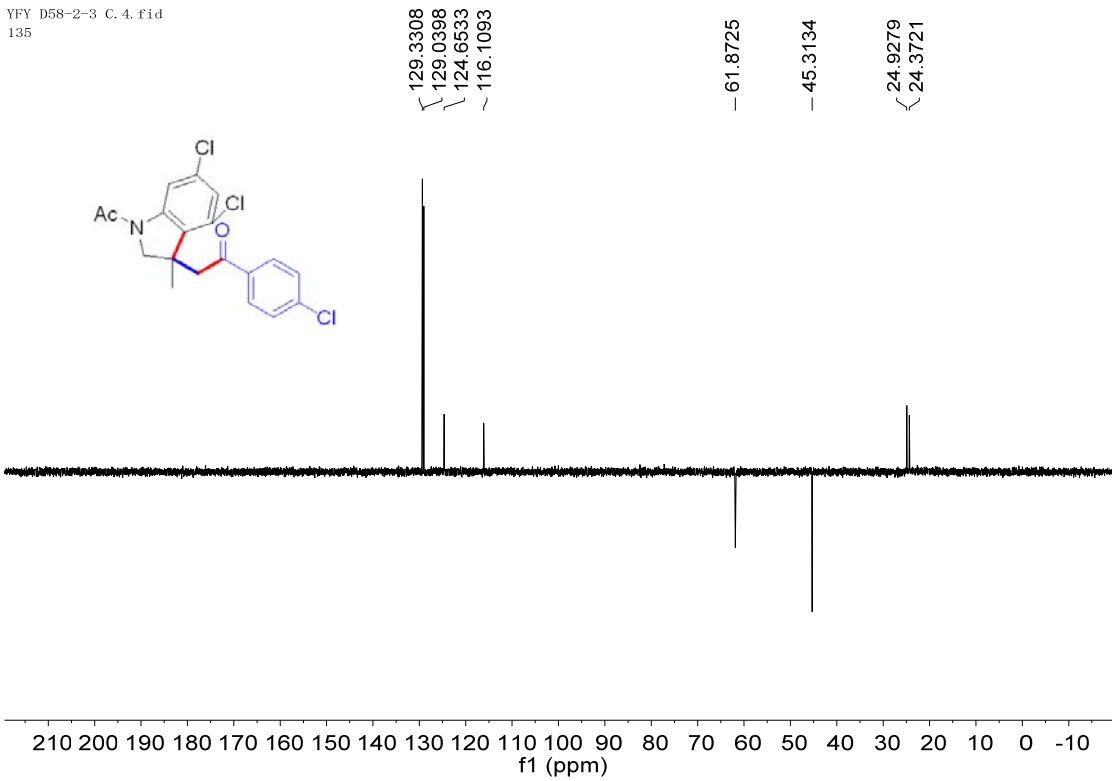
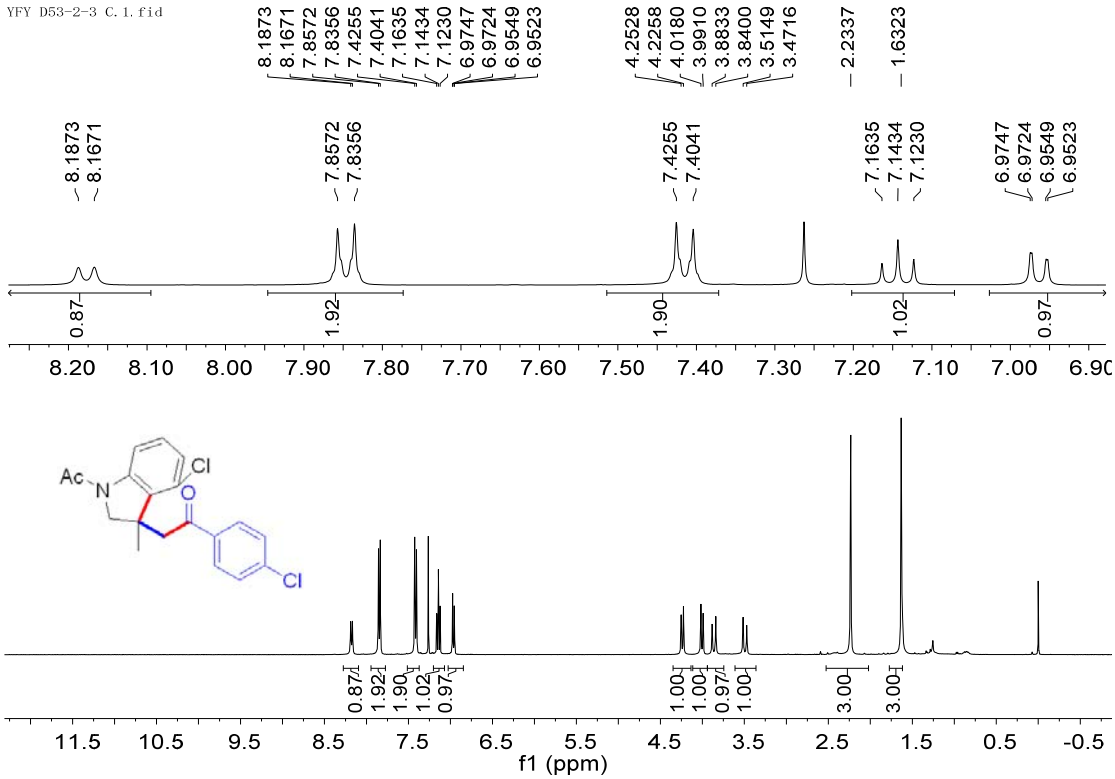


3h, ^{1}H NMR



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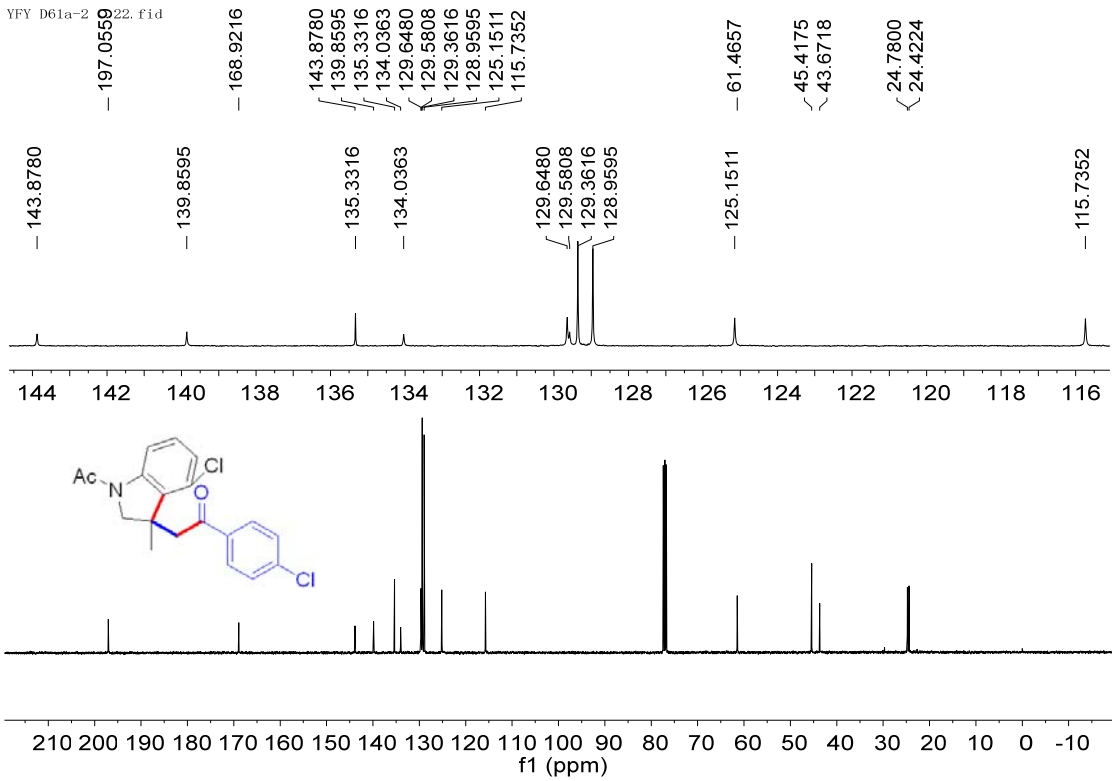

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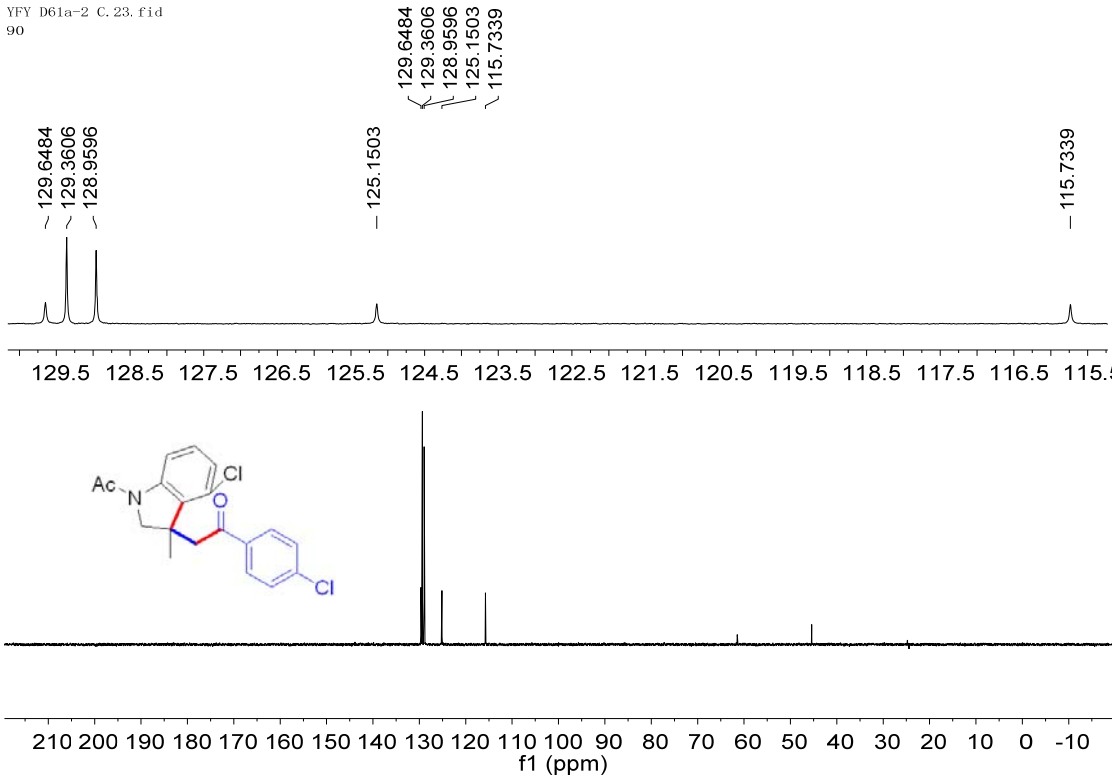

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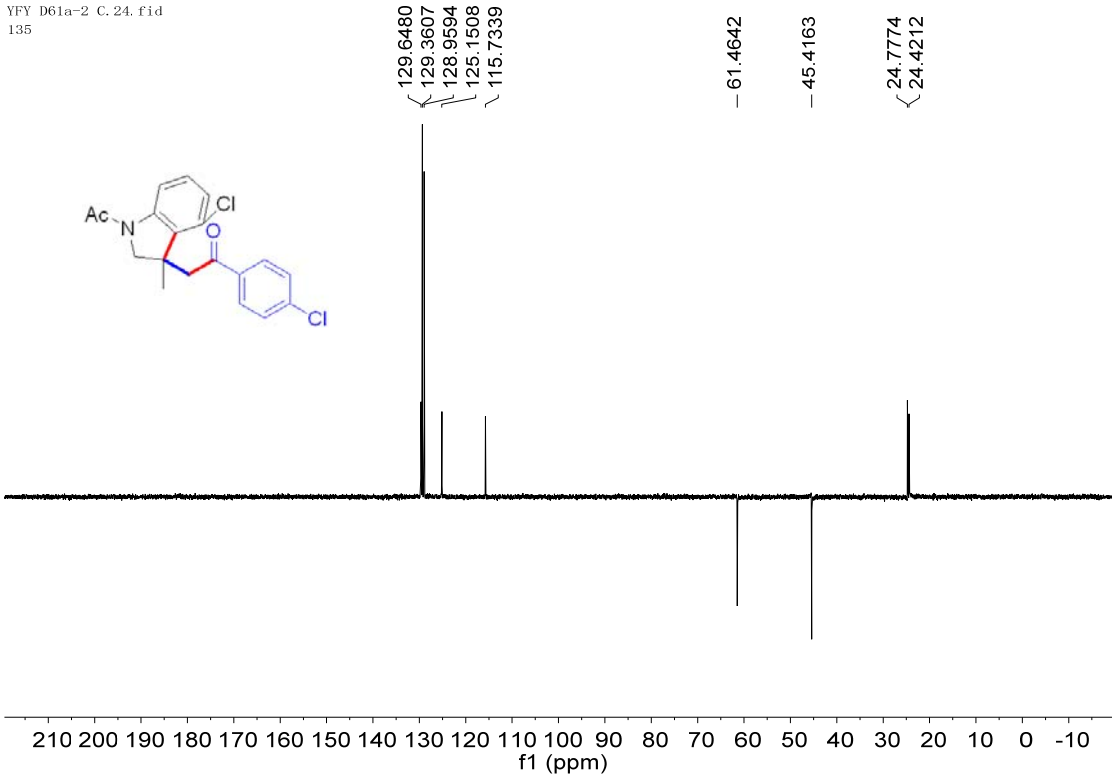
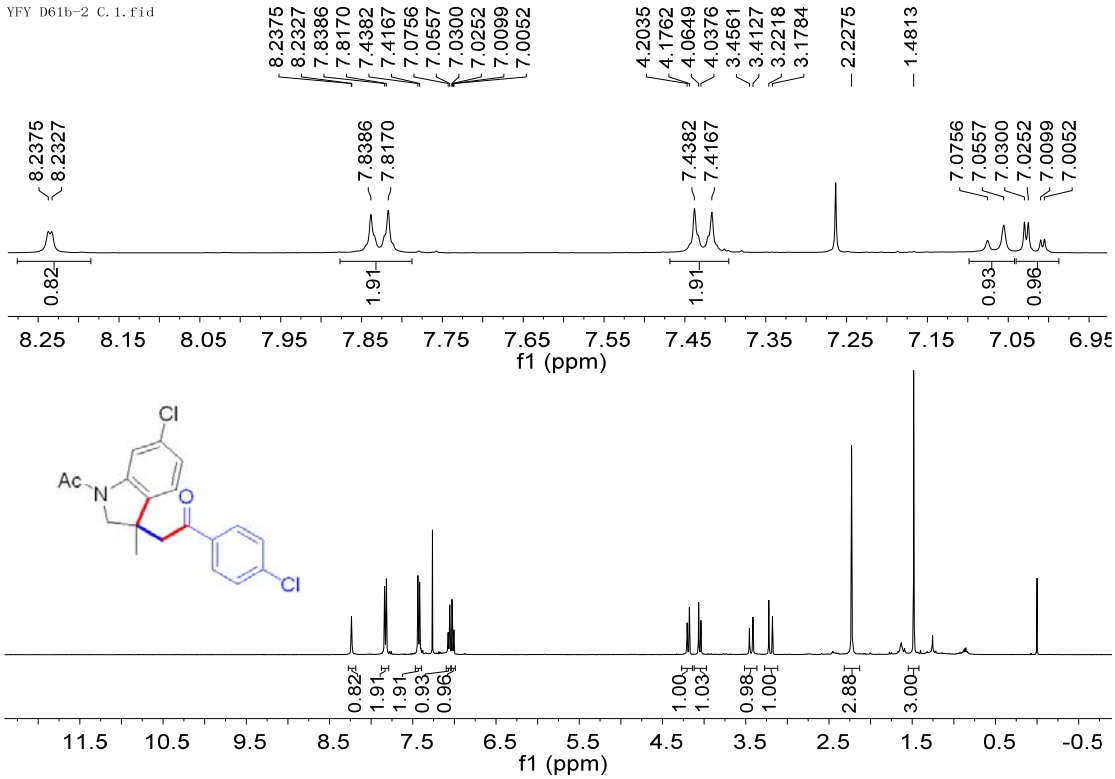


3h', ^{1}H NMR



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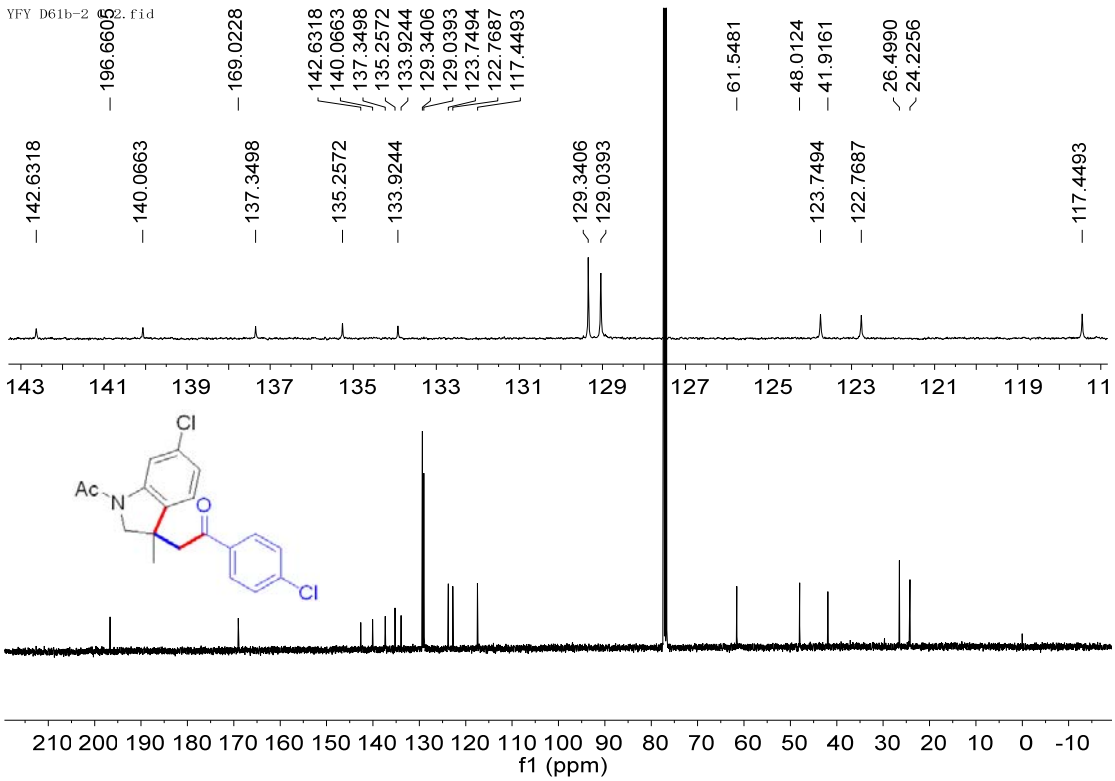

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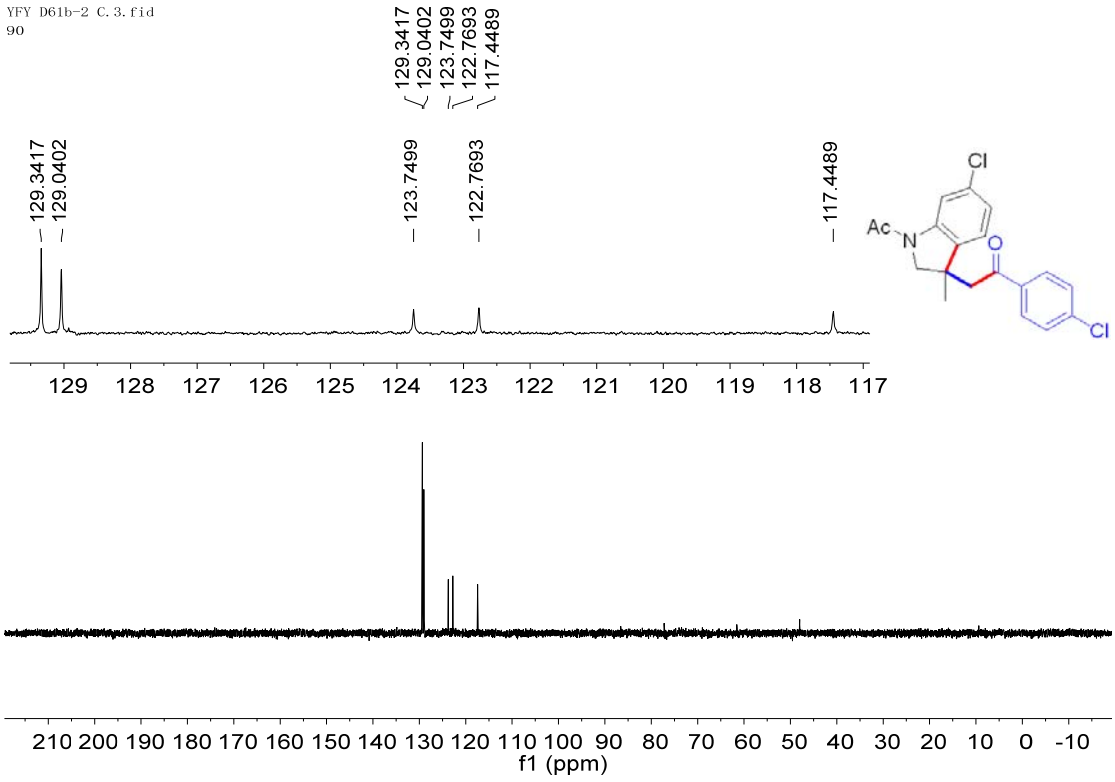

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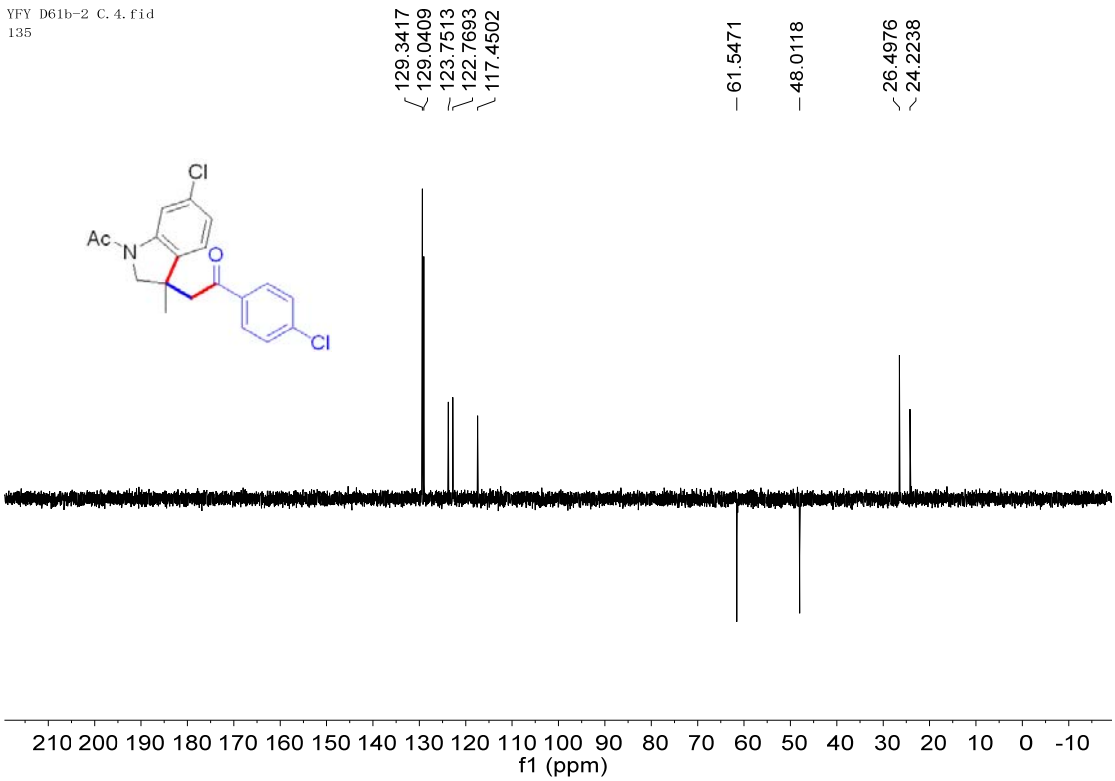
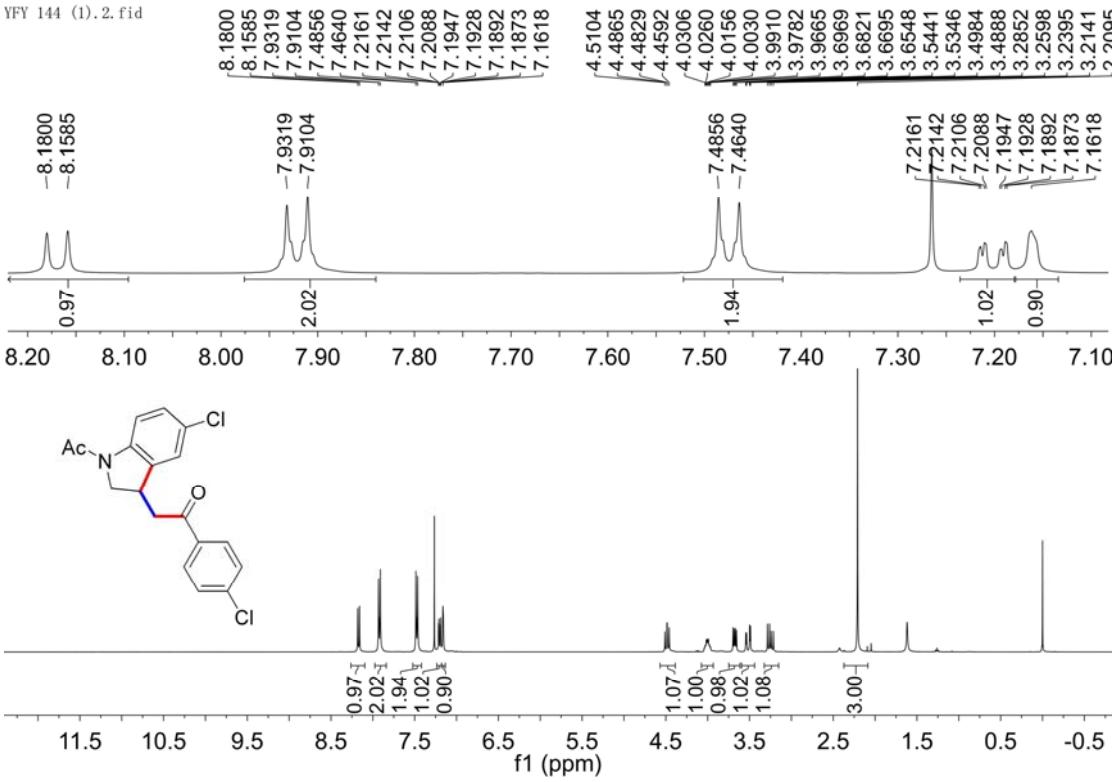


3i1 ^{1}H NMR



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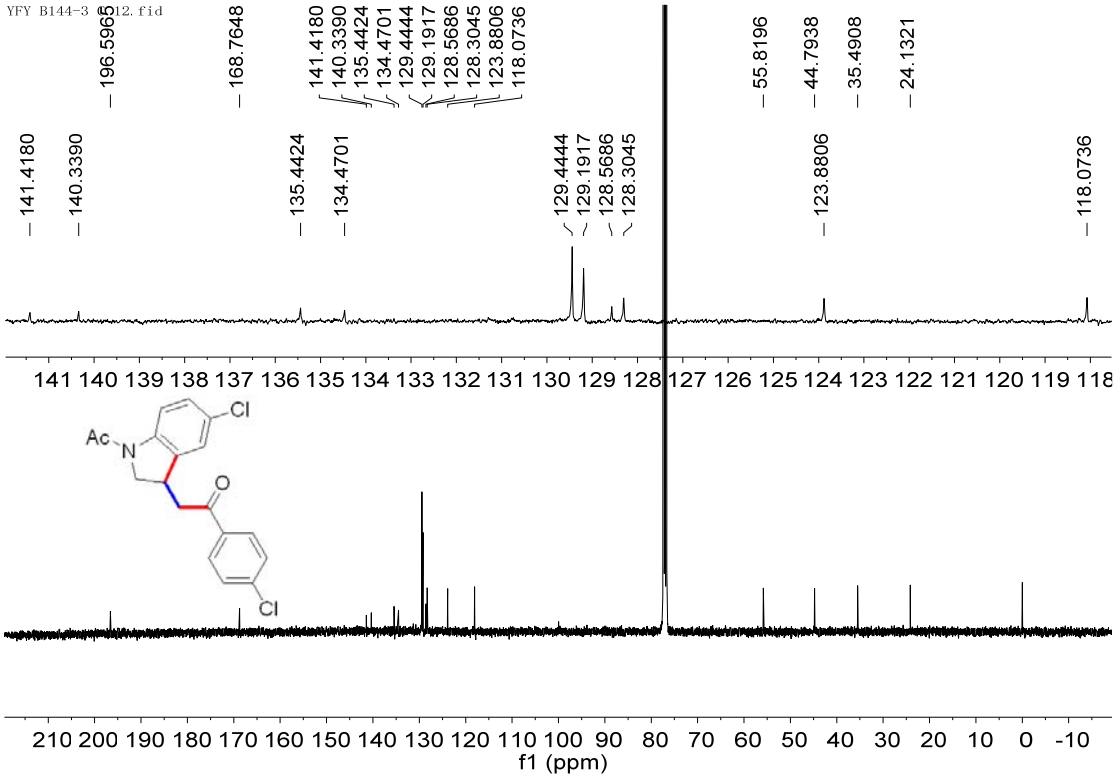

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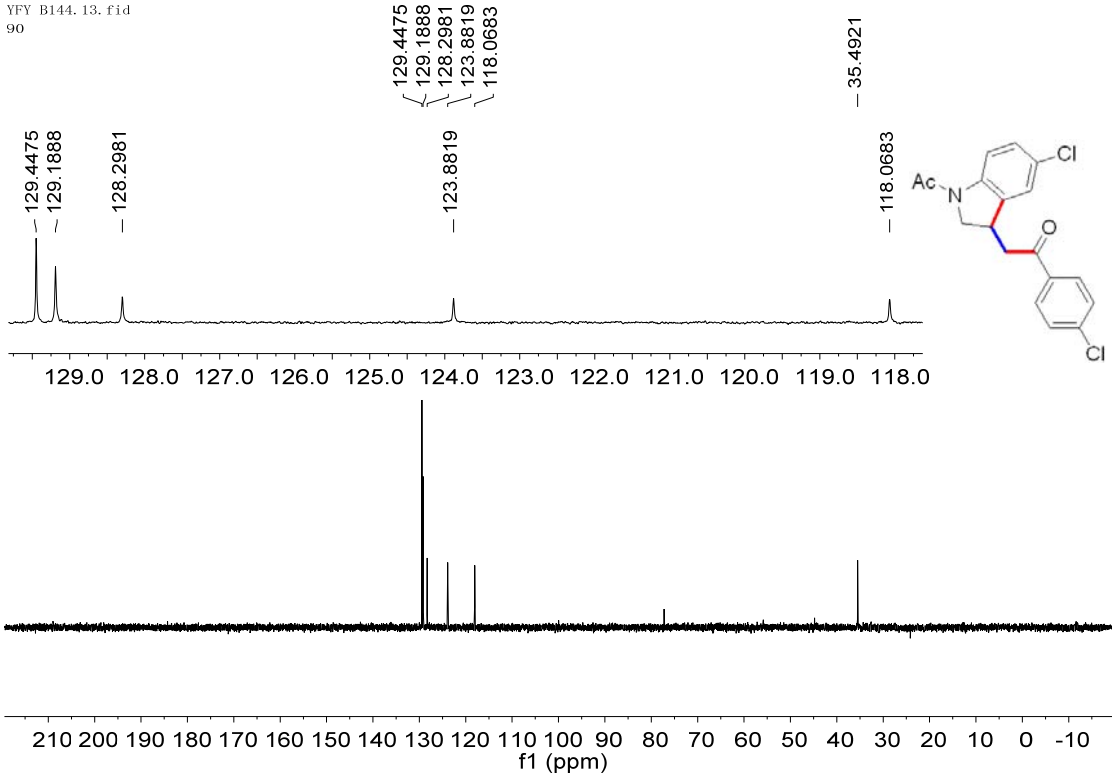

