Electrochemically enabled dearomative [2+2] cycloadditions of indoles with alkynes to access cyclobutene-fused 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 10 min 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, ^{13}C NMR, ^{19}F NMR, and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer using tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). Electrolysis was performed using a DJS-292B dual display potentiostat (Shanghai Xinrui Instruments Co., China). The indole derivatives used as substrates were synthesized following established methods, and their NMR data were consistent with the literature.[1-4] The electrochemical setup used in this research is shown in Figure S1.

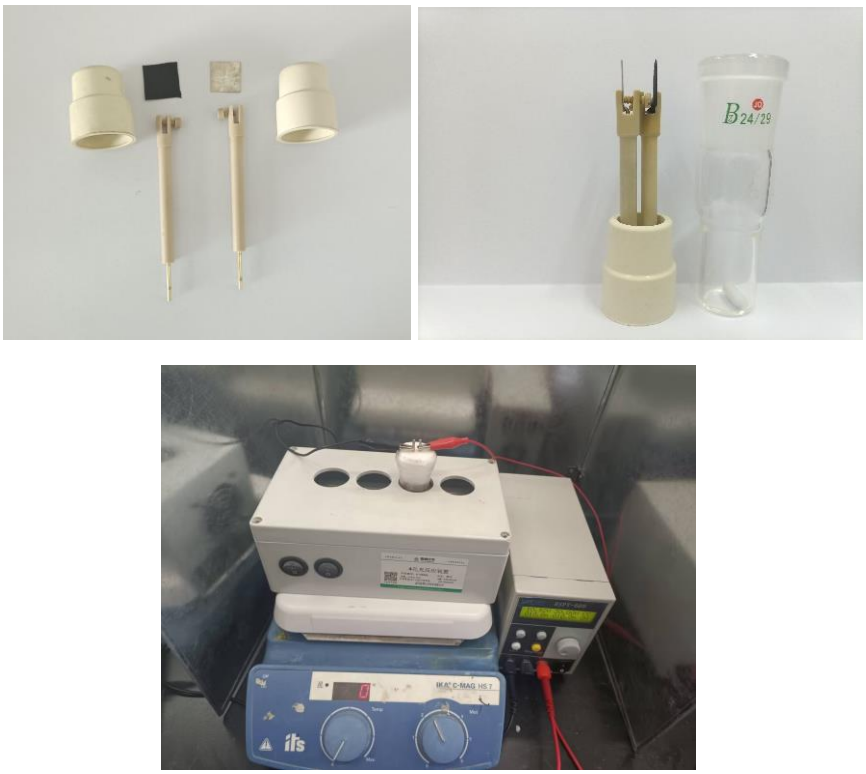
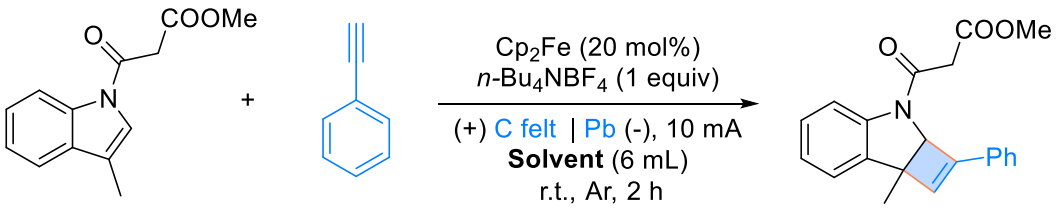


Figure S1 Electrochemical setup

II. Optimization of reaction condition

Table S1 Solvent screening.[a]

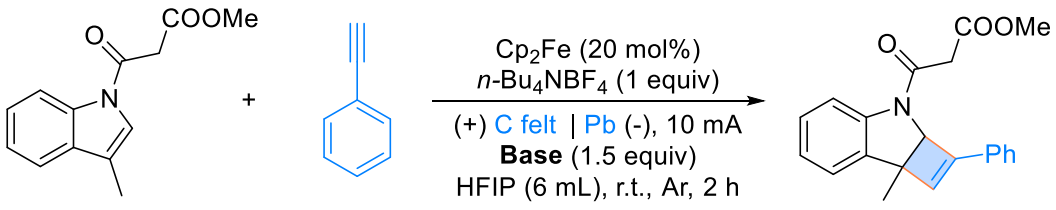


1a: 0.5 mmol **2a:** 1.0 mmol **3a**

Entry	Solvent	Yield (%)[b]
1	DCE	0%
2	MeCN	0%
3	$MeNO_2$	0%
4	acetone	0%
5	THF	0%
6	1,4-dioxane	0%
7	DMF	0%
8	DMA	0%
9	DMSO	0%
10	MeOH	0%
11	CF_3CH_2OH	0%
12	HFIP	16%

[a] Reaction conditions: undivided cell, carbon felt anode, Pb cathode, electrodes (15 mm × 15 mm × 0.3 mm), constant current electrolysis at 10.0 mA, **1a** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NOAc (0.5 mmol), Cp_2Fe (0.1 mmol, 0.2 equiv), solvent (6.0 mL), under argon, room temperature, 2 h. [b] ^1H NMR yield with isoquinoline as an internal standard.

Table S2 Base screening.[a]



1a: 0.5 mmol **2a:** 1.0 mmol **3a**

Entry	Base	Yield (%)[b]
1	none	16
2	KOAc	7
3	NaOAc	1

4	NaOAc	6
5	$NaHCO_3$	0
6	$KHCO_3$	0
7	KF	6
8	Cs_2CO_3	3
9	K_2CO_3	1
10	Na_2CO_3	3
11	Li_2CO_3	15
12	K_2HPO_4	6
13	K_3PO_4	2
14	KOH	0
15	*t*-BuOK	8
16	*t*-BuONa	4
17	*t*-BuOLi	2
18	DABCO	0
19	DBU	0

[a] Reaction conditions: undivided cell, carbon felt anode, Pb cathode, electrodes (15 mm × 15 mm × 0.3 mm), constant current electrolysis at 10.0 mA, **1a** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NOAc (0.5 mmol), base (0.45 mmol, 1.5 equiv), Cp_2Fe (0.1 mmol, 0.2 equiv), HFIP (6.0 mL), under argon, room temperature, 2 h. [b] ^1H NMR yield with isoquinoline as an internal standard.

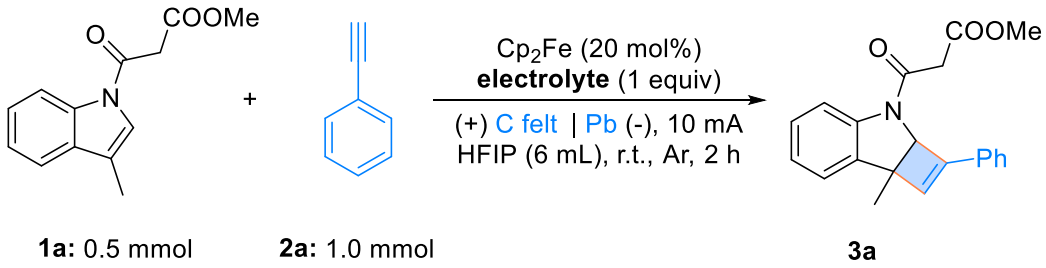


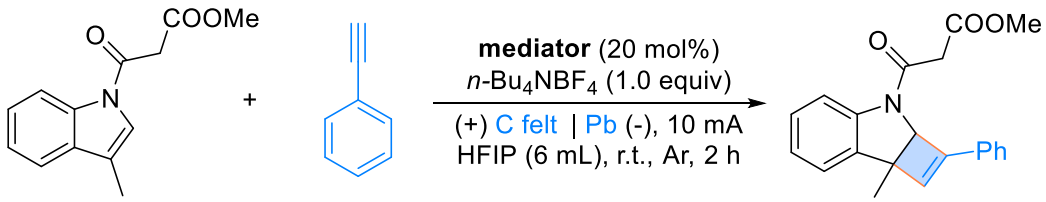
Table S3 electrolyte screening.[a]

Entry	Electrolyte	Yield (%)[b]
1	none	0
2	$LiClO_4$	0
3	KPF_6	0
4	***n*-Bu_4NBF_4**	**10**
5	*n*-Et_4NBF_4	5
6	*n*-Bu_4NPF_6	0
7	*n*-Bu_4NOAc	0
8	*n*-Bu_4NClO_4	0
9	TBAI	0

[a] Reaction conditions: undivided cell, carbon felt anode, Pb cathode, electrodes (15 mm × 15 mm × 0.3 mm), constant current electrolysis at 10.0 mA, **1a** (0.5 mmol), **2a** (1.0 mmol), electrolyte (0.5 mmol), Cp_2Fe (0.1 mmol, 0.2 equiv), HFIP (6.0 mL),

under argon, room temperature, 2 h. [b] ^{1}H NMR yield with isoquinoline as an internal standard.

Table S4 Optimization of mediator.[a]

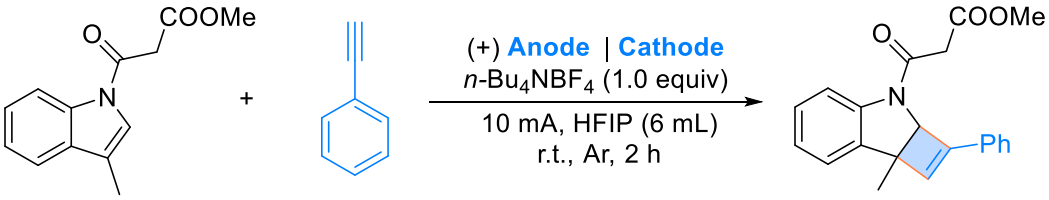


1a: 0.5 mmol **2a:** 1.0 mmol **3a**

Entry	Mediator	Yield (%)[b]
1	Cp_2Fe	16
2	TEMPO	20
3	NHPI	54
4	TBAI	2
5	TBAB	40
6	DDQ	7
7	Ph_3N	6
8	**none**	**54**

[a] Reaction conditions: undivided cell, carbon felt anode, Pb cathode, electrodes (15 mm × 15 mm × 0.3 mm), constant current electrolysis at 10.0 mA, **1a** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NOAc (0.5 mmol), mediator (0.1 mmol, 0.2 equiv), HFIP (6.0 mL), under argon, room temperature, 2 h. [b] ^{1}H NMR yield with isoquinoline as an internal standard.

Table S5 Optimization of electrodes.[a]



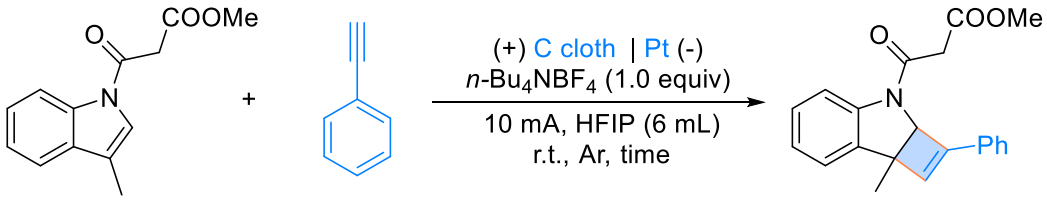
1a: 0.5 mmol **2a:** 1.0 mmol **3a**

Entry	Anode/Cathode	Yield (%)[b]
1	Pt/Pb	3
2	C cloth/Pb	58
3	C felt/Pb	25
4	C rod/Pb	19
5	C RVC/Pb	52
6	**C cloth/Pt**	**61**
7	C cloth/Ni	13
8	C cloth/Ni foam	51

9	C cloth/Stainless steel	60
10	C cloth/C cloth	52
11	C cloth/C felt	54
12	C cloth/C rod	49
13	C cloth/Zn	47
14	C cloth/Fe	4

[a] Reaction conditions: undivided cell, electrodes (15 mm × 15 mm × 0.3 mm), constant current electrolysis at 10.0 mA, **1a** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NOAc (0.3 mmol), HFIP (6.0 mL), under argon, room temperature, 2 h. [b] ^1H NMR yield with isoquinoline as an internal standard.

Table S6 Optimization of constant current.[a]

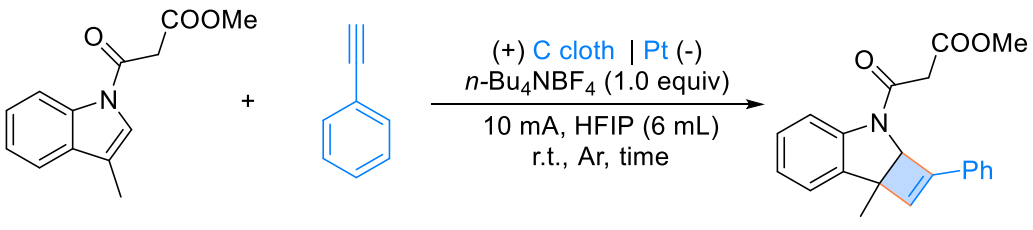


1a: 0.5 mmol **2a:** 1.0 mmol **3a**

Entry	Constant current (mA), reaction time	Yield (%)[b]
1	0 mA, 24 h	NR
2	2 mA, 8 h	45
3	4 mA, 4.0 h	51
4	5 mA, 3.2 h	52
5	7.5 mA, 2.7 h	57
6	10 mA, 2.0 h	61
7	12.5 mA, 1.6 h	61

[a] Reaction conditions: undivided cell, carbon cloth anode (15 mm × 15 mm × 0.33 mm), Pt cathode (15 mm × 15 mm × 0.3 mm), **1a** (0.5 mmol), **2a** (1.0 mmol), *n*-Bu_4NOAc (0.5 mmol), HFIP (6.0 mL), under argon, room temperature. [b] ^1H NMR yield with isoquinoline as an internal standard.

Table S7 Optimization of substrate loading.[a]



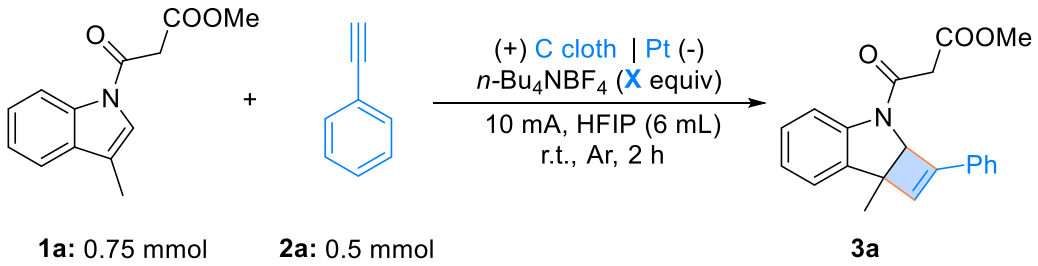
1a **2a** **3a**

Entry	**1a**/**2a** (mmol)	Yield (%)[b]
1	0.5:0.5	53%
2	0.5:0.55	58%

3	0.5:0.6	62%
4	0.5:0.65	59%
5	0.5:0.75	62%
6	0.5:0.9	61%
7	0.5:1.0	60%
8	0.6:0.5	62%
9	**0.75:0.5**	**68%**
10	0.9:0.5	69%
11	1.0:0.5	69%

[a] Reaction conditions: undivided cell, carbon cloth anode (15 mm × 15 mm × 0.33 mm), Pt cathode, electrodes (15 mm × 15 mm × 0.33 mm), *n*-Bu_4NOAc (0.5 mmol), HFIP (6.0 mL), under argon, room temperature, 2 h. [b] ^1H NMR yield with isoquinoline as an internal standard.

Table S8 Optimization of electrolyte loading.[a]



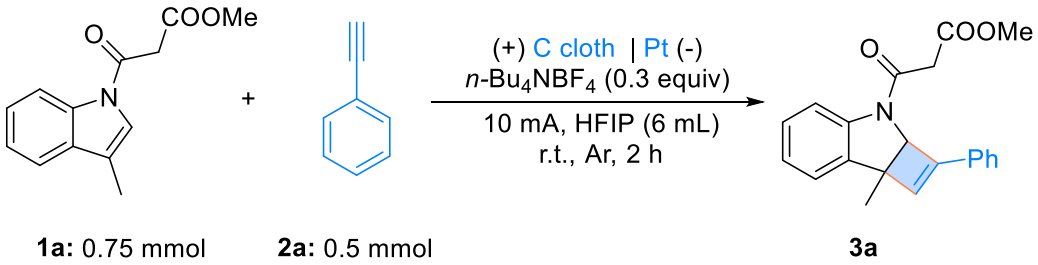
1a: 0.75 mmol **2a:** 0.5 mmol **3a**

Entry	Electrolyte (**X** equiv)	Yield (%)[b]
1	none	0
2	*n*-Bu_4NBF_4 (0.015 equiv)	44
3	*n*-Bu_4NBF_4 (0.15 equiv)	60
4	***n*-Bu_4NBF_4 (0.3 equiv)**	**76**
5	*n*-Bu_4NBF_4 (0.45 equiv)	70
6	*n*-Bu_4NBF_4 (0.6 equiv)	60
7	*n*-Bu_4NBF_4 (0.3 equiv)	62[c]

[a] Reaction conditions: undivided cell, carbon cloth anode (15 mm × 15 mm × 0.33 mm), Pt cathode, electrodes (15 mm × 15 mm × 0.3 mm), HFIP (6.0 mL), under argon, room temperature, 2 h. [b] ^1H NMR yield with isoquinoline as an internal standard. [c]The reaction was run under an air atmosphere.

III. Experimental procedures

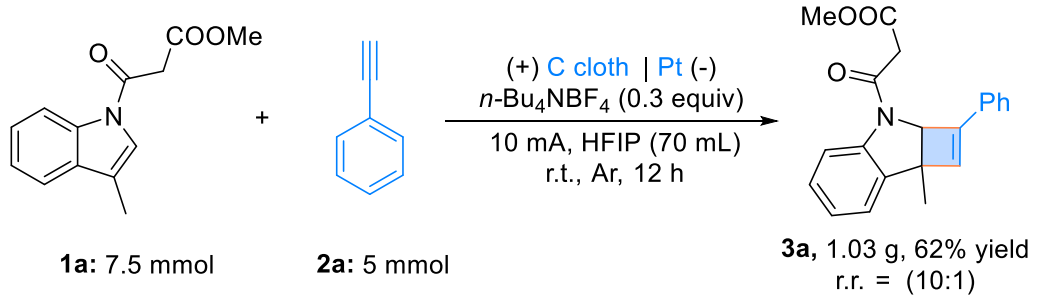
1. General procedure of for the synthesis of 3



1a: 0.75 mmol **2a:** 0.5 mmol **3a**

A custom-made undivided cell, equipped with a magnetic stirring bar, a C cloth anode (15 mm × 15 mm × 0.33 mm) and a Pt cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged with substrate **1** (1.5 equiv, 0.75 mmol), electrolyte *n*-Bu_4NOAc (0.3 equiv, 0.15 mmol, 49.4 mg), alkyne **2** (1.0 equiv, 0.5 mmol), and HFIP (6.0 mL). The mixture was electrolyzed with stirring using a constant current of 10.0 mA at room temperature for 2 hours. When the reaction was complete, ethyl acetate (10 mL) was added, and the solvent was removed under low pressure. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel to afford product **3**.

2. Gram-scale synthesis



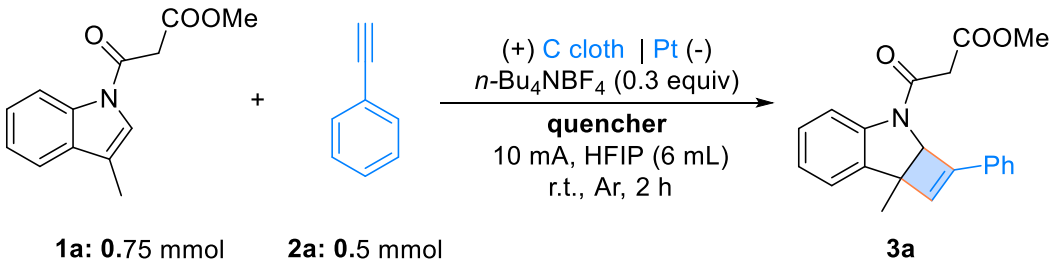
1a: 7.5 mmol **2a:** 5 mmol **3a,** 1.03 g, 62% yield
r.r. = (10:1)

A 100-mL double-neck round-bottom flask, a C cloth anode (15 mm × 15 mm × 0.33 mm) and a Pt cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged with substrate **1a** (1.5 equiv, 7.5 mmol), electrolyte *n*-Bu_4NOAc (0.3 equiv, 1.5 mmol, 494.0 mg), alkyne **2a** (1.0 equiv, 5.0 mmol), and HFIP (70.0 mL). The mixture was electrolyzed with stirring using a constant current of 10.0 mA at room temperature for **12 hours**. When the reaction was complete, ethyl acetate (10 mL) was added, and the solvent was removed under low pressure. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel to afford product **3a** (1.03 g, 62% yield).

Figure S2 Setup for gram-scale synthesis

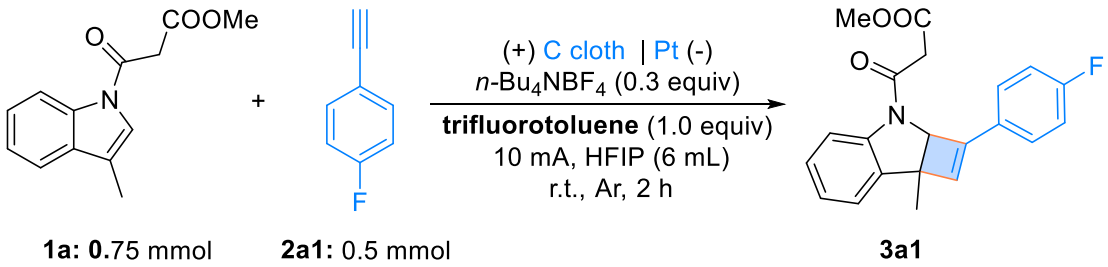
IV. Mechanistic investigations

1. Quenching experiments



A custom-made undivided cell, equipped with a magnetic stirring bar, a C cloth anode (15 mm × 15 mm × 0.33 mm), and a Pt cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged with substrate **1a** (1.5 equiv, 0.75 mmol), electrolyte *n*-Bu$_4$NOAc (0.3 equiv, 0.15 mmol, 49.4 mg), alkyne **2a** (1.0 equiv, 0.5 mmol), a **quencher**, and HFIP (6.0 mL). The mixture was electrolyzed with stirring using a constant current of 10.0 mA at room temperature for 2 hours. The yield of product **3a** formed was determined by ^{1}H NMR analysis based on an isoquinoline internal standard.

2. Electricity on-off experiments



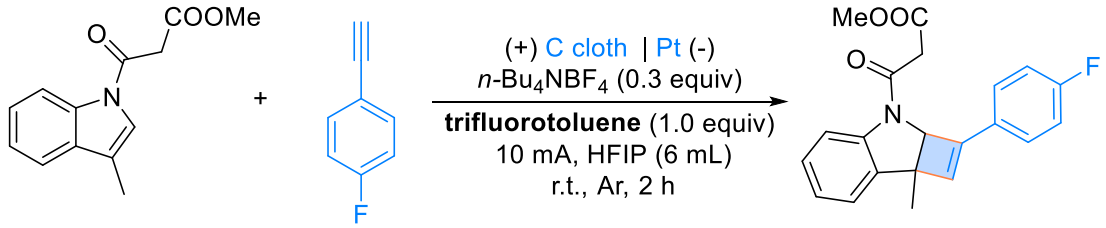
Trifluorotoluene (1 equiv) was added as an internal standard to the reaction mixture before electrolysis, 0.1 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ^{19}F NMR analysis.

	A(X)	B(Y)
Long Name	time	19F NMR Yield
Units	min	%
Comments		
F(x)=		Electricity on/off
1	0	0
2	20	17.02
3	40	17.6
4	60	27.58
5	80	28.18
6	100	33.6
7	120	34.4

Figure S3 Electricity on-off experiments

3. Reaction kinetic profiles

Benzotrifluoride (1 equiv) was added as an internal standard to the reaction mixture before electrolysis using 4-(Trifluoromethyl)benzenesulfonyl chloride as the radical precursor. 0.05 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ^{1}H NMR analysis.



1a: 0.75 mmol **2a:** 0.5 mmol **3a**

Long Name	time	1H NMR Yield of 3a1	1H NMR remaining amount of 2a1	1H NMR remaining amount of 1a
Units	min	%	%	%
Comments				
F(x)=				
1	0	0	100	150
2	20	24	71	112
3	40	43	38	90
4	60	47	29	80
5	80	56	16	38
6	100	61	9	36
7	120	62	3	27

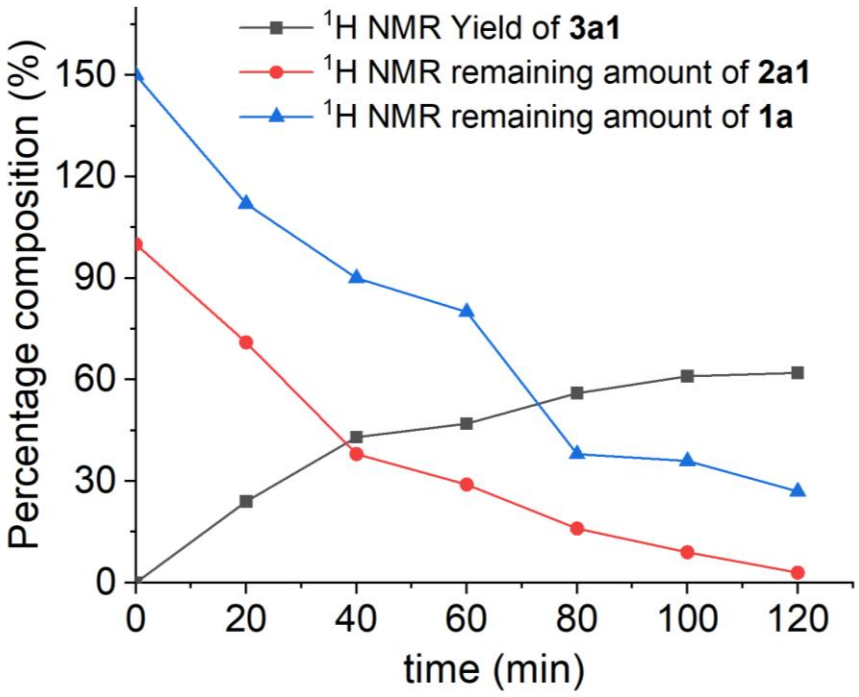


Figure S4 Reaction kinetic profiles

4. Cyclic voltammetry studies

General procedure: Cyclic voltammetries were performed in a three-electrode cell at room temperature. The working electrode was a glassy carbon (GC, d = 3 mm) disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution, and separated from reactions by a salt bridge. 10 mL solution containing 0.1 mmol *n*-Bu_4NBF_4 was poured into the electrochemical cell in all experiments under argon. The scan rate was 0.05 V/s.

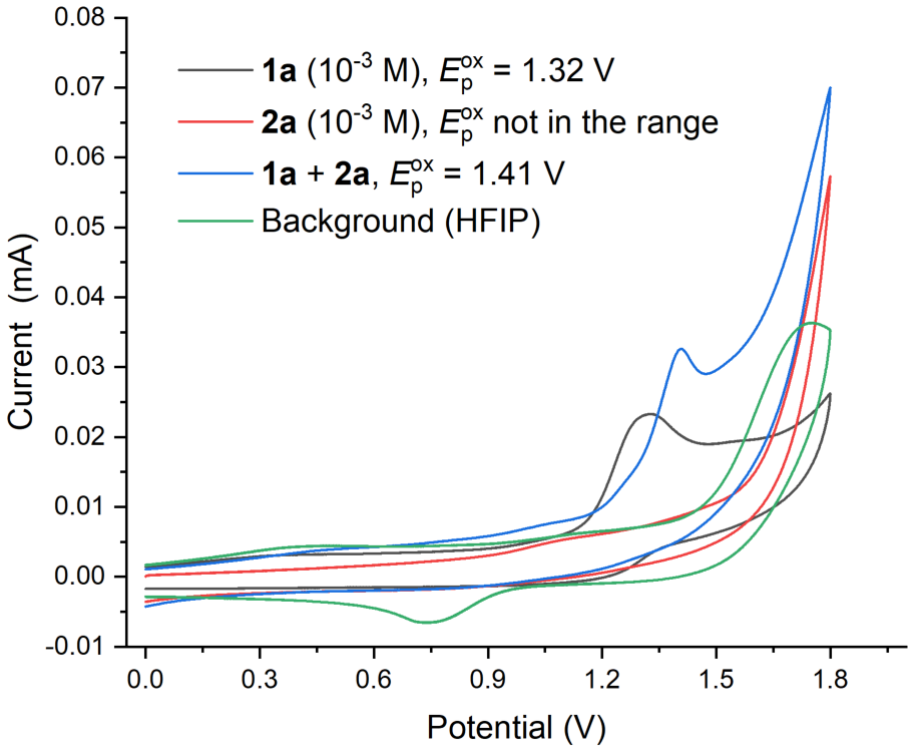
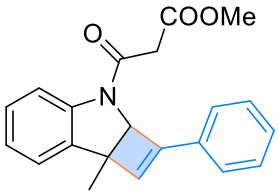
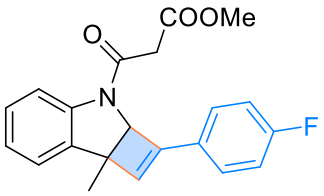


Figure S5 Anodic voltammograms of **1a** and **2a** (10^{-3} M) in HFIP.

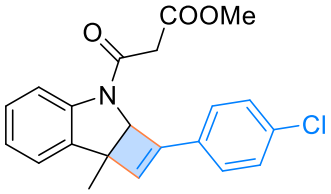
V. Spectral data of products



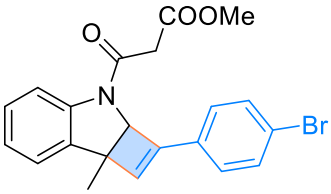
Methyl 3-(7b-methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 70% yield (117.3 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.43 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.25 – 7.19 (m, 1H), 7.09 (td, *J* = 7.5, 0.9 Hz, 1H), 6.32 (s, 1H), 4.73 (s, 1H), 3.82 (s, 3H), 3.66 (q, *J* = 15.1 Hz, 2H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.75, 163.94, 156.94, 143.61, 134.46, 131.73, 129.35, 128.83, 128.67, 125.99, 124.27, 124.11, 121.85, 118.88, 66.97, 56.53, 52.79, 43.53, 20.66. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_3^+$ ($[M+H]^+$) 334.1438. Found 334.1444.



Methyl 3-(2-(4-fluorophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), white solid, m.p. = 168.1-168.3 °C, 62% yield (108.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.39 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.12 – 7.03 (m, 3H), 6.26 (s, 1H), 4.73 (s, 1H), 3.82 (s, 3H), 3.65 (q, *J* = 15.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.73, 163.93,163.23 (d, *J* = 251.0 Hz), 155.87, 143.60, 134.23, 128.78, 128.03 (d, *J* = 3.4 Hz), 127.88 (d, *J* = 8.4 Hz), 124.30, 123.92, 121.44 (d, *J* = 2.2 Hz), 118.94, 116.00(d, *J* = 21.9 Hz), 66.89, 56.47, 52.82, 43.52, 20.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.76. HRMS (ESI-TOF) Calcd for $C_{21}H_{19}FNO_3^+$ ($[M+H]^+$) 352.1343. Found 352.1343.

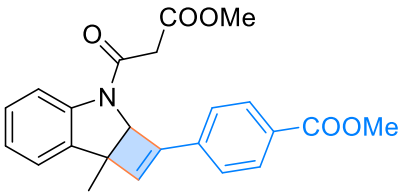


Methyl 3-(2-(4-chlorophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), white solid, m.p. = 151.5-151.7 °C, 81% yield (148.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.36 – 7.30 (m, 2H), 7.26 – 7.21 (m, 1H), 7.09 (td, *J* = 7.5, 0.9 Hz, 1H), 6.31 (s, 1H), 4.73 (s, 1H), 3.81 (s, 3H), 3.65 (q, *J* = 15.1 Hz, 2H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.61, 163.83, 155.65, 143.46, 135.07, 134.04, 130.06, 129.02, 128.70, 127.15, 124.22, 123.83, 122.43, 118.81, 66.79, 56.37, 52.71, 43.41, 20.40. HRMS (ESI-TOF) Calcd for $C_{21}H_{19}ClNO_3^+$ ($[M+H]^+$) 368.1048. Found 368.1052.

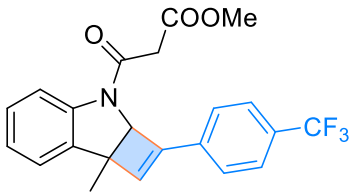


Methyl 3-(2-(4-bromophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a3**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow solid, m.p. = 189.3-189.9 °C, 75% yield

(153.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.38 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.23 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.09 (td, *J* = 7.5, 0.9 Hz, 1H), 6.33 (s, 1H), 4.72 (s, 1H), 3.81 (s, 3H), 3.65 (q, *J* = 15.1 Hz, 2H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.60, 163.81, 155.73, 143.44, 134.01, 131.97, 130.48, 128.72, 127.38, 124.23, 123.81, 123.37, 122.57, 118.83, 66.80, 56.37, 52.72, 43.41, 20.40. HRMS (ESI-TOF) Calcd for $C_{21}H_{19}BrNO_3^+$ ($[M+H]^+$) 412.0543. Found 412.0540.

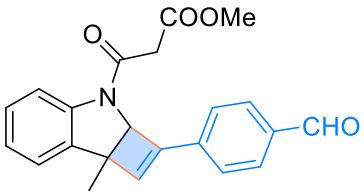


Methyl 4-(3-(3-methoxy-3-oxopropanoyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-2-yl)benzoate (**3a4**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), white solid, m.p. = 150.3-151.7 °C, yield (141.1 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.27 – 7.21 (m, 1H), 7.10 (td, *J* = 7.5, 0.9 Hz, 1H), 6.45 (s, 1H), 4.76 (s, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.66 (q, *J* = 15.1 Hz, 2H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 166.48, 163.81, 155.86, 143.43, 135.70, 133.93, 130.42, 130.00, 128.75, 125.77, 124.54, 124.28, 123.90, 118.81, 66.81, 56.51, 52.72, 52.28, 43.42, 20.43. HRMS (ESI-TOF) Calcd for $C_{23}H_{22}NO_5^+$ ($[M+H]^+$) 392.1492. Found 392.1491.

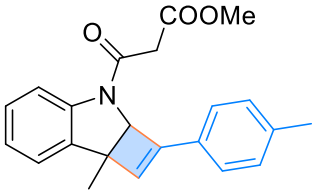


methyl 3-(7b-methyl-2-(4-(trifluoromethyl)phenyl)-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a5**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow solid, m.p. = 164.1-164.7 °C, 86% yield (172.6 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.61 (q, *J* = 8.3 Hz, 4H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 6.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.45 (s, 1H), 4.77 (s, 1H), 3.82 (s, 3H), 3.66 (q, *J* = 15.1 Hz, 2H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.55, 163.78, 155.49, 143.45, 134.91, 133.80, 130.87 (q, *J* = 32.7 Hz), 128.82, 126.11, 125.74 (q, *J* = 3.7 Hz), 124.58, 124.28, 123.86 (q, *J* = 273.2 Hz), 123.79, 118.86, 66.78, 56.54, 52.71, 43.41, 20.35. HRMS (ESI-TOF) Calcd for $C_{22}H_{19}F_3NO_3^+$ ($[M+H]^+$) 402.1312. Found

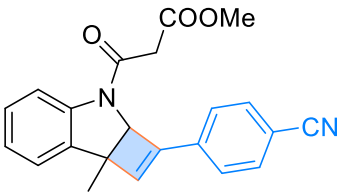
402.1313.



Methyl 3-(2-(4-formylphenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a6**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 62% yield (125.0 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.30 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.39 (m, 1H), 7.27 – 7.22 (m, 1H), 7.11 (td, *J* = 7.5, 0.9 Hz, 1H), 6.51 (s, 1H), 4.78 (s, 1H), 3.82 (s, 3H), 3.67 (q, *J* = 15.1 Hz, 2H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.49, 167.57, 163.85, 155.66, 143.42, 137.12, 136.35, 133.80, 130.12, 128.83, 126.37, 125.59, 124.33, 123.85, 118.85, 66.81, 56.57, 52.74, 43.40, 20.40. HRMS (ESI-TOF) Calcd for $C_{22}H_{20}NO_4^+$ ([M+H]$^+$) 362.1387. Found 362.1387.

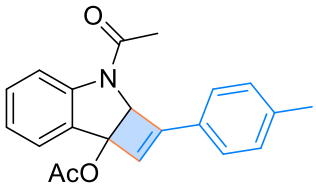


Methyl 3-(7b-methyl-2-(*p*-tolyl)-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a7**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 39% yield (67.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.24 – 7.20 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 – 7.06 (m, 1H), 6.25 (s, 1H), 4.71 (s, 1H), 3.81 (s, 3H), 3.70 – 3.60 (m, 2H), 2.34 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.67, 163.85, 156.77, 143.49, 139.40, 134.48, 129.41, 128.48, 125.83, 124.13, 123.98, 120.60, 118.75, 66.91, 56.33, 52.66, 43.40, 21.44, 20.56. HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_3^+$ ([M+H]$^+$) 348.1594. Found 348.1595.

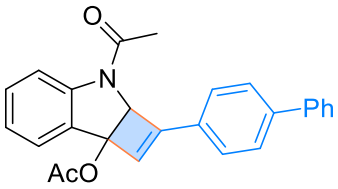


Methyl 3-(2-(4-cyanophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3a8**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 48% yield (86.0 mg), ^{1}H NMR (400 MHz,

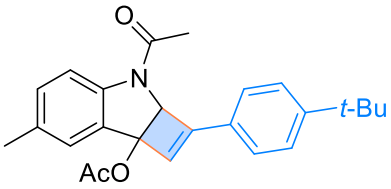
$CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.11 (td, *J* = 7.5, 0.9 Hz, 1H), 6.49 (s, 1H), 4.78 (s, 1H), 3.82 (s, 3H), 3.66 (q, *J* = 15.0 Hz, 2H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 163.75, 155.07, 143.41, 135.73, 133.51, 132.58, 128.96, 126.35, 125.88, 124.36, 123.72, 118.92, 118.45, 112.51, 66.74, 56.58, 52.77, 43.43, 20.32. HRMS (ESI-TOF) Calcd for $C_{22}H_{19}N_2O_3^+$ ($[M+H]^+$) 359.1390. Found 359.1392.



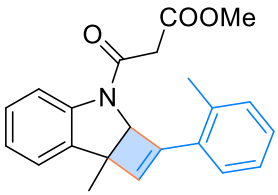
3-Acetyl-2-(*p*-tolyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3b1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 71% yield (118.3 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.07 – 7.01 (m, 1H), 6.21 (s, 1H), 5.33 (s, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.39, 168.18, 151.85, 143.24, 139.95, 130.20, 129.51, 128.71, 127.34, 126.21, 123.59, 123.45, 120.56, 118.53, 85.52, 65.29, 24.03, 21.52, 21.40. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_3^+$ ($[M+H]^+$) 334.1438. Found 334.1434.



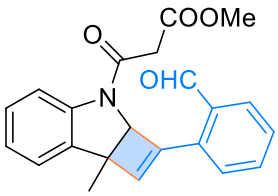
2-([1,1'-Biphenyl]-4-yl)-3-acetyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3b2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), white solid, m.p. = 216.1-216.9 °C, 56% yield (110.1 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.65 – 7.61 (m, 2H), 7.60 – 7.57 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.29 (m, 2H), 7.07 (td, *J* = 7.5, 0.7 Hz, 1H), 6.28 (s, 1H), 5.36 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.39, 168.20, 151.58, 143.27, 142.49, 140.29, 130.31, 128.98, 128.93, 128.65, 127.82, 127.52, 127.06, 126.73, 123.60, 123.54, 121.70, 118.58, 85.55, 65.36, 24.06, 21.42. HRMS (ESI-TOF) Calcd for $C_{26}H_{22}NO_3^+$ ($[M+H]^+$) 396.1594. Found 396.1597.



3-Acetyl-2-(4-(*tert*-butyl)phenyl)-6-methyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3c**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 44% yield (82.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 7.10 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.22 (s, 1H), 5.31 (s, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.12 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.41, 167.88, 153.02, 151.75, 141.06, 133.05, 130.89, 128.71, 127.38, 126.03, 125.79, 124.08, 120.87, 118.24, 85.65, 65.51, 34.89, 31.20, 23.93, 21.44, 21.16. HRMS (ESI-TOF) Calcd for $C_{25}H_{28}NO_3^+$ ([M+H]$^+$) 390.2064. Found 390.2064.

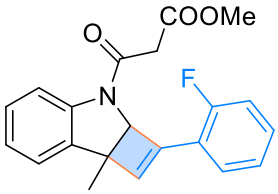


Methyl 3-(7b-methyl-2-(*o*-tolyl)-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3d1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 55% yield (95.9 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.17 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.21 (s, 1H), 4.73 (s, 1H), 3.81 (s, 3H), 3.67 (q, *J* = 15.1 Hz, 2H), 2.32 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.66, 163.79, 156.49, 143.67, 138.71, 134.47, 131.44, 130.47, 128.72, 128.57, 127.25, 126.39, 125.77, 124.30, 124.12, 118.72, 67.33, 57.69, 52.66, 43.45, 22.18, 21.14. HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_3^+$ ([M+H]$^+$) 348.1594. Found 348.1595.

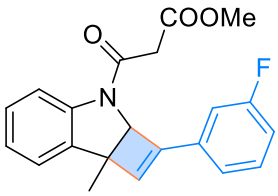


Methyl 3-(2-(2-formylphenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3d2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→5:1), pale yellow oil, 60% yield (180.7 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.61 (td, *J* = 7.6, 1.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.32 –

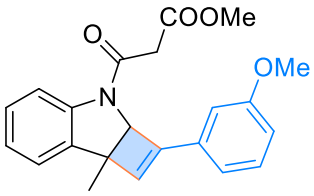
7.27 (m, 1H), 7.23 – 7.18 (m, 1H), 7.10 (td, *J* = 7.5, 0.8 Hz, 1H), 6.29 (s, 1H), 4.85 (s, 1H), 3.81 (s, 3H), 3.67 (q, *J* = 15.1 Hz, 2H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.04, 167.47, 163.80, 154.25, 143.29, 135.52, 134.83, 133.61, 130.64, 129.06, 129.04, 128.56, 128.20, 124.33, 123.68, 118.96, 66.81, 59.05, 52.73, 43.42, 20.04. HRMS (ESI-TOF) Calcd for $C_{22}H_{20}NO_4^+$ ([M+H]$^+$) 362.1387. Found 362.1387.



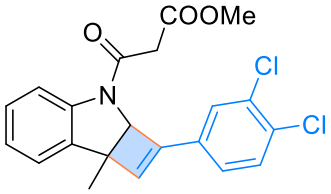
Methyl 3-(2-(2-fluorophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3d3**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 82% yield (143.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.53 (td, *J* = 7.6, 1.5 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.19 – 7.13 (m, 1H), 7.11 – 7.03 (m, 2H), 6.43 (d, *J* = 3.5 Hz, 1H), 4.77 (s, 1H), 3.81 (s, 3H), 3.65 (q, *J* = 15.2 Hz, 2H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.59, 163.83, 161.74 (d, *J* = 254.4 Hz), 151.18, 143.60, 134.05, 130.50 (d, *J* = 8.7 Hz), 128.67, 127.52, 127.46 (d, *J* = 12.0 Hz), 124.14, 124.10, 124.03, 119.71 (d, *J* = 13.8 Hz), 118.73, 116.24 (d, *J* = 21.5 Hz), 67.81, 57.08, 52.66, 43.40, 20.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.29 (s, 1F). HRMS (ESI-TOF) Calcd for $C_{21}H_{19}FNO_3^+$ ([M+H]$^+$) 352.1343. Found 352.1343.



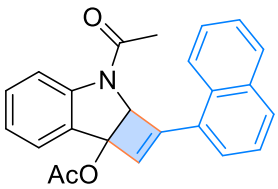
Methyl 3-(2-(3-fluorophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3e1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 80% yield (140.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 13.8, 7.8 Hz, 1H), 7.24 (dd, *J* = 15.3, 7.6 Hz, 2H), 7.15 (d, *J* = 9.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 8.2 Hz, 1H), 6.35 (s, 1H), 4.74 (s, 1H), 3.81 (s, 3H), 3.65 (q, *J* = 15.1 Hz, 2H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 164.93 (d, *J* = 247.7 Hz), 163.83, 155.68 (d, *J* = 2.4 Hz), 155.67, 143.46, 133.98, 133.73 (d, *J* = 7.1 Hz), 130.37 (d, *J* = 8.3 Hz), 128.70, 124.25, 123.89, 123.33, 121.64 (d, *J* = 2.9 Hz), 118.80, 116.15 (d, *J* = 21.4 Hz), 112.66 (d, *J* = 21.9 Hz), 66.75, 56.46, 52.68, 43.40, 20.36. Calcd for $C_{21}H_{19}FNO_3^+$ ([M+H]$^+$) 352.1343. Found 352.1343.



Methyl 3-(2-(3-methoxyphenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3e2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 60% yield (109.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.07 (dd, *J* = 11.8, 4.2 Hz, 2H), 7.03 – 6.98 (m, 1H), 6.86 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.31 (s, 1H), 4.71 (s, 1H), 3.81 (s, 3H), 3.81 (s, 3H), 3.65 (q, *J* = 15.1 Hz, 2H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.64, 163.84, 159.79, 156.69, 143.50, 134.32, 132.91, 129.80, 128.56, 124.18, 123.99, 122.19, 118.75, 118.40, 114.64, 111.52, 66.81, 56.43, 55.30, 52.66, 43.40, 20.53. HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_4^+$ ([M+H]$^+$) 364.1543. Found 364.1544.

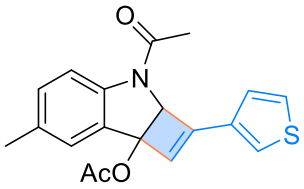


Methyl 3-(2-(3,4-dichlorophenyl)-7b-methyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3f**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 76% yield (151.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.35 (s, 1H), 4.74 (s, 1H), 3.81 (s, 3H), 3.70 – 3.58 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 163.84, 154.52, 143.40, 133.72, 133.15, 133.06, 131.58, 130.80, 128.83, 127.68, 125.04, 124.33, 123.97, 123.74, 118.84, 66.73, 56.45, 52.70, 43.37, 20.27. HRMS (ESI-TOF) Calcd for $C_{21}H_{18}Cl_2NO_3^+$ ([M+H]$^+$) 402.0658. Found 402.0662.

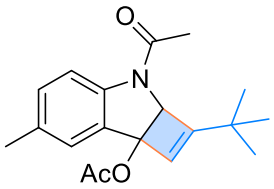


3-Acetyl-2-(naphthalen-1-yl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3g**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow solid, m.p. = 222.3-222.8 ^{o}C, 75% yield (68.0 mg), ^{1}H NMR (400 MHz,

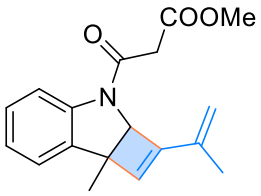
$CDCl_3$) δ 8.36 (d, *J* = 8.2 Hz, 1H), 8.23 – 8.12 (m, 1H), 8.04 – 7.94 (m, 1H), 7.87 (t, *J* = 5.0 Hz, 2H), 7.58 – 7.48 (m, 3H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.55 (s, 1H), 5.46 (s, 1H), 2.41 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.38, 168.20, 151.00, 143.30, 133.92, 131.49, 130.35, 130.28, 128.98, 128.72, 127.13, 126.78, 126.68, 126.17, 125.07, 124.51, 123.69, 123.52, 118.55, 87.10, 65.88, 24.11, 21.50. HRMS (ESI-TOF) Calcd for $C_{24}H_{20}NO_3^+$ ($[M+H]^+$) 370.1438. Found 370.1441.



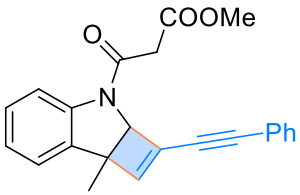
3-Acetyl-6-methyl-2-(thiophen-3-yl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3h**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow solid, m.p. = 208.5-208.8 °C, 53% yield (90.7 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.23 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.03 (s, 1H), 5.33 (s, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 167.84, 147.21, 141.01, 133.11, 132.05, 131.00, 128.57, 126.67, 125.54, 124.63, 123.72, 120.38, 118.31, 85.42, 65.95, 23.92, 21.39, 21.13. HRMS (ESI-TOF) Calcd for $C_{19}H_{18}NO_3S^+$ ($[M+H]^+$) 340.1002. Found 340.1003.



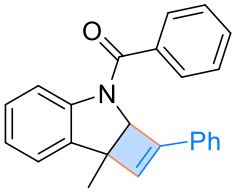
3-Acetyl-2-(*tert*-butyl)-6-methyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3i**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow solid, m.p. = 123.5-123.9 °C, 54% yield (81.6 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.15 (s, 1H), 7.10 (dd, *J* = 8.4, 1.1 Hz, 1H), 5.82 (s, 1H), 5.06 (s, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 2.08 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.41, 167.82, 164.18, 141.11, 132.59, 130.47, 128.92, 124.61, 122.69, 117.95, 86.68, 64.52, 33.57, 28.51, 23.77, 21.53, 21.12. HRMS (ESI-TOF) Calcd for $C_{19}H_{24}NO_3^+$ ($[M+H]^+$) 314.1751. Found 314.1750.



Methyl 3-(7b-methyl-2-(prop-1-en-2-yl)-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3j**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 49% yield (73.3 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.95 (s, 1H), 5.33 (s, 1H), 5.14 (s, 1H), 4.61 (s, 1H), 3.79 (s, 3H), 3.61 (q, *J* = 15.1 Hz, 2H), 1.77 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.63, 163.82, 158.41, 143.35, 135.78, 134.53, 128.42, 124.07, 124.02, 123.06, 118.69, 116.31, 66.62, 56.08, 52.62, 43.34, 20.41, 18.52. HRMS (ESI-TOF) Calcd for $C_{18}H_{20}NO_3^+$ ($[M+H]^+$) 298.1438. Found 298.1436.

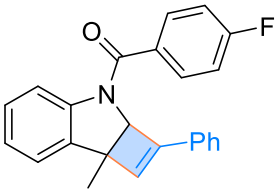


Methyl 3-(7b-methyl-2-(phenylethynyl)-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3k**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 75% yield (134.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.46 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.35 – 7.24 (m, 5H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.17 (s, 1H), 4.72 (s, 1H), 3.79 (s, 3H), 3.60 (q, *J* = 15.1 Hz, 2H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 163.75, 142.93, 140.95, 133.99, 132.24, 131.90, 129.22, 128.82, 128.46, 124.46, 123.05, 121.99, 118.60, 96.89, 80.47, 67.15, 58.94, 52.68, 43.41, 19.19. HRMS (ESI-TOF) Calcd for $C_{23}H_{20}NO_3^+$ ($[M+H]^+$) 358.1438. Found 358.1438.

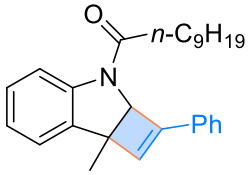


(7b-Methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)(phenyl)methanone (**3l1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→5:1), pale yellow solid, m.p. = 175.0-175.4 °C, 45% yield (76.1 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.62 (d, *J* = 6.5 Hz, 2H), 7.50 (d, *J* = 7.0 Hz, 5H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.18 (m, 2H), 7.10 (d, *J* = 6.6

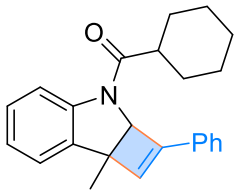
Hz, 1H), 6.26 (s, 1H), 4.56 (s, 1H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.92, 156.87, 143.41, 137.31, 135.61, 131.83, 130.35, 129.04, 128.68, 128.61, 128.25, 127.11, 125.83, 124.12, 123.38, 119.41, 68.23, 56.20, 20.12. HRMS (ESI-TOF) Calcd for $C_{24}H_{20}NO^+$ ([M+H]$^+$) 338.1539. Found 338.1540.



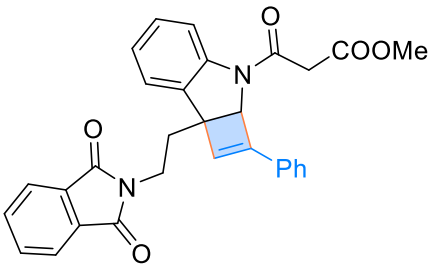
(4-Fluorophenyl)(7b-methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)methanone (**3l2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 51% yield (90.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.64 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.46 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.39 – 7.22 (m, 4H), 7.17 (t, *J* = 8.6 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.26 (s, 1H), 4.58 (s, 1H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.87, 163.89 (d, *J* = 251.7 Hz), 157.12, 143.35, 135.64, 133.39, 131.75, 129.53 (d, *J* = 9.1 Hz), 129.13, 128.95, 128.72, 128.26, 128.19, 125.86, 124.18, 123.08, 119.35, 115.75 (d, *J* = 21.2 Hz), 68.27, 20.12. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.19. HRMS (ESI-TOF) Calcd for $C_{24}H_{19}FNO^+$ ([M+H]$^+$) 356.1445. Found 356.1449.



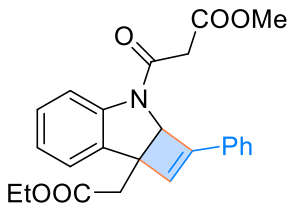
1-(7b-Methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)decan-1-one (**3m1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 60% yield (102.9 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.04 (td, *J* = 7.5, 0.9 Hz, 1H), 6.33 (s, 1H), 4.71 (s, 1H), 2.63 – 2.41 (m, 2H), 1.82 (s, 3H), 1.80 – 1.74 (m, 2H), 1.44 – 1.27 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.59, 156.30, 144.09, 134.06, 131.88, 129.04, 128.68, 128.45, 125.84, 123.93, 123.36, 122.31, 118.45, 66.56, 56.14, 35.89, 31.92, 29.57, 29.54, 29.52, 29.34, 24.82, 22.71, 20.67, 14.15. HRMS (ESI-TOF) Calcd for $C_{27}H_{34}NO^+$ ([M+H]$^+$) 388.2635. Found 388.2635.



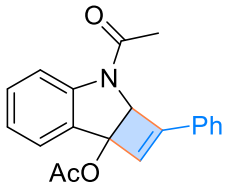
Cyclohexyl(7b-methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)methanone (**3m2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1→30:1), pale yellow solid, m.p. = 189.3-189.9 °C, 60% yield (102.9 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.33 (s, 1H), 4.75 (s, 1H), 2.56 (t, *J* = 11.5 Hz, 1H), 1.95 – 1.85 (m, 4H), 1.82 (s, 3H), 1.78 – 1.71 (m, 2H), 1.42 – 1.23 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.05, 156.45, 144.23, 134.30, 131.88, 129.05, 128.68, 128.44, 125.86, 123.92, 123.41, 122.54, 118.74, 66.51, 56.05, 44.35, 29.69, 29.46, 25.93, 25.80, 20.69. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}NO^{+}$ ($[M+H]^{+}$) 344.2009. Found 344.2009.



