

Supporting Information for

Rh(III)-Catalyzed Substrate-Dependent Oxidative (Spiro)annulation of Isoquinolones with Diazonaphthoquinones: Selective Access to New Spirocyclic and Oxepine-Fused Polycyclic Compounds

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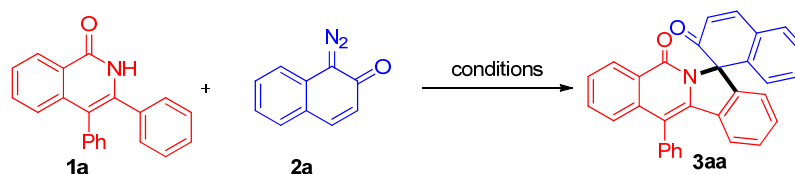
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1. General Information

Isoquinolones (**1**),¹ diazo compounds (**2**),² and [Cp*RhCl₂]₂³ were prepared according to the reported procedures. Unless noted, other commercial reagents and solvents were used without further purification. Melting points were recorded with a micro melting point apparatus and uncorrected. The ¹H NMR spectra were recorded at 400 or 600 MHz. The ¹³C NMR spectra were recorded at 100 or 150 MHz. High-resolution mass spectra (HRMS) were collected in ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

2. Table S1. Detailed Optimization Table for Synthesis of Spirocyclic Product 3aa^a

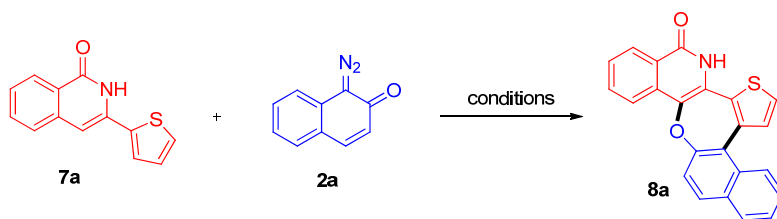


entry	catalyst	oxidant	additive	solvent	yield (%) ^b
1	[Cp*RhCl ₂] ₂	AgOAc	PivOH	1,4-dioxane	27
2	[Cp*RhCl ₂] ₂	AgOAc	PivOH	DCE	32
3	[Cp*RhCl ₂] ₂	AgOAc	PivOH	DCM	23
4	[Cp*RhCl ₂] ₂	AgOAc	PivOH	CHCl ₃	24
5	[Cp*RhCl ₂] ₂	AgOAc	PivOH	PhCH ₃	0
6	[Cp*RhCl ₂] ₂	AgOAc	PivOH	PhCF ₃	0
7	[Cp*RhCl ₂] ₂	AgOAc	PivOH	PhCl	27
8	[Cp*RhCl ₂] ₂	AgOAc	PivOH	CH ₃ CN	48
9	[Cp*RhCl ₂] ₂	AgOAc	PivOH	THF	28
10	[Cp*RhCl ₂] ₂	AgOAc	PivOH	acetone	21
11	[Cp*RhCl ₂] ₂	AgOAc	PivOH	EA	10
12	[Cp*RhCl ₂] ₂	AgOAc	PivOH	MeOH	35
13	[Cp*RhCl ₂] ₂	AgOAc	PivOH	EtOH	26
14	[Cp*RhCl ₂] ₂	AgOAc	PivOH	<i>i</i> PrOH	0
15	[Cp*RhCl ₂] ₂	AgOAc	PivOH	DMSO	0
16	[Cp*RhCl ₂] ₂	AgOAc	PivOH	DMF	58
17	[Cp*RhCl ₂] ₂	AgOAc	HOAc	DMF	40
18	[Cp*RhCl ₂] ₂	AgOAc	PhCO ₂ H	DMF	38
19	[Cp*RhCl ₂] ₂	AgOAc	MesCO ₂ H	DMF	40
20	[Cp*RhCl ₂] ₂	AgOAc	1-AdCO ₂ H	DMF	52
21	[Cp*RhCl ₂] ₂	AgOAc	TfOH	DMF	10
22	[Cp*RhCl ₂] ₂	AgOAc	TFA	DMF	0
23	[Cp*RhCl ₂] ₂	AgF	PivOH	DMF	55
24	[Cp*RhCl ₂] ₂	Ag ₂ CO ₃	PivOH	DMF	33

25	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	75
26	[Cp*RhCl ₂] ₂	K ₂ S ₂ O ₈	PivOH	DMF	0
27	[Cp*RhCl ₂] ₂	Cu(OAc) ₂	PivOH	DMF	0
28	[Cp*IrCl ₂] ₂	Ag ₂ O	PivOH	DMF	66
29	[Cp*Co(CO)I ₂]	Ag ₂ O	PivOH	DMF	0
30	[Cp*Rh(CH ₃ CN) ₃](SbF ₆) ₂	Ag ₂ O	PivOH	DMF	41
31	RhCl ₃ ·3H ₂ O	Ag ₂ O	PivOH	DMF	0
32	[RuCl ₂ (<i>p</i> -cymene)] ₂	Ag ₂ O	PivOH	DMF	0
33	Pd(OAc) ₂	Ag ₂ O	PivOH	DMF	0
34		Ag ₂ O	PivOH	DMF	0
35	[Cp*RhCl ₂] ₂		PivOH	DMF	0
36	[Cp*RhCl ₂] ₂	Ag ₂ O		DMF	46
37 ^c	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	0
38 ^d	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	25
39 ^e	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	12
40 ^f	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	38
41 ^g	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	29
42 ^h	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	62
43 ⁱ	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	48
44 ^j	[Cp*RhCl ₂] ₂	Ag ₂ O	PivOH	DMF	44

^aThe reactions were run with: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (0.005 mmol), oxidant (0.4 mmol), additive (0.4 mmol), solvent (2 mL), air, 100 °C, 3 h. ^bIsolated yields. ^cThe reaction was run at 80 °C for 12 h. ^dThe reaction was run at 120 °C. ^eThe reaction was run at 140 °C. ^f**1a:2a** = 1:1.5. ^g**1a:2a** = 1:3.0. ^hAg₂O (0.2 mmol) was used. ⁱPivOH (0.2 mmol) was used. ^jAg₂O (0.2 mmol) and PivOH (0.2 mmol) was used.

3. Table S2. Optimization of Reaction Conditions for the Synthesis of 8a^a

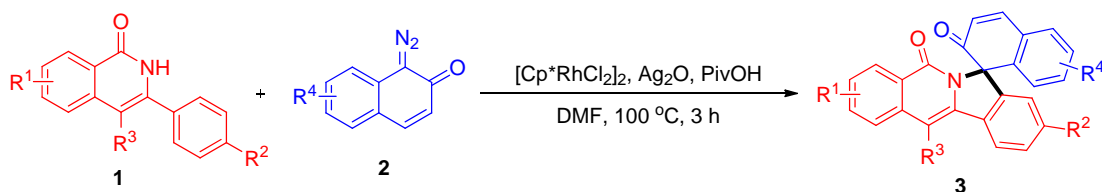


entry	catalyst	oxidant	solvent	T (°C)	yield (%) ^b
1 ^c	[Cp*RhCl ₂] ₂	Ag ₂ O	DMF	100	38
2	[Cp*RhCl₂]₂	Ag₂O	DMF	100	43
3 ^d	[Cp*RhCl ₂] ₂	Ag ₂ O	DMF	100	38
4 ^e	[Cp*RhCl ₂] ₂	Ag ₂ O	DMF	100	29
5	[Cp*RhCl ₂] ₂	AgOAc	DMF	100	26
6	[Cp*RhCl ₂] ₂	AgF	DMF	100	13
7	[Cp*RhCl ₂] ₂	Ag ₂ CO ₃	DMF	100	18
8	[Cp*RhCl ₂] ₂	AgSbF ₆	DMF	100	0
9	[Cp*RhCl ₂] ₂	AgOTf	DMF	100	0
10	[Cp*RhCl ₂] ₂	Ag ₂ O	DCE	100	15
11	[Cp*RhCl ₂] ₂	Ag ₂ O	1,4-dioxane	100	37
12	[Cp*RhCl ₂] ₂	Ag ₂ O	toluene	100	23
13	[Cp*RhCl ₂] ₂	Ag ₂ O	MeCN	100	messy
14	[Cp*RhCl ₂] ₂	Ag ₂ O	THF	100	messy
15	[Cp*RhCl ₂] ₂	Ag ₂ O	DMSO	100	0
16	[Cp*RhCl ₂] ₂	Ag ₂ O	DMA	100	37
17	[Cp*RhCl ₂] ₂	Ag ₂ O	NMP	100	39
18	[Cp*IrCl ₂] ₂	Ag ₂ O	DMF	100	37
19	[Cp*RhCl ₂] ₂	Ag ₂ O	DMF	80	25
20	[Cp*RhCl ₂] ₂	Ag ₂ O	DMF	120	19

^aThe reactions were run with: **7a** (0.2 mmol), **2a** (0.4 mmol), catalyst (0.005 mmol), oxidant (0.4 mmol), solvent (2 mL), air, 100 °C, 3 h. ^bIsolated yields. ^cPivOH (0.4 mmol) was used as an additive. ^d[Cp*RhCl₂]₂ (0.01 mmol) was used. ^e[Cp*RhCl₂]₂ (0.002 mmol) was used.

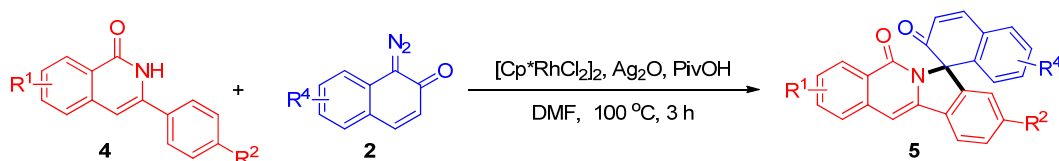
4. General Procedure for the Preparation of 3, 5, 8 and 11-14

4.1 General Procedure for the Preparation of Compounds 3



To a reaction tube (15 mL) equipped with a stirring bar were charged with 3,4-disubstituted isoquinolone **1** (0.2 mmol), 1-diazonaphthalen-2(1H)-one **2** (0.4 mmol), DMF (2 mL), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), Ag_2O (93 mg, 0.4 mmol), and PivOH (41 mg, 0.4 mmol). Then the tube was sealed, and the resulting mixture was stirred at $100\text{ }^\circ\text{C}$ under air for 3 h until isoquinolone **1** was consumed completely. Next, the reaction was quenched with NaHCO_3 and extracted with dichloromethane. The organic layer was washed with water and brine and then dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/ethyl acetate as eluent to give the corresponding product **3**.

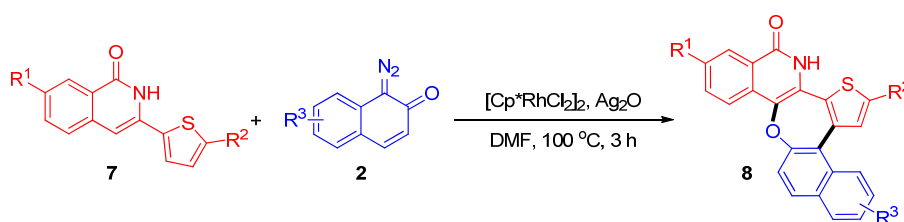
4.2 General Procedure for the Preparation of Compounds 5



To a reaction tube (15 mL) equipped with a stirring bar were charged with 4-unsubstituted isoquinolone **4** (0.2 mmol), 1-diazonaphthalen-2(1H)-one **2** (0.4 mmol), DMF (2 mL), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), Ag_2O (93 mg, 0.4 mmol), and PivOH (41 mg, 0.4 mmol). Then the tube was sealed, and the resulting mixture was stirred at $100\text{ }^\circ\text{C}$ under air for 3 h

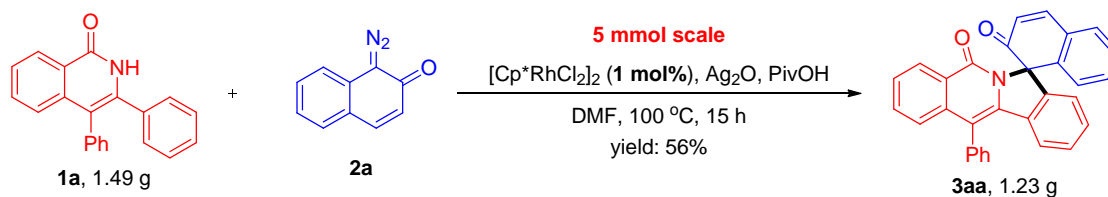
until isoquinolone **4** was consumed completely. Next, the reaction was quenched with NaHCO_3 and extracted with dichloromethane. The organic layer was washed with water and brine and then dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/ethyl acetate as eluent to give the corresponding product **5**.

4.3 General Procedure for the Preparation of Compounds **8**



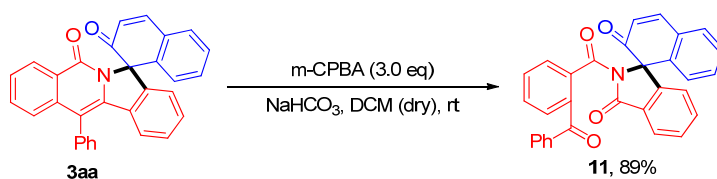
To a reaction tube (15 mL) equipped with a stirring bar were charged with 3-heteroaryl substituted isoquinolone **7** (0.2 mmol), 1-diazonaphthalen-2(1H)-one **2** (0.4 mmol), DMF (2 mL), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), and Ag_2O (93 mg, 0.4 mmol). Then the tube was sealed, and the resulting mixture was stirred at $100\text{ }^\circ\text{C}$ under air for 3 h until isoquinolone **7** was consumed completely. Next, the reaction was quenched with H_2O and extracted with dichloromethane. The organic layer was washed with water and brine and then dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether /ethyl acetate as eluent to give the corresponding product **8**.

4.4 Gram-Scale Synthesis of **3aa**



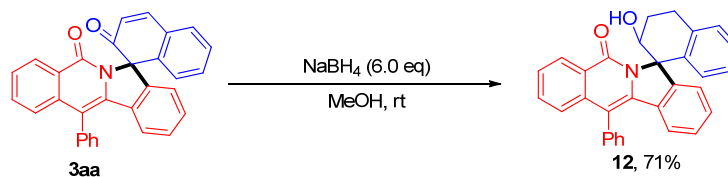
To a reaction tube (100 mL) equipped with a stirring bar were charged with **1a** (1.49 g, 5.0 mmol), **2a** (1.7 g, 10 mmol), DMF (50 mL), [Cp*RhCl₂]₂ (31 mg, 0.05 mmol), Ag₂O (2.3 g, 10 mmol), and PivOH (1.0 g, 10 mmol). Then the tube was sealed, and the resulting mixture was stirred at 100 °C (oil bath) under air for 15 h until **1a** was consumed completely. Next, the reaction was quenched with NaHCO₃ and extracted with dichloromethane. The organic layer was washed with water and brine and then dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/ethyl acetate (30:1) as eluent to afford **3aa** (1.23 g) as brown solid in 56% yield.

4.5 Synthesis of Compound **11**⁴



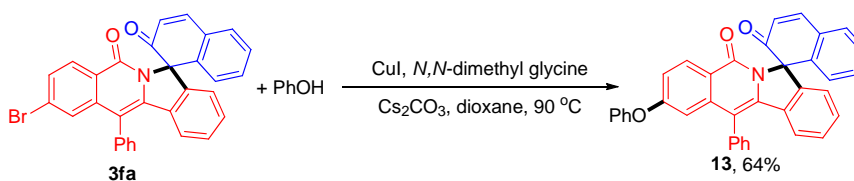
To a stirred suspension of NaHCO₃ (134 mg, 1.6 mmol) in dry dichloromethane (5 mL) was added *m*-CPBA (85% purity, 122 mg, 0.6 mmol) and then the mixture was stirred at room temperature for 15 minutes. Next, **3aa** (88 mg, 0.2 mmol) was added and the resulting mixture was stirred at room temperature for 30 h. The reaction was diluted with dichloromethane and washed with saturated NaHCO₃ and brine. After being dried over anhydrous Na₂SO₄, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **11** (84 mg) as white solid in 89% yield.

4.6 Synthesis of Compound **12**⁵



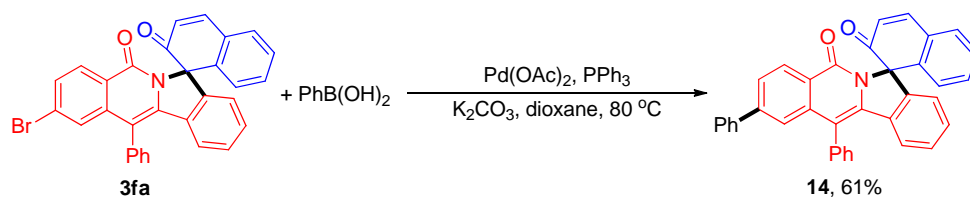
To a solution of **3aa** (88 mg, 0.2 mmol) in methanol (2 mL) was added NaBH₄ (45 mg, 1.2 mmol) at room temperature. Then the reaction mixture was stirred at the same temperature for 24 h until the complete consumption of **3aa**. Next, the reaction was quenched with water and extracted with EtOAc three times, and the combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. Then, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (5:1) as eluent to afford **12** (63 mg) as white solid in 71% yield.

4.7 Synthesis of Compound 13⁶



To a reaction tube (15 mL) equipped with a stirring bar were added **3fa** (51.6 mg, 0.1 mmol), phenol (28.2 mg, 0.3 mmol), *N,N*-dimethyl glycine hydrochloride (4.2 mg, 0.03 mmol), Cs₂CO₃ (65.2 mg, 0.2 mmol), CuI (1.9 mg, 0.01 mmol) and dioxane (1 mL). Then the resulting mixture was stirred at 90 °C for 24 h under argon atmosphere. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (2:1) as eluent to afford **13** (34 mg) as yellow solid in 64% yield.

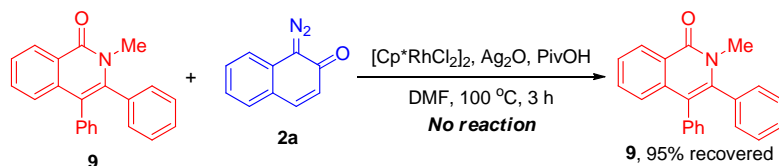
4.8 Synthesis of Compound **14**⁶



To a reaction tube (15 mL) equipped with a stirring bar were added **3fa** (51.6 mg, 0.1 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), PPh_3 (15.7 mg, 0.06 mmol), K_2CO_3 (55.3 mg, 0.4 mmol), Pd(OAc)_2 (2.2 mg, 0.01 mmol) and dioxane (1 mL). After the tube was sealed, the mixture was stirred at $80\text{ }^\circ\text{C}$ (oil bath) for 24 h. Upon completion, it was diluted with ethyl acetate (10 mL) and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) as the eluent to give **14** (32 mg) as white solid in 61% yield.

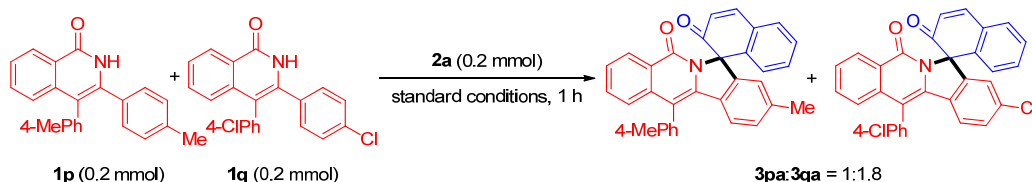
5. Mechanistic Studies

5.1 Control Experiment



To a reaction tube (15 mL) equipped with a stirring bar were charged with *N*-methyl substituted isoquinolone **9** (62 mg, 0.2 mmol), **2a** (68 mg, 0.4 mmol), DMF (2 mL), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), Ag_2O (93 mg, 0.4 mmol), and PivOH (41 mg, 0.4 mmol). Then the tube was sealed, and the resulting mixture was stirred at 100 °C under air for 3 h. After isolation and purification, isoquinolone **9** was recovered in 95% yield, implying that the *NH* unit of isoquinolone is crucial for the ortho $\text{C}(\text{sp}^2)\text{-H}$ bond activation.

5.2 Competitive Reaction



To a reaction tube (15 mL) equipped with a stirring bar were charged with **1p** (0.2 mmol), **1q** (0.2 mmol), **2a** (0.2 mmol), DMF (4 mL), $[\text{Cp}^*\text{RhCl}_2]_2$ (0.01 mmol), Ag_2O (0.8 mmol), and PivOH (0.8 mmol). Then the tube was sealed, and the resulting mixture was stirred at 100 °C for 1 h until **2a** was consumed completely. Next, the reaction was quenched with NaHCO_3 and extracted with dichloromethane. The organic layer was washed with water and brine and then dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the

residue was purified by silica gel chromatography using dichloromethane/ethyl acetate (30:1) as eluent to give a mixture of **3pa** and **3qa** (78 mg). Upon analyzing the ^1H NMR spectra as shown in Figure S1, the ratio of **3pa** and **3qa** was determined as 1:1.8, indicating that the ortho C-H bond cleavage might occur through a concerted metalation-deprotonation (CMD) mechanism.

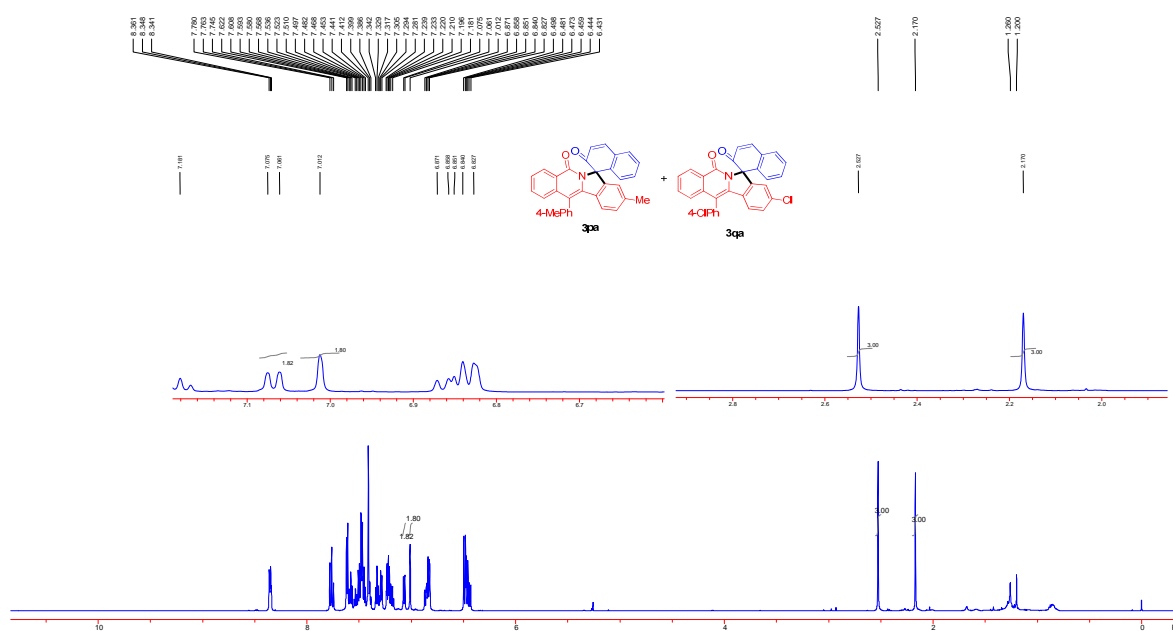


Figure S1. The ^1H NMR spectra of a mixture of **3pa** and **3qa**

5.3 Intermolecular KIE



To a reaction tube (15 mL) equipped with a stirring bar were charged with **1a** (0.2 mmol), **1a-d₁₀** (0.2 mmol), **2a** (0.2 mmol), DMF (4 mL), $[\text{Cp}^*\text{RhCl}_2]_2$ (0.01 mmol), Ag_2O (0.8 mmol), and PivOH (0.8 mmol). Then the tube was sealed, and the resulting mixture was stirred at 100 $^\circ\text{C}$ for 1 h until **2a** was consumed completely. Next, the reaction was quenched with NaHCO_3

and extracted with dichloromethane. The extract was washed with water and brine and then dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/ethyl acetate (30:1) as eluent to give a mixture of **3aa** and **3aa-d₉** (47 mg). Upon analyzing the ¹H NMR spectra as shown in Figure S2, the ratio of **3aa** and **3aa-d₉** was determined as 0.72:0.28. Accordingly, the KIE (kinetic isotopic effect) value was 2.57, suggesting that the C(sp²)-H bond activation might be involved in the turnover-limiting step.

