Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Exploring the regioselectivity for the cyanoalkylation of 3-aza-1,5-dienes: photoinduced synthesis of 3-cyanoalkyl-4-pyrrolin-2-ones

Jia-Qin He, Zhi-Xian Yang, Xue-Lu Zhou, Yanni Li, Shulin Gao, Lou Shi* and Deqiang Liang*

School of Chemistry and Chemical Engineering, Kunming University, Kunming 650214, China

E-mail: shil090@nenu.edu.cn, liangdq695@nenu.edu.cn

Table of Contents

I. General considerations **3**
II. Optimization of reaction conditions **4**
III. 2D NMR for 3y **7**
IV. 2D NMR for 3z **10**
V. Experimental procedures **12**
1. General procedure for the synthesis of 3-cyanoalkyl-4-pyrrolin-2-ones 12
2. Gram-scale synthesis 12
3. Natural sunlight experiment 13
4. General procedure for the synthesis of *N*-vinylacrylamide substrates **1** 14
5. General procedure for the synthesis of oxime esters **2** 28
VI. Mechanistic investigations **31**
1. KIE experiments 31
2. Quenching experiments 32
3. Light on-off experiments 32
4. Quantum yield measurements 33
5. Stern-Volmer experiments 34
6. Cyclic voltammetry studies 36
7. Determination of the excited-state oxidation potential of $Ir(ppy)_3$ in MeCN 39
VII. Spectral data of products **39**
VIII. Copies of ^{1}H, ^{19}F, ^{13}C and DEPT NMR spectra **63**

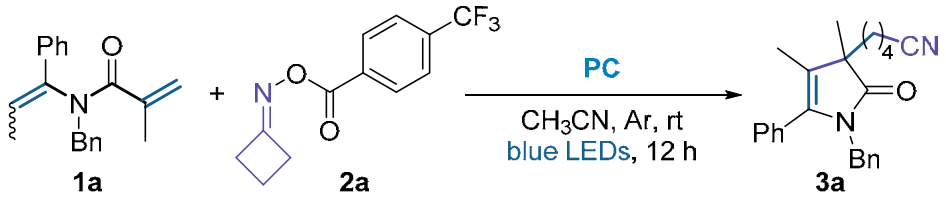
I. General considerations

Unless otherwise stated, commercially available chemicals were used without treatment. Solvents were degassed by bubbling Ar for 10 minutes before use. Reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography over 300-400 mesh silica gel under a positive pressure of air. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer using TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). UV-Vis measurements were carried out on a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan). Cyclic voltammetry studies were carried out on a CHI600E electrochemical workstation (Shanghai CH Instruments Co., China). The emission spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). The photoreactors used in this research were bought from GeAo Chem (Figure S1, containing 24 small LEDs, 1 W for every LED, and every reaction tube is irradiated by 6 LEDs).

Figure S1 Photochemical setup

II. Optimization of reaction conditions

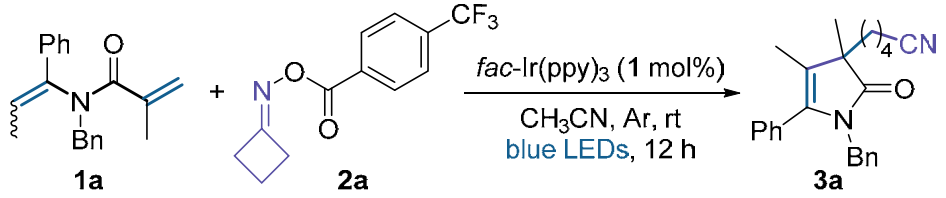
Table S1 Photocatalyst screening[a]



entry	photocatalyst (mol%)	yield[b] (%)
1	none	nr
2	***fac*-Ir(ppy)$_3$ (1)**	**50**
3	[Ir(dtbbpy)(ppy)$_2$]PF$_6$ (1)	41
4	(Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (1)	0 (decomposition)
5	Ru(bpy)$_3$Cl$_2$ (1)	15
6	Mes-Acr$^+$ClO$_4^-$ (1)	31
7	4CzIPN (1)	28
8	Eosin Y (5)	38
9	Rose bengal (5)	nr

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), MeCN (3.0 mL), 6 W blue LEDs (455 nm), Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.

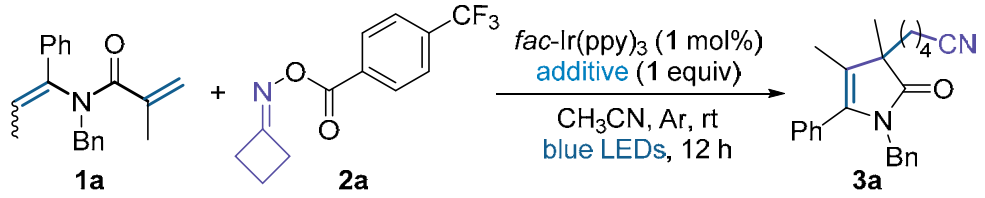
Table S2 Optimization of the loadings of the starting materials[a]



entry	**1a** (mmol)	**2a** (mmol)	yield[b] (%)
1	0.3	0.36	49
2	0.3	0.45	34
3	0.36	0.3	56
4	**0.45**	**0.3**	**68**
5	0.525	0.3	68

[a] Reaction conditions: *fac*-Ir(ppy)$_3$ (0.003 mmol), MeCN (3.0 mL), 6 W blue LEDs (455 nm), Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.

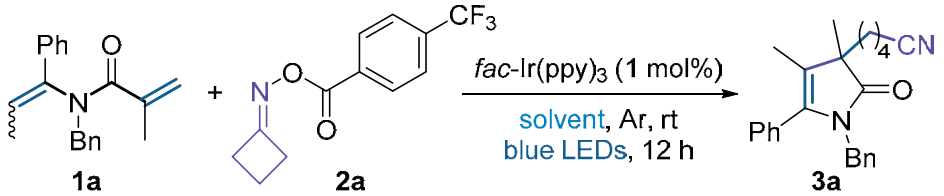
Table S3 Additive screening[a]



entry	additive (equiv)	yield[b] (%)
1	K_2CO_3	59
2	KOAc	54
3	2,6-lutidine	44
4	DABCO	35
5	HOAc	51
6	$PhCO_2H$	34

[a] Reaction conditions: **1a** (0.45 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.003 mmol), MeCN (3.0 mL), 6 W blue LEDs (455 nm), Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.

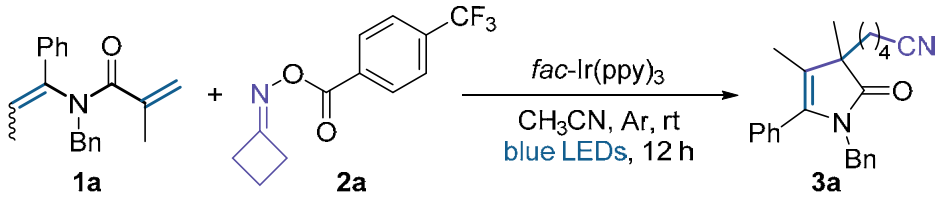
Table S4 Solvent screening[a]



entry	solvent	yield[b] (%)
1	DCE	60
2	toluene	52
3	$PhCF_3$	52
4	EtOAc	65
5	THF	50
6	**acetone**	67
7	CH_3NO_2	nr
8	DMA	39
9	DMSO	55

[a] Reaction conditions: **1a** (0.45 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.003 mmol), 6 W blue LEDs (455 nm), Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.

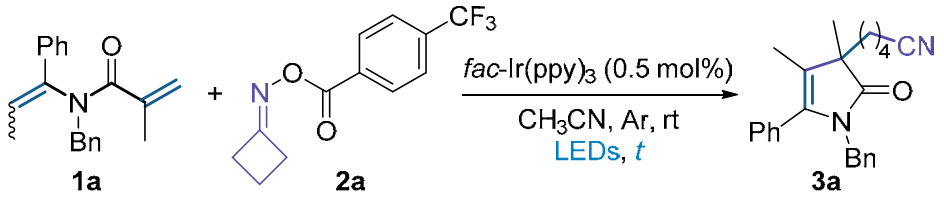
Table S5 Optimization of the loading of the PC and the volume of the solvent[a]



entry	PC (mol%)	solvent (mL)	yield[b] (%)
1	0.2	3	55
2	**0.5**	**3**	**69**
3	2	3	63
4	0.5	1	65
5	**0.5**	**2**	**74 (70)[c]**
6	0.5	4	68
7	0.5	5	69
8	0.5	7.5	66
9	0.5	10	60

[a] Reaction conditions: **1a** (0.45 mmol), **2a** (0.3 mmol), 6 W blue LEDs (455 nm), Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield.

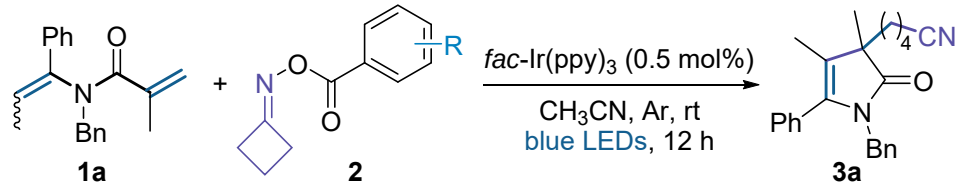
Table S6 Optimization of the reaction time and LEDs[a]



entry	*t* (h)	LEDs	yield[b] (%)
1	9	blue	63
2	18	blue	75
3	24	blue	74
4	12	violet (395 nm)	65
5	12	white	72
6	12	green (525 nm)	67
7	12	none (in the dark)	nr
8[c]	12	blue	trace
9[d]	12	blue	74

[a] Reaction conditions: **1a** (0.45 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.0015 mmol), MeCN (2.0 mL), 6 W LEDs, Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard. [c] The reaction was run under air atmosphere. [d] The reaction was run under N_2 atmosphere.

Table S7 Optimization of the leaving group of the cyclobutanone oxime ester[a]

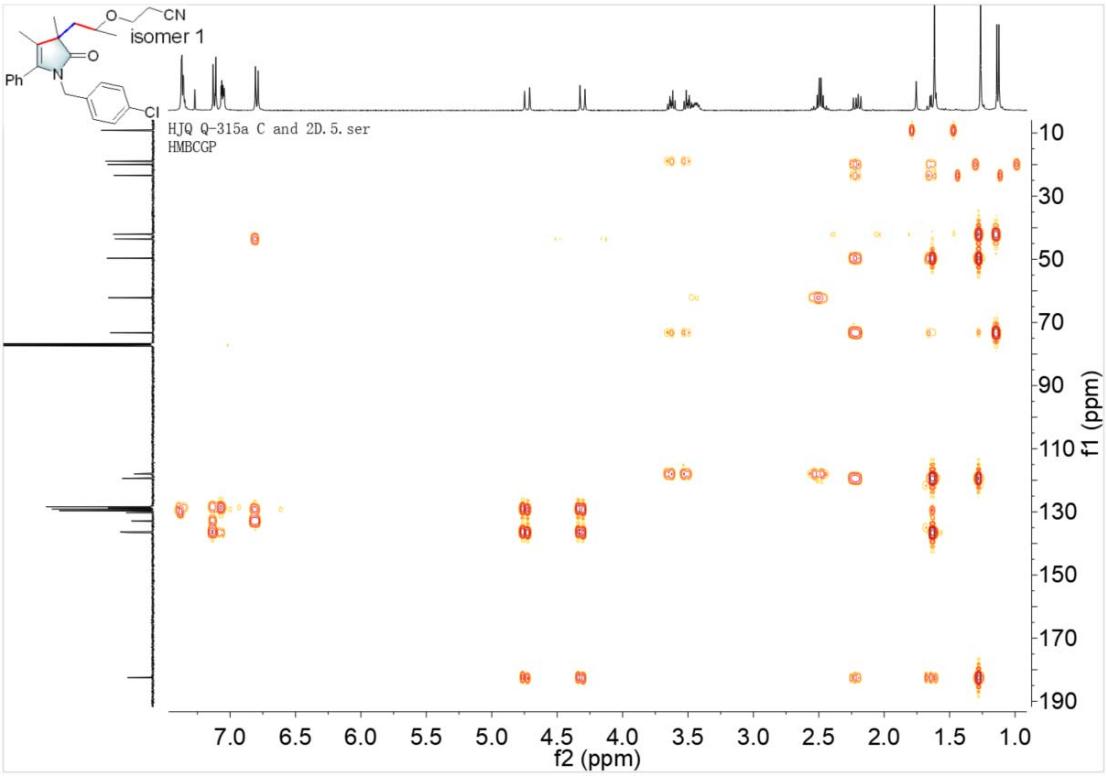


entry	R	yield[b] (%)
1	4-Me	57
2	4-MeO	48
3	H	45
4	4-Br	55
5	4-Cl	66
6	**2,4-Cl_2**	72

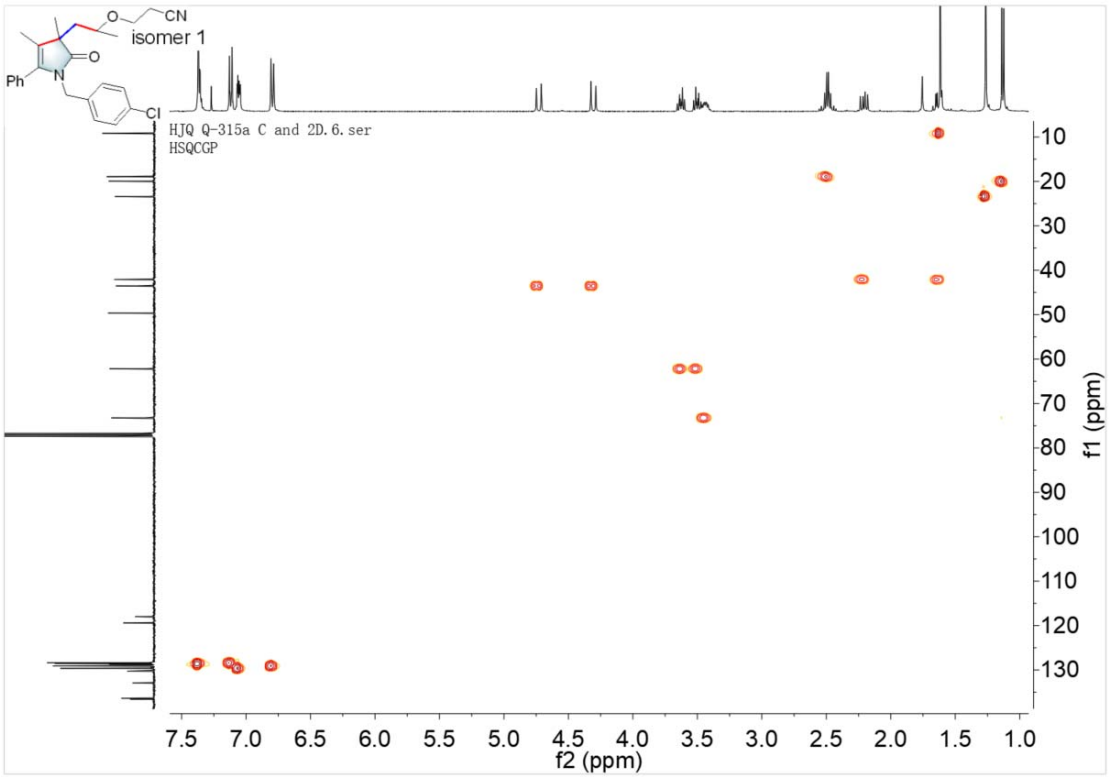
[a] Reaction conditions: **1a** (0.45 mmol), **2** (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.0015 mmol), MeCN (2.0 mL), 6 W blue LEDs, Ar, room temperature, 12 h. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.

III. 2D NMR for 3y

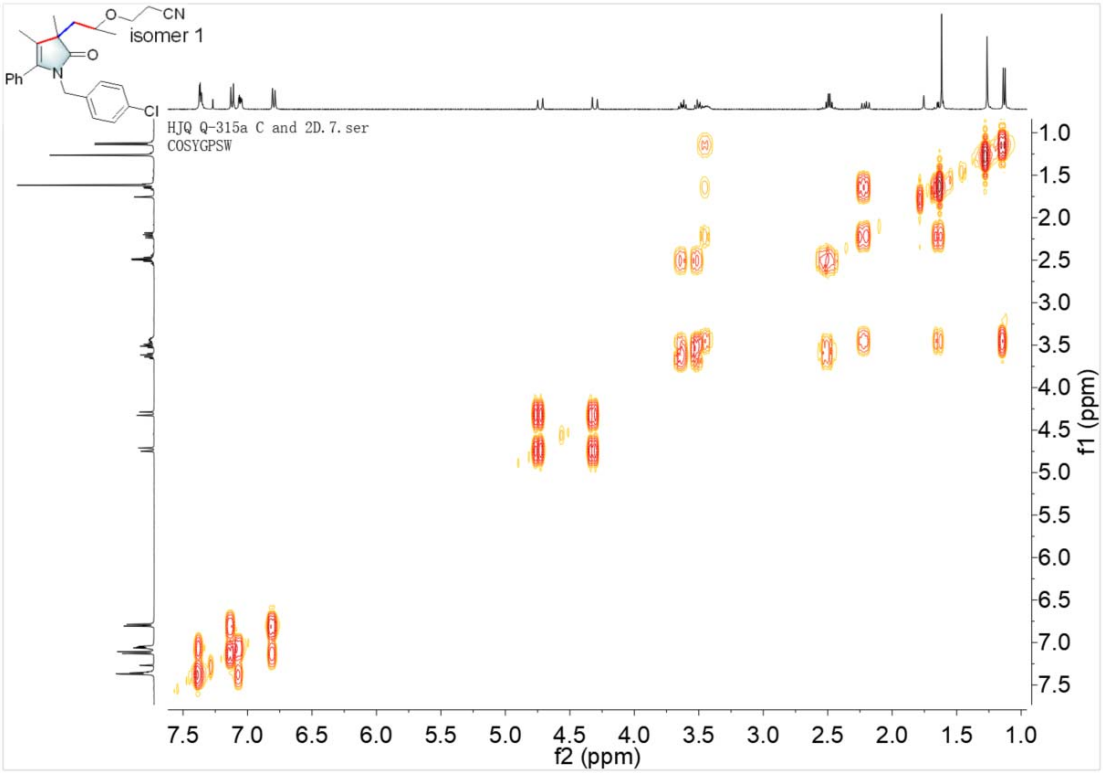
3y, isomer 1, HMBC



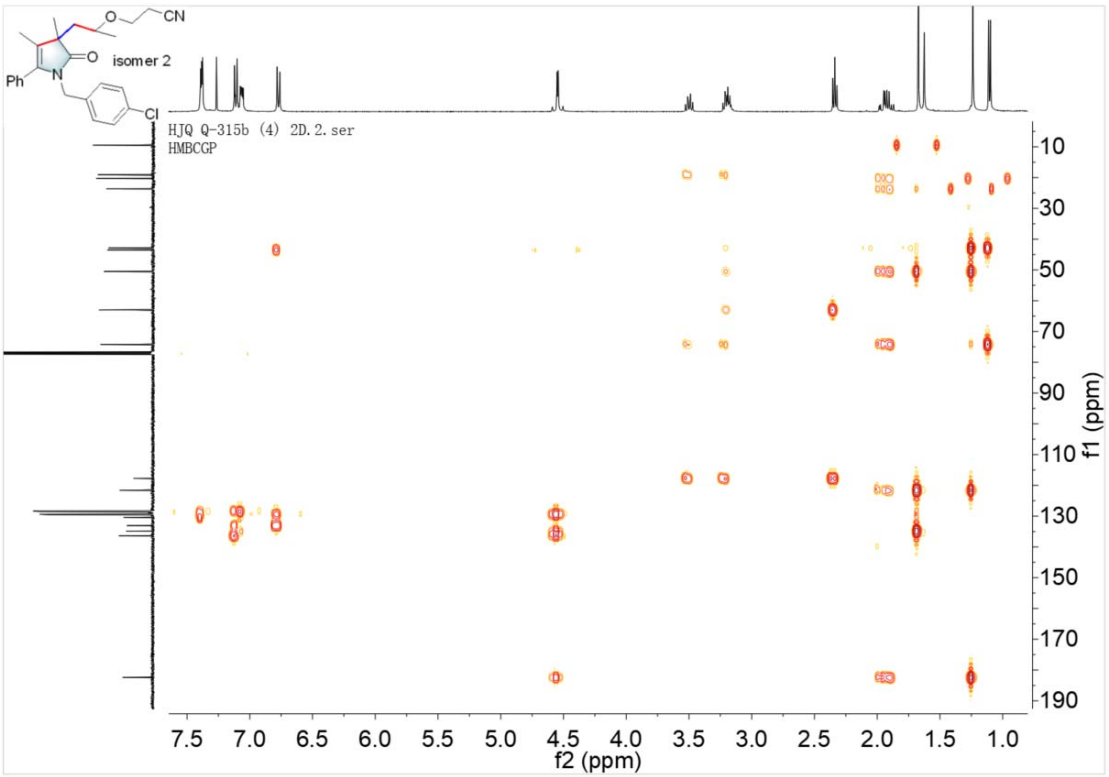
HSQC


isomer 1
HJQ Q-315a C and 2D.6.ser
HSQCGP
f2 (ppm)
f1 (ppm)

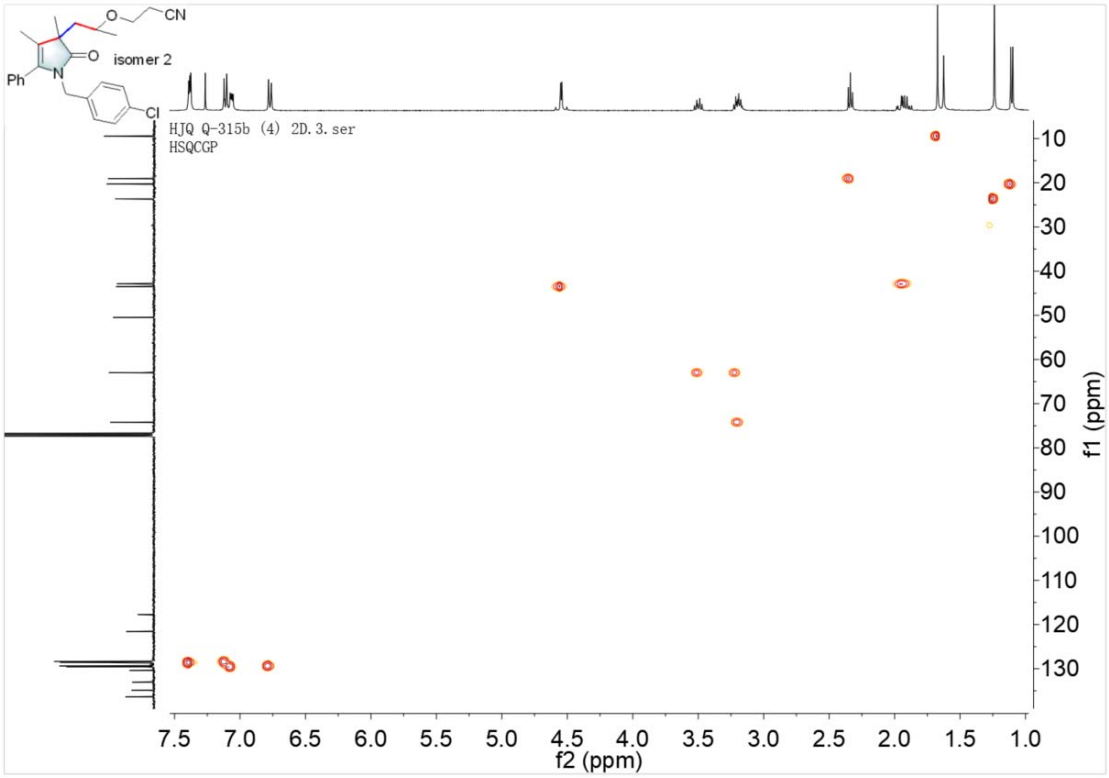
COSY


isomer 1
HJQ Q-315a C and 2D.7.ser
COSYGPSW
f2 (ppm)
f1 (ppm)

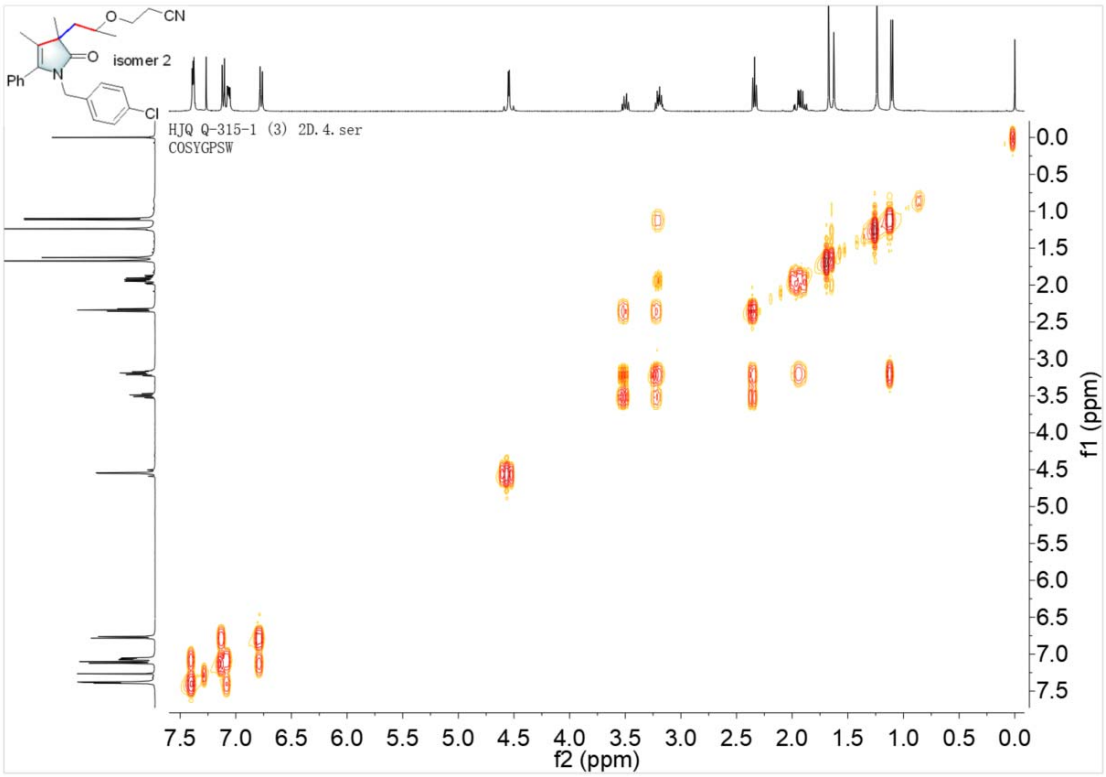
3y, isomer 2, HMBC



HSQC

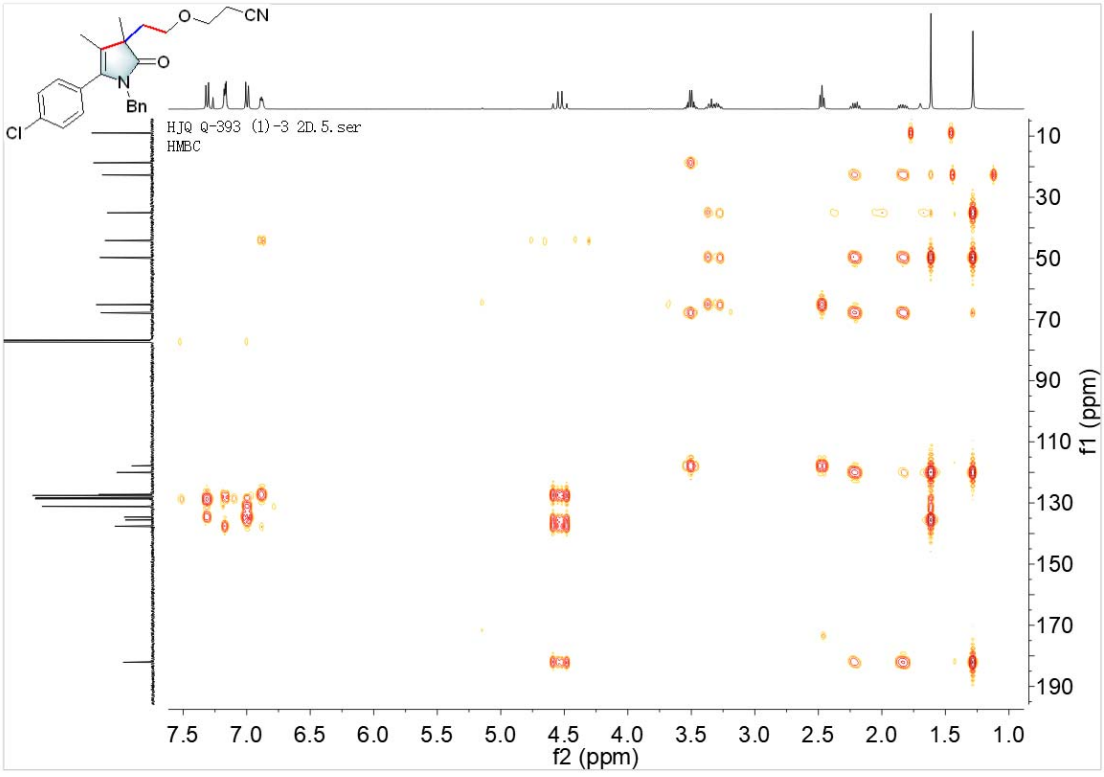


COSY

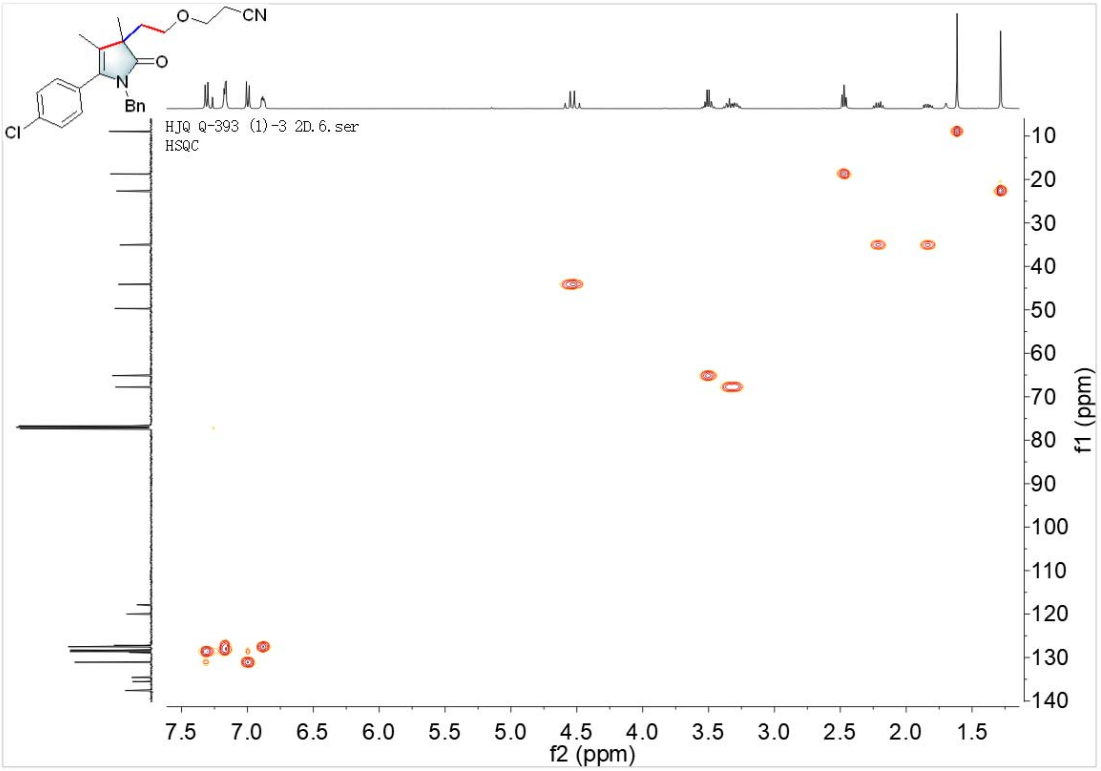


IV. 2D NMR for 3z

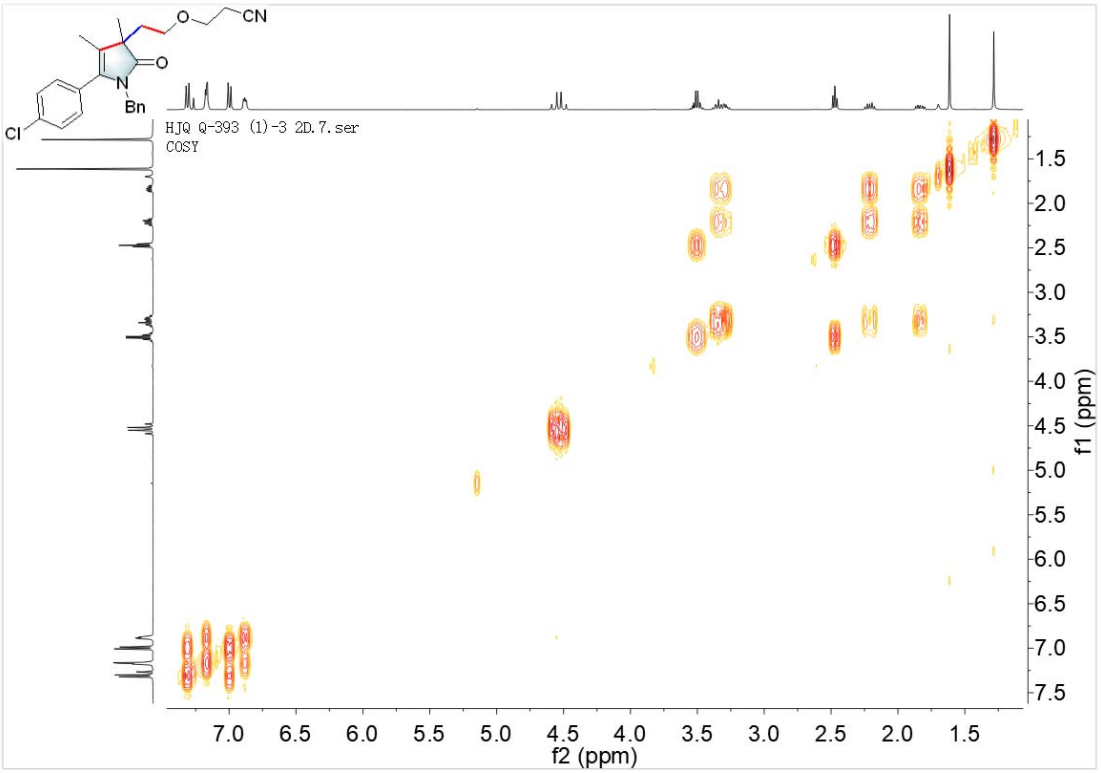
3z, HMBC



HSQC


HJQ Q-393 (1)-3 2D.6.ser
HSQC
f2 (ppm)
f1 (ppm)

COSY


HJQ Q-393 (1)-3 2D.7.ser
COSY
f2 (ppm)
f1 (ppm)

V. Experimental procedures

1. General procedure for the synthesis of 3-cyanoalkyl-4-pyrrolin-2-ones

A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with oxime ester **2** (0.3 mmol), *N*-vinylacrylamide **1** (1.5 equiv, 0.45 mmol), and *fac*-Ir(ppy)$_3$ (0.5 mol%, 0.0015 mmol, 1 mg) under argon, followed by the addition of degassed MeCN (2.0 mL). A strictly oxygen-free environment is necessary. The mixture was stirred at room temperature under blue LED irradiation for 12 h, then it was quenched with water (20.0 mL), and extracted with CH_2Cl_2 (20.0 mL × 4) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate, mostly 21:1) to afford the product.

2. Gram-scale synthesis

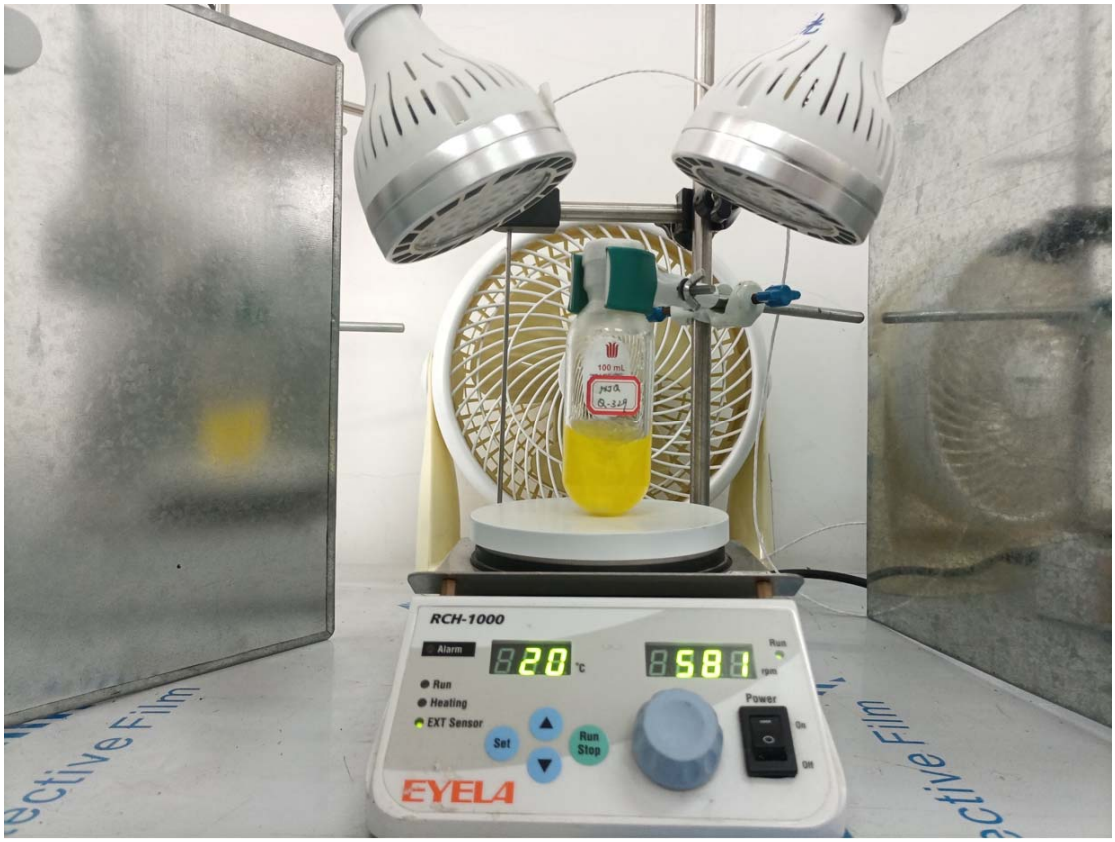


Figure S2 Setup for gram-scale synthesis

A 100-mL reaction tube, equipped with a magnetic stirring bar, was charged

sequentially with oxime ester **2a** (4 mmol, 1.029 g), *N*-vinylacrylamide **1j3** (1.5 equiv, 6 mmol, 1.955 g), and *fac*-Ir(ppy)$_3$ (0.5 mol%, 0.02 mmol, 13 mg) under argon, followed by the addition of degassed MeCN (27.0 mL). The mixture was stirred at room temperature under blue LED irradiation for 14 h (25 W × 2, 455 nm, Figure S2), then it was quenched with water (100.0 mL), and extracted with CH_2Cl_2 (50.0 mL × 4) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 21:1) to afford 5-(1-(4-chlorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)penta nenitrile **3j3** as a colorless oil (1.106 g, 70% yield).

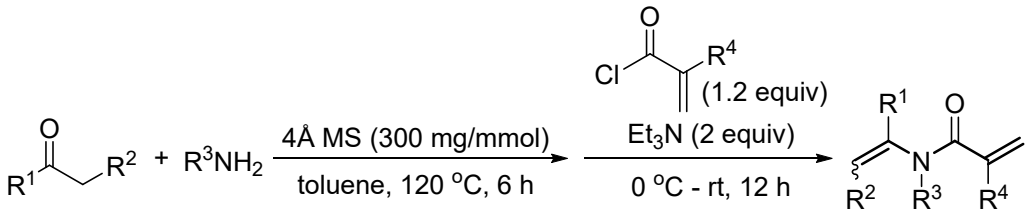
3. Natural sunlight experiment

Figure S3 Setup for natural sunlight experiment

A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with oxime ester **2a** (0.3 mmol, 77 mg), *N*-vinylacrylamide **1a** (1.5 equiv, 0.45 mmol, 131 mg), and *fac*-Ir(ppy)$_3$ (0.5 mol%, 0.0015 mmol, 1 mg) under argon, followed by the addition of degassed MeCN (2.0 mL). The mixture was stirred at room temperature under natural sunlight irradiation for 12 h (2020.12.24 (6 h, 10:30-16:30) and 2020.12.25 (6 h, 10:30-16:30), Kunming, Figure S3), then it was

quenched with water (20.0 mL), and extracted with CH_2Cl_2 (20.0 mL × 4) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 21:1) to afford 5-(1-benzyl-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile **3a** as a colorless oil (71 mg, 66% yield).

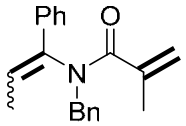
4. General procedure for the synthesis of *N*-vinylacrylamide substrates 1



Substrates **1** were synthesized according to the literature procedure.[1]

A mixture of primary amine (13.9 mmol), ketone (13.9 mmol) and 4Å molecular sieves (4.5 g) in toluene (14 mL) was stirred at 120 °C for 6 h, which furnished the corresponding crude imine. After cooling, the mixture was filtrated and washed with toluene (3 mL). To the filtrate were added triethylamine (2 equiv, 27.8 mmol) and methacryloyl chloride (1.2 equiv, 16.7 mmol) at 0 °C, and the mixture was allowed to warm to room temperature and stirred for another 12 h. Then, it was quenched with water (50 mL) and extracted with CH_2Cl_2 (25 mL × 4). The residue obtained after evaporation of the solvent was purified on silica gel (petroleum ether–ethyl acetate) to afford the *N*-vinylacrylamides.

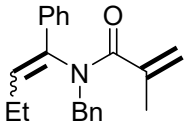
New compounds:



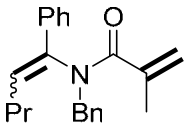
1a, *N*-benzyl-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 10H), 5.44 (q, *J* = 7.3 Hz, 1H), 5.34 (s, 1H), 5.10 (t, *J* = 1.6 Hz, 1H), 4.65 (s, 2H), 1.76 (s, 3H), 1.72 (d, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H}

1 M. Kobayashi, T. Suda, K. Noguchi and K. Tanaka, *Angew. Chem., Int. Ed.*, 2011, **50**, 1664–1667.

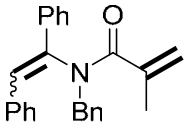
NMR (101 MHz, $CDCl_3$) δ 172.6, 141.8, 139.9 (br), 137.8, 135.3, 129.3, 128.7, 128.6, 128.4, 128.3, 128.1, 127.2, 123.8 (br), 117.6 (br), 50.5 (br), 20.2, 14.6. HRMS (ESI-TOF) Calcd for $C_{20}H_{22}NO^+$ ($[M+H]^+$) 292.1696. Found 292.1699.



1b1, *N*-benzyl-*N*-(1-phenylbut-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), yellowish solid: mp 74−75 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 10H), 5.34 (s, 1H), 5.30 (t, *J* = 7.6 Hz, 1H), 5.09 (t, *J* = 1.6 Hz, 1H), 4.63 (s, 2H), 2.16 (p, *J* = 7.5 Hz, 2H), 1.79 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.7, 141.8, 138.5 (br), 137.6, 135.4, 131.3 (br), 129.2, 128.9, 128.4, 128.3, 128.2, 127.2, 117.4 (br), 50.2 (br), 22.1, 20.4, 13.6. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO^+$ ($[M+H]^+$) 306.1852. Found 306.1860.

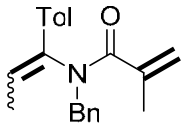


1b2, *N*-benzyl-*N*-(1-phenylpent-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), off-white solid: mp 49−50 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 10H), 5.35 (s, 1H), 5.32 (t, *J* = 7.6 Hz, 1H), 5.09 (p, *J* = 1.6 Hz, 1H), 4.63 (s, 2H), 2.12 (q, *J* = 7.5 Hz, 2H), 1.79 (s, 3H), 1.30 (h, *J* = 7.3 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.6, 141.8, 138.9 (br), 137.7, 135.5, 129.9 (br), 129.3, 128.9, 128.4, 128.3, 128.2, 127.2, 117.5 (br), 50.3 (br), 30.8, 22.6, 20.4, 13.8. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO^+$ ($[M+H]^+$) 320.2009. Found 320.1998.

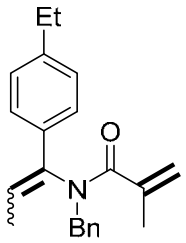


1b3, *N*-benzyl-*N*-(1,2-diphenylvinyl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 10H), 7.13 – 7.10 (m, 3H), 6.95 – 6.93 (m, 2H), 6.19 (s, 1H), 5.51 (t, *J* = 1.2 Hz, 1H), 5.14 (t, *J* = 1.5 Hz, 1H), 4.66 (s, 2H), 1.86 (t, *J* =

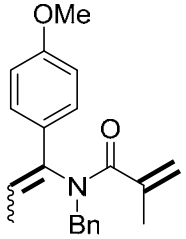
1.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.7, 141.8, 140.0, 137.3, 135.8, 134.8, 130.2, 129.1, 129.1, 128.8, 128.6, 128.3, 128.2, 127.39, 127.36, 127.2, 118.0, 49.9, 20.4. HRMS (ESI-TOF) Calcd for $C_{25}H_{24}NO^+$ ($[M+H]^+$) 354.1852. Found 354.1853.



1d1, *N*-benzyl-*N*-(1-(*p*-tolyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 9H), 5.37 (q, *J* = 7.3 Hz, 1H), 5.33 (s, 1H), 5.09 (s, 1H), 4.62 (s, 2H), 2.37 (s, 3H), 1.79 (s, 3H), 1.71 (d, *J* = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.6, 141.9, 139.6 (br), 138.1, 137.8, 132.2, 129.2, 129.1, 128.8, 128.3, 127.1, 123.4 (br), 117.4 (br), 50.2 (br), 21.3, 20.3, 14.5. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO^+$ ($[M+H]^+$) 306.1852. Found 306.1861.

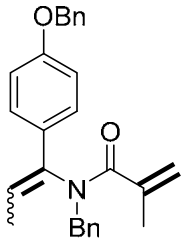


1d2, *N*-benzyl-*N*-(1-(4-ethylphenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 9H), 5.38 (q, *J* = 7.3 Hz, 1H), 5.33 (s, 1H), 5.09 (p, *J* = 1.5 Hz, 1H), 4.62 (s, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.78 (s, 3H), 1.72 (d, *J* = 7.4 Hz, 3H), 1.26 (t, *J* = 7.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.6, 144.4, 141.8, 139.7 (br), 137.8, 132.4, 129.3, 128.8, 128.2, 127.9, 127.1, 123.4 (br), 117.3 (br), 50.2 (br), 28.6, 20.2, 15.4, 14.5. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO^+$ ($[M+H]^+$) 320.2009. Found 320.2013.

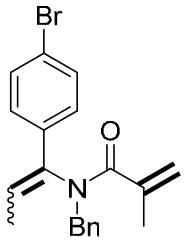


1d3, *N*-benzyl-*N*-(1-(4-methoxyphenyl)prop-1-en-1-yl)methacrylamide, isolated by

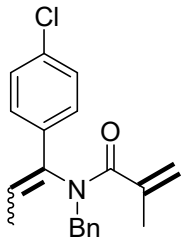
flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 5H), 7.18 – 7.15 (m, 2H), 6.90 – 6.87 (m, 2H), 5.34 (q, *J* = 6.6 Hz, 1H), 5.33 (s, 1H), 5.08 (t, *J* = 1.6 Hz, 1H), 4.63 (s, 2H), 3.78 (s, 3H), 1.78 (s, 3H), 1.69 (d, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 159.3, 141.9, 139.4 (br), 137.8, 130.6, 128.8, 128.3, 127.5, 127.1, 122.7 (br), 117.3 (br), 113.8, 55.3, 50.2 (br), 20.3, 14.5. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO_2^+$ ($[M+H]^+$) 322.1802. Found 322.1804.



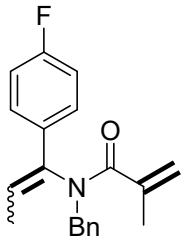
1d4, *N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), yellowish solid: mp 88−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.14 (m, 8H), 6.98 – 6.94 (m, 2H), 5.37 – 5.32 (m, 2H), 5.07 – 5.06 (m, 3H), 4.63 (s, 2H), 1.77 (s, 3H), 1.69 (d, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 158.6, 141.9, 139.5 (br), 137.8, 136.8, 130.7, 128.8, 128.7, 128.3, 128.1, 127.8, 127.6, 127.2, 122.7 (br), 117.4 (br), 114.8, 70.1, 50.3 (br), 20.3, 14.6. HRMS (ESI-TOF) Calcd for $C_{27}H_{28}NO_2^+$ ($[M+H]^+$) 398.2115. Found 398.2121.



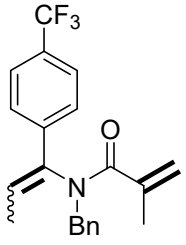
1d5, *N*-benzyl-*N*-(1-(4-bromophenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), off-white solid: mp 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.31 – 7.17 (m, 5H), 7.10 – 7.06 (m, 2H), 5.48 (q, *J* = 7.3 Hz, 1H), 5.31 (s, 1H), 5.11 (t, *J* = 1.5 Hz, 1H), 4.65 (s, 2H), 1.76 (s, 3H), 1.71 (d, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 141.6, 138.9 (br), 137.5, 134.3, 131.6, 130.8, 128.7, 128.4, 127.3, 124.4 (br), 122.1, 117.7 (br), 50.5 (br), 20.2, 14.5. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}BrNO^+$ ($[M+H]^+$) 370.0801. Found 370.0809.



1d6, *N*-benzyl-*N*-(1-(4-chlorophenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow solid: mp 63−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.28 – 7.18 (m, 5H), 7.16 – 7.12 (m, 2H), 5.48 (q, *J* = 7.3 Hz, 1H), 5.32 (t, *J* = 1.2 Hz, 1H), 5.09 (s, 1H), 4.66 (s, 2H), 1.74 (s, 3H), 1.68 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 141.7, 139.0 (br), 137.6, 133.9, 133.8, 130.6, 128.7, 128.6, 128.4, 127.3, 124.2 (br), 117.6 (br), 50.6 (br), 20.1, 14.5. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO^+$ ([M+H]$^+$) 326.1306. Found 326.1306.

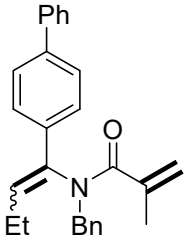


1d7, *N*-benzyl-*N*-(1-(4-fluorophenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), white solid: mp 71−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 7H), 7.03 (dddd, *J* = 8.6, 8.6, 3.1, 2.2 Hz, 2H), 5.46 (q, *J* = 7.3 Hz, 1H), 5.32 (t, *J* = 1.2 Hz, 1H), 5.10 (t, *J* = 1.6 Hz, 1H), 4.66 (s, 2H), 1.75 (s, 3H), 1.69 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 162.2 (d, *J* = 248.5 Hz), 141.8, 139.0 (br), 137.6, 131.4 (d, *J* = 3.4 Hz), 131.1 (d, *J* = 8.2 Hz), 128.7, 128.4, 127.3, 123.6 (br), 117.6 (br), 115.4 (d, *J* = 21.6 Hz), 50.5 (br), 20.2, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.74 (s, 1F). HRMS (ESI-TOF) Calcd for $C_{20}H_{21}FNO^+$ ([M+H]$^+$) 310.1602. Found 310.1600.

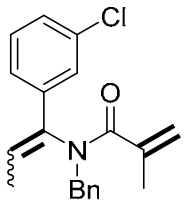


1d8, *N*-benzyl-*N*-(1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1),

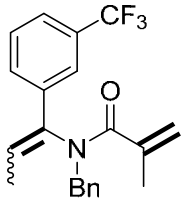
pale yellow solid: mp 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.23 (m, 7H), 5.60 (q, *J* = 7.3 Hz, 1H), 5.33 (s, 1H), 5.12 (s, 1H), 4.70 (s, 2H), 1.75 – 1.72 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 141.6, 139.3, 138.9 (br), 137.4, 129.9 (q, *J* = 32.5 Hz), 129.6, 128.7, 128.4, 127.4, 125.5 (br), 125.3 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.1 Hz), 117.9 (br), 50.8 (br), 20.0, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.62 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{21}H_{21}F_3NO^+$ ($[M+H]^+$) 360.1570. Found 360.1572.



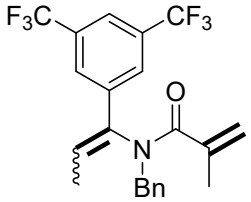
1d9, *N*-(1-([1,1'-biphenyl]-4-yl)but-1-en-1-yl)-*N*-benzylmethacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow solid: mp 90−91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.3, 7.3 Hz, 4H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.35 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.31 – 7.22 (m, 7H), 5.37 (s, 1H), 5.31 (t, *J* = 7.6 Hz, 1H), 5.10 (s, 1H), 4.67 (s, 2H), 2.21 (p, *J* = 7.5 Hz, 2H), 1.83 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.7 (br), 141.9, 141.0, 140.3, 138.2 (br), 137.7, 134.4, 131.6 (br), 129.7, 129.0, 128.9, 128.3, 127.7, 127.3, 127.0, 117.5 (br), 50.3 (br), 22.2, 20.5, 13.7. HRMS (ESI-TOF) Calcd for $C_{27}H_{28}NO^+$ ($[M+H]^+$) 382.2165. Found 382.2166.



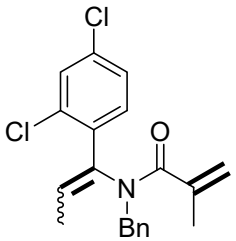
1d10, *N*-benzyl-*N*-(1-(3-chlorophenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 7H), 7.18 (ddd, *J* = 2.6, 1.0, 1.0 Hz, 1H), 7.12 – 7.07 (m, 1H), 5.51 (q, *J* = 7.4 Hz, 1H), 5.31 (s, 1H), 5.11 (p, *J* = 1.6 Hz, 1H), 4.66 (s, 2H), 1.75 (s, 3H), 1.72 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 141.6, 138.8 (br), 137.5, 137.3, 134.4, 129.7, 129.2, 128.7, 128.4, 128.2, 127.5, 127.4, 124.9 (br), 117.8 (br), 50.7 (br), 20.2, 14.5. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO^+$ ($[M+H]^+$) 326.1306. Found 326.1305.



1d11, *N*-benzyl-*N*-(1-(3-(trifluoromethyl)phenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.47 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.32 – 7.22 (m, 5H), 5.61 (q, *J* = 7.4 Hz, 1H), 5.31 (t, *J* = 1.2 Hz, 1H), 5.12 (t, *J* = 1.6 Hz, 1H), 4.71 (s, 2H), 1.73 (d, *J* = 7.4 Hz, 3H), 1.70 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 141.7, 138.9 (br), 137.4, 136.5, 132.5 (d, *J* = 1.5 Hz), 130.9 (q, *J* = 32.4 Hz), 128.9, 128.7, 128.5, 127.5, 126.0 (q, *J* = 3.9 Hz), 125.0 (br), 124.7 (q, *J* = 3.8 Hz), 123.9 (d, *J* = 272.4 Hz), 117.8 (br), 51.0 (br), 20.0, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{21}H_{21}F_3NO^+$ ([M+H]$^+$) 360.1570. Found 360.1561.

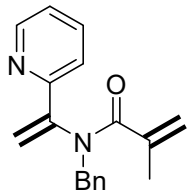


1d12, *N*-benzyl-*N*-(1-(3,5-bis(trifluoromethyl)phenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), white solid: mp 71−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.45 (s, 2H), 7.33 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 5.79 (q, *J* = 7.4 Hz, 1H), 5.26 (s, 1H), 5.14 (s, 1H), 4.78 (s, 2H), 1.76 (d, *J* = 7.5 Hz, 3H), 1.65 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 141.6, 138.3, 138.1 (br), 137.0, 131.7 (q, *J* = 33.5 Hz), 129.2 (d, *J* = 3.0 Hz), 128.8, 128.7, 127.8, 126.3 (br), 123.0 (q, *J* = 272.8 Hz), 121.5 (dt, *J* = 7.6, 3.8 Hz), 118.1 (br), 51.8 (br), 19.8, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.96 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{22}H_{20}F_6NO^+$ ([M+H]$^+$) 428.1444. Found 428.1457.

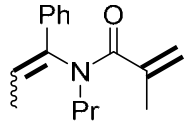


1d13, *N*-benzyl-*N*-(1-(2,4-dichlorophenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), off-white solid:

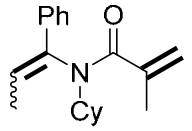
mp 58−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.5, 1.5 Hz, 1H), 7.32 – 7.21 (m, 5H), 7.17 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.75 (q, *J* = 7.2 Hz, 1H), 5.26 (s, 1H), 5.14 (s, 1H), 4.85 (s, 2H), 1.55 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 141.1, 138.3, 137.5 (br), 134.8, 134.5, 133.8, 132.9, 129.8, 128.6, 127.7, 127.2, 126.9, 123.2 (br), 117.8 (br), 53.4, 19.4, 14.5. HRMS (ESI-TOF) Calcd for $C_{20}H_{20}Cl_2NO^+$ ([M+H]$^+$) 360.0916. Found 360.0914.



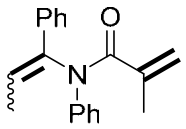
1e, *N*-benzyl-*N*-(1-(pyridin-2-yl)vinyl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.66 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.33 – 7.27 (m, 5H), 7.25 – 7.20 (m, 2H), 5.93 (s, 1H), 5.26 (s, 1H), 5.06 (s, 1H), 5.02 (t, *J* = 1.5 Hz, 1H), 4.85 (s, 2H), 1.78 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 154.4, 149.7, 147.0 (br), 140.9, 137.6, 136.7, 128.8, 128.4, 127.4, 123.1, 120.4, 118.0 (br), 115.1, 51.4 (br), 20.1. HRMS (ESI-TOF) Calcd for $C_{18}H_{19}N_2O^+$ ([M+H]$^+$) 279.1492. Found 279.1494.



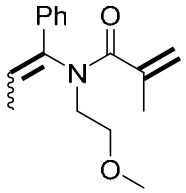
1g1, *N*-(1-phenylprop-1-en-1-yl)-*N*-propylmethacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.39 (m, 2H), 7.34 – 7.31 (m, 3H), 5.62 (q, *J* = 7.2 Hz, 1H), 5.16 (s, 1H), 5.03 (s, 1H), 3.25 (t, *J* = 7.7 Hz, 2H), 1.75 (d, *J* = 7.3 Hz, 3H), 1.68 (s, 3H), 1.47 (h, *J* = 7.4 Hz, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 171.6, 142.3, 140.1 (br), 135.4, 129.3, 128.8, 128.5, 122.9 (br), 116.3 (br), 48.1 (br), 21.0, 20.4, 14.8, 11.6. HRMS (ESI-TOF) Calcd for $C_{16}H_{22}NO^+$ ([M+H]$^+$) 244.1696. Found 244.1693.



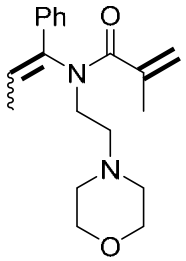
1g2, *N*-cyclohexyl-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 5.62 (q, *J* = 7.3 Hz, 1H), 5.18 (s, 1H), 5.00 (s, 1H), 4.05 (s, 1H), 1.87 (d, *J* = 7.4 Hz, 3H), 1.75 – 1.20 (m, 12H), 0.97 (qt, *J* = 12.7, 3.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 142.7, 138.7 (br), 137.1 (br), 129.5, 128.0, 127.8, 125.4 (br), 115.7 (br), 57.2 (br), 31.2 (br), 26.1, 25.5, 20.6, 14.9. HRMS (ESI-TOF) Calcd for $C_{19}H_{26}NO^{+}$ ([M+H]$^{+}$) 284.2009. Found 284.2010.



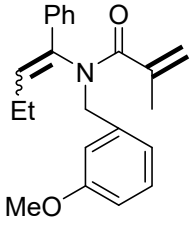
1g3, *N*-phenyl-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.34 – 7.20 (m, 7H), 7.16 – 7.12 (m, 1H), 5.70 (q, *J* = 7.3 Hz, 1H), 5.34 (s, 1H), 5.15 (t, *J* = 1.5 Hz, 1H), 1.84 (d, *J* = 7.3 Hz, 3H), 1.76 (t, *J* = 1.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 143.1 (br), 141.74 (br), 141.66, 136.1, 129.0, 128.9, 128.2, 127.8, 126.4, 126.0, 124.7, 119.8 (br), 19.6, 14.5. HRMS (ESI-TOF) Calcd for $C_{19}H_{20}NO^{+}$ ([M+H]$^{+}$) 278.1539. Found 278.1540.



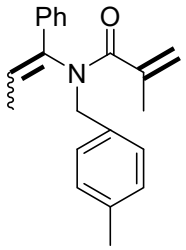
1h, *N*-(2-methoxyethyl)-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 3H), 5.73 (q, *J* = 7.3 Hz, 1H), 5.27 (s, 1H), 5.07 (s, 1H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 3.32 (s, 3H), 1.83 (d, *J* = 7.4 Hz, 3H), 1.69 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 141.9, 140.6 (br), 135.5, 129.2, 128.3, 128.0, 123.0 (br), 117.4 (br), 69.7, 58.6, 46.8 (br), 20.0, 14.6. HRMS (ESI-TOF) Calcd for $C_{16}H_{22}NO_2^{+}$ ([M+H]$^{+}$) 260.1645. Found 260.1643.



1i, *N*-(2-morpholinoethyl)-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.67 (q, *J* = 7.4 Hz, 1H), 5.28 (s, 1H), 5.08 (t, *J* = 1.6 Hz, 1H), 3.67 – 3.65 (m, 4H), 3.56 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.45 – 2.43 (m, 4H), 1.84 (d, *J* = 7.4 Hz, 3H), 1.76 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 141.8, 140.0 (br), 135.1, 129.2, 128.3, 128.1, 123.1 (br), 117.2 (br), 66.9, 55.8, 53.7, 53.5, 43.5 (br), 20.1, 14.6. HRMS (ESI-TOF) Calcd for $C_{19}H_{27}N_2O_2^+$ ([M+H]$^+$) 315.2067. Found 315.2064.

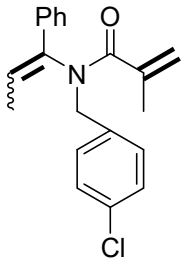


1j1, *N*-(3-methoxybenzyl)-*N*-(1-phenylbut-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.26 – 7.16 (m, 3H), 6.82 – 6.77 (m, 3H), 5.35 – 5.31 (m, 2H), 5.08 (p, *J* = 1.6 Hz, 1H), 4.62 (s, 2H), 3.75 (s, 3H), 2.16 (p, *J* = 7.5 Hz, 2H), 1.79 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 159.6, 141.8, 139.3, 138.6 (br), 135.5, 131.1 (br), 129.25, 129.22, 128.4, 128.2, 121.2, 117.4 (br), 114.2, 112.9, 55.2, 50.3 (br), 22.1, 20.4, 13.6. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_2^+$ ([M+H]$^+$) 336.1958. Found 336.1948.

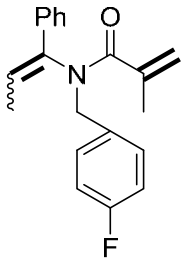


1j2, *N*-(4-methylbenzyl)-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by

flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 7.13 – 7.07 (m, 4H), 5.43 (q, *J* = 7.3 Hz, 1H), 5.32 (s, 1H), 5.08 (p, *J* = 1.6 Hz, 1H), 4.60 (s, 2H), 2.32 (s, 3H), 1.75 (s, 3H), 1.72 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 141.9, 139.9 (br), 136.7, 135.3, 134.7, 129.3, 129.0, 128.7, 128.4, 128.1, 123.7 (br), 117.4 (br), 50.2 (br), 21.2, 20.2, 14.5. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO^+$ ([M+H]$^+$) 306.1852. Found 306.1855.

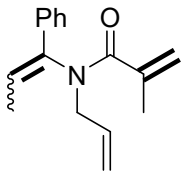


1j3, *N*-(4-chlorobenzyl)-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.32 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.26 – 7.23 (m, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 5.40 (q, *J* = 7.4 Hz, 1H), 5.35 (s, 1H), 5.12 (s, 1H), 4.57 (s, 2H), 1.79 (s, 3H), 1.74 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 141.6, 139.6 (br), 136.2, 134.9, 133.0, 130.2, 129.3, 128.5, 128.45, 128.41, 128.3, 124.0 (br), 117.8 (br), 49.6 (br), 20.2, 14.6. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO^+$ ([M+H]$^+$) 326.1306. Found 326.1309.

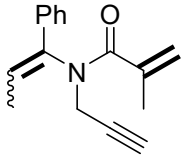


1j4, *N*-(4-fluorobenzyl)-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (tt, *J* = 8.0, 2.0 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 2H), 6.99 – 6.93 (m, 2H), 5.40 (q, *J* = 7.3 Hz, 1H), 5.34 (s, 1H), 5.11 (t, *J* = 1.5 Hz, 1H), 4.58 (s, 2H), 1.78 (s, 3H), 1.74 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 162.1 (d, *J* = 245.2 Hz), 141.7, 139.6 (br), 135.0, 133.5 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 8.0 Hz), 129.3, 128.5, 128.2, 124.0 (br),

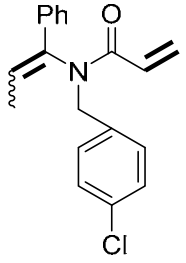
117.7 (br), 115.1 (d, J = 21.3 Hz), 49.5 (br), 20.2, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.41 (p, J = 7.8 Hz, 1F). HRMS (ESI-TOF) Calcd for $C_{20}H_{21}FNO^+$ ([M+H]$^+$) 310.1602. Found 310.1614.



1k, *N*-allyl-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 3H), 5.86 (ddt, J = 16.6, 10.2, 6.2 Hz, 1H), 5.64 (q, J = 7.3 Hz, 1H), 5.31 (s, 1H), 5.12 (dq, J = 10.2, 1.3 Hz, 1H), 5.09 (q, J = 1.6 Hz, 1H), 5.05 (dq, J = 17.1, 1.6 Hz, 1H), 4.05 (d, J = 6.2 Hz, 2H), 1.81 (d, J = 7.4 Hz, 3H), 1.74 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 141.8 (br), 140.2, 135.5, 133.3, 129.3, 128.3, 128.1, 123.1 (br), 117.60 (br), 117.56, 50.2, 20.1, 14.5. HRMS (ESI-TOF) Calcd for $C_{16}H_{20}NO^+$ ([M+H]$^+$) 242.1539. Found 242.1537.

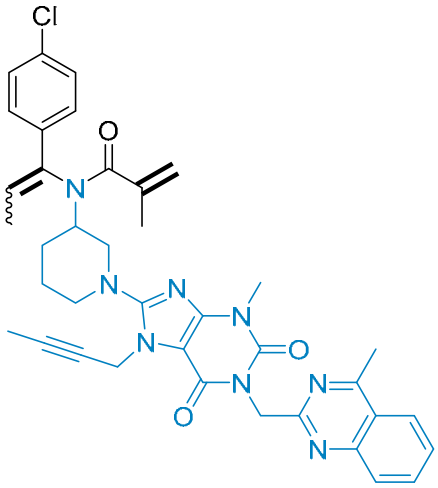


1l, *N*-(1-phenylprop-1-en-1-yl)-*N*-(prop-2-yn-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.76 (q, J = 7.3 Hz, 1H), 5.35 (s, 1H), 5.12 (s, 1H), 4.26 (d, J = 2.5 Hz, 2H), 2.22 (t, J = 2.5 Hz, 1H), 1.86 (d, J = 7.3 Hz, 3H), 1.73 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 141.1 (br), 139.6, 135.0, 129.3, 128.4, 128.2, 123.6 (br), 118.4 (br), 79.2, 71.6, 37.2 (br), 19.8, 14.6. HRMS (ESI-TOF) Calcd for $C_{16}H_{18}NO^+$ ([M+H]$^+$) 240.1383. Found 240.1385.

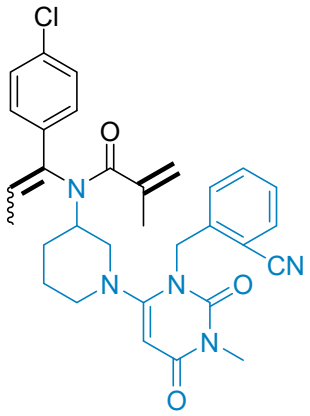


1m, *N*-(4-chlorobenzyl)-*N*-(1-phenylprop-1-en-1-yl)acrylamide, isolated by flash

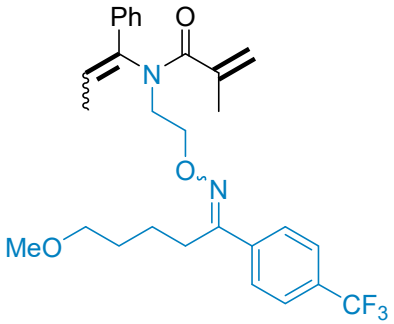
column chromatography (petroleum ether/ethyl acetate = 100:1), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 3H), 7.17 – 7.13 (m, 2H), 7.11 – 7.08 (m, 2H), 7.04 – 7.01 (m, 2H), 6.57 (dd, *J* = 16.8, 10.2 Hz, 1H), 6.38 (dd, *J* = 16.8, 2.2 Hz, 1H), 5.56 (dd, *J* = 10.2, 2.2 Hz, 1H), 5.25 (q, *J* = 7.3 Hz, 1H), 4.34 (s, 2H), 1.64 (d, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.3, 137.9, 136.0, 134.4, 133.0, 130.4, 128.8, 128.73, 128.68, 128.66, 128.4, 128.0, 127.7, 48.3, 14.5. HRMS (ESI-TOF) Calcd for $C_{19}H_{19}ClNO^+$ ([M+H]$^+$) 312.1150. Found 312.1151.



1n, *N*-(1-(7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-8-yl)piperidin-3-yl)-*N*-(1-(4-chlorophenyl)prop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1), white solid: mp 122−123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (dddd, *J* = 8.2, 8.2, 1.4, 1.4 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 5.70 (q, *J* = 7.3 Hz, 1H), 5.56 (s, 2H), 5.25 (s, 1H), 5.08 (s, 1H), 4.90 – 4.79 (m, 2H), 4.25 (t, *J* = 10.8 Hz, 1H), 3.83 (d, *J* = 12.0 Hz, 1H), 3.72 (d, *J* = 12.8 Hz, 1H), 3.53 (s, 3H), 3.18 (s, 1H), 2.88 – 2.83 (m, 4H), 1.89 – 1.65 (m, 13H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.9, 168.5, 161.1, 155.6, 154.4, 151.9, 150.0, 147.9, 142.1, 137.9 (br), 134.9 (br), 134.1, 133.2, 130.6, 128.9, 128.6, 126.7, 126.5 (br), 124.8, 123.1, 116.8 (br), 104.6, 81.1, 73.3, 55.0 (br), 53.1 (br), 50.1, 46.3, 35.8, 29.7, 28.1 (br), 25.1, 21.8, 20.5, 15.0, 3.7. HRMS (ESI-TOF) Calcd for $C_{38}H_{40}ClN_8O_3^+$ ([M+H]$^+$) 691.2906. Found 691.2919.



1o, *N*-(1-(4-chlorophenyl)prop-1-en-1-yl)-*N*-(1-(3-(2-cyanobenzyl)-1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)piperidin-3-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1), white solid: mp 89−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.25 – 7.22 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 5.54 (q, *J* = 7.3 Hz, 1H), 5.32 (s, 1H), 5.29 (d, *J* = 16.0 Hz, 1H), 5.20 – 5.16 (m, 2H), 5.05 (s, 1H), 4.03 (s, 1H), 3.27 (s, 3H), 3.20 (d, *J* = 9.7 Hz, 1H), 3.04 (d, *J* = 11.8 Hz, 1H), 2.76 (t, *J* = 10.3 Hz, 1H), 2.46 (t, *J* = 11.7 Hz, 1H), 1.84 (d, *J* = 7.4 Hz, 3H), 1.77 – 1.58 (m, 7H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 163.0, 159.2, 152.5, 141.8, 140.6, 137.7 (br), 134.6 (br), 134.3, 133.2, 133.0, 130.4, 128.7, 127.9, 127.4, 126.7 (br), 117.10, 117.07, 111.0, 90.2, 54.7 (br), 54.1 (br), 51.2, 46.5, 27.9, 27.6 (br), 24.5, 20.5, 14.9. HRMS (ESI-TOF) Calcd for $C_{31}H_{33}ClN_5O_3^+$ ($[M+H]^+$) 558.2266. Found 558.2284.



1p, *N*-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)-*N*-(1-phenylprop-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 12:1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.28 (m, 5H), 5.70 (q, *J* = 7.3 Hz, 1H), 5.28 (s, 1H), 5.08 (s, 1H), 4.39 (t, *J* = 5.7 Hz, 2H), 3.81 (t, *J* = 5.7 Hz, 2H), 3.35 (t, *J* = 6.0 Hz, 2H), 3.30 (s, 3H), 2.74 (t, *J* = 7.4 Hz, 2H), 1.80 (d, *J* = 7.4 Hz, 3H),

1.73 (s, 3H), 1.65 – 1.52 (m, 4H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.7, 156.1, 140.8, 139.6 (br), 138.1 (d, *J* = 1.0 Hz), 134.3, 129.7 (q, *J* = 32.4 Hz), 128.2, 127.3, 127.1, 125.5, 124.3 (q, *J* = 3.8 Hz), 123.0 (q, *J* = 272.1 Hz), 121.9 (br), 116.4 (br), 71.2, 70.7, 57.5, 45.7, 28.6, 25.1, 22.1, 19.0, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.71 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{28}H_{34}F_3N_2O_3^+$ ($[M+H]^+$) 503.2516. Found 503.2509.

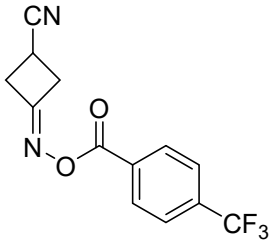
5. General procedure for the synthesis of oxime esters 2

Substrates **2** were synthesized according to the literature procedure.[2]

The ketone (5.0 mmol, 1.0 equiv) and hydroxylamine hydrochloride (5.5 mmol, 1.1 equiv) were placed in a 100-mL flask equipped with stirrer. The pH of the solution was held at 7–8 by adding saturated aq. sodium carbonate (10 mL). The resulting solution was stirred at 40 °C. After extraction with CH_2Cl_2, the solution was evaporated to provide crude products which were used in the next step without further purification.

To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) was added *p*-CF_3benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with CH_2Cl_2. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with PE-EtOAc as an eluent to give the cyclobutanone oxime esters.

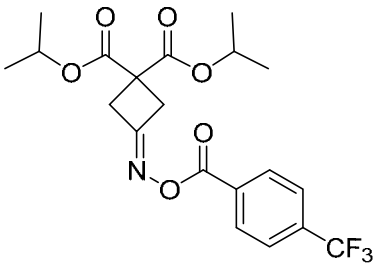
New compounds:



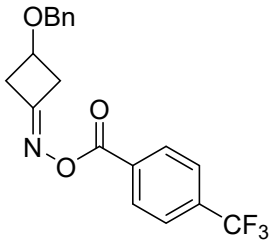
2q, 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutane-1-carbonitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 40:1), white solid: mp 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 3.69 – 3.53 (m, 4H), 3.35 (tt, *J* = 9.3, 6.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz,

2 X.-Y. Yu, J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2018, **57**, 738–743.

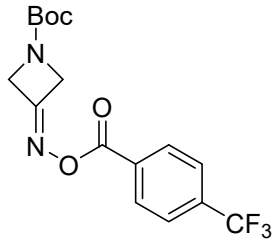
$CDCl_3$) δ 162.2, 162.1, 135.1 (q, *J* = 32.8 Hz), 131.5 (d, *J* = 1.0 Hz), 130.1, 125.7 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.9 Hz), 120.1, 37.4, 37.3, 16.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.25 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{13}H_{10}F_3N_2O_2^+$ ($[M+H]^+$) 283.0689. Found 283.0691.



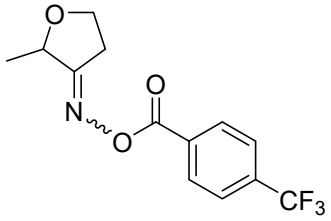
2t, diisopropyl 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutane-1,1-dicarboxylate, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), white solid: mp 75−76 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 5.12 (hept, *J* = 6.3 Hz, 2H), 3.67 – 3.64 (m, 4H), 1.29 (d, *J* = 6.3 Hz, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.1, 162.6, 162.3, 134.9 (q, *J* = 32.8 Hz), 131.9 (d, *J* = 1.0 Hz), 130.1, 125.6 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz), 70.2, 46.8, 39.63, 39.55, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{20}H_{23}F_3NO_6^+$ ($[M+H]^+$) 430.1472. Found 430.1470.



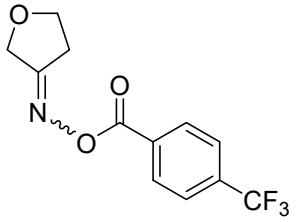
2v, 3-(benzyloxy)cyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime, isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1), white solid: mp 50−51 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.31 (m, 5H), 4.52 (dd, *J* = 14.6, 12.0 Hz, 2H), 4.31 (p, *J* = 6.2 Hz, 1H), 3.41 (dddt, *J* = 23.8, 20.9, 6.9, 3.7 Hz, 2H), 3.19 – 3.09 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.0, 162.8, 137.0, 134.8 (q, *J* = 32.8 Hz), 132.1 (d, *J* = 0.9 Hz), 130.0, 128.6, 128.2, 127.9, 125.6 (q, *J* = 3.7 Hz), 123.5 (d, *J* = 272.7 Hz), 71.2, 66.5, 40.39, 40.37. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{19}H_{17}F_3NO_3^+$ ($[M+H]^+$) 364.1155. Found 364.1152.



2x, *tert*-butyl 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)azetidine-1-carboxylate, isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1), white solid: mp 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 4.81 – 4.85 (m, 4H), 1.49 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 159.4, 155.9, 135.2 (d, *J* = 0.9 Hz), 131.4 (q, *J* = 33.0 Hz), 130.1, 125.7 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.9 Hz), 81.3, 58.2 (br), 28.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.28 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{16}H_{18}F_3N_2O_4^+$ ($[M+H]^+$) 359.1213. Found 359.1222.



2y, 2-methyldihydrofuran-3(2*H*)-one *O*-(4-(trifluoromethyl)benzoyl) oxime, isolated by flash column chromatography (petroleum ether/ethyl acetate = 100:1), white solid: mp 50−51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 4.58 (q, *J* = 6.4 Hz, 1H), 4.24 (ddd, *J* = 9.1, 8.0, 4.2 Hz, 1H), 3.96 (td, *J* = 8.8, 7.2 Hz, 1H), 3.11 – 2.96 (m, 2H), 1.54 (d, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1, 162.3, 134.7 (q, *J* = 32.7 Hz), 132.0 (d, *J* = 0.9 Hz), 129.9, 125.5 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.7 Hz), 74.8, 65.4, 29.9, 17.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.30 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{13}H_{13}F_3NO_3^+$ ($[M+H]^+$) 288.0842. Found 288.0845.



2z, dihydrofuran-3(2*H*)-one *O*-(4-(trifluoromethyl)benzoyl) oxime, isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1), white solid: mp

136−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 4.64 (s, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 2.96 (td, *J* = 7.0, 1.5 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 162.3, 135.0 (q, *J* = 32.8 Hz), 131.8 (d, *J* = 1.0 Hz), 130.0, 125.7 (q, *J* = 3.7 Hz), 123.5 (d, *J* = 272.8 Hz), 68.0, 67.1, 30.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.25 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{12}H_{11}F_3NO_3^+$ ([M+H]$^+$) 274.0686. Found 274.0689.

VI. Mechanistic investigations

1. KIE experiments

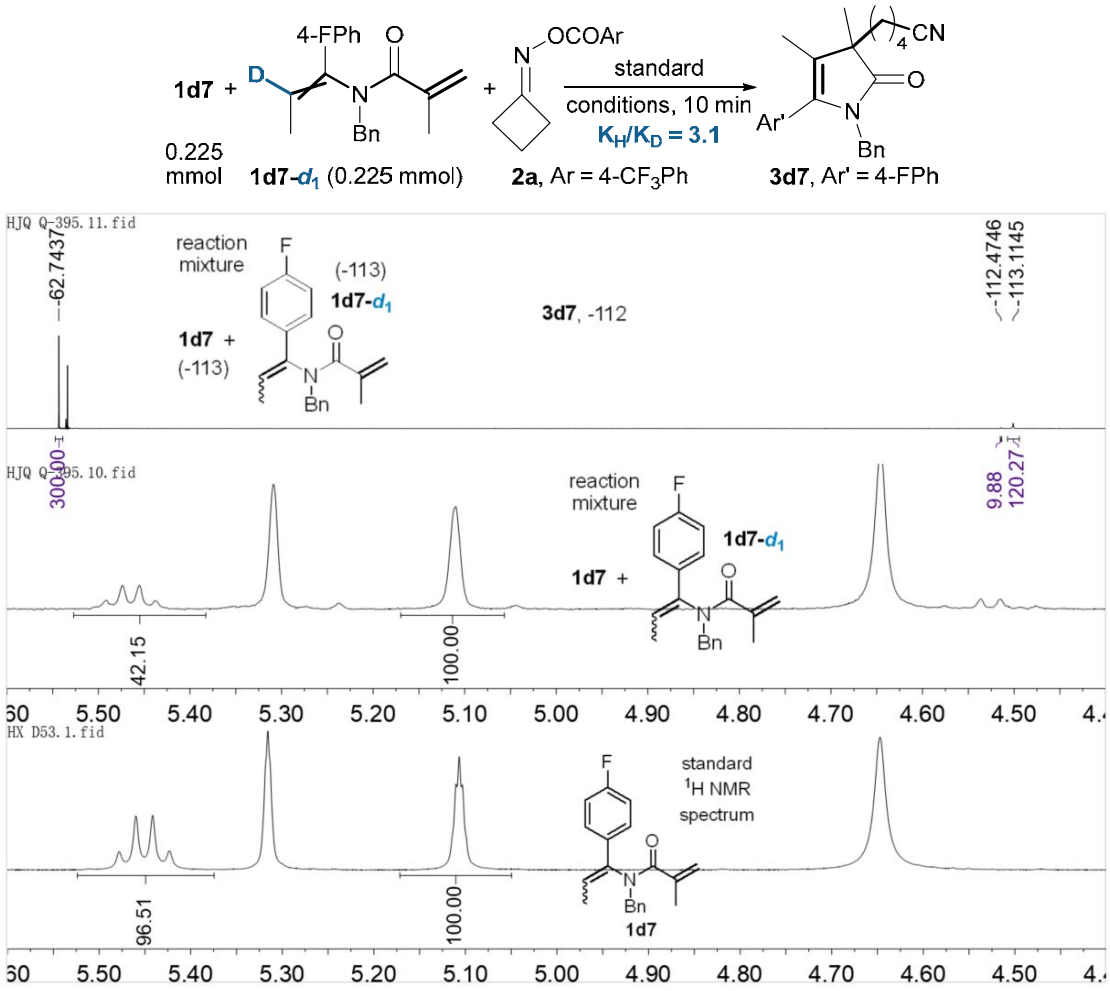


Figure S4 ^{19}F and ^{1}H NMR analyses for the reaction mixture of the KIE experiments

A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with oxime ester **2a** (0.3 mmol, 77 mg), *N*-benzyl-*N*-(1-(4-fluorophenyl)prop-1-en-1-yl)methacrylamide **1d7** (0.75 equiv,

0.225 mmol, 70 mg), *N*-benzyl-*N*-(1-(4-fluorophenyl)prop-1-en-1-yl-2-*d*)methacrylamide **1d7-*d*$_1$** (0.75 equiv, 0.225 mmol, 70 mg), and *fac*-Ir(ppy)$_3$ (0.5 mol%, 0.0015 mmol, 1 mg) under argon, followed by the addition of degassed MeCN (2.0 mL). The mixture was stirred at room temperature under blue LED irradiation for 10 min.

The yields of the product **3d7** formed, which is 9.88%, were determined by ^{19}F NMR analysis based on a benzotrifluoride standard, and 0.36 (120.27%*0.3) mmol of the substrates remained (Figure S4). ^{1}H NMR analyses of the reaction mixture showed that the ratio of the remaining *N*-vinylacrylamide **1d7** (0.1576 mmol) to its deuterated counterpart **1d7-*d*$_1$** (0.2032 mmol) is 42.15/(96.51-42.15) = 42.15/54.36, thus the consumption ratio of **1d7**/**1d7-*d*$_1$** is (0.225-0.1576)/(0.225-0.2032) = 3.1:1.

2. Quenching experiments

A 25-mL Schlenk tube, equipped with a magnetic stirring bar, was charged sequentially with oxime ester **2a** (0.3 mmol, 77 mg), *N*-vinylacrylamide **1d7** (1.5 equiv, 0.45 mmol, 139 mg), *fac*-Ir(ppy)$_3$ (0.5 mol%, 0.0015 mmol, 1 mg) and a scavenger (1.0 equiv, 0.3 mmol) under argon, followed by the addition of degassed MeCN (2.0 mL). The mixture was stirred at room temperature under blue LED irradiation for 12 h. The yields of the product **3d7** formed were determined by ^{19}F NMR analysis based on a benzotrifluoride standard. In the cases of BHT and DPE experiments, the reaction was then quenched with water (20.0 mL), and extracted with CH_2Cl_2 (20.0 mL × 4) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 42:1) to afford the radical adducts.

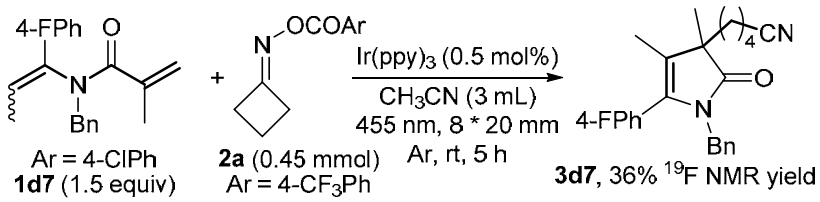
3. Light on-off experiments

To study the necessity of continuous irradiation with visible light for the progress of the reaction, we started a reaction with successive irradiation and black periods. Benzotrifluoride (1.0 equiv) was added as an internal standard to the reaction of **1d7** with **2a** before irradiation. 0.05 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ^{19}F NMR analysis after filtered by a filter membrane with pore size of 0.45 μm. These results demonstrated that light is necessary and a radical chain process is not the major reaction pathway.

Table S8 Light on-off experiments

	A(X)	B(Y)
Long Name	time	19F NMR yield
Units	h	%
Comments		
1	0	0
2	0.5	9.9
3	1	9.04
4	1.5	14.91
5	2	14.75
6	2.5	18.75
7	3	19.25
8	3.5	23.49
9	4	23.61

4. Quantum yield measurements



A quartz cuvette (10 × 10 × 45 mm), equipped with a magnetic stirring bar, was charged under argon sequentially with oxime ester **2a** (0.45 mmol, 116 mg), *N*-vinylacrylamide **1d7** (1.5 equiv, 0.675 mmol, 209 mg), and *fac*-Ir(ppy)$_3$ (0.5 mol%, 0.00225 mmol, 1.5 mg) under argon, followed by the addition of degassed MeCN (3.0 mL). The mixture was irradiated (λ = 455 nm, slit width = 8.0 mm, slit height 20.0 mm with the light intensity of 93.5 mW·cm^{-2}) in a dark room for 18000 s, and the yield of the product **3d7** formed (36.10%) was determined by ^{19}F NMR analysis based on a benzotrifluoride standard.

The set up used for this chemical actinometry is shown in Figure S5, and the light intensity was measured in the PAR-range (Photosynthetic active radiation, 400–700 nm) using a PAR sensor (FZ-A, Photoelectric Instrument Factory of Beijing Normal University).[3]

The fraction of photons absorbed by the reaction solution was recorded using a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan) in a 1 cm quartz cell, and the absorbance of the reaction mixture at 455 nm is 0.826.

---

3 (*a*) J. Liu, L.-Q. Lu, Y. Luo, W. Zhao, P.-C. Sun, W. Jin, X. Qi, Y. Cheng and W.-J. Xiao, *ACS Catal.* 2022, **12**, 1879–1885; (*b*) R. Kong, T. Fu, R. Yang, D. Chen, D. Liang, Y. Dong, W. Li and B. Wang, *ChemCatChem*, 2021, **13**, 2952–2958.

Figure S5 Set up for the chemical actinometry

The quantum yield is determined as follows.[3]

ϕ = Mole number of product/Mole number of absorbed photons = 0.012

$$\phi = \frac{n_{3d7} N_A / t}{f P \lambda / hc}$$

n_{3d7}: the mole number of the product **3d7**; t: reaction time (t = 18000 s); N_A: 6.02 × 10^{23}/mol; f: 1-10^{-A} (455 nm, A = 0.826); P: P = E × S (E: illumination intensity, E = 0.0935 W/cm^2; S: the area that irradiated, S = 1.60 cm^2); λ: wavelength (λ = 4.55×10^{-7} m); h: planck constant (h = 6.626 × 10^{-34} J*s); c: velocity of light (c = 3 × 10^8 m/s).

5. Stern-Volmer experiments

Fluorescence spectra were collected on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies).

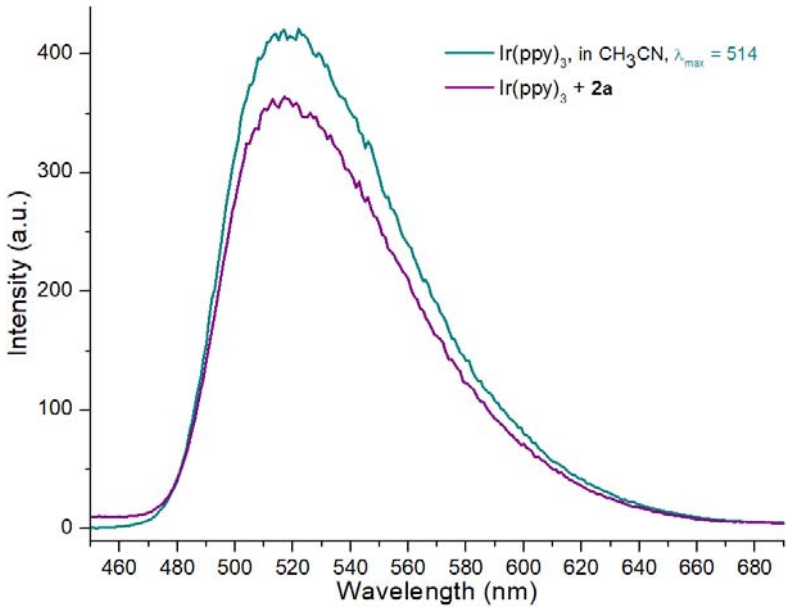


Figure S6 Fluorescence quenching of Ir(ppy)$_3$ (10^{-3} M in MeCN) in the presence of **2a** (1.0 equiv). The solutions were excited at 344 nm (ex. slit 10 nm, em. slit 10 nm).

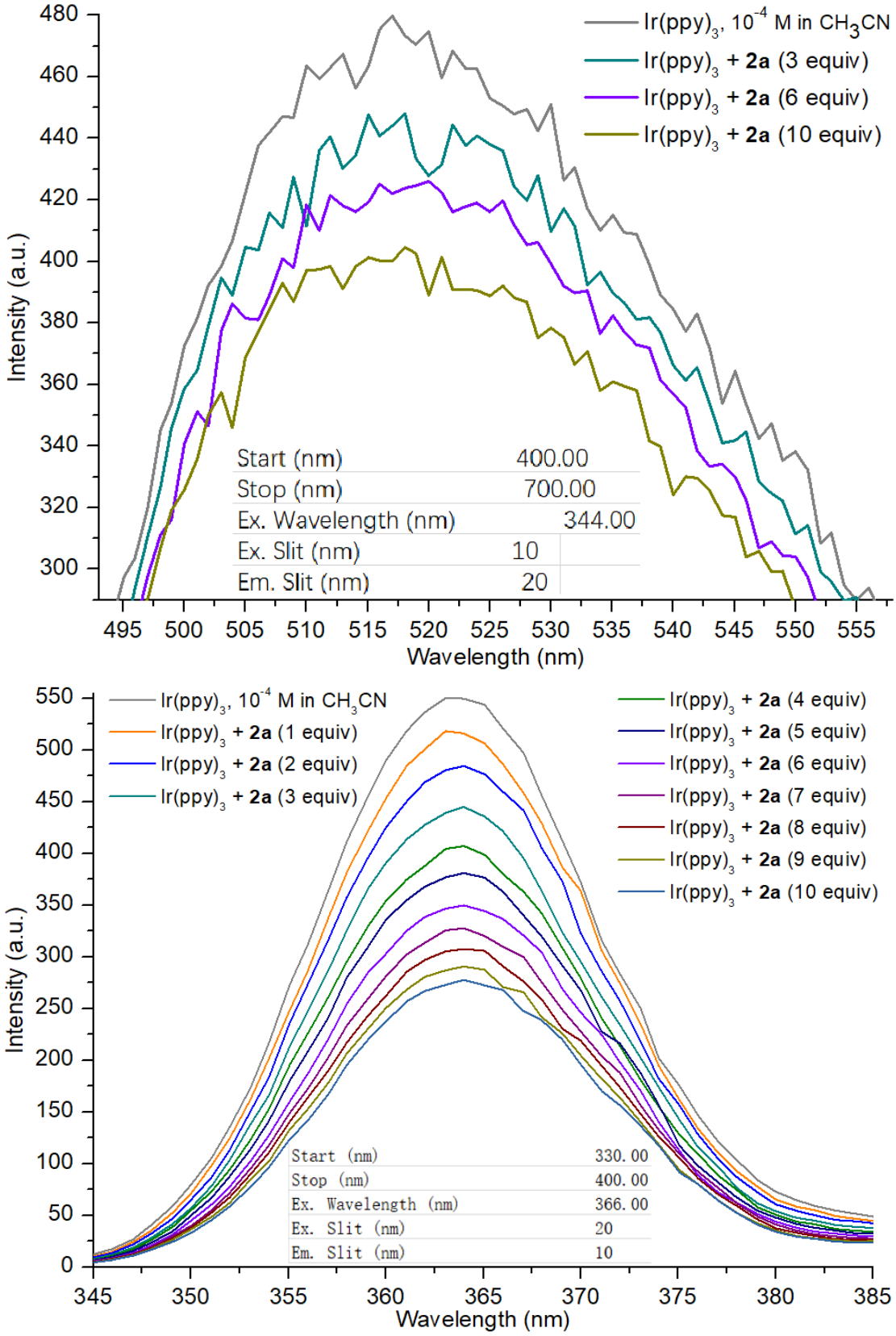


Figure S7 Fluorescence quenching of $Ir(ppy)_3$ (10^{-4} M in MeCN) in the presence of **2a**.

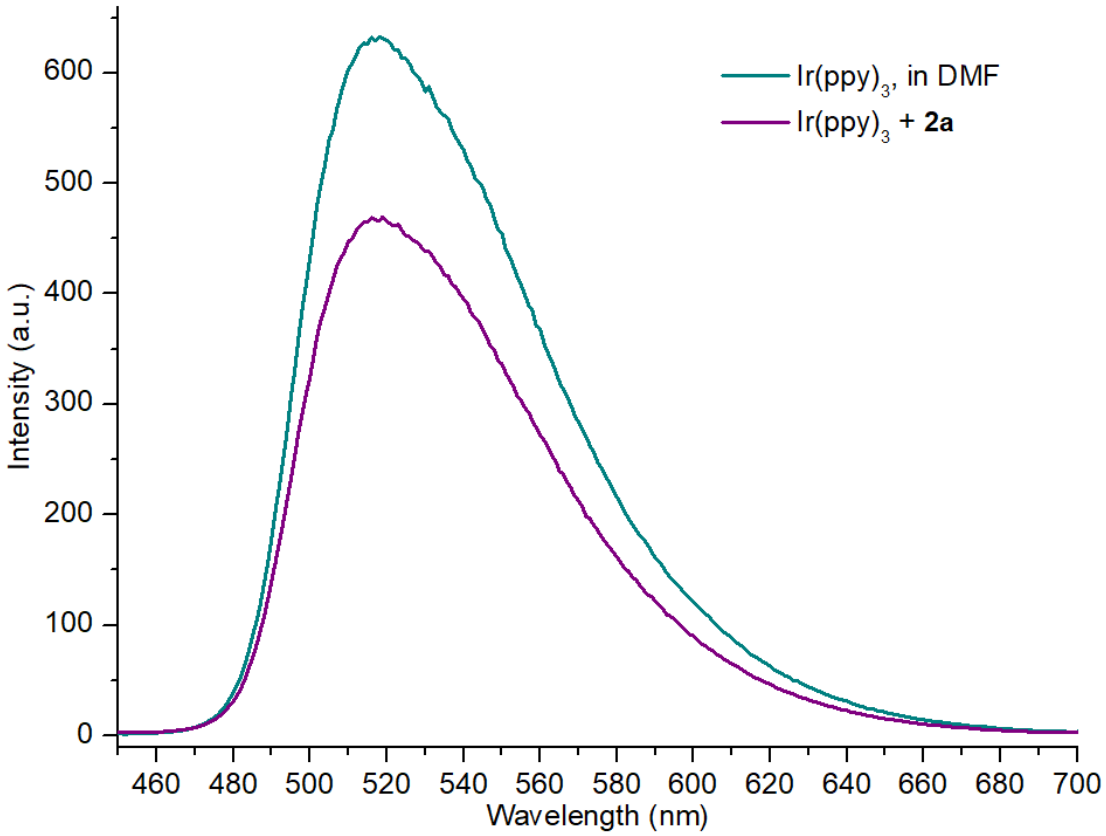


Figure S8 Fluorescence quenching of $Ir(ppy)_3$ (10^{-3} M in DMF) in the presence of **2a** (1.0 equiv). The solutions were excited at 366 nm (ex. slit 20 nm, em. slit 5 nm).

6. 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 1.0 mmol nBu$_4$NBF$_4$ was poured into the electrochemical cell in all experiments. The scan rate was 0.05 V/s.

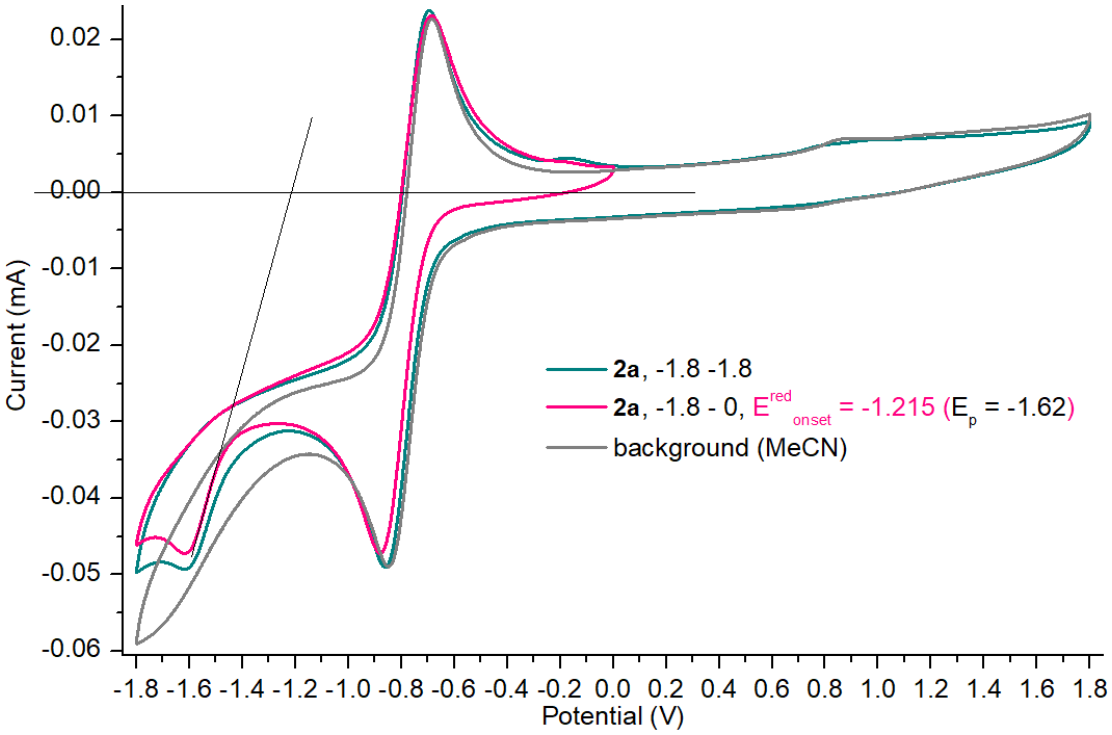


Figure S9 Cyclic voltammograms of **2a** (10^{-3} M) in CH_3CN

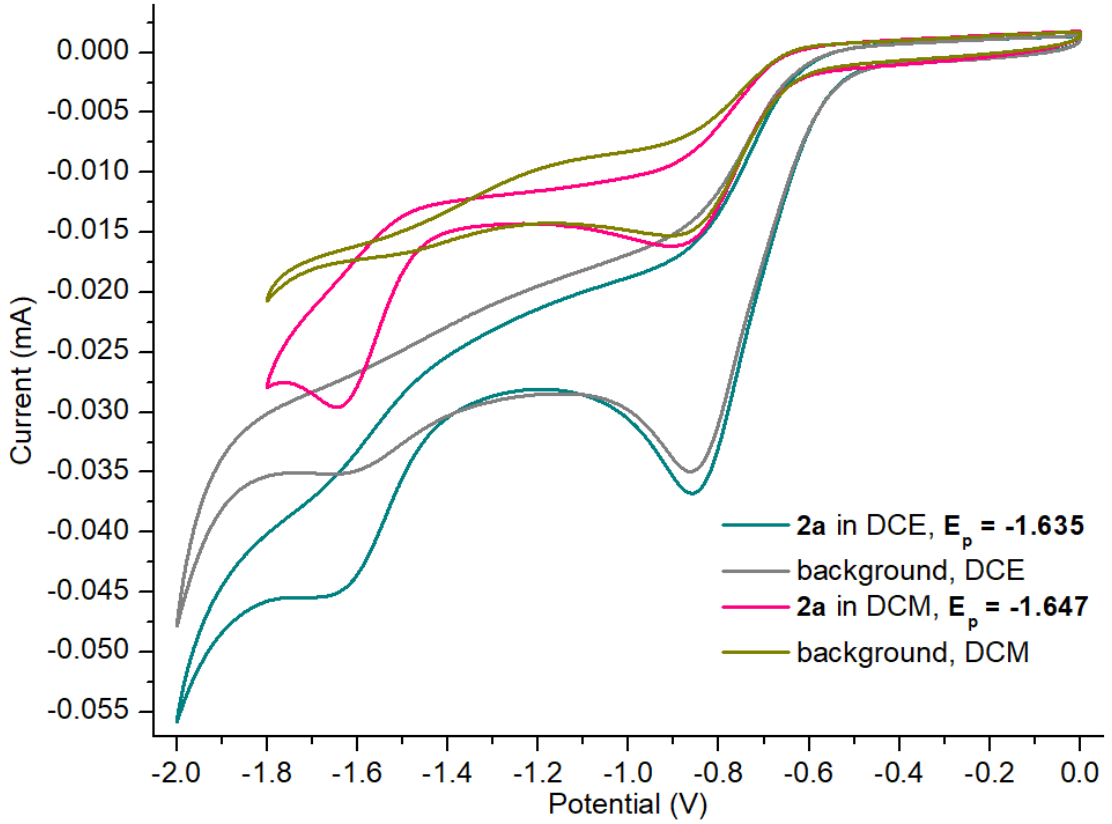


Figure S10 Cyclic voltammograms of **2a** (10^{-3} M) in CH_2Cl_2 or 1,2-dichloroethane

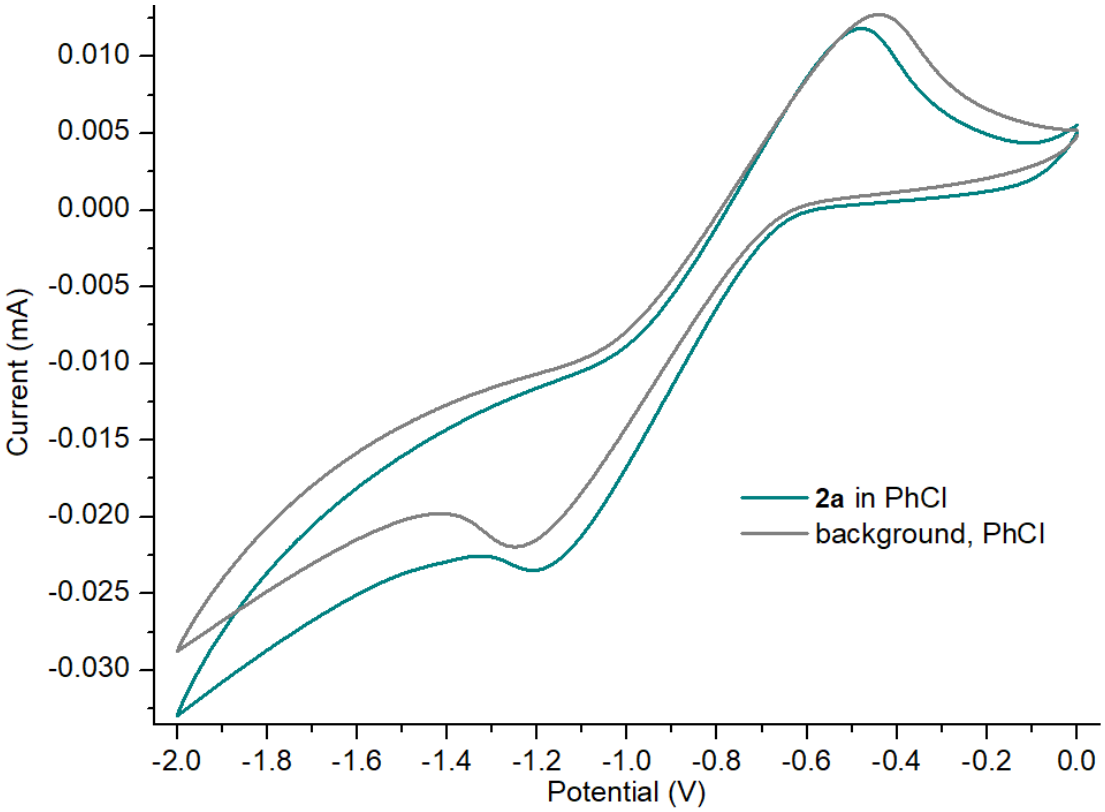


Figure S11 Cyclic voltammograms of **2a** (10^{-3} M) in PhCl

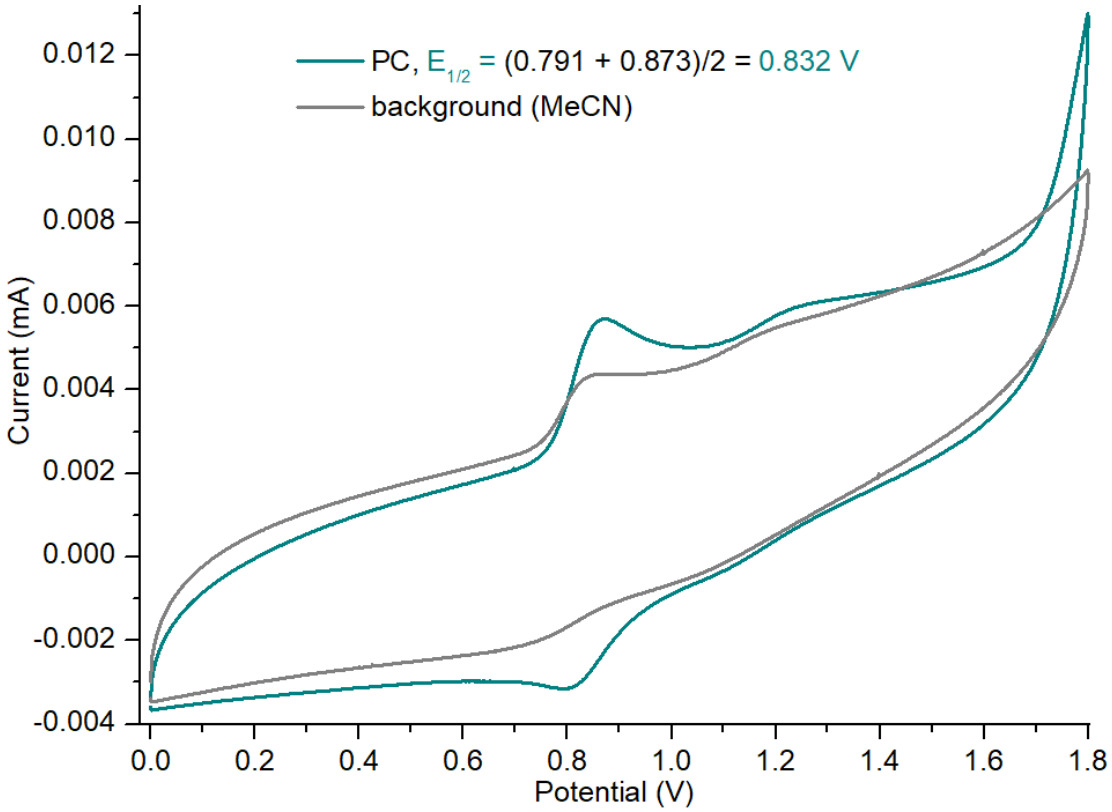


Figure S12 Anodic cyclic voltammogram of $Ir(ppy)_3$ (10^{-3} M) in MeCN

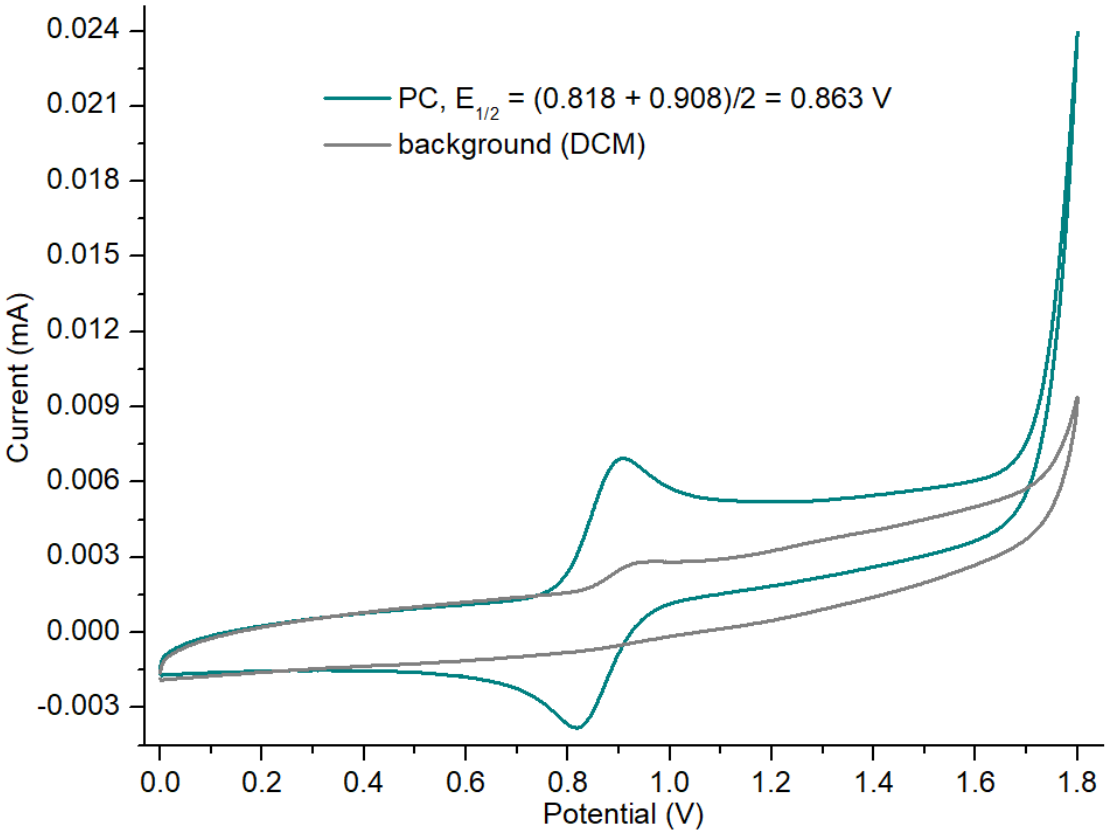


Figure S13 Anodic cyclic voltammogram of $Ir(ppy)_3$ (10^{-3} M) in CH_2Cl_2

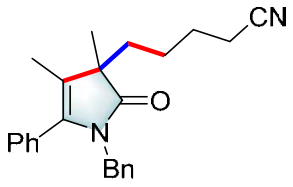
7. Determination of the excited-state oxidation potential of $Ir(ppy)_3$ in MeCN

The excited-state oxidation potential of $Ir(ppy)_3$ ($E[Ir^{IV}/Ir^{III}*]$) is estimated to be -1.58 V vs. Ag/AgCl according to the following equations:

$E_{1/2}$ ($Ir^{IV}/Ir^{III}*$) = E^{ox} - $E_{0,0}$

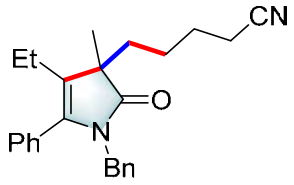
where E^{ox} (0.832 V) was obtained from its cyclic voltammetry spectrum (Figure S12); $E_{0,0}$ is caculated from its photoluminescence maximum (514 nm as shown in Figure S6) using the equation $E_{0,0} = hc/\lambda_{max}$ = 1240 nm/514 nm.

VII. Spectral data of products

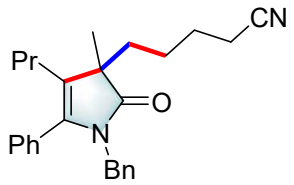


3a, 5-(1-benzyl-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 70% yield (76 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H),

7.19 – 7.12 (m, 3H), 7.10 – 7.05 (m, 2H), 6.88 – 6.84 (m, 2H), 4.59 – 4.50 (m, 2H), 2.26 (qt, *J* = 16.9, 7.1 Hz, 2H), 1.83 (ddd, *J* = 13.3, 11.5, 5.1 Hz, 1H), 1.64 – 1.51 (m, 6H), 1.26 (s, 3H), 1.25 – 1.11 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.4, 137.7, 137.0, 130.3, 129.9, 128.6, 128.4, 128.2, 127.7, 127.1, 119.5, 119.1, 51.2, 44.1, 35.1, 25.4, 23.8, 22.3, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{24}H_{27}N_2O^+$ ($[M+H]^+$) 359.2118. Found 359.2116.

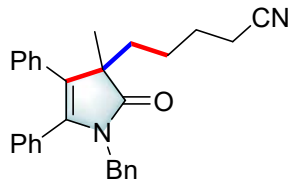


3b1, 5-(1-benzyl-4-ethyl-3-methyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 69% yield (77 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.15 (dddd, *J* = 5.8, 4.0, 2.2, 2.2 Hz, 3H), 7.10 – 7.07 (m, 2H), 6.87 – 6.83 (m, 2H), 4.50 (s, 2H), 2.34 – 2.17 (m, 2H), 2.04 (ddt, *J* = 32.9, 14.7, 7.4 Hz, 2H), 1.85 (ddd, *J* = 13.3, 11.8, 5.0 Hz, 1H), 1.68 – 1.51 (m, 3H), 1.31 (s, 3H), 1.30 – 1.22 (m, 1H), 1.19 – 1.08 (m, 1H), 0.92 (t, *J* = 7.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.0, 137.9, 137.7, 130.7, 129.9, 128.7, 128.3, 128.2, 127.7, 127.1, 124.5, 119.6, 51.8, 44.1, 35.8, 25.5, 23.9, 23.2, 17.6, 17.1, 15.1. HRMS (ESI-TOF) Calcd for $C_{25}H_{29}N_2O^+$ ($[M+H]^+$) 373.2274. Found 373.2277.

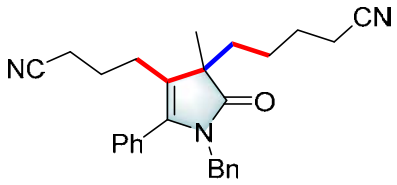


3b2, 5-(1-benzyl-3-methyl-2-oxo-5-phenyl-4-propyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 78% yield (91 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 3H), 7.15 (dddd, *J* = 5.7, 4.0, 2.1, 2.1 Hz, 3H), 7.08 – 7.05 (m, 2H), 6.87 – 6.82 (m, 2H), 4.50 (s, 2H), 2.34 – 2.17 (m, 2H), 2.02 (ddd, *J* = 14.4, 10.3, 6.4 Hz, 1H), 1.94 – 1.80 (m, 2H), 1.68 – 1.50 (m, 3H), 1.40 – 1.21 (m, 6H), 1.12 (dddd, *J* = 14.9, 12.6, 10.3, 5.4 Hz, 1H), 0.76 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.1, 138.3, 137.7, 130.7, 130.0, 128.6, 128.3, 128.2, 127.7, 127.1, 123.1, 119.6, 51.7, 44.1, 35.8, 26.9, 25.5, 23.9, 23.4, 23.1, 17.1, 14.5. HRMS (ESI-TOF) Calcd for $C_{26}H_{31}N_2O^+$

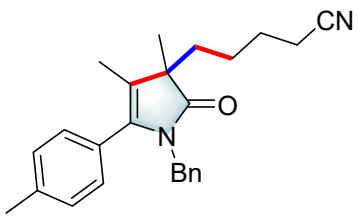
([M+H]$^+$) 387.2431. Found 387.2443.



3b3, 5-(1-benzyl-3-methyl-2-oxo-4,5-diphenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 60% yield (76 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.11 (m, 9H), 7.07 – 7.03 (m, 2H), 7.02 – 6.99 (m, 2H), 6.94 – 6.89 (m, 2H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.62 (d, *J* = 15.2 Hz, 1H), 2.28 – 2.14 (m, 2H), 1.87 (ddd, *J* = 13.3, 11.8, 4.9 Hz, 1H), 1.68 – 1.50 (m, 3H), 1.49 – 1.36 (m, 4H), 1.27 – 1.15 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.2, 139.9, 137.5, 133.8, 130.5, 130.1, 129.4, 128.7, 128.4, 128.3, 128.2, 127.7, 127.2, 126.8, 123.8, 119.6, 52.6, 44.3, 35.9, 25.4, 23.9, 23.5, 17.0. HRMS (ESI-TOF) Calcd for $C_{29}H_{29}N_2O^+$ ([M+H]$^+$) 421.2274. Found 421.2271.

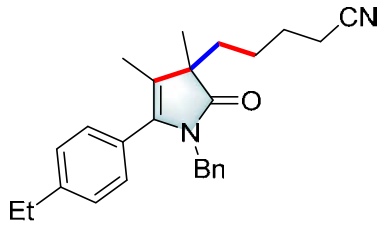


3c, 5-(1-benzyl-4-(3-cyanopropyl)-3-methyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 36% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 3H), 7.17 – 7.14 (m, 3H), 7.06 (ddd, *J* = 6.6, 1.6, 1.6 Hz, 2H), 6.85 – 6.82 (m, 2H), 4.50 (s, 2H), 2.36 – 2.06 (m, 6H), 1.87 (ddd, *J* = 13.4, 11.6, 5.1 Hz, 1H), 1.67 – 1.51 (m, 5H), 1.34 – 1.12 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.6, 139.8, 137.4, 130.2, 129.7, 129.2, 128.7, 128.2, 127.7, 127.2, 120.4, 119.4, 119.1, 51.6, 44.1, 35.7, 25.6, 25.3, 23.7, 23.6, 23.0, 17.2, 17.0. HRMS (ESI-TOF) Calcd for $C_{27}H_{30}N_3O^+$ ([M+H]$^+$) 412.2383. Found 412.2370.

