

Electrophotocatalytic tri- or difluoromethylative cyclization of alkenes

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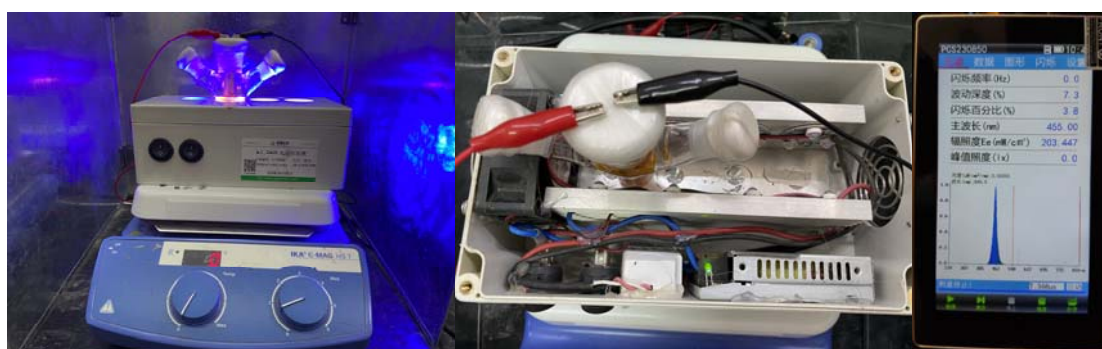
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I. General considerations

Unless otherwise stated, commercially available chemicals were used without treatment. Solvents were degassed by bubbling Ar for 10 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. ^1H NMR, ^{19}F NMR, ^{13}C NMR and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend™ 400 spectrometer using tetramethyl silane (TMS) as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). Cyclic voltammetry studies were carried out on a CHI600E electrochemical workstation (Shanghai CH Instruments Co., China). UV-Vis measurements were carried out on a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan). The emission spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). The photoelectrochemical setup used in this research is shown in [Figure S1](#). Photoreactors were bought from GeAo Chem (containing 24 small LEDs, 1 W for every LED, and every reaction tube is irradiated by 6 LEDs), and electrolysis was performed using a DJS-292B dual display potentiostat (Shanghai Xinrui Instruments Co., China). Allylated (**1a**, **1c-1l**, **4a**, **8a-8c**, **12a** and **16**) or homoallylated substrates (**10**)^[1] and methacryloylated substrates (**1b**, **1m**, **4b-4e**, **6**, **8d-8f**, **12b** and **14**)^[2] were prepared according to literature procedures.



[1] G. Kundu, T. Sperger, K. Rissanen and F. Schoenebeck, *Angew. Chem. Int. Ed.* 2020, **59**, 21930–21934.

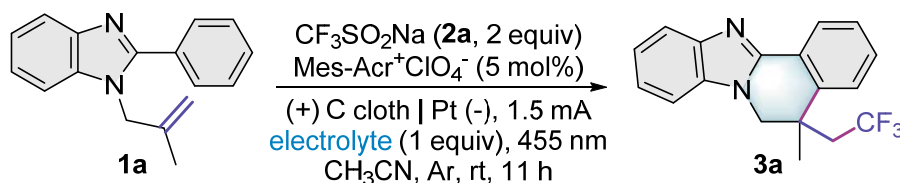
[2] Y. Yuan, Y. Zheng, B. Xu, J. Liao, F. Bu, S. Wang, J.-G. Hu and A. Lei, *ACS Catal.*, 2020, **10**, 6676–6681.



Figure S1 Photoelectrochemical setup

II. Optimization of reaction conditions

Table S1 Electrolyte screening^a

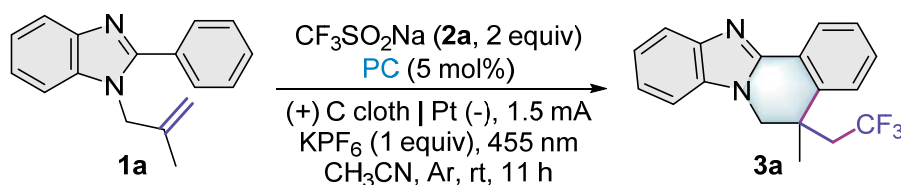


entry	supporting electrolyte	yield (%) ^b
1	Bu ₄ NBF ₄	29
2	Et ₄ NBF ₄	14
3	Bu ₄ NPF ₆	33
4	Bu ₄ NOAc	26
5	Bu ₄ NClO ₄	34
6	LiClO ₄	37
7	KPF₆	43
8	TBAI	2

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Mes-Acr⁺ClO₄⁻ (0.015 mmol), electrolyte (0.3 mmol), MeCN (9.0 mL), 6 W blue LEDs (455 nm), carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h.

^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

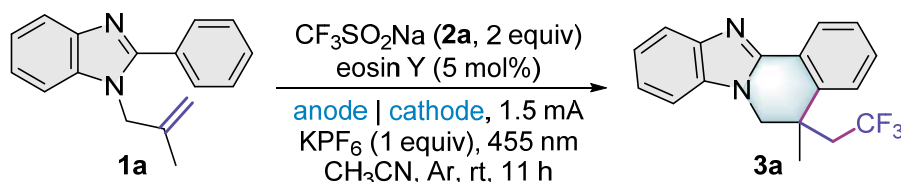
Table S2 PC screening^a



entry	PC	yield (%) ^b
1	4CzIPN	54
2	Ir(ppy) ₃	48
3	[Ir(dtbbpy)(ppy) ₂]PF ₆	49
4	(Ir[dF(CF ₃)ppy] ₂ (dtbpy))PF ₆	59
5	Ru(bpy) ₃ Cl ₂	22
6	eosin Y	74
7	eosin Y disodium	70
8	eosin B	66
9	rose bengal	10
10	rhodamine B	34
11	fluorescein	64
12	methylene blue	20
13	thioxanthone	34
14	–	27

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), PC (0.015 mmol), KPF₆ (0.3 mmol), MeCN (9.0 mL), 6 W blue LEDs (455 nm), carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

Table S3 Electrode screening^a

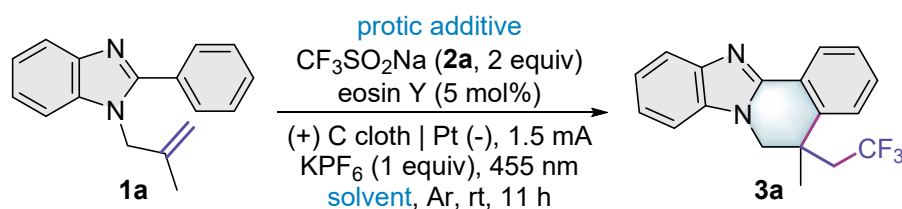


entry	anode	cathode	yield (%) ^b
1	C felt	Pt plate	62
2	C rod	Pt plate	34
3	RVC	Pt plate	6
4	Pt plate	Pt plate	36
5	C cloth	Ni plate	62
6	C cloth	Ni foam	3
7	C cloth	stainless steel	68
8	C cloth	C cloth	62
9	C cloth	C felt	3
10	C cloth	C rod	57

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Mes-Acr⁺ClO₄⁻ (0.015 mmol), electrolyte (0.3 mmol), MeCN (9.0 mL), 6 W blue LEDs (455 nm), anode (15 mm × 15 mm), cathode (15 mm × 15 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal

standard.

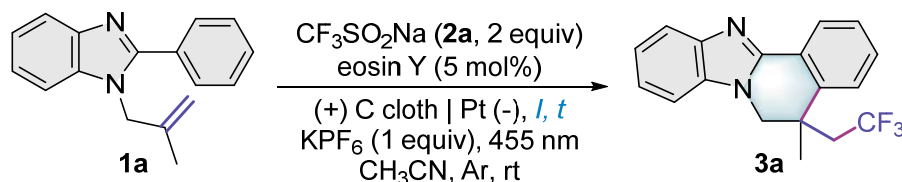
Table S4 Optimization of the solvent and proton source^a



entry	solvent	protic additive (equiv)	yield (%) ^b
1	DCE	–	48
2	CH ₃ NO ₂	–	19
3	acetone	–	68
4	THF	–	5
5	DMA	–	16
6	DMSO	–	69
7	MeOH	–	24
8	HFIP	–	7
9	CH ₃ CN/H ₂ O (9 : 1, v/v)	–	50
10	CH ₃ CN	H ₂ O (2)	67
11	CH ₃ CN	MeOH (2)	58
12	CH ₃ CN	HFIP (2)	36
13	CH ₃ CN	TFA (2)	26

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), eosin Y (0.015 mmol), KPF₆ (0.3 mmol), solvent (9.0 mL), 6 W blue LEDs (455 nm), carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

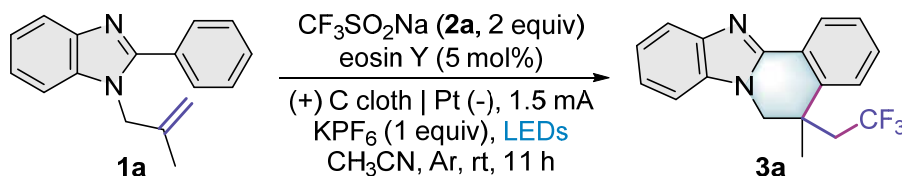
Table S5 Current and time optimization^a



entry	<i>I</i> (mA), <i>t</i> (h)	yield (%) ^b
1	1, 16.5	68
2	2, 8.25	70
3	3, 5.5	64
4	4, 4.125	62
5	5, 3.3	47
6	1.5, 10.73	72

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), eosin Y (0.015 mmol), KPF₆ (0.3 mmol), MeCN (9.0 mL), 6 W blue LEDs (455 nm), carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current, Ar, room temperature. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

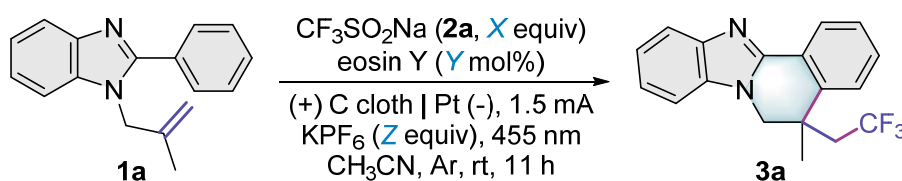
Table S6 LED screening^a



entry	LEDs	yield (%) ^b
1	violet (395 nm)	59
2	white	72
3	green (525 nm)	55
4	yellow (585 nm)	32

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), eosin Y (0.015 mmol), KPF₆ (0.3 mmol), MeCN (9.0 mL), 6 W LEDs, carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

Table S7 Optimization of the loadings of **2a**, eosin Y and the electrolyte^a

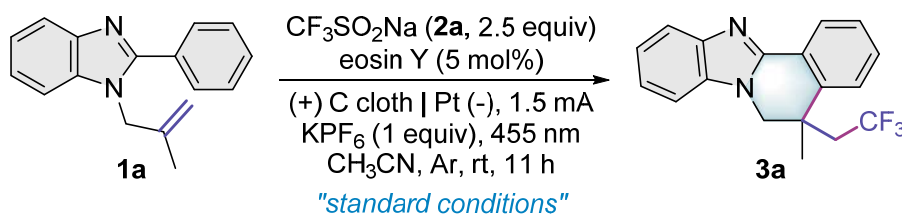


entry	X	Y	Z	yield (%) ^b
1	1.1	5	1	38
2	1.5	5	1	56
3	2.5	5	1	83
4	3	5	1	80
5	2.5	1	1	62
6	2.5	2.5	1	73
7	2.5	7.5	1	82
8	2.5	10	1	80
9	2.5	5	0	67
10	2.5	5	0.3	71

11	2.5	5	0.5	79
12	2.5	5	1.5	83
13	2.5	5	2	77

^aReaction conditions: **1a** (0.3 mmol), **2a**, eosin Y, KPF₆, MeCN (9.0 mL), 6 W blue LEDs (455 nm), carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

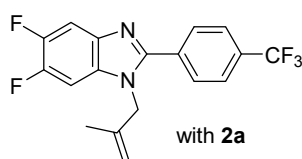
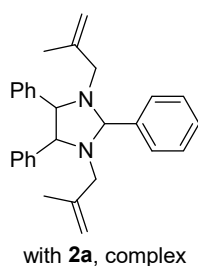
Table S8 Other control experiments^a



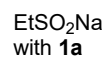
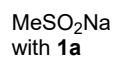
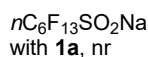
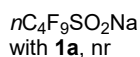
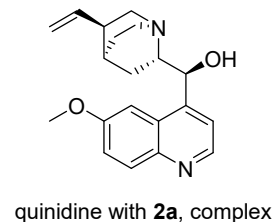
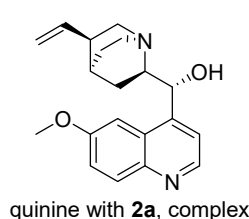
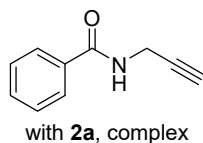
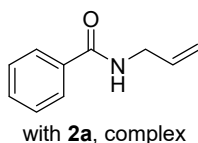
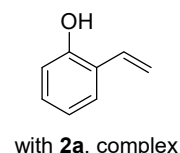
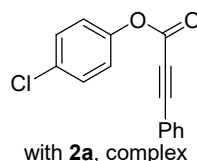
entry	variation from the standard conditions	yield (%) ^b
1	no electric current	6
2	no light	38
3	no PC and in the dark	33
4	under an air atmosphere	76
5	no electricity and under air	20

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.75 mmol), eosin Y (0.015 mmol), KPF₆ (0.3 mmol), MeCN (9.0 mL), 6 W blue LEDs (455 nm), carbon cloth anode (15 mm × 15 mm × 0.33 mm, WOS1009, Taiwan CeTech), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 1.5 mA, Ar, room temperature, 11 h. ^bYields were determined by ¹⁹F NMR analysis using trifluorotoluene as an internal standard.

III. Unsuccessful substrates



The product was isolated in 83% yield (104.5 mg, yellowish solid, mp. 126-127 °C), yet we failed to obtain its NMR spectra due to its poor solubility in various solvents.



substrate **1a** recovered
trace amounts of an unidentified product

IV. Experimental procedures

1. General procedure for the photoelectrochemical synthesis (**3a** as an example)

A custom-made undivided cell, equipped with a magnetic stirring bar, a C cloth anode (15 mm × 15 mm × 0.33 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged sequentially with *N*-allylated 2-arylbenzimidazole **1a** (0.3 mmol, 74.5 mg), $\text{CF}_3\text{SO}_2\text{Na}$ **2a** (2.5 equiv, 0.75 mmol, 117.1 mg), eosin Y (5 mol%, 0.015 mmol, 9.7 mg) and electrolyte KPF_6 (1 equiv, 0.3 mmol, 55.2 mg) under argon, followed by the addition of MeCN (9.0 mL). The mixture was electrolyzed with stirring using a constant current of 1.5 mA under blue LED irradiation at room temperature for 11 h (2.05 F/mol). The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1) to afford 5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline **3a** as a colorless oil (79.1 mg, 83% yield).

2. Gram-scale synthesis

A 100-mL two-necked flask, equipped with a magnetic stirring bar, a C cloth anode (15 mm × 15 mm × 0.33 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged sequentially with *N*-allylated 2-arylbenzimidazole **1a** (5 mmol, 1241.7 mg), CF₃SO₂Na **2a** (2.5 equiv, 12.5 mmol, 1950.7 mg), eosin Y (5 mol%, 0.25 mmol, 162.0 mg) and electrolyte KPF₆ (1 equiv, 5 mmol, 920.3 mg) under argon, followed by the addition of MeCN (150.0 mL). The mixture was electrolyzed with stirring using a constant current of 20.0 mA under blue LED irradiation (25 W × 2, 455 nm, Figure S2) at room temperature for 14 h. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 15:1) to afford 5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline **3a** as a colorless oil (1214.9 mg, 77% yield).

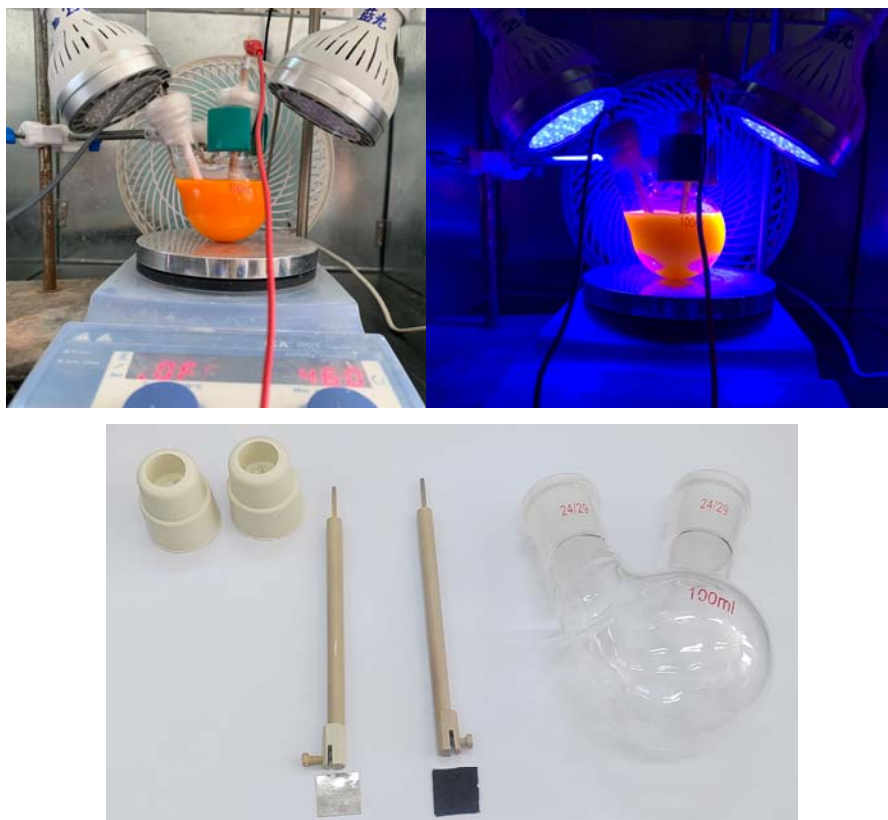


Figure S2 Setup for gram-scale synthesis

3. Sunlight experiment

A custom-made undivided cell, equipped with a magnetic stirring bar, a C cloth anode (15 mm × 15 mm × 0.33 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged sequentially with *N*-allylated 2-arylbenzimidazole **1a**

(0.3 mmol, 74.5 mg), $\text{CF}_3\text{SO}_2\text{Na}$ **2a** (2.5 equiv, 0.75 mmol, 117.1 mg), eosin Y (5 mol%, 0.015 mmol, 9.7 mg) and electrolyte KPF_6 (1 equiv, 0.3 mmol, 55.2 mg) under argon, followed by the addition of MeCN (9.0 mL). The mixture was electrolyzed with stirring using a constant current of 1.5 mA under sunlight irradiation (2021-09-11 (5.5 h, 11:56-17:26) and 2021-09-12 (5.5 h, 11:50-17:20), Kunming, [Figure S3](#)) at room temperature for 11 h. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1) to afford 5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline **3a** as a colorless oil (81.4 mg, 86% yield).

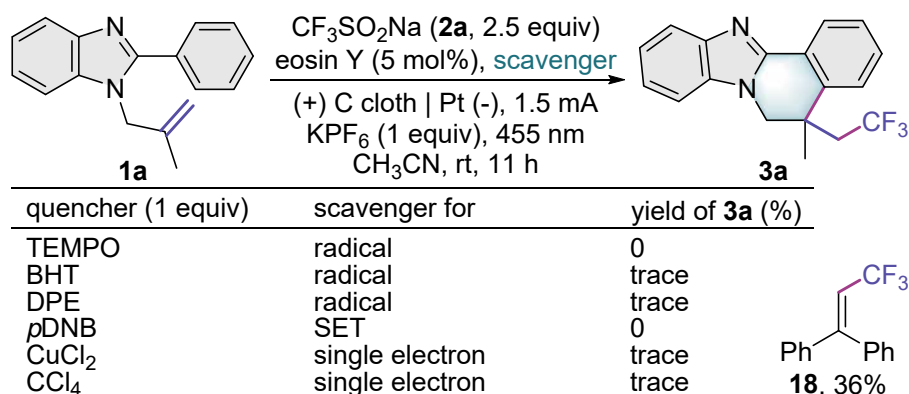


2021-09-11 星期六	26°C	17°C	晴	南风 2级
2021-09-12 星期日	27°C	16°C	晴	东南风 2级

Figure S3 Setup for natural sunlight experiment

V. Mechanistic investigations

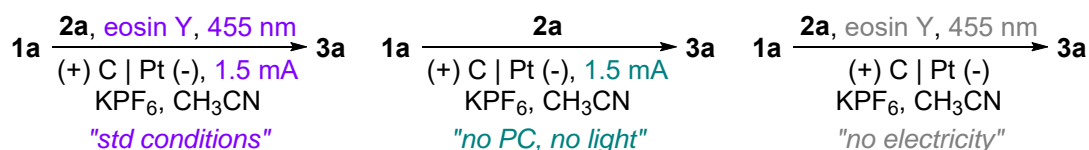
1. Quenching experiments

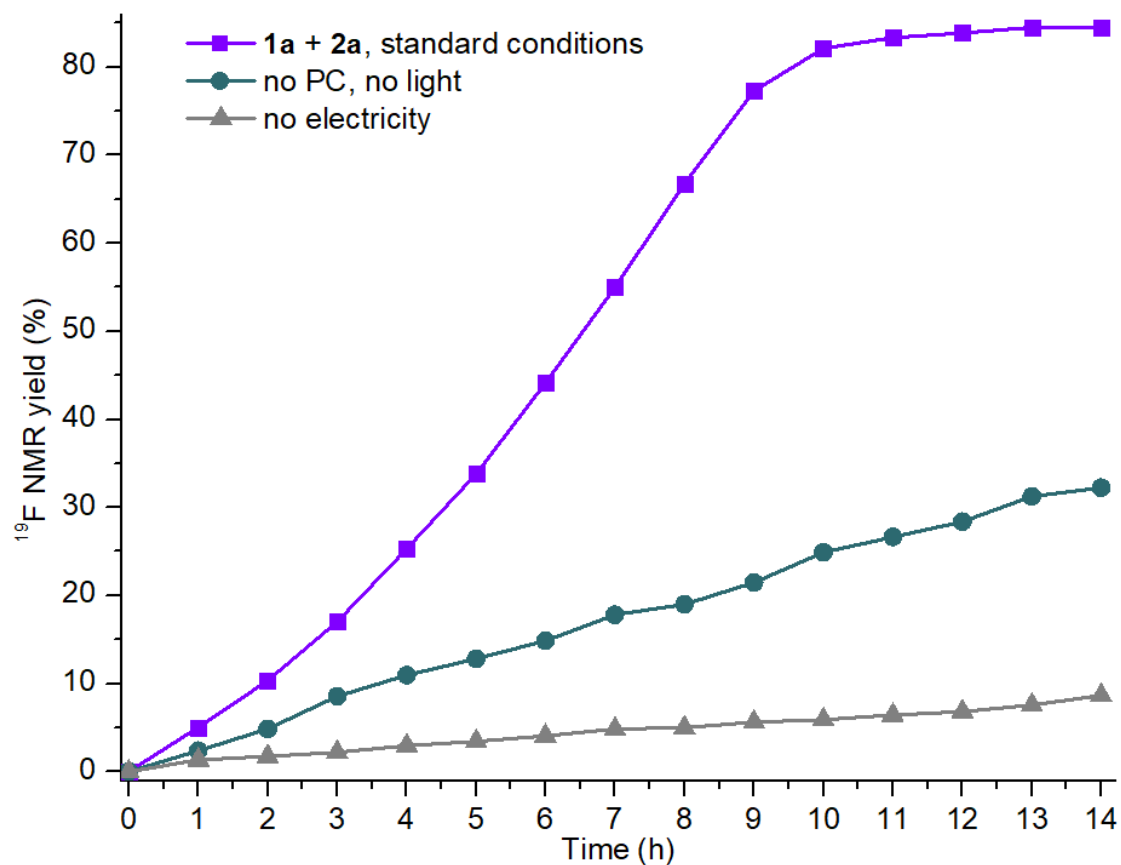


A custom-made undivided cell, equipped with a magnetic stirring bar, a C cloth anode (15 mm × 15 mm × 0.33 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged sequentially with *N*-allylated 2-arylbenzimidazole **1a** (0.3 mmol, 74.5 mg), CF₃SO₂Na **2a** (2.5 equiv, 0.75 mmol, 117.1 mg), eosin Y (5 mol%, 0.015 mmol, 9.7 mg), KPF₆ (1 equiv, 0.3 mmol, 55.2 mg) and a scavenger (1.0 equiv, 0.3 mmol) under argon, followed by the addition of MeCN (9.0 mL). The mixture was electrolyzed with stirring using a constant current of 1.5 mA under blue LED irradiation at room temperature for 11 h. In the case of DPE experiment, the residue obtained after evaporation of the solvent was purified by column chromatography on silica gel using petroleum ether to afford (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene **18** as a colorless oil (26.8 mg, 36% yield).

2. Reaction profiles

(Trifluoromethyl)benzene (1 equiv) was added to the reactions of **1a** and **2a** as an internal standard before reaction. 0.05 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ¹⁹F NMR analysis after filtered by a filter membrane with pore size of 0.45 μm.





	A(X)	D1(Y)	C1(Y)	B(Y)
Long Name	Time	19F NMR yield	19F NMR yield	19F NMR yield
Units	h	%	%	%
Comments		1a + 2a, standard conditions	no PC, no light	no electricity
1	0	0.00	0.00	0.00
2	1	5.04	2.39	1.34
3	2	10.35	4.85	1.76
4	3	17.05	8.55	2.20
5	4	25.32	10.96	2.96
6	5	33.84	12.83	3.44
7	6	44.15	14.86	4.06
8	7	55.00	17.83	4.84
9	8	66.78	19.01	5.01
10	9	77.29	21.48	5.62
11	10	82.15	24.91	5.92
12	11	83.35	26.65	6.44
13	12	83.89	28.40	6.83
14	13	84.51	31.25	7.57
15	14	84.45	32.24	8.65

Figure S4 Reaction kinetic profiles

3. On-off experiments

	A(X)	B(Y)	G1(Y)	D1(Y)
Long Name	Time	¹⁹ F NMR yield	¹⁹ F NMR yield	¹⁹ F NMR yield
Units	h	%	%	%
Comments		both on-off	electricity on-off	light on-off
1	0	0	0	0
2	1	5.07	5.59	4.88
3	2	5.05	7.73	8.8
4	3	12.11	16.03	20.5
5	4	12.26	18.48	24.84
6	5	25.68	27.42	45.28
7	6	25.16	29.88	52.12

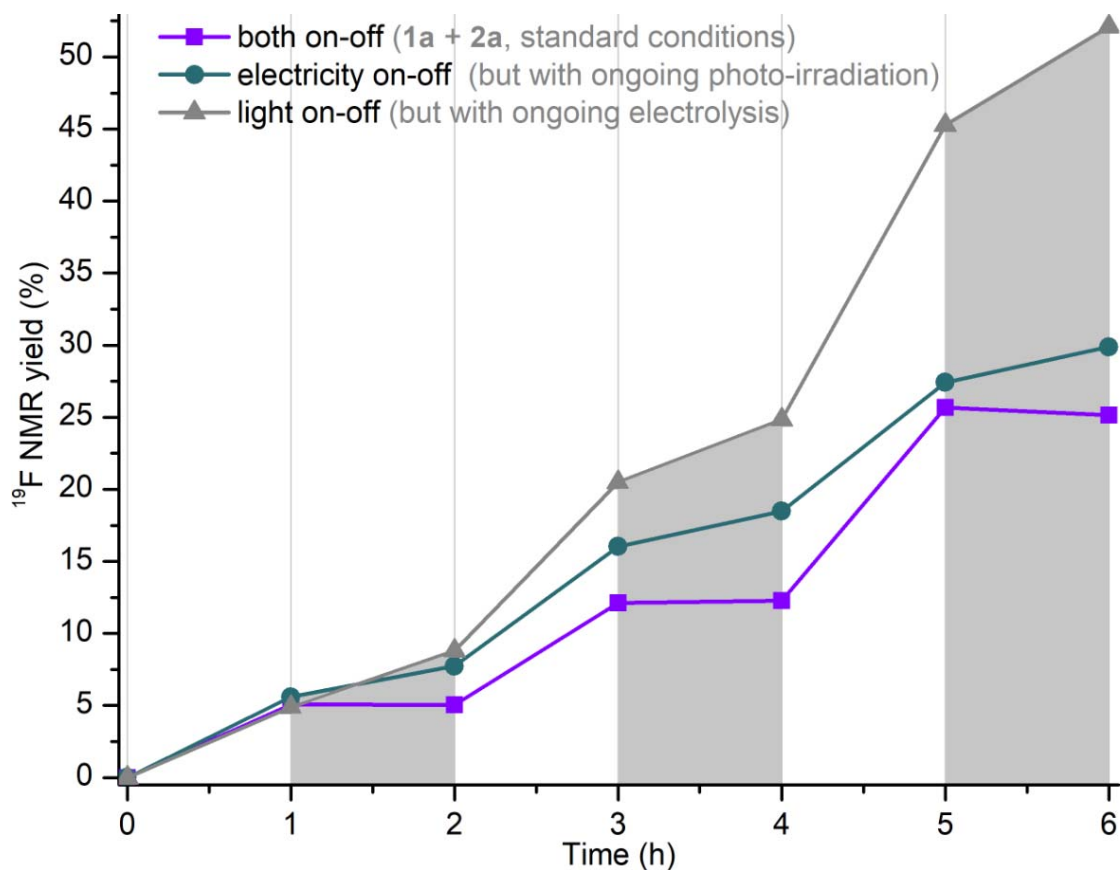


Figure S5 On-off experiments

Benzotrifluoride (1.0 equiv) was added as an internal standard to the reactions of **1a** with **2a** before reaction. 0.05 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ¹⁹F NMR analysis after filtered by a filter membrane with pore size of 0.45 μm.

4. Cyclic voltammetry studies

General procedure: Cyclic voltammograms 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. 12 mL solution containing 1.2 mmol $n\text{Bu}_4\text{NBF}_4$ was poured into the electrochemical cell in all experiments. The scan rate was 0.05 V/s.

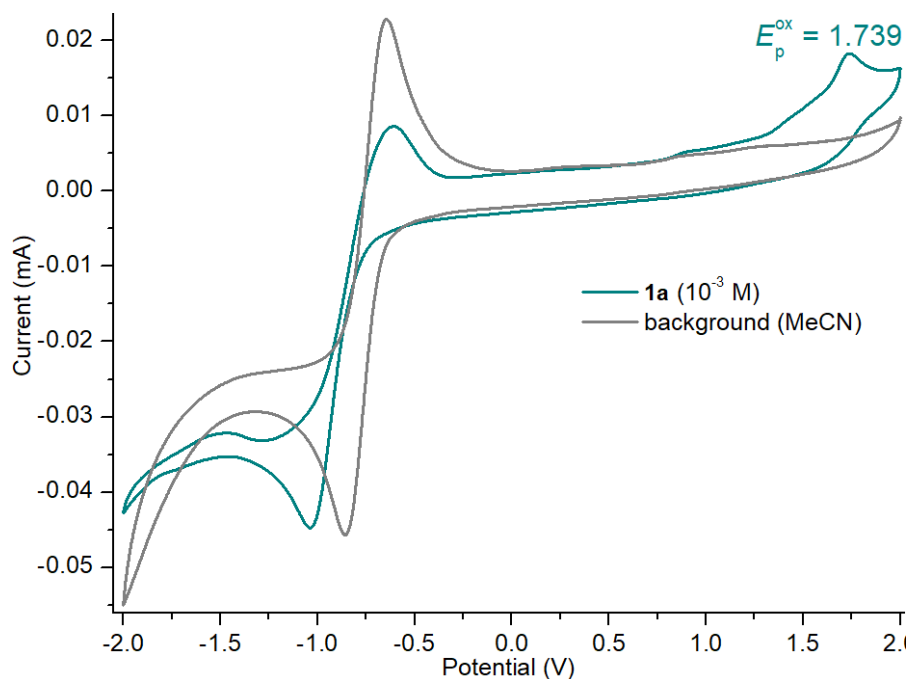


Figure S6 Cyclic voltammograms of **1a** (10^{-3} M) in CH_3CN

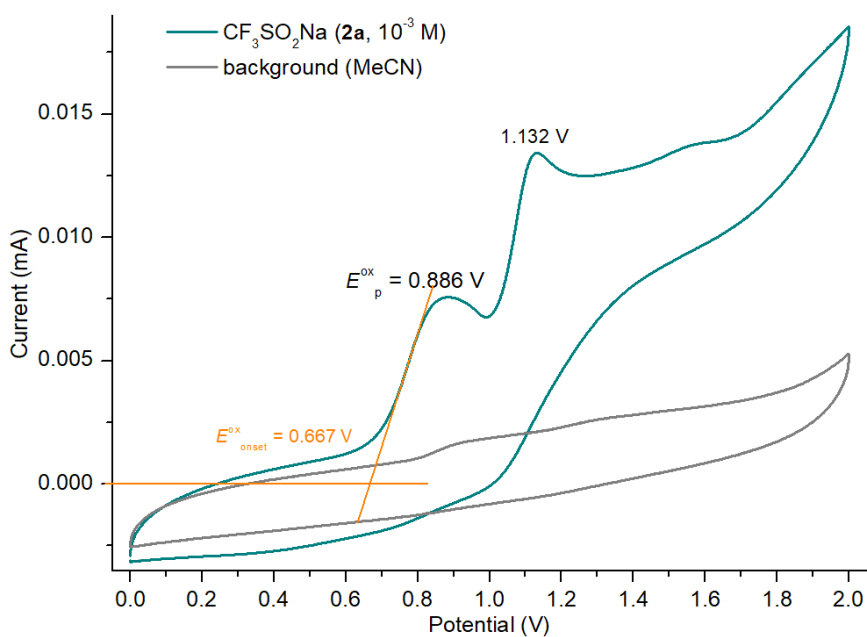


Figure S7 Anodic cyclic voltammograms of **2a** (10^{-3} M) in CH_3CN

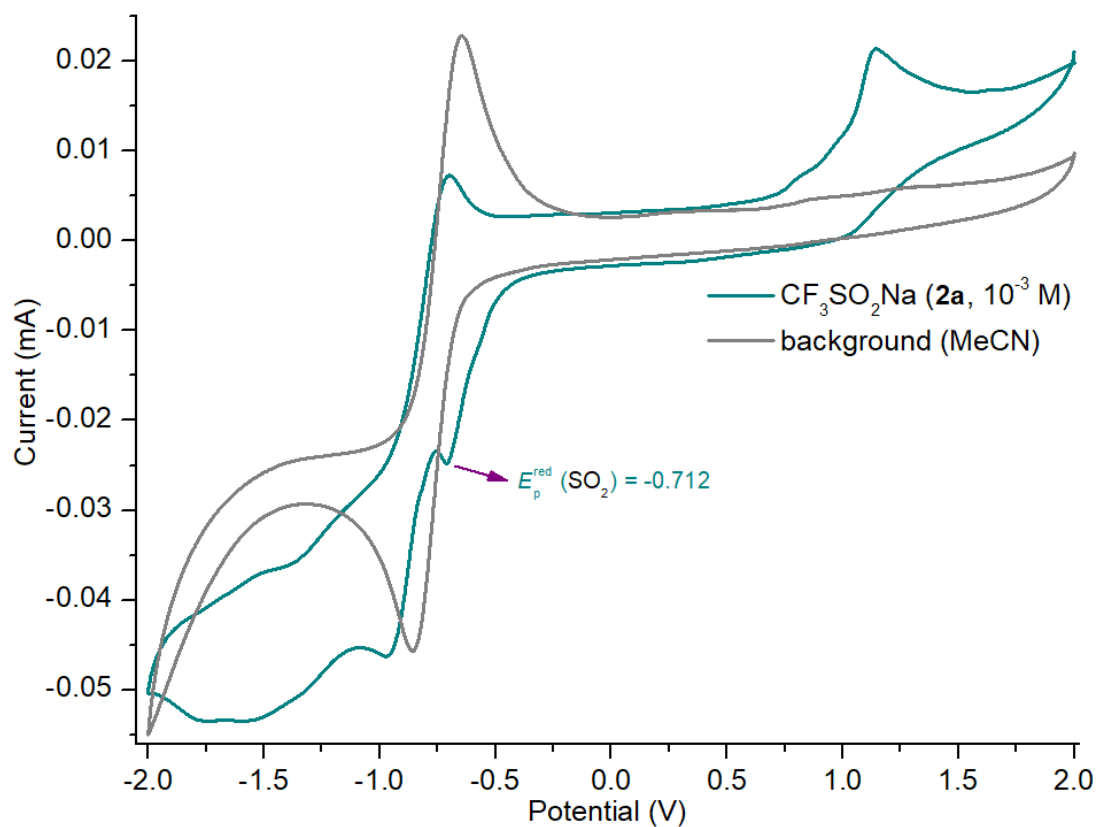


Figure S8 Cyclic voltammograms of **2a** (10^{-3} M) in CH_3CN ranging from -2 to 2 V

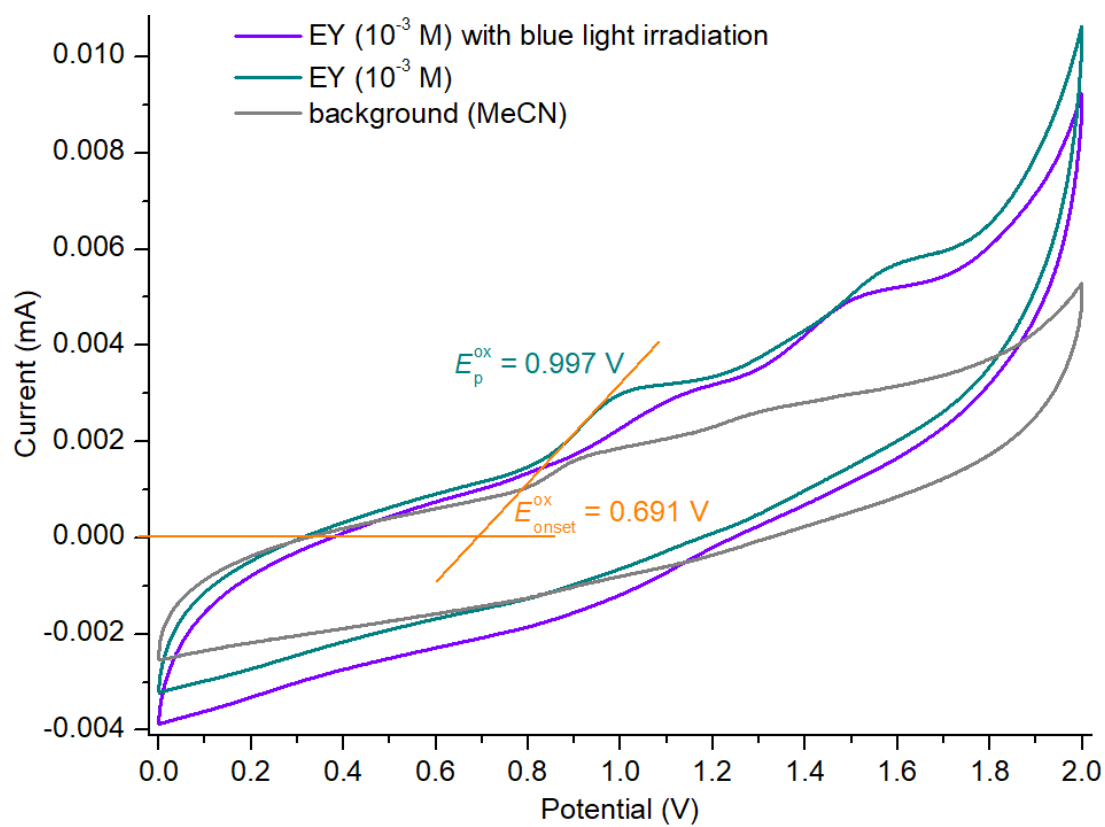


Figure S9 Anodic cyclic voltammograms of eosin Y (10^{-3} M) in CH_3CN

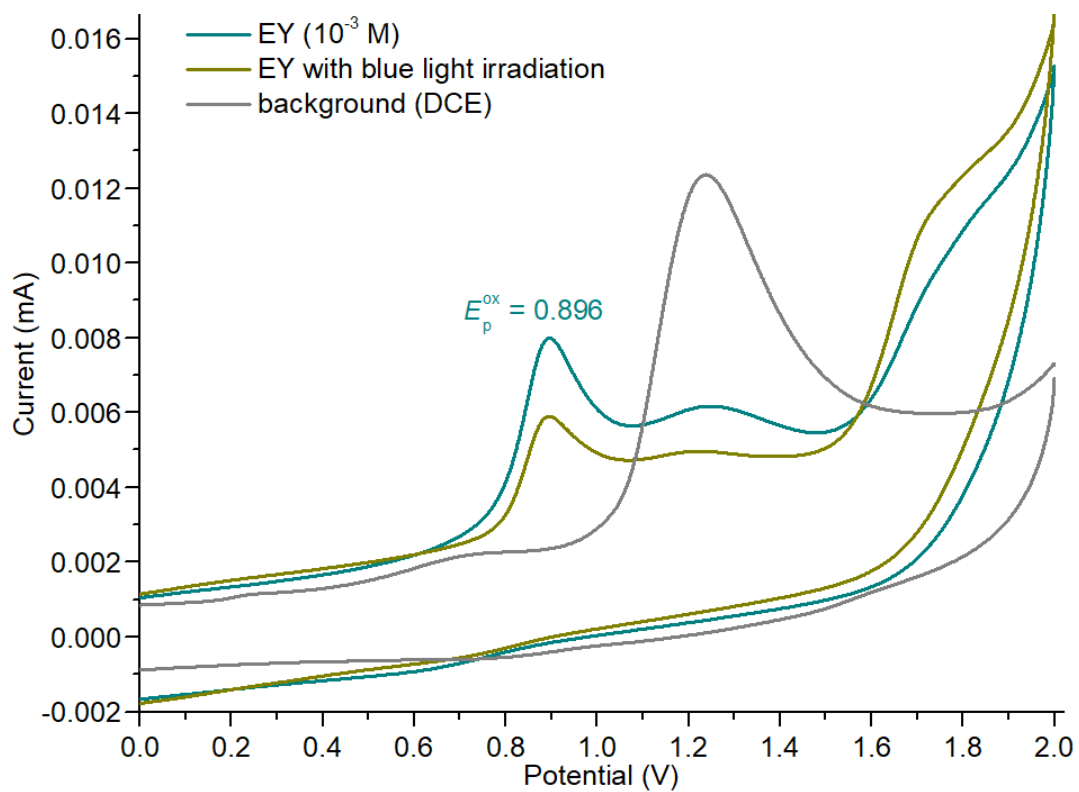


Figure S10 Anodic cyclic voltammograms of eosin Y (10^{-3} M) in DCE ranging from -2 to 2 V

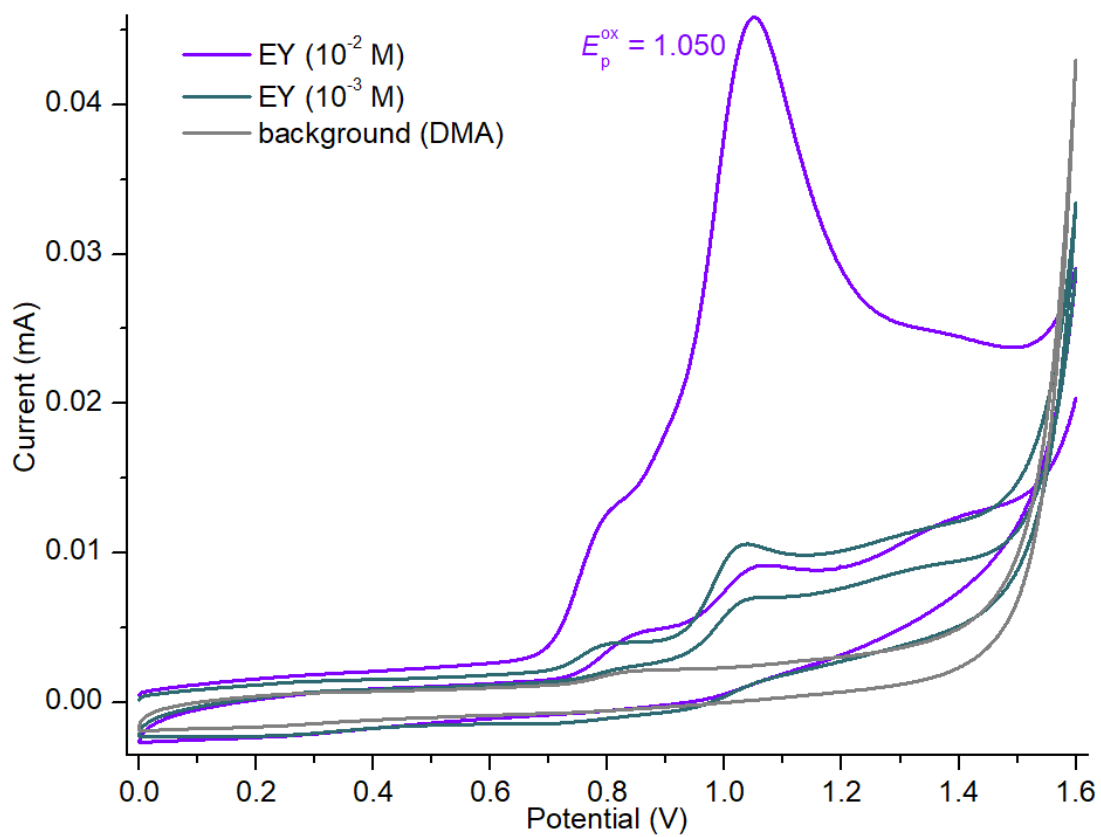


Figure S11 Anodic cyclic voltammograms of eosin Y in DMA

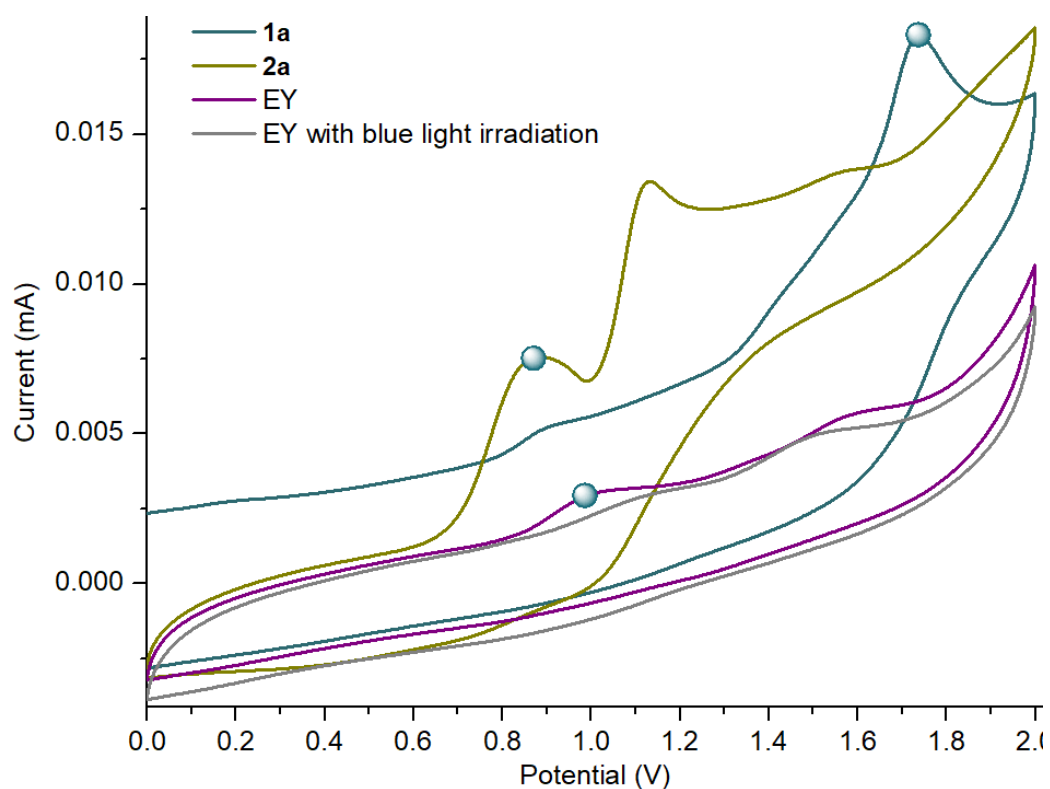


Figure S12 Anodic cyclic voltammograms of **1a** (10^{-3} M), **2a** (10^{-3} M), eosin Y (10^{-3} M) in CH_3CN

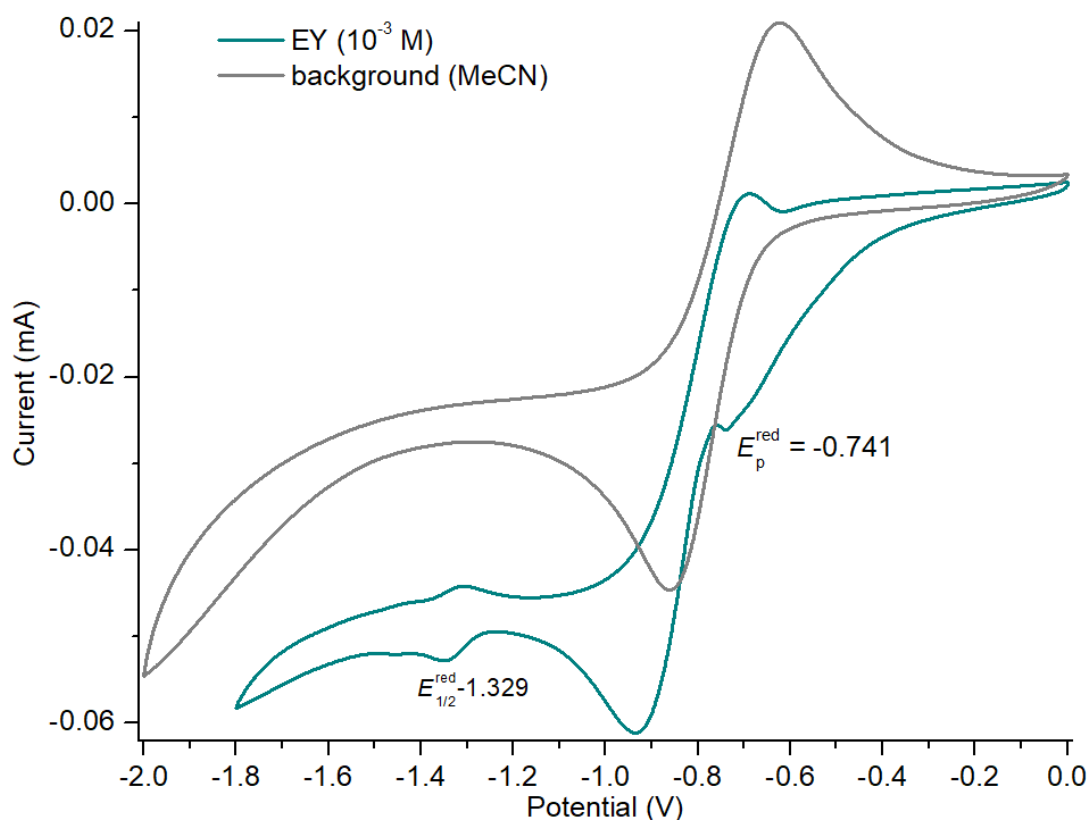


Figure S13 Cathodic cyclic voltammograms of eosin Y (10^{-3} M) in CH_3CN

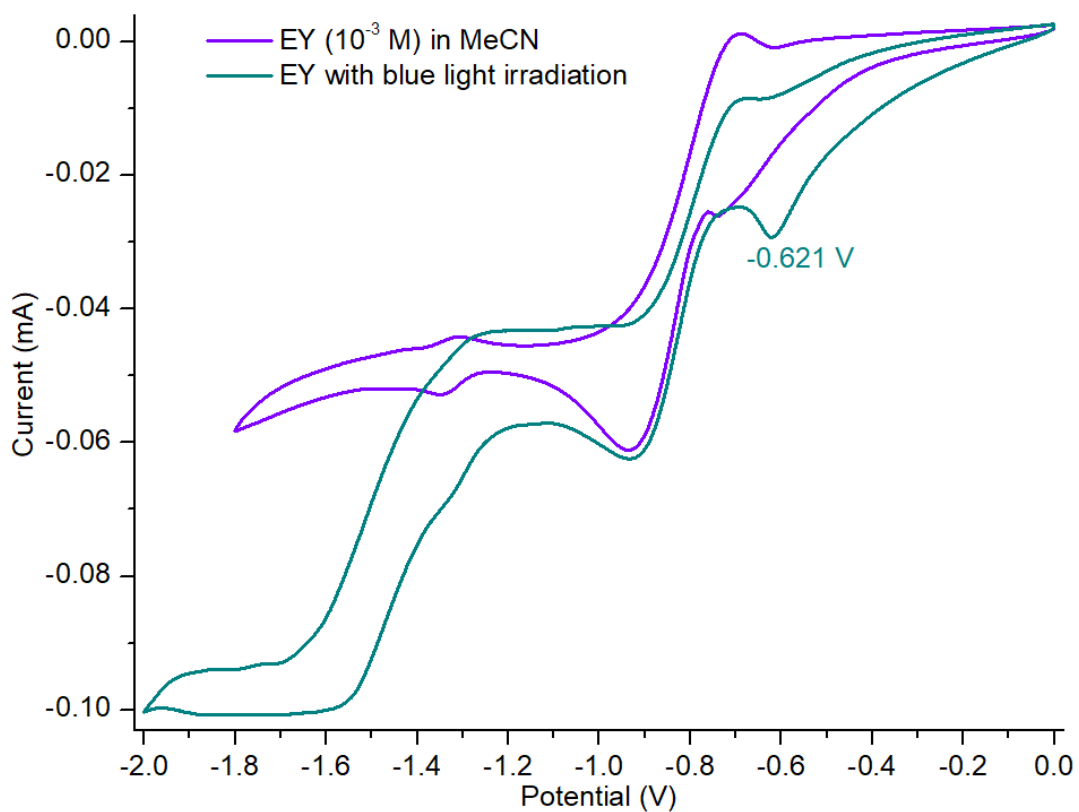


Figure S14 Cathodic cyclic voltammograms of eosin Y (10^{-3} M) in CH_3CN with or without blue light irradiation

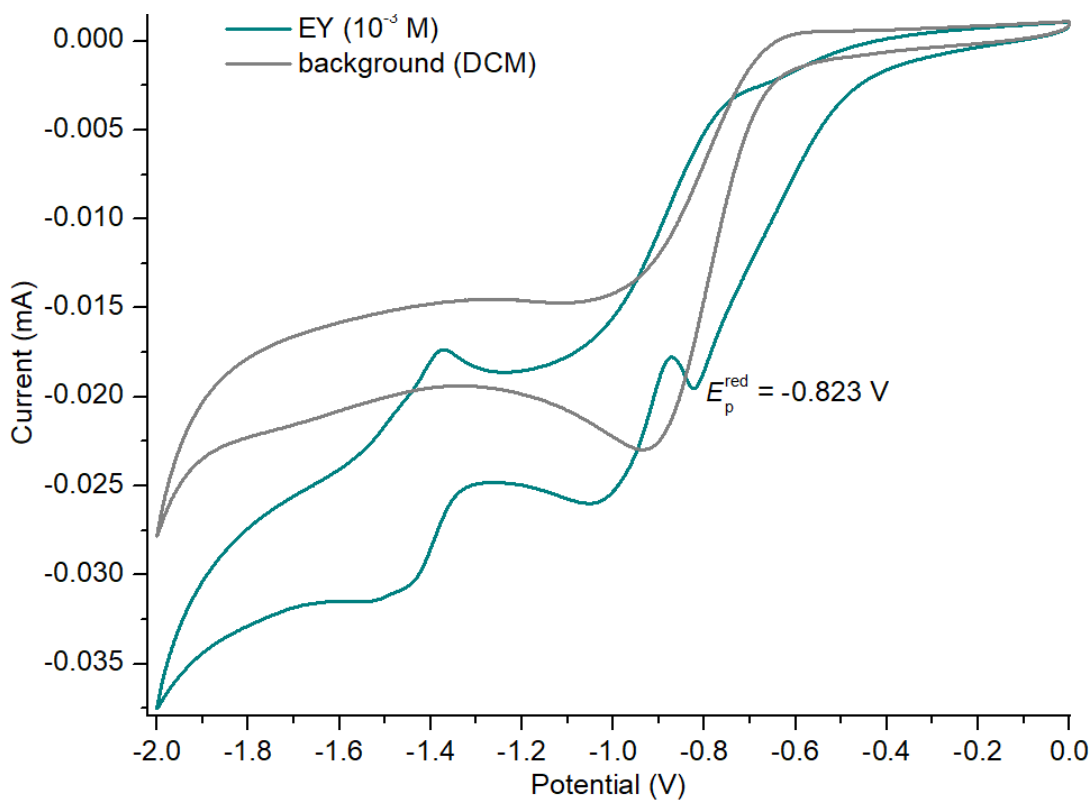


Figure S15 Cathodic cyclic voltammograms of eosin Y (10^{-3} M) in CH_2Cl_2

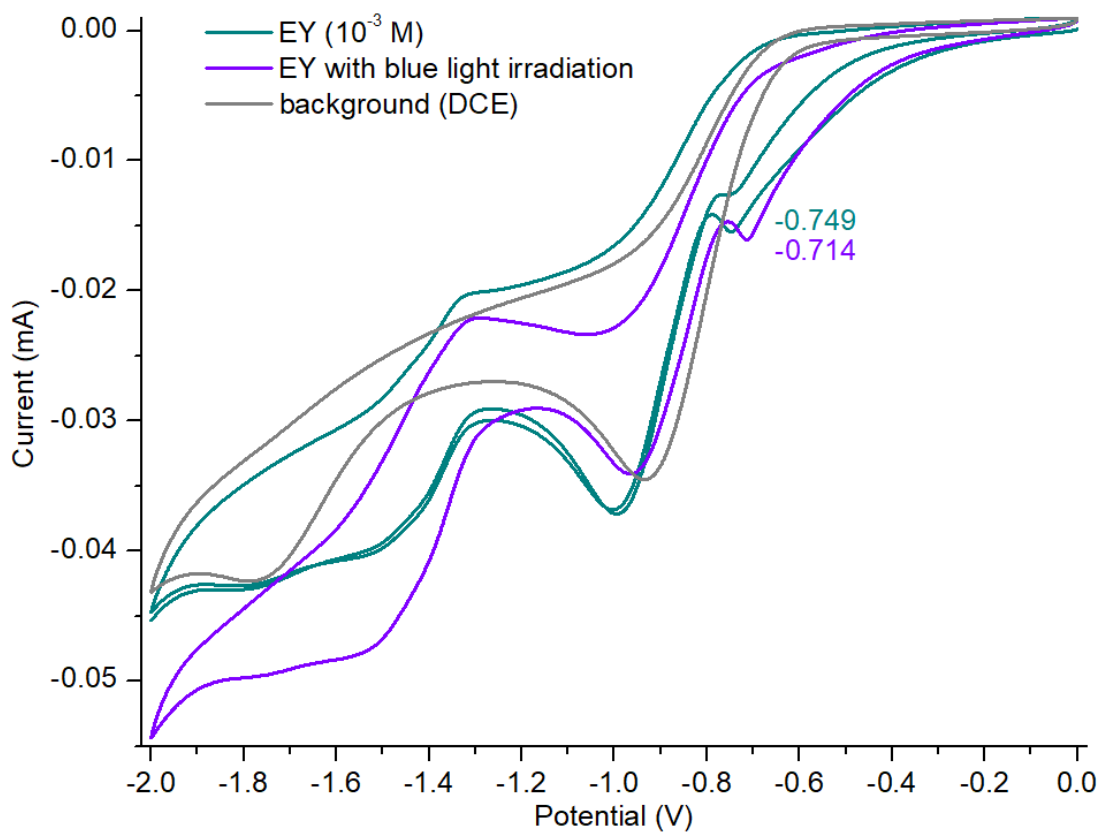


Figure S16 Cathodic cyclic voltammograms of eosin Y (10^{-3} M) in DCE

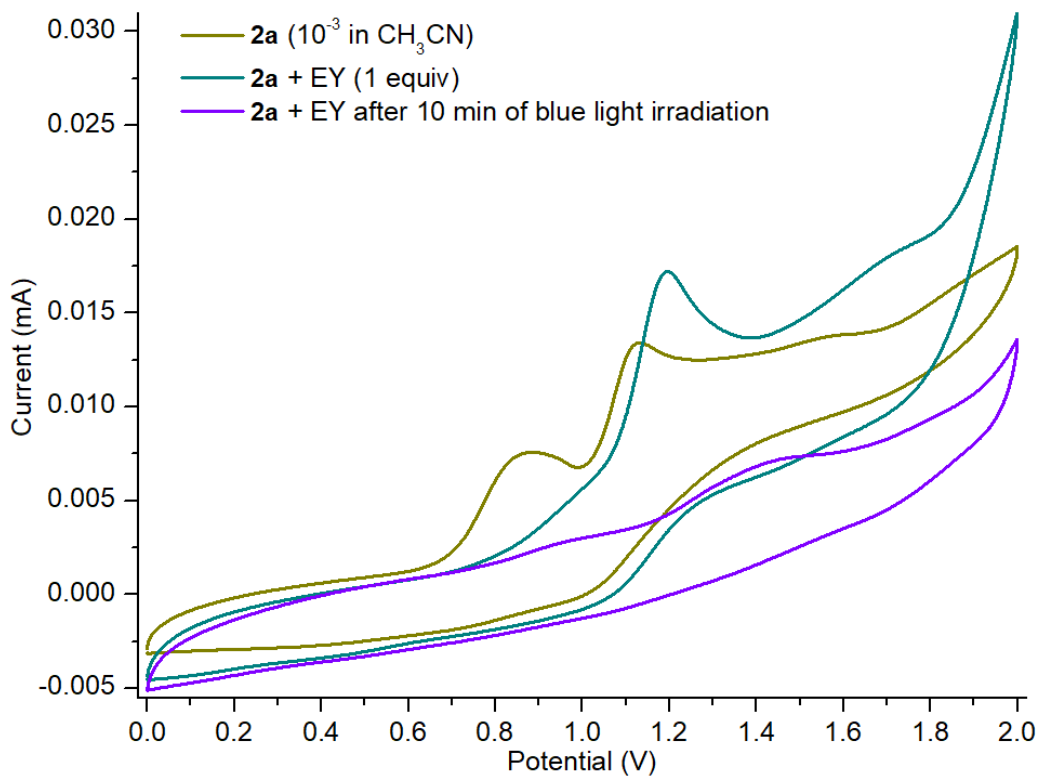


Figure S17 Anodic cyclic voltammogram of **2a** (10^{-3} M) and an equimolar mixture of **2a** and EY (10^{-3} M) with or without 10 min of blue light irradiation

5. Fluorescence spectra

Fluorescence spectra were collected on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). It has been established that **2a** could attenuate eosin Y fluorescence,^[3] although those experiments were troubled by aggregation-induced emission (AIE).

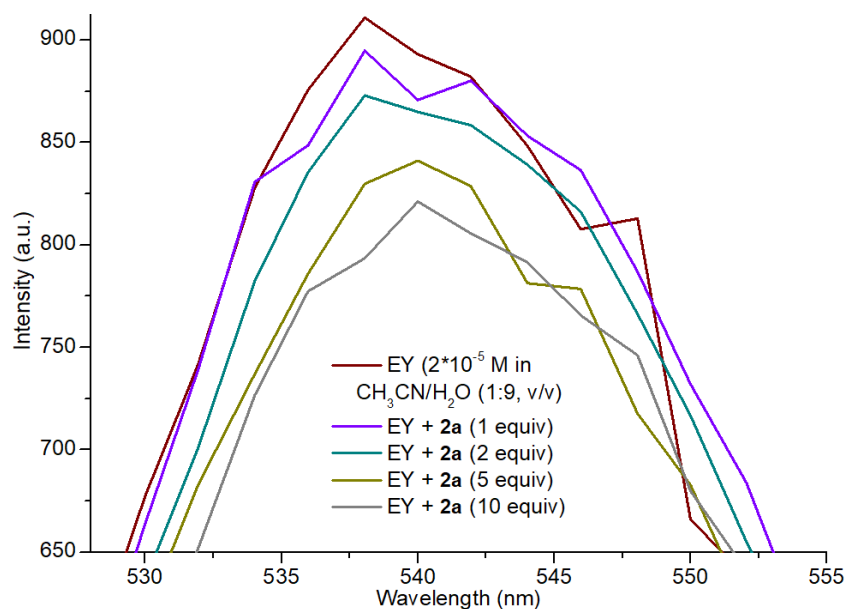


Figure S18 Fluorescence quenching of eosin Y (2×10^{-5} M) in the presence of **2a** in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:9, v/v). The solution was excited at 455 nm (ex. slit 10 nm, em. slit 10 nm).

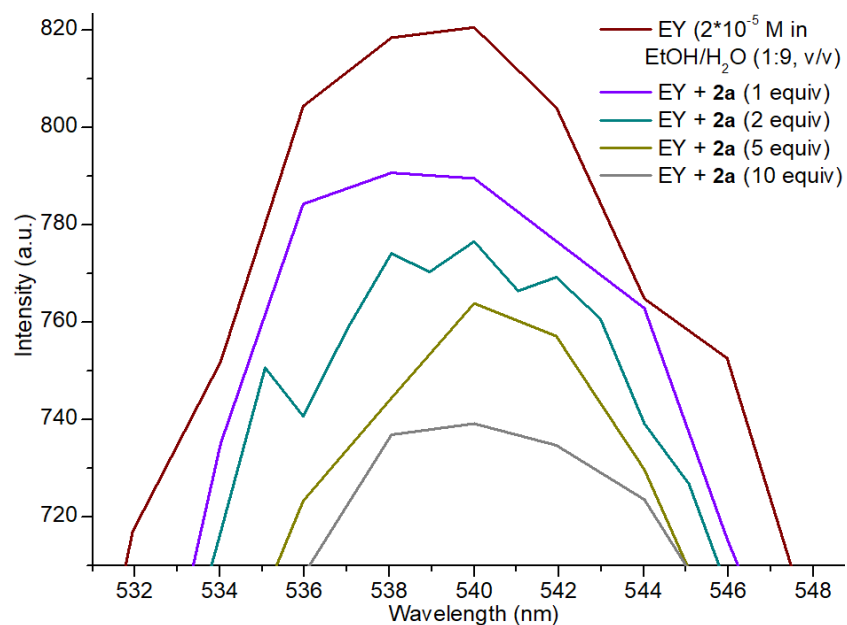


Figure S19 Fluorescence quenching of eosin Y (2×10^{-5} M) in the presence of **2a** in $\text{EtOH}/\text{H}_2\text{O}$ (1:9, v/v). The solution was excited at 455 nm (ex. slit 10 nm, em. slit 10 nm).

[3] a) J. Jeon, Y.-T. He, S. Shin and S. Hong, *Angew. Chem. Int. Ed.*, 2020, **59**, 281–285; b) Y.-T. He, D. Kang, I. Kim and S. Hong, *Green Chem.*, 2018, **20**, 5209–5214.

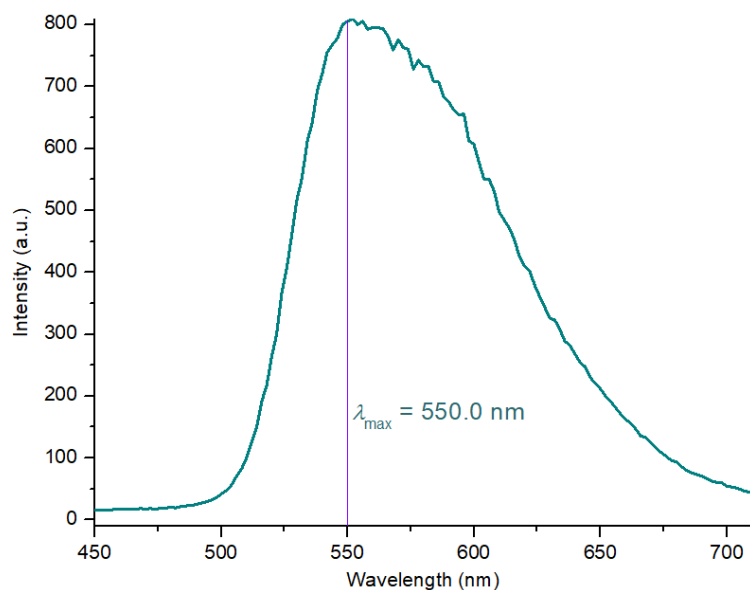


Figure S20 Fluorescence of eosin Y (10^{-3} M) in CH_3CN . The solution was excited at 366 nm (ex. slit 10 nm, em. slit 10 nm)

6. UV-Vis spectroscopic measurements

The UV-Vis absorption spectra were collected on a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan). A significant bathochromic shift was observed upon mixing eosin Y with **2a**.

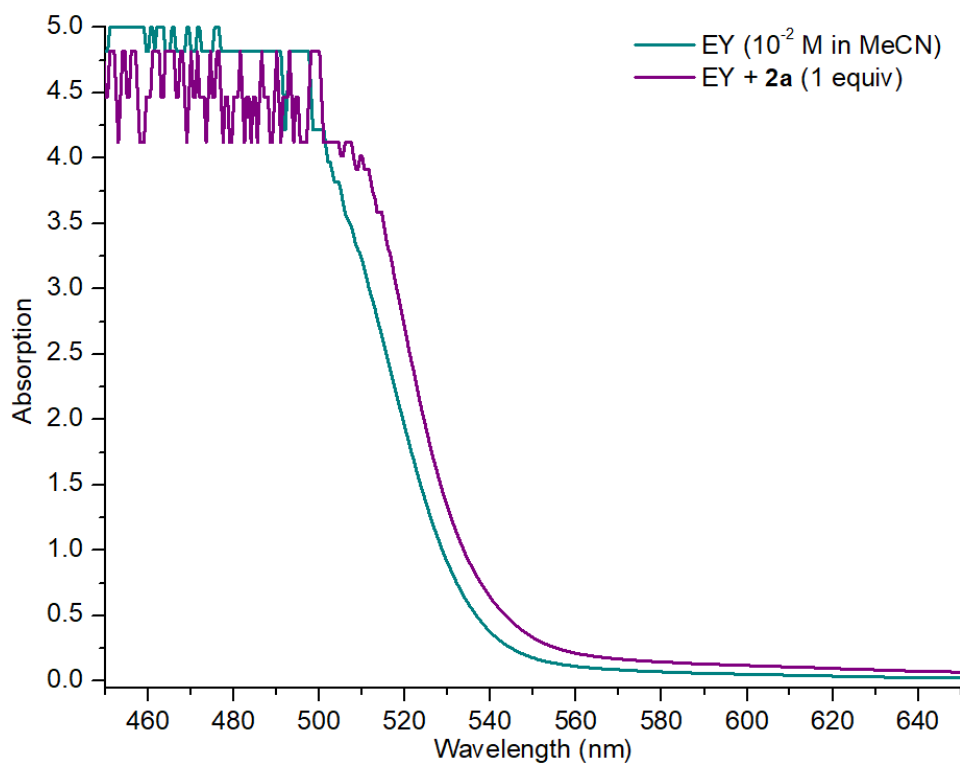


Figure S21 UV-vis spectra of EY (10^{-2} M) and an equimolar mixture of EY and **2a** (10^{-2} M) in CH_3CN

7. Determination of the excited-state reduction potential of eosin Y in MeCN

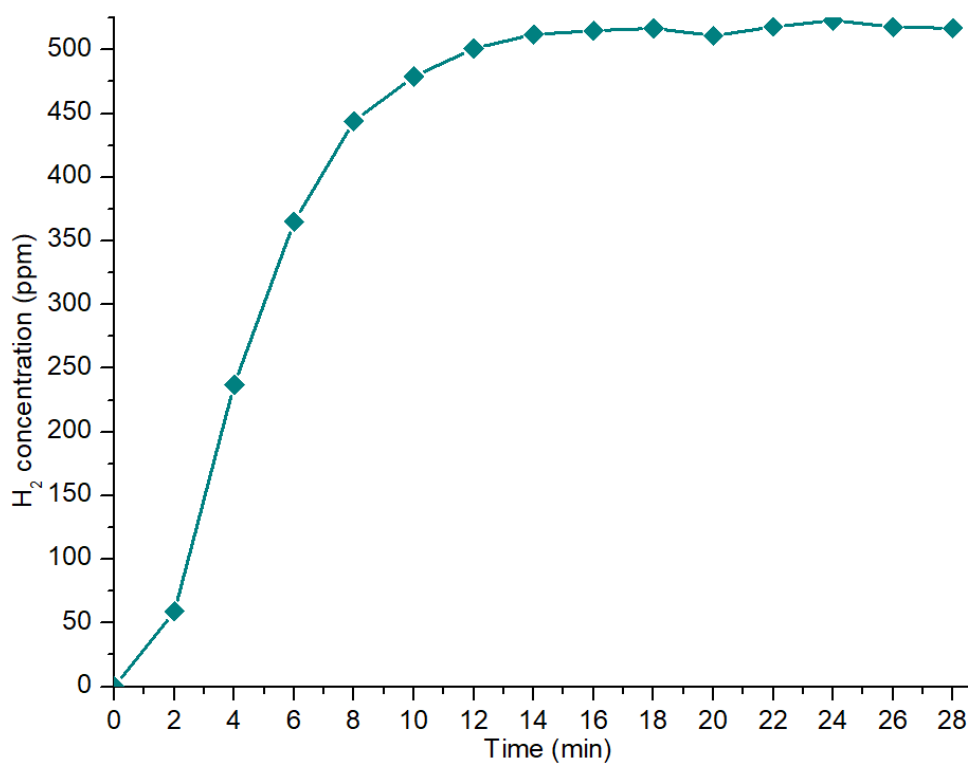
The excited-state reduction potential of eosin Y ($E[\text{EY}^*/\text{EY}^{\bullet-}]$) is estimated to be 1.51 V vs. Ag/AgCl according to the following equations:

$$E^{\text{red}*}(\text{EY}^*/\text{EY}^{\bullet-}) = E^{\text{red}}(\text{EY}^*/\text{EY}^{\bullet-}) + E_{0,0}$$

where $E^{\text{red}}(\text{EY}^*/\text{EY}^{\bullet-}, -0.741 \text{ V})$ was obtained from its cyclic voltammetry spectrum (Figure S13); $E_{0,0}$ is calculated from its photoluminescence maximum (550 nm as shown in Figure S20) using the equation $E_{0,0} = hc/\lambda_{\text{max}} = 1240 \text{ nm}/550 \text{ nm}$.

8. Hydrogen detection tests

The hydrogen detection tests were conducted with a H_2 detector (XLA-BX-H2), which was connected with the model reaction under standard conditions by a syringe with the pump on. The detector readings were recorded (Figure S22).

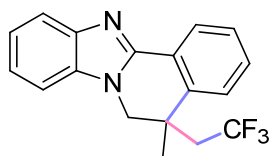


	A(X)	B(Y)
Long Name	Time	H2 concentration
Units	min	ppm
Comments		
1	0	0
2	2	59
3	4	237
4	6	365
5	8	444
6	10	479
7	12	501
8	14	512
9	16	515
10	18	517
11	20	511
12	22	518
13	24	523
14	26	518
15	28	517

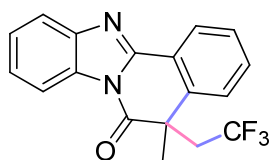


Figure S22 Hydrogen detection tests

VI. Spectral data of products and new compounds



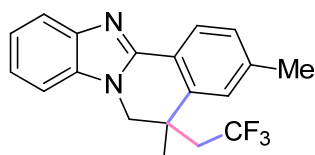
5-Methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3a**),^[4] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 83% yield (79.1 mg), colorless oil. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.37 – 8.35 (m, 1H), 7.87 – 7.83 (m, 1H), 7.52 – 7.45 (m, 3H), 7.41 – 7.36 (m, 1H), 7.35 – 7.29 (m, 2H), 4.47 (d, *J* = 13.0 Hz, 1H), 3.98 (d, *J* = 12.9 Hz, 1H), 2.43 – 2.23 (m, 2H), 1.74 (d, *J* = 1.4 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.4, 143.9, 140.7, 134.6, 130.9, 128.4, 126.3, 126.0 (q, *J* = 277.4 Hz), 125.3, 124.8, 123.1, 122.8, 119.9, 109.1, 49.4 (q, *J* = 2.1 Hz), 41.6 (q, *J* = 26.9 Hz), 36.3 (q, *J* = 1.6 Hz), 22.6 (q, *J* = 1.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -59.65 (t, *J* = 11.8 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₈H₁₆F₃N₂⁺ ([M+H]⁺) 317.1260. Found 317.1258.



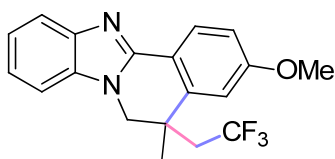
5-Methyl-5-(2,2,2-trifluoroethyl)benzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one (**3b**),^[5] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 64% yield (63.3 mg), colorless oil. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.52 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.38 – 8.33 (m, 1H), 7.85 – 7.82 (m, 1H), 7.62 – 7.58 (m, 1H), 7.55 – 7.51 (m, 1H), 7.49 – 7.42 (m, 3H), 3.54 – 3.42 (m, 1H), 3.00 – 2.89 (m, 1H), 1.77 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 171.0, 149.2, 144.0, 138.4, 131.6, 131.4, 128.4, 126.5, 126.3, 126.2, 125.8, 125.4, 124.9 (q, *J* = 277.0 Hz), 122.4, 120.0, 115.7, 45.2 (q, *J* = 2.3 Hz), 43.9 (q, *J* = 27.5 Hz), 31.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.36 (t, *J* = 9.0 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₈H₁₄F₃N₂O⁺ ([M+H]⁺) 331.1053. Found 331.1041.

[4] R. Kong, T. Fu, R. Yang, D. Chen, D. Liang, Y. Dong, W. Li and B. Wang, *ChemCatChem*, 2021, **13**, 2952–2958.

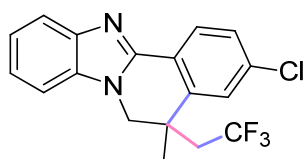
[5] K. Sun, G. Li, S. Guo, Z. Zhang and G. Zhang, *Org. Biomol. Chem.*, 2021, **19**, 375–378.



3,5-Dimethyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3c1**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 72% yield (71.7 mg), pale yellow solid: mp 97 – 98 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.39 – 7.35 (m, 1H), 7.32 – 7.28 (m, 3H), 7.26 (d, *J* = 1.4 Hz, 1H), 4.46 (d, *J* = 12.9 Hz, 1H), 3.94 (d, *J* = 12.9 Hz, 1H), 2.45 (s, 3H), 2.40 – 2.25 (m, 2H), 1.73 (d, *J* = 1.3 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.7, 143.9, 141.3, 140.8, 134.6, 129.2, 126.3, 126.0 (q, *J* = 277.4 Hz), 125.4, 122.9, 122.7, 122.5, 119.7, 109.0, 49.3 (q, *J* = 2.2 Hz), 41.5 (q, *J* = 26.8 Hz), 36.2 (q, *J* = 1.8 Hz), 22.5 (q, *J* = 1.9 Hz), 21.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -59.66 (t, *J* = 10.8 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₉H₁₈F₃N₂⁺ ([M+H]⁺) 331.1417. Found 331.1420.

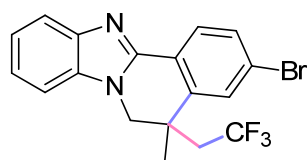


3-Methoxy-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3c2**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 77% yield (63.9 mg), pale yellow solid: mp 124 – 125 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.36 – 7.33 (m, 1H), 7.31 – 7.28 (m, 2H), 7.01 – 6.97 (m, 2H), 4.45 (d, *J* = 12.9 Hz, 1H), 3.93 (d, *J* = 12.9 Hz, 1H), 3.90 (s, 3H), 2.42 – 2.21 (m, 2H), 1.71 (d, *J* = 1.3 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.7, 148.7, 143.9, 142.8, 134.6, 128.1, 126.0 (q, *J* = 279.0 Hz), 122.6 (q, *J* = 3.0 Hz), 119.5, 118.0, 112.8, 111.6, 108.9, 55.5, 49.31 (q, *J* = 2.1 Hz), 41.5 (q, *J* = 27.1 Hz), 36.38 (q, *J* = 1.8 Hz), 22.5 (q, *J* = 1.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -59.64 (t, *J* = 11.2 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₉H₁₈F₃N₂O⁺ ([M+H]⁺) 347.1366. Found 347.1370.

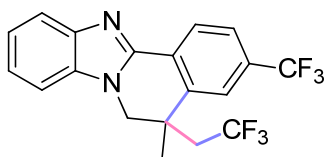


3-Chloro-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoqu

inoline (**3c3**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 68% yield (71.1 mg), white solid: mp 142 – 143 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.28 (dd, $J = 7.0, 0.8$ Hz, 1H), 7.85 – 7.80 (m, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.38 – 7.29 (m, 3H), 4.45 (d, $J = 13.0$ Hz, 1H), 3.95 (d, $J = 13.0$ Hz, 1H), 2.41 – 2.22 (m, 2H), 1.72 (d, $J = 1.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.5, 143.8, 142.3, 136.8, 134.6, 128.8, 127.7, 125.8 (q, $J = 277.3$ Hz), 125.4, 123.9, 123.4, 123.0, 120.0, 109.1, 49.3 (d, $J = 2.2$ Hz), 41.4 (q, $J = 27.2$ Hz), 36.5 (q, $J = 1.6$ Hz), 22.5 (q, $J = 1.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.63 (t, $J = 10.5$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 351.0870. Found 351.0872.

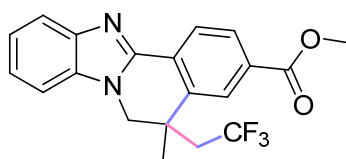


3-Bromo-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3c4**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 81% yield (95.9 mg), white solid: mp 143 – 144 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.1$ Hz, 1H), 7.85 – 7.80 (m, 1H), 7.63 – 7.58 (m, 2H), 7.38 – 7.28 (m, 3H), 4.44 (d, $J = 13.0$ Hz, 1H), 3.93 (d, $J = 13.0$ Hz, 1H), 2.40 – 2.21 (m, 2H), 1.72 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.5, 143.8, 142.5, 134.6, 131.7, 128.3, 127.8, 125.8 (q, $J = 277.3$ Hz), 125.1, 124.3, 123.4, 123.0, 120.0, 109.2, 49.2 (q, $J = 2.2$ Hz), 41.4 (q, $J = 27.1$ Hz), 36.4 (q, $J = 1.6$ Hz), 22.4 (q, $J = 1.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.62 (t, $J = 11.1$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{15}\text{BrF}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 395.0365. Found 395.0361.



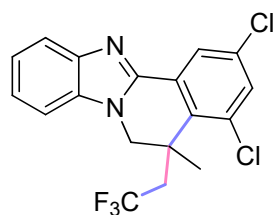
5-Methyl-5-(2,2,2-trifluoroethyl)-3-(trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3c5**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 87% yield (100.2 mg), white solid: mp 160 – 161 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, $J = 8.1$ Hz, 1H), 7.89 – 7.84 (m, 1H), 7.74 (d, $J = 8.2$ Hz, 1H), 7.70 (s, 1H), 7.43 – 7.39 (m, 1H), 7.39 – 7.32 (m, 2H), 4.51 (d, $J = 13.1$ Hz, 1H), 4.01 (d, $J = 13.0$ Hz, 1H),

2.45 – 2.26 (m, 2H), 1.79 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 146.9, 143.9, 141.1, 134.6, 132.3 (q, $J = 32.6$ Hz), 128.6 (q, $J = 1.6$ Hz), 126.7, 125.4 (q, $J = 3.7$ Hz), 125.8 (q, $J = 279.0$ Hz), 123.8, 123.7 (q, $J = 272.6$ Hz), 123.3, 122.1 (q, $J = 3.8$ Hz), 120.3, 109.3, 49.4 (q, $J = 2.0$ Hz), 41.5 (q, $J = 27.4$ Hz), 36.5 (q, $J = 1.6$ Hz), 22.5 (q, $J = 2.1$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.66 (t, $J = 11.2$ Hz, 3F), -62.79 (s, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_6\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 385.1134. Found 385.1135.



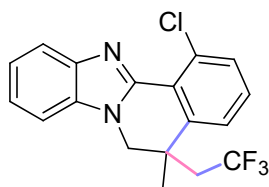
Methyl

5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline-3-carboxylate (**3c6**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 75% yield (84.5 mg), white solid: mp 186 – 187 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 8.0$ Hz, 1H), 8.15 – 8.12 (m, 2H), 7.88 – 7.84 (m, 1H), 7.43 – 7.31 (m, 3H), 4.51 (d, $J = 13.0$ Hz, 1H), 4.02 (d, $J = 13.1$ Hz, 1H), 3.97 (s, 3H), 2.46 – 2.28 (m, 2H), 1.79 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.3, 147.3, 144.0, 140.7, 134.7, 131.9, 129.5, 129.3, 126.32, 126.28, 125.9 (q, $J = 277.2$ Hz), 123.7, 123.2, 120.3, 109.3, 52.5, 49.3 (d, $J = 2.0$ Hz), 41.5 (q, $J = 27.0$ Hz), 36.5 (d, $J = 1.7$ Hz), 22.7 (d, $J = 2.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.63 (t, $J = 10.7$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 375.1315. Found 375.1313.

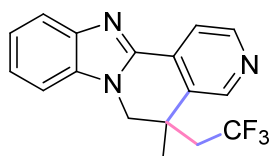


2,4-Dichloro-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3d**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 62% yield (71.4 mg), white solid: mp 219 – 220 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 2.3$ Hz, 1H), 7.84 – 7.80 (m, 1H), 7.49 (d, $J = 2.3$ Hz, 1H), 7.42 – 7.38 (m, 1H), 7.37 – 7.31 (m, 2H), 4.55 (d, $J = 13.3$ Hz, 1H), 3.97 (d, $J = 13.4$ Hz, 1H), 2.70 – 2.49 (m, 2H), 1.95 (s,

3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.0, 143.9, 135.9, 135.0, 134.5, 134.1, 133.2, 129.3, 125.8 (q, $J = 277.4$ Hz), 125.3, 123.8, 123.3, 120.1, 109.4, 49.5 (q, $J = 2.3$ Hz), 38.7 (q, $J = 27.1$ Hz), 38.0 (q, $J = 1.9$ Hz), 24.3 (q, $J = 1.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.63 (t, $J = 10.7$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 385.0481. Found 385.0484.

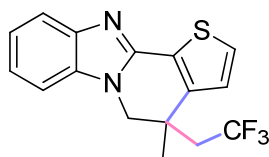


1-Chloro-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3e**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 62% yield (65.0 mg), white solid: mp 157 – 158 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.95 (m, 1H), 7.58 – 7.54 (m, 1H), 7.40 (s, 1H), 7.39 (d, $J = 2.2$ Hz, 1H), 7.38 – 7.30 (m, 3H), 4.44 (d, $J = 13.1$ Hz, 1H), 3.99 (dd, $J = 13.1, 1.1$ Hz, 1H), 2.20 – 2.11 (m, 2H), 1.72 (d, $J = 1.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 145.5, 143.7, 143.5, 133.6, 133.4, 131.5, 130.5, 125.8 (q, $J = 277.3$ Hz), 123.9, 123.8, 123.6, 122.8, 120.9, 108.9, 49.1 (q, $J = 1.9$ Hz), 40.8 (q, $J = 27.2$ Hz), 37.1 (q, $J = 1.8$ Hz), 22.5 (q, $J = 2.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.56 (t, $J = 11.7$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 351.0870. Found 351.0868.

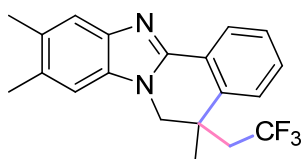


5-Methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*][2,6]naphthyridine (**3f**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 88% yield (83.5 mg), brown solid: mp 128 – 129 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.79 – 8.74 (m, 2H), 8.15 (d, $J = 4.9$ Hz, 1H), 7.90 – 7.86 (m, 1H), 7.44 – 7.34 (m, 3H), 4.51 (d, $J = 13.1$ Hz, 1H), 4.05 (d, $J = 13.0$ Hz, 1H), 2.49 – 2.32 (m, 2H), 1.83 (d, $J = 1.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.0, 147.0, 145.7, 143.9, 134.7, 134.4, 132.3, 125.7 (q, $J = 277.1$ Hz), 124.3, 123.5, 120.6, 118.9, 109.5, 49.7 (q, $J = 2.1$ Hz), 41.6 (q, $J = 27.2$ Hz), 35.3, 22.4 (q, $J = 1.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.63 (t, $J = 10.6$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{N}_3^+$ ($[\text{M}+\text{H}]^+$) 318.1213. Found

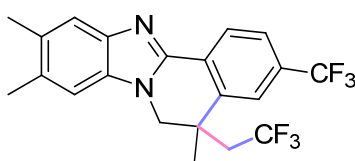
318.1216.



4-Methyl-4-(2,2,2-trifluoroethyl)-4,5-dihydrobenzo[4,5]imidazo[1,2-*a*]thieno[2,3-*c*]pyridine (**3g**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 42% yield (40.4 mg), pale yellow oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.78 (m, 1H), 7.47 (d, $J = 5.1$ Hz, 1H), 7.35 – 7.26 (m, 3H), 7.09 (d, $J = 5.1$ Hz, 1H), 4.41 (d, $J = 12.9$ Hz, 1H), 3.95 (d, $J = 12.9$ Hz, 1H), 2.42 (q, $J = 11.2$ Hz, 2H), 1.68 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 145.9, 145.3, 143.9, 134.4, 128.8, 126.2, 126.0 (q, $J = 277.1$ Hz), 124.8, 123.2, 122.7, 119.8, 109.0, 51.0 (q, $J = 2.2$ Hz), 41.4 (q, $J = 27.0$ Hz), 36.0 (q, $J = 1.9$ Hz), 23.3 (q, $J = 1.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.74 (t, $J = 10.8$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_2\text{S}^+$ ($[\text{M}+\text{H}]^+$) 323.0824. Found 323.0829.

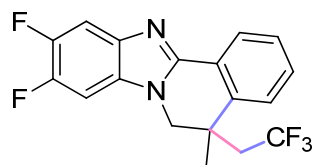


5,9,10-Trimethyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3h1**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 72% yield (74.6 mg), yellowish solid: mp 133 – 134 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.33 – 8.30 (m, 1H), 7.60 (s, 1H), 7.49 – 7.42 (m, 3H), 7.14 (s, 1H), 4.41 (d, $J = 12.9$ Hz, 1H), 3.93 (d, $J = 12.9$ Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.37 – 2.24 (m, 2H), 1.72 (d, $J = 1.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.6, 142.5, 140.4, 133.2, 132.4, 131.7, 130.4, 128.3, 126.1, 126.0 (q, $J = 277.3$ Hz), 125.6, 124.7, 119.9, 109.3, 49.4 (q, $J = 1.6$ Hz), 41.5 (q, $J = 26.9$ Hz), 36.3 (q, $J = 1.4$ Hz), 22.5 (q, $J = 1.3$ Hz), 20.6, 20.4. ^{19}F NMR (376 MHz, CDCl_3) δ -59.64 (t, $J = 11.4$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 345.1573. Found 345.1588.

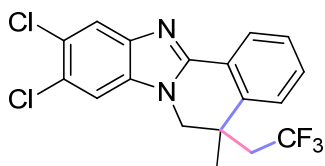


5,9,10-Trimethyl-5-(2,2,2-trifluoroethyl)-3-(trifluoromethyl)-5,6-dihydrobenzo[4,5]i

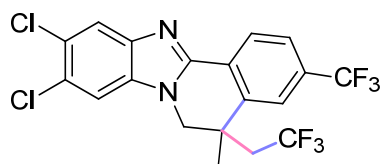
midazo[2,1-*a*]isoquinoline (**3h2**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 69% yield (84.8 mg), white solid: mp 180 – 181 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.61 (s, 1H), 7.16 (s, 1H), 4.45 (d, *J* = 13.0 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.38 – 2.24 (m, 2H), 1.77 (d, *J* = 1.4 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.1, 142.5, 140.8, 133.3, 133.2, 132.4, 131.9 (d, *J* = 32.4 Hz), 128.9, 126.4, 125.8 (q, *J* = 277.2 Hz), 125.3 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.8 Hz), 122.0 (q, *J* = 3.8 Hz), 120.2, 109.4, 49.3 (q, *J* = 2.1 Hz), 41.4 (q, *J* = 27.1 Hz), 36.5 (q, *J* = 1.8 Hz), 22.4 (q, *J* = 1.9 Hz), 20.7, 20.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -59.64 (t, *J* = 11.8 Hz, 3F), -62.73 (s, 3F). HRMS (ESI-TOF) Calcd for C₂₁H₁₉F₆N₂⁺ ([M+H]⁺) 413.1447. Found 413.1451.



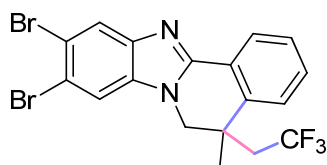
9,10-Difluoro-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3i**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 83% yield (87.3 mg), white solid: mp 178 – 179 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.27 (m, 1H), 7.60 (dd, *J* = 10.5, 7.2 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.16 (dd, *J* = 9.6, 6.8 Hz, 1H), 4.38 (d, *J* = 13.0 Hz, 1H), 3.96 (d, *J* = 12.9 Hz, 1H), 2.41 – 2.23 (m, 2H), 1.75 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 149.8 (d, *J* = 3.3 Hz), 149.4 (q, *J* = 13.9 Hz), 147.0 (q, *J* = 11.1 Hz), 140.4, 139.0 (q, *J* = 9.4 Hz), 131.1, 130.0 (d, *J* = 11.0 Hz), 128.5, 126.1, 125.8 (q, *J* = 277.3 Hz), 124.75, 124.70, 107.1 (q, *J* = 19.8 Hz), 97.0 (d, *J* = 23.0 Hz), 49.4 (q, *J* = 2.2 Hz), 41.6 (q, *J* = 27.1 Hz), 36.2 (q, *J* = 1.4 Hz), 22.5 (d, *J* = 2.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -59.82 (t, *J* = 10.7 Hz, 3F), -140.77 – -140.87 (m, 1F), -142.79 – -142.89 (m, 1F). HRMS (ESI-TOF) Calcd for C₁₈H₁₄F₅N₂⁺ ([M+H]⁺) 353.1072. Found 353.1071.



9,10-Dichloro-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3j1**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 81% yield (93.7 mg), yellowish solid: mp 184 – 185 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.29 – 8.27 (m, 1H), 7.87 (s, 1H), 7.56 – 7.46 (m, 4H), 4.39 (d, *J* = 13.0 Hz, 1H), 3.95 (d, *J* = 12.9 Hz, 1H), 2.41 – 2.23 (m, 2H), 1.73 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.2, 143.2, 140.7, 133.9, 131.5, 128.6, 127.0, 126.8, 126.5, 125.9 (q, *J* = 277.3 Hz), 124.8, 124.5, 120.9, 110.5, 49.5 (q, *J* = 2.0 Hz), 41.7 (q, *J* = 27.1 Hz), 36.2 (q, *J* = 1.7 Hz), 22.7 (q, *J* = 2.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -59.69 (t, *J* = 11.7 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₈H₁₄Cl₂F₃N₂⁺ ([M+H]⁺) 385.0481. Found 385.0488.

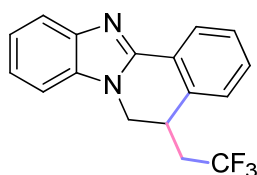


9,10-Dichloro-5-methyl-5-(2,2,2-trifluoroethyl)-3-(trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3j2**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 92% yield (125.0 mg), white solid: mp 209 – 210 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.45 – 8.43 (m, 1H), 7.93 (s, 1H), 7.76 (ddd, *J* = 8.1, 1.7, 0.8 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.52 (s, 1H), 4.45 (d, *J* = 13.1 Hz, 1H), 4.01 (d, *J* = 13.1 Hz, 1H), 2.41 – 2.30 (m, 2H), 1.79 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.7, 143.2, 141.2, 133.8, 133.1, 132.8, 128.0, 127.5, 127.1, 125.63 (q, *J* = 277.2 Hz), 125.58 (q, *J* = 3.9 Hz), 123.6 (q, *J* = 271.1 Hz), 122.1 (q, *J* = 4.0 Hz), 121.4, 110.7, 49.5 (q, *J* = 1.6 Hz), 41.6 (q, *J* = 27.5 Hz), 36.5 (q, *J* = 1.0 Hz), 22.6 (q, *J* = 1.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -59.68 (t, *J* = 10.3 Hz, 3F), -62.88 (s, 3F). HRMS (ESI-TOF) Calcd for C₁₉H₁₃Cl₂F₆N₂⁺ ([M+H]⁺) 453.0354. Found 453.0355.

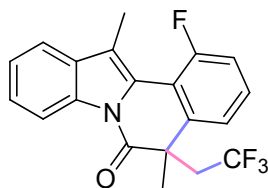


9,10-Dibromo-5-methyl-5-(2,2,2-trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3k**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 72% yield (101.7 mg), white solid: mp 196 – 197 °C. *R_f* (petroleum

ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.30 – 8.28 (m, 1H), 8.07 (s, 1H), 7.66 (s, 1H), 7.56 – 7.46 (m, 3H), 4.39 (d, J = 13.0 Hz, 1H), 3.94 (d, J = 13.0 Hz, 1H), 2.38 – 2.26 (m, 2H), 1.73 (d, J = 0.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.1, 144.2, 140.8, 134.8, 131.6, 128.6, 126.6, 125.8 (q, J = 277.2 Hz), 124.9, 124.5, 124.2, 118.2, 118.0, 113.6, 49.5 (q, J = 2.0 Hz), 41.7 (q, J = 27.0 Hz), 36.2 (q, J = 1.8 Hz), 22.7 (q, J = 1.9 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.67 (t, J = 11.0 Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{14}\text{Br}_2\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 472.9470. Found 472.9466.

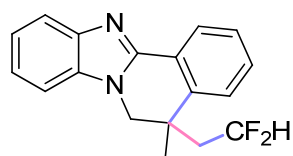


5-(2,2,2-Trifluoroethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3l**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 79% yield (71.8 mg), colorless oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.34 – 8.31 (m, 1H), 7.86 – 7.84 (m, 1H), 7.52 – 7.45 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 4.57 (dd, J = 13.0, 2.2 Hz, 1H), 4.28 (dd, J = 13.0, 4.2 Hz, 1H), 3.67 – 3.62 (m, 2H), 2.47 – 2.24 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.3, 144.0, 136.3, 134.9, 130.8, 128.8, 127.7, 126.2 (q, J = 276.2 Hz), 126.1, 125.9, 123.2, 122.8, 120.0, 109.1, 43.7, 37.5 (q, J = 27.8 Hz), 33.4 (q, J = 2.9 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -63.54 (t, J = 10.6 Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 303.1104. Found 303.1105.

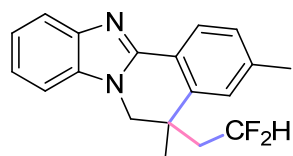


1-Fluoro-5,12-dimethyl-5-(2,2,2-trifluoroethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (**3m**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 69% yield (75.0 mg), white solid: mp 96 – 97 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.51 – 8.48 (m, 1H), 7.63 – 7.61 (m, 1H), 7.45 – 7.35 (m, 3H), 7.26 – 7.24 (m, 1H), 7.17 – 7.12 (m, 1H), 3.29 – 3.17 (m, 1H), 2.82 – 2.71 (m, 1H), 2.51 (d, J = 10.0 Hz, 3H), 1.72 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 169.6, 159.2, 156.7, 138.1 (d, J = 3.2 Hz), 135.1, 132.8, 129.3 (d, J = 9.1

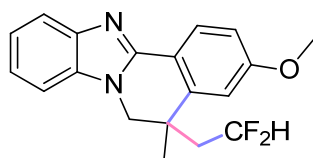
Hz), 126.4, 125.1 (q, $J = 277.3$ Hz), 124.5, 122.0 (d, $J = 3.1$ Hz), 119.1, 118.8 (d, $J = 1.8$ Hz), 116.3, 115.5 (d, $J = 23.6$ Hz), 114.9 (d, $J = 15.5$ Hz), 45.5 (p, $J = 2.2$ Hz), 43.5 (q, $J = 27.7$ Hz), 28.2, 11.7 (d, $J = 21.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -60.33 (t, $J = 10.3$ Hz, 3F), -105.40 – -105.52 (m, 1F). HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{16}\text{F}_4\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 362.1163. Found 362.1175.



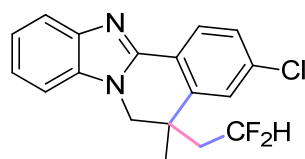
5-(2,2-Difluoroethyl)-5-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3n1**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 83% yield (74.2 mg), brown oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.39 – 8.36 (m, 1H), 7.86 – 7.82 (m, 1H), 7.52 – 7.43 (m, 3H), 7.39 – 7.35 (m, 1H), 7.33 – 7.29 (m, 2H), 5.75 – 5.45 (m, 1H), 4.29 (d, $J = 12.7$ Hz, 1H), 4.02 – 3.98 (m, 1H), 2.15 – 2.05 (m, 2H), 1.66 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.3, 143.9, 139.9, 134.7, 130.8, 128.3, 126.5, 125.5, 124.9, 123.0, 122.8, 119.9, 115.9 (t, $J = 238.1$ Hz), 109.0, 50.8, 42.6 (t, $J = 20.8$ Hz), 36.2 (t, $J = 4.5$ Hz), 23.5. ^{19}F NMR (376 MHz, CDCl_3) δ -112.01 – -112.27 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{17}\text{F}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 299.1354. Found 299.1352.



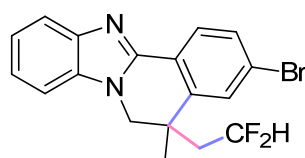
5-(2,2-Difluoroethyl)-3,5-dimethyl-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3n2**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 68% yield (63.8 mg), colorless oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 7.9$ Hz, 1H), 7.85 – 7.81 (m, 1H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 3H), 7.24 (d, $J = 1.5$ Hz, 1H), 5.76 – 5.46 (m, 1H), 4.28 (d, $J = 12.7$ Hz, 1H), 3.99 – 3.96 (m, 1H), 2.45 (s, 3H), 2.14 – 2.04 (m, 2H), 1.64 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.6, 143.9, 141.1, 139.9, 134.7, 129.1, 126.5, 125.5, 122.80, 122.78, 122.7, 119.7, 115.9 (t, $J = 238.0$ Hz), 108.9, 50.8, 42.6 (t, $J = 20.8$ Hz), 36.1 (q, $J = 1.2$ Hz), 23.5, 22.0. ^{19}F NMR (376 MHz, CDCl_3) δ -111.98 – -112.25 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 313.1511. Found 313.1500.