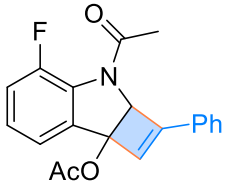
Methyl 3-(7b-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3n**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 38% yield (78.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 1H), 7.68 (dt, *J* = 7.2, 3.7 Hz, 2H), 7.63 (dd, *J* = 7.9, 4.9 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 3H), 7.29 – 7.25 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 5.11 (s, 1H), 3.85 (s, 3H), 3.83 – 3.78 (m, 2H), 3.78 – 3.66 (m, 2H), 2.70 (dd, *J* = 14.5, 7.2 Hz, 1H), 2.62 (dd, *J* = 14.5, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.99, 167.61, 163.94, 155.41, 143.50, 133.75, 132.29, 131.81, 131.27, 129.26, 128.65, 125.76, 124.19, 123.95, 123.09, 122.54, 118.95, 63.56, 58.89, 52.72, 43.50, 34.69, 31.18. HRMS (ESI-TOF) Calcd for $C_{30}H_{25}N_2O_5^{+}$ ($[M+H]^{+}$) 493.1758. Found 493.1759.



Methyl 3-(7b-(2-ethoxy-2-oxoethyl)-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indol-3-yl)-3-oxopropanoate (**3o**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 12% yield (24.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 5.21 (s, 1H), 4.01 – 3.91 (m, 2H), 3.82 (s, 3H), 3.68 (q, *J* = 15.2 Hz, 2H), 3.28 (d, *J* = 15.2 Hz, 1H), 3.11 (d, *J* = 15.2 Hz, 1H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.03, 167.55, 163.83, 154.84, 143.78, 131.81, 131.35, 129.37, 129.03, 128.73, 125.87, 124.06, 123.89, 122.94, 118.93, 64.96, 60.70, 57.24, 52.66, 43.45, 38.78, 13.77. HRMS (ESI-TOF) Calcd for $C_{24}H_{24}NO_5^+$ ([M+H]$^+$) 406.1649. Found 406.1649.

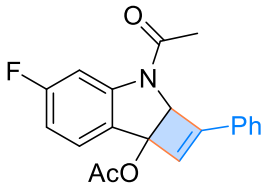


3-Acetyl-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3p1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), white solid, m.p. = 195.2-195.7 °C, 71% yield (141.1 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.27 (s, 1H), 5.34 (s, 1H), 2.34 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.37, 168.20, 151.92, 143.24, 130.26, 130.10, 129.71, 128.81, 128.62, 126.25, 123.60, 123.50, 121.73, 118.54, 85.54, 65.26, 24.03, 21.39. HRMS (ESI-TOF) Calcd for $C_{20}H_{18}NO_3^+$ ([M+H]$^+$) 320.1281. Found 320.1283.

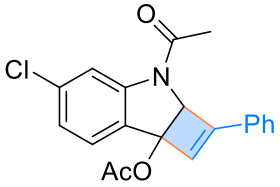


3-Acetyl-4-fluoro-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3p2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale yellow oil, 72% yield (121.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2

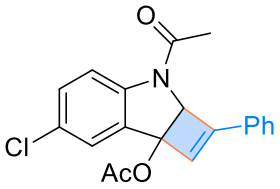
Hz, 1H), 7.77 – 7.69 (m, 2H), 7.40 (tt, *J* = 8.9, 4.5 Hz, 3H), 7.30 – 7.22 (m, 1H), 6.72 (t, *J* = 8.9 Hz, 1H), 6.32 (s, 1H), 5.29 (s, 1H), 2.34 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.53, 168.25, 158.8 (d, *J* = 247.9 Hz), 152.10, 145.30 (d, *J* = 7.6 Hz), 131.85 (d, *J* = 8.5 Hz), 129.92, 129.86, 128.67, 126.42 (d, *J* = 4.5 Hz), 121.93, 114.28, 110.64 (d, *J* = 20.3 Hz), 84.12, 65.56, 24.04, 21.12. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.02. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}FNO_3^+$ ($[M+H]^+$) 338.1187. Found 338.1191.



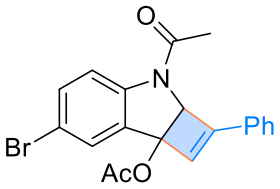
3-Acetyl-5-fluoro-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3q1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 53% yield (118.5 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.46 – 7.36 (m, 3H), 7.16 (dd, *J* = 7.8, 2.7 Hz, 1H), 6.99 (td, *J* = 8.9, 2.7 Hz, 1H), 6.28 (s, 1H), 5.34 (s, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.30, 167.95, 158.92 (d, *J* = 243.4 Hz), 151.56, 139.31, 130.28 (d, *J* = 7.6 Hz), 129.92, 129.84, 128.94, 126.19, 121.97, 119.65 (d, *J* = 7.8 Hz), 116.70 (d, *J* = 22.7 Hz), 110.70 (d, *J* = 24.4 Hz), 84.98, 65.61, 23.77, 21.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.66. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}FNO_3^+$ ($[M+H]^+$) 338.1187. Found 338.1191.



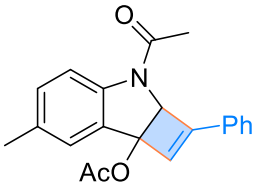
3-Acetyl-5-chloro-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3q2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), pale pink solid, m.p. = 115.5-116.4 °C, 89% yield (158.0 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.3 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.02 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.27 (s, 1H), 5.33 (s, 1H), 2.34 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.32, 168.29, 151.79, 144.09, 135.80, 129.91, 129.82, 128.89, 127.19, 126.22, 124.22, 123.63, 121.77, 118.78, 84.92, 65.63, 23.95, 21.33. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}ClNO_3^+$ ($[M+H]^+$) 354.0891. Found 354.0894.



3-Acetyl-6-chloro-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3r1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow solid, m.p. = 155.5-156.5 °C, 63% yield (113.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.42 (tt, *J* = 9.3, 4.5 Hz, 4H), 7.28 – 7.23 (m, 1H), 6.28 (s, 1H), 5.32 (s, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.28, 168.13, 151.58, 141.86, 130.37, 130.20, 129.95, 129.78, 128.97, 128.40, 126.21, 123.66, 121.91, 119.60, 84.93, 65.51, 23.89, 21.32. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}ClNO_3^+$ ([M+H]$^+$) 354.0891. Found 354.0894.

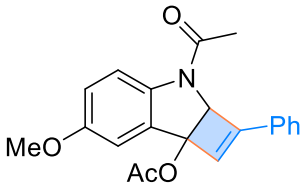


3-Acetyl-6-bromo-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3r2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow solid, m.p. = 190.2-191.1 °C, 65% yield (130.0 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.55 (s, 1H), 7.41 (dt, *J* = 8.8, 6.9 Hz, 4H), 6.27 (s, 1H), 5.31 (s, 1H), 2.33 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.28, 168.21, 151.59, 142.34, 133.10, 130.79, 129.96, 129.76, 128.98, 126.53, 126.21, 121.92, 120.03, 115.89, 84.85, 65.45, 23.92, 21.33. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}BrNO_3^+$ ([M+H]$^+$) 398.0386. Found 398.0395.

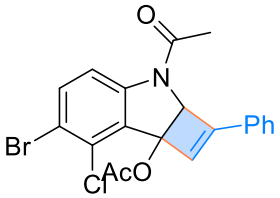


3-Acetyl-6-methyl-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3r3**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), purple solid, m.p. = 190.2-191.2 °C, 81% yield (135.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.45 – 7.35 (m, 3H), 7.14 – 7.08 (m, 1H), 6.28 (s, 1H), 5.32 (s, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.40, 167.88, 151.87, 141.03, 133.12, 130.95, 130.18, 129.66, 128.82, 128.59, 126.25, 124.02, 121.80, 118.25, 85.64, 65.44, 23.92, 21.43,

21.13. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_3^+$ ([M+H]$^+$) 334.1438. Found 334.1439.



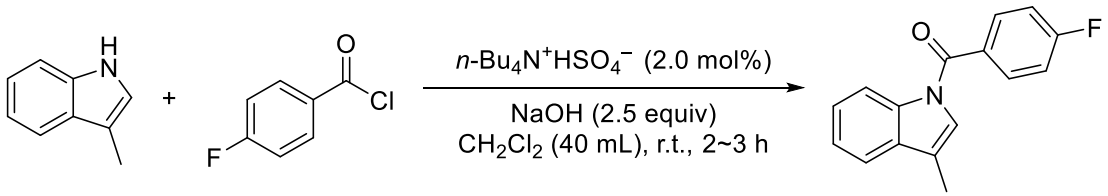
3-Acetyl-6-methoxy-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3r4**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow solid, m.p. = 204.1-204.2 °C, 79% yield (136.9 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.0 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.44 – 7.33 (m, 3H), 7.02 (d, *J* = 2.7 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.28 (s, 1H), 5.32 (s, 1H), 3.76 (s, 3H), 2.32 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 167.53, 155.89, 151.65, 137.03, 130.11, 130.01, 129.71, 128.84, 126.23, 122.03, 119.24, 114.26, 110.20, 85.49, 65.57, 55.66, 23.75, 21.37. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_4^+$ ([M+H]$^+$) 350.1387. Found 350.1388.



3-Acetyl-6-bromo-7-chloro-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl acetate (**3s**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1→9:1), yellow oil, 56% yield (120.0 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 1H), 7.81 – 7.67 (m, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.41 – 7.33 (m, 3H), 6.30 (s, 1H), 5.17 (s, 1H), 2.32 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.35, 168.26, 152.49, 144.03, 134.92, 130.69, 129.85, 128.36, 127.51, 127.24, 123.88, 117.89, 117.04, 85.87, 64.98, 23.97, 20.86. HRMS (ESI-TOF) Calcd for $C_{20}H_{16}BrClNO_3^+$ ([M+H]$^+$) 431.9997. Found 431.9998.

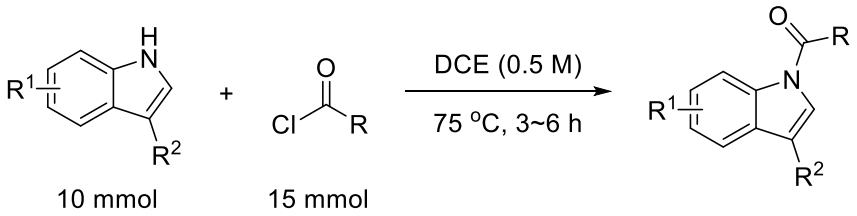
VI. General procedure for the synthesis of substrates 1

Most of the substrates 1 are previously reported compounds and were synthesized following established procedures.[1-4] The remaining substrates listed below are new compounds.

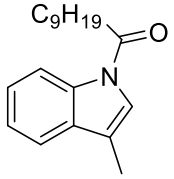


In a 100 mL round-bottom flask, add 10 mmol of 3-methylindole, tetrabutylammonium hydrogen sulfate (*n*-$Bu_4N^+HSO_4^-$, 2.0 mol%), NaOH (2.5 equiv), and 40 mL of dichloromethane. Stir vigorously, then add 4-fluorobenzoyl chloride (1.5 equiv) dropwise. Continue stirring at room temperature for 2~3 hours. After the reaction was complete (monitored by TLC), the mixture was cooled down to room temperature. Pour the mixture into 100 mL of water and extract twice with 30 mL of dichloromethane. The residue obtained after evaporation of the solvent was purified on silica gel (petroleum ether–ethyl acetate) to afford substrates **1l2**.

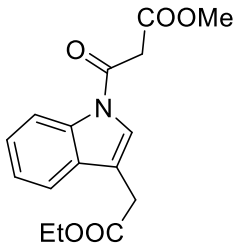
(4-Fluorophenyl)(3-methyl-1*H*-indol-1-yl)methanone (**1l2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 5:1→15:1), white solid, m.p. = 105.8-106.2 °C, 64% yield (1.624 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.33 (dtd, *J* = 20.9, 7.4, 1.1 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.00 (d, *J* = 1.1 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.23, 164.70 (d, *J* = 254.0 Hz), 136.36, 131.84, 131.63 (d, *J* = 8.9 Hz), 131.09 (d, *J* = 3.3 Hz), 125.11, 124.19, 123.83, 119.00, 118.14, 116.45, 115.79 (d, *J* = 22.0 Hz), 9.70. HRMS (ESI-TOF) Calcd for $C_{16}H_{13}FNO_5^+$ ([M+H]$^+$) 254.0976. Found 254.0974.



A mixture of an indole derivative (10.0 mmol), acyl chloride (15 mmol, 1.5 equiv), and DCE (20.0 mL) was stirred at 75 °C for 3~6 hours. After the reaction was complete (monitored by TLC), the mixture was cooled down to room temperature. The residue obtained after evaporation of the solvent was purified on silica gel (petroleum ether–ethyl acetate) to afford substrates **1m1** and **1o**.



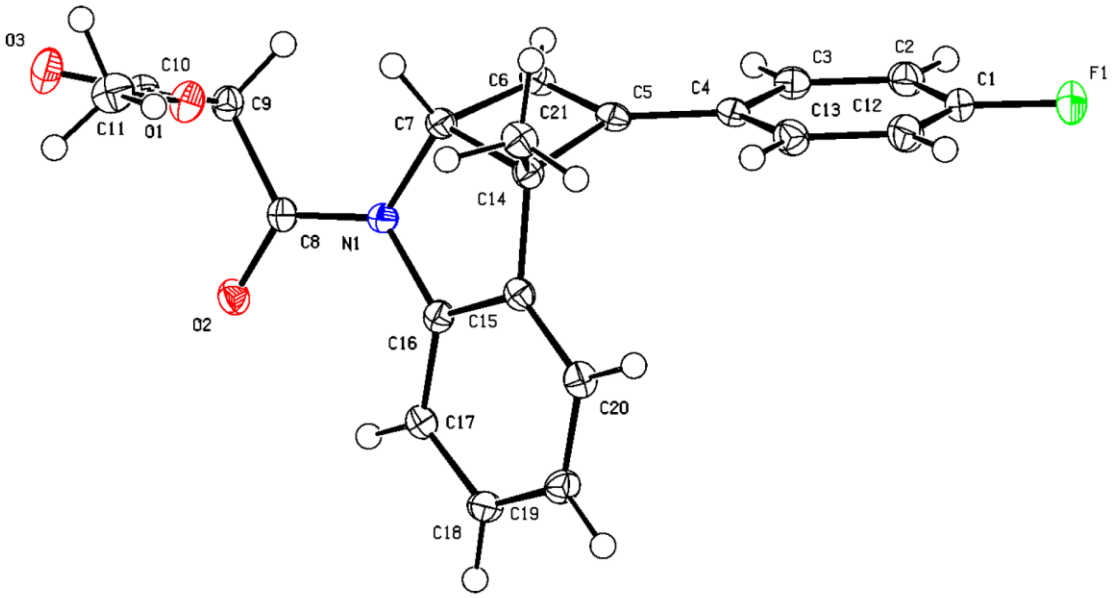
1-(3-Methyl-1*H*-indol-1-yl)decan-1-one (**1m1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1→20:1), yellow oil, 40% yield (1.136 g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.21 – 7.16 (m, 1H), 7.10 (s, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.79 – 1.66 (m, 2H), 1.38 – 1.09 (m, 14H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.33, 135.94, 131.33, 125.12, 123.28, 121.69, 118.76, 118.14, 116.69, 35.91, 31.93, 29.51, 29.48, 29.35, 29.31, 24.75, 22.73, 14.18, 9.76. HRMS (ESI-TOF) Calcd for $C_{19}H_{28}NO^{+}$ ($[M+H]^{+}$) 286.2165. Found 286.2164.



Methyl 3-(3-(2-ethoxy-2-oxoethyl)-1*H*-indol-1-yl)-3-oxopropanoate (**1o**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1→30:1), yellow oil, 27% yield (825.6 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 (s, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 3.77 (s, 3H), 3.69 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 166.71, 163.82, 135.83, 130.23, 125.76, 124.14, 123.21, 119.04, 116.76, 116.21, 61.16, 52.84, 43.41, 30.94, 14.18. HRMS (ESI-TOF) Calcd for $C_{16}H_{18}NO_5^{+}$ ($[M+H]^{+}$) 304.1179. Found 304.1179.

VII. Crystallographic Data

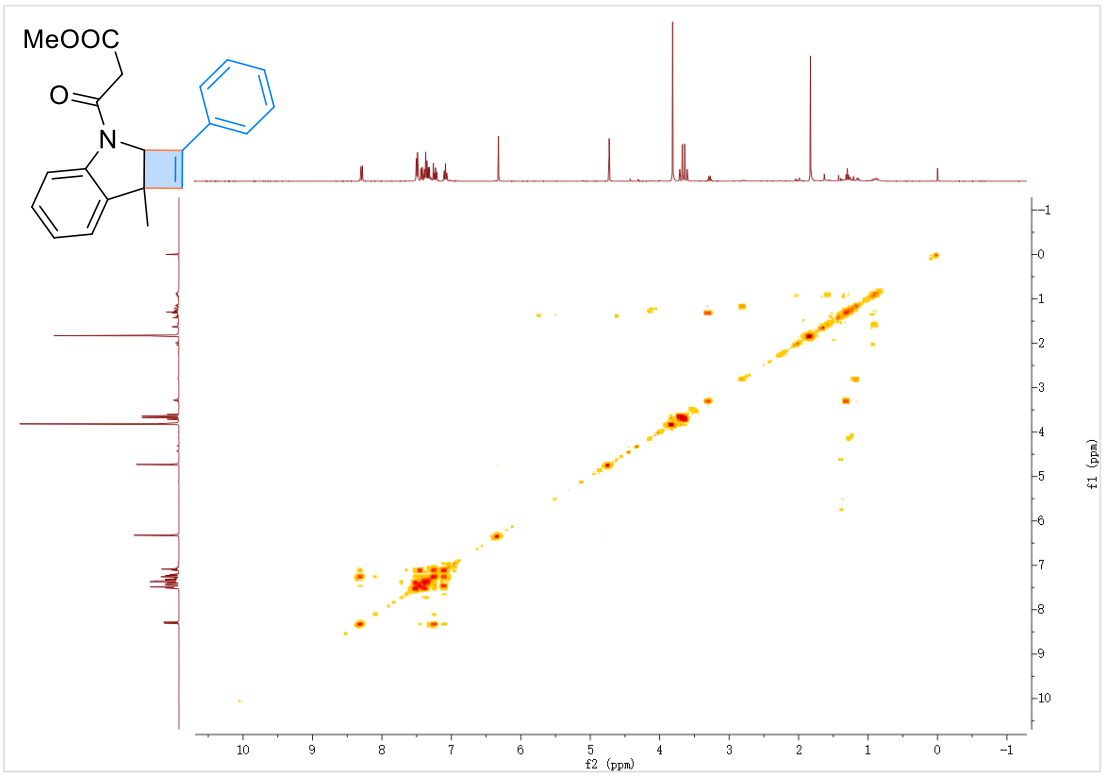
X-ray crystallographic data for compound **3a1** (CDCC number: 2366793)



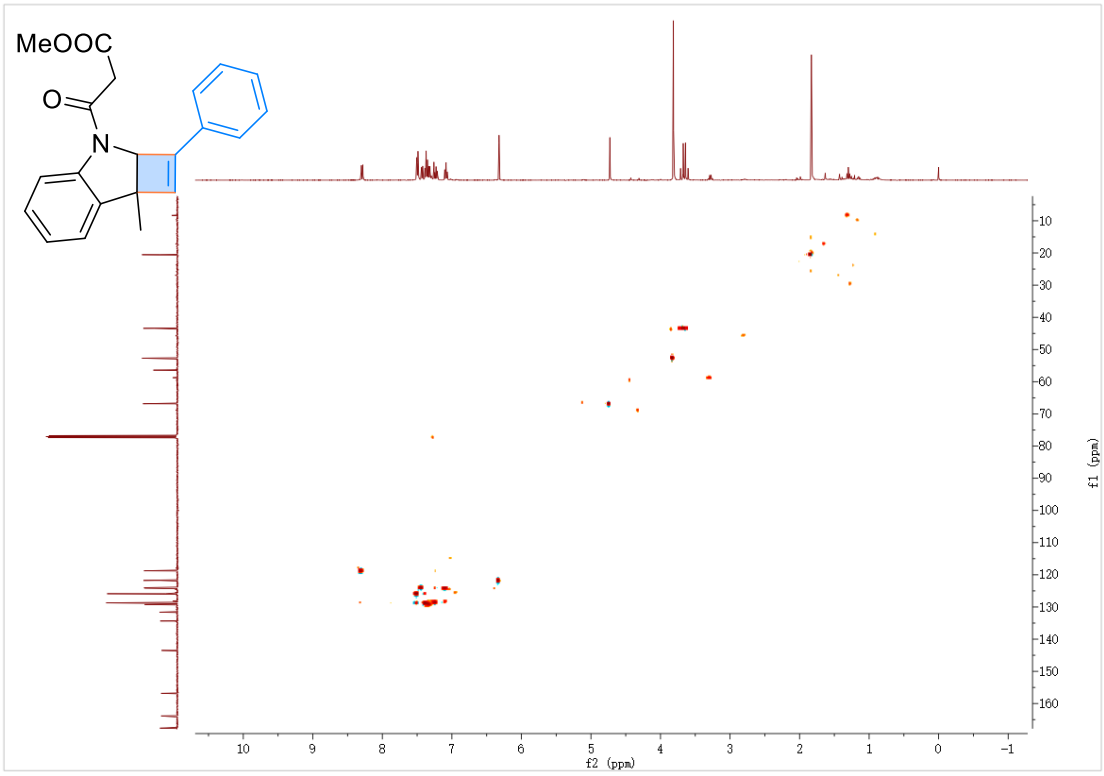
Empirical formula	$C_{21}H_{18}FNO_3$
Formula weight	351.12
Temperature/K	100
Crystal system	triclinic
Space group	P 21/n
a/Å	12.5984(6)
b/Å	10.5934(5)
c/Å	13.2326(6)
α/°	90
β/°	108.318(2)
γ/°	90
Volume/Å^3	1676.53(14)
Z	4
ρ_{calc}g/cm^3	1.392
μ/mm^{-1}	0.529
F(000)	736.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54186)
2Θ range for data collection/°	9.836 to 143.998
Index ranges	-10 ⩽ h ⩽ 10, -11 ⩽ k ⩽ 7, -11 ⩽ l ⩽ 11
Reflections collected	6988
Independent reflections	2750 [R_{int} = 0.0122, R_{sigma} = 0.0115]
Data/restraints/parameters	2750/0/196
Goodness-of-fit on F^2	1.149
Final R indexes [I>=2σ (I)]	R_1 = 0.0329, wR_2 = 0.0832
Final R indexes [all data]	R_1 = 0.0313, wR_2 = 0.0343
Largest diff. peak/hole / e Å^{-3}	0.27/-0.18