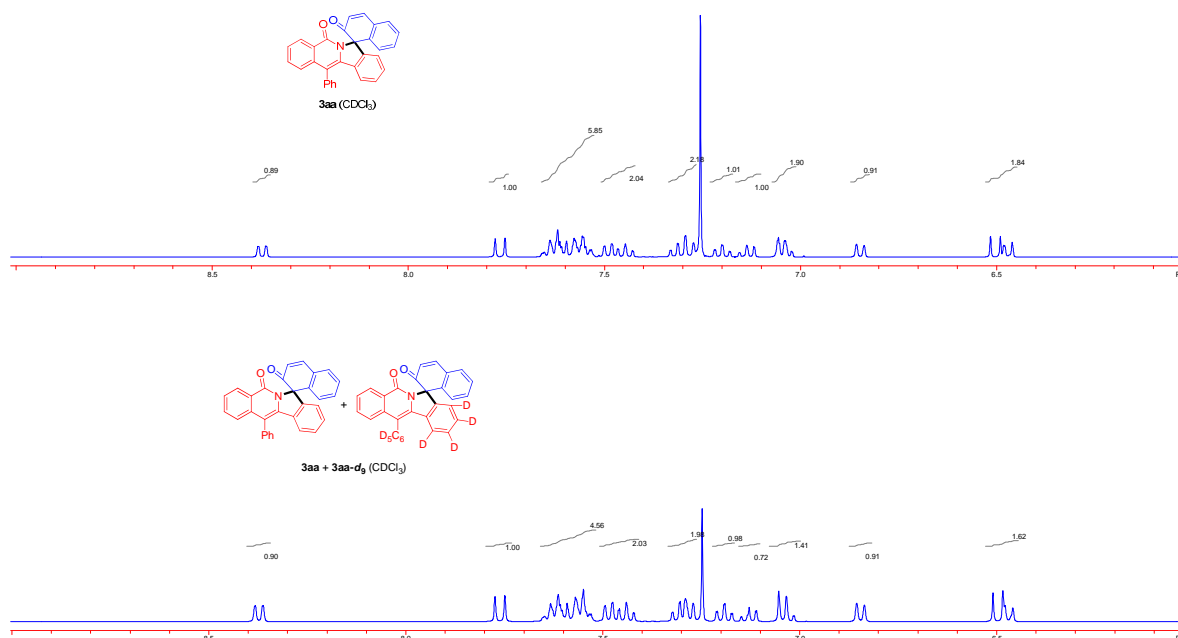
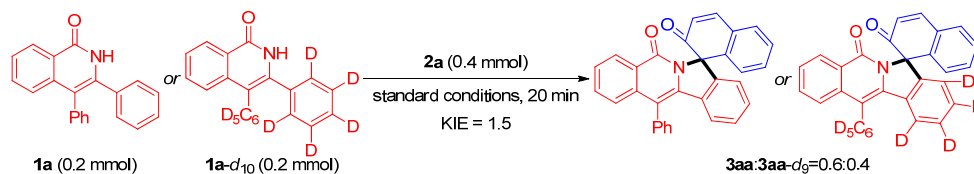


Figure S2. The ¹H NMR spectra of a mixture of **3aa** and **3aa-d₉**

5.4 Parallel KIE Study



Two parallel reactions with **1a** or deuterated substrate **1a-d₁₀** were performed under the standard conditions. Suspensions of **1a** (0.2 mmol) or **1a-d₁₀** (0.2 mmol), **2a** (0.4 mmol), DMF (2 mL), [Cp*RhCl₂]₂ (0.05 mmol), Ag₂O (0.4 mmol), PivOH (0.4 mmol) were stirred side-by-side at 100 °C for 20 min. Both reactions were quenched with saturated NaHCO₃ and combined rapidly. The mixture was extracted with dichloromethane. The extract was washed with water and brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using dichloromethane/ethyl acetate (30:1) as eluent to afford a mixture of **3aa** and **3aa-d₉** (54 mg). Upon analyzing the ¹H NMR spectra as shown in Figure S3, the ratio of **3aa** and **3aa-d₉** was determined as 0.6:0.4 and a value of $k_H/k_D = 1.5$ (parallel KIE) was calculated, suggesting that the C(sp²)-H bond activation might be involved in the turnover-limiting step.

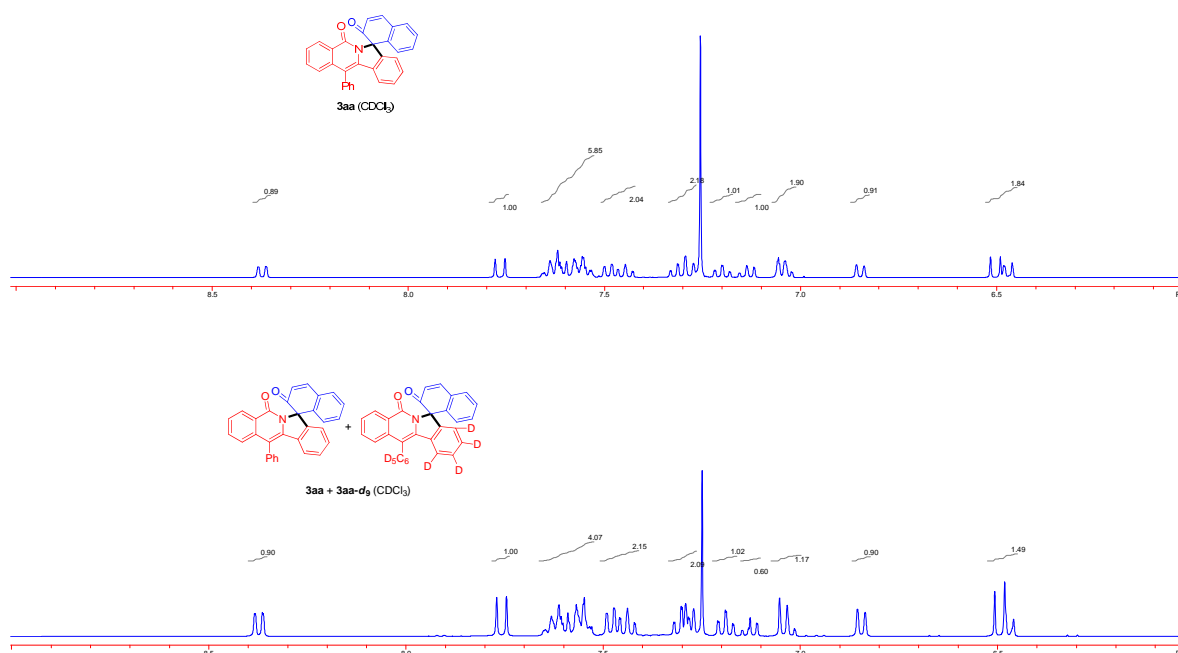


Figure S3. The ¹H NMR spectra of a mixture of **3aa** and **3aa-d₉**

6. X-Ray Crystal Structure and Data of 3aa, 5a, 8e, and 10

(1) Compound 3aa

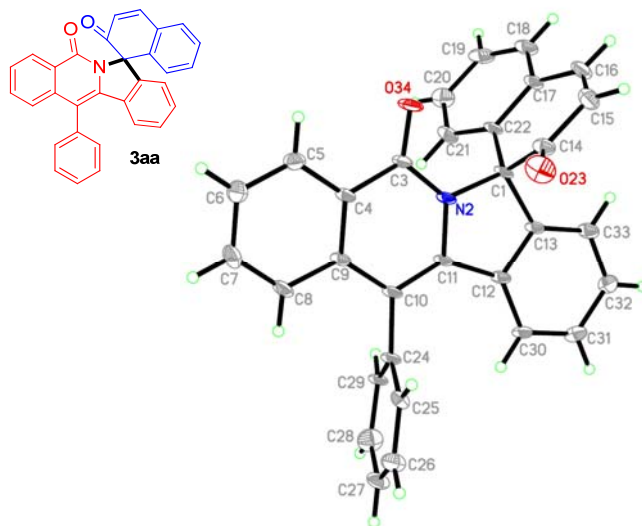


Figure S4. X-Ray Crystal Structure of **3aa** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (3:1) solution of **3aa**. Crystal data collection and refinement parameters of **3aa** are summarized in Table S3. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing Method and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S3. Crystallographic Data and Structure Refinement Results of 3aa

Empirical formula	2(C ₃₁ H ₁₉ NO ₂)
Formula weight	874.94
Temp, K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> , Å	10.3989(2)
<i>b</i> , Å	28.6103(4)
<i>c</i> , Å	15.0726(2)
α (°)	90
β (°)	102.494(2)
γ (°)	90
Volume, Å ³	4378.14(12)
<i>Z</i>	4
<i>d</i> _{calc} , g cm ⁻³	1.327
λ , Å	1.54184
μ , mm ⁻¹	0.654
No. of data collected	18749
No. of unique data	7566
<i>R</i> _{int}	0.0660
Goodness-of-fit on <i>F</i> ²	1.055
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0896, 0.2495
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1104, 0.2774

(2) Compound 5a

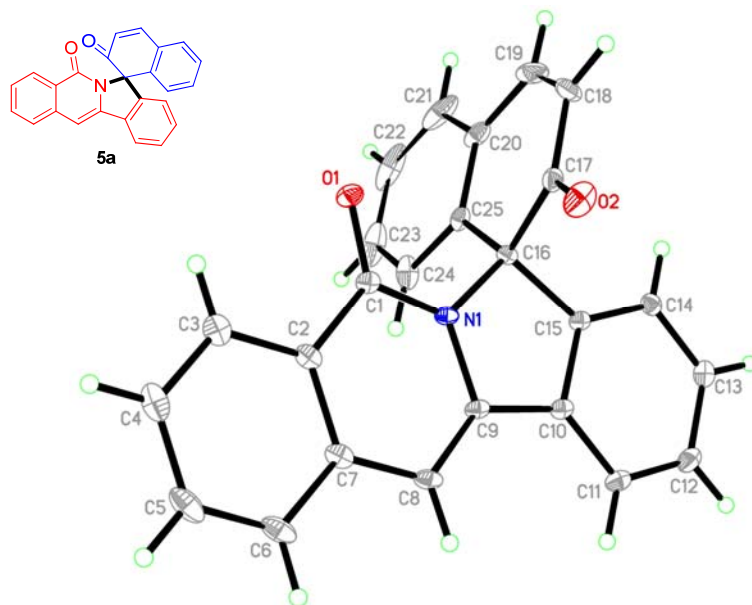


Figure S5. X-Ray Crystal Structure of **5a** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a dichloromethane/ethyl acetate (30:1) solution of **5a**. Crystal data collection and refinement parameters of **5a** are summarized in Table S4. Intensity data were collected at 150 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184$ Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing Method and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S4. Crystallographic Data and Structure Refinement Results of 5a

Empirical formula	C ₂₅ H ₁₅ NO ₂
Formula weight	361.38
Temp, K	149.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> , Å	12.4723(3)
<i>b</i> , Å	13.8610(3)
<i>c</i> , Å	10.2625(2)
α (°)	90
β (°)	101.425(2)
γ (°)	90
Volume, Å ³	1739.01(7)
<i>Z</i>	4
<i>d</i> _{calc} , g cm ⁻³	1.380
λ , Å	1.54184
μ , mm ⁻¹	0.699
No. of data collected	6920
No. of unique data	3307
<i>R</i> _{int}	0.0230
Goodness-of-fit on <i>F</i> ²	1.054
<i>R</i> ₁ , w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0556, 0.1548
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0609, 0.1608

(3) Compound **8e**

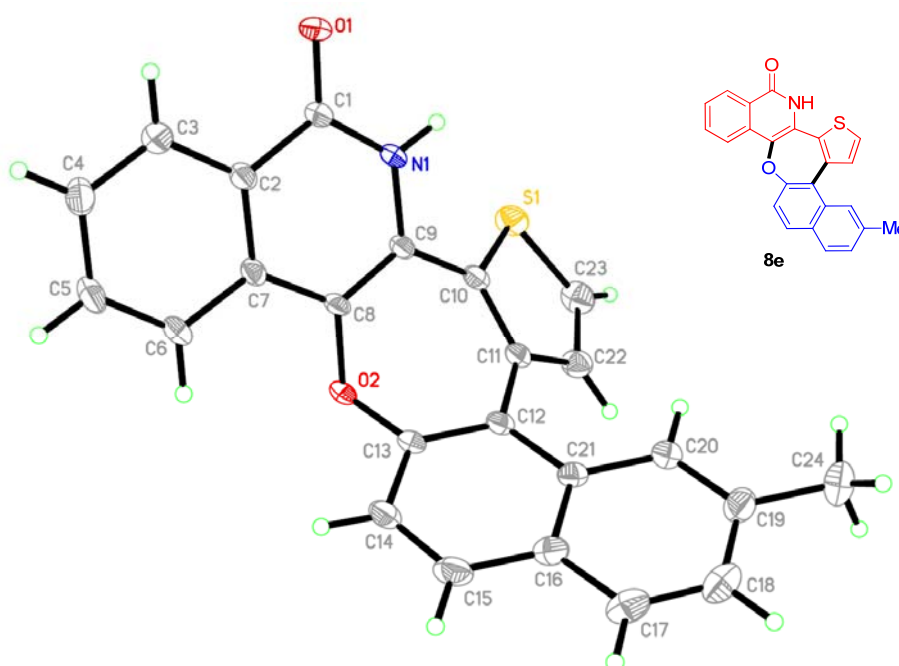


Figure S6. X-Ray Crystal Structure of **8e** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (3:1) solution of **8e**. Crystal data collection and refinement parameters of **8e** are summarized in Table S5. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing Method and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S5. Crystallographic Data and Structure Refinement Results of 8e

Empirical formula	C ₂₄ H ₁₅ NO ₂ S
Formula weight	381.43
Temp, K	293(2)
Crystal system	triclinic
Space group	P-1
<i>a</i> , Å	8.1960(4)
<i>b</i> , Å	9.4755(5)
<i>c</i> , Å	13.0705(7)
α (°)	77.839(4)
β (°)	78.582(4)
γ (°)	76.499(4)
Volume, Å ³	952.98(9)
<i>Z</i>	2
<i>d</i> _{calc} , g cm ⁻³	1.329
λ , Å	1.54184
μ , mm ⁻¹	1.662
No. of data collected	7306
No. of unique data	3622
<i>R</i> _{int}	0.0316
Goodness-of-fit on <i>F</i> ²	1.059
<i>R</i> ₁ , w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0562, 0.1480
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0636, 0.1563

(4) Compound 10

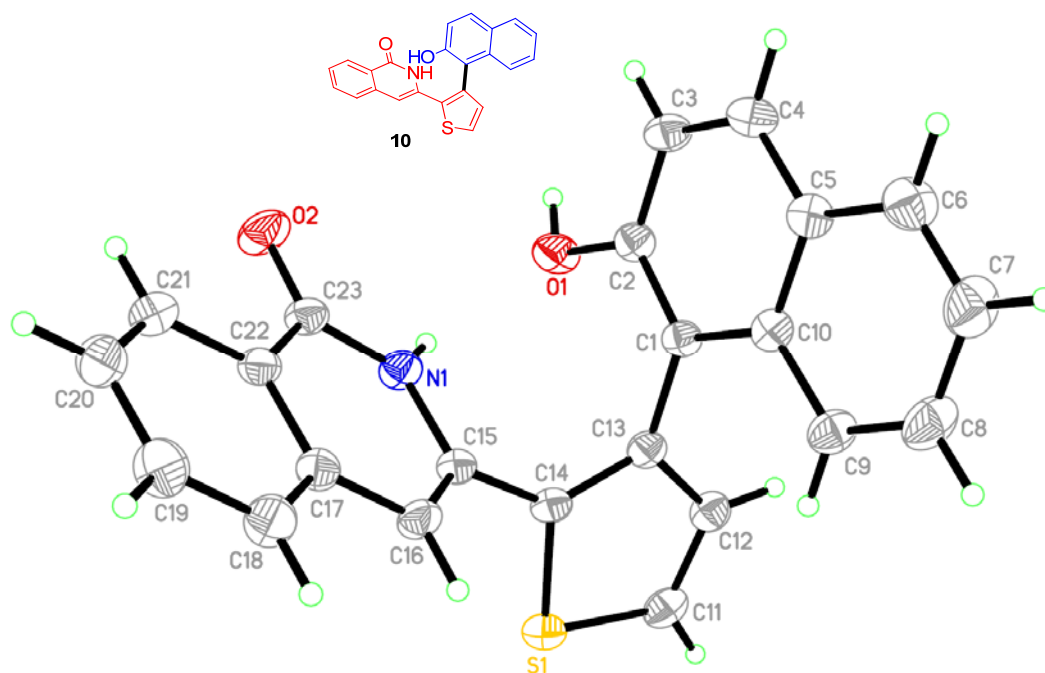


Figure S7. X-Ray Crystal Structure of **10** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (3:1) solution of **10**. Crystal data collection and refinement parameters of **10** are summarized in Table S6. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing Method and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

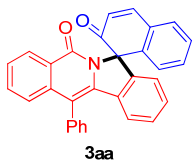
Table S6. Crystallographic Data and Structure Refinement Results of 10

Empirical formula	C ₂₃ H ₁₅ NO ₂ S
Formula weight	369.42
Temp, K	293(2)
Crystal system	triclinic
Space group	P-1
<i>a</i> , Å	8.8200(4)
<i>b</i> , Å	10.4849(5)
<i>c</i> , Å	10.5524(4)
α (°)	96.384(4)
β (°)	111.049(4)
γ (°)	90.540(4)
Volume, Å ³	903.81(7)
<i>Z</i>	2
<i>d</i> _{calc} , g cm ⁻³	1.357
λ , Å	1.54184
μ , mm ⁻¹	1.732
No. of data collected	6160
No. of unique data	3422
<i>R</i> _{int}	0.0256
Goodness-of-fit on <i>F</i> ²	1.073
<i>R</i> ₁ , w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0438, 0.1151
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0504, 0.1207

7. References

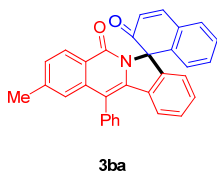
- (1) (a) Guimond, N.; Gouliaras, C.; Fagnou, K. Rhodium(III)-Catalyzed Isoquinolone Synthesis: The N-O Bond as a Handle for C-N Bond Formation and Catalyst Turnover. *J. Am. Chem. Soc.* **2010**, *132*, 6908–6909. (b) Guimond, N.; Gorelsky, S. I.; Fagnou, K. Rhodium(III)-Catalyzed Heterocycle Synthesis Using an Internal Oxidant: Improved Reactivity and Mechanistic Studies. *J. Am. Chem. Soc.* **2011**, *133*, 6449–6457. (c) Shi, Y.; Zhu, X.; Mao, H.; Hu, H.; Zhu, C.; Cheng, Y. Synthesis of Functionalized Isoquinolin-1(2*H*)-ones by Copper-Catalyzed α -Arylation of Ketones with 2-Halobenzamides. *Chem. Eur. J.* **2013**, *19*, 11553–11557.
- (2) Bera, S.; Roy, S.; Pal, S. C.; Anoop, A.; Samanta, R. Iridium(III)-Catalyzed Intermolecular Mild N-Arylation of Aliphatic Amides Using Quinoid Carbene: A Migratory Insertion-Based Approach. *ACS Catal.* **2021**, *11*, 10847–10854.
- (3) Fujita, K.-i.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. Synthesis of Five-, Six-, and Seven-Membered Ring Lactams by Cp*Rh Complex-Catalyzed Oxidative N-Heterocyclization of Amino Alcohols. *Org. Lett.* **2004**, *6*, 2785–2788.
- (4) Guo, S.; Sun, L.; Liu, Y.; Ma, N.; Zhang, X.; Fan, X. Rh(III)-Catalyzed Oxidative Spirocyclization of Isoquinolones with α -Diazo-1,3-indandiones. *Org. Lett.* **2019**, *21*, 4082–4086.
- (5) Han, X.; Kong, L.; Feng, J.; Li, X. Rhodium(III)-Catalyzed Synthesis of Spirocyclic Isoindole *N*-Oxides and Isobenzofuranones via C–H Activation and Spiroannulation. *Chem. Commun.* **2020**, *56*, 5528–5531.
- (6) Song, X.; Zhou, Q.; Zhao, J.; Jiang, Y.; Zhang, X.; Zhang, X.; Fan, X. Synthesis of 1,3-Benzodiazepines through [5 + 2] Annulation of N-Aryl Amidines with Propargylic Esters. *Org. Lett.* **2020**, *22*, 9506–9512.

8. Characterization Data of 3aa-3sa, 3ab-3ap, 5a-5j, 8a-8n, and 10-14



12-Phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3aa):

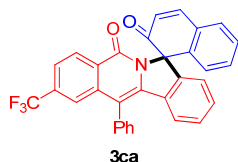
Dichloromethane/ethyl acetate (30:1) as eluent; brown solid (65 mg, 75%), mp >300 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.17 (dd, *J* = 7.6, 0.8 Hz, 1H), 8.09 (d, *J* = 10.0 Hz, 1H), 7.76-7.65 (m, 6H), 7.58-7.50 (m, 2H), 7.41 (td, *J* = 7.6, 0.8 Hz, 1H), 7.29-7.15 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 10.0 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 192.9, 159.3, 146.4, 142.4, 140.4, 139.1, 138.9, 134.9, 133.5, 132.5, 131.4, 131.1, 130.9, 130.1, 129.8, 129.7, 129.5, 129.4, 128.9, 128.6, 128.4, 127.9, 126.6, 125.60, 125.56, 125.3, 125.2, 124.9, 121.6, 114.6, 76.1. HRMS (ESI) calcd for C₃₁H₁₉NNaO₂ [M + Na]⁺ 460.1308, found 460.1301.



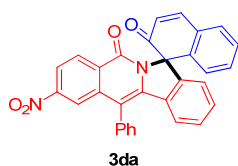
2-Methyl-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-di

one (3ba): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (56 mg, 62%), mp 201-202 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 10.0 Hz, 1H), 7.67-7.60 (m, 3H), 7.57-7.52 (m, 2H), 7.48 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.32-7.26 (m, 2H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14-7.10 (m, 1H), 7.05-7.01 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 6.43-6.41 (m, 1H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.0, 159.2, 146.3, 143.1, 142.4, 140.6, 139.2, 138.9, 135.0, 133.6, 131.4, 131.1, 130.8, 130.1,

129.6, 129.5, 129.4, 128.8, 128.5, 128.3, 128.2, 127.9, 125.3, 125.23, 125.15, 124.9, 123.4, 121.5, 114.4, 76.0, 22.0 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{21}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 474.1464, found 474.1443.

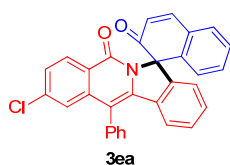


12-Phenyl-2-(trifluoromethyl)-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (3ca): Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (76 mg, 75%), mp 193-194 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.48 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 9.6$ Hz, 1H), 7.68-7.63 (m, 4H), 7.56-7.54 (m, 3H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.33 (td, $J = 7.8$, 1.2 Hz, 1H), 7.22 (td, $J = 7.8$, 1.2 Hz, 1H), 7.19-7.16 (m, 1H), 7.08-7.06 (m, 2H), 6.83 (d, $J = 7.8$ Hz, 1H), 6.51 (d, $J = 10.2$ Hz, 1H), 6.47 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.5, 158.5, 146.6, 142.5, 140.5, 139.8, 139.3, 134.1 (q, $J = 31.8$ Hz, 1C), 133.8, 132.9, 131.2, 130.99, 130.98, 130.31, 130.28, 130.0, 129.7, 129.5, 129.13, 129.06, 129.0, 128.6, 127.5, 125.2, 125.1, 123.7 (q, $J = 271.2$ Hz, 1C), 122.6 (q, $J = 4.4$ Hz, 1C), 122.5 (q, $J = 3.3$ Hz, 1C), 121.7, 114.1, 76.4 (one ^{13}C signal was not observed). ^{19}F NMR (CDCl_3 , 564 MHz) δ -62.95 (s). HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{18}\text{F}_3\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 528.1182, found 528.1170.

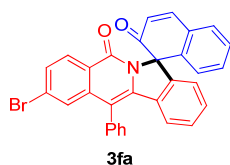


2-Nitro-12-phenyl-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (3da): Dichloromethane/ethyl acetate (30:1) as eluent; yellow solid (83 mg, 86%), mp >300 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.50 (d, $J = 9.0$ Hz, 1H), 8.17 (dd, $J = 8.4$, 2.4 Hz, 1H),

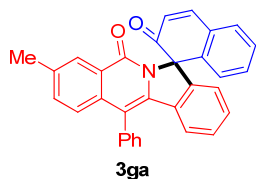
8.13 (d, $J = 2.4$ Hz, 1H), 7.80 (d, $J = 9.6$ Hz, 1H), 7.70-7.66 (m, 3H), 7.56-7.55 (m, 2H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.24-7.19 (m, 2H), 7.09 (t, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.52-6.49 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.2, 158.1, 150.5, 146.7, 142.5, 141.4, 140.0, 139.5, 133.3, 132.6, 131.2, 131.04, 130.96, 130.7, 130.4, 130.2, 129.92, 129.90, 129.5, 129.4, 129.2, 128.9, 128.8, 125.4, 125.2, 125.0, 121.7, 120.9, 120.1, 114.0, 76.6. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{18}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 505.1159, found 505.1130.



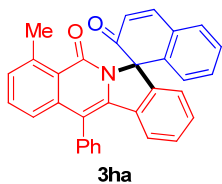
2-Chloro-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ea): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (89 mg, 94%), mp >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.28 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 10.0$ Hz, 1H), 7.66-7.61 (m, 3H), 7.55-7.48 (m, 3H), 7.38 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.23-7.13 (m, 3H), 7.06-7.03 (m, 2H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.49 (d, $J = 10.0$ Hz, 1H), 6.45 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 192.6, 158.7, 146.5, 142.6, 140.6, 140.3, 140.1, 139.3, 134.1, 133.1, 131.3, 131.0, 130.9, 130.23, 130.16, 129.9, 129.6, 129.5, 129.0, 128.5, 127.1, 125.2, 125.15, 125.08, 124.9, 123.9, 121.6, 113.6, 76.2 (two ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{18}\text{ClNNaO}_2$ $[\text{M} + \text{Na}]^+$ 494.0918, found 494.0900.



