Supporting Information

Electroreductive Synthesis of Polyfunctionalized Pyridin-2-Ones from Acetoacetanilides and Carbon Disulfide with Oxygen Evolution

Lichun Xu, Zhongxiao Ma, Xi Hu, Xin Zhang, Shulin Gao, Deqiang Liang,* Baoling Wang, Weili Li, and Yanni Li*

[a] School of Chemistry and Chemical Engineering, Kunming University, Kunming 650214, China

E-mail: liangdq695@nenu.edu.cn, liyanni@kmu.edu.cn

Table of Contents

I. General considerations **3**

II. Optimization of reaction conditions **4**

III. Experimental details **7**

1. General procedure for the electrosynthesis of pyridin-2-ones **2** 7

2. General procedure for quenching experiments 8

3. Procedure for gram-scale experiment 8

4. Electricity on-off experiments 9

4. Reaction kinetic profiles 10

5. Procedures for Br_2 detection experiments 10

6. Oxygen detection tests 11

IV. Cyclic voltammetry studies **13**

V. Spectral data of products **21**

VI. Single crystal X-ray diffraction studies **32**

VII. UV-vis spectra **39**

VIII. IR spectra **41**

IX. Copies of ^{1}H, ^{19}F, ^{13}C and DEPT NMR spectra **44**

I. General considerations

Unless otherwise stated, commercially available chemicals were used without treatment. Reactions were monitored by thin layer chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography over 300-400 mesh silica gel under a positive pressure of air. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer using TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). Cyclic voltammetry studies were carried out on a CHI600E electrochemical workstation (Shanghai CH Instruments Co., China). UV-Vis measurements were carried out on a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan), and the IR spectra were recorded from KBr pellets in the wavenumbers of 4000~400 cm^{-1} using Cary 600 Series FTIR Spectrometer (Agilent Technologies Inc., USA). Electrolysis was performed using a DJS-292B dual display potentiostat (Shanghai Xinrui Instruments Co., China, Figure S1).

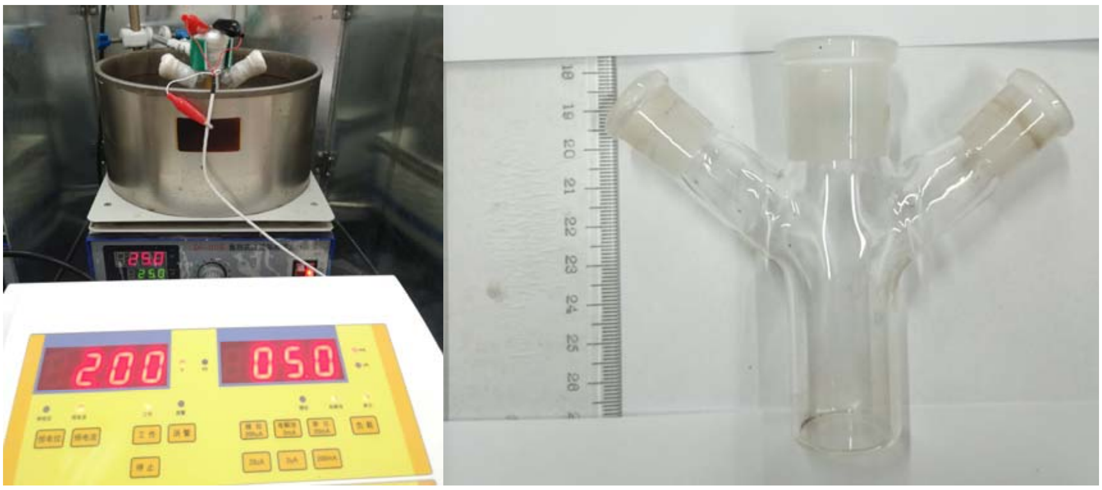
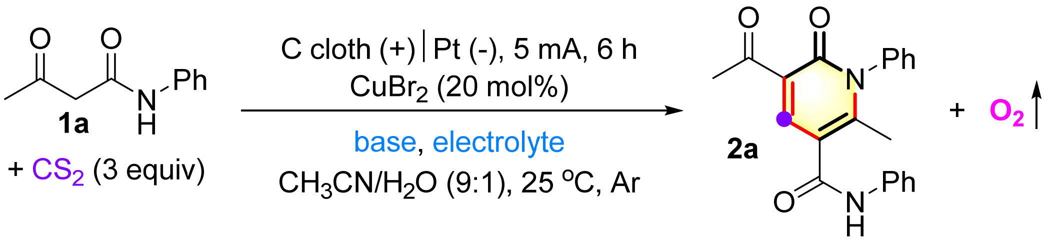


Figure S1 Electrochemical setup

II. Optimization of reaction conditions

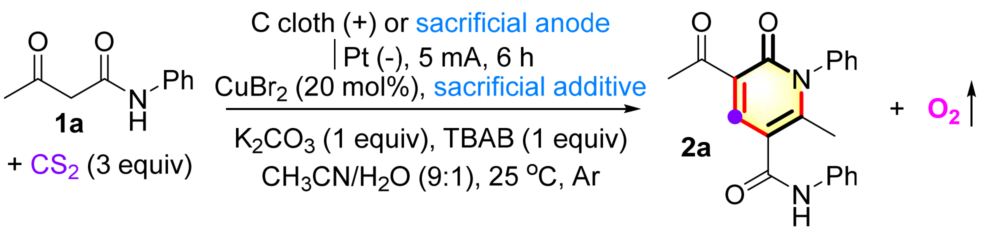
Table S1 Electrolyte and base screenings[a]



entry	electrolyte (equiv)	base (equiv)	isolated yield (%)
1	none	K_2CO_3 (1)	trace
2	**TBAB (1)**	**K_2CO_3 (1)**	44
3	CsBr (1)	K_2CO_3 (1)	22
4	TBAI (1)	K_2CO_3 (1)	trace
5	TBAC (1)	K_2CO_3 (1)	trace
6	*n*Bu_4NBF_4 (1)	K_2CO_3 (1)	22
7	$LiClO_4$ (1)	K_2CO_3 (1)	trace
8	TBAB (0.5)	K_2CO_3 (1)	38
9	*n*Bu_4NBF_4 (1) + TBAB (0.2)	K_2CO_3 (1)	27
10	TBAB (1)	none	nr
11	TBAB (1)	Na_2CO_3 (1)	40
12	TBAB (1)	Cs_2CO_3 (1)	41
13	TBAB (1)	$KHCO_3$ (1)	trace
14	TBAB (1)	K_3PO_4 (1)	20
15	TBAB (1)	*t*-BuOK (1)	37
16	TBAB (1)	2,6-lutidine	nr
17	TBAB (1)	Et_3N (1)	trace
18	TBAB (1)	K_2CO_3 (0.5)	37

[a] Undivided cell, carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), constant current = 5.0 mA, **1a** (0.5 mmol), CS_2 (1.5 mmol), $CuBr_2$ (0.1 mmol), CH_3CN/H_2O (9:1, v/v, 12.0 mL), Ar, 25 °C, 6 h.

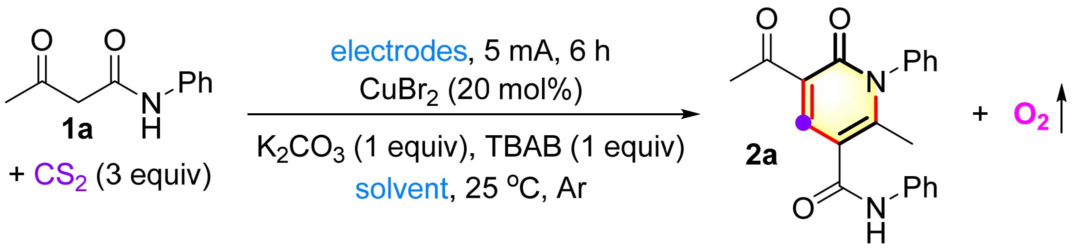
Table S2 Sacrificial anode and agent screenings[a]



entry	anode	sacrifice (equiv)	isolated yield (%)
1	C cloth	*i*Pr_2NEt (0.5)	16
2	C cloth	HBpin (0.5)	27
3	Cu	none	trace
4	stainless steel	none	trace
5	Ni	none	trace

[a] Undivided cell, platinum plate cathode (15 mm × 15 mm × 0.3 mm), constant current = 5.0 mA, **1a** (0.5 mmol), CS_2 (1.5 mmol), $CuBr_2$ (0.1 mmol), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol), CH_3CN/H_2O (9:1, v/v, 12.0 mL), Ar, 25 °C, 6 h.

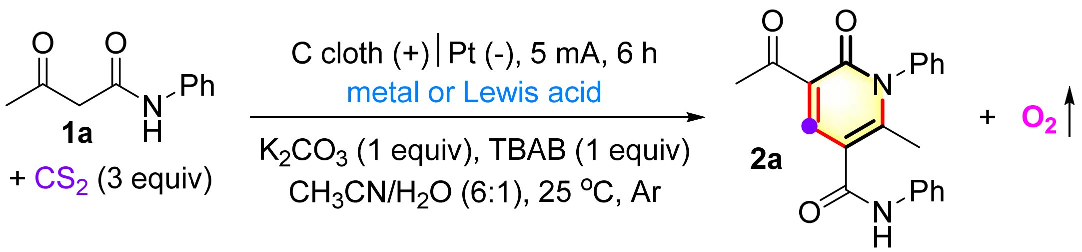
Table S3 Electrode and solvent screenings[a]



entry	anode	cathode	solvent	isolated yield (%)
1	C cloth	Pt	DCE/H_2O (9:1)	28
2	C cloth	Pt	THF/H_2O (9:1)	0
3	C cloth	Pt	DMF/H_2O (9:1)	11
4	C cloth	Pt	$DMSO/H_2O$ (9:1)	17
5	C cloth	Pt	$MeOH/H_2O$ (9:1)	trace
6	C cloth	Pt	$CH_3CN/MeOH$ (9:1)	trace
7	C cloth	Pt	CH_3CN/H_2O (4:1)	38
8	C cloth	Pt	**CH_3CN/H_2O (6:1)**	54
9	C cloth	Pt	CH_3CN/H_2O (11:1)	32
10	Pt	Pt	CH_3CN/H_2O (6:1)	25
11	graphite rod	Pt	CH_3CN/H_2O (6:1)	20
12	graphite felt	Pt	CH_3CN/H_2O (6:1)	21
13	graphite paper	Pt	CH_3CN/H_2O (6:1)	31
14	C cloth	Ni	CH_3CN/H_2O (6:1)	51
15	C cloth	Ni foam	CH_3CN/H_2O (6:1)	25
16	C cloth	stainless steel	CH_3CN/H_2O (6:1)	49
17	C cloth	Cu	CH_3CN/H_2O (6:1)	30
18	C cloth	graphite rod	CH_3CN/H_2O (6:1)	42
19	C cloth	C cloth	CH_3CN/H_2O (6:1)	46
20	C cloth	graphite paper	CH_3CN/H_2O (6:1)	50

[a] Undivided cell, electrodes, constant current = 5.0 mA, **1a** (0.5 mmol), CS_2 (1.5 mmol), $CuBr_2$ (0.1 mmol), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol), solvent (12.0 mL), Ar, 25 °C, 6 h.

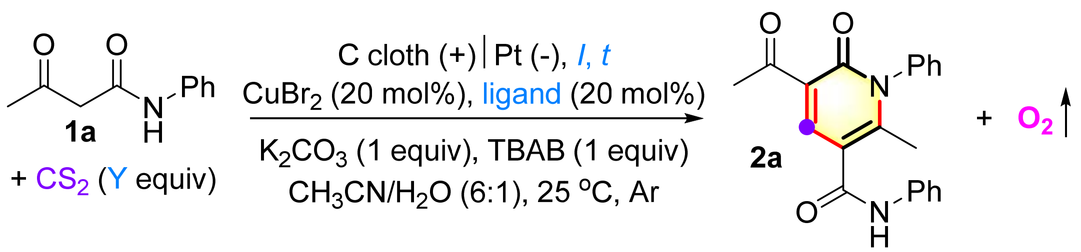
Table S4 Metal or Lewis acid screenings[a]



entry	metal or Lewis acid (mol%)	isolated yield (%)
1	none	nr
2	CuBr (20)	23
3	$CuCl_2$ (20)	50
4	$CuSO_4$ (20)	46
5	$Cu(acac)_2$ (20)	nr
6	CuTc (20)	33
7	$Pd(OAc)_2$ (20)	0
8	$CoCl_2$ (20)	trace
9	$NiCl_2$ (20)	42
10	$AgNO_3$ (20)	trace
11	$MnCl_2$ (20)	trace
12	$FeCl_3$ (20)	trace
13	$SnCl_4$ (20)	40
14	$CuBr_2$ (10)	11

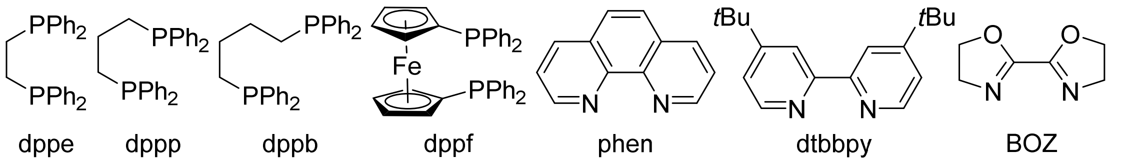
[a] Undivided cell, carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), constant current = 5.0 mA, **1a** (0.5 mmol), CS_2 (1.5 mmol), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol), CH_3CN/H_2O (6:1, v/v, 12.0 mL), Ar, 25 °C, 6 h.

Table S5 CS_2, current, time and ligand optimization[a]



entry	Y	*I* (mA), *t* (h)	ligand	isolated yield (%)
1	2	5, 6	_	51
2	3	3, 10	_	52
3	3	7.5, 4	_	51
4	3	**5, 7.5**	_	61
5	3	5, 9	_	54
6	3	5, 7.5	PPh_3	55

7	3	5, 7.5	PCy_3	40
8	3	5, 7.5	dppe	57
9	3	5, 7.5	dppp	50
10	**3**	**5, 7.5**	**dppb**	68
11	3	5, 7.5	dppf	57
12	3	5, 7.5	phen	37
13	3	5, 7.5	dtbbpy	52
14	3	5, 7.5	BOZ	43



[a] Undivided cell, carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), constant current, **1a** (0.5 mmol), CS_2, $CuBr_2$ (0.1 mmol), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol), CH_3CN/H_2O (6:1, v/v, 12.0 mL), Ar, 25 °C.

III. Experimental details

1. General procedure for the electrosynthesis of pyridin-2-ones 2

A custom-made undivided cell (Figure S1), equipped with a magnetic stirring bar, a carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, new or carefully polished until shining), was charged under argon sequentially with β-keto amide **1** (0.5 mmol), tetrabutylammonium bromide (TBAB, 1.0 equiv, 0.5 mmol, 161 mg), K_2CO_3 (1.0 equiv, 0.5 mmol, 69 mg), 1,4-bis(diphenylphosphino)butane (dppb, 20 mol%, 0.1 mmol, 43 mg), CH_3CN (10.3 mL), and a solution of $CuBr_2$ (20 mol%, 0.1 mmol, 22 mg) in H_2O (1.7 mL), followed by the addition of CS_2 (3.0 equiv, 1.5 mmol, 0.091 mL). The mixture was electrolyzed with stirring using a constant current of 5.0 mA at 25 °C (oil bath) for 7.5 h; then it was quenched with water (50.0 mL) and extracted with CH_2Cl_2 (30.0 mL) four times. The residue obtained after evaporation of the combined organic solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate–dichloromethane–triethylamine = 75:15:10:2) to afford pyridin-2-ones **2**.

This reaction is sensitive to electrode state and stirring conditions. New or carefully polished platinum plate cathode is necessary probably due to the passivation by sulfur-containing species, and there are reproducibility issues when the electrodes are wrapped in black paste.

2. General procedure for quenching experiments

A custom-made undivided cell, equipped with a magnetic stirring bar, a carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, new or carefully polished until shining), was charged under argon sequentially with *N*-(4-fluorophenyl)-3-oxobutanamide **1b4** (0.5 mmol, 98 mg), TBAB (1.0 equiv, 0.5 mmol, 161 mg), K_2CO_3 (1.0 equiv, 0.5 mmol, 69 mg), dppb (20 mol%, 0.1 mmol, 43 mg), a quencher, CH_3CN (10.3 mL), and a solution of $CuBr_2$ (20 mol%, 0.1 mmol, 22 mg) in H_2O (1.7 mL), followed by the addition of CS_2 (3.0 equiv, 1.5 mmol, 0.091 mL). The mixture was electrolyzed with stirring using a constant current of 5.0 mA at 25 °C (oil bath) for 7.5 h, and the yield of product **2b4** formed was determined by ^{19}F NMR analysis based on a 4,4'-difluoro-1,1'-biphenyl internal standard.

3. Procedure for gram-scale experiment

A 100-mL two-necked flask (Figure S2), equipped with a magnetic stirring bar, a carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, new or carefully polished until shining), was charged under argon sequentially with 3-oxo-*N*-(*p*-tolyl)butanamide **1b1** (6.0 mmol, 1.15 g), TBAB (1.0 equiv, 1.93 g), K_2CO_3 (1.0 equiv, 0.83 g), dppb (20 mol%, 0.51 g), CH_3CN (94.3 mL), and a solution of $CuBr_2$ (20 mol%, 0.27 g) in H_2O (15.7 mL), followed by the addition of CS_2 (3.0 equiv, 1.092 mL). The mixture was electrolyzed with stirring using a constant current of 60.0 mA at 25 °C (oil bath) for 7.5 h, *during which the electrodes were replaced with new ones at 1.5 h intervals*. Then, the reaction was quenched with water (300.0 mL) and extracted with CH_2Cl_2 (200.0 mL) four times. The residue obtained after evaporation of the combined organic solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate–dichloromethane–triethylamine = 75:15:10:2) to afford pyridin-2-ones **2b1** (54%, 607 mg). The current efficiency is 19%.

Figure S2 Setup for gram-scale experiment

4. Electricity on-off experiments

4,4'-Difluoro-1,1'-biphenyl (1 equiv) was added as an internal standard to the reaction mixture before electrolysis using **1b4** as the substrate. 0.05 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	h	%
Comments		
1	0	0
2	2	16
3	4	19
4	6	46
5	8	51
6	10	75
7	12	70

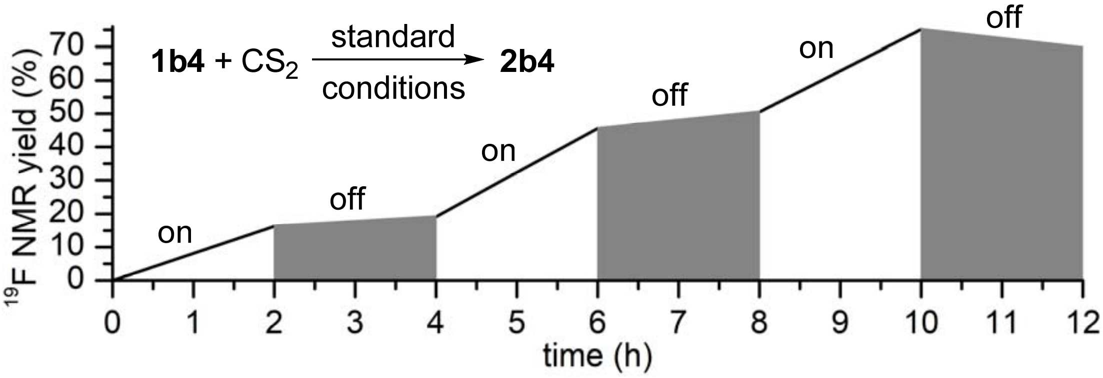


Figure S3 Intermittent electrolysis experiments

4. Reaction kinetic profiles

4,4'-Difluoro-1,1'-biphenyl (1 equiv) was added as an internal standard to the reaction mixture before electrolysis using **1b4** as the substrate. 0.05 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	h	%
Comments		
1	0	0
2	2	13
3	4	36
4	6	84
5	8	97
6	10	84
7	12	85

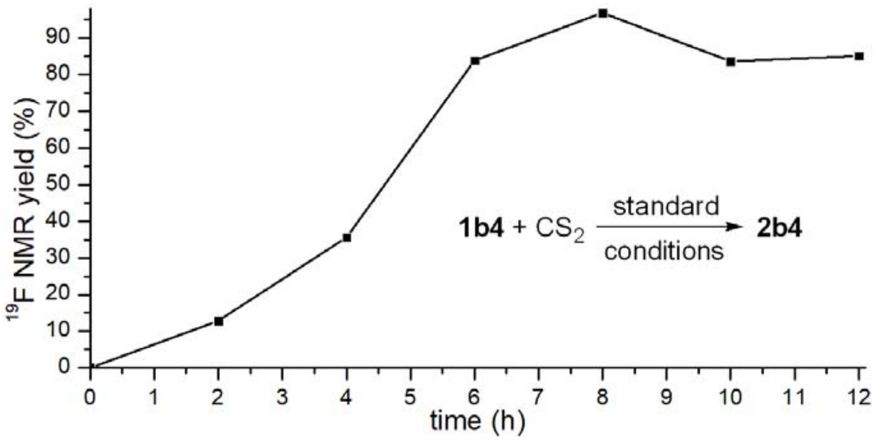
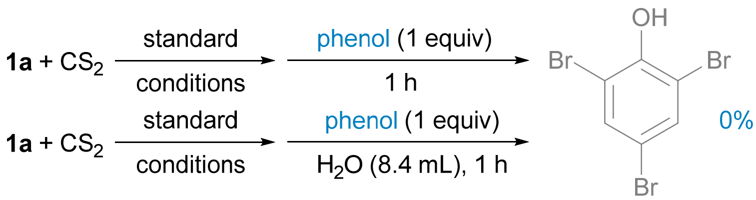


Figure S4 Reaction kinetic profiles

5. Procedures for Br_2 detection experiments

Conditions 1: A custom-made undivided cell, equipped with a magnetic stirring bar, a carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, new or carefully polished until shining), was charged under argon sequentially with 3-oxo-*N*-phenylbutanamide **1a** (0.5 mmol, 89 mg), TBAB (1.0 equiv, 0.5 mmol, 161 mg), K_2CO_3 (1.0 equiv, 0.5 mmol, 69 mg), dppb (20 mol%, 0.1 mmol, 43 mg), a quencher, CH_3CN (10.3 mL), and a solution of $CuBr_2$ (20 mol%, 0.1 mmol, 22 mg) in H_2O (1.7 mL), followed by the addition of CS_2 (3.0 equiv, 1.5 mmol, 0.091 mL). The mixture was electrolyzed with stirring using a constant current of 5.0 mA at 25 °C (oil bath) for 7.5 h. Then, phenol (1.0 equiv, 0.5 mmol, 47 mg) was added, and the resultant mixture was stirred at room temperature for another 1 h under air. The formation of 2,4,6-tribromophenol was checked by comparing with the purchased standard product through TLC and gas chromatography-mass spectrometry (GC-MS) analyses.

Conditions 2: A custom-made undivided cell, equipped with a magnetic stirring bar, a carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, new or carefully polished until shining), was charged under argon sequentially with 3-oxo-*N*-phenylbutanamide **1a** (0.5 mmol, 89 mg), TBAB (1.0 equiv, 0.5 mmol, 161 mg), K_2CO_3 (1.0 equiv, 0.5 mmol, 69 mg), dppb (20 mol%, 0.1 mmol, 43 mg), a quencher, CH_3CN (10.3 mL), and a solution of $CuBr_2$ (20 mol%, 0.1 mmol, 22 mg) in H_2O (1.7 mL), followed by the addition of CS_2 (3.0 equiv, 1.5 mmol, 0.091 mL). The mixture was electrolyzed with stirring using a constant current of 5.0 mA at 25 °C (oil bath) for 7.5 h. Then, H_2O (8.4 mL) and phenol (1.0 equiv, 0.5 mmol, 47 mg) was added, and the resultant mixture was stirred at room temperature for another 1 h under air. The formation of 2,4,6-tribromophenol was checked by comparing with the purchased standard product through TLC and GC-MS analyses.



Scheme S1 Br_2 detection

6. Oxygen detection tests

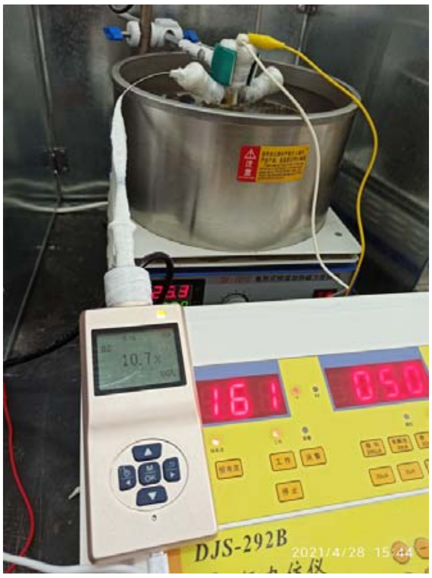


Figure S5 Setup for oxygen detection tests

The oxygen detection tests were conducted with an O_2 detector (XLA-BX-O2, Figure S5), which was connected with the model reaction under standard conditions by a syringe with pumping on.

	A(X)	G1(Y)	G2(Y)	F1(Y)	F2(Y)	E1(Y)	E2(Y)	D1(Y)	D2(Y)	C1(Y)	B(Y)
Long Name	time	oxygen conc	oxygen conc	oxygen conc	oxygen conc	oxygen conc	oxygen conc	oxygen conc	oxygen conc	oxygen conc	oxygen conc
Units	min	vol%	vol%	vol%	vol%	vol%	vol%	vol%	vol%	vol%	vol%
Comments		run 5, electricity off	run 5, electricity on	run 4, off	run 4, on	run 3, off	run 3, on	run 2, off	run 2, on	run 1, off	run 1, on
1	0	0	0.4	0	0	0	0	0	0	0	0.3
2	1	0	0.7	0	0.1	0	0.1	0	0.1	0	0.4
3	2	0.1	0.8	0	0.2	0.1	0.4	0	0.4	0	0.9
4	3	0.1	1	0	0.4	0.1	0.7	0	0.8	0	1.2
5	4	0.2	1.2	0	0.6	0.2	1	0	1	0.2	1.6
6	5	0.4	1.4	0.1	0.8	0.2	1.4	0	1.2	0.4	2
7	6	0.4	1.6	0.2	1.1	0.3	1.8	0	1.3	0.4	2.4
8	7	0.5	1.8	0.3	1.3	0.3	2.2	0	1.4	0.4	3
9	8	0.5	2	0.4	1.4	0.4	2.3	0	1.6	0.4	3.2
10	9	0.6	2.3	0.5	1.6	0.4	2.3	0	1.7	0.4	3.4
11	10	0.6	2.4	0.6	2	0.4	2.4	0	2	0.5	3.8
12	11		2.7								
13	12		2.8								
14	13		2.9								
15	14		3.1								
16	15		3.3								
17	16		3.5								
18	17		3.7								
19	18		3.9								
20	19		4								
21	20		4.5								

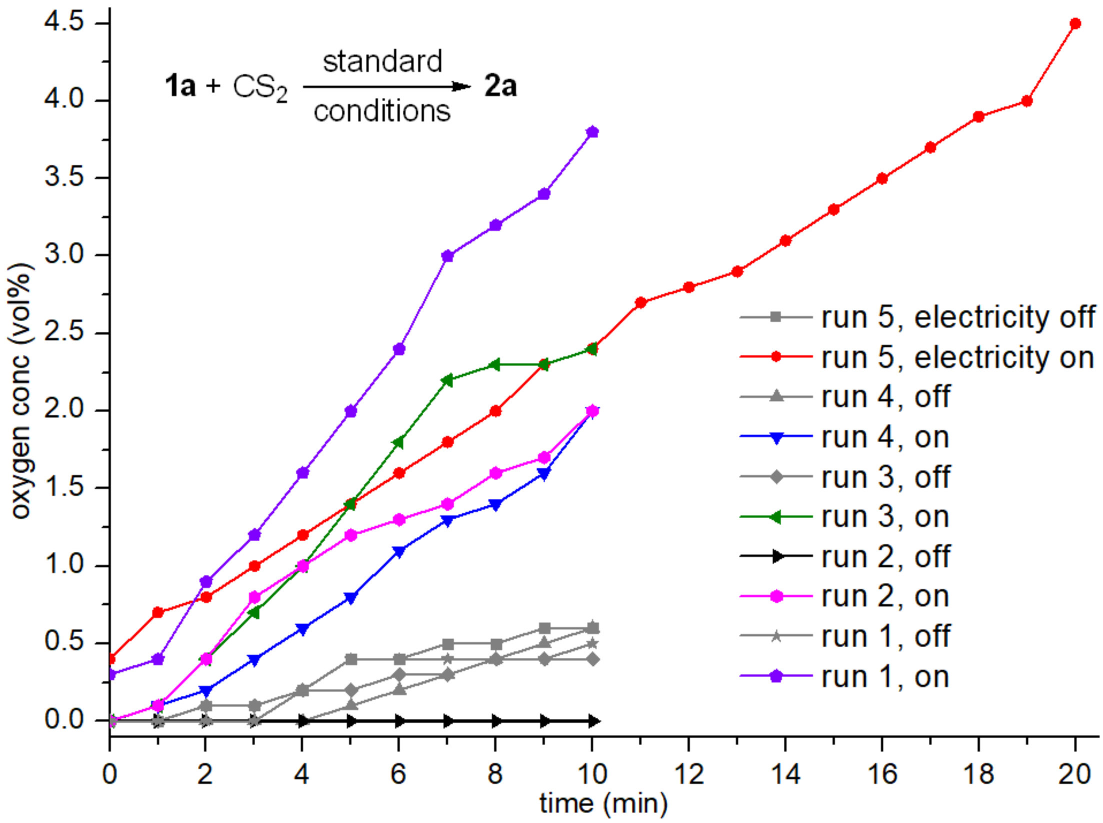


Figure S6 Oxygen detection

IV. Cyclic voltammetry studies

General procedure: Cyclic voltammetries were performed in a three-electrode cell (Figure S1) at room temperature. The working electrode was a glassy carbon (GC) disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl (KCl) electrode submerged in a saturated aqueous KCl solution, and separated from reactions by a salt bridge. 10 mL of CH_3CN/H_2O (6:1, v/v) or CH_3CN solution containing 1.0 mmol *n*Bu_4NBF_4 was poured into the electrochemical cell. The scan was started at 0 V and then the potential was then scanned in the negative direction at a scan rate of 100 mV s^{-1} unless stated otherwise.

In the cyclic voltammogram of CH_3CN/H_2O (6:1) in the region of -2.0–2.0 V vs. Ag/AgCl (red line, Figure S7), the oxidation wave of water is significant.

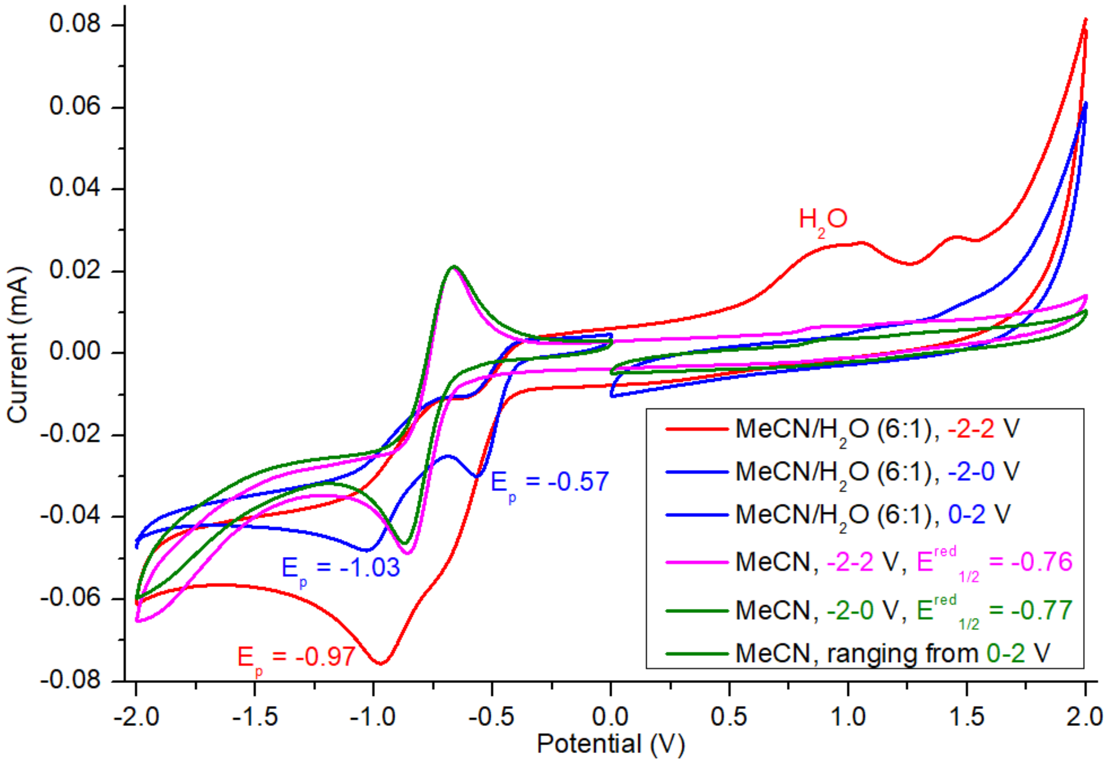
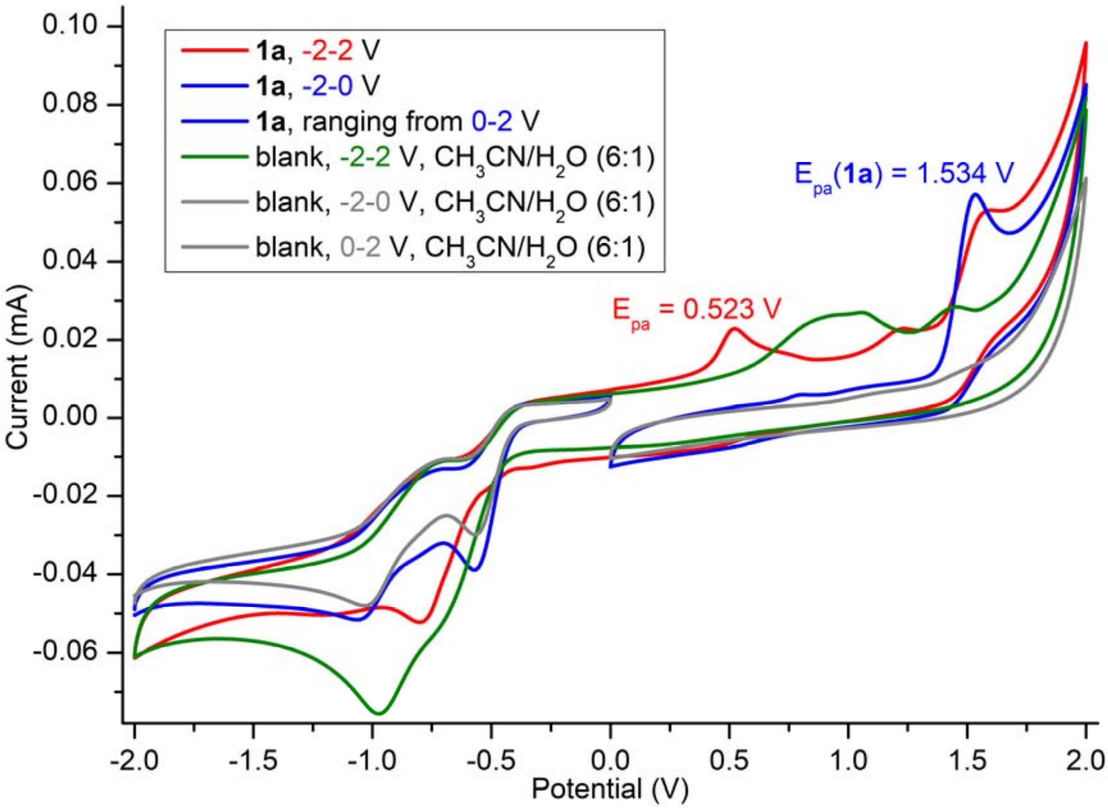
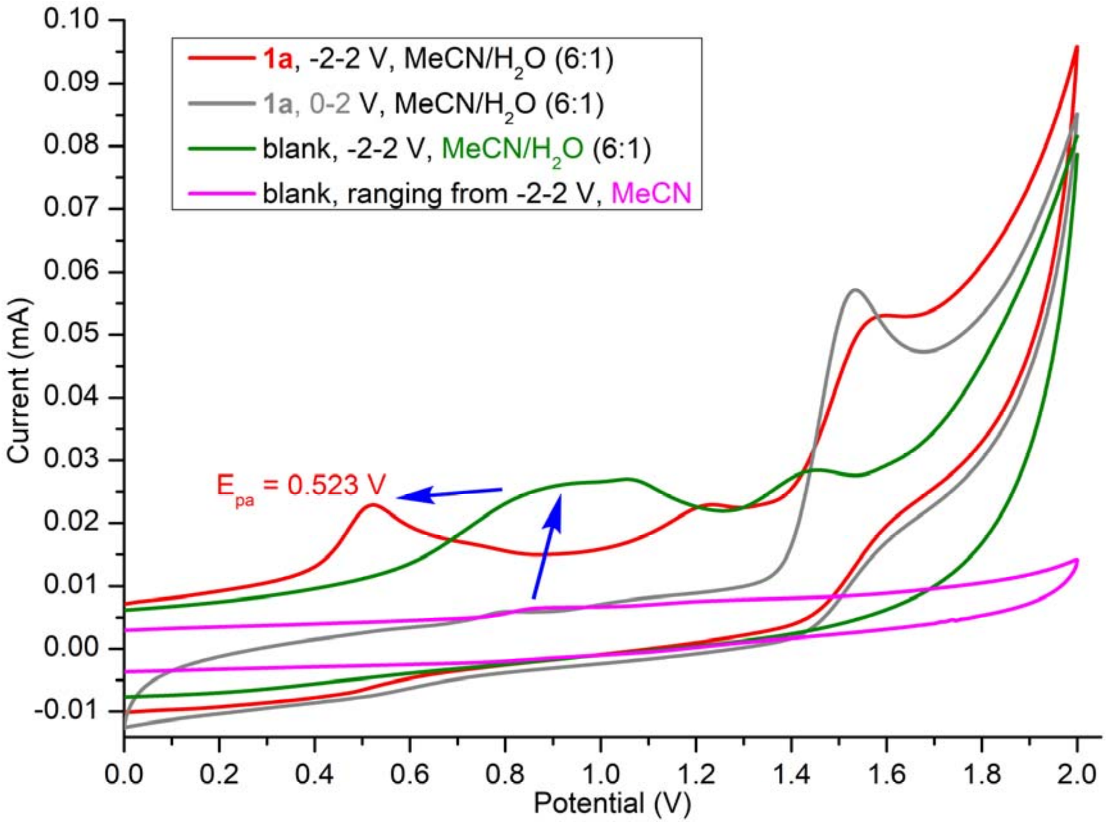


Figure S7 Cyclic voltammograms of the **solvent** CH_3CN and the CH_3CN/H_2O mixture (6:1, v/v)) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference electrode in 0.1 M *n*Bu_4NBF_4

New oxidation waves were observed at 0.52 V (in aqueous CH_3CN) or 0.43 V (in CH_3CN) upon addition of **1a**, the oxidation potentials of which are 1.53 V (in aqueous CH_3CN) or 1.85 V (in CH_3CN) vs. Ag/AgCl (Figures S8 and S9). It seems that the oxidation potentials of H_2O decreased upon addition of **1a**.



1a, -2-2 V
1a, -2-0 V
1a, ranging from 0-2 V
blank, -2-2 V, CH3CN/H2O (6:1)
blank, -2-0 V, CH3CN/H2O (6:1)
blank, 0-2 V, CH3CN/H2O (6:1)
Epa(1a) = 1.534 V
Epa = 0.523 V
Current (mA)
Potential (V)



1a, -2-2 V, MeCN/H2O (6:1)
1a, 0-2 V, MeCN/H2O (6:1)
blank, -2-2 V, MeCN/H2O (6:1)
blank, ranging from -2-2 V, MeCN
Epa = 0.523 V
Current (mA)
Potential (V)

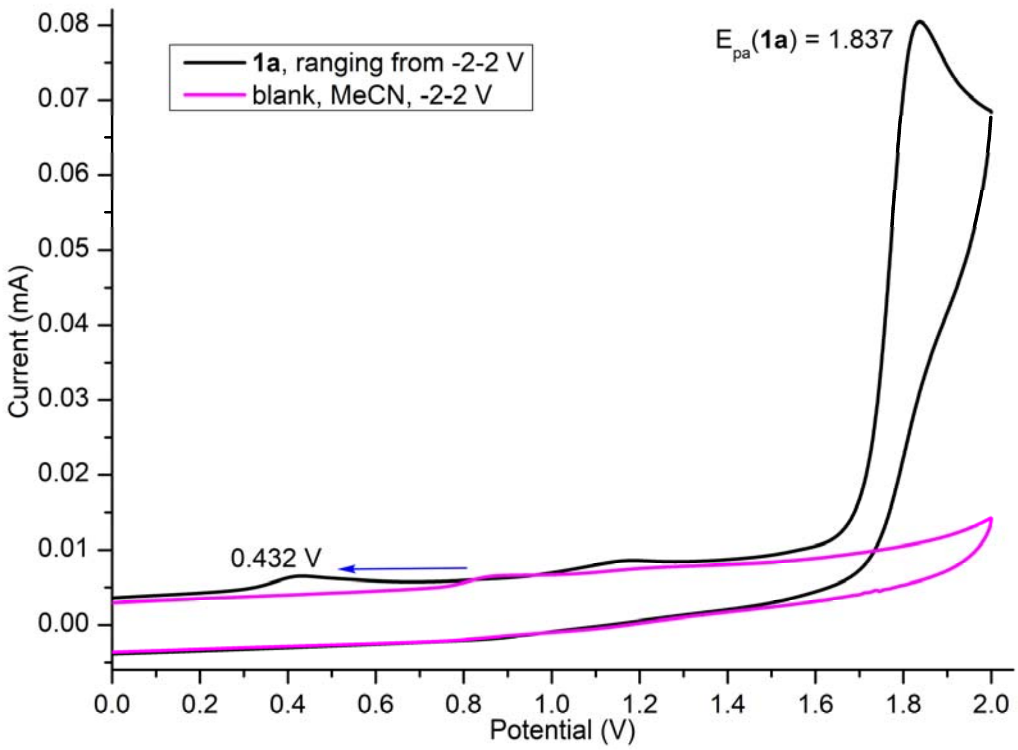


Figure S8 Cyclic voltammograms of **1a** (10^{-3} M) in CH_3CN or **CH_3CN/H_2O** (6:1, v/v)) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

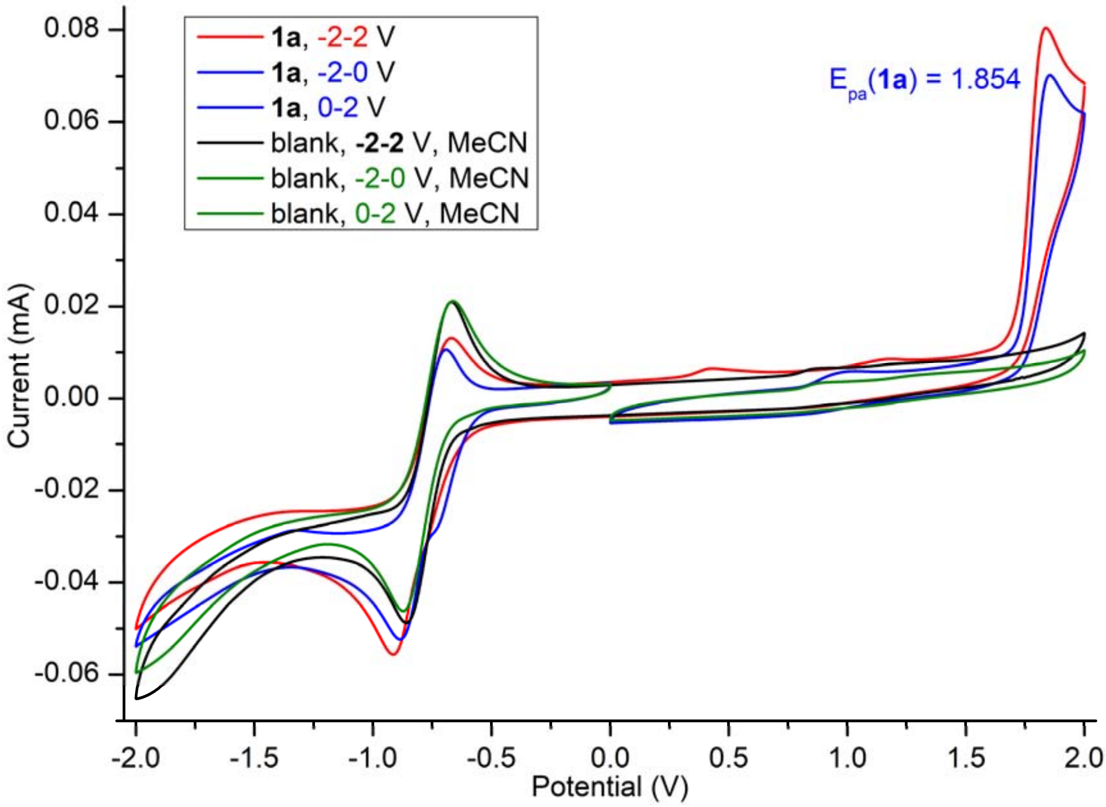


Figure S9 Cyclic voltammograms of **1a** (10^{-3} M) **in CH_3CN**

In CH_3CN/H_2O (6:1, v/v), higher current responses were observed upon introduction of K_2CO_3, and the reduction potentials decreased (red line and pink line, Figure S10).