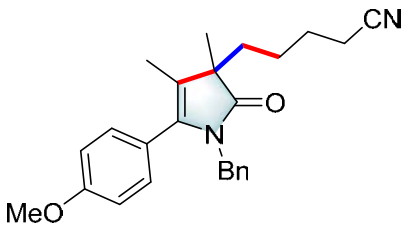


3d1, 5-(1-benzyl-3,4-dimethyl-2-oxo-5-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile,

isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 58% yield (65 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 5H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.90 (dd, *J* = 6.6, 3.0 Hz, 2H), 4.58 – 4.49 (m, 2H), 2.38 (s, 3H), 2.25 (qt, *J* = 16.9, 7.1 Hz, 2H), 1.81 (ddd, *J* = 13.4, 11.7, 5.0 Hz, 1H), 1.64 – 1.51 (m, 6H), 1.25 (s, 3H), 1.23 – 1.05 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 138.5, 137.8, 137.0, 129.8, 129.1, 128.2, 127.7, 127.3, 127.0, 119.5, 118.8, 51.2, 44.1, 35.1, 25.4, 23.8, 22.3, 21.3, 17.0, 8.9. HRMS (ESI-TOF) Calcd for $C_{25}H_{29}N_2O^+$ ([M+H]$^+$) 373.2274. Found 373.2277.

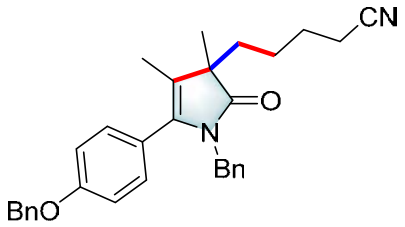


3d2, 5-(1-benzyl-5-(4-ethylphenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 71% yield (83 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 5H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.89 – 6.87 (m, 2H), 4.58 – 4.50 (m, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.25 (qt, *J* = 16.9, 7.1 Hz, 2H), 1.81 (ddd, *J* = 13.3, 11.5, 5.1 Hz, 1H), 1.67 – 1.48 (m, 6H), 1.30 – 1.24 (m, 6H), 1.24 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 144.8, 137.8, 137.0, 129.8, 128.2, 127.8, 127.7, 127.5, 127.0, 119.5, 118.8, 51.2, 44.1, 35.1, 28.7, 25.4, 23.8, 22.3, 17.0, 15.5, 8.9. HRMS (ESI-TOF) Calcd for $C_{26}H_{31}N_2O^+$ ([M+H]$^+$) 387.2431. Found 387.2449.

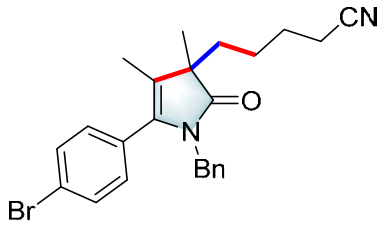


3d3, 5-(1-benzyl-5-(4-methoxyphenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 76% yield (89 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 3H), 7.02 – 6.98 (m, 2H), 6.90 (dd, *J* = 6.9, 2.7 Hz, 2H), 6.88 – 6.84 (m, 2H), 4.57 – 4.48 (m, 2H), 3.83 (s, 3H), 2.25 (qt, *J* = 16.9, 7.1 Hz, 2H), 1.81 (ddd, *J* = 13.3, 11.4, 5.1 Hz, 1H), 1.64 – 1.52 (m, 6H), 1.29 – 1.07 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 159.7, 137.9, 136.7, 131.2, 128.2, 127.6, 127.0, 122.5,

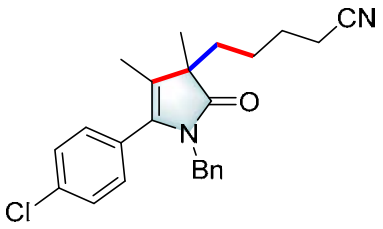
119.5, 118.8, 113.8, 55.3, 51.2, 44.1, 35.1, 25.4, 23.8, 22.3, 17.0, 8.9. HRMS (ESI-TOF) Calcd for $C_{25}H_{29}N_2O_2^+$ ([M+H]$^+$) 389.2224. Found 389.2228.



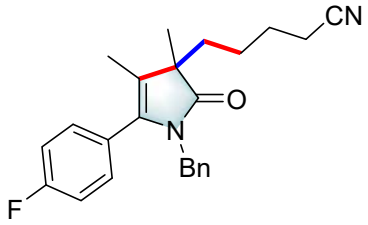
3d4, 5-(1-benzyl-5-(4-(benzyloxy)phenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 63% yield (87 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 5H), 7.17 – 7.14 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.88 (dd, *J* = 6.7, 3.0 Hz, 2H), 5.08 (s, 2H), 4.57 – 4.48 (m, 2H), 2.25 (qt, *J* = 16.9, 7.1 Hz, 2H), 1.81 (ddd, *J* = 13.2, 11.4, 5.1 Hz, 1H), 1.66 – 1.52 (m, 6H), 1.25 (s, 3H), 1.23 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 158.9, 137.9, 136.7, 136.6, 131.2, 128.6, 128.2, 128.1, 127.6, 127.5, 127.0, 122.8, 119.5, 118.8, 114.7, 70.0, 51.2, 44.1, 35.1, 25.4, 23.8, 22.3, 17.0, 8.9. HRMS (ESI-TOF) Calcd for $C_{31}H_{33}N_2O_2^+$ ([M+H]$^+$) 465.2537. Found 465.2539.



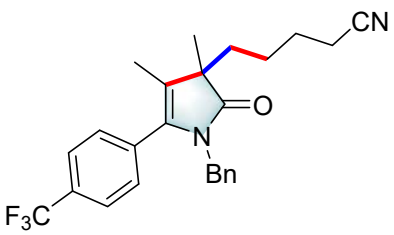
3d5, 5-(1-benzyl-5-(4-bromophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 60% yield (79 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.19 – 7.15 (m, 3H), 6.95 – 6.92 (m, 2H), 6.89 – 6.86 (m, 2H), 4.58 – 4.48 (m, 2H), 2.27 (qt, *J* = 16.9, 7.0 Hz, 2H), 1.83 (ddd, *J* = 13.3, 11.4, 5.3 Hz, 1H), 1.67 – 1.51 (m, 6H), 1.26 (s, 3H), 1.25 – 1.10 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.2, 137.5, 135.9, 131.6, 131.4, 129.3, 128.3, 127.5, 127.2, 122.8, 119.9, 119.5, 51.3, 44.2, 35.1, 25.4, 23.8, 22.3, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}BrN_2O^+$ ([M+H]$^+$) 437.1223. Found 437.1222.



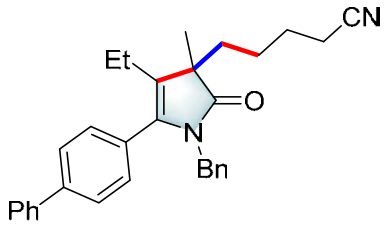
3d6, 5-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 75% yield (88 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.19 – 7.15 (m, 3H), 7.01 – 6.98 (m, 2H), 6.89 – 6.86 (m, 2H), 4.58 – 4.48 (m, 2H), 2.27 (qt, *J* = 17.0, 7.1 Hz, 2H), 1.83 (ddd, *J* = 13.4, 11.4, 5.3 Hz, 1H), 1.65 – 1.54 (m, 6H), 1.26 (s, 3H), 1.25 – 1.10 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.2, 137.5, 135.9, 134.6, 131.2, 128.8, 128.6, 128.3, 127.5, 127.2, 119.9, 119.5, 51.3, 44.2, 35.1, 25.4, 23.8, 22.3, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}ClN_2O^+$ ([M+H]$^+$) 393.1728. Found 393.1728.



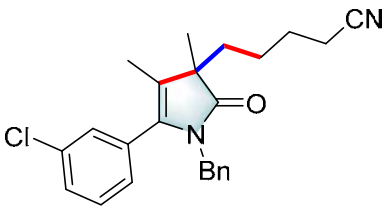
3d7, 5-(1-benzyl-5-(4-fluorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 71% yield (81 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 3H), 7.05 – 6.99 (m, 4H), 6.89 – 6.84 (m, 2H), 4.58 – 4.48 (m, 2H), 2.28 (qt, *J* = 16.9, 7.1 Hz, 2H), 1.84 (ddd, *J* = 13.3, 11.4, 5.2 Hz, 1H), 1.64 – 1.54 (m, 6H), 1.31 – 1.10 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.2, 162.7 (d, *J* = 248.7 Hz), 137.6, 136.0, 131.8 (d, *J* = 8.2 Hz), 128.3, 127.5, 127.2, 126.3 (d, *J* = 3.5 Hz), 119.6, 119.5, 115.5 (d, *J* = 21.6 Hz), 51.2, 44.1, 35.1, 25.4, 23.8, 22.3, 17.0, 8.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.24 (p, *J* = 7.1 Hz, 1F). HRMS (ESI-TOF) Calcd for $C_{24}H_{26}FN_2O^+$ ([M+H]$^+$) 377.2024. Found 377.2020.



3d8, 5-(1-benzyl-3,4-dimethyl-2-oxo-5-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 74% yield (95 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.15 (m, 5H), 6.85 – 6.82 (m, 2H), 4.61 – 4.50 (m, 2H), 2.37 – 2.21 (m, 2H), 1.86 (ddd, *J* = 13.3, 11.2, 5.4 Hz, 1H), 1.67 – 1.55 (m, 6H), 1.30 – 1.15 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.2, 137.3, 135.7, 134.1 (d, *J* = 1.1 Hz), 130.6 (d, *J* = 32.8 Hz), 130.2, 128.4, 127.5, 127.3, 125.3 (q, *J* = 3.7 Hz), 123.9 (d, *J* = 272.3 Hz), 120.6, 119.4, 51.4, 44.3, 35.1, 25.3, 23.8, 22.3, 17.0, 8.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{25}H_{26}F_3N_2O^+$ ($[M+H]^+$) 427.1992. Found 427.2007.

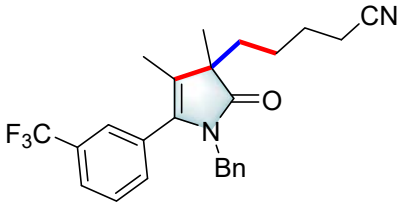


3d9, 5-(5-([1,1'-biphenyl]-4-yl)-1-benzyl-4-ethyl-3-methyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 50% yield (67 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.58 – 7.55 (m, 2H), 7.49 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 7.18 – 7.13 (m, 5H), 6.91 – 6.89 (m, 2H), 4.54 (s, 2H), 2.35 – 1.99 (m, 4H), 1.86 (ddd, *J* = 13.3, 11.7, 5.0 Hz, 1H), 1.71 – 1.54 (m, 3H), 1.36 – 1.24 (m, 4H), 1.21 – 1.10 (m, 1H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.0, 141.4, 140.3, 137.7, 130.3, 129.6, 128.9, 128.2, 127.71, 127.69, 127.1, 127.05, 126.95, 124.8, 119.5, 51.8, 44.1, 35.9, 25.5, 23.9, 23.2, 17.7, 17.1, 15.1. HRMS (ESI-TOF) Calcd for $C_{31}H_{33}N_2O^+$ ($[M+H]^+$) 449.2587. Found 449.2587.

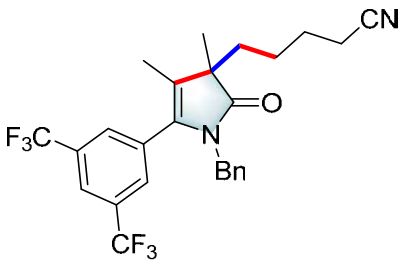


3d10, 5-(1-benzyl-5-(3-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 63% yield (74 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (ddd, *J* = 8.1, 2.1, 1.2 Hz, 1H), 7.27 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.17 (ddd, *J* = 6.6,

2.9, 2.9 Hz, 3H), 7.01 (dd, *J* = 1.8, 1.8 Hz, 1H), 6.95 (ddd, *J* = 7.5, 1.4, 1.4 Hz, 1H), 6.86 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.59 – 4.49 (m, 2H), 2.36 – 2.21 (m, 2H), 1.84 (ddd, *J* = 13.3, 11.3, 5.4 Hz, 1H), 1.67 – 1.54 (m, 6H), 1.27 (s, 3H), 1.25 – 1.10 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.2, 137.5, 135.7, 134.3, 132.1, 129.9, 129.6, 128.8, 128.3, 128.1, 127.6, 127.3, 120.1, 119.5, 51.3, 44.3, 35.0, 25.4, 23.8, 22.3, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}ClN_2O^+$ ($[M+H]^+$) 393.1728. Found 393.1724.

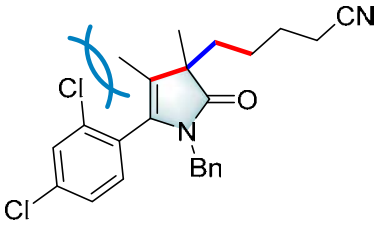


3d11, 5-(1-benzyl-3,4-dimethyl-2-oxo-5-(3-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 62% yield (79 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.46 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.17 – 7.13 (m, 3H), 6.82 – 6.79 (m, 2H), 4.58 (d, *J* = 15.3 Hz, 1H), 4.49 (d, *J* = 15.3 Hz, 1H), 2.38 – 2.24 (m, 2H), 1.86 (ddd, *J* = 13.3, 11.0, 5.7 Hz, 1H), 1.71 – 1.55 (m, 5H), 1.33 – 1.19 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.1, 137.3, 135.6, 133.2 (d, *J* = 0.7 Hz), 131.3, 130.9 (q, *J* = 32.6 Hz), 128.9, 128.4, 127.4, 127.3, 126.6 (q, *J* = 3.7 Hz), 125.3 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.6 Hz), 120.5, 119.4, 51.4, 44.3, 35.0, 25.4, 23.8, 22.3, 17.0, 8.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{25}H_{26}F_3N_2O^+$ ($[M+H]^+$) 427.1992. Found 427.1993.

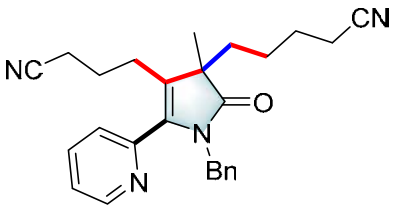


3d12, 5-(1-benzyl-5-(3,5-bis(trifluoromethyl)phenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 59% yield (88 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.41 (s, 2H), 7.17 – 7.14 (m, 3H), 6.77 (dd, *J* = 6.7, 2.8 Hz, 2H), 4.60 (d, *J* = 15.5 Hz, 1H), 4.48 (d, *J* = 15.5 Hz, 1H), 2.35 (td, *J* = 7.1, 4.0 Hz,

2H), 1.90 (dt, *J* = 13.4, 8.3 Hz, 1H), 1.77 – 1.55 (m, 6H), 1.37 – 1.25 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.9, 136.8, 134.4, 132.7, 131.9 (q, *J* = 33.6 Hz), 129.9 (q, *J* = 2.6 Hz), 128.6, 127.6, 127.2, 122.9 (q, *J* = 272.9 Hz), 122.3 (dq, *J* = 7.6, 3.7 Hz), 122.0, 119.4, 51.6, 44.5, 34.9, 25.4, 23.8, 22.4, 17.0, 8.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94 (s, 6F). HRMS (ESI-TOF) Calcd for $C_{26}H_{25}F_6N_2O^+$ ($[M+H]^+$) 495.1866. Found 495.1864.

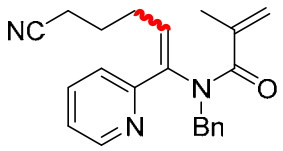


3d13, 5-(1-benzyl-5-(2,4-dichlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, 1:1 mixture of diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 70% yield (90 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 4.8, 2.1 Hz, 2H), 7.17 – 7.09 (m, 8H), 6.87 – 6.77 (m, 6H), 4.78 (dd, *J* = 15.3, 7.2 Hz, 2H), 4.17 (t, *J* = 15.4 Hz, 2H), 2.37 – 2.20 (m, 4H), 1.91 – 1.83 (m, 2H), 1.71 – 1.56 (m, 6H), 1.505 (s, 3H), 1.501 (s, 3H), 1.41 – 1.17 (m, 10H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.7, 181.6, 137.40, 137.36, 135.72, 135.68, 135.66, 135.64, 133.3, 133.12, 133.08, 133.0, 129.52, 129.45, 128.29, 128.26, 128.07, 128.06, 127.7, 127.4, 127.32, 127.27, 127.0, 126.9, 121.6, 121.4, 119.5, 119.4, 51.64, 51.56, 44.3, 44.1, 35.2, 34.8, 25.5, 25.3, 24.2, 24.0, 22.4, 22.3, 17.07, 17.05, 8.84, 8.81. HRMS (ESI-TOF) Calcd for $C_{24}H_{25}Cl_2N_2O^+$ ($[M+H]^+$) 427.1338. Found 427.1340.

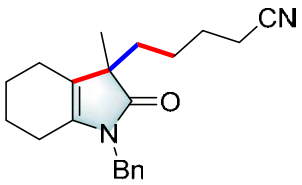


3e, 5-(1-benzyl-4-(3-cyanopropyl)-3-methyl-2-oxo-5-(pyridin-2-yl)-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, 1:4 mixture of rotamers due to the restricted rotation of the pyridyl C–C bond, isolated by flash column chromatography (petroleum ether/ethyl acetate = 14:1) in 45% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.72 (stack, 1H major and 1H minor), 7.69 – 7.60 (stack, 1H major and 1H minor), 7.34 – 7.28 (stack, 1H major and 1H minor), 7.24 – 7.06 (stack, 4H major and 4H minor),

6.82 – 6.76 (stack, 2H major and 2H minor), 4.86 (d, J = 15.0 Hz, 1H minor), 4.82 (d, J = 15.2 Hz, 1H major), 4.68 (d, J = 15.1 Hz, 1H major), 4.66 (d, J = 15.0 Hz, 1H minor), 2.51 – 1.85 (stack, 7H major and 7H minor), 1.72 – 1.49 (stack, 5H major and 5H minor), 1.36 – 1.15 (stack, 5H major and 5H minor). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.3 (major), 180.0 (minor), 149.92 (minor), 149.87 (major), 149.8 (major), 149.4 (minor), 139.2 (minor), 138.5 (major), 137.5 (major), 137.2 (minor), 136.9 (minor), 136.7 (major), 128.4 (minor), 128.2 (major), 127.6 (major), 127.5 (minor), 127.4 (minor), 127.2 (major), 125.23 (minor), 125.20 (major), 123.8 (minor), 123.5 (major), 122.3 (major), 121.0 (minor), 119.4 (major), 119.2 (minor), 119.0 (major), 118.8 (minor), 51.9 (major), 51.1 (minor), 44.1 (minor), 44.0 (major), 35.7 (major), 31.6 (minor), 25.63 (minor), 25.57 (major), 25.4, 23.8, 23.5 (minor), 23.4, 22.9, 22.2 (minor), 17.05 (major), 17.02 (minor), 16.98 (major), 12.8 (minor). HRMS (ESI-TOF) Calcd for $C_{26}H_{29}N_4O^+$ ($[M+H]^+$) 413.2336. Found 413.2338.

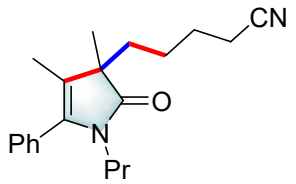


3e', *N*-benzyl-*N*-(5-cyano-1-(pyridin-2-yl)pent-1-en-1-yl)methacrylamide, isolated by flash column chromatography (petroleum ether/ethyl acetate = 14:1) in 28% yield (29 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, J = 5.4, 1.9 Hz, 1H), 7.70 (ddd, J = 7.8, 7.8, 1.9 Hz, 1H), 7.32 – 7.22 (m, 7H), 5.34 – 5.27 (m, 2H), 5.09 (s, 1H), 4.70 (s, 2H), 2.52 (q, J = 7.5 Hz, 2H), 2.17 (t, J = 7.2 Hz, 2H), 1.83 (s, 3H), 1.66 (p, J = 7.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.5, 154.1, 149.6, 141.2, 139.6 (br), 137.3, 136.4, 131.7, 129.0, 128.4, 127.5, 123.2, 122.8, 119.5, 117.6 (br), 50.6 (br), 27.1, 25.0, 20.4, 16.4. HRMS (ESI-TOF) Calcd for $C_{22}H_{24}N_3O^+$ ($[M+H]^+$) 346.1914. Found 346.1917.

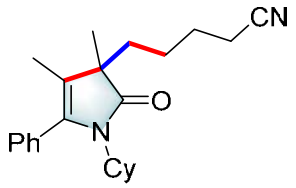


3f, 5-(1-benzyl-3-methyl-2-oxo-2,3,4,5,6,7-hexahydro-1*H*-indol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 65% yield (63 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 5H), 4.63 (s, 2H), 2.34 – 2.19 (m, 2H), 2.17 – 1.87 (m, 4H), 1.77 – 1.41 (m, 8H), 1.24 –

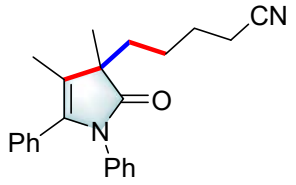
1.07 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.6, 138.1, 135.4, 128.6, 127.3, 127.1, 119.6, 118.9, 50.2, 43.1, 34.9, 25.4, 24.0, 22.54, 22.46, 22.2, 21.4, 19.8, 17.0. HRMS (ESI-TOF) Calcd for $C_{21}H_{27}N_2O^+$ ($[M+H]^+$) 323.2118. Found 323.2122.



3g1, 5-(3,4-dimethyl-2-oxo-5-phenyl-1-propyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 62% yield (58 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.27 – 7.24 (m, 2H), 3.39 – 3.26 (m, 2H), 2.40 – 2.25 (m, 2H), 1.83 – 1.76 (m, 1H), 1.73 – 1.51 (m, 6H), 1.34 – 1.14 (m, 7H), 0.68 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.2, 137.0, 130.7, 129.6, 128.54, 128.52, 119.5, 118.9, 51.2, 42.0, 34.9, 25.4, 23.7, 22.3, 22.0, 17.0, 11.1, 8.8. HRMS (ESI-TOF) Calcd for $C_{20}H_{27}N_2O^+$ ($[M+H]^+$) 311.2118. Found 311.2120.

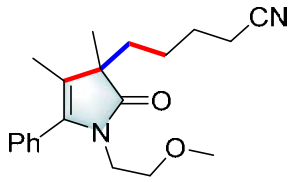


3g2, 5-(1-cyclohexyl-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1) in 59% yield (62 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.24 – 7.21 (m, 2H), 3.19 (tt, *J* = 12.1, 3.8 Hz, 1H), 2.40 – 2.26 (m, 2H), 2.12 (qdd, *J* = 11.6, 8.7, 3.2 Hz, 2H), 1.79 – 1.48 (m, 12H), 1.34 – 1.15 (m, 5H), 1.13 – 0.95 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.5, 138.0, 131.3, 129.9, 128.55, 128.52, 119.5, 118.7, 54.2, 51.2, 35.1, 29.9, 29.8, 26.08, 26.06, 25.4, 25.1, 23.6, 22.2, 17.0, 9.1. HRMS (ESI-TOF) Calcd for $C_{23}H_{31}N_2O^+$ ($[M+H]^+$) 351.2431. Found 351.2418.

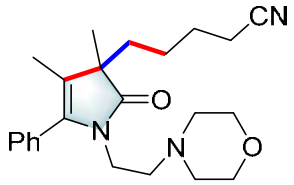


3g3, 5-(3,4-dimethyl-2-oxo-1,5-diphenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile,

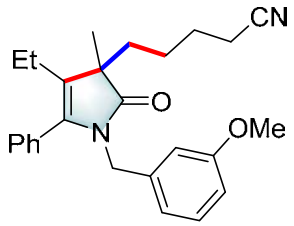
isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1) in 44% yield (45 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 5H), 7.14 – 7.06 (m, 3H), 6.98 – 6.94 (m, 2H), 2.40 – 2.25 (m, 2H), 1.88 (ddd, *J* = 13.3, 11.5, 5.1 Hz, 1H), 1.80 (s, 3H), 1.73 – 1.59 (m, 3H), 1.48 – 1.27 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.5, 137.0, 135.6, 130.3, 129.4, 128.5, 128.1, 128.0, 126.6, 126.4, 119.9, 119.5, 51.8, 35.5, 25.4, 23.7, 22.3, 17.0, 9.3. HRMS (ESI-TOF) Calcd for $C_{23}H_{25}N_2O^+$ ([M+H]$^+$) 345.1961. Found 345.1962.



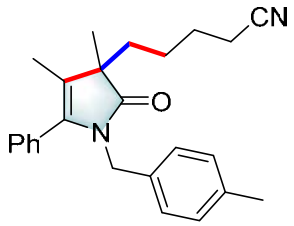
3h, 5-(1-(2-methoxyethyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1) in 42% yield (42 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 3H), 7.30 – 7.27 (m, 2H), 3.63 (dt, *J* = 14.2, 6.1 Hz, 1H), 3.49 (dt, *J* = 14.2, 5.9 Hz, 1H), 3.24 (qt, *J* = 10.1, 6.0 Hz, 2H), 3.16 (s, 3H), 2.40 – 2.25 (m, 2H), 1.79 (ddd, *J* = 13.3, 11.1, 5.5 Hz, 1H), 1.72 – 1.52 (m, 6H), 1.32 – 1.17 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.6, 136.9, 130.5, 129.8, 128.6, 128.5, 119.5, 118.8, 69.6, 58.4, 51.2, 39.7, 35.0, 25.4, 23.6, 22.2, 17.0, 8.9. HRMS (ESI-TOF) Calcd for $C_{20}H_{27}N_2O_2^+$ ([M+H]$^+$) 327.2067. Found 327.2069.



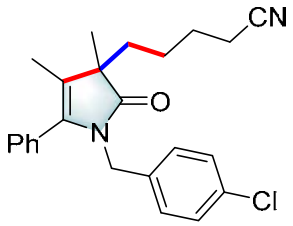
3i, 5-(3,4-dimethyl-1-(2-morpholinoethyl)-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 52% yield (60 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.29 – 7.27 (m, 2H), 3.57 – 3.45 (m, 6H), 2.40 – 2.16 (m, 8H), 1.78 (ddd, *J* = 13.3, 10.2, 6.4 Hz, 1H), 1.72 – 1.52 (m, 6H), 1.33 – 1.20 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.5, 136.7, 130.6, 129.6, 128.64, 128.59, 119.5, 119.0, 66.9, 56.7, 53.4, 51.2, 37.2, 34.9, 25.4, 23.6, 22.4, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{23}H_{32}N_3O_2^+$ ([M+H]$^+$) 382.2489. Found 382.2501.



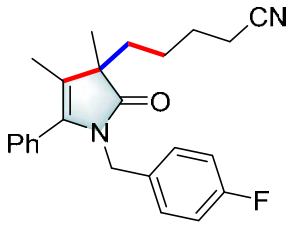
3j1, 5-(4-ethyl-1-(3-methoxybenzyl)-3-methyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 63% yield (76 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 3H), 7.12 – 7.08 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.70 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 6.47 (ddd, *J* = 7.6, 1.7, 0.9 Hz, 1H), 6.38 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.47 (s, 2H), 3.68 (s, 3H), 2.35 – 2.18 (m, 2H), 2.04 (ddt, *J* = 32.9, 14.7, 7.5 Hz, 2H), 1.85 (ddd, *J* = 13.3, 11.7, 5.0 Hz, 1H), 1.69 – 1.52 (m, 3H), 1.35 – 1.23 (s, 4H), 1.22 – 1.10 (m, 1H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.0, 159.4, 139.3, 137.9, 130.7, 130.0, 129.2, 128.7, 128.3, 124.5, 120.0, 119.6, 113.0, 112.9, 55.1, 51.8, 44.0, 35.8, 25.5, 23.9, 23.2, 17.6, 17.0, 15.0. HRMS (ESI-TOF) Calcd for $C_{26}H_{31}N_2O_2^+$ ([M+H]$^+$) 403.2380. Found 403.2383.



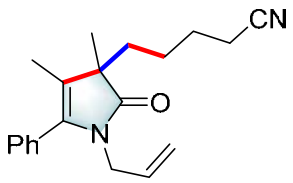
3j2, 5-(3,4-dimethyl-1-(4-methylbenzyl)-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 61% yield (66 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.10 – 7.08 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 2.34 – 2.17 (m, 5H), 1.82 (ddd, *J* = 13.3, 11.5, 5.1 Hz, 1H), 1.65 – 1.53 (m, 6H), 1.29 – 1.08 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 137.0, 136.6, 134.7, 130.4, 129.9, 128.9, 128.5, 128.3, 127.6, 119.5, 119.0, 51.2, 43.9, 35.1, 25.4, 23.8, 22.3, 21.1, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{25}H_{29}N_2O^+$ ([M+H]$^+$) 373.2274. Found 373.2275.



3j3, 5-(1-(4-chlorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 75% yield (89 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.14 – 7.11 (m, 2H), 7.10 – 7.07 (m, 2H), 6.80 – 6.77 (m, 2H), 4.56 – 4.46 (m, 2H), 2.36 – 2.21 (m, 2H), 1.82 (ddd, *J* = 13.3, 11.6, 5.0 Hz, 1H), 1.67 – 1.54 (m, 6H), 1.28 – 1.07 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 136.7, 136.2, 132.9, 130.2, 129.8, 129.1, 128.7, 128.5, 128.4, 119.5, 119.3, 51.2, 43.5, 35.1, 25.4, 23.8, 22.3, 17.0, 8.8. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}ClN_2O^+$ ([M+H]$^+$) 393.1728. Found 393.1726.

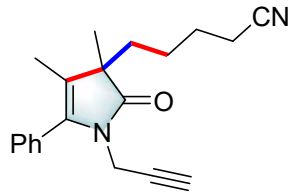


3j4, 5-(1-(4-fluorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 61% yield (69 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3H), 7.10 – 7.06 (m, 2H), 6.86 – 6.78 (m, 4H), 4.56 – 4.47 (m, 2H), 2.36 – 2.19 (m, 2H), 1.83 (ddd, *J* = 13.3, 11.6, 5.1 Hz, 1H), 1.66 – 1.54 (m, 6H), 1.25 (s, 3H), 1.24 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.4, 161.9 (d, *J* = 245.4 Hz), 136.7, 133.5 (d, *J* = 3.3 Hz), 130.3, 129.8, 129.4 (d, *J* = 8.1 Hz), 128.7, 128.4, 119.5, 119.3, 115.1 (d, *J* = 21.3 Hz), 51.2, 43.4, 35.1, 25.4, 23.8, 22.3, 17.0, 8.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.40 (p, *J* = 7.1, 6.4 Hz, 1F). HRMS (ESI-TOF) Calcd for $C_{24}H_{26}FN_2O^+$ ([M+H]$^+$) 377.2024. Found 377.2025.

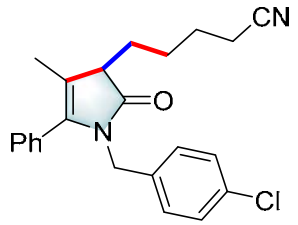


3k, 5-(1-allyl-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile,

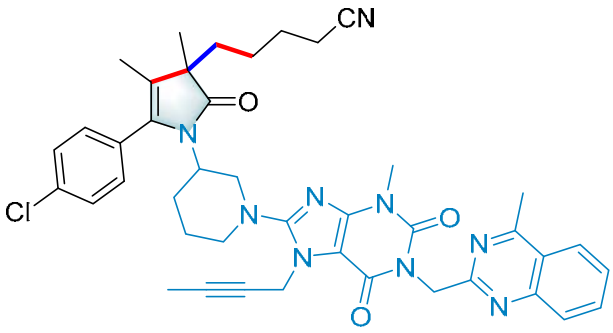
isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 36% yield (38 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.27 – 7.25 (m, 2H), 5.60 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 4.99 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.87 (dq, *J* = 17.1, 1.6 Hz, 1H), 3.96 (dt, *J* = 5.3, 1.6 Hz, 2H), 2.40 – 2.26 (m, 2H), 1.81 (ddd, *J* = 13.3, 11.5, 5.2 Hz, 1H), 1.70 – 1.54 (m, 6H), 1.35 – 1.16 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.1, 137.0, 133.2, 130.3, 129.8, 128.6, 128.4, 119.5, 118.9, 116.5, 51.2, 42.7, 35.0, 25.4, 23.8, 22.3, 17.0, 8.9. HRMS (ESI-TOF) Calcd for $C_{20}H_{25}N_2O^+$ ([M+H]$^+$) 309.1961. Found 309.1950.



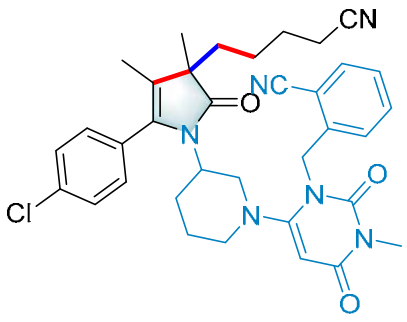
3l, 5-(3,4-dimethyl-2-oxo-5-phenyl-1-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 35% yield (32 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 5H), 4.19 (dd, *J* = 17.6, 2.5 Hz, 1H), 4.00 (dd, *J* = 17.5, 2.5 Hz, 1H), 2.39 – 2.25 (m, 2H), 2.09 (t, *J* = 2.4 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.73 – 1.55 (m, 6H), 1.36 – 1.18 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.1, 136.2, 129.78, 129.77, 128.8, 128.6, 119.5, 119.4, 78.9, 71.0, 51.2, 35.3, 30.3, 25.4, 23.7, 21.9, 17.0, 8.9. HRMS (ESI-TOF) Calcd for $C_{20}H_{23}N_2O^+$ ([M+H]$^+$) 307.1805. Found 307.1803.



3m, 5-(1-(4-chlorobenzyl)-4-methyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl) pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 53% yield (62 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3H), 7.27 – 7.23 (m, 2H), 7.04 – 6.98 (m, 4H), 5.07 (d, *J* = 15.0 Hz, 1H), 4.50 (s, 1H), 3.58 (d, *J* = 15.0 Hz, 1H), 2.45 – 2.37 (m, 4H), 1.75 – 1.72 (m, 4H), 1.69 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.9, 151.6, 136.1, 135.2, 133.2, 131.0, 129.7, 129.2, 128.8, 127.6 (br), 119.7, 67.1, 43.2, 27.6, 25.2, 22.9, 17.0, 12.2. HRMS (ESI-TOF) Calcd for $C_{23}H_{24}ClN_2O^+$ ([M+H]$^+$) 379.1572. Found 379.1585.

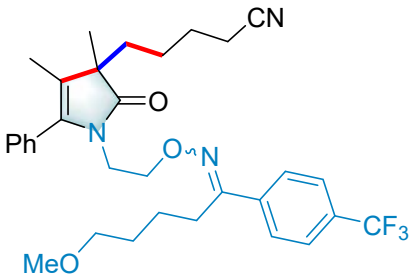


3n, 5-(1-(1-(7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-8-yl)piperidin-3-yl)-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)pentanenitrile, 1:1 mixture of diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1) in 51% yield (116 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 5.55 (s, 2H), 4.84 – 4.67 (m, 2H), 3.89 (dt, *J* = 22.7, 11.7 Hz, 1H), 3.72 – 3.51 (m, 3H), 3.47 (d, *J* = 9.0 Hz, 3H), 3.06 – 2.95 (m, 1H), 2.89 (s, 3H), 2.60 – 2.44 (m, 1H), 2.42 – 2.26 (m, 2H), 1.82 – 1.63 (m, 8H), 1.58 – 1.49 (m, 5H), 1.33 – 1.23 (m, 2H), 1.22 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.83, 182.80, 168.4, 161.2, 155.6, 155.5, 154.4, 151.8, 150.0, 147.87, 147.86, 136.5, 136.4, 135.1, 133.2, 131.10, 131.07, 129.23, 129.19, 129.03, 128.95, 128.9, 126.6, 124.8, 123.2, 120.2, 120.0, 119.4, 119.3, 104.52, 104.49, 81.3, 81.2, 73.20, 73.18, 51.53, 51.52, 51.3, 51.2, 51.0, 50.8, 49.9, 49.8, 46.3, 35.72, 35.69, 35.0, 34.8, 29.70, 29.68, 29.66, 26.99, 26.98, 25.3, 25.2, 24.84, 24.83, 23.5, 23.4, 22.27, 22.25, 21.8, 17.1, 16.9, 9.24, 9.22, 3.7, 3.6. HRMS (ESI-TOF) Calcd for $C_{42}H_{45}ClN_9O_3^+$ ([M+H]$^+$) 758.3328. Found 758.3320.

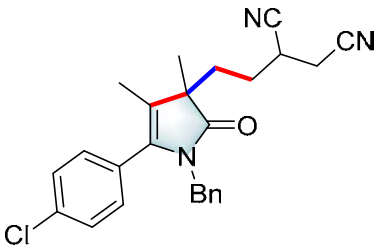


3o, 2-((6-(3-(5-(4-chlorophenyl)-3-(4-cyanobutyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-1-yl)piperidin-1-yl)-3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)methyl)benzonitrile, 1:1 mixture of diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1) in 64% yield (119 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (ddd, *J* = 7.7, 2.4, 1.4 Hz, 1H), 7.50

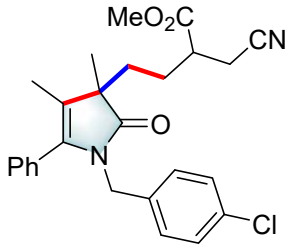
(dddd, J = 7.7, 7.7, 1.6, 1.6 Hz, 1H), 7.42 (dd, J = 8.6, 3.5 Hz, 2H), 7.37 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.11 (dd, J = 7.9, 6.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 1H), 5.37 (s, 1H), 5.13 – 5.00 (m, 2H), 3.60 – 3.44 (m, 1H), 3.34 – 3.23 (m, 4H), 3.03 (d, J = 11.9 Hz, 1H), 2.88 (td, J = 12.2, 3.6 Hz, 1H), 2.54 (td, J = 12.5, 4.2 Hz, 1H), 2.48 – 2.28 (m, 3H), 1.78 – 1.41 (m, 10H), 1.29 – 1.10 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.8, 182.7, 163.0, 162.9, 159.14, 159.10, 152.41, 152.38, 140.43, 140.42, 135.95, 135.89, 135.1, 133.2, 133.1, 133.04, 133.00, 131.0, 129.3, 128.63, 128.56, 128.0, 127.9, 127.0, 126.9, 120.4, 120.3, 119.5, 119.4, 117.05, 117.01, 110.8, 90.6, 90.5, 52.2, 52.1, 51.74, 51.72, 51.49, 51.47, 51.14, 51.08, 46.1, 46.0, 34.9, 34.8, 27.92, 27.90, 26.44, 26.39, 25.2, 24.4, 23.5, 23.4, 22.2, 22.1, 17.01, 16.97, 9.2. HRMS (ESI-TOF) Calcd for $C_{35}H_{38}ClN_6O_3^+$ ($[M+H]^+$) 625.2688. Found 625.2681.



3p, 5-(1-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1H-pyrrol-3-yl)pentanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1) in 81% yield (139 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.36 (dp, J = 6.1, 2.0 Hz, 3H), 7.17 – 7.12 (m, 2H), 3.99 – 3.86 (m, 2H), 3.72 (ddd, J = 14.4, 6.6, 5.2 Hz, 1H), 3.54 (dt, J = 14.4, 5.4 Hz, 1H), 3.32 (t, J = 6.4 Hz, 2H), 3.29 (s, 3H), 2.46 – 2.43 (m, 2H), 2.25 (qt, J = 16.9, 7.1 Hz, 2H), 1.74 (ddd, J = 13.3, 11.5, 5.1 Hz, 1H), 1.63 – 1.38 (m, 10H), 1.28 – 1.06 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.3, 156.3, 137.5 (d, J = 1.2 Hz), 136.8, 130.4 (q, J = 32.5 Hz), 130.2, 129.7, 128.6, 128.5, 128.3, 125.0 (q, J = 3.7 Hz), 123.91 (d, J = 272.1 Hz), 119.5, 118.8, 72.3, 71.1, 58.5, 51.0, 39.9, 35.1, 34.9, 29.0, 25.3, 23.5, 23.1, 21.9, 16.9, 8.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.79 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{32}H_{39}F_3N_3O_3^+$ ($[M+H]^+$) 570.2938. Found 570.2945.

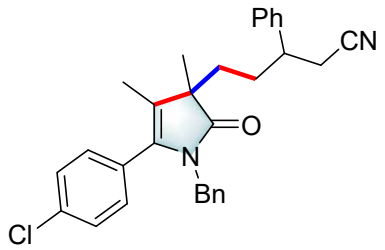


3q, 2-(2-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)ethyl)succinonitrile, 4:9 mixture of diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 35:1) in 65% yield (81 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (ddd, *J* = 9.0, 2.5, 2.5 Hz, 2H), 7.21 – 7.17 (m, 3H), 7.03 (dddd, *J* = 9.0, 9.0, 2.3, 2.3 Hz, 2H), 6.89 – 6.85 (m, 2H), 4.54 (dd, *J* = 15.6, 15.6 Hz, 2H), 2.87 – 2.77 (m, 1H), 2.74 – 2.51 (m, 2H), 2.04 – 1.81 (m, 1H), 1.71 – 1.64 (m, 2H), 1.62 – 1.33 (m, 4H), 1.30 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.7 (minor), 181.5 (major), 137.23 (minor), 137.21 (major), 136.53 (minor), 136.49 (major), 134.95 (major), 134.94 (minor), 131.14 (minor), 131.09 (major), 128.84 (minor), 128.83 (major), 128.49 (major), 128.46 (minor), 128.4, 127.7 (minor), 127.6 (major), 127.5 (major), 127.4 (minor), 119.3 (major), 119.2 (minor), 118.6 (minor), 118.5 (major), 115.4 (major), 115.2 (minor), 50.8 (minor), 50.6 (major), 44.3 (minor), 44.2 (major), 32.9 (minor), 32.0 (major), 28.5 (minor), 28.1 (major), 27.1 (minor), 26.3 (major), 22.1 (minor), 21.9 (major), 21.2 (minor), 20.5 (major), 8.83 (major), 8.77 (minor). HRMS (ESI-TOF) Calcd for $C_{25}H_{25}ClN_3O^+$ ($[M+H]^+$) 418.1681. Found 418.1678.

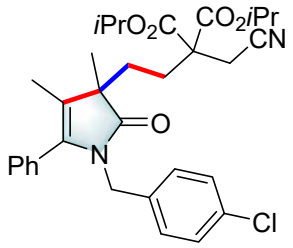


3r, methyl 4-(1-(4-chlorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)-2-(cyanomethyl)butanoate, 3:7 mixture of diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1) in 61% yield (83 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (stack, 3H major and 3H minor), 7.14 – 7.07 (stack, 4H major and 4H minor), 6.80 – 6.76 (stack, 2H major and 2H minor), 4.55 – 4.46 (stack, 2H major and 2H minor), 3.76 (s, 3H minor), 3.75 (s, 3H major), 2.72 – 2.48 (stack, 3H major and 3H minor), 1.87 – 1.76 (stack, 1H major

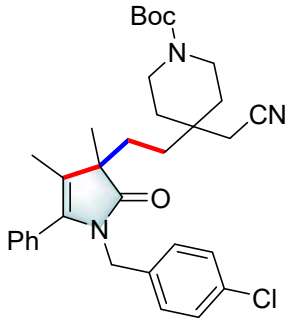
and 1H minor), 1.63 – 1.27 (stack, 6H major and 6H minor), 1.26 (s, 3H major), 1.25 (s, 3H minor). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.93 (minor), 181.88 (major), 172.7 (minor), 172.5 (major), 137.0 (major), 136.9 (minor), 136.20 (minor), 136.18 (major), 133.0 (major and minor), 130.1 (minor), 130.0 (major), 129.8 (major and minor), 129.2 (major), 129.1 (minor), 128.80 (major), 128.77 (minor), 128.5, 128.48 (minor), 128.39 (major), 118.9 (minor), 118.8 (major), 117.5 (major), 117.3 (minor), 52.47 (major), 52.45 (minor), 51.0 (minor), 50.9 (major), 43.51 (minor), 43.49 (major), 41.2 (minor), 41.1 (major), 32.7 (minor), 32.4 (major), 26.3 (minor), 26.0 (major), 22.19 (major), 22.16 (minor), 19.7 (minor), 18.8 (major), 8.71 (major), 8.67 (minor). HRMS (ESI-TOF) Calcd for $C_{26}H_{28}ClN_2O_3^+$ ($[M+H]^+$) 451.1783. Found 451.1784.



3s, 5-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)-3-phenylpentanenitrile, separable 1:1 diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 35:1). *Isomer 1*: colorless oil, 40% yield (57 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 7.20 – 7.13 (m, 5H), 7.03 (d, J = 7.3 Hz, 2H), 6.89 – 6.87 (m, 2H), 4.57 (d, J = 15.3 Hz, 1H), 4.51 (d, J = 15.3 Hz, 1H), 2.84 (p, J = 7.0 Hz, 1H), 2.57 (dd, J = 16.7, 6.5 Hz, 1H), 2.45 (dd, J = 16.8, 6.9 Hz, 1H), 1.75 – 1.40 (m, 7H), 1.20 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.0, 141.2, 137.5, 136.0, 134.6, 131.2, 129.0, 128.8, 128.7, 128.3, 127.64, 127.56, 127.2, 127.1, 119.8, 118.4, 51.2, 44.2, 42.0, 33.5, 29.2, 25.1, 22.1, 8.8. HRMS (ESI-TOF) Calcd for $C_{30}H_{30}ClN_2O^+$ ($[M+H]^+$) 469.2041. Found 469.2059. *Isomer 2*: colorless oil, 38% yield (53 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 7.20 – 7.15 (m, 5H), 7.02 – 6.99 (m, 2H), 6.90 – 6.87 (m, 2H), 4.59 (d, J = 15.3 Hz, 1H), 4.51 (d, J = 15.3 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.56 – 2.44 (m, 2H), 1.77 – 1.70 (m, 1H), 1.52 – 1.46 (m, 2H), 1.40 (s, 3H), 1.31 (ddd, J = 13.1, 11.0, 5.4 Hz, 1H), 1.17 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.2, 141.2, 137.5, 135.9, 134.7, 131.2, 129.0, 128.8, 128.7, 128.4, 127.62, 127.58, 127.23, 127.20, 119.8, 118.2, 51.2, 44.2, 42.0, 33.4, 29.8, 25.5, 22.1, 8.6. HRMS (ESI-TOF) Calcd for $C_{30}H_{30}ClN_2O^+$ ($[M+H]^+$) 469.2041. Found 469.2046.

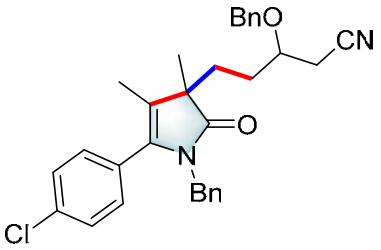


3t, diisopropyl 2-(2-(1-(4-chlorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)ethyl)-2-(cyanomethyl)malonate, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 57% yield (97 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.14 – 7.11 (m, 2H), 7.10 – 7.07 (m, 2H), 6.82 – 6.79 (m, 2H), 5.10 (heptd, *J* = 6.3, 2.1 Hz, 2H), 4.58 (d, *J* = 15.3 Hz, 1H), 4.45 (d, *J* = 15.3 Hz, 1H), 2.97 – 2.88 (m, 2H), 1.92 – 1.84 (m, 1H), 1.70 (qd, *J* = 13.0, 3.7 Hz, 2H), 1.63 (s, 3H), 1.55 (td, *J* = 13.0, 4.3 Hz, 1H), 1.27 (td, *J* = 6.2, 3.1 Hz, 15H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 181.6, 168.1, 168.0, 137.1, 136.3, 132.8, 130.1, 129.9, 129.1, 128.7, 128.4, 118.6, 116.2, 70.5, 70.3, 54.7, 50.8, 43.5, 30.3, 27.8, 22.1, 21.9, 21.5, 21.4, 8.7. HRMS (ESI-TOF) Calcd for $C_{32}H_{38}ClN_2O_5^+$ ($[M+H]^+$) 565.2464. Found 565.2466.

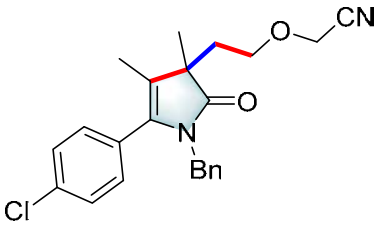


3u, *tert*-butyl 4-(2-(1-(4-chlorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)ethyl)-4-(cyanomethyl)piperidine-1-carboxylate, isolated by flash column chromatography (petroleum ether/ethyl acetate = 10:1) in 47% yield (77 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 3H), 7.12 – 7.09 (m, 4H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.59 (d, *J* = 15.2 Hz, 1H), 4.44 (d, *J* = 15.3 Hz, 1H), 3.45 – 3.39 (m, 2H), 3.30 – 3.18 (m, 2H), 2.36 (d, *J* = 16.9 Hz, 1H), 2.27 (d, *J* = 16.9 Hz, 1H), 1.75 (td, *J* = 12.5, 4.6 Hz, 1H), 1.63 (s, 3H), 1.52 – 1.39 (s, 14H), 1.27 (s, 3H), 1.15 (ddt, *J* = 27.2, 16.4, 9.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.1, 154.6, 136.9, 136.2, 133.1, 130.1, 129.8, 129.3, 128.8, 128.5, 128.4, 119.0, 117.4, 79.8, 50.9, 43.5, 39.4 (br), 38.8 (br), 34.6, 33.7, 33.6 (br), 30.4, 29.2, 28.4, 26.2, 22.3, 8.8. HRMS (ESI-TOF) Calcd for $C_{33}H_{41}ClN_3O_3^+$ ($[M+H]^+$) 562.2831. Found

562.2828.

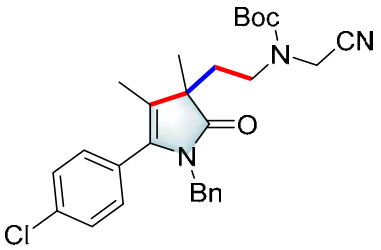


3v, 5-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)-3-(benzyloxy)pentanenitrile, 4:5 mixture of diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 23% yield (34 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 7H), 7.18 – 7.15 (m, 3H), 7.02 – 6.97 (m, 2H), 6.87 (dd, *J* = 6.4, 2.8 Hz, 2H), 4.62 – 4.47 (m, 4H), 3.61 (ddt, *J* = 17.4, 9.5, 5.2 Hz, 1H), 2.54 – 2.36 (m, 2H), 1.92 – 1.69 (m, 2H), 1.58 (d, *J* = 4.4 Hz, 3H), 1.53 – 1.34 (m, 2H), 1.26 (d, *J* = 4.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 182.2 (major), 182.0 (minor), 137.50, 137.47, 136.1 (minor), 136.0 (major), 134.71 (minor), 134.68 (major), 131.22 (major), 131.19 (minor), 128.73 (major), 128.72 (minor), 128.674 (major), 128.665 (minor), 128.5 (major and minor), 128.37 (minor), 128.36 (major), 128.03 (major), 127.98 (minor), 127.9 (major), 127.8 (minor), 127.6 (major), 127.5 (minor), 127.2 (major and minor), 119.8 (major), 119.7 (minor), 117.4 (minor), 117.3 (major), 74.2 (minor), 74.1 (major), 72.1 (major), 71.5 (minor), 51.0 (major), 50.9 (minor), 44.2 (major and minor), 31.2 (major), 30.8 (minor), 29.4 (major), 28.6 (minor), 23.0 (major), 22.6 (minor), 22.2 (major), 22.1 (minor), 8.8 (minor), 8.7 (major). HRMS (ESI-TOF) Calcd for $C_{31}H_{32}ClN_2O_2^+$ ($[M+H]^+$) 499.2147. Found 499.2144.

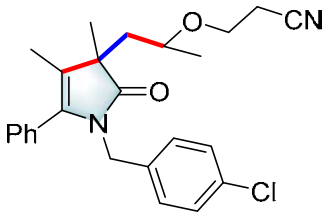


3w, 2-(2-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)ethoxy)acetonitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 52% yield (61 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.22 – 7.15 (m, 3H), 7.07 – 7.03 (m, 2H), 6.93 – 6.88 (m, 2H), 4.53 (dd, *J* = 15.4, 16.3 Hz, 2H), 4.00 (d, *J* = 16.1 Hz, 1H), 3.94 (d, *J* = 16.1

Hz, 1H), 3.40 (qdd, *J* = 9.3, 7.2, 5.6 Hz, 2H), 2.26 (ddd, *J* = 14.4, 7.9, 6.6 Hz, 1H), 1.85 (ddd, *J* = 14.2, 6.1, 5.2 Hz, 1H), 1.62 (s, 3H), 1.29 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 182.0, 137.5, 136.0, 134.7, 131.2, 128.73, 128.70, 128.4, 127.8, 127.3, 119.4, 115.9, 68.3, 55.9, 49.6, 44.2, 34.8, 22.8, 9.0. HRMS (ESI-TOF) Calcd for $C_{23}H_{24}ClN_2O_2^+$ ($[M+H]^+$) 395.1521. Found 395.1516.

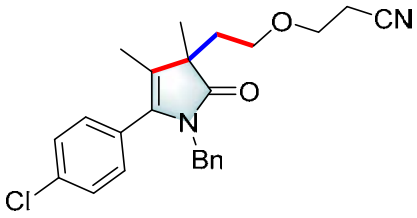


3x, *tert*-butyl (2-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)ethyl)(cyanomethyl)carbamate, 3:4 mixture of rotamers due to the slow rotation of the N-(CO) bond, isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1) in 40% yield (59 mg), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.87 (ddd, *J* = 5.3, 3.7, 3.7 Hz, 2H), 4.61 – 4.02 (m, 4H), 3.31 (brs, 1H major), 3.18 (brs, 1H minor), 2.93 (ddd, *J* = 14.2, 10.8, 5.8 Hz, 1H), 2.09 (ddd, *J* = 13.3, 10.9, 5.7 Hz, 1H), 1.87 (ddd, *J* = 13.2, 10.8, 4.7 Hz, 1H), 1.64 (s, 3H), 1.48 (s, 9H), 1.29 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.7 (br), 154.4 (br, minor), 153.9 (br, major), 137.4, 136.1, 134.8, 131.2 (br), 128.6, 128.52, 128.46, 127.3, 119.4 (br), 116.1, 81.9, 49.9, 44.3, 44.0 (br, minor), 43.7 (br, major), 35.6 (br), 33.6 (br, minor), 33.1 (br, major), 28.3, 22.5 (br), 8.8. HRMS (ESI-TOF) Calcd for $C_{28}H_{33}ClN_3O_3^+$ ($[M+H]^+$) 494.2205. Found 494.2201.

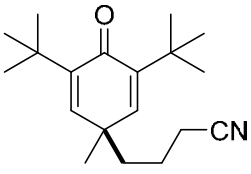


3y, 3-((1-(1-(4-chlorobenzyl)-3,4-dimethyl-2-oxo-5-phenyl-2,3-dihydro-1*H*-pyrrol-3-yl)propan-2-yl)oxy)propanenitrile, separable 1:1 diastereomers, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 47% yield (59 mg). Isomer 1: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 3H), 7.14 – 7.10 (m, 2H), 7.07 – 7.04 (m, 2H), 6.81 – 6.78 (m, 2H), 4.73 (d, *J* = 15.3 Hz, 1H), 4.31 (d, *J* = 15.3 Hz, 1H), 3.63 (dt, *J* = 9.2, 6.7 Hz, 1H), 3.53 – 3.40 (m, 2H), 2.55 –

2.43 (m, 2H), 2.21 (dd, J = 14.4, 8.2 Hz, 1H), 1.65 – 1.60 (s, 4H), 1.26 (s, 3H), 1.13 (d, J = 6.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 182.5, 136.6, 136.4, 132.9, 130.2, 129.6, 129.1, 128.7, 128.5, 128.4, 119.4, 118.0, 73.2, 62.2, 49.7, 43.5, 42.1, 23.4, 20.0, 18.9, 9.2. HRMS (ESI-TOF) Calcd for $C_{25}H_{28}ClN_2O_2^+$ ($[M+H]^+$) 423.1834. Found 423.1839. Isomer 2: colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 3H), 7.13 – 7.09 (m, 2H), 7.09 – 7.04 (m, 2H), 6.79 – 6.75 (m, 2H), 4.59 – 4.50 (m, 2H), 3.50 (dt, J = 9.0, 6.8 Hz, 1H), 3.23 – 3.15 (m, 2H), 2.34 (t, J = 6.5 Hz, 2H), 1.98 – 1.87 (m, 2H), 1.67 (s, 3H), 1.24 (s, 3H), 1.10 (d, J = 6.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 182.4, 136.3, 134.9, 133.1, 130.4, 129.6, 129.4, 128.62, 128.55, 128.3, 121.6, 117.7, 74.2, 63.0, 50.5, 43.5, 42.9, 23.7, 20.3, 19.1, 9.4. HRMS (ESI-TOF) Calcd for $C_{25}H_{28}ClN_2O_2^+$ ($[M+H]^+$) 423.1834. Found 423.1836.

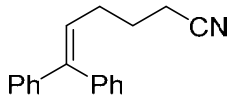


3z, 3-(2-(1-benzyl-5-(4-chlorophenyl)-3,4-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrol-3-yl)ethoxy)propanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1) in 17% yield (21 mg), colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.19 – 7.15 (m, 3H), 7.01 – 6.98 (m, 2H), 6.89 – 6.87 (m, 2H), 4.57 (d, J = 15.3 Hz, 1H), 4.50 (d, J = 15.3 Hz, 1H), 3.55 – 3.47 (m, 2H), 3.38 – 3.26 (m, 2H), 2.47 (t, J = 6.5 Hz, 2H), 2.21 (dt, J = 14.2, 7.2 Hz, 1H), 1.83 (ddd, J = 13.9, 7.2, 5.5 Hz, 1H), 1.61 (s, 3H), 1.28 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 182.1, 137.6, 135.6, 134.6, 131.1, 128.8, 128.6, 128.3, 127.5, 127.2, 120.0, 117.9, 67.8, 65.2, 49.7, 44.2, 35.1, 22.7, 18.7, 9.0. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}ClN_2O_2^+$ ($[M+H]^+$) 409.1677. Found 409.1669.



4, 4-(3,5-di-*tert*-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)butanenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 42:1) in 79% yield (68 mg), pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.39 (s, 2H), 2.29 (t, J = 6.9 Hz, 2H), 1.77 – 1.73 (m, 2H), 1.40 – 1.32 (m, 2H), 1.234 (s, 18 H), 1.226 (s, 3H).

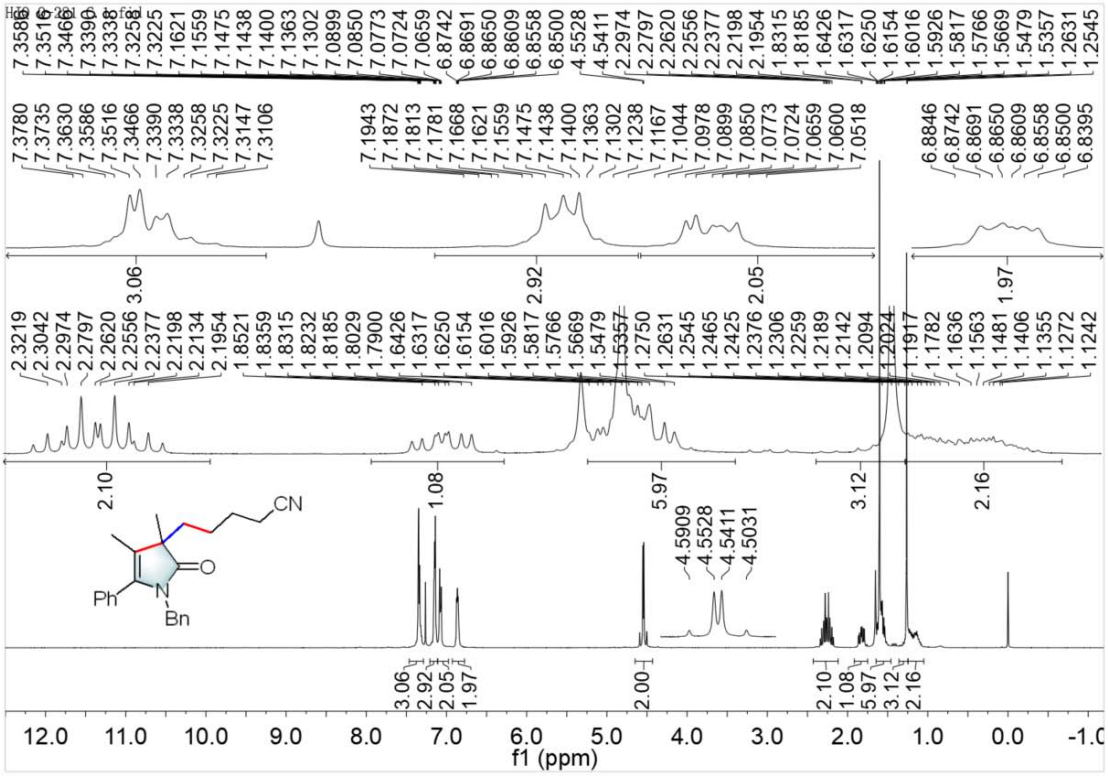
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 186.3, 147.4, 145.4, 119.2, 39.9, 39.6, 34.8, 29.5, 27.3, 20.9, 17.4.. HRMS (ESI-TOF) Calcd for $C_{19}H_{30}NO^+$ ($[M+H]^+$) 288.2322. Found 288.2323.



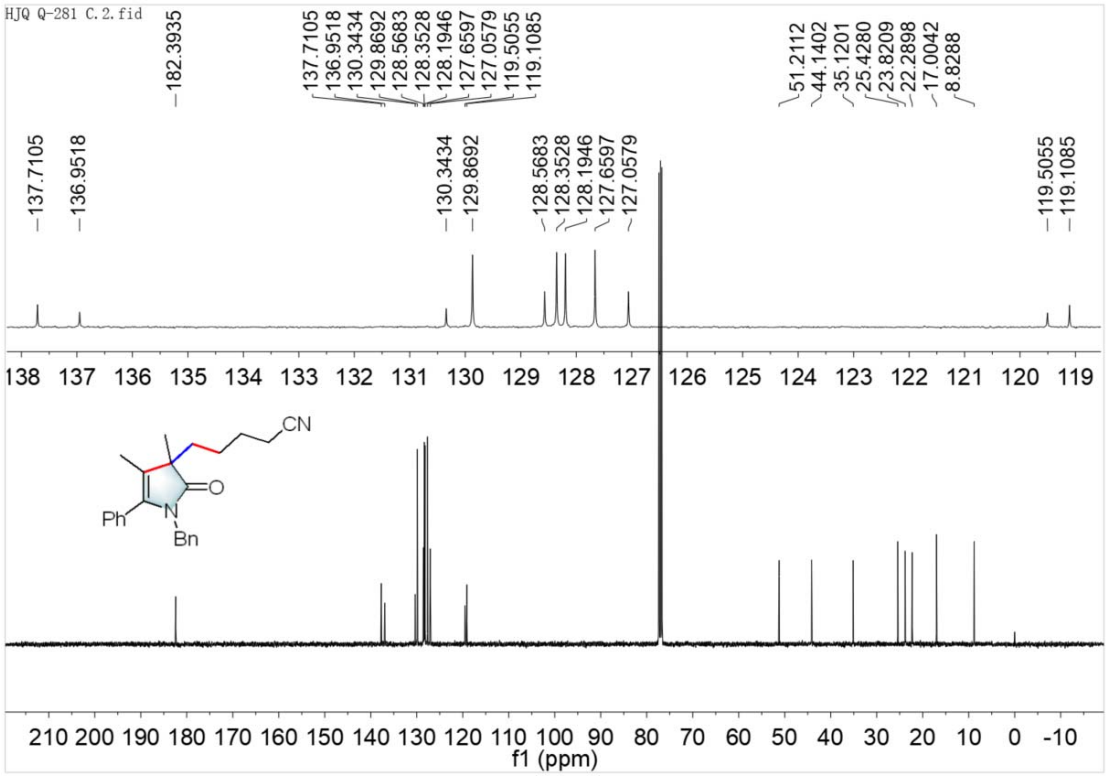
5,[2] 6,6-diphenylhex-5-enenitrile, isolated by flash column chromatography (petroleum ether/ethyl acetate = 42:1) in 59% yield (44 mg), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.14 (m, 10H), 6.01 (t, *J* = 7.4 Hz, 1H), 2.28 (dt, *J* = 19.9, 7.4 Hz, 4H), 1.80 (p, *J* = 7.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.8, 142.1, 139.6, 129.7, 128.4, 128.2, 127.27, 127.25, 127.19, 126.6, 119.5, 28.7, 25.8, 16.7. HRMS (ESI-TOF) Calcd for $C_{18}H_{18}N^+$ ($[M+H]^+$) 248.1434. Found 248.1432.