5-(2,2-Difluoroethyl)-3-methoxy-5-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3n3**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 84% yield (82.8 mg), white solid: mp 97 – 98 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, J = 8.5 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.36 – 7.26 (m, 3H), 7.01 – 6.95 (m, 2H), 5.77 – 5.46 (m, 1H), 4.25 (d, J = 12.7 Hz, 1H), 3.96 – 3.93 (m, 1H), 3.90 (s, 3H), 2.13 – 2.03 (m, 2H), 1.63 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 161.6, 148.6, 143.9, 141.9, 134.7, 128.3, 122.6, 119.5, 118.3, 115.9 (t, J = 238.0 Hz), 112.7, 111.7, 108.8, 55.5, 50.8, 42.4 (t, J = 20.7 Hz), 36.3 (t, J = 4.0 Hz), 23.4. ^{19}F NMR (376 MHz, CDCl_3) δ -112.00 – -112.26 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 329.1460. Found 329.1463.

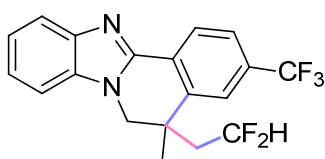


3-Chloro-5-(2,2-difluoroethyl)-5-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3n4**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 75% yield (75.0 mg), pale yellow solid: mp 101 – 102 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, J = 8.3 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.46 (dd, J = 8.3, 2.0 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.39 – 7.29 (m, 3H), 5.81 – 5.51 (m, 1H), 4.32 (d, J = 12.8 Hz, 1H), 4.01 – 3.97 (m, 1H), 2.15 – 2.04 (m, 2H), 1.66 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.5, 143.9, 141.9, 136.8, 134.7, 128.7, 127.8, 125.4, 124.1, 123.3, 123.0, 120.0, 115.6 (t, J = 238.4 Hz), 109.1, 50.5, 42.4 (t, J = 20.8 Hz), 36.4 (t, J = 4.7 Hz), 23.3. ^{19}F NMR (376 MHz, CDCl_3) δ -112.09 – -112.34 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{ClF}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 333.0965. Found 333.0979.

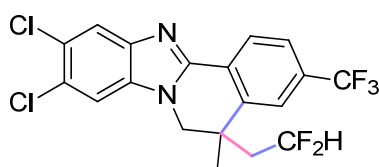


3-Bromo-5-(2,2-difluoroethyl)-5-methyl-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (**3n5**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1,

v/v) in 89% yield (100.7 mg), pale yellow solid: mp 131 – 132 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 8.3$ Hz, 1H), 7.88 – 7.85 (m, 1H), 7.63 (dd, $J = 8.3, 1.9$ Hz, 1H), 7.59 (d, $J = 1.8$ Hz, 1H), 7.41 – 7.32 (m, 3H), 5.84 – 5.54 (m, 1H), 4.36 (d, $J = 12.9$ Hz, 1H), 4.03 – 3.99 (m, 1H), 2.16 – 2.05 (m, 2H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.1, 142.1, 134.2, 131.8, 128.31, 128.27, 125.7, 123.7, 123.5, 119.6, 115.5 (t, $J = 238.5$ Hz), 109.3, 50.4, 42.4 (t, $J = 21.1$ Hz), 36.4 (t, $J = 4.5$ Hz), 23.3. ^{19}F NMR (376 MHz, CDCl_3) δ -112.17 – -112.41 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{BrF}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 377.0459. Found 377.0463.

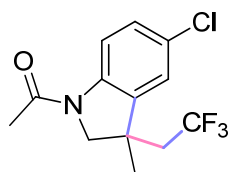


5-(2,2-Difluoroethyl)-5-methyl-3-(trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (**301**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 88% yield (96.2 mg), white solid: mp 97 – 98 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 8.1$ Hz, 1H), 7.89 – 7.84 (m, 1H), 7.75 – 7.73 (m, 1H), 7.67 (d, $J = 1.6$ Hz, 1H), 7.43 – 7.32 (m, 3H), 5.82 – 5.52 (m, 1H), 4.38 (d, $J = 12.8$ Hz, 1H), 4.06 – 4.02 (m, 1H), 2.22 – 2.03 (m, 2H), 1.71 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 146.9, 143.9, 140.9, 134.7, 132.3 (q, $J = 32.4$ Hz), 128.8 (q, $J = 0.4$ Hz), 126.8, 125.3 (q, $J = 3.9$ Hz), 125.1, 123.753 (q, $J = 270.9$ Hz), 123.752, 123.2, 122.0 (q, $J = 3.9$ Hz), 120.3, 115.5 (t, $J = 238.5$ Hz), 109.3, 50.4, 42.4 (t, $J = 20.8$ Hz), 36.5 (t, $J = 4.6$ Hz), 23.3. ^{19}F NMR (376 MHz, CDCl_3) δ -62.75 (s, 3F), -112.22 – -112.46 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{16}\text{F}_5\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 367.1228. Found 367.1230.

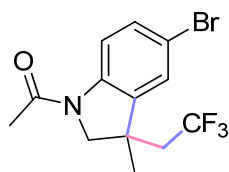


9,10-Dichloro-5-(2,2-difluoroethyl)-5-methyl-3-(trifluoromethyl)-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (**302**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 85% yield (110.5 mg), white solid: mp 223 – 224 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.34 (d, $J = 8.0$ Hz, 1H), 8.03 (d, $J = 9.5$ Hz, 2H), 7.92 (d, $J = 1.6$ Hz, 1H), 7.85 (dd, J

= 8.1, 1.6 Hz, 1H), 6.29 – 5.99 (m, 1H), 4.62 (d, $J = 13.2$ Hz, 1H), 4.22 (d, $J = 13.1$ Hz, 1H), 2.26 – 2.16 (m, 2H), 1.60 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO- d_6) δ 149.4, 143.3, 142.9, 134.8, 131.4 (q, $J = 31.7$ Hz), 128.5 (d, $J = 0.8$ Hz), 126.9, 126.0, 125.5, 125.3 (q, $J = 3.8$ Hz), 124.4 (q, $J = 271.1$ Hz), 123.3 (q, $J = 3.7$ Hz), 120.9, 116.6 (t, $J = 235.9$ Hz), 112.8, 49.8, 42.5 (t, $J = 20.7$ Hz), 36.5 (t, $J = 5.2$ Hz), 23.4. ^{19}F NMR (376 MHz, DMSO- d_6) δ -61.19 (s, 3F), -110.63 – -110.91 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{F}_5\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 435.0449. Found 435.0445.



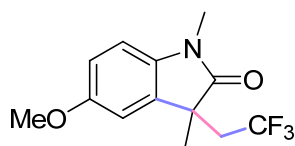
1-(5-Chloro-3-methyl-3-(2,2,2-trifluoroethyl)indolin-1-yl)ethanone (**5a1**),^[6] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 77% yield (67.5 mg), pale yellow oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.7$ Hz, 1H), 7.22 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.08 (d, $J = 2.2$ Hz, 1H), 4.13 (d, $J = 10.7$ Hz, 1H), 3.84 (d, $J = 10.8$ Hz, 1H), 2.59 – 2.39 (m, 2H), 2.24 (s, 3H), 1.47 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.6, 140.0, 139.3, 128.9, 128.7, 126.0 (q, $J = 276.8$ Hz), 122.4, 118.3, 61.1 (d, $J = 1.9$ Hz), 43.1 (q, $J = 26.8$ Hz), 41.1, 26.1, 24.1. ^{19}F NMR (376 MHz, CDCl_3) δ -60.44 (t, $J = 10.6$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{14}\text{ClF}_3\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 292.0711. Found 292.0712.



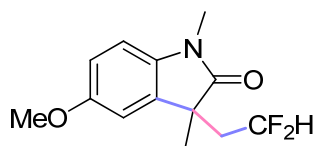
1-(5-Bromo-3-methyl-3-(2,2,2-trifluoroethyl)indolin-1-yl)ethanone (**5a2**),^[6] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 82% yield (82.7 mg), colorless oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.6$ Hz, 1H), 7.36 (dd, $J = 8.6, 2.1$ Hz, 1H), 7.23 (d, $J = 2.0$ Hz, 1H), 4.13 (d, $J = 10.8$ Hz, 1H), 3.83 (d, $J = 10.8$ Hz, 1H), 2.57 – 2.42 (m, 2H), 2.24 (s, 3H), 1.47 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.7, 140.4, 139.6, 131.6, 126.0 (q, $J = 276.7$ Hz), 125.3, 118.7, 116.3, 61.0 (q, $J = 2.4$ Hz), 43.1 (q, $J = 27.0$ Hz), 41.1 (d, $J = 1.4$ Hz), 26.1 (d, $J = 0.8$ Hz), 24.1. ^{19}F NMR (376 MHz, CDCl_3)

[6] J. Wang, K. Sun, X. Chen, T. Chen, Y. Liu, L. Qu, Y. Zhao and B. Yu, *Org. Lett.*, 2019, **21**, 1863–1867.

δ -65.18 (t, J = 10.4 Hz, 3F). HRMS (ESI-TOF) Calcd for $C_{13}H_{14}BrF_3NO^+$ ($[M+H]^+$) 336.0205. Found 336.0203.



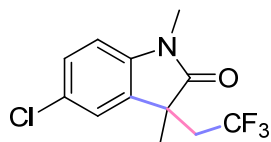
5-Methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**5b**),^[7] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 91% yield (74.7 mg), white solid: mp 105 – 106 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. 1H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 2.4 Hz, 1H), 6.84 (dd, J = 8.4, 2.5 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.21 (s, 3H), 2.87 – 2.75 (m, 1H), 2.68 – 2.57 (m, 1H), 1.40 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 178.1, 156.1, 136.4, 132.4, 125.2 (q, J = 276.5 Hz), 112.6, 111.3 (q, J = 1.6 Hz), 108.7, 55.8, 44.8 (q, J = 2.2 Hz), 40.6 (q, J = 28.2 Hz), 26.5, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.87 (t, J = 10.4 Hz, 3F). HRMS (ESI-TOF) Calcd for $C_{13}H_{15}F_3NO_2^+$ ($[M+H]^+$) 274.1049. Found 274.1036.



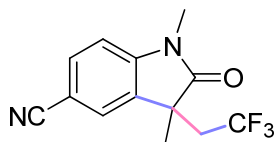
3-(2,2-Difluoroethyl)-5-methoxy-1,3-dimethylindolin-2-one (**5c**),^[8] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 89% yield (68.5 mg), pale yellow oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. 1H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.81 (m, 2H), 6.79 – 6.76 (m, 1H), 5.77 – 5.46 (m, 1H), 3.81 (s, 3H), 3.20 (s, 3H), 2.55 – 2.43 (m, 1H), 2.32 – 2.19 (m, 1H), 1.40 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 178.8, 156.2, 136.4, 133.5, 115.1 (t, J = 238.3 Hz), 112.4, 110.6, 108.7, 55.8, 45.0 (q, J = 0.9 Hz), 41.4 (t, J = 21.8 Hz), 26.4, 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.08 – -114.36 (m, 2F). HRMS (ESI-TOF) Calcd for $C_{13}H_{16}F_2NO_2^+$ ($[M+H]^+$) 256.1144. Found 256.1145.

[7] W. Fu, F. Xu, Y. Fu, C. Xu, S. Li and D. Zou, *Eur. J. Org. Chem.*, 2013, **2014**, 709–712.

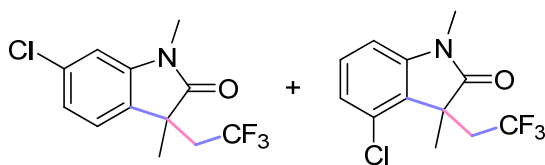
[8] H. Sun, Y. Jiang, Y.-S. Yang, Y.-Y. Li, L. Li, W.-X. Wang, T. Feng, Z.-H. Li and J.-K. Liu, *Org. Biomol. Chem.*, 2019, **17**, 6629–6638.



5-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**5d1**),^[9] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 68% yield (56.9 mg), white solid: mp 74 – 75 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.23 (s, 3H), 2.89 – 2.77 (m, 1H), 2.69 – 2.57 (m, 1H), 1.41 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 177.9, 141.4, 132.7, 128.5, 128.1, 125.1 (q, *J* = 278.1 Hz), 124.1 (q, *J* = 1.6 Hz), 109.4, 44.6 (q, *J* = 2.1 Hz), 41.6 (q, *J* = 28.5 Hz), 26.6, 24.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.97 (t, *J* = 10.4 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₂H₁₂ClF₃NO⁺ ([M+H]⁺) 278.0554. Found 278.0557.



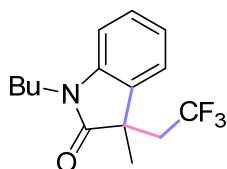
1,3-Dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (**5d2**),^[10] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 72% yield (57.9 mg), white solid: mp 105 – 106 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.53 (d, *J* = 1.5 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.28 (s, 3H), 2.93 – 2.81 (m, 1H), 2.74 – 2.63 (m, 1H), 1.44 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 178.1, 146.7, 133.9, 132.0, 127.0 (q, *J* = 1.6 Hz), 124.9 (q, *J* = 276.3 Hz), 119.0, 109.0, 106.0, 44.2 (q, *J* = 2.3 Hz), 40.5 (q, *J* = 28.4 Hz), 26.7, 24.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.04 (t, *J* = 10.4 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₃H₁₂F₃N₂O⁺ ([M+H]⁺) 269.0896. Found 269.0899.



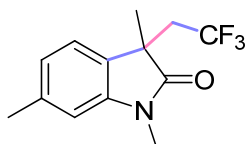
6-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one and 4-chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**5e**),^[9] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 65% yield (54.0 mg), 1:1 mixture of regioisomers, colorless oil. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33.

[9] L. Li, M. Deng, S.-C. Zheng, Y.-P. Xiong, B. Tan and X.-Y. Liu, *Org. Lett.*, 2013, **16**, 504–507.

^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.24 (m, 1H), 7.17 (d, $J = 7.9$ Hz, 1H), 7.07 (dd, $J = 7.9, 1.9$ Hz, 1H), 7.02 (dd, $J = 8.2, 0.9$ Hz, 1H), 6.89 (d, $J = 1.8$ Hz, 1H), 6.79 (dd, $J = 7.8, 0.8$ Hz, 1H), 3.23 (s, 3H), 3.22 (s, 3H), 3.18 – 3.10 (m, 1H), 2.93 – 2.76 (m, 2H), 2.69 – 2.57 (m, 1H), 1.53 (s, 3H), 1.39 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 178.4, 177.8, 144.6, 144.1, 134.4, 131.2, 129.8, 129.3, 127.2, 125.1 (q, $J = 276.4$ Hz), 125.0 (q, $J = 276.4$ Hz), 124.5 (q, $J = 1.5$ Hz), 123.6, 122.5, 109.3, 107.0, 45.4 (q, $J = 2.3$ Hz), 44.1 (q, $J = 2.2$ Hz), 40.6 (q, $J = 28.2$ Hz), 38.7 (q, $J = 28.2$ Hz), 26.7, 26.5, 24.9, 22.2. ^{19}F NMR (376 MHz, CDCl_3) δ -64.00 (t, $J = 10.2$ Hz, 3F), -61.96 (t, $J = 10.3$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{12}\text{ClF}_3\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 278.0554. Found 278.0551.

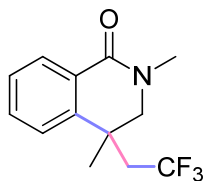


1-Butyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**7a**),^[7] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 56% yield (47.9 mg), colorless oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.25 (m, 2H), 7.09 – 7.05 (m, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 3.85 – 3.75 (m, 1H), 3.71 – 3.62 (m, 1H), 2.94 – 2.81 (m, 1H), 2.74 – 2.59 (m, 1H), 1.69 – 1.61 (m, 2H), 1.44 – 1.34 (m, 5H), 0.95 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 178.3, 142.3, 131.1, 128.4, 125.3 (q, $J = 276.6$ Hz), 123.7 (d, $J = 1.3$ Hz), 122.3, 108.7, 44.3 (q, $J = 2.2$ Hz), 40.6 (q, $J = 28.1$ Hz), 39.9, 29.3, 25.3, 20.1, 13.8. ^{19}F NMR (376 MHz, CDCl_3) δ -61.89 (t, $J = 10.6$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 286.1413. Found 286.1415.

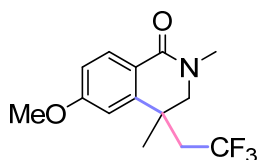


1,3,6-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**7b**),^[9] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 60% yield (47.1 mg), yellowish oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 7.5$ Hz, 1H), 6.91 – 6.89 (m, 1H), 6.71 (dd, $J = 0.9, 0.8$ Hz, 1H), 3.22 (s, 3H), 2.86 – 2.74 (m, 1H), 2.69 – 2.55 (m, 1H), 2.40 (s, 3H), 1.39 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 178.8, 142.9, 138.7, 128.1, 125.3 (q, $J = 276.3$ Hz), 123.3

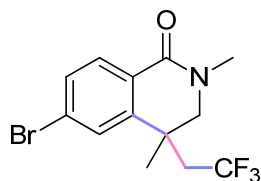
(q, $J = 1.4$ Hz), 123.2, 109.4, 44.2 (q, $J = 2.3$ Hz), 40.7 (q, $J = 28.0$ Hz), 26.4, 25.1, 21.8. ^{19}F NMR (376 MHz, CDCl_3) δ -61.93 (t, $J = 10.9$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 258.1100. Found 258.1096.



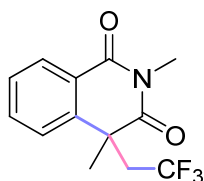
2,4-Dimethyl-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one (**9a**),^[6] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 62% yield (47.7 mg), colorless oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.50 (ddd, $J = 1.52, 6.1, 7.6$ Hz, 1H), 7.39 (ddd, $J = 1.2, 6.3, 7.5$ Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 1H), 3.55 (d, $J = 12.9$ Hz, 1H), 3.40 (d, $J = 13.0$ Hz, 1H), 3.18 (s, 3H), 2.58 – 2.46 (m, 1H), 2.39 – 2.27 (m, 1H), 1.55 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 164.4, 144.2, 132.3, 128.9, 128.0, 127.7, 126.1 (q, $J = 277.0$ Hz), 123.7, 57.2 (q, $J = 1.7$ Hz), 41.33 (q, $J = 27.1$ Hz), 35.2 (q, $J = 1.8$ Hz), 35.1, 22.1 (q, $J = 1.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.99 (t, $J = 11.2$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 258.1100. Found 258.1101.



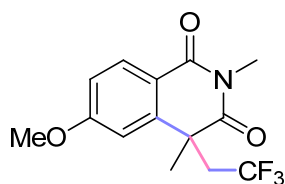
6-Methoxy-2,4-dimethyl-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one (**9b**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 64% yield (54.8 mg), white solid: mp 73 – 74 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.7$ Hz, 1H), 6.88 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.78 (d, $J = 2.4$ Hz, 1H), 3.86 (s, 3H), 3.52 (d, $J = 12.9$ Hz, 1H), 3.37 (d, $J = 13.0$ Hz, 1H), 3.15 (s, 3H), 2.58 – 2.45 (m, 1H), 2.36 – 2.23 (m, 1H), 1.61 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 164.4, 162.7, 146.4, 131.2, 126.1 (q, $J = 277.1$ Hz), 120.9, 112.1, 110.0, 57.2, 55.5, 41.2 (q, $J = 27.0$ Hz), 35.3 (q, $J = 1.4$ Hz), 34.9, 22.1 (q, $J = 1.5$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.96 (t, $J = 11.8$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 288.1206. Found 288.1215.



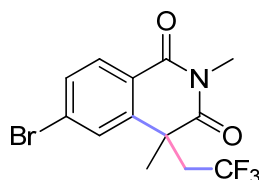
6-Bromo-2,4-dimethyl-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one (**9c**),^[6] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 75% yield (75.3 mg), white solid: mp 56 – 57 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.3$ Hz, 1H), 7.53 (dd, $J = 8.3, 1.9$ Hz, 1H), 7.44 (d, $J = 1.9$ Hz, 1H), 3.54 (d, $J = 13.0$ Hz, 1H), 3.39 (d, $J = 13.0$ Hz, 1H), 3.16 (s, 3H), 2.57 – 2.45 (m, 1H), 2.38 – 2.26 (m, 1H), 1.54 (d, $J = 1.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.6, 146.0, 131.1, 130.8, 127.2, 127.1, 127.0, 125.9 (q, $J = 277.1$ Hz), 125.7, 57.0 (d, $J = 2.0$ Hz), 41.2 (q, $J = 27.1$ Hz), 35.3 (d, $J = 1.7$ Hz), 35.1, 22.0 (d, $J = 2.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.97 (t, $J = 11.8$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{14}\text{BrF}_3\text{NO}^+$ ($[\text{M}+\text{H}]^+$) 336.0205. Found 336.0203.



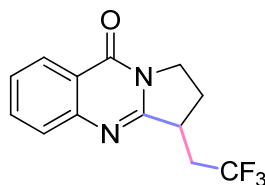
2,4-Dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (**9d**),^[9] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 65% yield (56.6 mg), white solid: mp 66 – 67 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.29 (ddd, $J = 7.9, 1.5, 0.5$ Hz, 1H), 7.67 (ddd, $J = 7.9, 7.3, 1.5$ Hz, 1H), 7.49 (ddd, $J = 7.9, 7.3, 1.1$ Hz, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 3.41 (s, 3H), 3.40 – 3.29 (m, 1H), 2.86 – 2.75 (m, 1H), 1.66 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 174.6, 163.7, 140.4, 133.8, 129.3, 128.1, 125.6, 125.0 (q, $J = 278.7$ Hz), 124.2, 44.4 (q, $J = 27.6$ Hz), 43.6 (q, $J = 2.3$ Hz), 31.2, 27.4. ^{19}F NMR (376 MHz, CDCl_3) δ -61.66 (t, $J = 9.7$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 272.0893. Found 272.0881.



6-Methoxy-2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2*H*,4*H*)-dione (**9e**),^[9] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 65% yield (59.0 mg), yellowish solid: mp 113 – 114 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.8 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 3.90 (s, 3H), 3.38 – 3.29 (m, 4H), 2.82 – 2.71 (m, 1H), 1.65 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 174.6, 164.0, 163.4, 142.6, 131.7, 125.0 (q, *J* = 277.1 Hz), 117.2, 113.6, 111.1, 55.6, 44.4 (q, *J* = 27.4 Hz), 43.7 (q, *J* = 2.3 Hz), 31.3, 27.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.61 (t, *J* = 10.3 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₄H₁₅F₃NO₃⁺ ([M+H]⁺) 302.0999. Found 302.0996.



6-Bromo-2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2*H*,4*H*)-dione (**9f**),^[10] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 73% yield (76.6 mg), white solid: mp 137 – 138 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.63 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 3.40 (s, 3H), 3.38 – 3.30 (m, 1H), 2.82 – 3.71 (m, 1H), 1.67 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.8, 163.0, 142.1, 131.7, 130.9, 129.1, 128.9, 124.8 (q, *J* = 277.0 Hz), 123.2, 44.4 (q, *J* = 27.6 Hz), 43.5 (q, *J* = 2.3 Hz), 31.0, 27.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.68 (t, *J* = 10.0 Hz, 3F). HRMS (ESI-TOF) Calcd for C₁₃H₁₂BrF₃NO₂⁺ ([M+H]⁺) 349.9998. Found 349.9999.

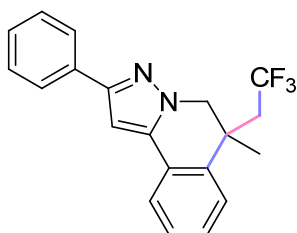


3-(2,2,2-Trifluoroethyl)-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**11**),^[11] isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 44% yield (35.8 mg), white solid: mp 118 – 119 °C. *R_f* (petroleum ether/EtOAc = 5:1, v/v) 0.33. ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 7.9 Hz, 1H), 7.75 (ddd, *J* = 1.5,

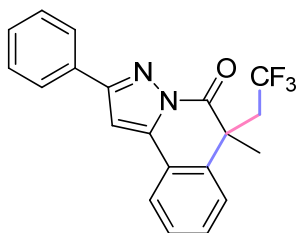
[10] Z. Zhang, L. Zhang, Y. Cao, F. Li, G. Bai, G. Liu, Y. Yang and F. Mo, *Org. Lett.*, 2019, **21**, 762–766.

[11] J. Zheng, Z. Deng, Y. Zhang and S. Cui, *Adv. Synth. Catal.*, 2016, **358**, 746–751.

7.1, 8.6 Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.48 (dd, $J = 7.6, 7.4$ Hz, 1H), 4.43 – 4.37 (m, 1H), 3.99 – 3.91 (m, 1H), 3.58 – 3.49 (m, 1H), 3.34 – 3.21 (m, 1H), 2.72 – 2.65 (m, 1H), 2.36 – 2.22 (m, 1H), 2.10 – 1.99 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.8, 158.5, 148.9, 134.3, 127.1, 126.7, 126.6 (q, $J = 276.8$ Hz), 126.5, 120.8, 44.7, 38.4 (q, $J = 2.8$ Hz), 36.0 (q, $J = 29.1$ Hz), 27.5. ^{19}F NMR (376 MHz, CDCl_3) δ -64.68 (t, $J = 10.5$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 269.0896. Found 269.0898.

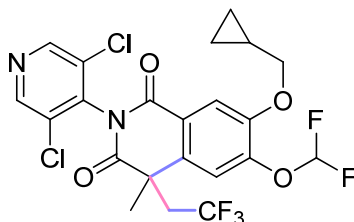


6-Methyl-2-phenyl-6-(2,2,2-trifluoroethyl)-5,6-dihydropyrazolo[5,1-*a*]isoquinoline (**13a**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 86% yield (88.8 mg), white solid: mp 107 – 108 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.85 (m, 2H), 7.65 – 7.63 (m, 1H), 7.47 – 7.30 (m, 6H), 6.88 (s, 1H), 4.42 (d, $J = 13.3$ Hz, 1H), 4.11 (dd, $J = 12.3, 1.0$ Hz, 1H), 2.40 (d, $J = 11.2$ Hz, 1H), 2.34 (dd, $J = 10.4, 0.7$ Hz, 1H), 1.66 (d, $J = 1.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 151.6, 139.2, 137.5, 133.2, 128.74, 128.67, 128.1, 127.8, 126.1 (q, $J = 277.1$ Hz), 125.8, 125.6, 125.3, 124.7, 98.0, 56.1 (q, $J = 1.2$ Hz), 41.2 (q, $J = 26.9$ Hz), 37.2 (d, $J = 1.7$ Hz), 22.5 (d, $J = 1.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -59.45 (t, $J = 11.8$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 343.1417. Found 343.1413.

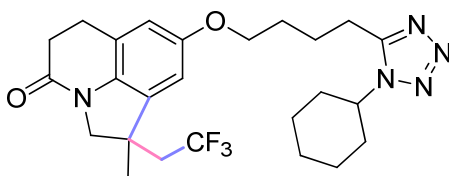


6-Methyl-2-phenyl-6-(2,2,2-trifluoroethyl)pyrazolo[5,1-*a*]isoquinolin-5(6*H*)-one (**13b**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 67% yield (72.0 mg), white solid: mp 59 – 60 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.05 – 8.03 (m, 2H), 7.84 – 7.82 (m, 1H), 7.52 – 7.42 (m, 6H), 7.15 (s, 1H), 3.57 – 3.45 (m, 1H), 2.98 – 2.87 (m, 1H), 1.76 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.3, 158.2, 143.7, 136.4, 131.0, 130.0,

129.9, 128.8, 128.3, 126.91, 126.86, 125.0 (q, $J = 277.2$ Hz), 124.8, 122.1, 101.8, 45.6 (q, $J = 2.2$ Hz), 44.0 (q, $J = 27.5$ Hz), 31.0. ^{19}F NMR (376 MHz, CDCl_3) δ -61.26 (p, $J = 5.2$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{16}\text{F}_3\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 357.1209. Found 357.1210.

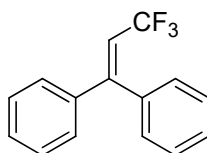


7-(Cyclopropylmethoxy)-2-(3,5-dichloropyridin-4-yl)-6-(difluoromethoxy)-4-methyl-4-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinolin-1(2H)-one (**15**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 66% yield (106.2 mg), white solid: mp 183 – 184 °C. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 8.69 (s, 1H), 8.67 (s, 1H), 7.79 (s, 1H), 7.28 (s, 1H), 6.83 (t, $J = 74.6$ Hz, 1H), 4.03 – 3.95 (m, 2H), 3.52 – 3.40 (m, 1H), 2.93 – 2.82 (m, 1H), 1.76 (s, 3H), 1.39 – 1.29 (m, 1H), 0.72 – 0.68 (m, 2H), 0.41 – 0.37 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.2, 160.6, 150.4, 148.6 (d, $J = 46.8$ Hz), 145.4 (t, $J = 3.1$ Hz), 139.1, 133.7, 132.3, 131.3, 124.7 (q, $J = 277.1$ Hz), 121.3, 120.1, 115.4 (t, $J = 261.3$ Hz), 113.5, 74.3, 44.7 (q, $J = 2.3$ Hz), 42.7 (q, $J = 27.9$ Hz), 32.3, 9.9, 3.38, 3.34. ^{19}F NMR (376 MHz, CDCl_3) δ -60.41 (t, $J = 9.4$ Hz, 3F), -82.16 – -82.41 (m, 2F). HRMS (ESI-TOF) Calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{F}_5\text{N}_2\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 539.0558. Found 539.0566.

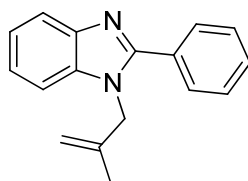


8-(4-(1-Cyclohexyl-1H-tetrazol-5-yl)butoxy)-1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-1H-pyrrolo[3,2,1-*ij*]quinolin-4(2H)-one (**17**), isolated by flash column chromatography (petroleum ether/EtOAc = 20:1, v/v) in 75% yield (110.8 mg), colorless oil. R_f (petroleum ether/EtOAc = 5:1, v/v) 0.33. ^1H NMR (400 MHz, CDCl_3) δ 6.61 – 6.60 (m, 1H), 6.57 (d, $J = 2.2$ Hz, 1H), 4.17 – 4.09 (m, 2H), 3.98 (t, $J = 6.0$ Hz, 2H), 3.87 (d, $J = 12.3$ Hz, 1H), 3.31 (q, $J = 7.2$ Hz, 1H), 2.98 – 2.90 (m, 3H), 2.68 (t, $J = 7.7$ Hz, 2H), 2.60 – 2.39 (m, 2H), 2.08 – 1.98 (m, 7H), 1.93 – 1.87 (m, 3H), 1.46 – 1.30 (m, 7H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.8, 156.2, 153.5, 135.8,

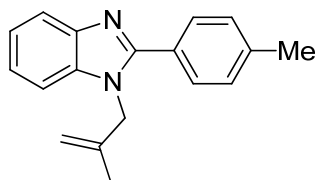
133.7, 126.0 (q, $J = 277.1$ Hz), 121.3, 112.9, 107.9, 68.1, 58.0 (q, $J = 2.1$ Hz), 57.6, 43.4 (q, $J = 26.9$ Hz), 42.4 (q, $J = 1.9$ Hz), 32.9, 31.3, 28.6, 26.7 (d, $J = 1.3$ Hz), 25.3, 24.8, 24.6, 24.0, 23.0. ^{19}F NMR (376 MHz, CDCl_3) δ -60.50 (t, $J = 11.8$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{25}\text{H}_{33}\text{F}_3\text{N}_5\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 492.2581. Found 492.2580.



(3,3,3-Trifluoroprop-1-ene-1,1-diyl)dibenzene (**18**),^[4] isolated by flash column chromatography (pure petroleum ether) in 36% yield (26.8 mg), colorless oil. R_f (pure petroleum ether) 0.50. ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.37 (m, 3H), 7.36 – 7.30 (m, 3H), 7.27 – 7.22 (m, 4H), 6.12 (q, $J = 8.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.5 (q, $J = 5.6$ Hz), 140.1, 137.3, 129.4, 129.1 (q, $J = 1.9$ Hz), 128.5 (d, $J = 1.5$ Hz), 128.03, 127.96, 123.1 (q, $J = 269.0$ Hz), 115.4 (q, $J = 33.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -55.60 (d, $J = 8.5$ Hz, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3^+$ ($[\text{M}+\text{H}]^+$) 249.0886. Found 249.0885.



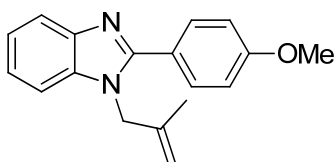
1-(2-Methylallyl)-2-phenyl-1H-benzo[*d*]imidazole (**1a**),^[12] white solid: mp 100 – 101 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.83 (m, 1H), 7.79 – 7.75 (m, 2H), 7.52 – 7.49 (m, 3H), 7.34 – 7.27 (m, 3H), 5.02 (p, $J = 1.5$ Hz, 1H), 4.69 (s, 2H), 4.64 (s, 1H), 1.81 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.0, 143.0, 139.8, 136.1, 130.2, 129.9, 129.1, 128.7, 122.9, 122.5, 119.9, 112.2, 110.5, 50.4, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 249.1386. Found 249.1381.



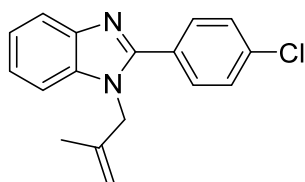
1-(2-Methylallyl)-2-(*p*-tolyl)-1H-benzo[*d*]imidazole (**1c1**), white solid: mp 110 –

[12] R. Kong, T. Fu, R. Yang, D. Chen, D. Liang, Y. Dong, W. Li and B. Wang, *ChemCatChem*, 2021, **13**, 2952–2958.

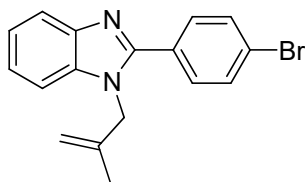
111 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (dd, $J = 3.9, 2.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.14 (m, 5H), 4.89 (s, 1H), 4.56 (s, 2H), 4.53 (s, 1H), 2.32 (s, 3H), 1.68 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.2, 143.0, 140.0, 139.8, 136.1, 129.4, 129.0, 127.3, 122.7, 122.4, 119.8, 112.1, 110.4, 50.3, 21.5, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 263.1543. Found 263.1541.



2-(4-Methoxyphenyl)-1-(2-methylallyl)-1*H*-benzo[*d*]imidazole (**1c2**), white solid: mp 108 – 109 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.73 (m, 1H), 7.63 (d, $J = 8.8$ Hz, 2H), δ 7.24 – 7.16 (m, 3H), 6.94 (d, $J = 8.8$ Hz, 2H), 4.93 (s, 1H), 4.58 (s, 2H), 4.55 (s, 1H), 3.79 (s, 3H), 1.73 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.9, 154.0, 143.0, 139.9, 136.1, 130.5, 122.6, 122.5, 122.4, 119.6, 114.2, 112.1, 110.3, 55.4, 50.4, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 279.1492. Found 279.1480.

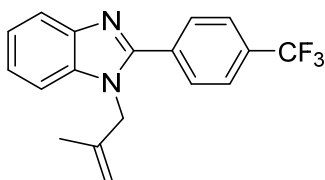


2-(4-Chlorophenyl)-1-(2-methylallyl)-1*H*-benzo[*d*]imidazole (**1c3**), white solid: mp 108 – 109 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.82 (m, 1H), 7.71 (ddd, $J = 8.5, 2.5, 2.0$ Hz, 2H), 7.48 (ddd, $J = 8.5, 2.5, 2.0$ Hz, 2H), 7.34 – 7.29 (m, 3H), 5.02 (s, 1H), 4.65 (s, 2H), 4.61 (s, 1H), 1.81 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.8, 142.9, 139.7, 136.1, 130.3, 129.0, 128.6, 123.2, 122.7, 119.9, 112.3, 110.4, 50.3, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{16}\text{ClN}_2^+$ ($[\text{M}+\text{H}]^+$) 283.0997. Found 283.0999.

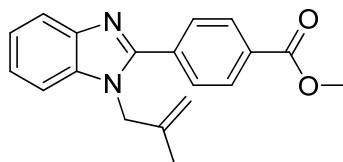


2-(4-Bromophenyl)-1-(2-methylallyl)-1*H*-benzo[*d*]imidazole (**1c4**), white solid: mp 91 – 92 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.72 (m, 1H), 7.58 – 7.53 (m, 4H),

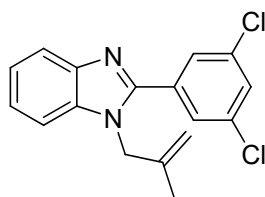
7.25 – 7.18 (m, 3H), 4.92 (dd, $J = 1.5, 1.6$ Hz, 1H), 4.56 (s, 2H), 4.51 (s, 1H), 1.72 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.8, 142.9, 139.7, 136.2, 132.0, 130.6, 129.1, 124.5, 123.2, 122.7, 120.0, 112.3, 110.4, 50.3, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{16}\text{BrN}_2^+$ ($[\text{M}+\text{H}]^+$) 327.0491. Found 327.0494.



1-(2-Methylallyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (**1c5**), white solid: mp 97 – 98 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.1$ Hz, 2H), 7.88 – 7.85 (m, 1H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.37 – 7.32 (m, 3H), 5.04 (s, 1H), 4.69 (s, 2H), 4.63 (s, 1H), 1.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 152.3, 142.9, 139.6, 136.2, 133.7 (q, $J = 1.5$ Hz), 131.7 (q, $J = 32.4$ Hz), 129.4, 125.7 (q, $J = 3.7$ Hz), 123.9 (q, $J = 270.8$ Hz), 123.5, 122.9, 120.1, 112.4, 110.5, 50.4, 20.2. ^{19}F NMR (376 MHz, CDCl_3) δ -62.79 (s, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 317.1260. Found 317.1271.

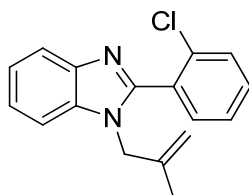


Methyl 4-(1-(2-methylallyl)-1*H*-benzo[*d*]imidazol-2-yl)benzoate (**1c6**), white solid: mp 96 – 97 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.19 – 8.16 (m, 2H), 7.88 – 7.85 (m, 3H), 7.36 – 7.30 (m, 3H), 5.03 (t, $J = 1.3$, 1H), 4.70 (s, 2H), 4.63 (s, 1H), 3.97 (s, 3H), 1.82 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 166.5, 152.7, 143.0, 139.6, 136.2, 134.4, 131.2, 129.9, 129.1, 123.4, 122.9, 120.1, 112.4, 110.5, 52.4, 50.4, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 307.1441. Found 307.1445.

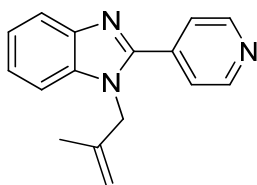


2-(3,5-Dichlorophenyl)-1-(2-methylallyl)-1*H*-benzo[*d*]imidazole (**1d**), pink solid: mp 79 – 80 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.82 (m, 1H), 7.70 (d, $J = 1.9$ Hz,

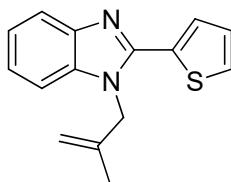
2H), 7.50 (dd, $J = 1.9, 1.8$ Hz, 1H), 7.37 – 7.31 (m, $J = 4.4, 2.1$ Hz, 3H), 5.06 (s, 1H), 4.69 (s, 2H), 4.60 (s, 1H), 1.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.9, 142.8, 139.5, 136.2, 135.5, 133.0, 129.8, 127.4, 123.7, 123.0, 120.2, 112.7, 110.5, 50.4, 20.1. HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 317.0607. Found 317.0609.



2-(2-Chlorophenyl)-1-(2-methylallyl)-1*H*-benzo[*d*]imidazole (**1e**), pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.83 (m, 1H), 7.54 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.37 (m, 2H), 7.35 – 7.28 (m, 2H), 4.86 (p, $J = 1.4$ Hz, 1H), 4.61 (t, $J = 1.2, 1.3$ Hz, 1H), 4.58 (s, 2H), 1.54 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 151.3, 143.0, 139.4, 134.9, 134.3, 132.3, 131.3, 130.0, 129.8, 126.9, 123.0, 122.4, 120.2, 113.2, 110.7, 50.4, 19.9. HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{16}\text{ClN}_2^+$ ($[\text{M}+\text{H}]^+$) 283.0997. Found 283.0999.

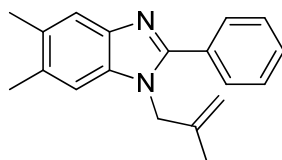


1-(2-Methylallyl)-2-(pyridin-4-yl)-1*H*-benzo[*d*]imidazole (**1f**), brown solid: mp 115 – 116 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.78 – 8.75 (m, 2H), 7.88 – 7.85 (m, 1H), 7.70 – 7.68 (m, 2H), 7.34 – 7.31 (m, 3H), 5.02 (s, 1H), 4.69 (s, 2H), 4.57 (s, 1H), 1.83 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 150.9, 150.3, 142.8, 139.4, 137.7, 136.3, 123.8, 123.1, 123.0, 120.3, 112.4, 110.6, 50.3, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3^+$ ($[\text{M}+\text{H}]^+$) 250.1339. Found 250.1335.

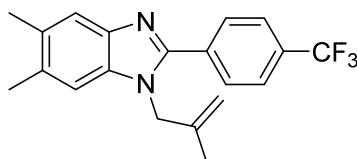


1-(2-Methylallyl)-2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole (**1g**), pale yellow solid: mp 121 – 122 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.71 (m, 1H), 7.37 (dd, $J =$

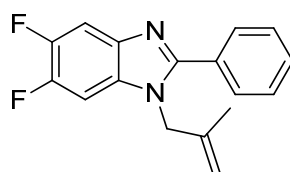
5.1, 1.1 Hz, 1H), 7.32 (dd, $J = 3.8, 1.1$ Hz, 1H), 7.20 – 7.13 (m, 3H), 7.03 (dd, $J = 5.1, 3.7$ Hz, 1H), 4.86 (s, 1H), 4.67 (s, 2H), 4.41 (s, 1H), 1.75 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.0, 142.9, 139.3, 136.2, 132.1, 128.7, 127.9, 127.7, 123.1, 122.7, 119.7, 112.0, 109.9, 50.0, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{S}^+$ ($[\text{M}+\text{H}]^+$) 255.0950. Found 255.0951.



5,6-Dimethyl-1-(2-methylallyl)-2-phenyl-1*H*-benzo[*d*]imidazole (**1h1**), yellowish solid: mp 237 – 238 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.72 (m, 2H), 7.59 (s, 1H), 7.51 – 7.46 (m, 3H), 7.07 (s, 1H), 5.00 (t, $J = 1.5, 1.6$ Hz, 1H), 4.63 (s, 3H), 2.40 (s, 6H), 1.81 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.2, 141.6, 140.0, 134.7, 132.0, 131.4, 130.5, 129.6, 129.0, 128.6, 119.9, 112.0, 110.5, 50.3, 20.6, 20.3, 20.2. HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 277.1699. Found 277.1709.

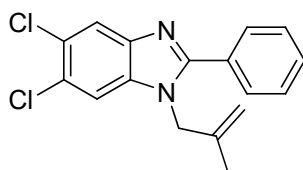


5,6-Dimethyl-1-(2-methylallyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (**1h2**), white solid: mp 123 – 124 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.85 (m, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.60 (s, 1H), 7.08 (s, 1H), 5.03 (dt, $J = 2.7, 1.4$ Hz, 1H), 4.63 (dd, $J = 2.1, 1.0$ Hz, 2H), 4.61 (dd, $J = 1.8, 1.0$ Hz, 1H), 2.40 (d, $J = 1.1$ Hz, 6H), 1.83 (t, $J = 1.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 151.5, 141.6, 139.8, 134.8, 134.0 (d, $J = 1.2$ Hz), 132.8, 131.9, 131.4 (q, $J = 32.7$ Hz), 129.3, 125.6 (q, $J = 3.7$ Hz), 123.9 (q, $J = 272.4$ Hz), 120.1, 112.2, 110.6, 50.3, 20.7, 20.3, 20.2. ^{19}F NMR (376 MHz, CDCl_3) δ -62.78 (s, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 345.1573. Found 345.1571.

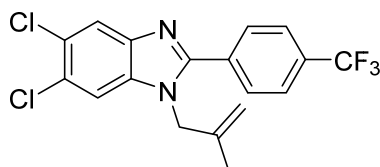


5,6-Difluoro-1-(2-methylallyl)-2-phenyl-1*H*-benzo[*d*]imidazole (**1i**), white solid: mp 103 – 104 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.69 (m, 2H), 7.59 (dd, $J = 10.4,$

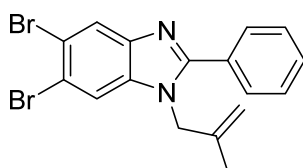
7.3 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.11 (dd, $J = 9.8, 6.9$ Hz, 1H), 5.05 (q, $J = 1.4$ Hz, 1H), 4.64 (s, 3H), 1.79 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.5 (d, $J = 3.1$ Hz), 149.3 (dd, $J = 4.1, 15.6$ Hz), 146.9 (dd, $J = 2.0, 15.6$ Hz), 139.2, 138.1 (d, $J = 10.4$ Hz), 131.4 (d, $J = 10.6$ Hz), 130.2, 129.6, 128.9, 128.8, 112.6, 107.2 (d, $J = 19.4$ Hz), 98.5 (d, $J = 22.8$ Hz), 50.7, 20.1. ^{19}F NMR (376 MHz, CDCl_3) δ -141.24 – -141.34 (m, 1F), δ -143.32 – -143.42 (m, 1F). HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{15}\text{F}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 285.1198. Found 285.1196.



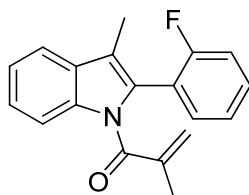
5,6-Dichloro-1-(2-methylallyl)-2-phenyl-1*H*-benzo[*d*]imidazole (**1j1**), brown solid: mp 158 – 159 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.75 – 7.70 (m, 2H), 7.55 – 7.48 (m, 3H), 7.40 (s, 1H), 5.04 (s, 1H), 4.63 (s, 2H), 4.60 (s, 1H), 1.79 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.9, 142.4, 139.2, 135.3, 130.4, 129.3, 129.0, 128.9, 126.8, 126.6, 121.0, 112.6, 111.8, 50.6, 20.1. HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 317.0607. Found 317.0611.



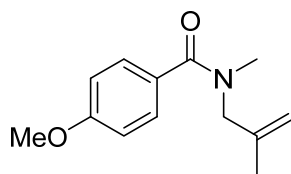
5,6-Dichloro-1-(2-methylallyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (**1j2**), yellowish solid: mp 147 – 148 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.90 – 7.85 (m, 2H), 7.79 (d, $J = 8.2$ Hz, 2H), 7.43 (s, 1H), 5.08 (q, $J = 1.6$ Hz, 1H), 4.64 (s, 2H), 4.60 (p, $J = 1.1$ Hz, 1H), 1.83 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.2, 142.2, 139.0, 135.4, 132.8 (q, $J = 1.1$ Hz), 132.3 (q, $J = 32.9$ Hz), 129.4, 127.5, 127.1, 125.9 (q, $J = 3.8$ Hz), 123.7 (q, $J = 272.5$ Hz), 121.3, 112.8, 111.9, 50.6, 20.1. ^{19}F NMR (376 MHz, CDCl_3) δ -62.91 (s, 3F). HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{F}_3\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 385.0481. Found 385.0476.



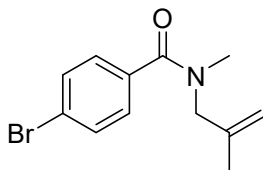
5,6-Dibromo-1-(2-methylallyl)-2-phenyl-1*H*-benzo[*d*]imidazole (**1k**), white solid: mp 193 – 194 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.14 (s, 1H), 8.07 (s, 1H), 7.77 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.58 (dd, *J* = 5.1, 1.9 Hz, 3H), 4.88 (t, *J* = 1.6 Hz, 1H), 4.86 (s, 2H), 4.26 (s, 1H), 1.71 (s, 3H). ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 155.7, 143.2, 141.1, 136.9, 130.8, 129.6, 129.4, 129.3, 123.9, 117.3, 117.0, 116.4, 111.2, 50.1, 20.3. HRMS (ESI-TOF) Calcd for C₁₇H₁₅Br₂N₂⁺ ([M+H]⁺) 404.9597. Found 404.9609.



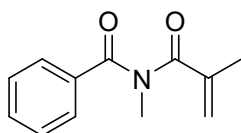
1-(2-(2-Fluorophenyl)-3-methyl-1*H*-indol-1-yl)-2-methylprop-2-en-1-one (**1m**), brown solid: mp 87 – 88 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.38 – 7.34 (m, 1H), 7.32 (dd, *J* = 4.4, 1.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.20 (ddd, *J* = 1.2, 6.1, 7.5 Hz, 1H), 7.13 – 7.09 (m, 1H), 5.34 (q, *J* = 1.7 Hz, 1H), 5.28 (s, 1H), 2.22 (s, 3H), 1.86 (t, *J* = 1.2 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 170.5, 160.8, 158.3, 140.8, 136.9, 131.6 (d, *J* = 12.2 Hz), 129.9 (q, *J* = 75.9 Hz), 124.8, 124.6, 124.1 (d, *J* = 14.2 Hz), 122.8, 121.8 (d, *J* = 60.5 Hz), 119.0, 118.0, 115.7 (d, *J* = 86.5 Hz), 114.5, 18.5, 9.3 (d, *J* = 5.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -112.64 – -112.69 (m, 1F). HRMS (ESI-TOF) Calcd for C₁₉H₁₇FNO⁺ ([M+H]⁺) 294.1289. Found 294.1289.



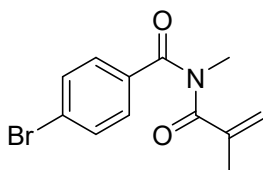
4-Methoxy-*N*-methyl-*N*-(2-methylallyl)benzamide (**8b**),^[12] 2:3 mixture of rotamers due to the restricted rotation of the N-(CO) bond, pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 4.98 (s, 1H), 4.92 (s, 1H), 4.11 (brs, 1H), 3.82 (s, 4H), 3.01 (brs, 3H major), 2.94 (brs, 3H minor), 1.76 (brs, 3H minor), 1.63 (brs, 3H major). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 172.2 (br, major), 171.3 (br, minor), 160.6, 140.6, 128.7 (br), 128.4 (br), 113.6, 112.3 (br, minor), 112.0 (br, major), 57.5 (br, major), 55.3, 53.1 (br, minor), 37.1 (br, minor), 33.6 (br, major), 20.0. HRMS (ESI-TOF) Calcd for C₁₃H₁₈NO₂⁺ ([M+H]⁺) 220.1332. Found 220.1330.



4-Bromo-*N*-methyl-*N*-(2-methylallyl)benzamide (**8c**),^[12] 2:3 mixture of rotamers due to the restricted rotation of the N-(CO) bond, pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, *J* = 13.2, 7.9 Hz, 2H major and 2 H minor), 7.41 – 7.17 (m, 2H major and 2 H minor), 4.97 – 4.87 (stack, 2H major and 2 H minor), 4.11 (s, 2H minor), 3.74 (s, 2H major), 3.03 (s, 3H major), 2.87 (s, 3H minor), 1.76 (s, 3H minor), 1.60 (s, 3H major). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 171.2 (major), 170.3 (minor), 140.3 (major), 140.0 (minor), 135.3 (minor), 135.0 (major), 131.5, 128.6 (minor), 128.4 (major), 123.9 (major), 123.8 (minor), 112.7 (minor), 112.2 (major), 57.2 (major), 52.9 (minor), 36.8 (minor), 33.5 (major), 19.9. HRMS (ESI-TOF) Calcd for C₁₂H₁₅BrNO⁺ ([M+H]⁺) 268.0332. Found 268.0335.

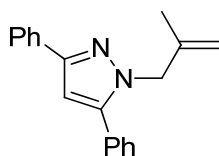


N-Methacryloyl-*N*-methylbenzamide (**8d**),^[13] yellowish oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 3H), 7.40 (dddd, *J* = 7.0, 7.0, 1.0, 1.0 Hz, 2H), 5.27 (s, 1H), 5.14 (q, *J* = 1.6 Hz, 1H), 3.40 (s, 3H), 1.67 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 175.3, 174.3, 143.0, 137.1, 131.9, 128.8, 128.5, 122.0, 33.4, 18.6. HRMS (ESI-TOF) Calcd for C₁₂H₁₄NO₂⁺ ([M+H]⁺) 204.2485. Found 204.2481.

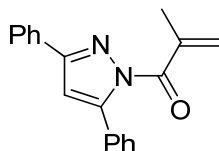


4-Bromo-*N*-methacryloyl-*N*-methylbenzamide (**8f**), white semisolid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.48 (m, 2H), 7.43 – 7.30 (m, 2H), 5.31 (s, 1H), 5.21 (q, *J* = 1.6 Hz, 1H), 3.39 (s, 3H), 1.71 (t, *J* = 1.3 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 174.9, 173.1, 142.7, 135.9, 132.0, 129.9, 126.6, 122.6, 33.5, 18.7. HRMS (ESI-TOF) Calcd for C₁₂H₁₃BrNO₂⁺ ([M+H]⁺) 282.0124. Found 282.0125.

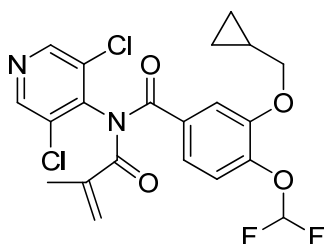
[13] X.-F. Xia, S.-L. Zhu, D. Wang and Y.-M. Liang, *Adv. Synth. Catal.*, 2017, **359**, 859–865.



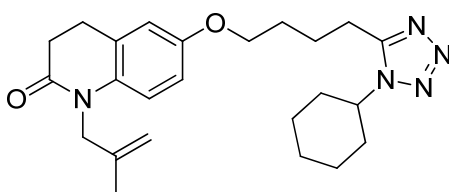
1-(2-Methylallyl)-3,5-diphenyl-1*H*-pyrazole (**12a**), white solid: mp 38 – 39 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.84 (m, 2H), 7.47 – 7.38 (m, 7H), 7.32 – 7.27 (m, 1H), 6.63 (s, 1H), 4.91 (dd, *J* = 1.4, 1.5 Hz, 1H), 4.69 (s, 2H), 4.57 (s, 1H), 1.71 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.8, 145.4, 141.7, 133.5, 130.8, 128.7, 128.62, 128.60, 127.6, 125.7, 112.2, 103.4, 55.2, 20.2. HRMS (ESI-TOF) Calcd for C₁₉H₁₉N₂⁺ ([M+H]⁺) 275.1543. Found 275.1540.



1-(3,5-Diphenyl-1*H*-pyrazol-1-yl)-2-methylprop-2-en-1-one (**12b**), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.86 (m, 2H), 7.46 – 7.36 (m, 9H), 6.79 (s, 1H), 6.09 (t, *J* = 1.1 Hz, 1H), 5.88 (p, *J* = 1.5 Hz, 1H), 2.18 (t, *J* = 1.2 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 153.4, 148.1, 138.8, 131.9, 130.8, 129.1, 128.78, 128.77, 128.4, 128.31, 128.28, 126.3, 108.8, 19.7. HRMS (ESI-TOF) Calcd for C₁₉H₁₇N₂O⁺ ([M+H]⁺) 289.1335. Found 289.1339.



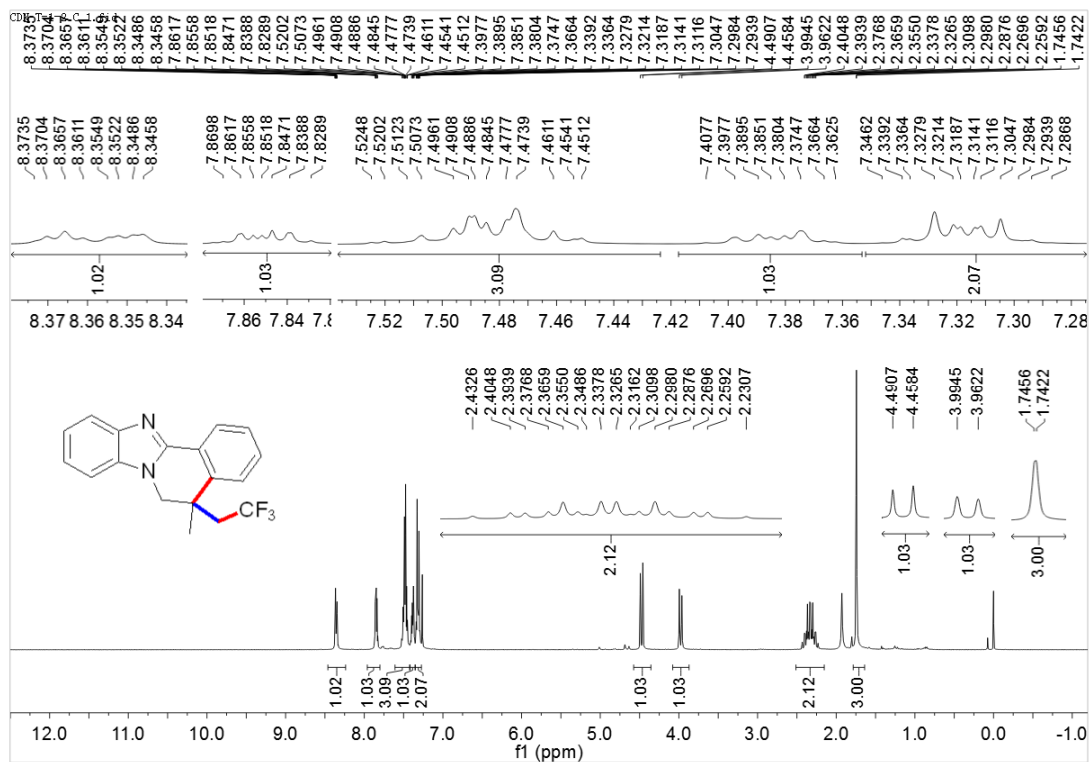
3-(Cyclopropylmethoxy)-*N*-(3,5-dichloropyridin-4-yl)-4-(difluoromethoxy)-*N*-methacryloylbenzamide (**14**), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 2H), 7.35 – 7.30 (m, 2H), 7.16 (d, *J* = 8.3 Hz, 1H), 6.71 (t, *J* = 74.6 Hz, 1H), 5.79 (d, *J* = 1.2 Hz, 1H), 5.49 (q, *J* = 1.5 Hz, 1H), 3.88 (d, *J* = 7.0 Hz, 2H), 1.94 (s, 3H), 1.30 – 1.23 (m, 1H), 0.67 – 0.62 (m, 2H), 0.37 – 0.33 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 172.0, 170.3, 150.5, 149.0, 143.98, 143.95, 143.91, 143.1, 140.4, 132.3, 131.4, 123.9, 121.72, 121.69, 115.6 (t, *J* = 1039.0 Hz), 114.6, 74.0, 18.5, 9.9, 3.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.98 (d, *J* = 74.4 Hz, 2F). HRMS (ESI-TOF) Calcd for C₂₁H₁₈Cl₂F₂N₂O₄⁺ ([M+H]⁺) 470.0612. Found 470.0611.



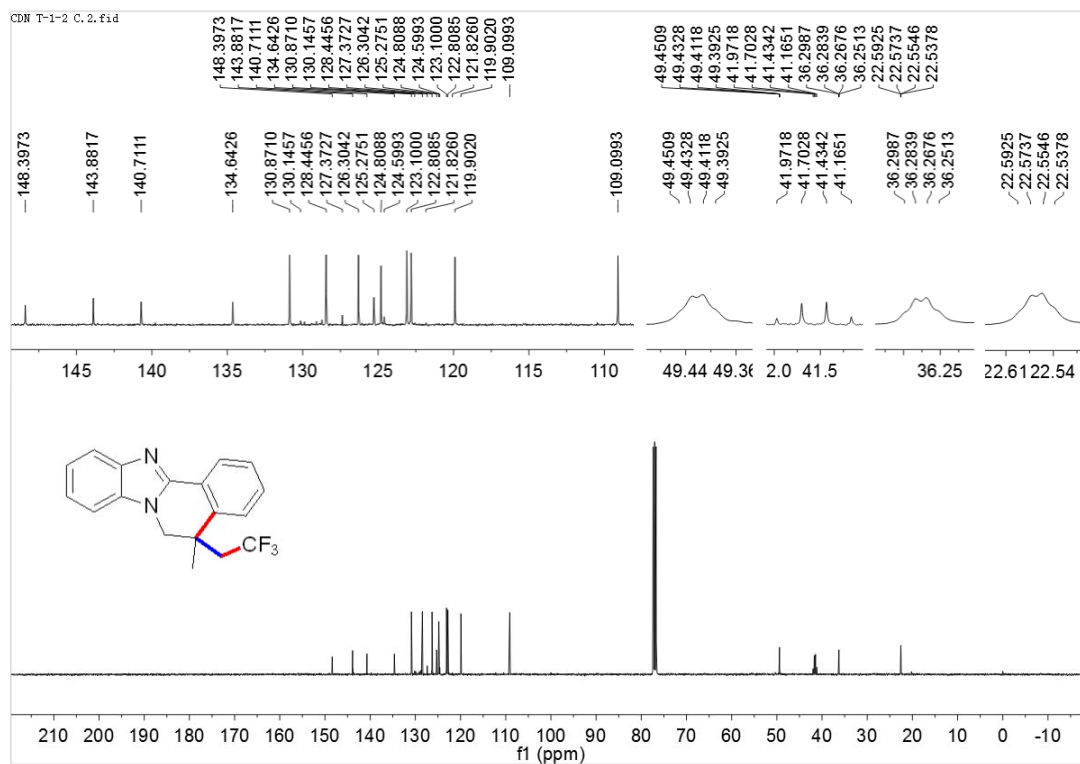
6-(4-(1-Cyclohexyl-1*H*-tetrazol-5-yl)butoxy)-1-(2-methylallyl)-3,4-dihydroquinolin-2(1*H*)-one (**16**), yellowish oil. ^1H NMR (400 MHz, CDCl_3) δ 6.84 (d, $J = 8.5$ Hz, 1H), 6.71 (d, $J = 8.9$ Hz, 2H), 4.87 (p, $J = 1.5$ Hz, 1H), 4.70 (s, 1H), 4.43 (s, 2H), 4.20 – 4.12 (m, 1H), 3.99 (t, $J = 6.0$ Hz, 2H), 2.96 – 2.87 (m, 4H), 2.69 – 2.65 (m, 2H), 2.07 – 1.98 (m, 7H), 1.95 – 1.87 (m, 3H), 1.75 (s, 4H), 1.46 – 1.30 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 169.6, 154.4, 153.6, 139.7, 133.4, 127.7, 116.5, 114.2, 112.5, 110.6, 67.4, 57.5, 48.0, 32.9, 31.7, 28.5, 25.8, 25.2, 24.8, 24.0, 22.9, 20.0. HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{34}\text{N}_5\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 424.2707. Found 424.2715.

VII. Copies of NMR spectra for products and new compounds

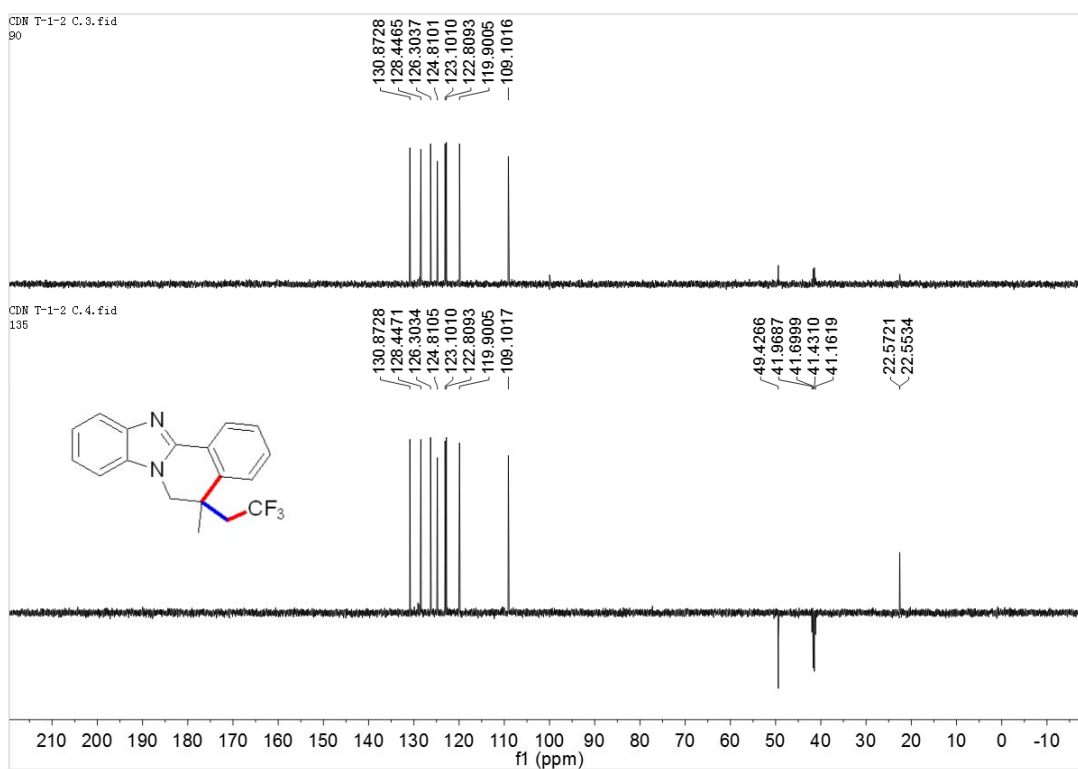
3a, ¹H NMR



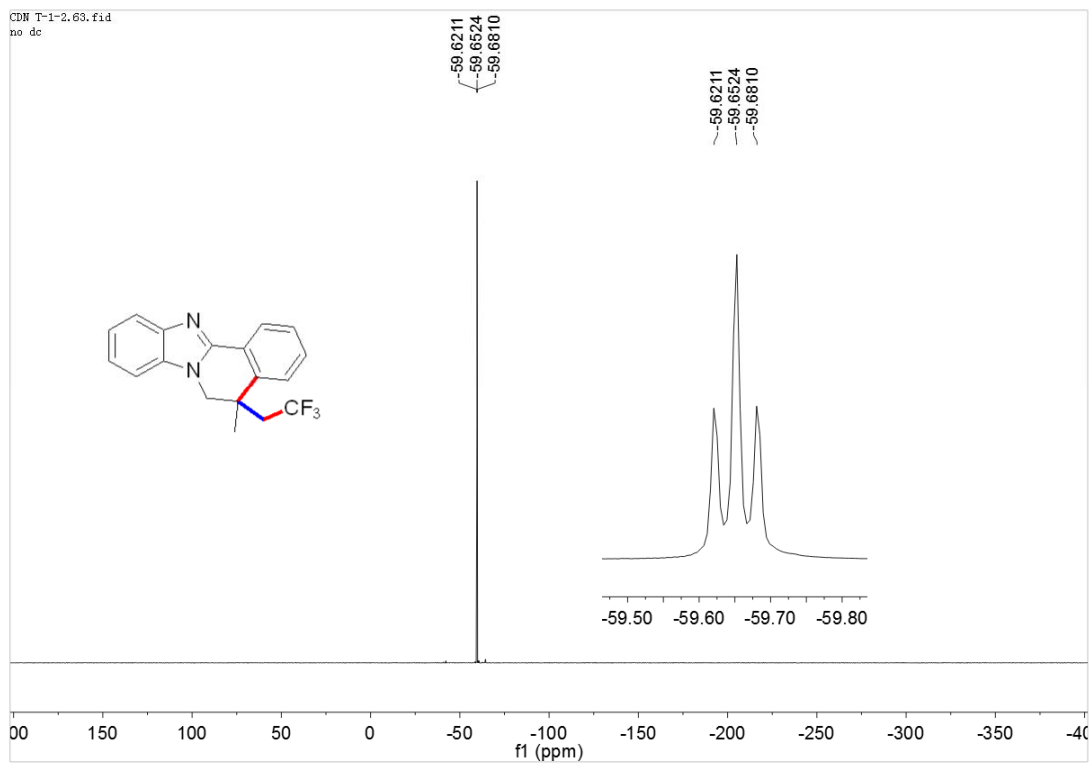
¹³C NMR



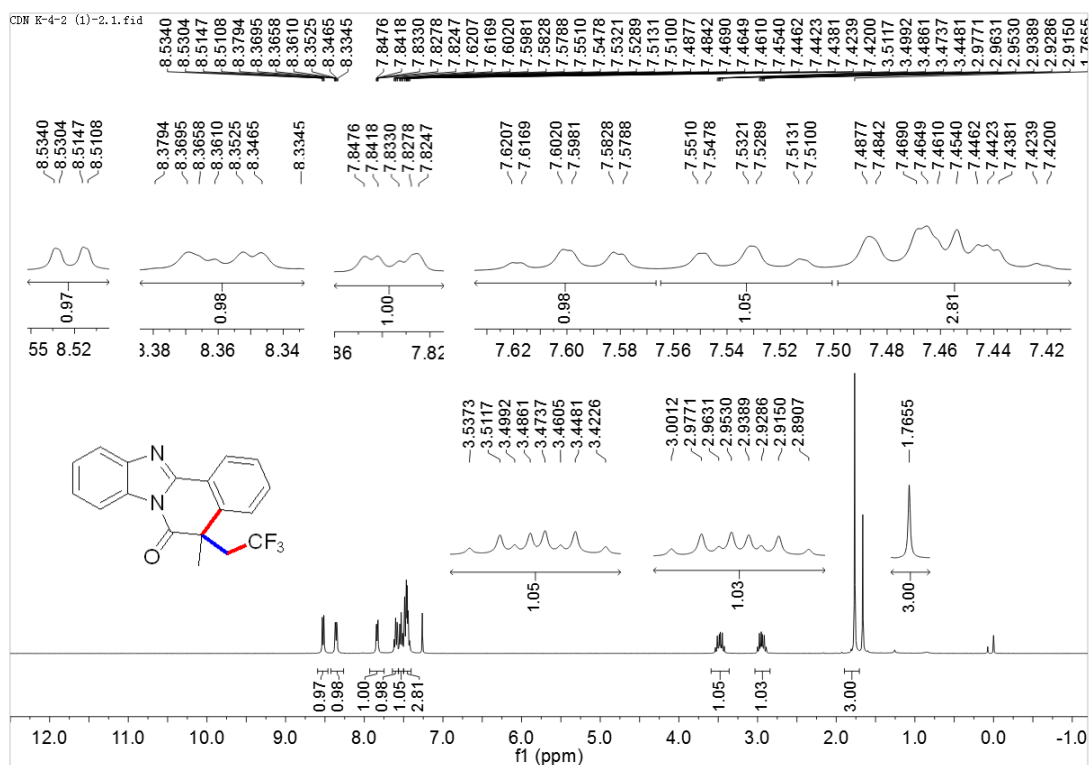
DEPT 90 and DEPT 135



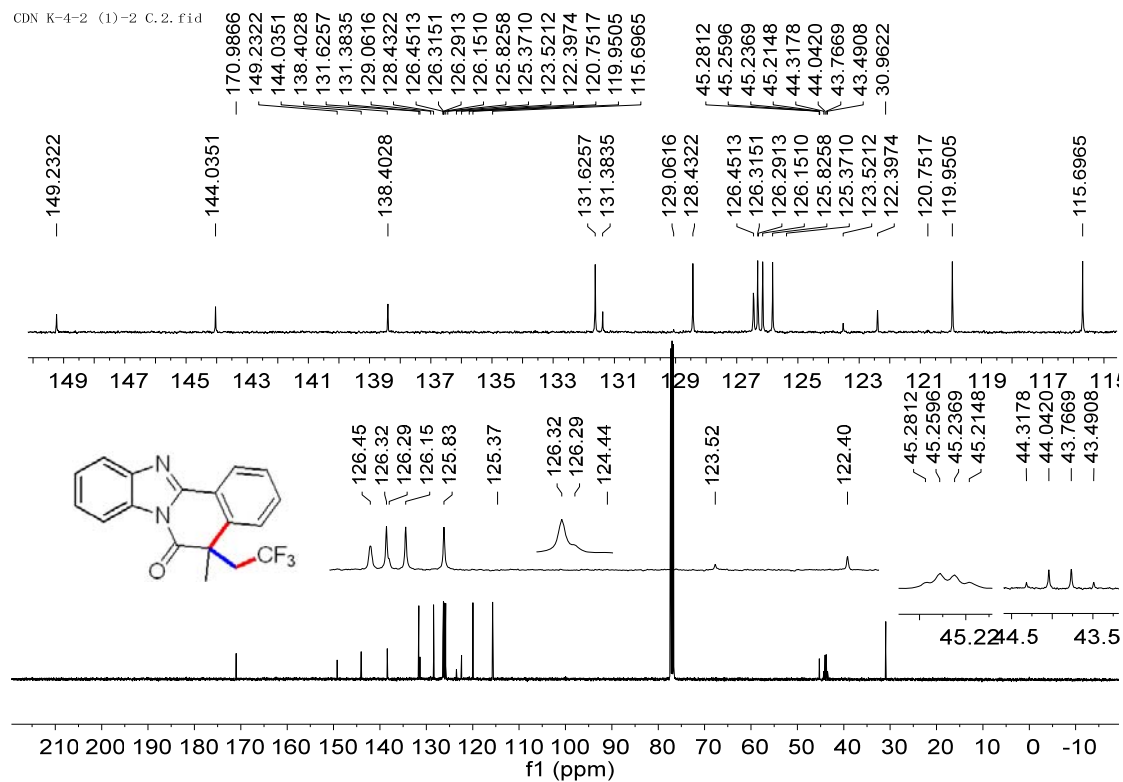
¹⁹F NMR



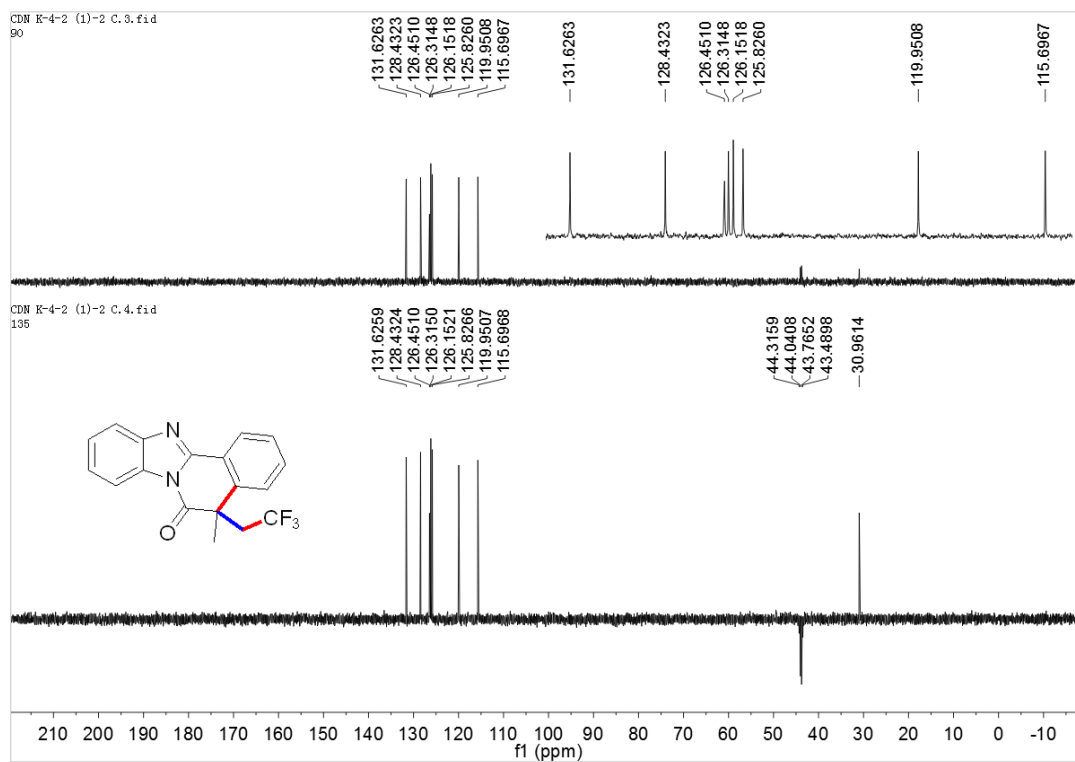
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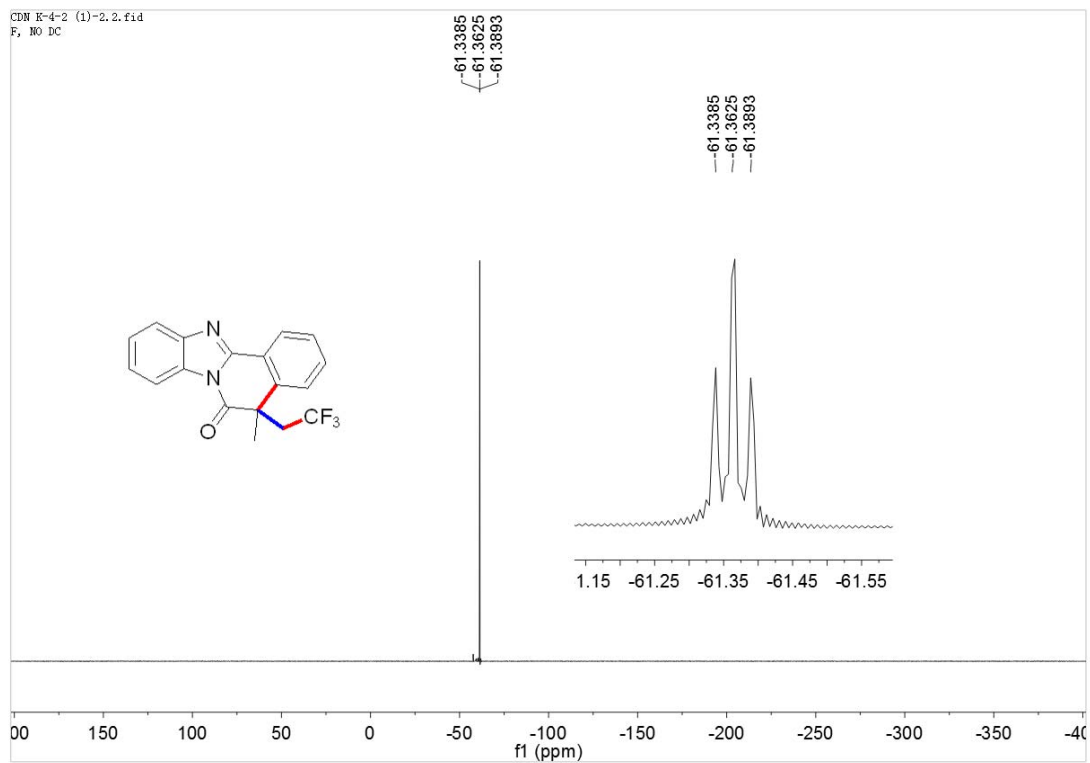
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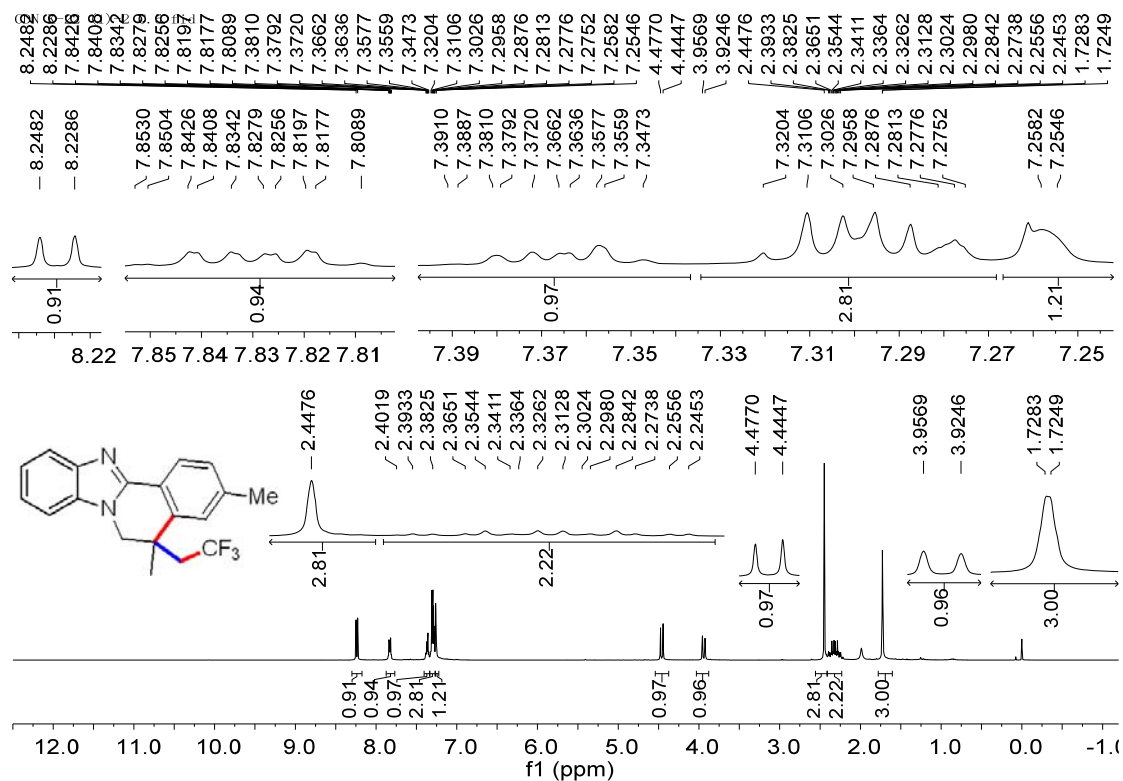
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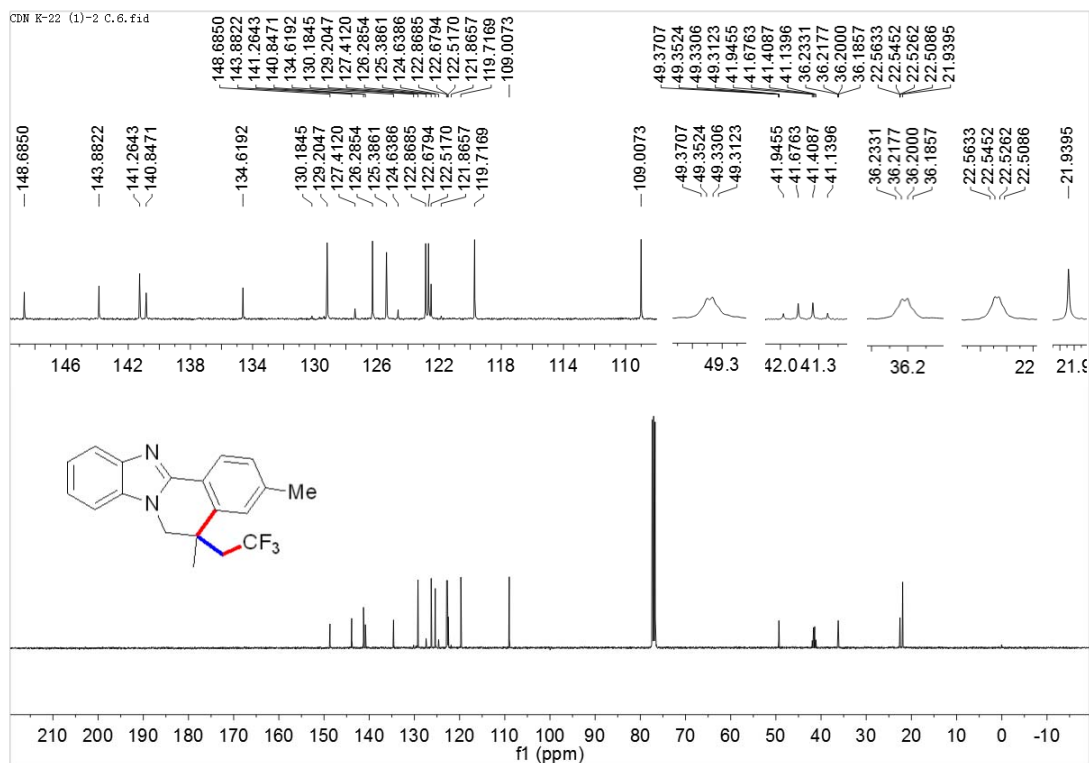
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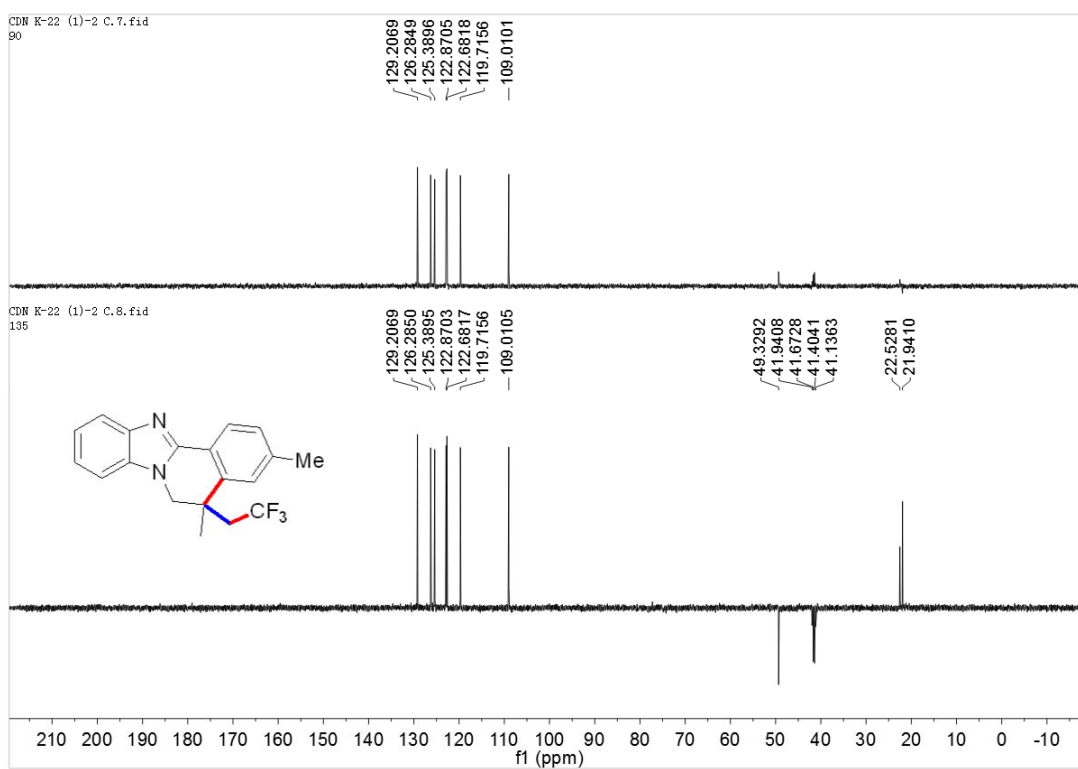
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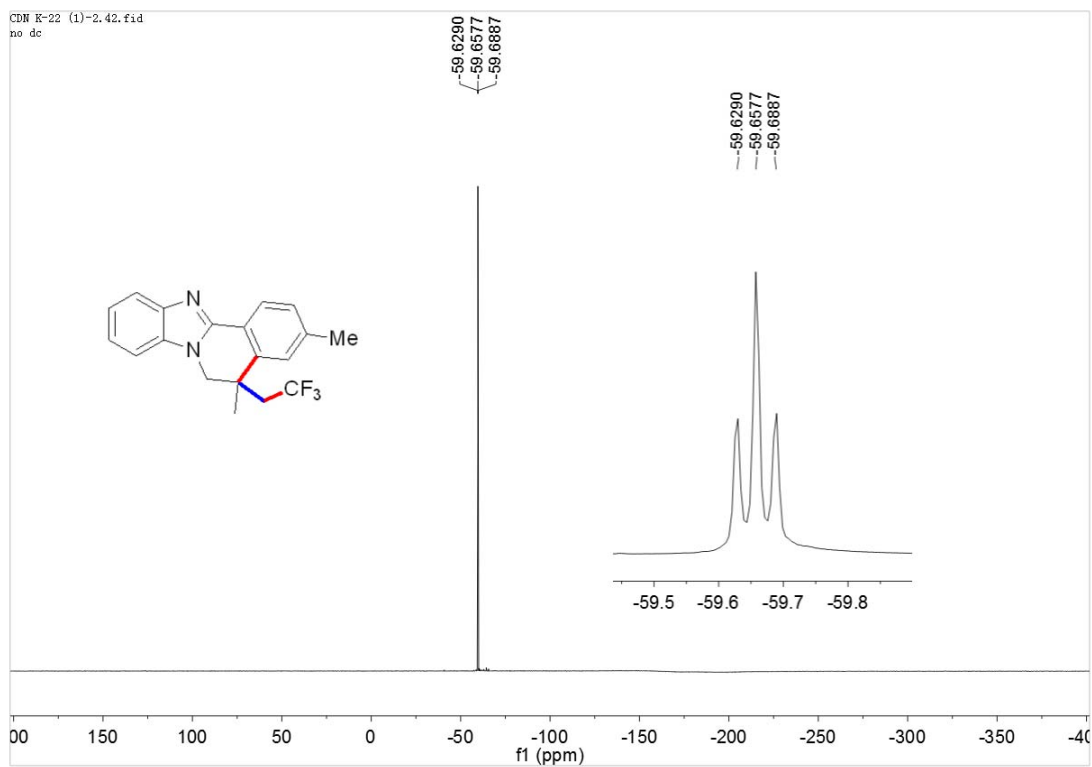
¹³C NMR



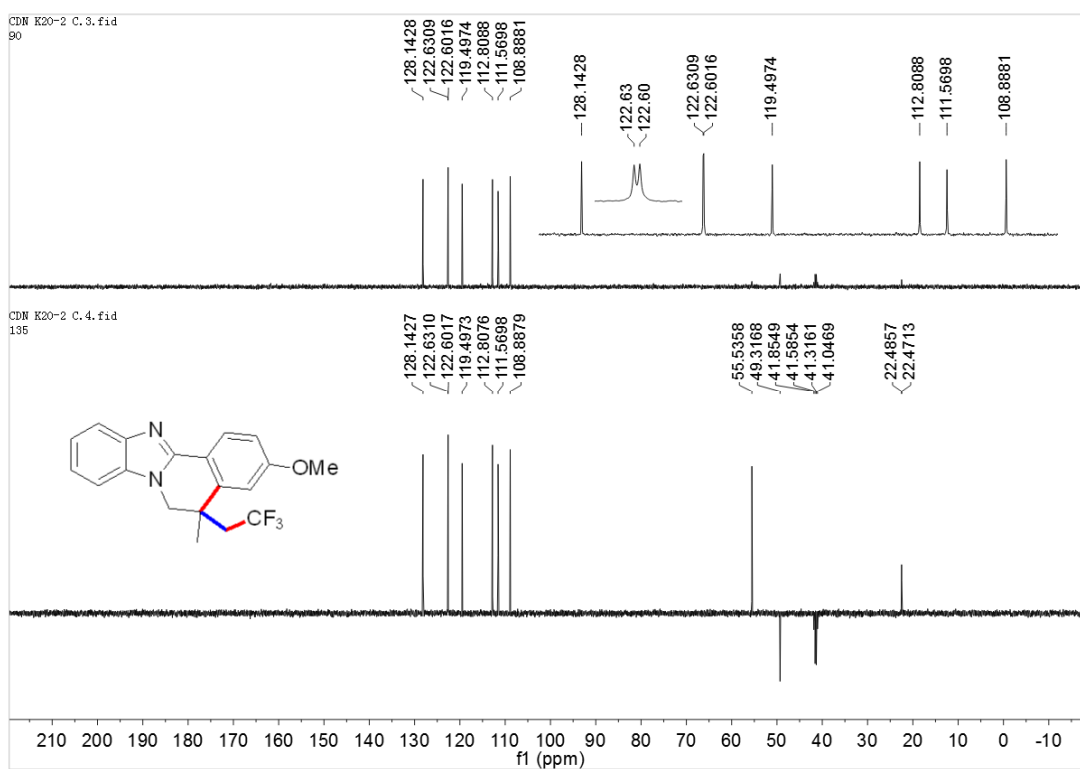
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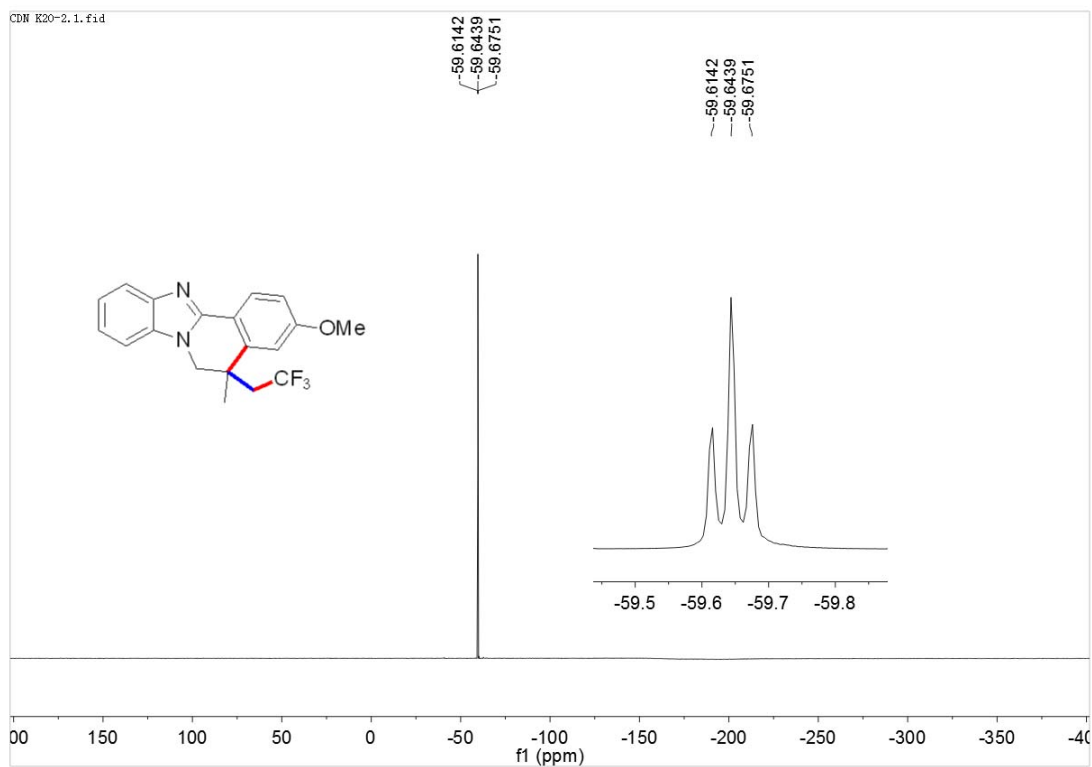
¹⁹F NMR



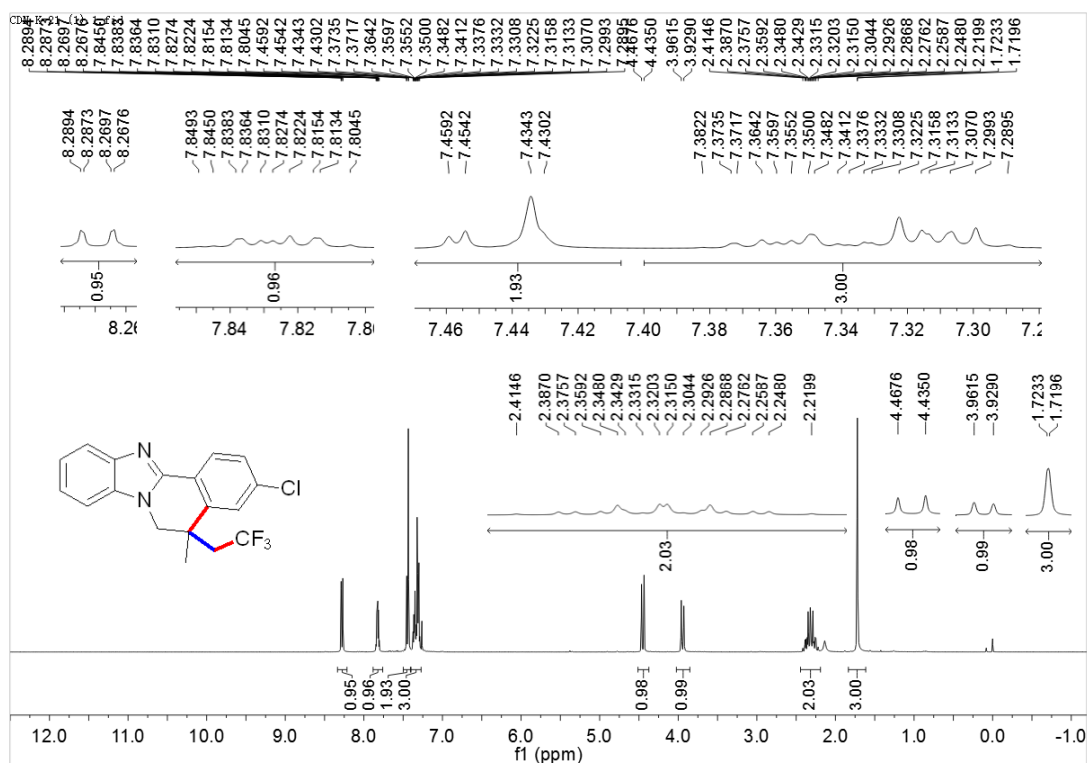
DEPT 90 and DEPT 135



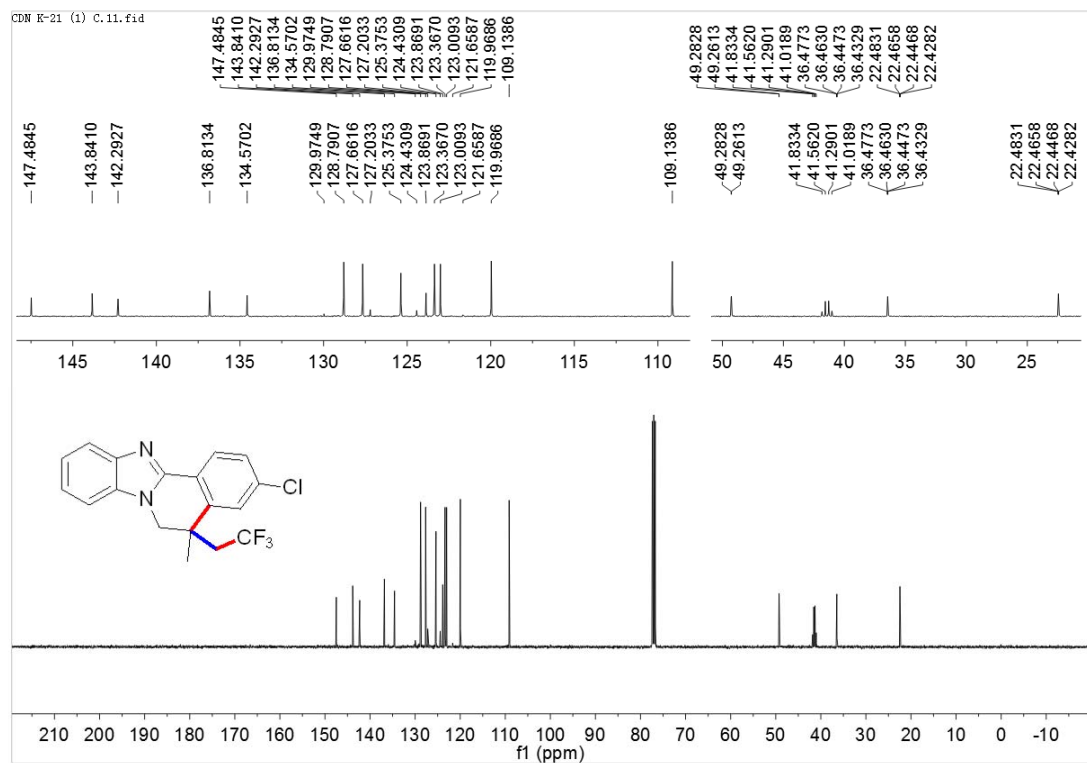
¹⁹F NMR



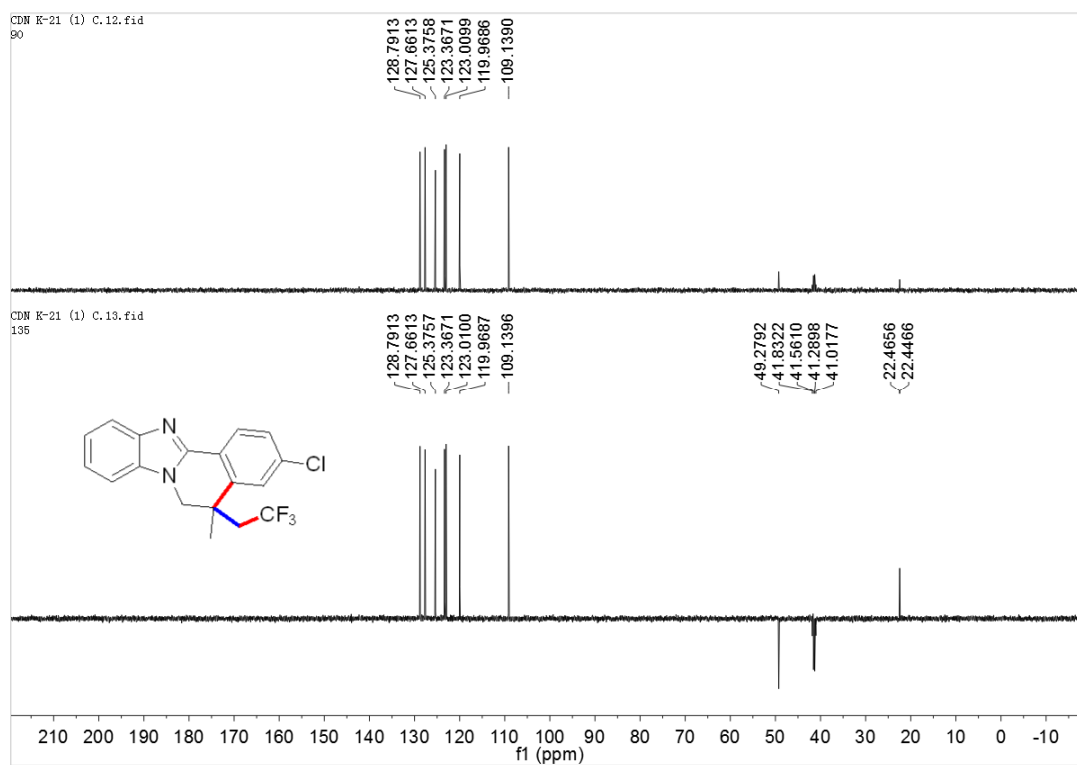
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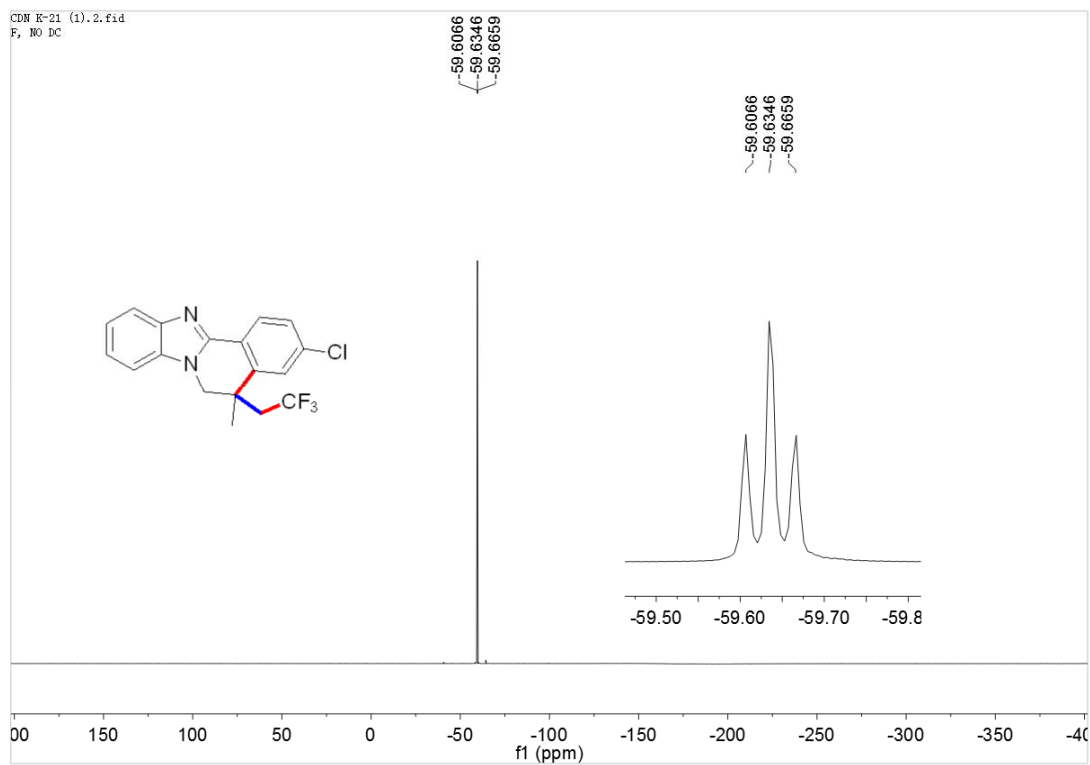
¹³C NMR