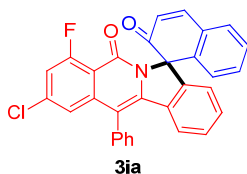
2-Bromo-12-phenyl-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (3fa): Dichloromethane/ethyl acetate (30:1) as eluent; brown solid (81 mg, 79%), mp >300 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 10.2 Hz, 1H), 7.66-7.62 (m, 3H), 7.55-7.49 (m, 4H), 7.40 (d, *J* = 1.8 Hz, 1H), 7.32 (td, *J* = 7.2, 0.6 Hz, 1H), 7.21 (td, *J* = 7.8, 1.2 Hz, 1H), 7.17-7.14 (m, 1H), 7.06-7.04 (m, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 10.2 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.6, 158.8, 146.5, 142.5, 140.7, 140.3, 140.0, 134.1, 133.1, 131.3, 131.0, 130.9, 130.22, 130.15, 129.9, 129.8, 129.64, 129.62, 129.5, 129.0, 128.5, 128.02, 127.97, 125.2, 125.14, 125.09, 124.2, 121.6, 113.4, 76.2 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₃₁H₁₈BrNNaO₂ [M + Na]⁺ 538.0413, found 538.0408.



3-Methyl-12-phenyl-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (3ga): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (52 mg, 58%), mp 196-197 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.18 (s, 1H), 7.75 (d, *J* = 10.0 Hz, 1H), 7.64-7.58 (m, 3H), 7.56-7.52 (m, 2H), 7.48 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.30 (td, *J* = 7.2, 1.2 Hz, 1H), 7.20-7.16 (m, 2H), 7.13-7.09 (m, 1H), 7.04-7.00 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 193.0, 159.2, 146.3, 142.3, 140.6, 138.0, 136.8, 135.0, 133.9, 133.6, 131.4, 131.1, 130.8, 130.1, 129.6, 129.5, 129.3, 128.8, 128.5, 128.3, 127.6, 125.5, 125.3, 125.2, 124.7, 121.6, 114.6, 76.0, 21.3 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₃₂H₂₁NNaO₂ [M + Na]⁺ 474.1464, found 474.1444.

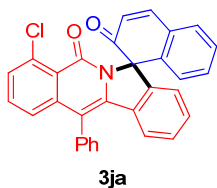


4-Methyl-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ha): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (35 mg, 39%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.75 (d, *J* = 10.0 Hz, 1H), 7.64-7.58 (m, 3H), 7.53-7.47 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21-7.18 (m, 2H), 7.12-7.08 (m, 2H), 7.03-6.99 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 10.0 Hz, 1H), 6.37 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.83 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 193.1, 159.9, 146.4, 142.3, 140.90, 140.87, 138.8, 135.6, 133.5, 131.5, 131.4, 131.2, 130.8, 130.2, 129.74, 129.66, 129.6, 129.4, 129.3, 128.8, 128.5, 128.2, 125.4, 125.0, 124.9, 124.2, 124.0, 121.5, 114.4, 76.3, 24.0 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₃₂H₂₁NNaO₂ [M + Na]⁺ 474.1464, found 474.1445.



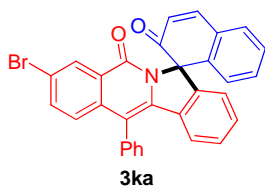
2-Chloro-4-fluoro-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ia): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (60 mg, 61%), mp 226-227 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.75 (d, *J* = 10.2 Hz, 1H), 7.66-7.62 (m, 3H), 7.52-7.50 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.33-7.30 (m, 1H), 7.23-7.20 (m, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.09-7.02 (m, 3H), 7.00 (s, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 10.2 Hz, 1H), 6.38 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.3, 163.0 (d, *J* = 266.9 Hz, 1C), 156.0 (d, *J* = 3.3 Hz, 1C), 146.5, 142.83, 142.80, 141.4, 139.7, 139.0 (d, *J* = 12.0 Hz, 1C),

134.0, 132.8, 131.3, 131.1, 130.9, 130.5, 130.3, 130.0, 129.7, 129.6, 129.1, 129.0, 128.5, 125.3, 125.2, 125.0, 121.7, 121.1 (d, $J = 3.3$ Hz, 1C), 114.3 (d, $J = 24.0$ Hz, 1C), 113.2 (d, $J = 5.4$ Hz, 1C), 112.6 (d, $J = 2.3$ Hz, 1C), 76.2. ^{19}F NMR (CDCl_3 , 376 MHz) δ -107.67 (d, $J = 9.4$ Hz). HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{17}\text{ClFNNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 512.0824, found 512.0811.



4-Chloro-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ja):

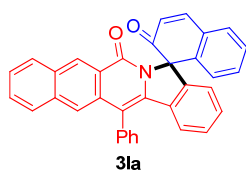
Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (58 mg, 61%), mp >300 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 7.74 (d, $J = 10.2$ Hz, 1H), 7.63-7.58 (m, 3H), 7.52-7.50 (m, 2H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.42 (d, $J = 6.6$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.04-7.02 (m, 2H), 6.86 (d, $J = 7.8$ Hz, 1H), 6.49 (d, $J = 10.2$ Hz, 1H), 6.36 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.5, 157.4, 146.5, 142.6, 142.3, 140.2, 140.0, 136.0, 135.0, 133.0, 131.9, 131.4, 131.2, 130.9, 130.3, 130.1, 129.8, 129.7, 129.6, 129.5, 128.9, 128.8, 128.3, 125.4, 125.1, 124.9, 124.8, 122.2, 121.6, 113.6, 76.5. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{18}\text{ClNNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 494.0918, found 494.0914.



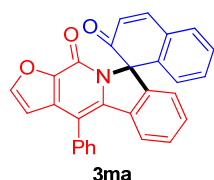
3-Bromo-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ka):

Dichloromethane/ethyl acetate (45:1) as eluent; white solid (89 mg, 86%), mp >300 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.49 (d, $J = 1.8$ Hz, 1H), 7.77 (d, $J = 10.2$ Hz, 1H),

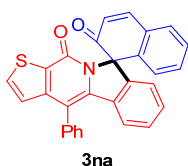
7.65-7.59 (m, 4H), 7.54-7.49 (m, 3H), 7.32 (td, $J = 7.2, 0.6$ Hz, 1H), 7.22-7.19 (m, 1H), 7.16-7.14 (m, 2H), 7.06-7.03 (m, 2H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.49 (d, $J = 10.2$ Hz, 1H), 6.46 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.6, 158.1, 146.5, 142.4, 140.0, 139.4, 137.9, 135.5, 134.3, 133.2, 131.3, 131.0, 130.9, 130.5, 130.2, 130.0, 129.8, 129.53, 129.52, 129.0, 128.9, 128.5, 127.3, 126.8, 125.2, 125.1, 125.0, 121.7, 120.7, 114.0, 76.3. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{18}\text{BrNNaO}_2$ $[\text{M} + \text{Na}]^+$ 538.0413, found 538.0402.



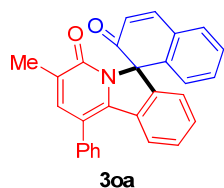
14-Phenyl-2'H,7H-spiro[benzo[g]isoindolo[2,1-b]isoquinoline-5,1'-naphthalene]-2',7-dione (3la): Dichloromethane/ethyl acetate (30:1) as eluent; yellow solid (67 mg, 69%), mp >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.97 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.78 (s, 1H), 7.76-7.75 (m, 1H), 7.69-7.60 (m, 6H), 7.53-7.44 (m, 3H), 7.31 (td, $J = 7.6, 0.8$ Hz, 1H), 7.20 (td, $J = 8.0, 1.2$ Hz, 1H), 7.15-7.11 (m, 1H), 7.06-7.02 (m, 2H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.50 (d, $J = 10.0$ Hz, 1H), 6.47-6.45 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.4, 159.9, 146.4, 142.4, 141.0, 137.7, 135.41, 135.36, 135.2, 133.5, 131.49, 131.46, 131.2, 130.9, 130.1, 129.8, 129.7, 129.49, 129.48, 129.4, 129.3, 128.9, 128.7, 128.4, 128.2, 128.0, 126.2, 125.3, 125.2, 125.0, 124.5, 124.0, 121.6, 114.6, 75.9. HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{21}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 510.1464, found 510.1446.



4-Phenyl-2*H*,11*H*-spiro[furo[3',2':4,5]pyrido[2,1-*a*]isoindole-9,1'-naphthalene]-2',11-dione (3ma): Dichloromethane/ethyl acetate (7:1) as eluent; brown solid (48 mg, 56%), mp 273-274 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.76 (d, *J* = 10.2 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.63-7.58 (m, 4H), 7.56-7.53 (m, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.32 (td, *J* = 7.8, 1.2 Hz, 1H), 7.21 (td, *J* = 7.8, 1.2 Hz, 1H), 7.15-7.12 (m, 1H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.93-6.92 (m, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.51-6.49 (m, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.5, 150.1, 148.6, 146.6, 142.7, 142.5, 139.9, 139.8, 136.6, 134.4, 133.0, 130.9, 130.4, 130.20, 130.18, 129.53, 129.48, 129.4, 129.1, 128.8, 128.7, 128.4, 125.3, 124.8, 124.1, 121.6, 110.8, 107.3, 76.4. HRMS (ESI) calcd for C₂₉H₁₇NNaO₃ [M + Na]⁺ 450.1101, found 450.1091.

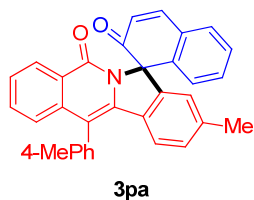


4'-Phenyl-2*H*,11'*H*-spiro[naphthalene-1,9'-thieno[3',2':4,5]pyrido[2,1-*a*]isoindole]-2,11'-dione (3na): Dichloromethane/ethyl acetate (15:1) as eluent; white solid (58 mg, 65%), mp >300 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.09 (d, *J* = 5.2 Hz, 1H), 8.08 (d, *J* = 10.0 Hz, 1H), 7.73-7.64 (m, 5H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.42 (td, *J* = 7.6, 0.8 Hz, 1H), 7.31-7.25 (m, 2H), 7.22-7.18 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 10.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 192.6, 155.4, 148.3, 146.4, 142.4, 140.7, 139.9, 135.1, 133.4, 133.2, 130.9, 130.7, 130.4, 130.1, 129.7, 129.53, 129.45, 129.2, 128.9, 128.8, 128.7, 128.4, 125.3, 125.1, 124.5, 124.4, 121.7, 113.5, 76.0. HRMS (ESI) calcd for C₂₉H₁₇NNaO₂S [M + Na]⁺ 466.0872, found 466.0864.



3'-Methyl-1'-phenyl-2*H*,4'*H*-spiro[naphthalene-1,6'-pyrido[2,1-*a*]isoindole]-2,4'-dione

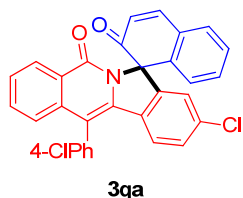
(3oa): Dichloromethane/ethyl acetate (15:1) as eluent; brown solid (39 mg, 48%), mp 236-237 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.74 (d, *J* = 9.6 Hz, 1H), 7.56-7.51 (m, 4H), 7.49-7.46 (m, 2H), 7.36 (s, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.10-7.07 (m, 1H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 2.16 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.1, 159.7, 146.3, 142.5, 142.1, 141.5, 139.4, 136.9, 133.3, 130.9, 130.1, 129.9, 129.7, 129.6, 128.9, 128.75, 128.73, 128.4, 128.2, 125.5, 124.8, 124.1, 121.7, 116.6, 76.6, 16.3. HRMS (ESI) calcd for C₂₈H₁₉NNaO₂ [M + Na]⁺ 424.1308, found 424.1290.



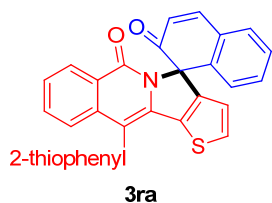
9-Methyl-12-(*p*-tolyl)-2'*H*,5'*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5'-dione

(3pa): Dichloromethane/ethyl acetate (30:1) as eluent; yellow solid (68 mg, 73%), mp 206-207 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.35 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.76 (d, *J* = 10.2 Hz, 1H), 7.56-7.54 (m, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.42-7.40 (m, 5H), 7.32-7.28 (m, 2H), 7.19 (td, *J* = 7.8, 0.6 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.82 (s, 1H), 6.50 (d, *J* = 10.2 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 2.54 (s, 3H), 2.18 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.1, 159.3, 146.3, 142.7, 140.6, 140.3, 139.4, 139.1, 138.2, 132.3, 131.9, 131.2,

131.0, 130.92, 130.85, 130.3, 130.1, 130.0, 129.9, 129.5, 128.3, 127.8, 126.3, 125.44, 125.42, 125.37, 125.2, 124.8, 121.8, 113.8, 75.9, 21.54, 21.52. HRMS (ESI) calcd for C₃₃H₂₃NNaO₂ [M + Na]⁺ 488.1621, found 488.1601.

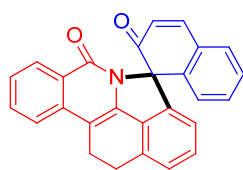


9-Chloro-12-(4-chlorophenyl)-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalen e]-2',5-dione (3qa): Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (68 mg, 67%), mp >300 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.36 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 10.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.59 (td, *J* = 8.4, 1.2 Hz, 1H), 7.52-7.45 (m, 4H), 7.35 (td, *J* = 7.2, 0.6 Hz, 1H), 7.24-7.21 (m, 2H), 7.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 10.2 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.2, 159.1, 146.7, 143.8, 139.5, 138.7, 138.1, 135.9, 135.0, 133.1, 132.8, 132.7, 132.5, 131.7, 131.1, 130.4, 130.1, 129.9, 129.5, 129.4, 128.8, 128.0, 127.0, 125.7, 125.6, 125.3, 125.2, 125.1, 122.1, 113.3, 75.7. HRMS (ESI) calcd for C₃₁H₁₇Cl₂NNaO₂ [M + Na]⁺ 528.0529, found 528.0501.



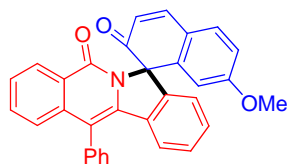
11'-(Thiophen-2-yl)-2H,6'H-spiro[naphthalene-1,4'-thieno[2',3':3,4]pyrrolo[1,2-b]isoquinoline]-2,6'-dione (3ra): Dichloromethane/ethyl acetate (45:1) as eluent; yellow solid (59 mg, 66%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.25 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 10.0

Hz, 1H), 7.54 (m, 2H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.39-7.33 (m, 2H), 7.26-7.20 (m, 3H), 7.17-7.14 (m, 2H), 6.86 (d, $J = 7.2$ Hz, 1H), 6.55 (d, $J = 4.8$ Hz, 1H), 6.40 (d, $J = 10.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 191.3, 159.1, 148.4, 146.2, 139.3, 139.0, 138.1, 134.9, 134.0, 132.8, 130.9, 130.2, 129.8, 129.5, 128.7, 128.1, 127.9, 126.5, 125.3, 125.13, 125.10, 118.9, 104.0, 75.6 (three ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{15}\text{NNaO}_2\text{S}_2$ [$\text{M} + \text{Na}$] $^+$ 472.0436, found 472.0430.



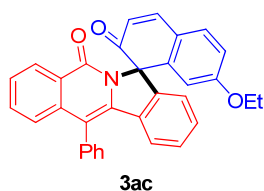
3sa

11,12-Dihydro-2'*H*,6*H*-spiro[isoindolo[7,1,2-*cde*]phenanthridine-4,1'-naphthalene]-2',6-dione (3sa): Dichloromethane/ethyl acetate (60:1) as eluent; yellow solid (38 mg, 49%), mp >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.40 (dd, $J = 8.0, 0.4$ Hz, 1H), 7.74 (d, $J = 10.4$ Hz, 1H), 7.69 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.65 (d, $J = 7.2$ Hz, 1H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.44-7.40 (m, 1H), 7.31 (td, $J = 7.2, 1.2$ Hz, 1H), 7.21-7.11 (m, 3H), 6.89 (t, $J = 6.8$ Hz, 2H), 6.44 (d, $J = 10.0$ Hz, 1H), 3.32-3.21 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 192.3, 159.3, 146.5, 139.4, 138.9, 138.4, 137.9, 133.5, 132.4, 130.85, 130.76, 130.5, 130.1, 129.24, 129.21, 128.6, 127.7, 127.2, 125.7, 125.6, 125.0, 122.1, 119.3, 103.4, 79.8, 25.5, 21.5. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{17}\text{NNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 410.1151, found 410.1147.

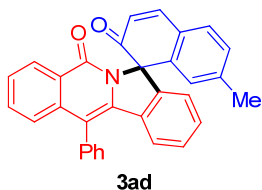


3ab

7'-Methoxy-12-phenyl-2'*H*,5*H*-spiro[isindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ab): Dichloromethane/ethyl acetate (30:1) as eluent; pink solid (82 mg, 88%), mp >300 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 9.6 Hz, 1H), 7.64-7.53 (m, 6H), 7.46-7.43 (m, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.39 (d, *J* = 2.4 Hz, 1H), 6.36 (d, *J* = 10.2 Hz, 1H), 3.65 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.7, 161.8, 159.3, 146.3, 142.7, 142.5, 139.2, 138.9, 134.9, 133.3, 132.4, 131.9, 131.4, 131.1, 129.7, 129.6, 129.4, 128.8, 128.6, 127.9, 126.6, 125.6, 125.5, 124.9, 122.9, 122.7, 121.6, 114.5, 112.7, 112.0, 76.2, 55.3. HRMS (ESI) calcd for C₃₂H₂₁NNaO₃ [M + Na]⁺ 490.1414, found 490.1399.



7'-Ethoxy-12-phenyl-2'*H*,5*H*-spiro[isindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ac): Dichloromethane/ethyl acetate (30:1) as eluent; pink solid (95 mg, 98%), mp 183-184 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.39 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.71 (d, *J* = 10.2 Hz, 1H), 7.65-7.55 (m, 6H), 7.46-7.42 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.03 (td, *J* = 8.4, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 6.39 (d, *J* = 2.4 Hz, 1H), 6.36 (d, *J* = 10.2 Hz, 1H), 3.92-3.86 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.8, 161.2, 159.3, 146.4, 142.6, 142.5, 139.2, 138.9, 134.9, 133.4, 132.4, 131.9, 131.4, 131.2, 129.7, 129.6, 129.4, 128.8, 128.6, 127.9, 126.5, 125.6, 125.5, 124.9, 122.7, 122.5, 121.6, 114.5, 113.2, 112.3, 76.3, 63.6, 14.6. HRMS (ESI) calcd for C₃₃H₂₃NNaO₃ [M + Na]⁺ 504.1570, found 504.1549.



7'-Methyl-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-di

one (3ad): Dichloromethane/ethyl acetate (30:1) as eluent; yellow solid (44 mg, 49%),

mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.39 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.74 (d, *J* = 9.6 Hz,

1H), 7.66-7.55 (m, 6H), 7.46 (td, *J* = 8.0, 1.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* =

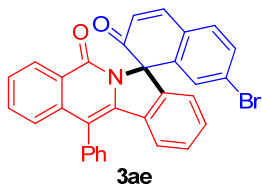
8.0 Hz, 1H), 7.16-7.10 (m, 2H), 7.06-7.02 (m, 2H), 6.61 (s, 1H), 6.49-6.47 (m, 1H), 6.43 (d, *J*

= 9.6 Hz, 1H), 2.16 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 193.0, 159.3, 146.5, 142.5, 141.5,

140.3, 139.2, 139.0, 134.9, 133.4, 132.4, 131.4, 131.1, 130.2, 129.72, 129.66, 129.4, 129.3,

128.8, 128.6, 128.0, 127.0, 126.5, 125.71, 125.67, 125.5, 124.9, 124.2, 121.6, 114.4, 76.3,

21.7. HRMS (ESI) calcd for C₃₂H₂₁NNaO₂ [M + Na]⁺ 474.1464, found 474.1456.



7'-Bromo-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-di

one (3ae): Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (37 mg, 36%),

mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 10.0 Hz, 1H),

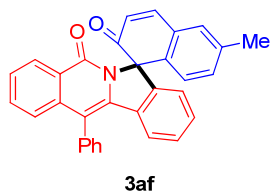
7.68-7.58 (m, 5H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.50-7.44 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31

(d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H),

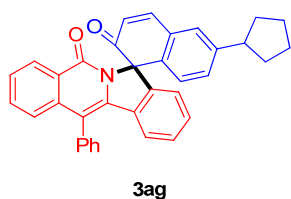
6.95 (d, *J* = 1.2 Hz, 1H), 6.52-6.48 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 192.0, 159.4,

145.2, 142.3, 141.6, 139.2, 138.6, 134.7, 133.5, 132.6, 131.8, 131.31, 131.28, 131.2, 129.8,

129.7, 129.4, 129.2, 128.7, 128.5, 128.3, 127.9, 126.8, 125.69, 125.66, 125.6, 125.5, 125.1, 121.6, 114.9, 75.7. HRMS (ESI) calcd for C₃₁H₁₈BrNNaO₂ [M + Na]⁺ 538.0413, found 538.0416.

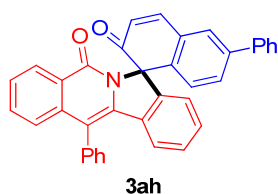


6'-Methyl-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3af): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (51 mg, 56%), mp 198-199 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 10.2 Hz, 1H), 7.64-7.53 (m, 6H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.04-6.99 (m, 3H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.49-6.46 (m, 2H), 2.32 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.2, 159.3, 146.5, 142.7, 139.1, 138.9, 138.2, 137.4, 135.0, 133.5, 132.4, 131.7, 131.4, 131.1, 130.8, 129.8, 129.7, 129.4, 128.8, 128.6, 127.9, 126.5, 125.6, 125.5, 125.3, 125.1, 124.9, 121.6, 114.5, 76.0, 21.0 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₃₂H₂₁NNaO₂ [M + Na]⁺ 474.1464, found 474.1457.



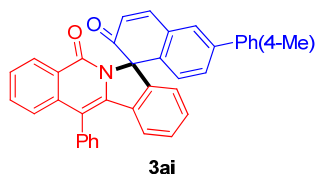
6'-Cyclopentyl-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ag): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (63 mg, 63%), mp 272-273 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 10.2 Hz, 1H), 7.64-7.53 (m, 6H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 1.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H),

7.13 (t, $J = 7.2$ Hz, 1H), 7.06-7.01 (m, 3H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.48 (d, $J = 10.2$ Hz, 1H), 6.46 (d, $J = 7.8$ Hz, 1H), 2.98-2.92 (m, 1H), 2.06-2.02 (m, 2H), 1.81-1.75 (m, 2H), 1.70-1.63 (m, 2H), 1.58-1.51 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 193.2, 159.3, 146.8, 146.7, 142.7, 139.1, 139.0, 137.6, 135.0, 133.4, 132.4, 131.4, 131.1, 129.9, 129.7, 129.6, 129.4, 129.3, 129.0, 128.7, 128.6, 127.9, 126.5, 125.6, 125.5, 125.1, 125.0, 124.9, 121.7, 114.5, 76.0, 45.4, 34.40, 34.35, 25.4. HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{27}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 528.1934, found 528.1904.

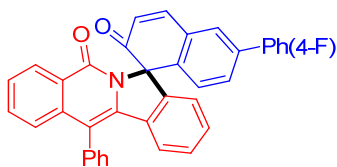


6',12-Diphenyl-2'H,5H-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione

(3ah): Dichloromethane/ethyl acetate (45:1) as eluent; grey solid (51 mg, 49%), mp >300 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.39 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 9.6$ Hz, 1H), 7.69 (s, 1H), 7.66-7.56 (m, 6H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.47-7.39 (m, 4H), 7.36 (t, $J = 7.2$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.8$ Hz, 1H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.55 (d, $J = 10.2$ Hz, 1H), 6.49 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.9, 159.3, 146.3, 142.4, 141.6, 139.9, 139.2, 139.1, 138.9, 134.9, 133.5, 132.5, 131.4, 131.1, 129.9, 129.8, 129.7, 129.6, 129.4, 128.93, 128.86, 128.7, 127.9, 127.8, 127.1, 126.7, 125.71, 125.68, 125.6, 125.0, 121.7, 114.6, 76.0. HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{23}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 536.1621, found 536.1603.



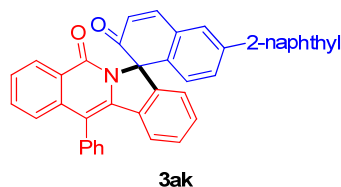
12-Phenyl-6'-(*p*-tolyl)-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ai): Dichloromethane/ethyl acetate (30:1) as eluent; yellow solid (63 mg, 60%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.39 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.81 (d, *J* = 10.0 Hz, 1H), 7.66-7.54 (m, 7H), 7.46-7.41 (m, 3H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (td, *J* = 8.0, 0.8 Hz, 1H), 7.10-7.02 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 10.0 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 193.0, 159.3, 146.5, 142.5, 141.5, 139.2, 138.9, 138.8, 137.7, 137.0, 134.9, 133.5, 132.5, 131.4, 131.1, 129.9, 129.8, 129.7, 129.43, 129.40, 128.9, 128.67, 128.66, 127.9, 126.9, 126.6, 125.7, 125.61, 125.58, 125.0, 121.7, 114.6, 76.0, 21.2. HRMS (ESI) calcd for C₃₈H₂₅NNaO₂ [M + Na]⁺ 550.1777, found 550.1756.



