Supporting Information

Photo-induced [2+2+n] Radical Cascade for the Synthesis of Alkylated/Spirocyclic Polycyclic Quinolinone via Iron-Catalyzed Decarboxylation

Zhuoheng Song,[a] Jiawen Yin,[a] Jinrui Bai,[a] Dan Qi,[a] Lin Guo,[a] Chao Yang,[a,*] and Wujiong Xia[a,b,*]

[a] State Key Lab of Urban Water Resource and Environment, School of Science, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, People's Republic of China
E-mail: xyyang@hit.edu.cn; xiawj@hit.edu.cn
[b] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, People's Republic of China

Table Content

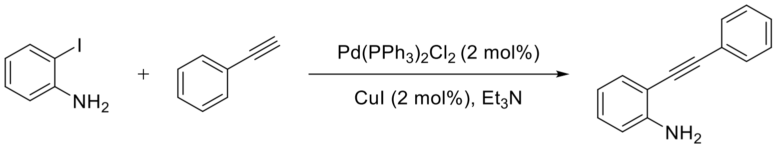
1 General Information

Unless otherwise mentioned, all reagents were purchased from commercial sources and used as received. The visible-light mediated reactions were performed on WPTEC-1020L instruments which are purchased from WATTCAS, China. All yields of products refer to the isolated yields after chromatography. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker AV-400 spectrometer or a Quantum-I Plus 400 in $CDCl_3$. For ^{1}H NMR, $CDCl_3$ ($\delta = 7.26$ ppm) or tetramethylsilane (TMS, $\delta = 0$ ppm) serves as the internal standard; for ^{13}C NMR, $CDCl_3$ ($\delta = 77.16$ ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration. GC analysis was performed on a 7890B/Agilent, while GC-MS analysis was performed on a 7890A-5975C/Agilent. HRMS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization. NMR yields of the screening part were calculated using 1,3,5-trimethoxybenzene as the internal standard. All yields of products refer to the isolated yields after chromatography.

2 General Synthetic Procedure

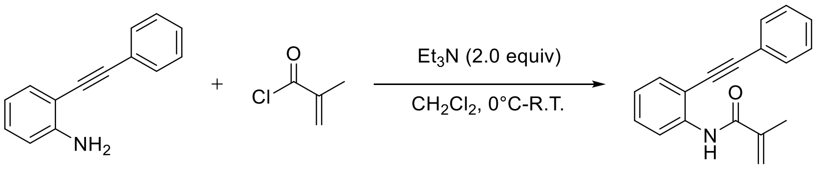
2.1 General procedure for synthesis of N-methyl-N-(2-(phenylethynyl)phenyl)methacrylamide

It is necessary to synthesize appropriate 1,7-enyne compounds as substrates. According to the synthesis steps published by Nishida et al., a suitable 1,7-enyne was prepared in three steps on a gram scale starting from the inexpensive commercially available reagent orthoiodoaniline. The specific synthesis method takes the synthesis pathway of substrate **1a** as an example.



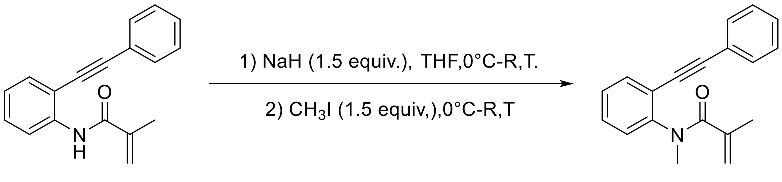
Scheme S1. Synthesis of 2-(phenylethynyl)aniline

Step one, add ortho iodoaniline (1.10 g, 5 mmol), Pd $(PPh_3)_2Cl_2$ (70.2 mg, 2 mol%), CuI (19.1 mg, 2 mol%) to a 100 mL round bottom flask equipped with a magnetic stirrer, and then add dry triethylamine as a solvent (20 mL), After stirring evenly, slowly add phenylacetylene (7.5 mmol, 1.5 equiv) dropwise to the reaction system and stir at room temperature for 8 hours. After confirming the complete consumption of raw materials through TLC detection, the reaction mixture was filtered through a short silica gel column, washed with ethyl acetate solvent, and the organic phase was collected and concentrated under reduced pressure. The crude product was completely converted and can be directly put into the next reaction step without purification.



Scheme S2. Synthesis of N-(2-(phenylethynyl)phenyl)methacrylamide

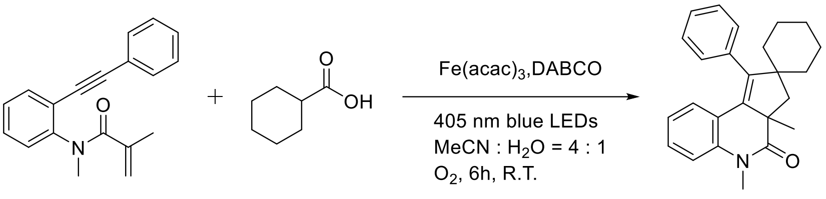
Step two, add the crude product obtained in step one into a 100 mL round bottom flask equipped with a magnetic stirrer, and then add dry triethylamine (2.0 equiv), Then add dry CH_2Cl_2 solvent (20 mL) to the reaction flask. Subsequently, the reaction flask was placed in an ice water bath. After the reaction system cooled to 0 ℃, methacryloyl chloride (10 mmol, 2.0 equiv) was slowly added dropwise to the reaction system. After the dropwise addition was complete, the ice water bath was removed to gradually restore the reaction system to room temperature, and the mixture was stirred for 12 hours. After the reaction is complete, filter the reaction mixture through a short silica gel column, wash with ethyl acetate solvent, collect the organic phase, and concentrate under reduced pressure to obtain the crude intermediate product. The crude intermediate product can be directly put into the next reaction step without purification.



Scheme S3. Synthesis of N-methyl-N-(2-(phenylethynyl)phenyl)methacrylamide

Step three, at 0 ℃, dissolve the crude intermediate product obtained from the first step reaction in THF (20 mL), add a magnetic stirrer and start stirring. After the solid is completely dissolved, cool the reaction system in an ice water bath to 0 ℃. Slowly add 60% NaH (300 mg, 7.5 mmol, 1.5 times equivalent) in batches and stir for 30 minutes. Then add iodomethane (1.07 g, 7.5 mmol, 1.5 times equivalent), and remove the ice water bath to gradually restore the reaction system to room temperature. After stirring for 8 hours, the reaction mixture was concentrated under reduced pressure to remove the THF solution. Then quench the reaction with water (20 mL) and extract the aqueous phase three times with EA (10 mL x 3). The merged organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The concentrated crude product was purified by column chromatography gradient elution using PE/EA as the developing agent, VPE:VEA = 10: 1-3:1), a yellow solid reaction template substrate **1a** N-methyl-N - (2-(phenylacetynyl) phenyl) methacrylamide (1.10g, 4mmol) was obtained, with a total yield of 75% in the three-step reaction. Most substrates follow the reaction pathway of **1a**.

2.2 General procedure for preparation of alkyl/spirocyclic polycyclic quinolinone



Scheme S4. Procedure for preparation of 3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one

Add a magnetic stirrer to a 10mL quartz light tube dried in an oven, and then sequentially add substrate **1a** (0.1 mmol, 27.5mg), free radical precursor cyclohexanecarboxylic acid **2a** (0.5 mmol, 5 equiv), a mixed solvent of acetonitrile and water in a volume ratio of 4:1 (1.0 mL), photocatalyst acetylacetonate iron (10 mol%, 3.5 mg), DABCO (50 mol%, 2 mg). Place the light tube in the light irradiation slot of the photoreactor, insert a balloon filled with O_2, seal it and ventilate it five times to fill the reaction tube with O_2, and then start to irradiate it with a 10W 405 nm LED light reaction chip. During the irradiation process, use the fan and water cooling device of the photoreactor to cool the tube. Maintain the temperature near room temperature while keeping the O_2 balloon continuously supplying oxygen to the reaction system. After 6 hours of reaction, stop the light irradiation and remove the reaction tube. Concentrate the reaction solution under reduced pressure, remove the solvent MeCN, add water (10mL), and extract three times with EA (5 mL * 3 ·). Collect the organic phase, dry it, and concentrate under reduced pressure. The concentrated crude product was purified by column chromatography gradient elution using PE/EA as the developing agent, VPE:VEA = 20: 1-5:1), a yellow solid 3a', 5' - dimethyl-1 '- phenyl-3', 3a '- dihydrospiro [cyclohexane-1,2' - cyclopentanol [c] quinoline] -4 '(5'*H*) - one (28.9 mg) was obtained with a yield of 81%.

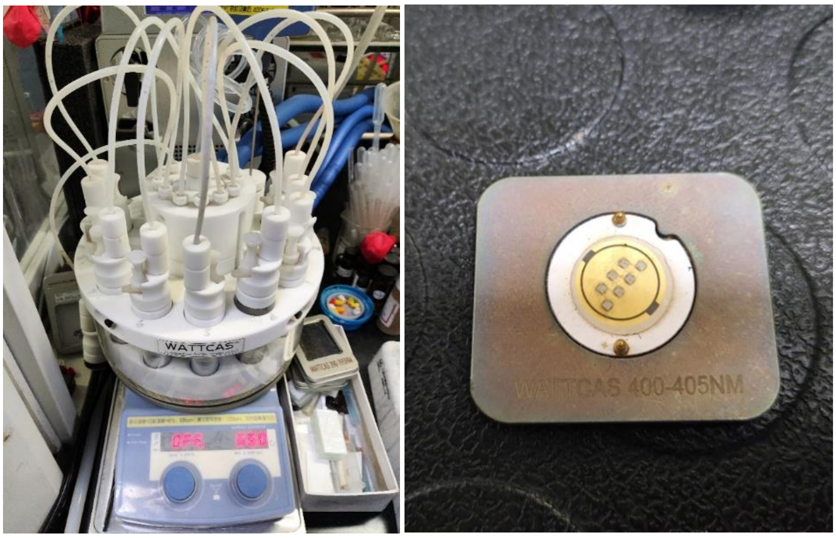


Figure S1. Photo reactor device and 405 nm 10 W blue LED chip

2.3 General procedure for gram-scale flow reaction

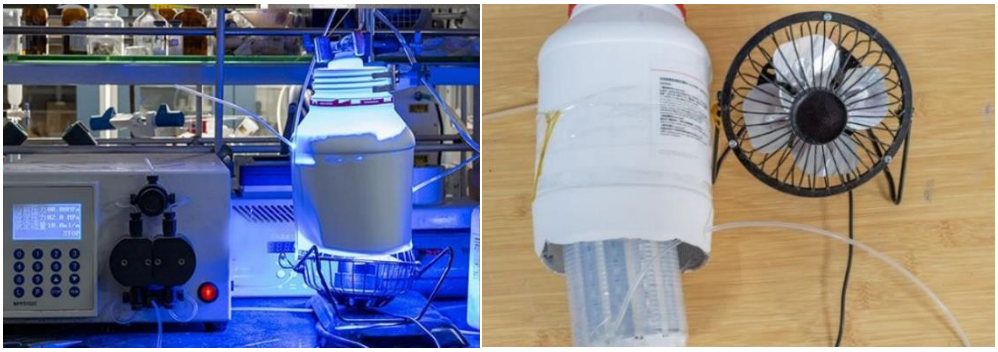
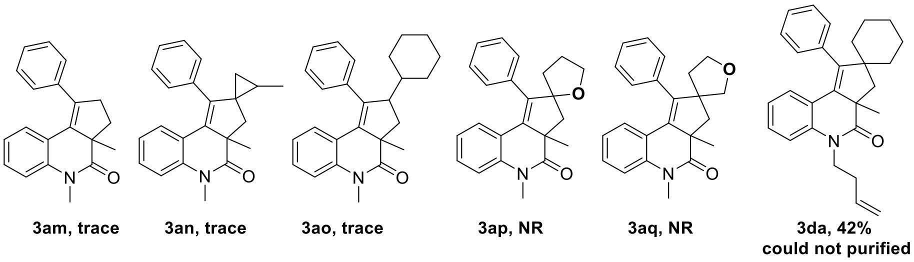


Figure S2. Example figure of gram scale flow reactor of photoreactions

The construction of the photoreaction device followed Qi, et al[2]. An oven dried 200 mL round bottom flask was charged with a stir bar. Substrate **1a** (1.38 g, 5 mmol, 1.0 equiv.), **2a** (25 mmol, 5.0 equiv.), Fe(acac)$_3$ (10 mol%), DABCO (50 mol%) and $Na_2S_2O_8$ (2 equiv) was added with 40 mL MeCN and 10 mL water. The reaction mixture was pumped into PTFE transparent coil and irradiated with commercially available 410 nm blue light bulbs and flow pump for 6 hours. After the reaction was complete, all reactants were filtered through a short silica gel column, washed with EtOAc, and the crude product was concentrated under reduced pressure, then purified by column chromatography (1:10 to 1:3 EtOAc : petroleum ether). Affording product γ-lactam **3aa** (62% yield) as a yellow solid.

2.4 Typical unsuccessful reaction samples



Scheme S5. Typical unsuccessful reaction samples

3 Optimization of Reaction Conditions

Table 1S. Optimization of solvent.[a]

Entry	Solvent	Yield (%) [b]
1	MeCN	24
2	MeCN:Water = 2:1	19
3	MeCN:Water = 4:1	34
4	MeCN:Water = 9:1	25
5	DMSO	Trace
6	DMSO:Water = 4:1	18
7	DMSO:MeCN = 1:1	Trace
8	Acetone	Trace
9	MeCN:Acetone = 1:1	20
10	DMF	Trace

a) Reaction conditions: substrate **1a** (0.2 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), $Fe(OAc)_2OH$ (10 mol%), DBU (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under Air. 2.0 mL solvent added. b) yield detected by GC-MS.

Table 2S. Optimization of photo catalyst.[a]

Entry	Photocatalyst	Yield (%) [b]
1	$Fe(OH)(OAc)_2$	34
2	$Fe(acac)_3$	39
3	$Fe(OH)\ (OAc)_2$+LiCl	25
4	$FeCl_3$	Trace
5	$Fe(NO_3)_3$	24
6	$FeCl_2$	Trace
7	$FeBr_3$	31
8	Fac-Ir(ppy)$_3$	N.R.
9	Mes-Acr$^+$ClO$_4^-$	N.R.

a) Reaction conditions: substrate **1a** (0.2 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), Photo cat (10 mol%), DBU (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under Air, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS.

Table 3S. Optimization of Oxidant.[a]

Entry	Possible Oxidant	Atmosphere	Yield (%) [b]
1	O_2 in air	Air	39
2	O_2	O_2	51
3	$Na_2S_2O_8$	N_2	46

4	$K_2S_2O_8$	N_2	44
5	$(NH_4)_2S_2O_8$	N_2	33
6	NFSI	N_2	trace
7	None	N_2	trace
8	PhSSPh	N_2	trace

a) Reaction conditions: substrate **1a** (0.2 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), $Fe(acac)_3$ (10 mol%), DBU (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under Air, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS.

Table 4S. Optimization of substrate and reactant dosage.[a]

Entry	1,7-enyne（mmol）	Acid（mmol）	Yield (%) [b]
1	0.2	1	51
2	0.2	2	48
3	0.2	3	33
4	0.1	0.5	55
5	0.1	1	45
6	0.3	1.5	48

a) Reaction conditions: substrate **1a**, Cyclohexanecarboxylic acid (**2a**), $Fe(acac)_3$ (10 mol%), DBU (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under O_2 atmosphere, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS.

Table 5S. Optimization of base.[a]

Entry	Base	Yield (%) [b]
1	None	trace
2	DBU	55
3	DABCO	58
4	Quinuclidine	48
5	Et_3N	trace
6	LDA	34
7	Na_2CO_3	30
8	Cs_2CO_3	37
9	K_2HPO_4	22

a) Reaction conditions: substrate **1a** (0.1 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), $Fe(acac)_3$ (10 mol%), base (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under O_2 atmosphere, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS.

Table 6S. Optimization of base dosage.[a]

Entry	DABCO（equiv.）	Yield (%) [b]
1	0.5	58
2	1.0	57
3	1.5	53
4	0.2	51
5	0.1	36

a) Reaction conditions: substrate **1a** (0.1 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), Fe(acac)$_3$ (10 mol%), DABCO (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under O_2 atmosphere, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS.

Table 7S. Optimization of light resourse.[a]

Entry	Light Source	Yield (%) [b]
1	380 nm	30
2	390 nm	58
3	400 nm	62
4	405 nm	70
5	410 nm	68
6	420 nm	52
7	460 nm	n.d.

a) Reaction conditions: substrate **1a** (0.1 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), Fe(acac)$_3$ (10 mol%), DABCO (0.5 equiv.), 10 W 390 nm LEDs at room temperature for 12 hours under O_2 atmosphere, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS.

Table 9S. Optimization of react time and additives.[a]

Entry	Other changes	Yield (%) [b]
1	12 h react time	70
2	16 h react time	50
3	20 h react time	28
4	24 h react time	Trace
5	8 h react time	75
6	6 h react time	81[c]
7	4 h react time	57
8	2 h react time	30
9	7 h react time	79[c]
10	60°C temp	60
11	5 W radiation strength	36

a) Reaction conditions: substrate **1a** (0.1 mmol), Cyclohexanecarboxylic acid (**2a**) (5.0 equiv.), Fe(acac)$_3$ (10 mol%), DABCO (0.5 equiv.), 10 W 405 nm LEDs at room temperature under O_2 atmosphere, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) yield detected by GC-MS. c) isolated yield.

.

Table 10S. Verifying of optimalized conditions.[a]

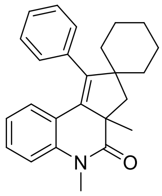
Entry	Variation from standard conditions[b]	Yield (%) [c]
1	None	81[d]
2	Fe(OH)(OAc)$_2$ as photo catalyst	68
3	Fac-Ir(ppy)$_3$ as photo catalyst	N.R.
4	Mes-Acr$^+$ClO$_4^-$ as photo catalyst	N.R.
5	390 nm LED	69
6	410 nm LED	78[d]
7	DMSO : H_2O = 2 : 1 as solvent	68
8	DMSO : H_2O = 9 : 1 as solvent	75

9	DBU as base	78[d]
10	Cs_2CO_3 as base	46
11	3 equiv. **2a**	54
12	10 equiv. **2a**	72[d]
13	Open to air	51
14	No Photo Catalyst	N.R.
15	React in dark	N.R.

a) Standard reaction conditions: substrate **1a** (0.1 mmol), Cyclohexanecarboxylic acid **2a** (5.0 equiv.), Fe(acac)$_3$ (10 mol%), DABCO (0.5 equiv.), 10 W 405 nm LEDs at room temperature for 6 hours under O_2 atmosphere, 2.0 mL mix solvent (MeCN : Water = 4 : 1) added. b) Each entry only changed the condition represented. c) yield detected by GC-MS. d) isolated yield.

4 Product Characterization

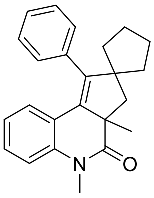
3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'*H*)-one (**3aa**)



3aa

Yellow solid (81% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, J = 6.6 Hz, 3H), 7.18 – 7.06 (m, 3H), 6.97 (d, J = 8.2 Hz, 1H), 6.68 (d, J = 4.4 Hz, 2H), 3.40 (s, 3H), 2.46 (d, J = 13.8 Hz, 1H), 2.28 (d, J = 13.8 Hz, 1H), 1.71 – 1.64 (m, 3H), 1.55 – 1.38 (m, 3H), 1.32 (s, 3H), 1.27 – 0.85 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.05, 148.84, 139.84, 136.90, 129.55, 128.24, 127.93, 127.58, 127.12, 122.28, 114.75, 52.28, 51.96, 43.63, 37.70, 35.94, 30.05, 27.37, 25.48, 23.55, 22.44. HRMS (ESI, m/z): calcd for [M+H]$^+$ 358.2165, found 358.2166.

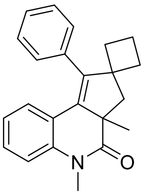
3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclopentane-1,2'-cyclopenta[c]quinolin]-4'(5'*H*)-one (**3ab**)



3ab

Yellow solid (81% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (q, J = 7.4, 6.7 Hz, 3H), 7.19 – 7.10 (m, 3H), 6.98 (d, J = 8.2 Hz, 1H), 6.78 – 6.66 (m, 2H), 3.40 (s, 3H), 2.44 (d, J = 13.4 Hz, 1H), 2.15 (d, J = 13.4 Hz, 1H), 1.82 – 1.72 (m, 2H), 1.62 (ddd, J = 18.3, 8.0, 4.1 Hz, 3H), 1.55 – 1.38 (m, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.96, 139.83, 136.96, 134.00, 129.49, 128.36, 127.98, 127.50, 127.17, 122.31, 121.70, 114.81, 58.85, 52.09, 48.91, 39.04, 38.48, 30.00, 26.57, 24.29, 24.00. HRMS (ESI, m/z): calcd for [M+H]$^+$ 344.2009, found 344.2013.

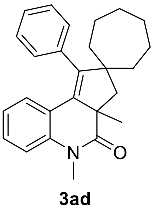
3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclobutane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ac**)



3ac

Yellow solid (79% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.33 (m, 3H), 7.25 – 7.21 (m, 2H), 7.15 (td, J = 7.9, 7.3, 1.7 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.80 (dd, J = 7.8, 1.6 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H), 3.39 (s, 3H), 2.56 (d, J = 5.5 Hz, 2H), 2.37 – 2.29 (m, 2H), 2.11 – 2.01 (m, 2H), 2.01 – 1.85 (m, 3H), 1.54 (ddd, J = 10.2, 6.1, 4.5 Hz, 1H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.61, 139.99, 137.15, 129.06, 128.59, 128.15, 127.47, 127.32, 122.35, 121.36, 114.90, 54.20, 52.02, 50.24, 35.09, 31.93, 29.93, 25.80, 25.28, 18.44, 16.77. HRMS (ESI, m/z): calcd for [M+H]$^+$ 330.1852, found 330.1855.

3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cycloheptane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ad**)

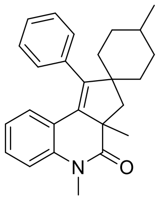


3ad

Yellow solid (61% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dd, J = 5.0, 2.8 Hz, 3H), 7.13 (td, J = 5.3, 2.9 Hz, 3H), 6.97 (d, J = 8.2 Hz, 1H), 6.72 – 6.65 (m, 2H), 3.39 (s, 3H), 2.46 (d, J = 13.7 Hz, 1H), 2.24 (d, J = 13.7 Hz, 1H), 2.07 – 1.87 (m, 3H), 1.52 – 1.44 (m, 4H), 1.40 (dd, J = 18.5, 7.4 Hz, 4H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-

d) δ 149.66, 139.93, 137.30, 129.44, 128.29, 127.87, 127.63, 127.10, 122.26, 114.74, 54.76, 51.79, 45.84, 40.92, 40.34, 30.02, 29.75, 29.00, 28.70, 26.41, 24.43, 23.81. HRMS (ESI, m/z): calcd for $[M+H]^+$ 372.2322, found 372.2318.

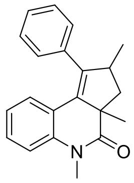
3a',4,5'-trimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ae**)



3ae

Yellow solid (75% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (td, J = 6.1, 2.9 Hz, 3H), 7.13 (dq, J = 9.0, 4.7 Hz, 3H), 6.97 (d, J = 8.2 Hz, 1H), 6.69 (d, J = 4.4 Hz, 2H), 3.40 (s, 3H), 2.44 (d, J = 13.8 Hz, 1H), 2.31 (d, J = 13.8 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.91 – 1.67 (m, 4H), 1.45 (d, J = 3.8 Hz, 4H), 1.32 (s, 4H), 0.76 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.06, 148.91, 137.03, 129.43, 128.29, 127.91, 127.66, 127.12, 122.27, 121.87, 114.73, 52.43, 51.88, 43.71, 31.68, 30.29, 30.04, 28.89, 27.82, 27.28, 26.11, 17.23. HRMS (ESI, m/z): calcd for $[M+H]^+$ 372.2322, found 372.2323.