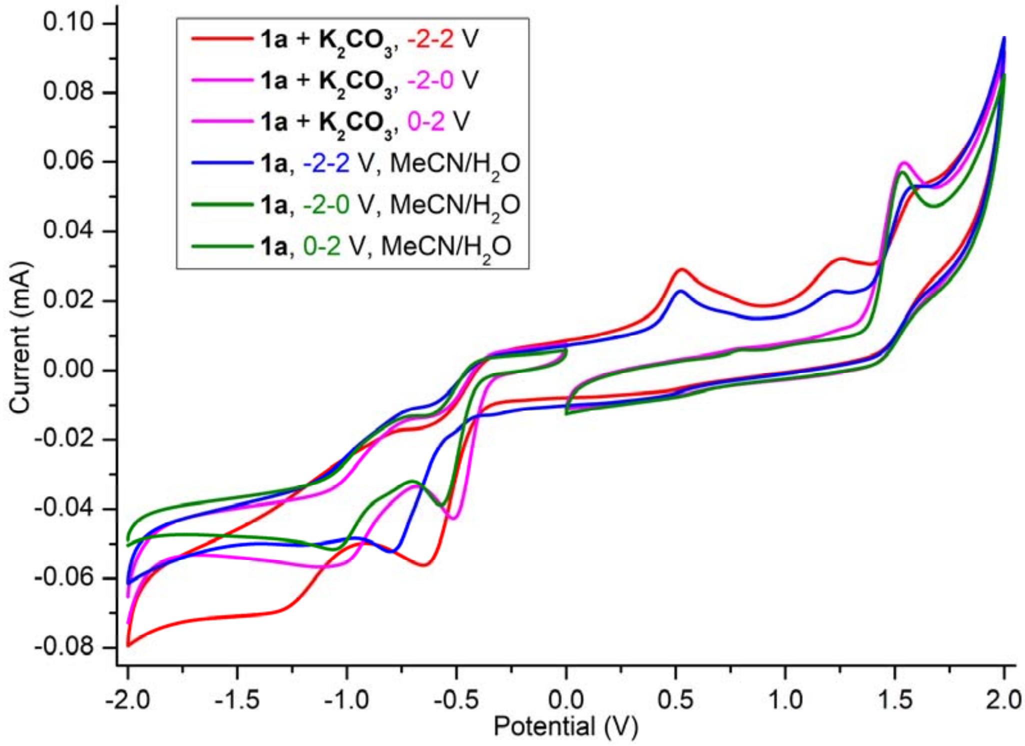


Figure S10 Cyclic voltammograms of **1a** (10^{-3} M **in CH_3CN/H_2O (6:1**, v/v)) in the presence or absence of K_2CO_3 (10^{-3} M) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

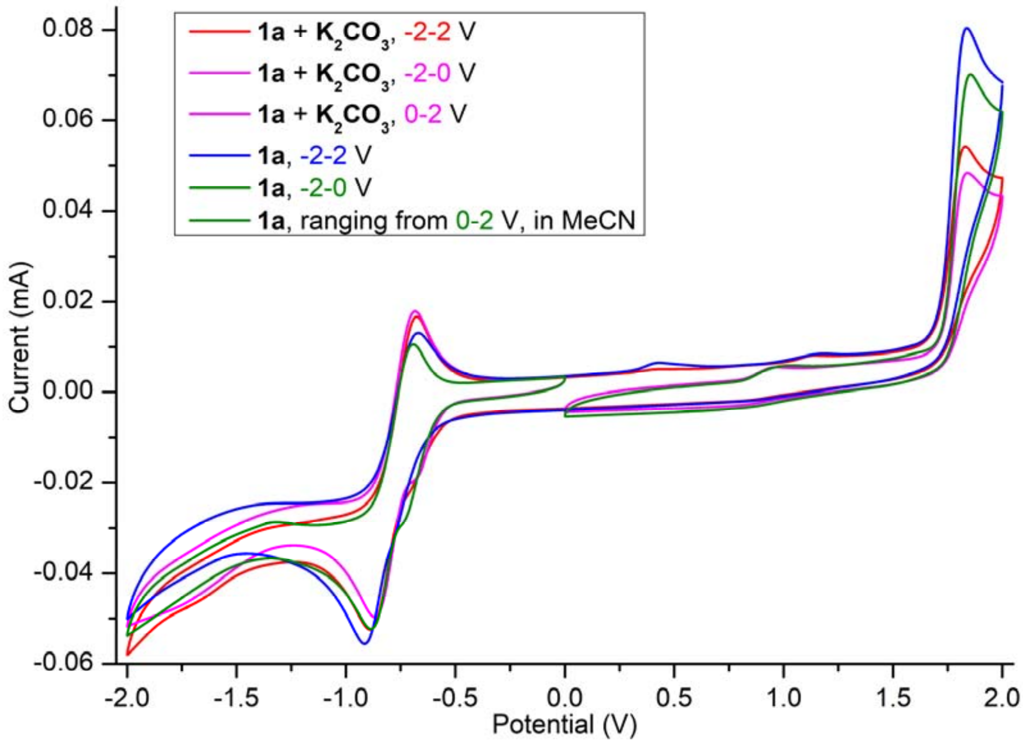


Figure S11 Cyclic voltammograms of **1a** (10^{-3} M **in CH_3CN**) in the presence or absence of K_2CO_3 (10^{-3} M) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

The oxidation potentials of H_2O decreased as well upon addition of CS_2 (Figures S12-S14).

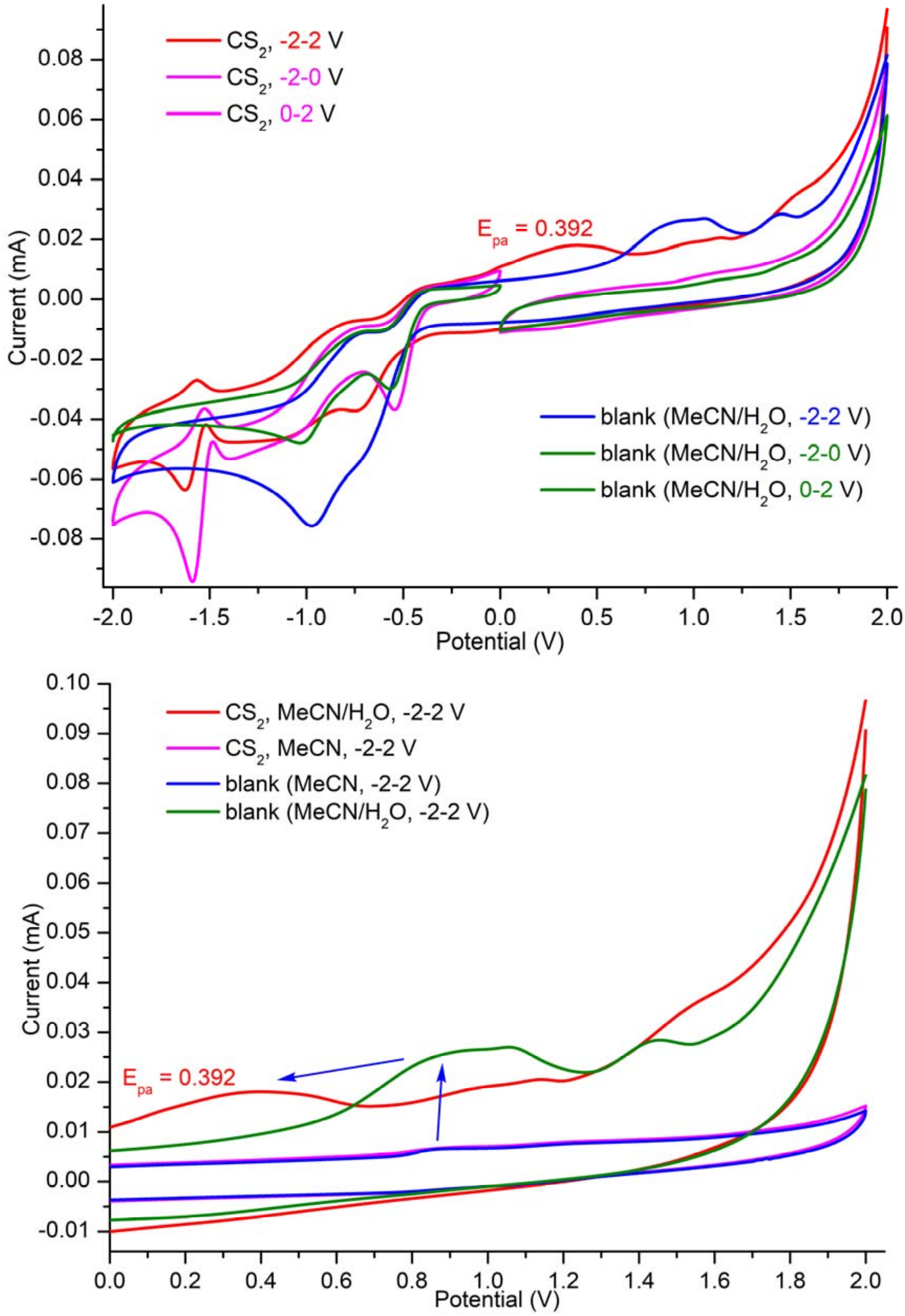


Figure S12 Cyclic voltammograms of CS_2 (10^{-3} M) in CH_3CN or $\mathbf{CH_3CN/H_2O}$ (6:1, v/v)) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M nBu$_4$NBF$_4$

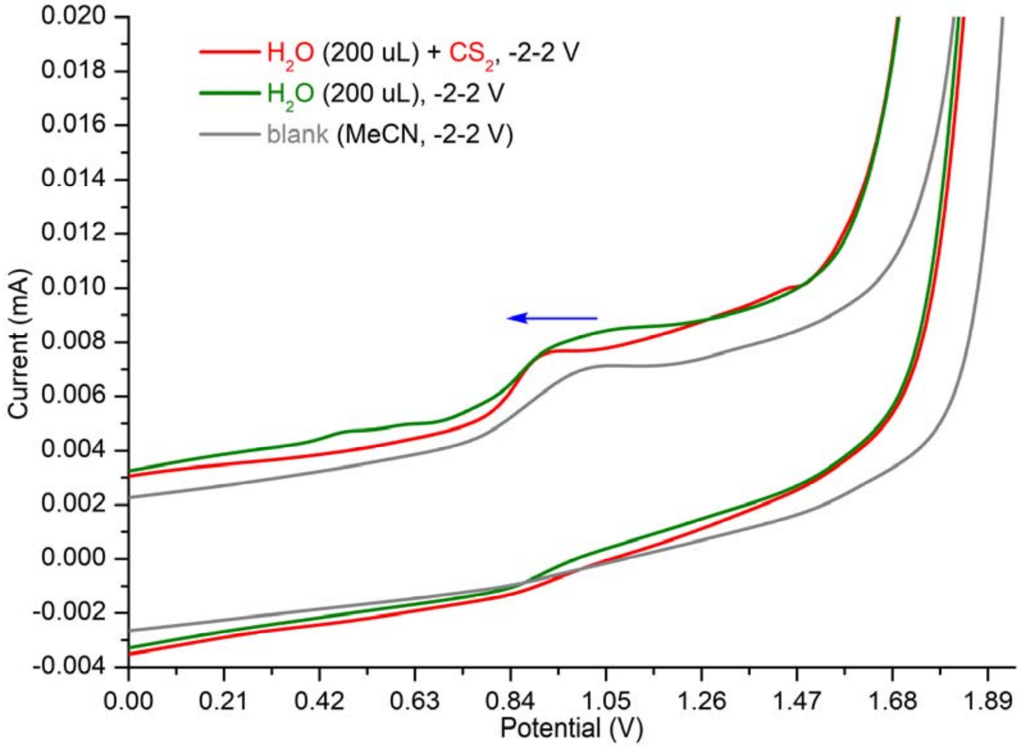


Figure S13 Cyclic voltammograms of H_2O (200 uL) in CH_3CN in the presence or absence of CS_2 (10^{-3} M) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

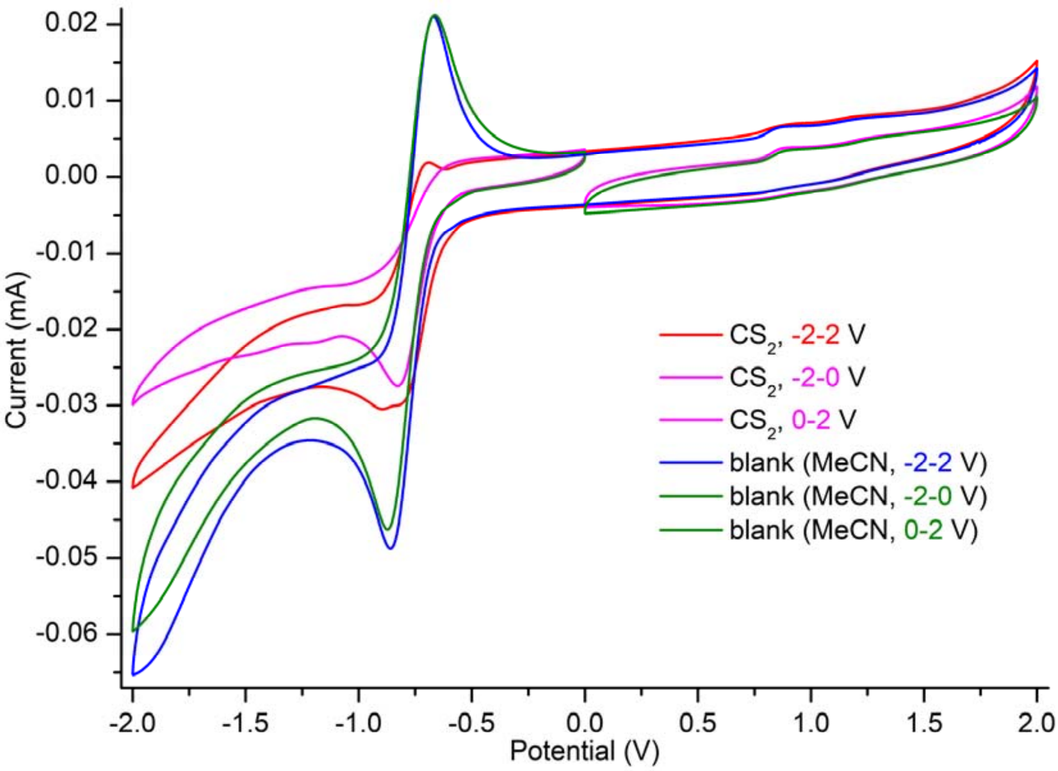


Figure S14 Cyclic voltammograms of CS_2 (10^{-3} M) in CH_3CN with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

In the presence of the ligand dppb, the CV tests of $CuBr_2$ showed no obvious redox wave in aqueous CH_3CN in the region of -1.60–1.85 V vs. Ag/AgCl (Figure S15).

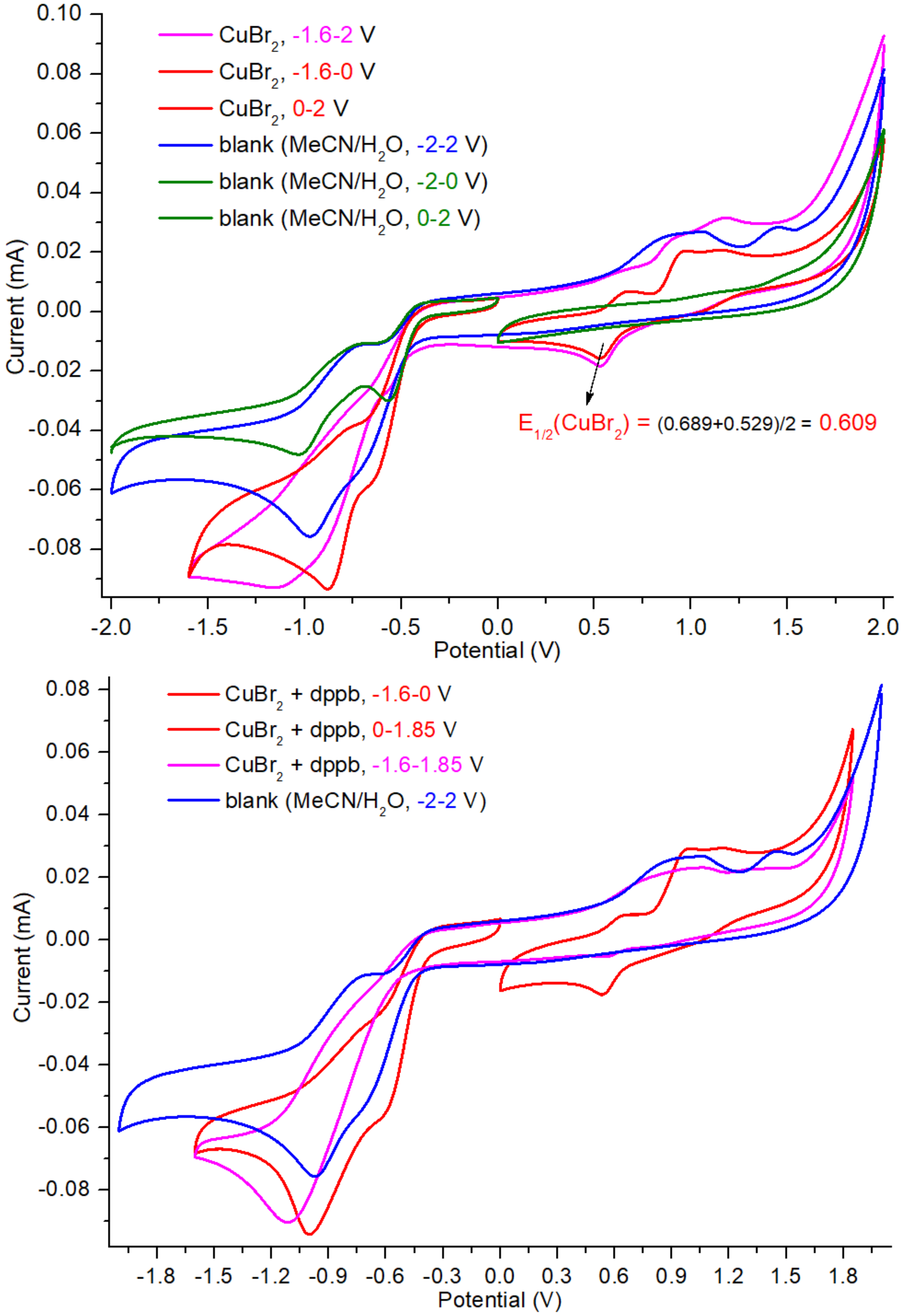


Figure S15 Cyclic voltammograms of $CuBr_2$ (10^{-3} M in CH_3CN/H_2O (6:1, v/v)) in the presence or absence of dppb (10^{-3} M) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

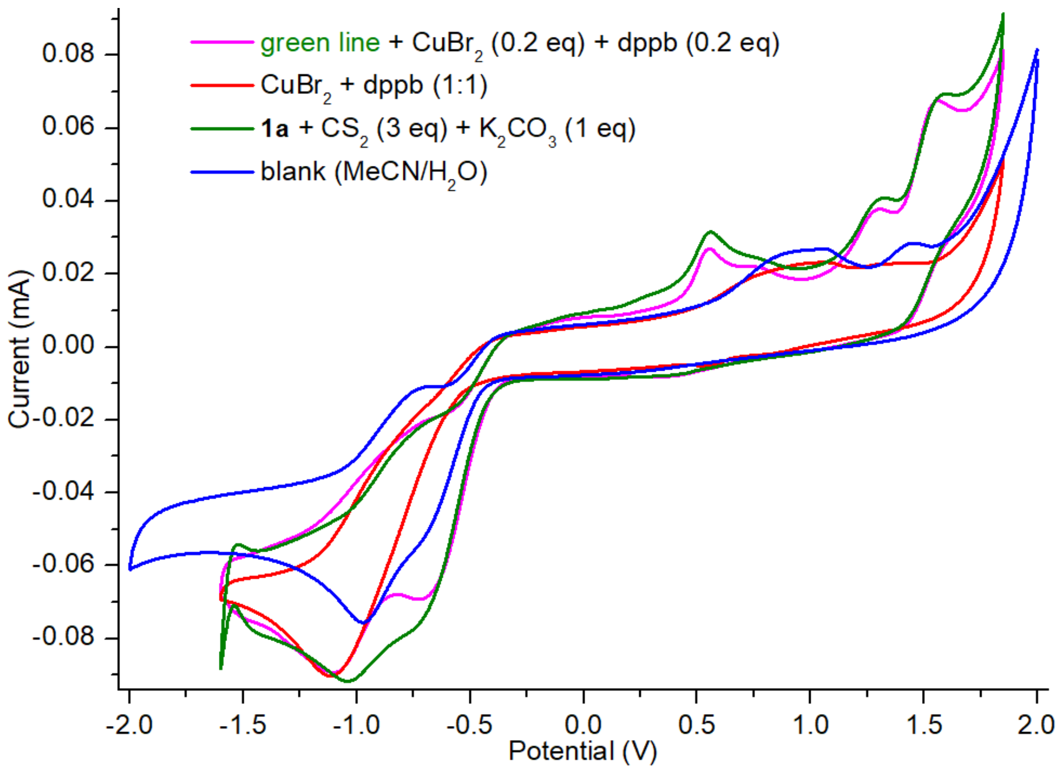


Figure S16 Key cyclic voltammograms of reaction mixtures (10^{-3} M) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

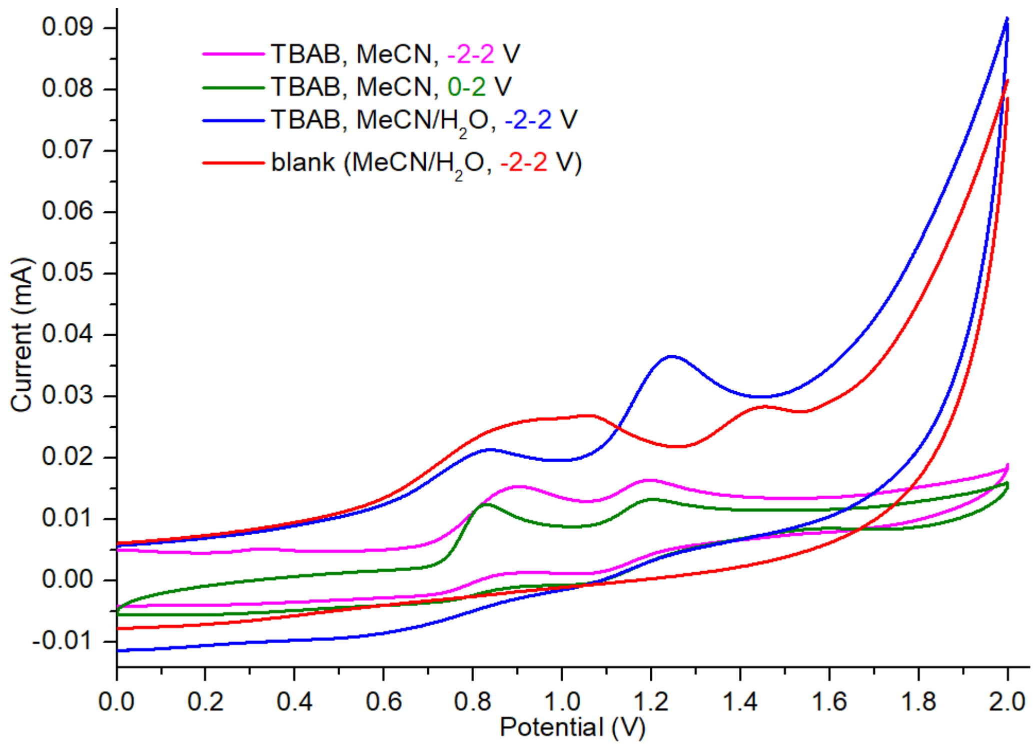
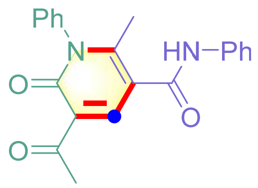
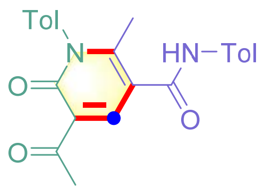


Figure S17 Key cyclic voltammograms of TBAB (10^{-3} M) with GC as the working electrode, Pt wire as the counter electrode, Ag/AgCl (KCl) as the reference in 0.1 M *n*Bu_4NBF_4

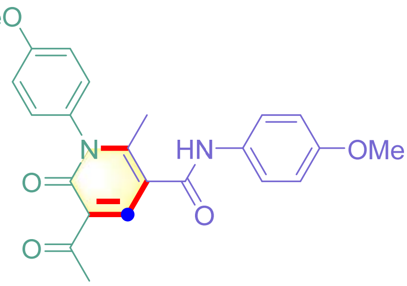
V. Spectral data of products



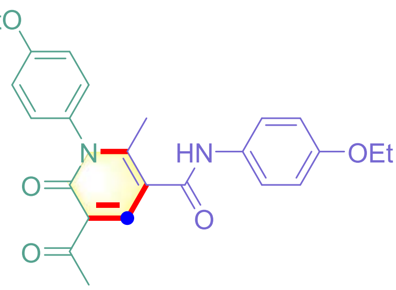
2a, 5-acetyl-2-methyl-6-oxo-*N*,1-diphenyl-1,6-dihydropyridine-3-carboxamide, pale yellow solid: mp 249–250 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.45 (s, 1H, NH), 8.27 (s, 1H, ArH), 7.68 (d, J = 7.5 Hz, 2H, ArH), 7.61 (dd, J = 8.3, 6.6 Hz, 2H, ArH), 7.54 (dddd, J = 7.4, 7.4, 2.6, 2.2 Hz, 1H, ArH), 7.37 – 7.33 (m, 4H, ArH), 7.11 (dd, J = 7.2, 7.2 Hz, 1H, ArH), 2.54 (s, 3H, CH_3), 2.15 (s, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 196.3 (MeCO), 165.1 (NCO), 161.2 (NCO), 155.3 (ArC), 142.7 (ArC), 139.4 (ArC), 138.7 (ArC), 130.3 (ArC), 129.5 (ArC), 129.2 (ArC), 128.4 (ArC), 124.3 (ArC), 123.4 (ArC), 120.3 (ArC), 115.7 (ArC), 31.1 (CH_3), 20.5 (CH_3). HRMS (ESI-TOF) Calcd for $C_{21}H_{19}N_2O_3^+$ ([M+H]$^+$) 347.1390. Found 347.1399.



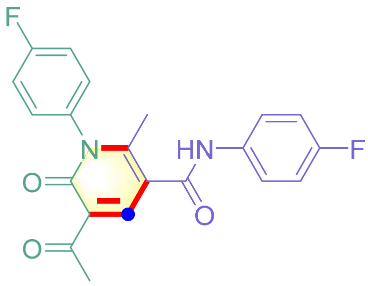
2b1, 5-acetyl-2-methyl-6-oxo-*N*,1-di-*p*-tolyl-1,6-dihydropyridine-3-carboxamide, pale yellow crystal: mp 292–293 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H, NH), 8.23 (s, 1H, ArH), 7.55 (d, J = 8.4 Hz, 2H, ArH), 7.40 (d, J = 8.1 Hz, 2H, ArH), 7.19 (d, J = 8.3 Hz, 2H, ArH), 7.15 (d, J = 8.3 Hz, 2H, ArH), 2.53 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.14 (s, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 196.4 (MeCO), 165.0 (NCO), 161.3 (NCO), 155.4 (ArC), 142.5 (ArC), 139.0 (ArC), 136.8 (ArC), 136.1 (ArC), 133.3 (ArC), 130.7 (ArC), 129.6 (ArC), 128.0 (ArC), 123.3 (ArC), 120.3 (ArC), 115.8 (ArC), 31.1 (CH_3), 21.2 (CH_3), 21.0 (CH_3), 20.5 (CH_3). HRMS (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_3^+$ ([M+H]$^+$) 375.1703. Found 375.1701.



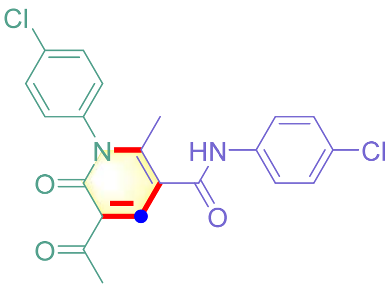
2b2, 5-acetyl-*N*,1-bis(4-methoxyphenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 250–251 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1H, NH), 8.23 (s, 1H, ArH), 7.58 (d, J = 9.0 Hz, 2H, ArH), 7.24 (ddd, J = 8.9, 3.2, 2.3 Hz, 2H, ArH), 7.12 (ddd, J = 8.9, 3.3, 2.2 Hz, 2H, ArH), 6.92 (ddd, J = 9.0, 3.5, 2.2 Hz, 2H, ArH), 3.84 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.53 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.5 (MeCO), 164.8 (NCO), 161.4 (NCO), 159.8 (ArC), 156.1 (ArC), 155.7 (ArC), 142.5 (ArC), 132.5 (ArC), 131.2 (ArC), 129.4 (ArC), 123.3 (ArC), 121.9 (ArC), 115.7 (ArC), 115.3 (ArC), 114.3 (ArC), 55.9 (OCH_3), 55.7 (OCH_3), 31.1 (CH_3), 20.5 (CH_3). HRMS (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_5^+$ ([M+H]$^+$) 407.1601. Found 407.1589.



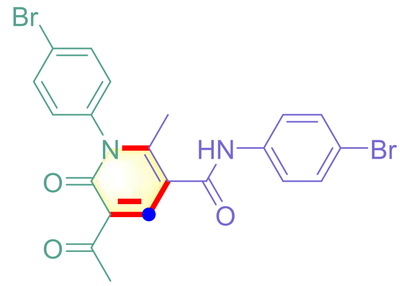
2b3, 5-acetyl-*N*,1-bis(4-ethoxyphenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, brown solid: mp 243–244 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H, NH), 8.22 (s, 1H, ArH), 7.57 (d, J = 9.0 Hz, 2H, ArH), 7.22 (ddd, J = 8.9, 3.2, 2.3 Hz, 2H, ArH), 7.10 (ddd, J = 8.9, 3.3, 2.3 Hz, 2H, ArH), 6.90 (ddd, J = 9.1, 3.5, 2.3 Hz, 2H, ArH), 4.10 (q, J = 7.0 Hz, 2H, OCH_2), 3.99 (q, J = 6.9 Hz, 2H, OCH_2), 2.53 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.37 (t, J = 7.0 Hz, 3H, CH_2CH_3), 1.31 (t, J = 7.0 Hz, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.5 (MeCO), 164.8 (NCO), 161.4 (NCO), 159.0 (ArC), 155.7 (ArC), 155.3 (ArC), 142.5 (ArC), 132.4 (ArC), 131.1 (ArC), 129.4 (ArC), 123.2 (ArC), 121.9 (ArC), 115.7 (ArC), 114.8 (ArC), 63.9 (OCH_2), 63.6 (OCH_2), 31.1 (CH_3), 20.5 (CH_3), 15.15 (CH_3), 15.09 (CH_3). IR (KBr): v = 2972, 2933, 1682, 1647, 1603, 1511, 1475, 1247, 1174, 1116, 1045. HRMS (ESI-TOF) Calcd for $C_{25}H_{27}N_2O_5^+$ ([M+H]$^+$) 435.1914. Found 435.1914.



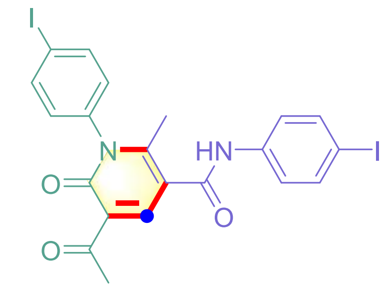
2b4, 5-acetyl-*N*,1-bis(4-fluorophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, brown solid: mp 222–223 °C. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 11.61 (s, 1H, NH), 8.74 (s, 1H, ArH), 8.03 (dd, *J* = 8.9, 4.9 Hz, 2H, ArH), 7.29 (dd, *J* = 8.6, 8.6 Hz, 2H, ArH), 7.22 (dd, *J* = 9.7, 6.9 Hz, 4H, ArH), 2.68 (s, 3H, CH_3), 2.31 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, Pyridine-d_5) δ 195.7 (MeCO), 165.4 (NCO), 162.6 (d, *J* = 248.0 Hz, ArC), 161.4 (NCO), 159.3 (d, *J* = 241.8 Hz, ArC), 155.2 (ArC), 142.8 (ArC), 136.2 (d, *J* = 2.7 Hz, ArC), 134.8 (d, *J* = 3.2 Hz, ArC), 130.1 (d, *J* = 8.8 Hz, ArC), 122.3 (d, *J* = 7.7 Hz, ArC), 116.9 (d, *J* = 23.1 Hz, ArC), 115.9 (ArC), 115.6 (d, *J* = 22.3 Hz, ArC), 30.9 (CH_3), 20.0 (CH_3). ^{19}F NMR (376 MHz, Pyridine-d_5) δ -112.18 – -112.25 (m, 1F), -118.32 (dt, *J* = 8.5, 5.0 Hz, 1F). HRMS (ESI-TOF) Calcd for $C_{21}H_{17}F_2N_2O_3^+$ ([M+H]$^+$) 383.1202. Found 383.1205.



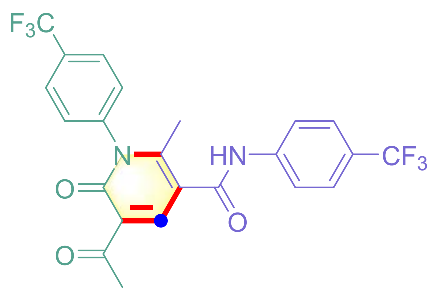
2b5, 5-acetyl-*N*,1-bis(4-chlorophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellowish solid: mp 196–197 °C (dec.). ^{1}H NMR (400 MHz, Pyridine-d_5) δ 11.69 (s, 1H, NH), 8.72 (s, 1H, ArH), 8.02 (d, *J* = 8.8 Hz, 2H, ArH), 7.53 (d, *J* = 8.9 Hz, 2H, ArH), 7.46 (d, *J* = 8.7 Hz, 2H, ArH), 7.15 (d, *J* = 8.6 Hz, 2H, ArH), 2.67 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, Pyridine-d_5) δ 195.6 (MeCO), 165.5 (NCO), 161.2 (NCO), 155.0 (ArC), 142.9 (ArC), 138.8 (ArC), 137.4 (ArC), 134.8 (ArC), 130.2 (ArC), 129.7 (ArC), 129.1 (ArC), 128.7 (ArC), 121.9 (ArC), 115.8 (ArC), 30.9 (CH_3), 20.0 (CH_3). HRMS (ESI-TOF) Calcd for $C_{21}H_{17}Cl_2N_2O_3^+$ ([M+H]$^+$) 415.0611. Found 415.0610.



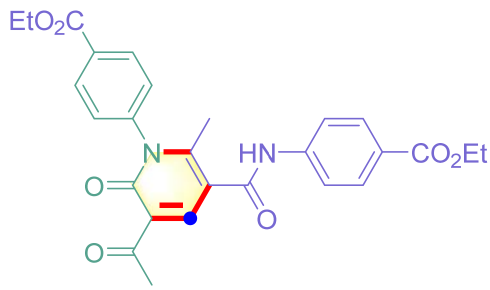
2b6, 5-acetyl-*N*,1-bis(4-bromophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, brown solid: mp 267–268 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.27 (s, 1H), 7.80 (ddd, J = 8.6, 2.9, 2.0 Hz, 2H), 7.65 (ddd, J = 8.9, 2.9, 2.0 Hz, 2H), 7.54 (ddd, J = 8.9, 2.9, 2.0 Hz, 2H), 7.34 (d, J = 8.7, 2.9, 2.0 Hz, 2H), 2.53 (s, 3H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.2, 165.1, 161.1, 155.5, 142.7, 138.7, 138.0, 133.3, 132.0, 130.8, 123.4, 122.7, 122.3, 116.0, 115.4, 31.1, 20.5. HRMS (ESI-TOF) Calcd for $C_{21}H_{17}Br_2N_2O_3^+$ ([M+H]$^+$) 502.9600. Found 502.9604.



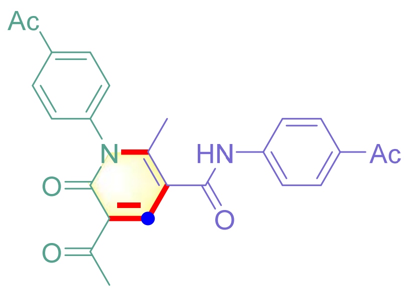
2b7, 5-acetyl-*N*,1-bis(4-iodophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellowish solid: mp 285–286 °C. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 11.68 (s, 1H), 8.72 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 2.67 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Pyridine-d_5) δ 195.6, 165.5, 161.1, 154.9, 142.8, 139.8, 139.2, 138.5, 138.0, 130.0, 122.5, 115.8, 95.9, 87.9, 30.9, 20.0. HRMS (ESI-TOF) Calcd for $C_{21}H_{17}I_2N_2O_3^+$ ([M+H]$^+$) 598.9323. Found 598.9325.



2b8, 5-acetyl-2-methyl-6-oxo-*N*,1-bis(4-(trifluoromethyl)phenyl)-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 233–234 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 8.34 (s, 1H), 8.00 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 2.54 (s, 3H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 196.1, 165.4, 161.1, 155.5, 143.0 (d, J = 0.9 Hz), 142.9, 142.3 (d, J = 1.3 Hz), 130.1 (q, J = 32.1 Hz), 129.8, 127.4 (q, J = 3.9 Hz), 126.5 (q, J = 4.0 Hz), 124.8 (q, J = 269.8 Hz), 124.34 (d, J = 272.4 Hz), 124.29 (q, J = 32.0 Hz), 123.5, 120.3, 115.3, 31.0, 20.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.38 (s, 1F), -61.13 (s, 1F). HRMS (ESI-TOF) Calcd for $C_{23}H_{17}F_6N_2O_3^+$ ($[M+H]^+$) 483.1138. Found 483.1135.

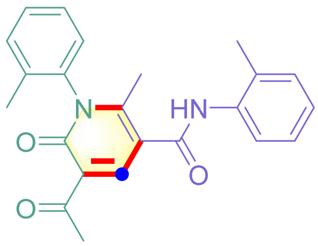


2b9, ethyl 4-(5-acetyl-1-(4-(ethoxycarbonyl)phenyl)-2-methyl-6-oxo-1,6-dihydro pyridine-3-carboxamido)benzoate, yellow solid: mp 227–228 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 8.32 (s, 1H), 8.17 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 2.54 (s, 3H), 2.16 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 196.1, 165.8, 165.5, 165.4, 161.0, 155.4, 143.8, 142.9, 142.8, 131.1, 131.0, 130.7, 129.1, 125.2, 123.4, 119.7, 115.4, 61.6, 61.0, 31.1, 20.5, 14.7, 14.6. HRMS (ESI-TOF) Calcd for $C_{27}H_{27}N_2O_7^+$ ($[M+H]^+$) 491.1813. Found 491.1814.

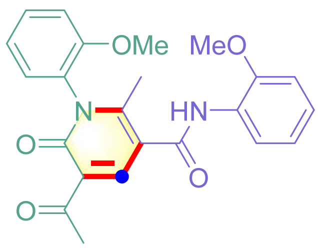


2b10, 5-acetyl-*N*,1-bis(4-acetylphenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellowish solid: mp 224–225 °C (dec.). ^1H NMR (400 MHz, DMSO-d_6) δ 10.76 (s, 1H), 8.32 (s, 1H), 8.17 (ddd, J = 8.5, 2.3, 2.0 Hz, 2H), 7.98 (ddd, J = 8.8, 2.3, 2.0 Hz, 2H), 7.83 (ddd, J = 8.8 Hz, 2H), 7.54 (ddd, J = 8.5, 2.3, 2.0 Hz, 2H), 2.67 (s, 3H), 2.55 (s, 3H), 2.54 (s, 3H), 2.17 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 197.8, 197.0, 196.2, 165.4, 161.1, 155.4, 143.7, 142.9, 142.7, 137.6, 132.7, 130.2, 129.9, 129.0, 123.4, 119.6, 115.3, 31.1, 27.4, 27.0, 20.5. HRMS (ESI-TOF) Calcd for

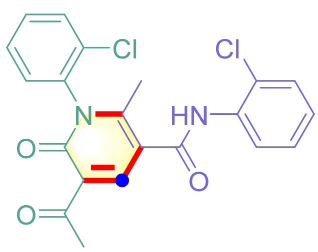
$C_{25}H_{23}N_2O_5^+$ ([M+H]$^+$) 431.1601. Found 431.1600.



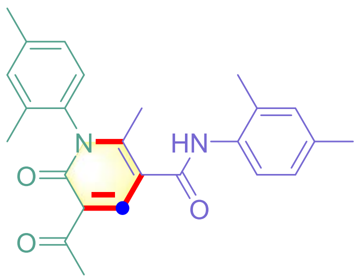
2c1, 5-acetyl-2-methyl-6-oxo-*N*,1-di-*o*-tolyl-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 201–202 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.34 (s, 1H), 7.49 – 7.37 (m, 4H), 7.28 – 7.14 (m, 4H), 2.55 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.5, 165.3, 160.6, 154.9, 142.9, 137.9, 136.4, 135.0, 133.5, 131.7, 130.9, 129.8, 128.2, 128.0, 126.54, 126.48, 123.5, 115.7, 31.1, 19.8, 18.5, 17.3. HRMS (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_3^+$ ([M+H]$^+$) 375.1703. Found 375.1703.



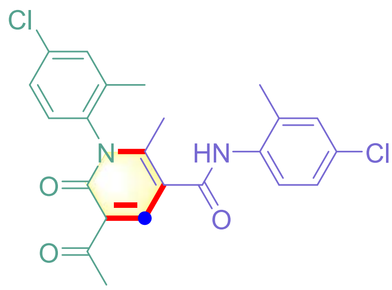
2c2, 5-acetyl-*N*,1-bis(2-methoxyphenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 171–172 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 (s, 1H), 8.25 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.27 (ddd, *J* = 7.7, 6.5, 1.4 Hz, 2H), 7.20 – 7.12 (m, 2H), 7.08 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.95 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.52 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.3, 165.4, 160.7, 155.7, 154.2, 152.2, 143.1, 131.2, 129.4, 127.0, 126.9, 126.5, 125.1, 123.1, 121.7, 120.6, 115.6, 113.1, 112.0, 56.3, 56.1, 31.1, 19.5. HRMS (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_5^+$ ([M+H]$^+$) 407.1601. Found 407.1599.



2c3, 5-acetyl-*N*,1-bis(2-chlorophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 181–182 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.31 (s, 1H), 8.41 (s, 1H), 7.80 – 7.75 (m, 1H), 7.62 – 7.57 (m, 4H), 7.56 (dd, J = 8.0, 1.6 Hz, 1H), 7.39 (ddd, J = 7.6, 7.6, 1.5 Hz, 1H), 7.30 (ddd, J = 7.7, 7.7, 1.7 Hz, 1H), 2.55 (s, 3H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.1, 165.3, 160.4, 155.4, 143.4, 136.1, 135.1, 131.7, 131.2, 130.8, 130.6, 130.1, 129.7, 129.4, 128.8, 128.1, 128.0, 123.6, 115.1, 31.0, 19.6. HRMS (ESI-TOF) Calcd for $C_{21}H_{17}Cl_2N_2O_3^+$ ([M+H]$^+$) 415.0611. Found 415.0612.

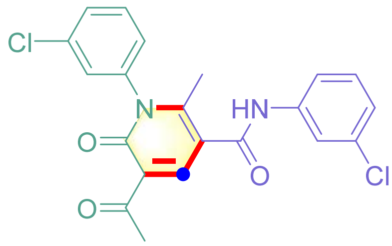


2d1, 5-acetyl-*N*,1-bis(2,4-dimethylphenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 181–182 °C. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 11.11 (s, 1H), 8.95 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.10 (dd, J = 8.0, 1.9 Hz, 2H), 7.05 (d, J = 11.2 Hz, 2H), 6.98 (d, J = 7.9 Hz, 1H), 2.75 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.21 (s, 6H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Pyridine-d_5) δ 196.1, 165.9, 161.0, 155.4, 143.0, 139.2, 135.7, 135.5, 134.6, 134.5, 133.2, 132.1, 131.5, 128.3, 127.4, 127.1, 126.2, 116.0, 31.0, 20.7, 20.6, 19.4, 18.3, 16.8. HRMS (ESI-TOF) Calcd for $C_{25}H_{27}N_2O_3^+$ ([M+H]$^+$) 403.2016. Found 403.2014.