VIII. Copies of NMR spectra

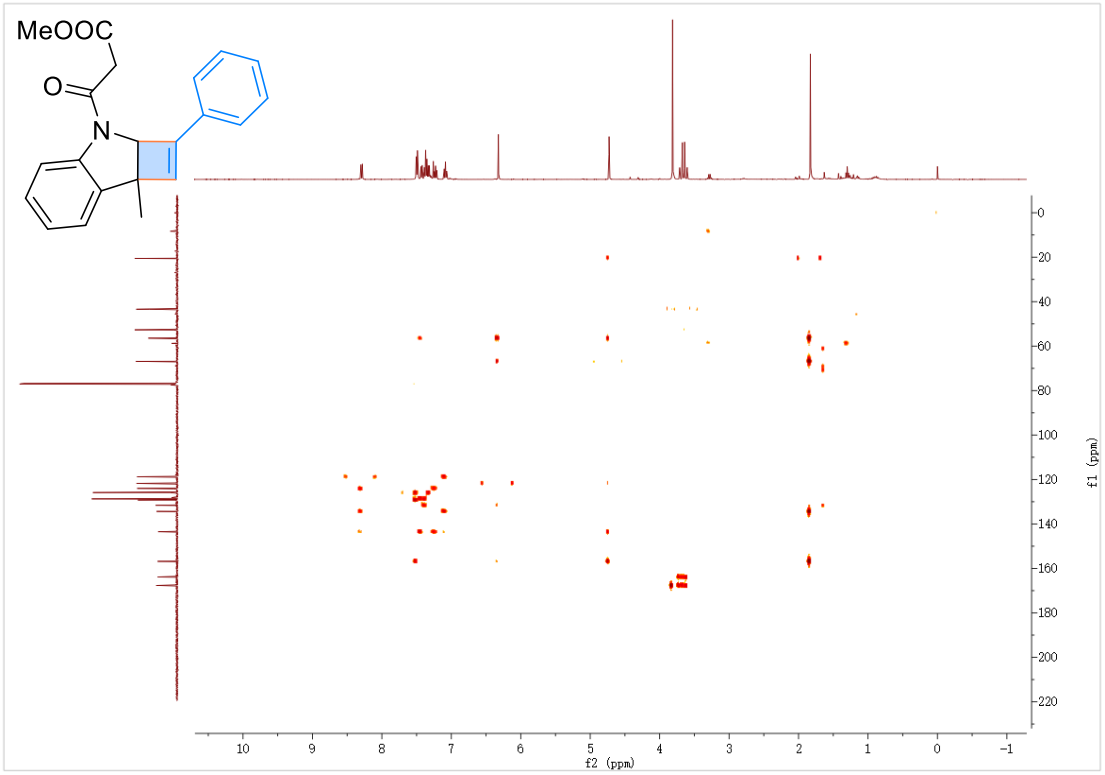
H/H-COSY Spectra of **3a**



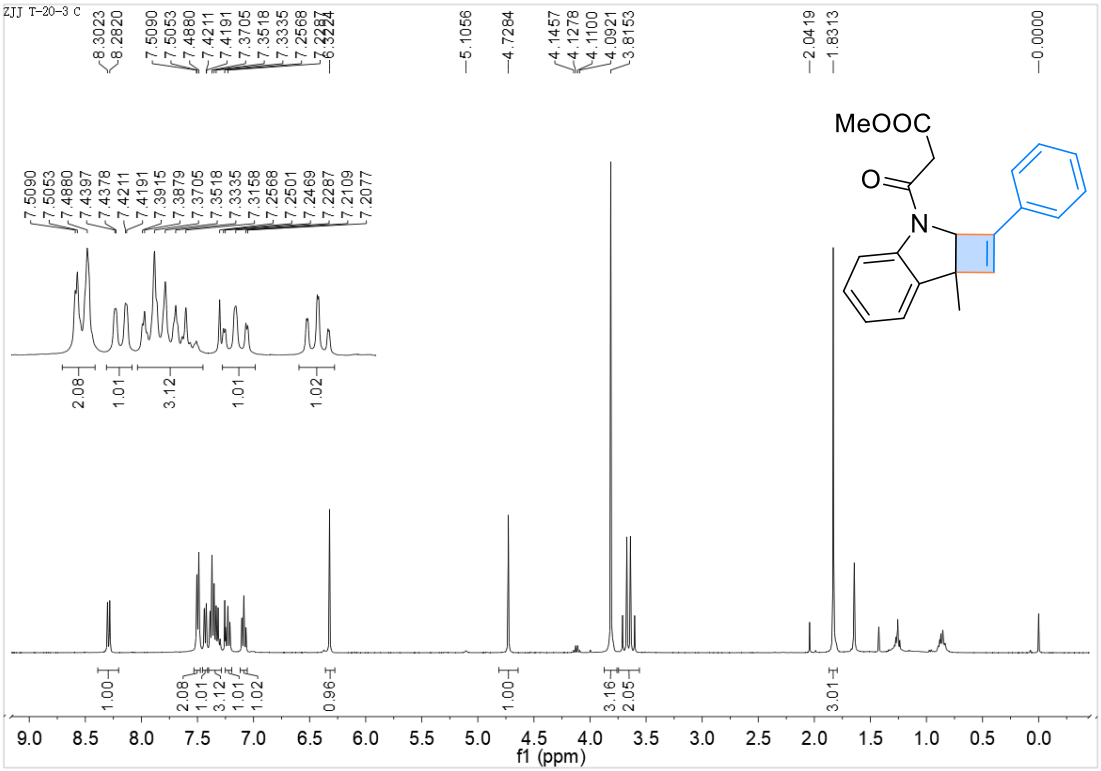
HSQC Spectra of **3a**



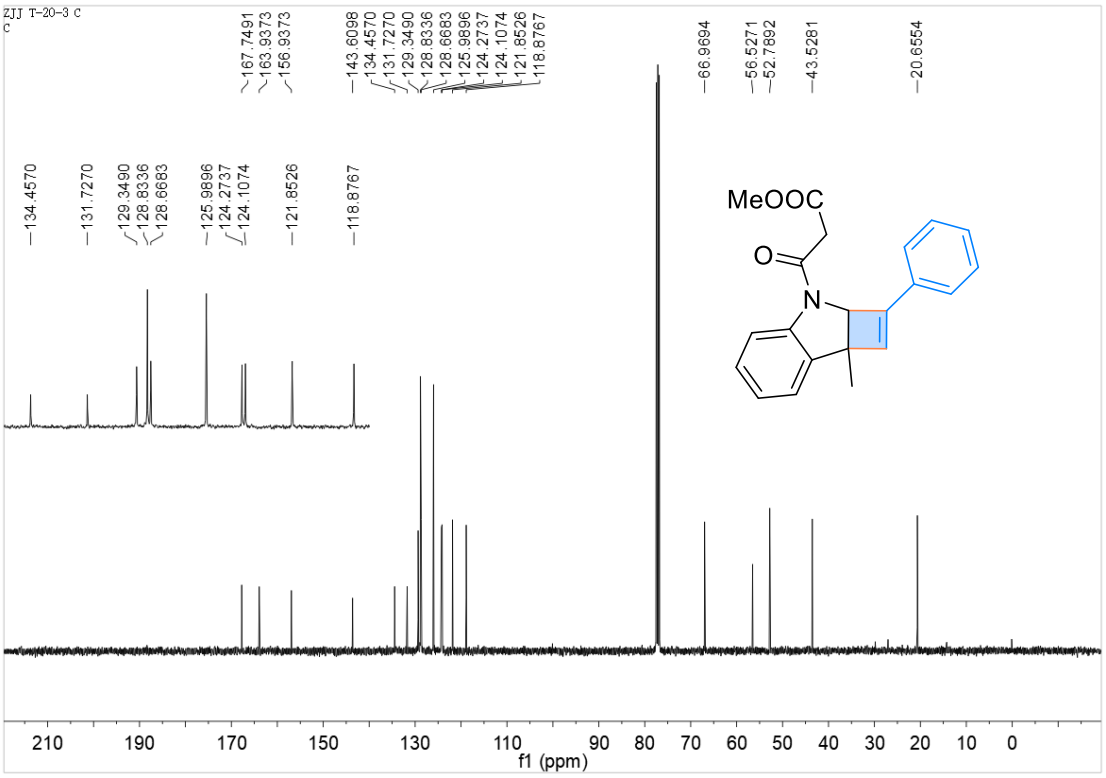
HMBC Spectra of **3a**



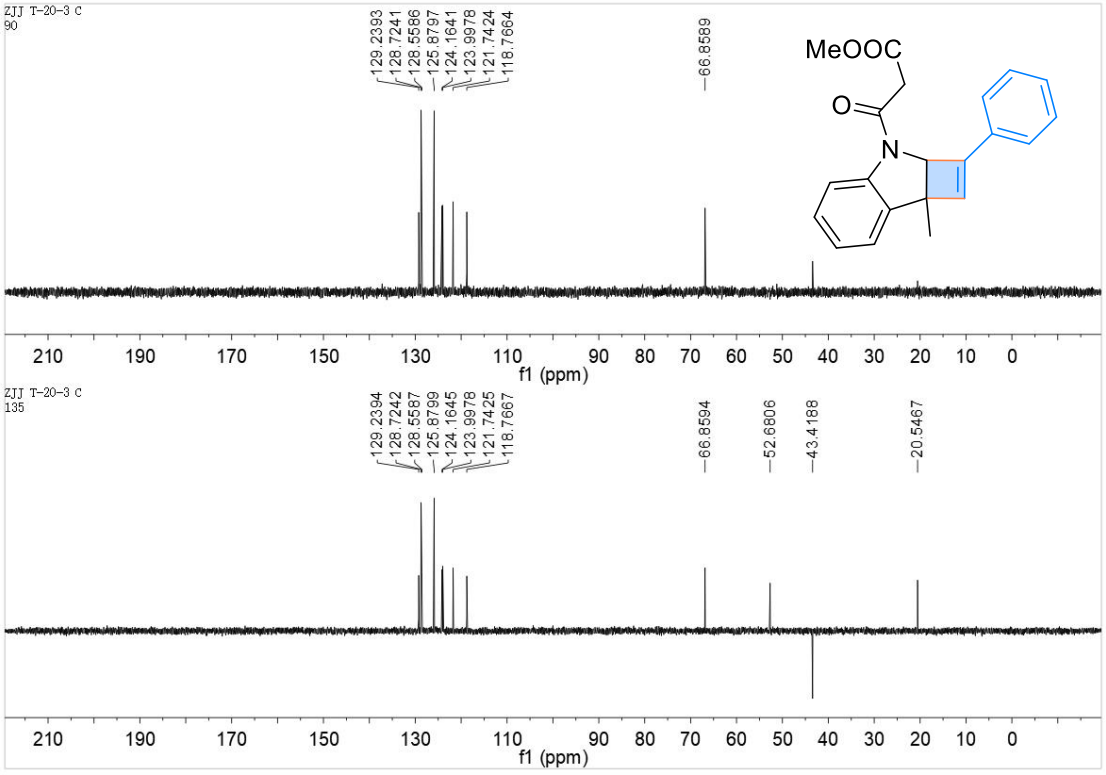
3a ^{1}H NMR



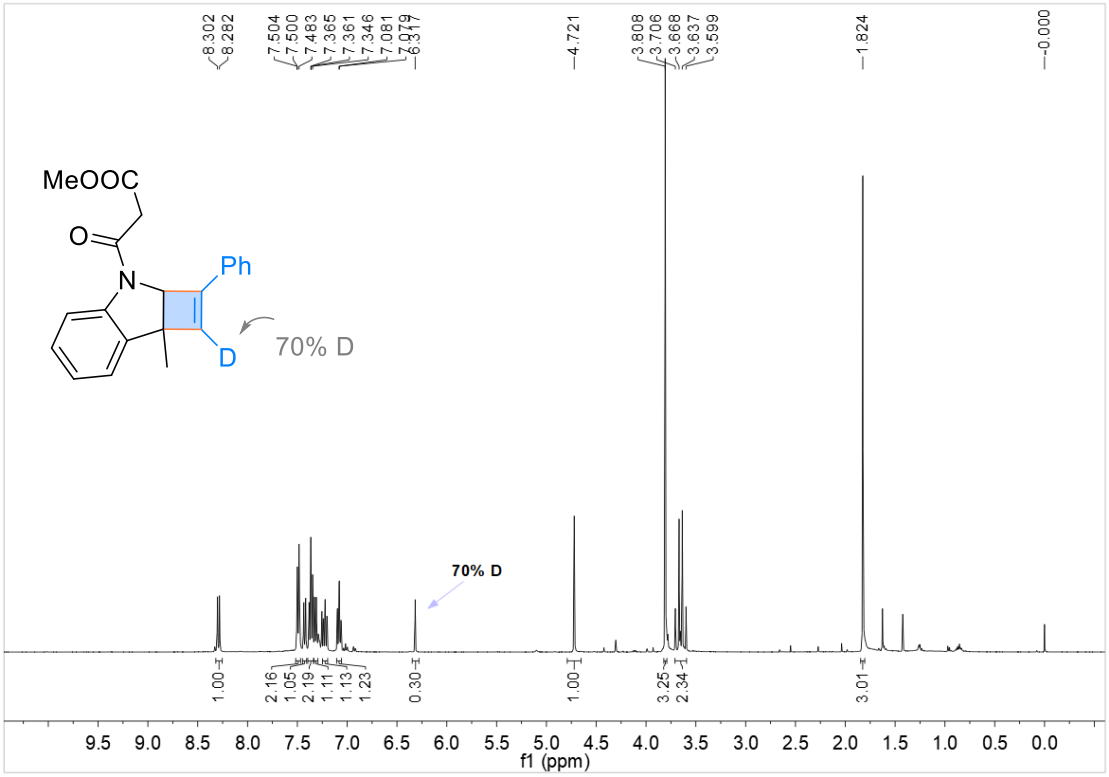
3a ^{13}C NMR



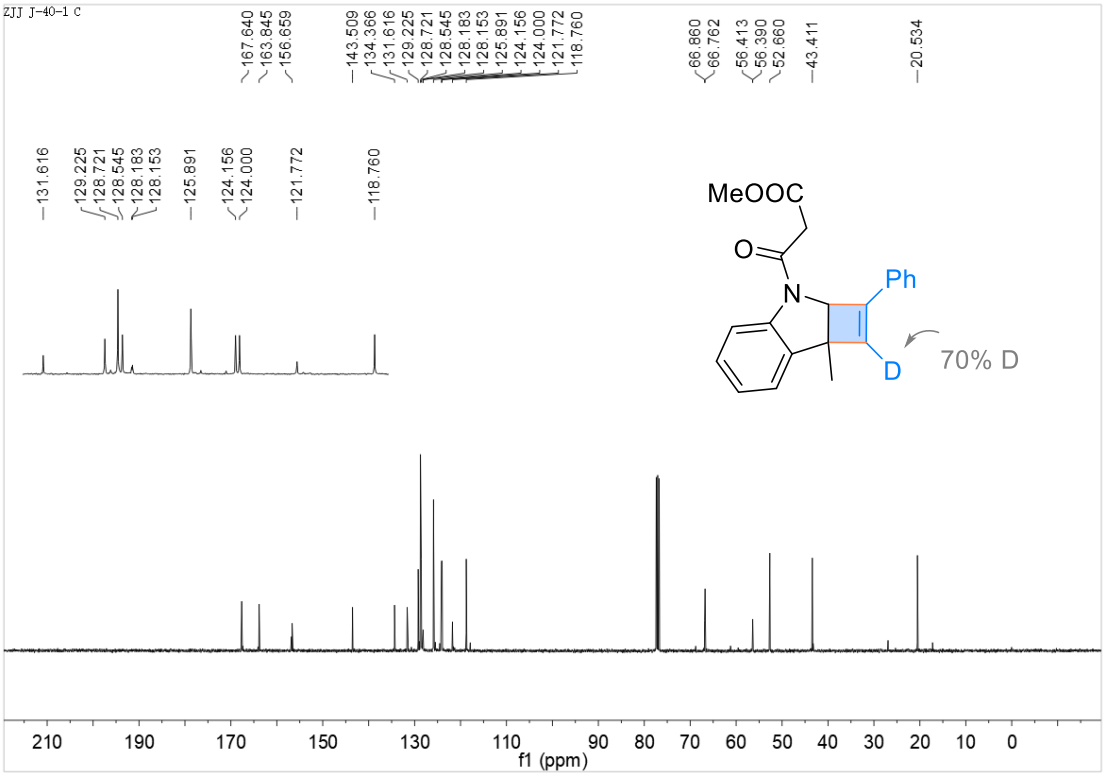
3a DEPT 90 and DEPT 135



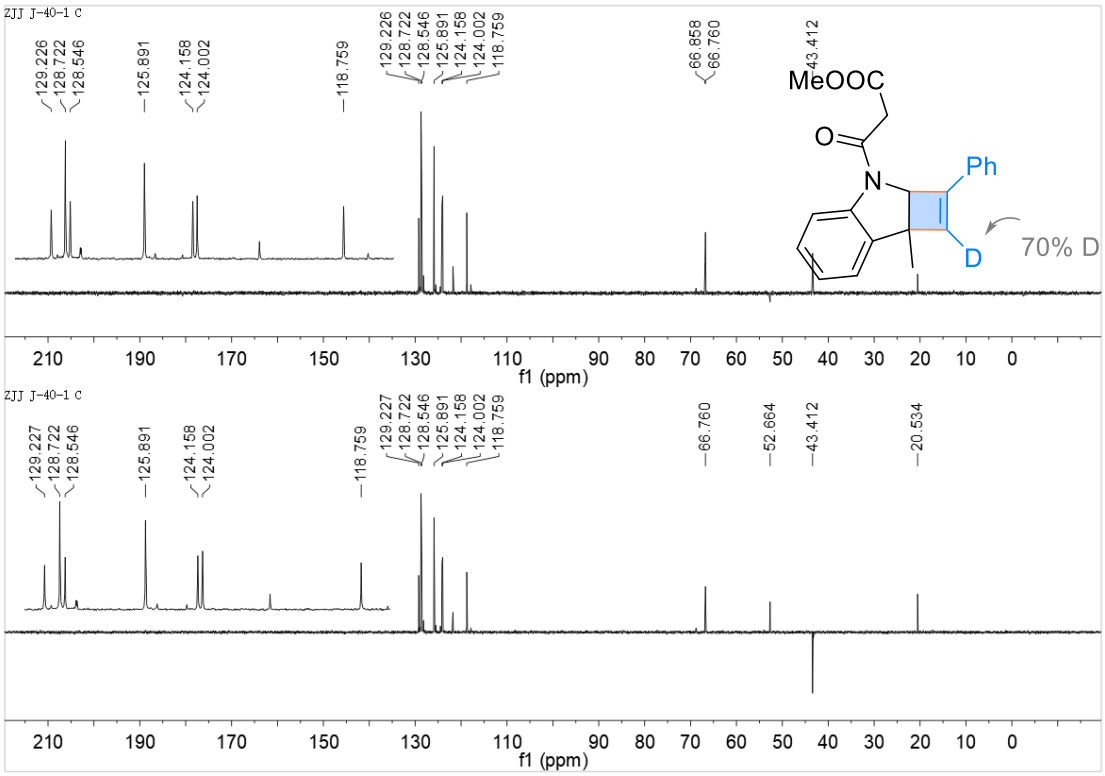
3a-D ^{1}H NMR



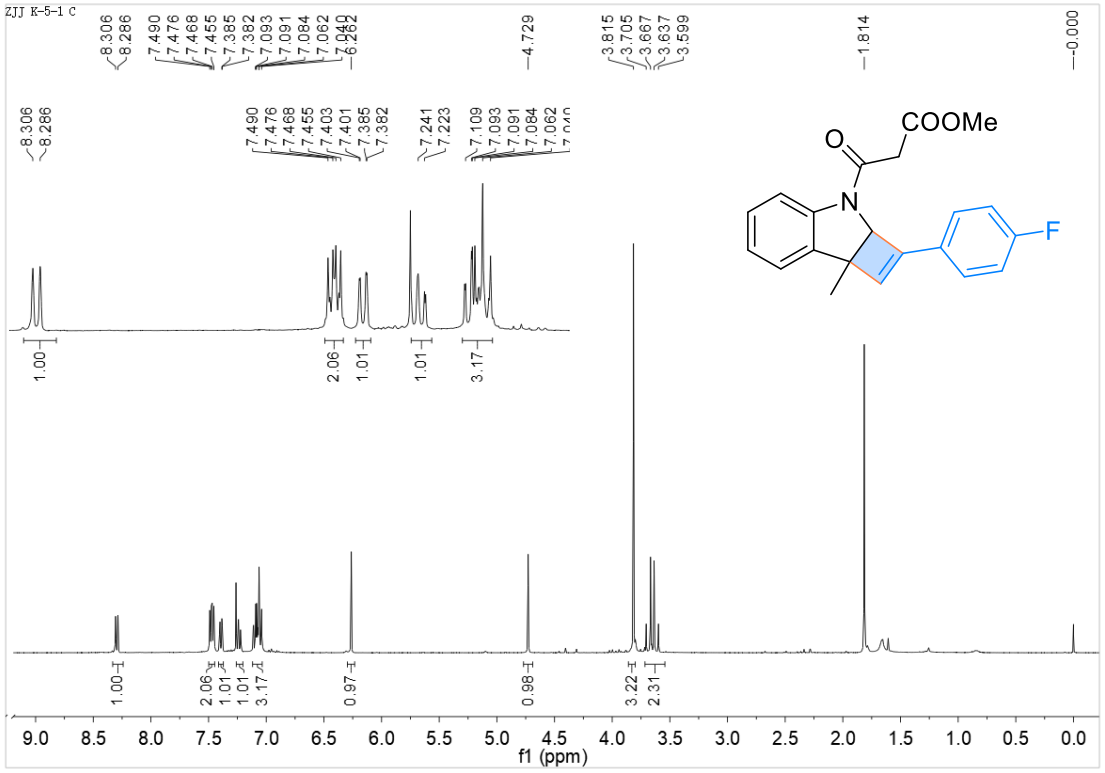
3a-D ^{13}C NMR



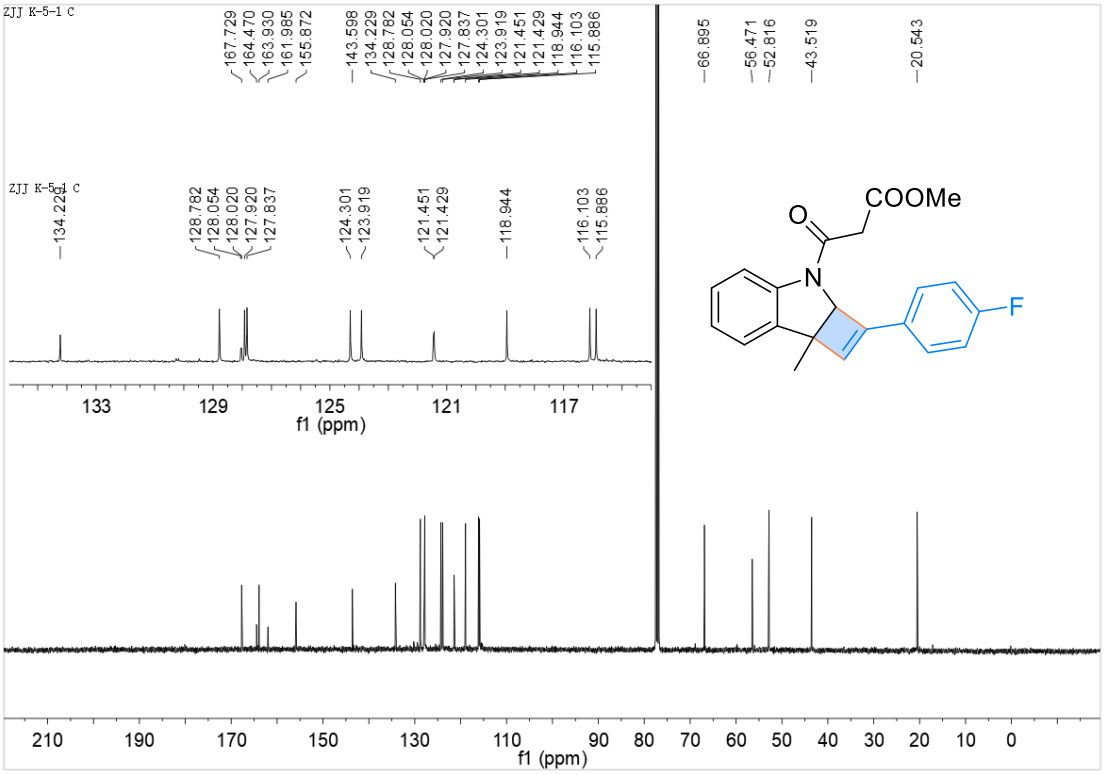
3a-D DEPT 90 and DEPT 135



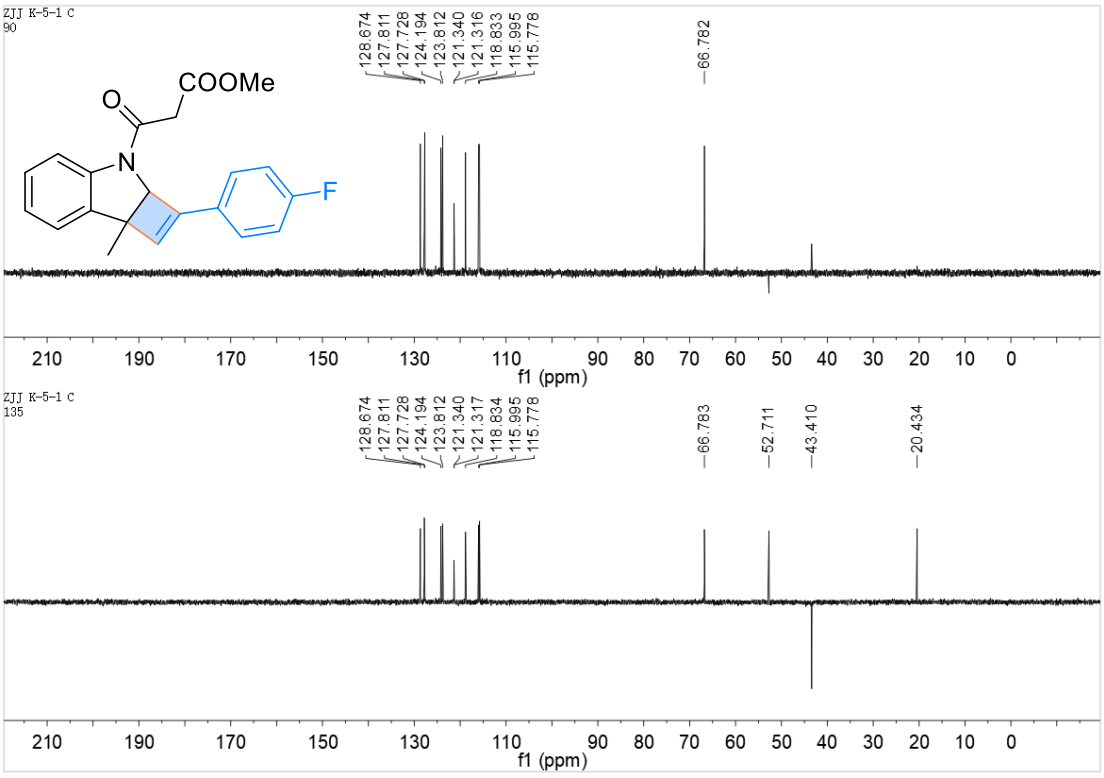
3a1 ^{1}H NMR



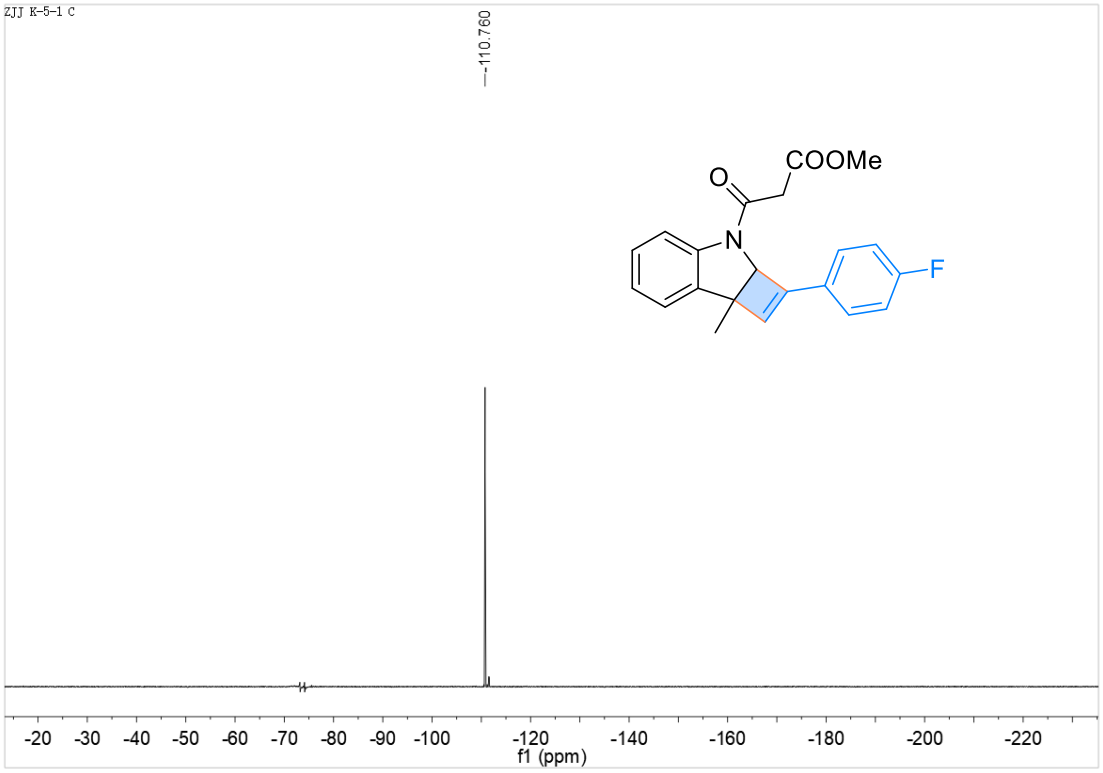
3a1 ^{13}C NMR



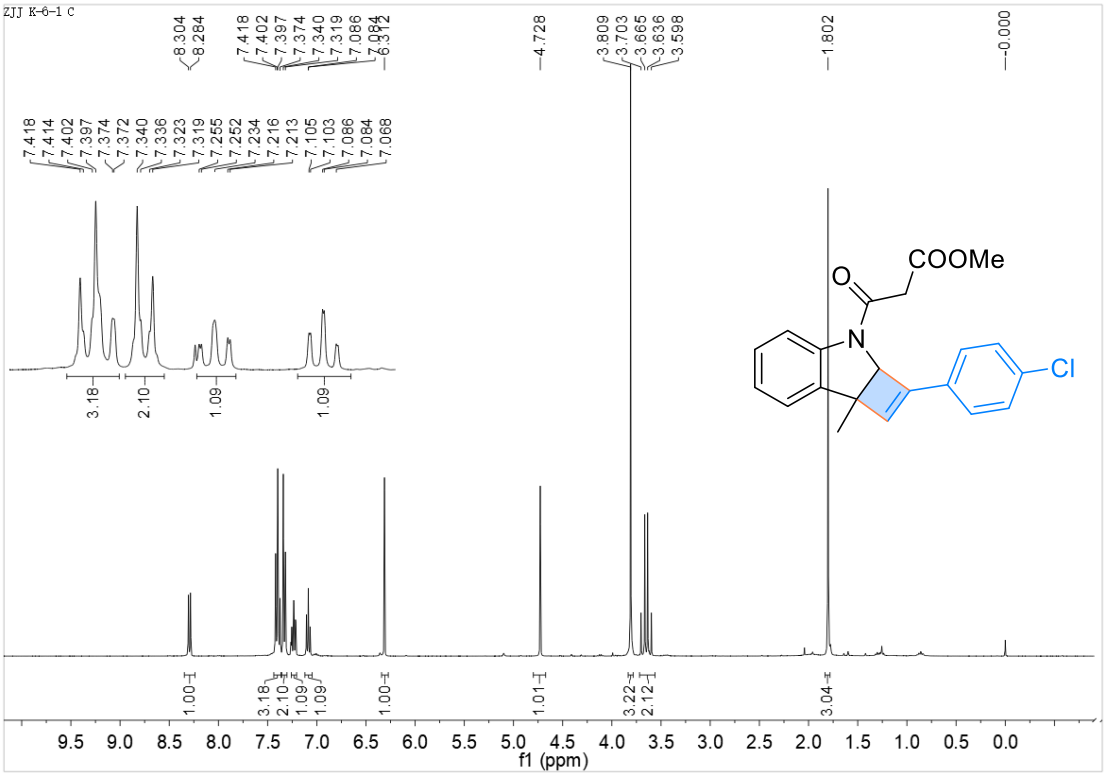
3a1 DEPT 90 and DEPT 135



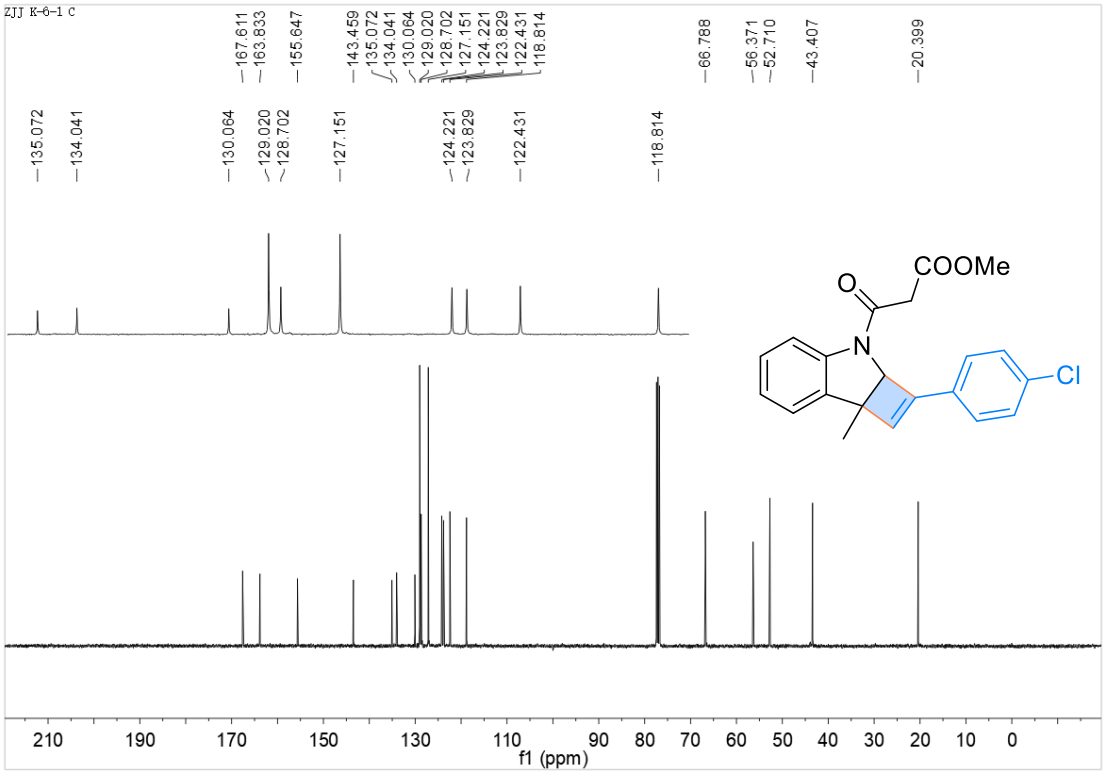
3a1 ^{19}F NMR



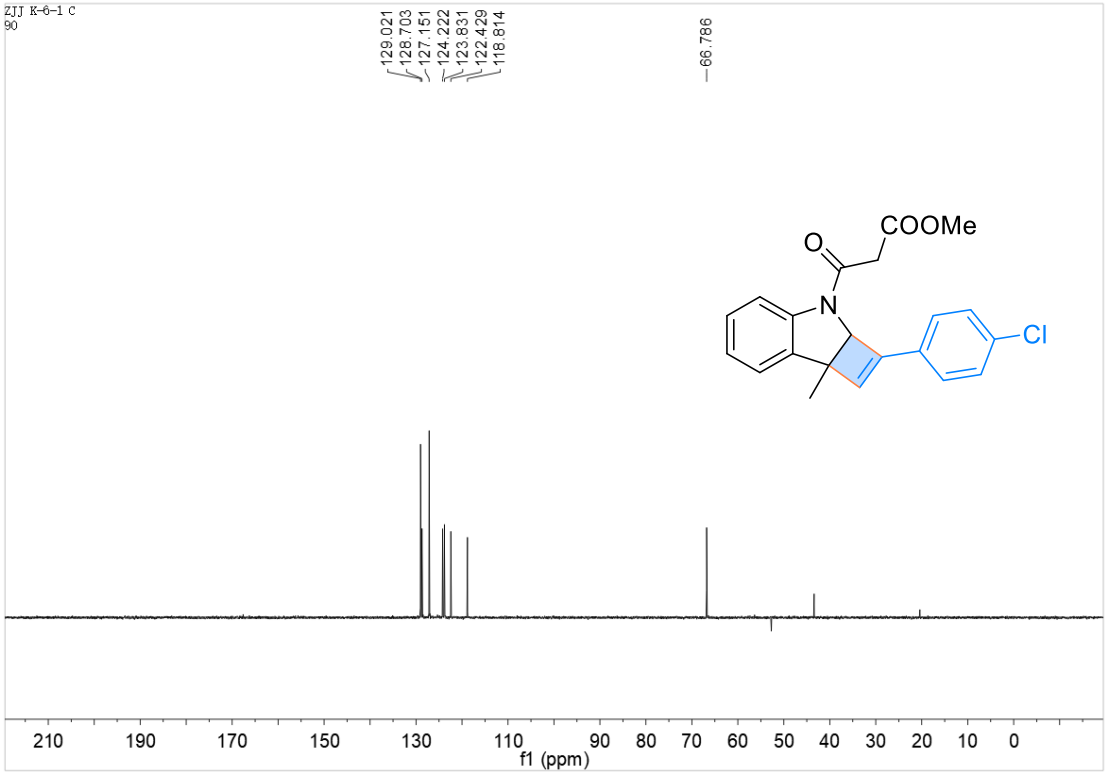
3a2 ^{1}H NMR



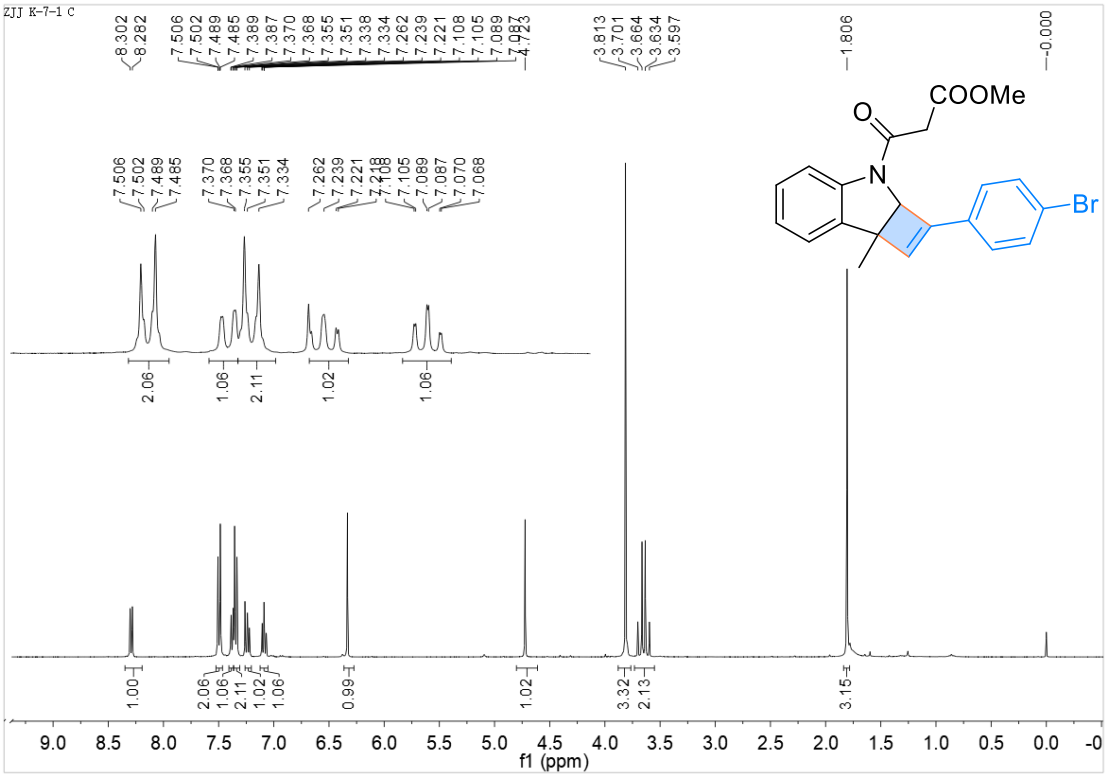
3a2 ^{13}C NMR



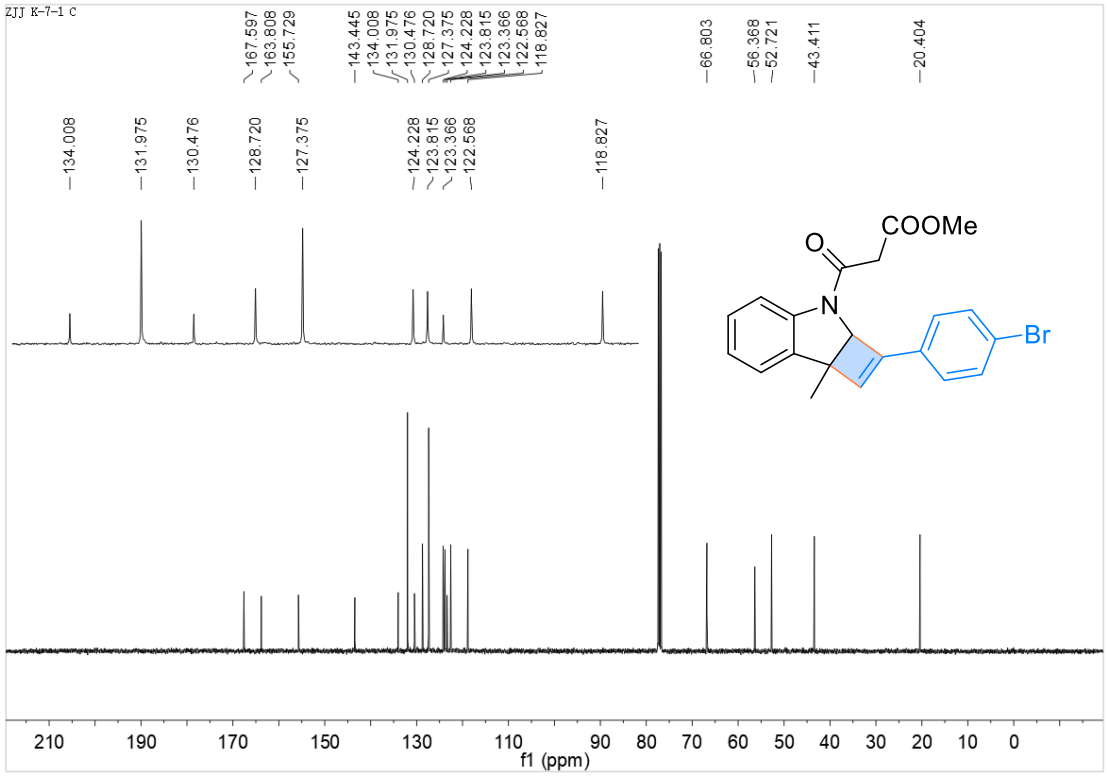
3a2 DEPT 90



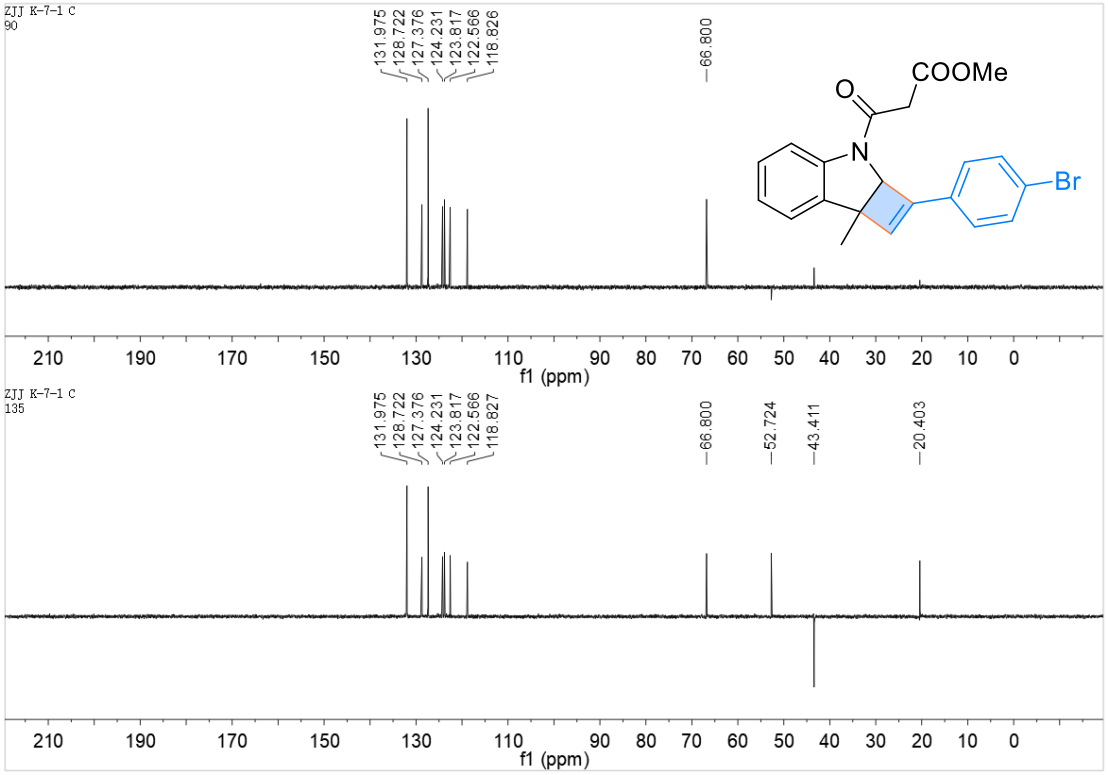
3a3 ^{1}H NMR



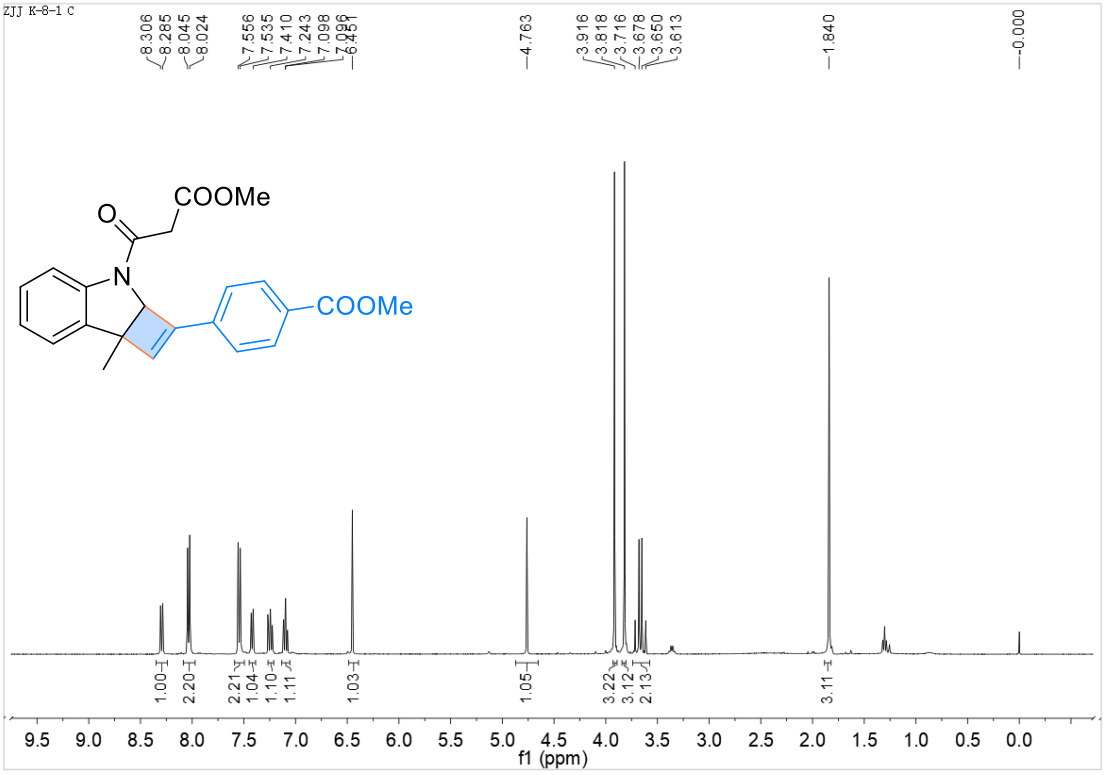
3a3 ^{13}C NMR



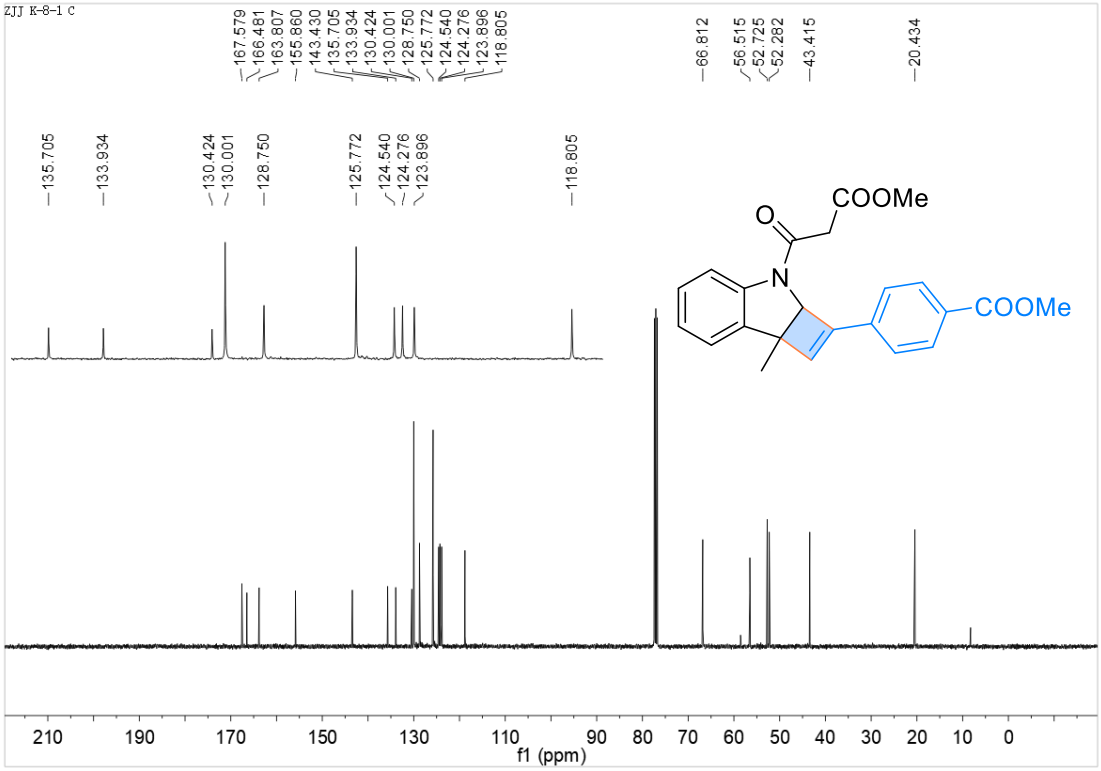
3a3 DEPT 90 and DEPT 135



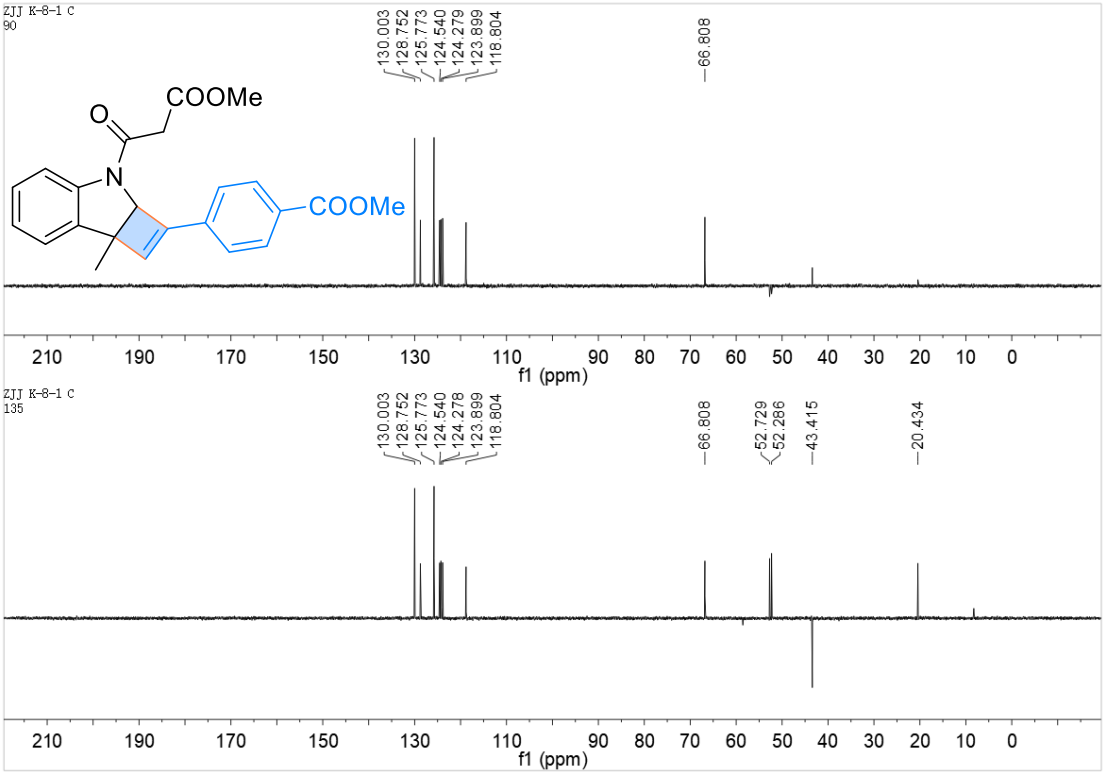
3a4 ^{1}H NMR



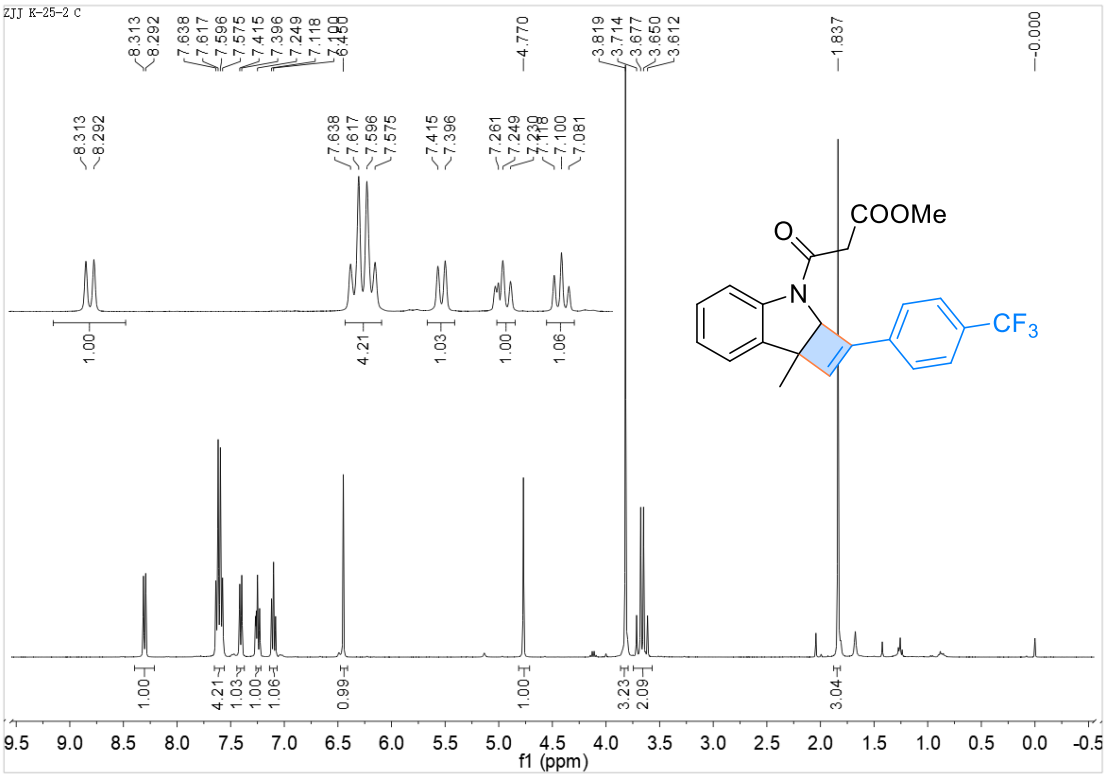
3a4 ^{13}C NMR



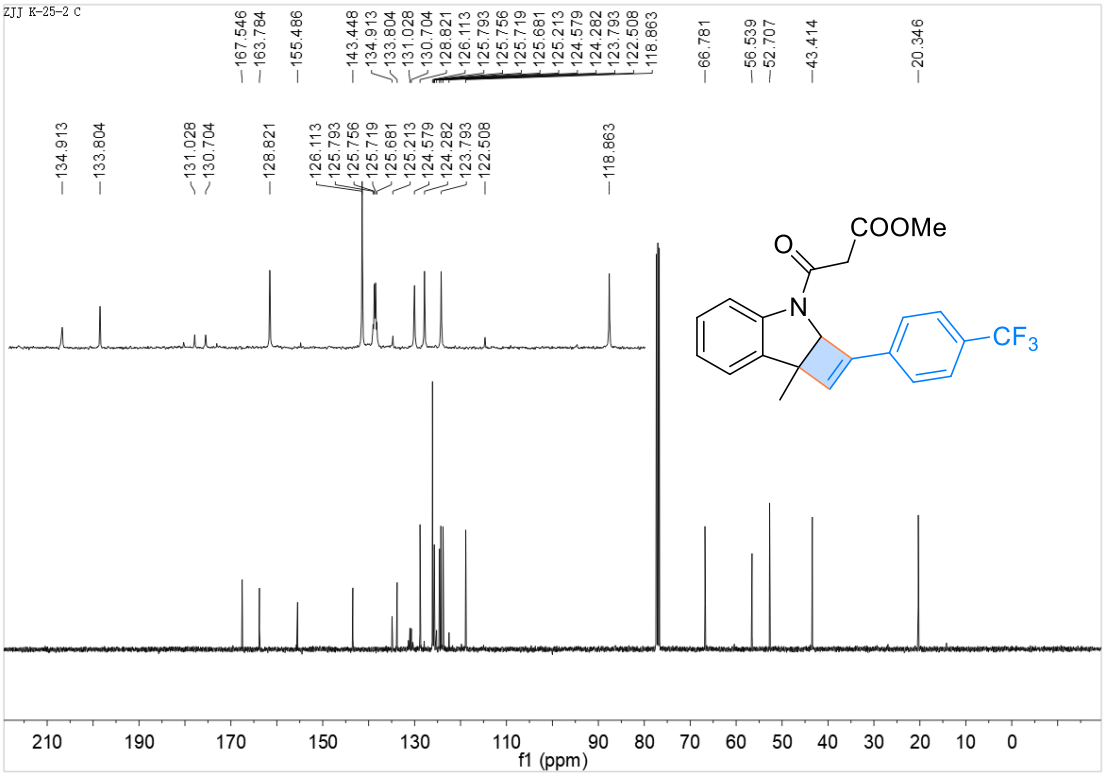
3a4 DEPT 90 and DEPT 135



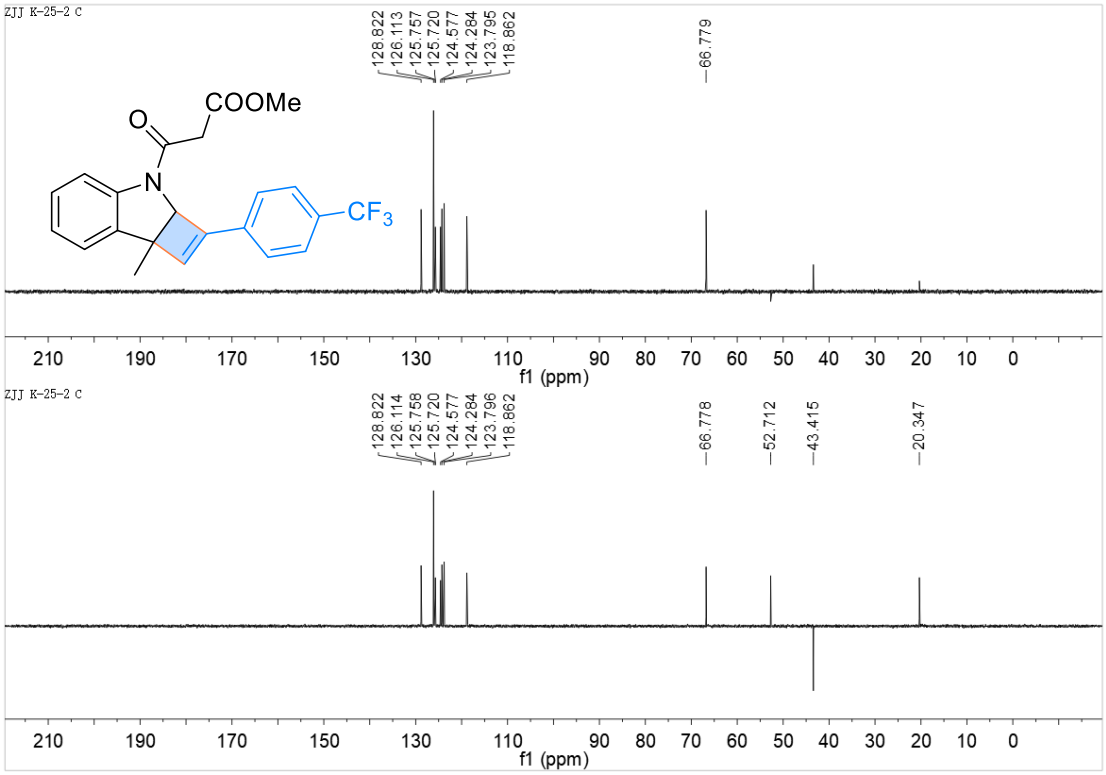
3a5 ^{1}H NMR



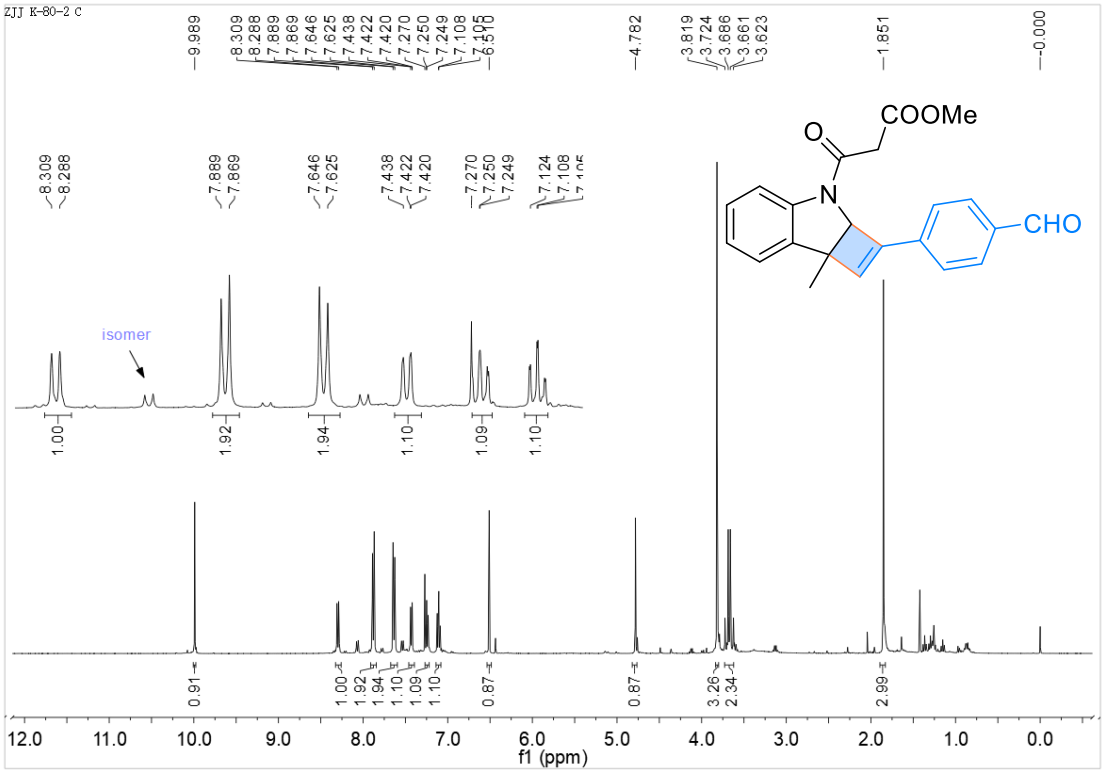
3a5 ^{13}C NMR



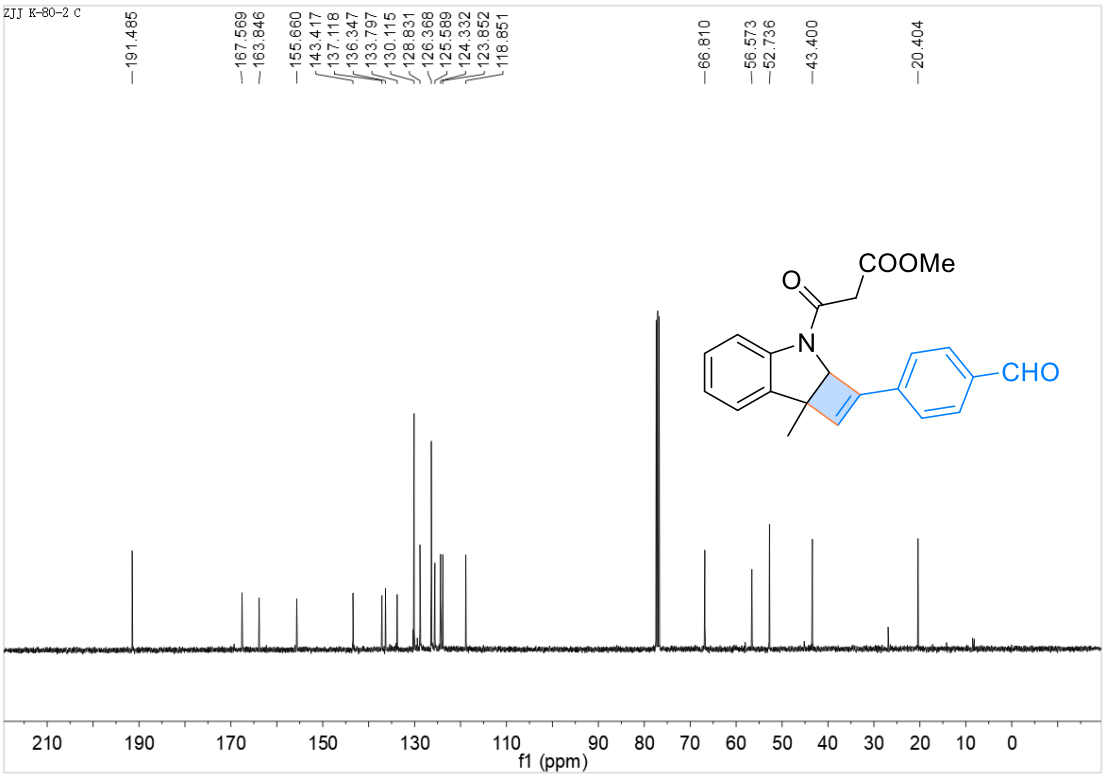
3a5 DEPT 90 and DEPT 135