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

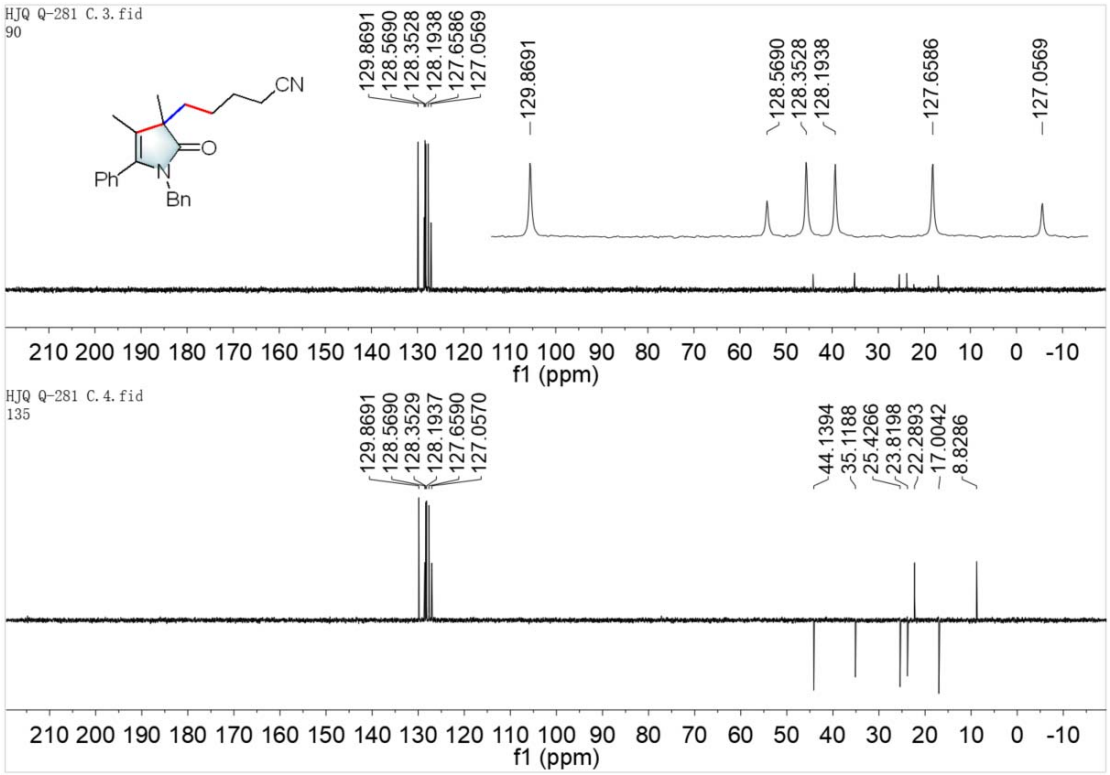
3a, ^{1}H NMR



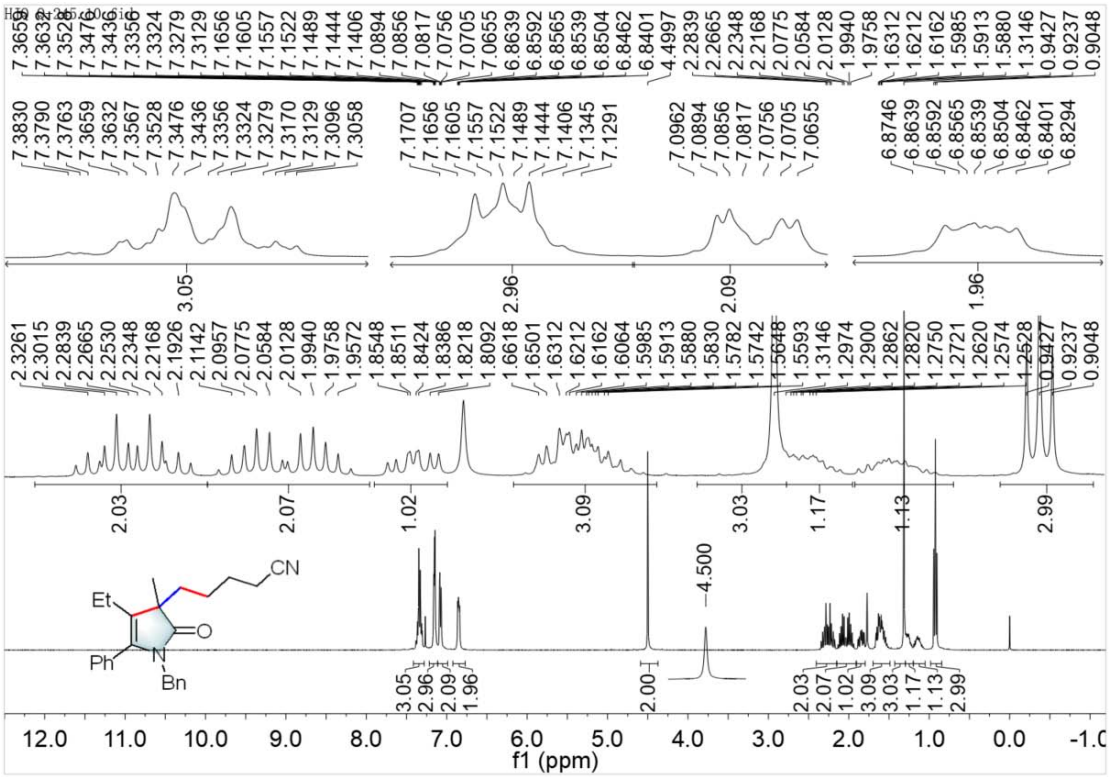
^{13}C NMR



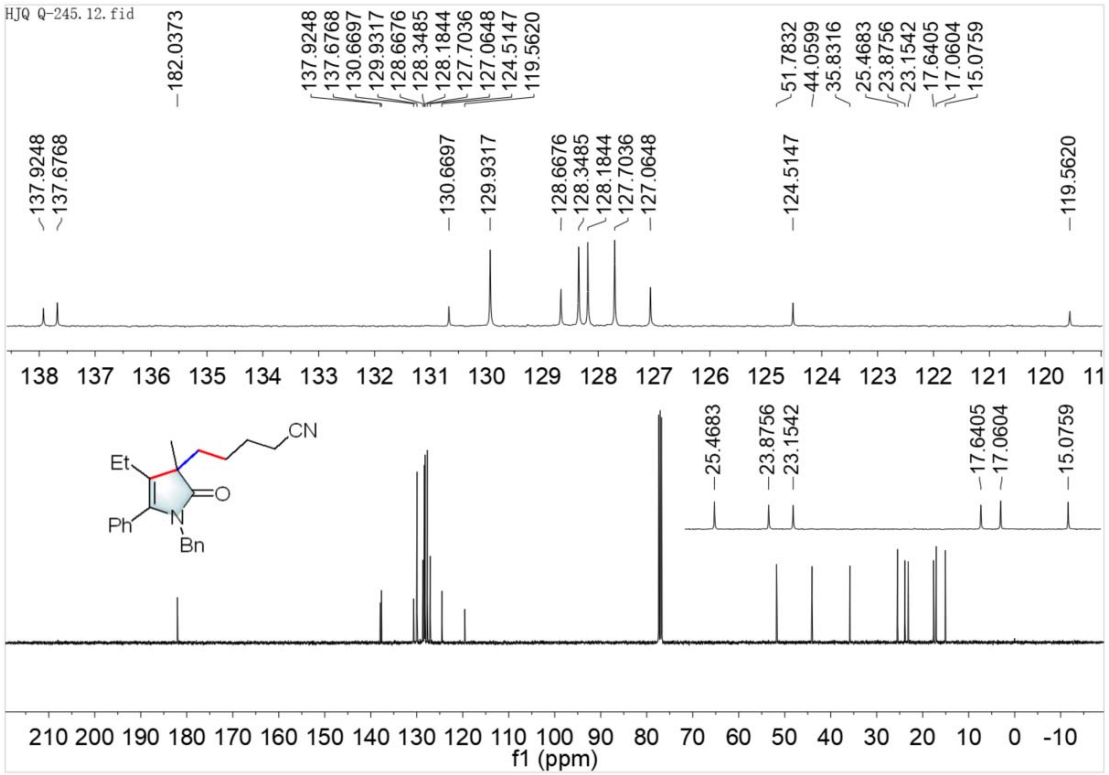
DEPT 90 and DEPT 135



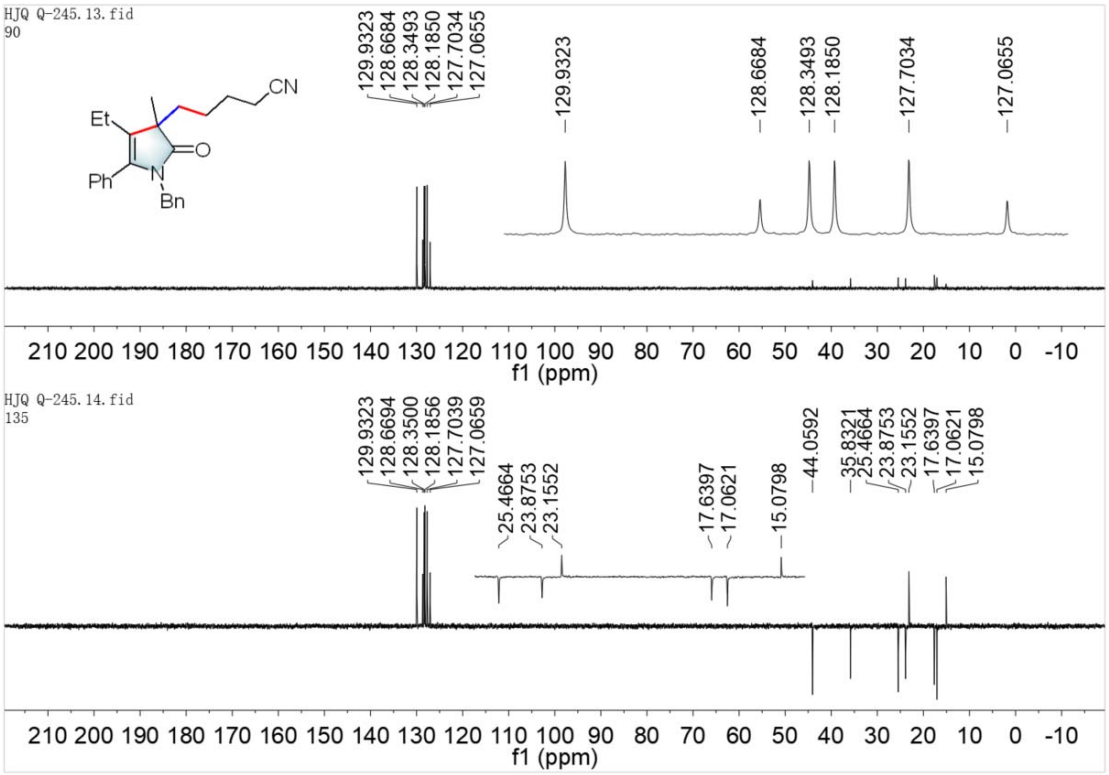
3b1, ^{1}H NMR



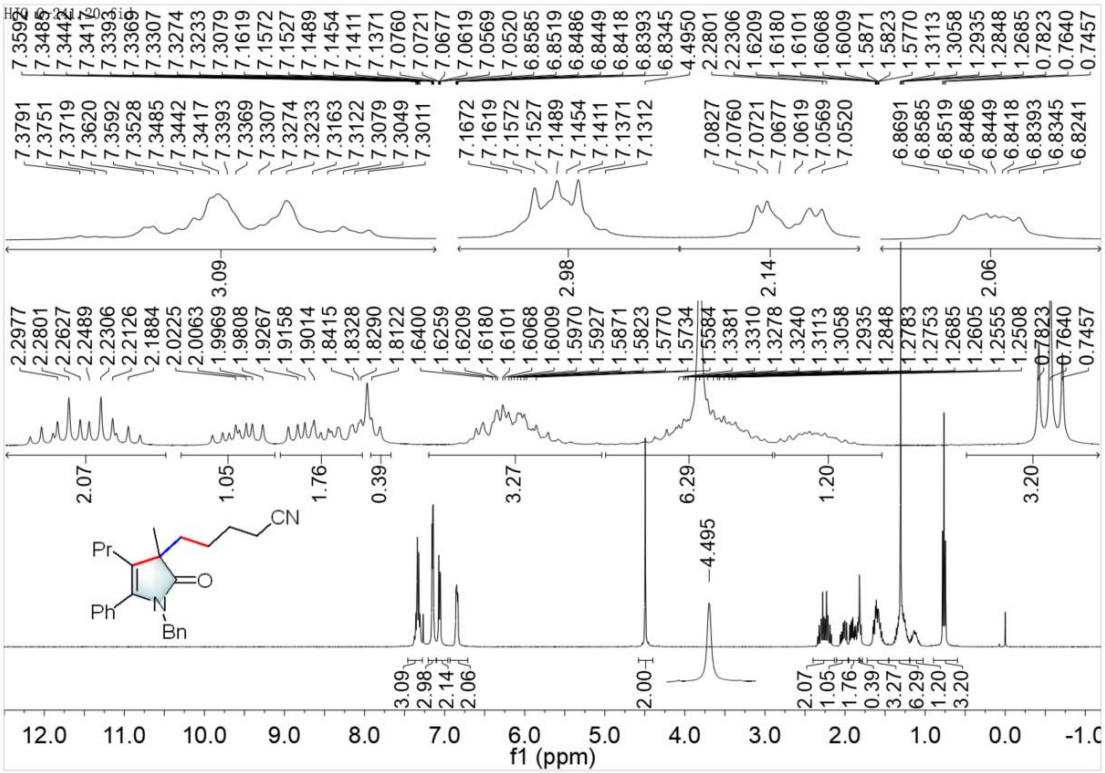
^{13}C NMR



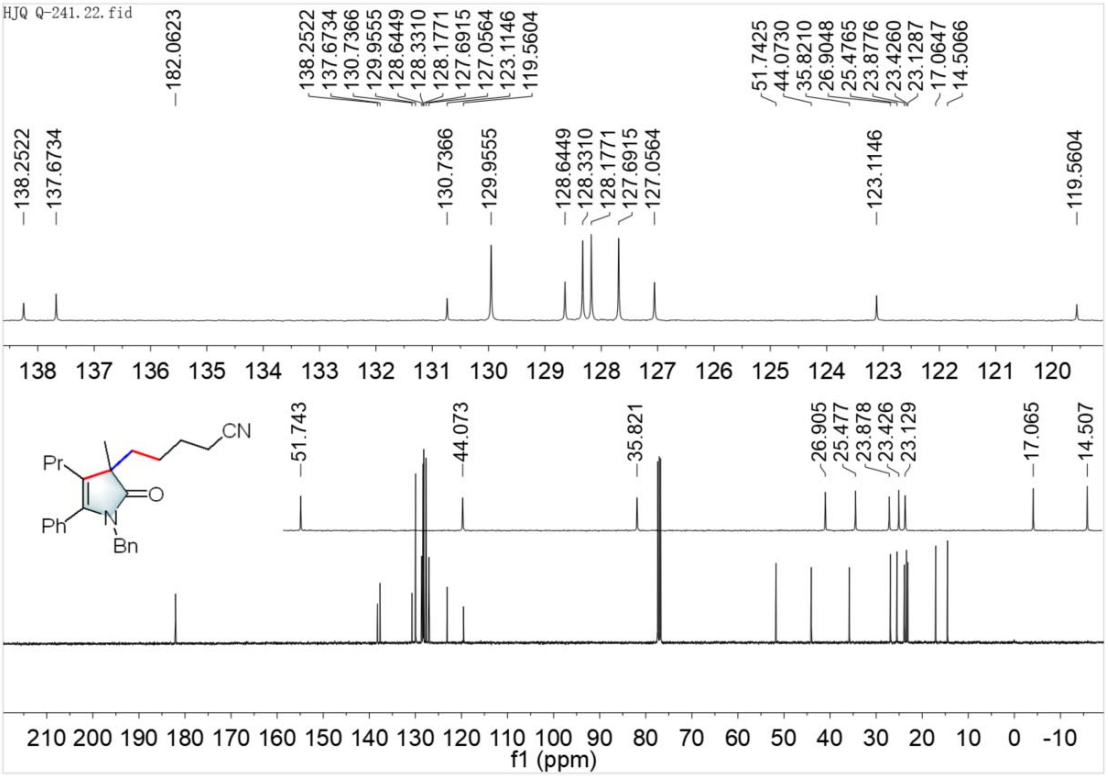
DEPT 90 and DEPT 135



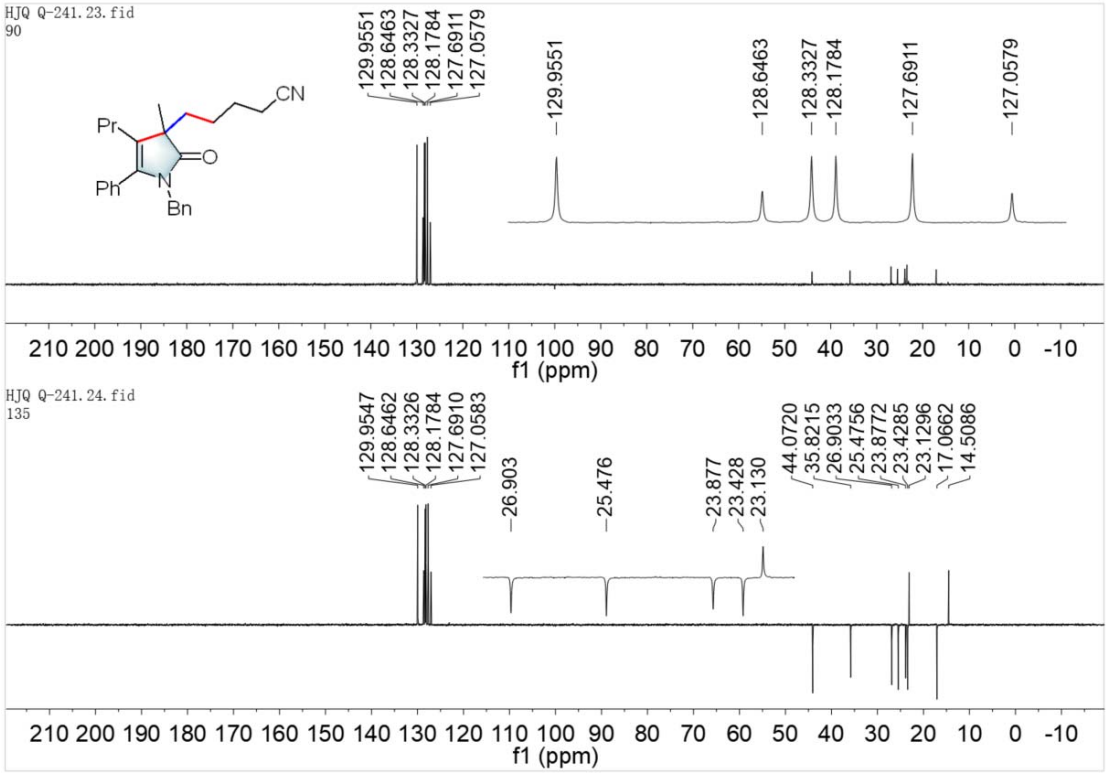
3b2, ^{1}H NMR



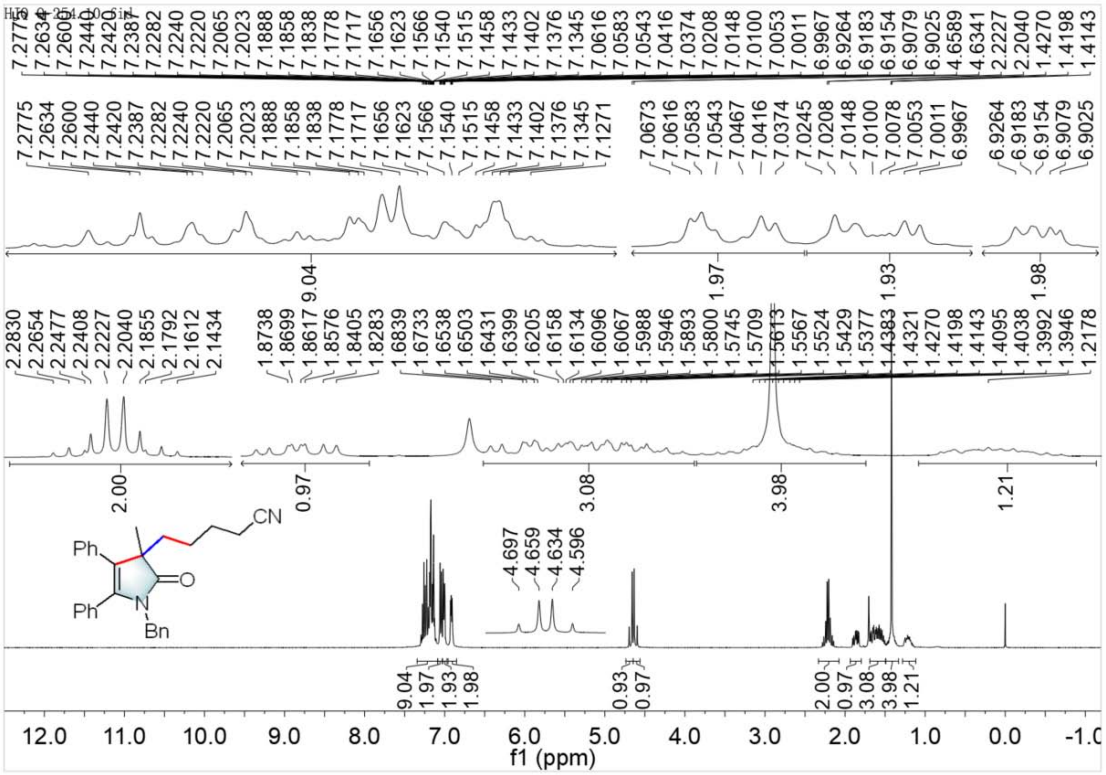
^{13}C NMR



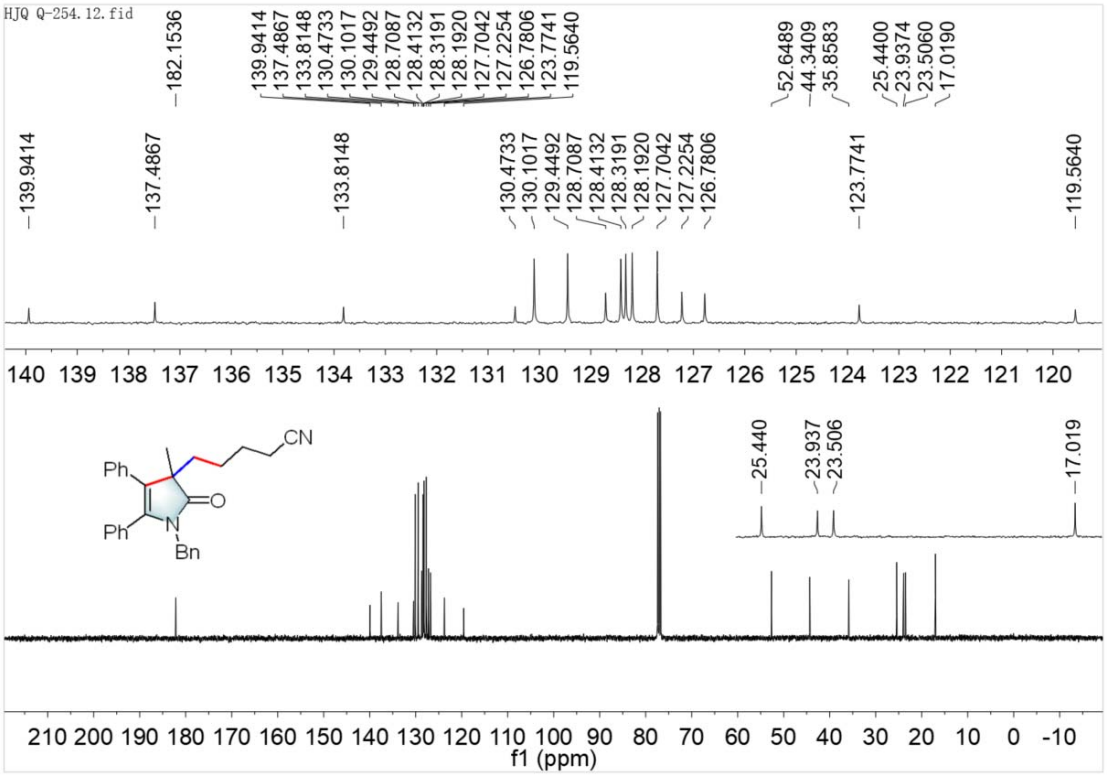
DEPT 90 and DEPT 135



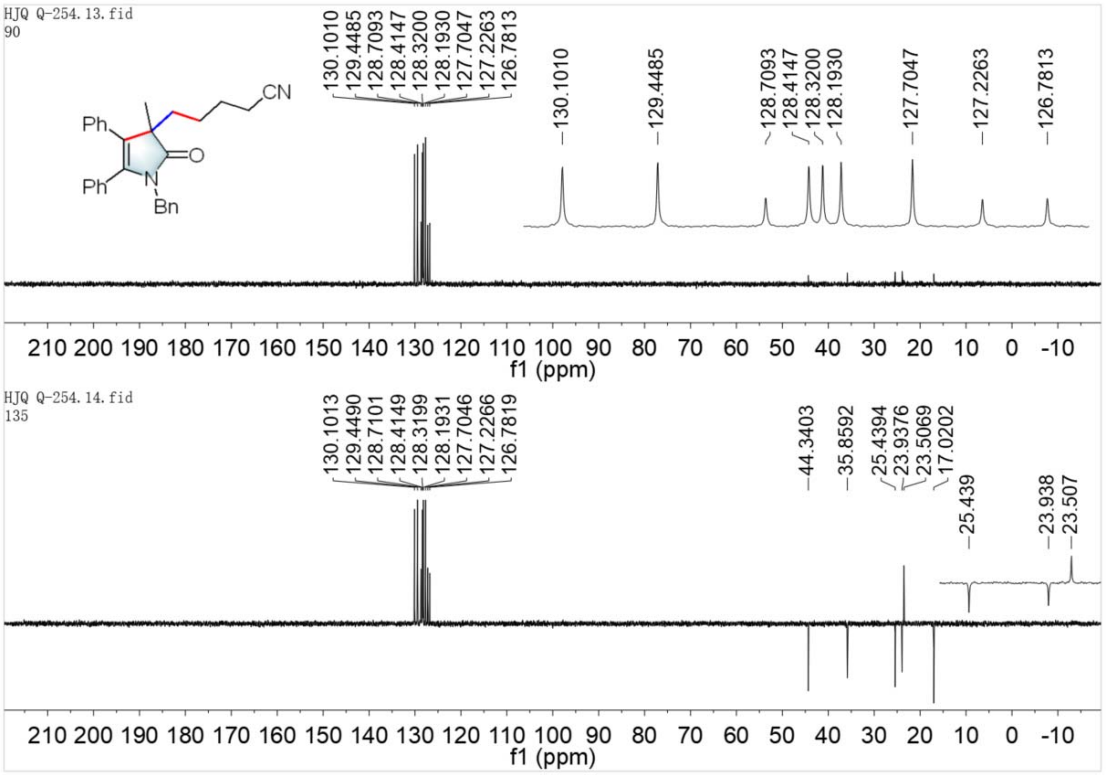
3b3, ^{1}H NMR



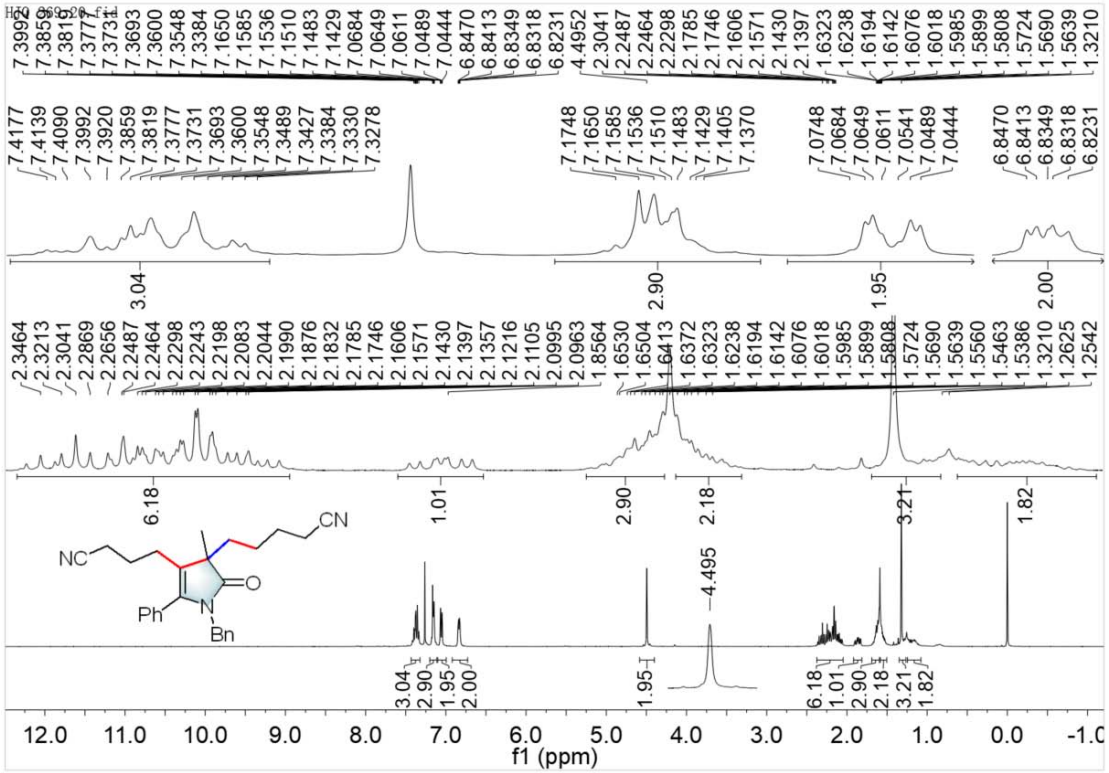
^{13}C NMR



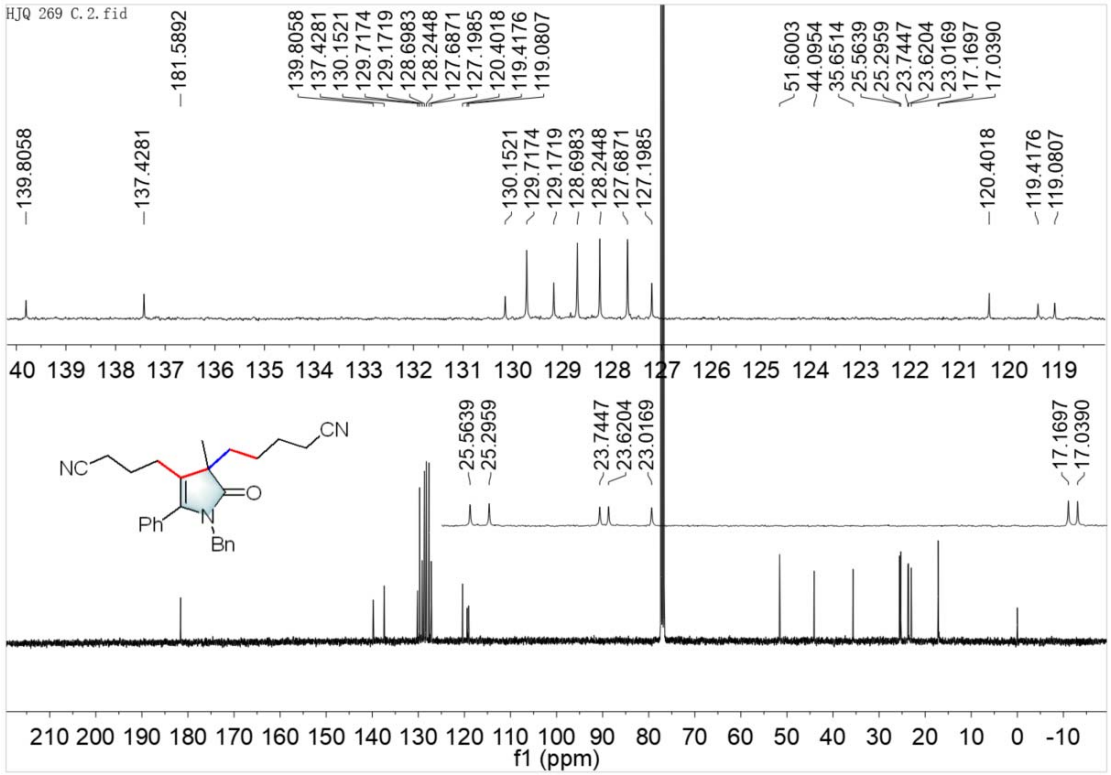
DEPT 90 and DEPT 135



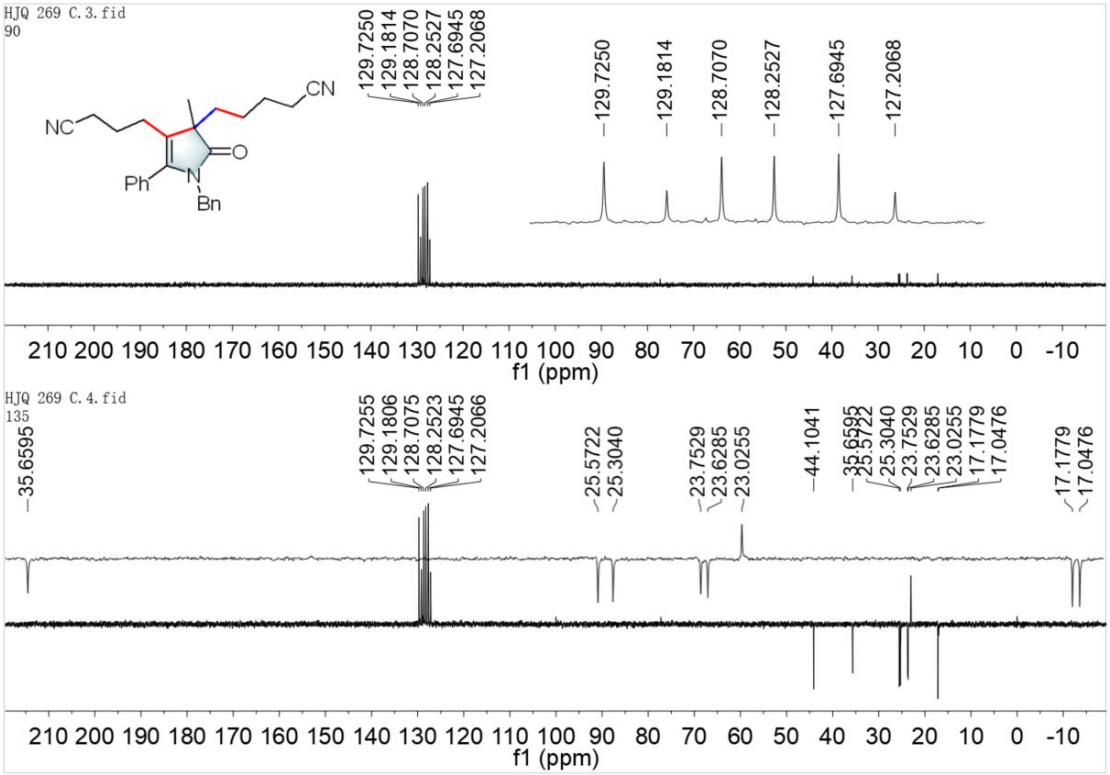
3c, ^{1}H NMR



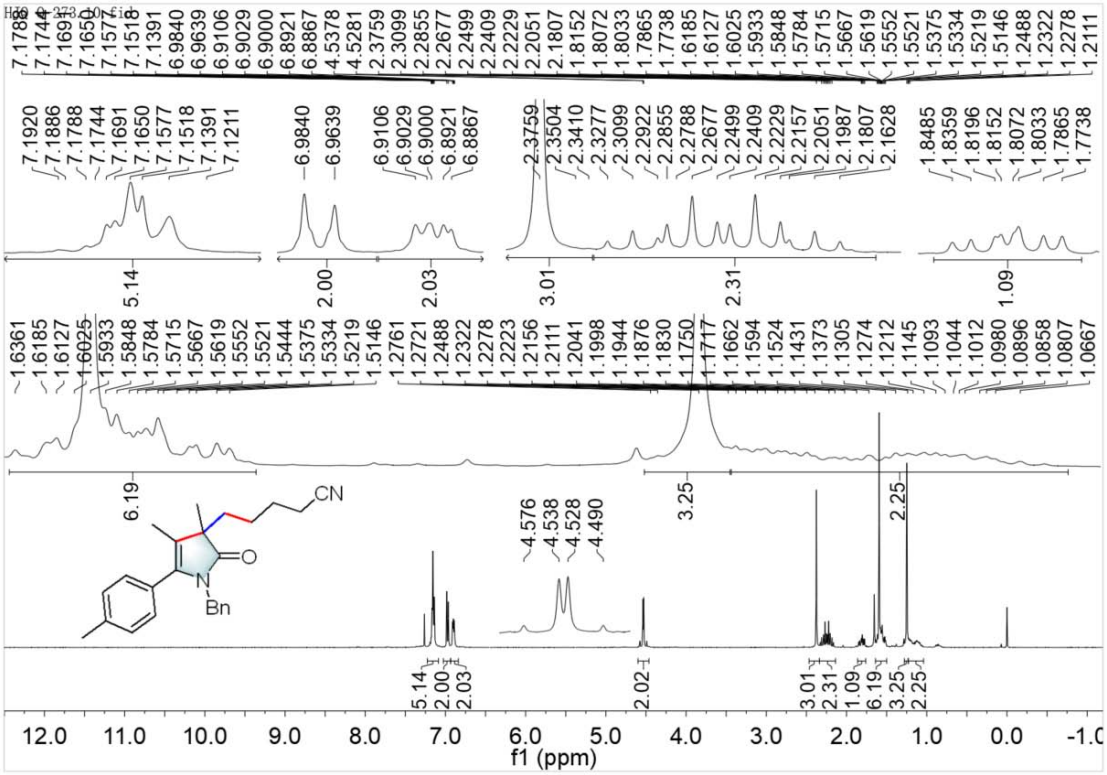
^{13}C NMR



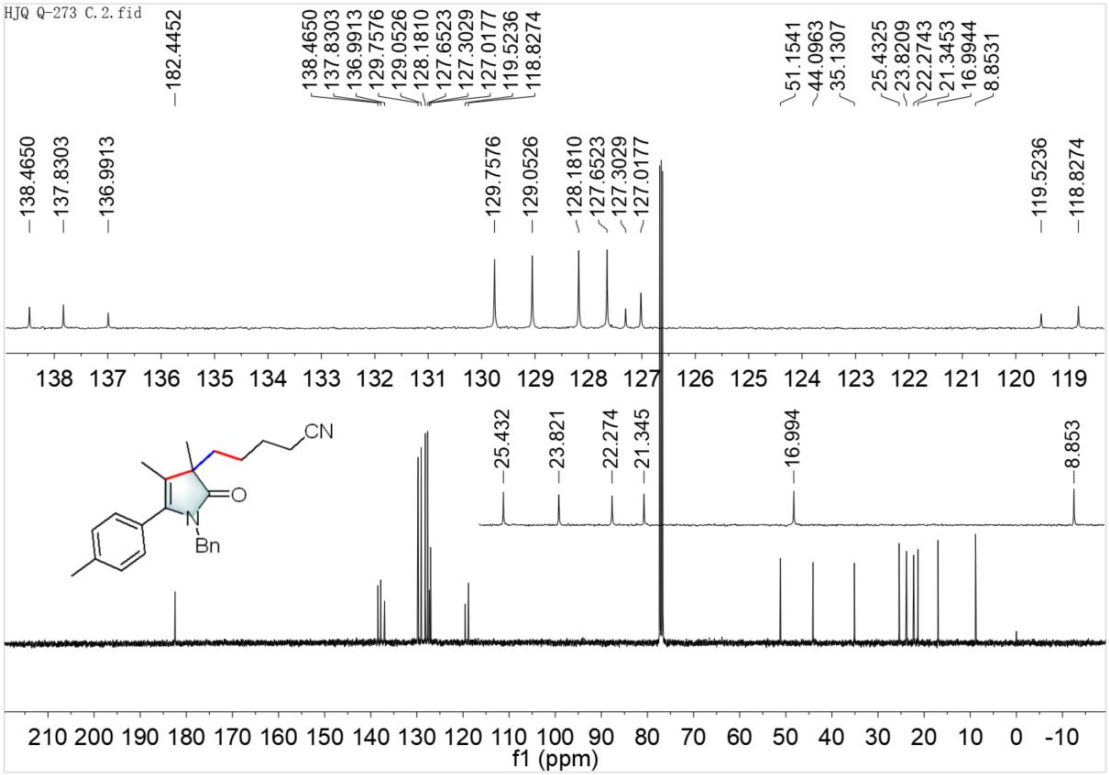
DEPT 90 and DEPT 135



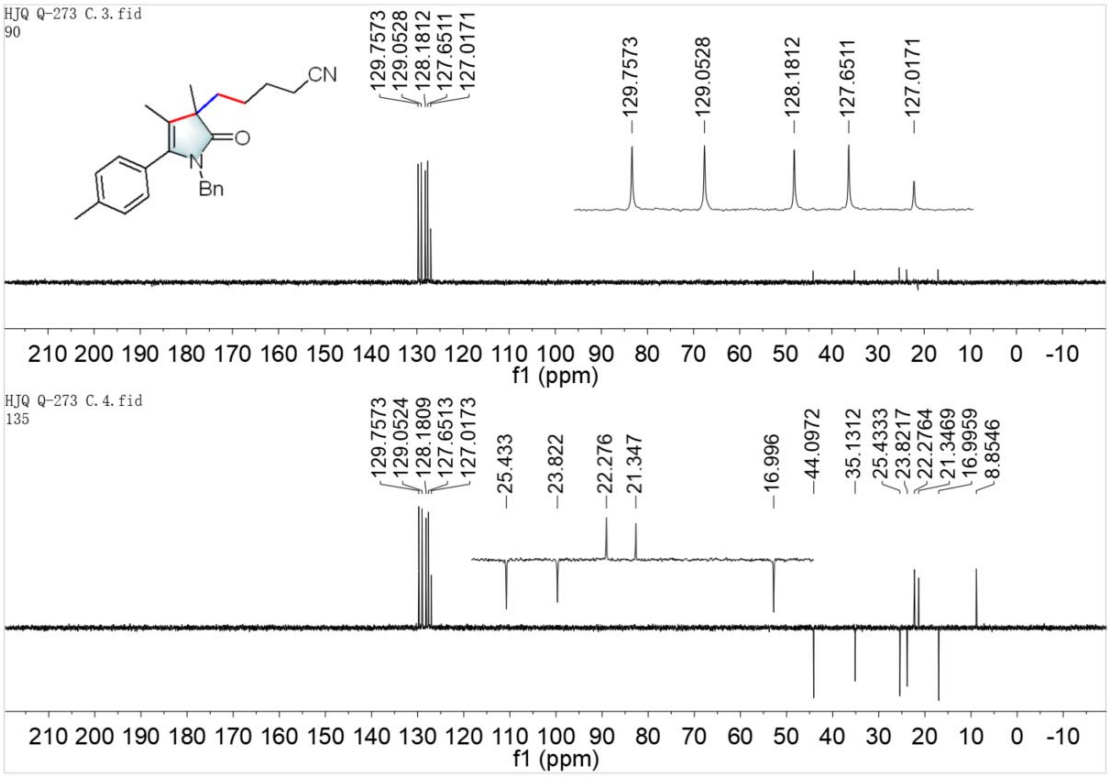
3d1, ^{1}H NMR



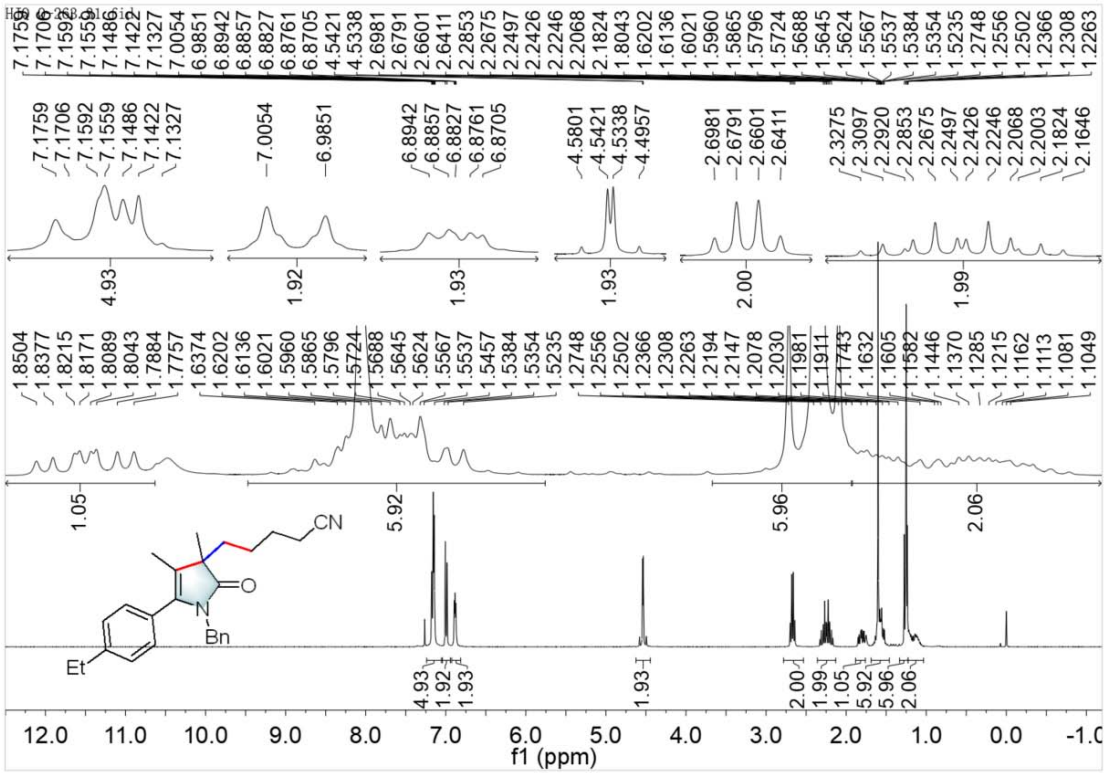
^{13}C NMR



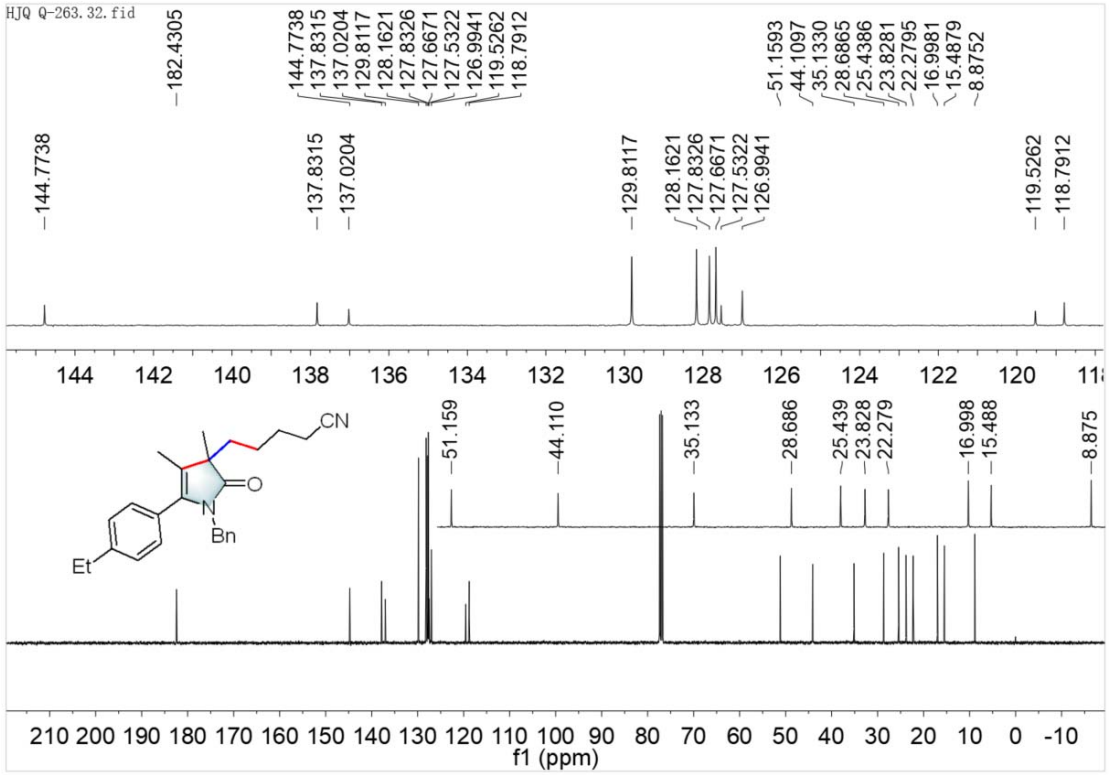
DEPT 90 and DEPT 135



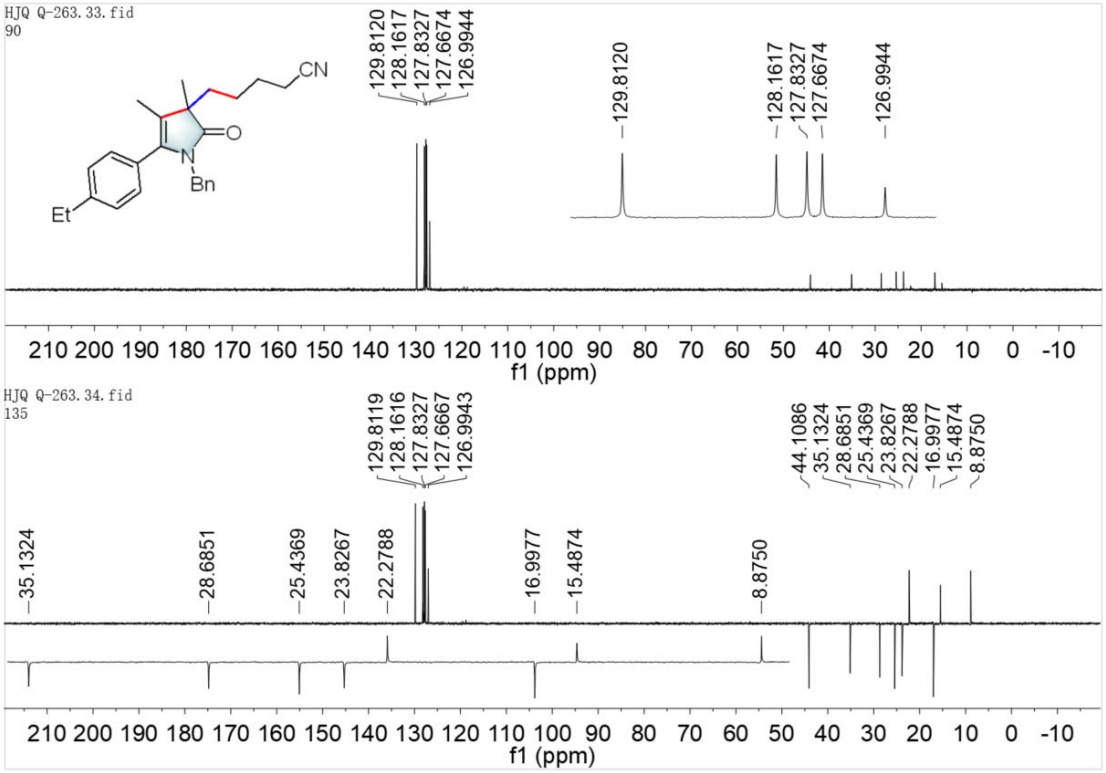
3d2, ^{1}H NMR



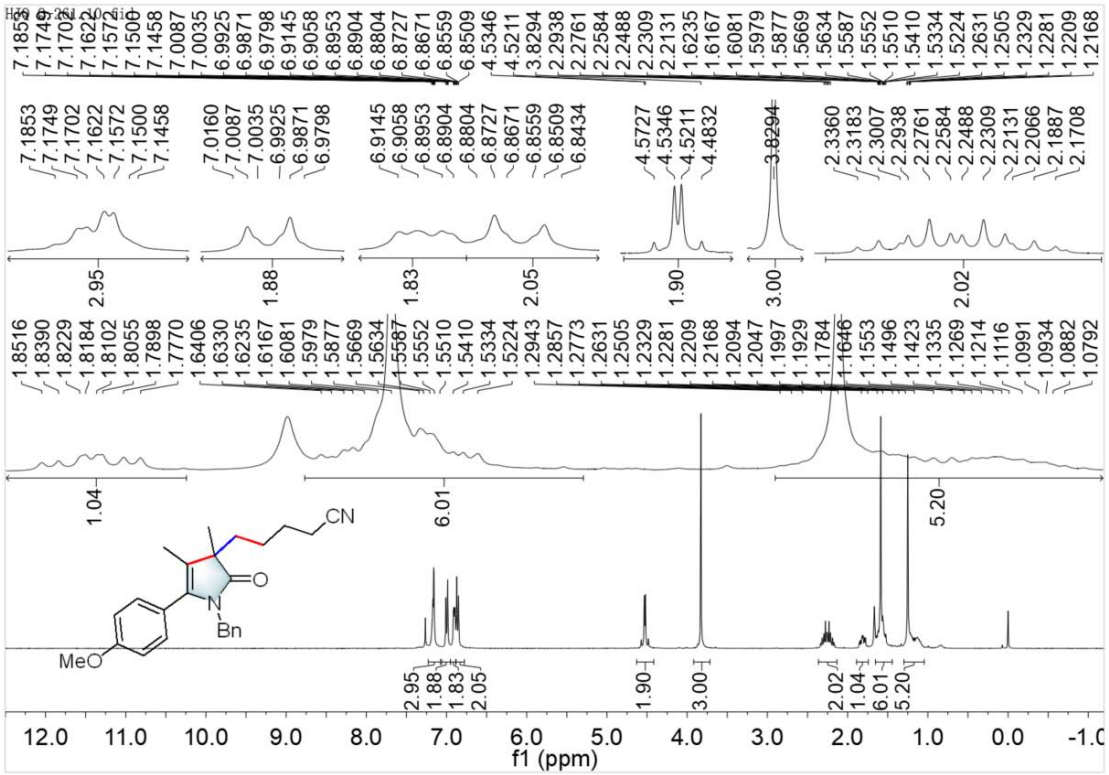
^{13}C NMR



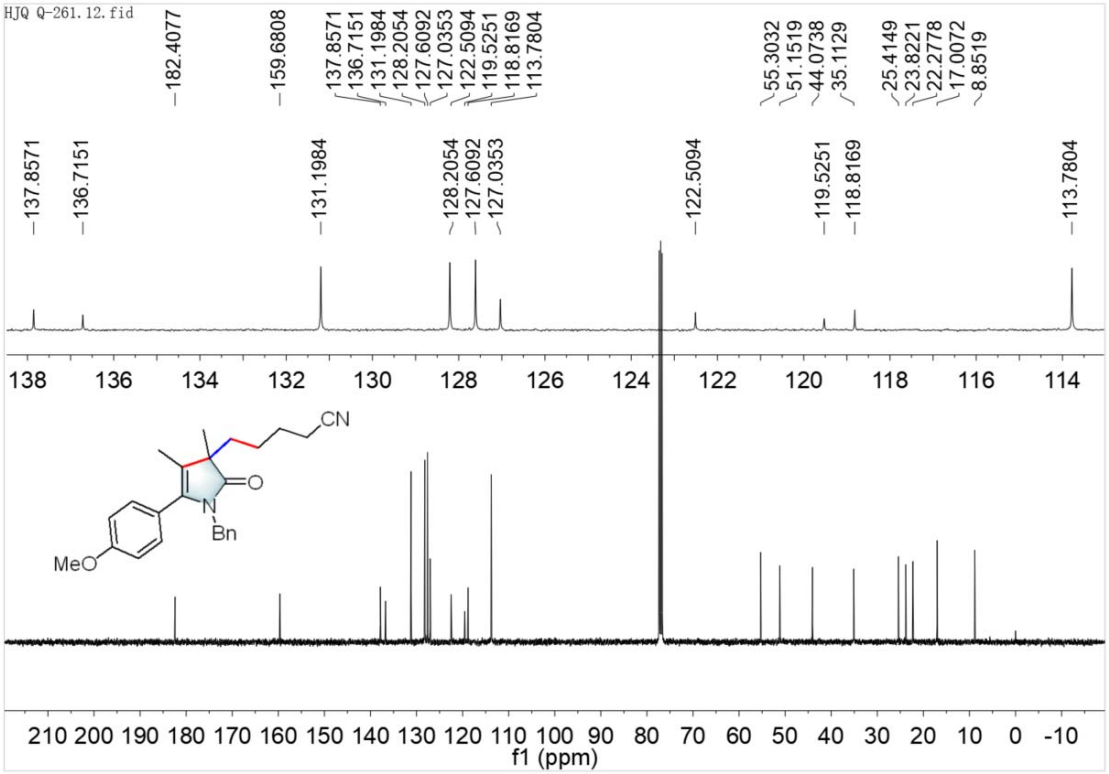
DEPT 90 and DEPT 135



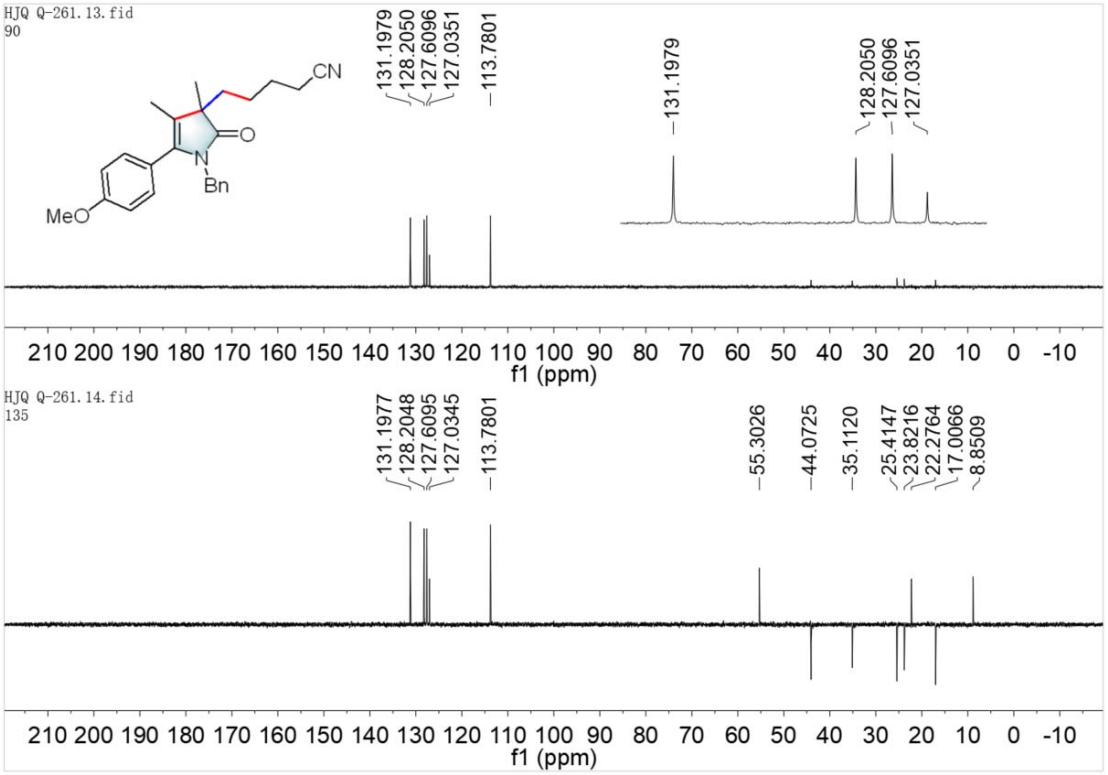
3d3, ^{1}H NMR



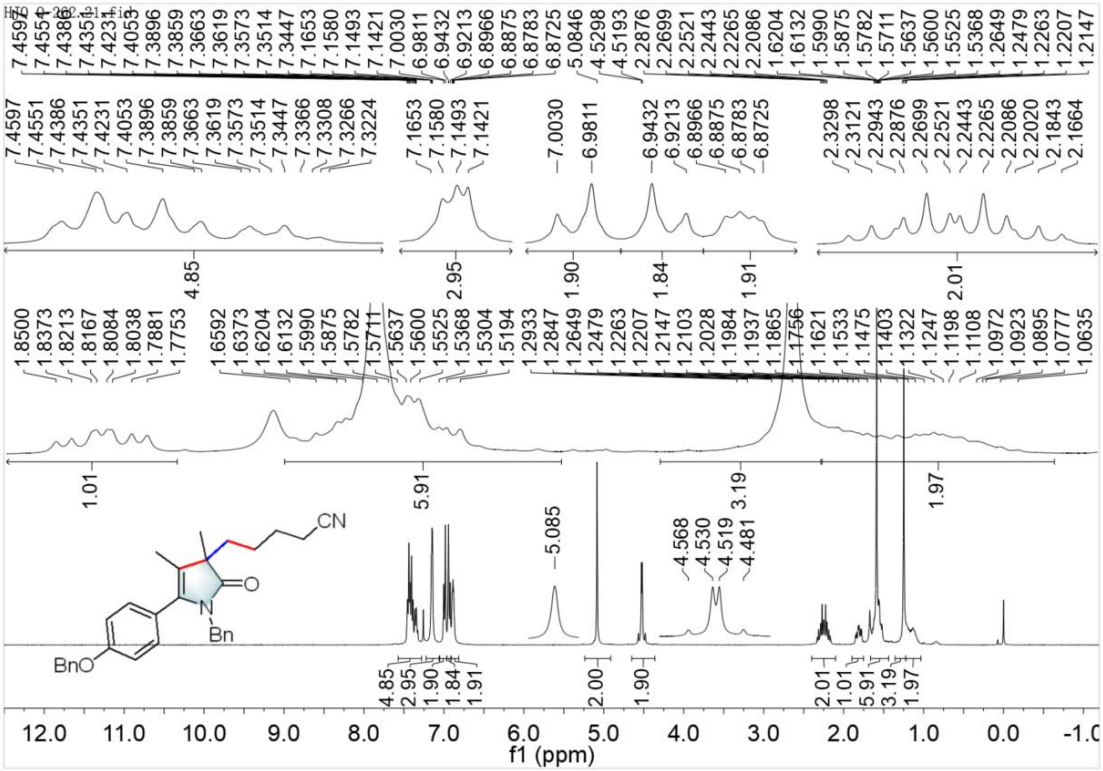
^{13}C NMR



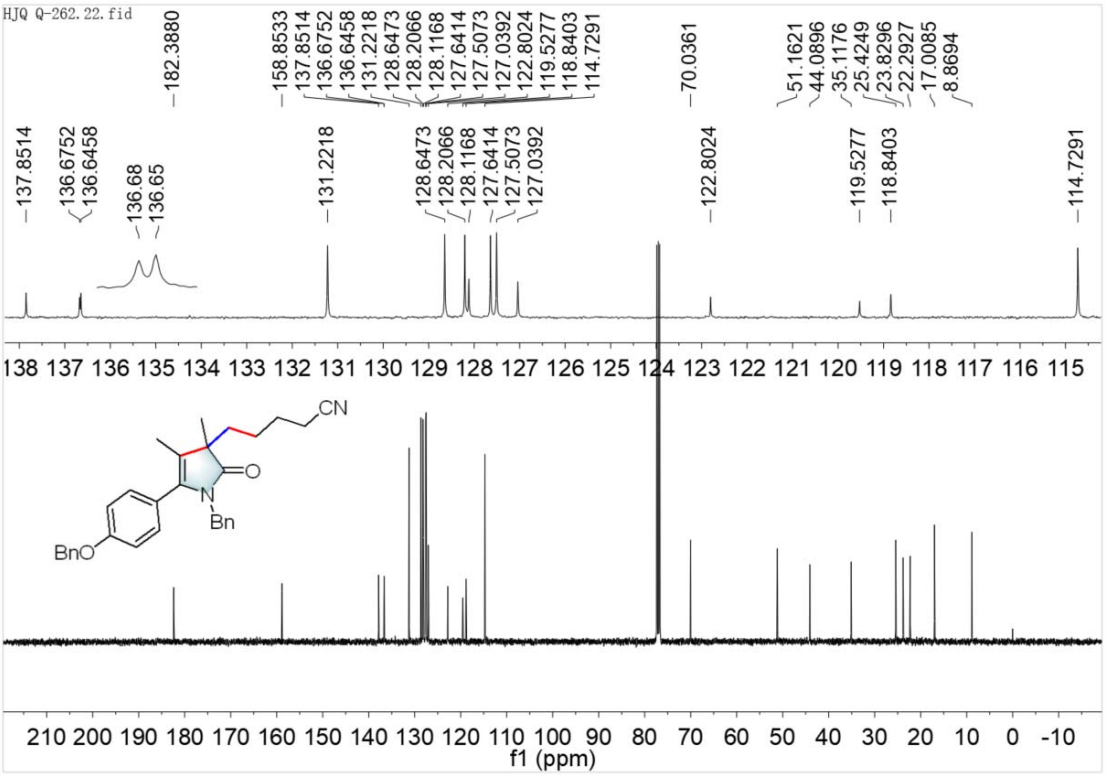
DEPT 90 and DEPT 135



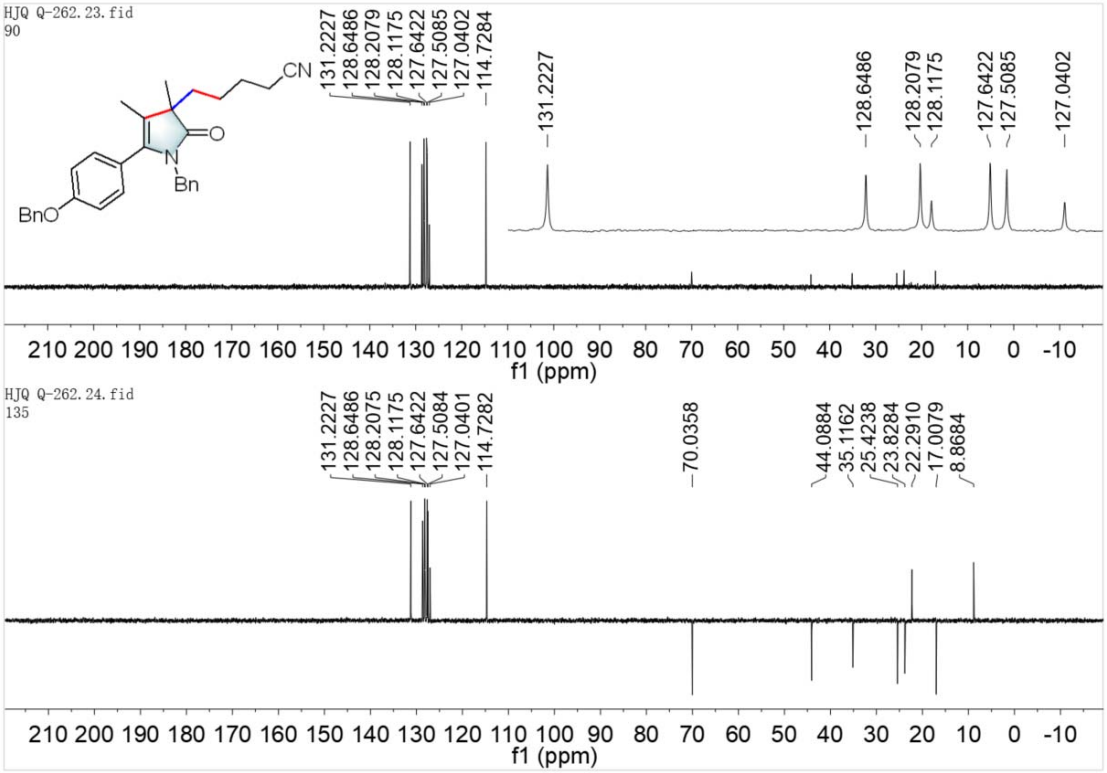
3d4, ^{1}H NMR



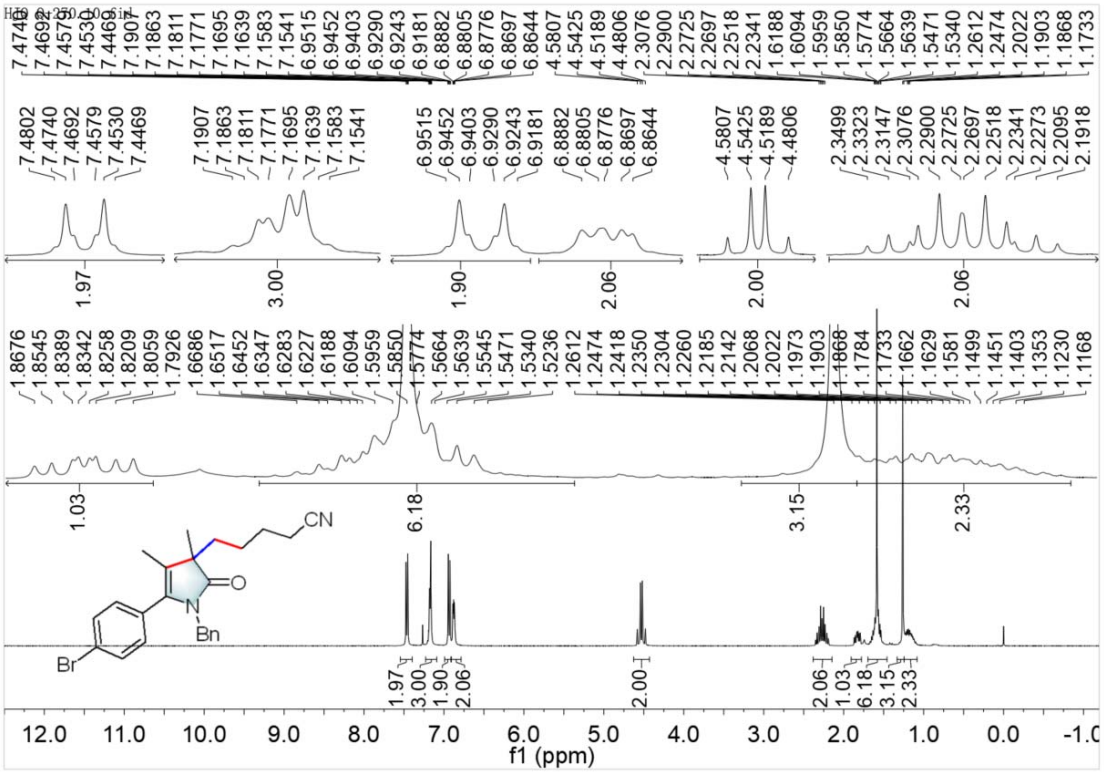
^{13}C NMR



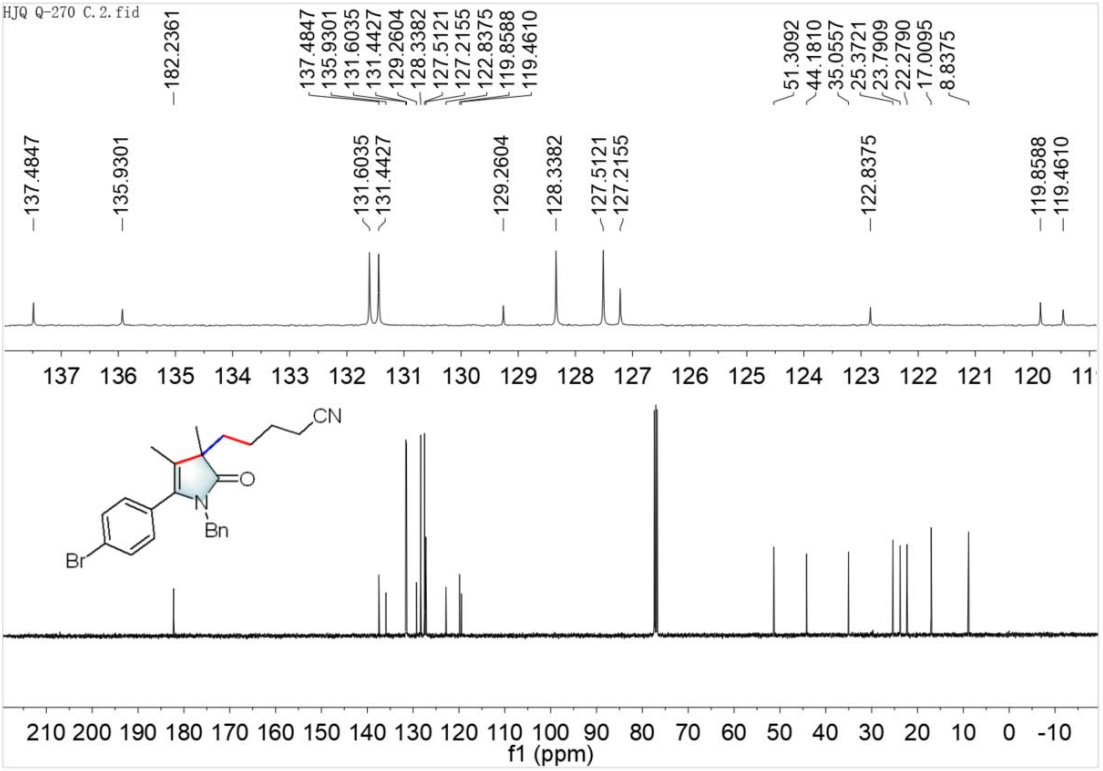
DEPT 90 and DEPT 135



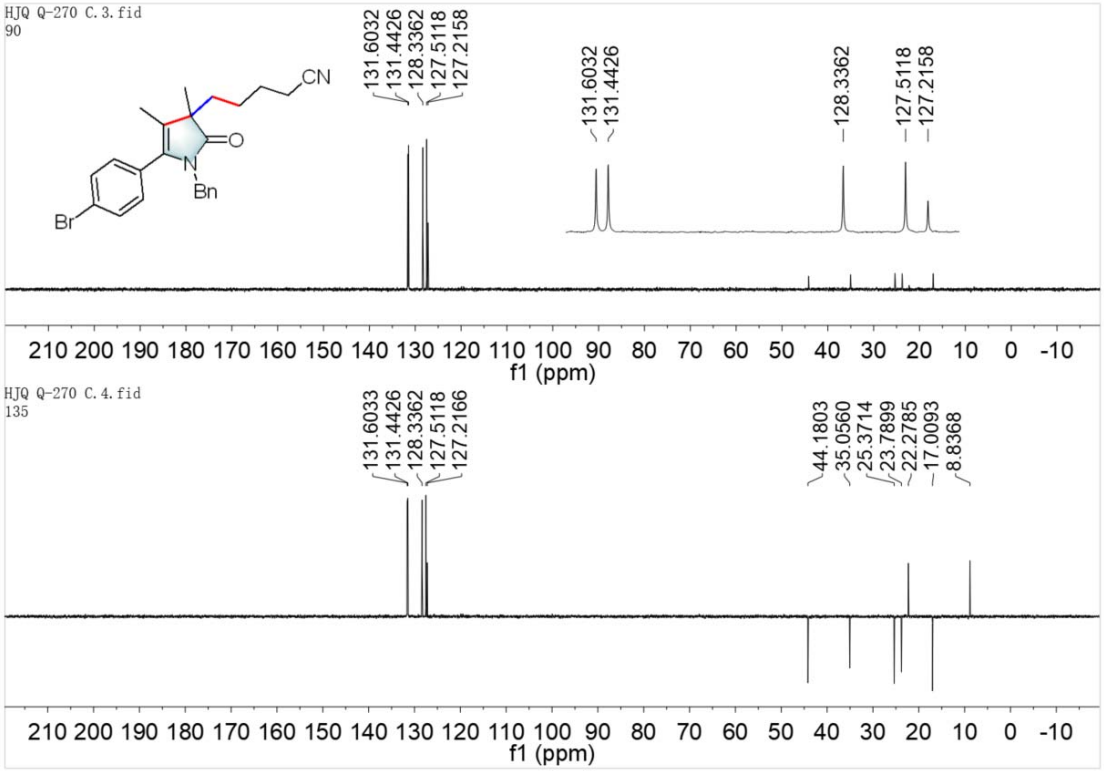
3d5, ^{1}H NMR



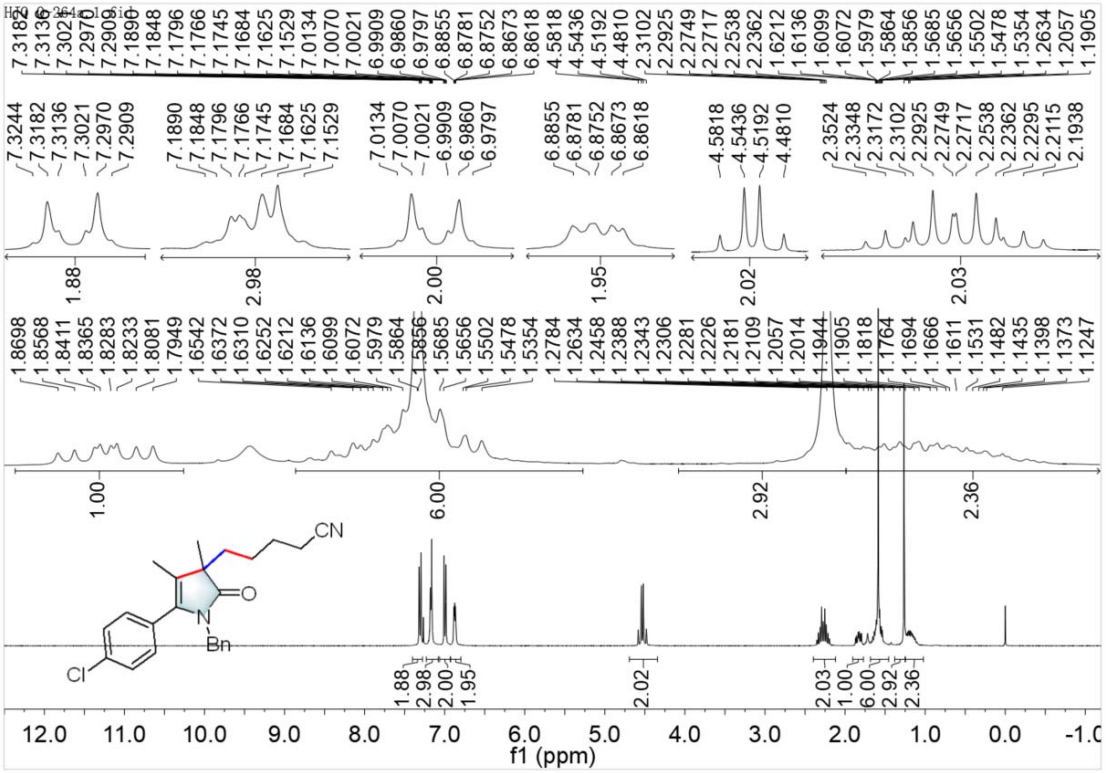
^{13}C NMR



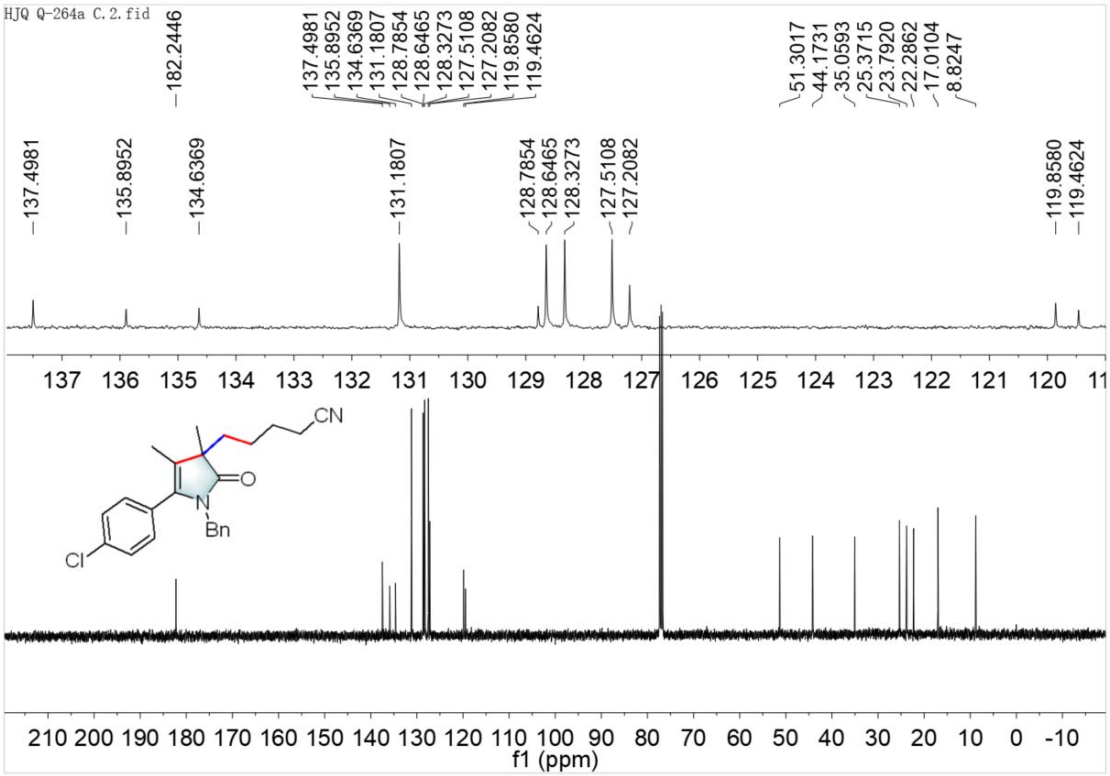
DEPT 90 and DEPT 135



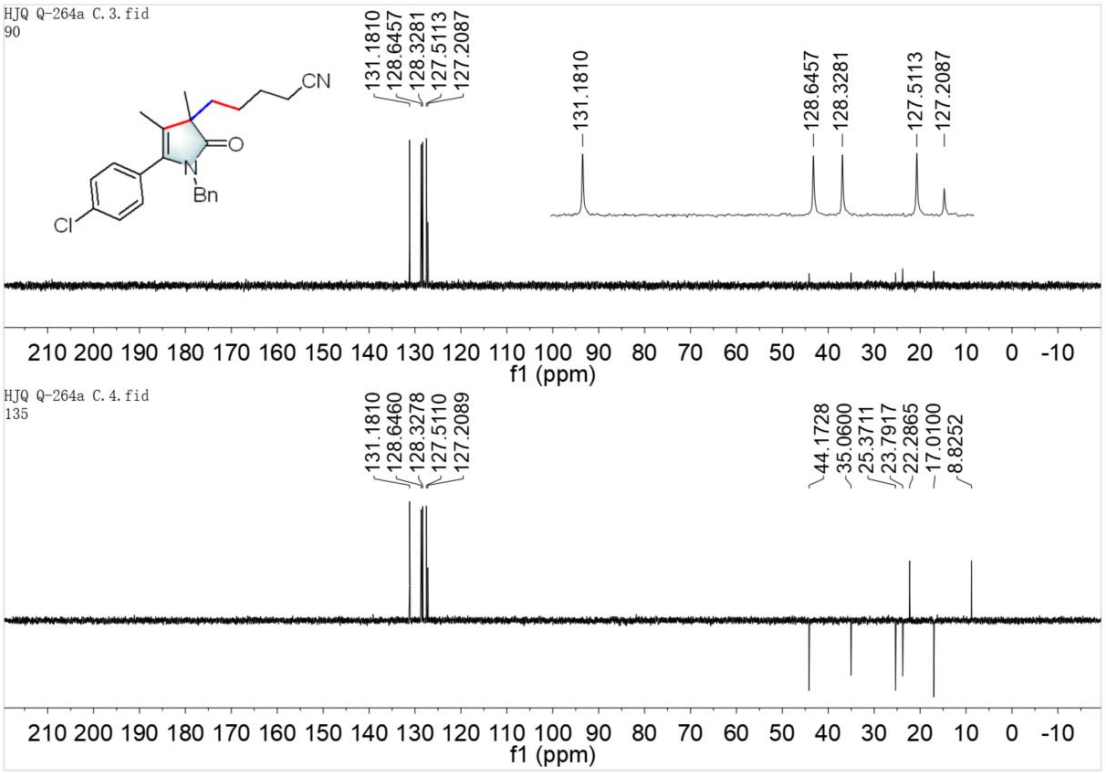
3d6, ^{1}H NMR



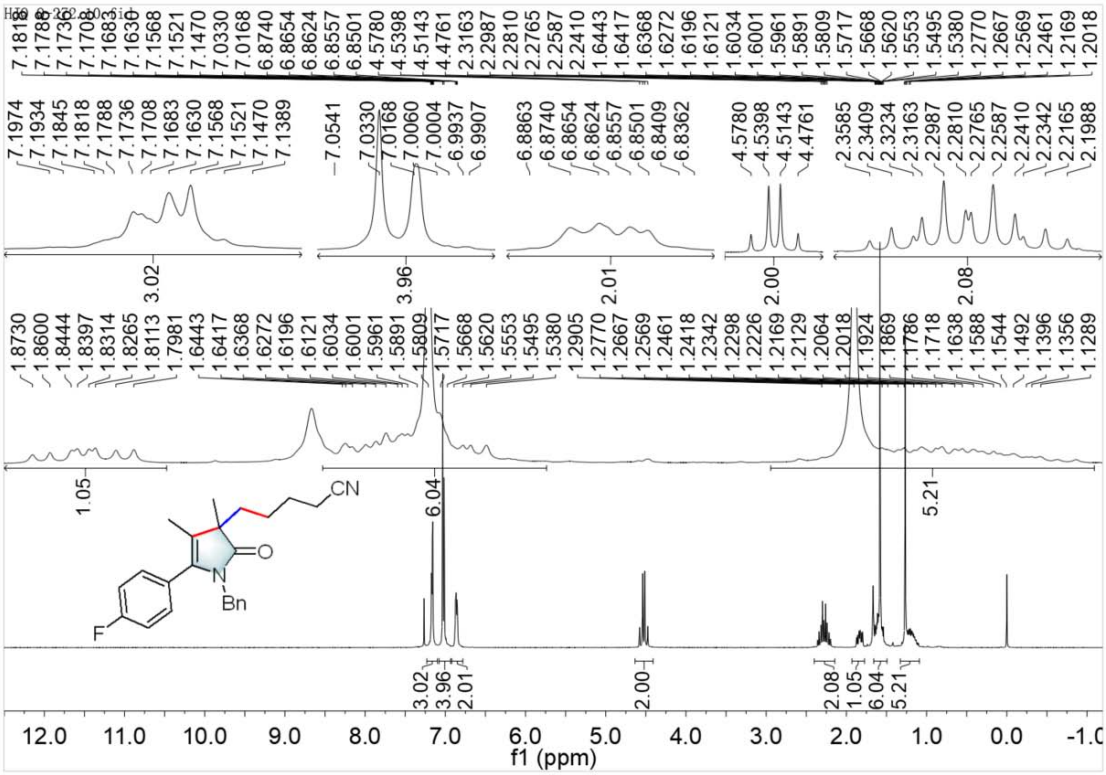
^{13}C NMR



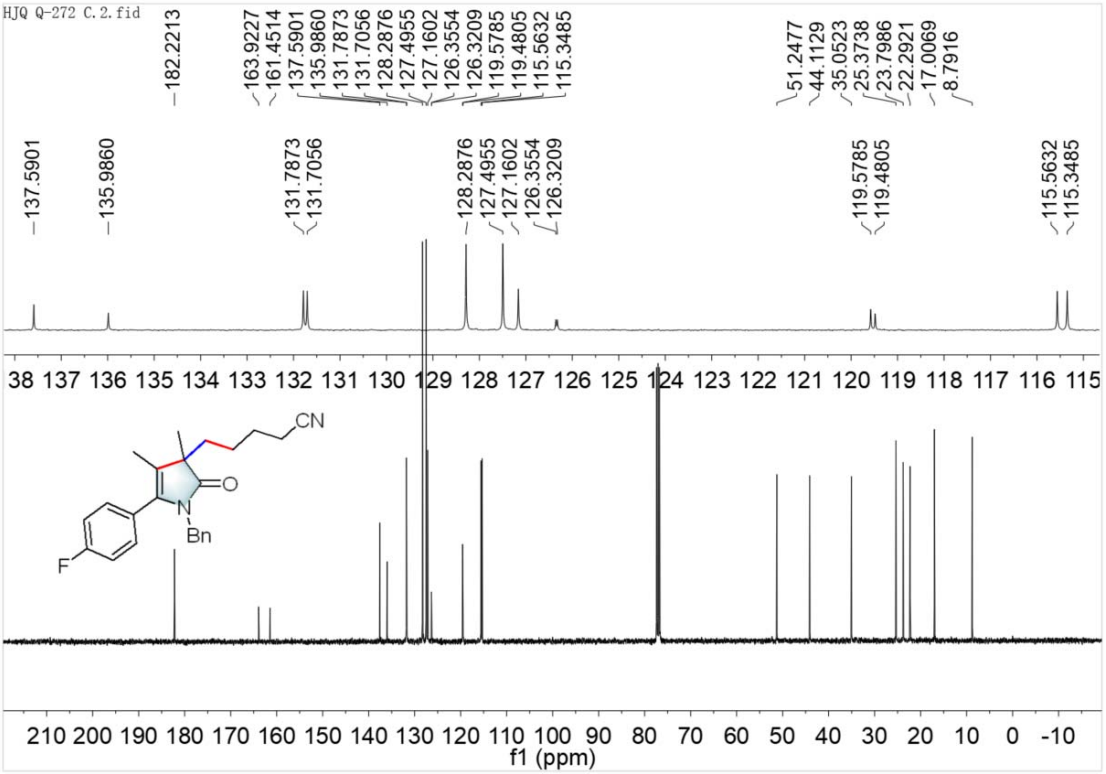
DEPT 90 and DEPT 135



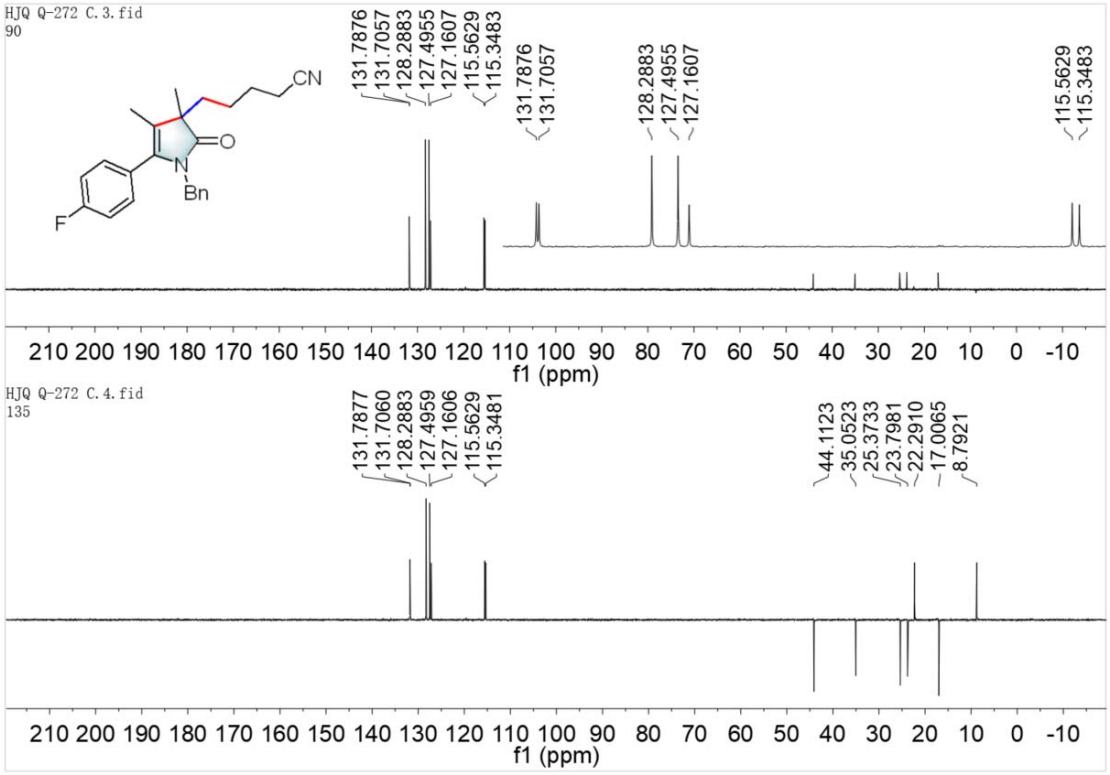
3d7, ^{1}H NMR



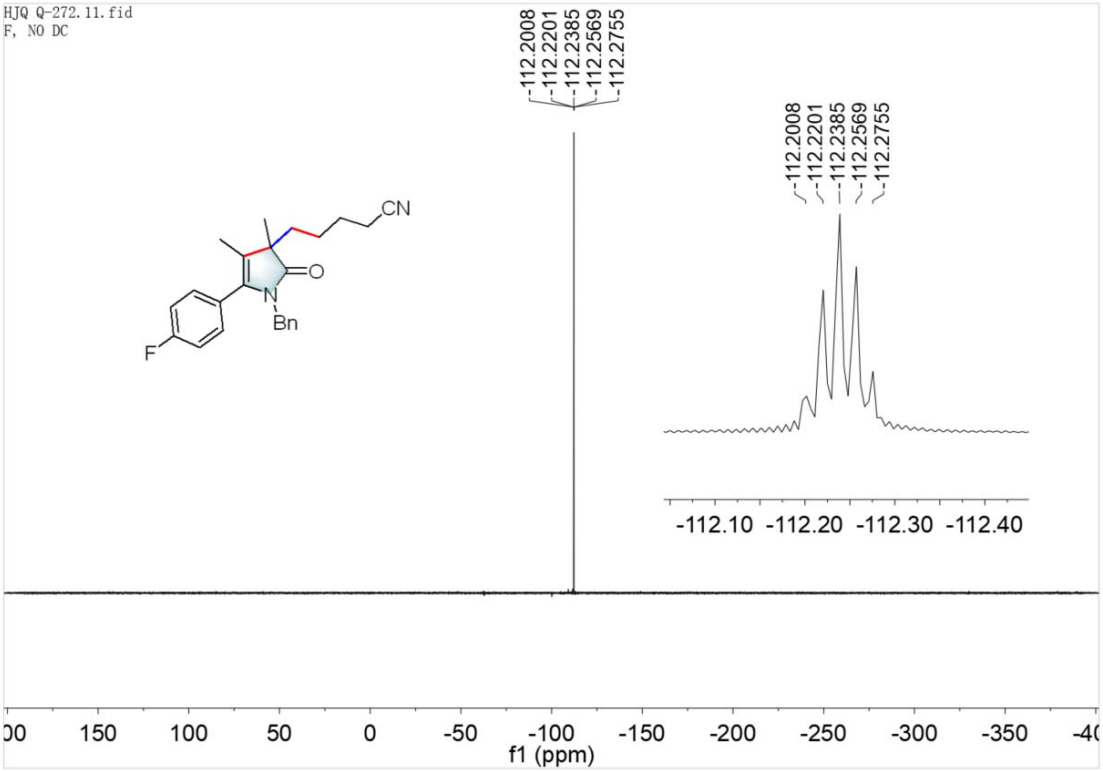
^{13}C NMR



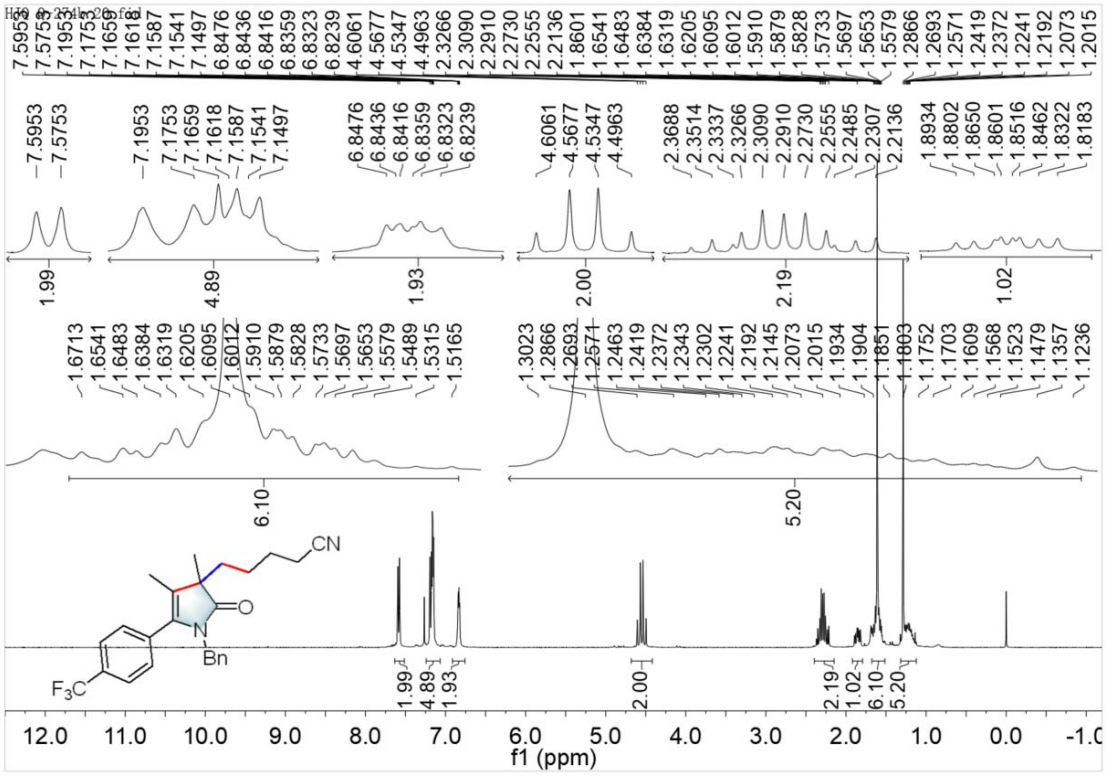
DEPT 90 and DEPT 135



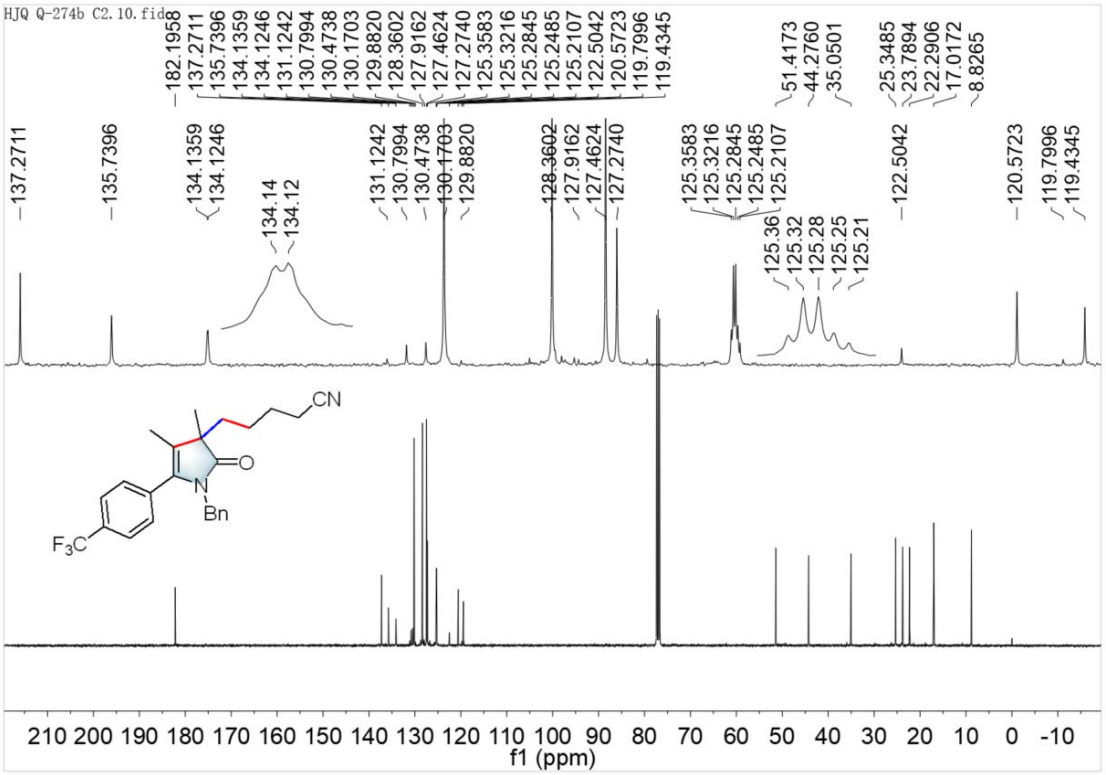
^{19}F NMR



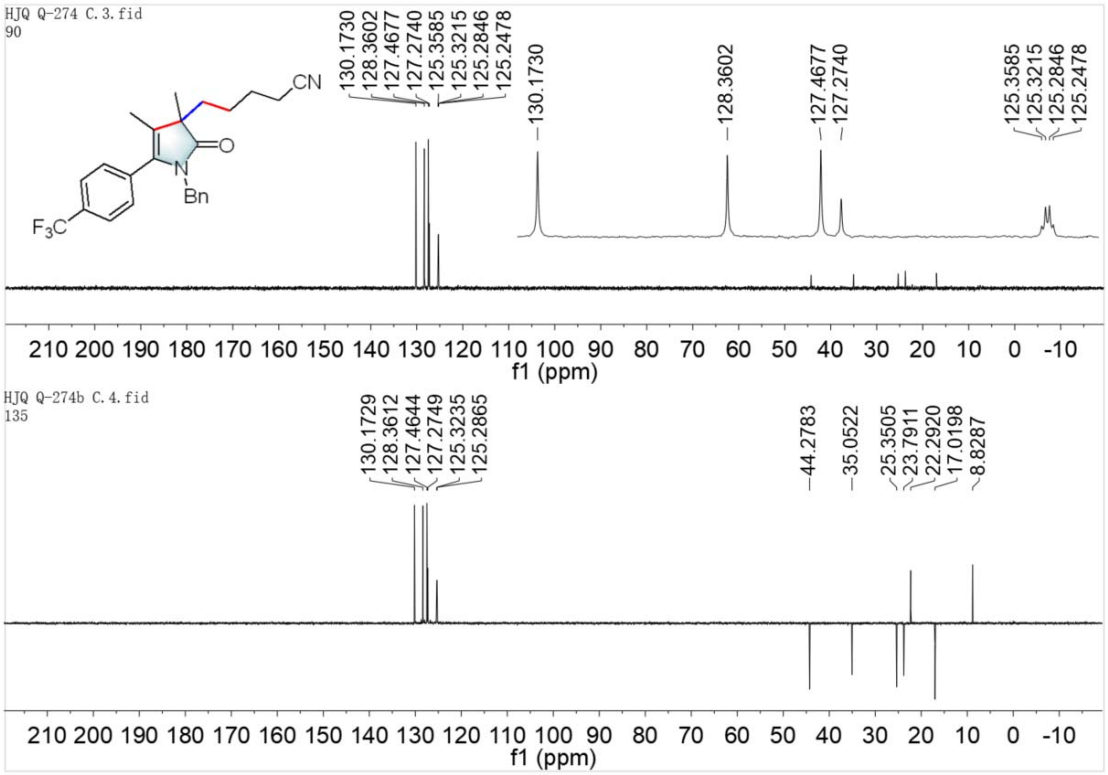
3d8, ^{1}H NMR



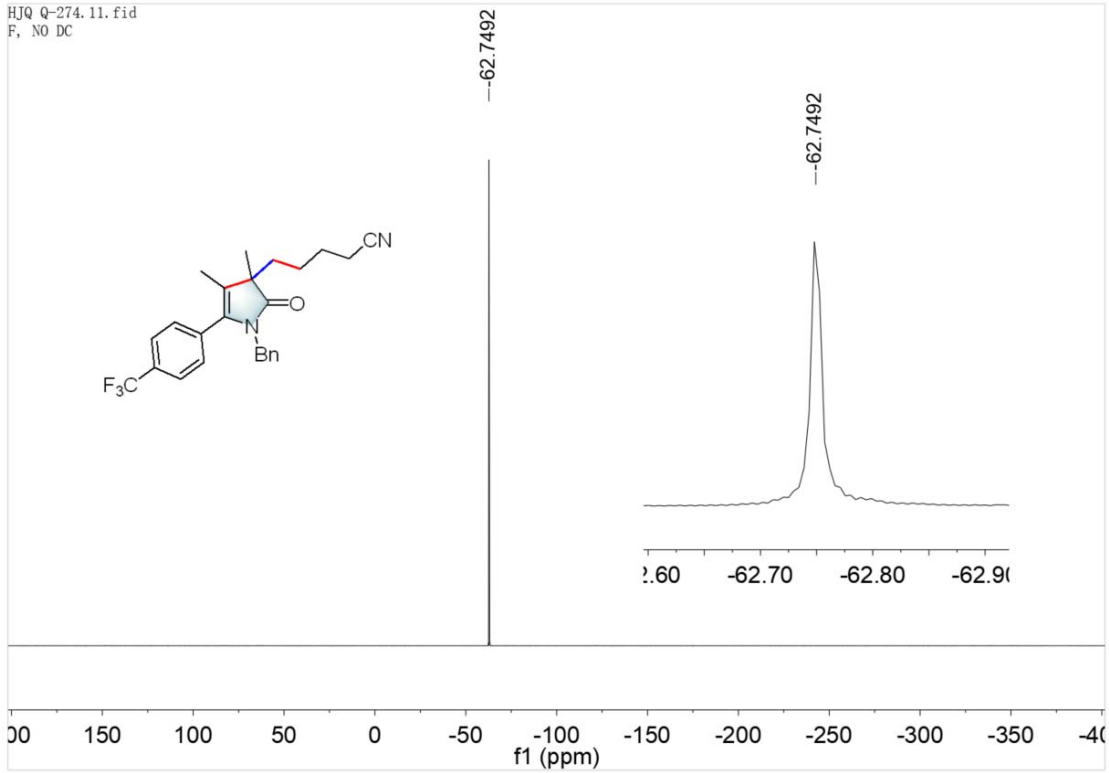
^{13}C NMR



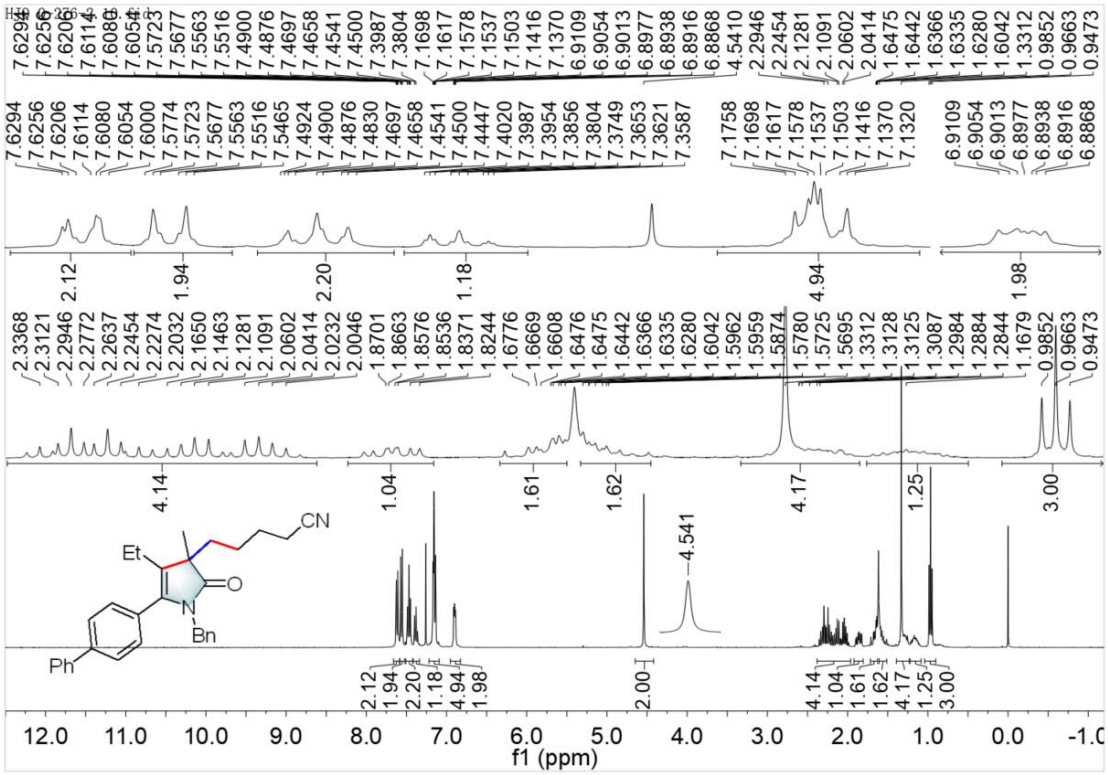
DEPT 90 and DEPT 135



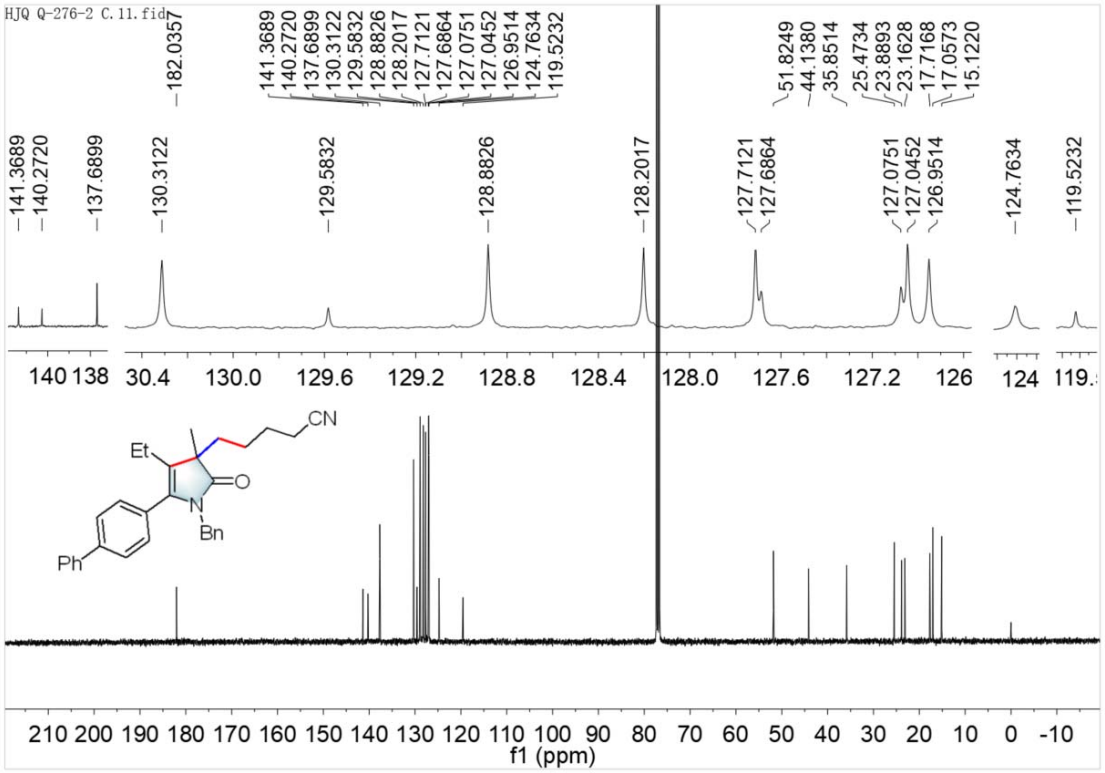
^{19}F NMR



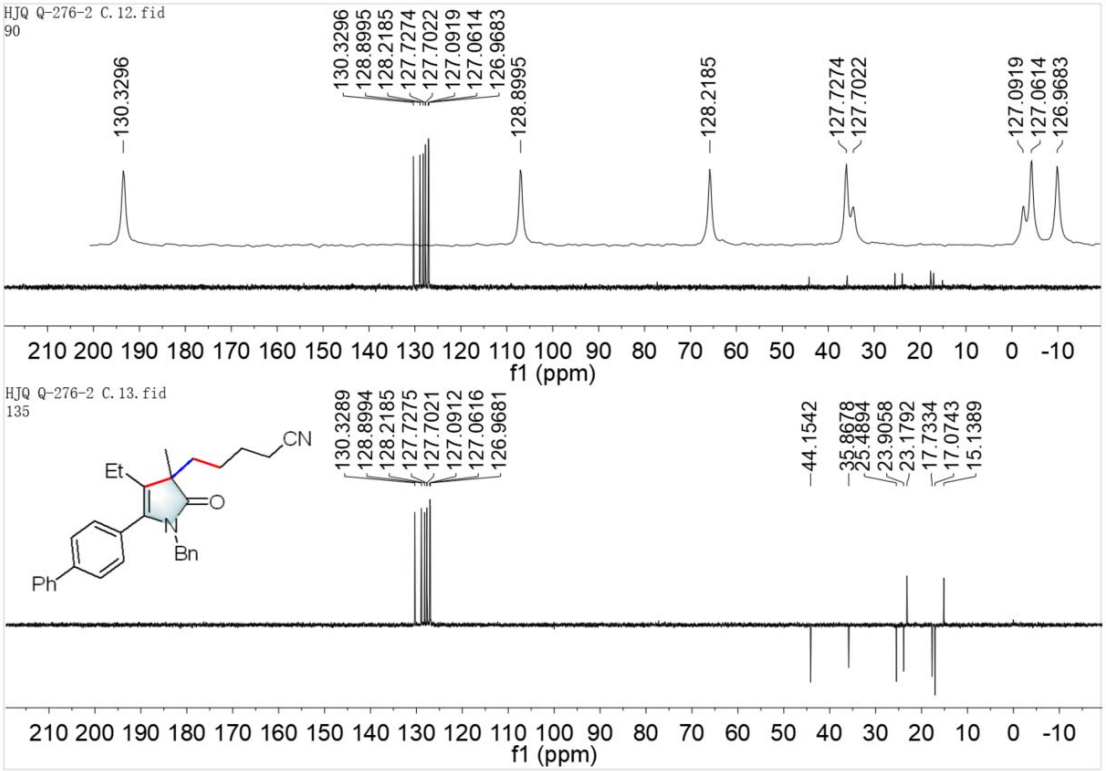
3d9, ^{1}H NMR



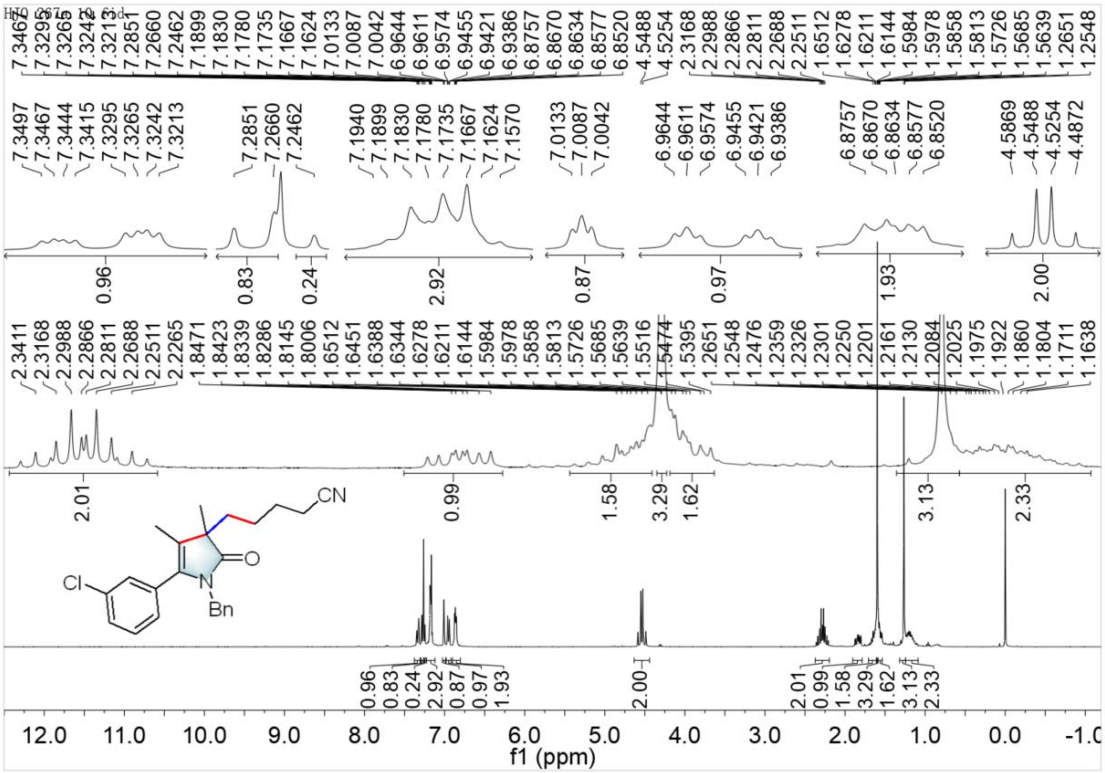
^{13}C NMR



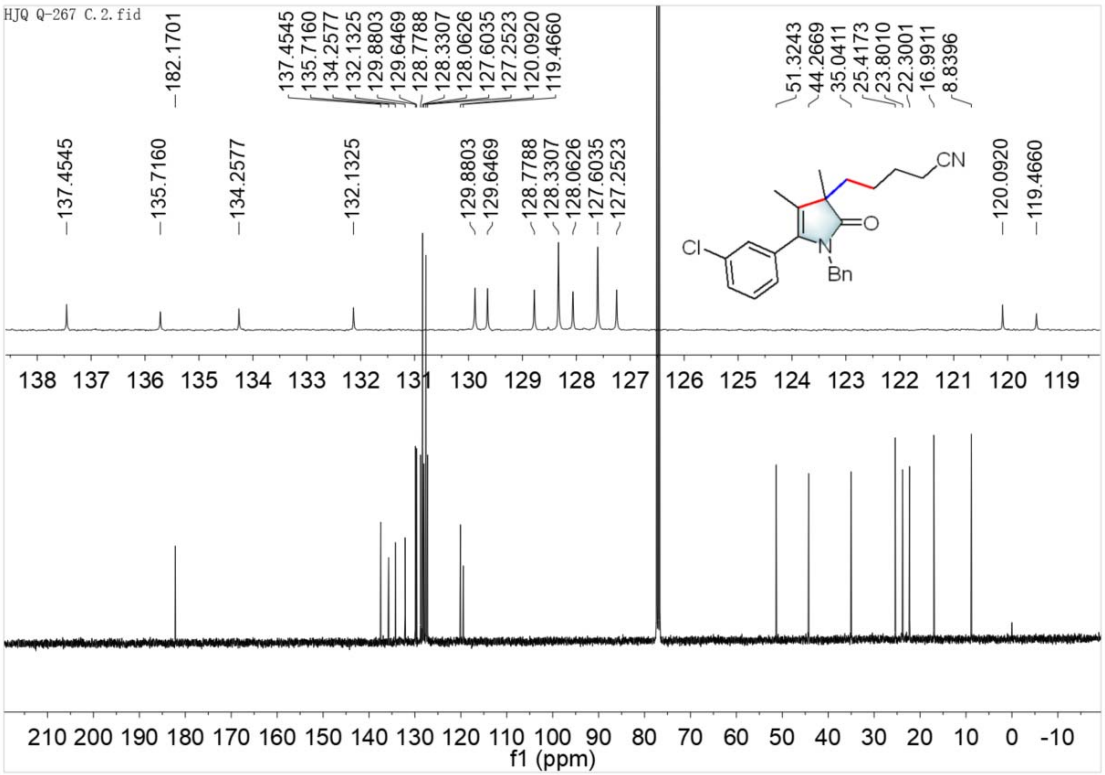
DEPT 90 and DEPT 135



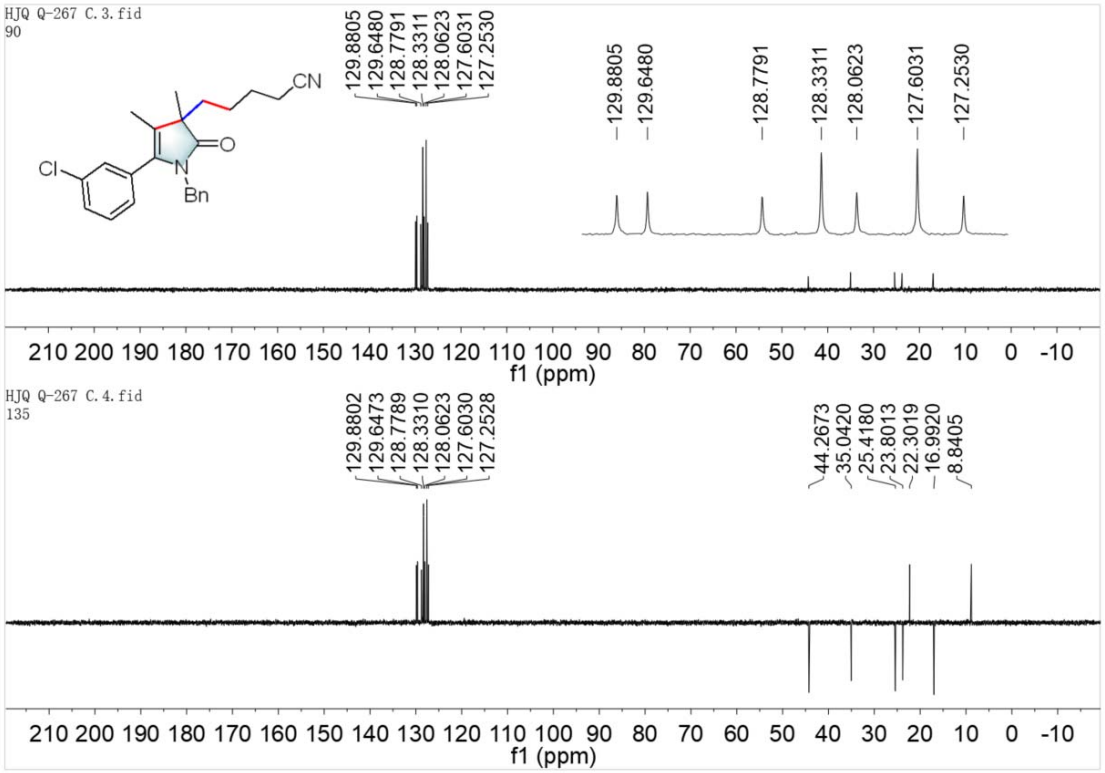
3d10, ^{1}H NMR



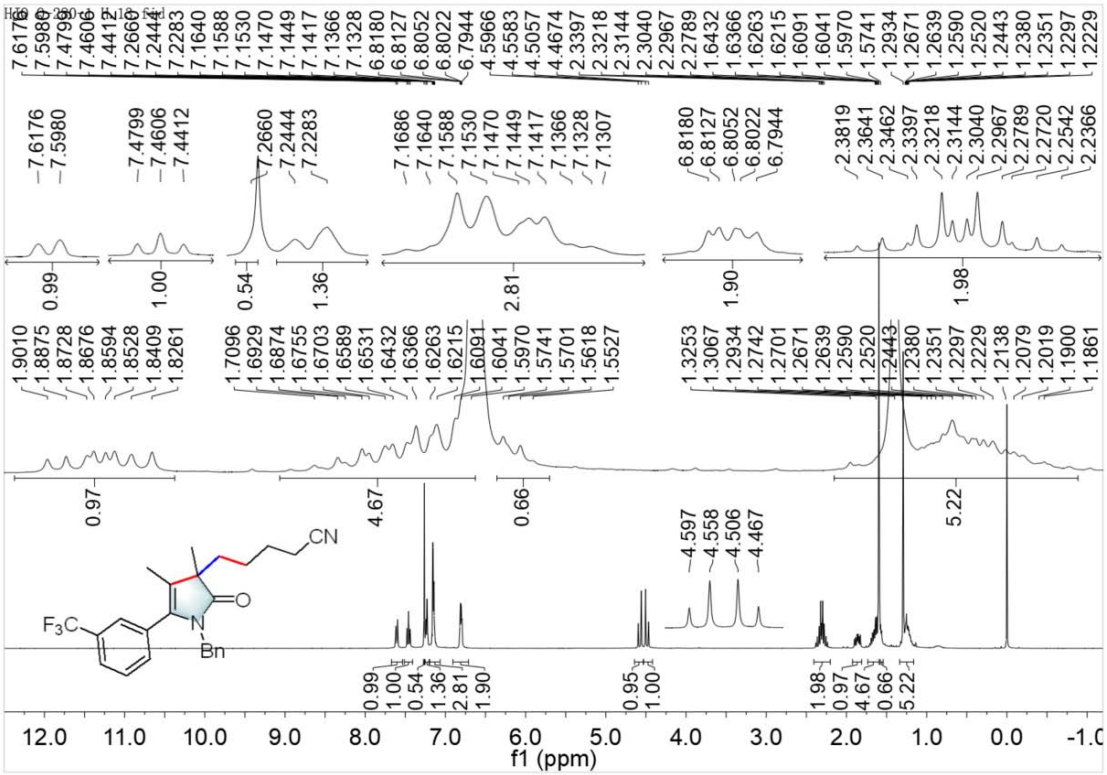
^{13}C NMR



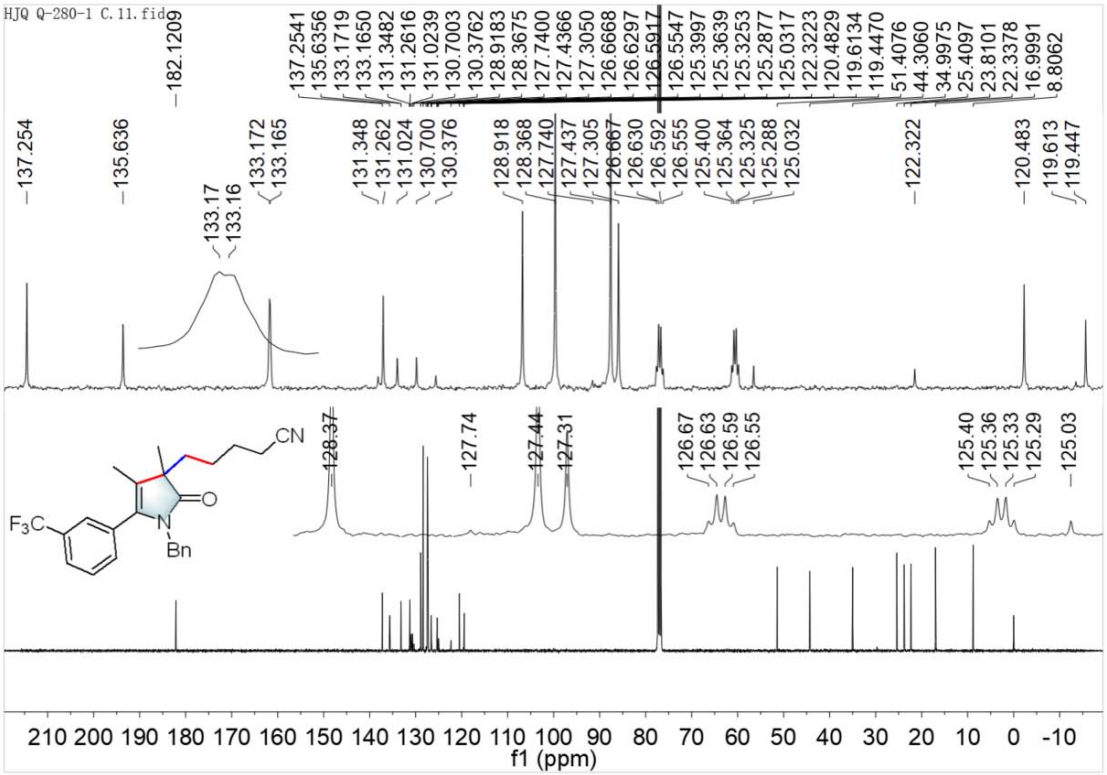
DEPT 90 and DEPT 135



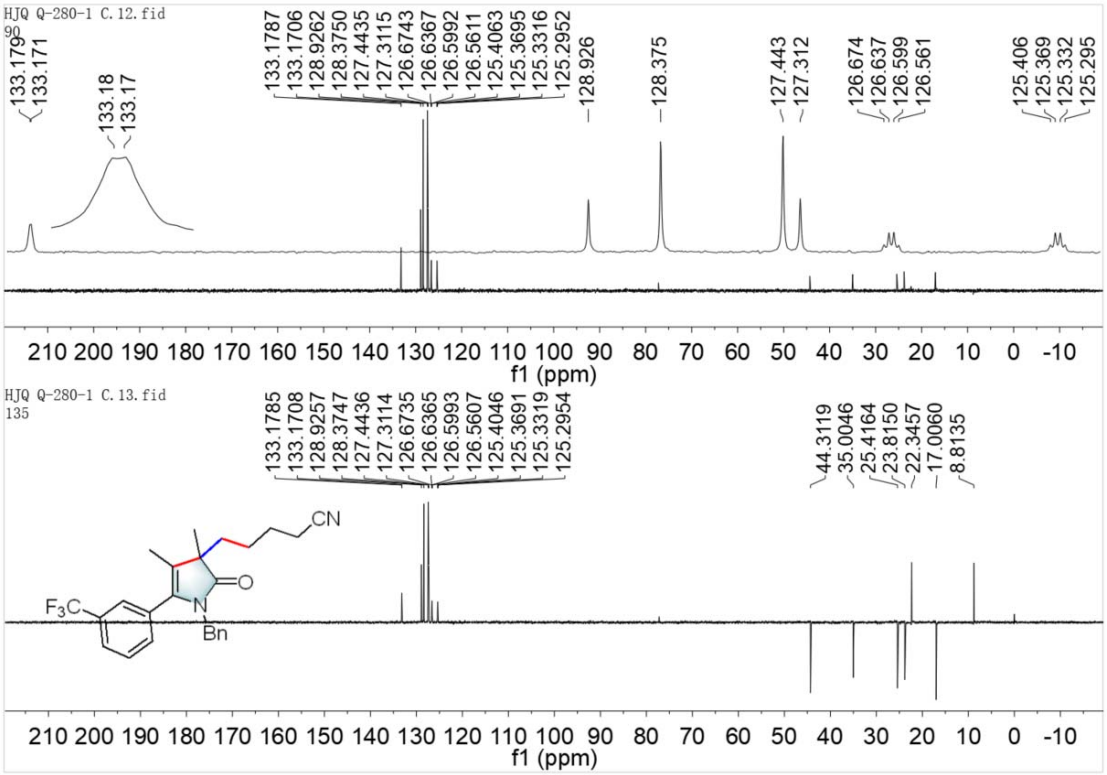
3d11, ^{1}H NMR



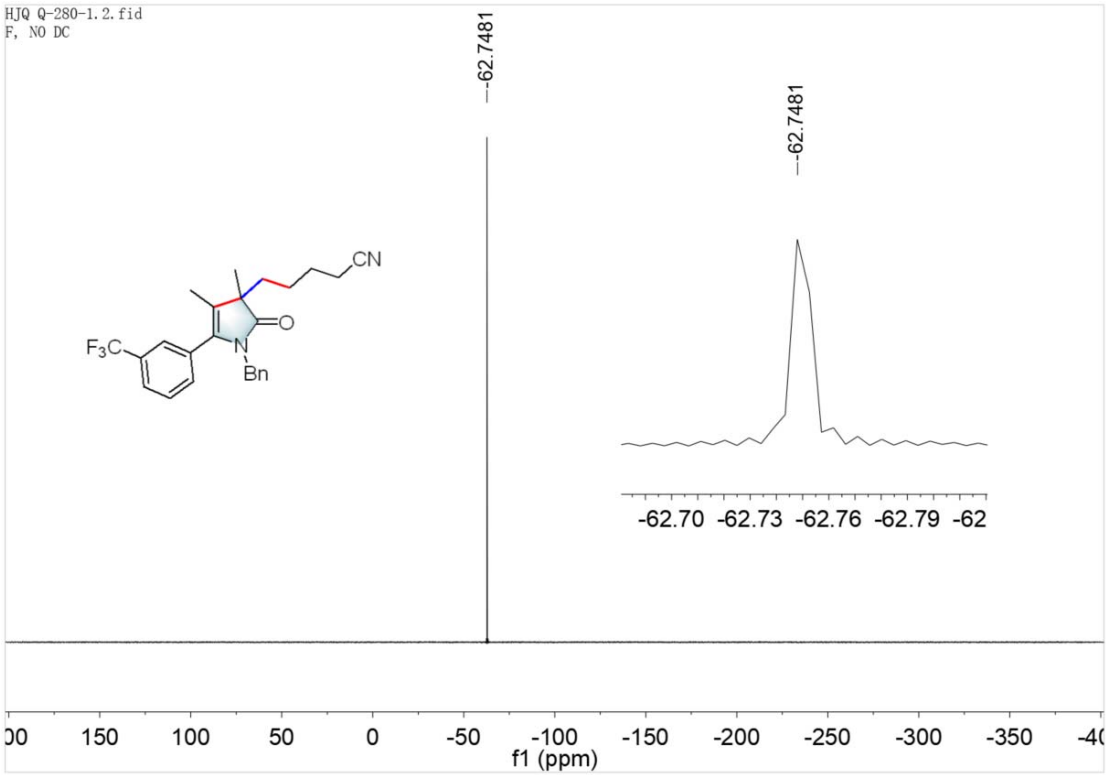
^{13}C NMR



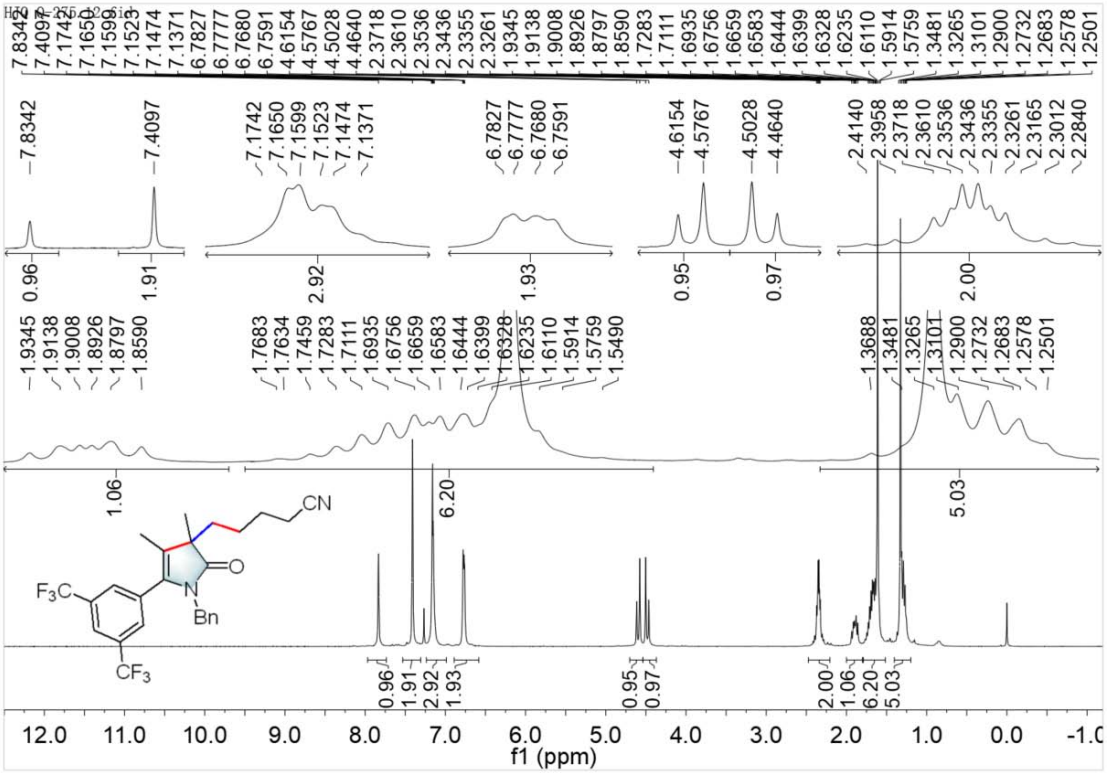
DEPT 90 and DEPT 135



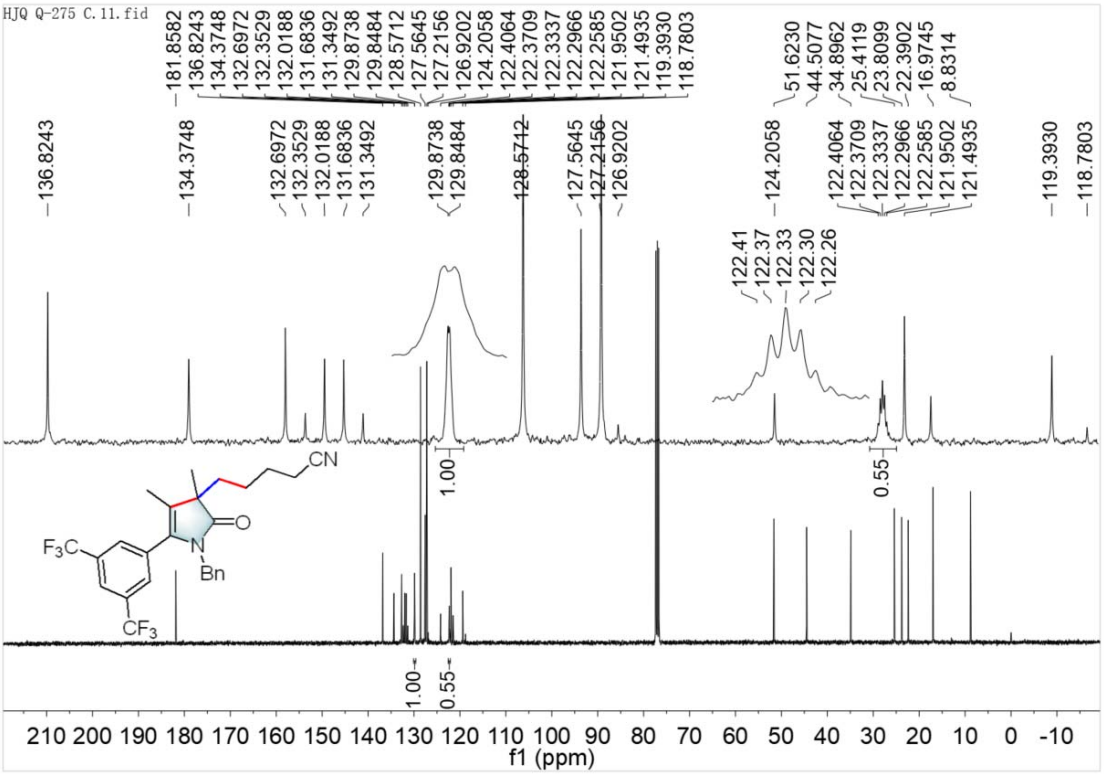
^{19}F NMR



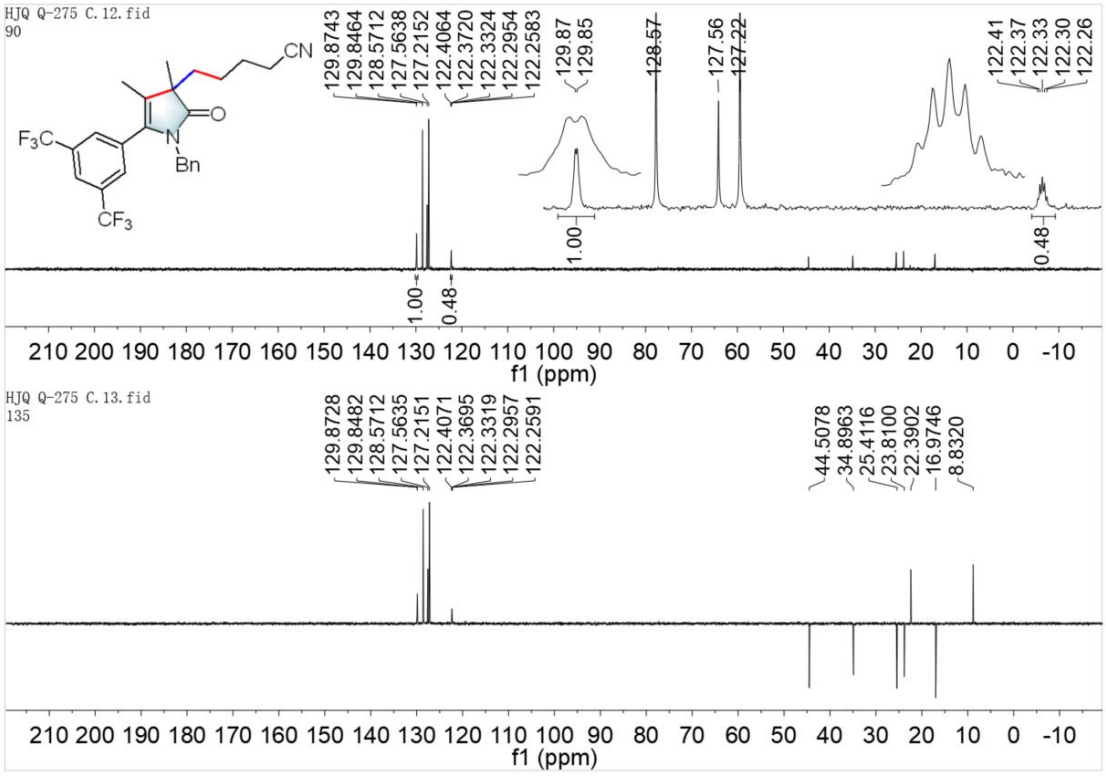
3d12, ^{1}H NMR



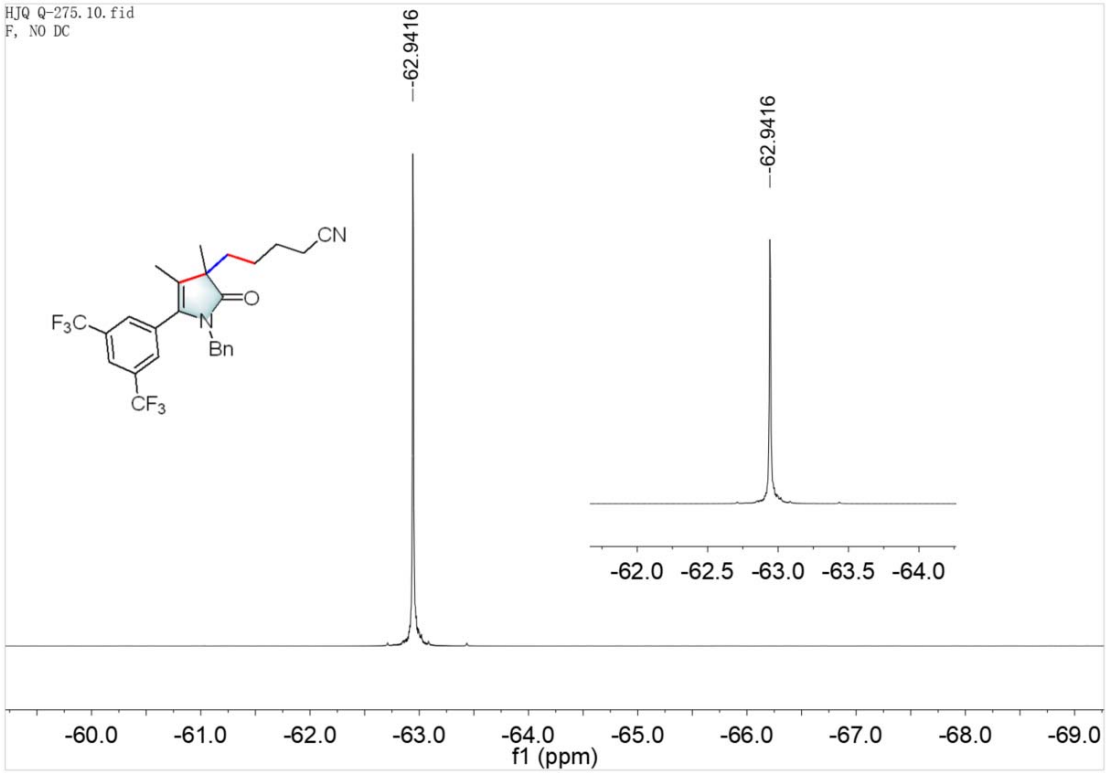
^{13}C NMR



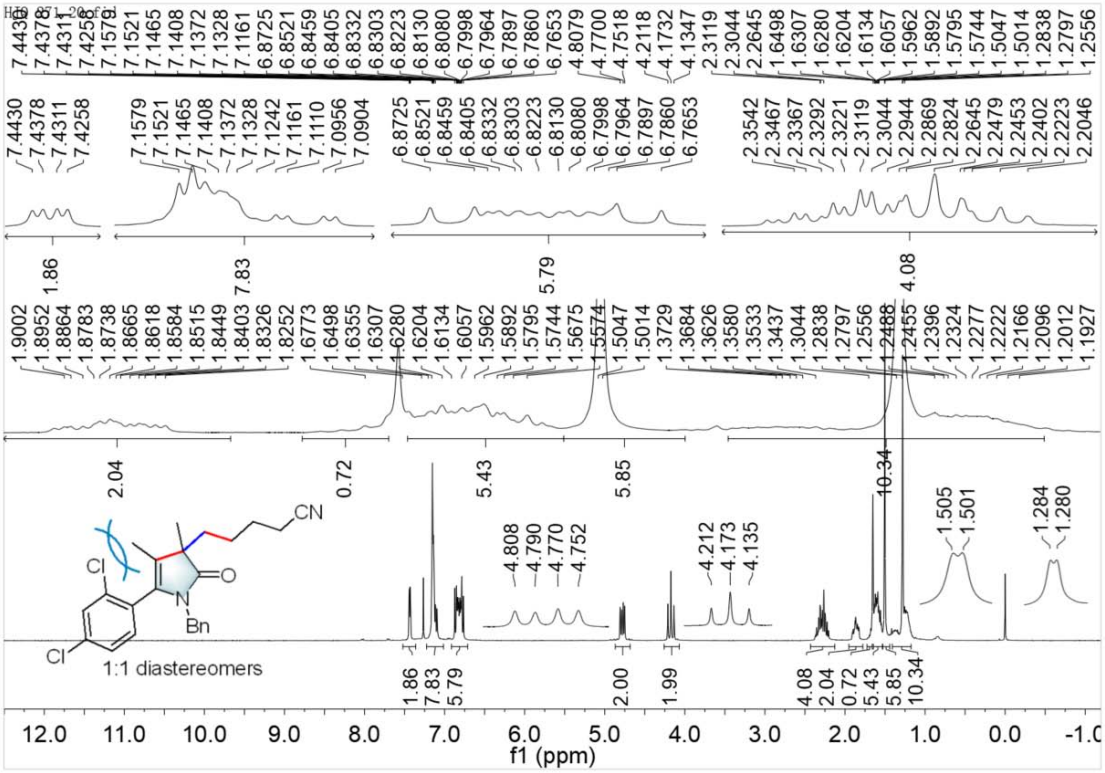
DEPT 90 and DEPT 135



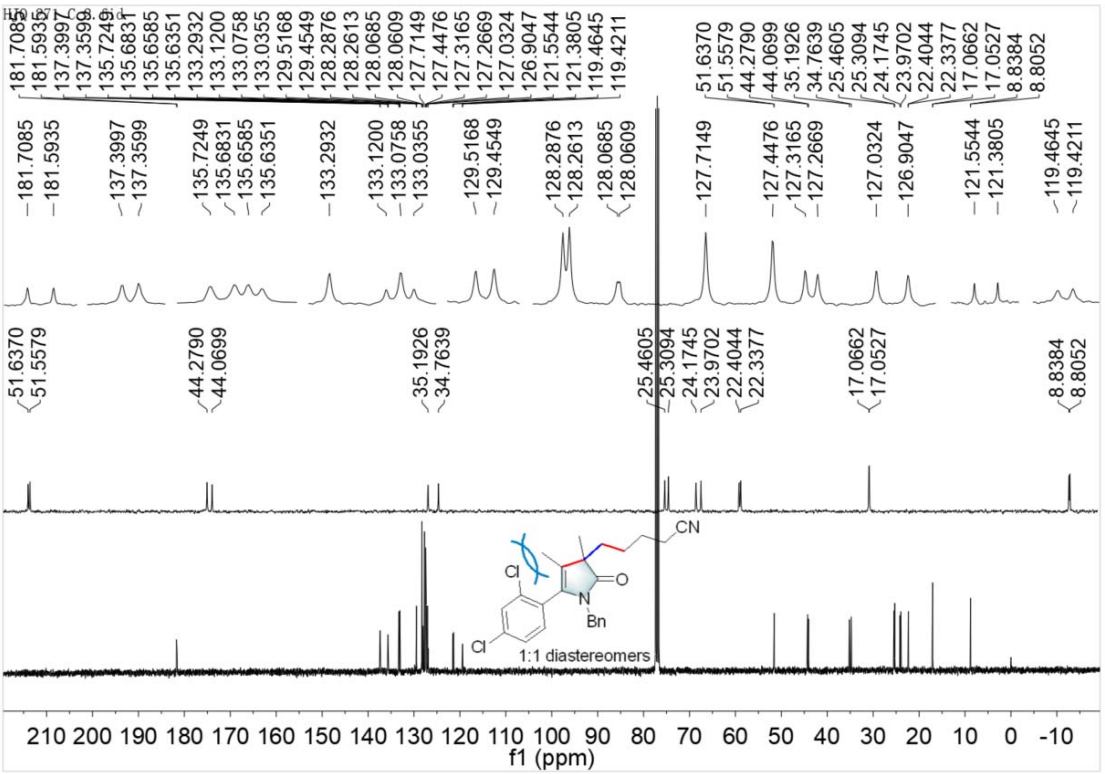
^{19}F NMR



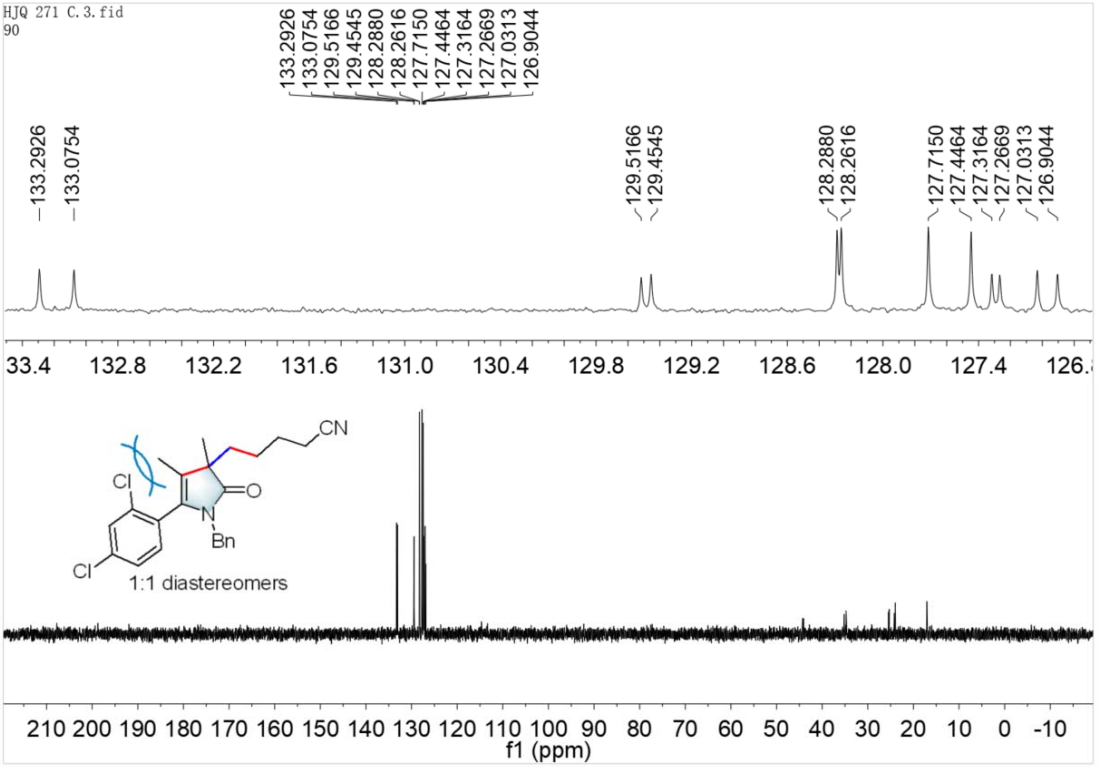
3d13, ^{1}H NMR



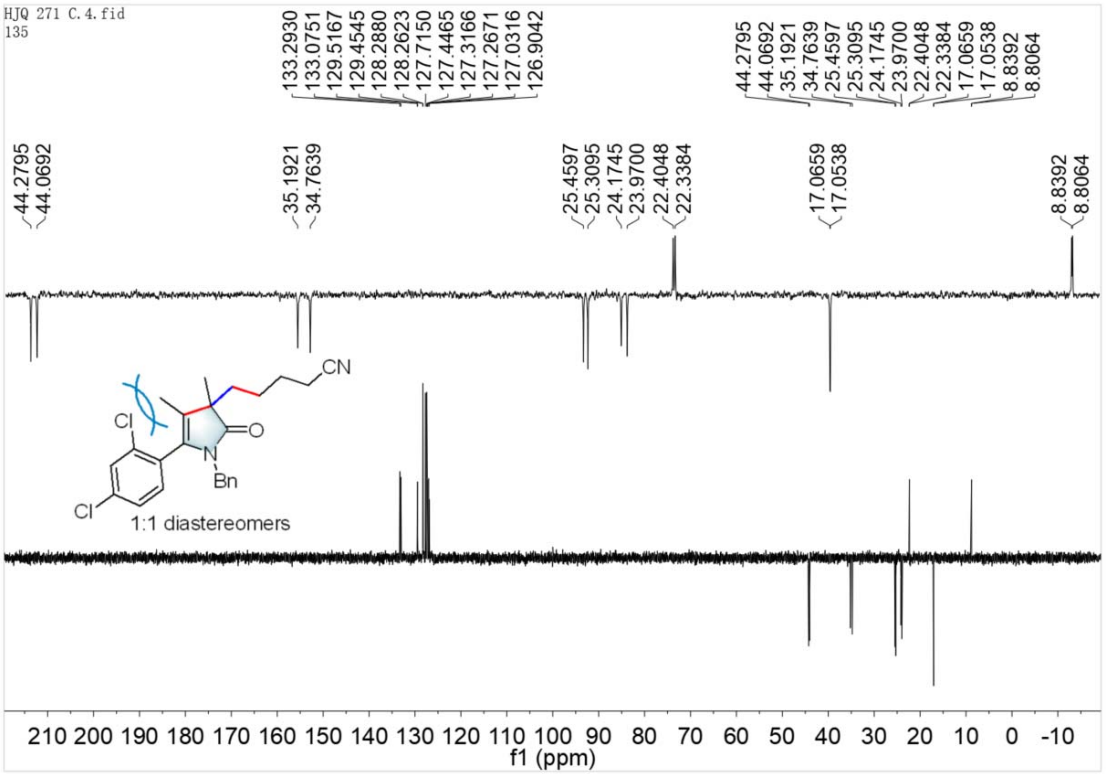
^{13}C NMR



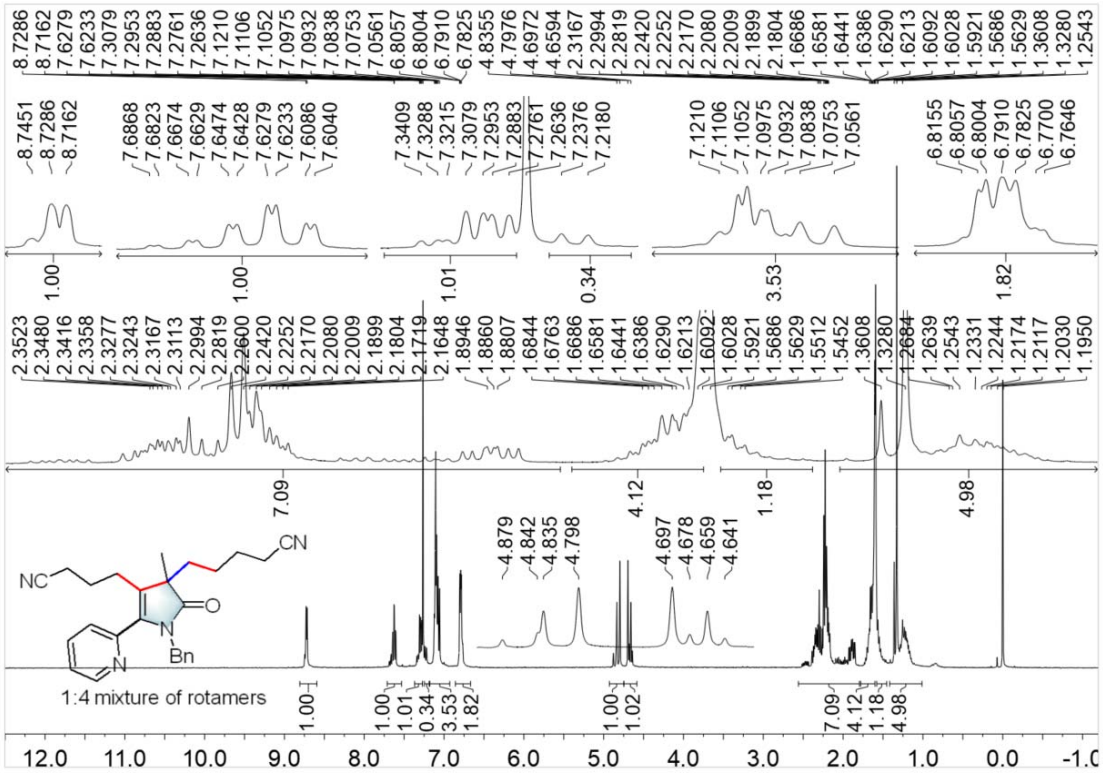
DEPT 90



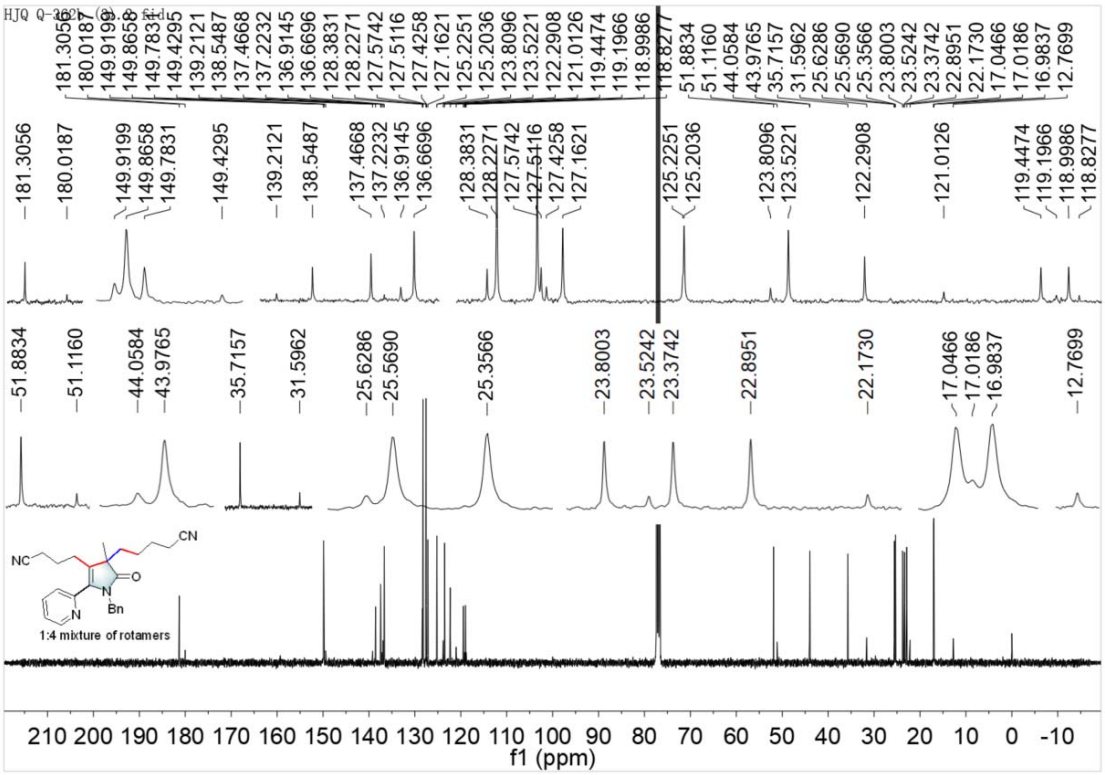
DEPT 135