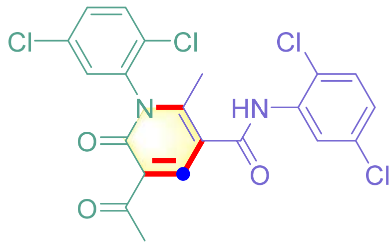


2d2, 5-acetyl-*N*,1-bis(4-chloro-2-methylphenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 253–254 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 1H), 8.35 (s, 1H), 7.61 (d, J = 2.3 Hz, 1H), 7.49 (dd, J = 8.4, 2.4 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.27 (dd, J = 8.5, 2.5 Hz, 1H), 2.54 (s, 3H), 2.25 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.3, 165.3, 160.5, 155.1, 143.1, 137.7, 136.8, 135.8, 135.5, 134.0, 131.4, 130.4, 130.3, 130.2, 128.04, 128.95, 126.4, 123.5, 115.5, 31.1, 19.9, 18.3, 17.2.

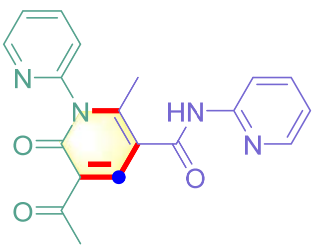
HRMS (ESI-TOF) Calcd for $C_{23}H_{21}Cl_2N_2O_3^+$ ($[M+H]^+$) 443.0924. Found 443.0935.



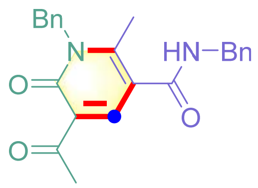
2e, 5-acetyl-*N*,1-bis(3-chlorophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 231–232 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.31 (s, 1H), 7.90 (dd, J = 2.1, 2.1 Hz, 1H), 7.66 – 7.56 (m, 4H), 7.41 – 7.36 (m, 2H), 7.18 (dd, J = 8.1, 2.1 Hz, 1H), 2.54 (s, 3H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.2, 165.2, 161.1, 155.7, 142.8, 140.8, 139.9, 134.4, 133.5, 131.8, 130.9, 129.7, 128.7, 127.4, 124.0, 123.4, 119.8, 118.7, 115.2, 31.1, 20.5. HRMS (ESI-TOF) Calcd for $C_{21}H_{17}Cl_2N_2O_3^+$ ($[M+H]^+$) 415.0611. Found 415.0614.



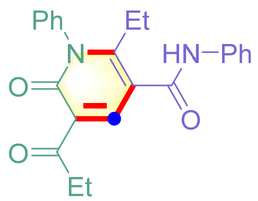
2f, 5-acetyl-*N*,1-bis(2,5-dichlorophenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 207–208 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 8.44 (s, 1H), 7.86 (d, J = 2.5 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.70 (dd, J = 8.7, 2.5 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H), 7.38 (dd, J = 8.6, 2.6 Hz, 1H), 2.55 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 195.9, 165.2, 160.3, 155.5, 143.7, 137.2, 136.4, 133.3, 132.2, 132.0, 131.7, 131.4, 130.6, 130.4, 128.13, 128.07, 127.7, 123.6, 114.8, 31.0, 19.6. IR (KBr): v = 2980, 1685, 1646, 1602, 1517, 1441, 1320, 1207, 753. HRMS (ESI-TOF) Calcd for $C_{21}H_{15}Cl_4N_2O_3^+$ ($[M+H]^+$) 482.9831. Found 482.9835.



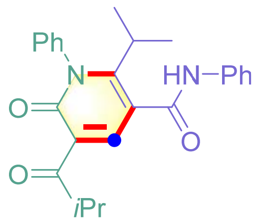
2g, 3-acetyl-6-methyl-2-oxo-*N*-(pyridin-2-yl)-2*H*-[1,2'-bipyridine]-5-carboxamide, yellowish solid: mp 219–220 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (s, 1H), 8.71 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 8.37 (ddd, J = 4.9, 2.0, 0.9 Hz, 1H), 8.31 (s, 1H), 8.16 – 8.11 (m, 2H), 7.84 (ddd, J = 8.4, 7.4, 2.0 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.17 (ddd, J = 7.4, 4.8, 1.1 Hz, 1H), 2.53 (s, 3H), 2.12 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 195.9, 165.6, 161.2, 154.8, 152.5, 151.7, 150.4, 148.5, 143.8, 140.1, 138.7, 125.3, 124.2, 123.3, 120.4, 115.1, 114.7, 31.1, 19.4. HRMS (ESI-TOF) Calcd for $C_{19}H_{17}N_4O_3^+$ ([M+H]$^+$) 349.1295. Found 349.1297.



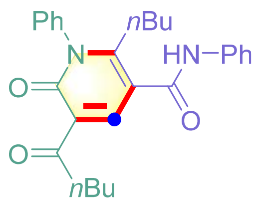
2h, 5-acetyl-*N*,1-dibenzyl-2-methyl-6-oxo-1,6-dihydropyridine-3-carboxamide, colorless oil. ^1H NMR (400 MHz, DMSO-d_6) δ 9.00 (t, J = 5.9 Hz, 1H), 8.09 (s, 1H), 7.38 – 7.23 (m, 8H), 7.16 (d, J = 7.0 Hz, 2H), 5.45 (s, 2H), 4.40 (d, J = 5.9 Hz, 2H), 2.58 (s, 3H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 196.7, 166.7, 161.2, 155.1, 141.8, 139.6, 136.5, 129.3, 128.9, 127.81, 127.78, 127.4, 126.7, 122.8, 116.0, 47.7, 43.2, 31.2, 18.6. HRMS (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_3^+$ ([M+H]$^+$) 375.1703. Found 375.1701.



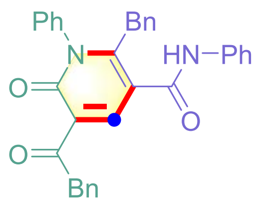
2i1, 2-ethyl-6-oxo-*N*,1-diphenyl-5-propionyl-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 216–217 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 8.25 (s, 1H), 7.68 (d, J = 7.3 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.39 – 7.33 (m, 4H), 7.11 (dd, J = 7.4, 7.4 Hz, 1H), 2.98 (q, J = 7.2 Hz, 2H), 2.57 (q, J = 7.4 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 199.5, 165.2, 161.1, 159.6, 142.8, 139.4, 138.1, 130.0, 129.6, 129.2, 128.8, 124.3, 123.4, 120.4, 115.1, 35.8, 25.2, 13.8, 8.7. IR (KBr): ν = 2979, 2938, 1685, 1646, 1602, 1541, 1517, 1499, 1441, 1390, 1320, 1207, 753. HRMS (ESI-TOF) Calcd for $C_{23}H_{23}N_2O_3^+$ ([M+H]$^+$) 375.1703. Found 375.1701.



2i2, 5-isobutyryl-2-isopropyl-6-oxo-*N*,1-diphenyl-1,6-dihydropyridine-3-carboxamide, yellowish solid: mp 225–226 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 8.06 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.61 (dd, *J* = 8.3, 6.5 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.38 – 7.32 (m, 4H), 7.12 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H), 3.72 (hept, *J* = 6.6 Hz, 1H), 2.73 (p, *J* = 7.1 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 6H), 1.04 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 203.2, 166.0, 160.9, 160.8, 143.6, 139.3, 138.7, 130.2, 129.5, 129.3, 128.6, 124.4, 123.3, 120.1, 116.5, 38.1, 33.0, 20.5, 18.7. HRMS (ESI-TOF) Calcd for $C_{25}H_{27}N_2O_3^+$ ([M+H]$^+$) 403.2016. Found 403.2018.

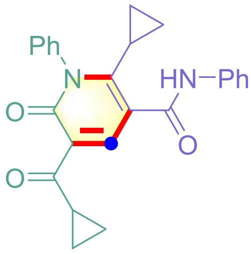


2i3, 2-butyl-6-oxo-5-pentanoyl-*N*,1-diphenyl-1,6-dihydropyridine-3-carboxamide, yellowish solid: mp 232–233 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.25 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.57 – 7.53 (m, 1H), 7.39 – 7.34 (m, 4H), 7.11 (dd, *J* = 7.4, 7.4 Hz, 1H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.57 – 2.53 (m, 2H), 1.54 (p, *J* = 7.4 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.29 (h, *J* = 7.4 Hz, 2H), 0.98 (h, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.53 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 199.0, 165.2, 161.1, 158.7, 142.8, 139.4, 138.1, 129.9, 129.5, 129.2, 128.9, 124.3, 123.4, 120.4, 115.4, 42.2, 31.1, 30.8, 26.2, 22.34, 22.32, 14.3, 13.4. HRMS (ESI-TOF) Calcd for $C_{27}H_{31}N_2O_3^+$ ([M+H]$^+$) 431.2329. Found 431.2325.

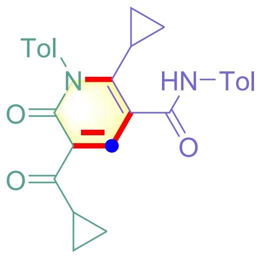


2i4, 2-benzyl-6-oxo-*N*,1-diphenyl-5-(2-phenylacetyl)-1,6-dihydropyridine-3-carboxamide, yellow solid: mp 193–194 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.37 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.39 – 7.28 (m, 6H), 7.25 –

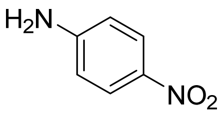
7.20 (m, 3H), 7.13 – 7.07 (m, 4H), 6.96 (dd, J = 8.3, 1.4 Hz, 2H), 6.73 – 6.70 (m, 2H), 4.37 (s, 2H), 4.09 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 196.6, 165.1, 161.3, 155.9, 143.1, 139.3, 137.7, 136.5, 135.6, 130.3, 129.5, 129.3, 129.2, 128.7, 128.64, 128.60, 128.5, 127.0, 126.9, 124.4, 124.2, 120.5, 117.1, 48.4, 37.0. HRMS (ESI-TOF) Calcd for $C_{33}H_{27}N_2O_3^+$ ([M+H]$^+$) 499.2016. Found 499.2017.



2j1, 5-(cyclopropanecarbonyl)-2-cyclopropyl-6-oxo-*N*,1-diphenyl-1,6-dihydropyridine -3-carboxamide, yellowish solid: mp 211–212 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.06 (s, 1H), 7.67 (d, J = 7.3 Hz, 2H), 7.59 (dd, J = 7.6, 7.6 Hz, 2H), 7.50 (dd, J = 7.4, 7.4 Hz, 1H), 7.42 (d, J = 7.1 Hz, 2H), 7.36 (dd, J = 8.5, 7.3 Hz, 2H), 7.11 (dd, J = 7.4, 7.4 Hz, 1H), 3.23 (tt, J = 7.8, 4.7 Hz, 1H), 1.82 – 1.75 (m, 1H), 1.03 – 0.94 (m, 4H), 0.56 (dt, J = 5.8, 2.6 Hz, 2H), 0.49 (qd, J = 7.2, 5.7, 3.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 199.4, 165.0, 161.4, 156.2, 142.5, 139.3, 138.9, 129.6, 129.3, 129.0, 128.9, 125.4, 124.3, 120.1, 117.7, 19.8, 16.1, 12.5, 9.6. HRMS (ESI-TOF) Calcd for $C_{25}H_{23}N_2O_3^+$ ([M+H]$^+$) 399.1703. Found 399.1716.



2j2, 5-(cyclopropanecarbonyl)-2-cyclopropyl-6-oxo-*N*,1-di-*p*-tolyl-1,6-dihydropyridine -3-carboxamide, yellow solid: mp 249–250 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.19 (s, 1H), 8.02 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 3.22 (tt, J = 7.7, 4.7 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 1.80 – 1.73 (m, 1H), 1.02 – 0.93 (m, 4H), 0.58 – 0.48 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 199.4, 164.9, 161.4, 156.3, 142.4, 138.3, 136.8, 136.3, 133.3, 130.0, 129.7, 128.6, 125.3, 120.1, 117.6, 21.3, 21.0, 19.7, 16.1, 12.5, 9.6. HRMS (ESI-TOF) Calcd for $C_{27}H_{27}N_2O_3^+$ ([M+H]$^+$) 427.2016. Found 427.2014.



3, 4-nitroaniline, yellow solid: mp 148–149 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (ddd, J = 9.2, 3.2, 3.3 Hz, 2H), 6.73 (s, 2H), 6.60 (ddd, J = 9.1, 3.2, 3.3 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 156.2, 136.1, 126.9, 112.8. HRMS (ESI-TOF) Calcd for $C_6H_7N_2O_2^+$ ([M+H]$^+$) 139.0502. Found 139.0496.

VI. Single crystal X-ray diffraction studies

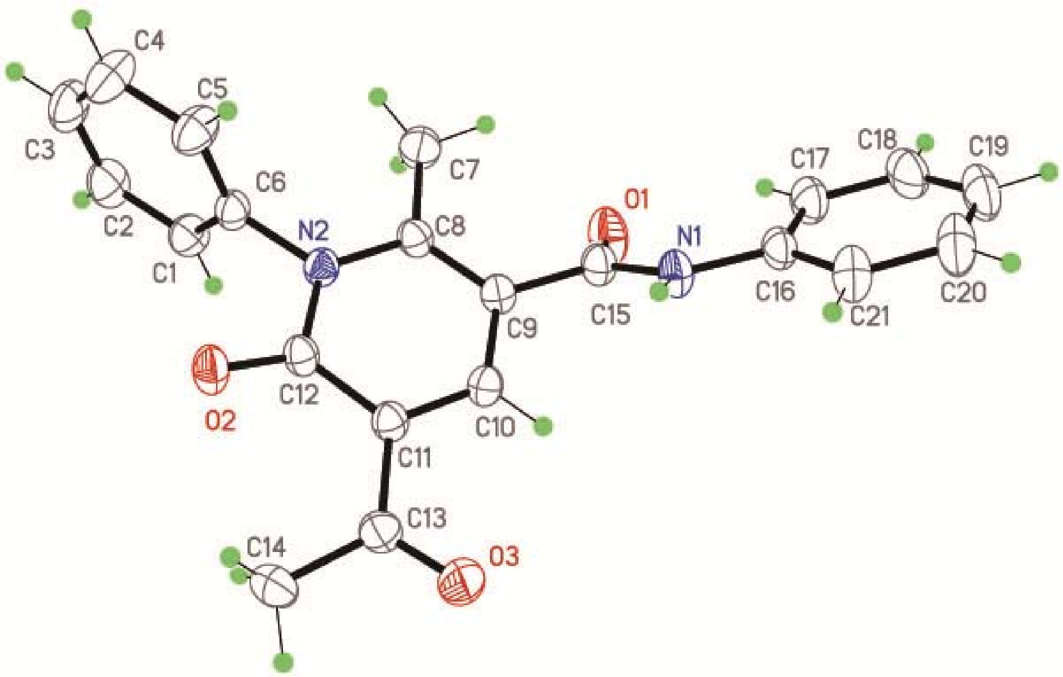


Figure S18 X-ray crystal structure of **2a**

The test name of crystal **2a** is exp_3536

Crystal structure determination of [exp_3536]

Crystal Data for $C_{21}H_{18}N_2O_3$ (M =346.37): triclinic, space group P-1 (no. 2), a = 8.1439(10) Å, b = 9.6588(8) Å, c = 11.5840(13) Å, α = 92.542(8)°, β = 98.729(10)°, γ = 97.055(9)°, V = 891.98(17) Å^3, Z = 2, T = 293(2) K, μ(Cu Kα) = 0.708 mm^{-1}, $Dcalc$ = 1.290 g/mm^3, 5461 reflections measured (7.74 ≤ 2Θ ≤ 134.14), 3166 unique (R_{int} = 0.0166) which were used in all calculations. The final R_1 was 0.0427 (>2sigma(I)) and wR_2 was 0.1247 (all data).

Table S6 Crystal data and structure refinement for exp_3536

Identification code	exp_3536
Empirical formula	$C_{21}H_{18}N_2O_3$
Formula weight	346.37
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.1439(10)
b/Å	9.6588(8)
c/Å	11.5840(13)
α/°	92.542(8)
β/°	98.729(10)
γ/°	97.055(9)
Volume/Å^3	891.98(17)
Z	2
ρ_{calc}mg/mm^3	1.290
m/mm^{-1}	0.708
F(000)	364.0
Crystal size/mm^3	0.26 × 0.12 × 0.11
2Θ range for data collection	7.74 to 134.14°
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 11, -13 ≤ l ≤ 10
Reflections collected	5461
Independent reflections	3166[R(int) = 0.0166]
Data/restraints/parameters	3166/0/238
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0516, wR_2 = 0.1247
Largest diff. peak/hole / e Å^{-3}	0.21/-0.16

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_3536. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	591(2)	1104.0(17)	-1910.8(15)	54.8(4)
C2	178(3)	115(2)	-2851.7(18)	68.4(5)
C3	1377(3)	-233(2)	-3479.0(18)	75.4(6)
C4	3000(3)	391(2)	-3179.3(19)	81.0(7)
C5	3435(2)	1382(2)	-2242.8(17)	66.0(5)
C6	2221(2)	1720.1(15)	-1621.8(13)	45.3(4)
C7	3263(3)	857.1(17)	621.8(16)	65.1(5)
C8	3164.8(19)	2377.9(15)	476.6(13)	44.1(4)
C9	3563.6(19)	3393.0(16)	1384.2(13)	43.9(4)
C10	3339.6(19)	4776.2(16)	1147.9(13)	43.9(4)
C11	2771.2(19)	5167.3(15)	53.8(13)	42.6(4)
C12	2539.6(18)	4161.7(15)	-928.2(13)	42.4(4)
C13	2390(2)	6629.4(16)	-79.2(15)	50.7(4)
C14	1414(3)	7030(2)	-1185.5(19)	76.7(6)
C15	4118(2)	3020.3(17)	2615.7(14)	48.9(4)
C16	6279(2)	3827.7(19)	4356.5(13)	50.6(4)
C17	6027(3)	2697(2)	5028.5(15)	63.3(5)
C18	7034(3)	2688(3)	6107.3(16)	75.1(6)
C19	8243(3)	3767(3)	6520.4(16)	79.0(7)
C20	8448(3)	4912(3)	5867.8(18)	80.4(7)
C21	7469(2)	4947(2)	4784.1(16)	67.5(5)
N1	5410.9(18)	3905.1(14)	3202.8(11)	51.7(4)
N2	2656.3(16)	2760.8(12)	-635.8(10)	42.1(3)
O1	3441.6(18)	1999.9(14)	3027.2(11)	73.6(4)
O2	2262.6(16)	4393.0(11)	-1968.3(9)	55.7(3)
O3	2809(2)	7485.3(13)	747.2(12)	80.0(5)

Table S8 Anisotropic Displacement Parameters (Å^2×10^3) for exp_3536. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+...+2hka×b×U$_{12}$]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	53.6(10)	49.9(9)	57.6(10)	-0.3(7)	4.0(8)	0.5(7)

C2	66.5(12)	58.2(11)	68.9(12)	-4.6(9)	-11.3(10)	-7.2(9)
C3	98.2(16)	62.6(12)	56.3(11)	-15.7(9)	-3.2(11)	0.4(11)
C4	87.8(16)	83.8(14)	70.2(13)	-25.3(11)	24.1(11)	2.9(12)
C5	59.2(11)	69.8(12)	65.0(12)	-16.2(9)	11.8(9)	-3.0(9)
C6	52.7(9)	39.9(7)	40.1(8)	0.5(6)	1.1(7)	1.9(6)
C7	93.0(14)	45.1(9)	55.9(10)	6.0(8)	2.8(10)	14.4(9)
C8	45.7(8)	42.9(8)	42.6(8)	6.9(6)	3.7(6)	4.4(6)
C9	45.0(8)	45.3(8)	39.5(8)	4.1(6)	2.5(6)	2.9(6)
C10	44.8(8)	44.2(8)	39.8(8)	-1.3(6)	3.2(6)	0.4(6)
C11	42.4(8)	41.5(8)	41.5(8)	2.6(6)	2.6(6)	1.1(6)
C12	42.5(8)	41.7(8)	39.5(8)	4.6(6)	0.5(6)	-1.1(6)
C13	53.3(9)	41.7(8)	54.4(9)	3.7(7)	3.0(7)	2.2(7)
C14	98.5(16)	57.9(11)	70.8(13)	7.1(9)	-11.7(11)	29.2(11)
C15	55.0(9)	50.5(9)	39.6(8)	5.6(7)	4.1(7)	3.2(7)
C16	49.7(9)	67.2(10)	35.1(8)	2.6(7)	4.0(7)	12.1(8)
C17	74.5(12)	70.8(11)	43.1(9)	8.7(8)	2.4(8)	10.8(9)
C18	84.2(15)	100.8(16)	44.4(10)	19.1(10)	5.5(10)	28.2(12)
C19	62.9(12)	133(2)	40.2(10)	4.7(11)	-1.5(9)	22.3(13)
C20	61.0(12)	120.2(19)	51.0(11)	-7.9(12)	-3.9(9)	-3.0(12)
C21	63.3(12)	85.6(13)	47.3(10)	1.5(9)	-0.5(8)	-3(1)
N1	55.9(8)	56.6(8)	38.1(7)	7.6(6)	-0.9(6)	-1.1(6)
N2	46.9(7)	38.7(6)	38.6(7)	0.8(5)	3.5(5)	2.2(5)
O1	84.6(10)	72.4(8)	53.4(7)	20.9(6)	-2.7(6)	-20.2(7)
O2	74.1(8)	49.7(6)	38.2(6)	6.8(5)	-1.1(5)	-1.2(5)
O3	115.3(12)	45.6(7)	70.2(9)	-7.4(6)	-14.0(8)	15.3(7)

Table S9 Bond Lengths for exp_3536.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.389(2)	C11	C13	1.492(2)
C1	C6	1.371(2)	C12	N2	1.4203(19)
C2	C3	1.367(3)	C12	O2	1.2273(18)
C3	C4	1.370(3)	C13	C14	1.495(2)
C4	C5	1.388(3)	C13	O3	1.216(2)

C5	C6	1.370(3)	C15	N1	1.346(2)
C6	N2	1.4589(19)	C15	O1	1.221(2)
C7	C8	1.496(2)	C16	C17	1.382(3)
C8	C9	1.378(2)	C16	C21	1.379(3)
C8	N2	1.3735(19)	C16	N1	1.4235(19)
C9	C10	1.404(2)	C17	C18	1.388(2)
C9	C15	1.503(2)	C18	C19	1.358(3)
C10	C11	1.368(2)	C19	C20	1.375(3)
C11	C12	1.437(2)	C20	C21	1.385(3)

Table S10 Bond Angles for exp_3536.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C1	C2	118.86(18)	O2	C12	N2	118.01(13)
C3	C2	C1	120.47(18)	C11	C13	C14	120.96(15)
C2	C3	C4	119.97(18)	O3	C13	C11	119.21(15)
C3	C4	C5	120.4(2)	O3	C13	C14	119.73(16)
C6	C5	C4	118.99(18)	N1	C15	C9	113.89(13)
C1	C6	N2	118.95(15)	O1	C15	C9	122.03(14)
C5	C6	C1	121.33(15)	O1	C15	N1	124.07(15)
C5	C6	N2	119.72(14)	C17	C16	N1	123.84(16)
C9	C8	C7	123.84(14)	C21	C16	C17	119.86(16)
N2	C8	C7	116.96(14)	C21	C16	N1	116.27(16)
N2	C8	C9	119.19(13)	C16	C17	C18	118.89(19)
C8	C9	C10	118.53(13)	C19	C18	C17	121.6(2)
C8	C9	C15	120.98(13)	C18	C19	C20	119.26(18)
C10	C9	C15	120.37(14)	C19	C20	C21	120.4(2)
C11	C10	C9	123.01(14)	C16	C21	C20	119.9(2)
C10	C11	C12	119.37(13)	C15	N1	C16	128.38(14)
C10	C11	C13	118.65(14)	C8	N2	C6	121.00(12)
C12	C11	C13	121.97(13)	C8	N2	C12	124.05(12)
N2	C12	C11	115.03(13)	C12	N2	C6	114.94(12)
O2	C12	C11	126.96(14)				

Table S11 Torsion Angles for exp_3536.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	0.1(3)	C10	C11	C12	N2	10.4(2)
C1	C6	N2	C8	90.50(19)	C10	C11	C12	O2	-169.35(16)
C1	C6	N2	C12	-90.61(17)	C10	C11	C13	C14	-166.07(18)
C2	C1	C6	C5	0.2(3)	C10	C11	C13	O3	10.2(3)
C2	C1	C6	N2	179.86(15)	C11	C12	N2	C6	172.87(13)
C2	C3	C4	C5	-0.2(4)	C11	C12	N2	C8	-8.3(2)
C3	C4	C5	C6	0.3(4)	C12	C11	C13	C14	13.2(3)
C4	C5	C6	C1	-0.2(3)	C12	C11	C13	O3	-170.57(16)
C4	C5	C6	N2	-179.92(18)	C13	C11	C12	N2	-168.82(13)
C5	C6	N2	C8	-89.8(2)	C13	C11	C12	O2	11.4(3)
C5	C6	N2	C12	89.06(19)	C15	C9	C10	C11	-177.21(14)
C6	C1	C2	C3	-0.1(3)	C16	C17	C18	C19	0.7(3)
C7	C8	C9	C10	-176.81(16)	C17	C16	C21	C20	2.3(3)
C7	C8	C9	C15	-0.8(2)	C17	C16	N1	C15	7.7(3)
C7	C8	N2	C6	0.5(2)	C17	C18	C19	C20	1.6(3)
C7	C8	N2	C12	-178.25(15)	C18	C19	C20	C21	-2.0(3)
C8	C9	C10	C11	-1.2(2)	C19	C20	C21	C16	0.1(3)
C8	C9	C15	N1	137.76(16)	C21	C16	C17	C18	-2.7(3)
C8	C9	C15	O1	-42.0(2)	C21	C16	N1	C15	-174.46(18)
C9	C8	N2	C6	-179.94(14)	N1	C16	C17	C18	175.10(17)
C9	C8	N2	C12	1.3(2)	N1	C16	C21	C20	-175.65(17)
C9	C10	C11	C12	-6.2(2)	N2	C8	C9	C10	3.7(2)
C9	C10	C11	C13	173.04(14)	N2	C8	C9	C15	179.72(14)
C9	C15	N1	C16	-177.24(15)	O1	C15	N1	C16	2.6(3)
C10	C9	C15	N1	-46.3(2)	O2	C12	N2	C6	-7.3(2)
C10	C9	C15	O1	133.89(19)	O2	C12	N2	C8	171.52(14)

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_3536.

Atom	*x*	*y*	*z*	U(eq)
H1	-223	1344	-1484	66

H2	-922	-312	-3056	82
H3	1091	-894	-4109	91
H4	3813	150	-3606	97
H5	4535	1810	-2040	79
H7A	2155	371	595	98
H7B	3928	744	1362	98
H7C	3769	480	2	98
H10	3589	5458	1763	53
H14A	1093	7942	-1062	115
H14B	428	6363	-1410	115
H14C	2094	7042	-1794	115
H1A	5939	4629	2750	92
H17	5196	1954	4762	76
H18	6877	1924	6559	90
H19	8924	3731	7237	95
H20	9249	5668	6155	97
H21	7614	5723	4346	81

VII. UV-vis spectra

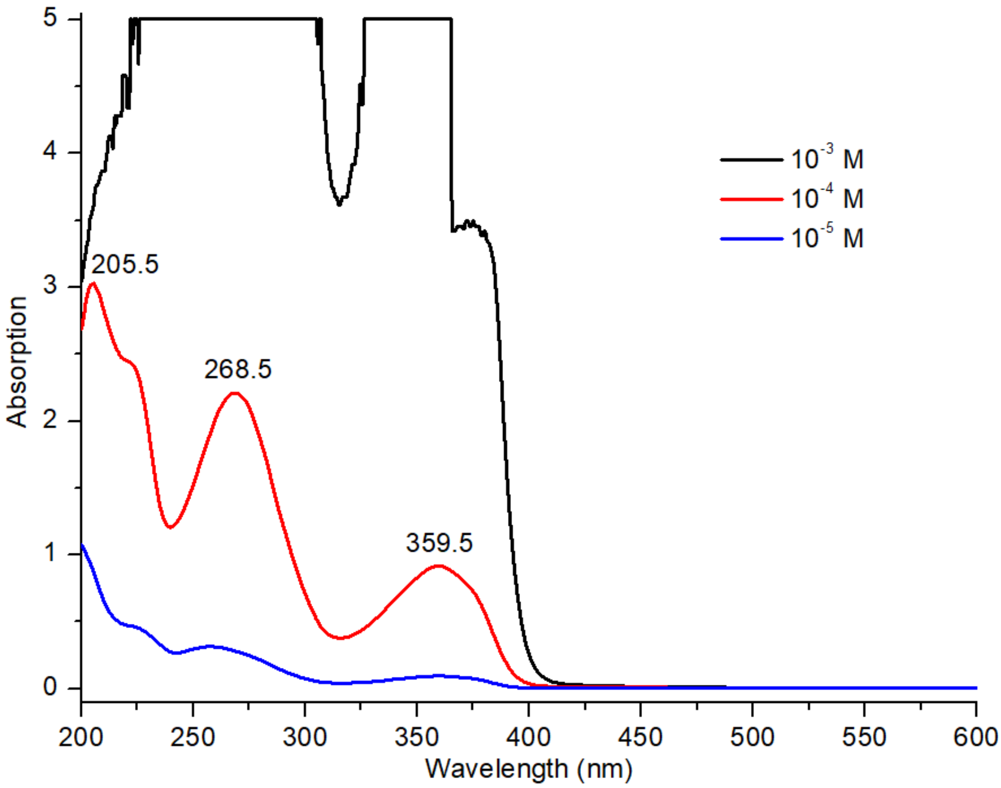


Figure S19 UV-vis spectra of **2b3** (in CH_3CN)

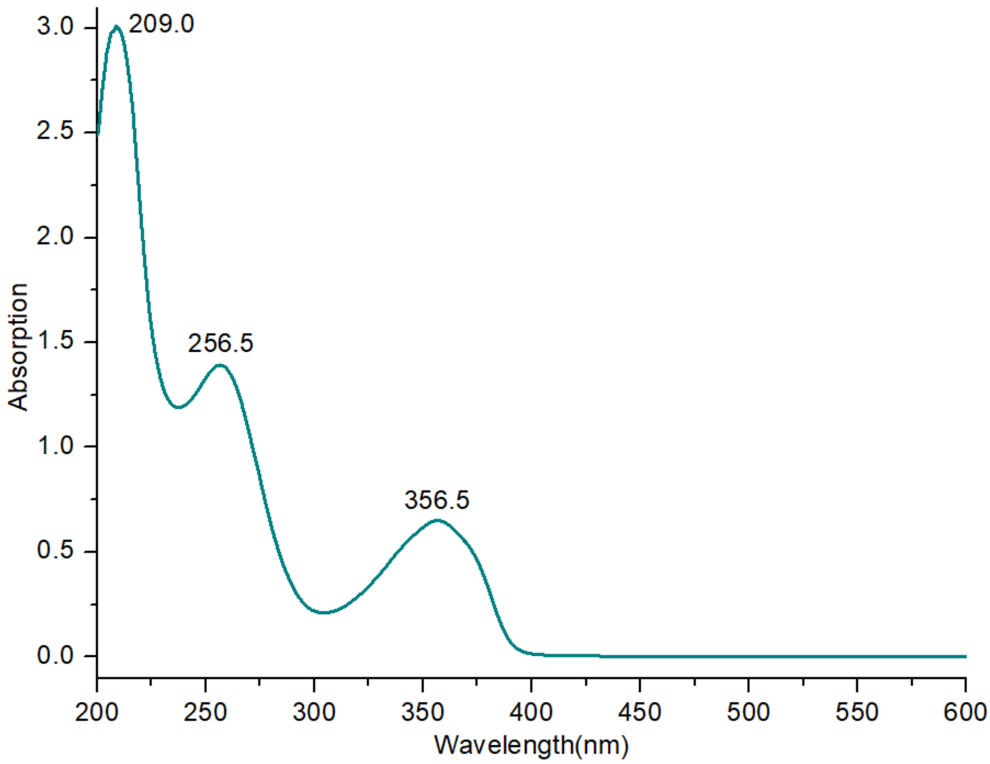


Figure S20 UV-vis spectra of **2d1** (10^{-4} M in CH_3CN)

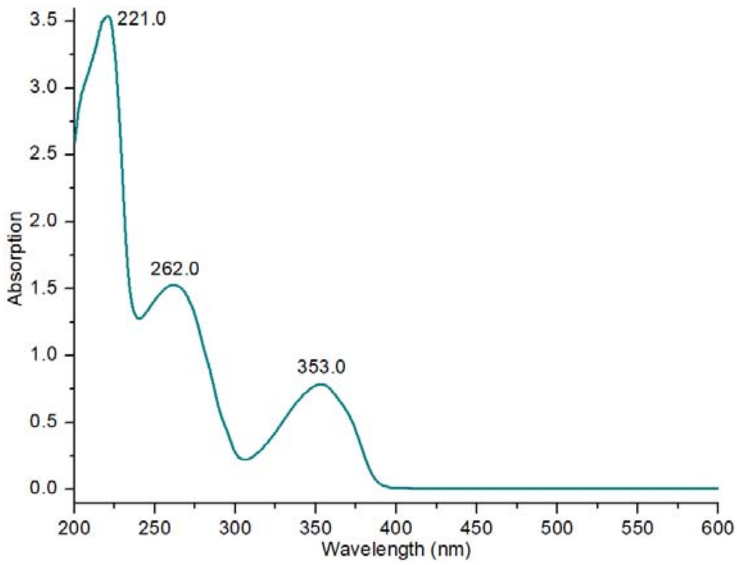


Figure S21 UV-vis spectra of **2f** (10^{-4} M in CH_3CN)

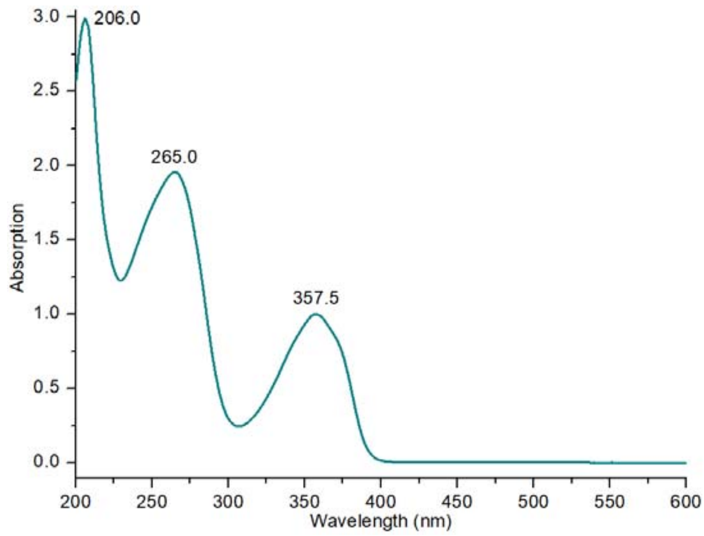


Figure S22 UV-vis spectra of **2i1** (10^{-4} M in CH_3CN)

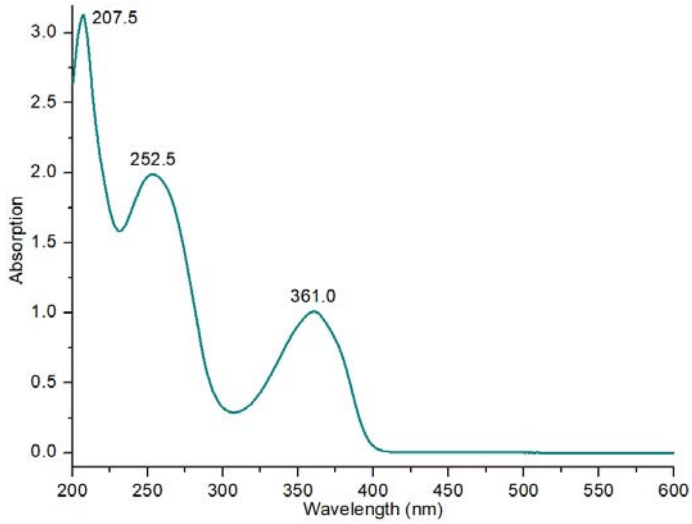


Figure S23 UV-vis spectra of **2j1** (10^{-4} M in CH_3CN)

VIII. IR spectra

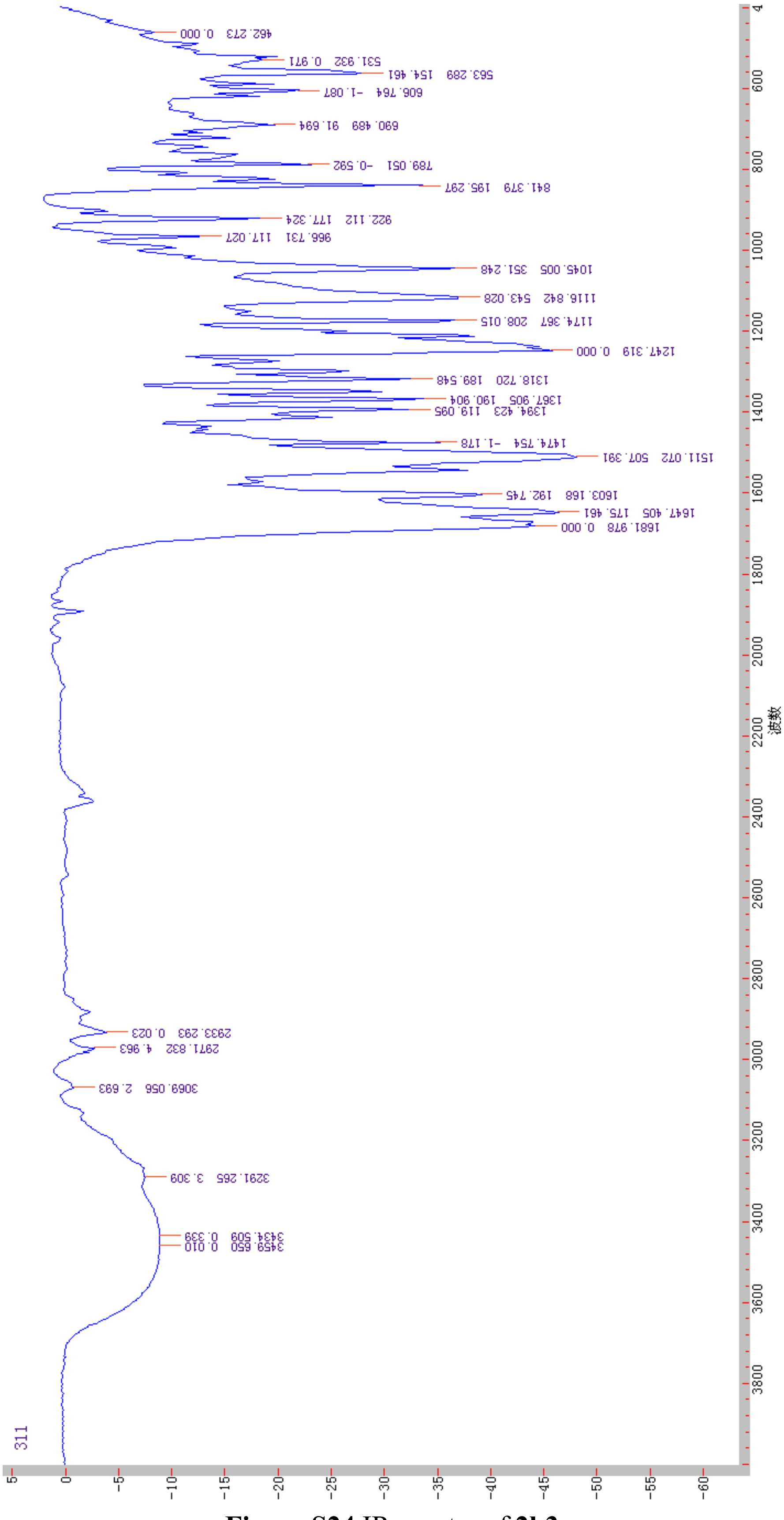


Figure S24 IR spectra of **2b3**

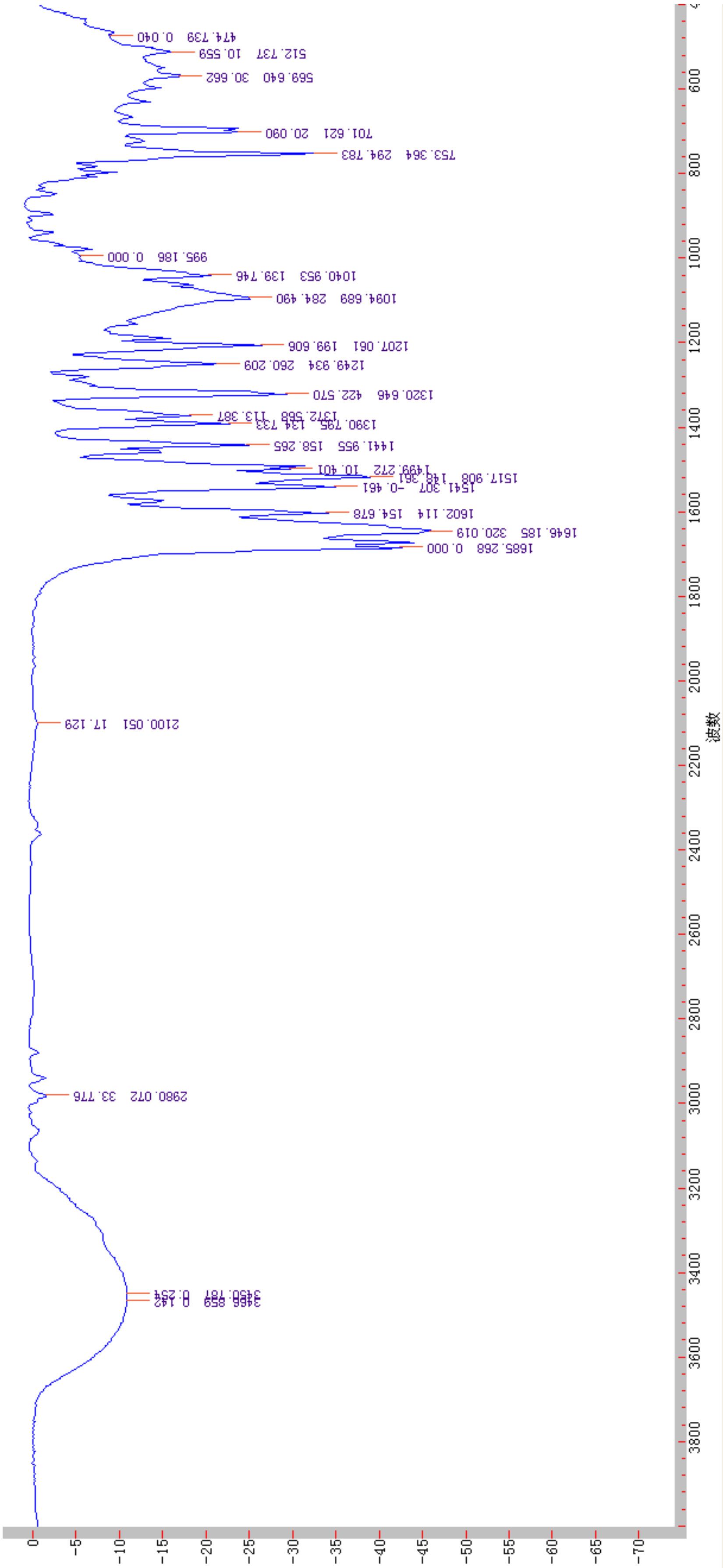


Figure S25 IR spectra of **2f**

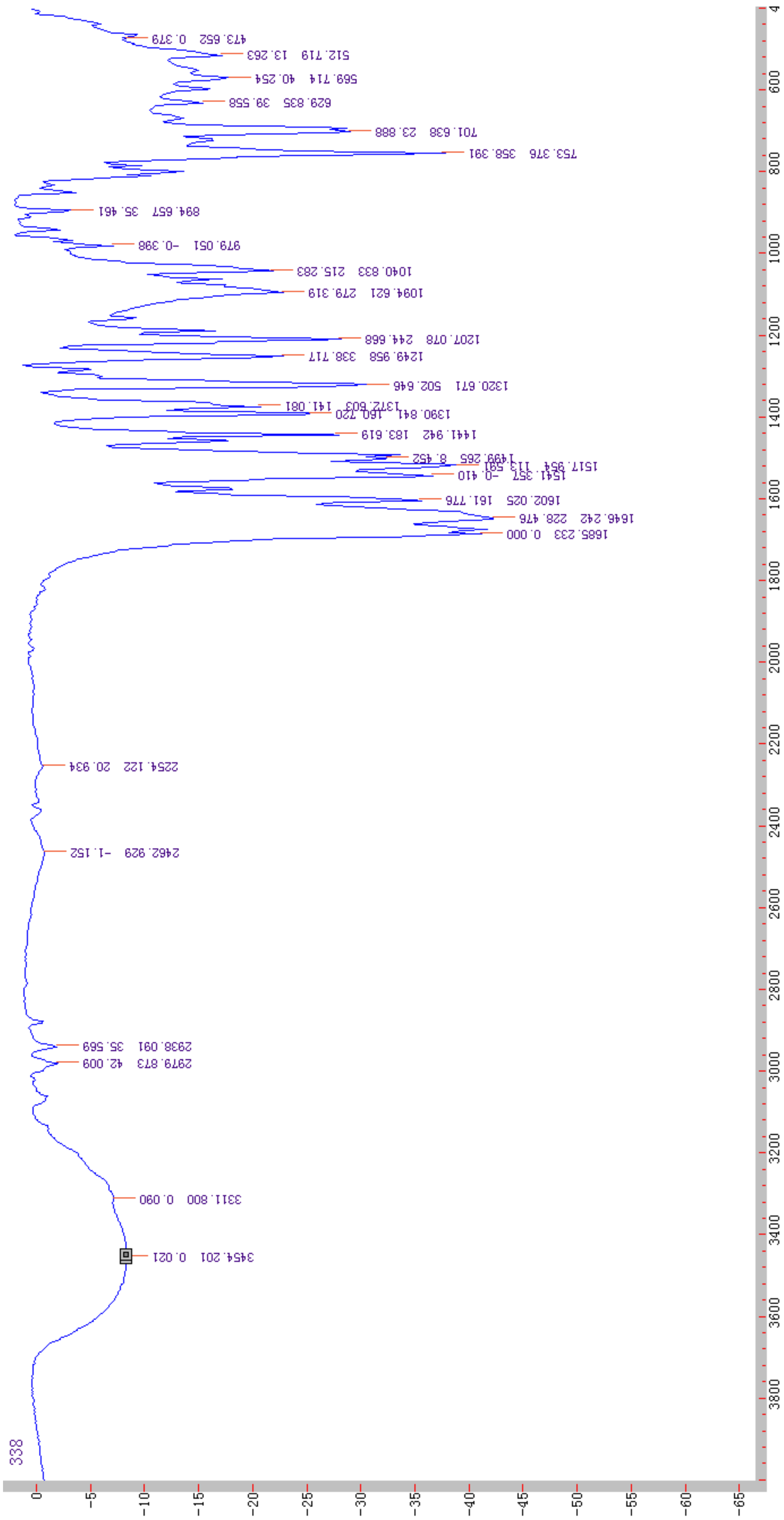
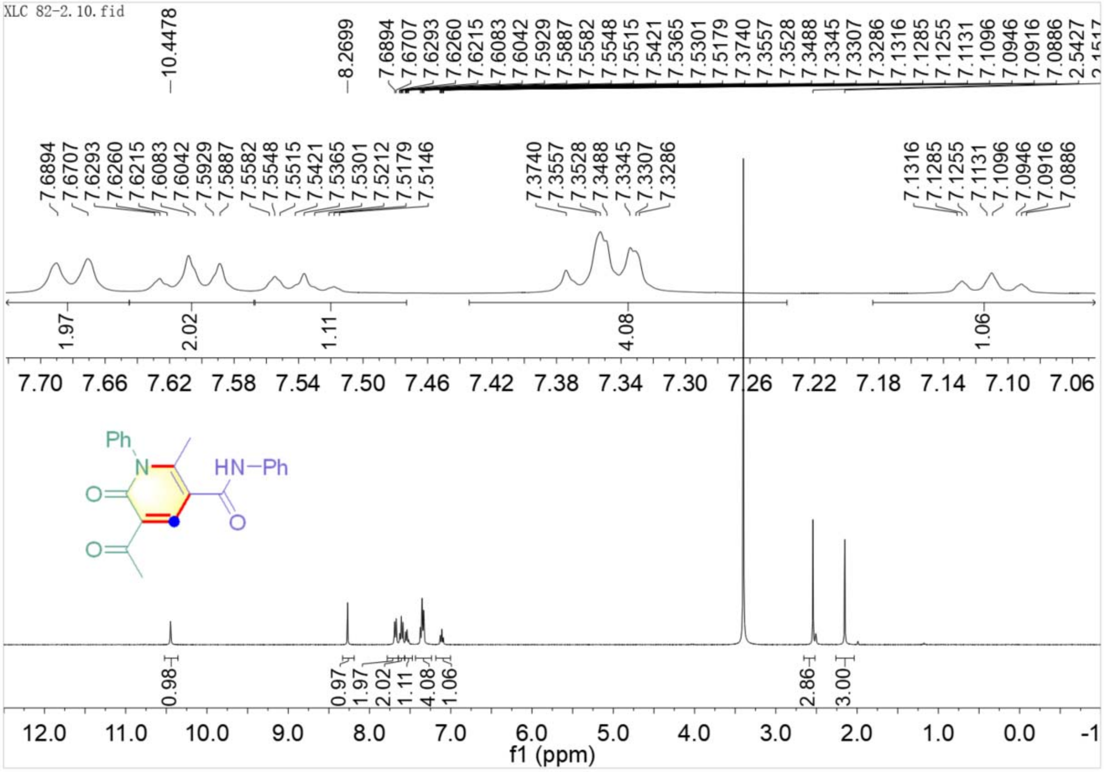


