

Supporting Information

Rhodium(I)-Catalyzed Aryl C–H Carboxylation of 2-Arylanilines with CO₂

Yuzhen Gao,[†] Zhihua Cai,[†] Shangda Li,[†] and Gang Li^{*†‡}

[†]Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[‡]State Key Laboratory of Structural Chemistry, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Email: gangli@fjirsm.ac.cn

Table of Contents

1. General information.....	S3
2. Experimental section.....	S3
2.1 Preparation of substrates.....	S3
2.2 Optimization of reaction conditions.....	S6
2.3 General procedure and characterization of products.....	S8
2.4 Mechanistic studies and control experiments.....	S13
2.5 Further transformations and characterization of products.....	S16
2.6 References.....	S19
3. NMR spectra of compounds.....	S20

1. General information

Unless otherwise noted, commercial available reagents were purchased from commercial suppliers (such as Adamas, Strem, J&K Chemical Co., Energy Chemical. etc), and used as received. Rhodium catalysts were purchased from Sinocompound. Sensitive reagents, such as *t*-BuOK, were stored and weighed in glove box. CO₂ was provided by Linde Gas (Xiamen) and its purity was \geq 99.995%. Solvents were generally dried over 4 Å molecular sieves and degassed. The reaction vessels used for C–H functionalization were 50 mL Schlenk sealed tube (Synthware). Purification of products was performed by flash chromatography (FC) using silica gel. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz and 100 MHz, respectively), and a JEOL ECZ600S (600 MHz and 151 MHz, respectively). Chemical shifts are reported parts per million (ppm) referenced to CDCl₃ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), DMSO-*d*₆ (δ 3.30 ppm) for ¹H NMR; CDCl₃ (δ 77.16 ppm), DMSO-*d*₆ (δ 39.5 ppm) for ¹³C NMR. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptaplet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Impact II UHR-TOF mass spectrometry equipped with an ESI source from Bruker at Fujian Institute of Research on the Structure of Matter.

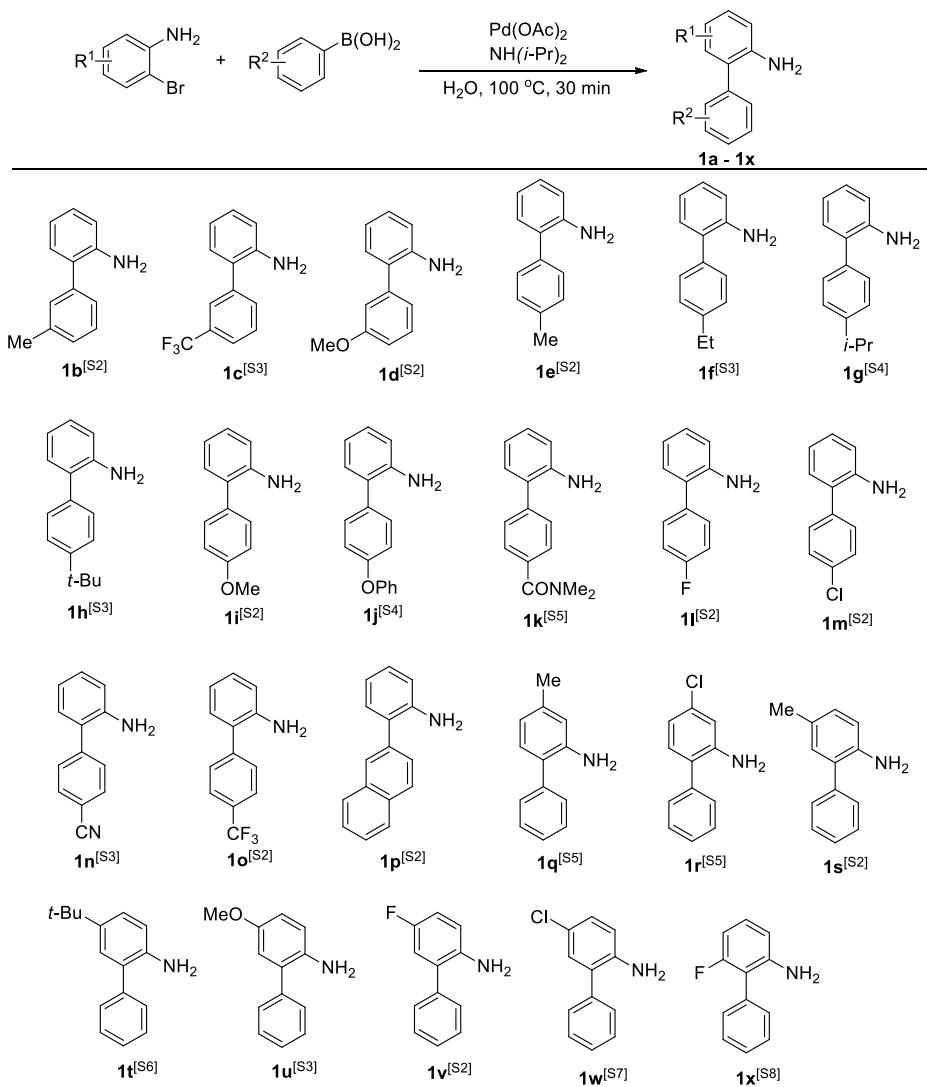
2. Experimental section

2.1 Preparation of substrates.

2.1.1 Synthesis of substrates 1b-1x^[S1]

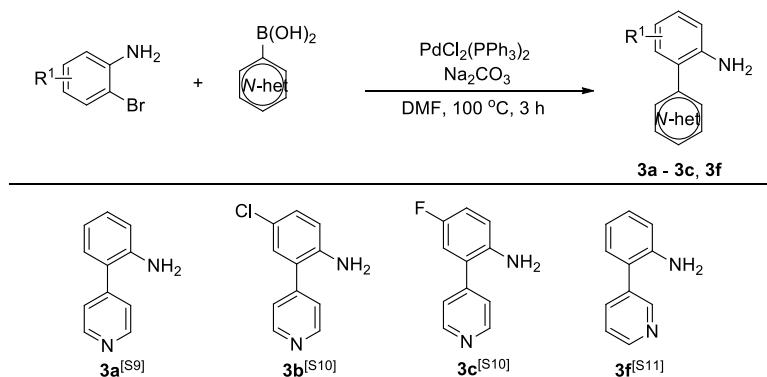
Substrates 1b-1x were prepared by Suzuki–Miyaura coupling between *o*-bromoanilines and corresponding arylboronic acids according to the literature procedure (see below equation). All the compounds are known.

General procedure A: A mixture of *o*-bromoanilines (3.0 mmol), arylboronic acids (4.5 mmol), base (6.0 mmol), Pd(OAc)₂ (0.25 mol%, 1.68 mg), H₂O (6.0 mL) was stirred at 100 °C for 0.5 h. The reaction mixture was added to brine (10 mL) and extracted with ethyl acetate (3 \times 20 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel column using petroleum ether/EtOAc (20:1 - 15:1) as the eluent.



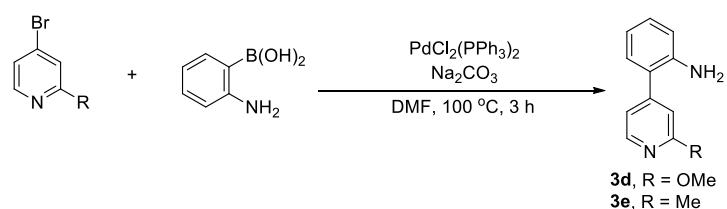
2.1.2 Synthesis of substrates 3a-3c, 3f^[S9]

The solution of *o*-bromoanilines (3 mmol) in DMF (8 mL) was degassed with nitrogen for 15 min followed by addition of Na₂CO₃ solution (5 mL, 2 M) under continuous flow of nitrogen. After 10 min, pyridine-boronic acid (3.6 mmol) and PdCl₂(PPh₃)₂ (0.21 mmol, 7 mol%) were added to the reaction mixture under a nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 3 h. The solution was diluted with H₂O (5 mL), and then the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified on a silica gel column using petroleum ether/EtOAc (2:1-3:2) as the eluent to afford the corresponding products. All the compounds are known.



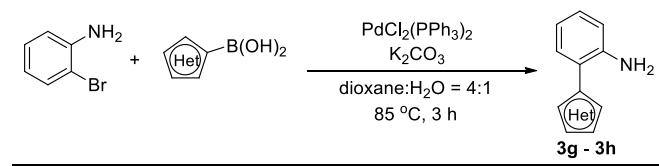
2.1.3 Synthesis of substrates 3d, 3e

Compound **3d**, **3e** was prepared from (2-aminophenyl)boronic acid using the same procedure as **3a-3c**. Both the compounds are known.



2.1.4 Synthesis of substrates 3g-3i^[S11]

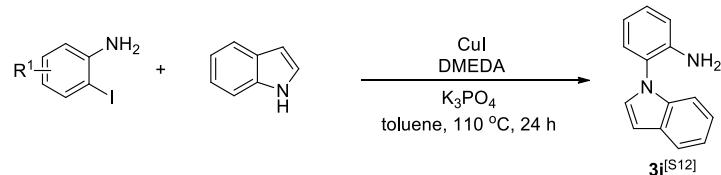
To an oven-dried schlenk tube was charged with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (105 mg, 0.15 mmol, 5 mol%), *o*-bromoanilines (3.0 mmol, 1 equiv), corresponding hetero-arylboronic acids (4.5 mmol, 1.5 equiv), and K_2CO_3 (1.24 g, 9.0 mmol, 3 equiv.). Degassed 1,4-dioxane/ H_2O (15 mL, *v/v* = 4/1) was added under Ar atmosphere. The reaction was heated at 85 °C for 3 h and then cooled to room temperature. 1N NaHCO_3 (20 mL) was added and the aqueous phase was extracted with EtOAc (20 mL \times 3). The combined organic layer was washed with H_2O (20 mL) and brine (10 mL), and then dried over Na_2SO_4 . After removal of volatile matter under reduced pressure, the residue was purified by flash silica gel column chromatography using petroleum ether/EtOAc (20:1) as the eluent to give the corresponding products. All the compounds are known.



2.1.5 Synthesis of substrate 3i^[S12]

Indole (702 mg, 6.0 mmol, 1.2 equiv) was added to a mixture of CuI (95 mg, 0.5 mmol, 0.1 equiv), K_3PO_4 (2.3 g, 10.5 mmol, 2.1 equiv), 2-iodoaniline (1.1 g, 5.0 mmol, 1.0 equiv) and *N,N*-dimethylmethane-1,2-diamine (DMEDA) (88.1 mg, 1.0 mmol, 0.2 equiv) in toluene (5 mL) at room temperature. The reaction tube was purged

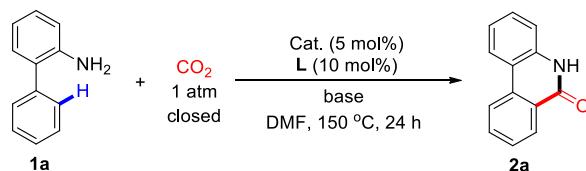
with Argon and sealed with PTFE cap. After been heated at 110 °C for 24 h, the mixture was cooled to room temperature, diluted with EtOAc (50 mL) and filtered through a plug of celite. The filtrate was concentrated in vacuo and the resulting residue was purified by silica gel column chromatography using petroleum ether/EtOAc (20:1) as the eluent to give corresponding products.



2.2 Optimization of reaction conditions.

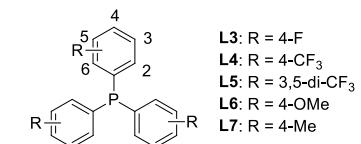
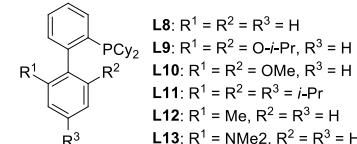
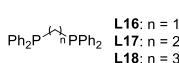
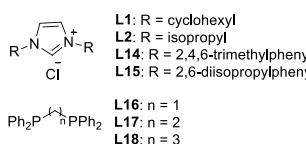
General procedure: In a glove box, compound **1a** (0.2 mmol), catalyst, ligand and base were added sequentially to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar. After taken out of the glove box, the tube was evacuated under vacuum and charged with CO₂ (1 atm, × 3). Then anhydrous solvent (2.0 mL) was added along the inside wall of the tube under a flow of CO₂. Again, the reaction tube was evacuated briefly under vacuum and charged with CO₂ (1 atm, × 3). The tube was capped and then placed into a hotplate. The reaction was stirred vigorously (Note: good stirring is important!) for 24 h and cooled to room temperature. After removal of volatile matter under reduced pressure, the residue was diluted with EtOAc (5 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 20 mL of EtOAc. The filtrate was concentrated in vacuo, and crude ¹H NMR spectrum was taken using CH₂Br₂ as the internal standard.

Table S1. Reaction conditions screening with compound **1a**



entry	cat. (5 mol%)	ligand (10 mol%)	solvent	base (equiv)	T (°C)	t (h)	yield (%)
1	[RhCl ₂ Cp ⁺] ₂	-	DMF	t-BuOK (4.5 eq)	150	24	11
2	RhCl(PPh ₃) ₃	-	DMF	t-BuOK (4.5 eq)	150	24	19
3	[Rh(OAc) ₂] ₂	-	DMF	t-BuOK (4.5 eq)	150	24	13
4	[RhCl(cod) ₂] ₂	-	DMF	t-BuOK (4.5 eq)	150	24	3
5	[RhCl(cod)] ₂	-	DMF	t-BuOK (4.5 eq)	150	24	44
6	[RhOAc(cod)] ₂	-	DMF	t-BuOK (4.5 eq)	150	24	38
7	Rh(acac)(CO) ₂	-	DMF	t-BuOK (4.5 eq)	150	24	30
8	[RhCl(cod)] ₂	L14	DMF	t-BuOK (4.5 eq)	150	24	11
9	[RhCl(cod)] ₂	L1	DMF	t-BuOK (4.5 eq)	150	24	8
10	[RhCl(cod)] ₂	L2	DMF	t-BuOK (4.5 eq)	150	24	38
11	[RhCl(cod)] ₂	L15	DMF	t-BuOK (4.5 eq)	150	24	25
12	[RhCl(cod)] ₂	L16	DMF	t-BuOK (4.5 eq)	150	24	22
13	[RhCl(cod)] ₂	L17	DMF	t-BuOK (4.5 eq)	150	24	27
14	[RhCl(cod)] ₂	L18	DMF	t-BuOK (4.5 eq)	150	24	22

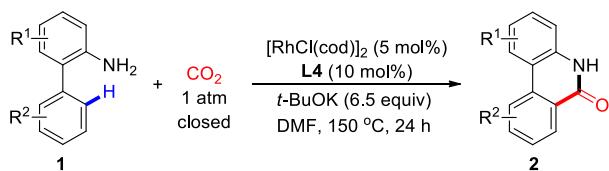
15	[RhCl(cod)] ₂	L8	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	21
16	[RhCl(cod)] ₂	L9	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	36
17	[RhCl(cod)] ₂	L10	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	46
18	[RhCl(cod)] ₂	L11	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	45
19	[RhCl(cod)] ₂	L12	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	46
20	[RhCl(cod)] ₂	L13	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	40
21	[RhCl(cod)] ₂	L14	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	60
22	[RhCl(cod)] ₂	L3	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	30
23	[RhCl(cod)] ₂	L15	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	49
24	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	69
25	[RhCl(cod)] ₂	L5	DMF	<i>t</i> -BuOK (4.5 eq)	150	24	52
26	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuONa (4.5 eq)	150	24	34
27	[RhCl(cod)] ₂	L4	DMF	Cs ₂ CO ₃ (4.5 eq)	150	24	0
28	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOLi (4.5 eq)	150	24	trace
29	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOLi (4.5 eq) Cs ₂ CO ₃ (1.5 eq)	150	24	21
30	[RhCl(cod)] ₂	L4	DMF	EtONa (4.5 eq)	150	24	0
31	[RhCl(cod)] ₂	L4	DMF	KOH (4.5 eq)	150	24	0
32	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (4.5 eq)	140	24	56
33	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (4.5 eq)	120	24	20
34	[RhCl(cod)] ₂	L4	DMA	<i>t</i> -BuOK (4.5 eq)	150	24	1
35	[RhCl(cod)] ₂	L4	diglyme	<i>t</i> -BuOK (4.5 eq)	150	24	27
36	[RhCl(cod)] ₂	L4	toluene	<i>t</i> -BuOK (4.5 eq)	150	24	0
37	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (3.0 eq)	150	24	19
38	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.0 eq)	150	24	75
39	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq)	150	24	84 (83)
40	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq)	150	2	20
41	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq)	150	12	65
42	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq)	150	18	82
43 ^b	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq)	150	24	0
44 ^c	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq)	150	24	62
45	[RhCl(cod)] ₂	L6	DMF	<i>t</i> -BuOK (6.5 eq)	150	24	80
46	[RhCl(cod)] ₂	L7	DMF	<i>t</i> -BuOK (6.5 eq)	150	24	77
47	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOLi (6.5 eq)	150	24	16
48	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOLi (6.5 eq) Cs ₂ CO ₃ (1.5 eq)	150	24	46
49	[RhCl(cod)] ₂	L4	DMF	<i>t</i> -BuOK (6.5 eq) Cs ₂ CO ₃ (1.5 eq)	150	24	70



^bCO (1 atm, closed) was used instead of CO₂. ^c[RhCl(cod)]₂ (2.5 mol%), **L4** (5 mol%).

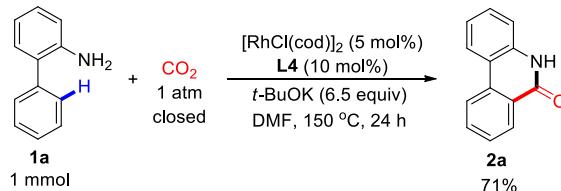
2.3 General procedure and characterization of products.

2.3.1 General procedure for the synthesis of products:



In a glove box, to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added **1** or **3** (0.2 mmol), $[\text{RhCl}(\text{cod})]_2$ (5 mol%), **L4** (10 mol%) and *t*-BuOK (1.30 mmol, 6.5 equiv) (Note: *t*-BuOK should be dry). After taken out of the glove box, the tube was evacuated under vacuum and charged with CO_2 (1 atm, $\times 3$). Then anhydrous solvent DMF (2.0 mL) was added along the inside wall of the tube under a flow of CO_2 . Afterwards, the reaction tube was evacuated briefly under vacuum and charged with CO_2 (1 atm, $\times 3$). The tube was capped and then placed into a preheated hotplate. The reaction was stirred vigorously (Note: good stirring is important!) for 24 h and cooled to room temperature. The reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional of 20 mL EtOAc. The filtrate was concentrated in vacuo, and purified by flash silica gel chromatography using petroleum ether/EtOAc (eluent gradient from 2:1 to 1:1) as the eluent.

2.3.2 1 mmol scale for the synthesis of **2a**:



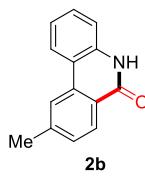
In a glove box, to an oven-dried 250 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added **1a** (1.0 mmol), $[\text{RhCl}(\text{cod})]_2$ (5 mol%), **L4** (10 mol%) and *t*-BuOK (6.5 mmol, 6.5 equiv) (Note: *t*-BuOK should be dry). After taken out of the glove box, the tube was evacuated under vacuum and charged with CO_2 (1 atm, $\times 3$). Then anhydrous solvent DMF (20.0 mL) was added along the inside wall of the tube under a flow of CO_2 . Afterwards, the reaction tube was evacuated briefly under vacuum and charged with CO_2 (1 atm, $\times 3$). The tube was capped and then placed into an oil bath (the tube was wrapped in foil). The reaction was stirred vigorously (Note: good stirring is important!) for 24 h and cooled to room temperature. The reaction was diluted with EtOAc (50 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional of 50 mL EtOAc. The filtrate was concentrated in vacuo, and purified by flash silica gel chromatography using petroleum ether/EtOAc (eluent gradient from 2:1 to 1:1) as the eluent to afford **2a** in 71% yield (139 mg).

2.3.3 Characterization of products:

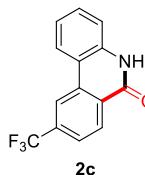


phenanthridin-6(5H)-one (known compound)^[S2]: quality: 32.4 mg; yield: 83%; white solid. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.68 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.66 – 7.62 (m, 1H), 7.51 – 7.47 (m, 1H), 7.37 (dd, *J*

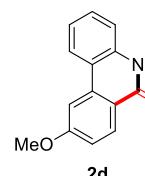
= 8.4, 1.2 Hz, 1H), 7.28 – 7.24 (m, 1H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 160.8, 136.5, 134.2, 132.8, 129.6, 127.9, 127.5, 125.7, 123.2, 122.6, 122.2, 117.5, 116.1.



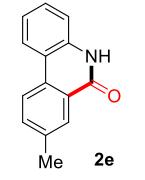
9-methylphenanthridin-6(5H)-one (known compound)^[S2]: quality: 29.3 mg; yield: 70%; white solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.59 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.31 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 2.52 (s, 3H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 160.9, 143.1, 136.8, 134.3, 129.5, 129.2, 127.5, 123.4, 123.2, 122.5, 122.2, 117.6, 116.1, 21.6.



9-(trifluoromethyl)phenanthridin-6(5H)-one (known compound)^[S13]: quality: 43.1 mg; yield: 82%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.93 (s, 1H), 8.85 (s, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 159.9, 136.9, 134.9, 132.7 (q, *J* = 31.7 Hz), 130.6, 129.0, 128.4, 124.0, 124.0 (q, *J* = 273.1 Hz), 123.8, 122.6, 120.2, 116.8, 116.3.



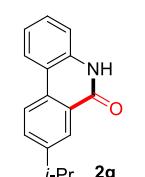
9-methoxyphenanthridin-6(5H)-one (known compound)^[S2]: quality: 18.0 mg; yield: 40%; white solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.51 (s, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.34 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.21 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.98 (s, 3H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 162.9, 160.7, 137.0, 136.4, 129.8, 129.6, 123.7, 122.0, 119.2, 117.5, 116.3, 116.1, 105.1, 55.8.



8-methylphenanthridin-6(5H)-one (known compound)^[S2]: quality: 25.9 mg; yield: 62%; white solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.64 (s, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.12 (s, 1H), 7.72 – 7.63 (m, 1H), 7.46 – 7.44 (m, 1H), 7.34 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.27 – 7.21 (m, 1H), 2.47 (s, 3H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 160.8, 137.6, 136.2, 133.9, 131.8, 129.1, 127.2, 125.6, 123.0, 122.6, 122.2, 117.7, 116.0, 20.9.



8-ethylphenanthridin-6(5H)-one (known compound)^[S14]: quality: 29.0 mg; yield: 65%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.63 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.15 (s, 1H), 7.70 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 160.9, 143.7, 136.2, 132.9, 132.1, 129.1, 125.9, 125.7, 123.0, 122.7, 122.2, 117.7, 116.0, 27.9, 15.3.



8-isopropylphenanthridin-6(5H)-one: quality: 28.9 mg; yield: 61%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.66 (s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.20 (m, 1H), 3.07 (h, *J* = 6.8 Hz, 1H), 1.29 (s, 3H), 1.28 (s, 3H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 161.0, 148.3, 136.3, 132.3, 131.7, 129.2, 125.6, 124.4, 123.1, 122.8, 122.2, 117.7, 116.0, 33.3, 23.7. HRMS (m/z, ESI-TOF): Calcd for C₁₆H₁₅NNaO⁺ [M+Na]⁺ 260.1046, found 260.1046.



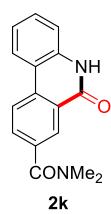
8-(tert-butyl)phenanthridin-6(5H)-one: quality: 39.2 mg; yield: 78%; light yellow solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.68 (s, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.38 – 8.28 (m, 2H), 7.90 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.26 – 7.22 (m, 1H), 1.37 (s, 9H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 161.0, 150.5, 136.3, 131.9, 130.5, 129.1, 125.3, 123.0, 123.0, 122.6, 122.2, 117.5, 116.0, 34.6, 30.9. HRMS (m/z, ESI-TOF): Calcd for C₁₇H₁₇NNaO⁺ [M+Na]⁺ 274.1202, found 274.1203.



8-methoxyphenanthridin-6(5H)-one (known compound)^[S2]: quality: 30.6 mg; yield: 68%; light yellow solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.70 (s, 1H), 8.43 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 3.2 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 3.91 (s, 3H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 160.6, 159.0, 135.5, 128.4, 127.7, 127.1, 124.6, 122.6, 122.3, 121.6, 117.7, 116.0, 108.7, 55.4.



8-phenoxyphenanthridin-6(5H)-one: quality: 51.1 mg; yield: 89%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.74 (s, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 2.8 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.51 – 7.43 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 160.3, 157.2, 155.6, 135.8, 130.4, 129.6, 129.1, 127.2, 125.3, 124.6, 123.8, 123.0, 122.5, 119.9, 117.4, 116.1, 113.7. HRMS (m/z, ESI-TOF): Calcd for C₁₉H₁₃NNaO₂⁺ [M+Na]⁺ 310.0838, found 310.0838.



N,N-dimethyl-6-oxo-5,6-dihydrophenanthridine-8-carboxamide: quality: 46.8 mg; yield: 88%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.80 (s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.23 (m, 1H), 3.04 (s, 3H), 2.97 (s, 3H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 169.2, 160.5, 136.8, 135.6, 135.0, 131.3, 130.1, 126.1, 125.4, 123.6, 122.9, 122.5, 117.1, 116.3, 34.9. HRMS (m/z, ESI-TOF): Calcd for C₁₆H₁₄N₂NaO₂⁺ [M+Na]⁺ 289.0947, found 289.0947.



8-fluorophenanthridin-6(5H)-one (known compound)^[S2]: quality: 37.1 mg; yield: 87%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.82 (s, 1H), 8.58 (dd, *J* = 9.0, 5.2 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.72 (td, *J* = 8.8, 2.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.37 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29 – 7.24 (m, 1H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 161.6 (d, *J* = 246.1 Hz), 159.9 (d, *J* = 3.0 Hz), 136.0, 131.1 (d, *J* = 2.5 Hz), 129.5, 127.6 (d, *J* = 7.6 Hz), 125.9 (d, *J* = 8.0 Hz), 123.3, 122.5, 121.0 (d, *J* = 22.8 Hz), 117.1, 116.2, 112.5 (d, *J* = 22.5 Hz).

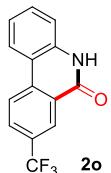


8-chlorophenanthridin-6(5H)-one (known compound)^[S2]: quality: 40.3 mg; yield: 88%; light yellow solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.84 (s, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 2.4 Hz, 1H), 7.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.26 (m, 1H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 159.7, 136.5, 133.1, 132.8, 132.7, 130.0, 127.2, 126.6, 125.2, 123.5, 122.6, 116.9, 116.2.

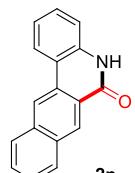


6-oxo-5,6-dihydrophenanthridine-8-carbonitrile (known compound)^[S14]: quality: 40.0 mg; yield: 91%; light yellow solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.94 (s, 1H), 8.65 – 8.63 (m, 1H), 8.59 (s, 1H), 8.42 – 8.39 (m, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.25 (m, 1H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 159.5, 137.9, 137.5, 134.9, 132.1, 131.4,

126.0, 124.3, 124.2, 122.8, 118.4, 116.44, 116.40, 110.27.



8-(trifluoromethyl)phenanthridin-6(5H)-one (known compound)^[S2]: quality: 46.3 mg; yield: 88%; light yellow solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.94 (s, 1H), 8.69 (d, *J* = 8.8 Hz, 1H), 8.53 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 156.0, 137.6, 137.3, 131.0, 128.7 (d, *J* = 3.6 Hz), 127.9 (q, *J* = 32.8 Hz), 125.8, 124.4 (d, *J* = 4.3 Hz), 124.4, 124.1, 124.0 (q, *J* = 272.2 Hz), 122.7, 116.5, 116.4.



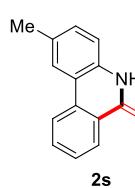
benzo[j]phenanthridin-6(5H)-one (known compound)^[S2]: quality: 16.2 mg; yield: 33%; light yellow solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.56 (s, 1H), 9.08 (s, 1H), 8.98 (s, 1H), 8.53 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.65 – 7.62 (m, 1H), 7.50 – 7.47 (m, 1H), 7.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.31 – 7.28 (m, 1H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 161.2, 136.4, 134.9, 131.7, 130.5, 129.6, 129.2, 128.7, 128.6, 128.2, 126.8, 124.1, 123.6, 122.5, 121.6, 118.0, 116.4.



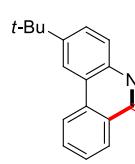
3-methylphenanthridin-6(5H)-one (known compound)^[S13]: quality: 25.5 mg; yield: 61%; white solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.63 (s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 2.37 (s, 3H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 161.0, 139.5, 136.6, 134.4, 132.8, 127.5, 125.3, 123.6, 123.2, 122.4, 116.0, 115.3, 21.2.



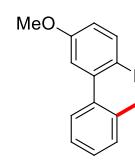
3-chlorophenanthridin-6(5H)-one (known compound)^[S1]: quality: 38.9 mg; yield: 85%; light yellow solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.77 (s, 1H), 8.47 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.30 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.67 – 7.64 (m, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.8 Hz, 1H). **¹³C NMR (151 MHz, DMSO-d₆)** δ 160.8, 137.6, 133.7, 133.5, 133.1, 128.4, 127.5, 125.5, 125.3, 122.8, 122.2, 116.6, 115.3.



2-methylphenanthridin-6(5H)-one (known compound)^[S2]: quality: 25.1 mg; yield: 60%; white solid. **¹H NMR (400 MHz, DMSO-d₆)** δ 11.59 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.20 (s, 1H), 7.92 – 7.77 (m, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.14 (m, 2H), 2.41 (s, 3H). **¹³C NMR (101 MHz, DMSO-d₆)** δ 160.7, 134.4, 134.2, 132.7, 131.2, 130.6, 127.8, 127.5, 125.7, 123.1, 122.5, 117.4, 116.0, 20.7.



2-(tert-butyl)phenanthridin-6(5H)-one (known compound): quality: 36.6 mg; yield: 73%; light yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 11.44 (s, 1H), 8.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 2.0 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.64 – 7.60 (m, 1H), 7.57 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 1.43 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 163.2, 145.8, 135.3, 134.0, 132.8, 128.5, 127.7, 127.4, 125.9, 122.0, 118.9, 118.1, 116.7, 34.9, 31.7.

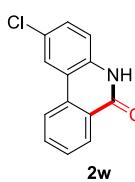


2-methoxyphenanthridin-6(5H)-one (known compound)^[S13]: quality: 35.1 mg; yield: 78%; white solid. **¹H NMR (600 MHz, DMSO-d₆)** δ 11.57 (s, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.32 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.65 – 7.63 (m, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.14

(dd, $J = 8.4, 2.4$ Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (151 MHz, DMSO- d_6)** δ 160.4, 154.8, 134.1, 132.6, 130.7, 128.0, 127.5, 125.9, 123.0, 118.3, 117.8, 117.4, 106.2, 55.7.