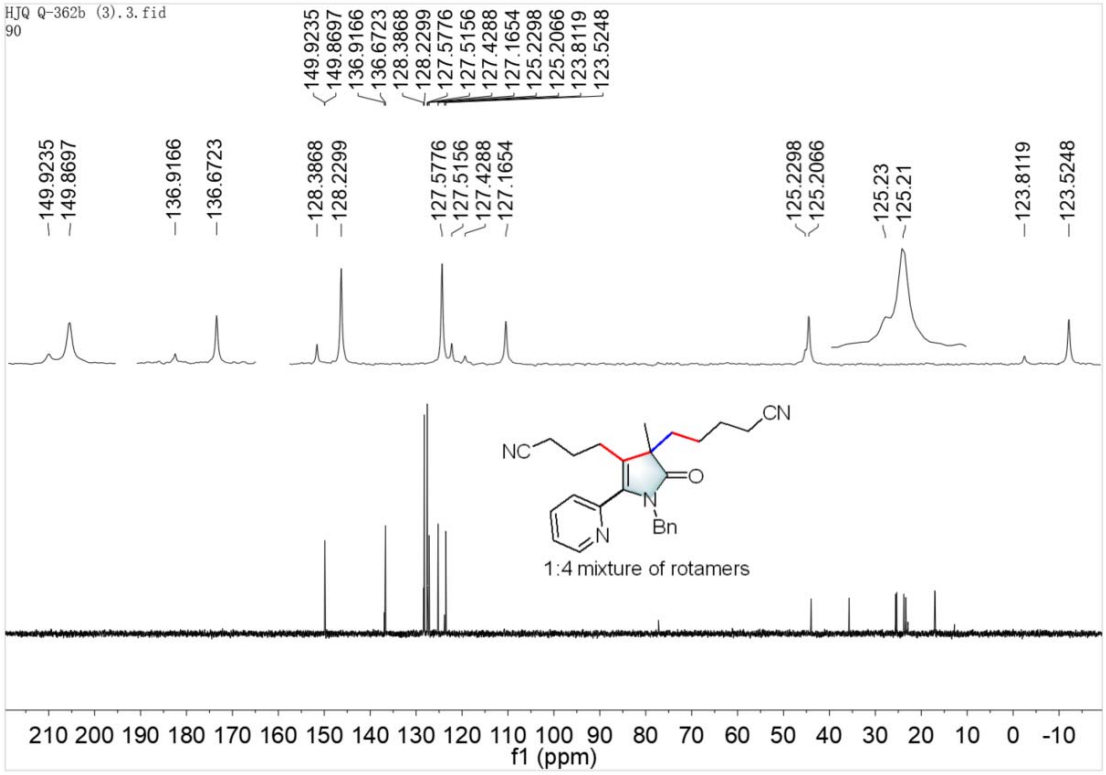
3e, ^{1}H NMR



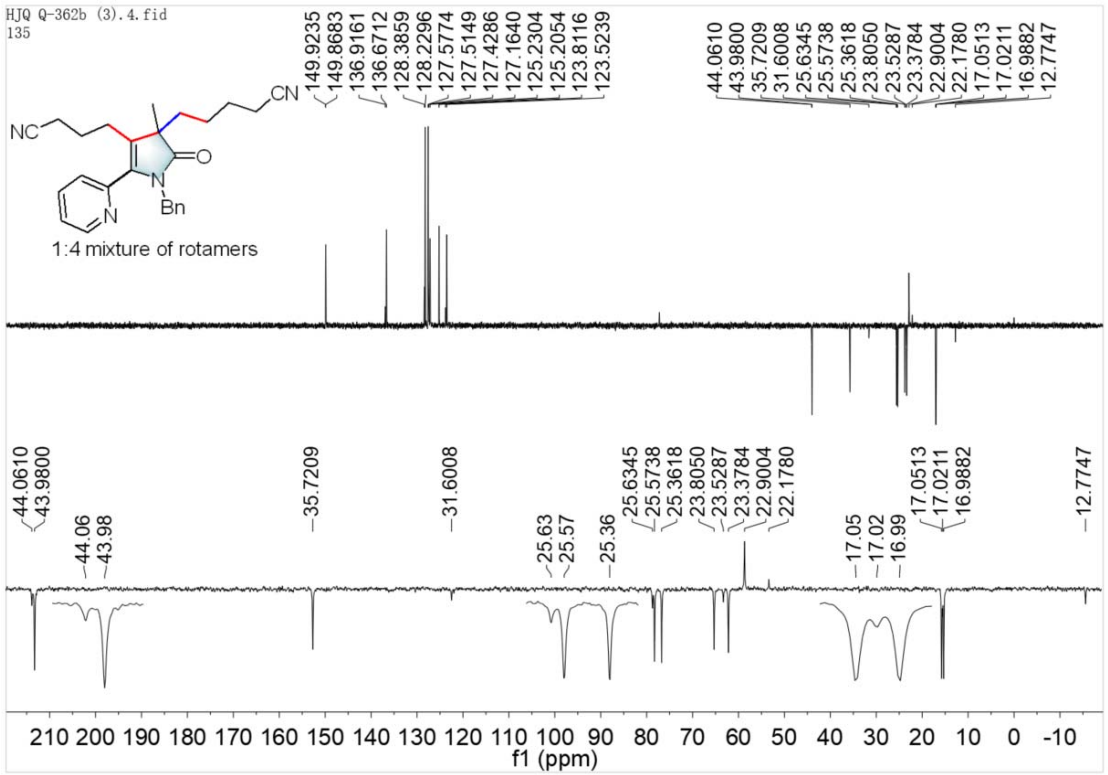
^{13}C NMR



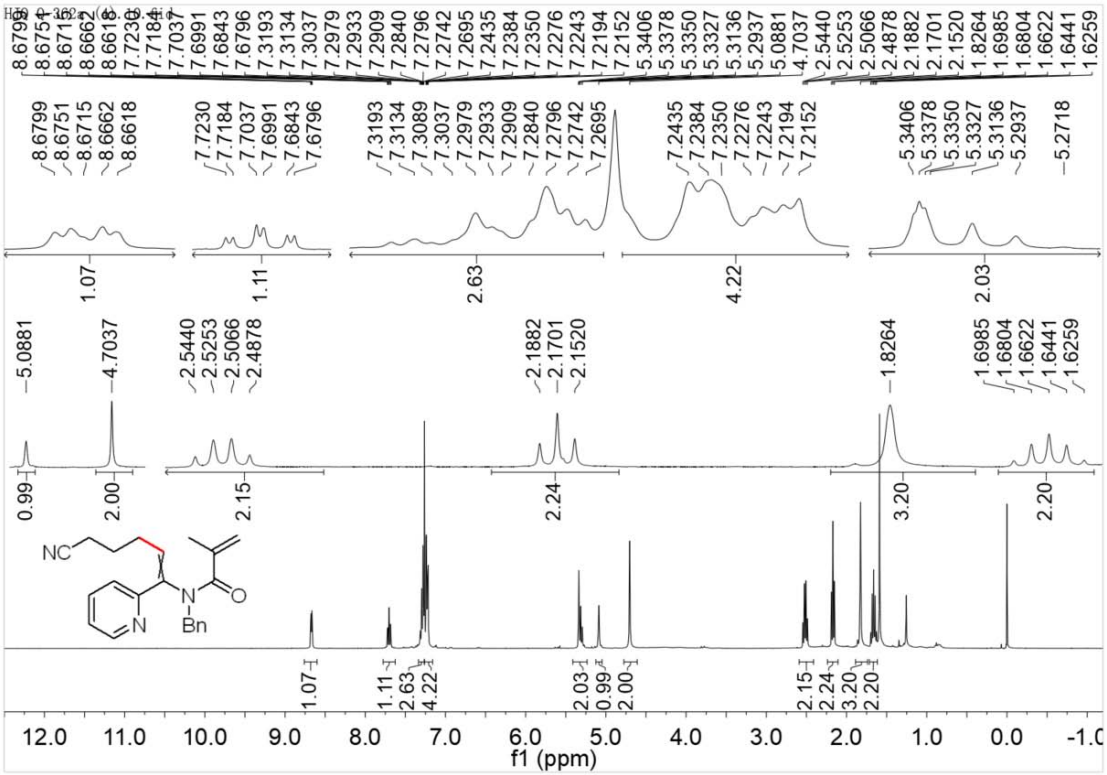
DEPT 90



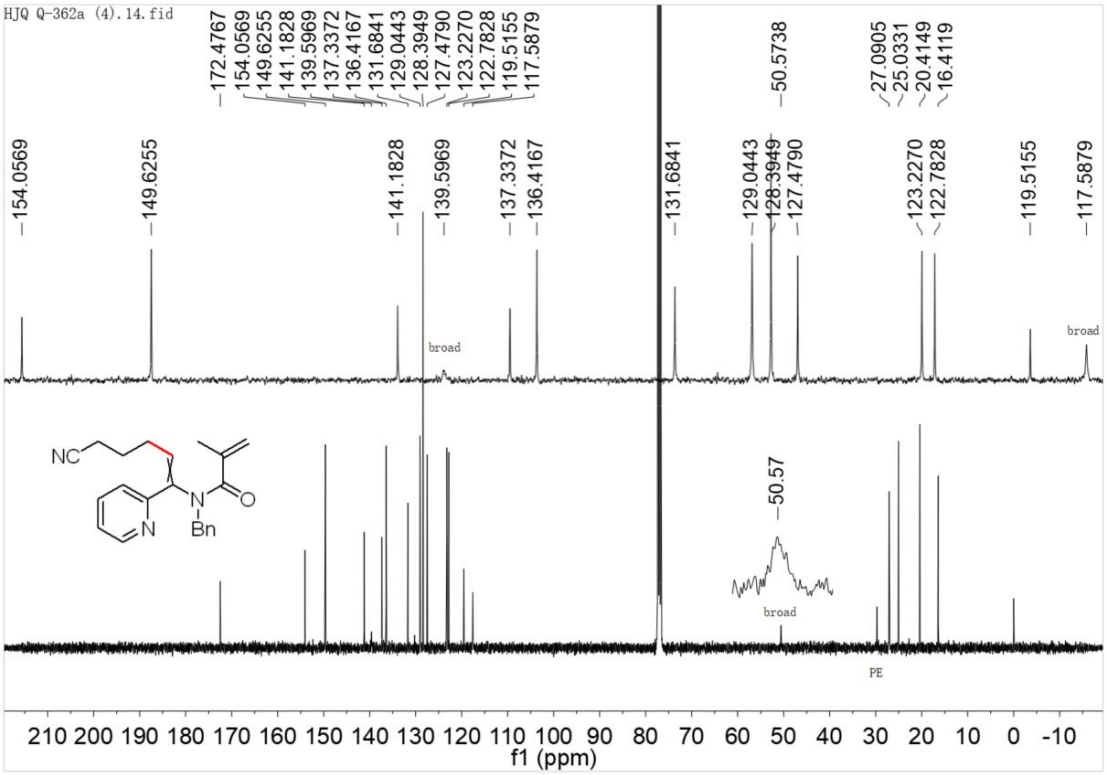
DEPT 135



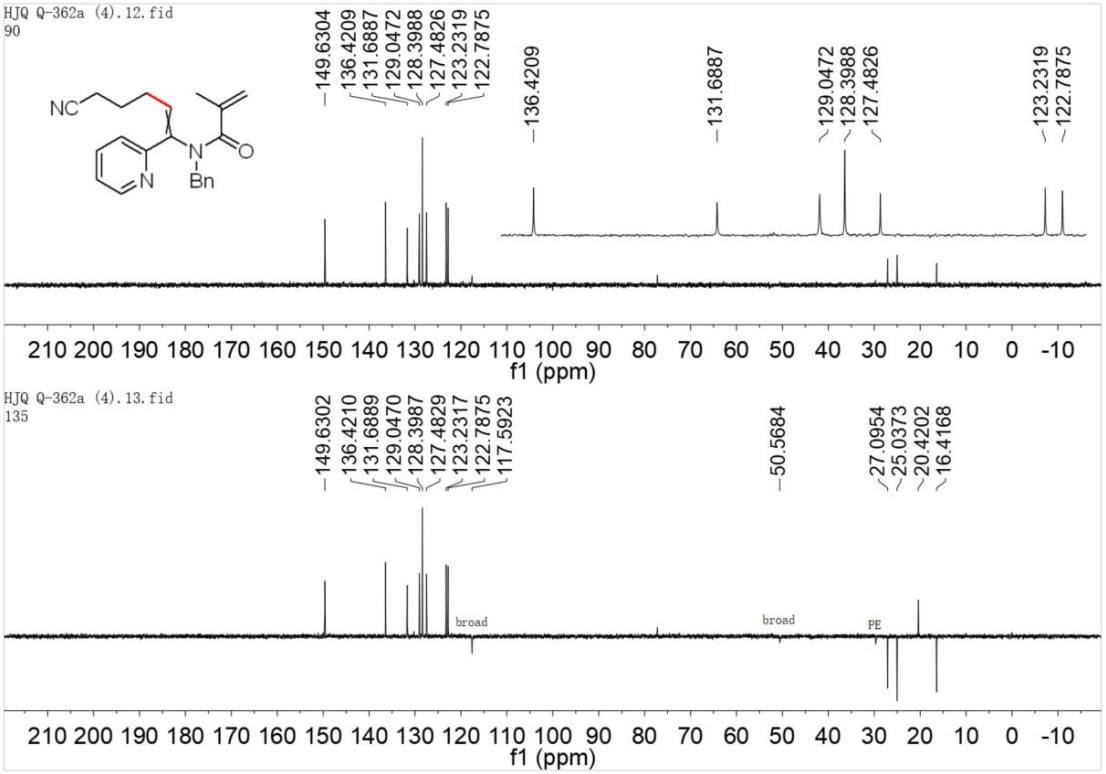
3e', ^{1}H NMR



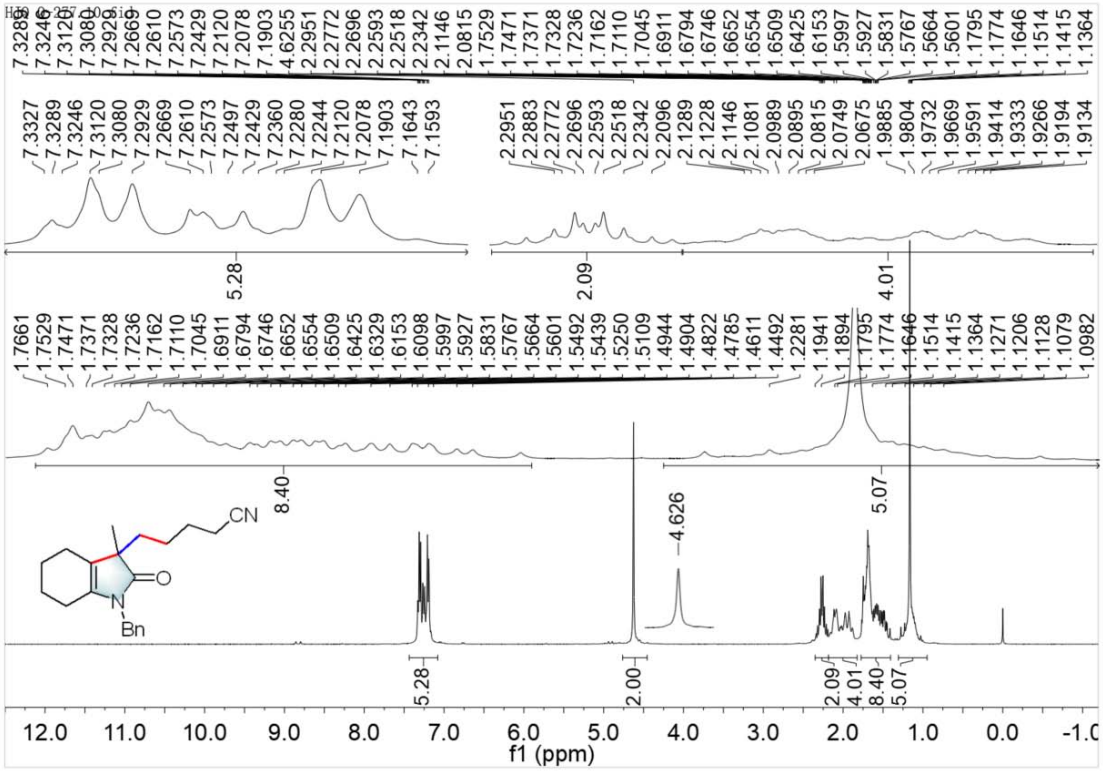
^{13}C NMR



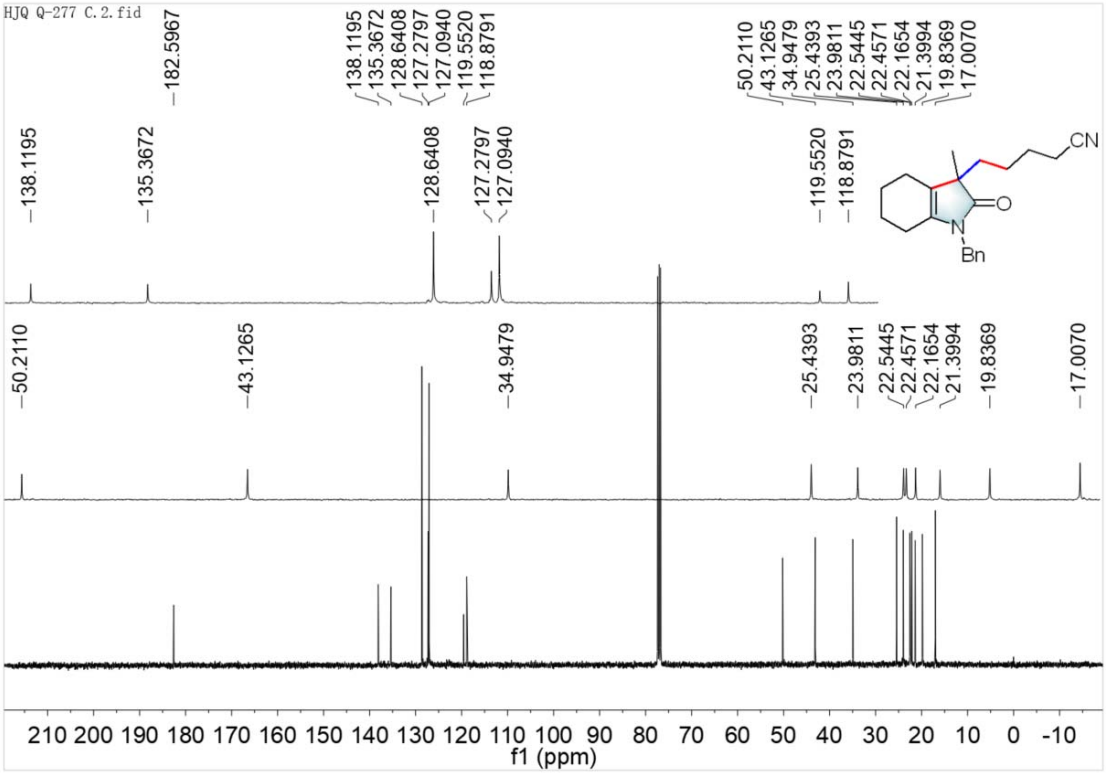
DEPT 90 and DEPT 135



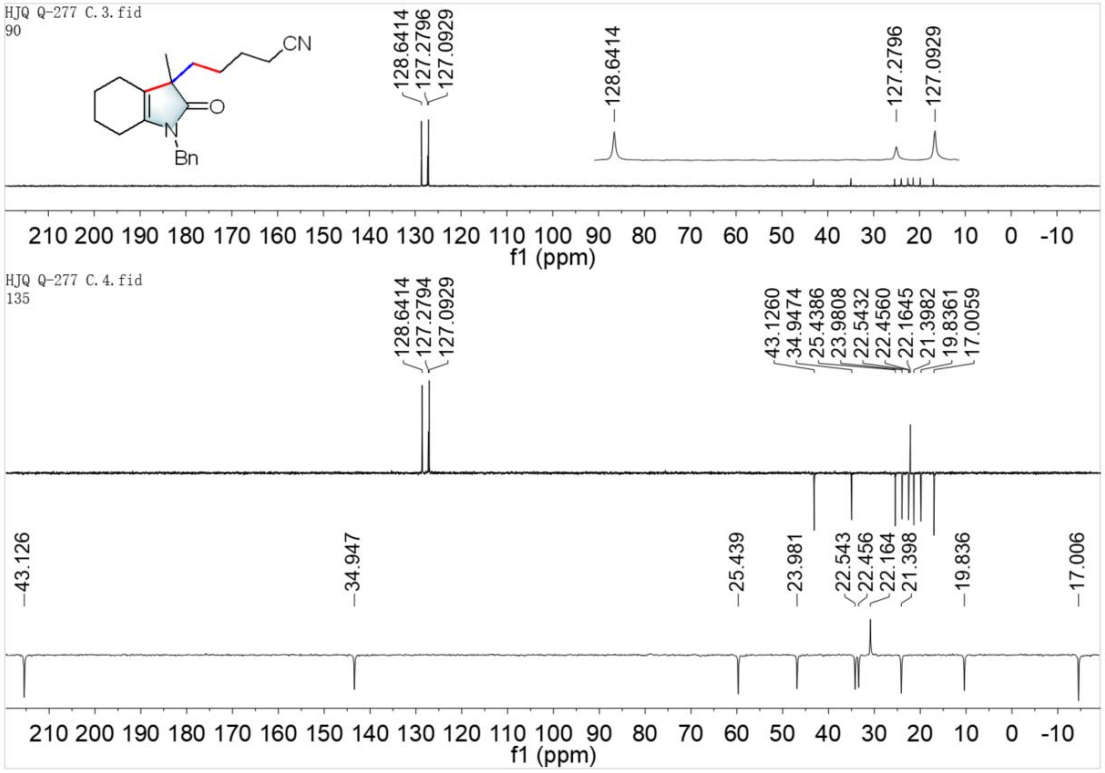
3f, ^{1}H NMR



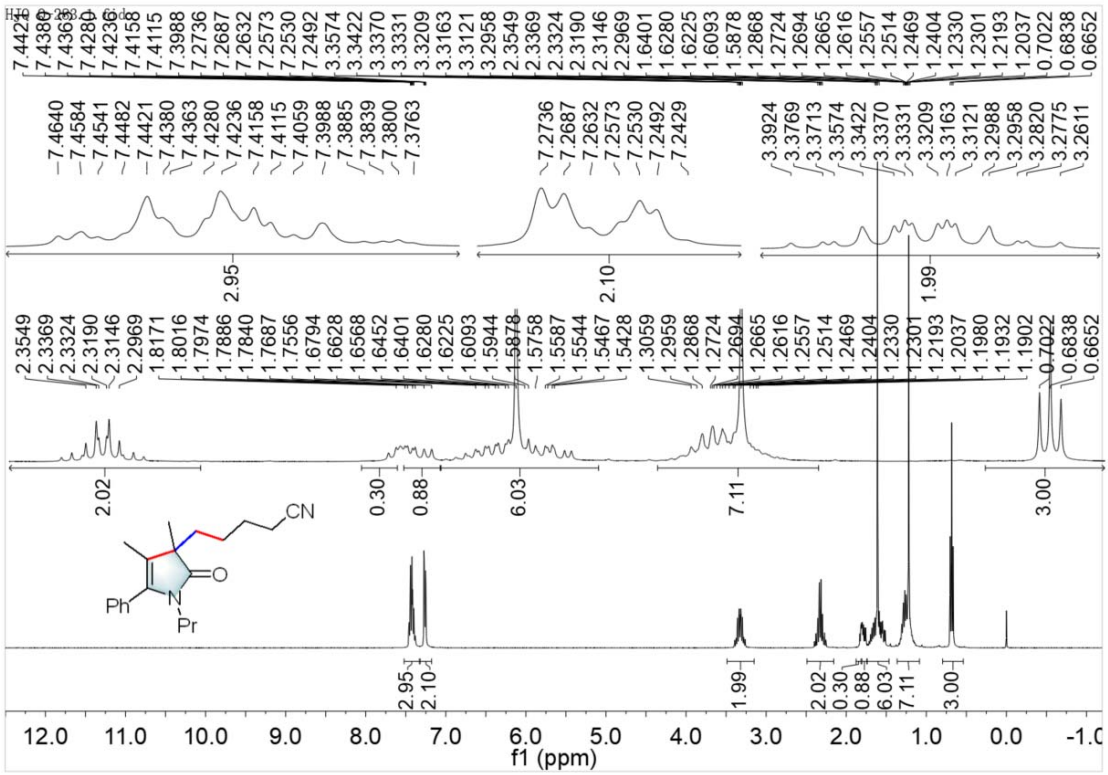
^{13}C NMR



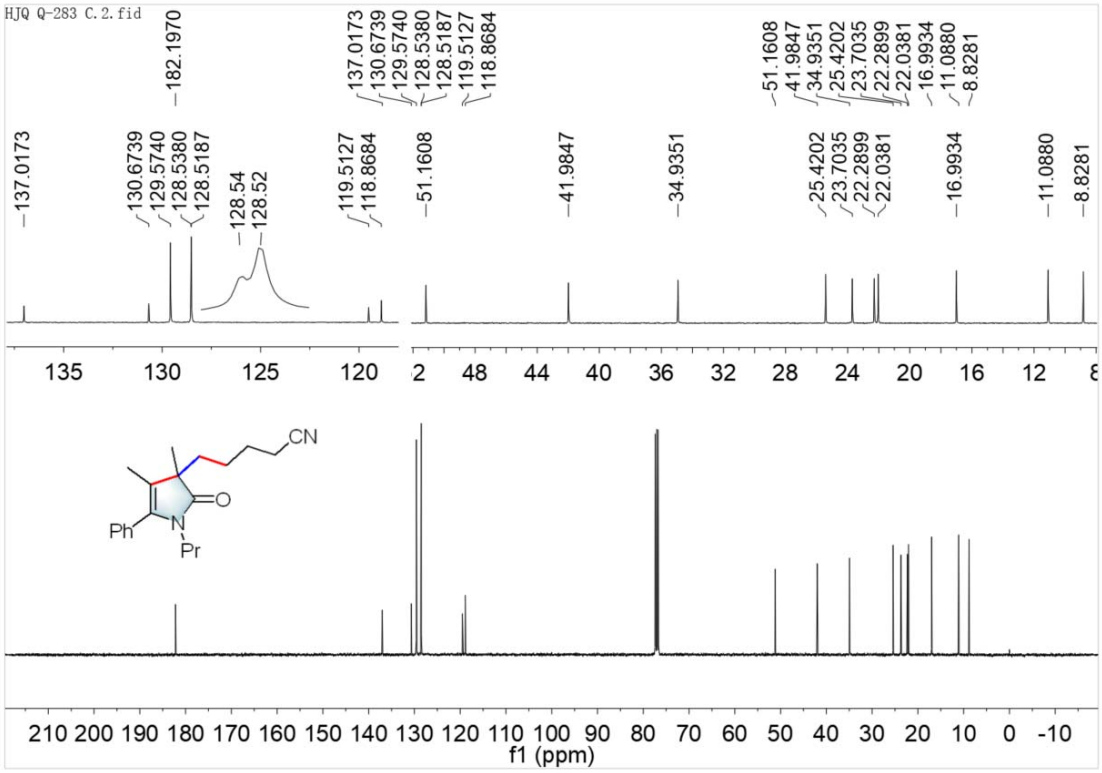
DEPT 90 and DEPT 135



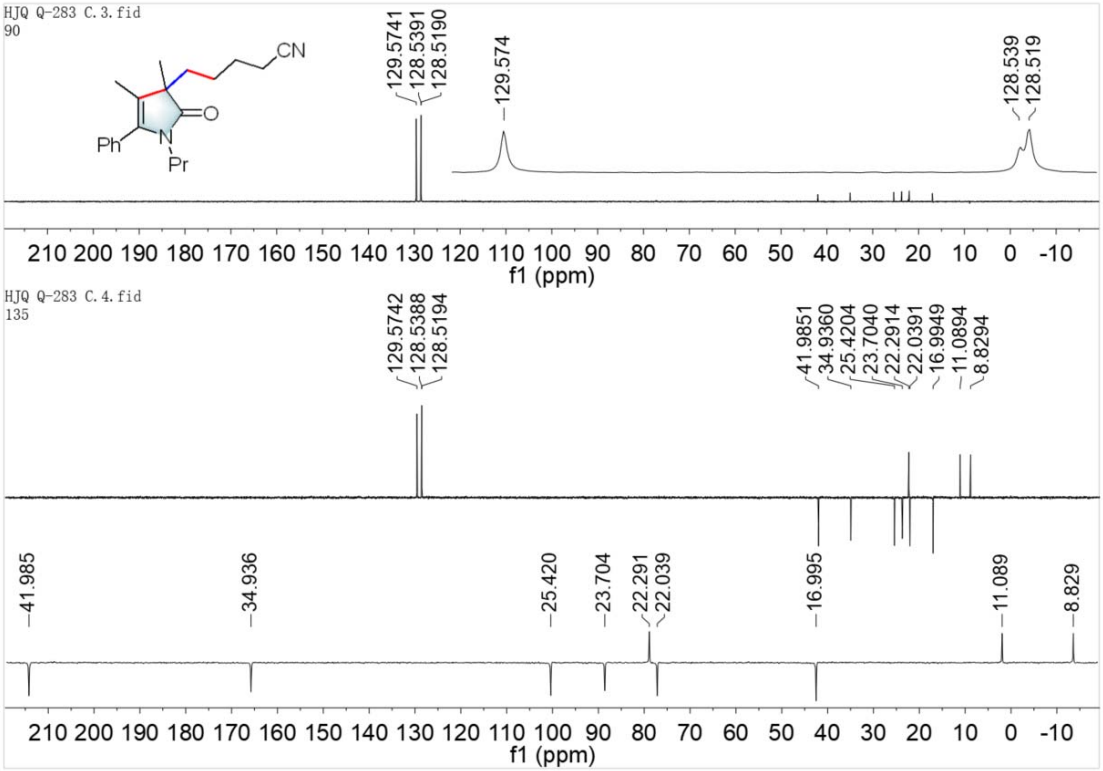
3g1, ^{1}H NMR



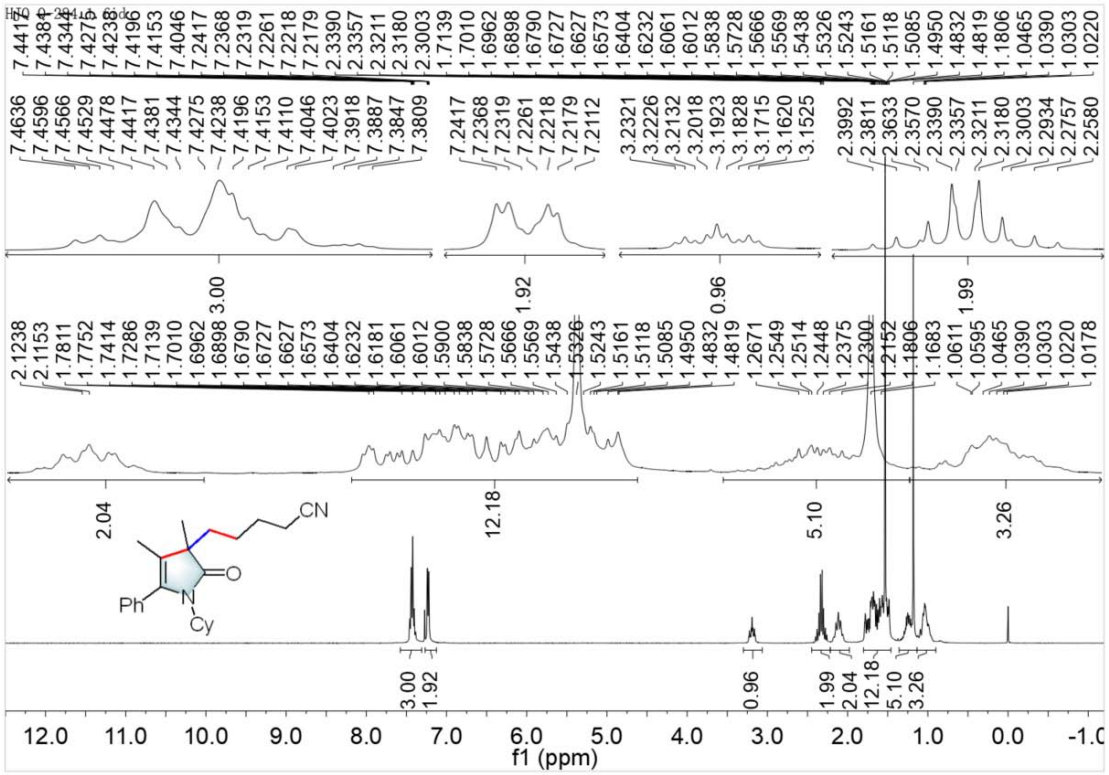
^{13}C NMR



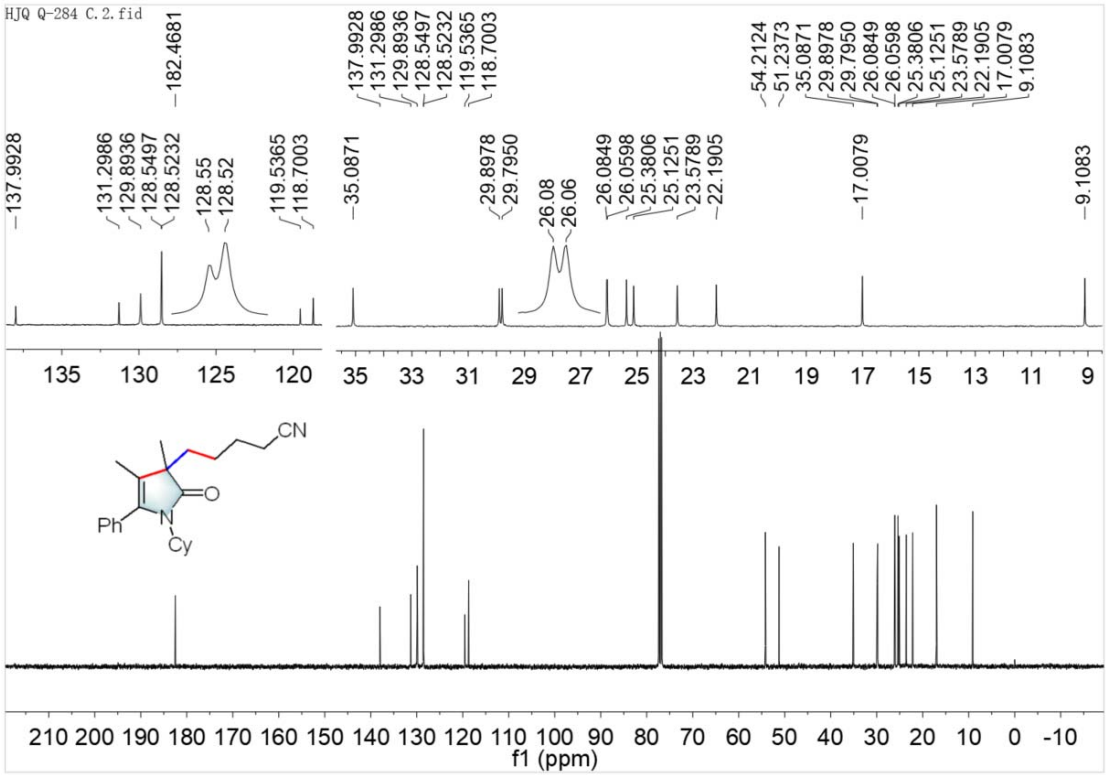
DEPT 90 and DEPT 135



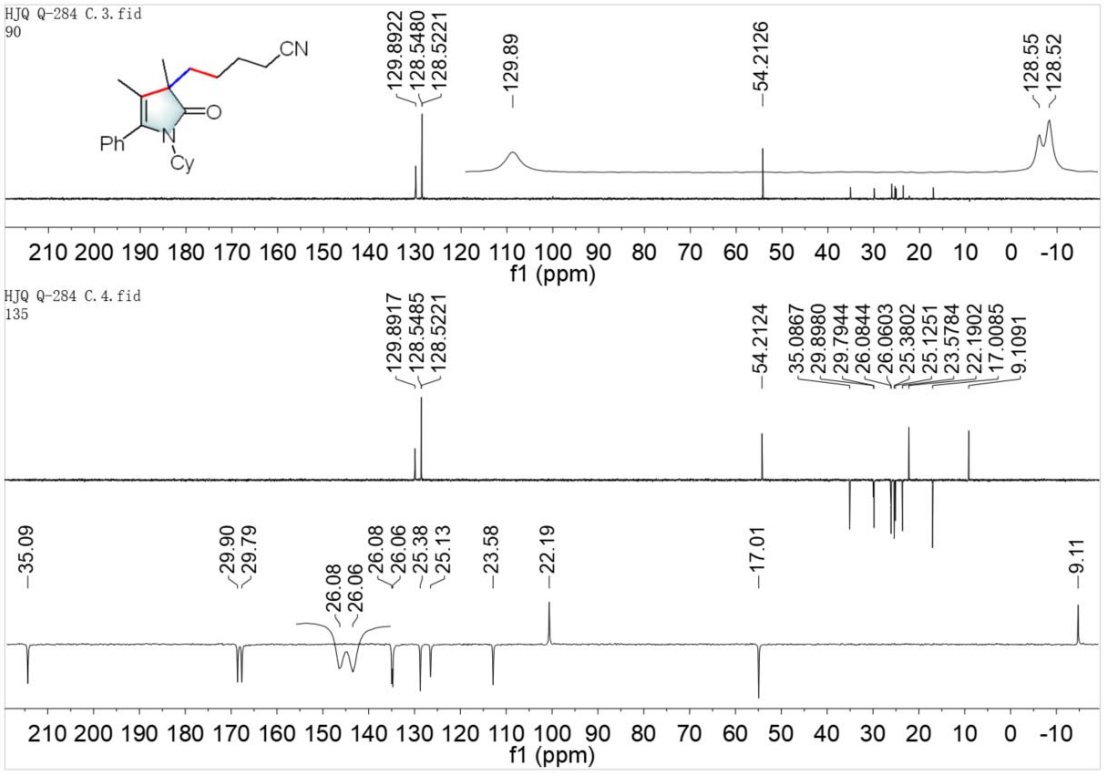
3g2, ^{1}H NMR



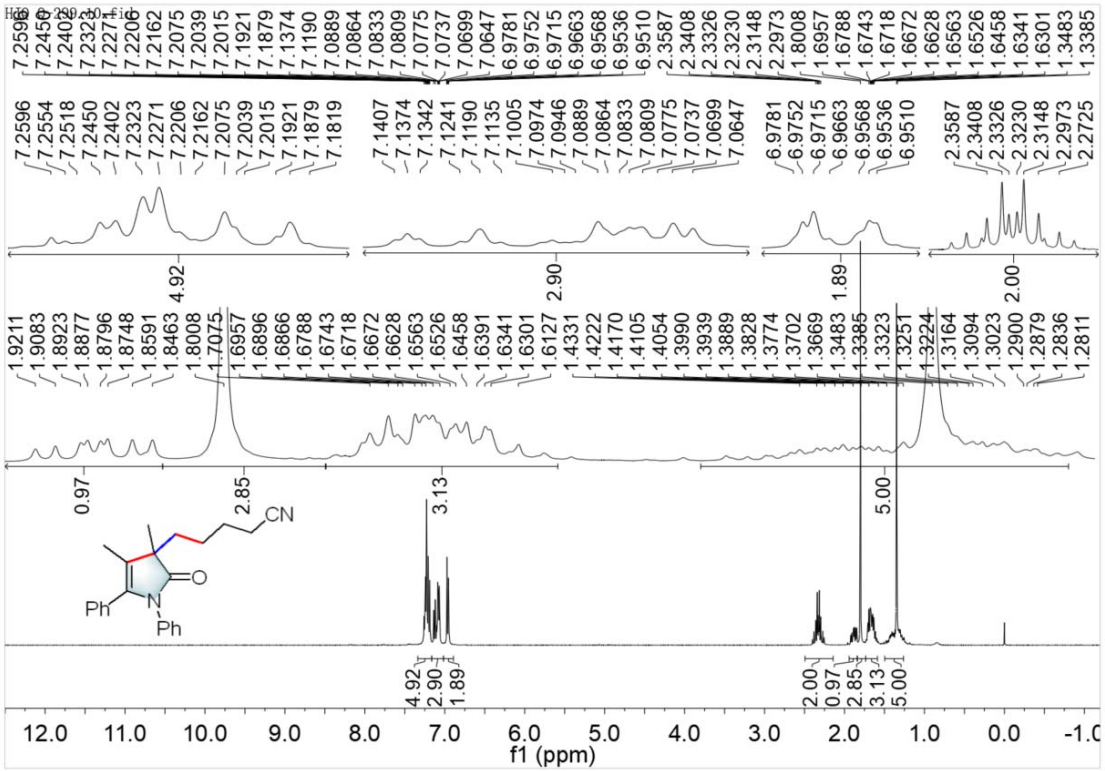
^{13}C NMR



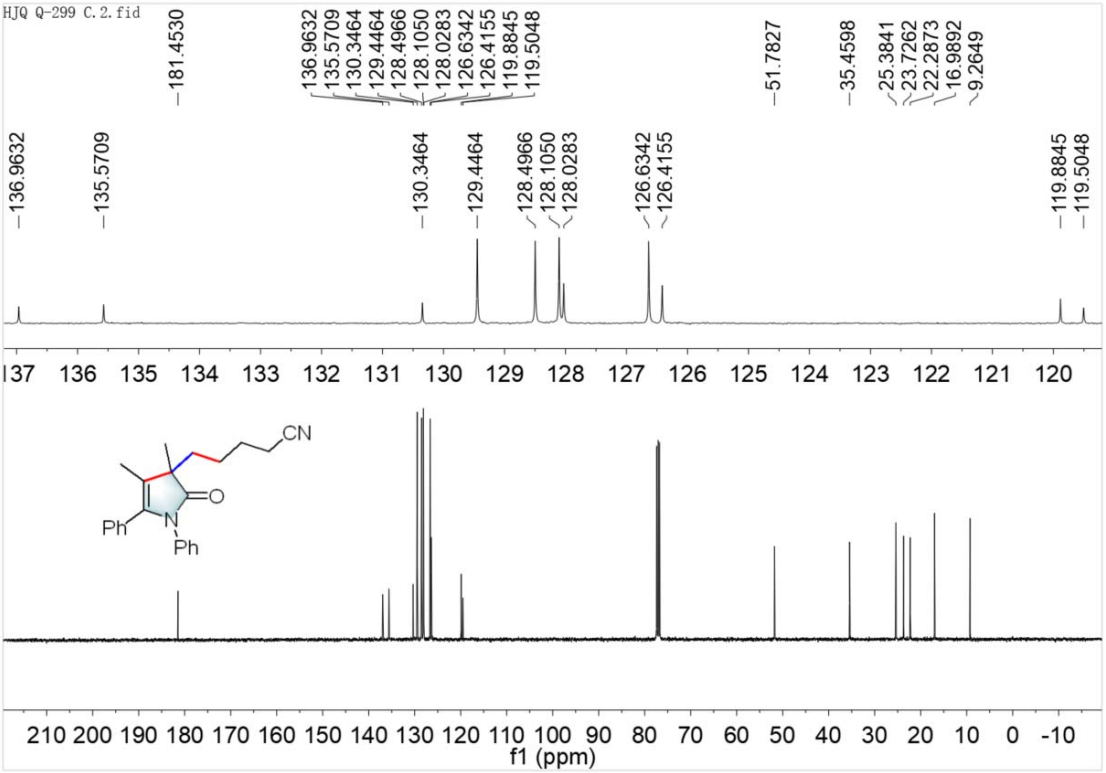
DEPT 90 and DEPT 135



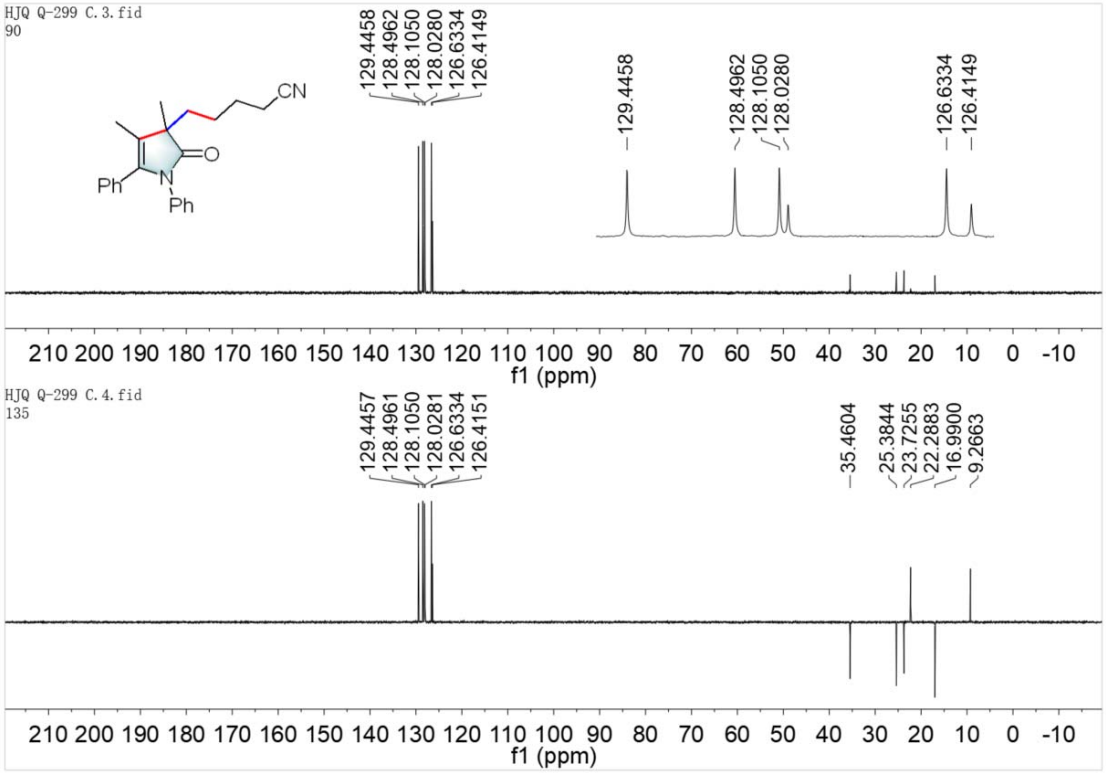
3g3, ^{1}H NMR



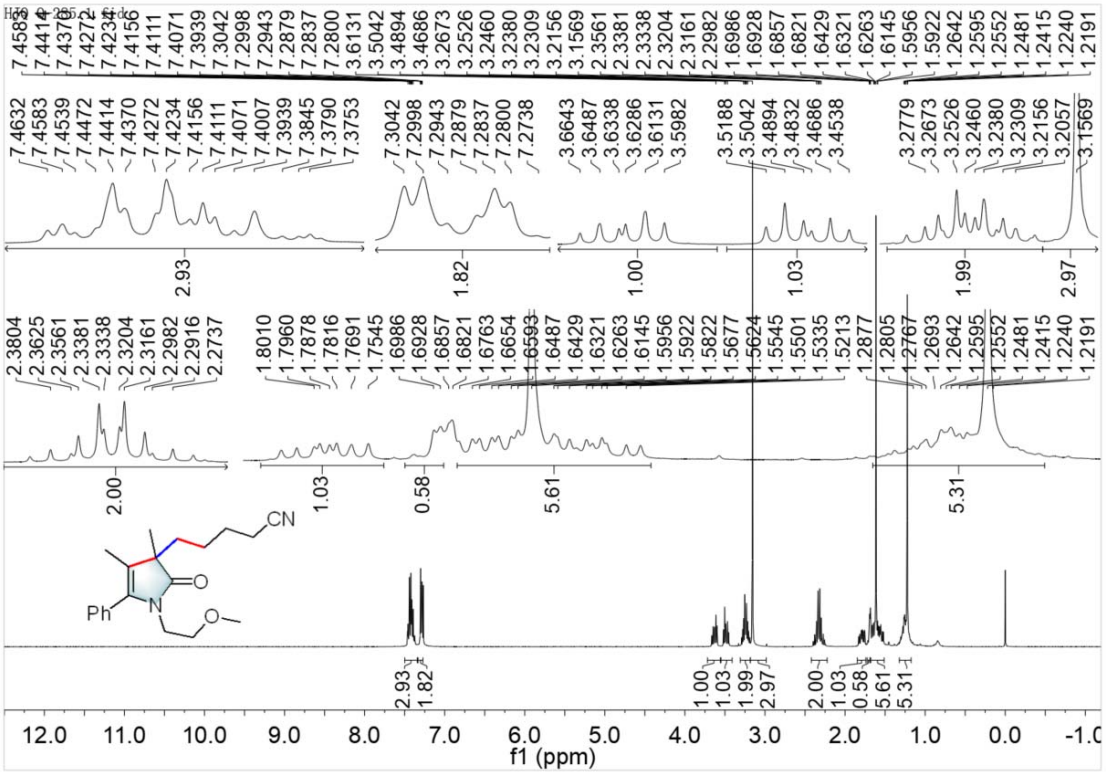
^{13}C NMR



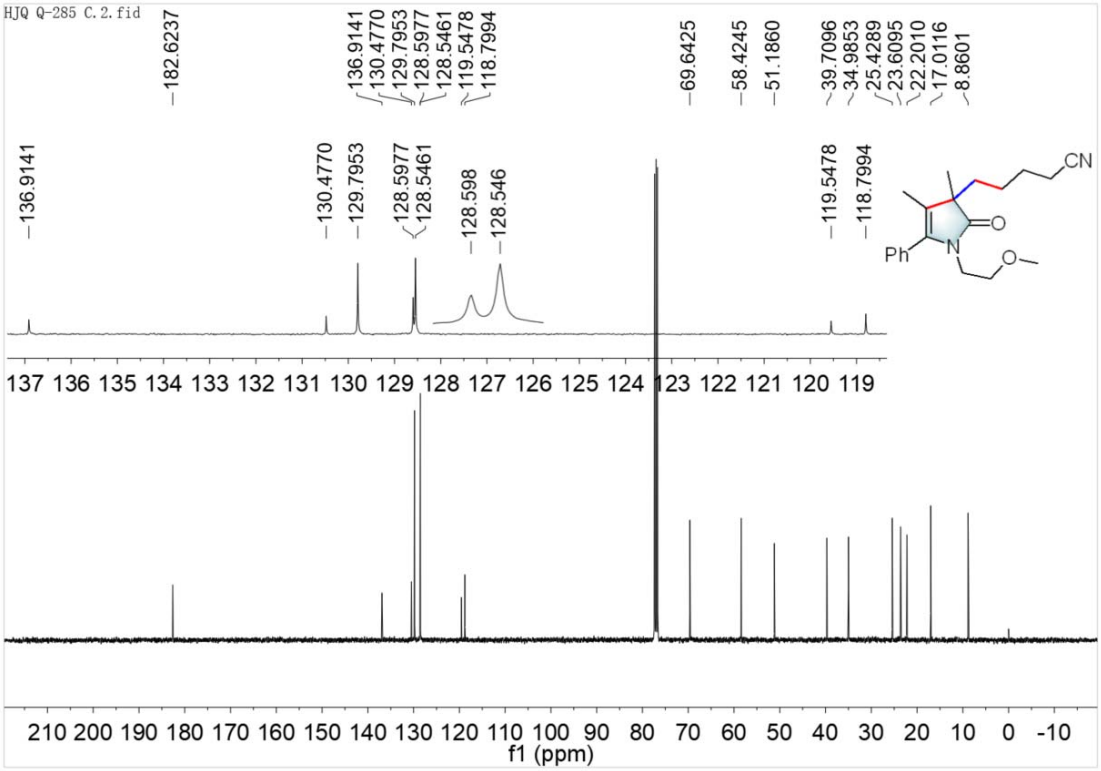
DEPT 90 and DEPT 135



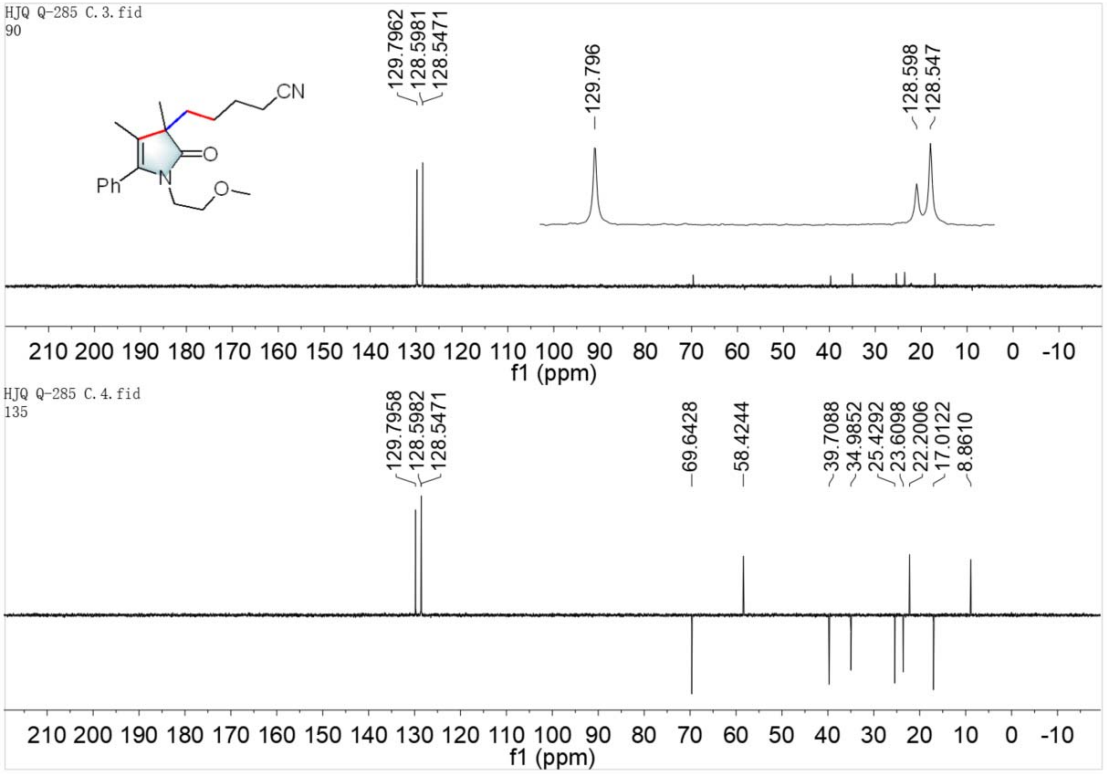
3h, ^{1}H NMR



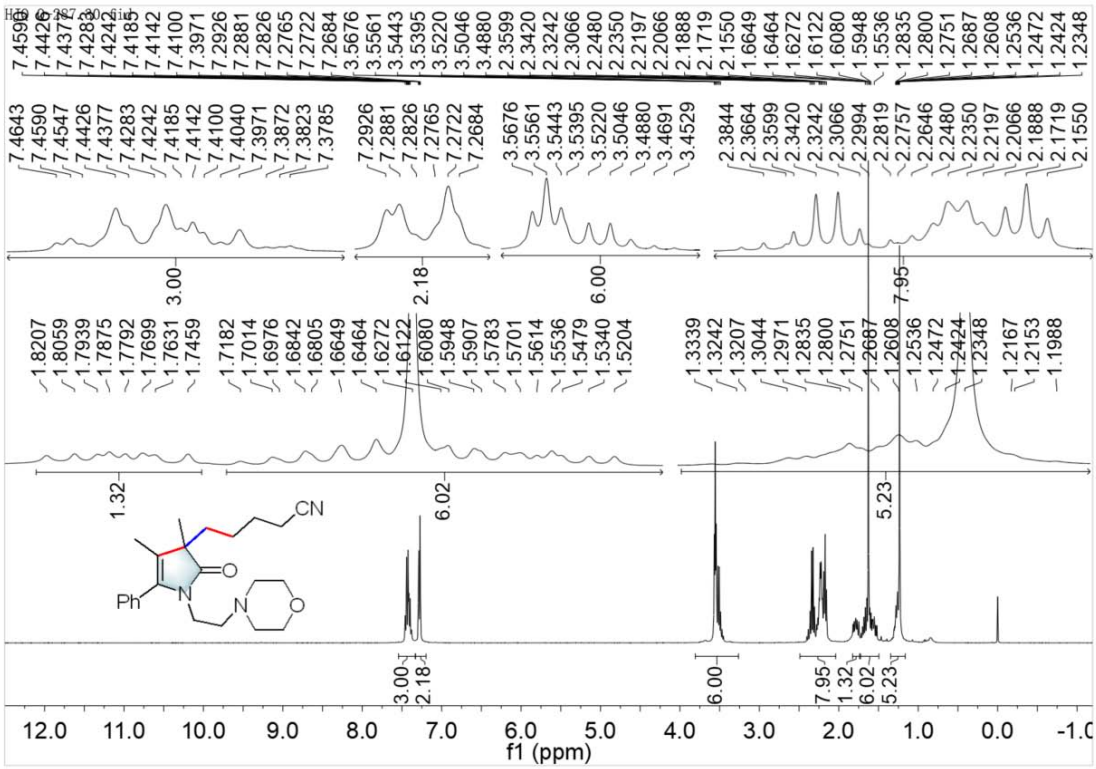
^{13}C NMR



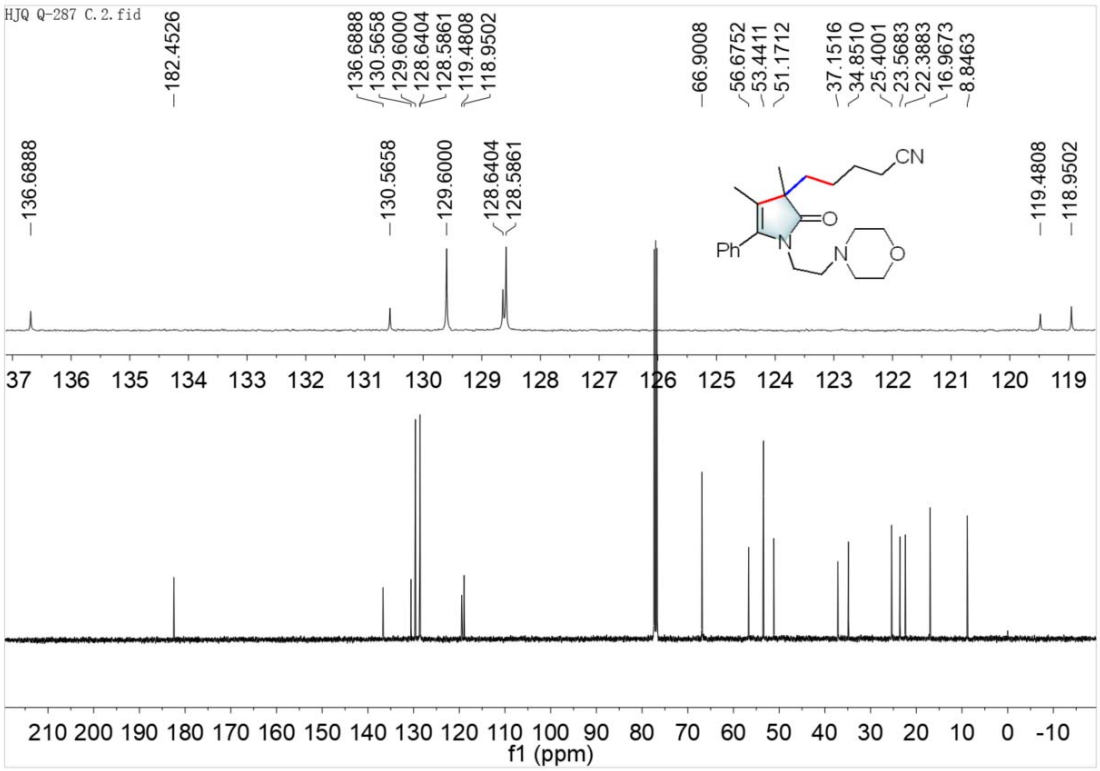
DEPT 90 and DEPT 135



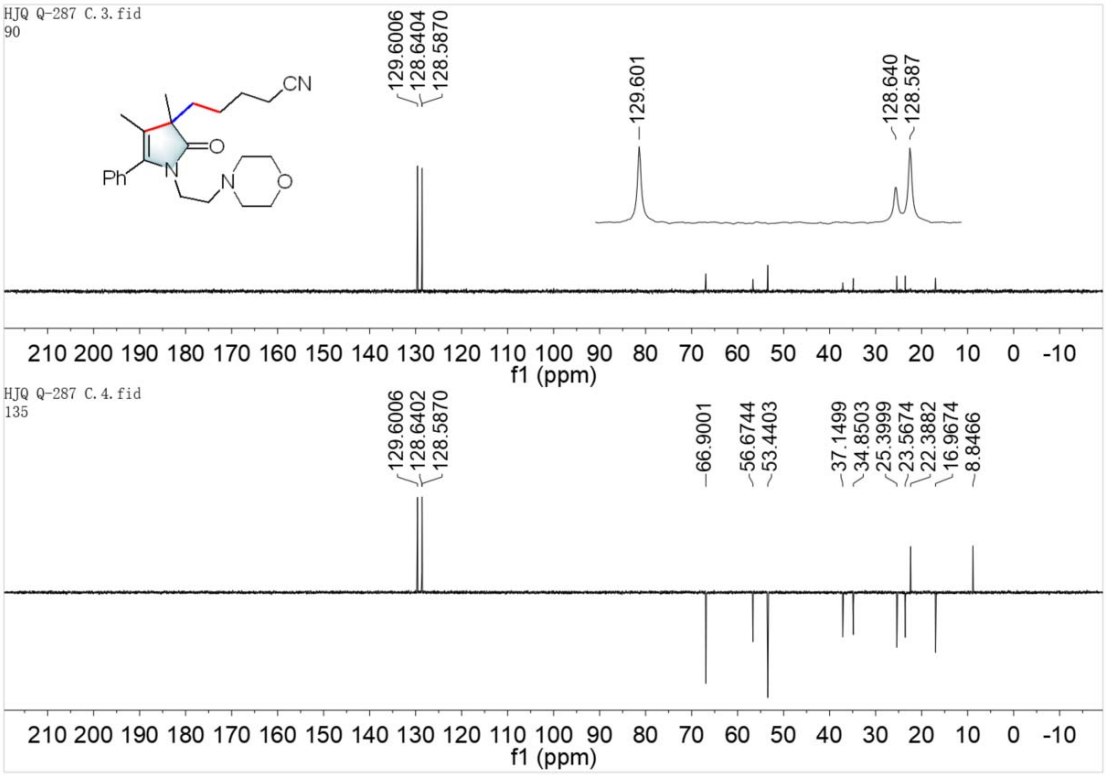
3i, ^{1}H NMR



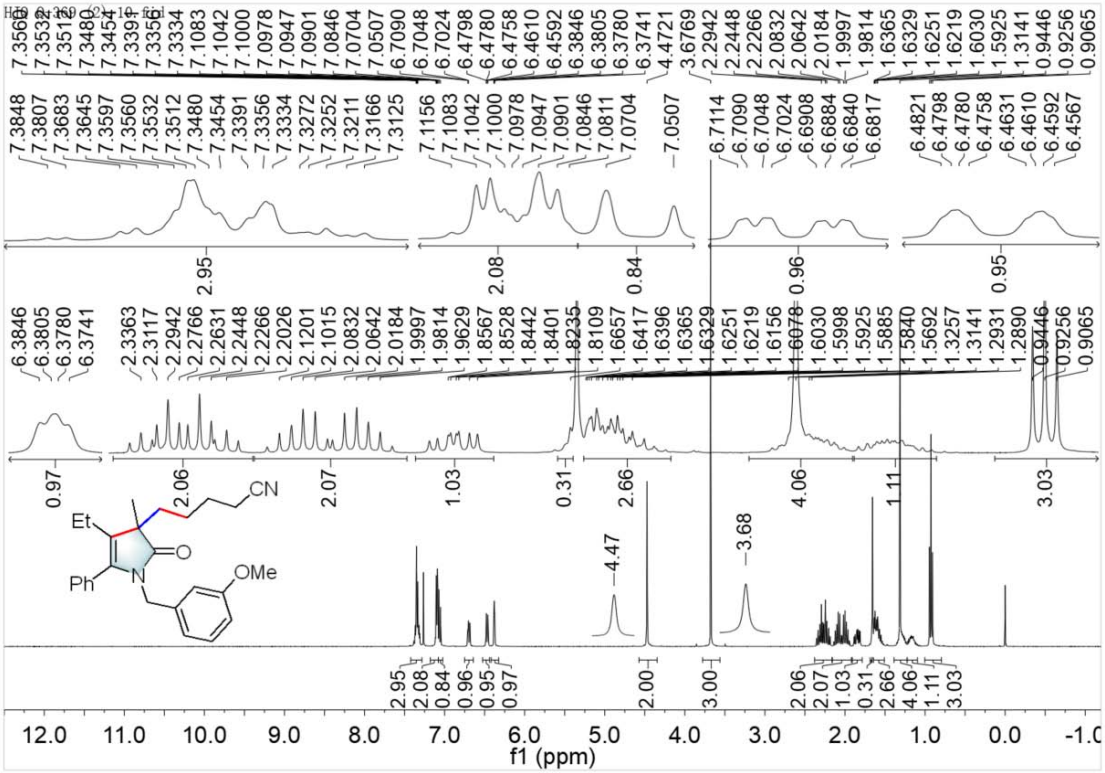
^{13}C NMR



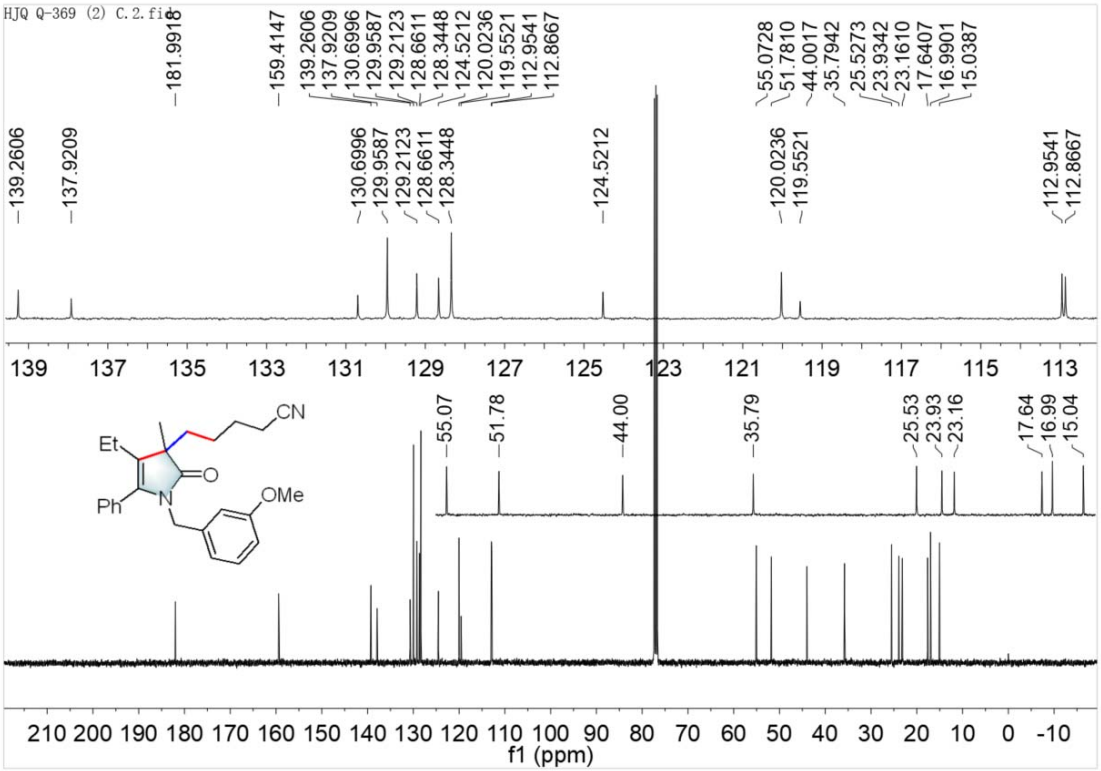
DEPT 90 and DEPT 135



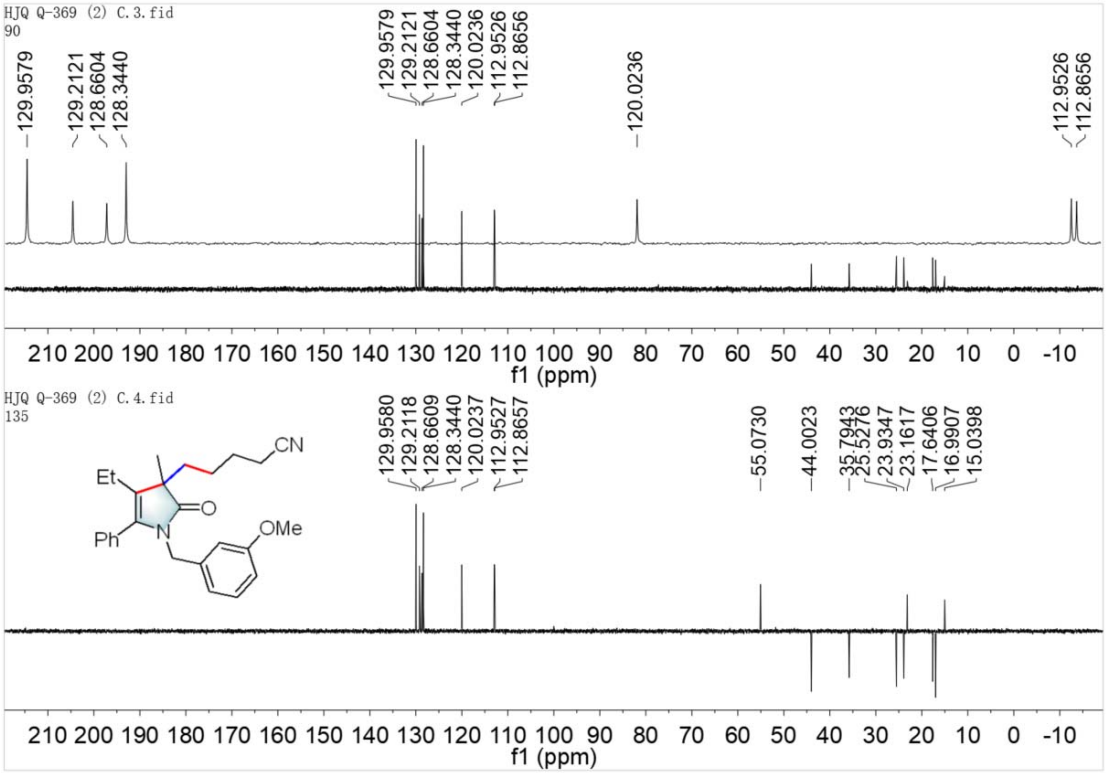
3j1, ^{1}H NMR



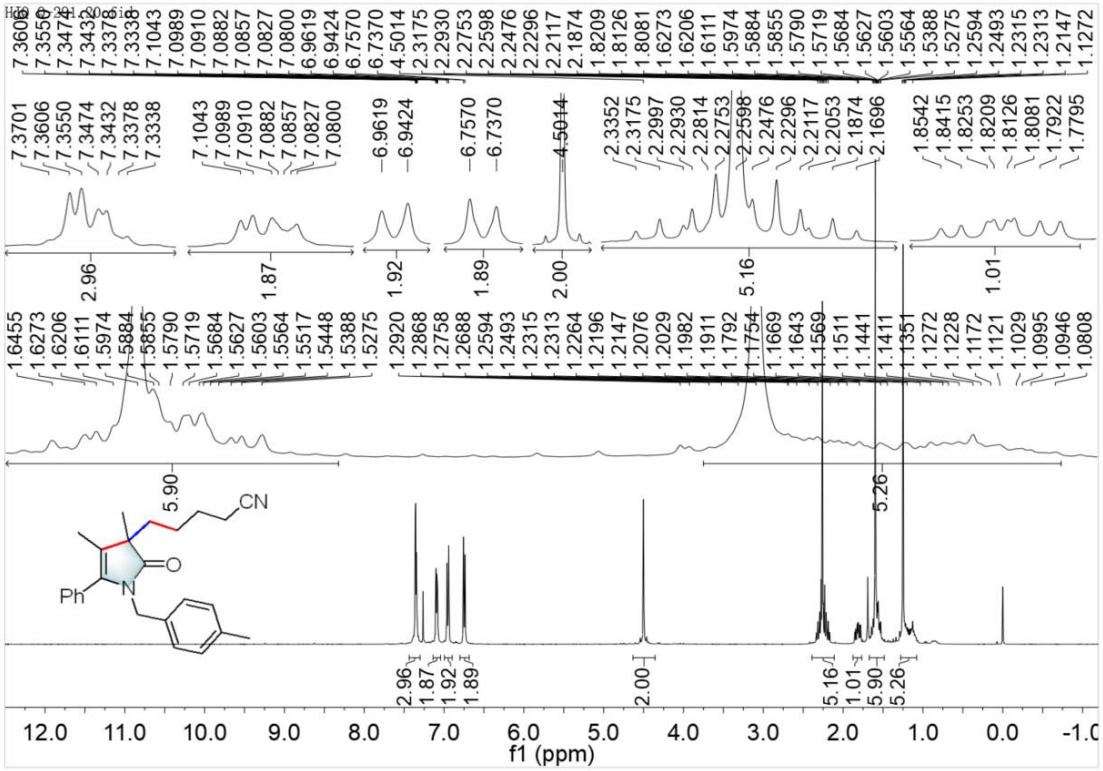
^{13}C NMR



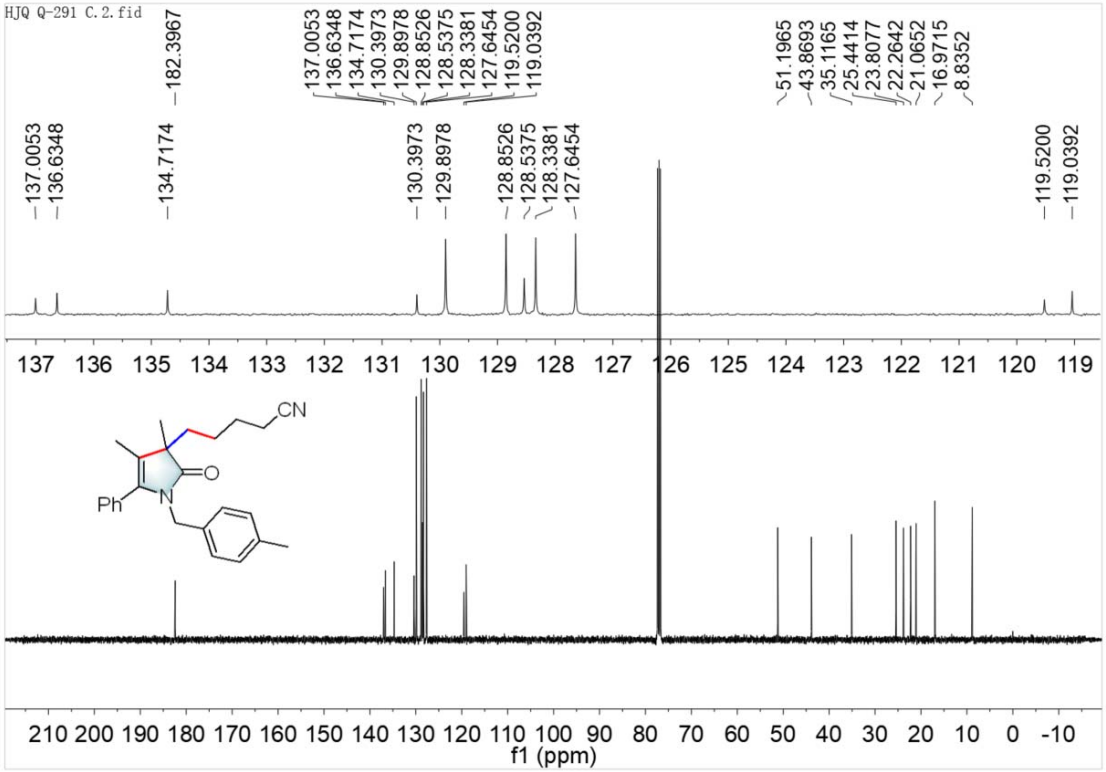
DEPT 90 and DEPT 135



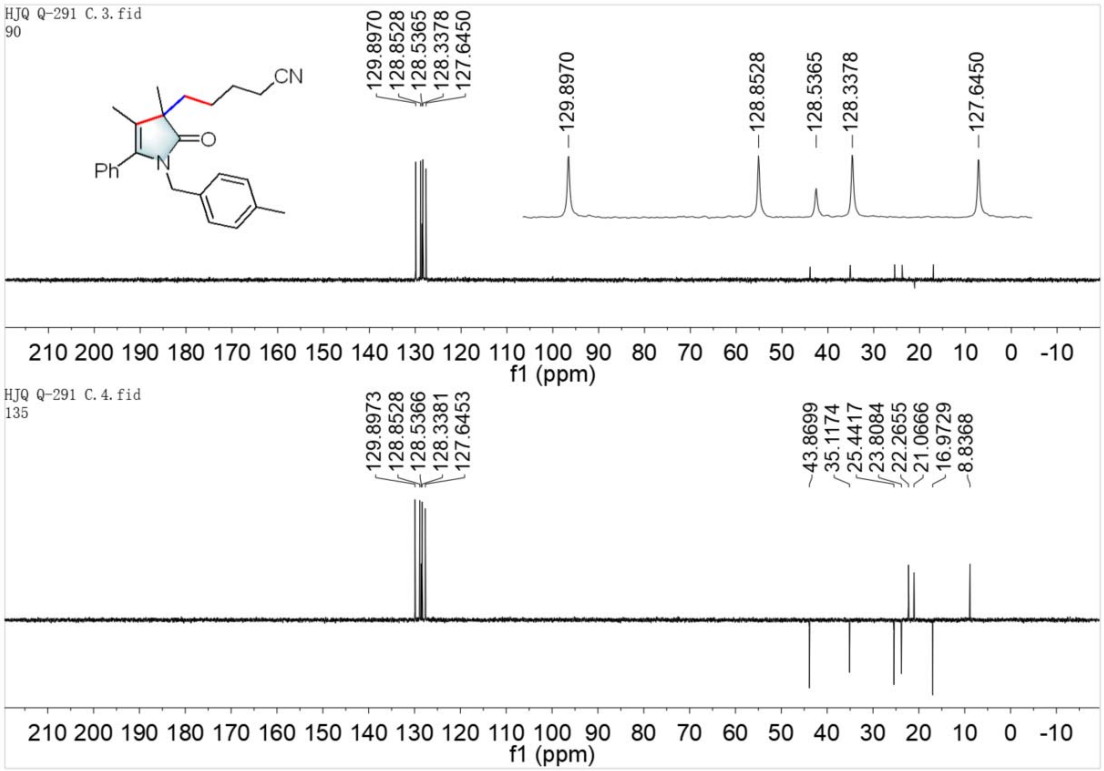
3j2, ^{1}H NMR



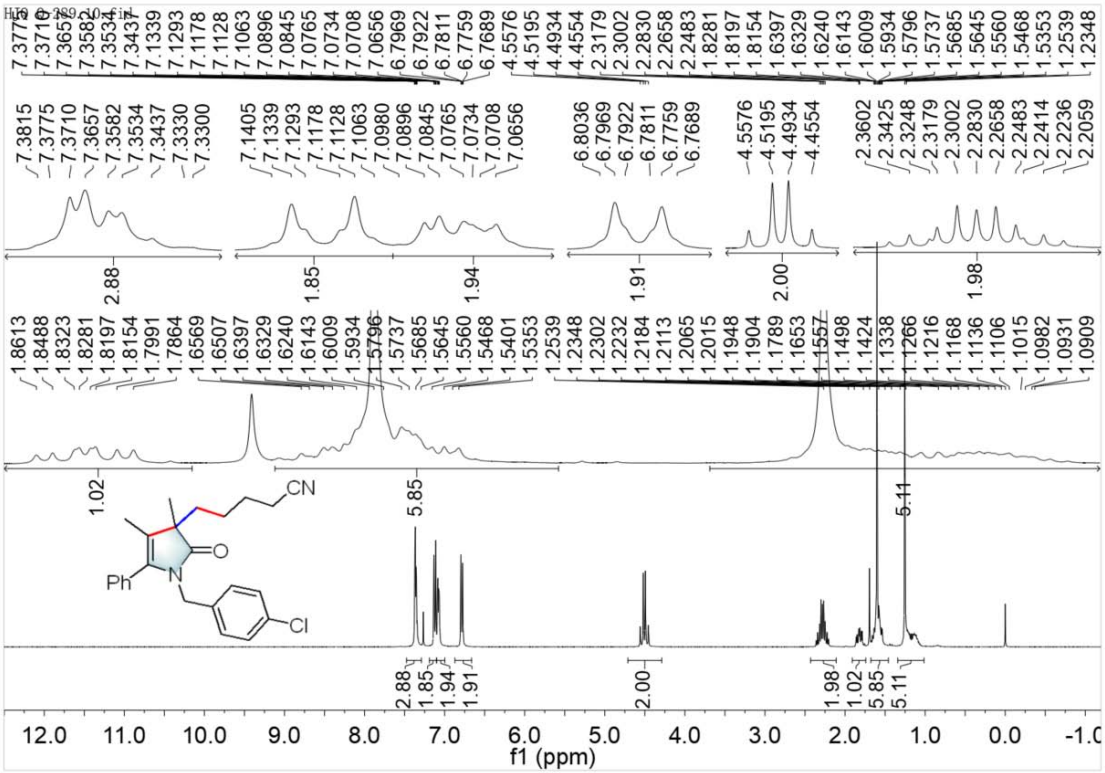
^{13}C NMR



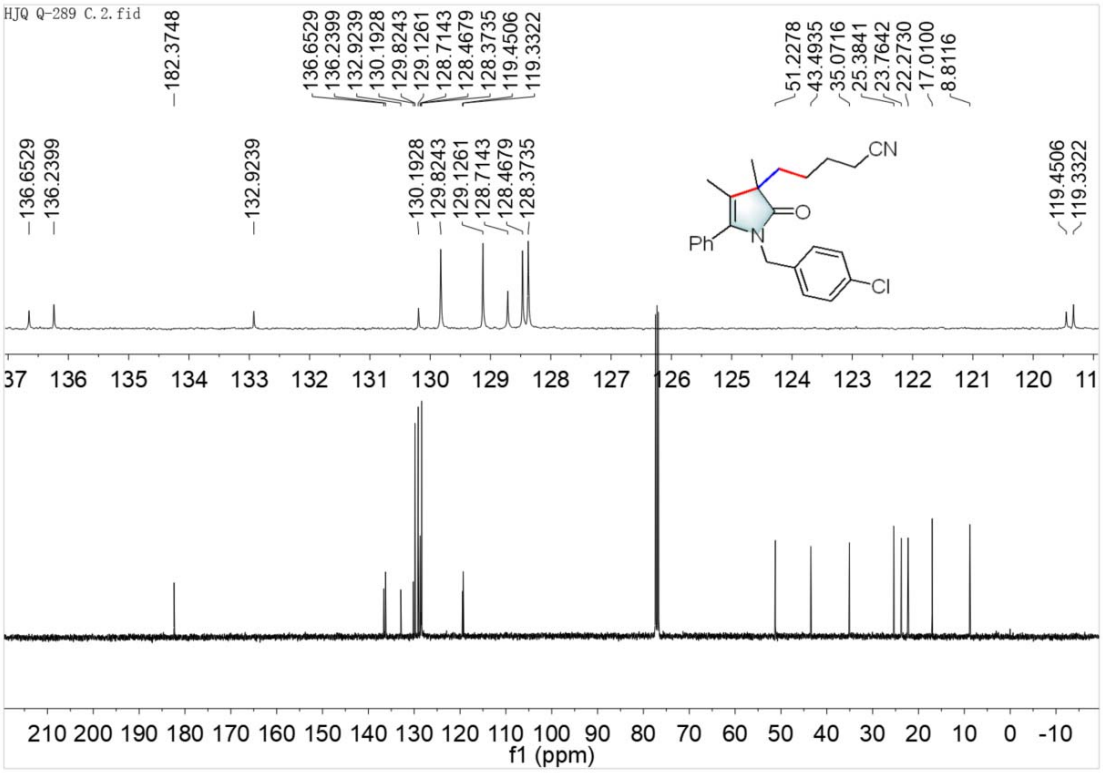
DEPT 90 and DEPT 135



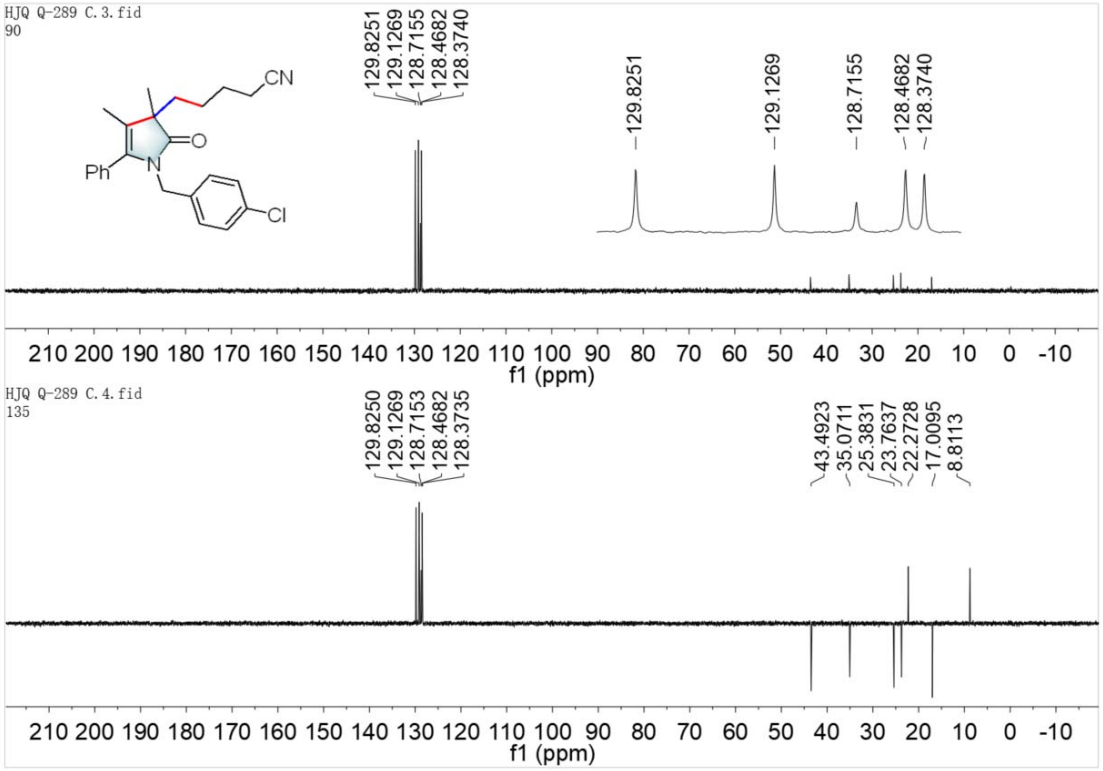
3j3, ^{1}H NMR



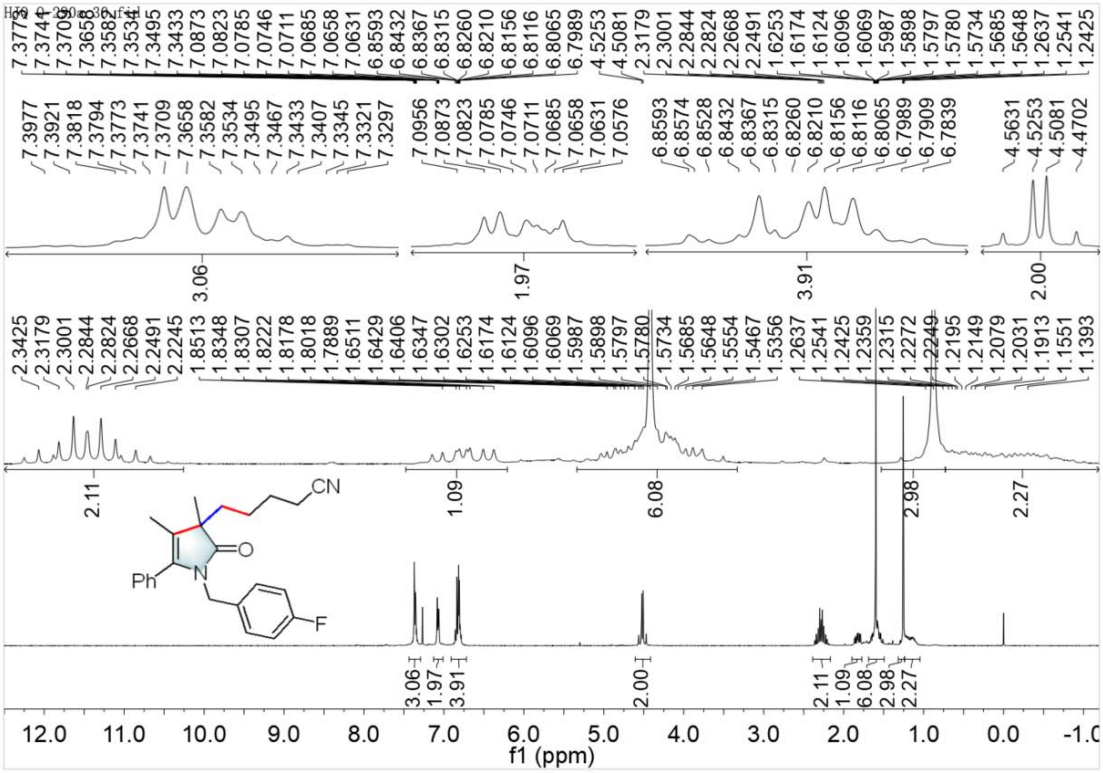
^{13}C NMR



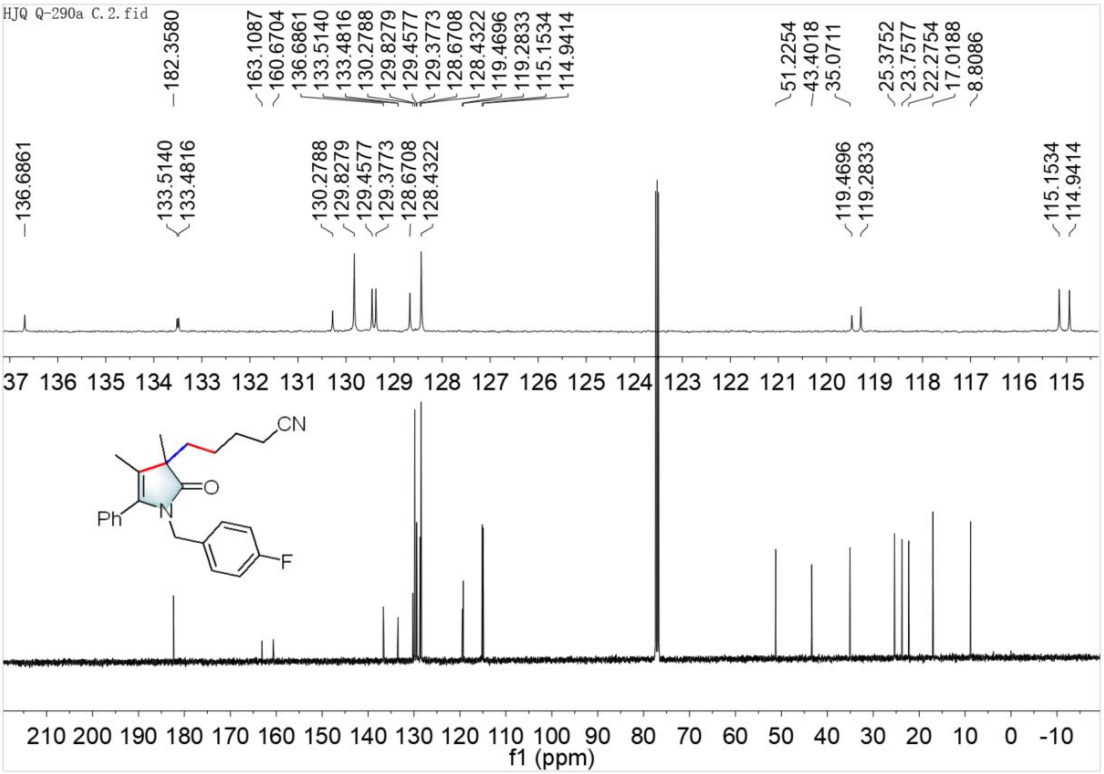
DEPT 90 and DEPT 135



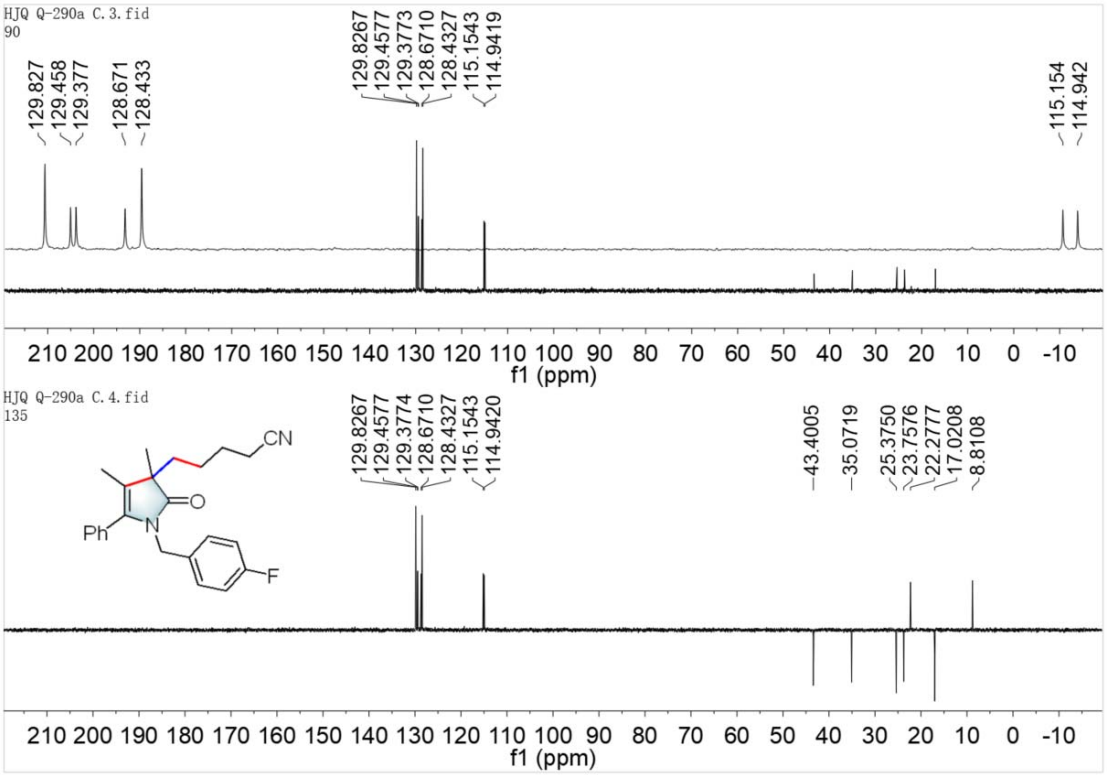
3j4, ^{1}H NMR



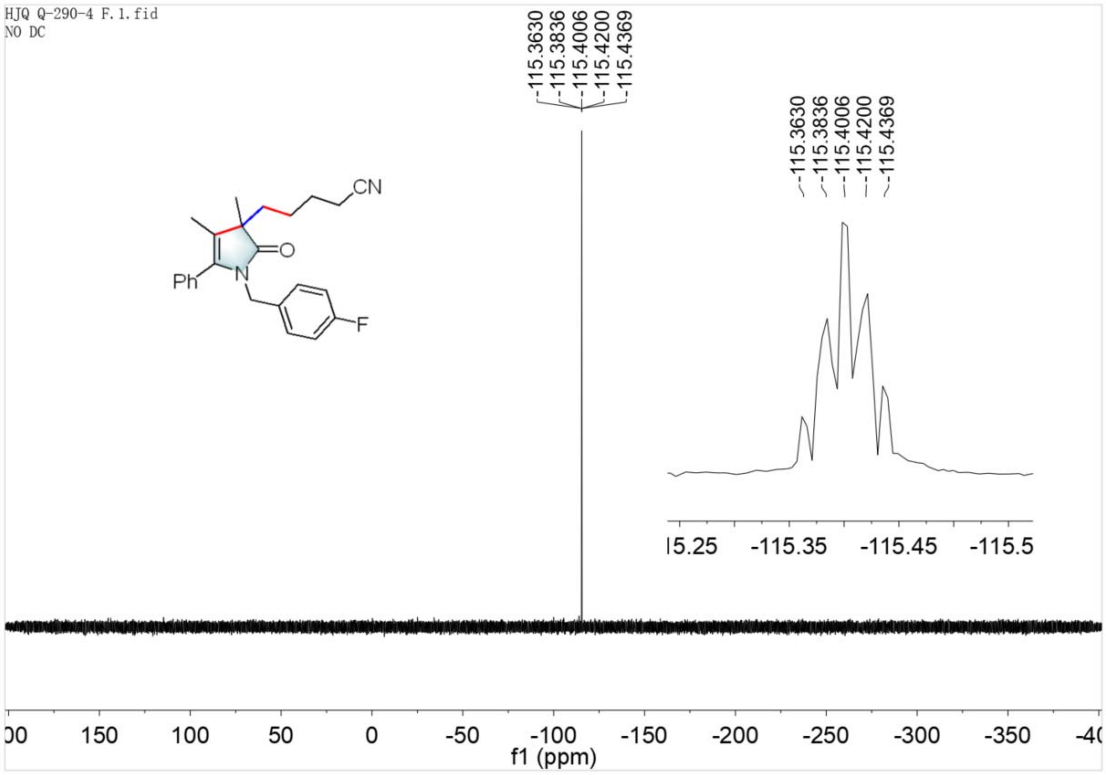
^{13}C NMR



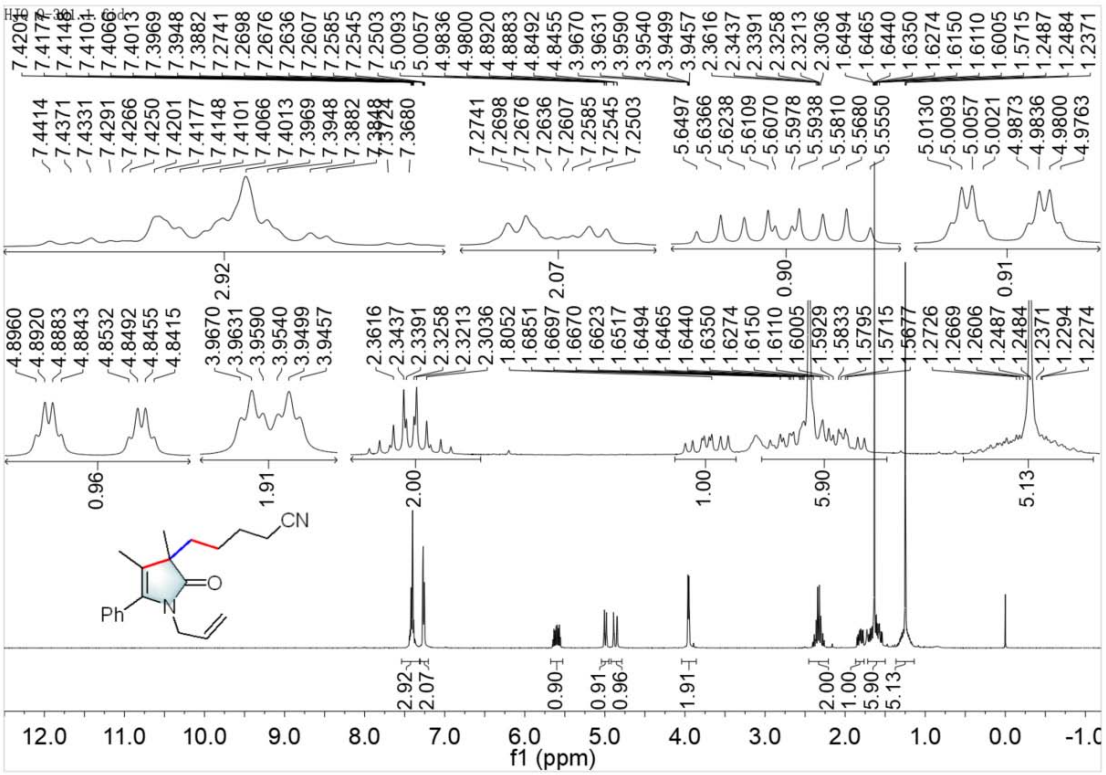
DEPT 90 and DEPT 135



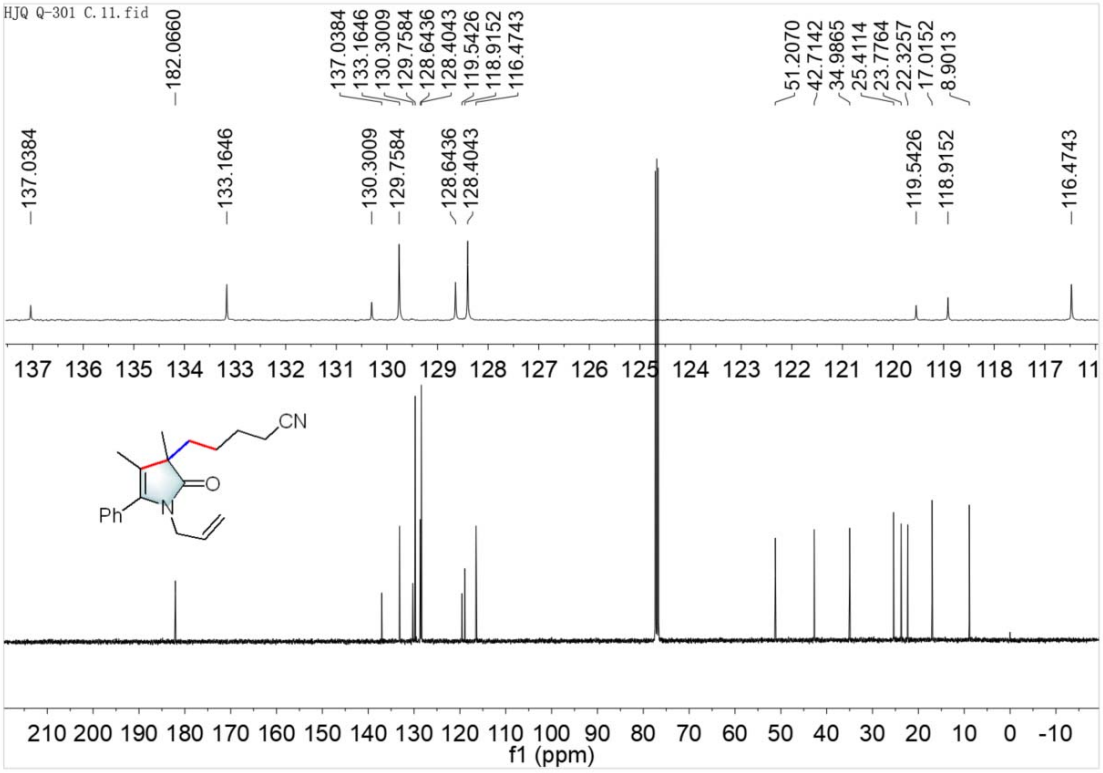
^{19}F NMR



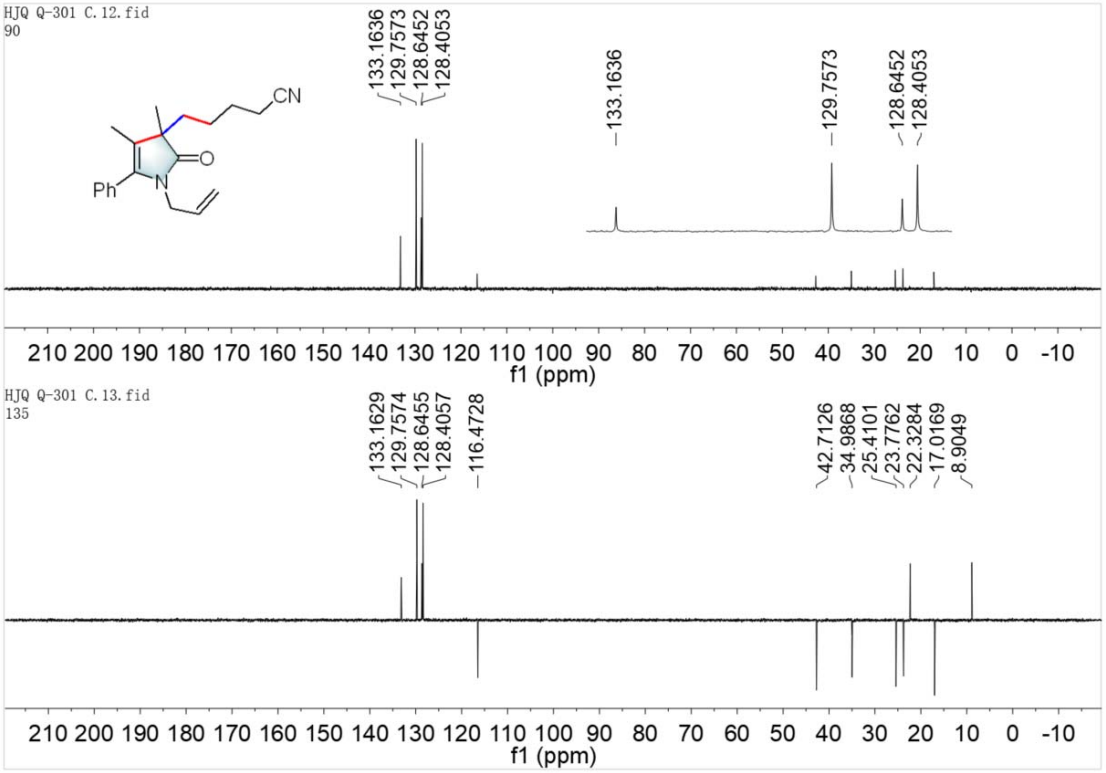
3k, ^{1}H NMR



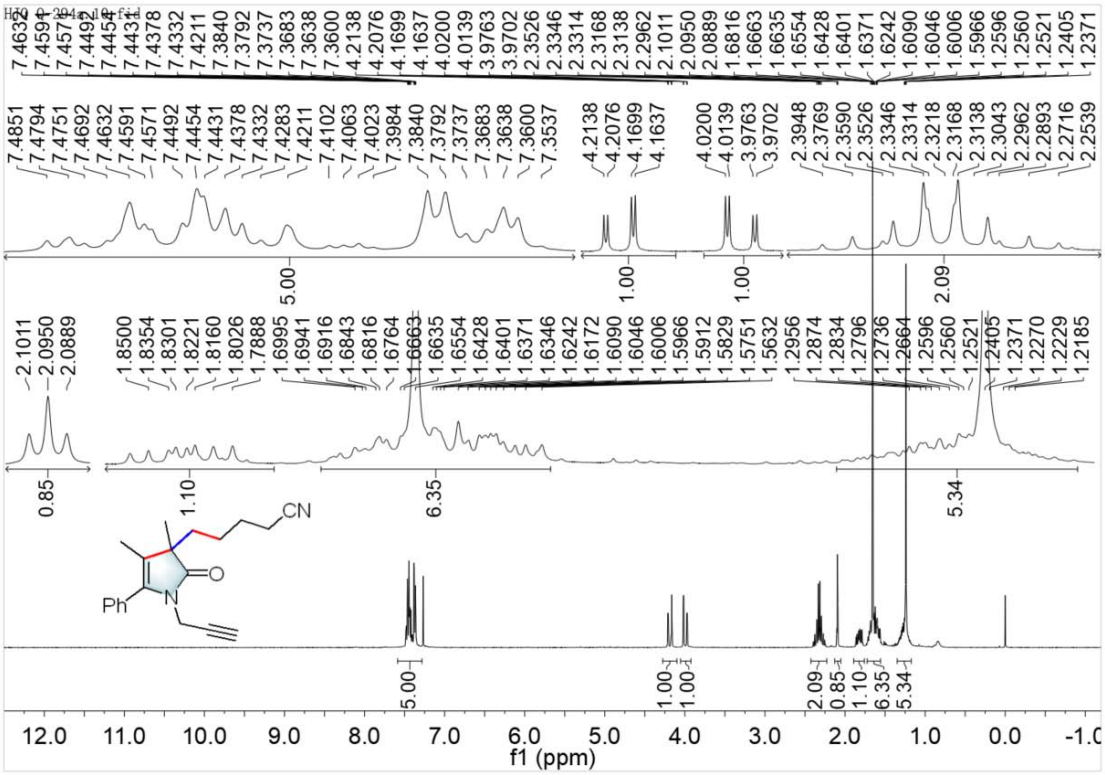
^{13}C NMR



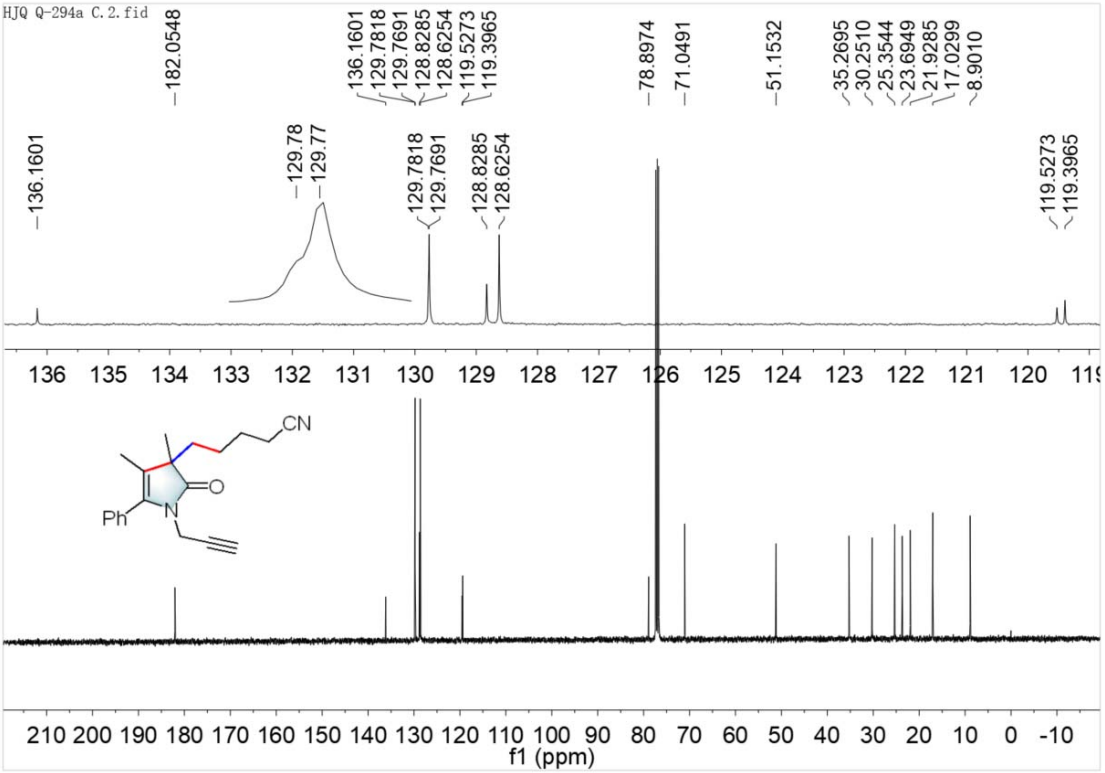
DEPT 90 and DEPT 135



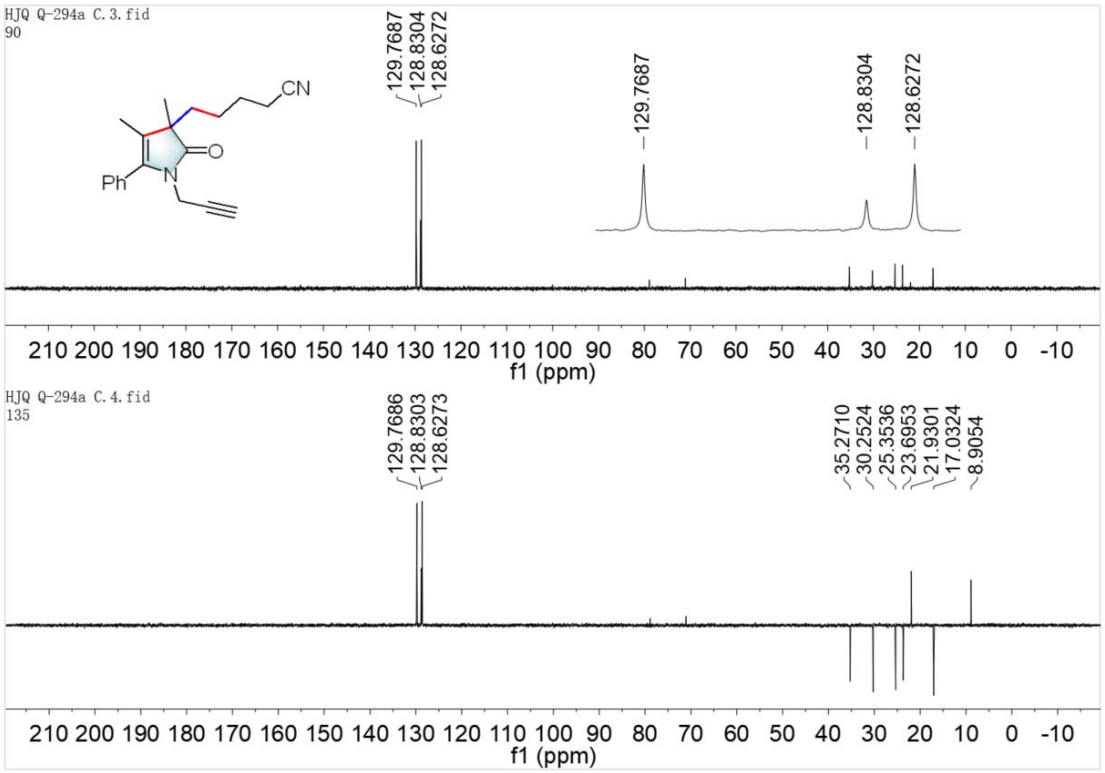
3l, ^{1}H NMR



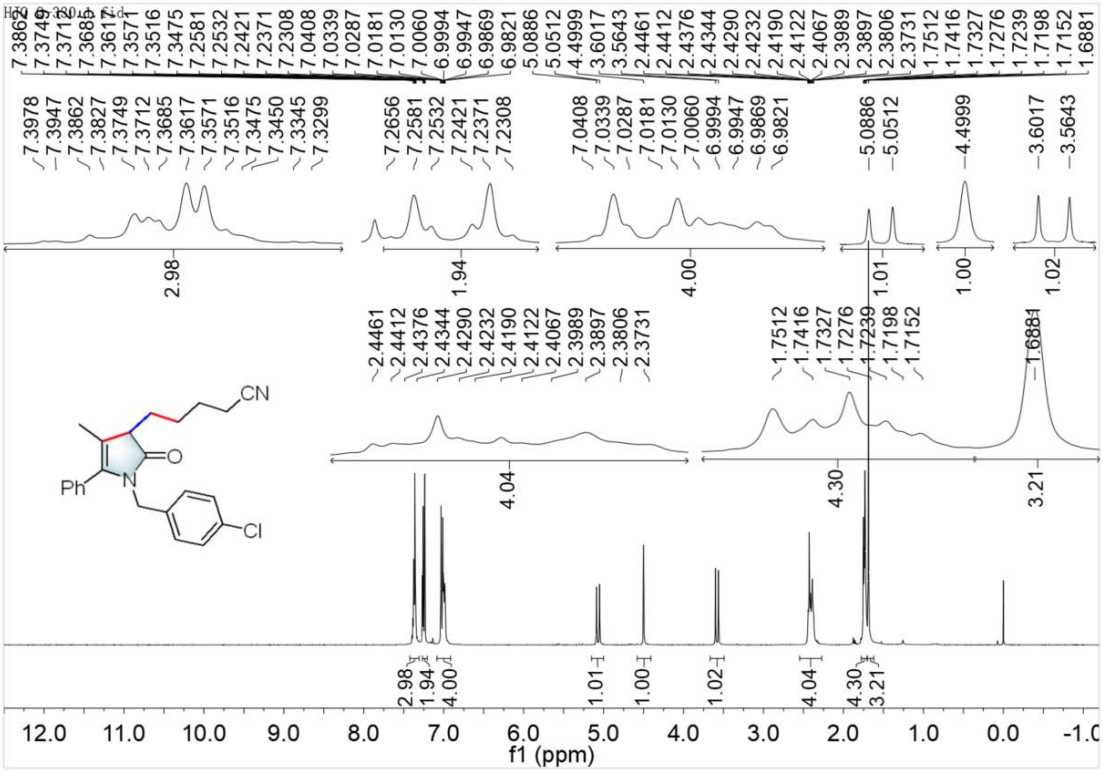
^{13}C NMR



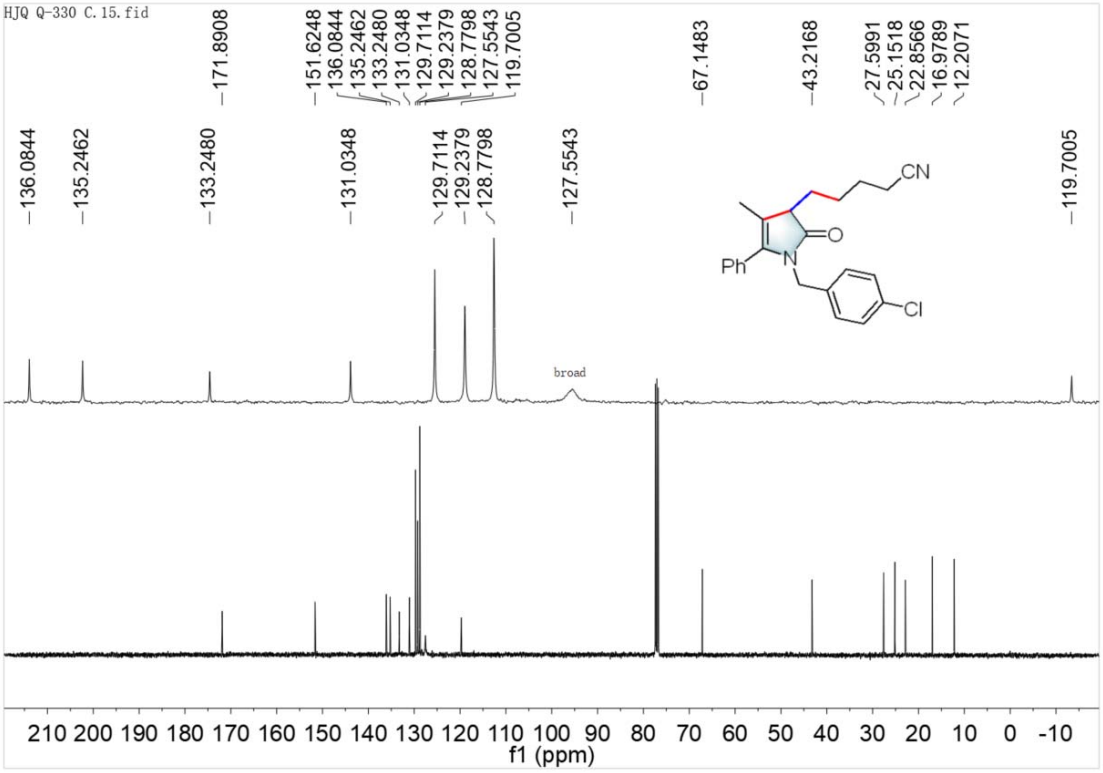
DEPT 90 and DEPT 135



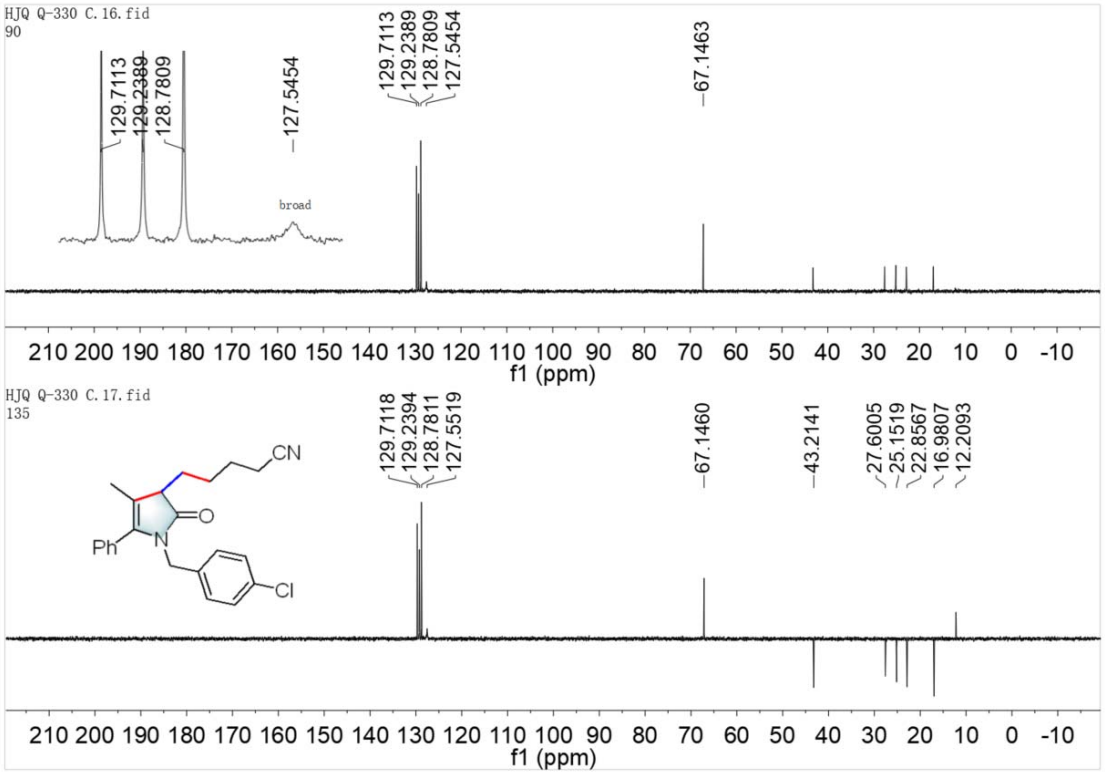
3m, ^{1}H NMR



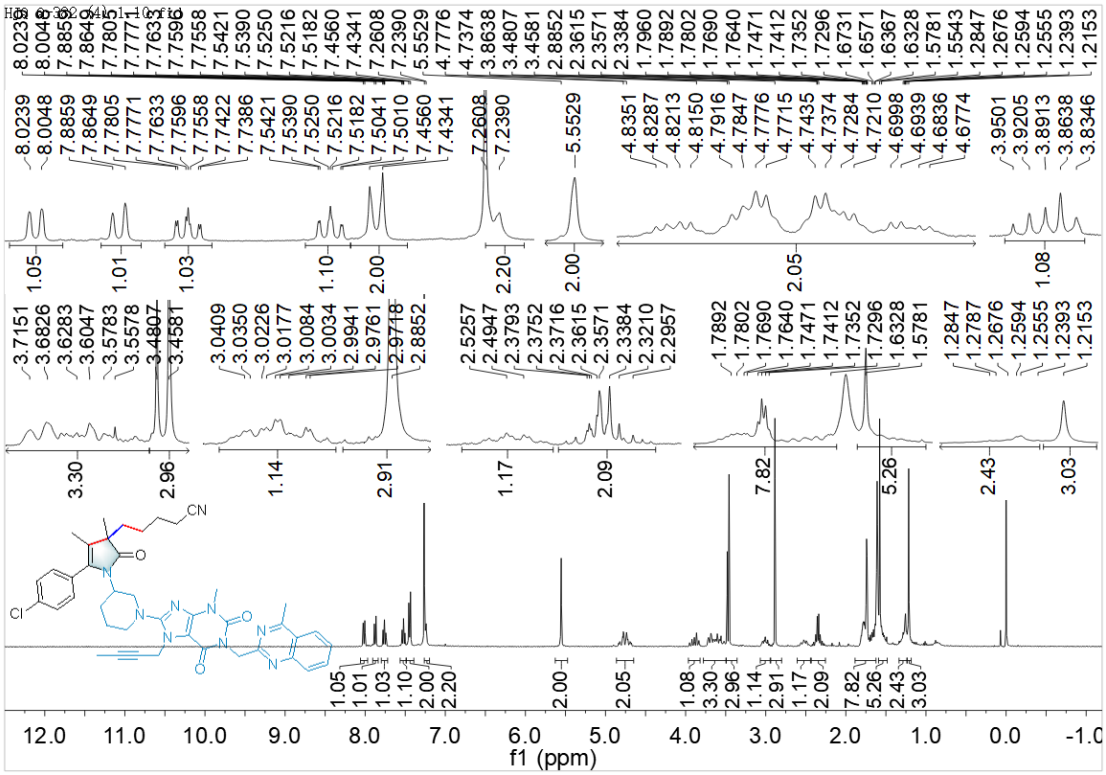
^{13}C NMR



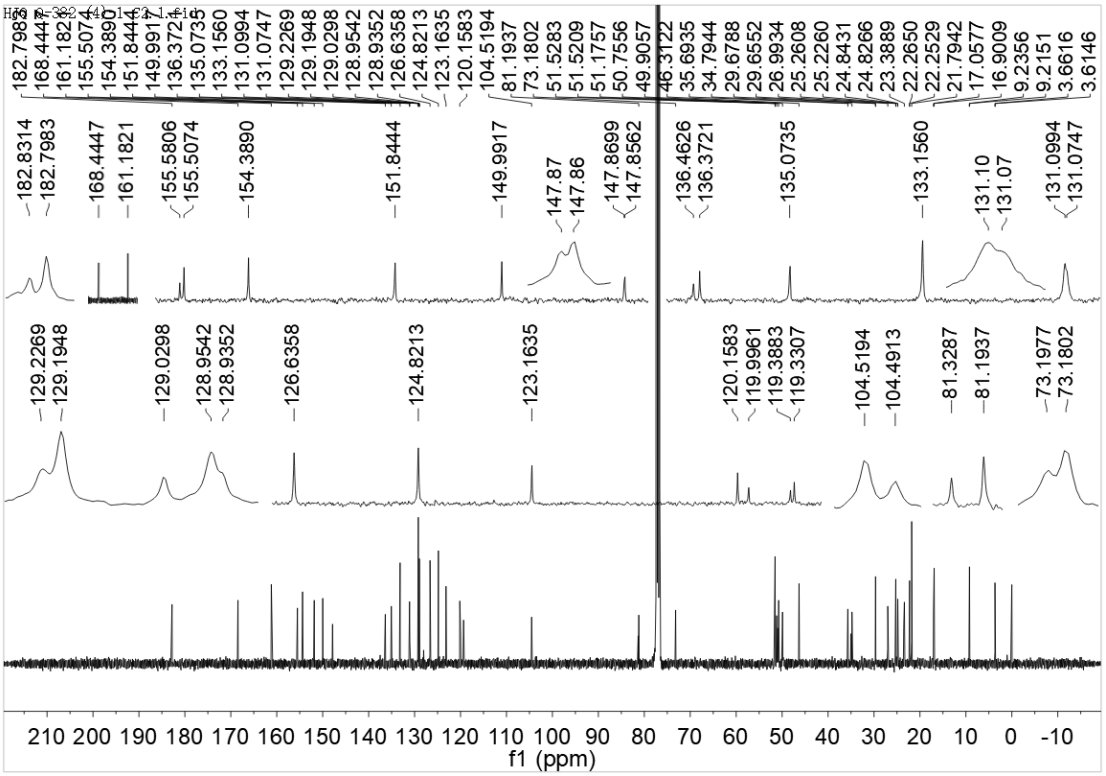
DEPT 90 and DEPT 135

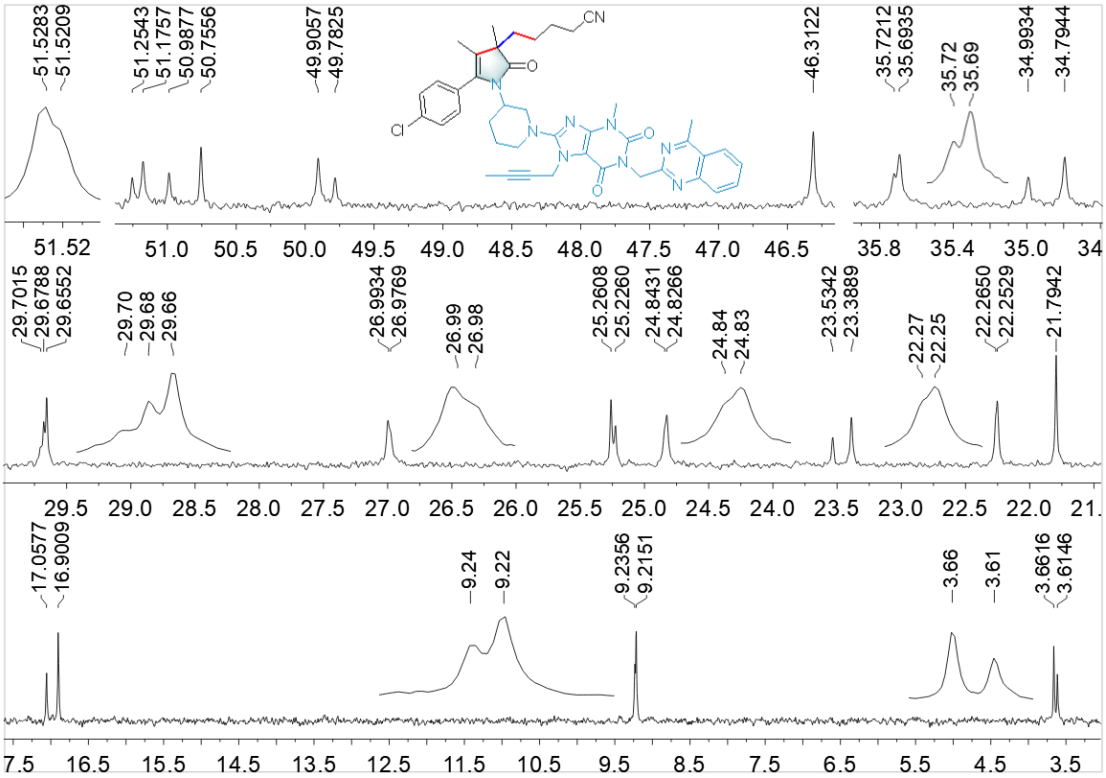


3n, ^{1}H NMR

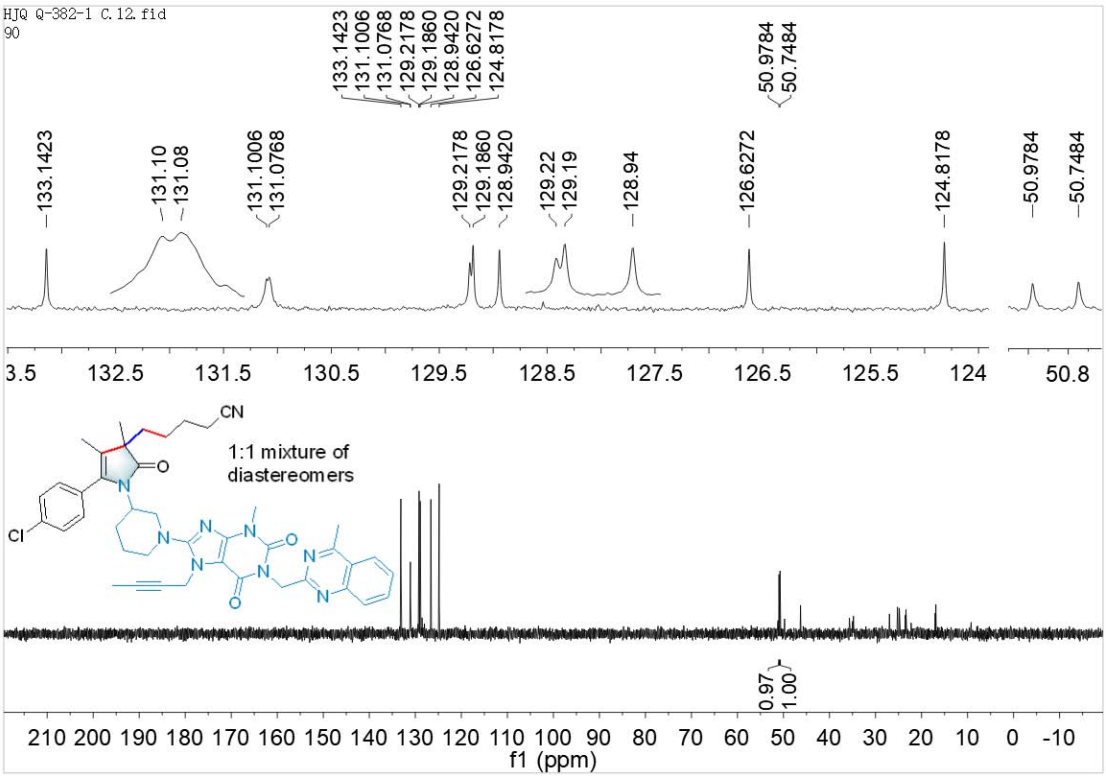


^{13}C NMR

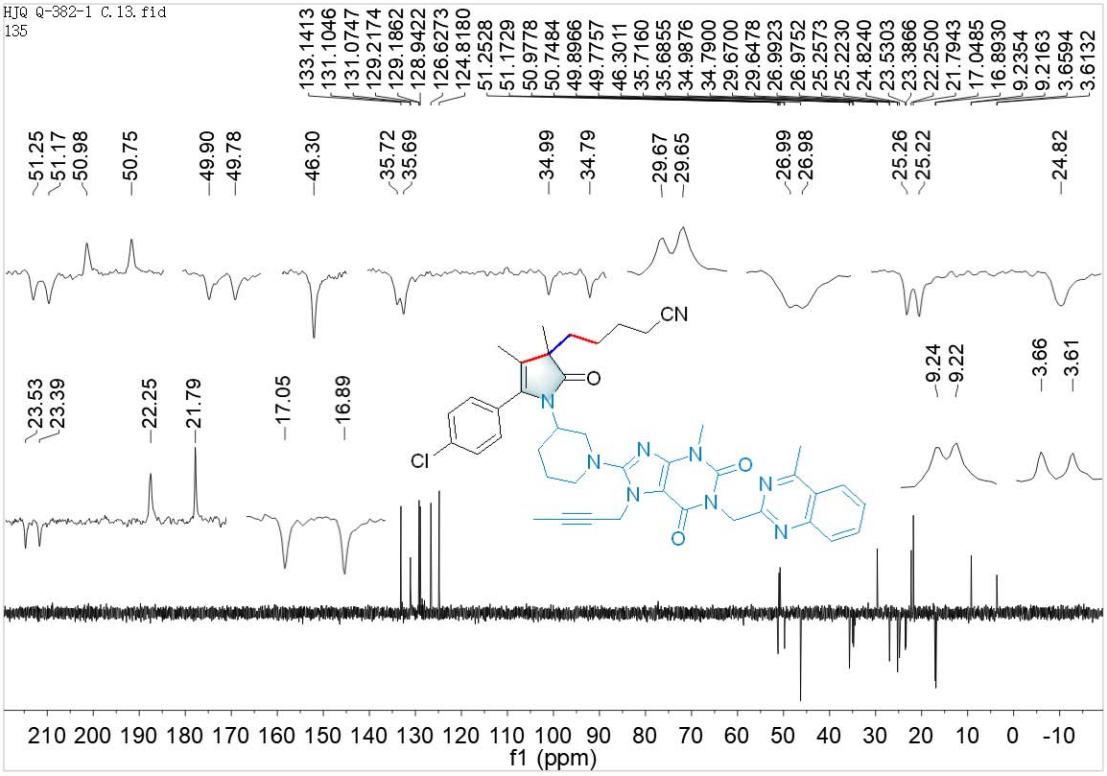



51.5283
51.5209
51.2543
51.1757
50.9877
50.7556
49.9057
49.7825
46.3122
35.7212
35.6935
35.72
35.69
34.9934
34.7944
29.7015
29.6788
29.6552
29.70
29.68
29.66
26.9934
26.9769
26.99
26.98
25.2608
25.2260
24.8431
24.8266
24.84
24.83
23.5342
23.3889
22.27
22.25
22.2650
22.2529
21.7942
17.0577
16.9009
9.24
9.22
9.2356
9.2151
3.66
3.61
3.6616
3.6146
CN
Cl

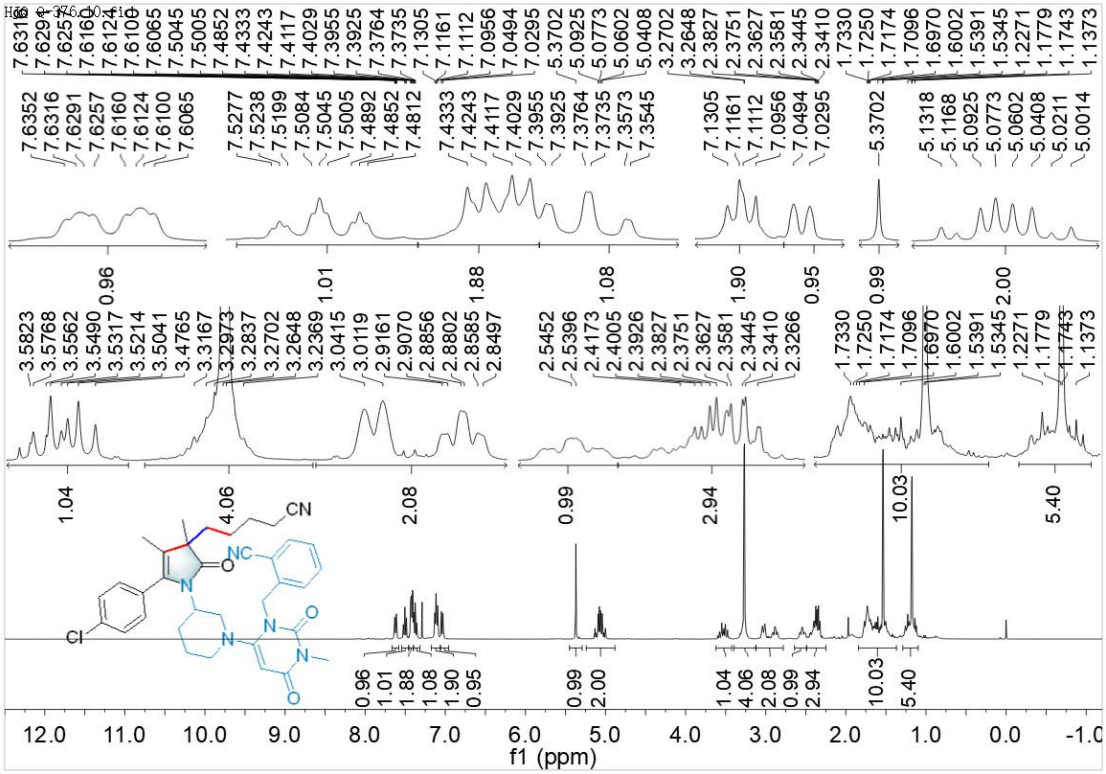
DEPT 90


HJQ Q-382-1 C.12.fid
90
133.1423
131.1006
131.0768
129.2178
129.1860
128.9420
126.6272
124.8178
50.9784
50.7484
131.10
131.08
129.22
129.19
128.94
CN
Cl
1:1 mixture of
diastereomers
0.97
1.00
f1 (ppm)