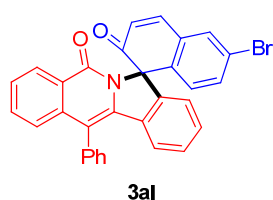
3aj

6'-(4-Fluorophenyl)-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3aj): Dichloromethane/ethyl acetate (30:1) as eluent; grey solid (54 mg, 51%), mp >300 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 10.2 Hz, 1H), 7.66-7.55 (m, 7H), 7.50-7.45 (m, 3H), 7.34 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.13-7.05 (m, 4H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 10.2 Hz, 1H), 6.49 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.8, 162.8 (d, *J* = 246.2 Hz, 1C), 159.3, 146.1, 142.3, 140.6, 139.2, 138.8, 136.0 (d, *J* = 3.3 Hz, 1C), 134.8, 133.5, 132.5, 131.4, 131.1, 129.9, 129.8, 129.7, 129.41, 129.40, 129.0, 128.75, 128.70, 128.67, 127.9, 126.7, 125.8 (d, *J* = 7.7 Hz, 2C), 125.60, 125.57, 125.0, 121.7, 115.9 (d, *J* = 20.7 Hz, 2C), 114.7, 75.9. ¹⁹F

NMR (CDCl₃, 376 MHz) δ -114.63– -114.70 (m). HRMS (ESI) calcd for C₃₇H₂₂FNNaO₂ [M + Na]⁺ 554.1527, found 554.1500.

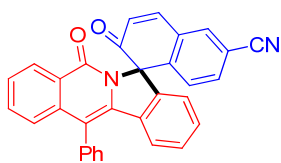


6'-(Naphthalen-2-yl)-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3ak): Dichloromethane/ethyl acetate (45:1) as eluent; white solid (83 mg, 73%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.41 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.90-7.84 (m, 4H), 7.80 (s, 1H), 7.66-7.56 (m, 7H), 7.51-7.43 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.18-7.10 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 10.0 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 192.9, 159.4, 146.4, 142.4, 141.5, 139.20, 139.18, 138.9, 137.2, 134.9, 133.6, 133.5, 132.8, 132.5, 131.4, 131.1, 130.0, 129.9, 129.8, 129.7, 129.4, 129.1, 129.0, 128.70, 128.67, 128.3, 127.9, 127.7, 126.7, 126.5, 126.3, 126.0, 125.79, 125.76, 125.6, 125.2, 125.0, 121.7, 114.7, 76.0 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₄₁H₂₅NNaO₂ [M + Na]⁺ 586.1777, found 586.1739.



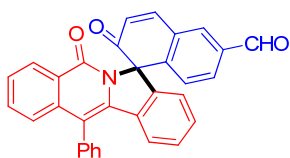
6'-Bromo-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (3al): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (44 mg, 43%), mp 190-191 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.36 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 10.2 Hz, 1H), 7.64-7.57 (m, 5H), 7.55-7.53 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.31-7.28 (m, 2H), 7.15 (t, *J* =

7.8 Hz, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 7.03 (d, $J = 7.8$ Hz, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 6.53 (d, $J = 10.2$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.3, 159.3, 144.6, 141.8, 139.3, 139.1, 138.6, 134.7, 133.6, 133.5, 132.6, 131.3, 131.0, 129.9, 129.7, 129.4, 129.1, 128.7, 127.9, 126.9, 126.8, 126.5, 125.6, 125.5, 125.0, 122.2, 121.6, 114.8, 75.7. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{18}\text{BrNNaO}_2$ $[\text{M} + \text{Na}]^+$ 538.0413, found 538.0407.



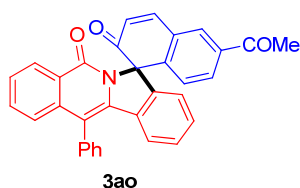
3am

2',5-Dioxo-12-phenyl-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-6'-carbonitrile (3am): Dichloromethane/ethyl acetate (30:1) as eluent; grey solid (38 mg, 41%), mp >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.35 (d, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 1.2$ Hz, 1H), 7.75 (d, $J = 10.0$ Hz, 1H), 7.67-7.59 (m, 4H), 7.56-7.53 (m, 2H), 7.50-7.46 (m, 2H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.17 (t, $J = 7.2$ Hz, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.62 (d, $J = 10.0$ Hz, 1H), 6.50 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 191.4, 159.3, 145.2, 143.7, 140.9, 139.1, 138.3, 134.5, 133.8, 133.7, 133.1, 132.8, 131.2, 130.9, 130.6, 130.0, 129.8, 129.5, 128.8, 127.8, 127.3, 127.0, 126.2, 125.8, 125.3, 125.2, 121.5, 117.7, 115.2, 112.7, 75.7 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{18}\text{N}_2\text{NaO}_2$ $[\text{M} + \text{Na}]^+$ 485.1260, found 485.1233.

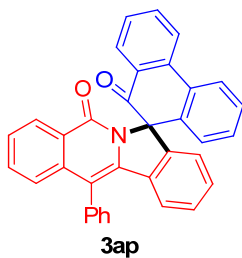


3an

2',5-Dioxo-12-phenyl-2'H,5H-spiro[isoidolo[2,1-b]isoquinoline-7,1'-naphthalene]-6'-carbaldehyde (3an): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (35 mg, 38%), mp >300 °C. ¹H NMR (CDCl₃, 600 MHz) δ 10.00 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 10.2 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.66-7.59 (m, 4H), 7.57-7.55 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 3.6 Hz, 1H), 7.04 (d, *J* = 3.6 Hz, 1H), 6.61 (d, *J* = 10.2 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 191.8, 190.8, 159.3, 146.5, 144.9, 141.2, 139.1, 138.5, 136.3, 134.6, 133.6, 132.7, 131.7, 131.3, 131.0, 130.7, 130.3, 129.9, 129.7, 129.4, 129.3, 128.7, 127.8, 126.9, 126.6, 126.0, 125.7, 125.4, 125.1, 121.5, 115.0, 76.0. HRMS (ESI) calcd for C₃₂H₁₉NNaO₃ [M + Na]⁺ 488.1257, found 488.1244.

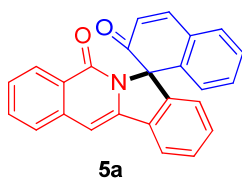


6'-Acetyl-12-phenyl-2'H,5H-spiro[isoidolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (3ao): Dichloromethane/ethyl acetate (30:1) as eluent; white solid (65 mg, 68%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.36 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.09 (d, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 10.0 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67-7.54 (m, 6H), 7.47 (td, *J* = 8.0, 0.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 7.09-7.03 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 10.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 2.58 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 196.7, 192.1, 159.3, 145.4, 145.1, 141.5, 139.1, 138.6, 137.1, 134.7, 133.6, 132.6, 131.3, 131.0, 130.5, 129.9, 129.84, 129.77, 129.7, 129.4, 129.2, 128.7, 127.9, 126.8, 126.3, 125.7, 125.6, 125.4, 125.1, 121.5, 114.9, 76.0, 26.6. HRMS (ESI) calcd for C₃₃H₂₁NNaO₃ [M + Na]⁺ 502.1414, found 502.1402.



12-Phenyl-5H,10'H-spiro[isoindolo[2,1-b]isoquinoline-7,9'-phenanthrene]-5,10'-dione

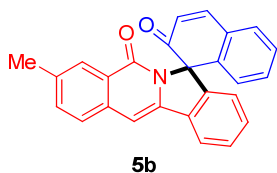
(3ap): Dichloromethane/ethyl acetate (100:1) as eluent; white solid (46 mg, 47%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.39 (d, *J* = 7.2 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.16-8.13 (m, 2H), 7.80 (td, *J* = 8.4, 0.8 Hz, 1H), 7.66-7.55 (m, 6H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.39 (td, *J* = 8.0, 0.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.04-6.98 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.84-6.82 (m, 1H), 6.47-6.45 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 191.2, 159.4, 142.6, 139.2, 138.9, 137.9, 137.3, 135.5, 135.0, 133.3, 132.4, 131.4, 131.2, 129.8, 129.69, 129.67, 129.45, 129.43, 129.38, 128.92, 128.85, 128.6, 128.5, 128.0, 126.6, 125.7, 125.5, 125.3, 124.9, 124.5, 123.6, 121.9, 114.7, 76.9 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₃₅H₂₁NNaO₂ [M + Na]⁺ 510.1464, found 510.1462.



2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (5a):

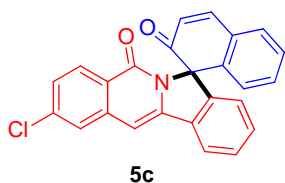
Dichloromethane/ethyl acetate (30:1) as eluent; brown solid (50 mg, 69%), mp >300 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 10.2 Hz, 1H), 7.69-7.65 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 6.6 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H),

7.10-7.09 (m, 2H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.48 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.7, 159.6, 146.5, 142.6, 142.2, 139.9, 138.2, 133.2, 132.6, 130.9, 130.4, 130.1, 129.5, 129.3, 128.5, 128.0, 126.7, 126.6, 126.1, 125.2, 122.0, 121.9, 98.5, 76.6 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{15}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 384.0995, found 384.0982.



3-Methyl-2'H,5H-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (5b):

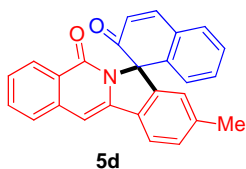
Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (41 mg, 54%), mp >300 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.11 (s, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.75 (d, $J = 9.6$ Hz, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.50-7.47 (m, 2H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 7.2$ Hz, 1H), 7.25 (t, $J = 7.2$ Hz, 1H), 7.16-7.14 (m, 1H), 7.09 (d, $J = 7.8$ Hz, 1H), 7.07 (s, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.48 (d, $J = 10.2$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.8, 159.5, 146.4, 142.1, 141.7, 140.1, 136.8, 135.8, 134.1, 133.3, 130.9, 130.10, 130.07, 129.5, 129.3, 128.4, 127.7, 126.7, 126.1, 125.2, 121.9, 121.8, 98.5, 76.5, 21.5 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 398.1151, found 398.1136.



2-Chloro-2'H,5H-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (5c):

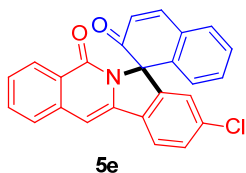
Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (52 mg, 65%), mp >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.21 (d, $J = 8.8$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J =$

10.0 Hz, 1H), 7.63 (d, $J = 2.0$ Hz, 1H), 7.49 (d, $J = 7.2$ Hz, 1H), 7.41 (td, $J = 7.6, 0.8$ Hz, 1H), 7.36 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.33-7.26 (m, 2H), 7.17 (td, $J = 7.6, 1.2$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.00 (s, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 6.49 (d, $J = 10.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 192.5, 159.0, 146.6, 144.0, 142.3, 139.6, 139.5, 139.1, 132.7, 131.0, 130.8, 130.2, 129.7, 129.4, 128.6, 127.0, 125.9, 125.1, 124.4, 122.2, 121.9, 97.4, 77.3 (two ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{14}\text{ClNNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 418.0605, found 418.0589.



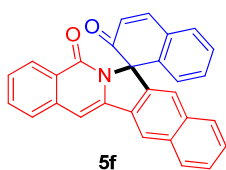
9-Methyl-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (5d):

Dichloromethane/ethyl acetate (45:1) as eluent; yellow solid (55 mg, 73%), mp >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.29 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 10.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.64-7.63 (m, 2H), 7.48 (d, $J = 7.2$ Hz, 1H), 7.42-7.38 (m, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.02 (s, 1H), 6.87 (s, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 6.48 (d, $J = 10.0$ Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 192.9, 159.6, 146.5, 142.8, 142.5, 141.0, 140.1, 138.3, 132.6, 130.9, 130.5, 130.4, 130.1, 129.5, 128.4, 128.0, 126.6, 126.3, 125.9, 125.3, 125.2, 122.2, 121.8, 97.9, 76.4, 21.8. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NNaO}_2$ [$\text{M} + \text{Na}$] $^+$ 398.1151, found 398.1142.



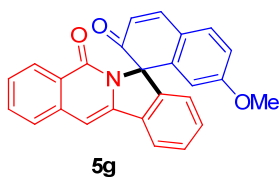
9-Chloro-2'*H*,5*H*-spiro[isindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (5e):

Dichloromethane/ethyl acetate (45:1) as eluent; yellow solid (58 mg, 73%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.30-8.28 (m, 1H), 7.78 (d, *J* = 10.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.67-7.66 (m, 2H), 7.50 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.47-7.43 (m, 1H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.33 (td, *J* = 7.2, 1.2 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (s, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 192.2, 159.5, 146.7, 143.4, 141.5, 139.2, 138.0, 136.1, 132.8, 131.7, 131.1, 130.4, 129.9, 129.4, 128.8, 128.0, 126.8, 126.1, 125.2, 125.0, 123.1, 122.4, 98.9, 76.1 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₂₅H₁₄ClNNaO₂ [M + Na]⁺ 418.0605, found 418.0598.



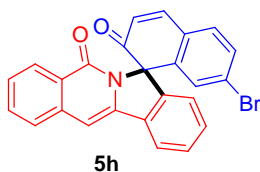
2'*H*,5*H*-Spiro[benzo[5,6]isindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (5f):

Dichloromethane/ethyl acetate (45:1) as eluent; yellow solid (43 mg, 52%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.33-8.31 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 10.0 Hz, 1H), 7.73-7.66 (m, 3H), 7.54-7.43 (m, 5H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 (s, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 10.0 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.9, 159.7, 146.6, 142.2, 140.9, 139.0, 138.2, 134.2, 133.6, 132.7, 131.1, 130.9, 130.2, 129.3, 128.6, 128.42, 128.35, 128.1, 127.3, 127.1, 126.8, 126.7, 126.3, 125.3, 125.0, 121.4, 121.1, 98.9, 76.0. HRMS (ESI) calcd for C₂₉H₁₇NNaO₂ [M + Na]⁺ 434.1151, found 434.1135.



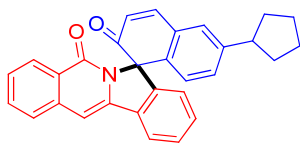
7'-Methoxy-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (5g):

Dichloromethane/ethyl acetate (45:1) as eluent; brown solid (35 mg, 44%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.32 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 10.0 Hz, 1H), 7.69-7.67 (m, 2H), 7.46-7.40 (m, 3H), 7.30-7.26 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 6.80 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 3.61 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.6, 161.8, 159.6, 146.5, 142.6, 142.3, 142.2, 138.2, 133.0, 132.6, 131.9, 130.3, 129.3, 128.1, 126.7, 126.6, 126.1, 122.8, 122.5, 122.0, 121.9, 112.6, 112.3, 98.5, 76.7, 55.3. HRMS (ESI) calcd for C₂₆H₁₇NNaO₃ [M + Na]⁺ 414.1101, found 414.1093.



7'-Bromo-2'H,5H-spiro[isoindolo[2,1-b]isoquinoline-7,1'-naphthalene]-2',5-dione (5h):

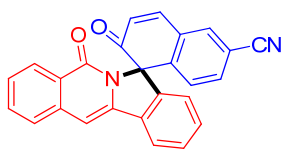
Dichloromethane/ethyl acetate (45:1) as eluent; yellow solid (37 mg, 42%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.71-7.68 (m, 3H), 7.47-7.42 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 1.2 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 191.8, 159.7, 145.3, 142.3, 141.8, 141.5, 138.2, 133.2, 132.8, 131.8, 131.3, 130.5, 129.6, 128.43, 128.39, 128.0, 126.9, 126.8, 126.0, 125.7, 125.5, 122.2, 121.9, 98.9, 76.0. HRMS (ESI) calcd for C₂₅H₁₄BrNNaO₂ [M + Na]⁺ 462.0100, found 462.0104.



5i

6'-Cyclopentyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione

(5i): Dichloromethane/ethyl acetate (100:1) as eluent; brown solid (30 mg, 34%), mp 164-165 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.68-7.63 (m, 2H), 7.44-7.38 (m, 2H), 7.32 (d, *J* = 1.2 Hz, 1H), 7.28-7.25 (m, 1H), 7.10-7.08 (m, 2H), 7.02 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 2.98-2.89 (m, 1H), 2.06-2.01 (m, 2H), 1.83-1.75 (m, 2H), 1.71-1.63 (m, 2H), 1.55-1.48 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 193.0, 159.6, 147.0, 146.8, 142.7, 142.5, 138.2, 137.0, 133.1, 132.6, 130.3, 129.9, 129.24, 129.20, 129.0, 128.0, 126.7, 126.5, 126.1, 125.1, 125.0, 122.0, 121.9, 98.4, 76.5, 45.4, 34.4, 34.3, 25.4. HRMS (ESI) calcd for C₃₀H₂₃NNaO₂ [M + Na]⁺ 452.1621, found 452.1603.

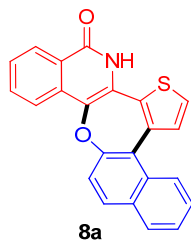


5j

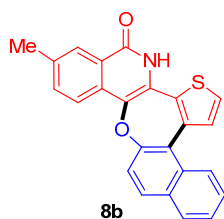
2',5-Dioxo-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-6'-carbonitrile

(5j): Dichloromethane/ethyl acetate (45:1) as eluent; yellow solid (27 mg, 34%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.78 (s, 1H), 7.74 (d, *J* = 10.4 Hz, 1H), 7.70 (d, *J* = 3.6 Hz, 2H), 7.49-7.42 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 191.2, 159.6, 144.7, 143.8, 142.1, 140.7, 138.1, 133.8, 133.3, 133.1, 133.0, 130.6, 130.5, 129.9, 128.0, 127.2, 126.98, 126.96, 126.2, 125.8, 122.3, 121.8,

117.7, 112.7, 99.1, 76.1. HRMS (ESI) calcd for C₂₆H₁₄N₂NaO₂ [M + Na]⁺ 409.0947, found 409.0941.

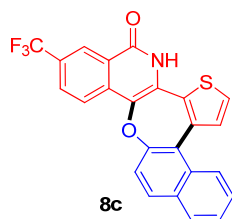


Naphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8a): Petroleum ether/ethyl acetate (3:1) as eluent; yellow solid (32 mg, 43%), mp >300 °C. ¹H NMR (DMSO-*d*₆, 600 MHz) δ 11.75 (s, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.08-8.06 (m, 2H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.94-7.91 (m, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 5.4 Hz, 1H), 7.64-7.60 (m, 2H), 7.56-7.54 (m, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 161.4, 158.0, 137.1, 136.6, 133.8, 133.2, 132.6, 132.0, 131.3, 131.2, 130.4, 129.1, 128.2, 128.0, 126.1, 125.8, 125.4, 123.4, 122.0, 121.3 (three ¹³C signals were not observed). HRMS (ESI) calcd for C₂₃H₁₃NNaO₂S [M + Na]⁺ 390.0559, found 390.0546.

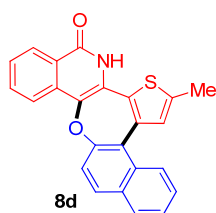


10-Methylnaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8b): Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (25 mg, 33%), mp 257-258 °C. ¹H NMR (DMSO-*d*₆, 600 MHz) δ 11.66 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 8.07-8.05 (m, 3H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.70 (d, *J* = 5.4 Hz, 1H), 7.62-7.59 (m, 1H), 7.56-7.53 (m, 1H), 2.49 (s, 3H); ¹³C

NMR (DMSO-*d*₆, 100 MHz) δ 161.3, 158.0, 137.9, 136.8, 135.1, 132.0, 131.3, 131.1, 130.9, 130.4, 129.1, 128.00, 127.95, 127.6, 126.1, 125.4, 123.4, 122.1, 121.3, 21.5 (four ¹³C signals were not observed). HRMS (ESI) calcd for C₂₄H₁₅NNaO₂S [M + Na]⁺ 404.0716, found 404.0714.

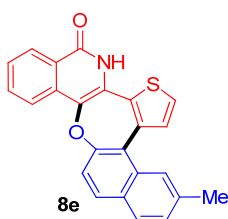


10-(Trifluoromethyl)naphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-*c*]isoquinolin-12(13*H*)-one (8c): Petroleum ether/ethyl acetate (5:1) as eluent; yellow solid (26 mg, 30%), mp 267-268 °C. ¹H NMR (DMSO-*d*₆, 600 MHz) δ 12.12 (s, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.46 (s, 1H), 8.17-8.13 (m, 3H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 5.4 Hz, 1H), 7.63-7.61 (m, 1H), 7.56 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 150 MHz) δ 160.8, 157.8, 137.9, 136.0, 132.1, 131.4, 131.3, 130.6, 129.6, 129.2, 129.1, 128.1, 127.7, 127.5, 126.2, 125.4, 125.3, 125.1, 123.6, 123.5, 123.2, 121.1; ¹⁹F NMR (DMSO-*d*₆, 564 MHz) δ -60.99 (s). HRMS (ESI) calcd for C₂₄H₁₂F₃NNaO₂S [M + Na]⁺ 458.0433, found 458.0431.



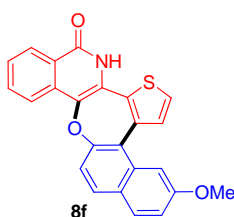
15-Methylnaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-*c*]isoquinolin-12(13*H*)-one (8d): Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (29 mg, 38%), mp 125-126 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.62 (s, 1H), 8.39 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H),

8.21 (d, $J = 8.4$ Hz, 1H), 7.88-7.81 (m, 3H), 7.58-7.45 (m, 4H), 7.34 (d, $J = 0.8$ Hz, 1H), 2.70 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 161.5, 157.8, 140.8, 137.8, 136.8, 133.7, 133.3, 131.9, 131.6, 130.5, 129.5, 129.3, 128.5, 128.4, 127.3, 127.1, 125.6, 125.5, 125.3, 123.5, 121.4, 120.9, 15.8 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{15}\text{NNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 404.0716, found 404.0717.



2-Methylnaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8e):

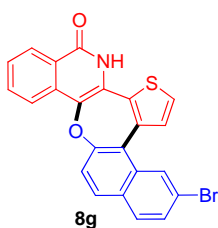
Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (22 mg, 29%), mp 119-120 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.94 (s, 1H), 8.43 (d, $J = 7.6$ Hz, 1H), 8.31 (d, $J = 8.0$ Hz, 1H), 7.97 (s, 1H), 7.86-7.81 (m, 2H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.68 (m, 2H), 7.58-7.54 (m, 1H), 7.51 (d, $J = 8.8$ Hz, 1H), 7.30 (dd, $J = 8.0, 0.8$ Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$, 150 MHz) δ 161.4, 158.2, 137.5, 137.3, 133.8, 133.2, 131.6, 130.9, 130.4, 130.2, 130.1, 129.0, 128.24, 128.21, 128.0, 124.4, 122.7, 122.0, 120.3, 22.2 (four ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{15}\text{NNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 404.0716, found 404.0718.



2-Methoxynaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8f):

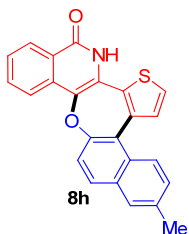
Petroleum ether/ethyl acetate (2:1) as eluent; brown solid (30 mg, 38%), mp 107-108 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.95 (s, 1H), 8.43 (d, $J = 7.2$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H),

7.87-7.82 (m, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 5.2$ Hz, 1H), 7.68 (d, $J = 5.2$ Hz, 1H), 7.59-7.53 (m, 2H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.13 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (DMSO- d_6 , 150 MHz) δ 161.4, 158.9, 158.8, 137.4, 133.8, 133.2, 132.9, 130.9, 130.8, 129.9, 128.4, 128.0, 127.4, 122.4, 122.0, 118.7, 118.3, 104.4, 55.5 (five ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{15}\text{NNaO}_3\text{S}$ $[\text{M} + \text{Na}]^+$ 420.0665, found 420.0657.



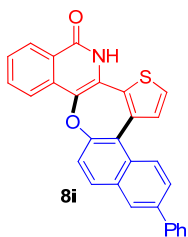
2-Bromonaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8g):

Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (37 mg, 41%), mp 151-152 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 10.27 (s, 1H), 8.44 (d, $J = 7.8$ Hz, 1H), 8.35 (s, 1H), 8.29 (d, $J = 8.4$ Hz, 1H), 7.86-7.82 (m, 2H), 7.72-7.71 (m, 2H), 7.63 (d, $J = 5.4$ Hz, 1H), 7.60-7.56 (m, 2H), 7.54 (dd, $J = 9.0, 1.8$ Hz, 1H); ^{13}C NMR (DMSO- d_6 , 150 MHz) δ 161.4, 158.7, 136.3, 133.8, 133.1, 132.6, 131.34, 131.29, 130.5, 130.0, 129.1, 128.8, 128.1, 128.0, 127.3, 122.8, 122.0, 121.7 (five ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{12}\text{BrNNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 467.9664, found 467.9662.



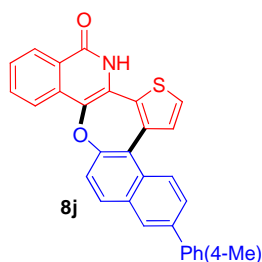
3-Methylnaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13*H*)-one (8h):

Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (36 mg, 47%), mp 145-146 °C. ¹H NMR (CDCl₃, 400 MHz) δ 10.59 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.66-7.62 (m, 2H), 7.60 (s, 1H), 7.57-7.52 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.4, 157.4, 137.8, 137.6, 135.1, 133.8, 133.2, 132.2, 131.9, 130.7, 129.8, 129.4, 128.3, 127.5, 127.4, 126.0, 125.63, 125.58, 125.4, 123.3, 121.5, 120.7, 21.3 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₂₄H₁₅NNaO₂S [M + Na]⁺ 404.0716, found 404.0712.