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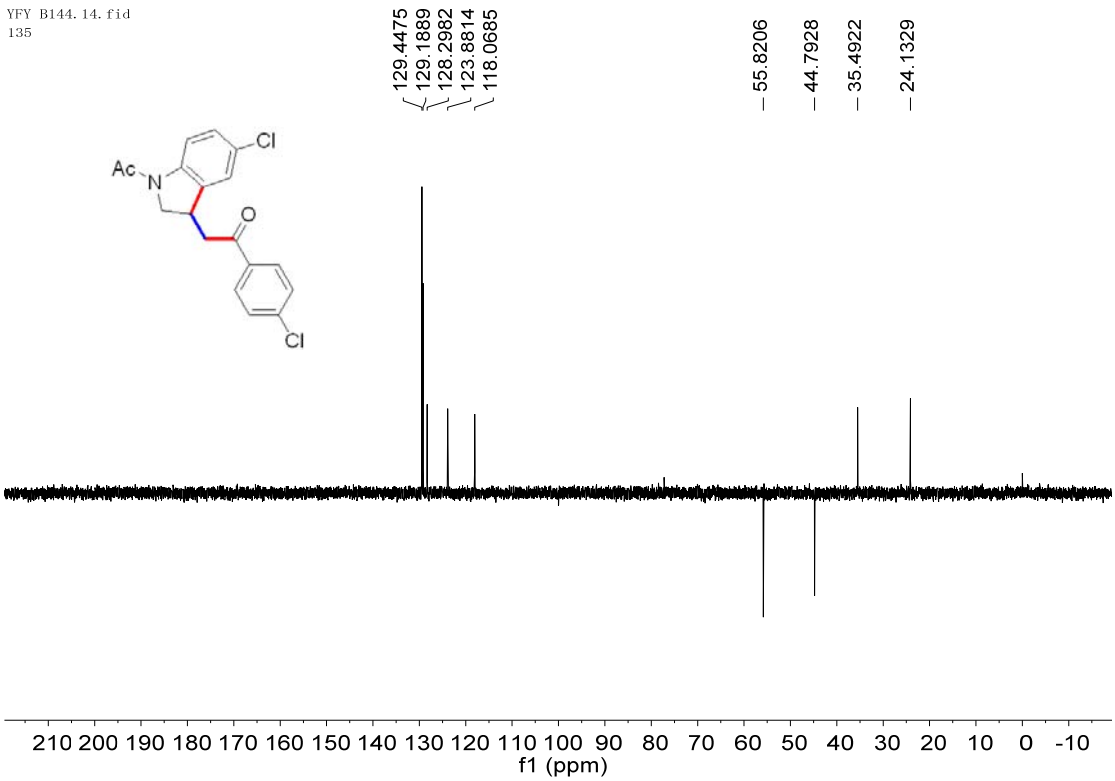
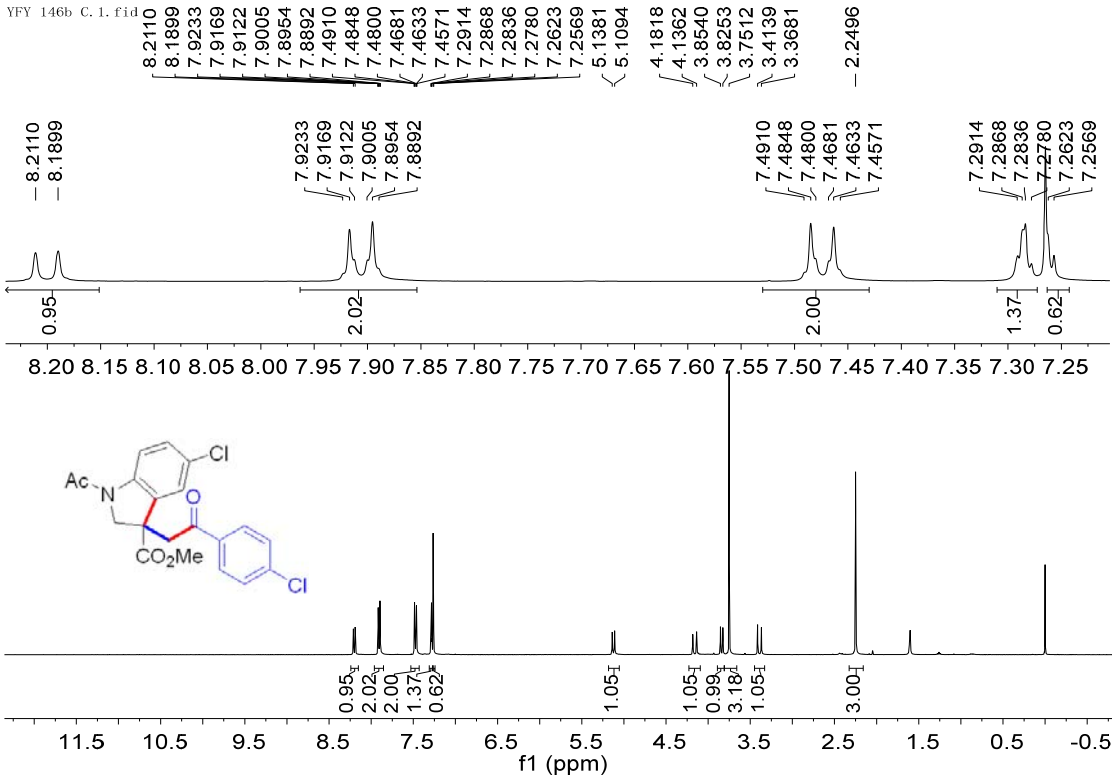


3i2, ^{1}H NMR



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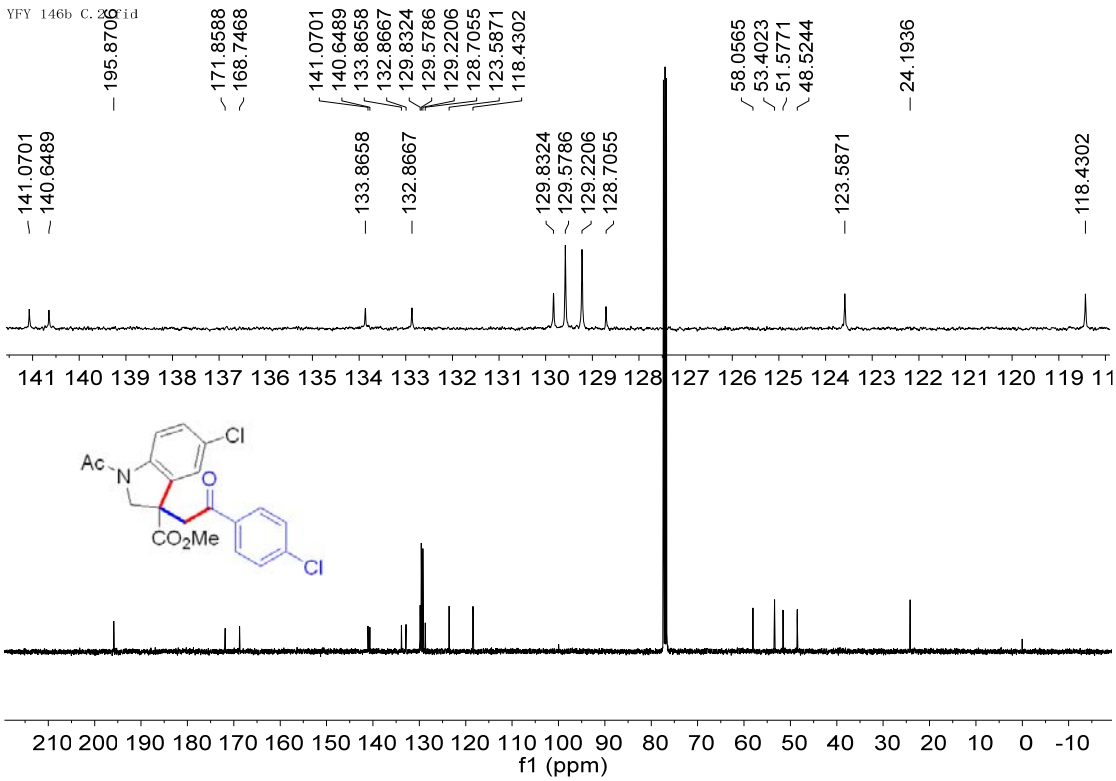

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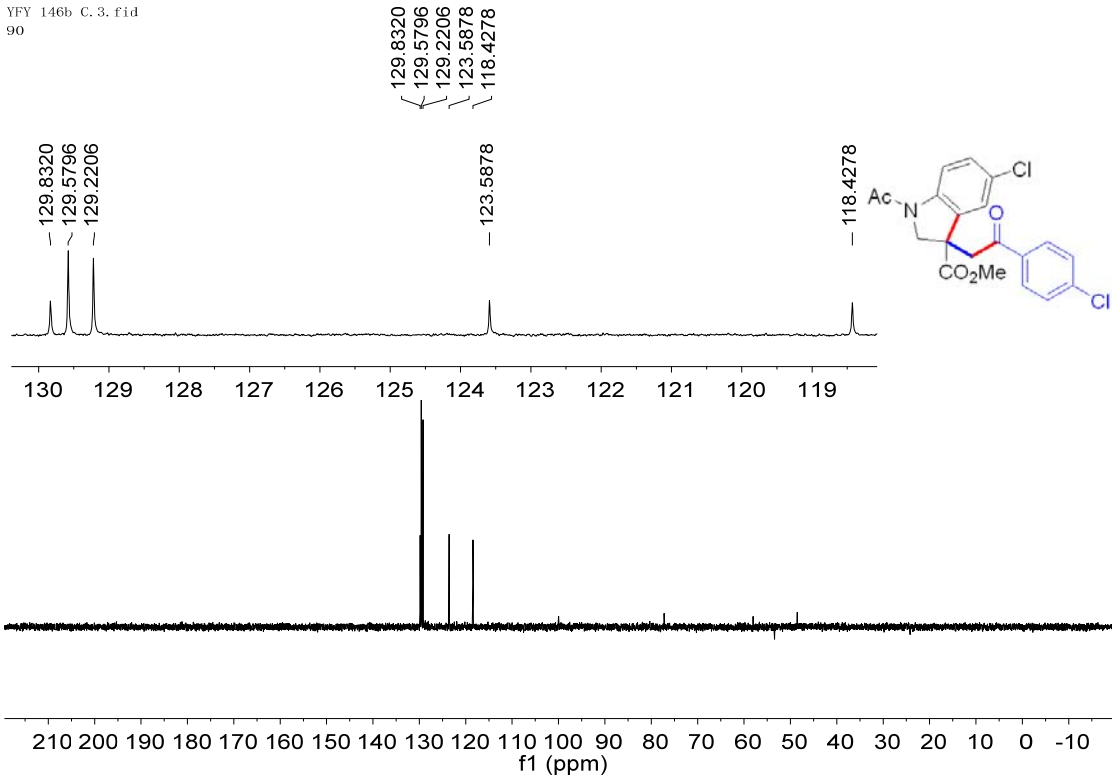

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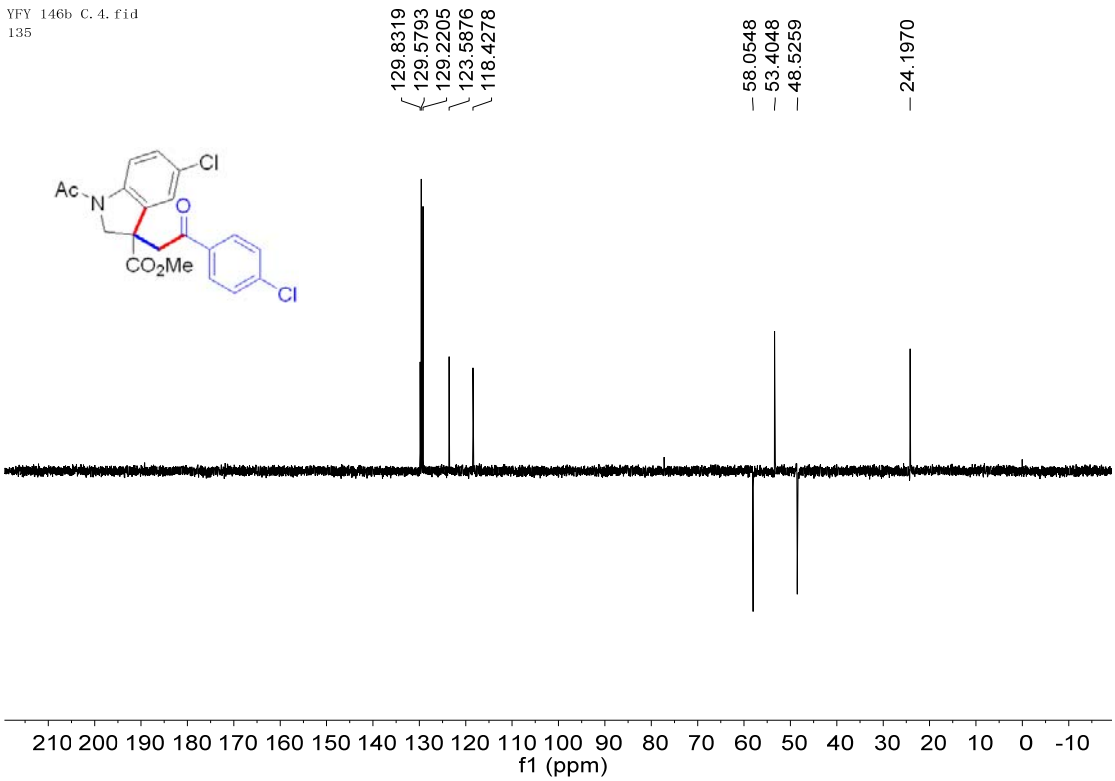
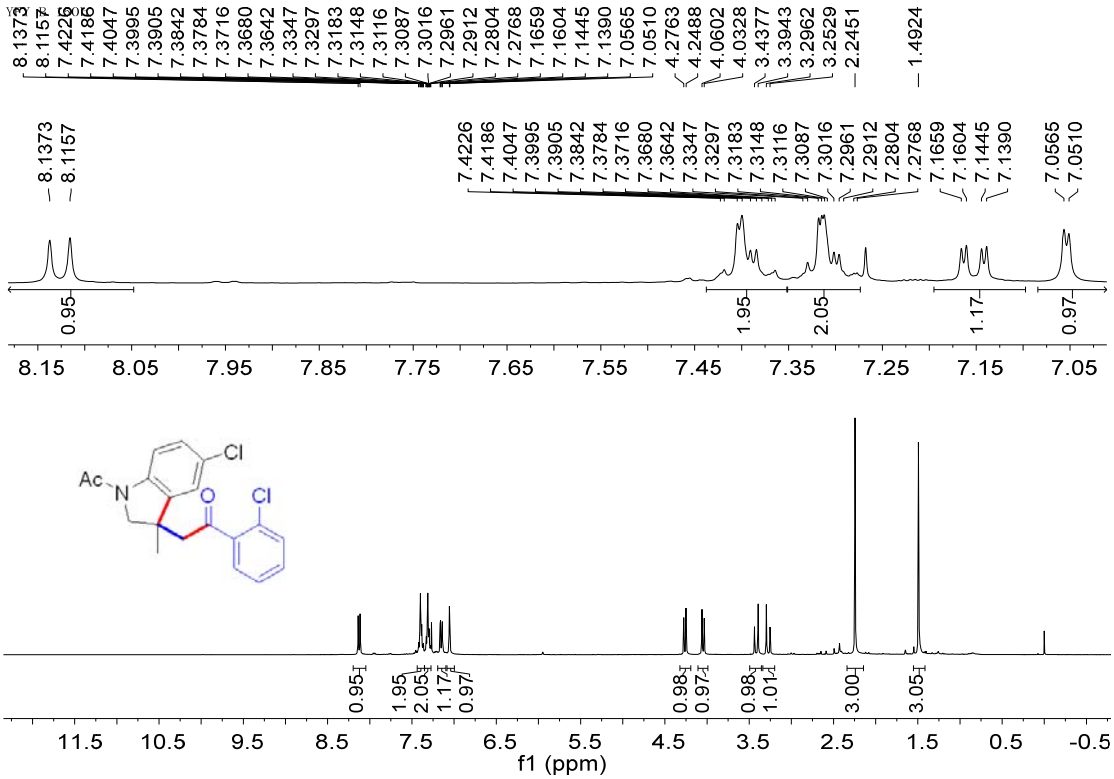


3j, ^{1}H NMR



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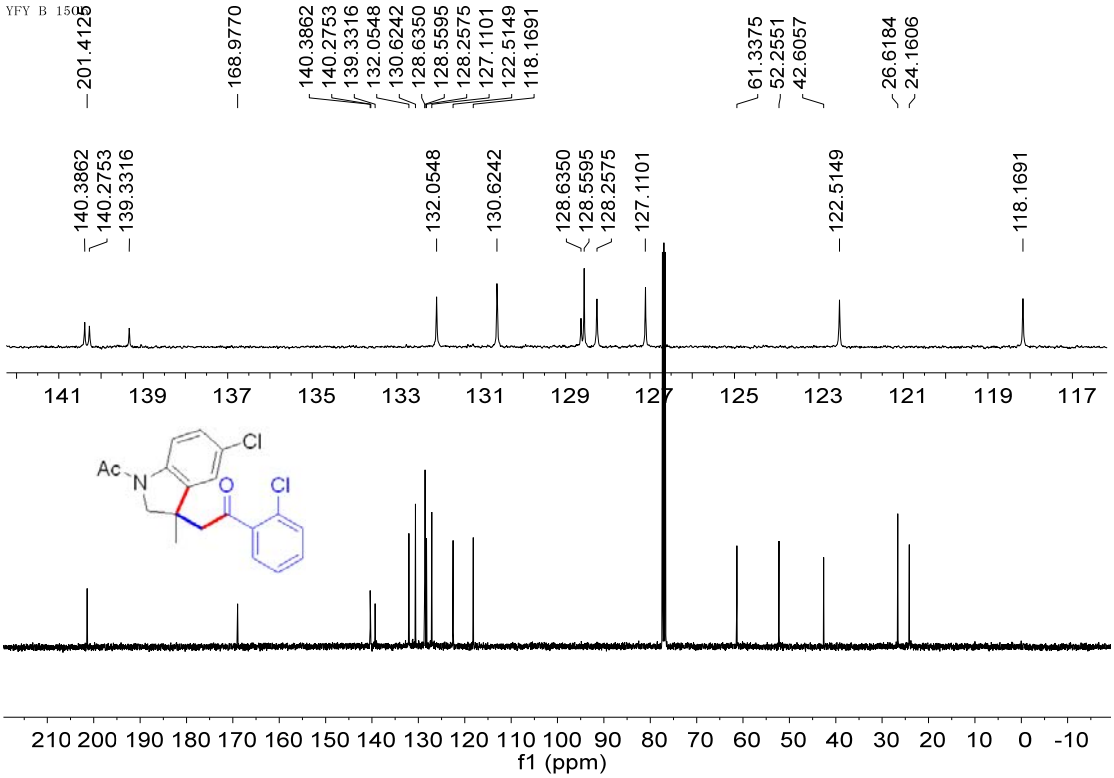

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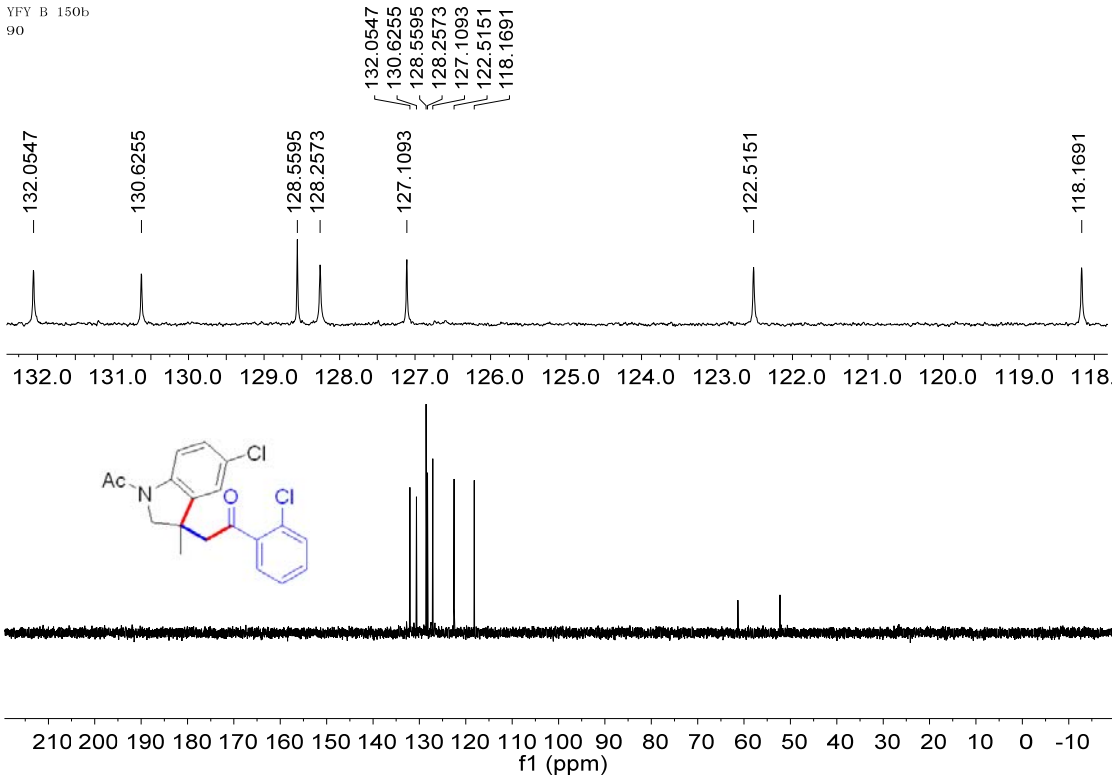

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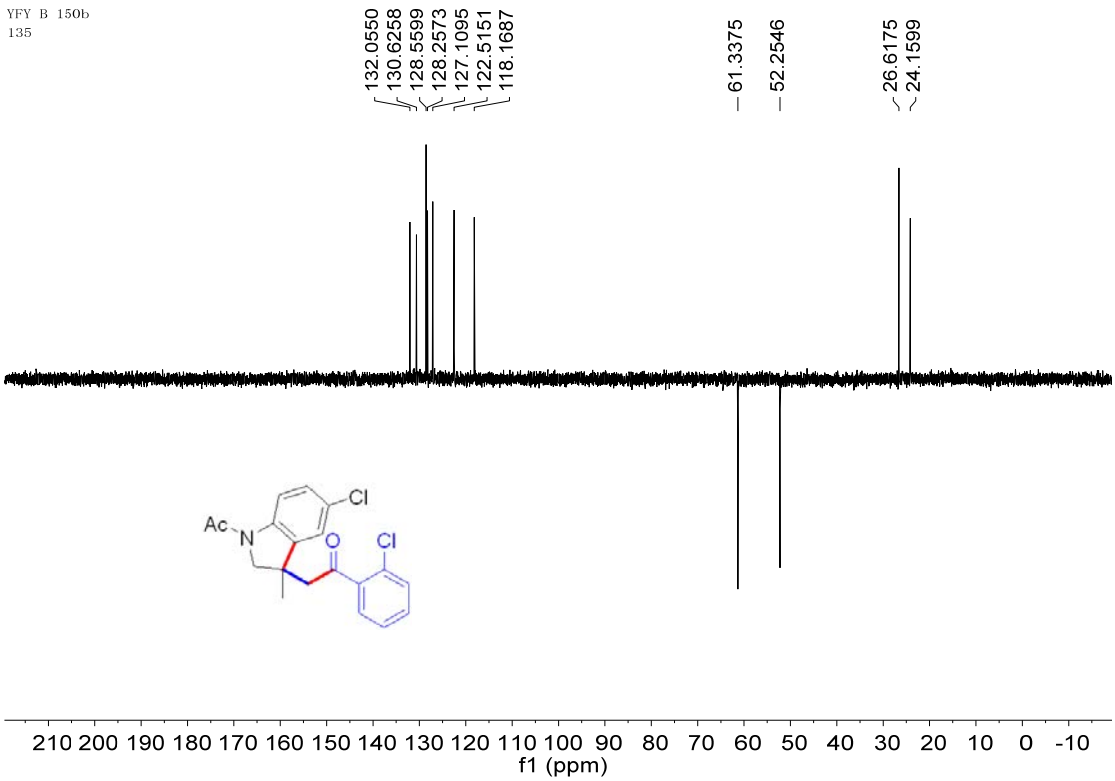
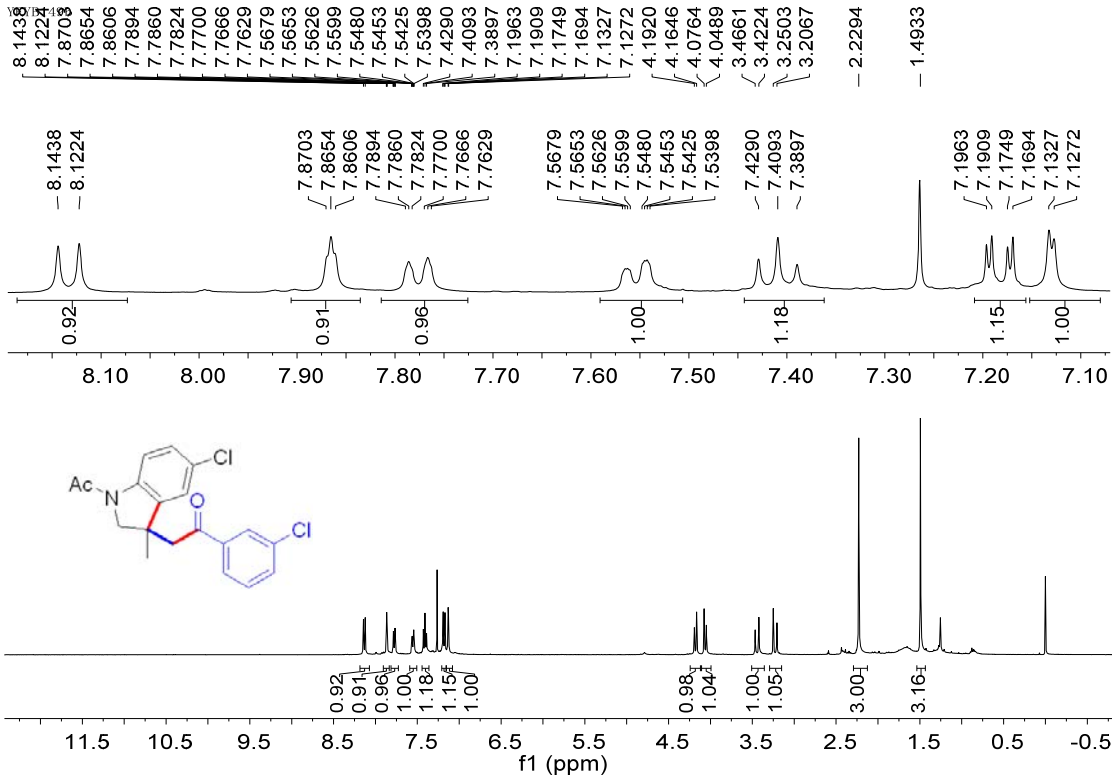
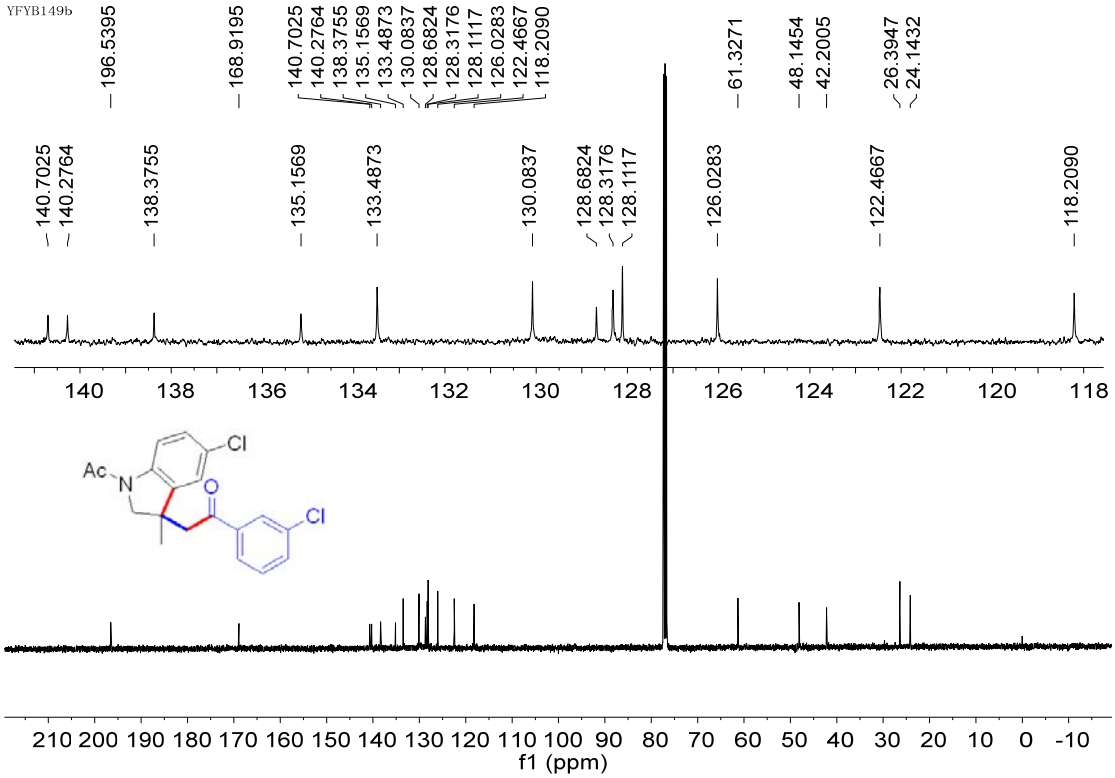


3k, ^{1}H NMR



^{13}C NMR



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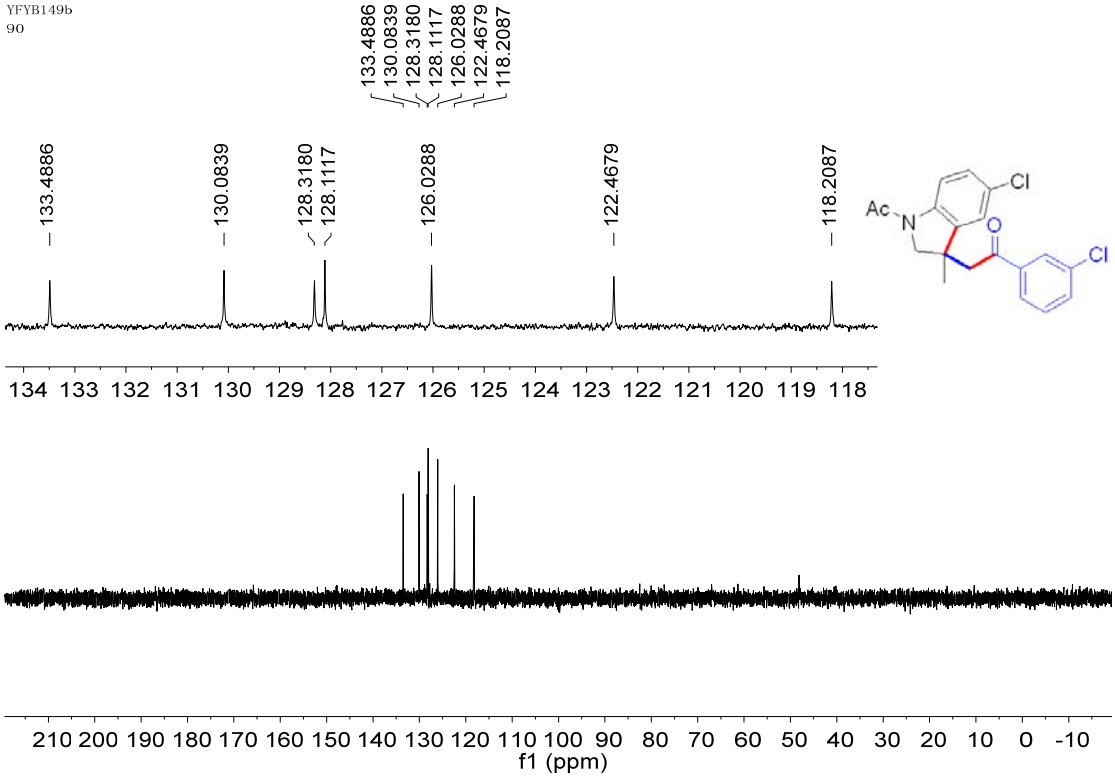