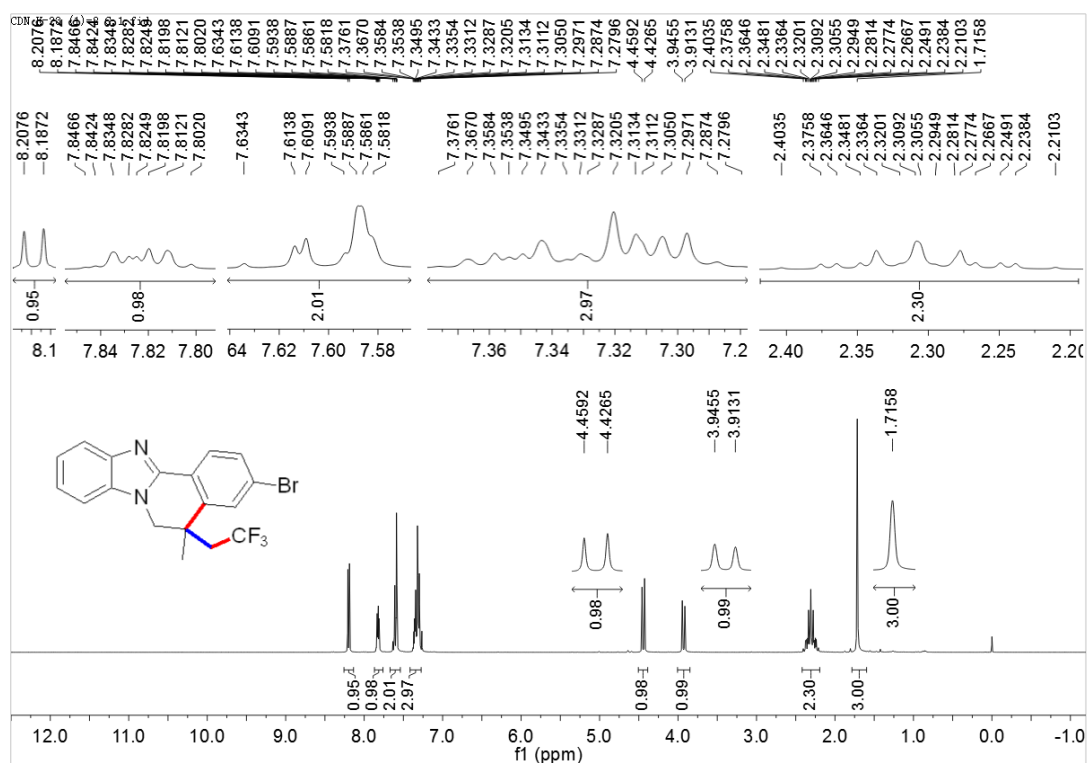
DEPT 90 and DEPT 135



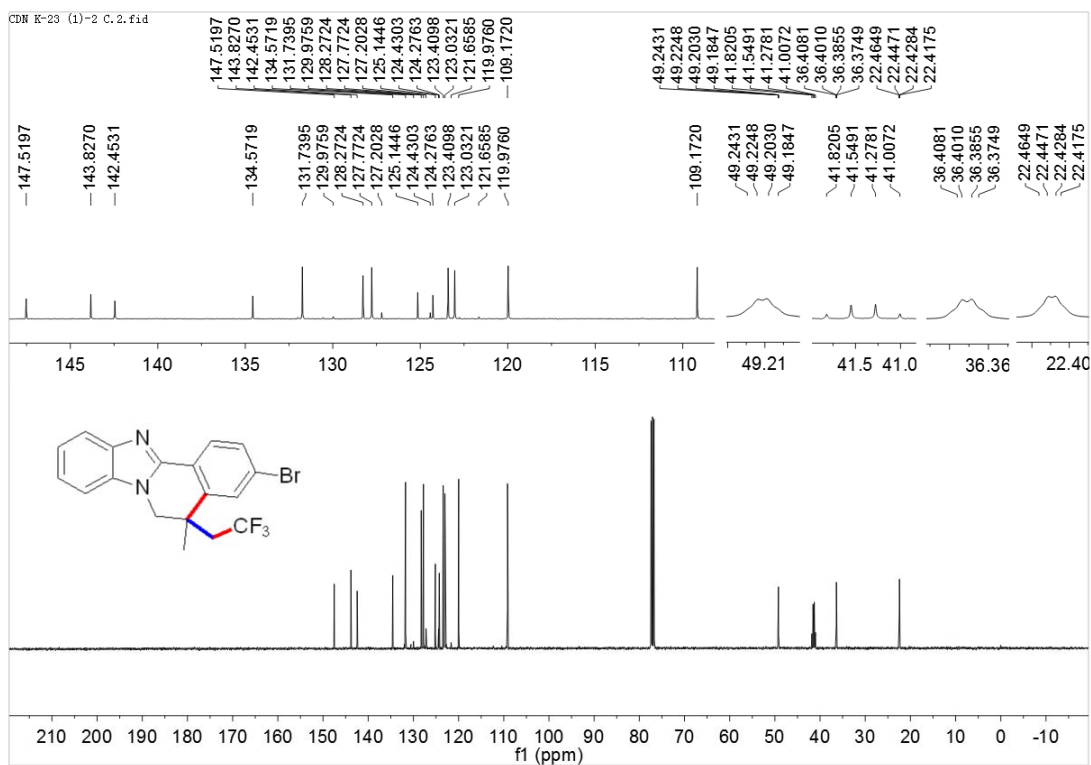
¹⁹F NMR



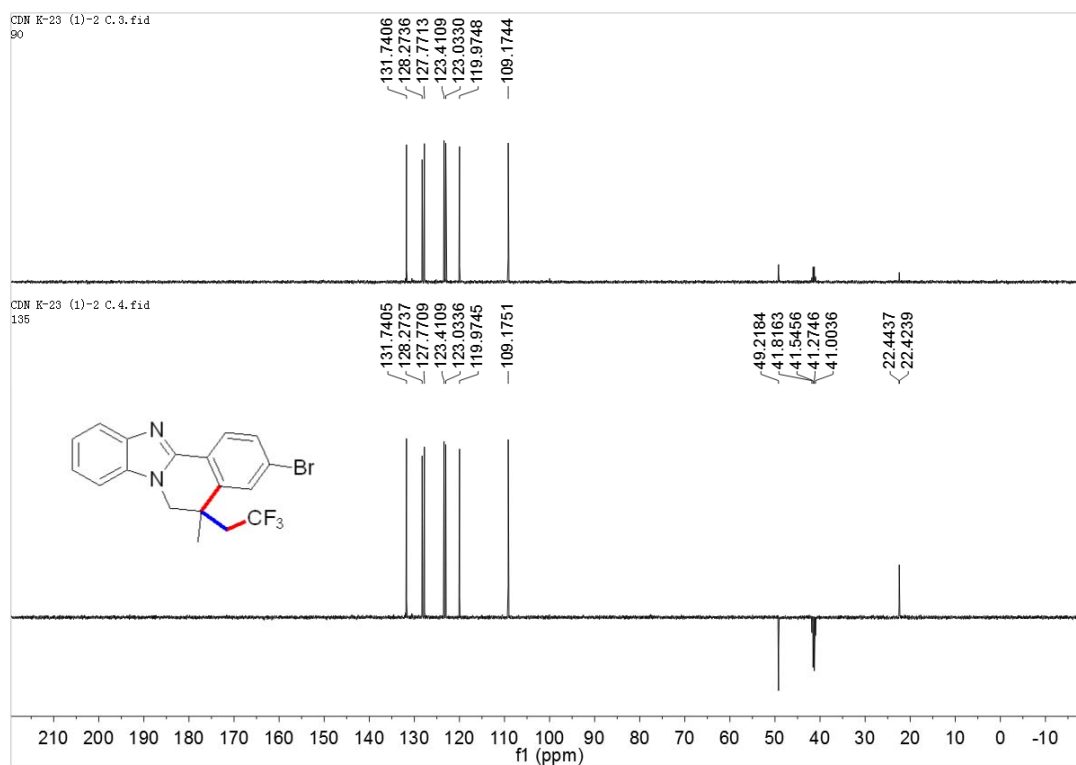
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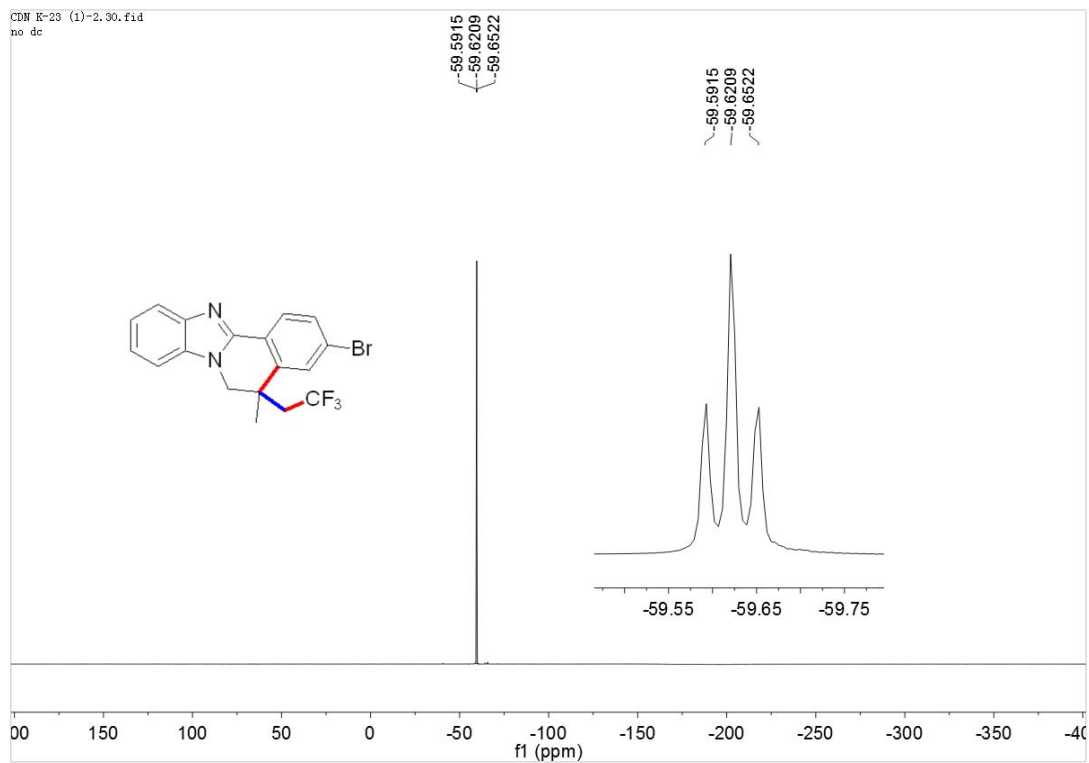
¹³C NMR



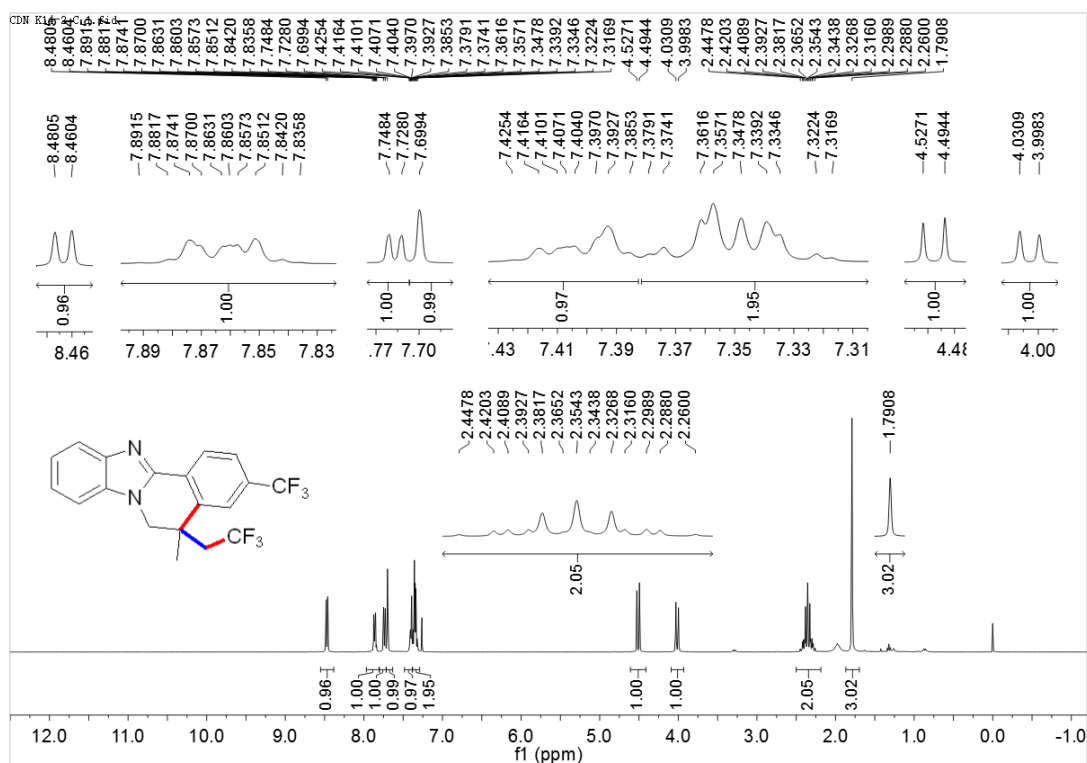
DEPT 90 and DEPT 135



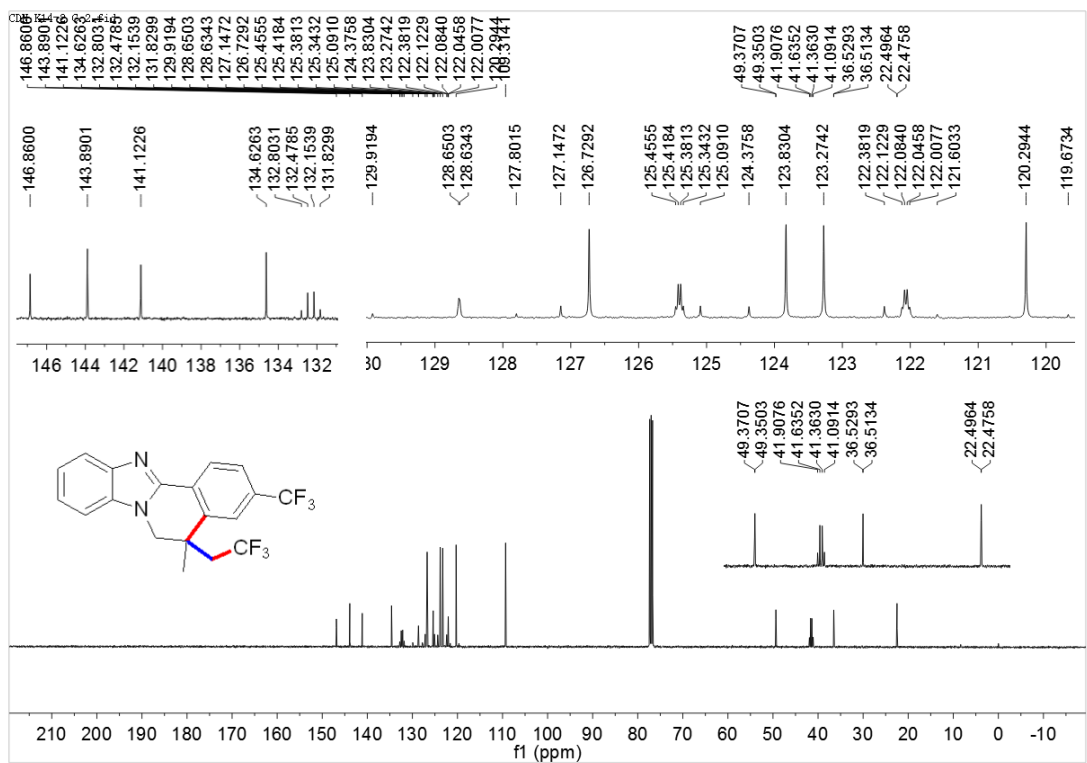
¹⁹F NMR



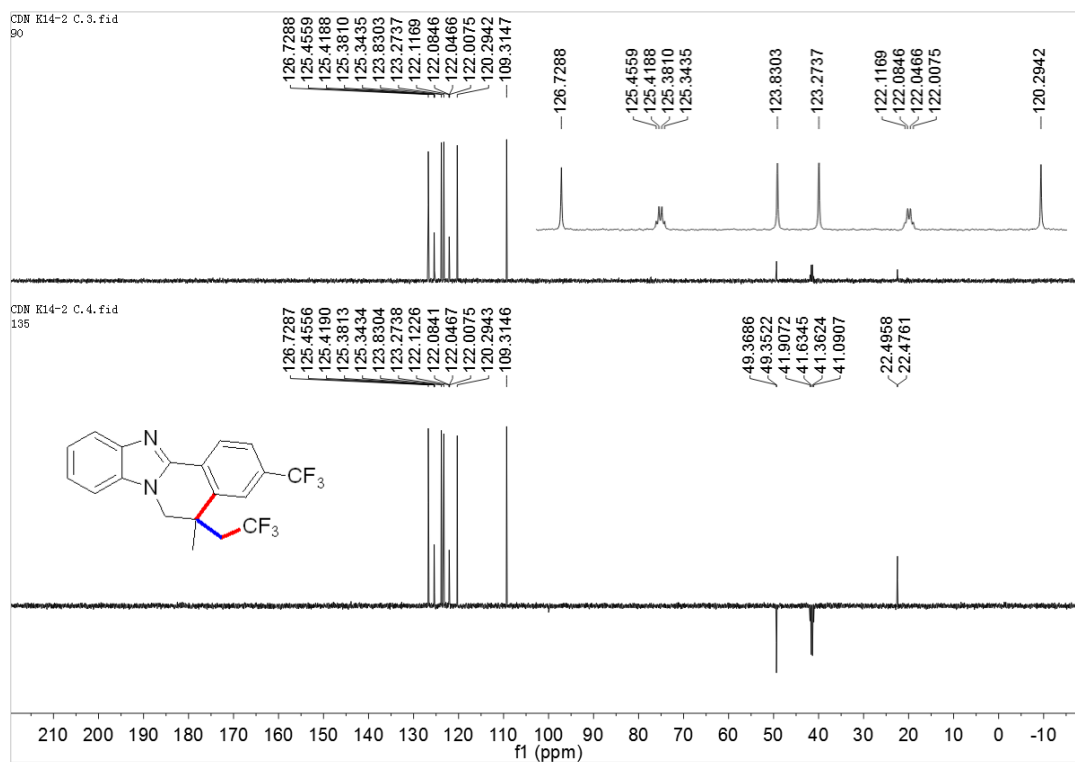
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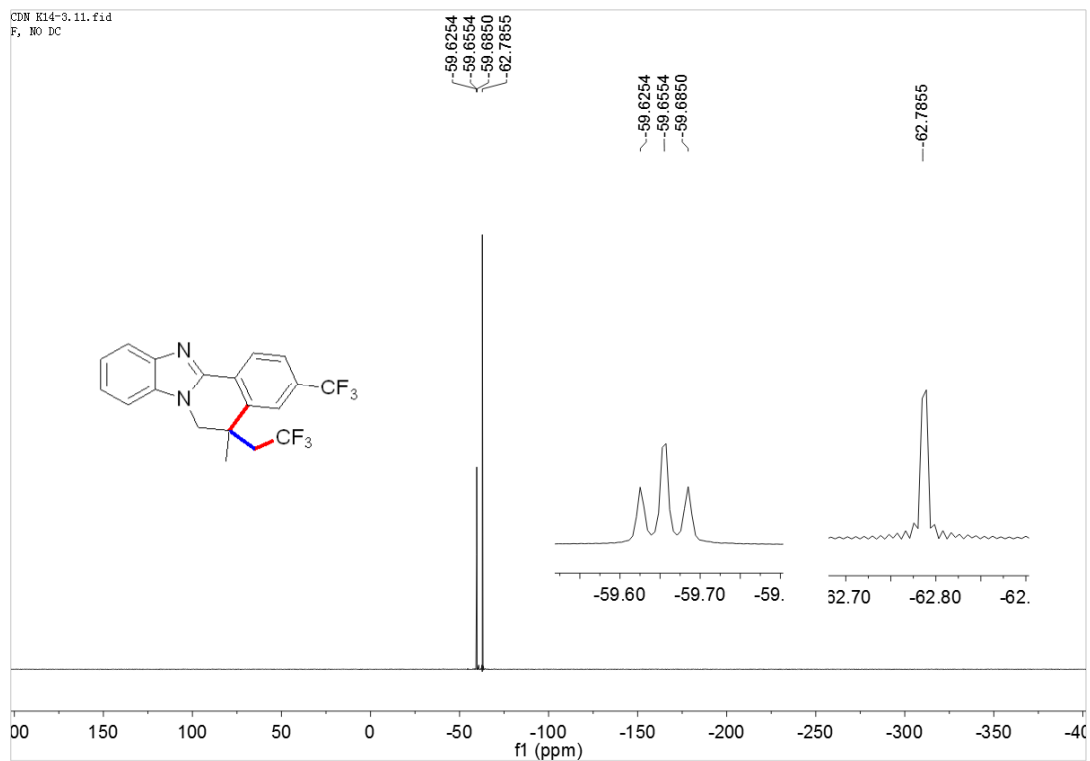
¹³C NMR



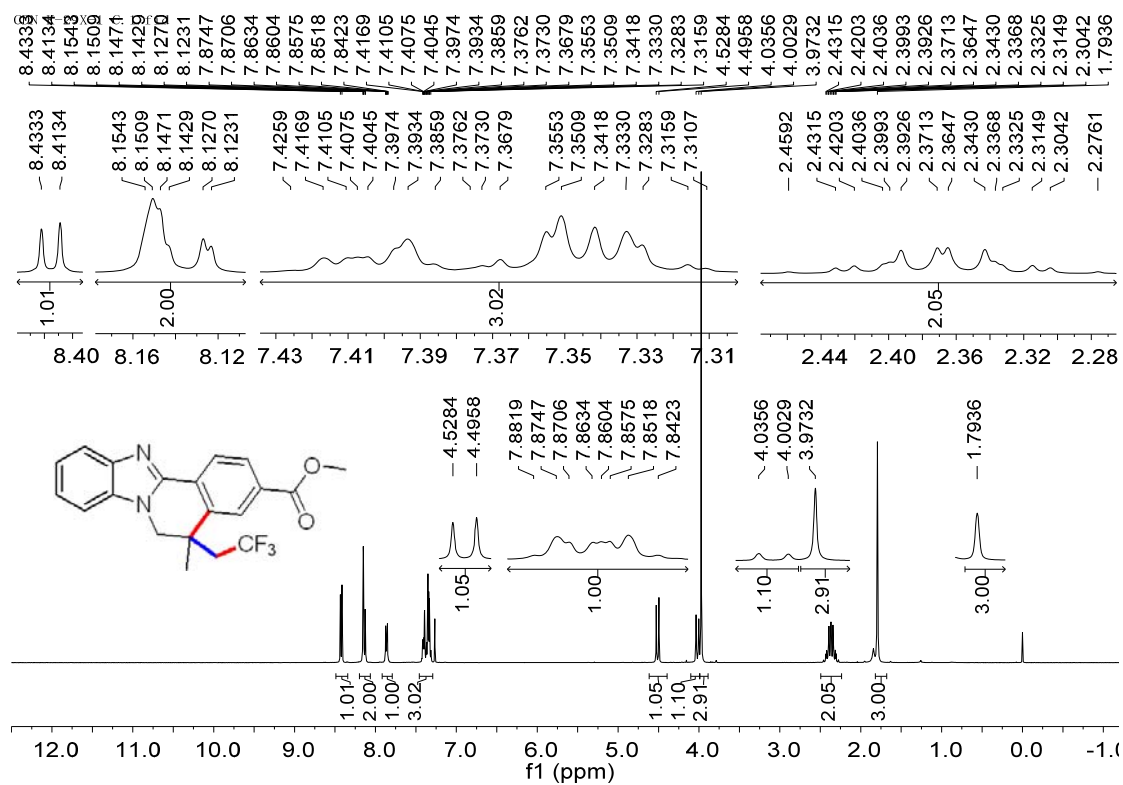
DEPT 90 and DEPT 135



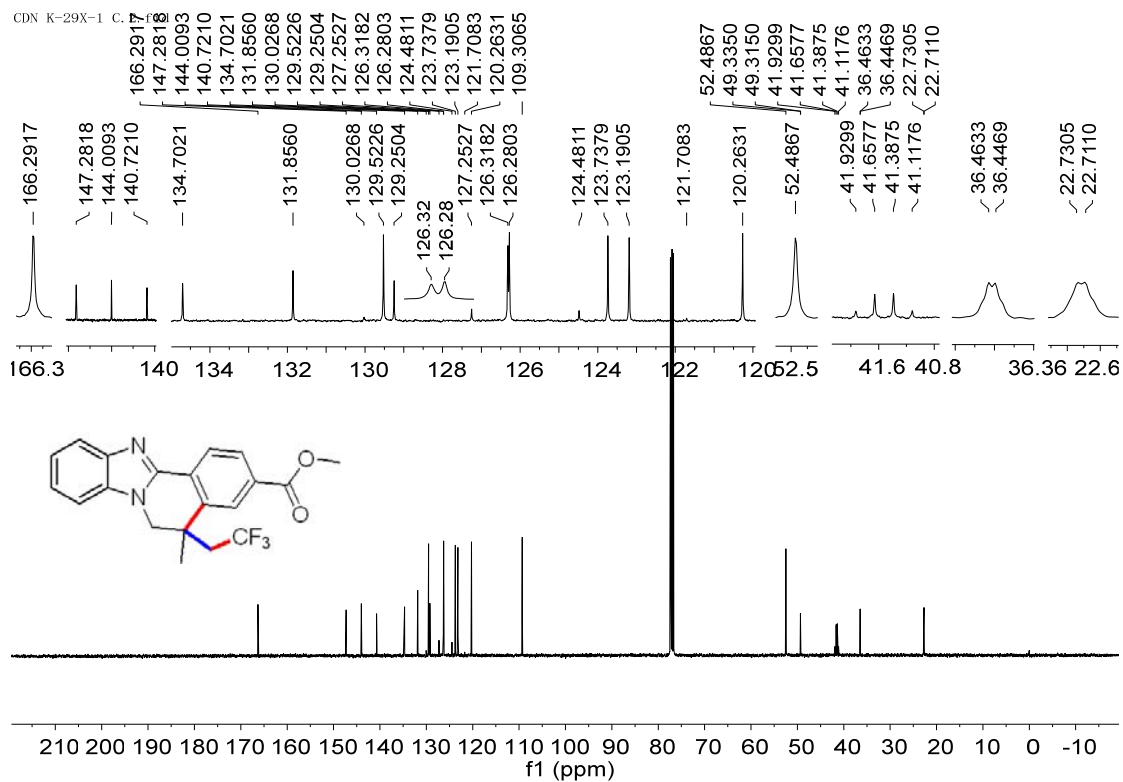
¹⁹F NMR



3c6, ¹H NMR



¹³C NMR



DEPT 90 and DEPT 135

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90

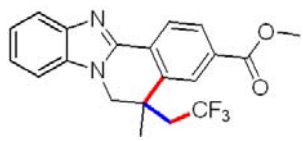
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123.1915
120.2625
109.3071

CDN K-29X-1 C. 4. fid
135

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126.3188
126.2801
123.7382
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109.3072

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41.1143
22.7168



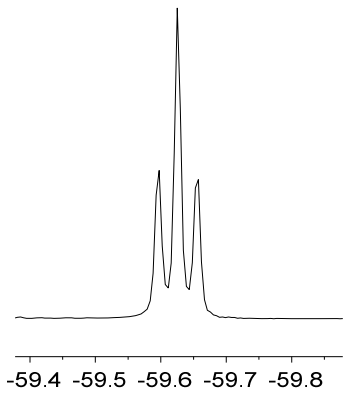
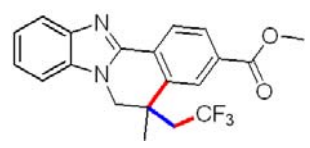
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f1 (ppm)

¹⁹F NMR

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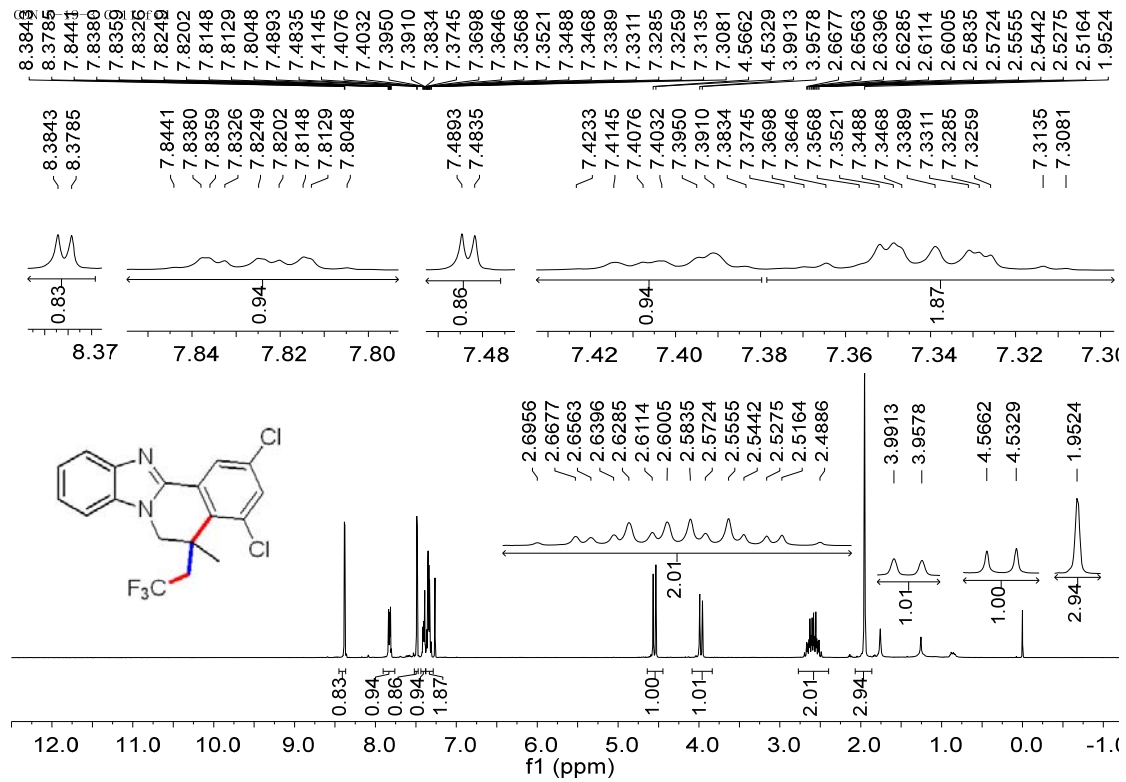
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-59.6253
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-59.5967
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-59.6550

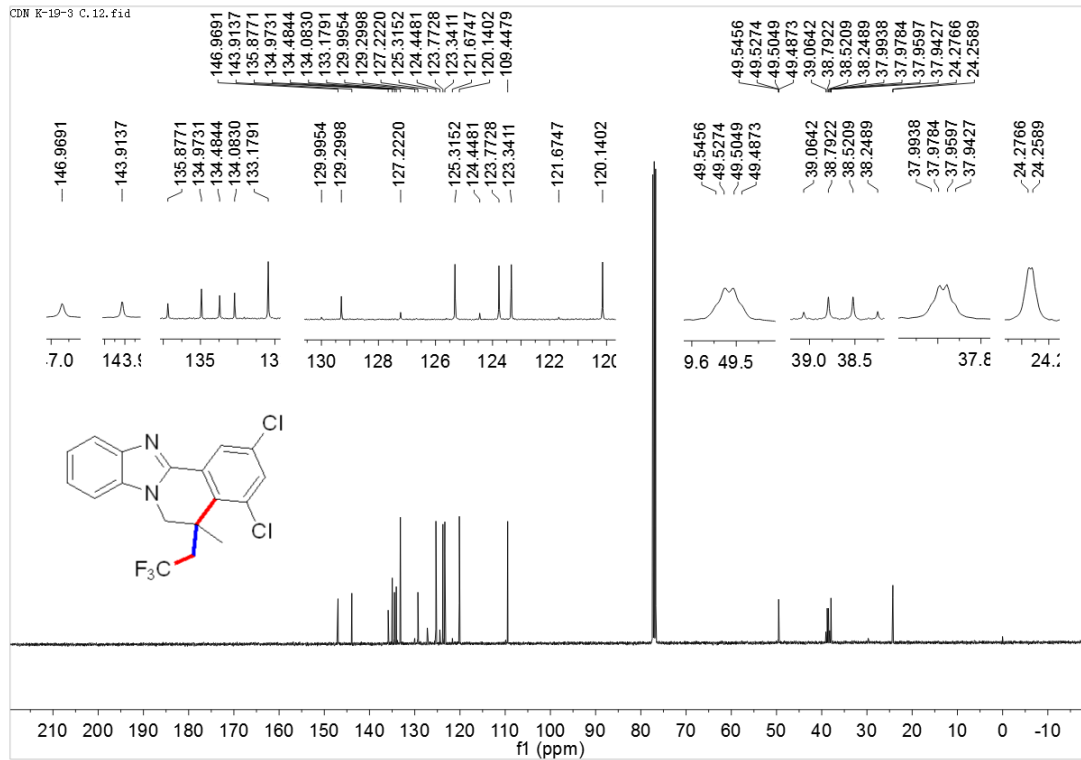


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f1 (ppm)

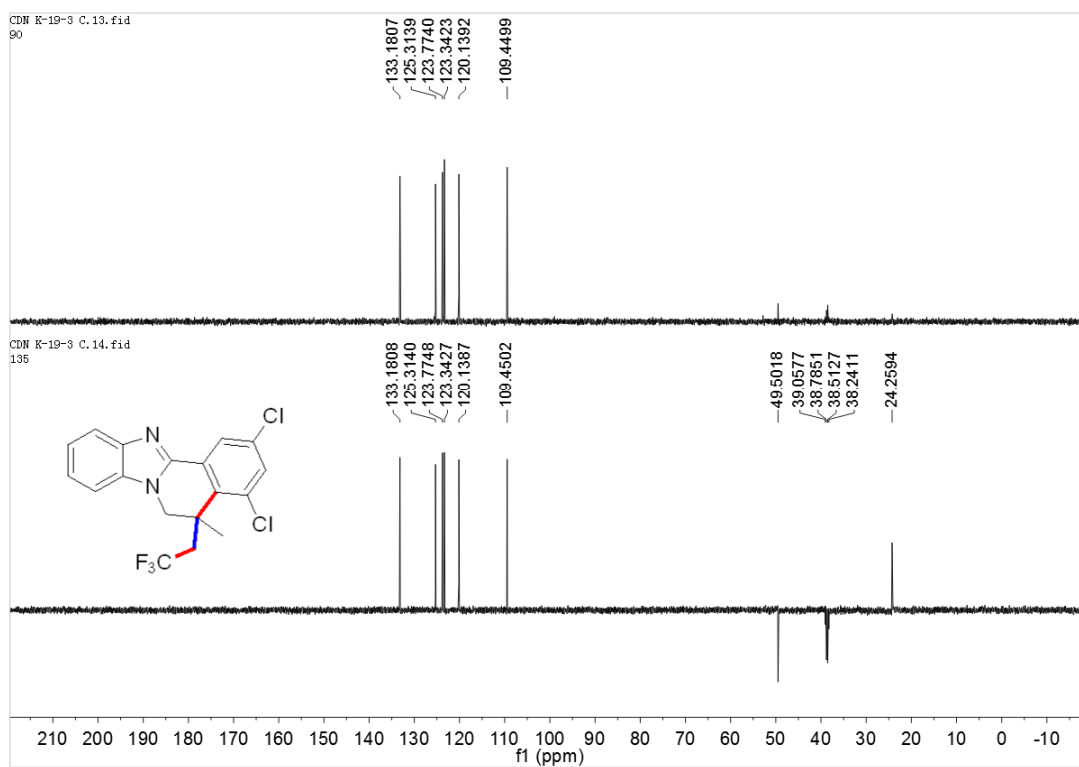
3d, ¹H NMR



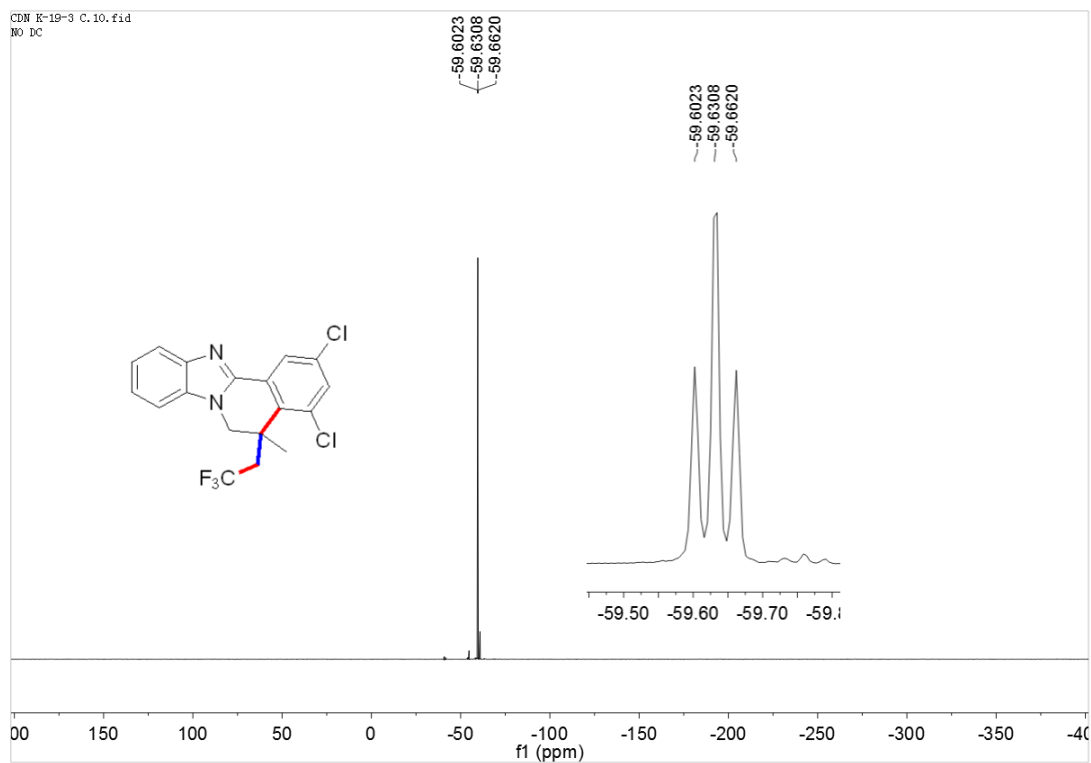
¹³C NMR



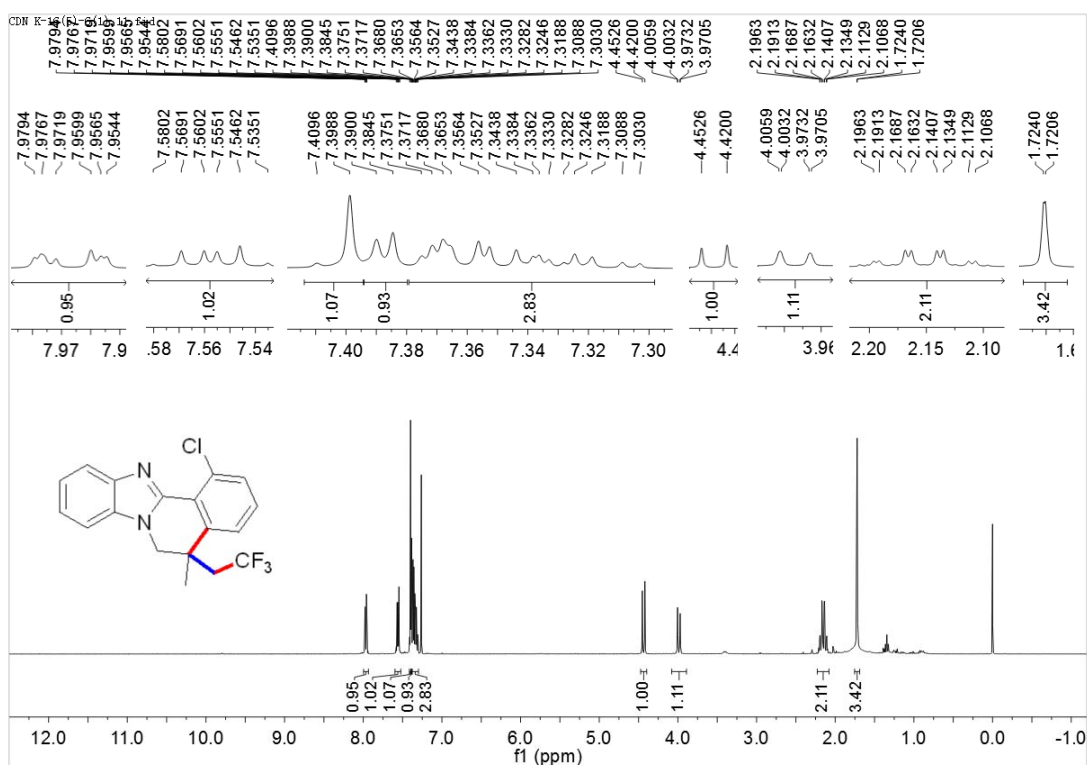
DEPT 90 and DEPT 135



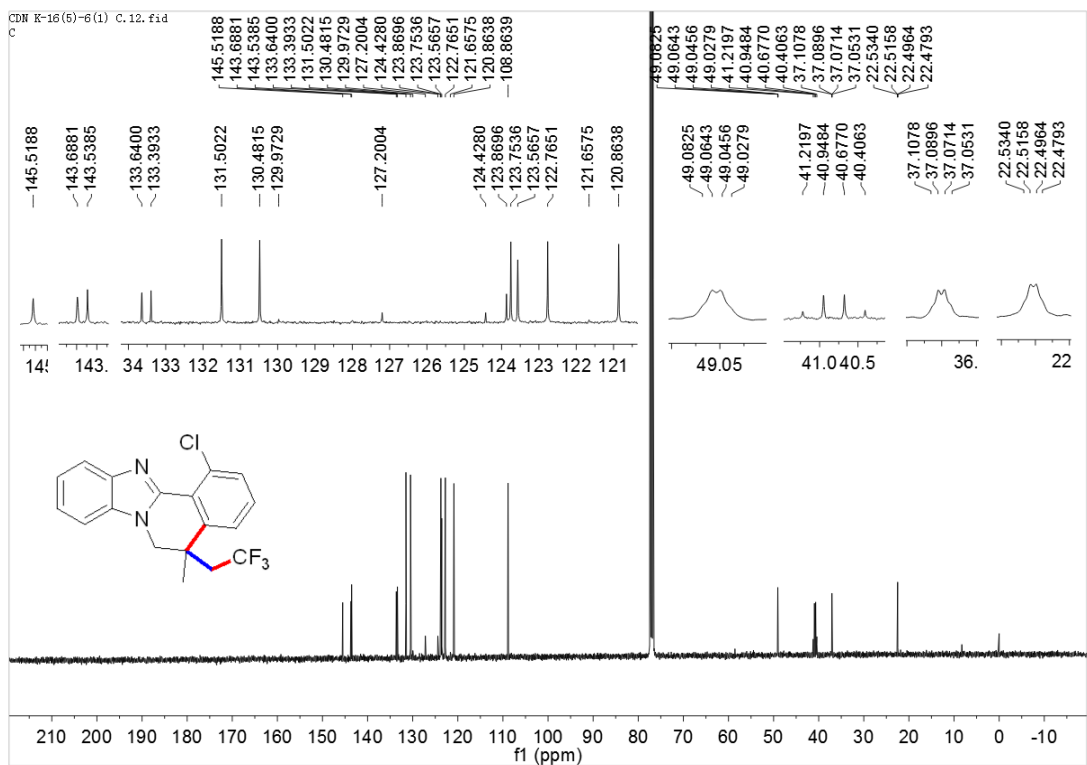
¹⁹F NMR



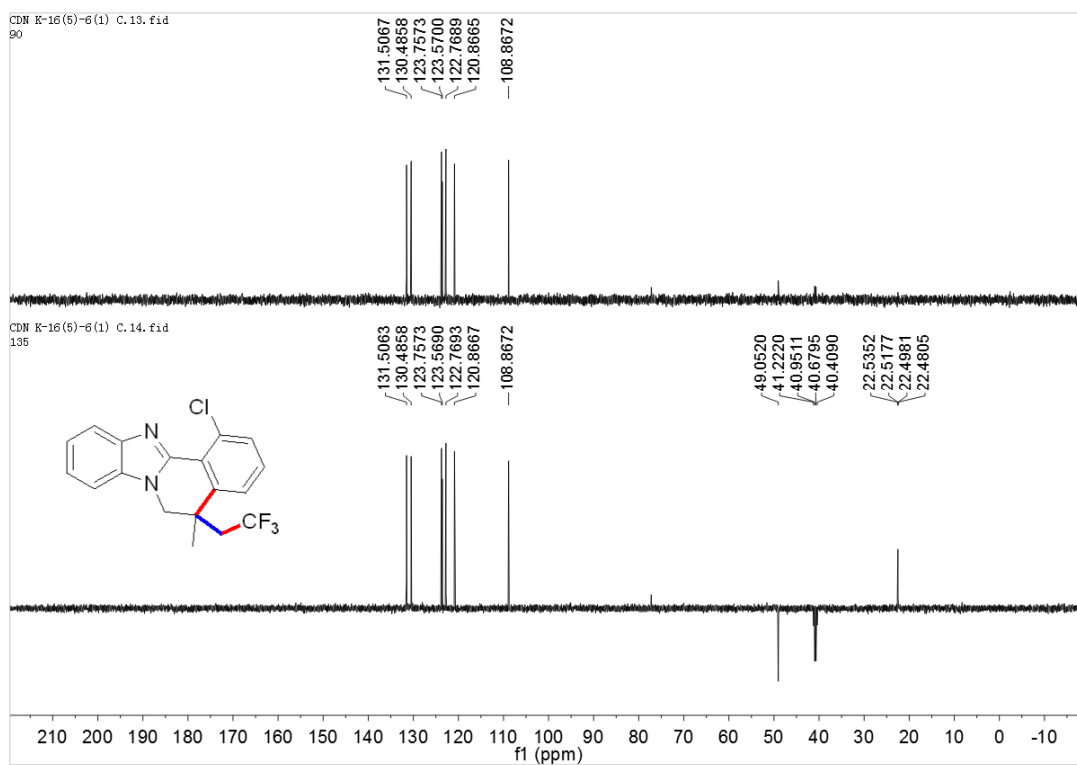
3e, ¹H NMR



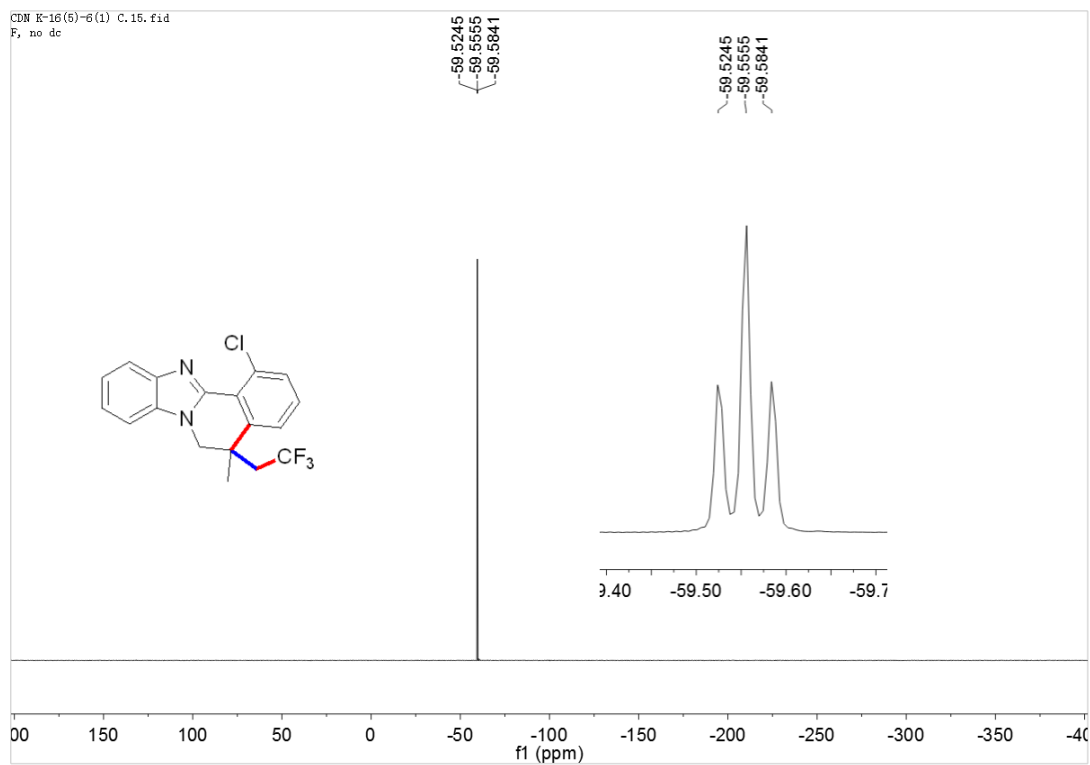
¹³C NMR



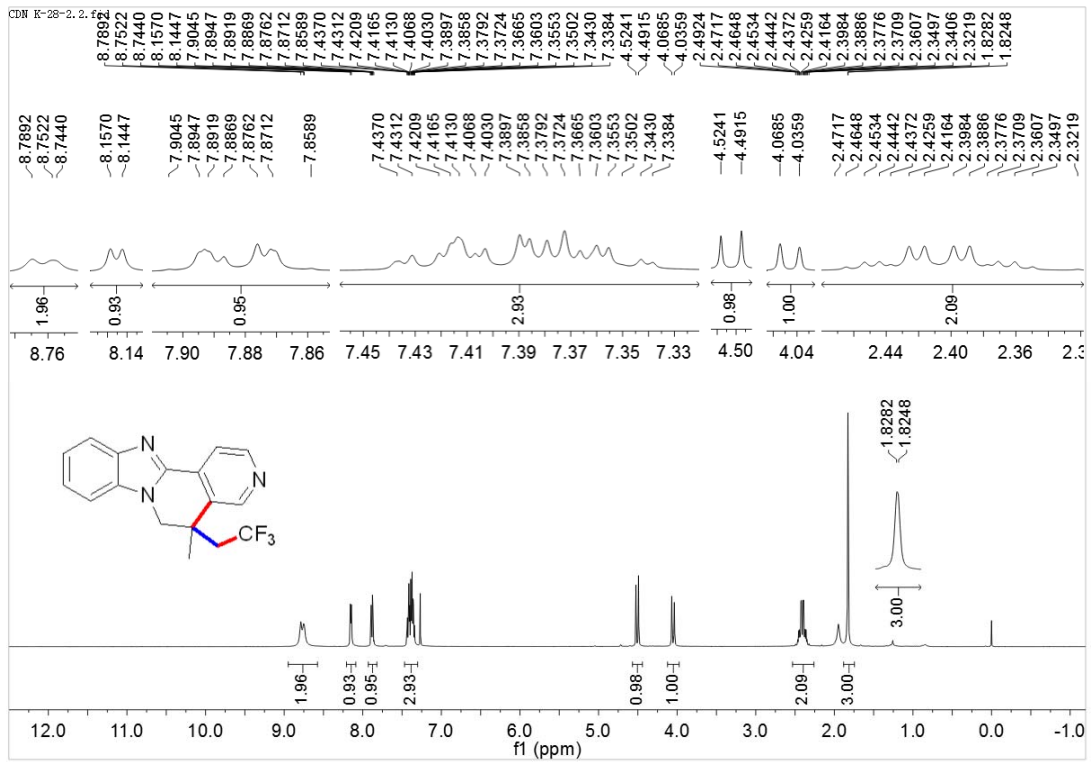
DEPT 90 and DEPT 135



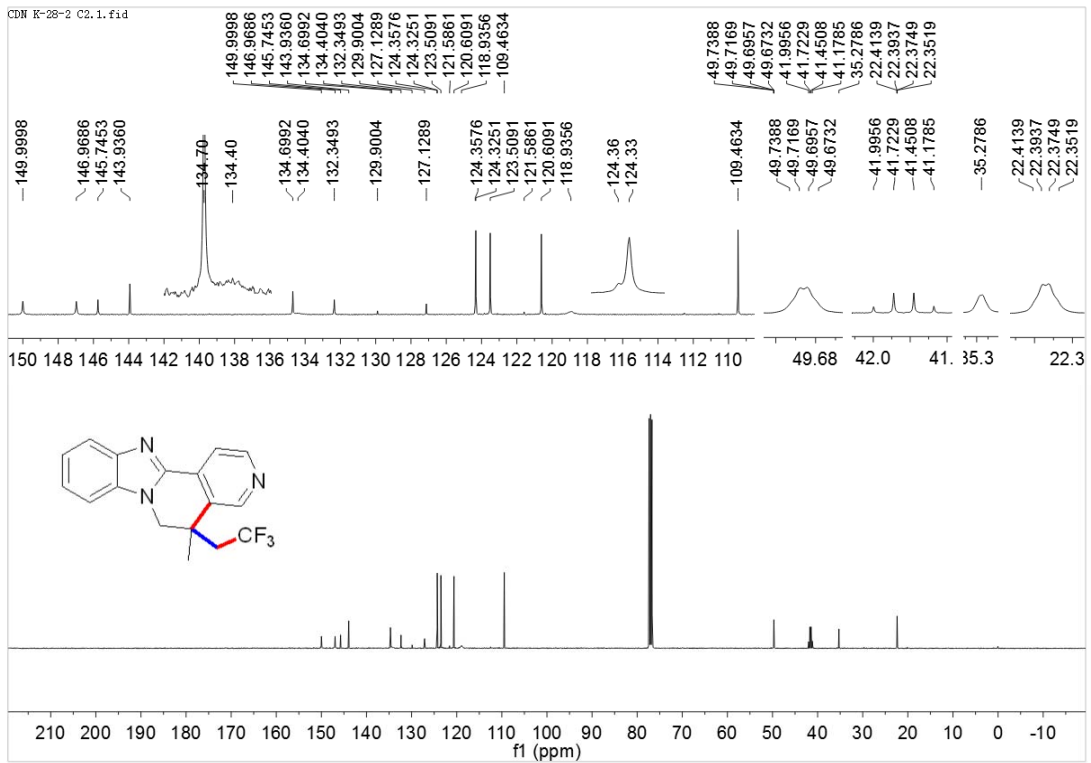
¹⁹F NMR



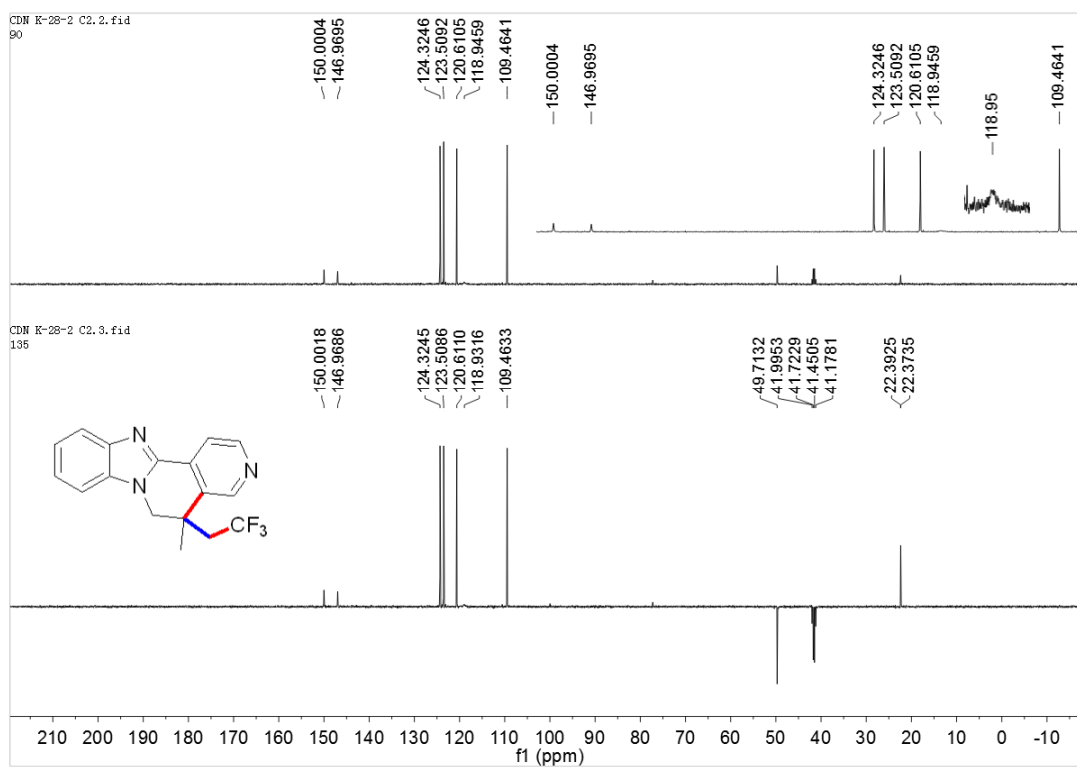
3f, ¹H NMR



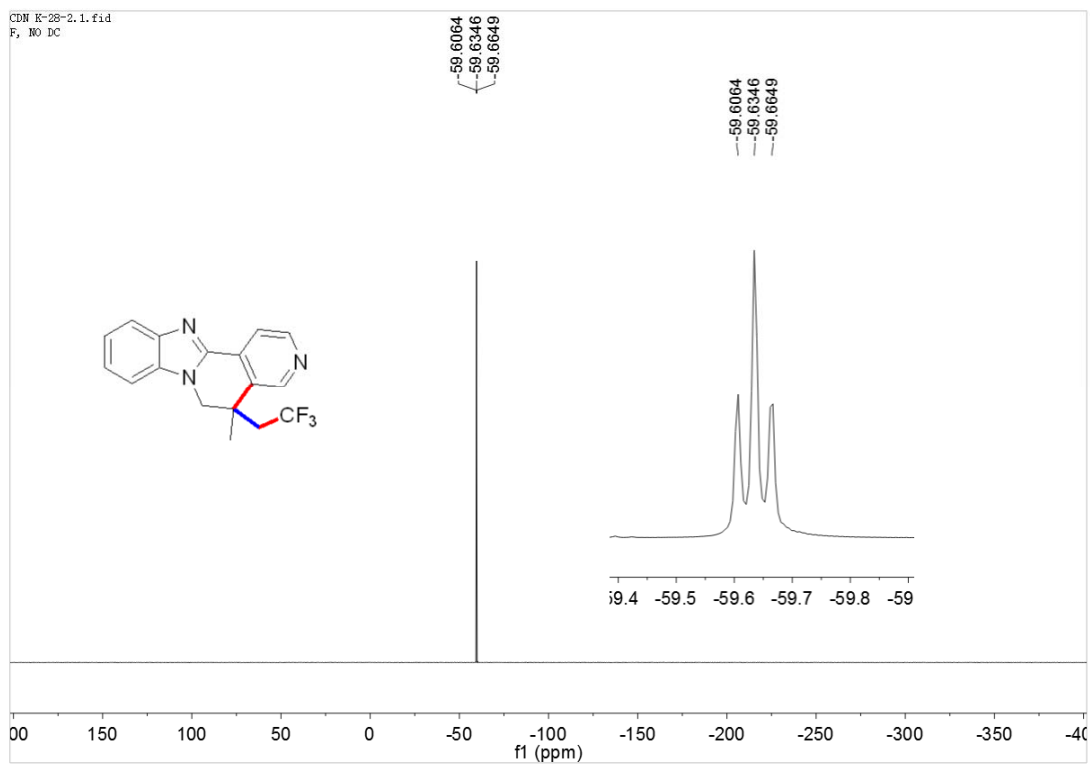
¹³C NMR



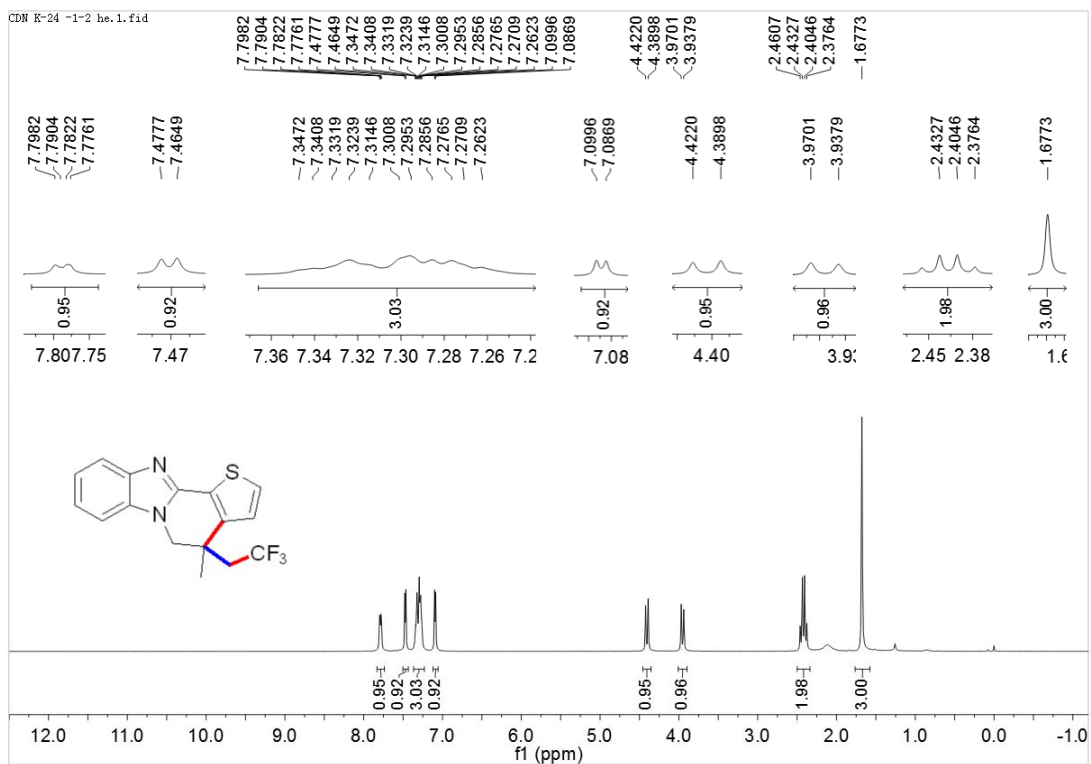
DEPT 90 and DEPT 135



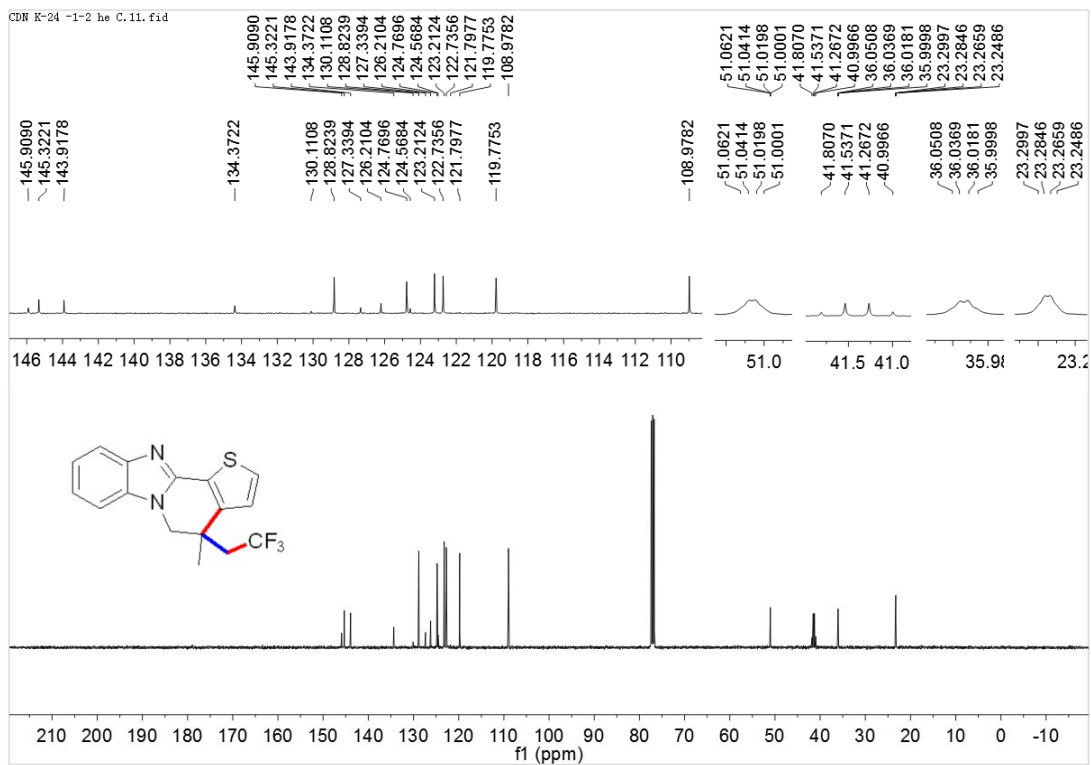
¹⁹F NMR



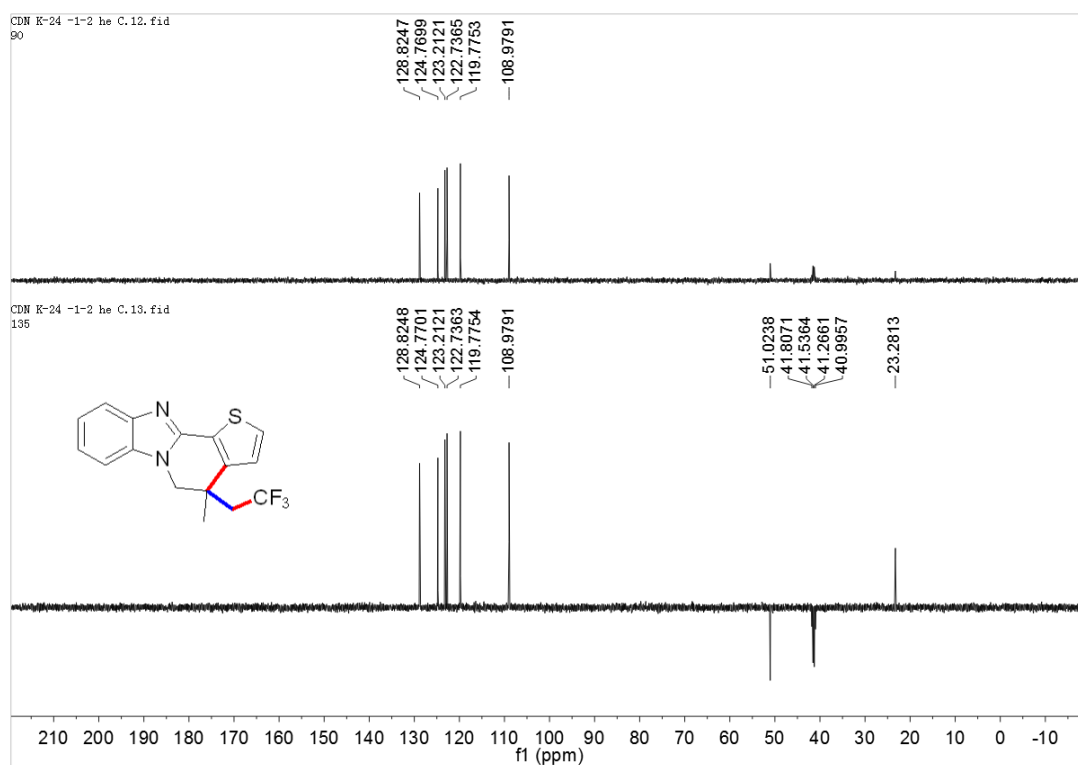
3g, ¹H NMR



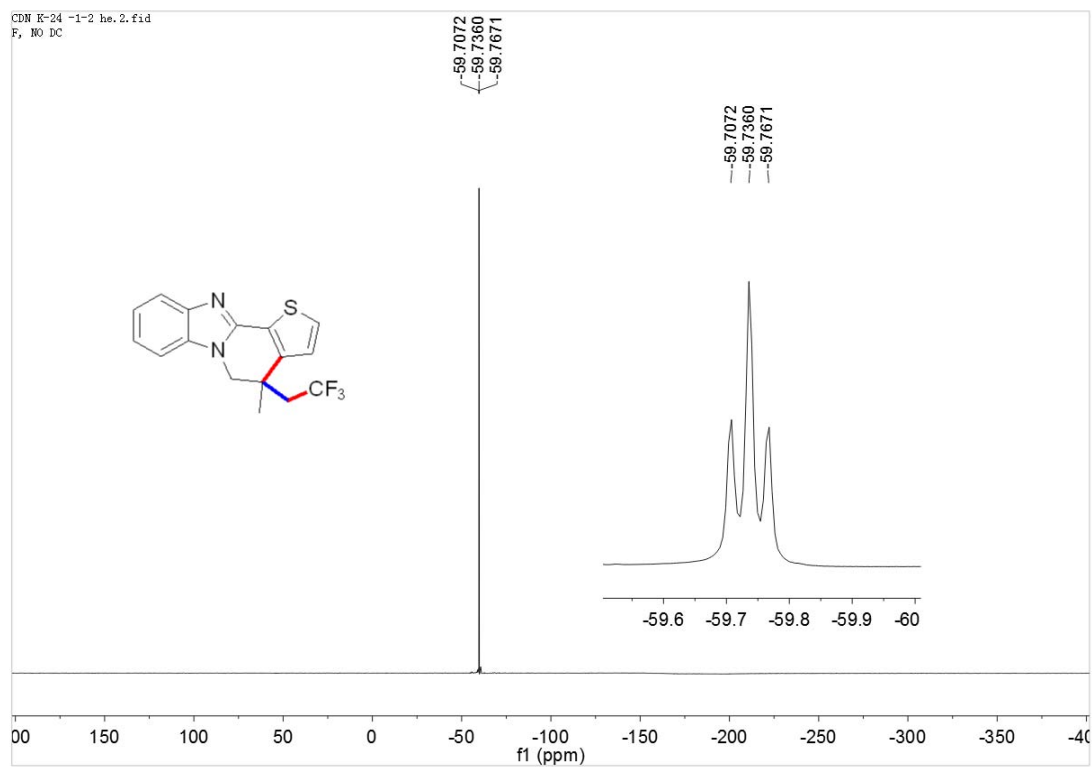
¹³C NMR



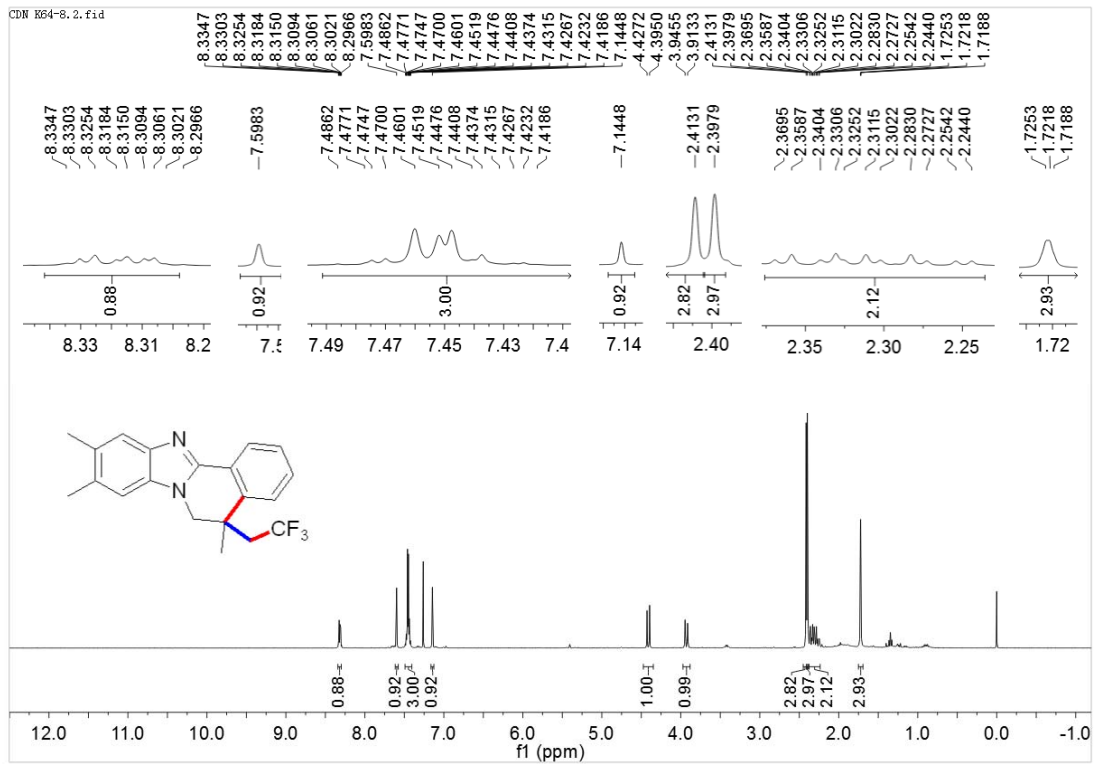
DEPT 90 and DEPT 135



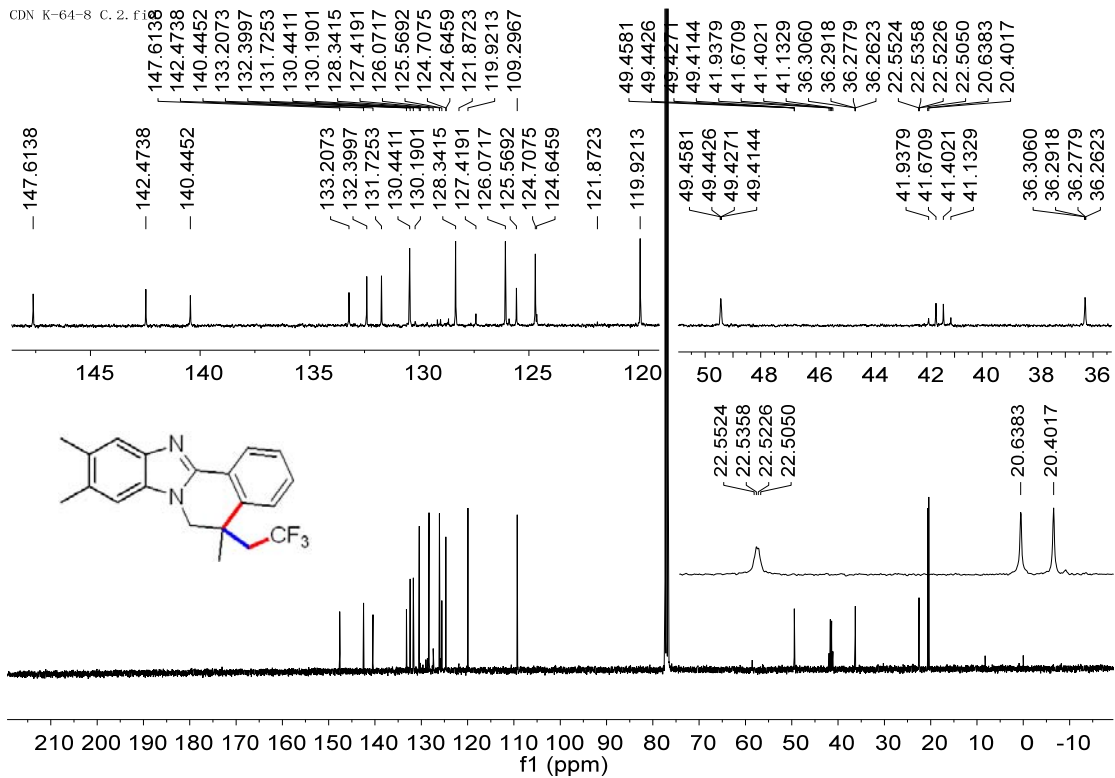
¹⁹F NMR



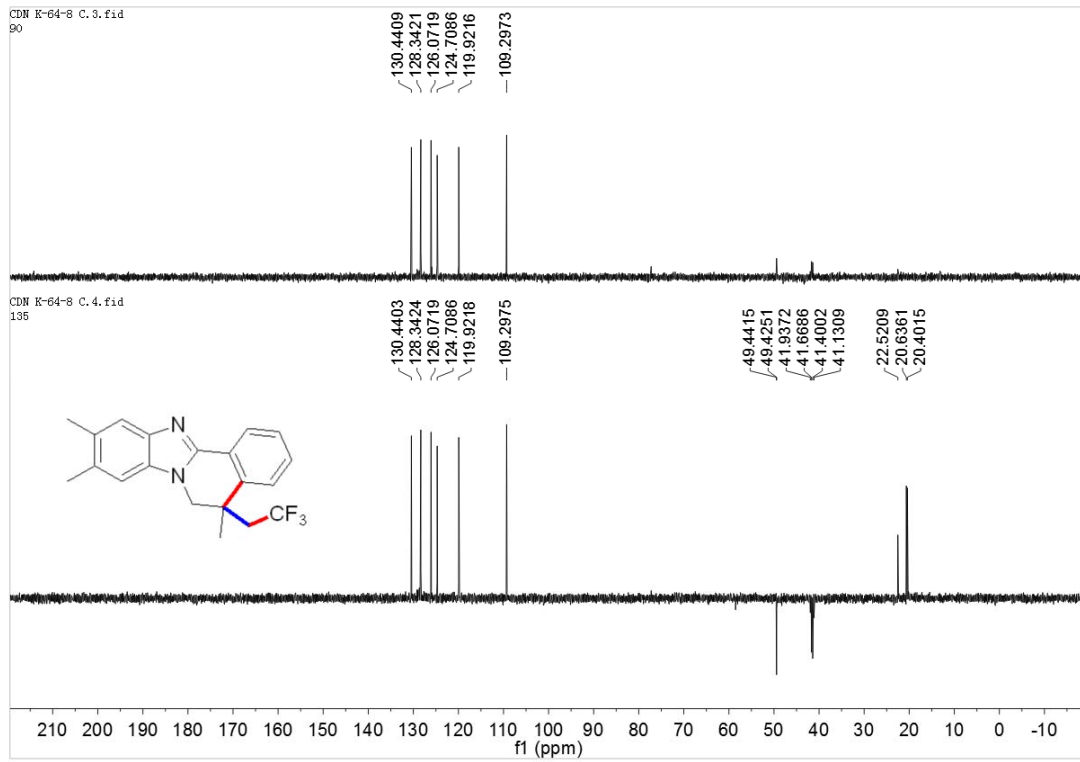
3h1, ¹H NMR



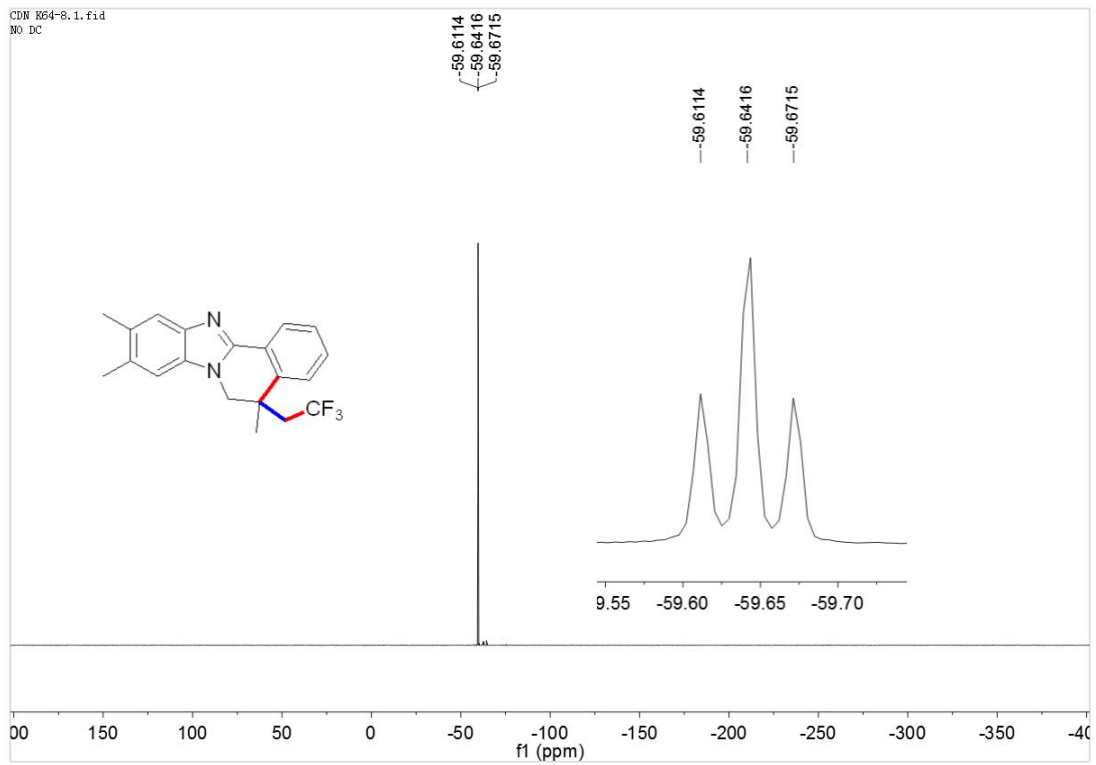
¹³C NMR



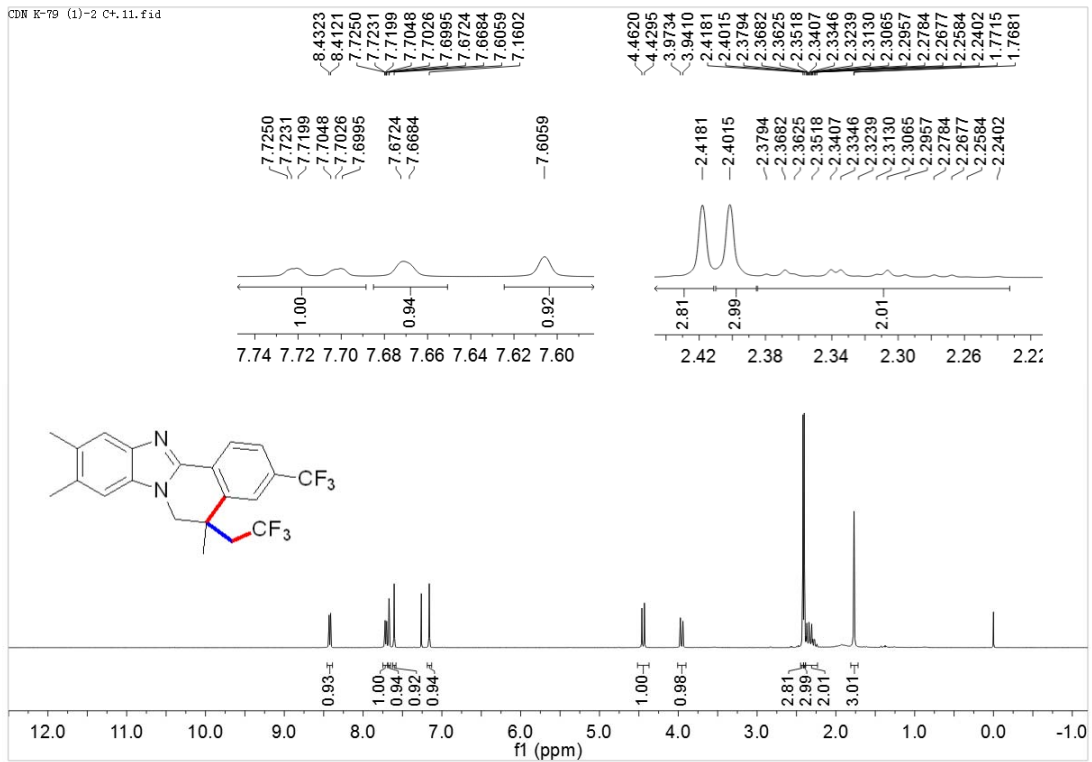
DEPT 90 and DEPT 135



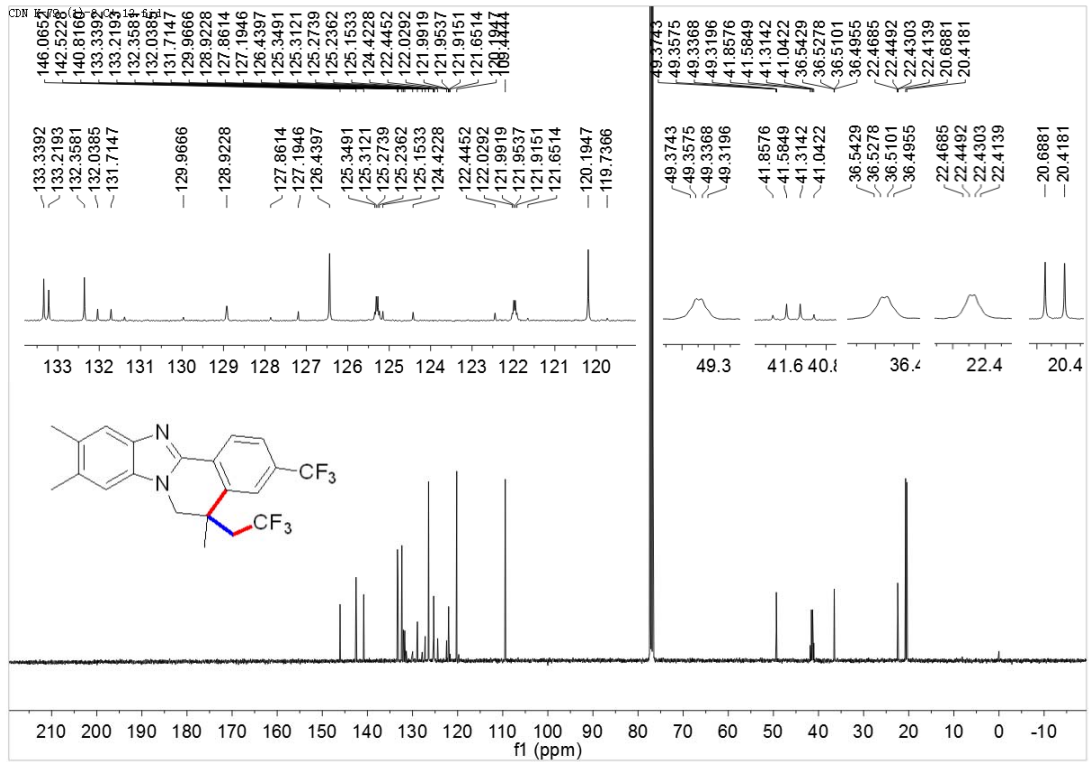
¹⁹F NMR



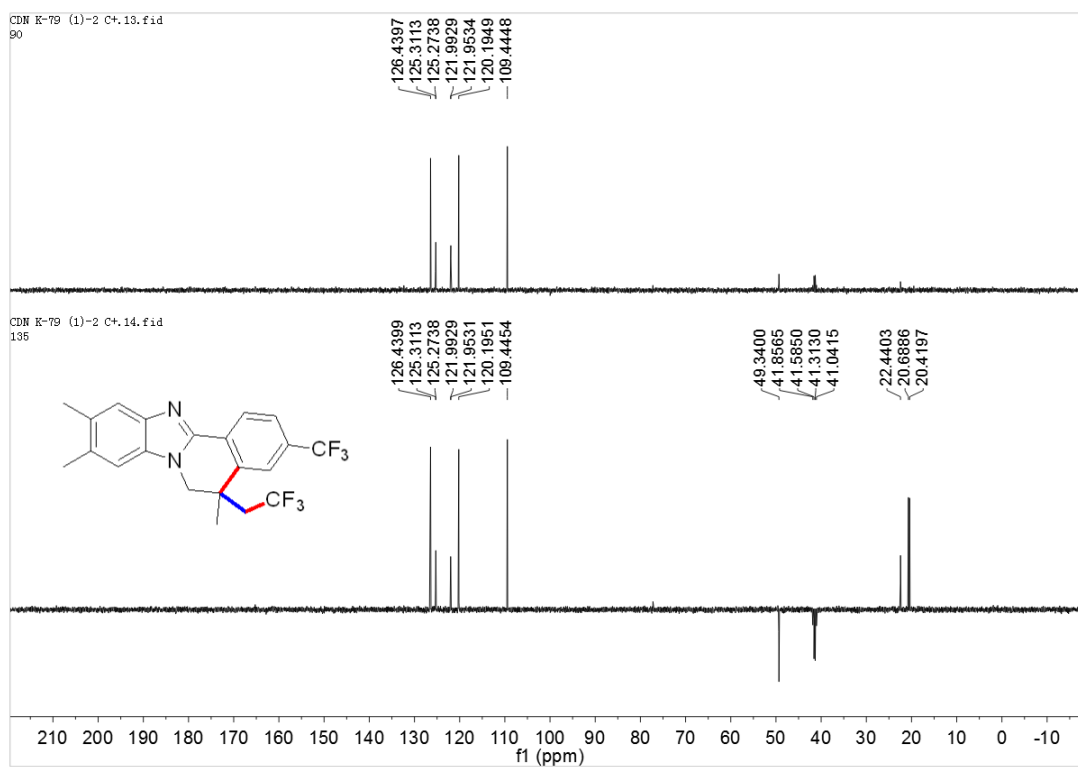
3h2, ¹H NMR



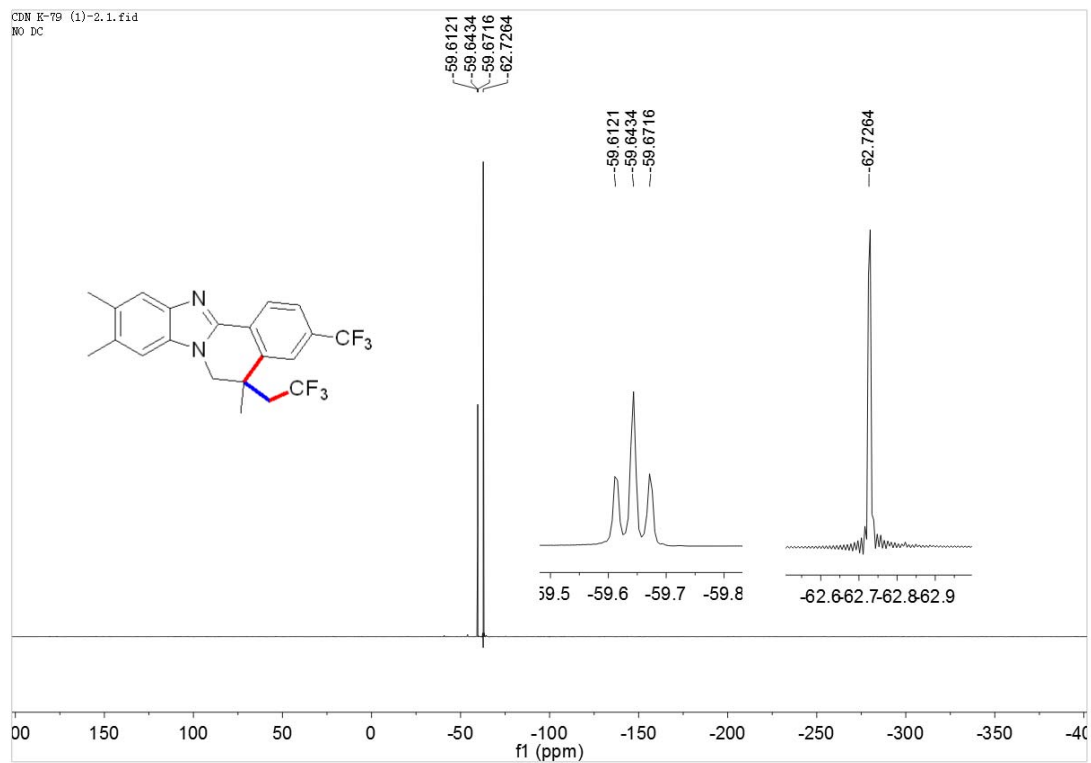
¹³C NMR



DEPT 90 and DEPT 135



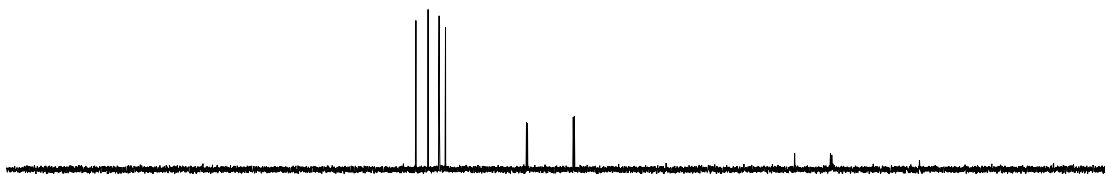
¹⁹F NMR



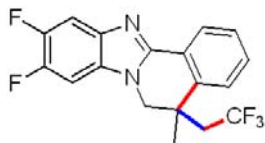
DEPT 90 and DEPT 135

CDN K-61-3-3.28. fid
90

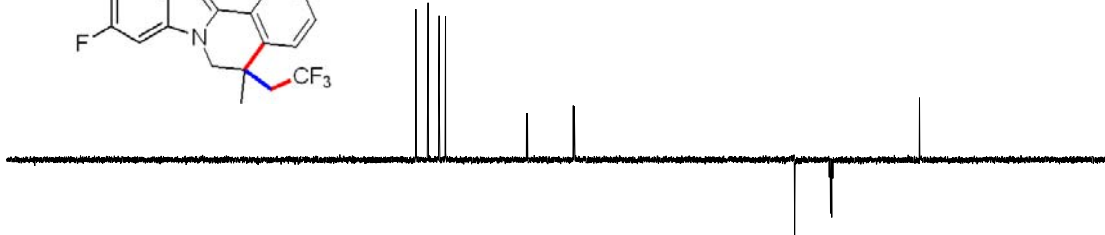
131.0753
128.4680
126.0785
124.7022
107.2204
107.0220
97.1482
96.9190



CDN K-61-3-3.29. fid
135



131.0753
128.4679
126.0784
124.7028
107.2194
107.0244
97.1466
96.9188
49.4343
41.9701
41.6996
41.4300
41.1604
22.5032

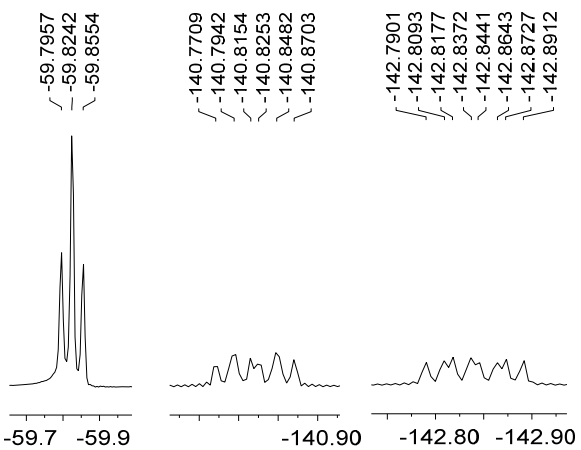
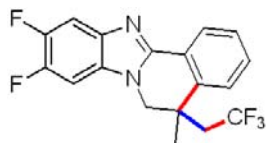


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

¹⁹F NMR

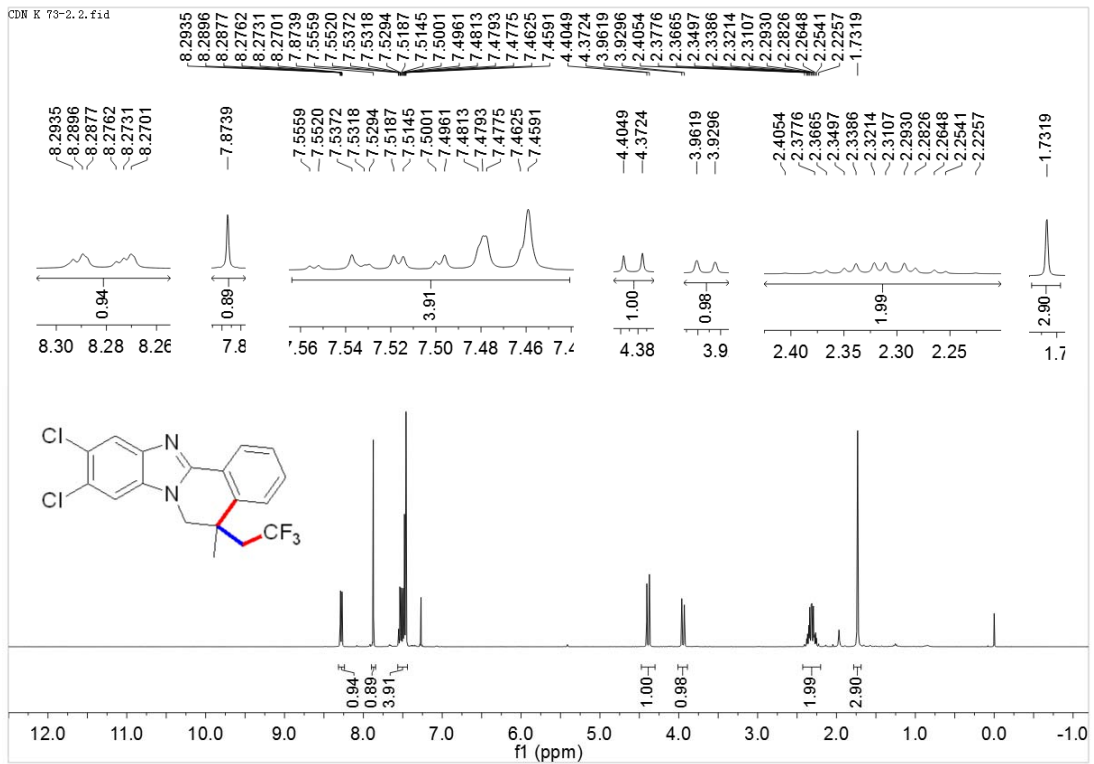
CDN K-61-3-3.2. fid

-59.7957
-59.8242
-59.8554
-140.7709
-140.7942
-140.8154
-140.8253
-140.8482
-140.8703
-142.7901
-142.8093
-142.8177
-142.8372
-142.8441
-142.8643
-142.8727
-142.8912

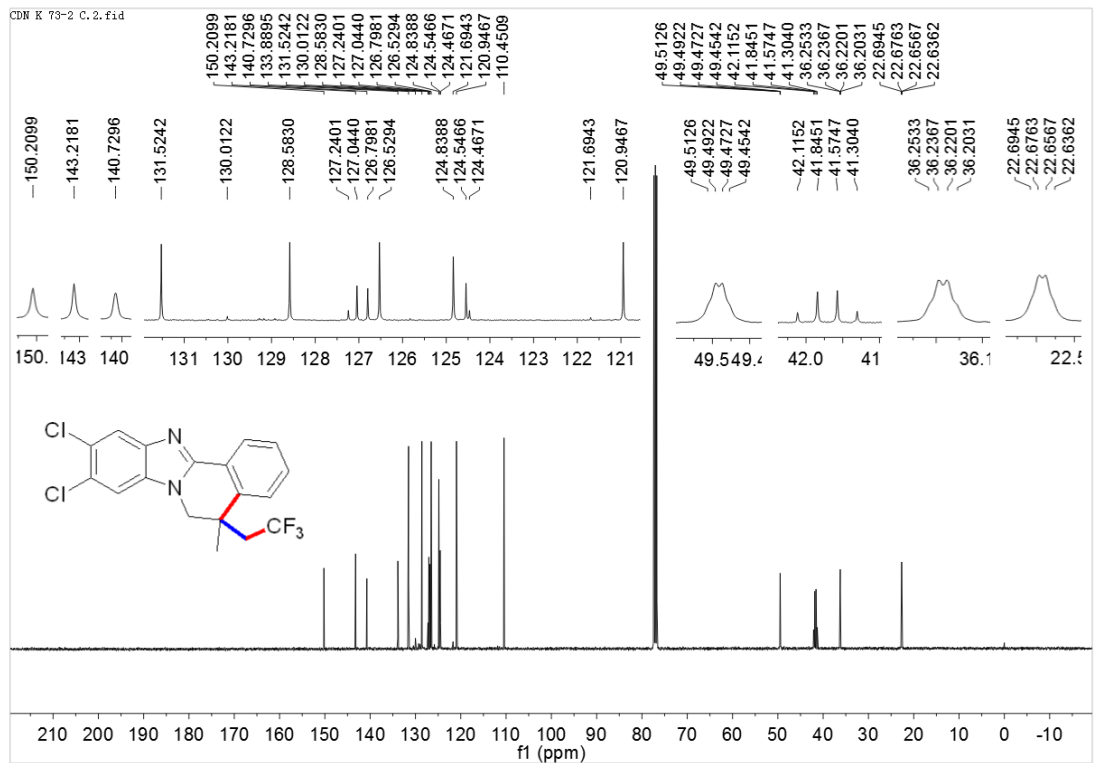


00 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -4
f1 (ppm)