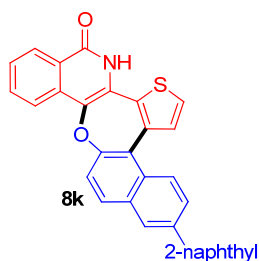
3-Phenylnaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13*H*)-one (8i):

Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (21 mg, 23%), mp 264-265 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.75 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 1.2 Hz, 1H), 8.23 (t, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 9.2 Hz, 1H), 8.09 (d, *J* = 5.2 Hz, 1H), 7.96-7.91 (m, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 5.2 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 161.4, 158.0, 139.7, 137.5, 137.0, 133.9, 133.2, 132.4, 131.6, 130.5, 130.4, 129.6, 128.4, 128.3, 128.0, 127.3, 126.9, 126.4, 126.2, 123.3, 122.0, 121.8 (five ¹³C signals were not observed). HRMS (ESI) calcd for C₂₉H₁₇NNaO₂S [M + Na]⁺ 466.0872, found 466.0867.



3-(4-Methylphenyl)naphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8j):

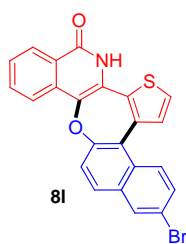
Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (31 mg, 34%), mp 136-137 °C. ¹H NMR (DMSO-*d*₆, 600 MHz) δ 11.78 (s, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 8.30 (s, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 8.09 (d, *J* = 5.4 Hz, 1H), 7.95-7.90 (m, 2H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 5.4 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (DMSO-*d*₆, 150 MHz) δ 161.4, 157.9, 137.6, 137.4, 137.1, 136.8, 133.8, 133.2, 132.4, 131.5, 130.37, 130.35, 130.1, 128.3, 128.0, 127.1, 126.8, 126.2, 125.9, 123.3, 122.0, 121.7, 21.2 (five ¹³C signals were not observed). HRMS (ESI) calcd for C₃₀H₁₉NNaO₂S [M + Na]⁺ 480.1029, found 480.1012.



3-(Naphthalen-2-yl)naphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8k):

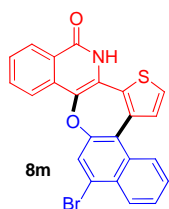
Petroleum ether/ethyl acetate (3:1) as eluent; yellow solid (34 mg, 34%), mp 143-144 °C. ¹H NMR (DMSO-*d*₆, 600 MHz) δ 11.78 (s, 1H), 8.48 (d, *J* = 1.2 Hz, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 8.37 (s, 1H), 8.27-8.23 (m, 2H), 8.17 (d, *J* = 9.0 Hz, 1H), 8.10-8.07 (m, 2H), 8.03 (t, *J* = 8.4 Hz, 2H), 7.99 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.96-7.92 (m, 2H), 7.87 (d, *J* = 9.0 Hz,

1H), 7.75 (d, $J = 4.8$ Hz, 1H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.57-7.52 (m, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 161.4, 158.1, 137.2, 137.04, 136.99, 133.8, 133.2, 132.9, 132.5, 131.6, 130.6, 130.4, 129.1, 128.7, 128.4, 128.0, 127.03, 127.01, 126.8, 126.7, 126.3, 126.0, 125.5, 123.4, 122.0, 121.8 (seven ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{20}\text{NO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 494.1209, found 494.1190.



3-Bromonaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8l):

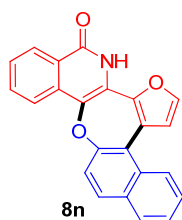
Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (28 mg, 32%), mp 124-125 °C. ^1H NMR (DMSO- d_6 , 400 MHz) δ 11.75 (s, 1H), 8.42 (d, $J = 8.4$ Hz, 1H), 8.32 (d, $J = 2.0$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 8.09-8.05 (m, 3H), 7.94-7.89 (m, 2H), 7.71 (dd, $J = 9.2, 2.4$ Hz, 1H), 7.68 (d, $J = 5.2$ Hz, 1H), 7.63 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (DMSO- d_6 , 150 MHz) δ 161.4, 158.2, 136.51, 136.47, 133.8, 133.3, 133.1, 130.81, 130.79, 130.4, 130.3, 130.0, 128.5, 128.1, 128.0, 127.95, 127.89, 123.8, 122.6, 122.0, 119.3 (two ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{12}\text{BrNNaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 467.9664, found 467.9669.



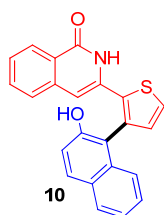
5-Bromonaphtho[1',2':6,7]thieno[2',3':4,5]oxepino[3,2-c]isoquinolin-12(13H)-one (8m):

Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (36 mg, 40%), mp 106-107 °C. ^1H NMR (DMSO- d_6 , 400 MHz) δ 11.80 (s, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.34 (s, 1H), 8.25 (d, J

= 7.6 Hz, 1H), 8.22-8.17 (m, 2H), 8.10 (d, $J = 4.8$ Hz, 1H), 7.96-7.92 (m, 1H), 7.72-7.68 (m, 3H), 7.66-7.62 (m, 1H); ^{13}C NMR (DMSO- d_6 , 150 MHz) δ 161.4, 157.1, 136.3, 133.9, 133.0, 131.9, 130.5, 130.1, 128.9, 128.6, 128.1, 128.0, 127.9, 127.5, 126.4, 125.3, 123.9, 123.8, 122.2 (four ^{13}C signals were not observed). HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{12}\text{BrNNaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 467.9664, found 467.9669.

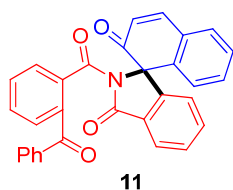


Furo[2',3':4,5]naphtho[1',2':6,7]oxepino[3,2-*c*]isoquinolin-12(13*H*)-one (8n): Petroleum ether/ethyl acetate (2:1) as eluent; yellow solid (25 mg, 35%), mp >300 °C. ^1H NMR (DMSO- d_6 , 400 MHz) δ 11.83 (s, 1H), 8.43 (d, $J = 8.0$ Hz, 1H), 8.33-8.24 (m, 3H), 8.08 (d, $J = 8.8$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.94-7.90 (m, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.66-7.62 (m, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (DMSO- d_6 , 150 MHz) δ 161.0, 155.6, 145.2, 144.4, 134.9, 133.8, 133.3, 131.9, 131.3, 131.0, 129.2, 128.2, 128.13, 128.08, 126.3, 126.2, 125.1, 122.7, 122.6, 122.1, 121.6, 120.4, 113.6. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{14}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 352.0968, found 352.0970.

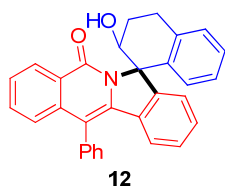


3-(3-(2-Hydroxynaphthalen-1-yl)thiophen-2-yl)isoquinolin-1(2*H*)-one (10): Petroleum ether/ethyl acetate (3:1) as eluent; brown solid (24 mg, 32%), mp 171-172 °C. ^1H NMR (DMSO- d_6 , 600 MHz) δ 10.68 (s, 1H), 10.22 (s, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 4.8$

Hz, 1H), 7.83 (d, $J = 9.0$ Hz, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.60-7.57 (m, 1H), 7.40-7.38 (m, 2H), 7.34-7.25 (m, 4H), 7.07 (d, $J = 4.8$ Hz, 1H), 6.48 (s, 1H); ^{13}C NMR (DMSO- d_6 , 150 MHz) δ 162.1, 152.9, 137.8, 135.4, 134.7, 134.1, 133.4, 133.2, 132.4, 130.2, 128.5, 128.4, 127.11, 127.07, 127.0, 126.9, 125.0, 124.3, 123.4, 118.6, 115.3, 105.2 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{15}\text{NNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 392.0716, found 392.0710.

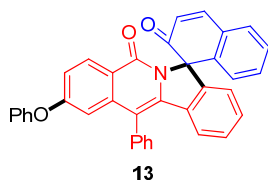


2-(2-Benzoylbenzoyl)-2'*H*-spiro[isoindoline-1,1'-naphthalene]-2',3-dione (11): Petroleum ether/ethyl acetate (3:1) as eluent; white solid (84 mg, 89%), mp 138-139 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 7.88 (d, $J = 7.2$ Hz, 2H), 7.79 (d, $J = 7.2$ Hz, 1H), 7.70 (d, $J = 9.6$ Hz, 1H), 7.65-7.62 (m, 3H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.53-7.50 (m, 1H), 7.47-7.37 (m, 5H), 7.33-7.29 (m, 3H), 7.08 (d, $J = 7.8$ Hz, 1H), 6.37 (d, $J = 9.6$ Hz, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 195.5, 192.4, 168.3, 167.0, 147.1, 145.0, 139.7, 137.4, 137.2, 136.7, 134.7, 132.5, 131.5, 131.1, 130.41, 130.39, 130.3, 129.5, 129.3, 129.04, 129.01, 128.45, 128.39, 128.3, 126.3, 125.9, 124.3, 121.6, 73.5. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{19}\text{NNaO}_4$ $[\text{M} + \text{Na}]^+$ 492.1206, found 492.1195.

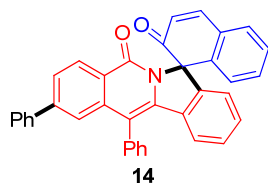


2'-Hydroxy-12-phenyl-3',4'-dihydro-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalen]-5-one (12): Petroleum ether/ethyl acetate (5:1) as eluent; white solid (63 mg, 71%), mp >300 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.41 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.66-7.61 (m, 3H),

7.59-7.56 (m, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.47-7.43 (m, 2H), 7.30 (d, $J = 7.8$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.21-7.17 (m, 2H), 7.05 (d, $J = 7.8$ Hz, 1H), 7.03-7.01 (m, 1H), 6.97 (t, $J = 7.8$ Hz, 1H), 6.61 (d, $J = 7.2$ Hz, 1H), 6.36 (d, $J = 8.4$ Hz, 1H), 5.60 (d, $J = 7.8$ Hz, 1H), 4.30-4.28 (m, 1H), 3.54-3.49 (m, 1H), 2.98 (dt, $J = 16.8, 4.8$ Hz, 1H), 2.53-2.48 (m, 1H), 2.41-2.36 (m, 1H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 163.4, 148.0, 138.7, 138.5, 137.1, 135.2, 134.3, 132.6, 131.8, 131.3, 130.8, 129.8, 129.6, 129.5, 129.1, 128.7, 128.20, 128.17, 127.6, 126.7, 126.2, 125.3, 125.2, 124.0, 123.8, 115.9, 76.7, 76.0, 28.7, 24.3 (one ^{13}C signal was not observed). HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{23}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 464.1621, found 464.1605.



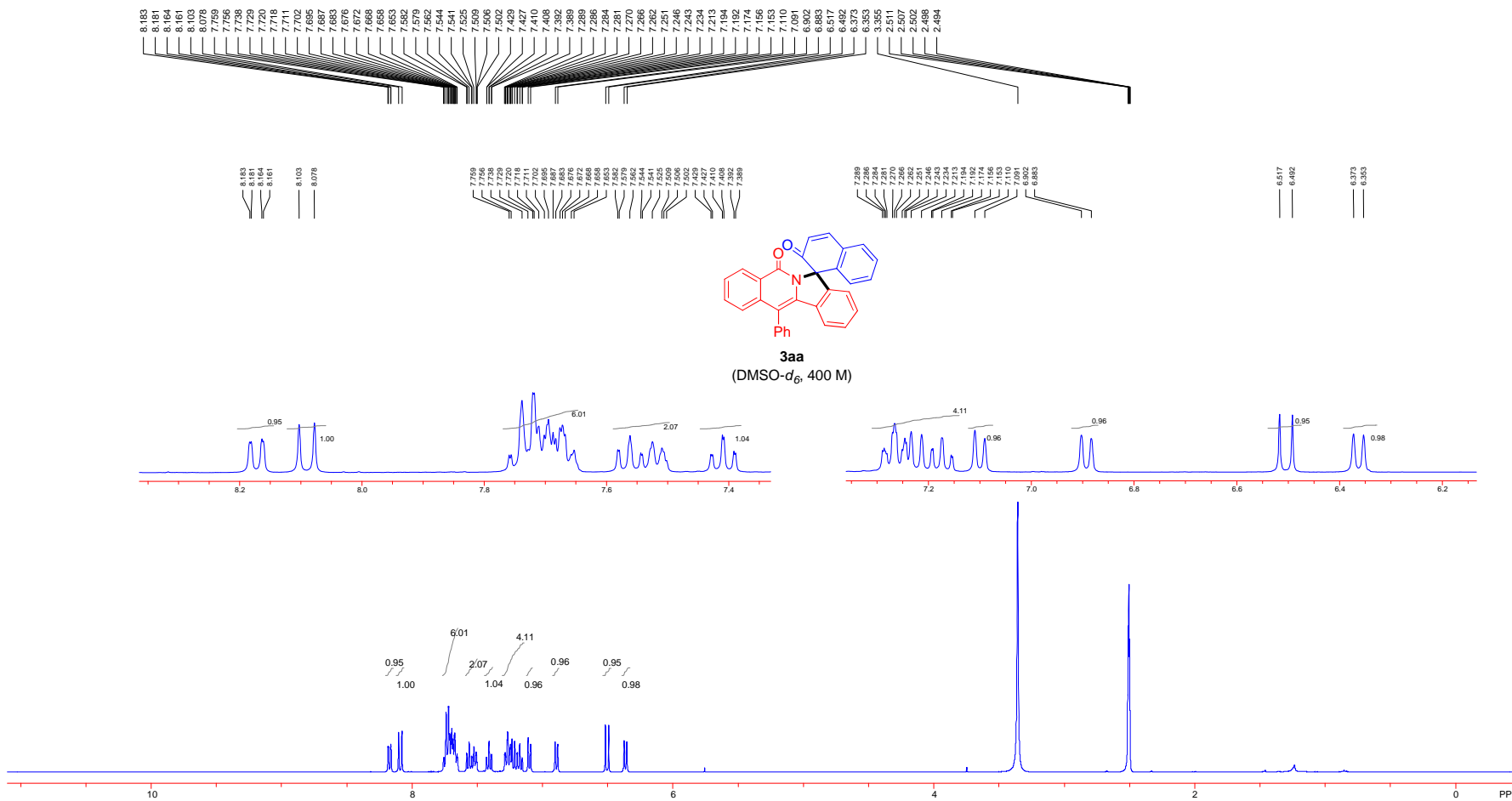
2-Phenoxy-12-phenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione (13): Petroleum ether/ethyl acetate (2:1) as eluent; yellow solid (34 mg, 64%), mp 170-171 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.23 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 10.0$ Hz, 1H), 7.52-7.40 (m, 6H), 7.26-7.21 (m, 3H), 7.13 (td, $J = 7.6, 1.2$ Hz, 1H), 7.08-7.02 (m, 2H), 6.97 (d, $J = 7.2$ Hz, 2H), 6.94-6.90 (m, 3H), 6.79-6.78 (m, 2H), 6.43-6.40 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 192.9, 161.1, 158.8, 155.9, 146.3, 142.6, 141.5, 140.5, 139.7, 134.6, 133.4, 131.3, 131.0, 130.9, 130.2, 130.1, 129.90, 129.87, 129.6, 129.5, 129.4, 128.8, 128.6, 128.4, 125.3, 125.2, 125.0, 124.2, 121.6, 121.1, 119.6, 117.1, 114.1, 113.6, 76.1. HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{23}\text{NNaO}_3$ $[\text{M} + \text{Na}]^+$ 552.1570, found 552.1549.

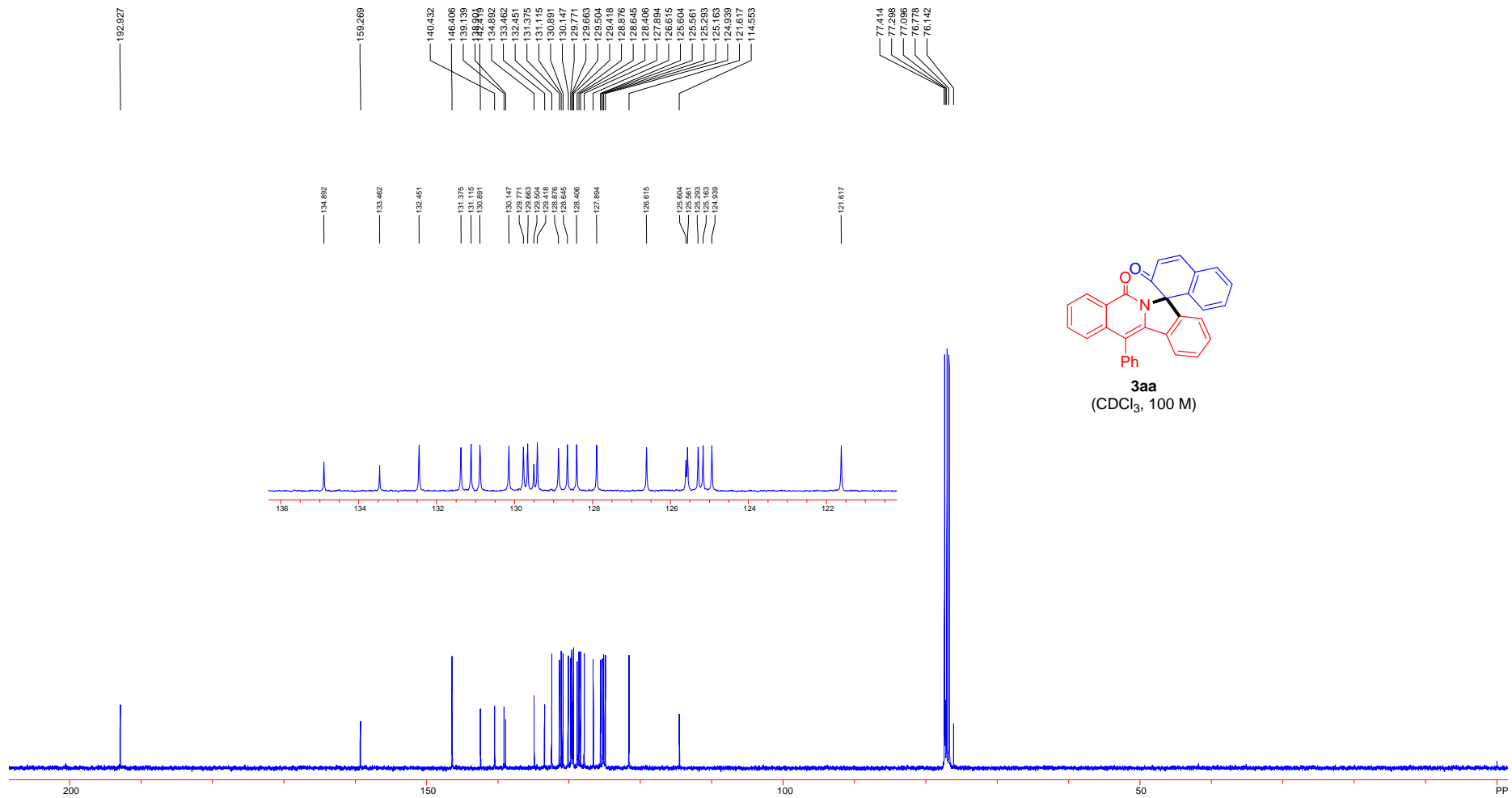


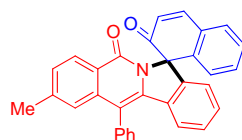
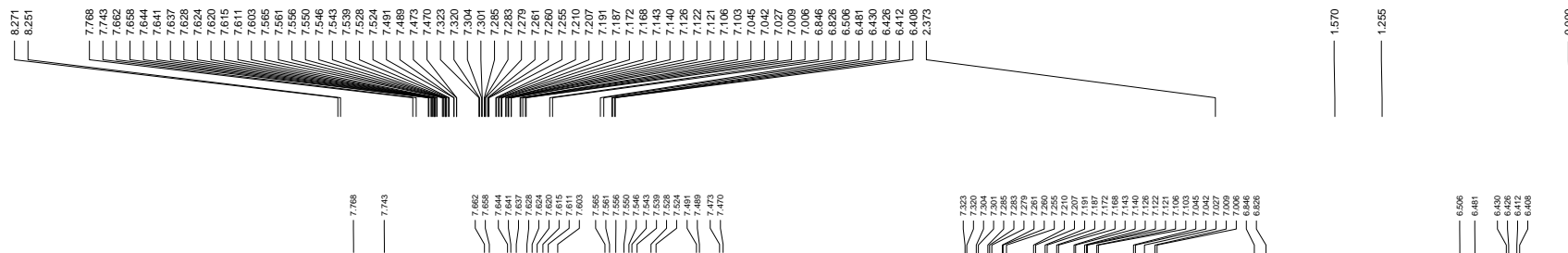
2,12-Diphenyl-2'*H*,5*H*-spiro[isoindolo[2,1-*b*]isoquinoline-7,1'-naphthalene]-2',5-dione

(14): Petroleum ether/ethyl acetate (2:1) as eluent; white solid (32 mg, 61%), mp >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.44 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 10.0 Hz, 1H), 7.69-7.57 (m, 6H), 7.52-7.49 (m, 3H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.43-7.39 (m, 2H), 7.37-7.30 (m, 2H), 7.23-7.19 (m, 1H), 7.16-7.12 (m, 1H), 7.06-7.03 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 192.9, 159.1, 146.4, 145.3, 142.5, 140.4, 139.6, 139.3, 134.8, 133.5, 131.4, 131.1, 130.9, 130.1, 129.8, 129.7, 129.51, 129.48, 128.90, 128.87, 128.7, 128.5, 128.4, 128.1, 127.6, 125.9, 125.3, 125.2, 125.0, 124.5, 123.8, 121.6, 114.7, 76.1 (one ¹³C signal was not observed). HRMS (ESI) calcd for C₃₇H₂₃NNaO₂ [M + Na]⁺ 536.1621, found 536.1604.

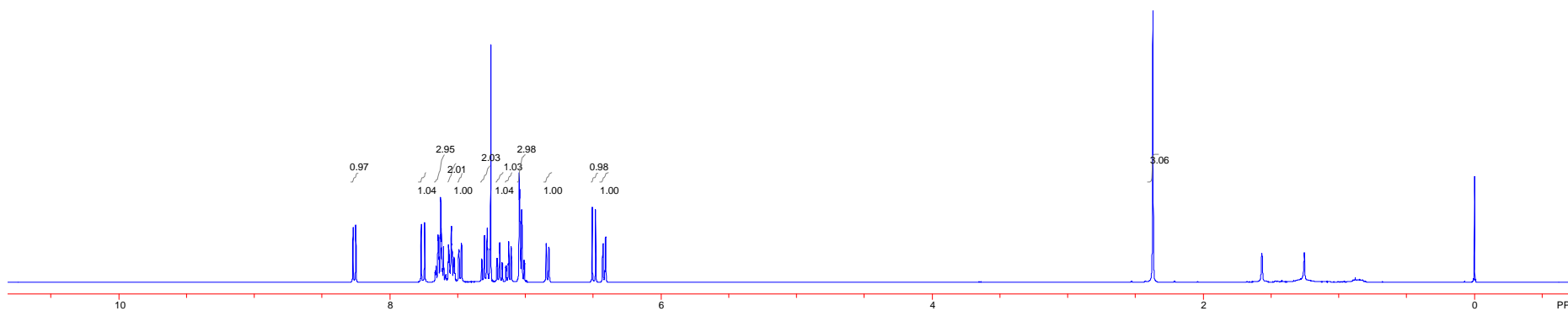
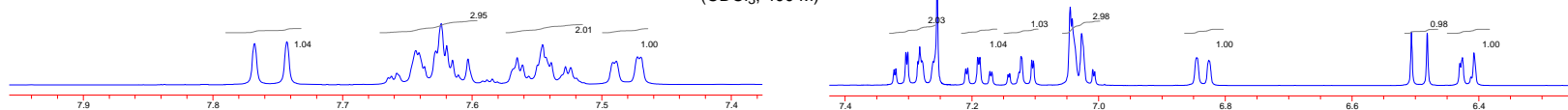
9. The ^1H , ^{13}C , and ^{19}F NMR Spectra of 3aa-3sa, 3ab-3ap, 5a-5j, 8a-8n, and 10-14