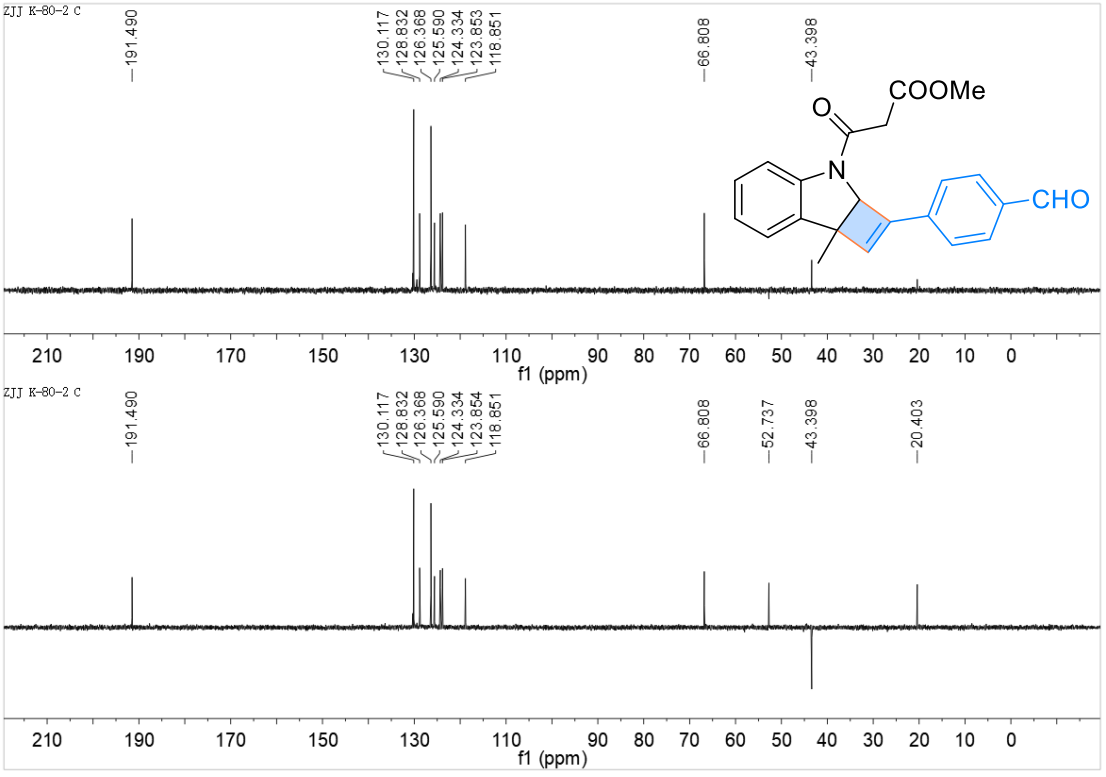
3a6 ^{1}H NMR



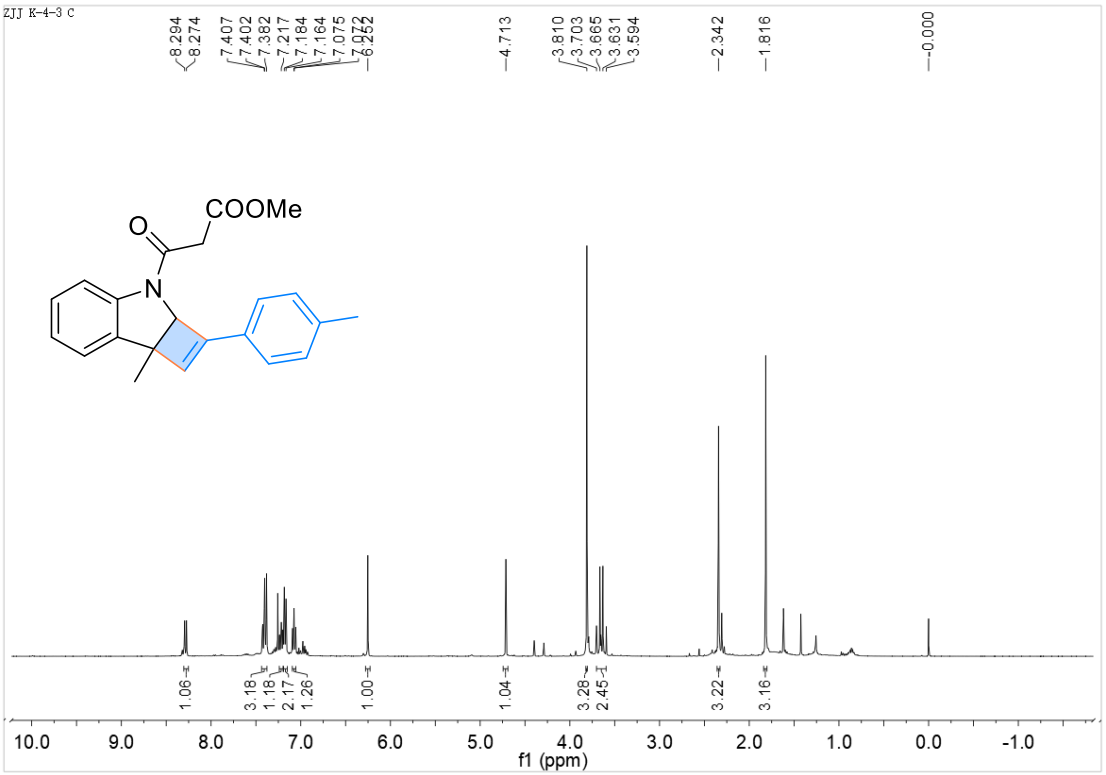
3a6 ^{13}C NMR



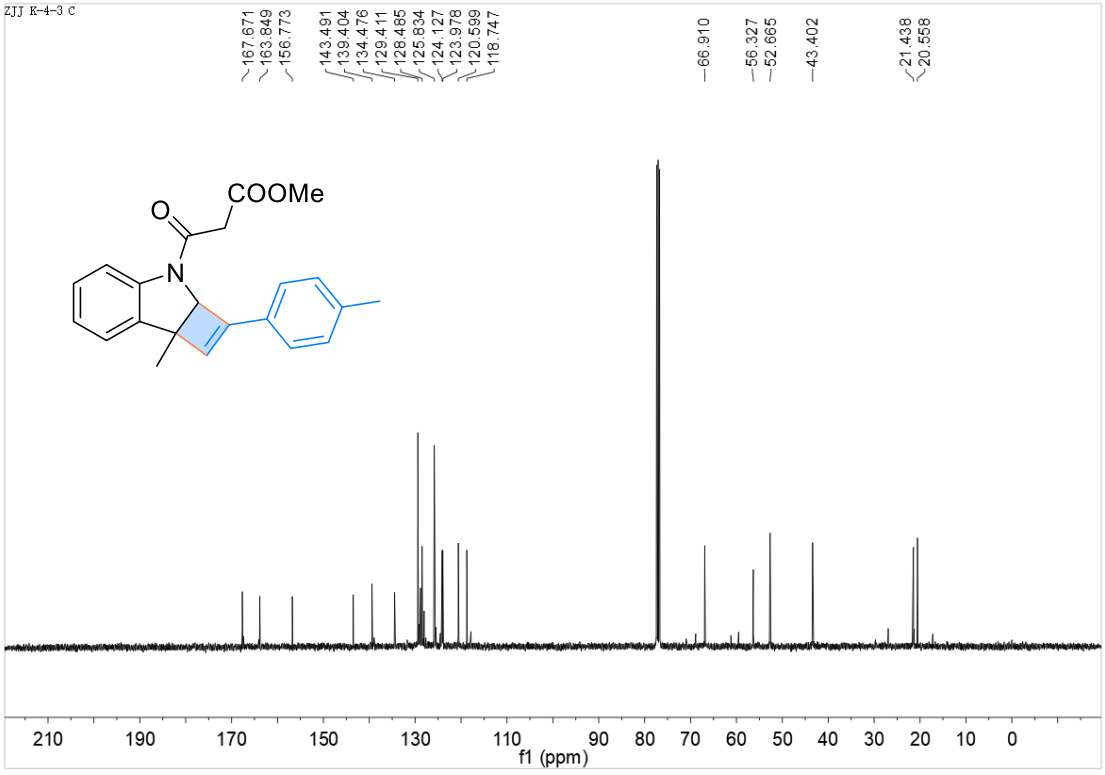
3a6 DEPT 90 and DEPT 135



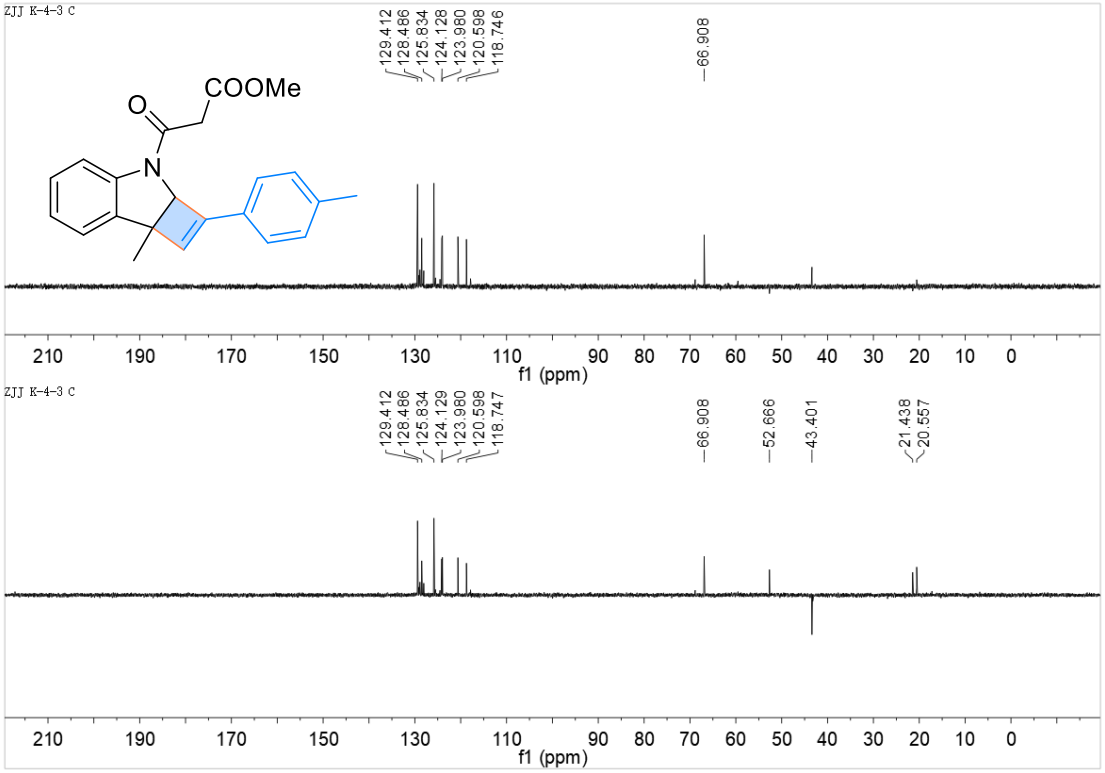
3a7 ^{1}H NMR



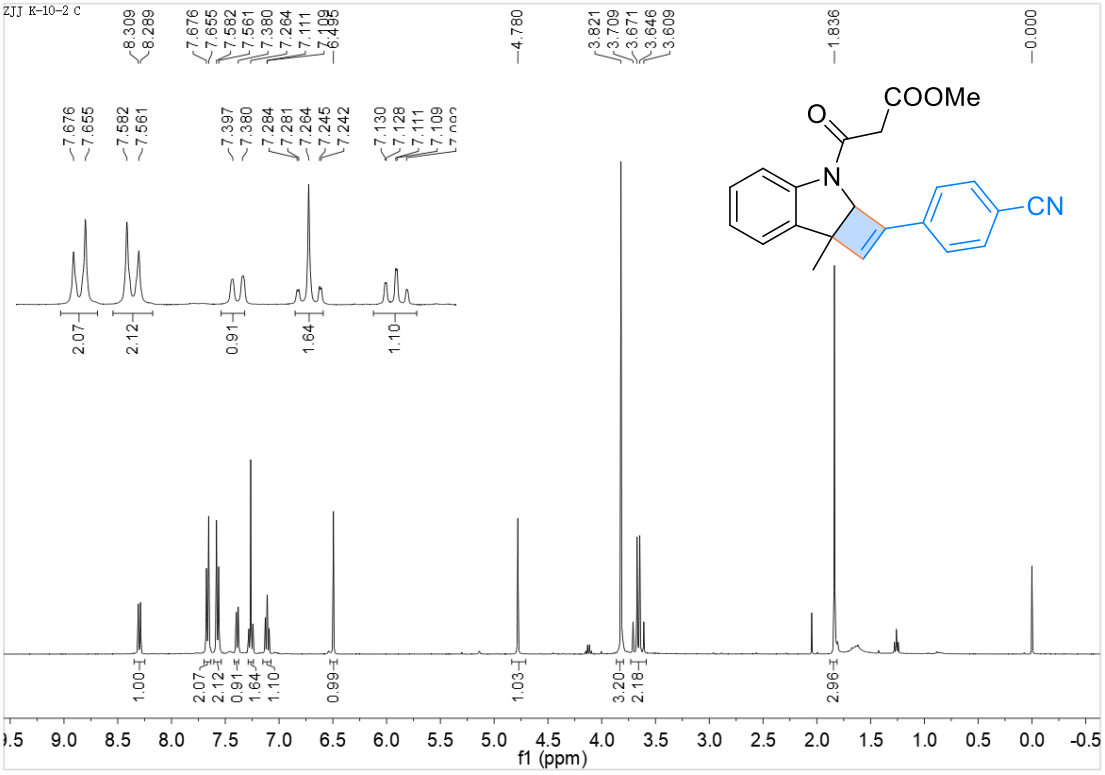
3a7 ^{13}C NMR



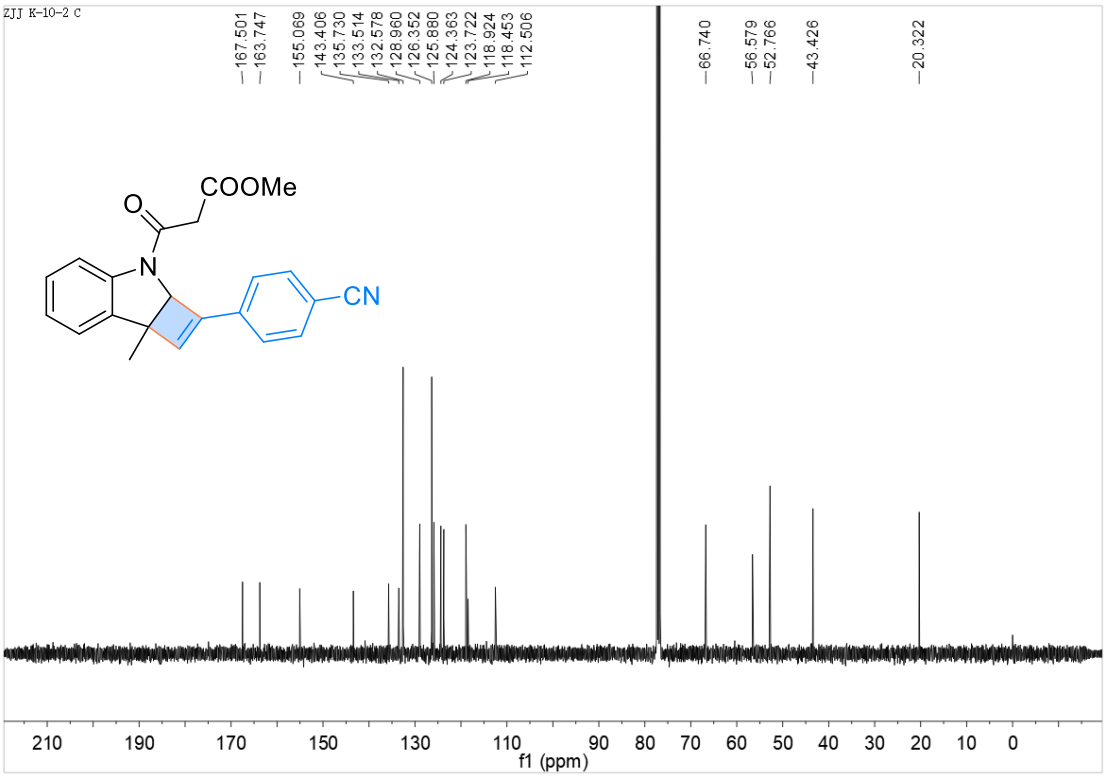
3a7 DEPT 90 and DEPT 135



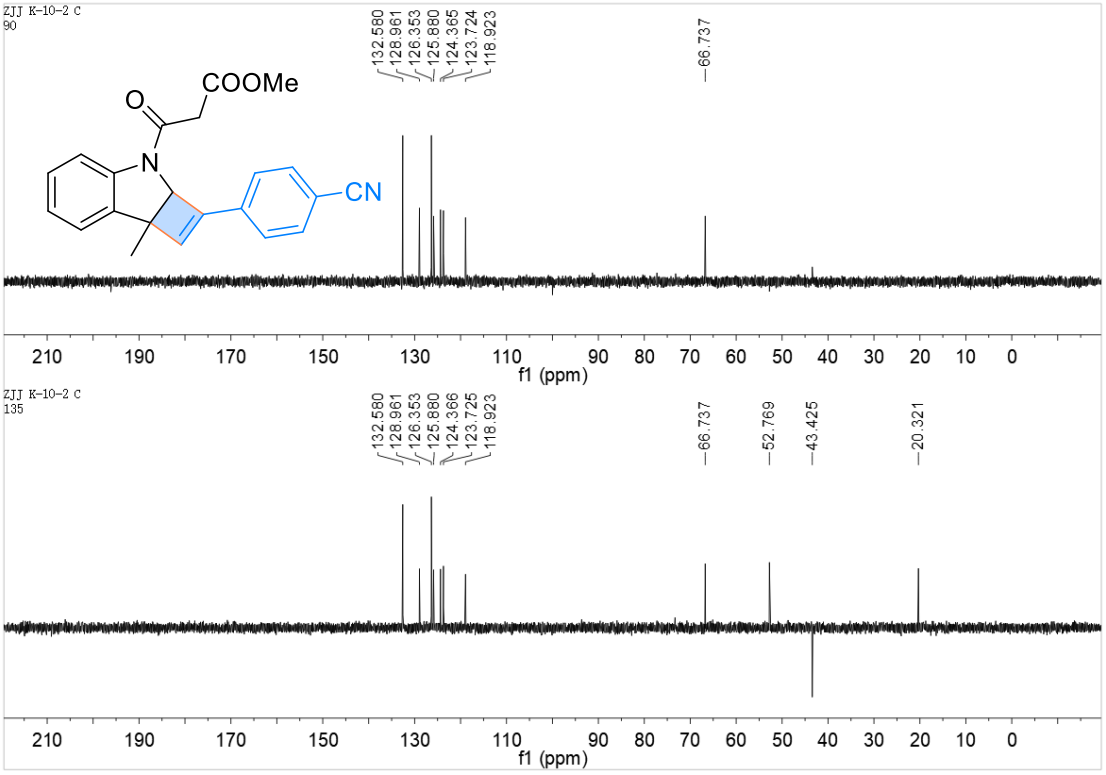
3a8 ^{1}H NMR



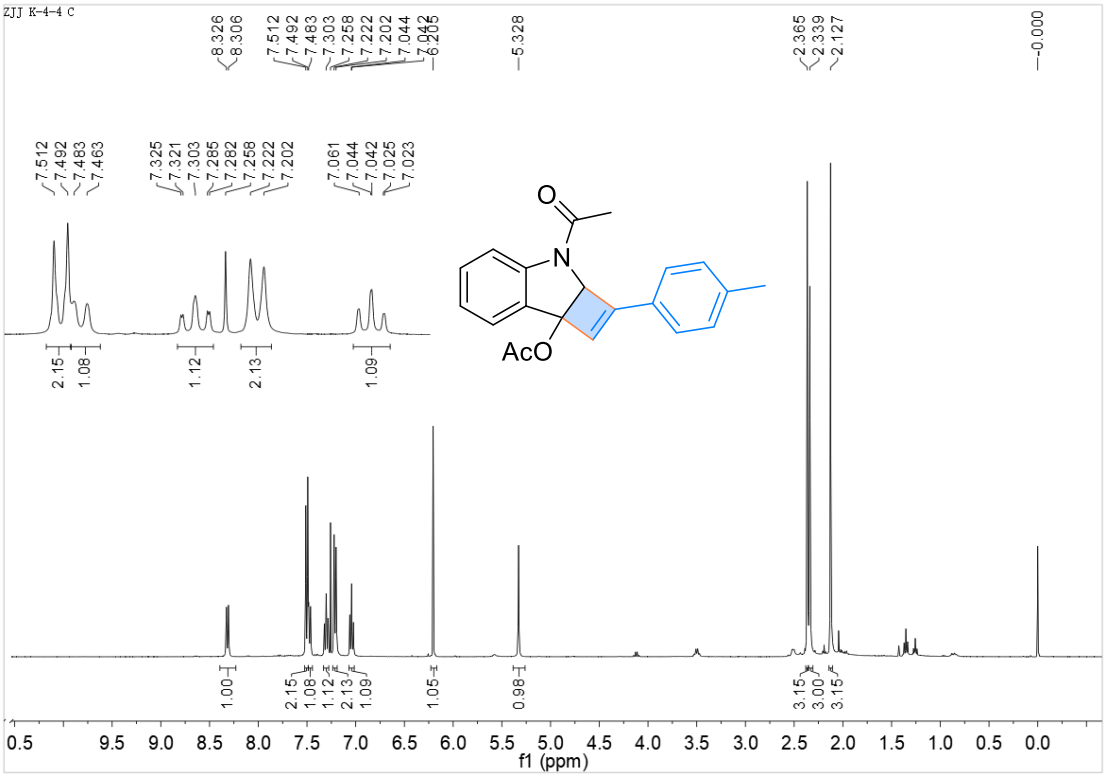
3a8 ^{13}C NMR



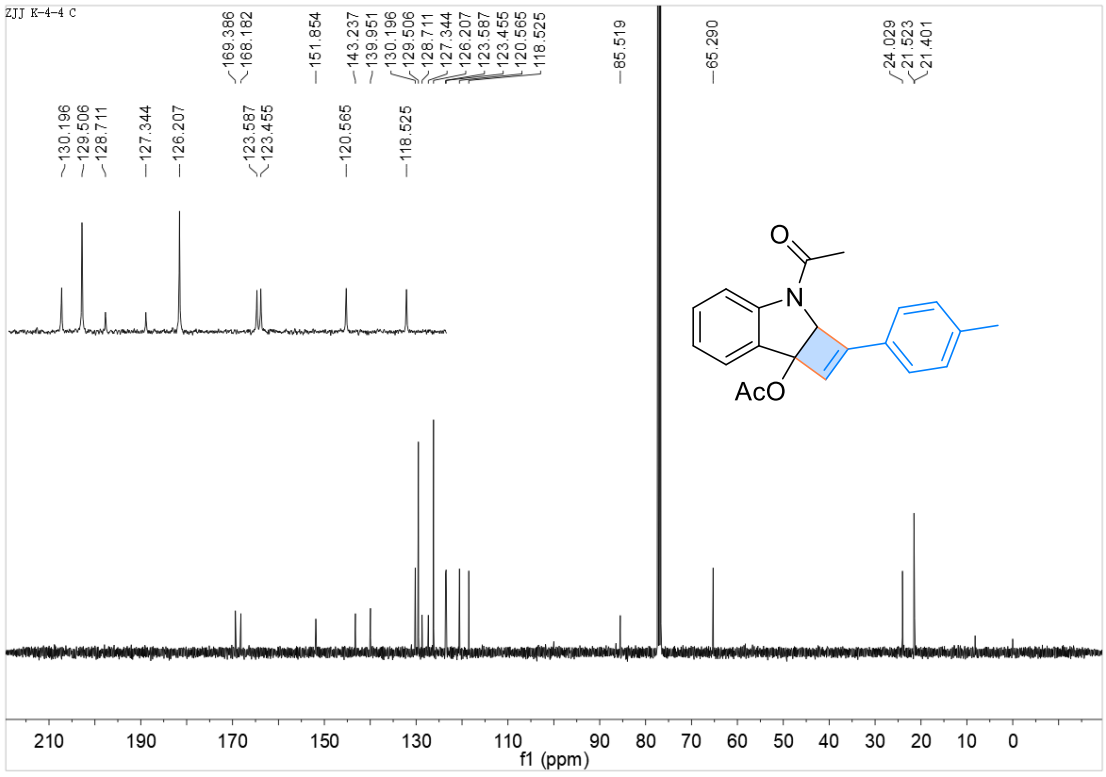
3a8 DEPT 90 and DEPT 135



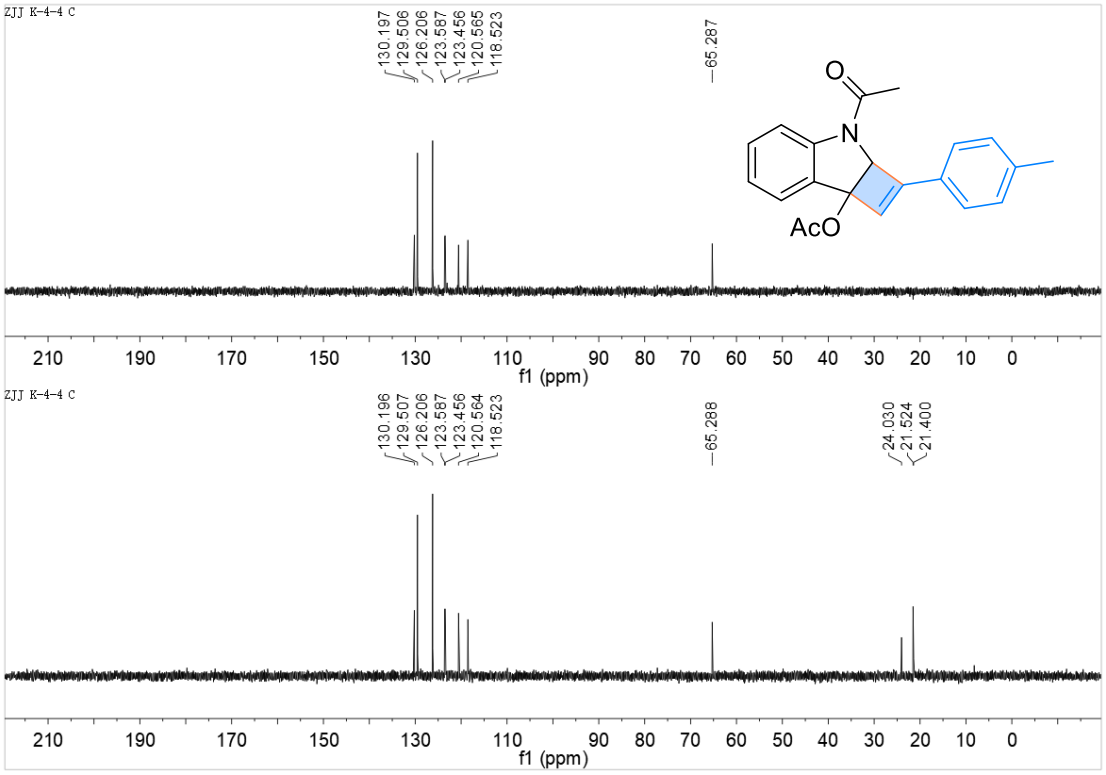
3b1 ^{1}H NMR



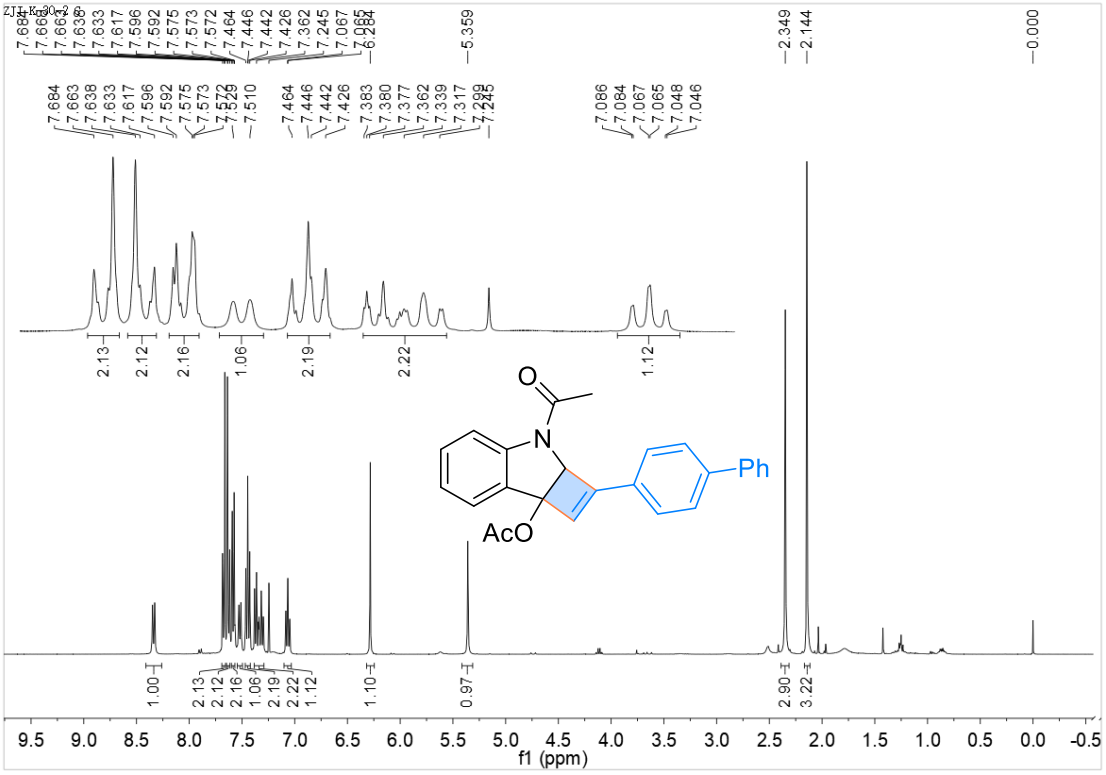
3b1 ^{13}C NMR



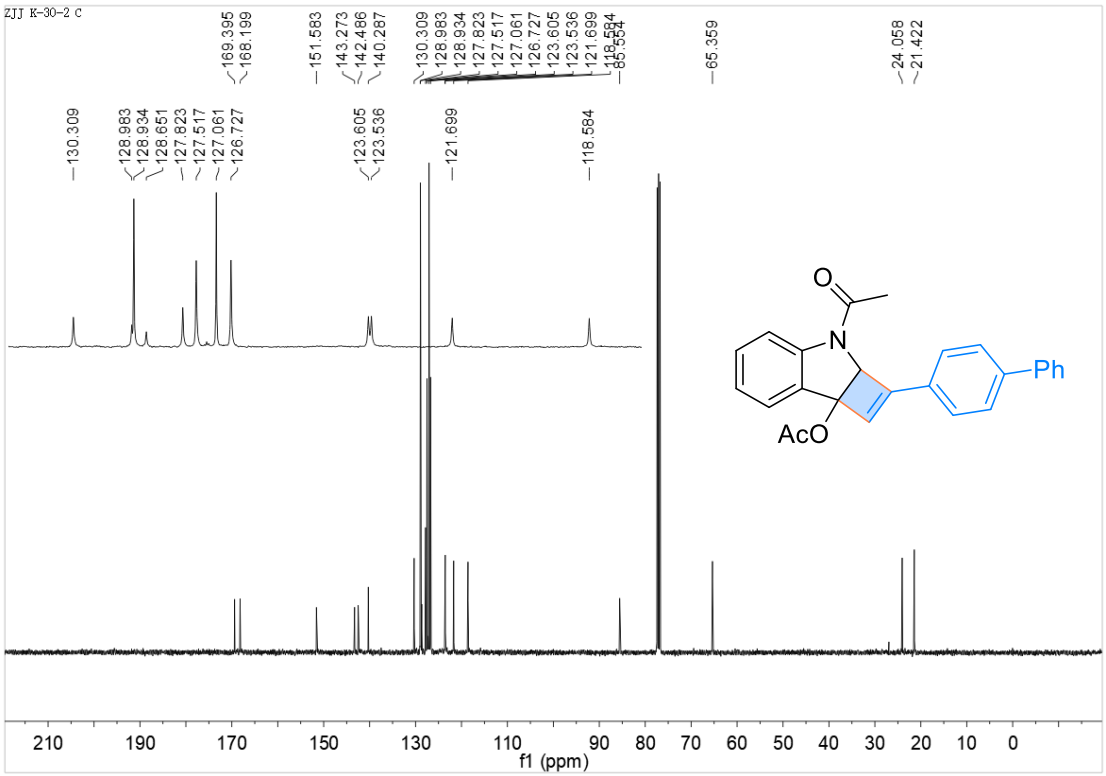
3b1 DEPT 90 and DEPT 135



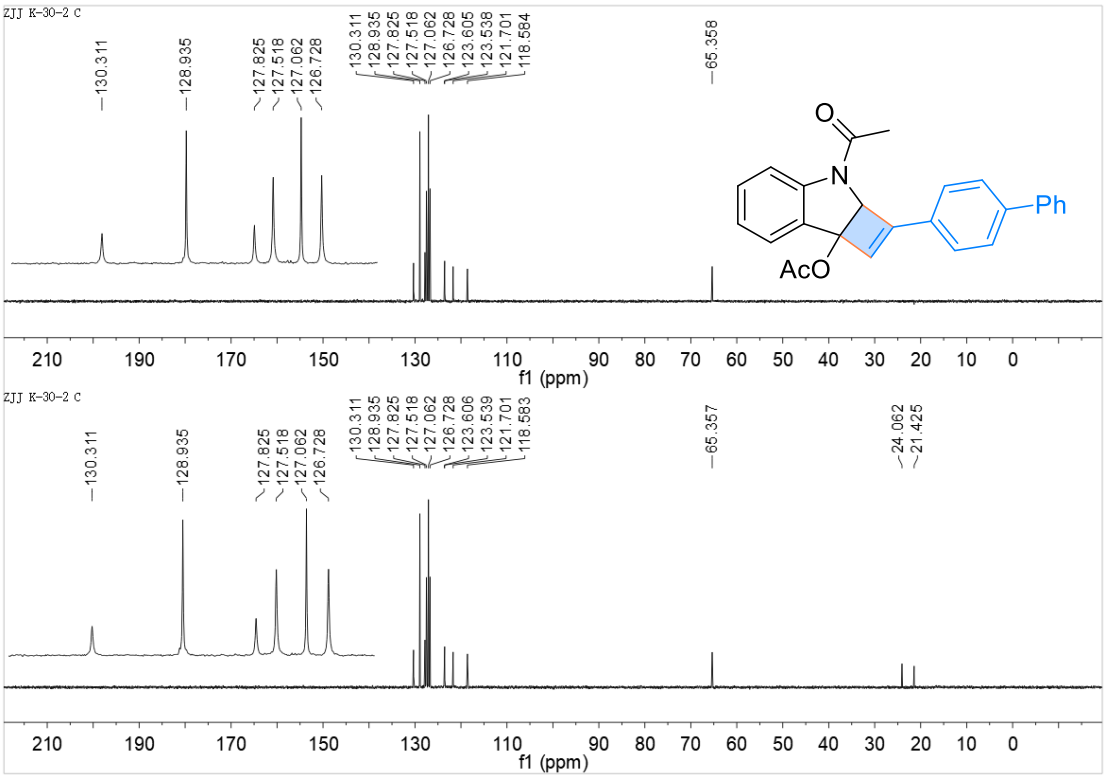
3b2 ^{1}H NMR



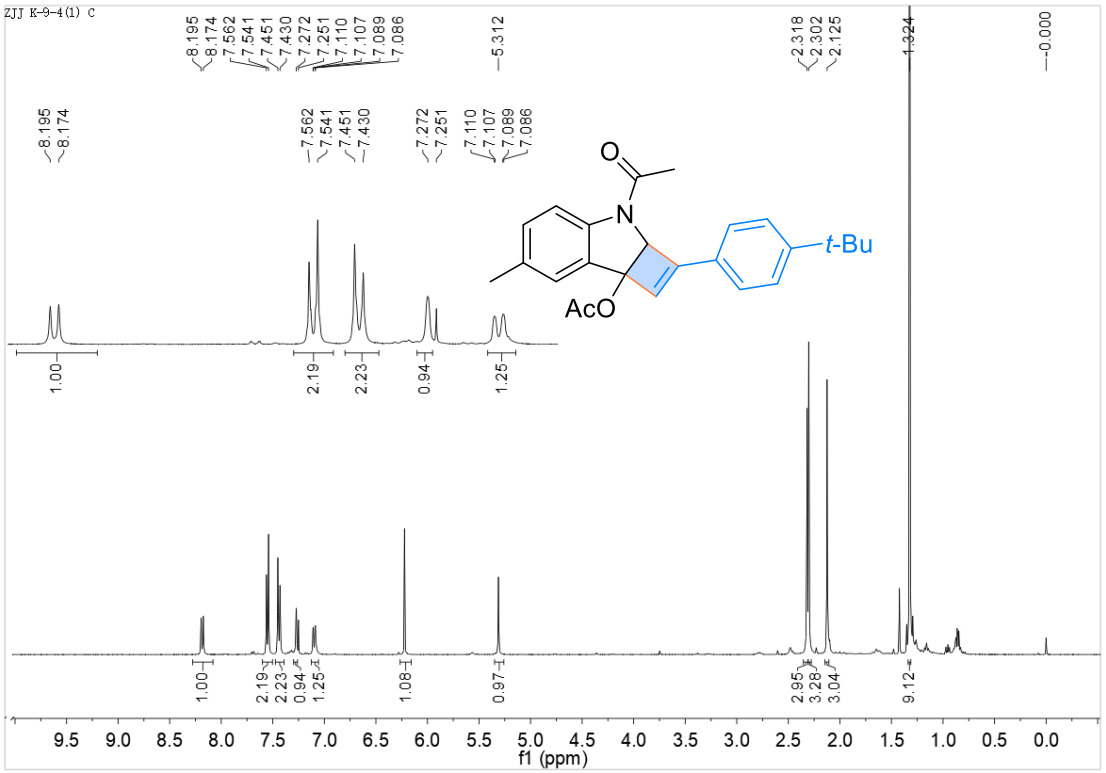
3b2 ^{13}C NMR



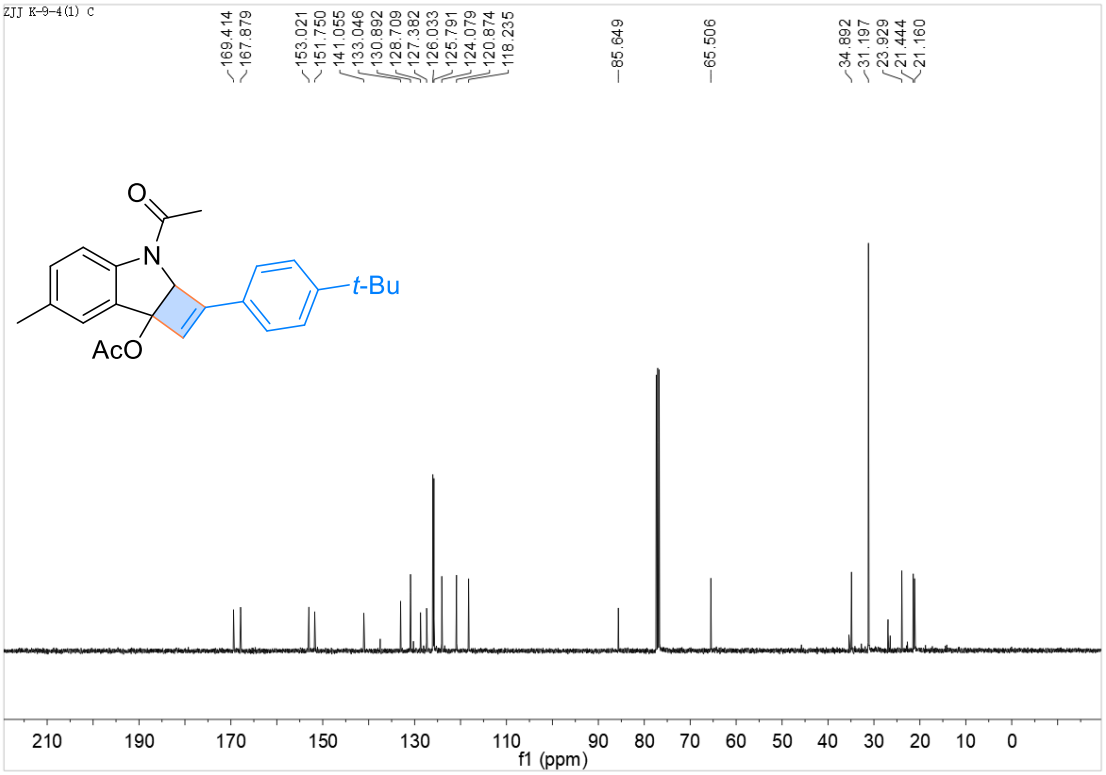
3b2 DEPT 90 and DEPT 135



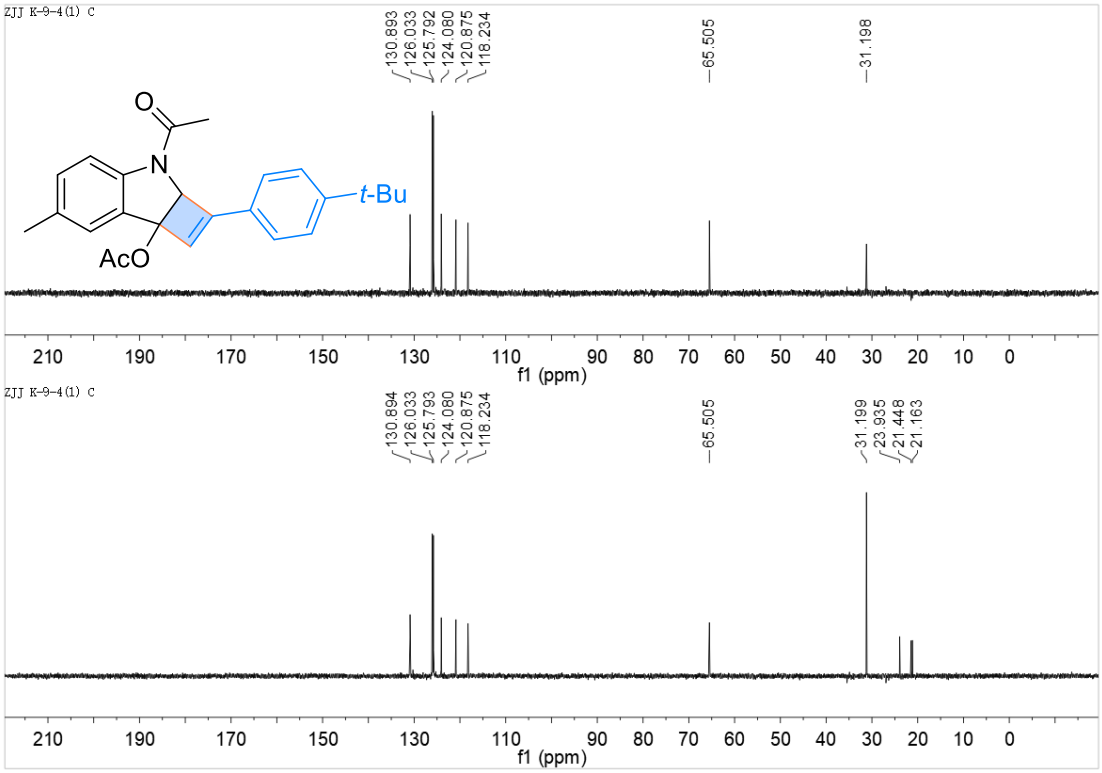
3c ^{1}H NMR



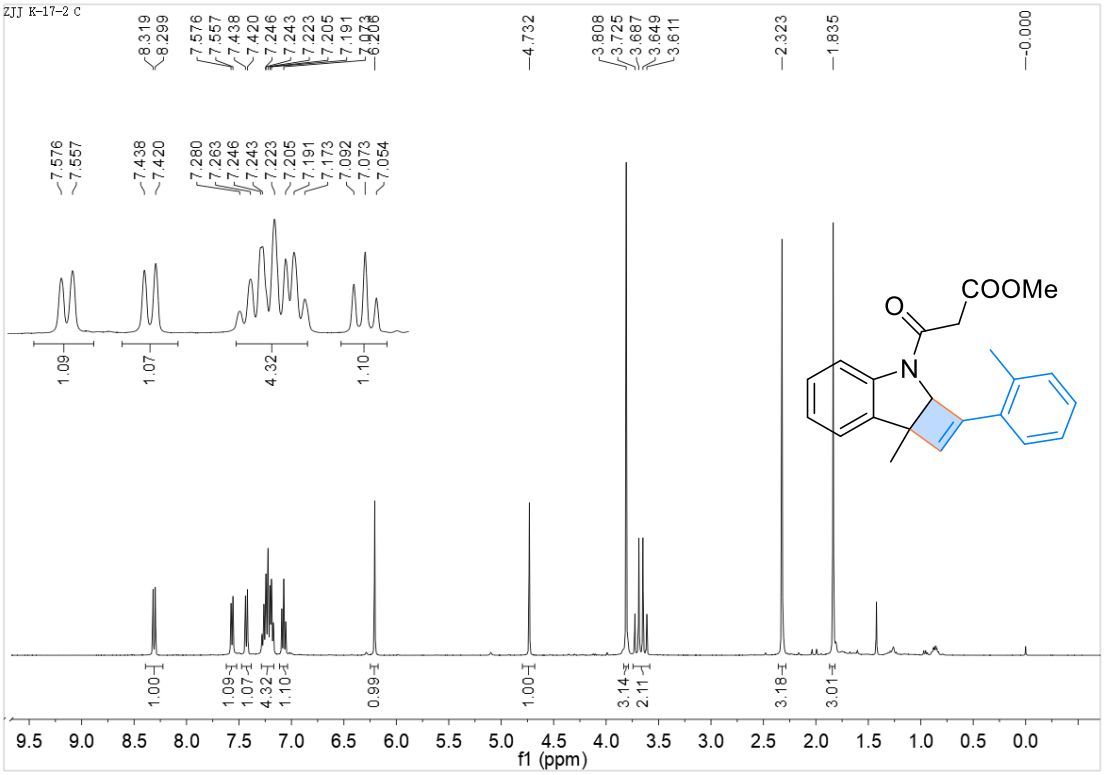
3c ^{13}C NMR



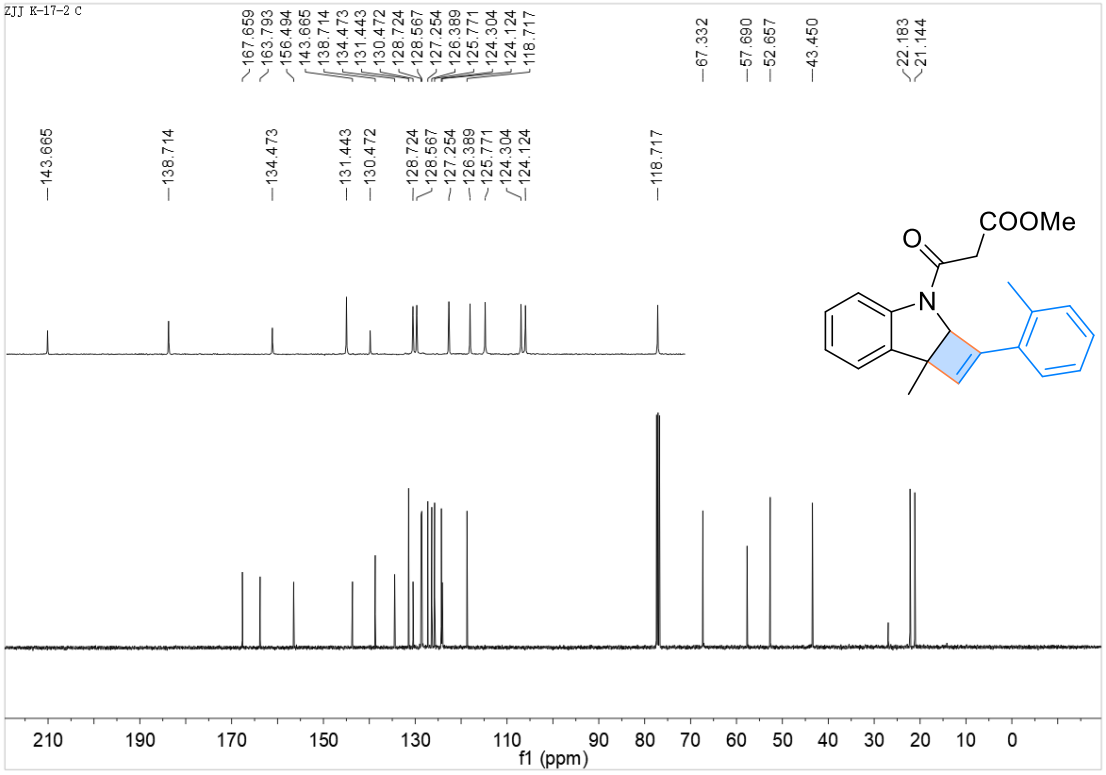
3c DEPT 90 and DEPT 135



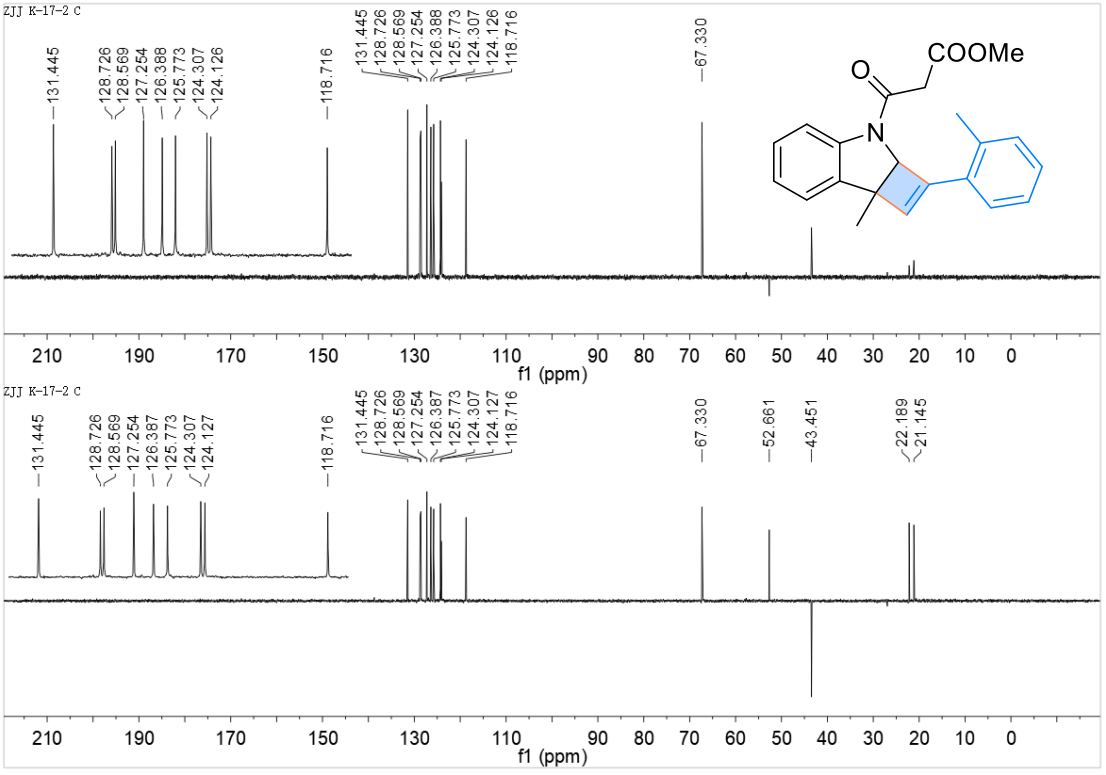
3d1 ^{1}H NMR



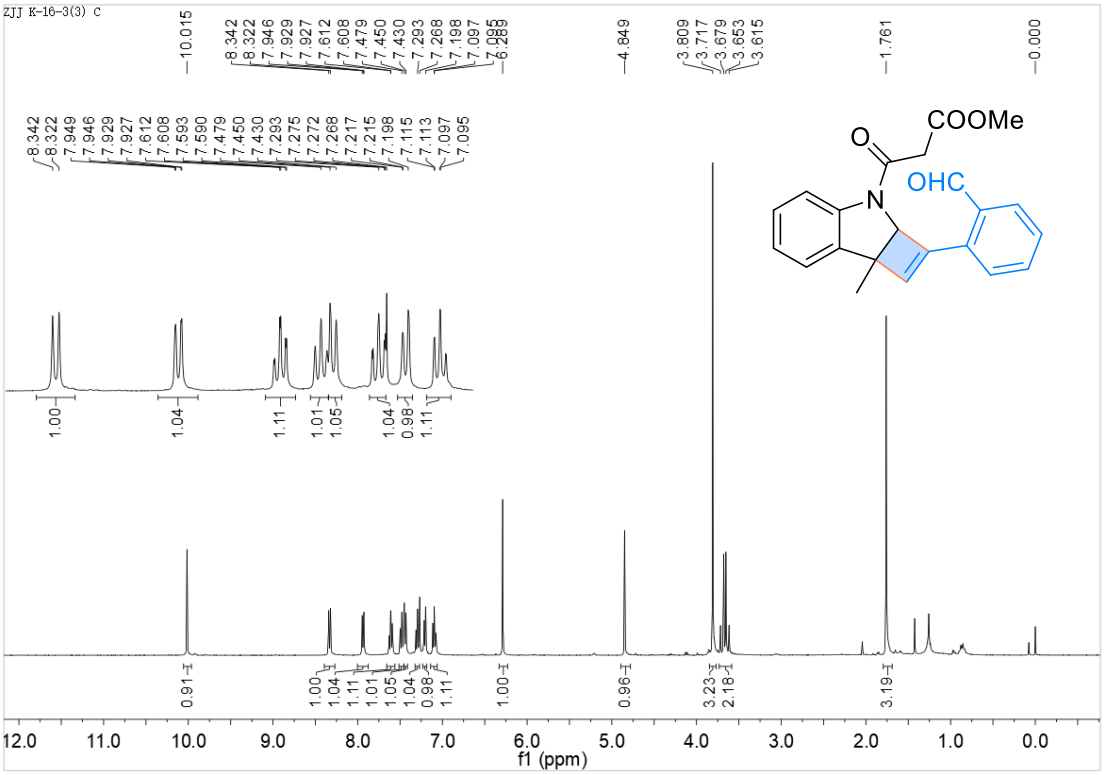
3d1 ^{13}C NMR



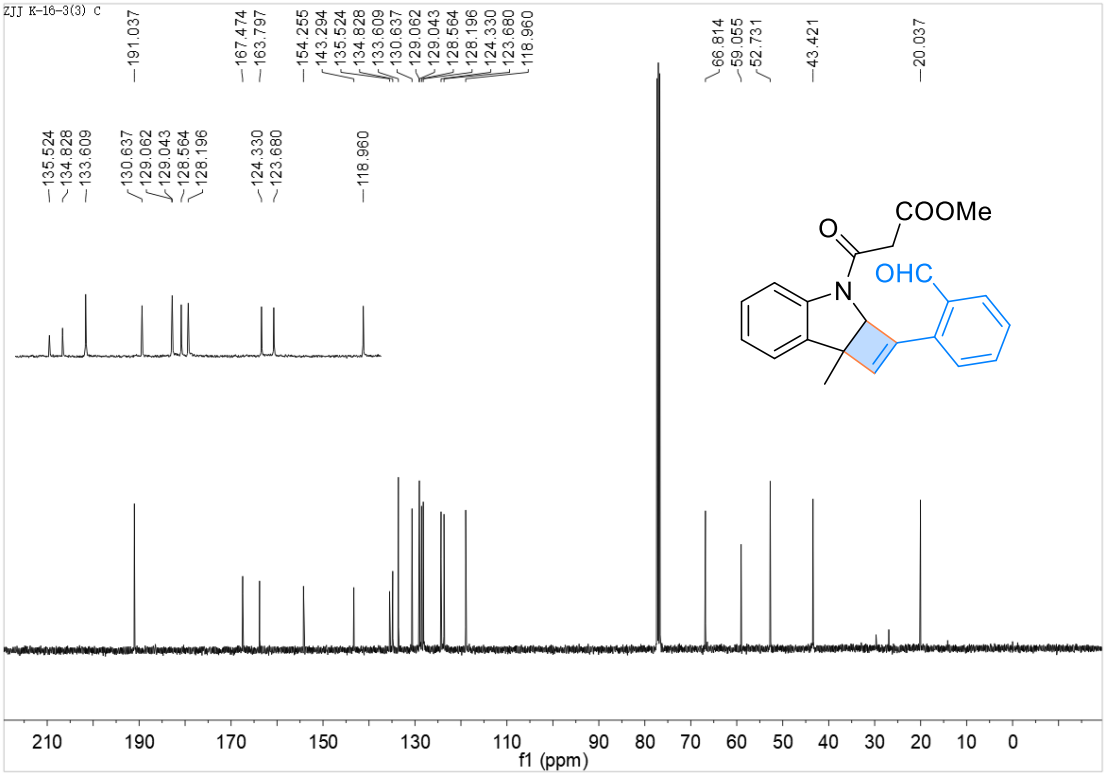
3d1 DEPT 90 and DEPT 135



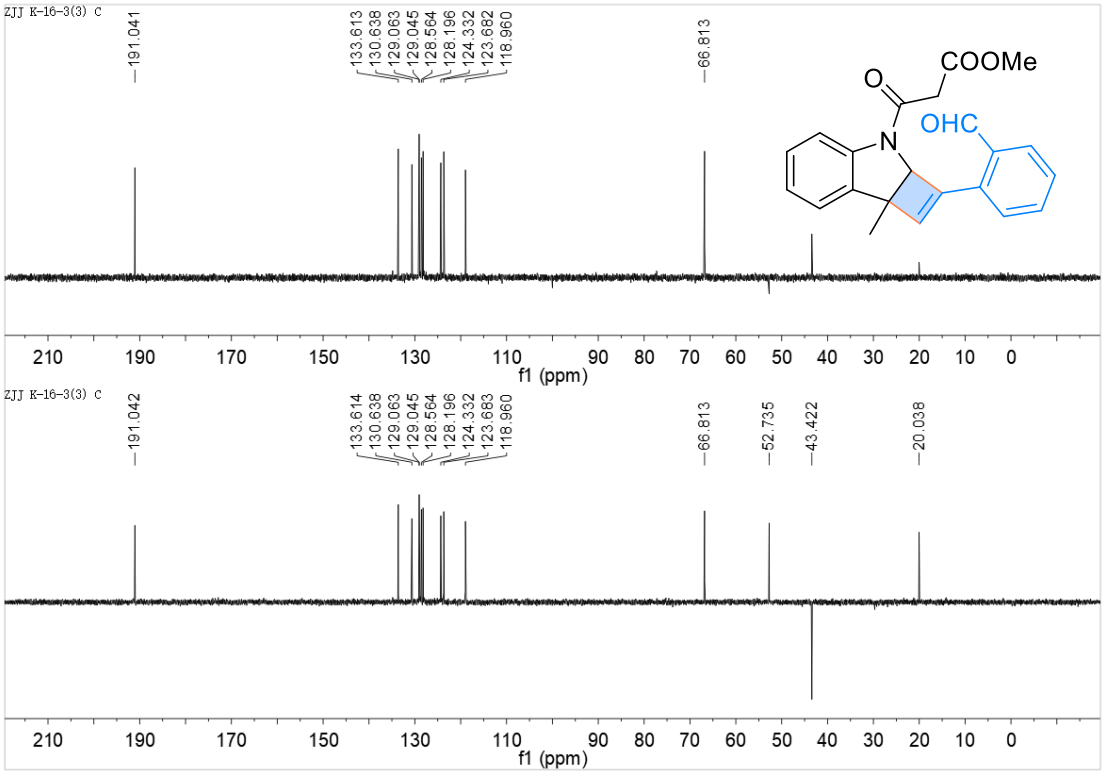
3d2 ^{1}H NMR



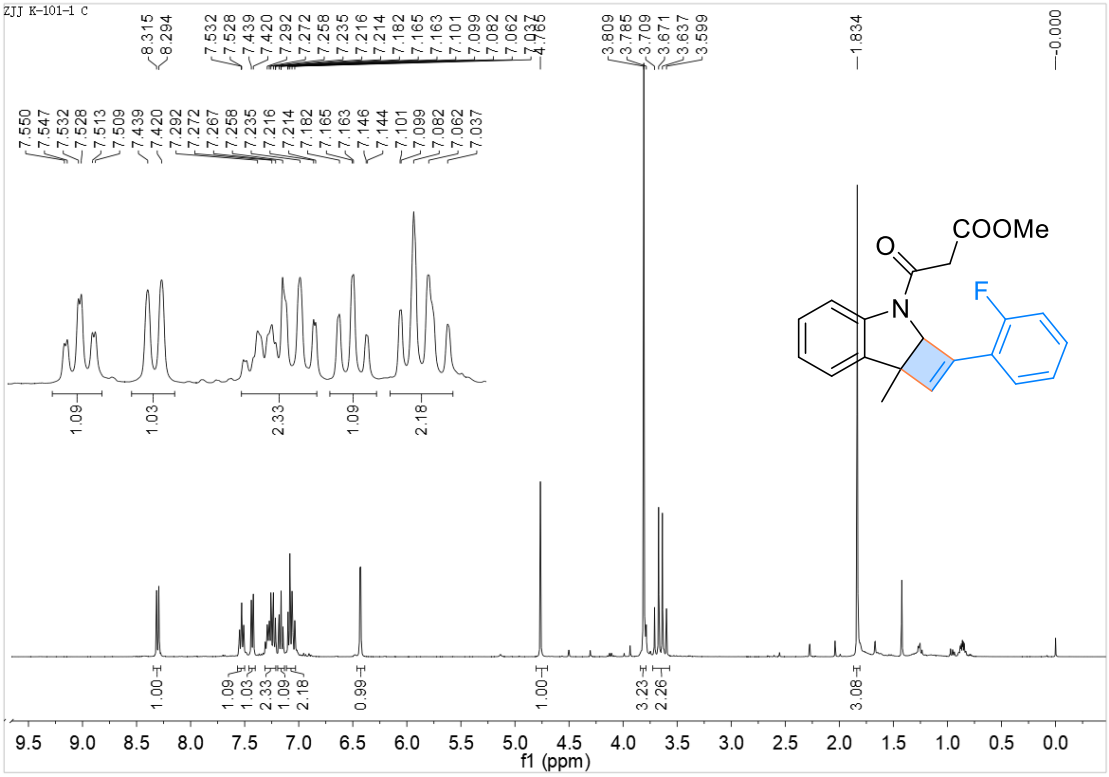
3d2 ^{13}C NMR



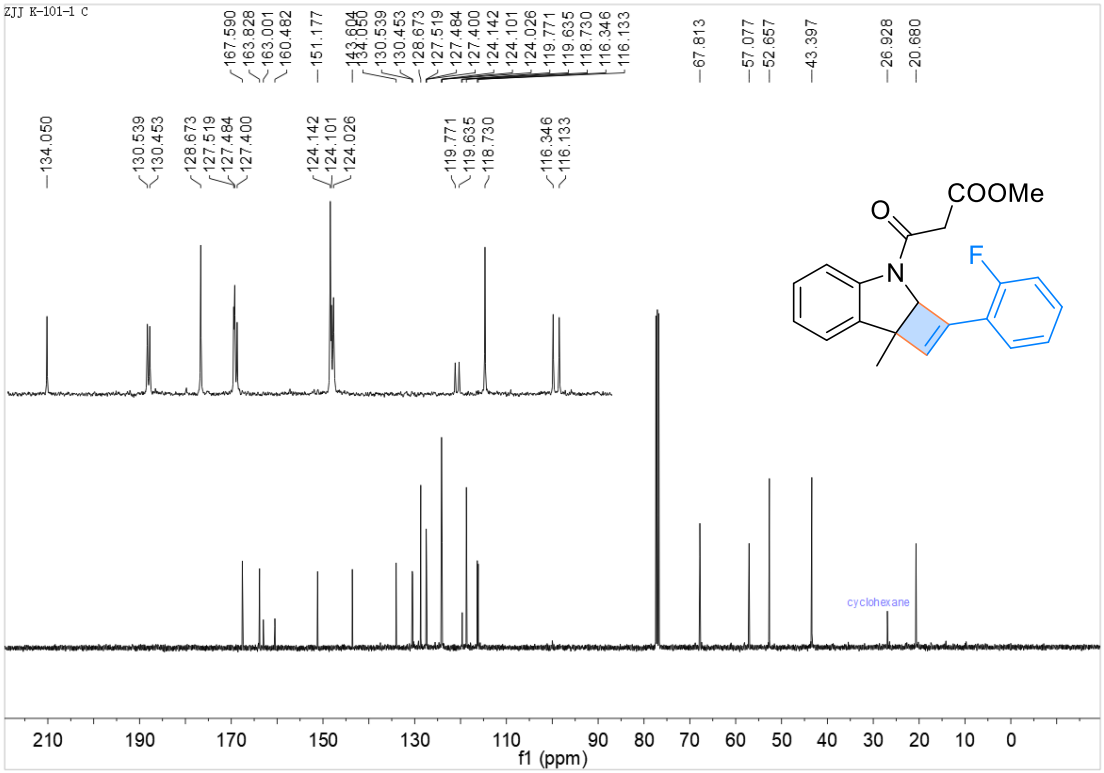
3d2 DEPT 90 and DEPT 135



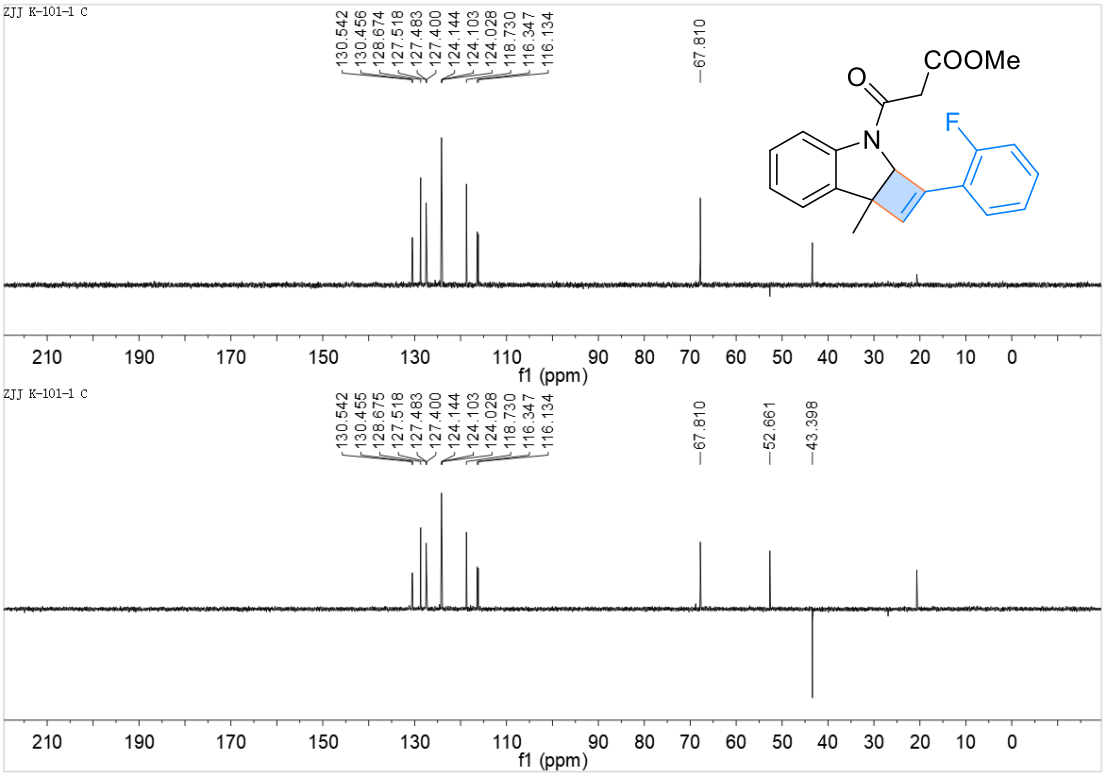
3d3 ^{1}H NMR



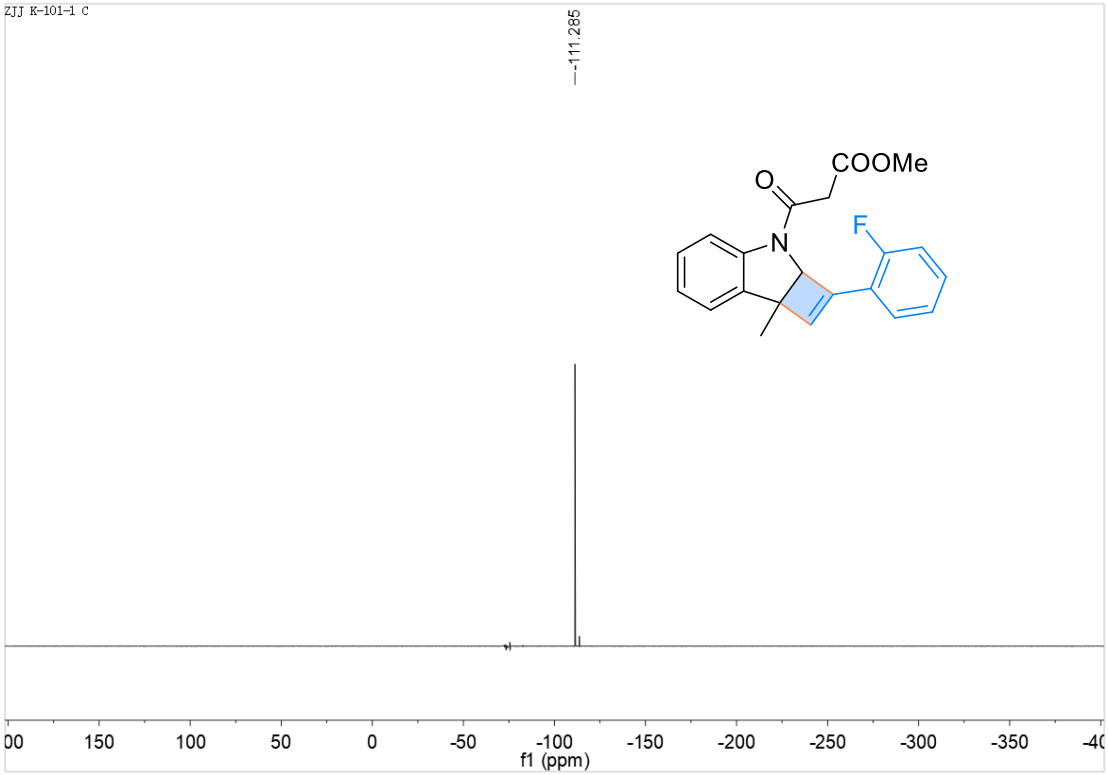