2-fluorophenanthridin-6(5H)-one (known compound)^[S2]: quality: 26.0 mg; yield: 61%; white solid. **^1H NMR (400 MHz, DMSO- d_6)** δ 11.73 (s, 1H), 8.42 (d, $J = 8.0$ Hz, 1H), 8.32 (d, $J = 7.6$ Hz, 1H), 8.26 (d, $J = 10.4$ Hz, 1H), 7.86 (t, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 7.0$ Hz, 2H). **^{13}C NMR (101 MHz, DMSO- d_6)** δ 160.5, 157.8 (d, $J = 237.5$ Hz), 133.6 (d, $J = 2.9$ Hz), 133.2, 132.8, 128.6, 127.5, 125.8, 123.2, 118.8 (d, $J = 8.4$ Hz), 117.8 (d, $J = 8.5$ Hz), 117.2 (d, $J = 24.1$ Hz), 109.2 (d, $J = 24.0$ Hz).



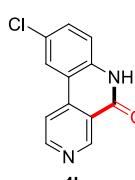
2-chlorophenanthridin-6(5H)-one (known compound)^[S13]: quality: 27.9 mg; yield: 61%; light yellow solid. **^1H NMR (400 MHz, DMSO- d_6)** δ 11.79 (s, 1H), 8.55 (d, $J = 8.0$ Hz, 1H), 8.47 (d, $J = 2.4$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H), 7.86 (t, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.53 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.37 (d, $J = 8.8$ Hz, 1H). **^{13}C NMR (101 MHz, DMSO- d_6)** δ 160.6, 135.3, 133.2, 133.0, 129.4, 128.7, 127.5, 126.6, 125.8, 123.1, 122.9, 119.2, 117.9.



1-fluorophenanthridin-6(5H)-one (known compound)^[S15]: quality: 15.3 mg; yield: 36%; white solid. **^1H NMR (600 MHz, DMSO- d_6)** δ 11.93 (s, 1H), 8.66 – 8.55 (m, 1H), 8.37 – 8.35 (m, 1H), 7.91 – 7.88 (m, 1H), 7.72 – 7.69 (m, 1H), 7.52 – 7.48 (m, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.14 – 7.10 (m, 1H). **^{13}C NMR (151 MHz, DMSO- d_6)** δ 160.6, 160.5 (d, $J = 249.9$ Hz), 138.5 (d, $J = 6.7$ Hz), 133.4, 131.7 (d, $J = 4.7$ Hz), 130.1 (d, $J = 11.4$ Hz), 128.4, 127.7, 126.5 (d, $J = 22.9$ Hz), 126.0, 112.5, 109.5 (d, $J = 24.0$ Hz), 106.8 (d, $J = 12.3$ Hz).



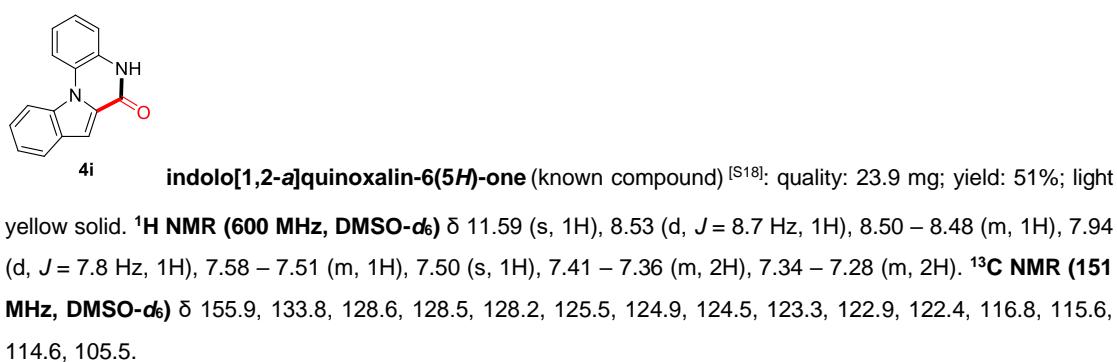
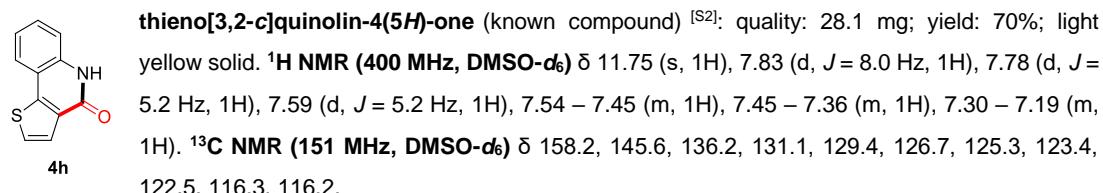
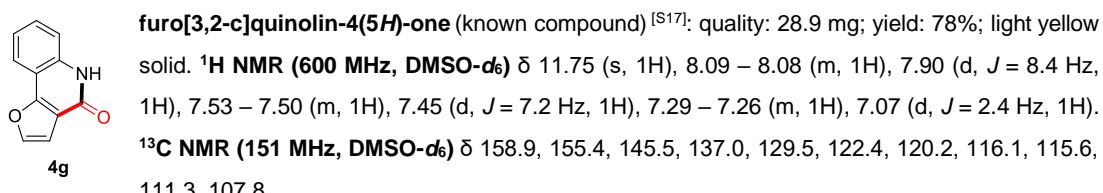
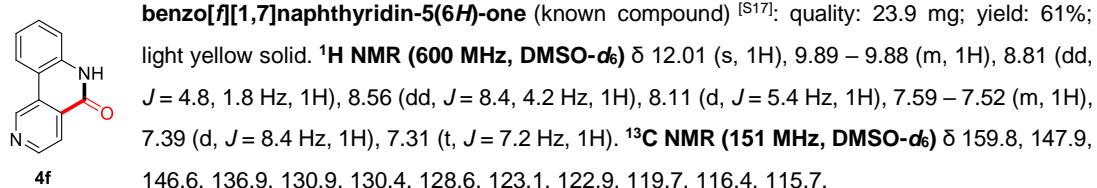
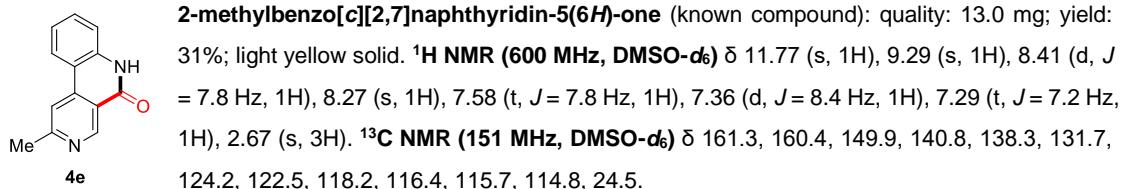
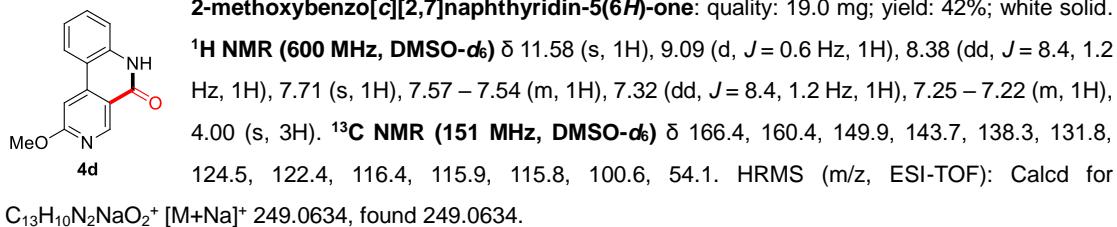
benzo[c][2,7]naphthyridin-5(6H)-one (known compound)^[S17]: quality: 34.1 mg; yield: 87%; light yellow solid. **^1H NMR (600 MHz, DMSO- d_6)** δ 11.91 (s, 1H), 9.42 (s, 1H), 8.89 (dd, $J = 5.4, 1.2$ Hz, 1H), 8.47 – 8.42 (m, 1H), 8.42 – 8.36 (m, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.38 (d, $J = 7.8$ Hz, 1H), 7.35 – 7.28 (m, 1H). **^{13}C NMR (151 MHz, DMSO- d_6)** δ 160.3, 151.9, 150.3, 140.6, 138.2, 131.9, 124.3, 122.6, 120.4, 116.4, 116.2, 115.7.



9-chlorobenzo[c][2,7]naphthyridin-5(6H)-one: quality: 29.0 mg; yield: 63%; white solid. **^1H NMR (600 MHz, DMSO- d_6)** δ 11.98 (s, 1H), 9.39 (d, $J = 1.2$ Hz, 1H), 8.89 (d, $J = 5.4$ Hz, 1H), 8.50 (d, $J = 2.4$ Hz, 1H), 8.42 (dd, $J = 6.0, 1.2$ Hz, 1H), 7.62 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 1H). **^{13}C NMR (151 MHz, DMSO- d_6)** δ 160.1, 152.1, 150.2, 139.7, 137.0, 131.7, 126.9, 123.8, 120.4, 118.2, 117.2, 116.5. HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{12}\text{H}_7\text{ClN}_2\text{NaO}^+$ $[\text{M}+\text{Na}]^+$ 253.0139, found 253.0138.

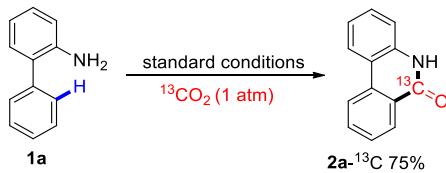


9-fluorobenzo[c][2,7]naphthyridin-5(6H)-one: quality: 38.9 mg; yield: 91%; white solid. **^1H NMR (600 MHz, DMSO- d_6)** δ 11.94 (s, 1H), 9.41 (s, 1H), 8.90 (d, $J = 6.0$ Hz, 1H), 8.39 (d, $J = 6.0$ Hz, 1H), 8.32 (d, $J = 9.6$ Hz, 1H), 7.49 (t, $J = 9.0$ Hz, 1H), 7.42 – 7.35 (m, 1H). **^{13}C NMR (151 MHz, DMSO- d_6)** δ 160.0, 157.8 (d, $J = 238.7$ Hz), 152.0, 150.3, 140.0 (d, $J = 2.9$ Hz), 134.9, 120.5, 119.7 (d, $J = 24.2$ Hz), 118.3 (d, $J = 8.3$ Hz), 116.9 (d, $J = 8.5$ Hz), 116.6, 110.1 (d, $J = 24.0$ Hz). HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{12}\text{H}_7\text{FN}_2\text{NaO}^+$ $[\text{M}+\text{Na}]^+$ 237.0435, found 237.0436.

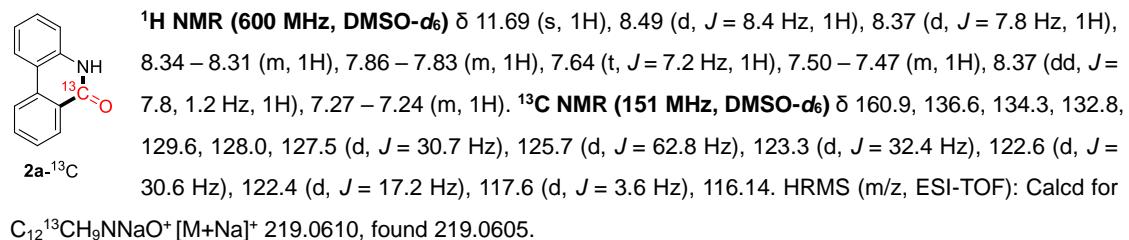


2.4 Mechanistic studies and control experiments

2.4.1 ¹³C-Labeling experiments

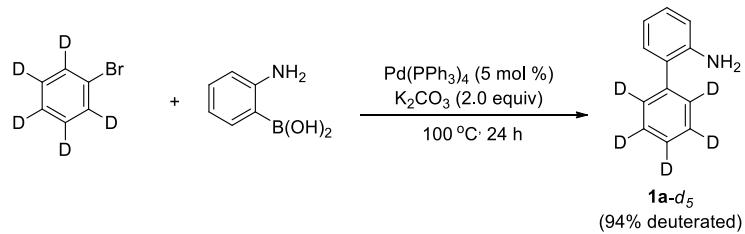


In a glove box, to an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added **1a** (0.2 mmol), $[\text{RhCl}(\text{cod})]_2$ (5 mol%), **L4** (10 mol%) and *t*-BuOK (1.30 mmol, 6.5 equiv) (Note: *t*-BuOK should be dry). After taken out of the glove box, the tube was evacuated under vacuum and charged with $^{13}\text{CO}_2$ (1 atm, $\times 3$). Then anhydrous DMF (2.0 mL) was added along the inside wall of the tube. Afterwards, the reaction tube was evacuated briefly under vacuum and charged with $^{13}\text{CO}_2$ (99.9%, 1 atm, $\times 3$). The tube was capped and then placed into a preheated hotplate. The reaction was stirred vigorously (Note: good stirring is important!) for 24 h and cooled to room temperature. The reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional of 20 mL EtOAc. The filtrate was concentrated in vacuo, and purified by flash silica gel chromatography using petroleum ether/EtOAc (2:1 to 1:1) as the eluent to afford white solid (**2a-}^{13}\text{C}**, 29.4 mg; 94% ^{13}C , calculated from GC-MS) in 75% yield.

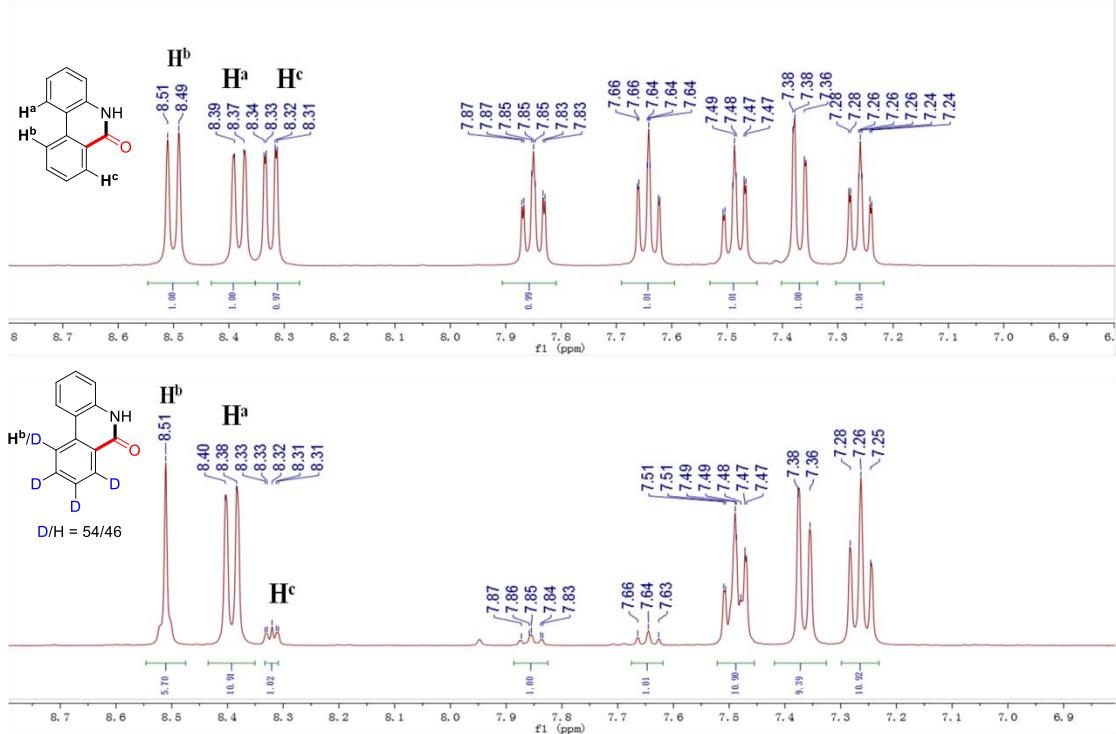
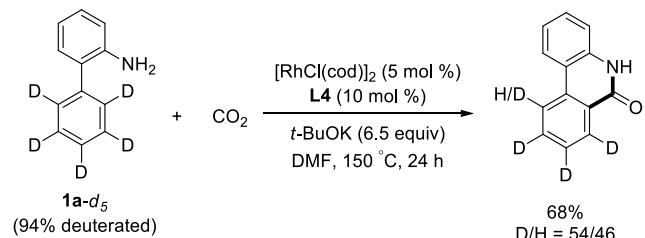


2.4.2 Preparation and reaction of **1a-d₅**

To a 50 mL round bottom flask, equipped with a magnetic stir bar, 2-amidoboronic acid (2.4 mmol, 1.2 equiv), K_2CO_3 (4.0 mmol, 2.0 equiv), and $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) were dissolved in 12.5 mL of toluene followed by the addition of 2.5 mL of H_2O and 5 mL of EtOH. Bromobenzene-*d*5 (2.0 mmol, 1.0 equiv) was then added and the resulting mixture was heated at 100 °C for 24 h. After cooling to room temperature, the solution was diluted with 15 mL of saturated aqueous NH_4Cl and 15 mL of DCM. The aqueous phase was extracted with an additional DCM (2 \times 30 mL), and the combined organic layers were washed with 15 mL of water and 15 mL of saturated aqueous NaHCO_3 . The organic phase was dried over MgSO_4 and filtered. The filtrate was concentrated in vacuo and purified by column chromatography using petroleum ether/EtOAc (20:1) as the eluent to afford **1a-d₅**. ^[S19]

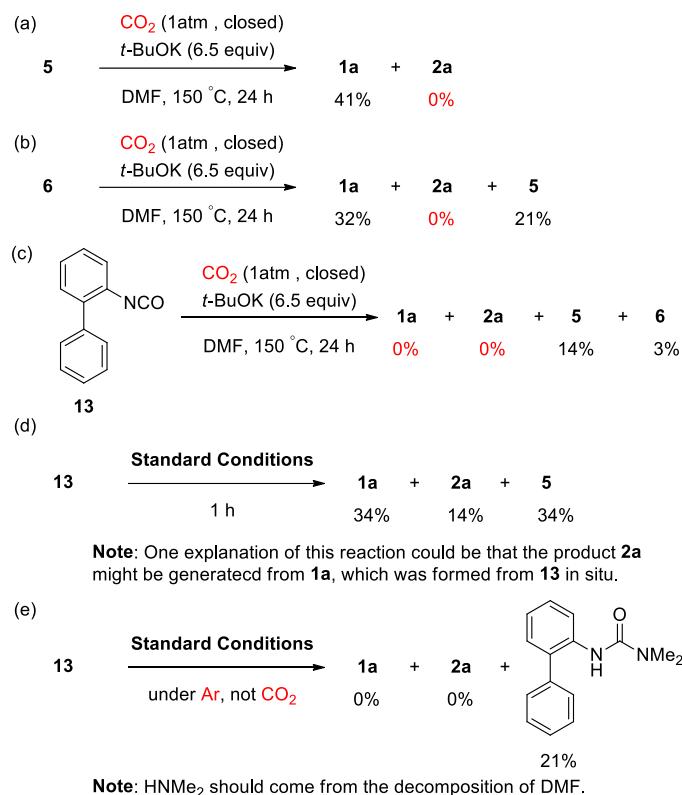


The reactions of **1a-d₅** was performed under the standard conditions (details see 2.3.1 in SI part). And the value of D/H is 54/46 (see attached).

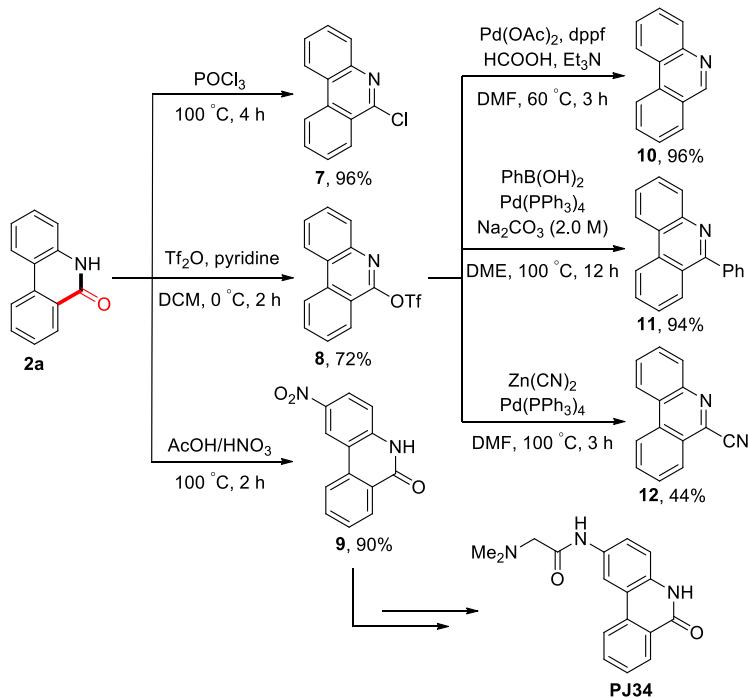


2.4.3 More control experiments

Compounds **5**, **6**, **13** were synthesized according to the reported literature^[S20-S22]. And the following yields were determined by ¹H NMR with CH_2Br_2 as the internal standard.



2.5 Further transformations and characterization of products.



Scheme S1 Synthetic elaboration.

To demonstrate the utility of our C–H carboxylation method, further elaboration was carried out for the synthesis of several synthetically useful compounds (Scheme S1). Firstly, 6-chlorophenanthridine **7** was afforded in excellent yield by subjecting **2a** to POCl_3 . Moreover, phenanthridine **10** and 6-substituted phenanthridines (**11** and **12**) could be obtained readily with well-established reaction conditions from triflate **8**.

that was generated from **2a** with triflate anhydride in good yields. Finally, nitration of **2a** in the presence of AcOH/HNO₃ provided 2-nitrophenanthridin-6(5*H*)-one **9** in 90% yield which is a key precursor for the preparation of a highly selective PARP-1 inhibitor **PJ34** which also possesses anti-cancer activity.

2.5.1 Procedure for synthesis of **7** ^[S23]

2a (0.3 mmol, 58.5 mg) was added to 6 mL POCl₃ and the mixture was heated to 100 °C for 4 h. Then the reaction mixture was cooled to room temperature and evaporation to dryness. POCl₃ was recycled and the residue was quenched with 10 mL water and extracted by DCM. The organic phase was dried over sodium sulfate, filtered, and evaporated to afford a residue. Separation of the residue by silica gel column chromatography using petroleum ether/EtOAc (30:1) as the eluent provided the corresponding product **7** (61.3 mg, 96% yield).

2.5.2 Procedure for synthesis of **8** ^[S24]

To a screw-capped vial were added **2a** (0.3 mmol, 58.5 mg) and pyridine (0.45 mmol, 1.5 equiv) in 3 mL DCM, and the solution was kept stirring at 0 °C. Tf₂O (0.36 mmol, 1.2 equiv) was dissolved in 2 mL DCM, then the mixture were slowly injected into the reaction mixture using a drip pump for two hours. Then the crude reaction mixture was diluted with DCM, extracted by NaHCO₃ aqueous solution. The combined organic layer was collected, dried over sodium sulfate, filtered, and evaporated to afford a residue. Separation of the residue by silica gel column chromatography using petroleum ether/EtOAc (30:1) as the eluent provided the corresponding product **8** (70.6 mg, 72% yield).

2.5.3 Procedure for synthesis of **9** ^[S25]

In a 25 mL round bottom flask fitted with a condenser, **2a** (97.5 mg, 0.5 mmol) was taken and dissolved in acetic acid (5.0 mL). Later, 90% of nitric acid (2.5 mL) was added into the mixture slowly in 10 min at the ambient temperature. The mixture was refluxed at 100 °C for 2 h, then cooled to ambient temperature. The solid was filtered and washed with ice acetic acid and water, and dried under vacuum to afford the corresponding product **9** (108.0 mg, 90% yield).

2.5.4 Procedure for synthesis of **10** ^[S24]

Reactions were conducted in glove box under nitrogen atmosphere. To a screw-capped vial (10-mL) were added compound **5c** (65.4 mg, 0.2 mmol), Pd(OAc)₂ (2.4 mg, 5.0 mol%), dppf (14.4 mg, 13 mol%) in 2 mL DMF. The reaction mixture was allowed to stir at room temperature for a while. Formic acid (HCO₂H, 22.2 mg, 2.4 equiv) and NEt₃ (60.6 mg, 3.0 equiv) were then slowly injected into the reaction. The vial was then sealed with cap and kept stirring at 60 °C for 3 h. The crude reaction mixture was diluted with DCM, extracted by NaHCO₃ aqueous solution (2 M). The combined organic layer was collected, dried over sodium sulfate, filtered, and evaporated to afford a residue. Separation of the residue by silica gel column chromatography using petroleum ether/EtOAc (30:1) as the eluent provided the corresponding product **10** (34.4 mg, 96% yield).

2.5.5 Procedure for synthesis of **11** ^[S26]

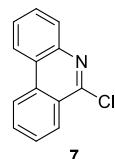
To a Schlenk tube was added **5c** (65.4 mg, 0.2 mmol), phenylboronic acid (29.2 mg, 0.24 mmol) and Pd(PPh₃)₄ (11.6 mg, 0.01 mmol), then replacement with Ar for three times. Under protecting by Ar, dry DME (0.8 mL) and 2M Na₂CO₃ aqueous solution (0.2 mL) was added. The reaction was reacted at 100 °C for 12 h. The crude reaction mixture was diluted with EtOAc and washed with water and brine. The combined organic layer was collected, dried over sodium sulfate, filtered, and evaporated to afford a residue. Separation of the

residue by silica gel column chromatography using petroleum ether/EtOAc (30:1) as the eluent provided the corresponding product **11** (47.9 mg, 94% yield).

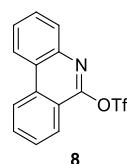
2.5.6 Procedure for synthesis of **12** [S26]

The mixture of **5c** (65.4 mg, 0.2 mmol), Zn(CN)₂ (31 mg, 0.26 mmol, 1.3 equiv) and Pd(PPh₃)₄ (23.2 mg, 0.02 mmol) in dry and degassed DMF (1 mL) was stirred at 100 °C for 3 h. Then the reaction was cooled to room temperature when completed, and it was diluted with EtOAc, washed with H₂O and brine respectively. The organic phase was dried over anhydrous Na₂SO₄, concentrated under vacuum and purified by flash silica gel chromatography using petroleum ether/EtOAc (30:1) as the eluent to give **12** (18.0 mg, 44%).

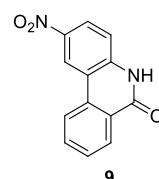
2.5.7 Characterization of 7-12



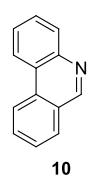
6-chlorophenanthridine (known compound)^[S27], white solid. **1H NMR (600 MHz, CDCl₃)** δ 8.51 – 8.49 (m, 1H), 8.46 – 8.42 (m, 1H), 8.41 – 8.39 (m, 1H), 8.06 – 8.04 (m, 1H), 7.85 – 7.82 (m, 1H), 7.72 – 7.67 (m, 2H), 7.64 – 7.62 (m, 1H). **13C NMR (151 MHz, CDCl₃)** δ 151.5, 143.3, 134.5, 131.8, 129.4, 129.3, 128.3, 127.7, 127.5, 124.9, 124.0, 122.28, 122.25.



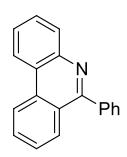
phenanthridin-6-yl trifluoromethanesulfonate (known compound)^[S27], white solid. **1H NMR (600 MHz, CDCl₃)** δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.45 – 8.44 (m, 1H), 8.18 – 8.16 (m, 1H), 8.04 – 8.02 (m, 1H), 7.91 – 7.88 (m, 1H), 7.74 – 7.71 (m, 1H), 7.69 – 7.66 (m, 1H). **13C NMR (151 MHz, CDCl₃)** δ 151.6, 141.0, 136.2, 132.5, 129.7, 129.5, 128.5, 128.0, 124.4, 124.0, 122.5, 122.3, 119.0 (q, *J* = 320.4 Hz), 118.4.



2-nitrophenanthridin-6(5H)-one (known compound)^[S2], light yellow solid. **1H NMR (600 MHz, DMSO-d₆)** δ 12.25 (s, 1H), 9.20 (d, *J* = 2.4 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.40 – 8.31 (m, 2H), 7.93 (t, *J* = 7.2 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H).



phenanthridine (known compound)^[S28], white solid. **1H NMR (600 MHz, CDCl₃)** δ 9.28 (s, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.57 – 8.55 (m, 1H), 8.20 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.76 – 7.73 (m, 1H), 7.71 – 7.68 (m, 1H), 7.68 – 7.66 (m, 1H). **13C NMR (151 MHz, CDCl₃)** δ 153.7, 144.6, 132.7, 131.1, 130.2, 128.9, 128.8, 127.6, 127.2, 126.5, 124.2, 122.3, 122.0.



6-phenylphenanthridine (known compound)^[S29], white solid. **1H NMR (600 MHz, CDCl₃)** δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.64 – 8.60 (m, 1H), 8.28 – 8.26 (m, 1H), 8.12 – 8.10 (m, 1H), 7.86 – 7.83 (m, 1H), 7.79 – 7.74 (m, 3H), 7.70 – 7.68 (m, 1H), 7.62 – 7.60 (m, 1H), 7.59 – 7.52 (m, 3H). **13C NMR (151 MHz, CDCl₃)** δ 161.4, 143.9, 139.9, 133.6, 130.7, 130.5, 129.9, 129.01, 128.95, 128.8, 128.5, 127.2, 127.0, 125.4, 123.9, 122.3, 122.1.