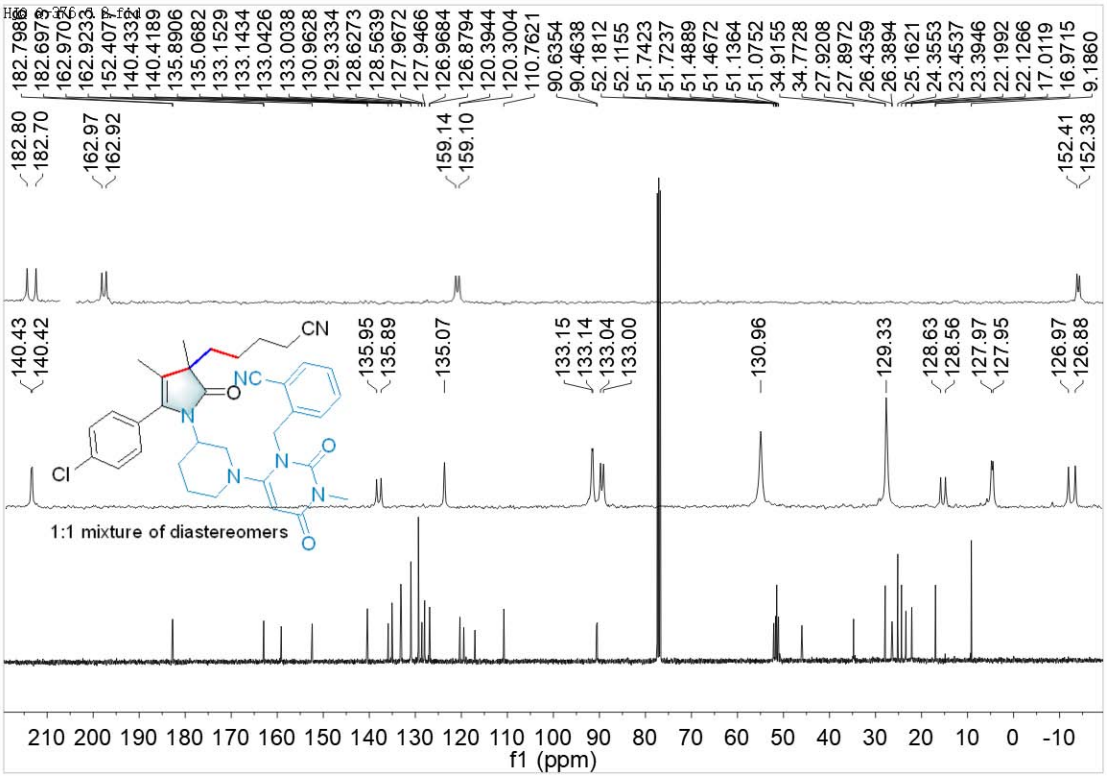
DEPT 135

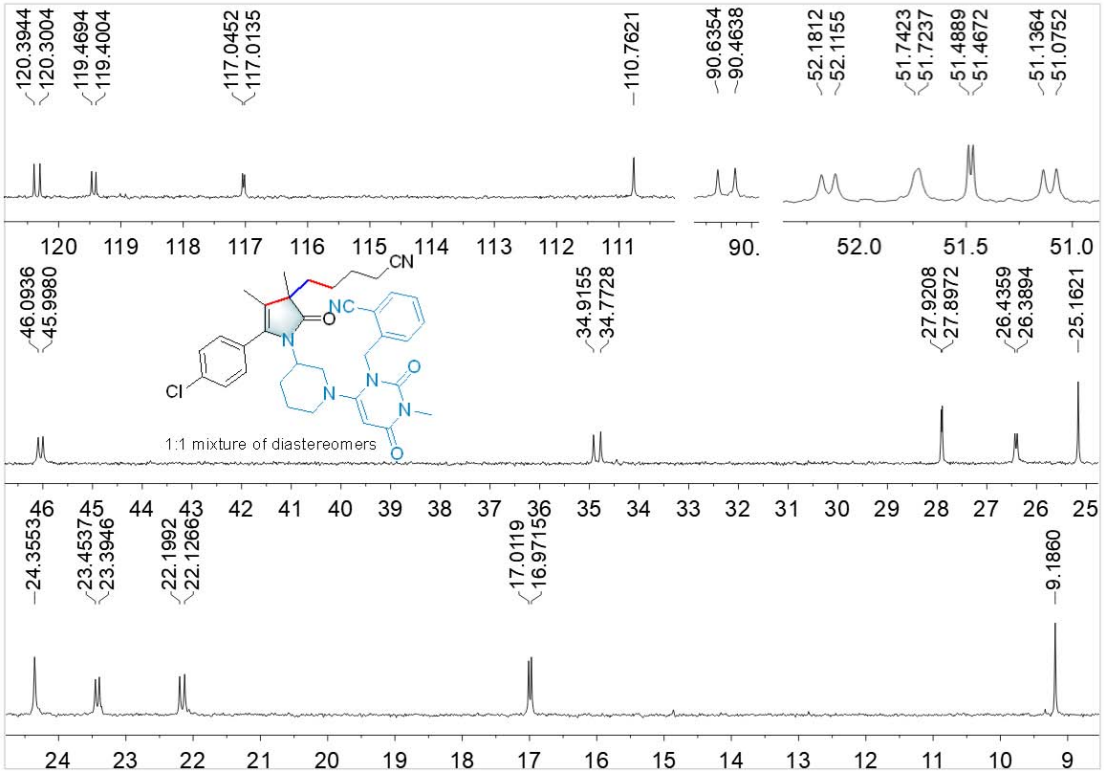

HJQ Q-382-1 C.13.fid
135
133.1413
131.1046
131.0747
129.2174
129.1862
128.9422
126.6273
124.8180
51.2528
51.1729
50.9778
50.7484
49.8966
49.7757
46.3011
35.7160
35.6855
34.9876
34.7900
29.6700
29.6478
26.9923
26.9752
25.2573
25.2230
24.8240
23.5303
23.3866
22.2500
21.7943
17.0485
16.8930
9.2354
9.2163
3.6594
3.6132
51.25
51.17
50.98
50.75
49.90
49.78
46.30
35.72
35.69
34.99
34.79
29.67
29.65
26.99
26.98
25.26
25.22
24.82
23.53
23.39
22.25
21.79
17.05
16.89
9.24
9.22
3.66
3.61
CN
O
N
Cl
N
N
N
N
O
N
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3o, ^{1}H NMR