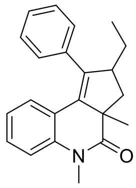
2,3a,5-trimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (**3af**)



3af

Yellow oil (42% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (qd, J = 7.2, 5.6, 2.7 Hz, 3H), 7.27 – 7.18 (m, 3H), 7.02 (dt, J = 7.5, 3.4 Hz, 2H), 6.79 (d, J = 7.5 Hz, 1H), 3.42 (s, 3H), 3.11 – 2.91 (m, 2H), 1.82 (dd, J = 11.8, 3.2 Hz, 1H), 1.37 (s, 3H), 1.35 (d, J = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.87, 145.06, 139.81, 133.72, 128.63, 128.43, 128.16, 127.48, 127.24, 122.35, 121.89, 114.83, 53.53, 44.98, 41.76, 30.05, 29.75, 27.39, 22.11. HRMS (ESI, m/z): calcd for $[M+H]^+$ 304.1696, found 304.1693.

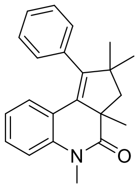
2-ethyl-3a,5-dimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (**3ag**)



3ag

Yellow oil (40% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dtt, J = 14.1, 7.3, 3.7 Hz, 3H), 7.22 – 7.15 (m, 3H), 7.03 – 6.91 (m, 2H), 6.75 (t, J = 7.5 Hz, 1H), 3.40 (d, J = 1.6 Hz, 3H), 3.27 – 2.77 (m, 2H), 2.40 – 2.05 (m, 1H), 1.89 (d, J = 13.2 Hz, 1H), 1.31 (d, J = 1.6 Hz, 3H), 0.98 (td, J = 7.3, 1.6 Hz, 3H), 0.86 – 0.76 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ13C NMR (101 MHz, Chloroform-d) δ 176.77, 144.36, 137.92, 128.89, 128.57, 128.36, 128.11, 127.38, 127.21, 122.34, 114.78, 53.60, 52.47, 37.67, 30.10, 29.94, 29.75, 27.79, 27.44, 26.40, 12.62, 11.19. HRMS (ESI, m/z): calcd for $[M+H]^+$ 318.1852, found 318.1854.

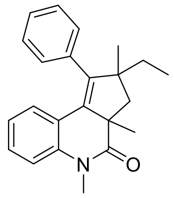
2,2,3a,5-tetramethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (**3ah**)



3ah

Yellow oil (86% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 3H), 7.19 – 7.09 (m, 3H), 6.98 (d, J = 8.3 Hz, 1H), 6.73 (dt, J = 10.3, 4.7 Hz, 2H), 3.40 (s, 3H), 2.58 (d, J = 13.6 Hz, 1H), 2.08 (d, J = 13.6 Hz, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) 175.91, 148.23, 139.96, 136.81, 132.92, 129.12, 128.36, 128.01, 127.58, 127.17, 122.28, 114.77, 51.83, 49.60, 47.85, 30.01, 29.65, 29.26, 26.40. HRMS (ESI, m/z): calcd for $[M+H]^+$ 318.1852, found 318.1852.

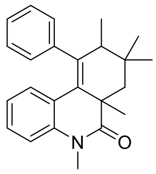
2-ethyl-2,3a,5-trimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (**3ai**)



3ai

Yellow oil (83% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.34 (m, 3H), 7.26 – 7.21 (m, 2H), 7.19 – 7.11 (m, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.81 (dd, J = 7.7, 1.6 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H), 3.39 (s, 3H), 2.57 (d, J = 6.4 Hz, 2H), 2.54 – 2.45 (m, 1H), 2.27 – 2.15 (m, 1H), 2.13 – 2.01 (m, 2H), 1.98 – 1.83 (m, 1H), 1.83 – 1.74 (m, 1H), 1.59 – 1.49 (m, 1H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.58, 140.02, 137.16, 134.06, 129.06, 128.60, 128.15, 127.47, 127.32, 127.15, 122.33, 121.35, 114.89, 54.20, 52.02, 50.25, 35.10, 31.94, 29.90, 25.82, 16.77.. HRMS (ESI, m/z): calcd for $[M+H]^+$ 332.2009, found 332.2012.

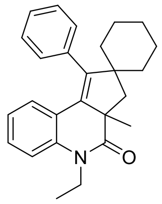
5,6a,8,8,9-pentamethyl-10-phenyl-6a,7,8,9-tetrahydrophenanthridin-6(5H)-one (**3aj**)



3aj

Yellow oil (65% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (ddd, J = 12.5, 7.3, 5.6 Hz, 3H), 7.15 – 6.99 (m, 3H), 6.89 (dd, J = 8.2, 1.2 Hz, 1H), 6.76 (dd, J = 7.7, 1.6 Hz, 1H), 6.61 (td, J = 7.5, 1.1 Hz, 1H), 3.39 (s, 3H), 2.79 (dd, J = 14.2, 1.8 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.26 (s, 3H), 1.05 (s, 3H), 0.99 (d, J = 2.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.27, 143.98, 138.76, 130.01, 128.99, 128.03, 127.15, 126.33, 125.80, 121.81, 113.53, 47.88, 42.79, 38.38, 31.89, 30.66, 27.90, 27.21, 26.90, 15.85. HRMS (ESI, m/z): calcd for $[M+H]^+$ 346.2165, found 346.2165.

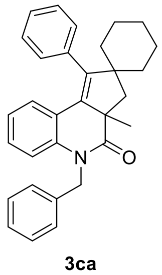
5'-ethyl-3a'-methyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ba**)



3ba

Yellow solid (83% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (td, J = 5.7, 2.7 Hz, 3H), 7.12 (ddd, J = 13.7, 7.8, 4.3 Hz, 3H), 6.98 (d, J = 8.2 Hz, 1H), 6.74 – 6.61 (m, 2H), 4.21 (dq, J = 14.2, 7.1 Hz, 1H), 3.81 (dq, J = 14.1, 7.0 Hz, 1H), 2.49 (d, J = 13.9 Hz, 1H), 2.25 (d, J = 13.8 Hz, 1H), 1.73 – 1.62 (m, 3H), 1.60 – 1.53 (m, 2H), 1.51 – 1.39 (m, 2H), 1.31 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.04 – 0.90 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ13C NMR (101 MHz, Chloroform-d) δ 175.42, 148.65, 138.77, 136.97, 129.58, 128.24, 127.96, 127.90, 127.11, 122.07, 122.03, 114.49, 52.28, 51.77, 43.36, 37.71, 37.64, 36.02, 27.19, 25.50, 23.55, 22.48, 12.73. HRMS (ESI, m/z): calcd for $[M+H]^+$ 372.2322, found 372.2326.

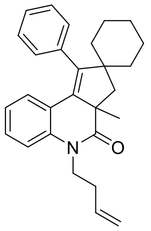
5'-benzyl-3a'-methyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ca**)



3ca

Yellow solid (82% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dt, J = 8.4, 4.2 Hz, 5H), 7.27 (d, J = 7.5 Hz, 3H), 7.16 (d, J = 6.9 Hz, 2H), 7.02 (t, J = 7.8 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 5.72 (d, J = 16.3 Hz, 1H), 4.76 (d, J = 16.3 Hz, 1H), 2.63 (d, J = 14.1 Hz, 1H), 2.36 (dd, J = 13.9, 1.8 Hz, 1H), 1.76 (d, J = 6.9 Hz, 3H), 1.71 – 1.57 (m, 3H), 1.51 (s, 3H), 1.41 (d, J = 13.0 Hz, 1H), 1.31 (td, J = 7.1, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.07, 149.10, 139.32, 137.56, 136.89, 129.59, 128.86, 128.30, 127.95, 127.67, 127.19, 127.10, 126.23, 122.42, 115.59, 52.43, 52.08, 46.70, 43.52, 37.68, 36.11, 27.48, 25.50, 23.56, 22.52. HRMS (ESI, m/z): calcd for $[M+H]^+$ 434.2478, found 434.2481.

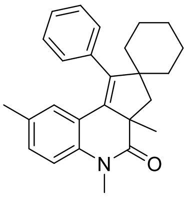
5'-(but-3-en-1-yl)-3a'-methyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'*H*)-one (**3da**)



3da

Yellow solid (42% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.09 (tt, *J* = 57.2, 5.0 Hz, 1H), 3.44 (s, 3H), 2.57 (td, *J* = 16.0, 5.0 Hz, 2H), 2.50 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.93, 173.36, 143.74, 139.68, 127.18, 125.87, 124.59, 123.13, 118.02, 115.64, 113.25, 54.01, 38.90, 38.67, 38.44, 37.48, 24.29, 21.97. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.69 (t, *J* = 16.1 Hz), -113.84 (t, *J* = 16.1 Hz). HRMS (ESI, m/z): calcd for $[M+H]^+$ 398.2478, found 398.2474.

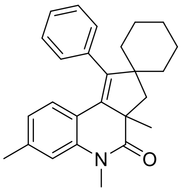
3a',5',8'-trimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'*H*)-one (**3ea**)



3ea

Yellow solid (76% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (td, J = 5.8, 2.8 Hz, 3H), 7.09 (d, J = 6.7 Hz, 2H), 6.93 (dd, J = 8.4, 2.1 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.45 (d, J = 2.1 Hz, 1H), 3.37 (s, 3H), 2.44 (d, J = 13.9 Hz, 1H), 2.28 (d, J = 13.8 Hz, 1H), 1.96 (s, 3H), 1.71 – 1.63 (m, 3H), 1.64 – 1.48 (m, 3H), 1.41 (dt, J = 13.2, 3.4 Hz, 1H), 1.31 (s, 3H), 1.16 (dd, J = 13.0, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.90, 148.58, 137.52, 137.00, 133.44, 131.54, 129.57, 128.46, 128.23, 128.16, 127.07, 121.65, 114.58, 52.22, 51.98, 43.63, 37.72, 35.95, 30.01, 27.42, 25.50, 23.57, 22.45, 20.54. HRMS (ESI, m/z): calcd for $[M+H]^+$ 372.2322, found 372.2319.

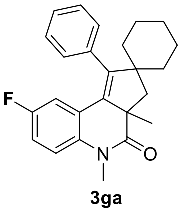
3a',5',7'-trimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'*H*)-one (**3fa**)



3fa

Yellow solid (62% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 3H), 7.09 (d, J = 6.7 Hz, 2H), 6.79 (s, 1H), 6.58 – 6.45 (m, 2H), 3.39 (s, 3H), 2.43 (d, J = 13.9 Hz, 1H), 2.29 (d, J = 7.1 Hz, 4H), 1.73 – 1.64 (m, 4H), 1.46 – 1.37 (m, 2H), 1.31 (s, 3H), 1.12 (d, J = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.18, 147.84, 137.93, 137.09, 133.22, 129.60, 129.55, 128.22, 127.37, 127.04, 123.06, 115.56, 52.18, 52.02, 43.63, 37.78, 35.95, 30.02, 27.42, 25.50, 23.57, 22.47, 21.73. HRMS (ESI, m/z): calcd for $[M+H]^+$ 372.2322, found 372.2323.

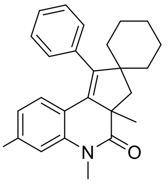
8'-fluoro-3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ga**)



3ga

Yellow solid (80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 6.6 Hz, 3H), 7.20 – 6.97 (m, 2H), 6.69 (dd, *J* = 11.0, 2.5 Hz, 1H), 6.62 (ddd, *J* = 7.6, 6.5, 1.1 Hz, 1H), 6.38 (td, *J* = 8.3, 2.2 Hz, 1H), 3.37 (s, 3H), 2.43 (d, *J* = 13.9 Hz, 1H), 2.28 (d, *J* = 13.9 Hz, 1H), 1.70 – 1.62 (m, 3H), 1.56 – 1.44 (m, 2H), 1.40 (dt, *J* = 13.4, 3.6 Hz, 1H), 1.31 (s, 3H), 1.12 (td, *J* = 13.0, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.93, 148.51, 136.67, 132.25, 129.50, 128.88, 128.78, 128.35, 127.25, 108.91, 108.69, 102.78, 102.51, 52.25, 51.95, 43.55, 37.69, 35.92, 30.12, 27.40, 25.45, 23.52, 22.44. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.09 (q, J = 8.3 Hz). HRMS (ESI, m/z): calcd for [M+H]$^+$ 376.2071, found 376.2072.

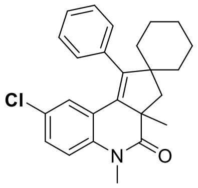
7'-fluoro-3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ha**)



3ha

Yellow solid (42% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (p, J = 5.5, 4.7 Hz, 3H), 7.10 (d, J = 6.7 Hz, 2H), 6.72 (dt, J = 11.0, 2.4 Hz, 1H), 6.65 (ddd, J = 8.6, 6.4, 2.1 Hz, 1H), 6.42 (tt, J = 8.5, 2.5 Hz, 1H), 3.40 (d, J = 2.1 Hz, 3H), 2.46 (dd, J = 13.8, 2.0 Hz, 1H), 2.31 (dd, J = 13.8, 2.1 Hz, 1H), 1.70 (d, J = 9.1 Hz, 3H), 1.53 – 1.39 (m, 2H), 1.34 (d, J = 2.1 Hz, 3H), 1.17 (dd, J = 13.1, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.94, 148.51, 136.66, 132.23, 129.49, 128.87, 128.77, 128.34, 127.24, 108.90, 108.69, 102.77, 102.50, 52.24, 51.94, 43.54, 37.68, 35.90, 30.12, 27.39, 25.44, 23.51, 22.43. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.14 (q, J = 8.6 Hz).. HRMS (ESI, m/z): calcd for [M+H]$^+$ 376.2071, found 376.2074.

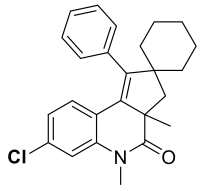
8'-chloro-3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ia**)



3ia

Yellow solid (82% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (q, J = 6.1 Hz, 3H), 7.09 (d, J = 6.8 Hz, 2H), 6.79 (s, 1H), 6.65 – 6.45 (m, 2H), 3.40 (d, J = 1.1 Hz, 3H), 2.41 (d, J = 13.8 Hz, 2H), 2.28 (d, J = 13.7 Hz, 1H), 1.81 (d, J = 9.2 Hz, 4H), 1.75 – 1.67 (m, 3H), 1.51 (d, J = 13.1 Hz, 3H), 1.32 (s, 3H), 1.12 (d, J = 4.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.15, 147.72, 139.75, 133.24, 129.66, 128.19, 127.29, 127.01, 120.73, 113.53, 52.16, 44.77, 43.54, 37.86, 35.89, 34.38, 34.32, 30.06, 27.59, 26.86, 26.14, 25.50, 23.57, 22.46. HRMS (ESI, m/z): calcd for [M+H]$^+$ 392.1776, found 392.1771.

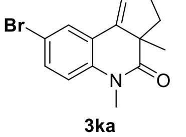
7'-chloro-3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ja**)



3ja

Yellow solid (53% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (td, J = 5.8, 5.0, 2.6 Hz, 3H), 7.11 – 7.02 (m, 2H), 6.96 (d, J = 2.0 Hz, 1H), 6.65 (dd, J = 8.3, 2.0 Hz, 1H), 6.58 (d, J = 8.3 Hz, 1H), 3.37 (s, 3H), 2.44 (d, J = 13.9 Hz, 1H), 2.28 (d, J = 13.9 Hz, 1H), 1.69 – 1.62 (m, 3H), 1.51 (dt, J = 12.0, 4.4 Hz, 2H), 1.40 (dt, J = 13.4, 3.5 Hz, 1H), 1.31 (s, 3H), 1.16 – 1.07 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.84, 149.55, 140.93, 136.51, 133.52, 132.26, 129.38, 128.48, 128.37, 127.33, 122.23, 120.26, 115.09, 52.36, 51.86, 43.59, 37.61, 35.88, 30.09, 27.37, 25.43, 23.50, 22.40. HRMS (ESI, m/z): calcd for [M+H]$^+$ 392.1776, found 392.1774.

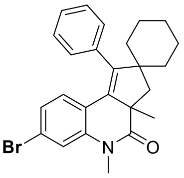
8'-bromo-3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ka**)



3ka

Yellow solid (68% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (t, J = 3.5 Hz, 3H), 7.23 (dd, J = 8.7, 2.3 Hz, 1H), 7.07 (d, J = 6.4 Hz, 2H), 6.83 (d, J = 8.7 Hz, 1H), 6.74 (d, J = 2.3 Hz, 1H), 3.37 (s, 3H), 2.47 – 2.25 (m, 2H), 1.71 – 1.62 (m, 3H), 1.51 – 1.36 (m, 2H), 1.31 (s, 3H), 1.15 (td, J = 13.0, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.67, 150.51, 136.09, 132.05, 130.56, 130.25, 129.27, 128.42, 127.52, 123.72, 116.29, 115.10, 52.40, 51.78, 43.59, 37.56, 35.83, 30.12, 27.36, 25.42, 23.48, 22.37. HRMS (ESI, m/z): calcd for [M+H]$^+$ 436.1271, found 436.1271.

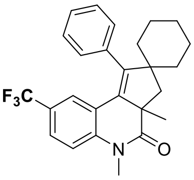
7'-bromo-3a',5'-dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3la**)



3la

Yellow solid (77% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 3H), 7.14 – 6.99 (m, 3H), 6.80 (dq, J = 8.3, 1.8 Hz, 1H), 6.56 – 6.40 (m, 1H), 3.41 – 3.33 (m, 3H), 2.48 – 2.22 (m, 2H), 1.67 (d, J = 9.3 Hz, 3H), 1.56 – 1.46 (m, 2H), 1.40 (dd, J = 13.1, 3.4 Hz, 1H), 1.33 – 1.29 (m, 3H), 1.16 – 1.07 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.82, 149.70, 141.03, 136.48, 132.31, 129.35, 128.72, 128.37, 127.34, 125.18, 121.57, 120.70, 117.91, 52.40, 51.82, 43.60, 37.58, 35.85, 30.11, 27.38, 25.43, 23.50, 22.39. HRMS (ESI, m/z): calcd for [M+H]$^+$ 436.1271, found 436.1267.

3a',5'-dimethyl-1'-phenyl-8'-(trifluoromethyl)-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[c]quinolin]-4'(5'H)-one (**3ma**)



3ma

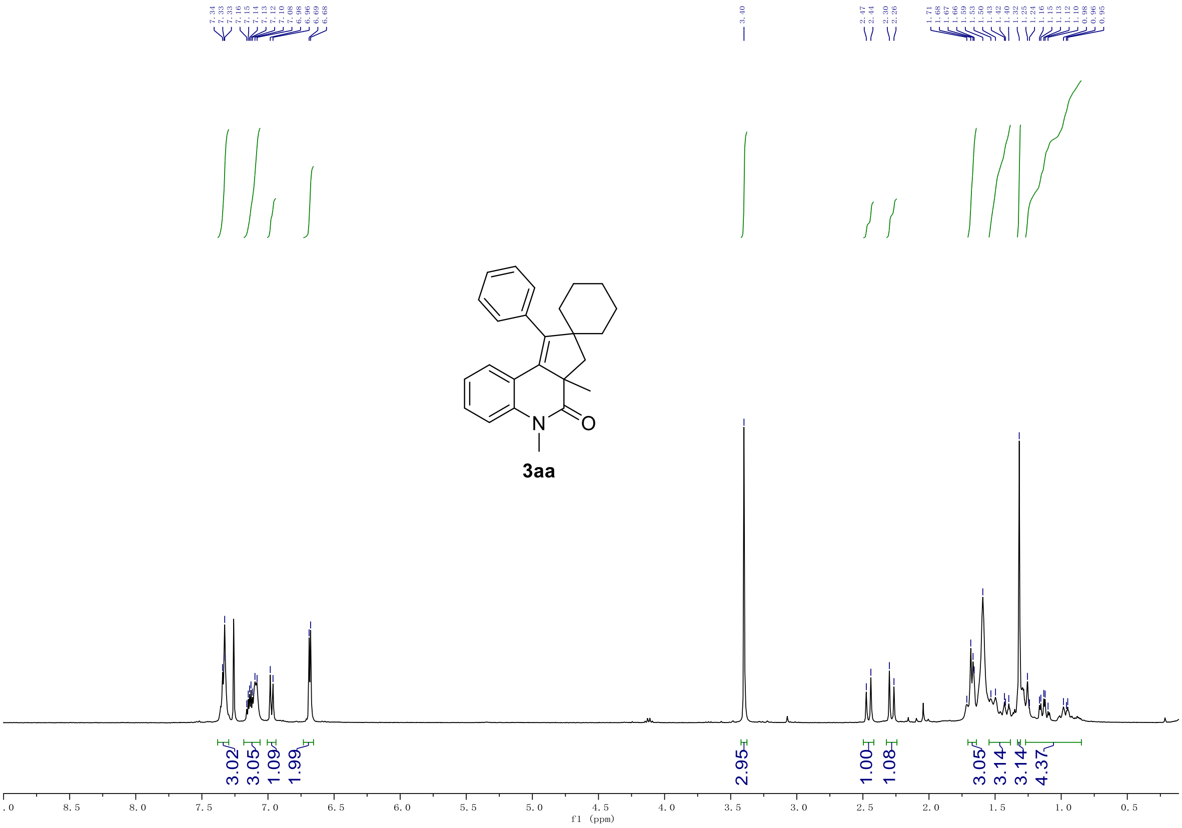
Yellow solid (79% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.35 (m, 4H), 7.16 – 6.99 (m, 3H), 6.91 (d, J = 2.2 Hz, 1H), 3.45 (s, 3H), 2.57 – 2.27 (m, 2H), 1.74 (q, J = 4.8, 3.2 Hz, 3H), 1.61 – 1.50 (m, 2H), 1.45 (dt, J = 13.2, 3.4 Hz, 1H), 1.36 (d, J = 5.3 Hz, 3H), 1.23 (td, J = 13.1, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.93, 151.04, 142.33, 135.94, 131.97, 129.21, 128.46, 127.58, 124.81, 124.78, 124.64, 121.98, 114.65, 52.43, 51.77, 43.65, 37.54, 35.82, 30.18, 27.45, 25.40, 23.49, 22.36. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.61. HRMS (ESI, m/z): calcd for [M+H]$^+$ 426.2039, found 426.2039.