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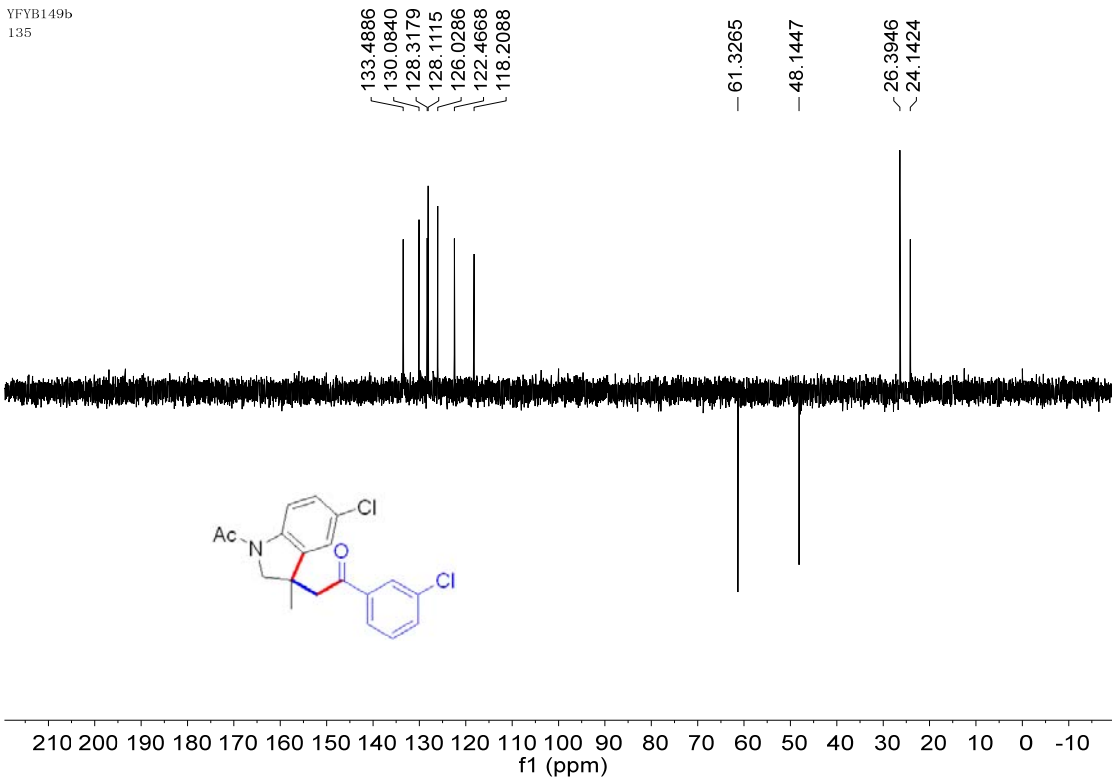
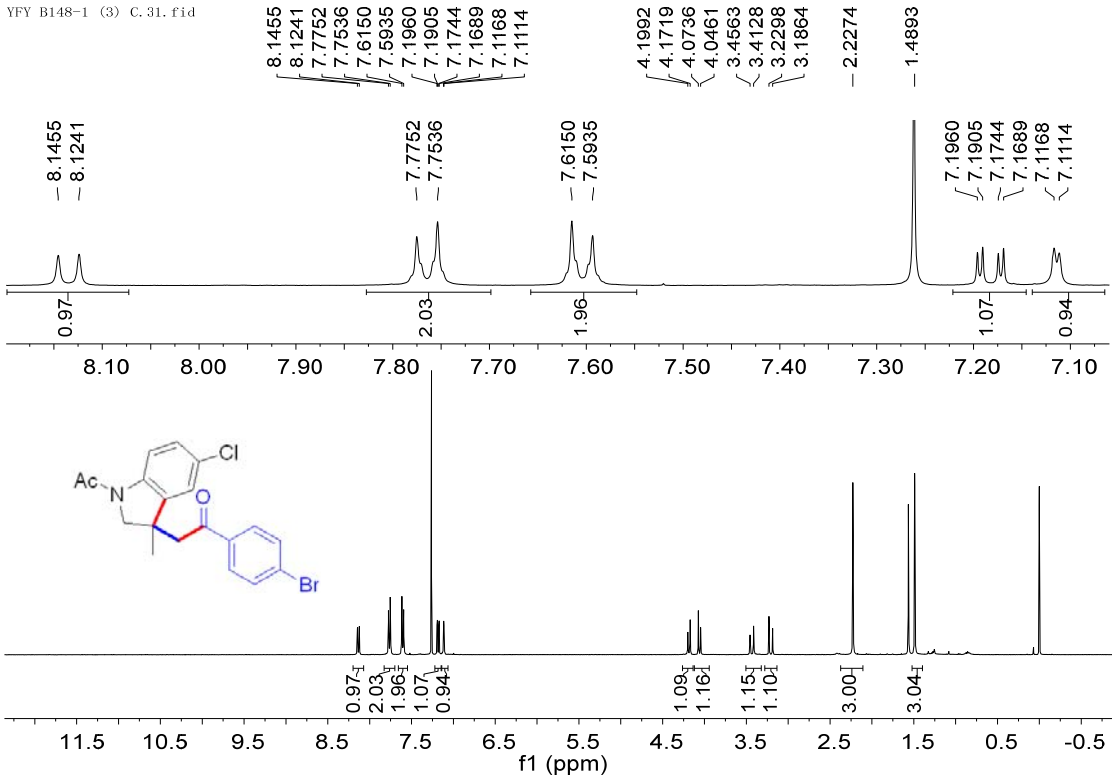
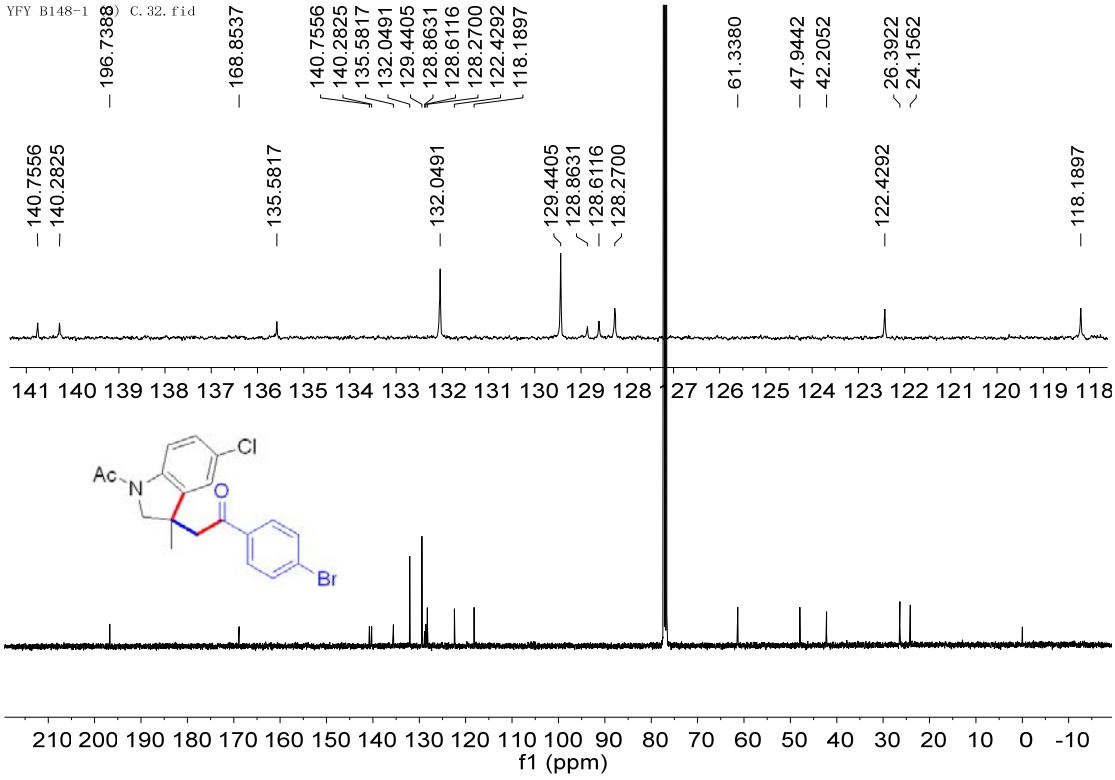


3ll, ^{1}H NMR



^{13}C NMR



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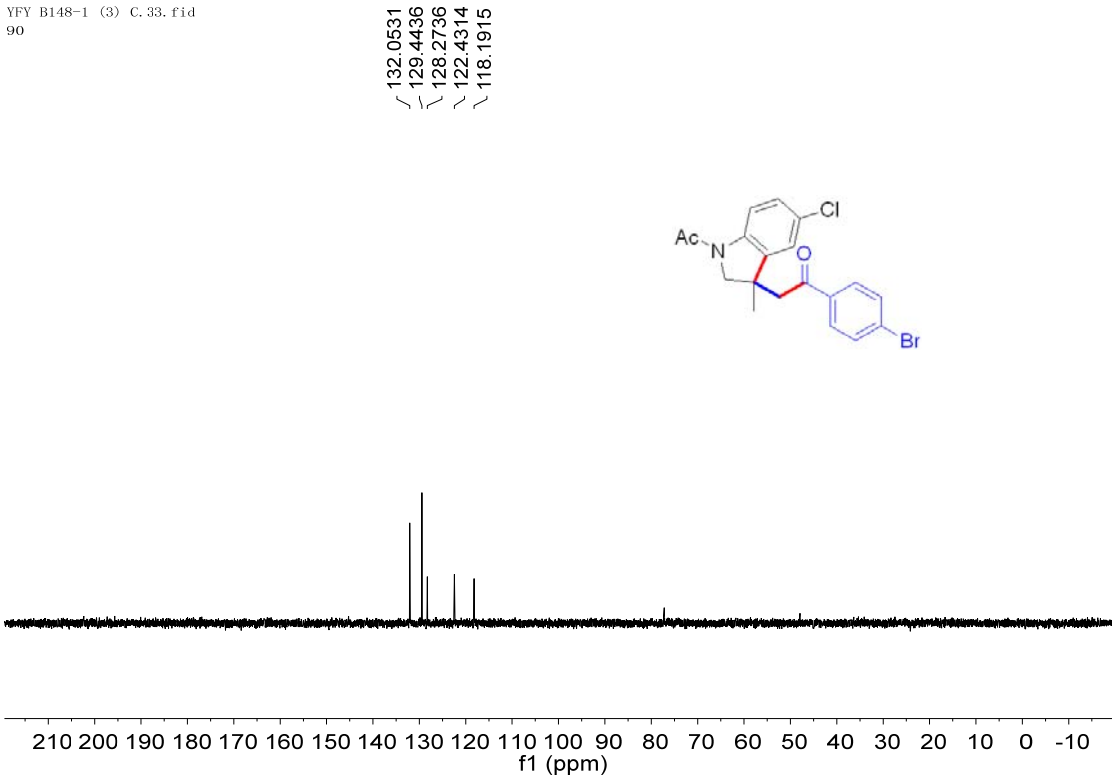

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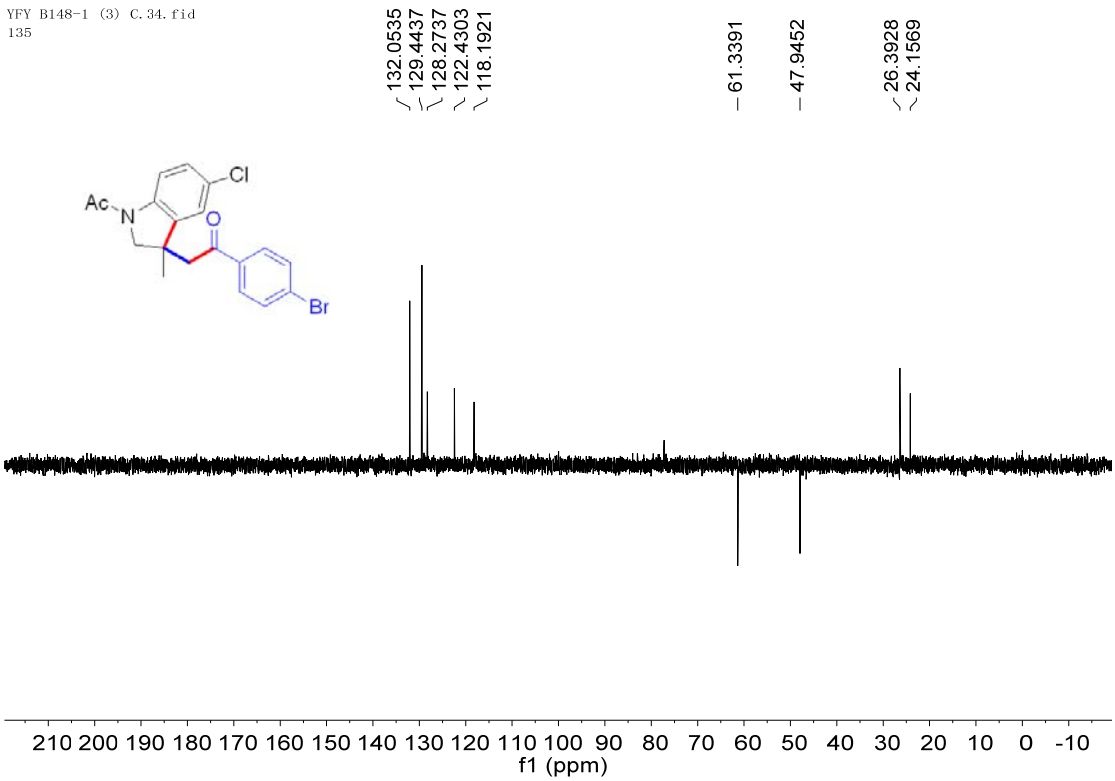

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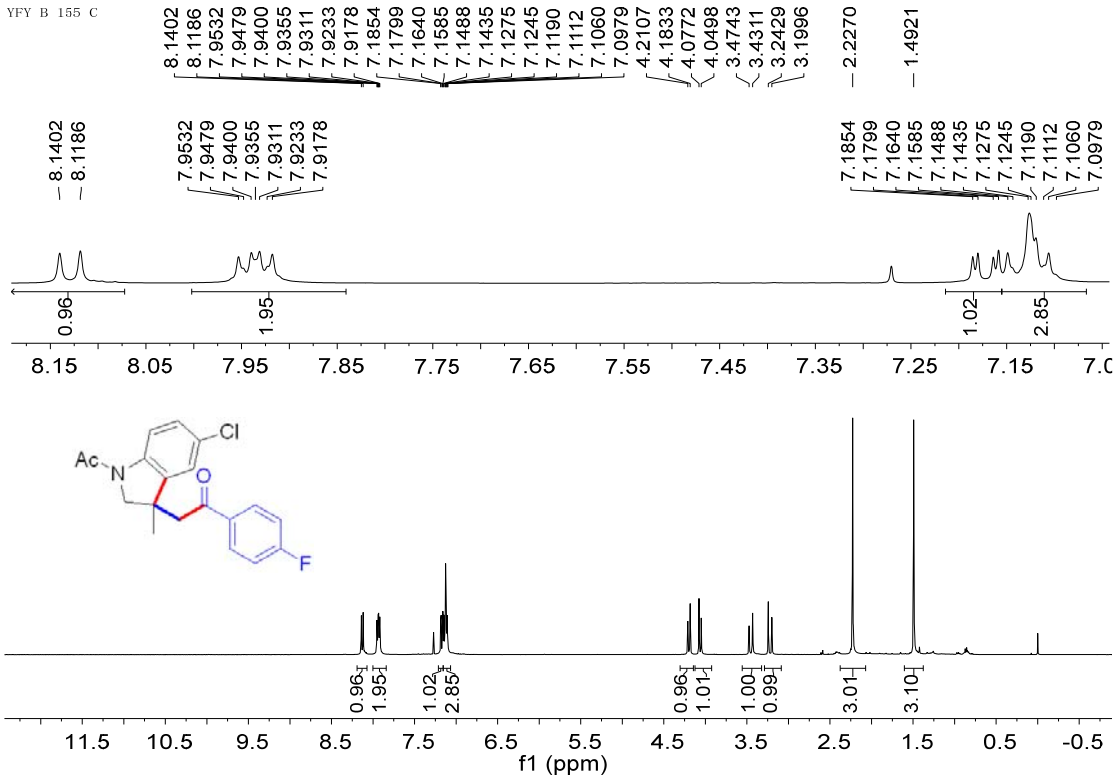
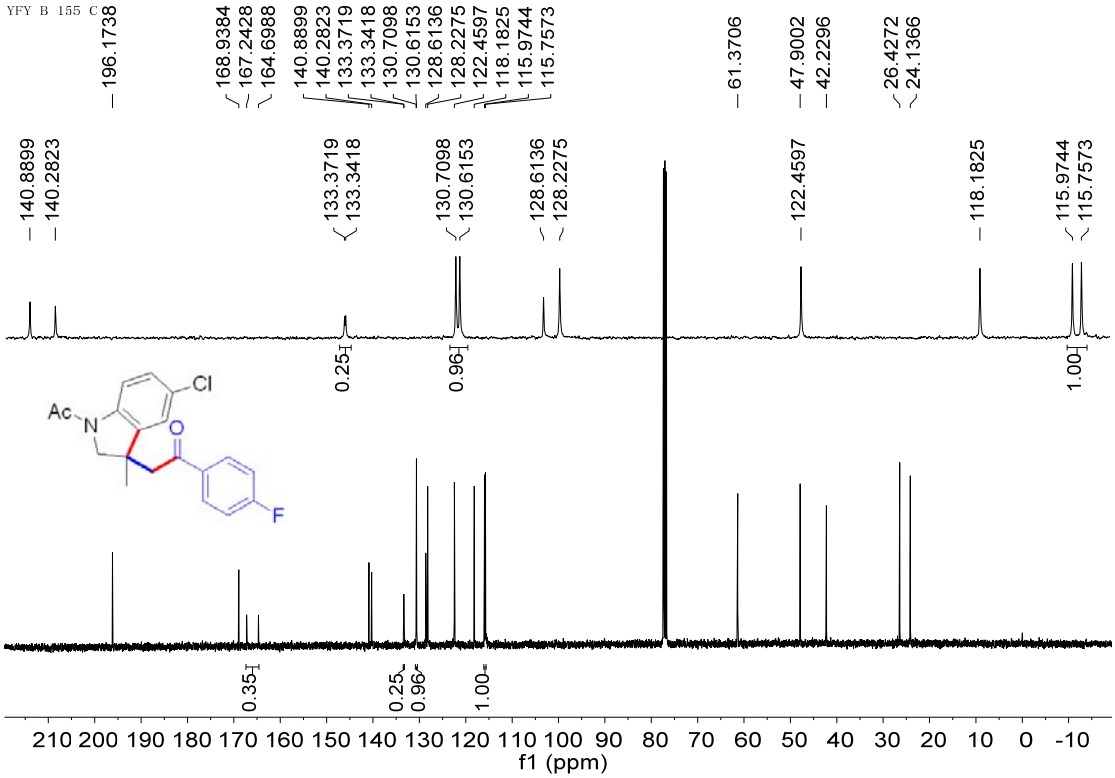


^{13}C NMR



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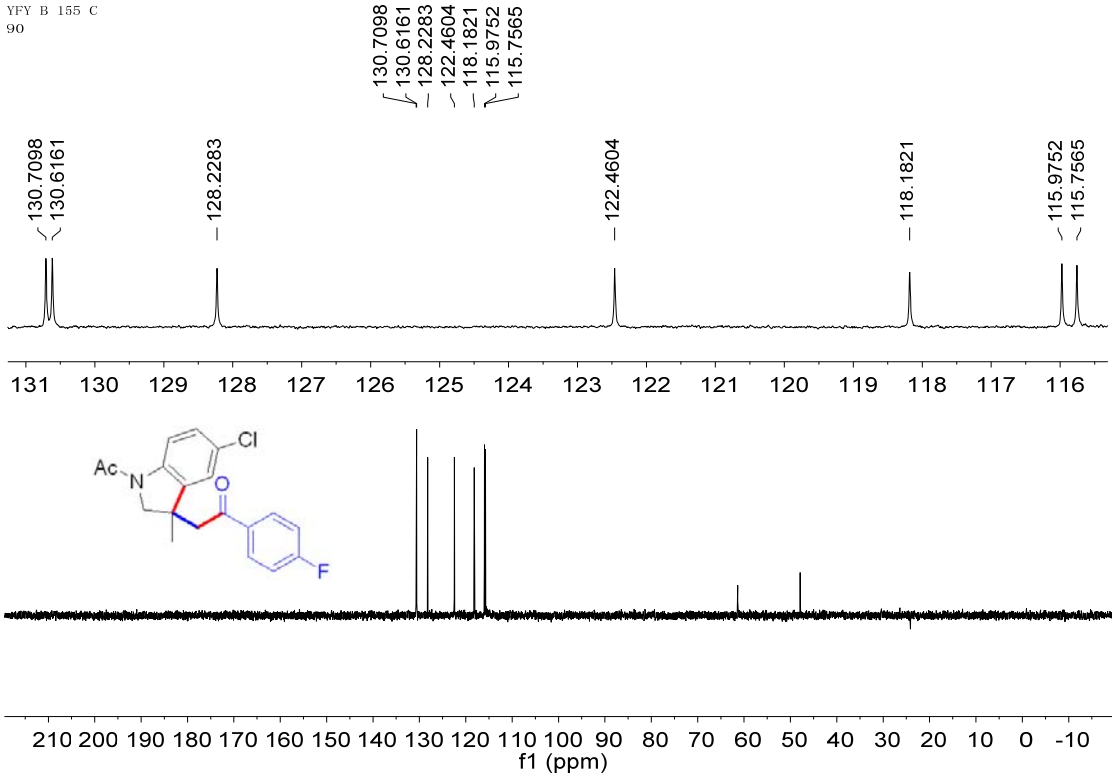

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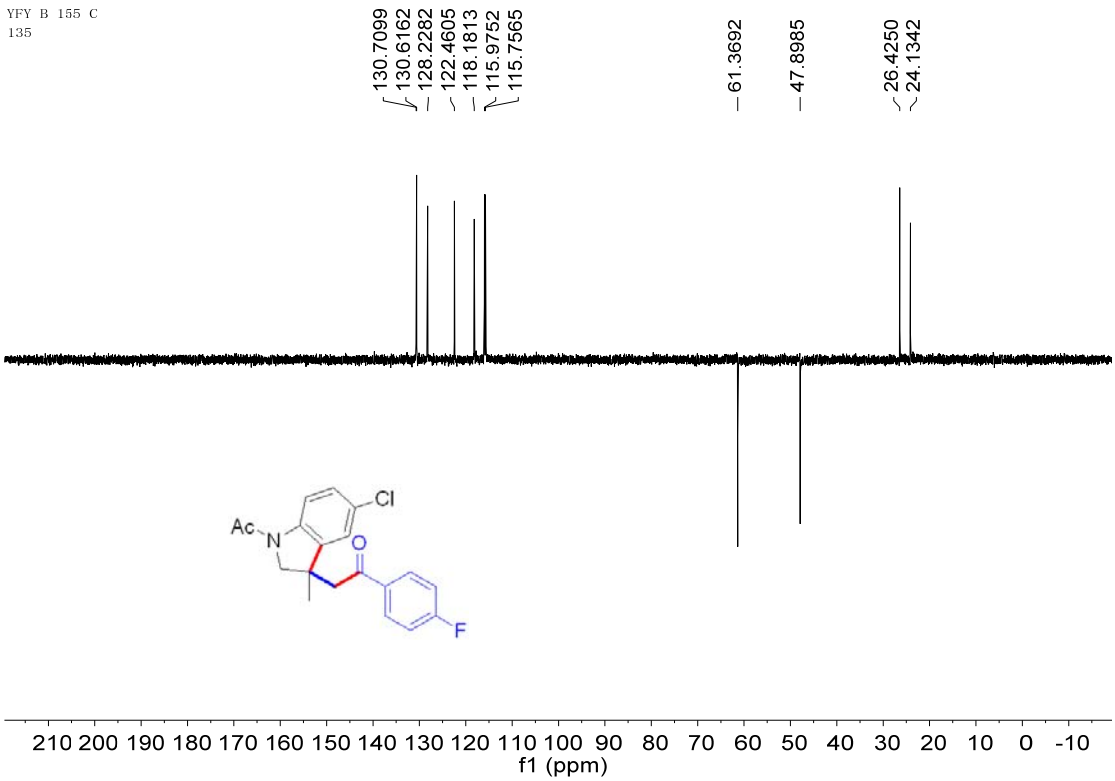
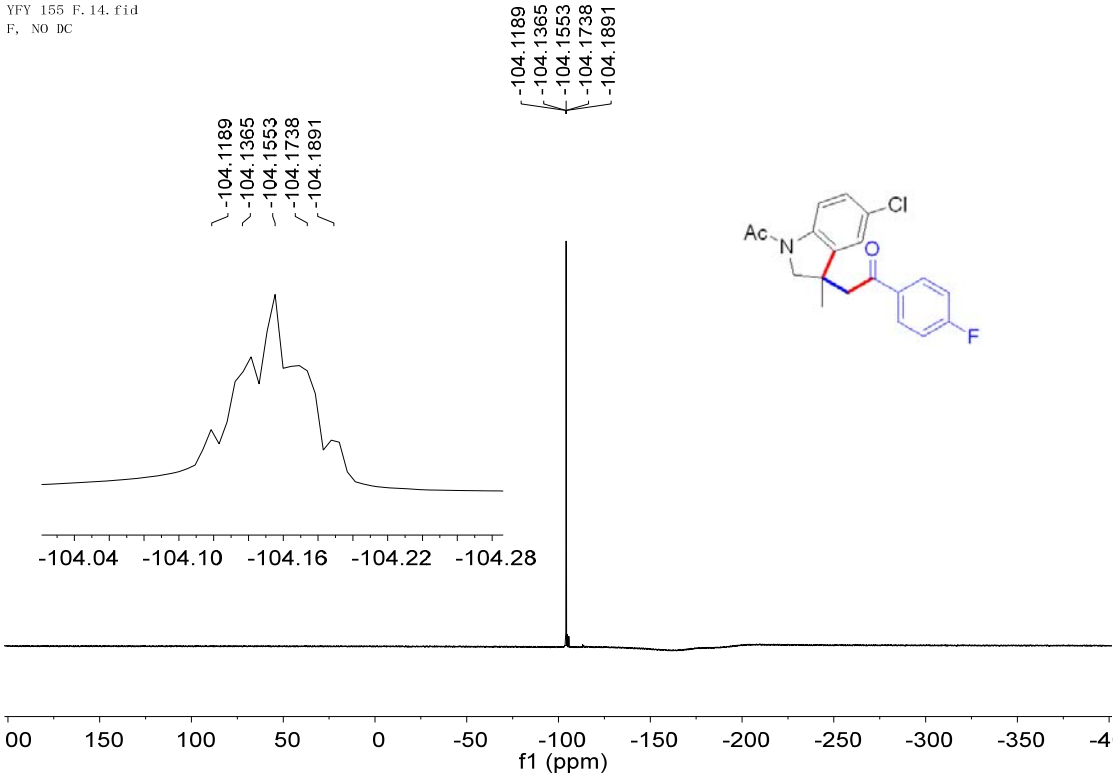
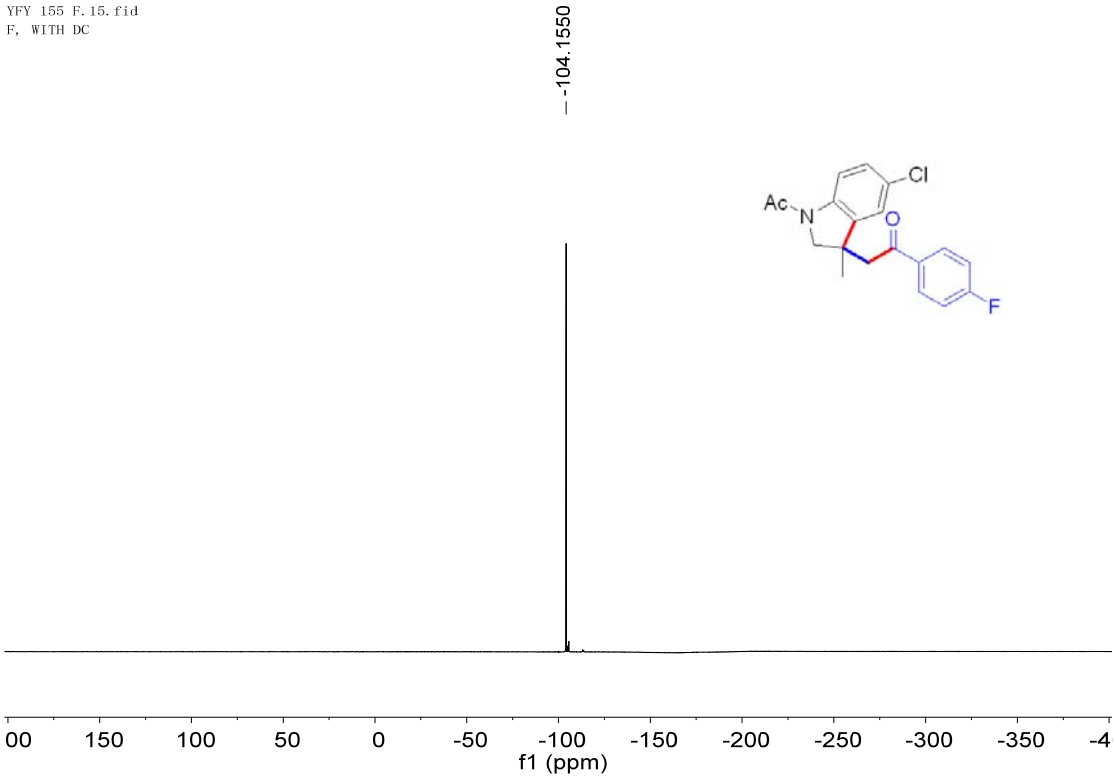


^{19}F NMR, no decoupling



^{19}F NMR, with pulse decoupling



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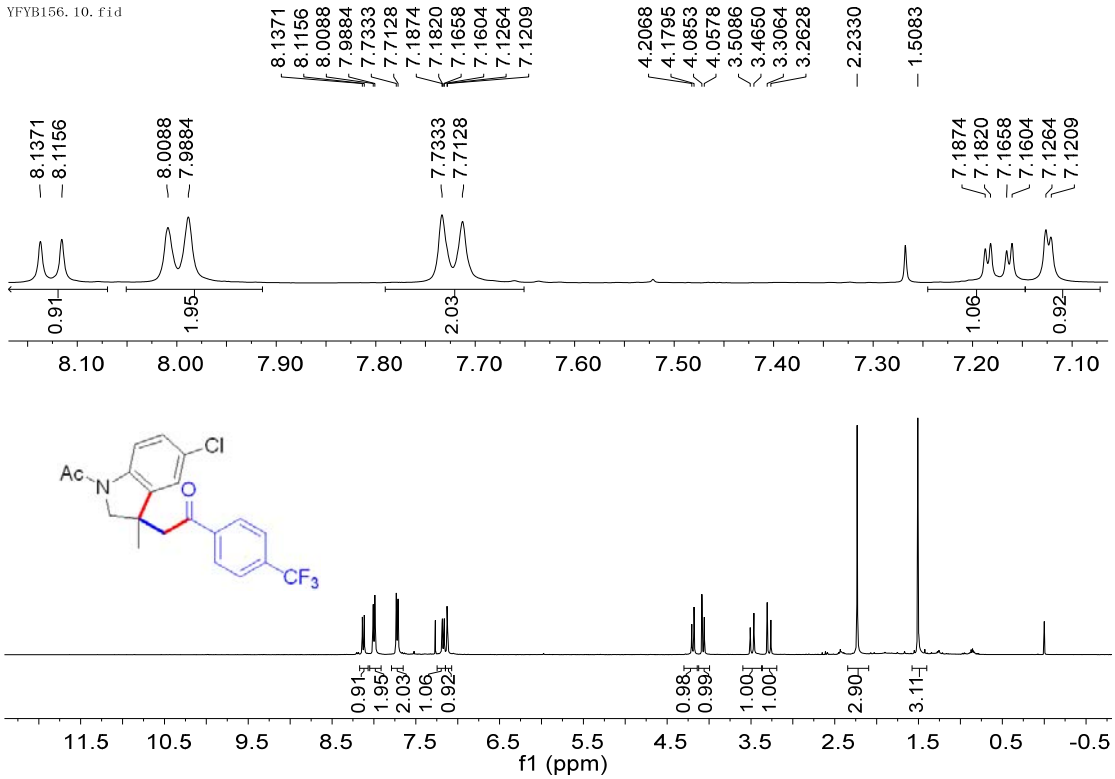
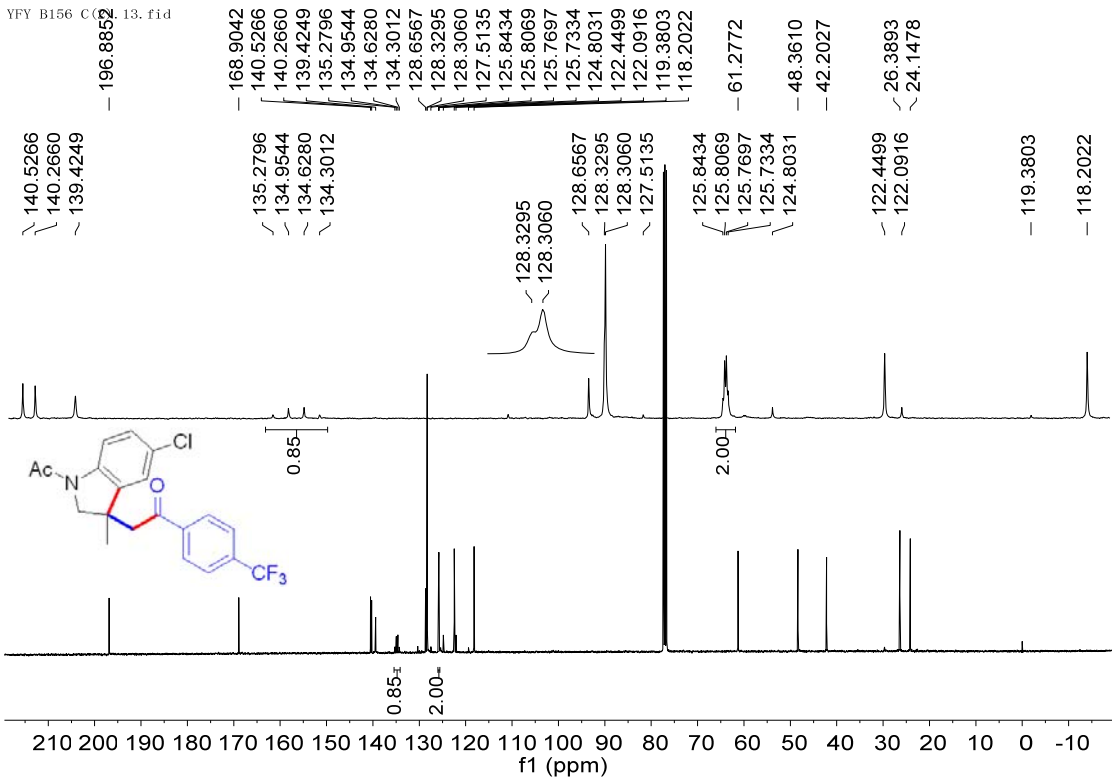