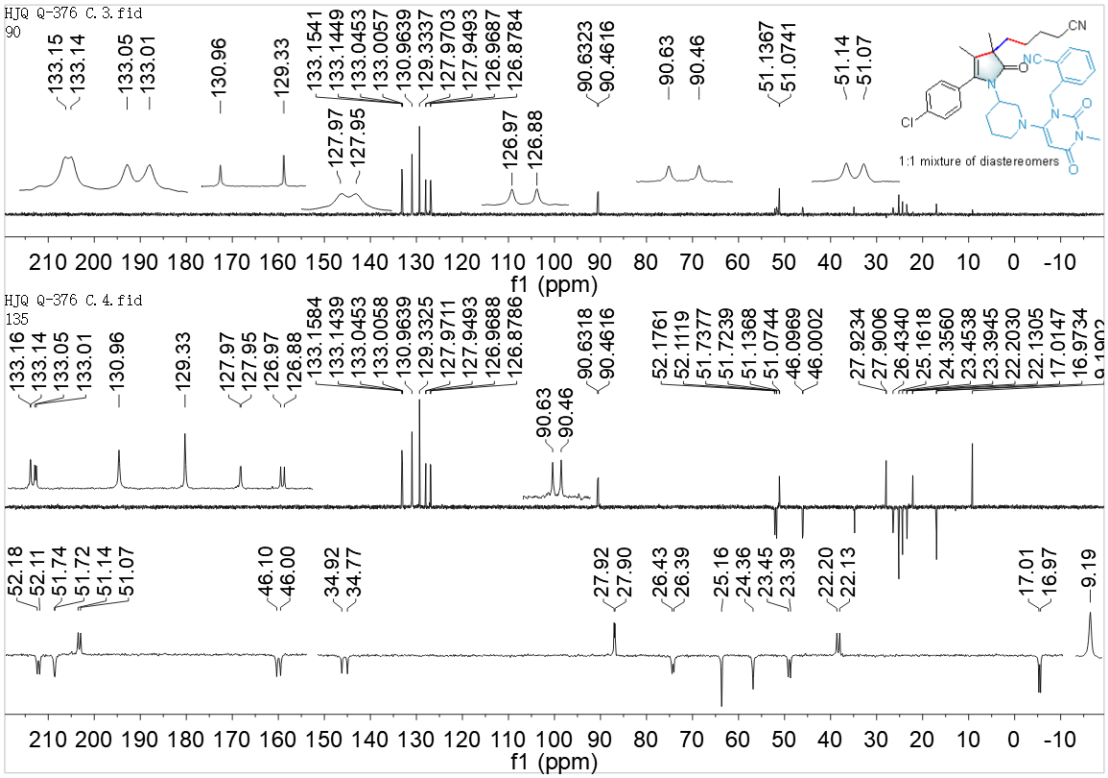


^{13}C NMR

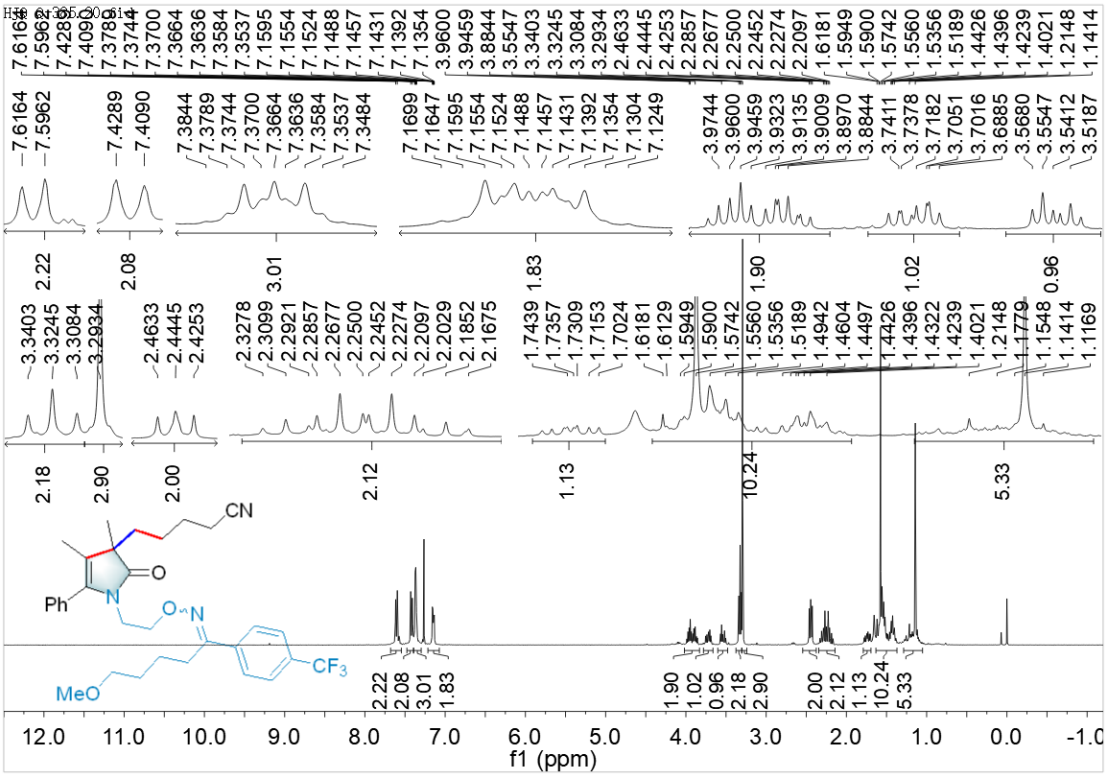




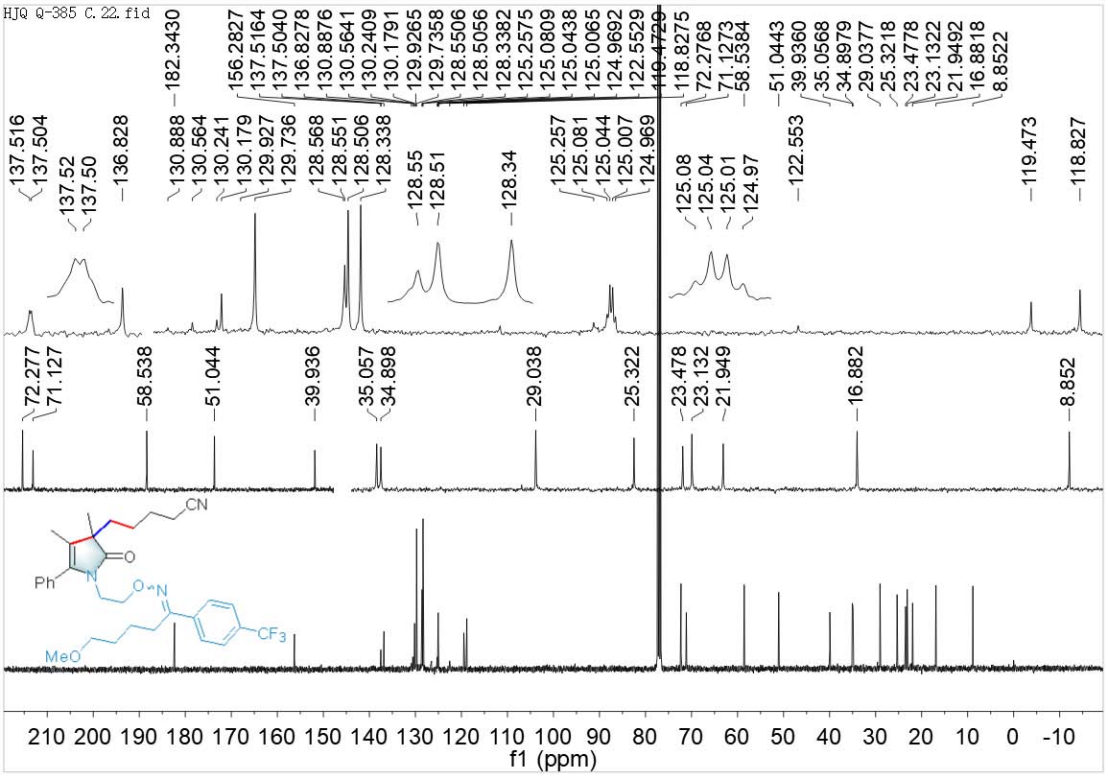
DEPT 90 and DEPT 135



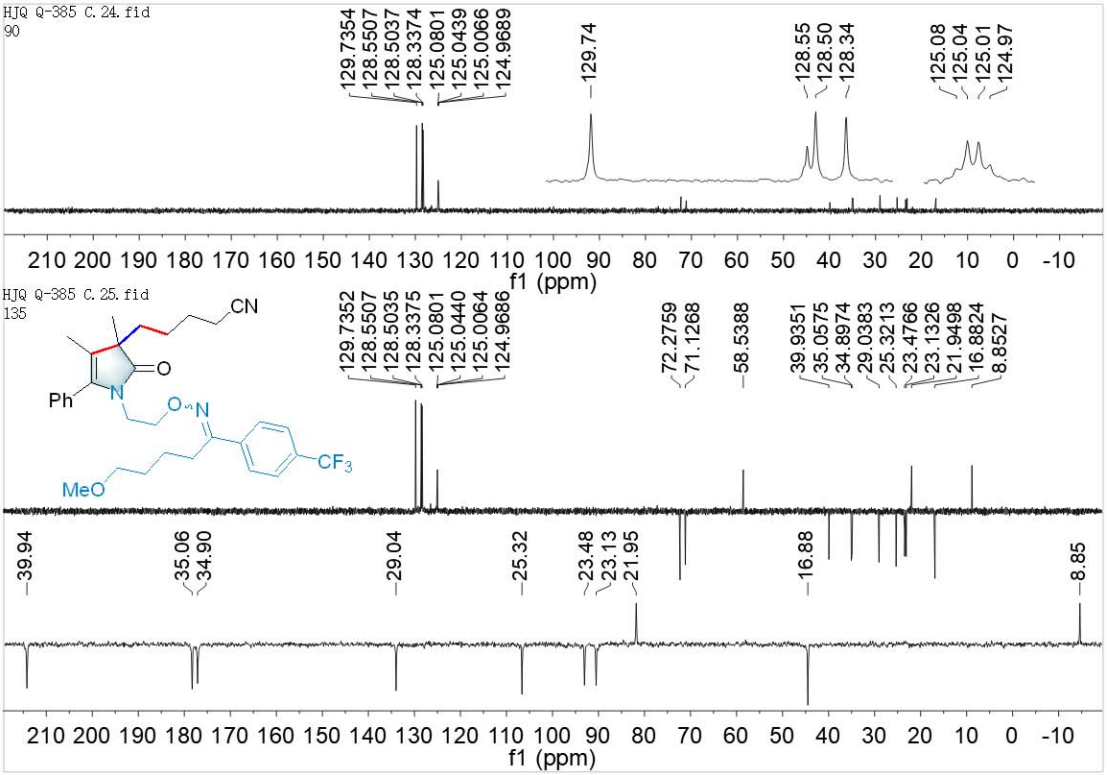
3p, ^{1}H NMR



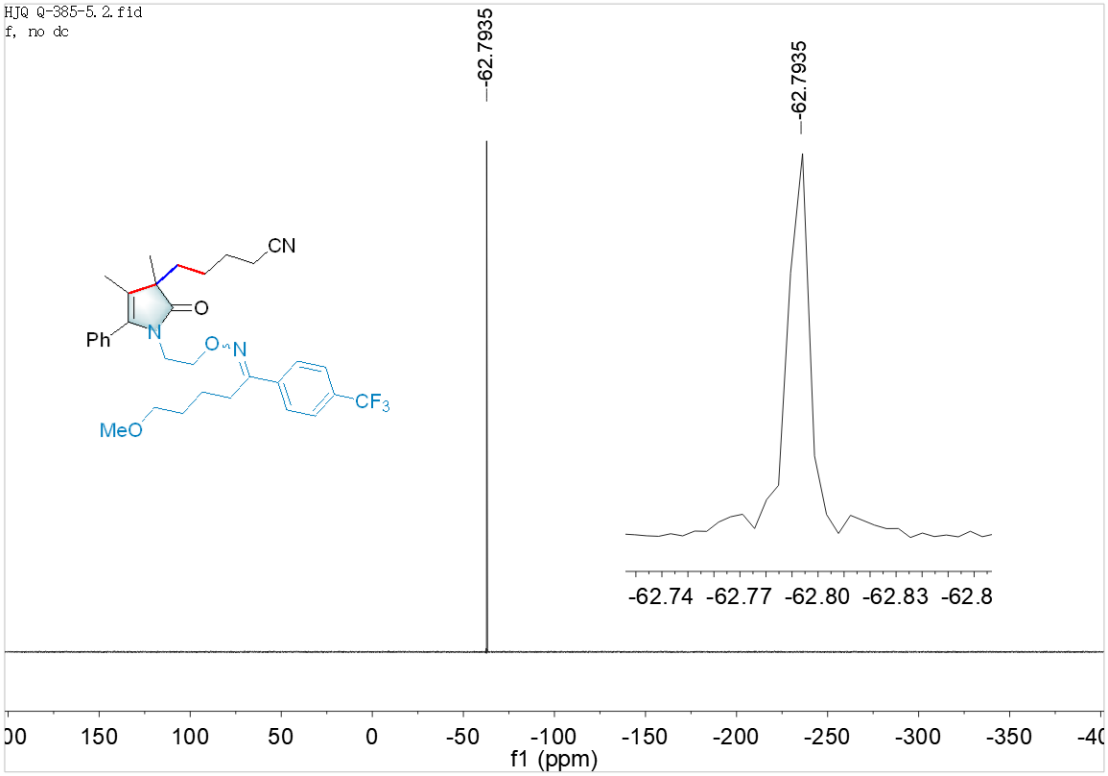
^{13}C NMR



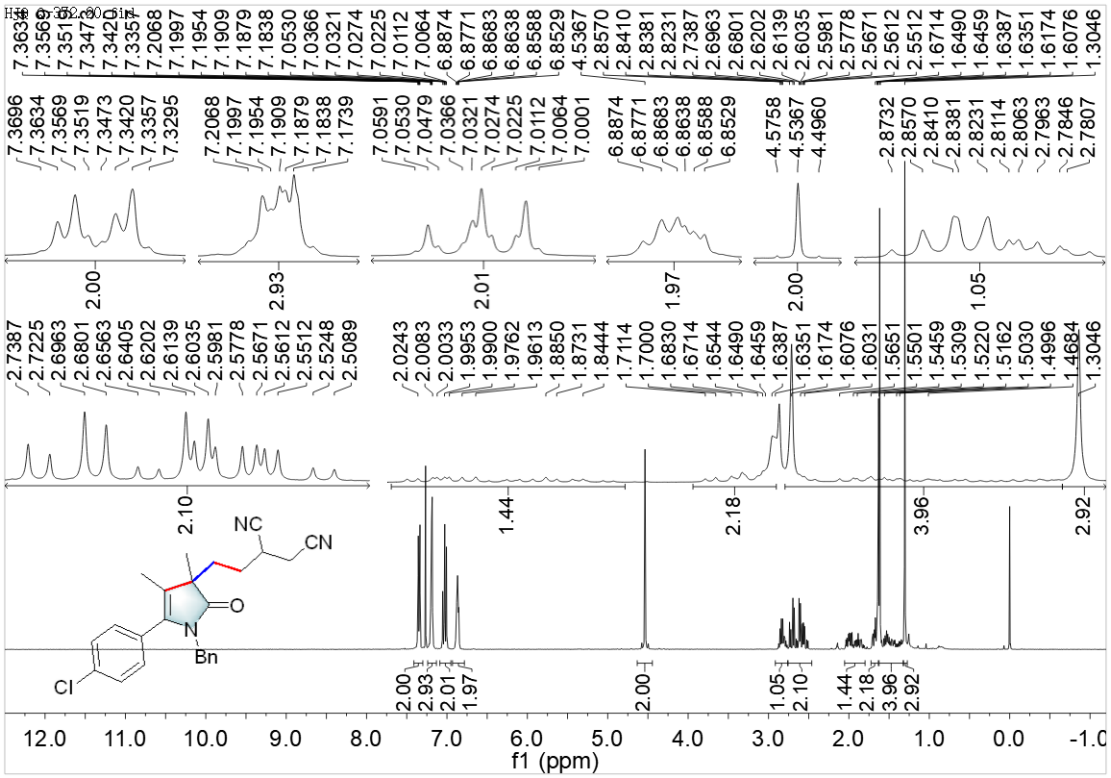
DEPT 90 and DEPT 135



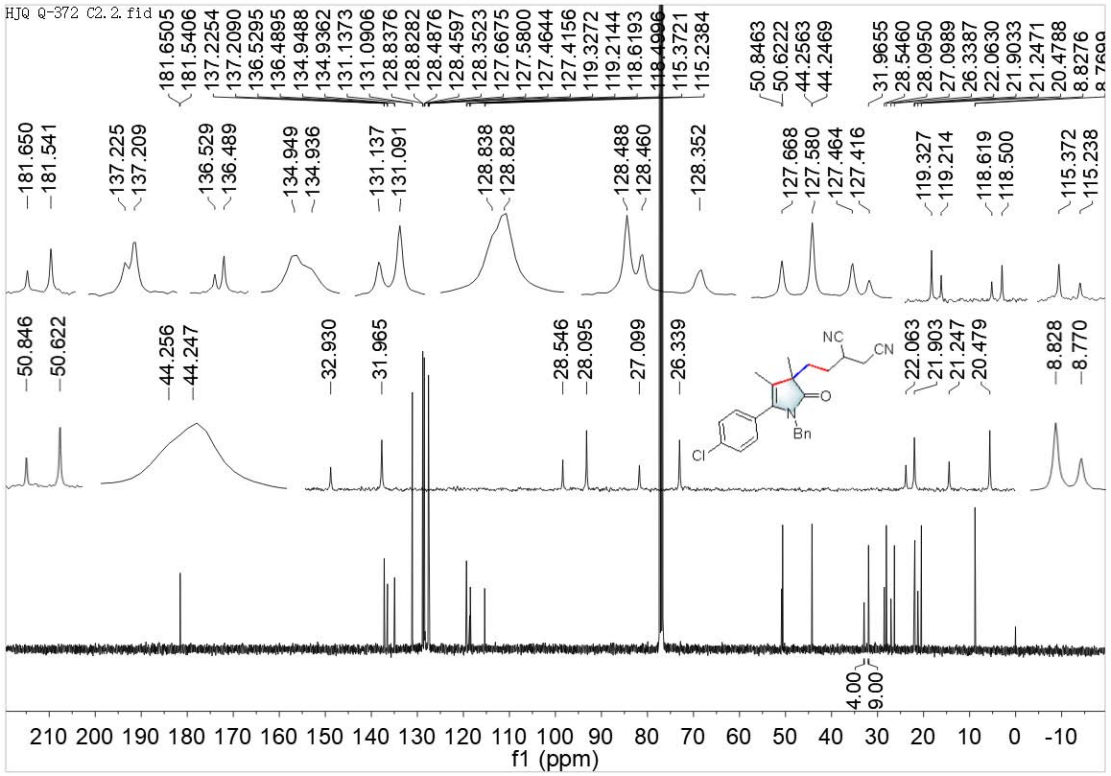
^{19}F NMR



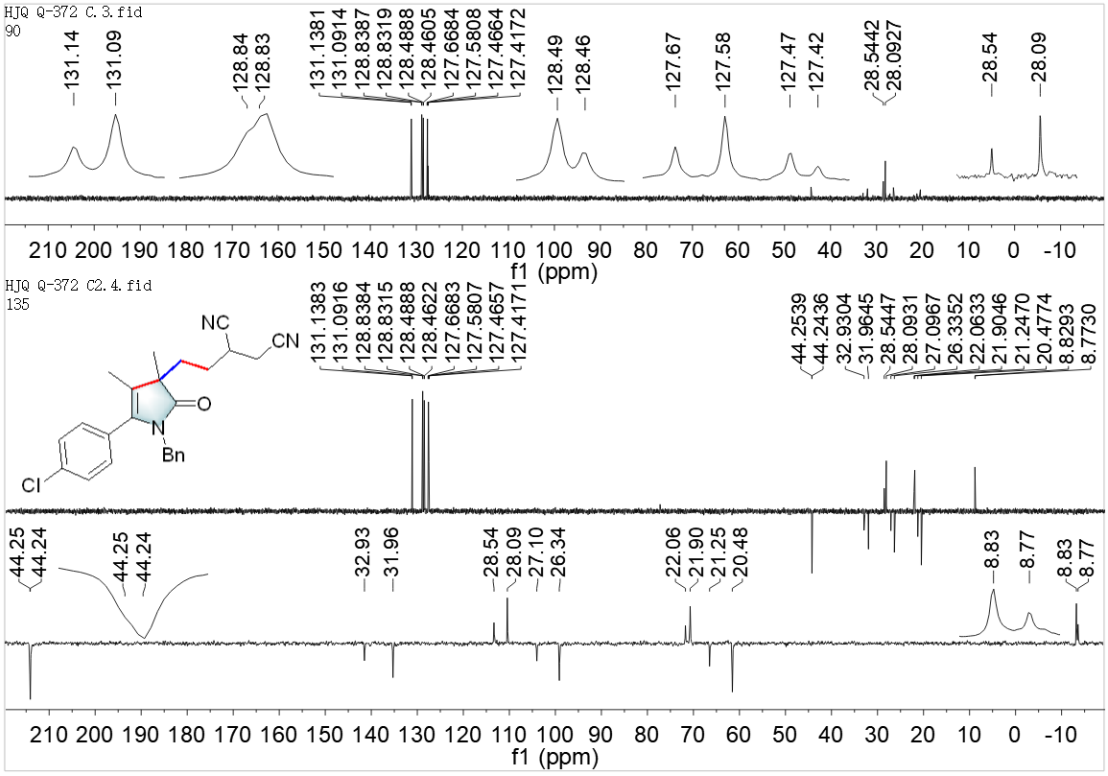
3q, ^{1}H NMR



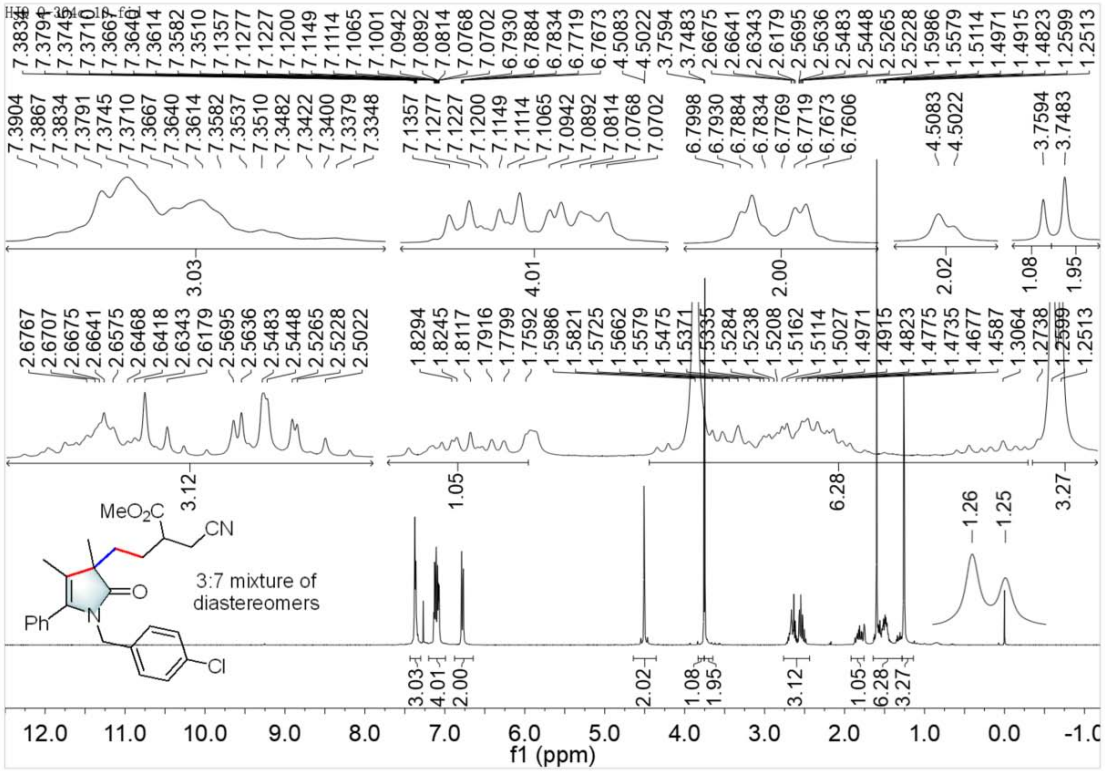
^{13}C NMR



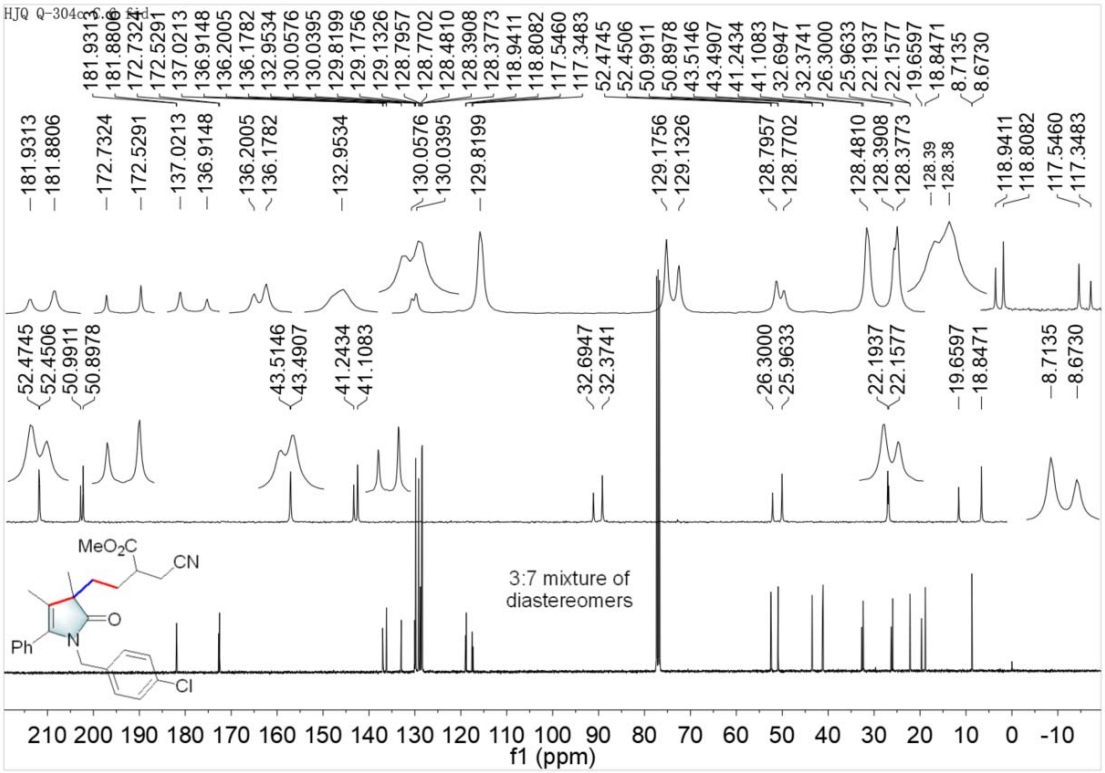
DEPT 90 and DEPT 135



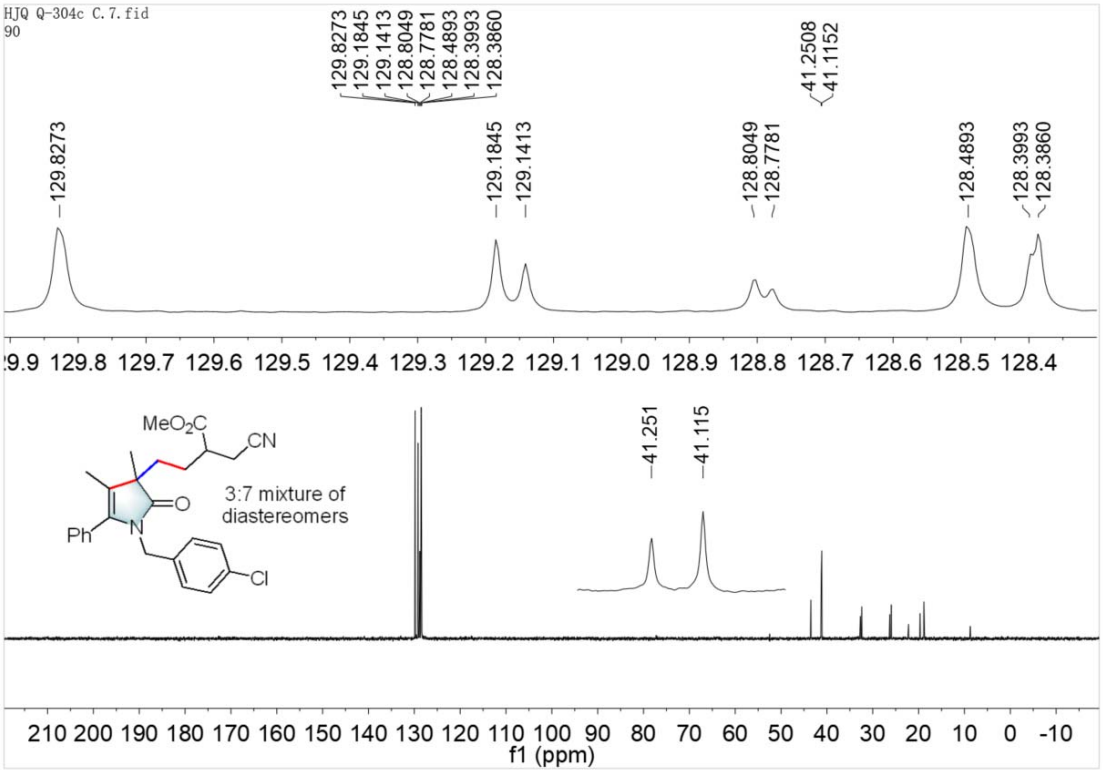
3r, ^{1}H NMR



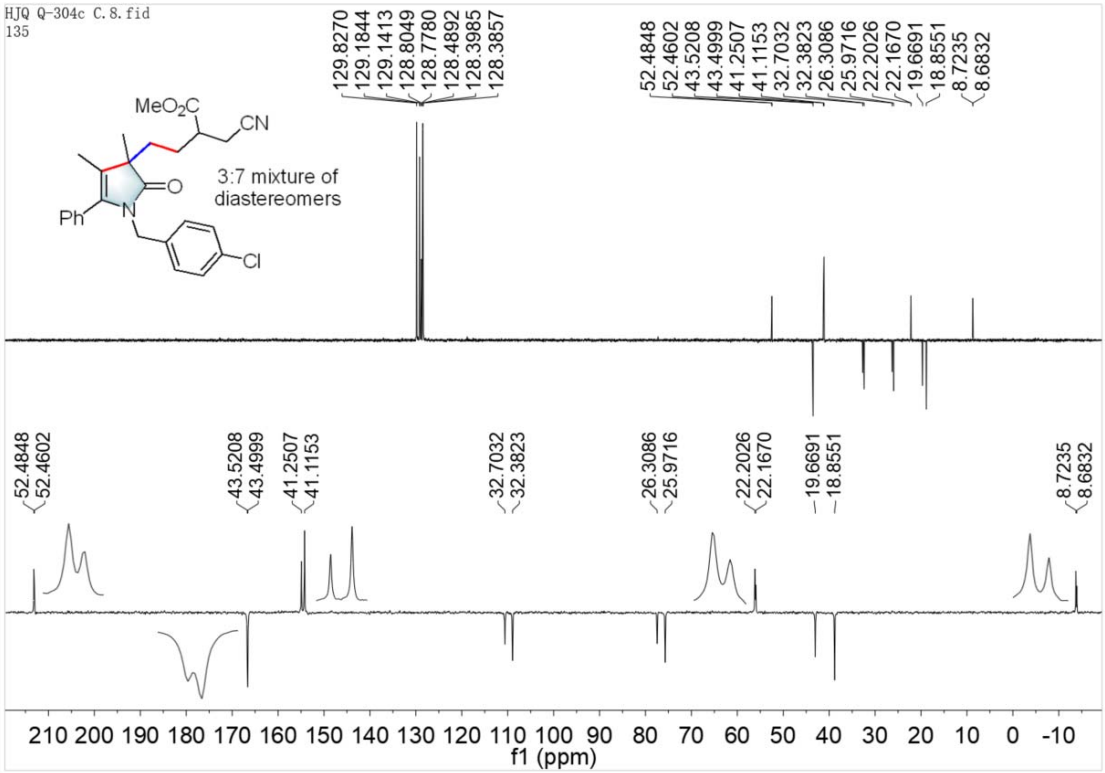
^{13}C NMR



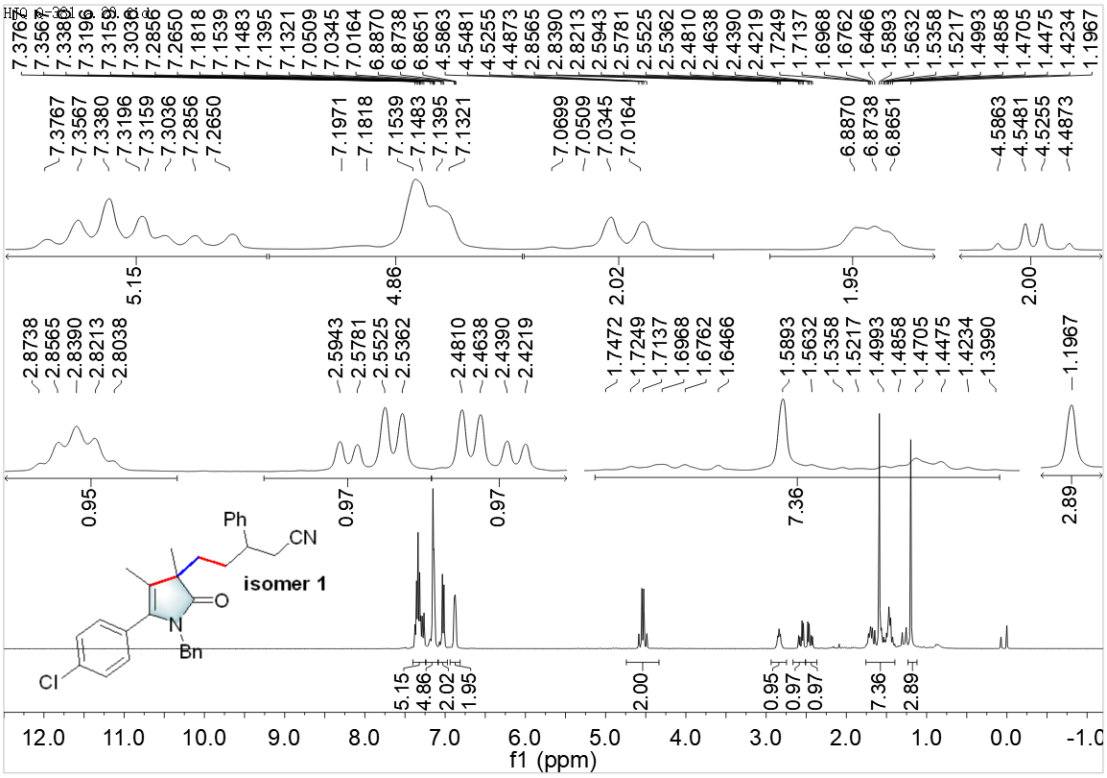
DEPT 90



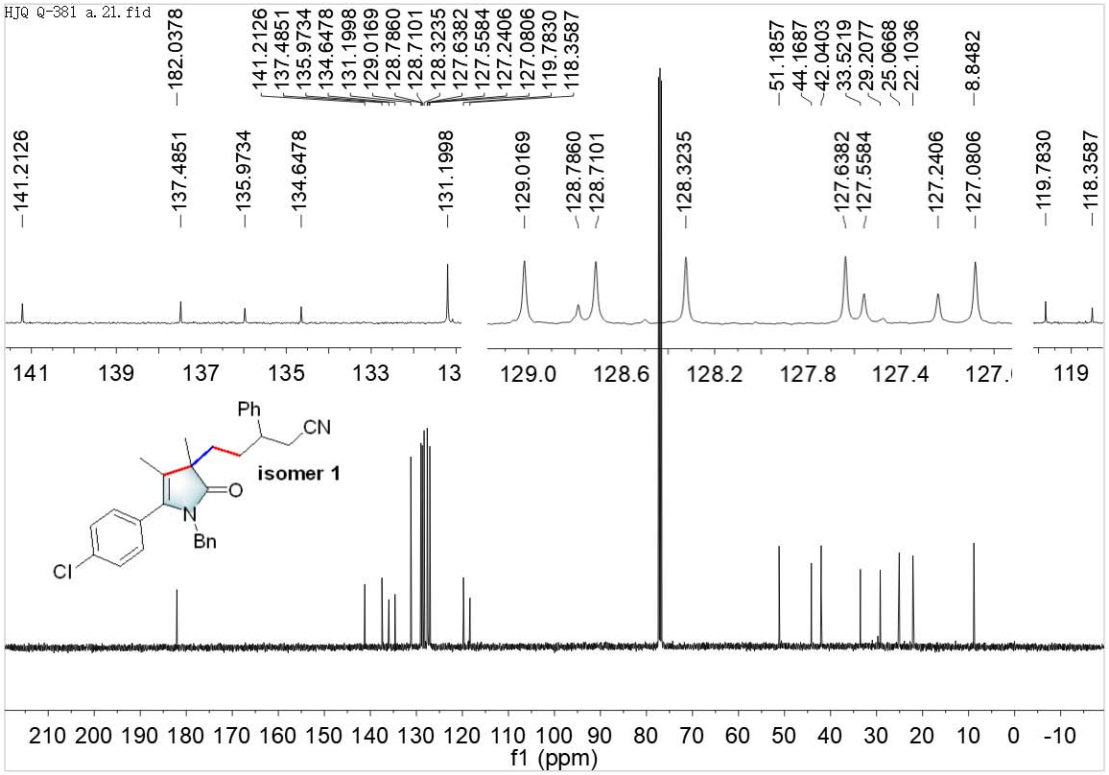
DEPT 135



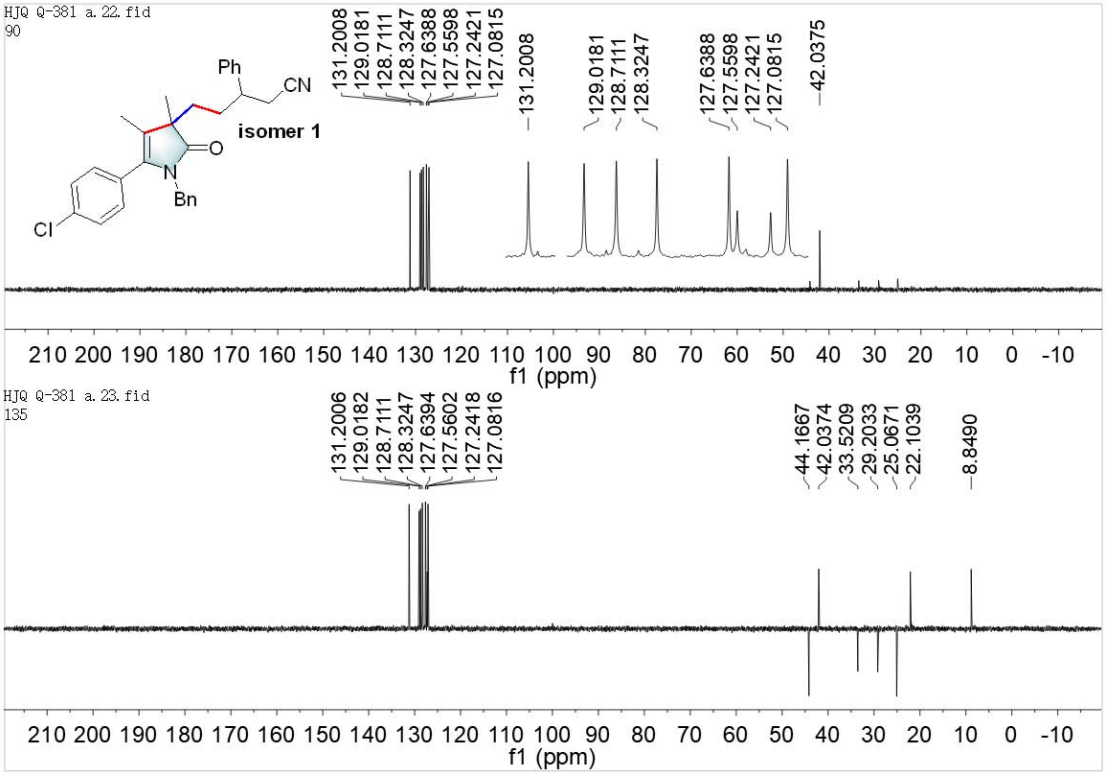
3s, isomer 1, ^{1}H NMR



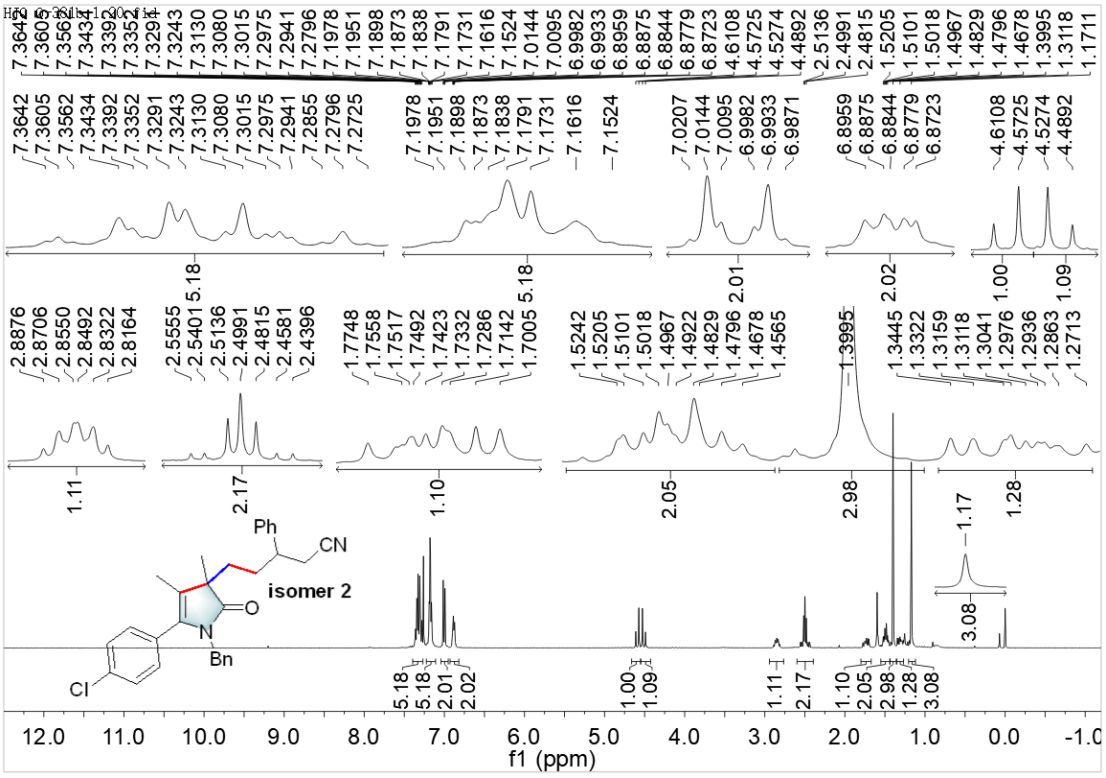
^{13}C NMR



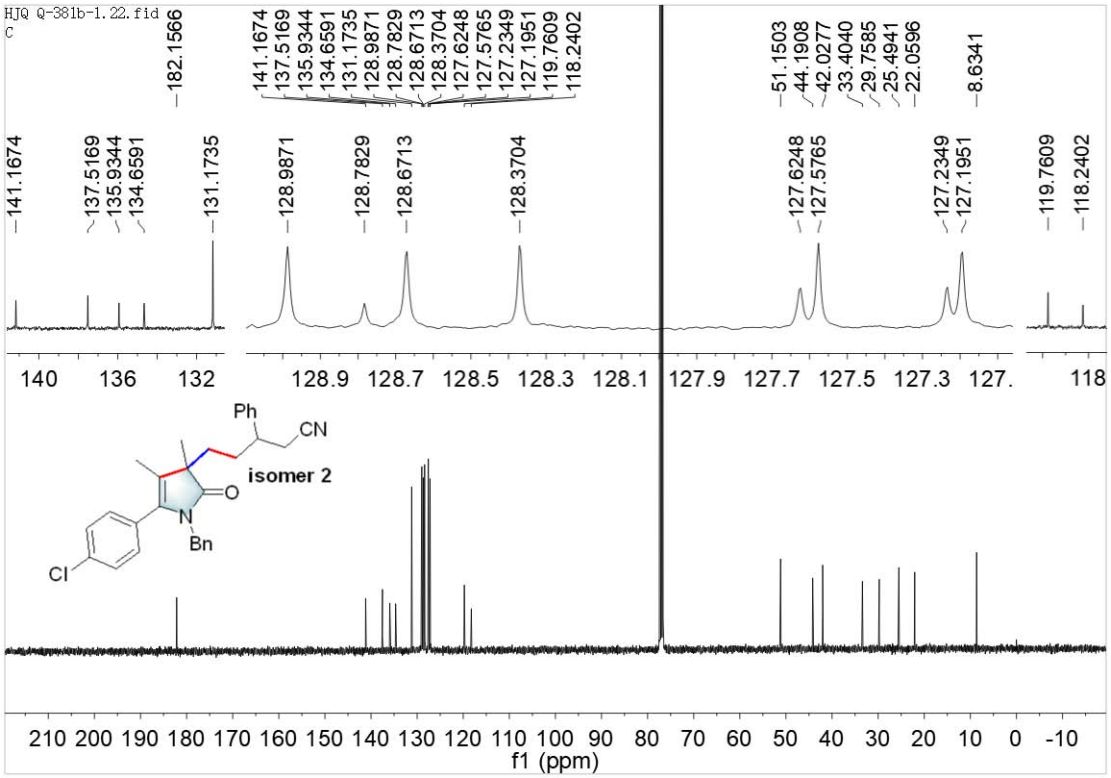
DEPT 90 and DEPT 135



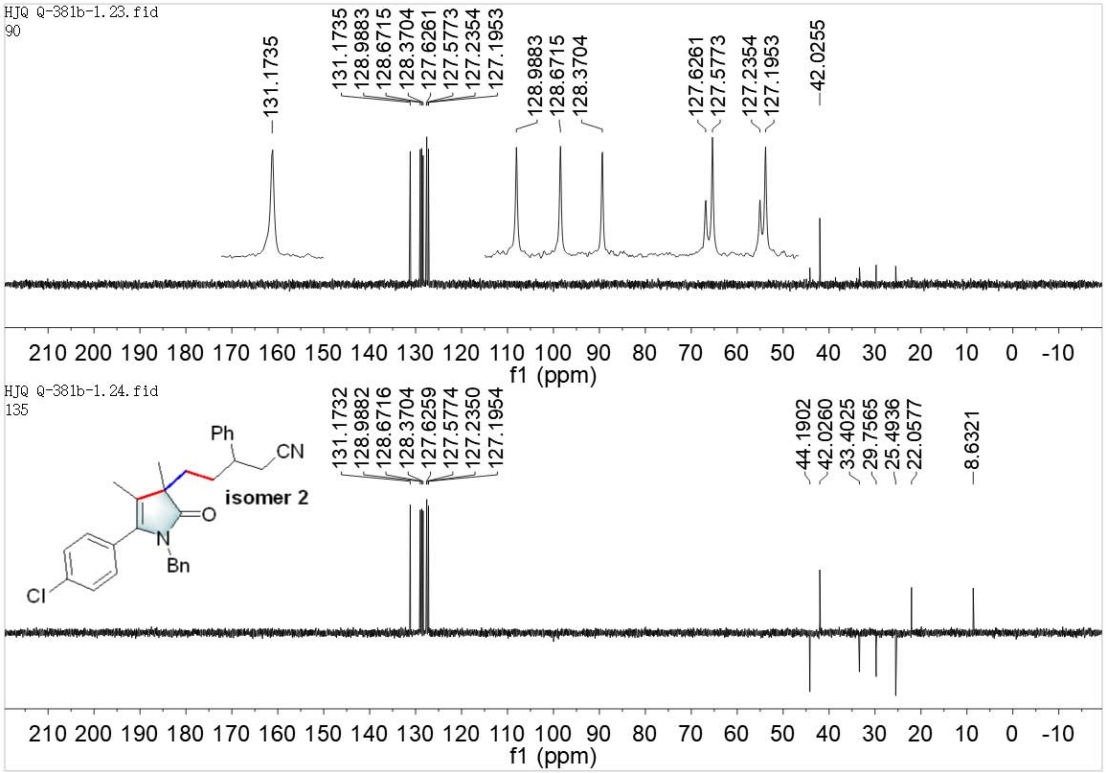
3s, isomer 2, ^{1}H NMR



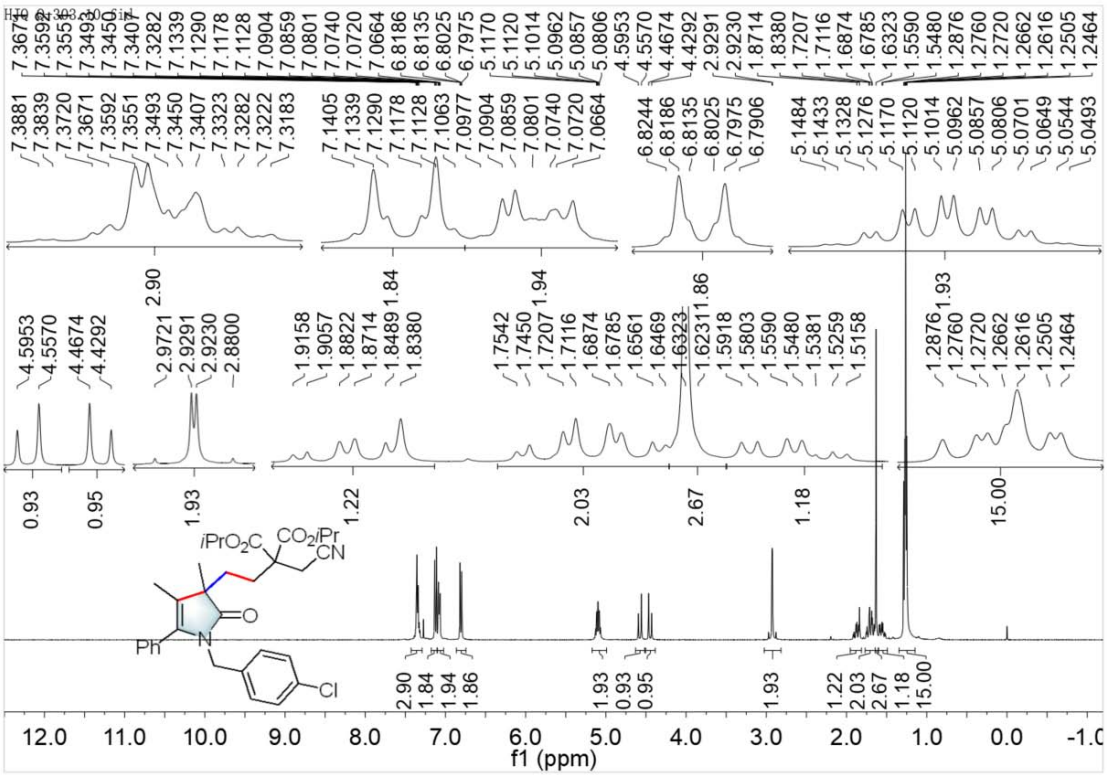
^{13}C NMR



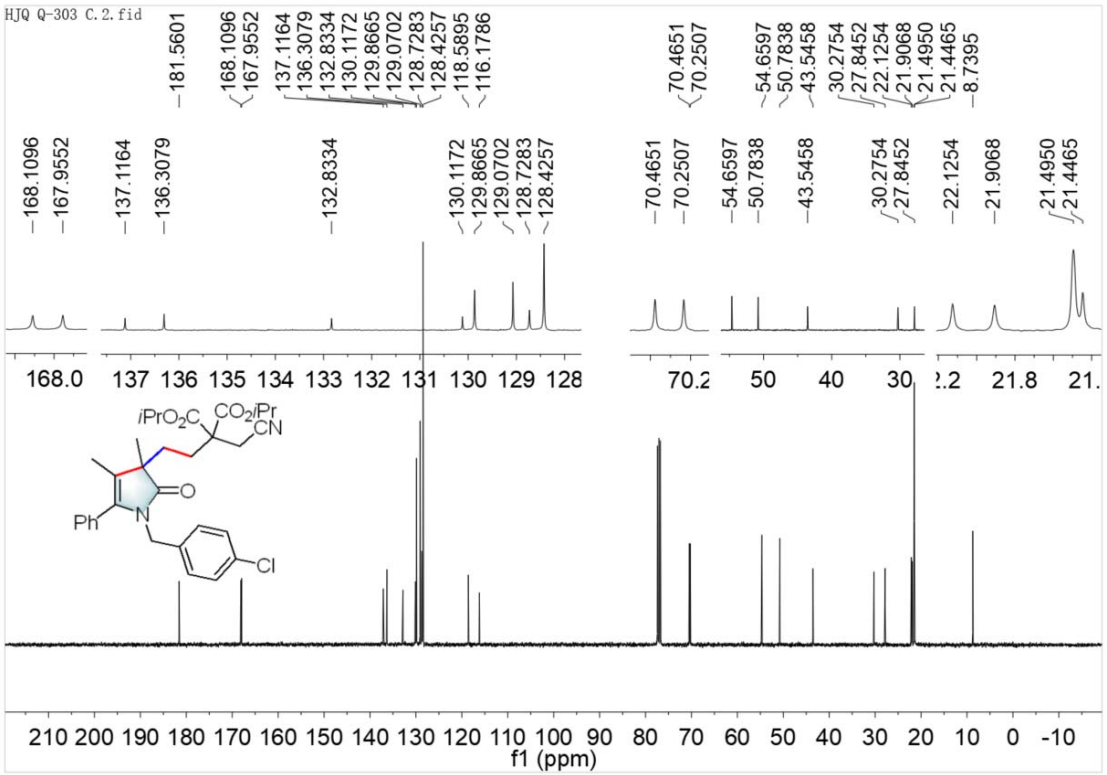
DEPT 90 and DEPT 135



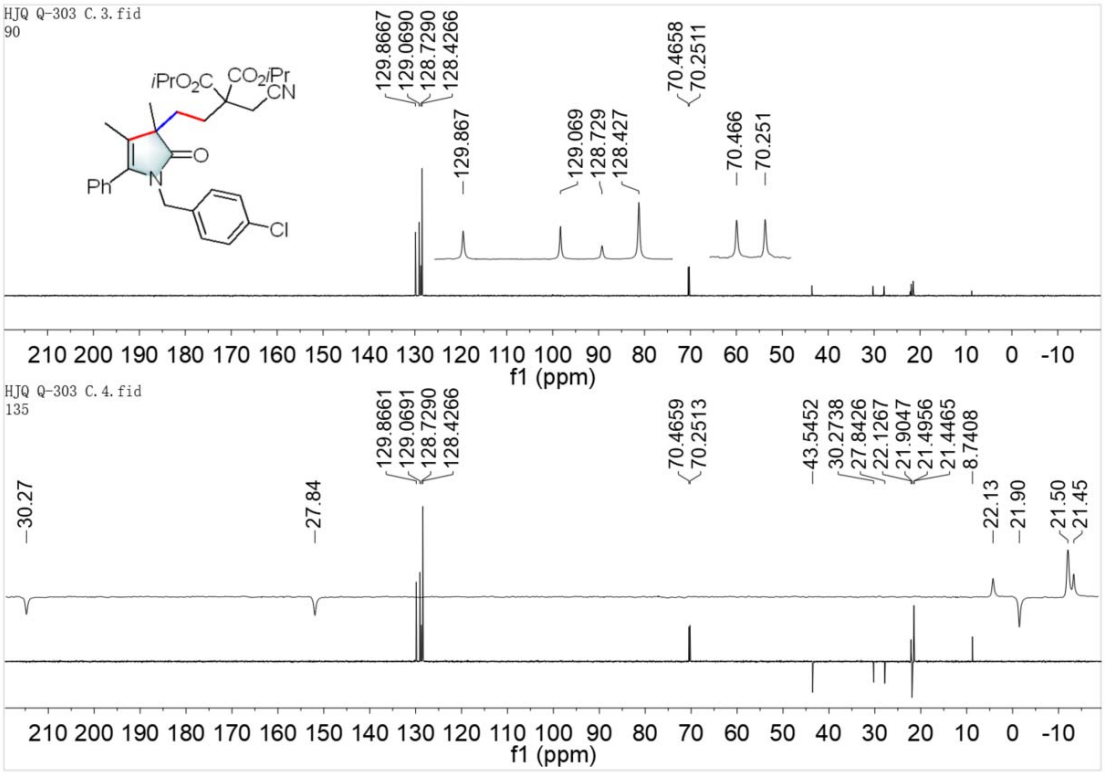
3t, ^{1}H NMR



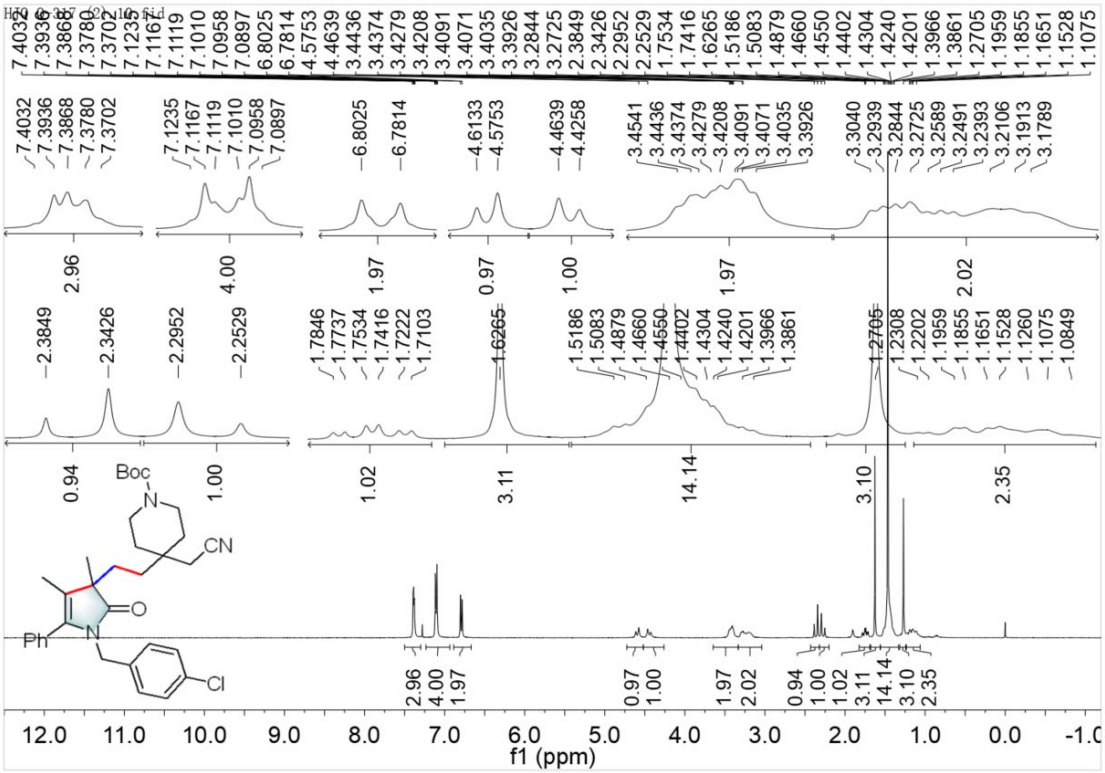
^{13}C NMR



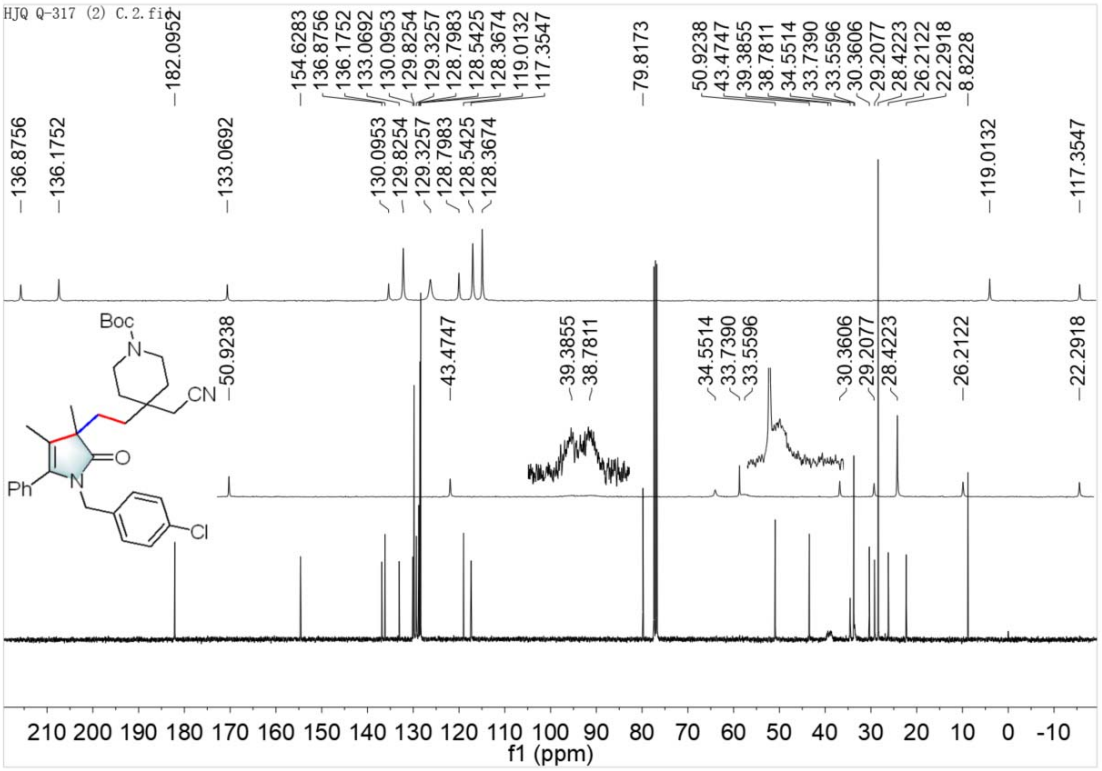
DEPT 90 and DEPT 135



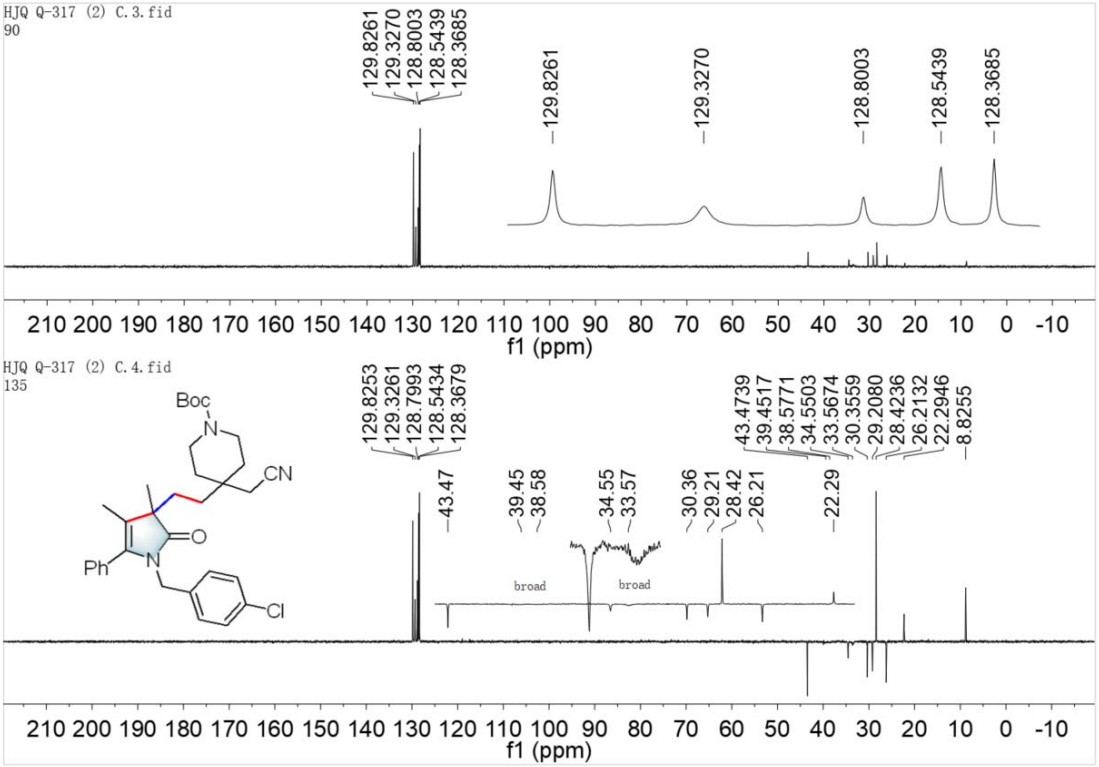
3u, ^{1}H NMR



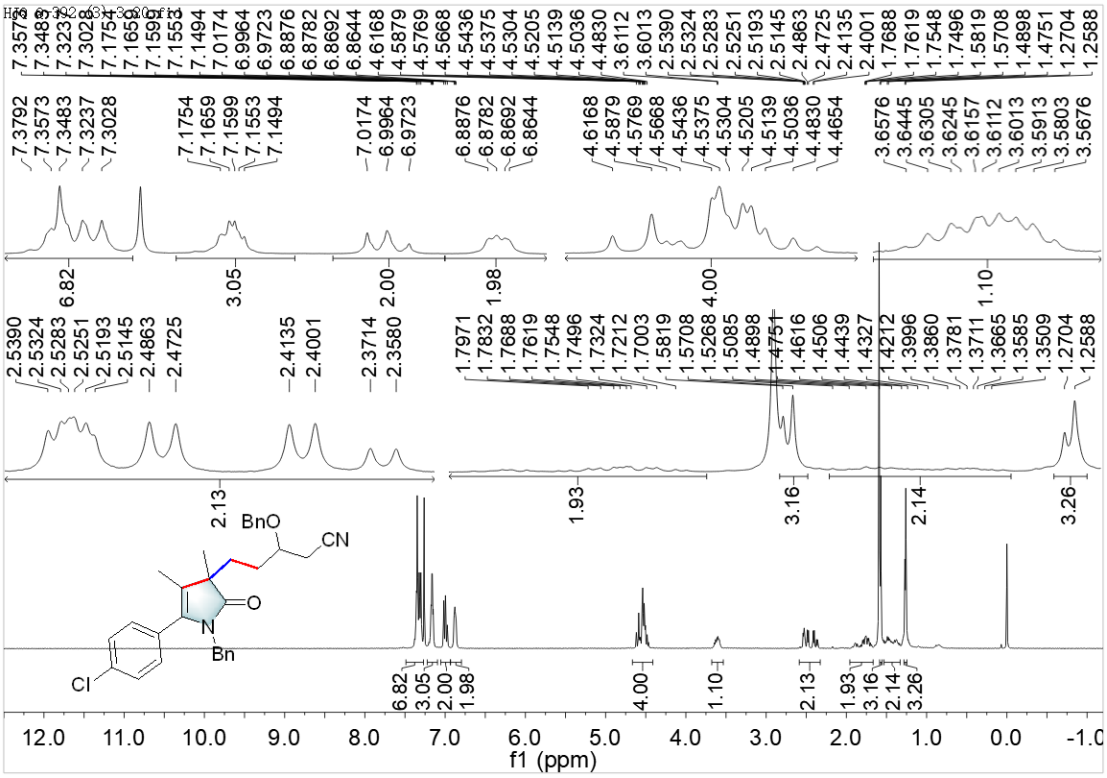
^{13}C NMR



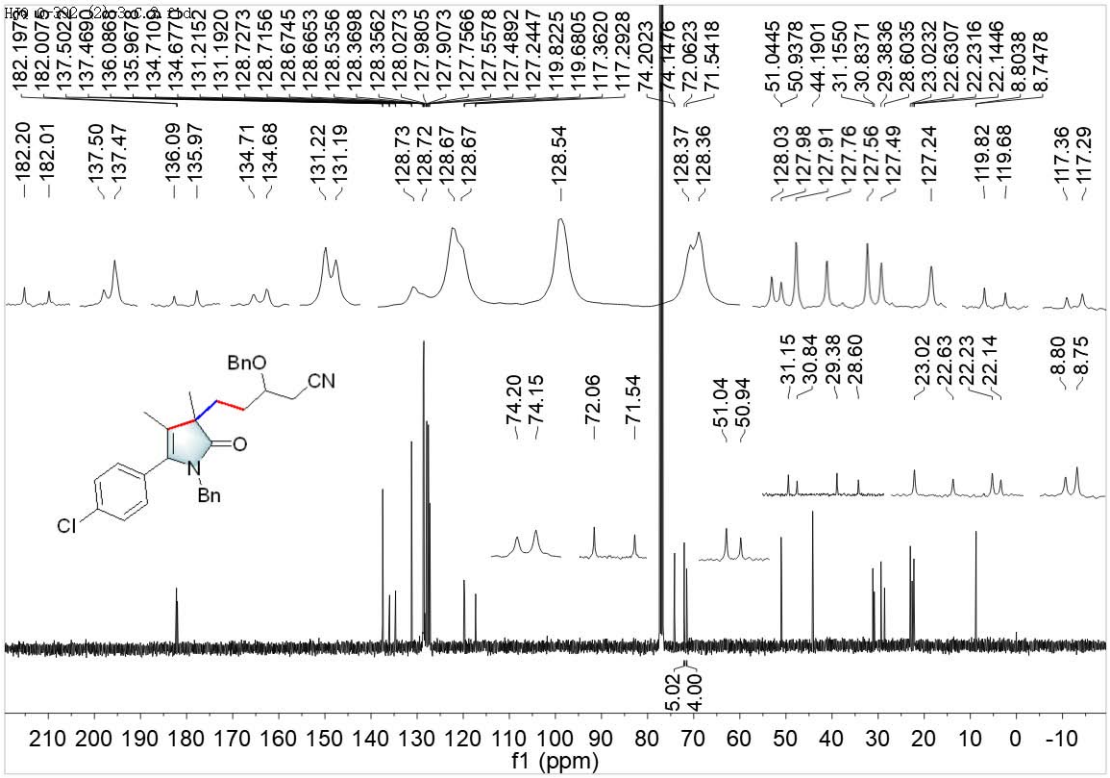
DEPT 90 and DEPT 135



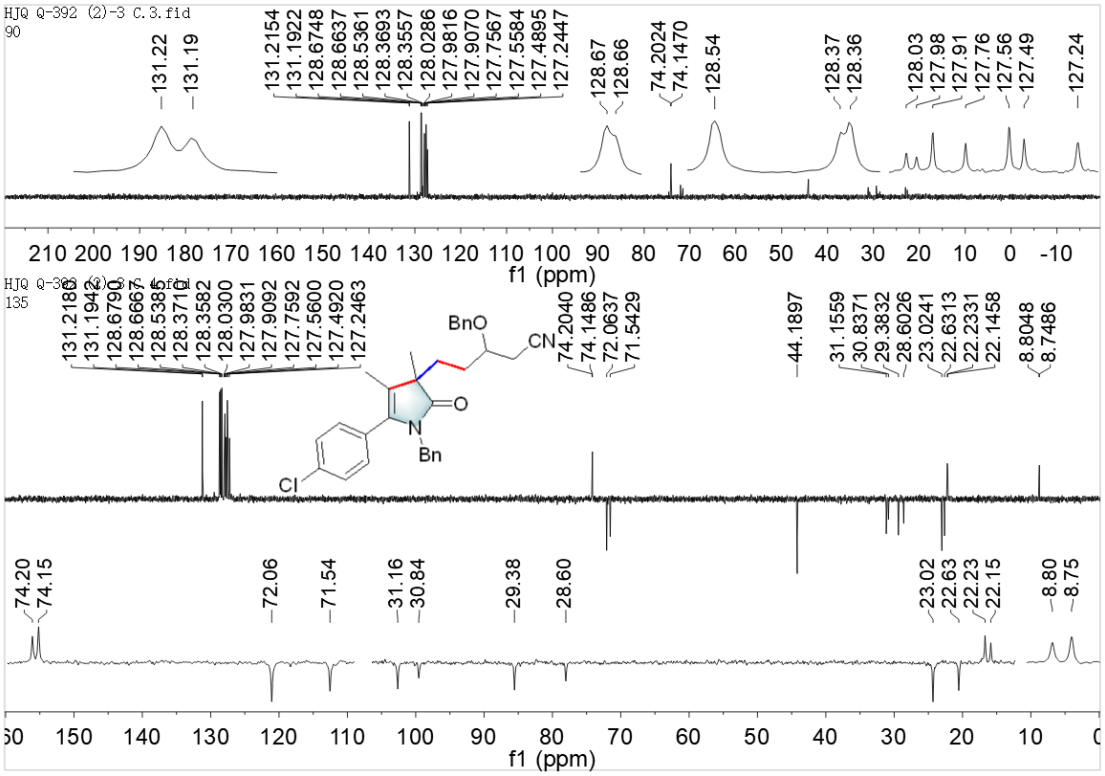
3v, ^{1}H NMR



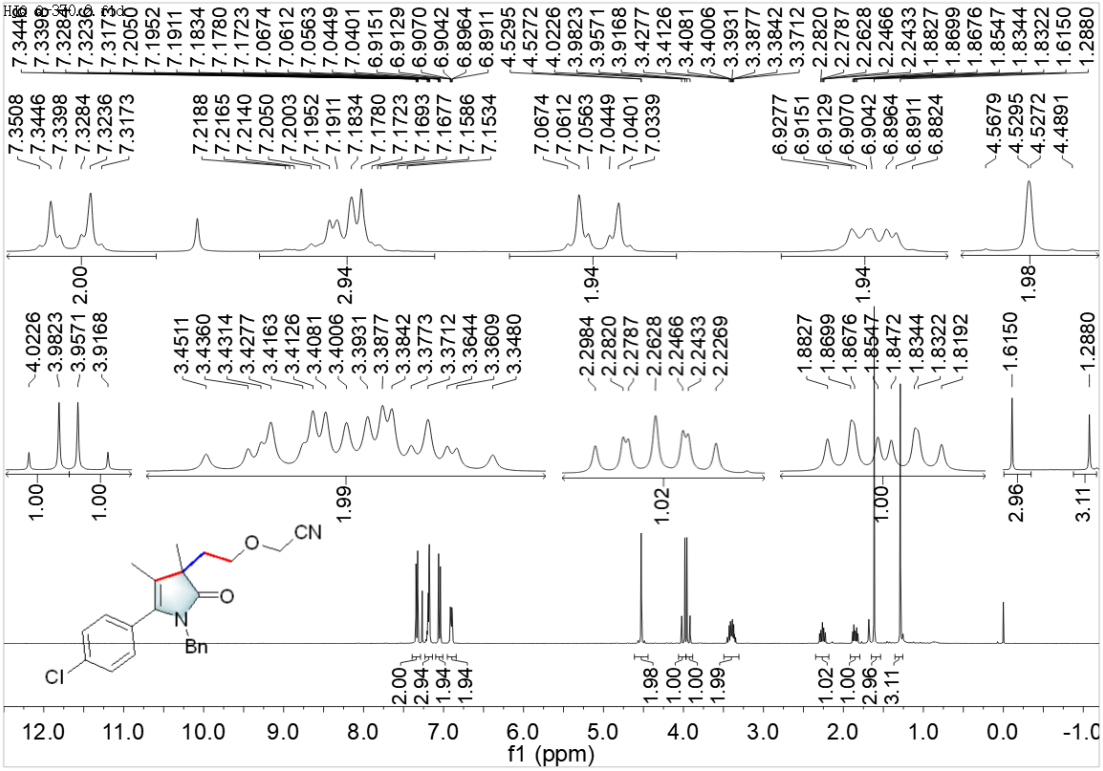
^{13}C NMR



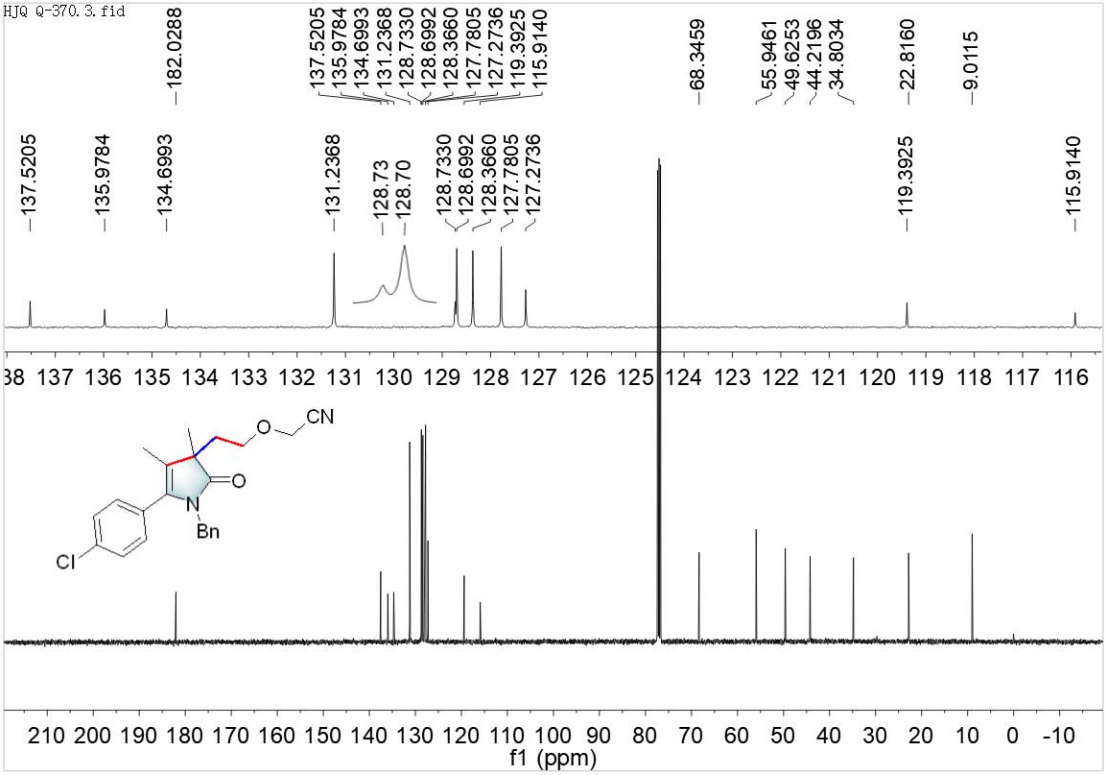
DEPT 90 and DEPT 135



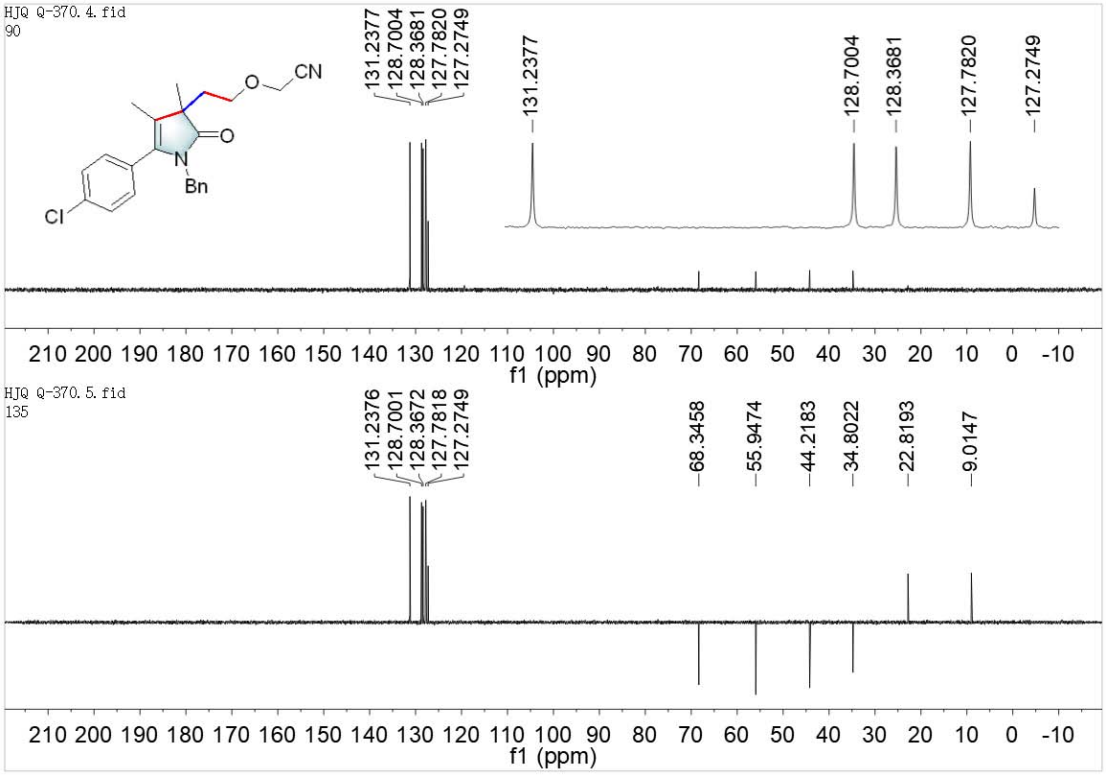
3w, ^{1}H NMR



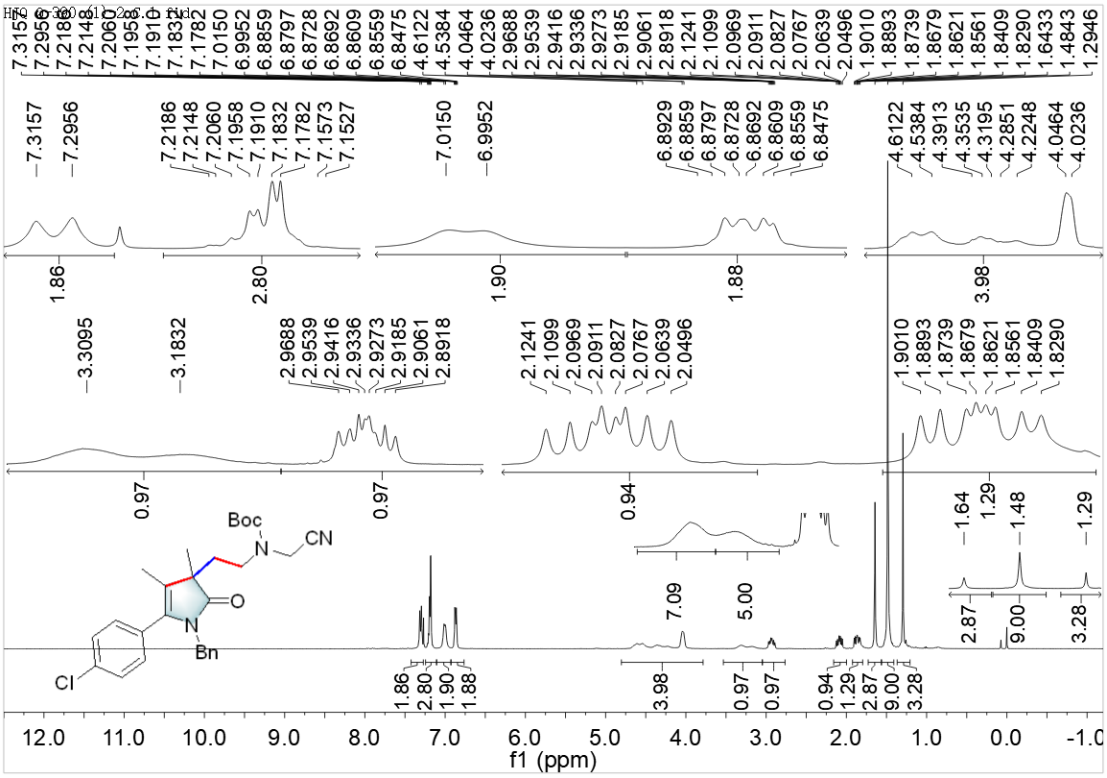
^{13}C NMR



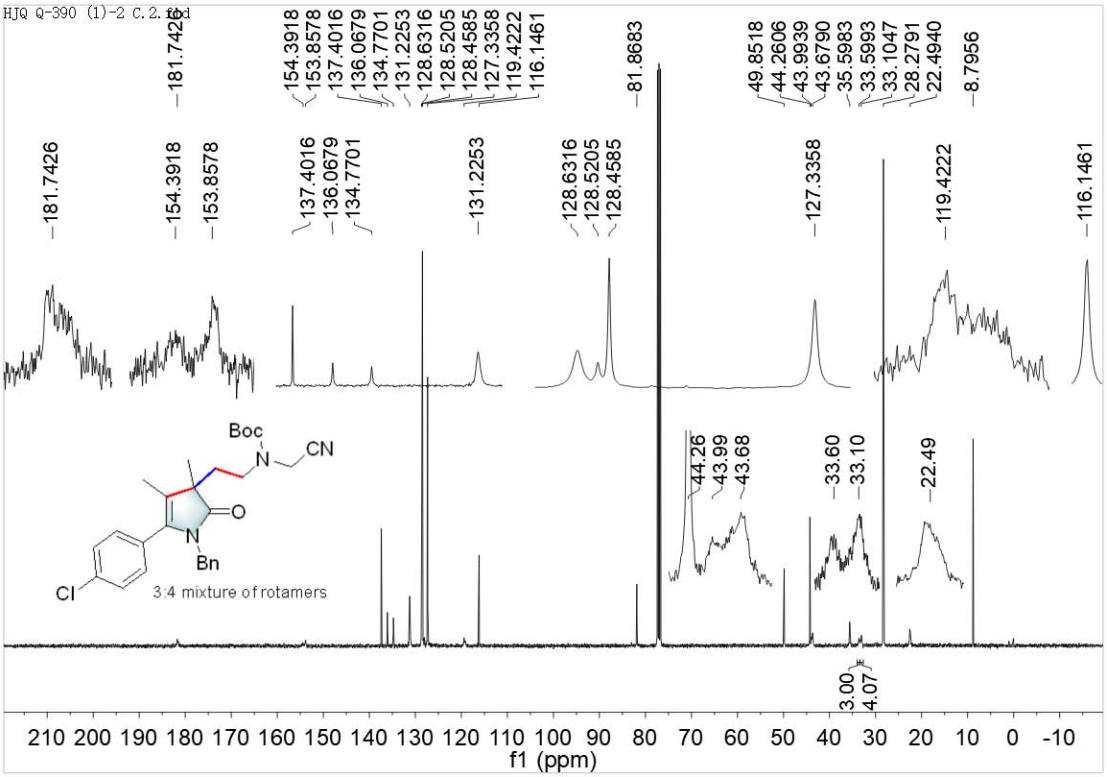
DEPT 90 and DEPT 135



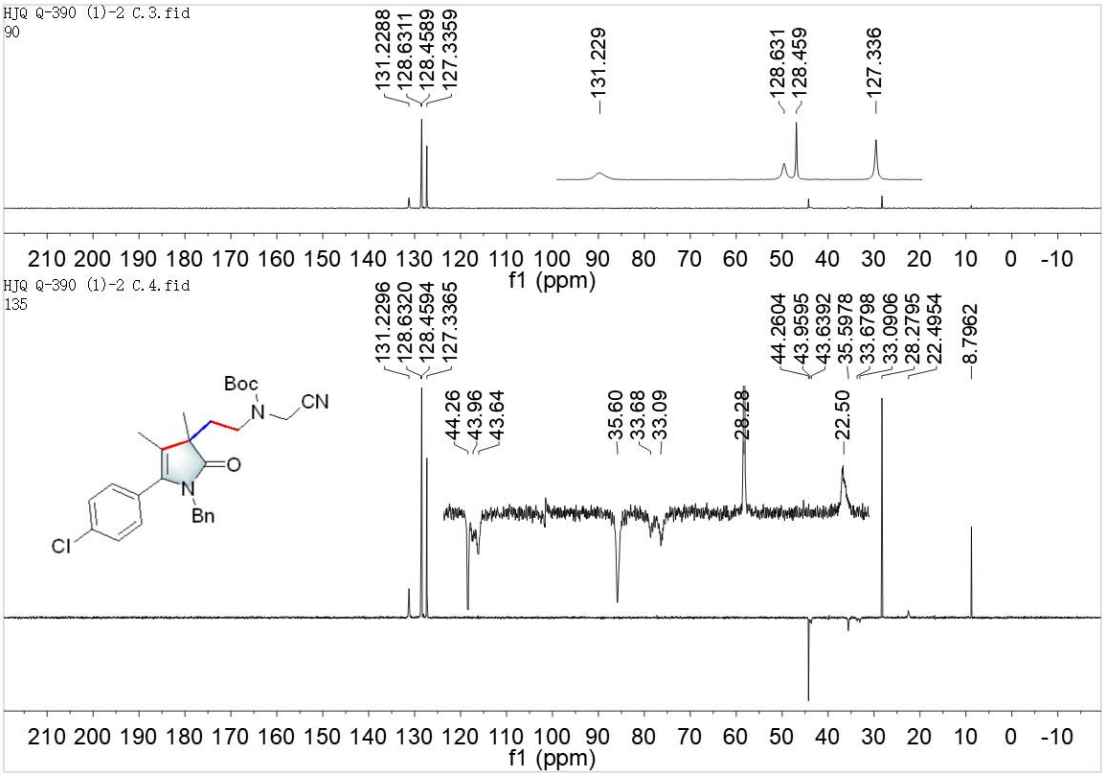
3x, ^{1}H NMR



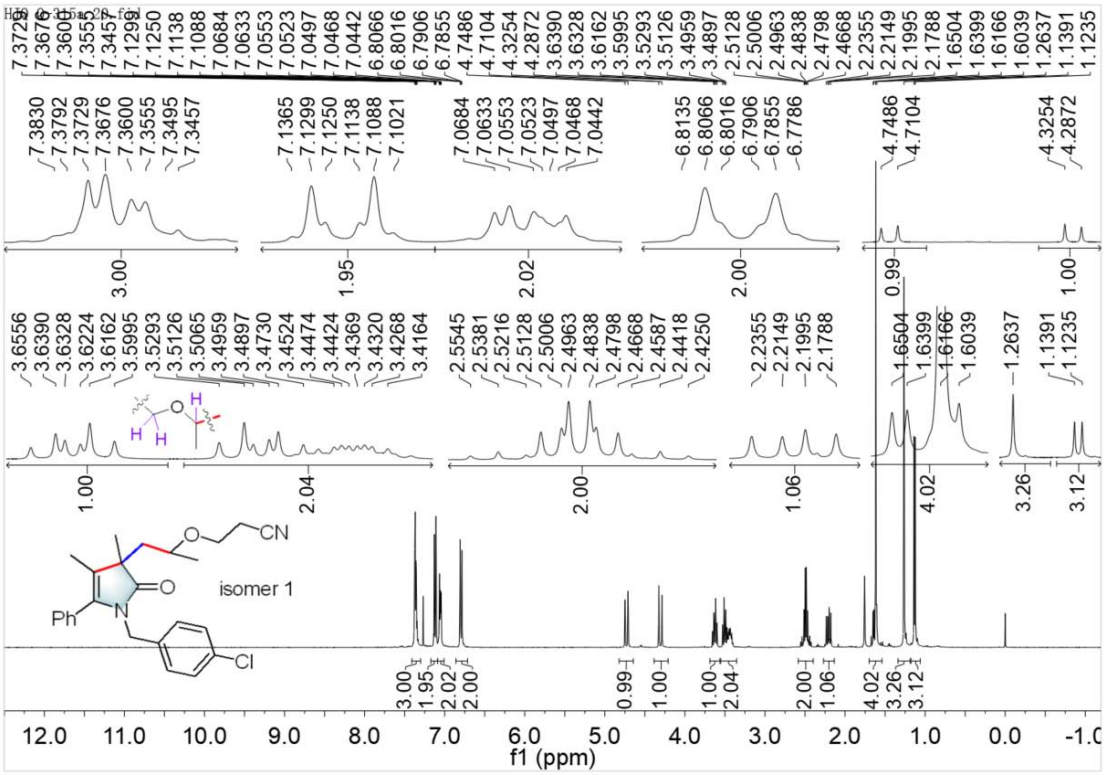
^{13}C NMR



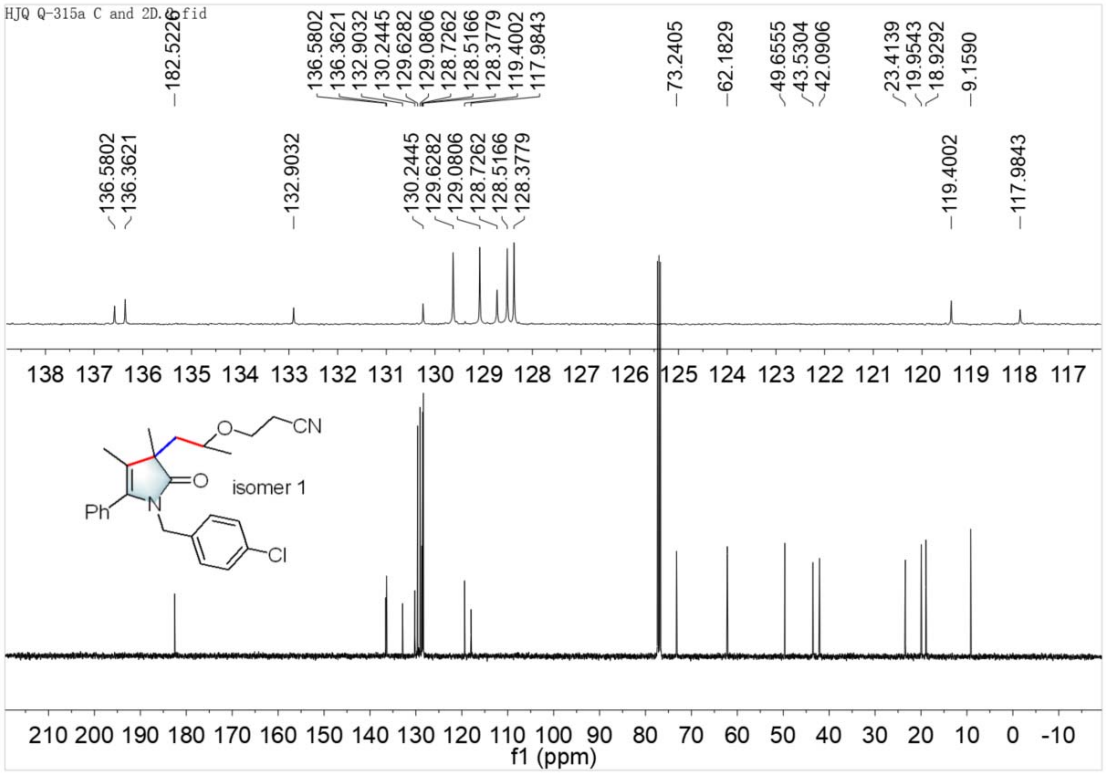
DEPT 90 and DEPT 135



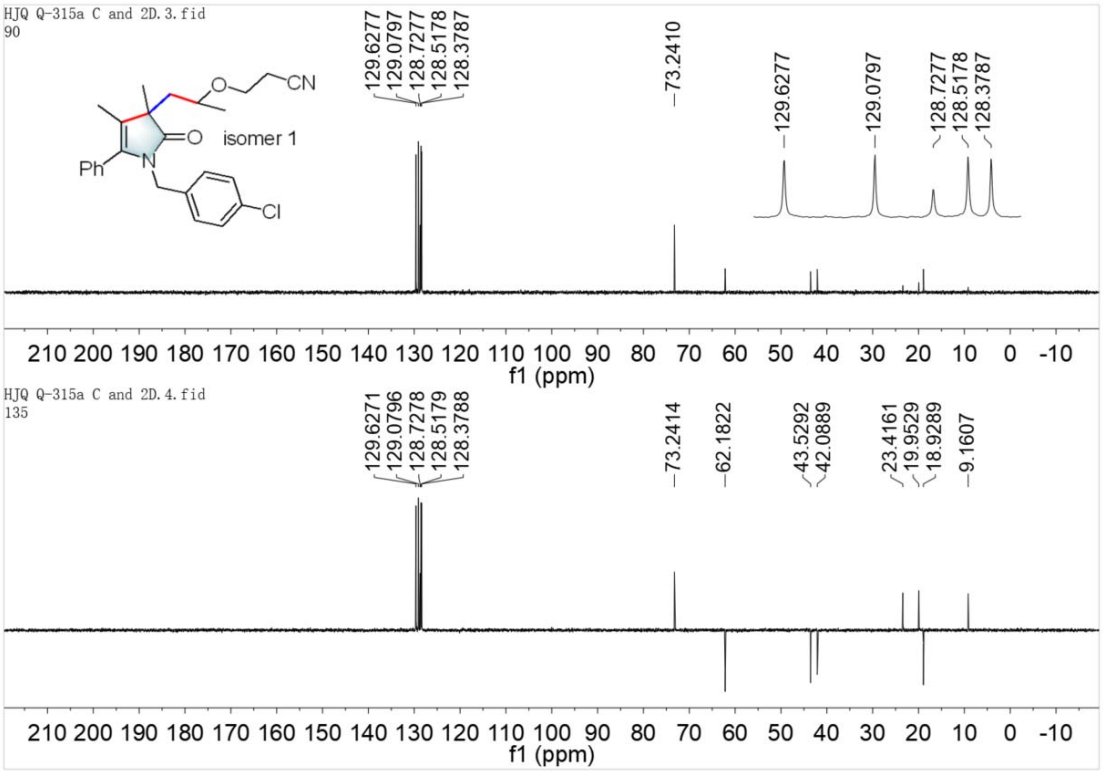
3y, isomer 1, ^{1}H NMR



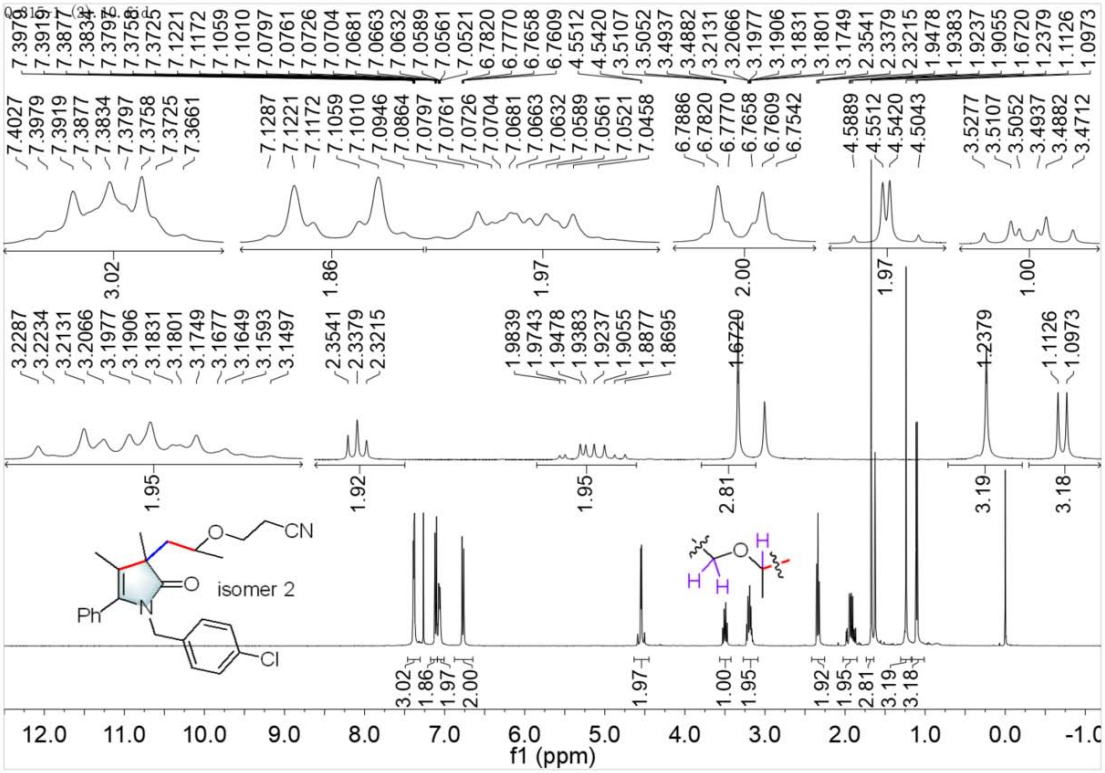
^{13}C NMR



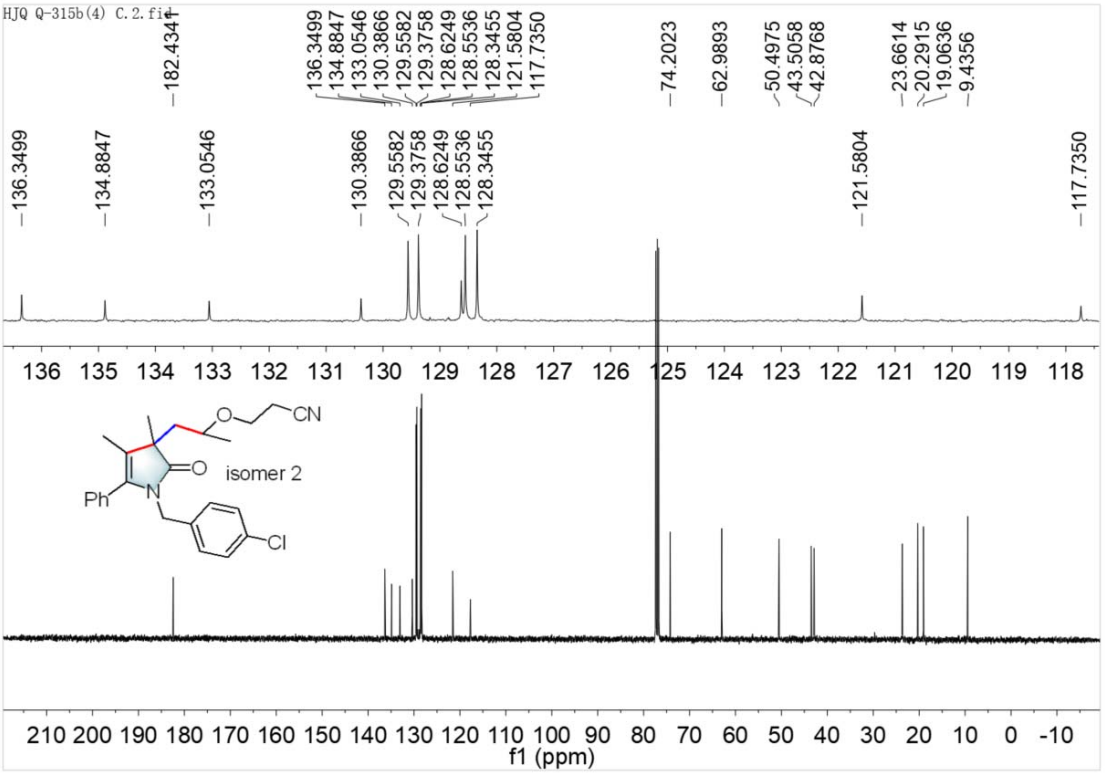
DEPT 90 and DEPT 135



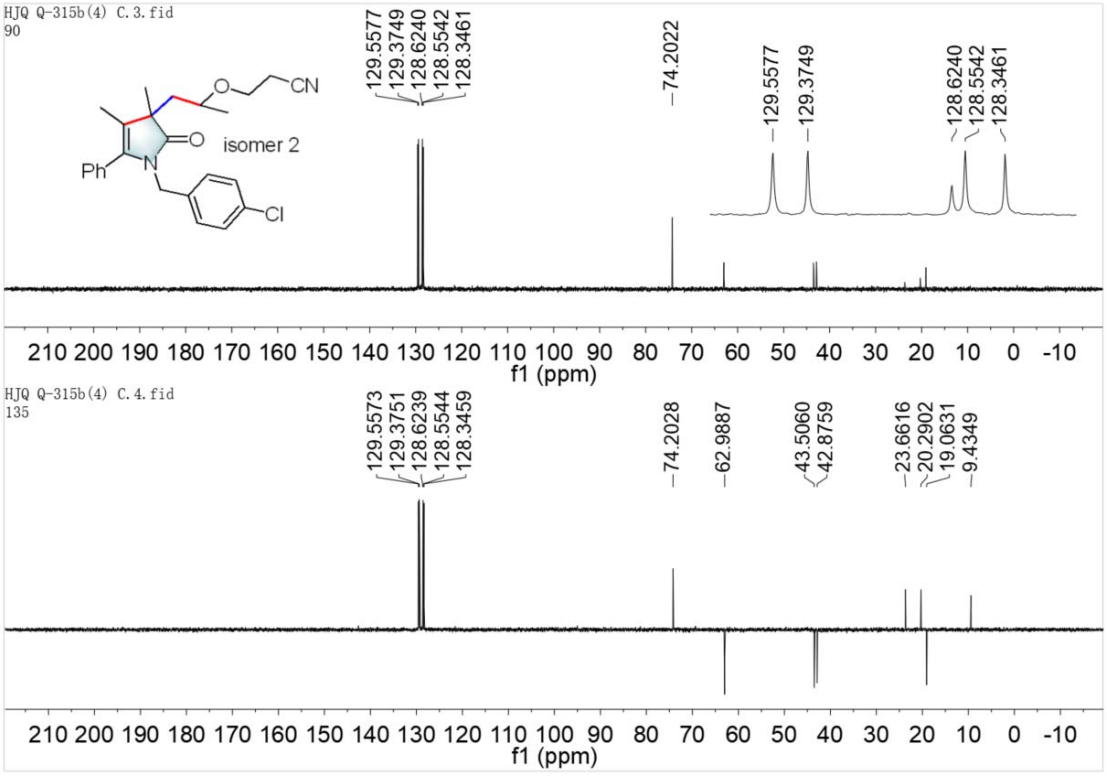
3y, isomer 2, ^{1}H NMR



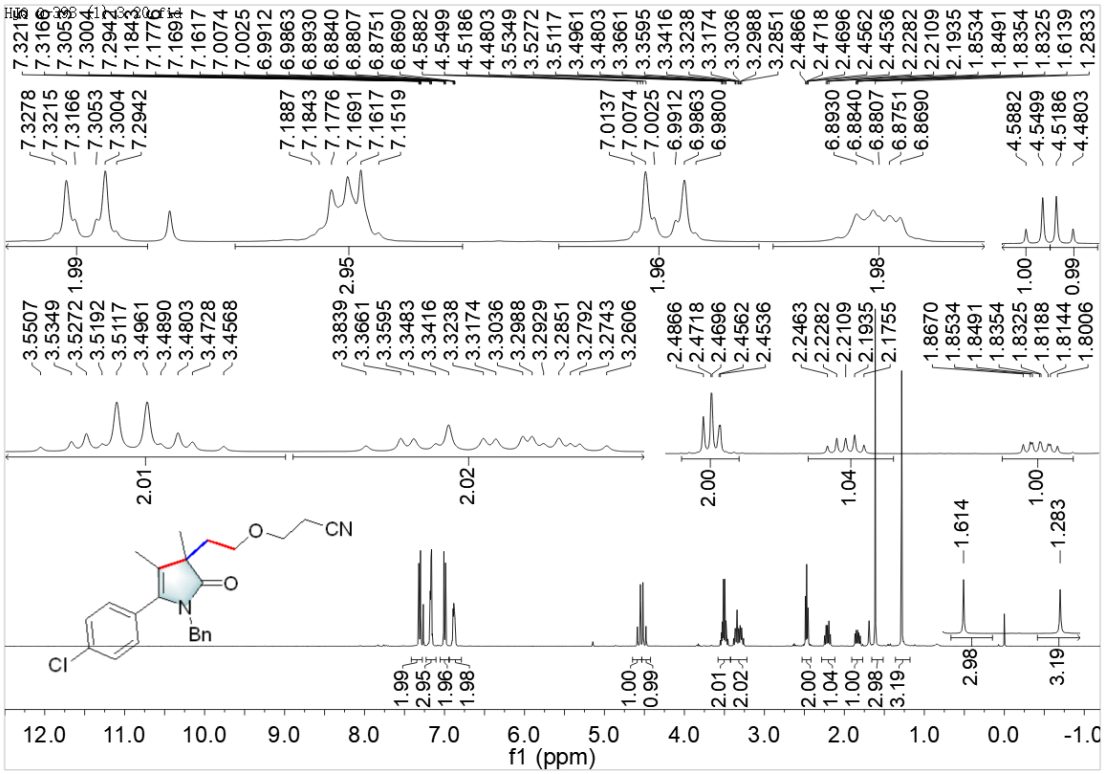
^{13}C NMR



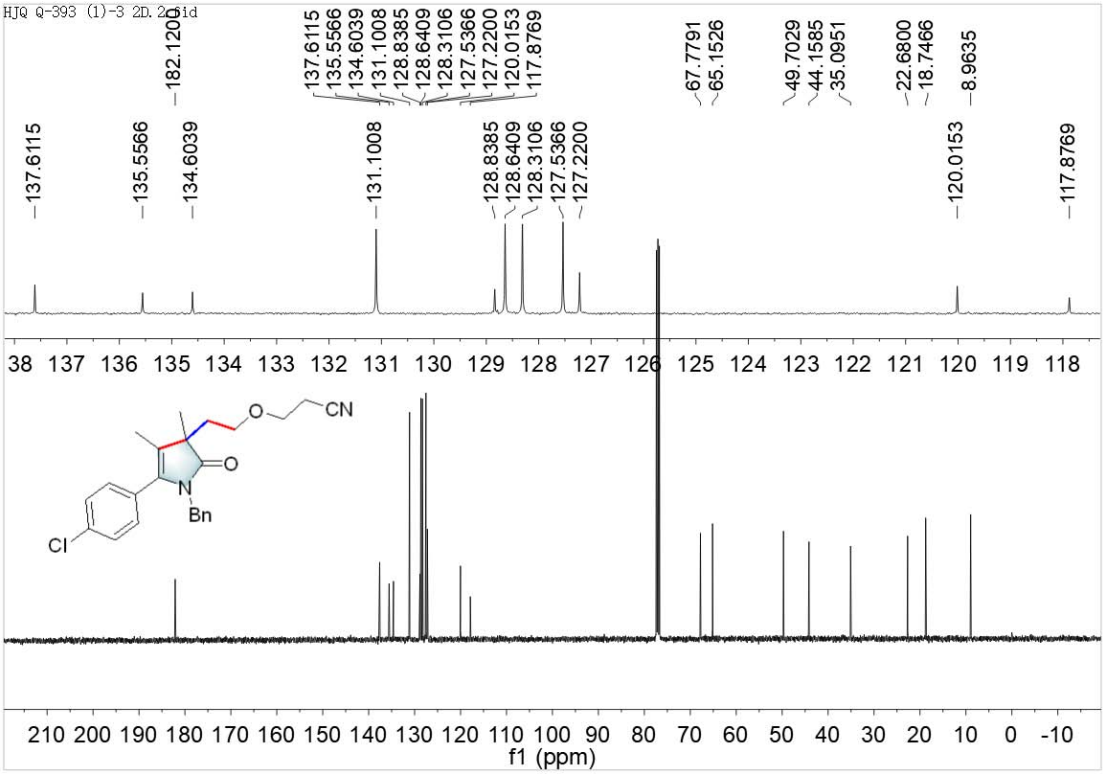
DEPT 90 and DEPT 135



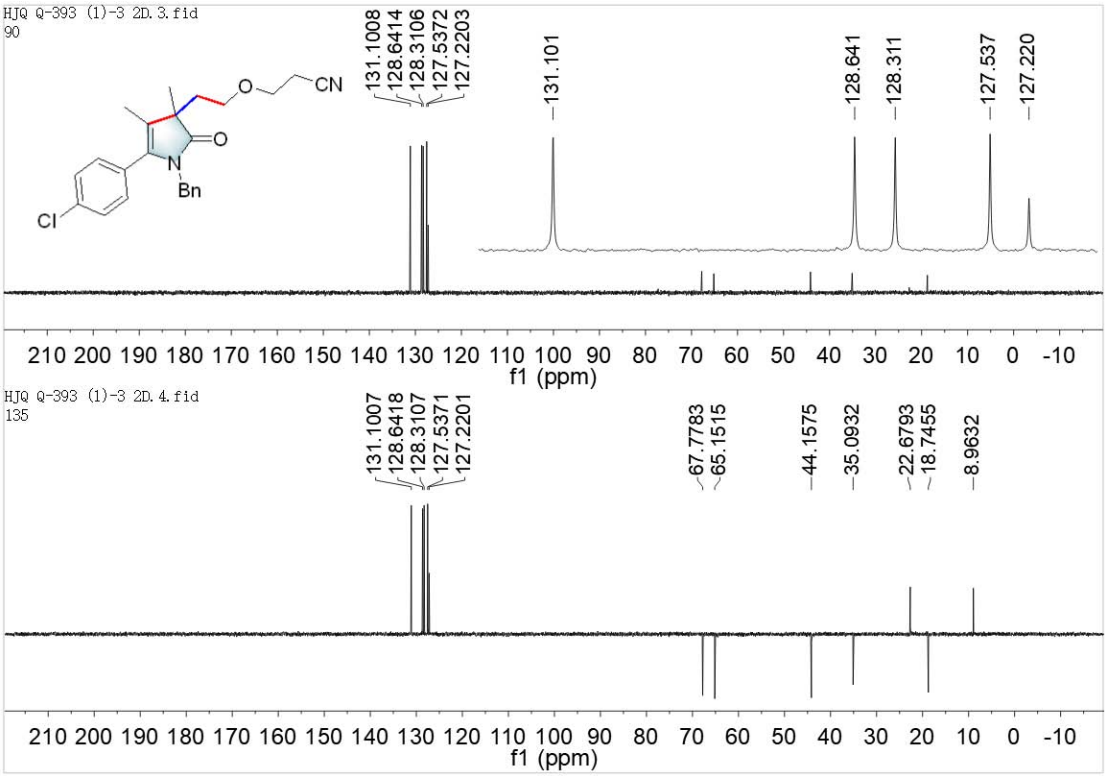
3z, ^{1}H NMR



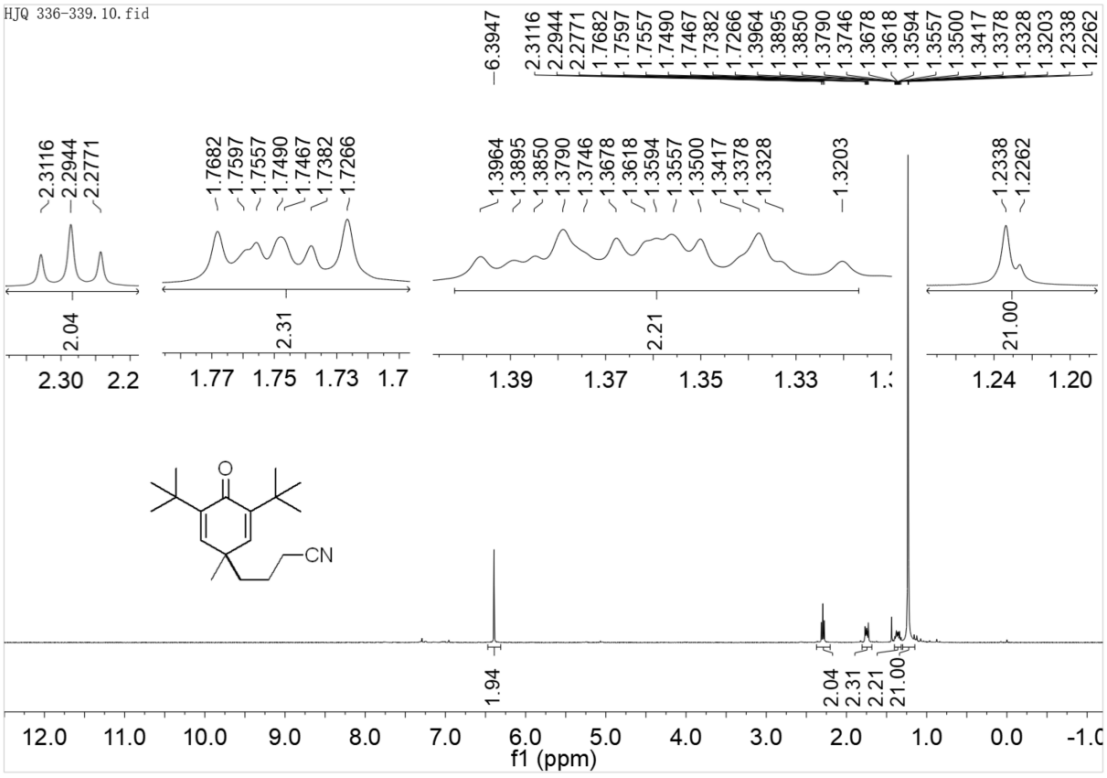
^{13}C NMR



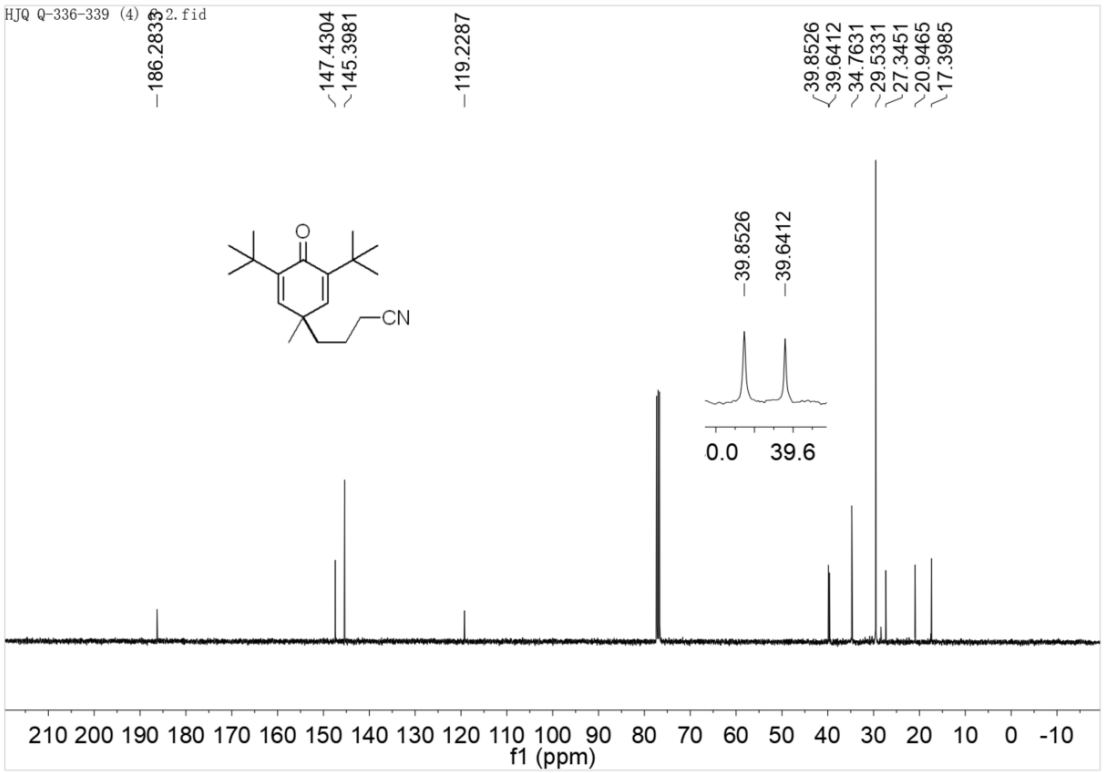
DEPT 90 and DEPT 135



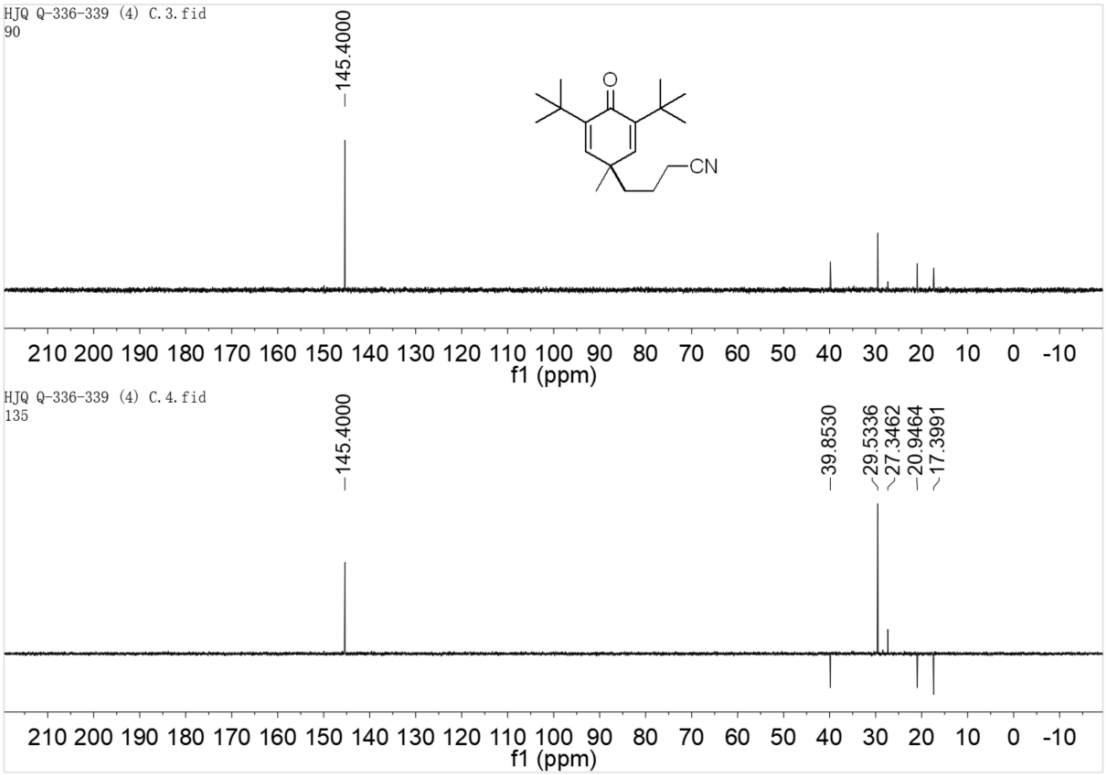
4, ^{1}H NMR



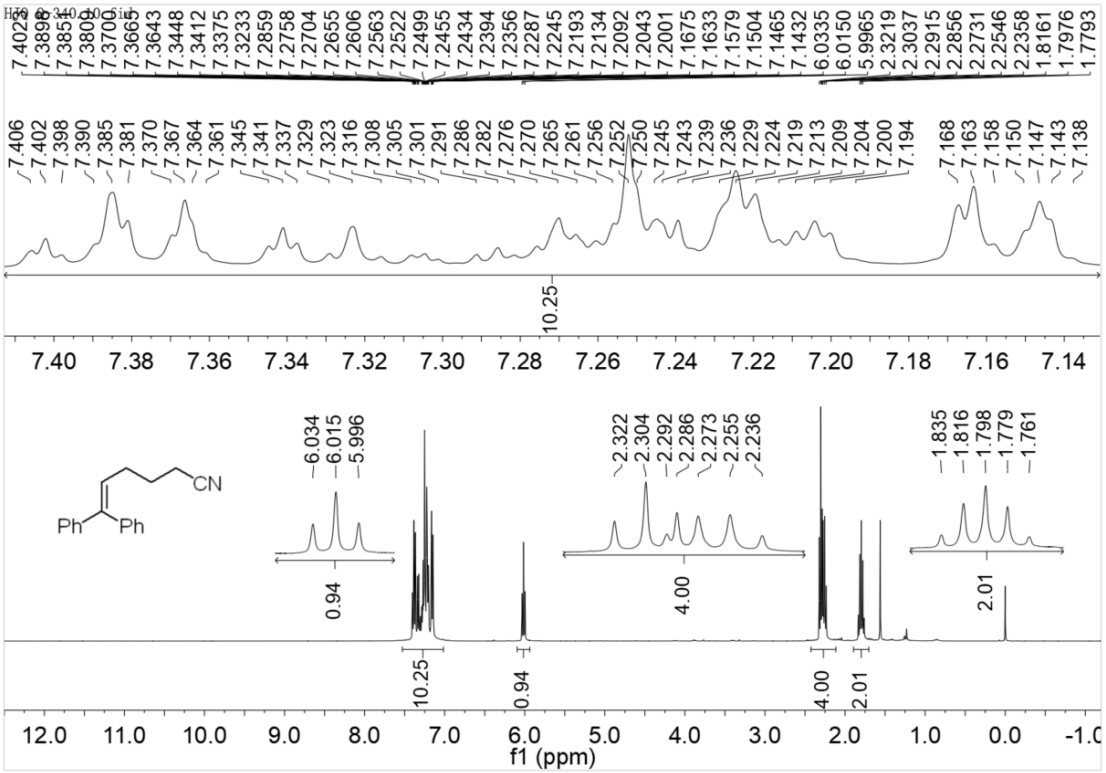
^{13}C NMR



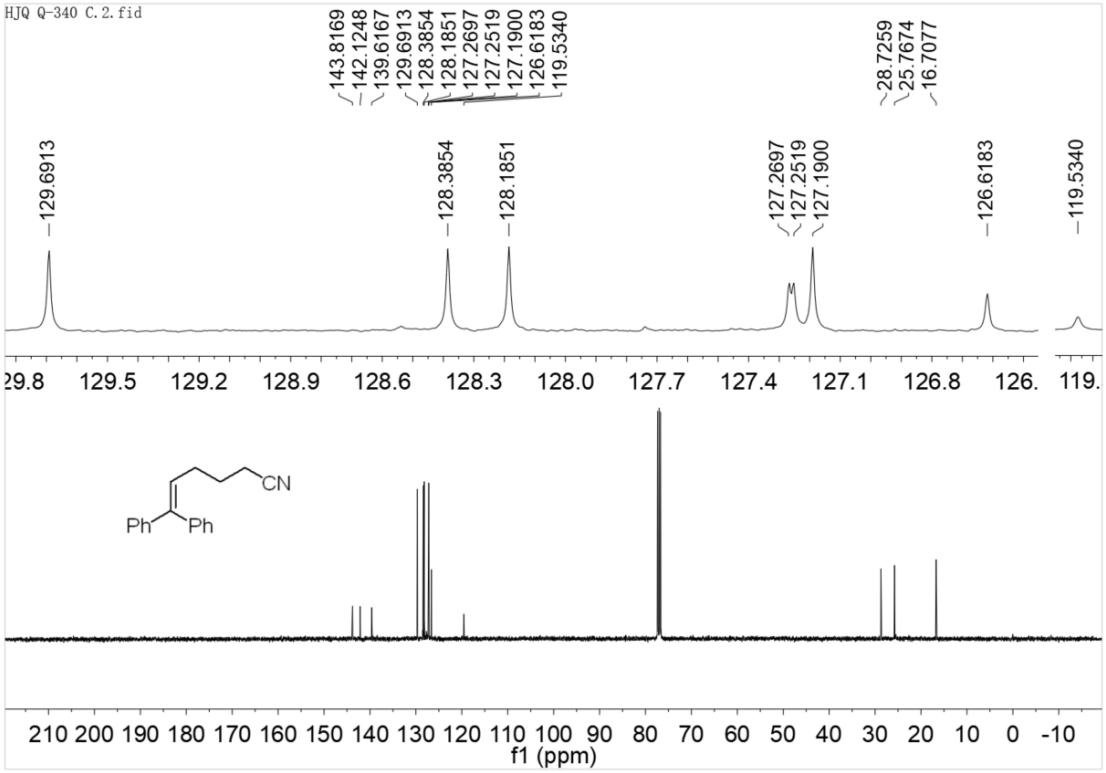
DEPT 90 and DEPT 135



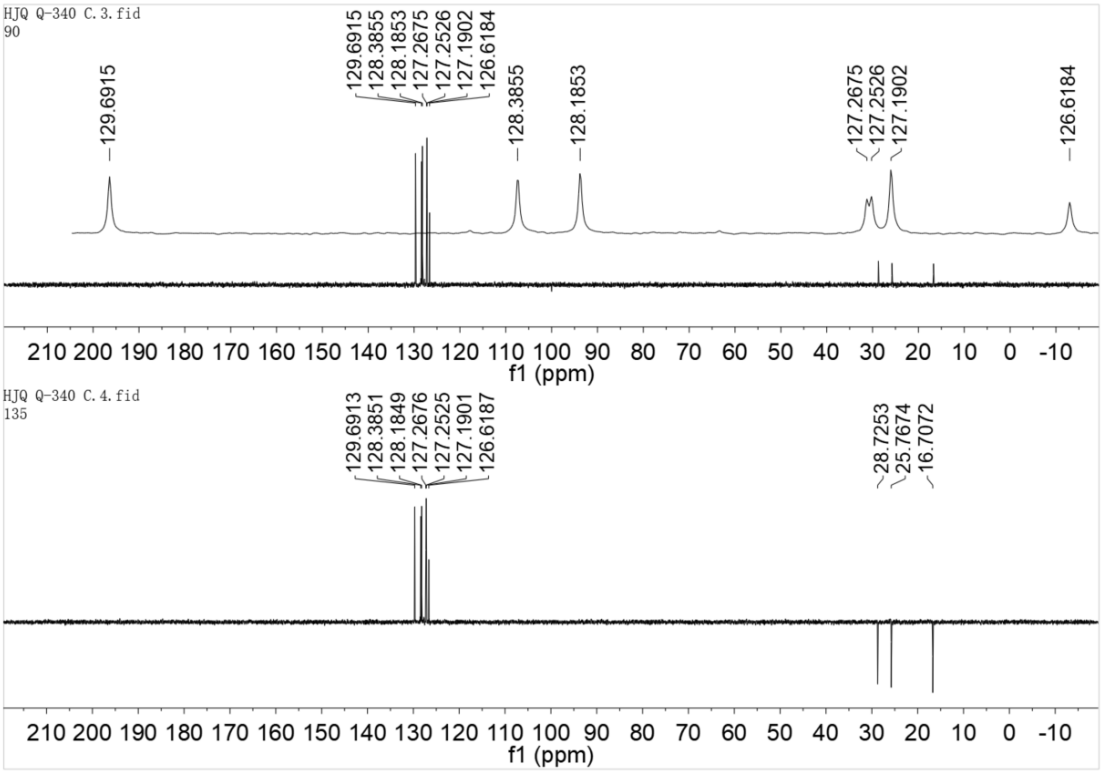
5, ^{1}H NMR



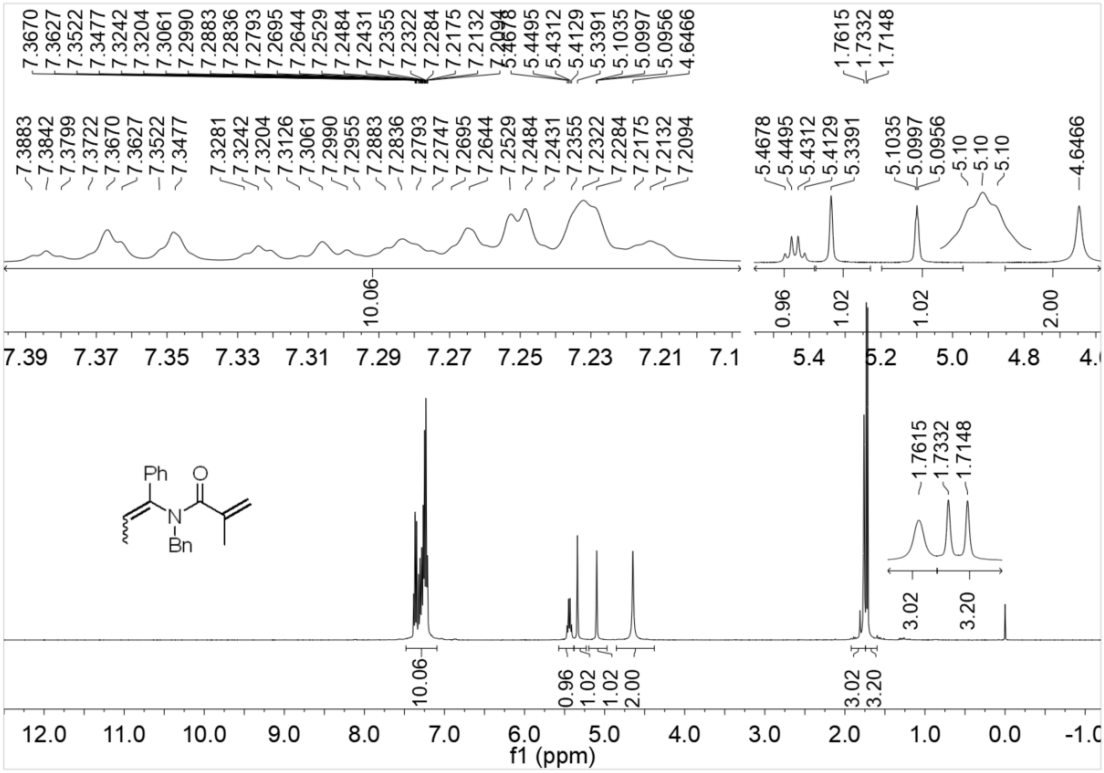
^{13}C NMR



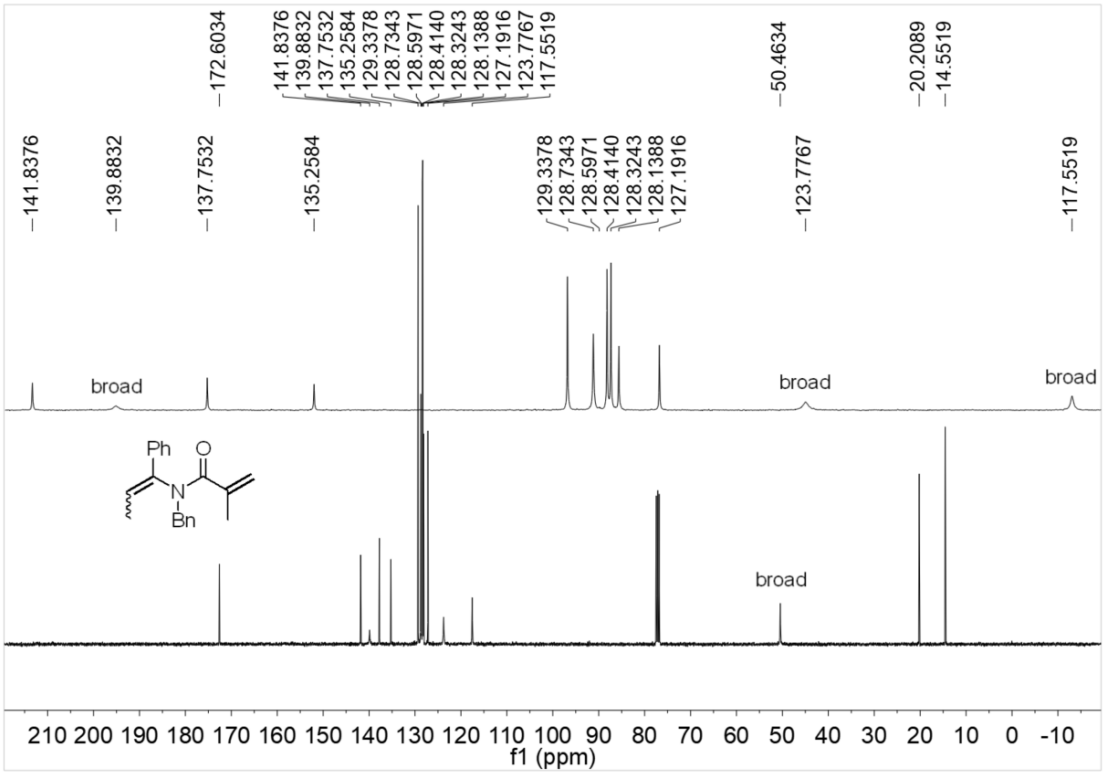
DEPT 90 and DEPT 135



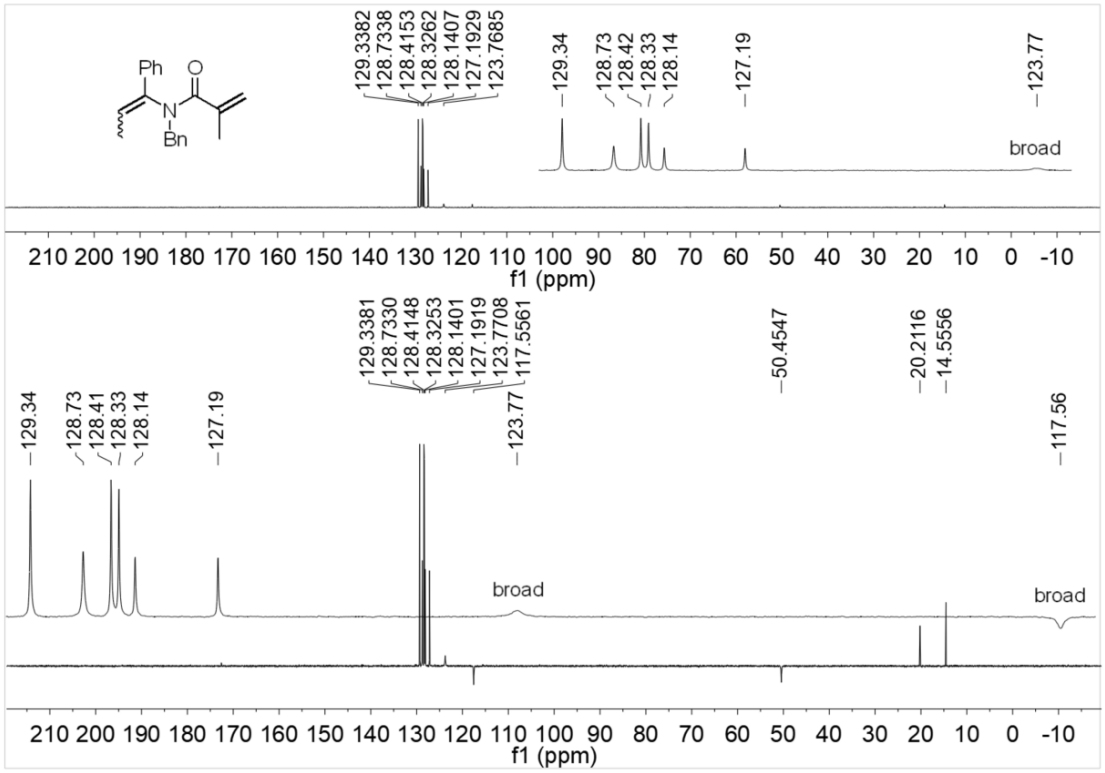
1a, ^{1}H NMR



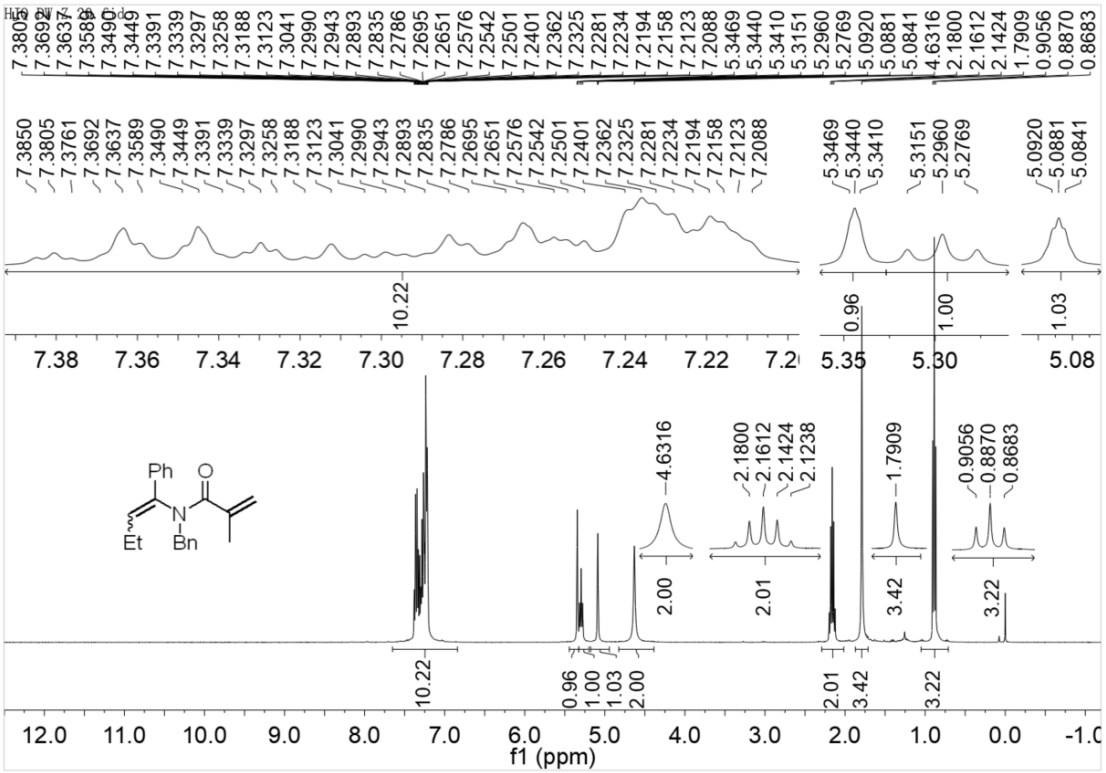
^{13}C NMR



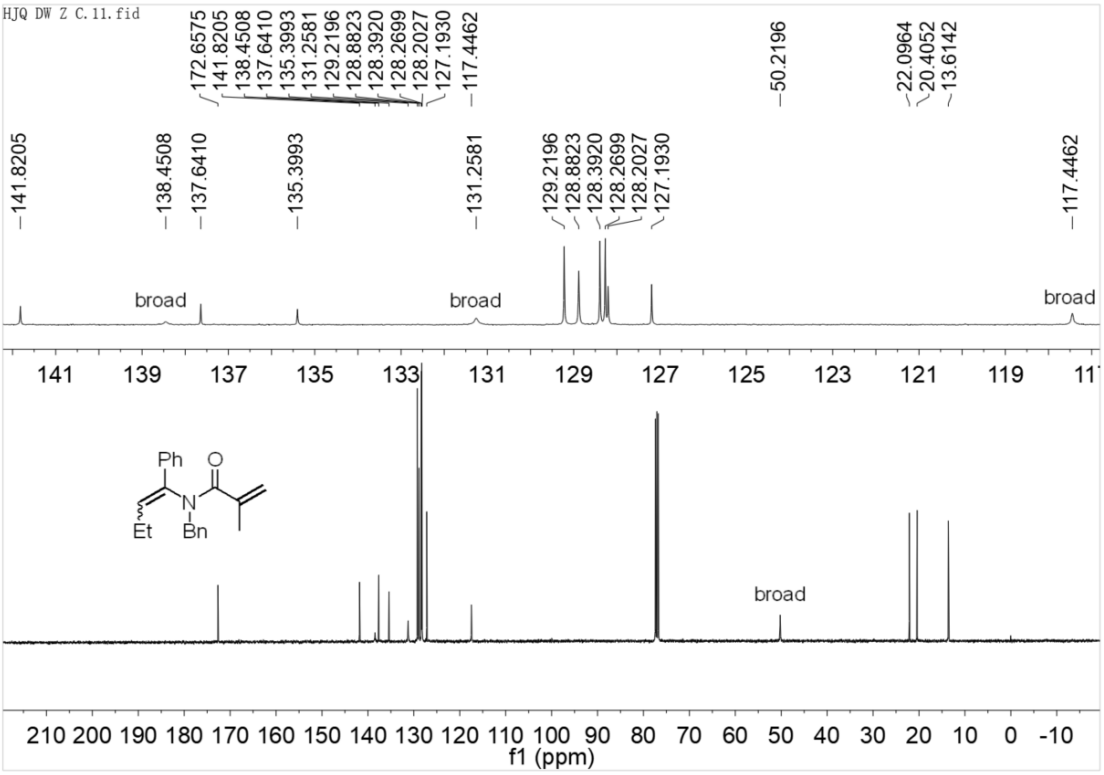
DEPT 90 and DEPT 135



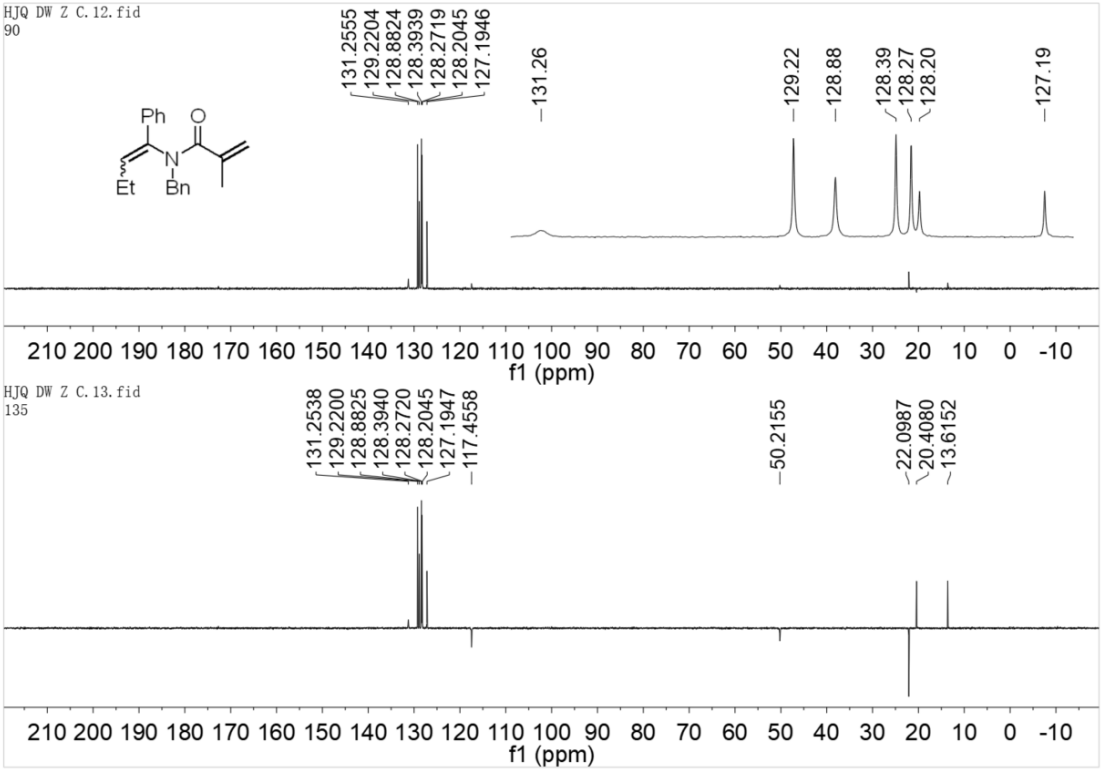
1b1, ^{1}H NMR



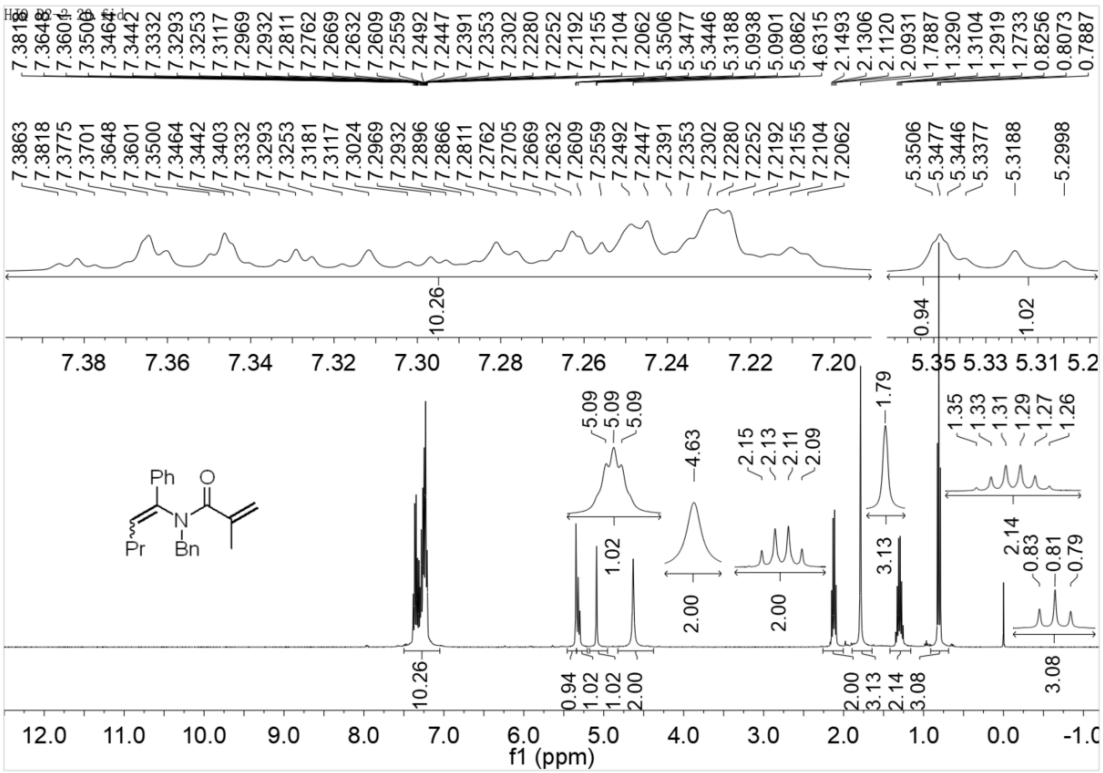
^{13}C NMR



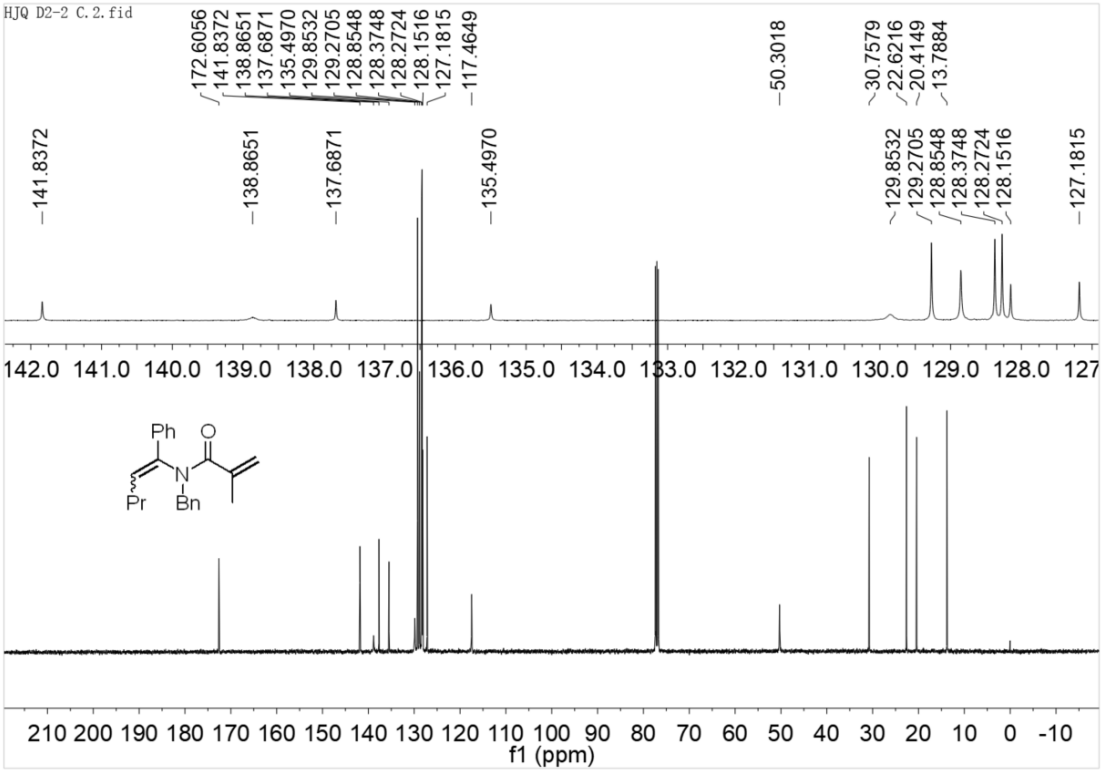
DEPT 90 and DEPT 135



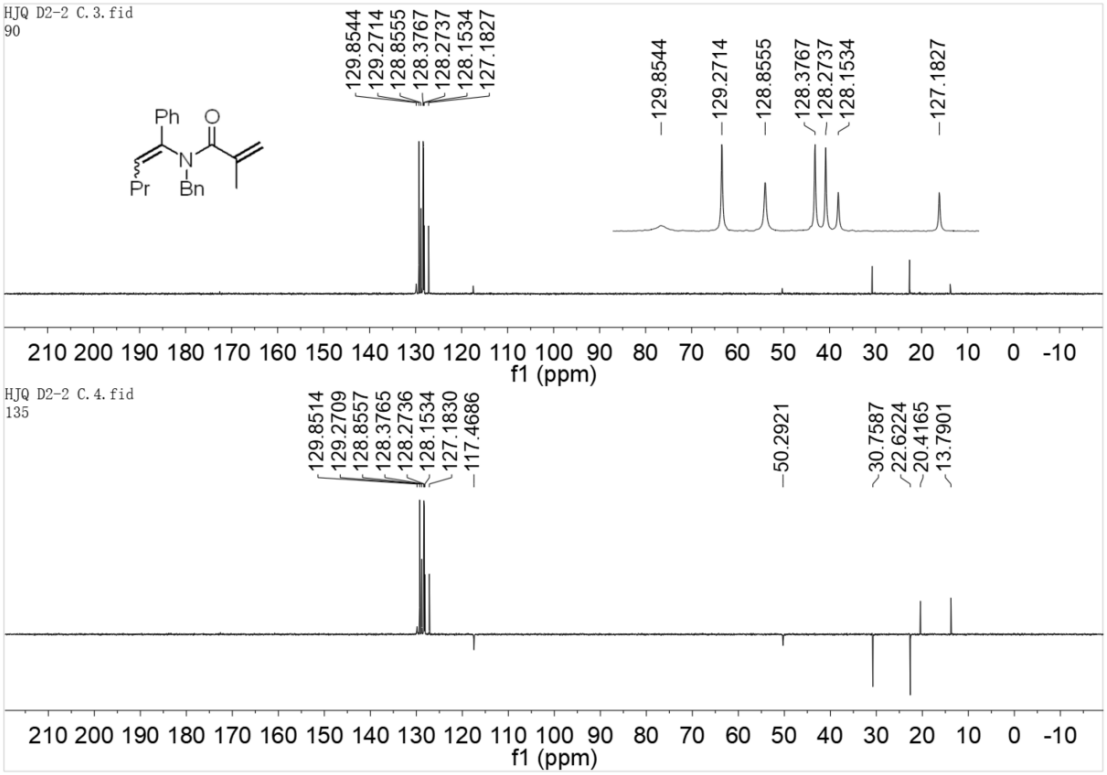
1b2, ^{1}H NMR



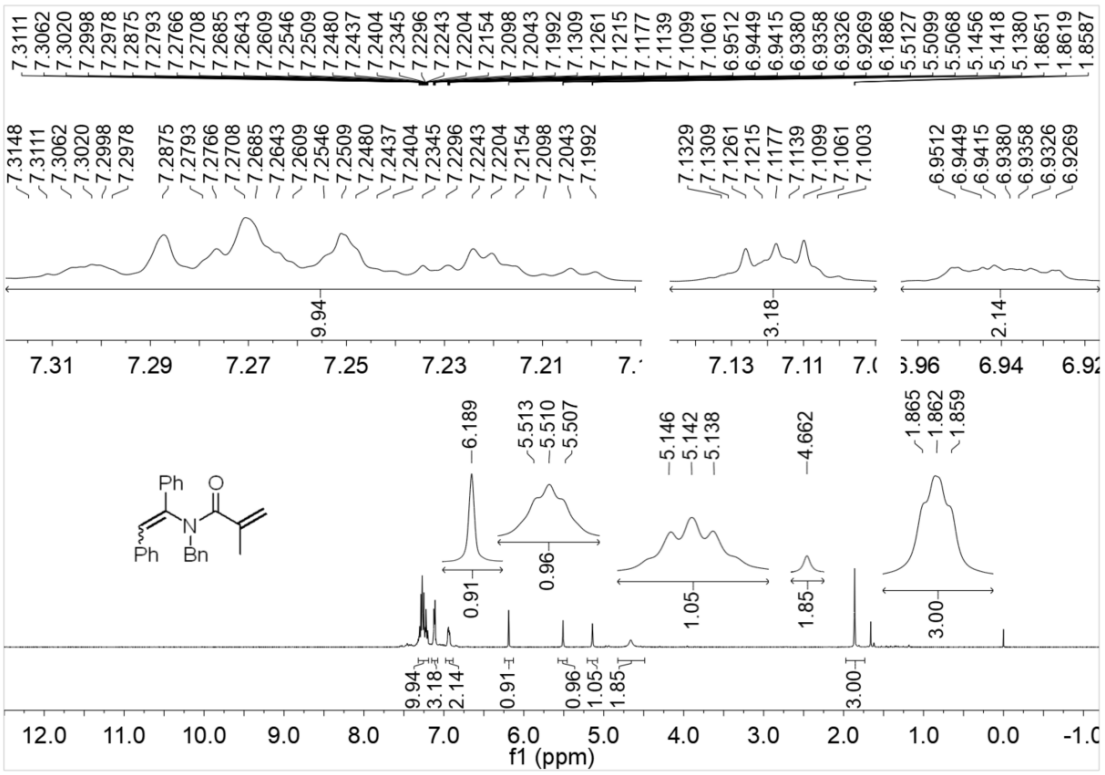
^{13}C NMR



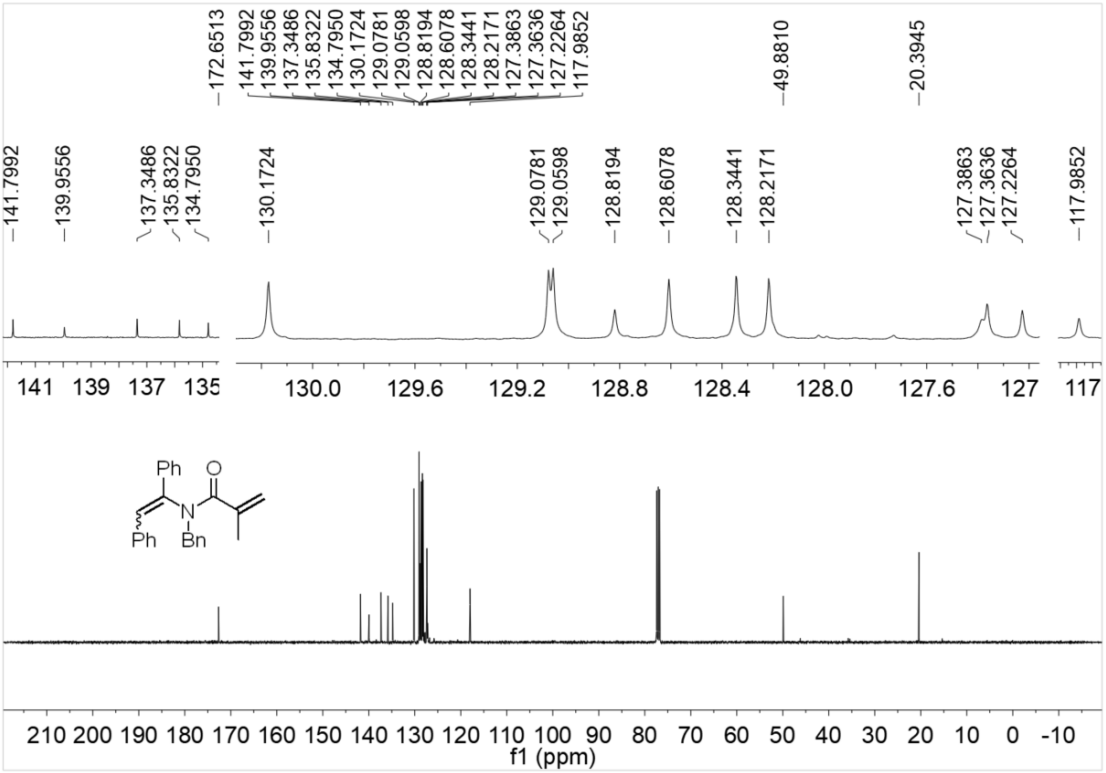