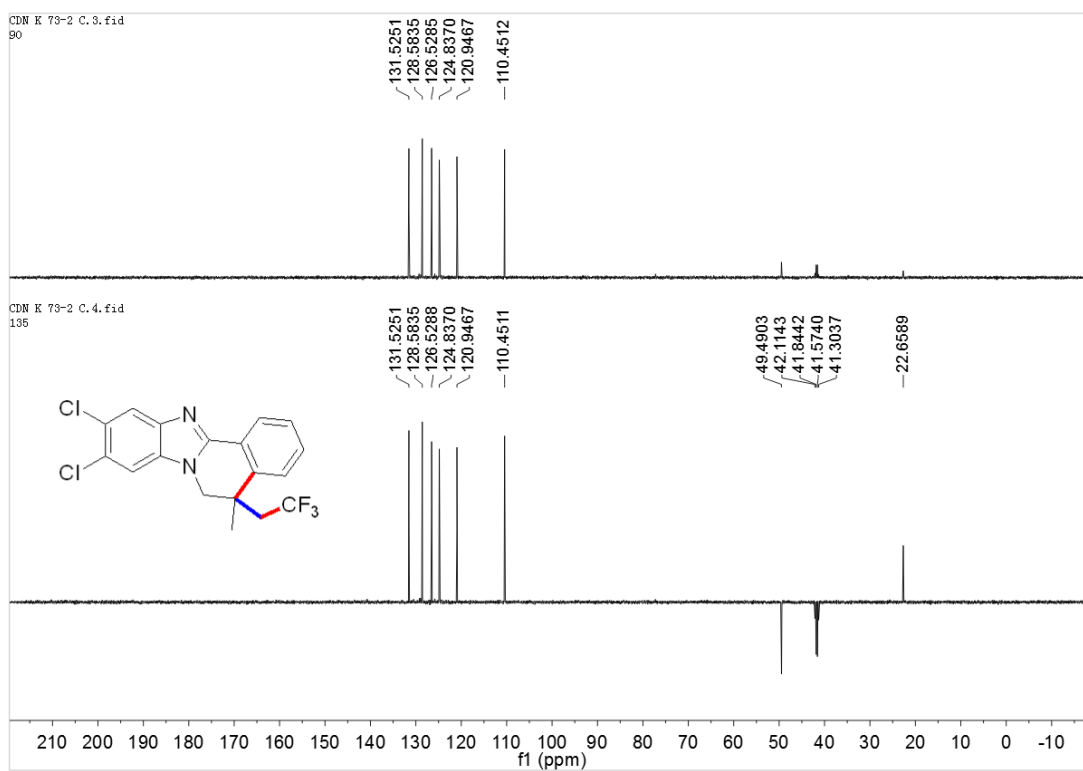
3j1, ¹H NMR



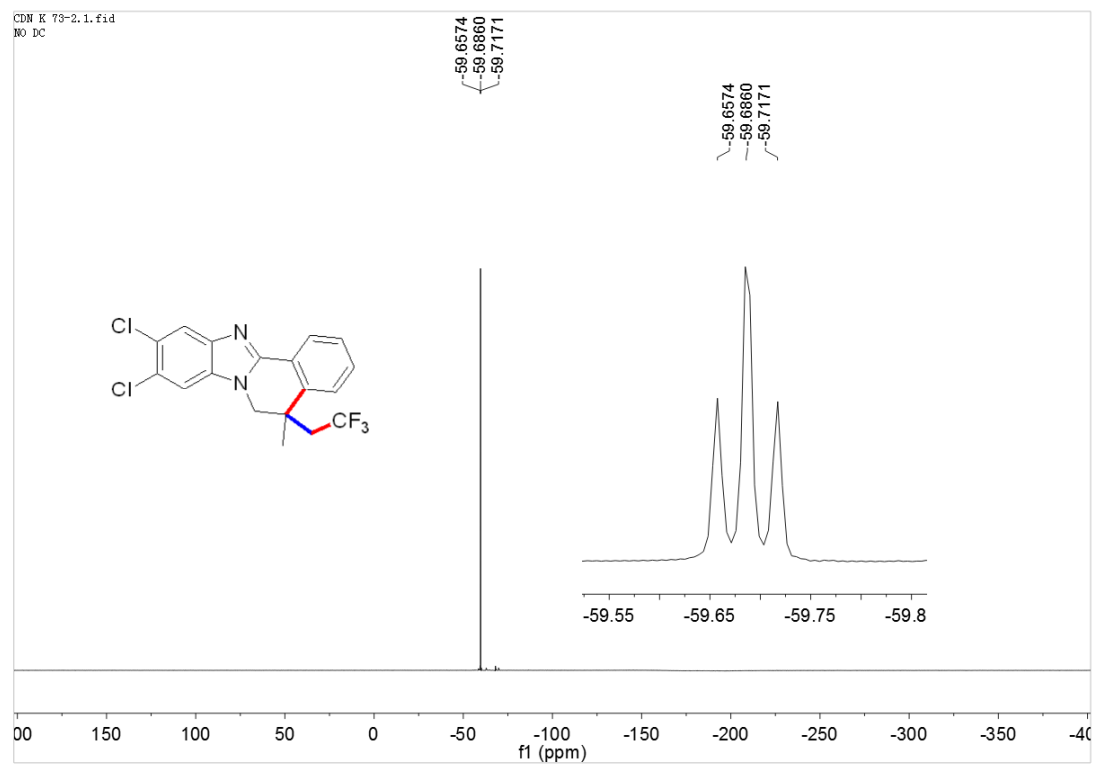
¹³C NMR



DEPT 90 and DEPT 135

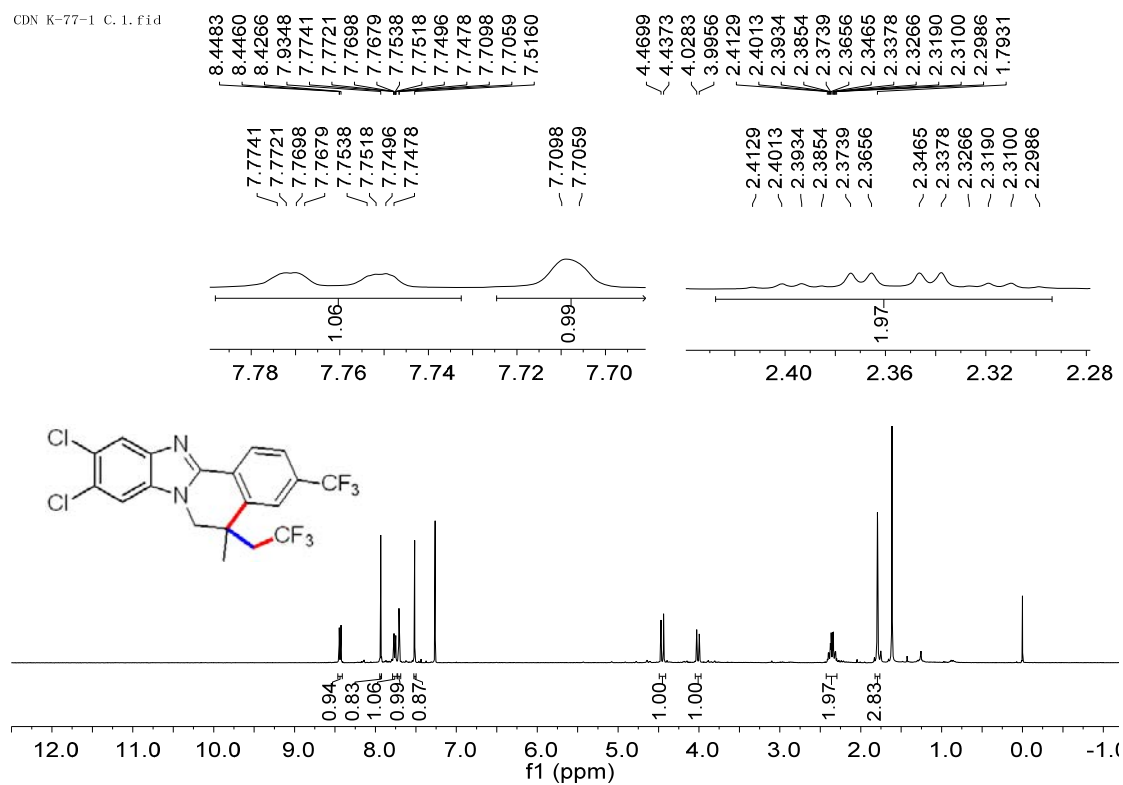


¹⁹F NMR

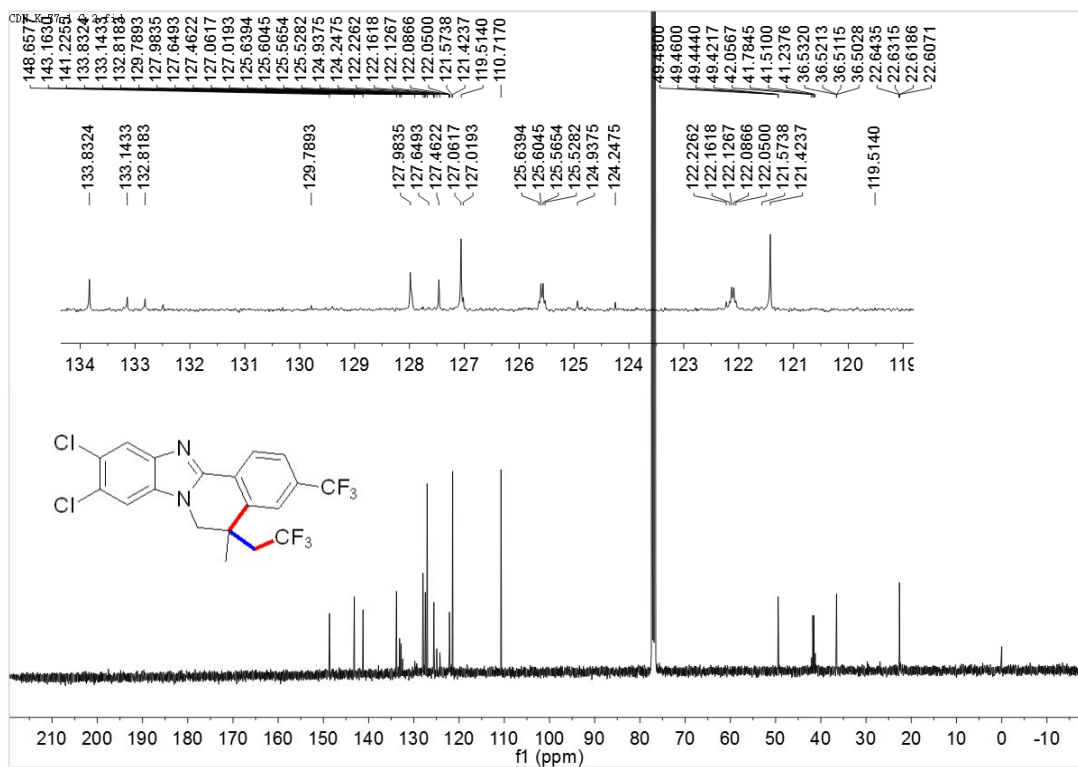


3j2, ¹H NMR

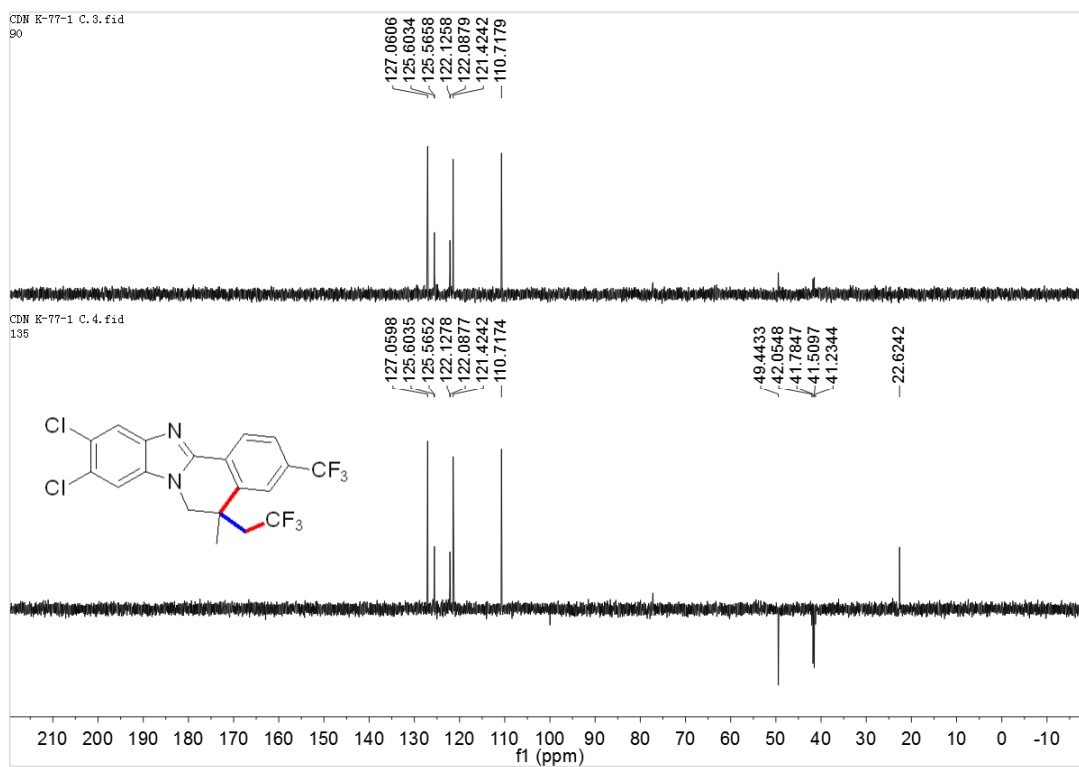
CDN K-77-1 C. 1. f1d



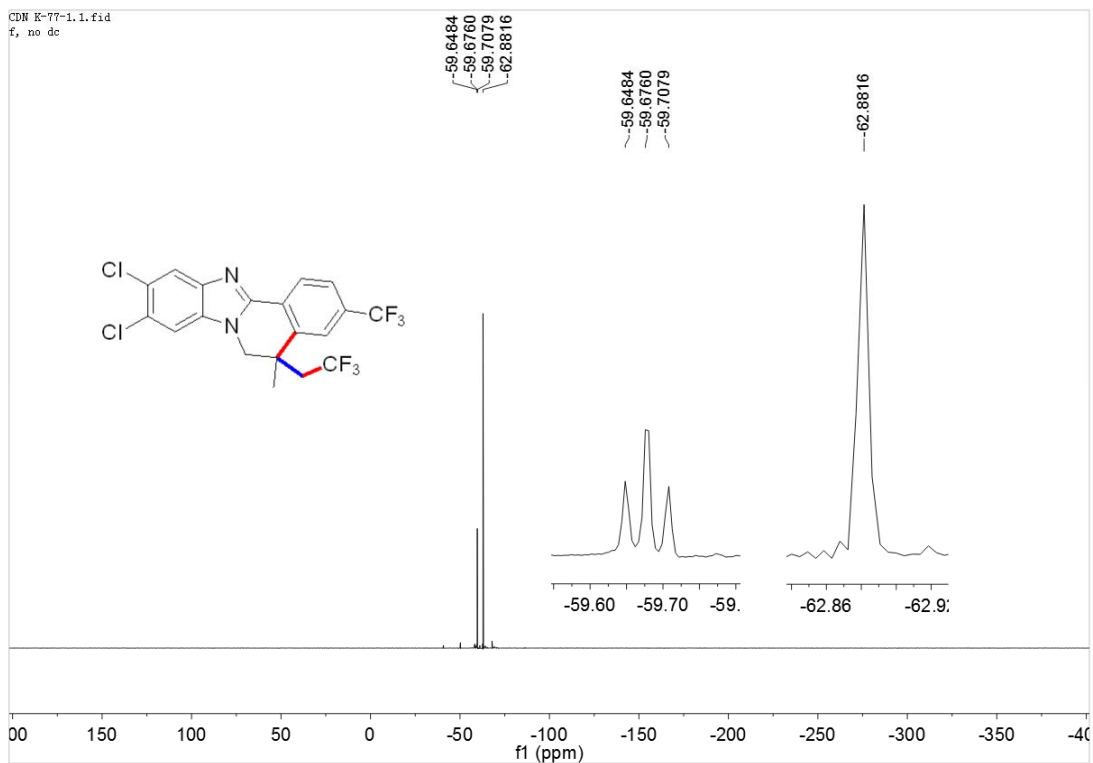
¹³C NMR



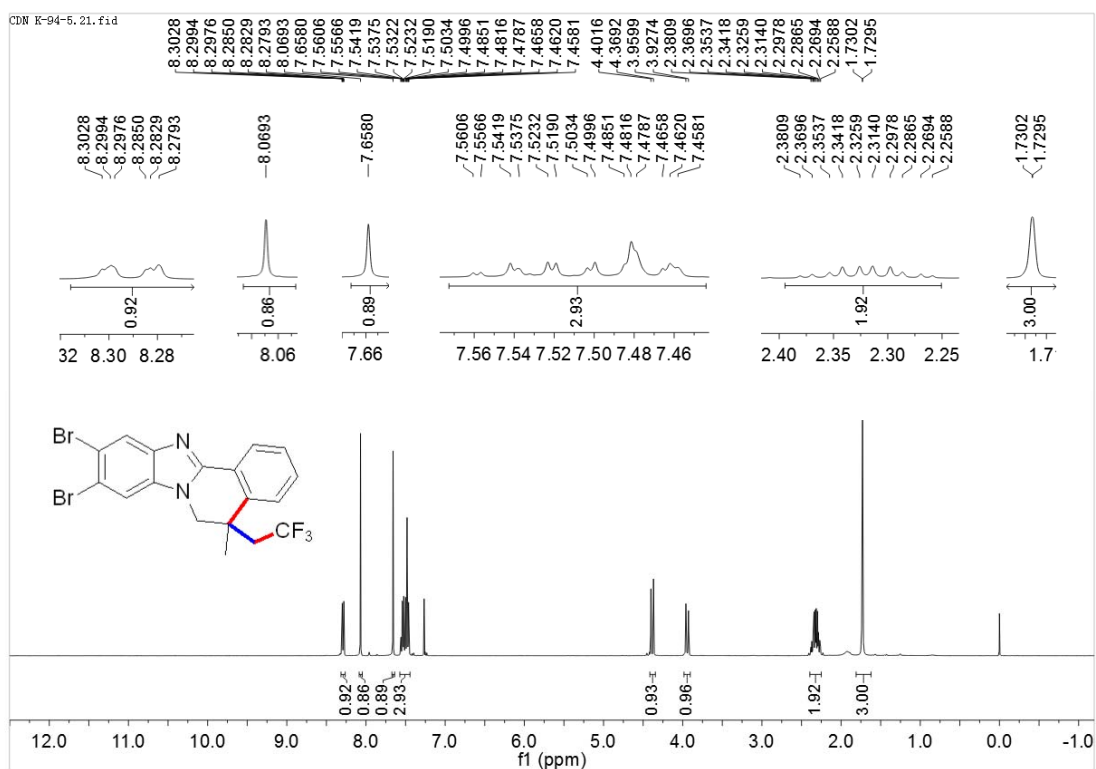
DEPT 90 and DEPT 135



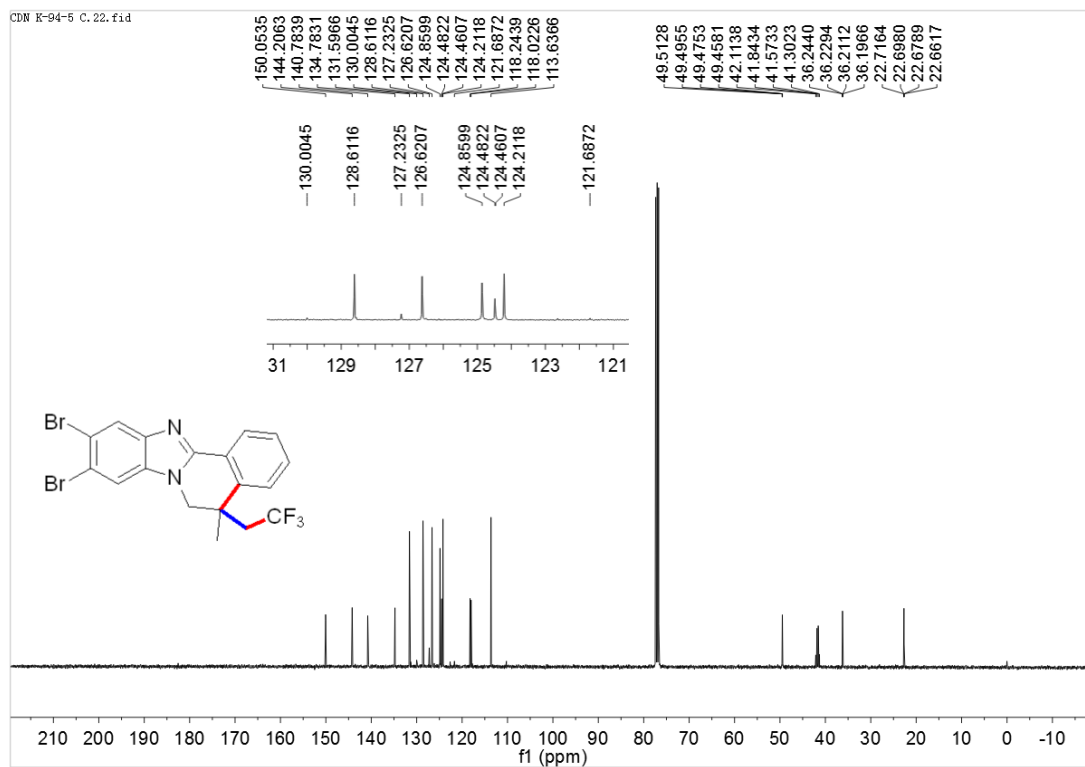
¹⁹F NMR



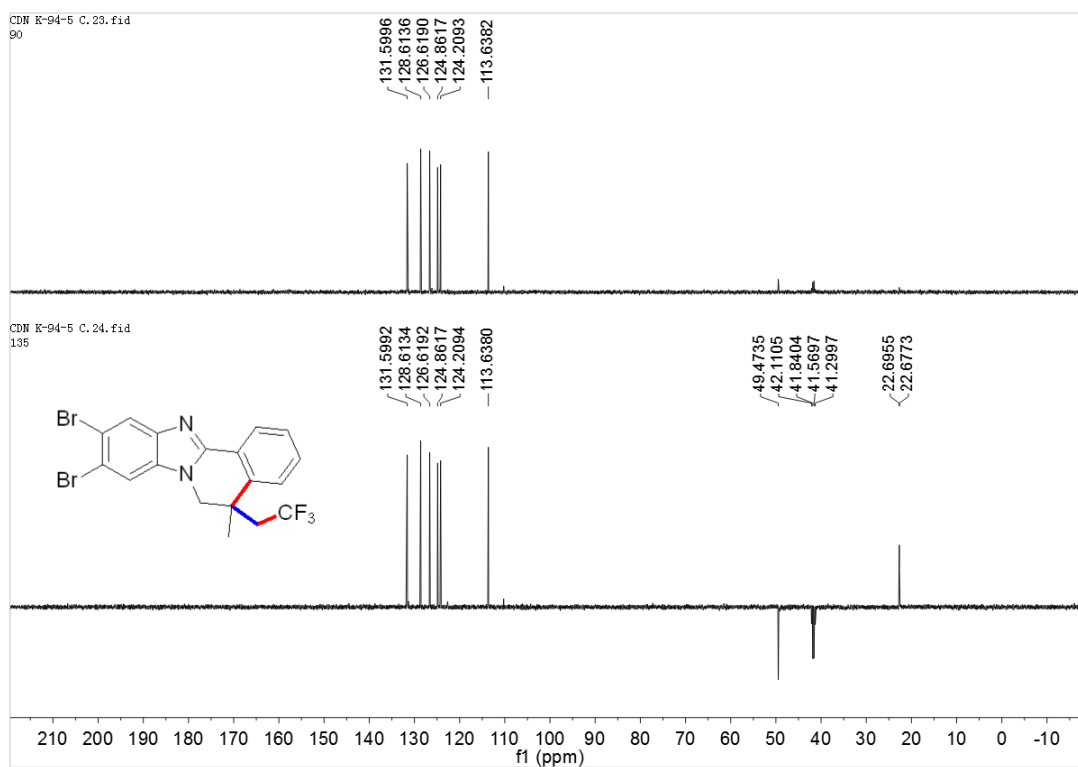
3k, ¹H NMR



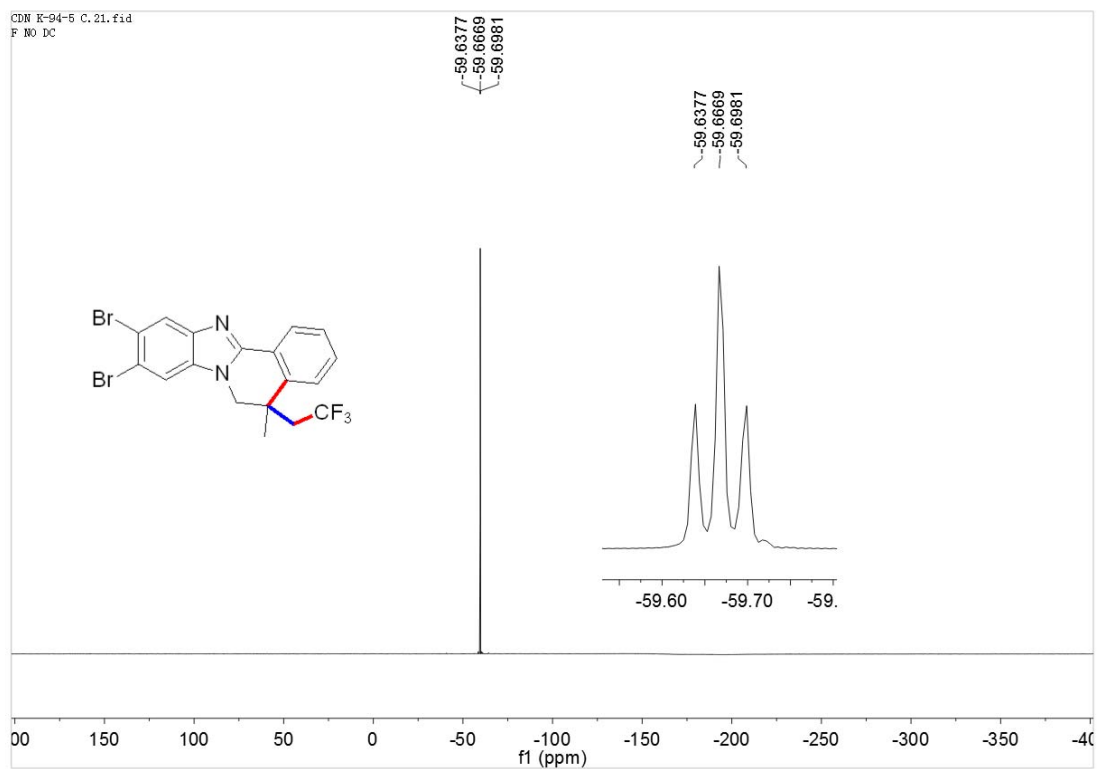
¹³C NMR



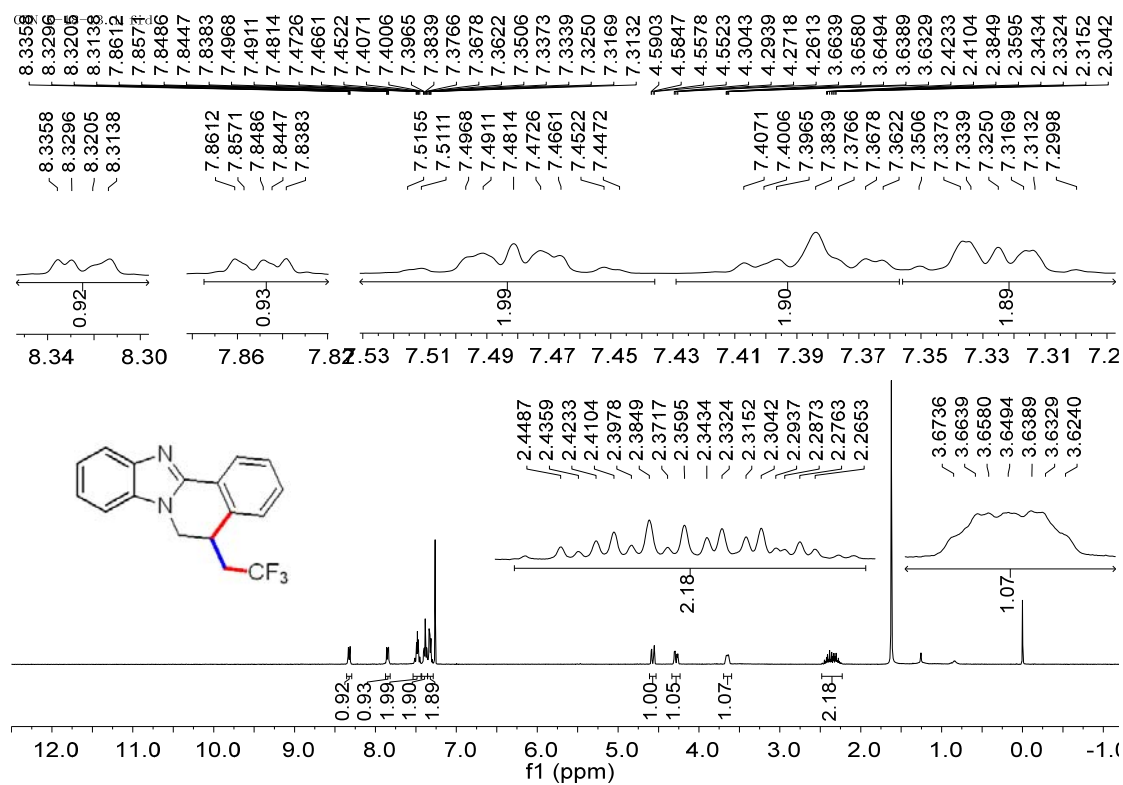
DEPT 90 and DEPT 135



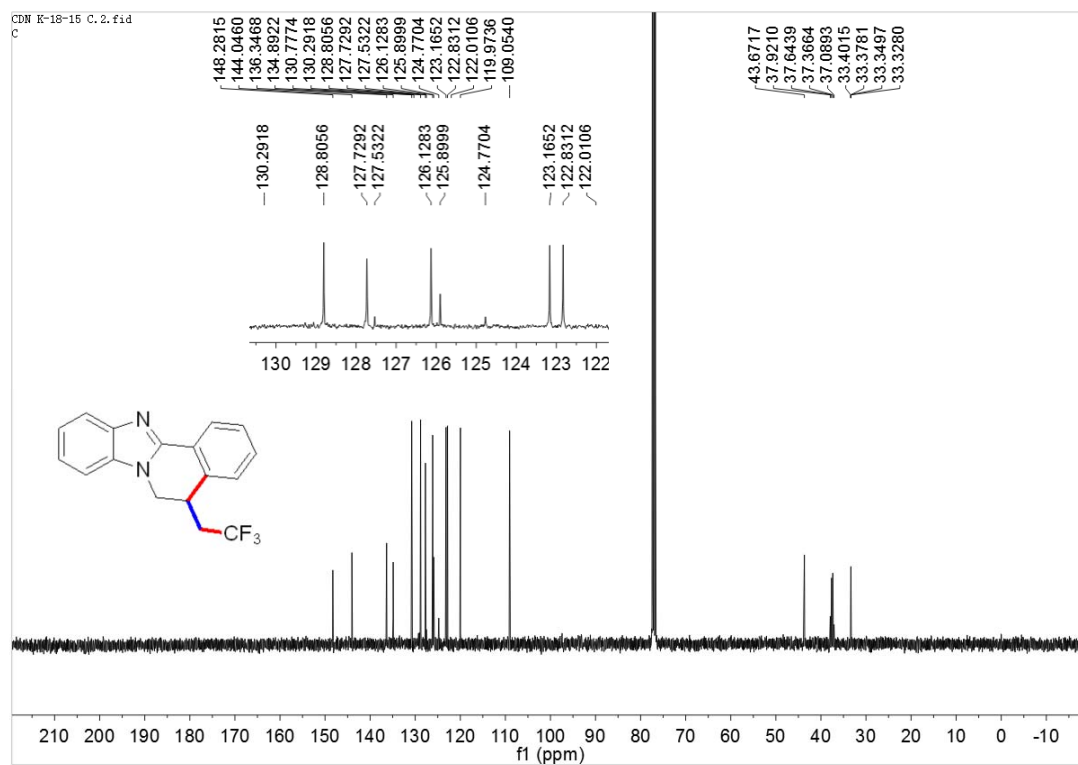
¹⁹F NMR



31, ¹H NMR



¹³C NMR



DEPT 90 and DEPT 135

CDN K-18-15 C. 3. fid
90

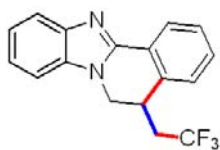
130.7778
128.8059
127.7294
126.1269
123.1641
122.8315
119.9735
-109.0535

33.4034
33.3785
33.3508
33.3255

CDN K-18-15 C. 4. fid
135

130.7780
128.8059
127.7302
126.1269
123.1642
122.8314
119.9737
-109.0536

43.6671
37.9230
37.6442
37.3665
37.0872
33.4006
33.3777
33.3519
33.3278



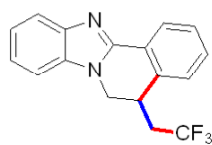
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

¹⁹F NMR

CDN K-18 (3)-8.12.fid
F, NO DC

63.5165
63.5448
63.5733

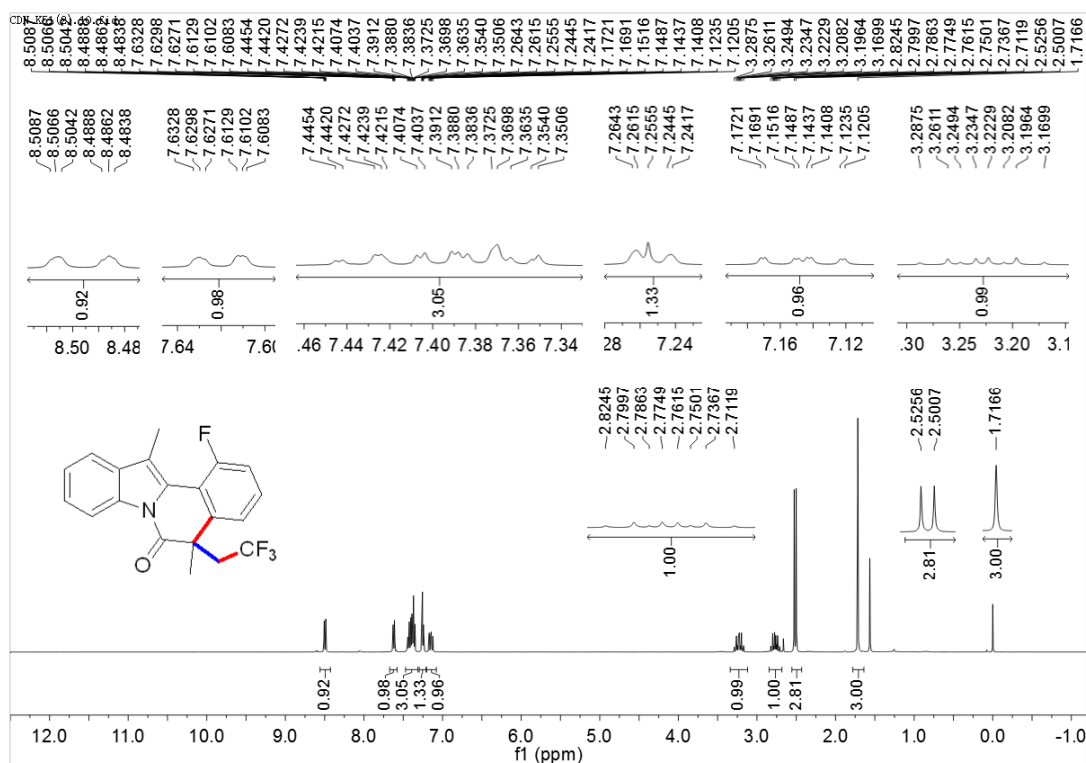
63.5165
63.5448
63.5733



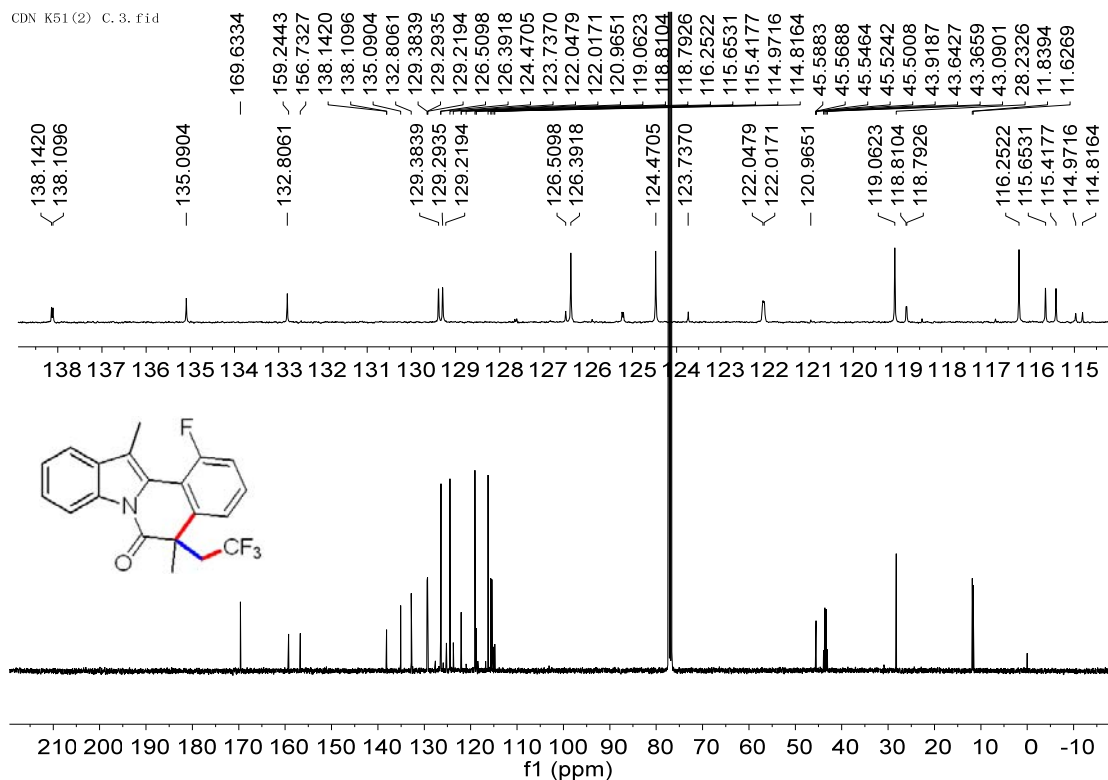
-63.45 -63.50 -63.55 -63.60 -63.65

00 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400
f1 (ppm)

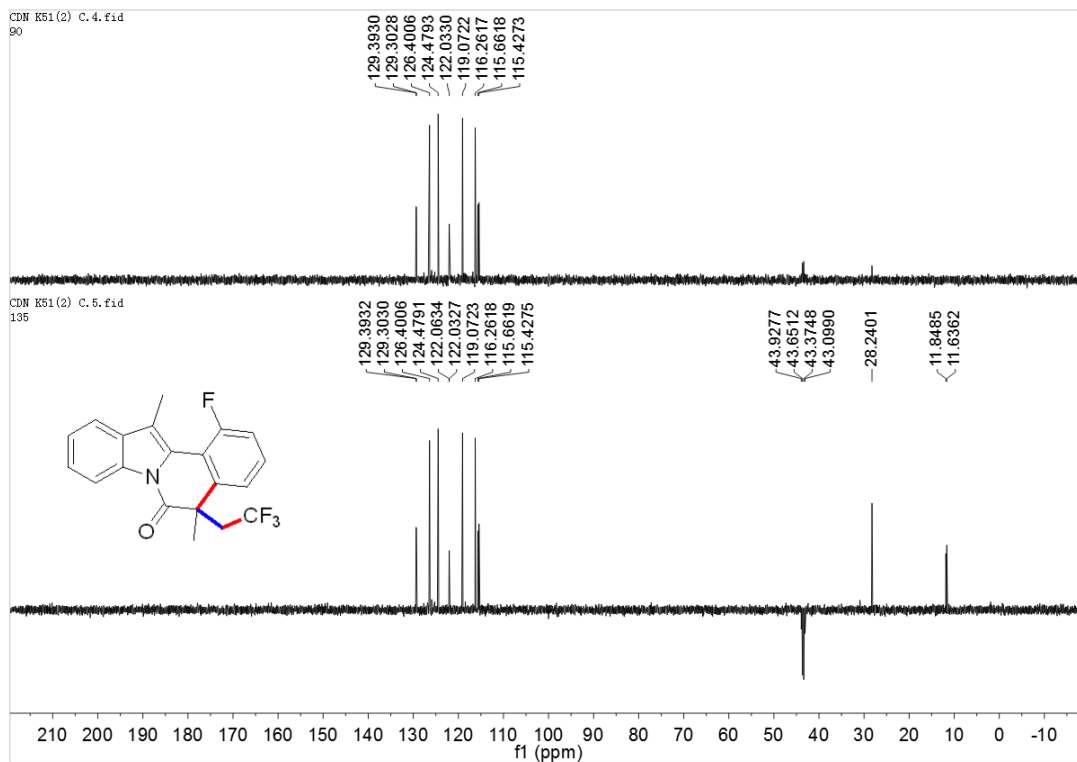
3m, ¹H NMR



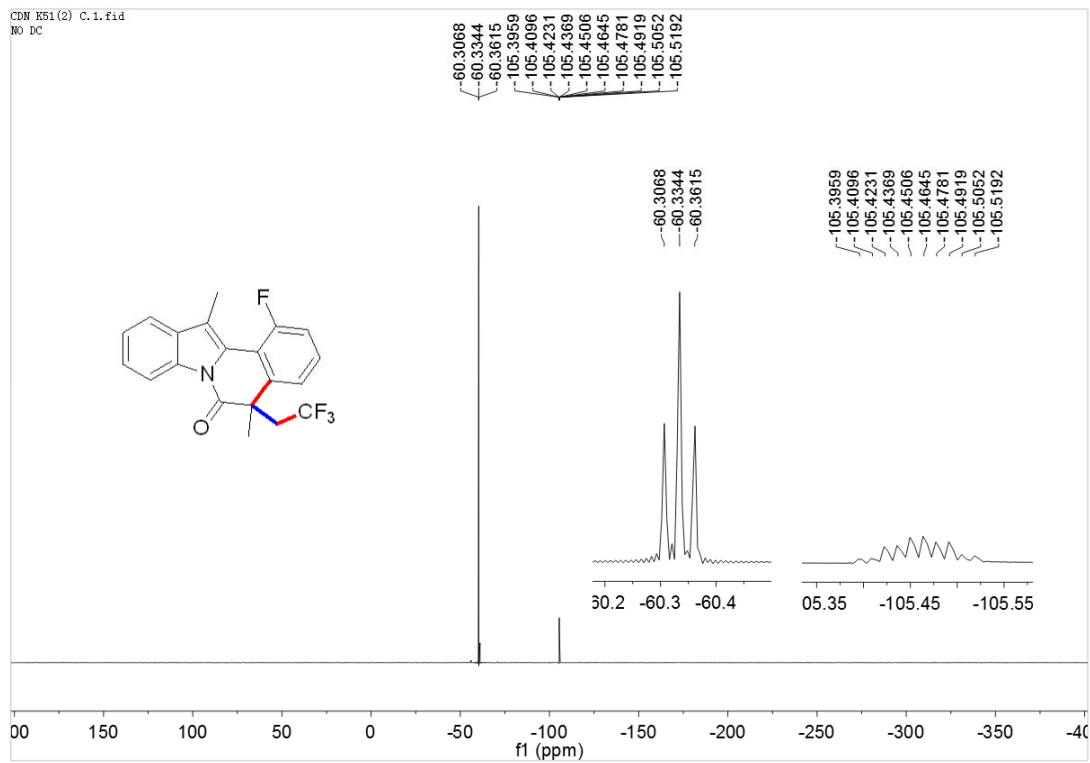
¹³C NMR



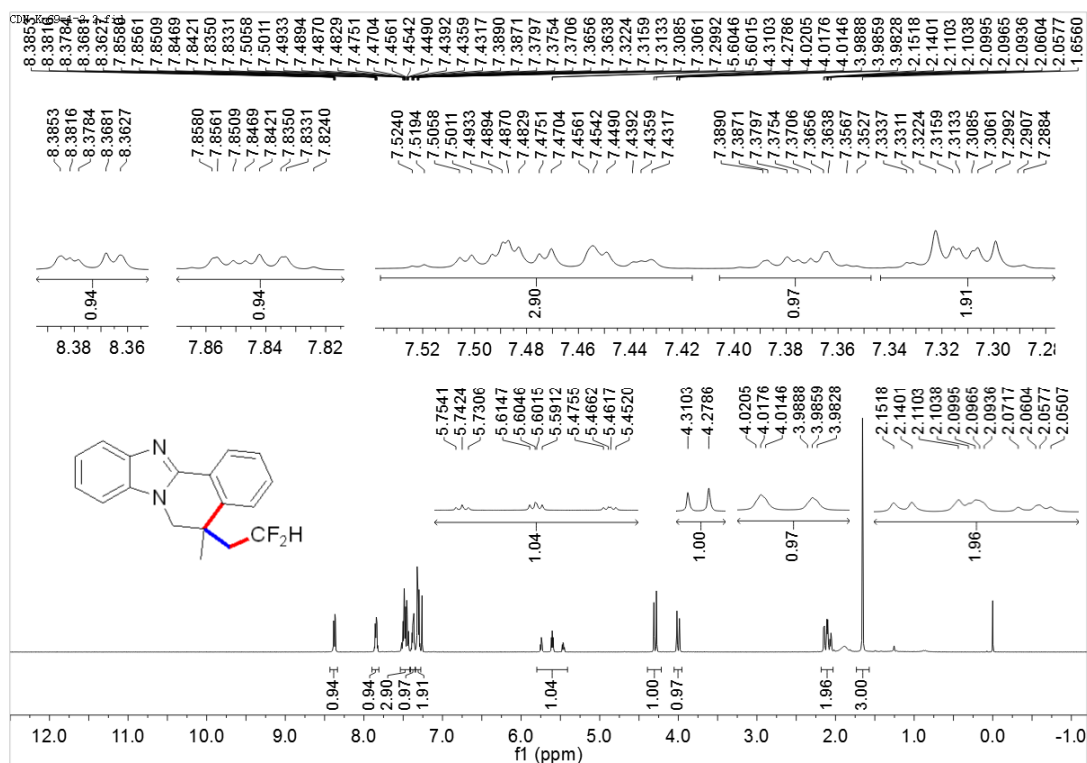
DEPT 90 and DEPT 135



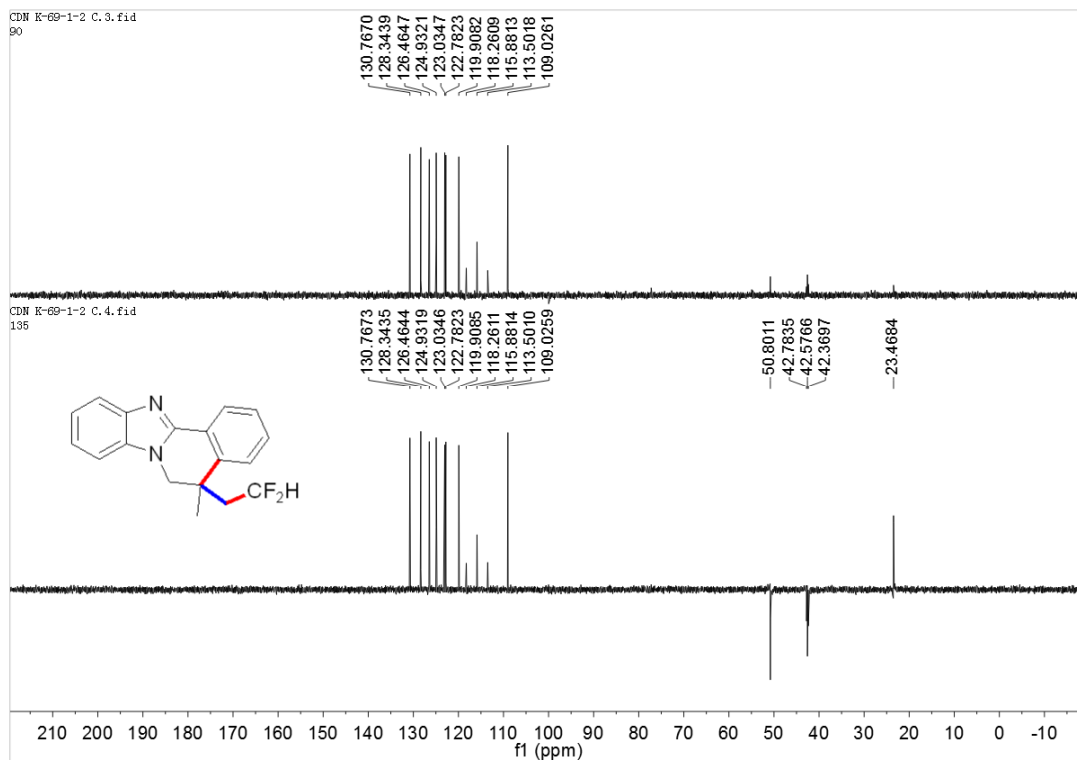
¹⁹F NMR



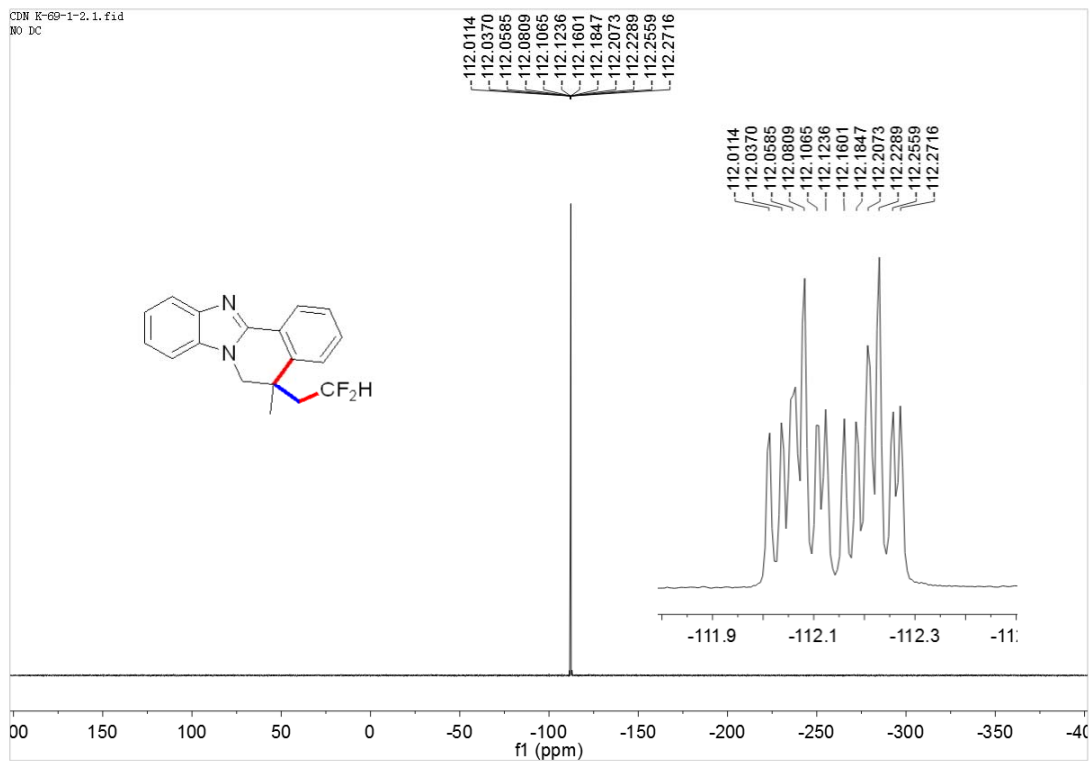
3n1, ¹H NMR



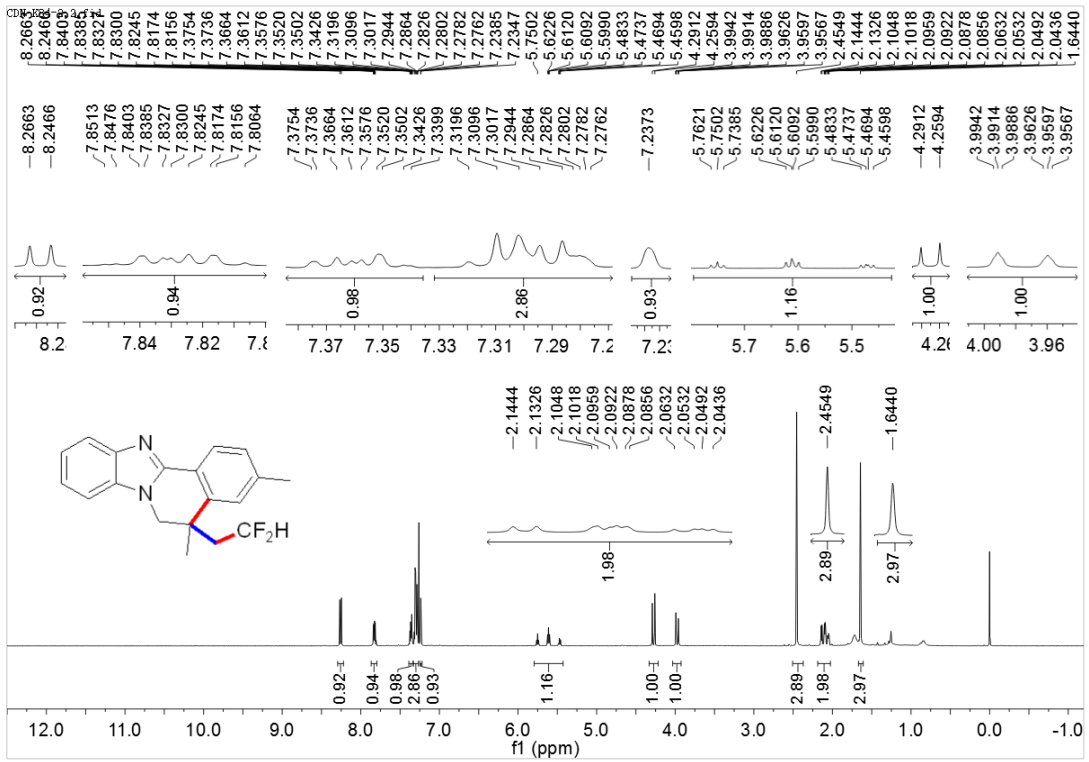
DEPT 90 and DEPT 135



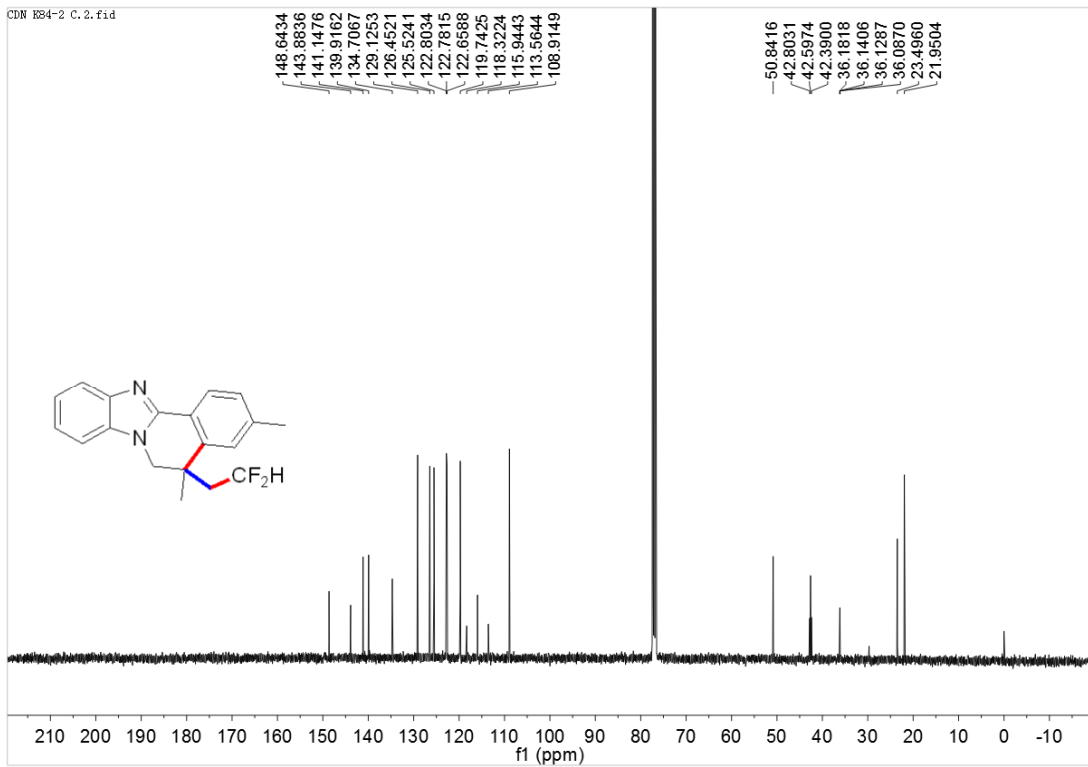
¹⁹F NMR



3n2, ¹H NMR



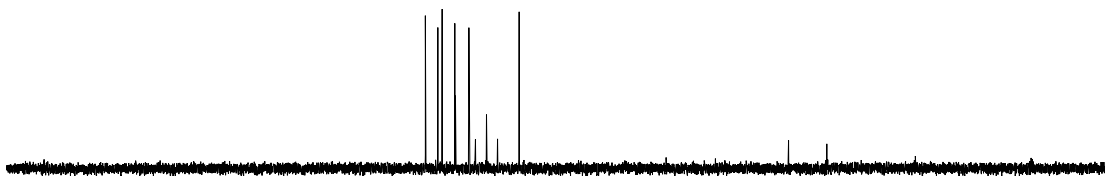
¹³C NMR



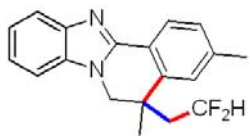
DEPT 90 and DEPT 135

CDN K84-2 C. 3. fid
90

129.1246
126.4510
125.5245
122.8027
122.6577
119.7420
118.3228
115.9438
113.5641
108.9146

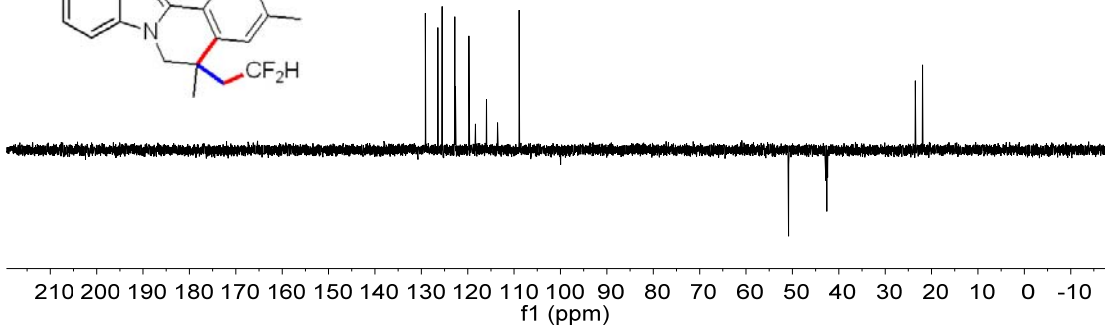


CDN K84-2 C. 4. fid
135



129.1247
126.4512
125.5247
122.8030
122.6582
119.7421
118.3221
115.9431
113.5650
108.9146

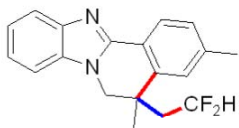
50.8413
42.8016
42.5954
42.3895
23.4949
21.9512



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)

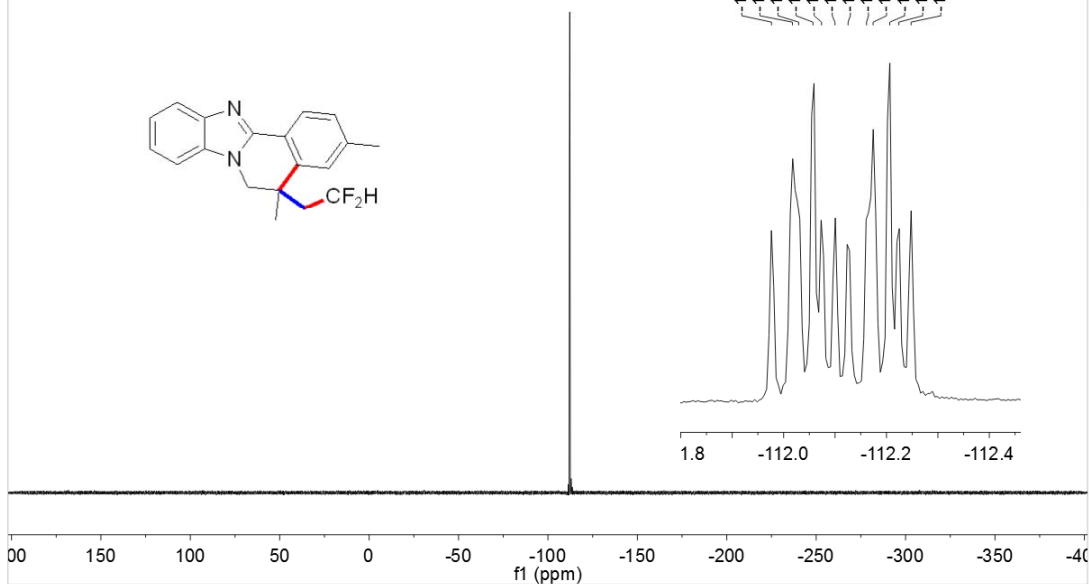
¹⁹F NMR

CDN E84-2.1.fid



-111.9765
-112.0171
-112.0293
-112.0571
-112.0738
-112.0999
-112.1254
-112.1613
-112.1740
-112.2064
-112.2240
-112.2478

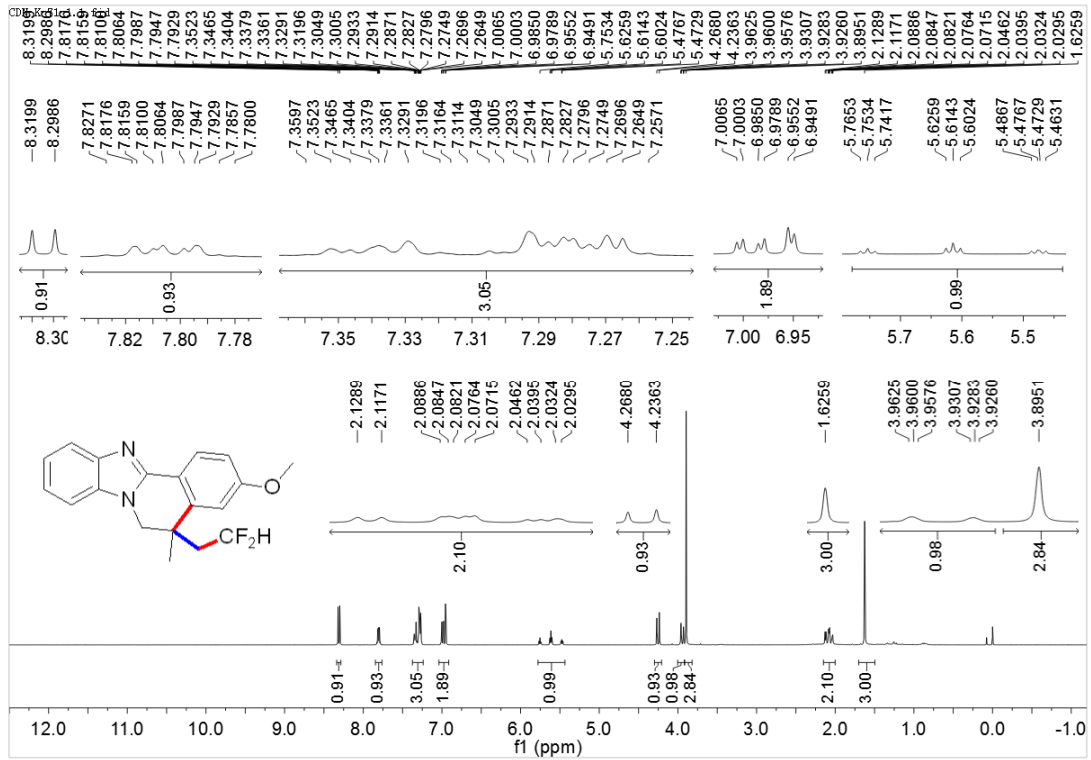
111.9765
112.0171
112.0293
112.0571
112.0738
112.0999
112.1254
112.1613
112.1740
112.2064
112.2240
112.2478



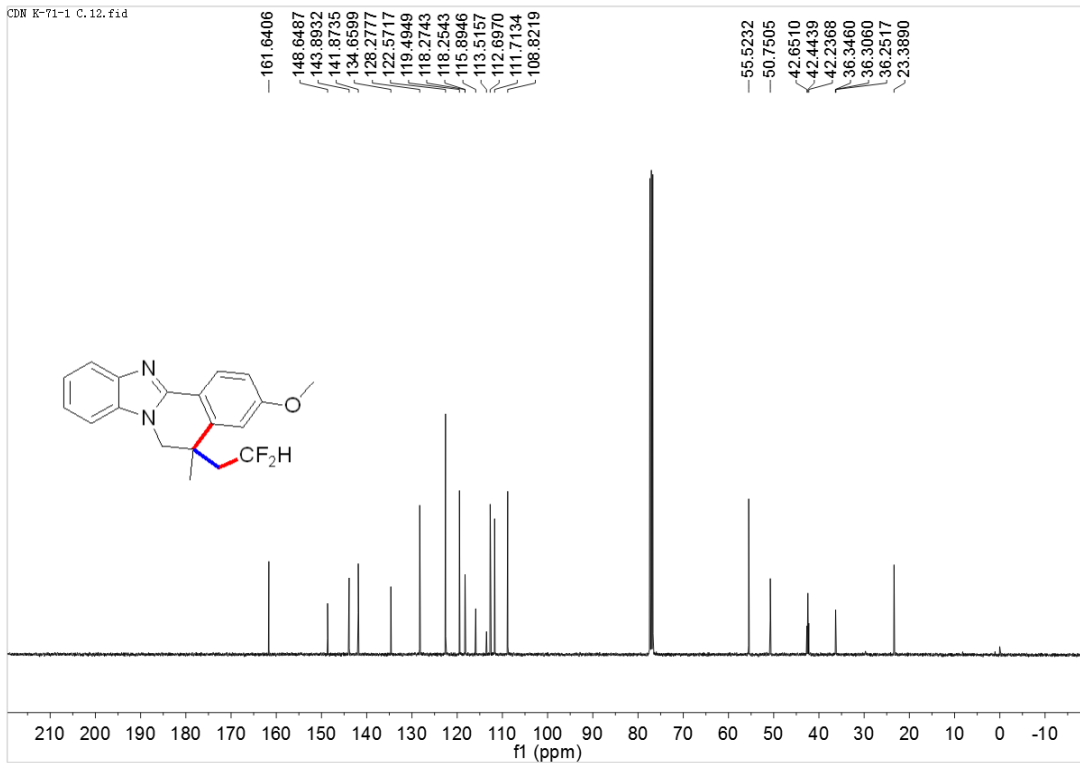
1.8 -112.0 -112.2 -112.4

00 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400
f1 (ppm)