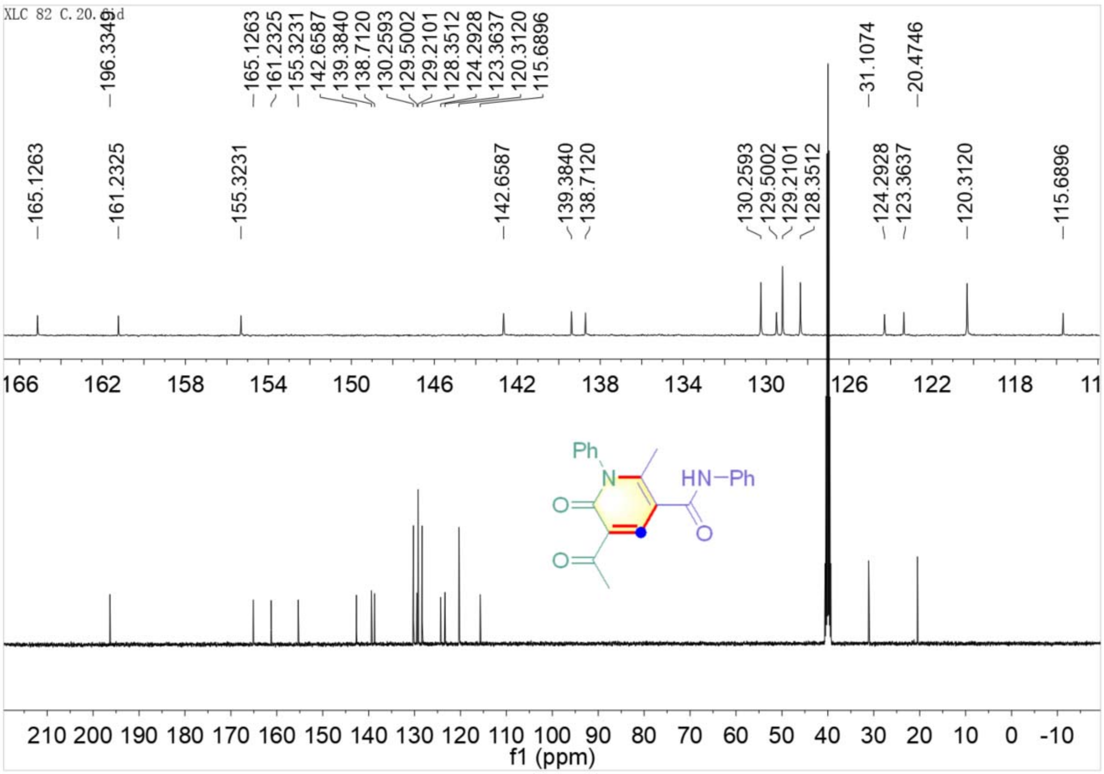
Figure S26 IR spectra of **2i1**

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

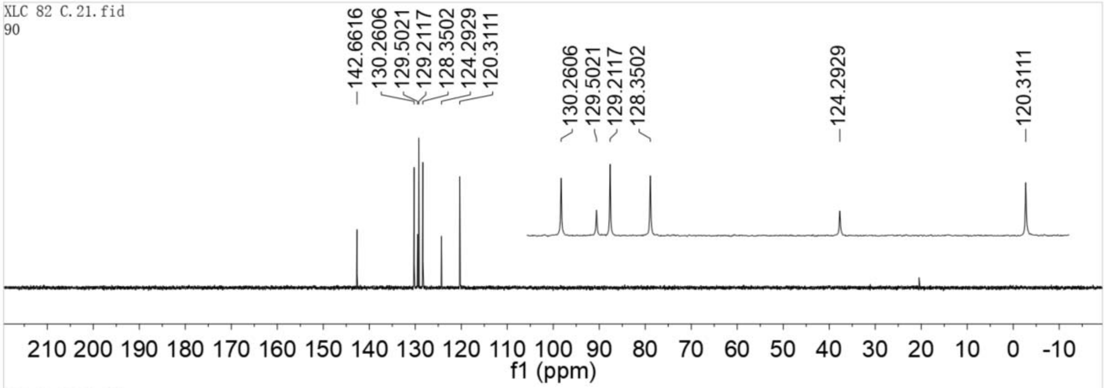
2a, ^{1}H NMR

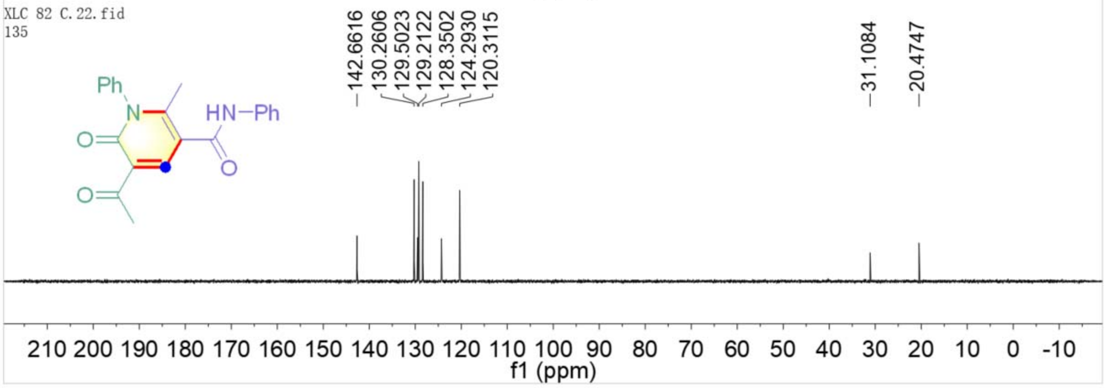


^{13}C NMR

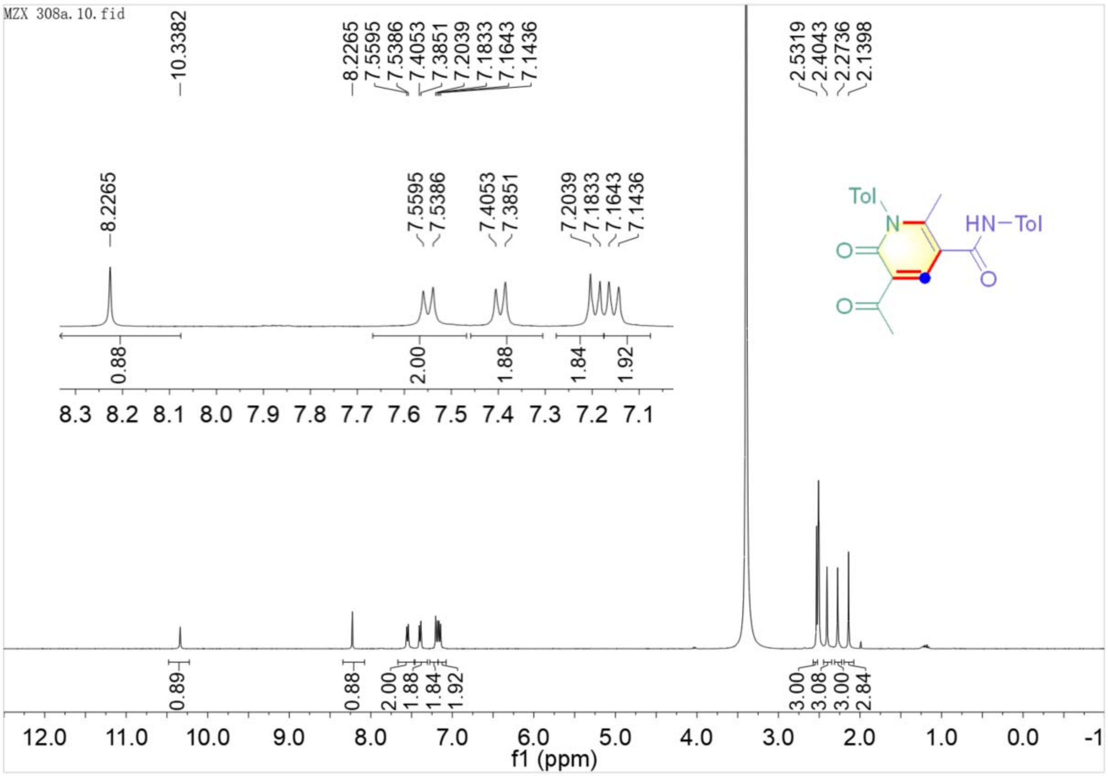


DEPT 90 and DEPT 135

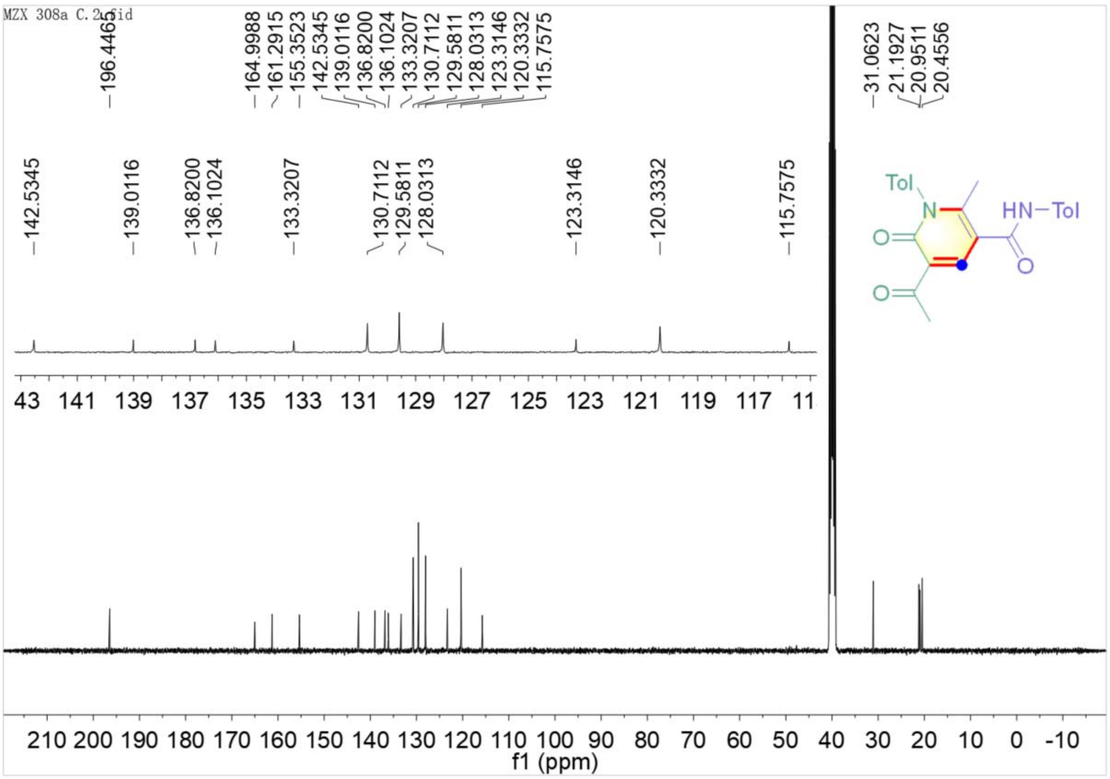




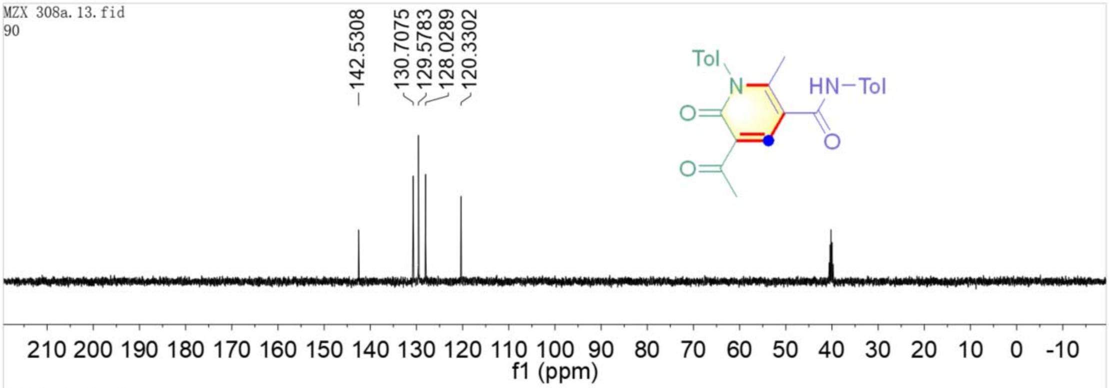
2b1, ^{1}H NMR

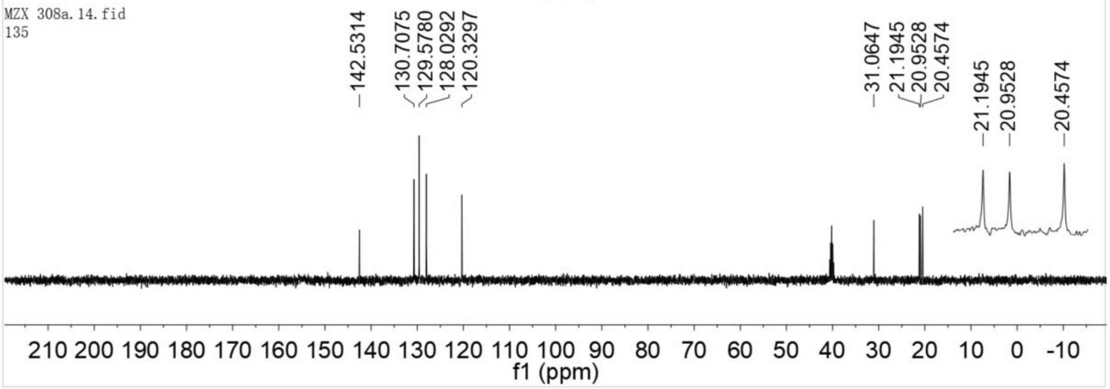


^{13}C NMR

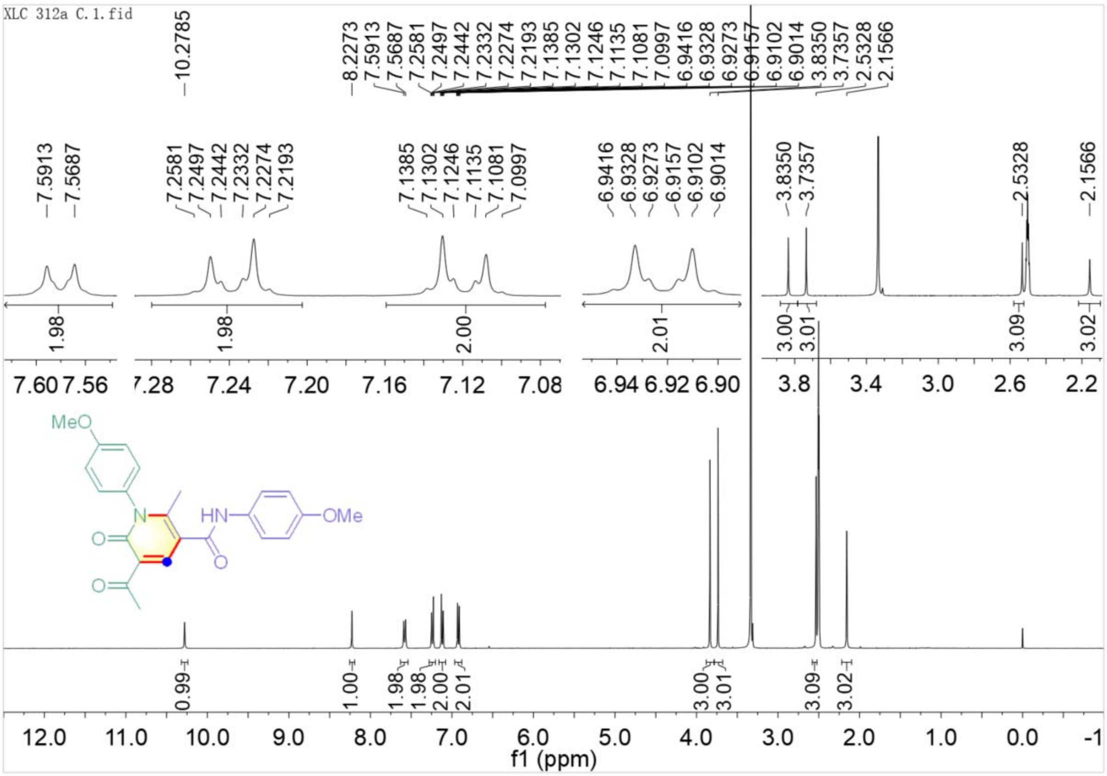


DEPT 90 and DEPT 135

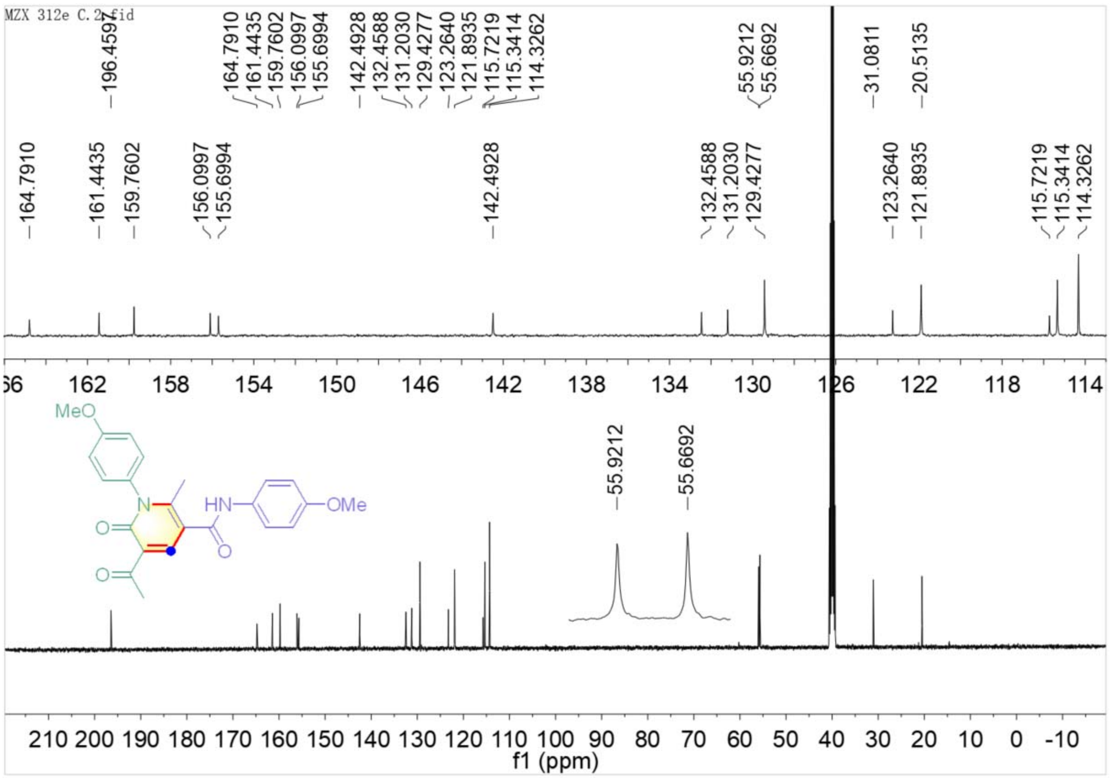




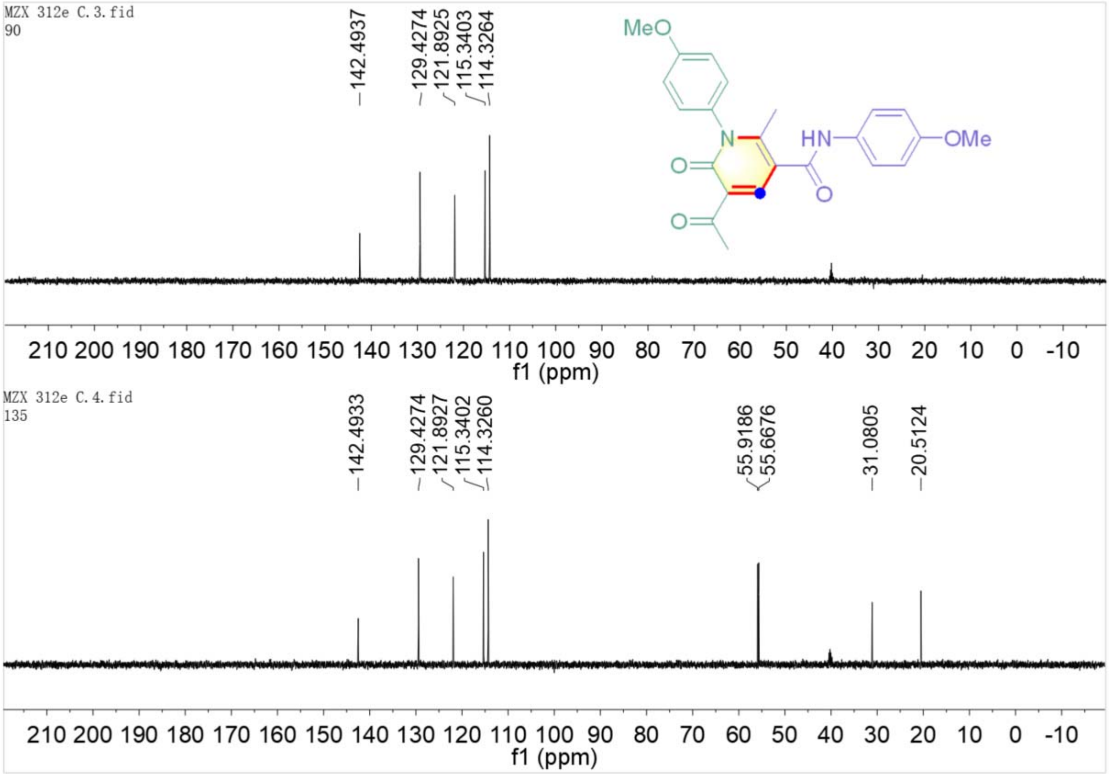
2b2, ^{1}H NMR



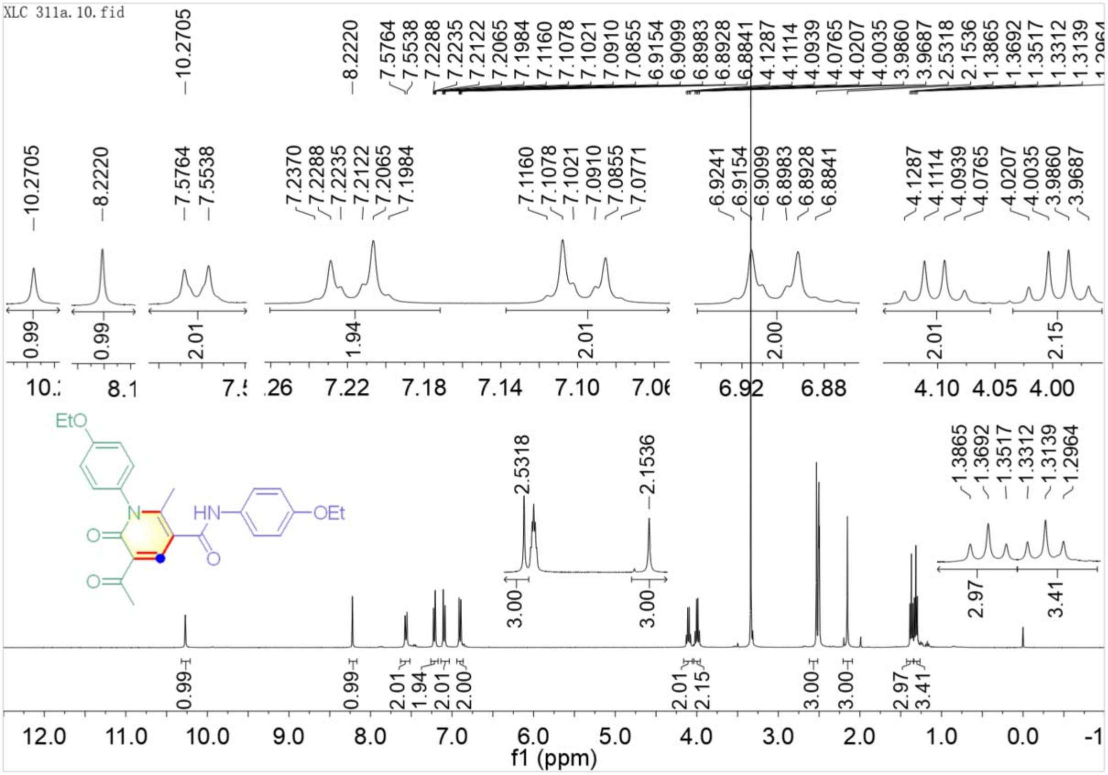
^{13}C NMR



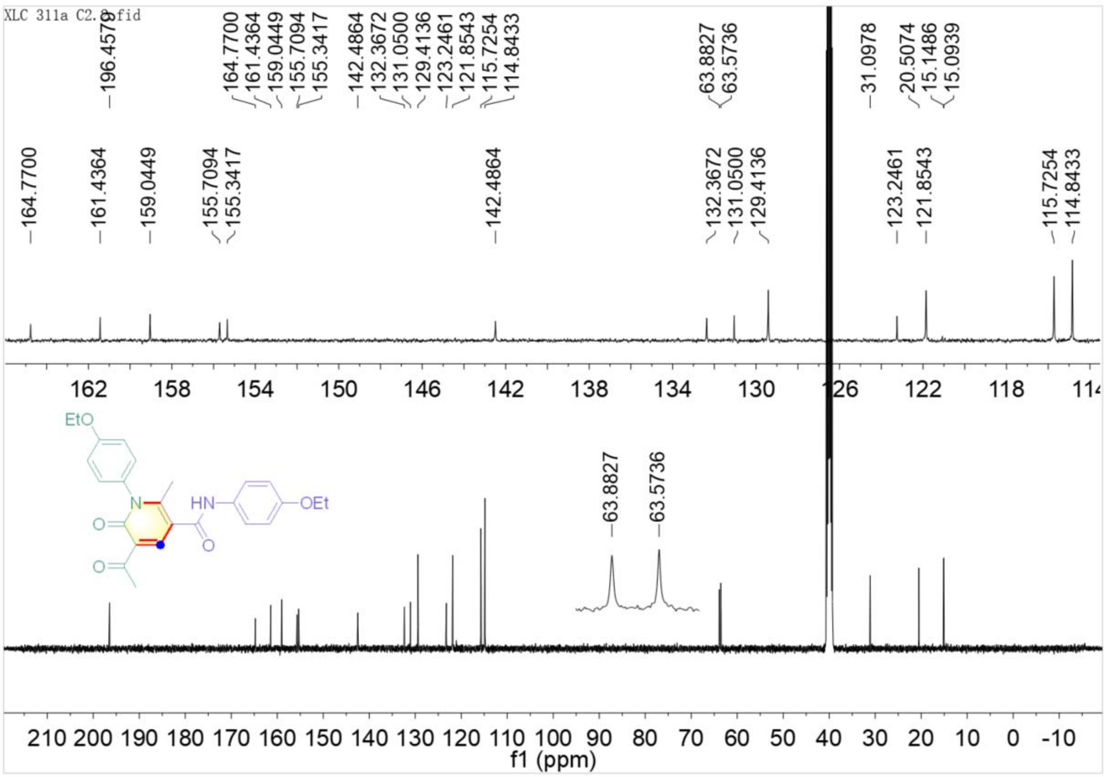
DEPT 90 and DEPT 135



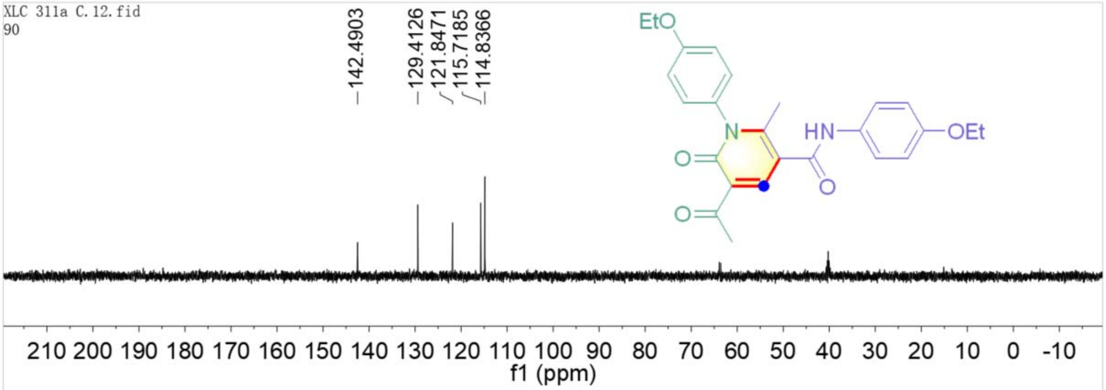
2b3, ^{1}H NMR

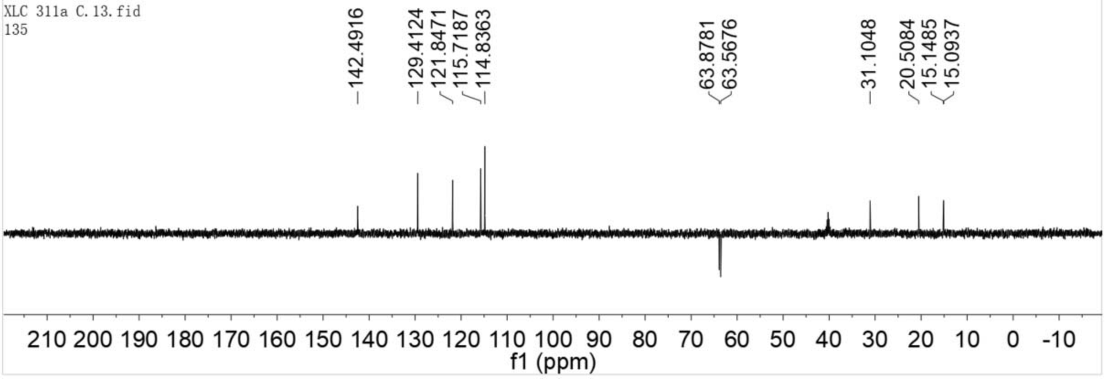


^{13}C NMR

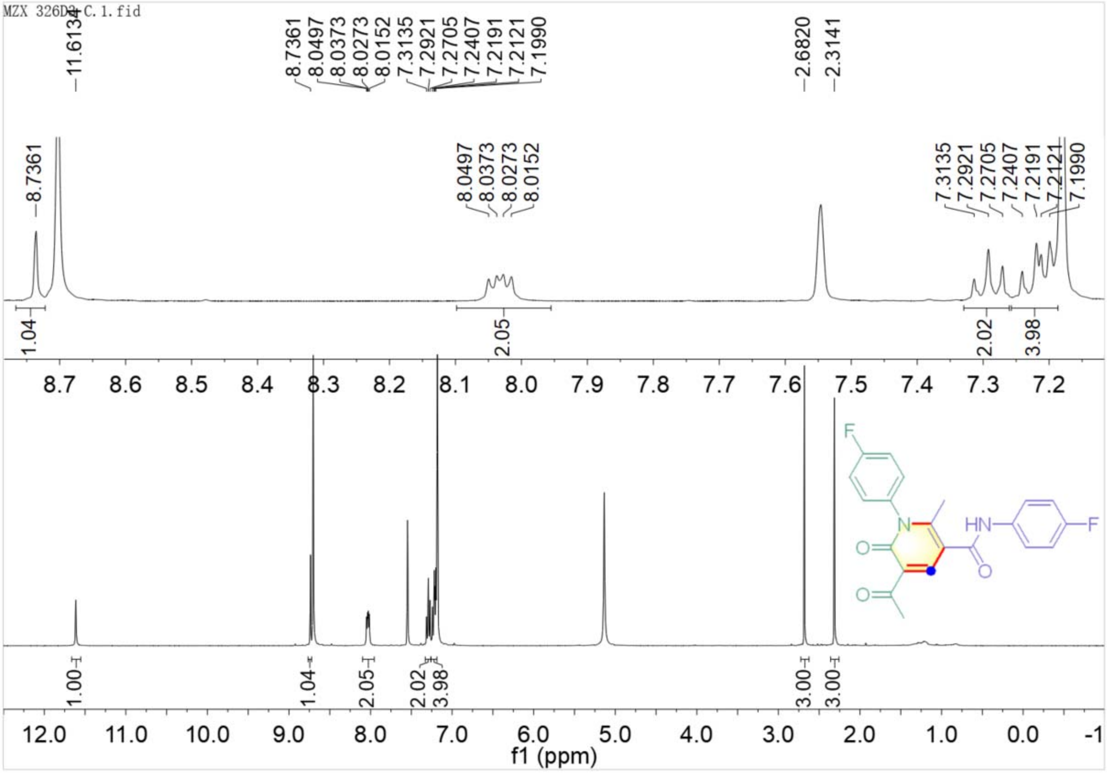


DEPT 90 and DEPT 135

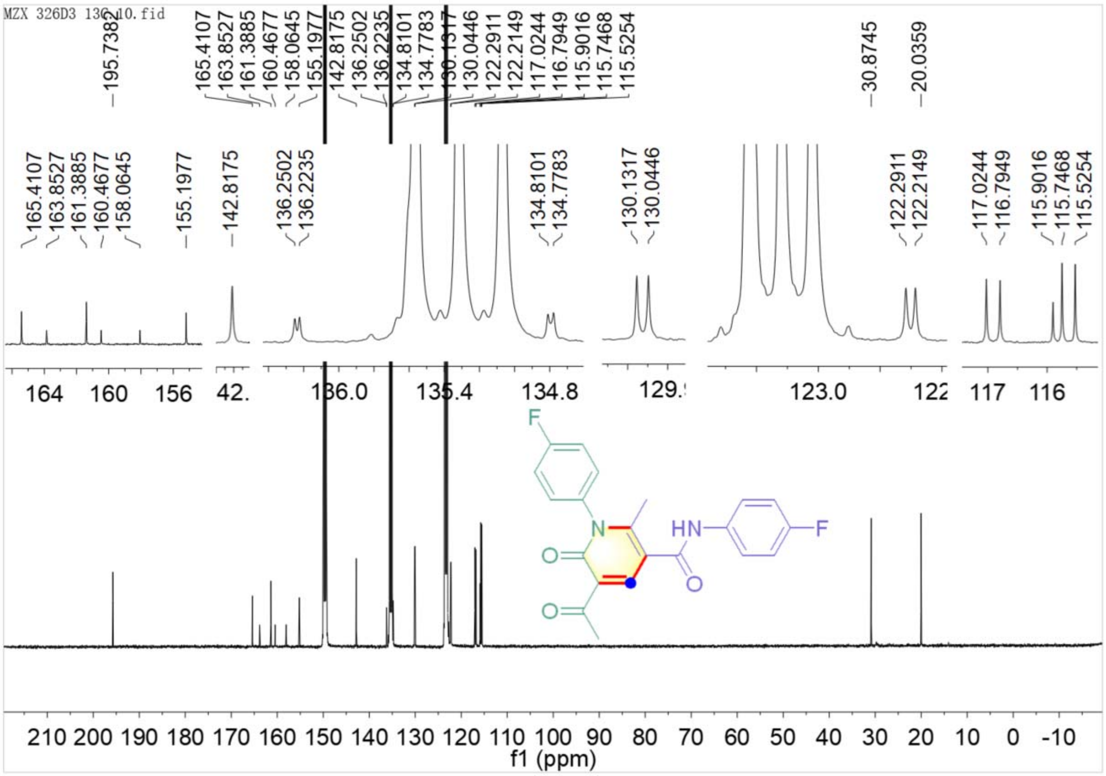




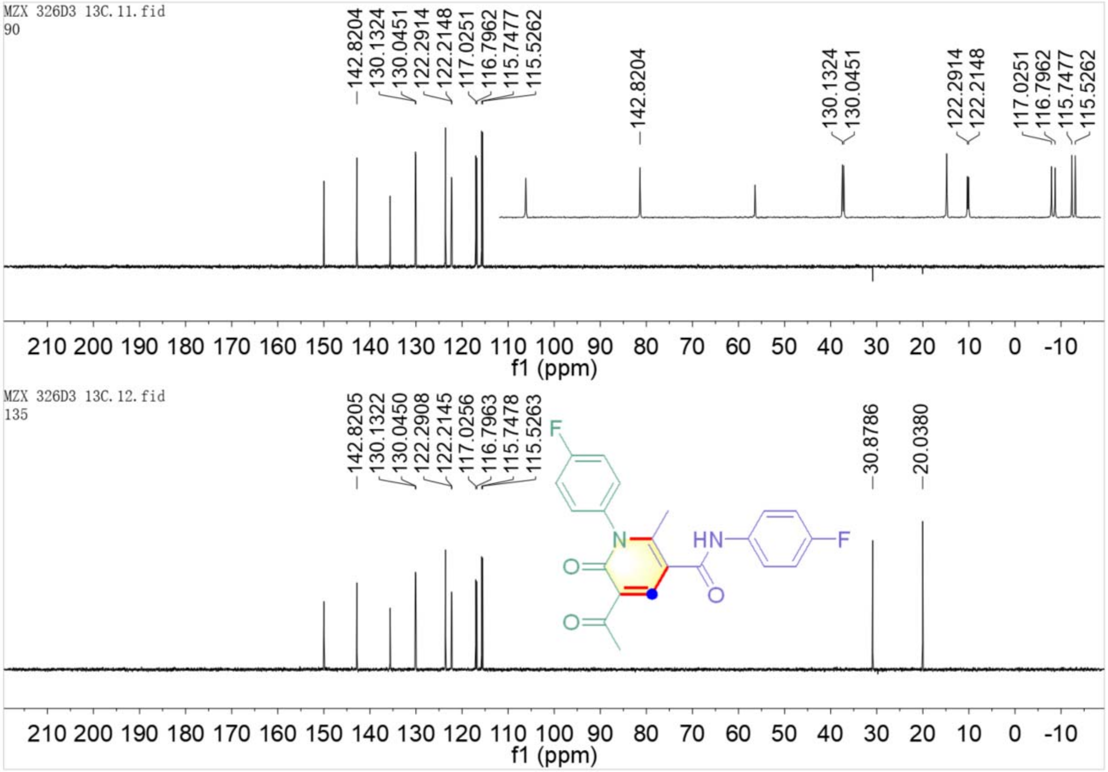
2b4, ^{1}H NMR (in pyridine-d_5)



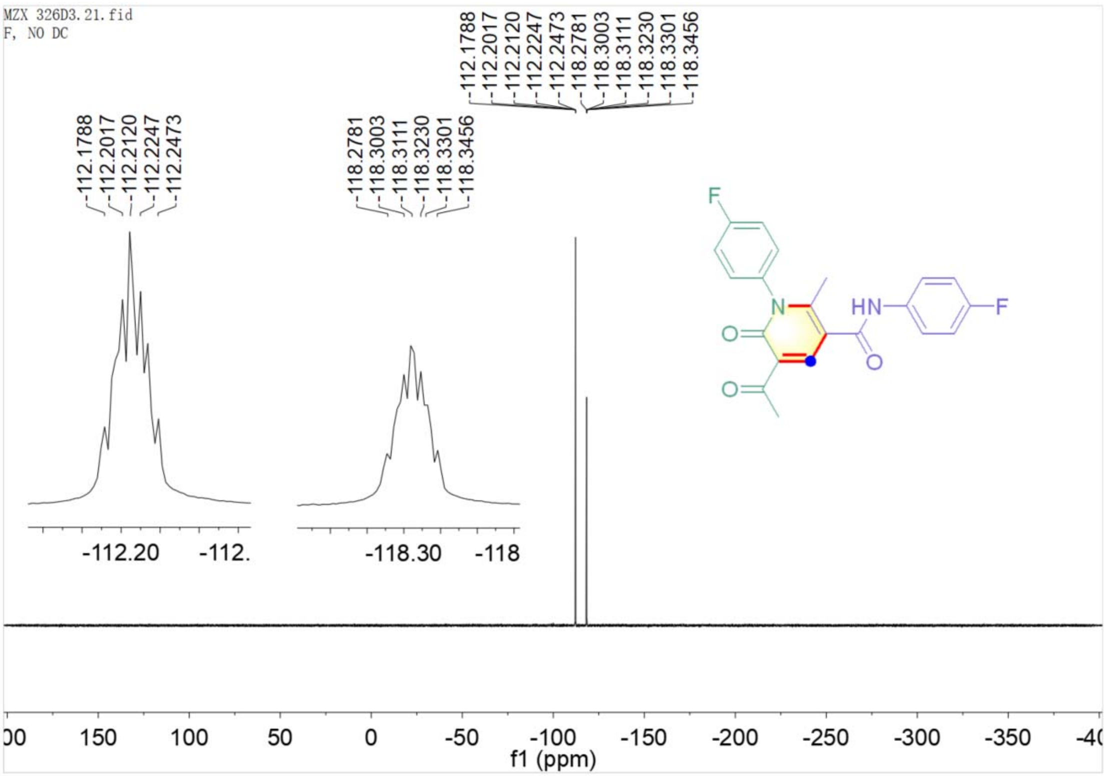
^{13}C NMR (in pyridine-d_5)