^{13}C NMR



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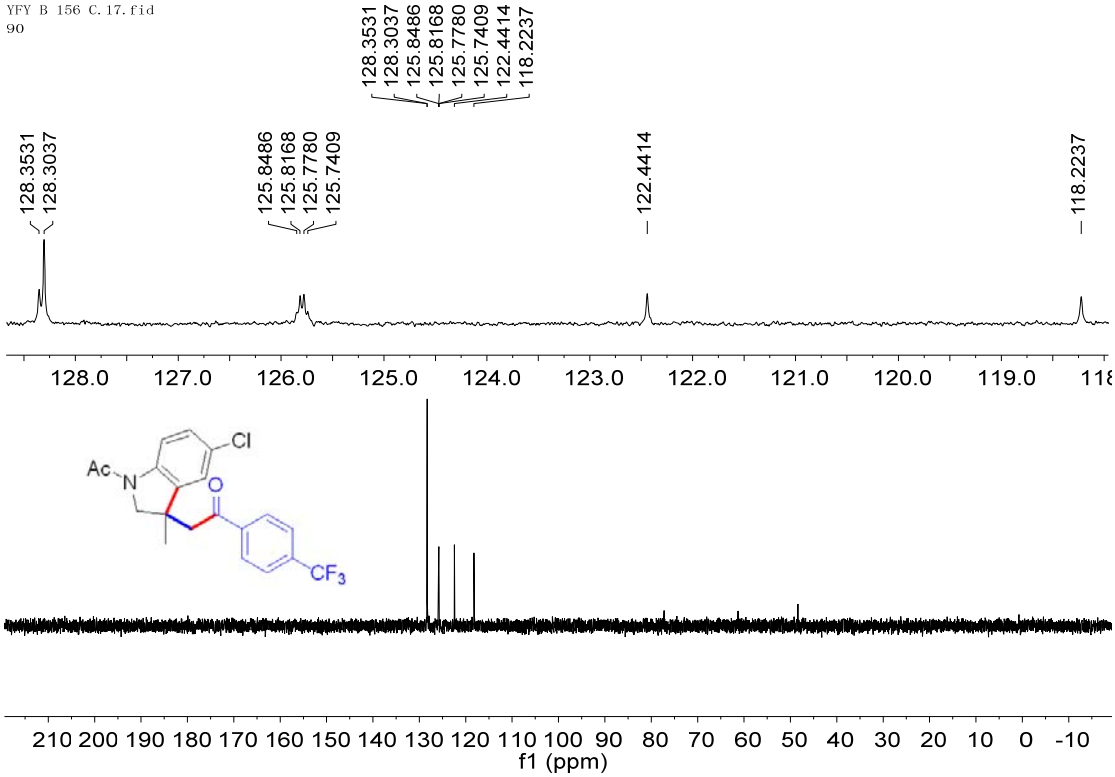

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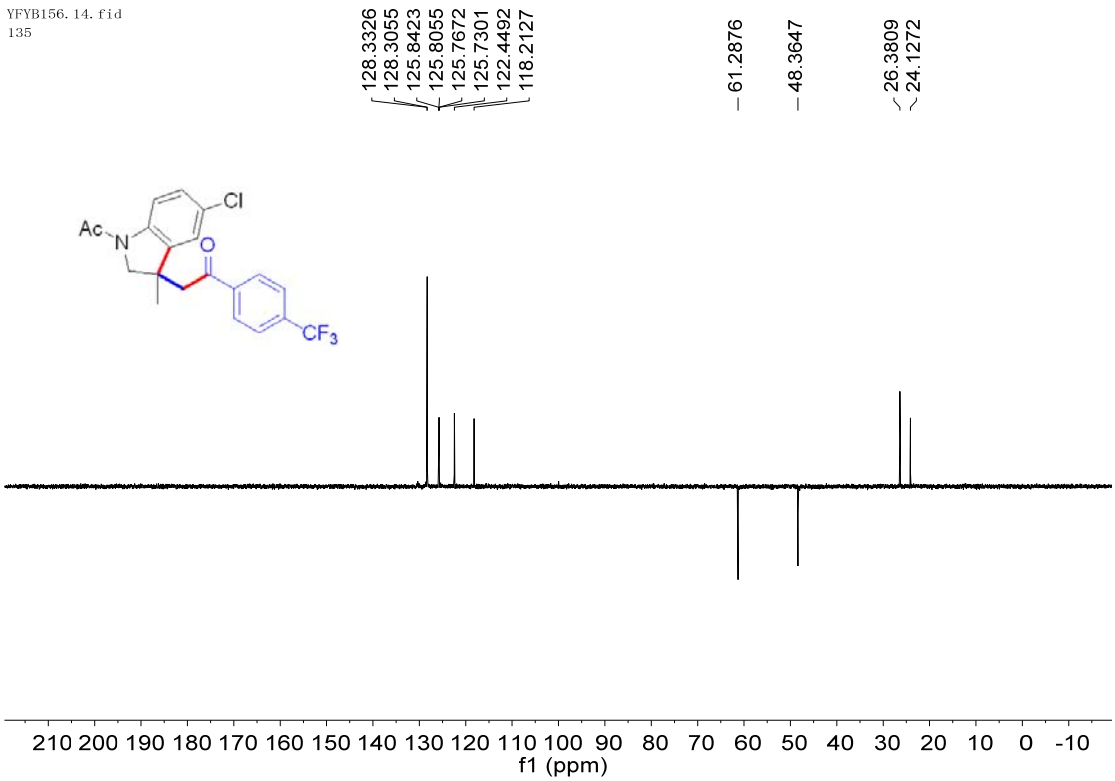
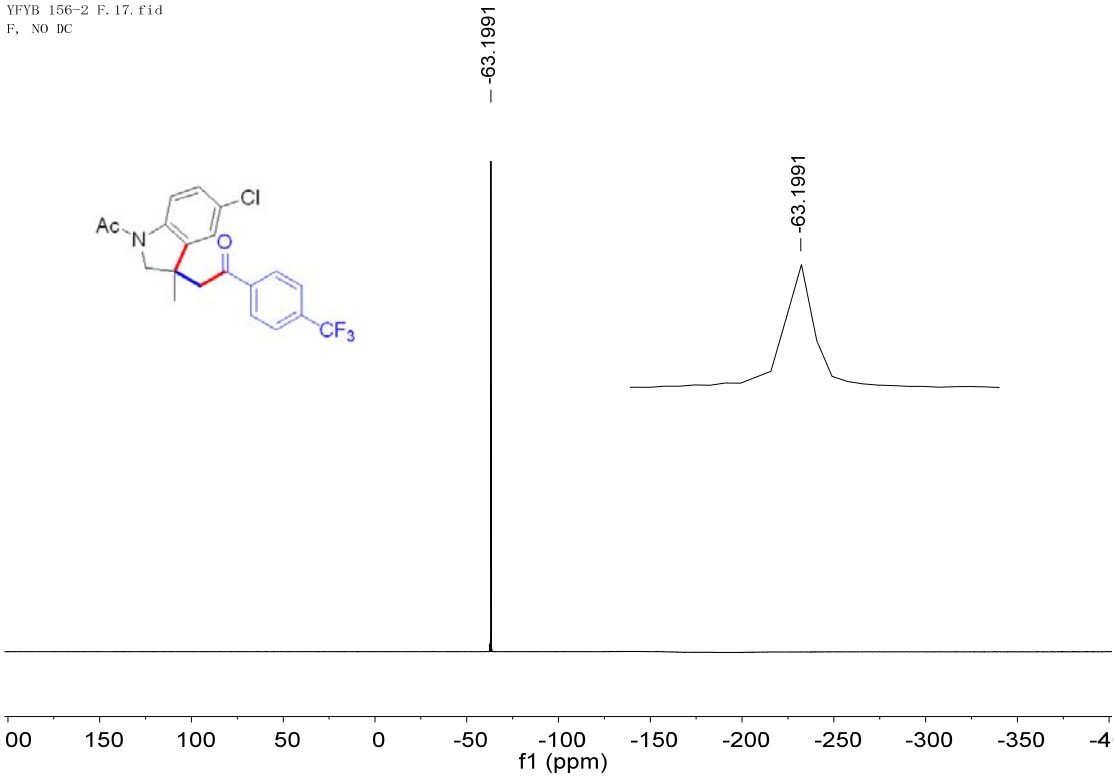
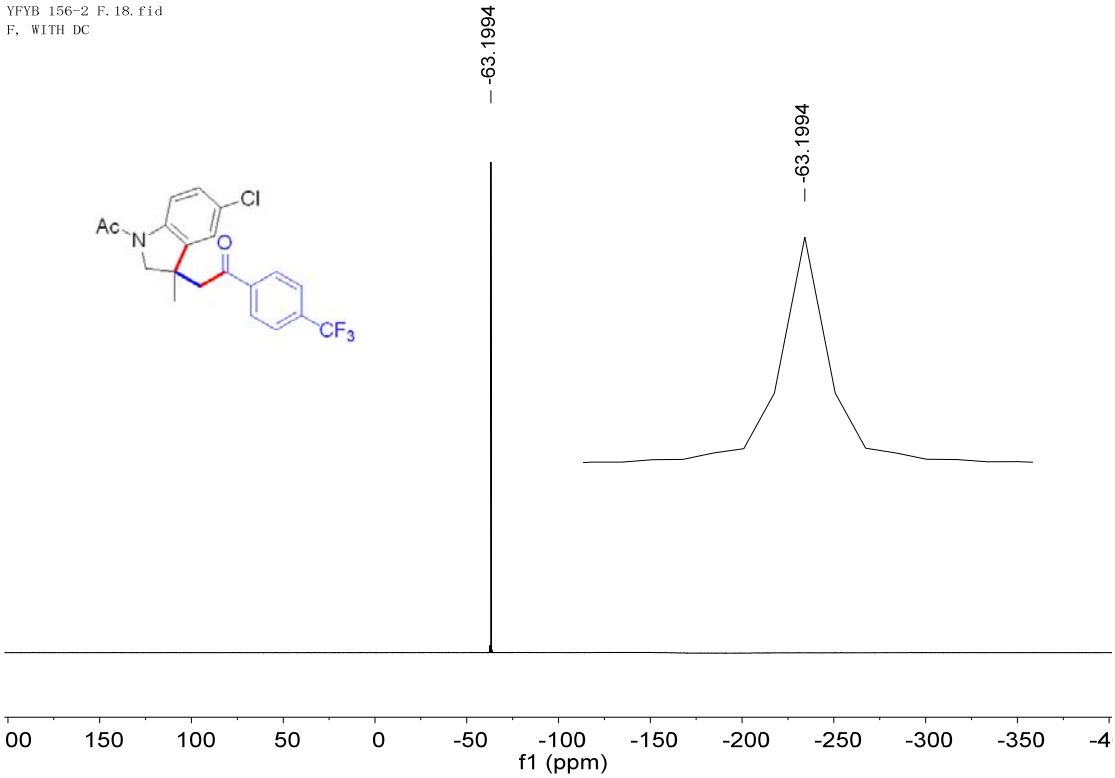


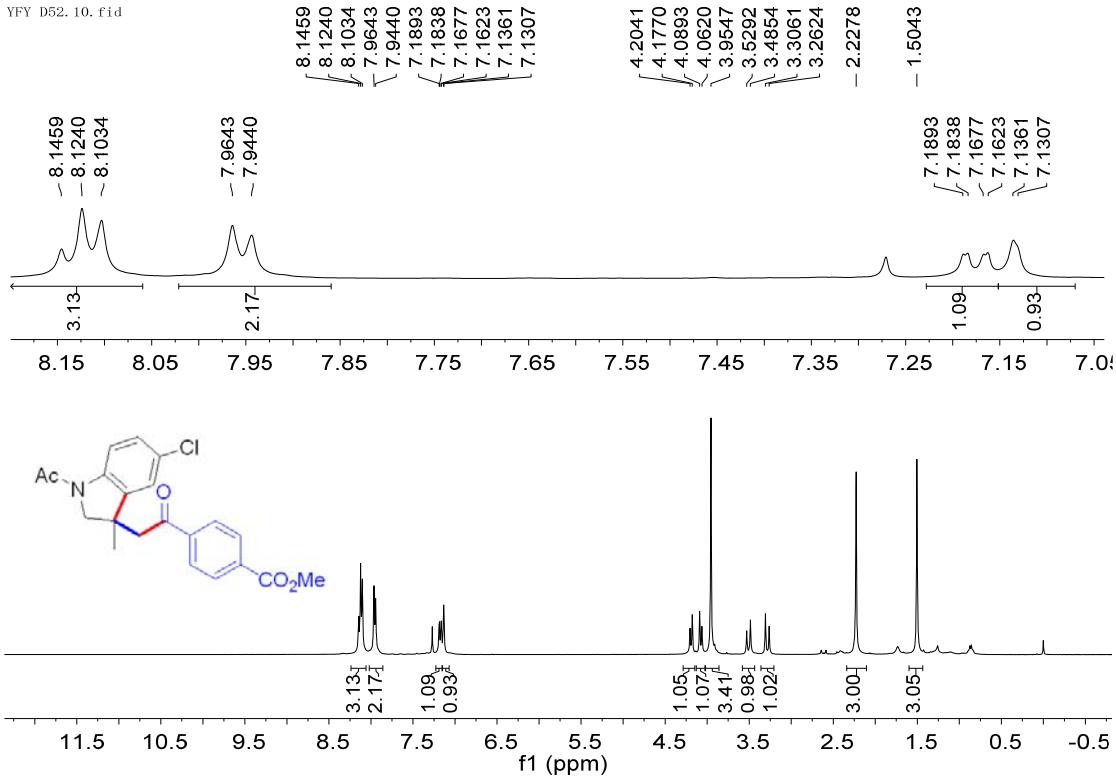
^{19}F NMR, no decoupling



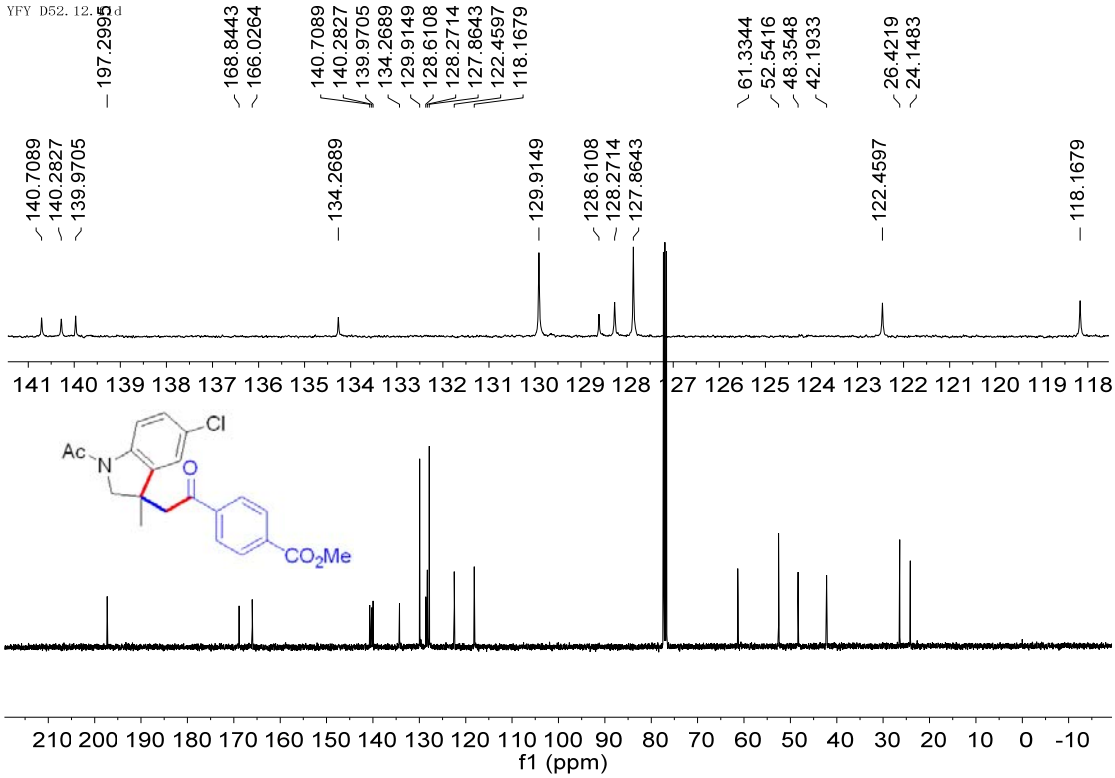
^{19}F NMR, with pulse decoupling



3l4, ^{1}H NMR



^{13}C NMR



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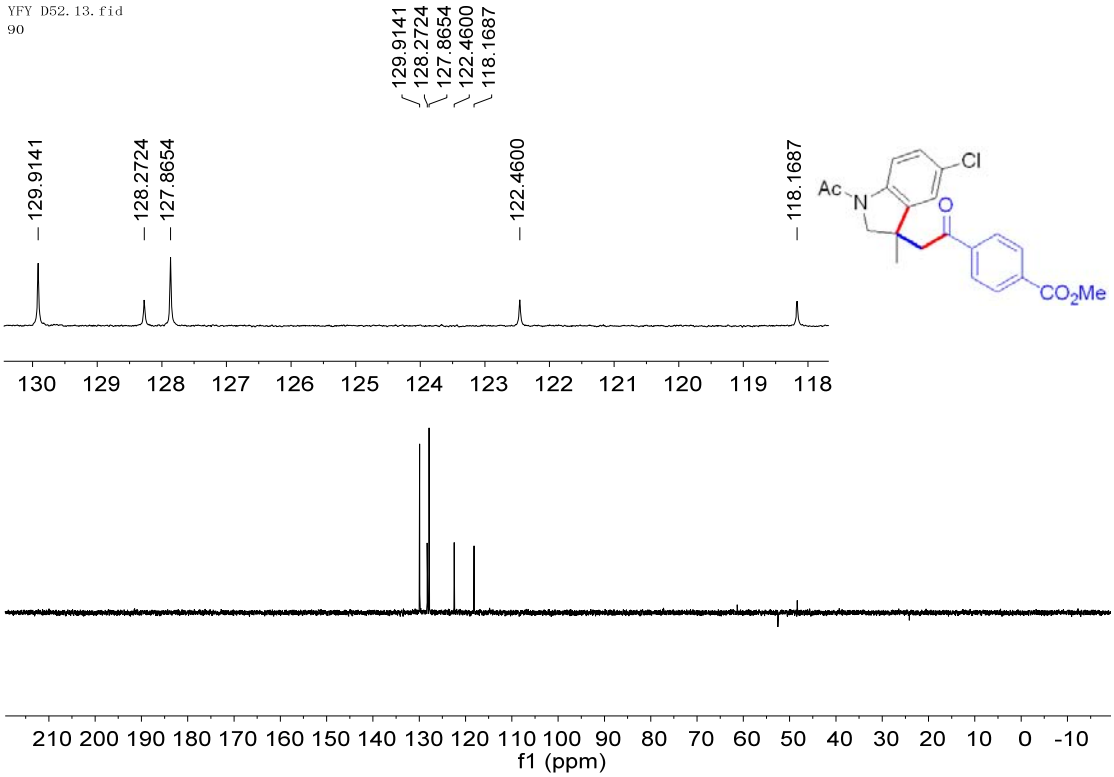

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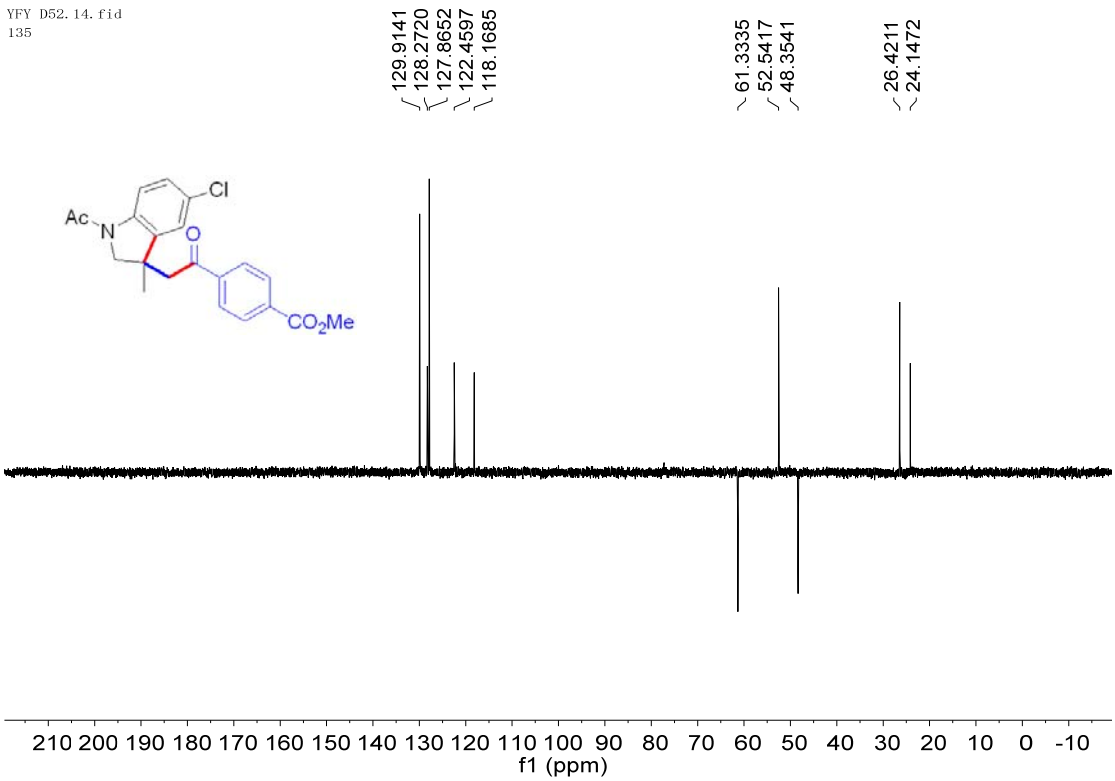
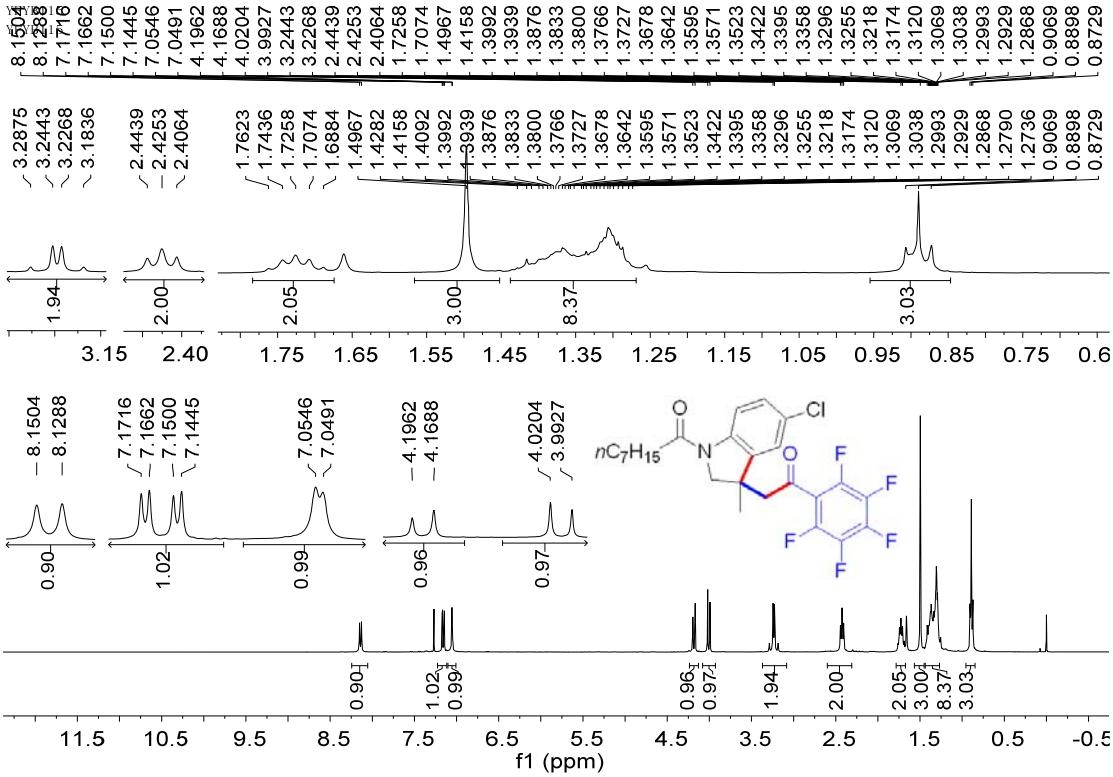
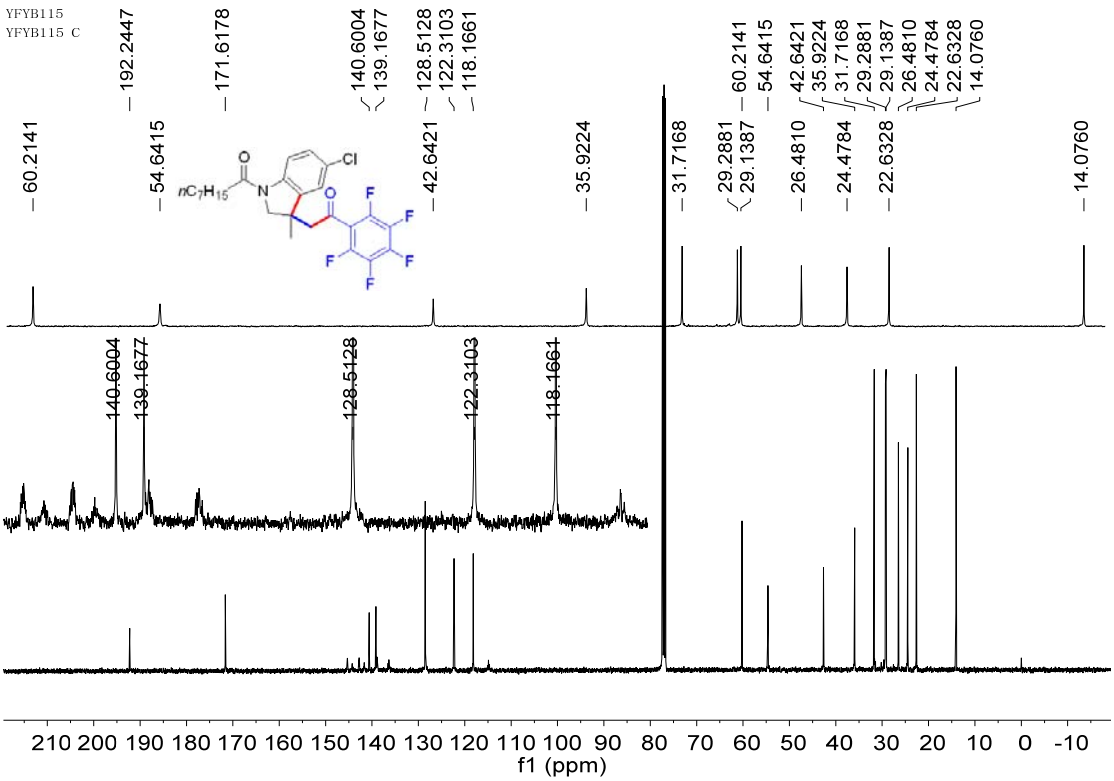


3m, ^{1}H NMR



^{13}C NMR



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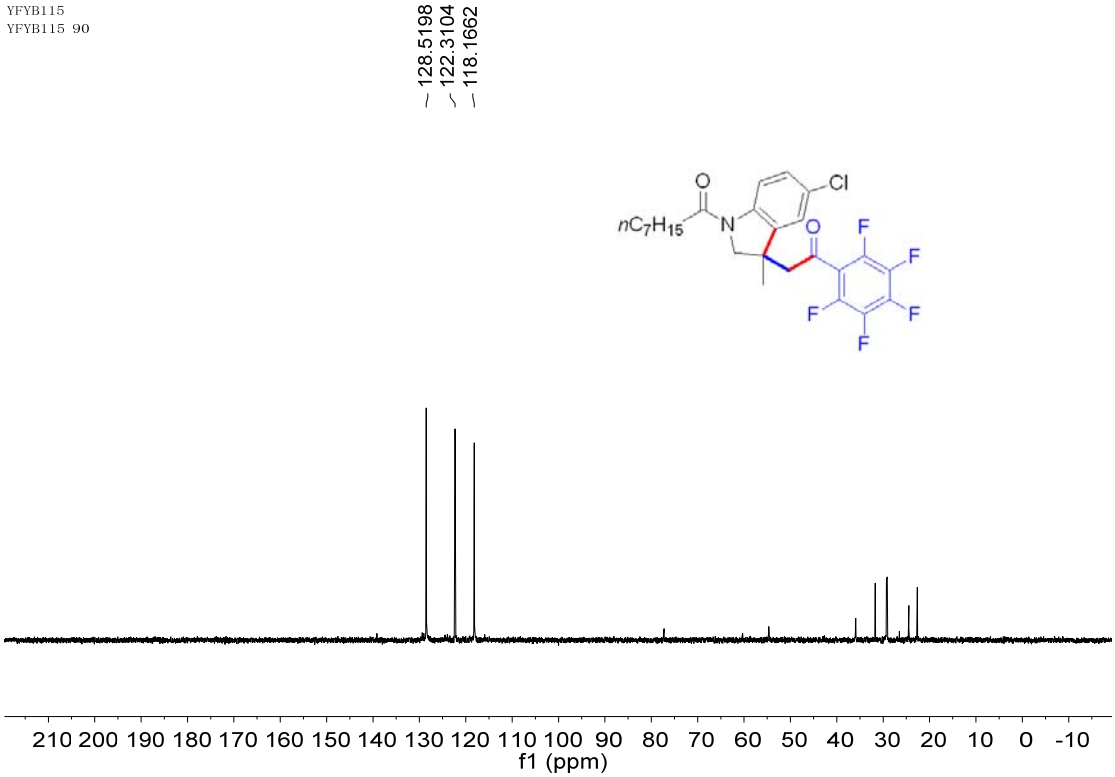