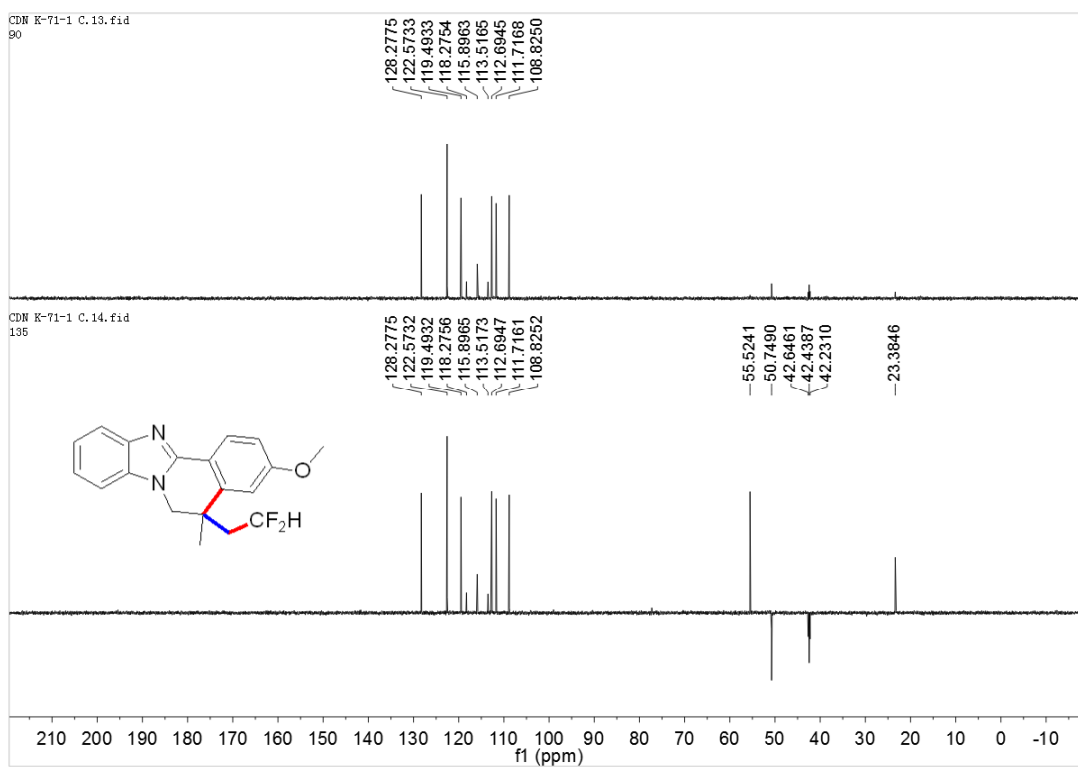
3n3, ¹H NMR



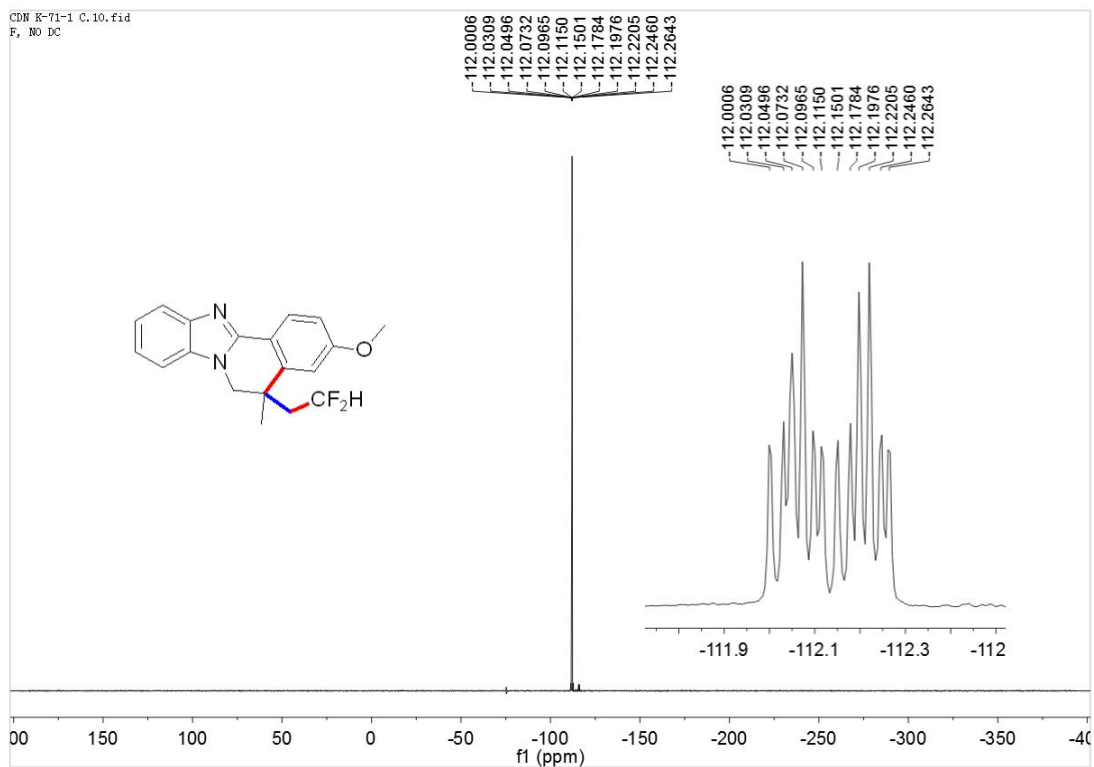
¹³C NMR



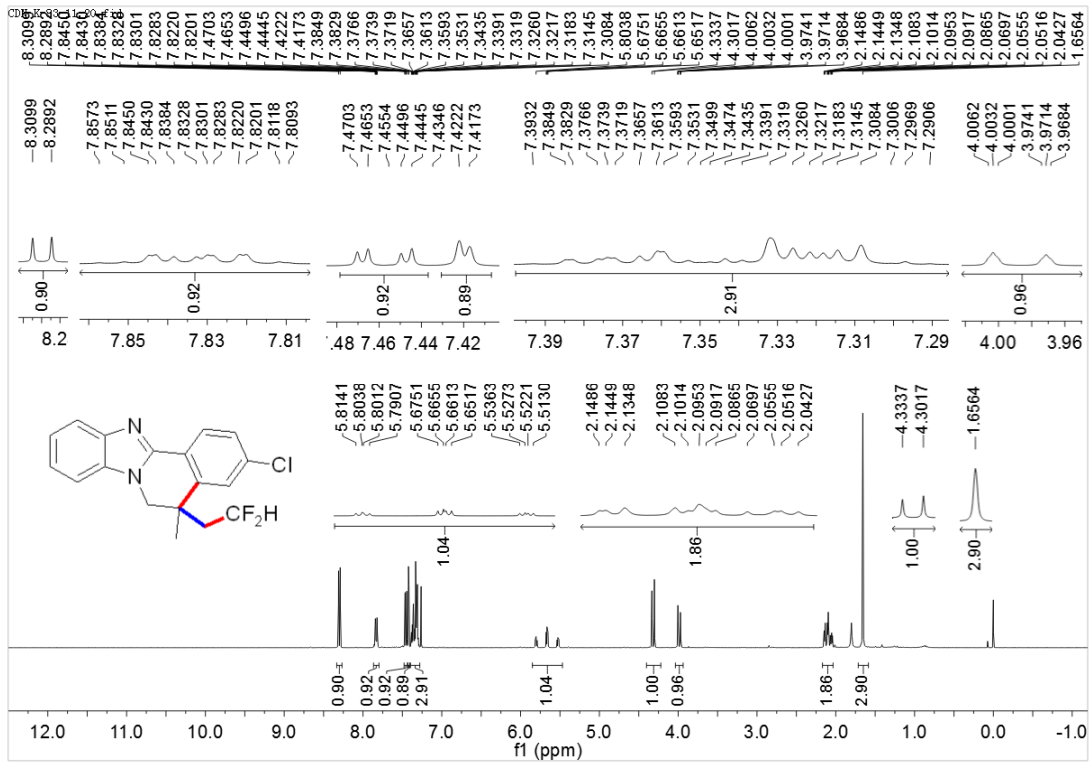
DEPT 90 and DEPT 135



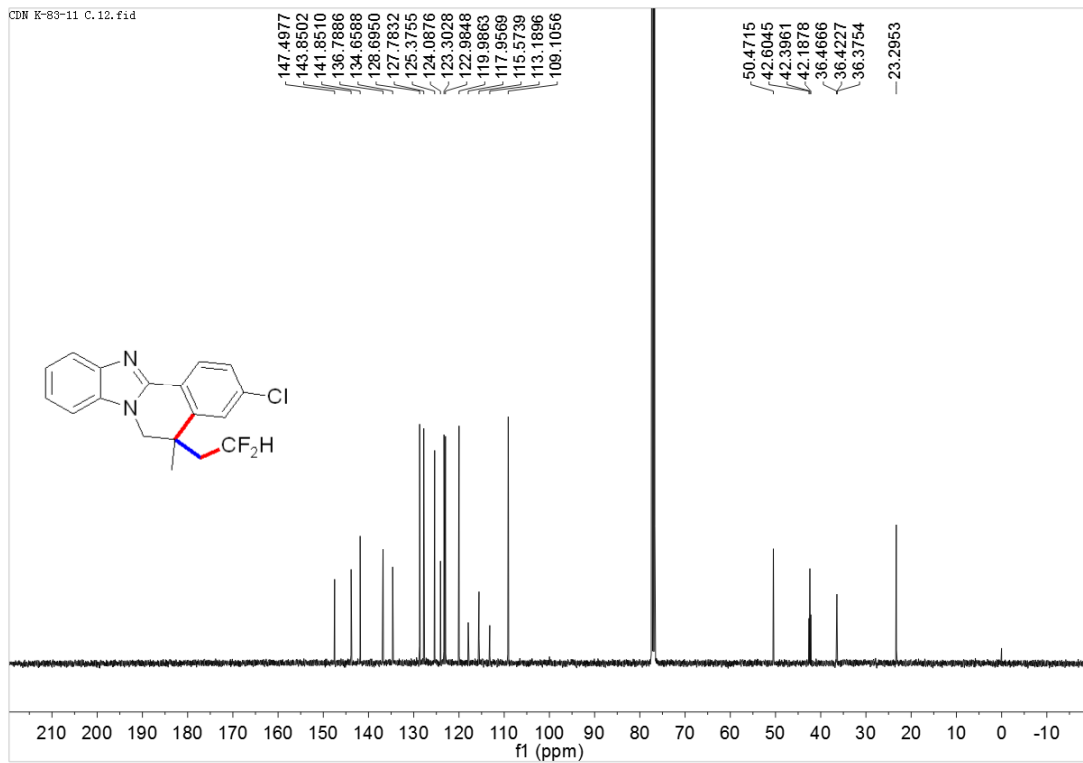
^{19}F NMR



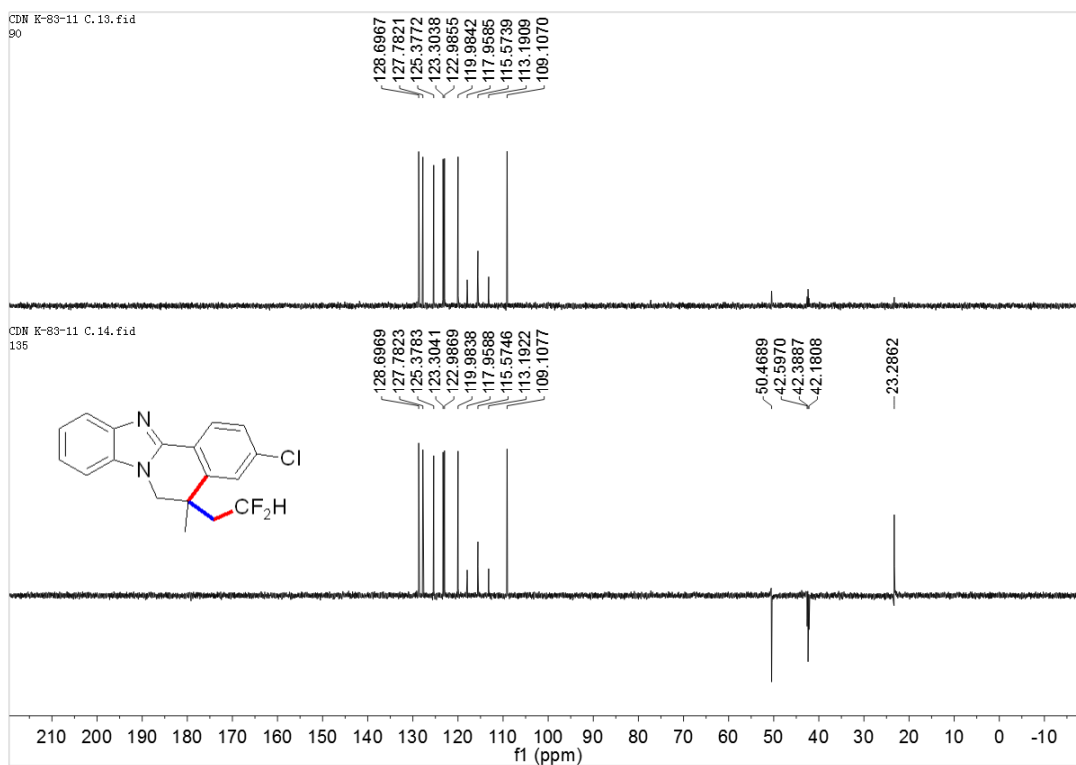
3n4, ¹H NMR



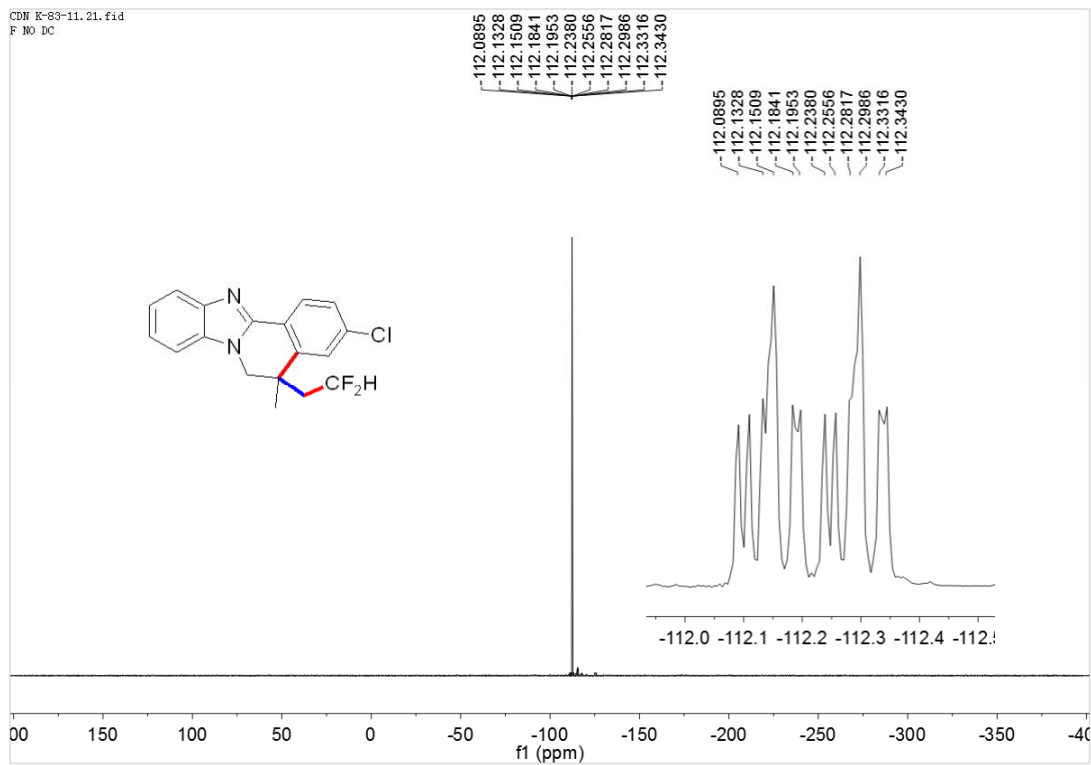
¹³C NMR



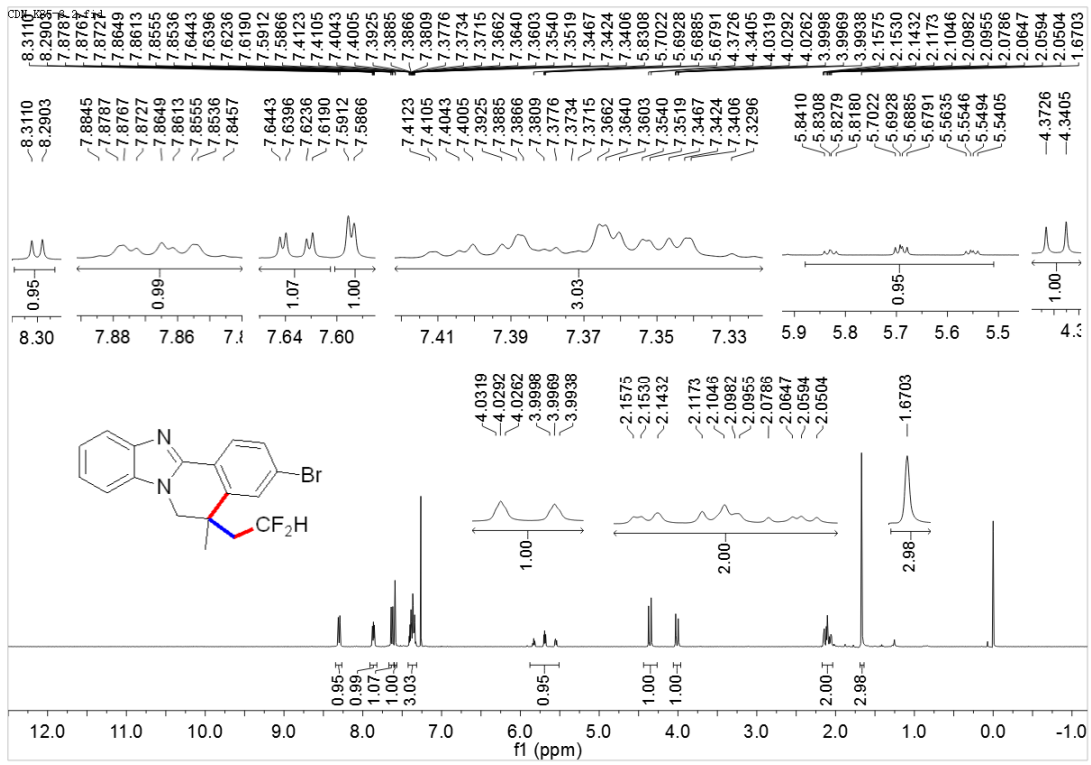
DEPT 90 and DEPT 135



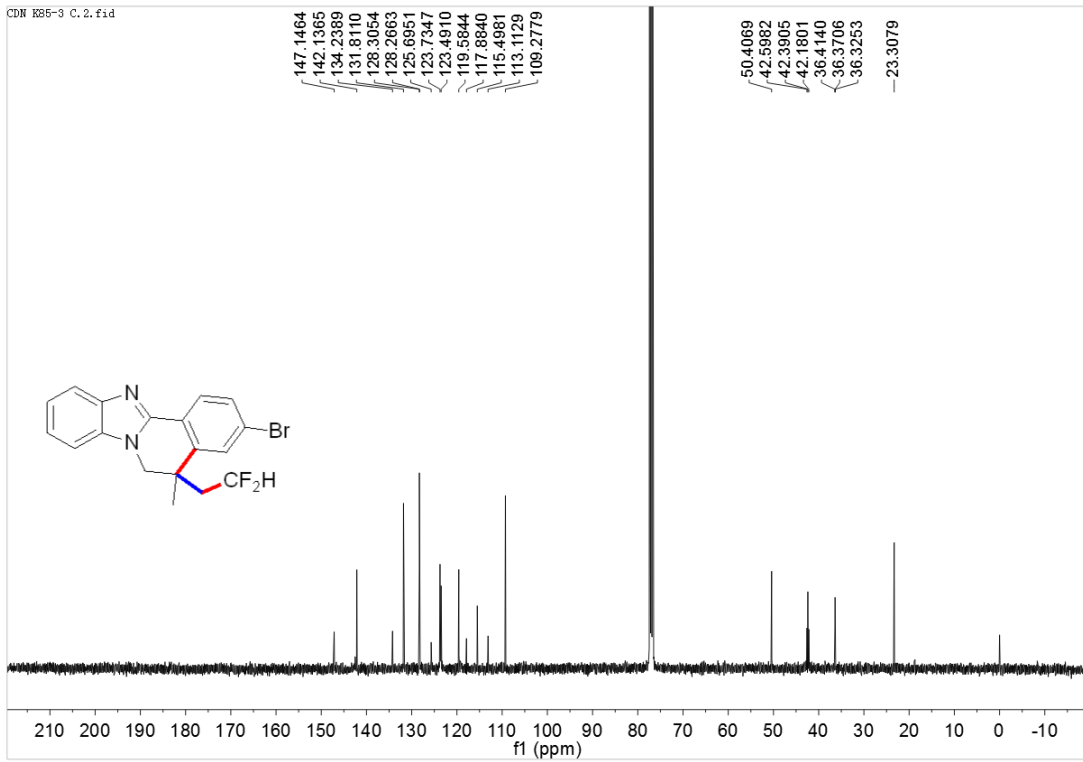
¹⁹F NMR



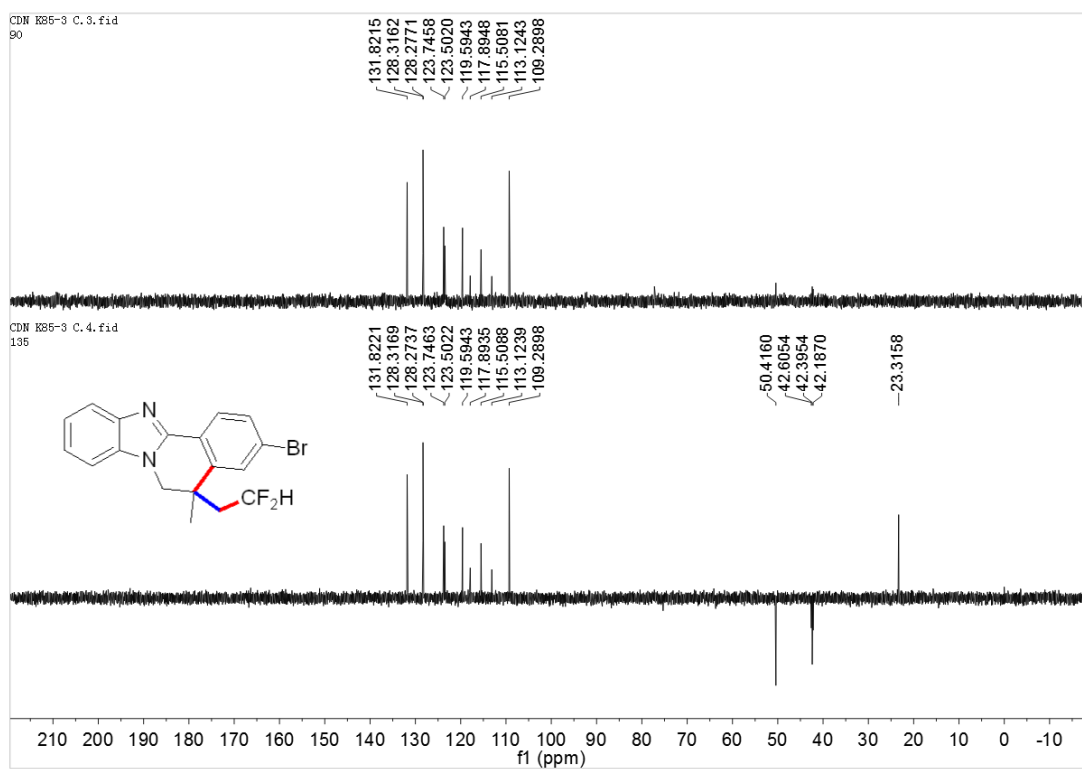
3n5, ¹H NMR



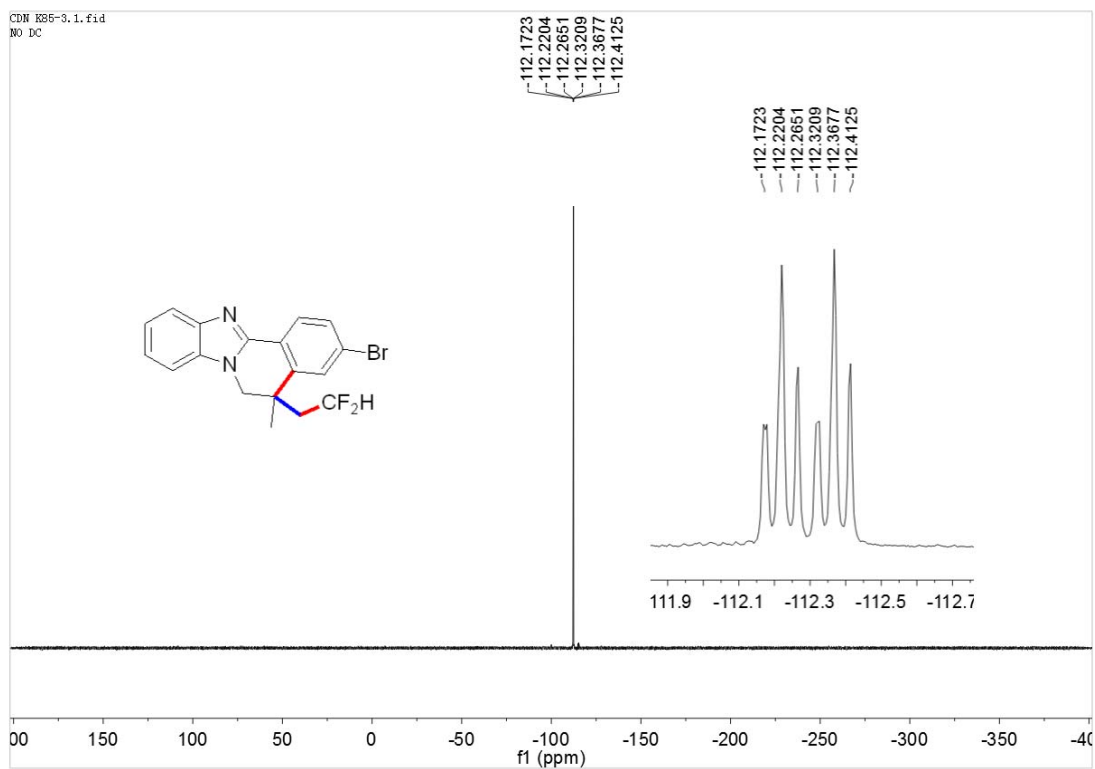
¹³C NMR



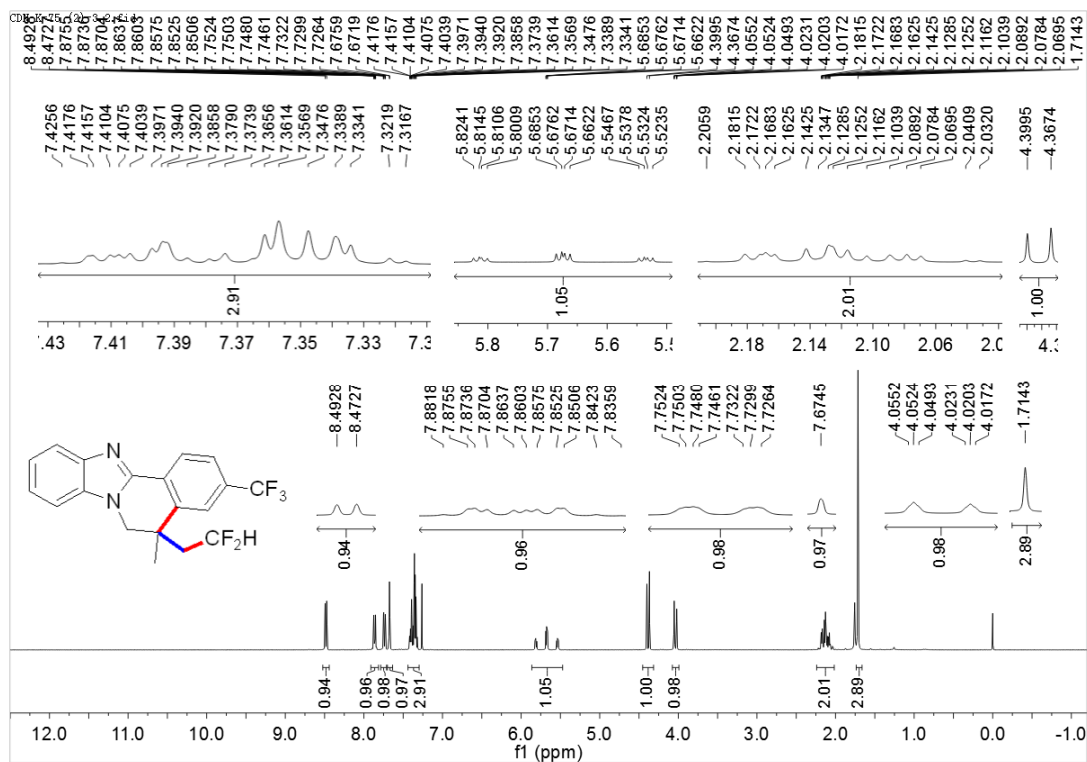
DEPT 90 and DEPT 135



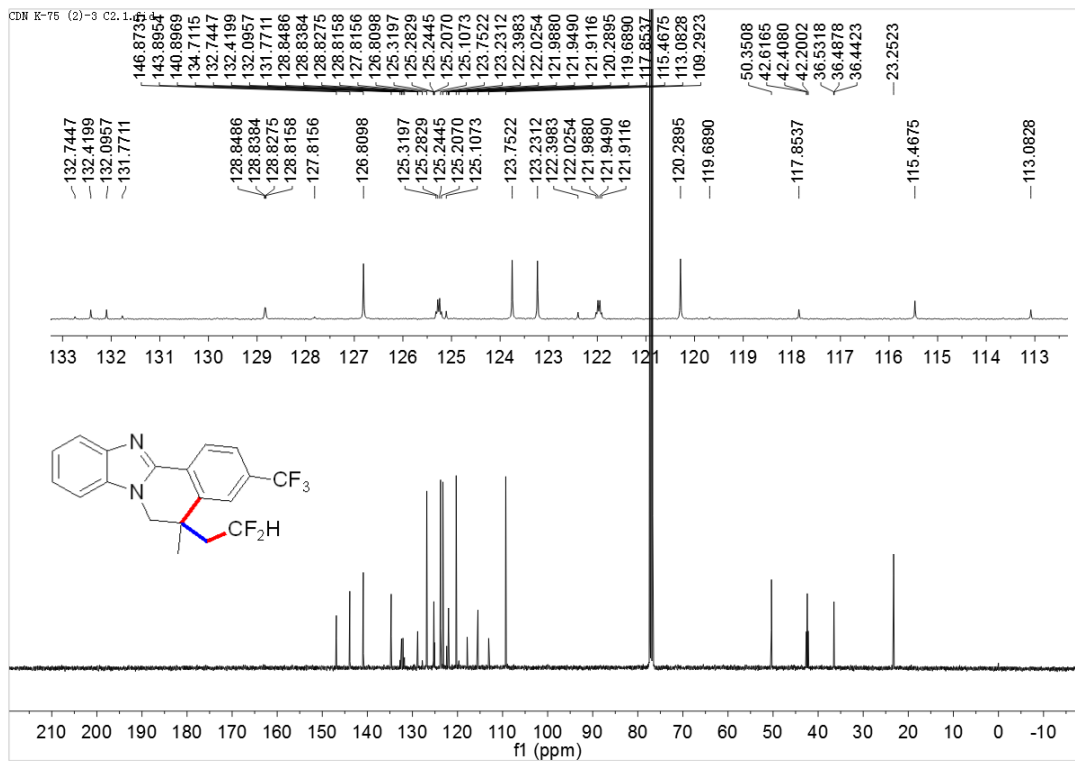
¹⁹F NMR



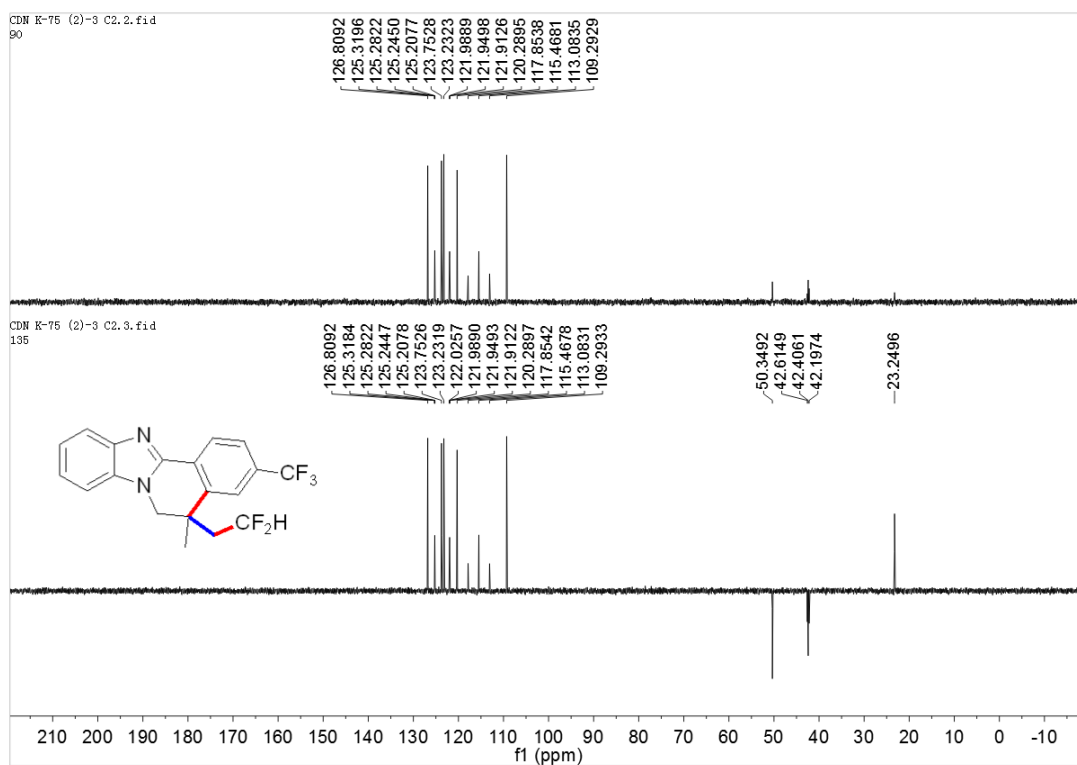
3o1, ¹H NMR



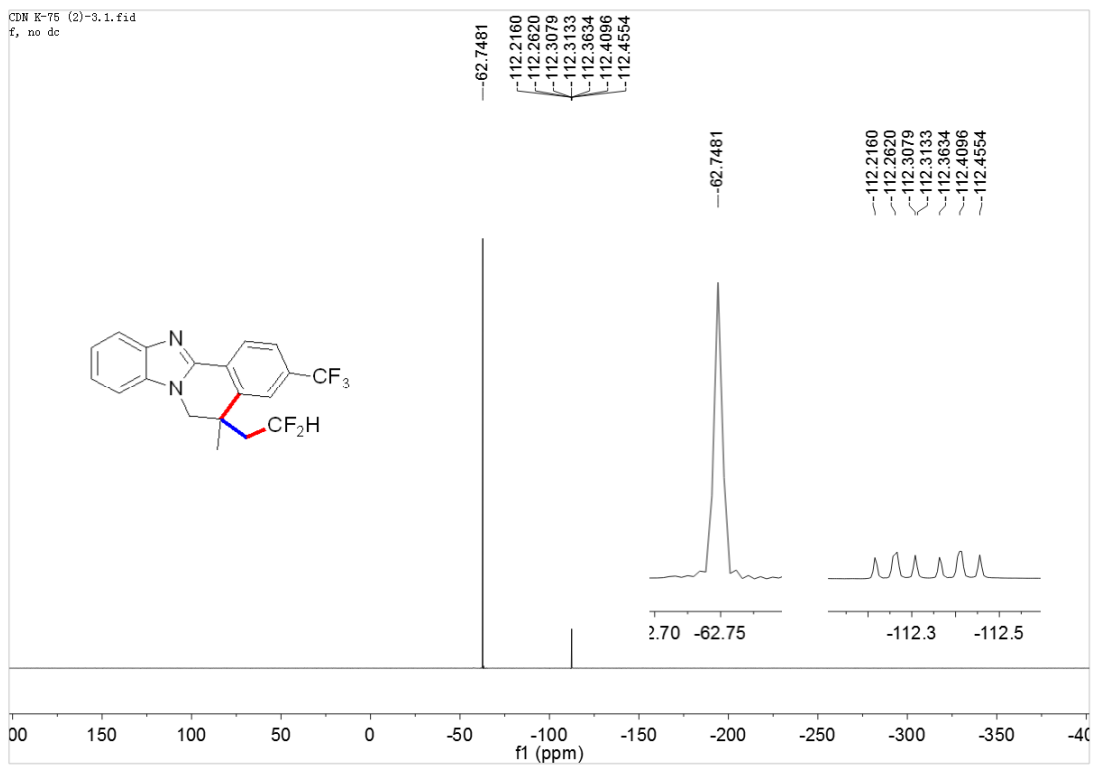
¹³C NMR



DEPT 90 and DEPT 135

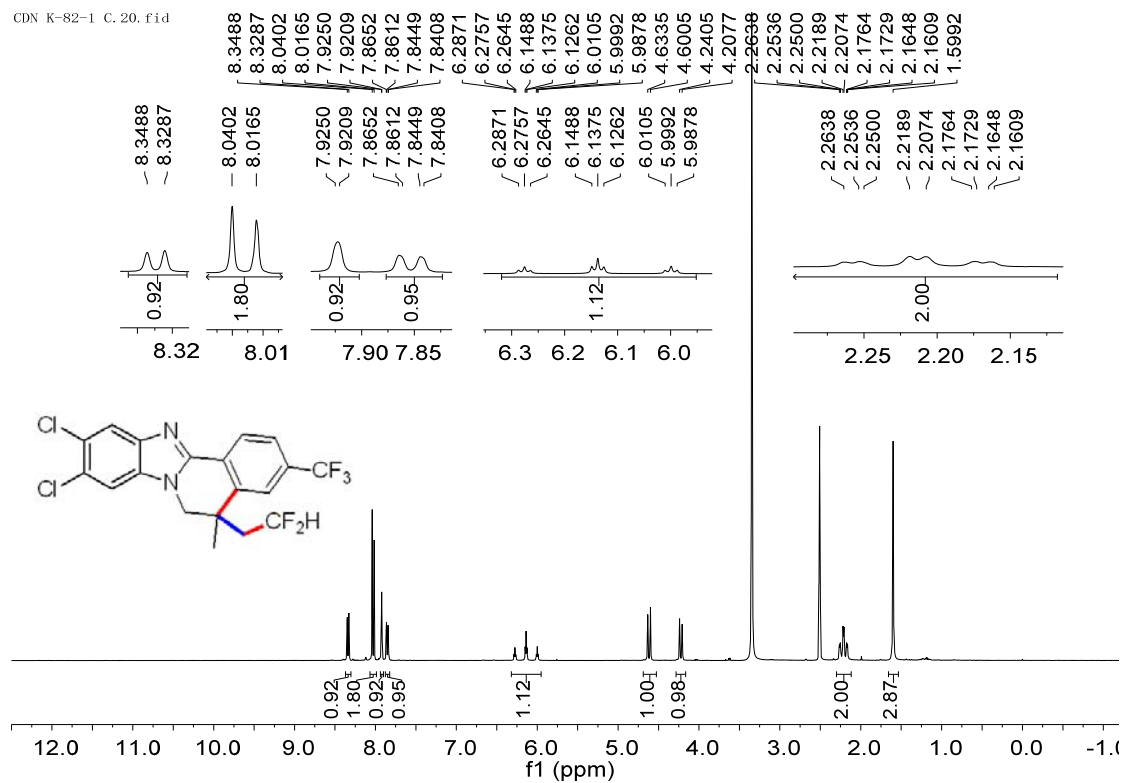


¹⁹F NMR



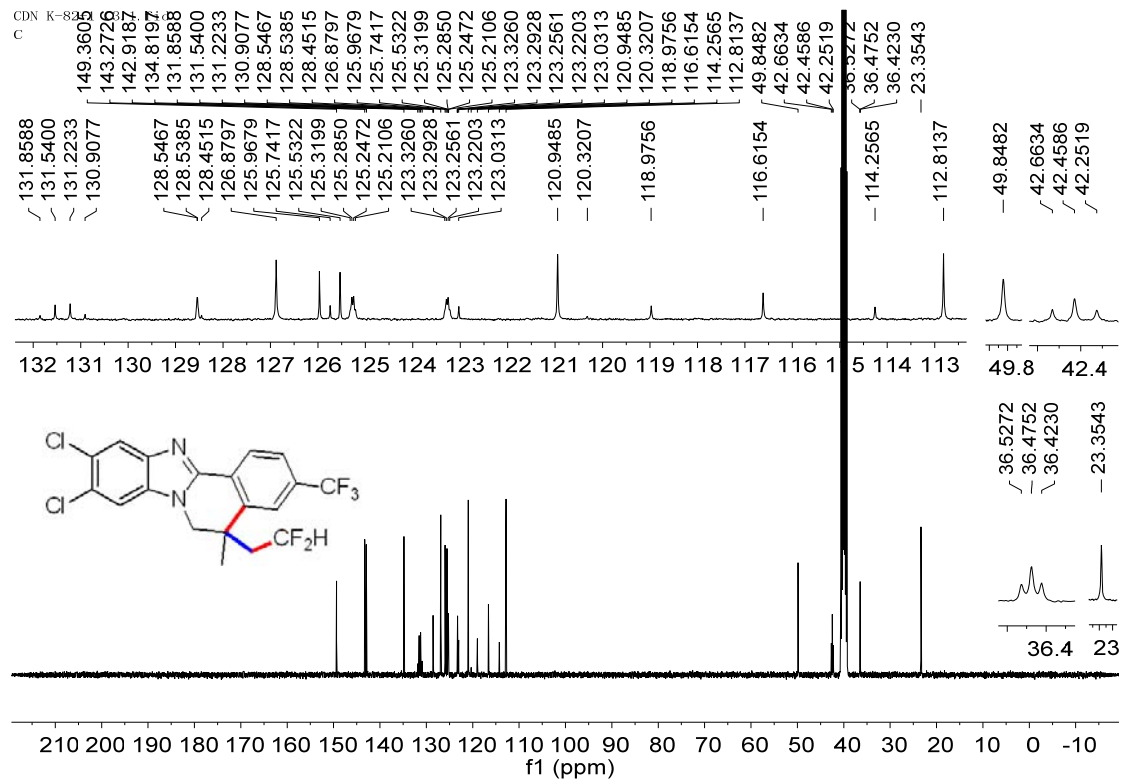
302, ¹H NMR

CDN K-82-1 C. 20. f1d

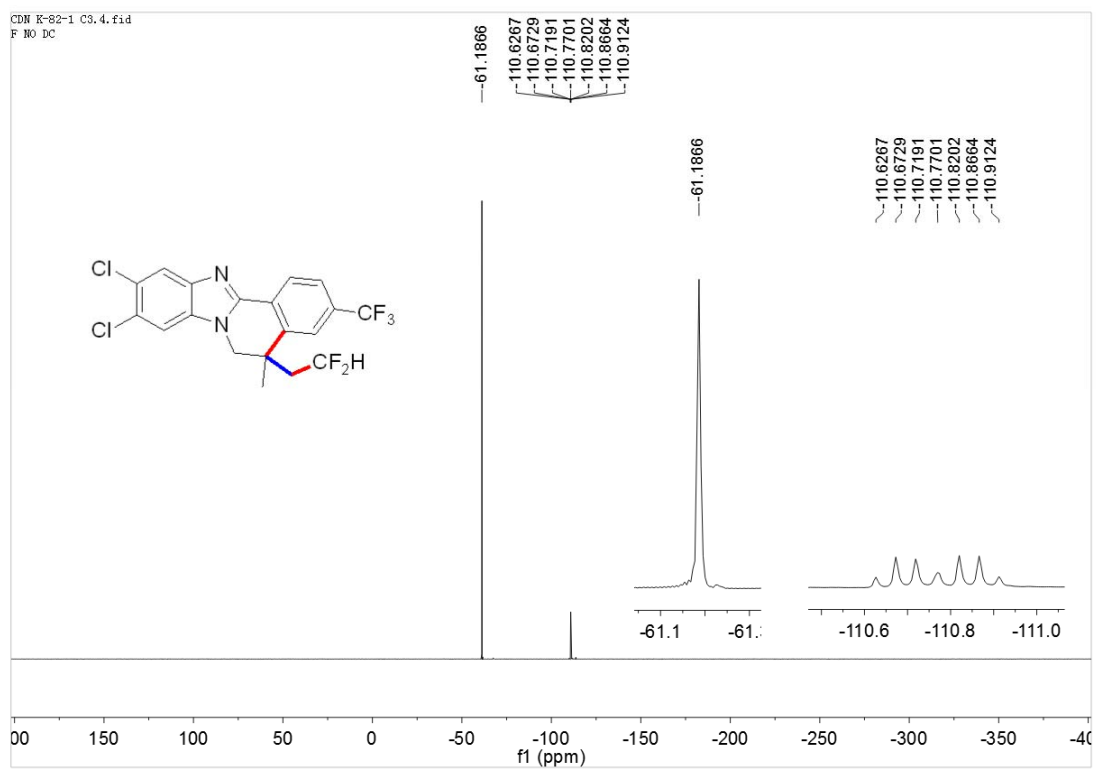


¹³C NMR

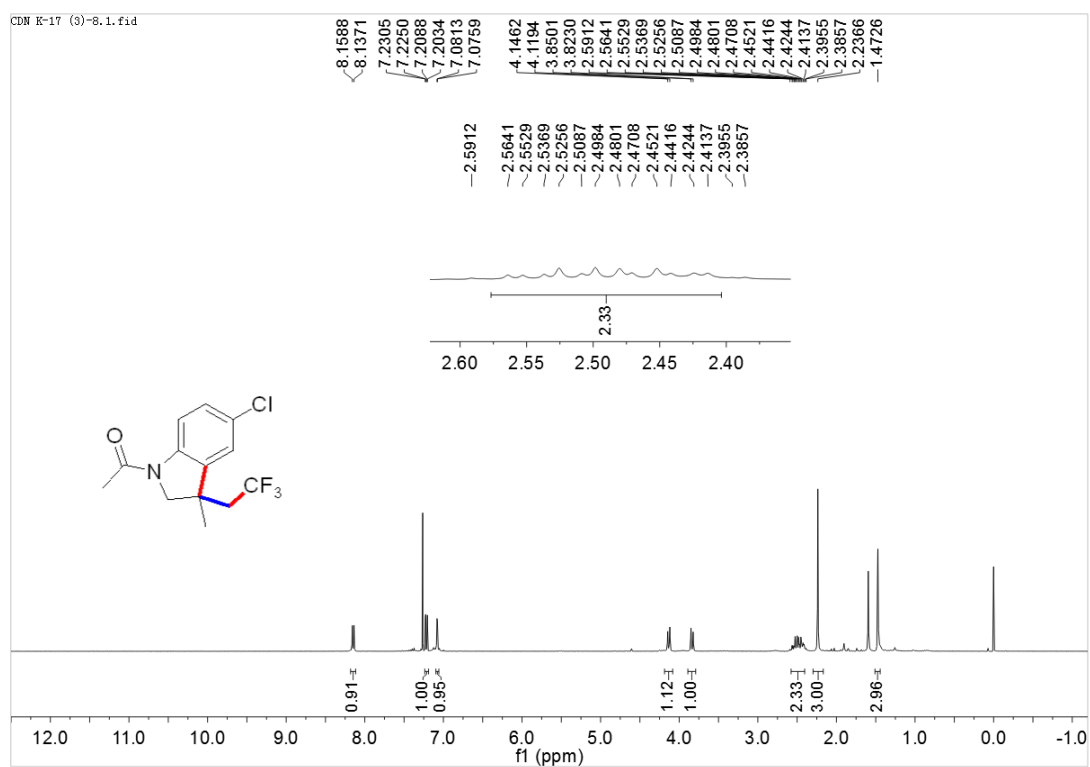
CDN K-82-1 C. 20. f1d



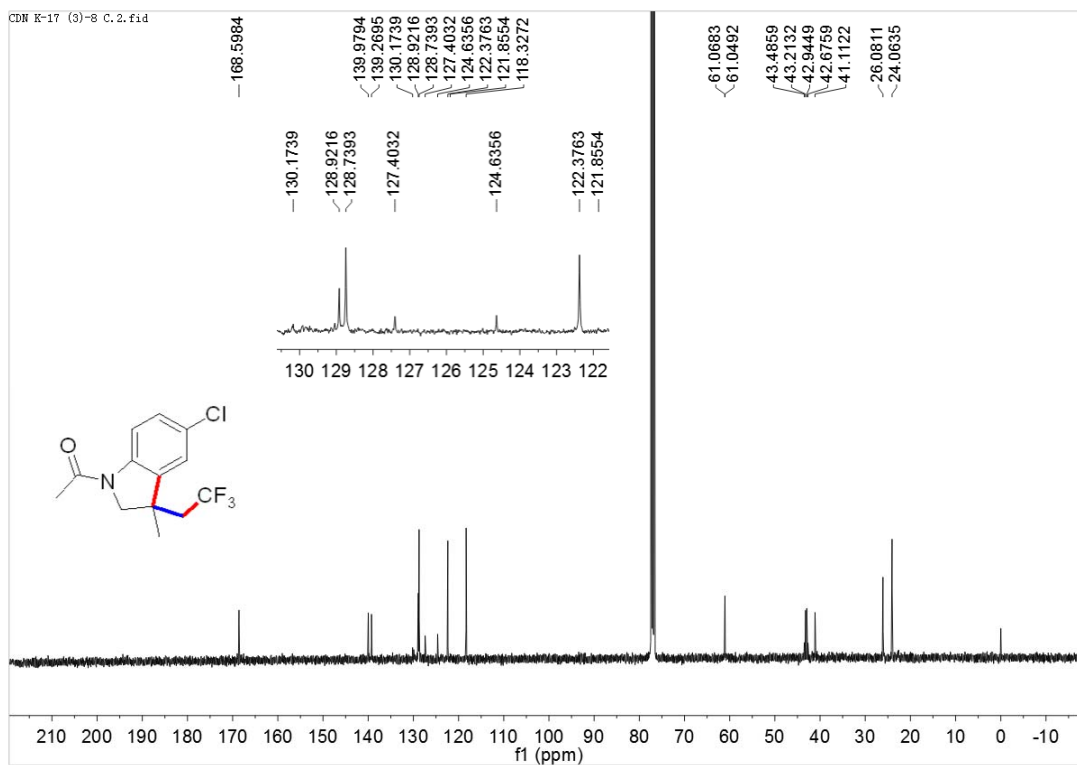
¹⁹F NMR



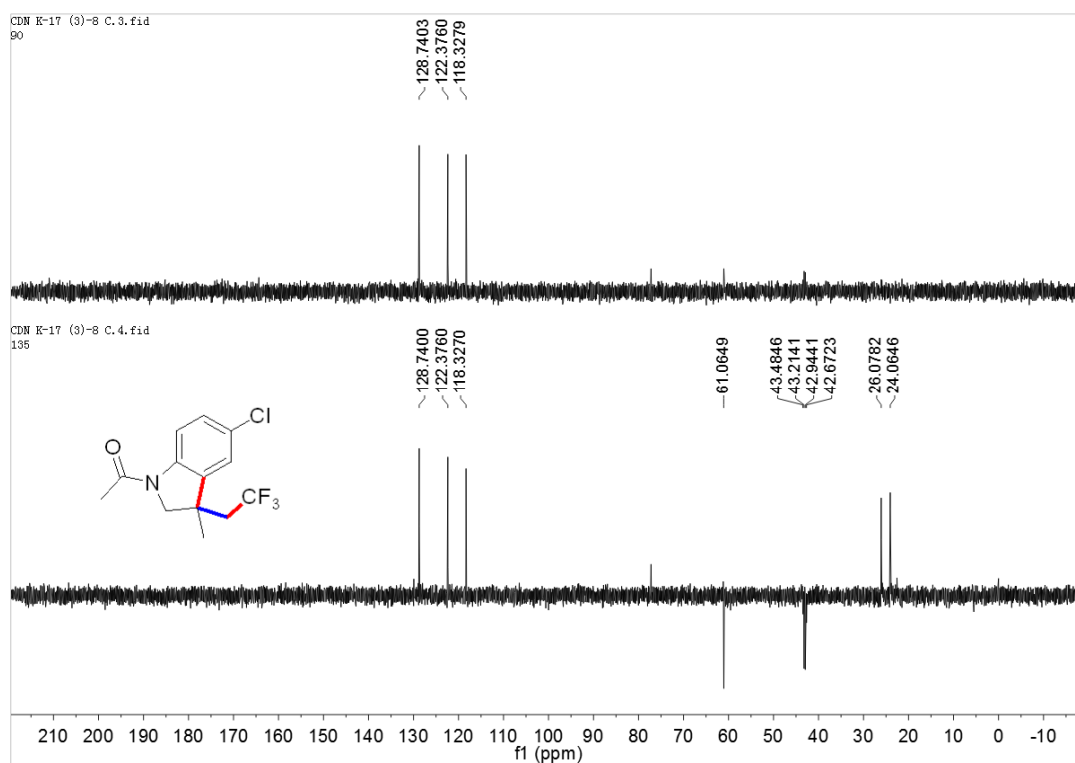
5a1, ¹H NMR



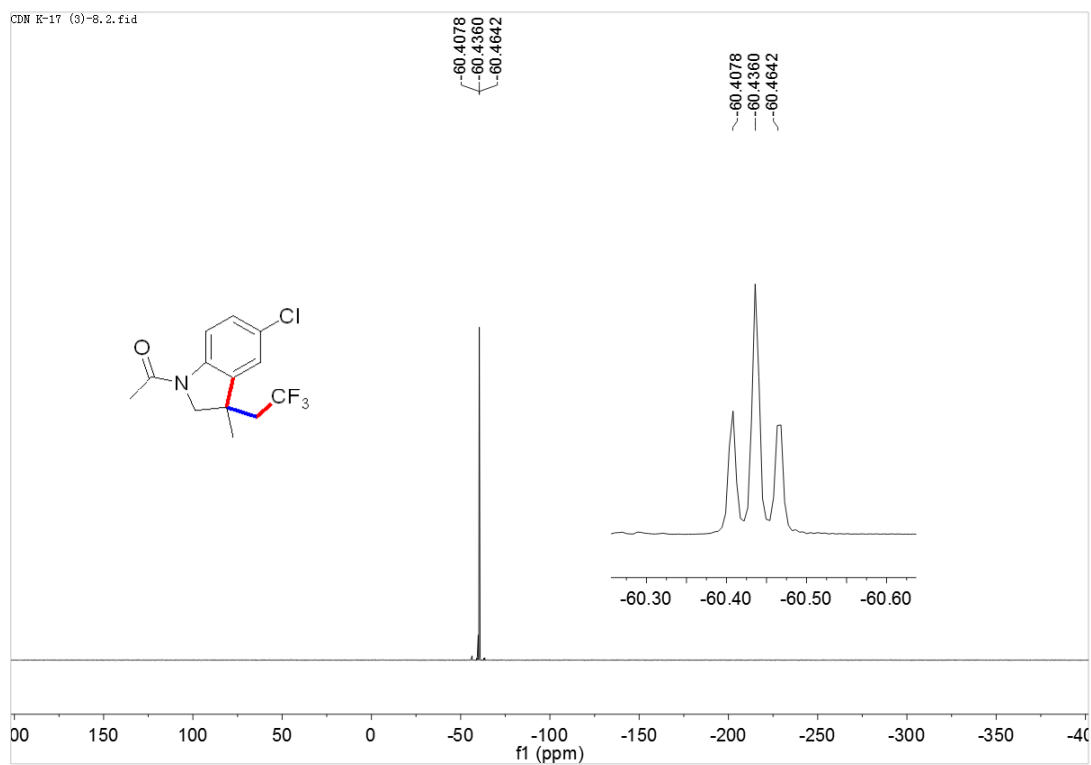
¹³C NMR



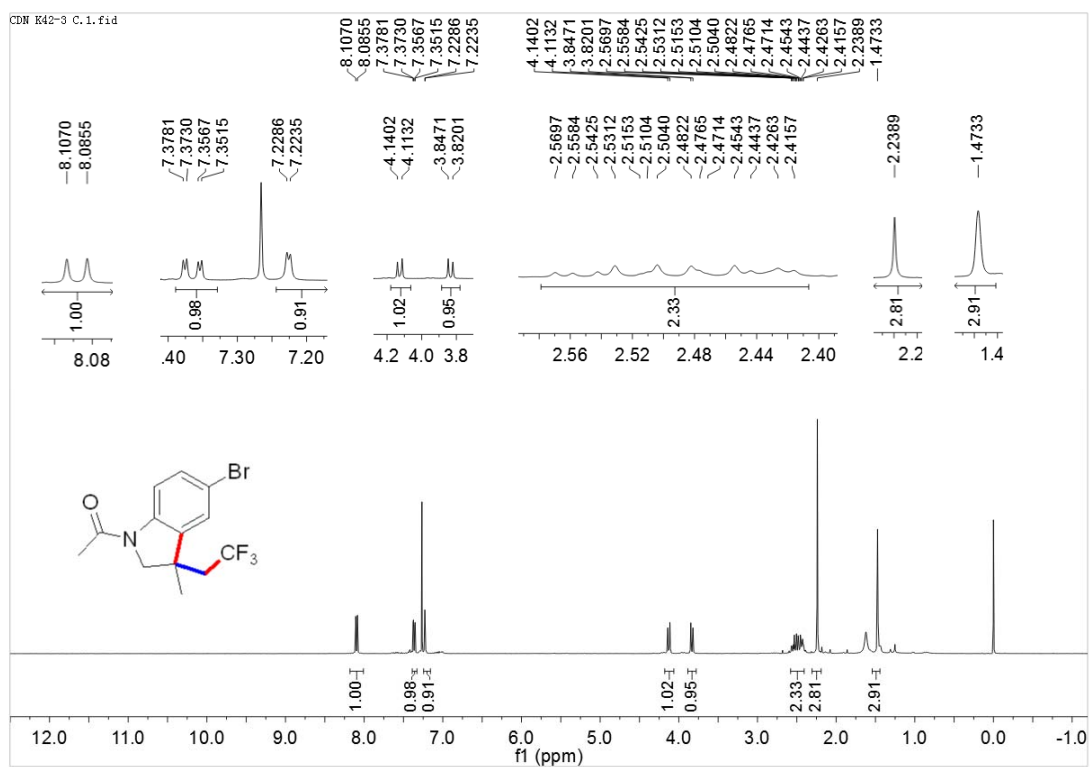
DEPT 90 and DEPT 135



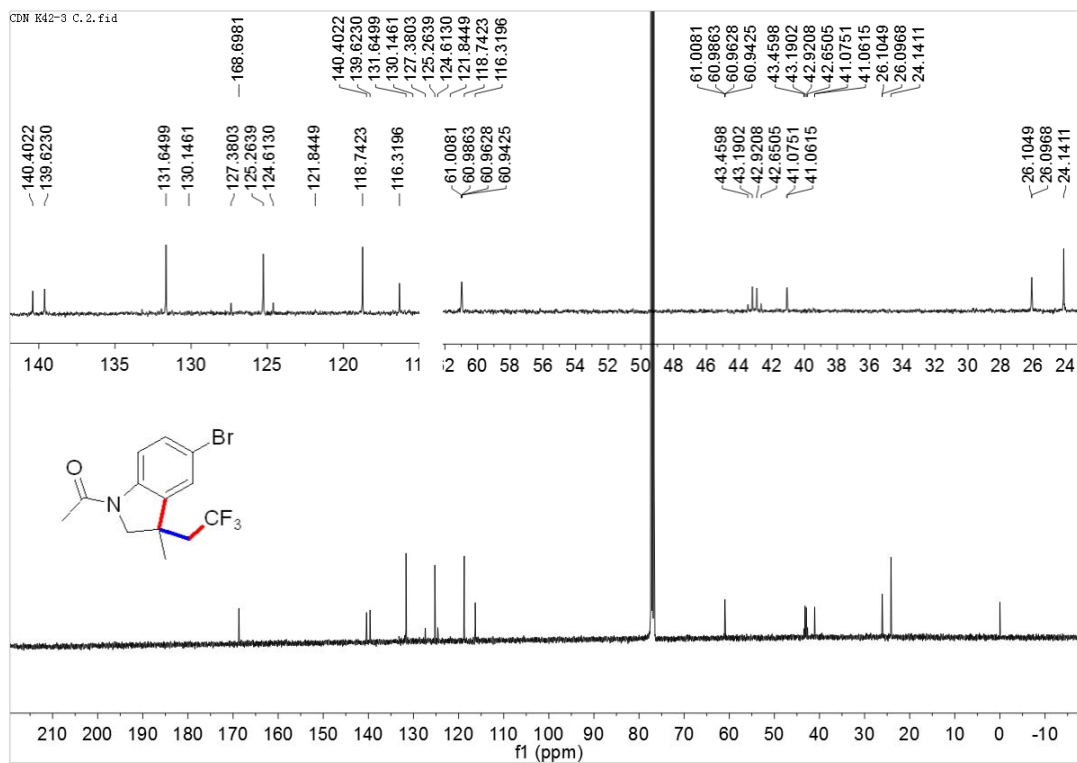
¹⁹F NMR



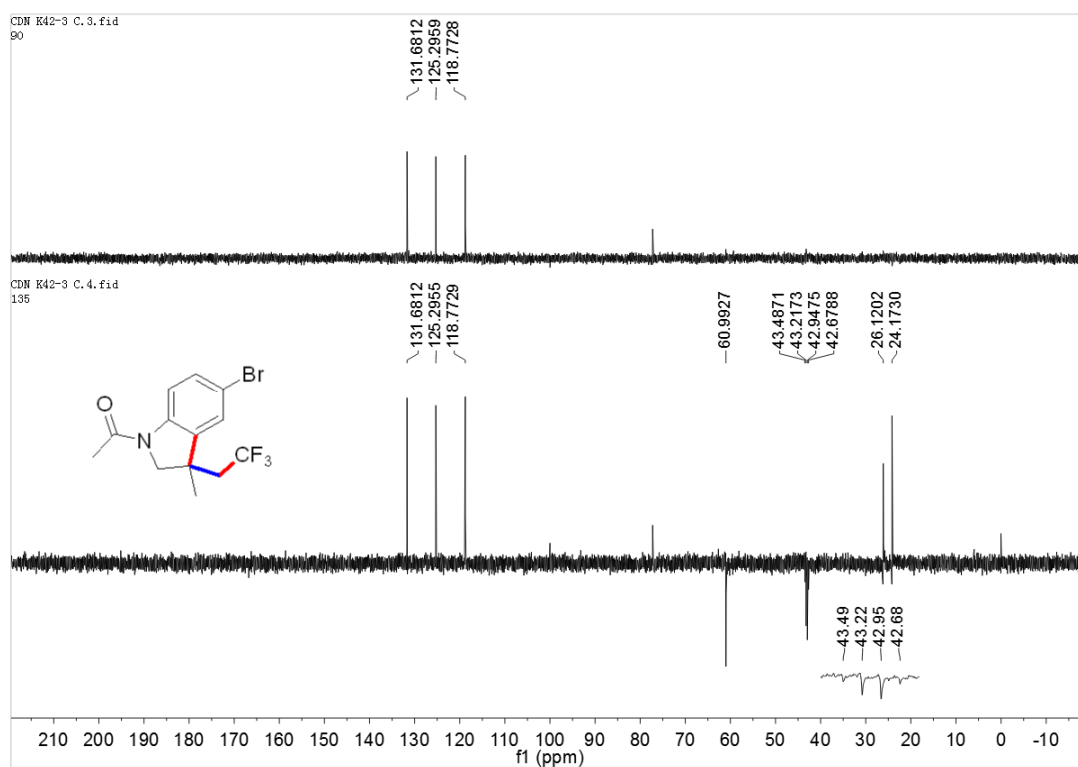
5a2, ¹H NMR



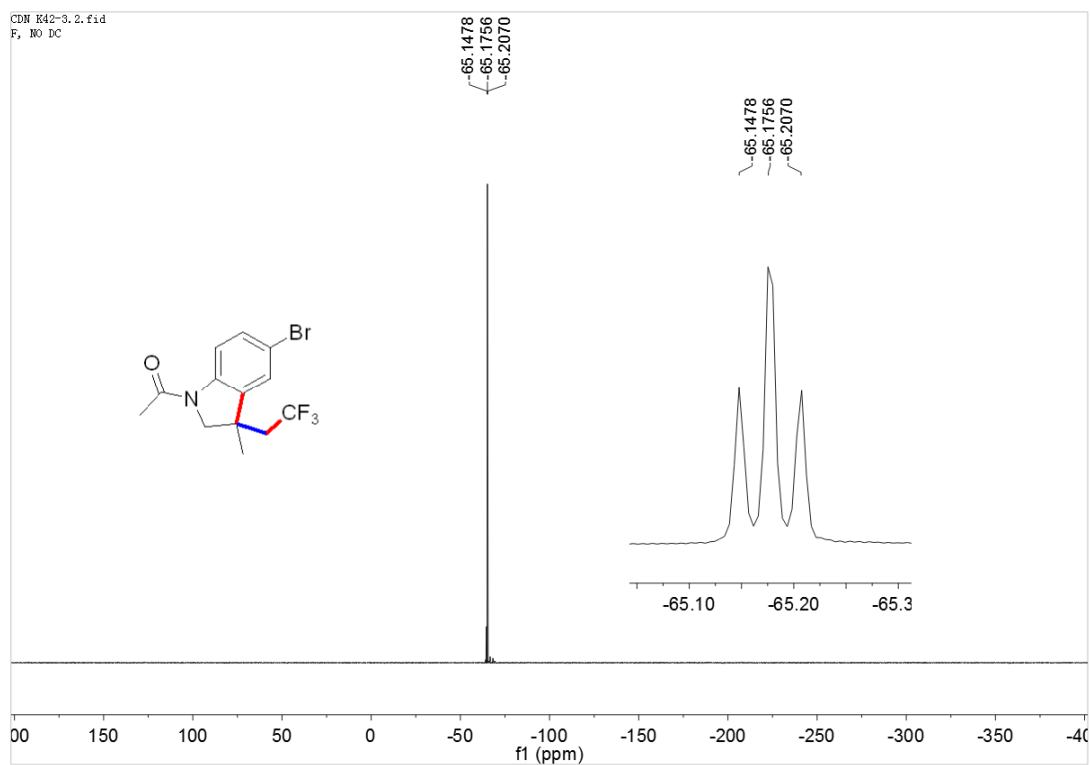
¹³C NMR



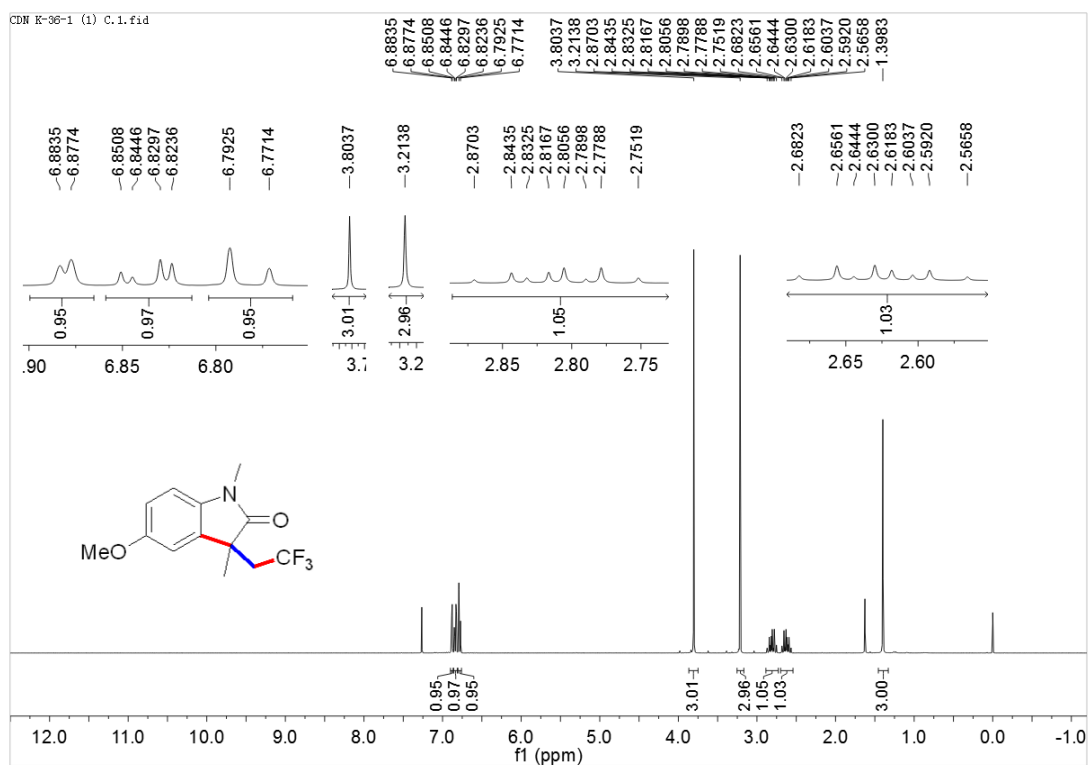
DEPT 90 and DEPT 135



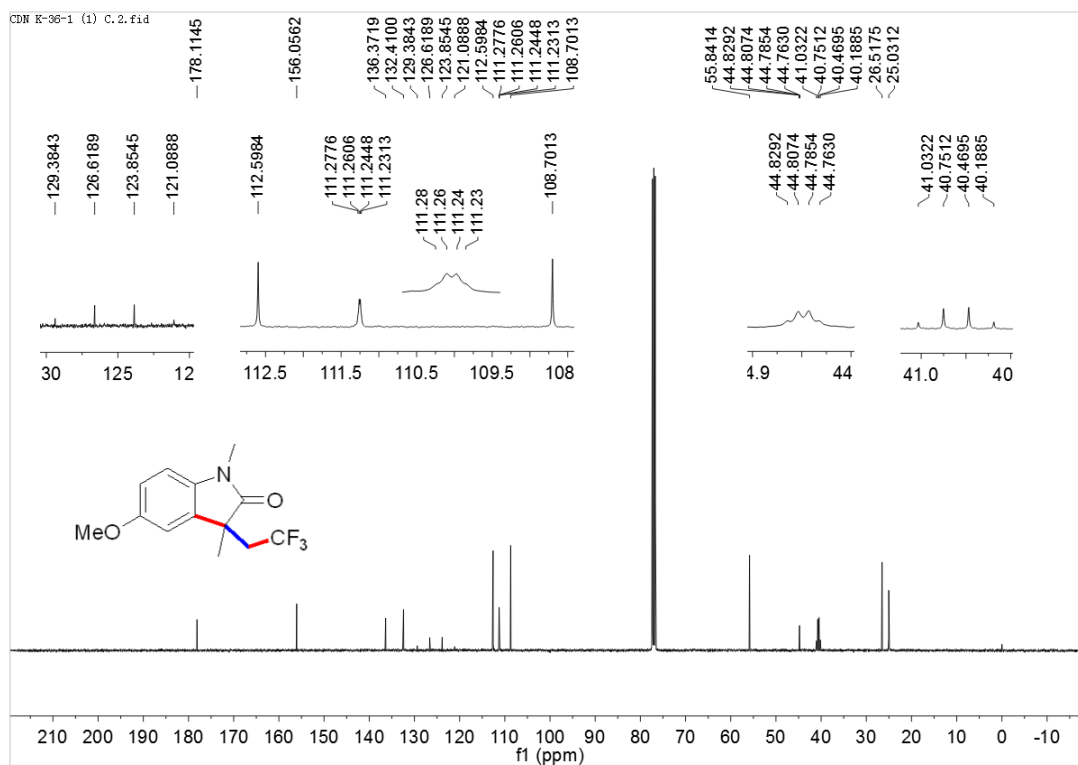
¹⁹F NMR



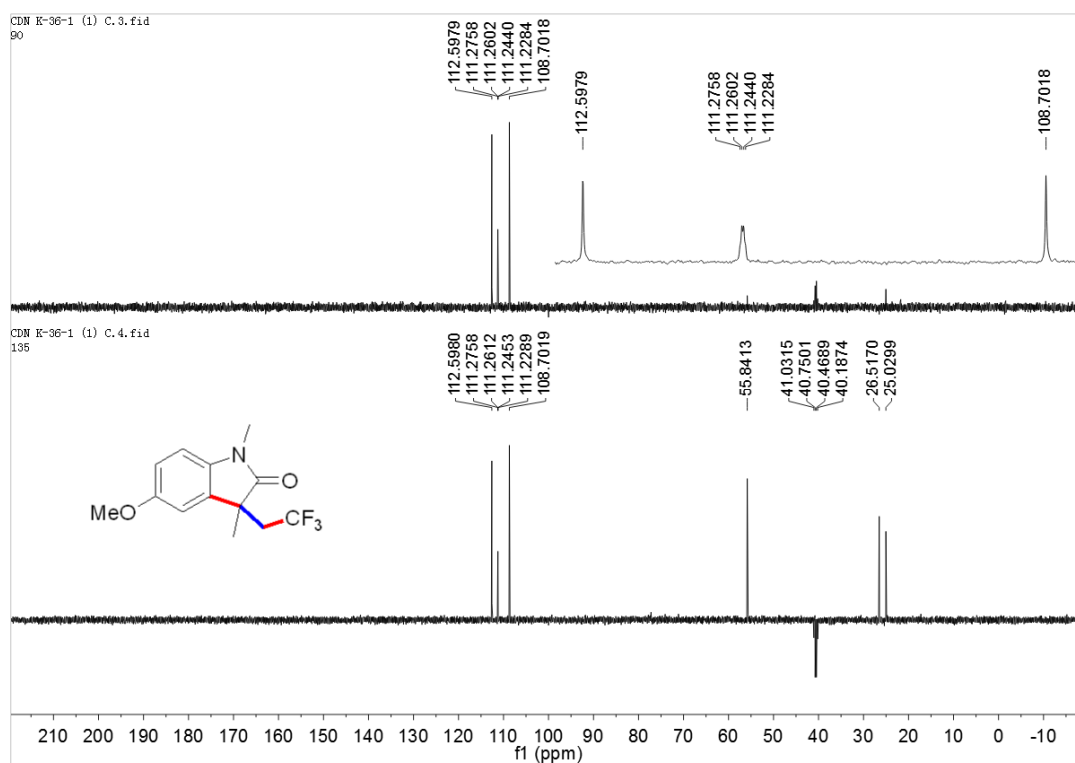
5b, ¹H NMR



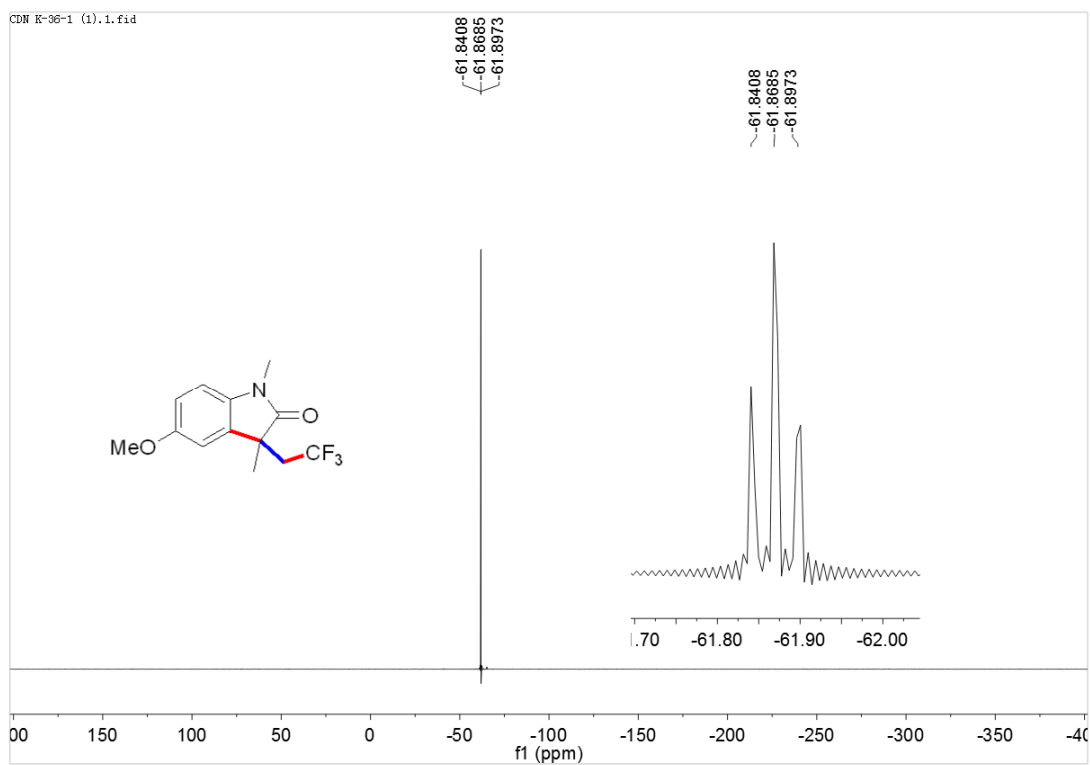
¹³C NMR



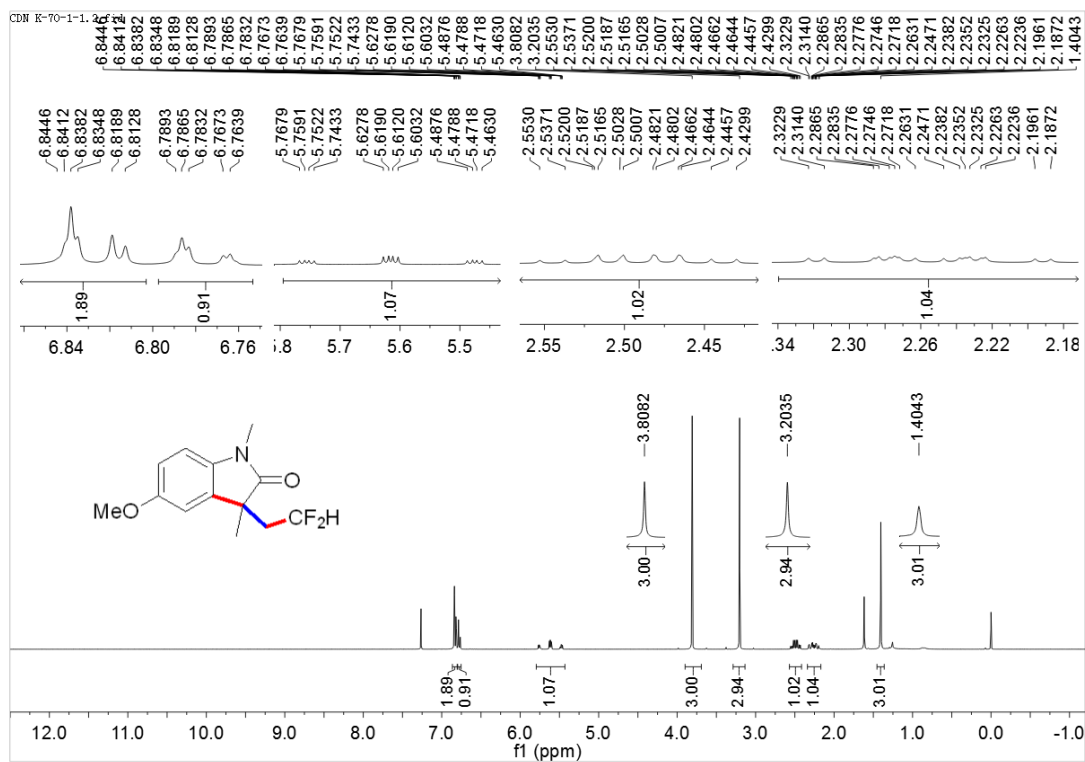
DEPT 90 and DEPT 135



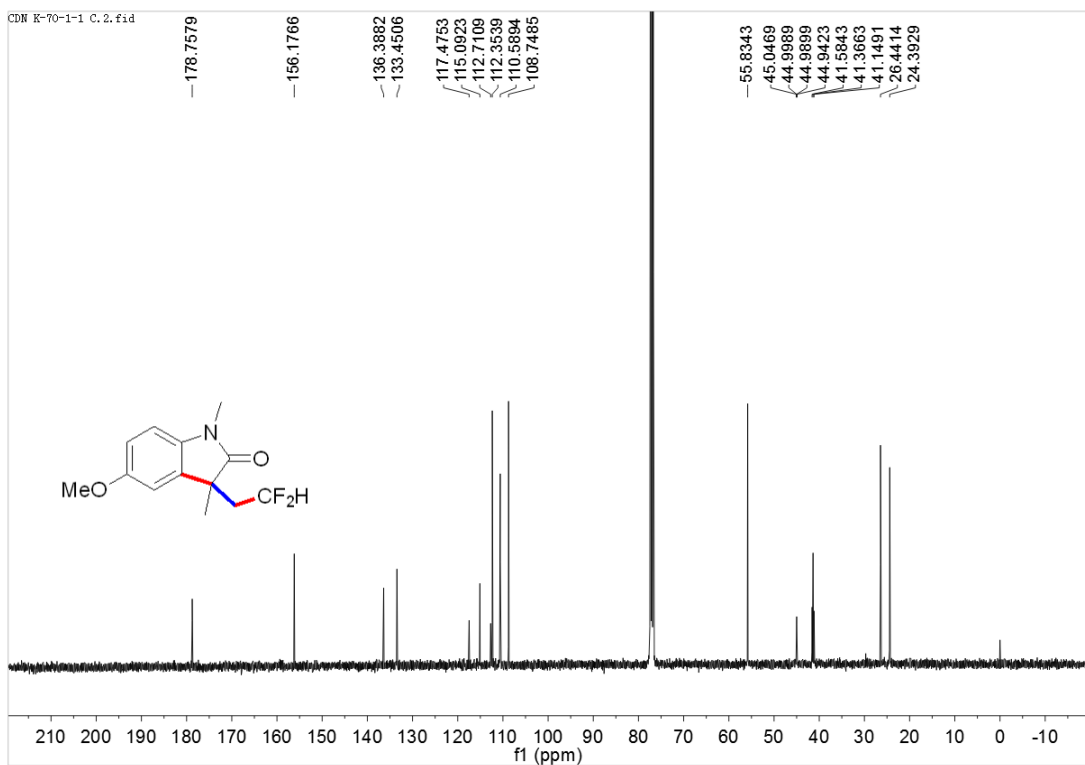
¹⁹F NMR



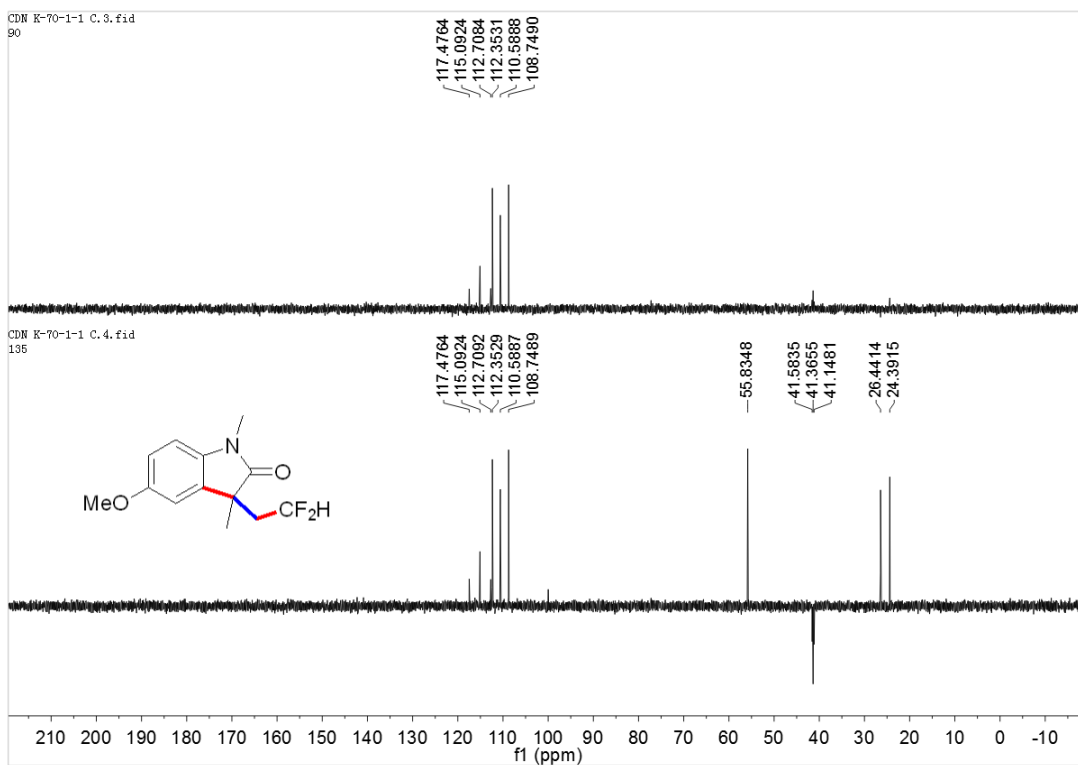
5c, ¹H NMR



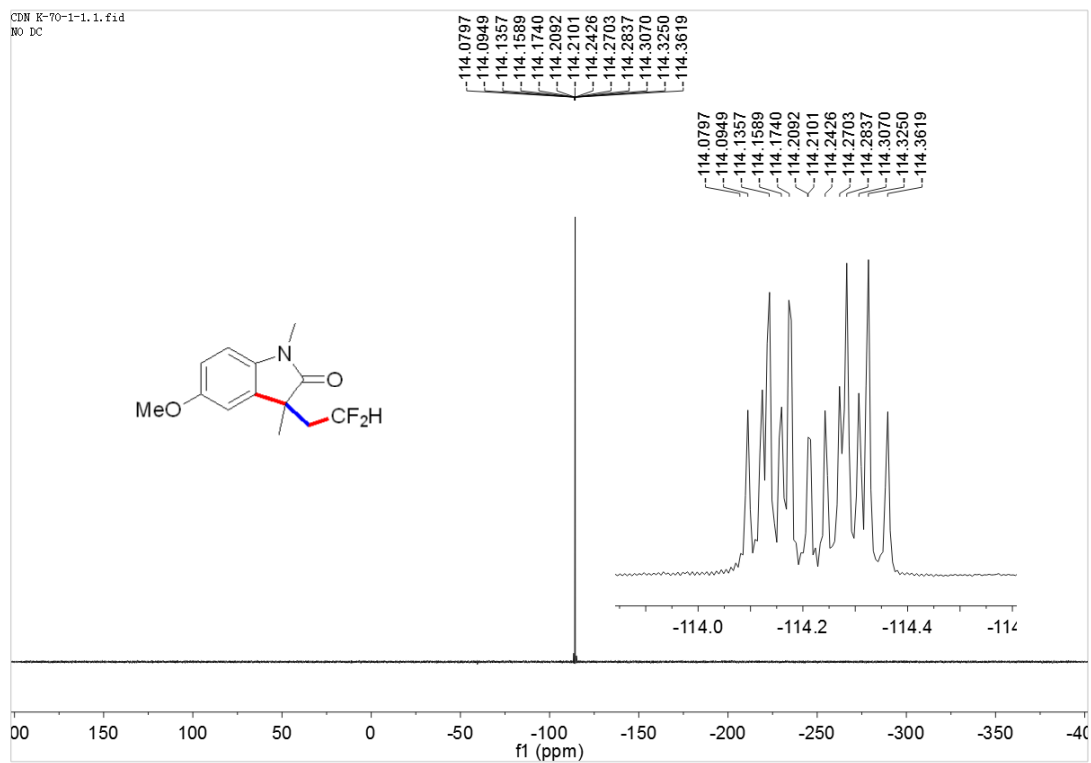
¹³C NMR



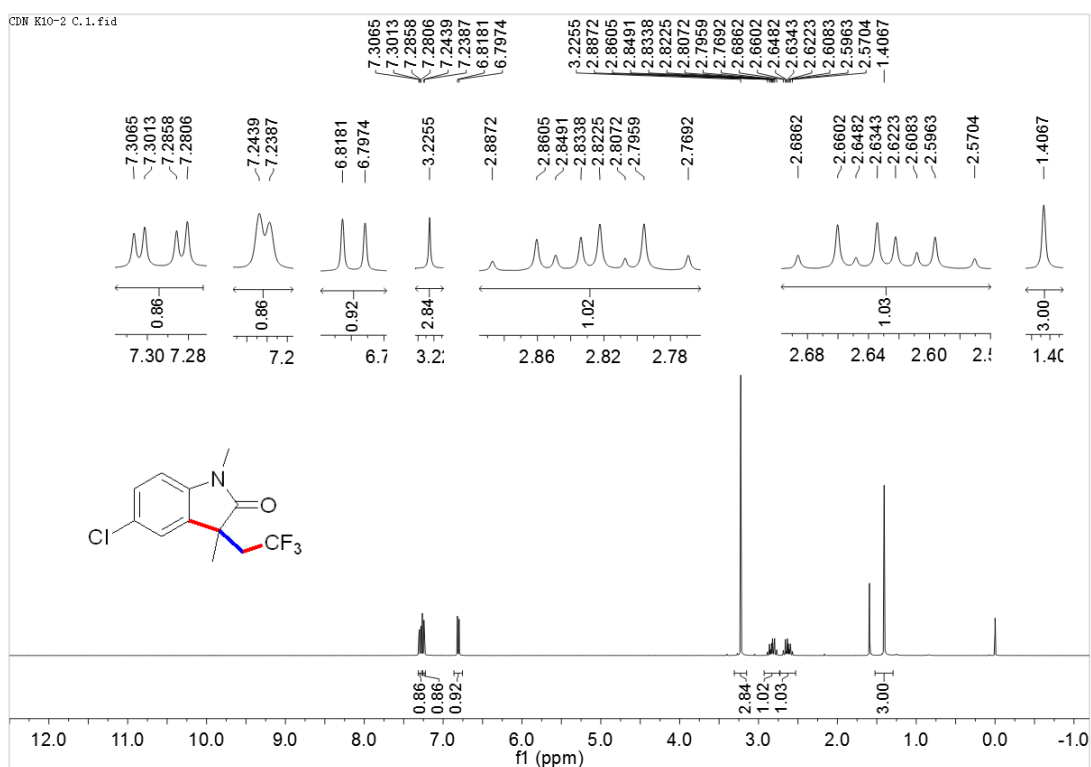
DEPT 90 and DEPT 135



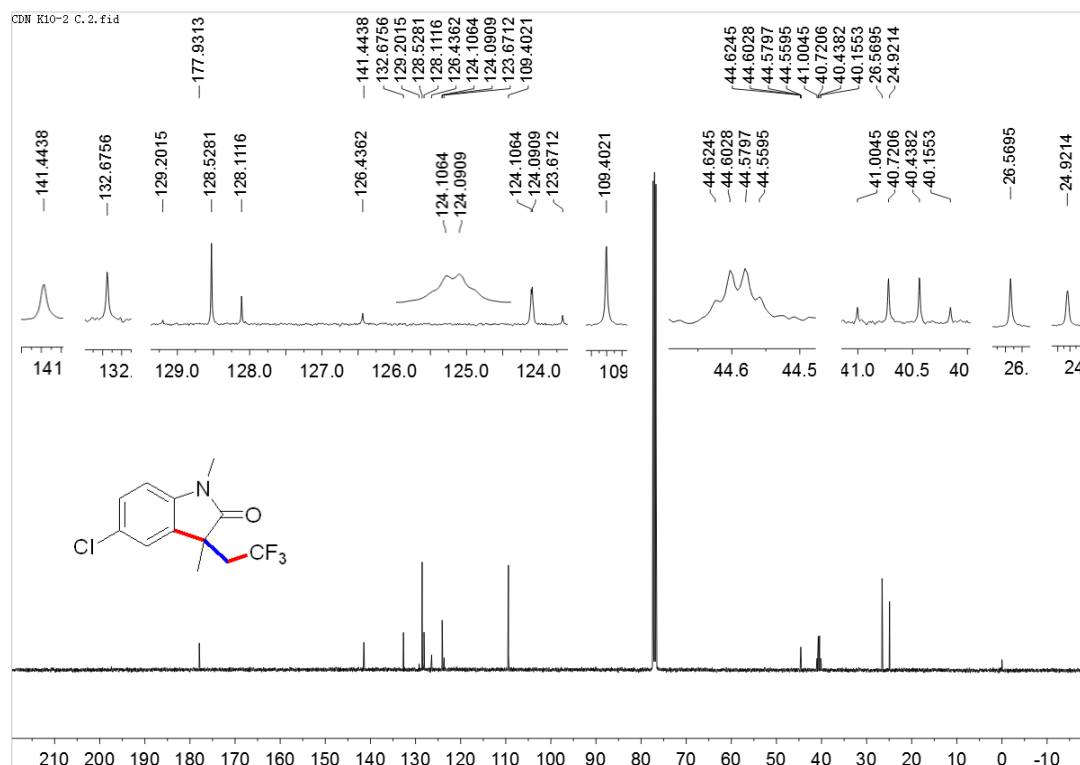
¹⁹F NMR



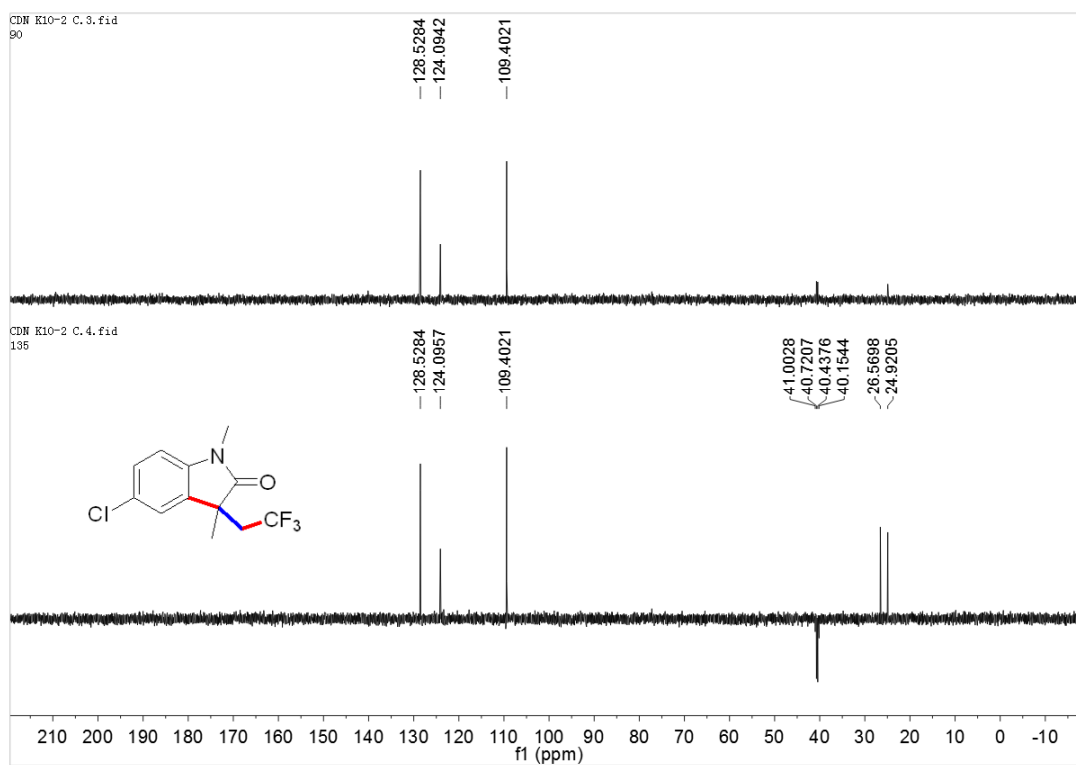
5d1, ¹H NMR



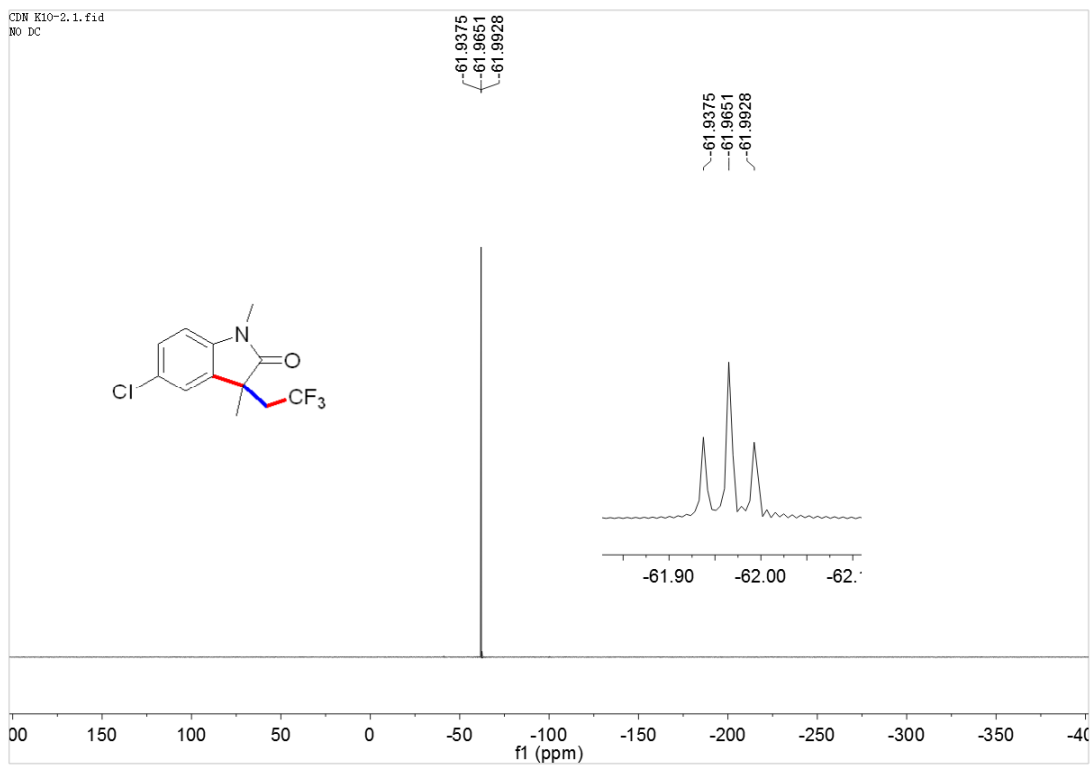
¹³C NMR



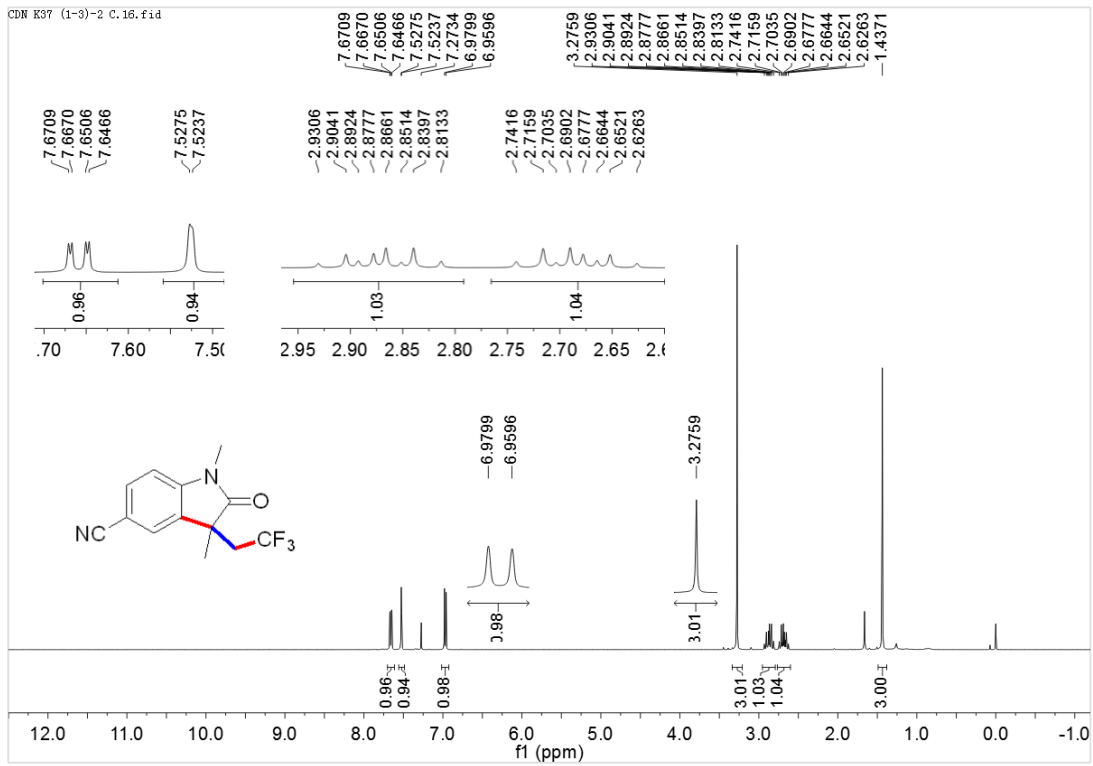
DEPT 90 and DEPT 135



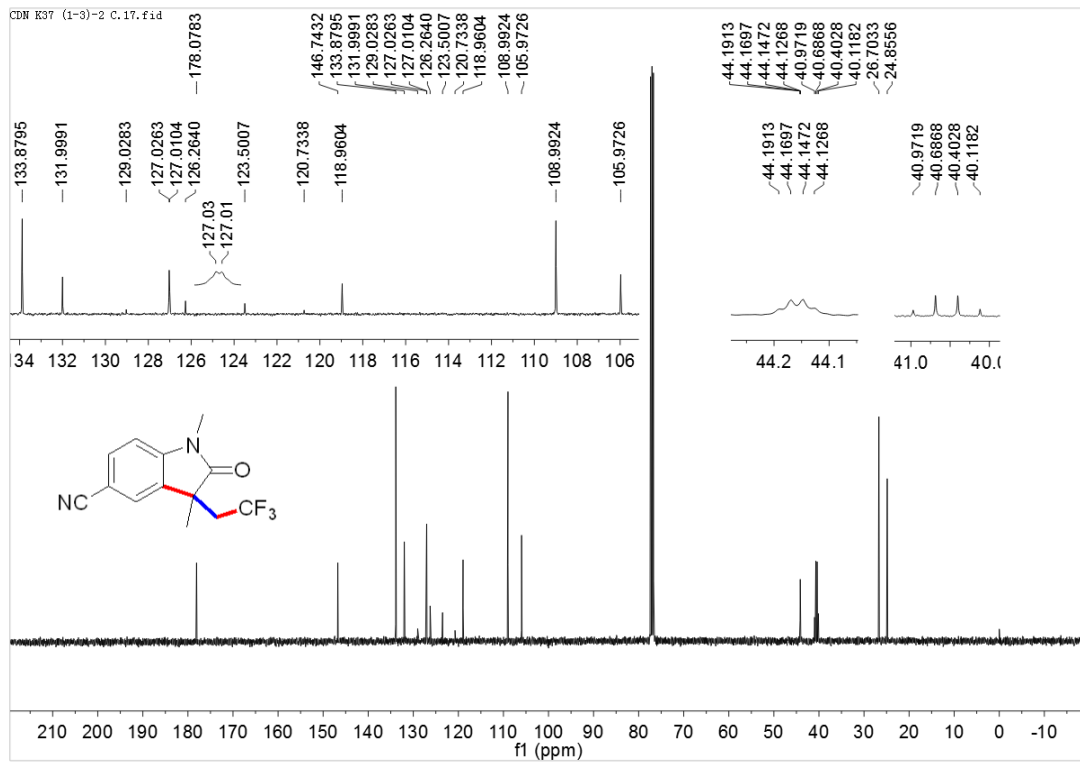
¹⁹F NMR



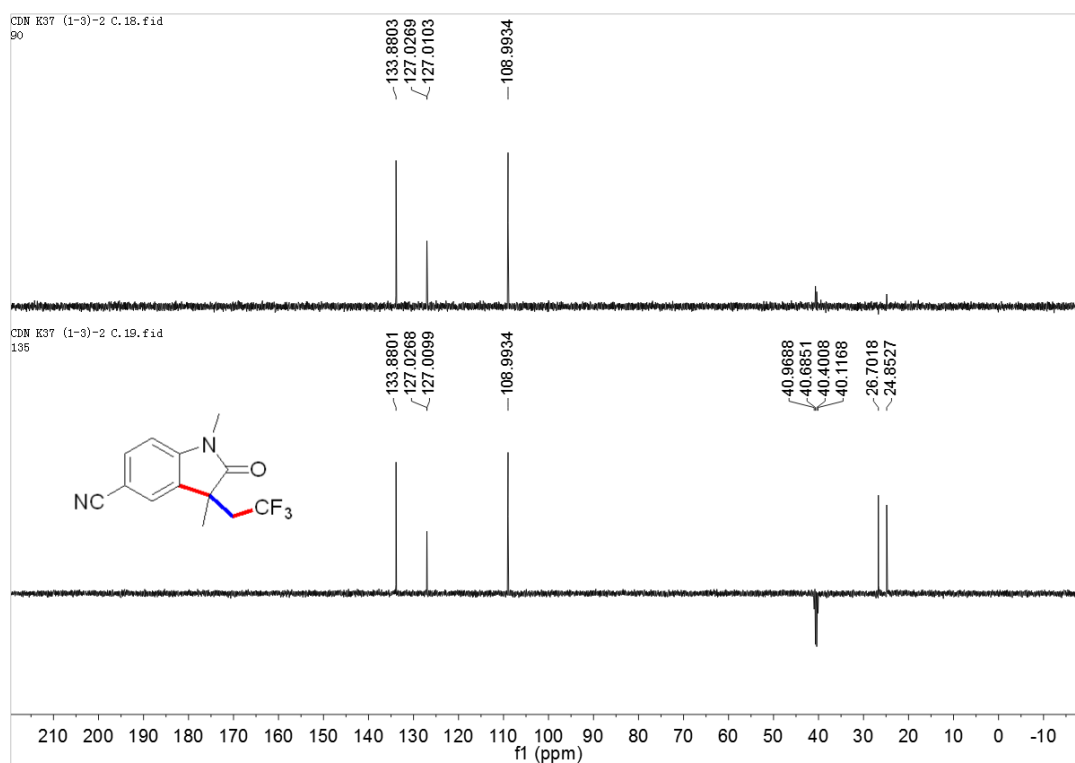
5d2, ¹H NMR



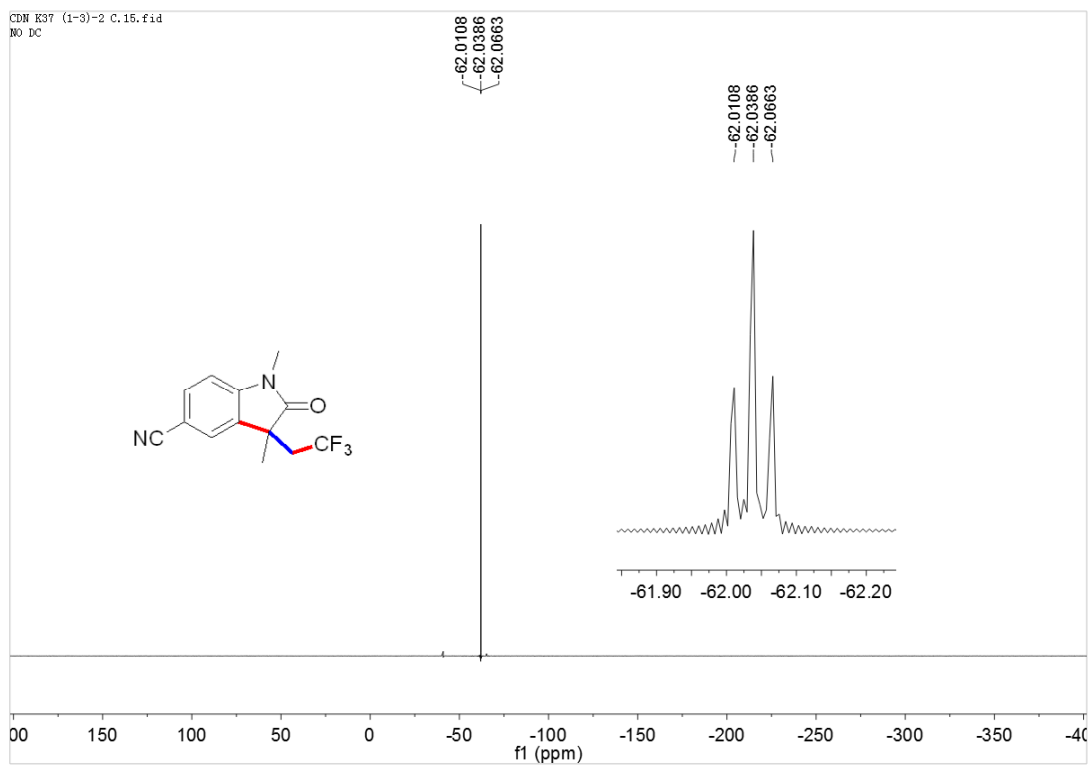
¹³C NMR



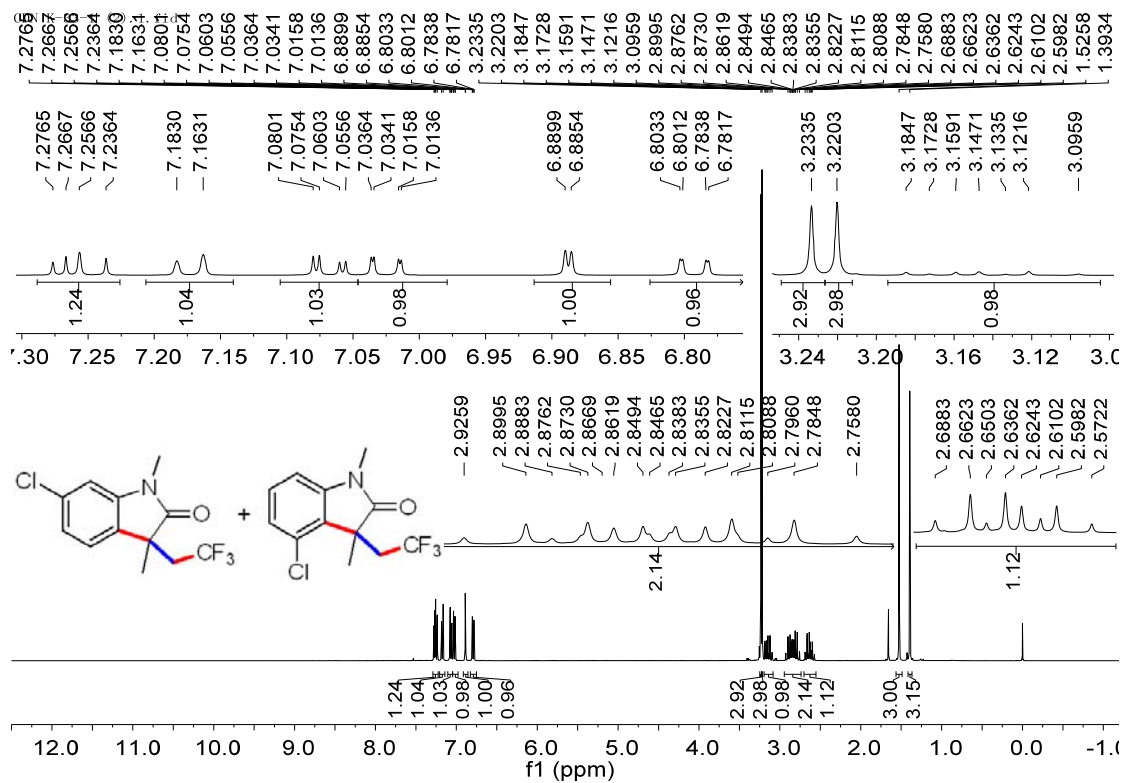
DEPT 90 and DEPT 135



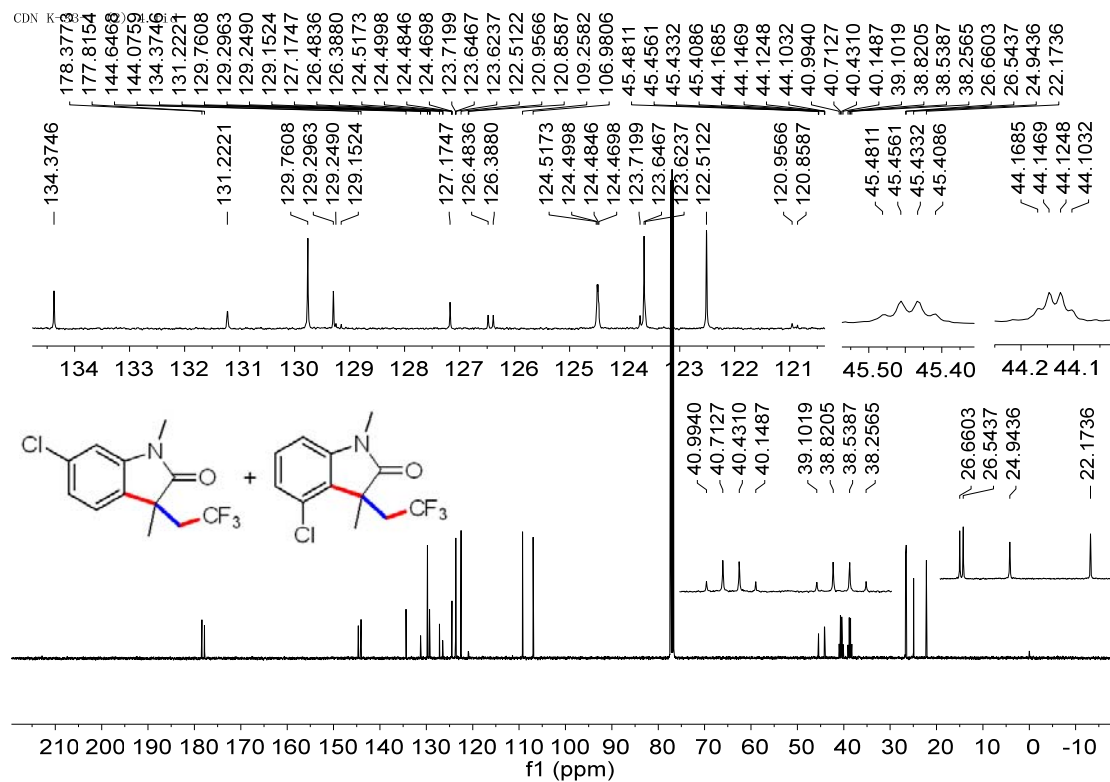
¹⁹F NMR



5e, ¹H NMR



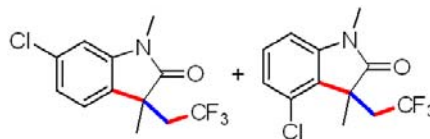
¹³C NMR



DEPT 90 and DEPT 135

CDN K-33-1 (2).5.fid
90

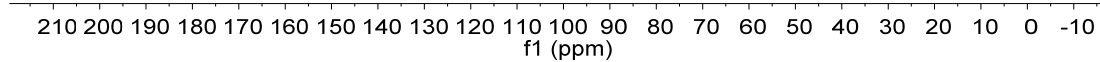
129.7612
124.5008
124.4826
123.6470
122.5116
109.2579
106.9815



CDN K-33-1 (2).6.fid
135

129.7612
124.5008
124.4832
123.6470
122.5116
109.2580
106.9814

40.9941
40.7120
40.4301
40.1488
39.1018
38.8194
38.5381
38.2567
26.6607
26.5441
24.9425
22.1738



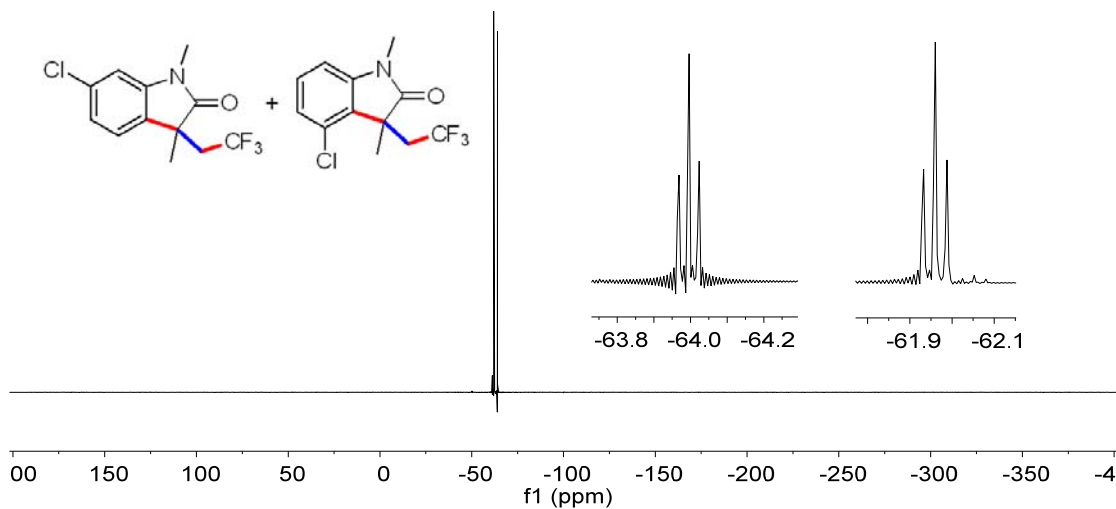
¹⁹F NMR

CDN K-33-1 (2).2.fid
F, NO DC

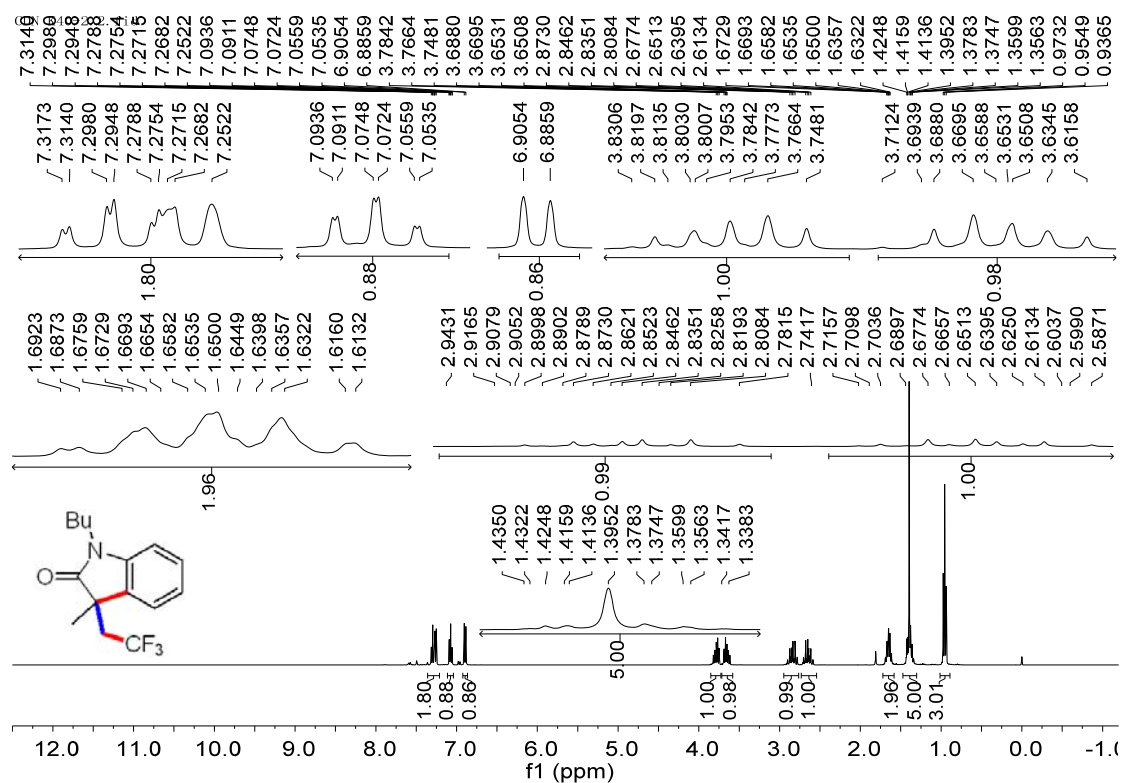
-61.9320
-61.9602
-61.9878
-63.9677
-63.9960
-64.0232

-63.9677
-63.9960
-64.0232

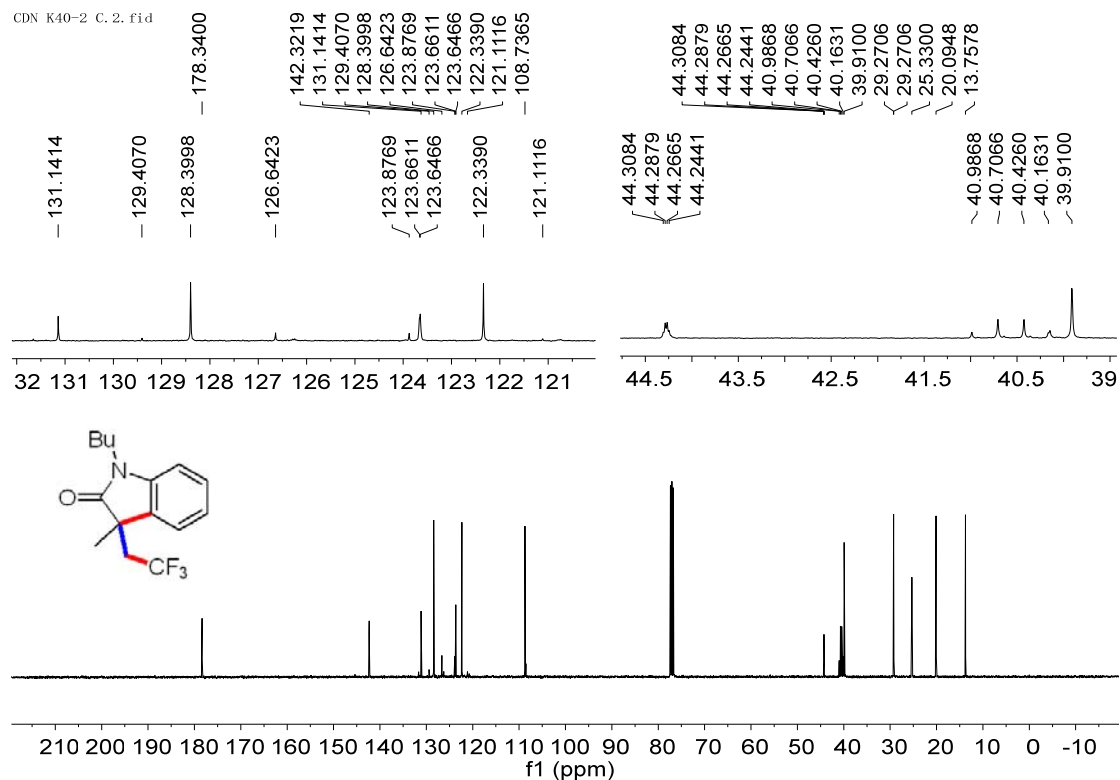
-61.9320
-61.9602
-61.9878



7a, ¹H NMR



¹³C NMR



DEPT 90 and DEPT 135

CDN K40-2 C. 3. fid
90

128.4011
123.6624
123.6475
122.3405
— 108.7384

CDN K40-2 C. 4. fid
135



128.4012
123.6635
123.6479
122.3416
— 108.7387

40.9842
40.7041
40.4238
40.1441
39.9099
29.2705
25.3333
20.0960
13.7611

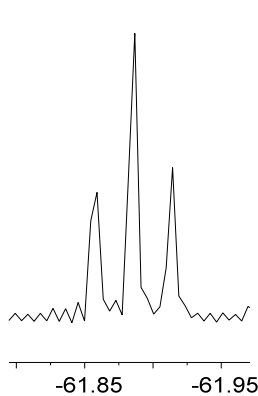
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

¹⁹F NMR

CDN K40-2. 1. fid
F, NO DC

-61.8577
-61.8860
-61.9140

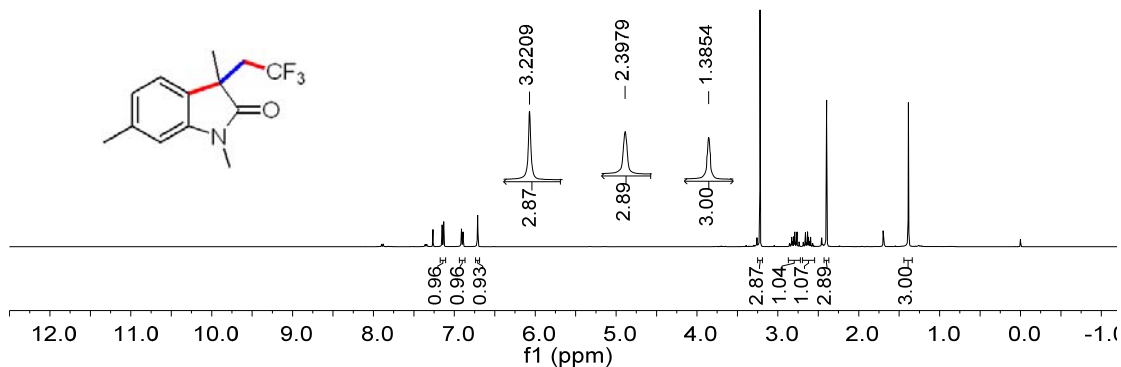
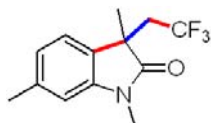
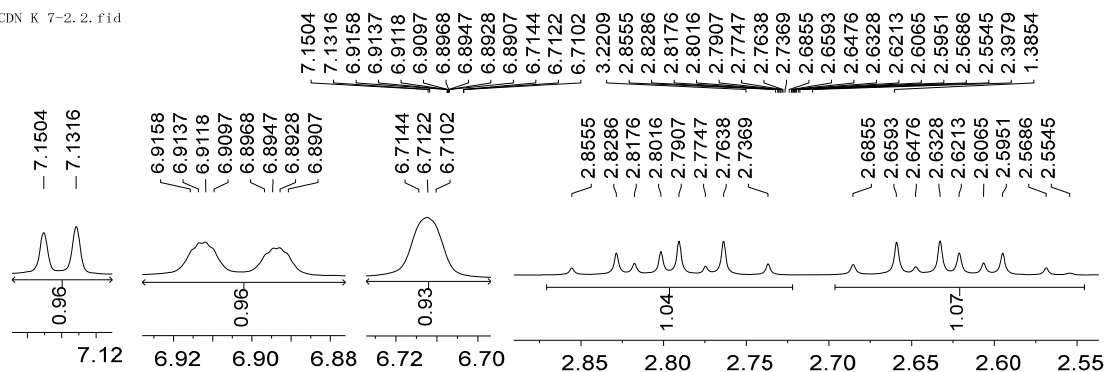
-61.8577
-61.8860
-61.9140



00 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -4
f1 (ppm)

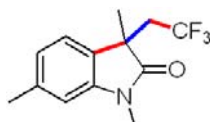
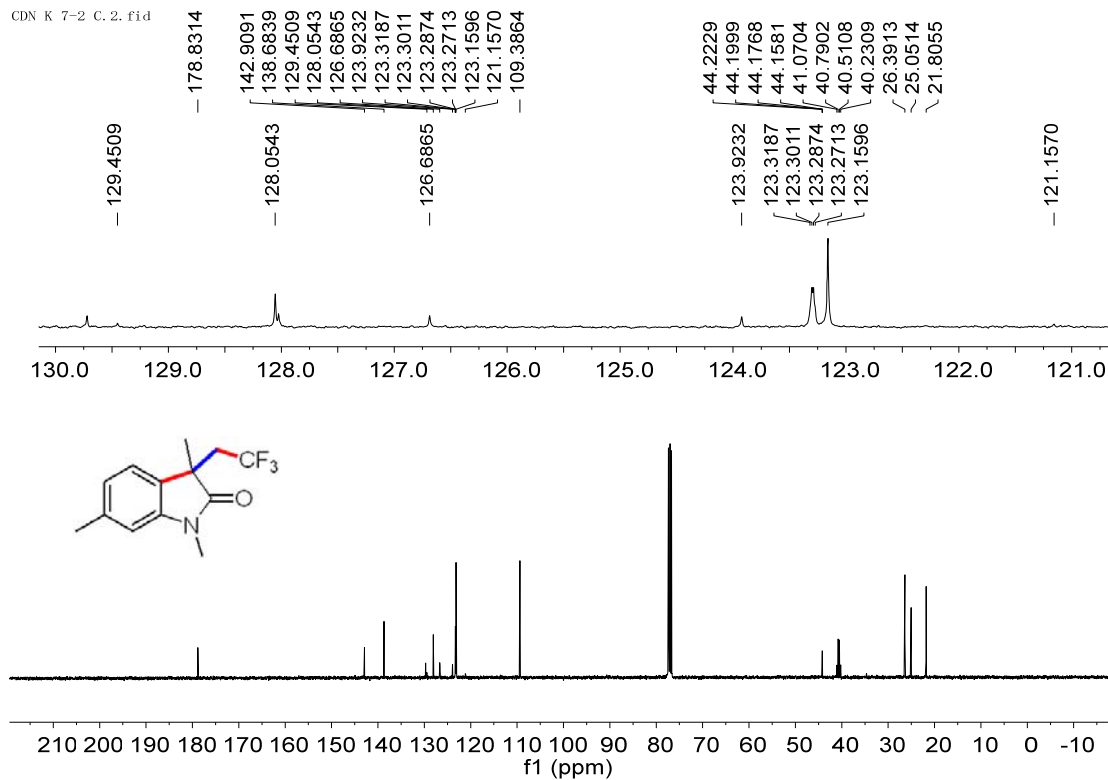
7b, ¹H NMR