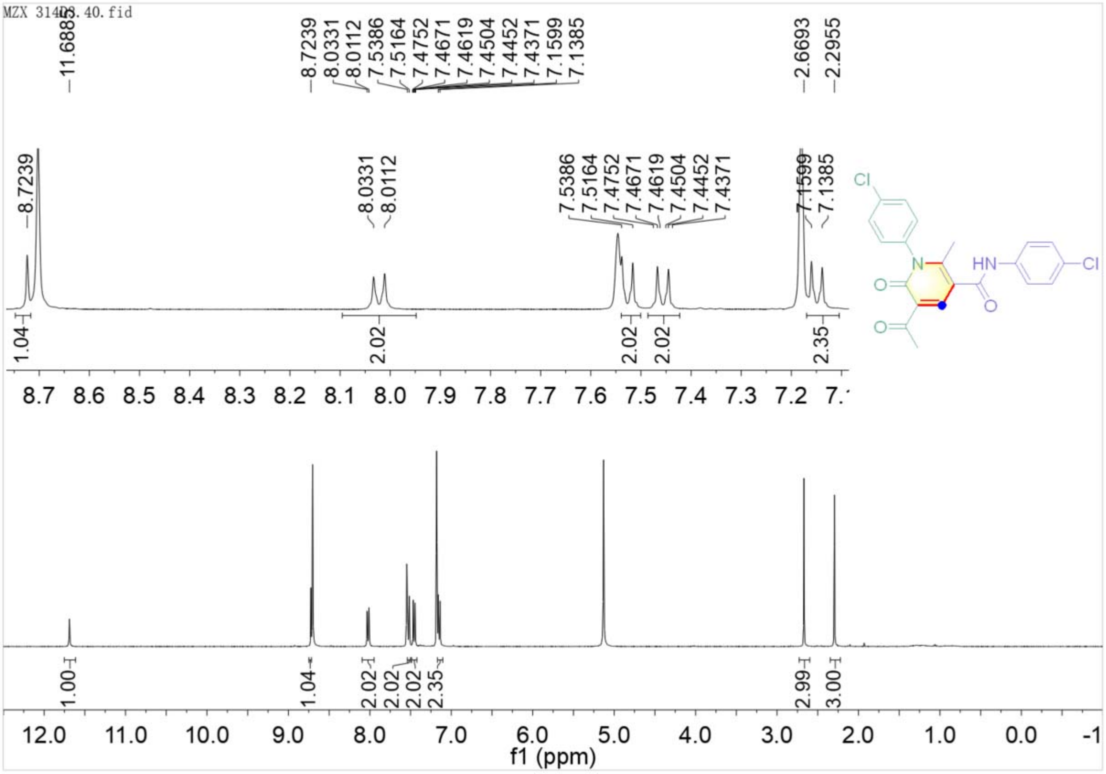
DEPT 90 and DEPT 135 (in pyridine-d_5)



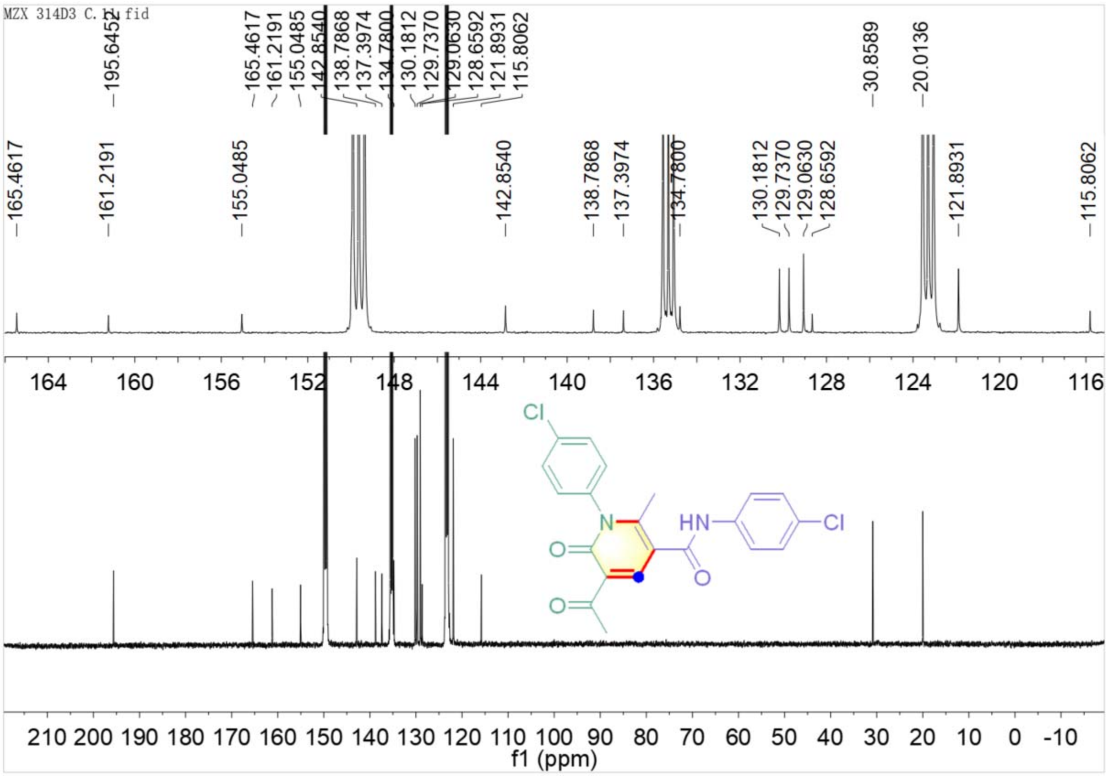
^{19}F NMR (in pyridine-d_5)



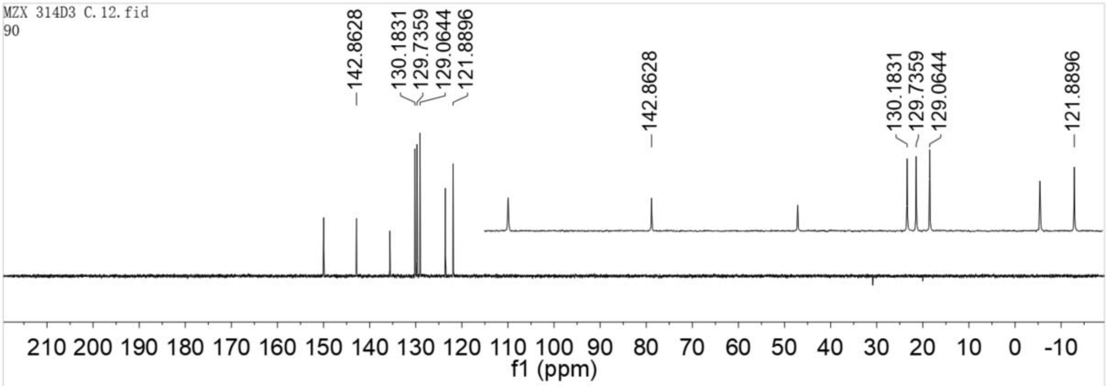
2b5, ^{1}H NMR (in pyridine-d_5)

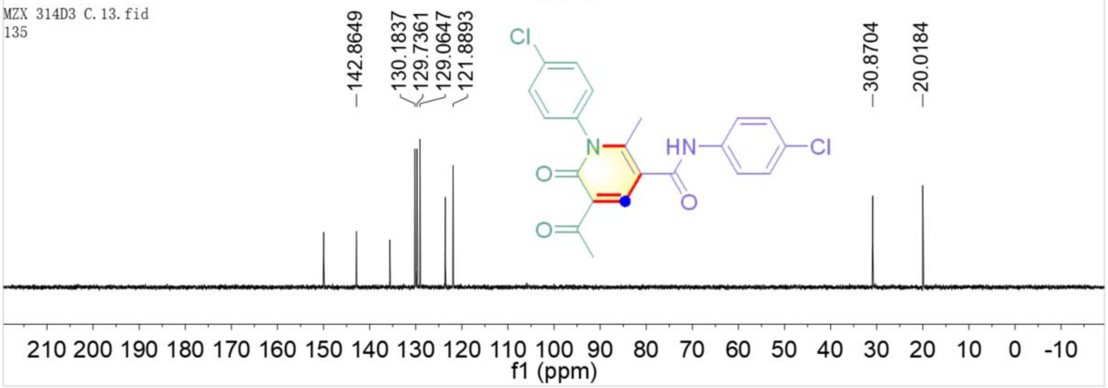


^{13}C NMR (in pyridine-d_5)

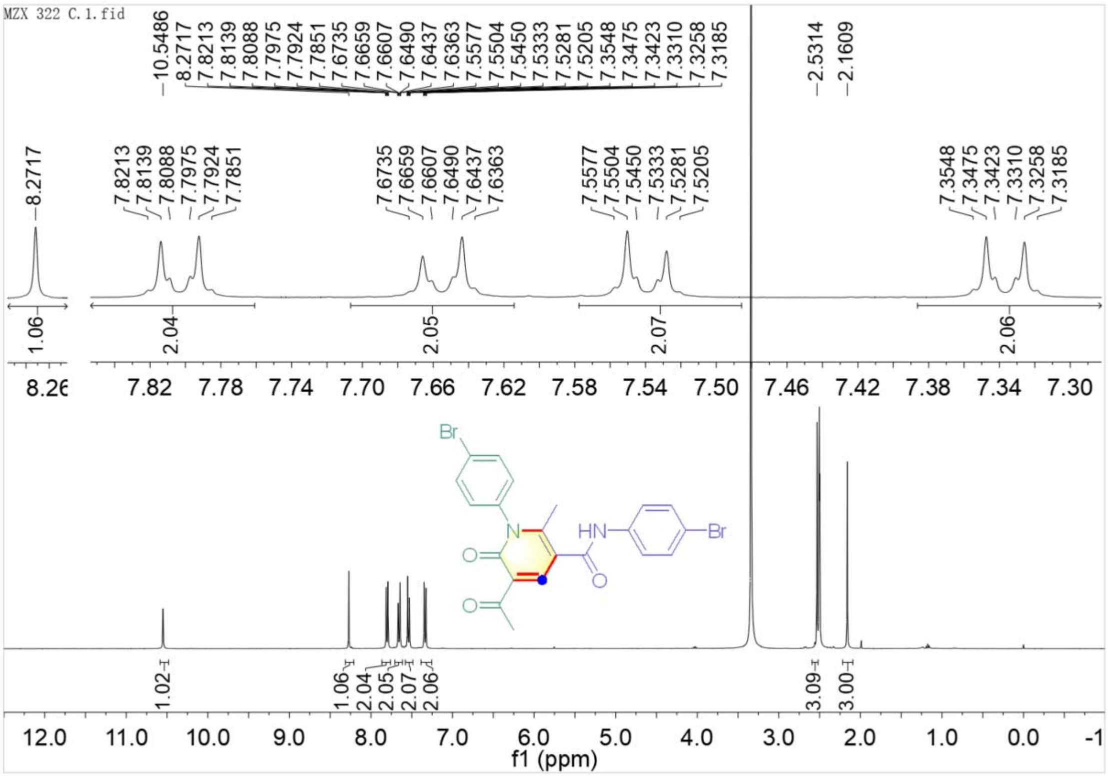


DEPT 90 and DEPT 135 (in pyridine-d_5)

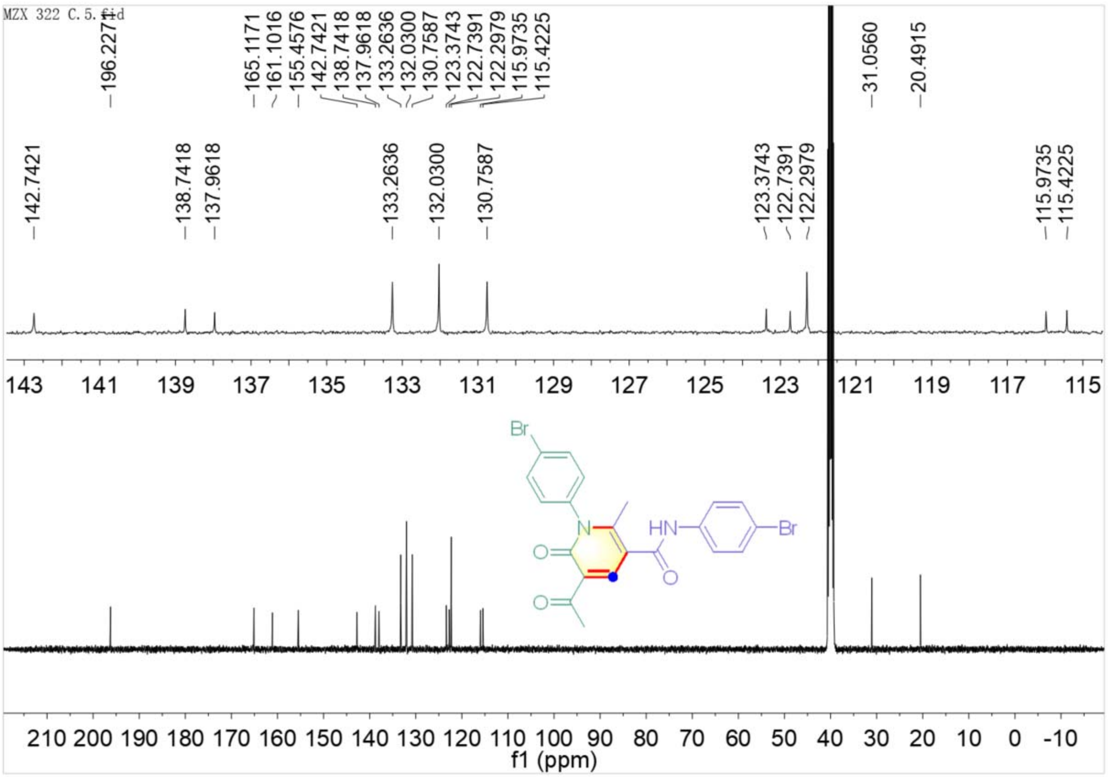




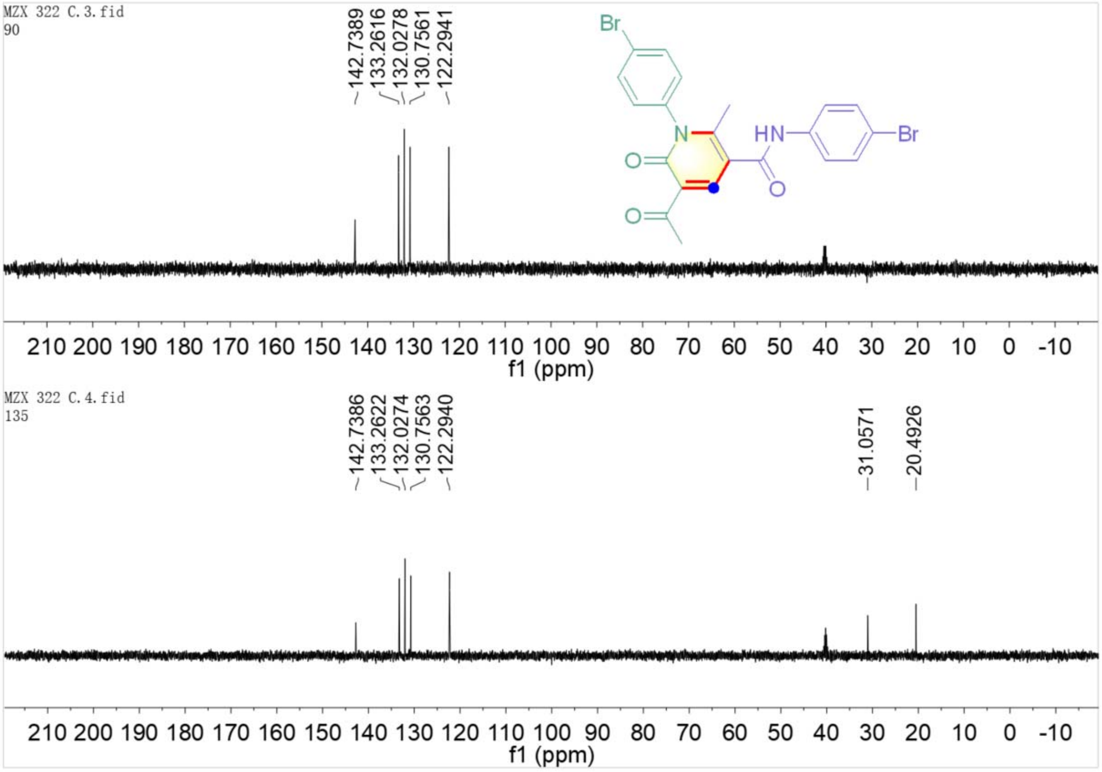
2b6, ¹H NMR



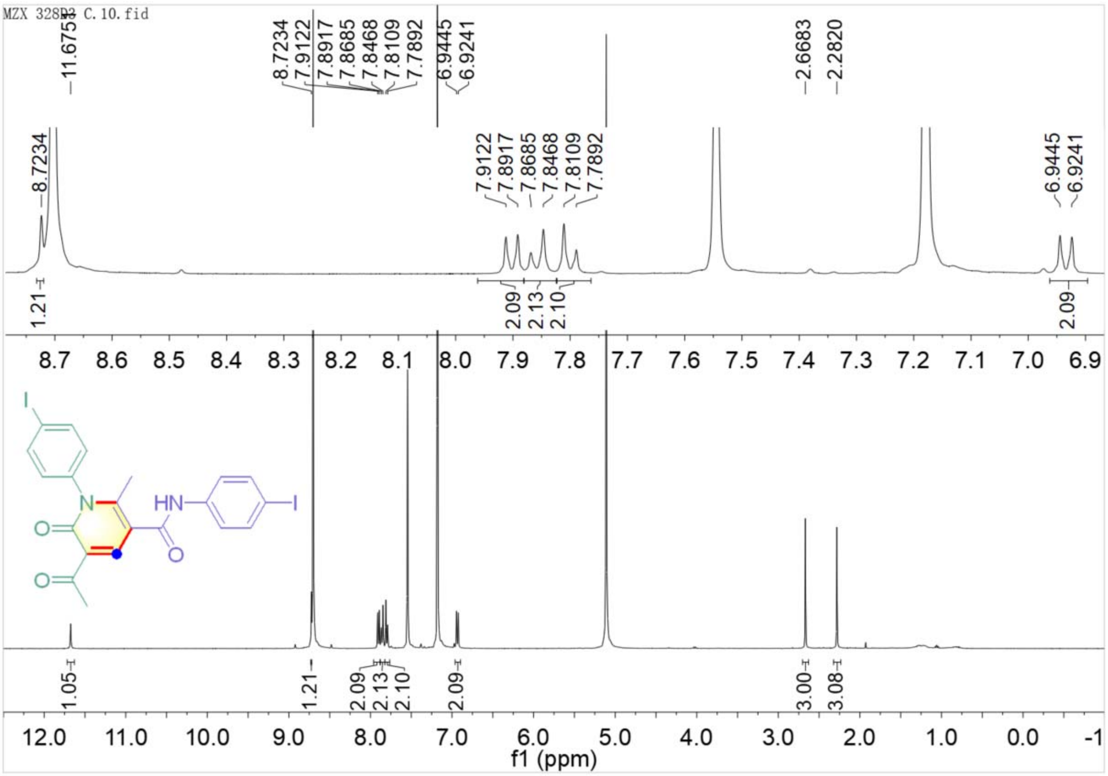
¹³C NMR



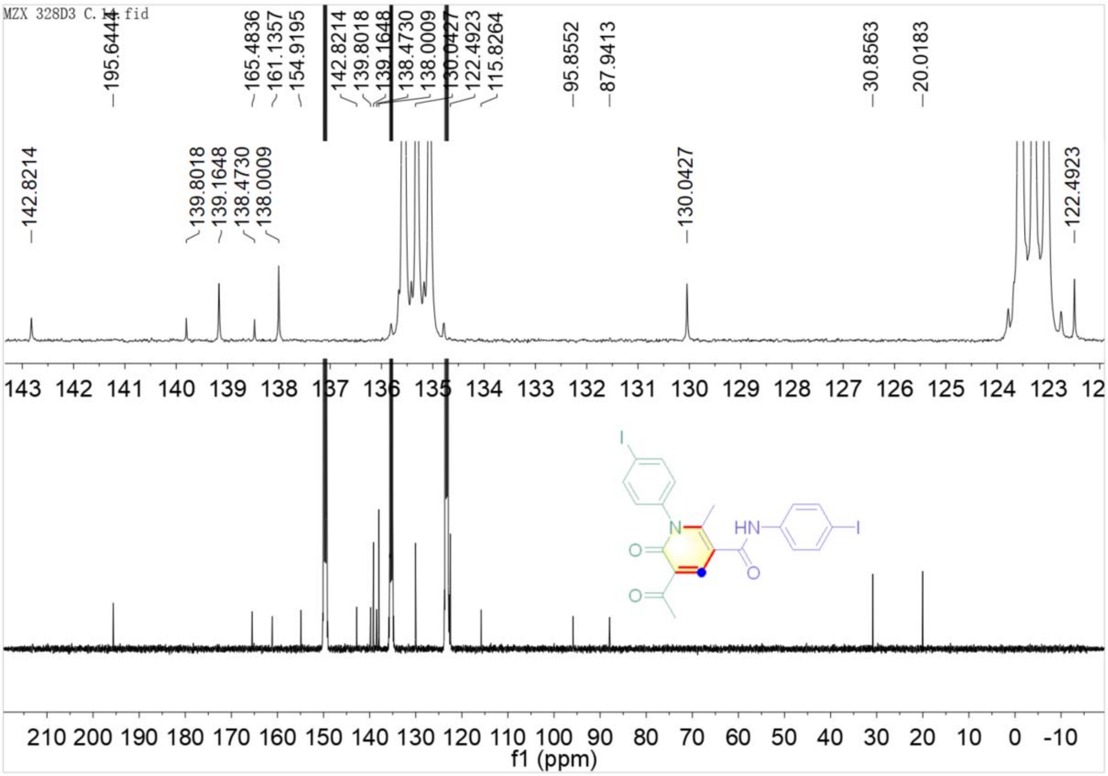
DEPT 90 and DEPT 135



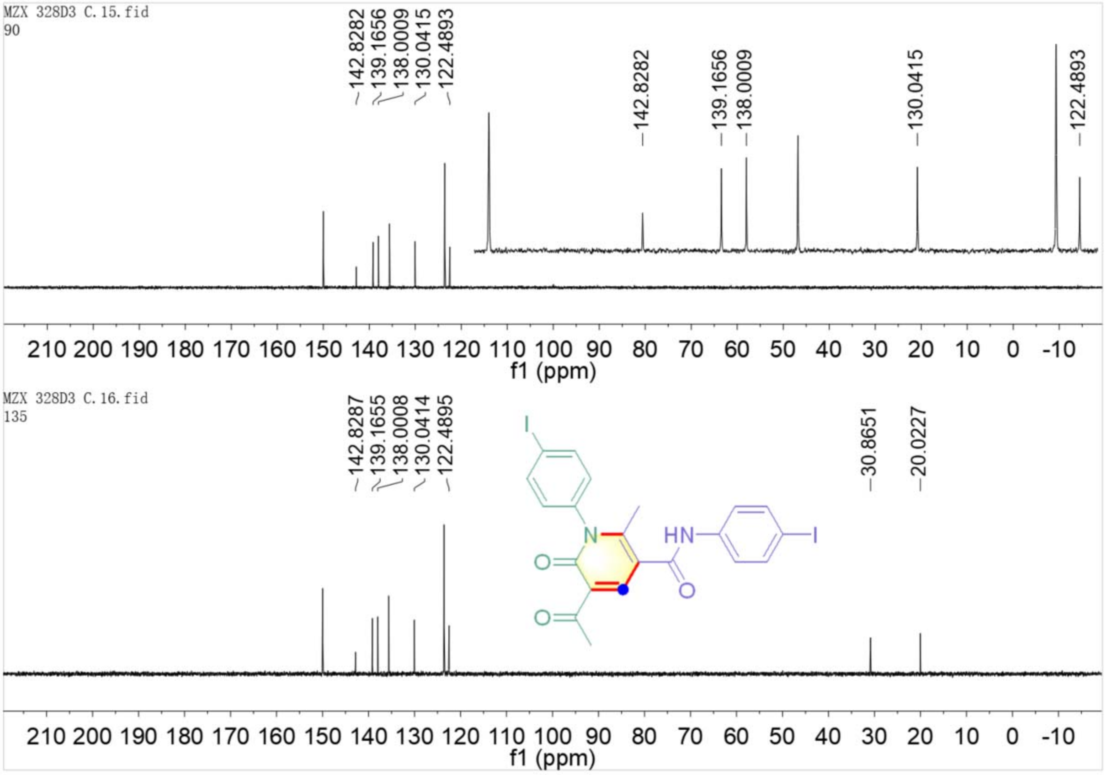
2b7, ^{1}H NMR (in pyridine-d_5)



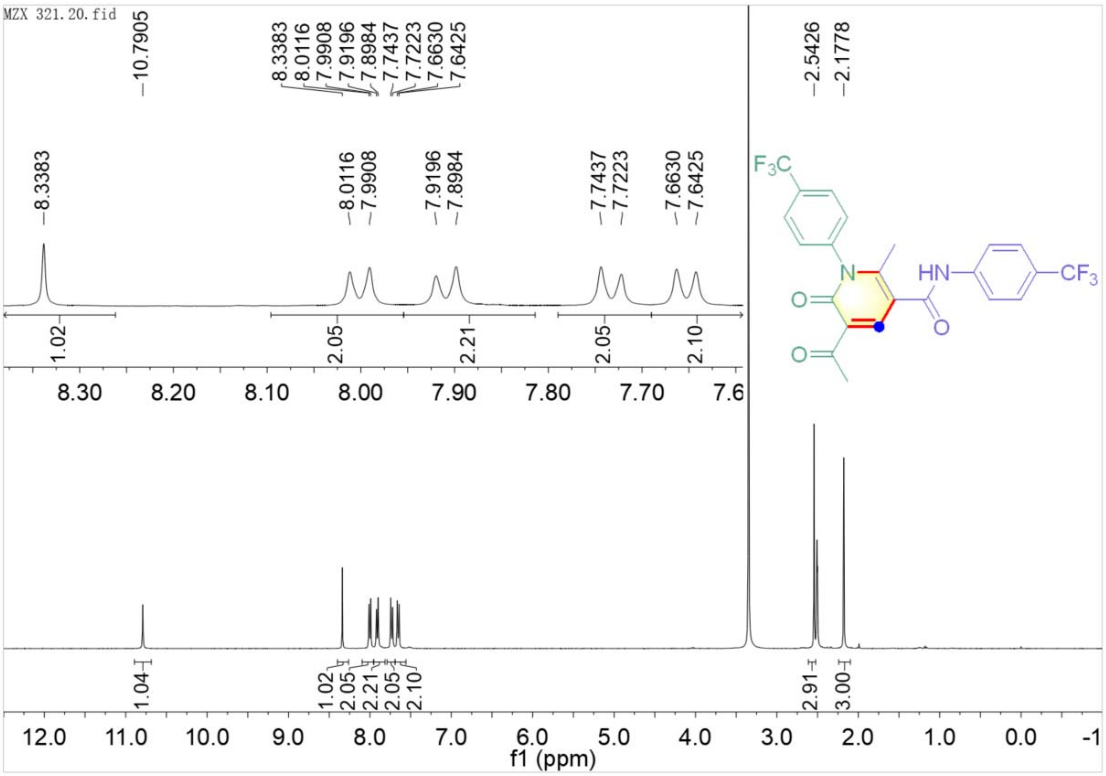
^{13}C NMR (in pyridine-d_5)



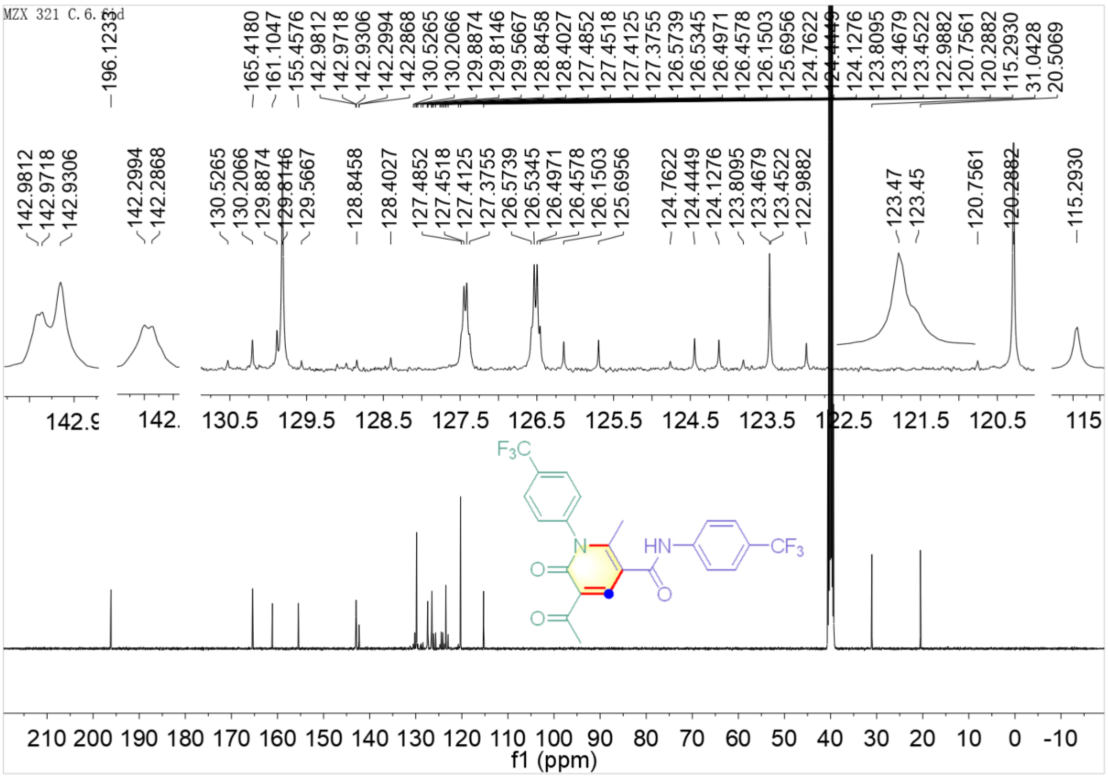
DEPT 90 and DEPT 135 (in pyridine-d_5)