DEPT 90 and DEPT 135



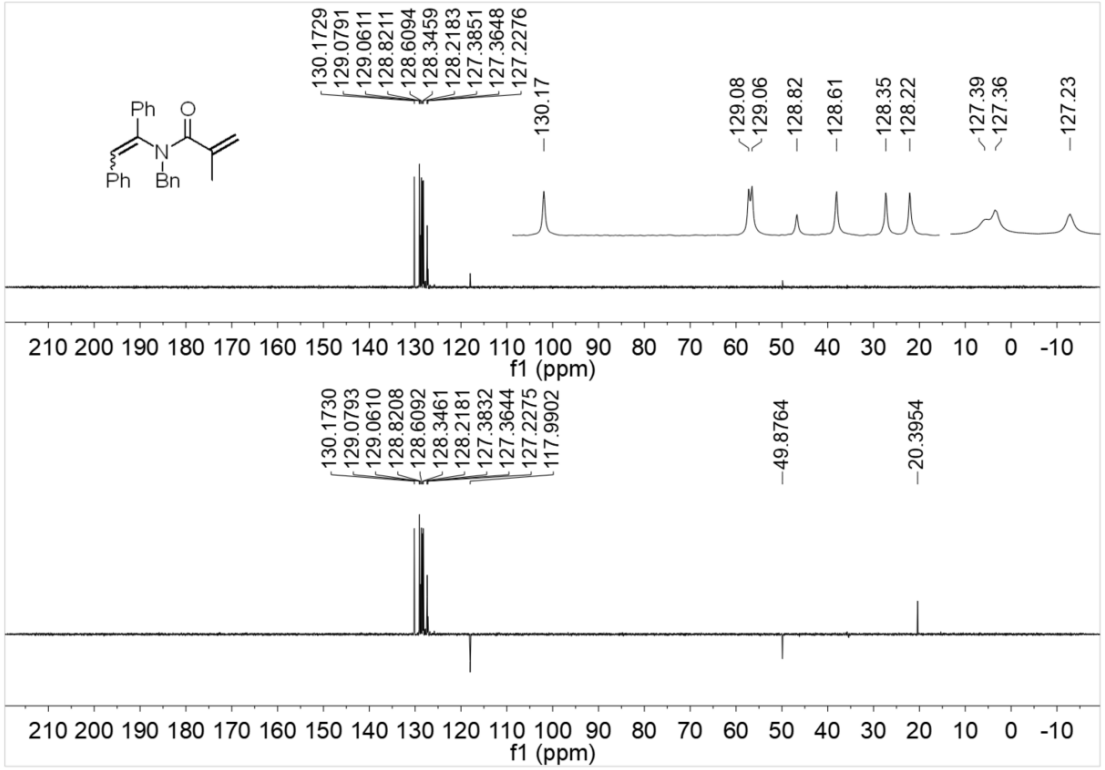
1b3, ^{1}H NMR



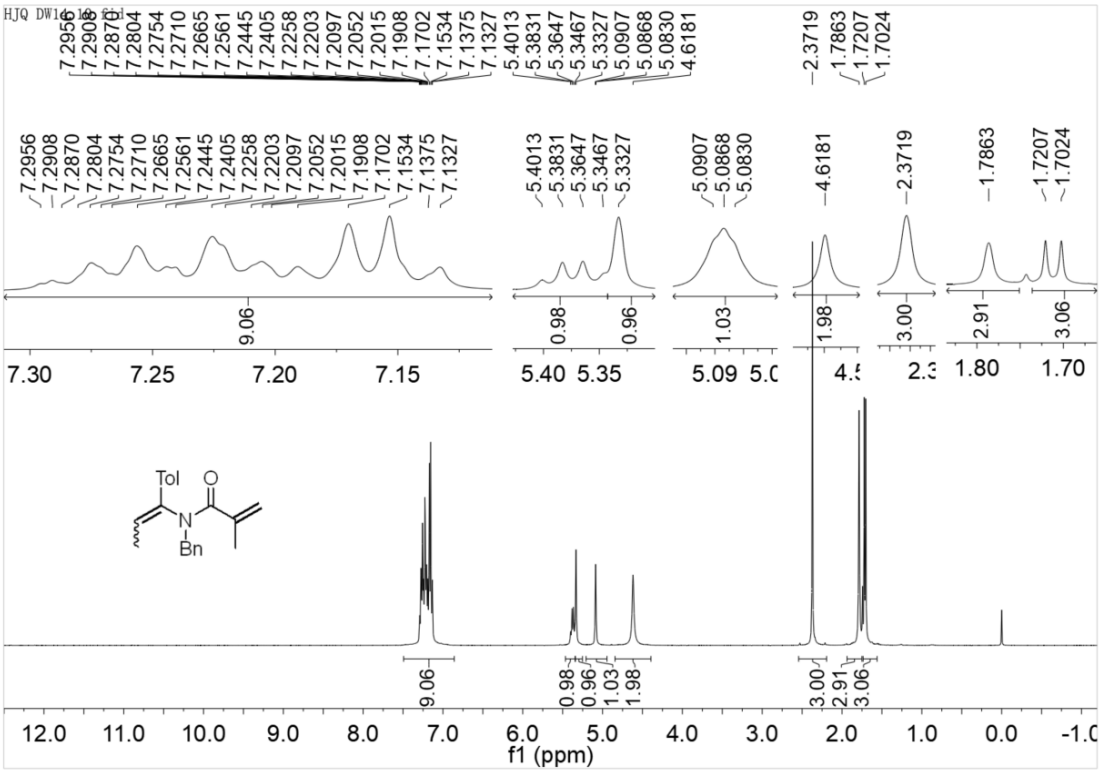
^{13}C NMR



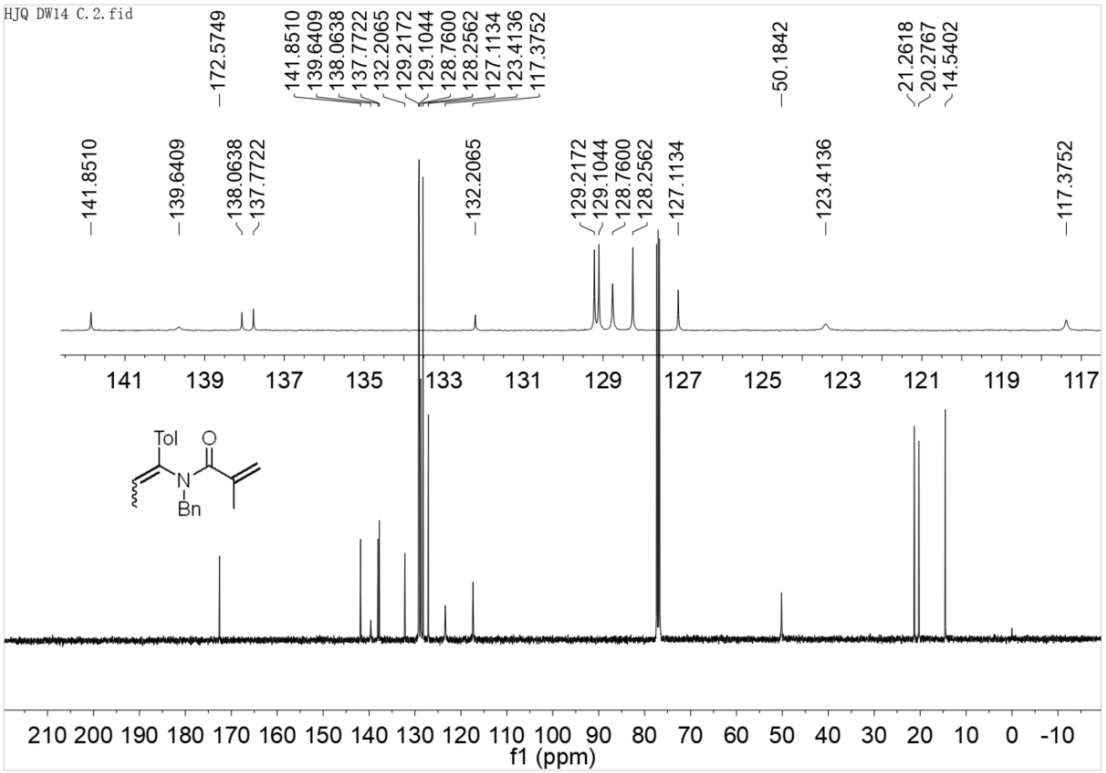
DEPT 90 and DEPT 135



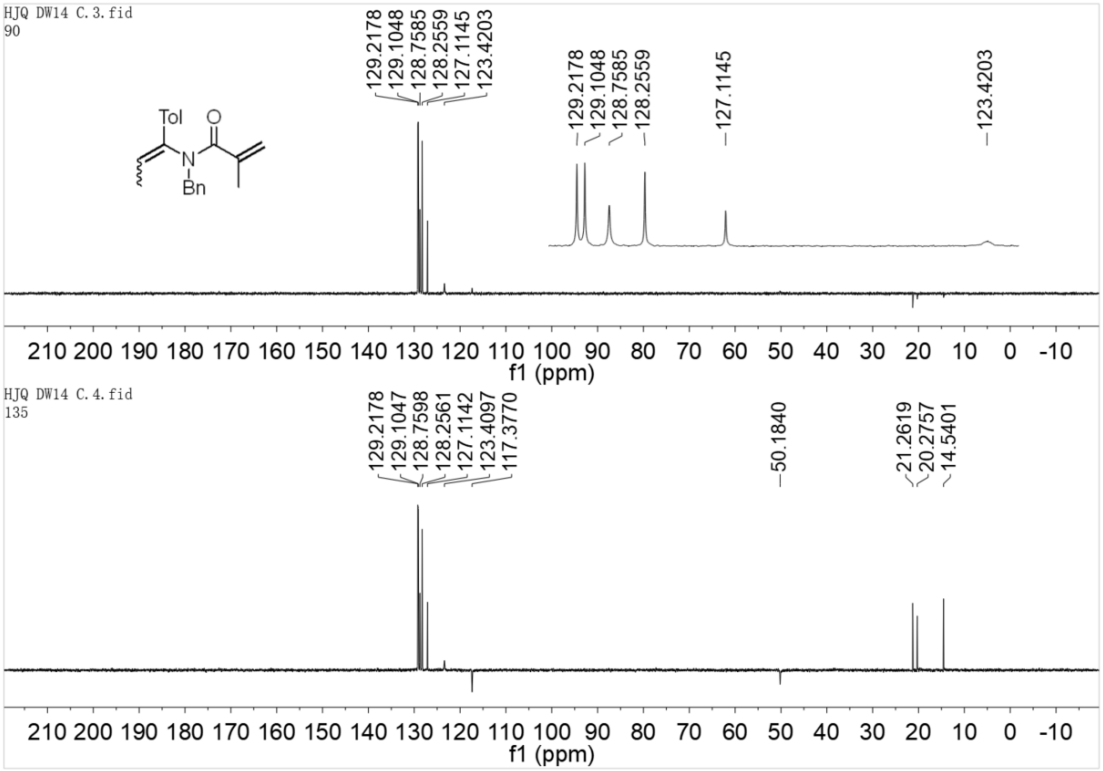
1d1, ^{1}H NMR



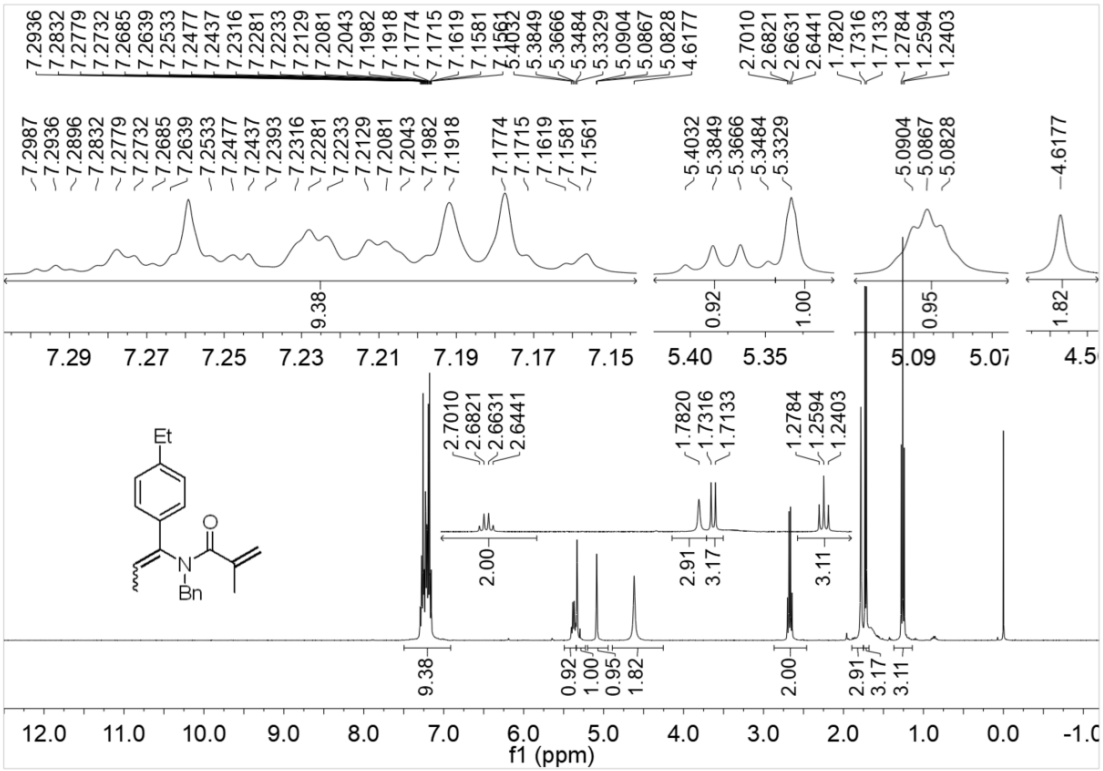
^{13}C NMR



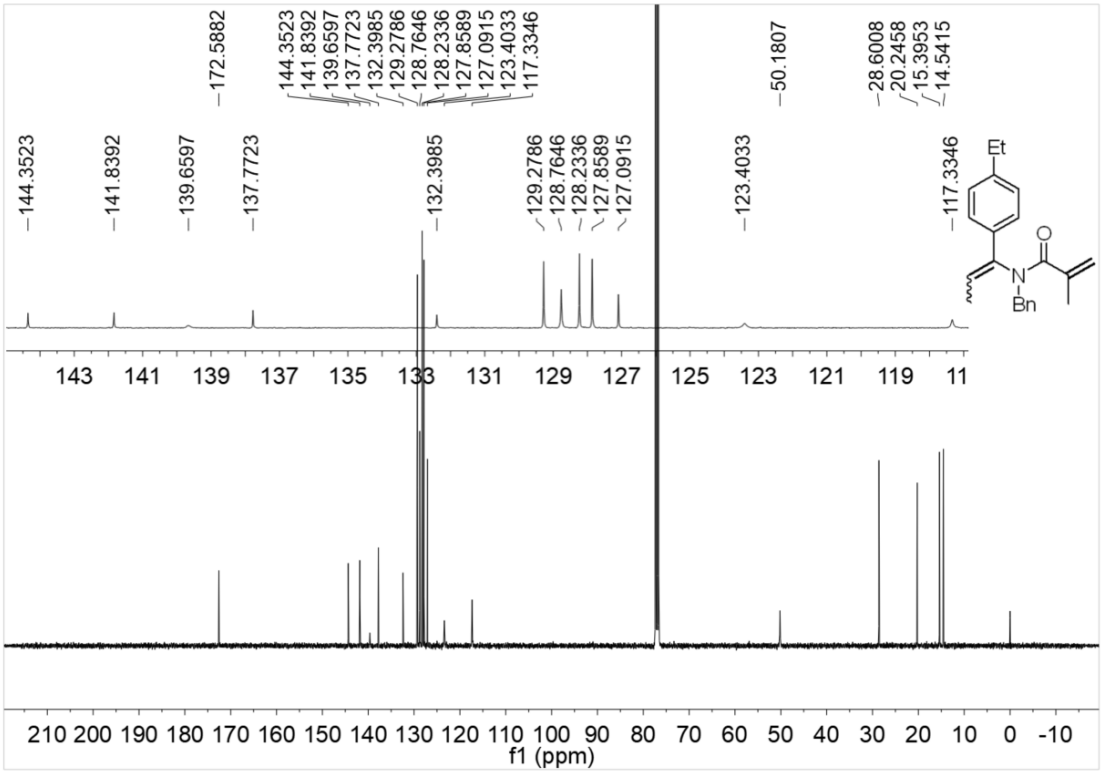
DEPT 90 and DEPT 135



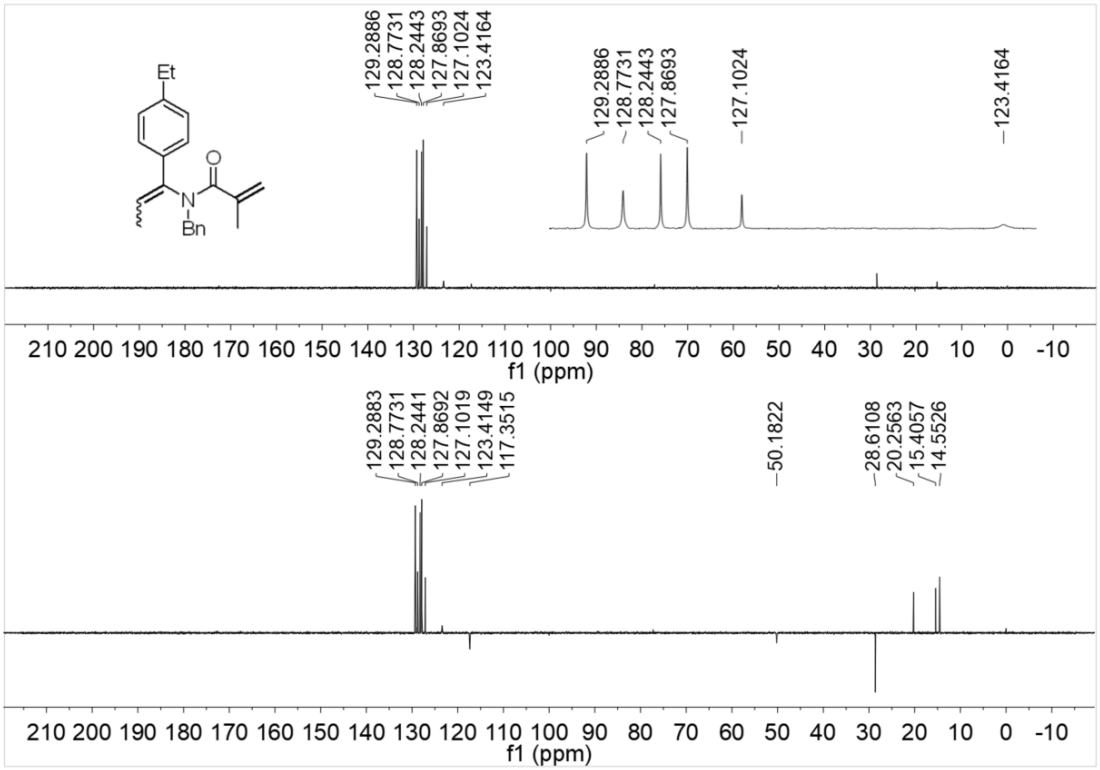
1d2, ^{1}H NMR



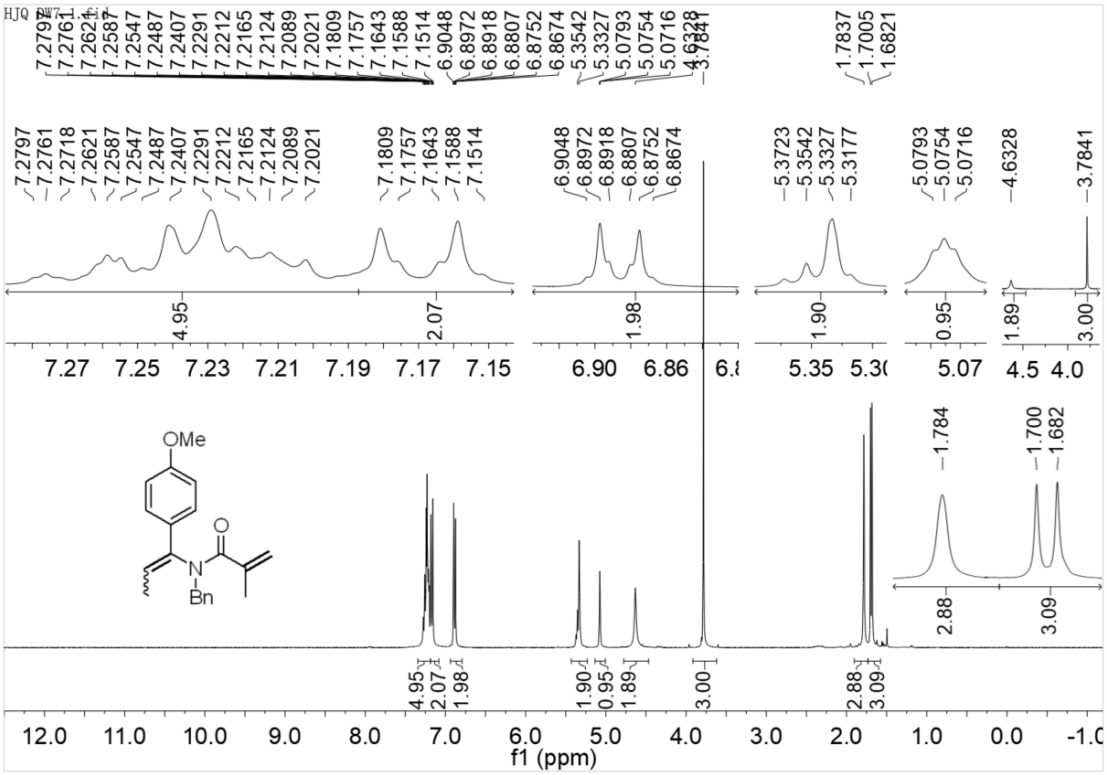
^{13}C NMR



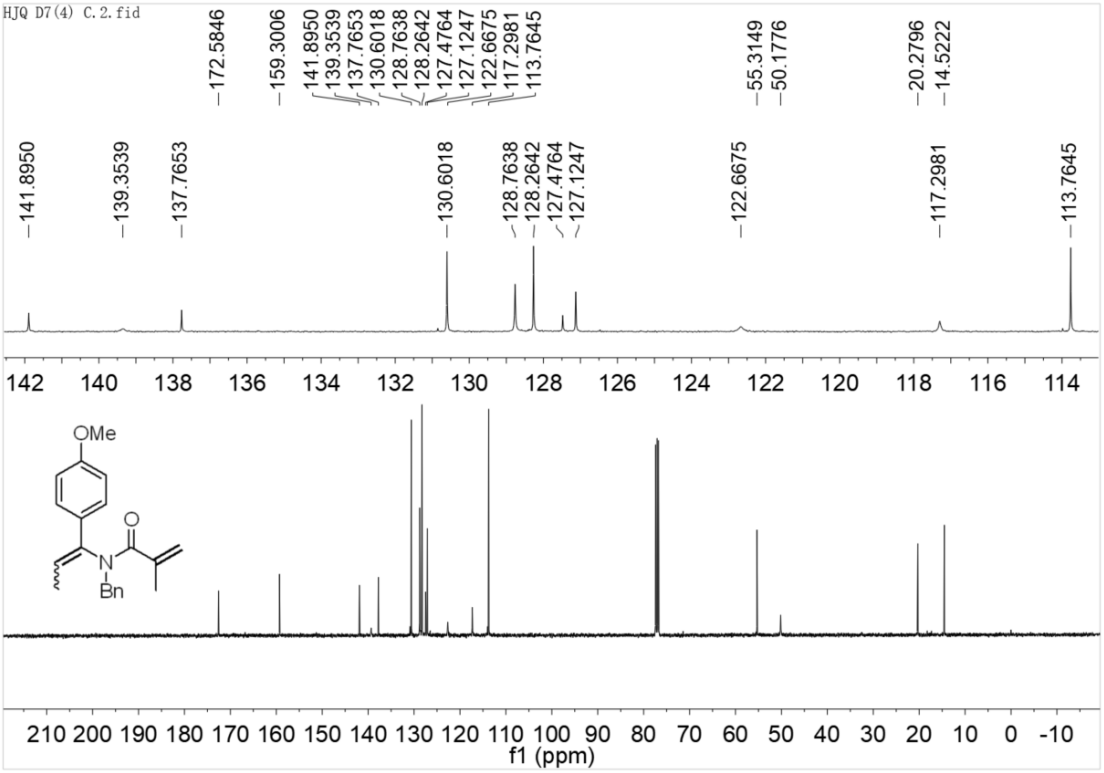
DEPT 90 and DEPT 135



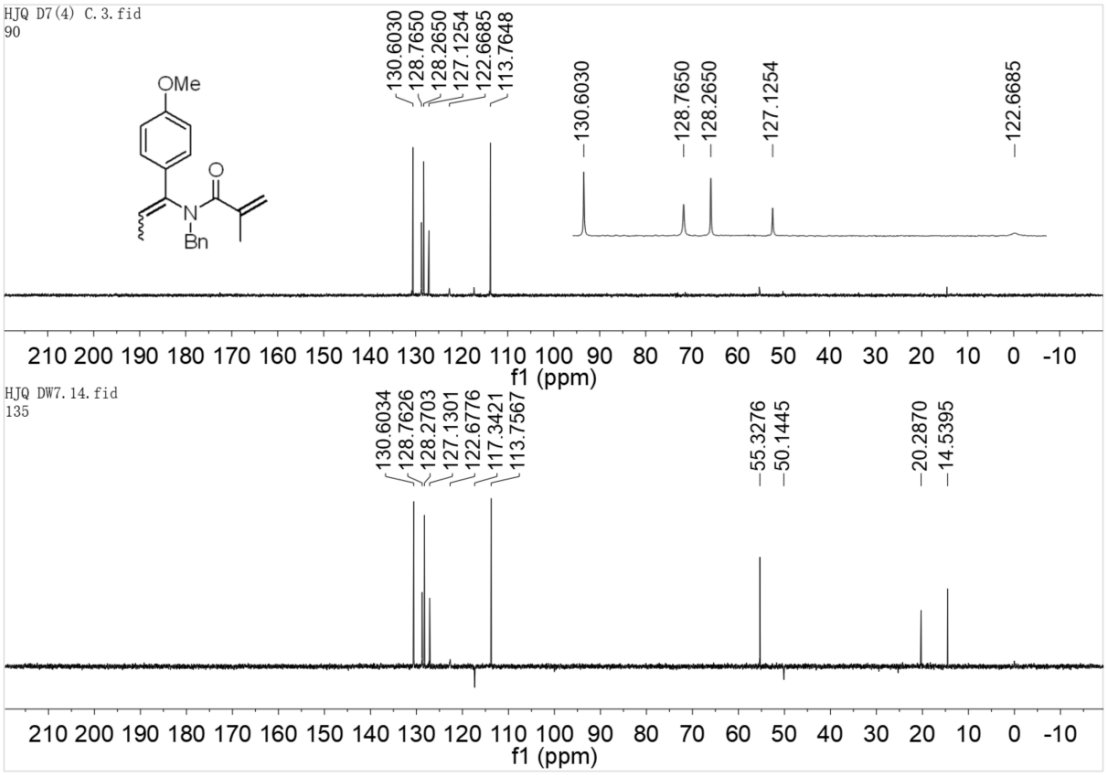
1d3, ^{1}H NMR



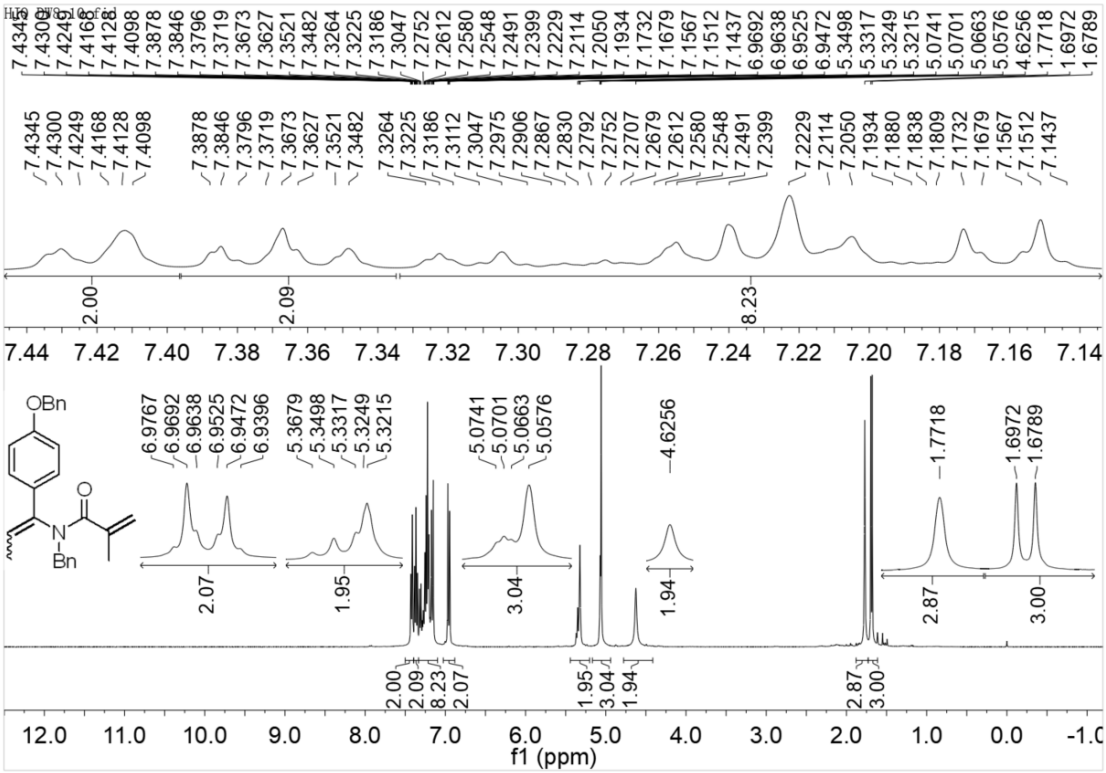
^{13}C NMR



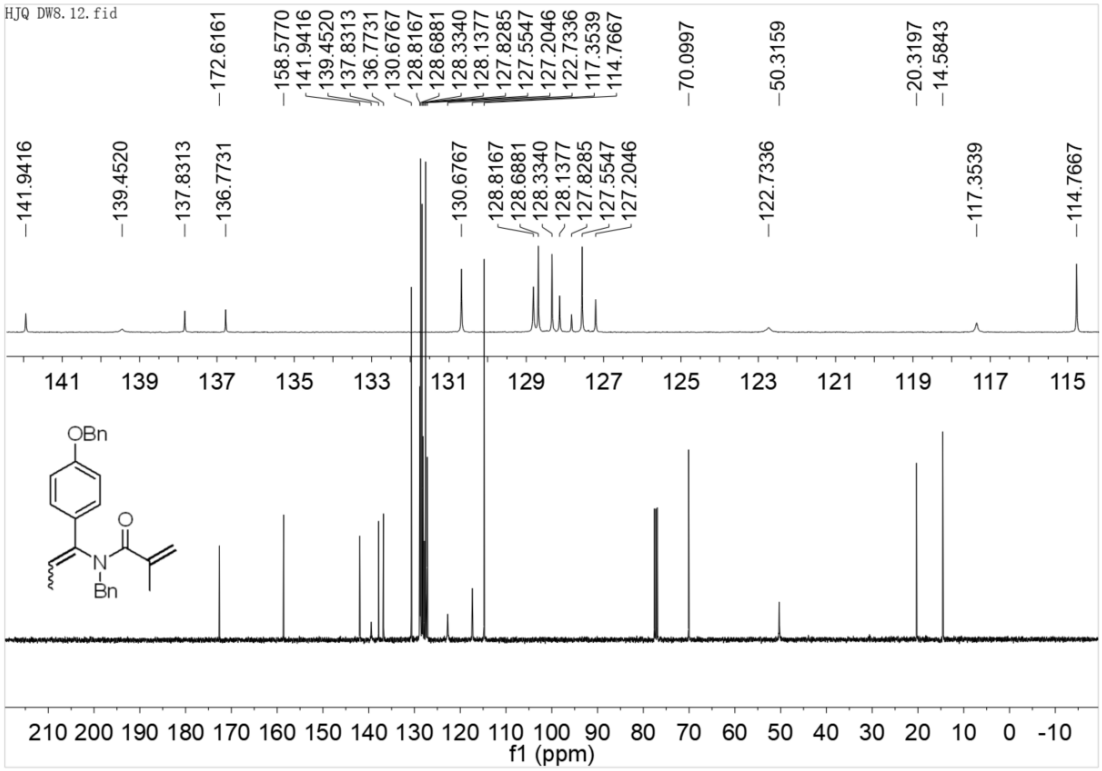
DEPT 90 and DEPT 135



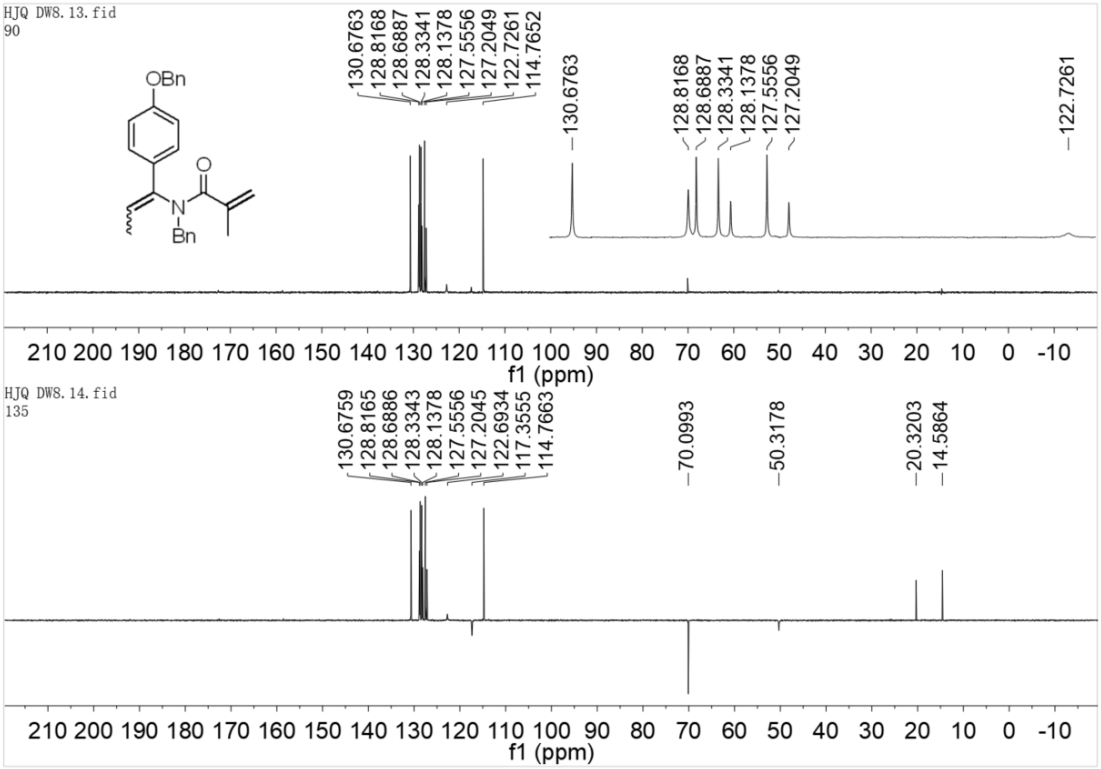
1d4, ^{1}H NMR



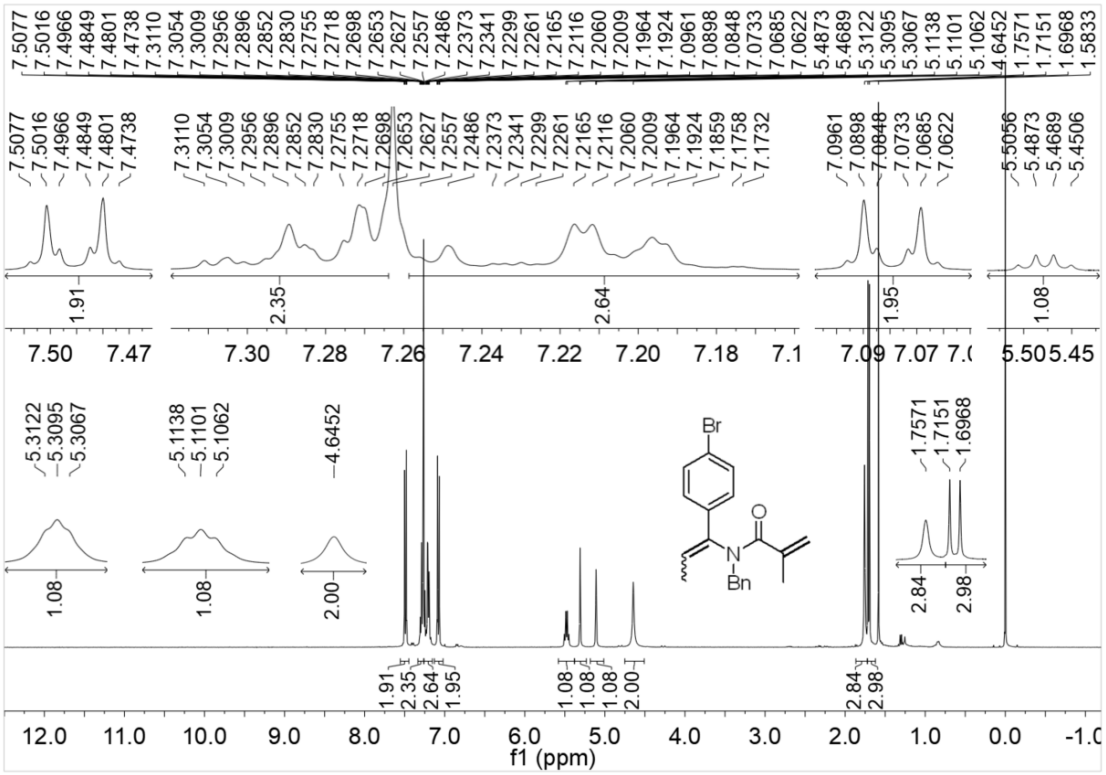
^{13}C NMR



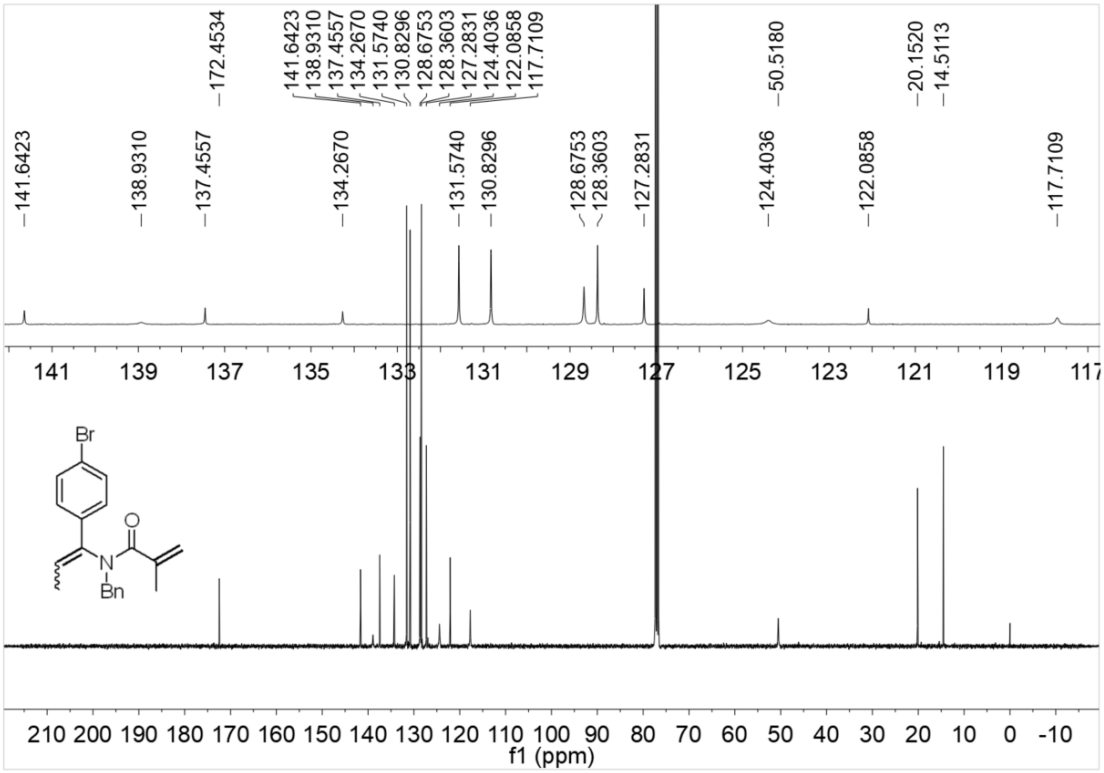
DEPT 90 and DEPT 135



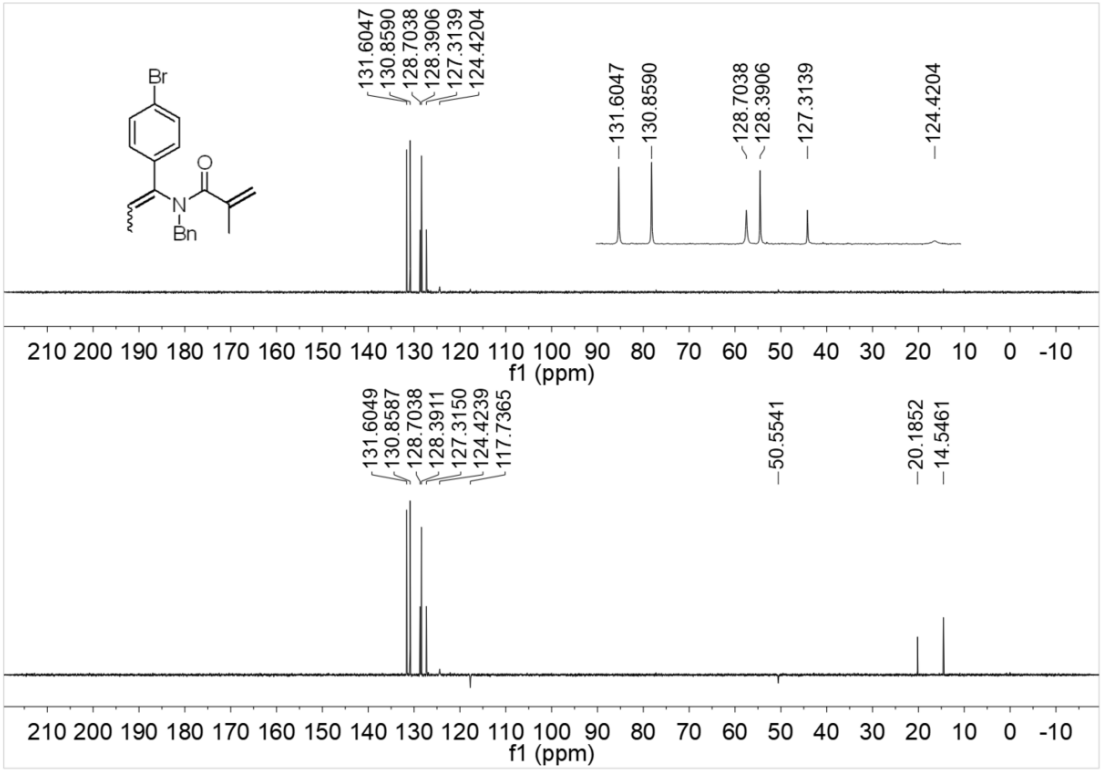
1d5, ^{1}H NMR



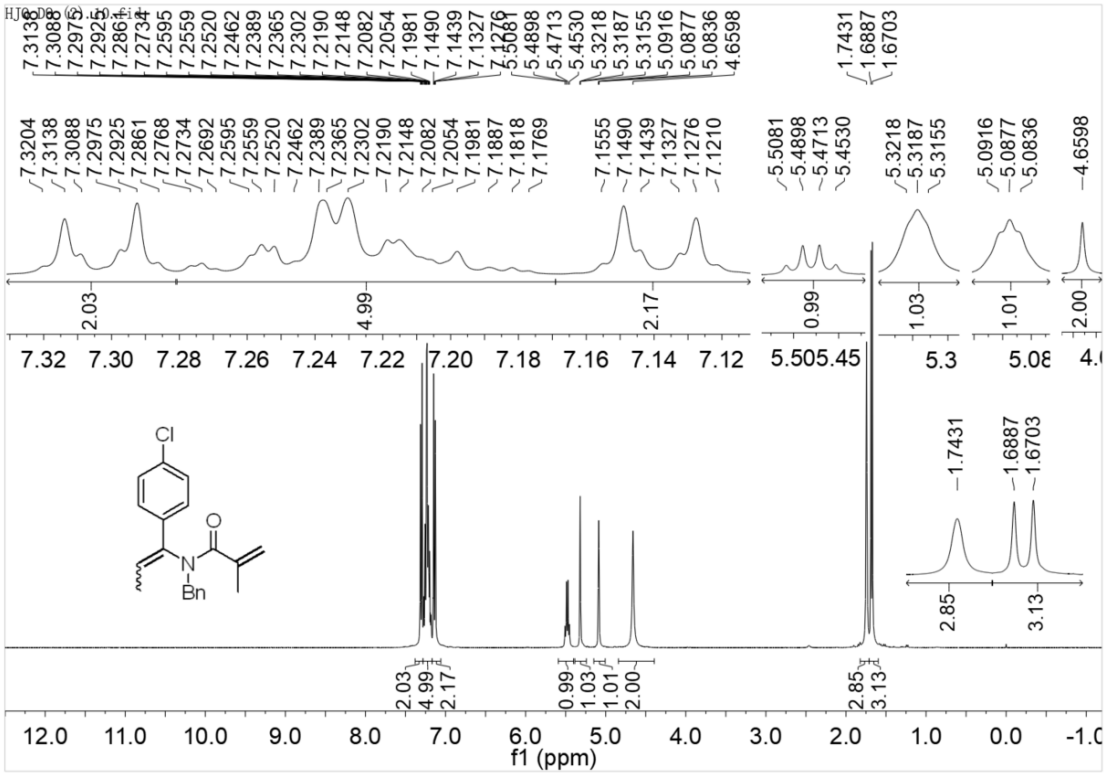
^{13}C NMR



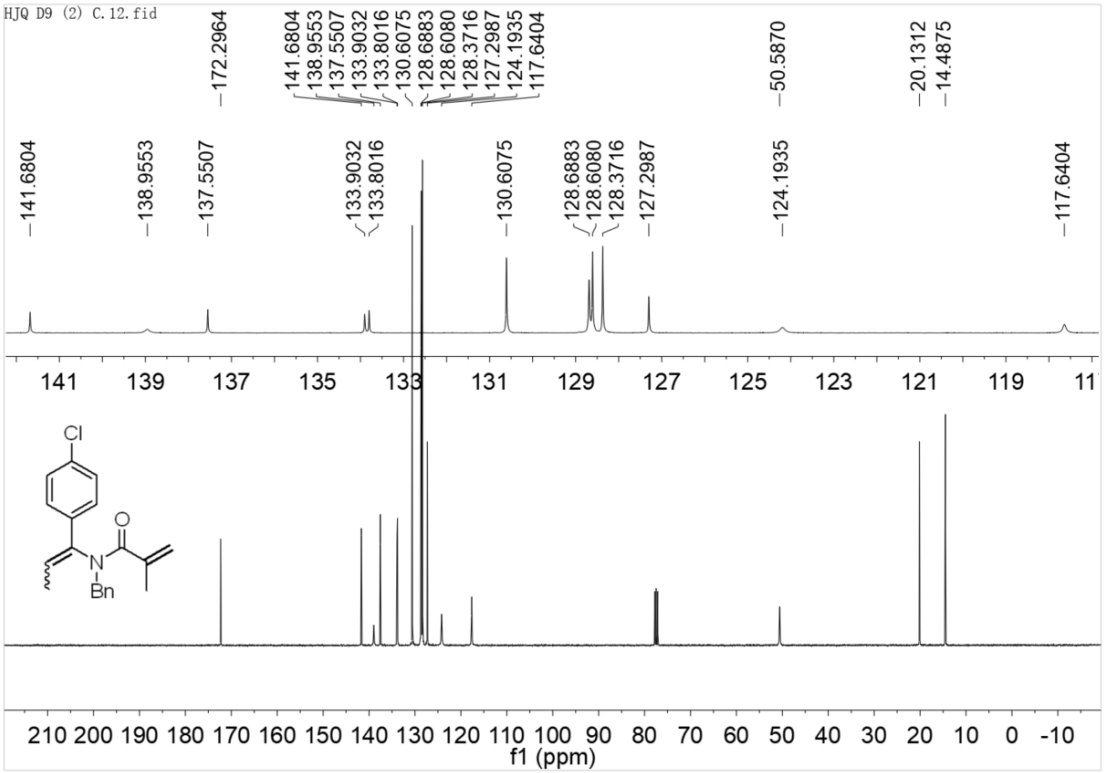
DEPT 90 and DEPT 135



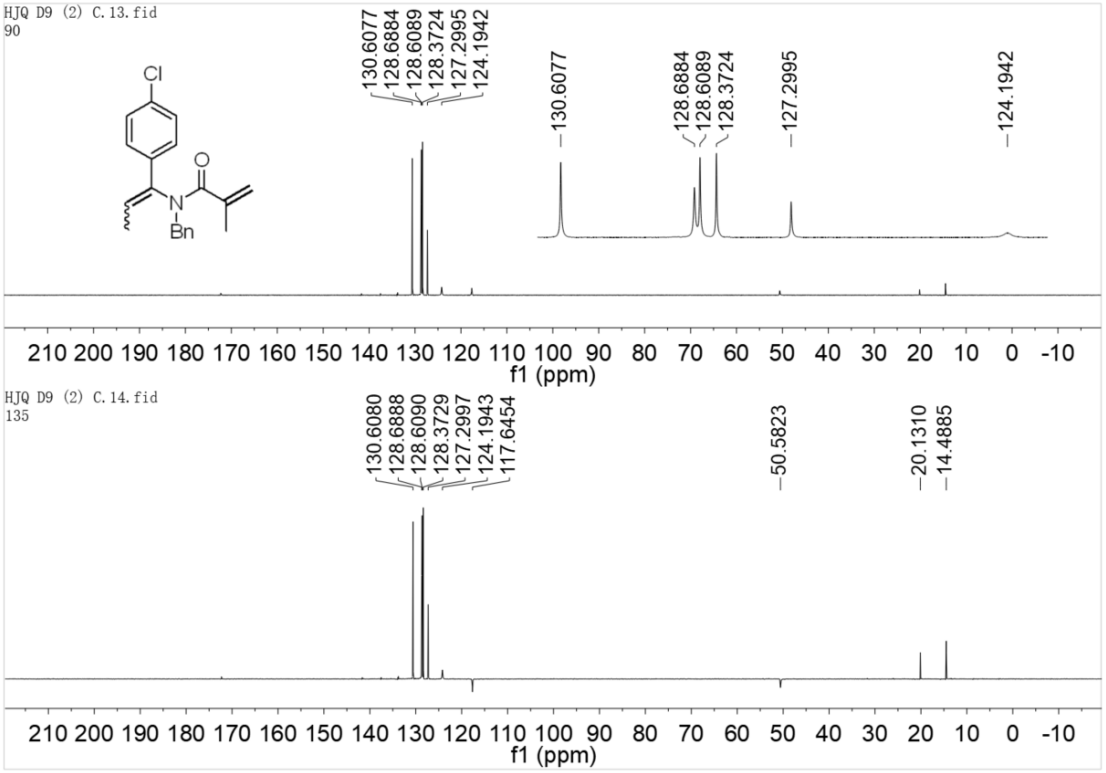
1d6, ^{1}H NMR



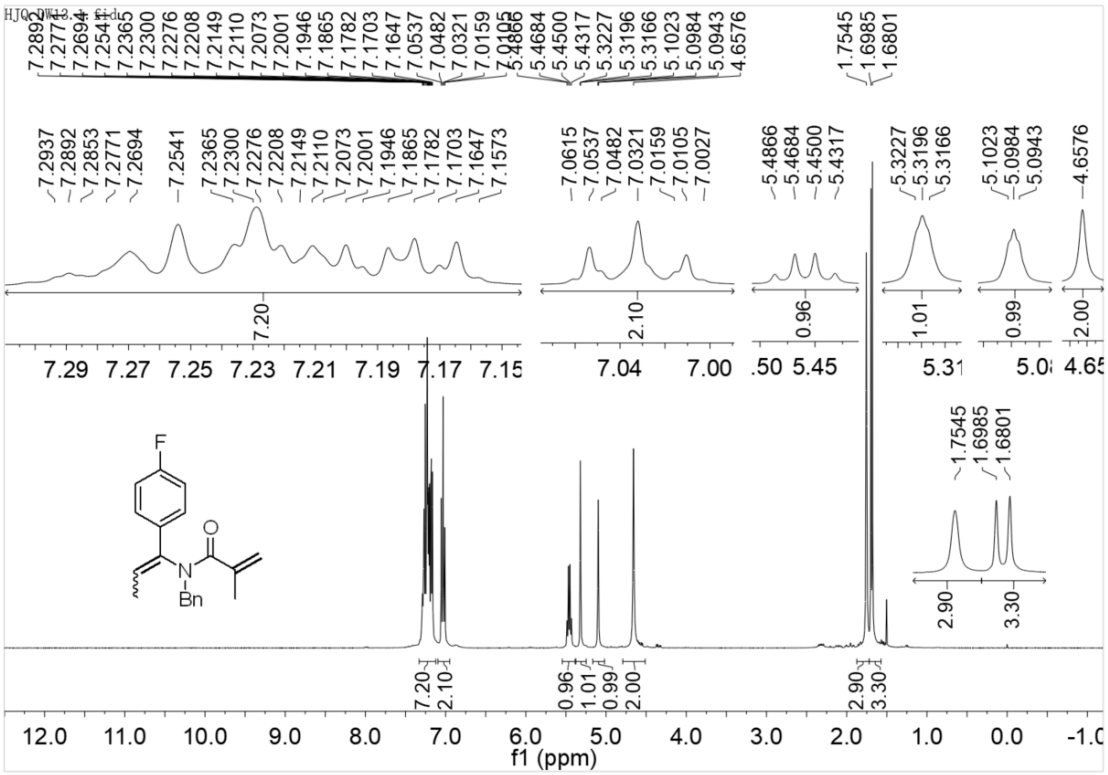
^{13}C NMR



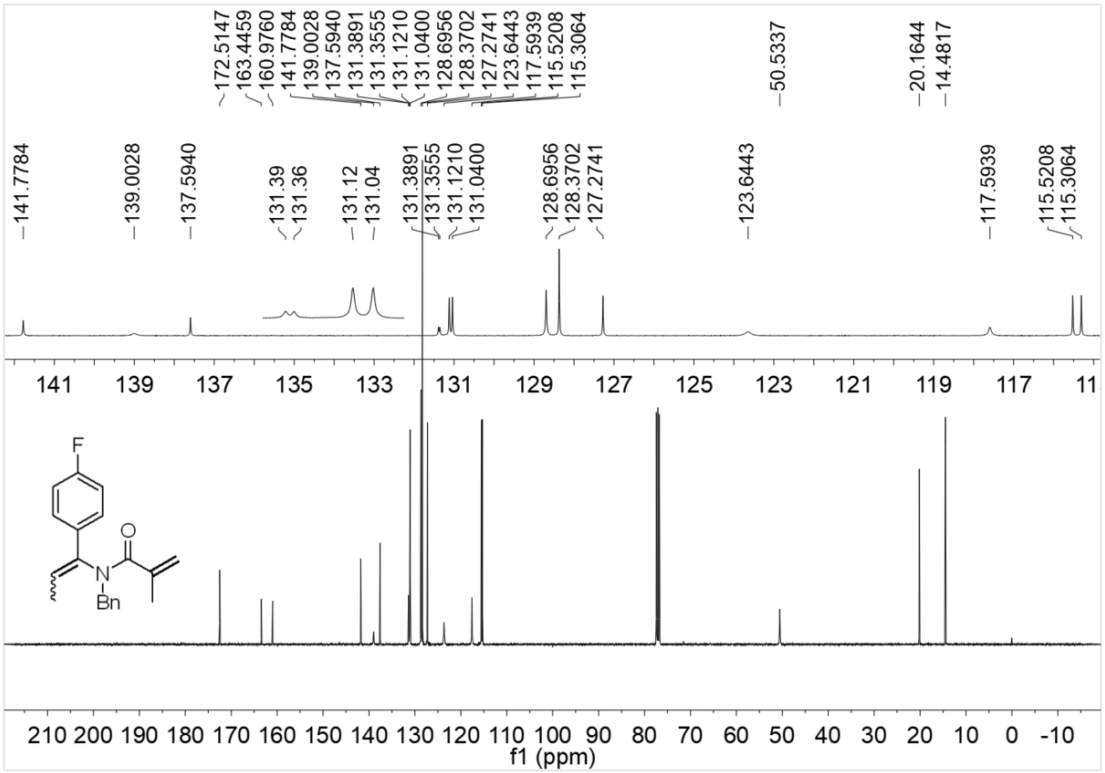
DEPT 90 and DEPT 135



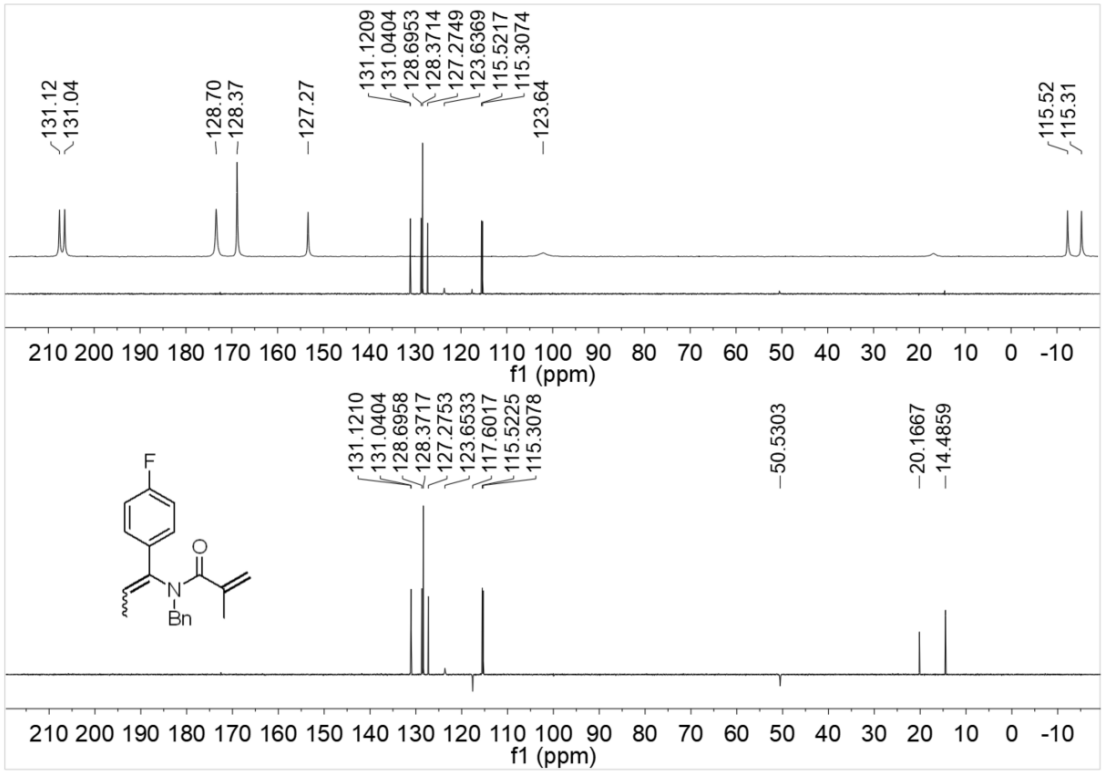
1d7, ^{1}H NMR



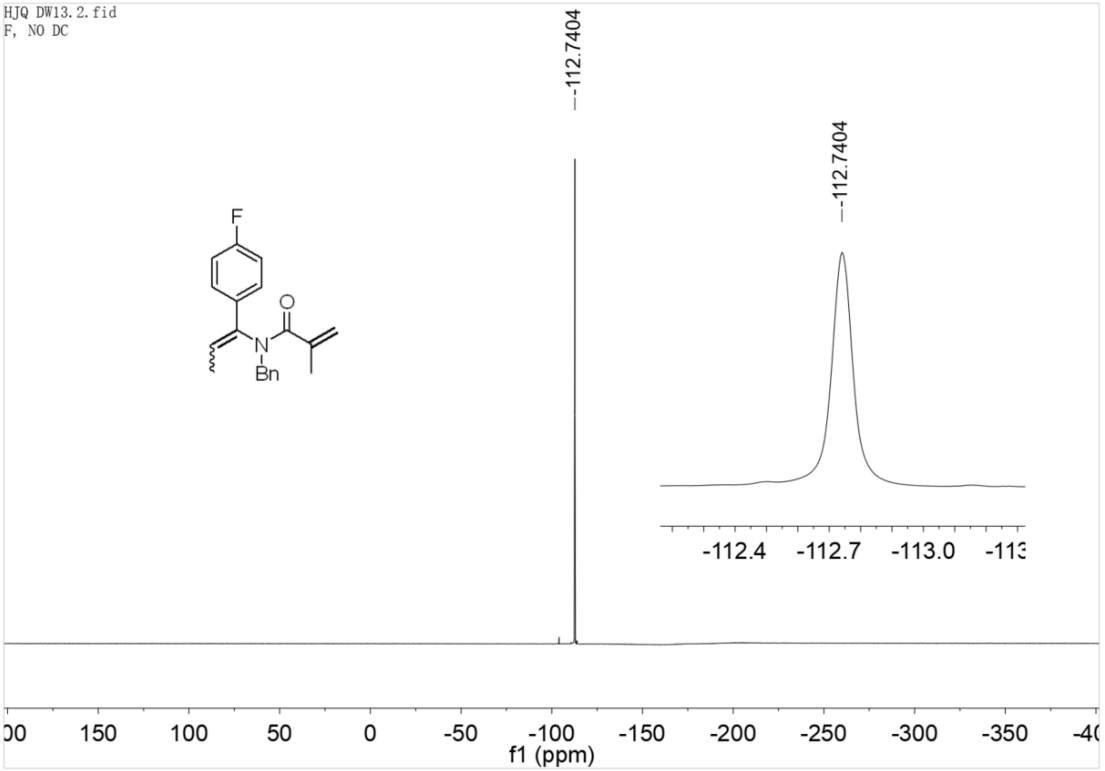
^{13}C NMR



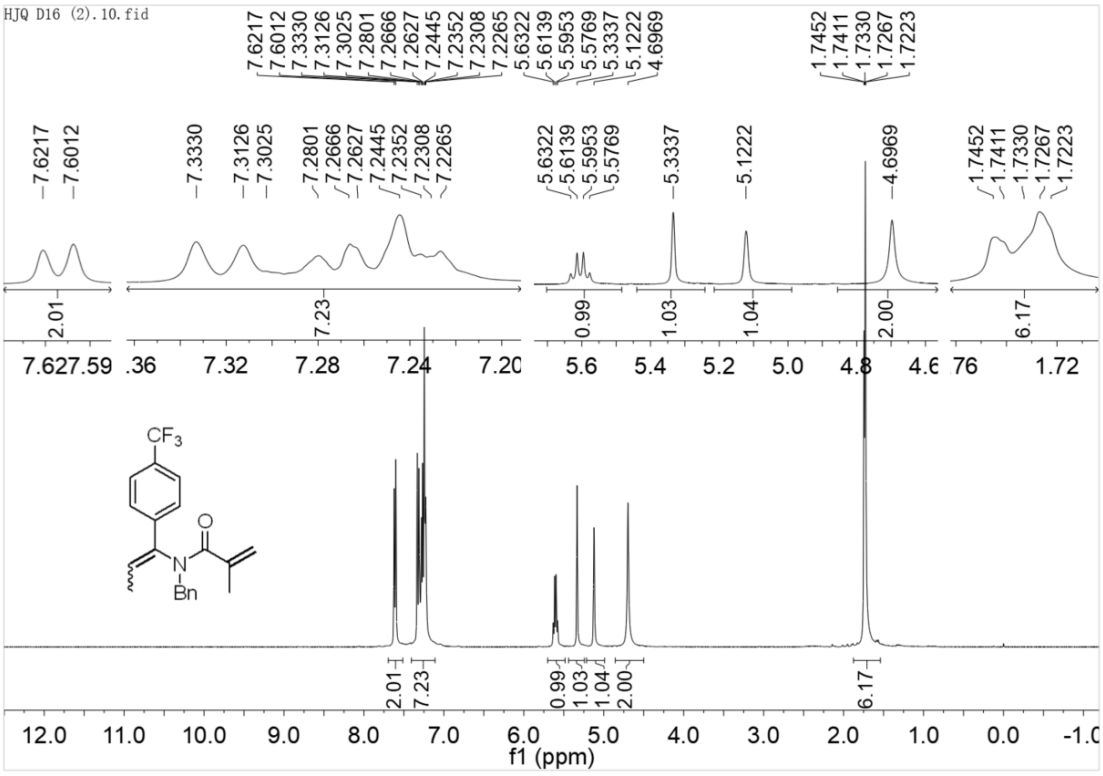
DEPT 90 and DEPT 135



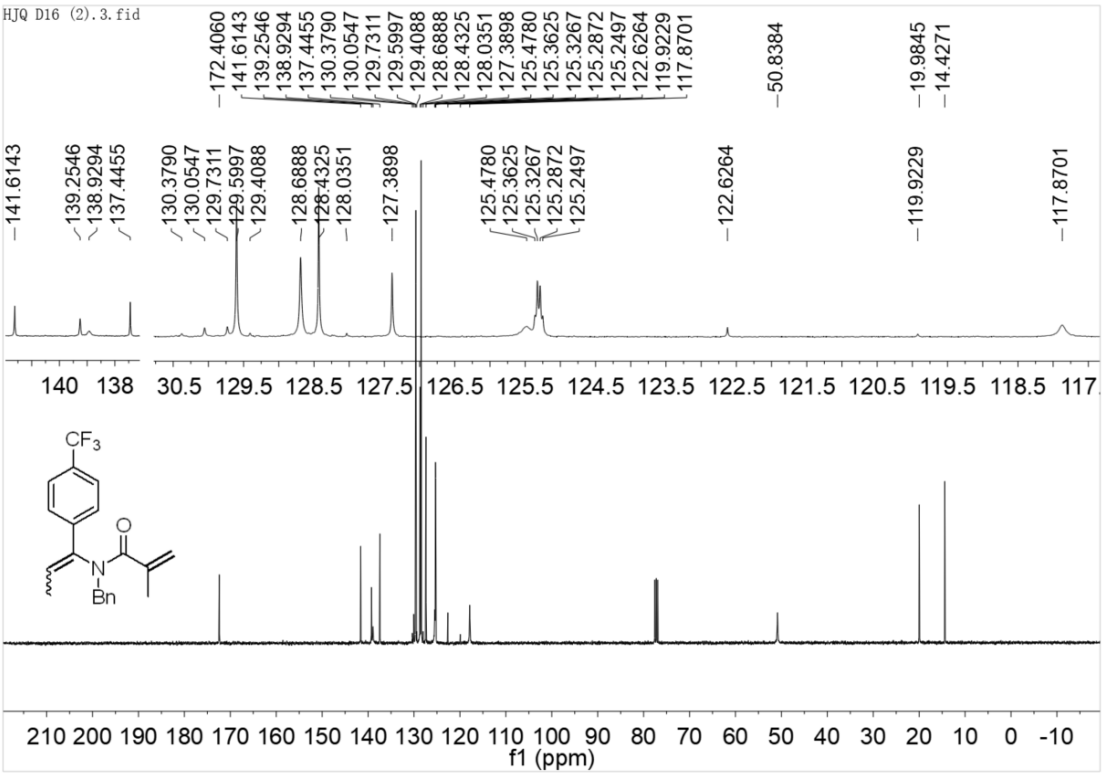
^{19}F NMR



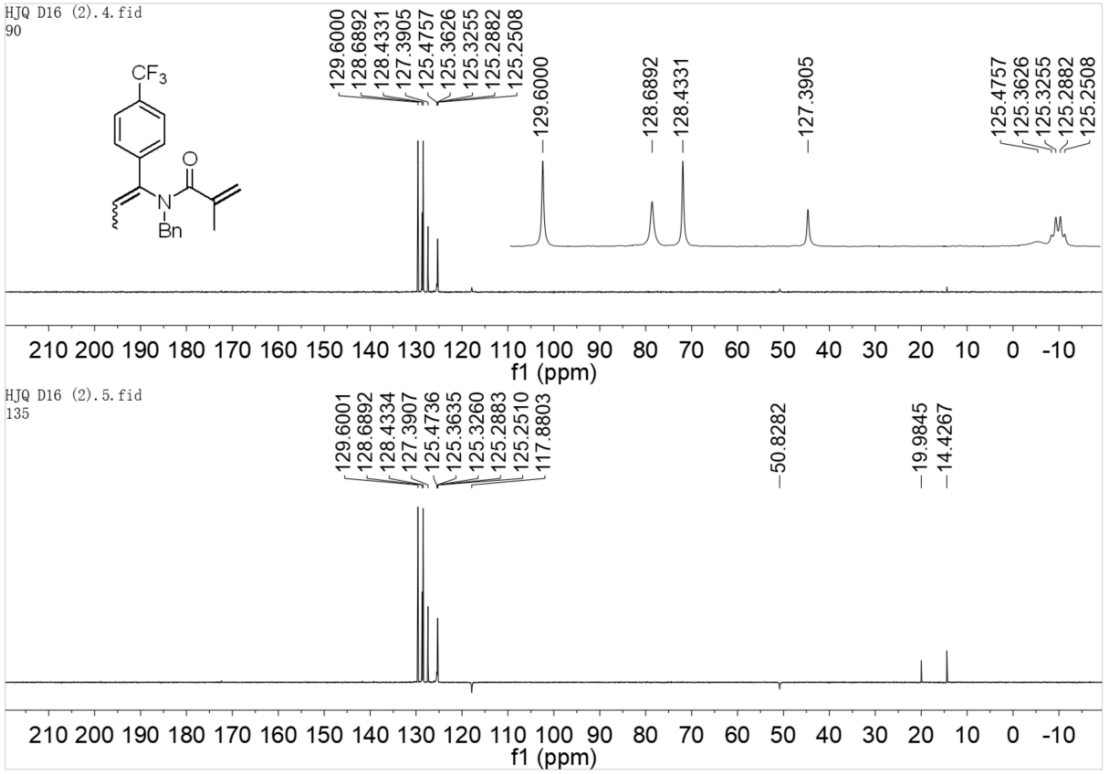
1d8, ^{1}H NMR



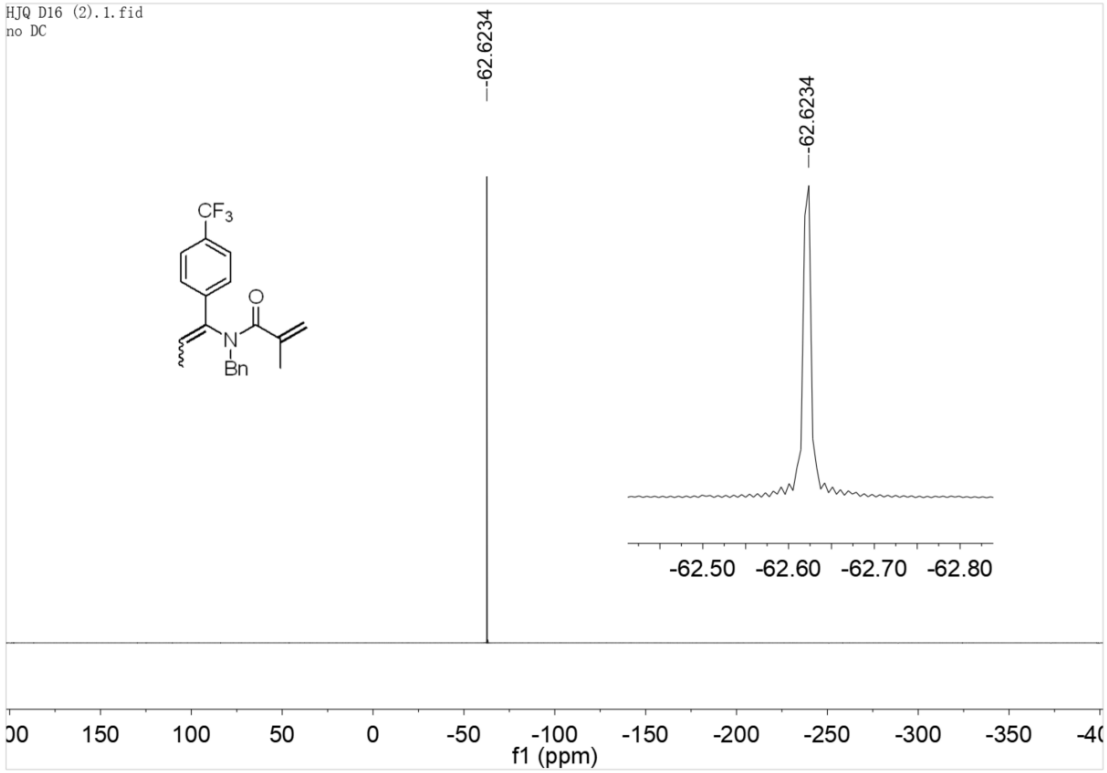
^{13}C NMR



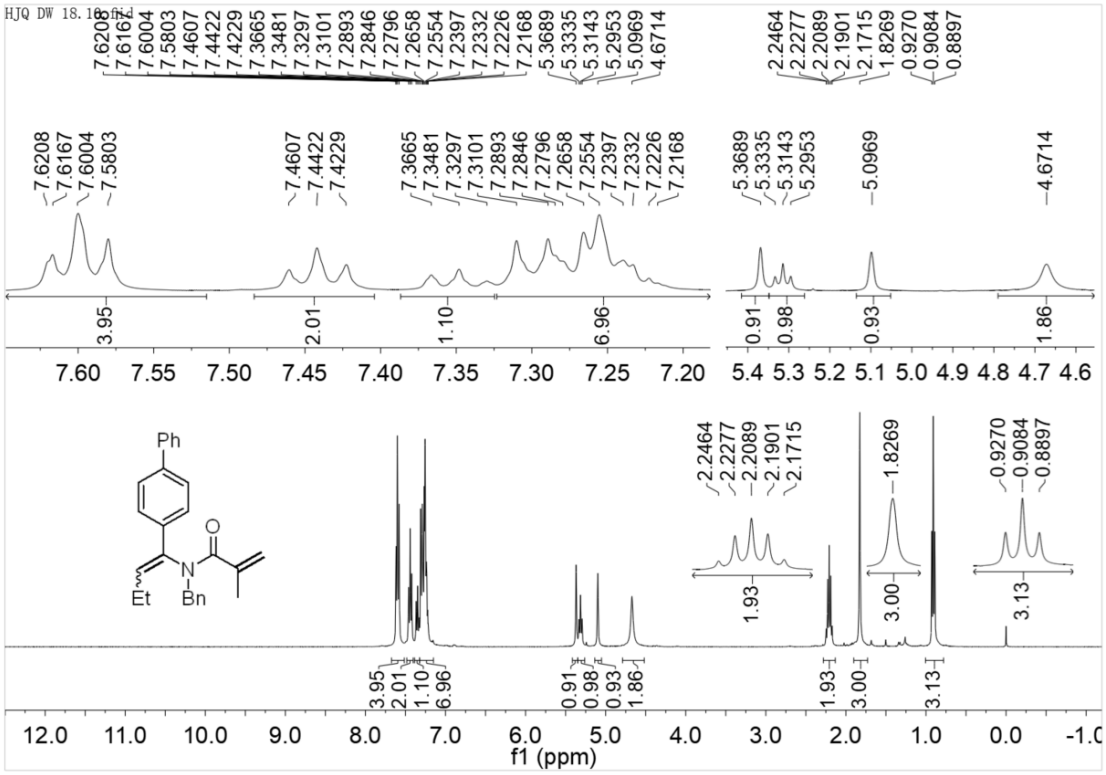
DEPT 90 and DEPT 135



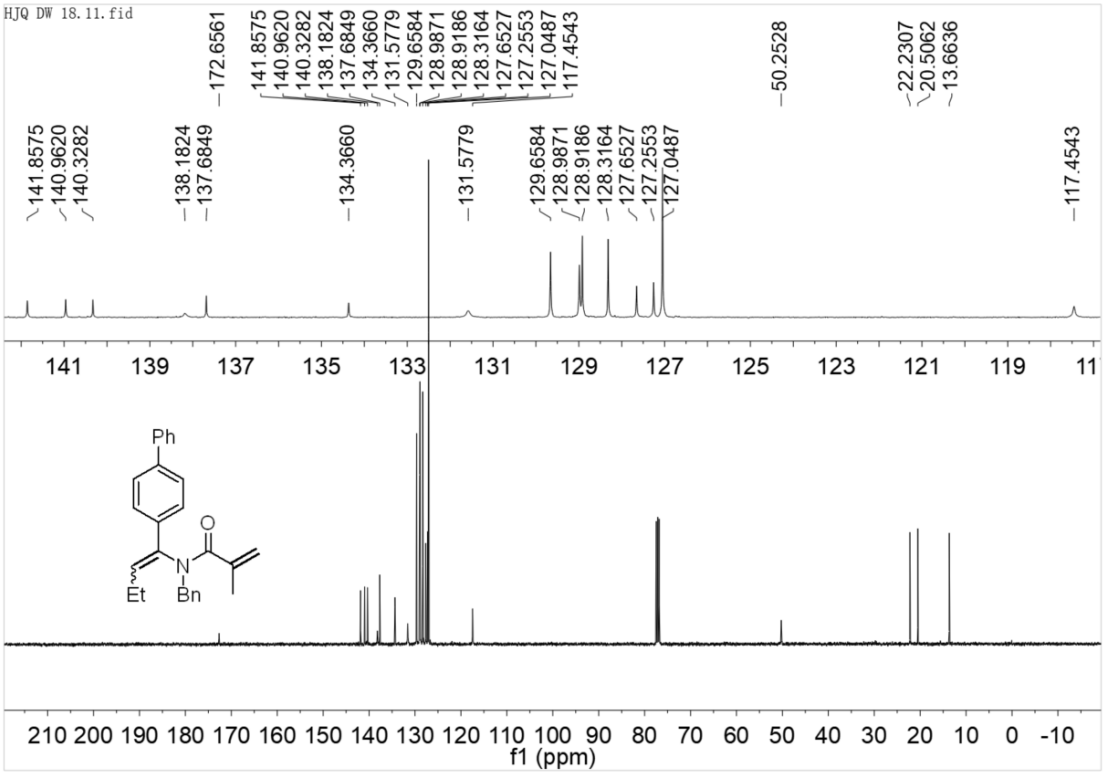
^{19}F NMR



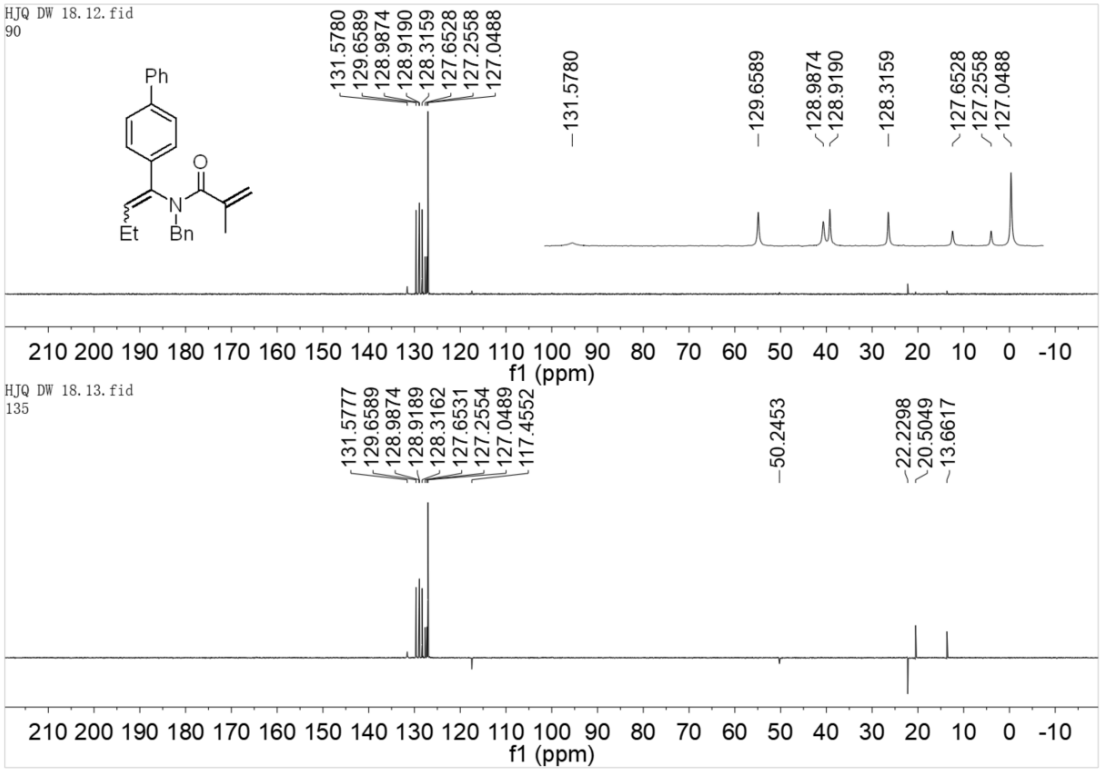
1d9, ^{1}H NMR



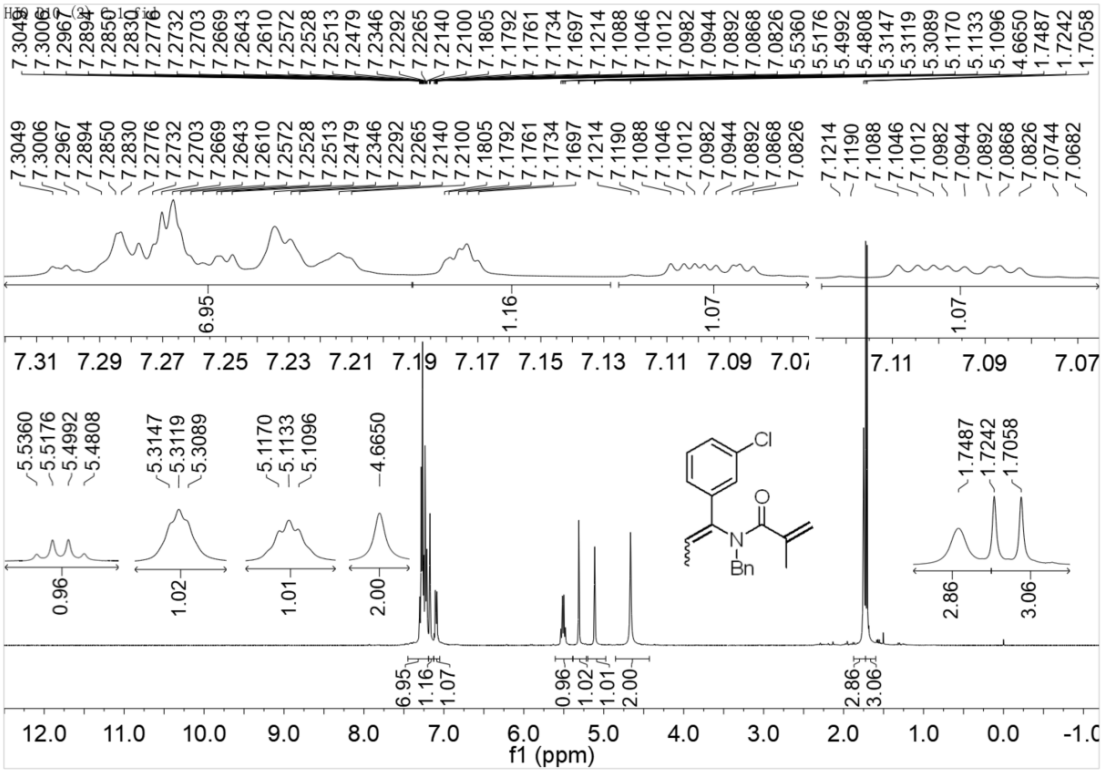
^{13}C NMR



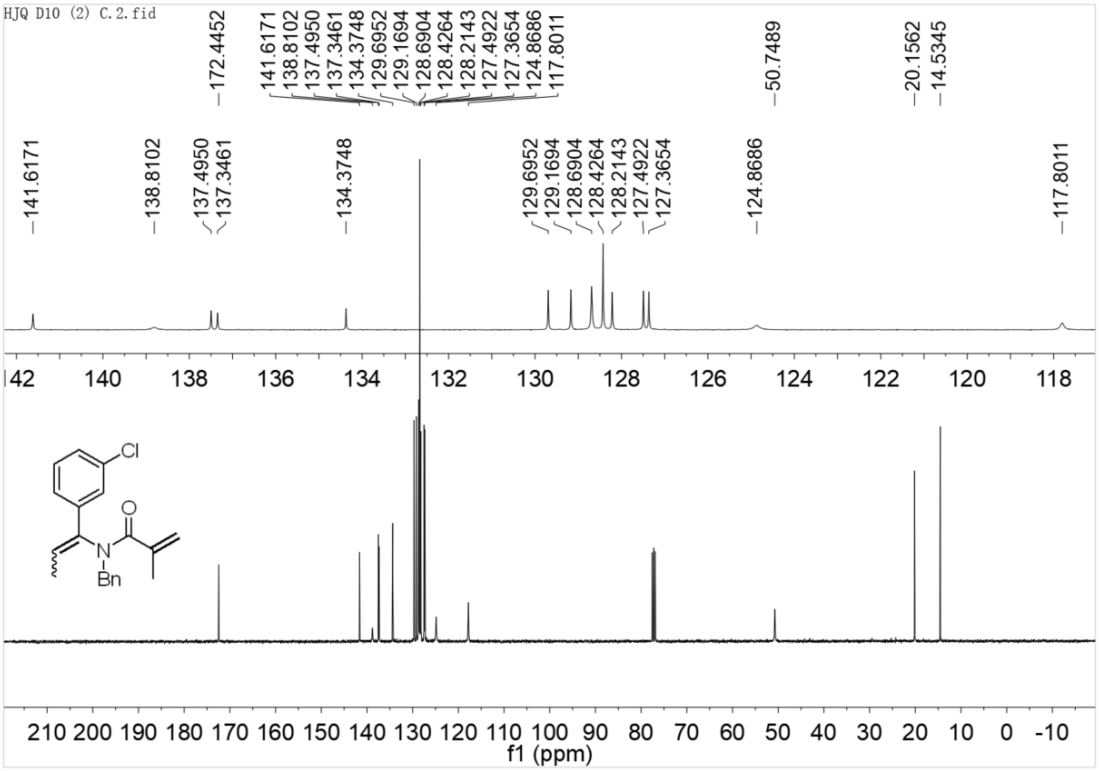
DEPT 90 and DEPT 135



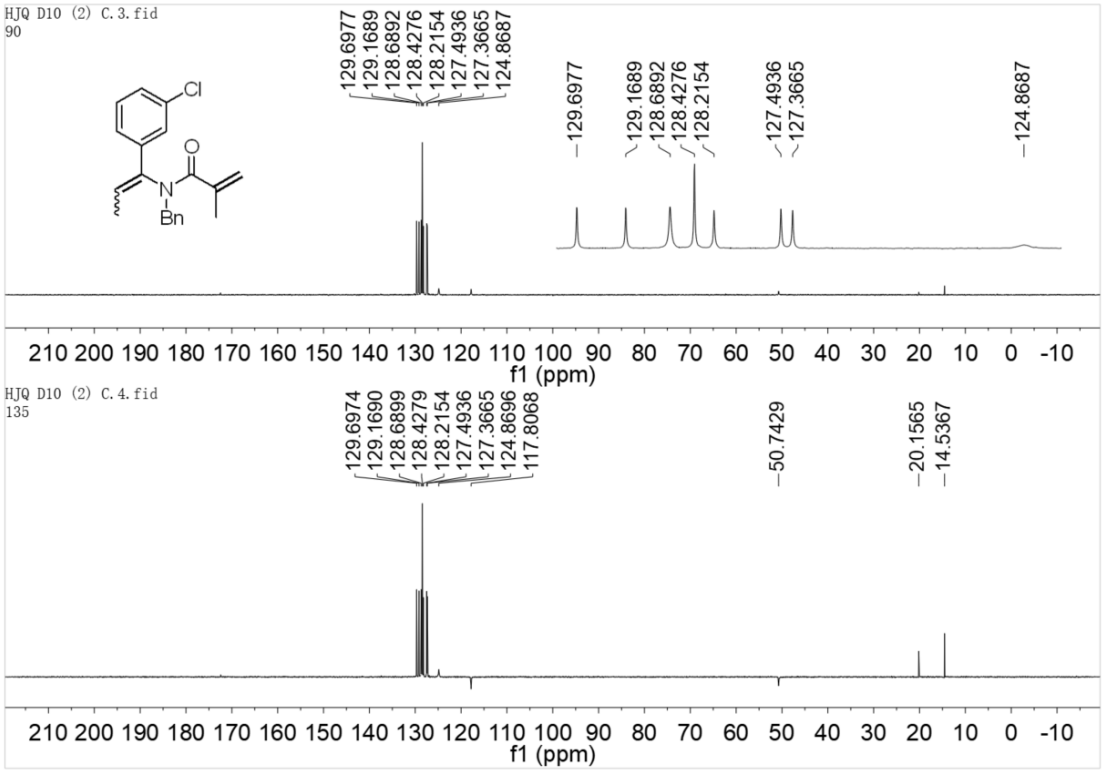
1d10, ^{1}H NMR



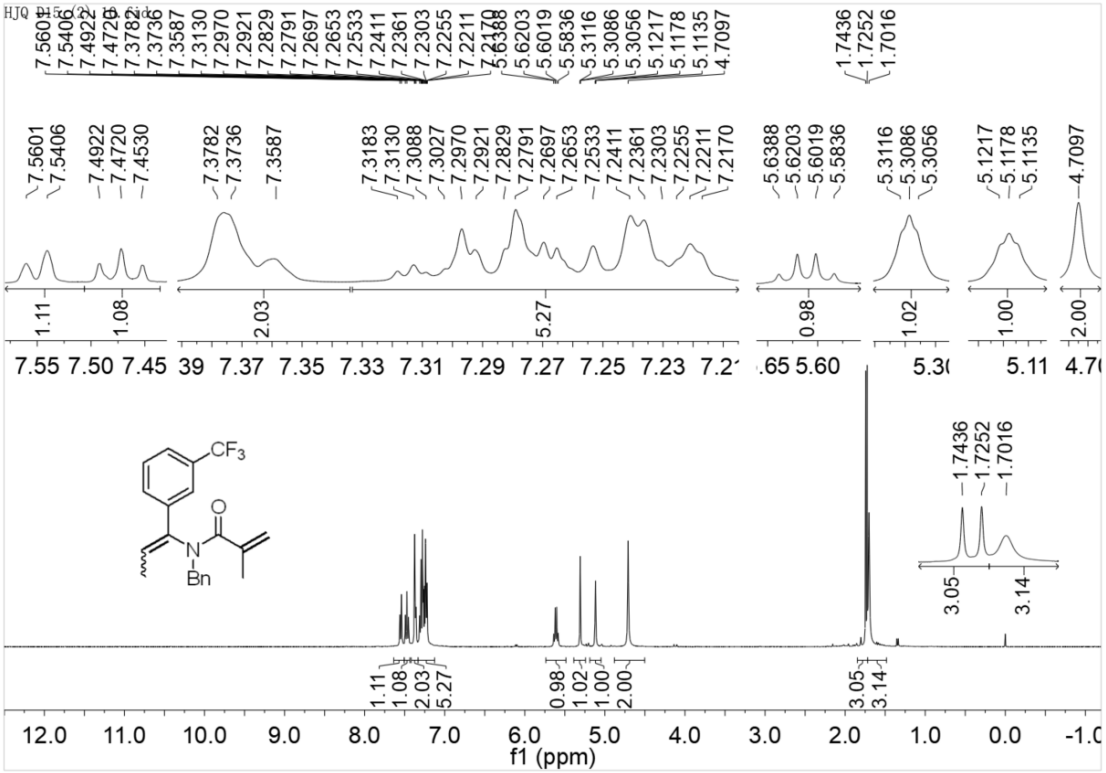
^{13}C NMR



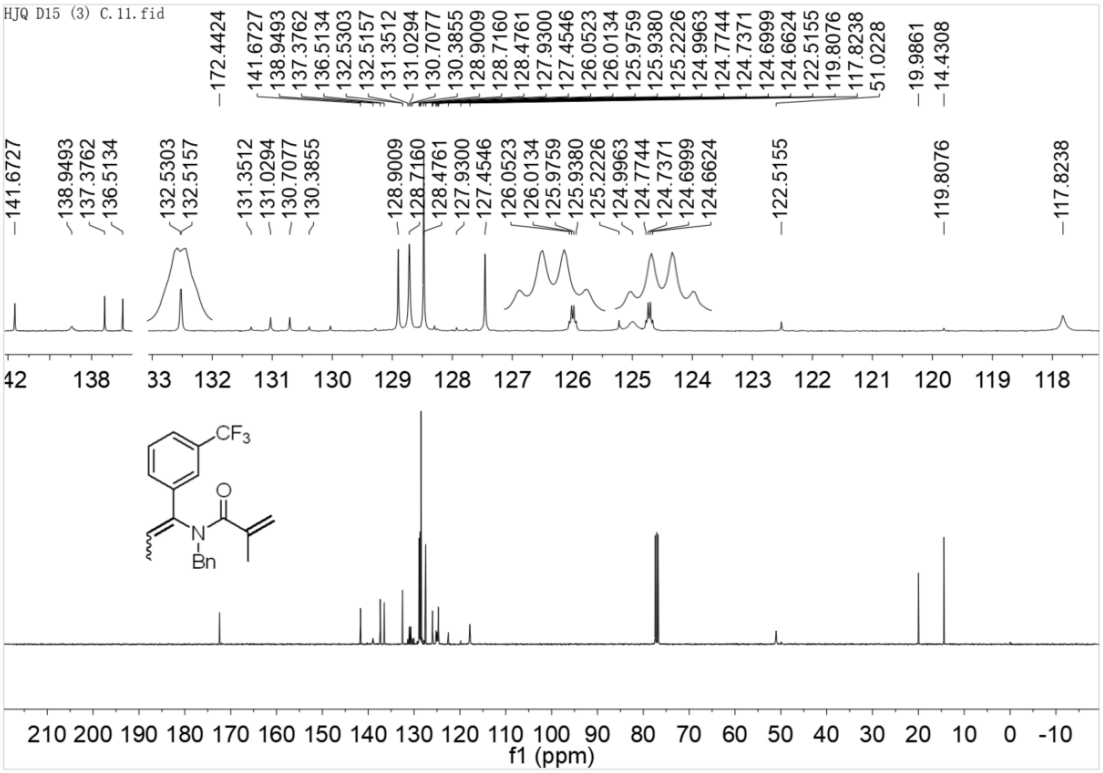
DEPT 90 and DEPT 135



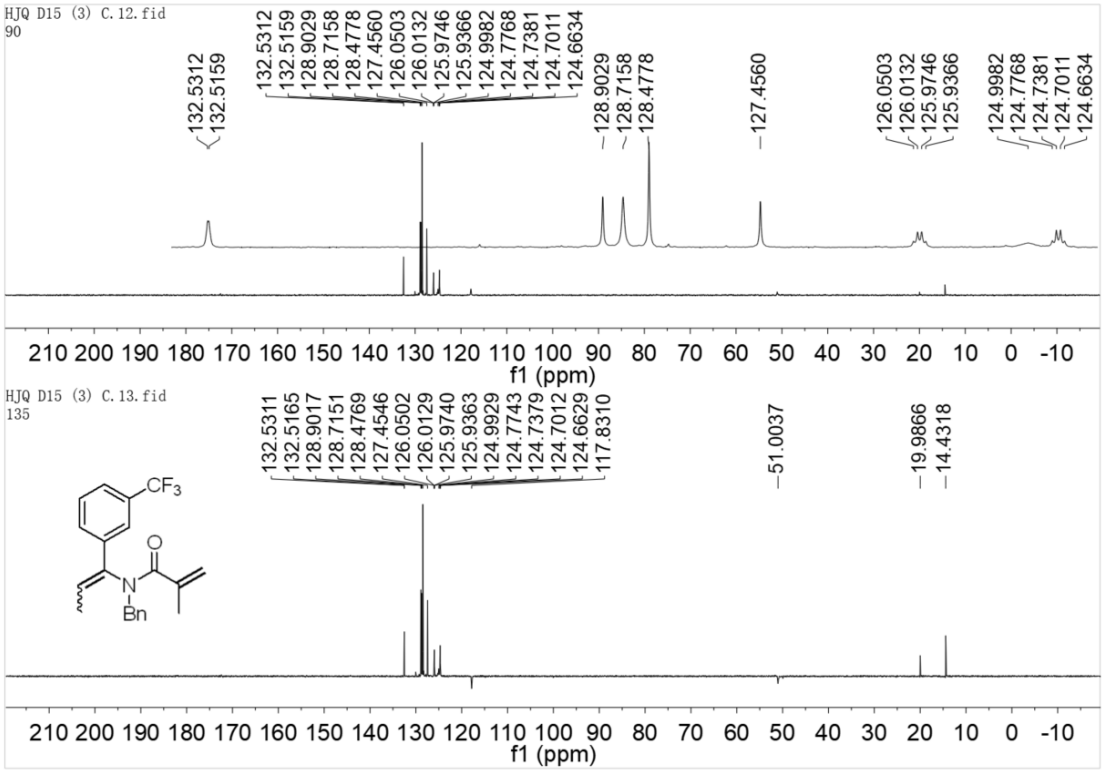
1d11, ^{1}H NMR



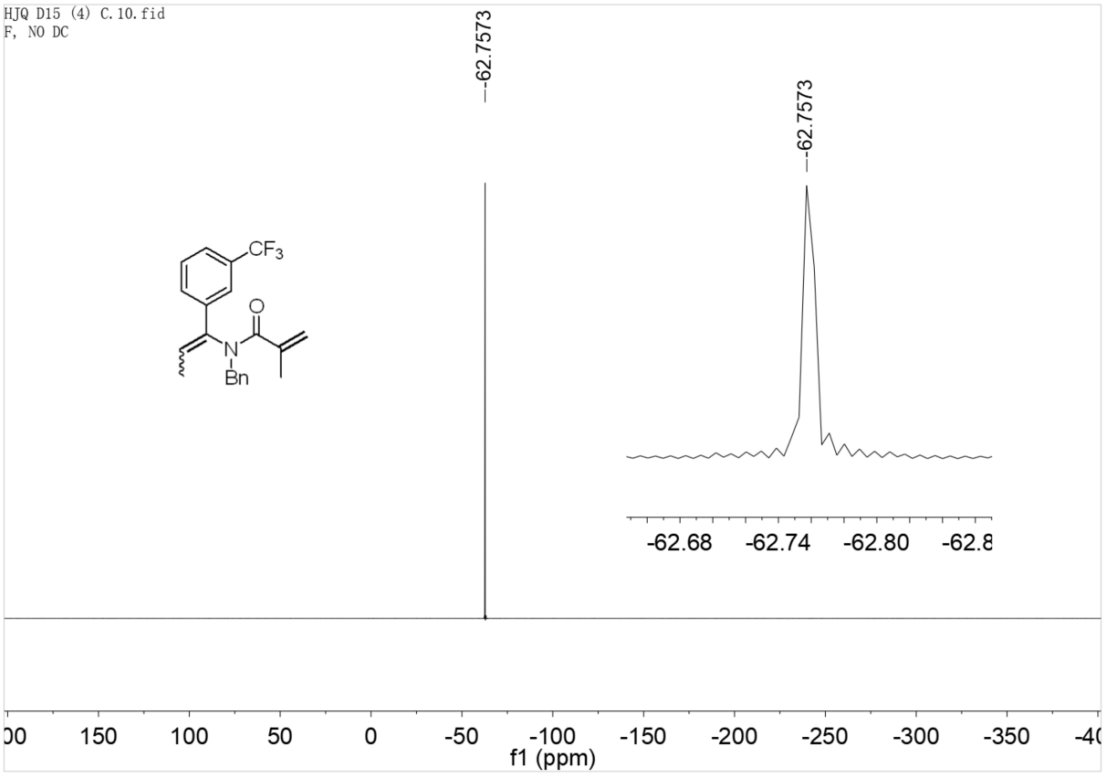
^{13}C NMR



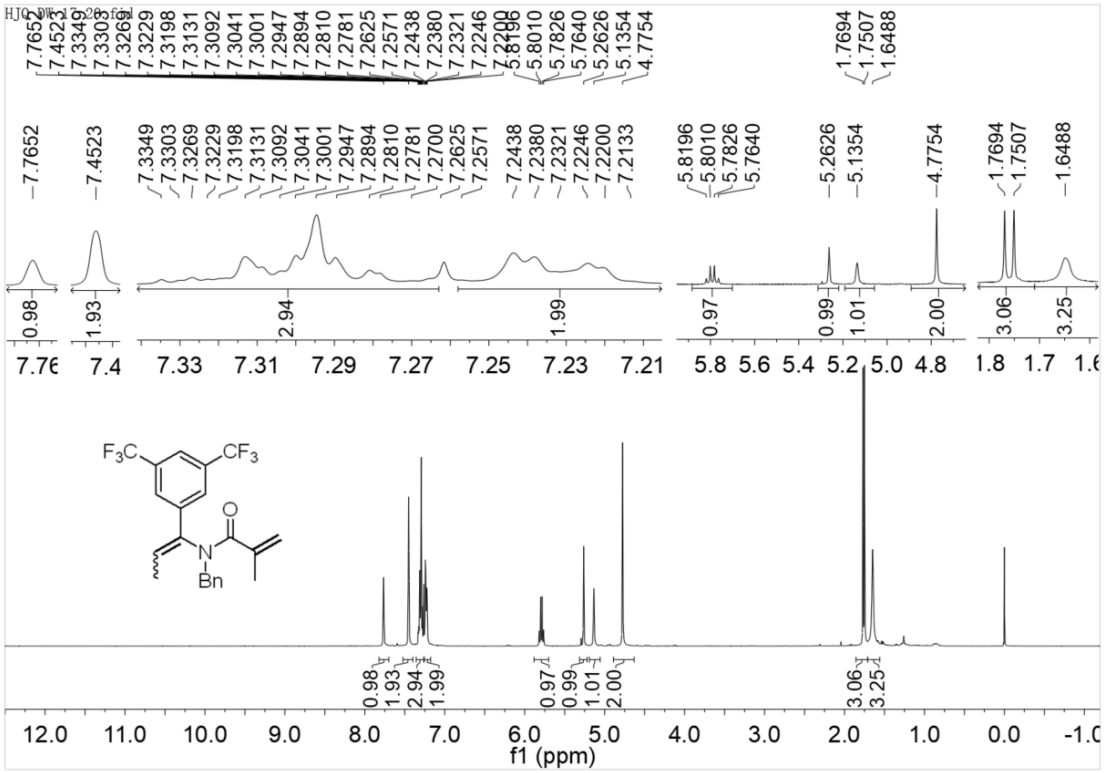
DEPT 90 and DEPT 135



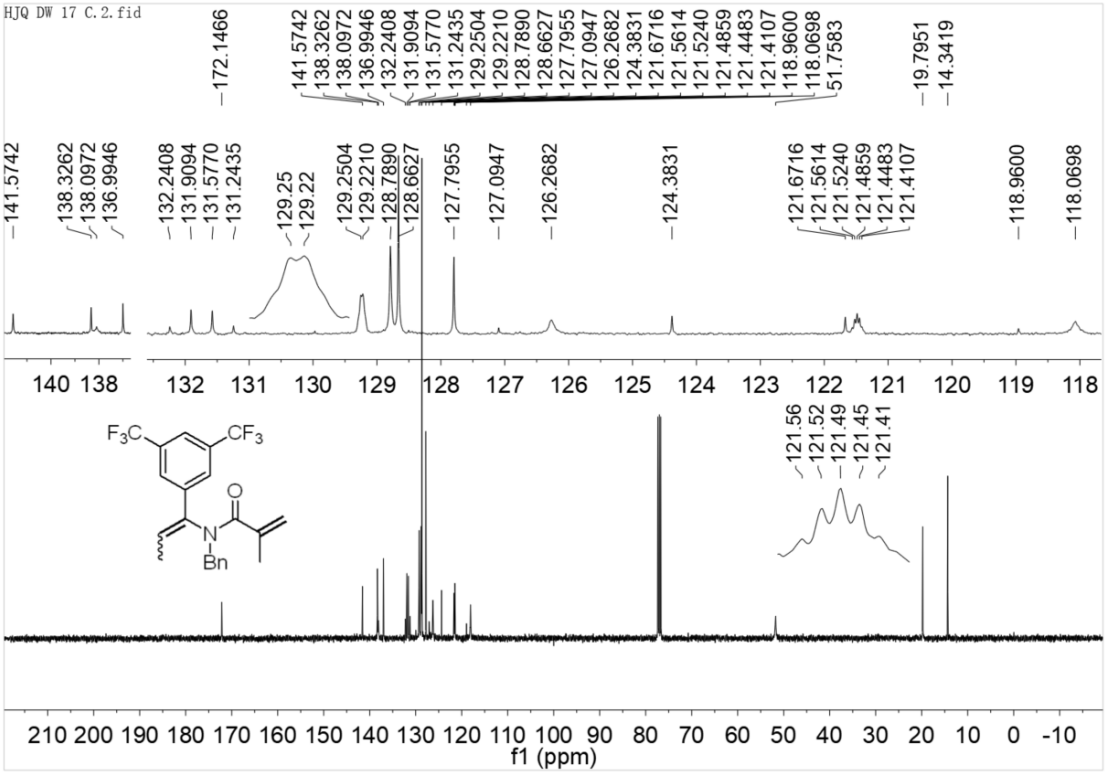
^{19}F NMR



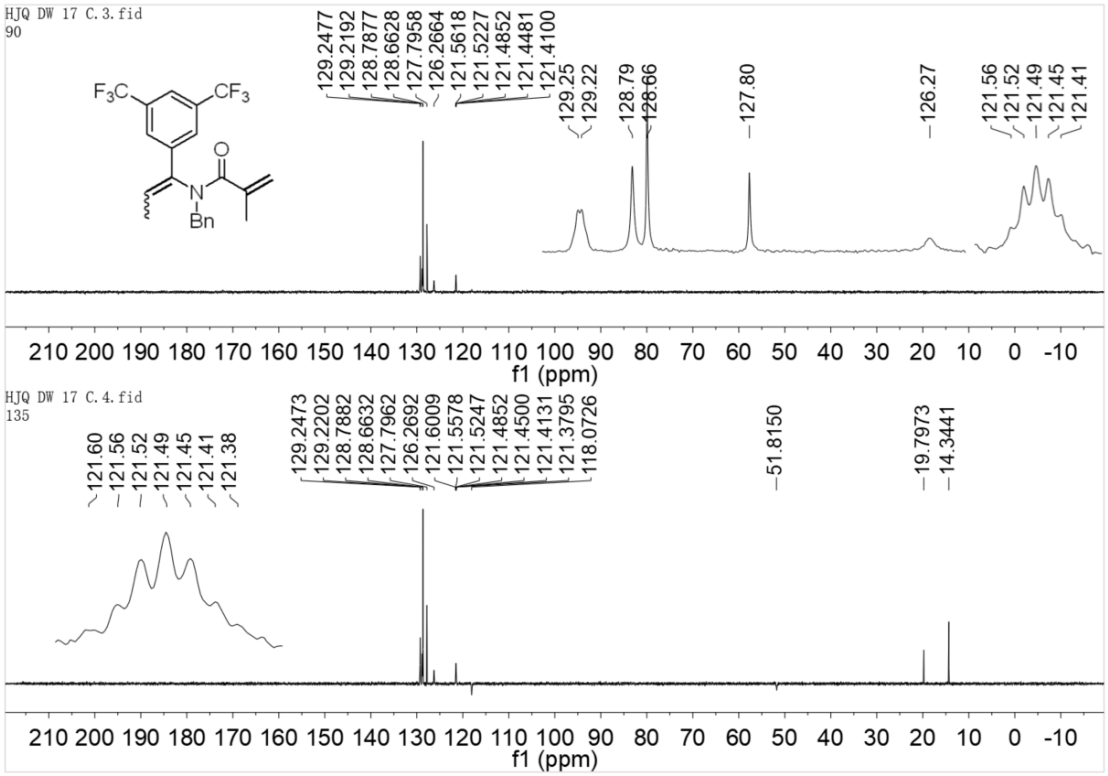
1d12, ^{1}H NMR



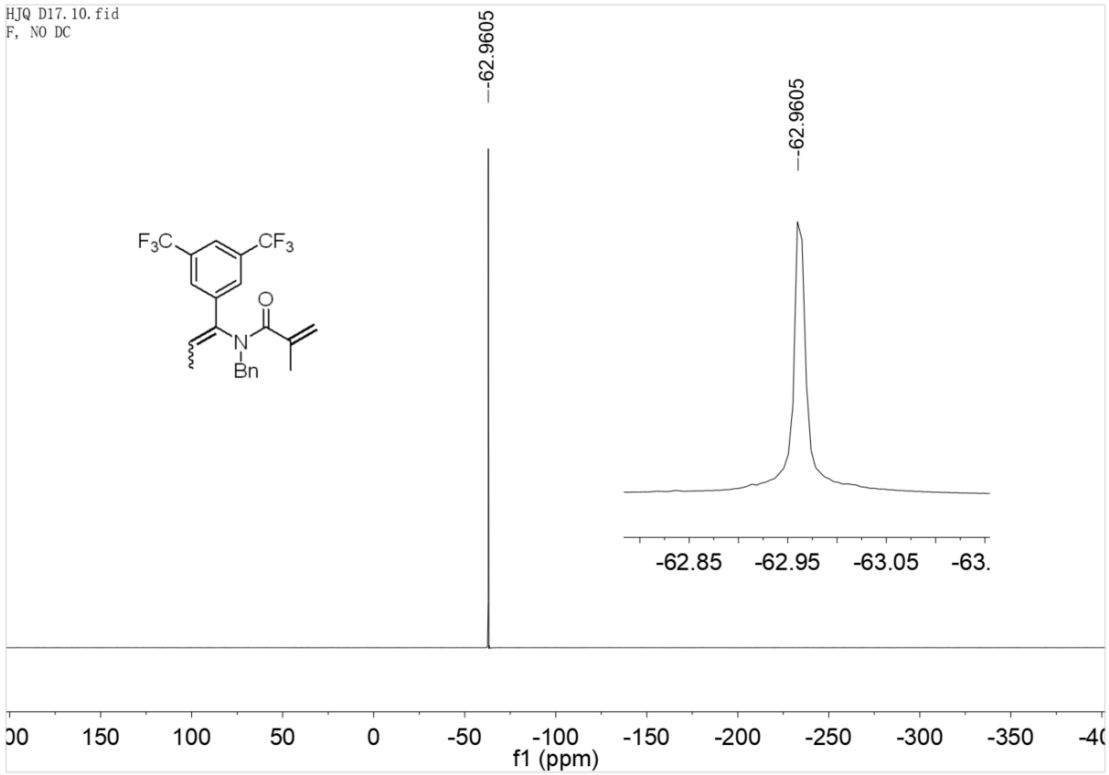
^{13}C NMR



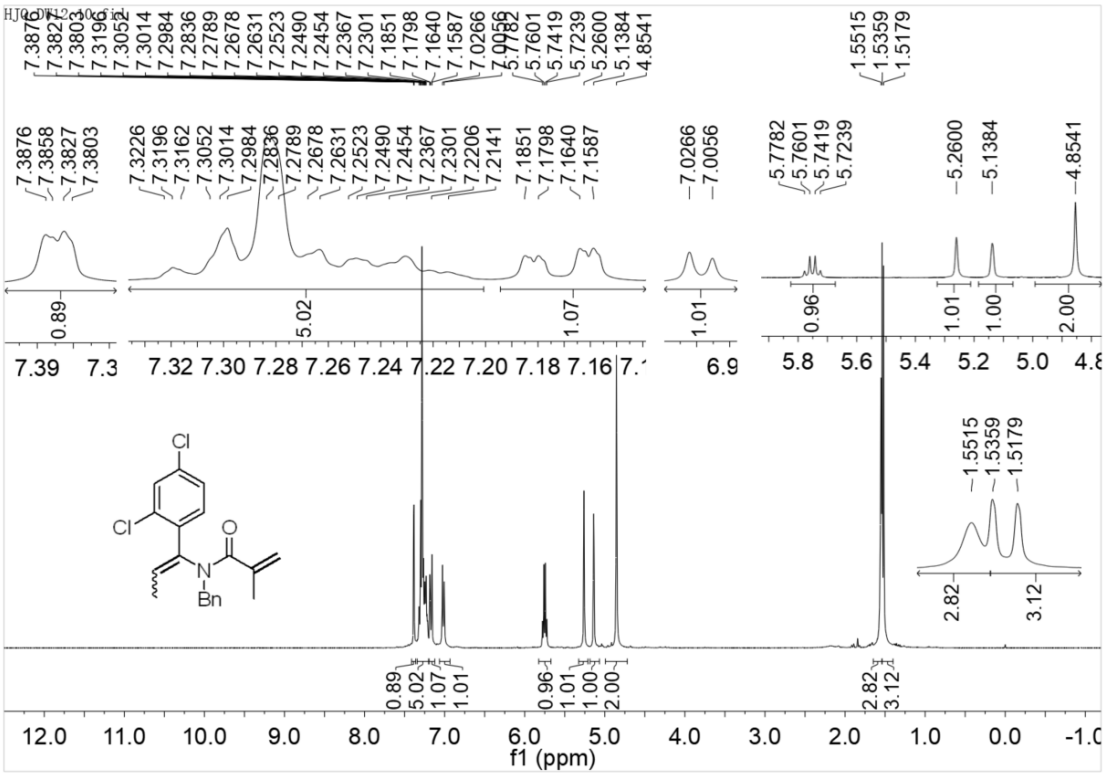
DEPT 90 and DEPT 135



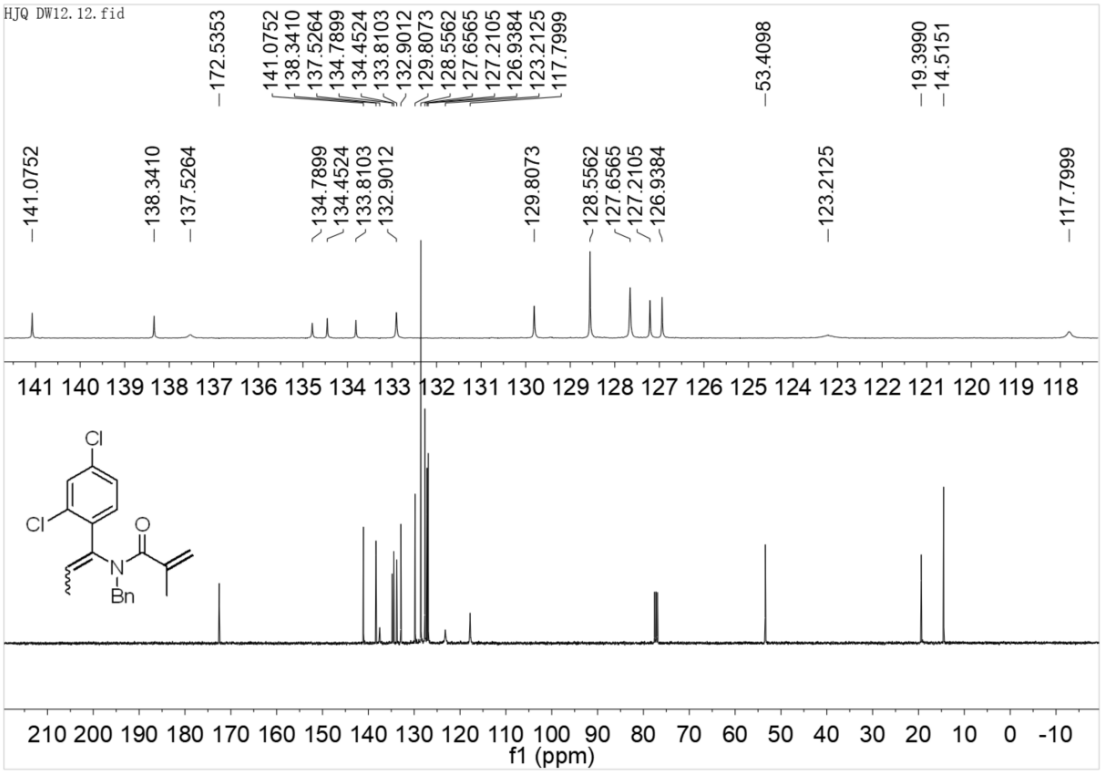
^{19}F NMR



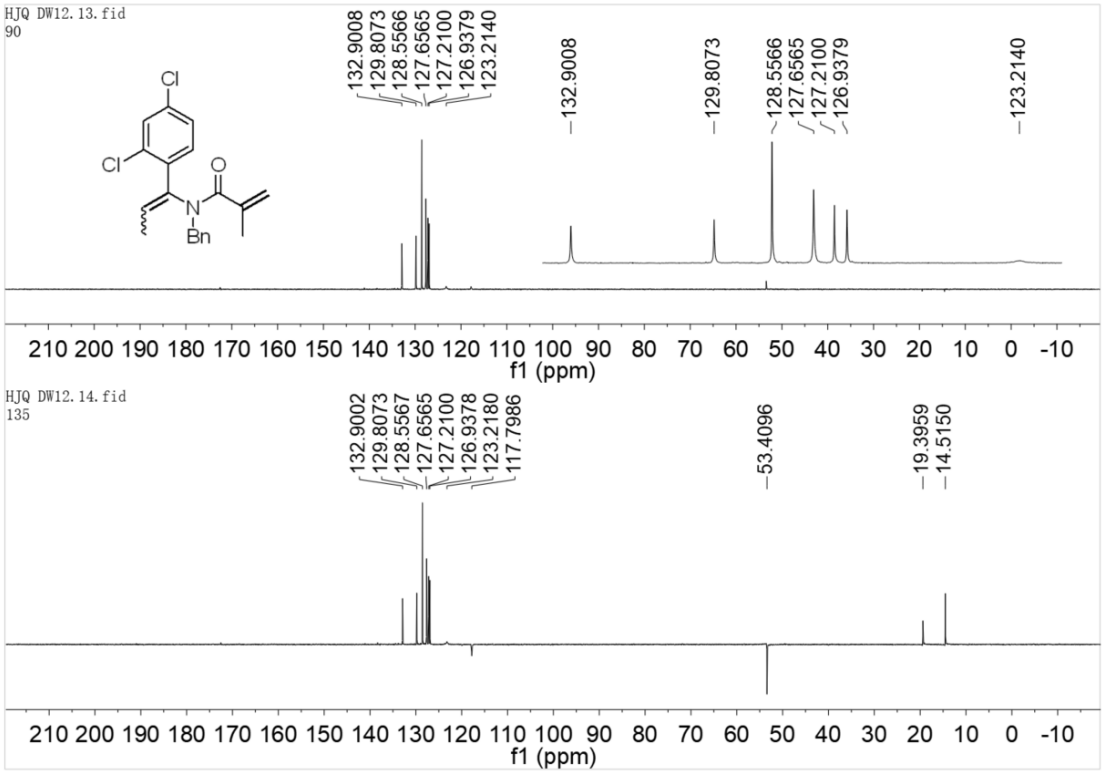
1d13, ^{1}H NMR



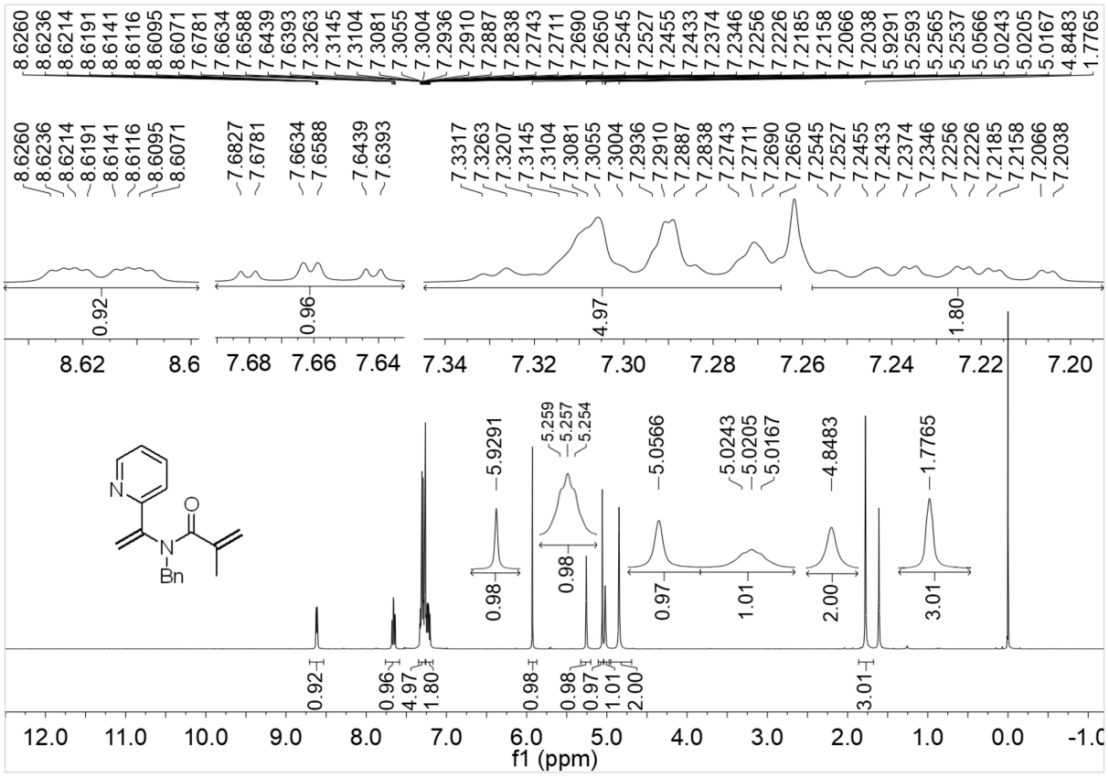
^{13}C NMR



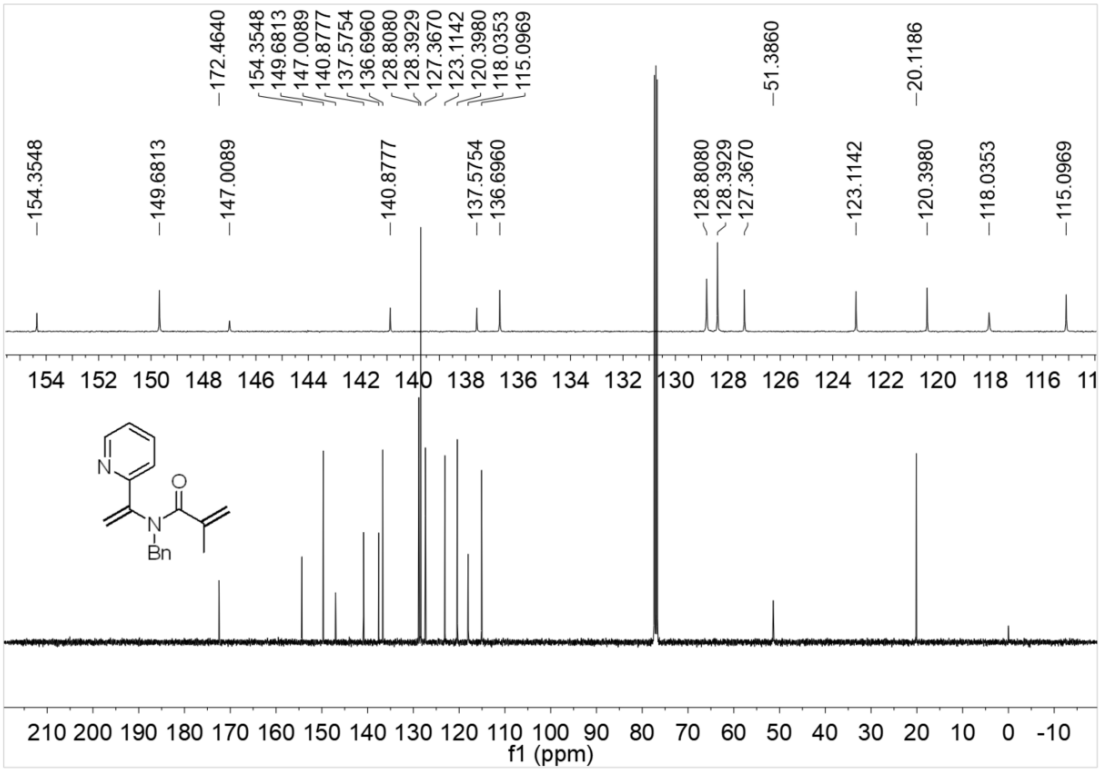
DEPT 90 and DEPT 135



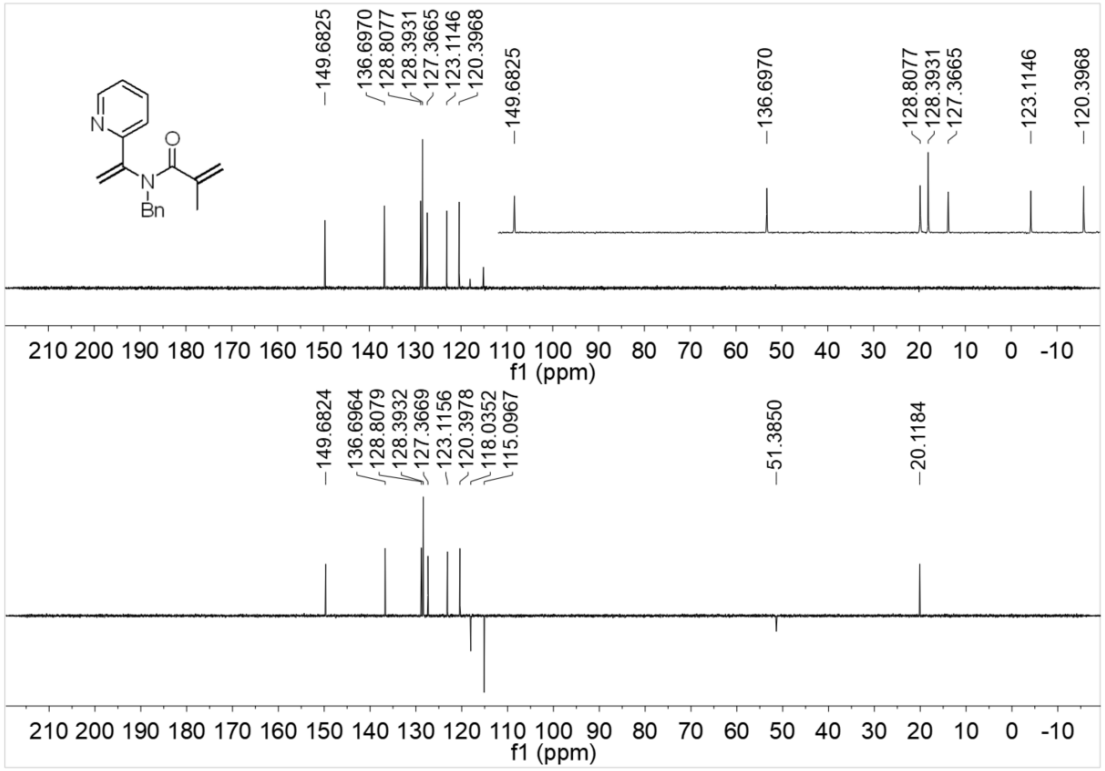
1e, ^{1}H NMR



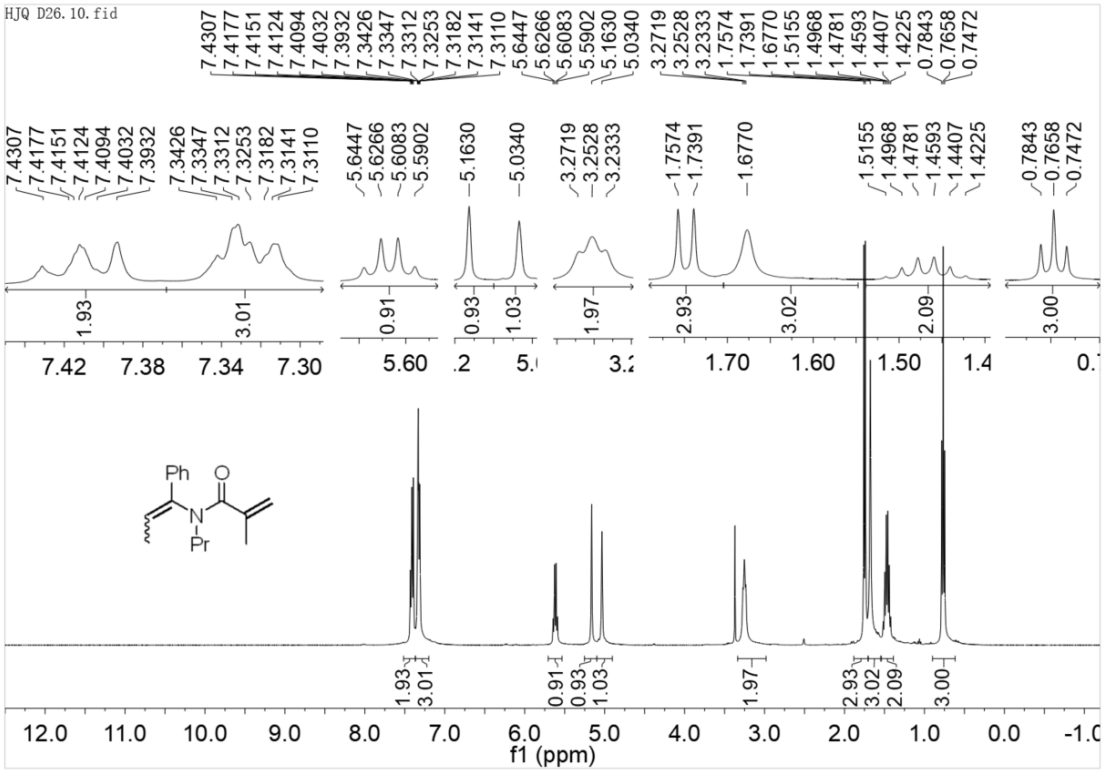
^{13}C NMR



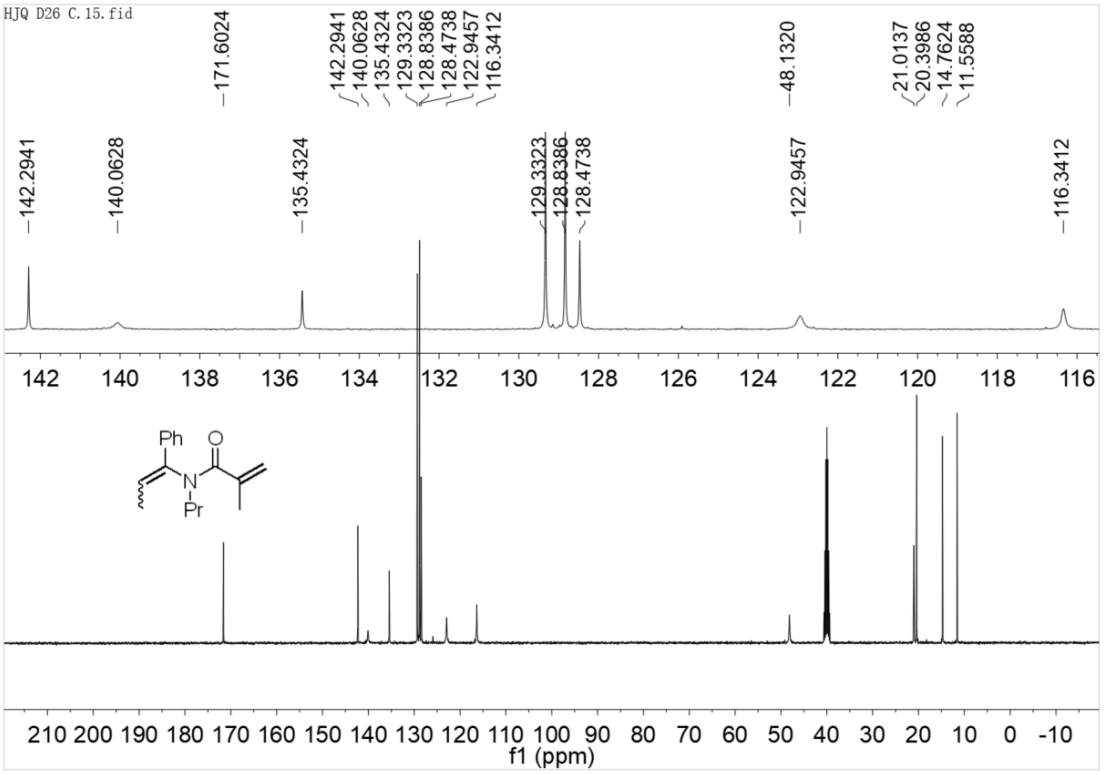
DEPT 90 and DEPT 135



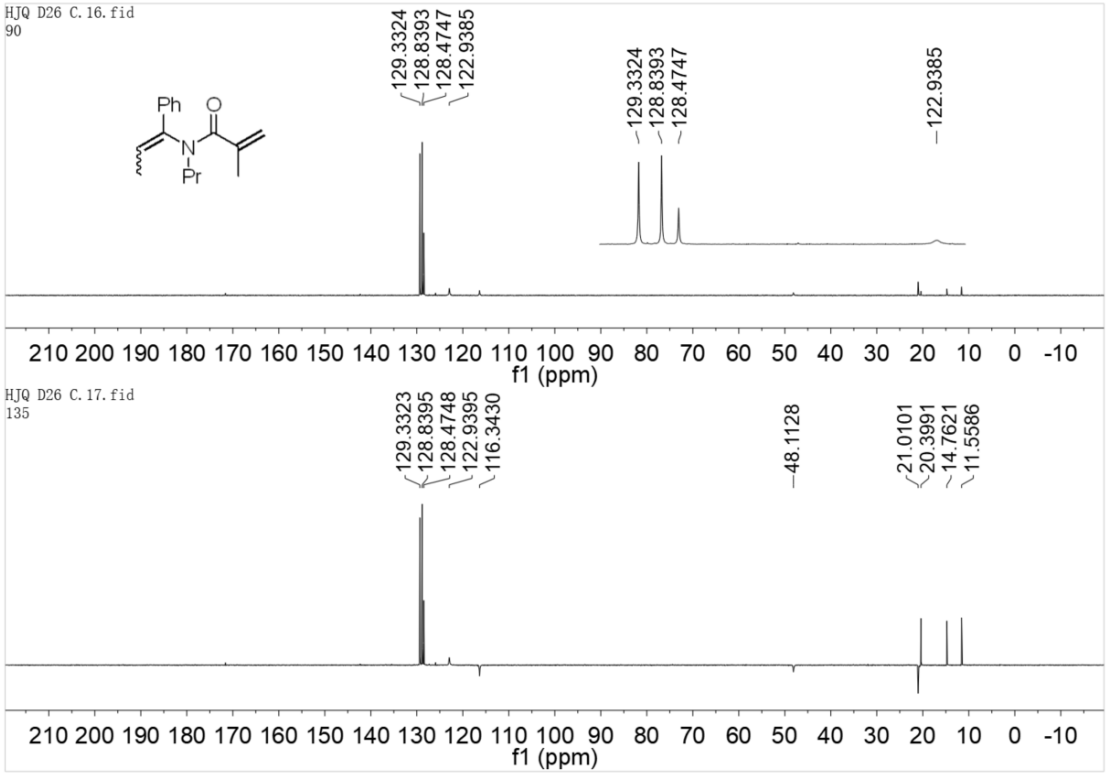
1g1, ^{1}H NMR



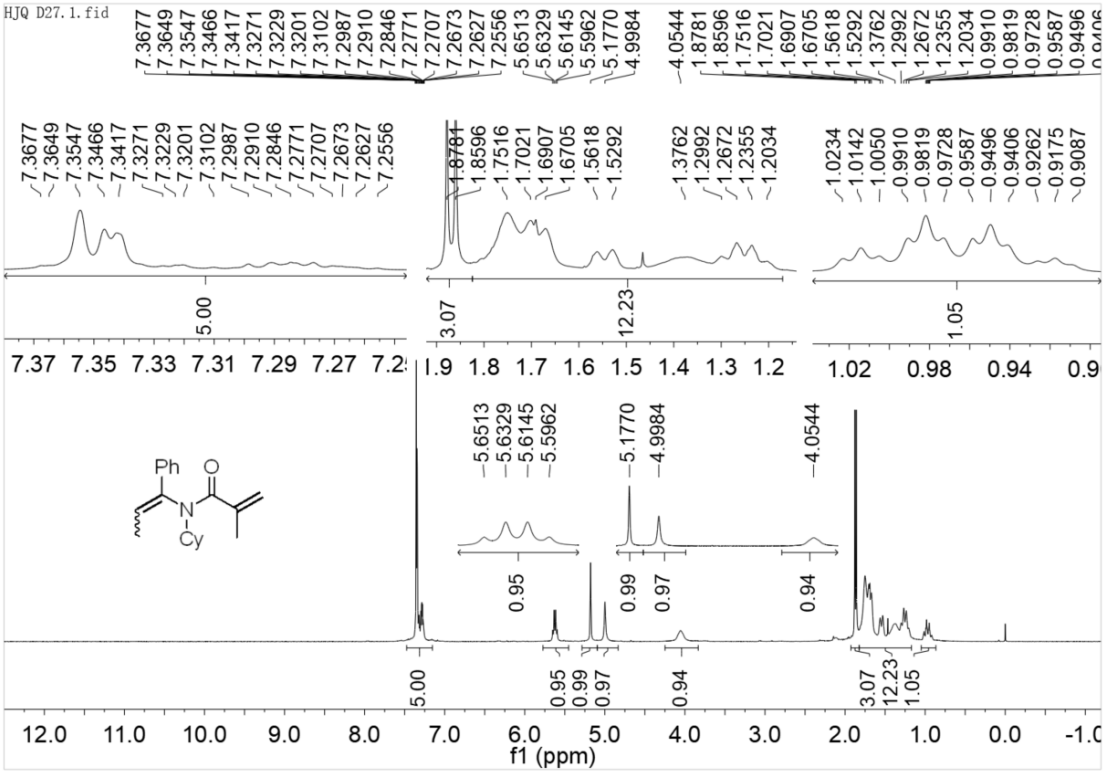
^{13}C NMR



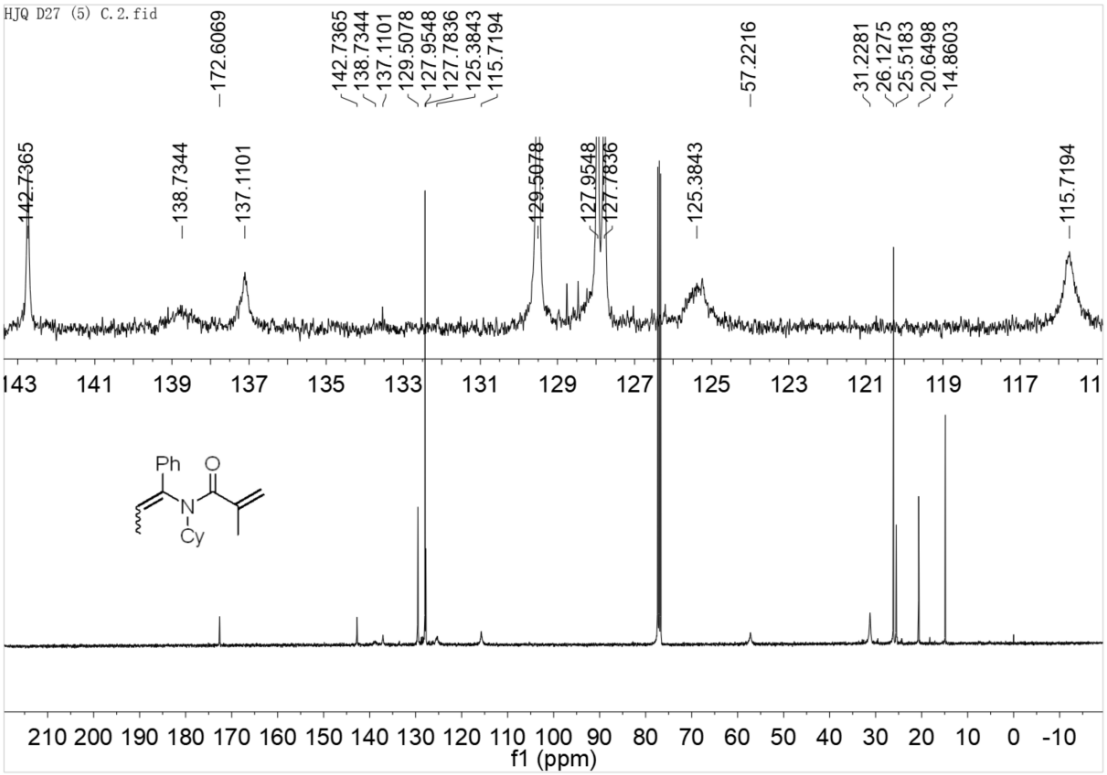
DEPT 90 and DEPT 135



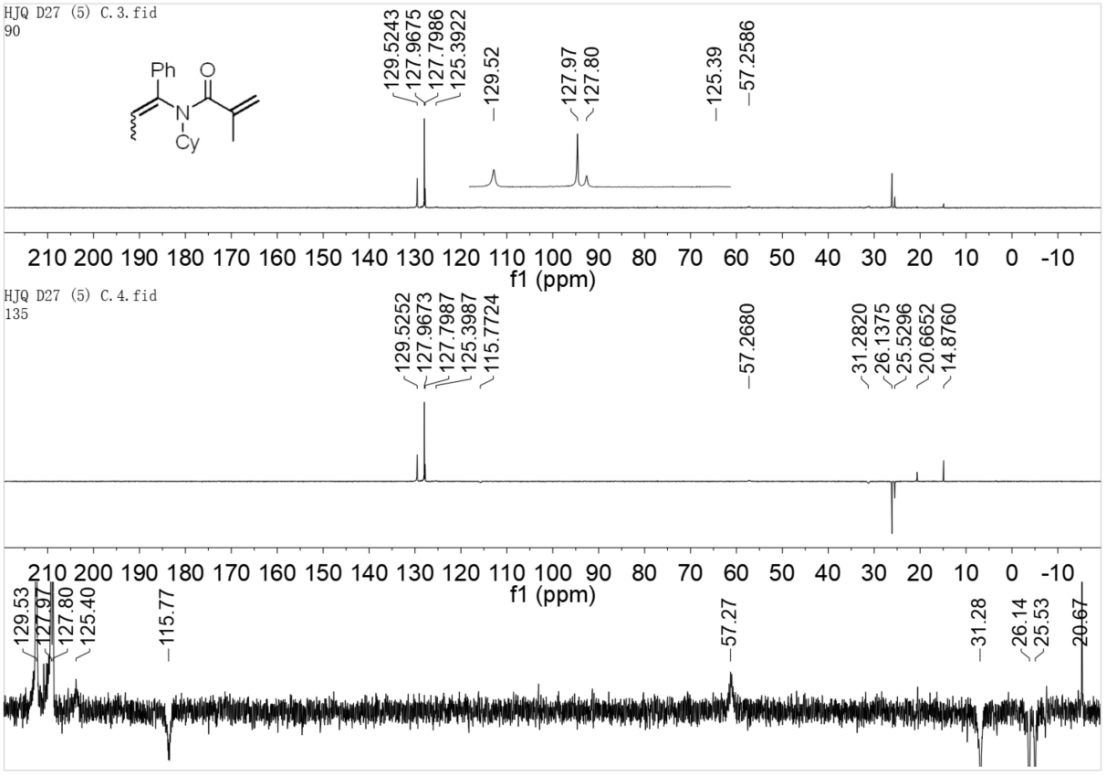
1g2, ^{1}H NMR



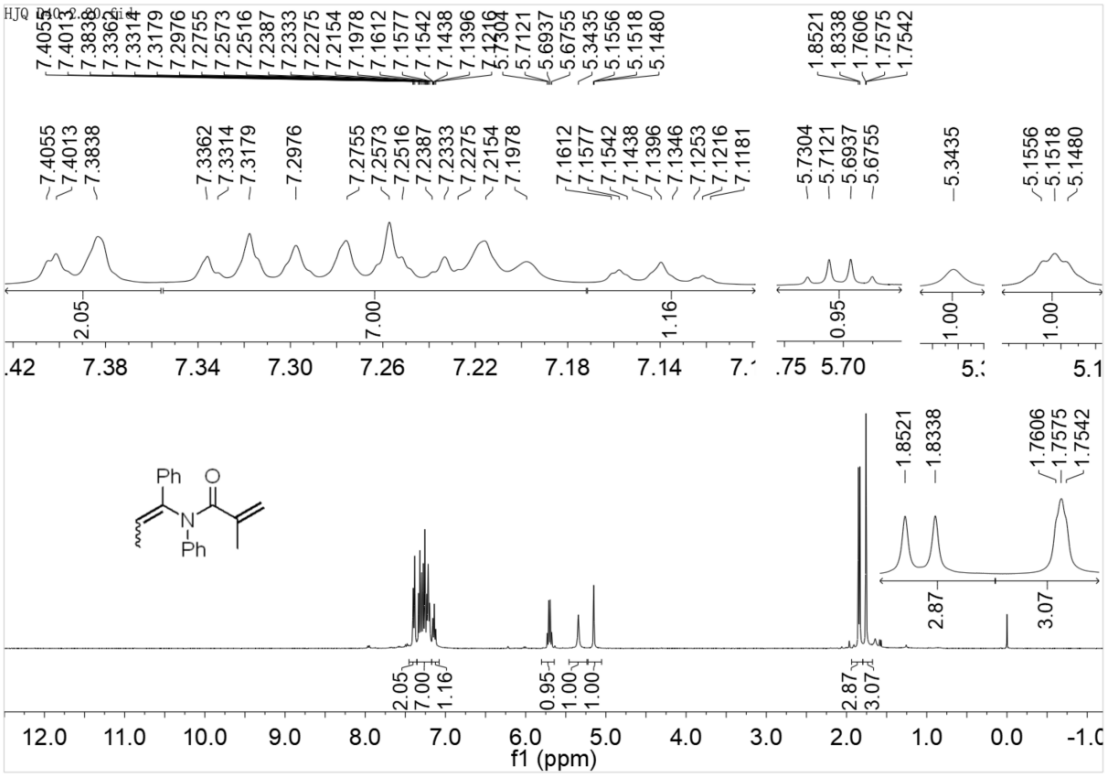
^{13}C NMR



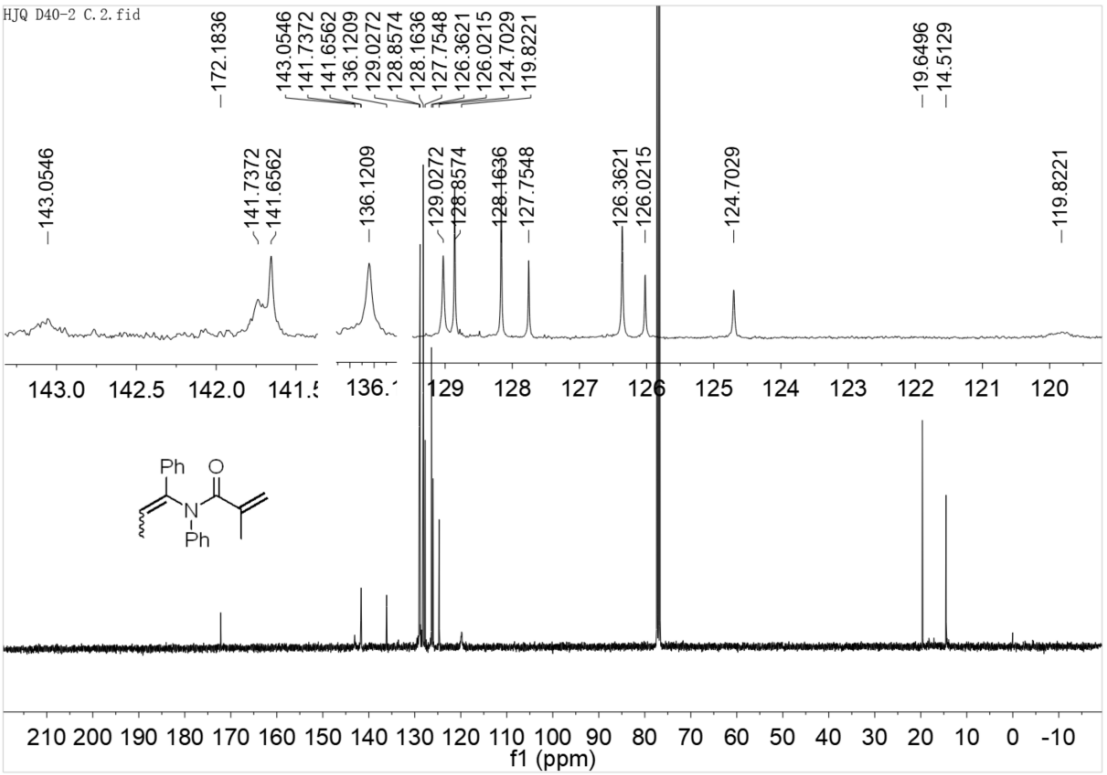
DEPT 90 and DEPT 135



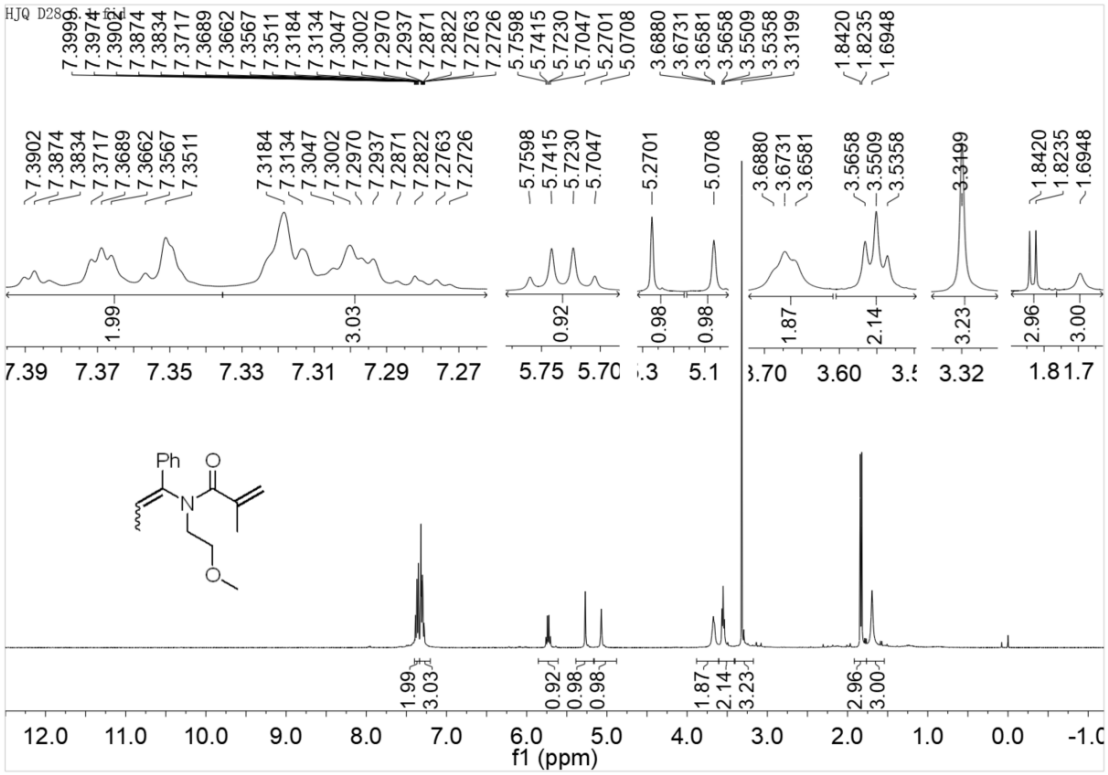
1g3, ^{1}H NMR



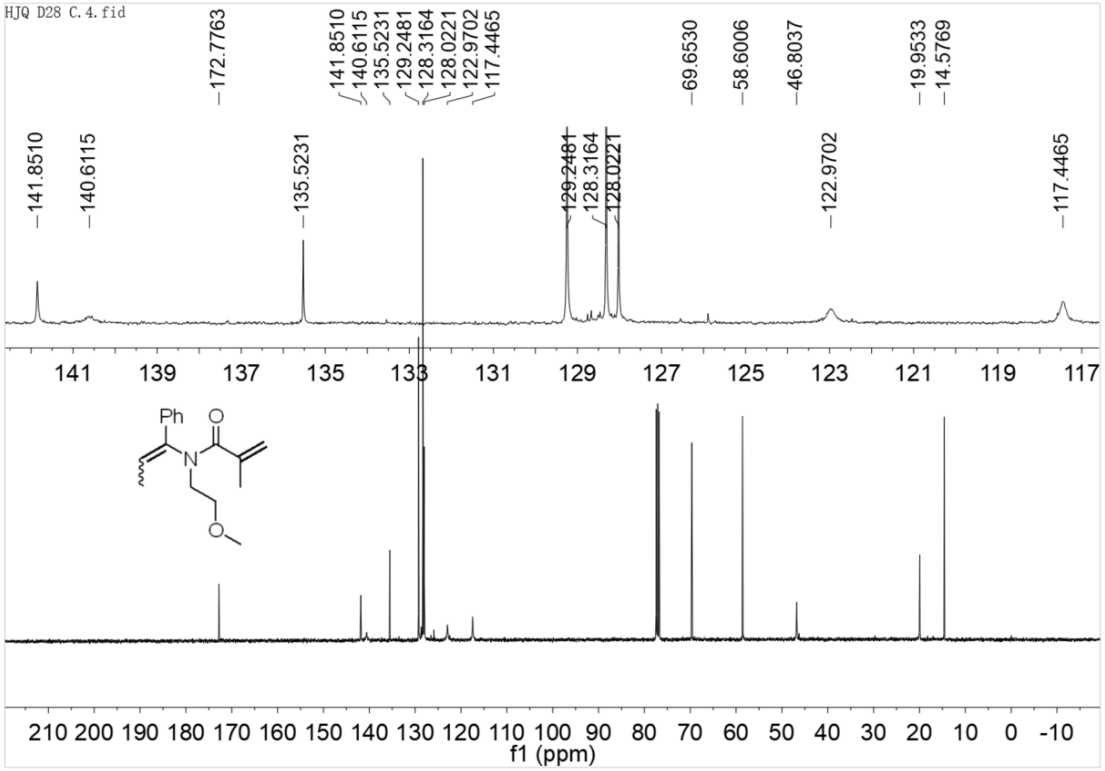
^{13}C NMR



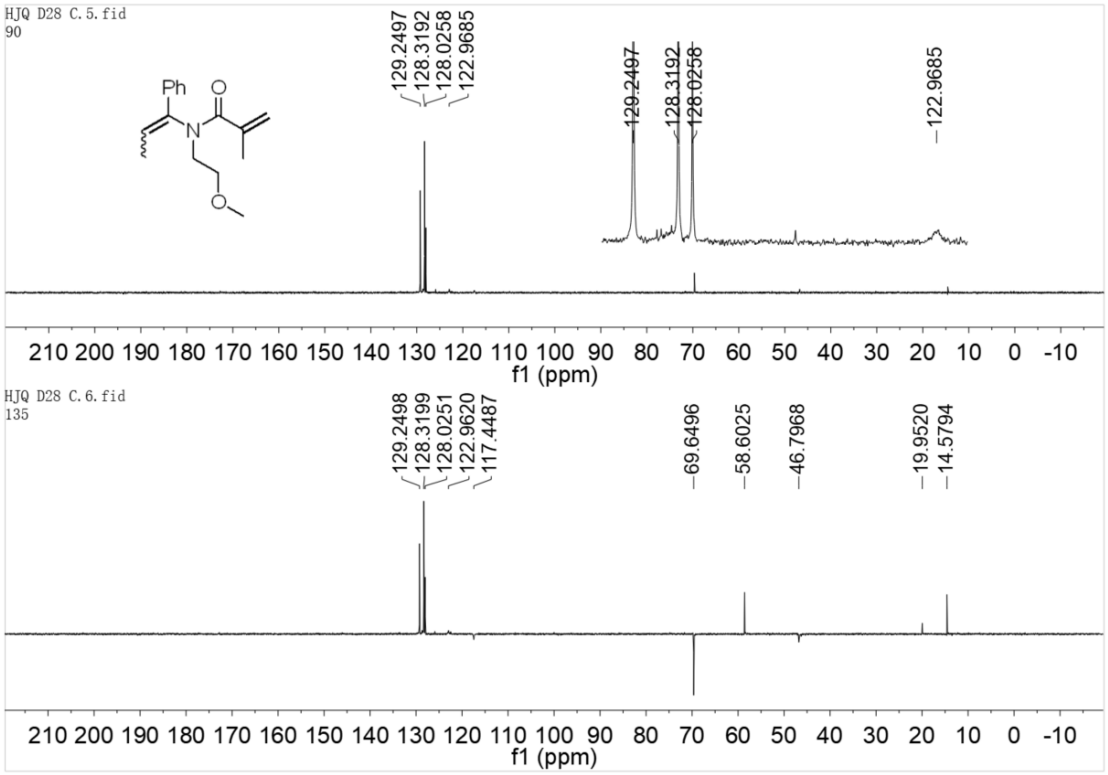
1h, ^{1}H NMR