CDN K 7-2.2. f1d



¹³C NMR

CDN K 7-2. C.2. f1d

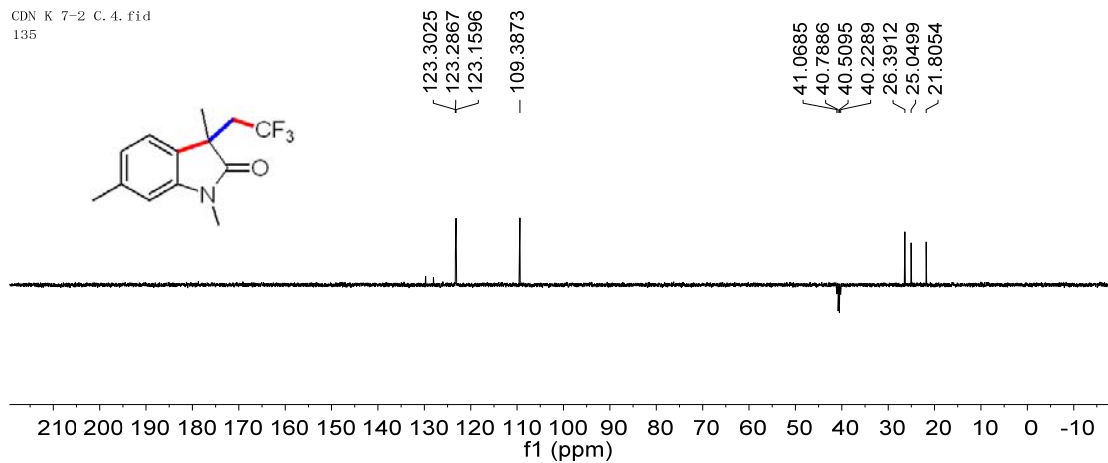


DEPT 90 and DEPT 135

CDN K 7-2 C. 3. fid
90

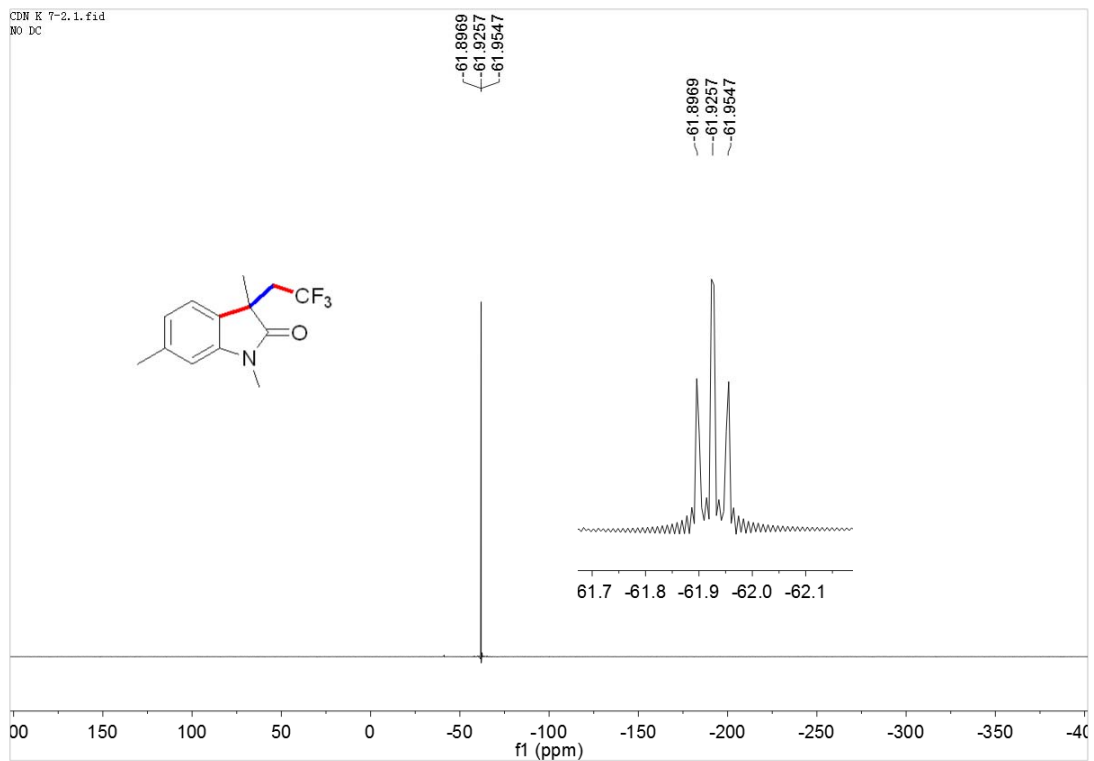


CDN K 7-2 C. 4. fid
135

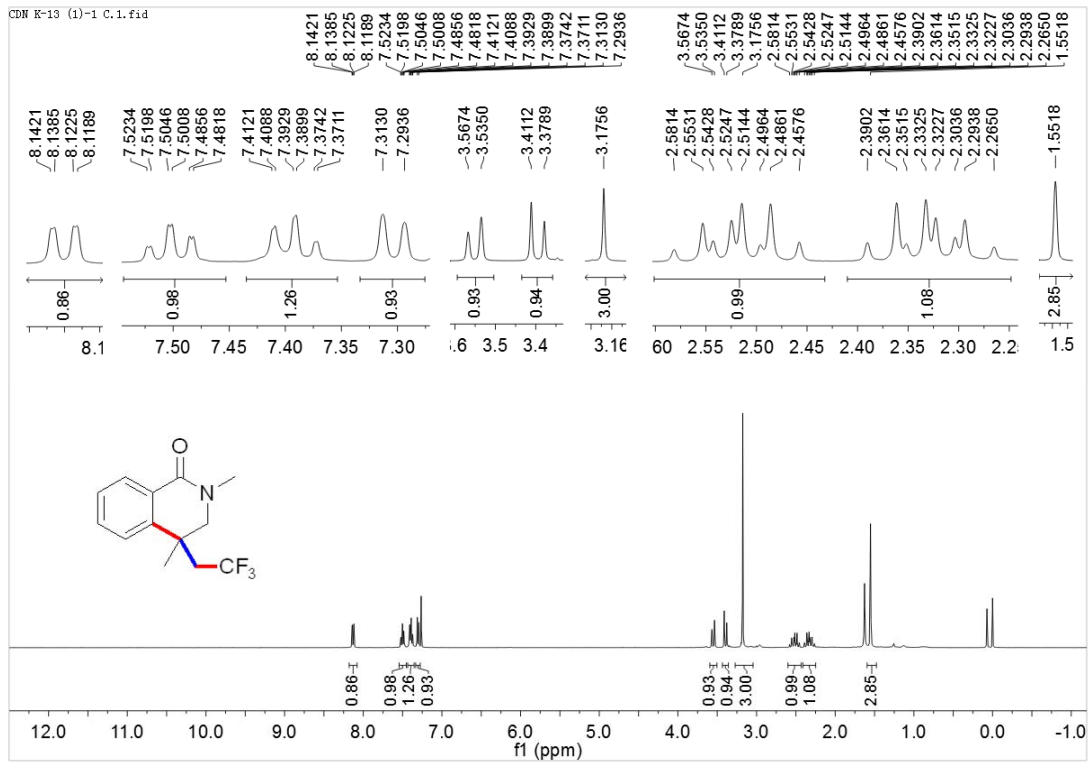


¹⁹F NMR

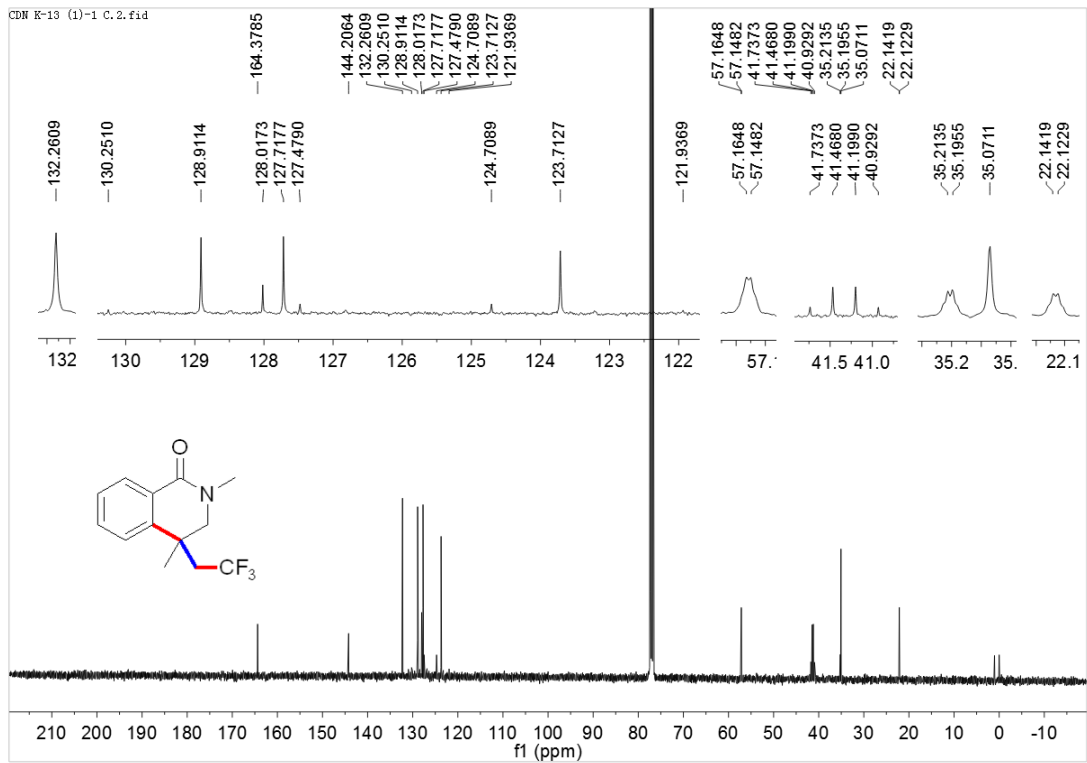
CDN K 7-2.1.fid
NO DC



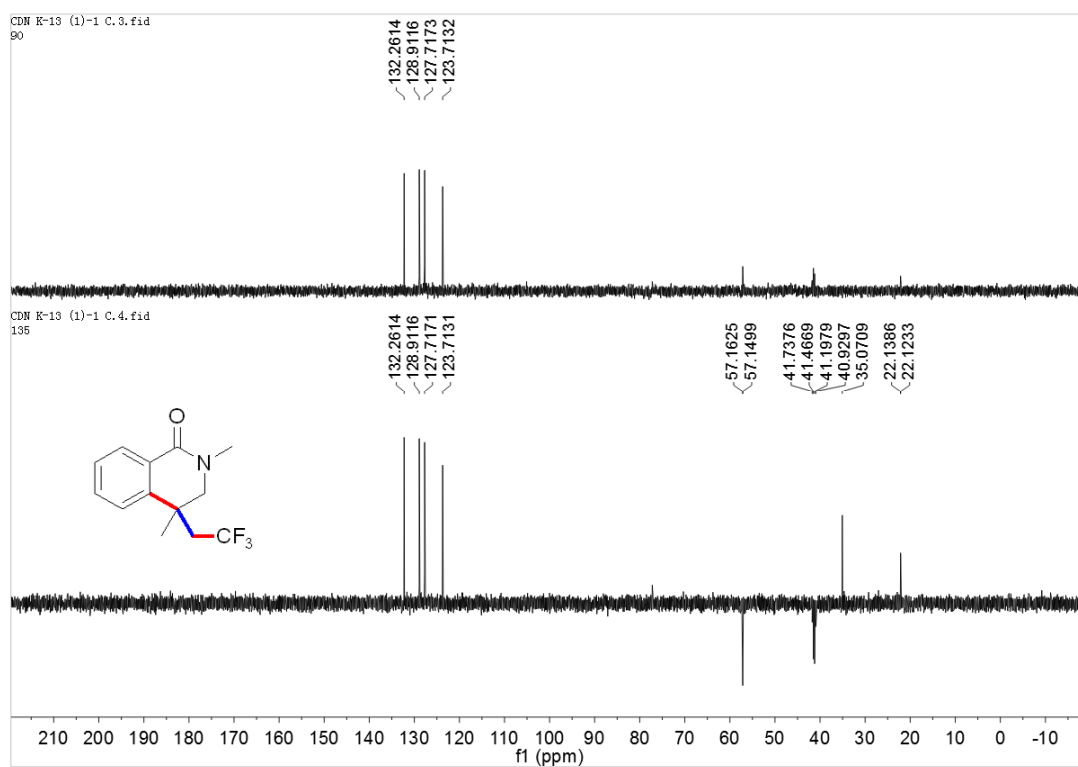
9a, ¹H NMR



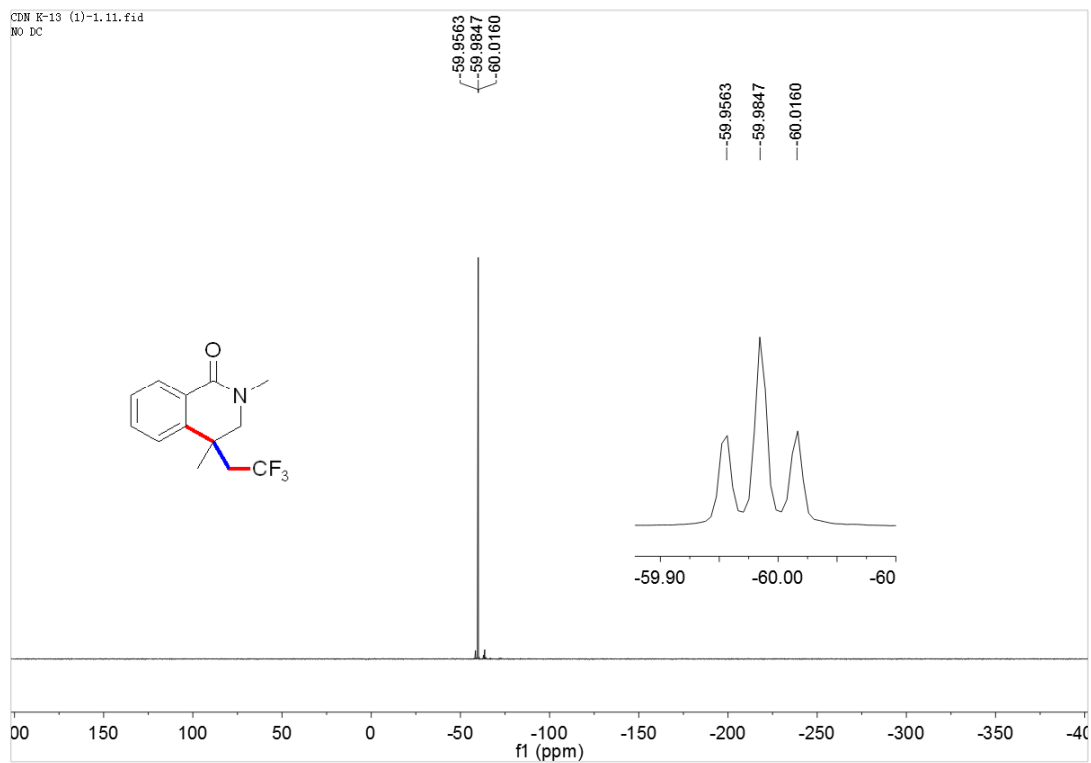
¹³C NMR



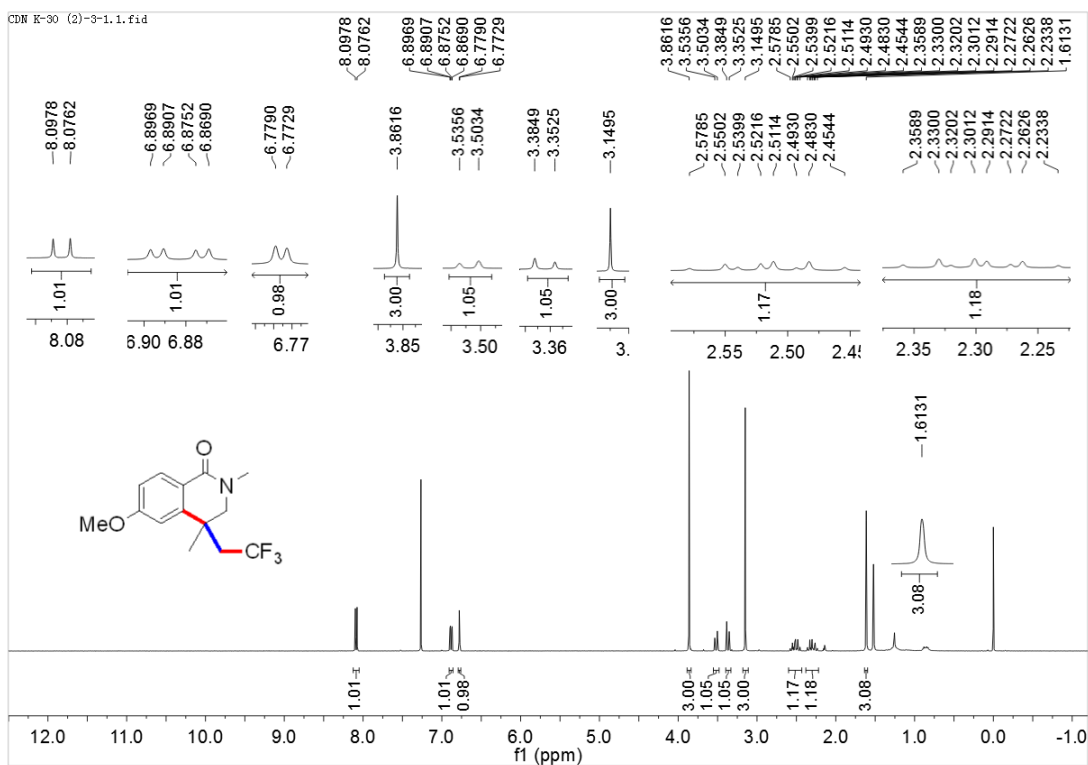
DEPT 90 and DEPT 135



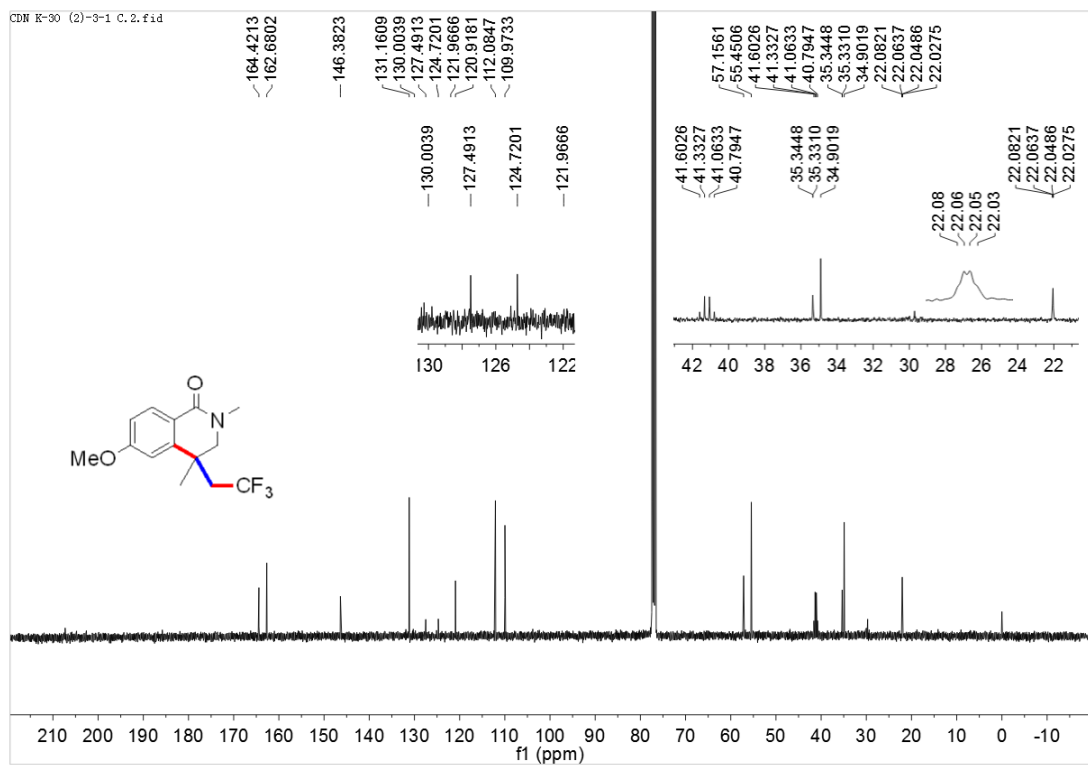
¹⁹F NMR



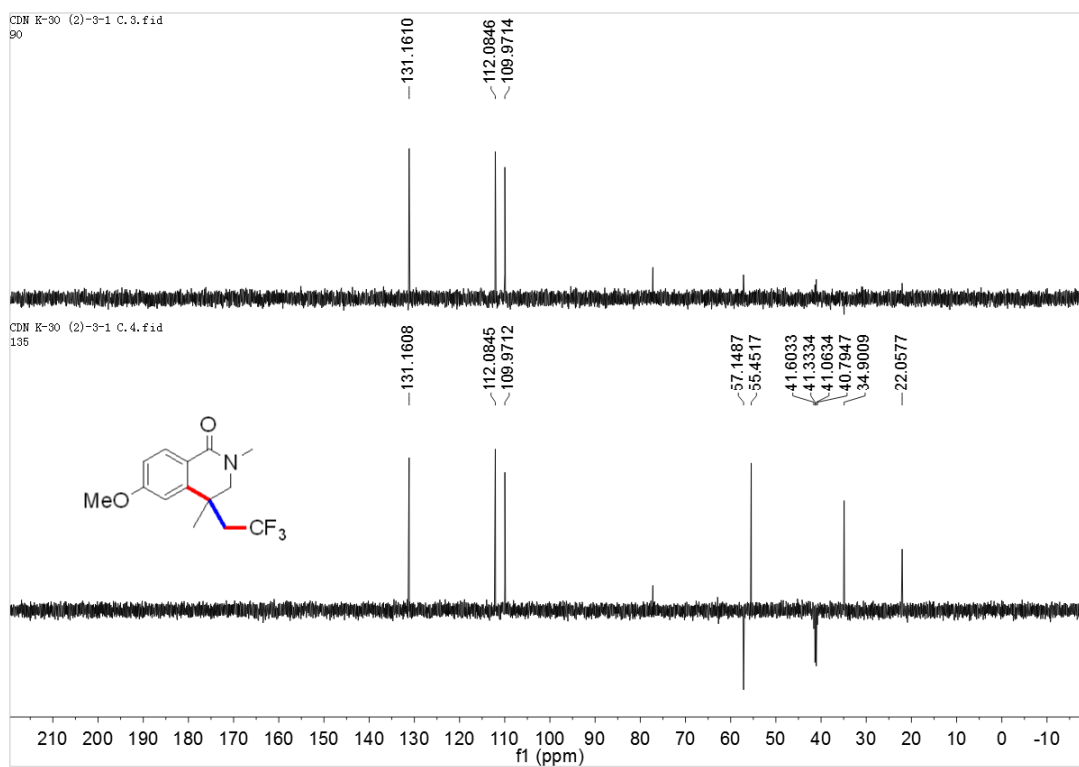
9b, ¹H NMR



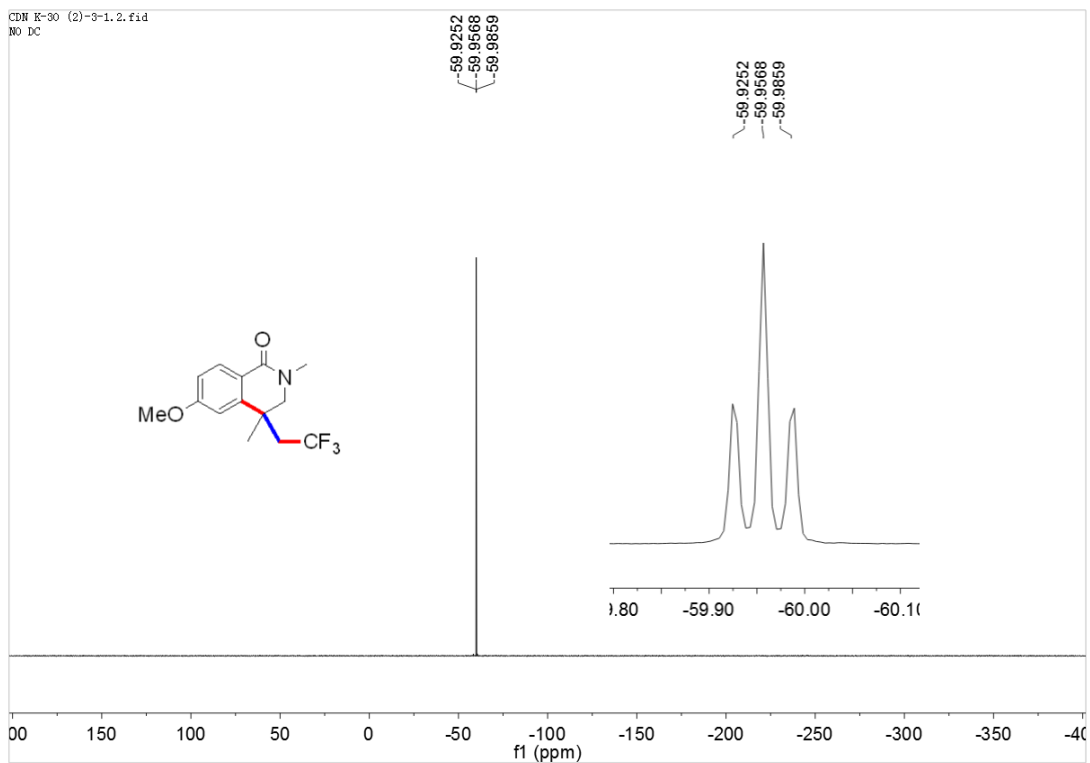
¹³C NMR



DEPT 90 and DEPT 135

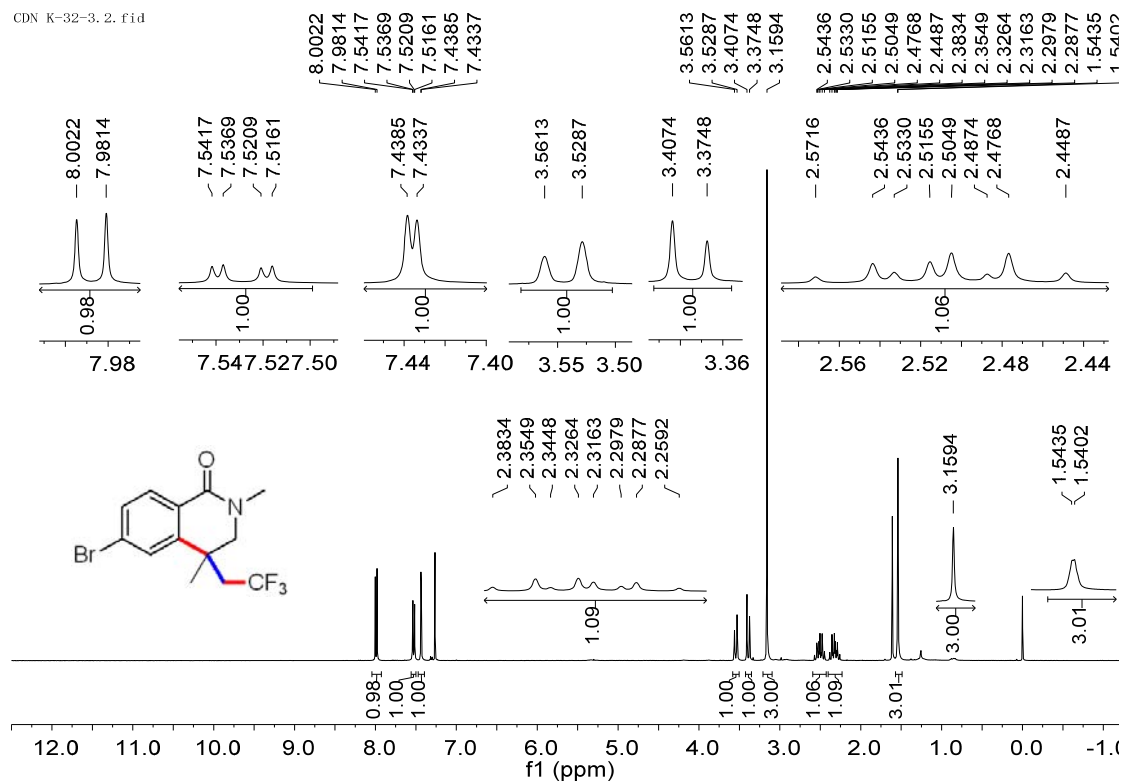


¹⁹F NMR



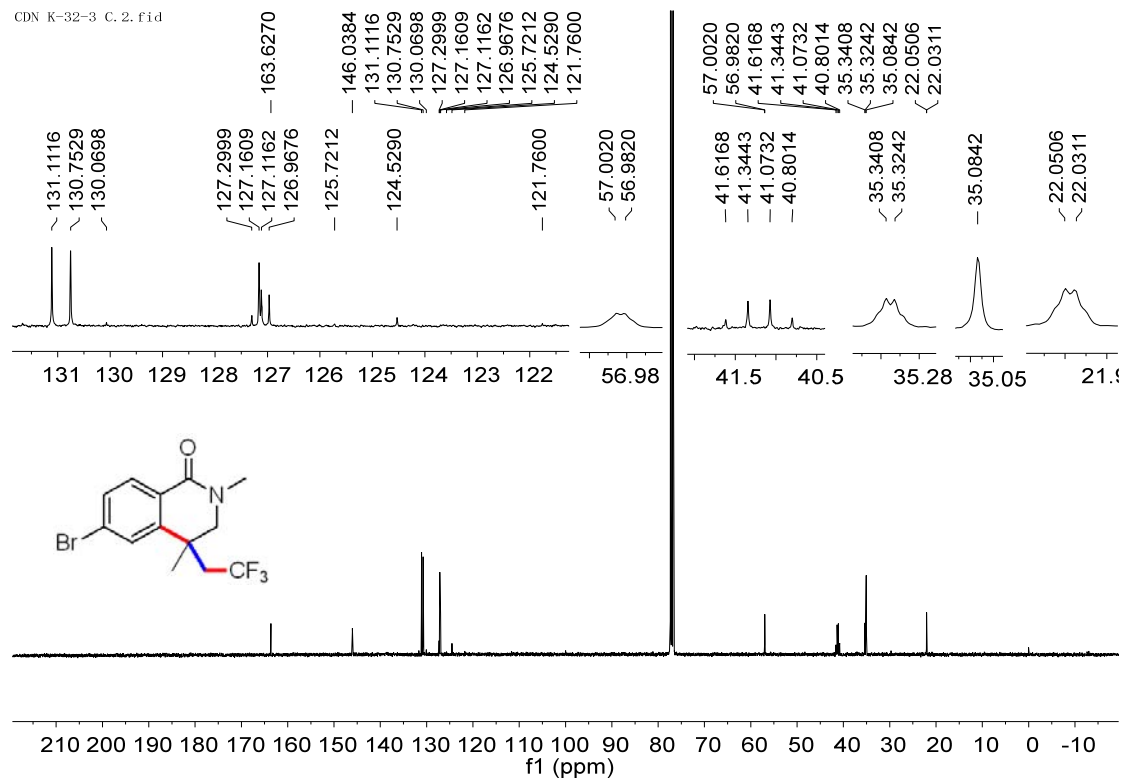
9c, ¹H NMR

CDN K-32-3. 2. fid

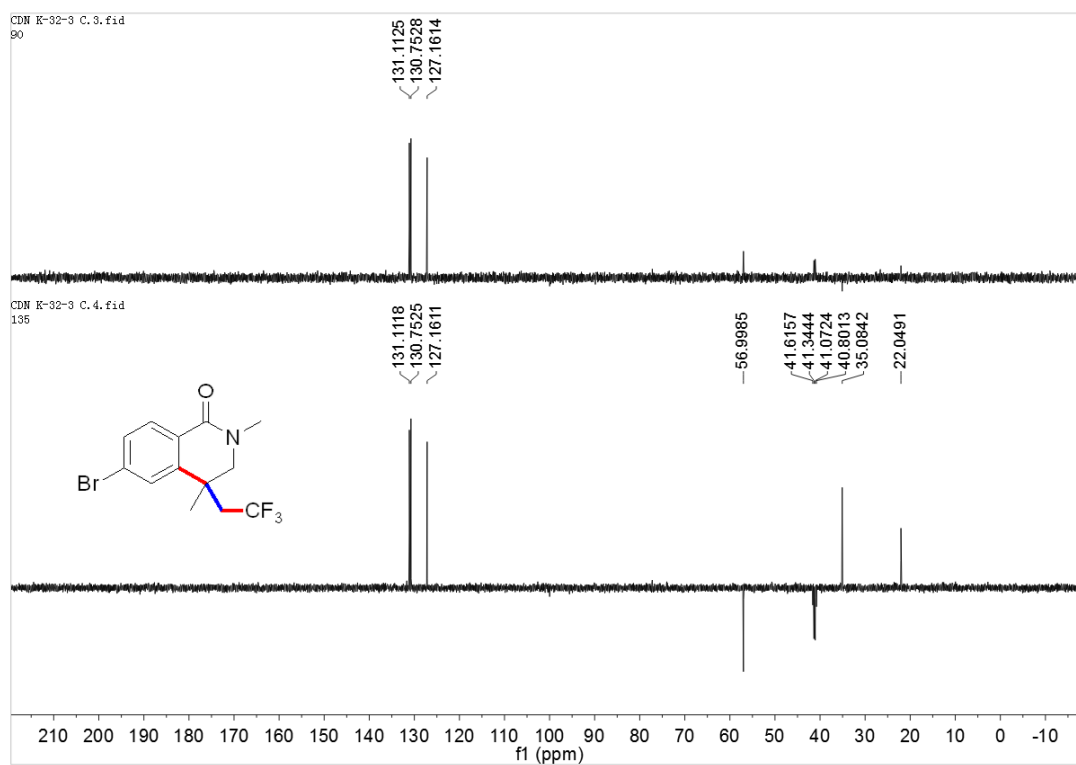


¹³C NMR

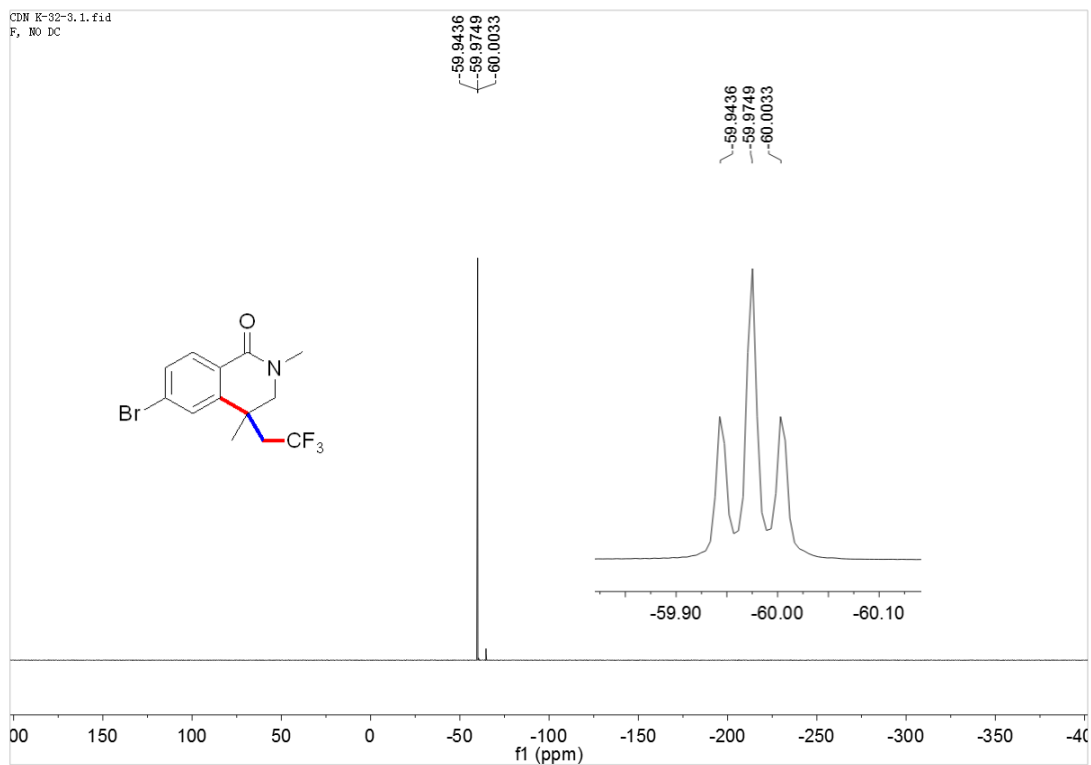
CDN K-32-3 C. 2. fid



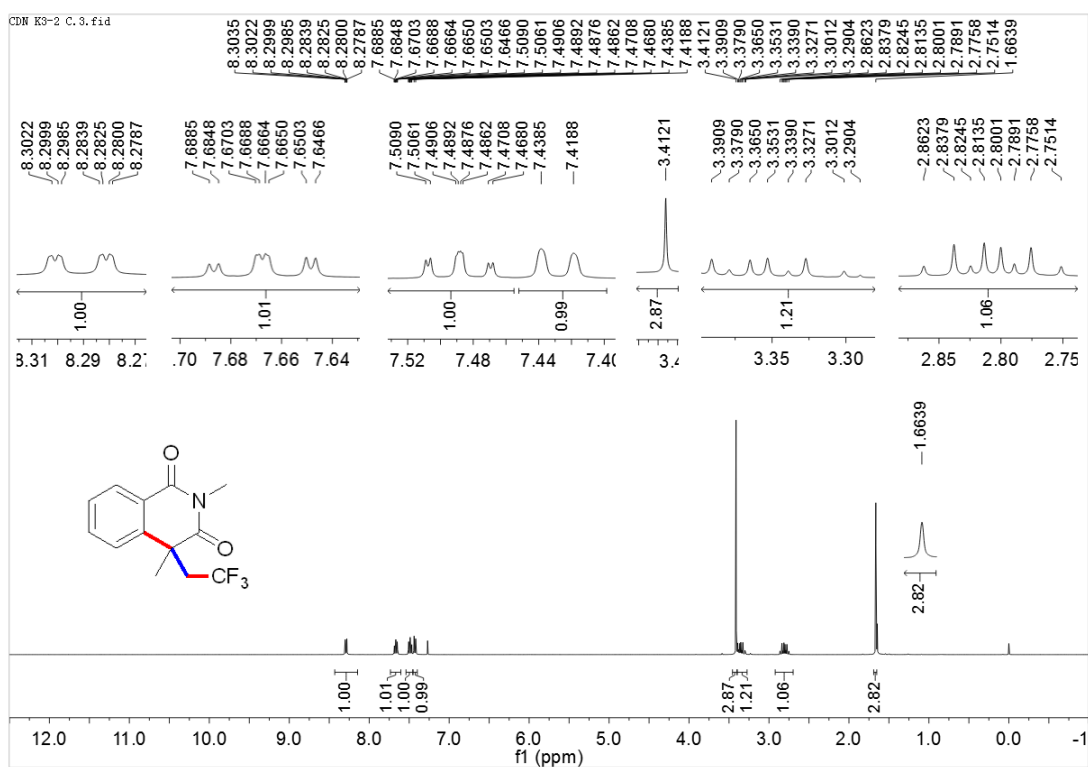
DEPT 90 and DEPT 135



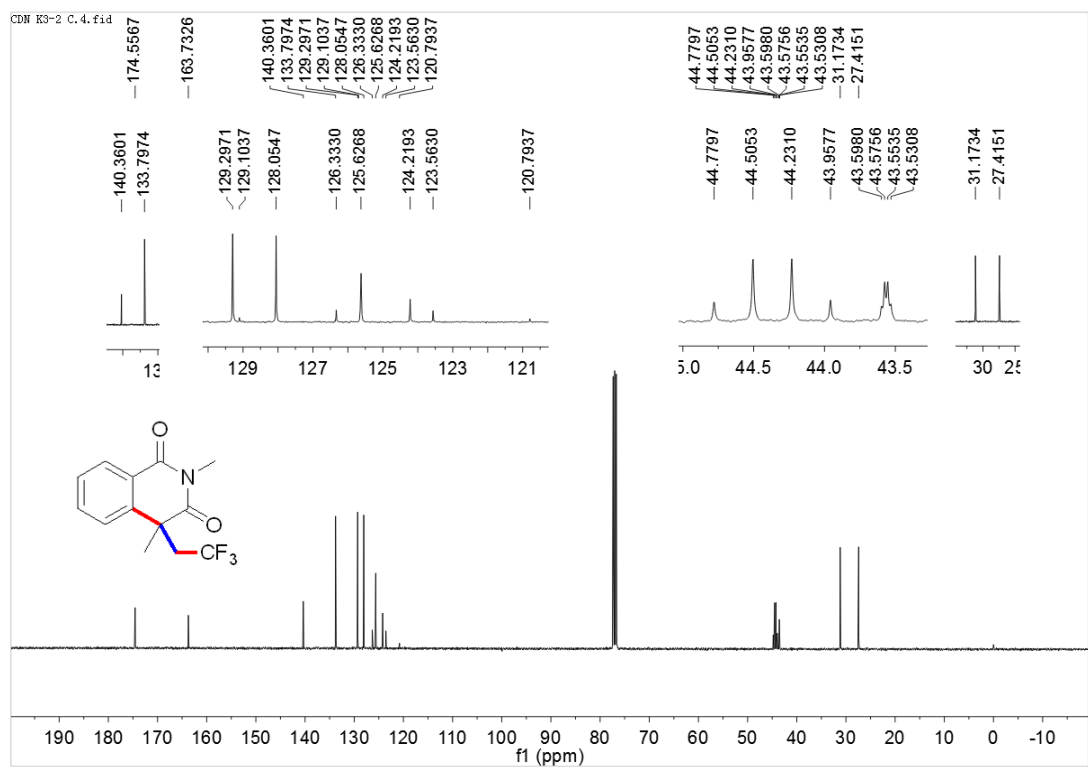
¹⁹F NMR



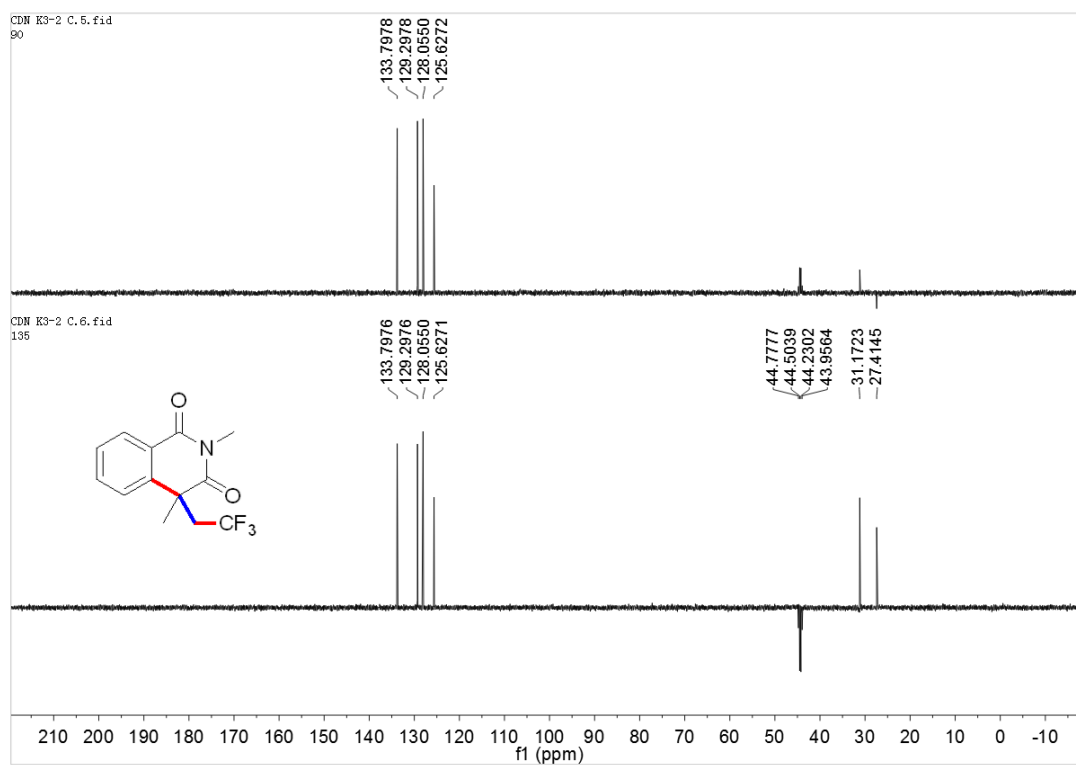
9d, ¹H NMR



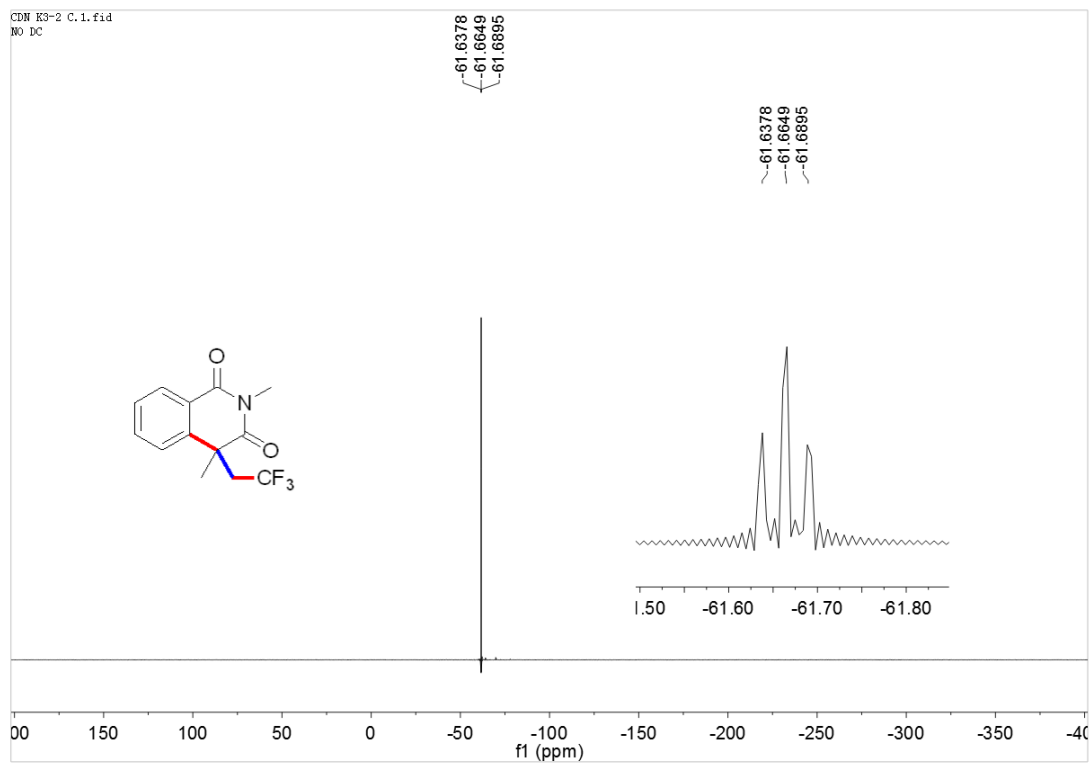
¹³C NMR



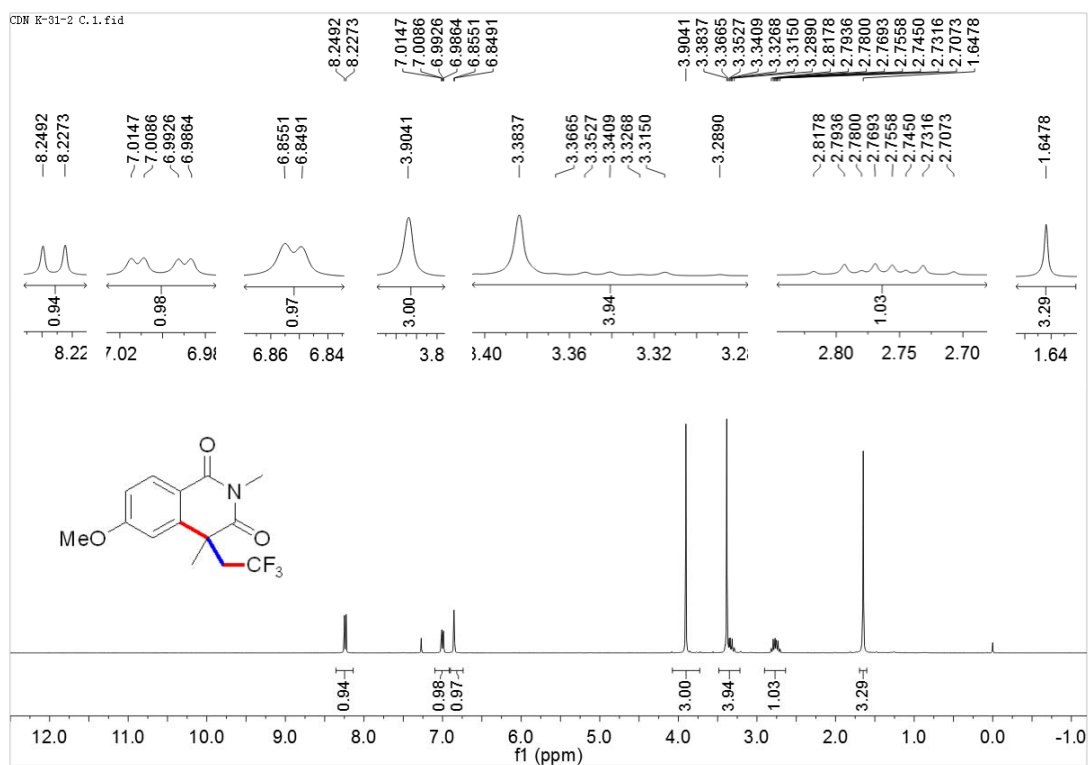
DEPT 90 and DEPT 135



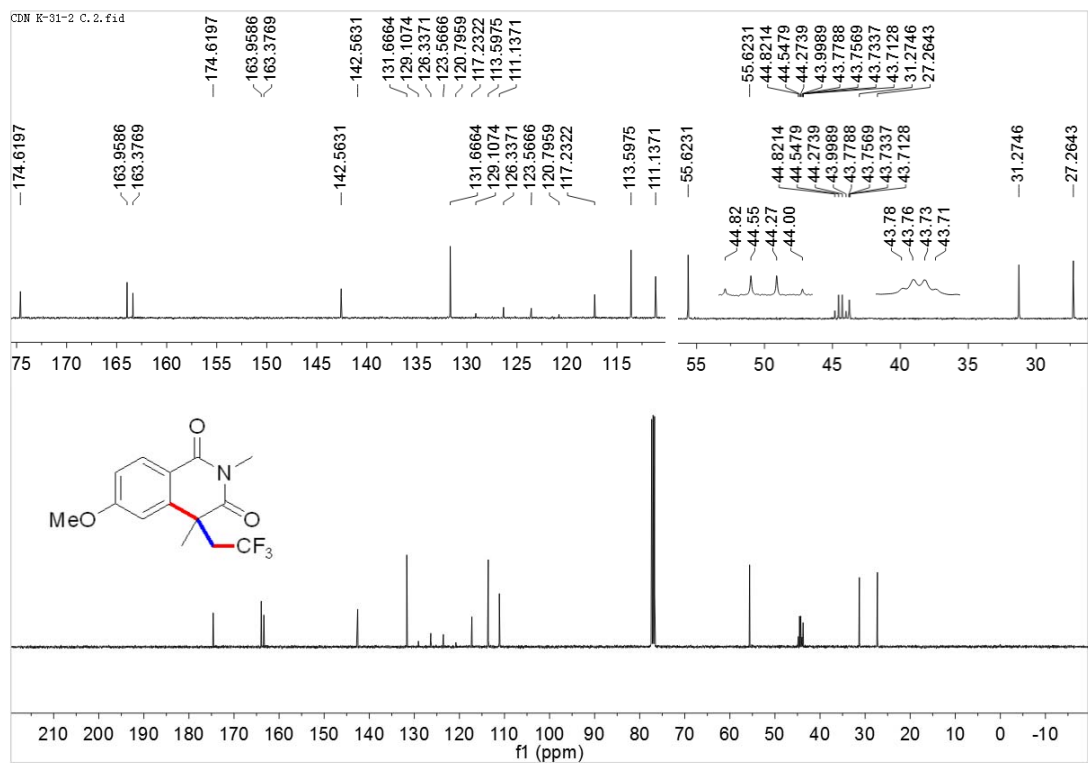
¹⁹F NMR



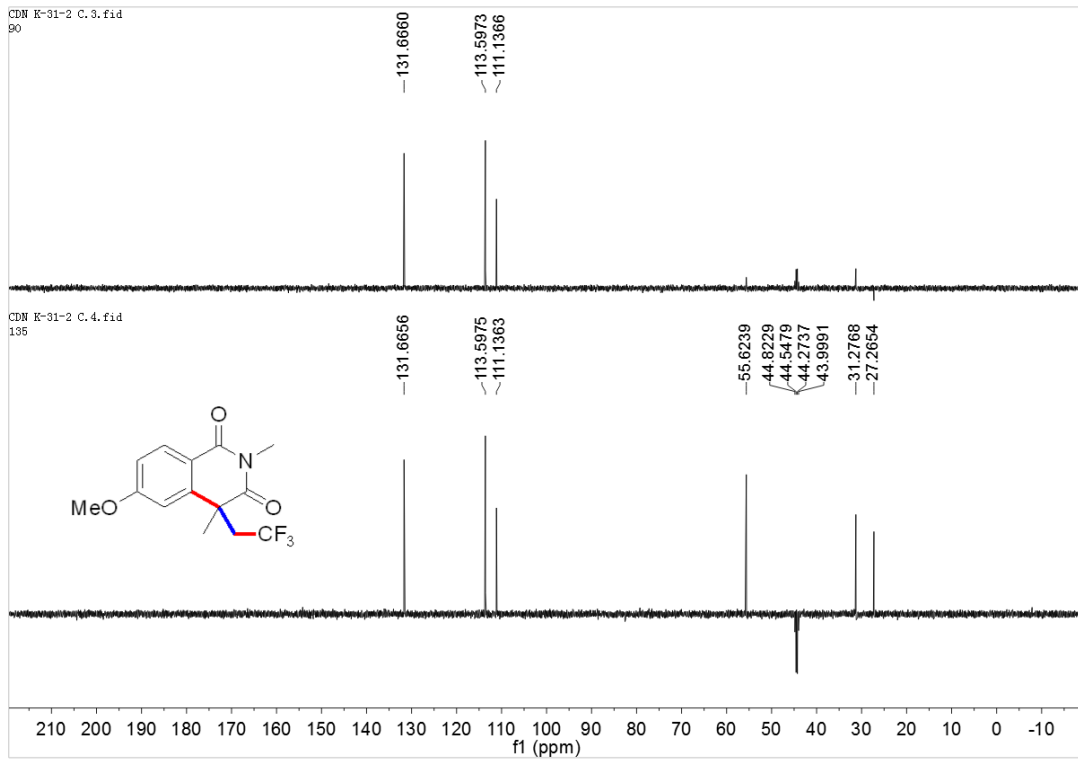
9e, ¹H NMR



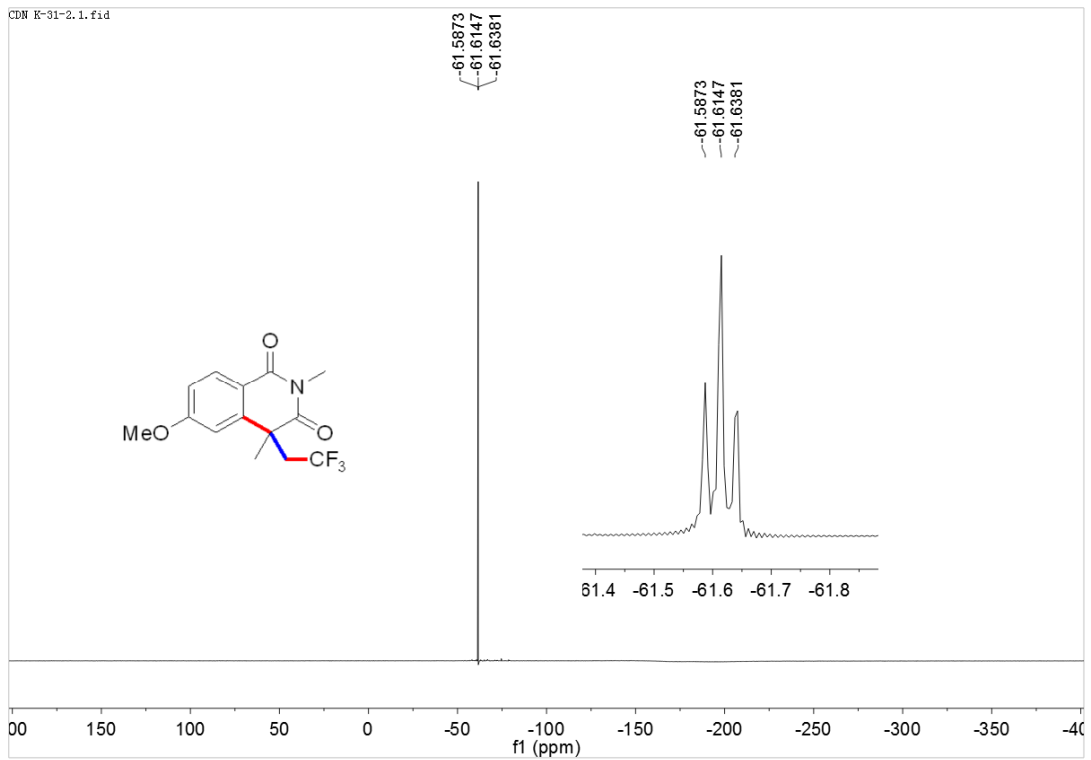
¹³C NMR



DEPT 90 and DEPT 135

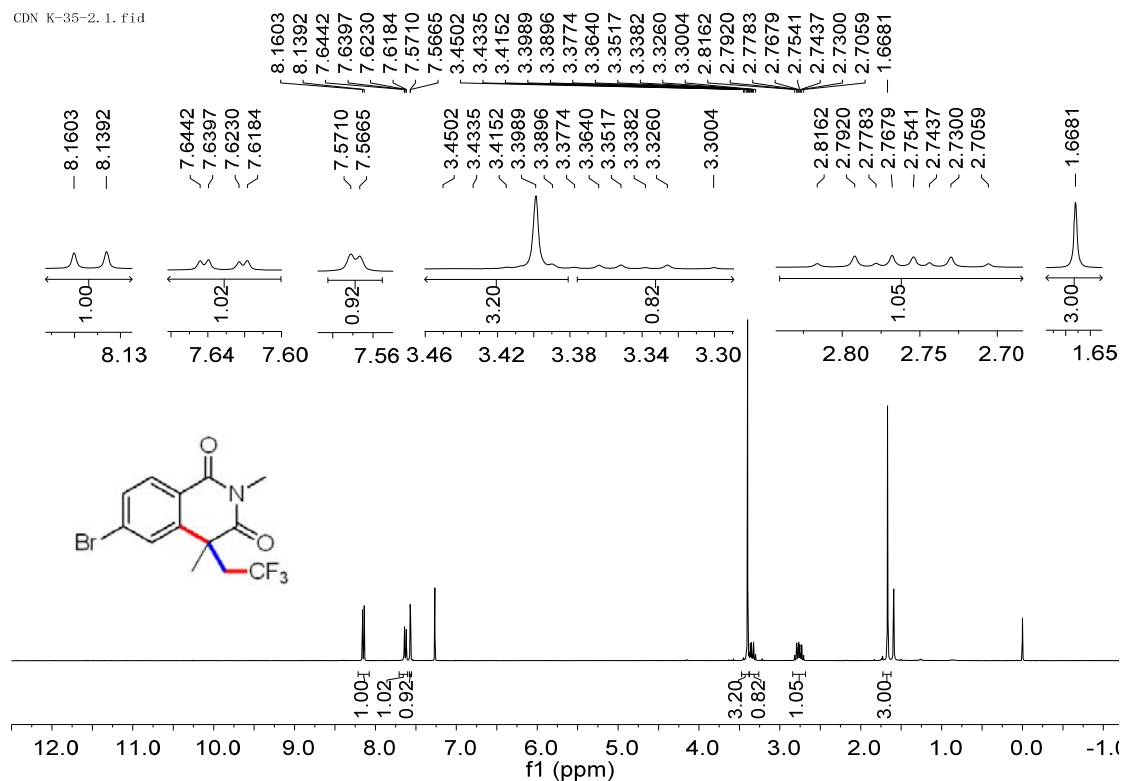


¹⁹F NMR



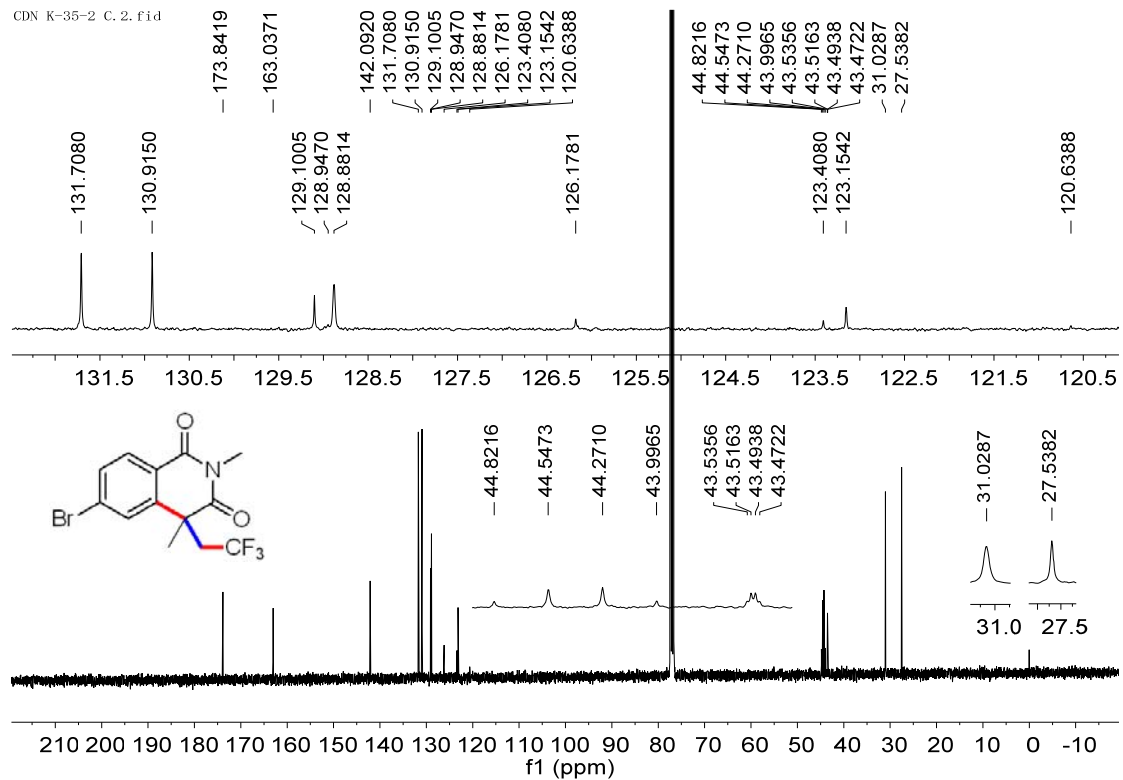
9f, ¹H NMR

CDN K-35-2. 1. fid

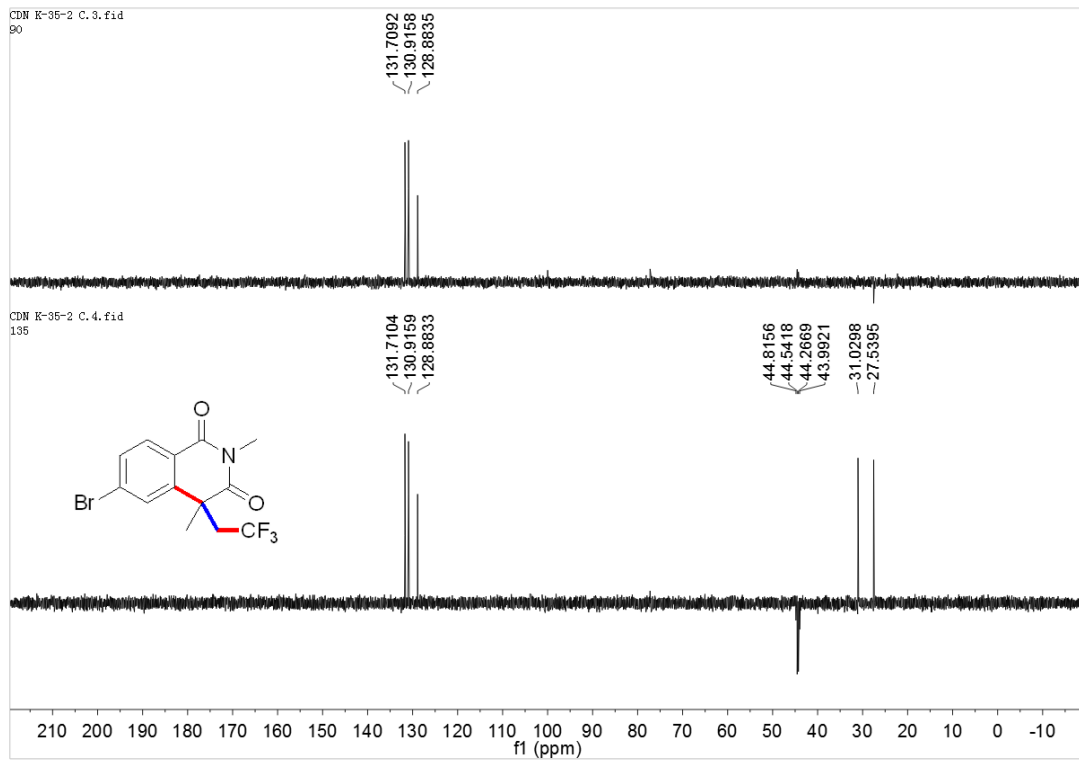


¹³C NMR

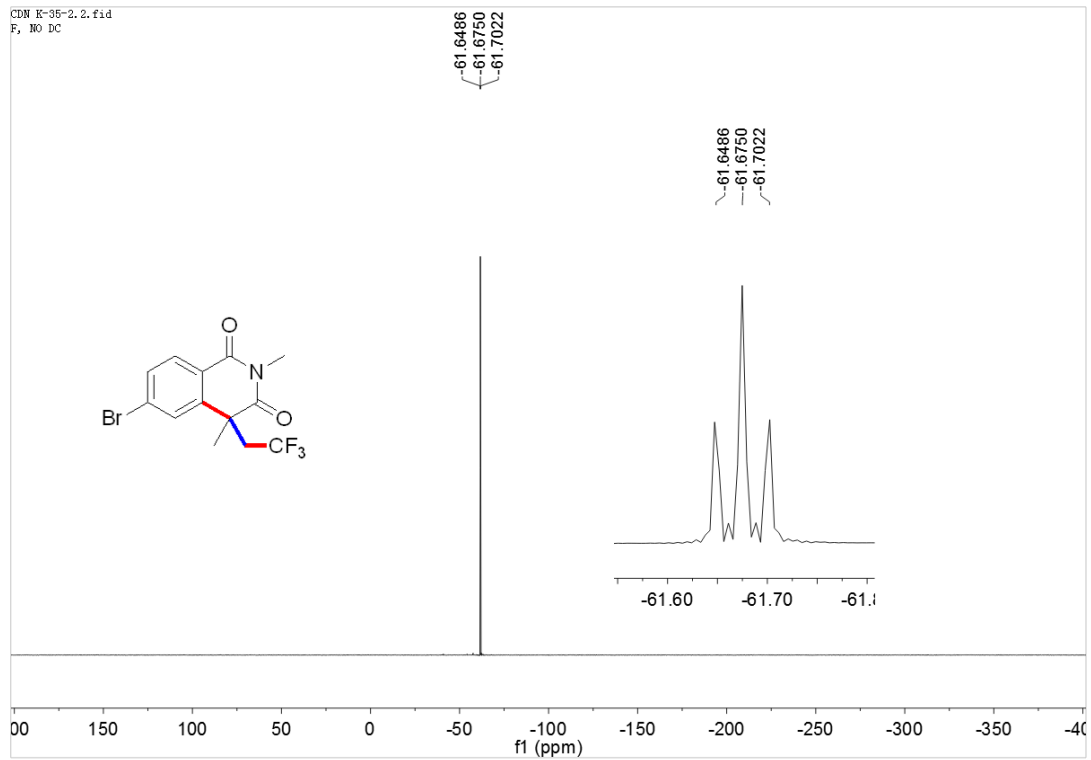
CDN K-35-2 C. 2. fid



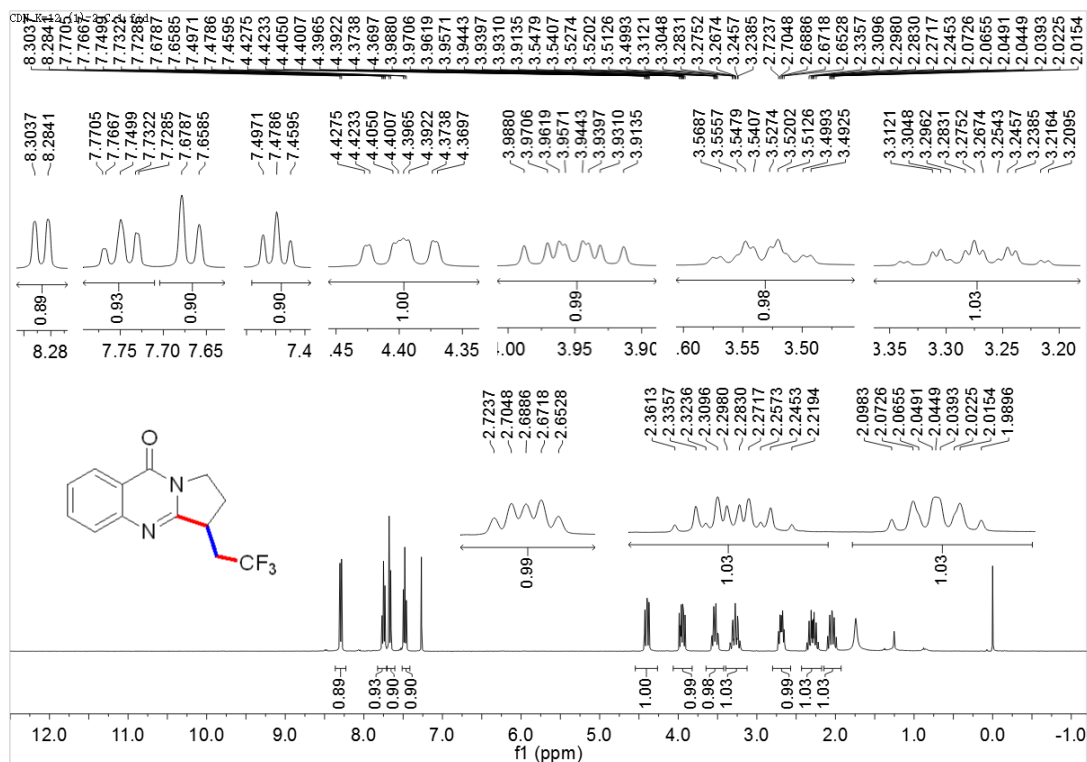
DEPT 90 and DEPT 135



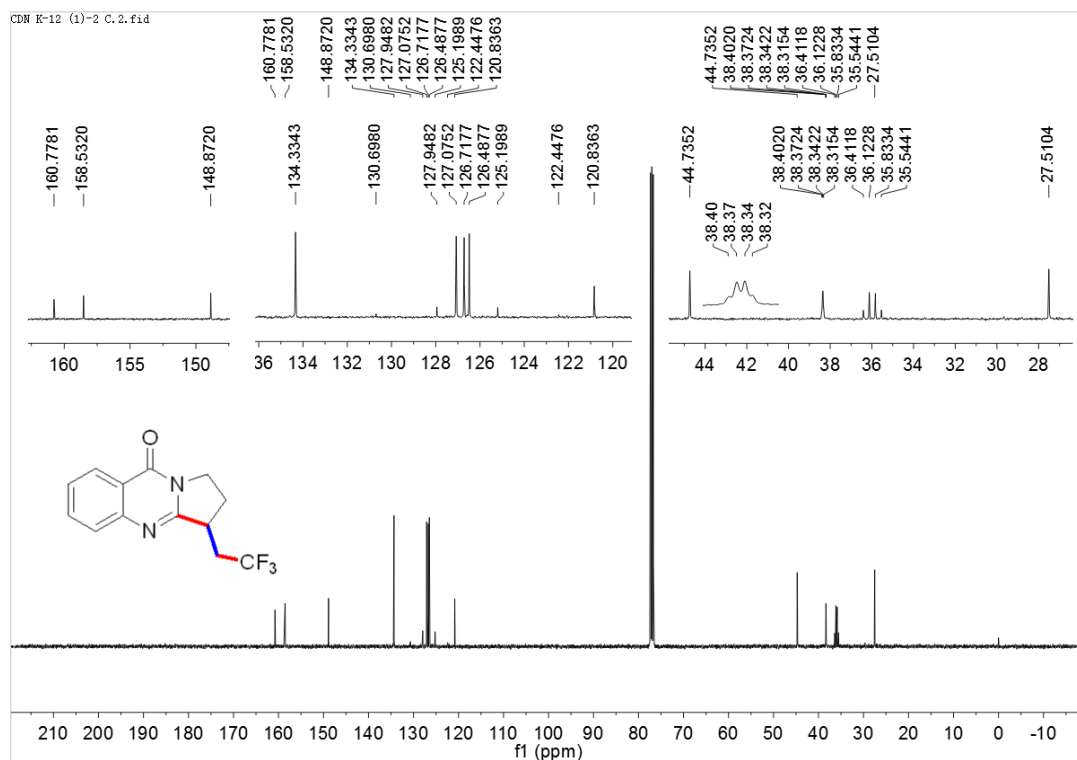
¹⁹F NMR



11, ¹H NMR

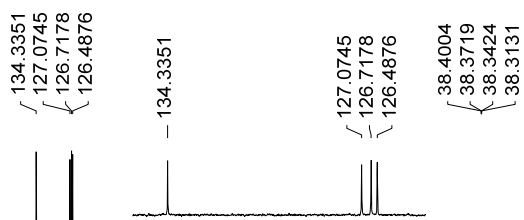


¹³C NMR

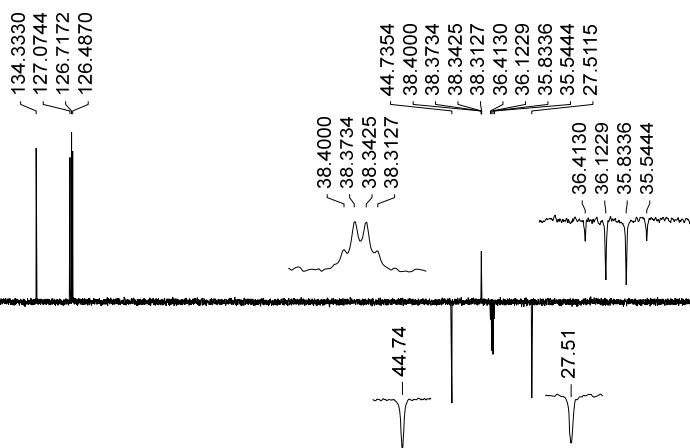
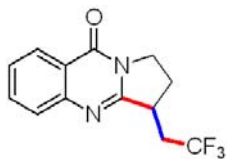


DEPT 90 and DEPT 135

CDN K-12 (1)-2 C. 3. fid
90



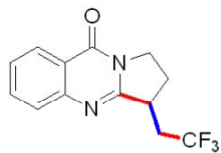
CDN K-12 (1)-2 C. 4. fid
135



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)

¹⁹F NMR

CDN K-12 (1)-2.2. fid



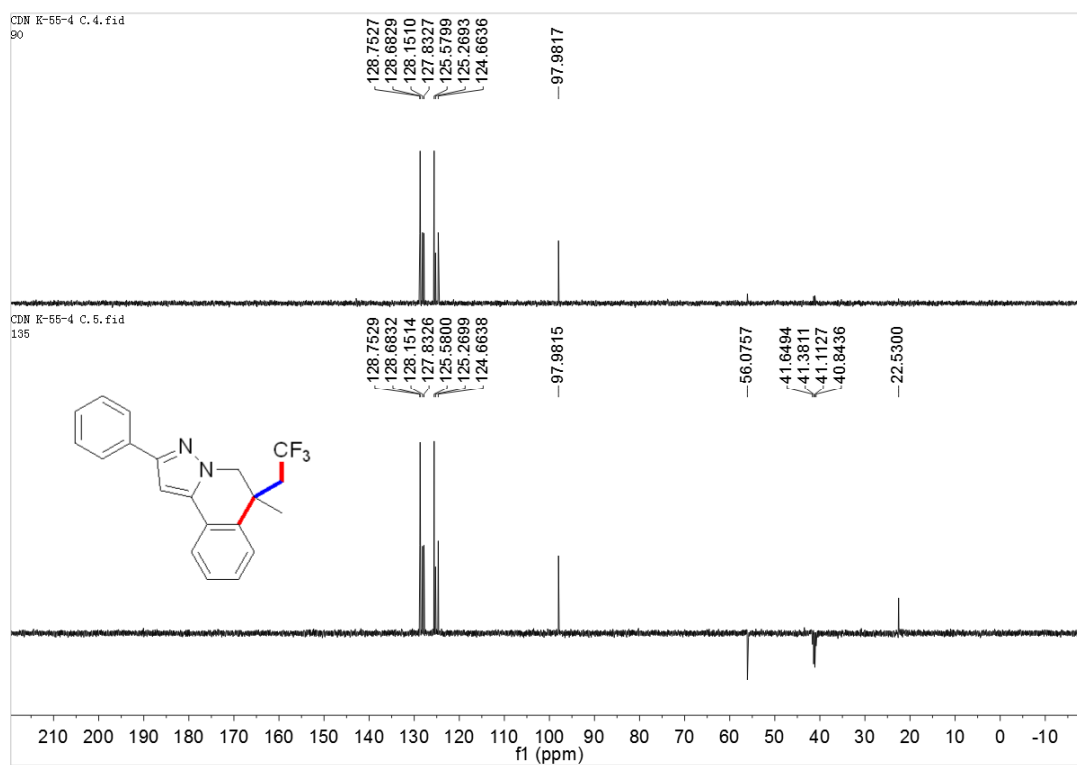
64.6548
64.6626
64.7108

64.6548
64.6626
64.7108

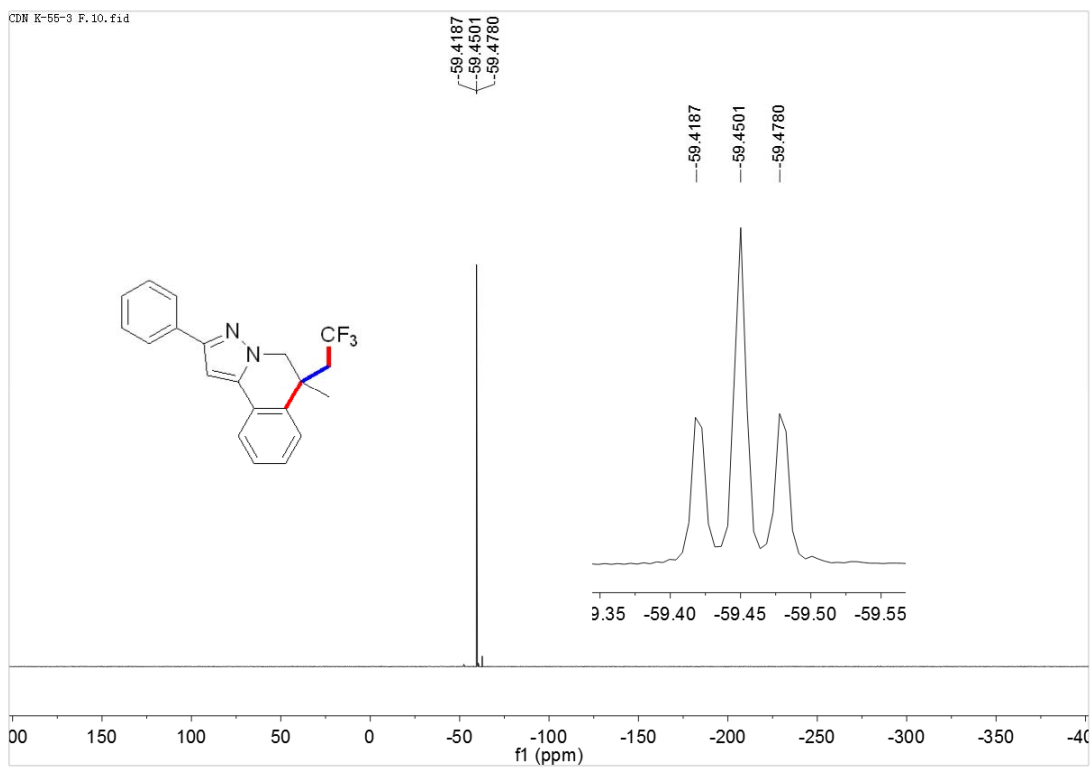
64.55 -64.65 -64.75 -64.1

00 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400
f1 (ppm)

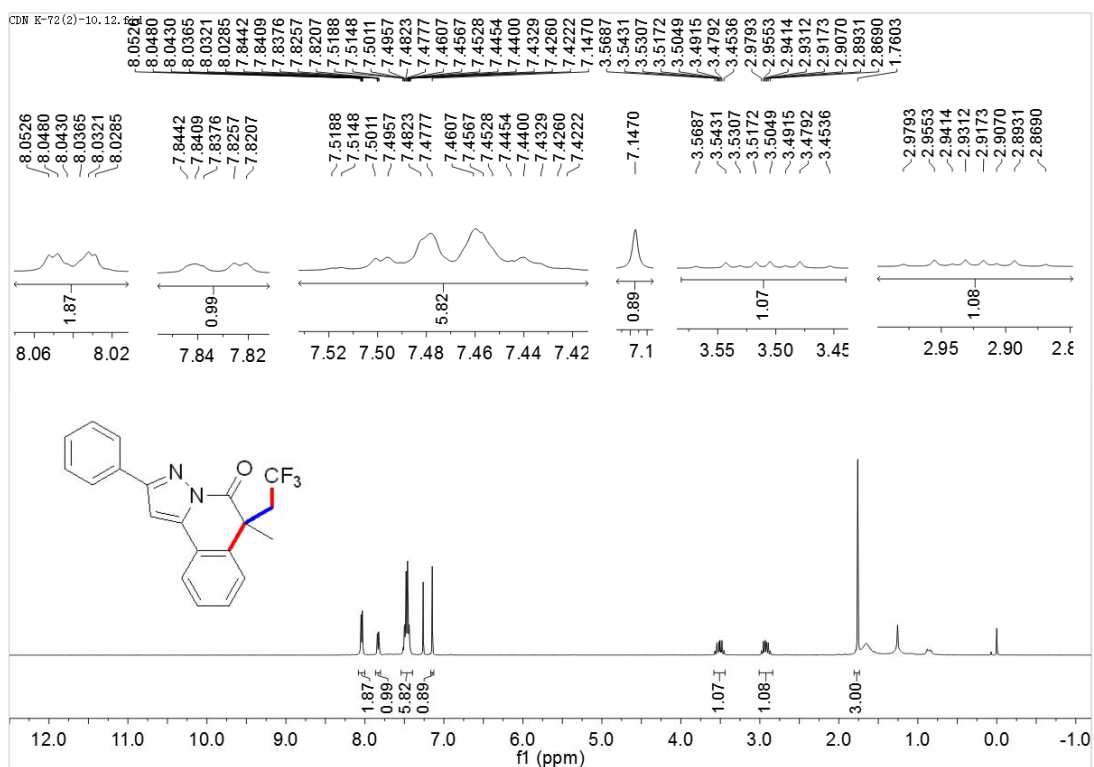
DEPT 90 and DEPT 135



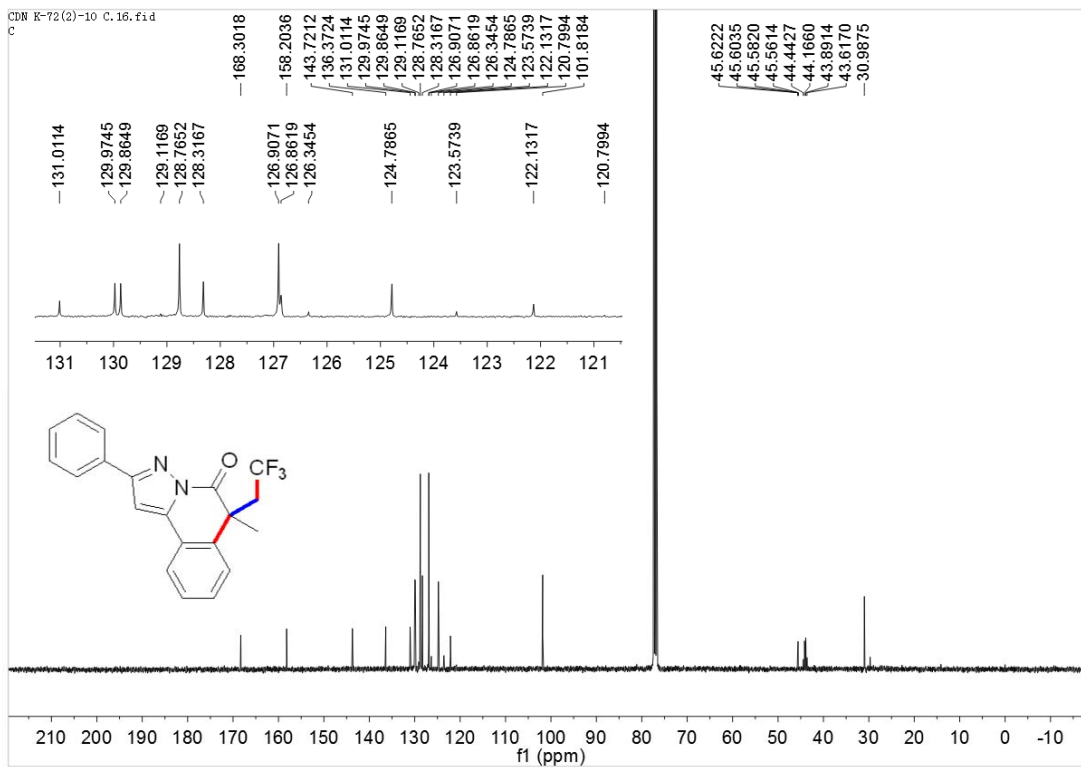
¹⁹F NMR



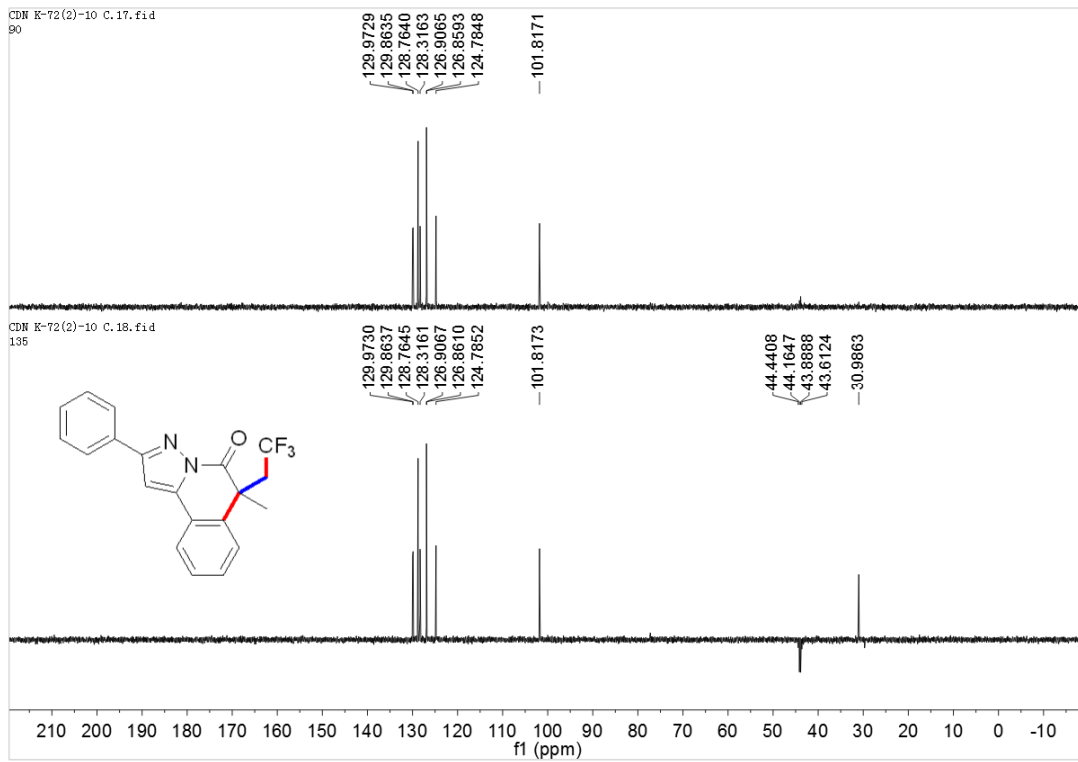
13b, ¹H NMR



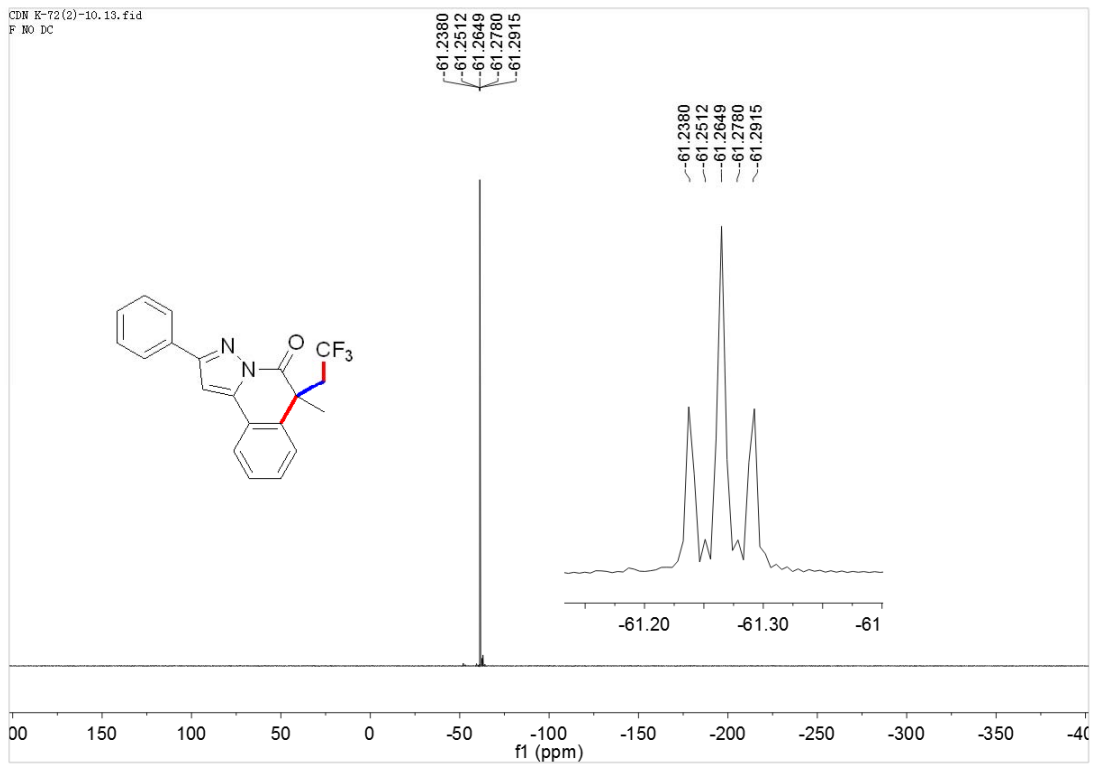
¹³C NMR



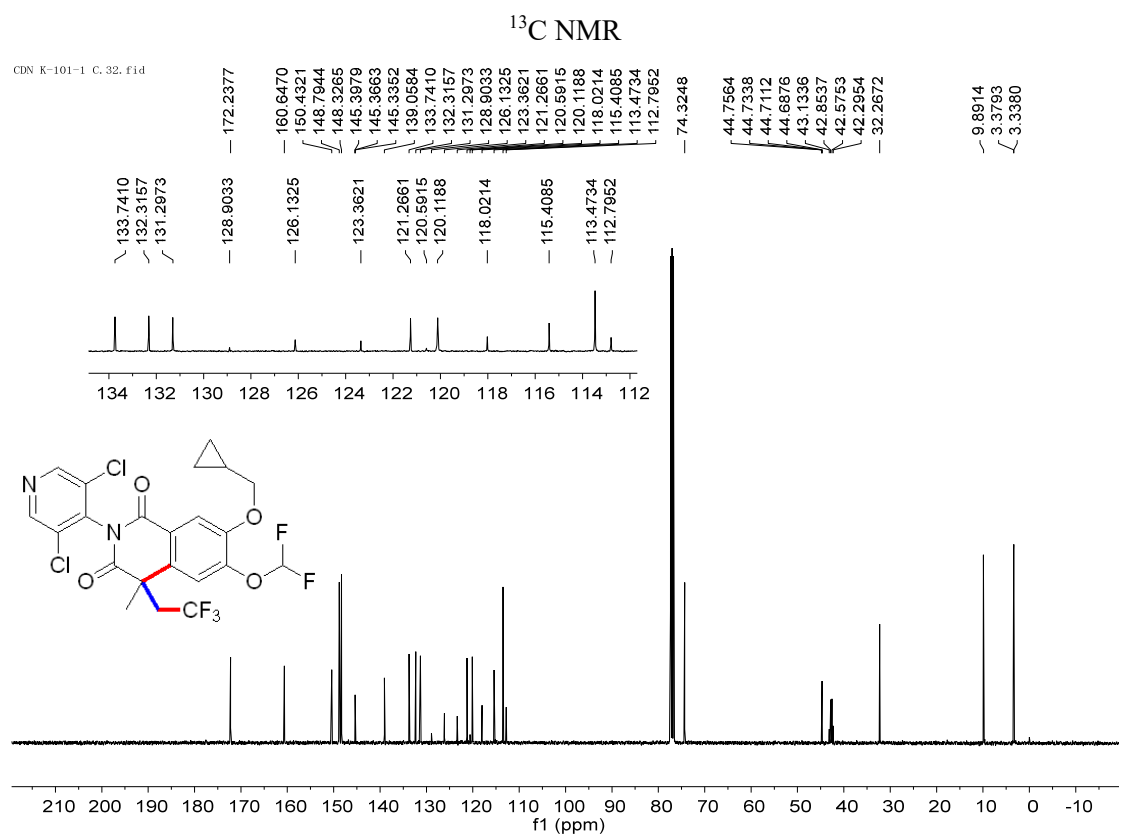
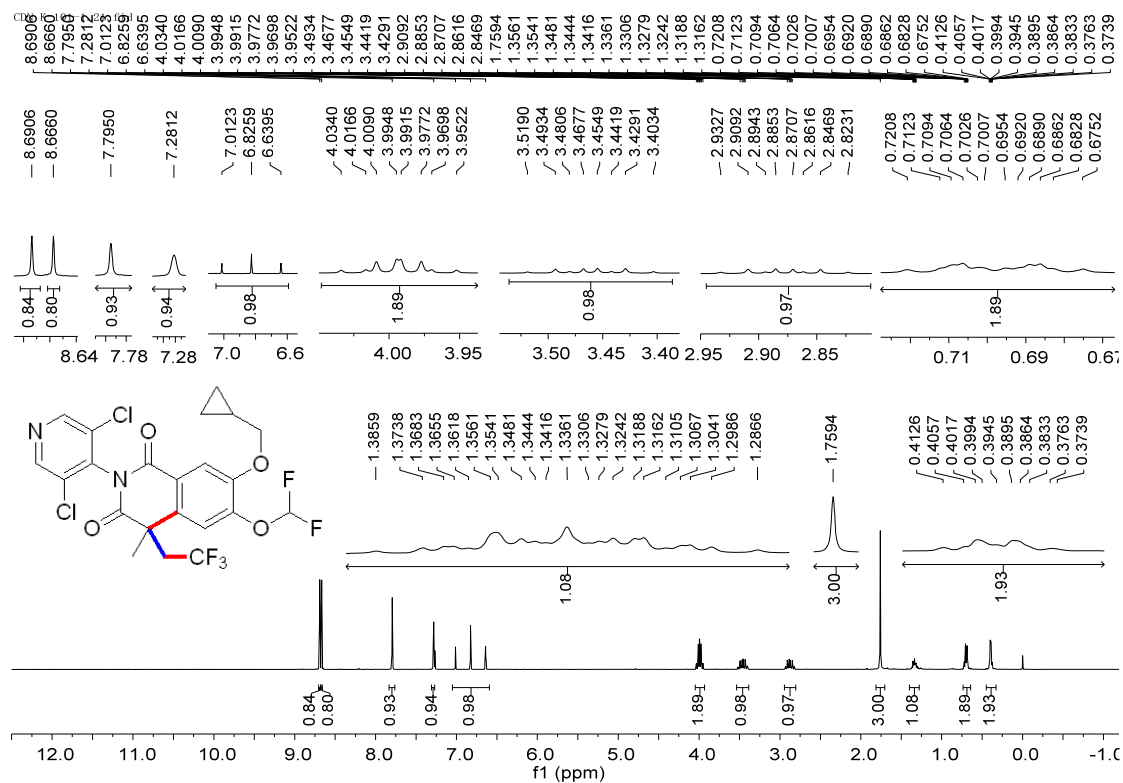
DEPT 90 and DEPT 135