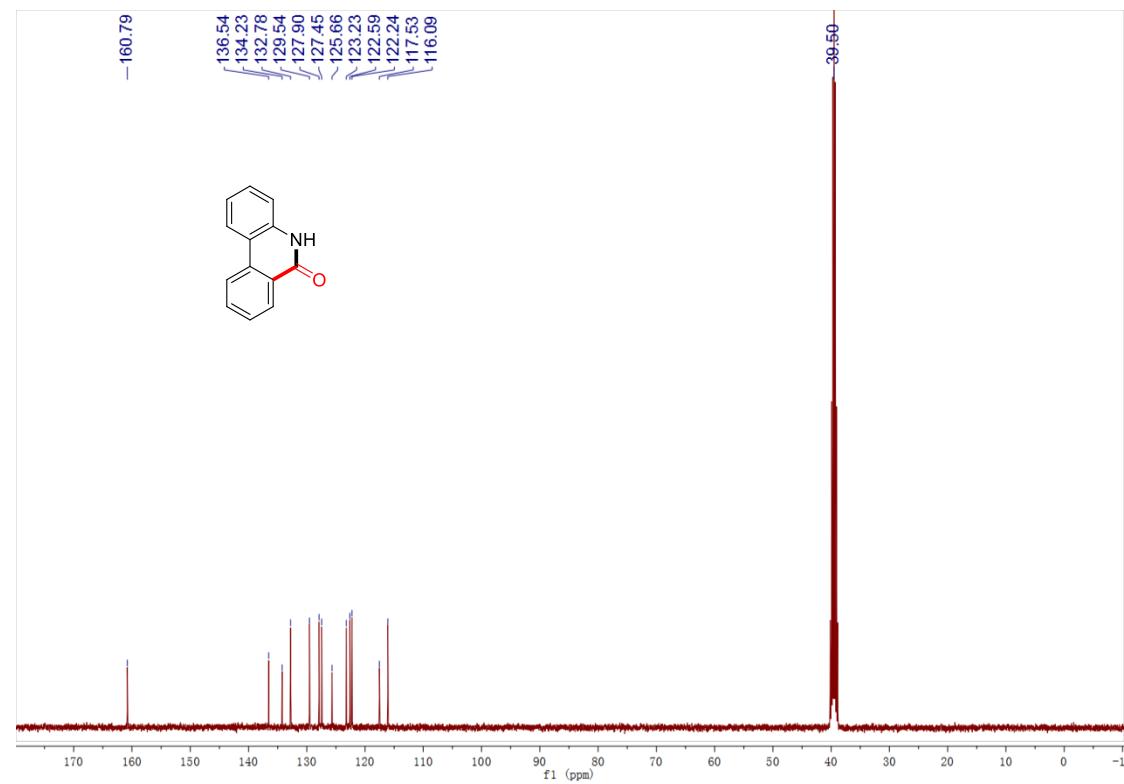
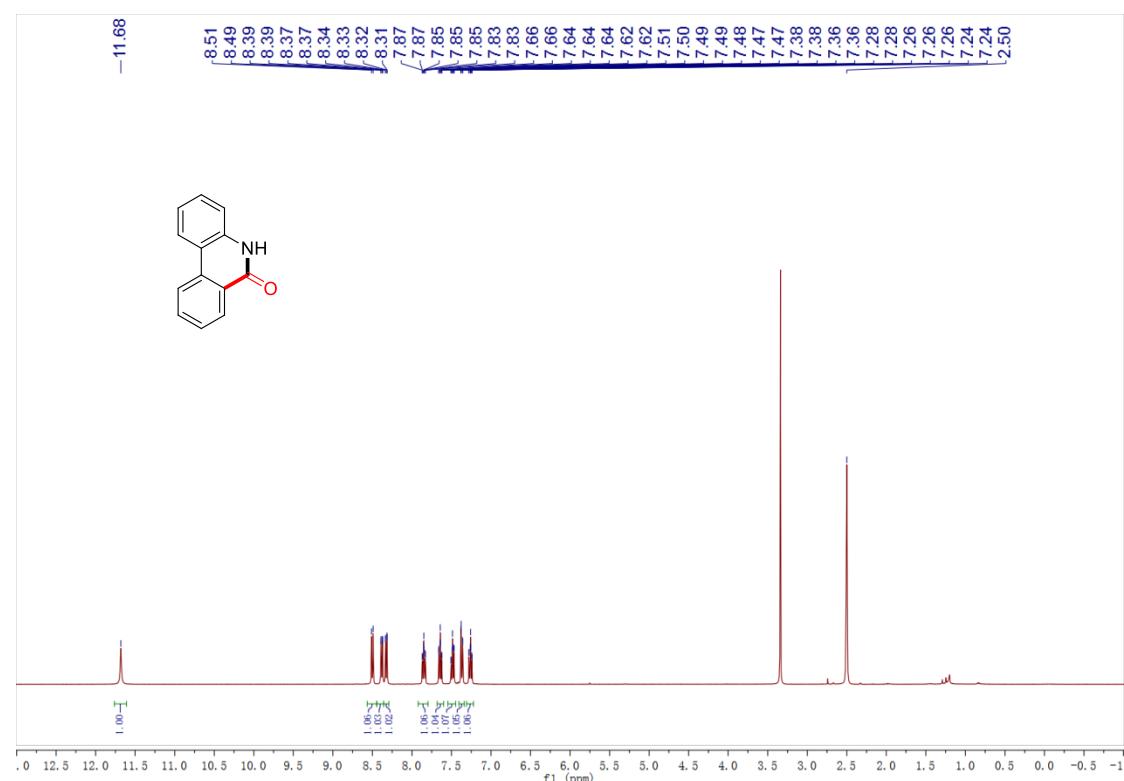
phenanthridine-6-carbonitrile (known compound)^[S30], white solid. **1H NMR (600 MHz, CDCl₃)** δ 8.67 – 8.65 (m, 1H), 8.62 – 8.58 (m, 1H), 8.44 – 8.43 (m, 1H), 8.27 – 8.22 (m, 1H), 7.99 – 7.96 (m, 1H), 7.86 – 7.81 (m, 3H). **13C NMR (151 MHz, CDCl₃)** δ 143.8, 135.9, 132.9, 132.4, 131.2, 130.1, 129.8, 129.0, 126.8, 125.6, 124.9, 122.5, 122.4, 116.0.

2.6 References

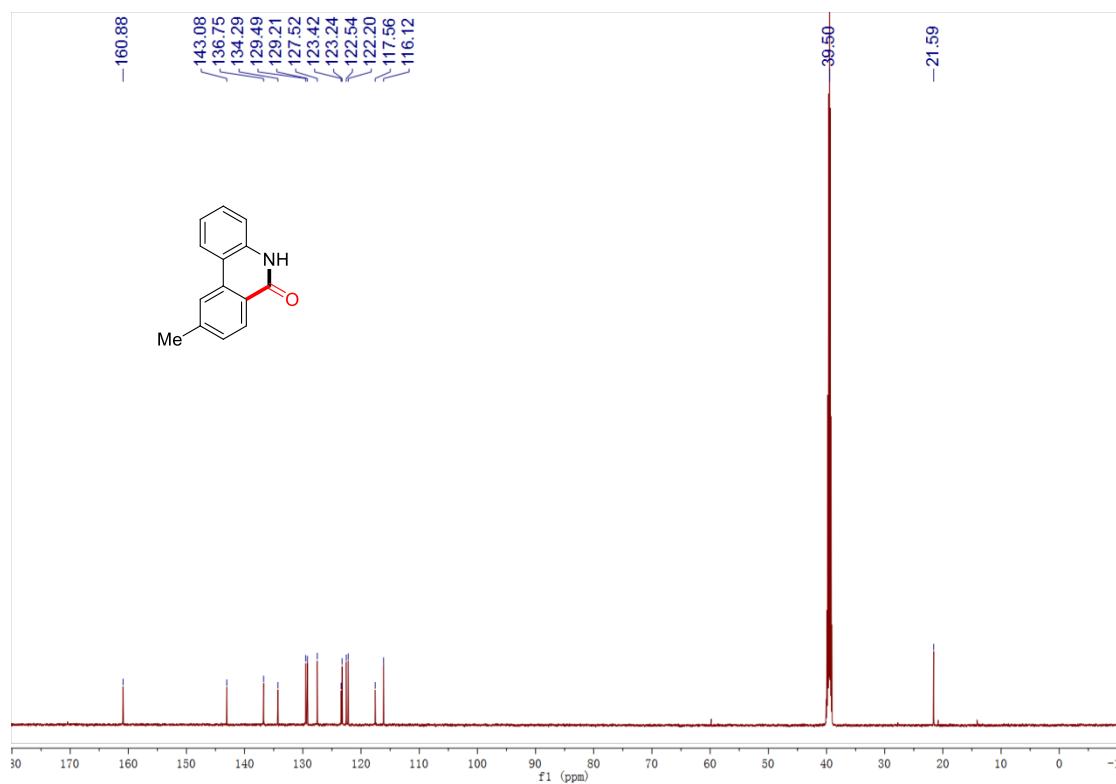
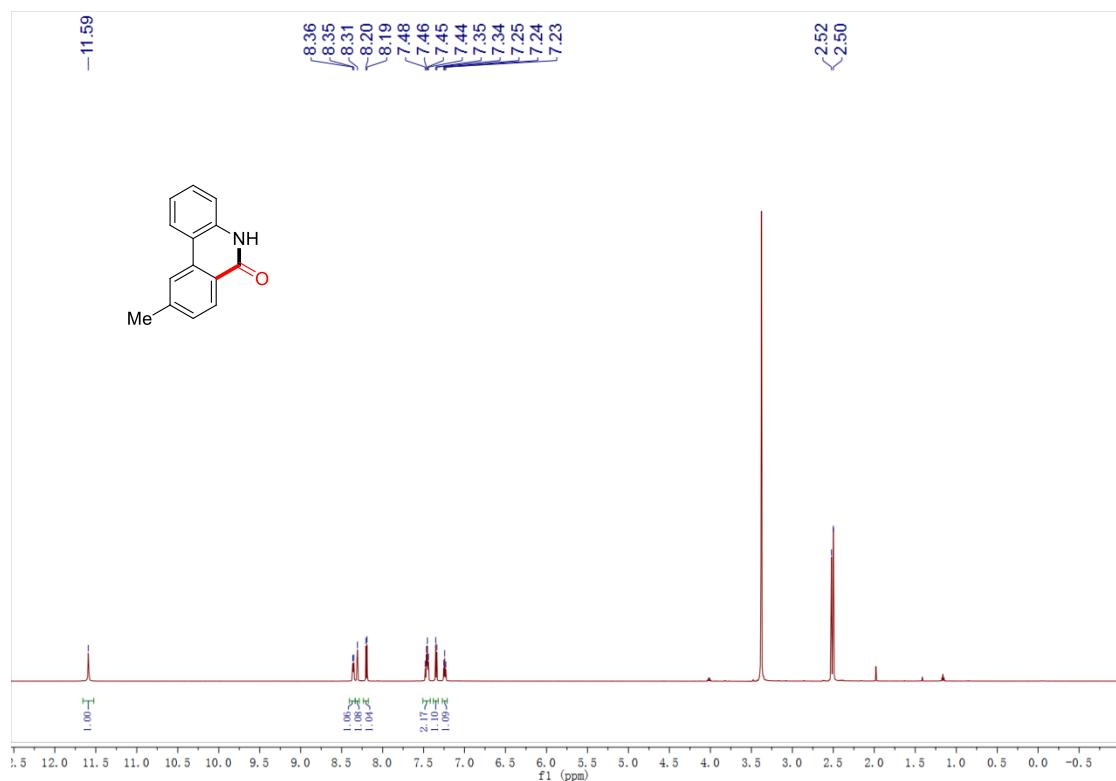
- [S1] C. Liu, Y. Zhang, N. Liu and J. Qiu, *Green Chem.*, 2012, **14**, 2999.
- [S2] Z. Liang, J. Zhang, Z. Liu, K. Wang and Y. Zhang, *Tetrahedron*, 2013, **69**, 6519.
- [S3] B. J. Stokes, B. Jovanović, H. Dong, K. J. Richert, R. D. Riell and T. G. Driver, *J. Org. Chem.*, 2009, **74**, 3225.
- [S4] U. Sheth, L. T. D. Fanning, M. M. D. Numa, H. Binch, D. Hurley, J. Zhou, S. S. H. Ruah, A. Hazlewood, A. Silina, R. Vairagounder, F. Van Goor, P. D. J. Grootenhuis and M. Botfield, WO 2011072241 A1, 2016.
- [S5] J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu and J. Hu, *Angew. Chem., Int. Ed.*, 2016, **55**, 2743.
- [S6] Z. Zuo, J. Liu, J. Nan, L. Fan, W. Sun, Y. Wang and X. Luan, *Angew. Chem., Int. Ed.*, 2015, **54**, 15385.
- [S7] J. Xie, X. Yuan, A. Abdukader, C. Zhu and J. Ma, *Org. Lett.*, 2014, **16**, 1768.
- [S8] M. J. S. Dewar and P. J. Grisdale, *J. Org. Chem.*, 1963, **28**, 1759.
- [S9] P. K. Agarwal, S. K. Sharma, D. Sawant and B. Kundu, *Tetrahedron*, 2009, **65**, 1153.
- [S10] A. L. Pumphrey, H. Dong and T. G. Driver, *Angew. Chem., Int. Ed.*, 2012, **51**, 5920.
- [S11] L. Fu, S. Li, Z. Cai, Y. Ding, X.-Q. Guo, L.-P. Zhou, D. Yuan, Q.-F. Sun and G. Li, *Nat. Catal.*, 2018, **1**, 469.
- [S12] Z. An, L. Zhao, M. Wu, J. Ni, Z. Qi, G. Yua and R. Yan, *Chem. Commun.*, 2017, **53**, 11572.
- [S13] E. Dubost, R. Magnelli, T. Cailly, R. Legay, F. Fabis and S. Rault, *Tetrahedron*, 2010, **66**, 5008.
- [S14] F. Ling, C. Zhang, C. Ai, Y. Lv and W. Zhong, *J. Org. Chem.*, 2018, **83**, 5698.
- [S15] B. S. Bhakuni, A. Kumar, S. J. Balkrishna, J. A. Sheikh, S. Konar and S. Kumar, *Org. Lett.*, 2012, **14**, 2838.
- [S16] T. Cailly, F. Fabis and S. Rault, *Tetrahedron*, 2006, **62**, 5862.
- [S17] B. Glover, K. A. Harvey, B. Liu, M. J. Sharp and M. F. Tymoschenko, *Org. Lett.*, 2003, **5**, 301.
- [S18] R. Chicharro, S. D. Castro, J. L. Reino and V. J. Arán, *Eur. J. Org. Chem.*, 2003, 2314.
- [S19] S. H. Cho, J. Yoon and S. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 5996.
- [S20] J. Pouessel, O. Jacquet and T. Cantat, *ChemCatChem*, 2013, **5**, 3552.
- [S21] S. W. Youn and Y. H. Kim, *Org. Lett.*, 2016, **18**, 6140.
- [S22] M. Pizzotti, S. Cenini, S. Quici and S. Tollari, *J. Chem. Soc. Perkin Trans. 2*, 1994, 913.
- [S23] Z. Zhang, L.-L. Liao, S.-S. Yan, L. Wang, Y.-Q. He, J.-H. Ye, J. Li, Y.-G. Zhi, D.-G. Yu, *Angew. Chem., Int. Ed.*, 2016, **55**, 7068.
- [S24] Y.-F. Chen, Y.-S. Wu, Y.-H. Jhan and J.-C. Hsieh, *Org. Chem. Front.*, 2014, **1**, 253.
- [S25] S. Pimparkar and M. Jeganmohan, *Chem. Commun.*, 2014, **50**, 12116.
- [S26] Z. Cai, S. Li, Y.; Gao and G. Li, *Adv. Synth. Catal.*, 2018, **360**, 4005.
- [S27] M. R. Sonawane, J. Vávra, D. Šaman, I. Císařová and F. Teplý, *Synthesis*, 2015, **47**, 3479.
- [S28] C. Tang, Y. Yuan and N. Jiao, *Org. Lett.*, 2015, **17**, 2206.
- [S29] Y.-F. Chen and J.-C. Hsieh, *Org. Lett.*, 2014, **16**, 4642.
- [S30] S. Guo, G. Wan, S. Sun, Y. Jiang, J.-T. Yua and J. Cheng, *Chem. Commun.*, 2015, **51**, 5085.

3 NMR spectra of compounds

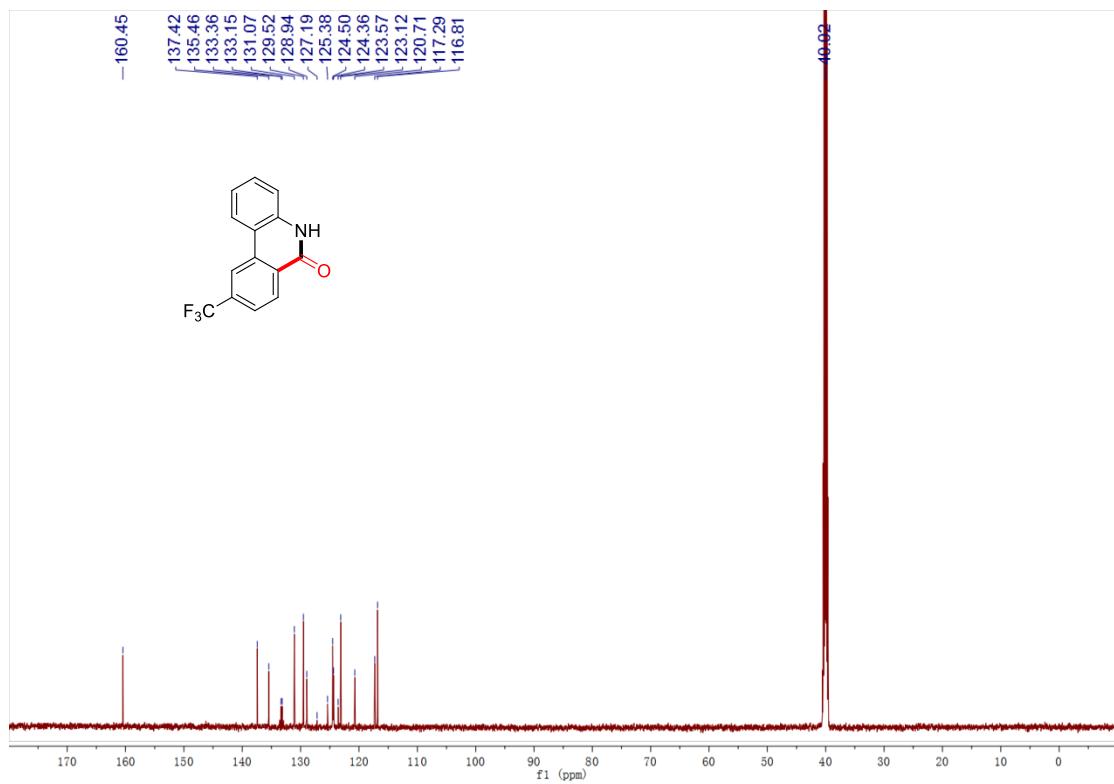
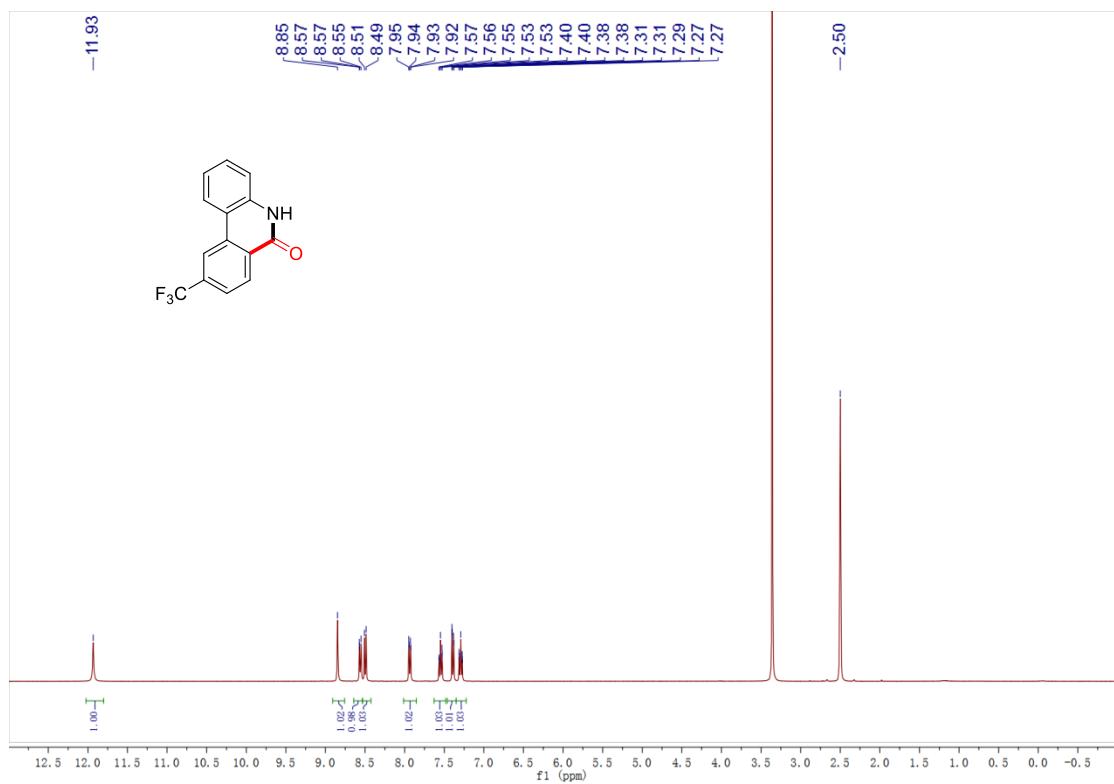
2a



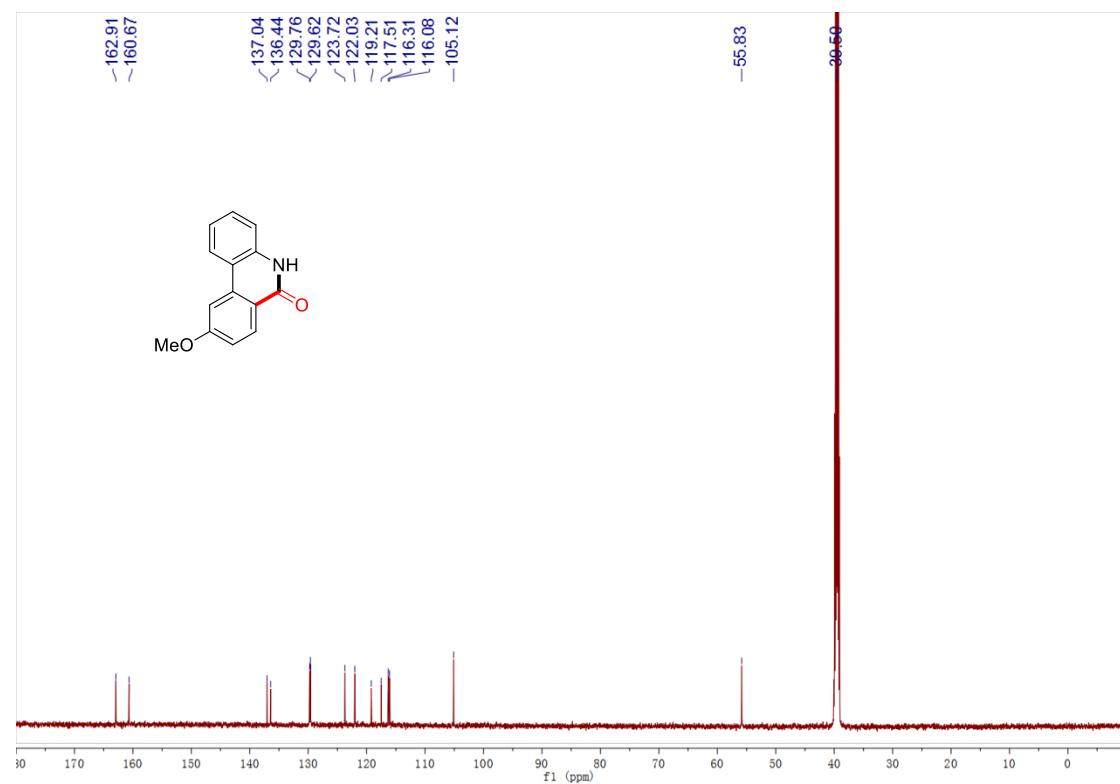
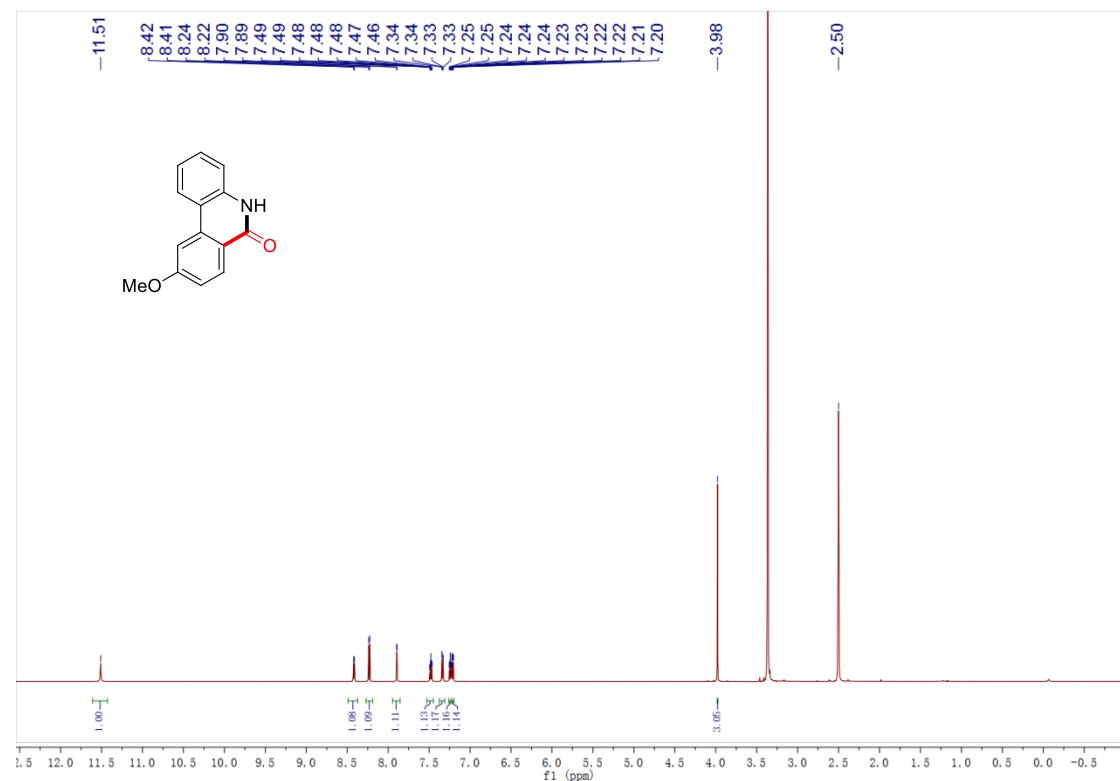
2b



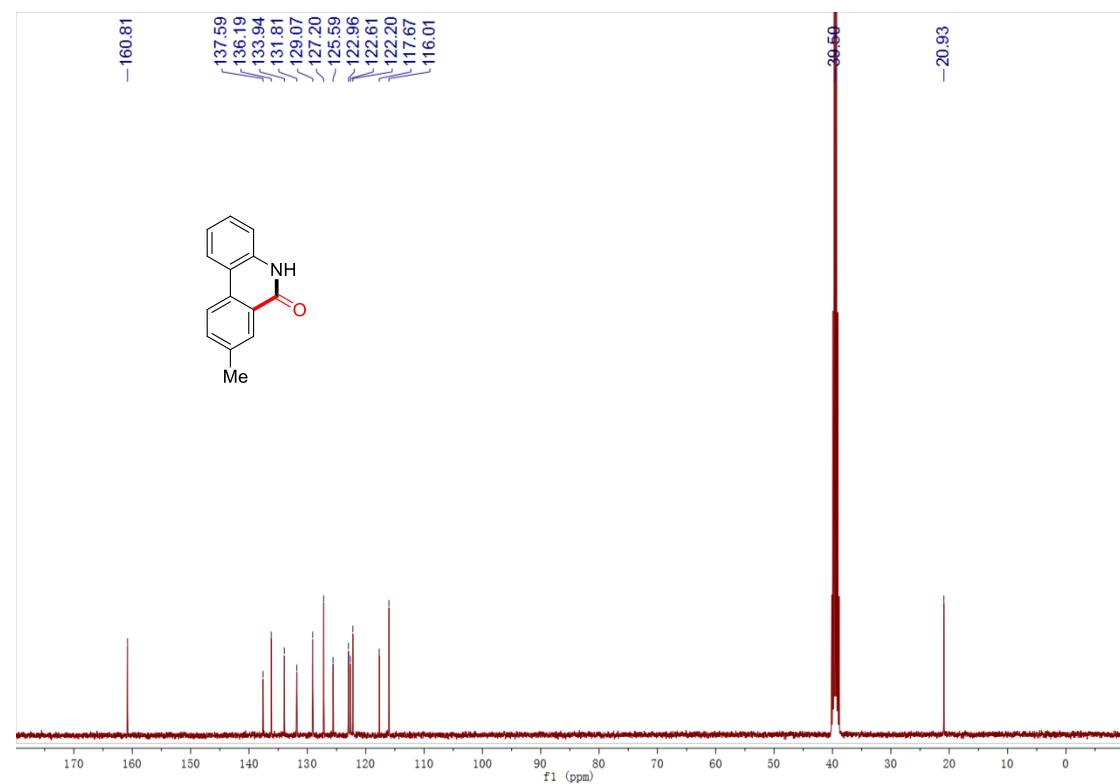
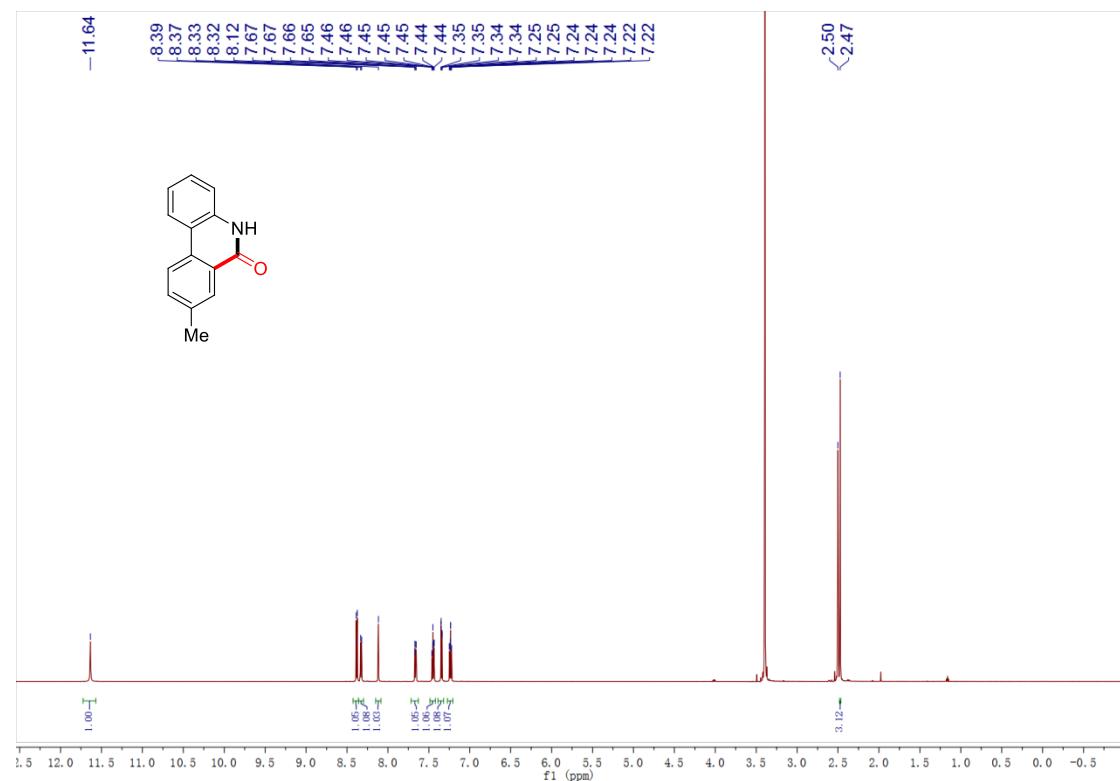
2c