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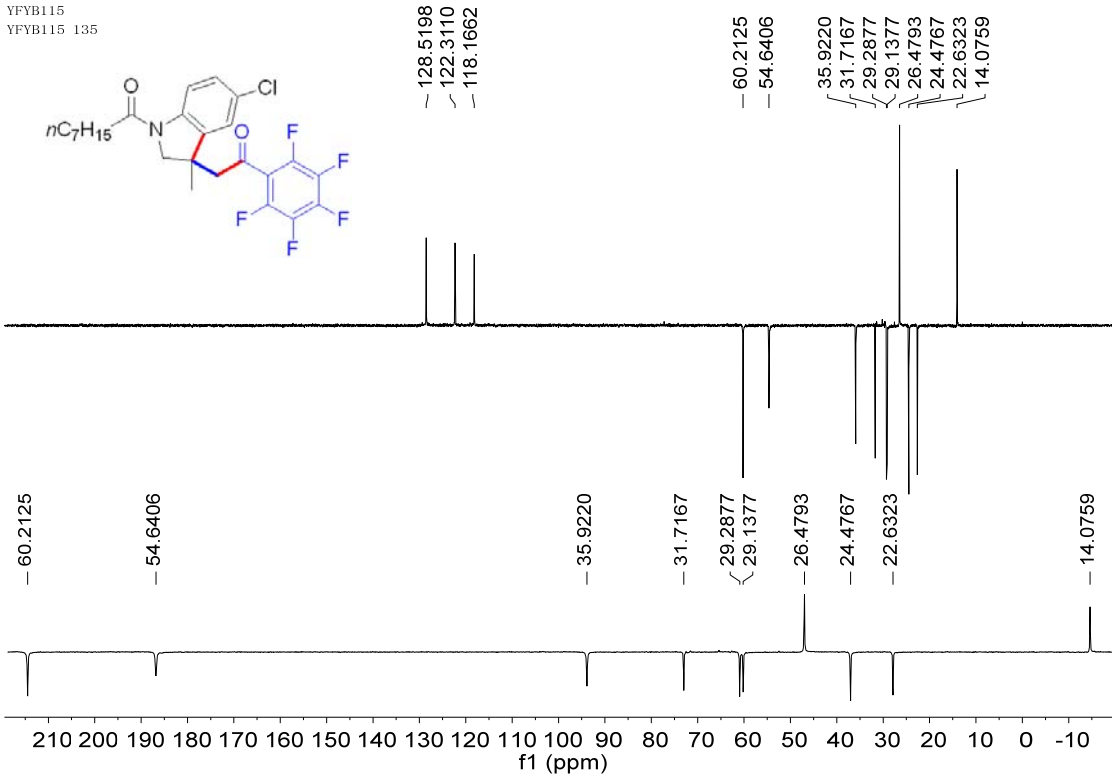
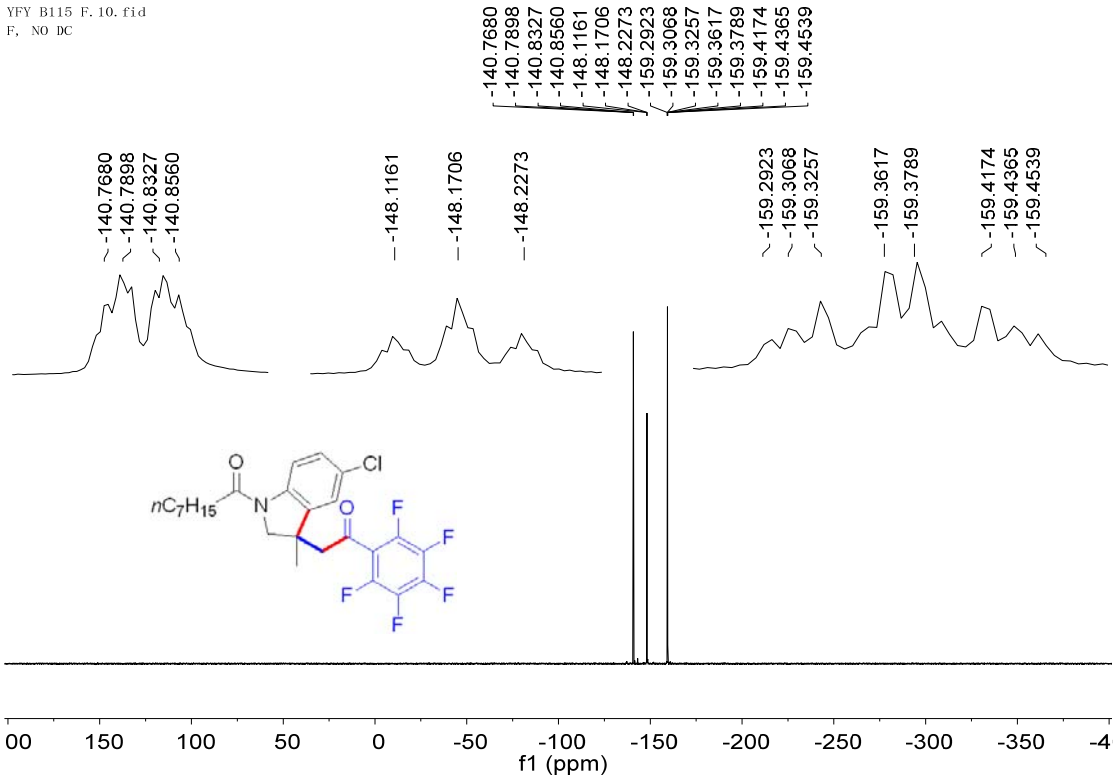
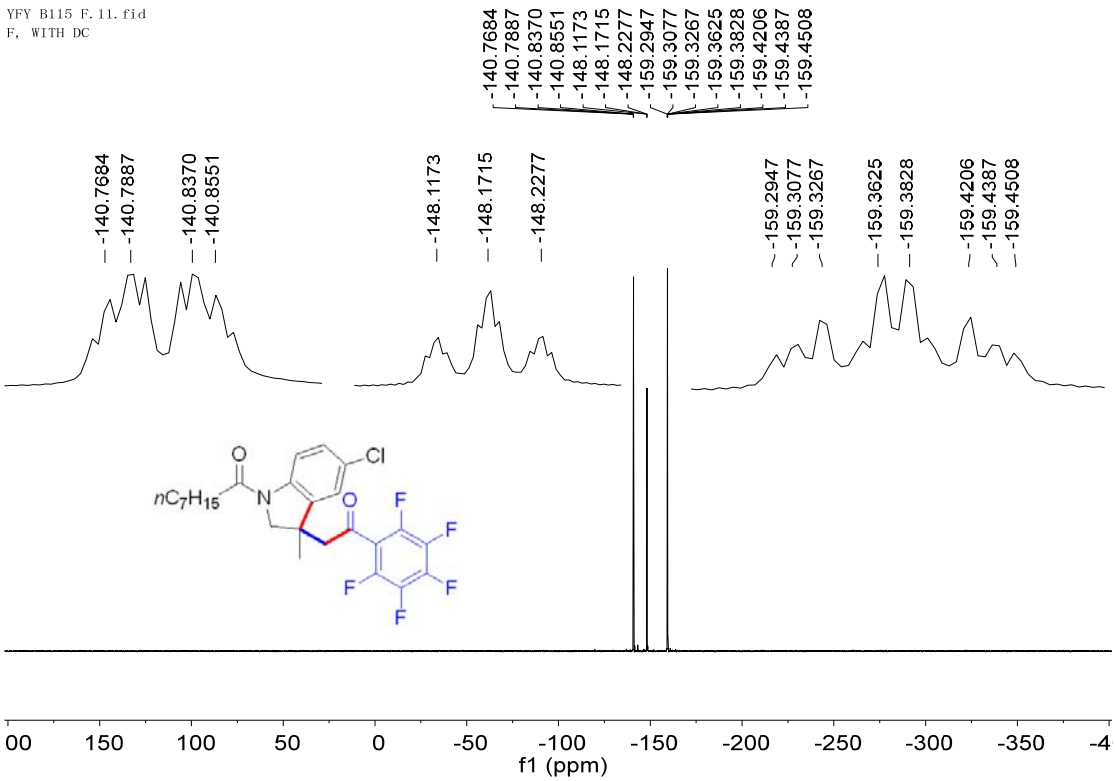


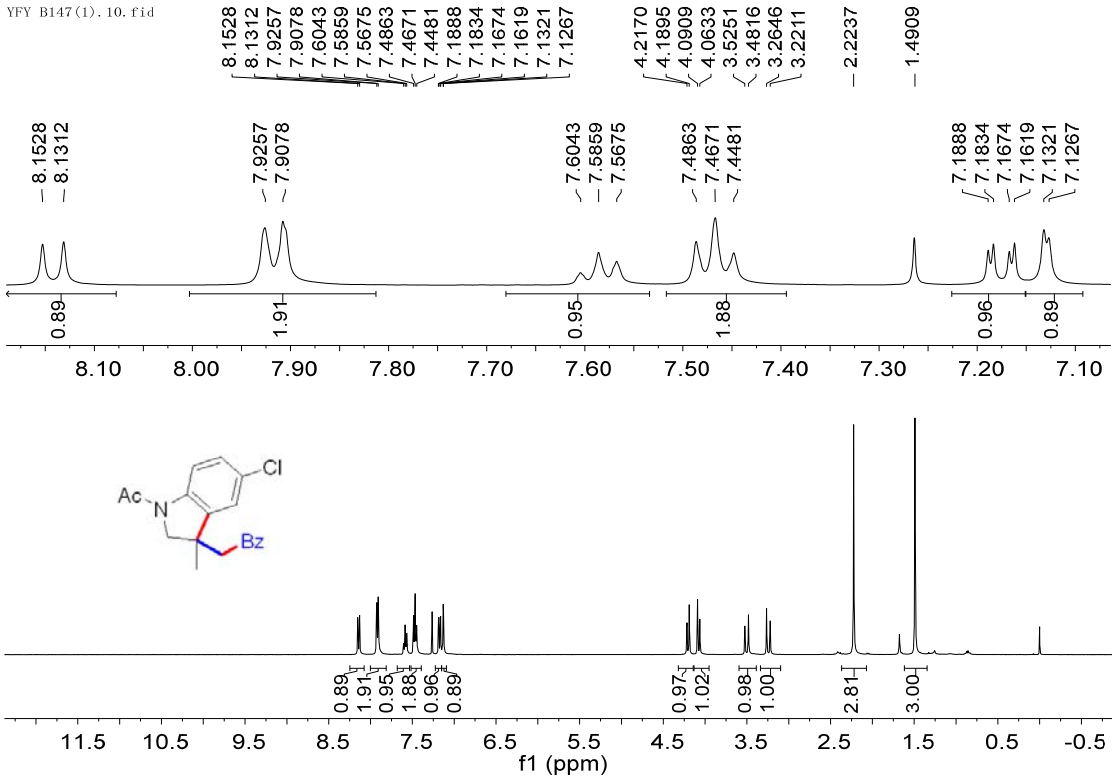
^{19}F NMR, no decoupling



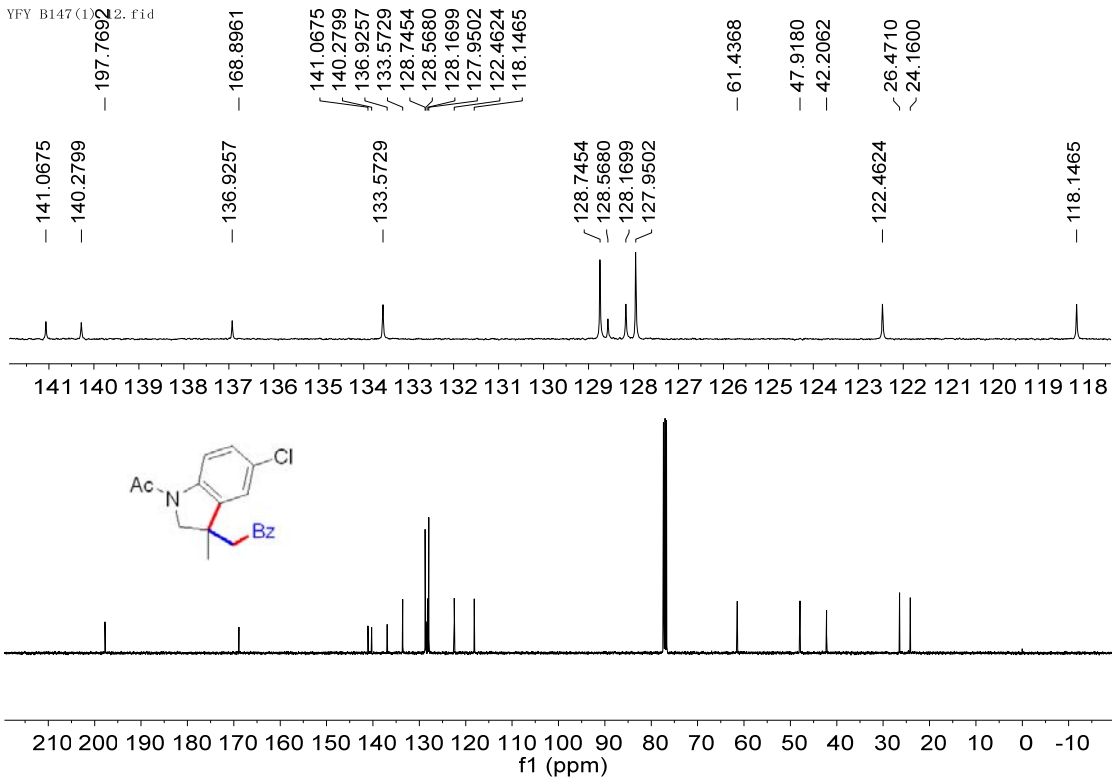
^{19}F NMR, with pulse decoupling



3n, ^{1}H NMR



^{13}C NMR



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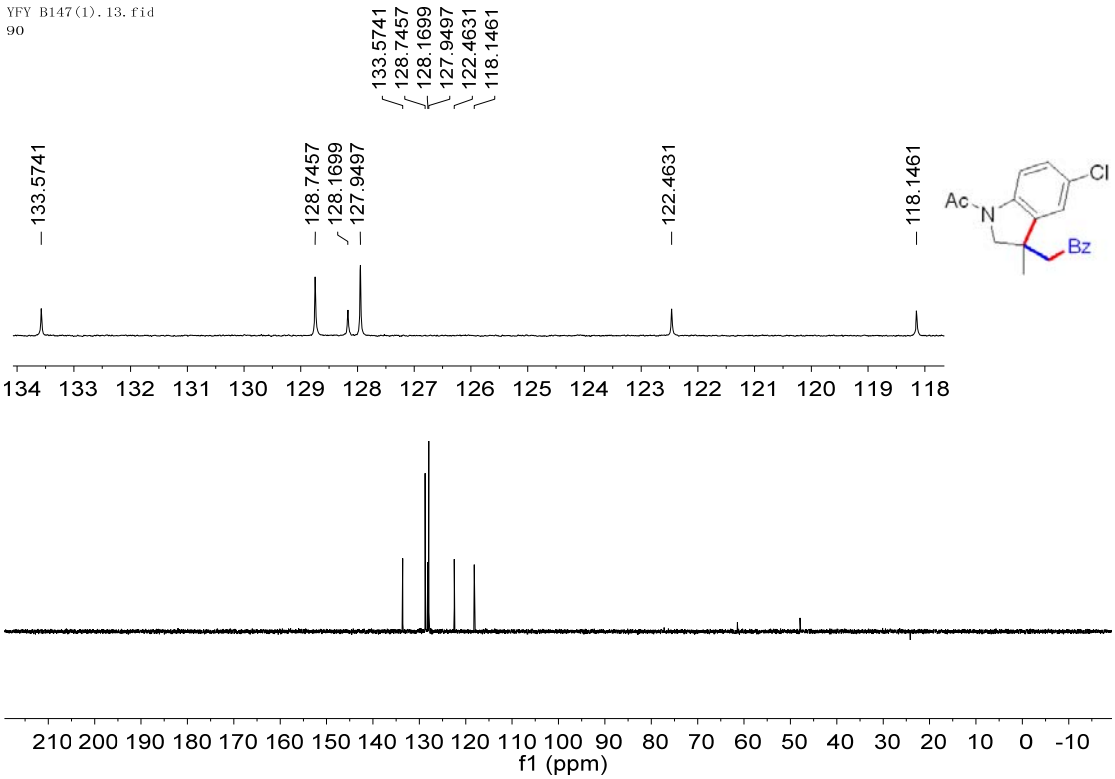

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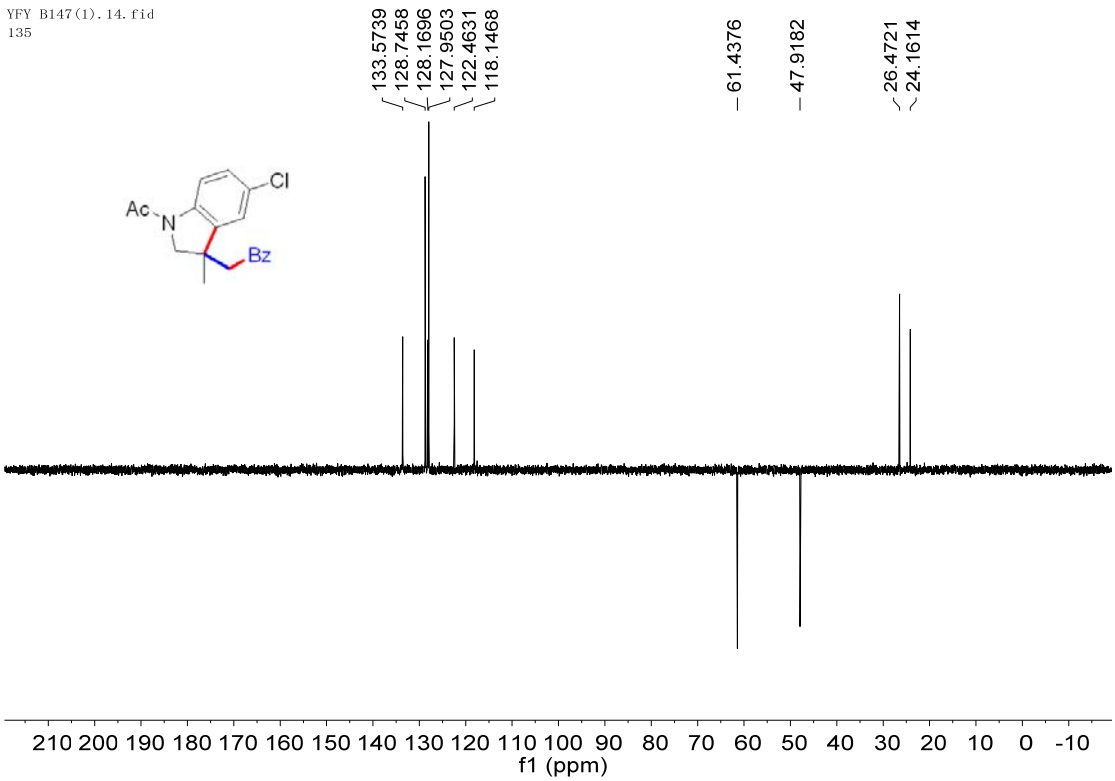
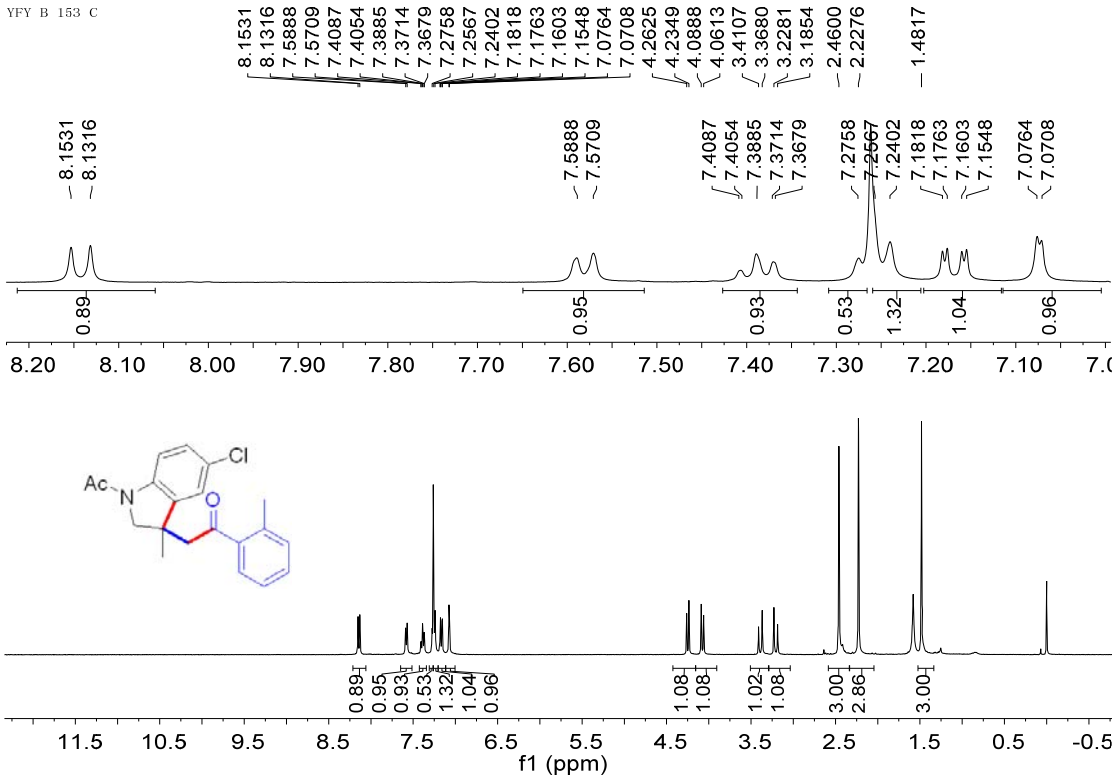


3o, ^{1}H NMR



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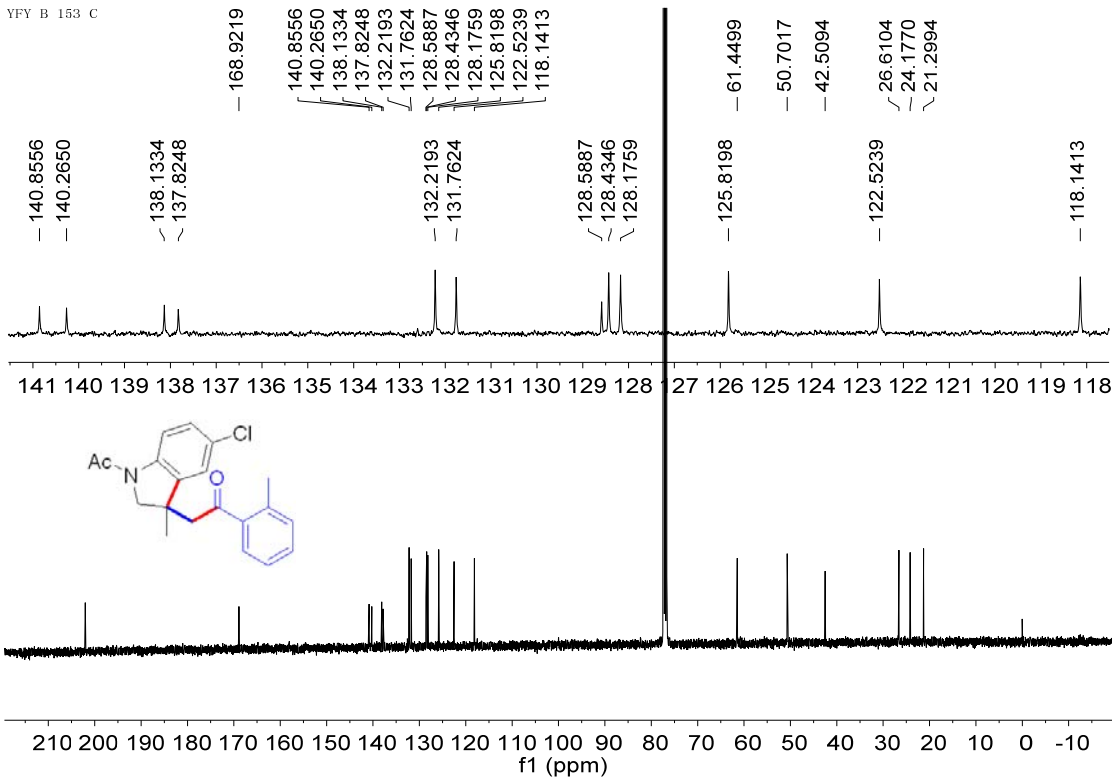

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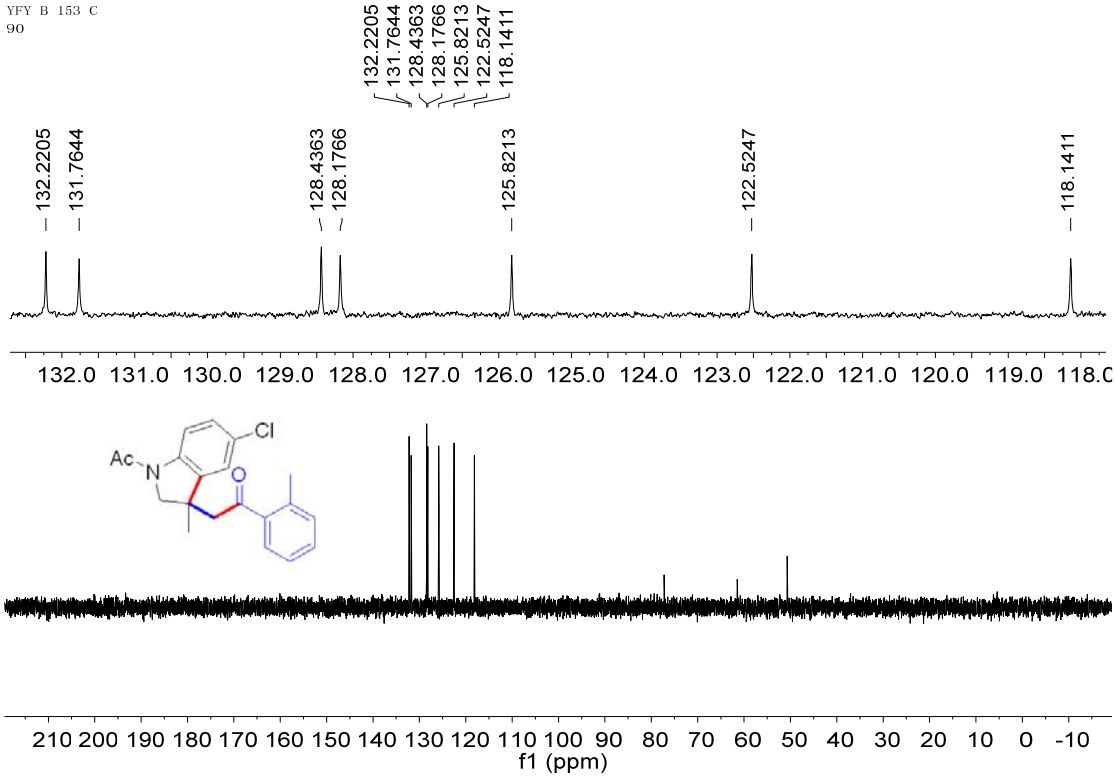

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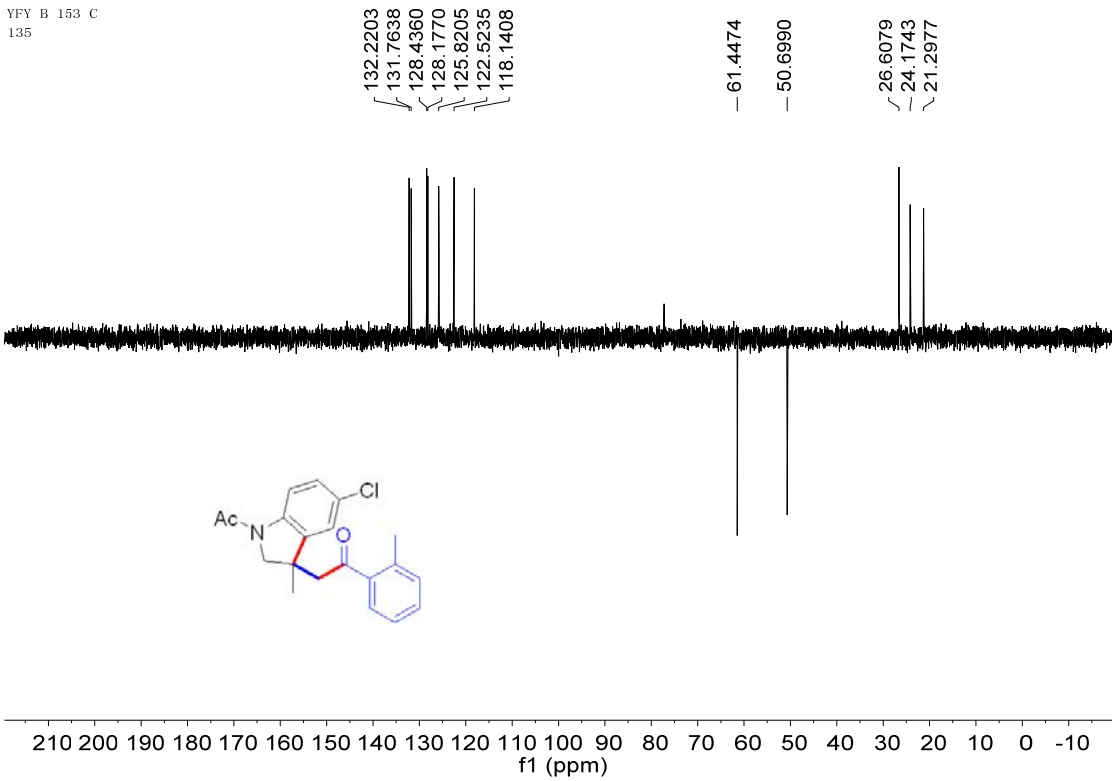
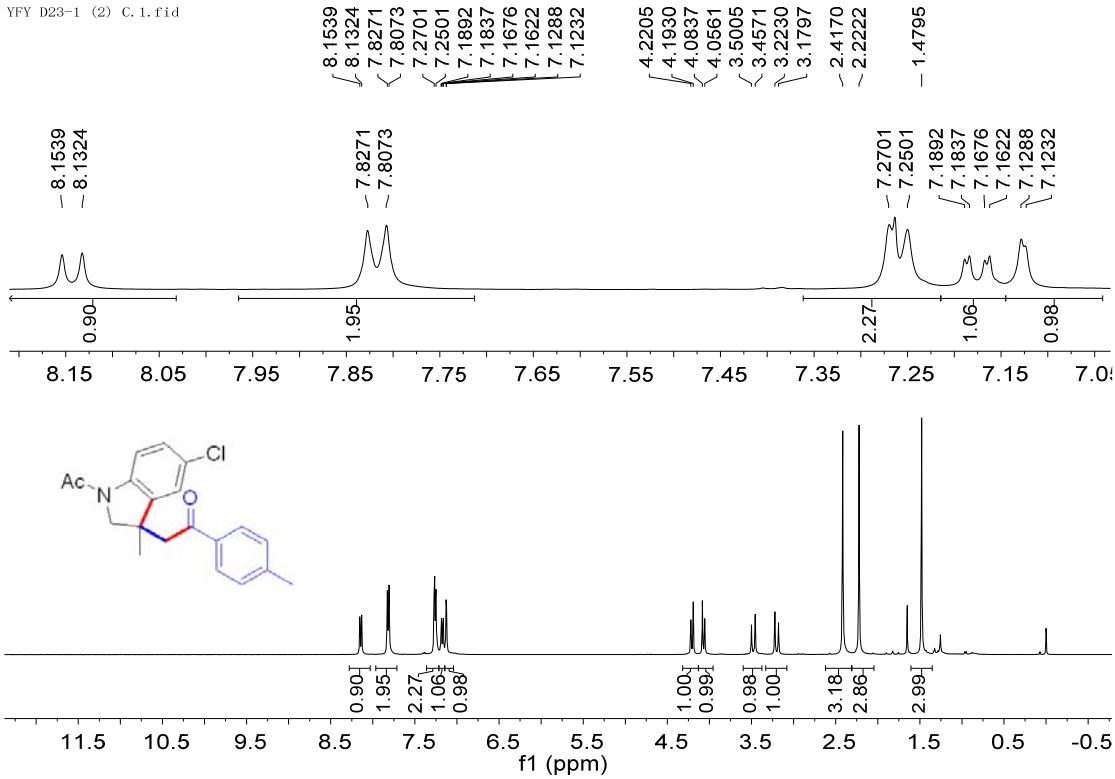
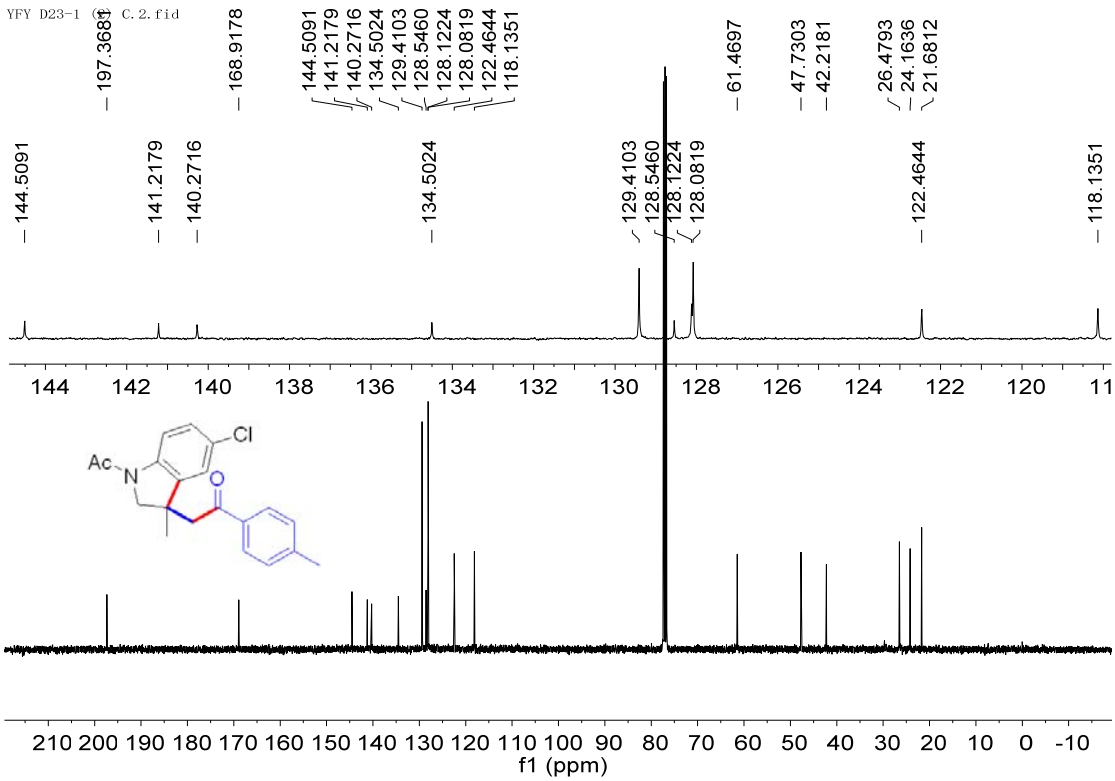