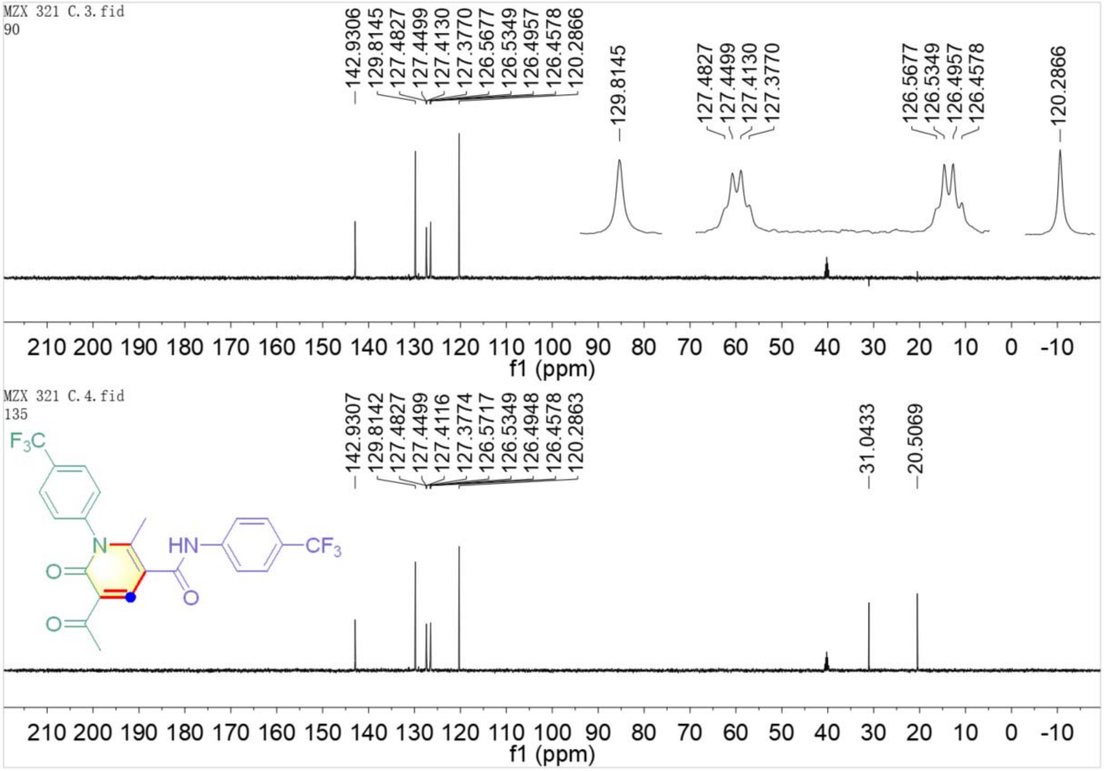
2b8, ^{1}H NMR



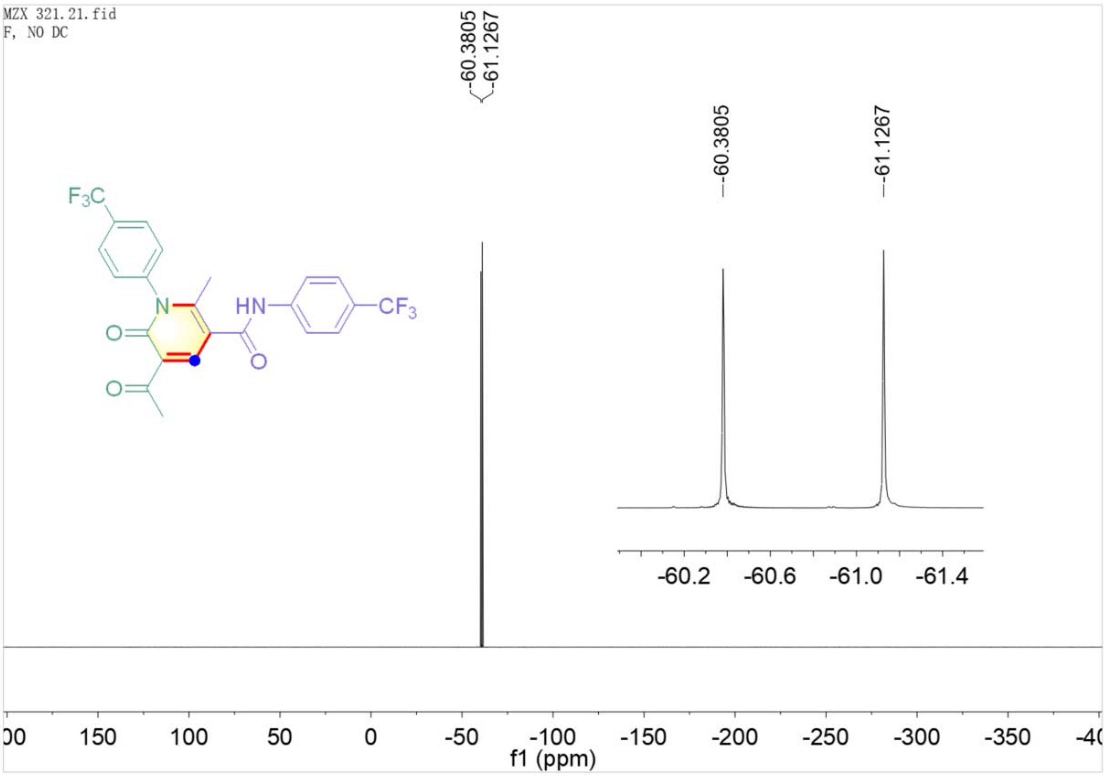
^{13}C NMR



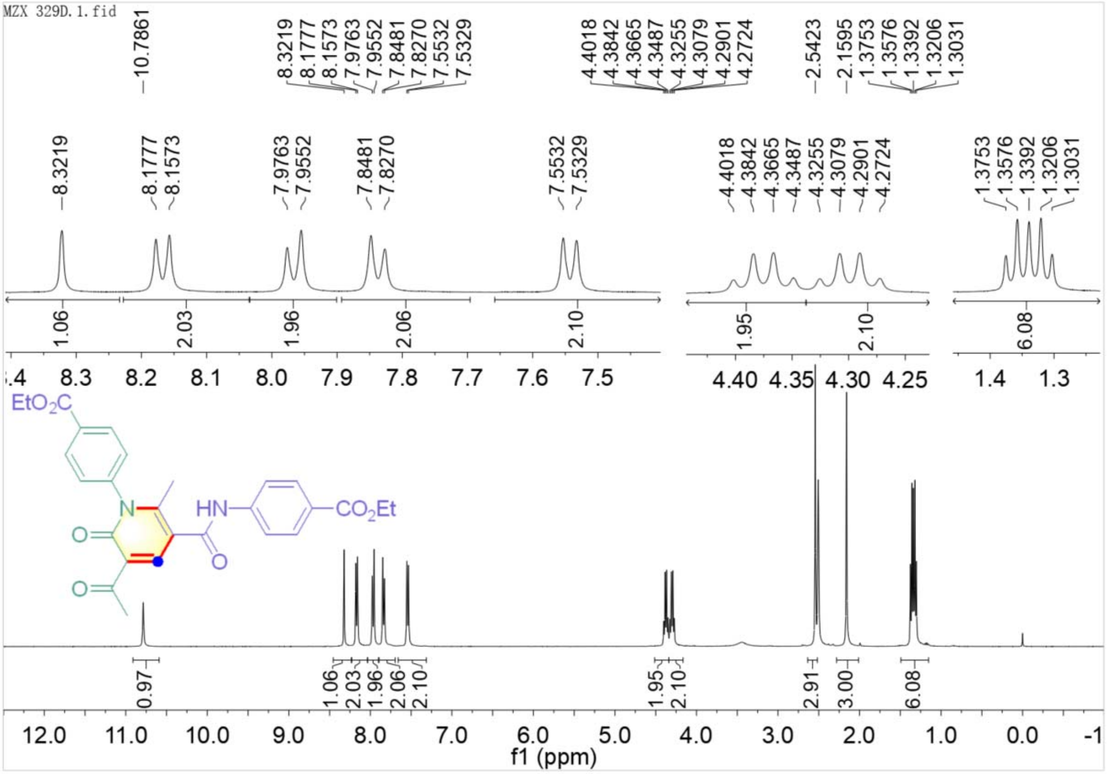
DEPT 90 and DEPT 135



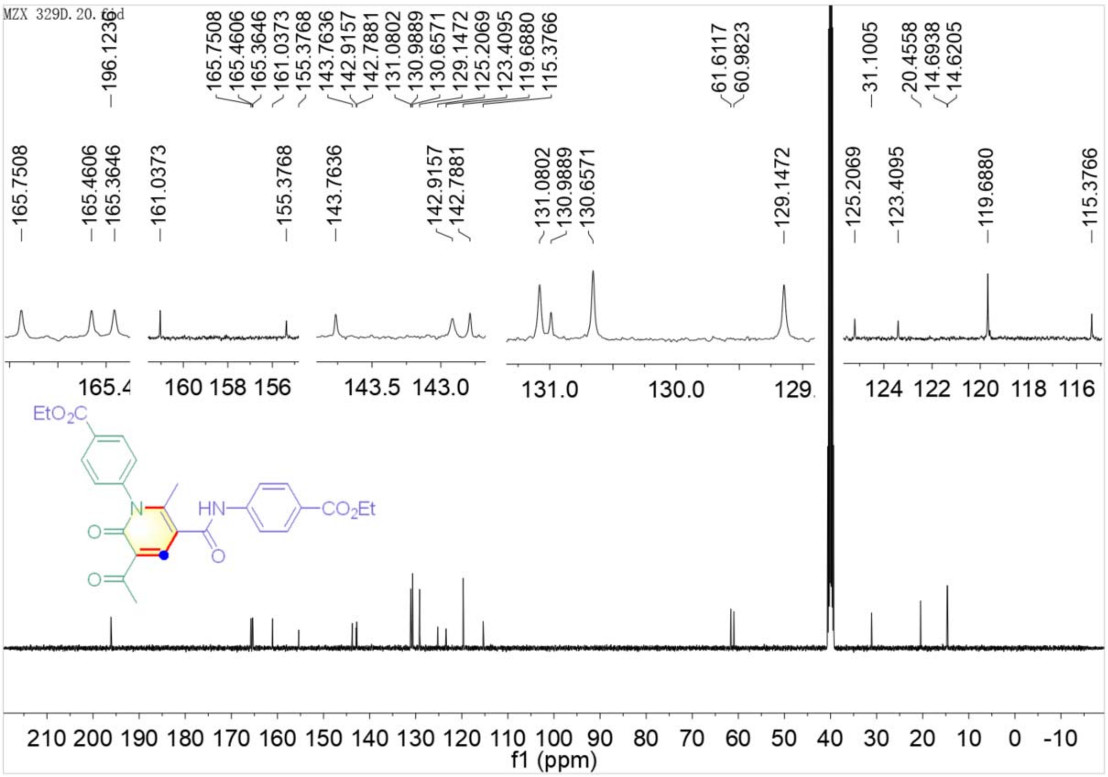
^{19}F NMR



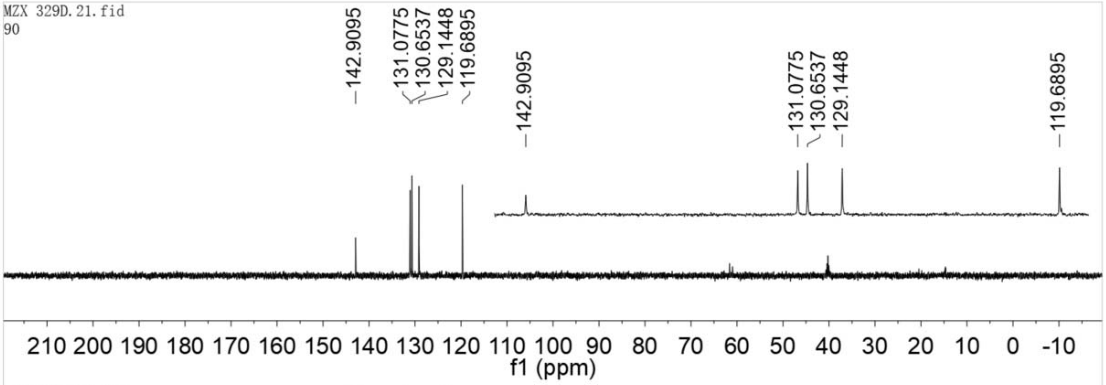
2b9, ^{1}H NMR

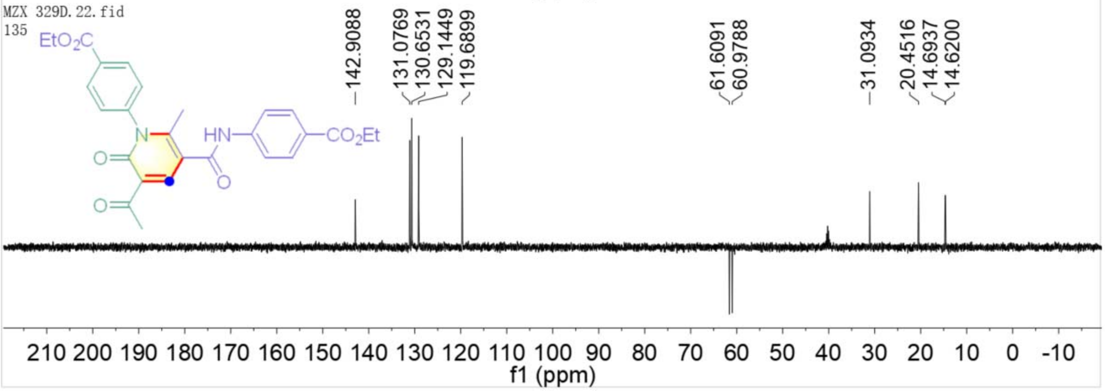


^{13}C NMR

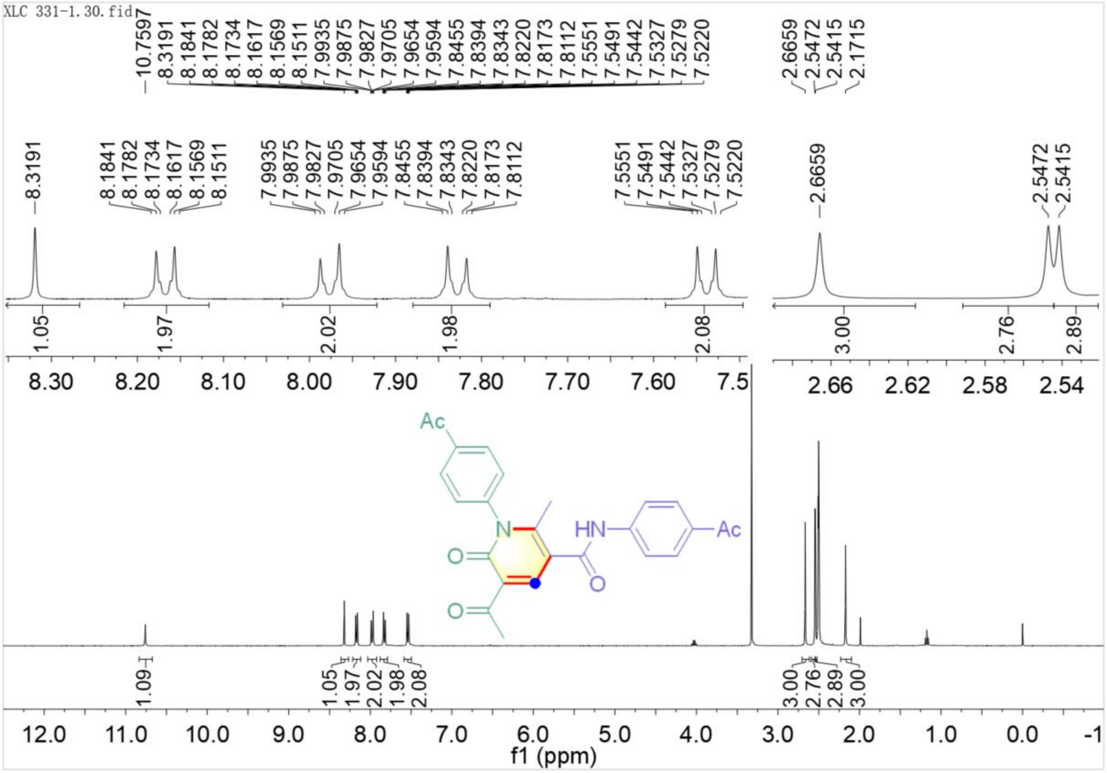


DEPT 90 and DEPT 135

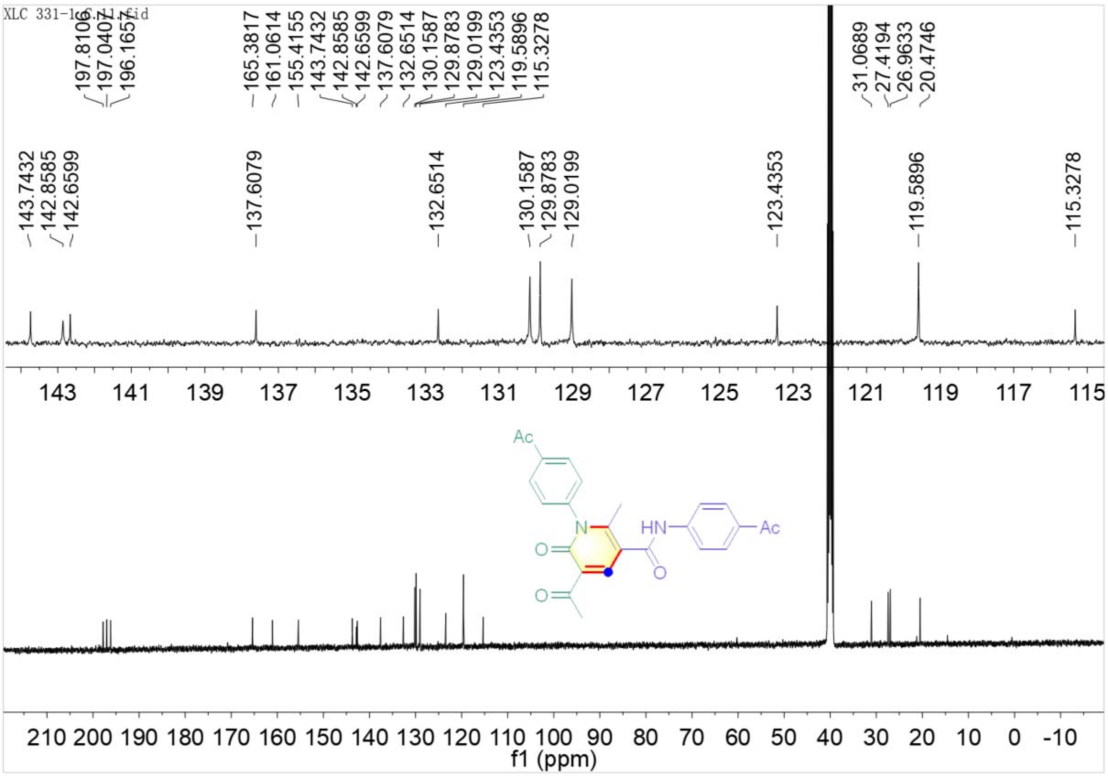




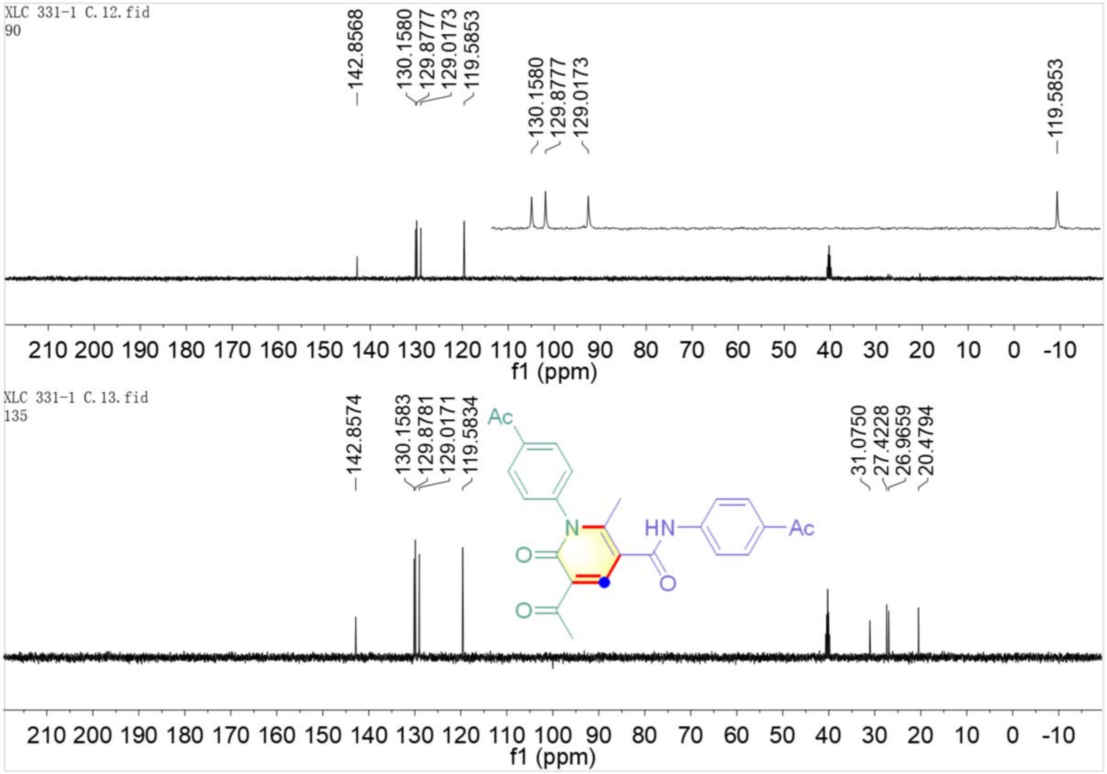
2b10, ^{1}H NMR



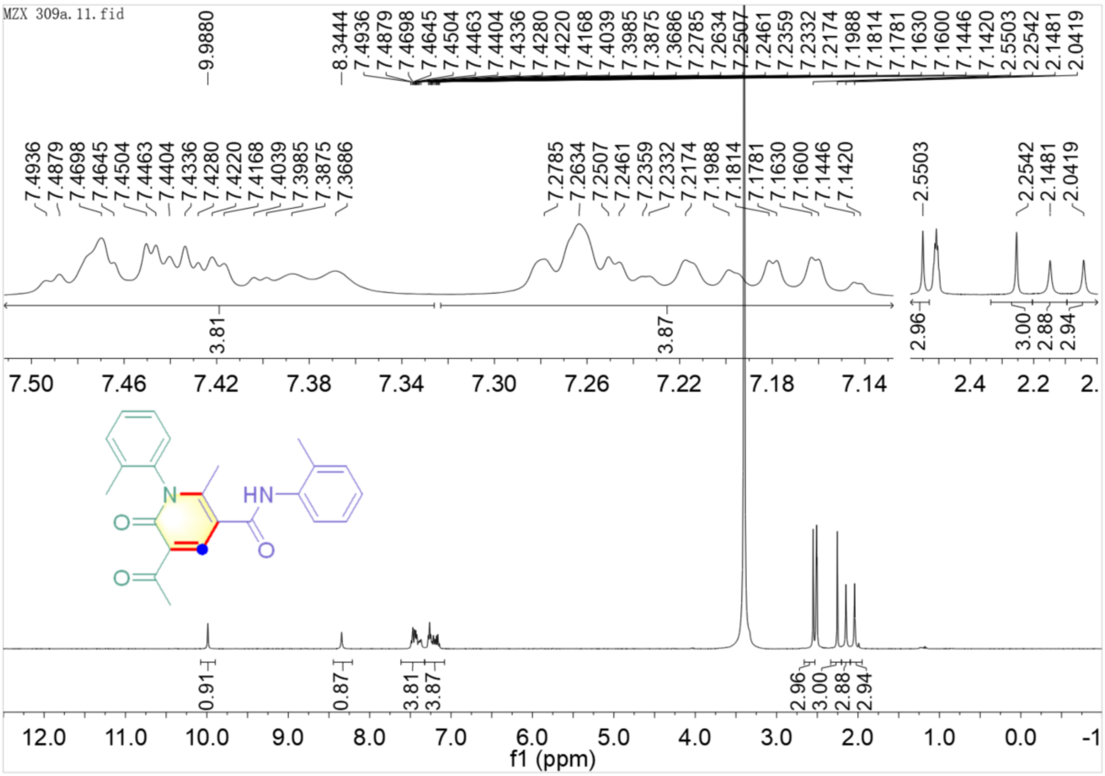
^{13}C NMR



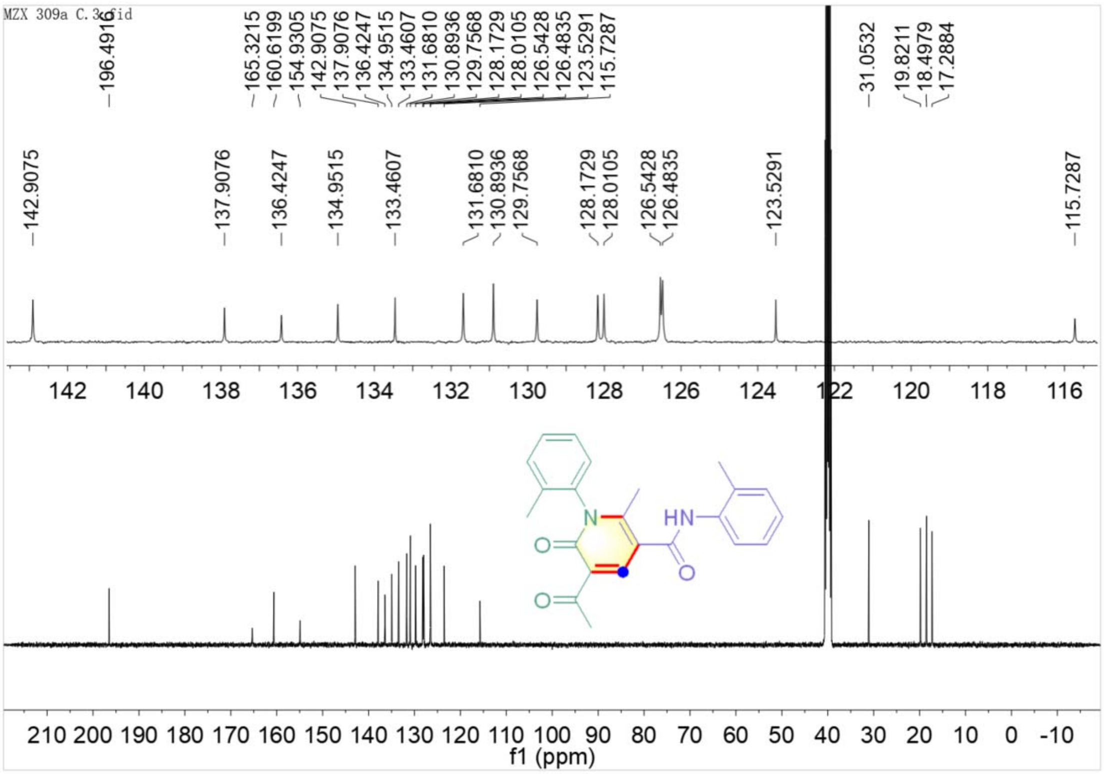
DEPT 90 and DEPT 135



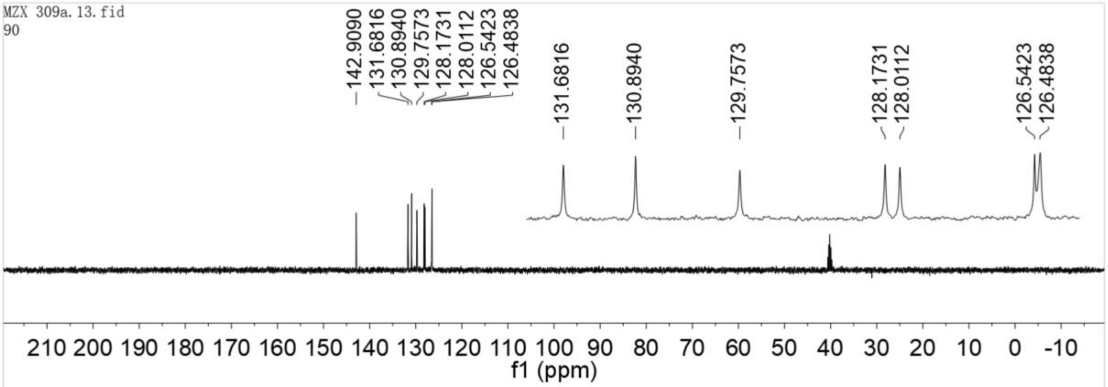
2c1, ^{1}H NMR

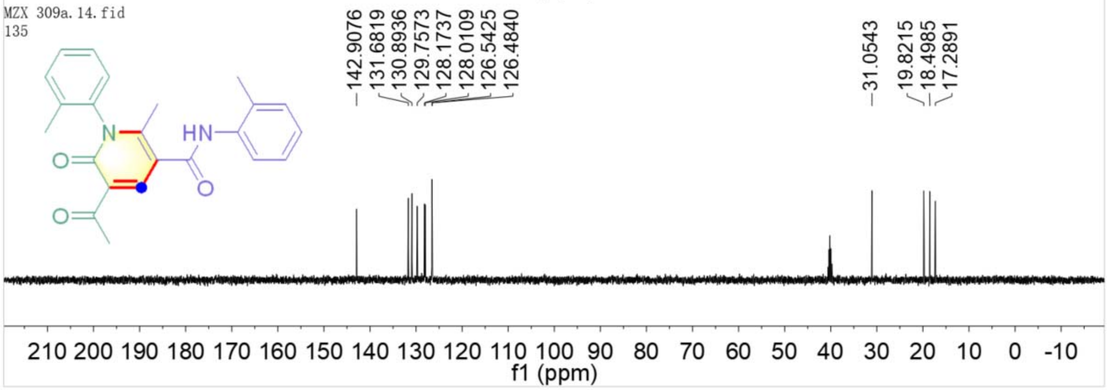


^{13}C NMR

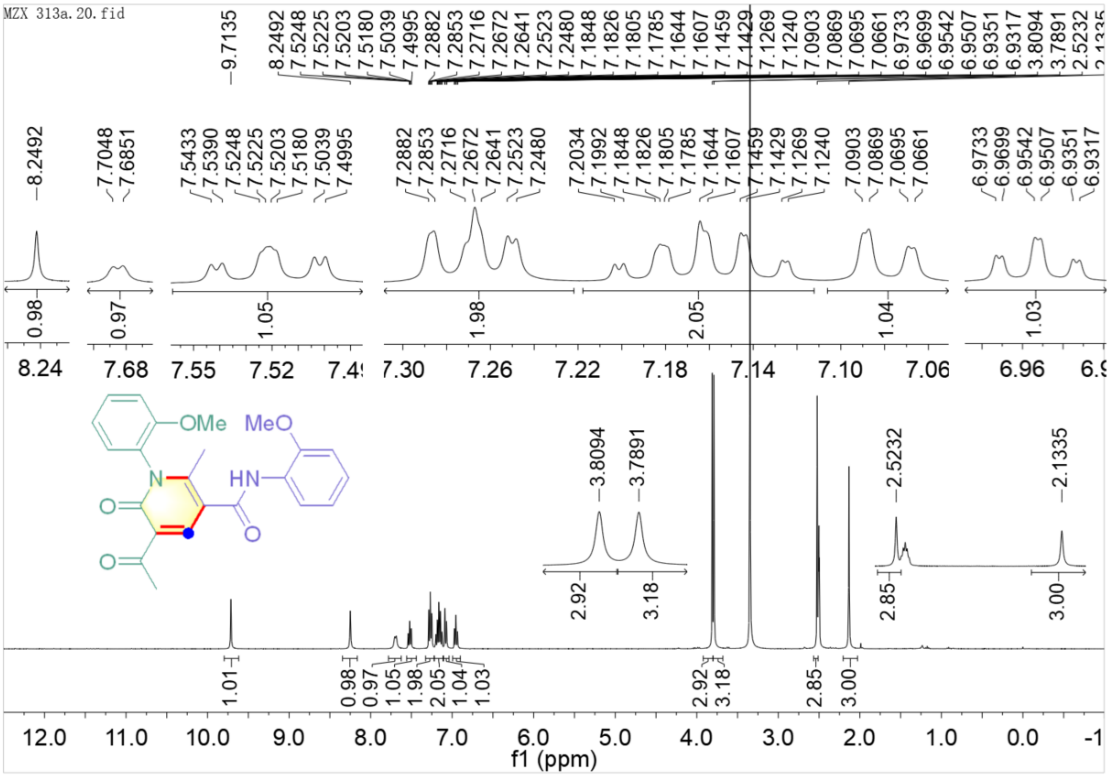


DEPT 90 and DEPT 135

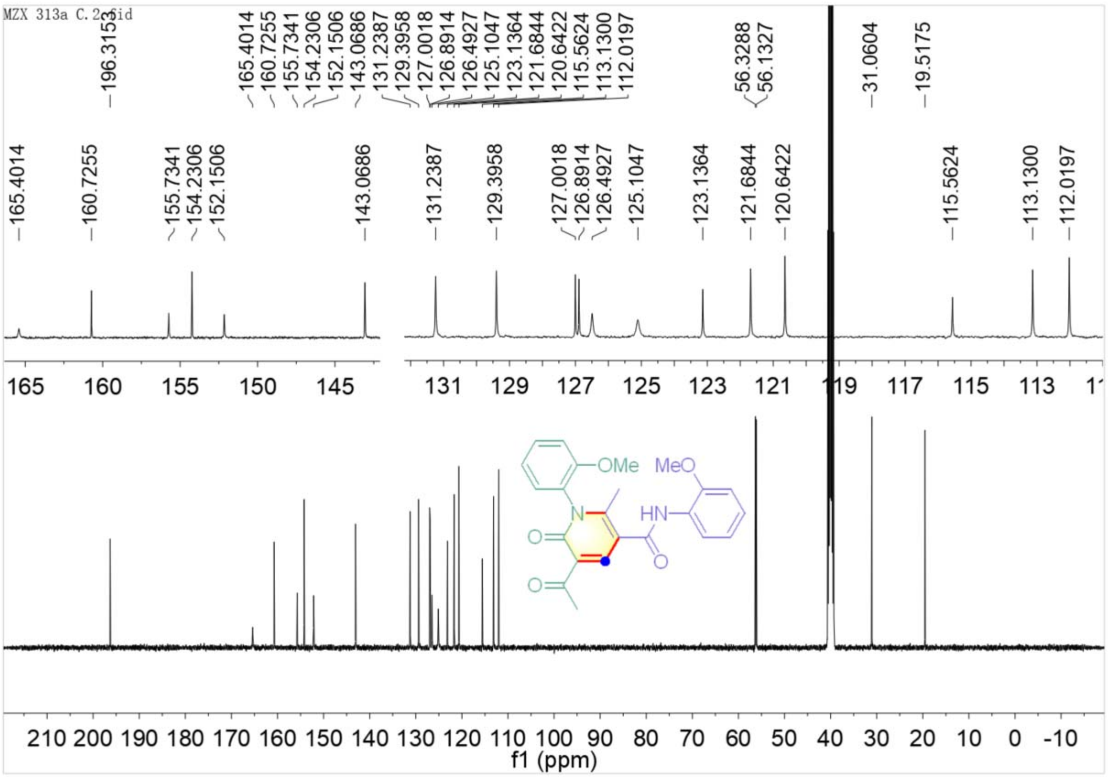




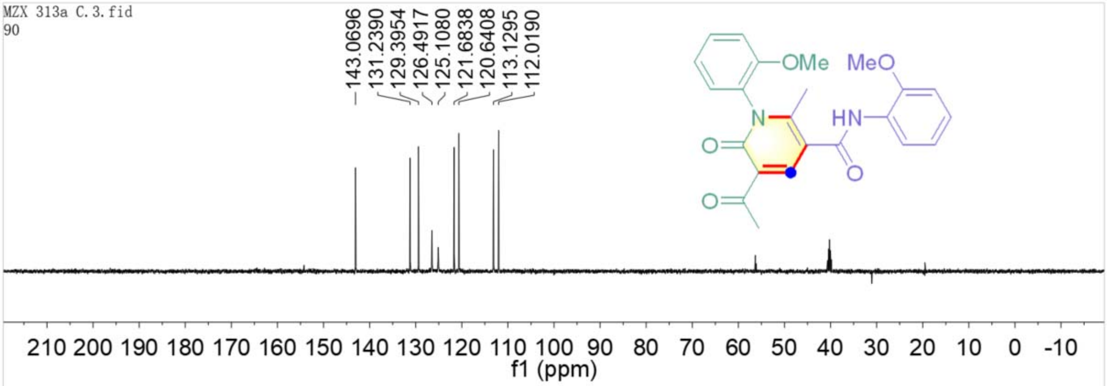
2c2, ^{1}H NMR

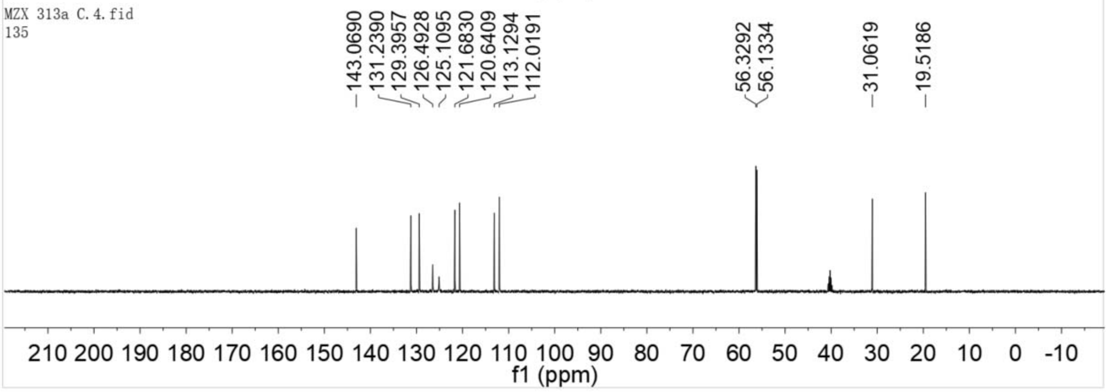


^{13}C NMR

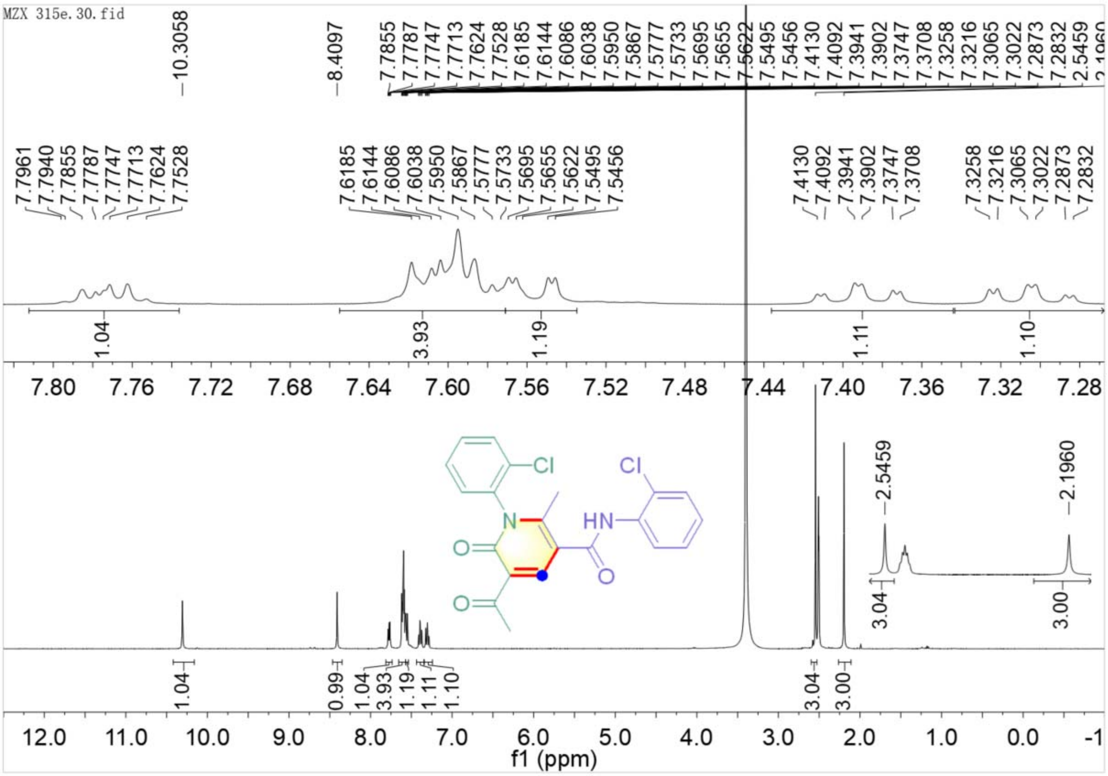


DEPT 90 and DEPT 135

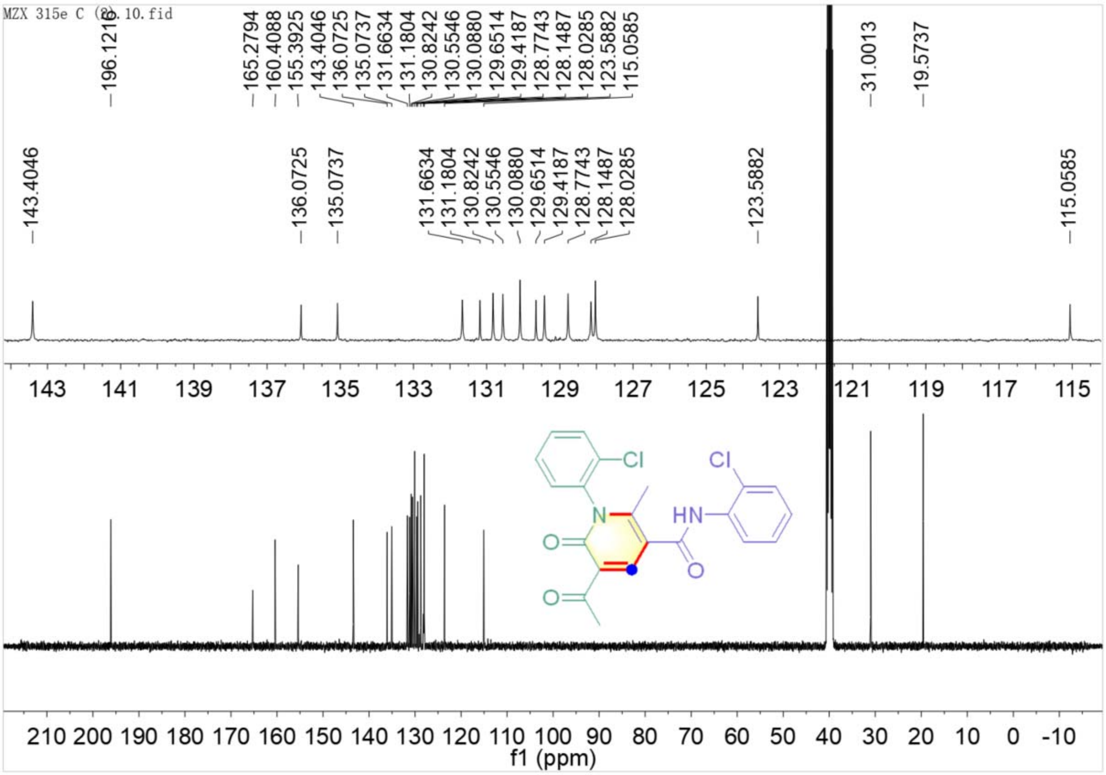




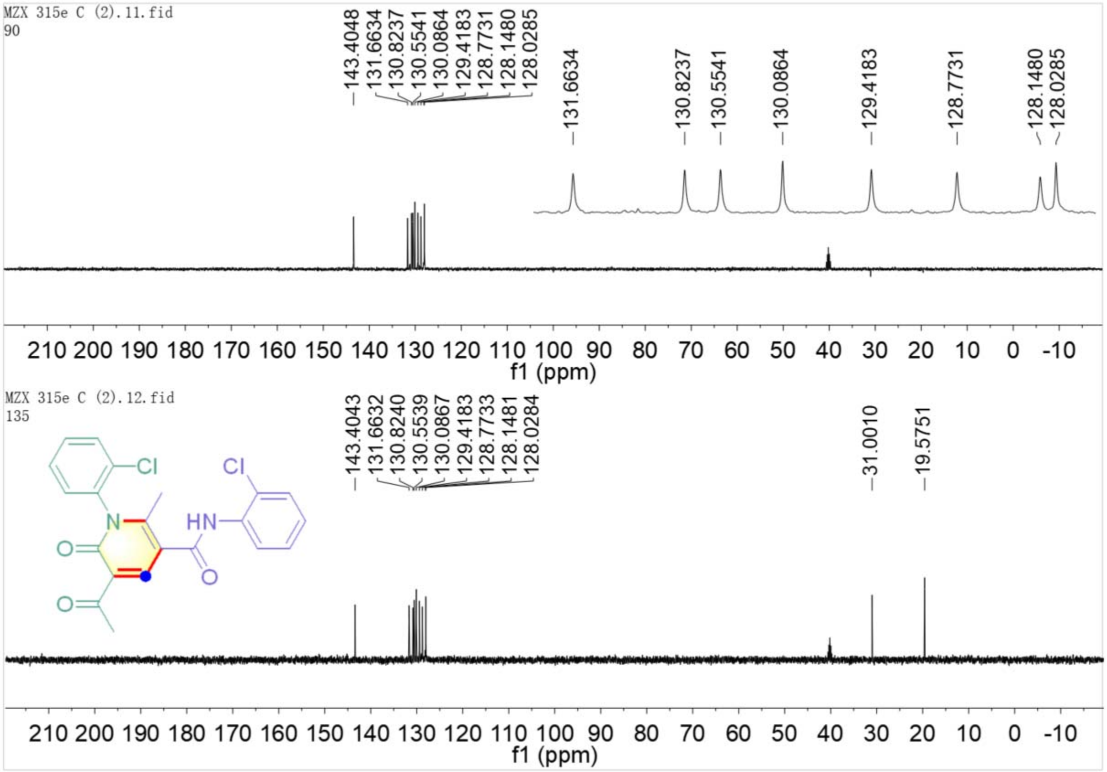
2c3, ^{1}H NMR



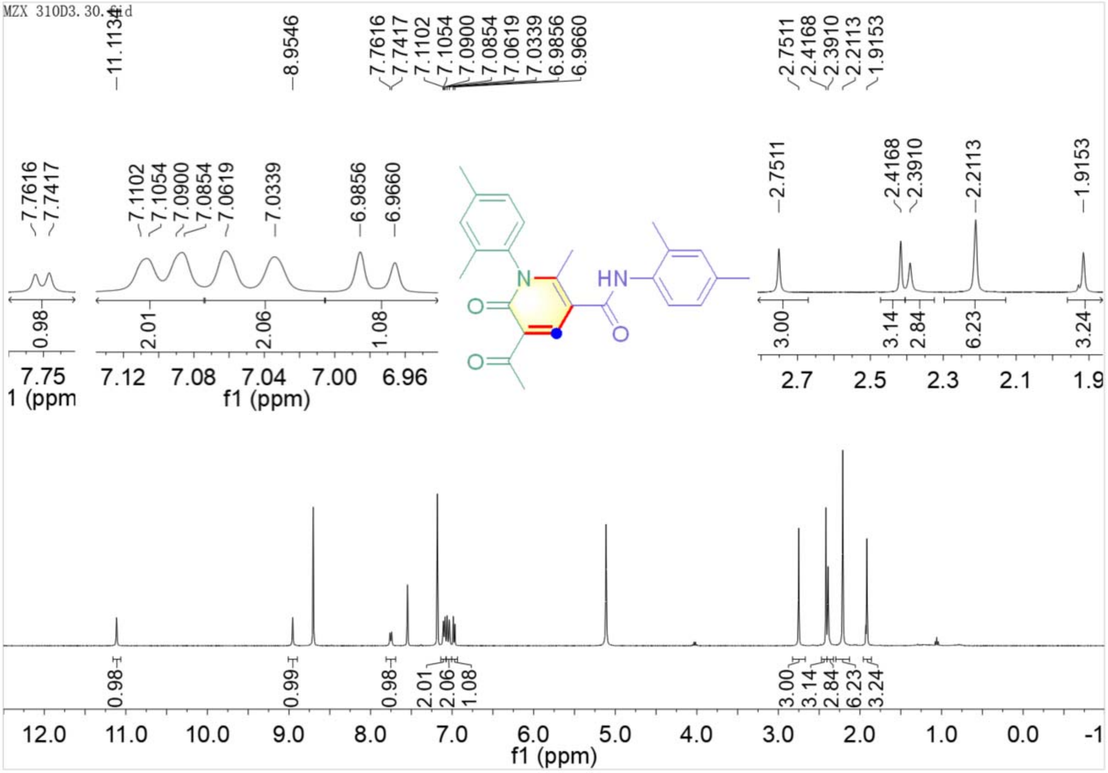
^{13}C NMR



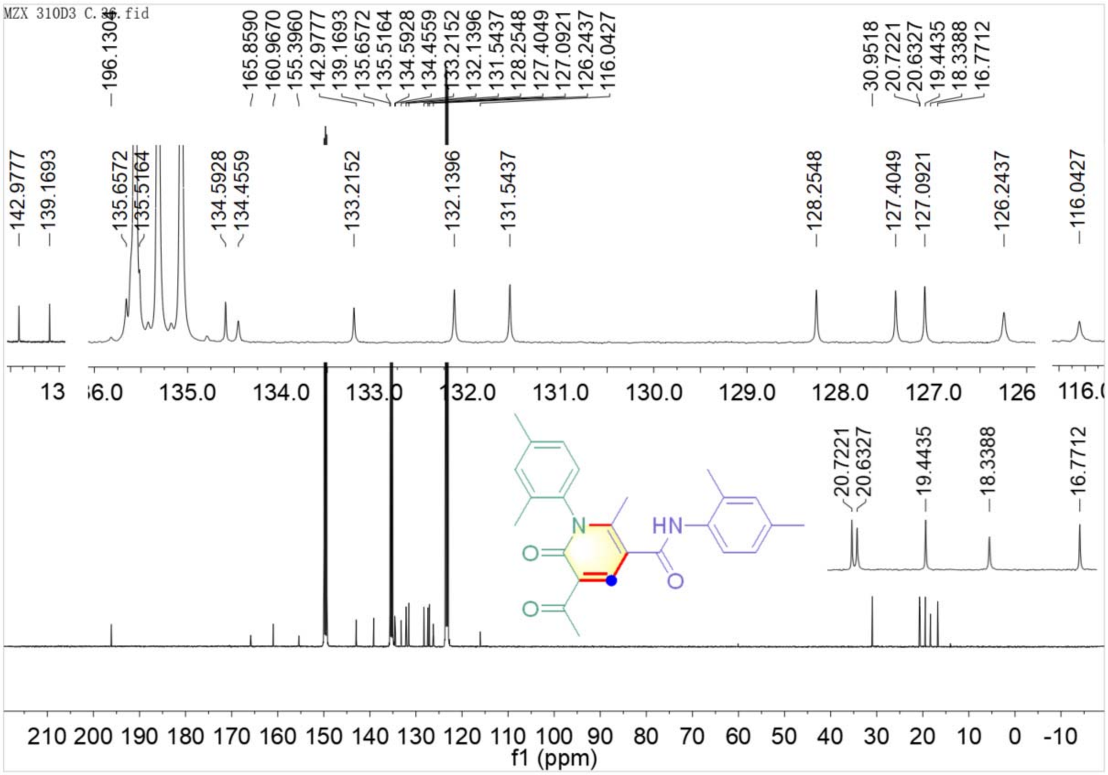
DEPT 90 and DEPT 135



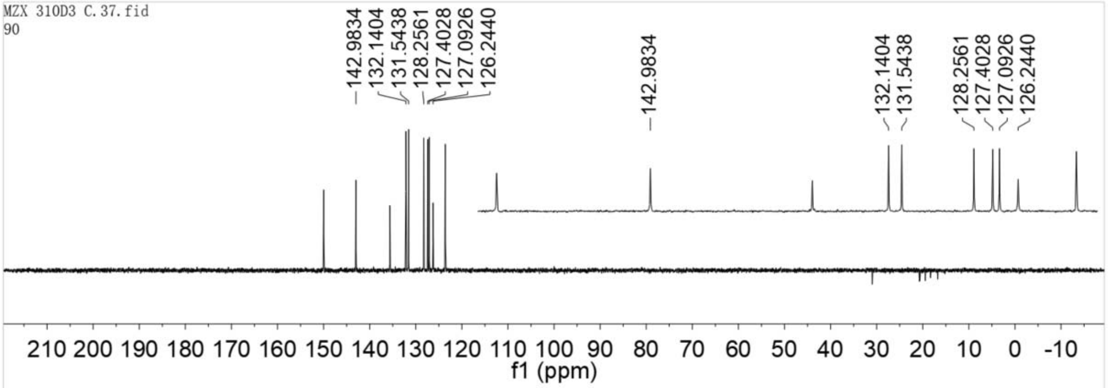
2d1, ^{1}H NMR (in pyridine-d_5)

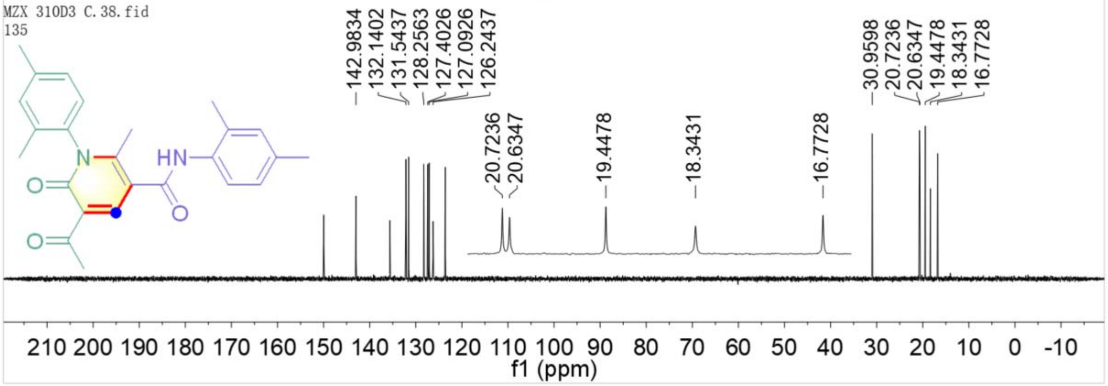


^{13}C NMR (in pyridine-d_5)

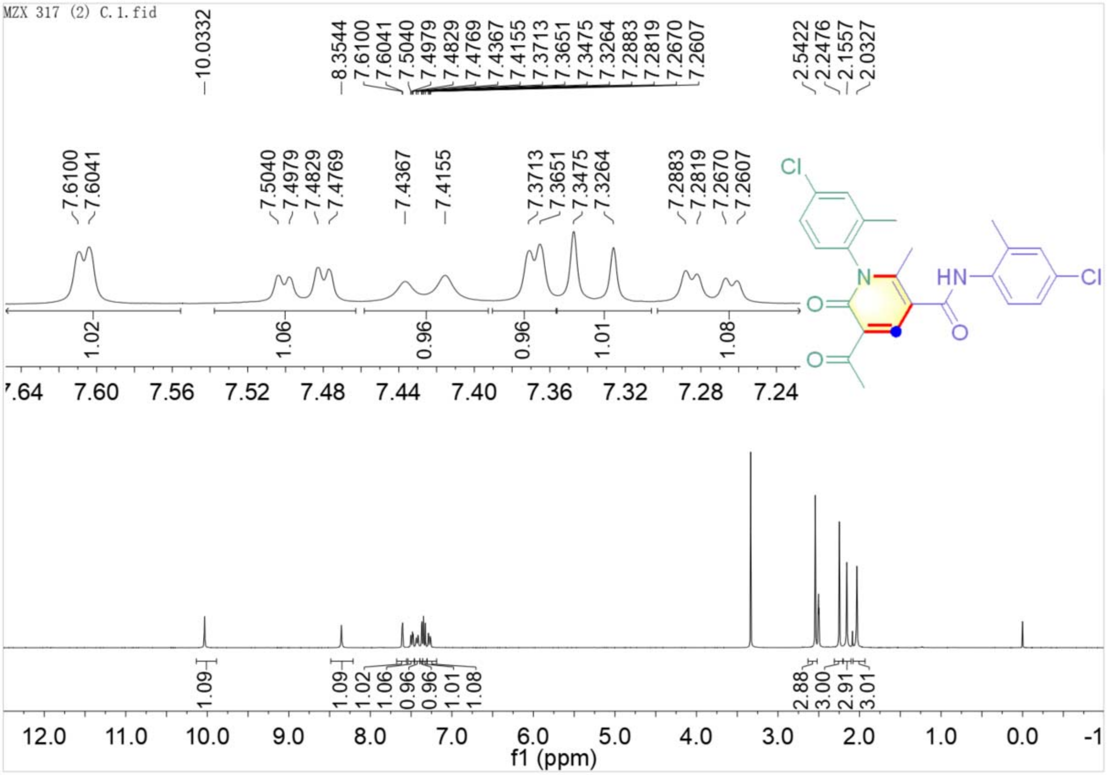


DEPT 90 and DEPT 135 (in pyridine-d_5)