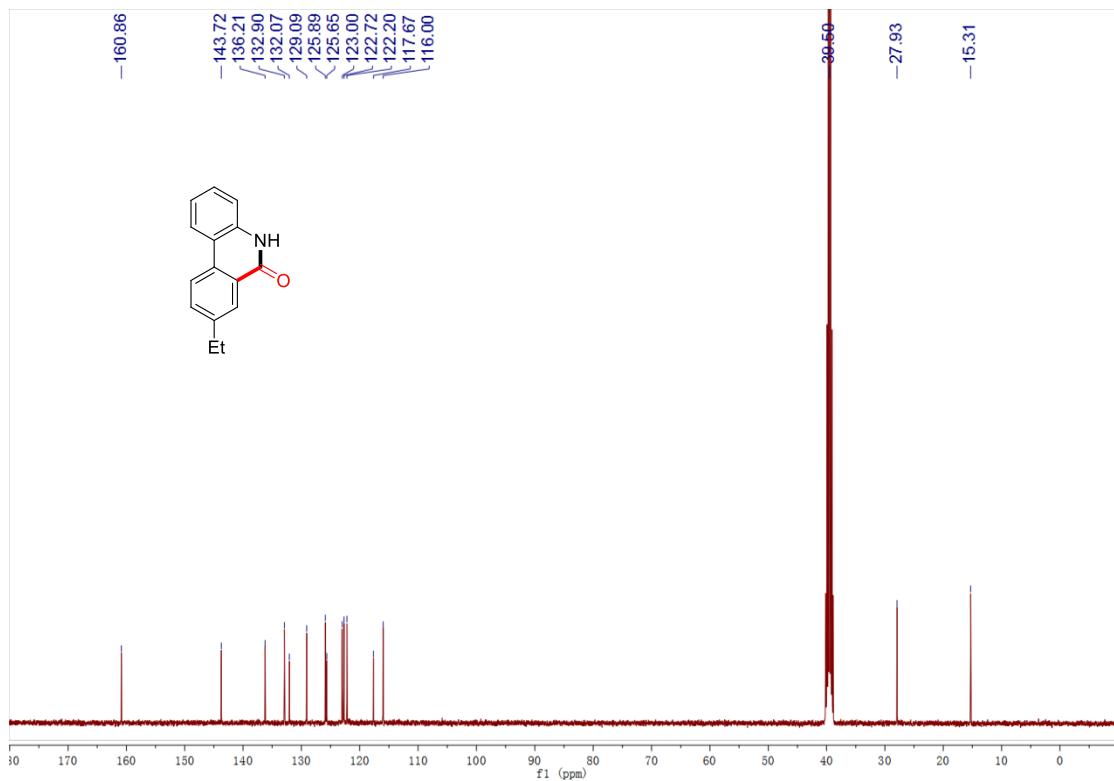
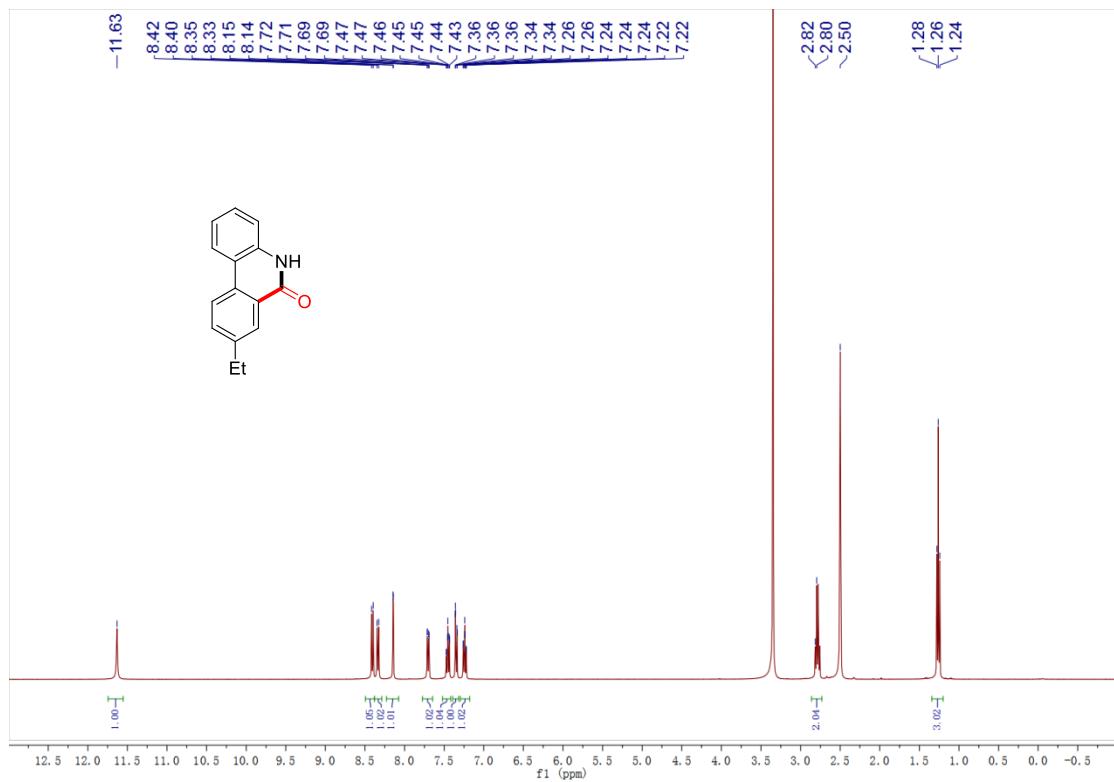


2d

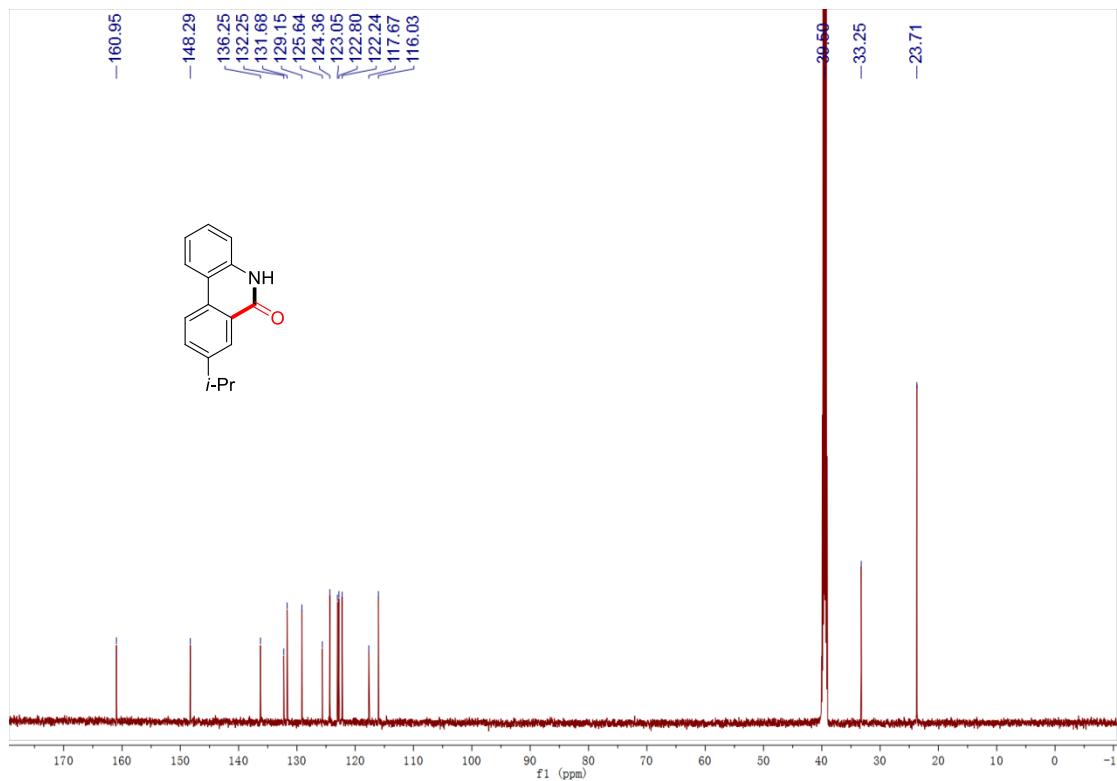
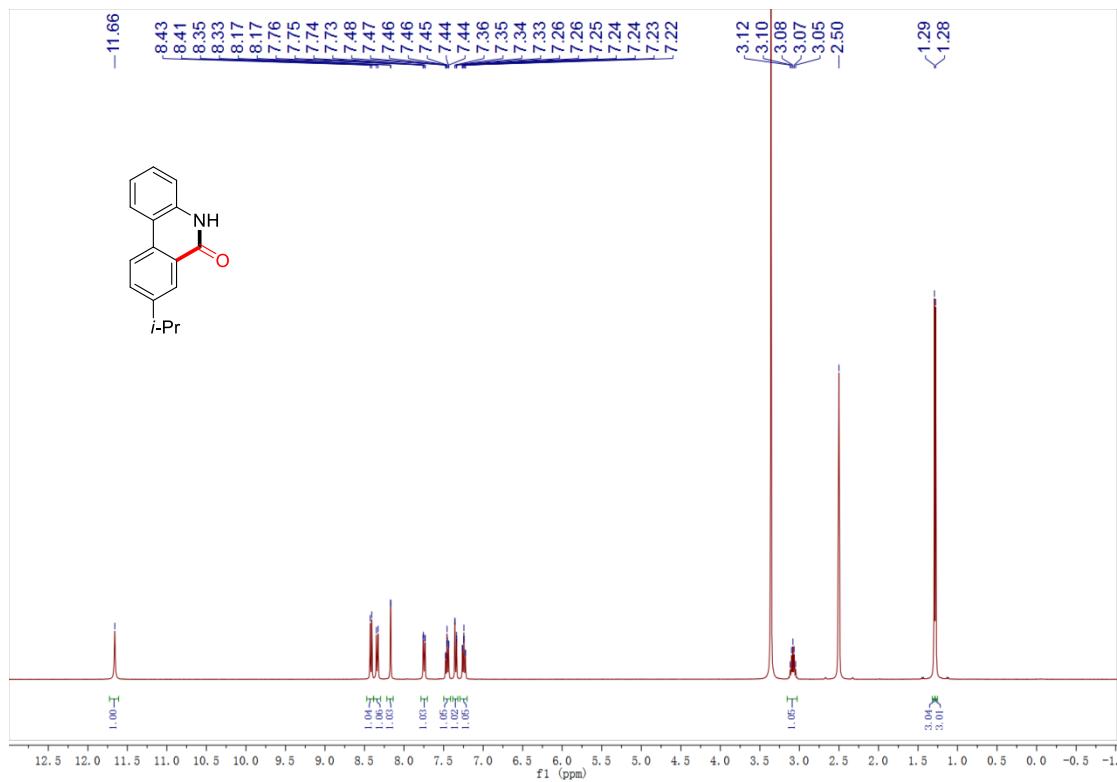


2e

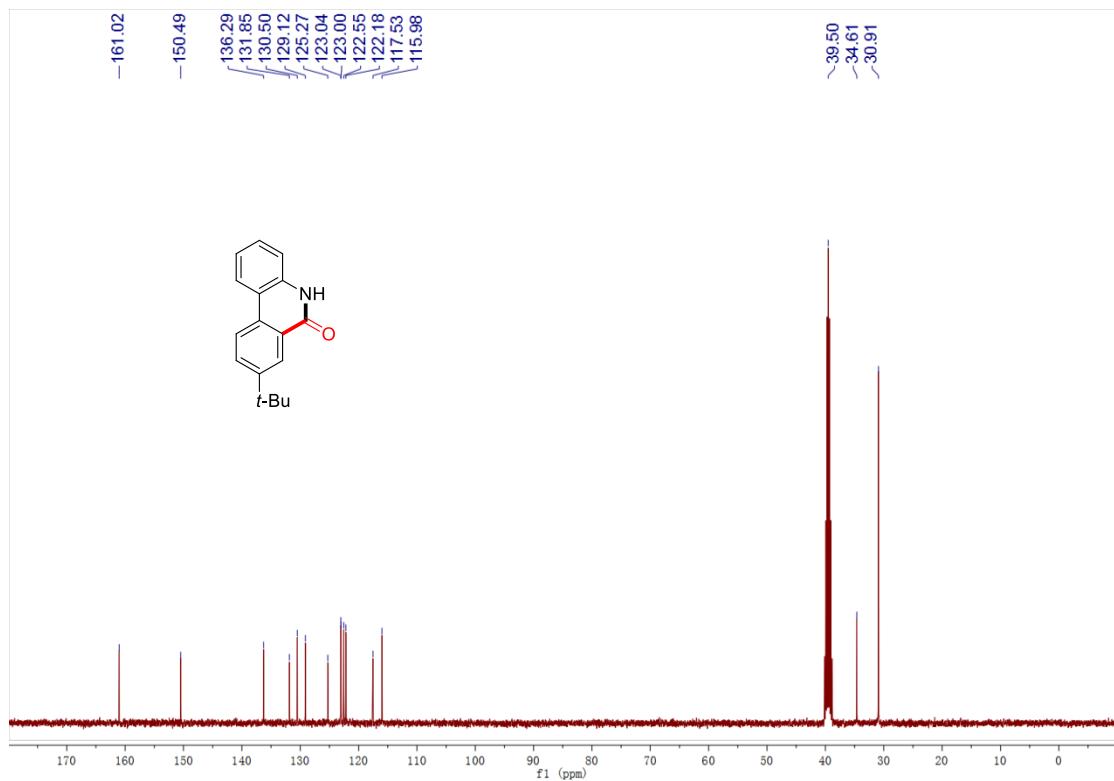
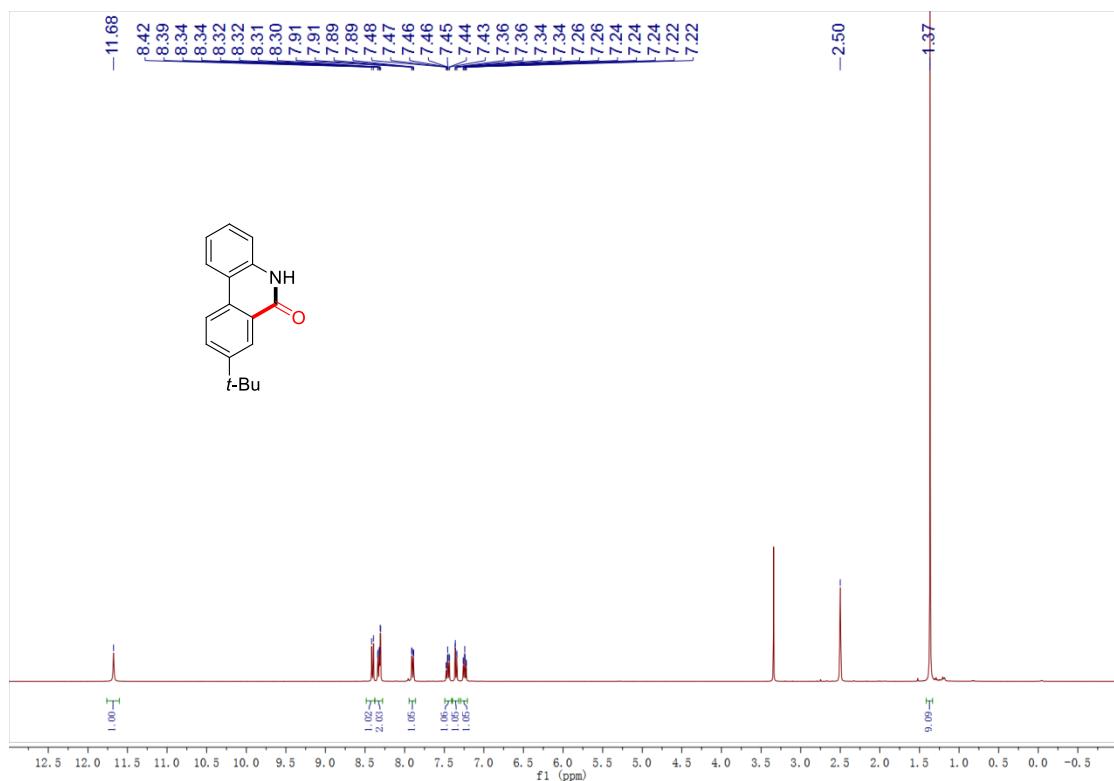


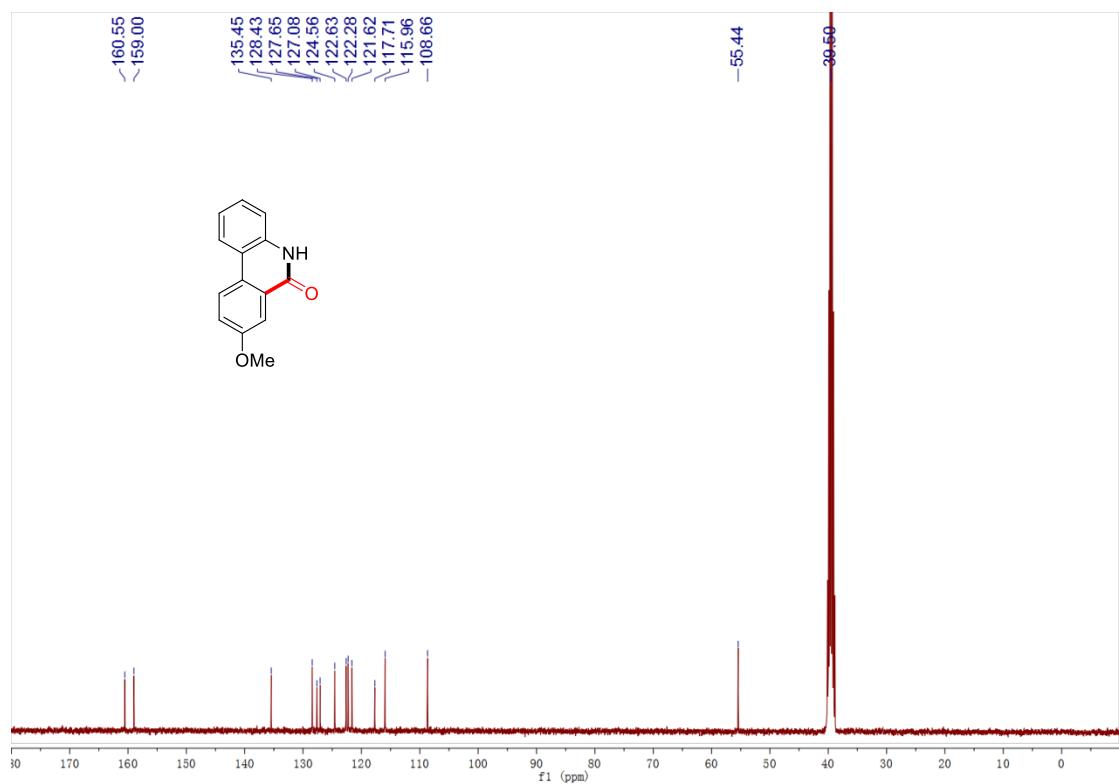
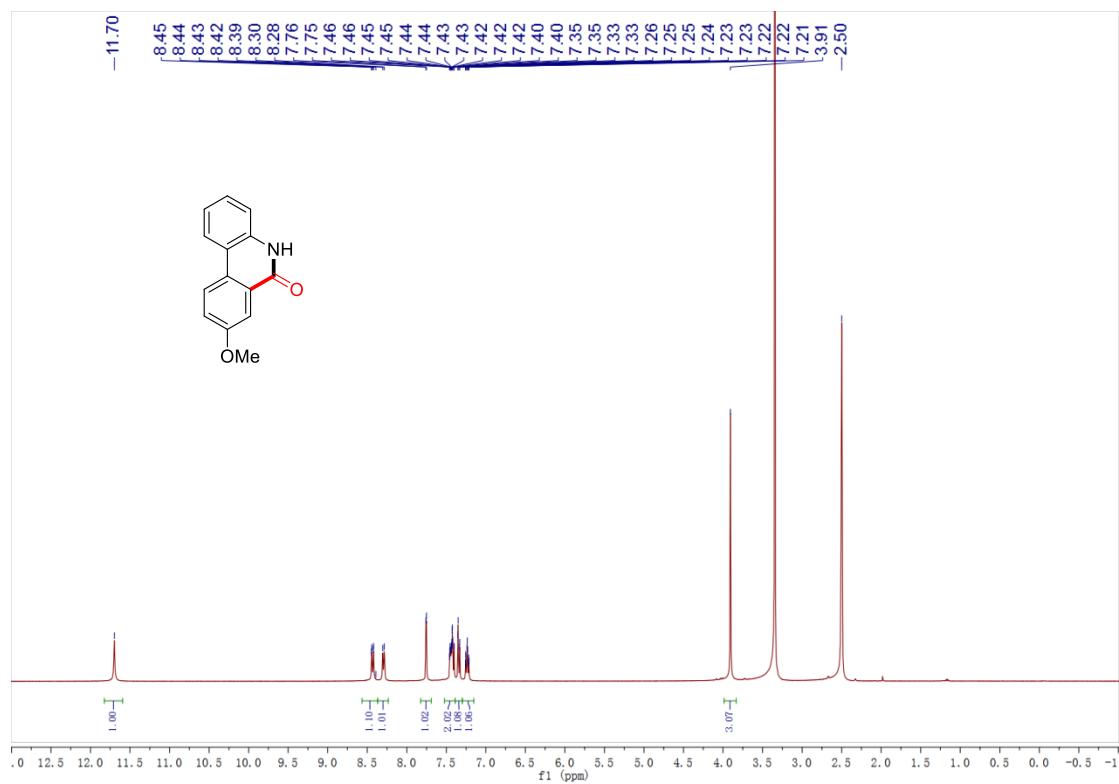


2g

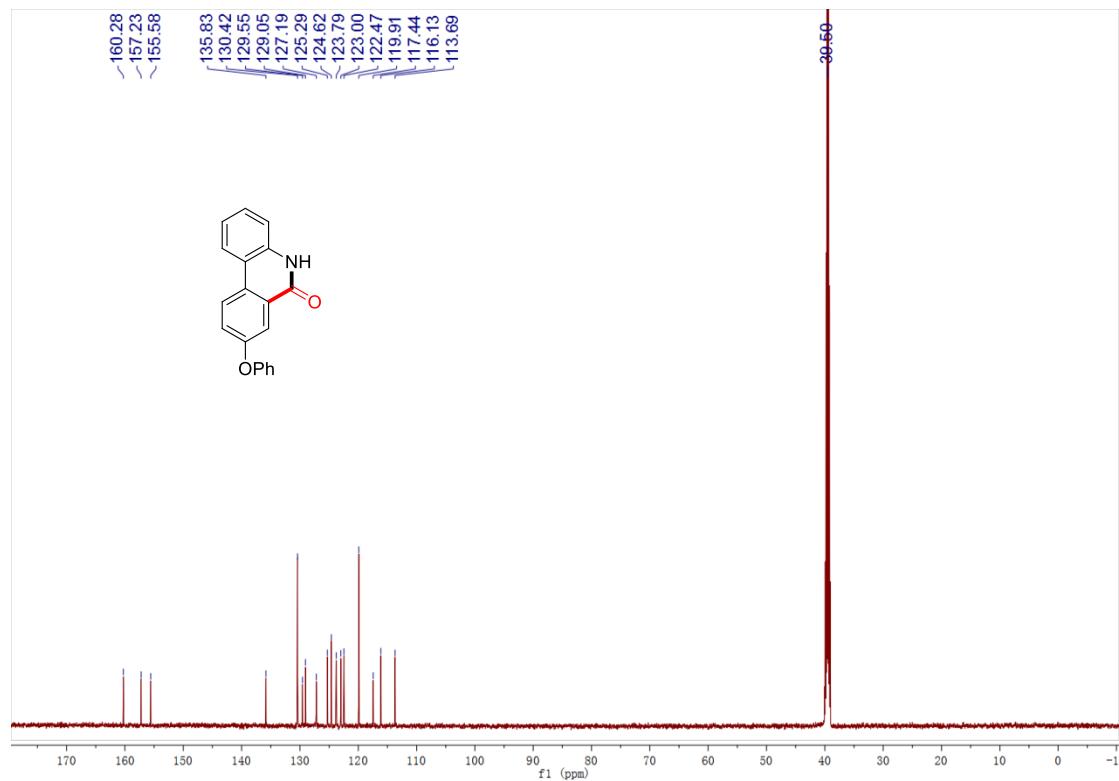
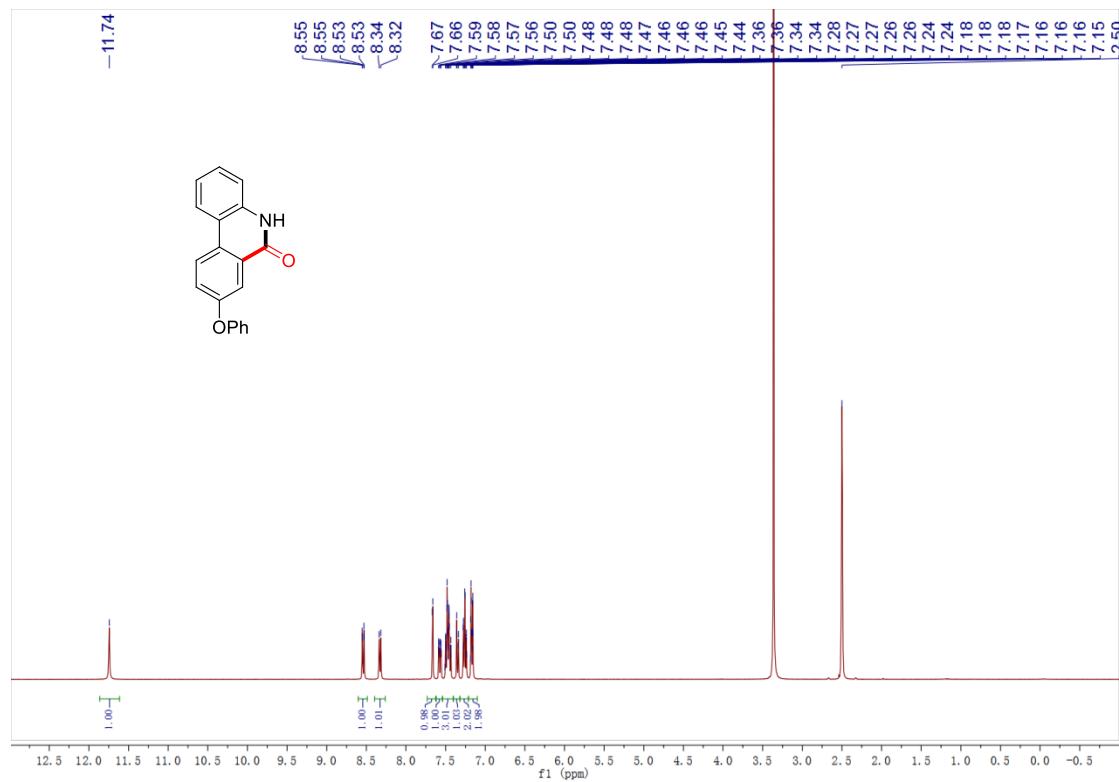


2h

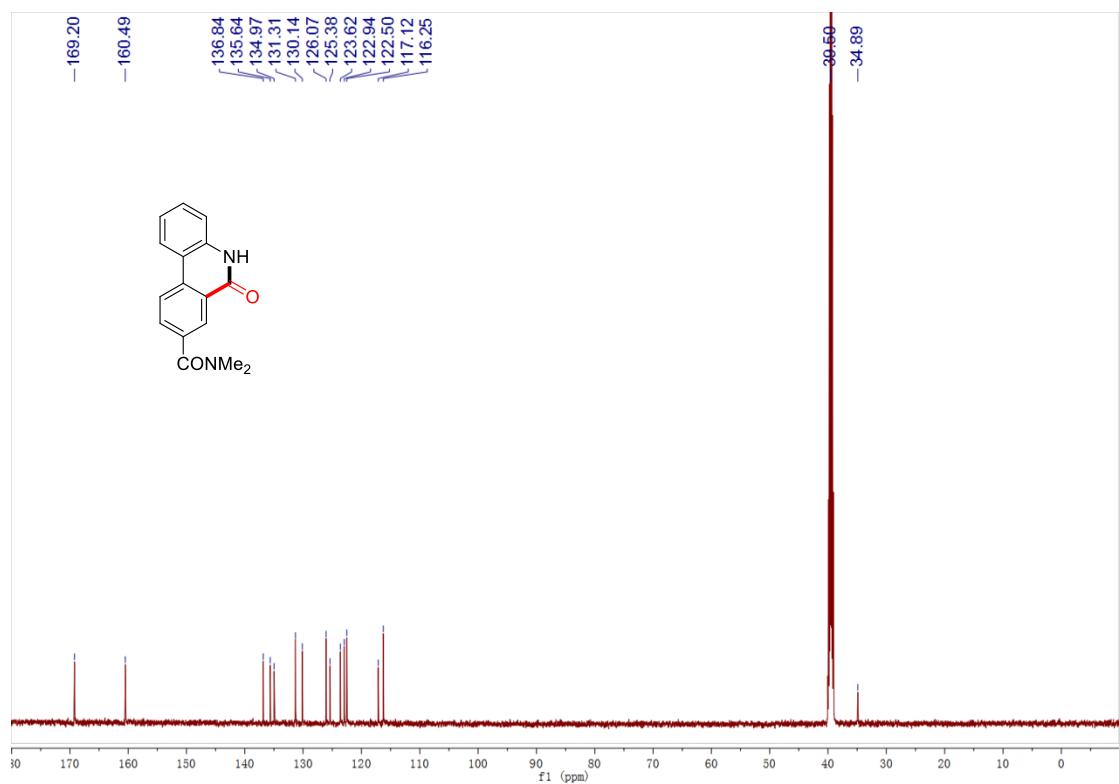
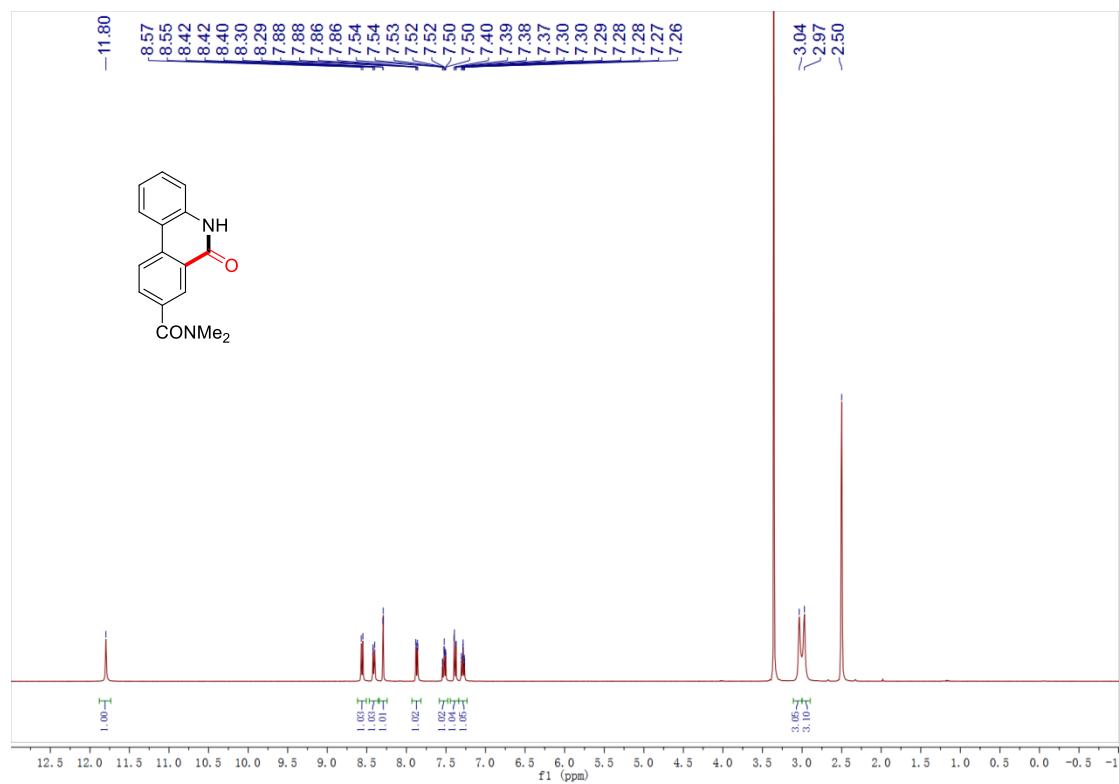