3p1, ^{1}H NMR



^{13}C NMR



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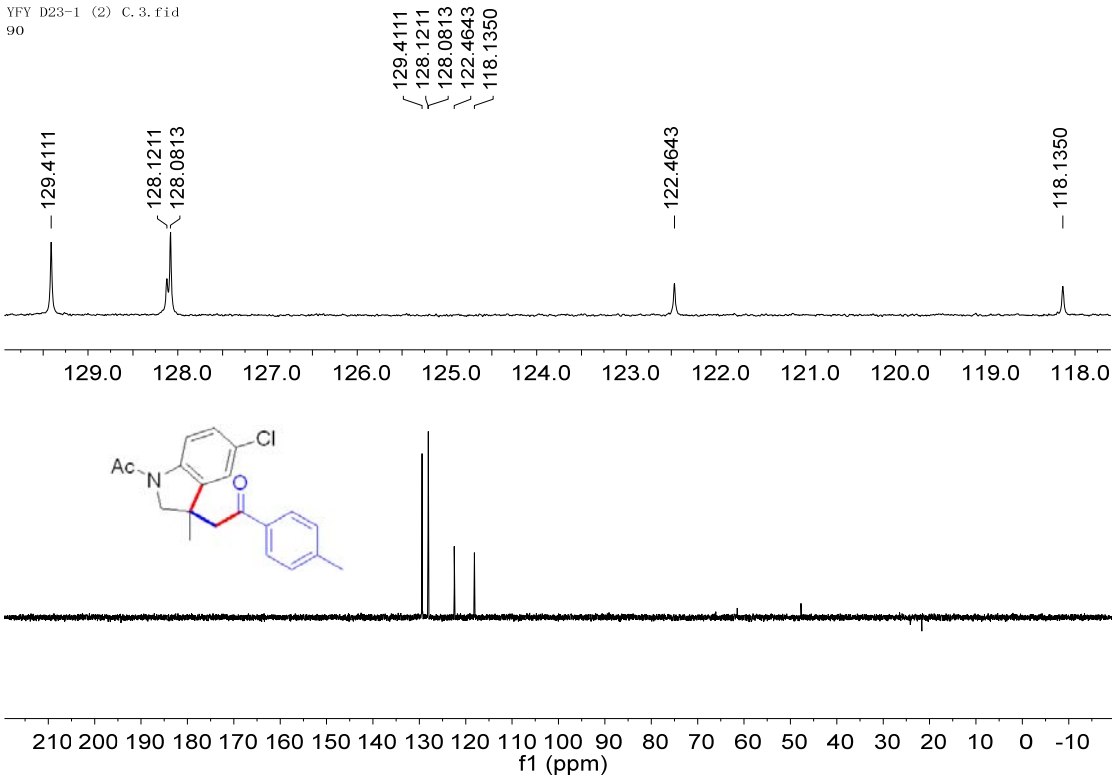

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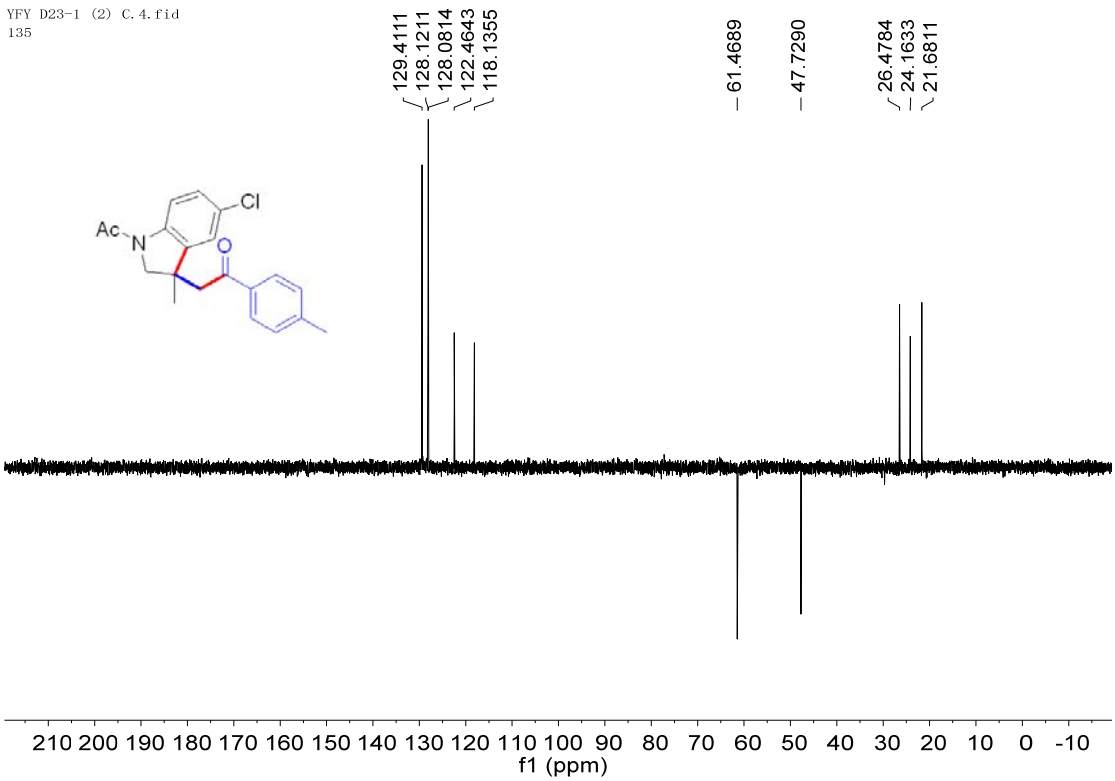
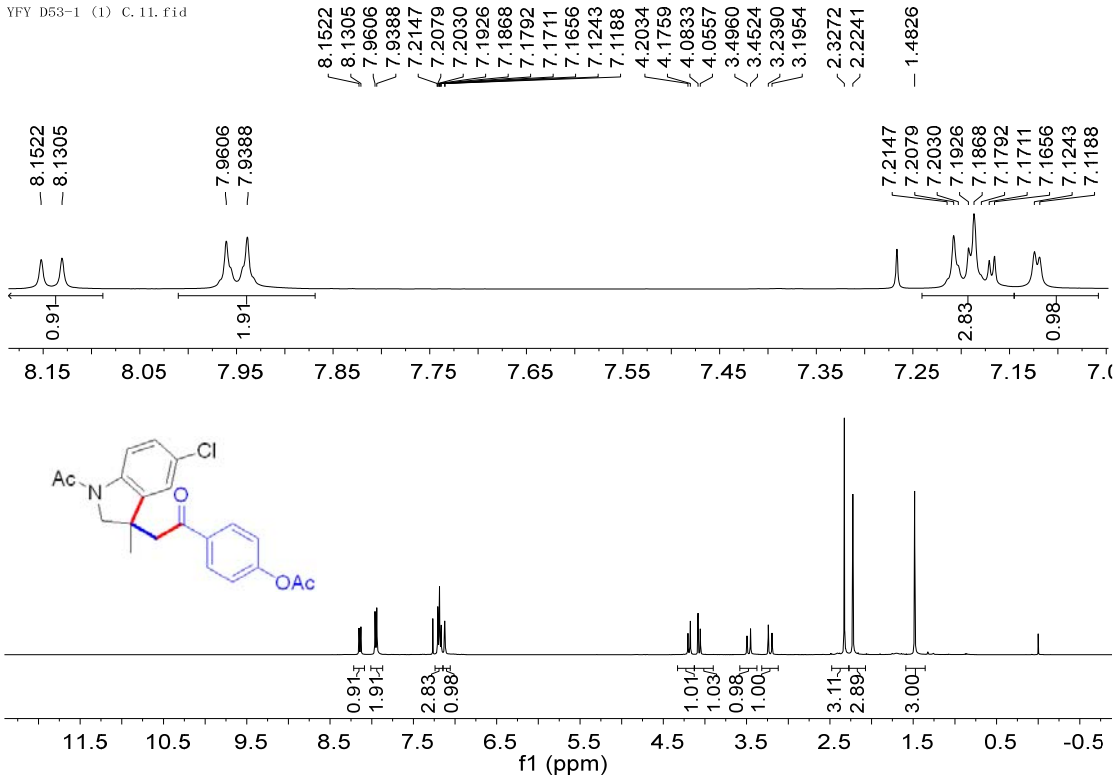
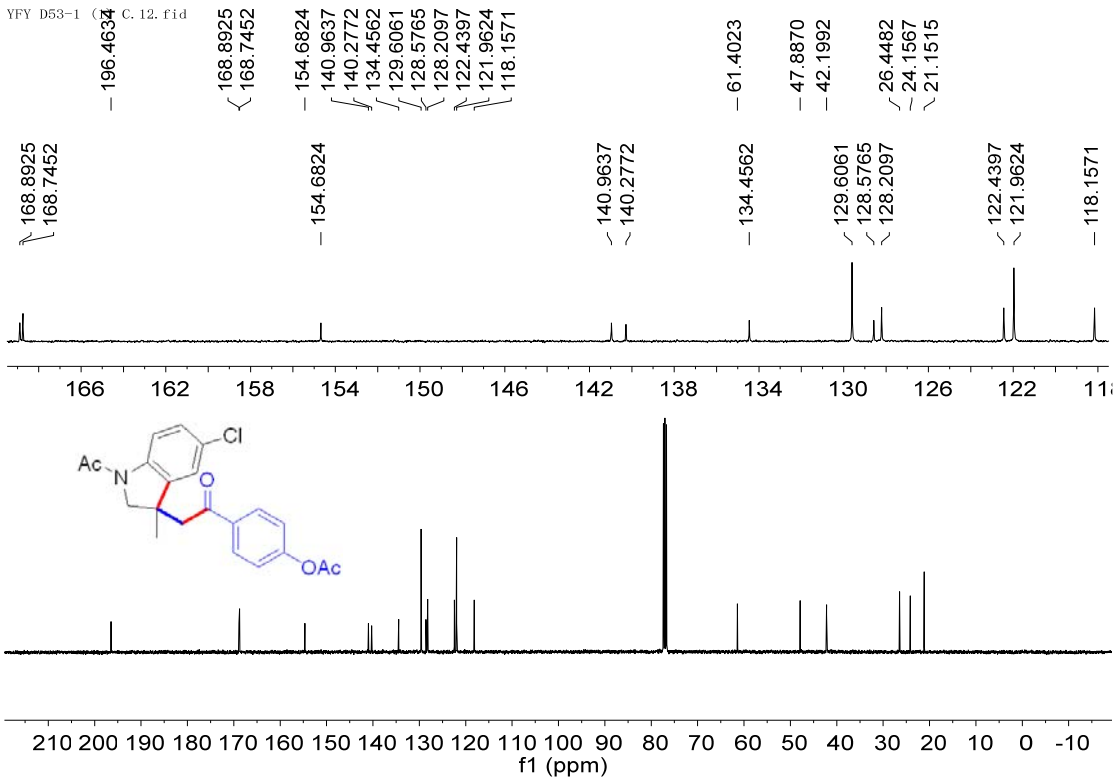


3p2, ^{1}H NMR



^{13}C NMR



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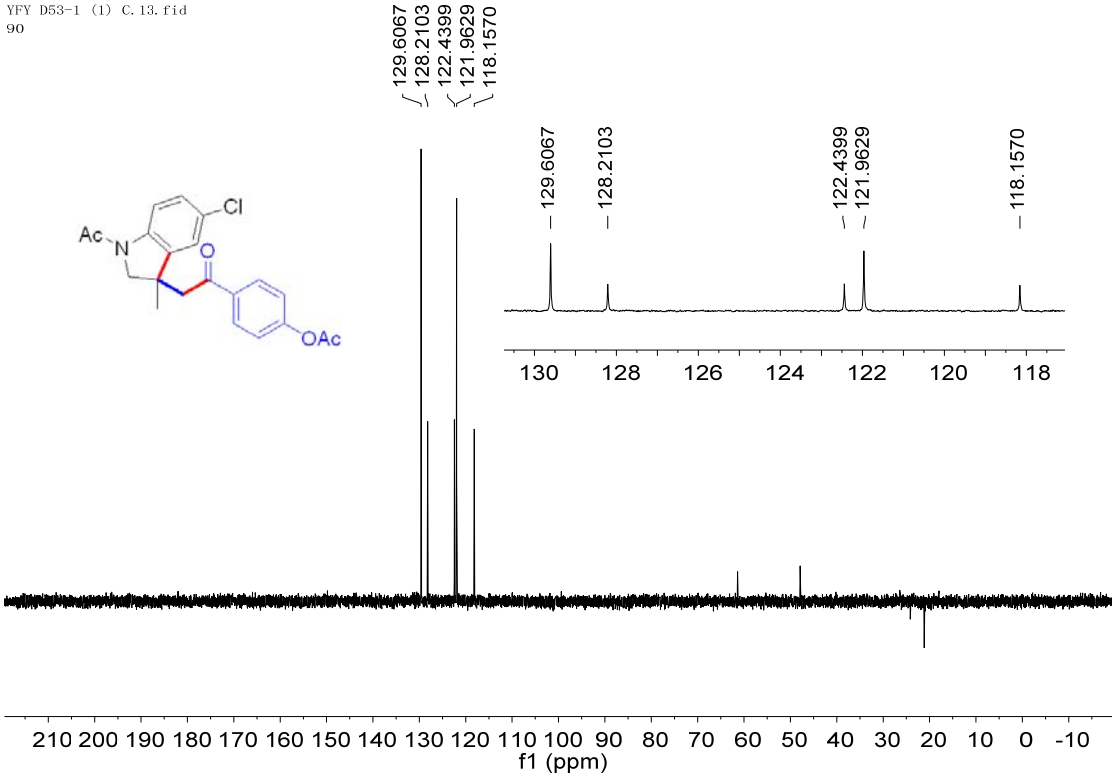

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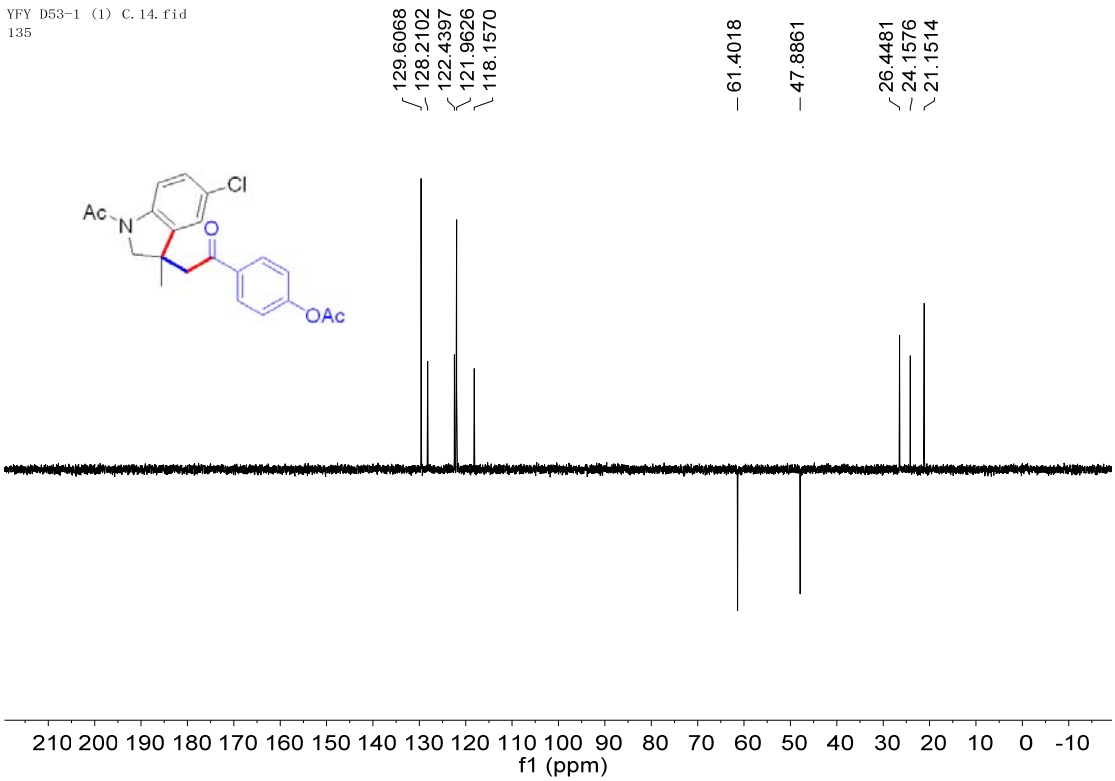
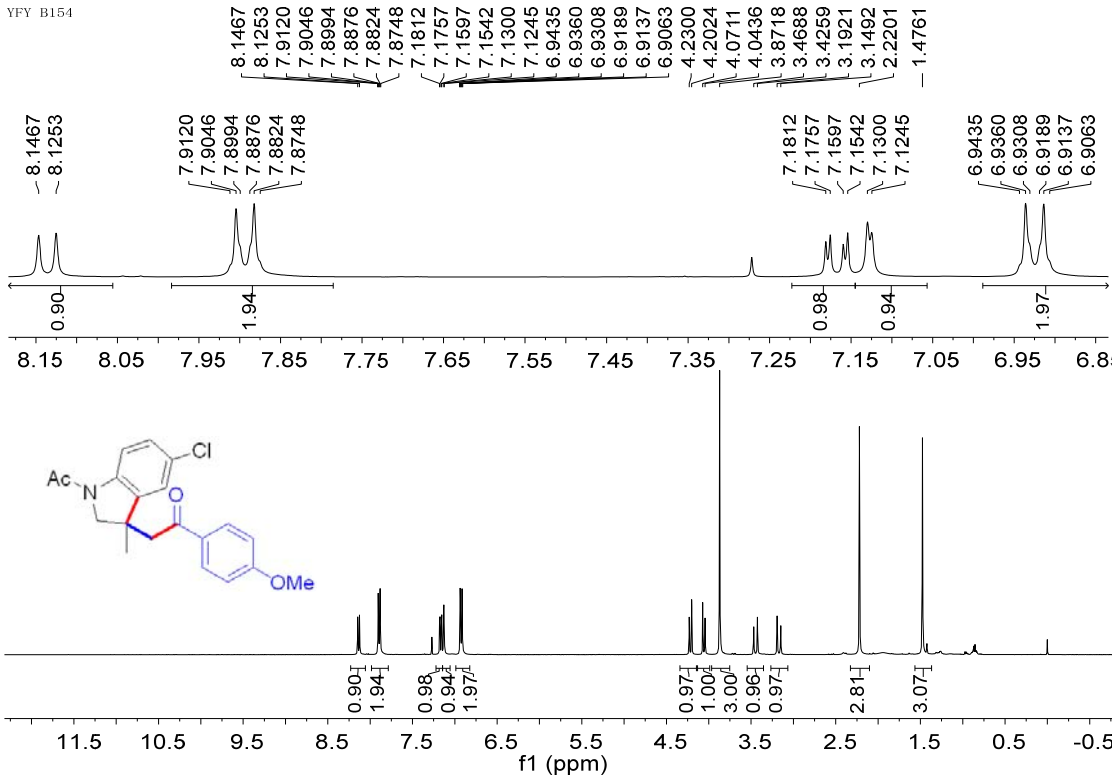


3p3, ^{1}H NMR



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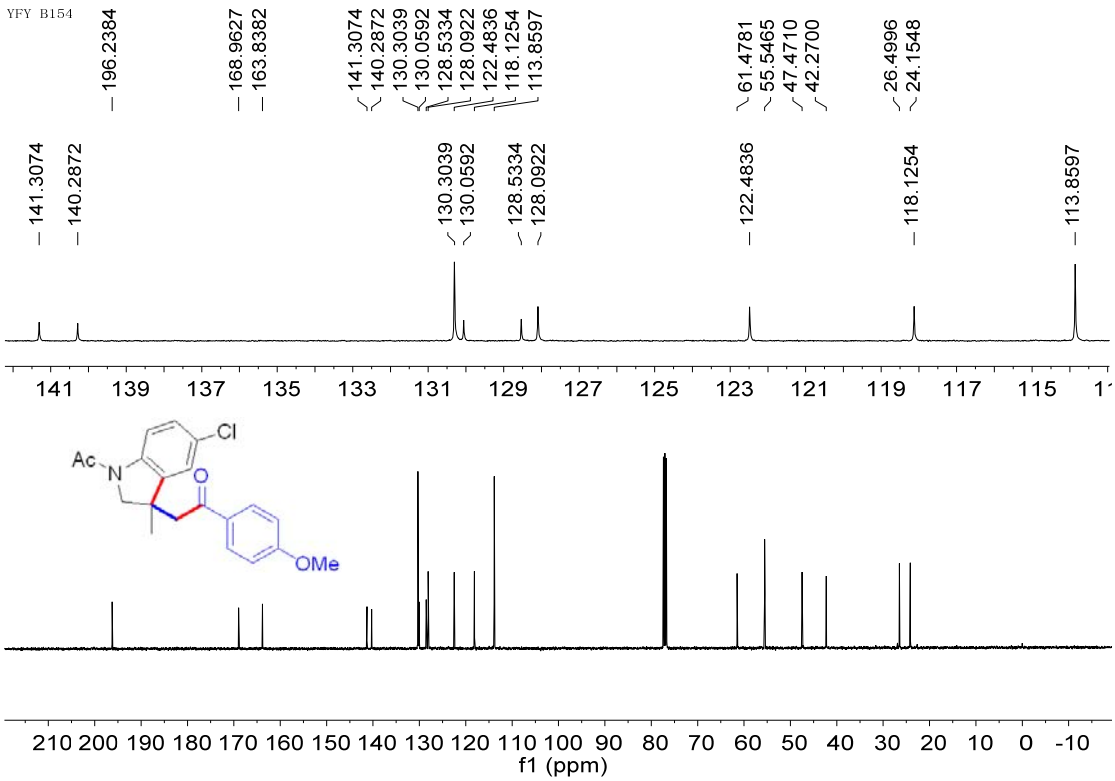

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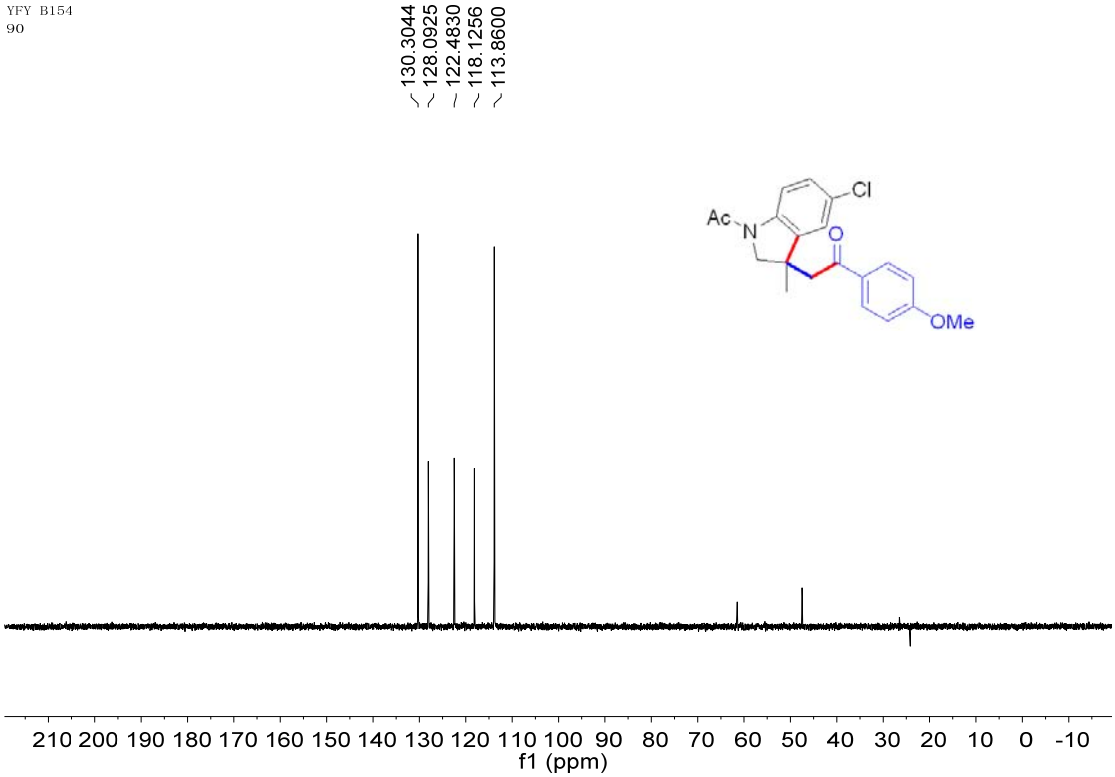

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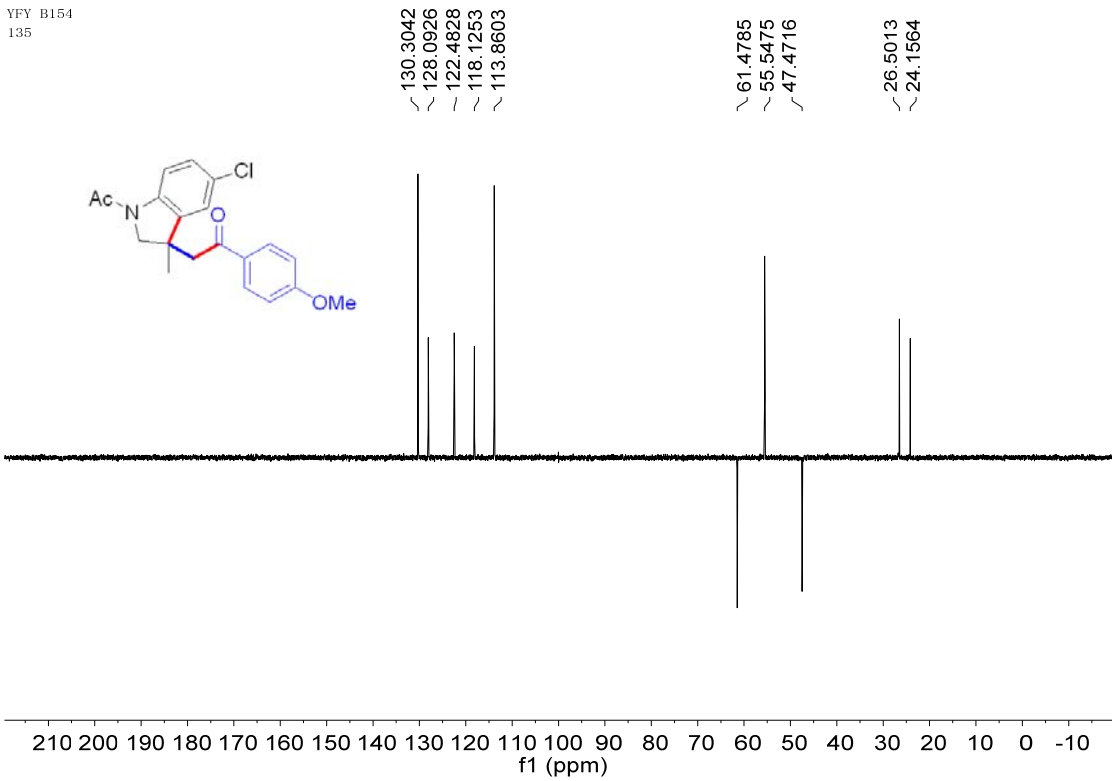
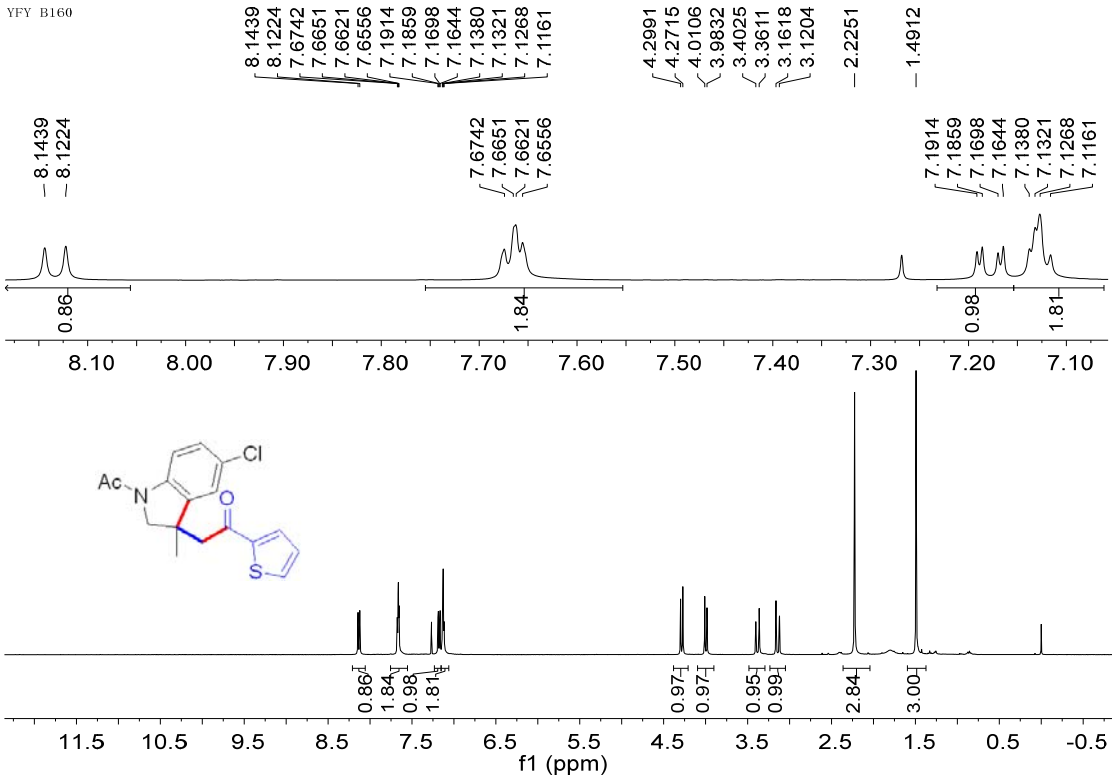
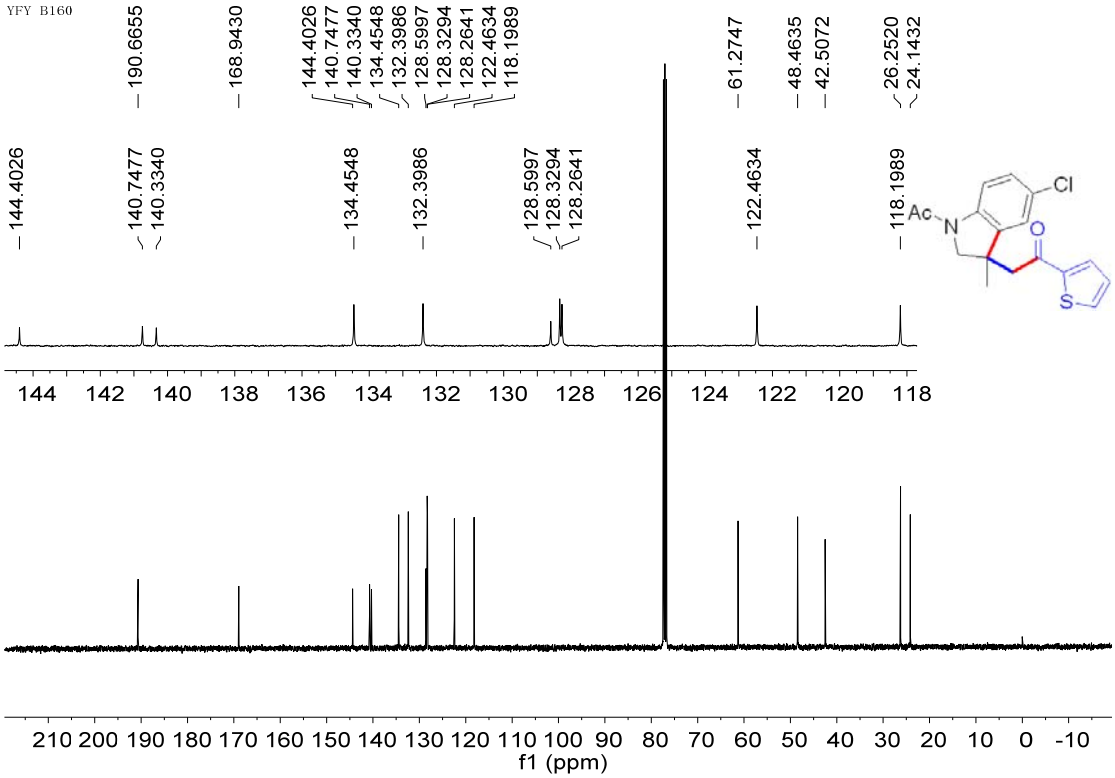


3q, ^{1}H NMR



^{13}C NMR



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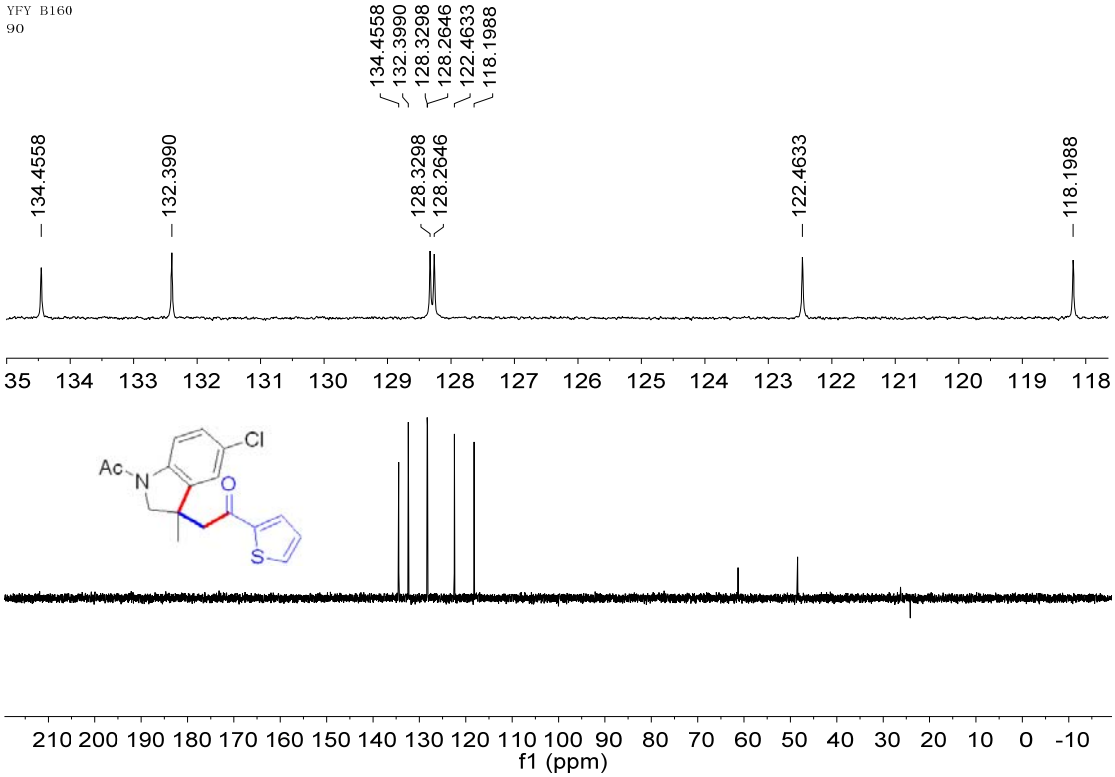