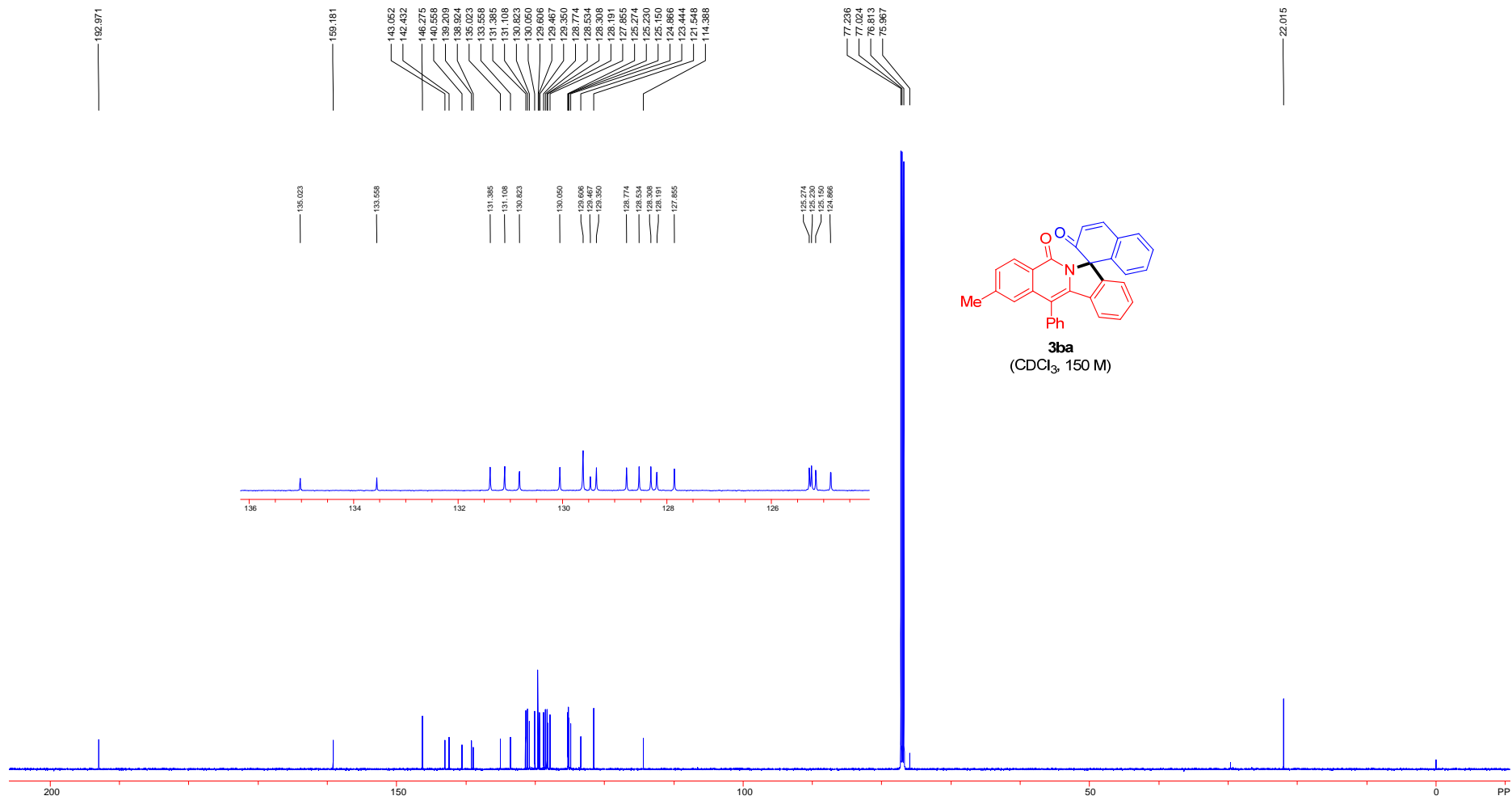


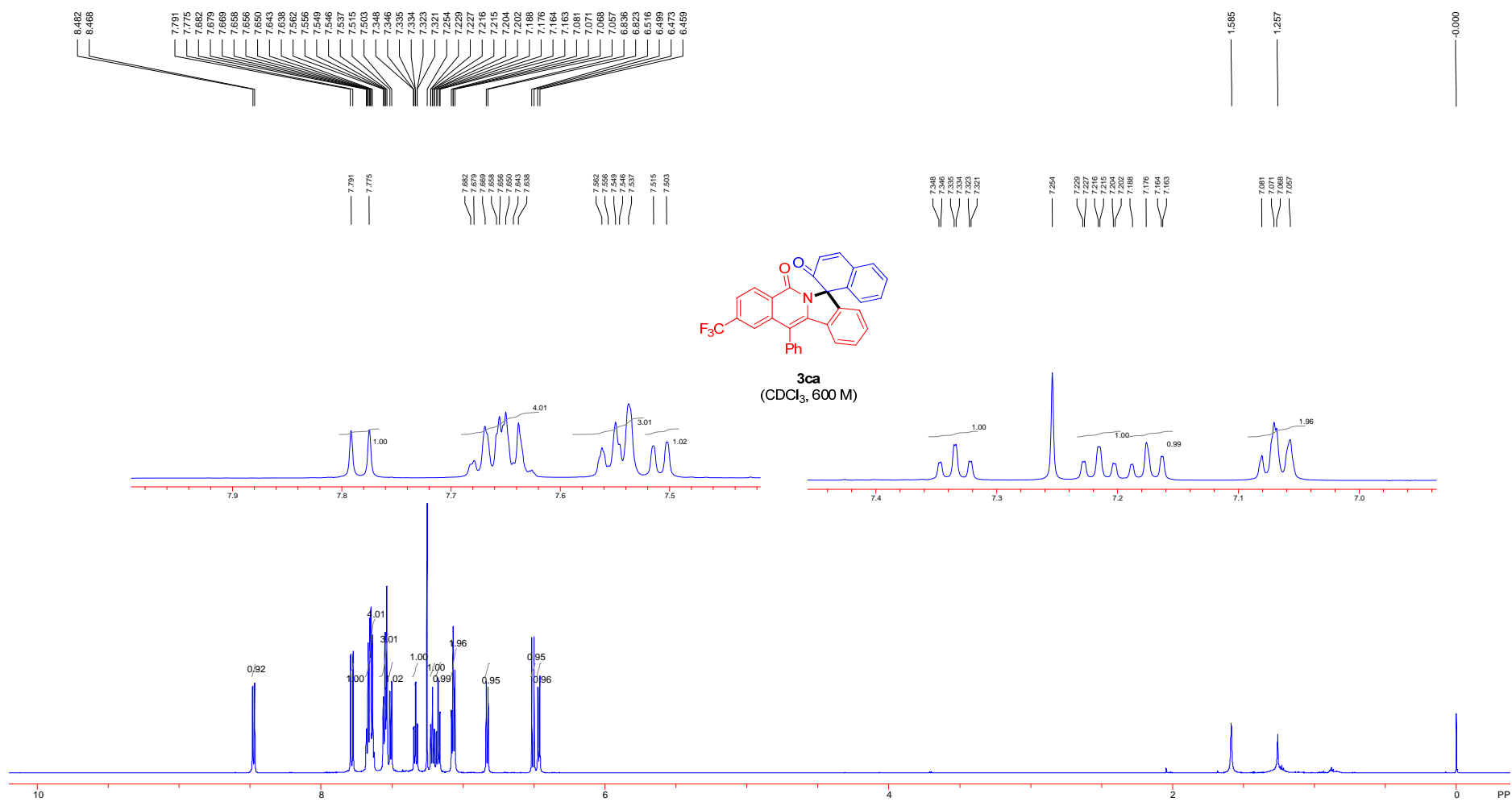


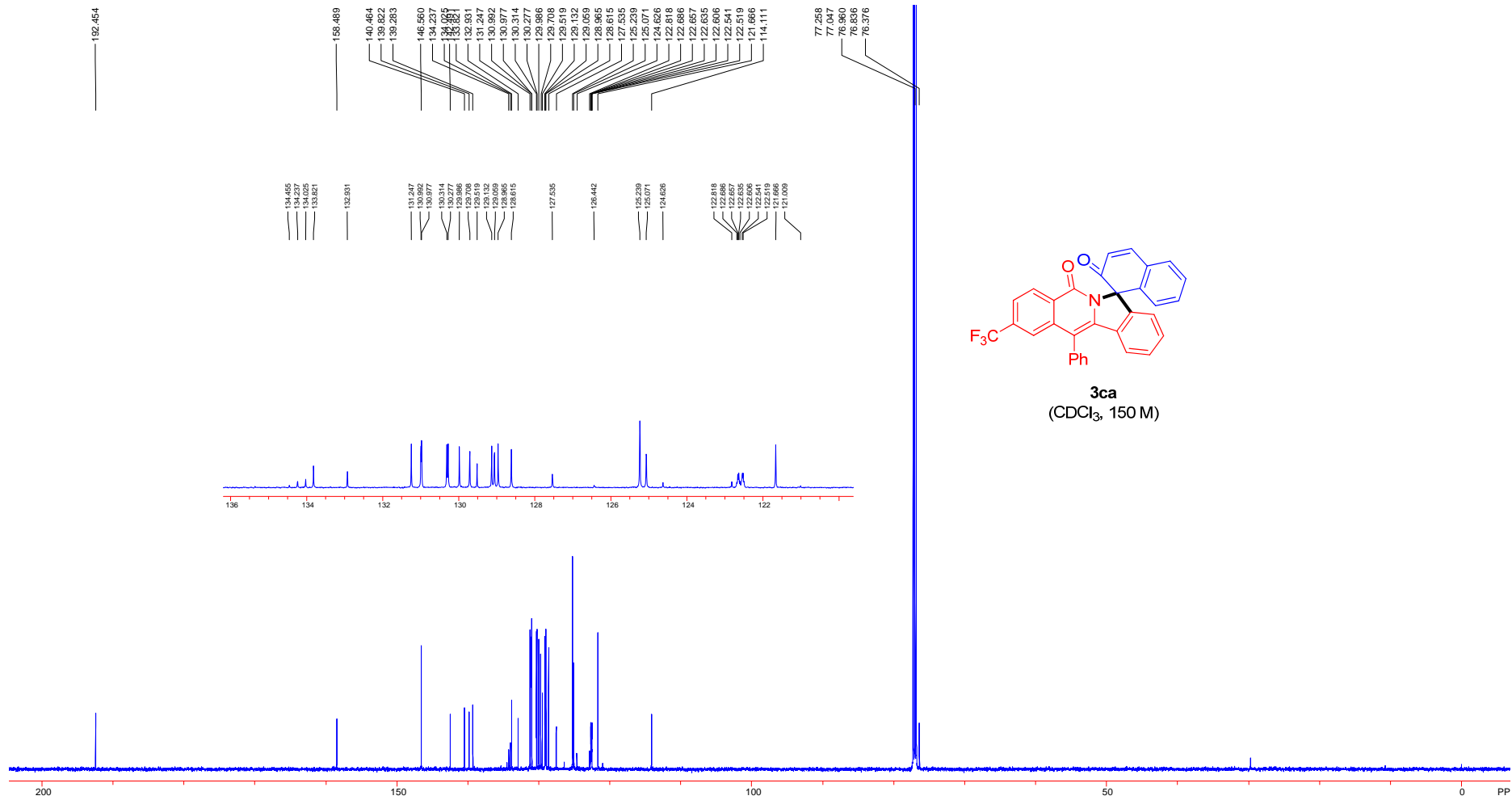


3ba
(CDCl₃, 400 M)

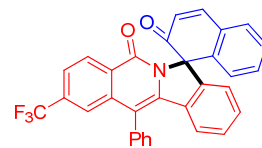




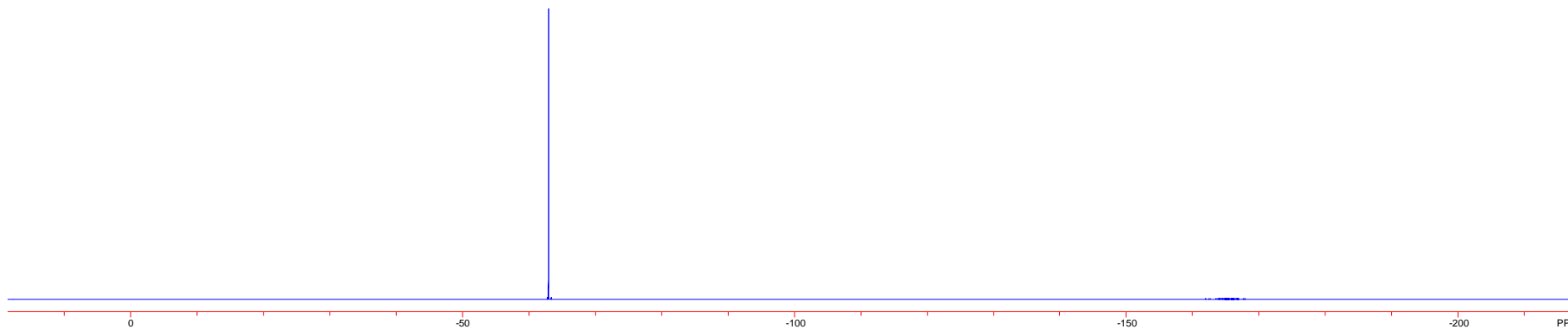


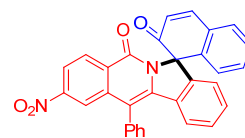
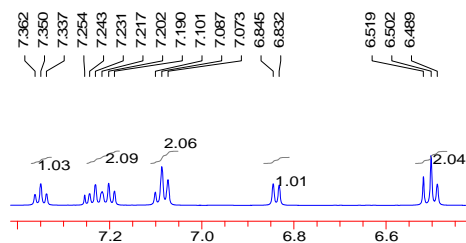
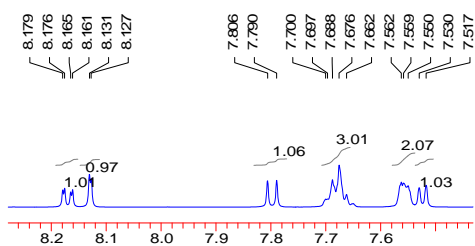
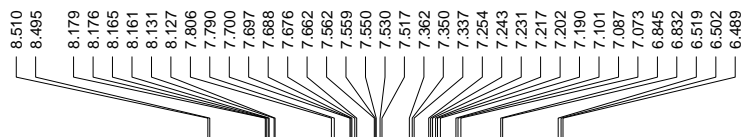


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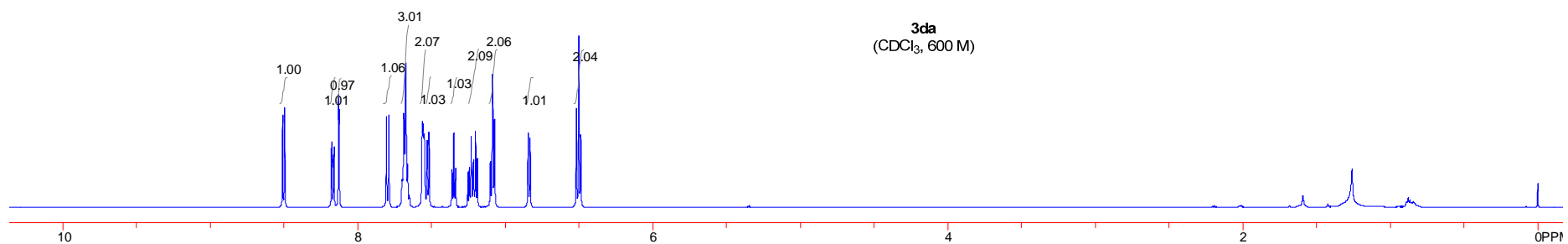


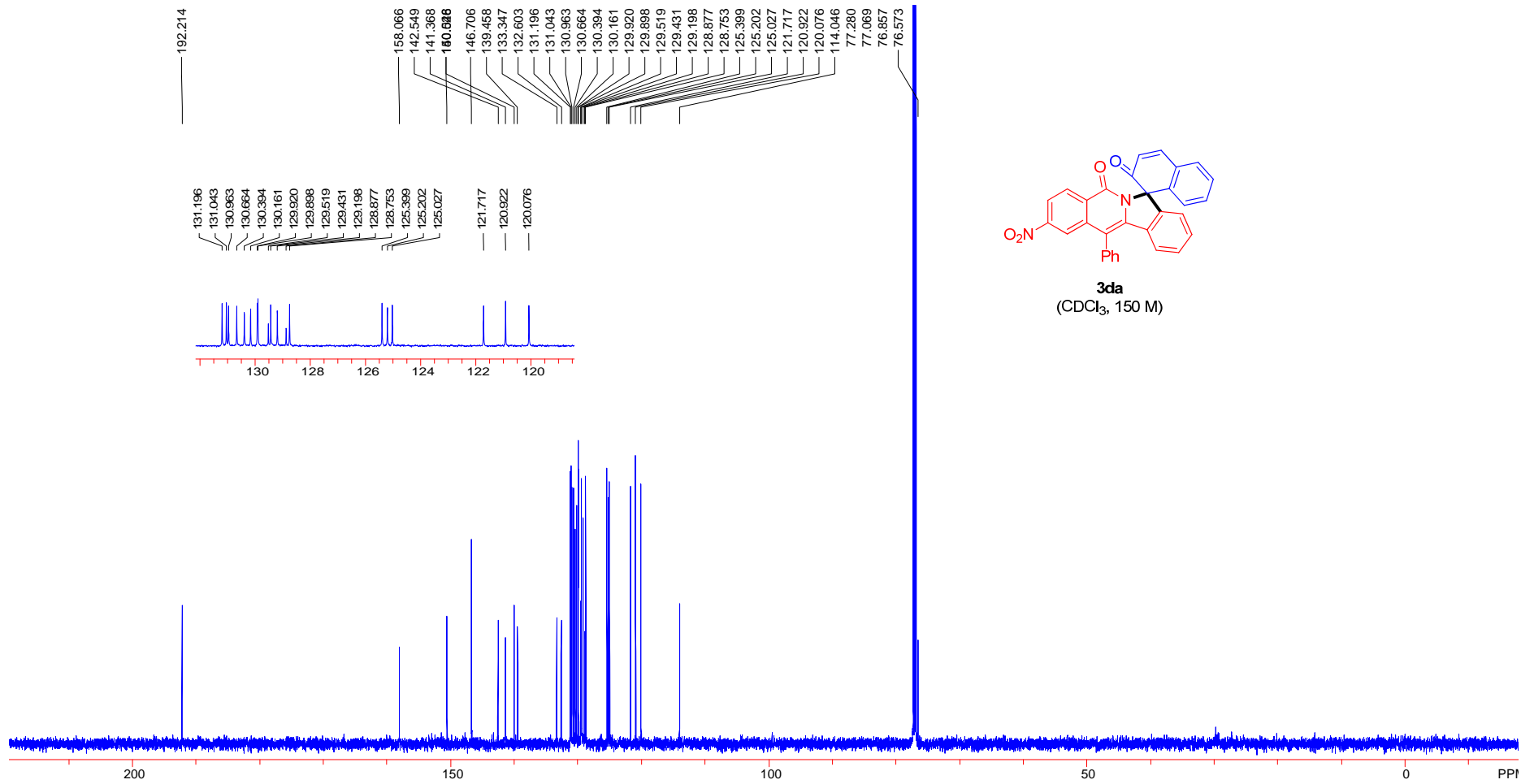
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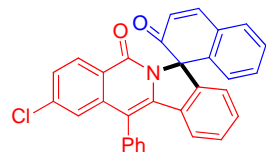




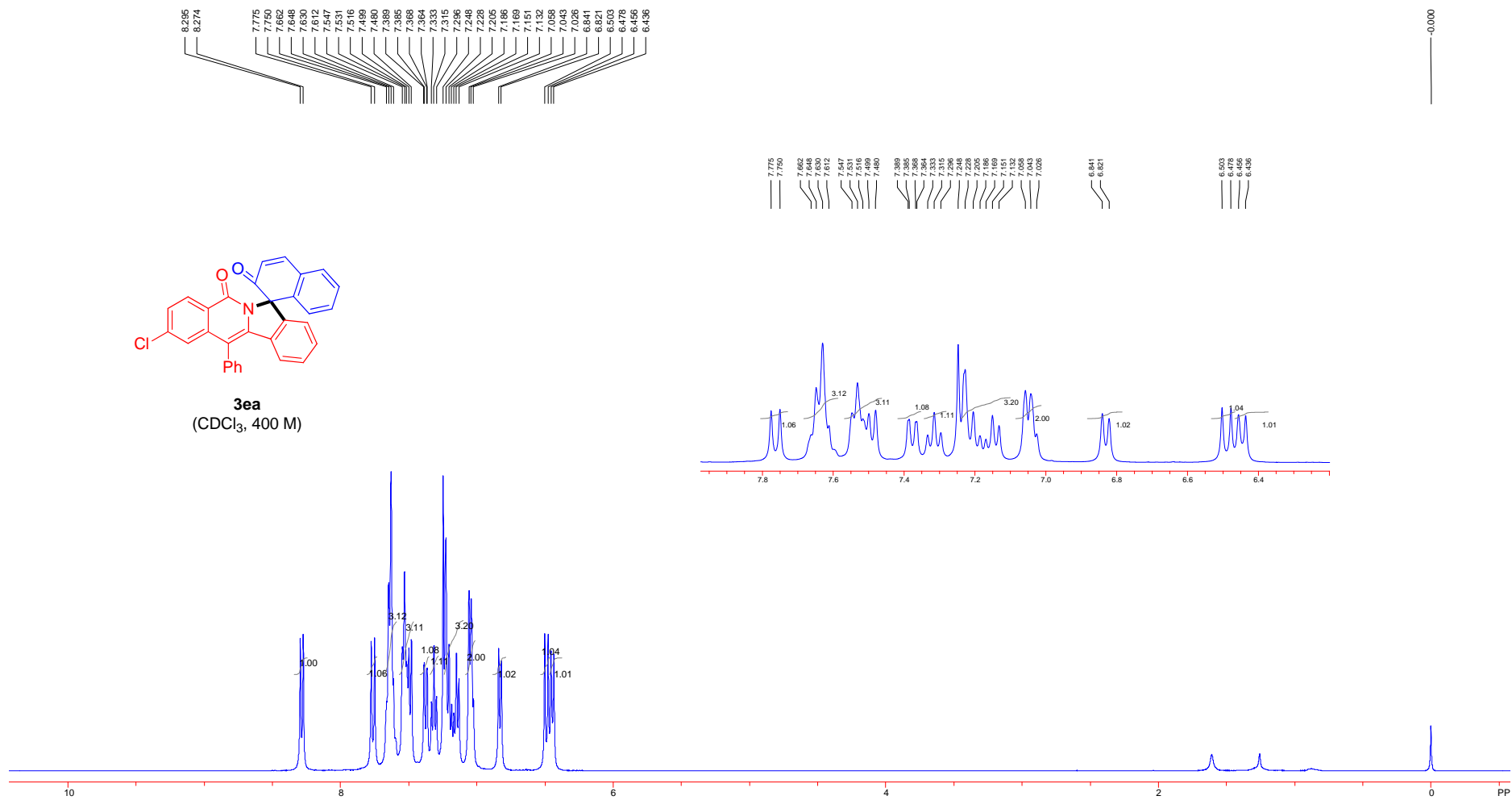
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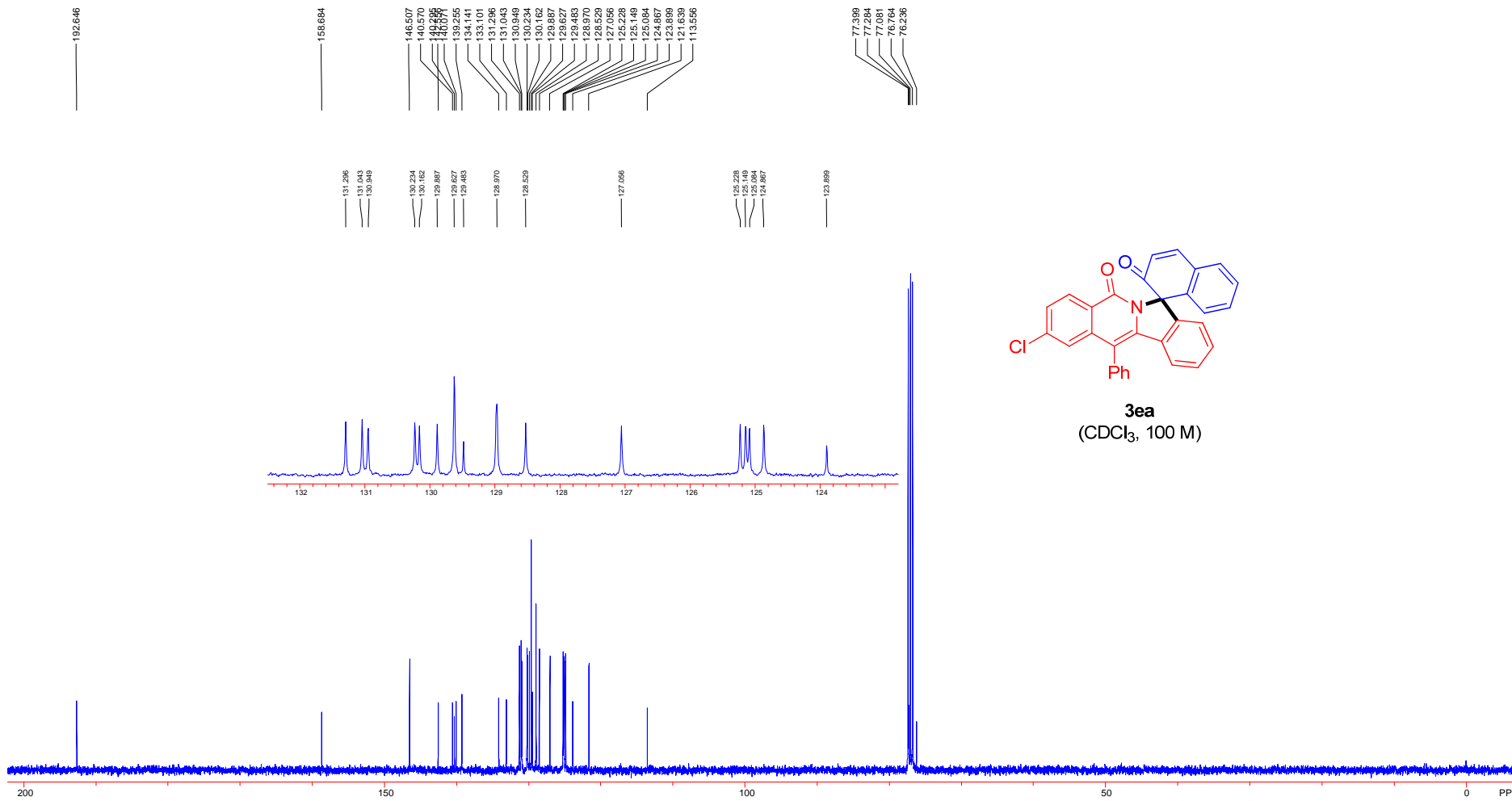