5 References

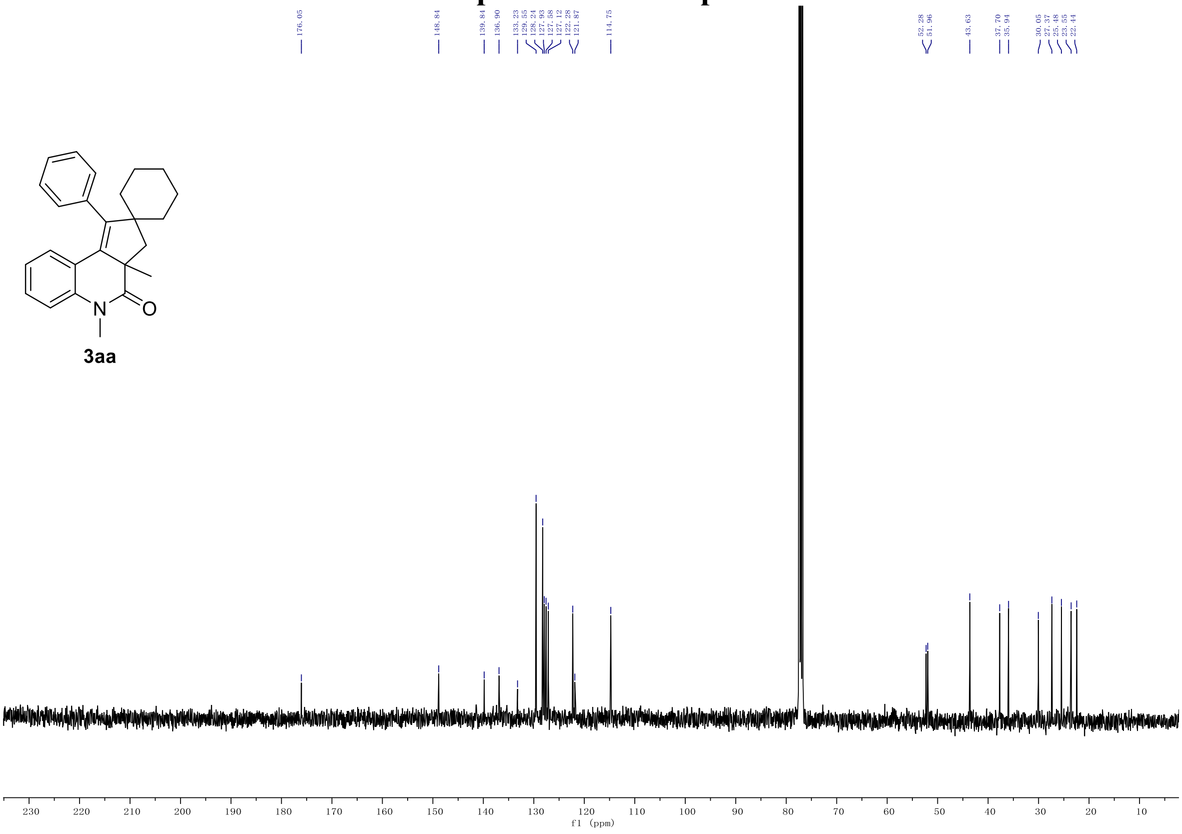
[1] S. Arai, Y. Koike, A. Nishida, *Advanced Synthesis & Catalysis* **2010**, *352*, 893-900.

[2] D. Qi, J. Bai, H. Zhang, B. Li, Z. Song, N. Ma, L. Guo, L. Song, W. Xia, *Green Chemistry* **2022**, *24*, 5046-5051.

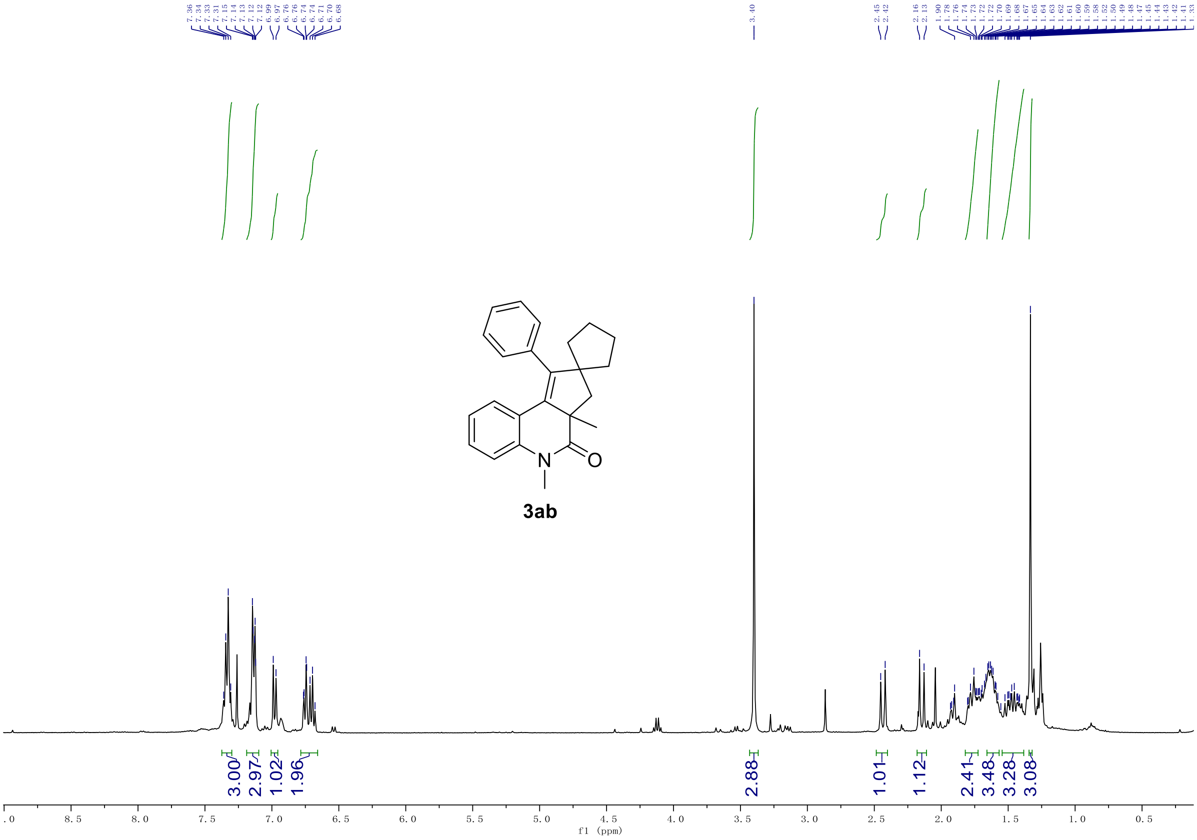
6 Copies of 1H, 13C and 19F NMR Spectra for Products