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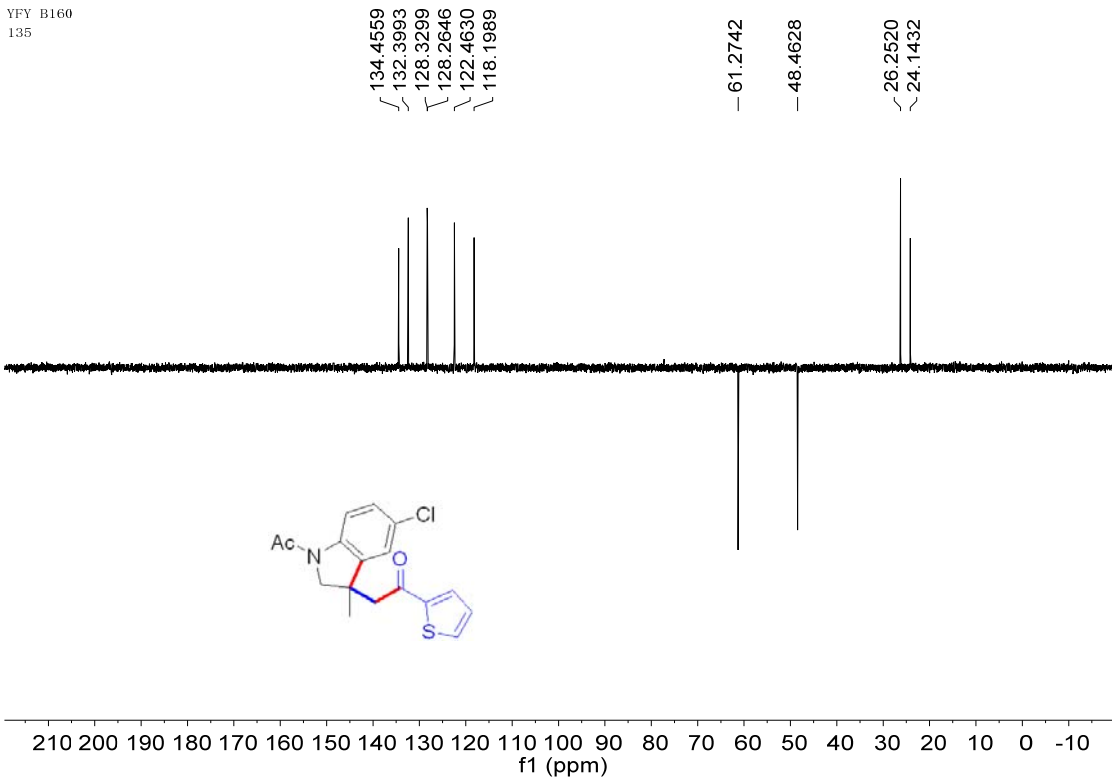
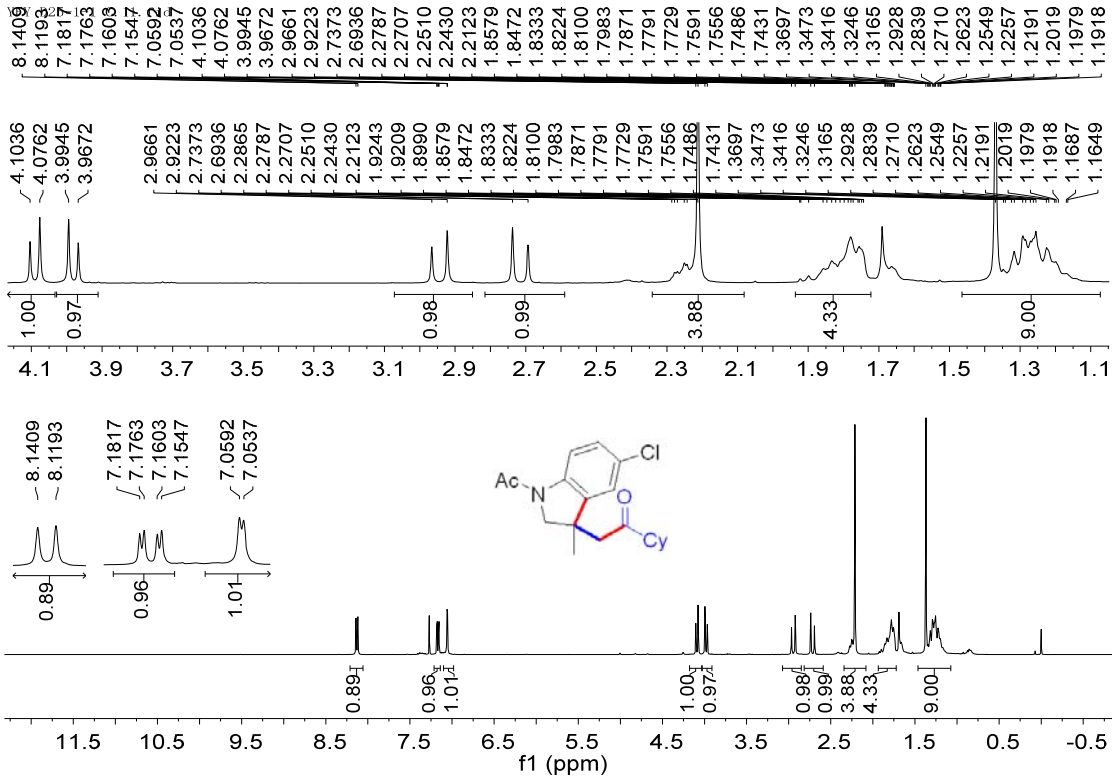
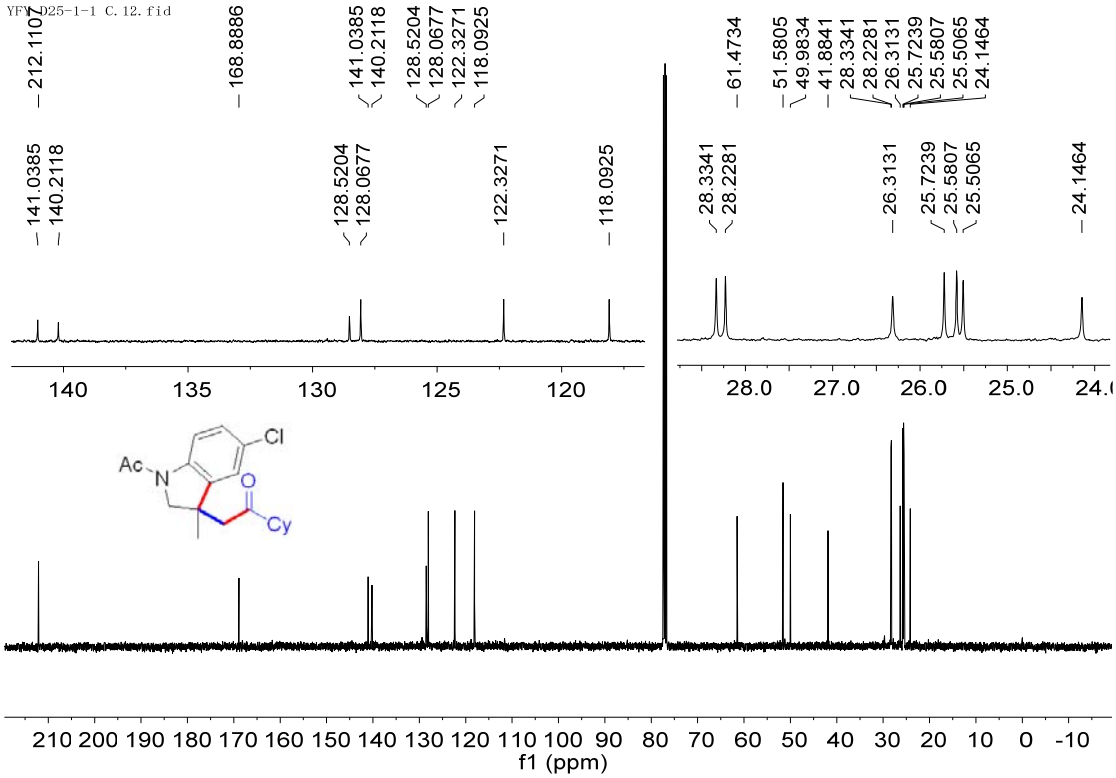


3r, ^{1}H NMR



^{13}C NMR



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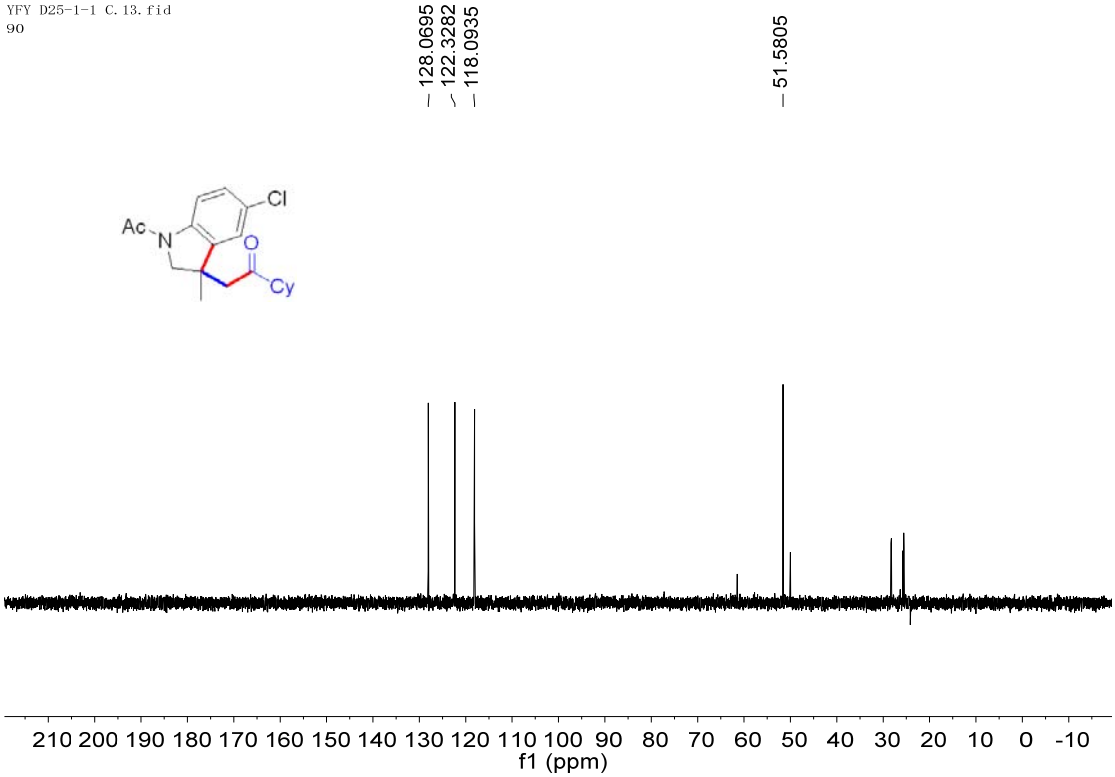

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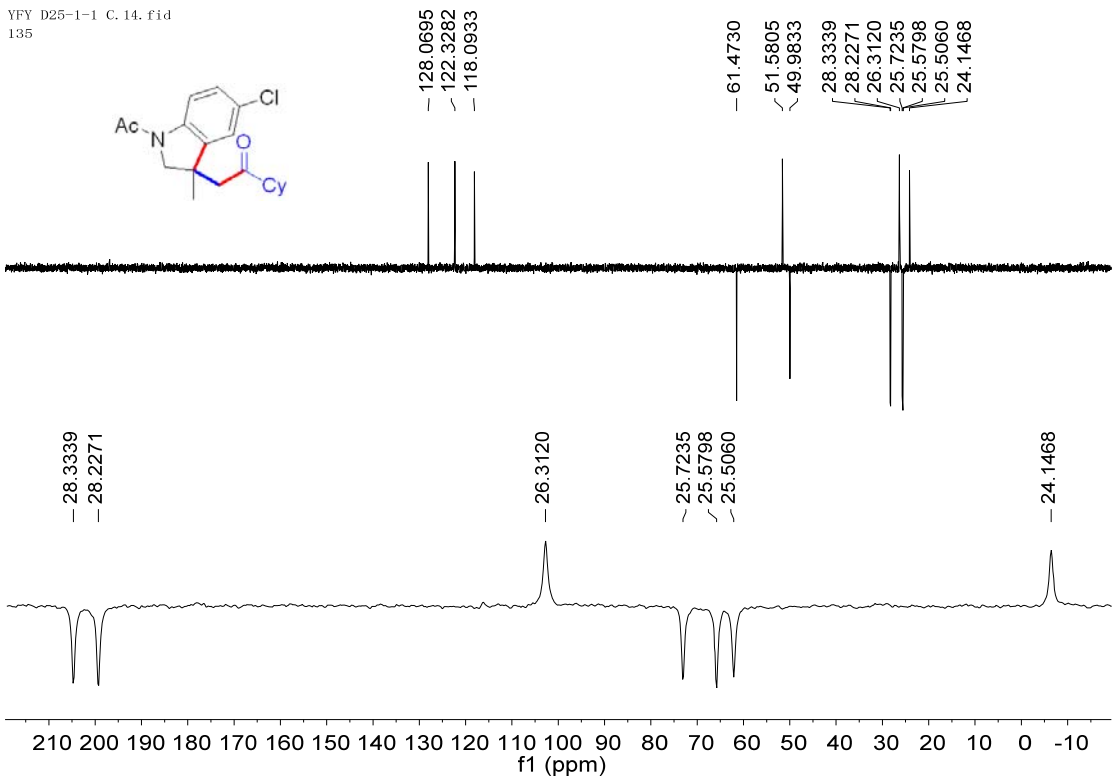
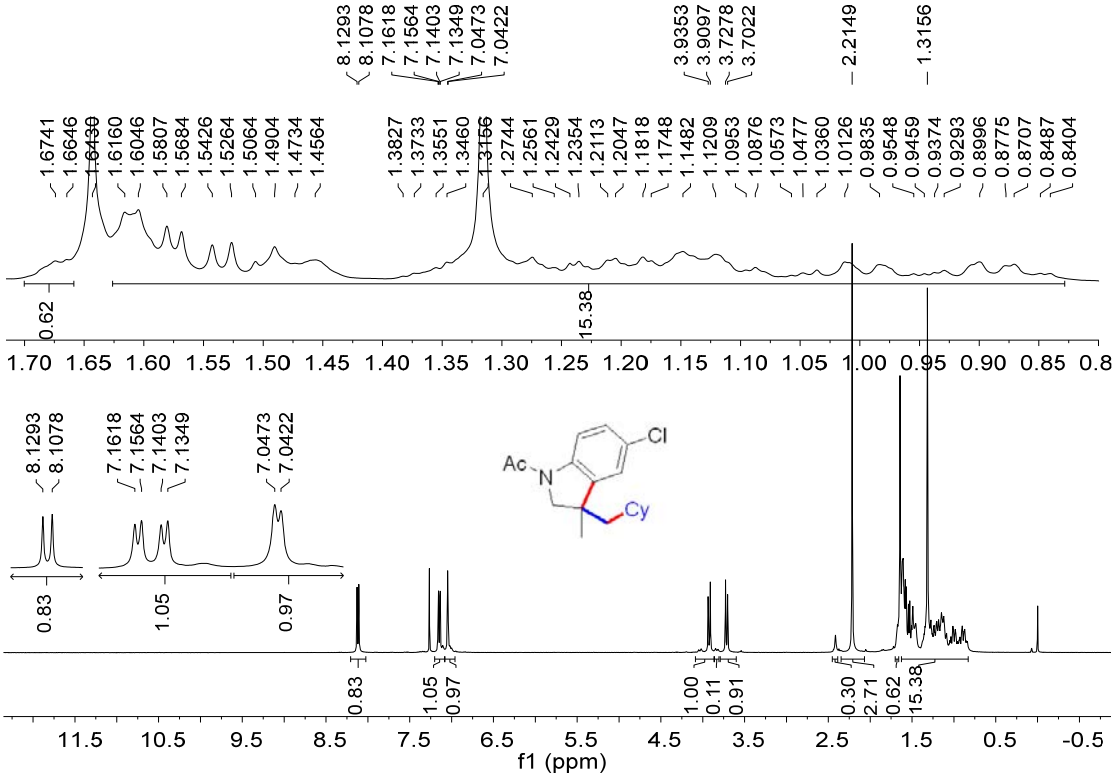
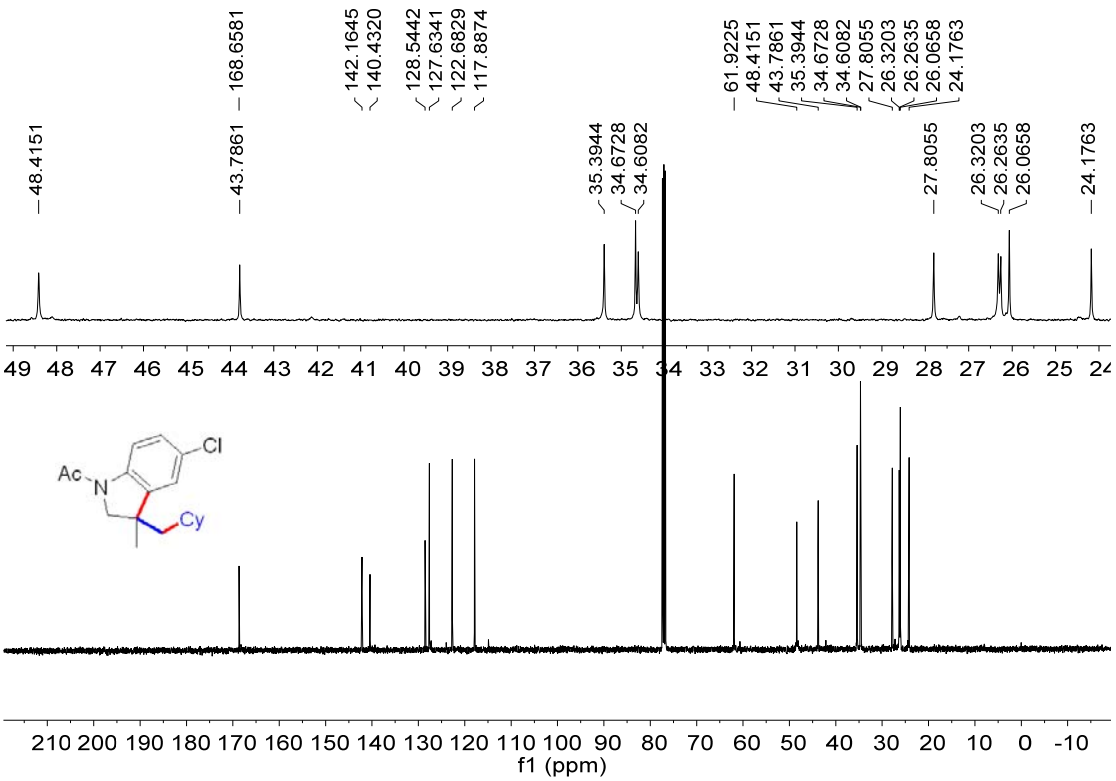


3r', ^{1}H NMR



^{13}C NMR



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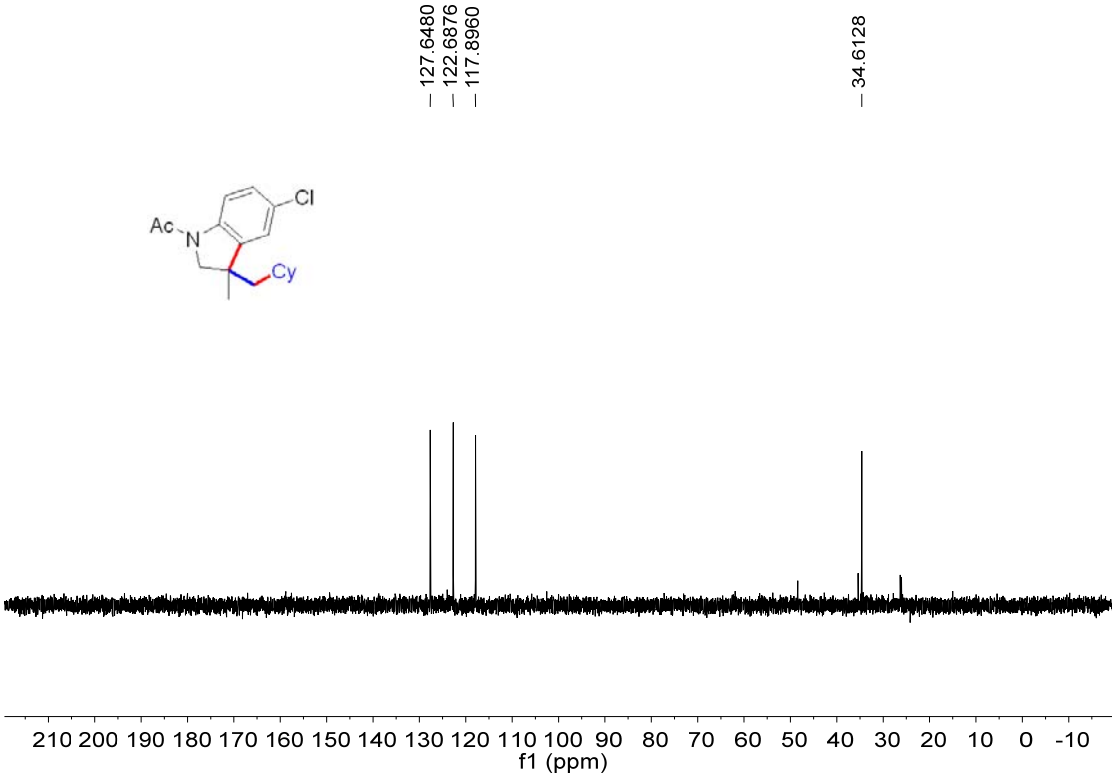

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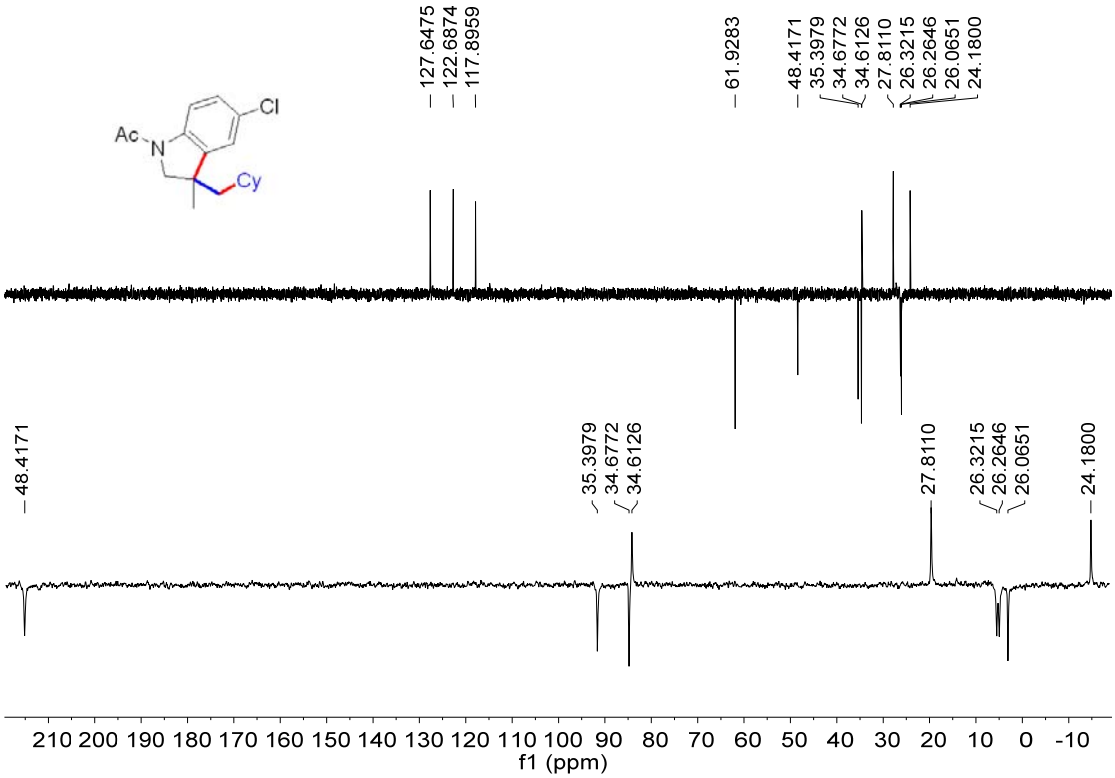
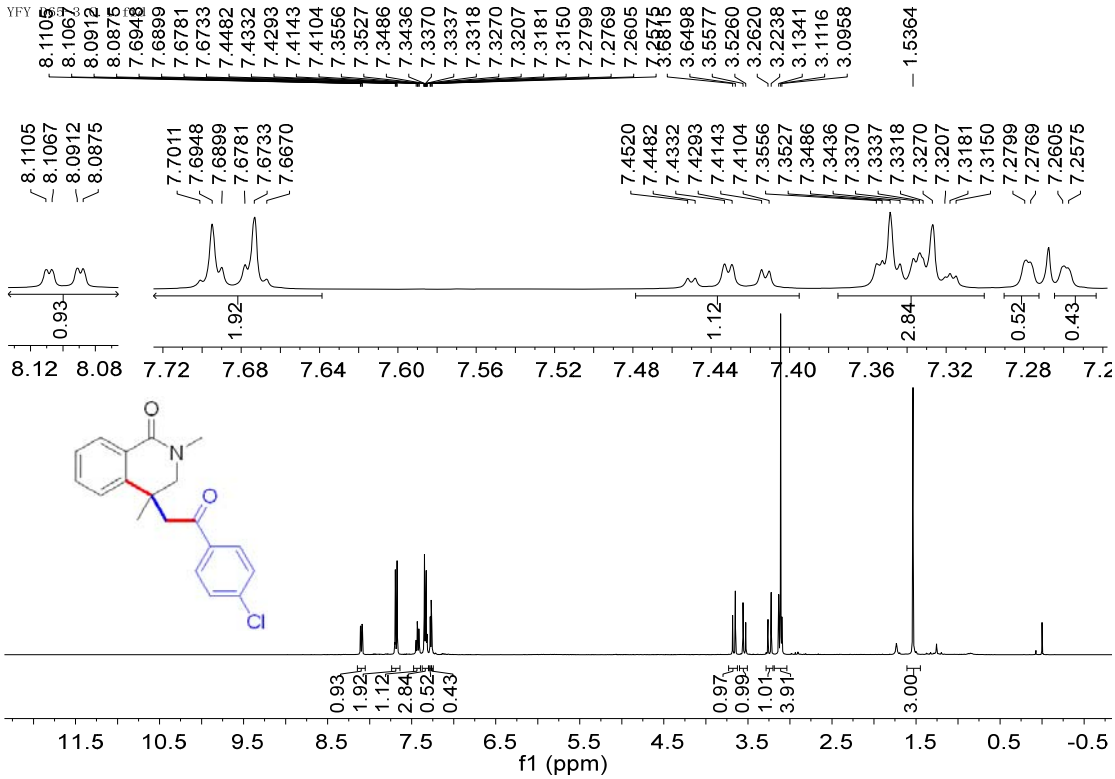
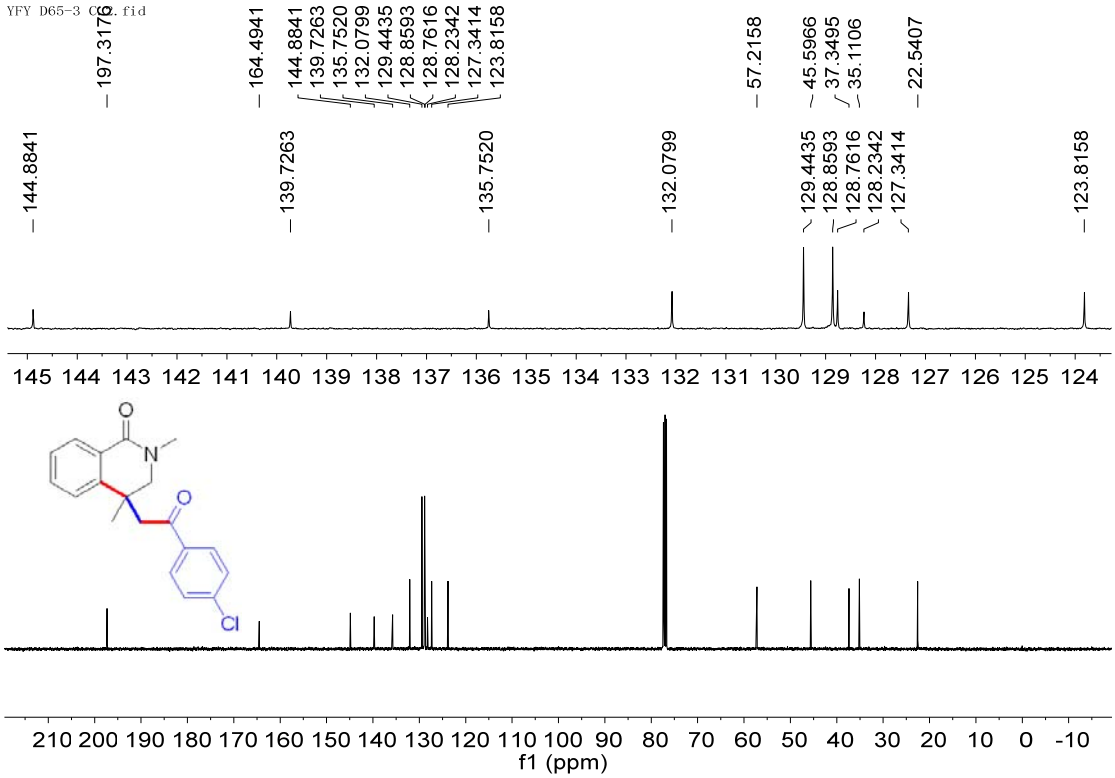