3d3 ^{13}C NMR



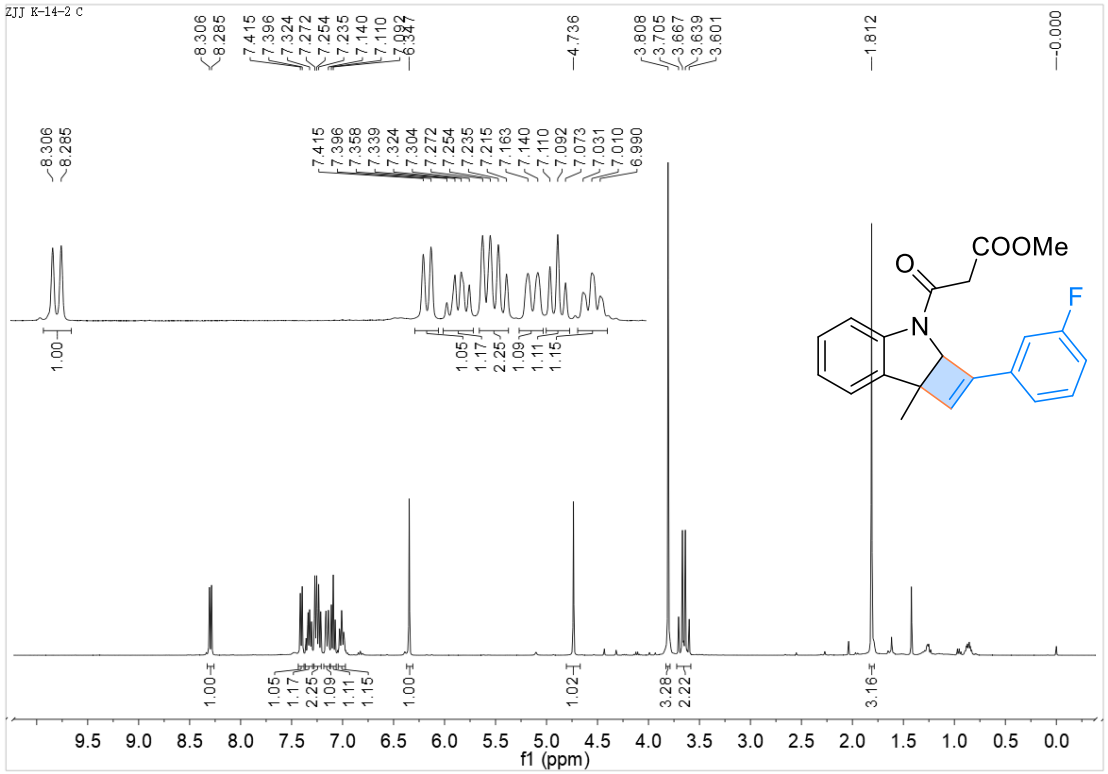
3d3 DEPT 90 and DEPT 135



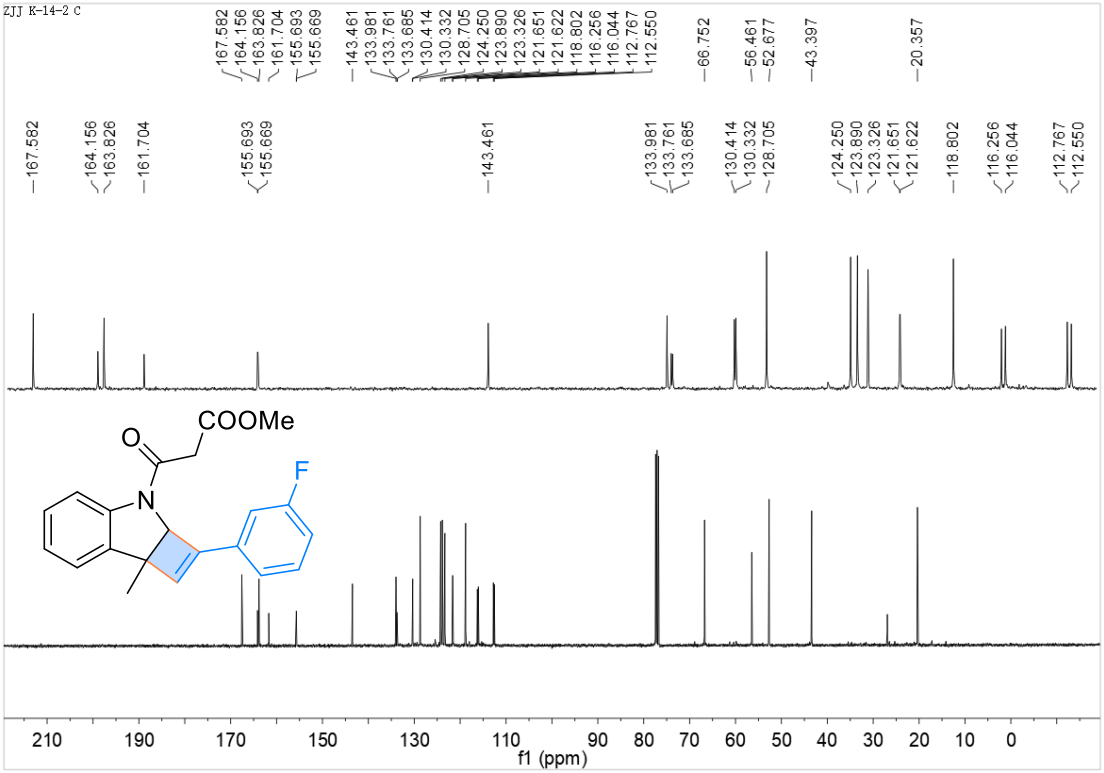
3d3 ^{19}F NMR



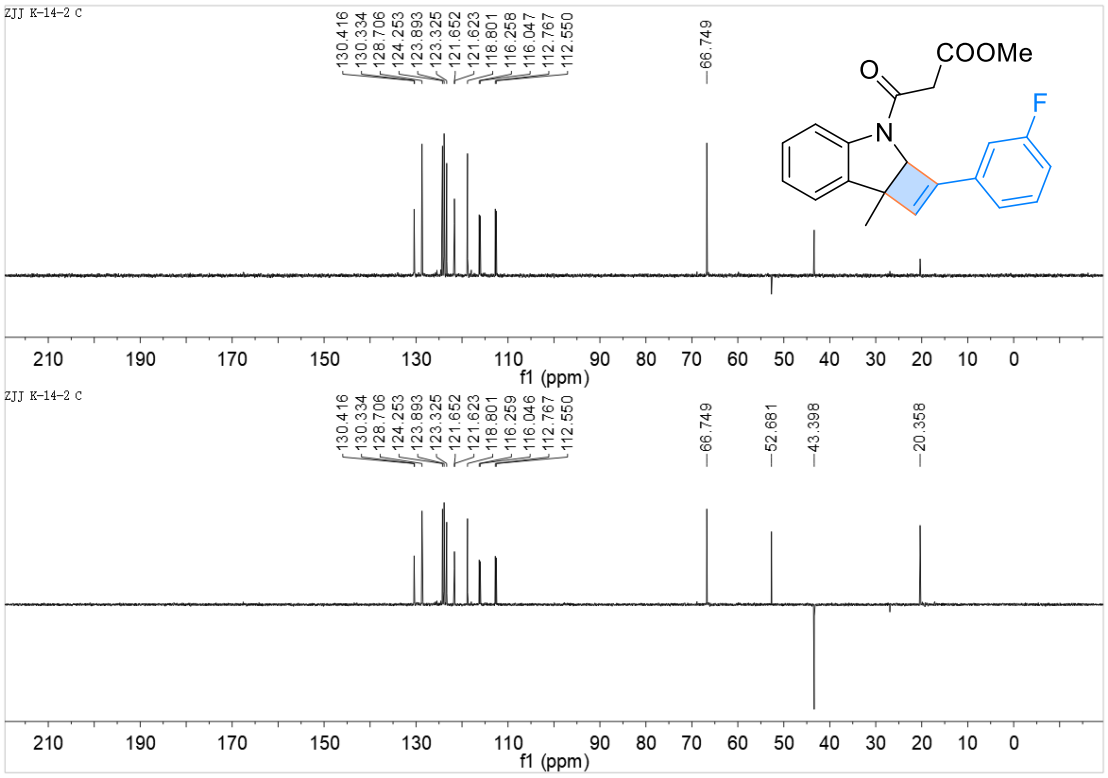
3e1 ^{1}H NMR



3e1^{13}C NMR



3e1 DEPT 90 and DEPT 135



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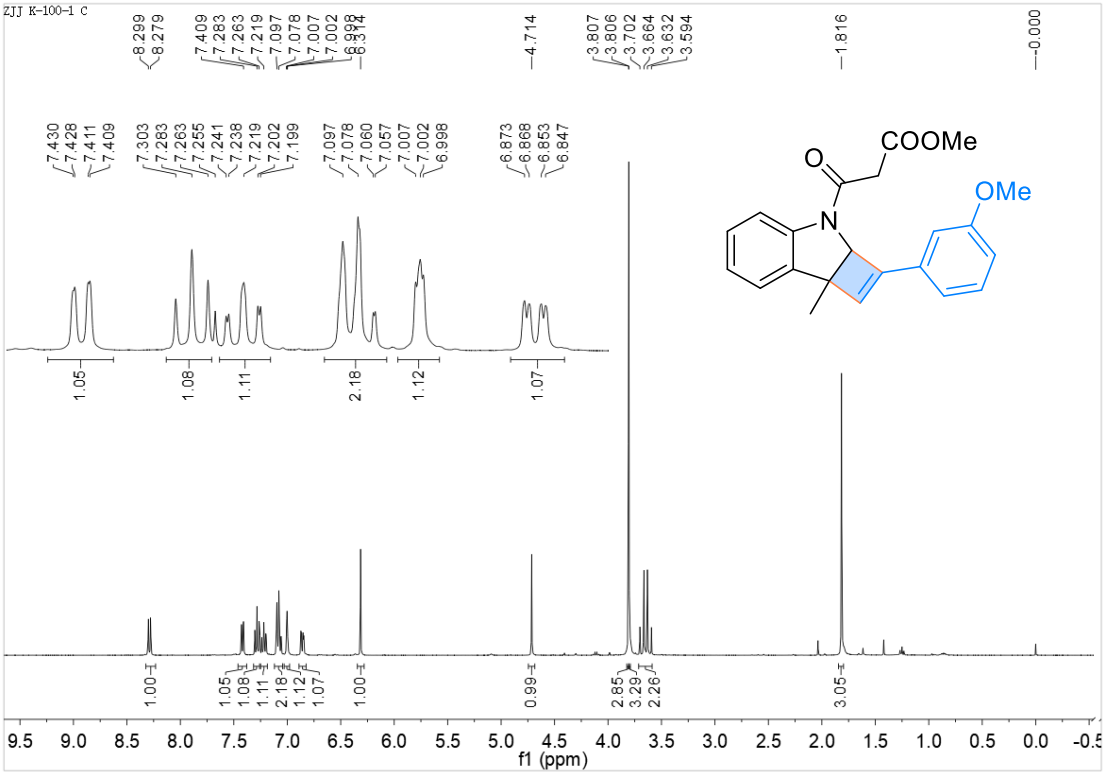
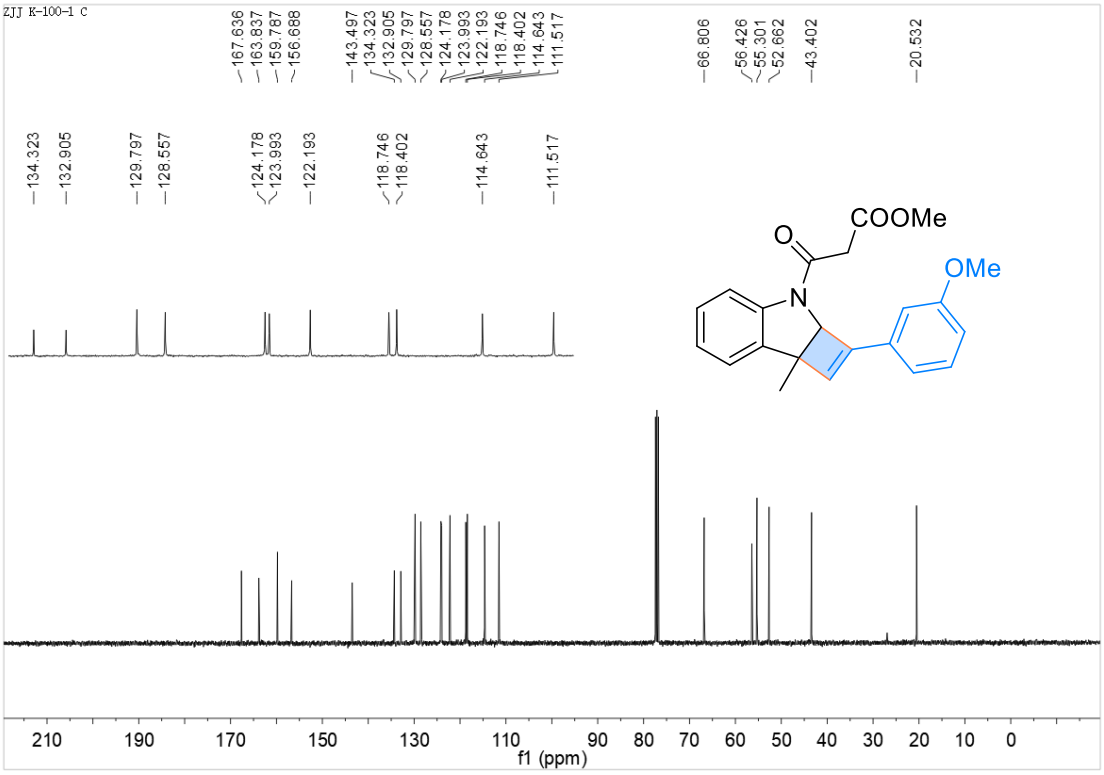
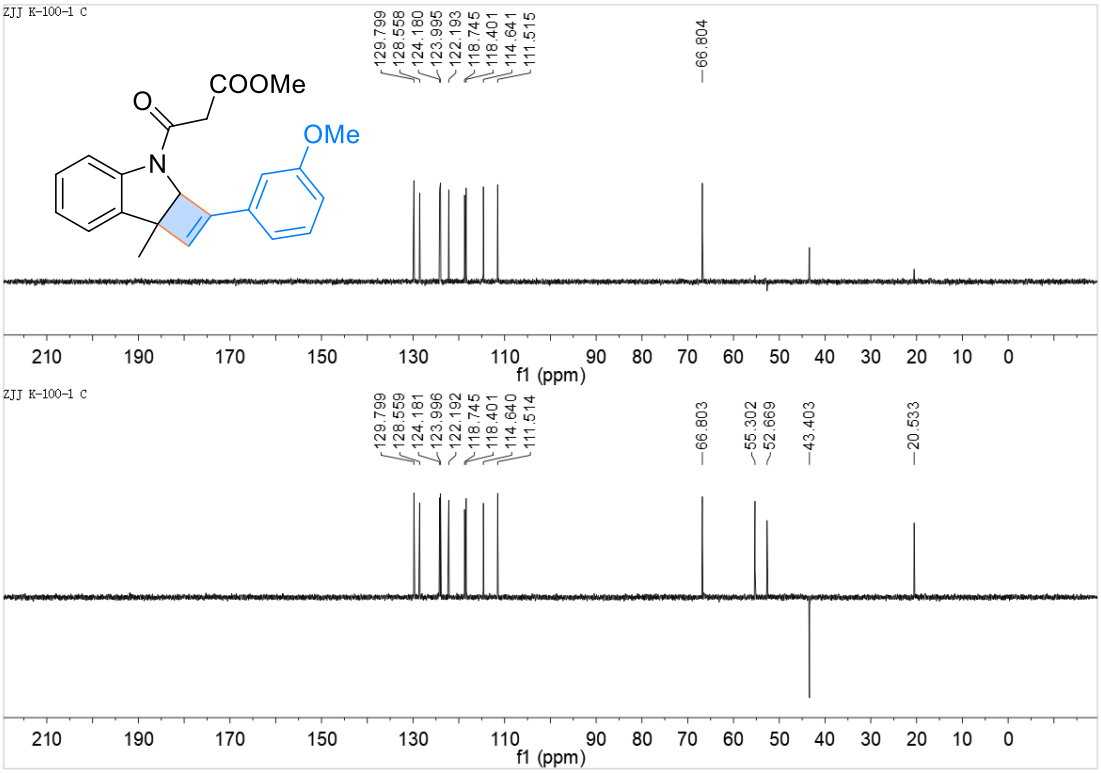


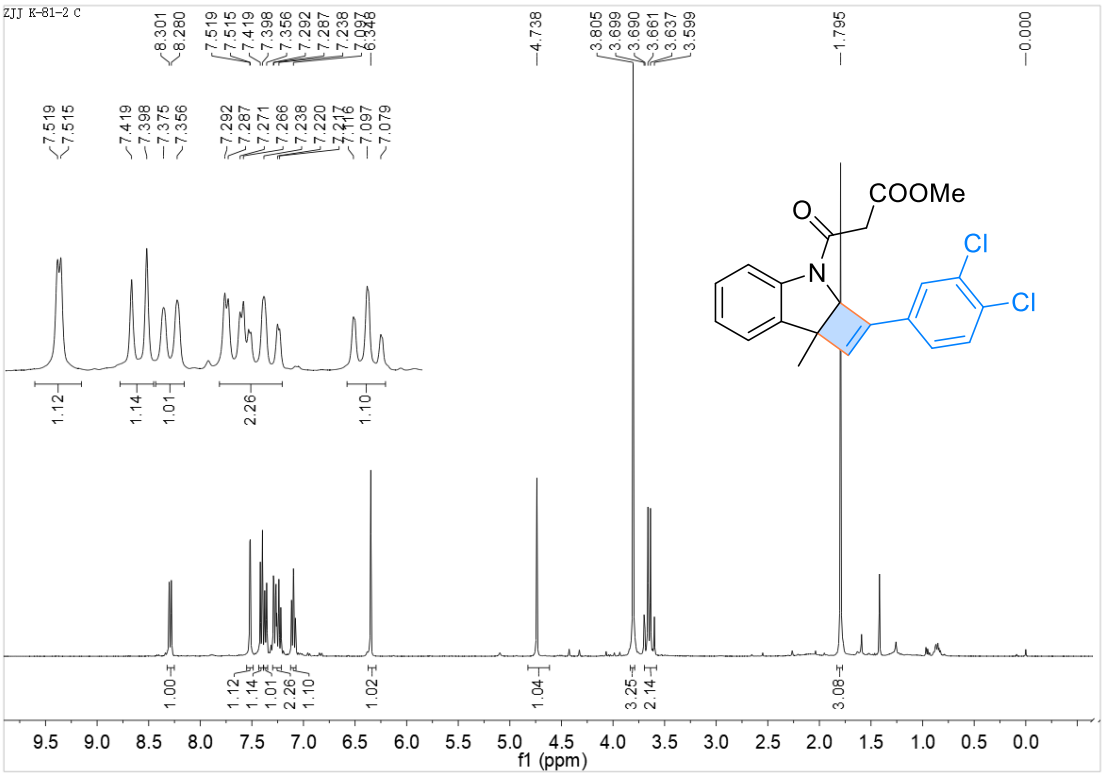
3e2 ^{13}C NMR



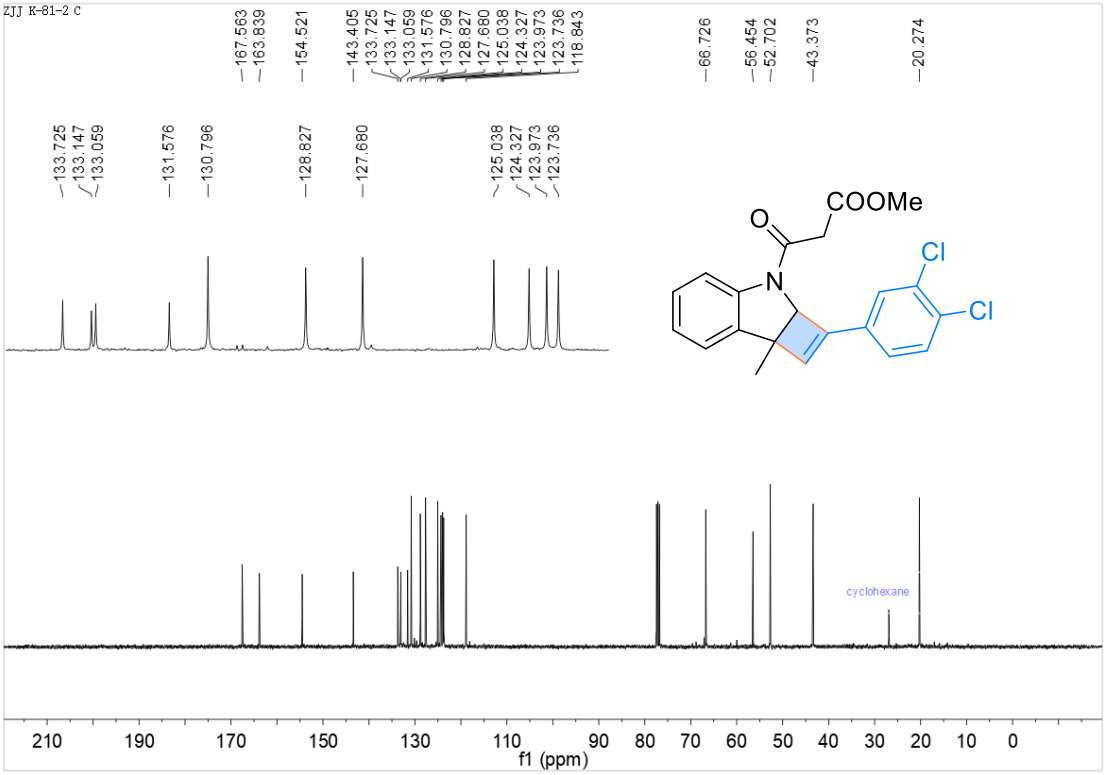
3e2 DEPT 90 and DEPT 135



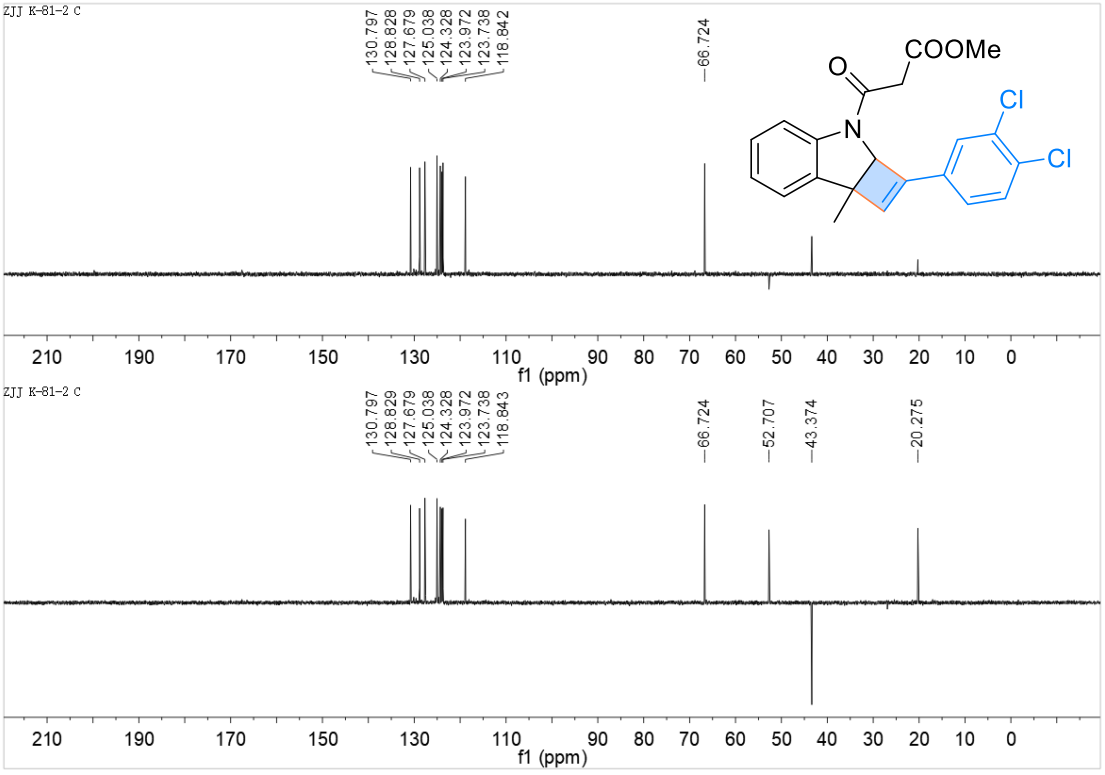
3f ^{1}H NMR



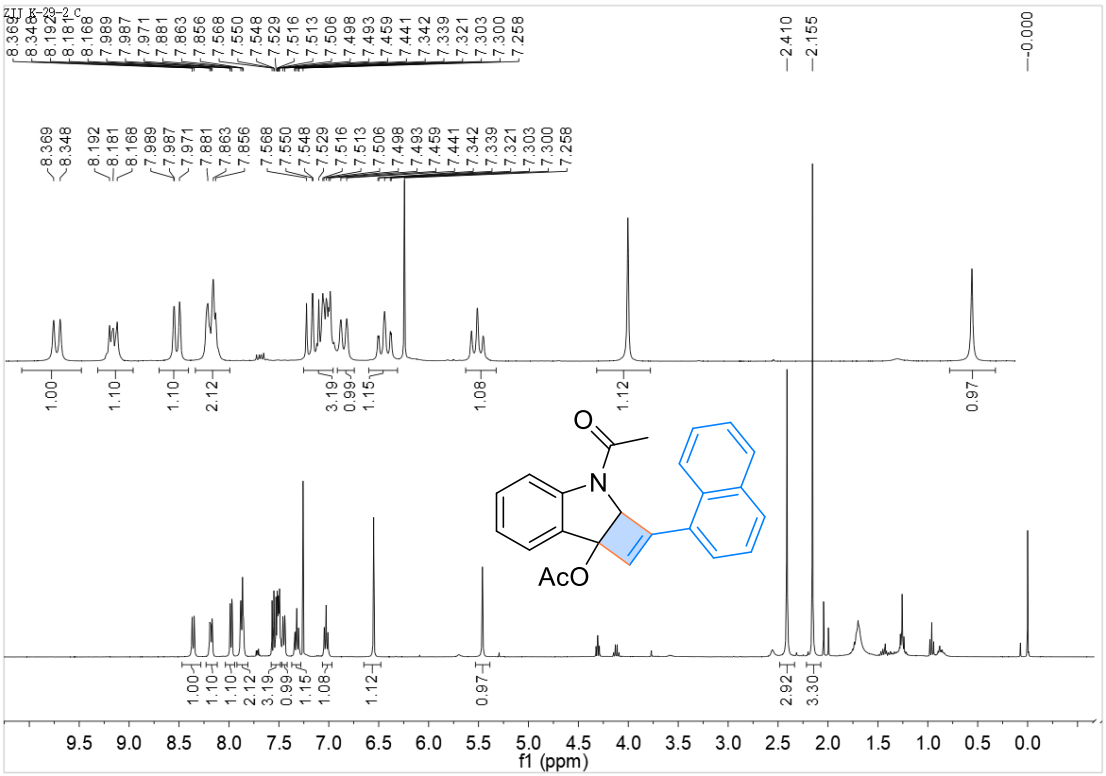
3f ^{13}C NMR



3f DEPT 90 and DEPT 135



3g ^{1}H NMR



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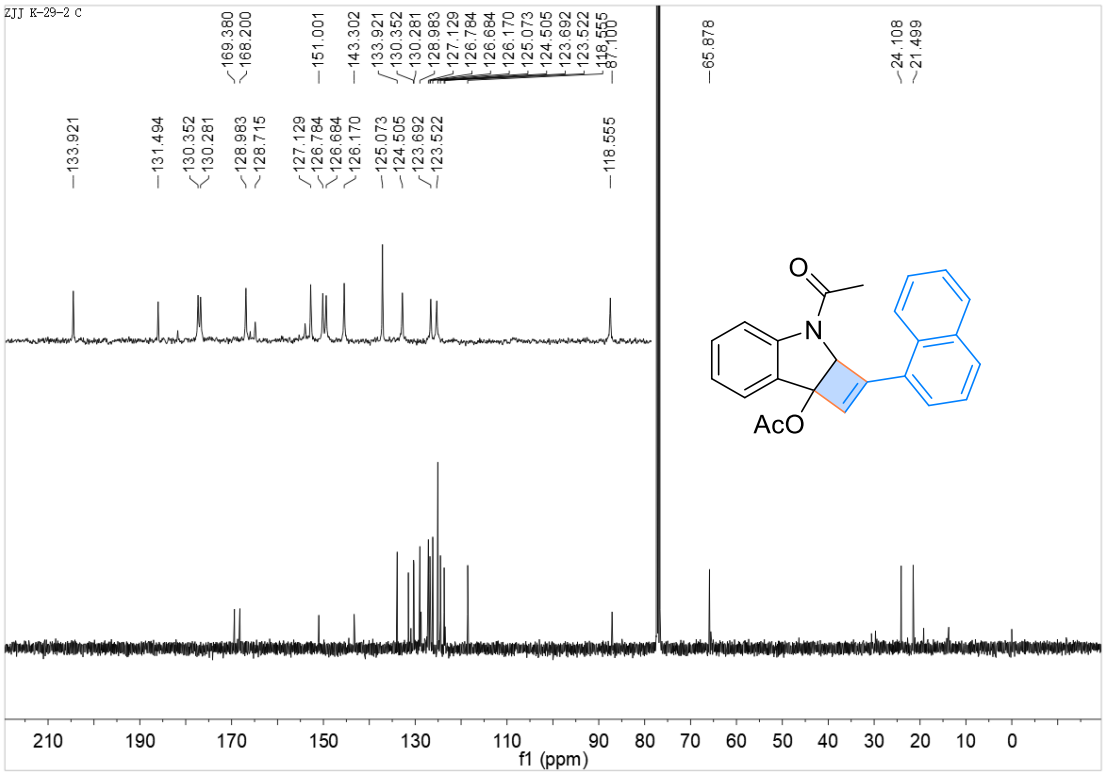
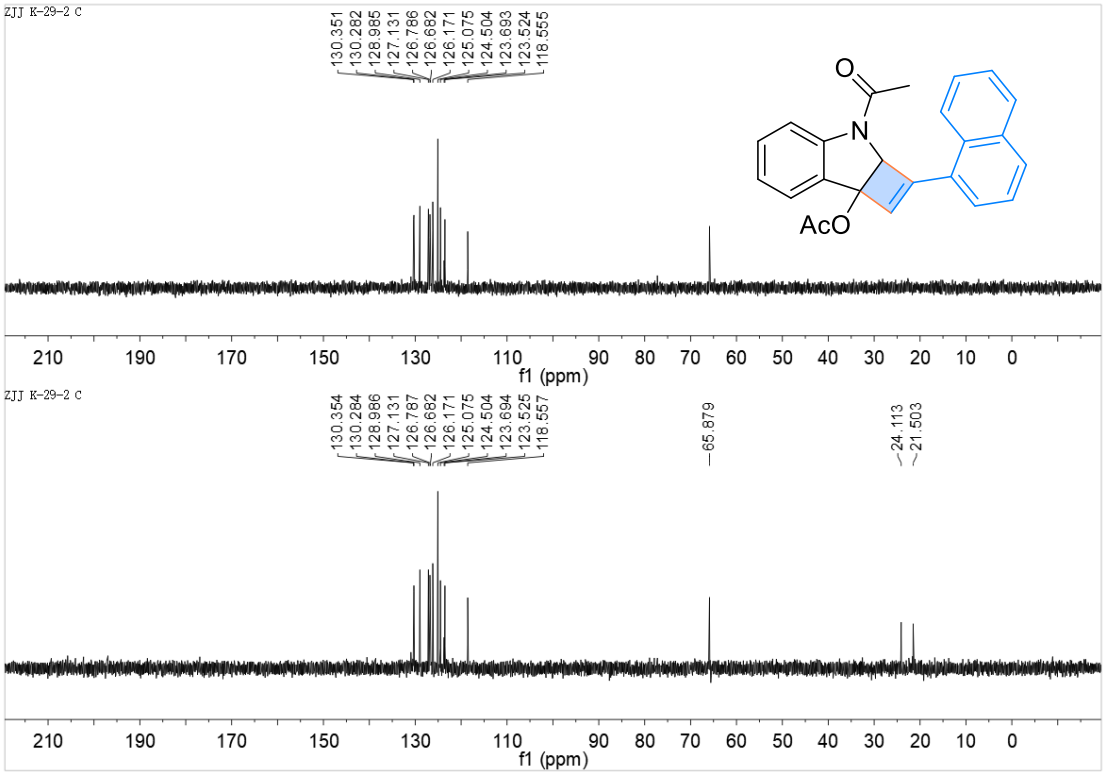
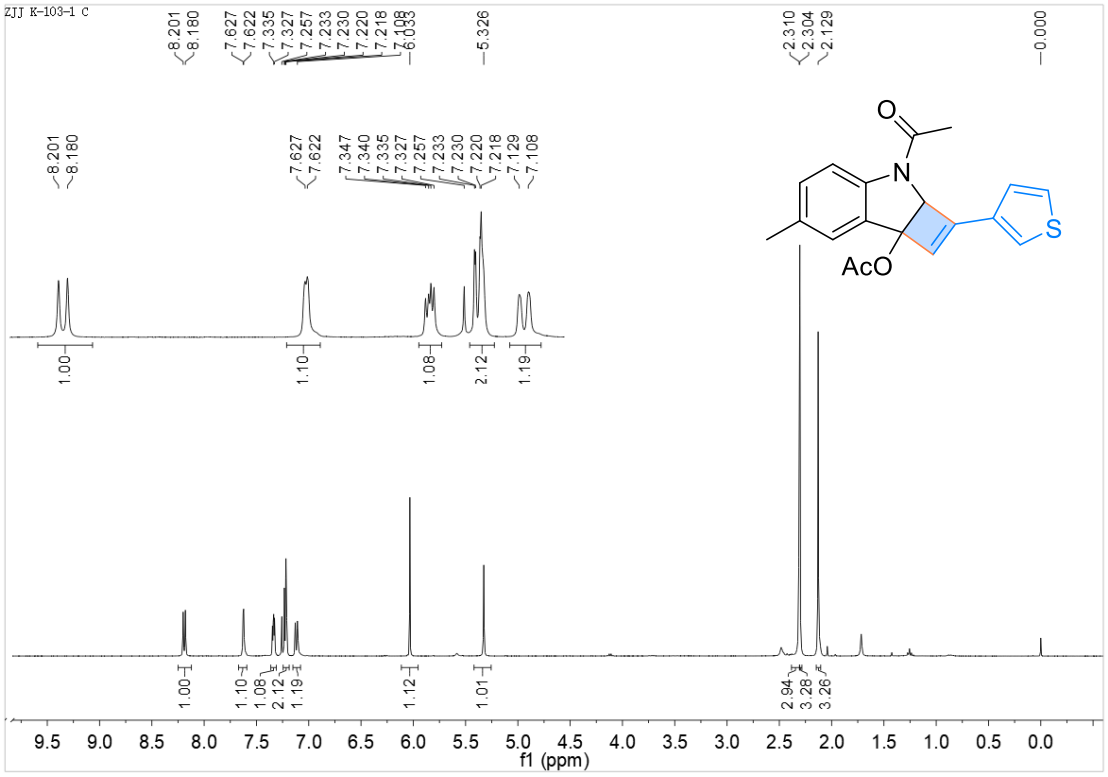


3g DEPT 90 and DEPT 135



3h ^{1}H NMR



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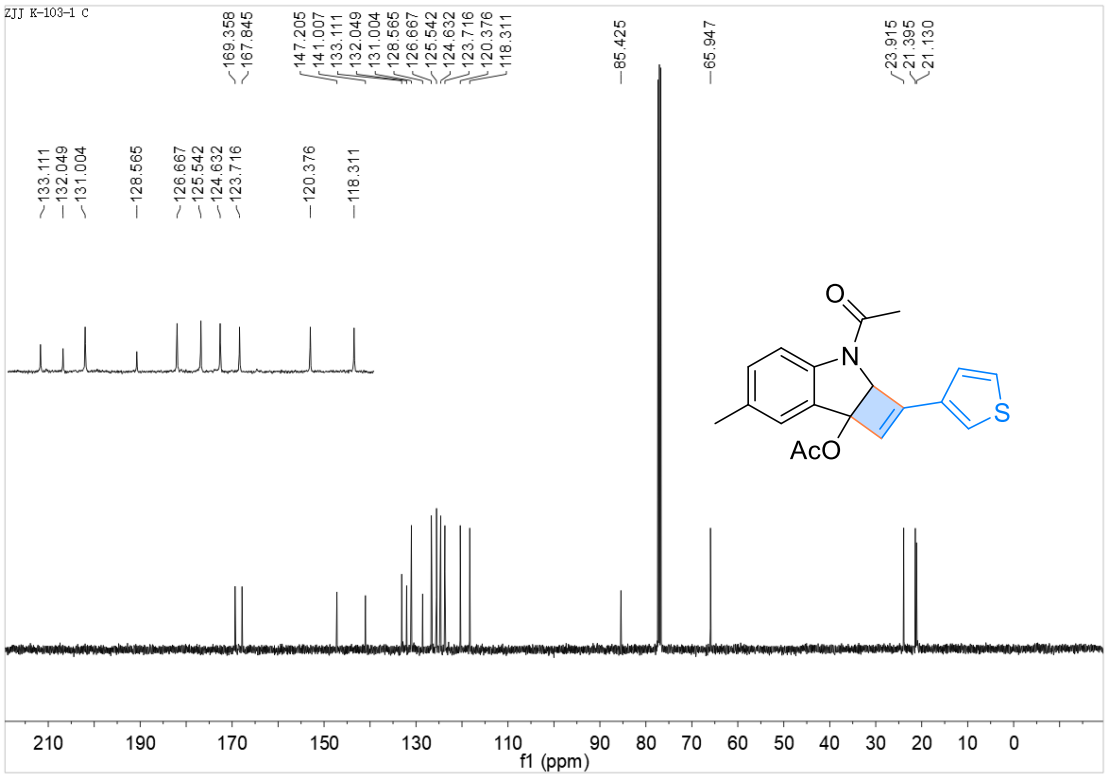
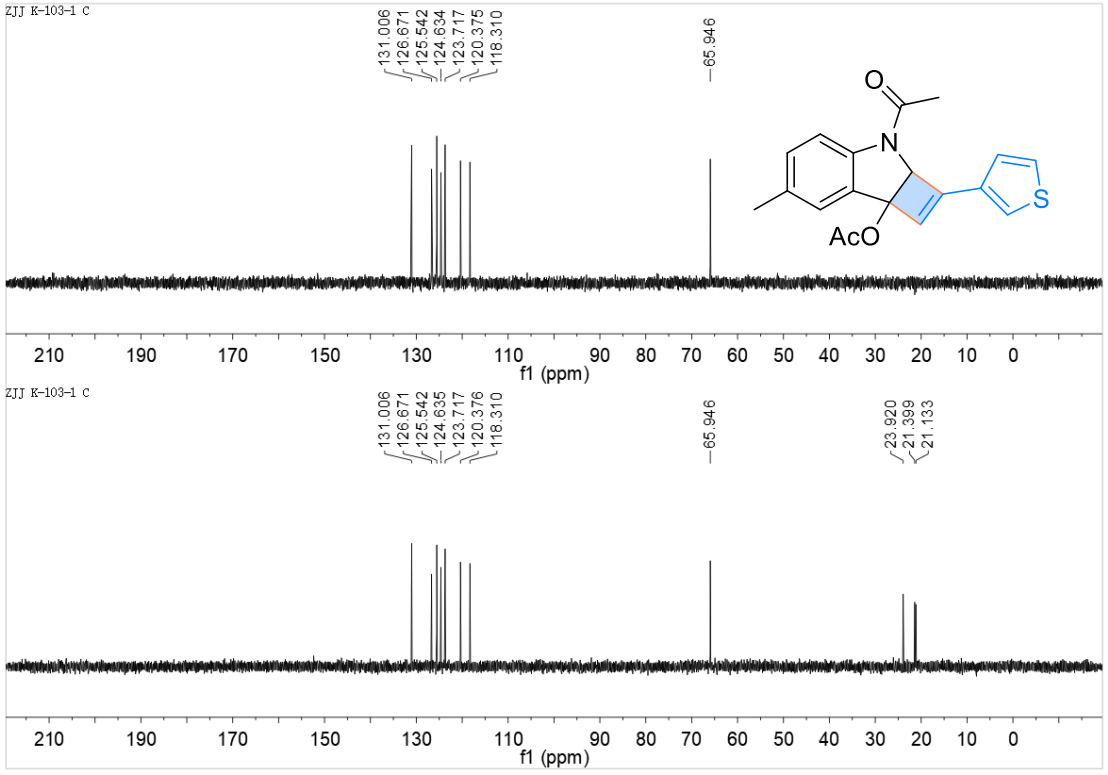
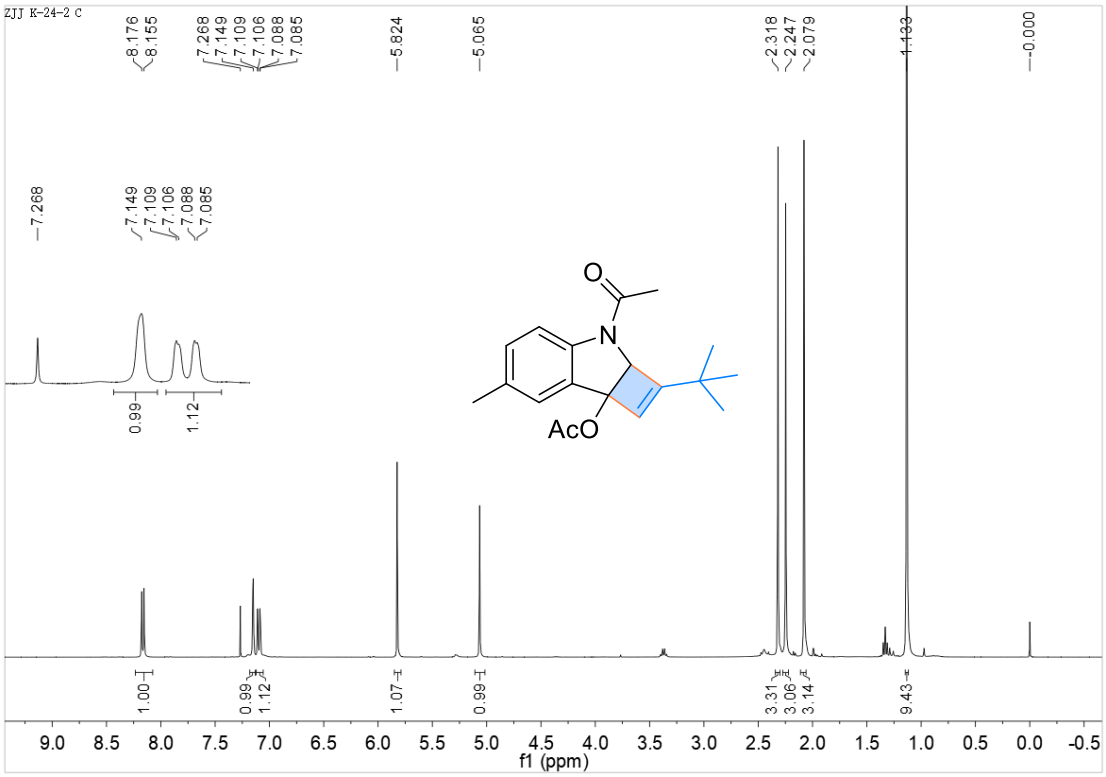


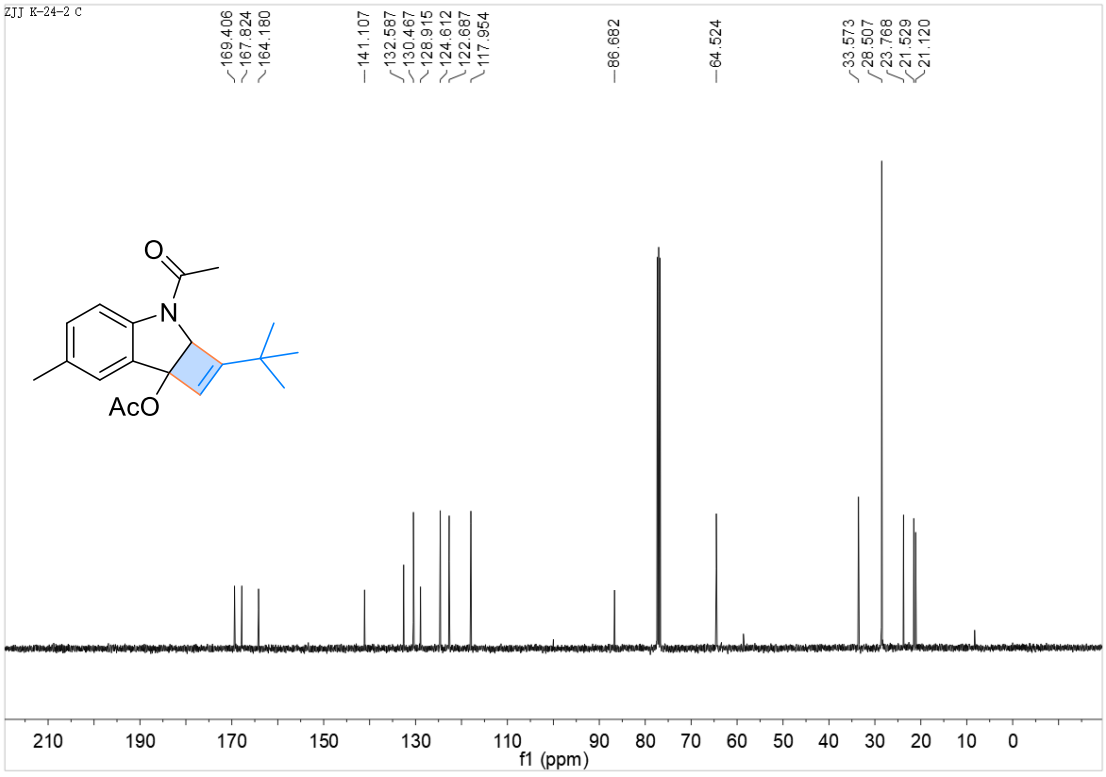
3h DEPT 90 and DEPT 135



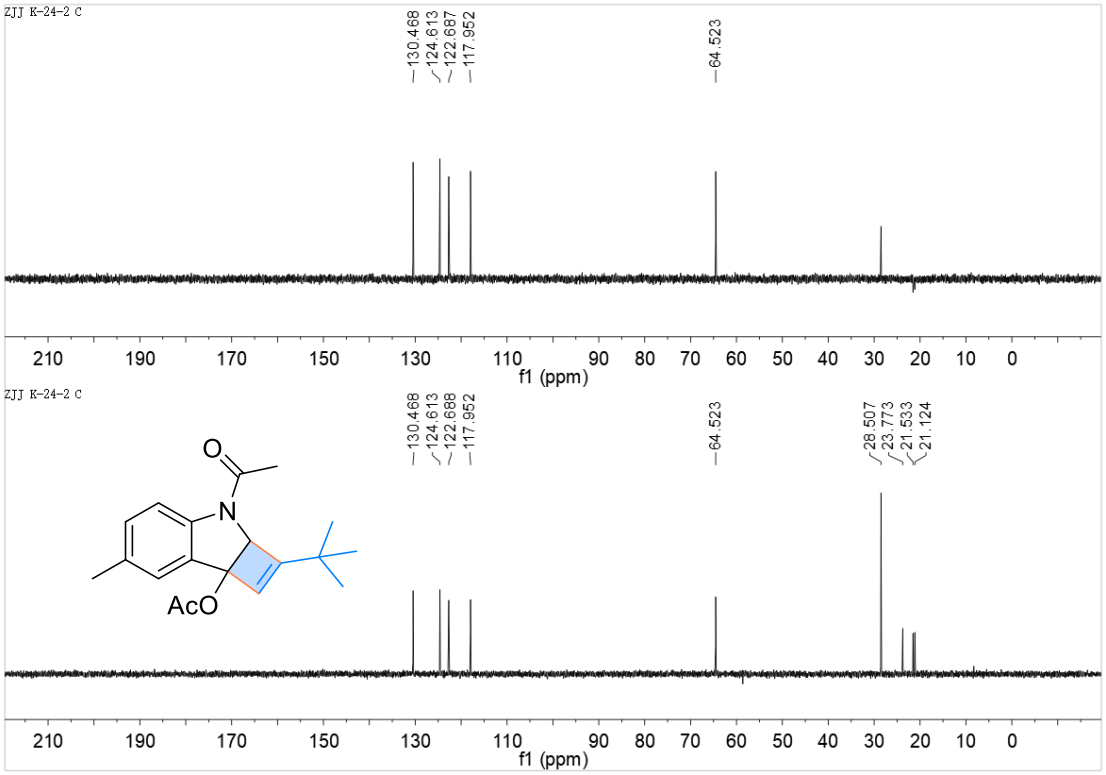
3i ^{1}H NMR



3i ^{13}C NMR



3i DEPT 90 and DEPT 135



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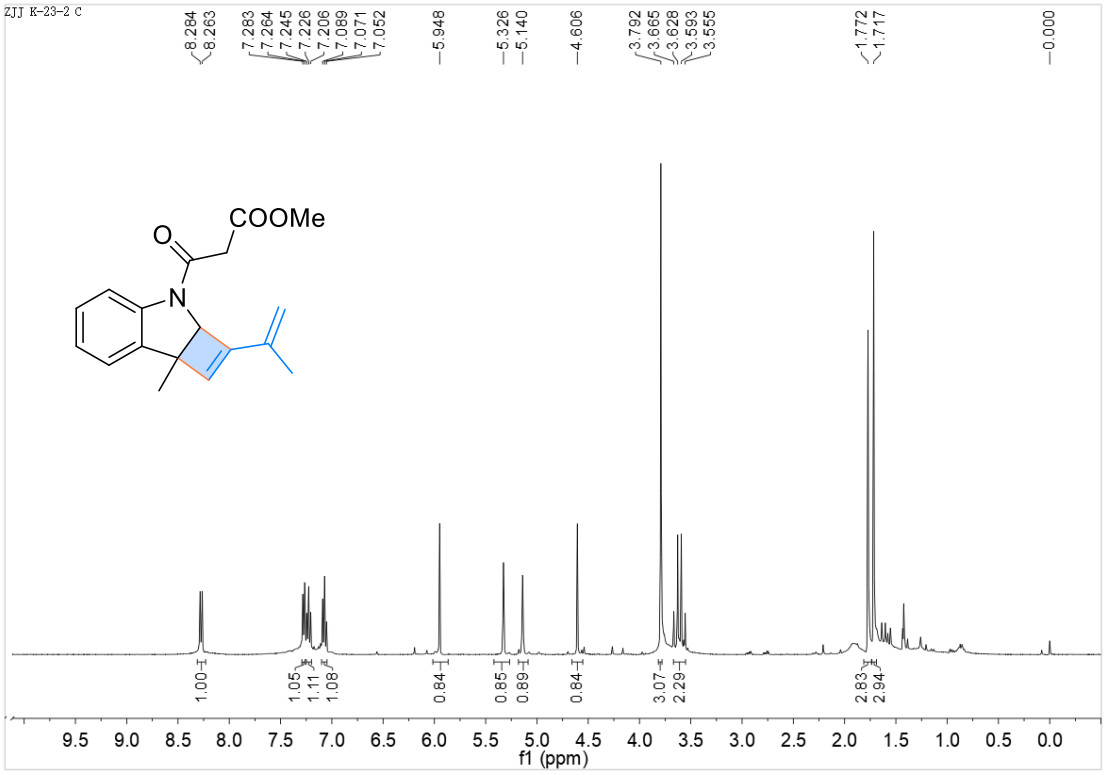

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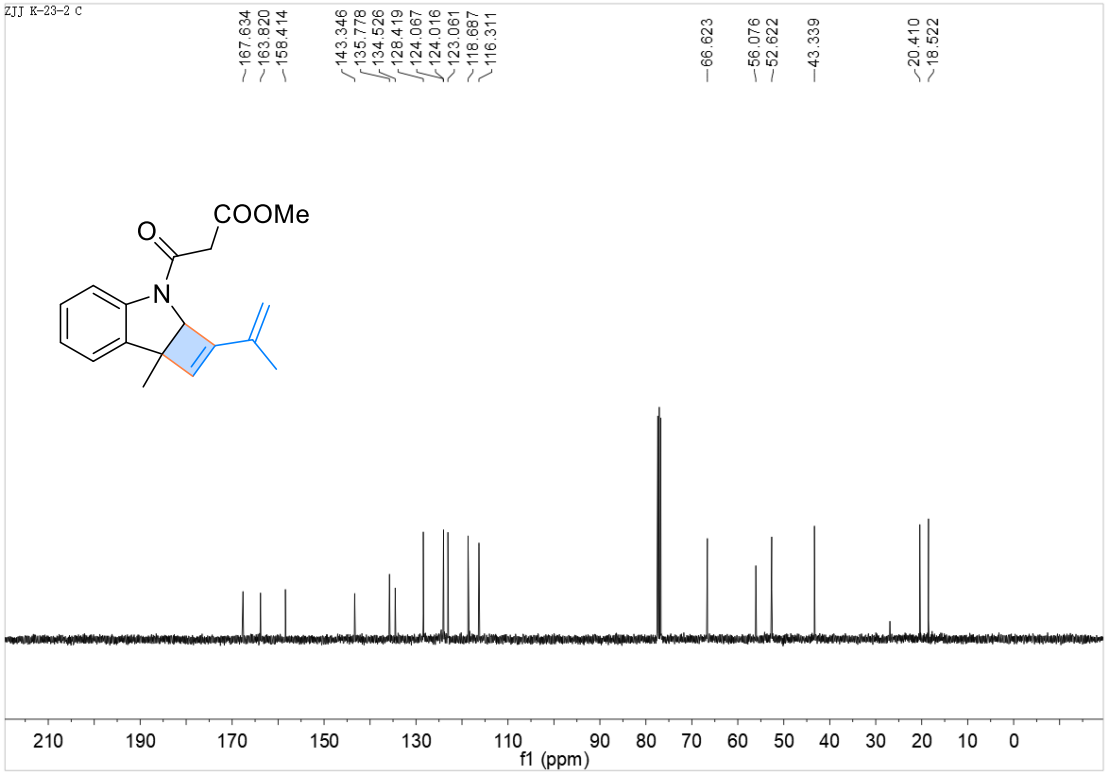

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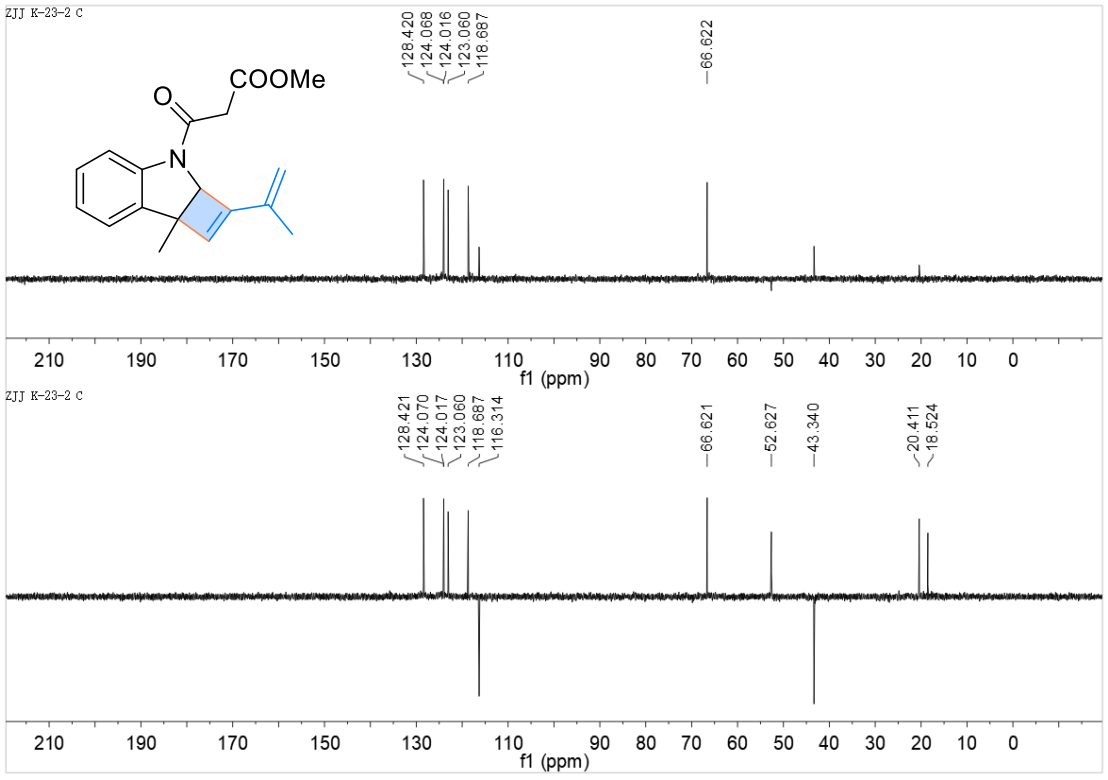