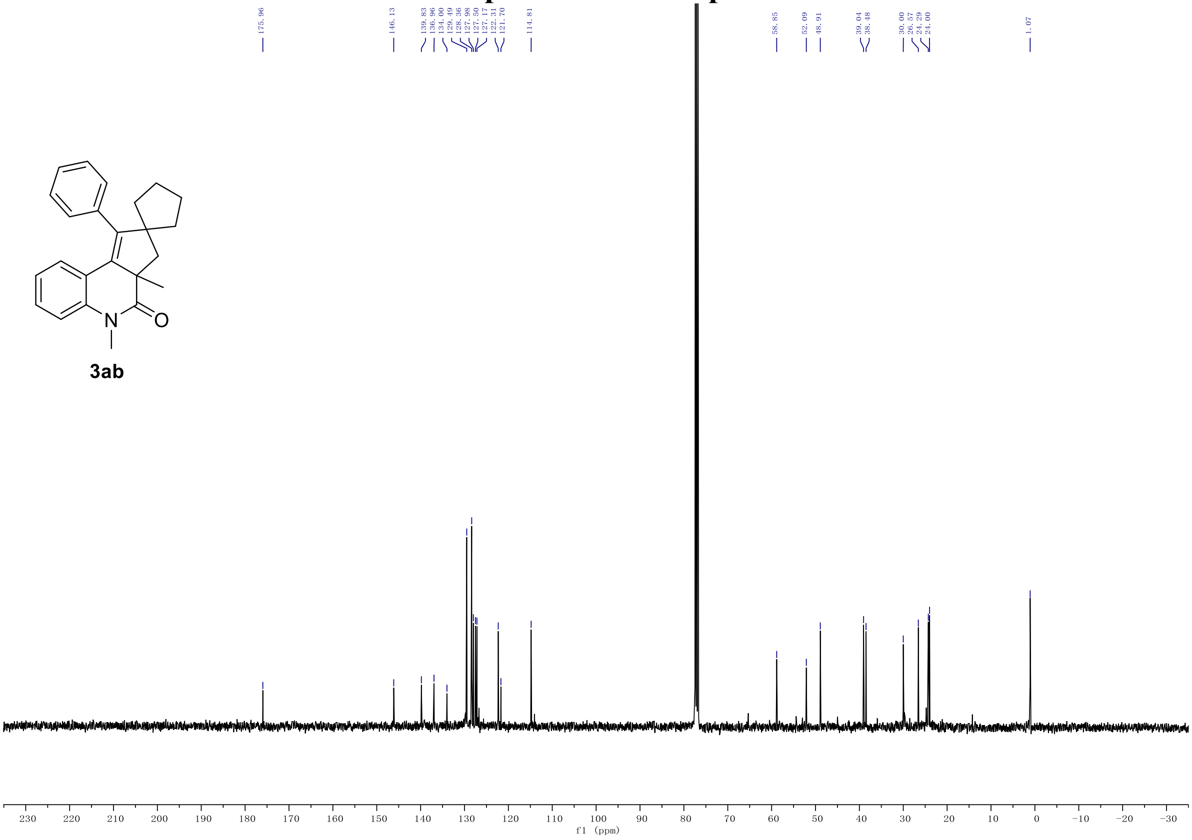
^{1}H NMR Spectrum of Compound 3aa



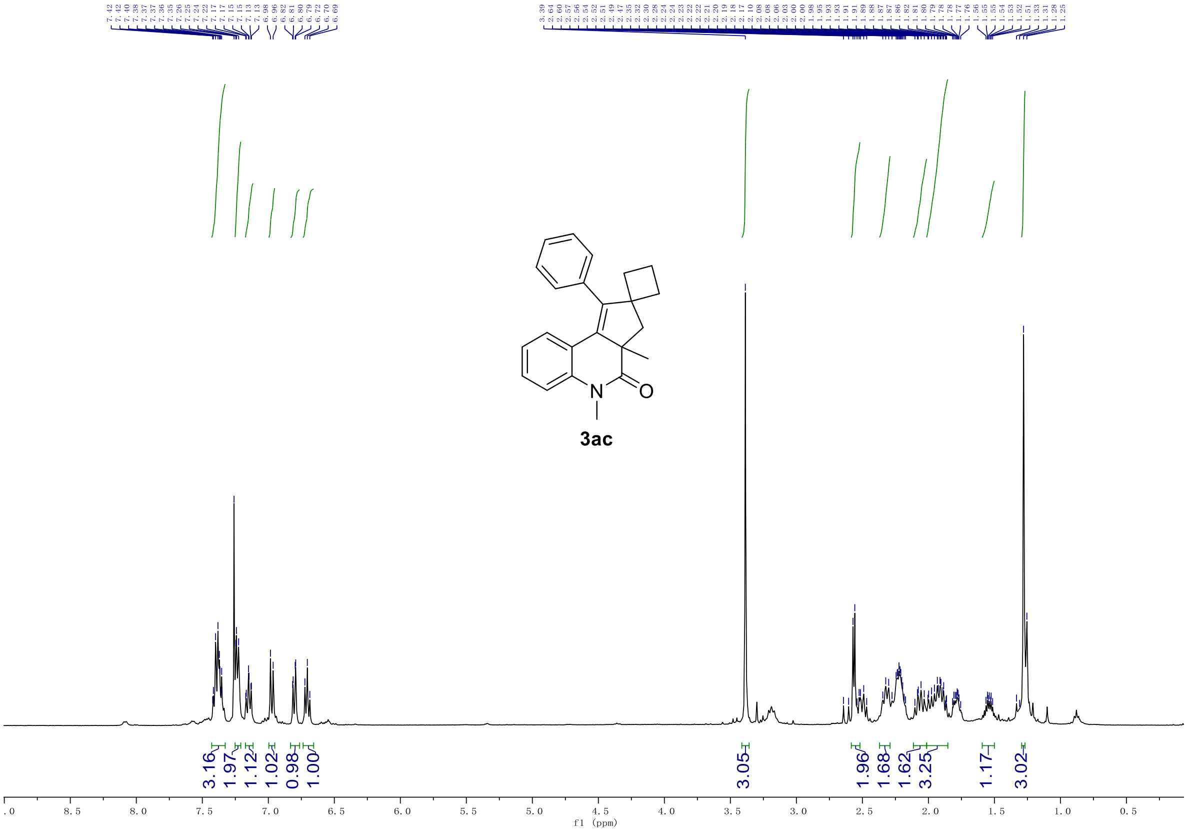
^{13}C NMR Spectrum of Compound 3aa



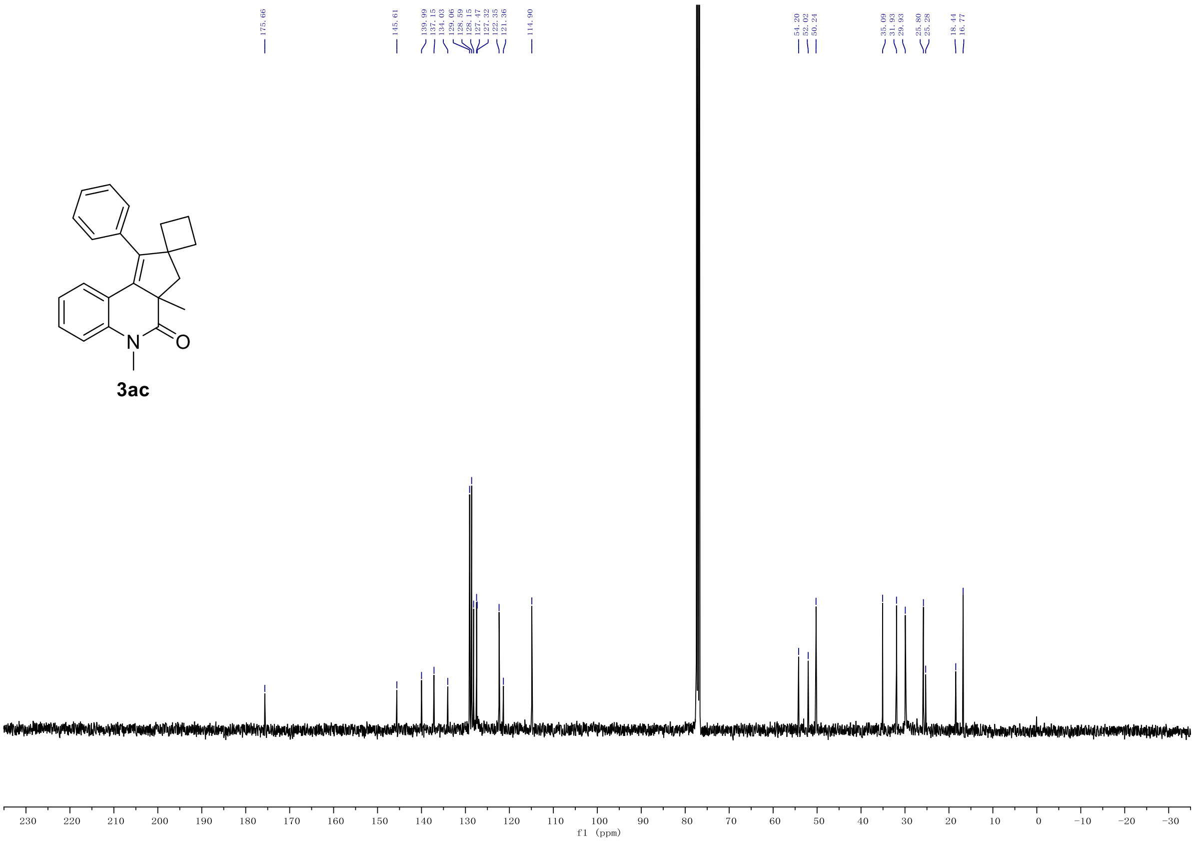
^{1}H NMR Spectrum of Compound 3ab



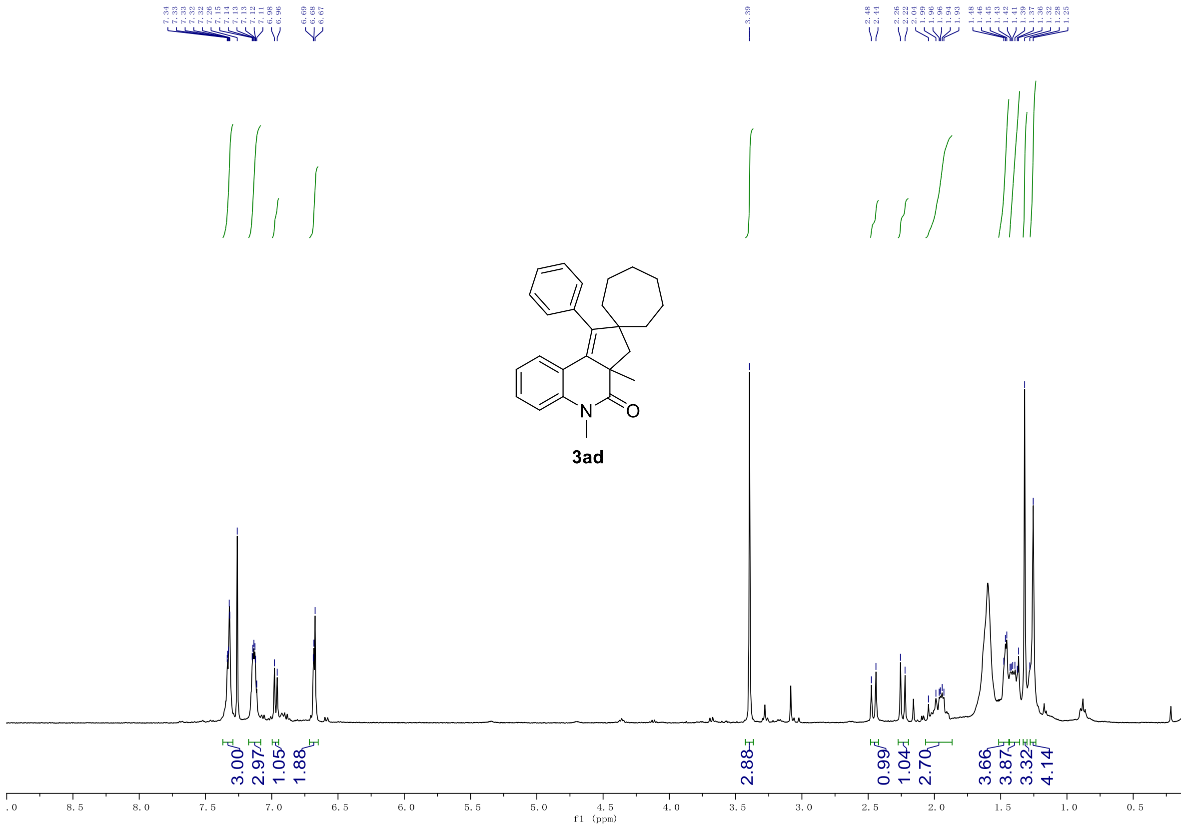
^{13}C NMR Spectrum of Compound 3ab



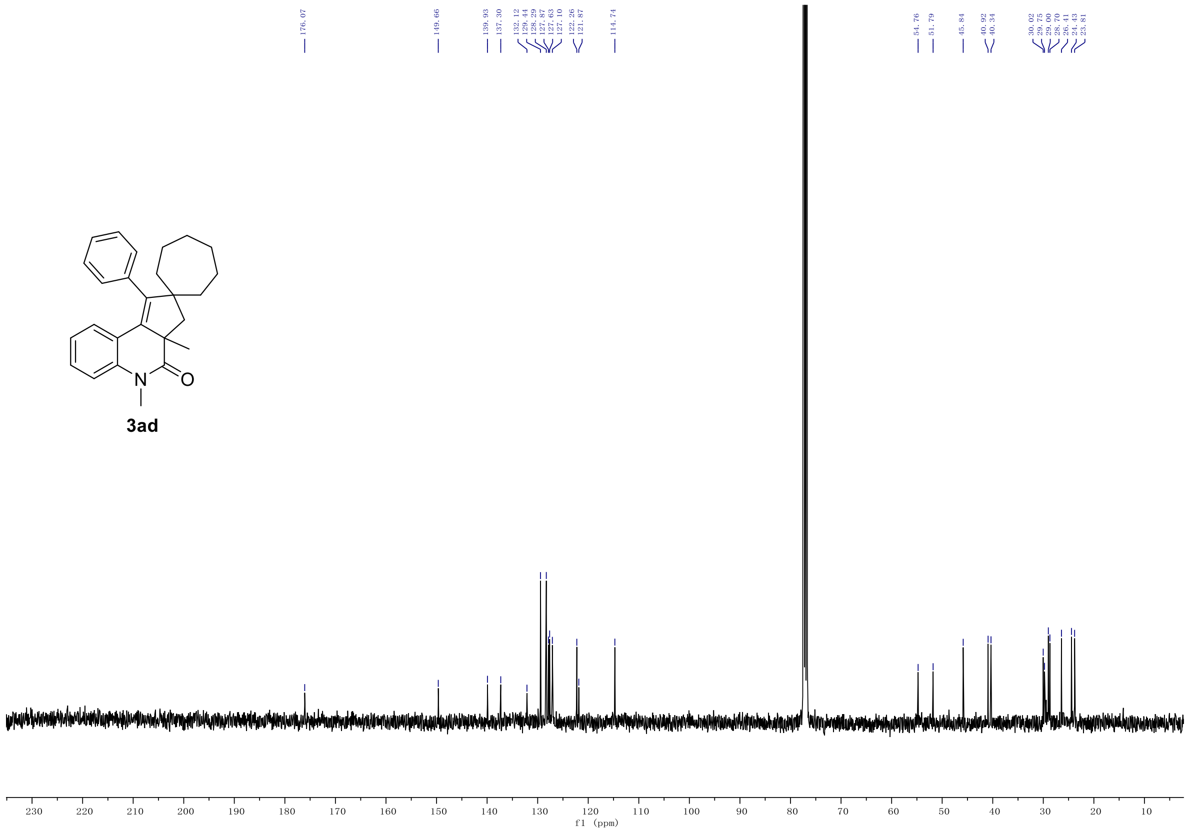
^{1}H NMR Spectrum of Compound 3ac



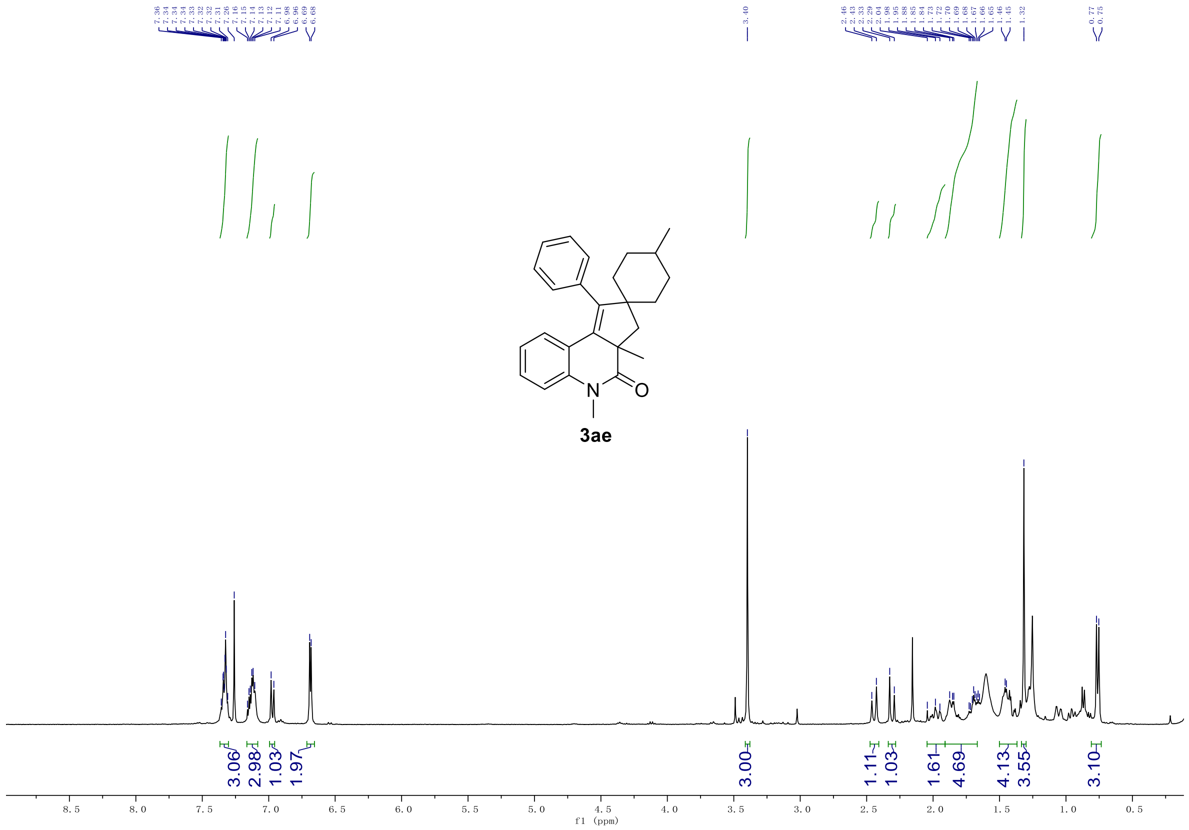
^{13}C NMR Spectrum of Compound 3ac



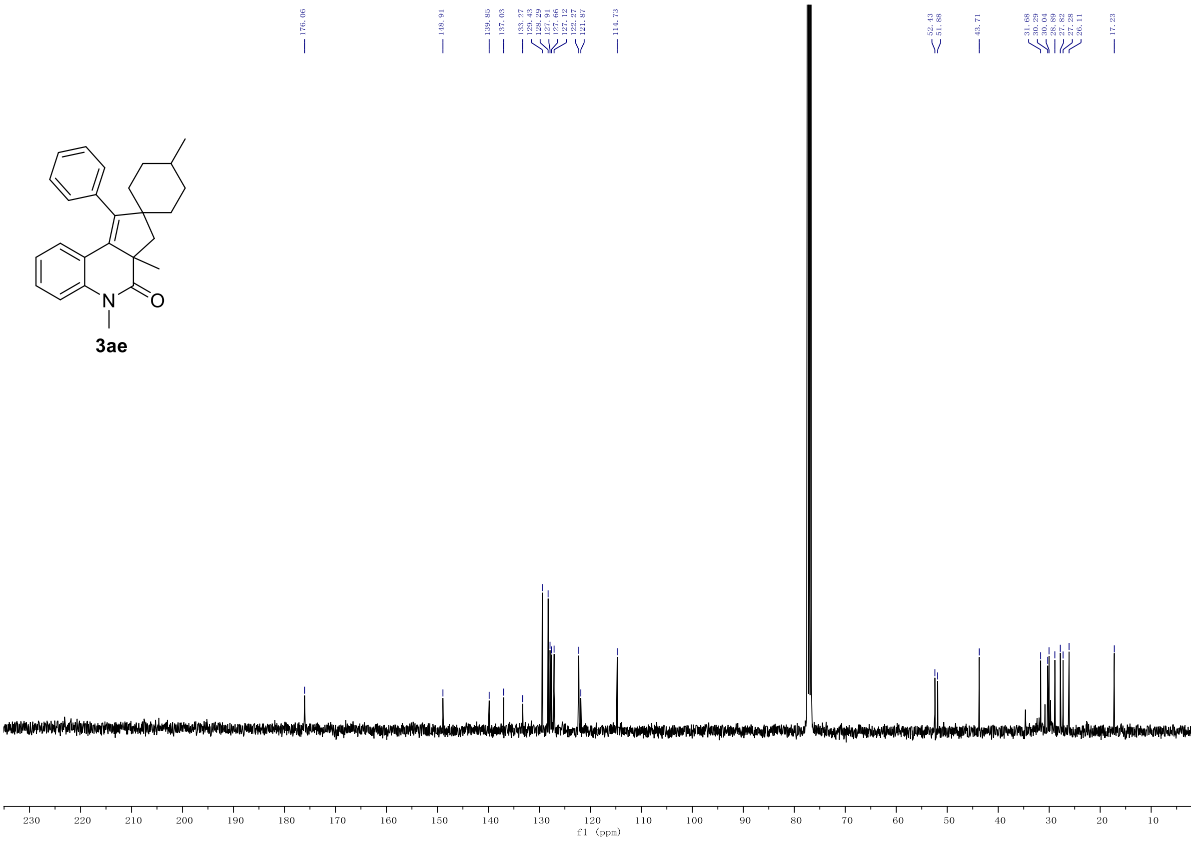
^{1}H NMR Spectrum of Compound 3ad



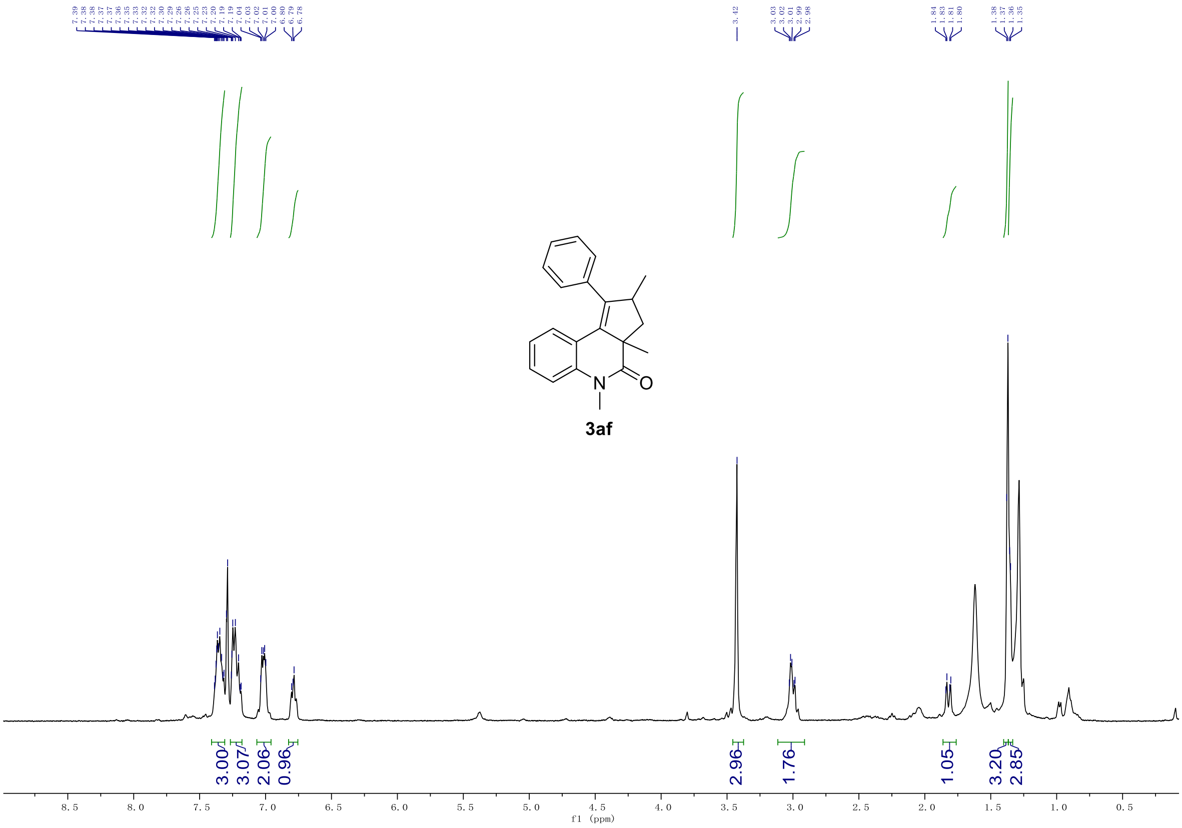
^{13}C NMR Spectrum of Compound 3ad



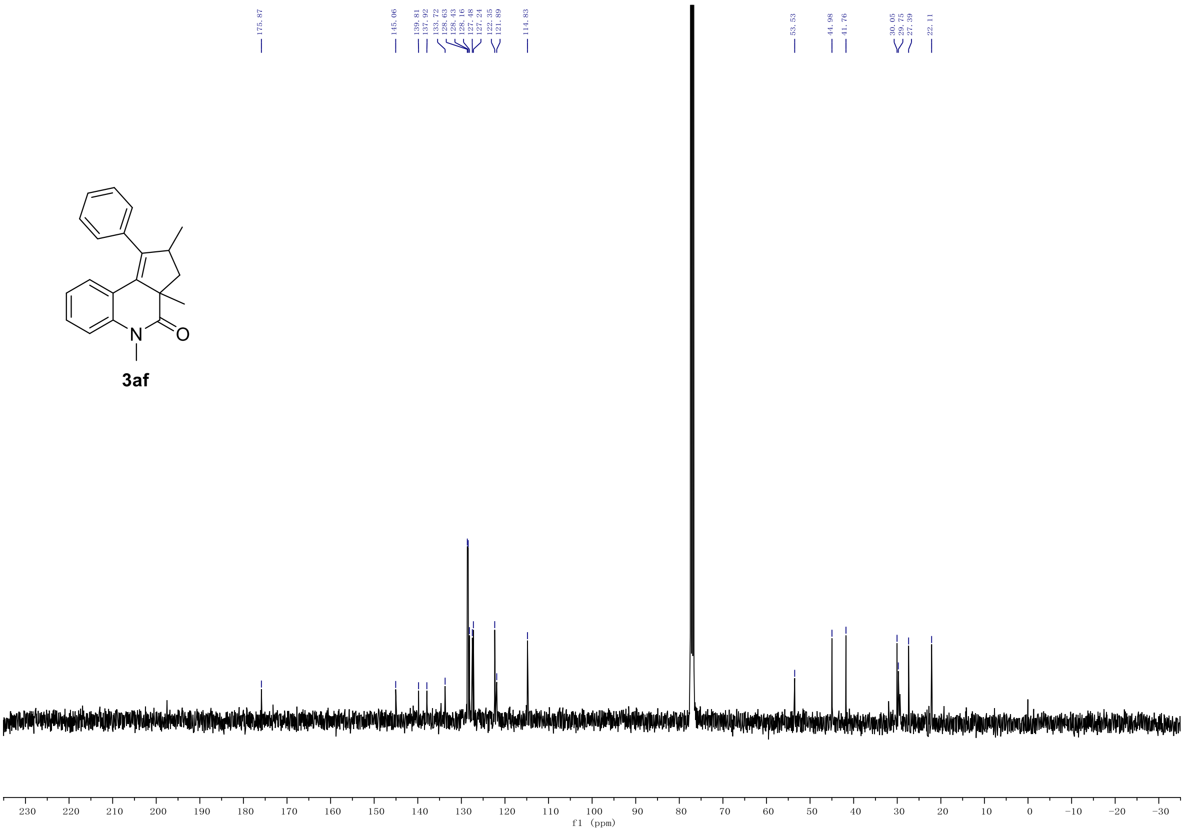