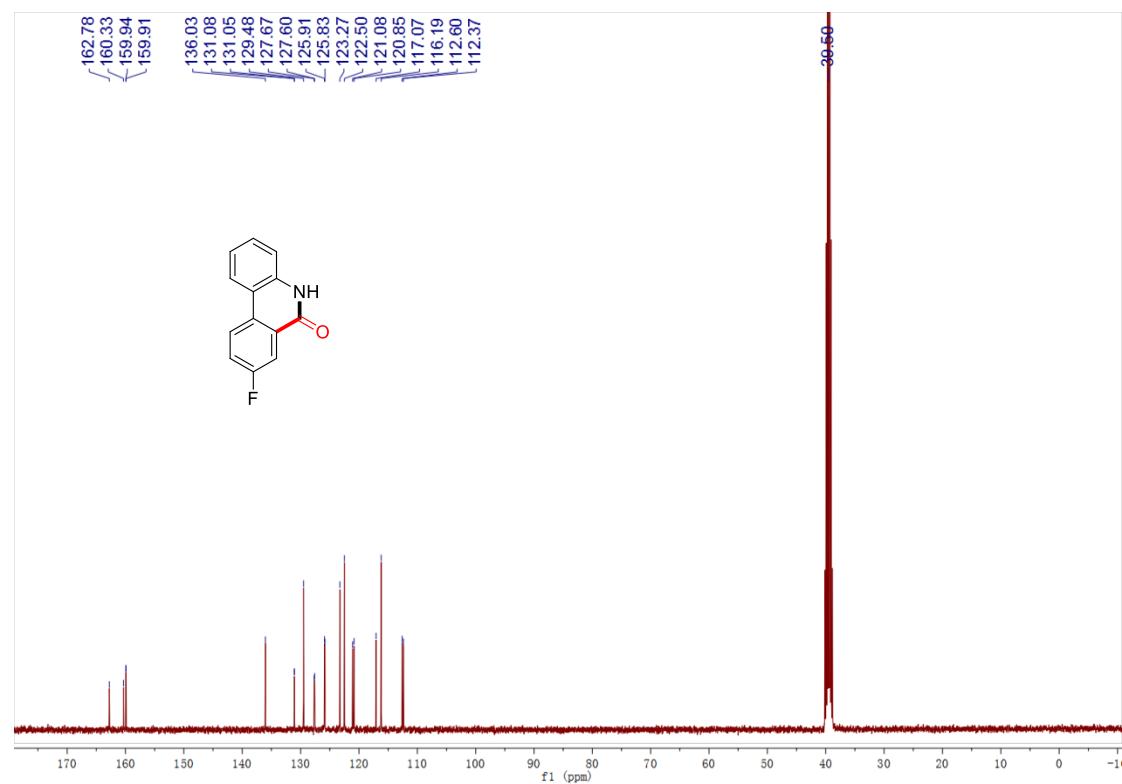
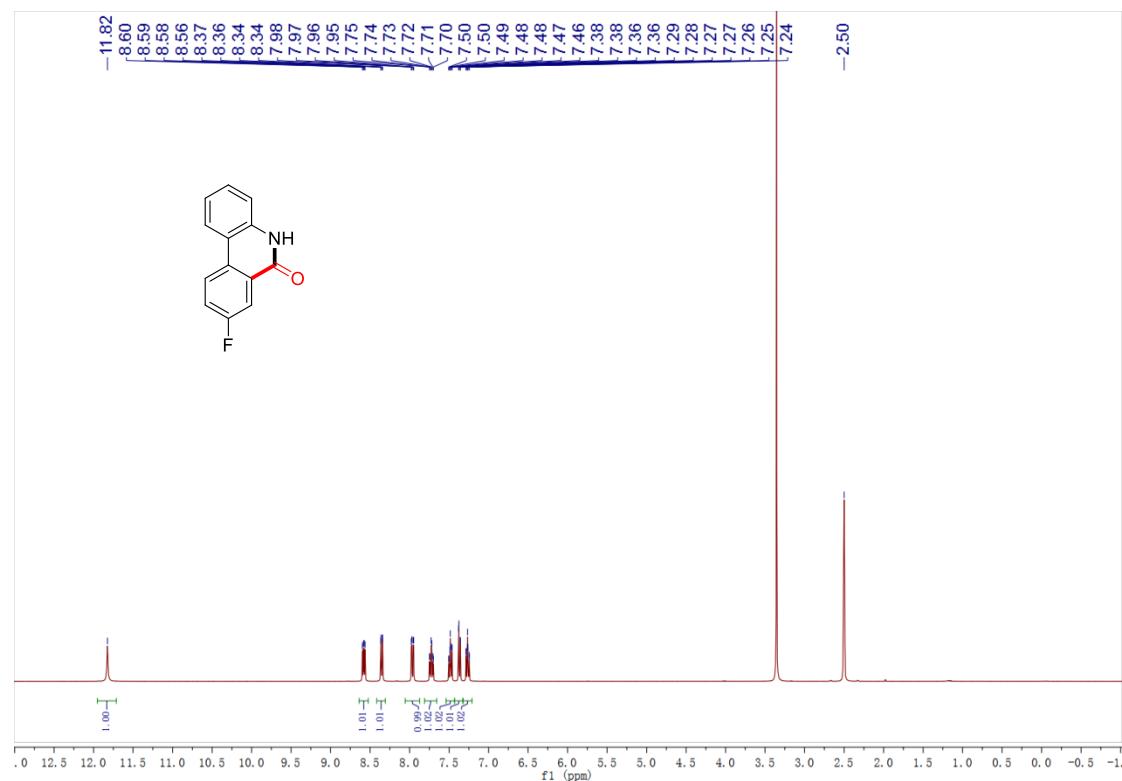


2j

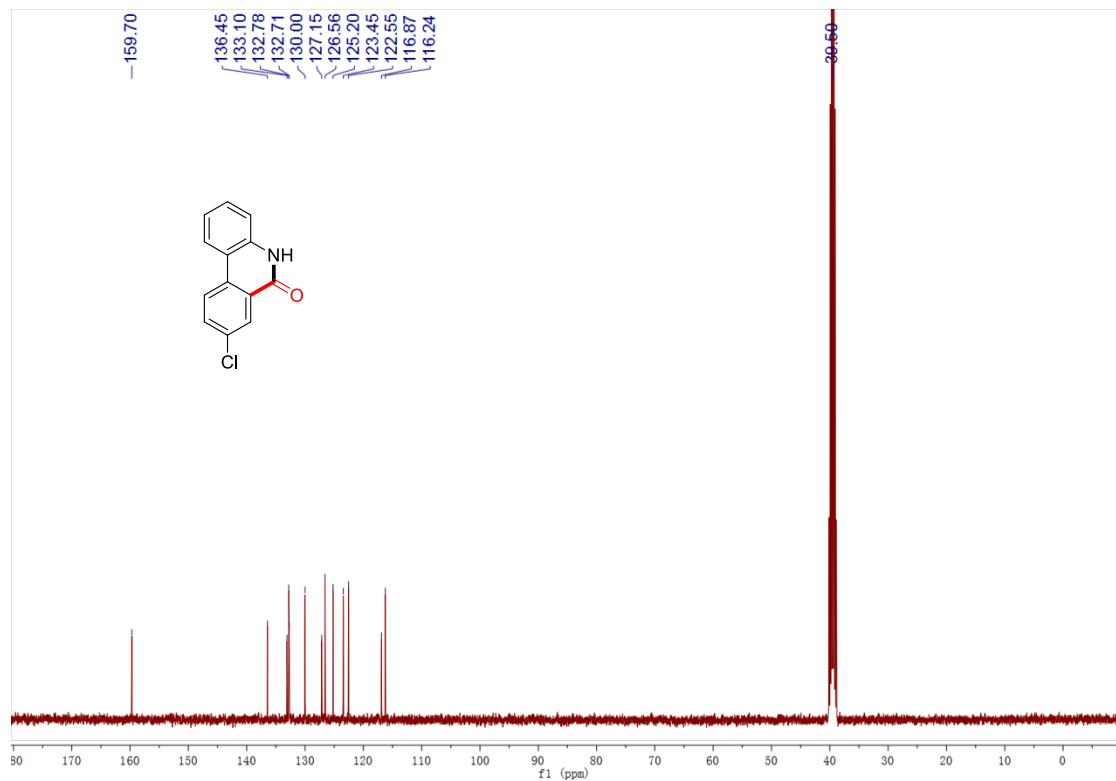
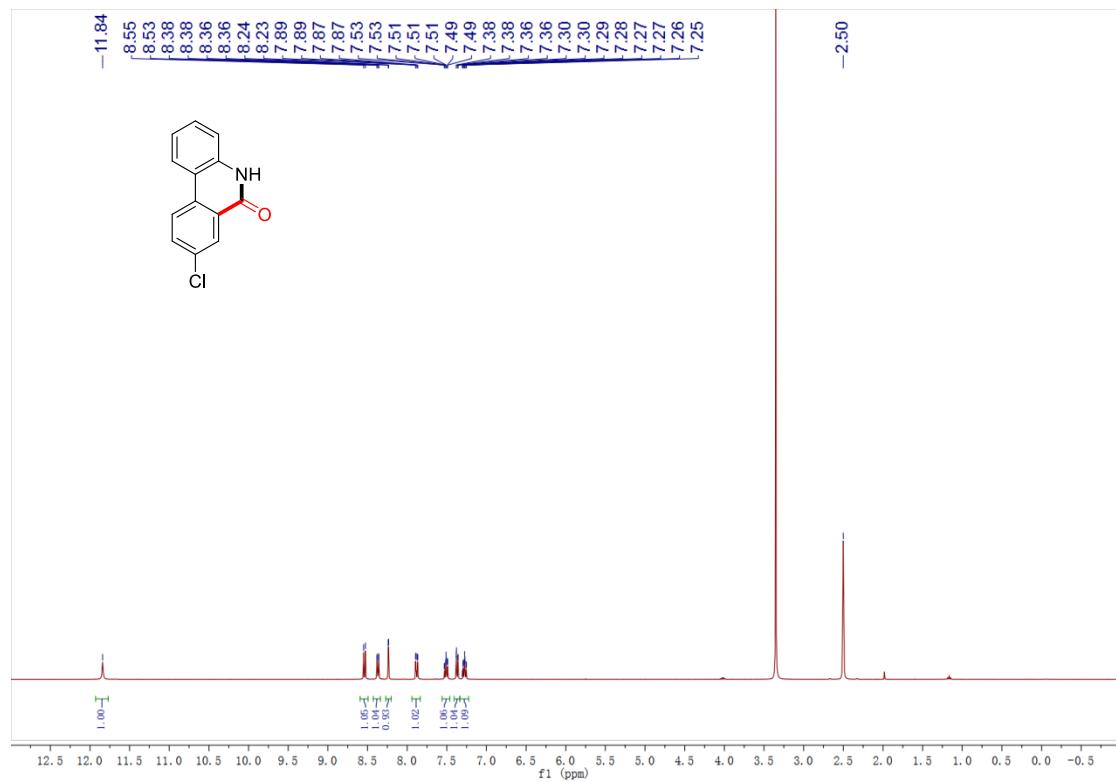


2k

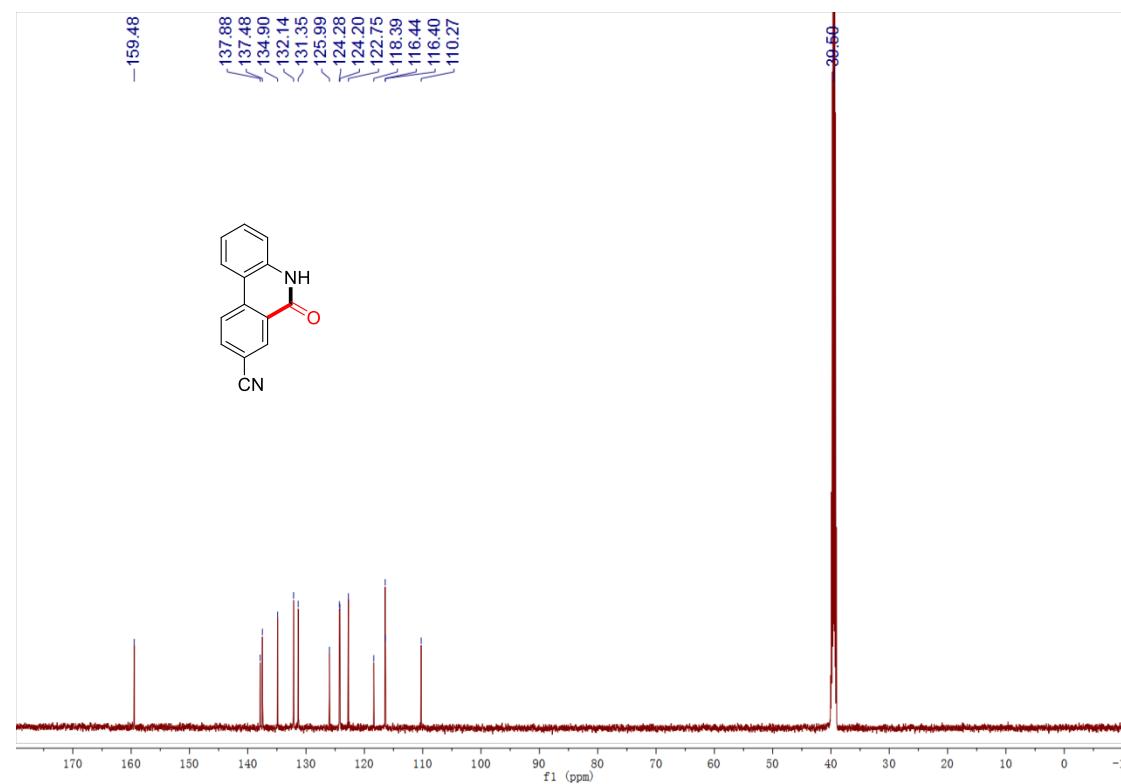
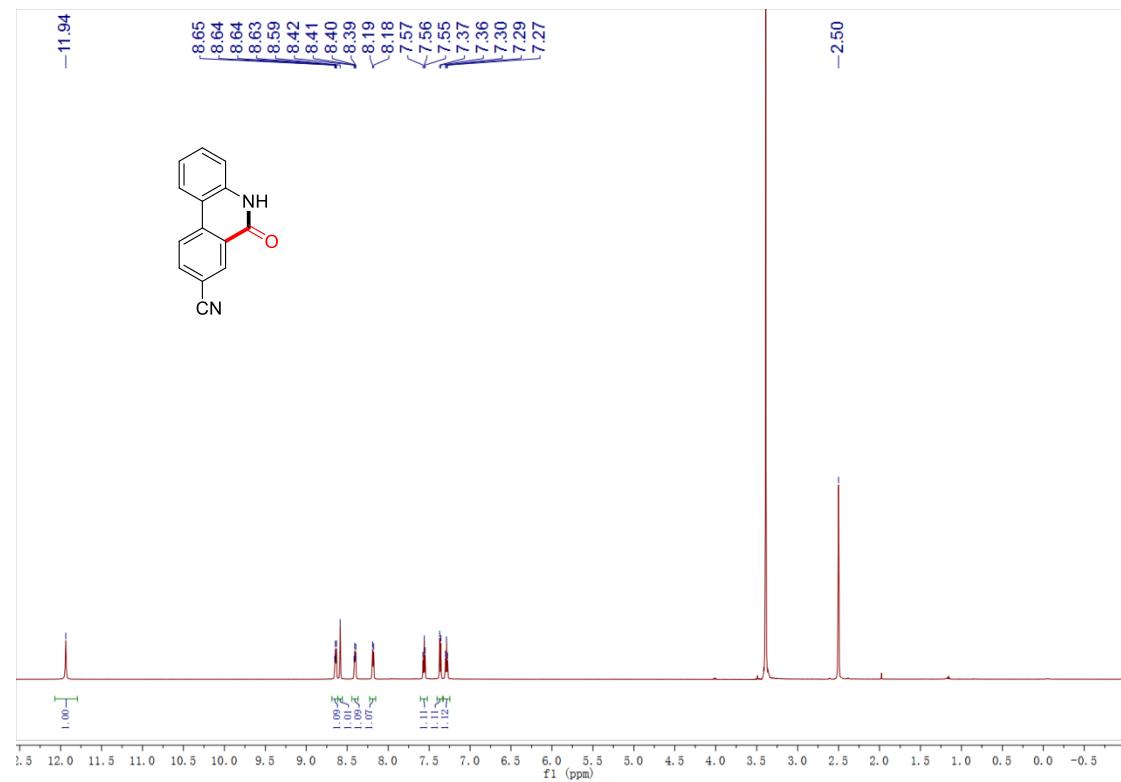


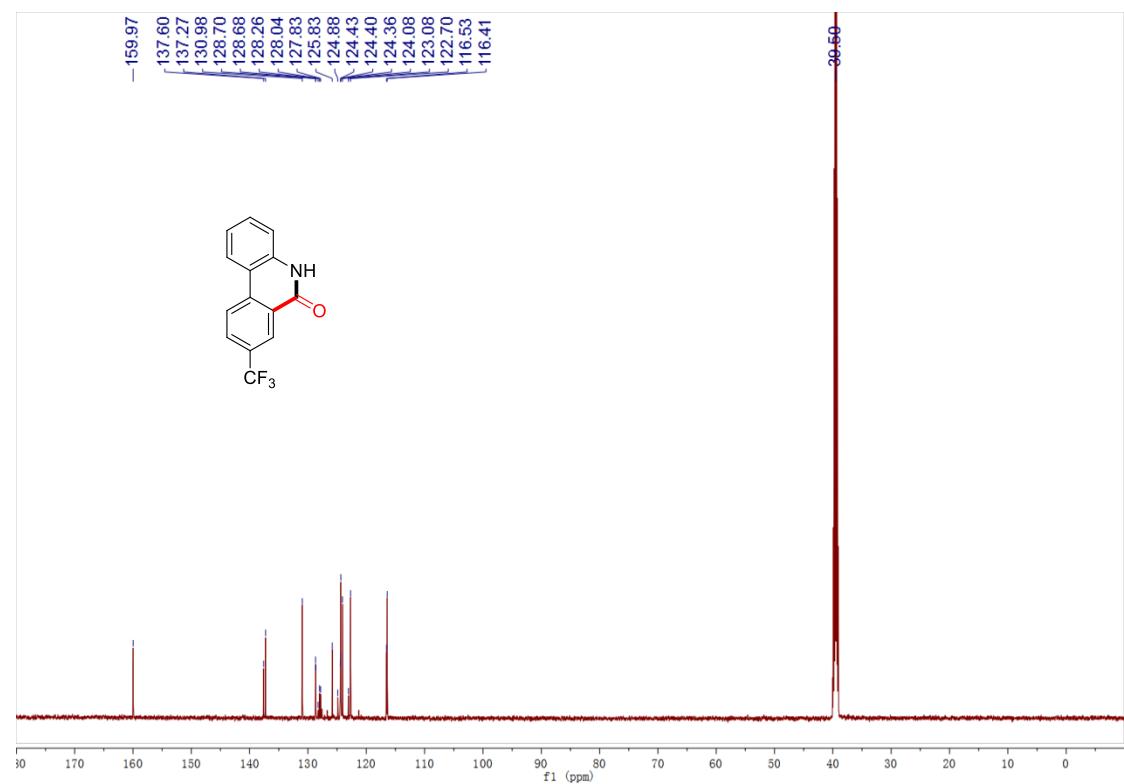
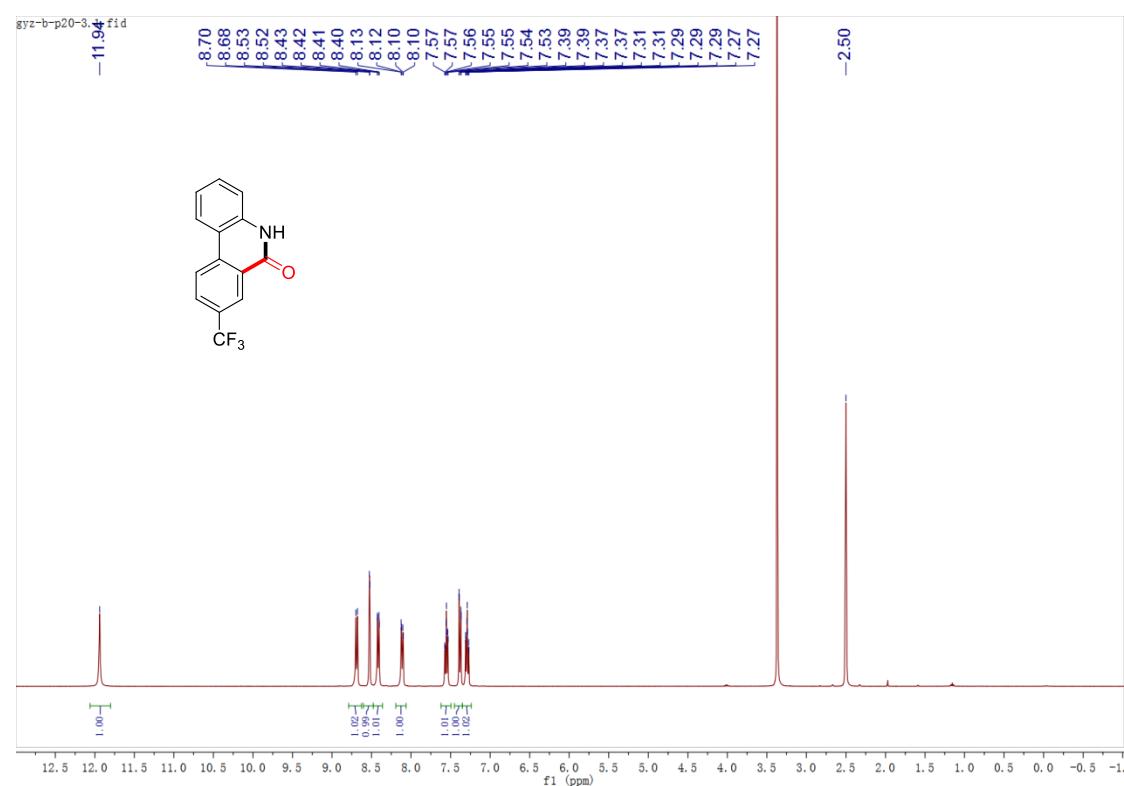


2m

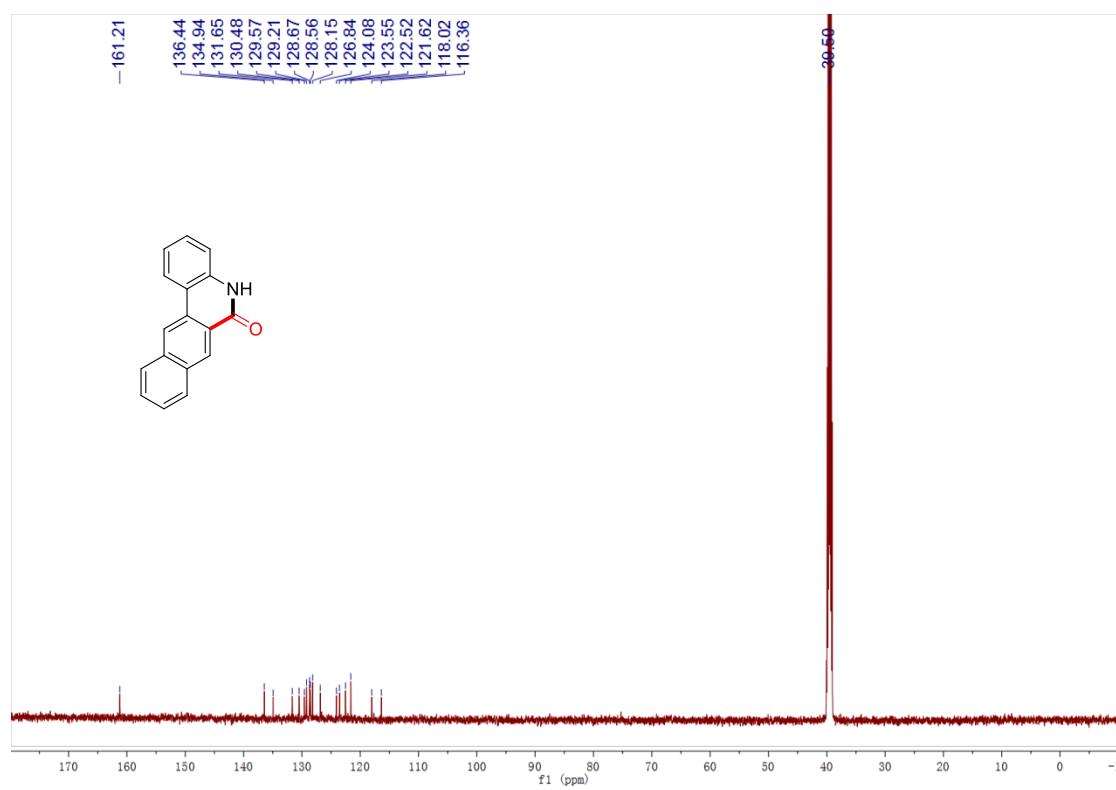
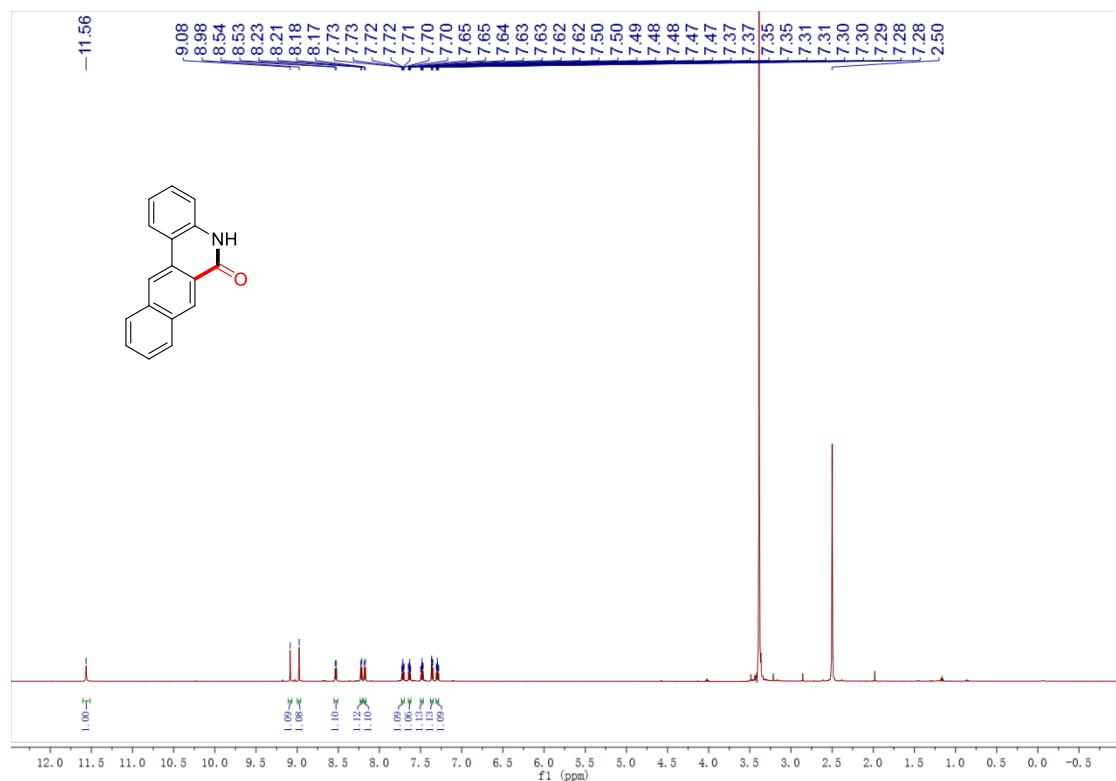