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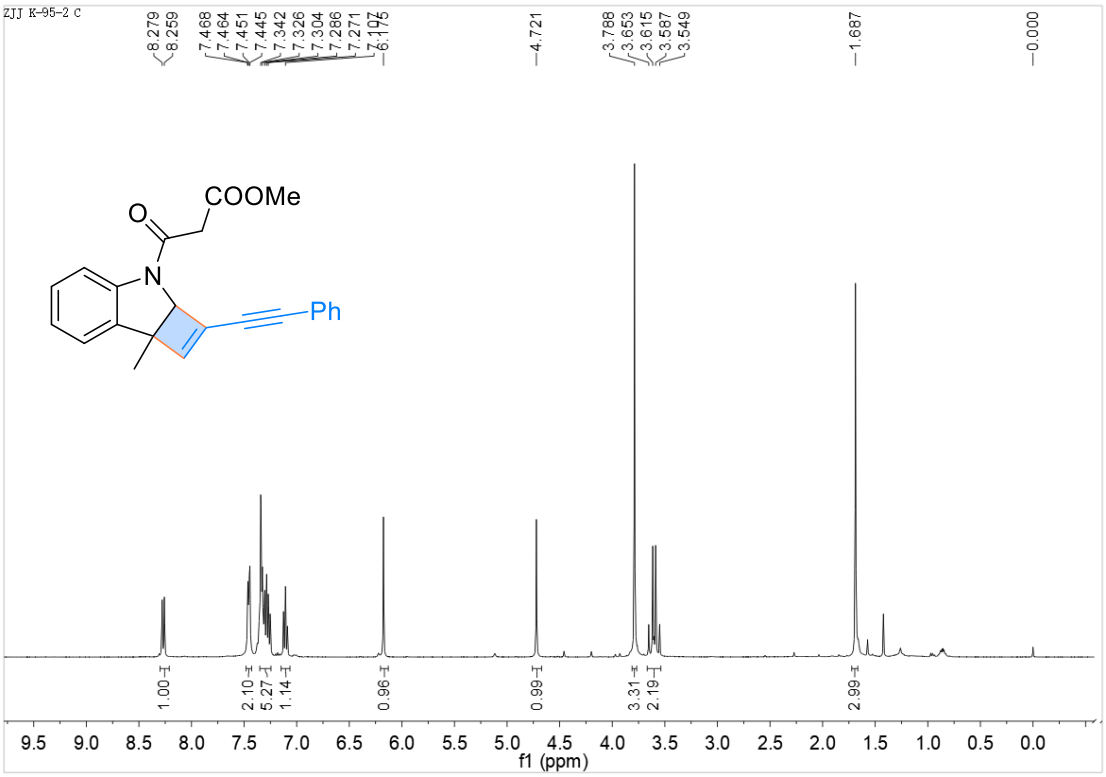
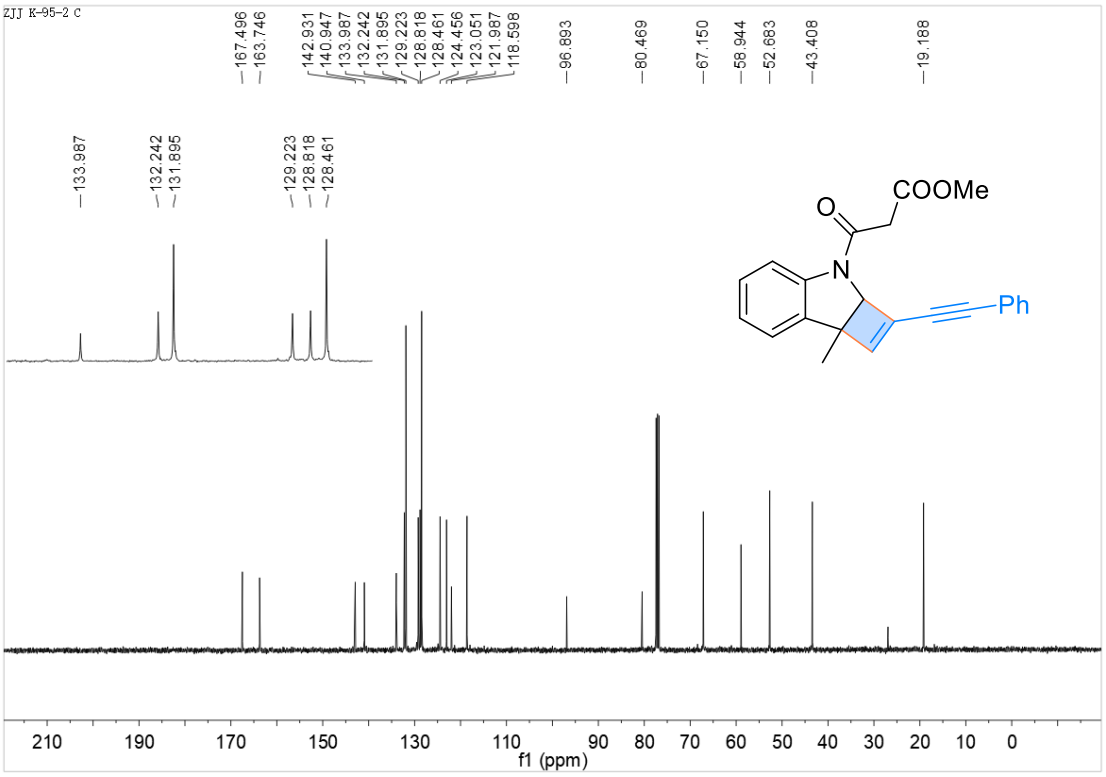
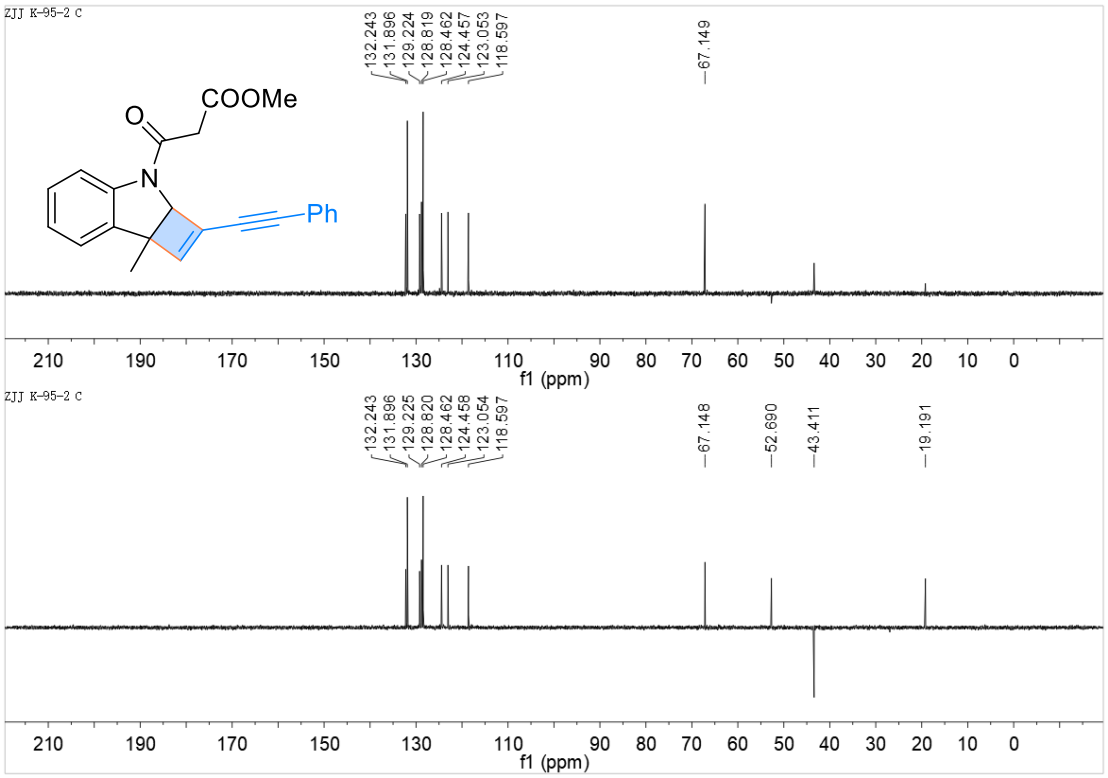


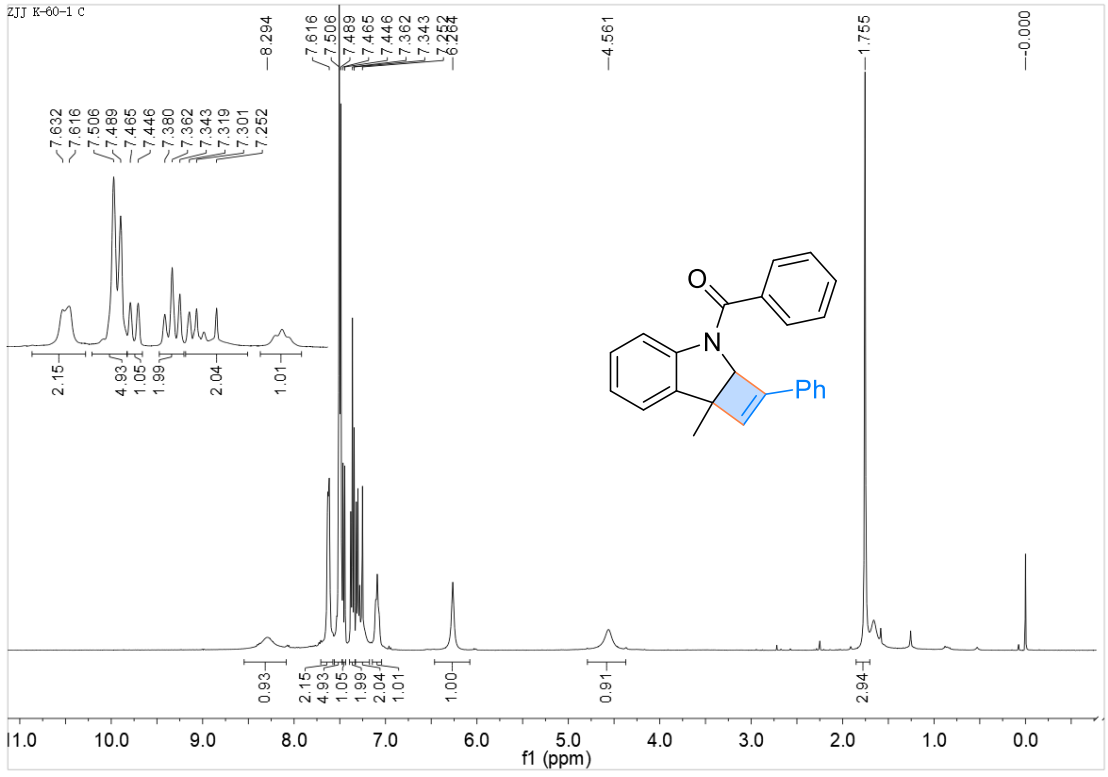
3k ^{13}C NMR



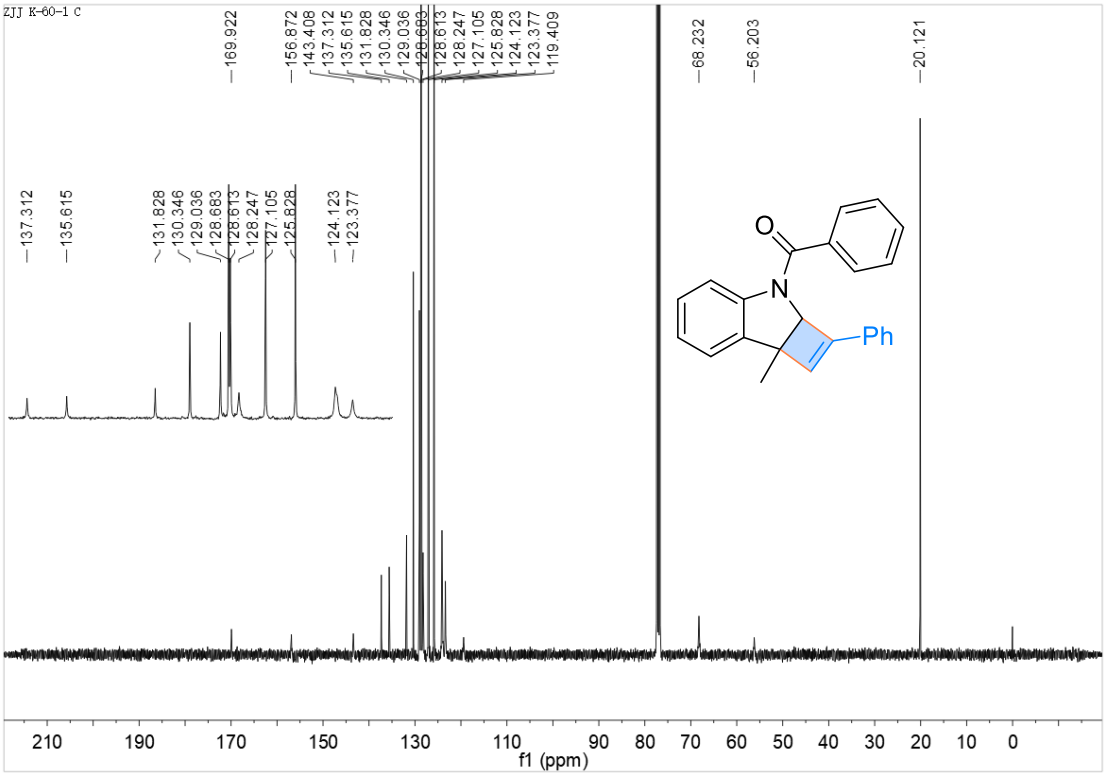
3k DEPT 90 and DEPT 135



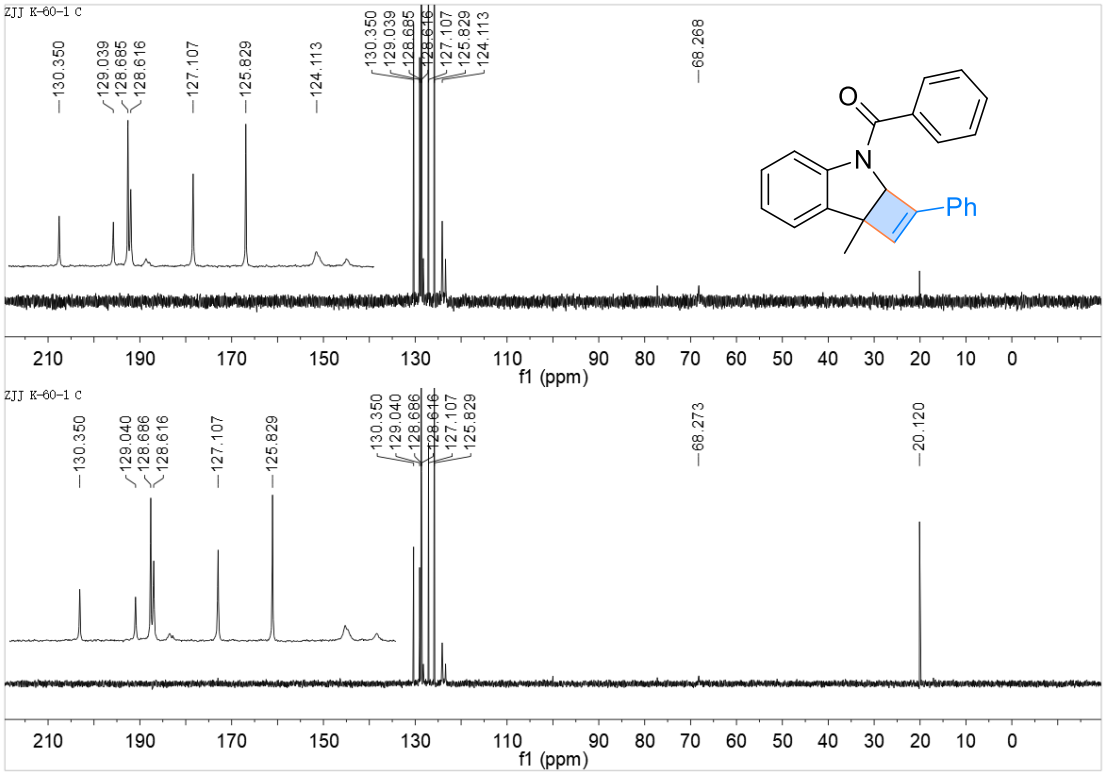
3l1 ^{1}H NMR



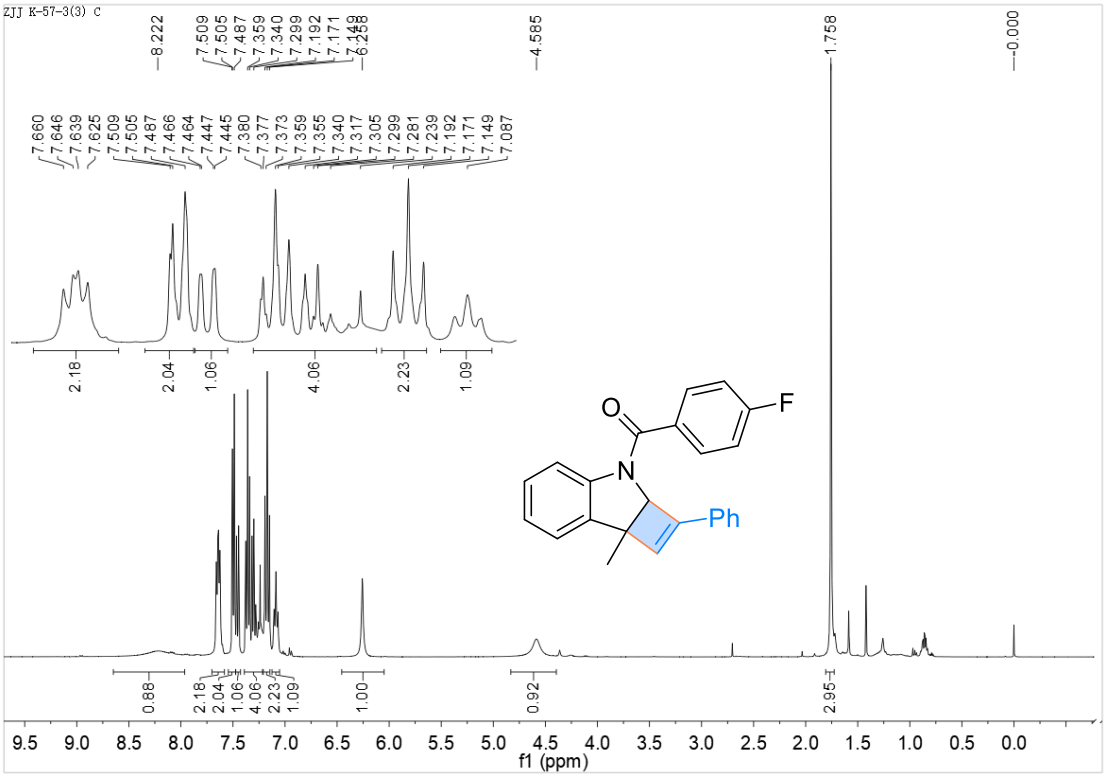
3l1 ^{13}C NMR



3l1 DEPT 90 and DEPT 135



3l2 ^{1}H NMR



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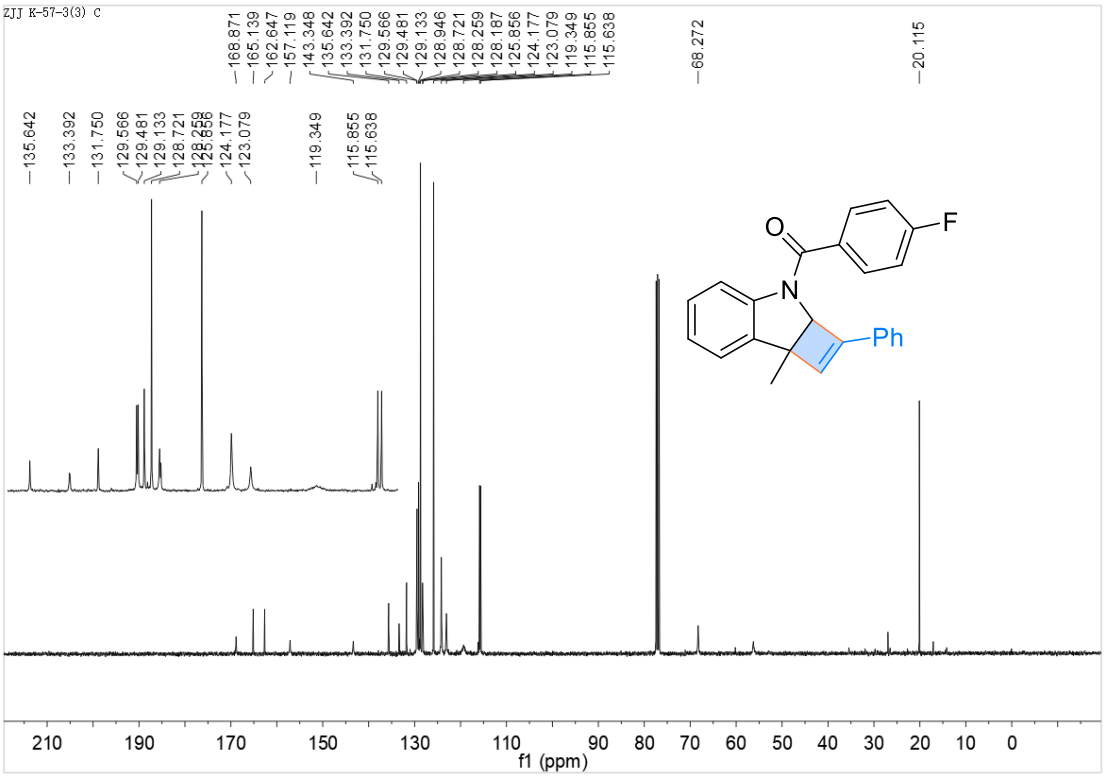

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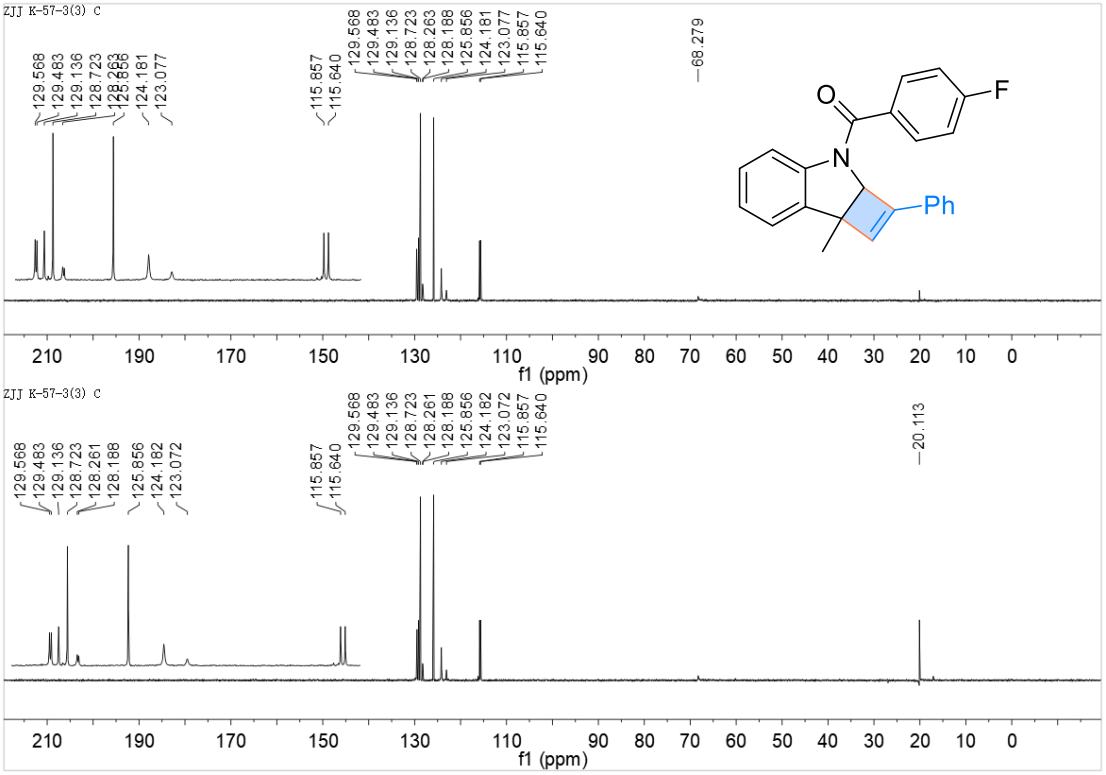
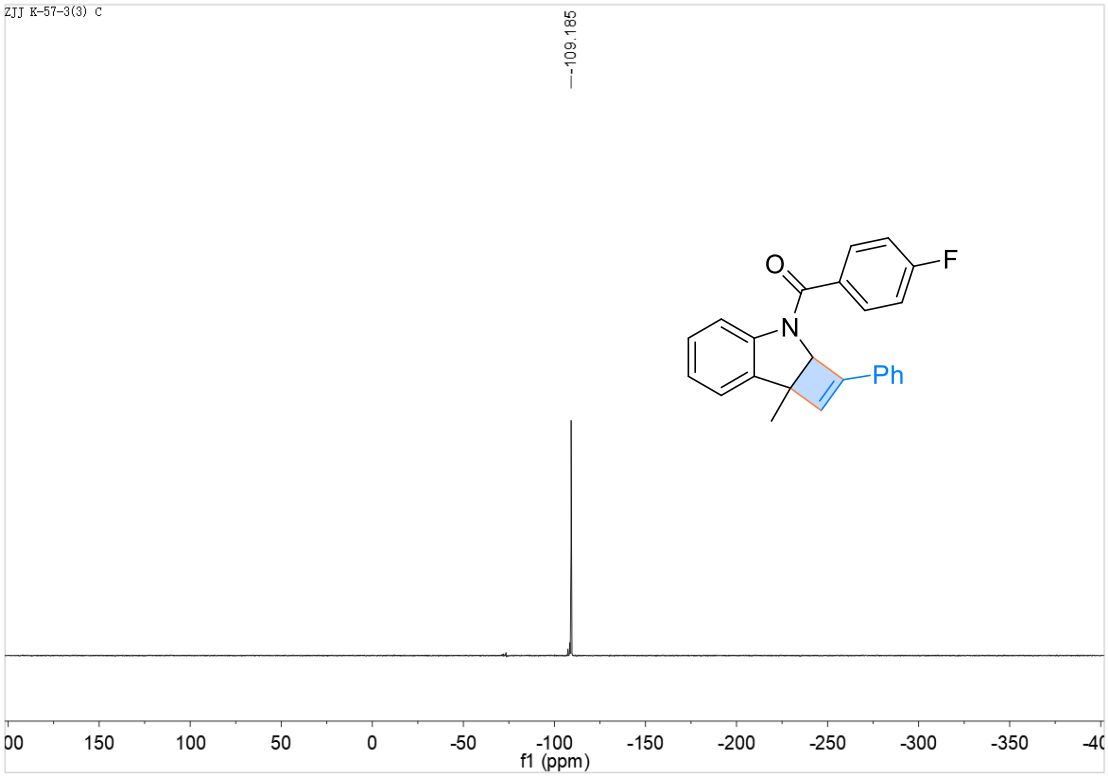
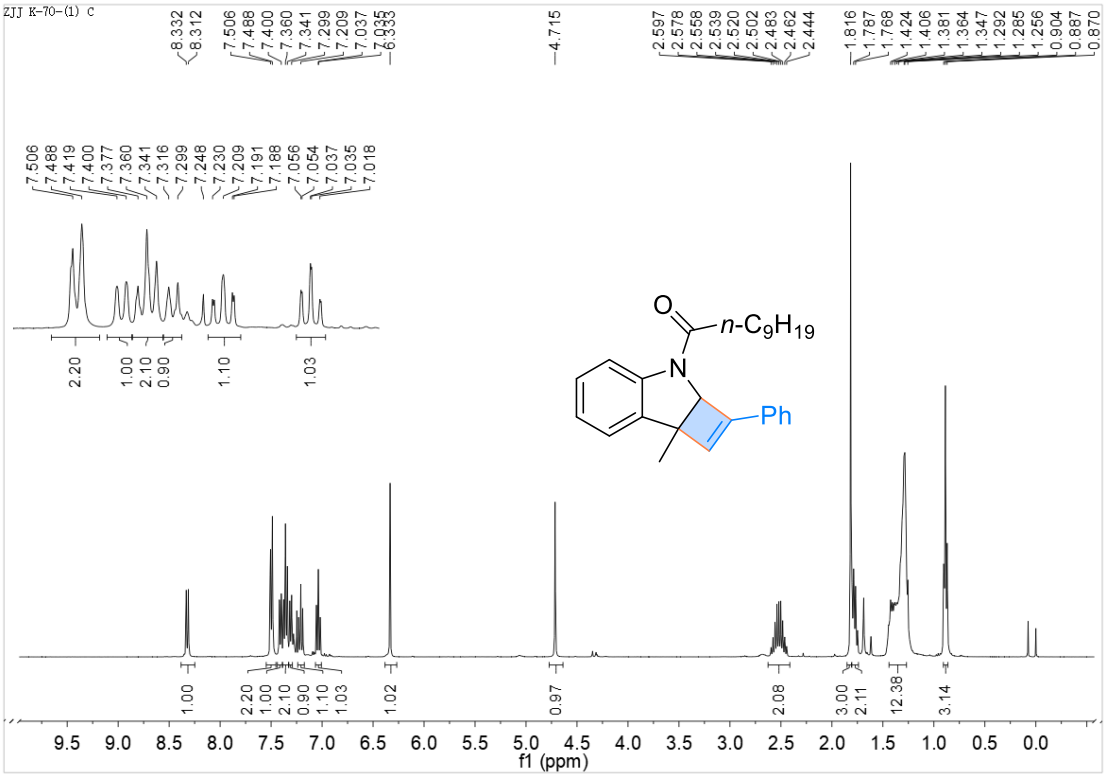


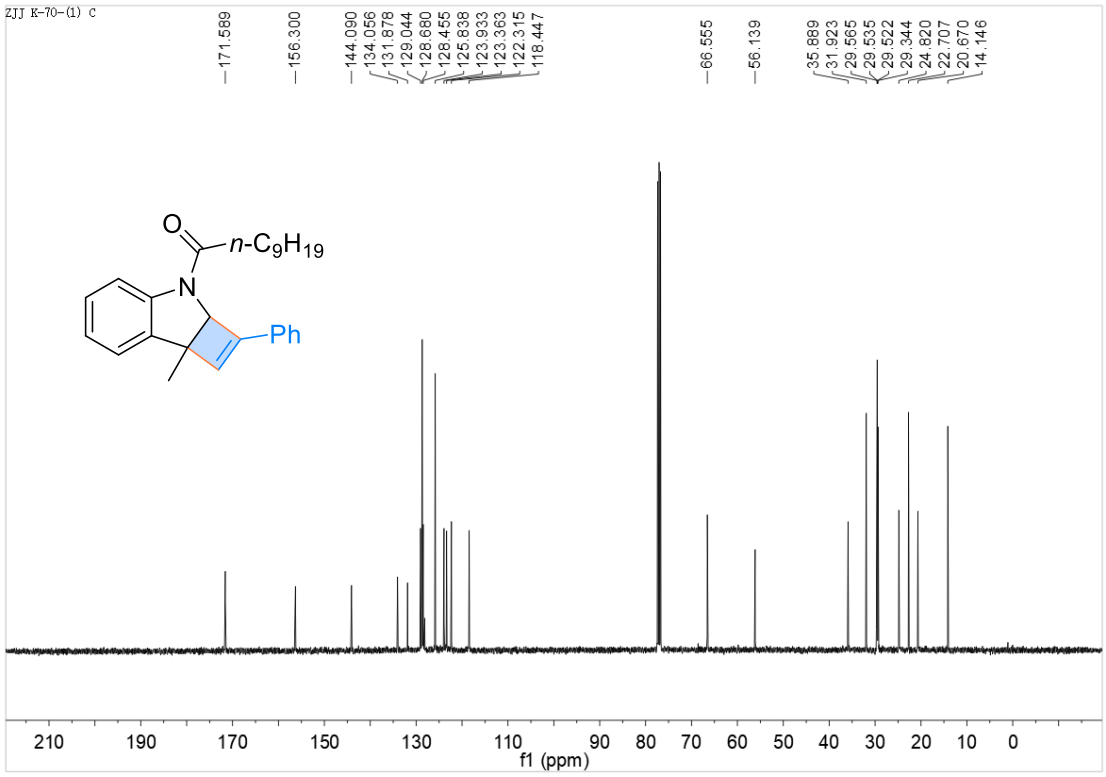
3l2 ^{19}F NMR



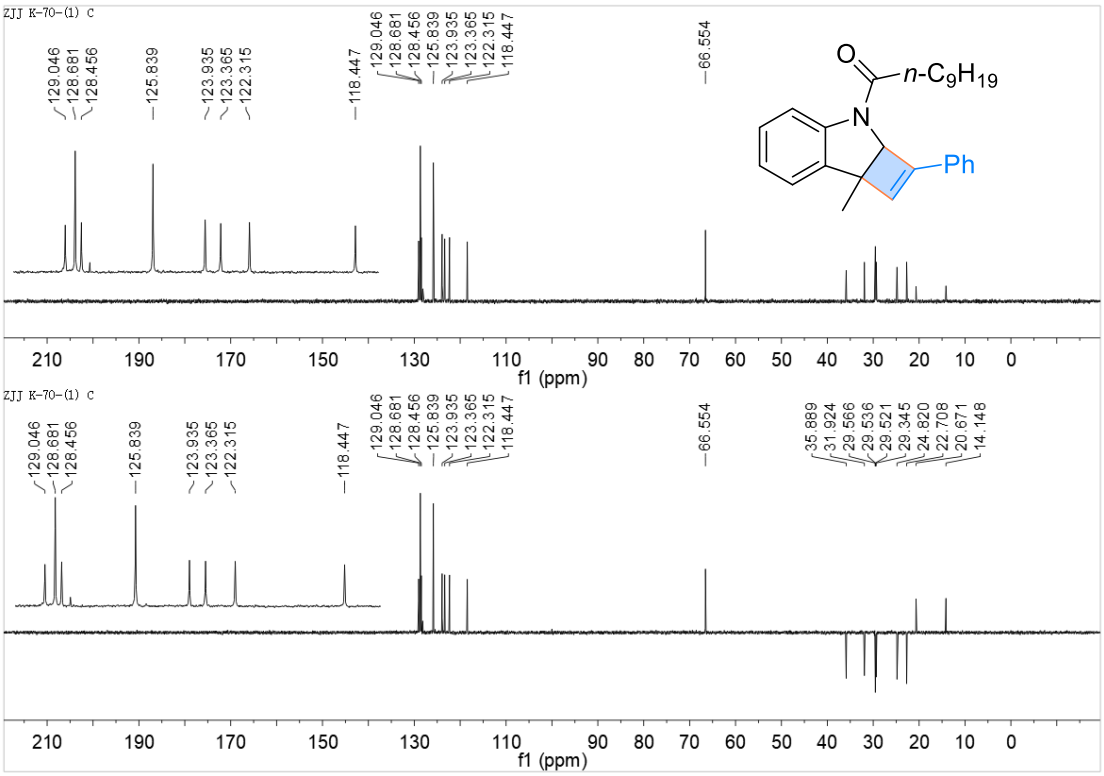
3m1 ^{1}H NMR



3m1 ^{13}C NMR



3m1 DEPT 90 and DEPT 135



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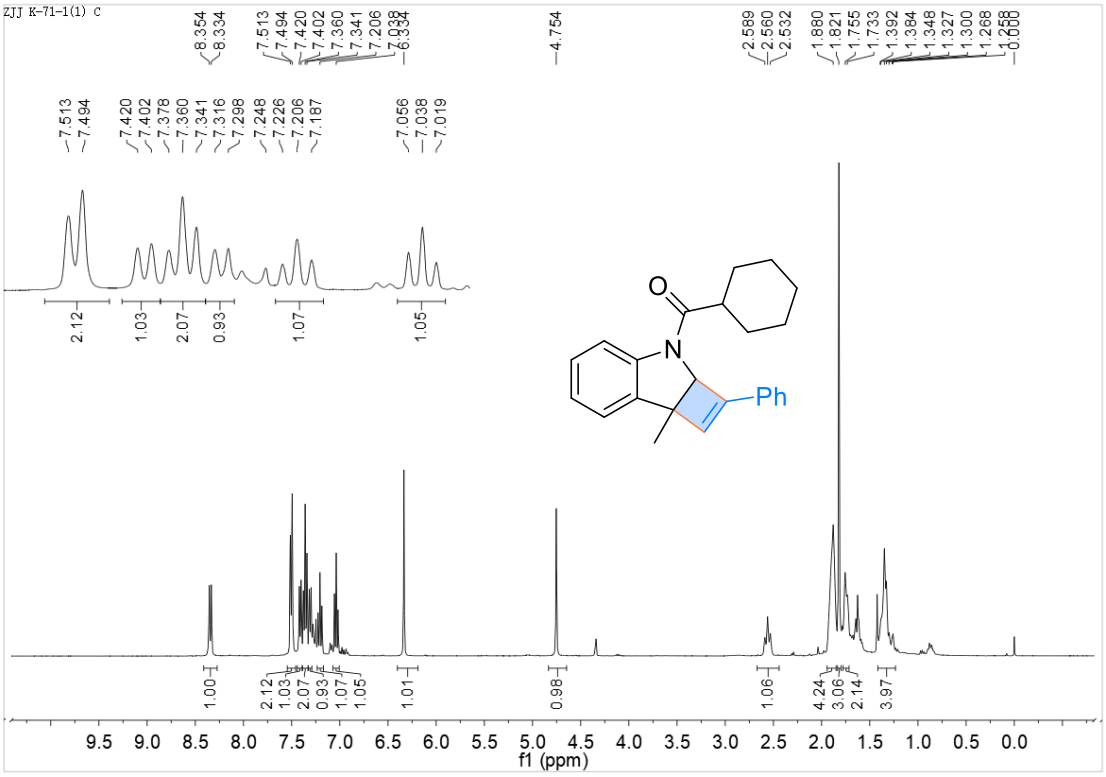

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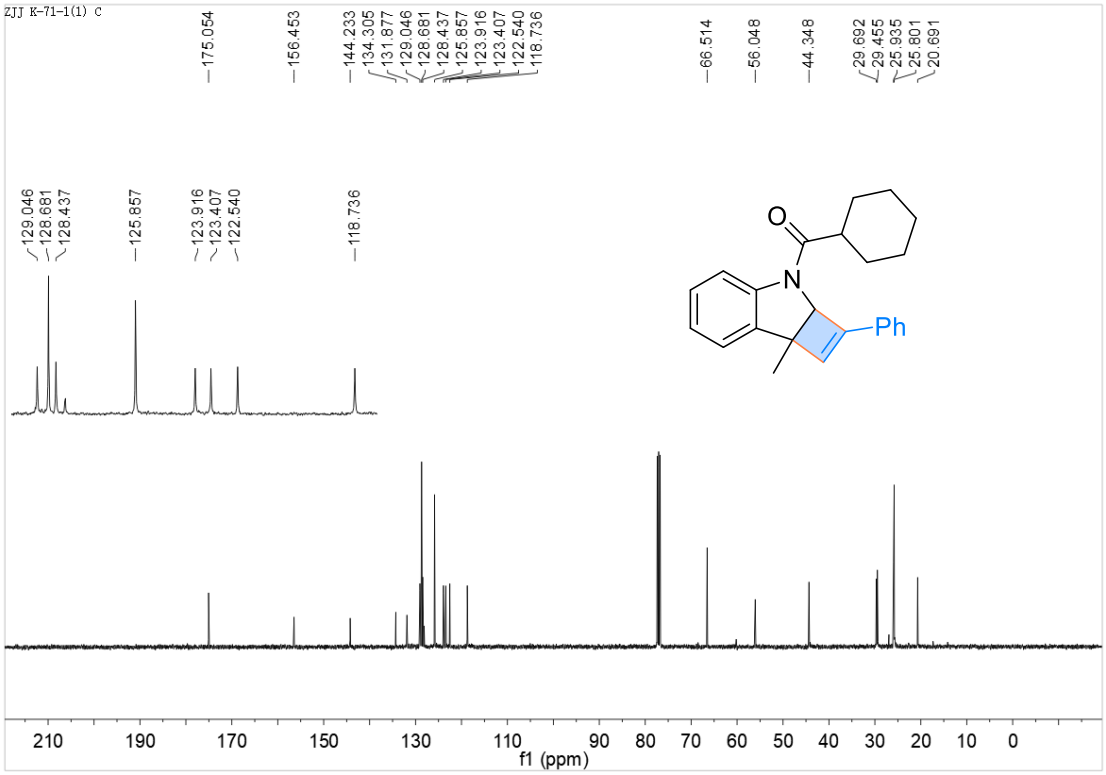
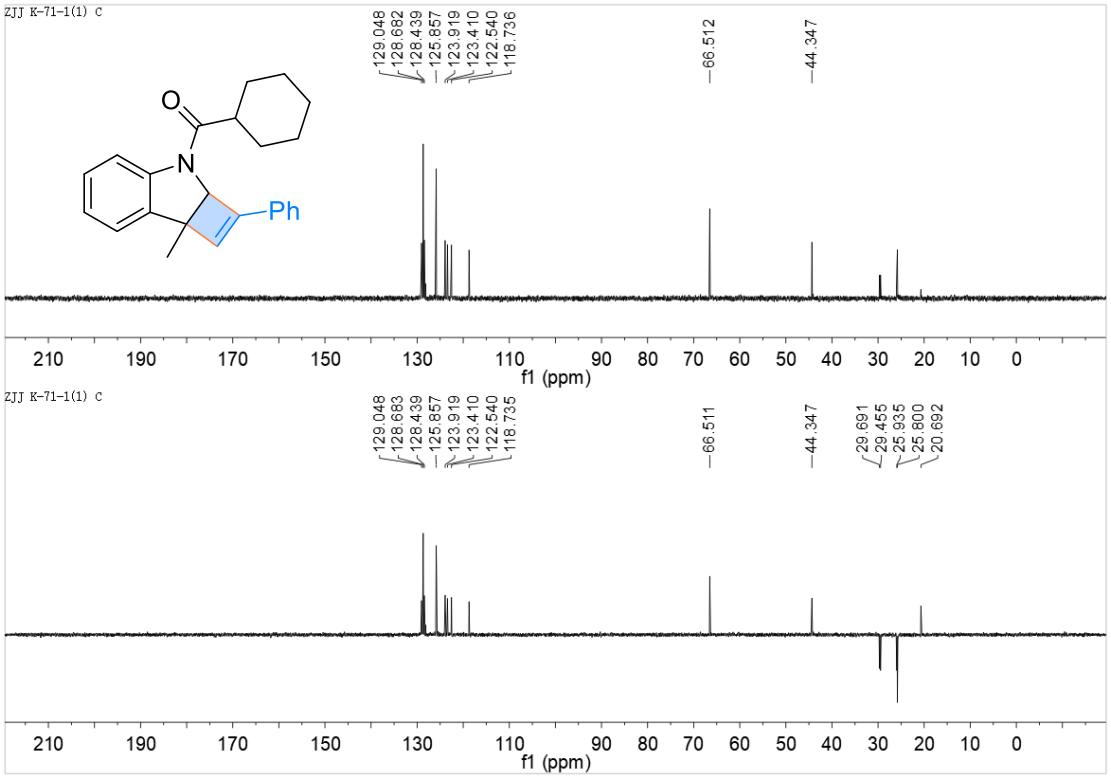
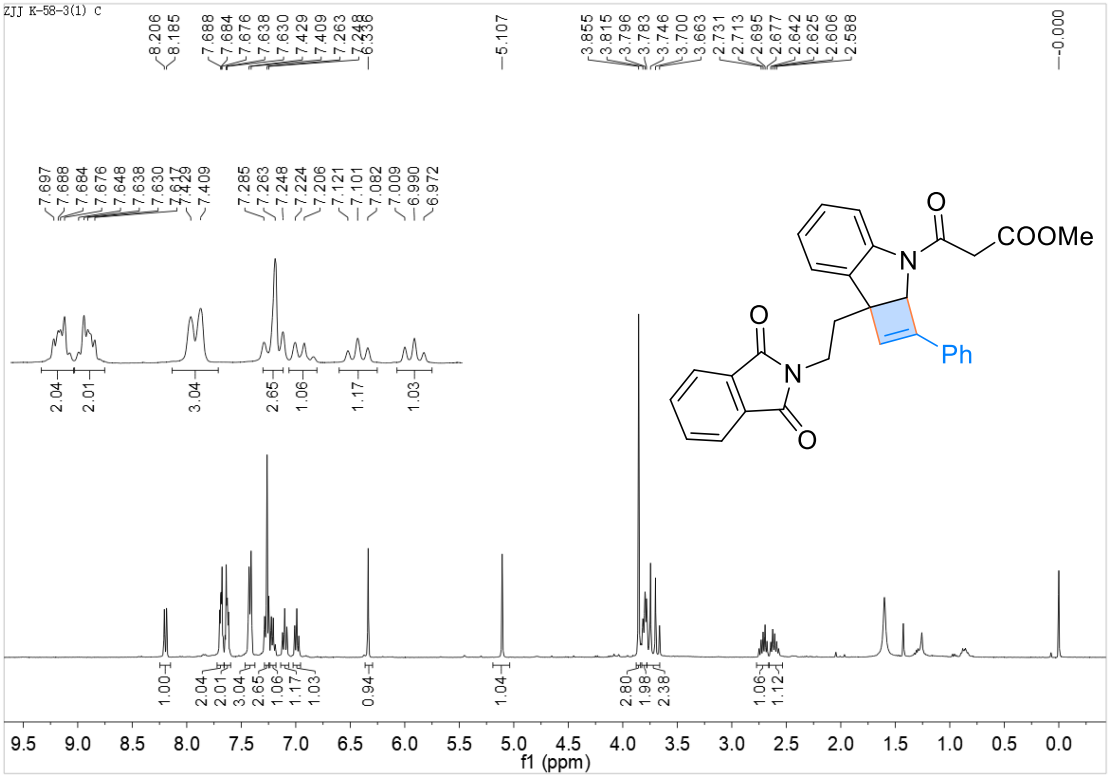