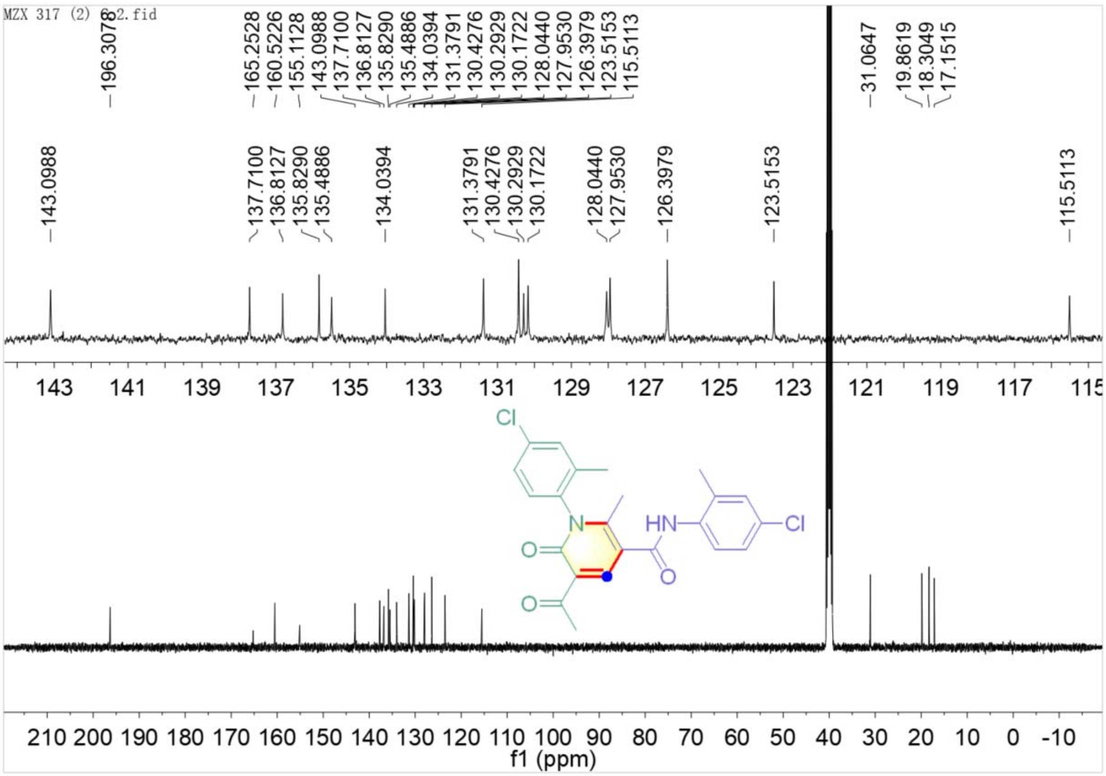




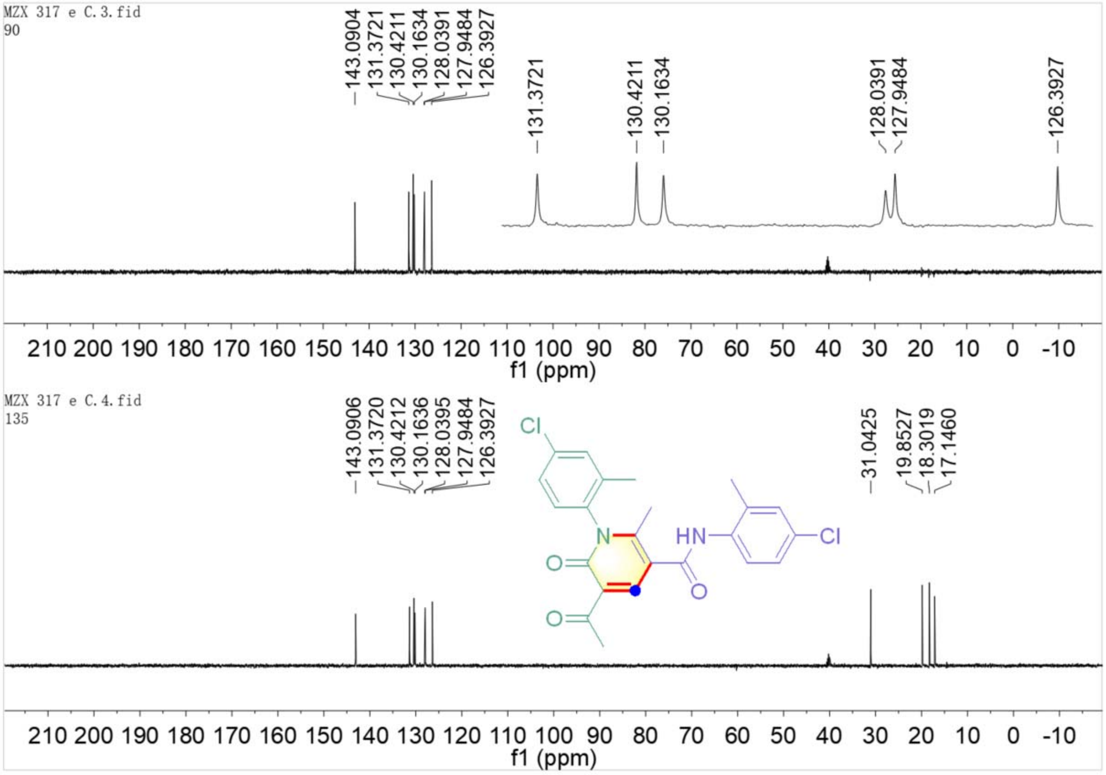
2d2, ^{1}H NMR



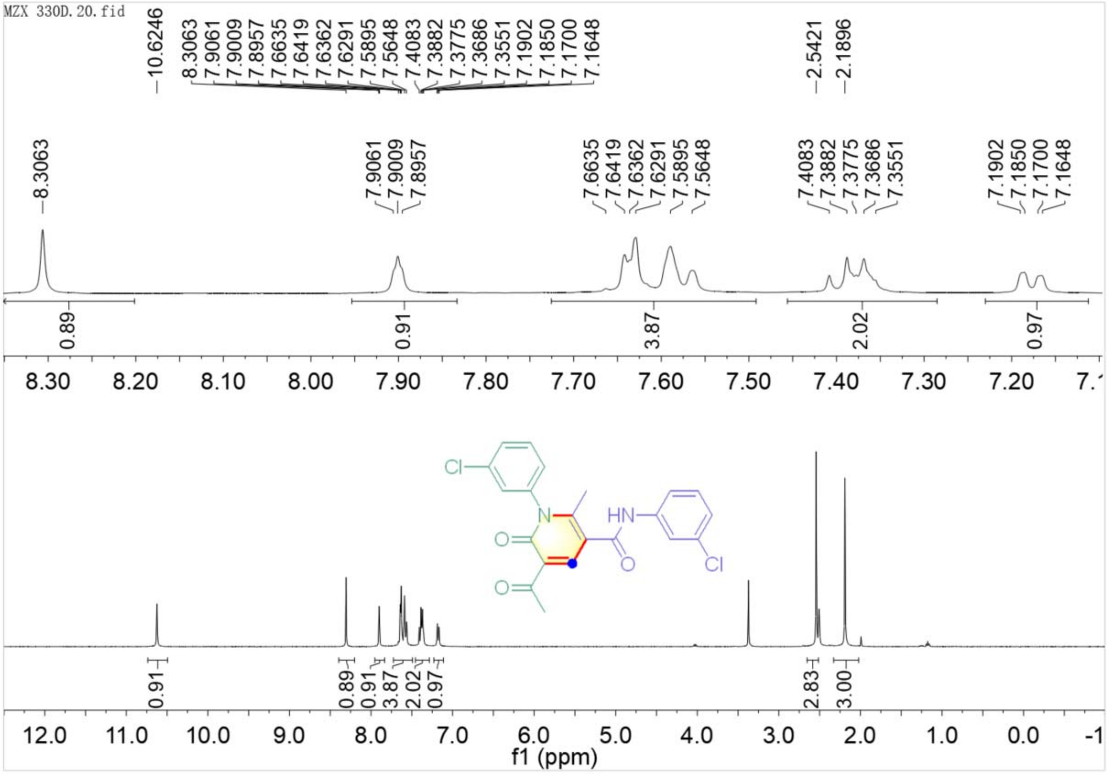
^{13}C NMR



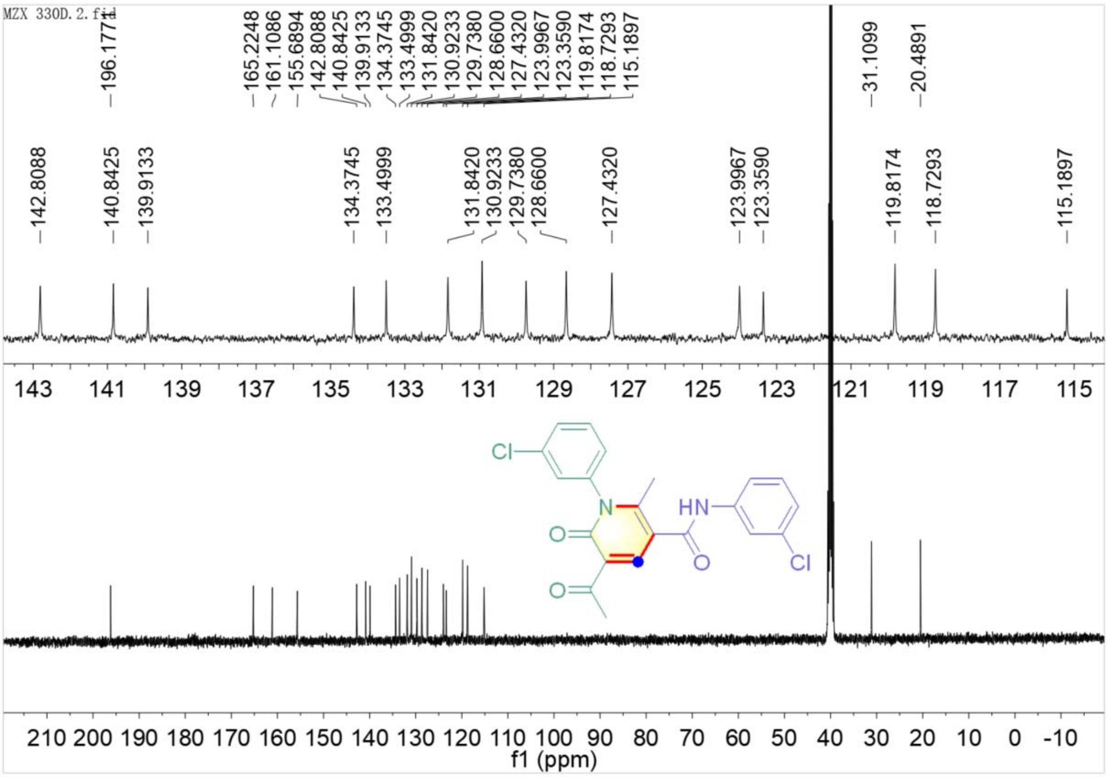
DEPT 90 and DEPT 135



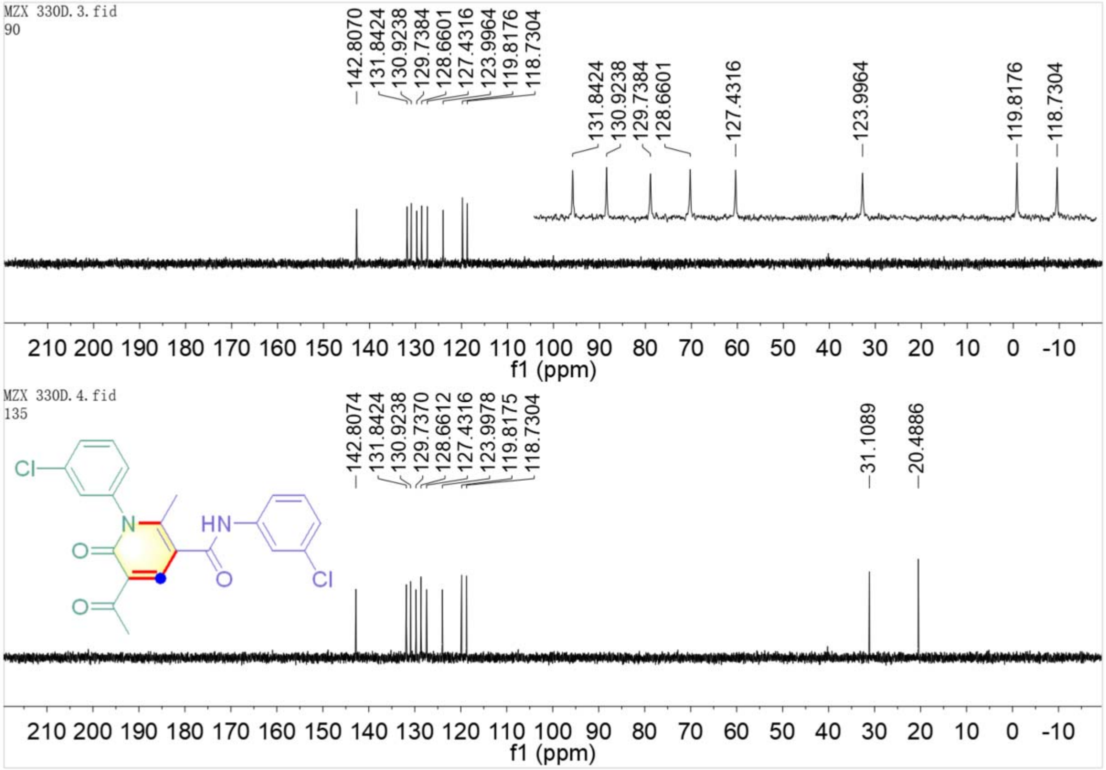
2e, ^{1}H NMR



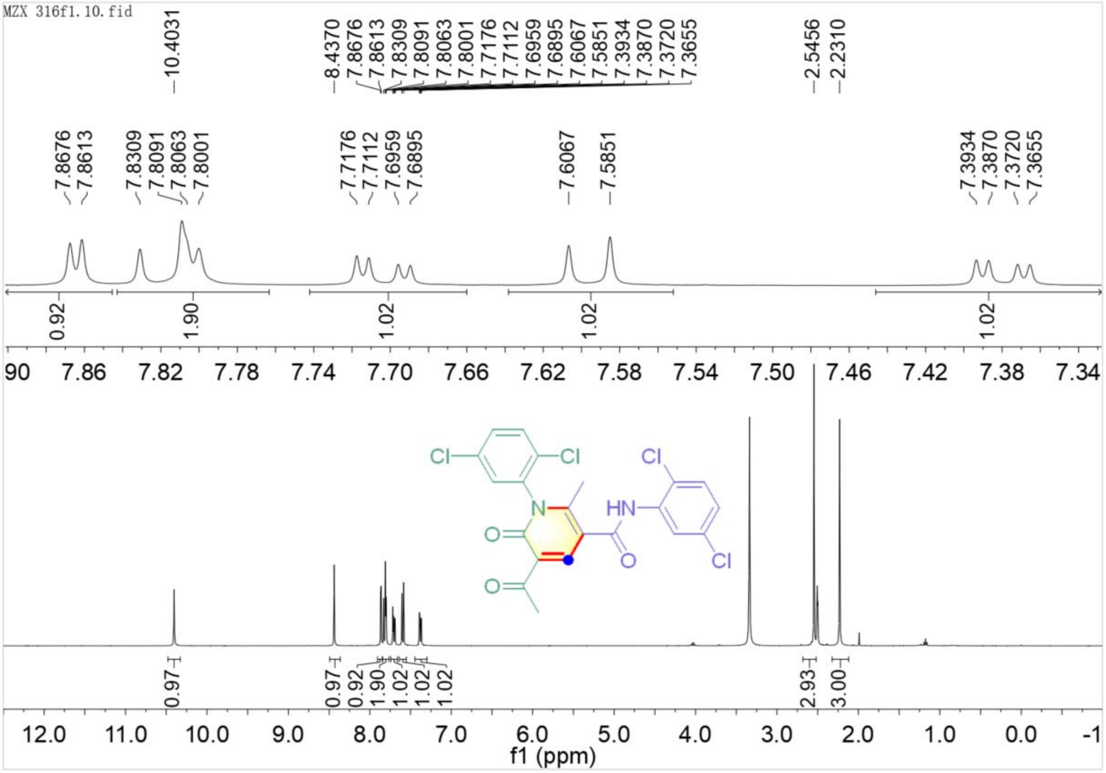
^{13}C NMR



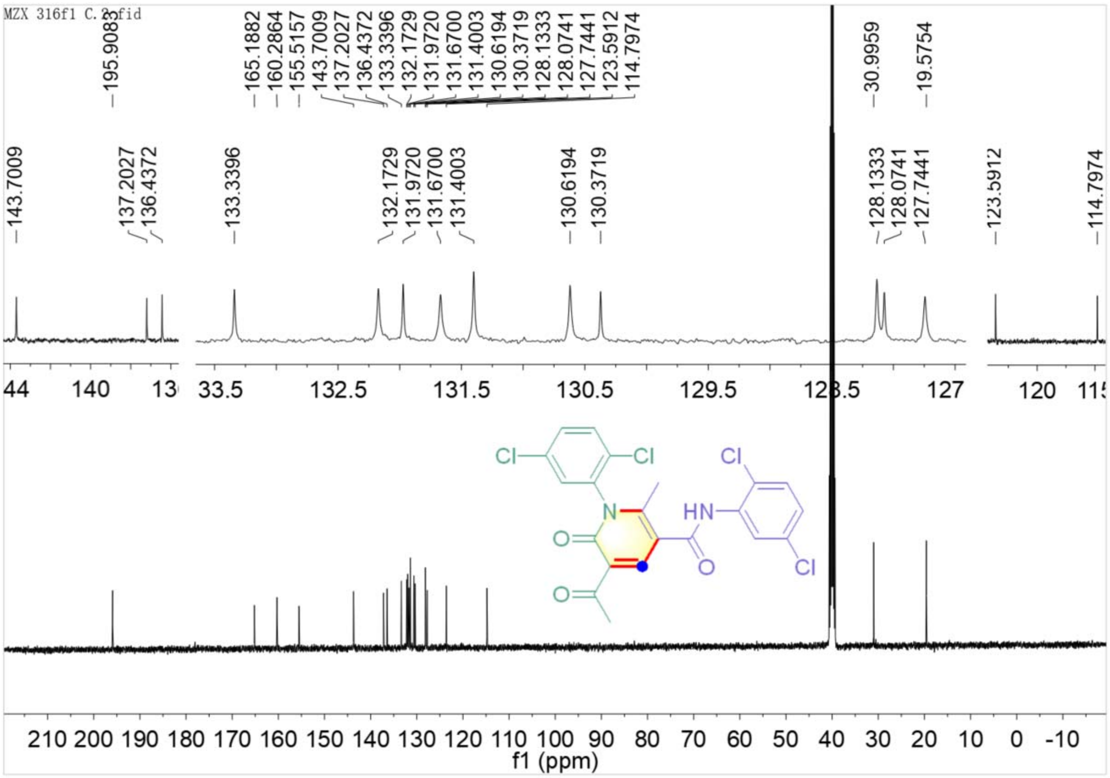
DEPT 90 and DEPT 135



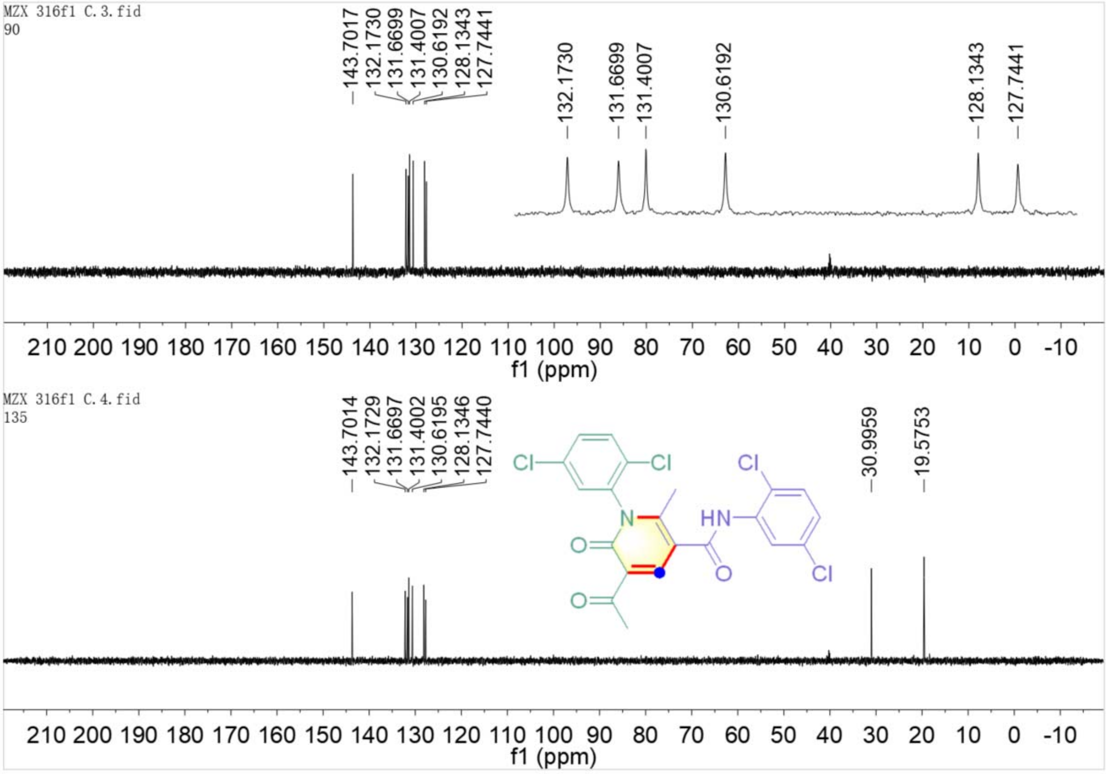
2f, ^{1}H NMR



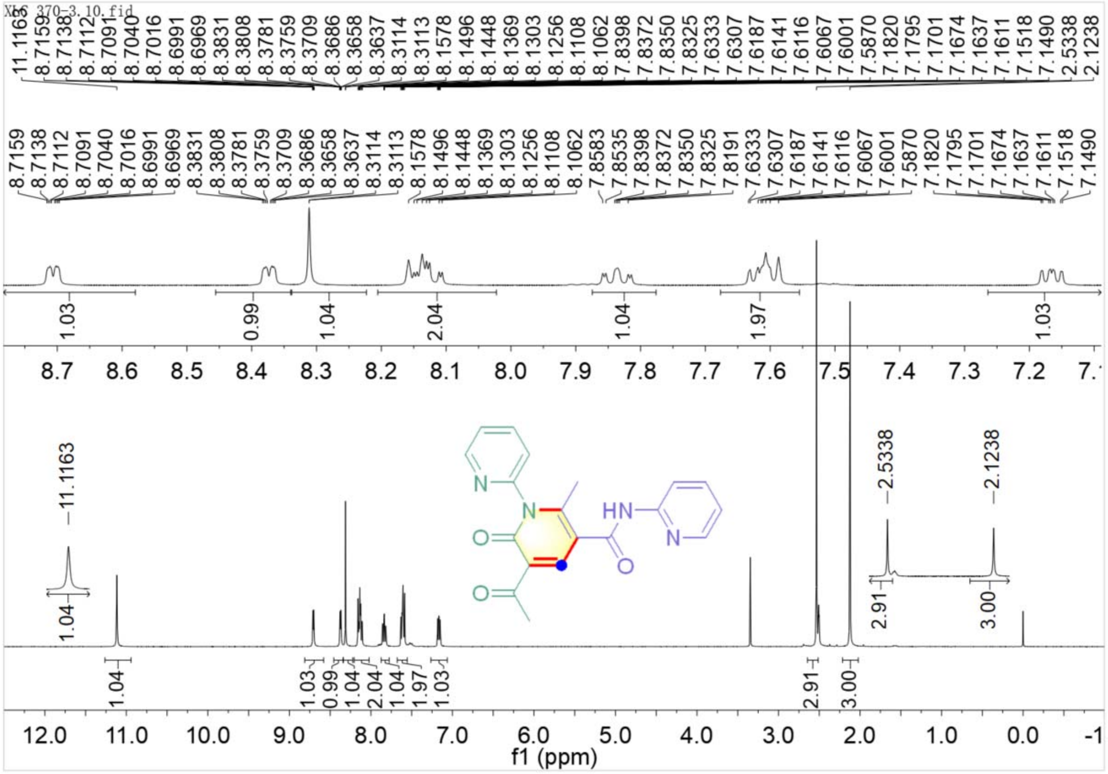
^{13}C NMR



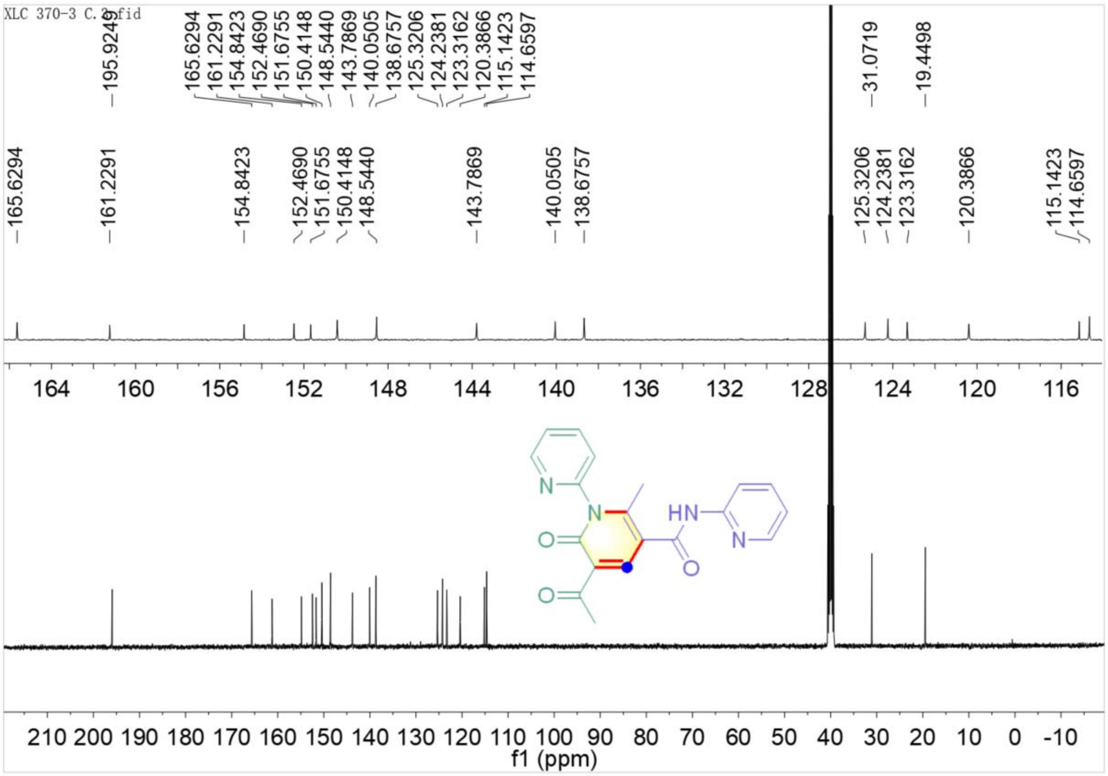
DEPT 90 and DEPT 135



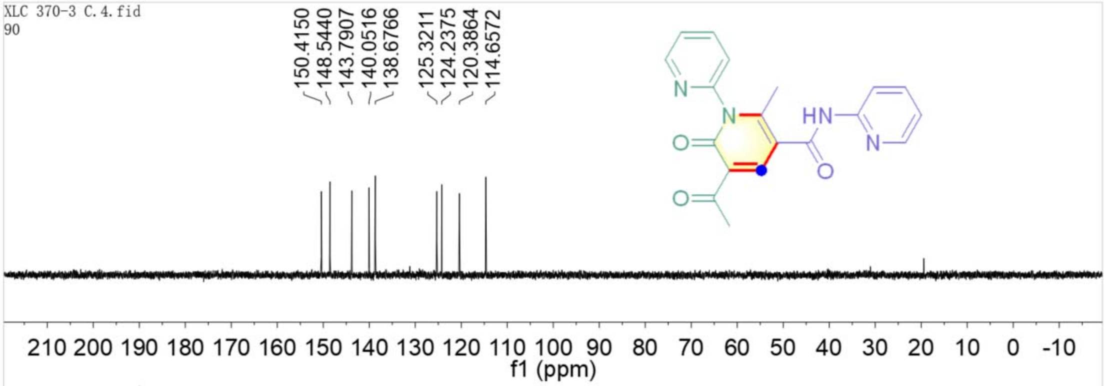
2g, ^{1}H NMR

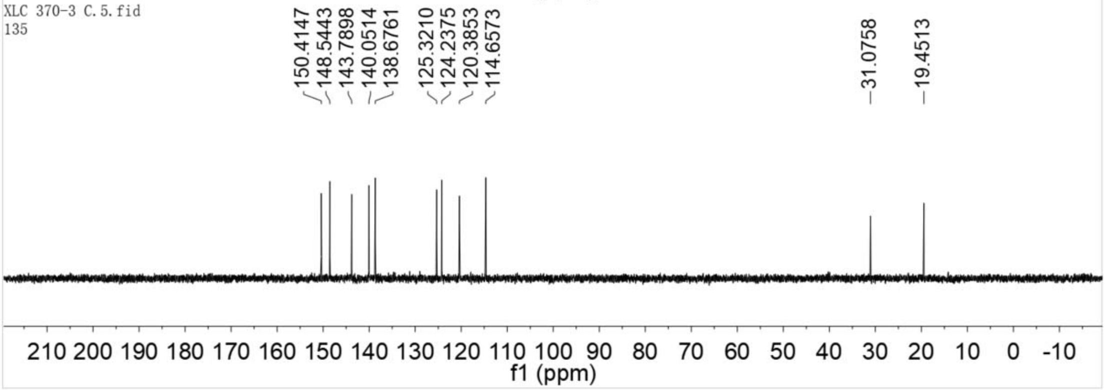


^{13}C NMR

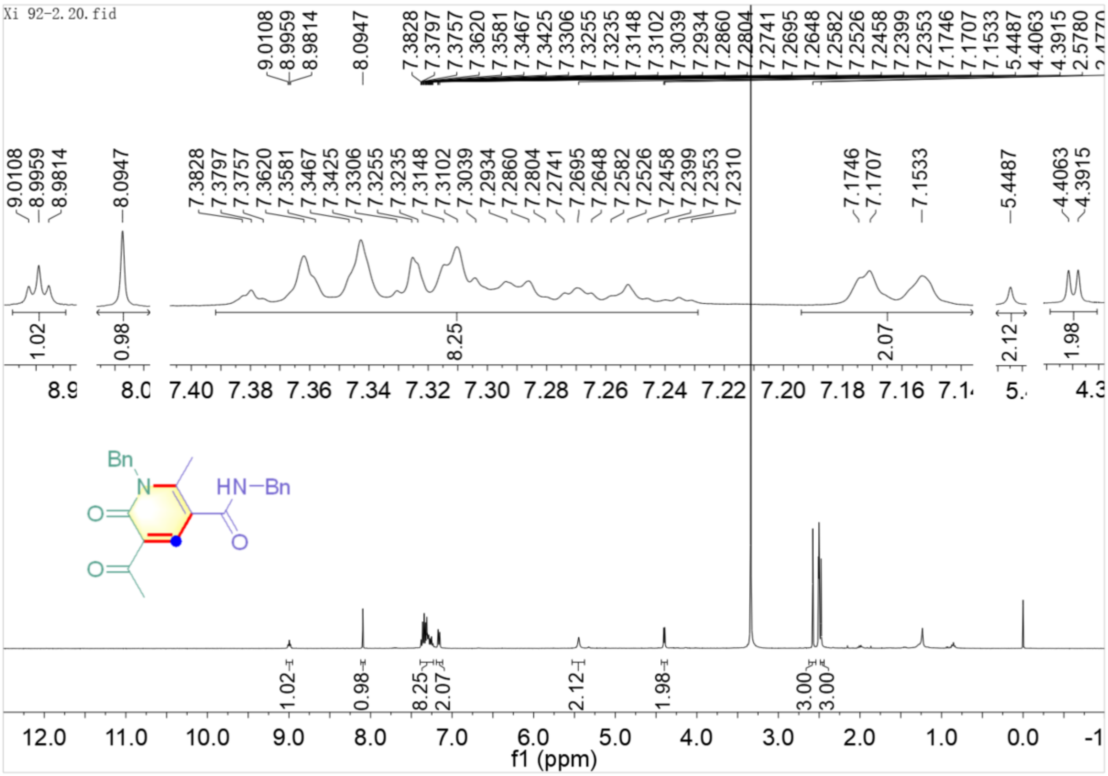


DEPT 90 and DEPT 135

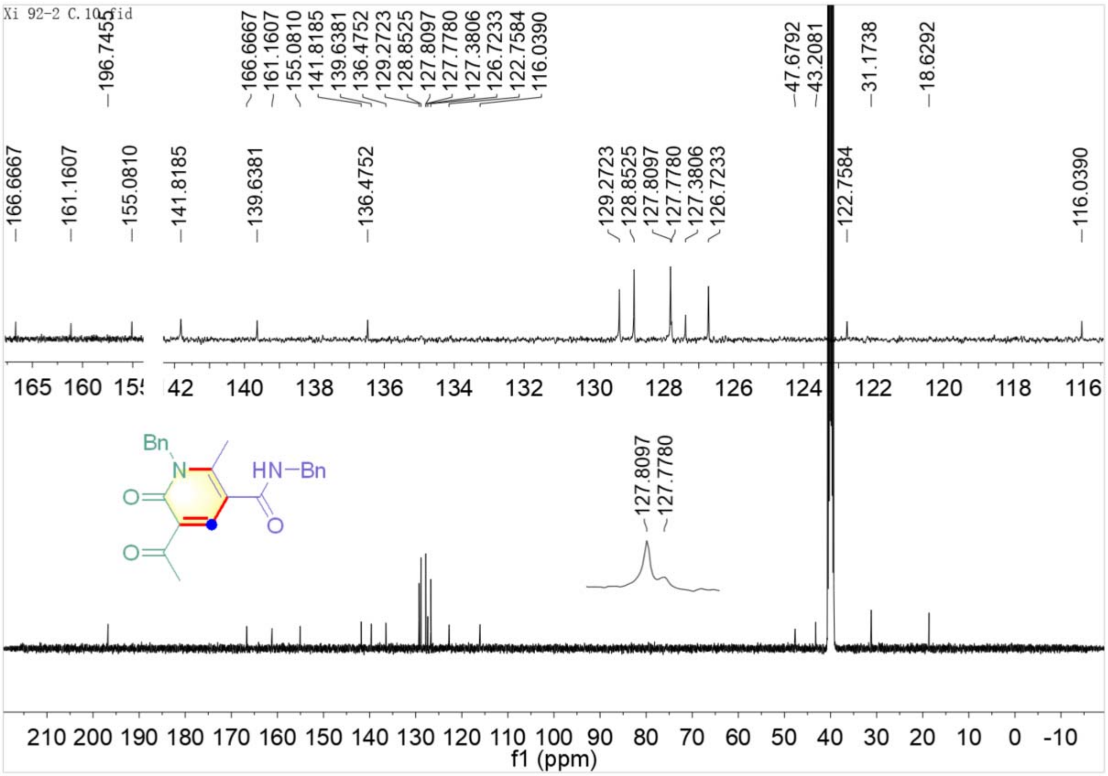




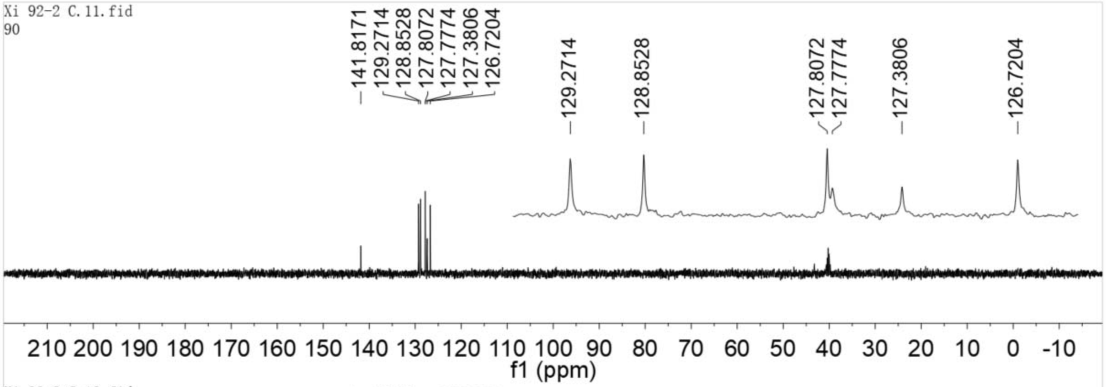
2h, ^{1}H NMR

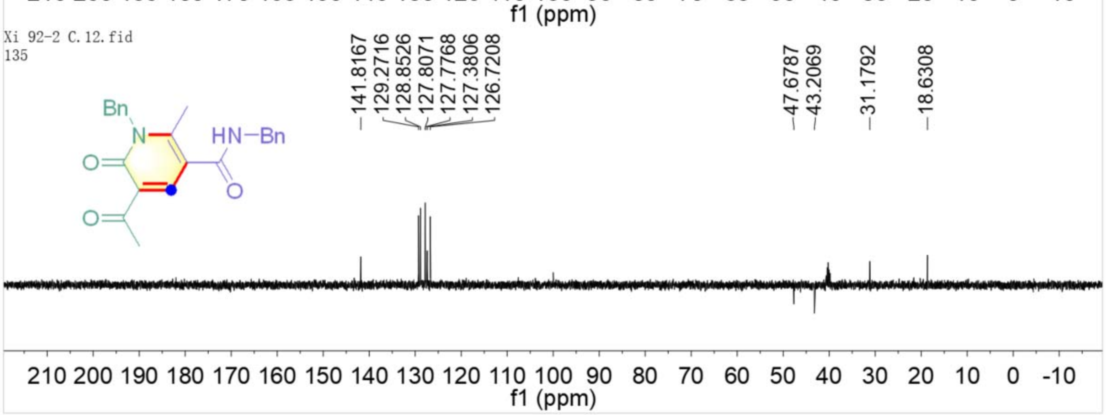


^{13}C NMR

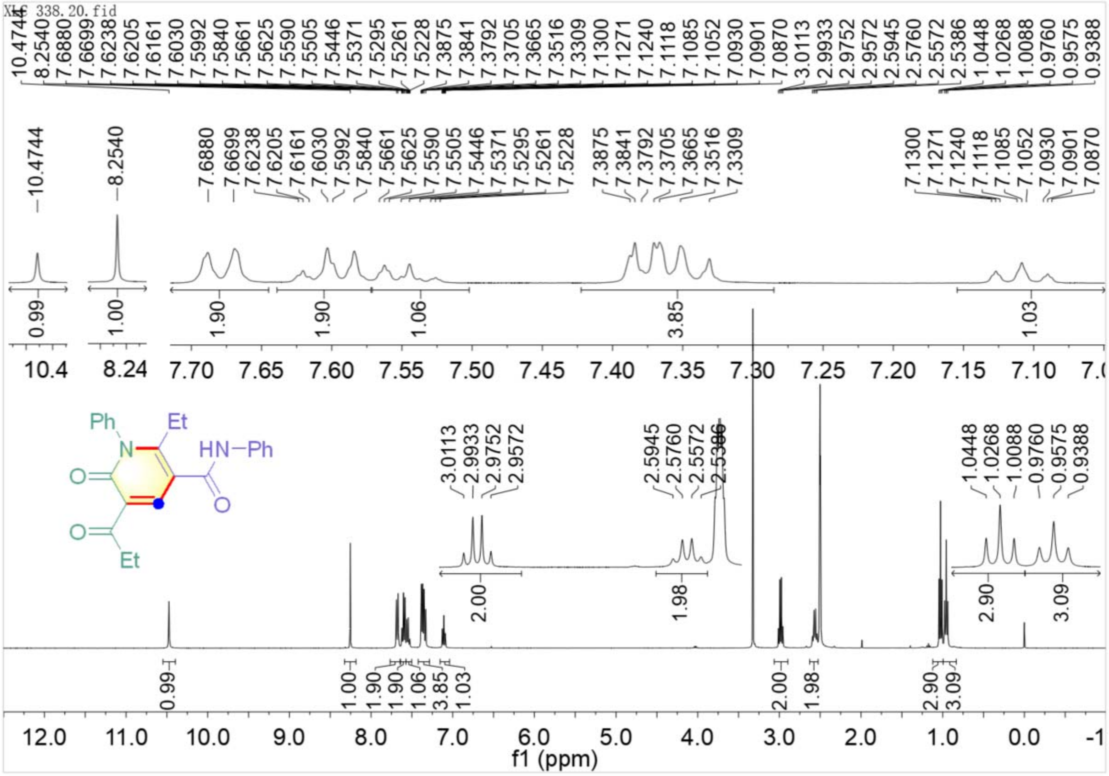


DEPT 90 and DEPT 135

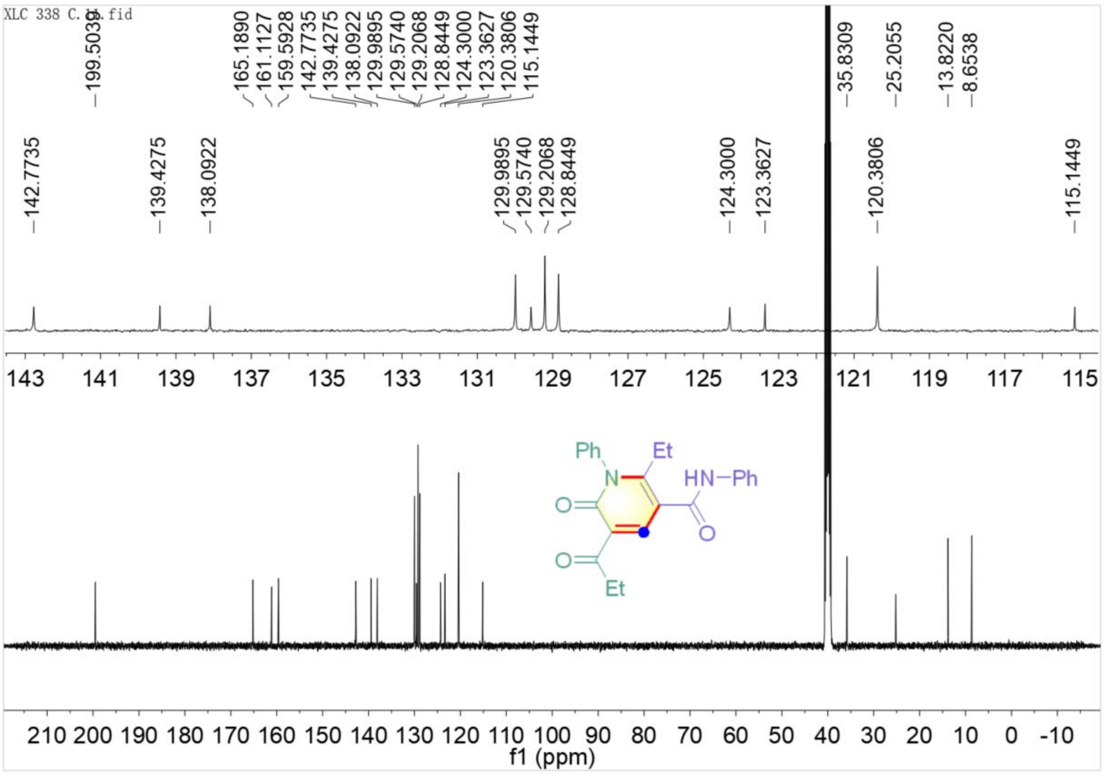




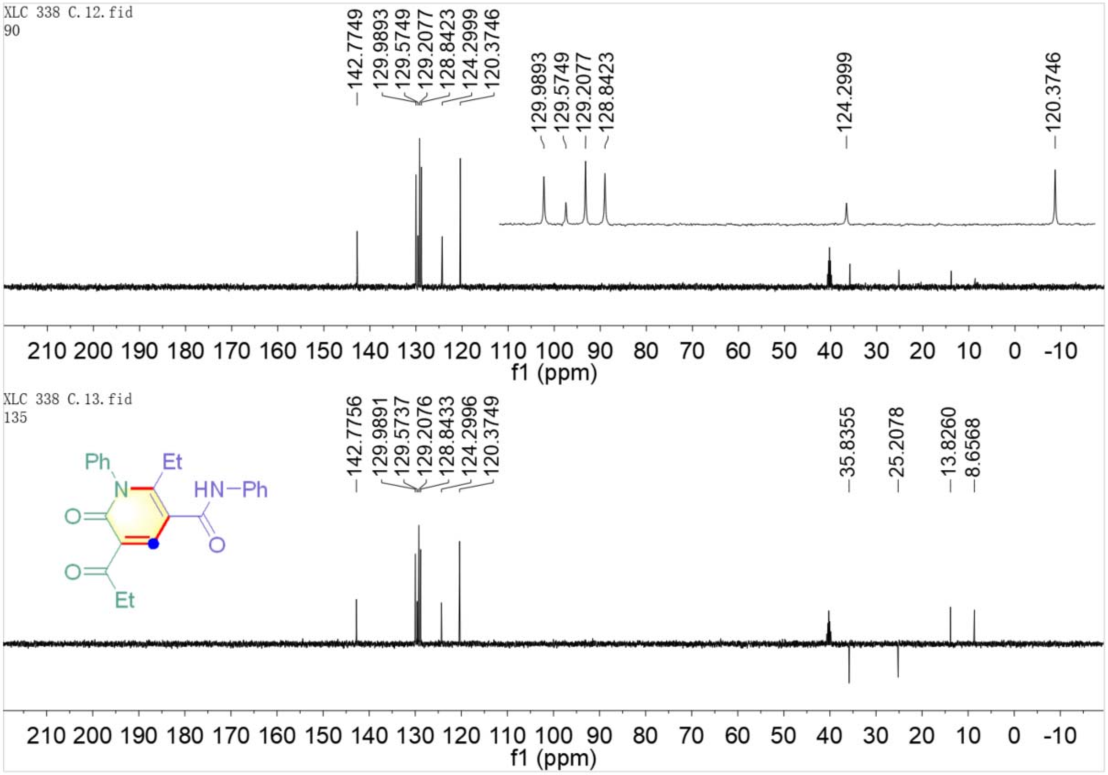
2i1, ^{1}H NMR



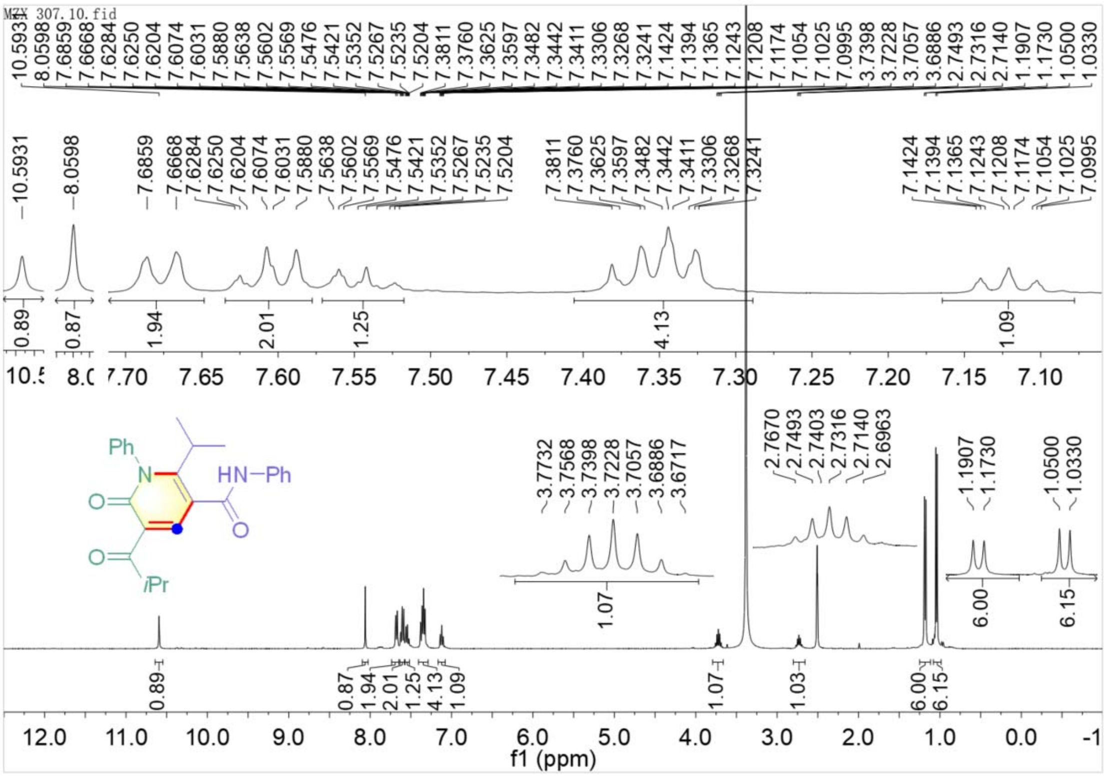
^{13}C NMR