¹⁹F NMR

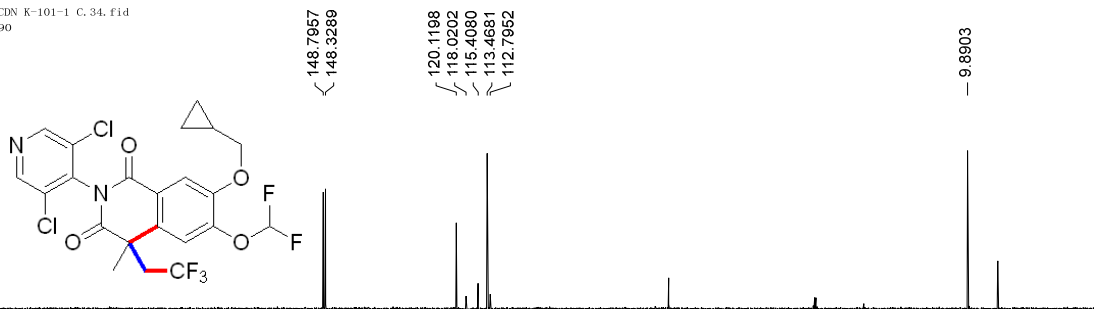


15, ¹H NMR

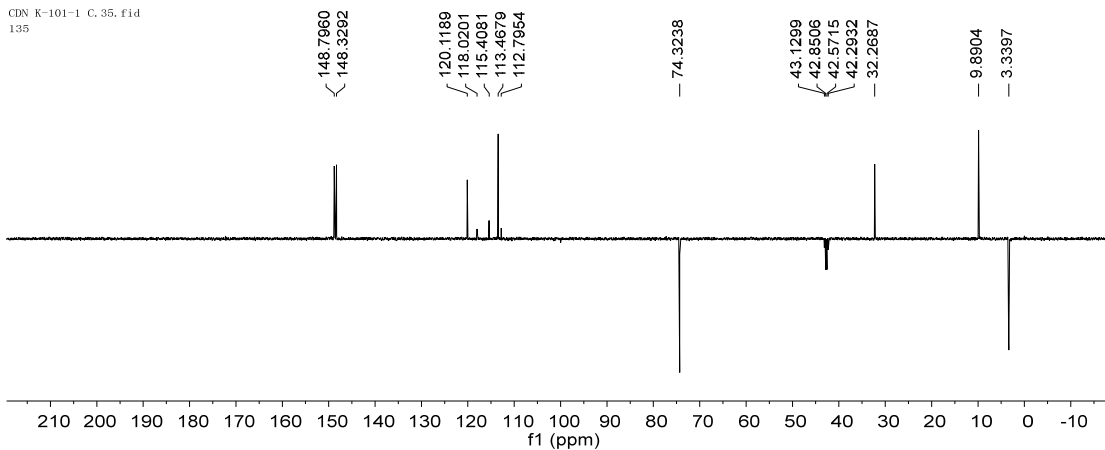


DEPT 90 and DEPT 135

CDN K-101-1 C. 34. fid
90

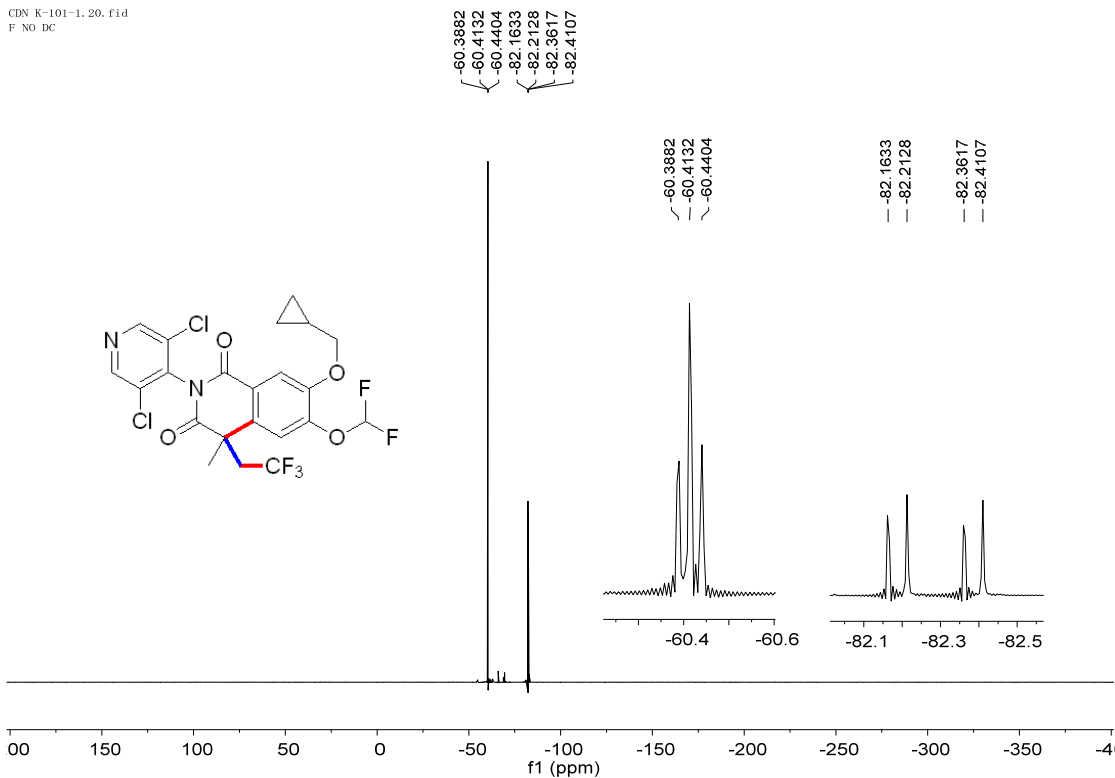


CDN K-101-1 C. 35. fid
135

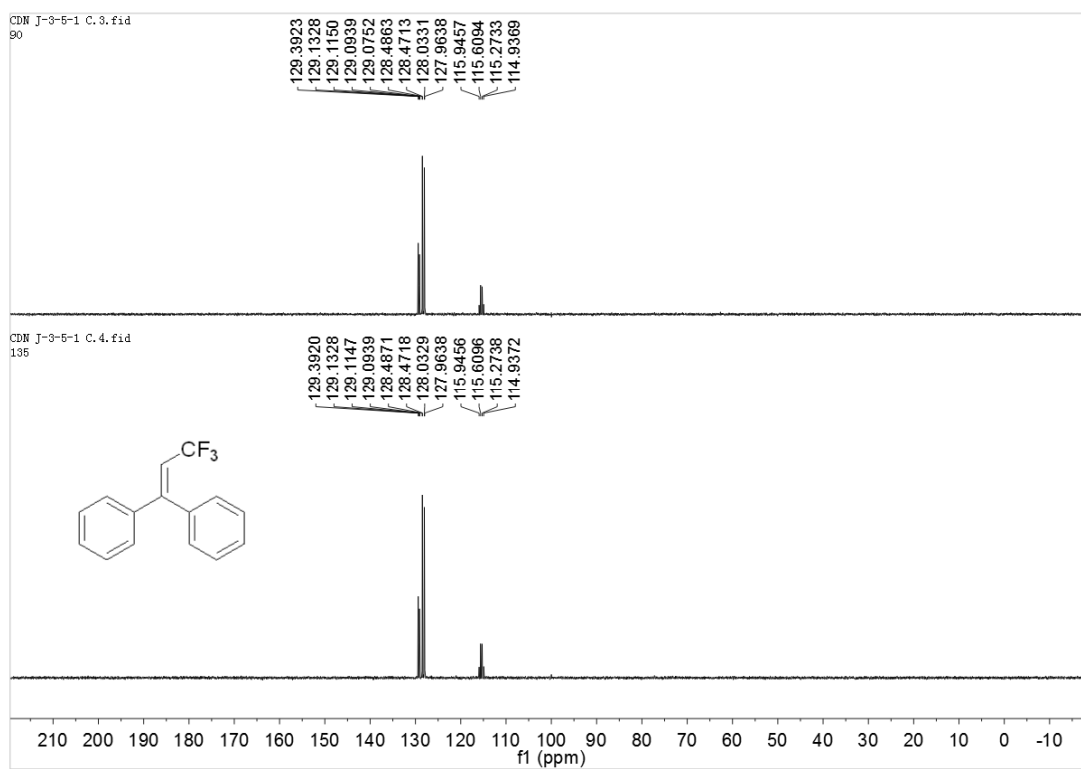


¹⁹F NMR

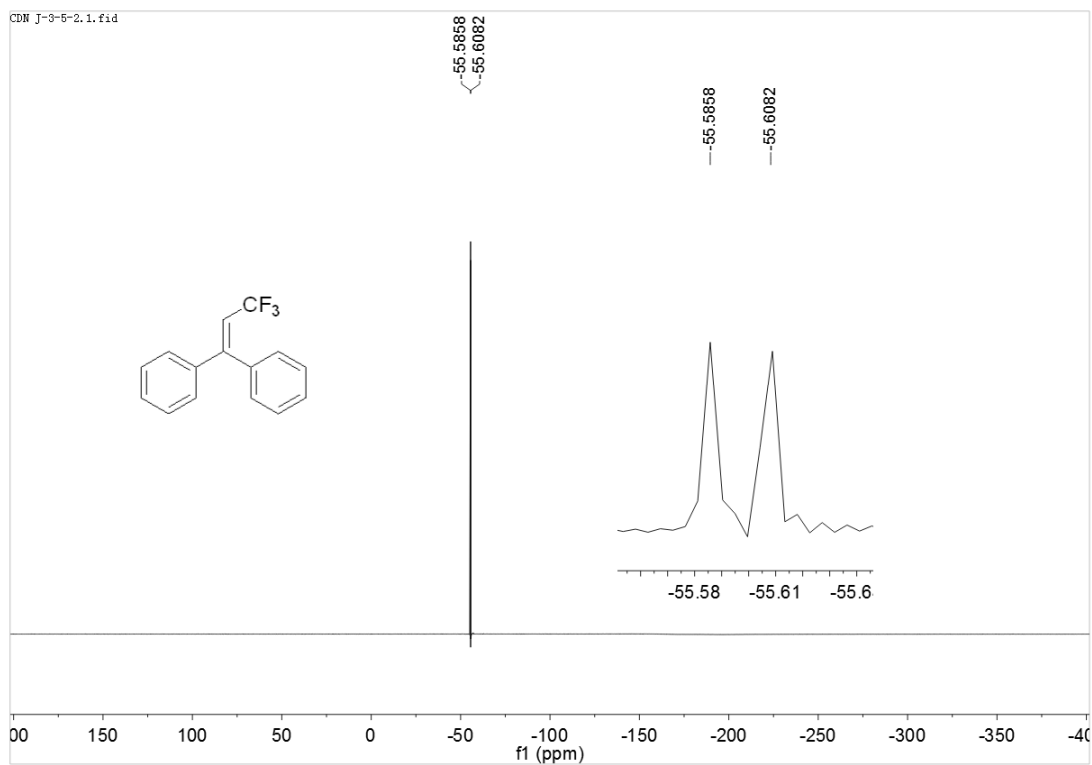
CDN K-101-1. 20. fid
F NO DC



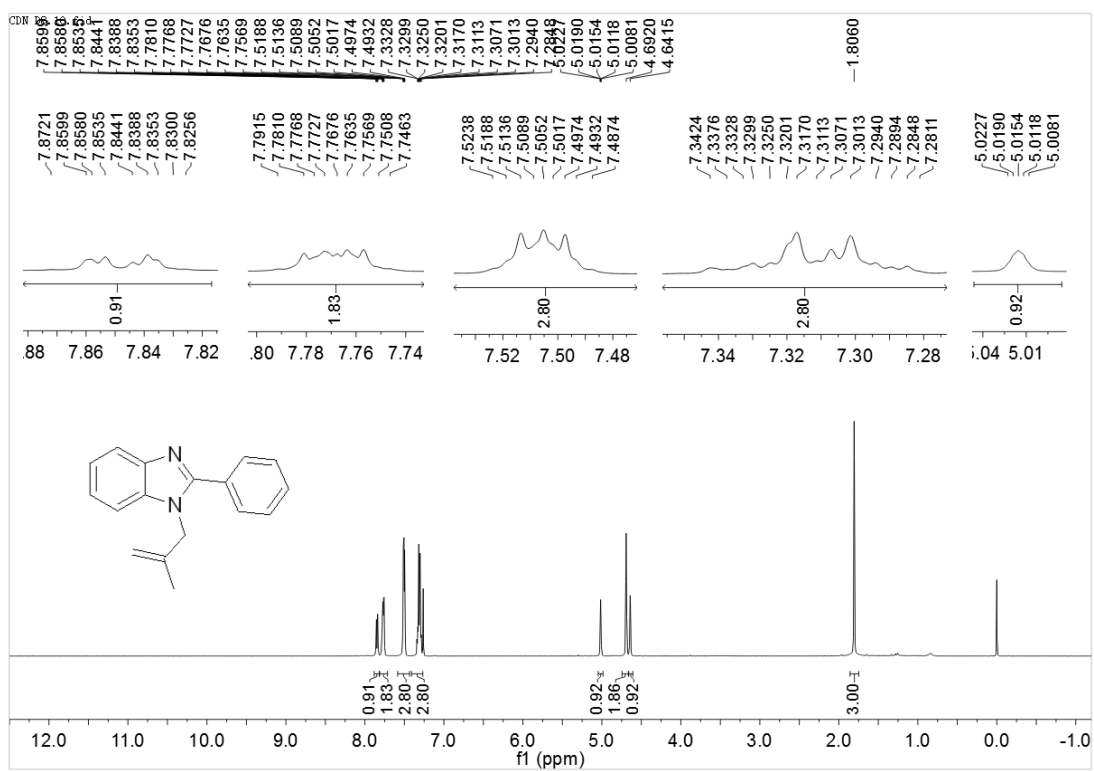
DEPT 90 and DEPT 135



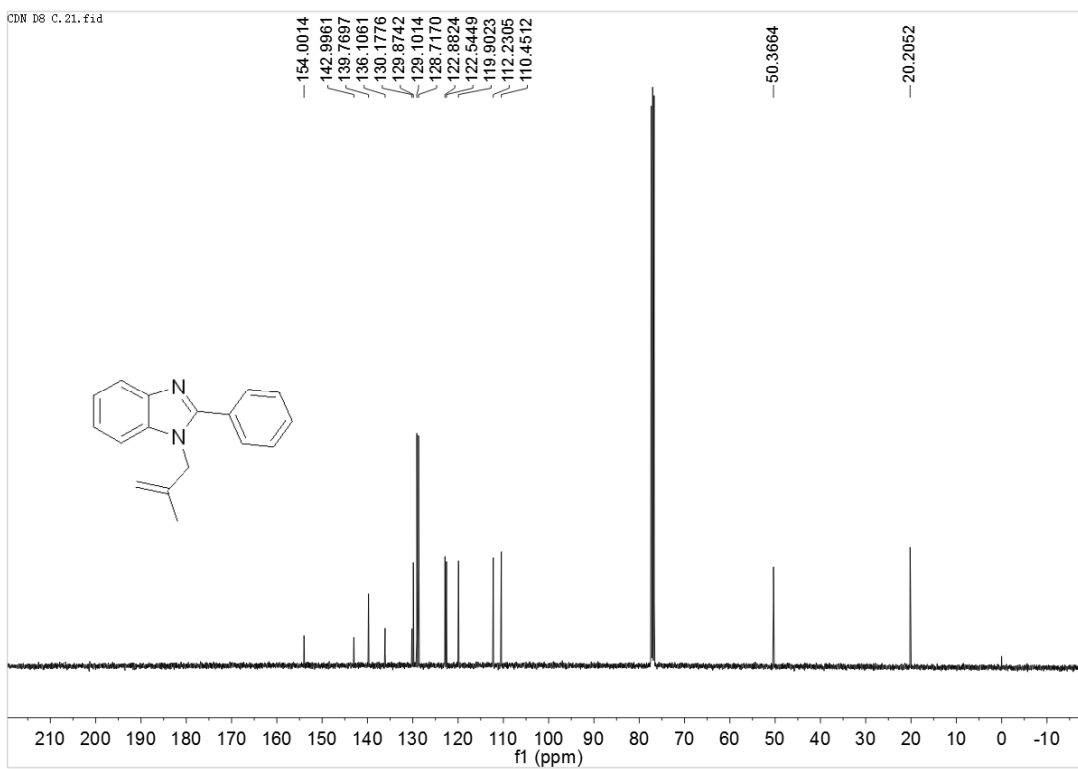
¹⁹F NMR



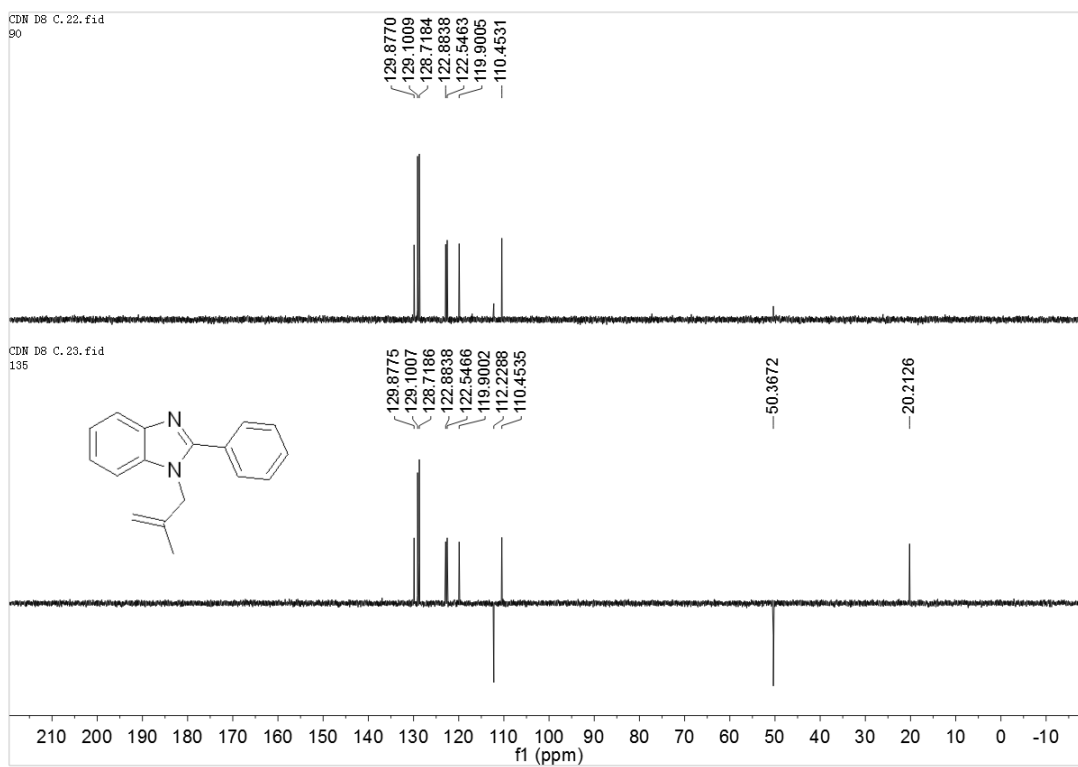
1a, ¹H NMR



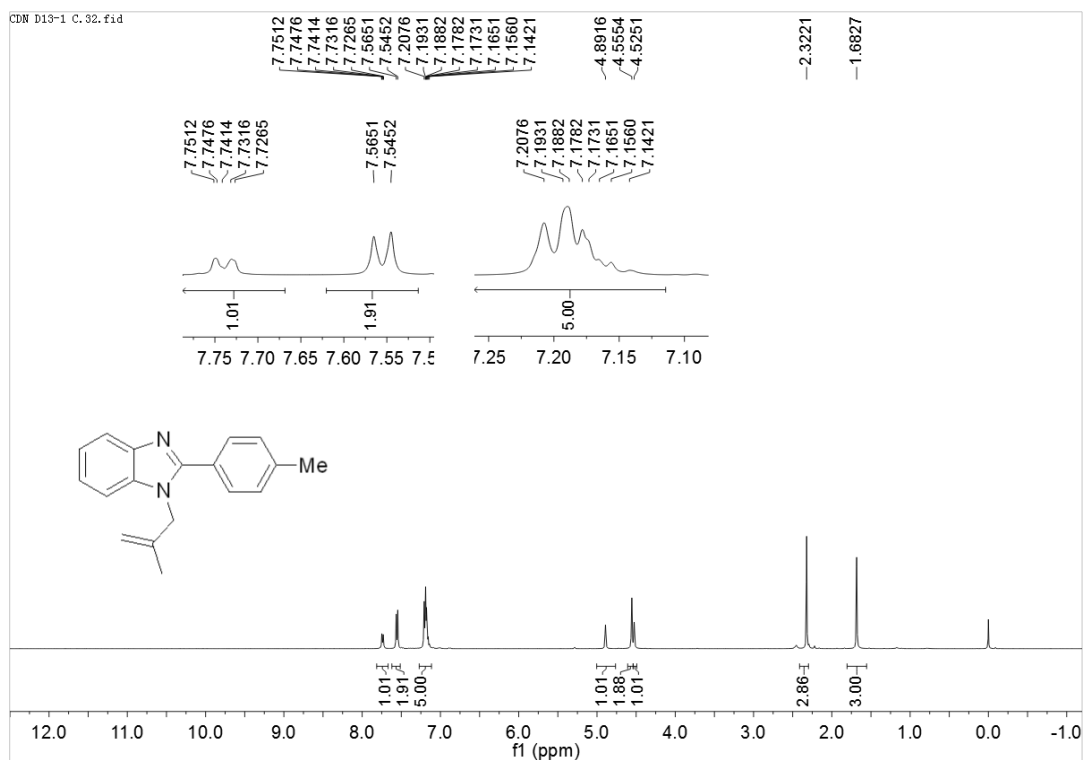
¹³C NMR



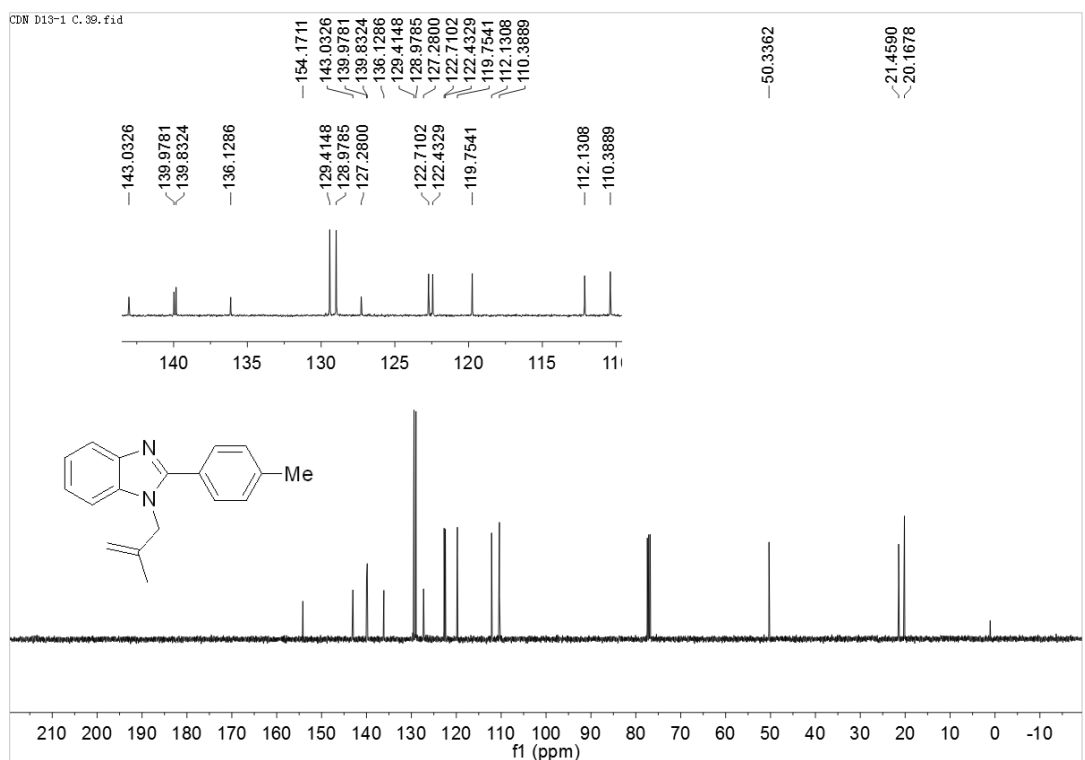
DEPT 90 and DEPT 135



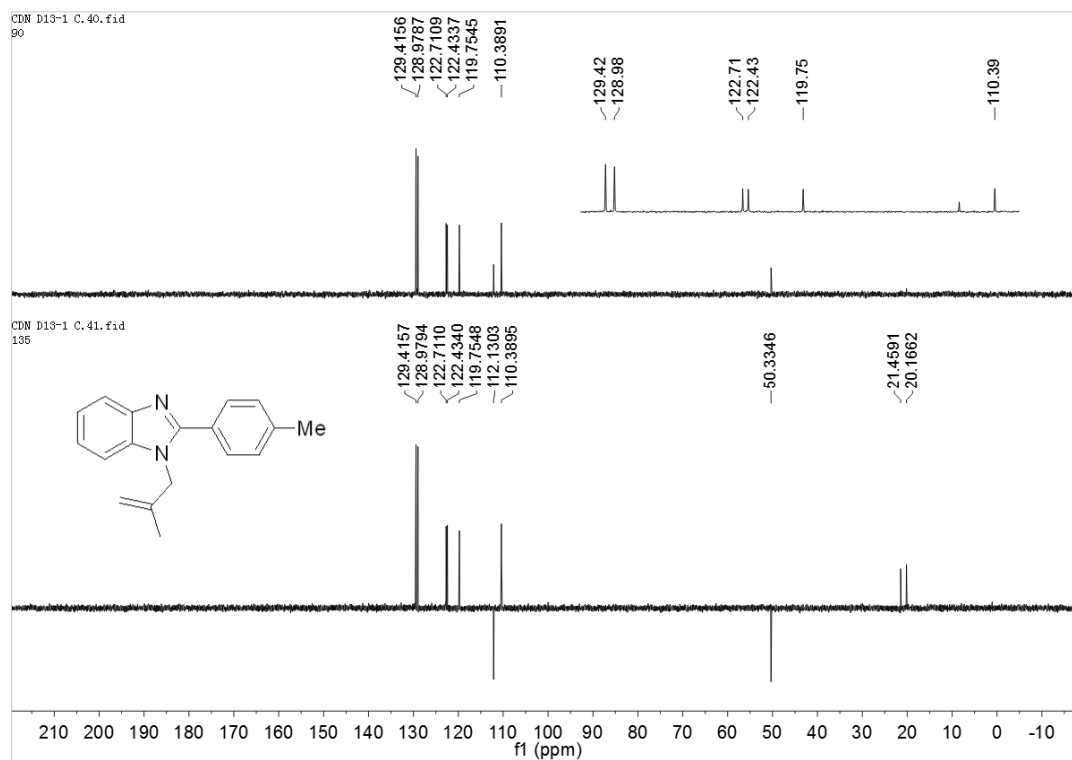
1c1, ¹H NMR



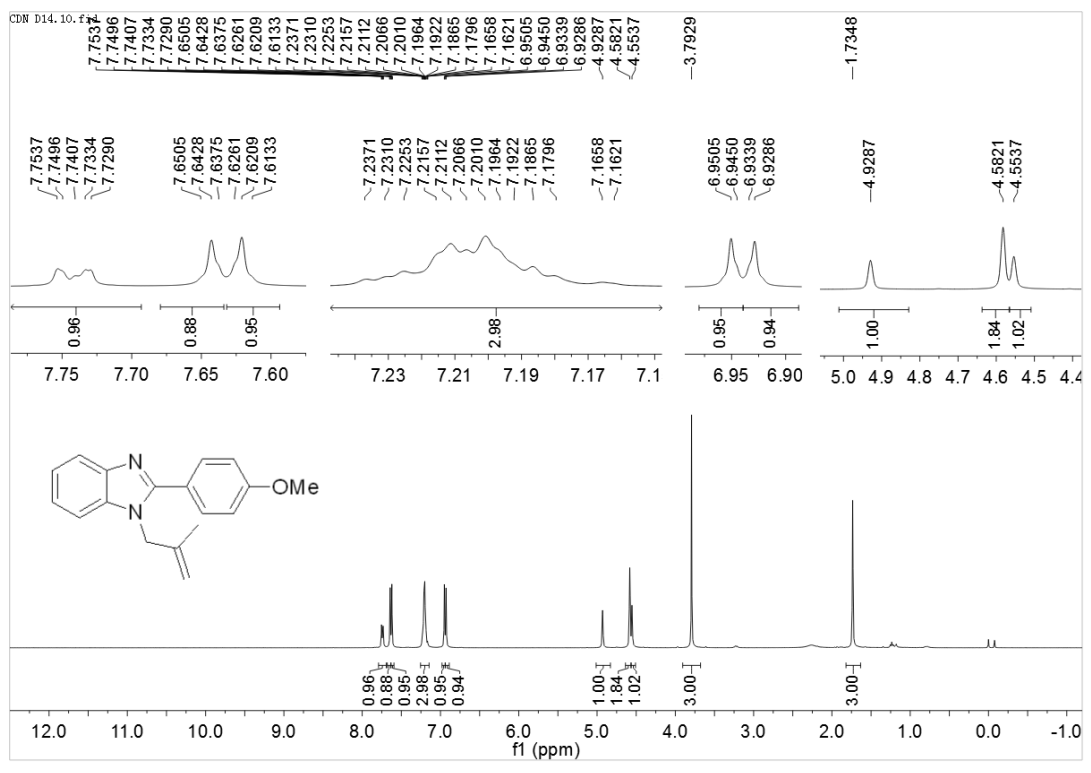
¹³C NMR



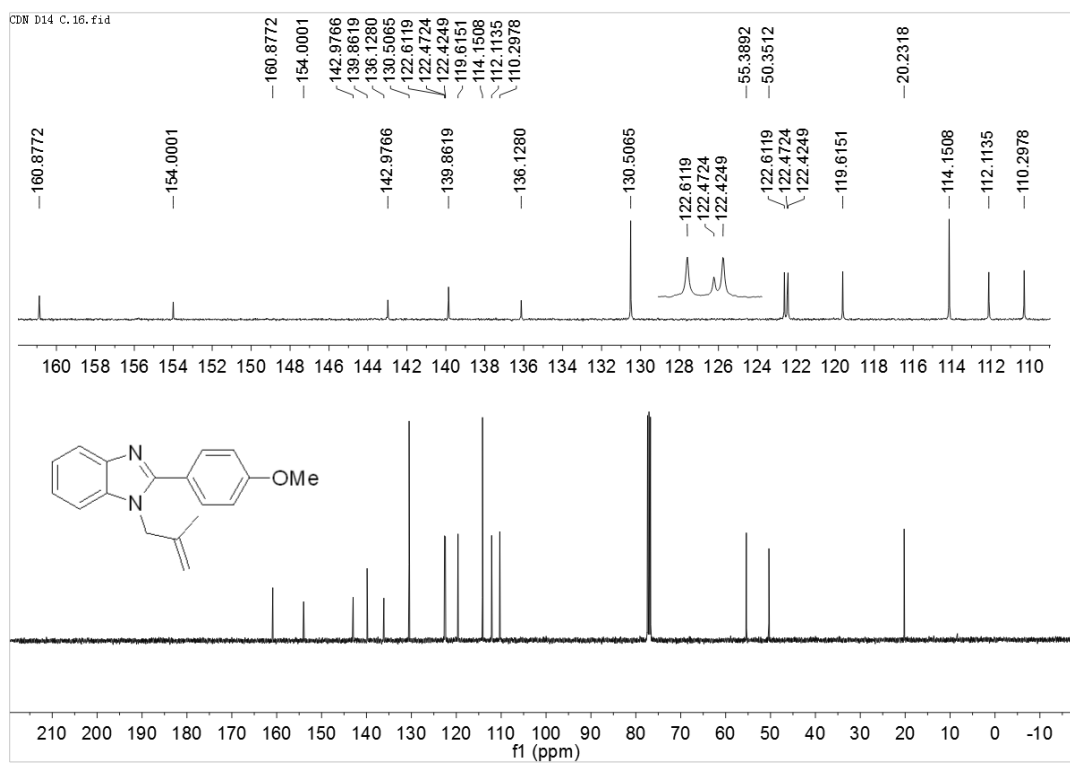
DEPT 90 and DEPT 135



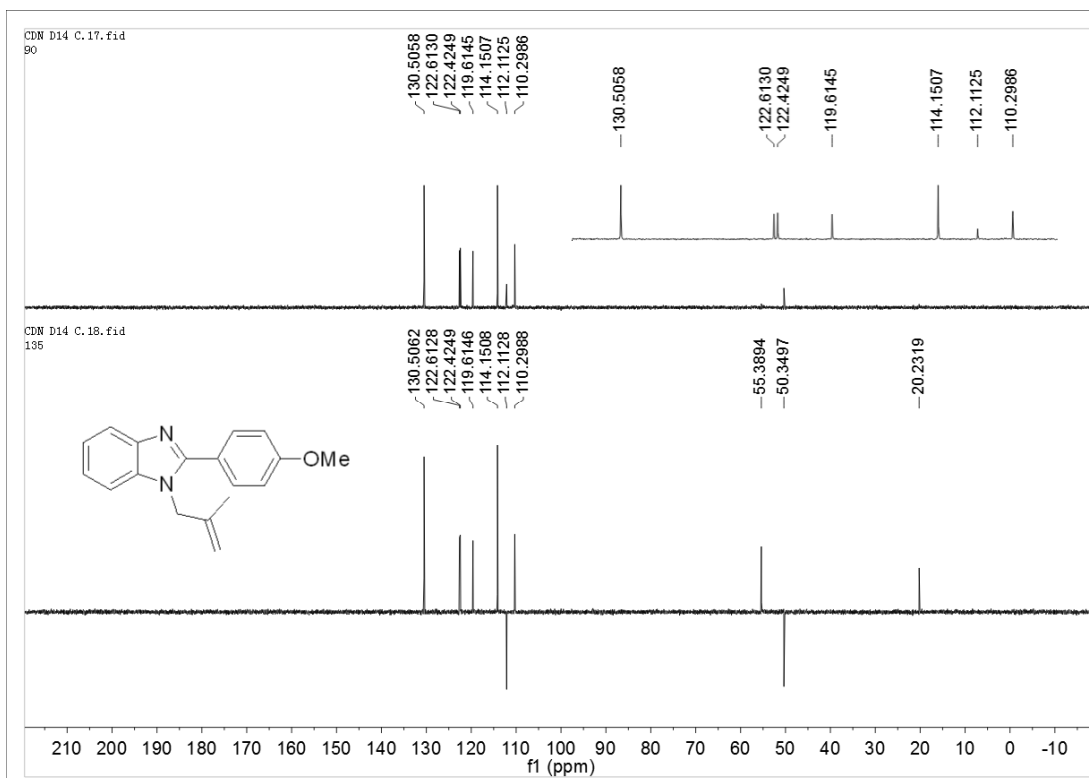
1c2, ¹H NMR



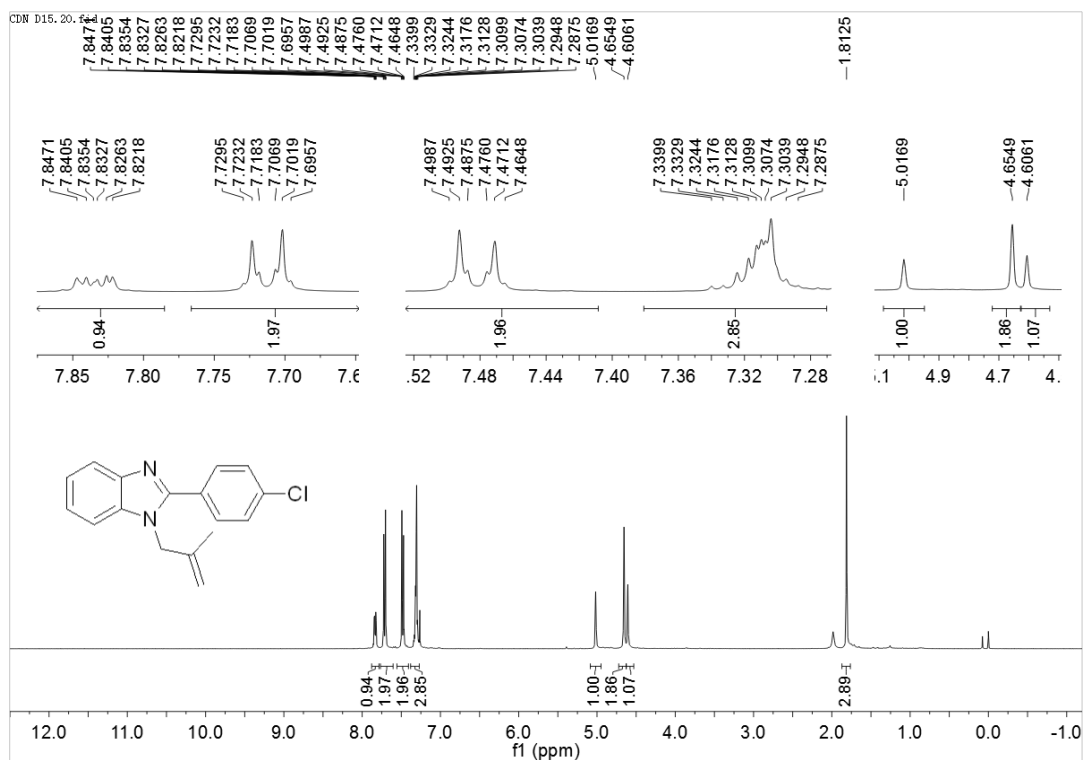
¹³C NMR



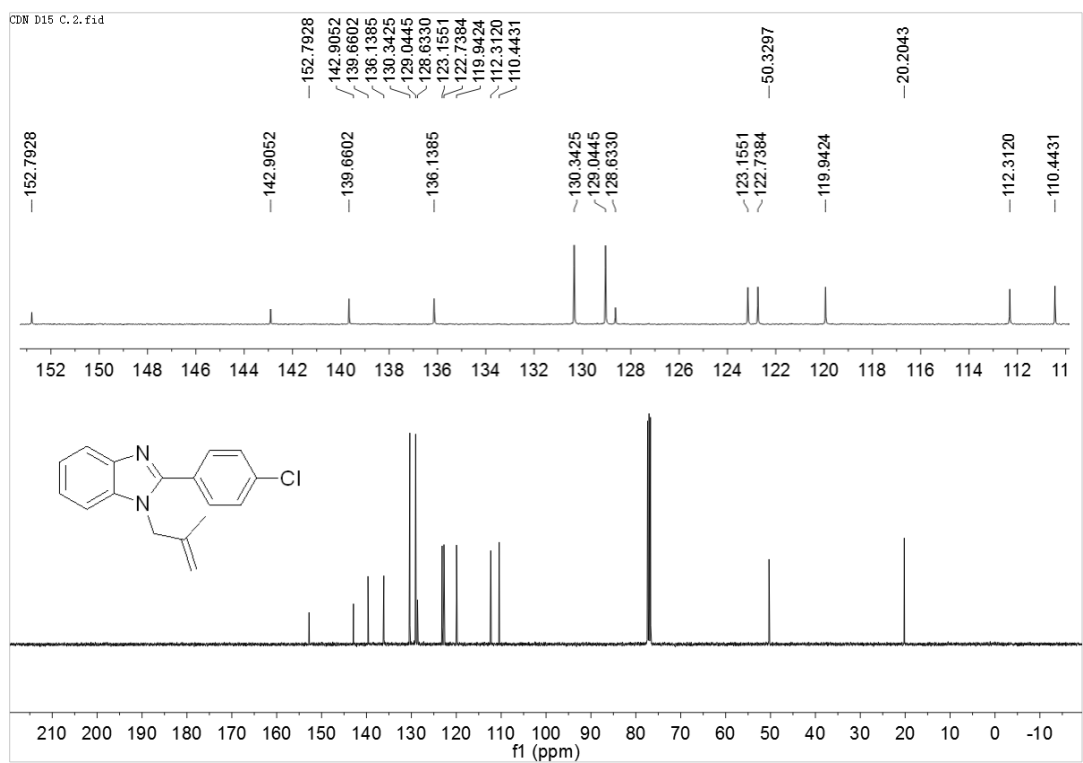
DEPT 90 and DEPT 135



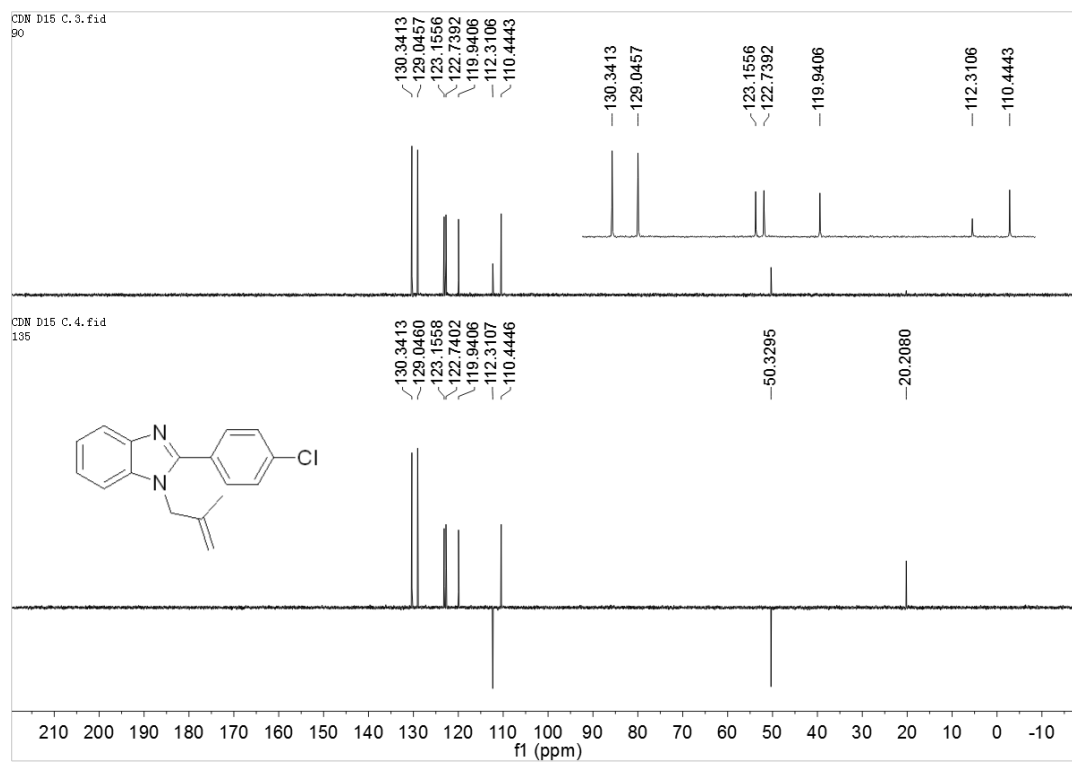
1c3, ¹H NMR



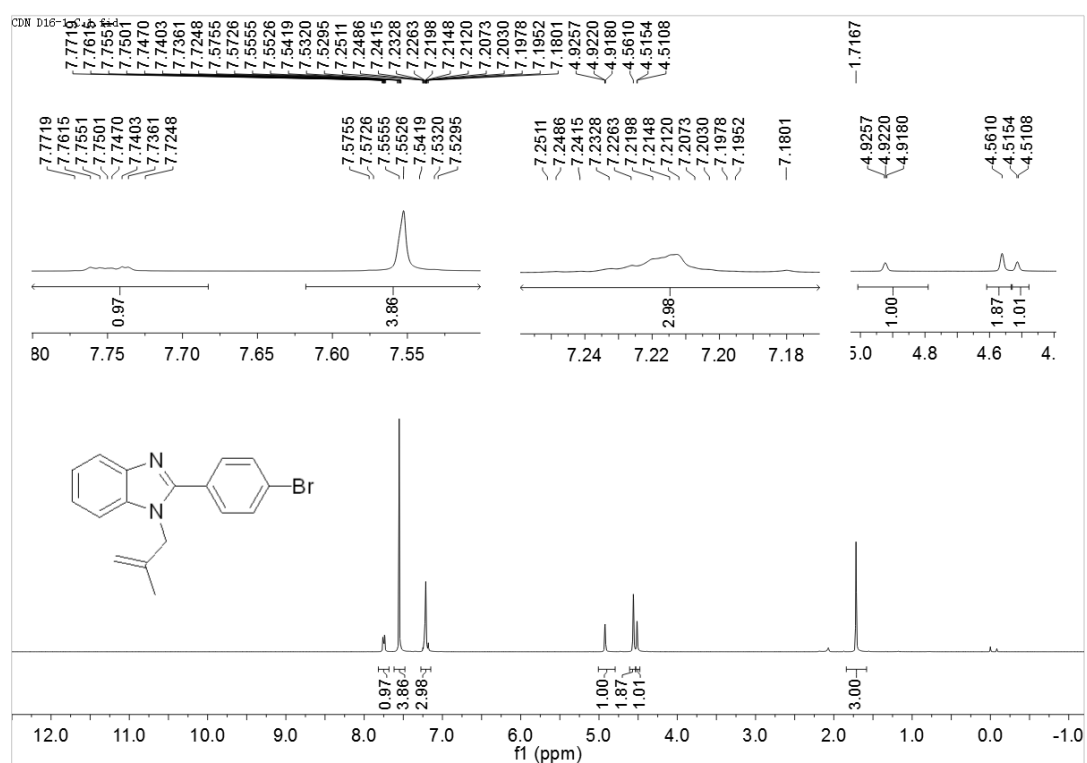
¹³C NMR



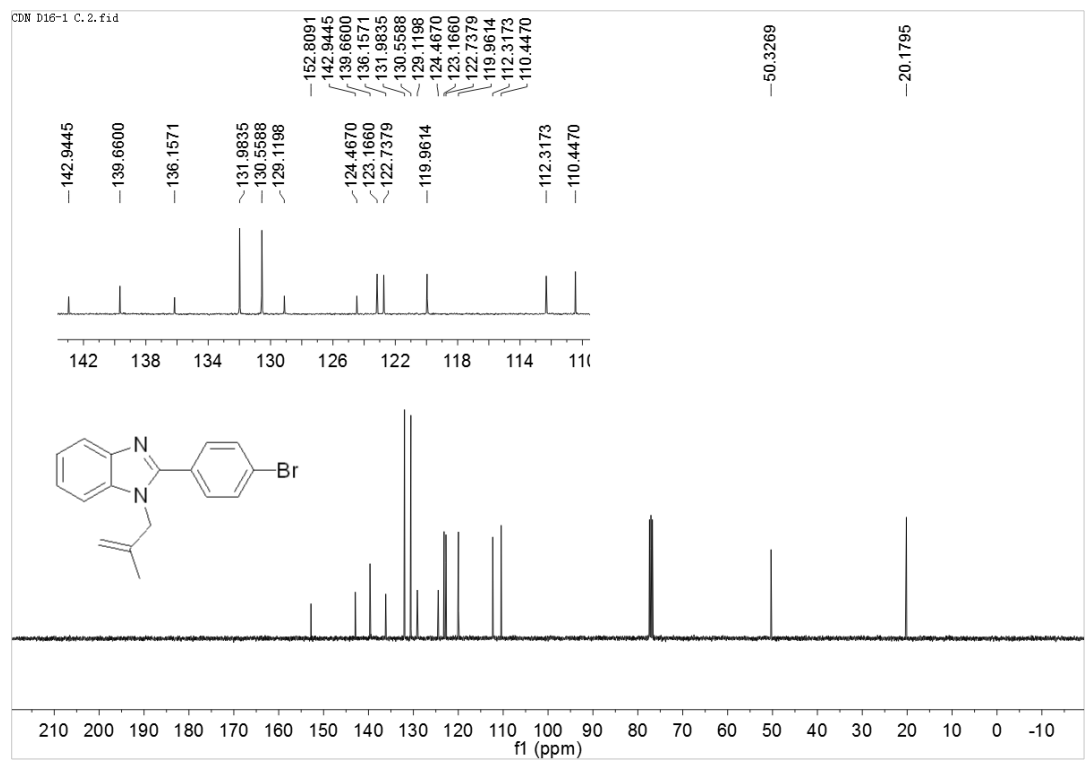
DEPT 90 and DEPT 135



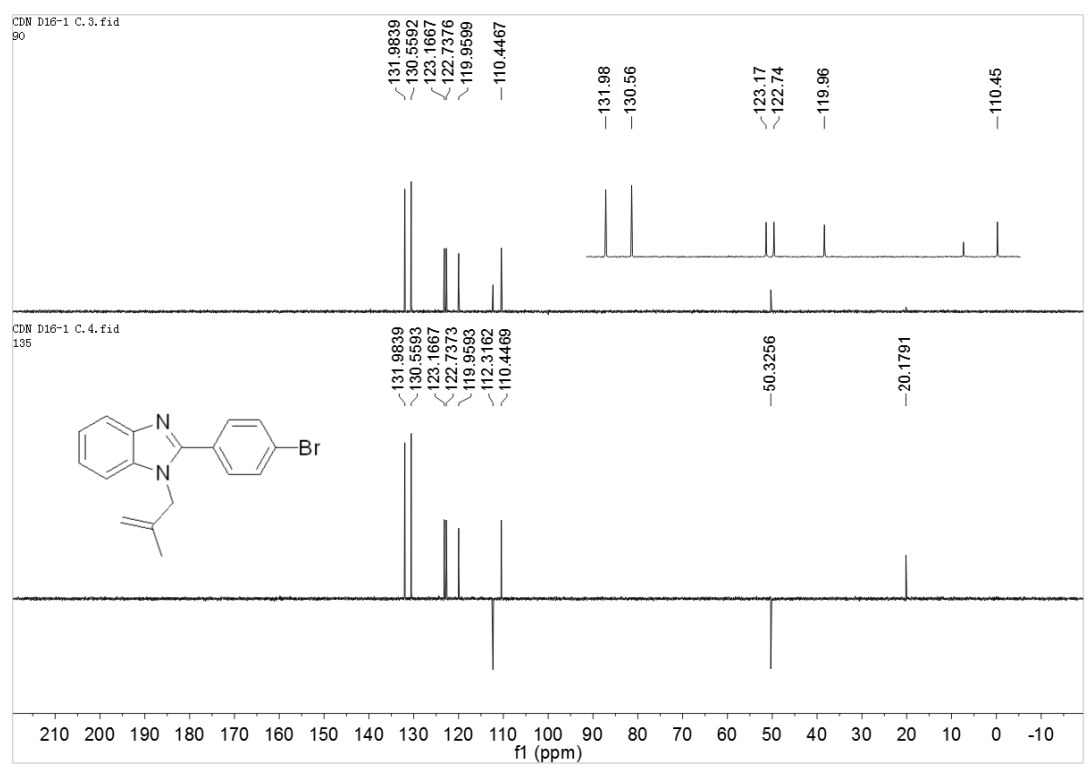
1c4, ¹H NMR



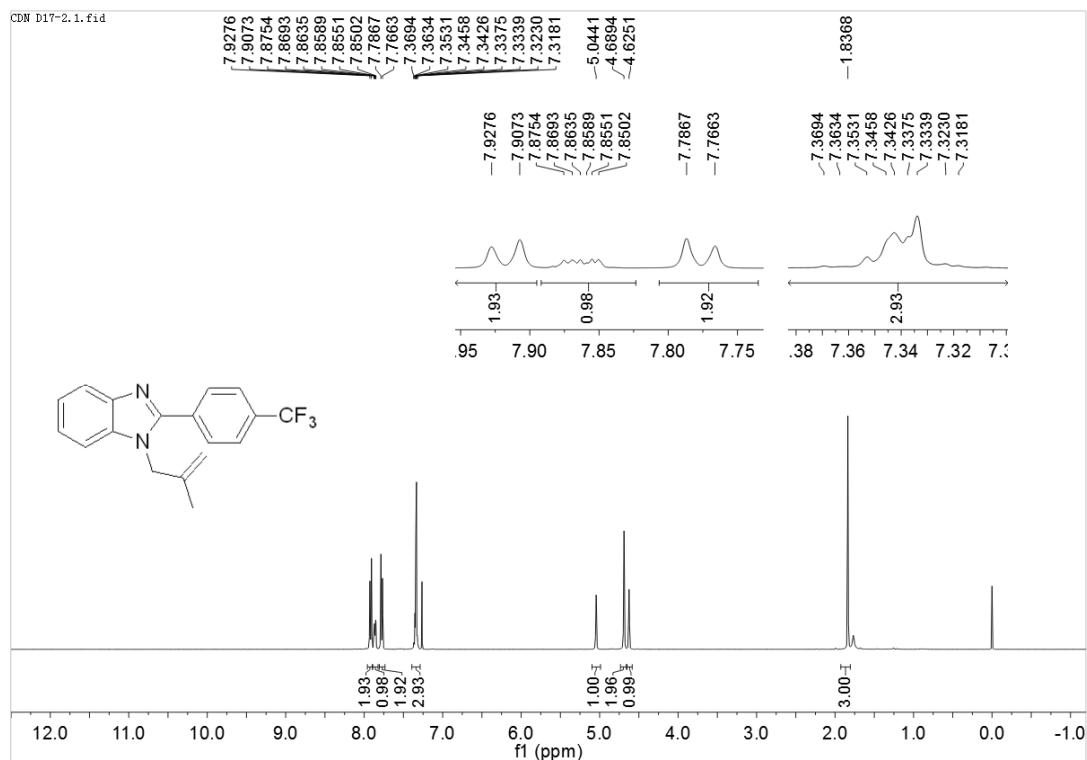
¹³C NMR



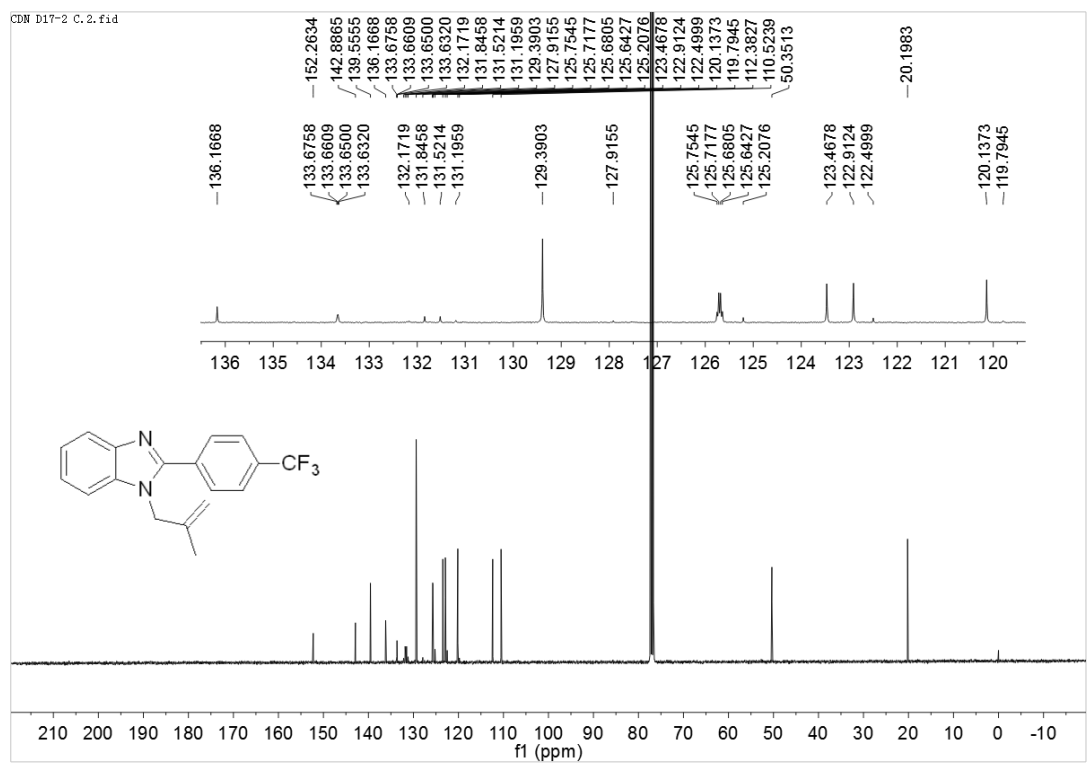
DEPT 90 and DEPT 135



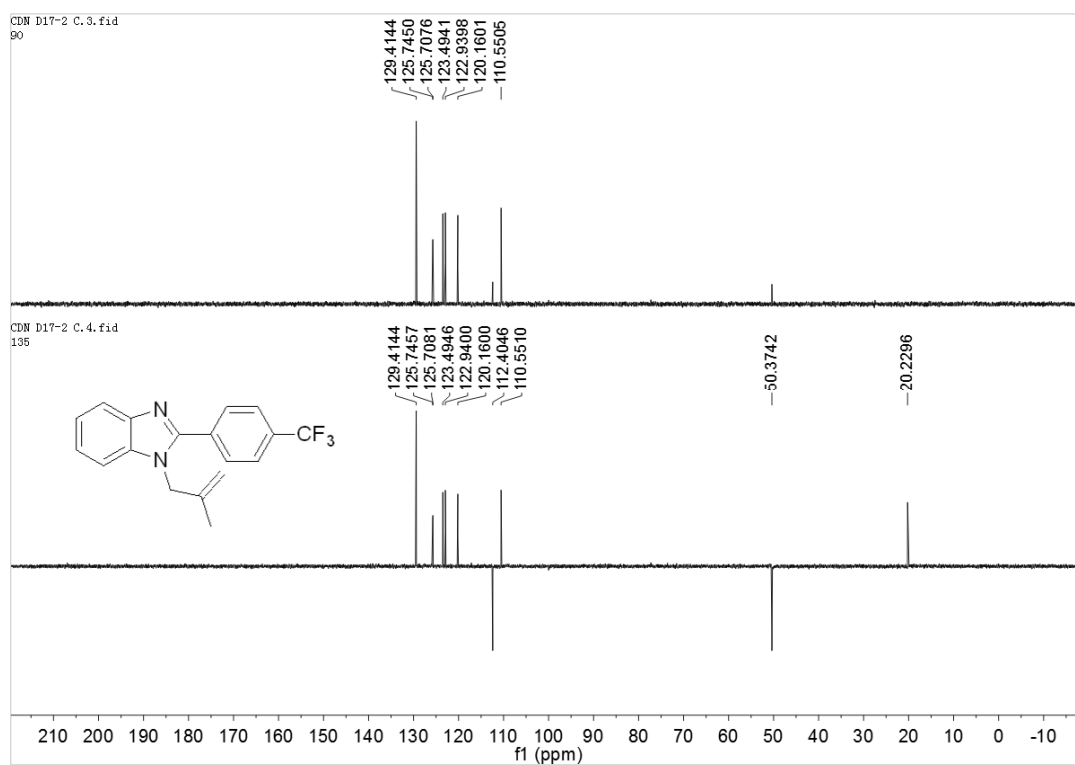
1c5, ¹H NMR



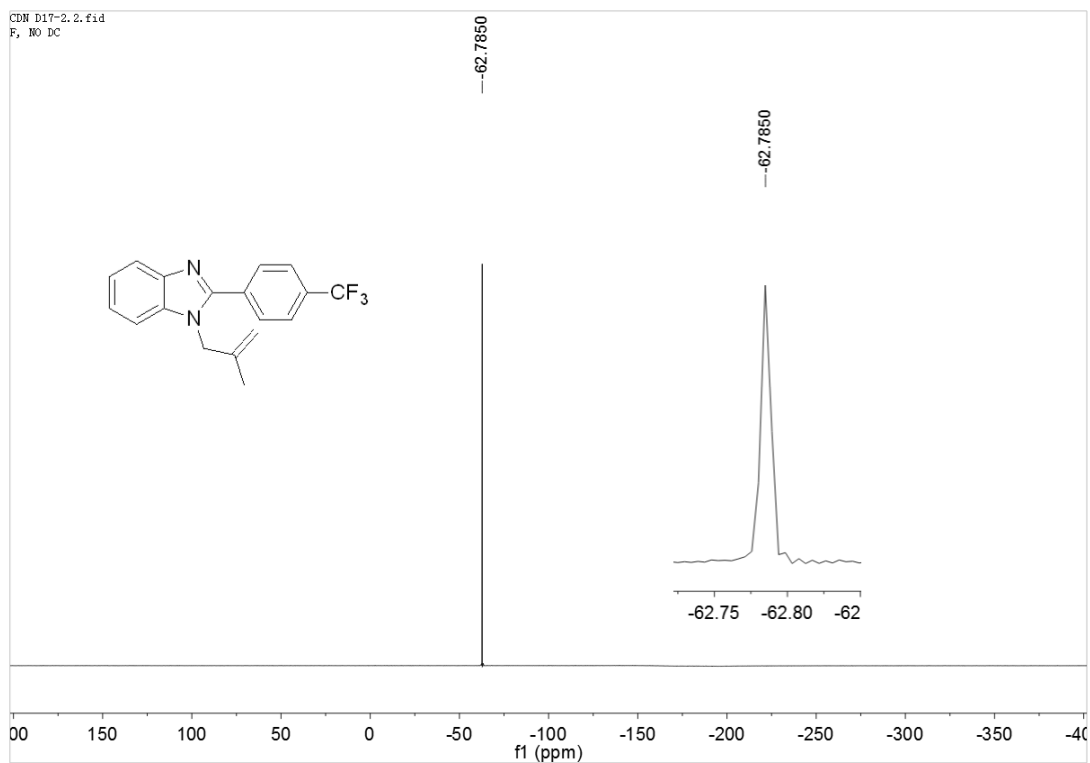
¹³C NMR



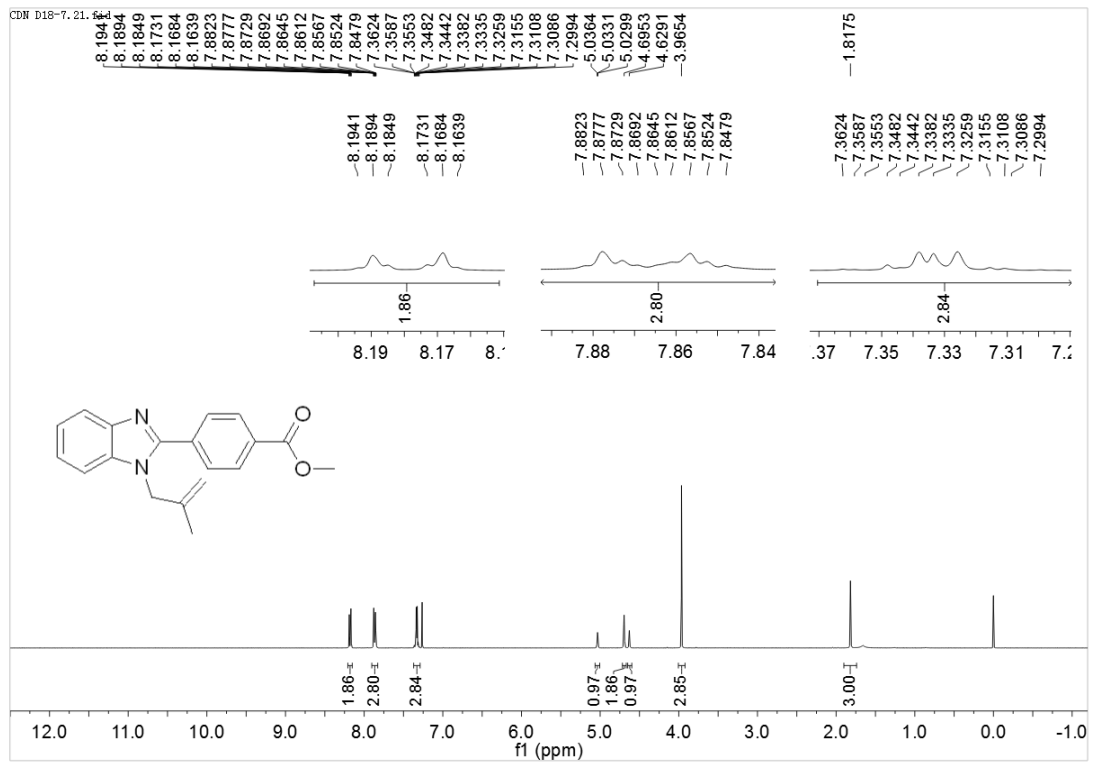
DEPT 90 and DEPT 135



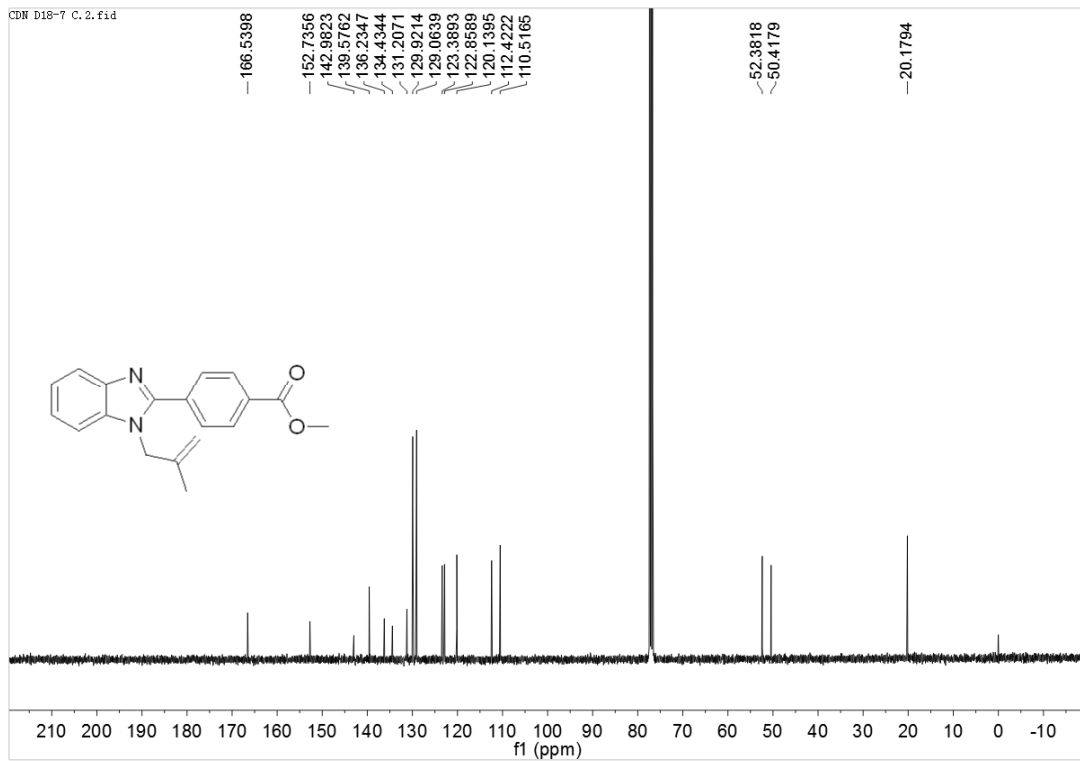
¹⁹F NMR



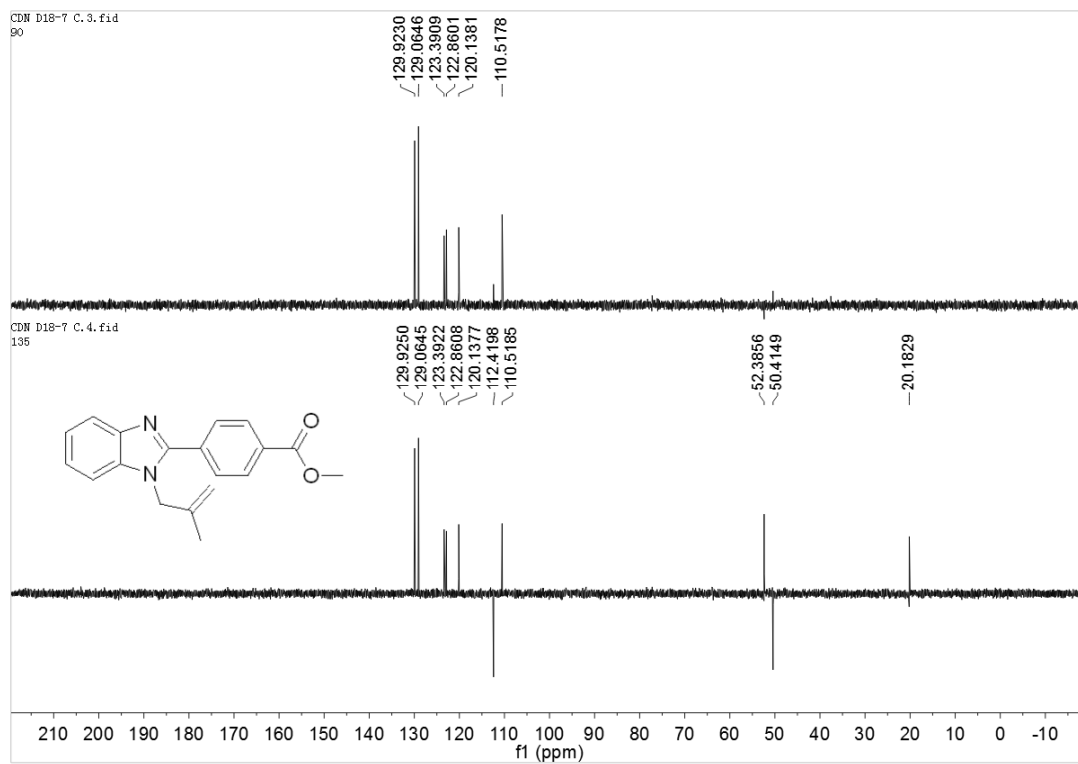
1c6, ¹H NMR



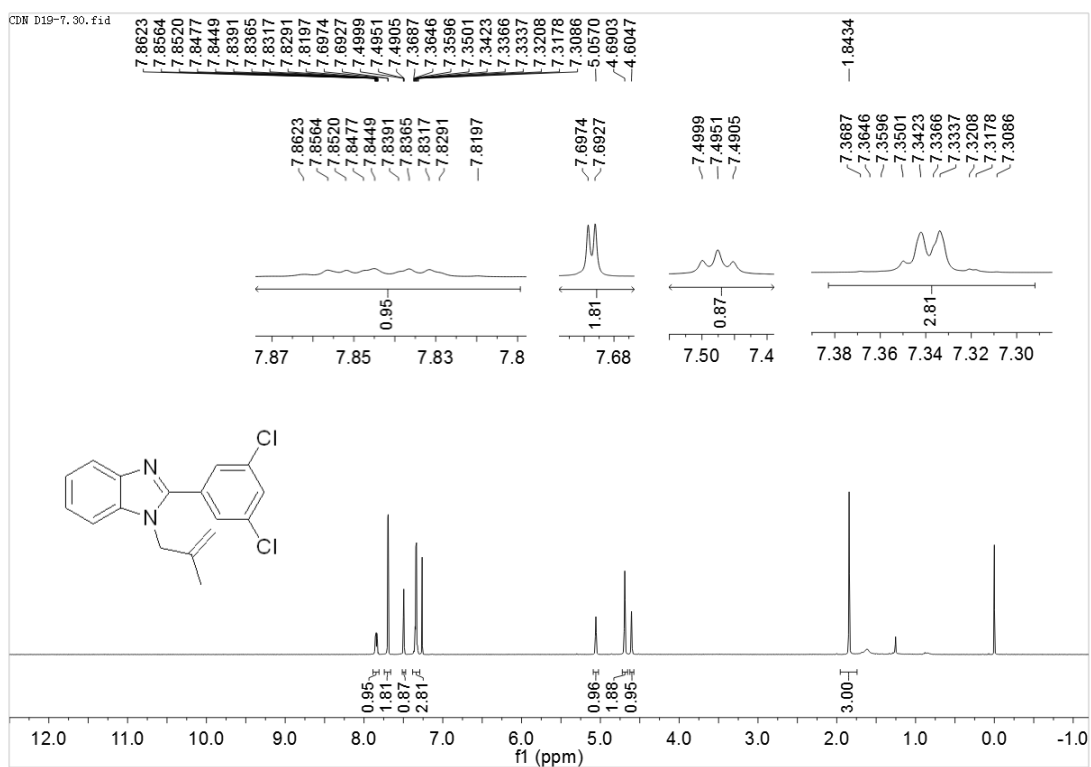
¹³C NMR



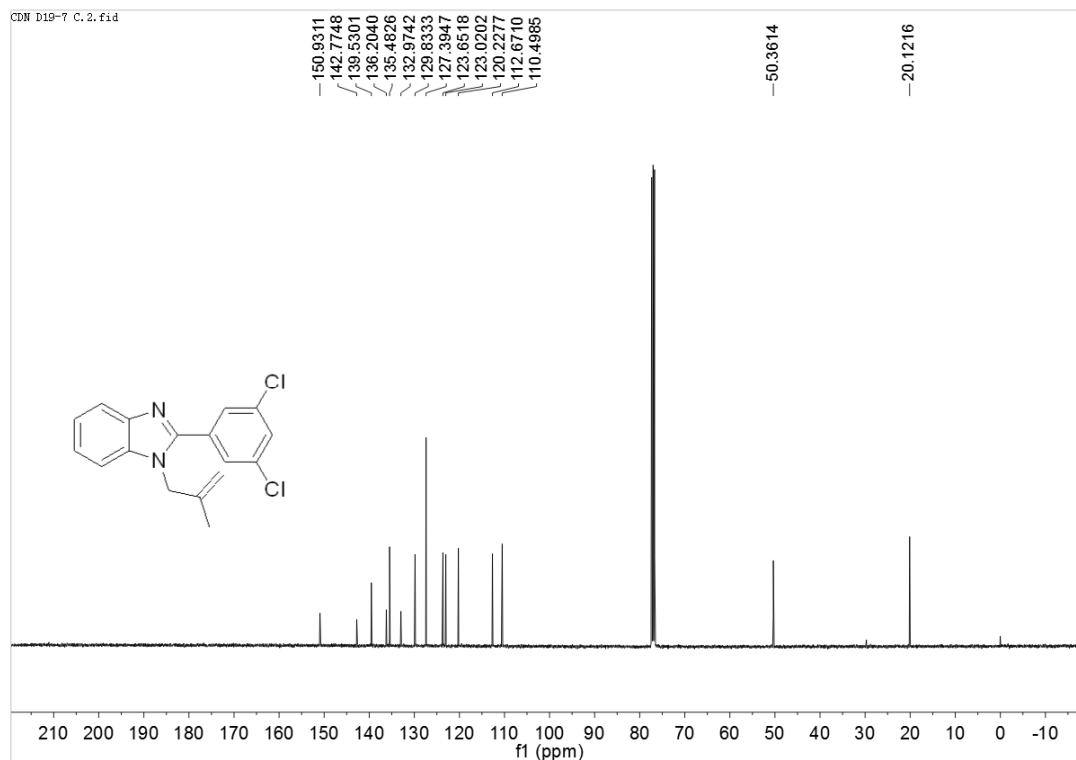
DEPT 90 and DEPT 135



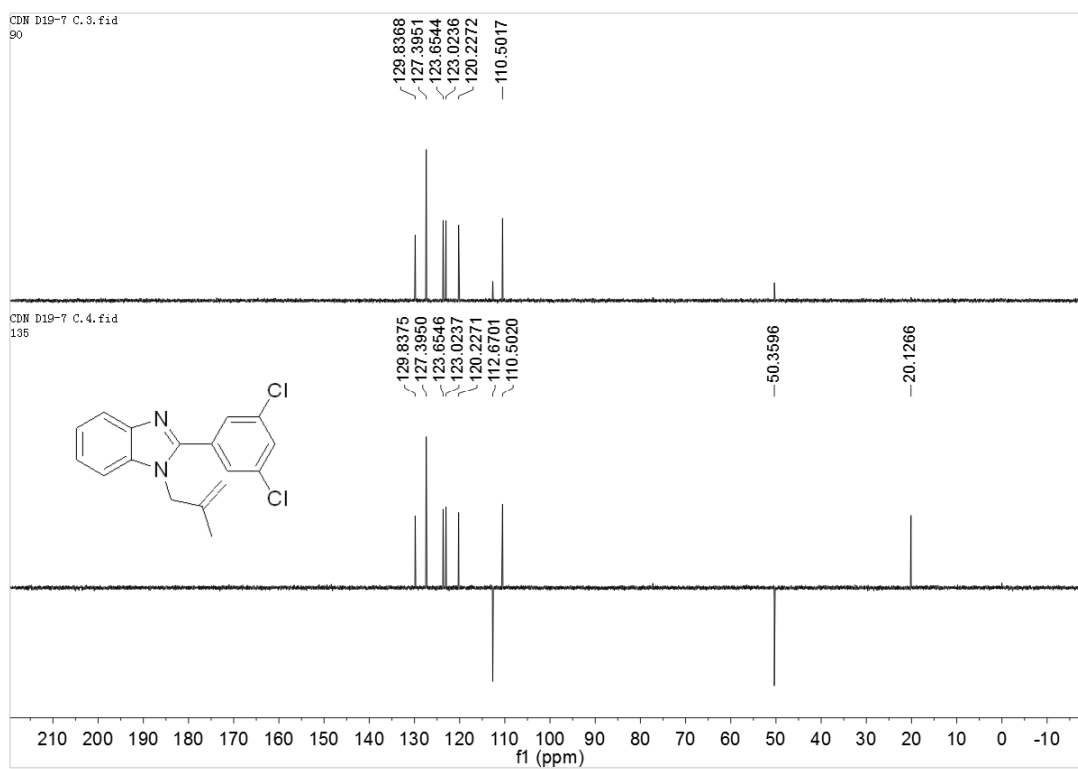
1d, ¹H NMR



¹³C NMR



DEPT 90 and DEPT 135

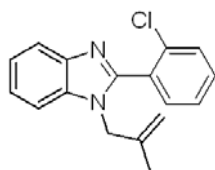


DEPT 90 and DEPT 135

CDN D20-7 C. 3. fid
90

132.2724
131.2890
129.8002
129.8001
126.8840
123.0237
122.4219
120.2137
110.6730

CDN D20-7 C. 4. fid
135



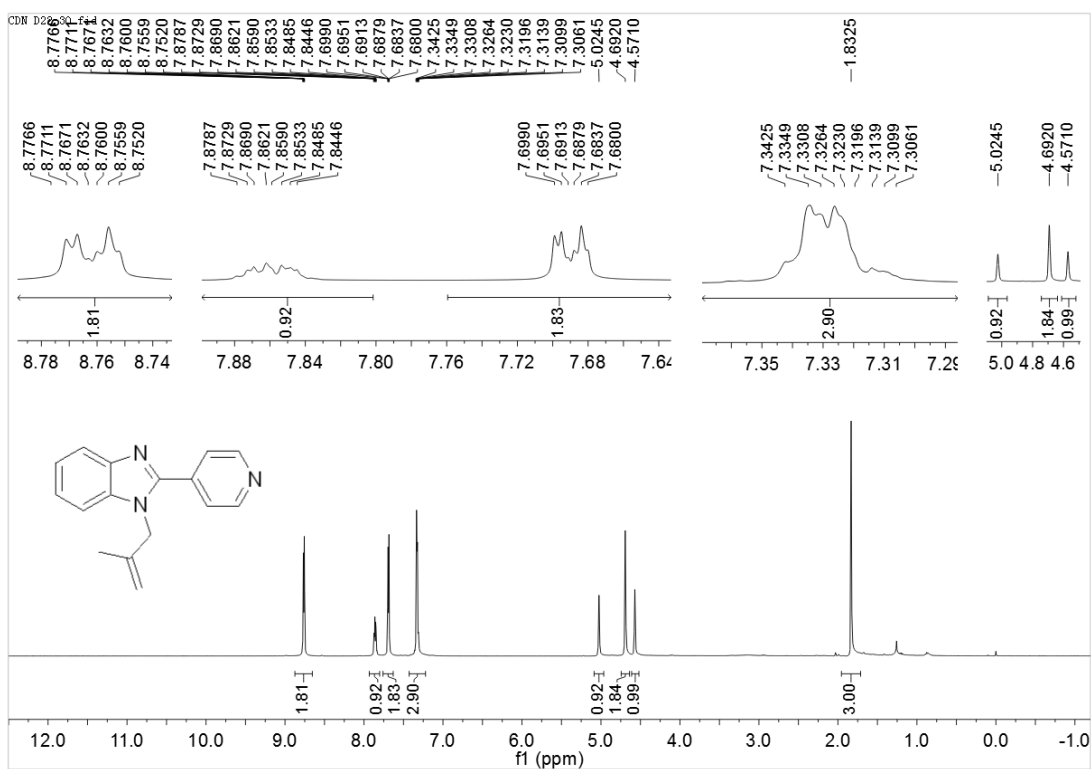
132.2724
131.2894
129.8002
126.8842
123.0236
122.4224
120.2136
113.1607
110.6732

50.4019

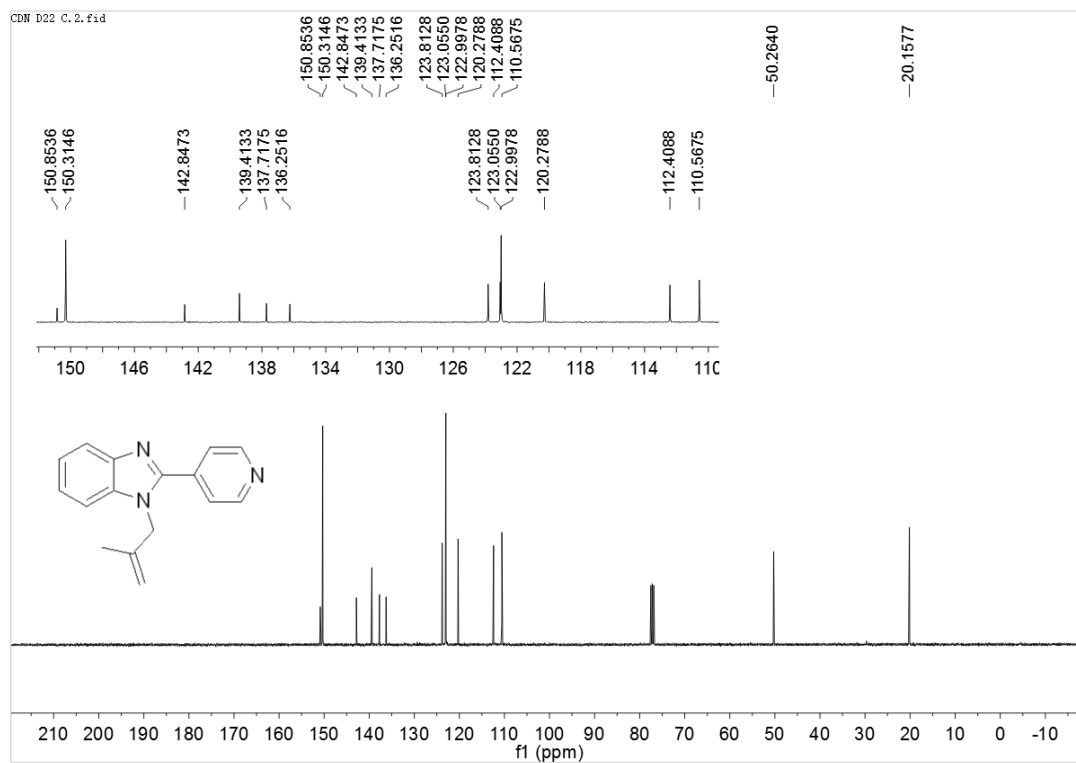
19.8656

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)

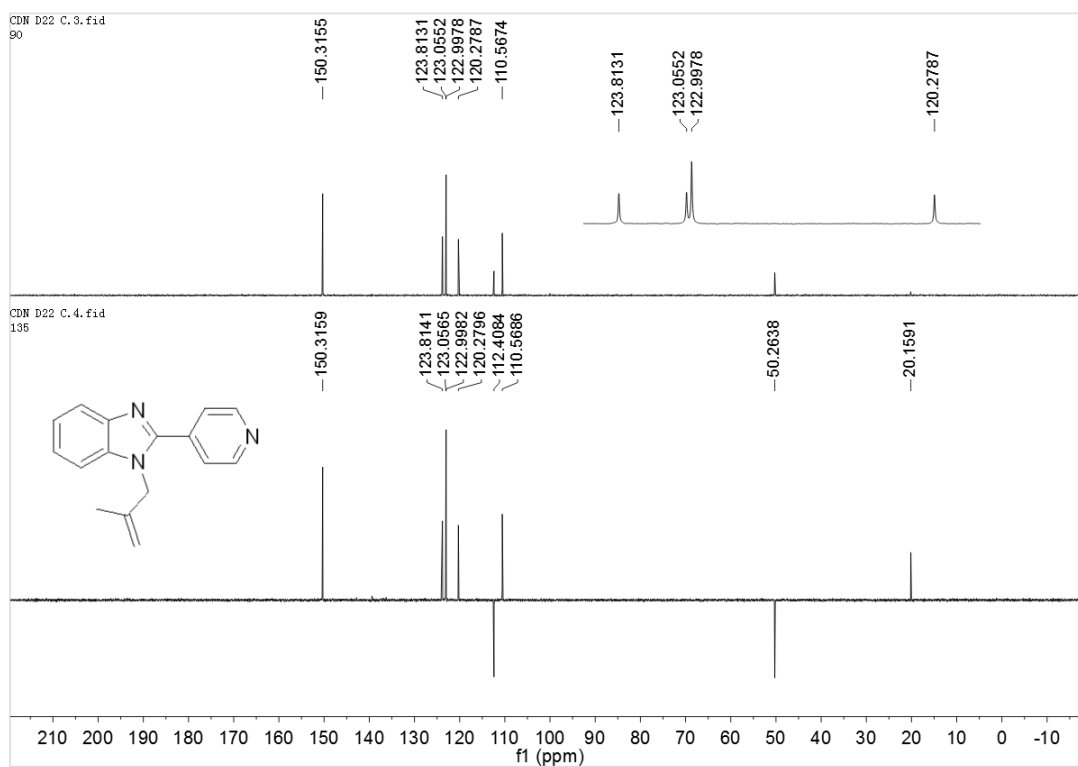
1f, ¹H NMR



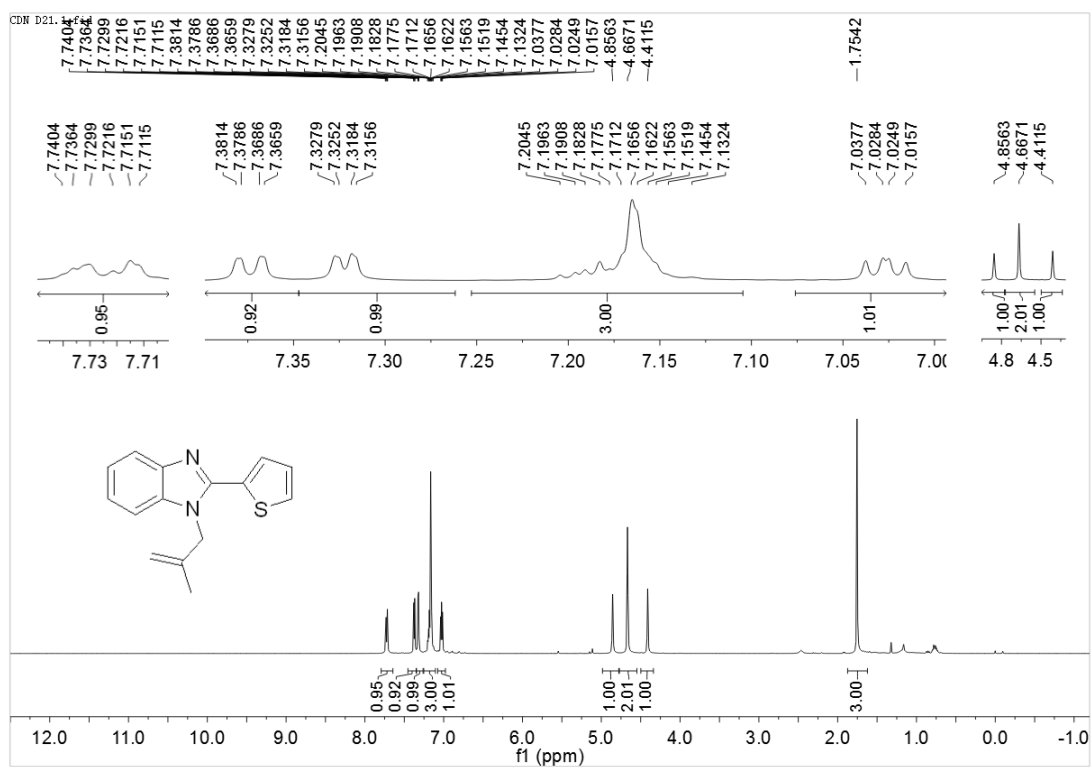
¹³C NMR



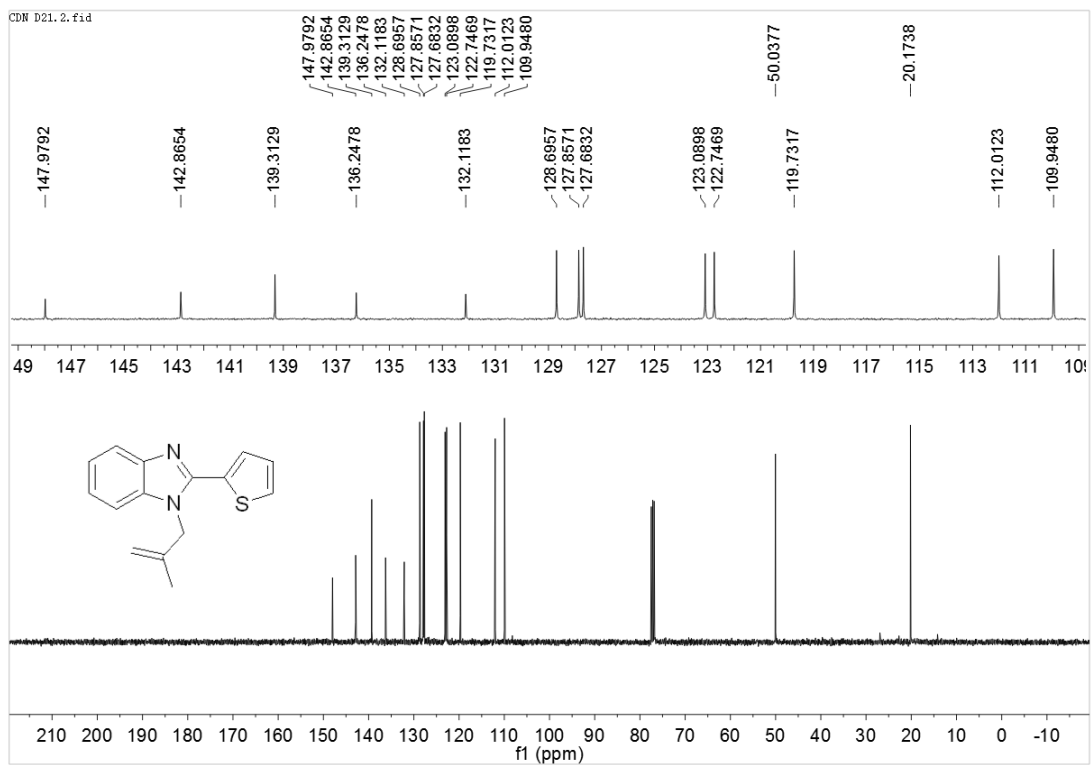
DEPT 90 and DEPT 135



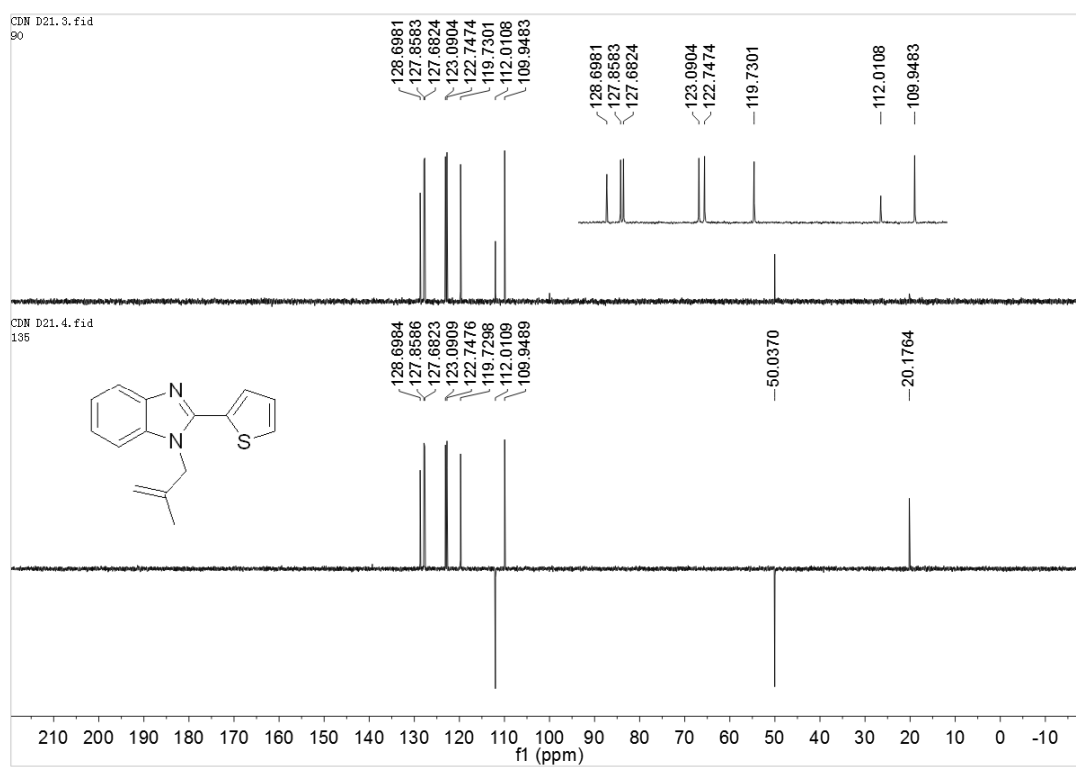
1g, ¹H NMR



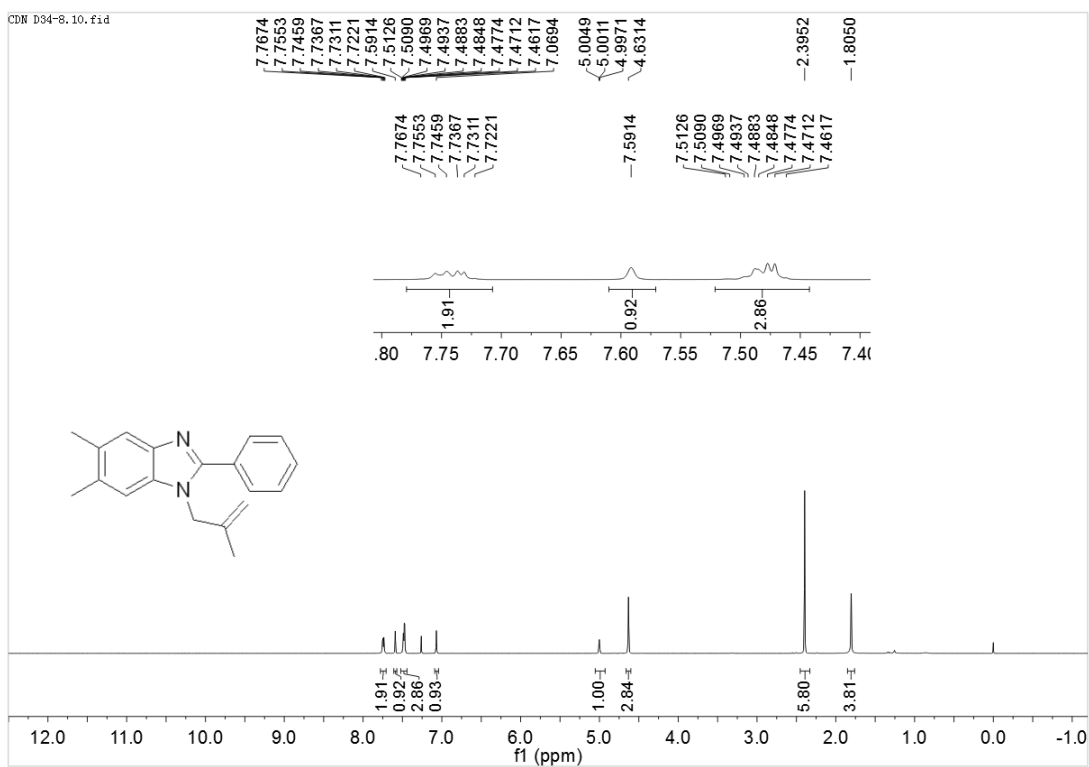
¹³C NMR



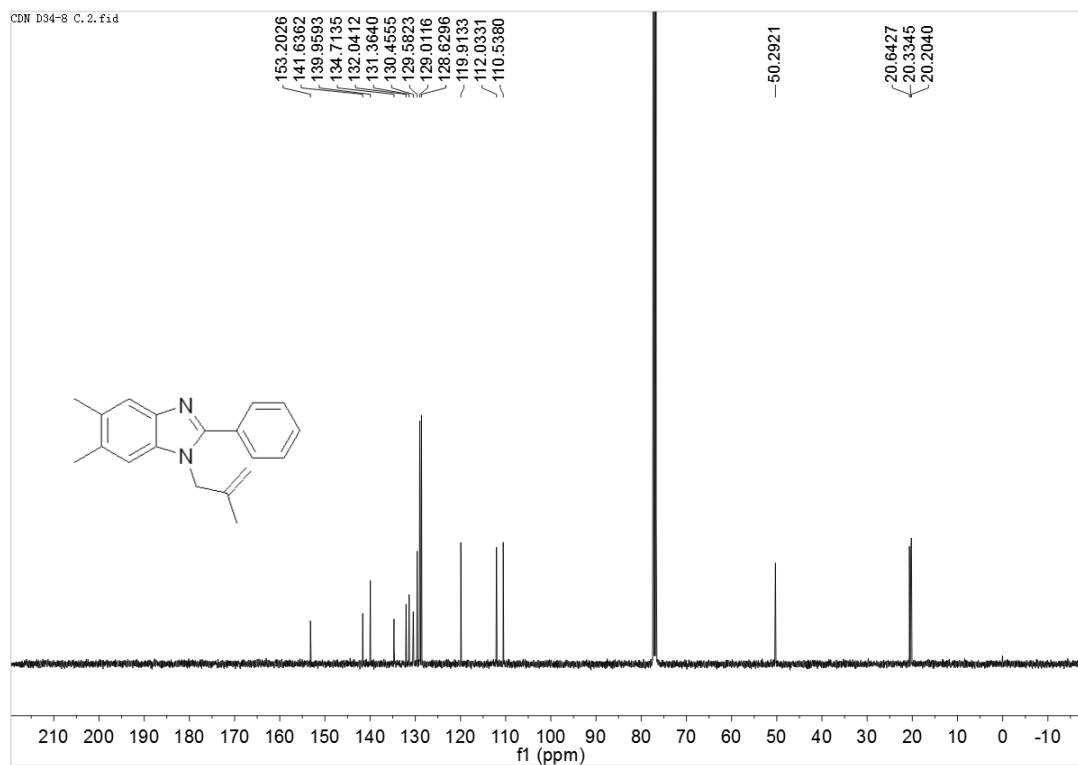
DEPT 90 and DEPT 135



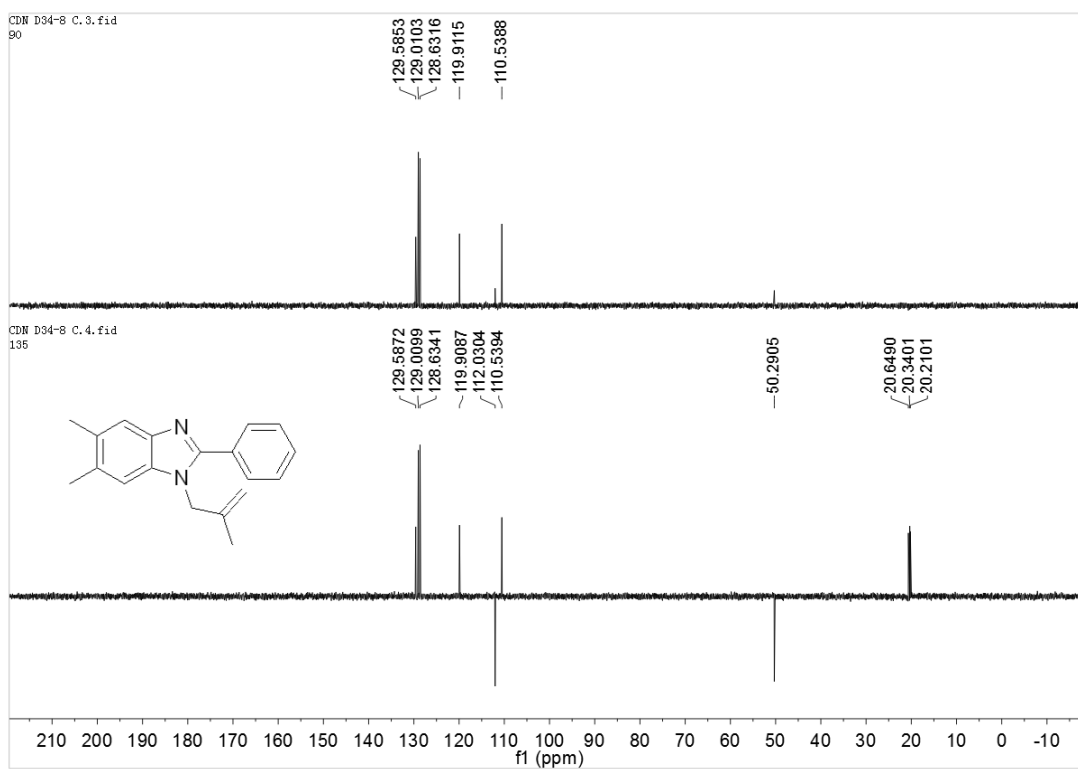
1h1, ¹H NMR



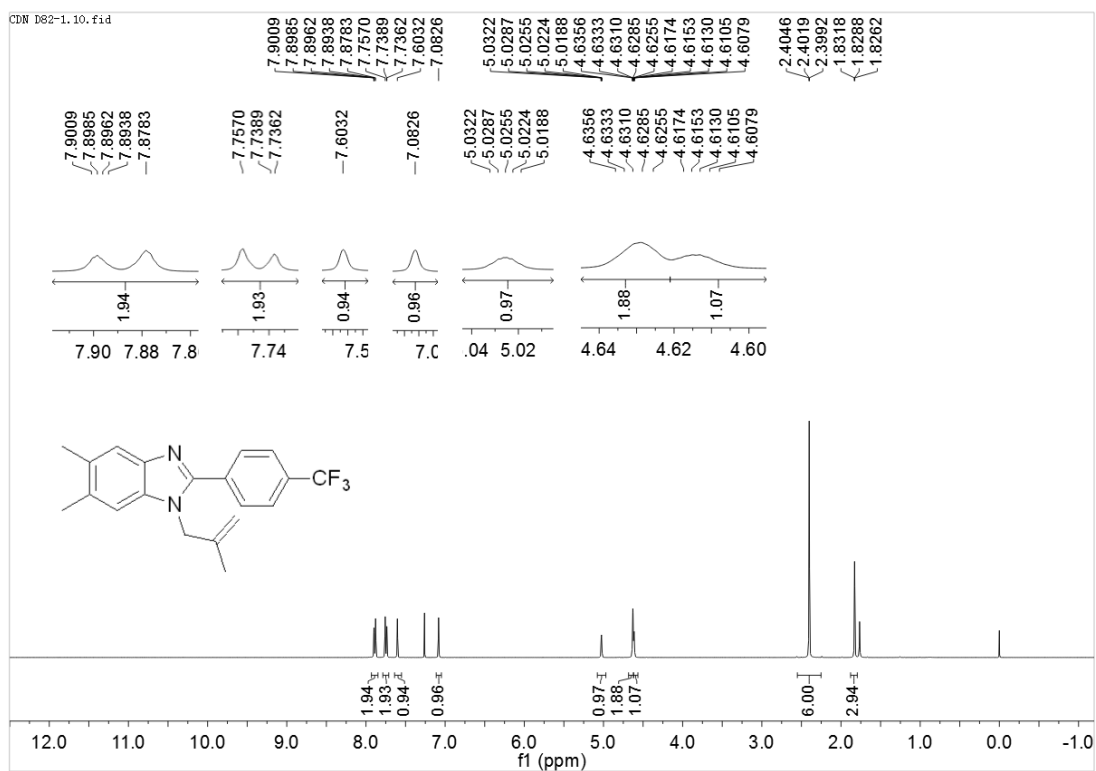
¹³C NMR



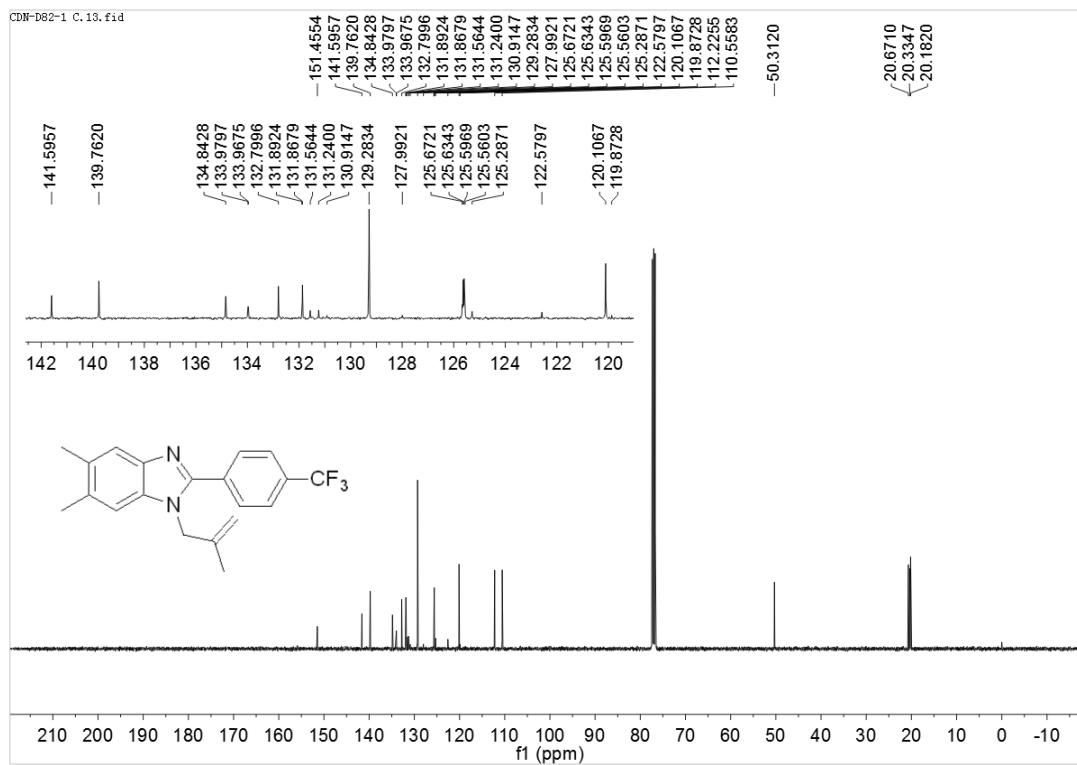
DEPT 90 and DEPT 135



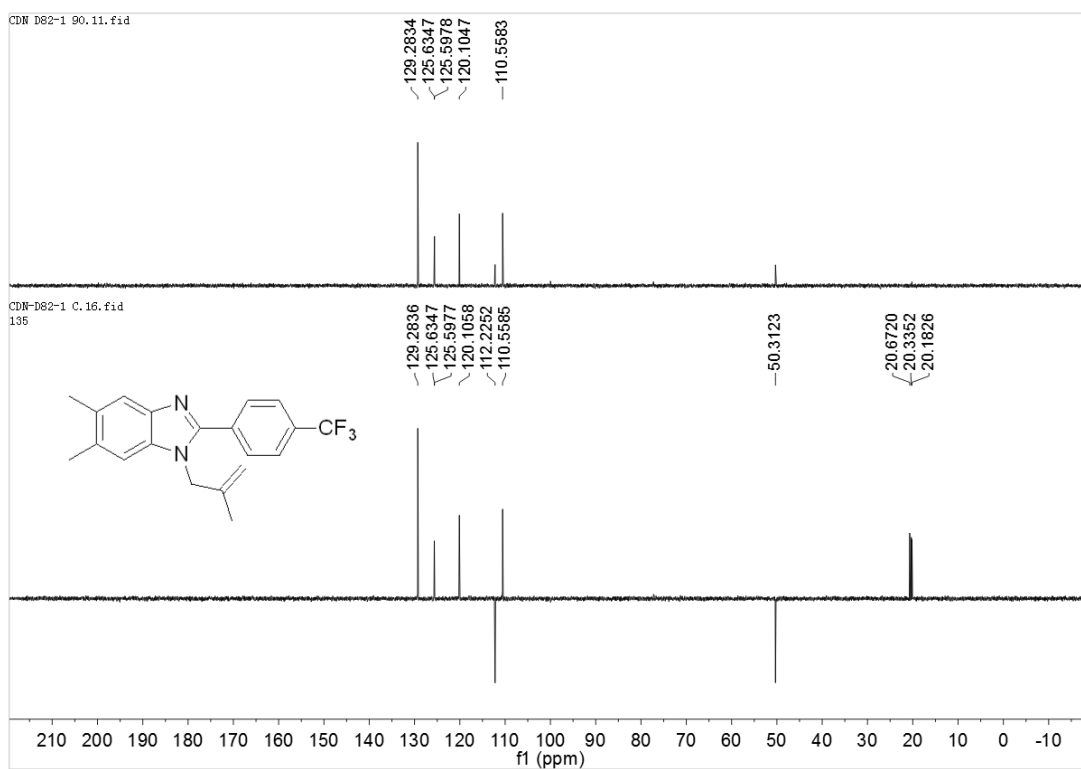
1h2, ¹H NMR



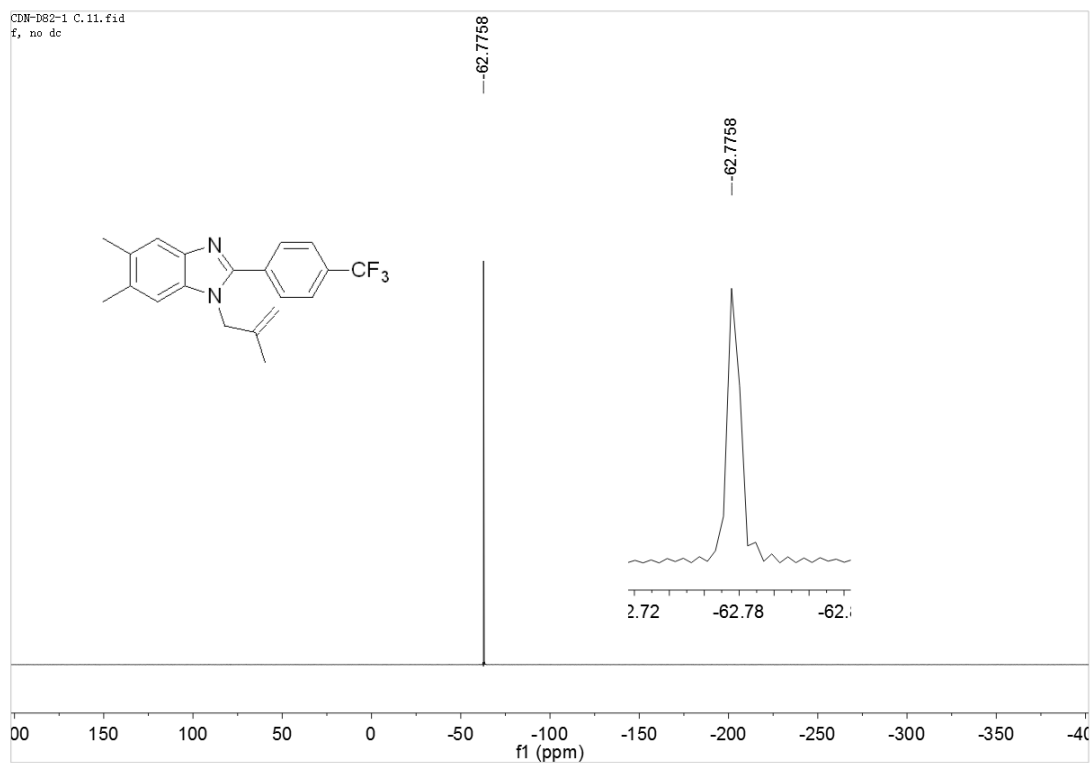
¹³C NMR



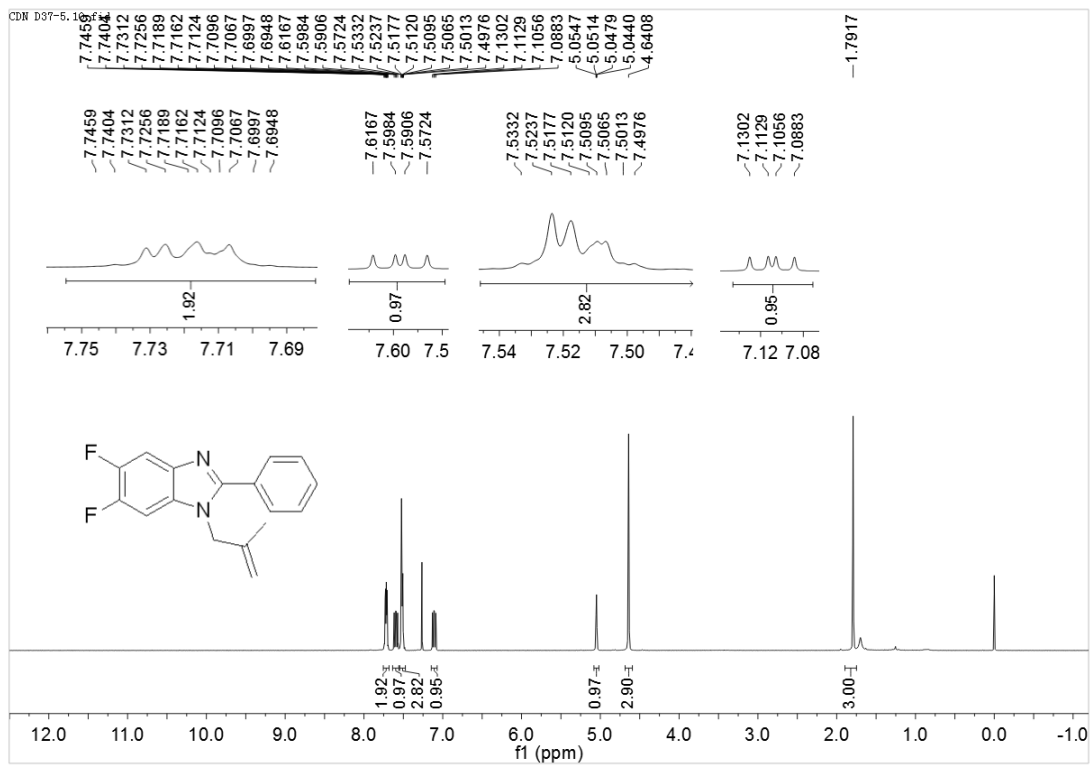
DEPT 90 and DEPT 135



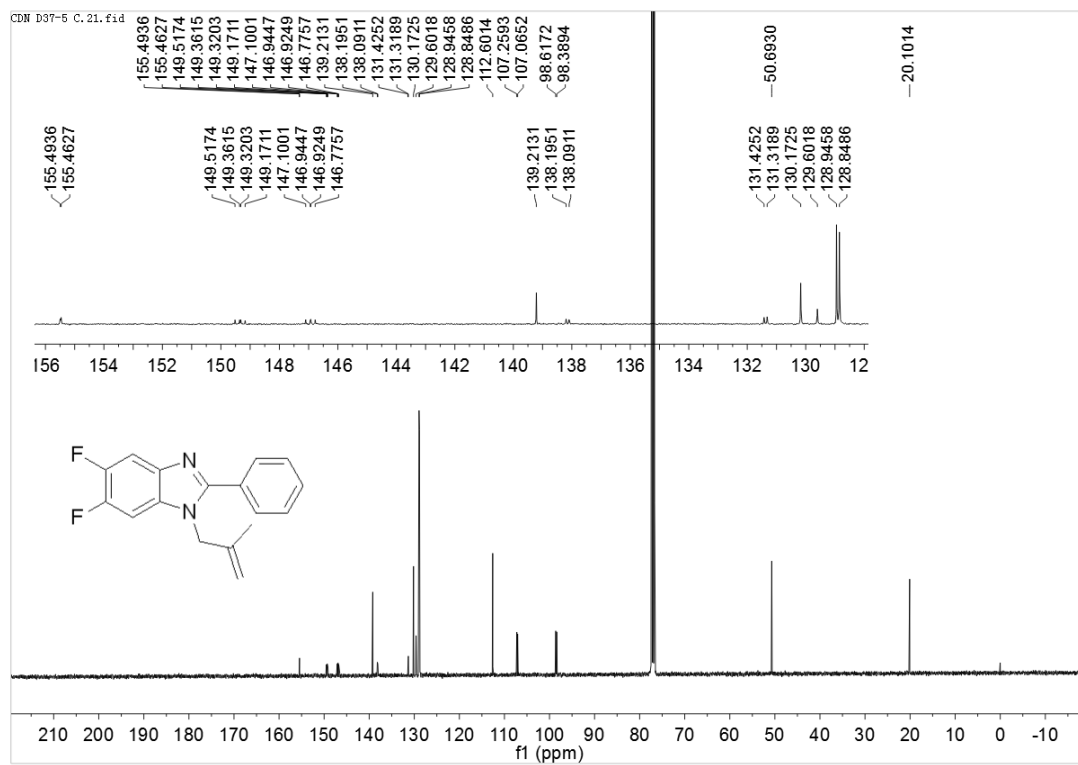
¹⁹F NMR



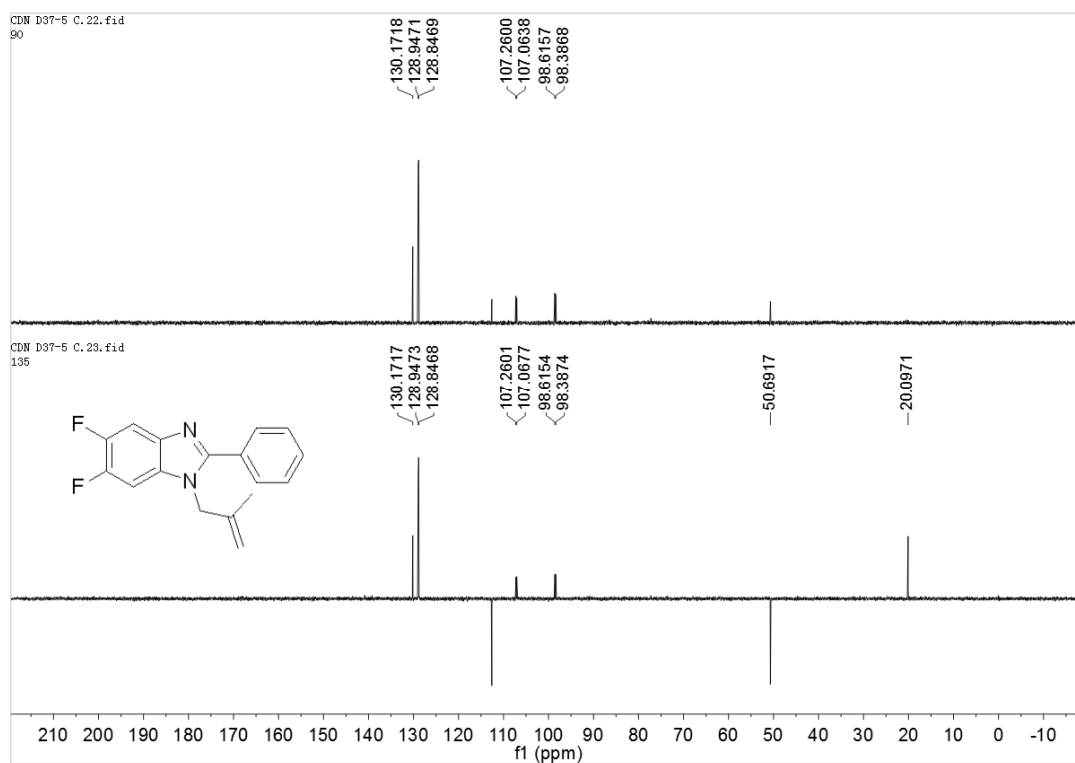
i, ¹H NMR



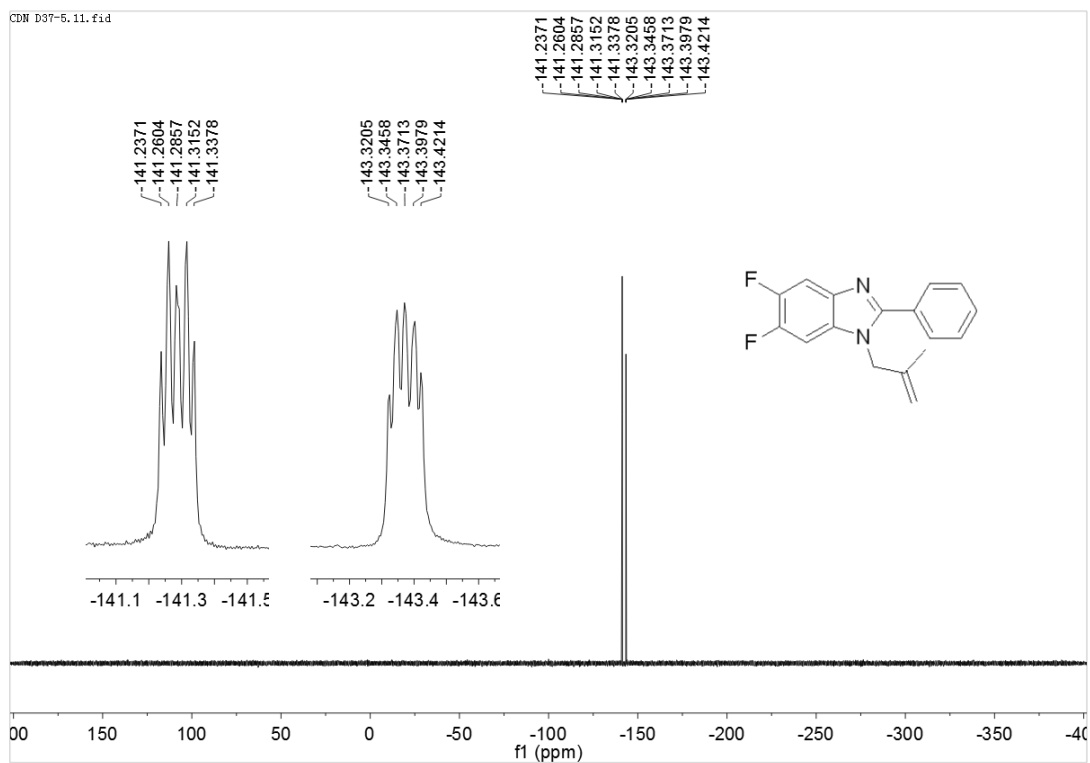
¹³C NMR



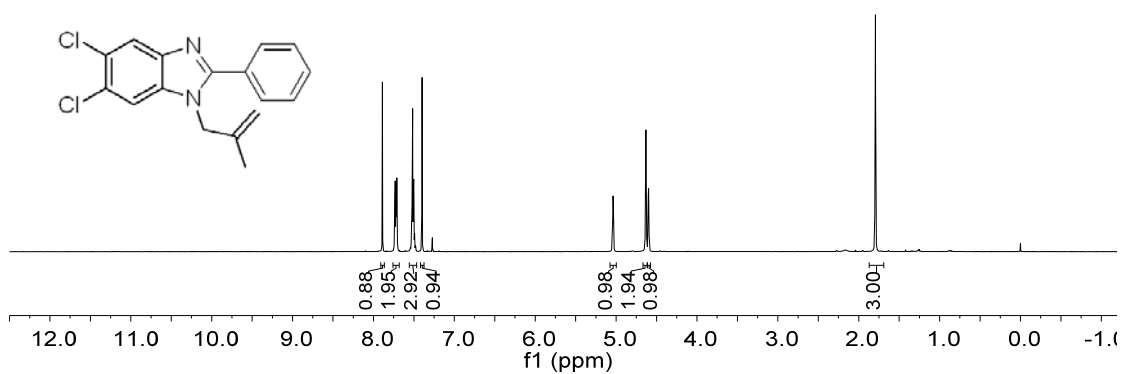
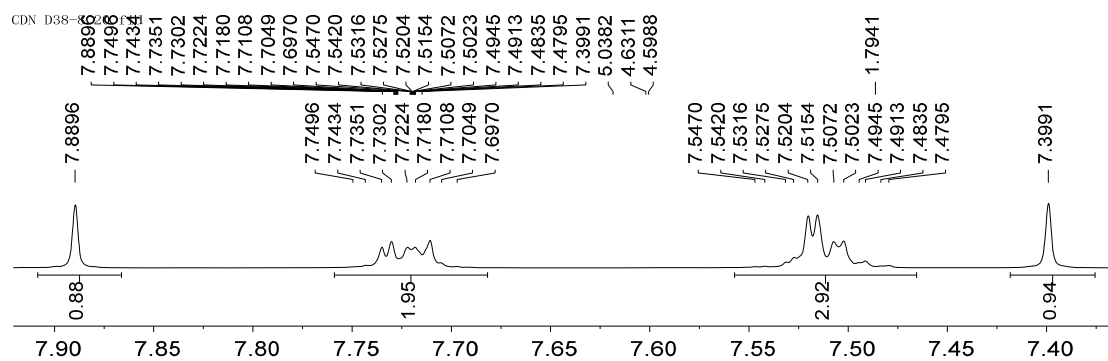
DEPT 90 and DEPT 135