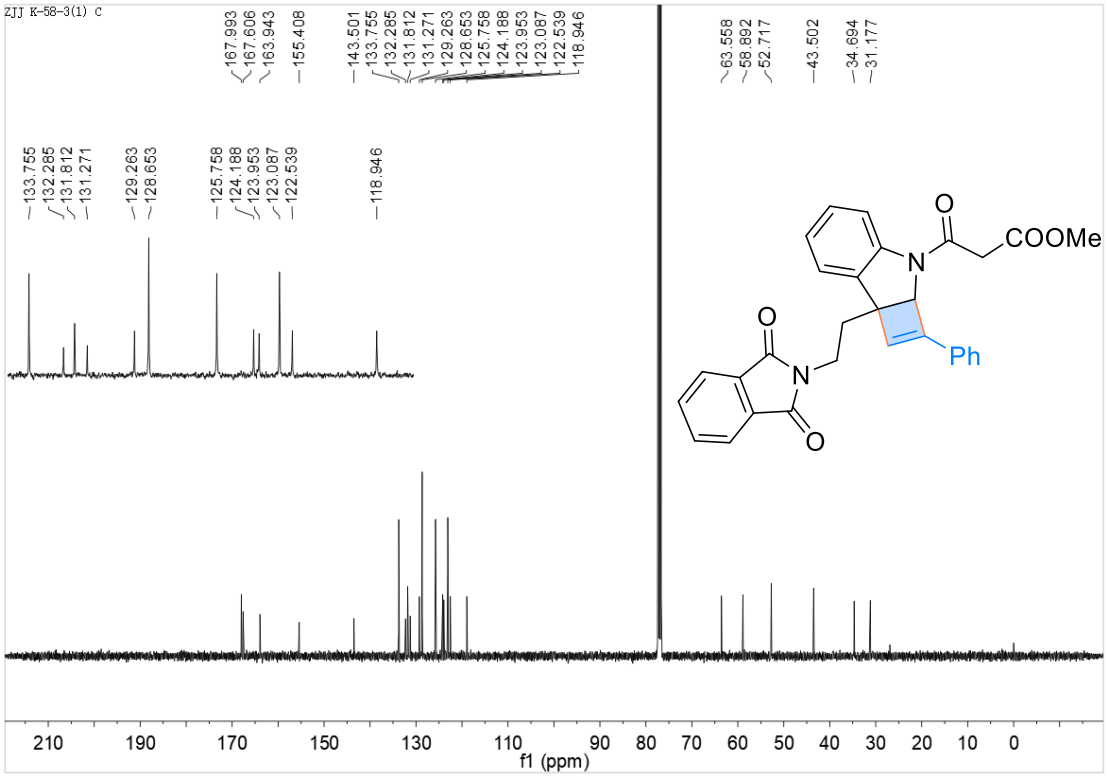
3m2 DEPT 90 and DEPT 135



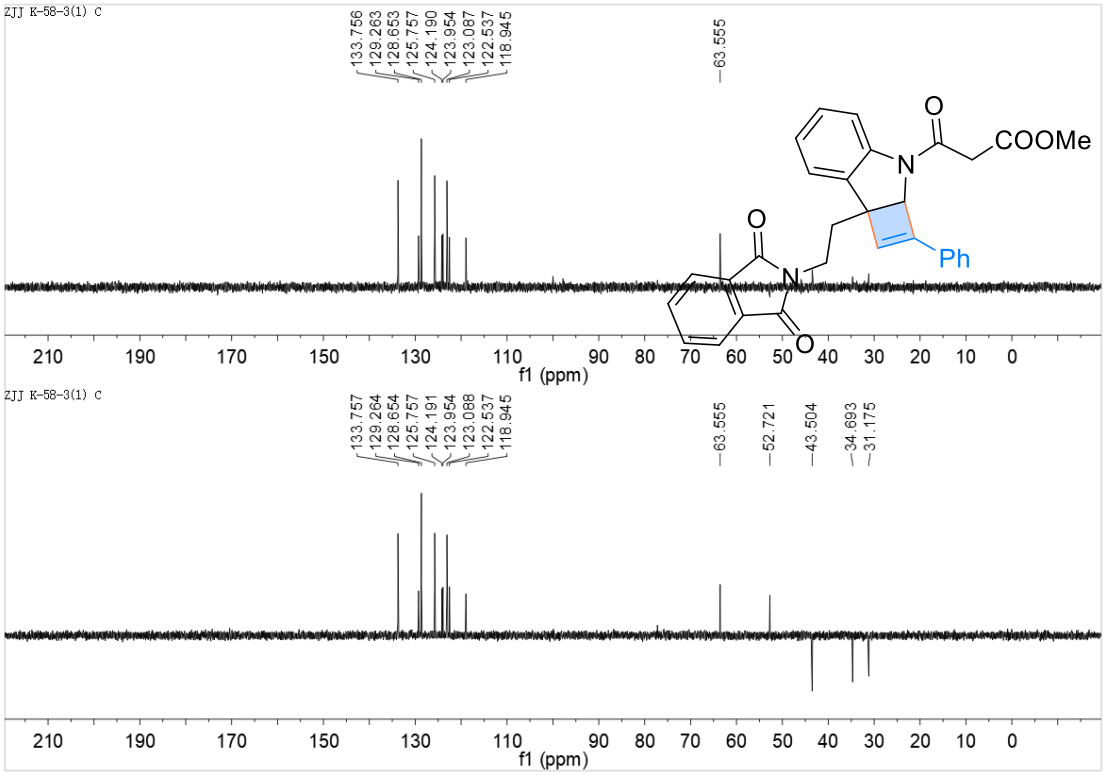
3n ^{1}H NMR



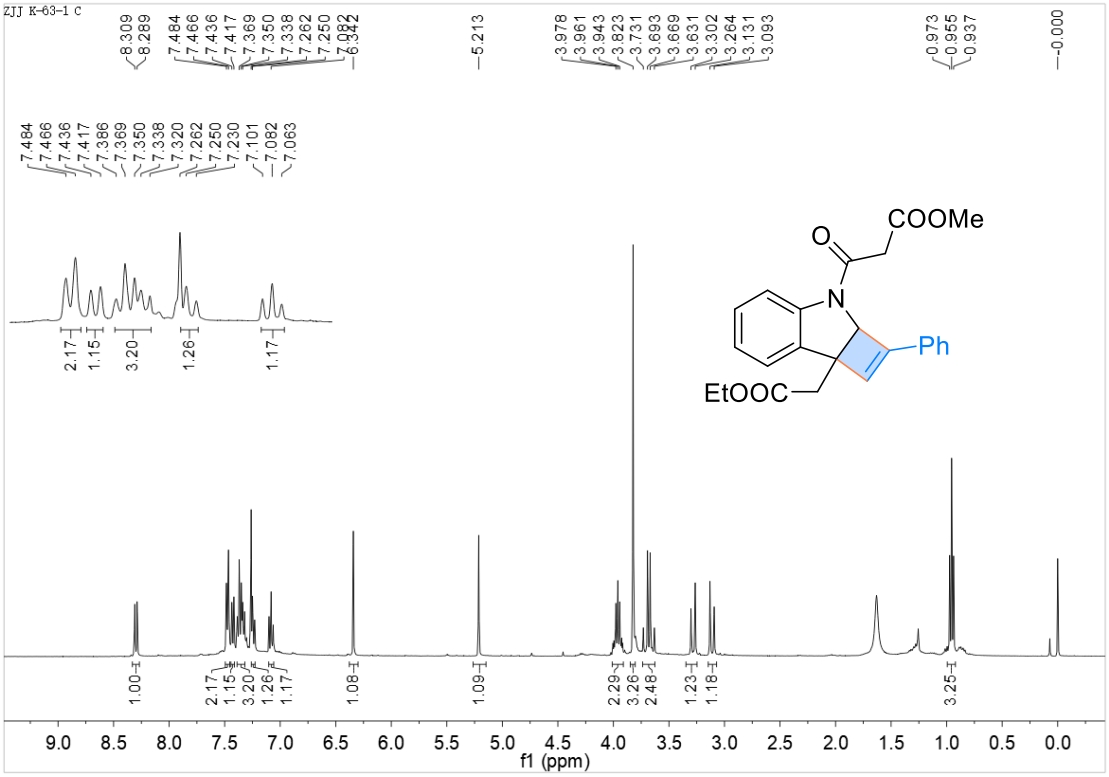
3n ^{13}C NMR



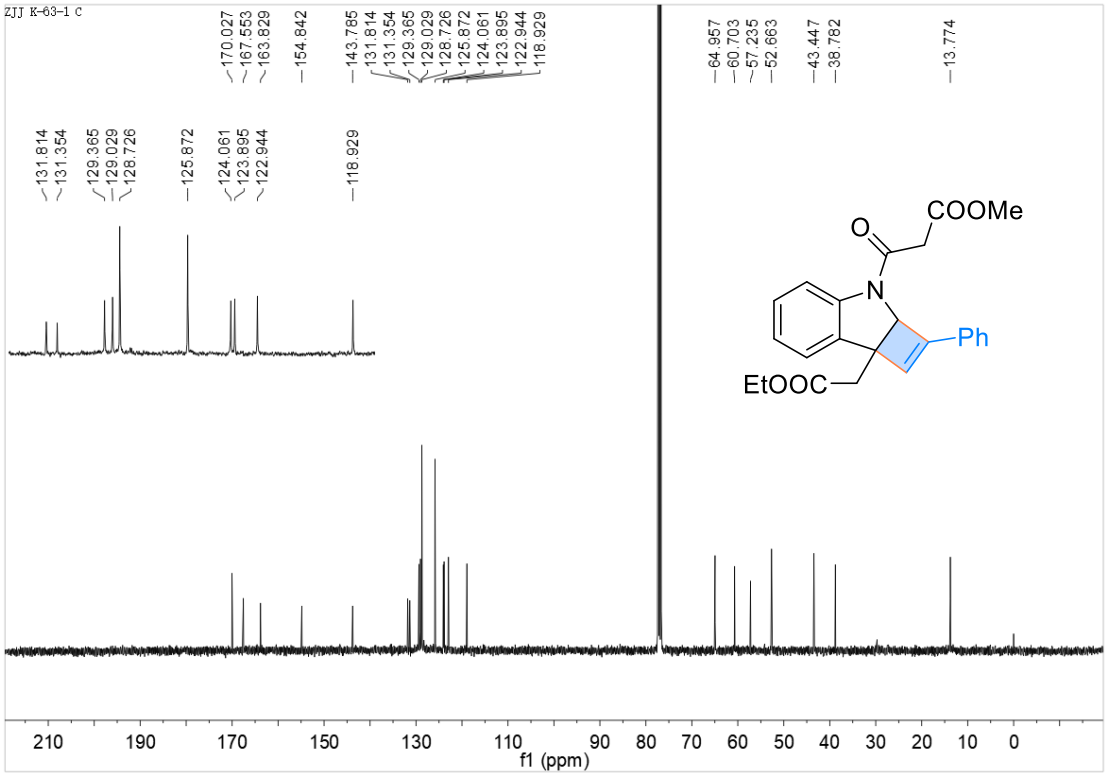
3n DEPT 90 and DEPT 135



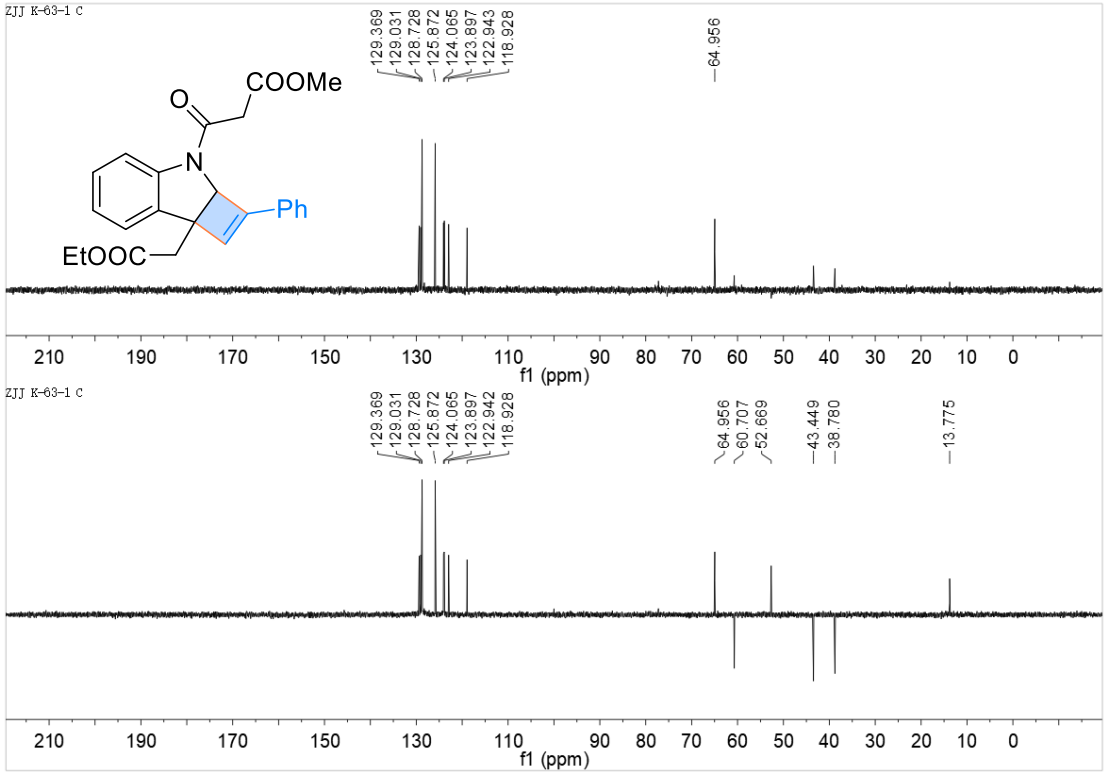
3o ^{1}H NMR



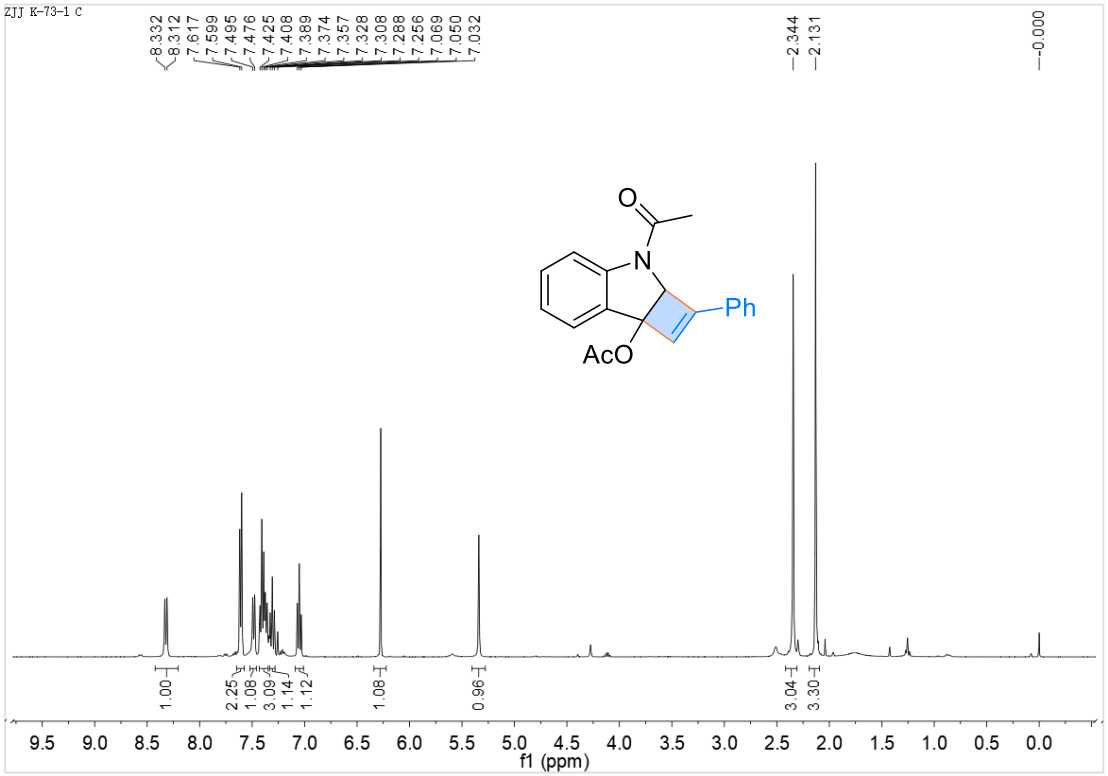
3o ^{13}C NMR



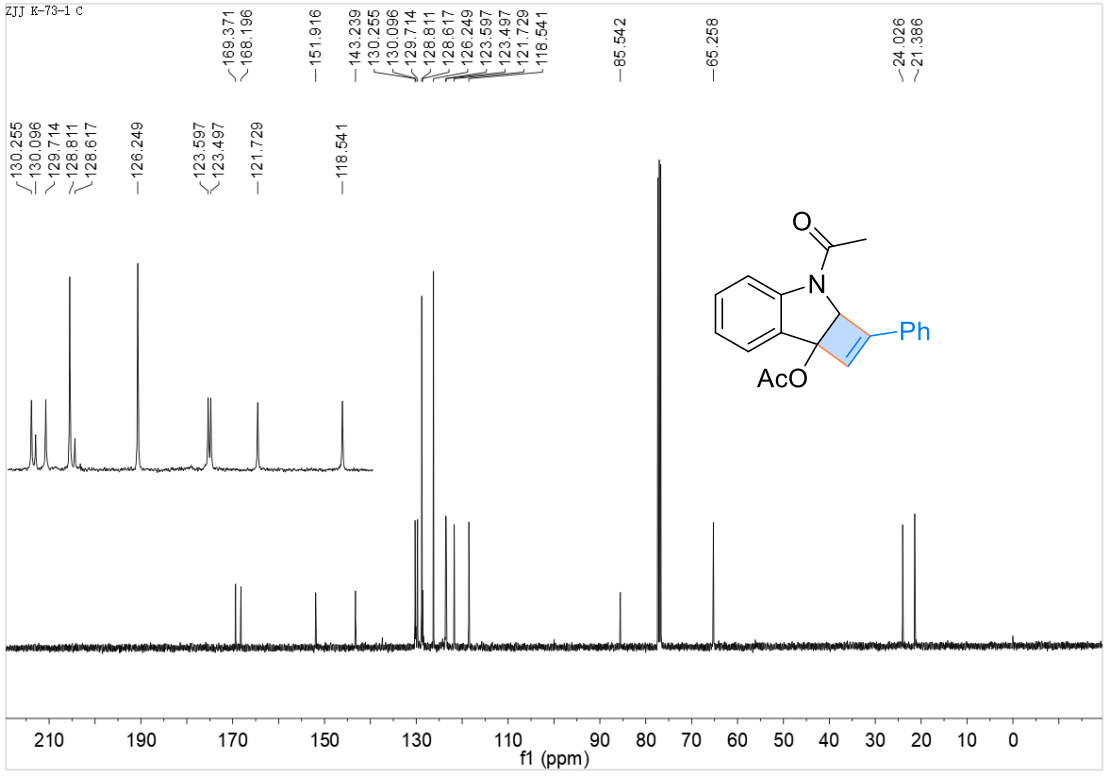
3o DEPT 90 and DEPT 135



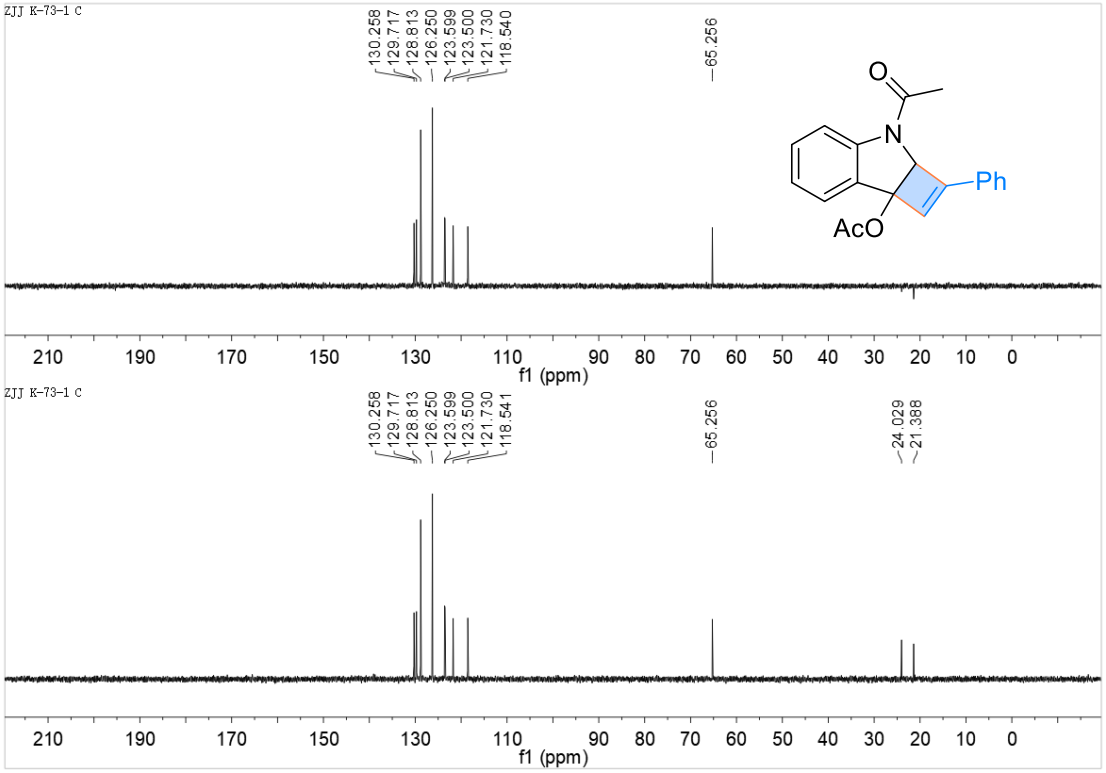
3p1 ^{1}H NMR



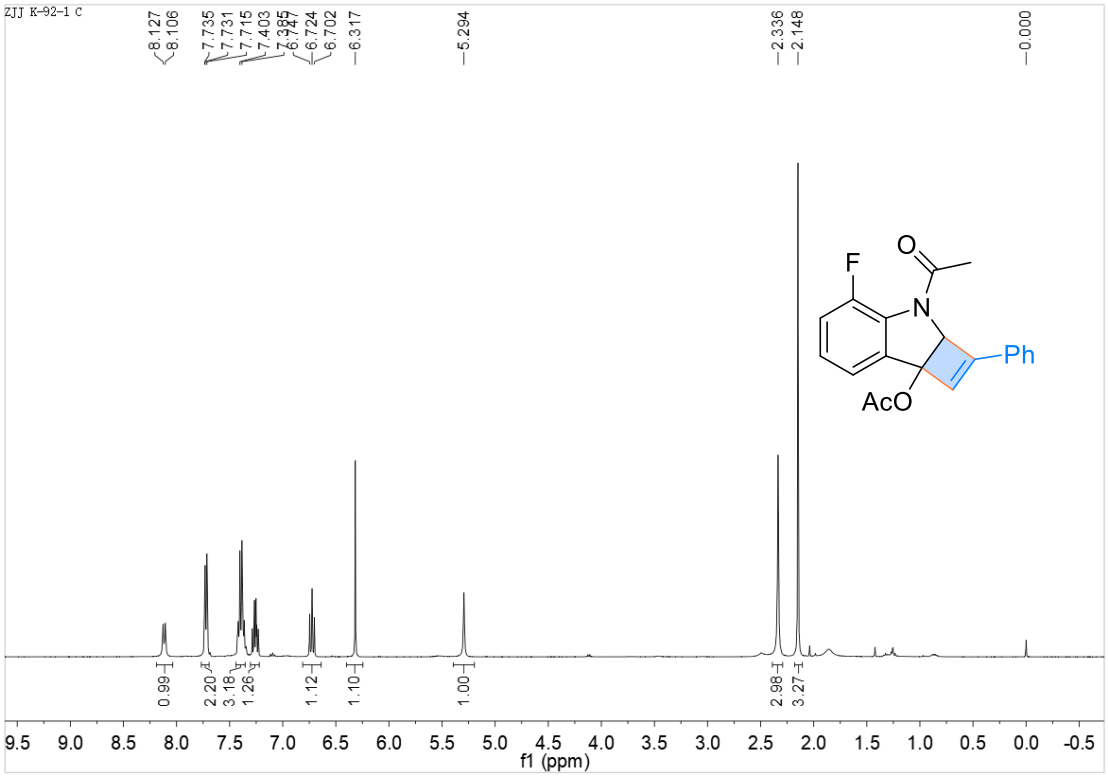
3p1 ^{13}C NMR



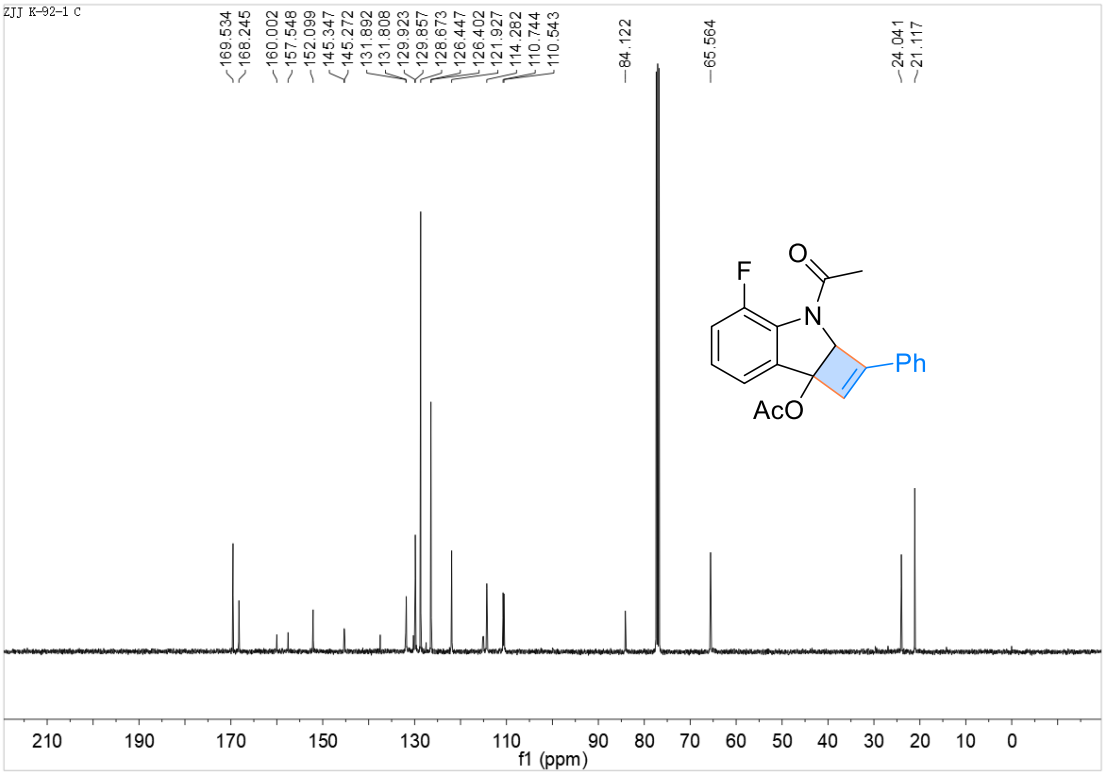
3p1 DEPT 90 and DEPT 135



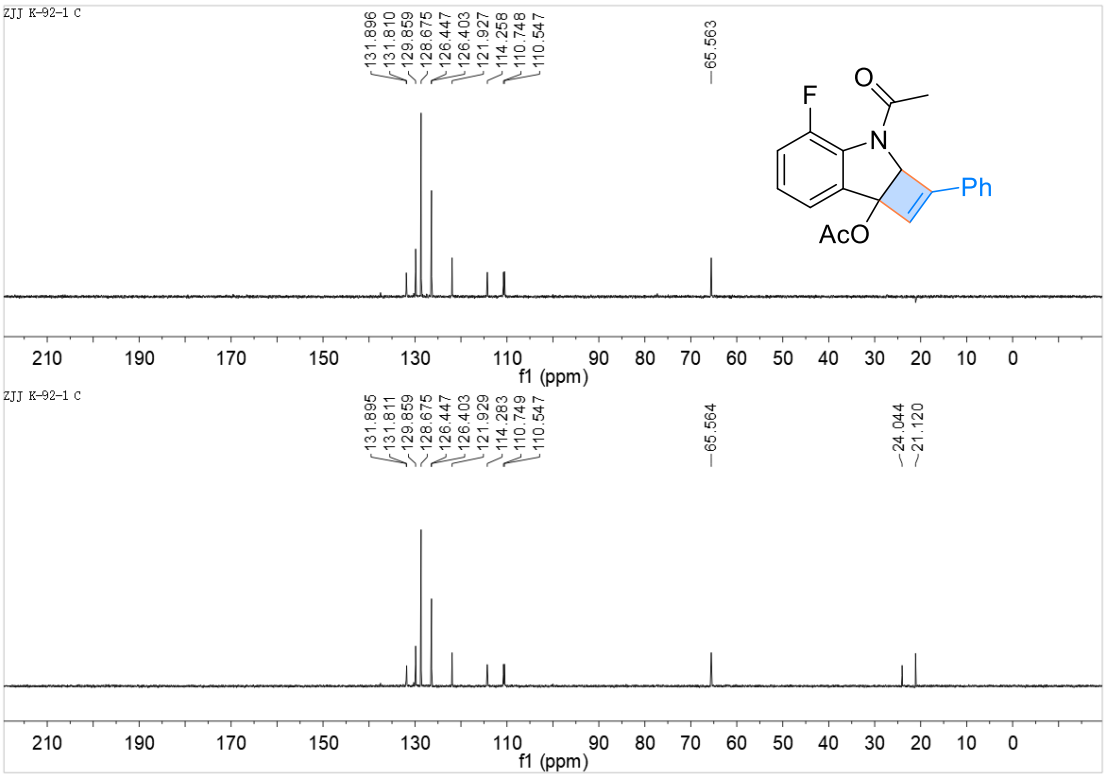
3p2 ^{1}H NMR



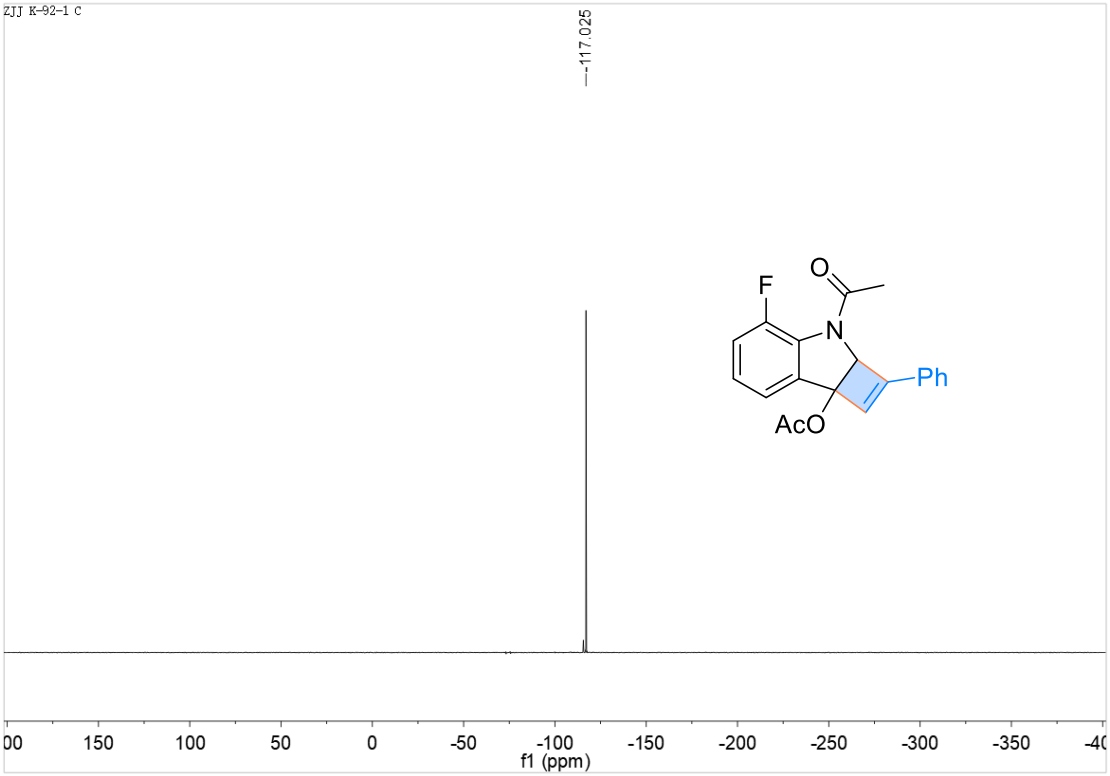
3p2 ^{13}C NMR



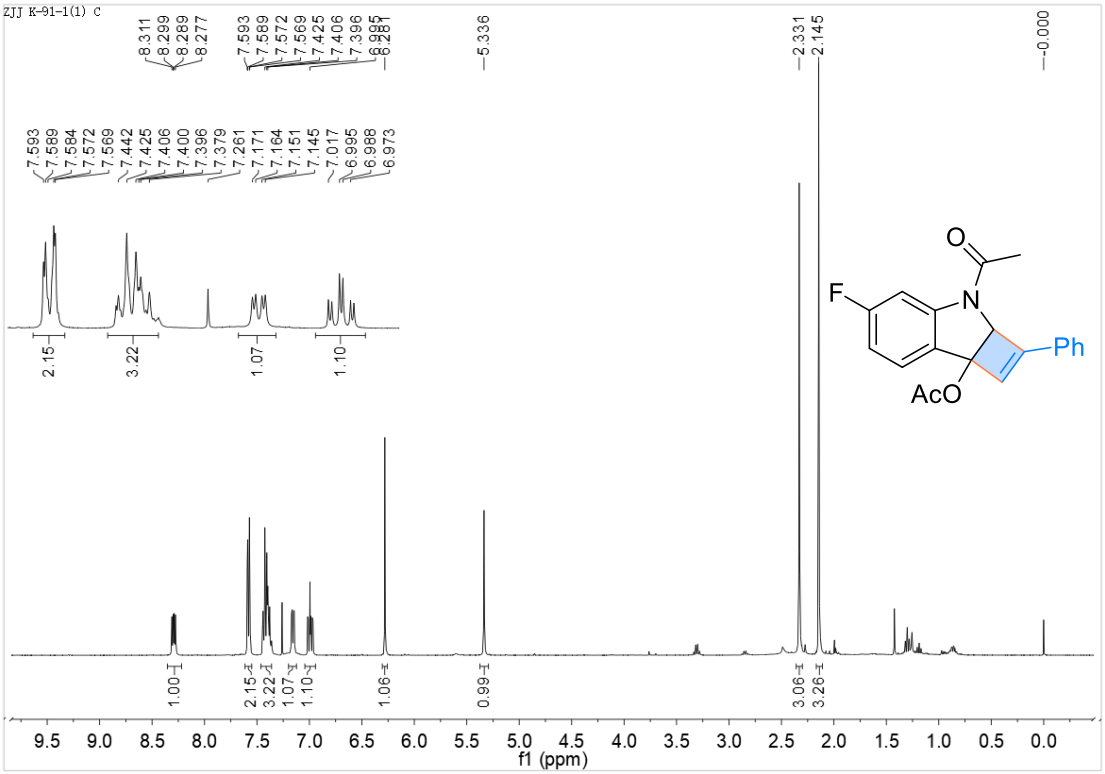
3p2 DEPT 90 and DEPT 135



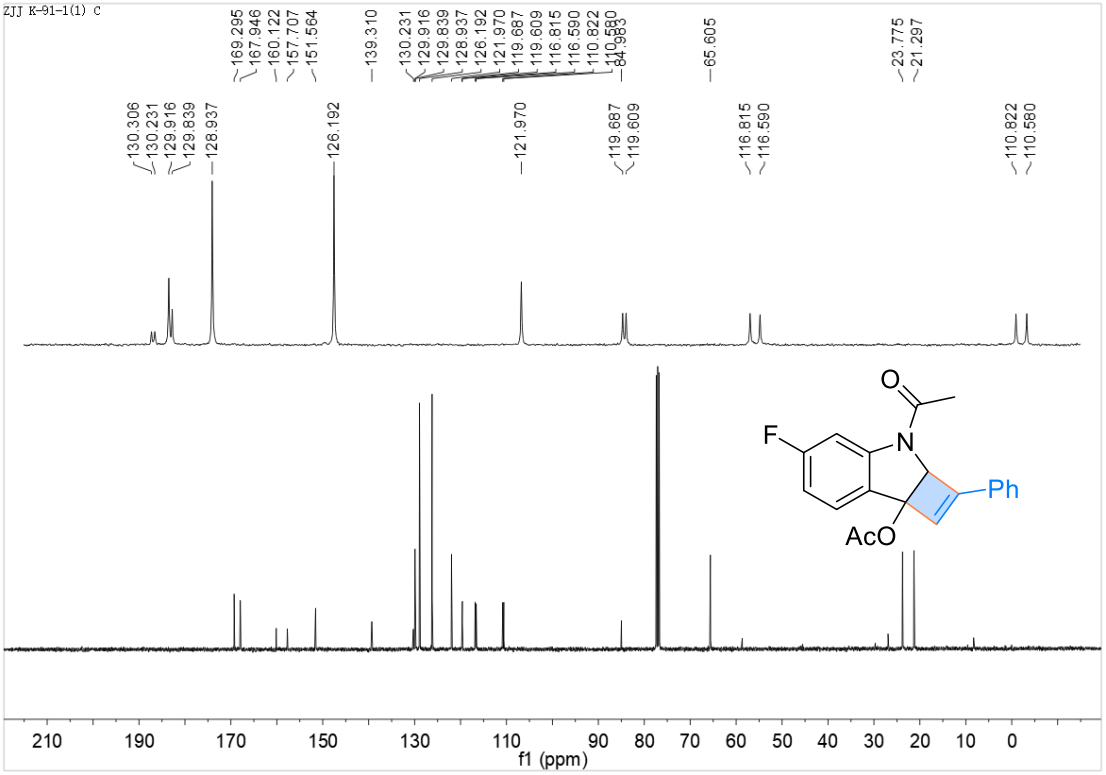
3p2 ^{19}F NMR



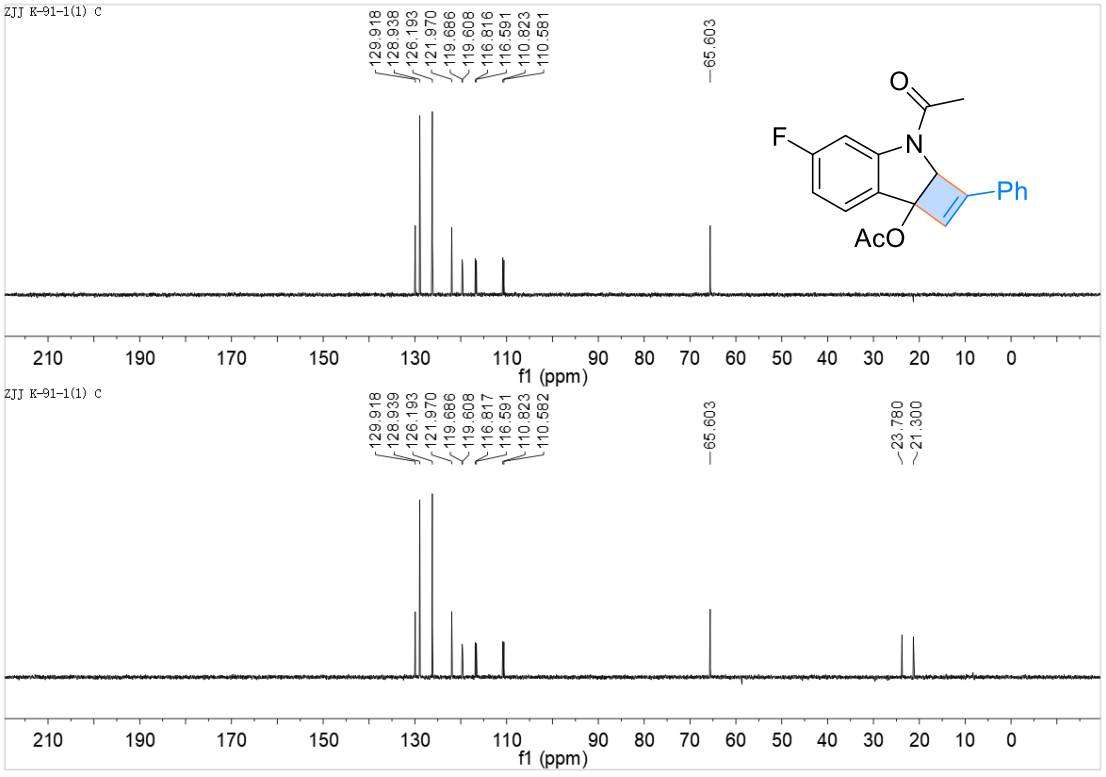
3q1 ^{1}H NMR



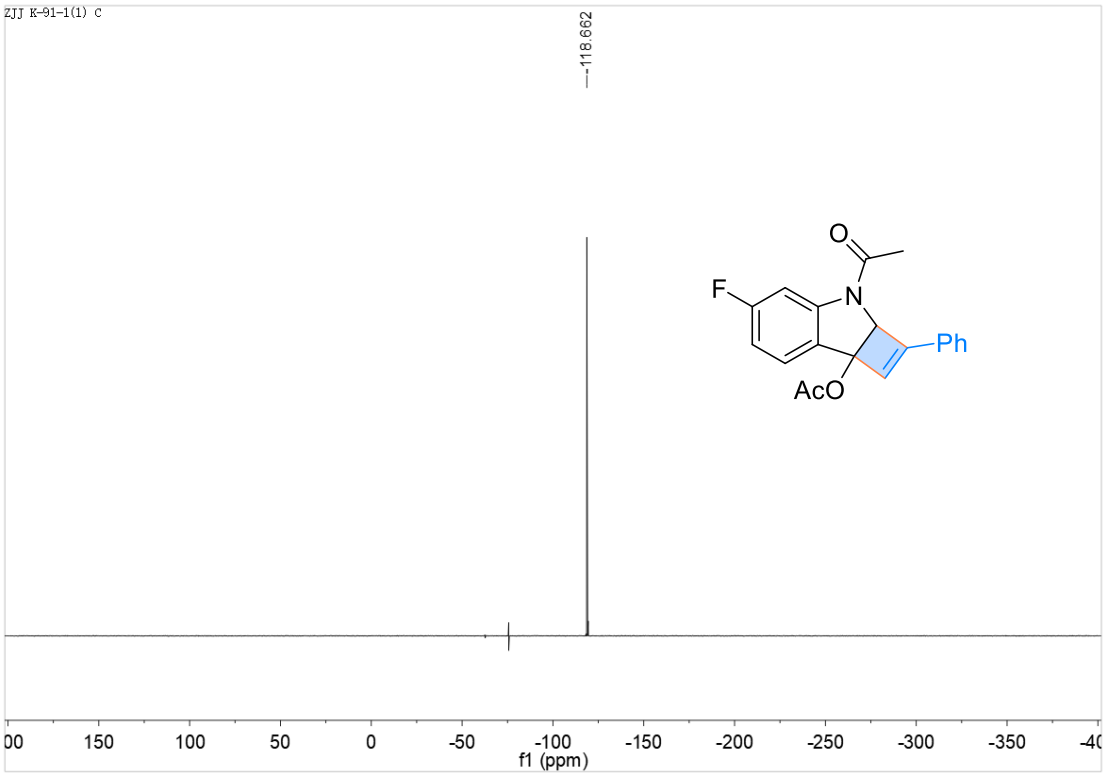
3q1 ^{13}C NMR



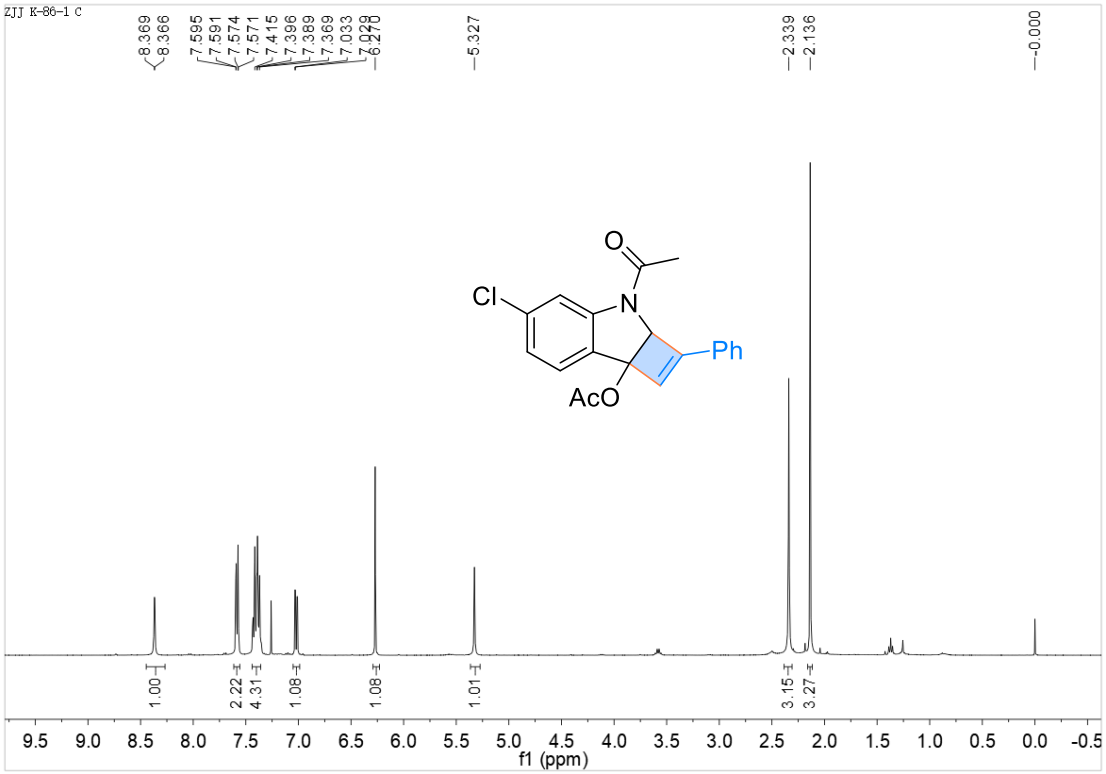
3q1 DEPT 90 and DEPT 135



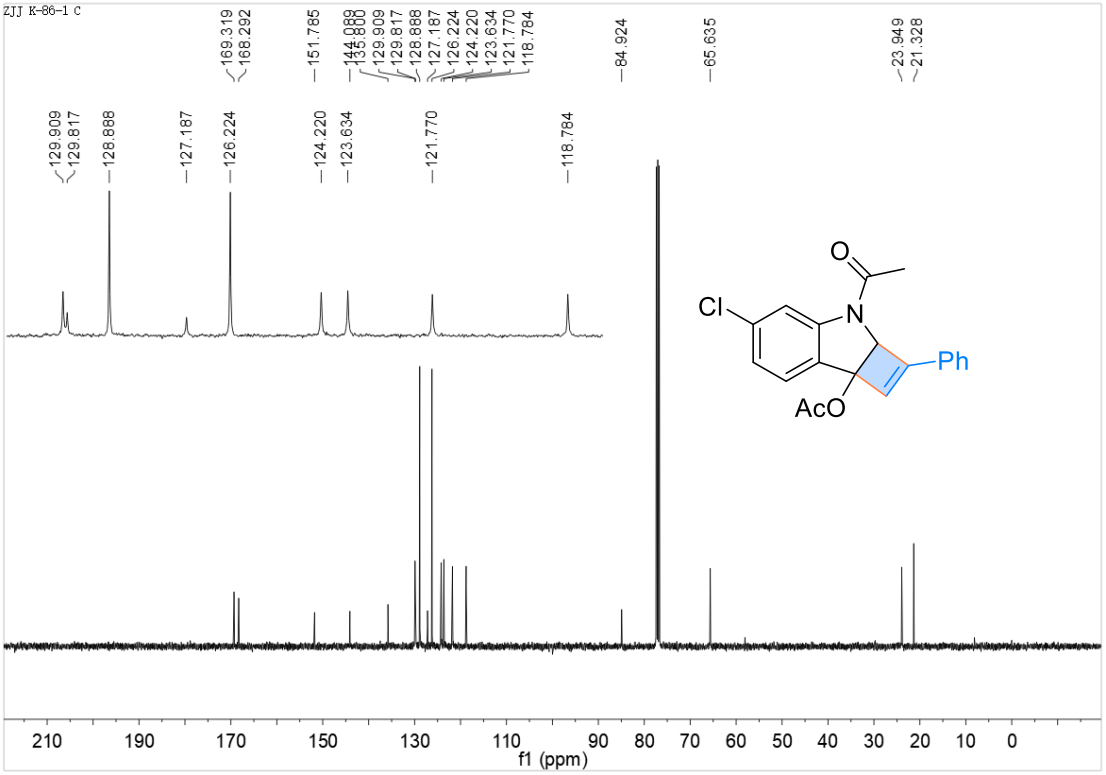
3q1 ^{19}F NMR



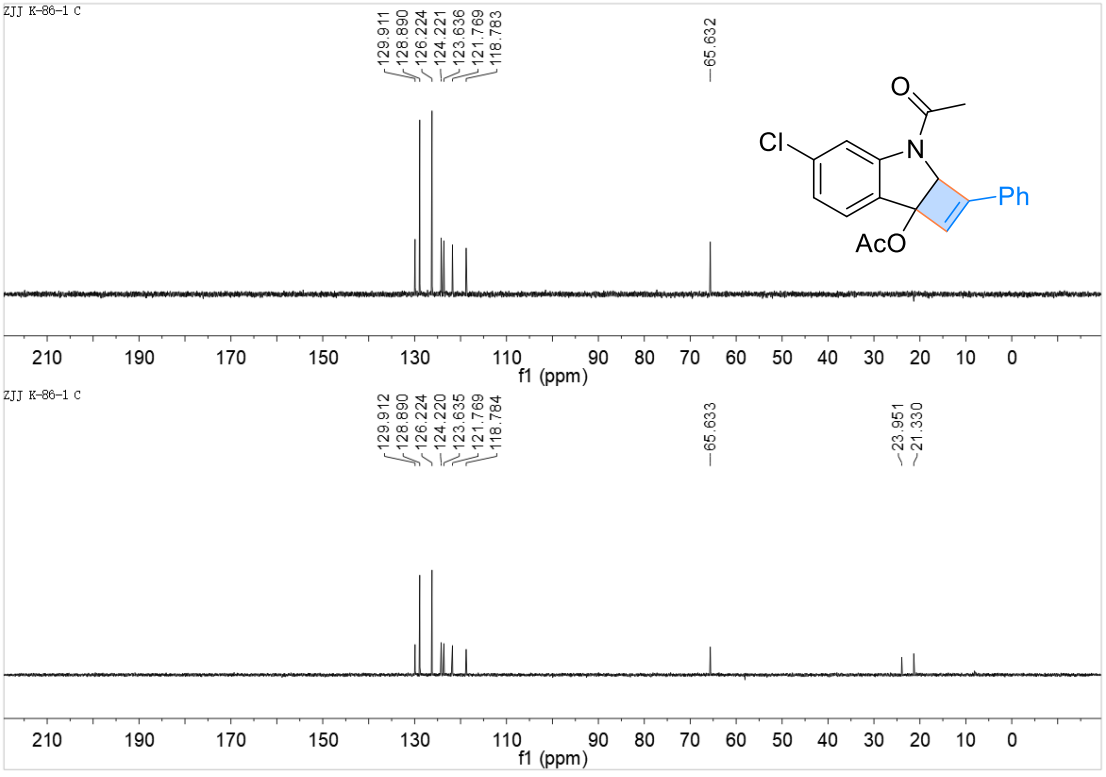
3q2 ^{1}H NMR



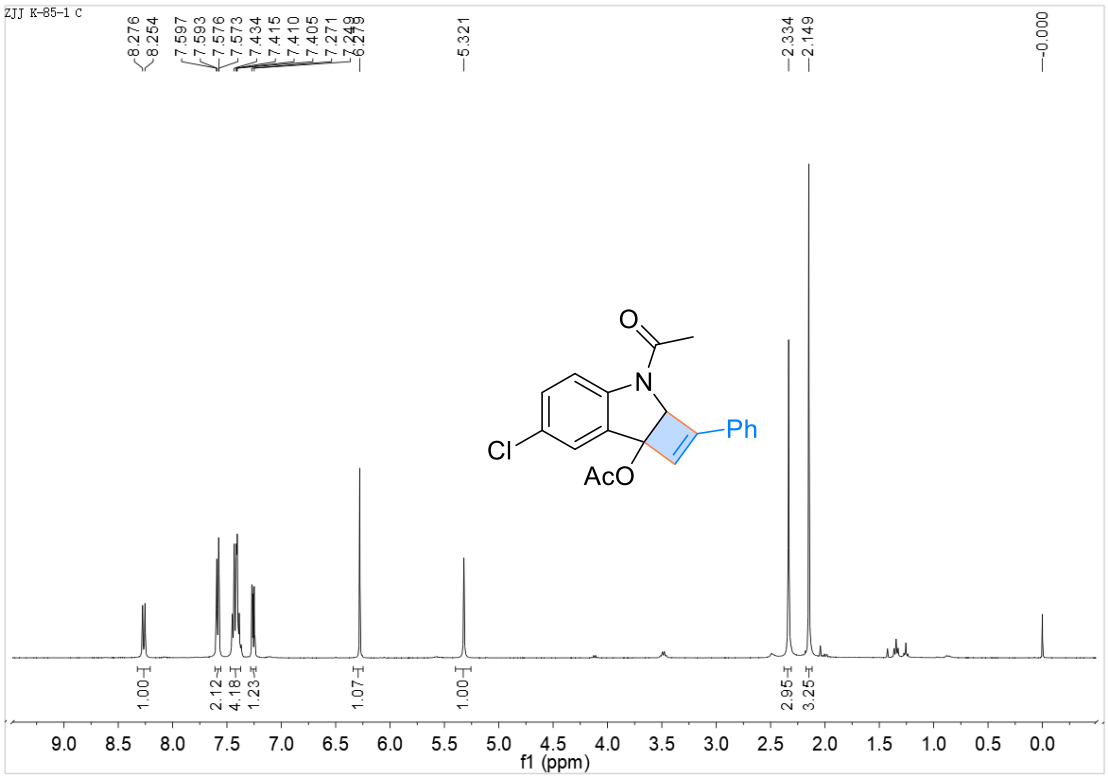
3q2 ^{13}C NMR



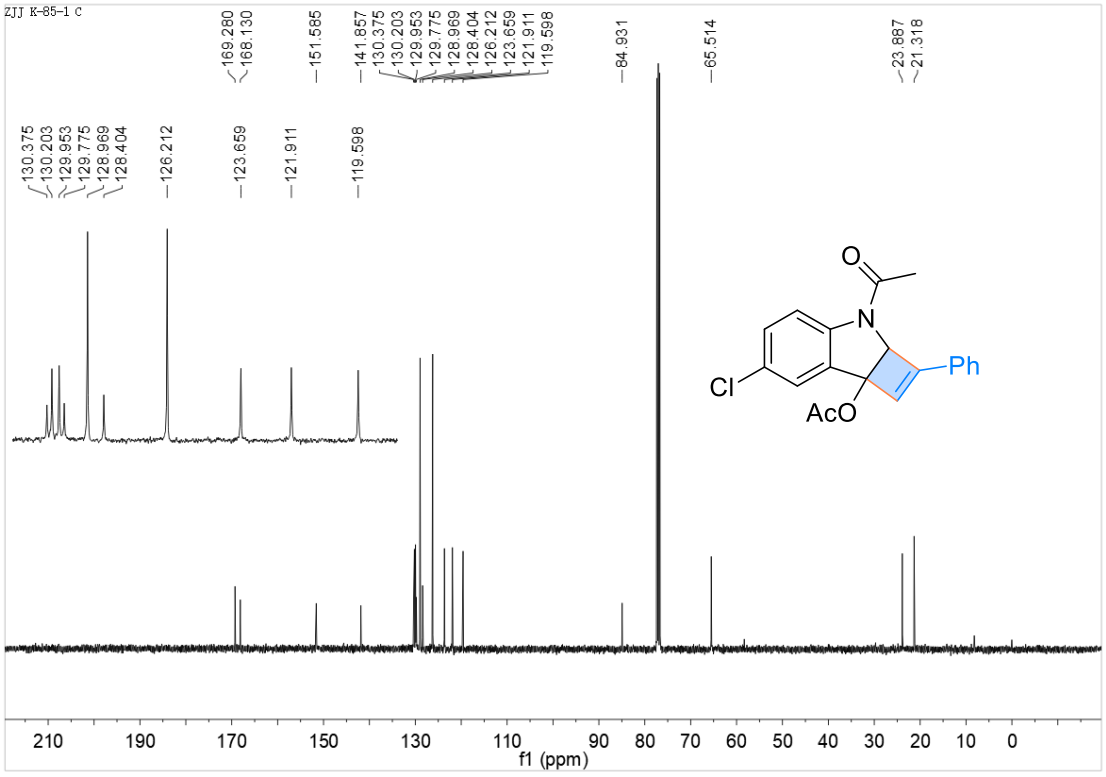
3q2 DEPT 90 and DEPT 135



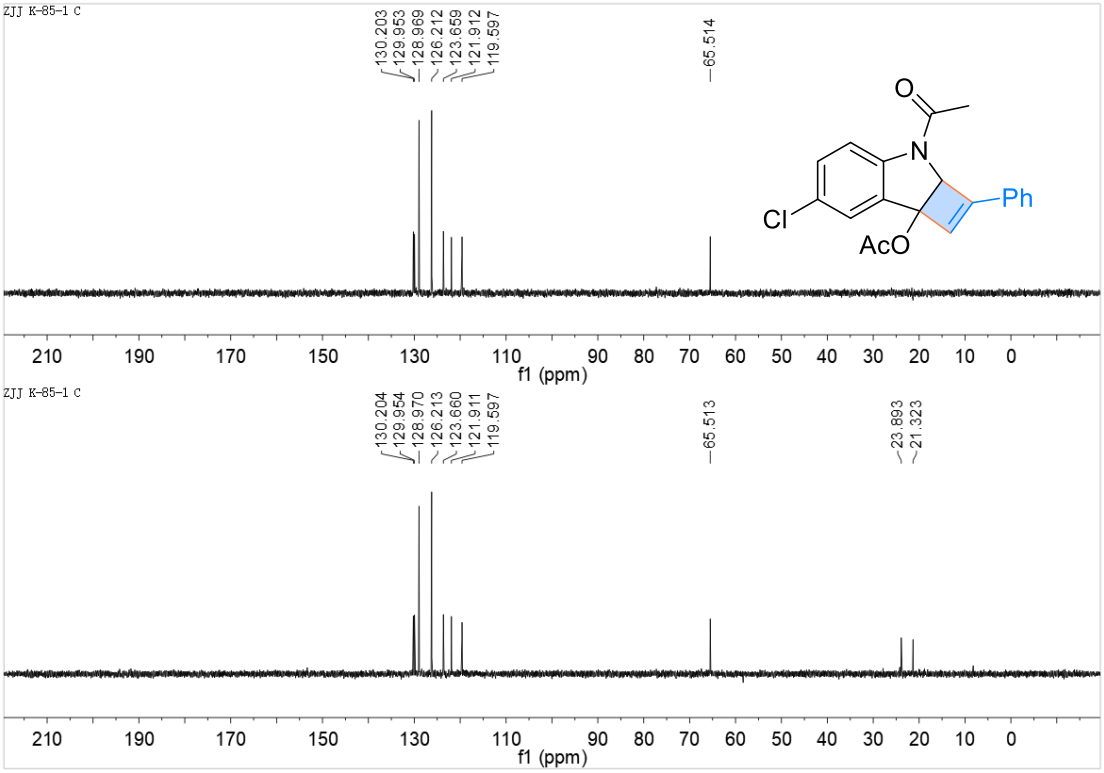
3r1 ^{1}H NMR



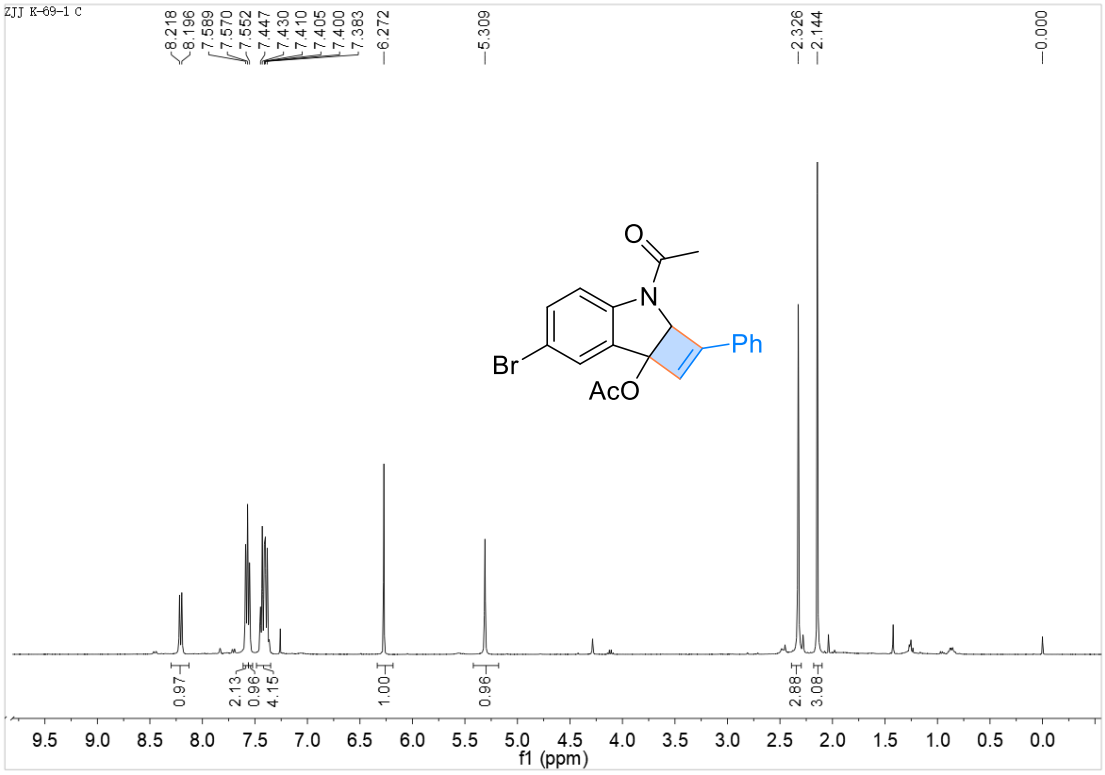
3r1 ^{13}C NMR



3r1 DEPT 90 and DEPT 135



3r2 ^{1}H NMR