^{1}H NMR Spectrum of Compound 3ae



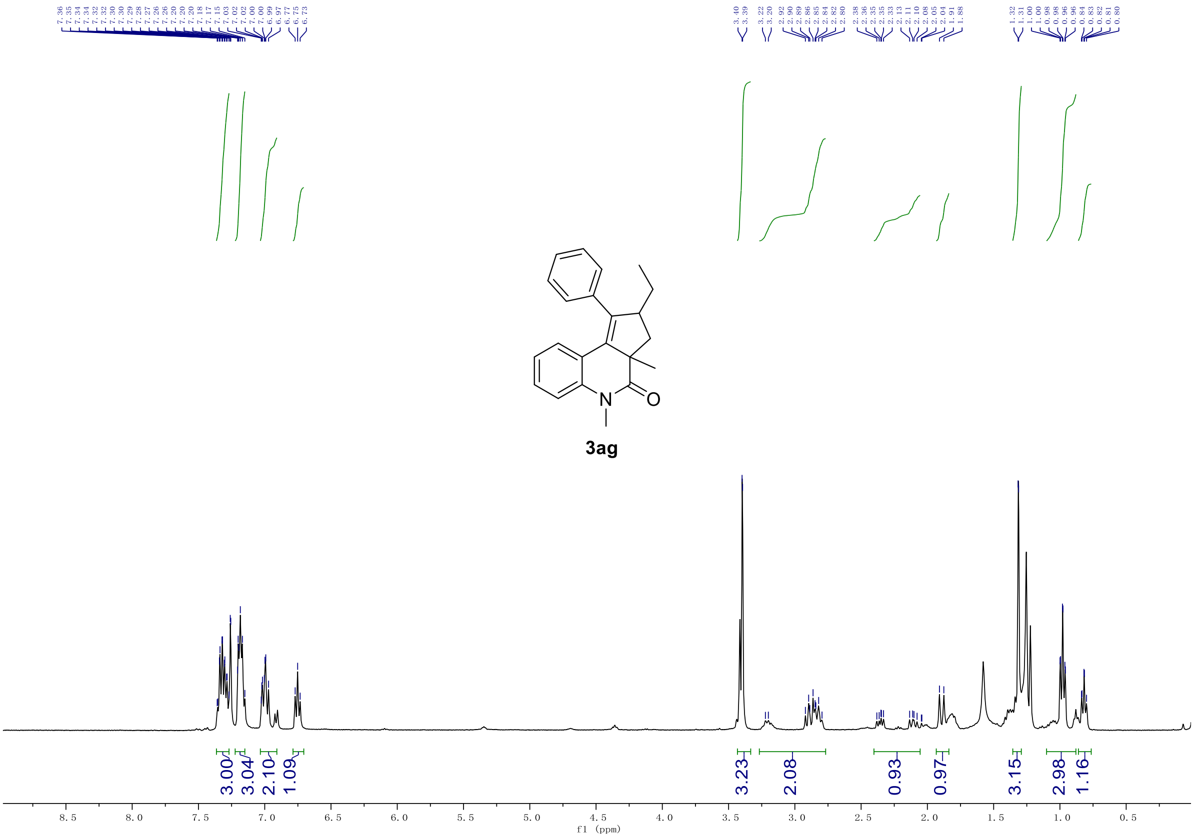
^{13}C NMR Spectrum of Compound 3ae



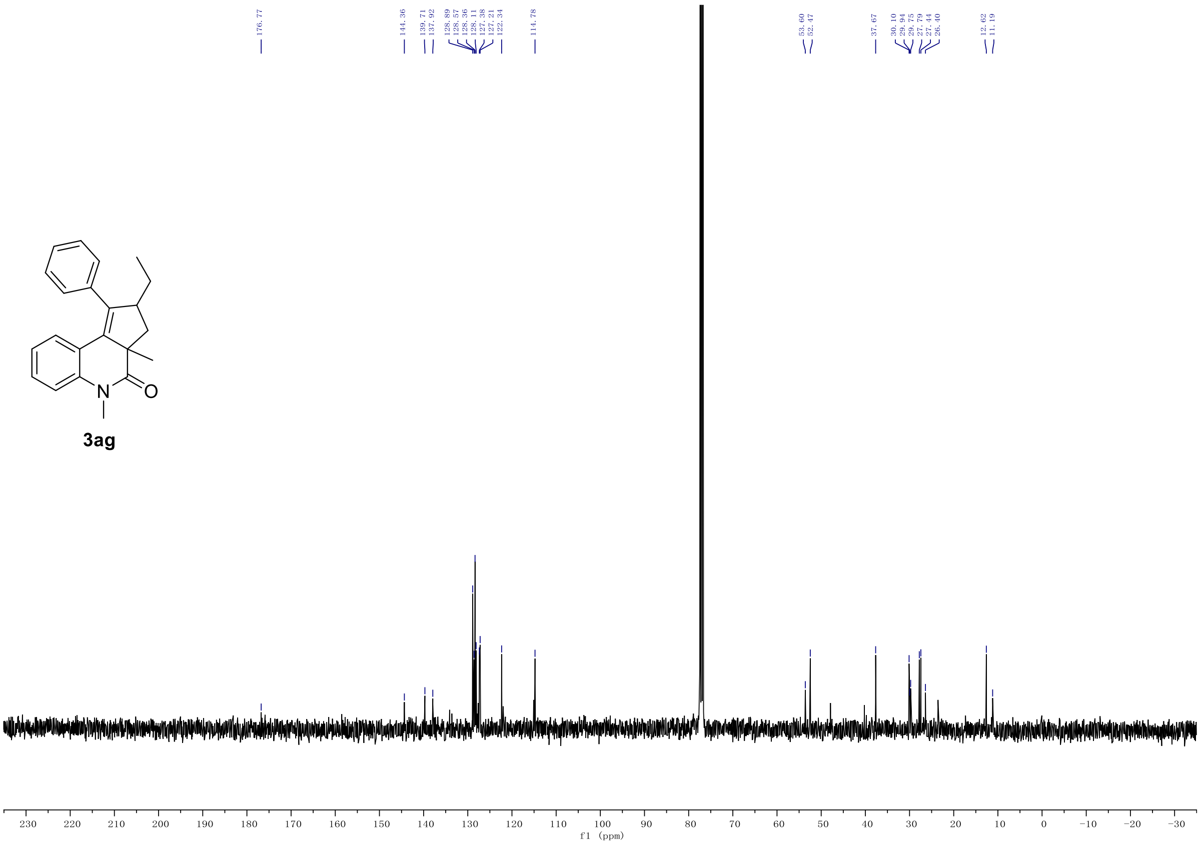
^{1}H NMR Spectrum of Compound 3af



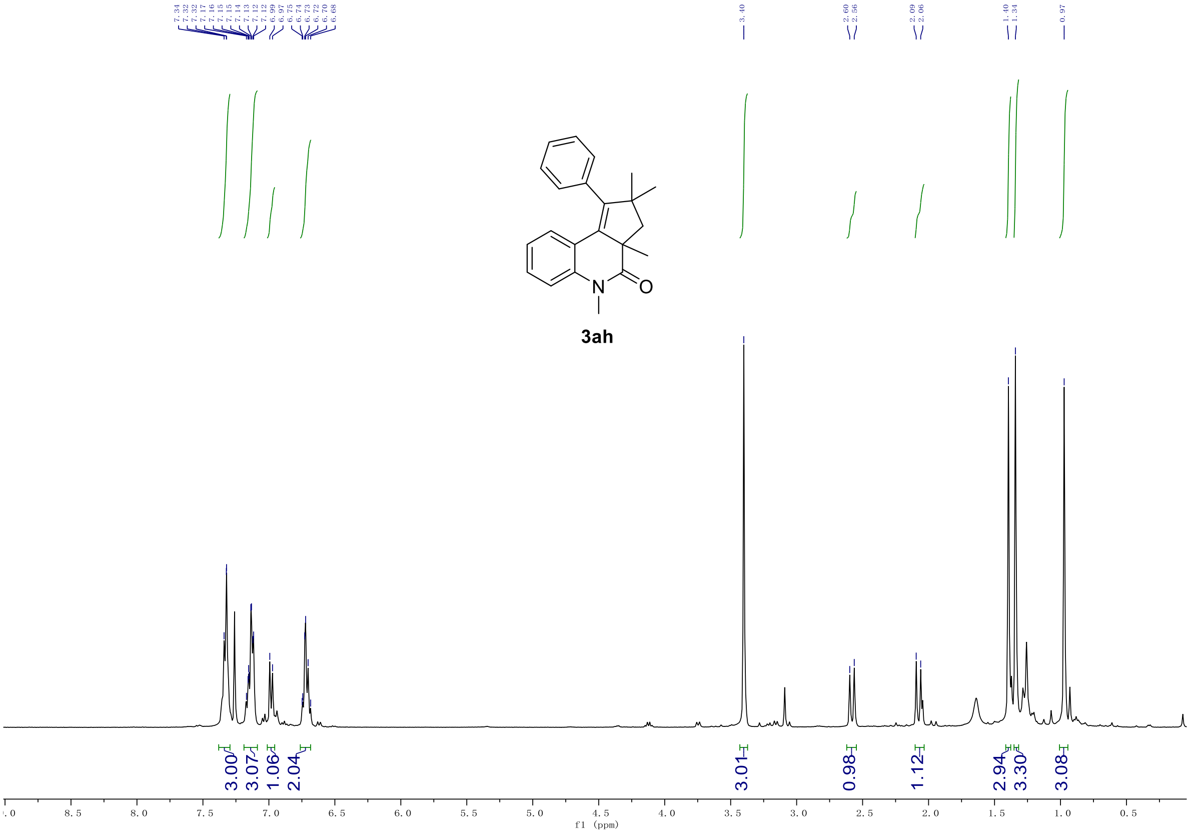
^{13}C NMR Spectrum of Compound 3af



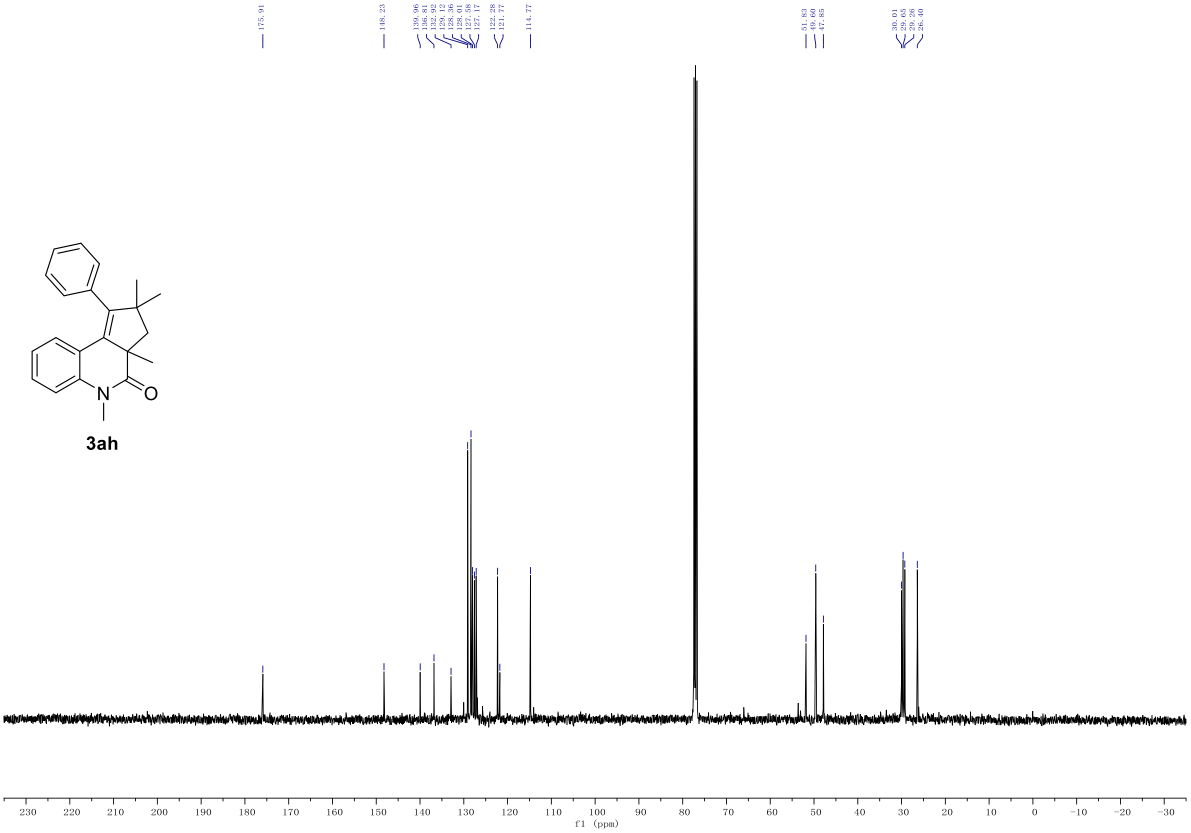
^{1}H NMR Spectrum of Compound 3ag



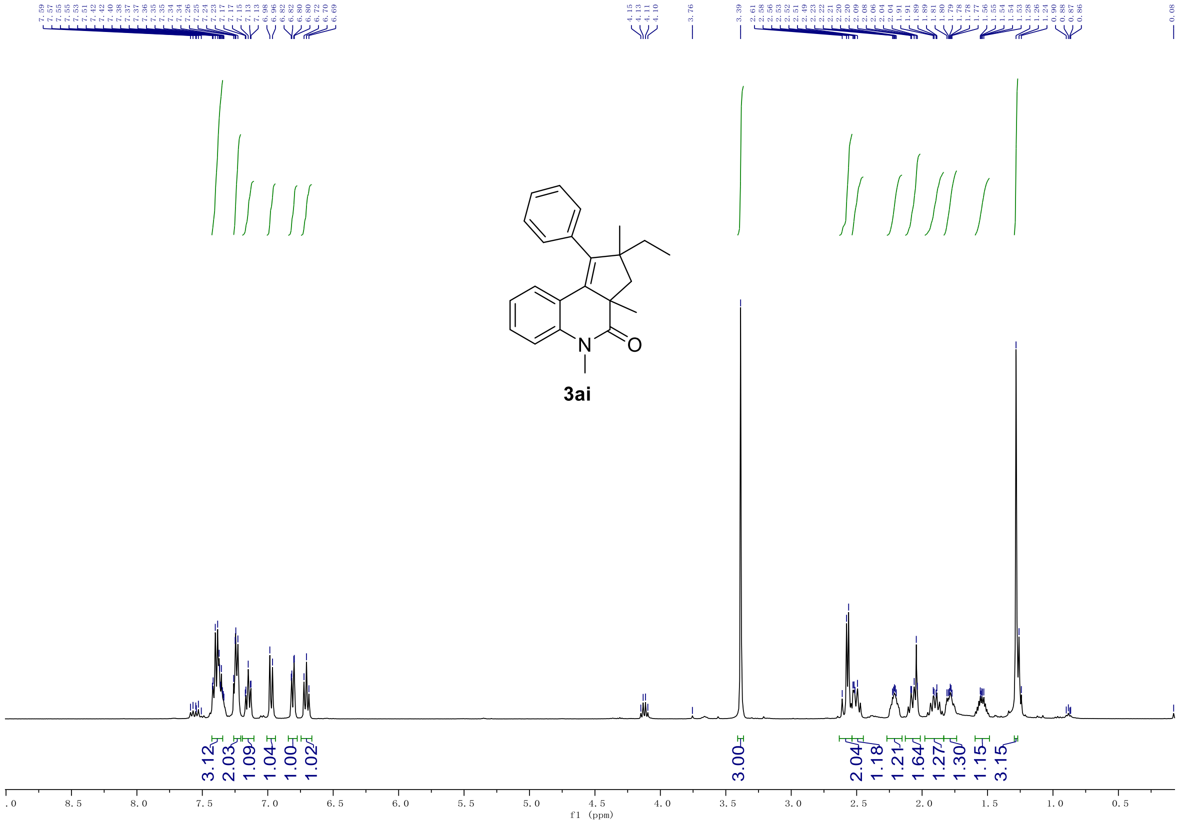
^{13}C NMR Spectrum of Compound 3ag



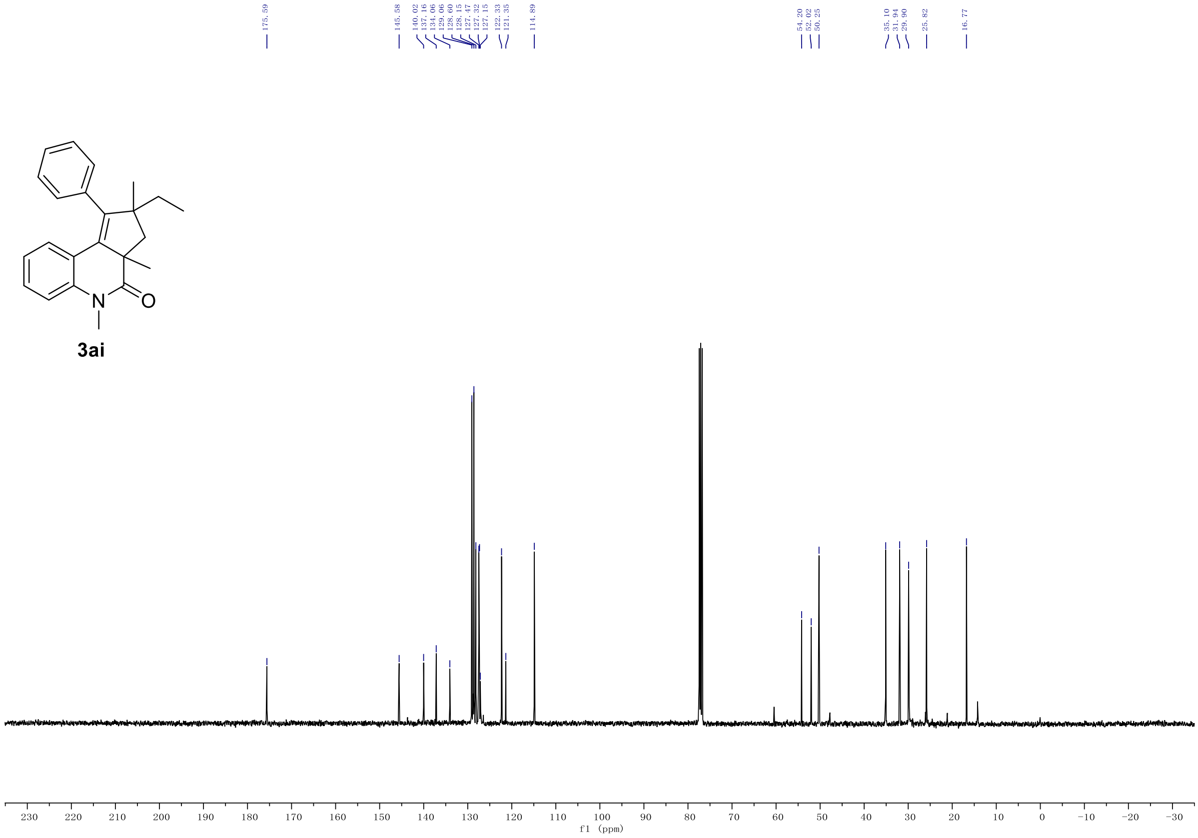
^{1}H NMR Spectrum of Compound 3ah



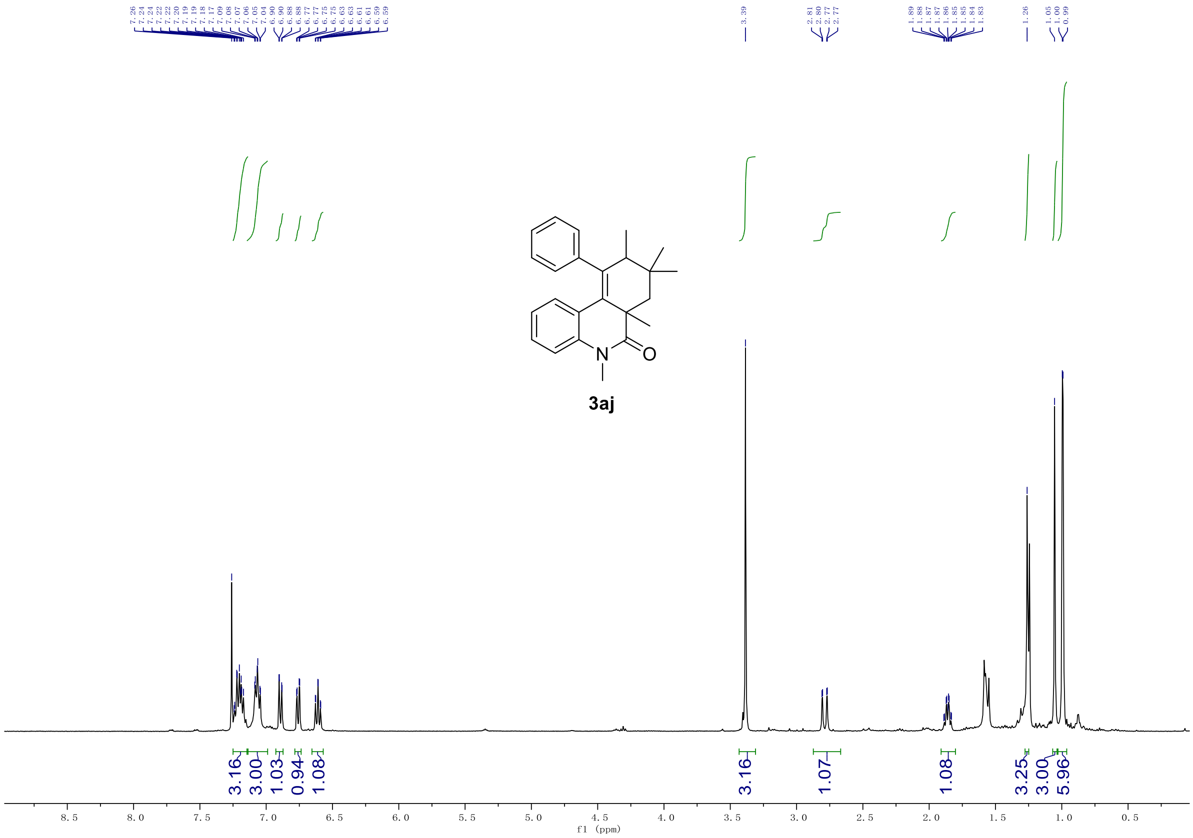
^{13}C NMR Spectrum of Compound 3ah



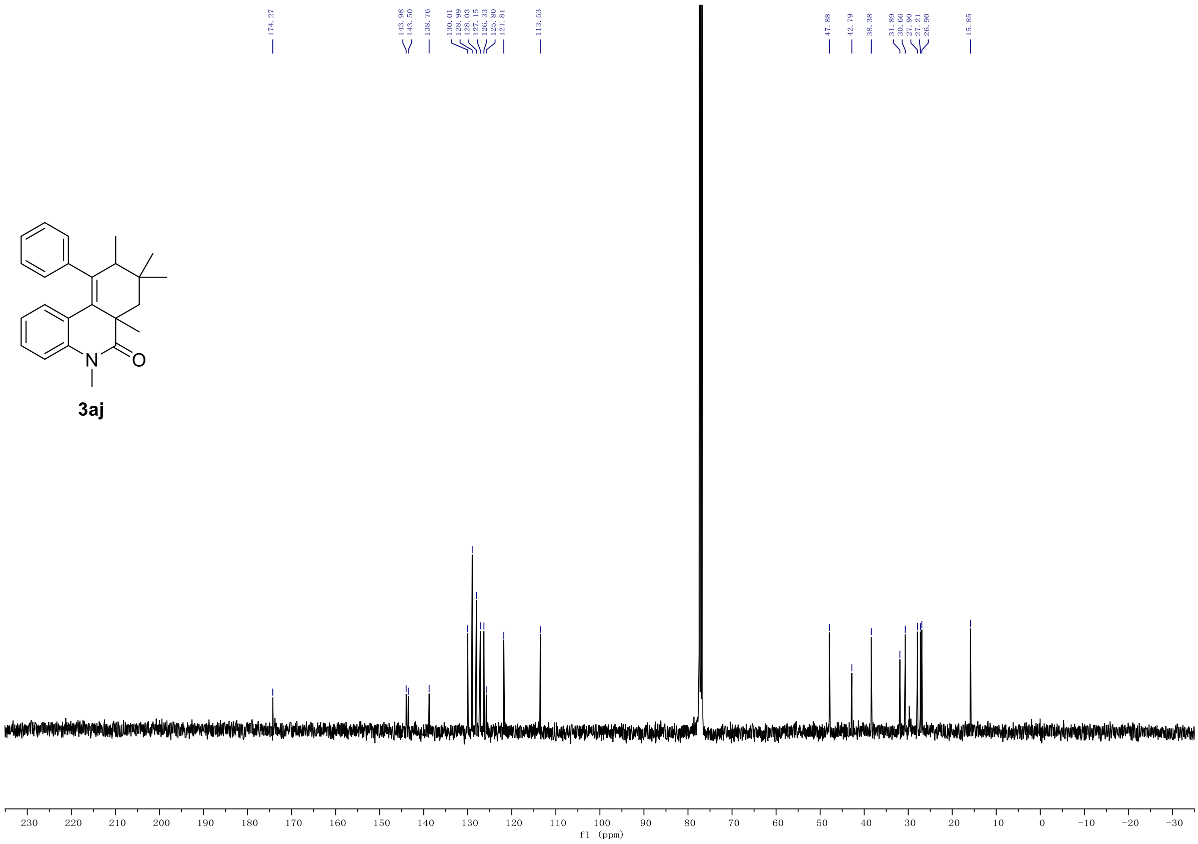
^{1}H NMR Spectrum of Compound 3ai



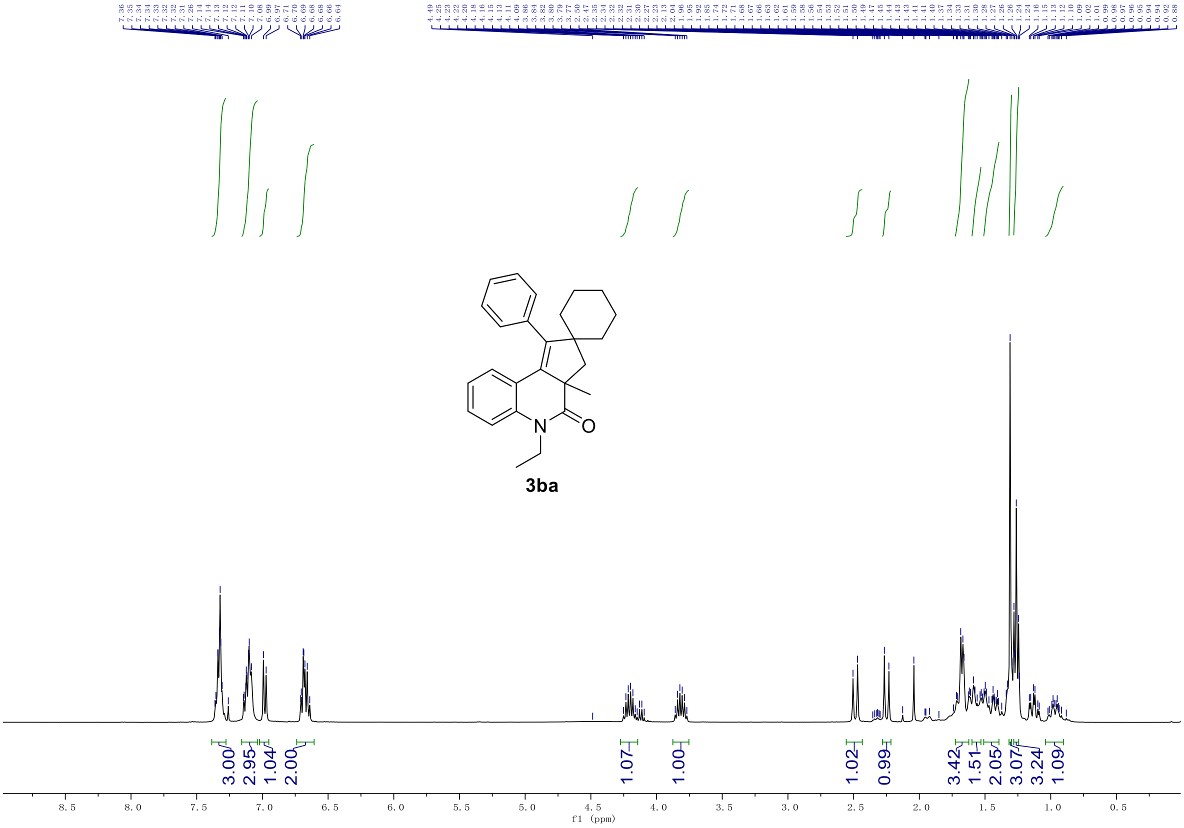