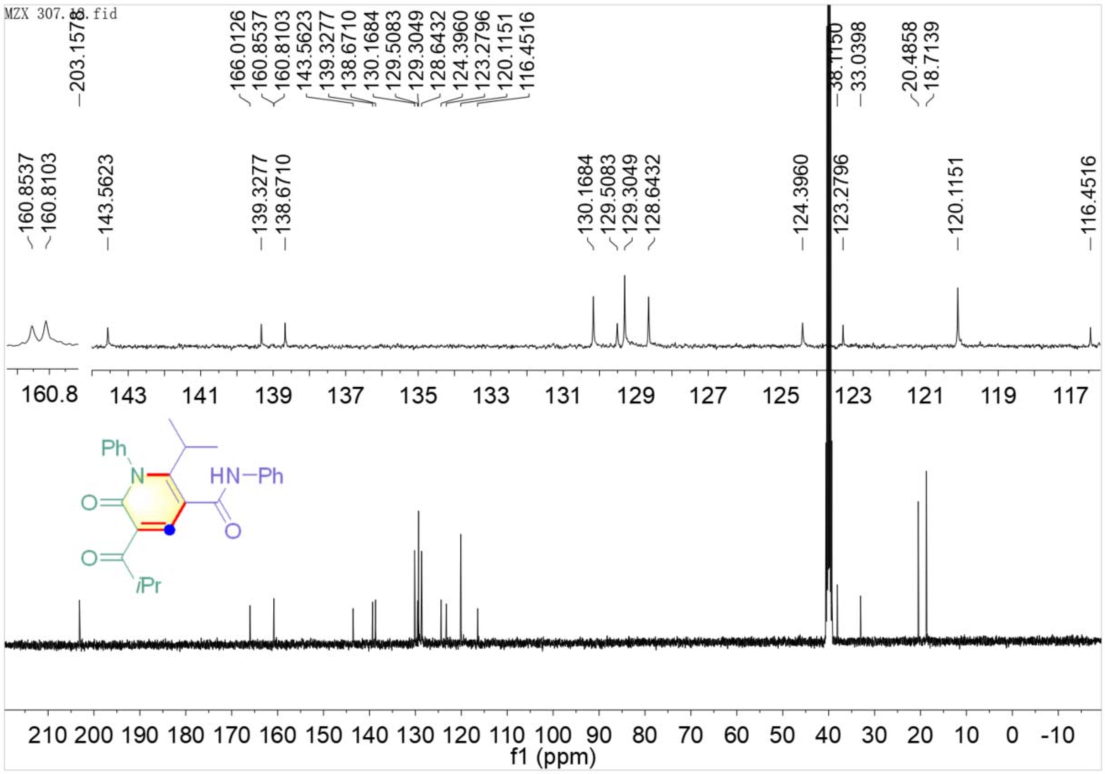
DEPT 90 and DEPT 135



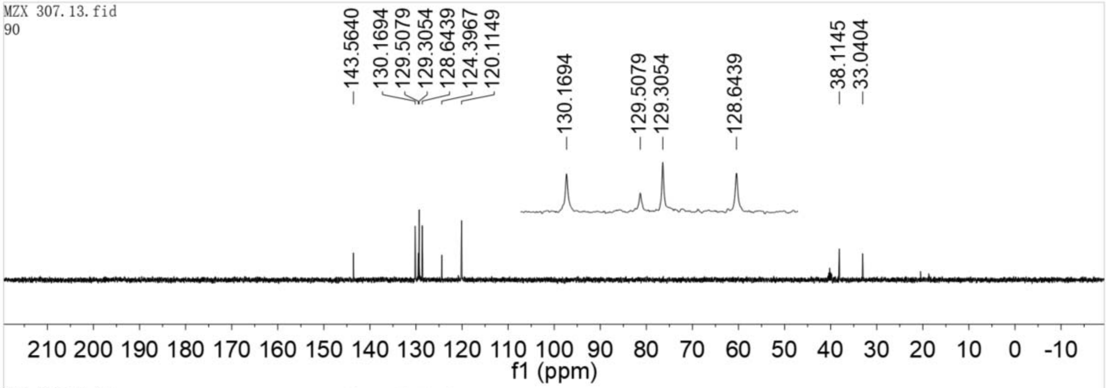
2i2, ^{1}H NMR

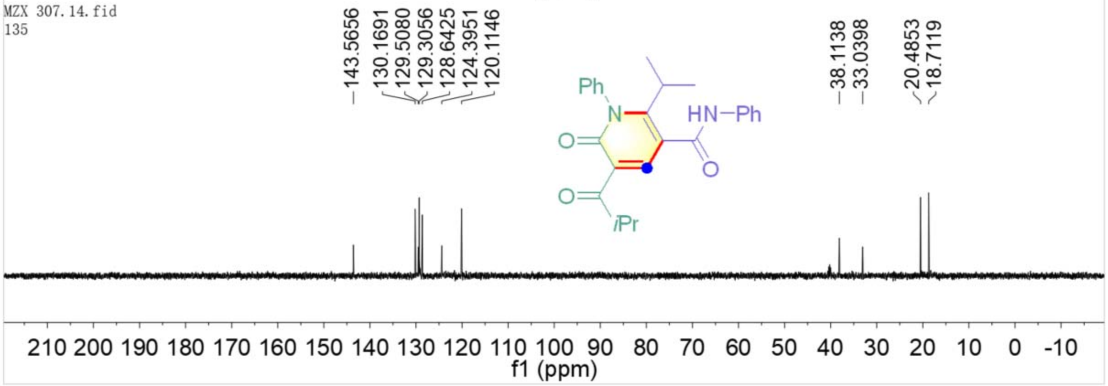


^{13}C NMR

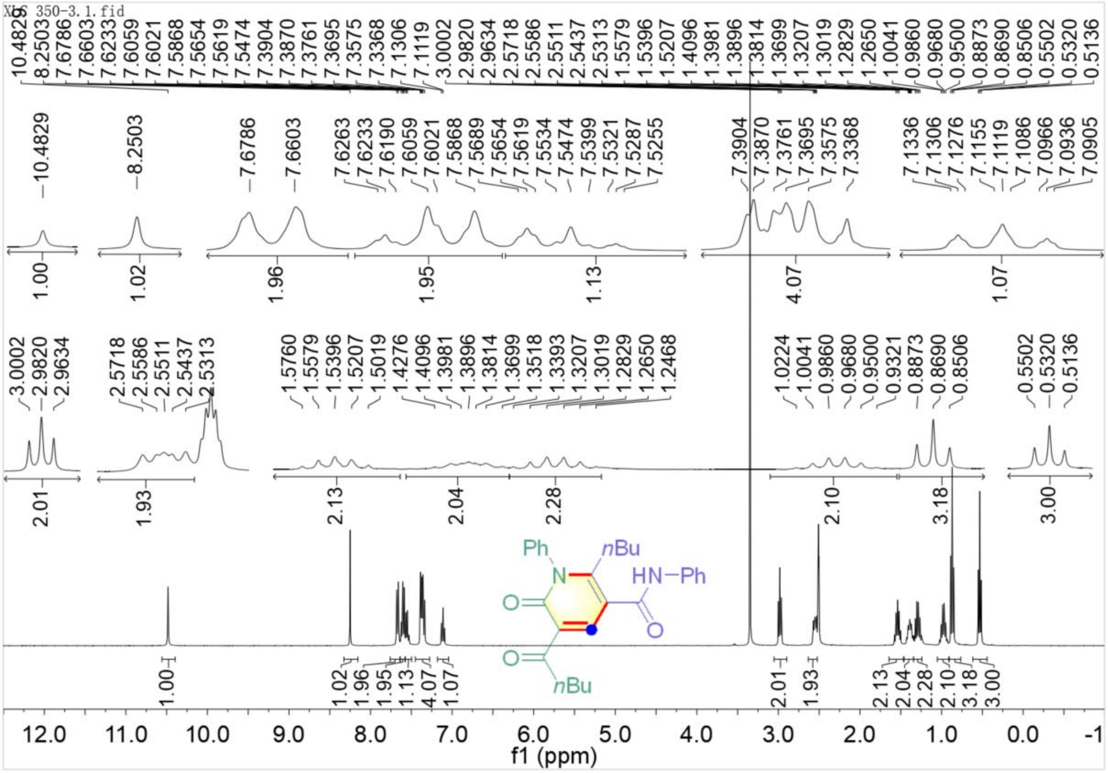


DEPT 90 and DEPT 135

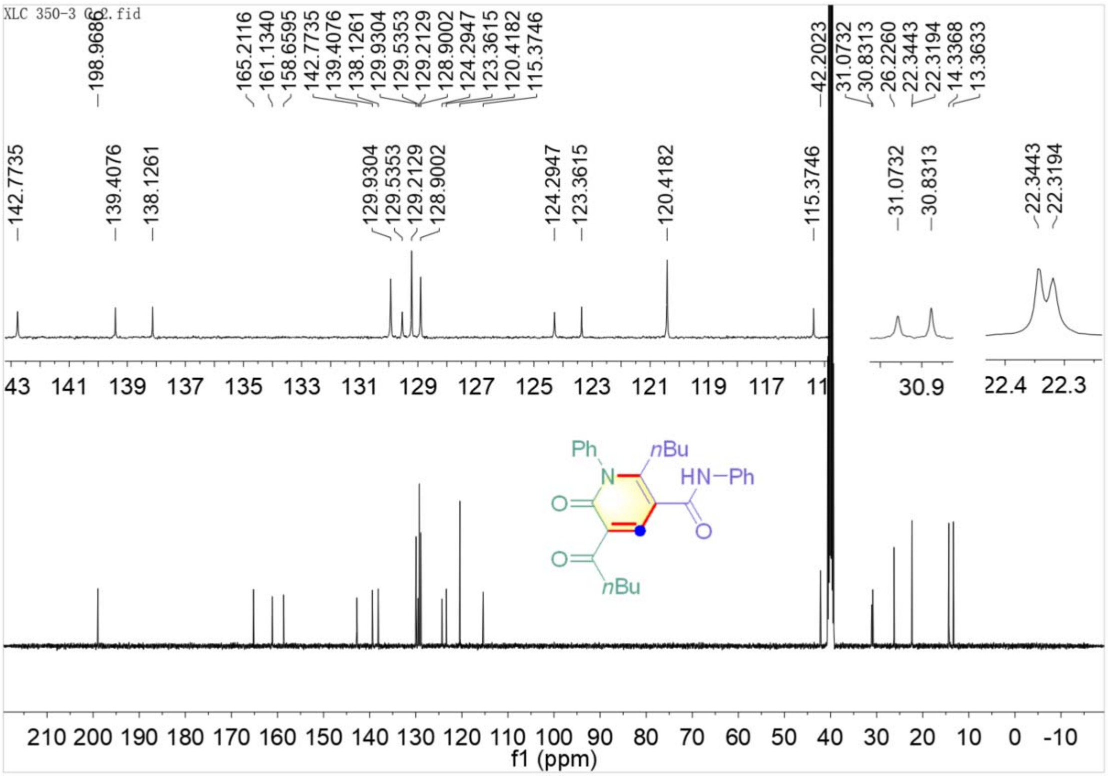




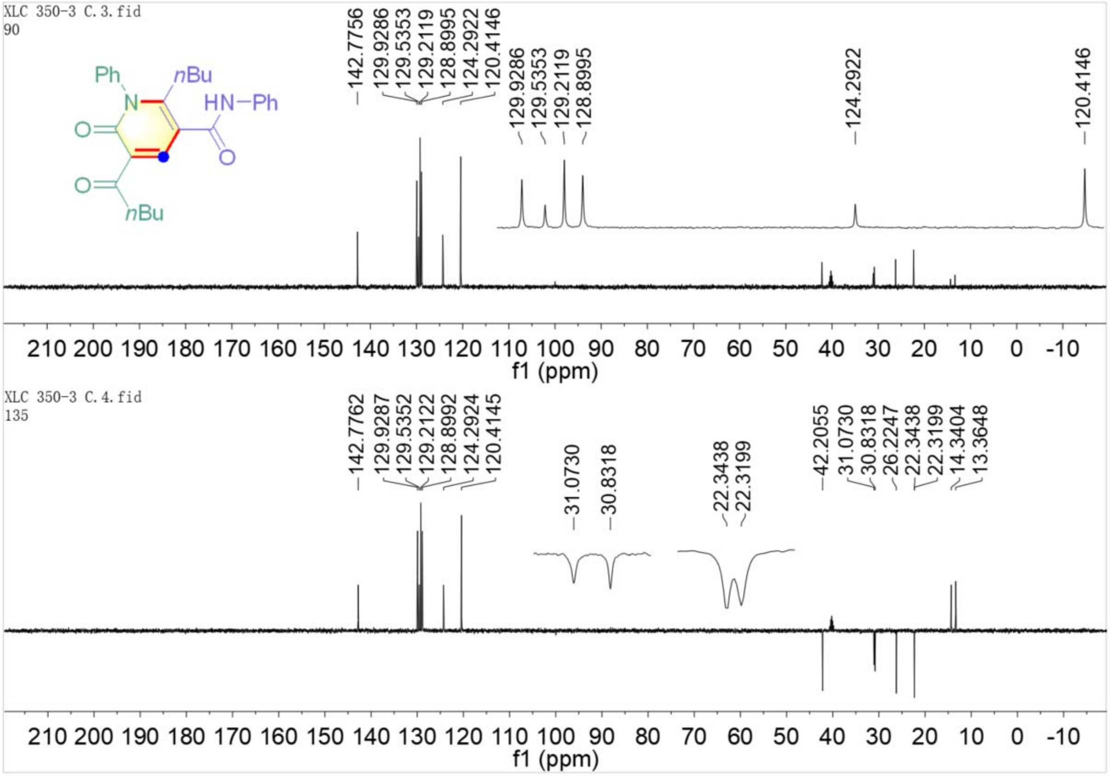
2i3, ^{1}H NMR



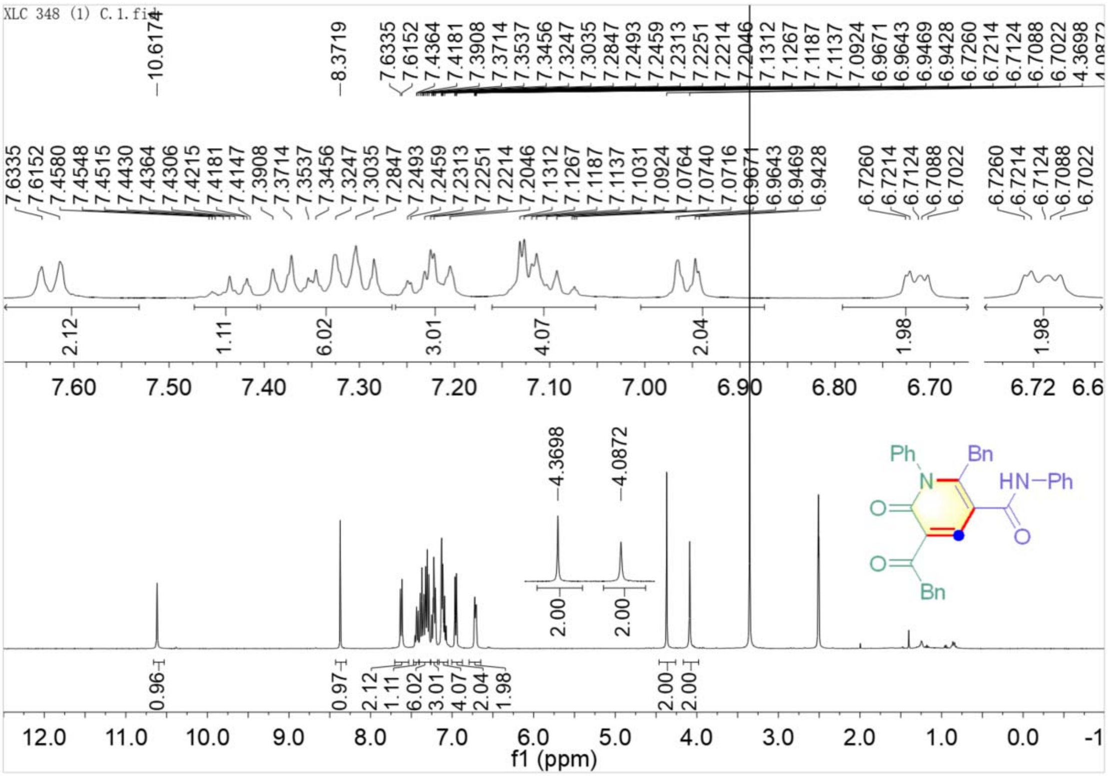
^{13}C NMR



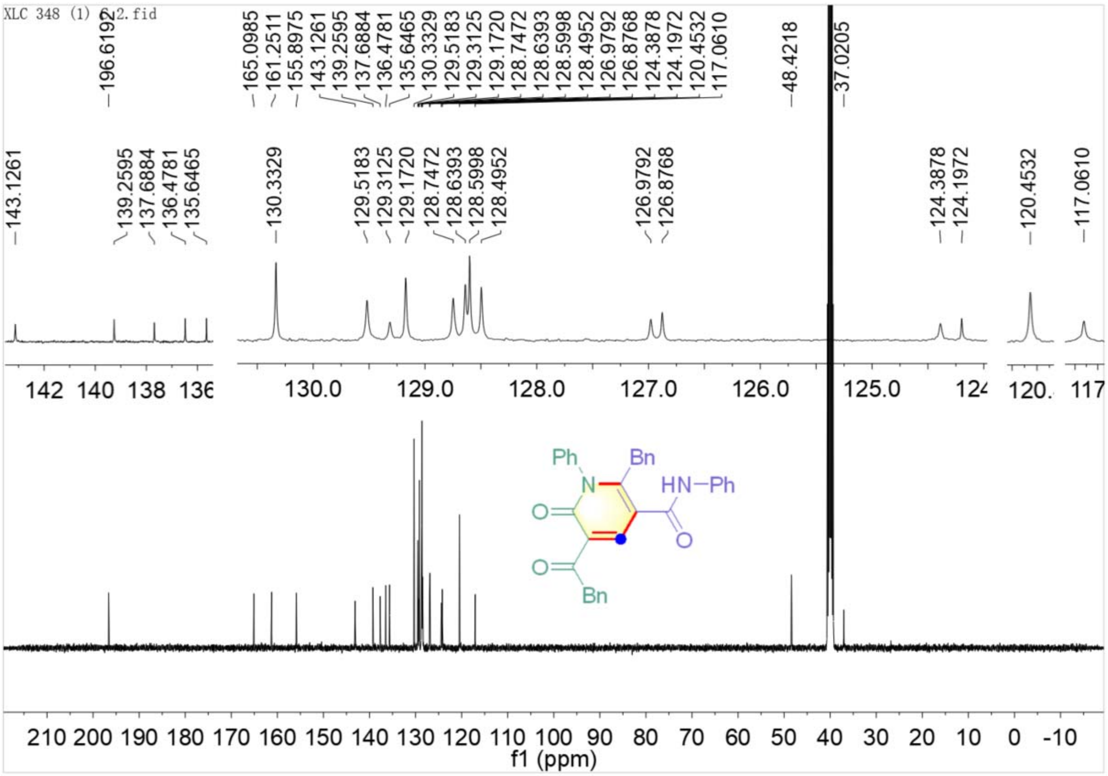
DEPT 90 and DEPT 135



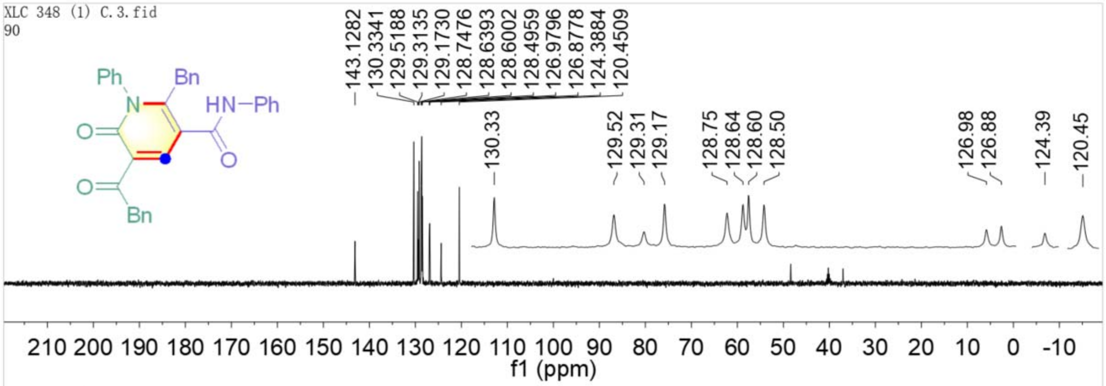
2i4, ^{1}H NMR

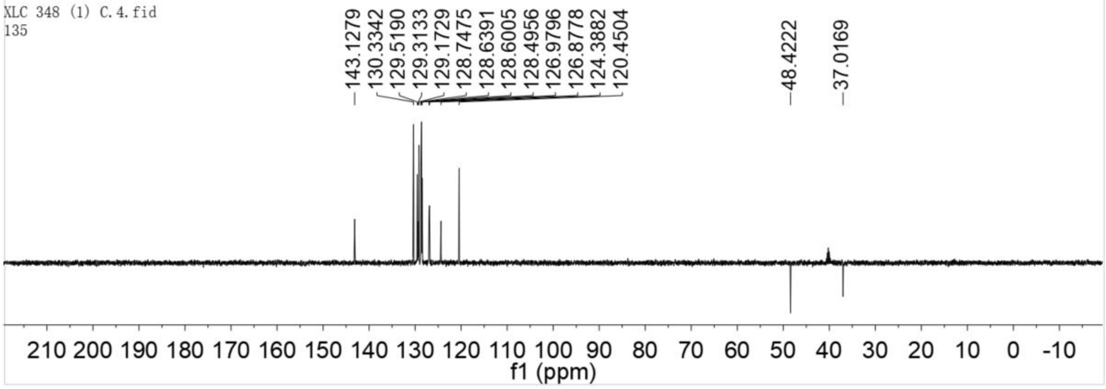


^{13}C NMR

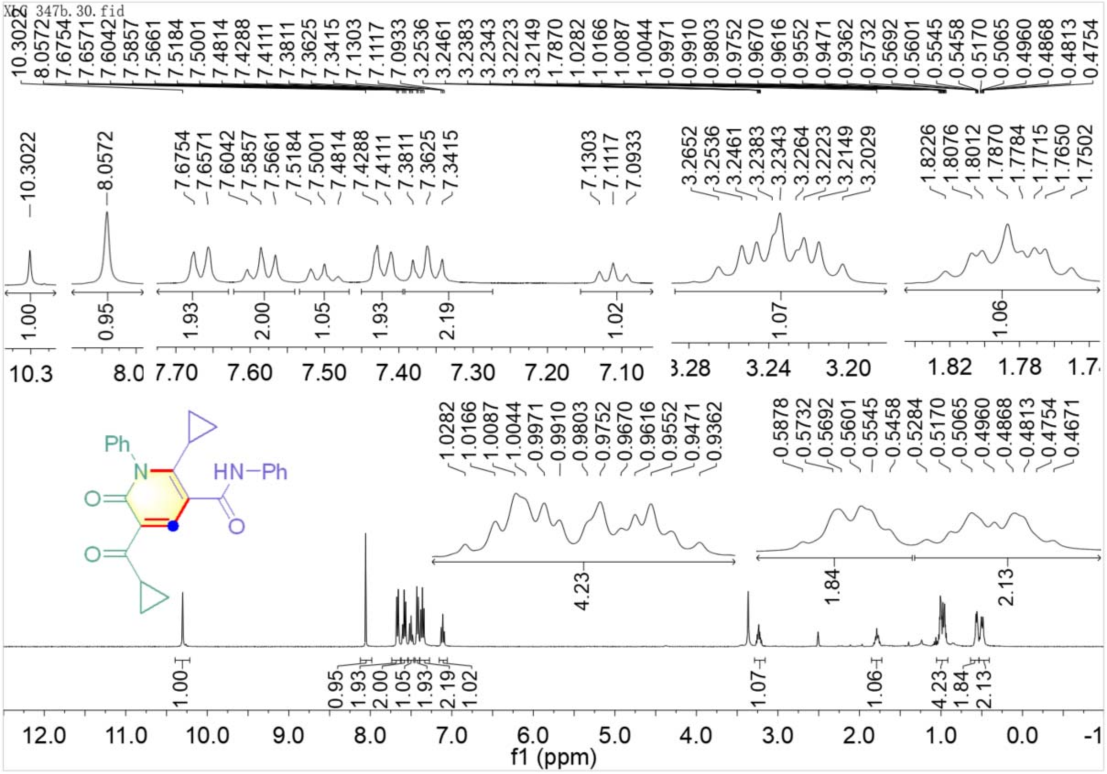


DEPT 90 and DEPT 135

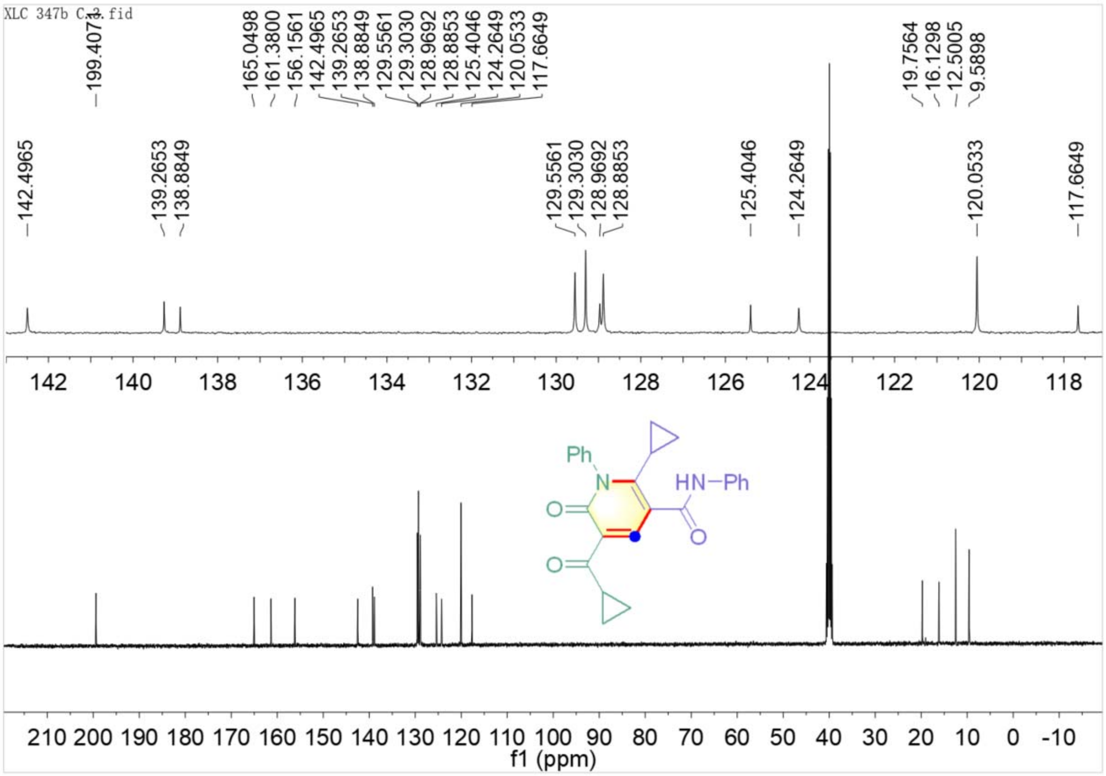




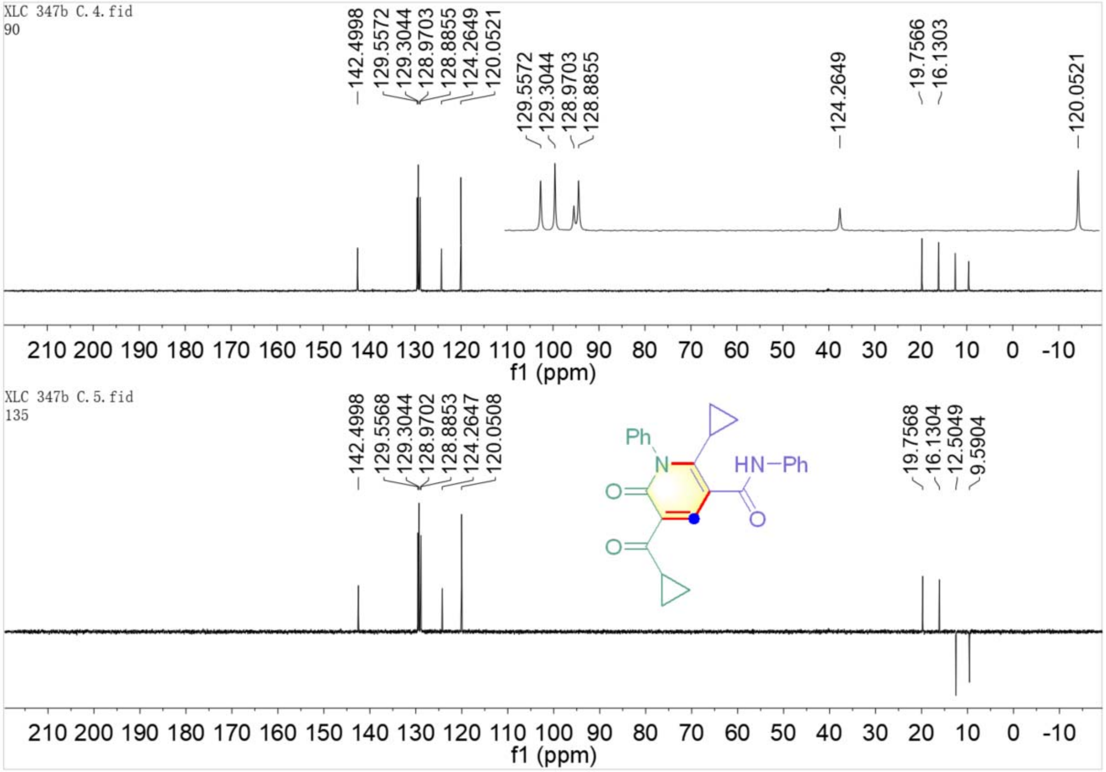
2j1, ^{1}H NMR



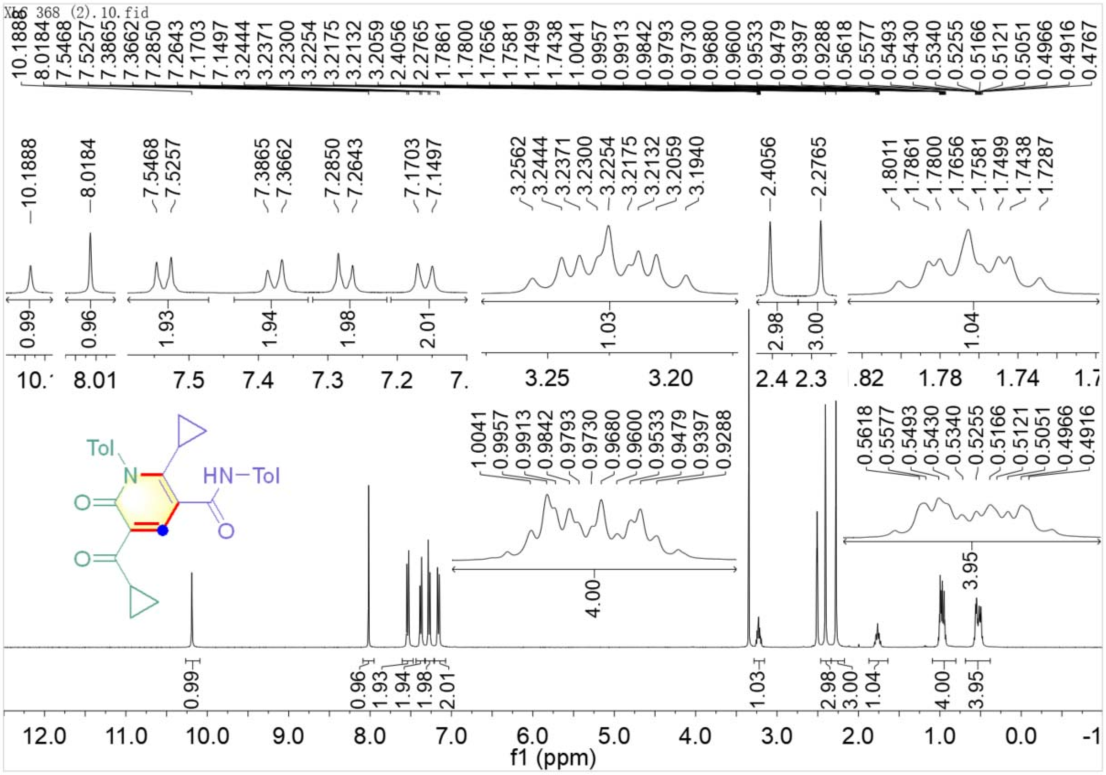
^{13}C NMR



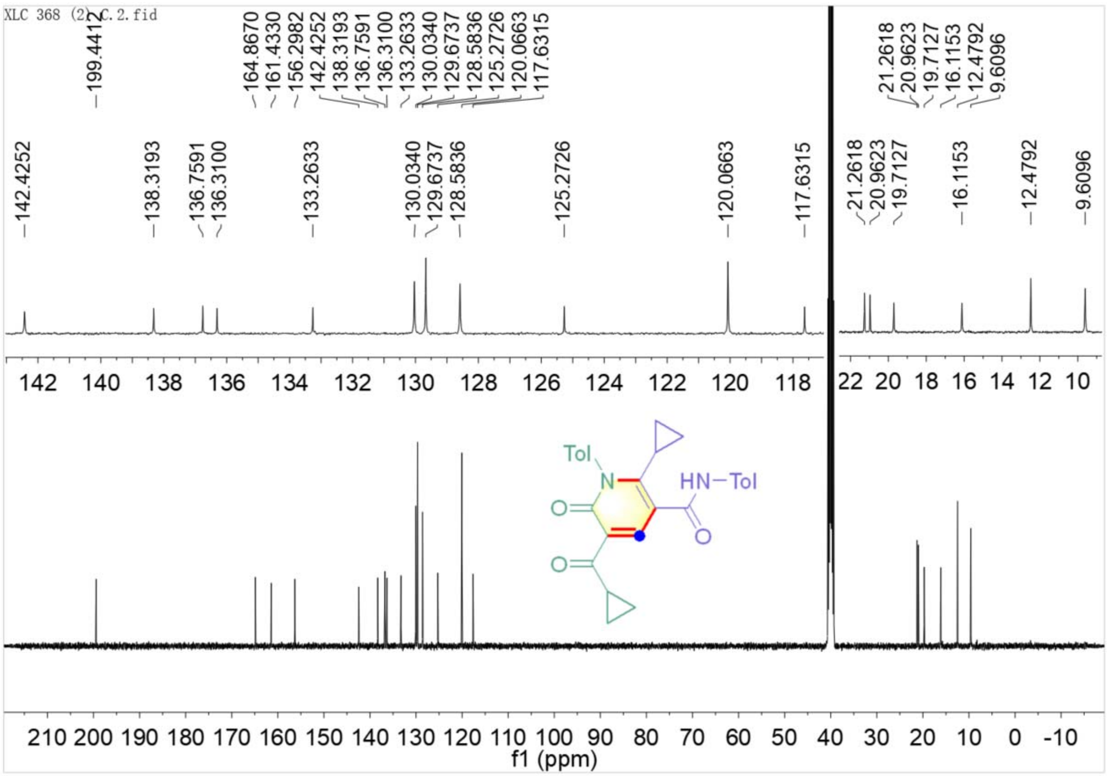
DEPT 90 and DEPT 135



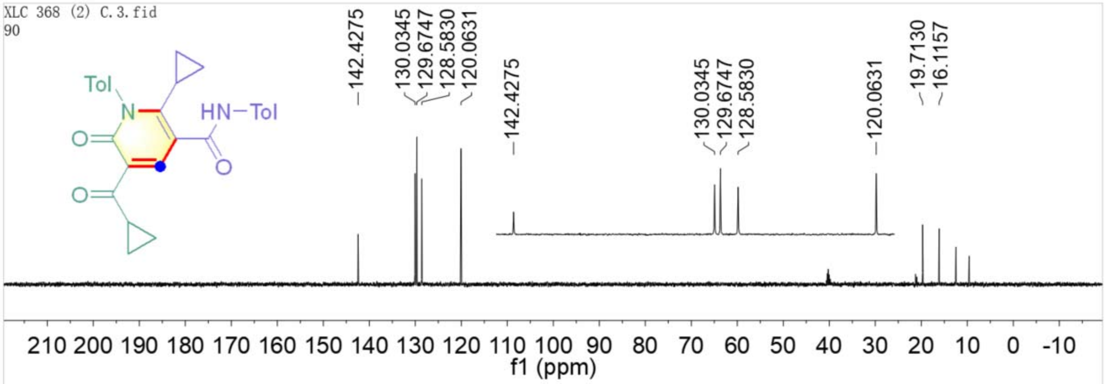
2j2, ^{1}H NMR

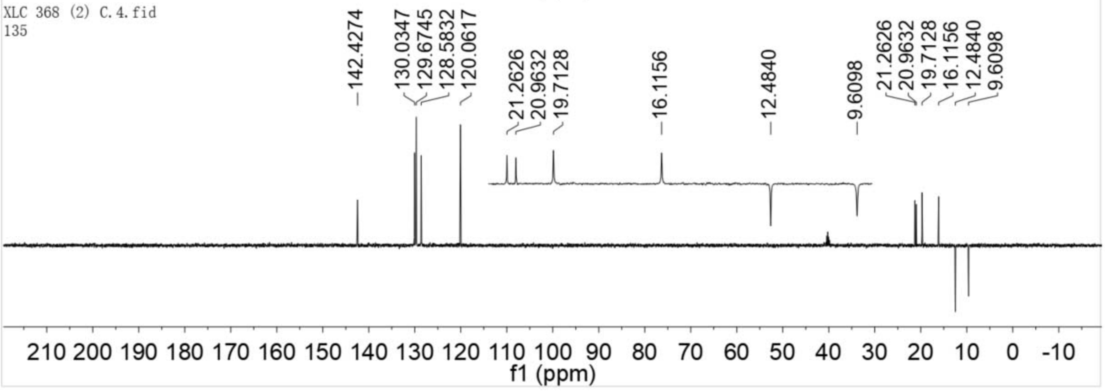


^{13}C NMR

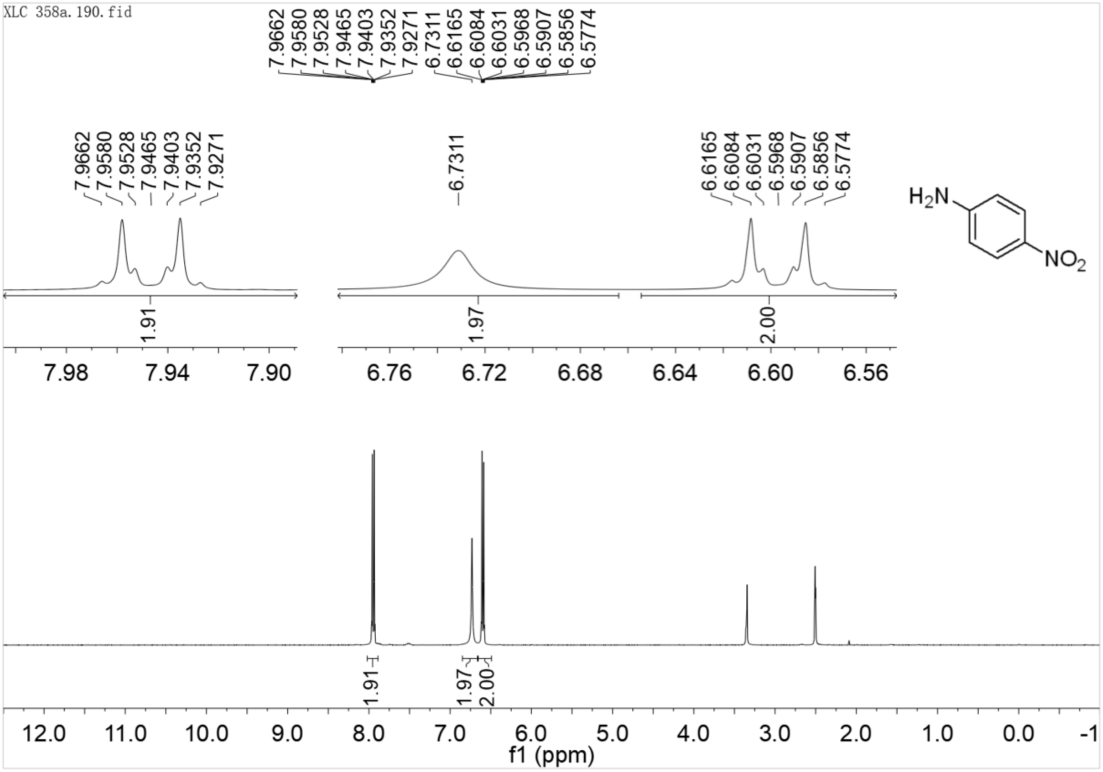


DEPT 90 and DEPT 135

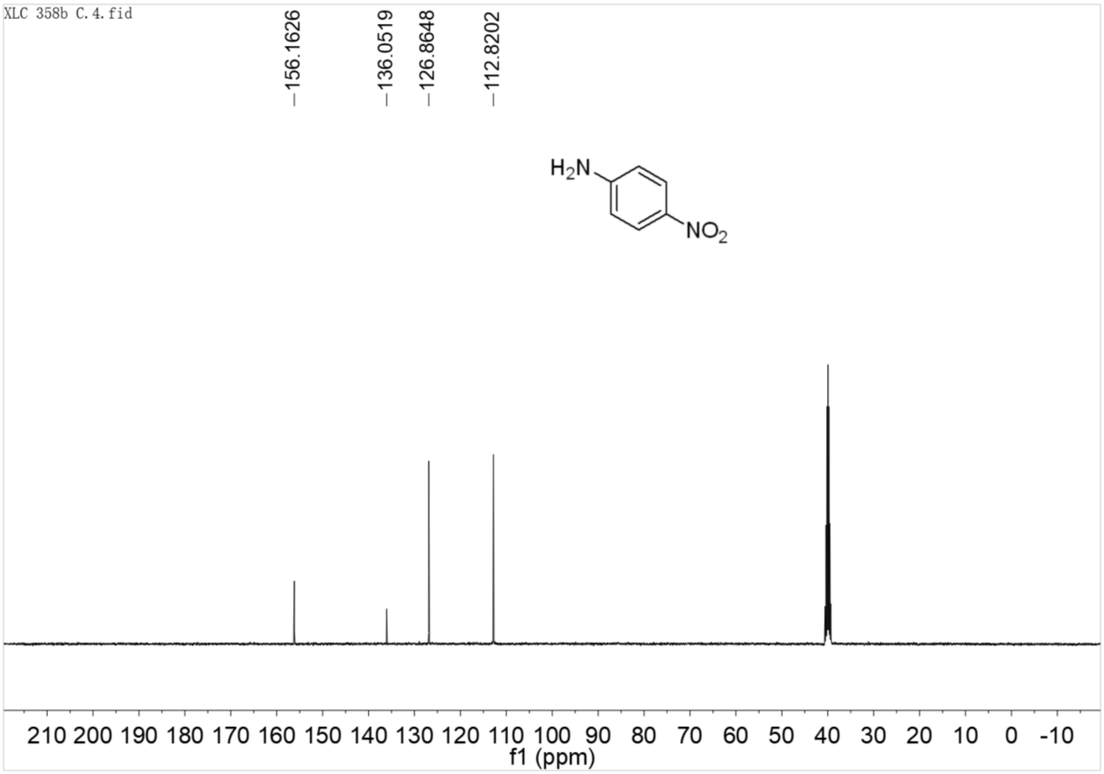




3 ^{1}H NMR



^{13}C NMR



DEPT 90 and DEPT 135