2n

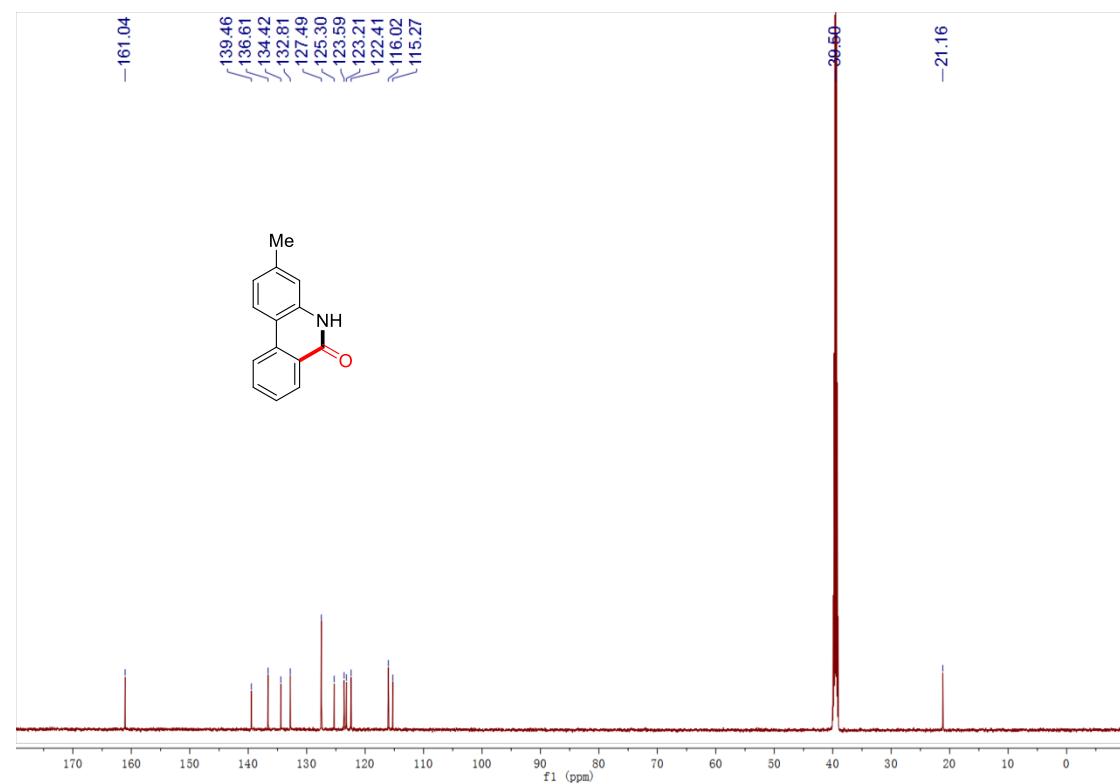
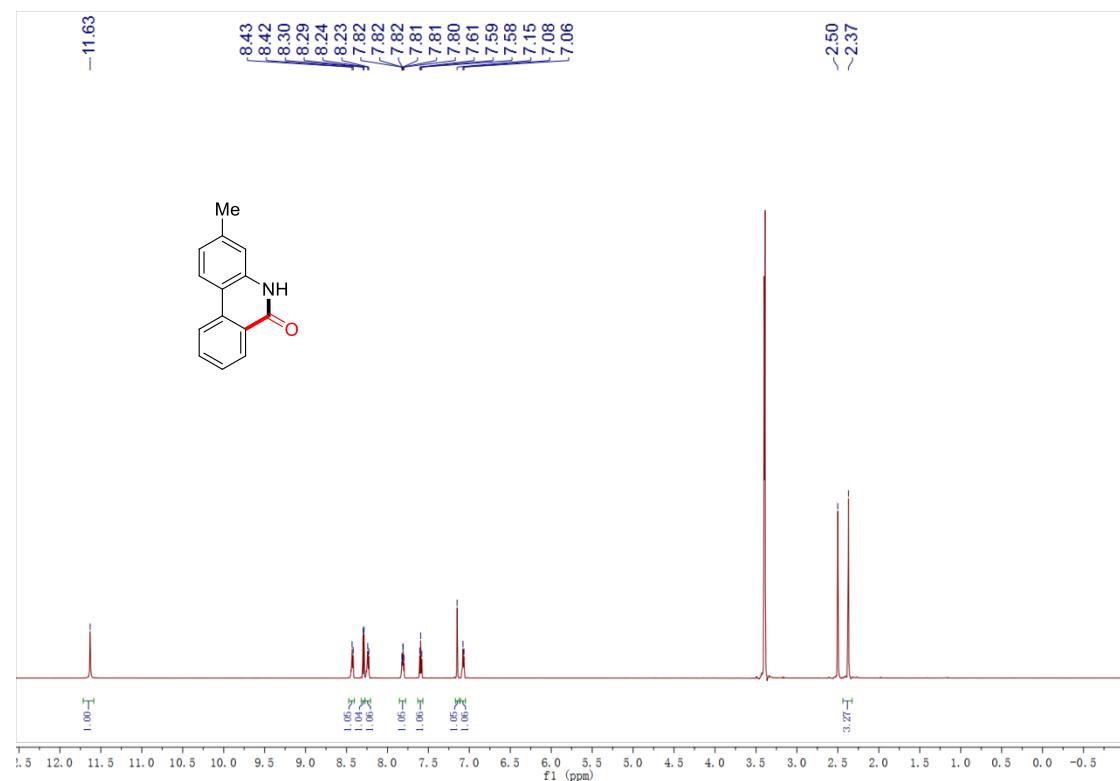




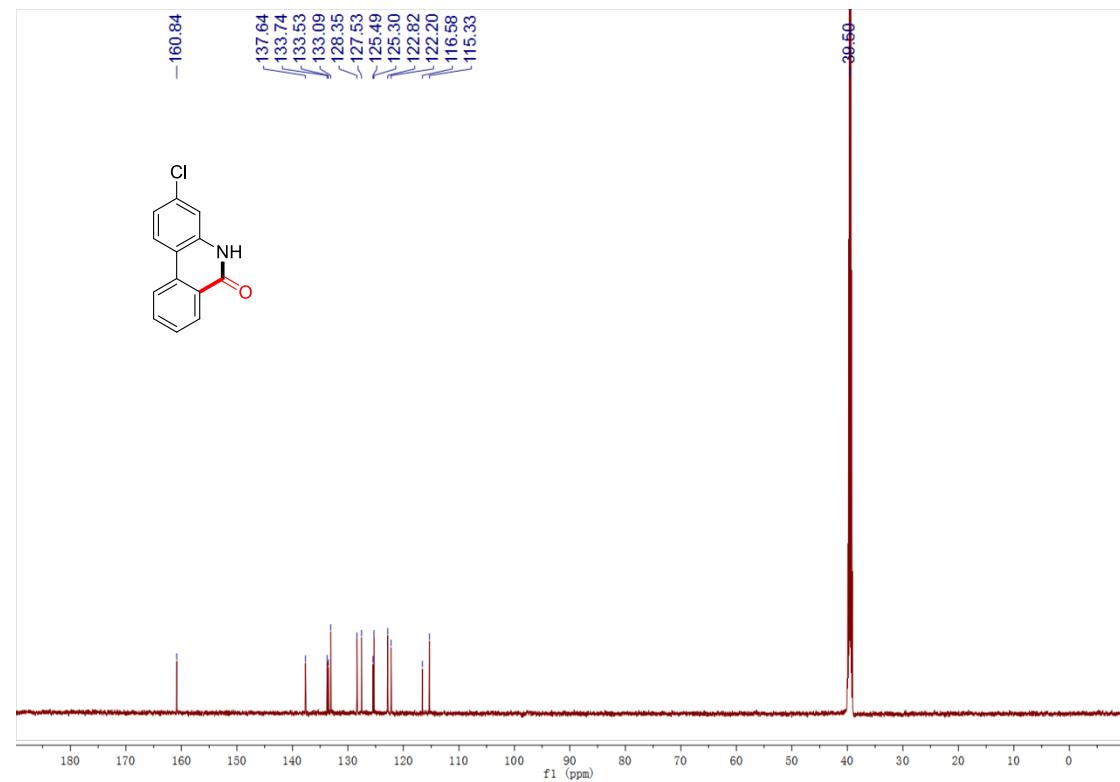
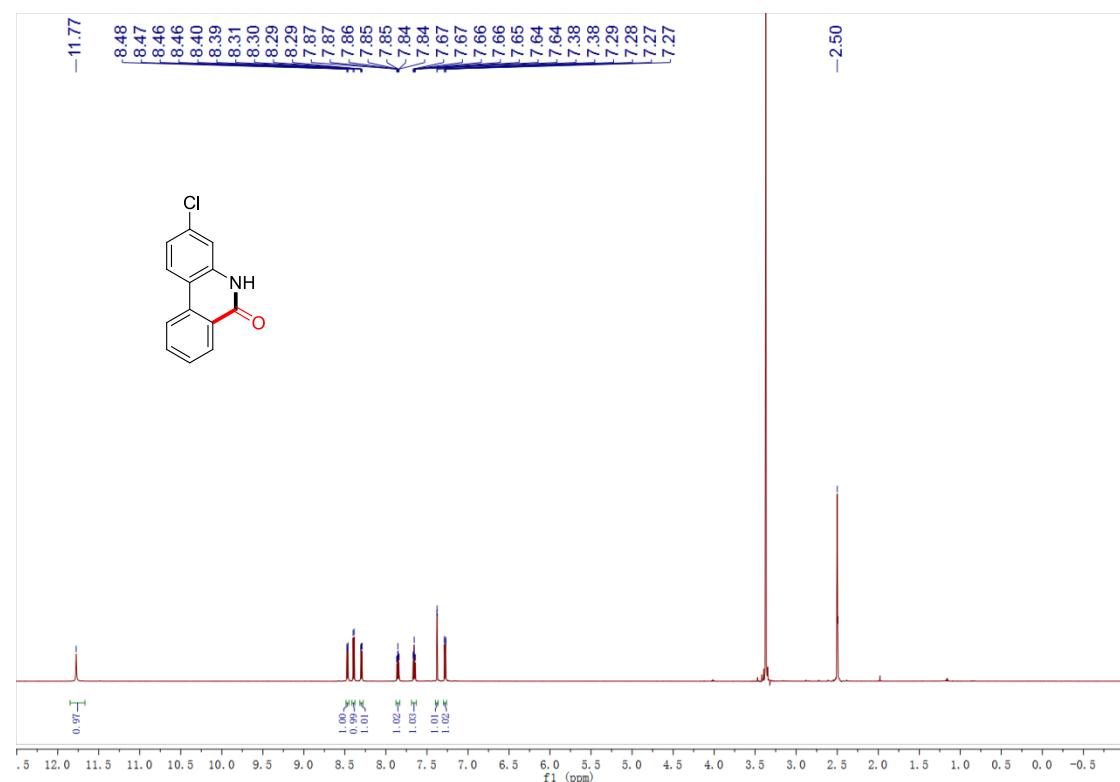
2p



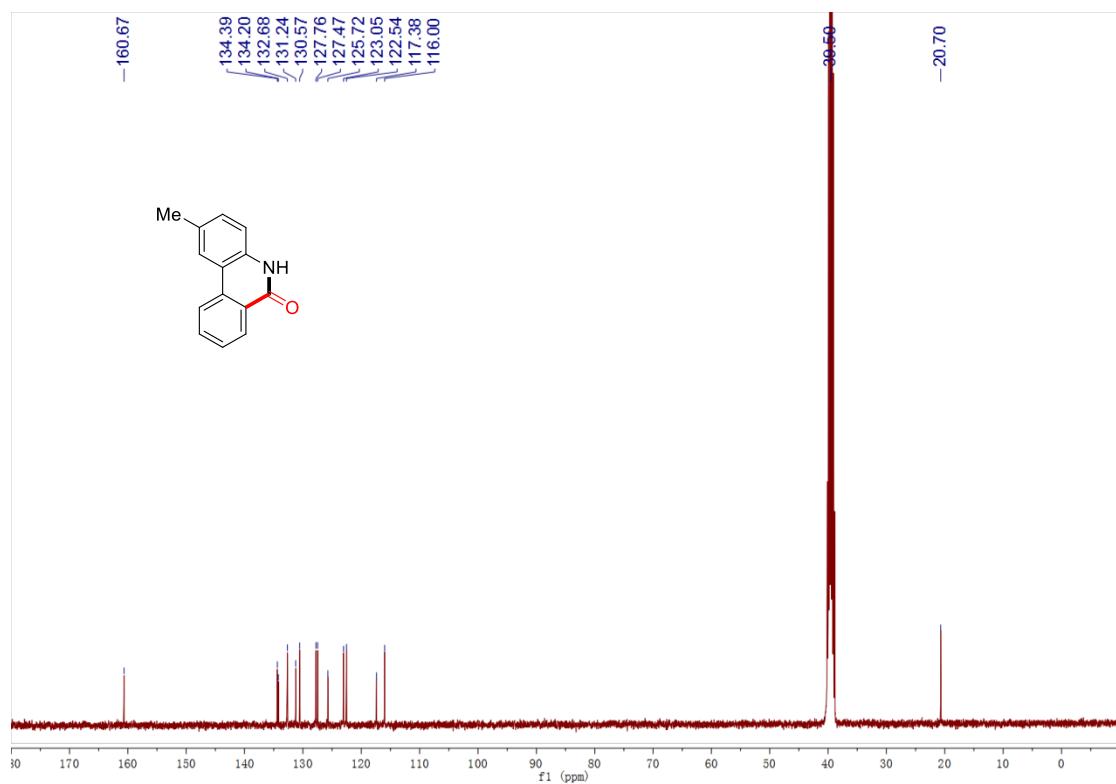
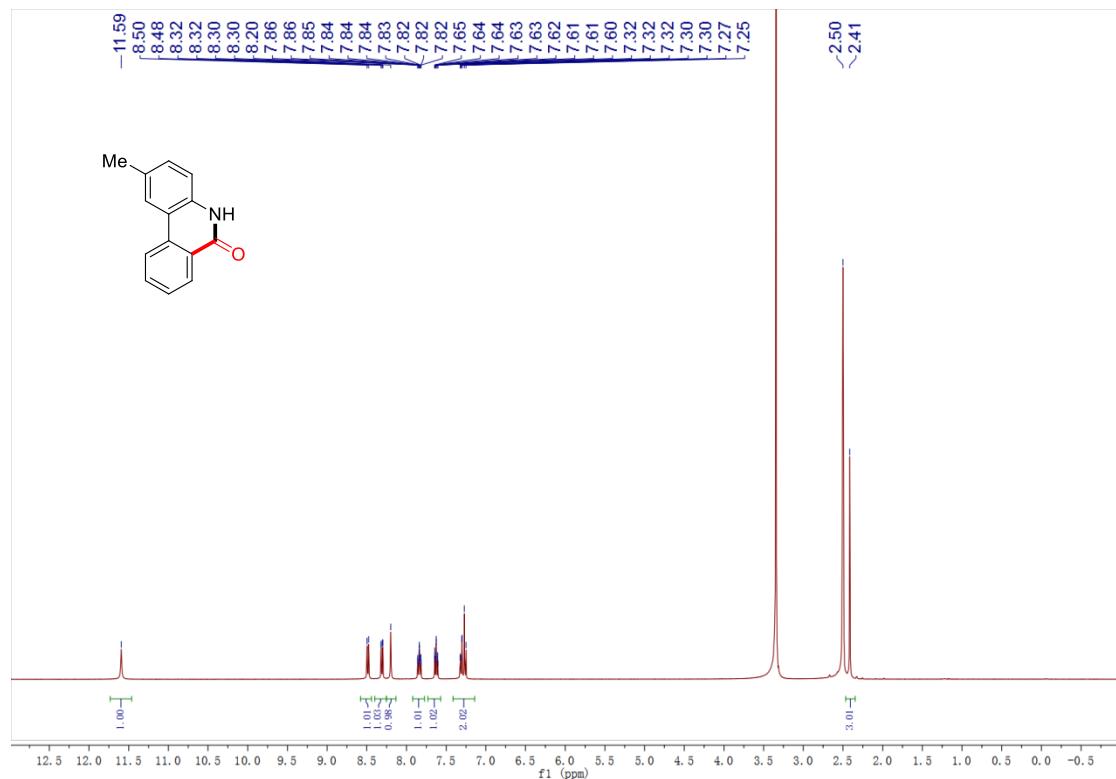
2q



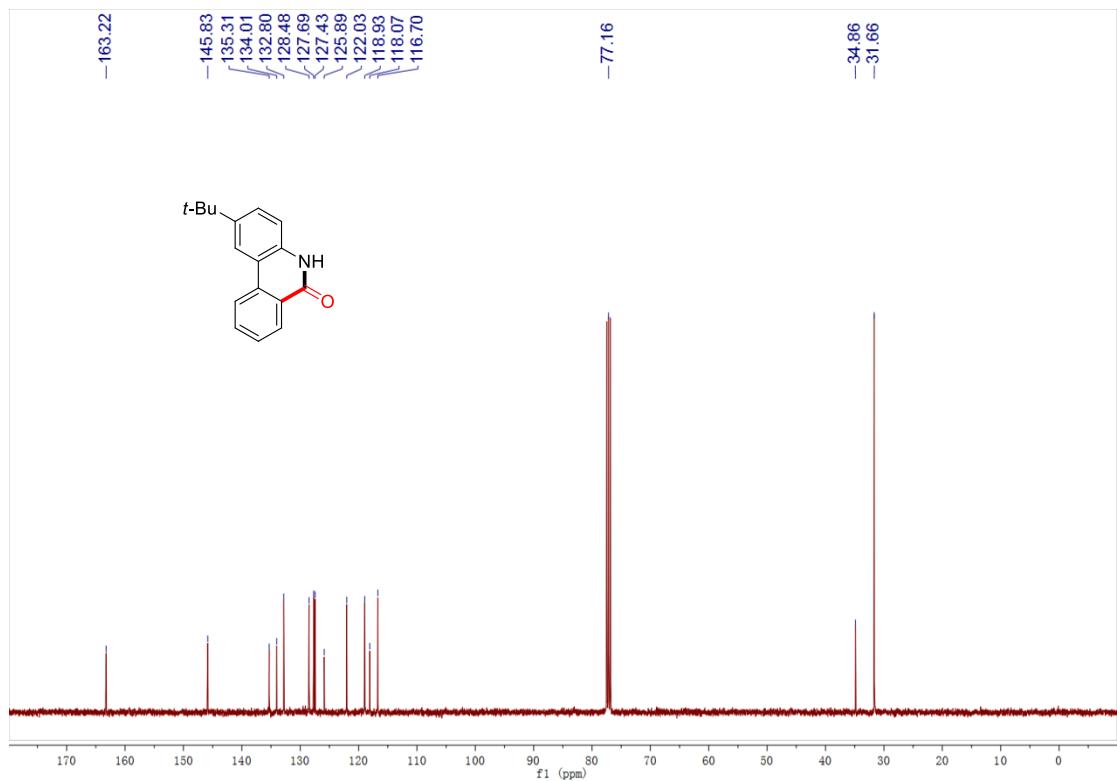
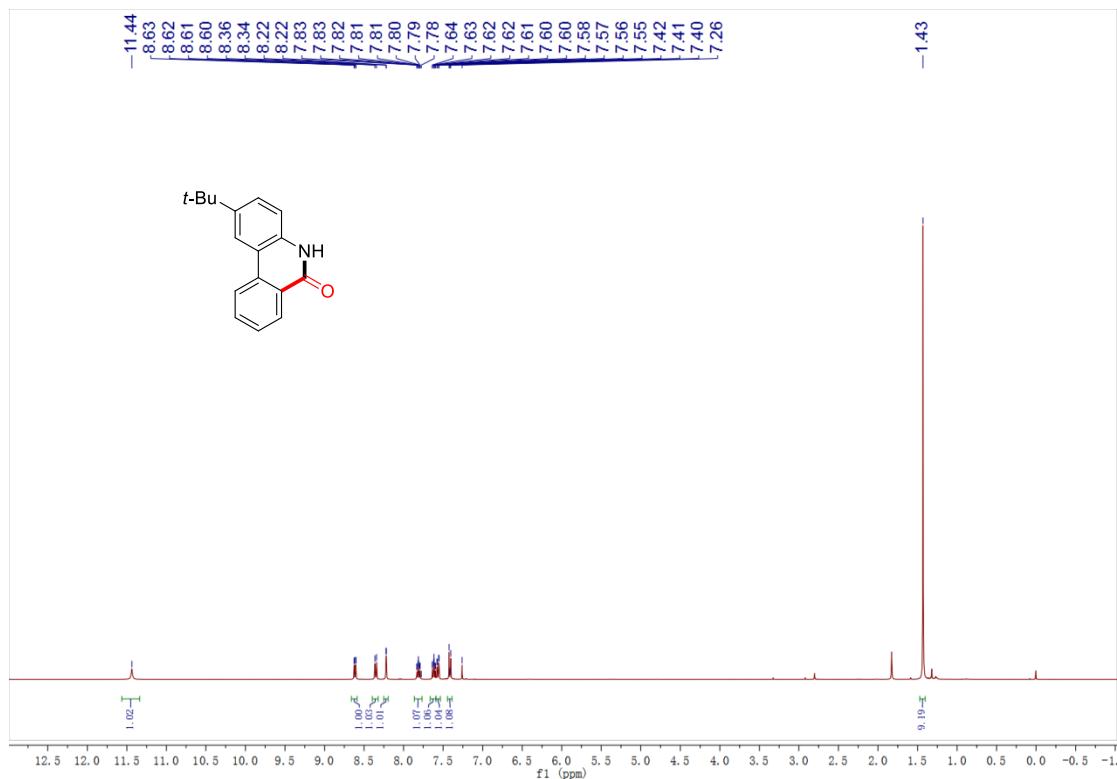
2r



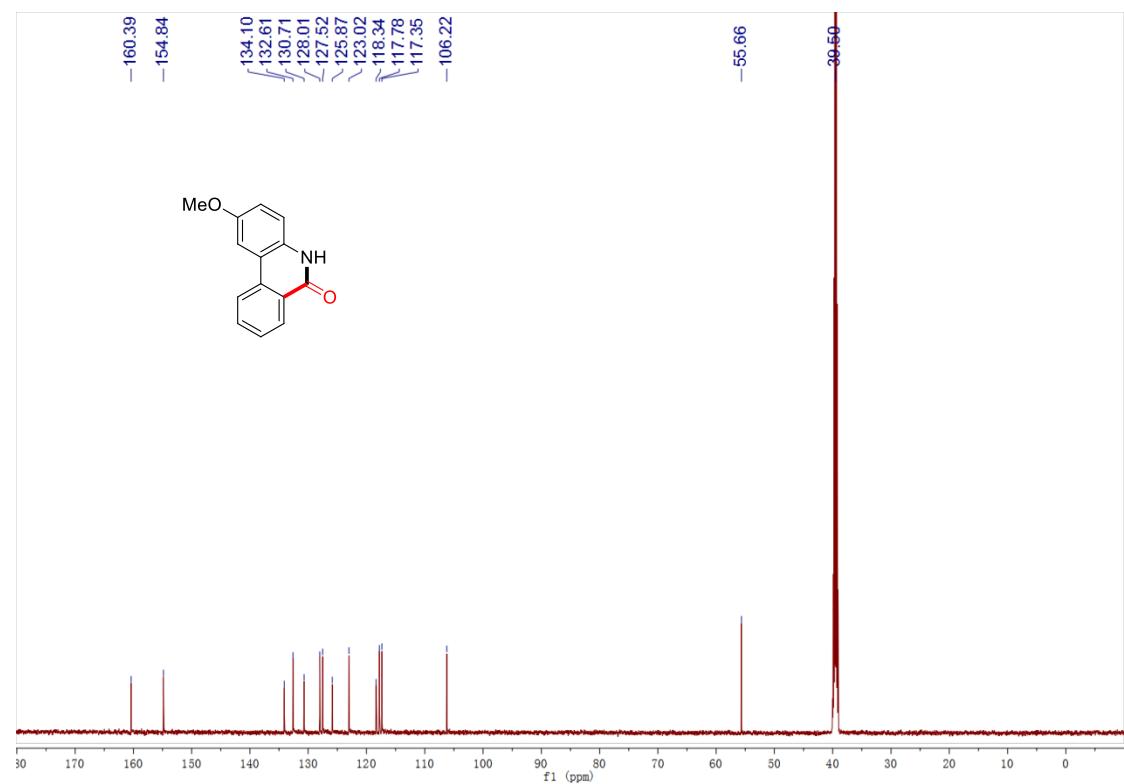
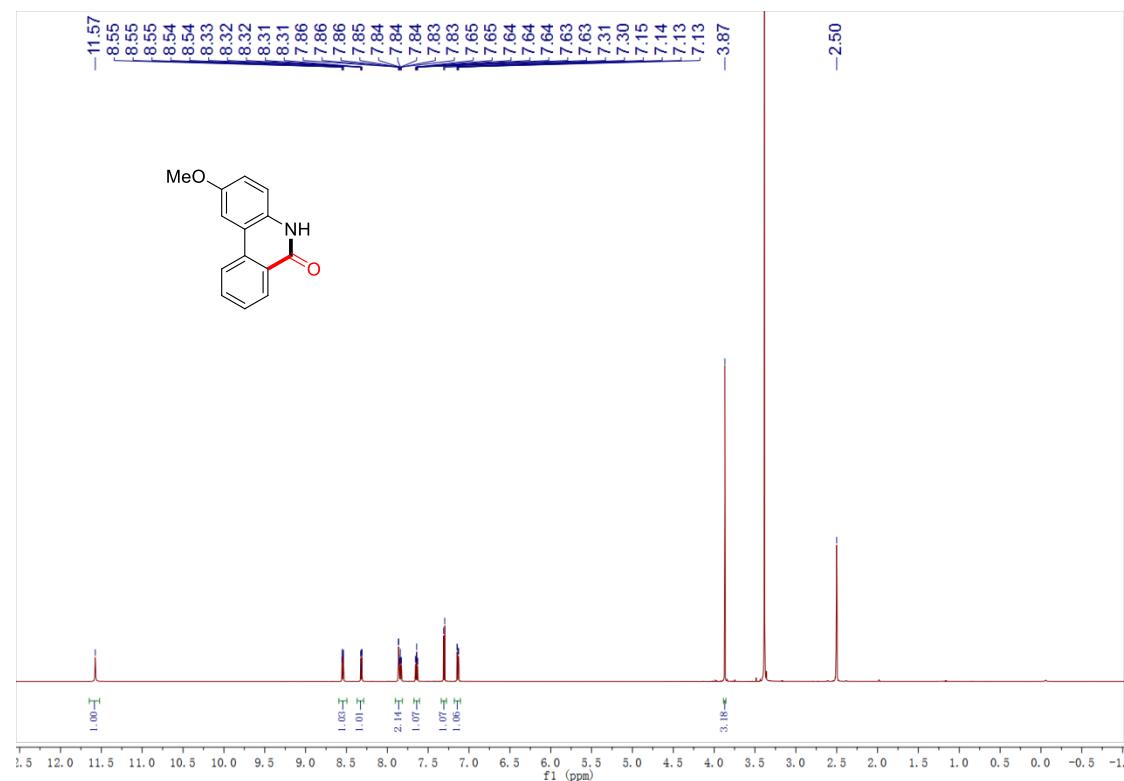
2s



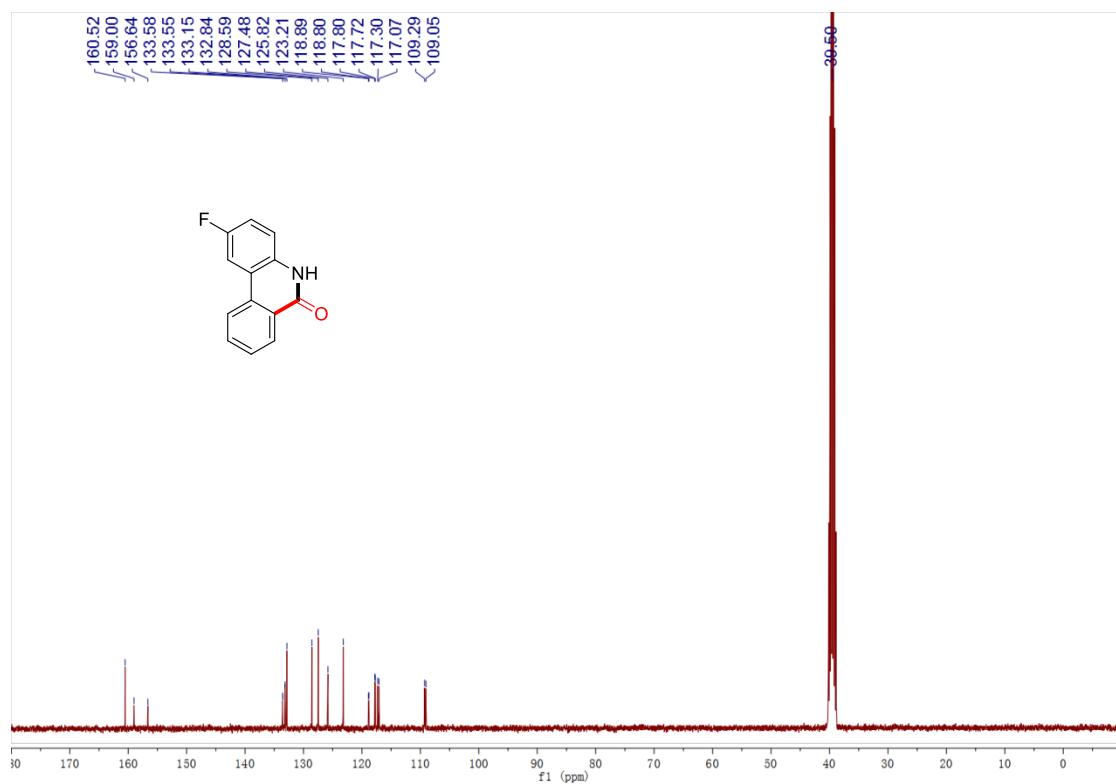
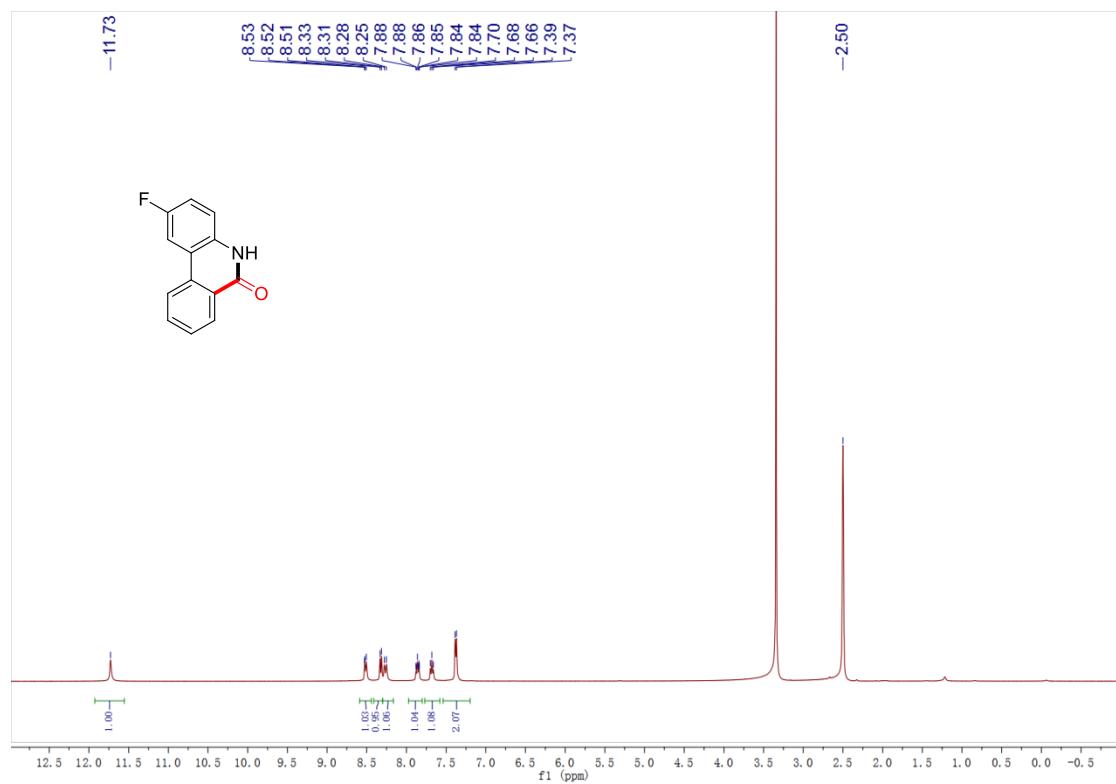
2t