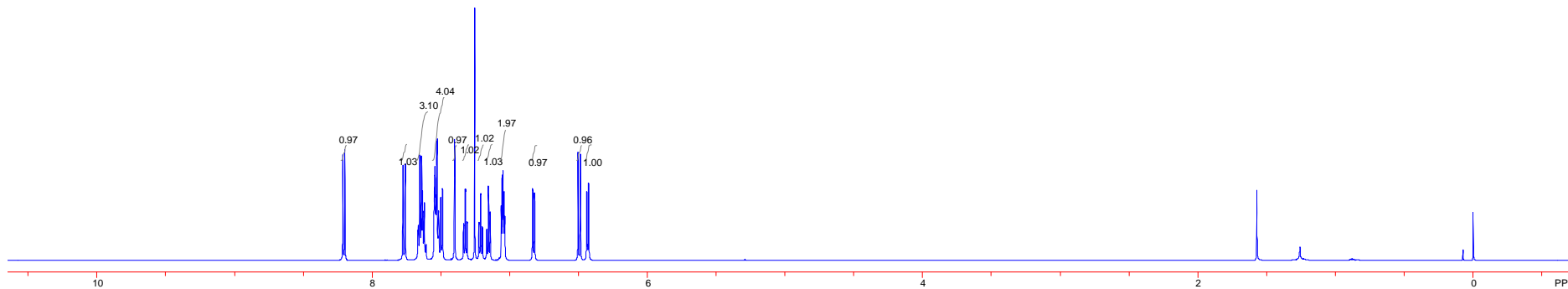
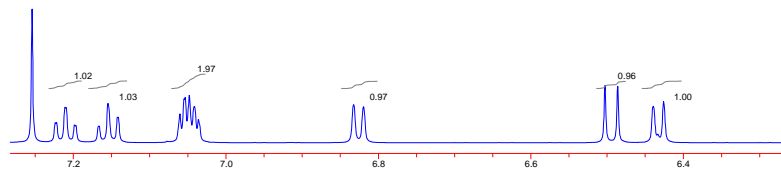
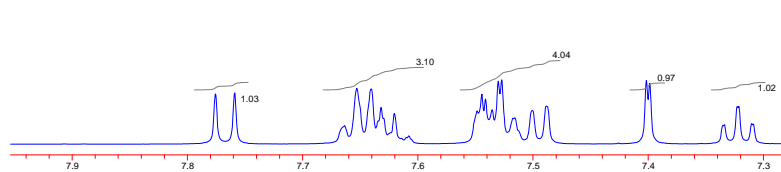
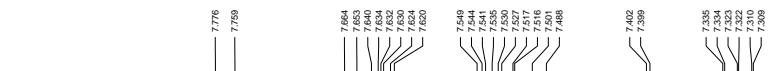
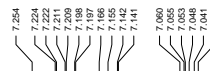
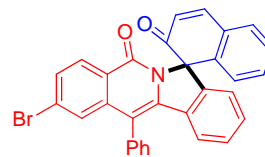
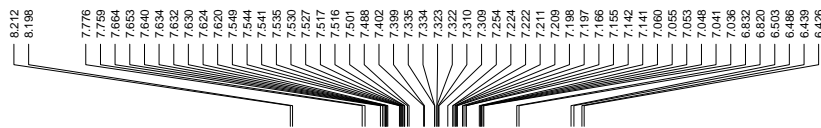


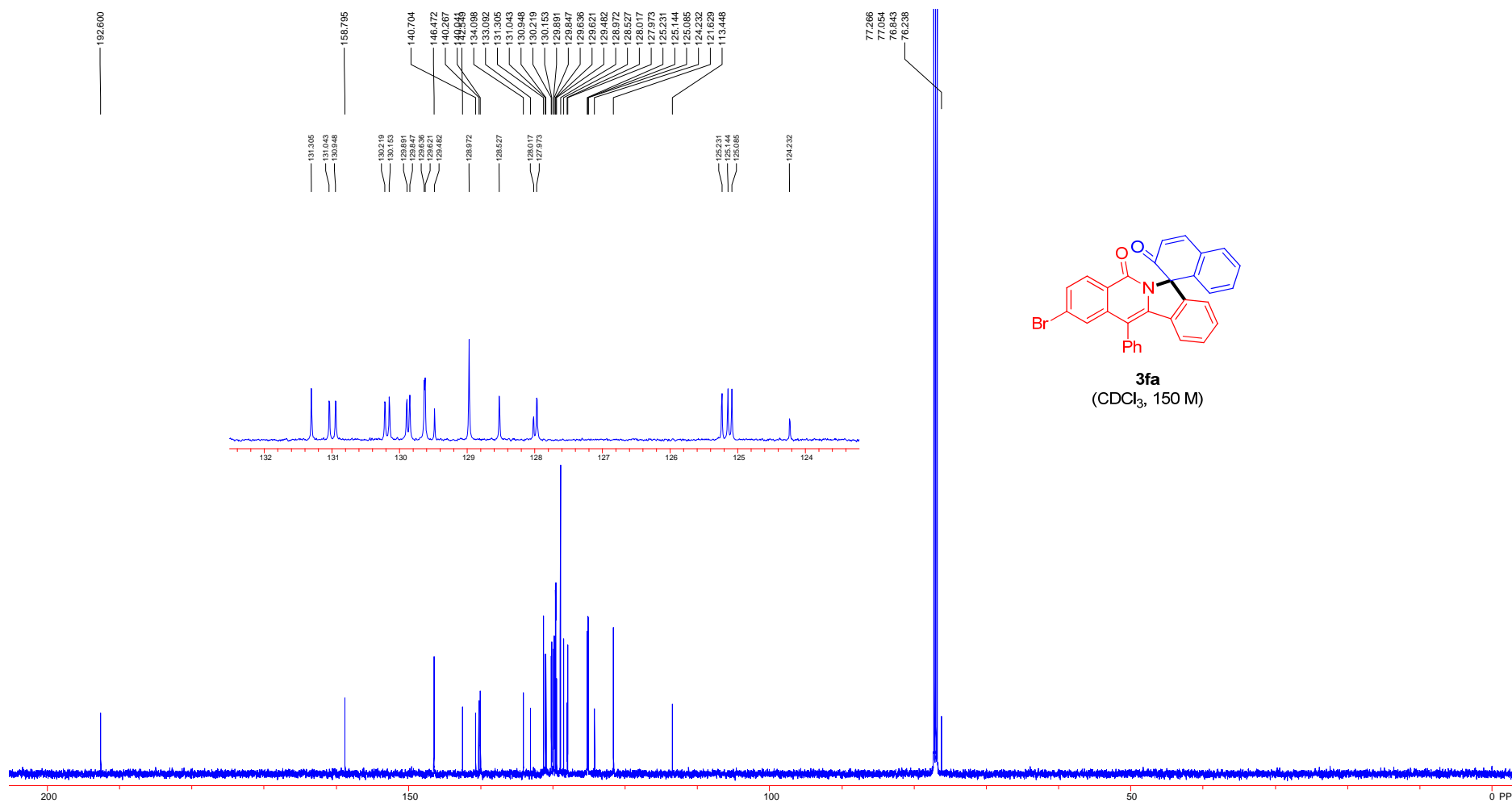


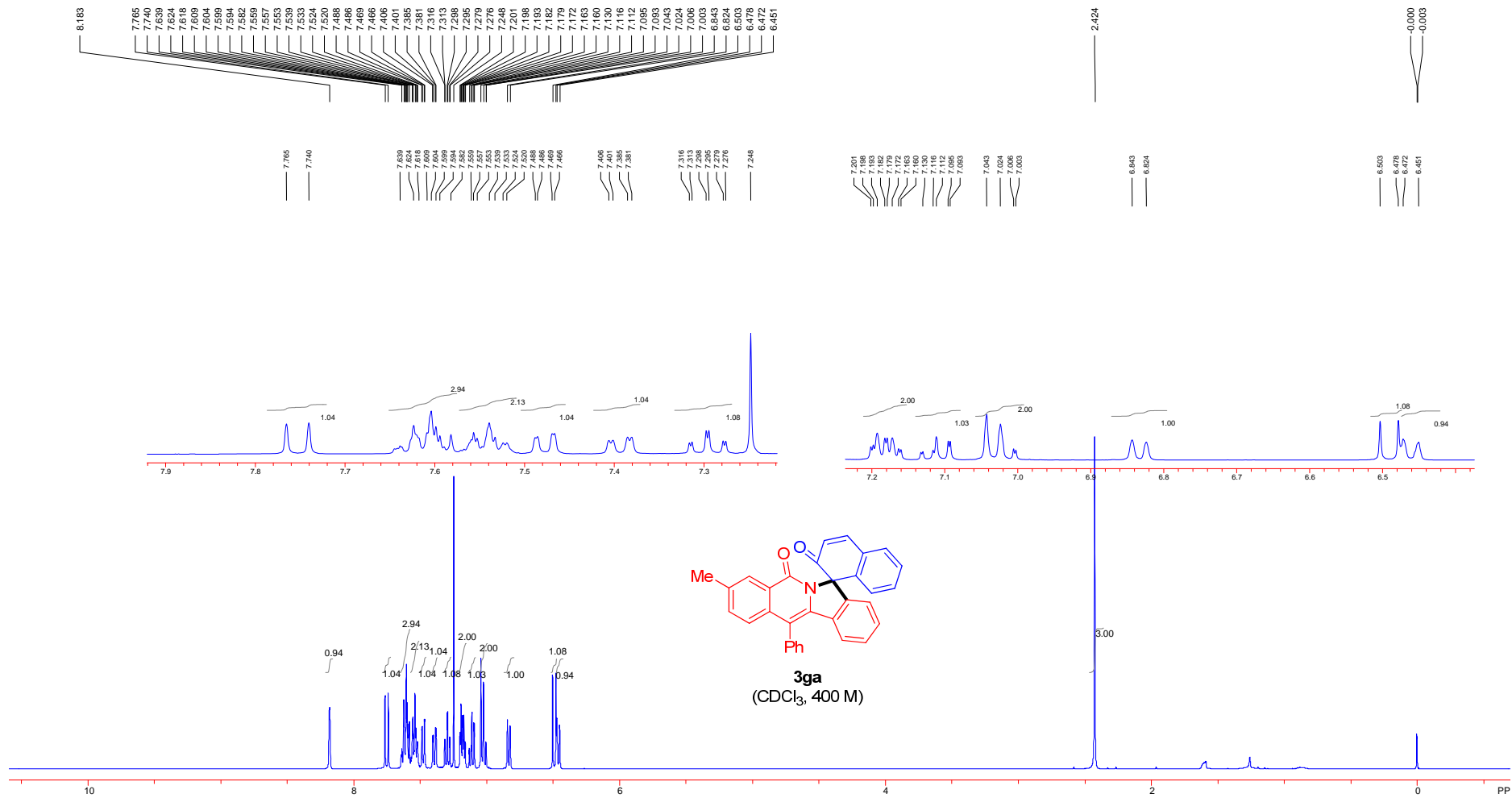
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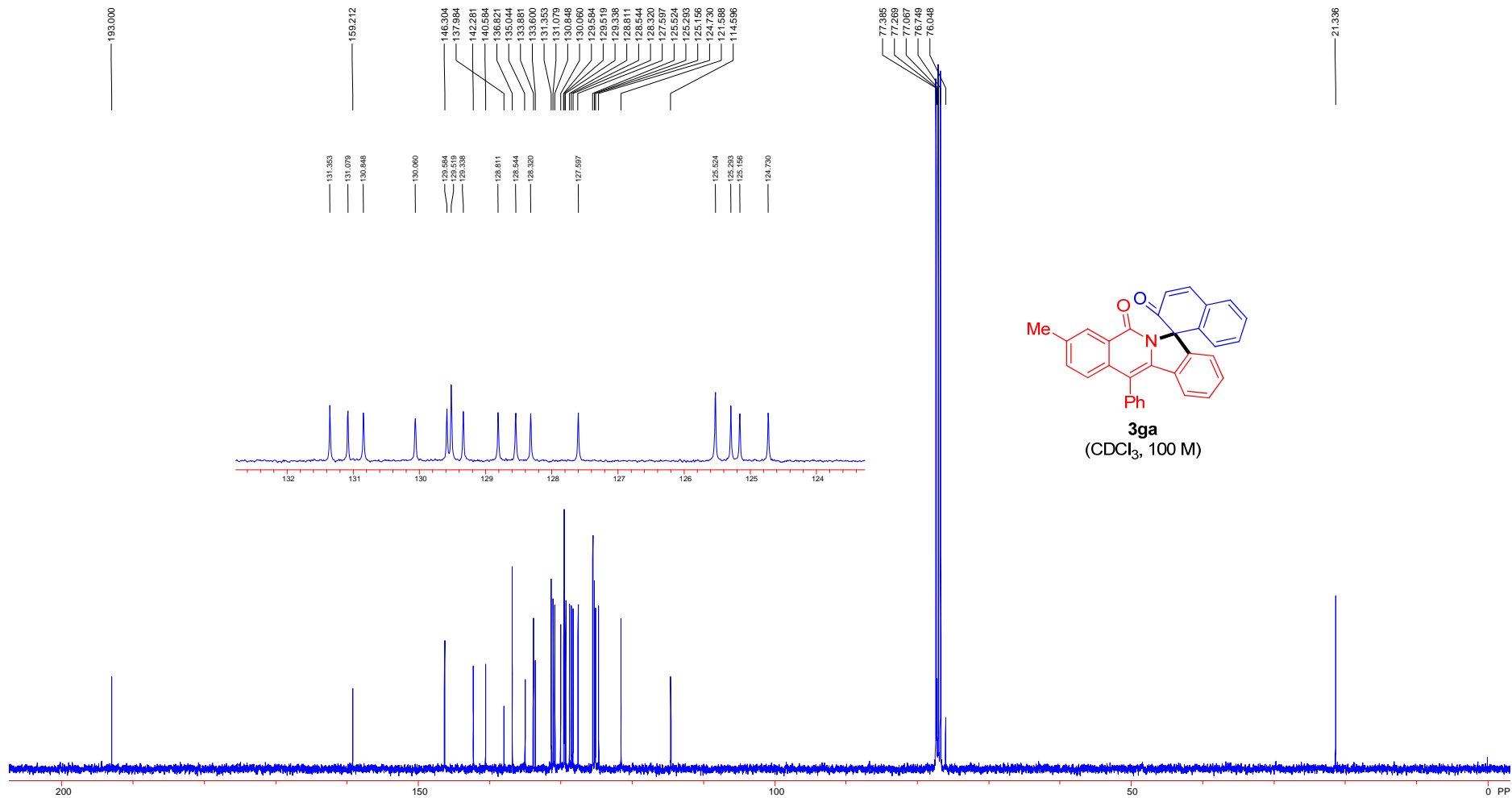


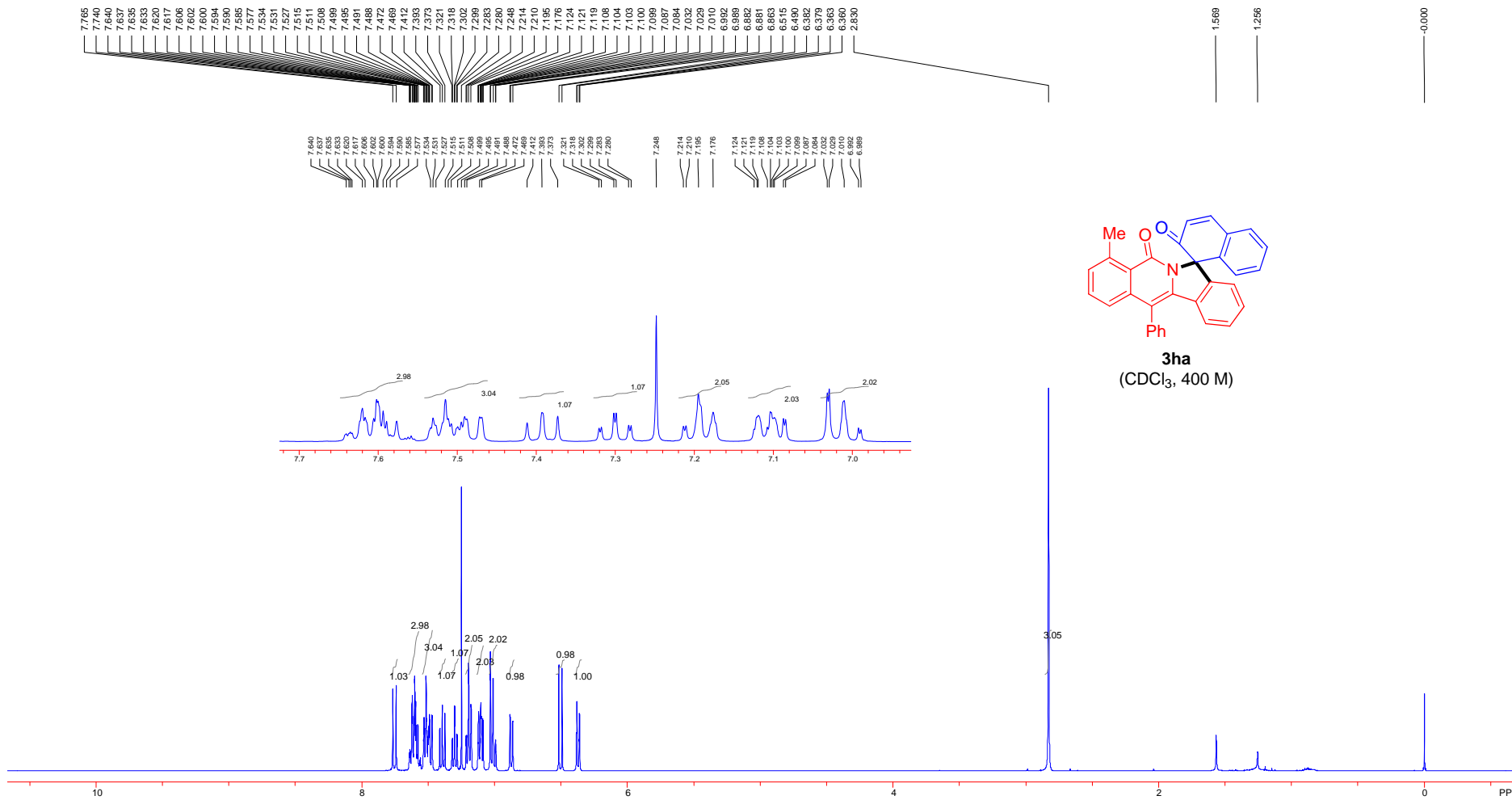


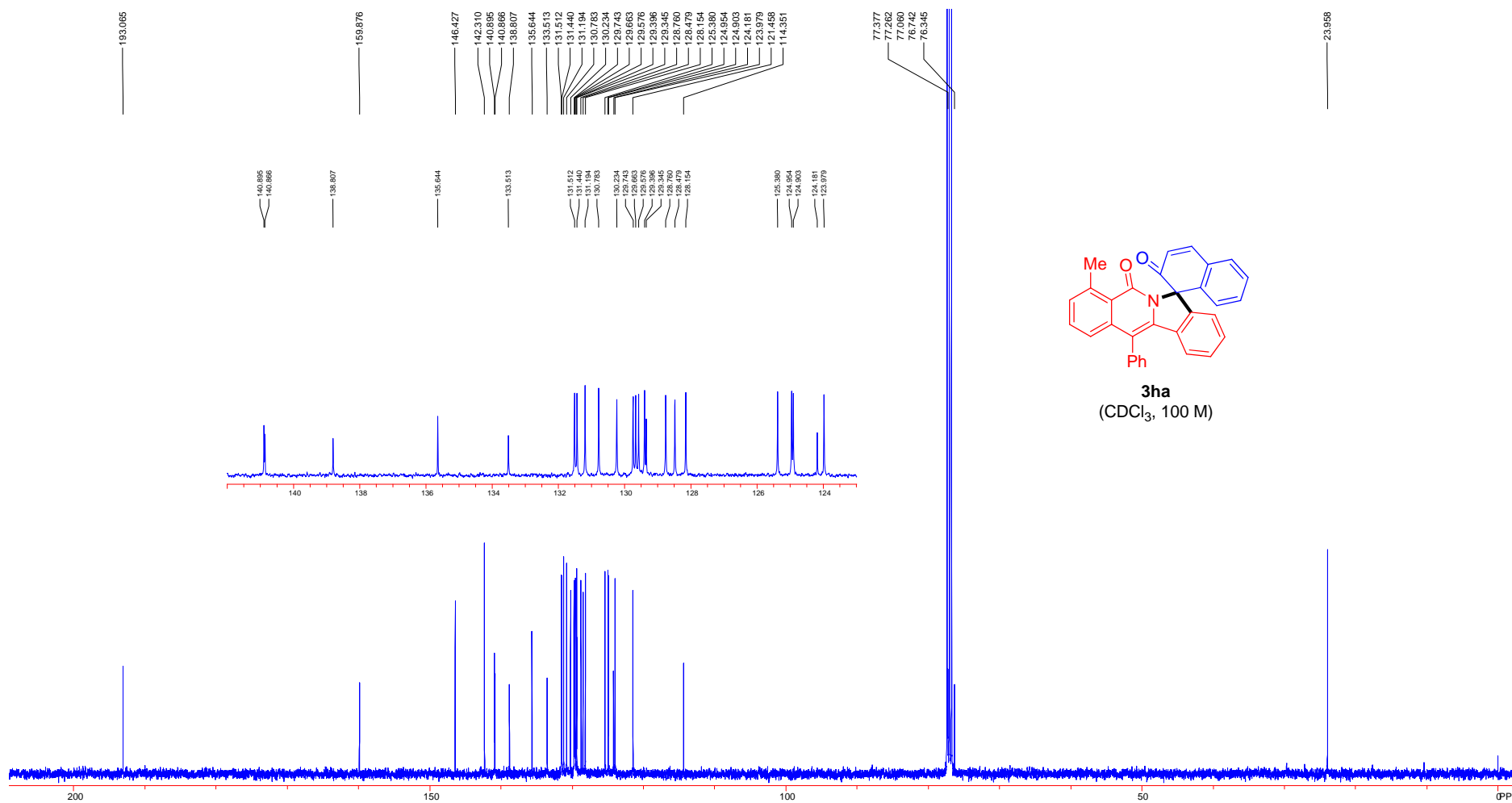


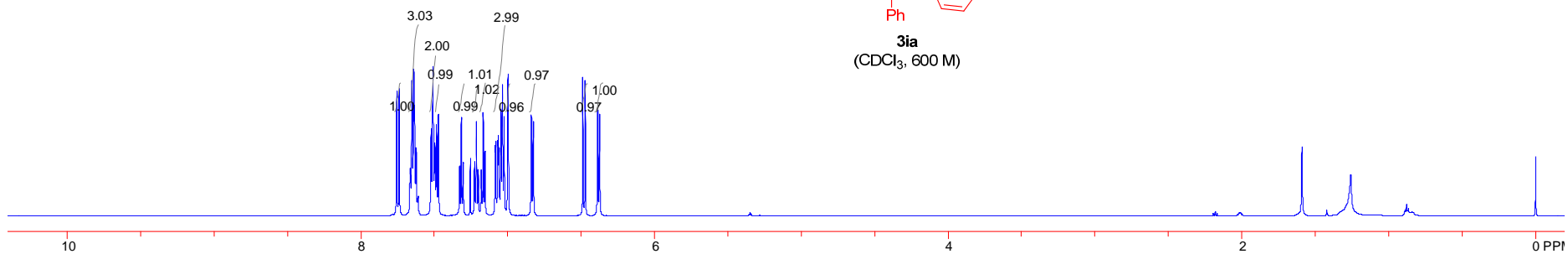
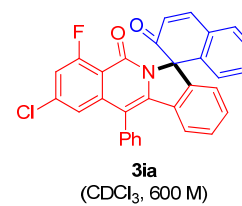
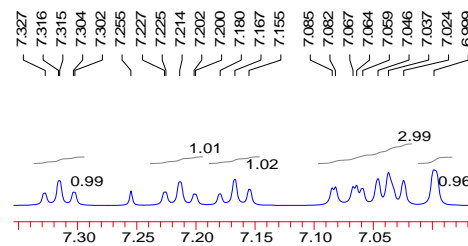
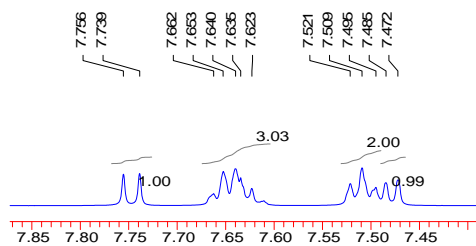
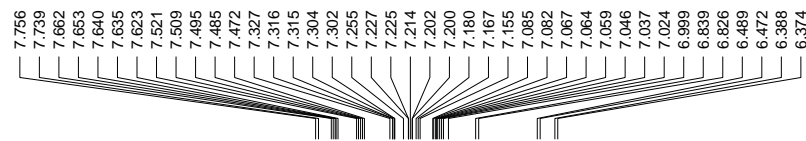