^{13}C NMR Spectrum of Compound 3ai



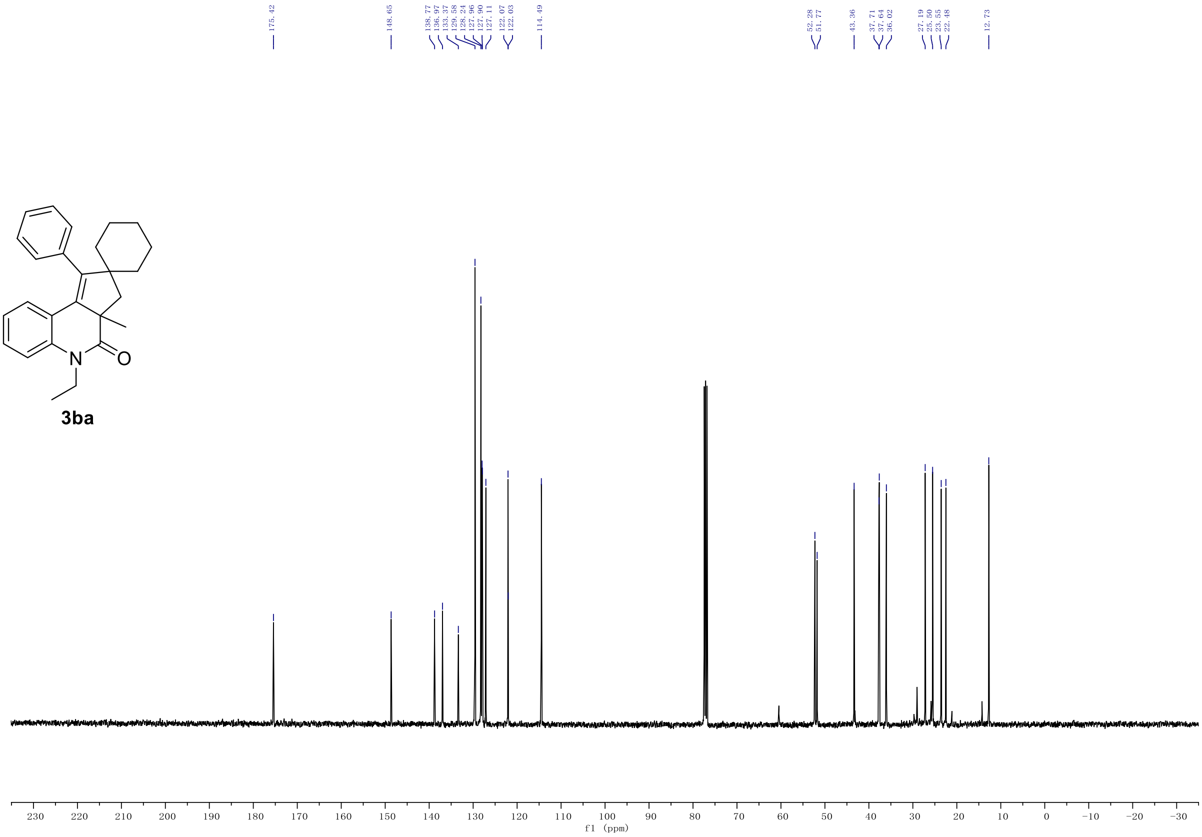
^{1}H NMR Spectrum of Compound 3aj



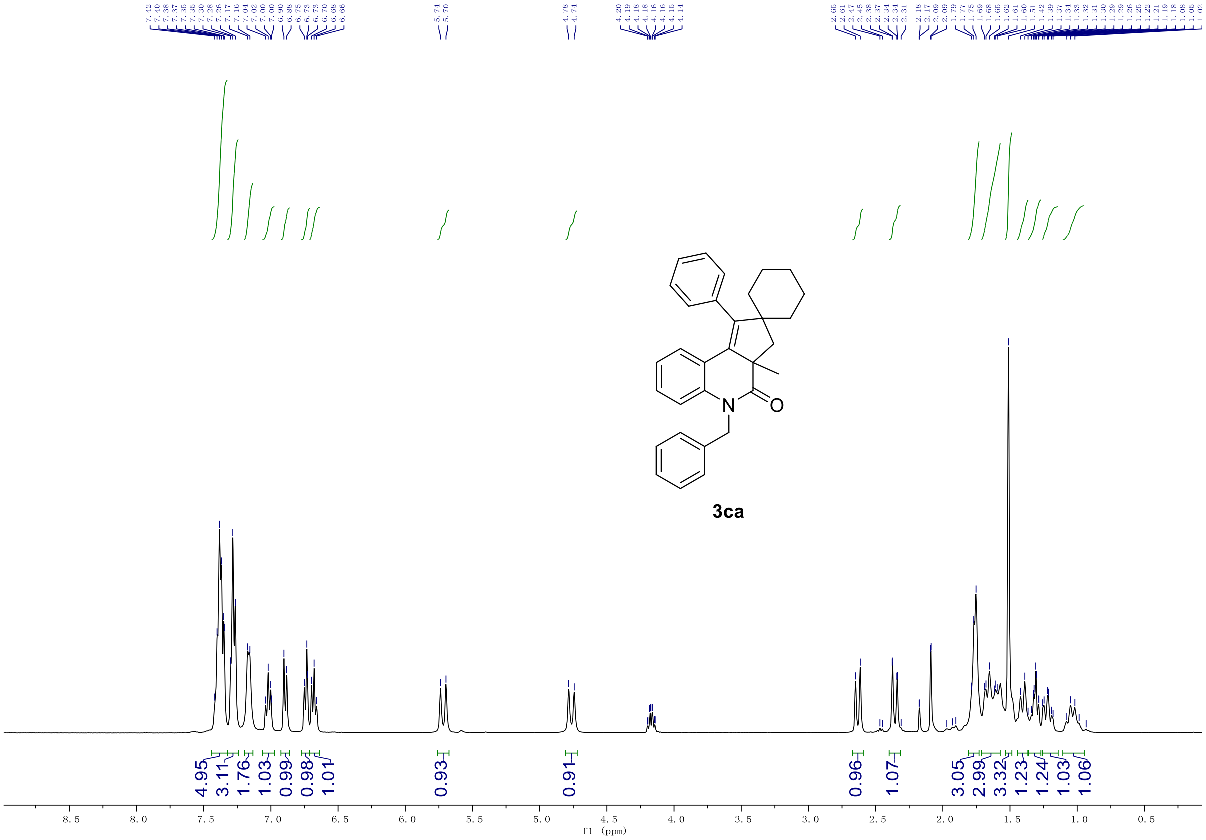
^{13}C NMR Spectrum of Compound 3aj



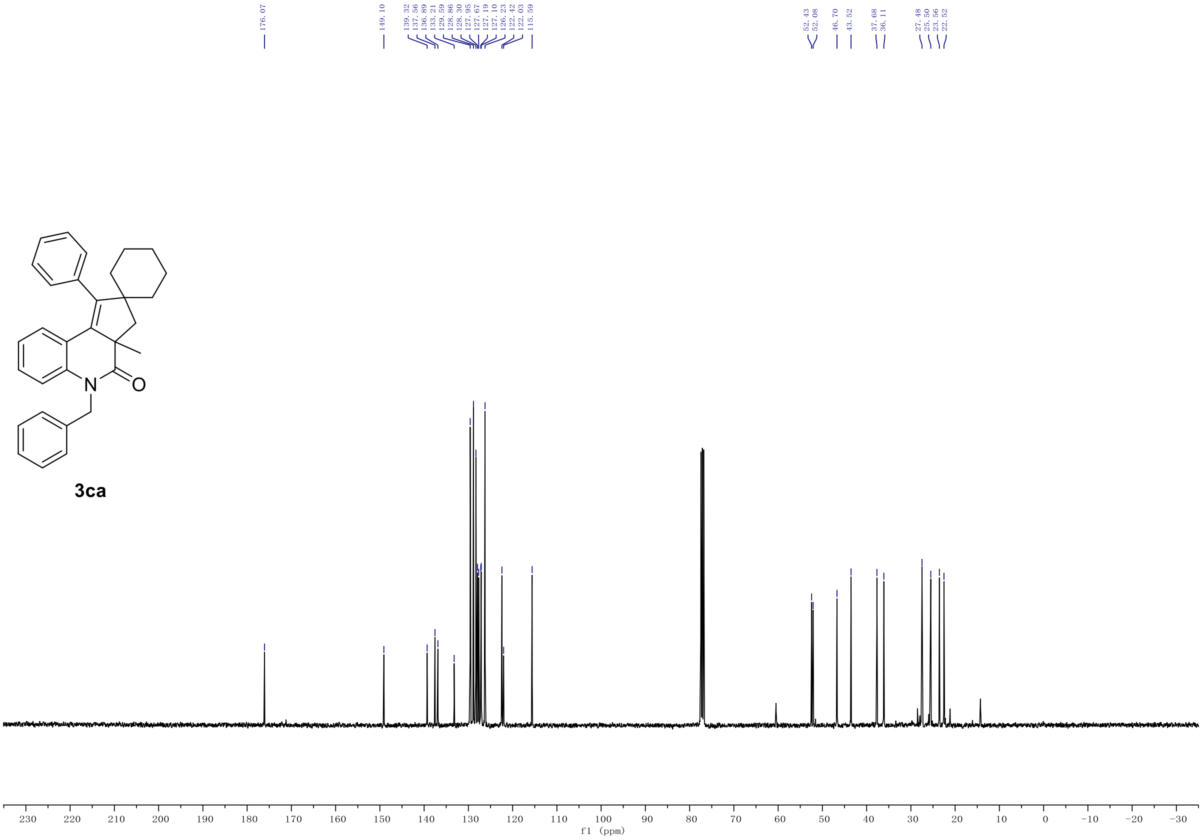
^{1}H NMR Spectrum of Compound 3ba



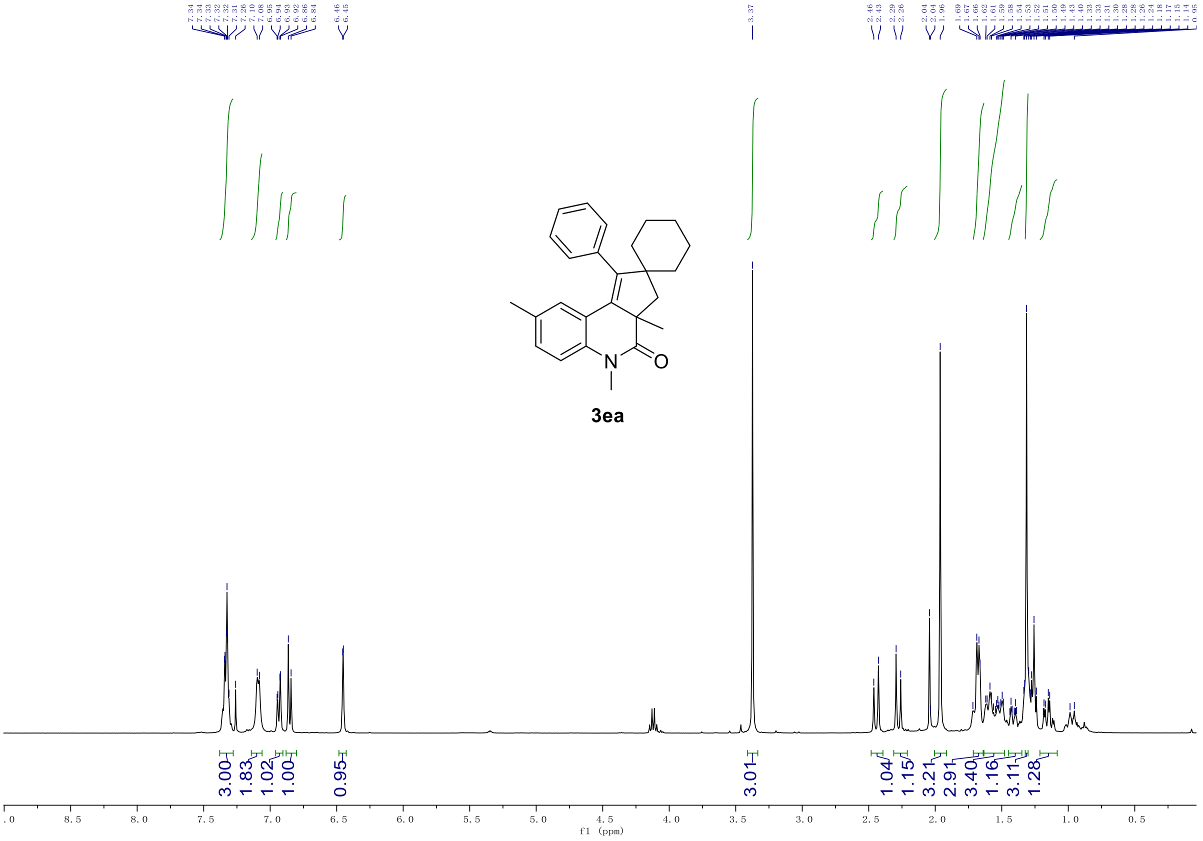
^{13}C NMR Spectrum of Compound 3ba



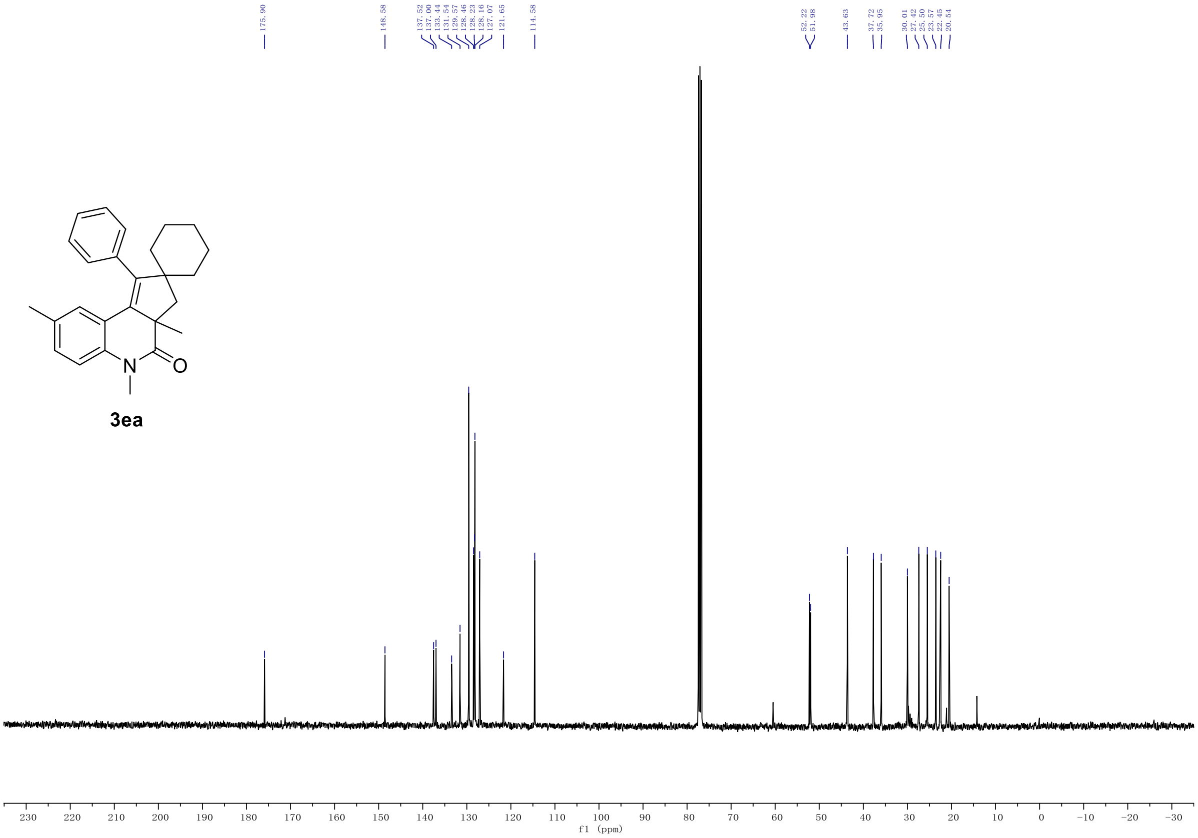
^{1}H NMR Spectrum of Compound 3ca



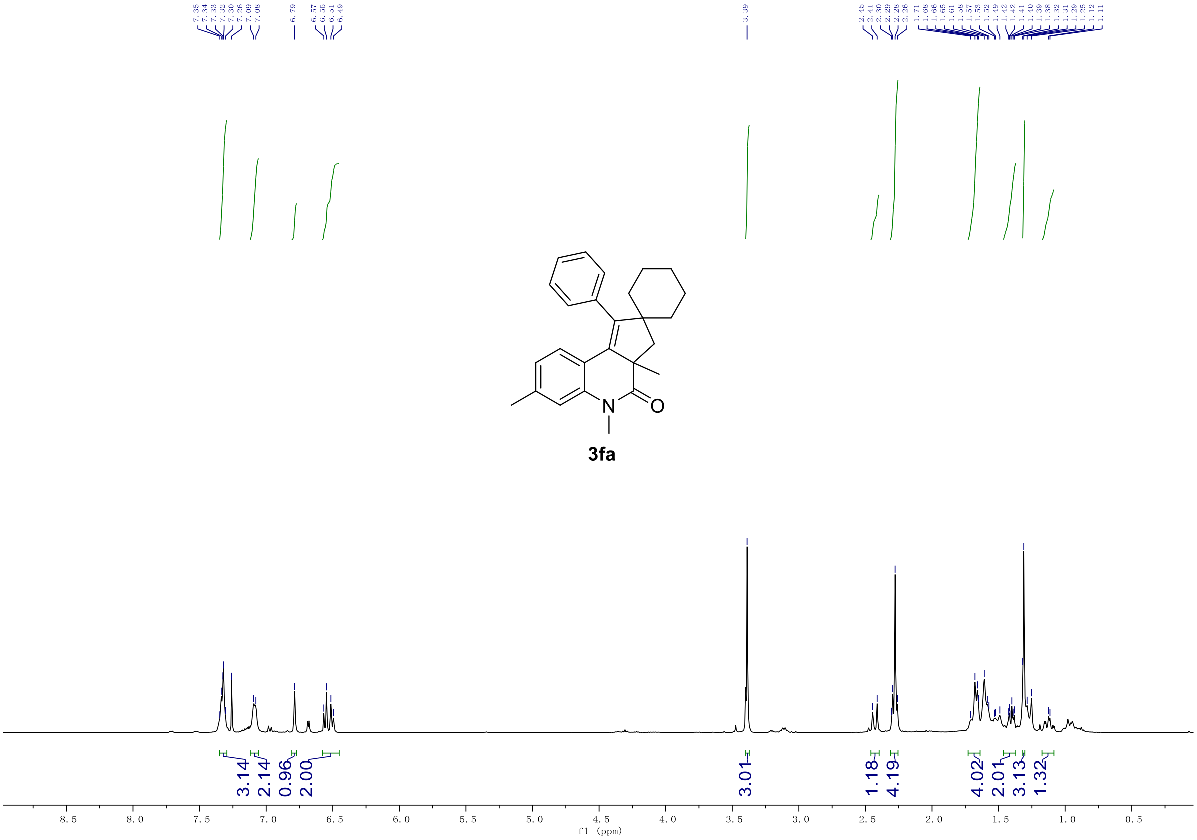
^{13}C NMR Spectrum of Compound 3ca



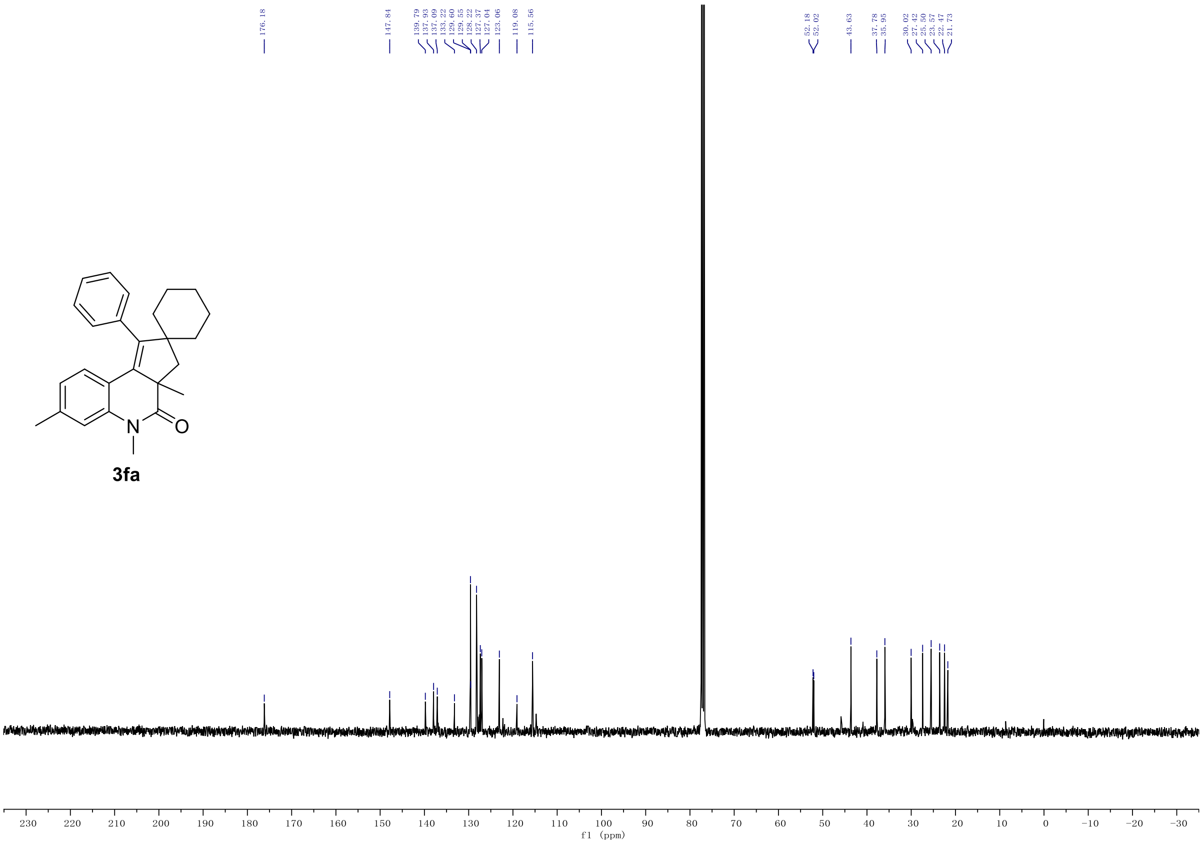
^{1}H NMR Spectrum of Compound 3ea



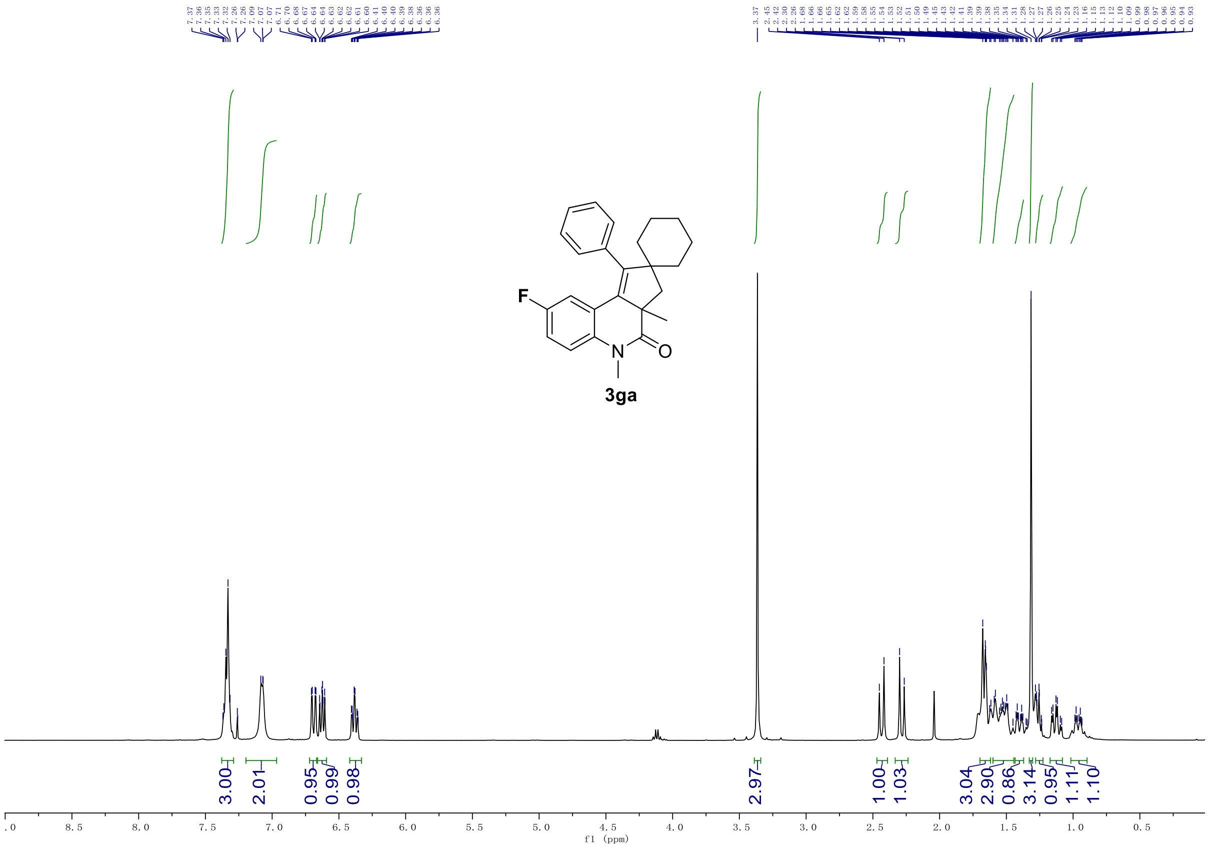
^{13}C NMR Spectrum of Compound 3ea