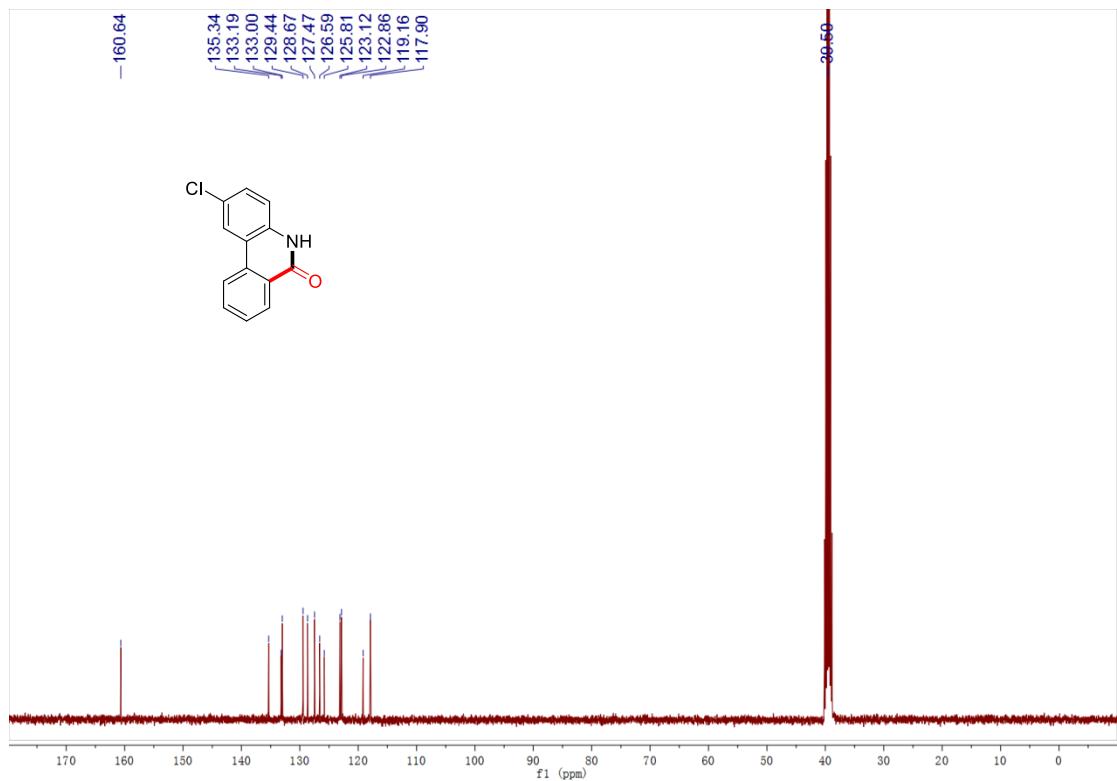
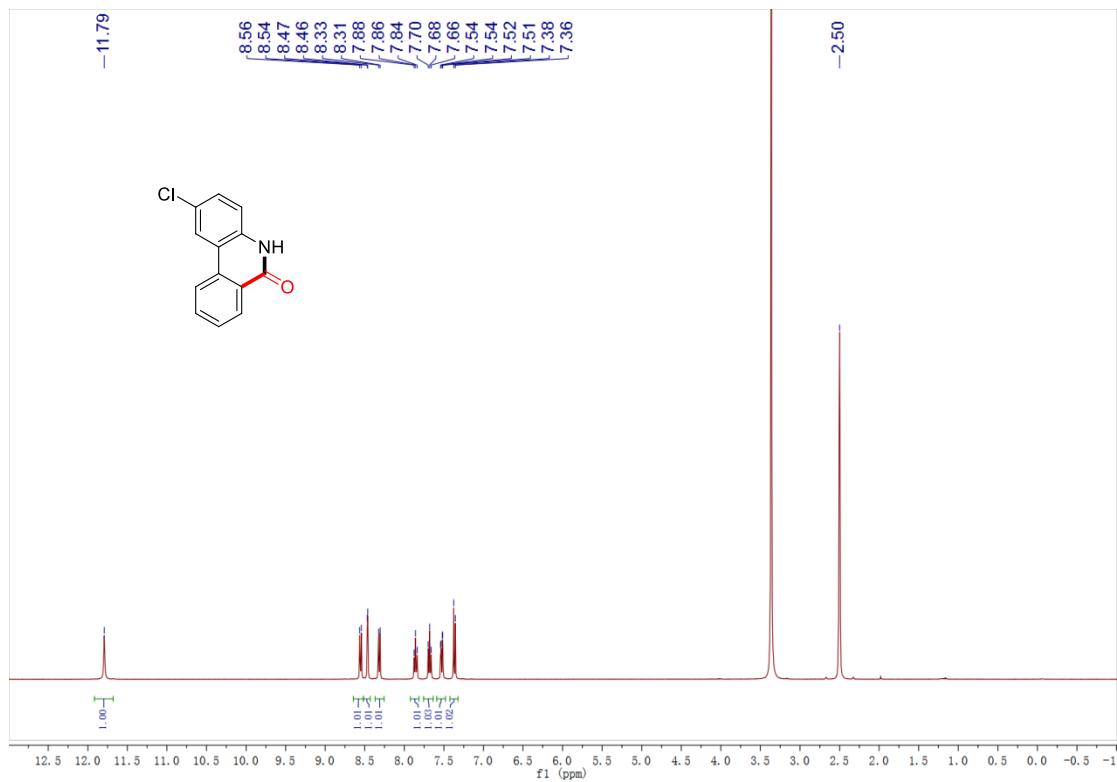
2u

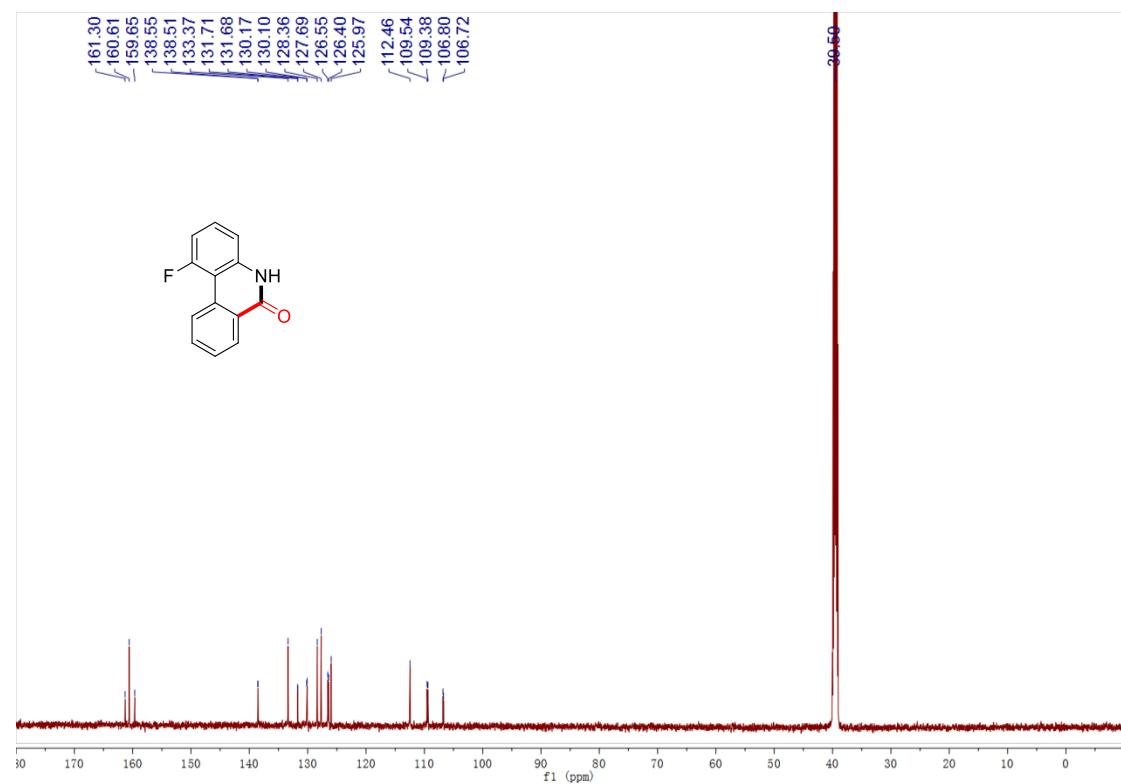
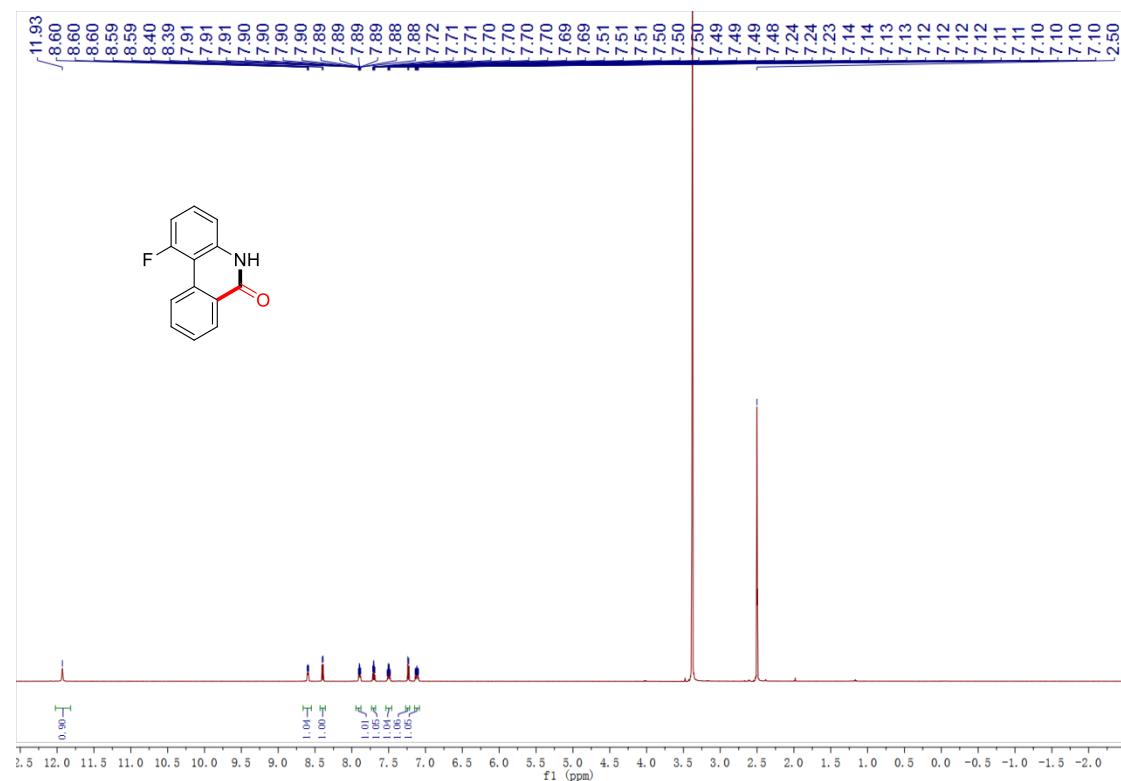


2v

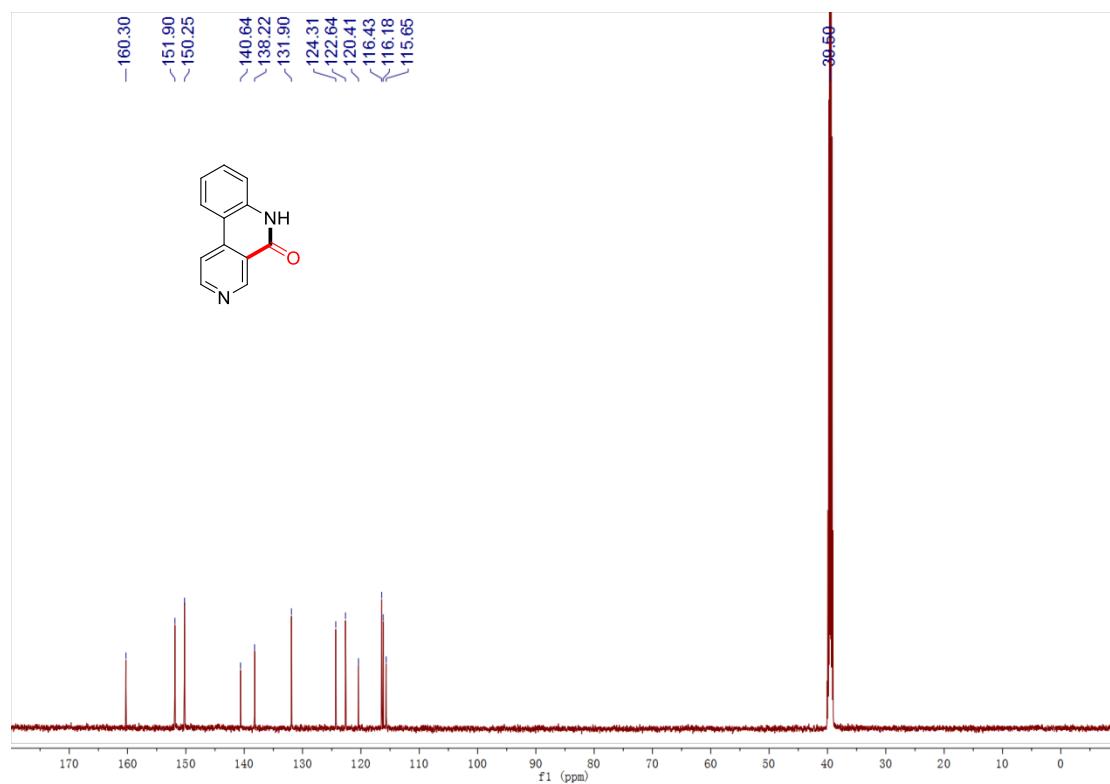
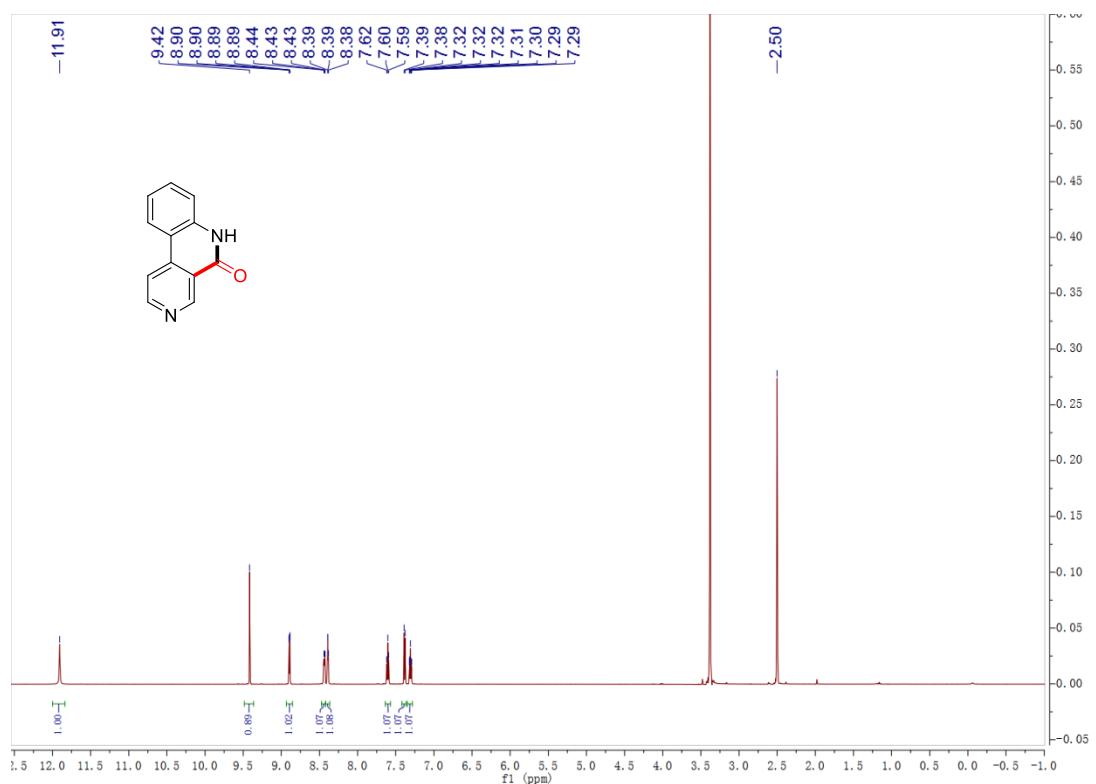


2w

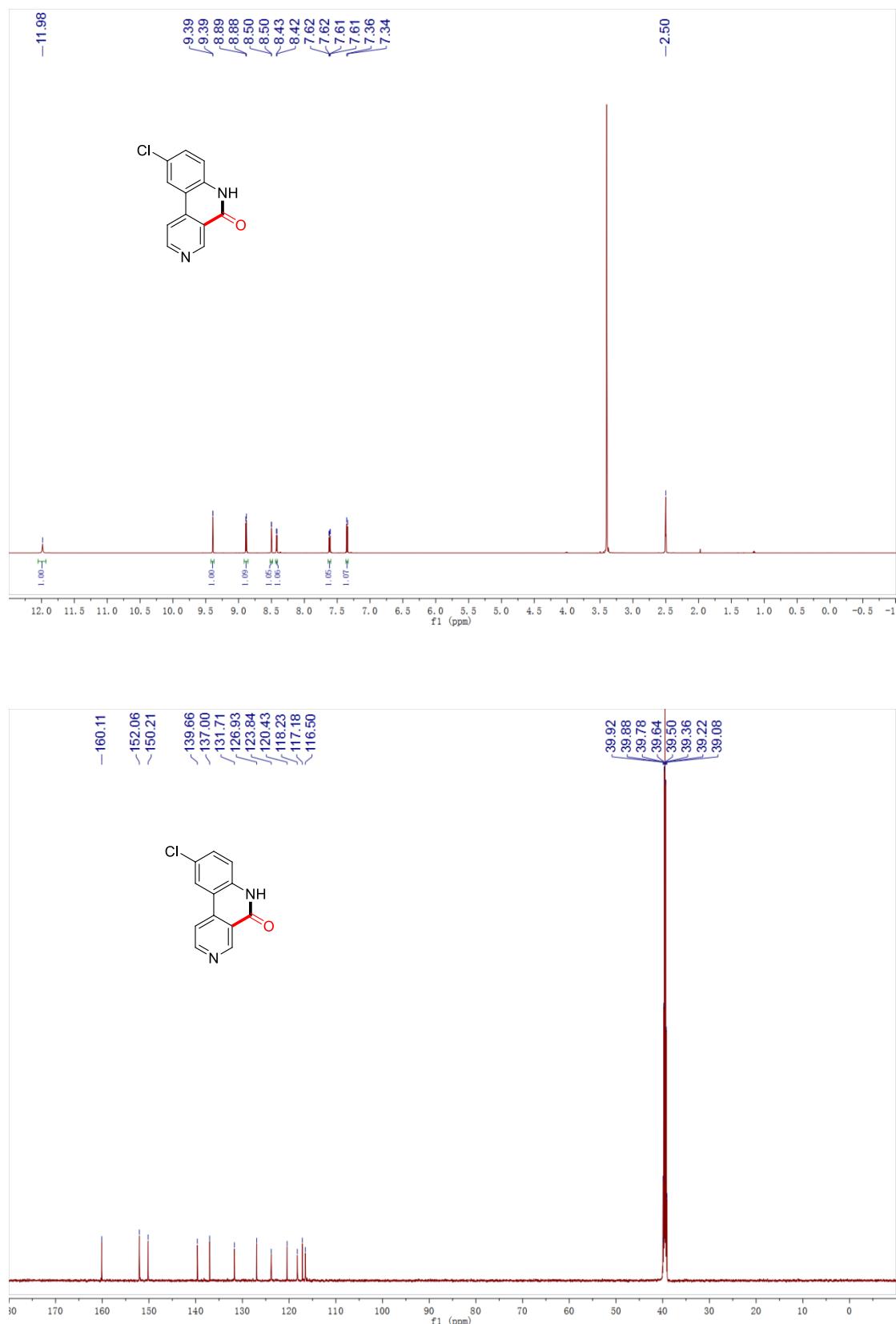




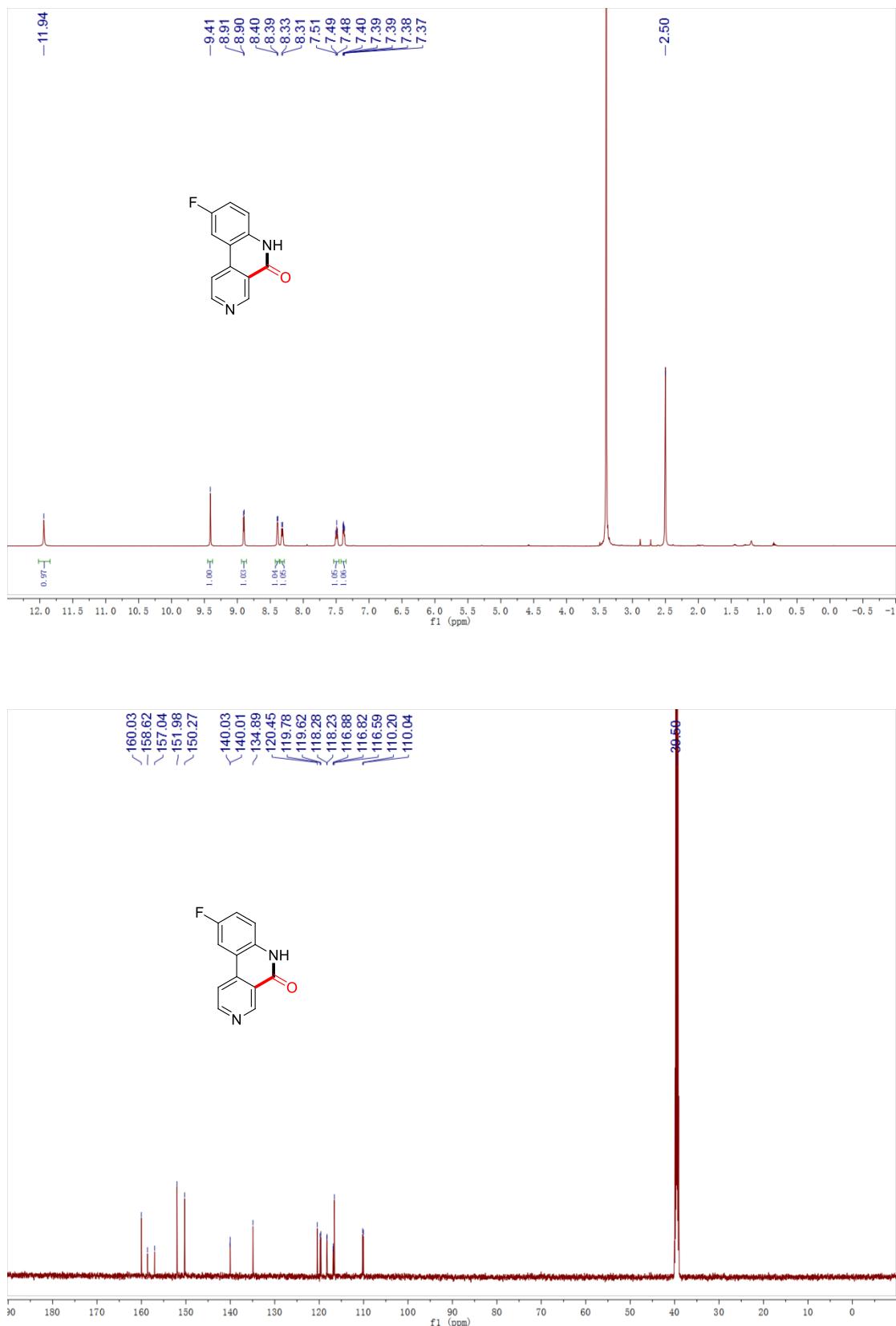
4a



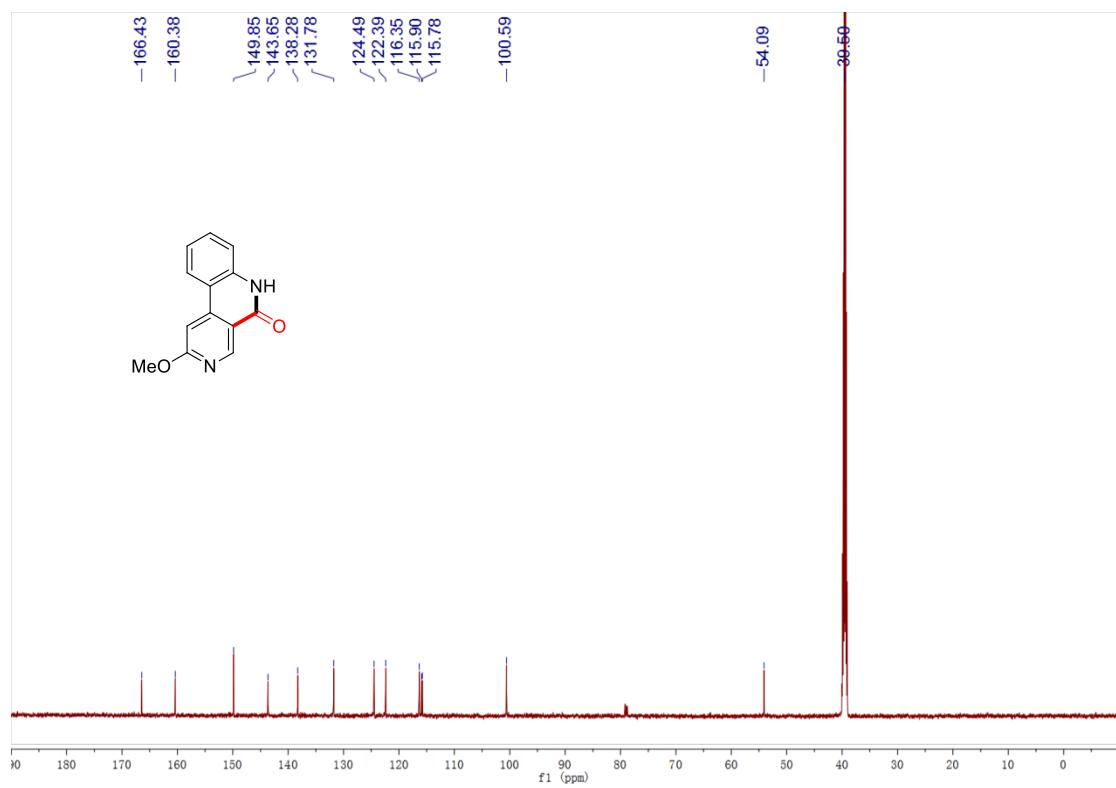
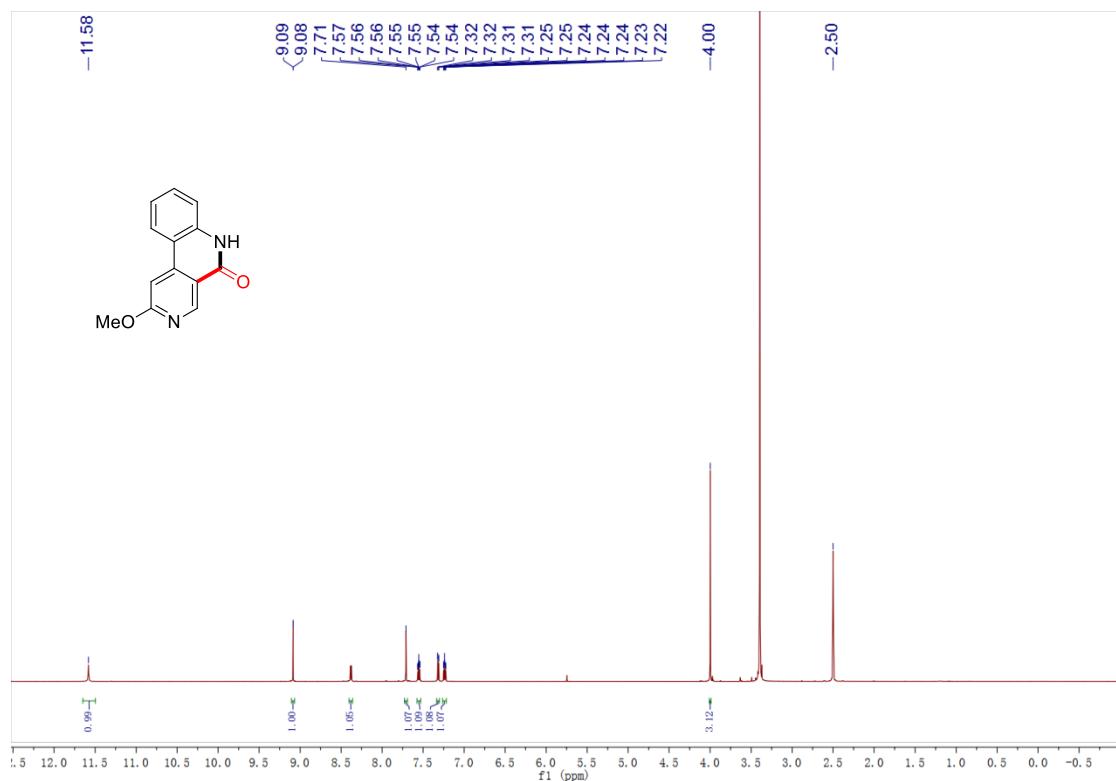
4b