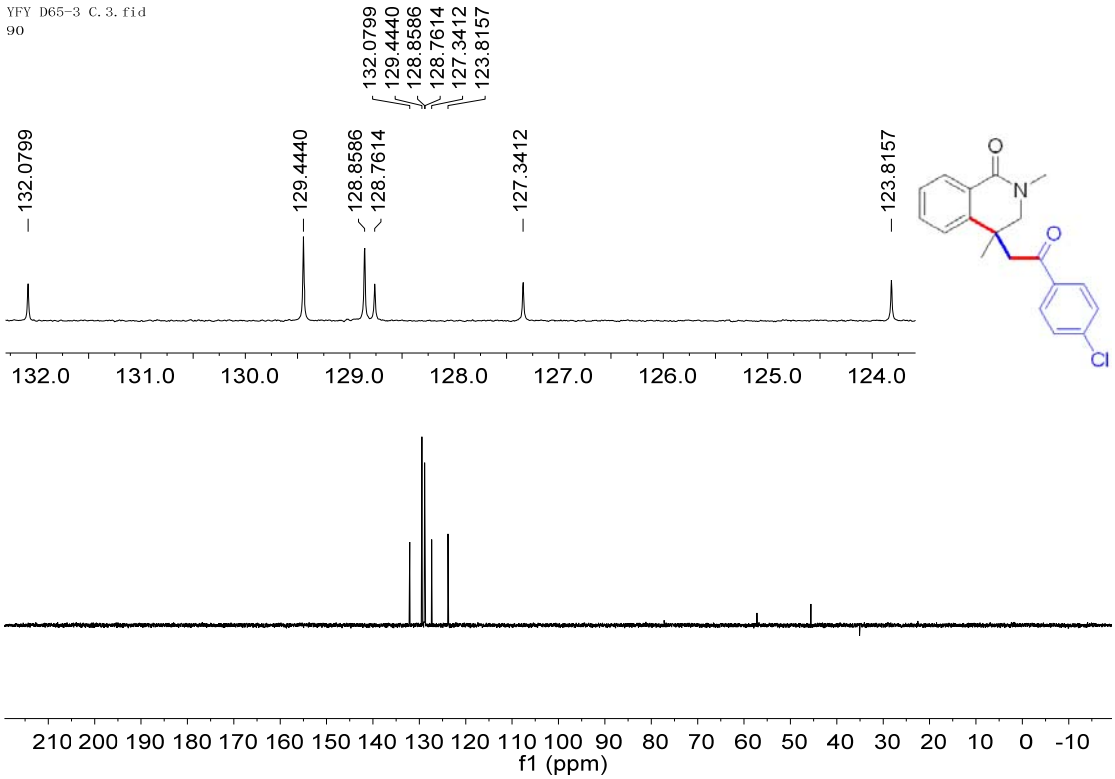
4a, ^{1}H NMR



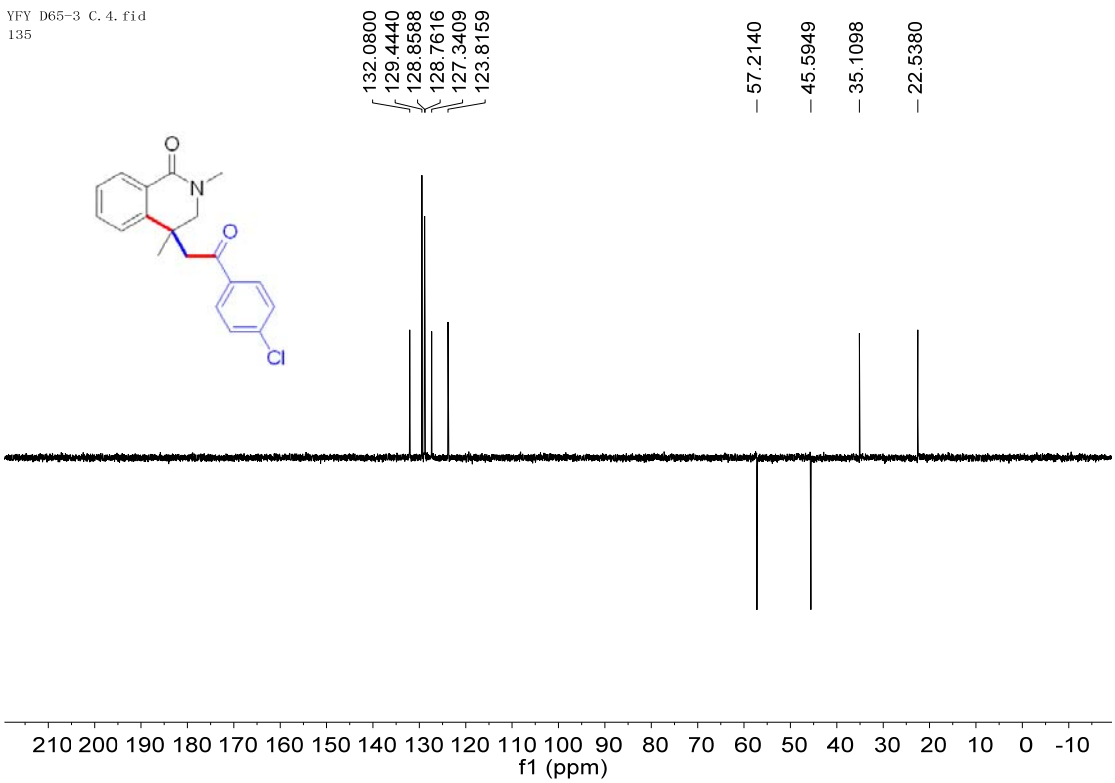
^{13}C NMR



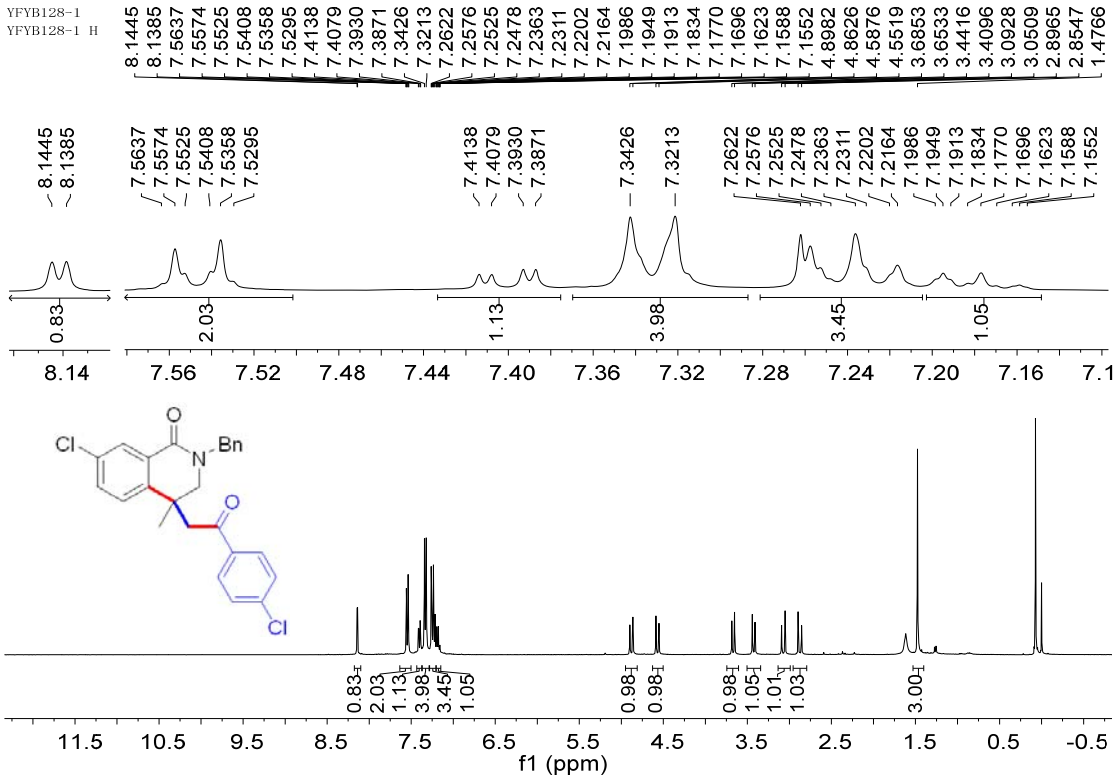
DEPT 90



DEPT 135



4b, ^{1}H NMR



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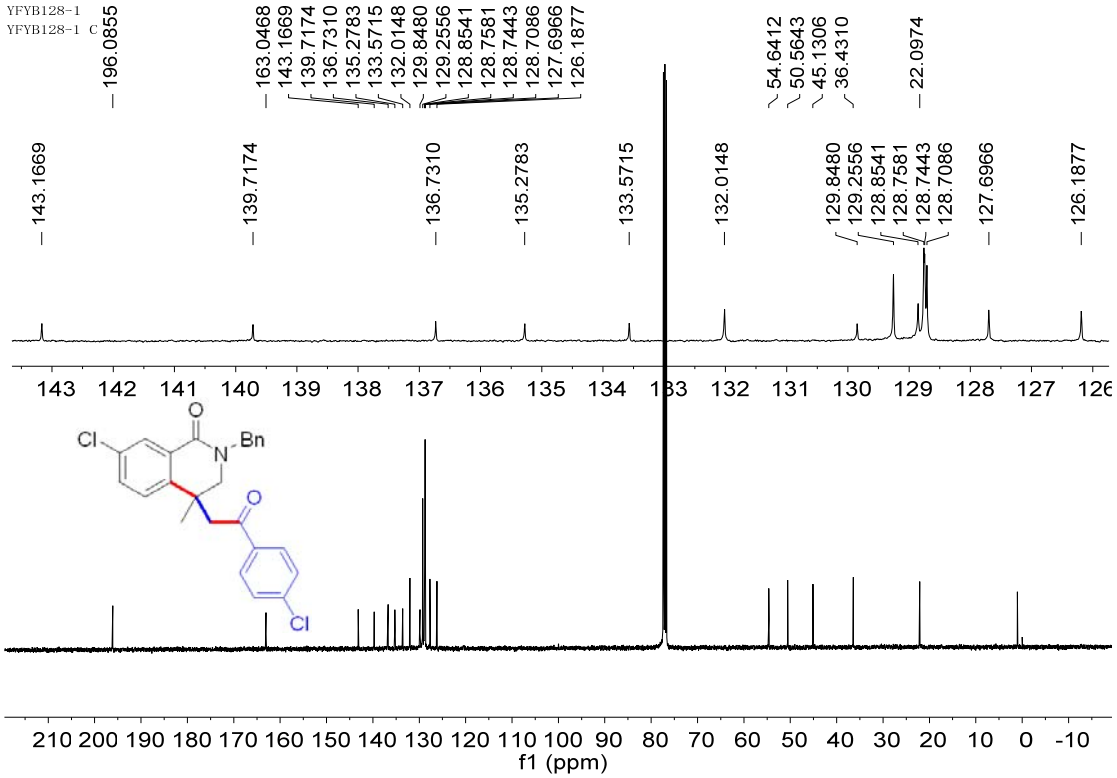

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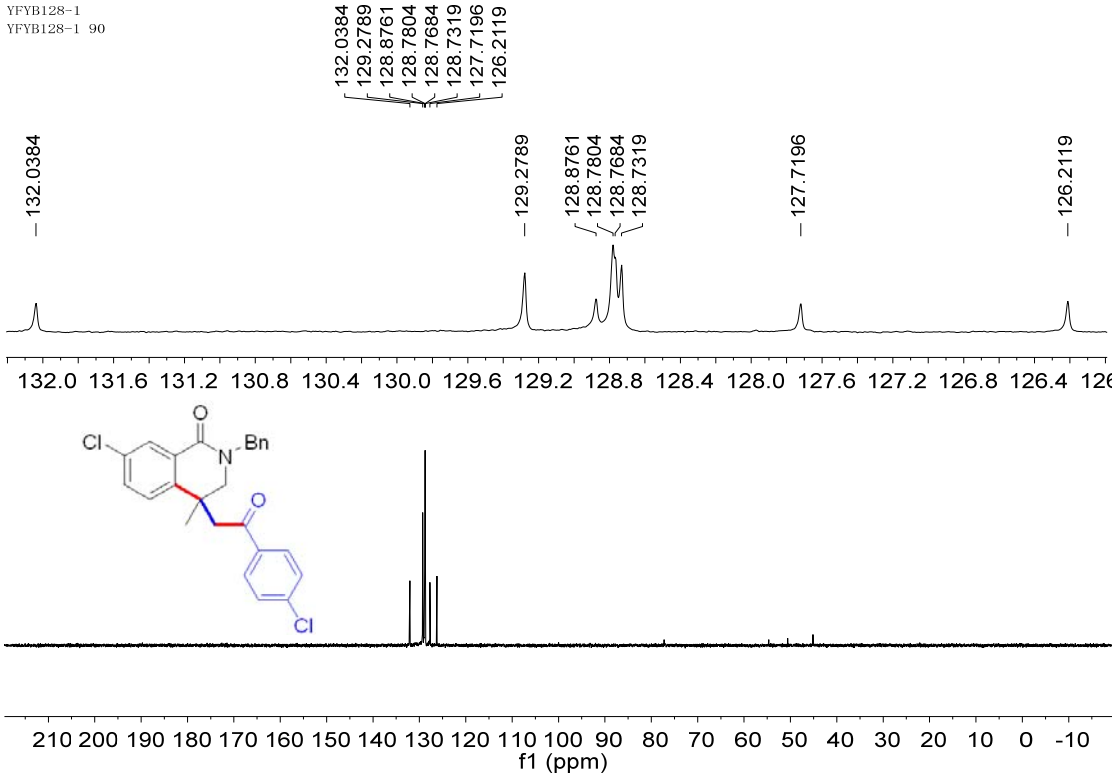

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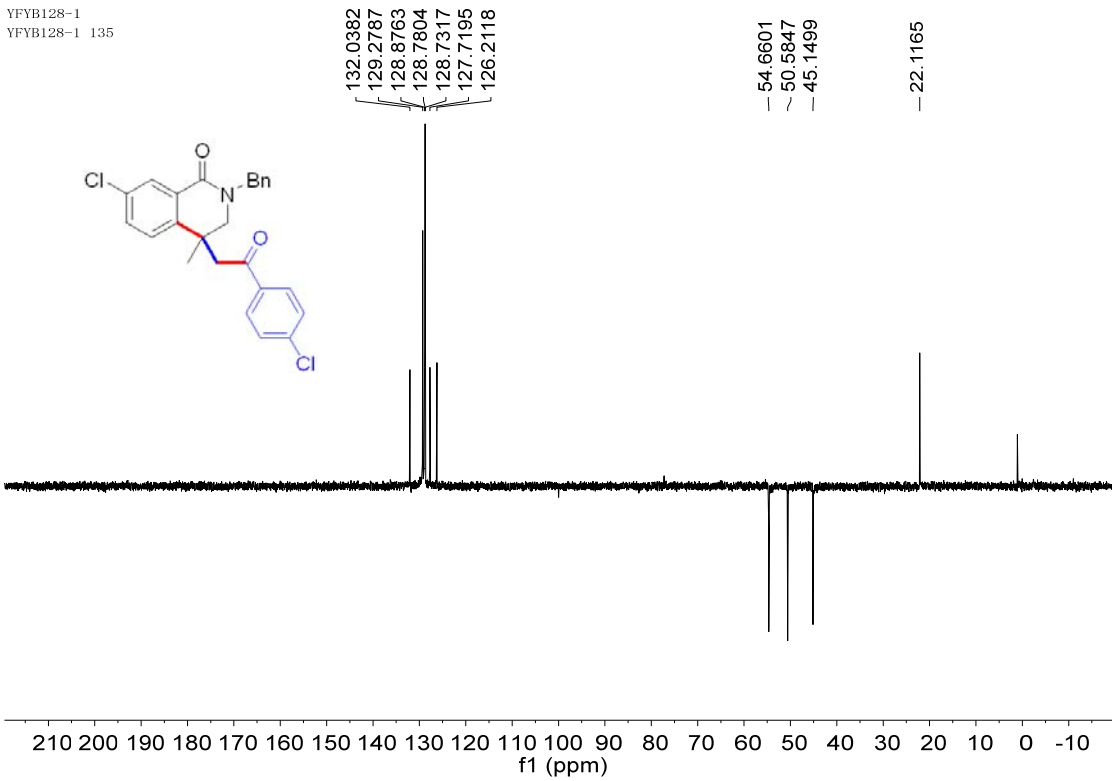
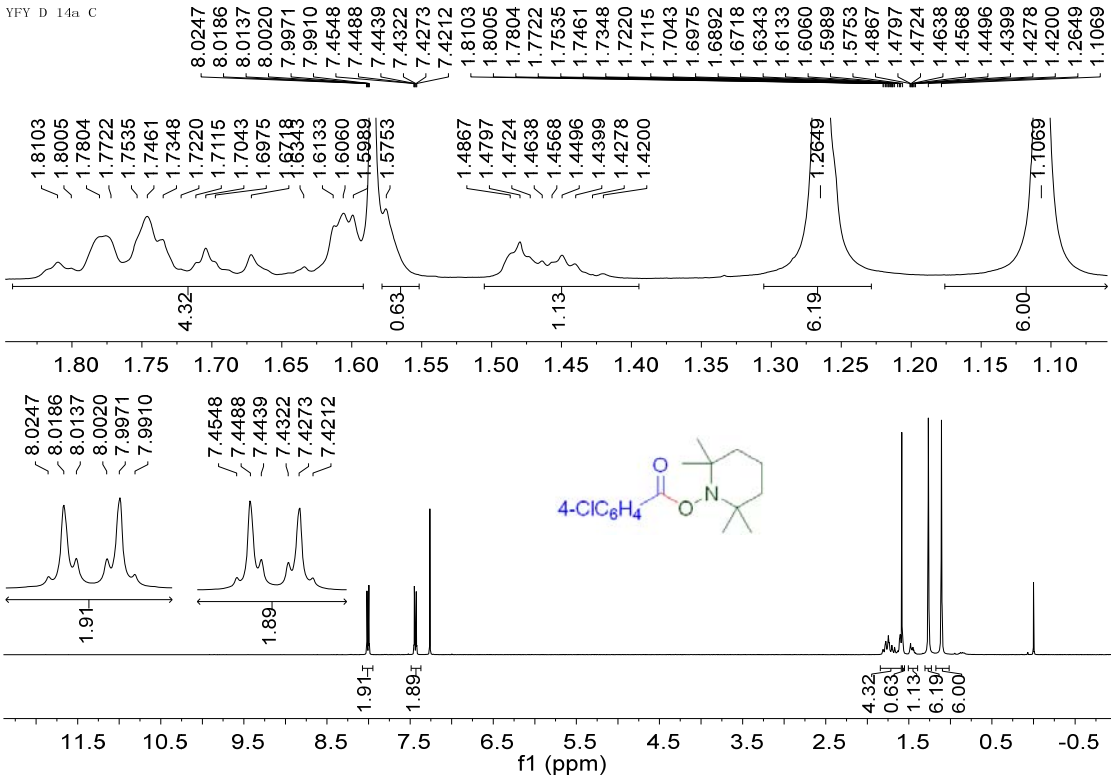


5a, ^{1}H NMR



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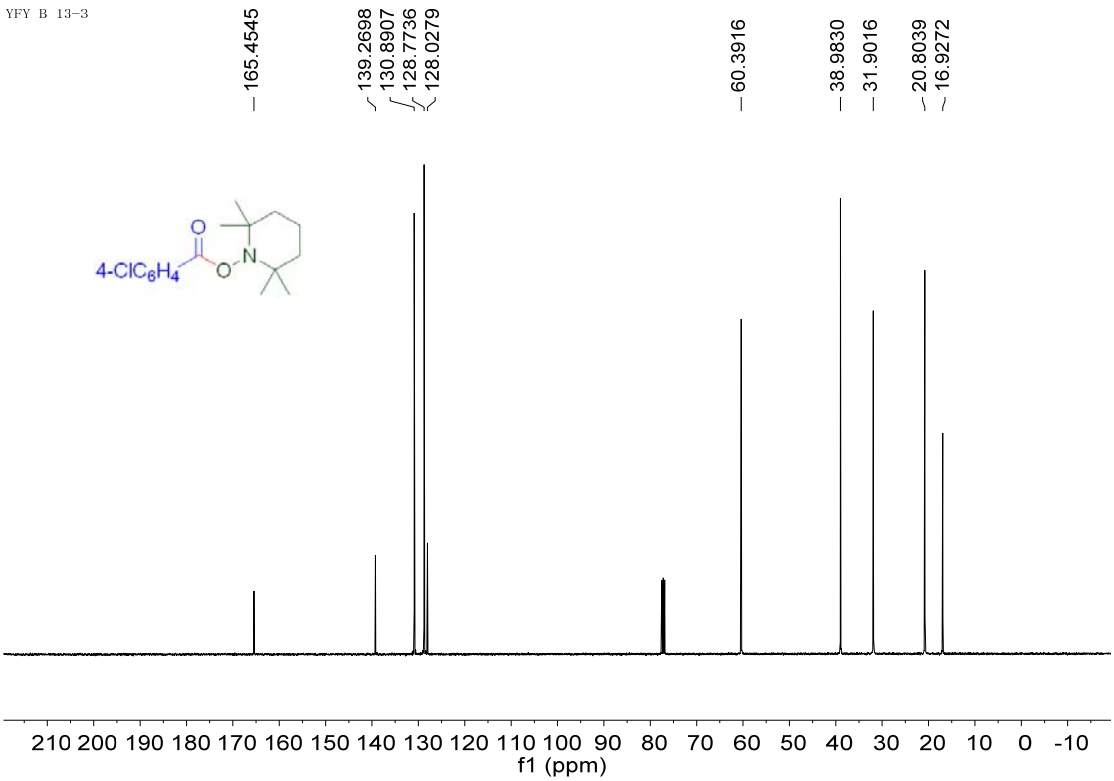

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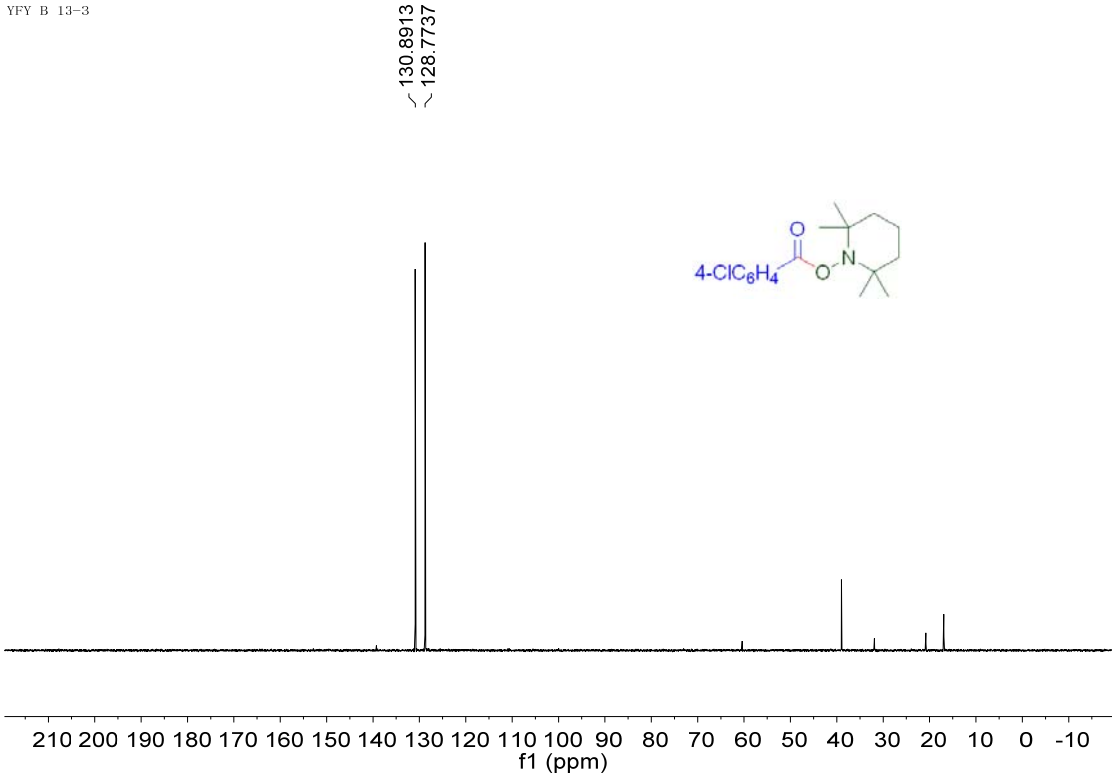

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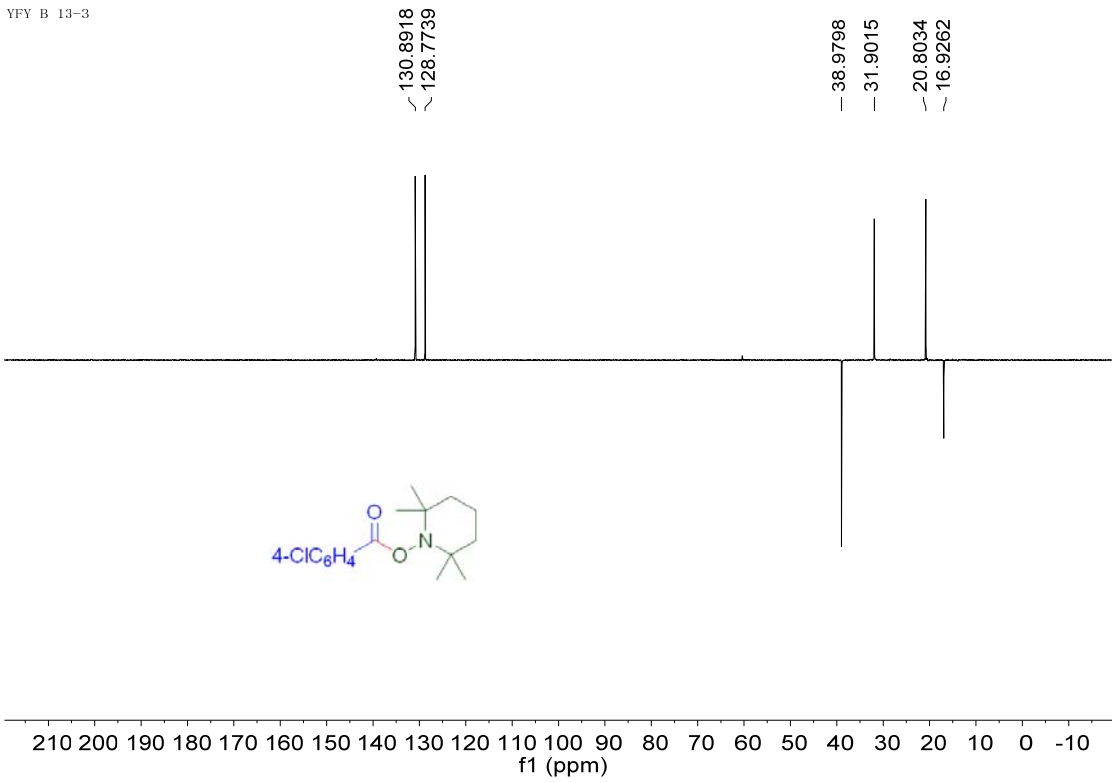
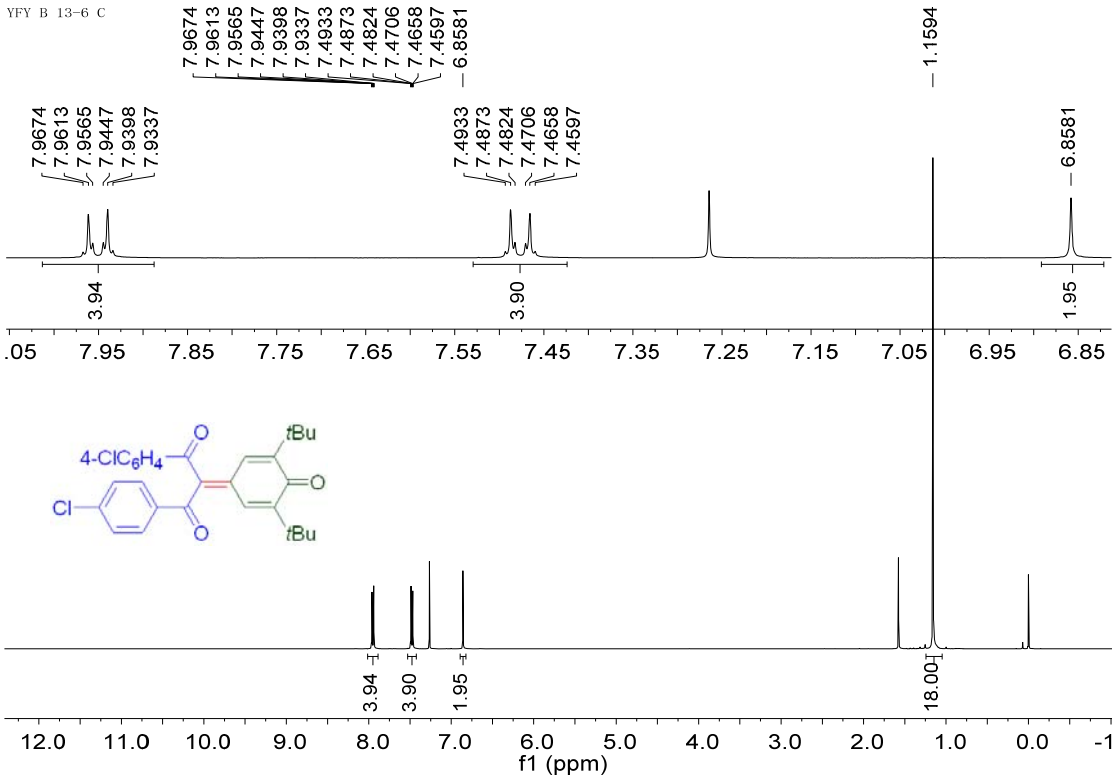
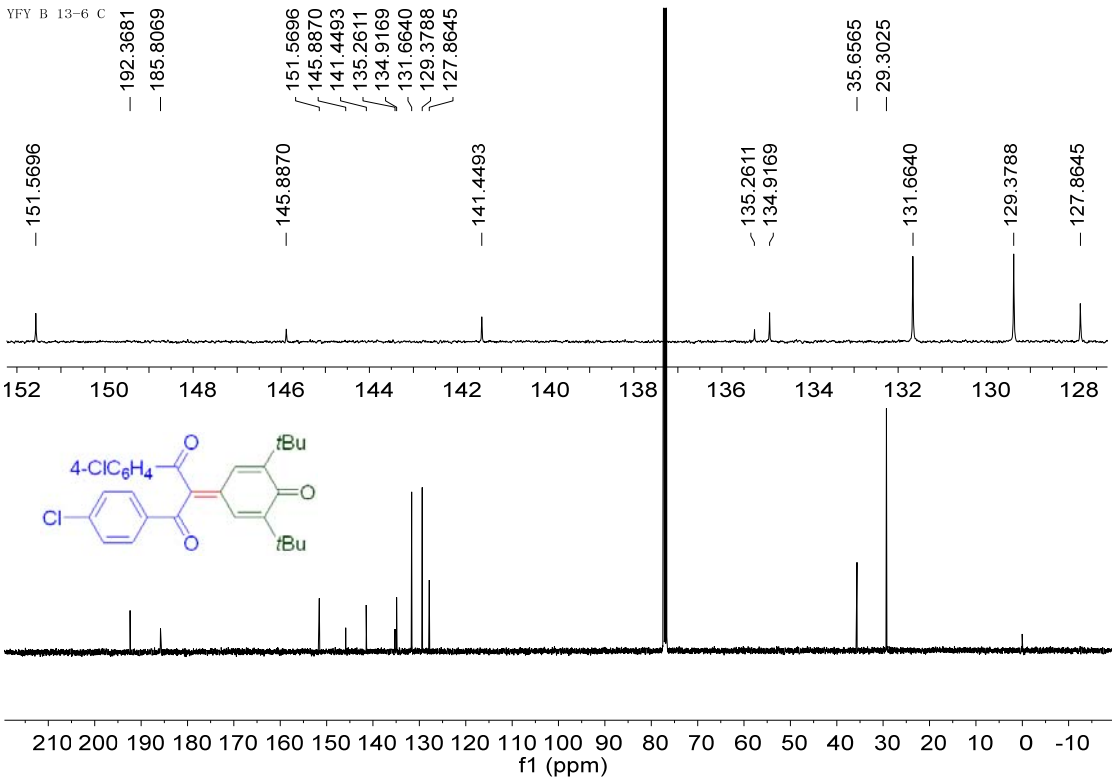


5b, ^{1}H NMR



^{13}C NMR



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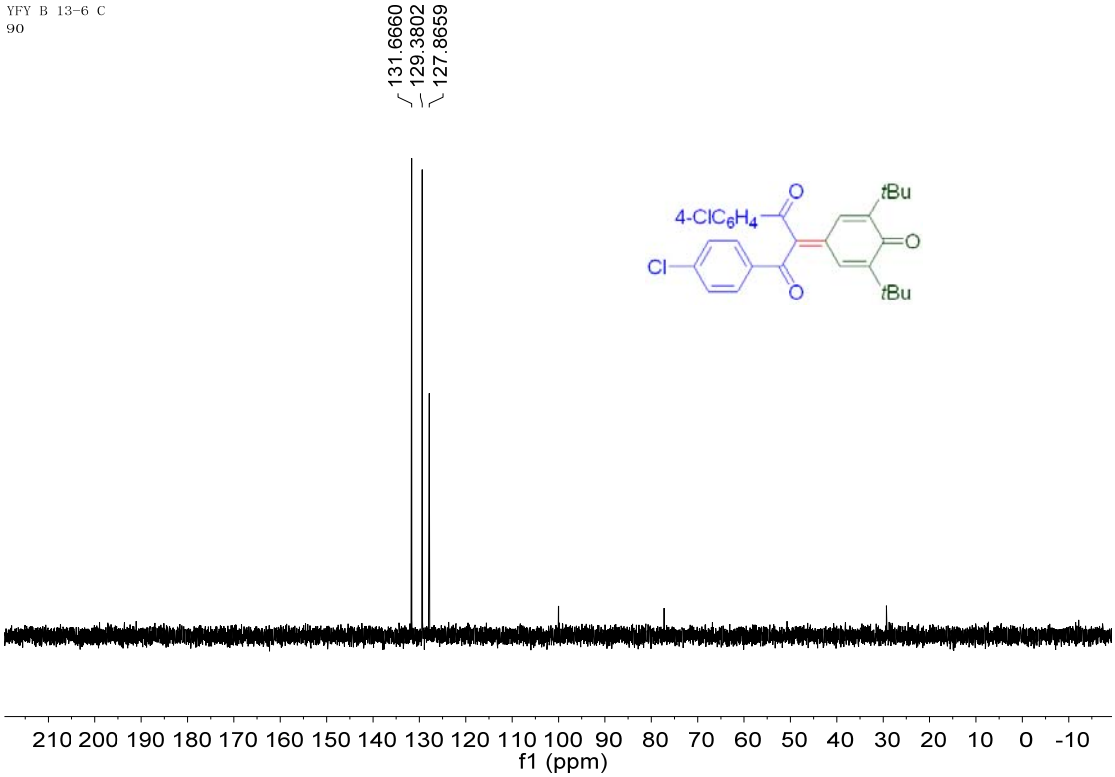

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