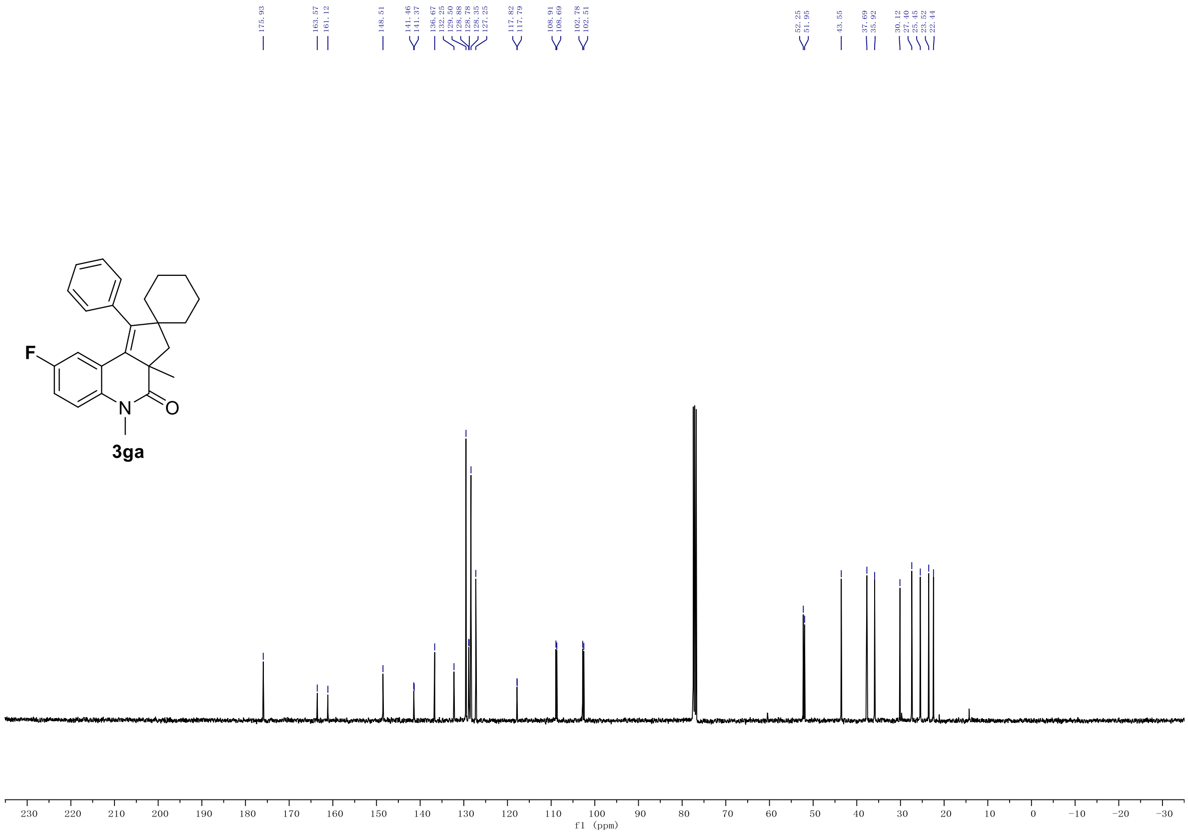
^{1}H NMR Spectrum of Compound 3fa



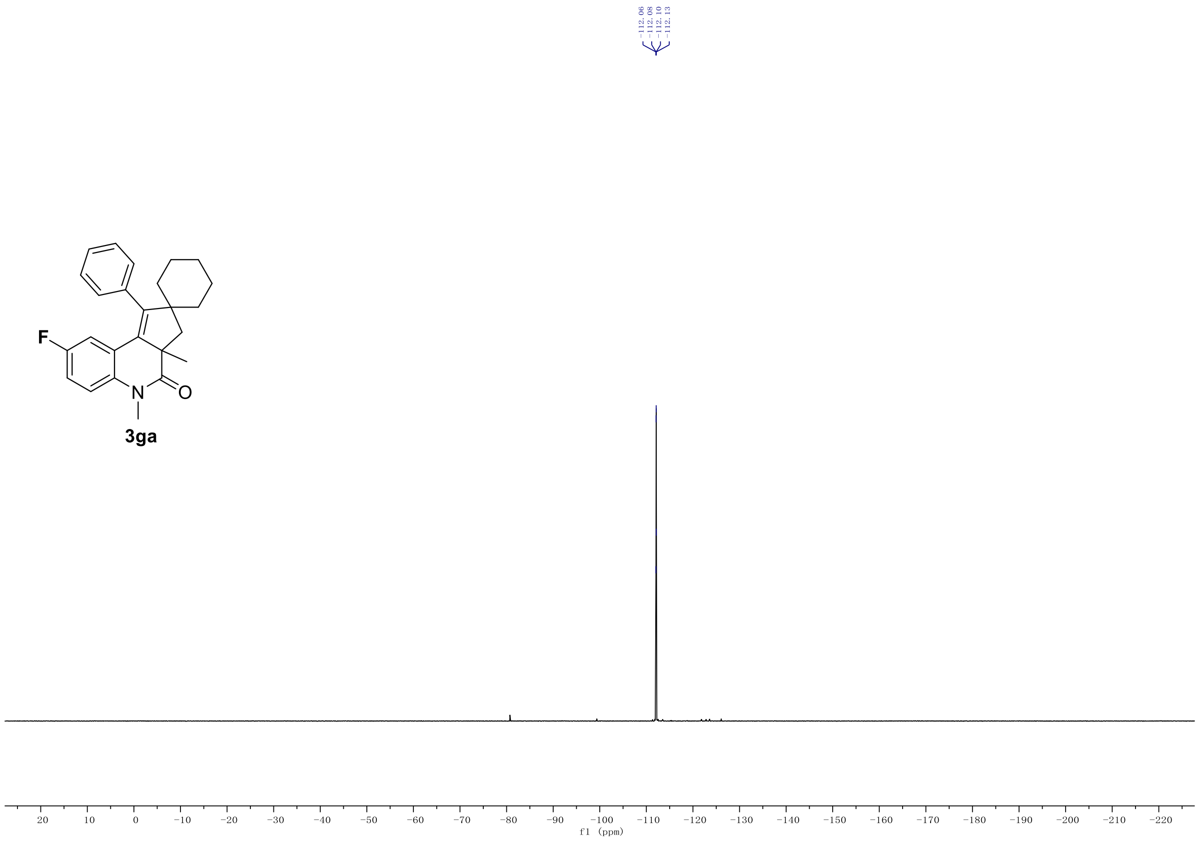
^{13}C NMR Spectrum of Compound 3fa



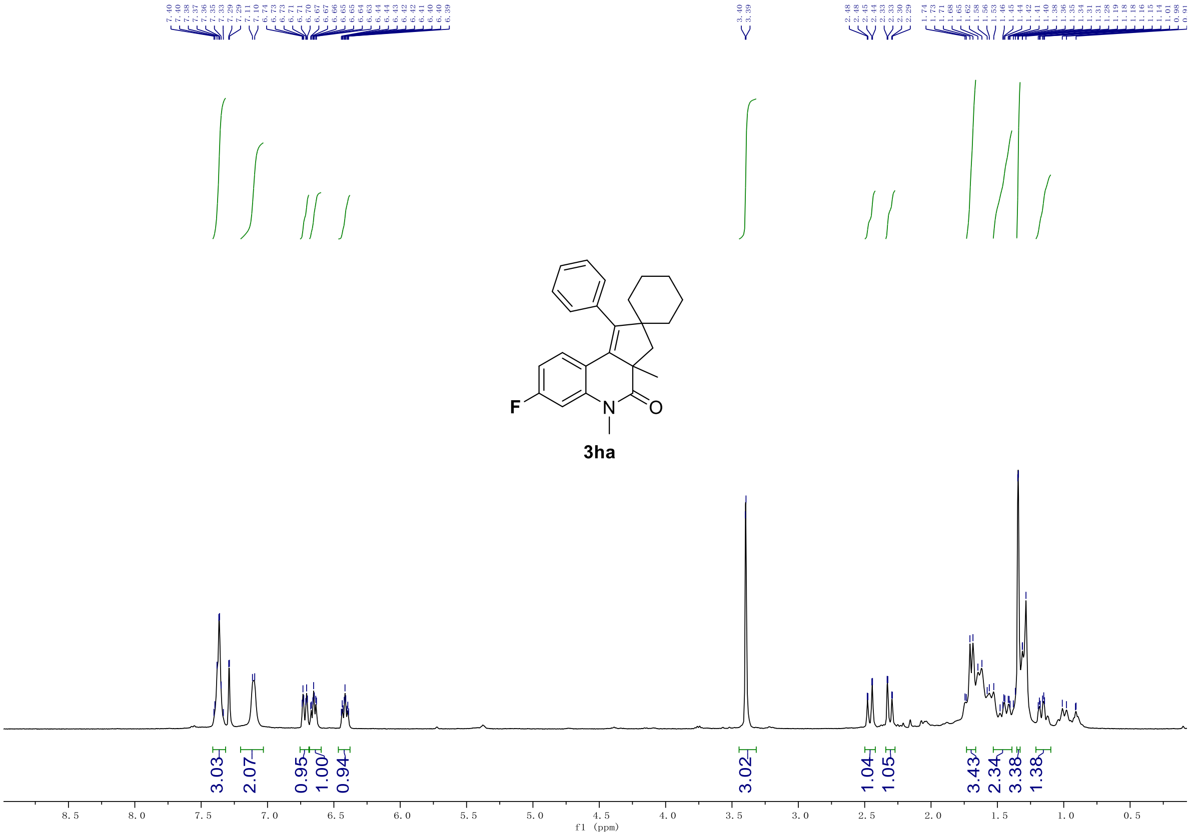
^{1}H NMR Spectrum of Compound 3ga



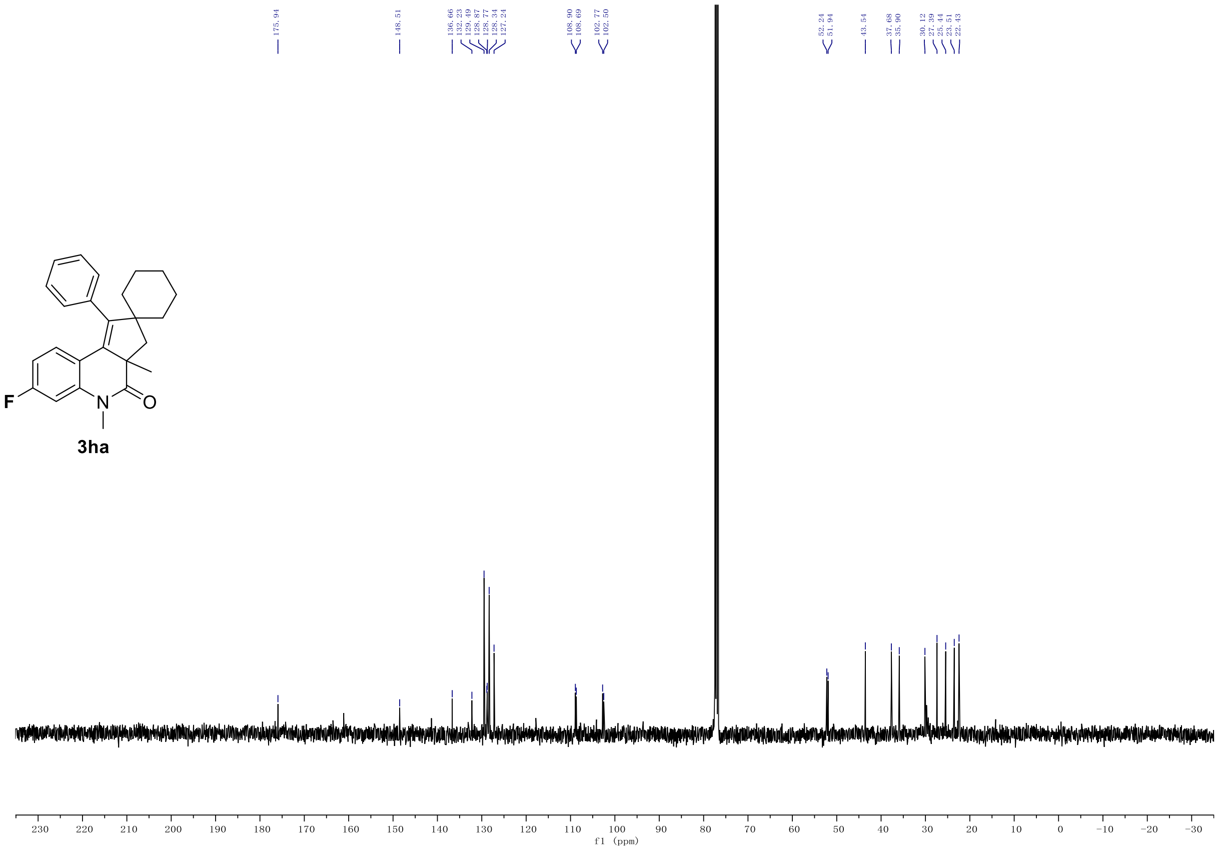
^{13}C NMR Spectrum of Compound 3ga



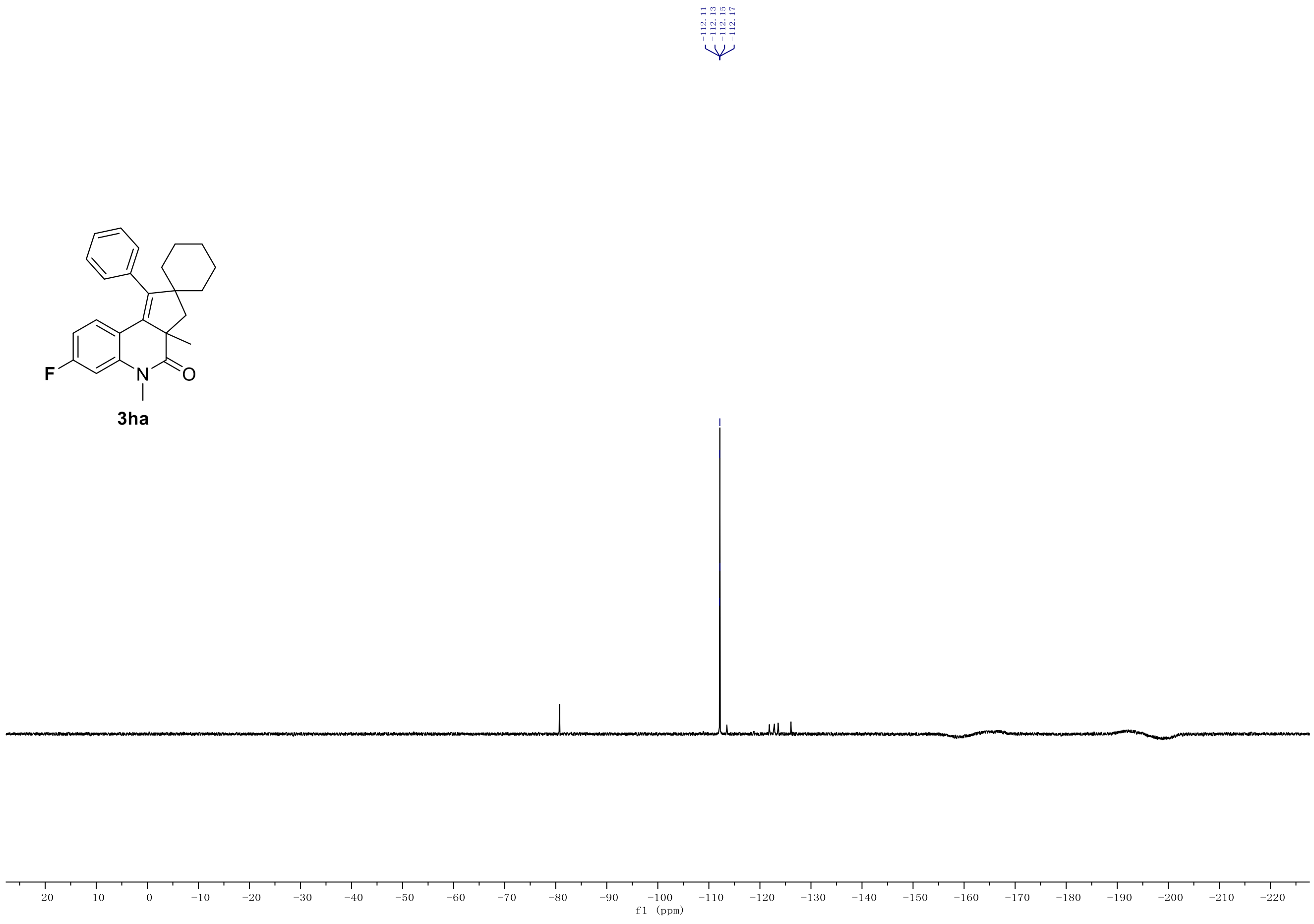
^{19}F NMR Spectrum of Compound 3ga



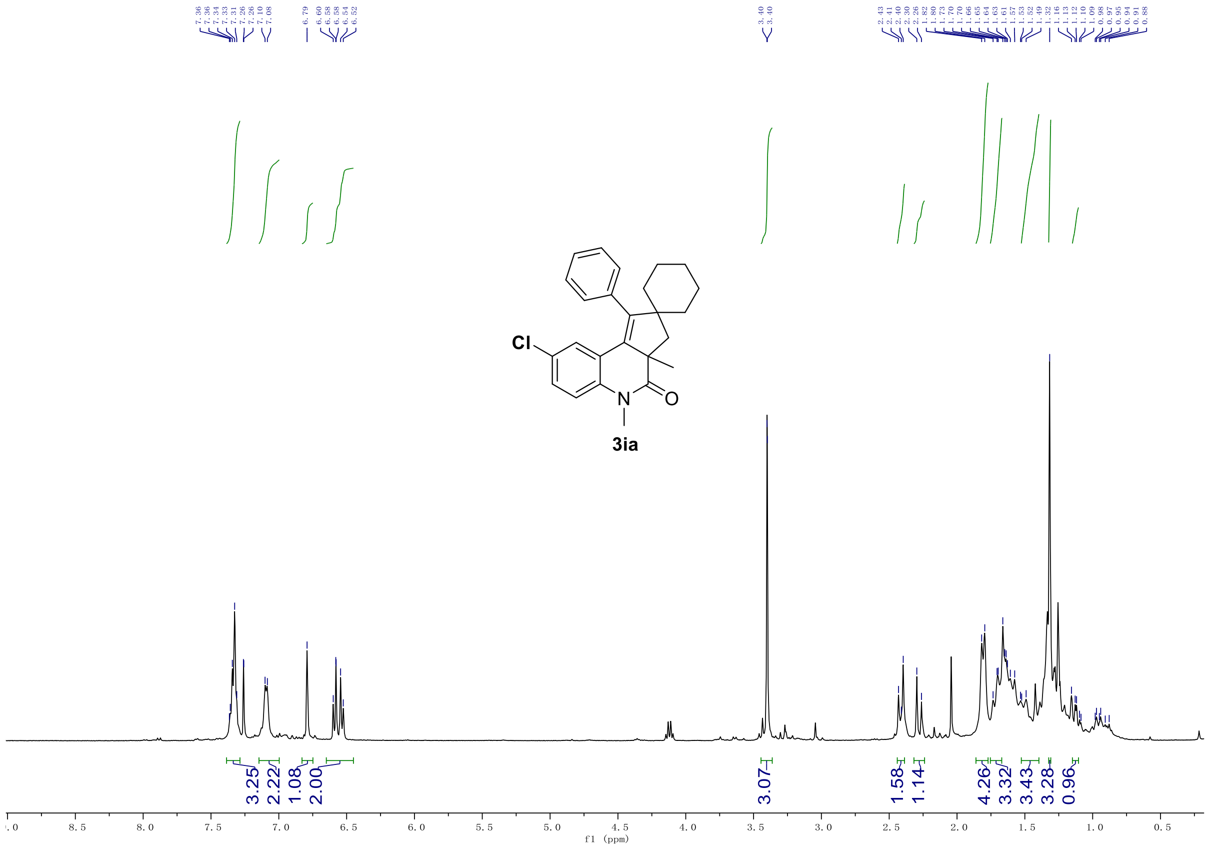
^{1}H NMR Spectrum of Compound 3ha



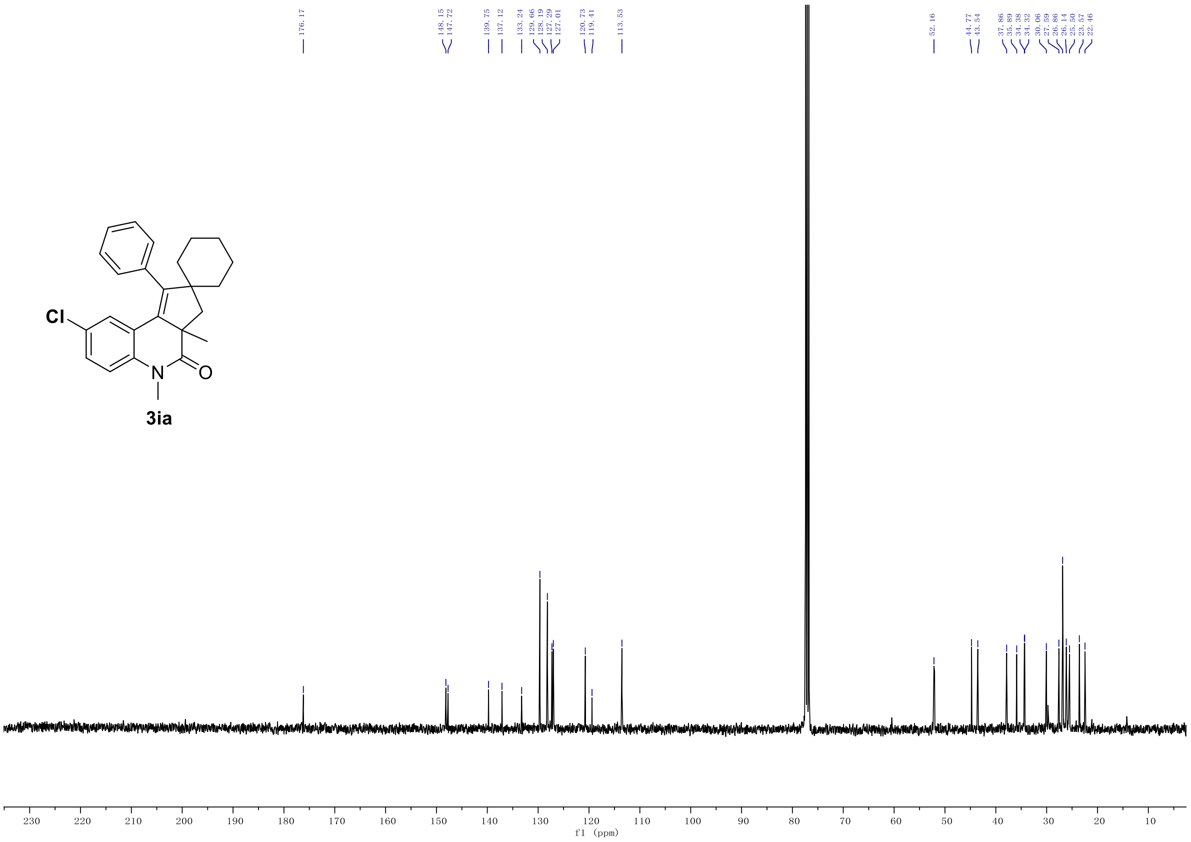
^{13}C NMR Spectrum of Compound 3ha



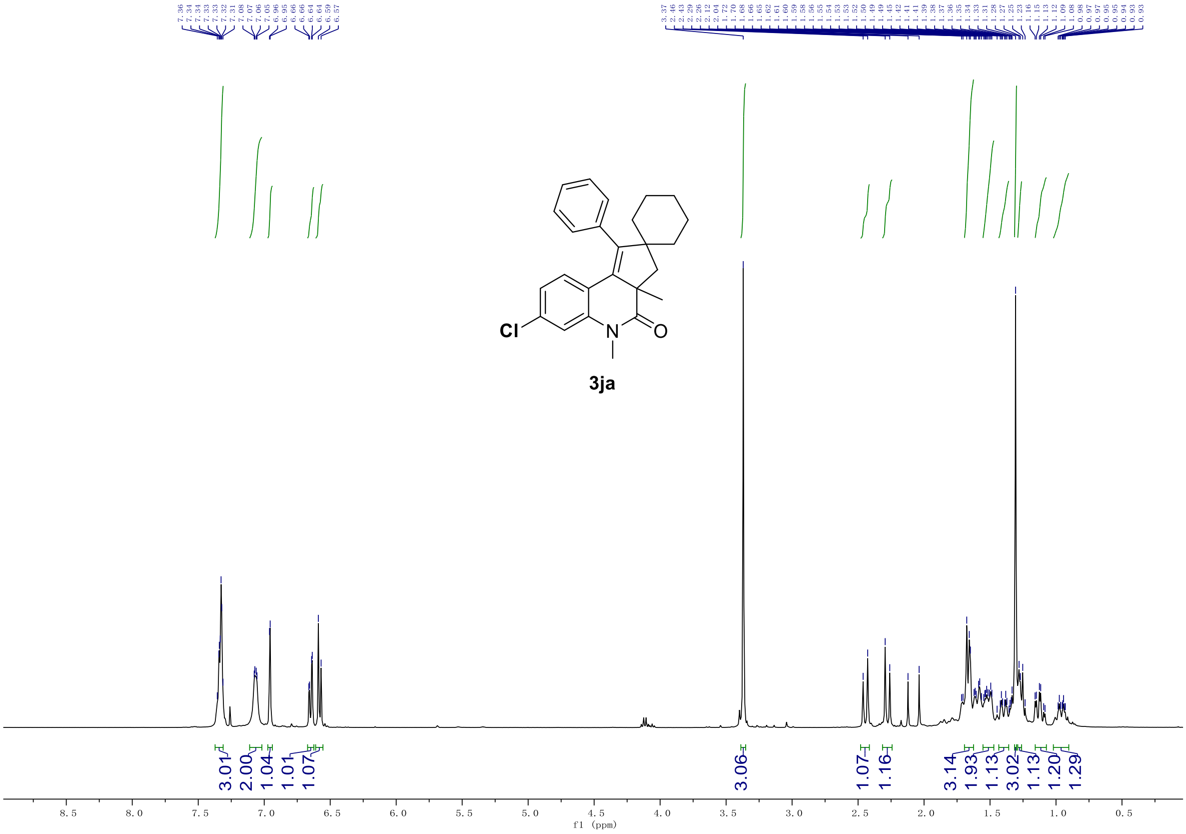
^{19}F NMR Spectrum of Compound 3ha



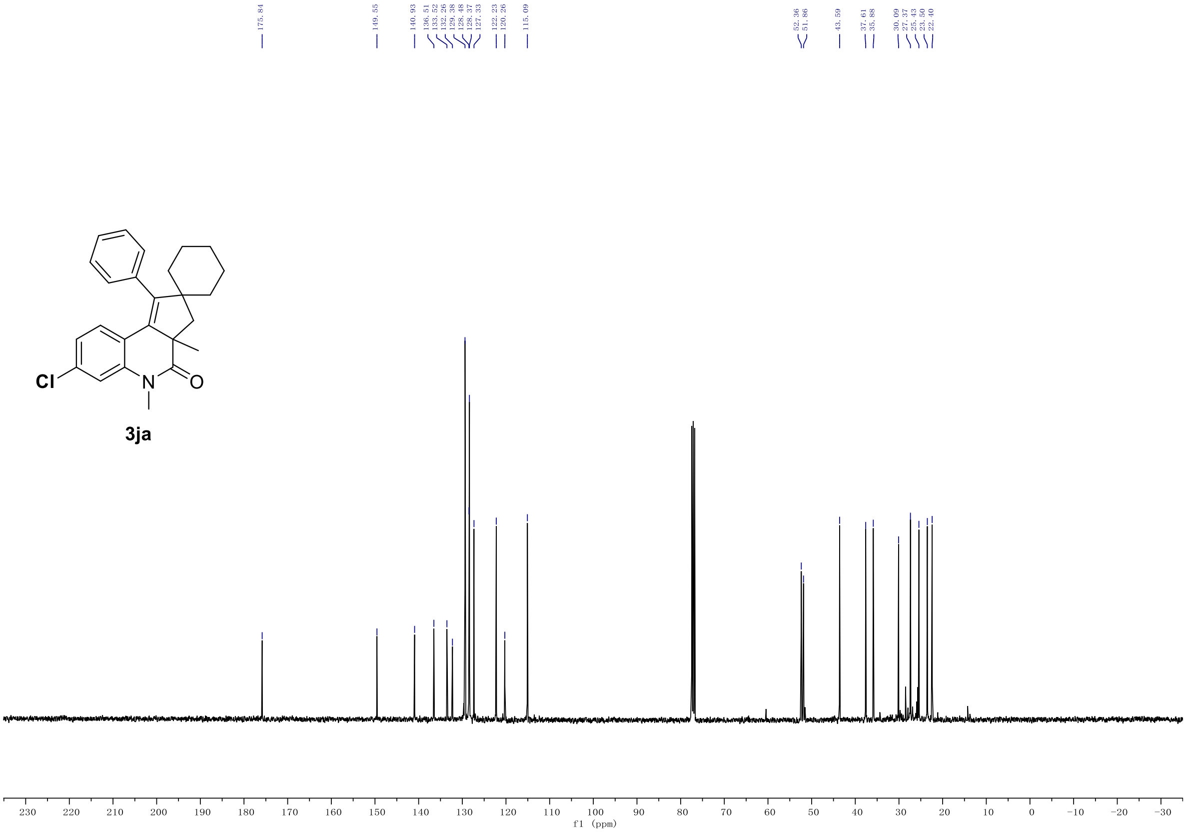