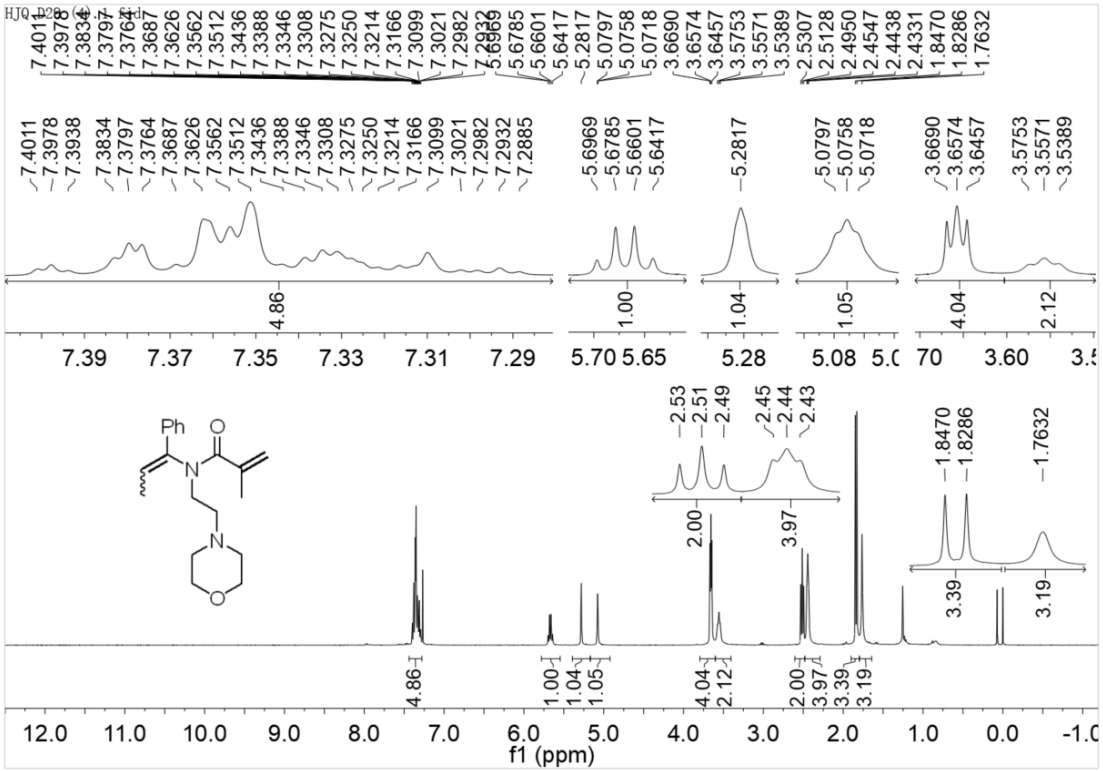
^{13}C NMR



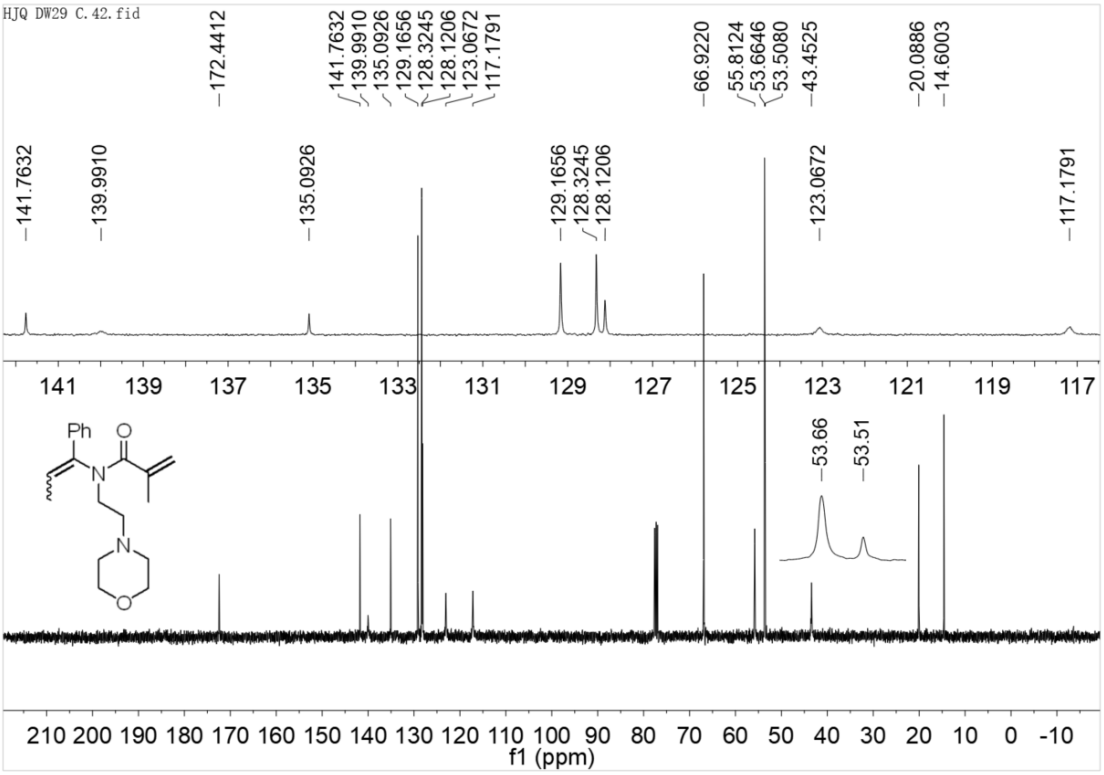
DEPT 90 and DEPT 135



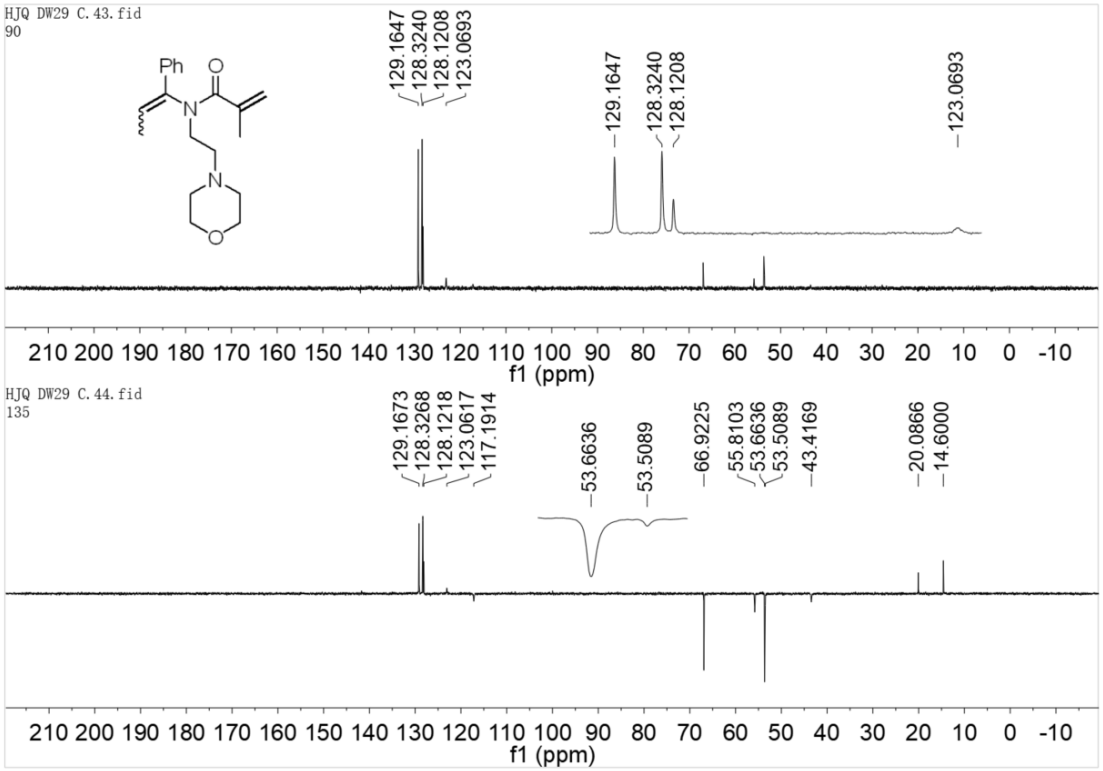
1i, ^{1}H NMR



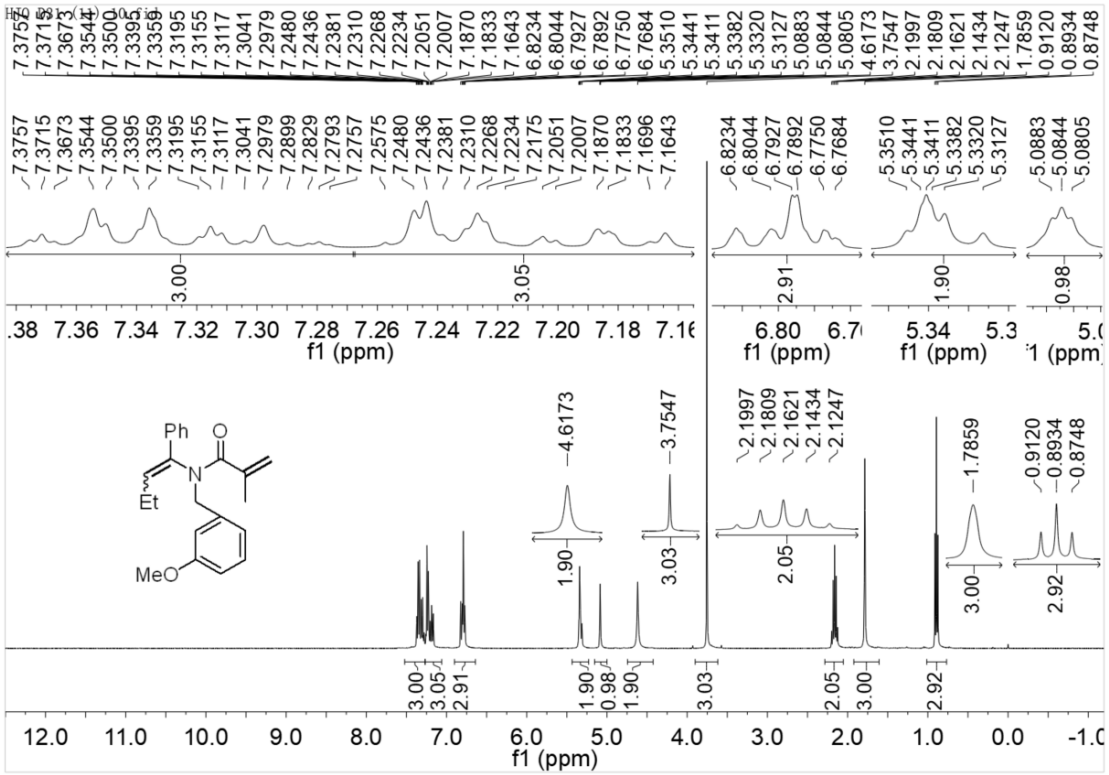
^{13}C NMR



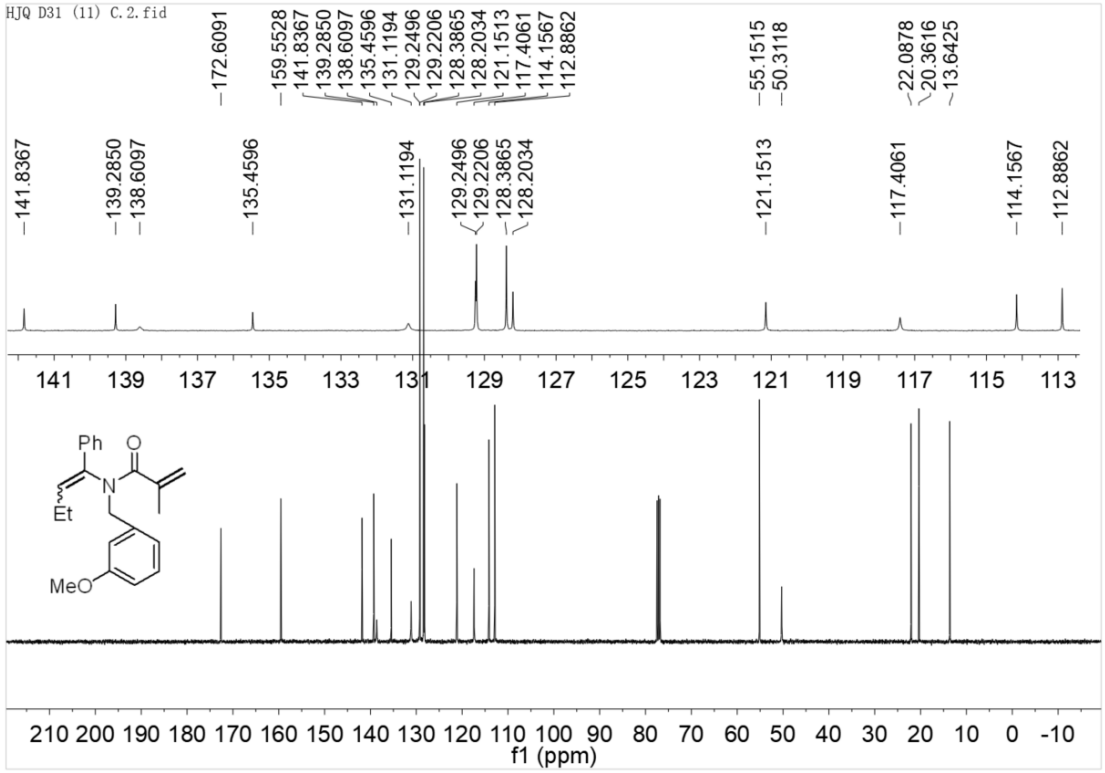
DEPT 90 and DEPT 135



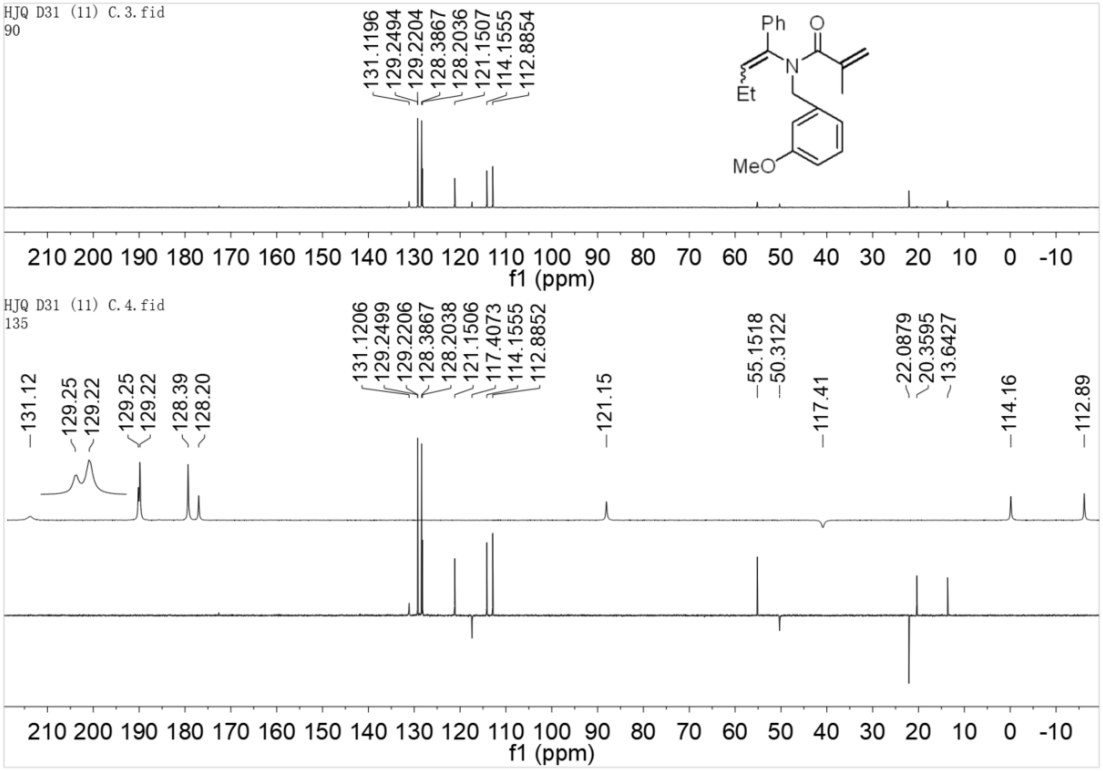
1j1, ^{1}H NMR



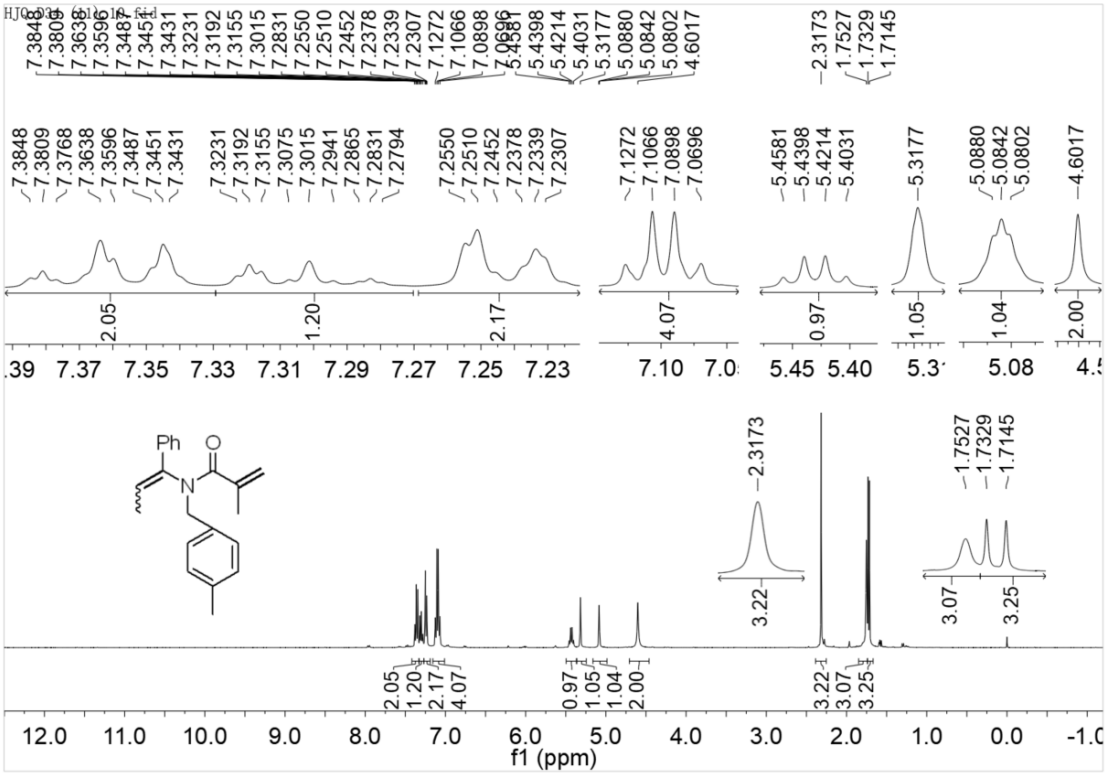
^{13}C NMR



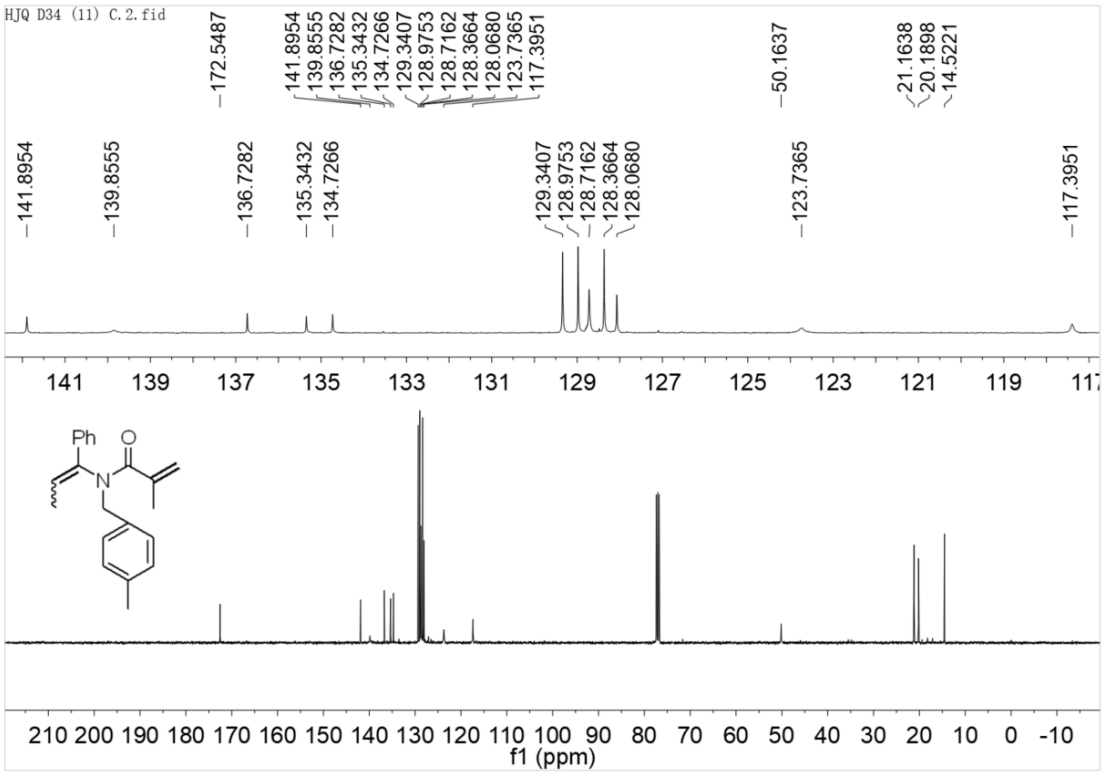
DEPT 90 and DEPT 135



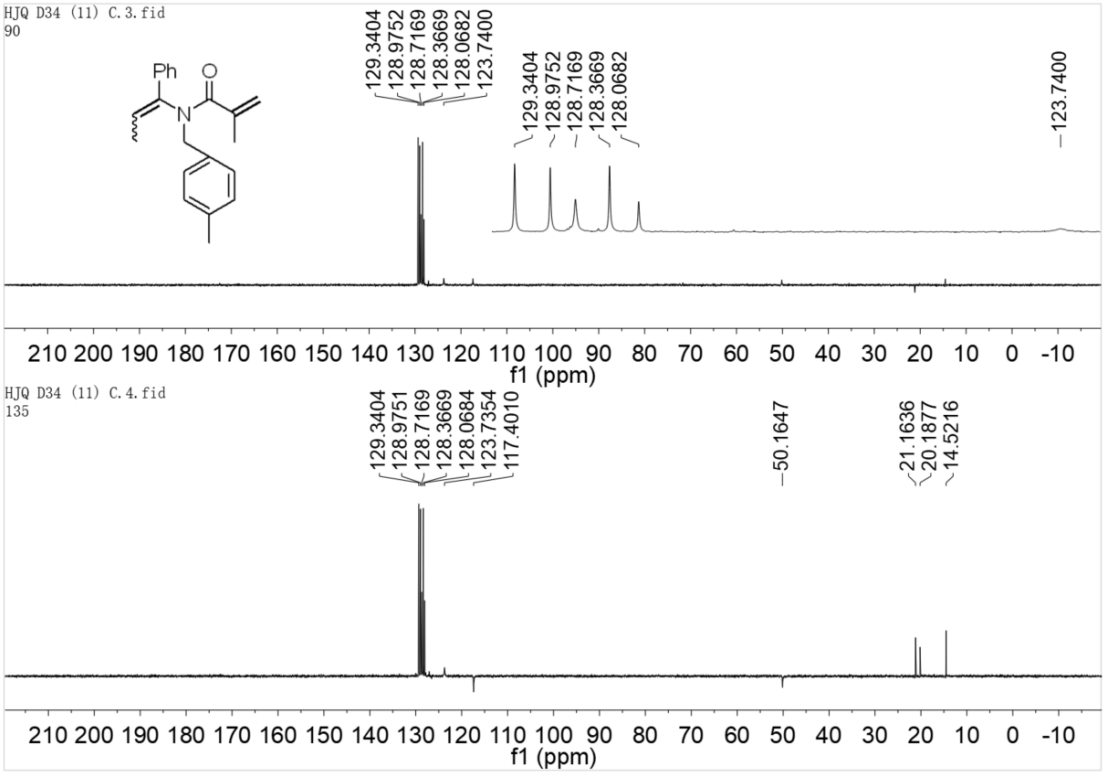
1j2, ^{1}H NMR



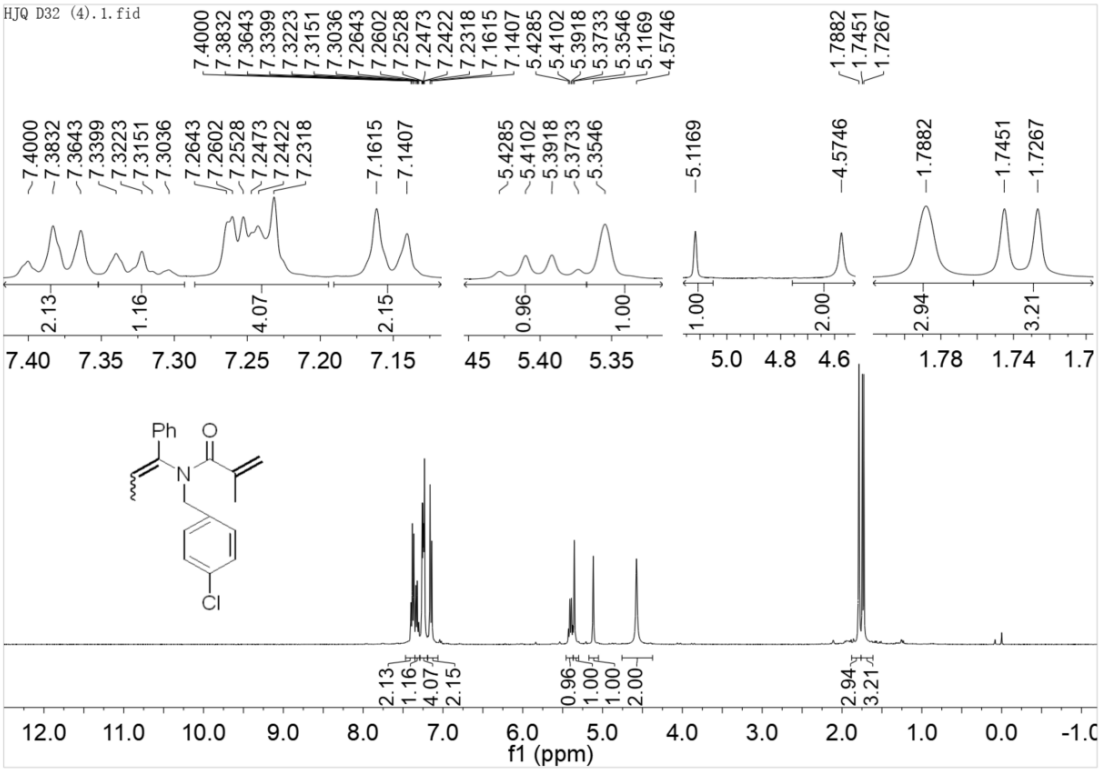
^{13}C NMR



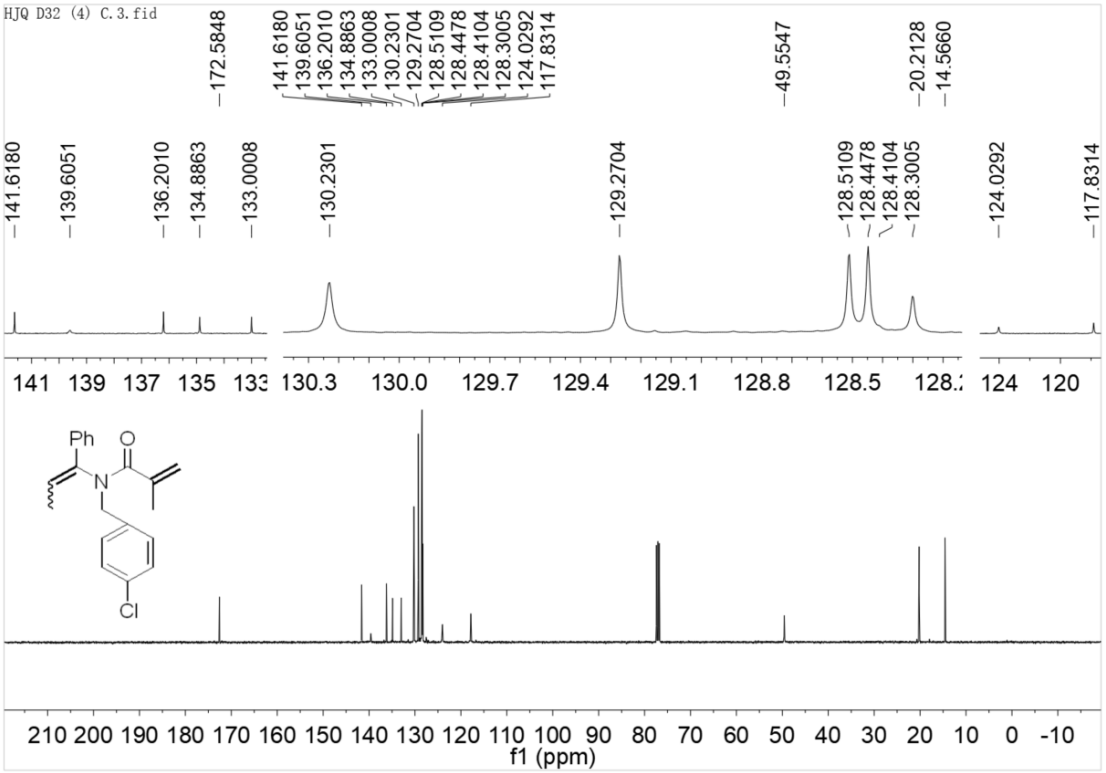
DEPT 90 and DEPT 135



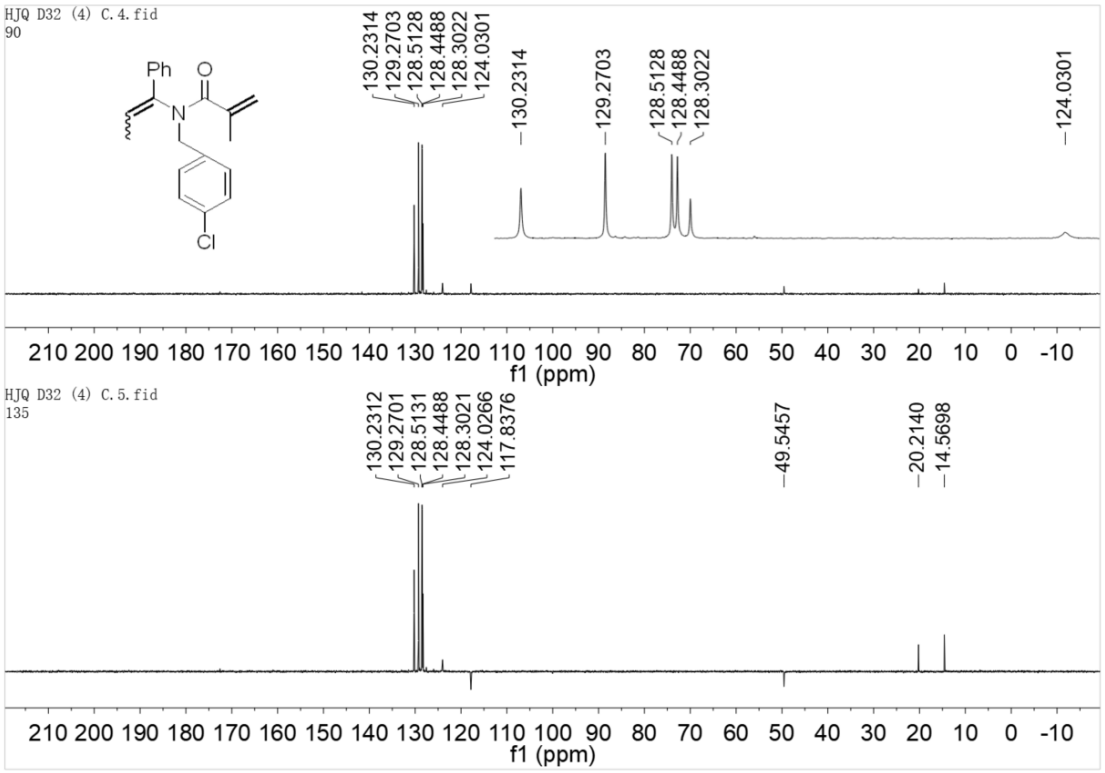
1j3, ^{1}H NMR



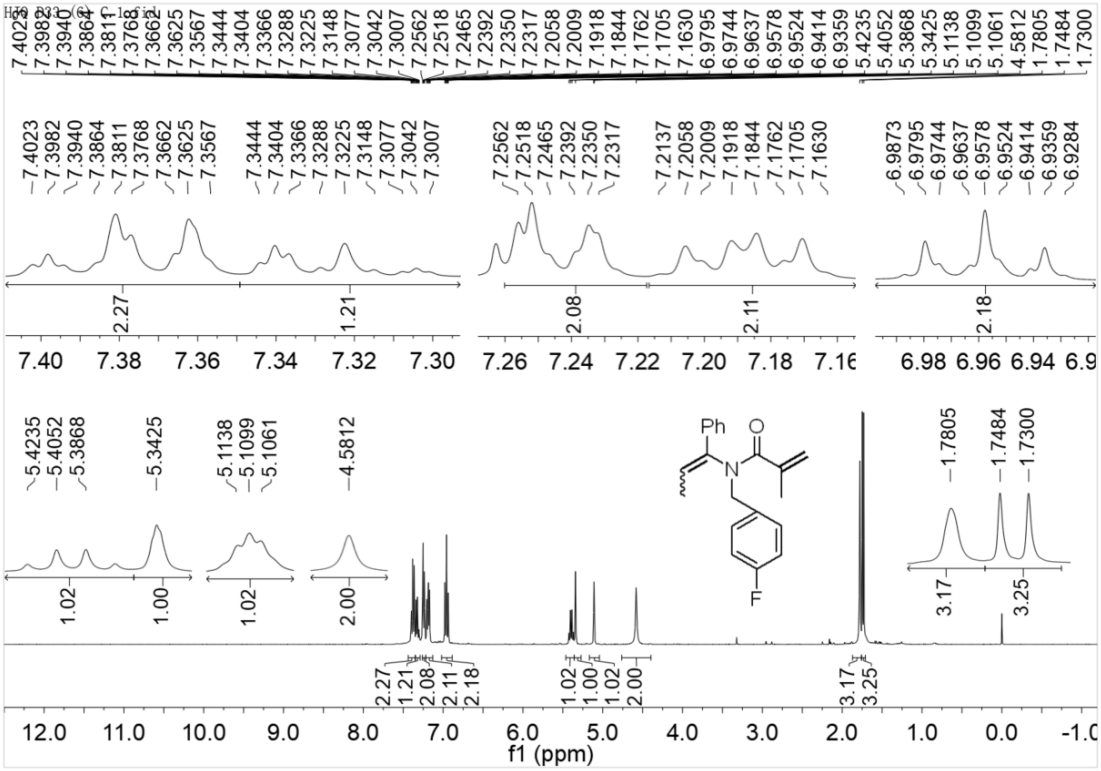
^{13}C NMR



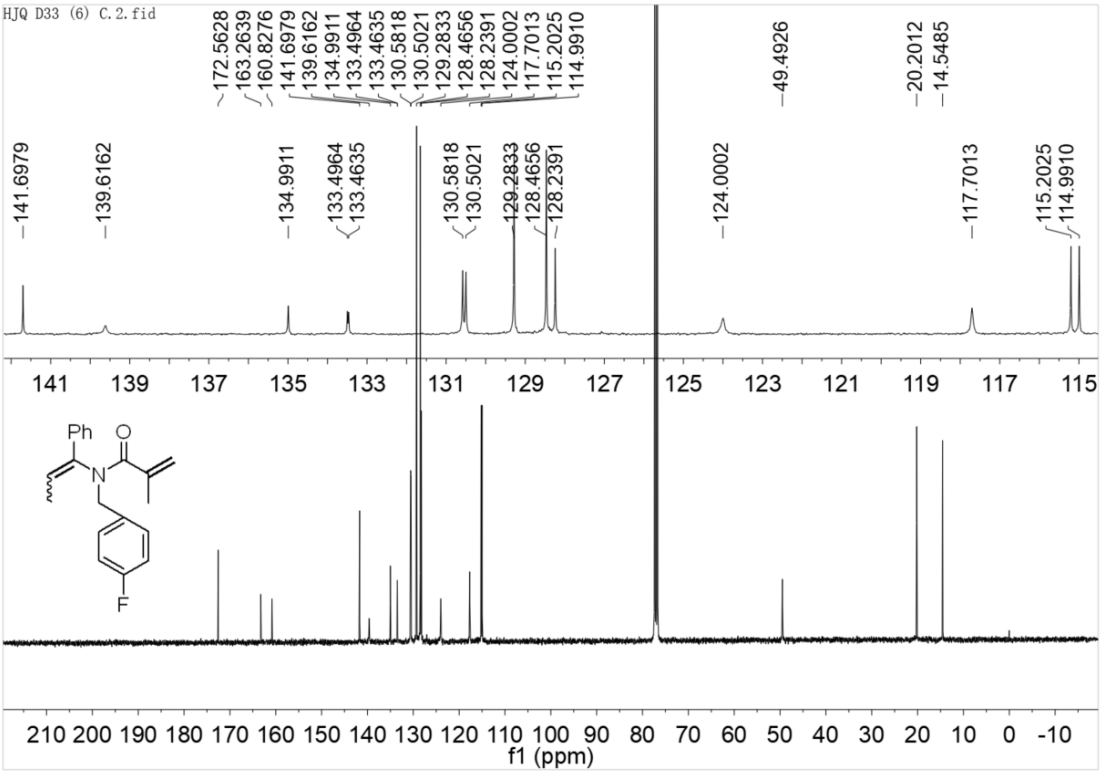
DEPT 90 and DEPT 135



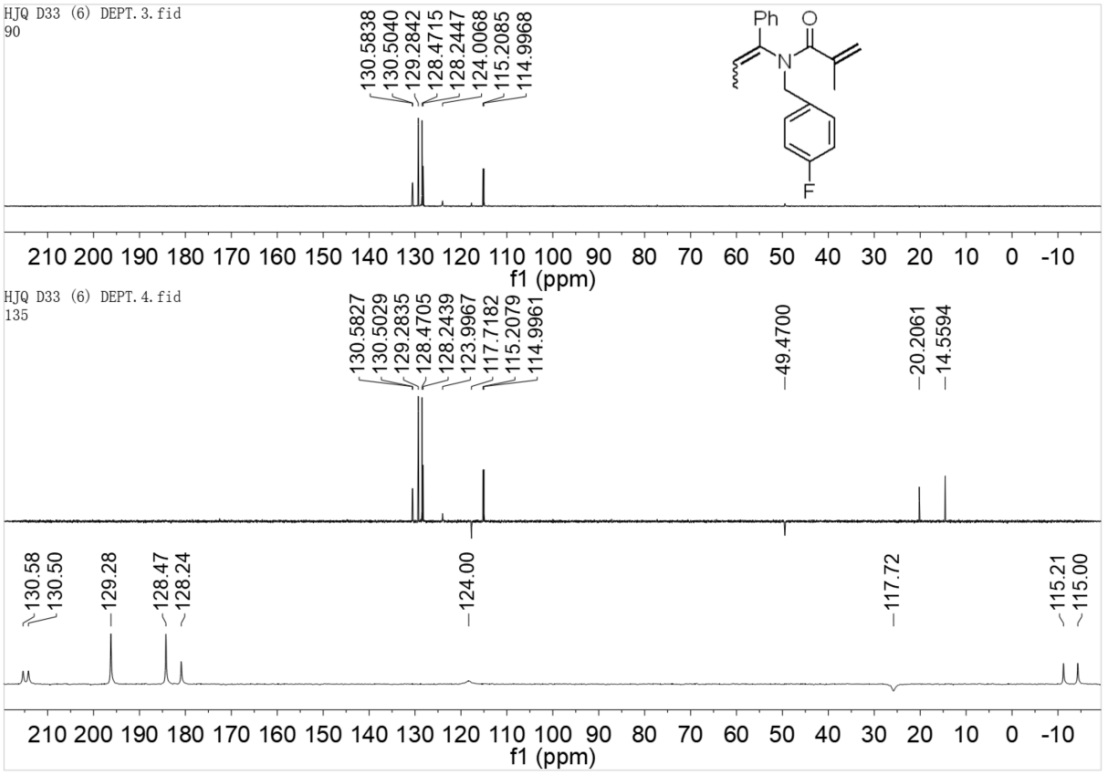
1j4, ^{1}H NMR



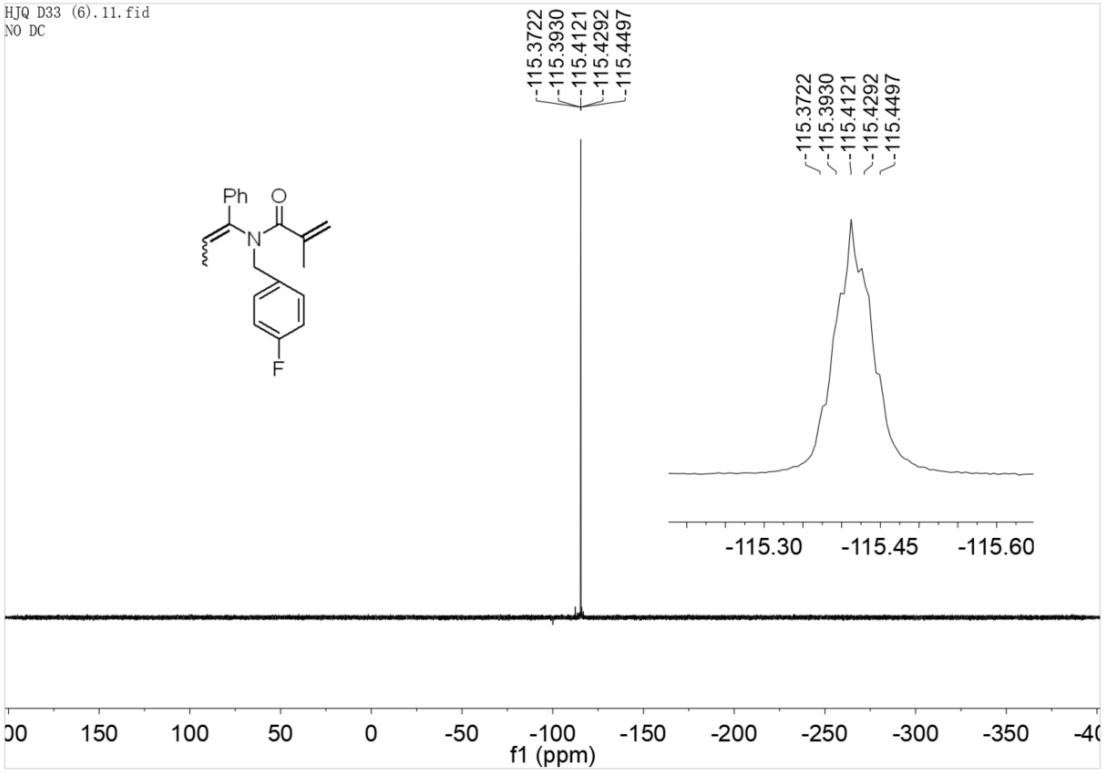
^{13}C NMR



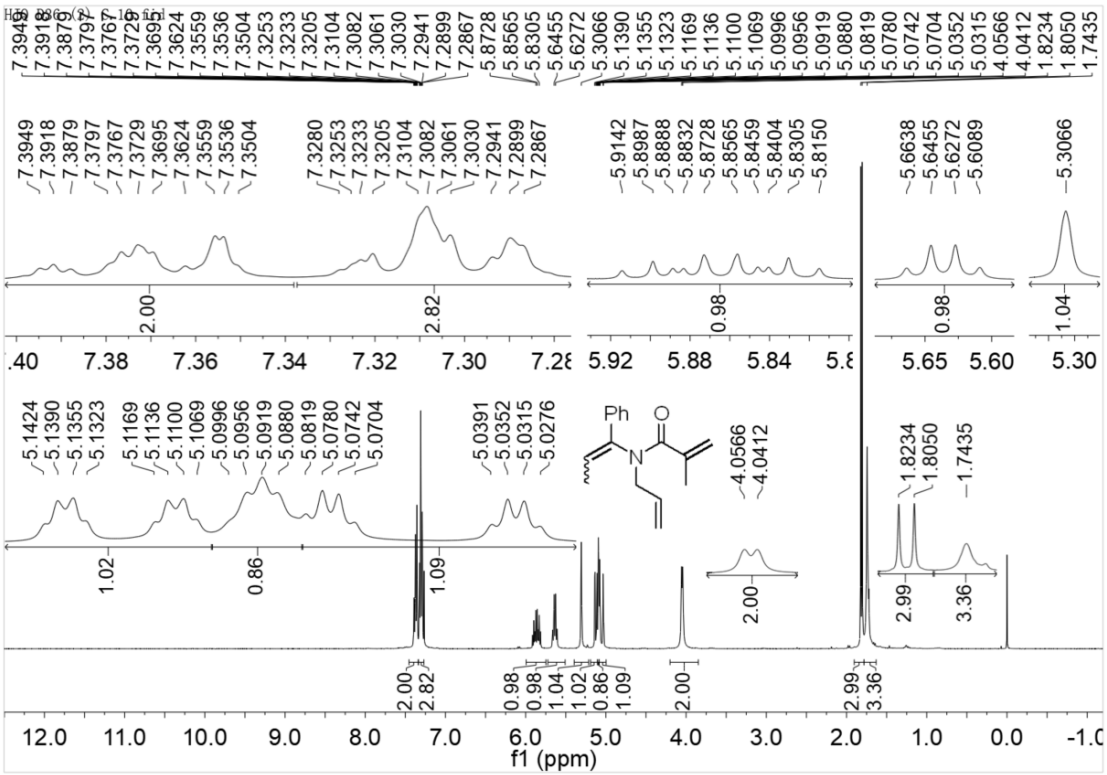
DEPT 90 and DEPT 135



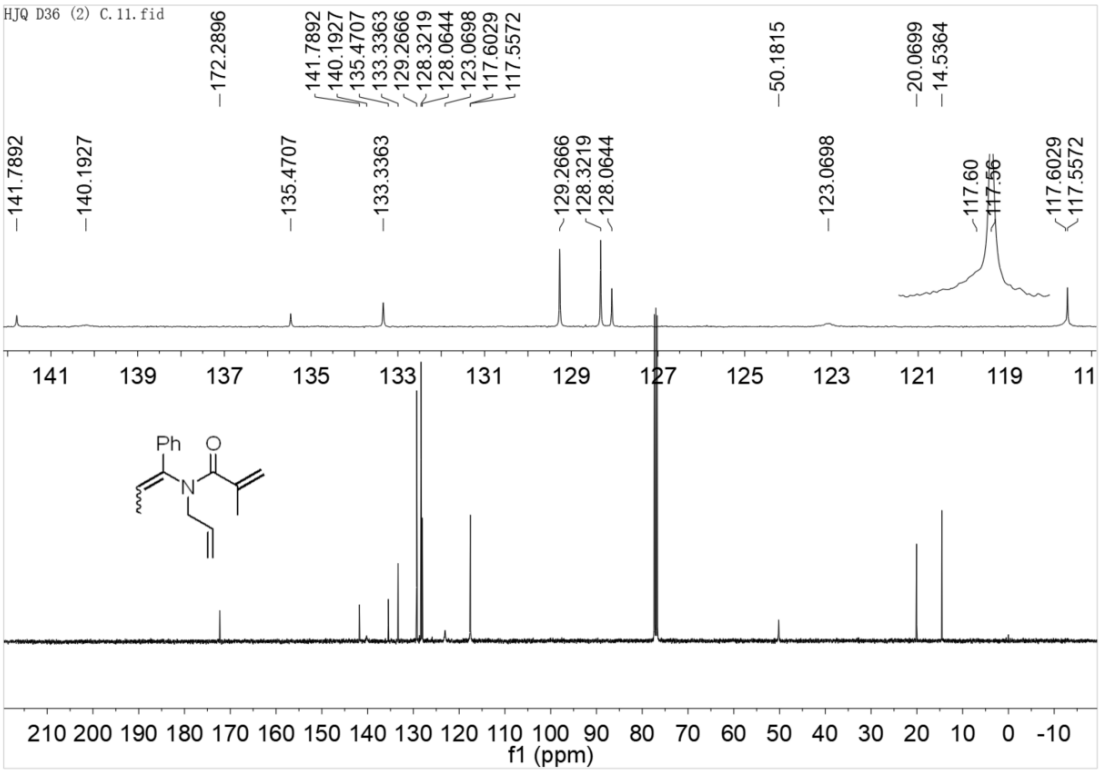
^{19}F NMR



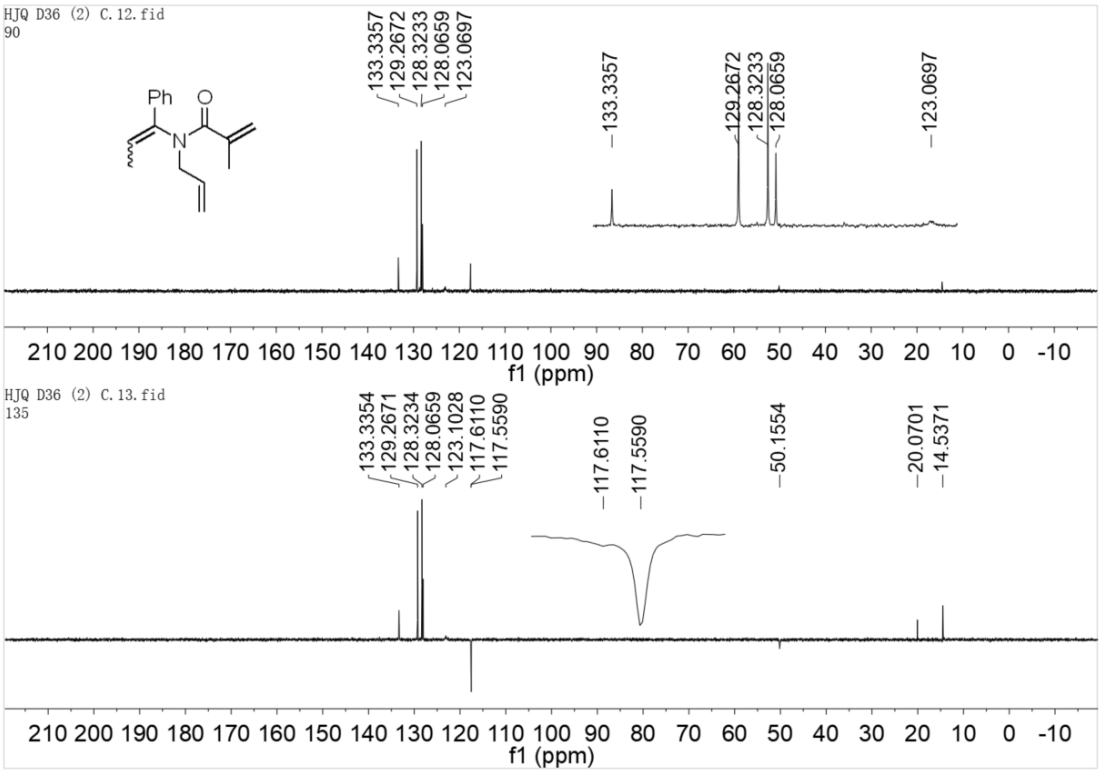
1k, ^{1}H NMR



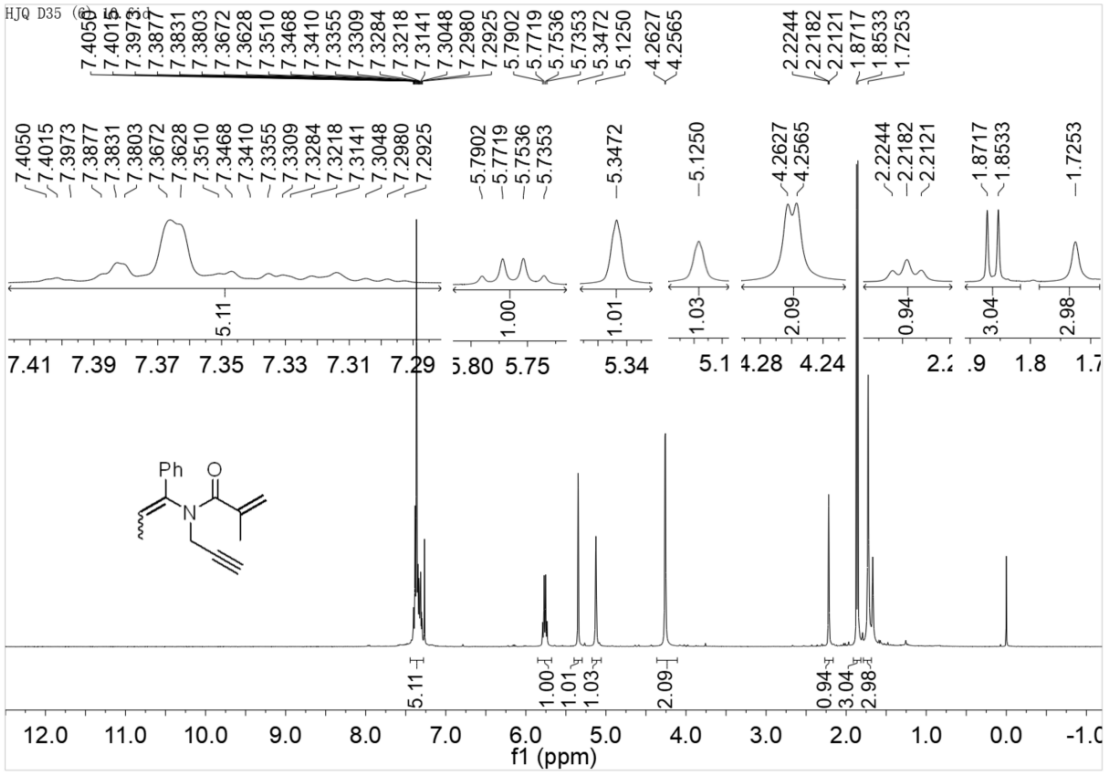
^{13}C NMR



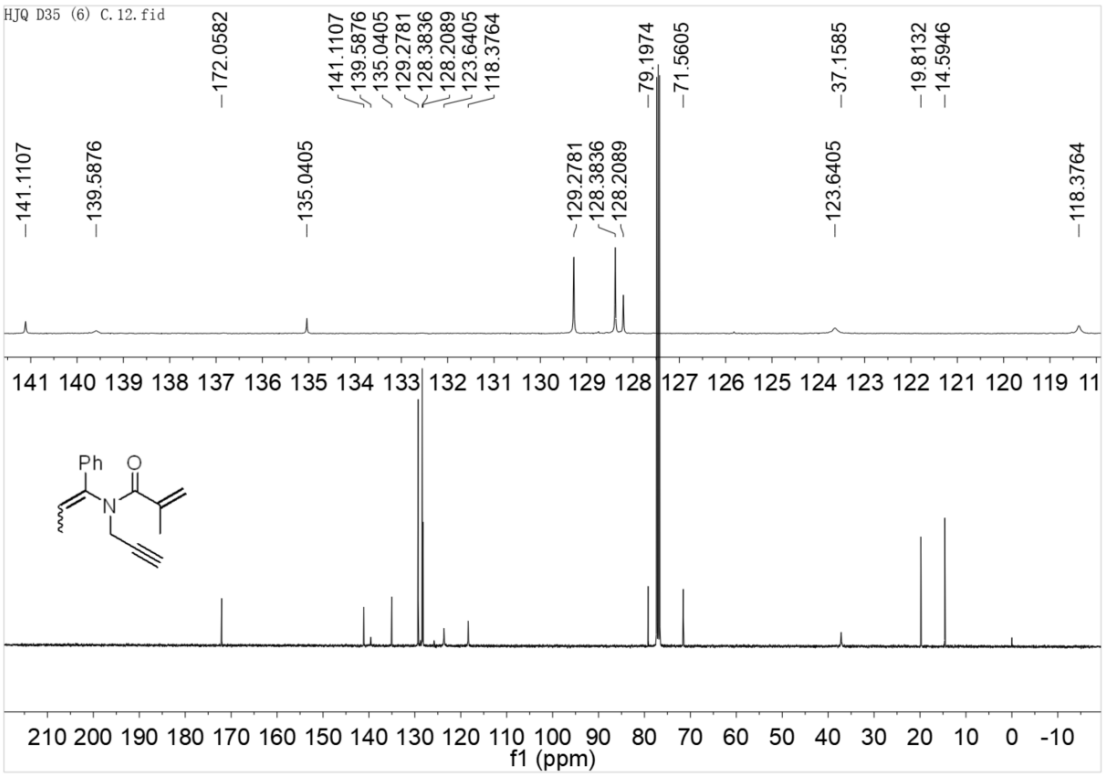
DEPT 90 and DEPT 135



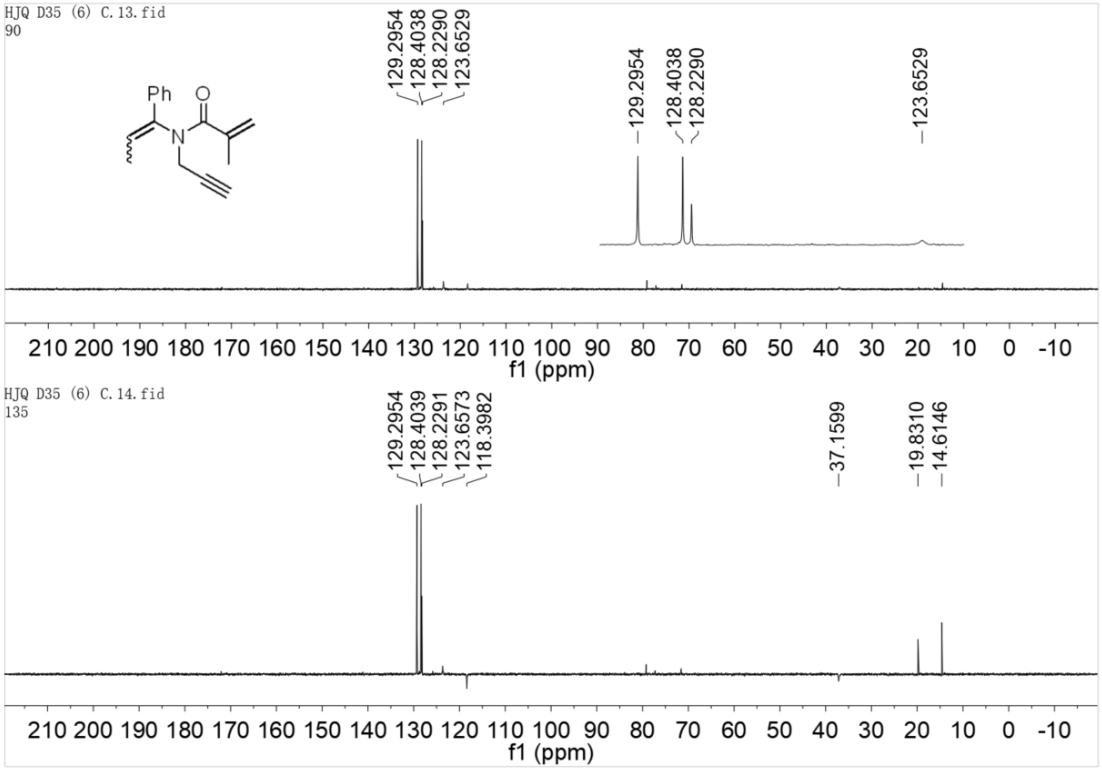
1l, ^{1}H NMR



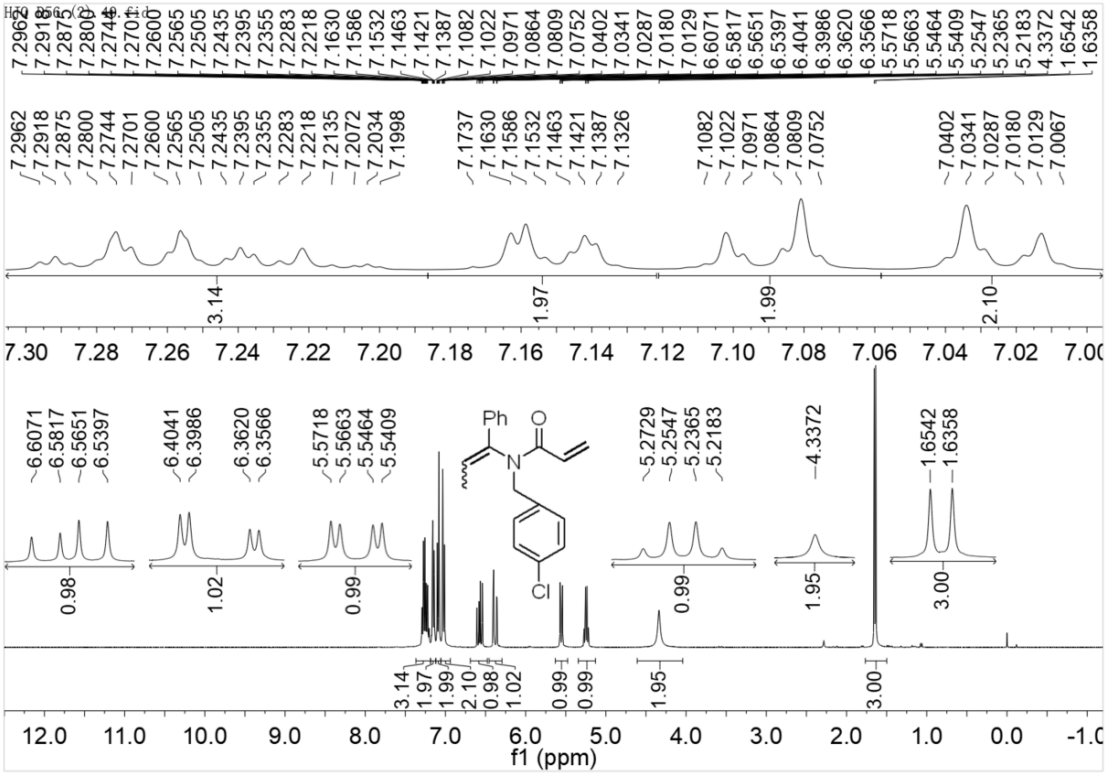
^{13}C NMR



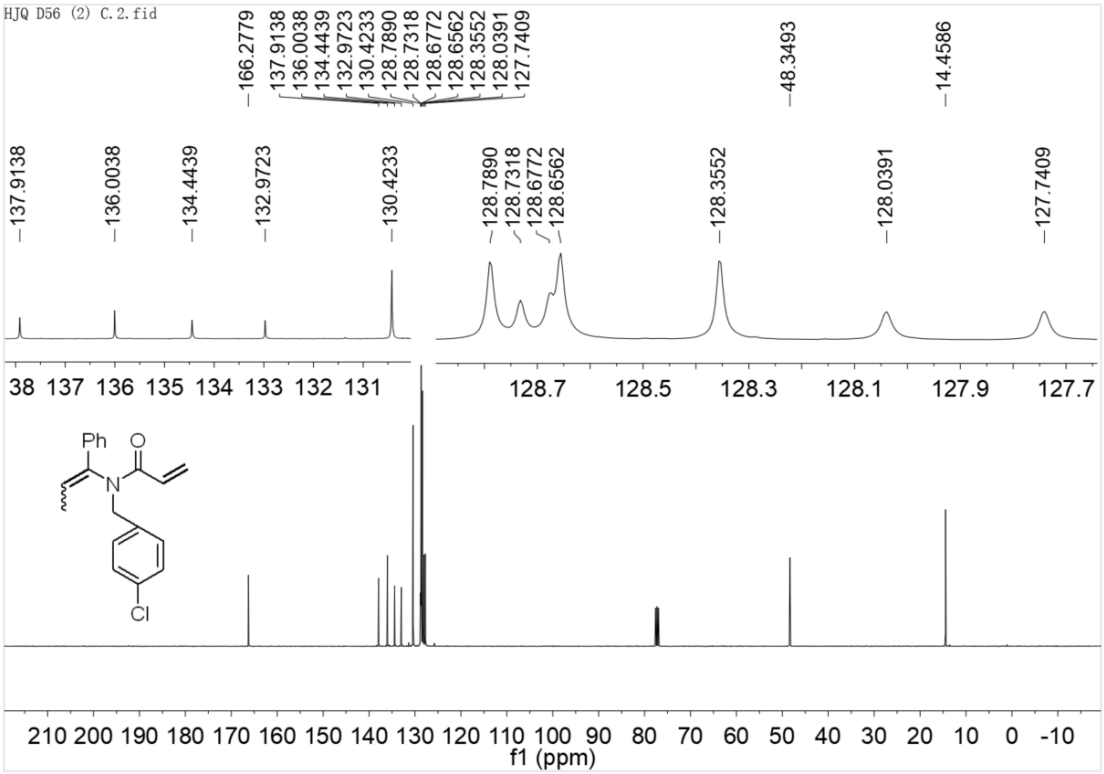
DEPT 90 and DEPT 135



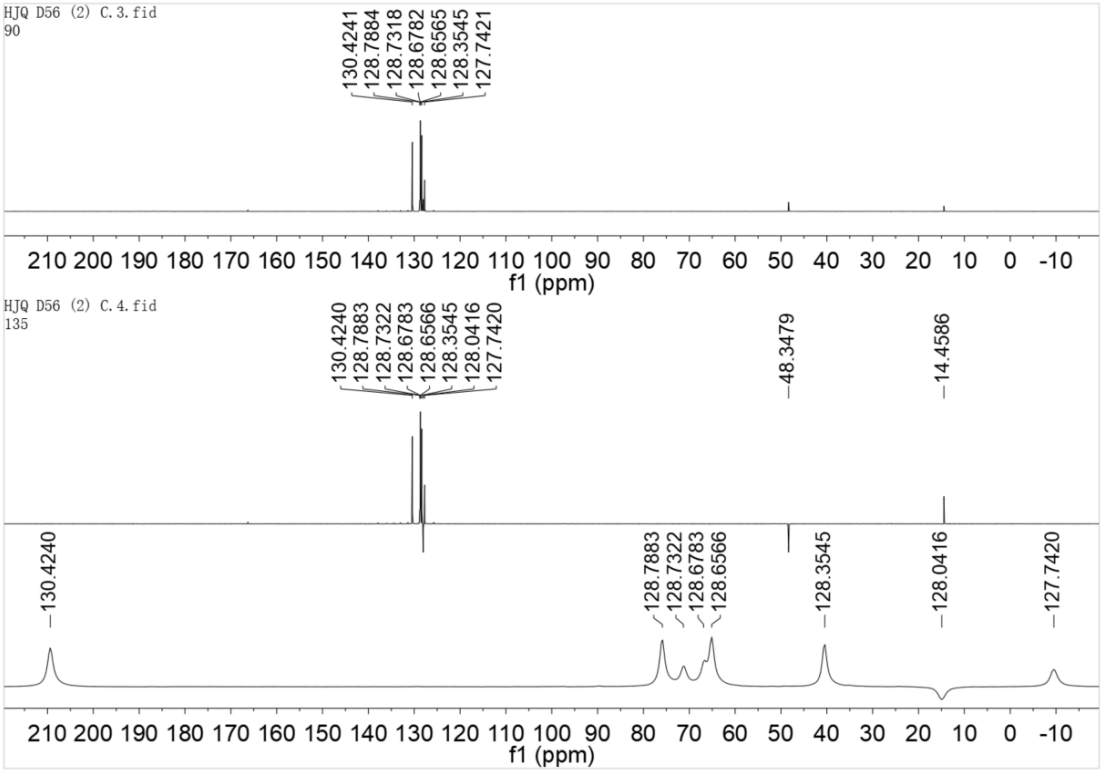
1m, ^{1}H NMR



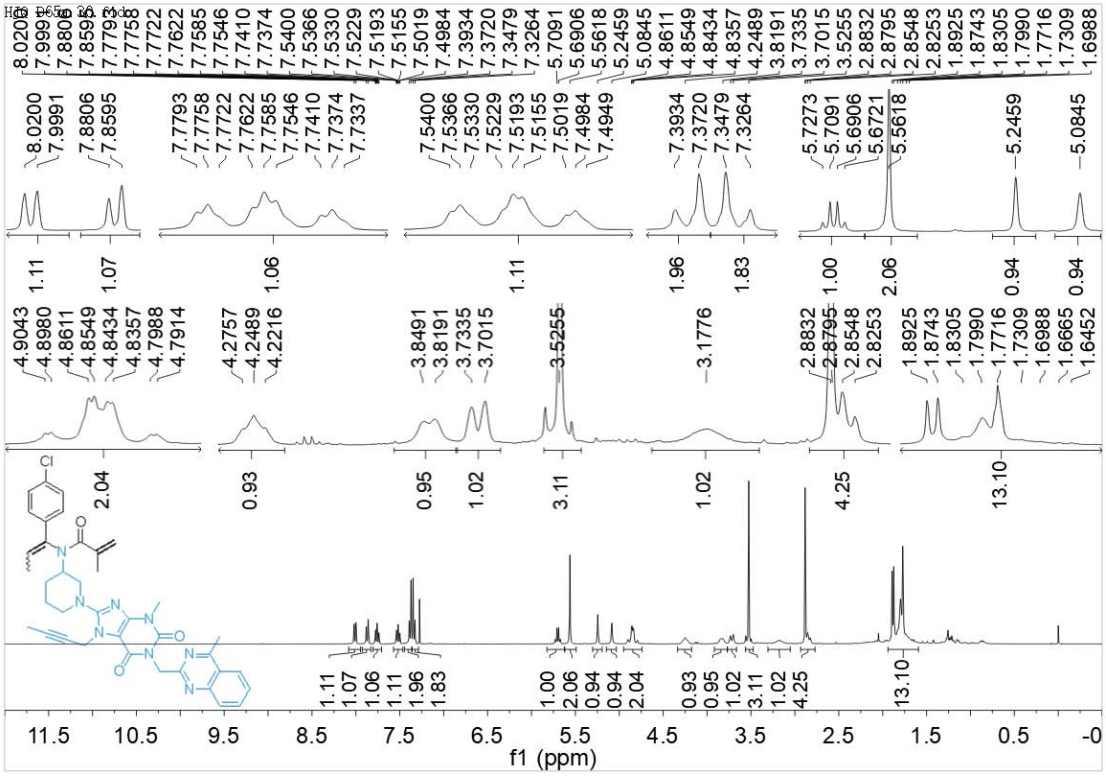
^{13}C NMR



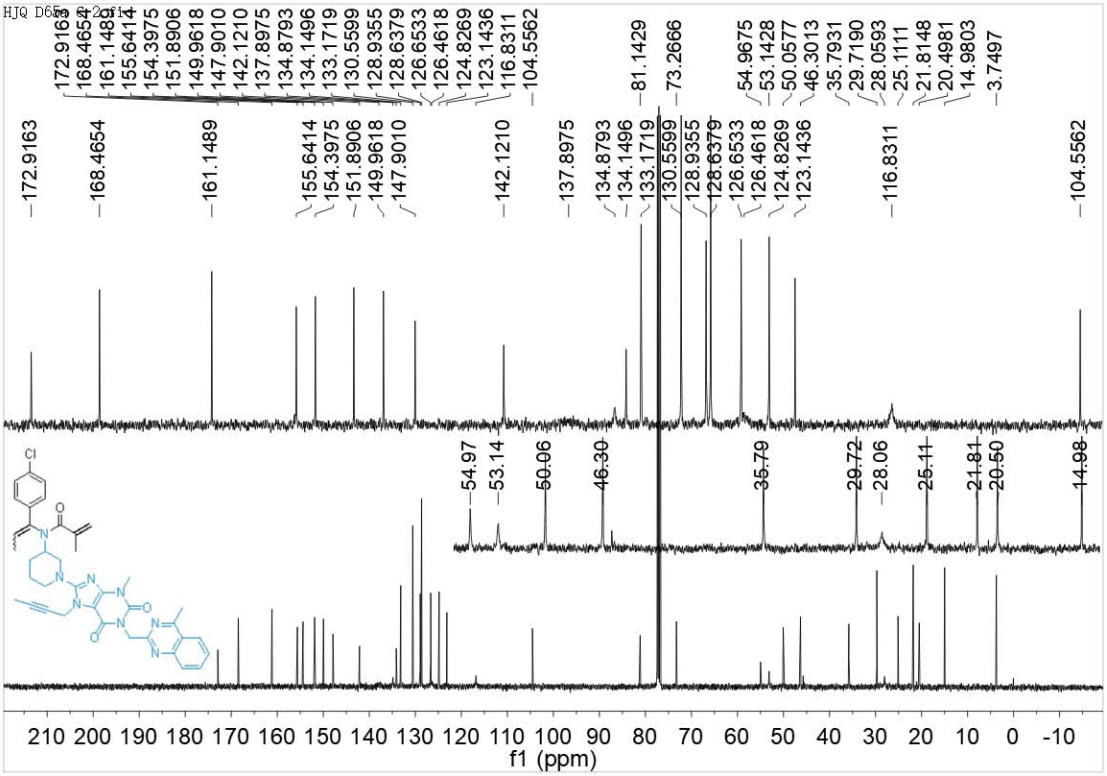
DEPT 90 and DEPT 135



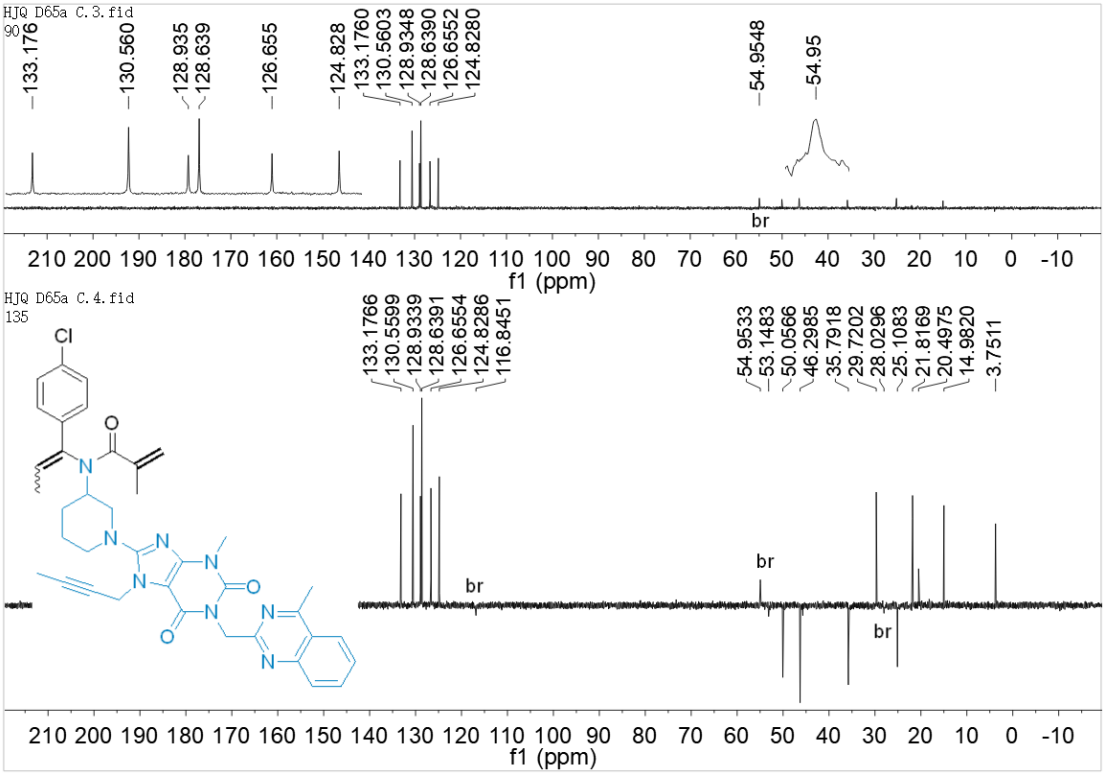
1n, ^{1}H NMR



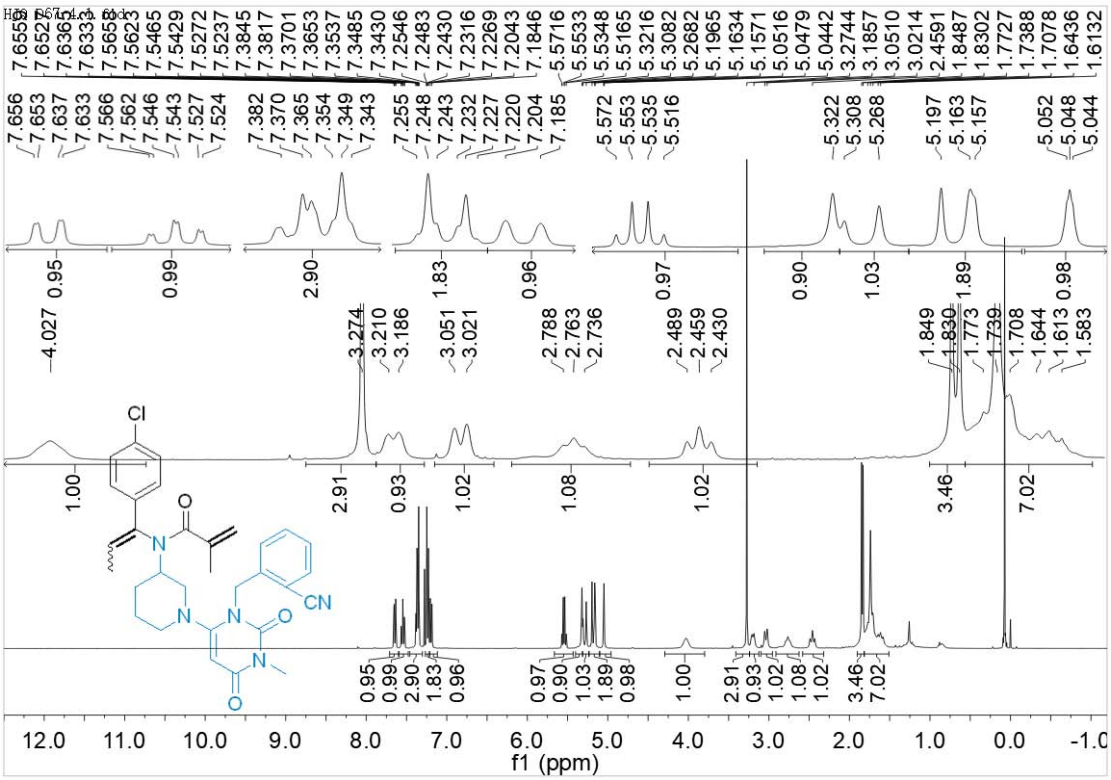
^{13}C NMR



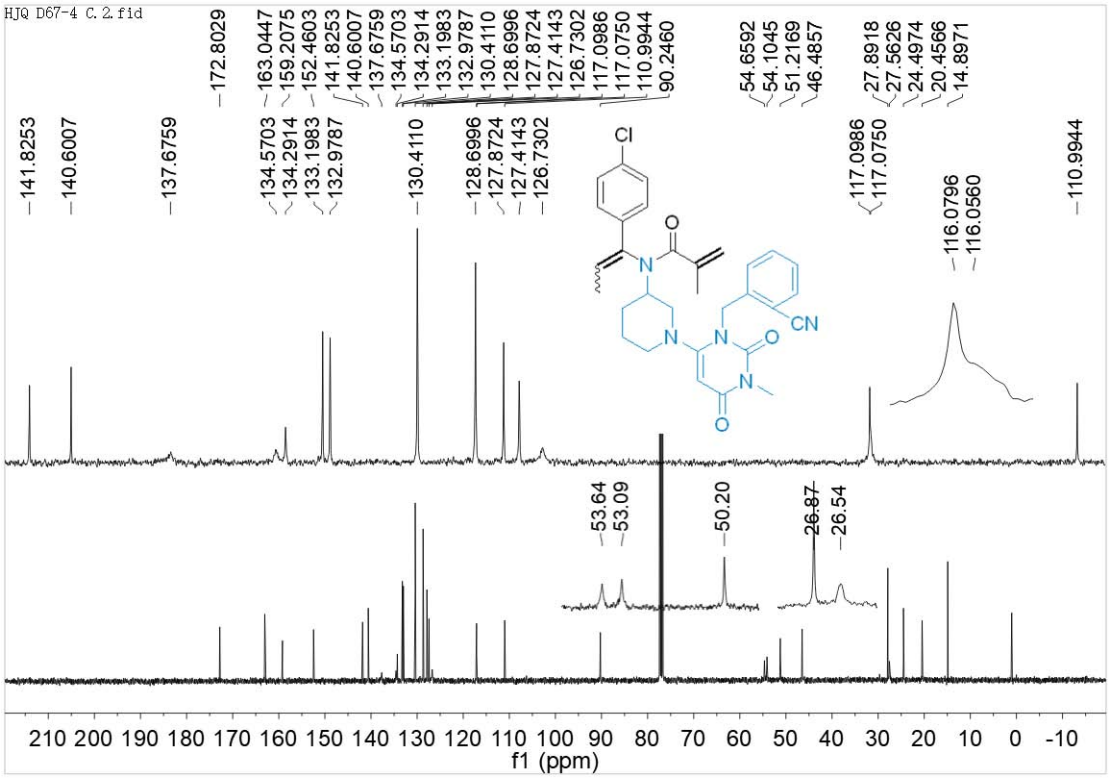
DEPT 90 and DEPT 135



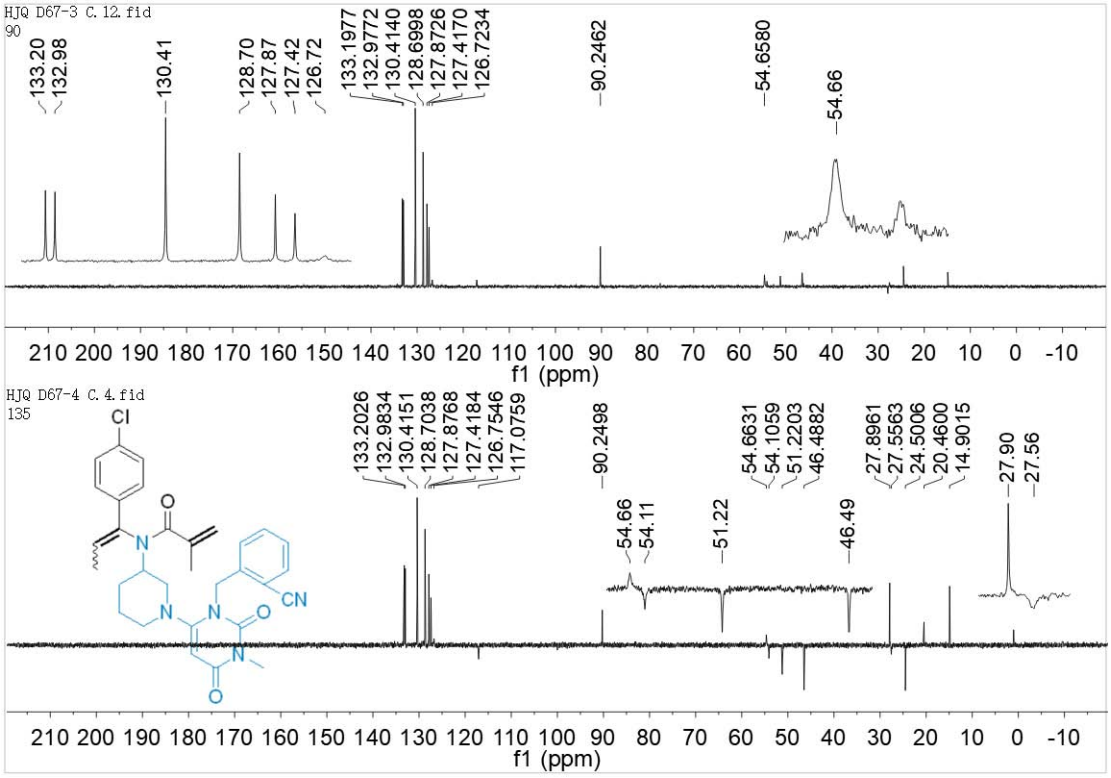
1o, ^{1}H NMR



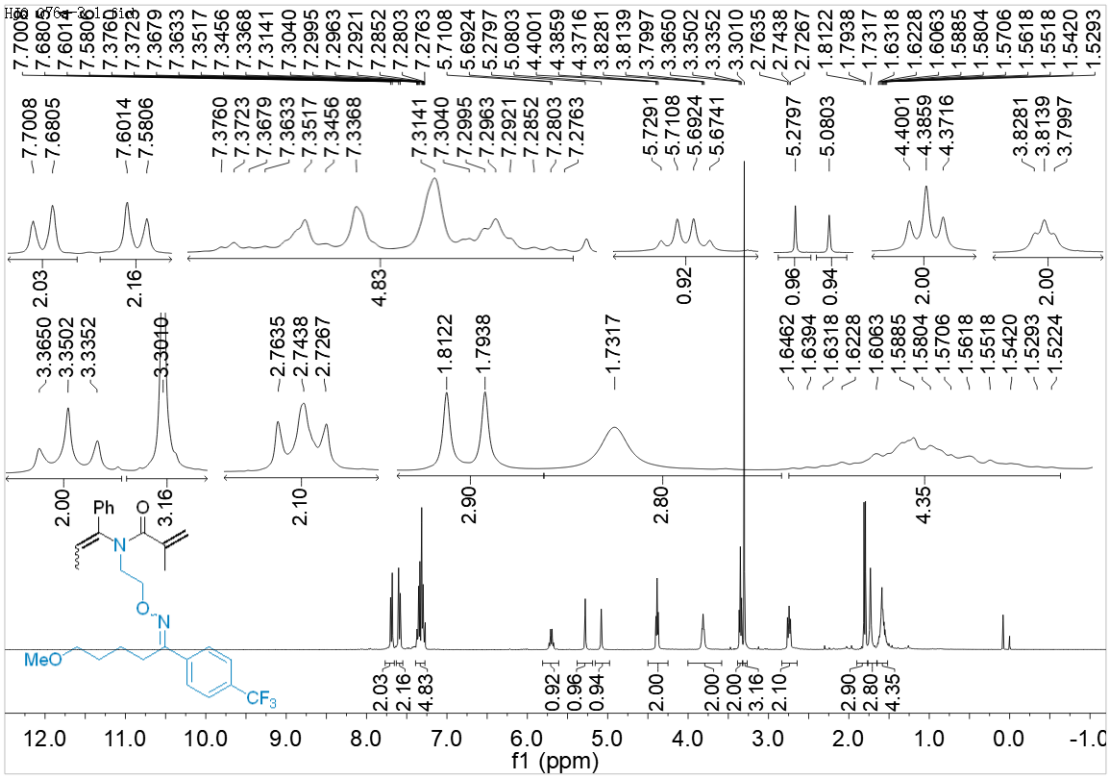
^{13}C NMR



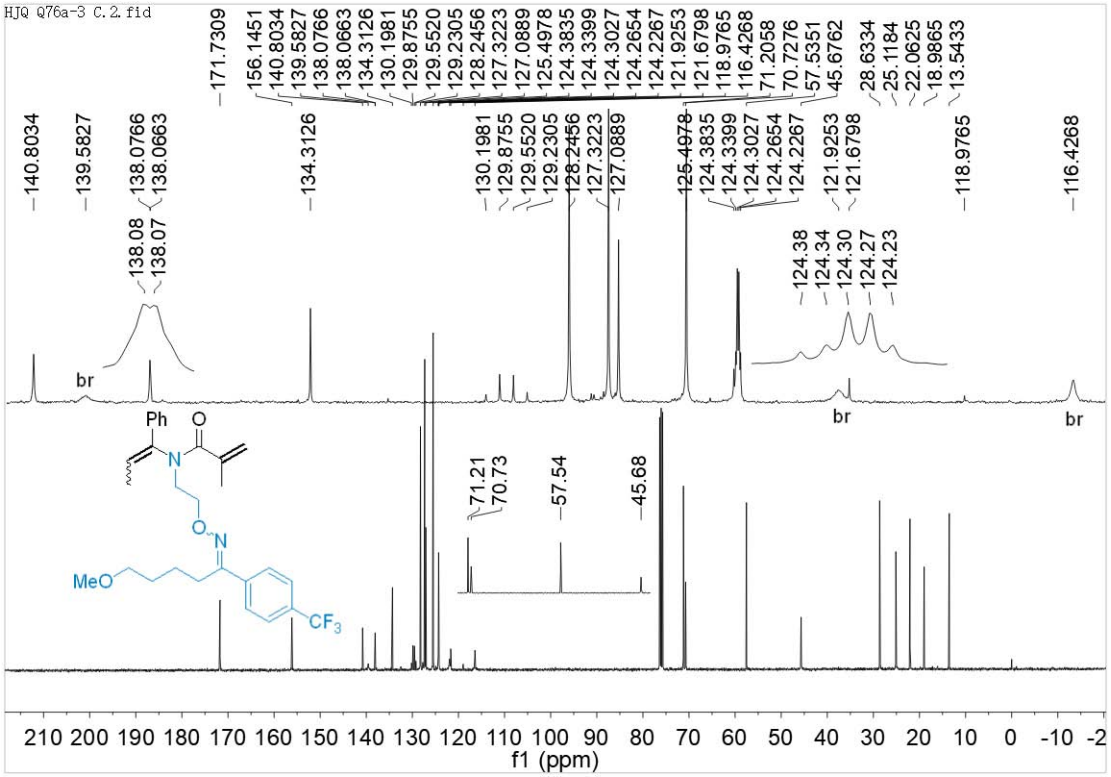
DEPT 90 and DEPT 135



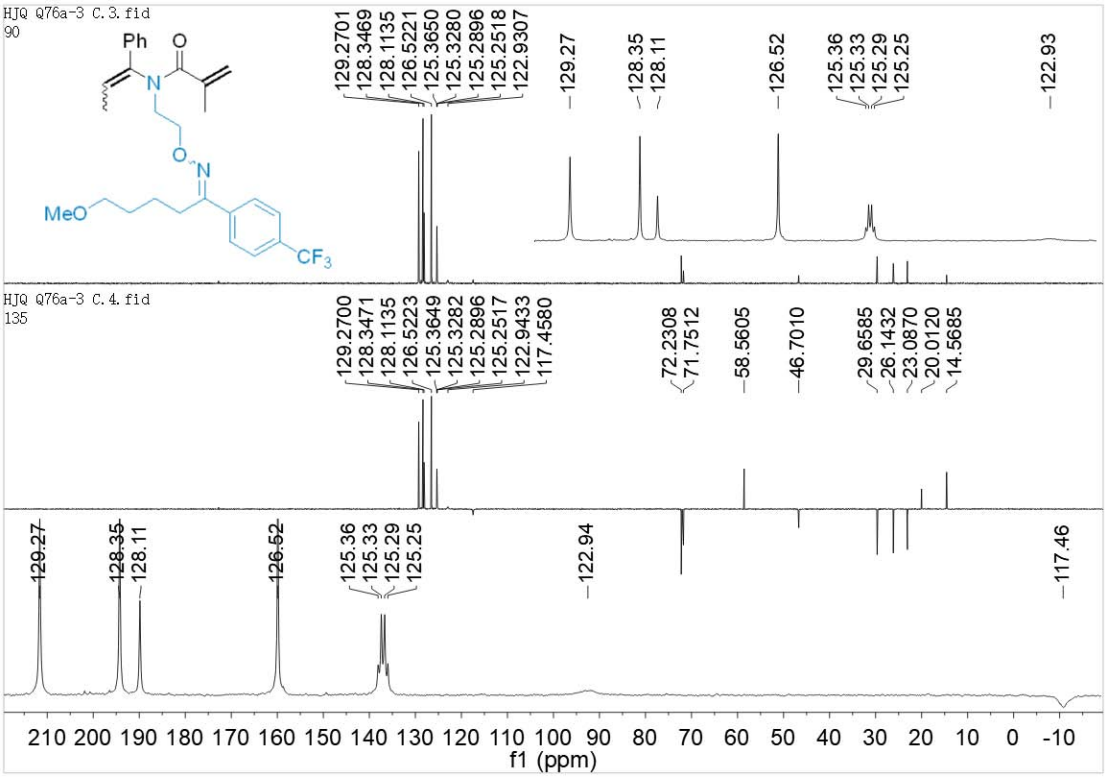
1p, ^{1}H NMR



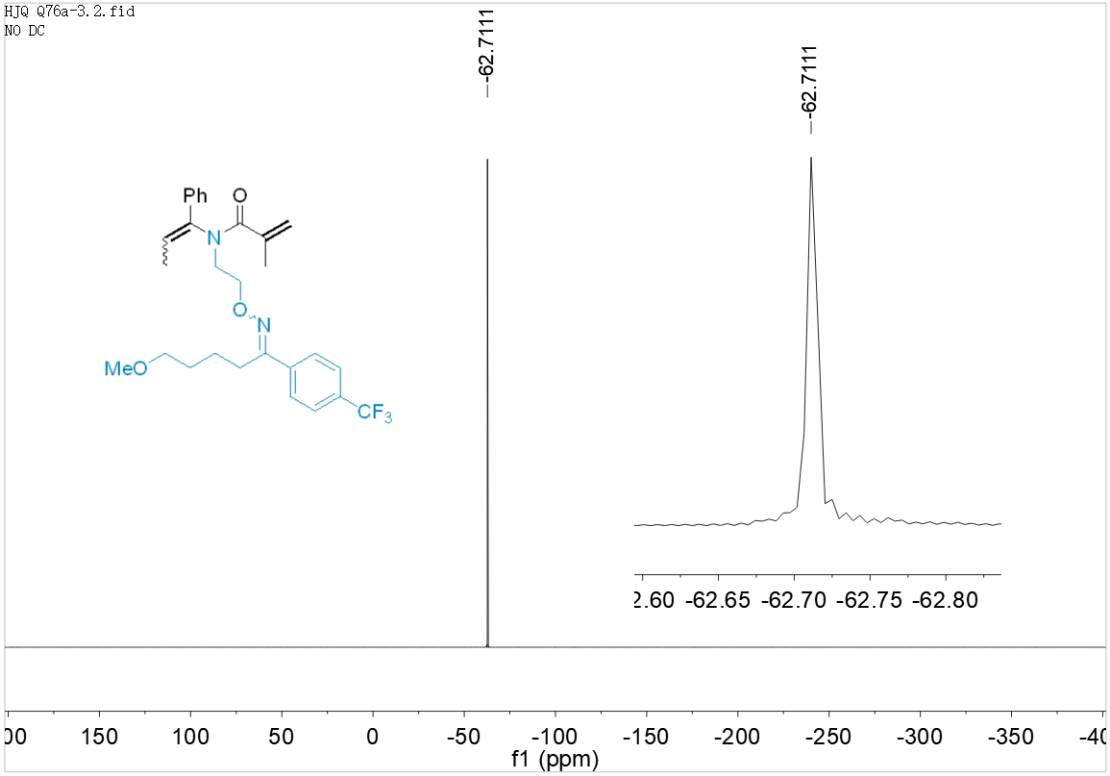
^{13}C NMR



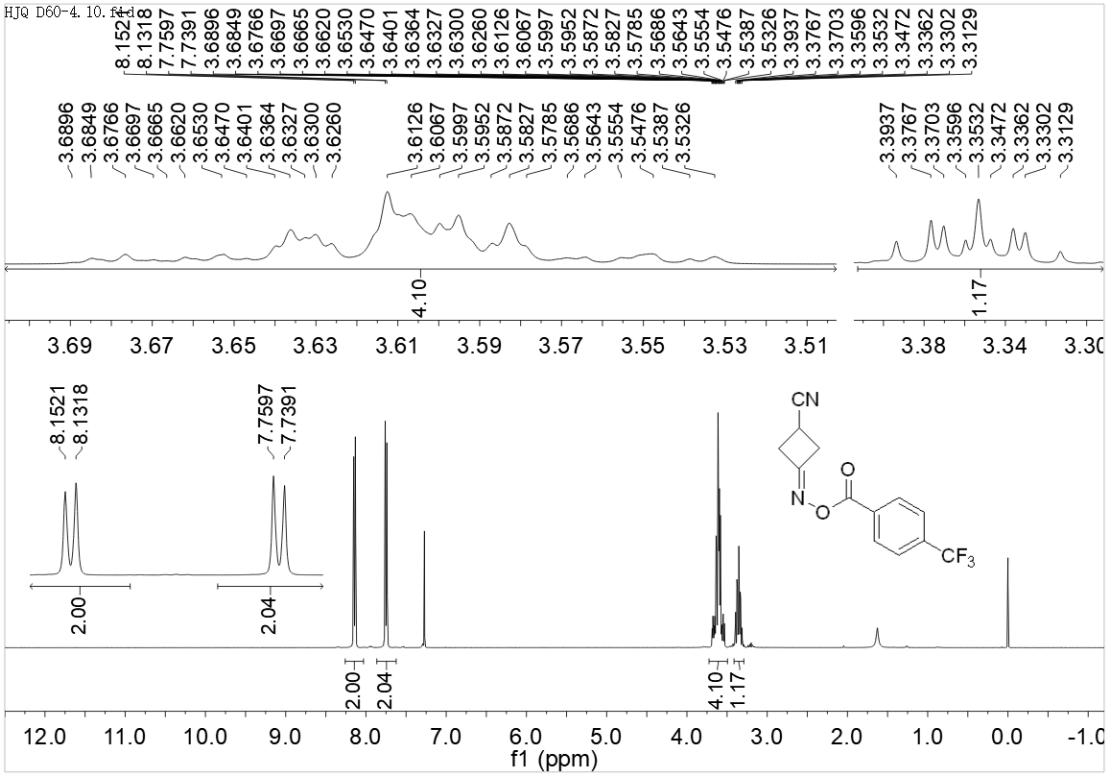
DEPT 90 and DEPT 135



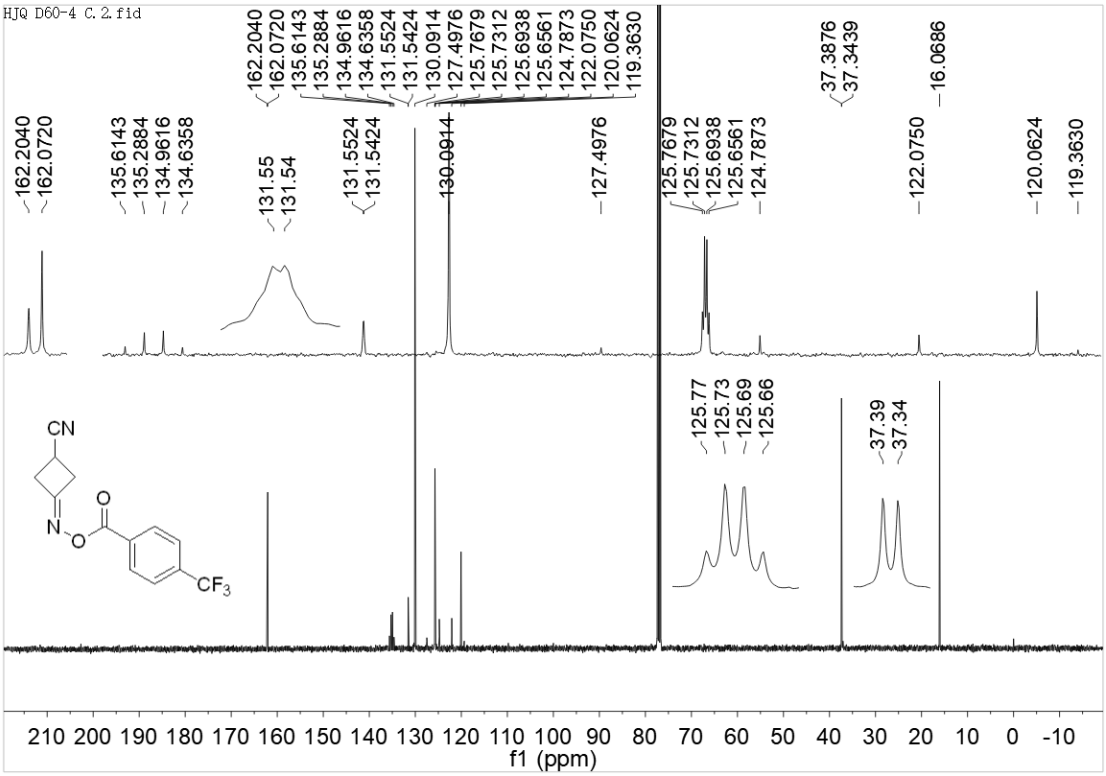
^{19}F NMR



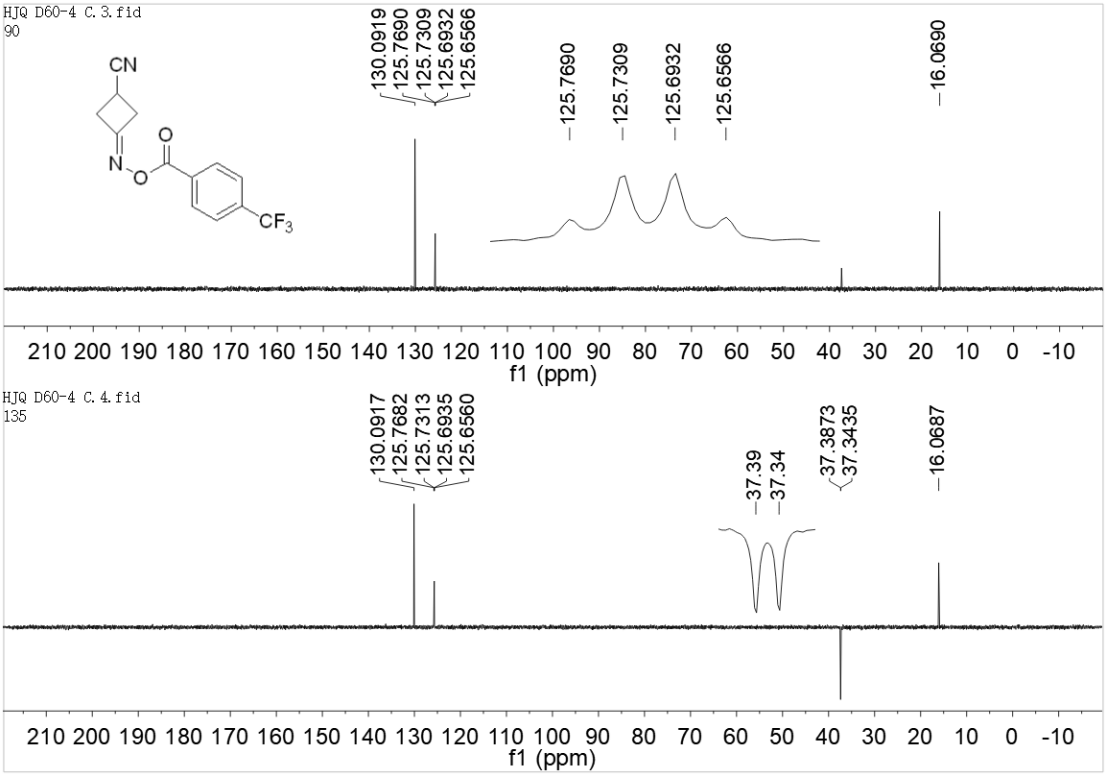
2q, ^{1}H NMR



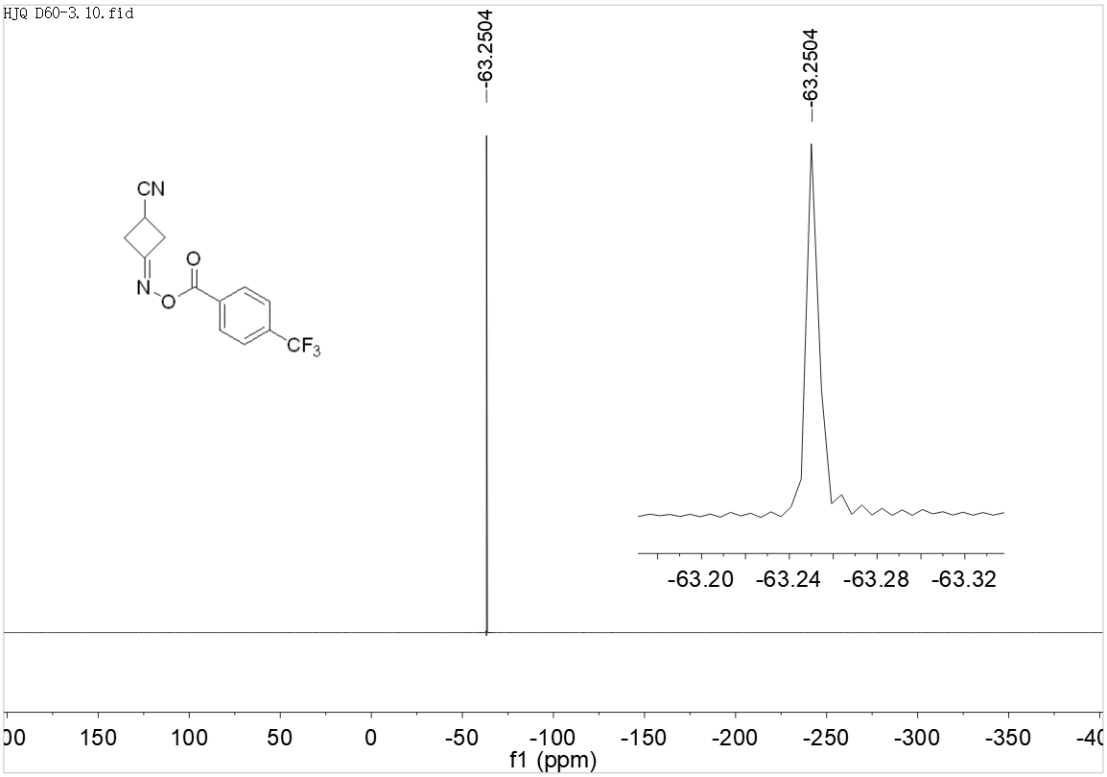
^{13}C NMR



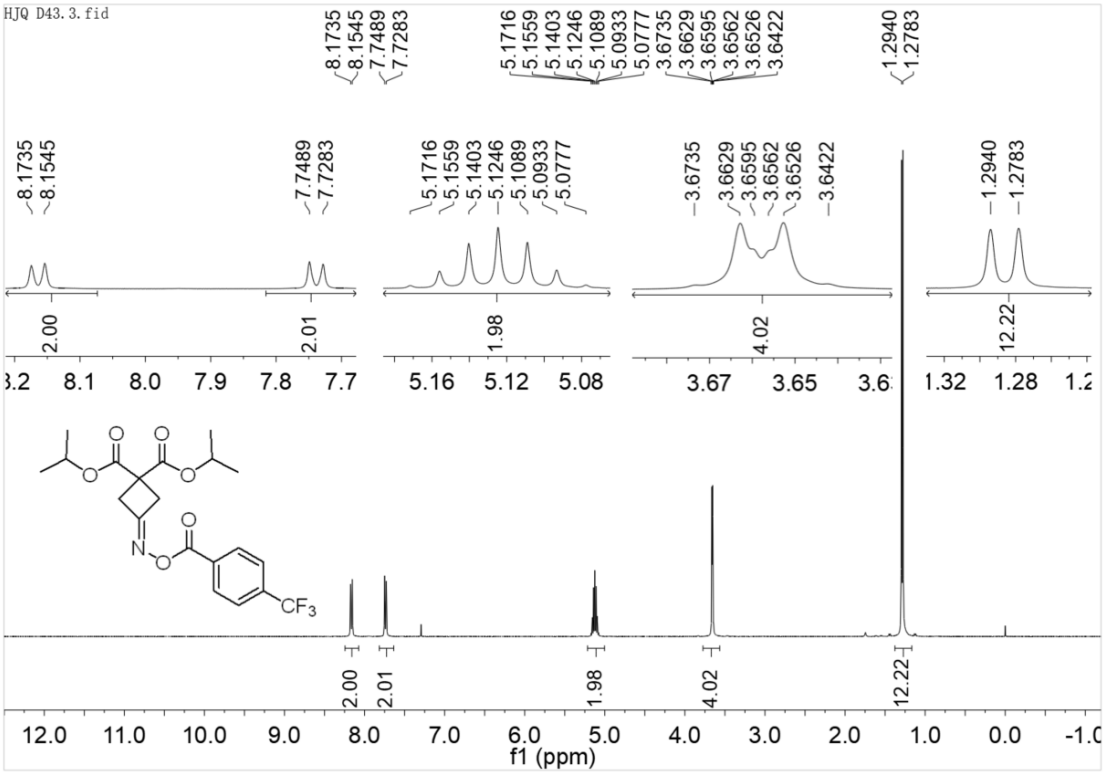
DEPT 90 and DEPT 135



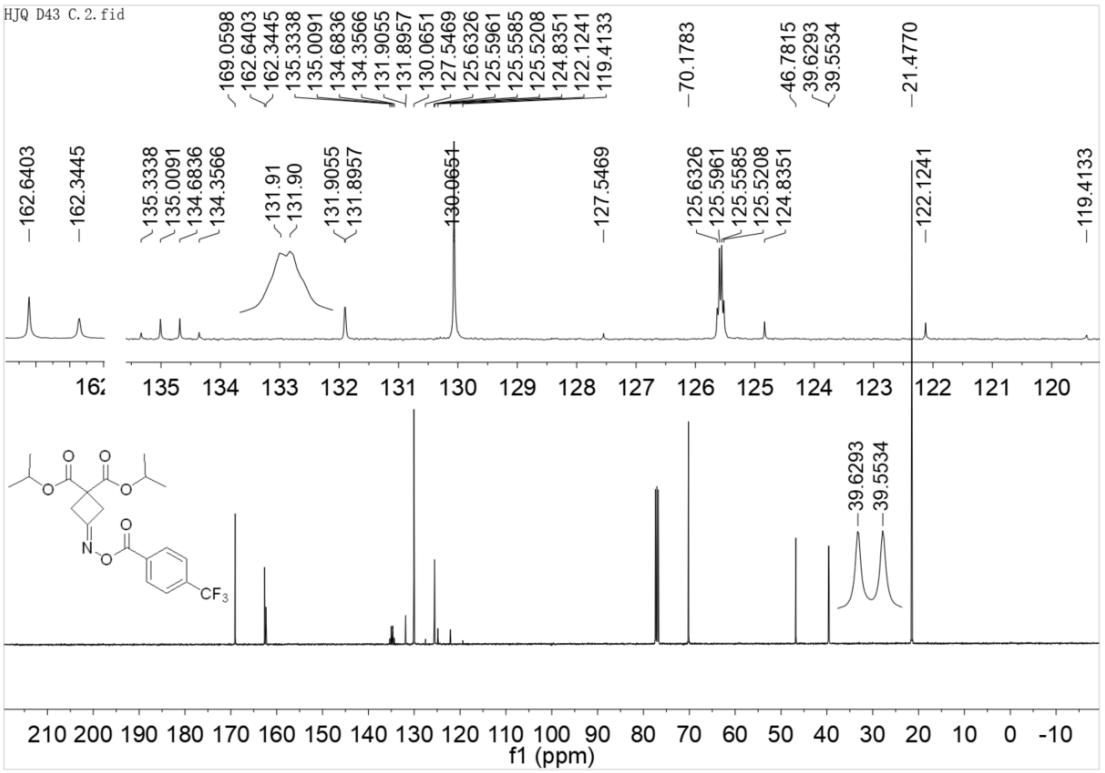
^{19}F NMR



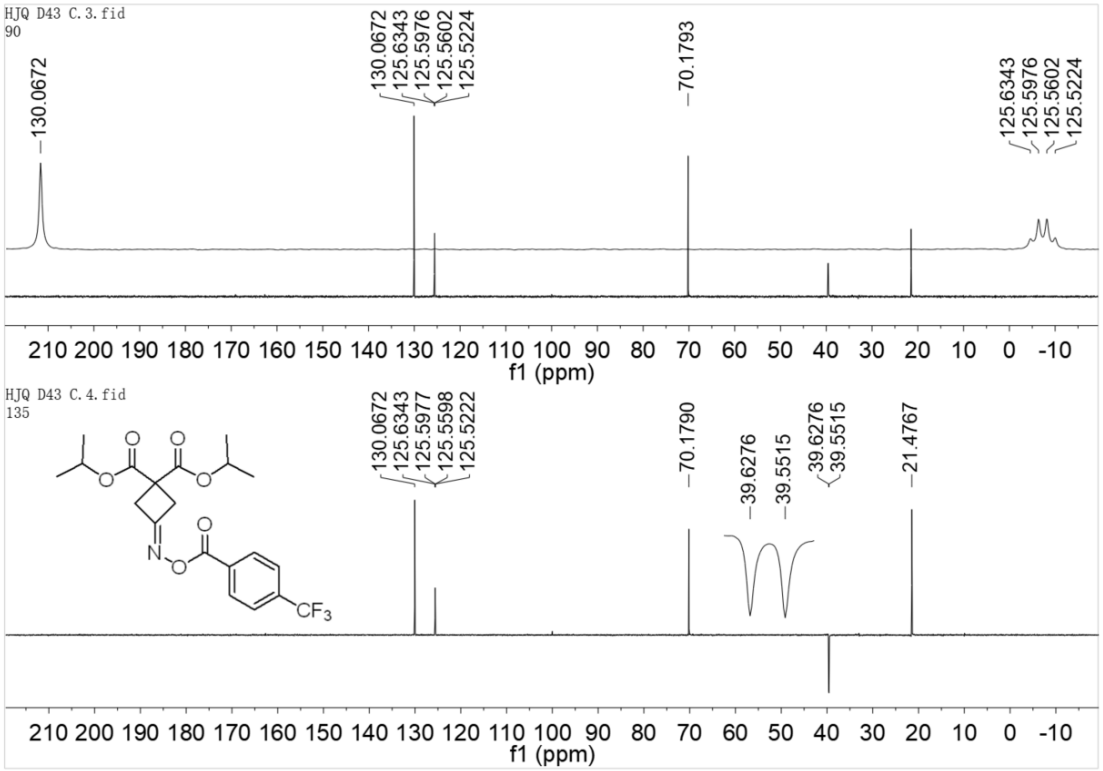
2t, ^{1}H NMR



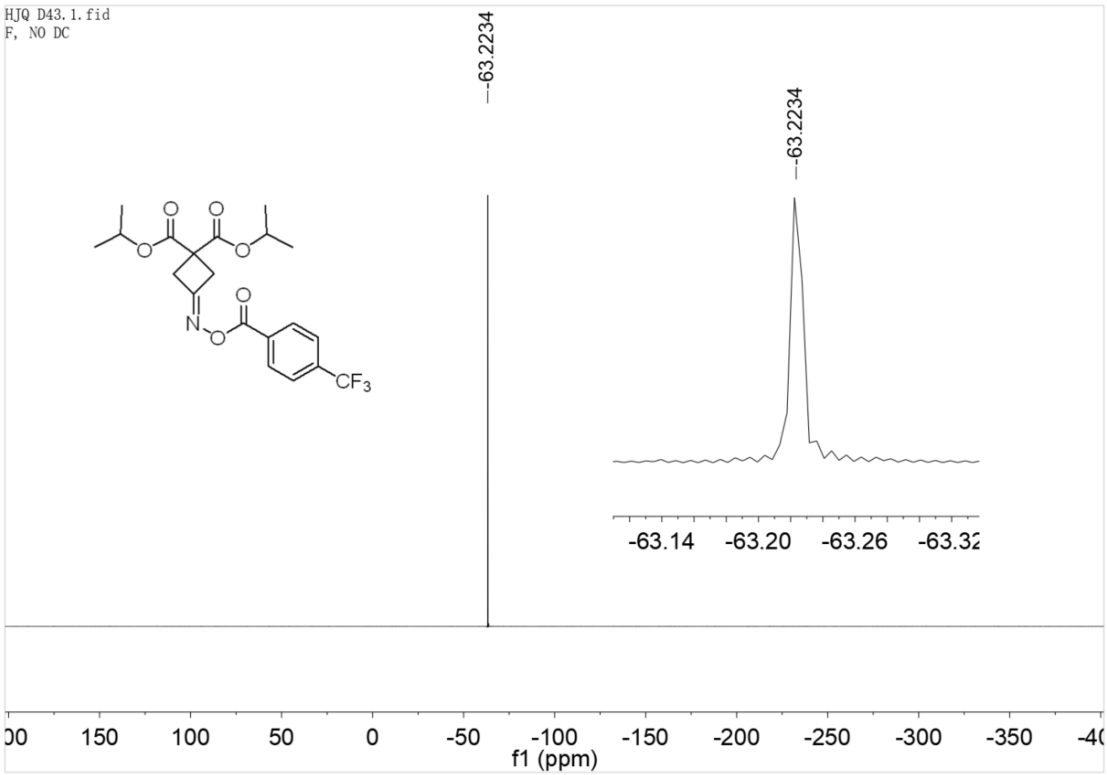
^{13}C NMR



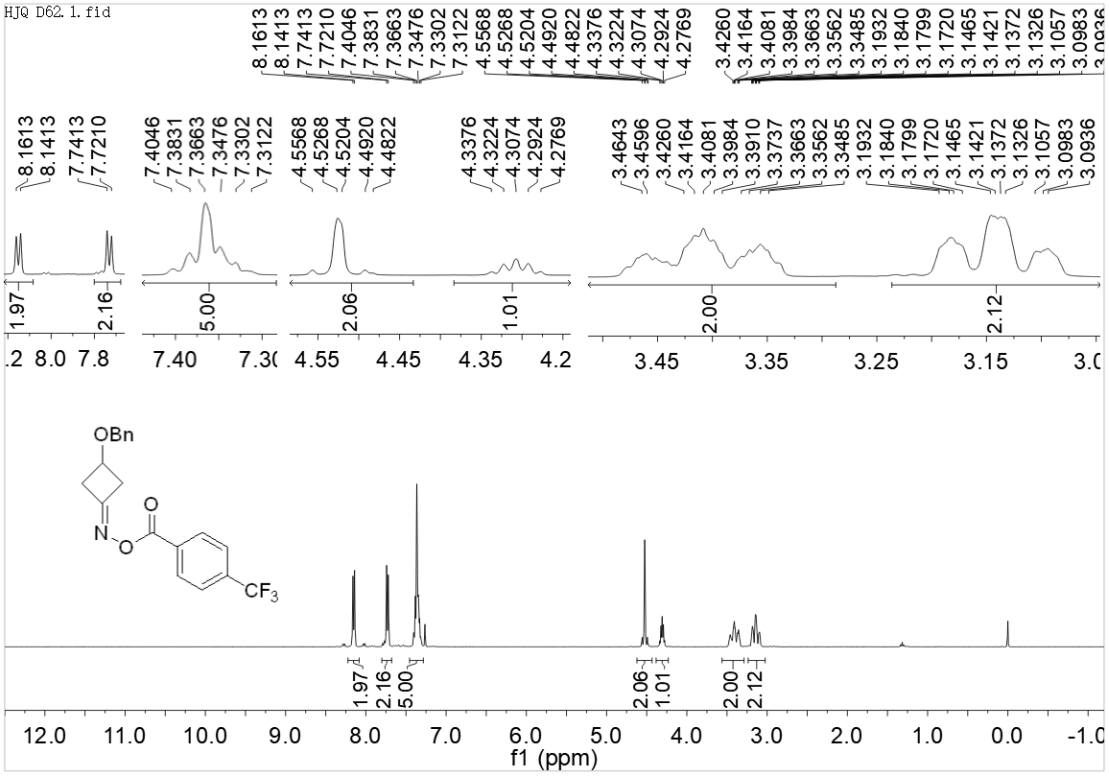
DEPT 90 and DEPT 135



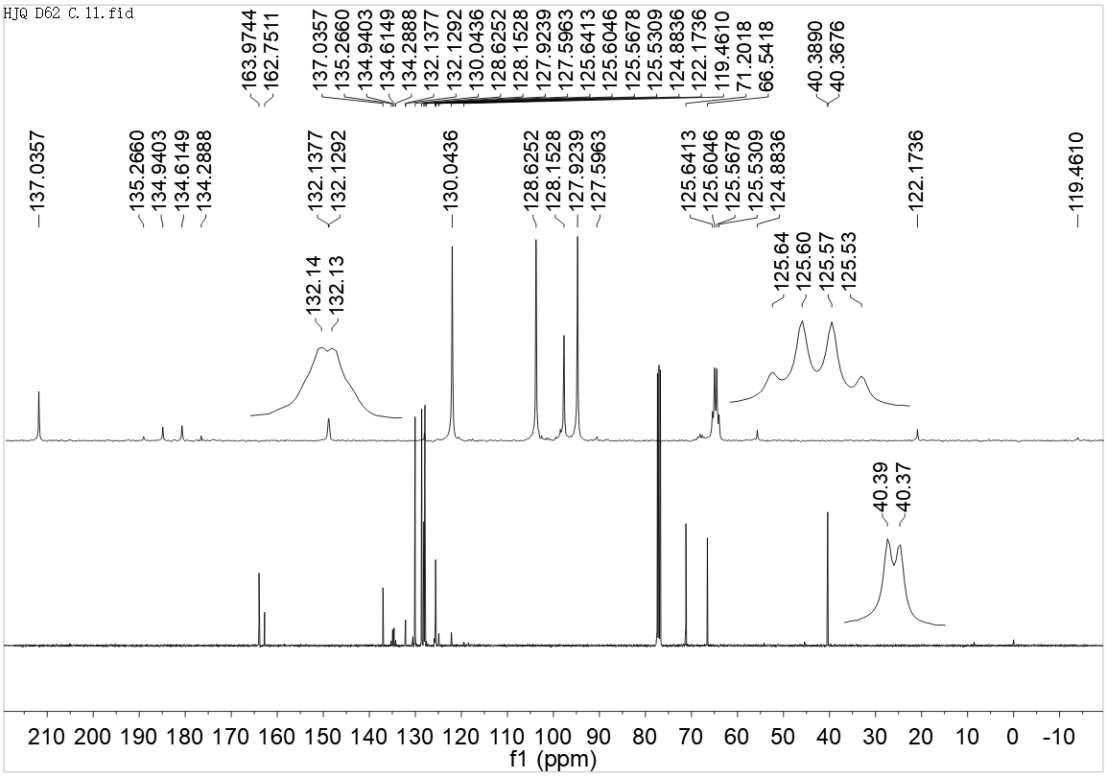
^{19}F NMR



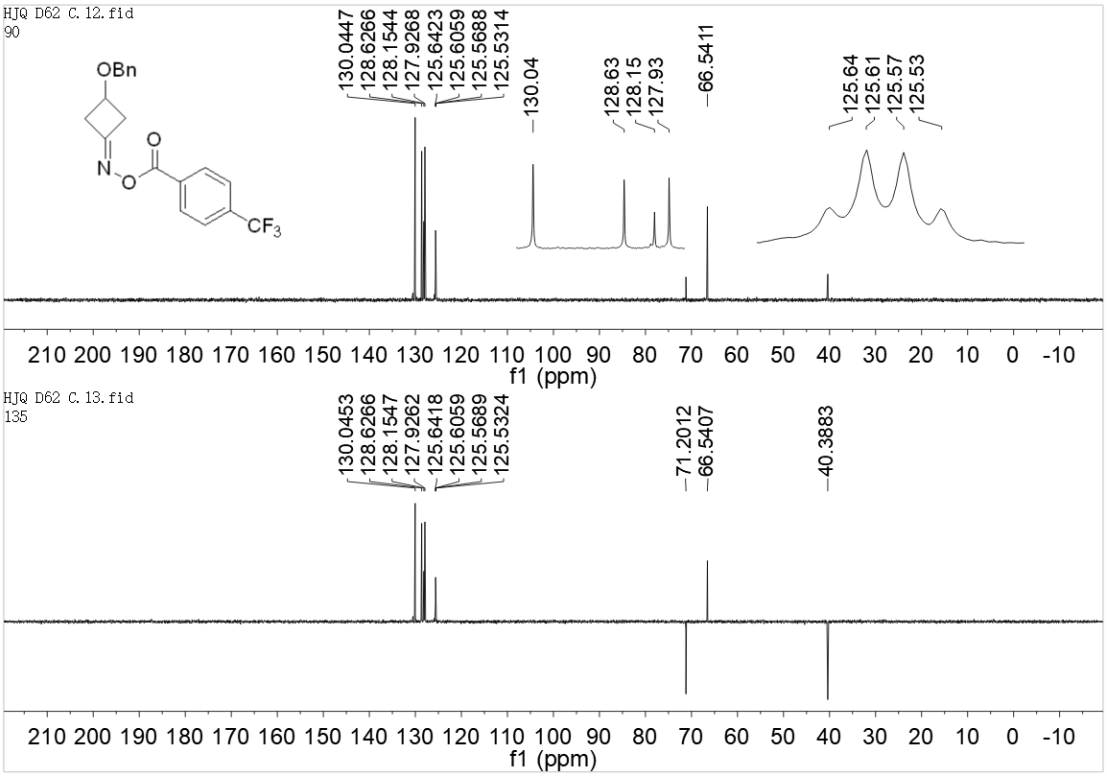
2v, ^{1}H NMR



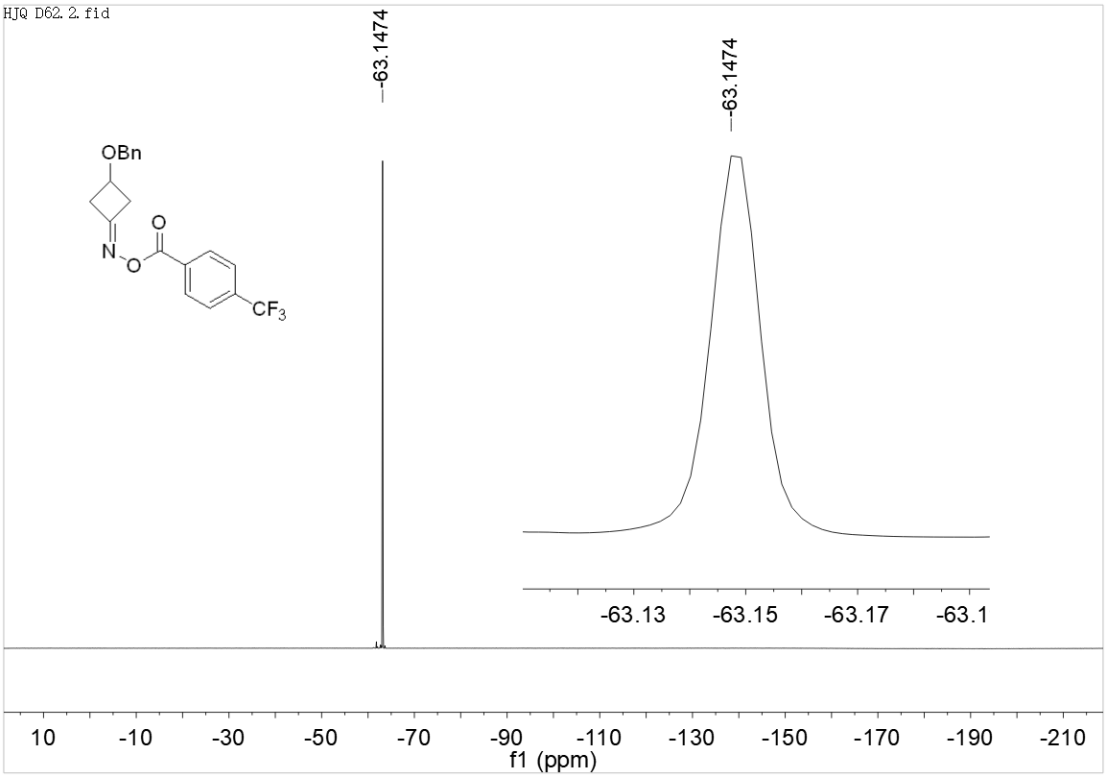
^{13}C NMR



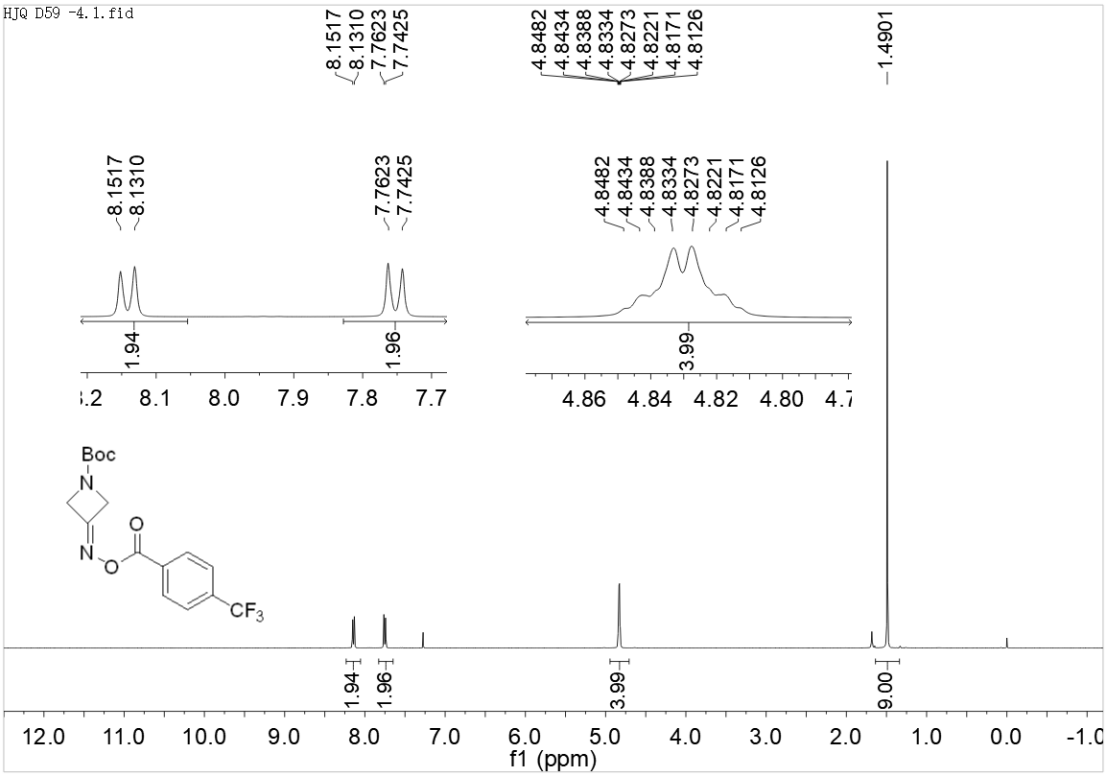
DEPT 90 and DEPT 135



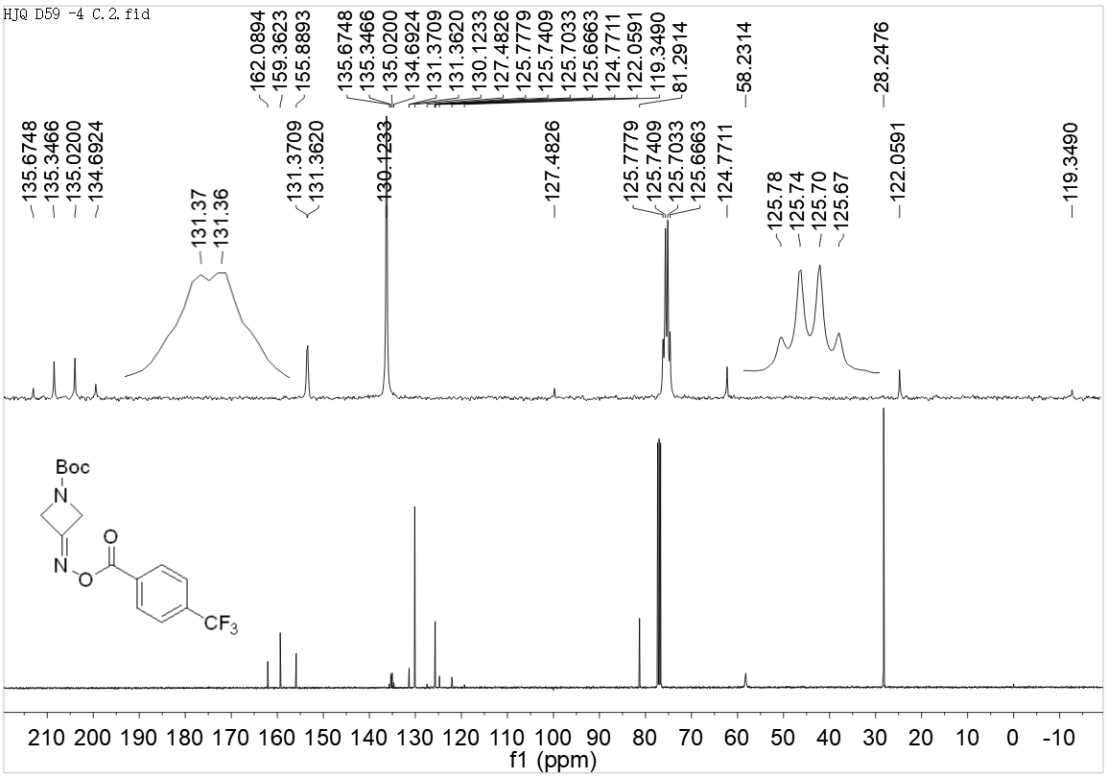
^{19}F NMR



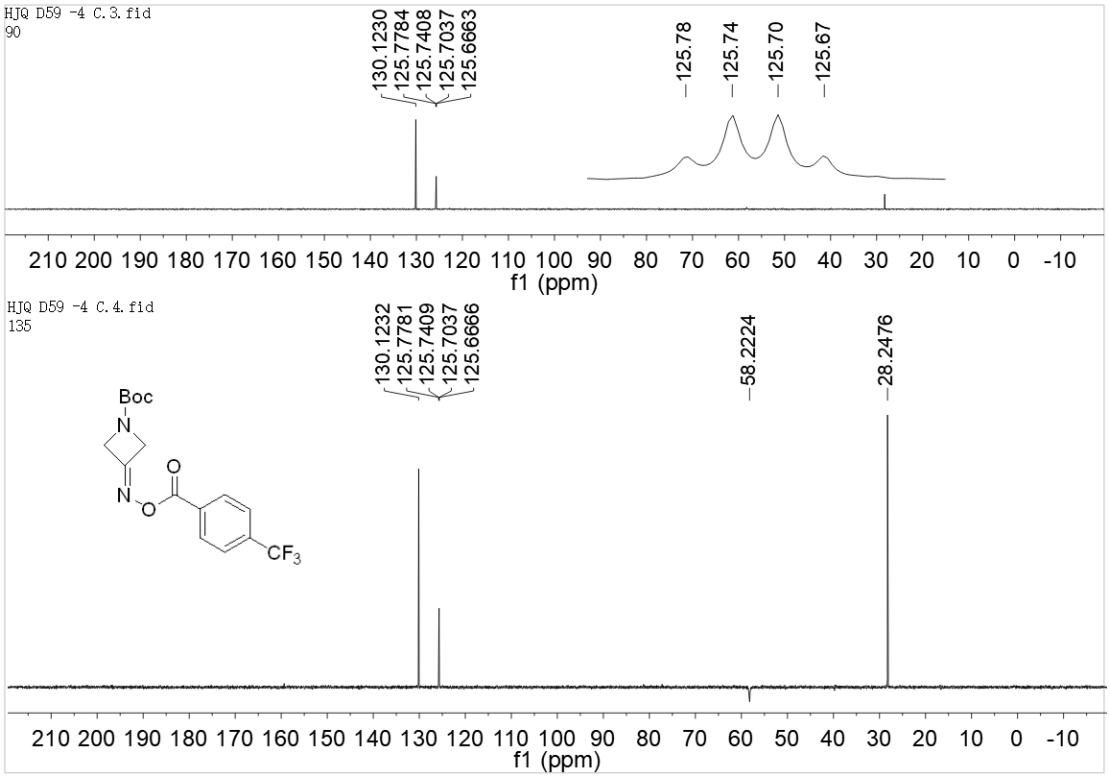
2x, ^{1}H NMR



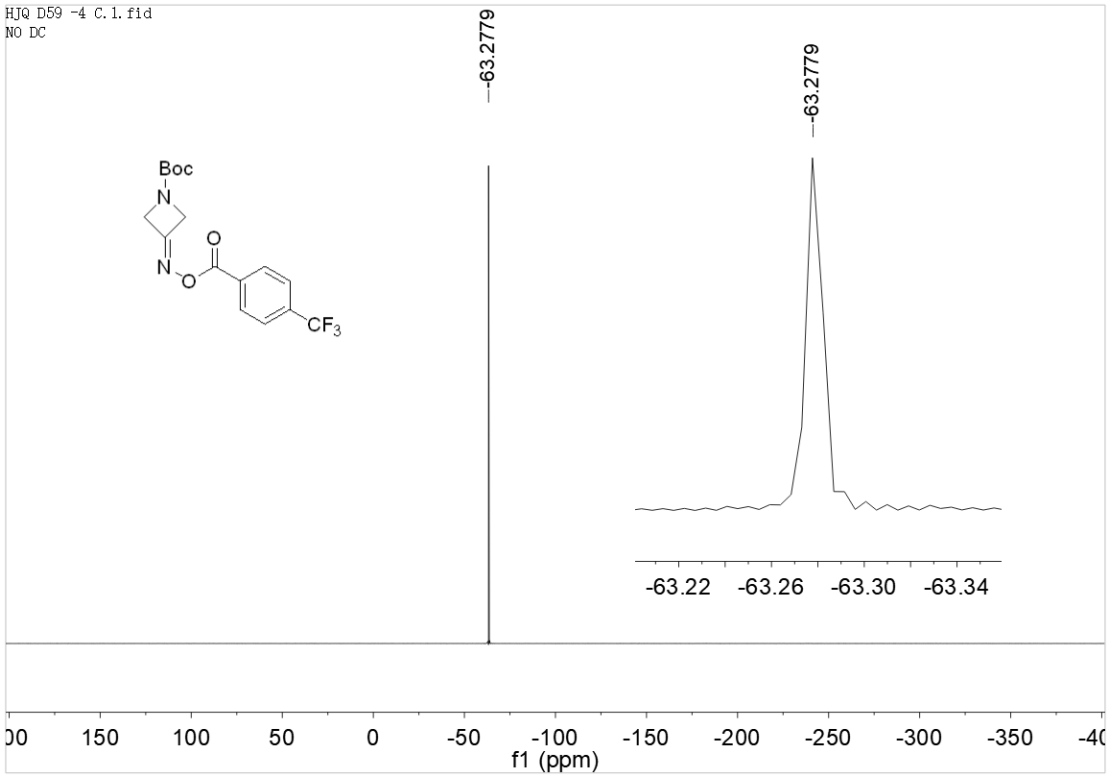
^{13}C NMR



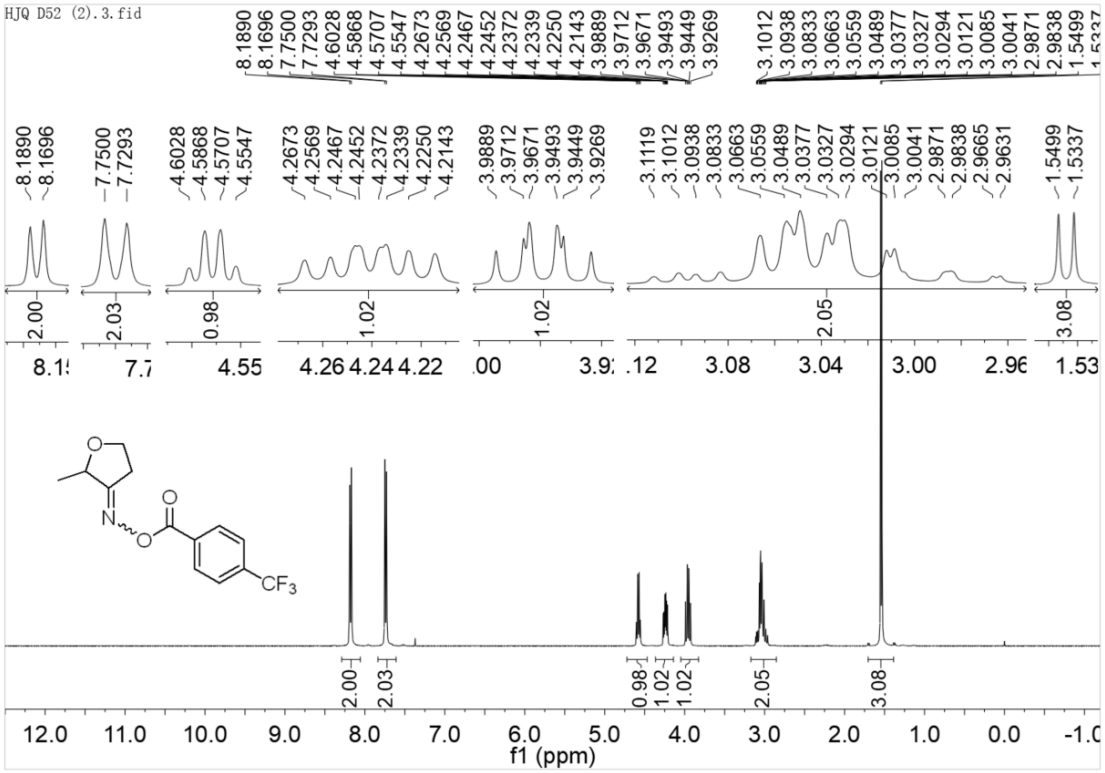
DEPT 90 and DEPT 135



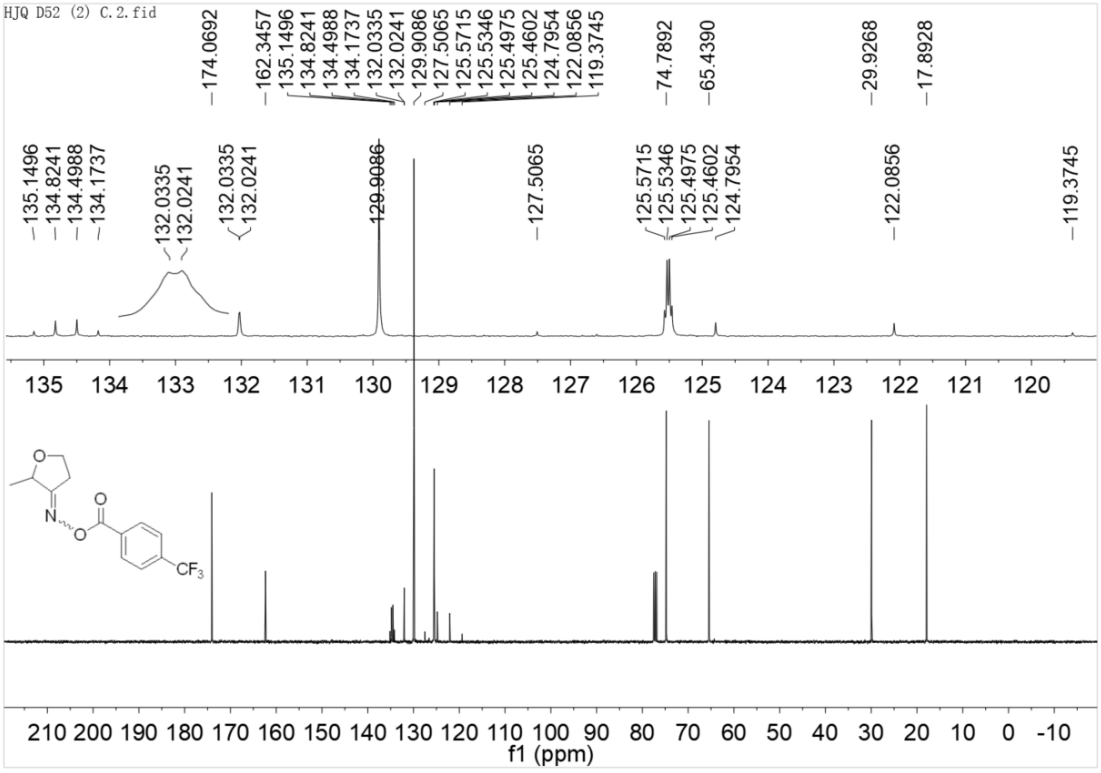
^{19}F NMR



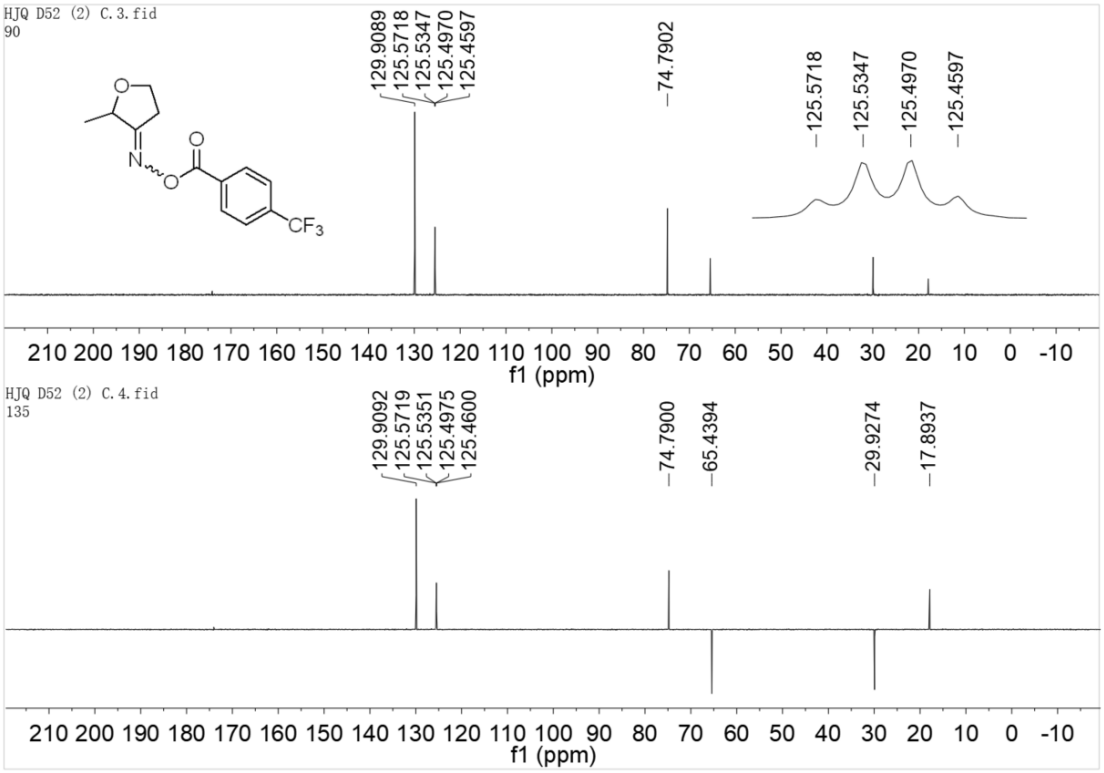
2y, ^{1}H NMR



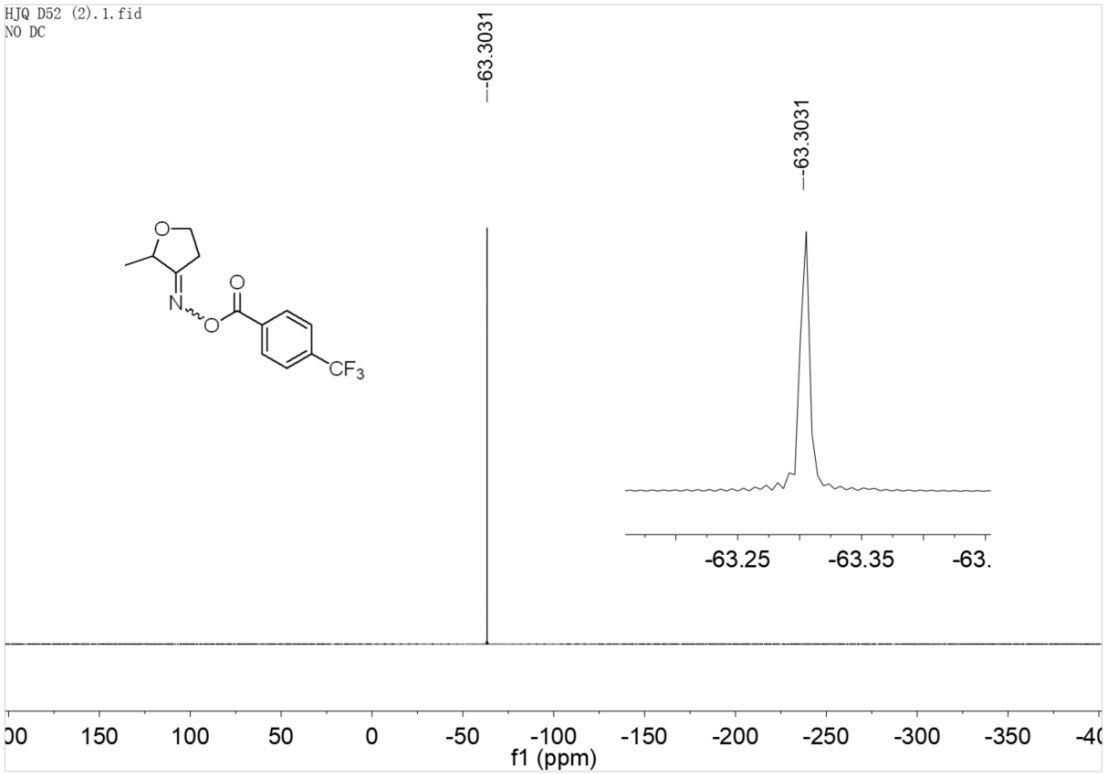
^{13}C NMR



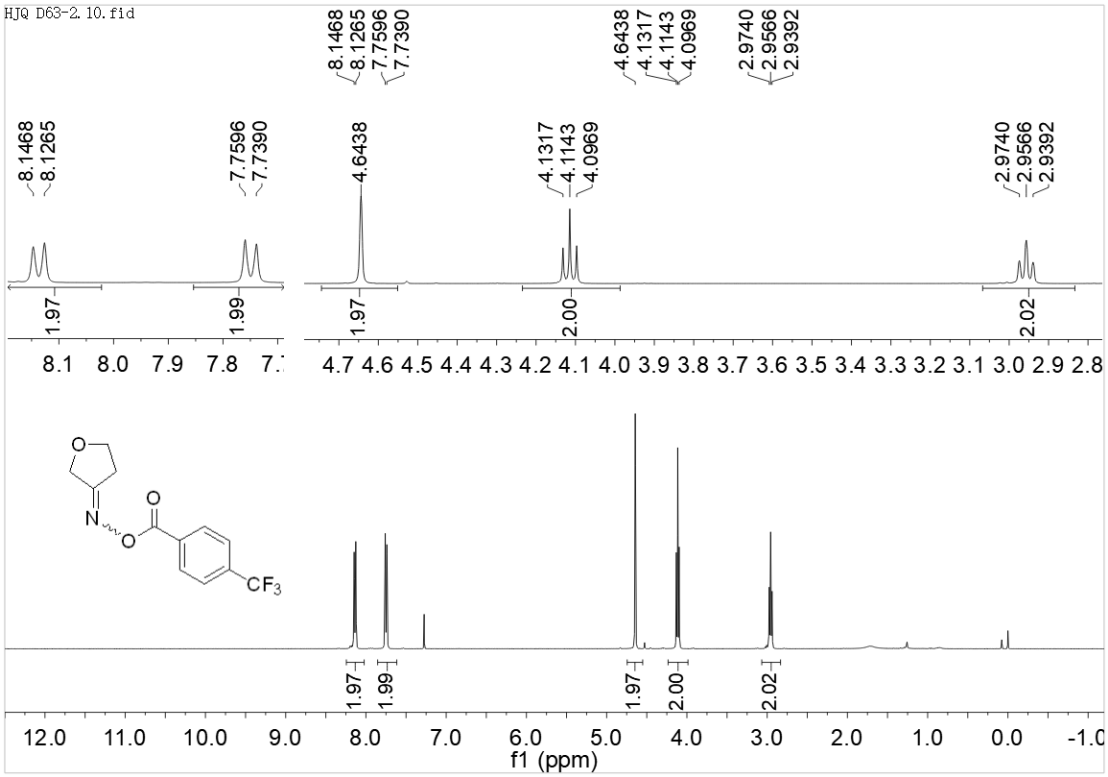
DEPT 90 and DEPT 135



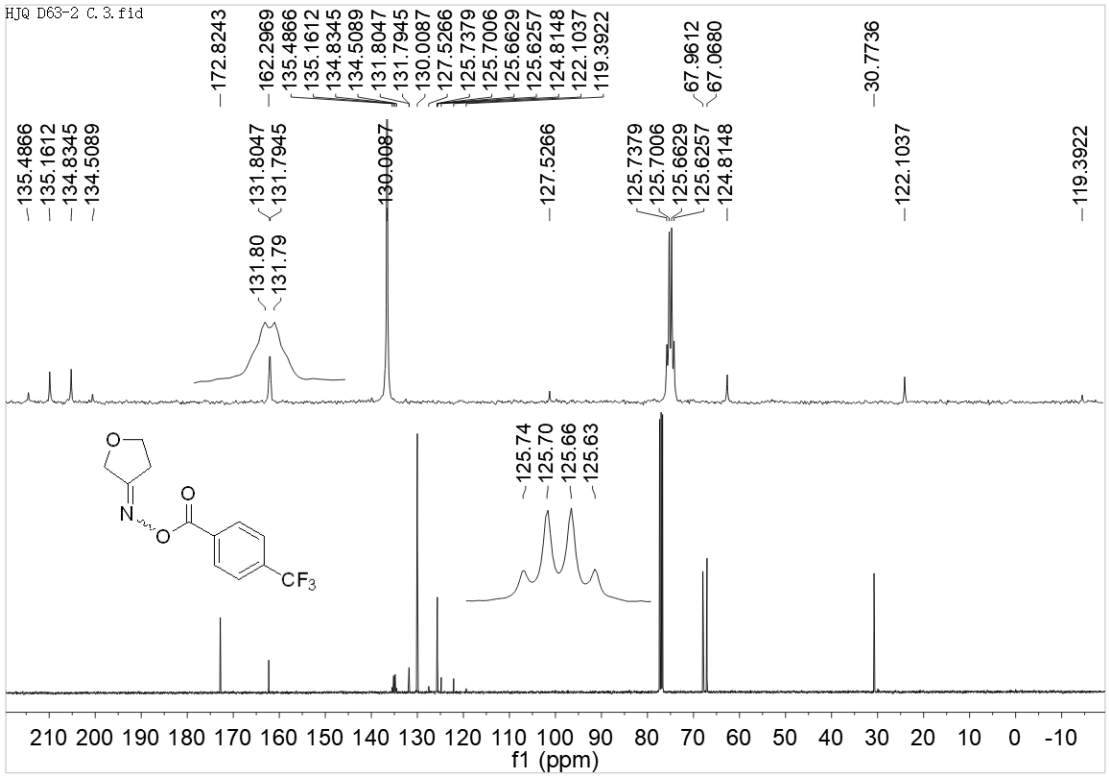
^{19}F NMR



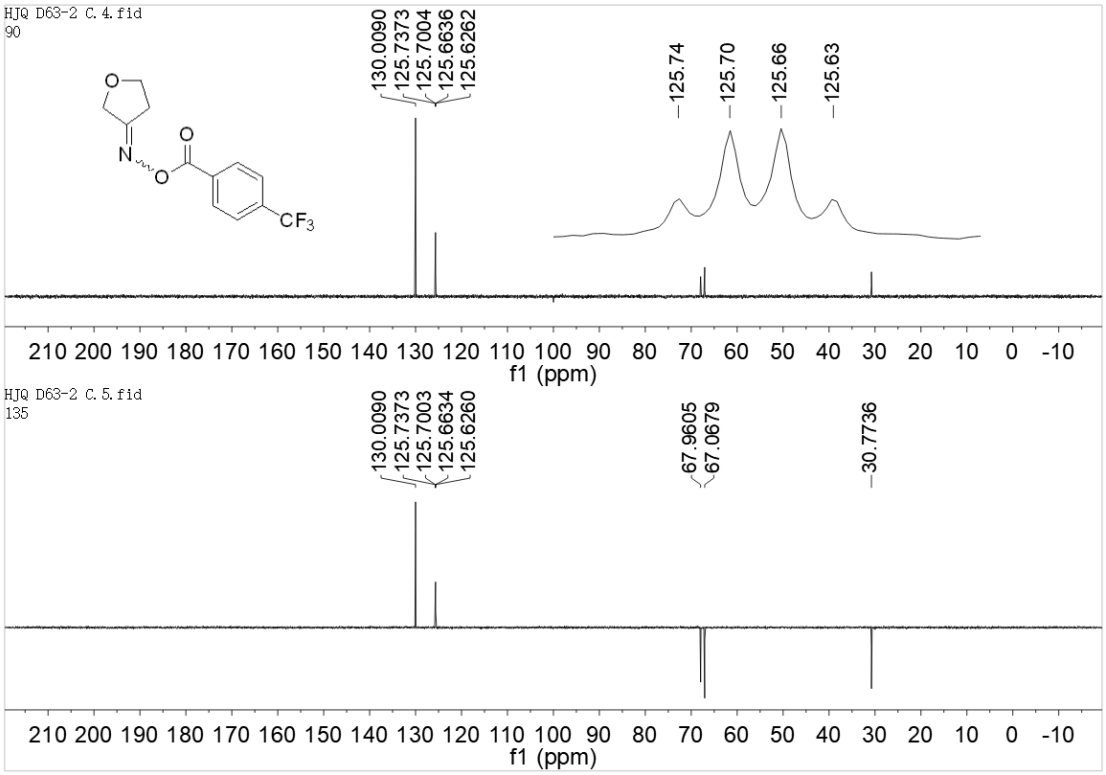
2z, ^{1}H NMR



^{13}C NMR



DEPT 90 and DEPT 135



^{19}F NMR