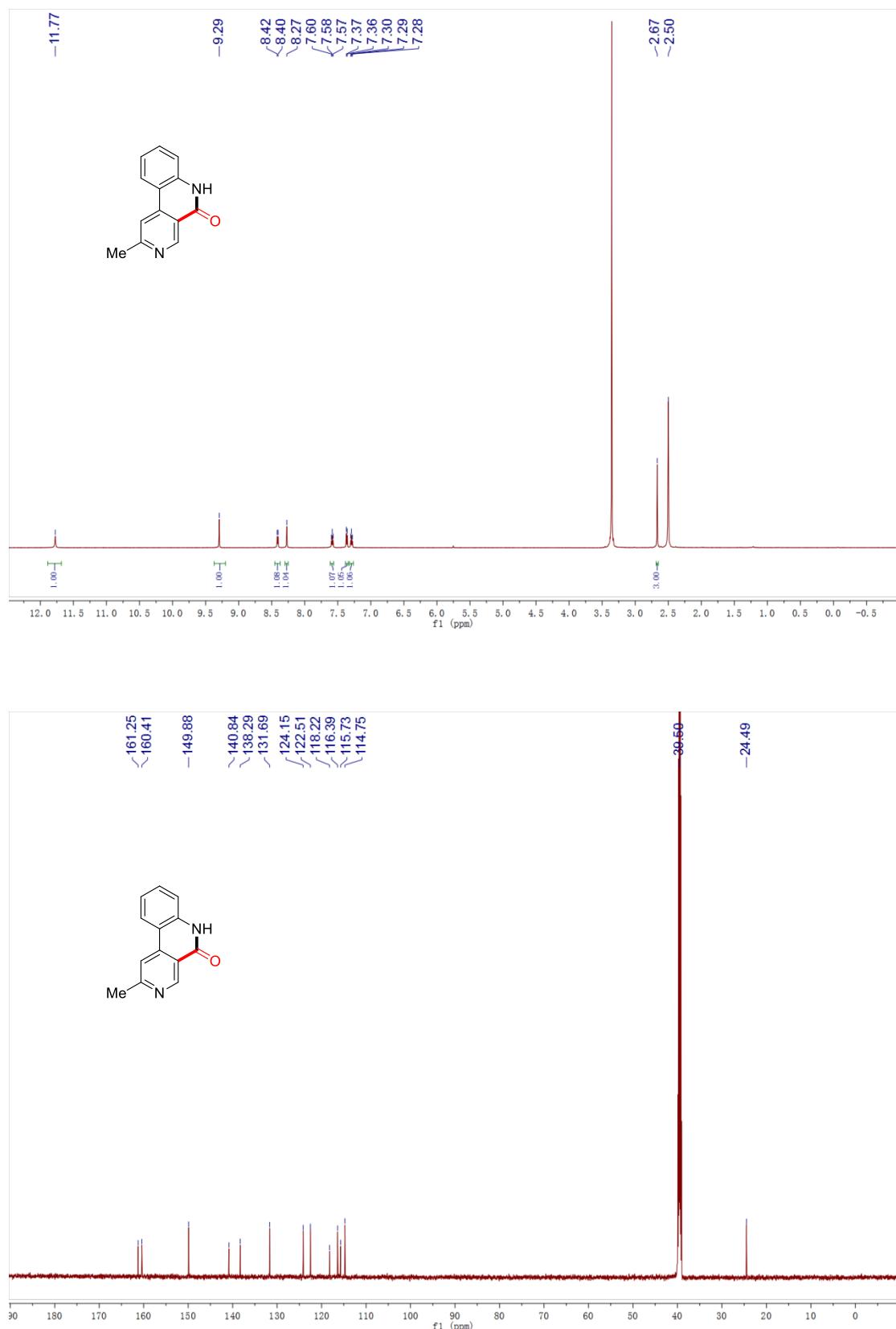
4c



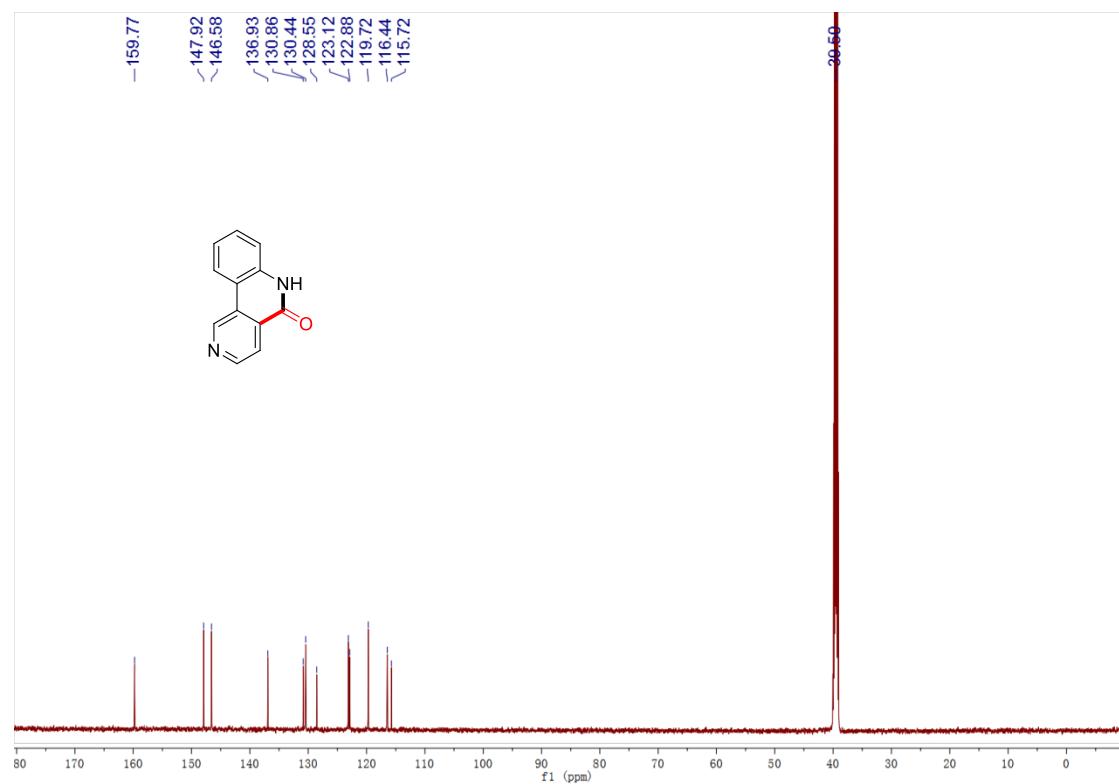
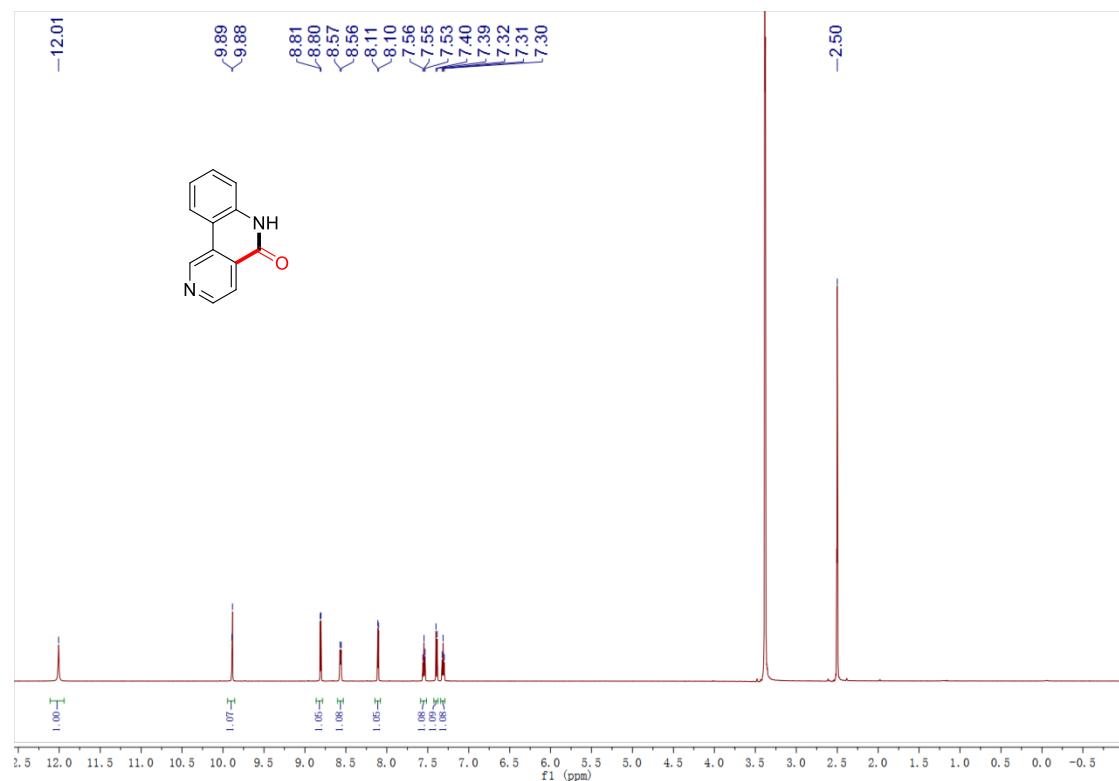
4d



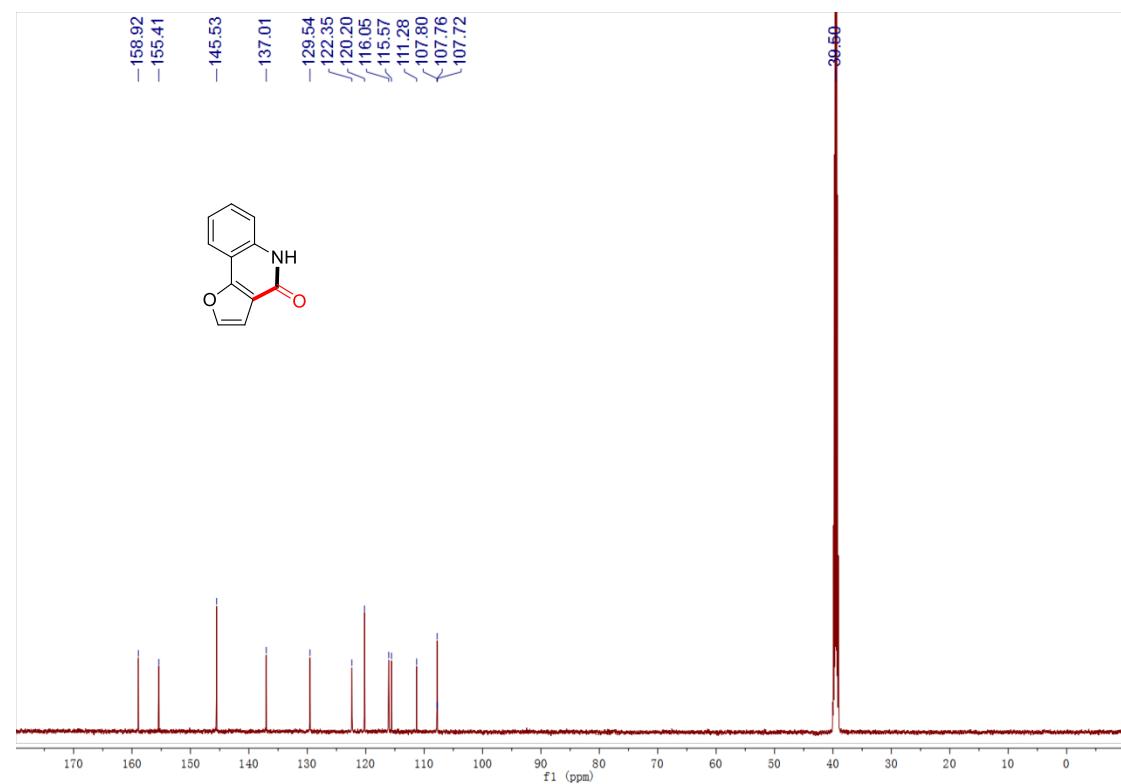
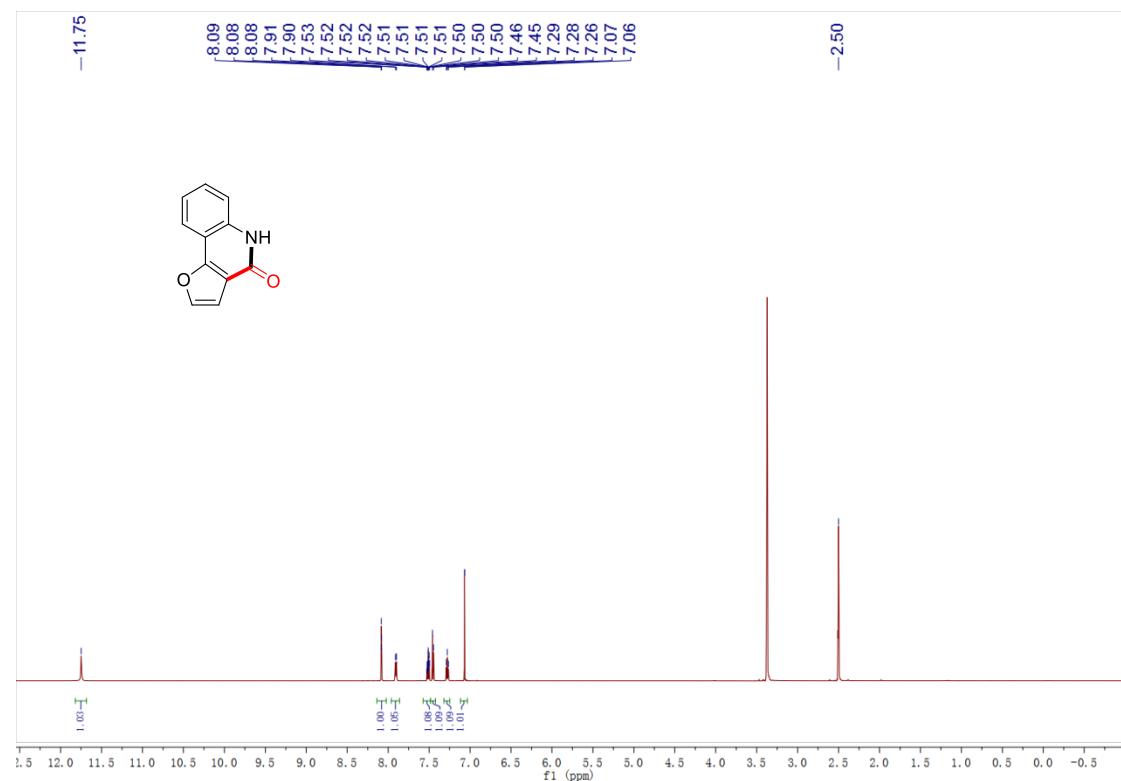
4e



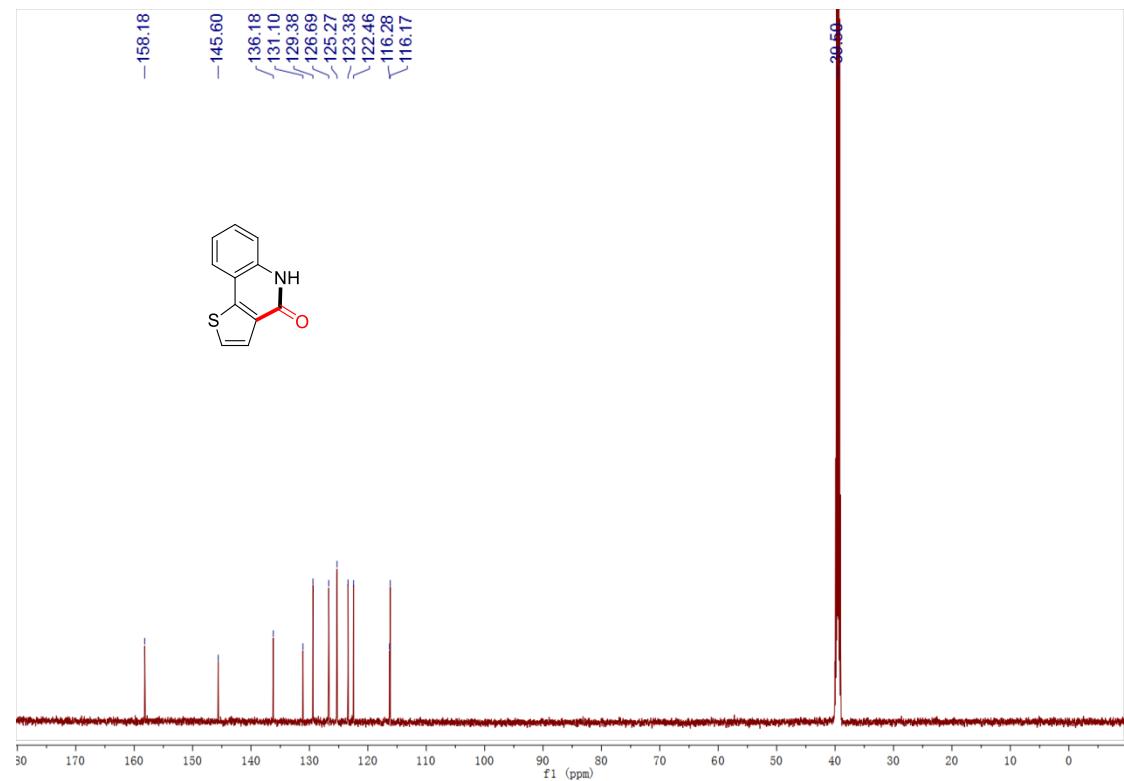
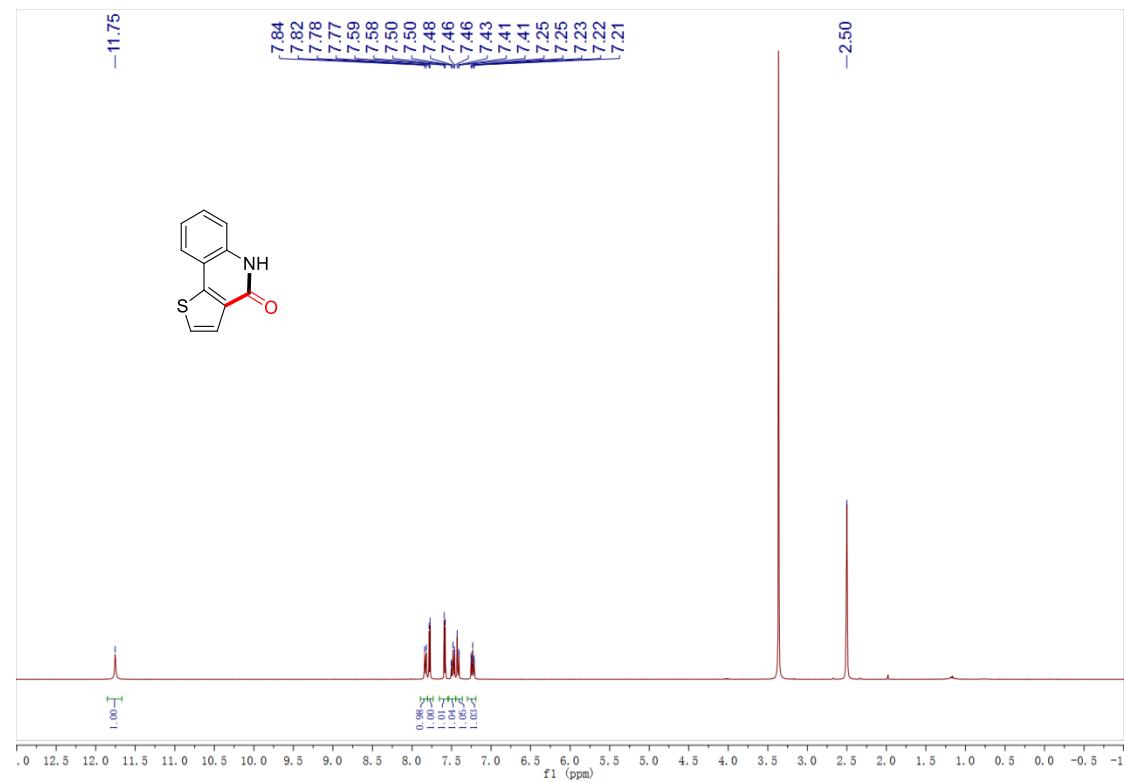
4f



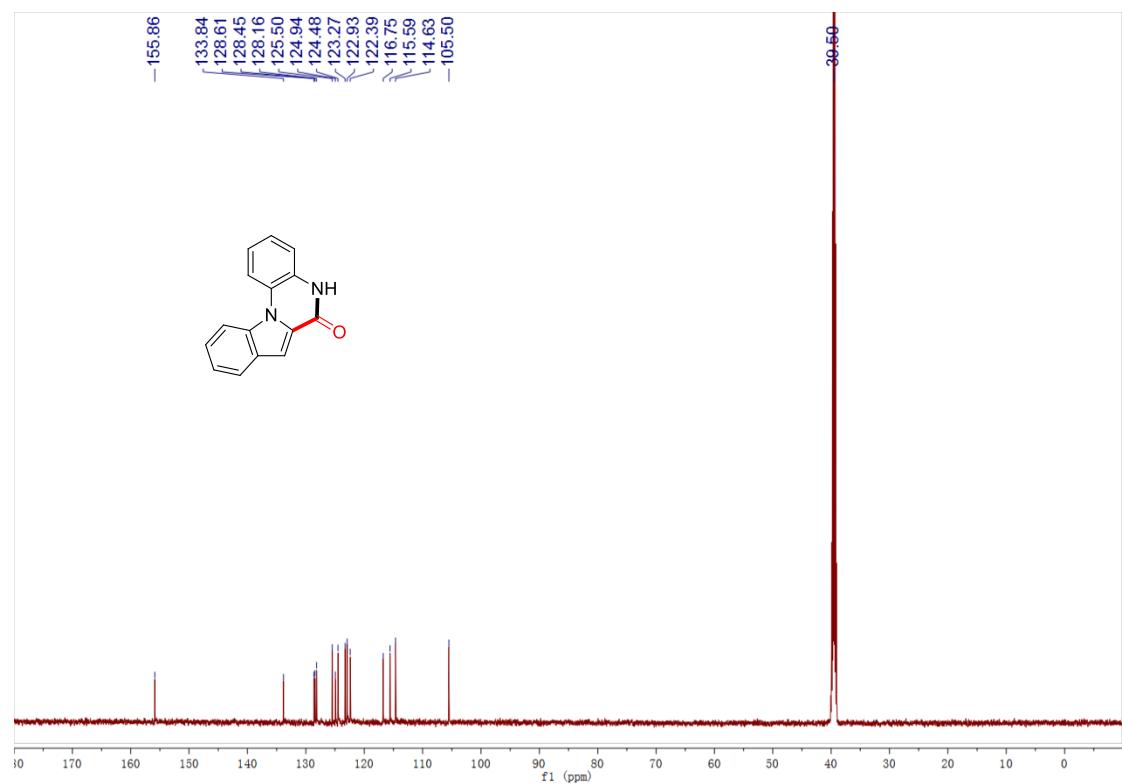
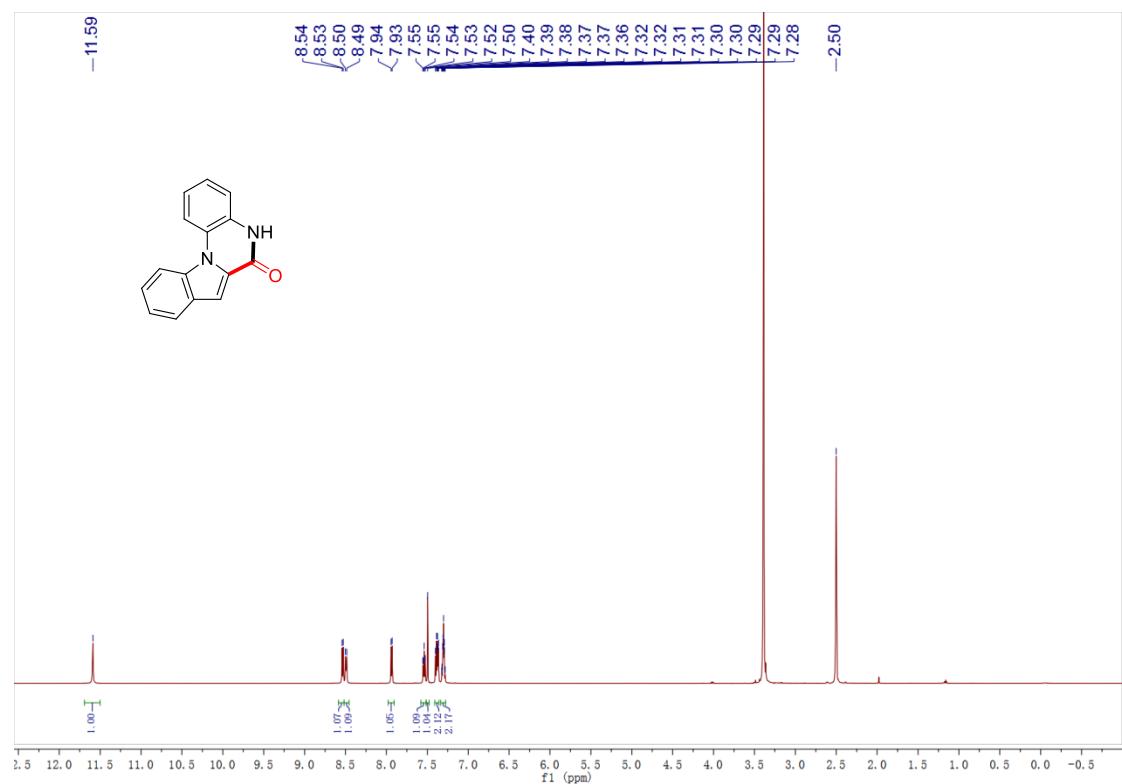
4g



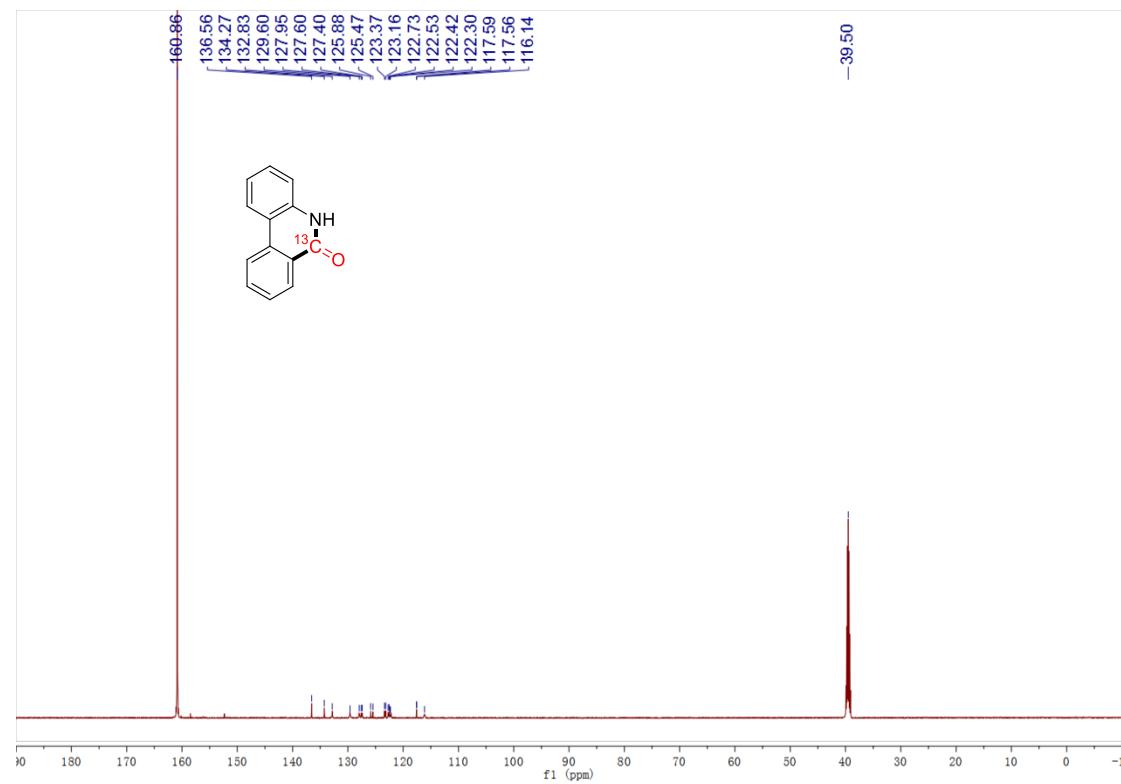
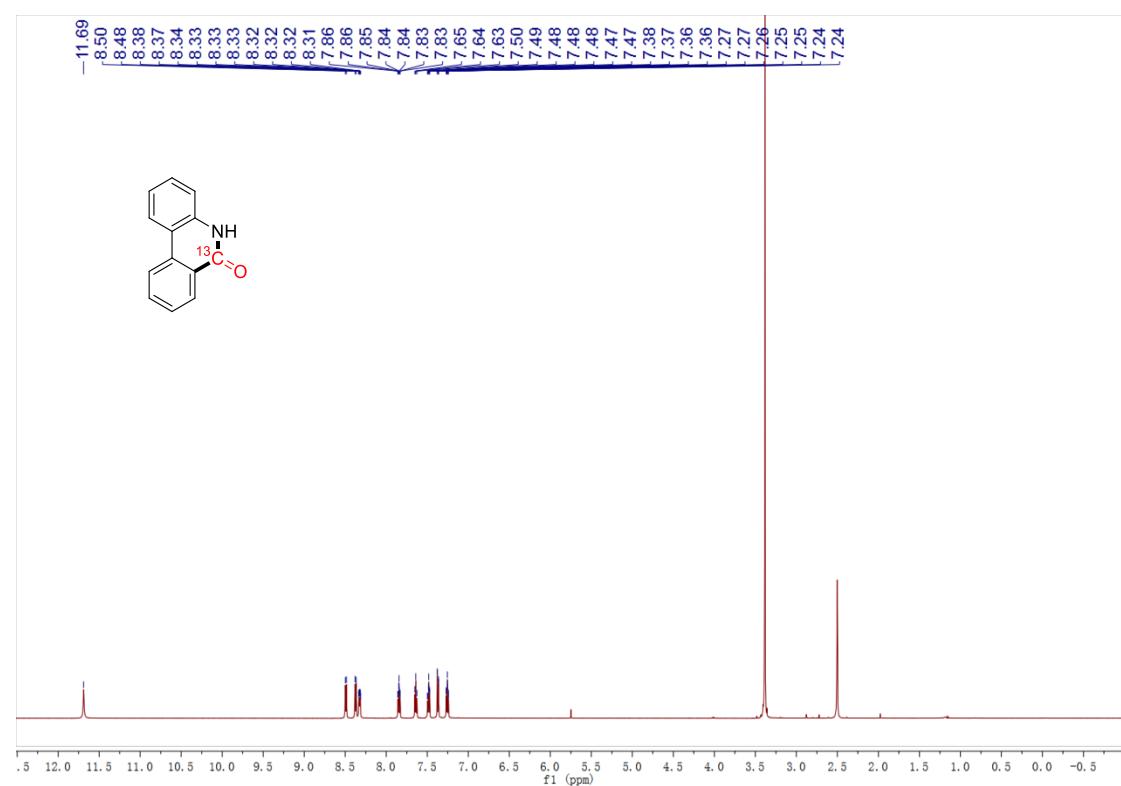
4h



4i



2a-¹³C



1a-d₅