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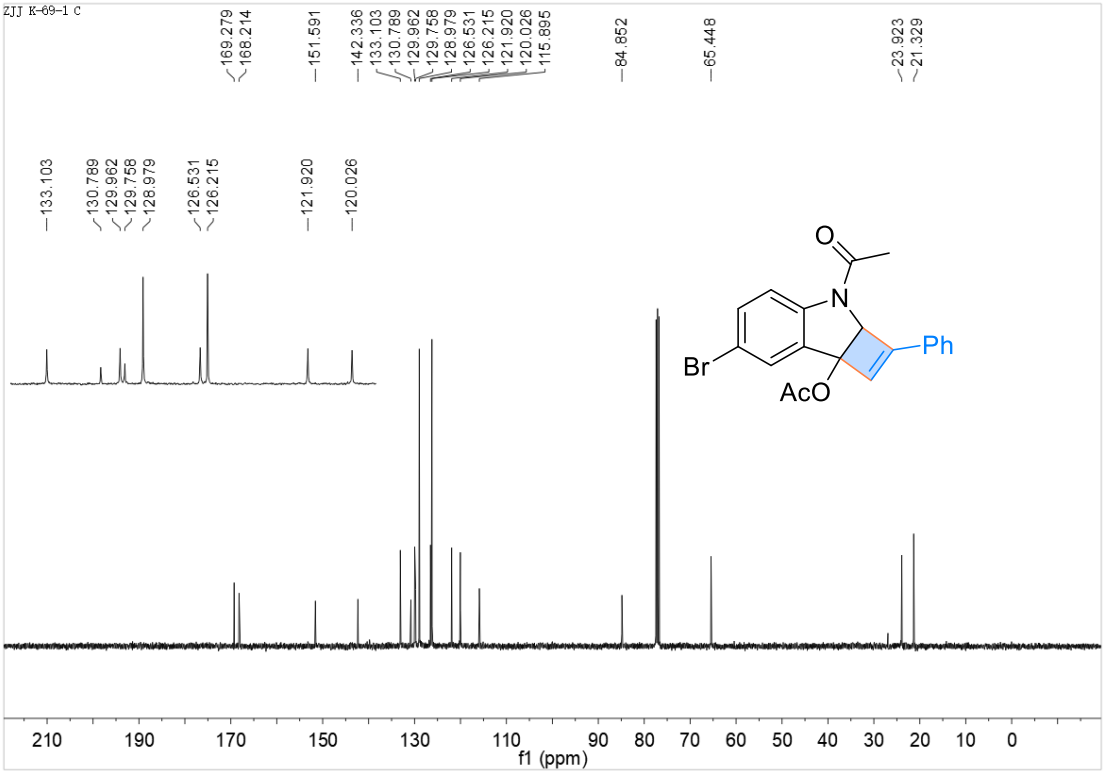
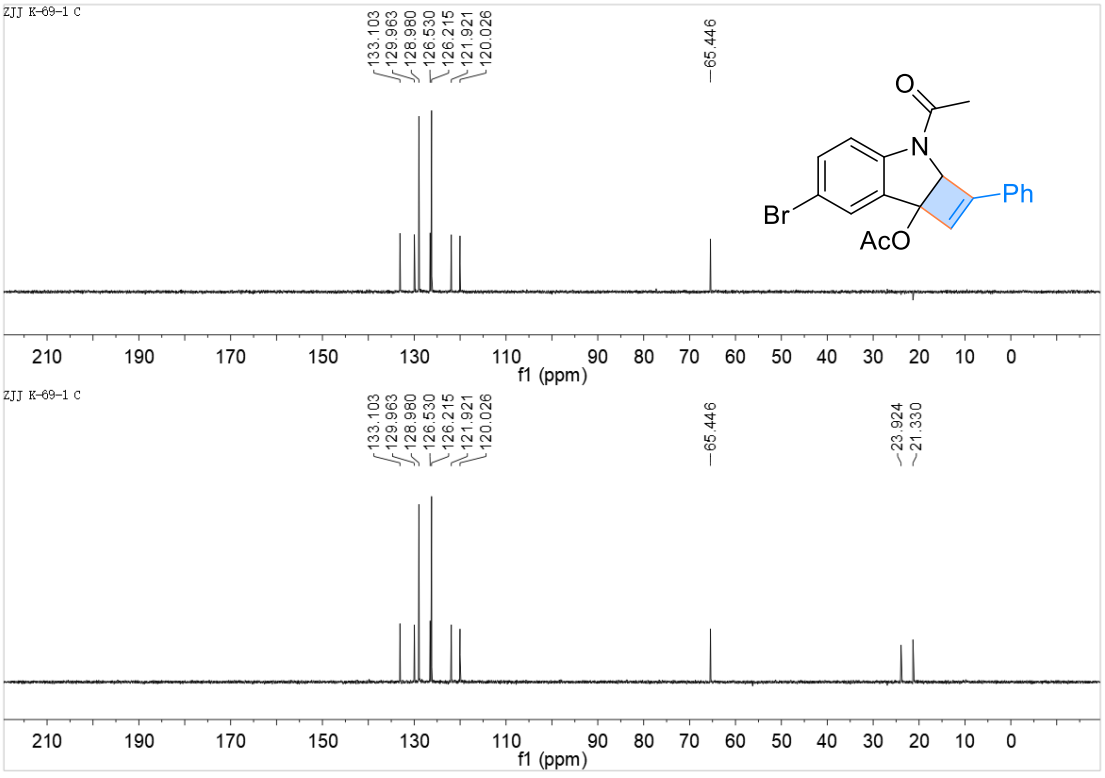
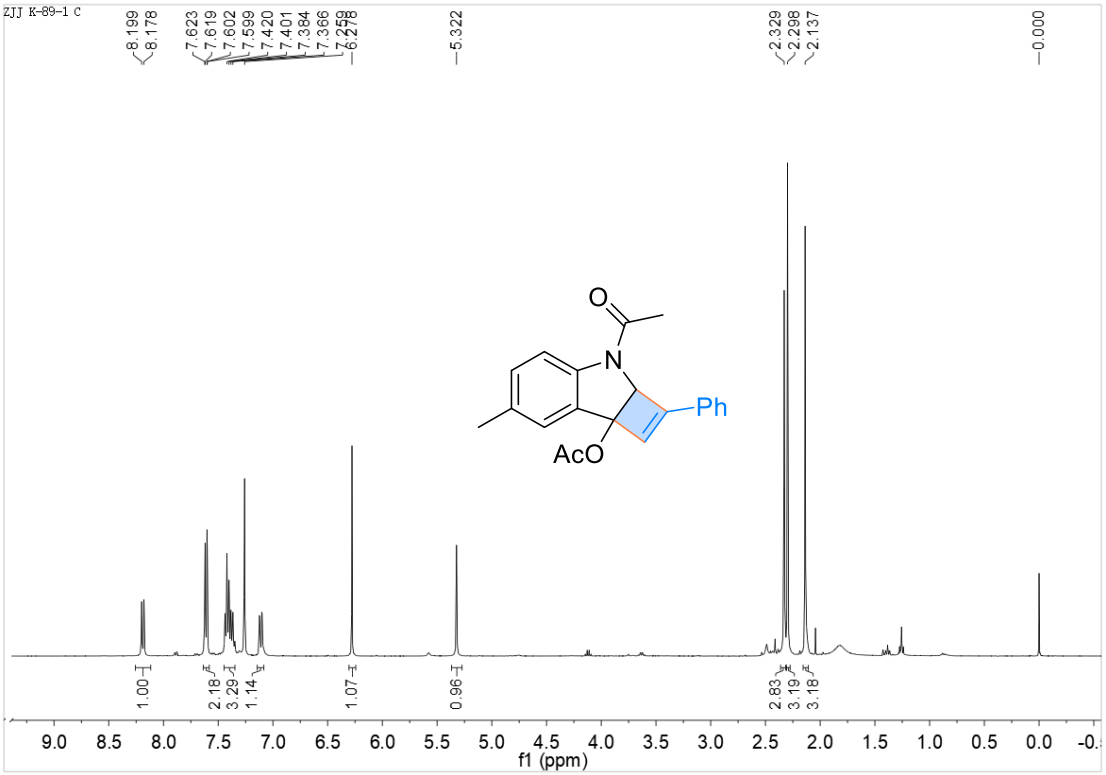


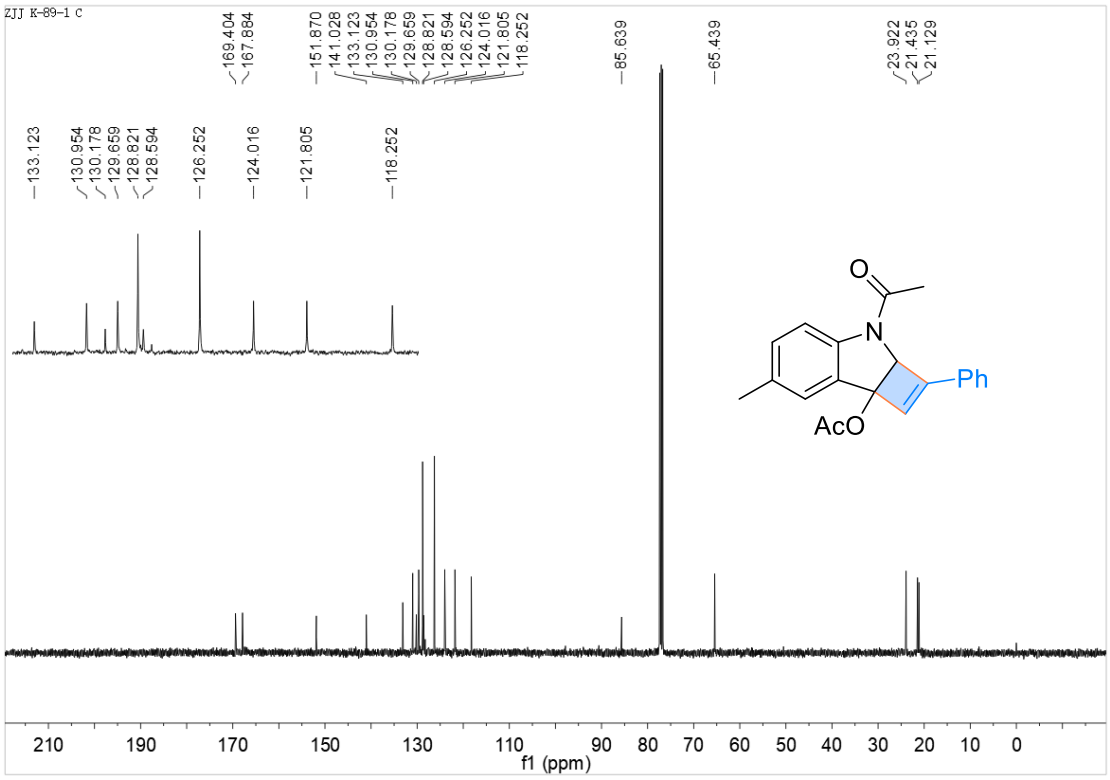
3r2 DEPT 90 and DEPT 135



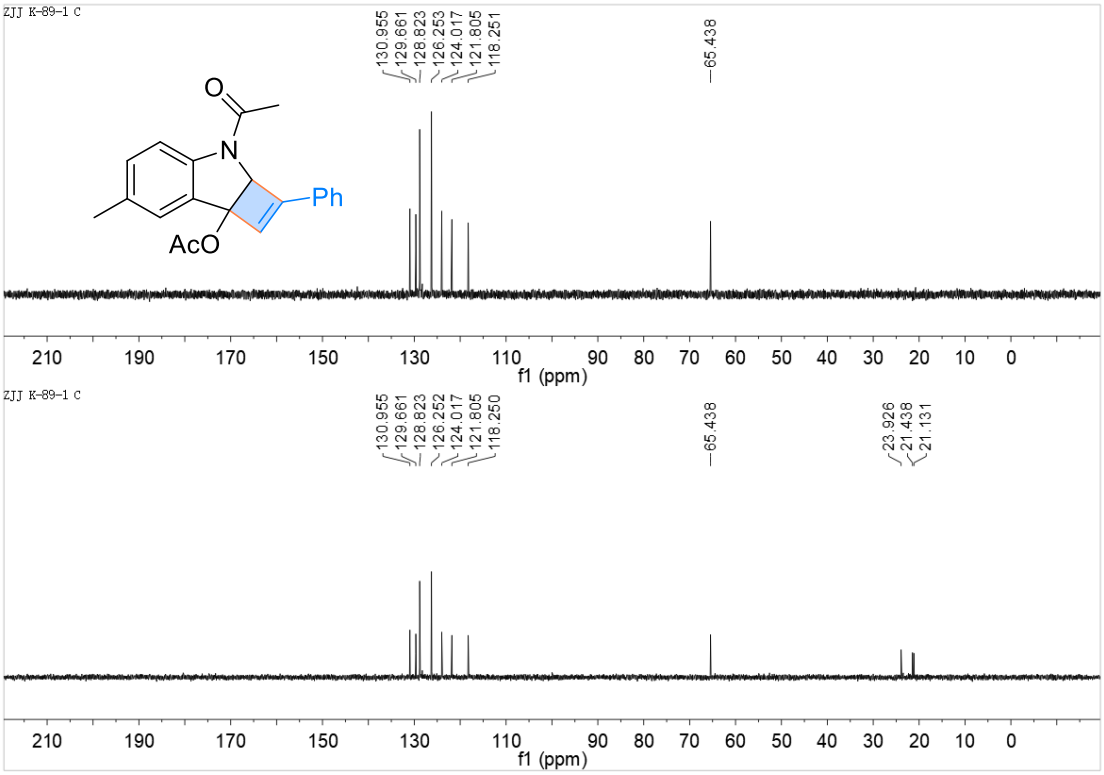
3r3 ^{1}H NMR



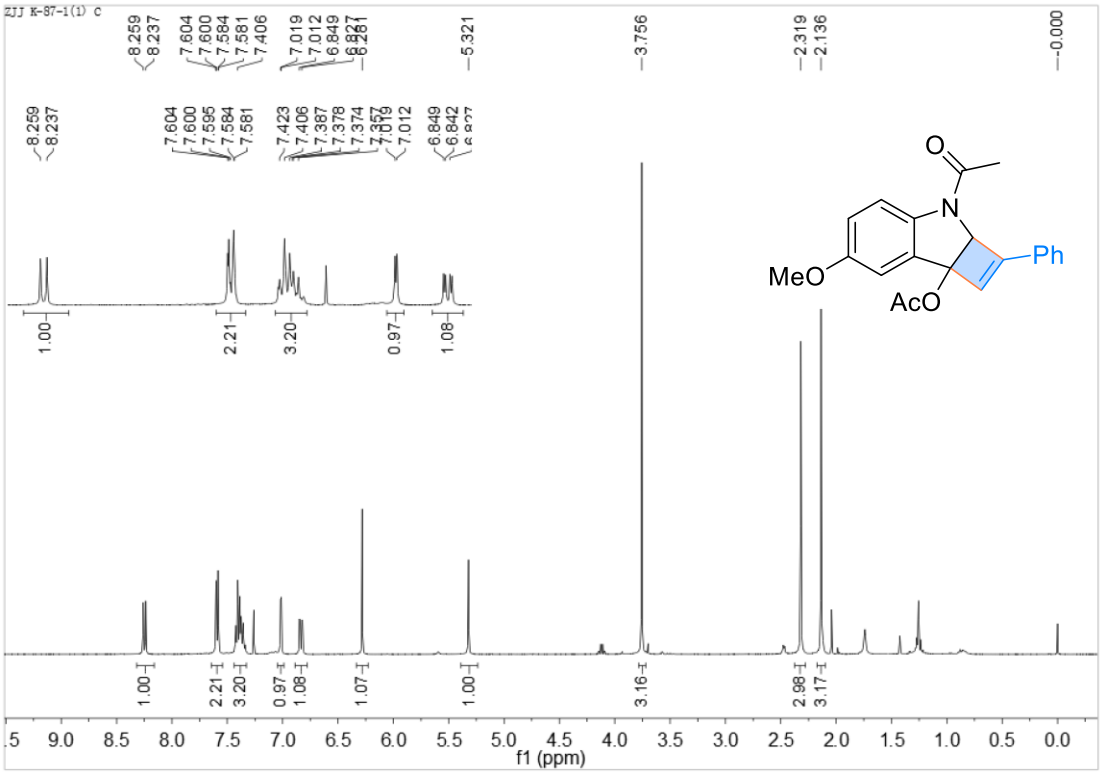
3r3 ^{13}C NMR



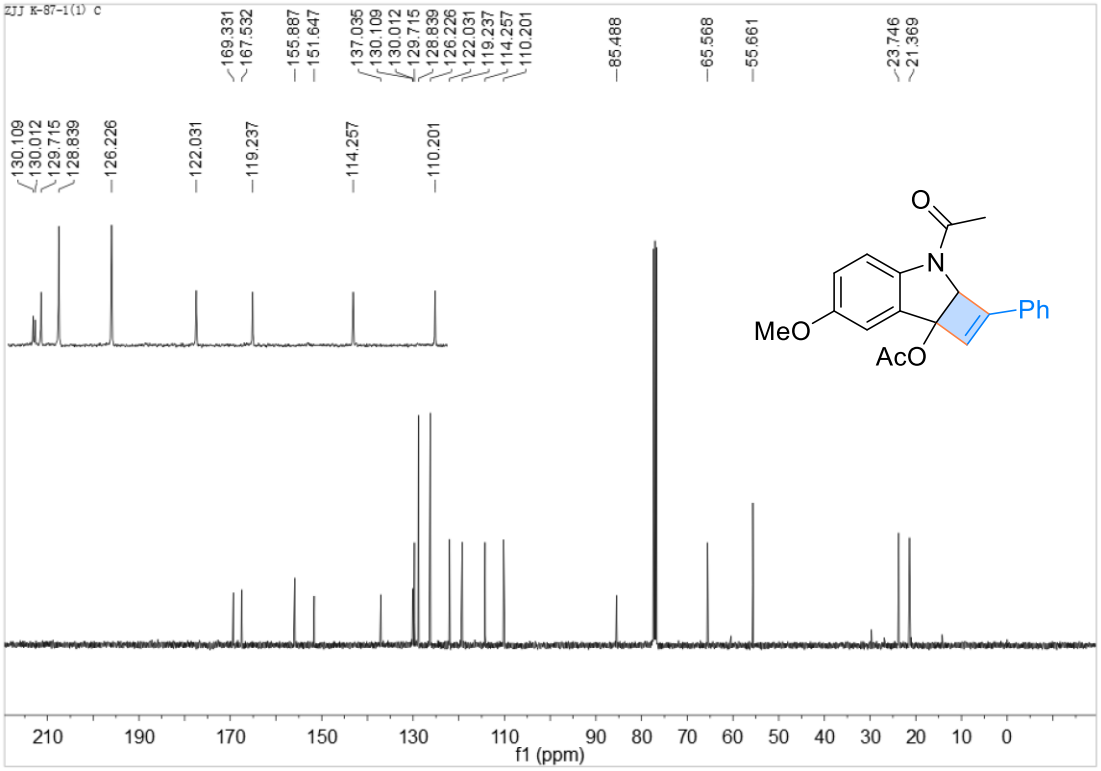
3r3 DEPT 90 and DEPT 135



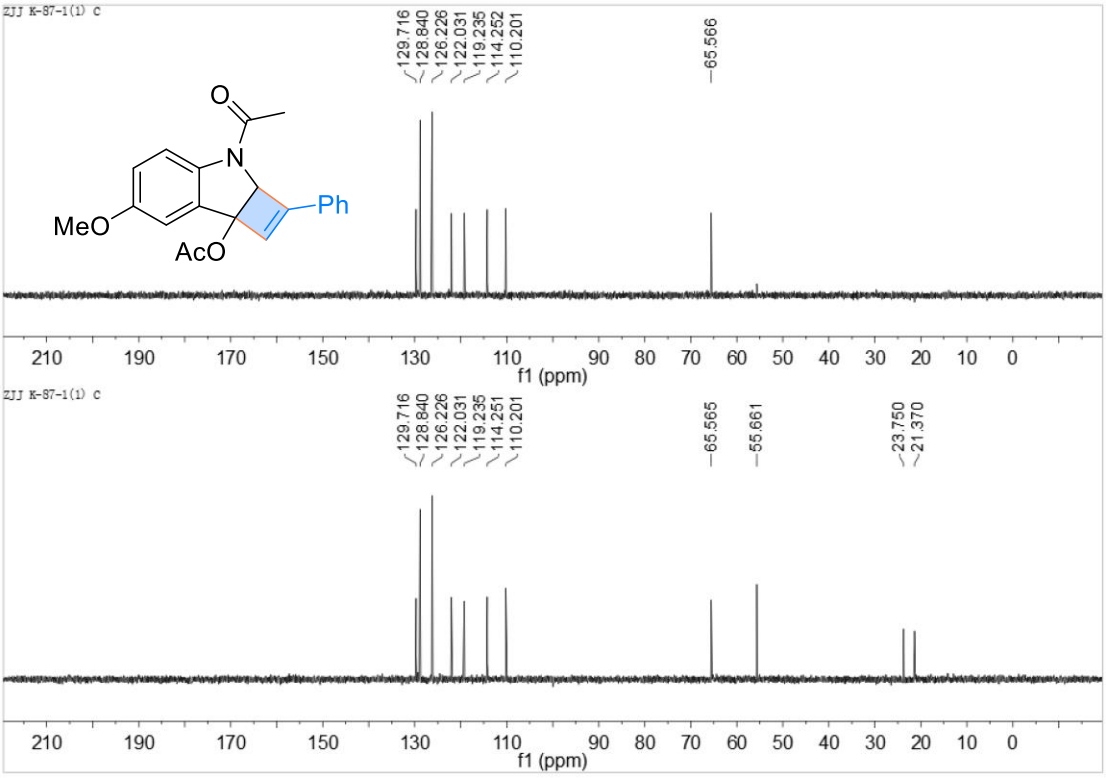
3r4 ^{1}H NMR



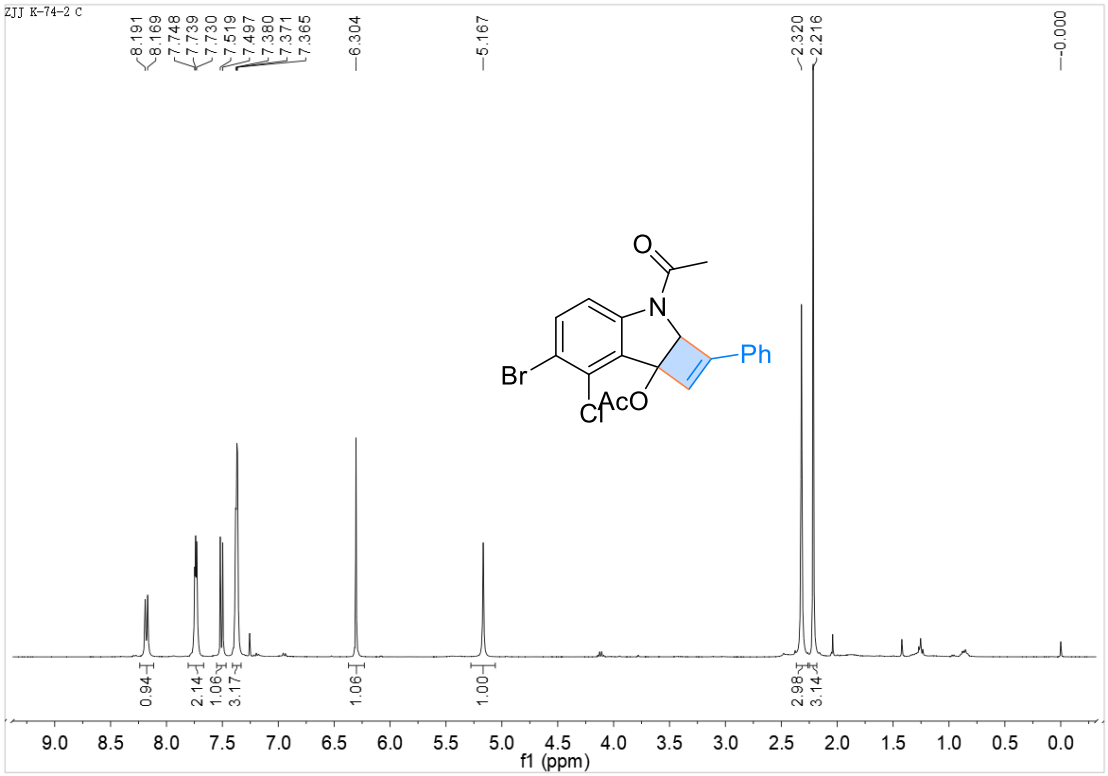
3r4 ^{13}C NMR



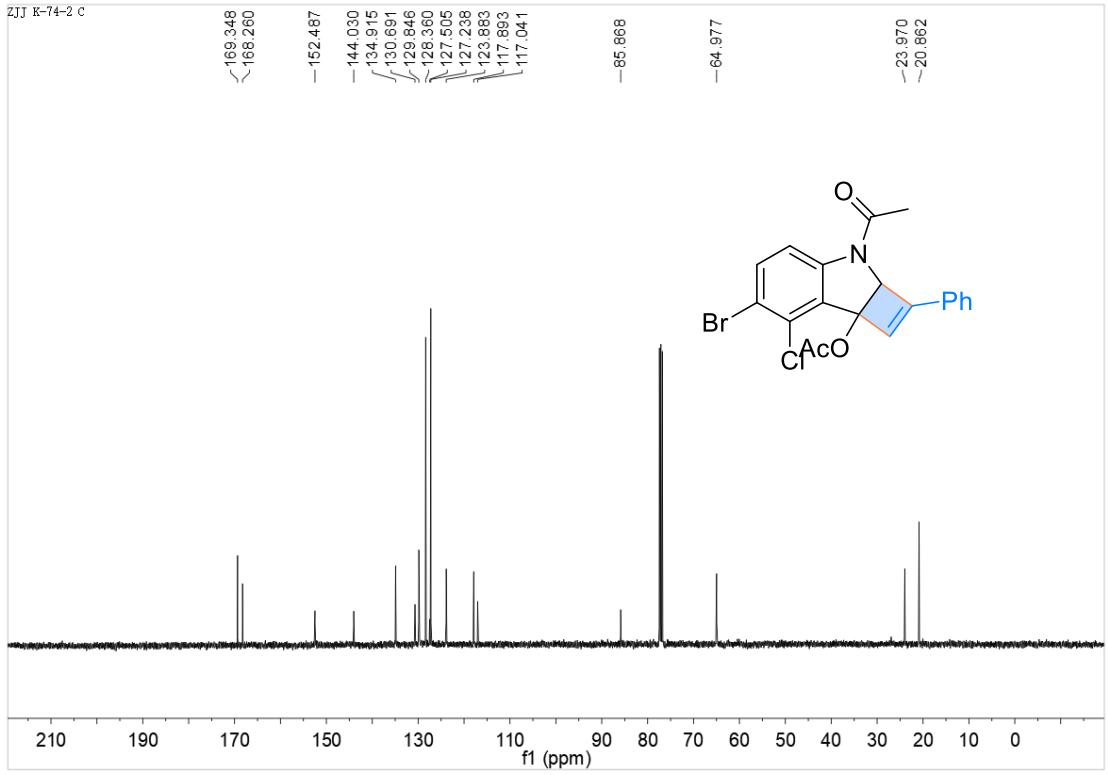
3r4 DEPT 90 and DEPT 135



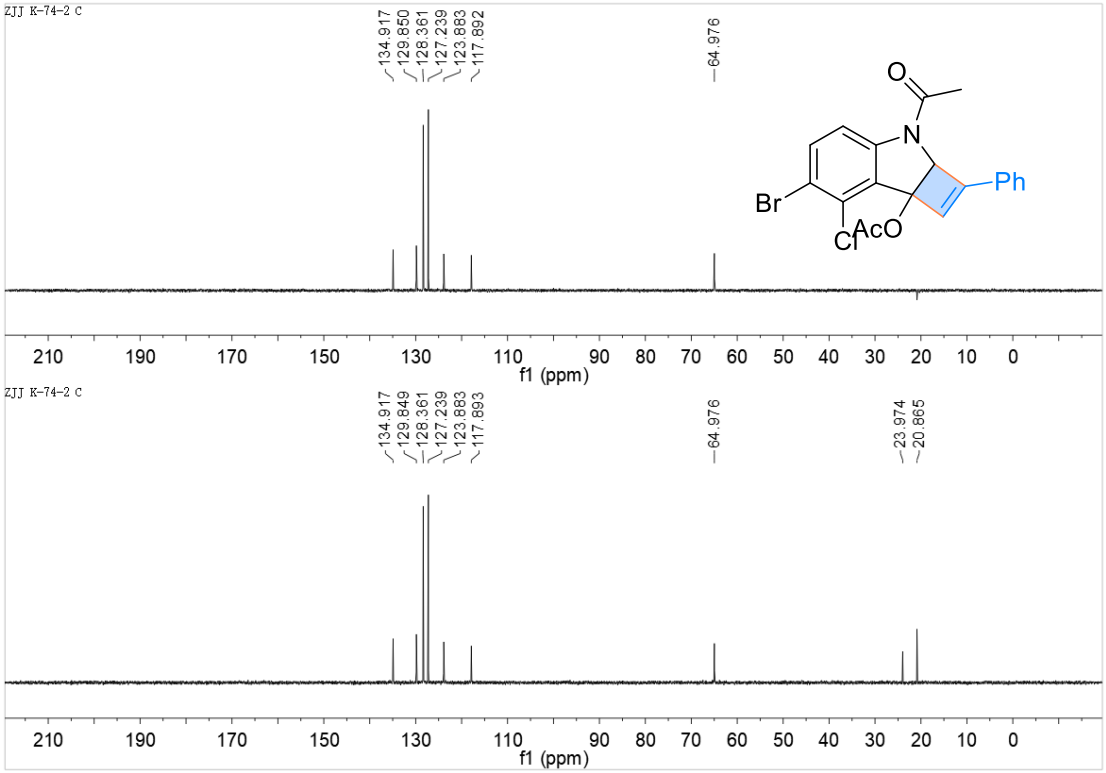
3s ^{1}H NMR



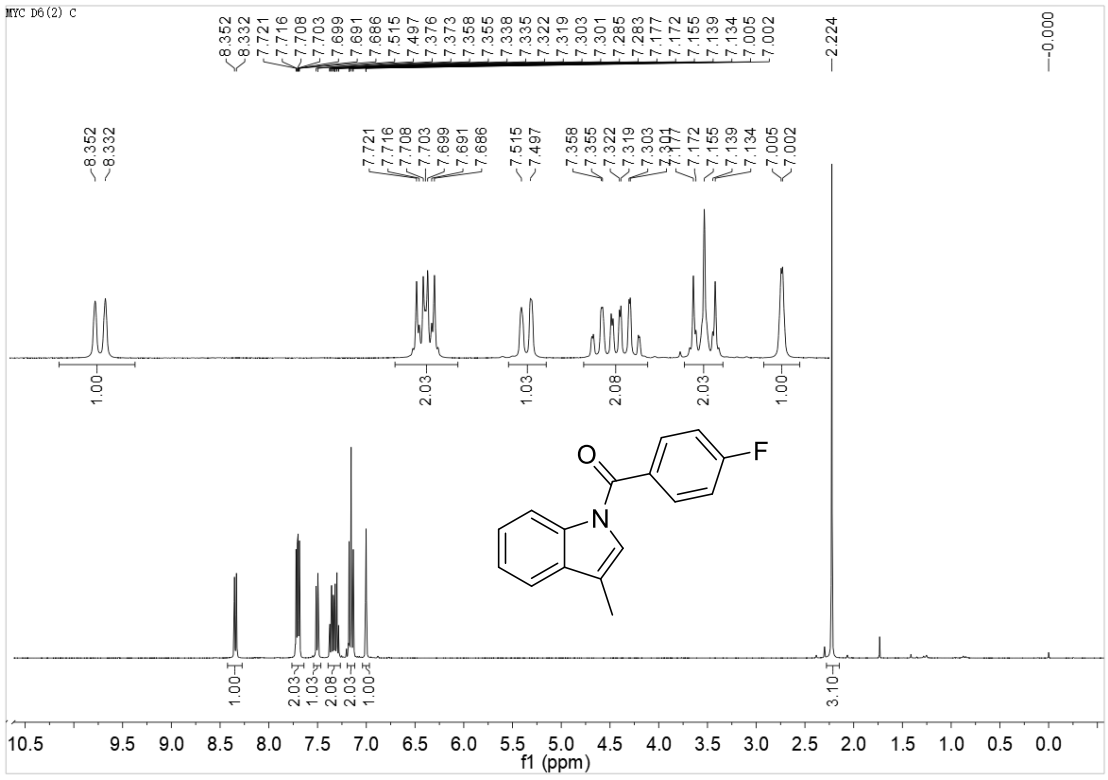
3s ^{13}C NMR



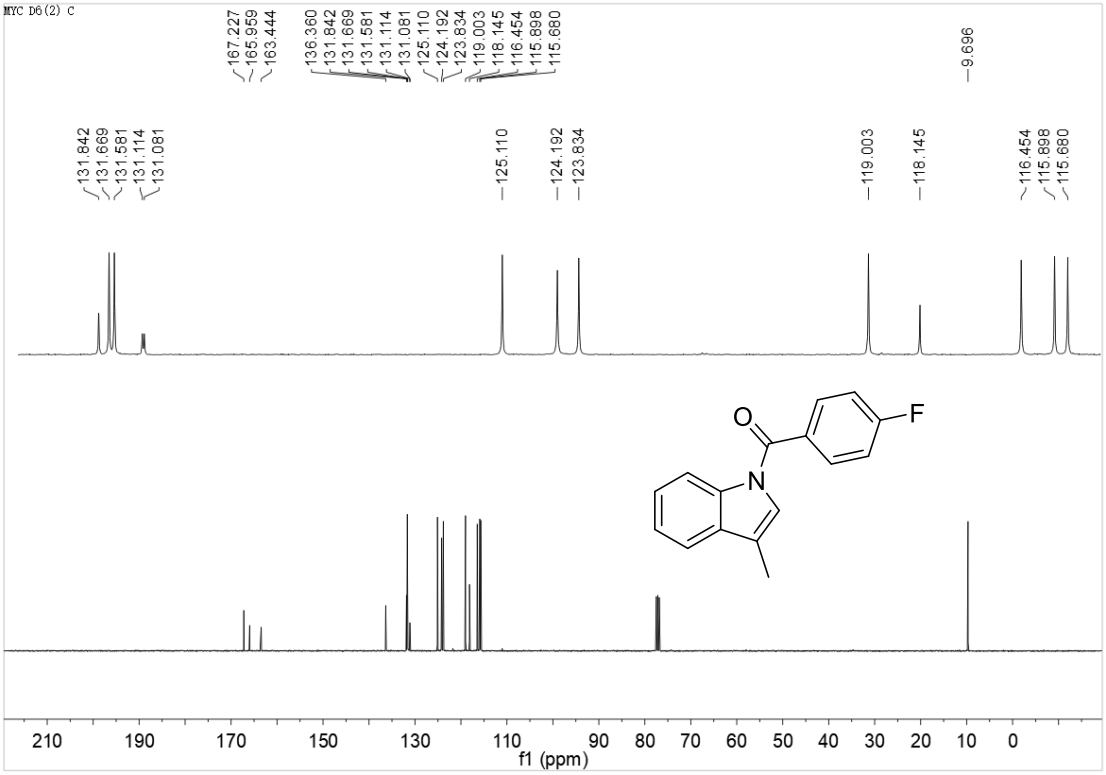
3s DEPT 90 and DEPT 135



1l2 ^{1}H NMR



1l2 ^{13}C NMR



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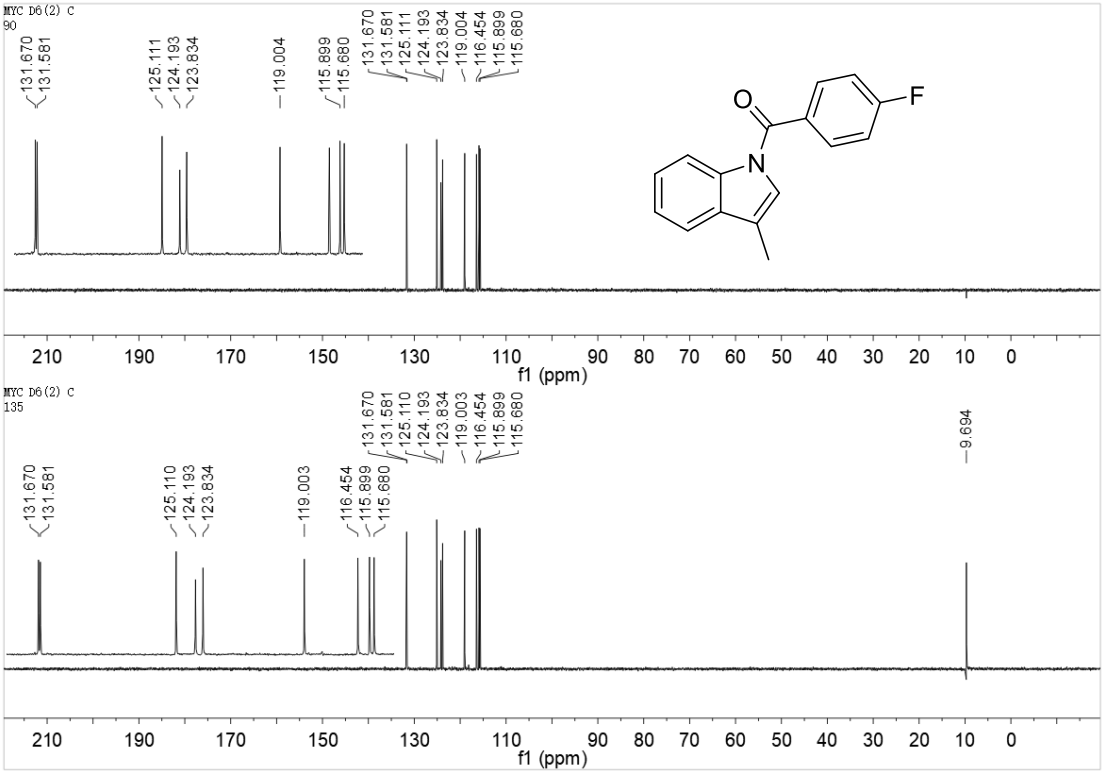
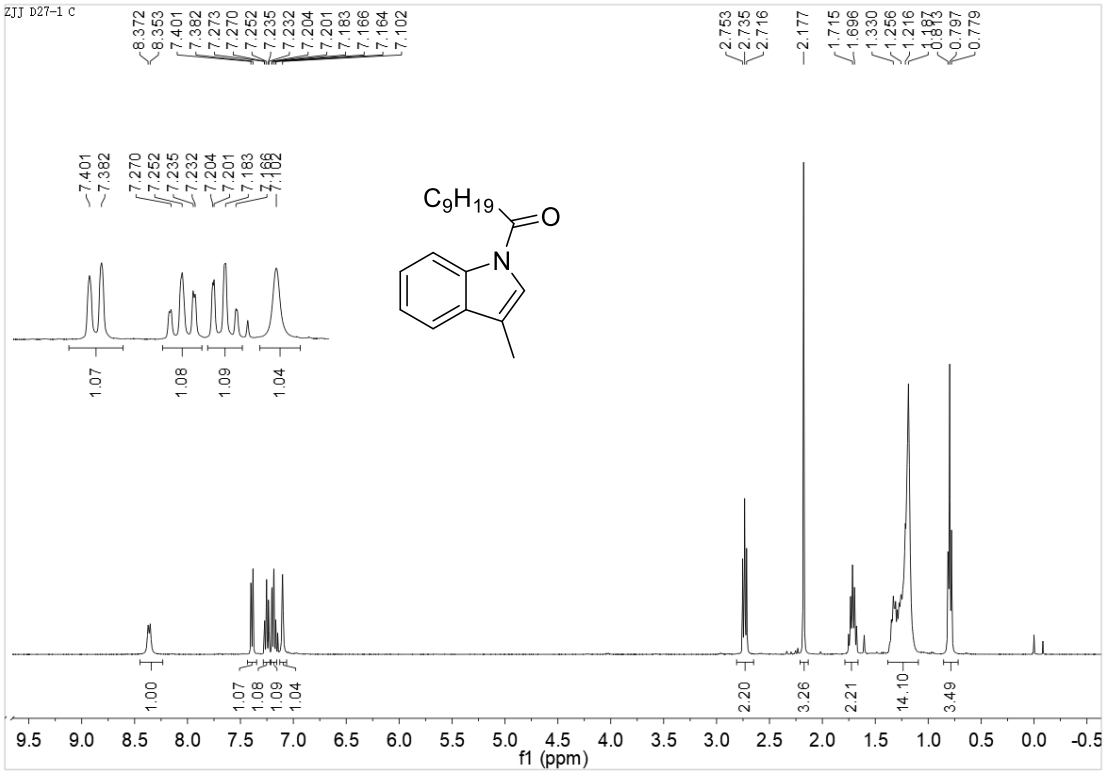


1m1 ^{1}H NMR



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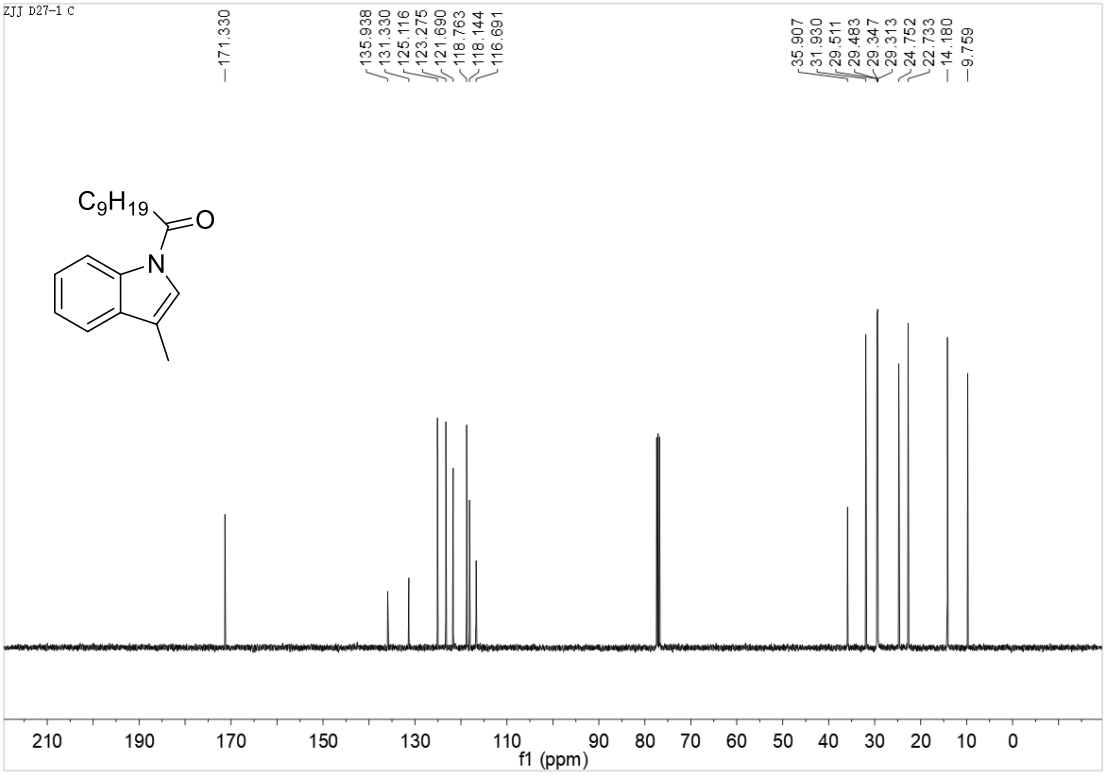

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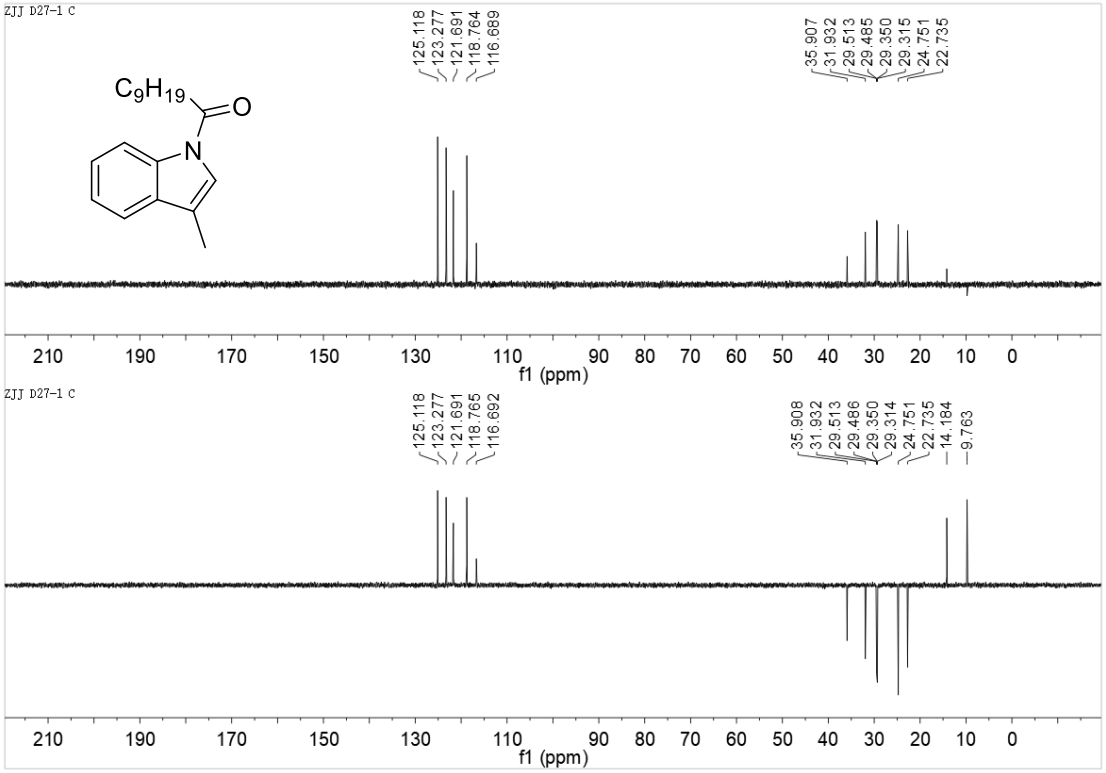
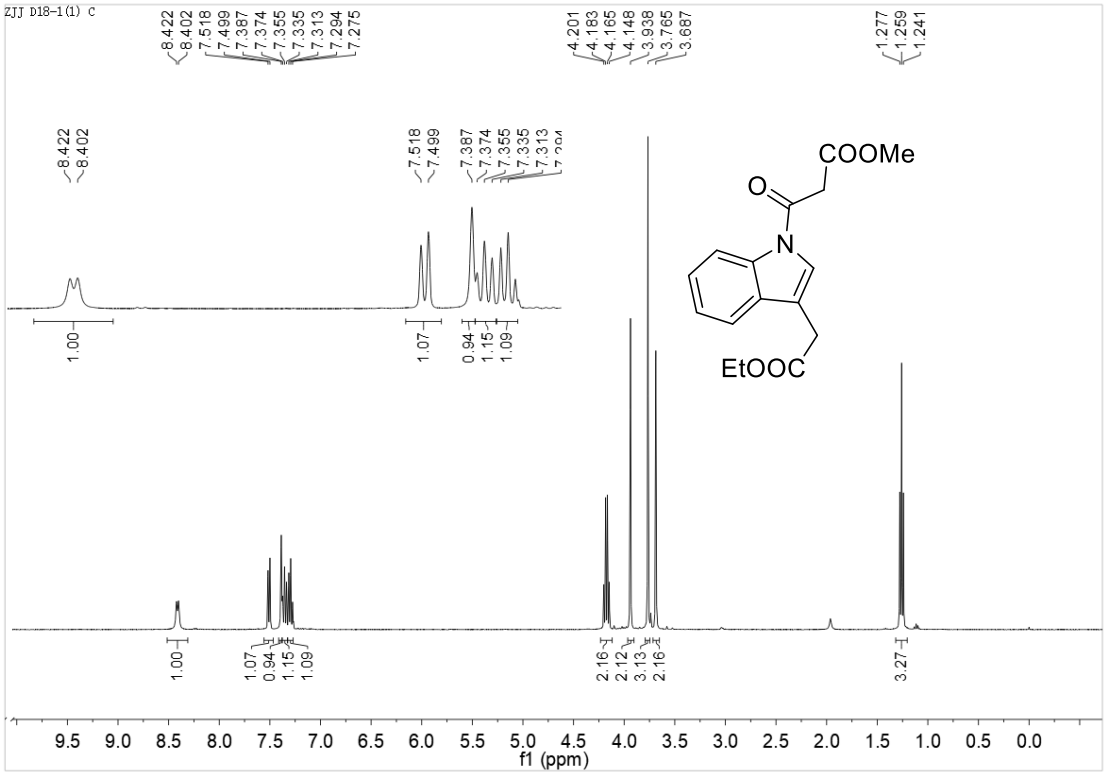


1o ^{1}H NMR



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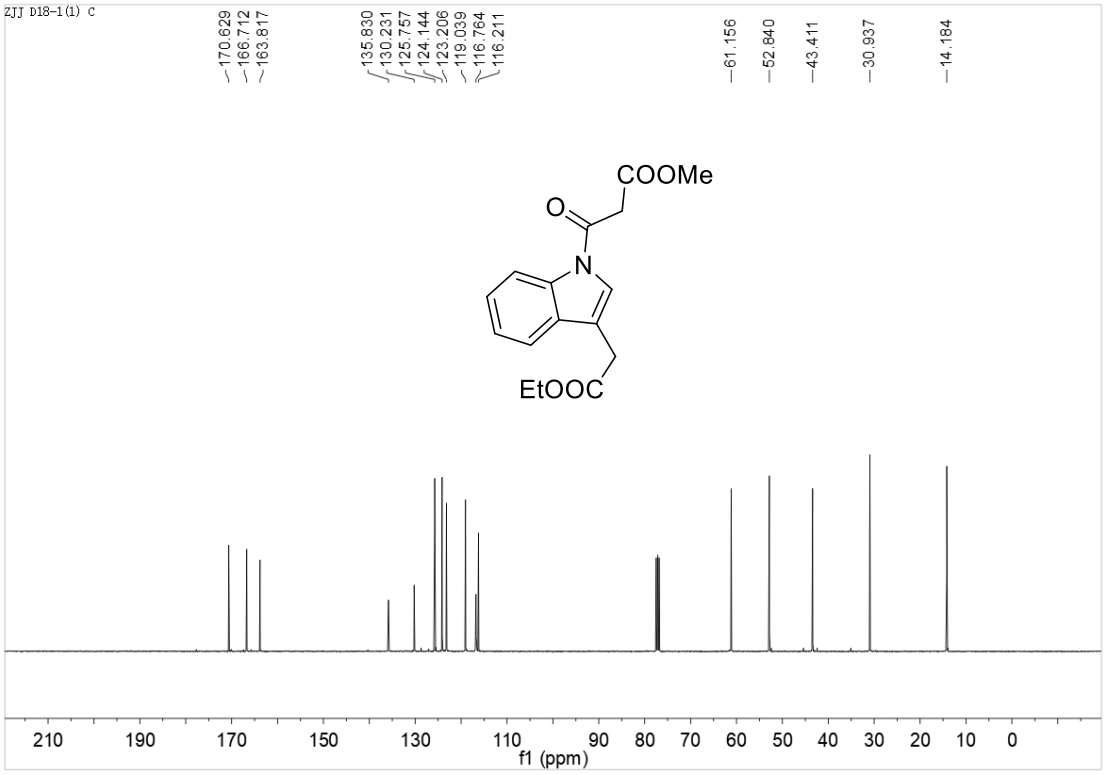

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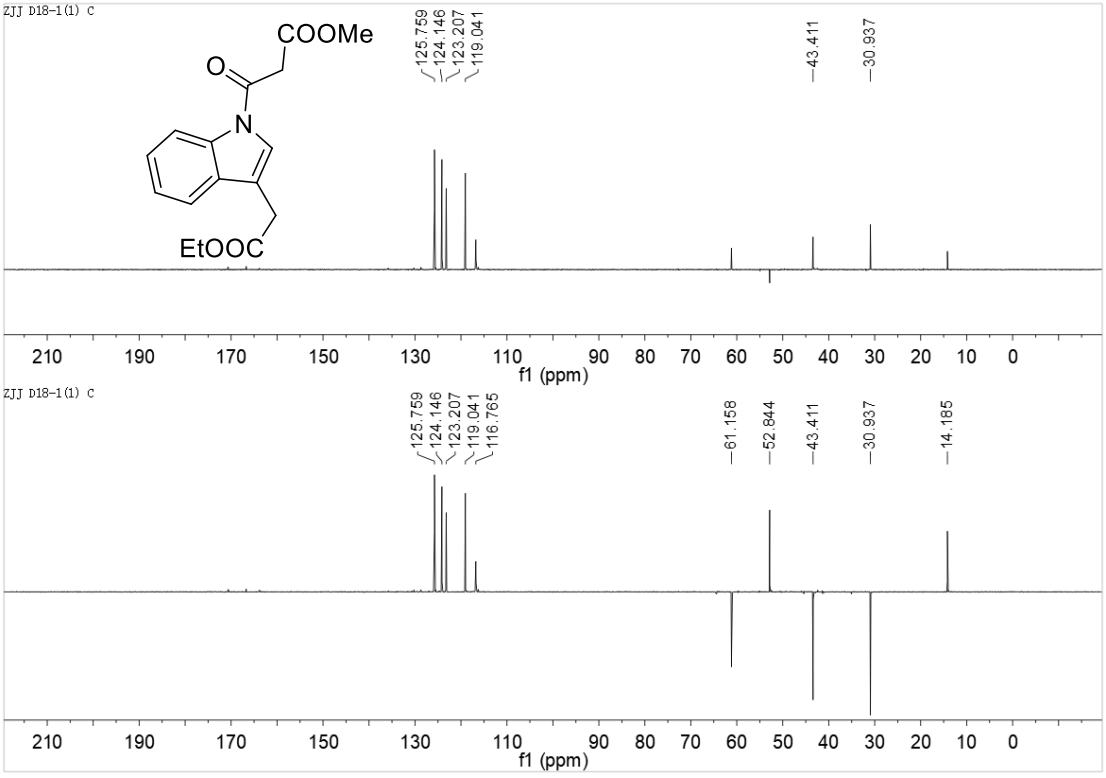

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