^{1}H NMR Spectrum of Compound 3ia



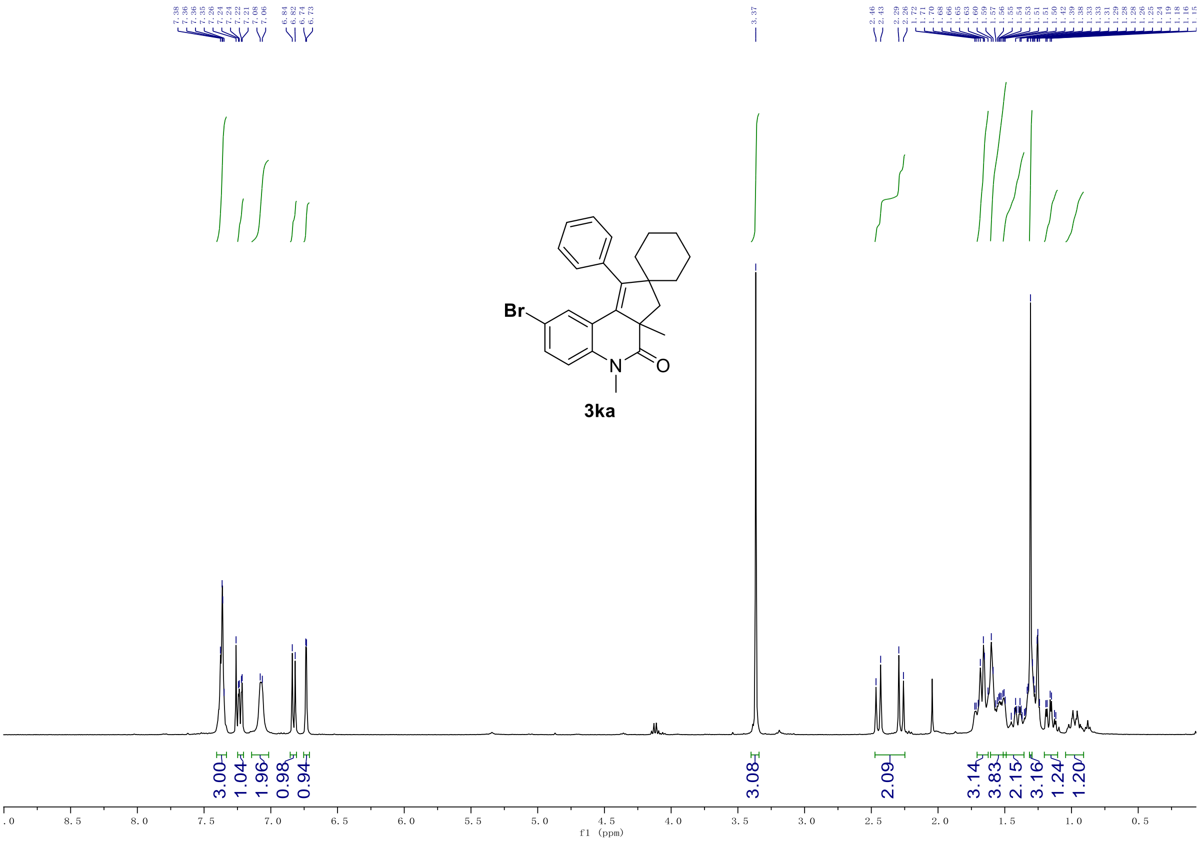
^{13}C NMR Spectrum of Compound 3ia



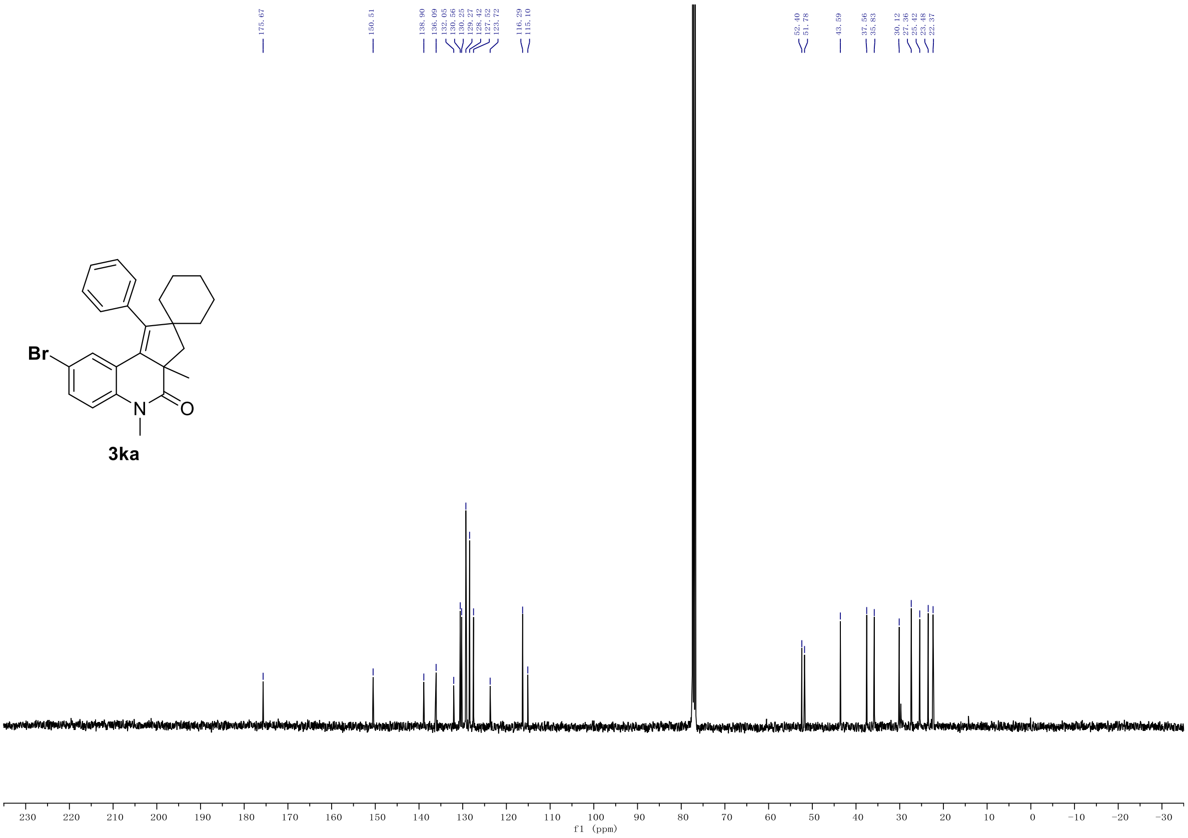
^{1}H NMR Spectrum of Compound 3ja



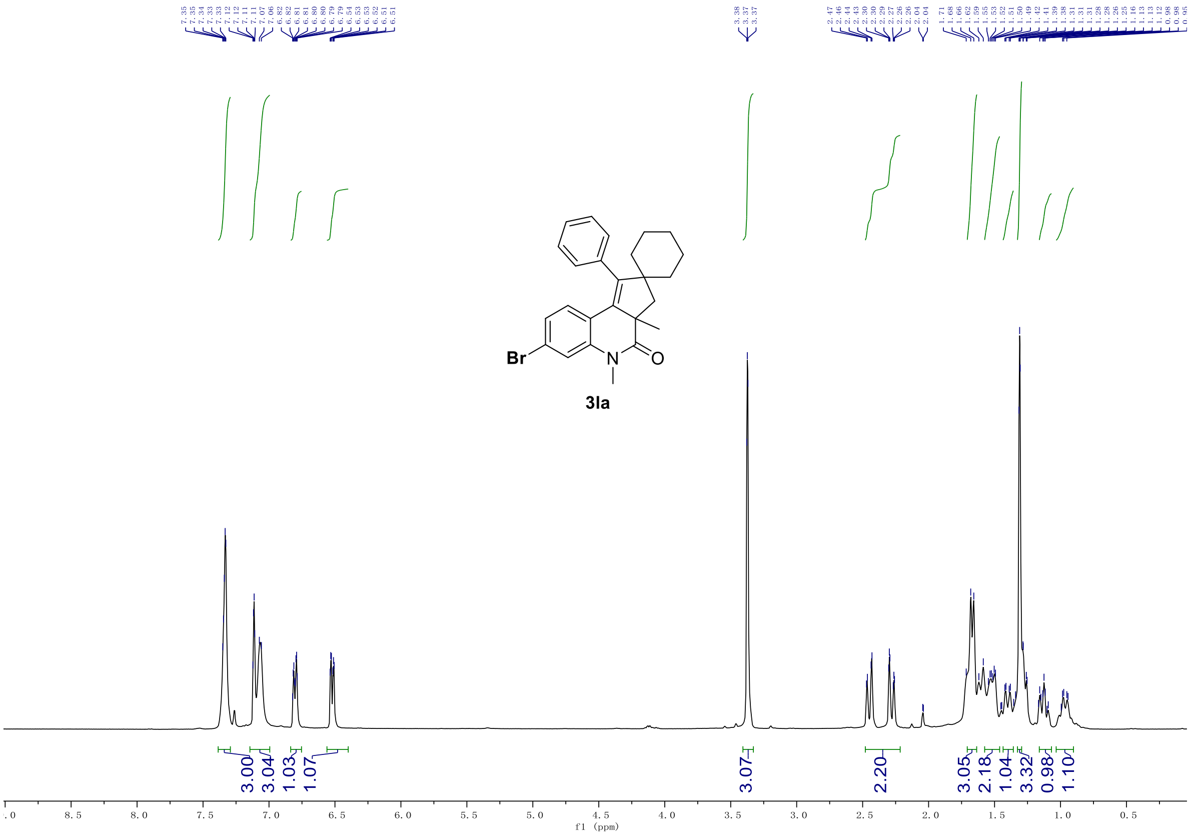
^{13}C NMR Spectrum of Compound 3ja



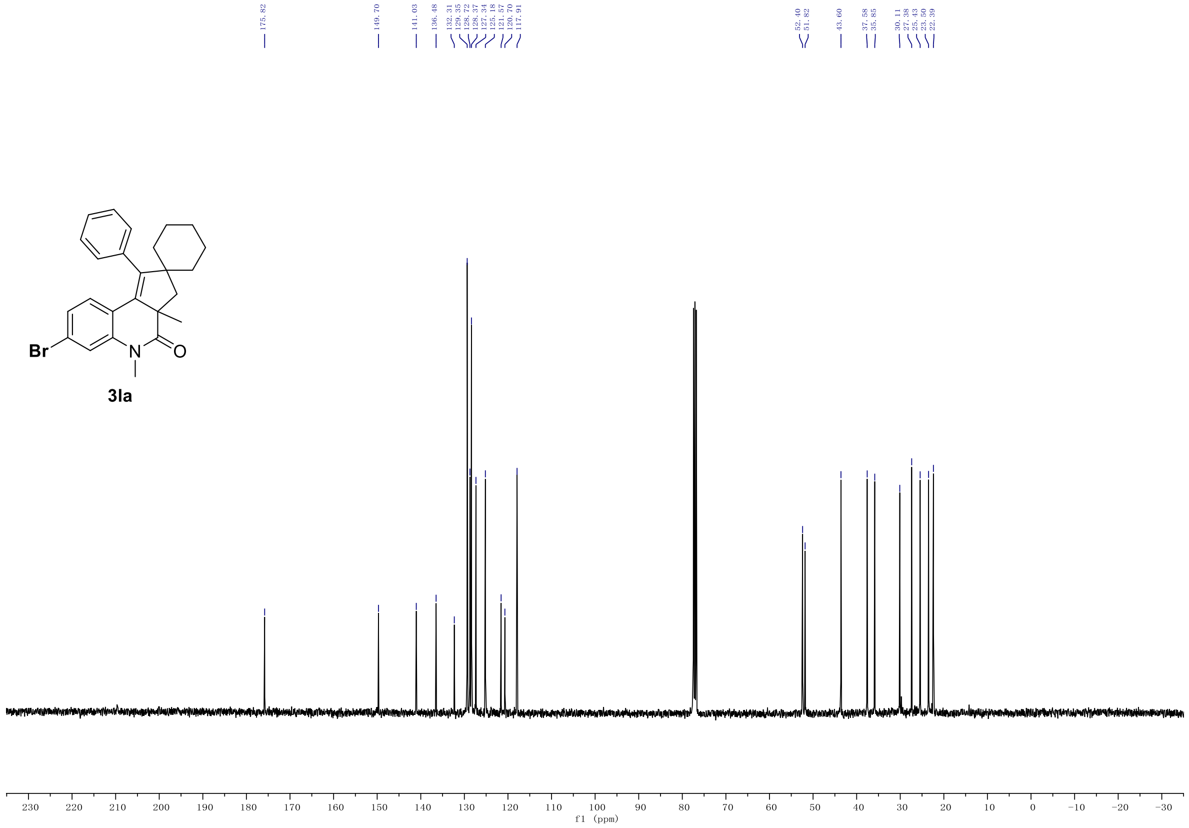
^{1}H NMR Spectrum of Compound 3ka



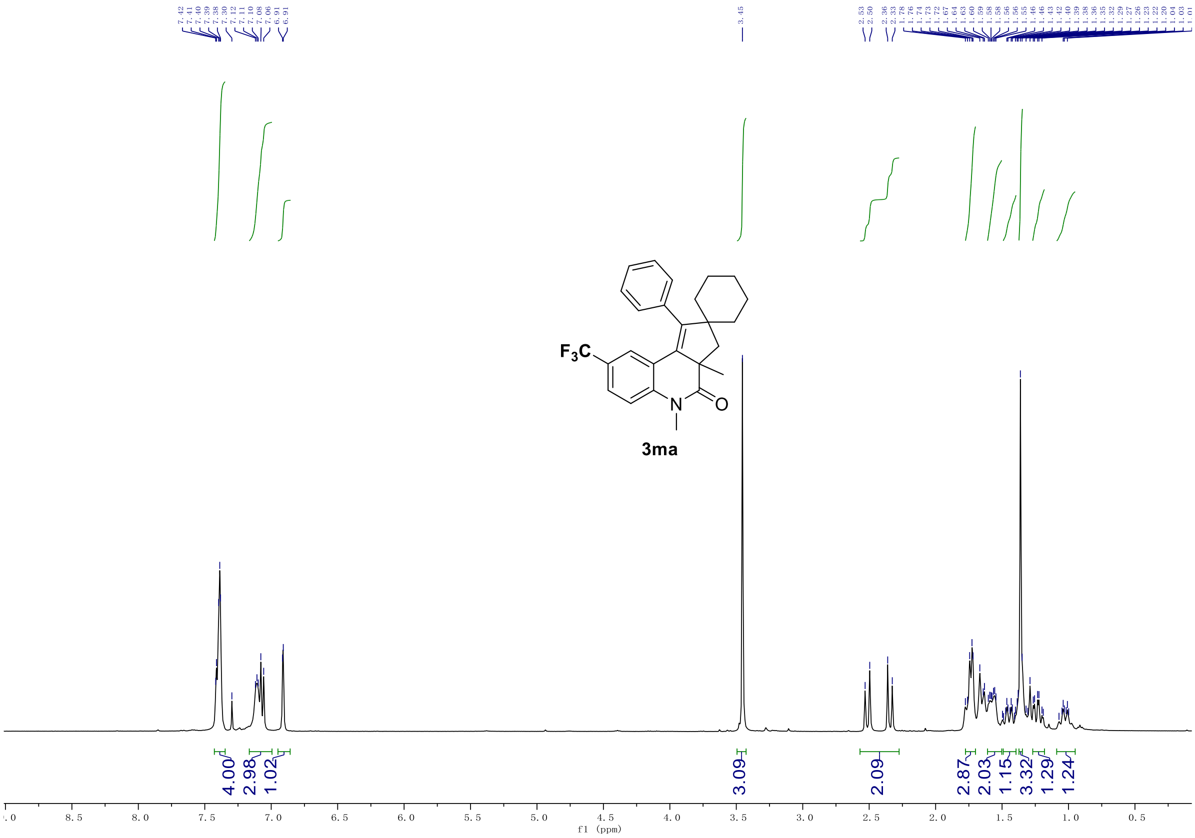
^{13}C NMR Spectrum of Compound 3ka



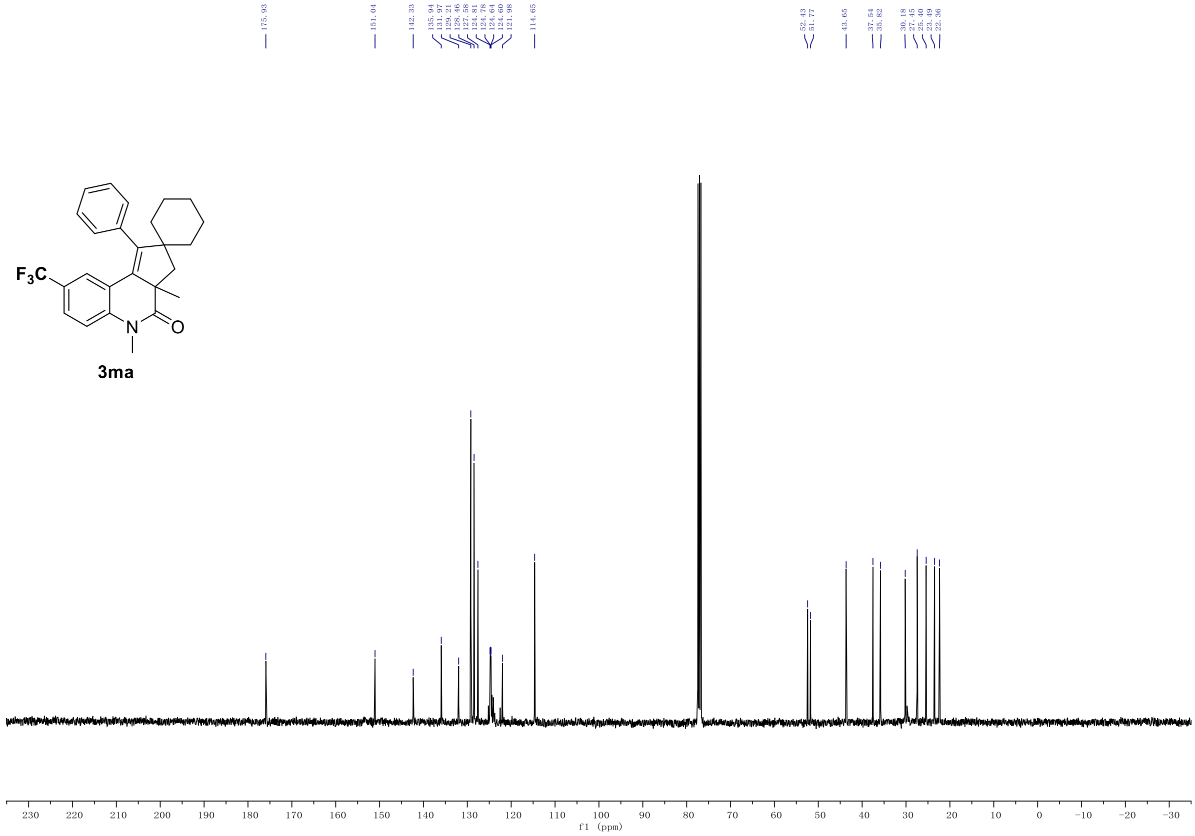
^{1}H NMR Spectrum of Compound 3la



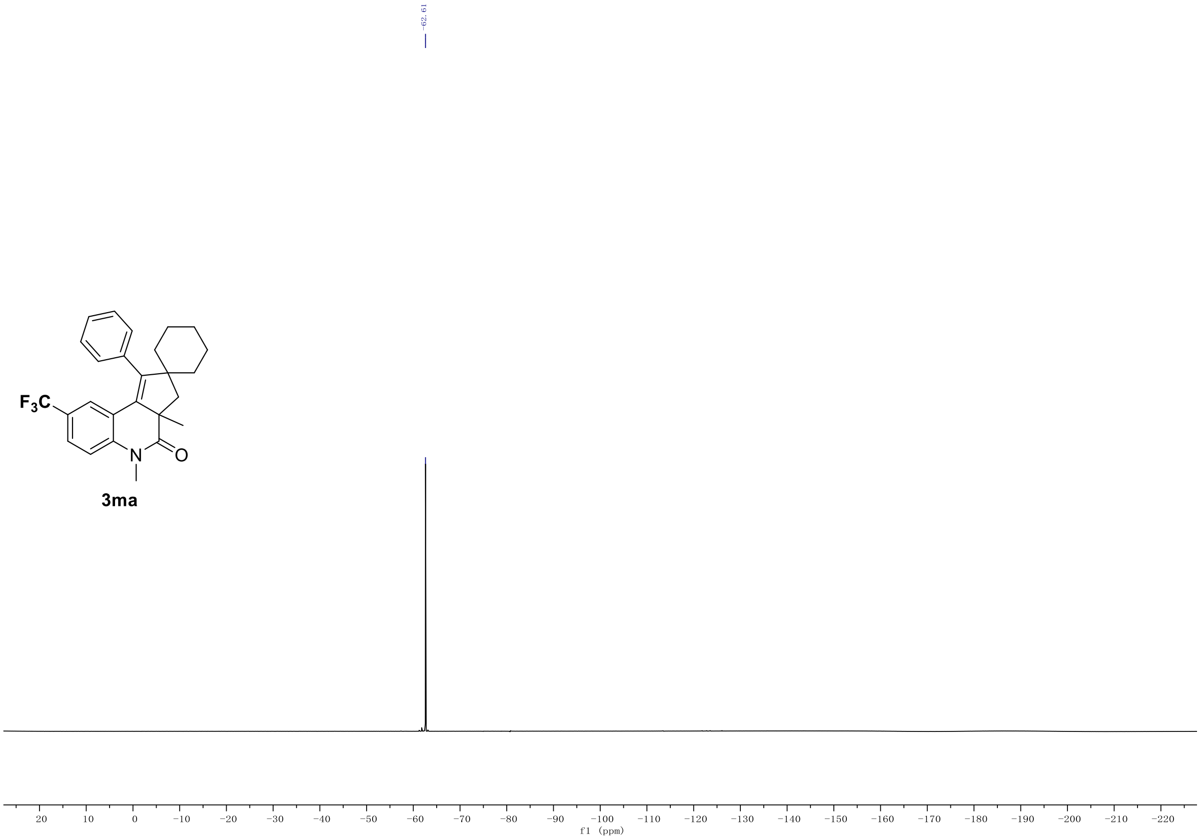
^{13}C NMR Spectrum of Compound 3la



^{1}H NMR Spectrum of Compound 3ma



^{13}C NMR Spectrum of Compound 3ma



^{19}F NMR Spectrum of Compound 3ma