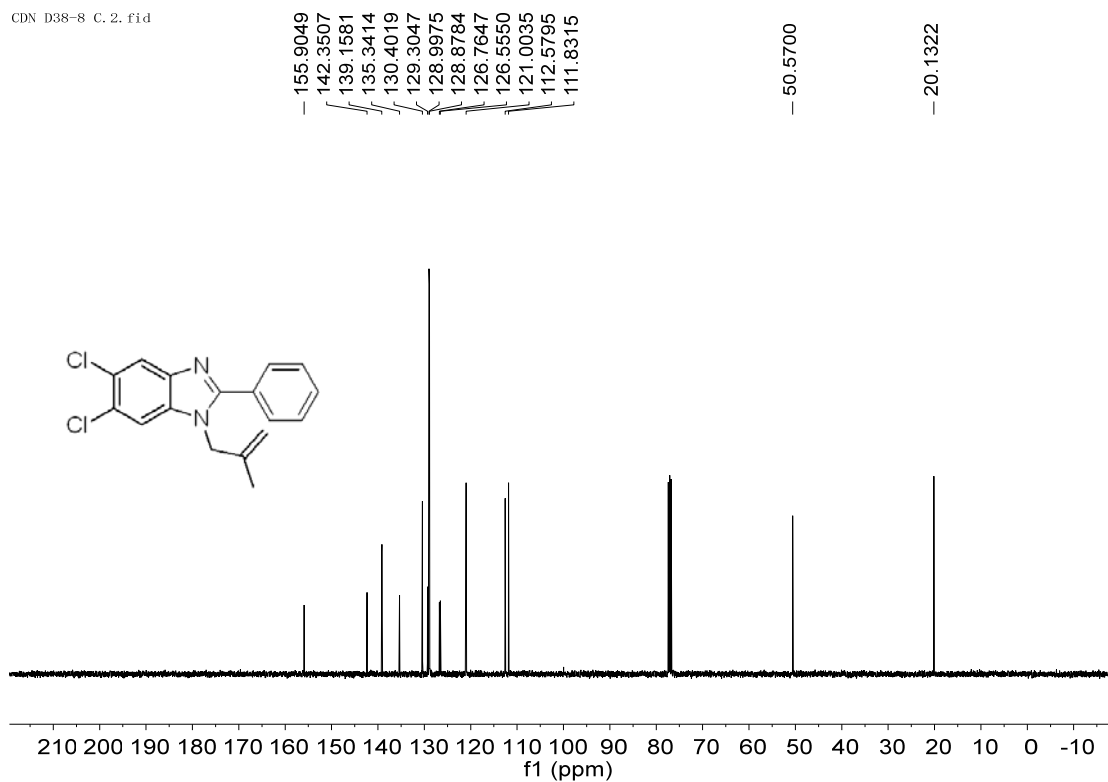
¹⁹F NMR



1j1, ¹H NMR



¹³C NMR

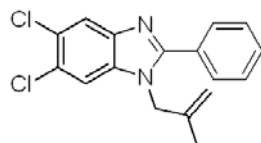


DEPT 90 and DEPT 135

CDN D38-8 C. 3. fid
90

130.4043
128.9967
128.8801
121.0023
111.8324

CDN D38-8 C. 4. fid
135



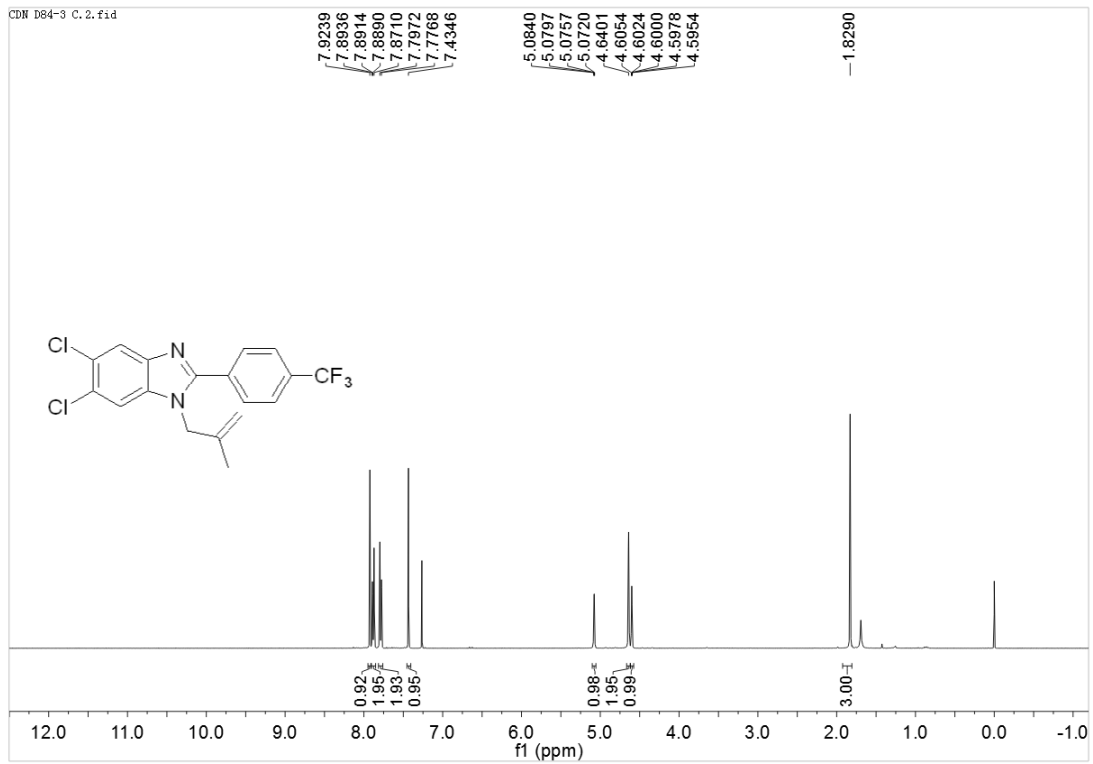
130.4049
128.9962
128.8804
121.0016
112.5776
111.8327

- 50.5687

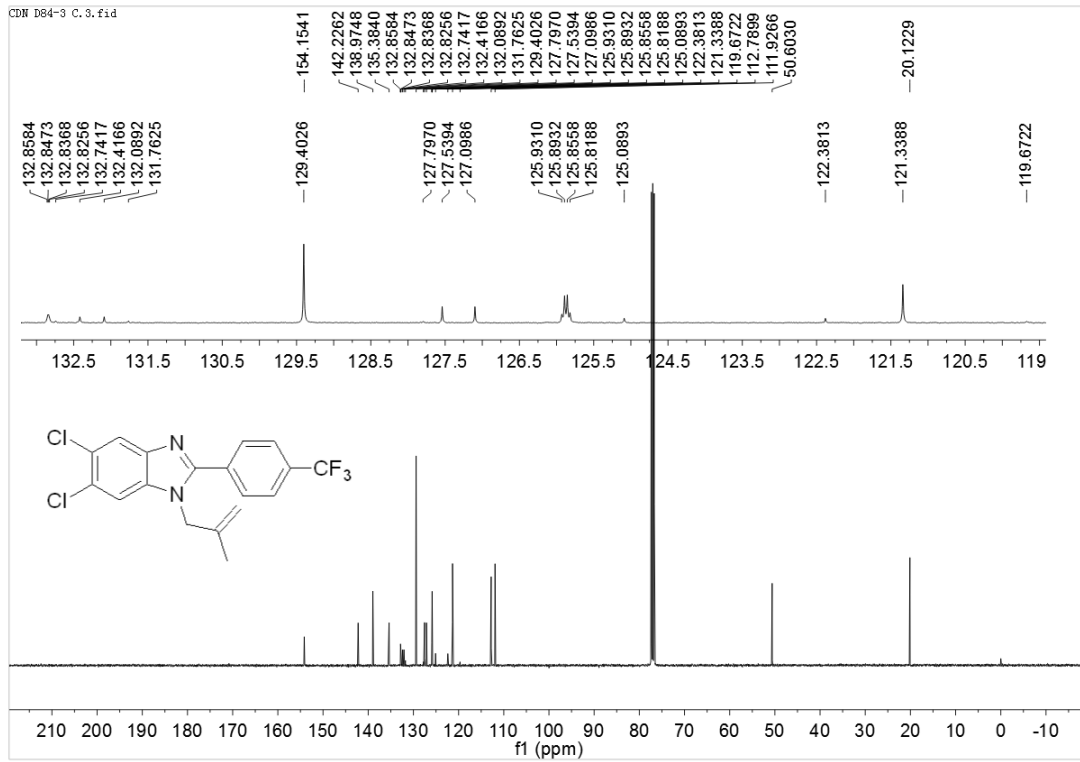
- 20.1363

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)

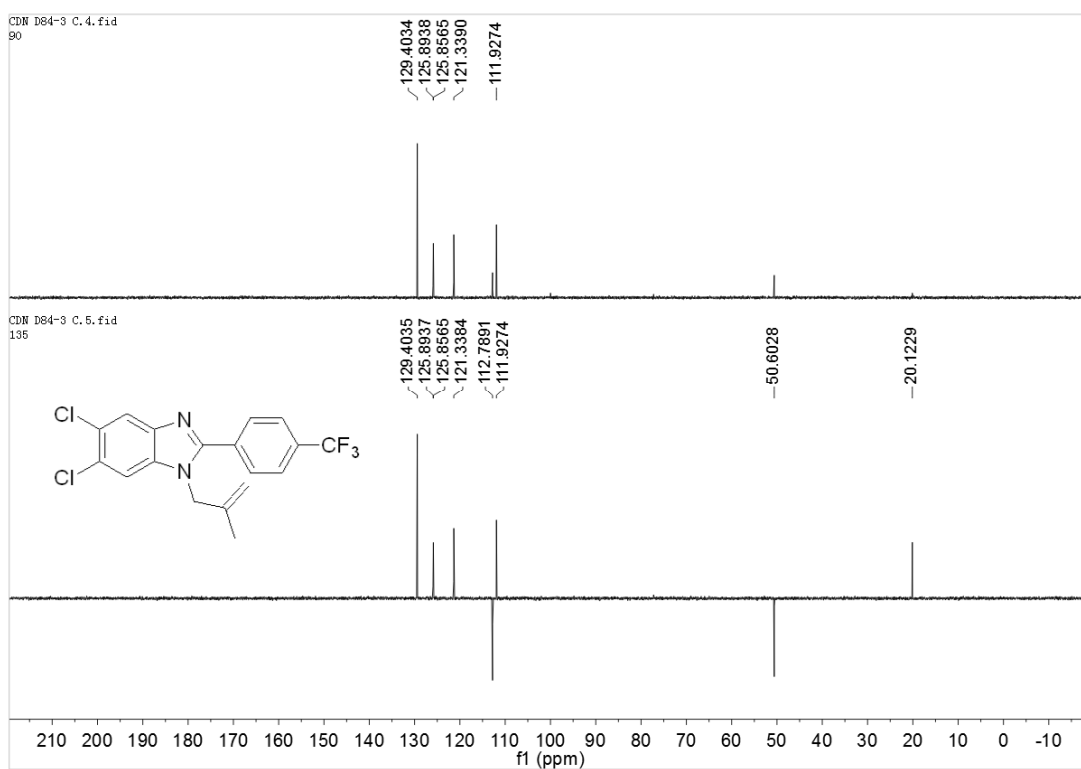
1j2, ¹H NMR



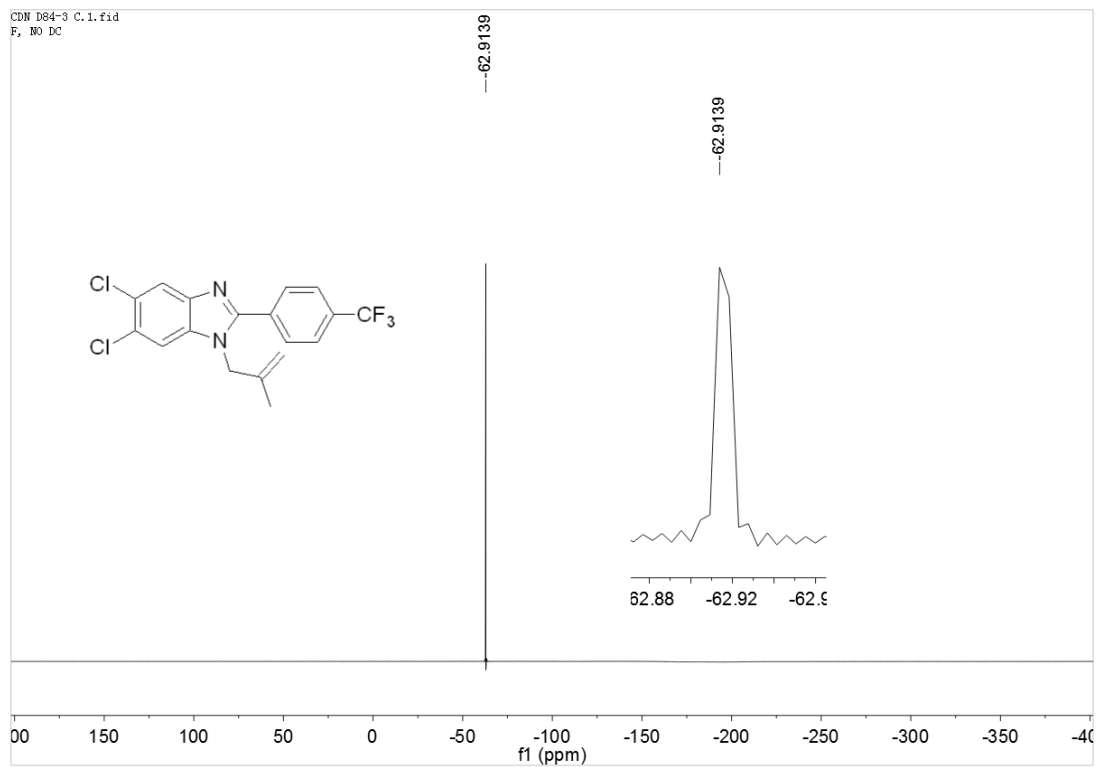
¹³C NMR



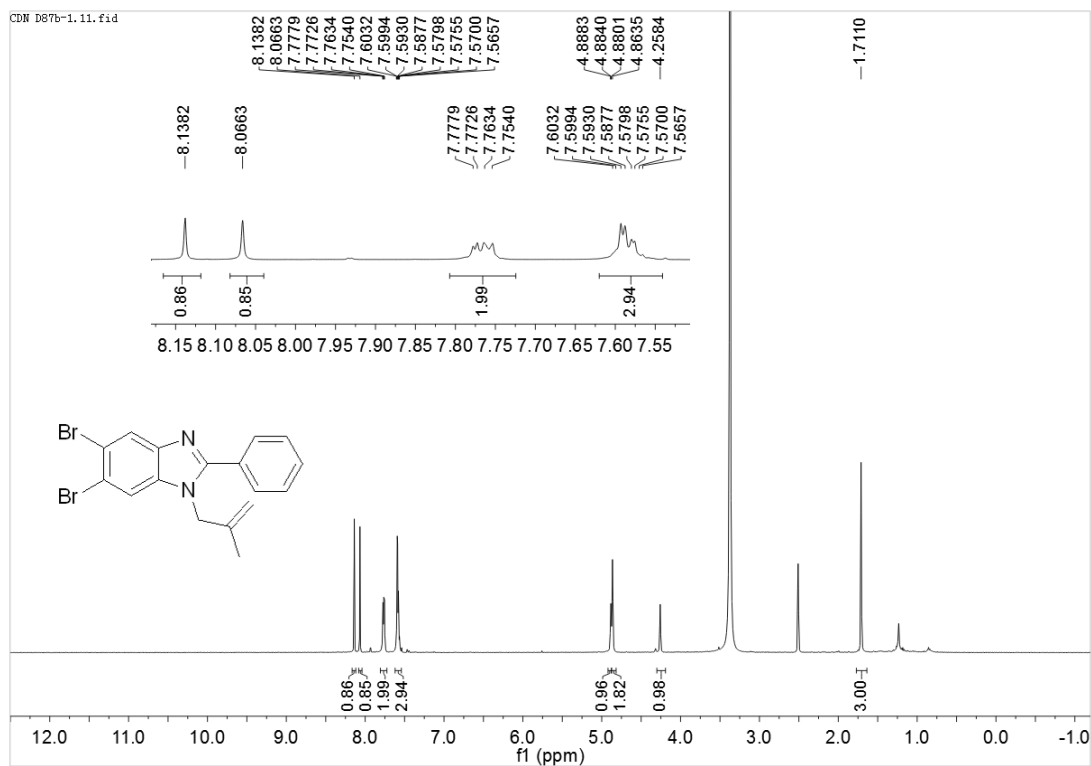
DEPT 90 and DEPT 135



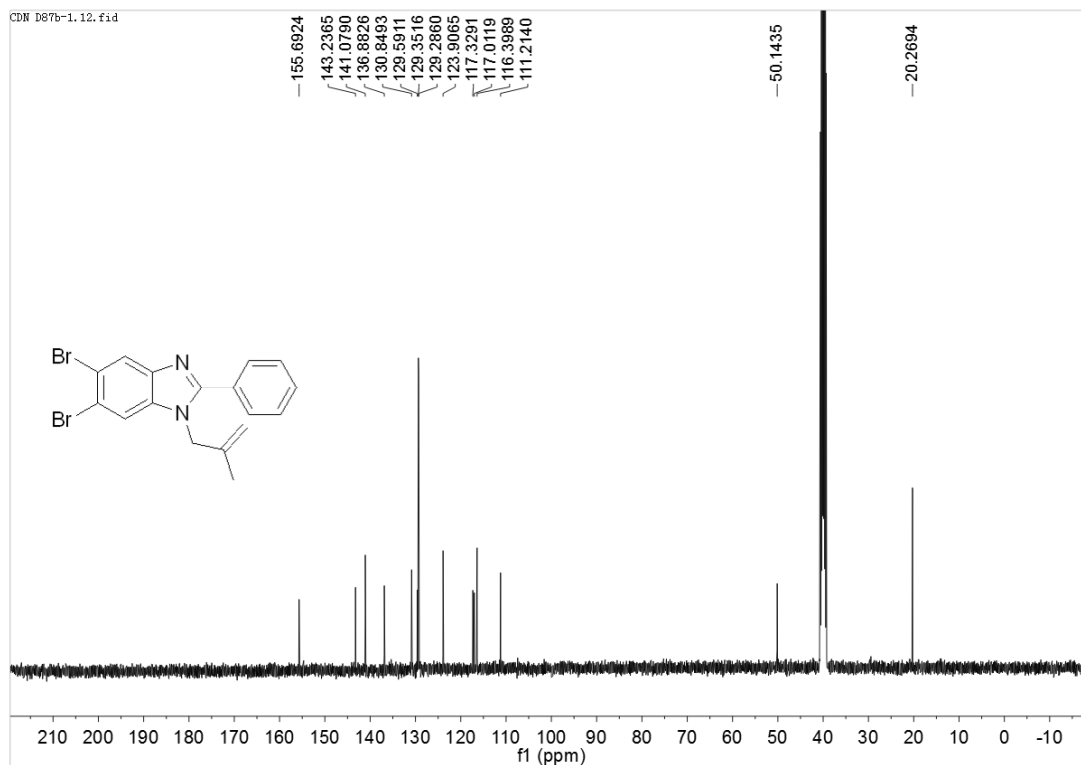
¹⁹F NMR



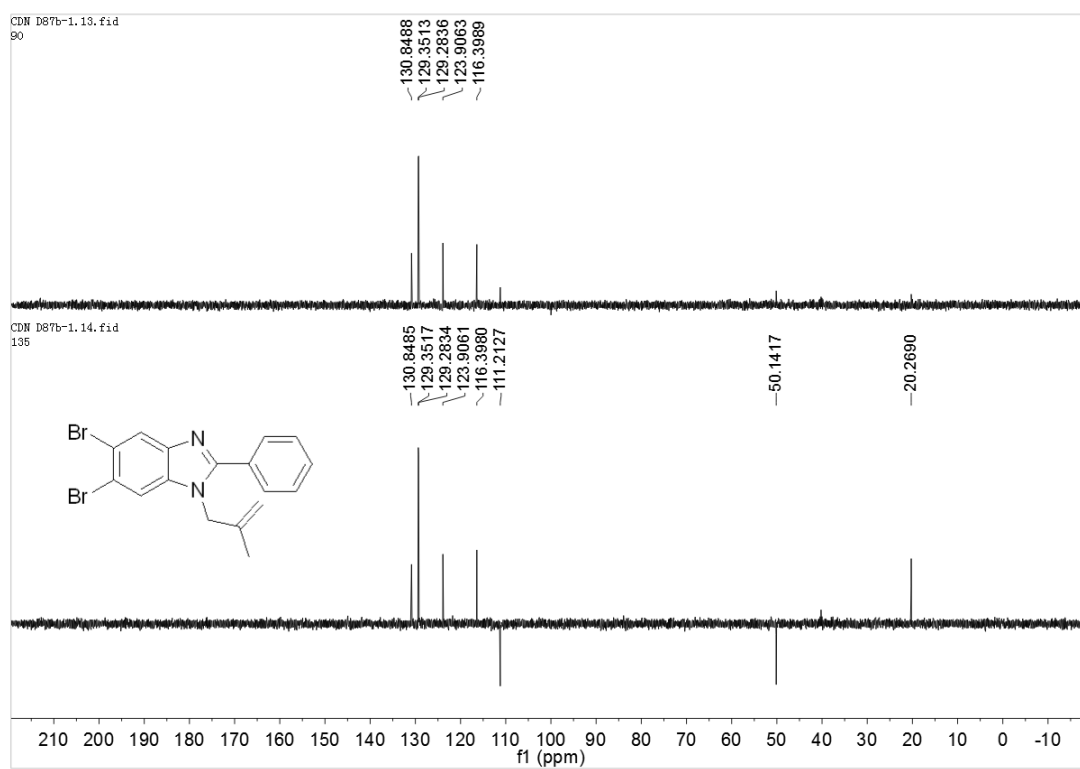
1k, ¹H NMR



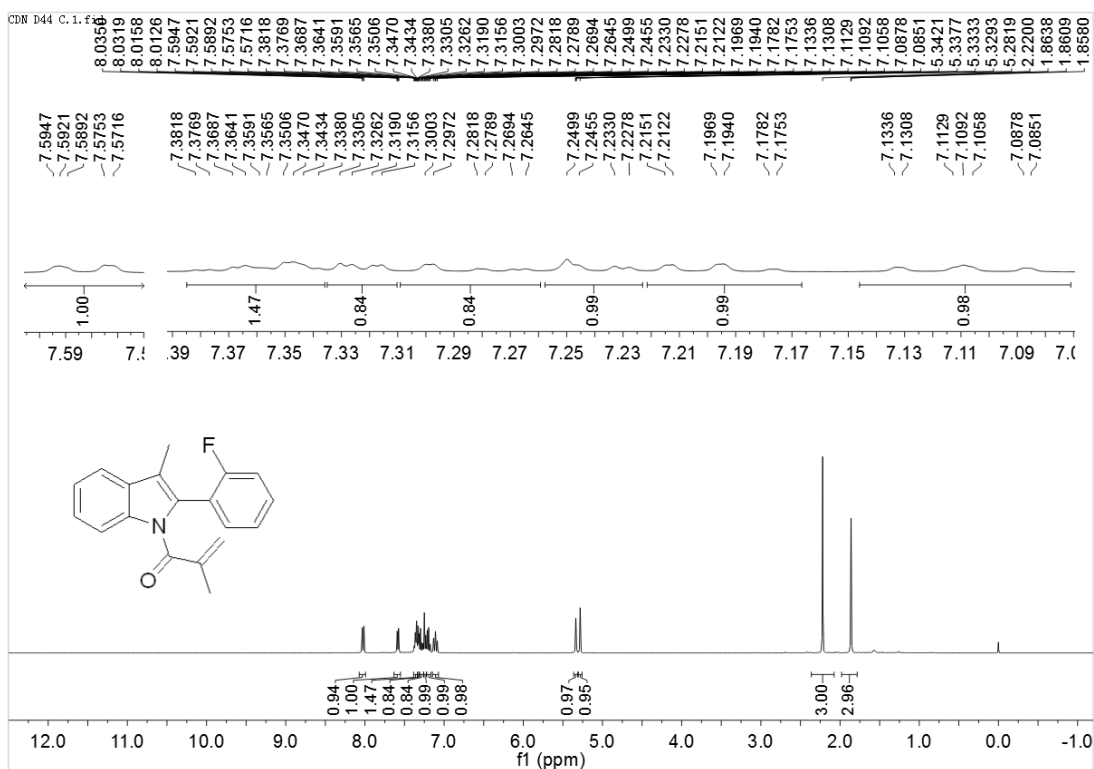
¹³C NMR



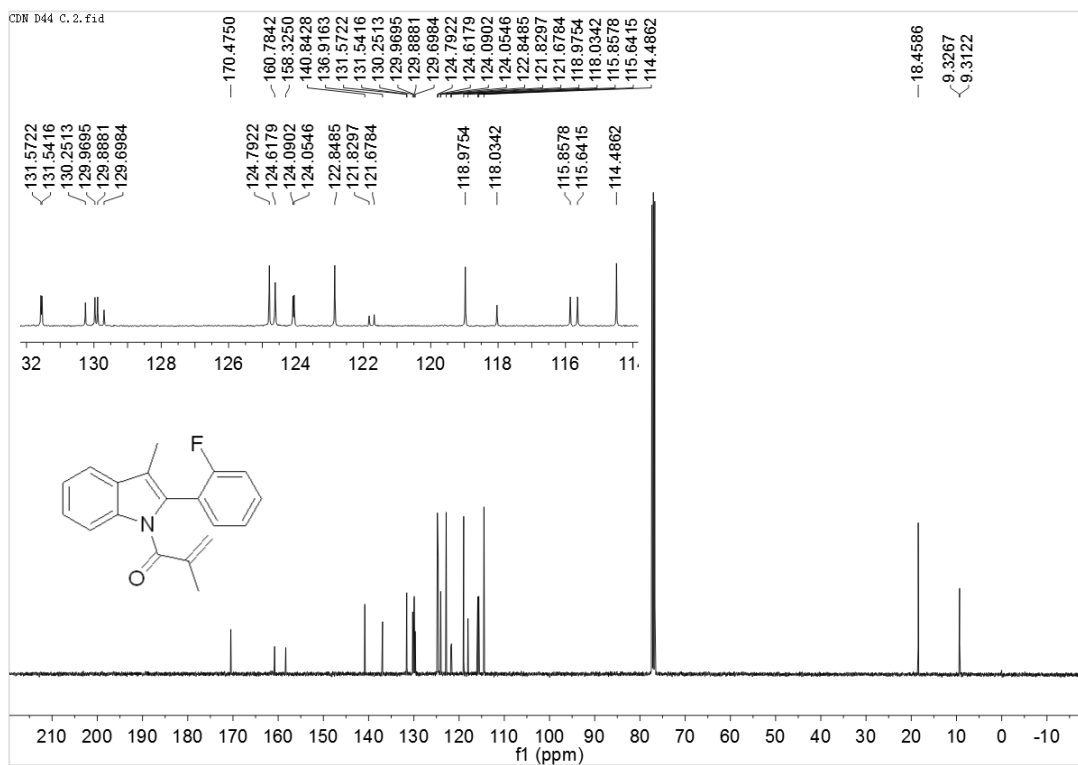
DEPT 90 and DEPT 135



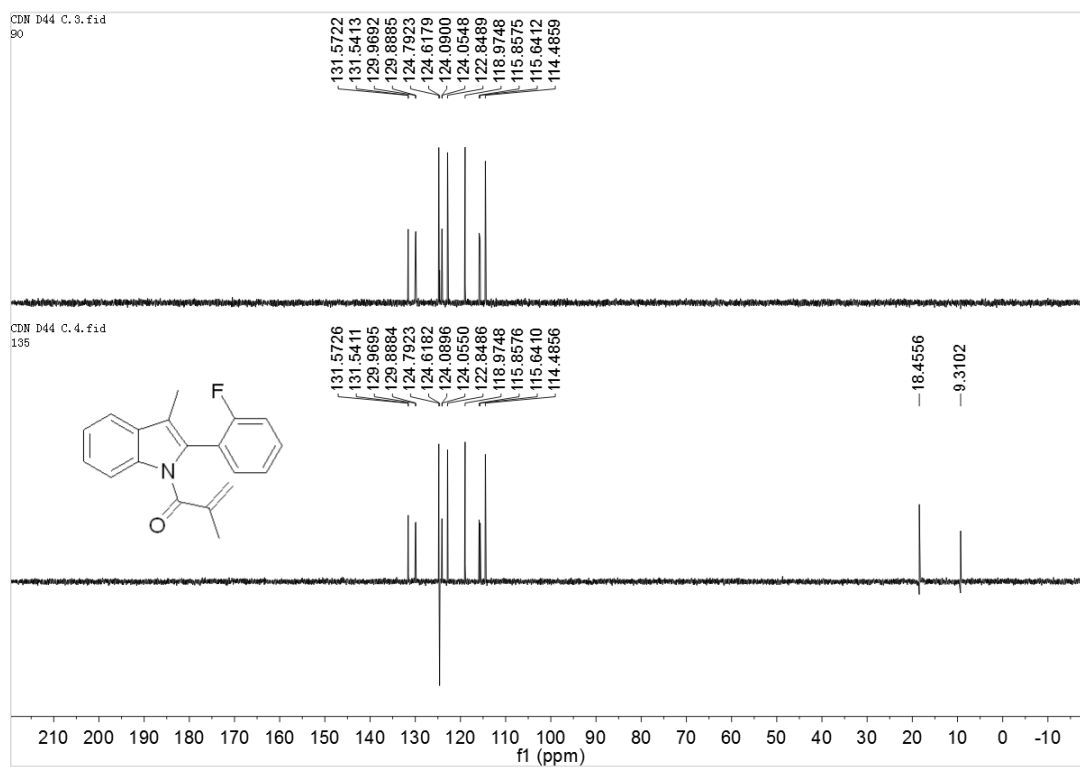
1m, ¹H NMR



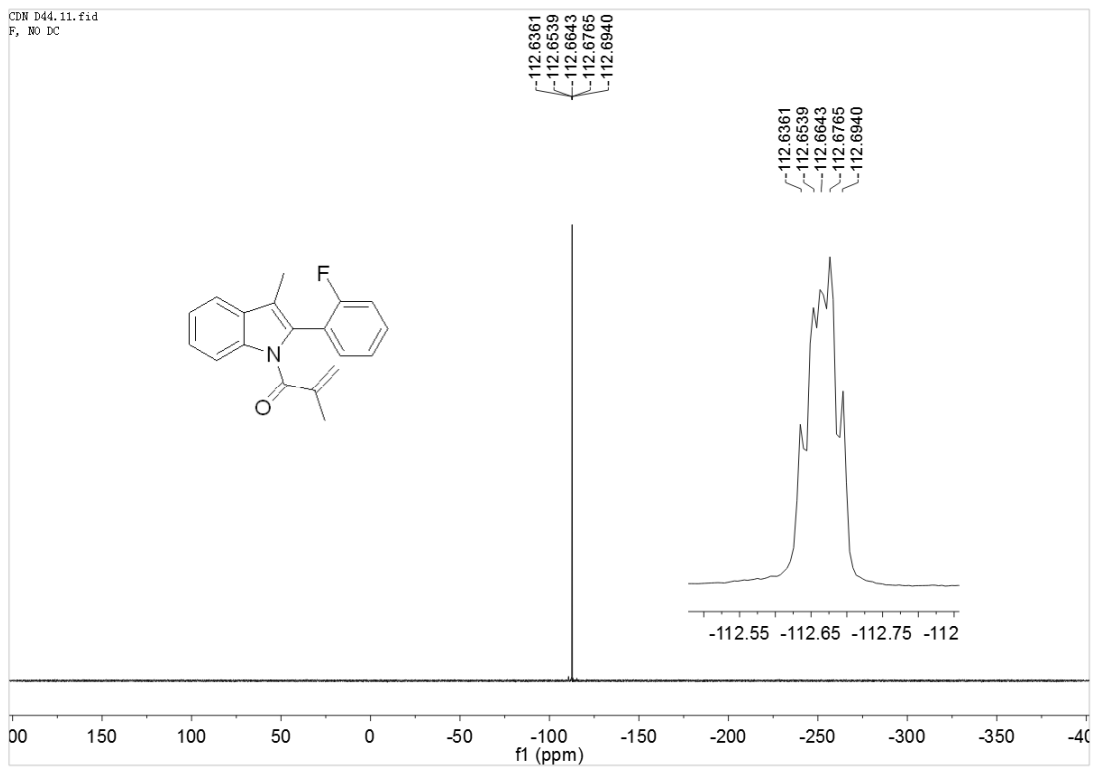
¹³C NMR



DEPT 90 and DEPT 135

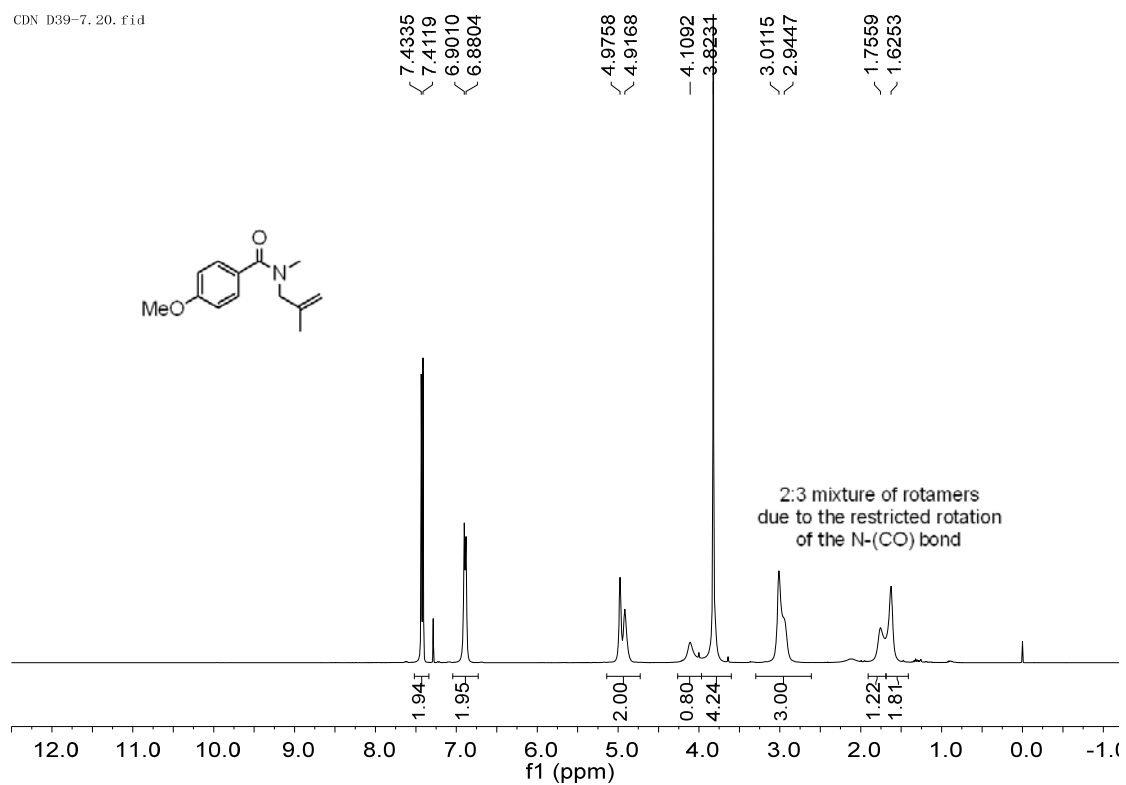


¹⁹F NMR



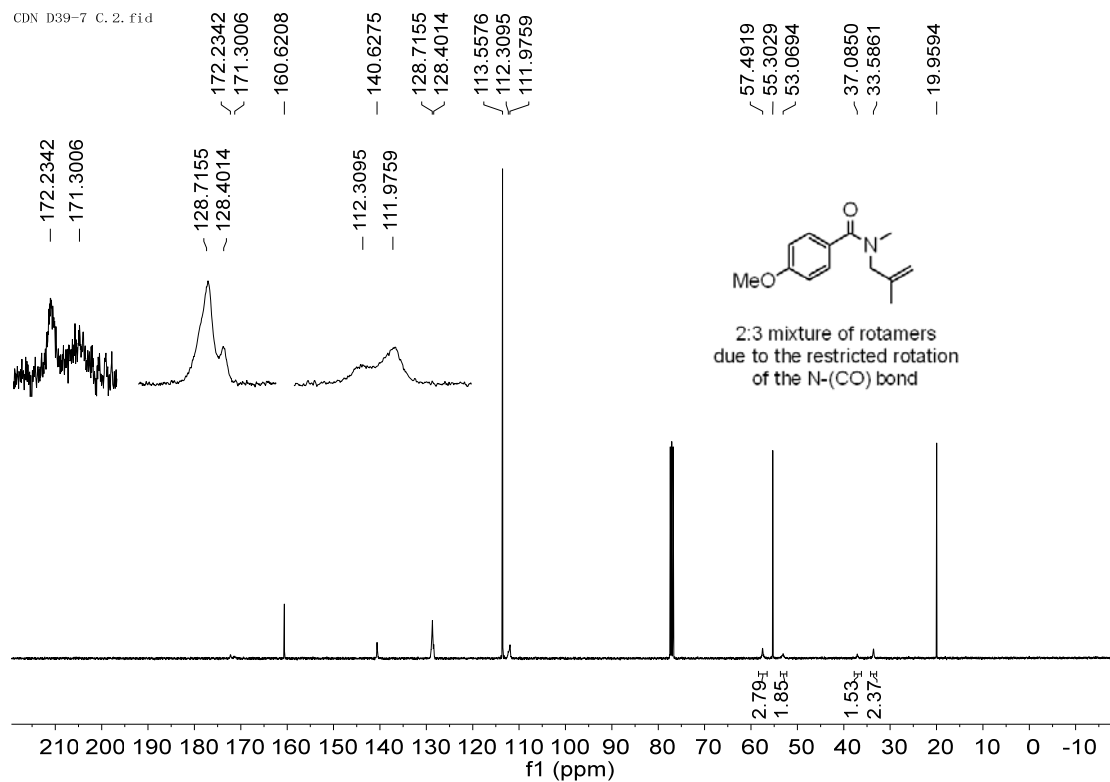
8b, ¹H NMR

CDN D39-7. 20. fid



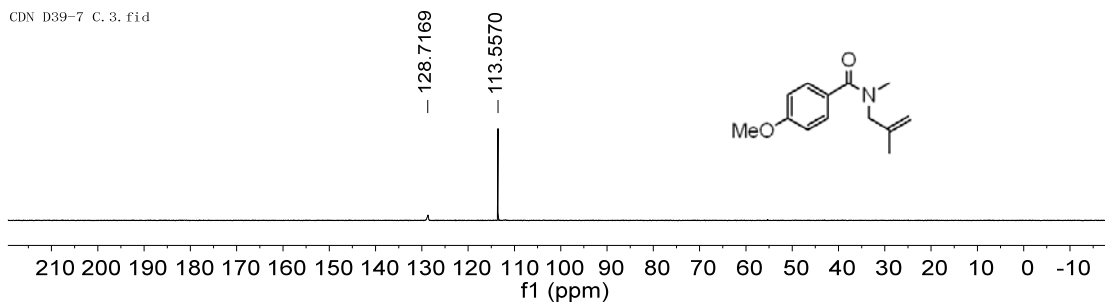
¹³C NMR

CDN D39-7 C. 2. fid

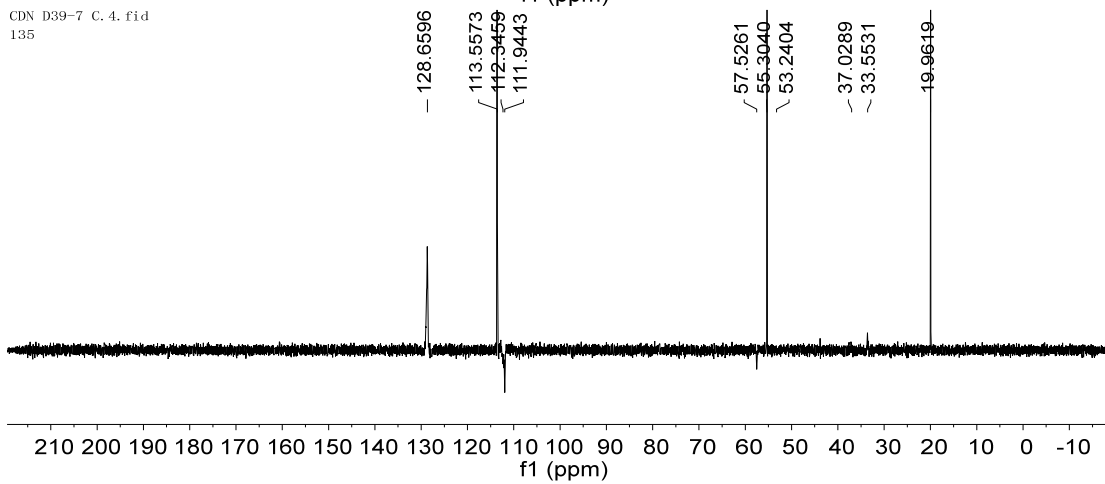


DEPT 90 and DEPT 135

CDN D39-7 C. 3. fid

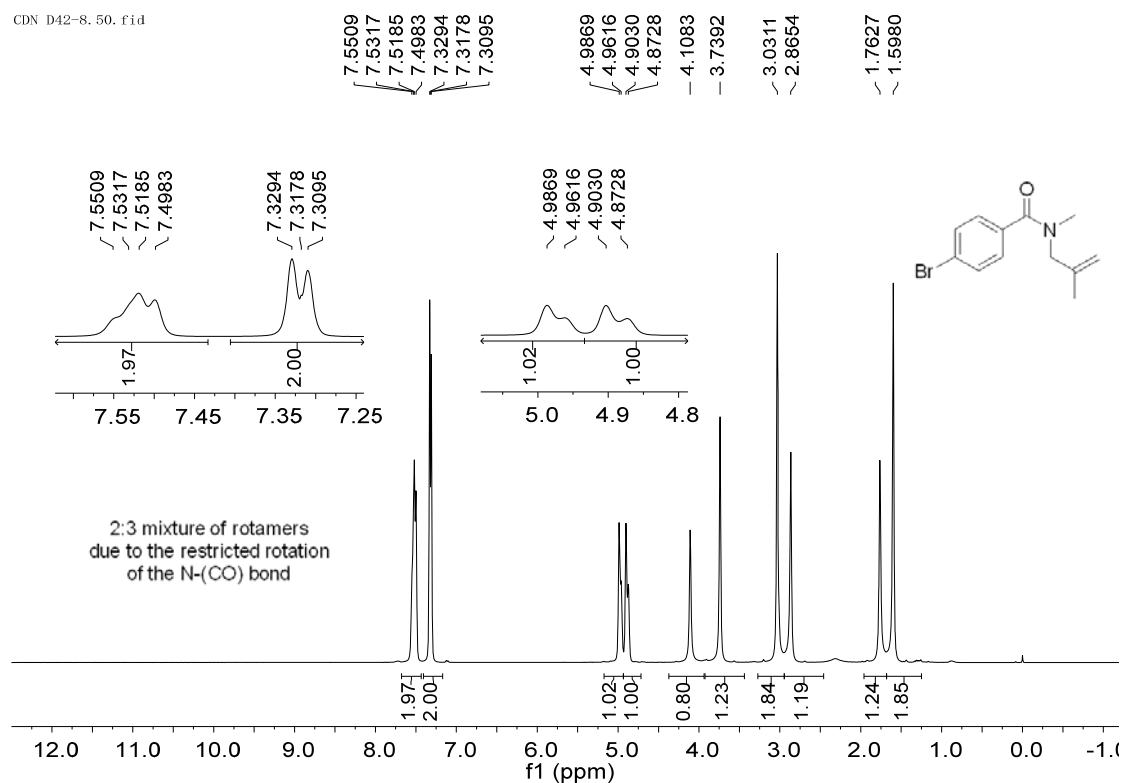


CDN D39-7 C. 4. fid
135



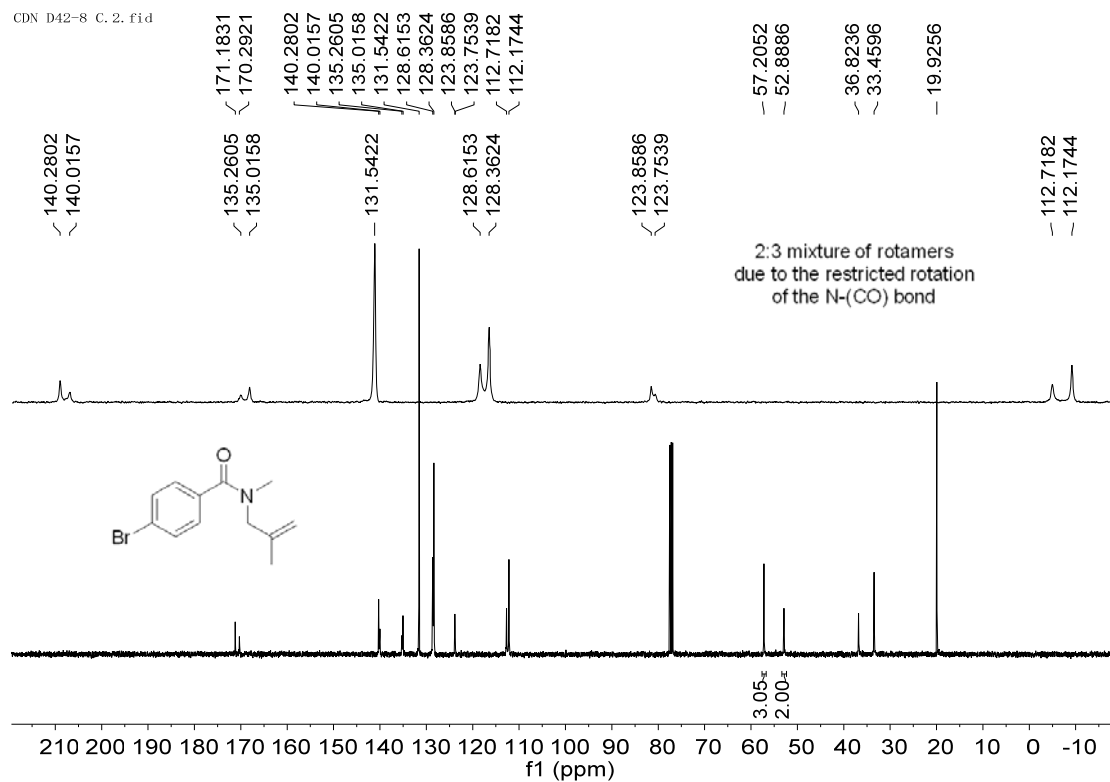
8c, ¹H NMR

CDN D42-8. 50. fid



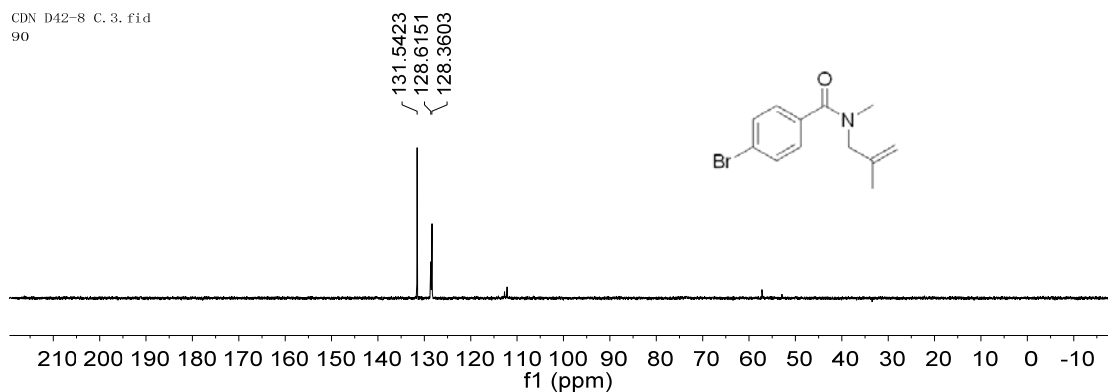
¹³C NMR

CDN D42-8 C. 2. fid

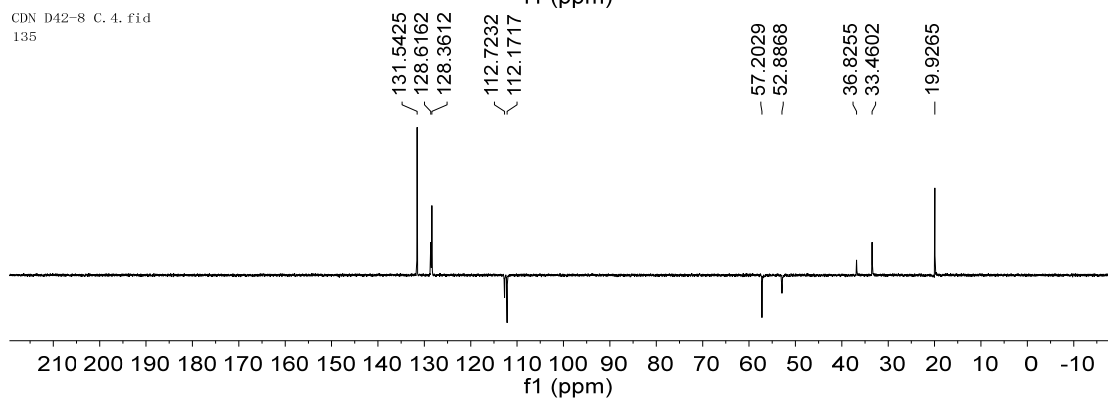


DEPT 90 and DEPT 135

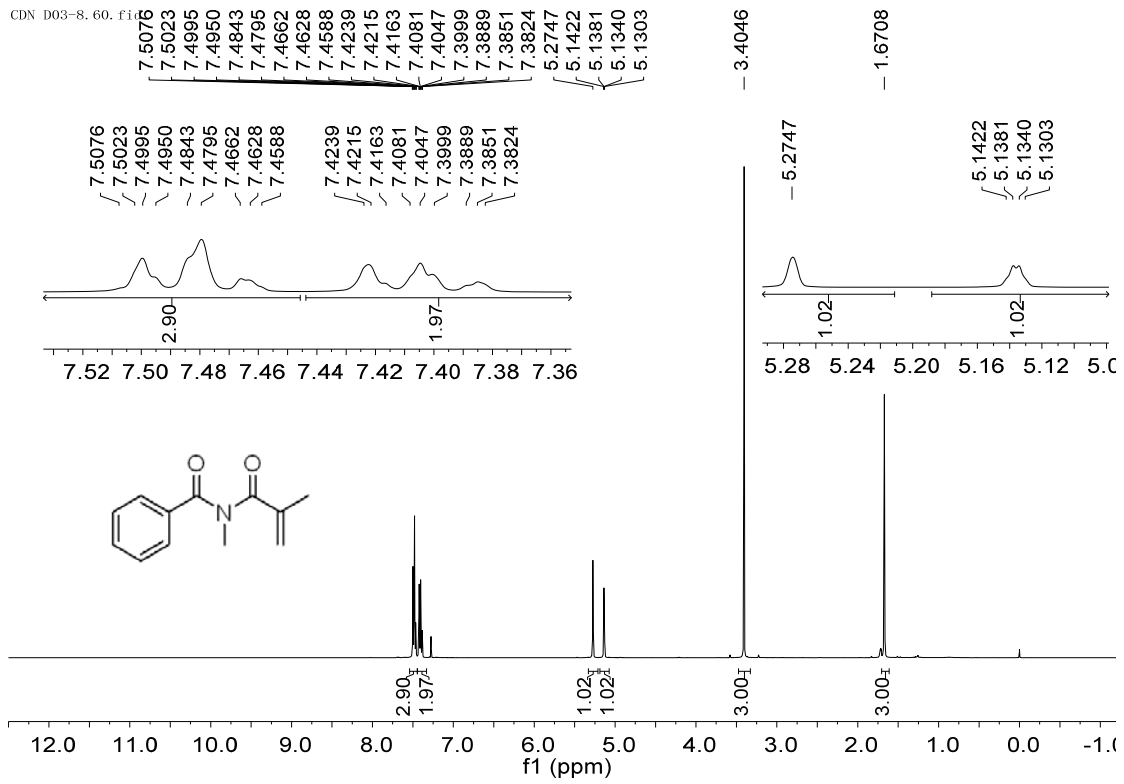
CDN D42-8 C. 3. fid
90



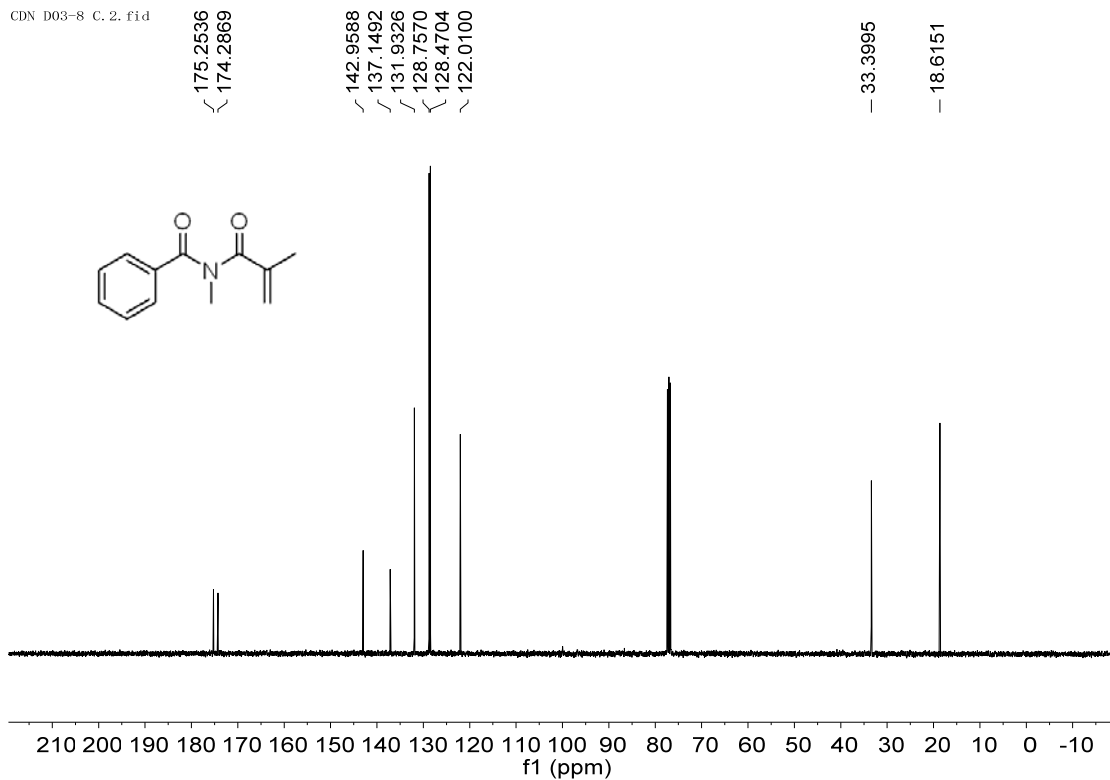
CDN D42-8 C. 4. fid
135



8d, ¹H NMR

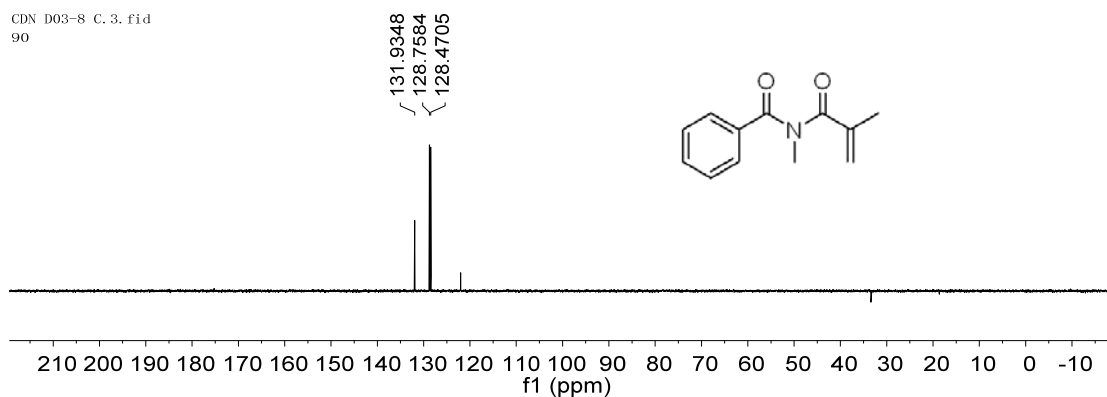


¹³C NMR

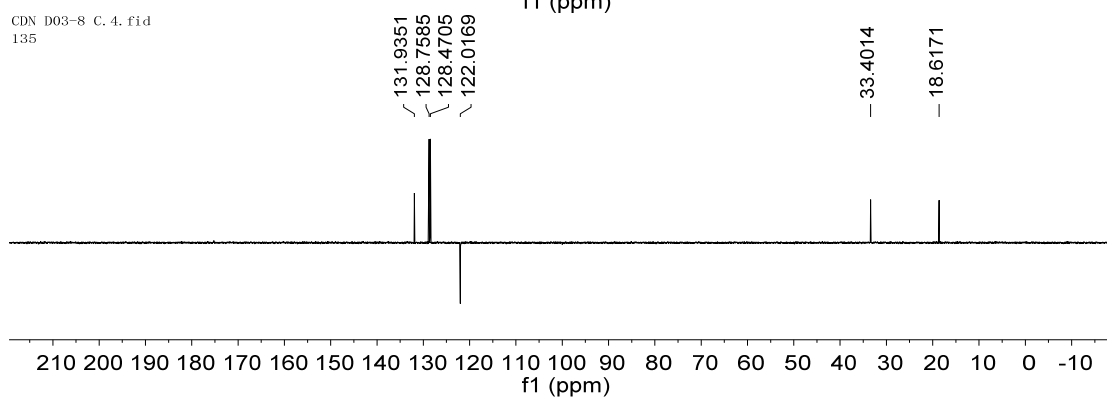


DEPT 90 and DEPT 135

CDN D03-8 C. 3. fid
90

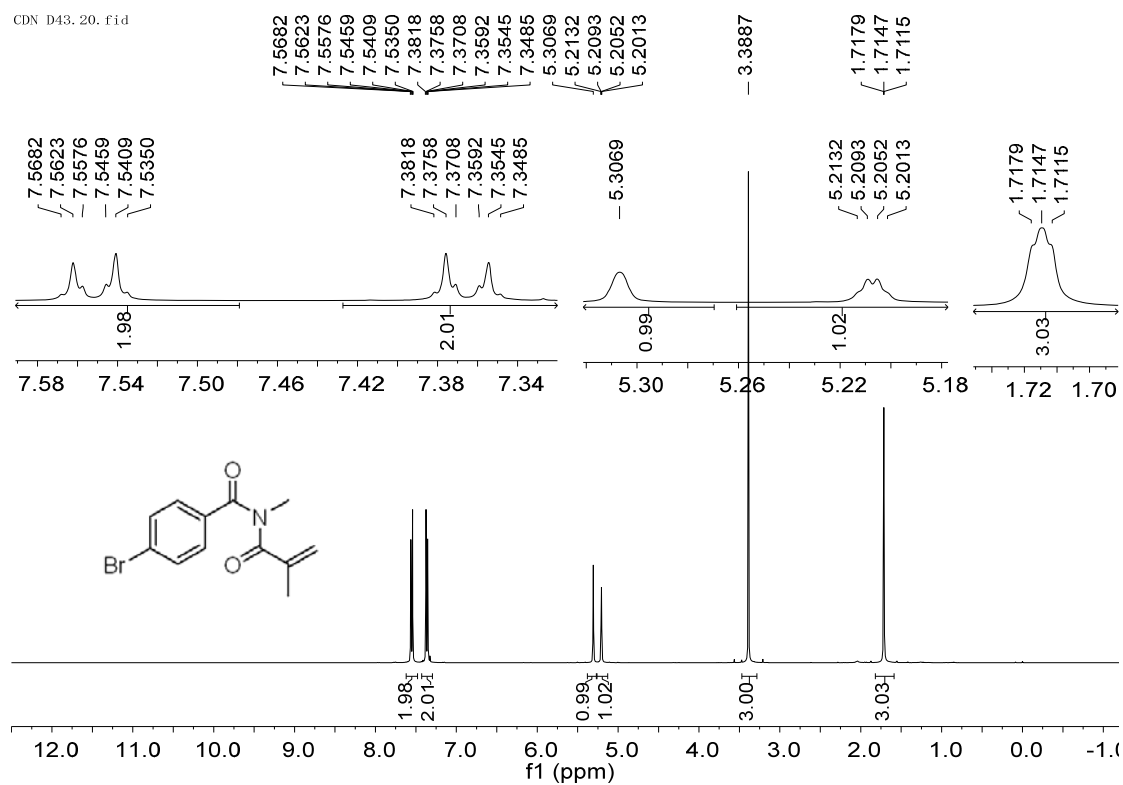


CDN D03-8 C. 4. fid
135



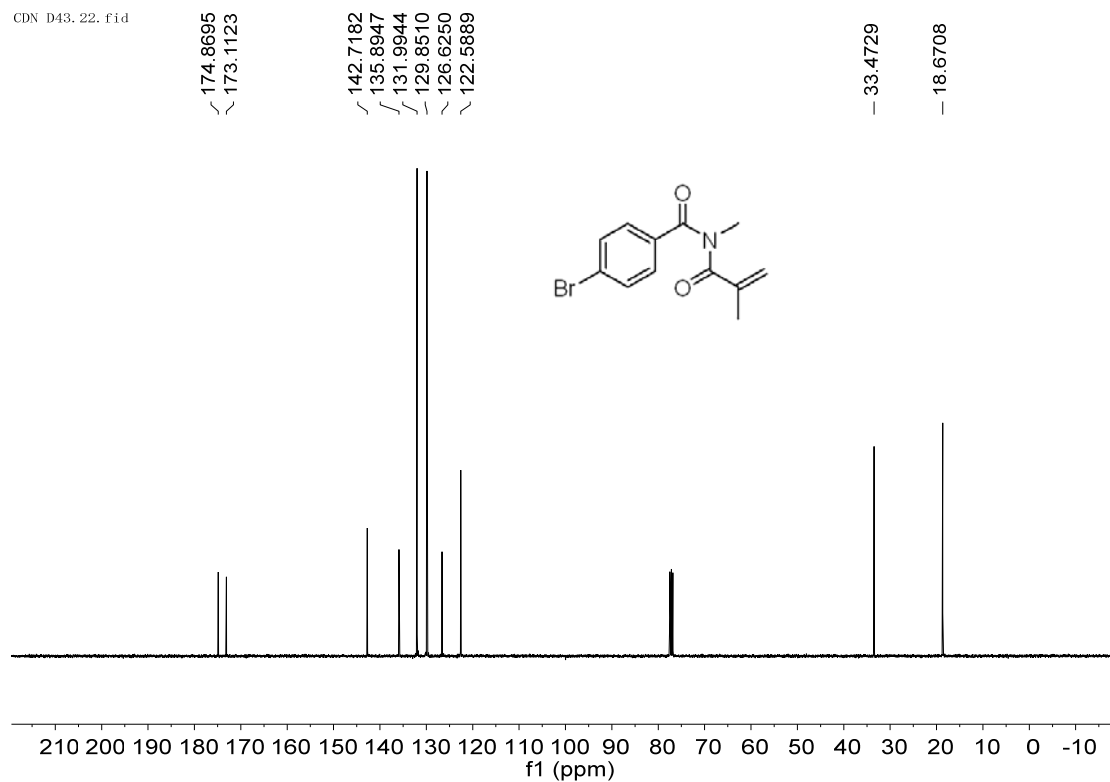
8f, ¹H NMR

CDN D43. 20. fid



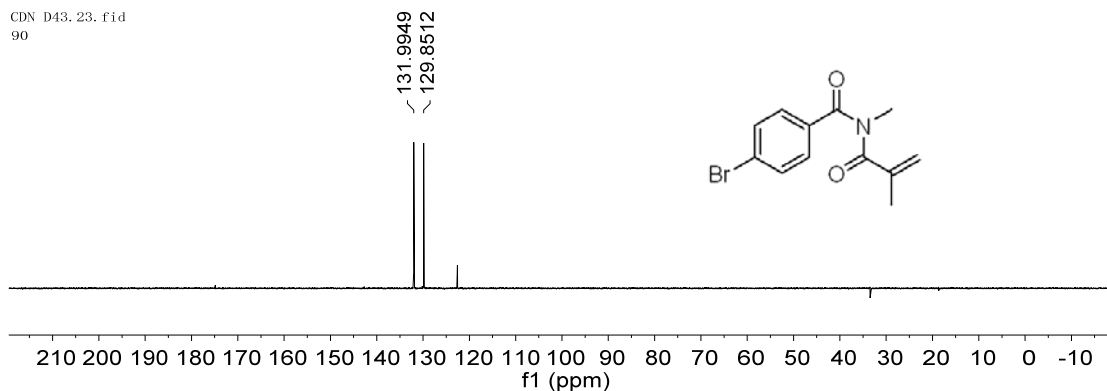
¹³C NMR

CDN D43. 22. fid

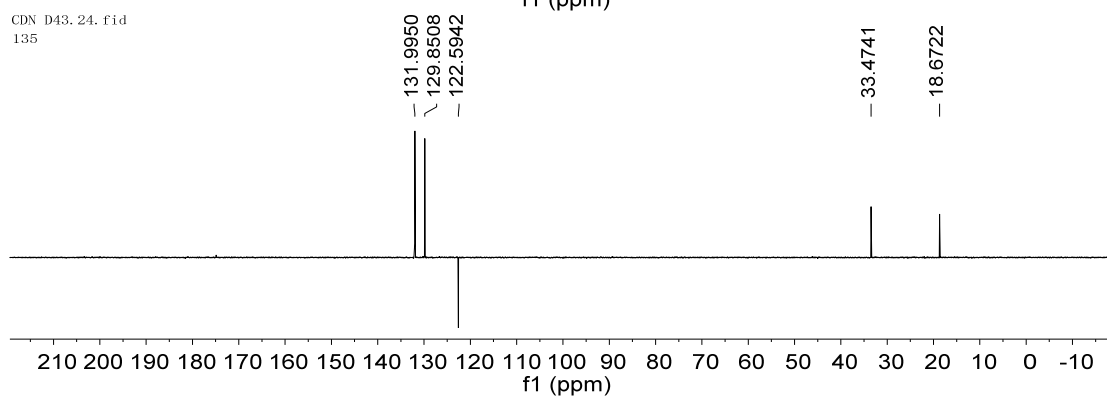


DEPT 90 and DEPT 135

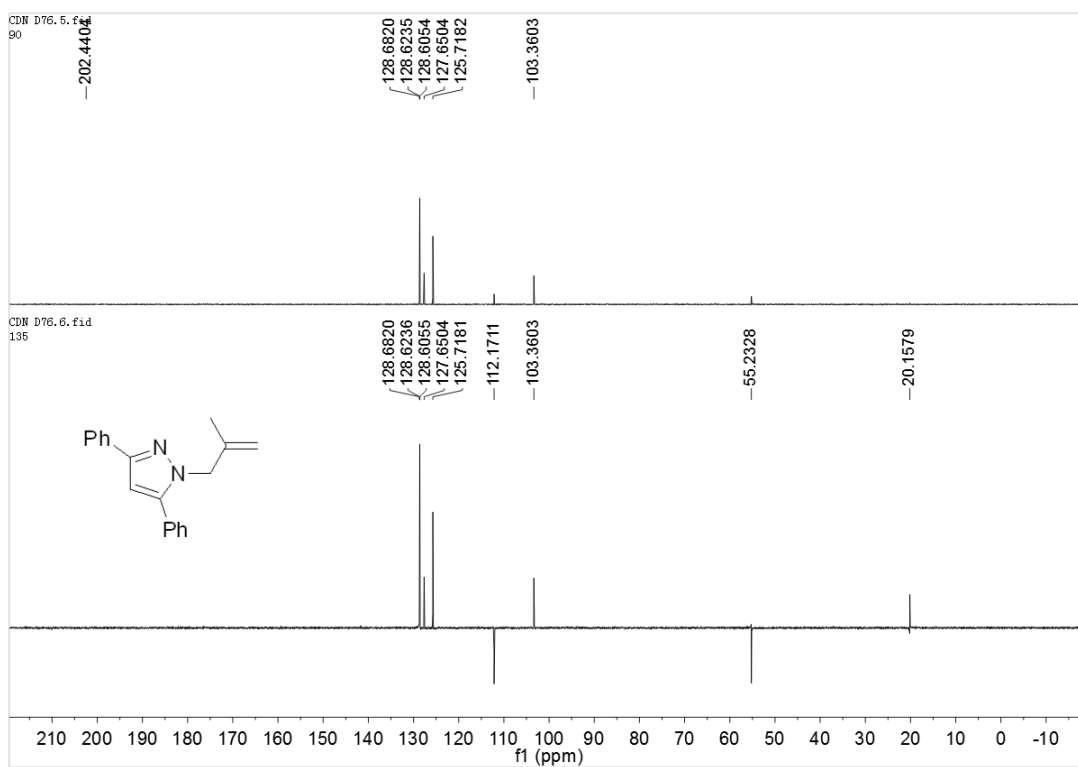
CDN D43. 23. fid
90



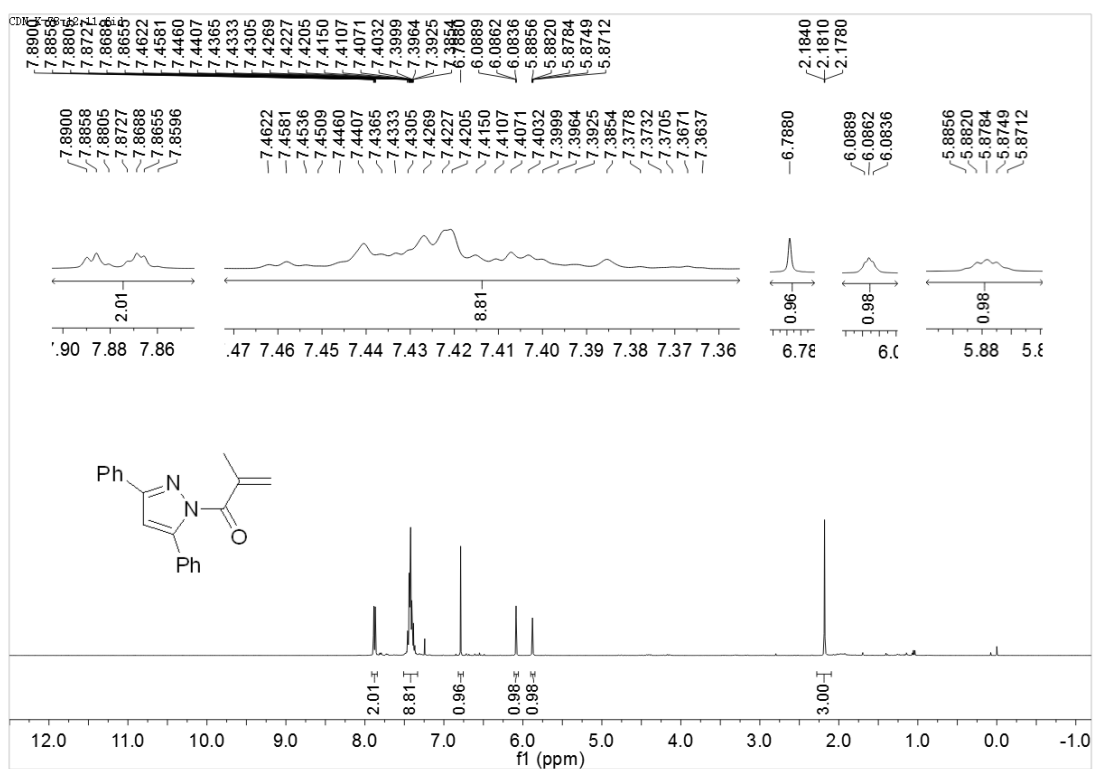
CDN D43. 24. fid
135



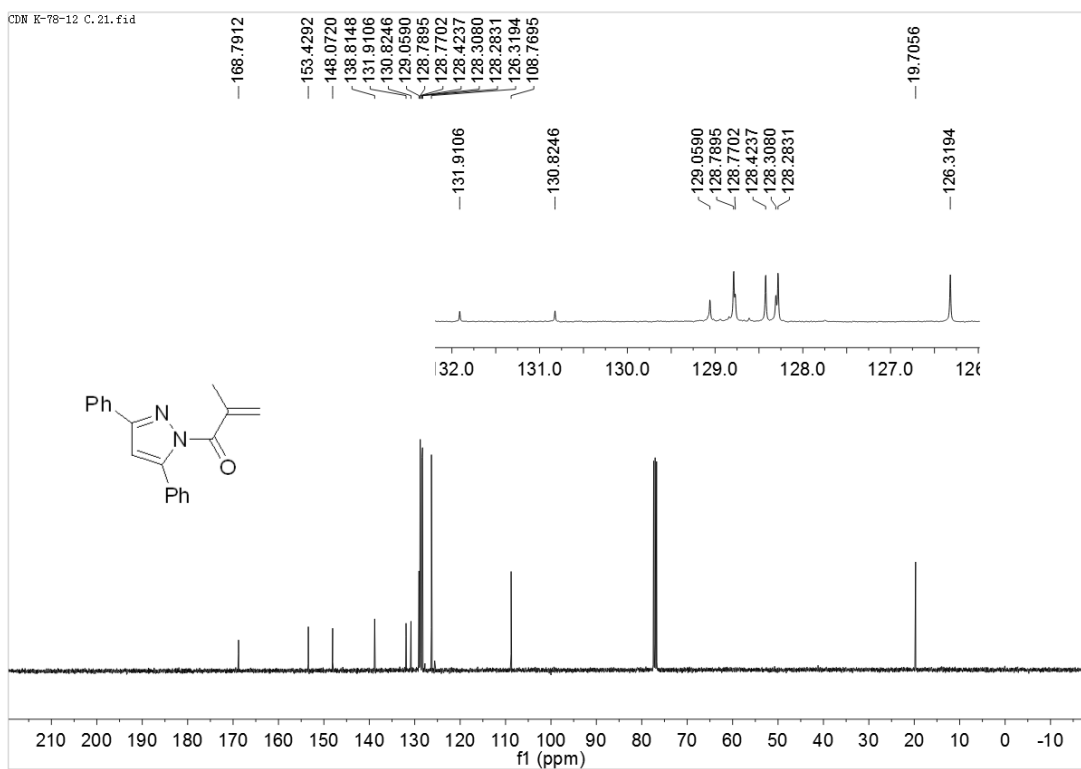
DEPT 90 and DEPT 135



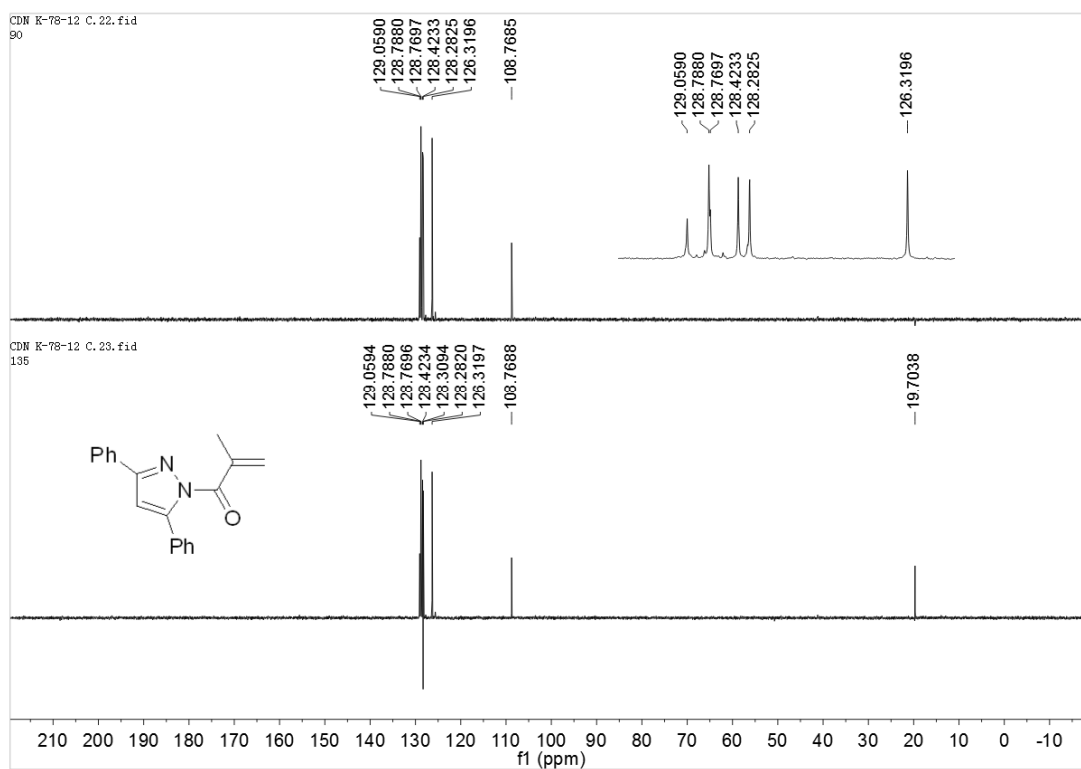
12b, ¹H NMR



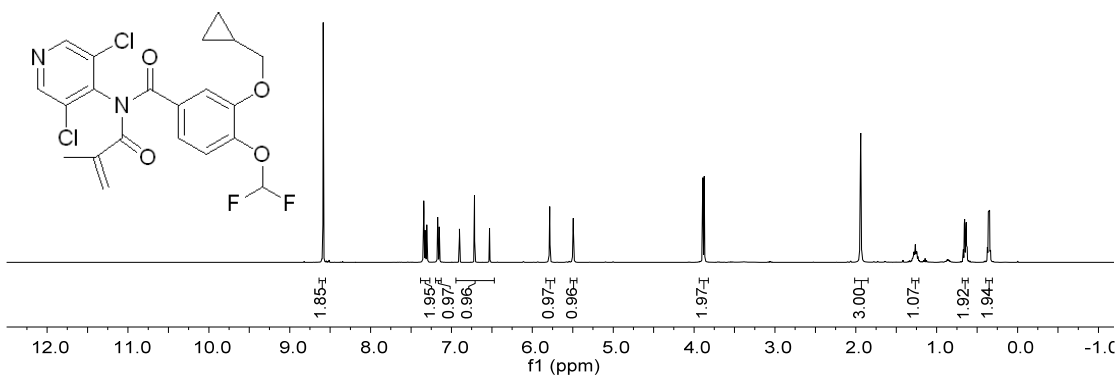
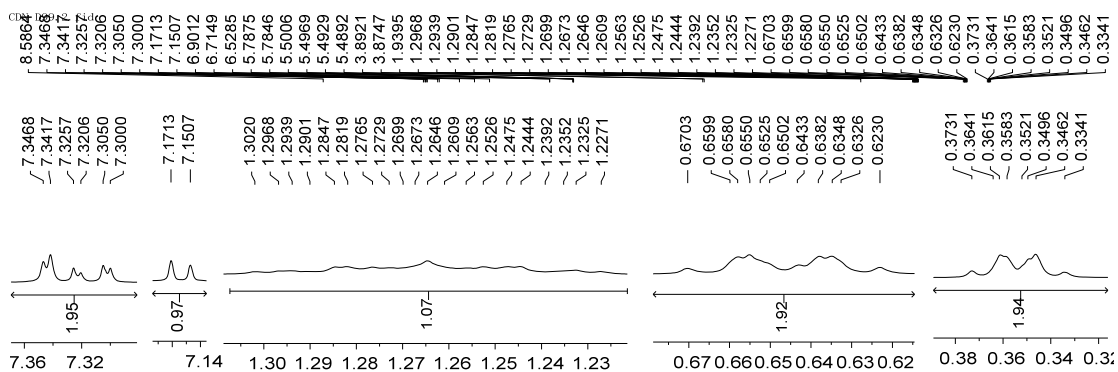
¹³C NMR



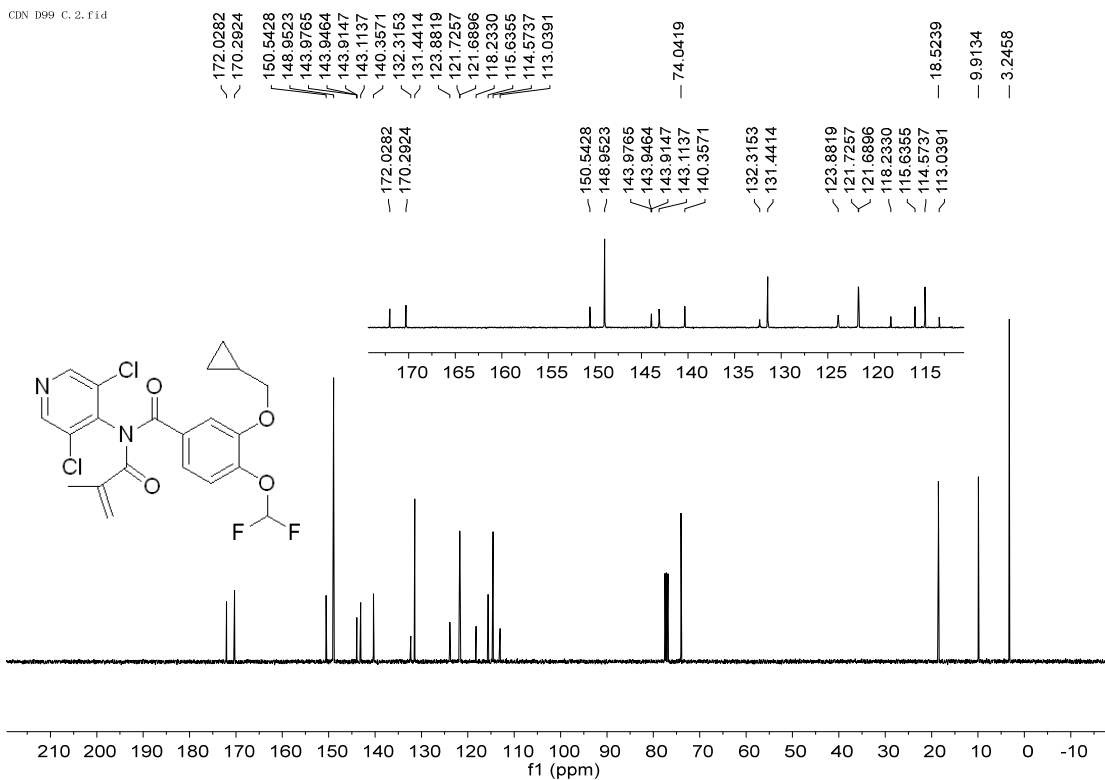
DEPT 90 and DEPT 135



14, ¹H NMR

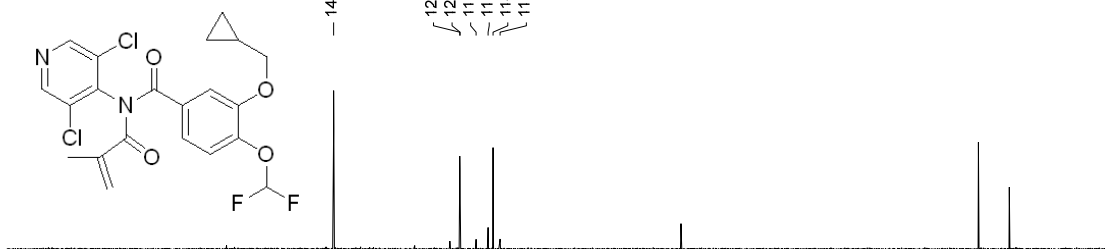


13C NMR

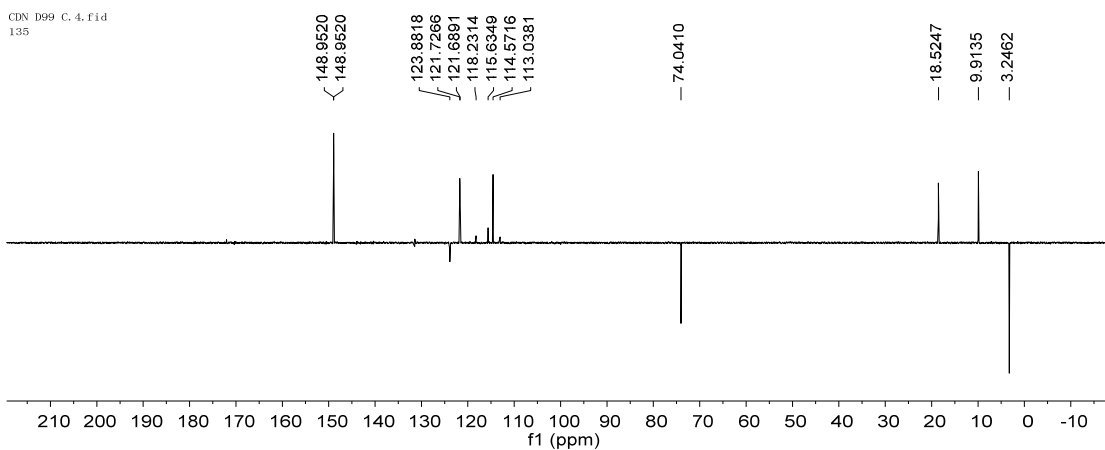


DEPT 90 and DEPT 135

CDN D99 C. 3. fid
90

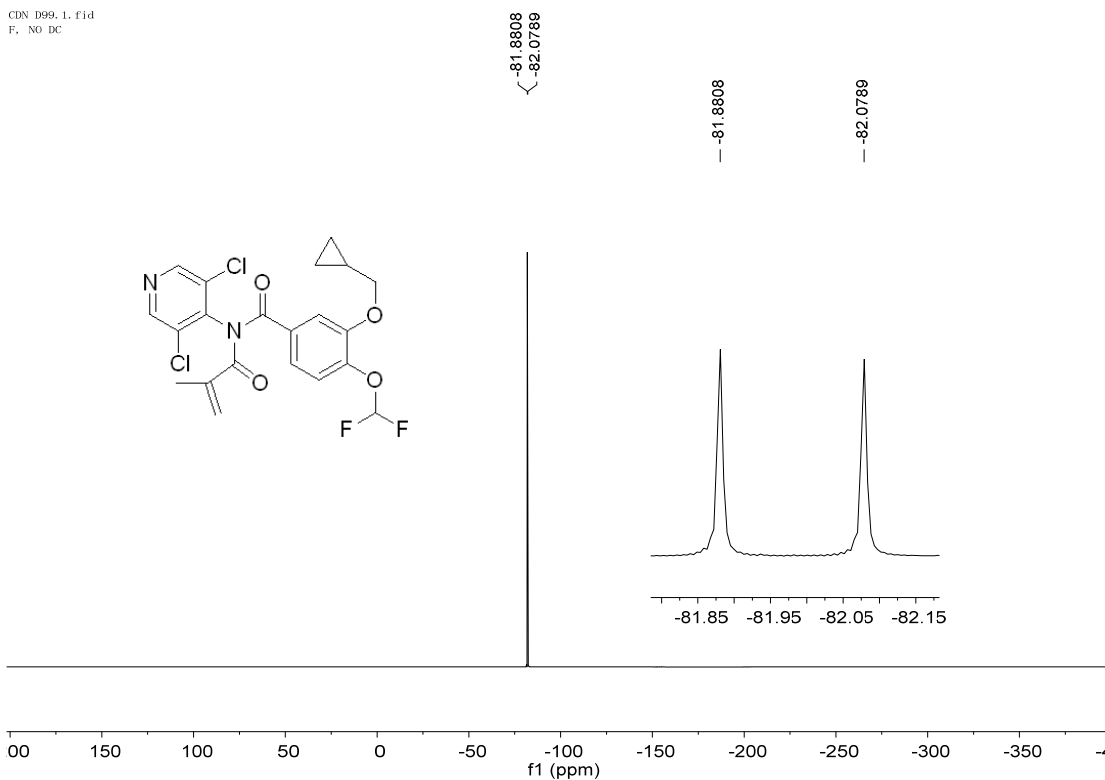


CDN D99 C. 4. fid
135

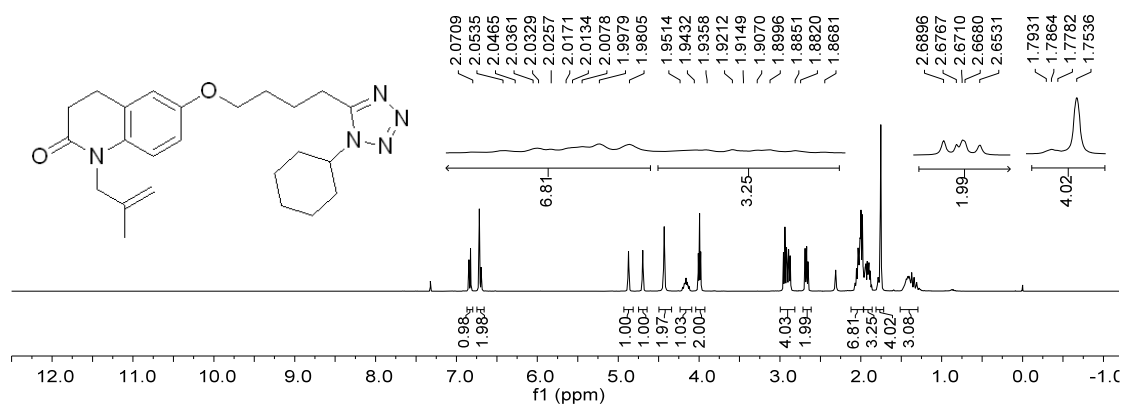
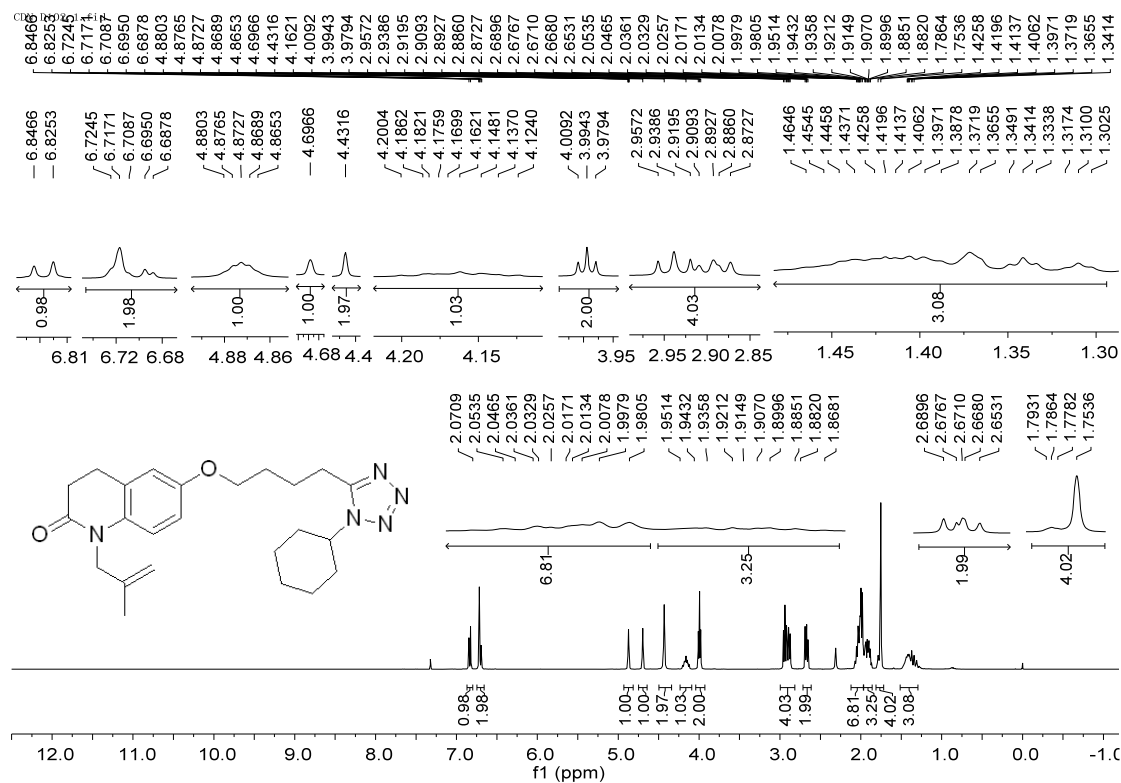


¹⁹F NMR

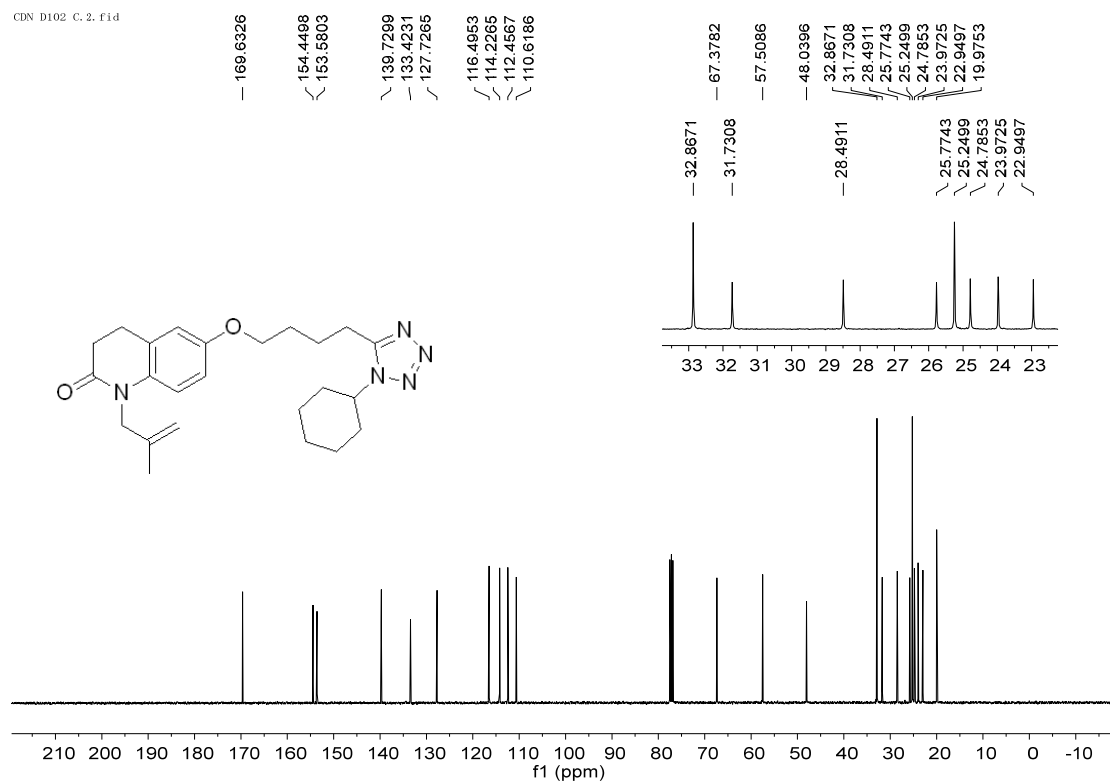
CDN D99. 1. fid
F, NO DC



16, ¹H NMR

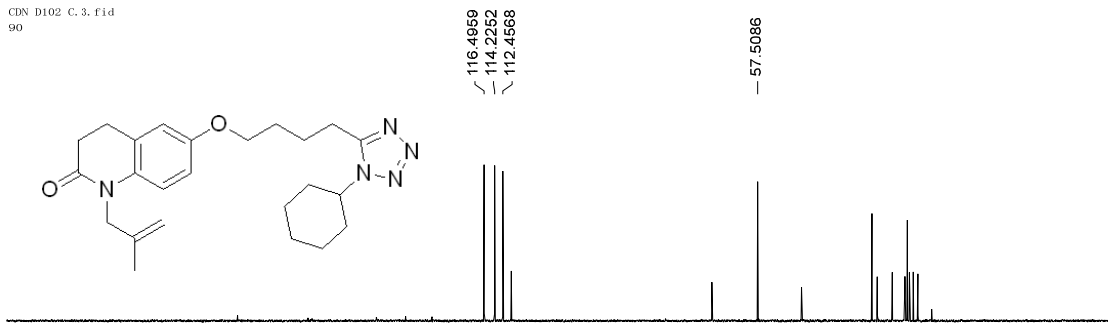


¹³C NMR



DEPT 90 and DEPT 135

CDN D102 C. 3. F1d
90



CDN D102 C. 4. F1d
135