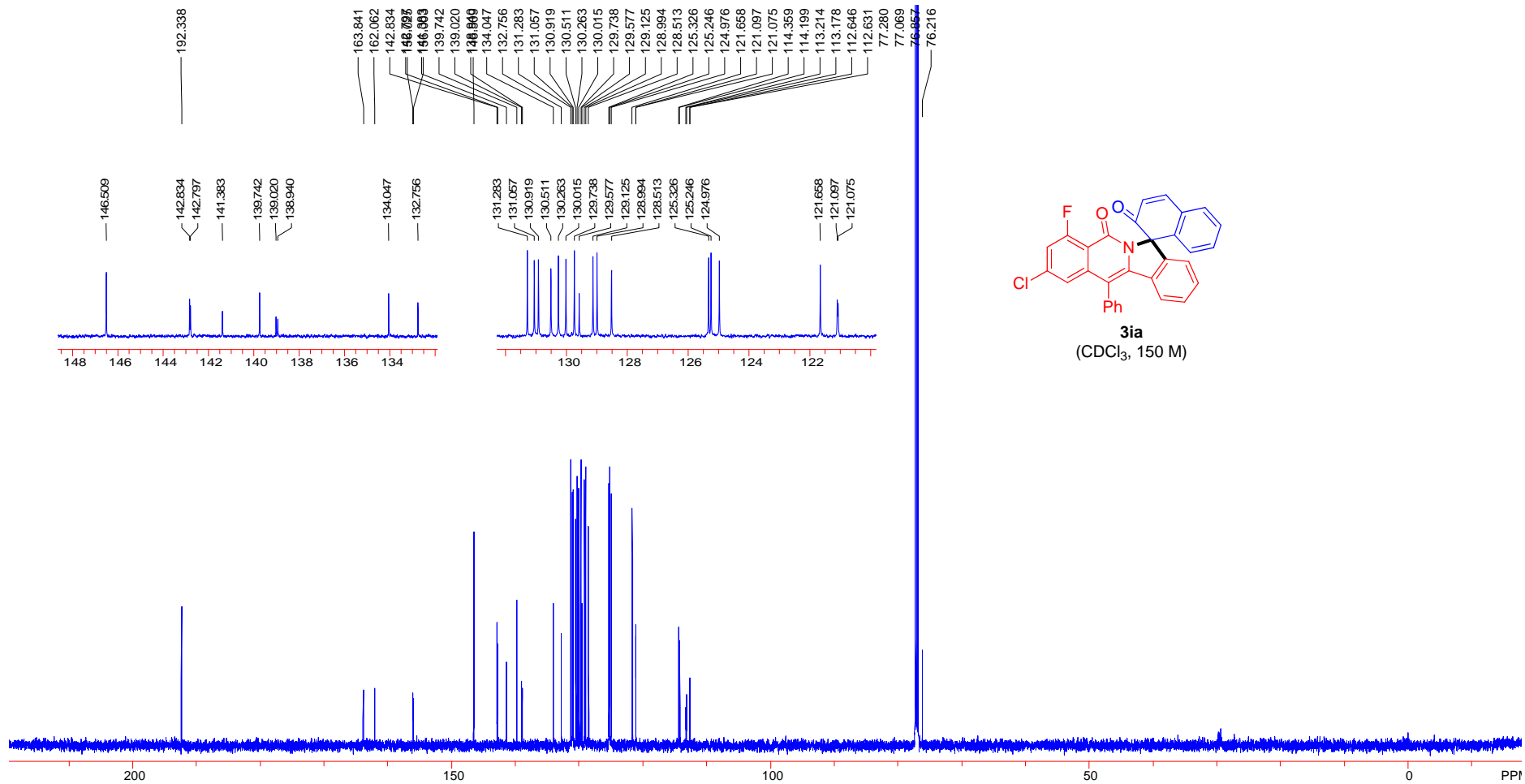


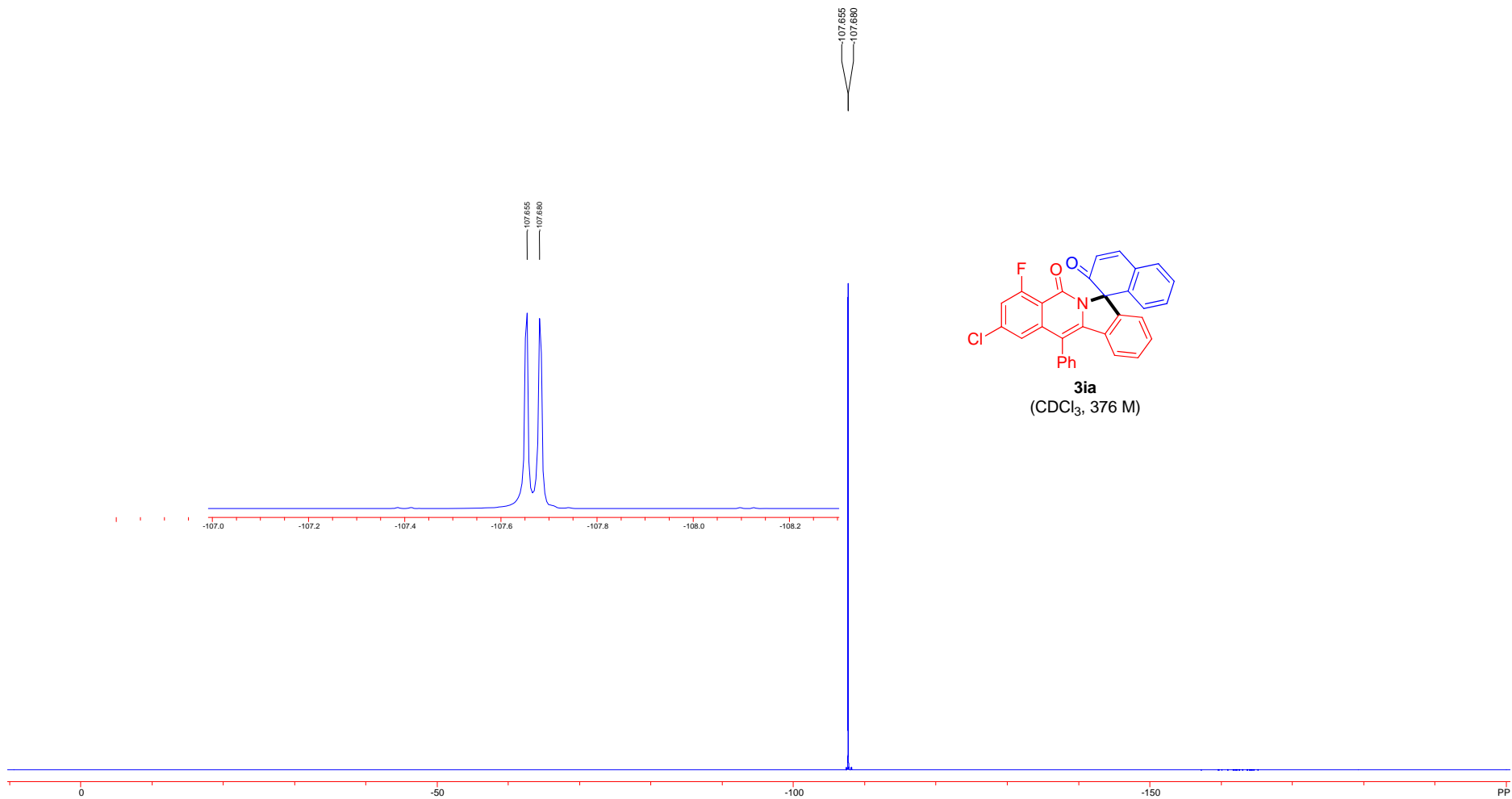


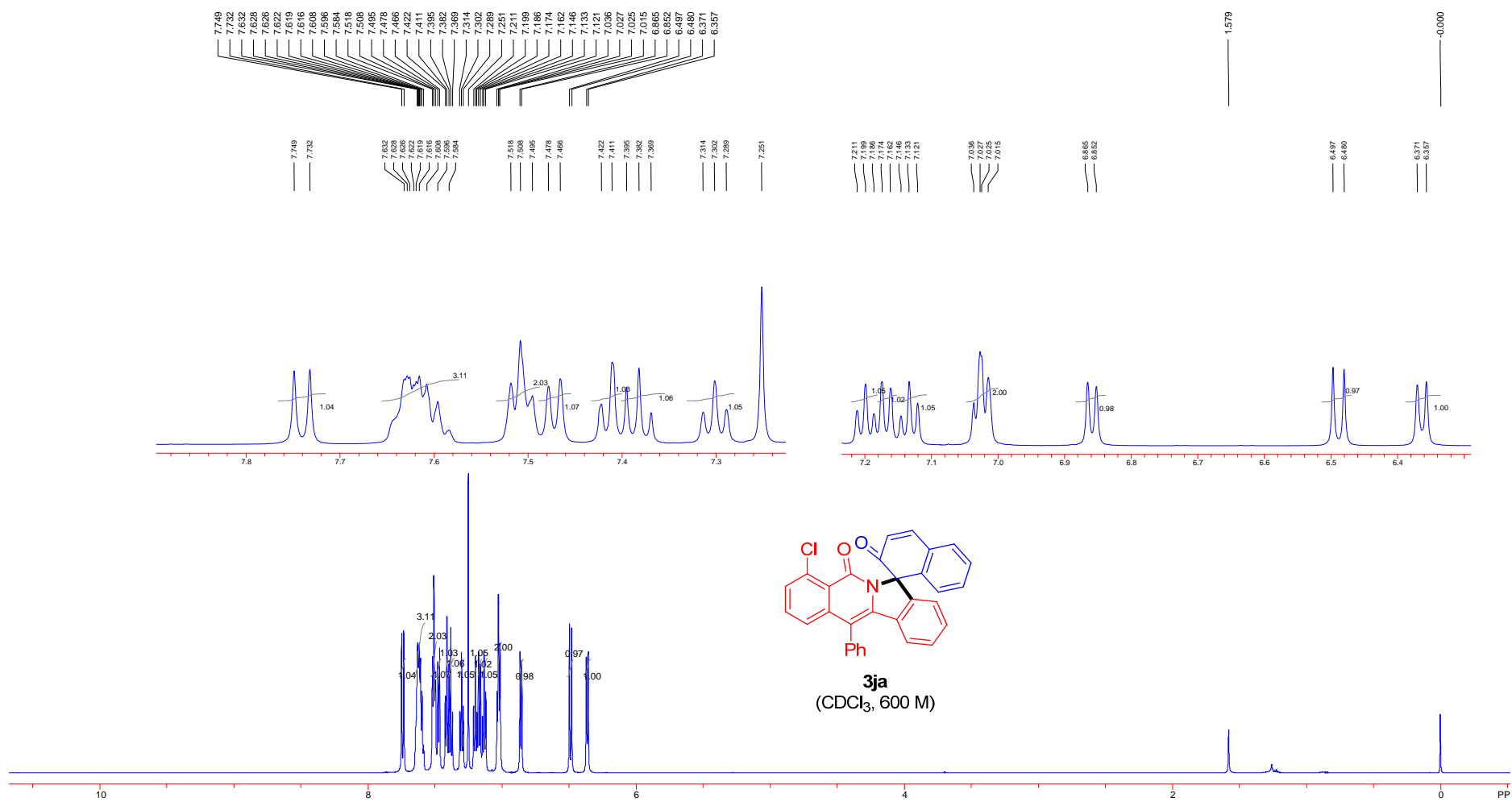


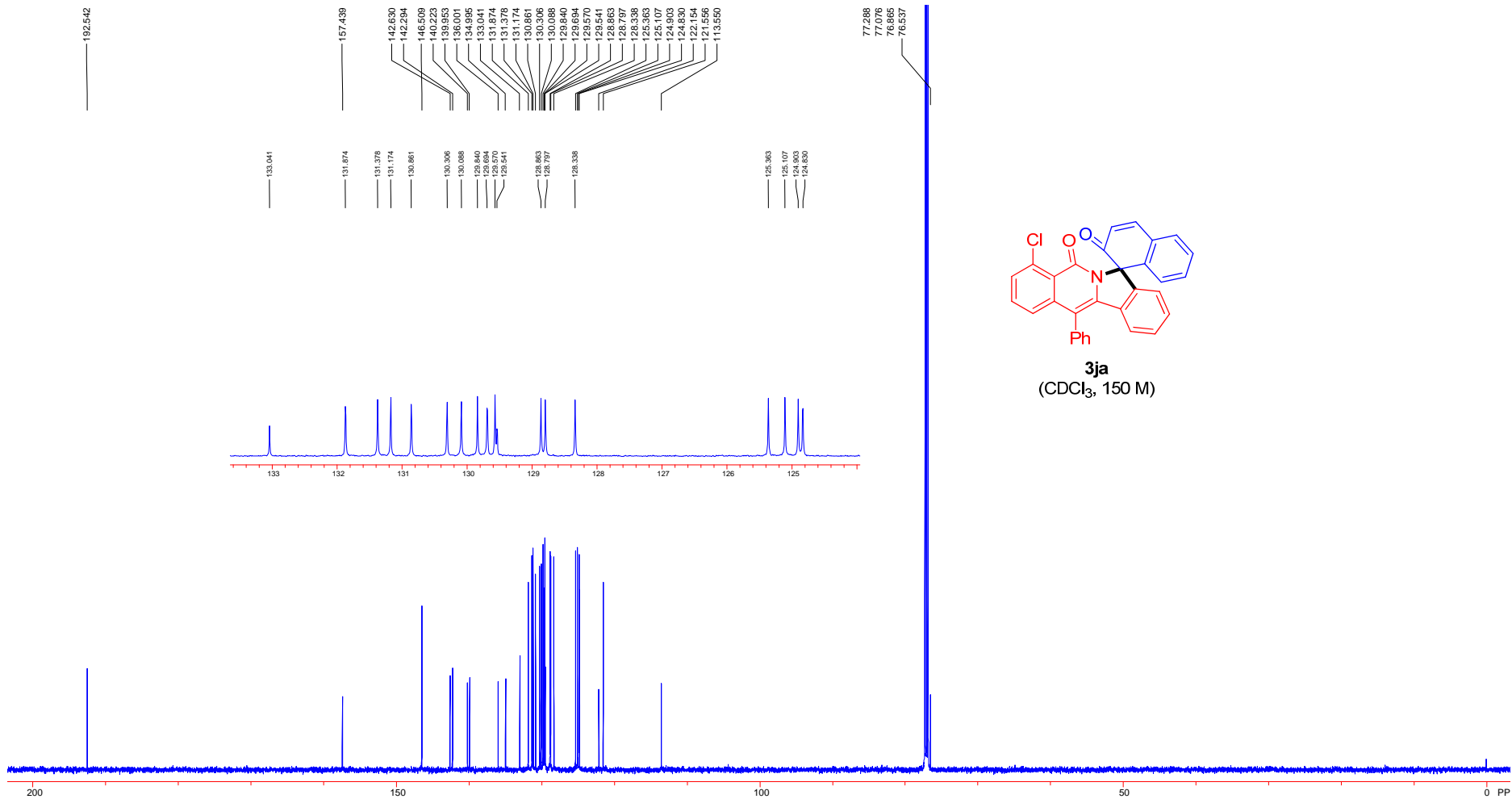


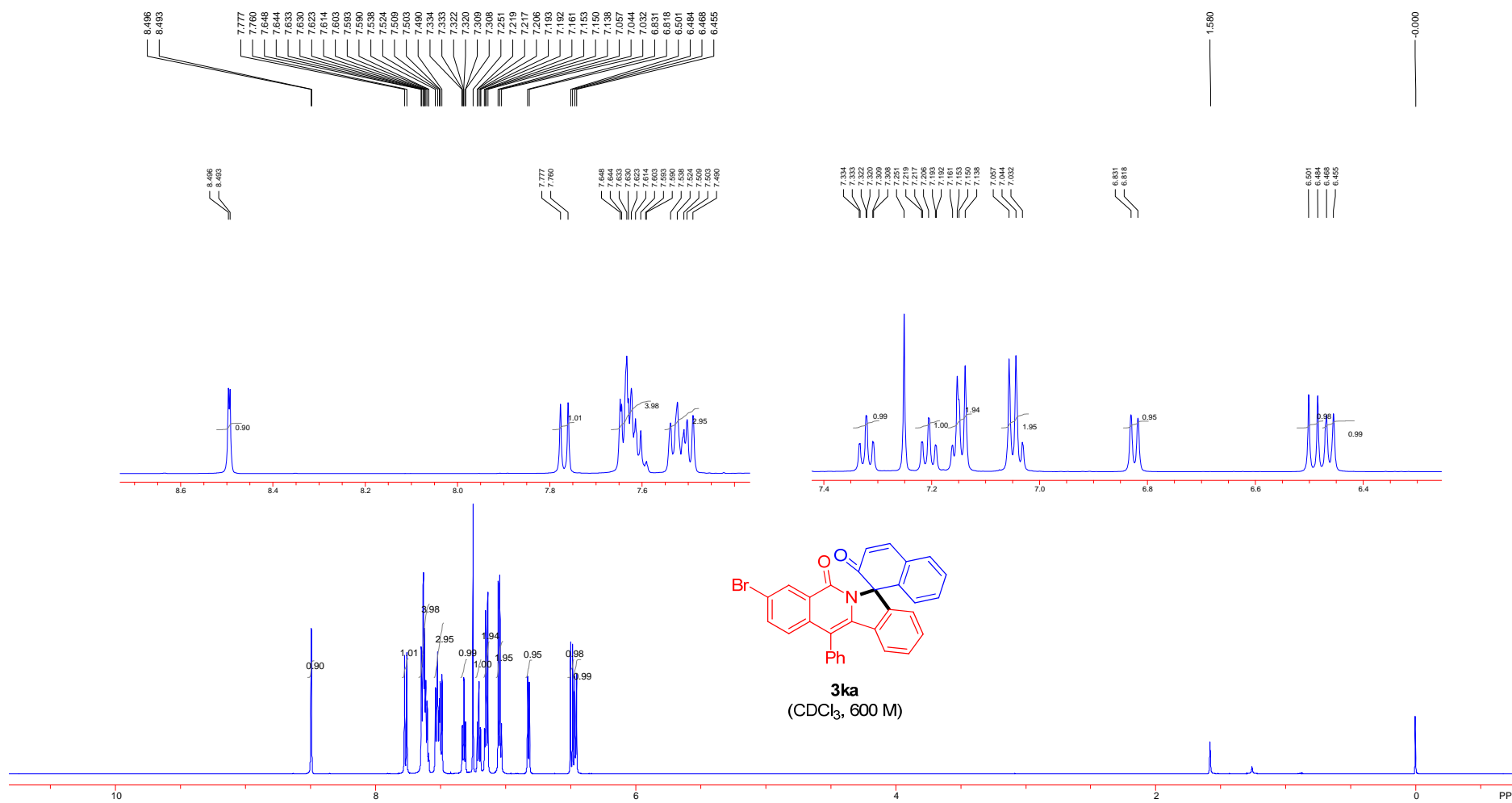


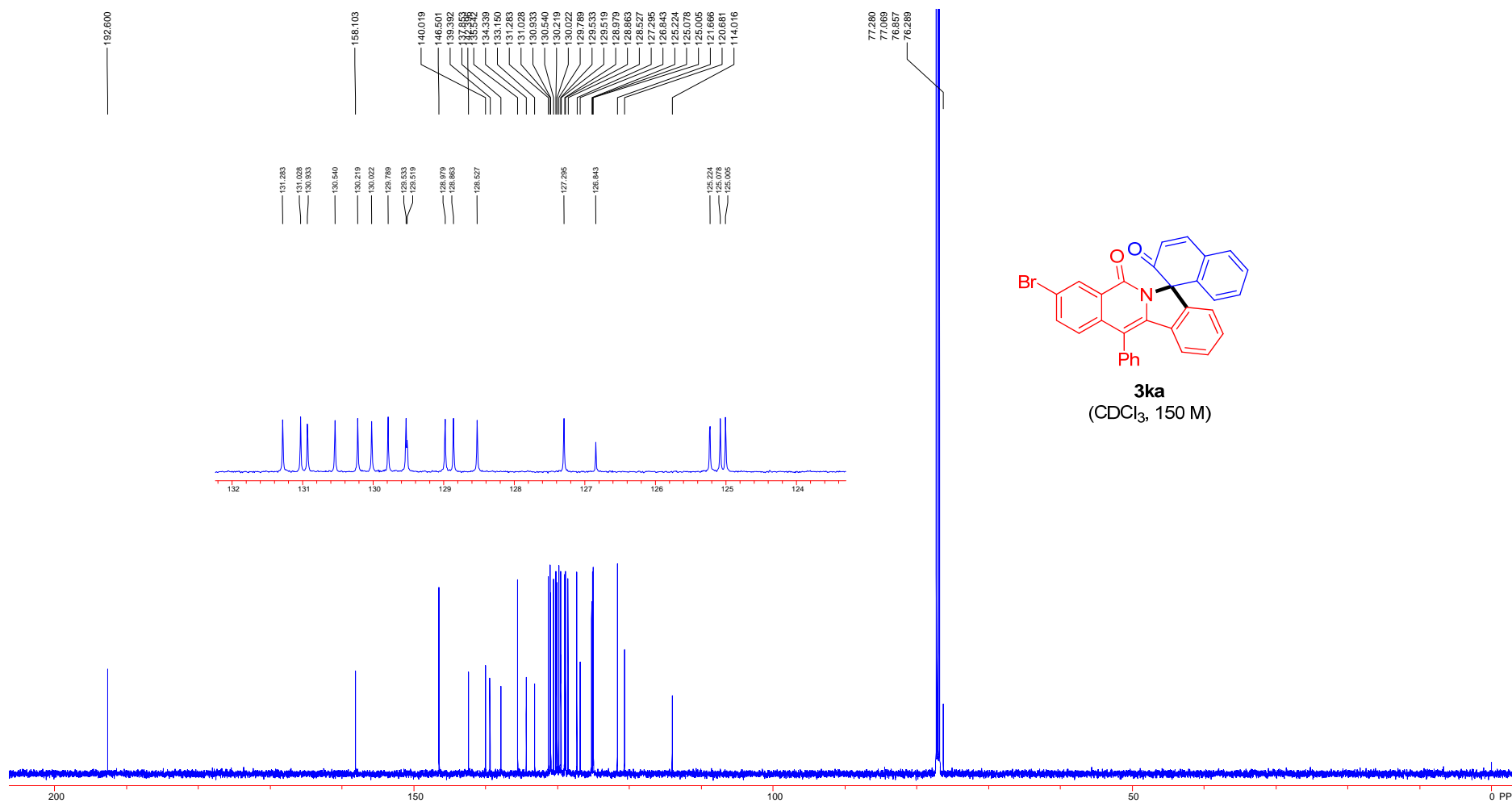


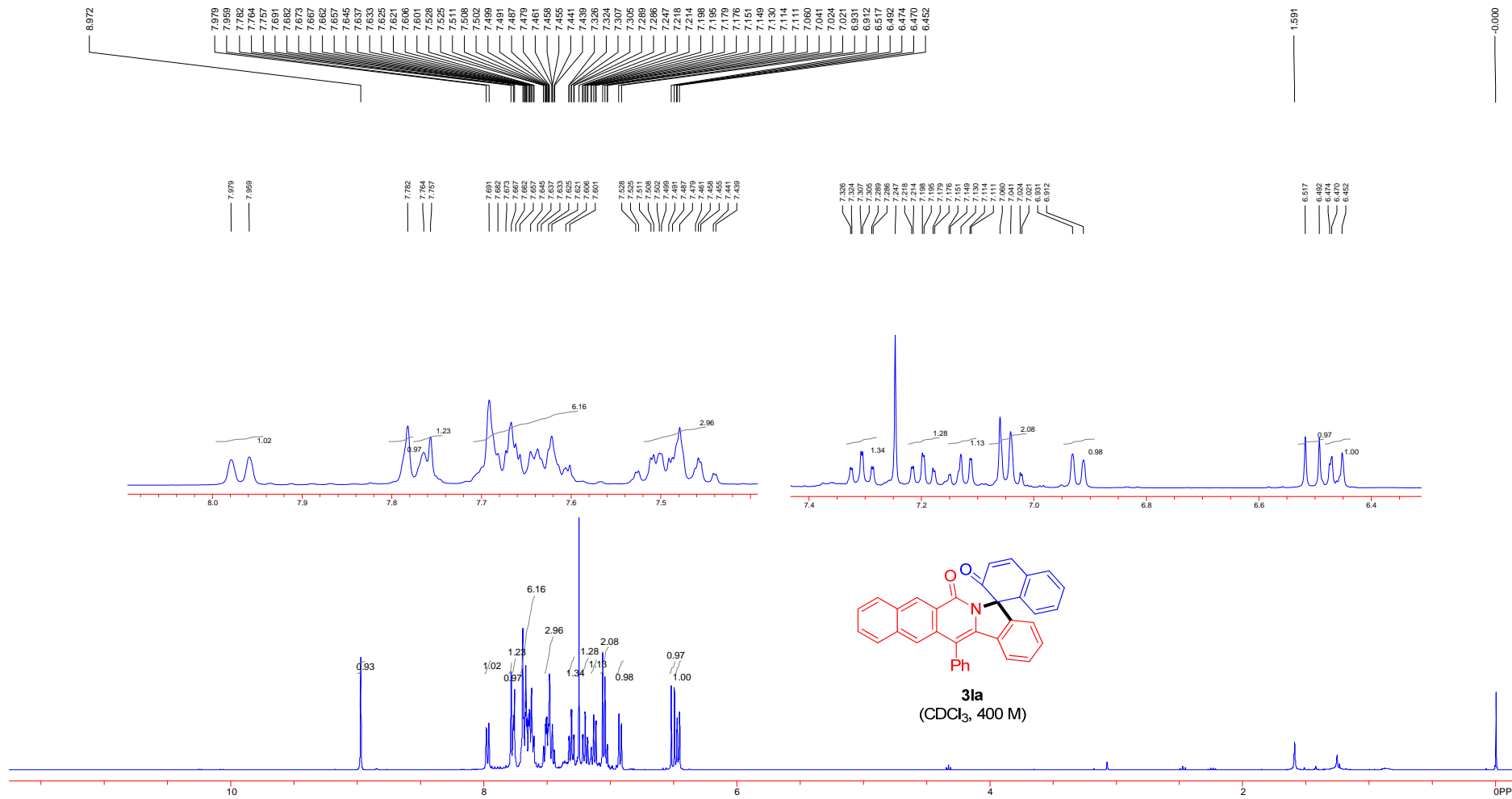


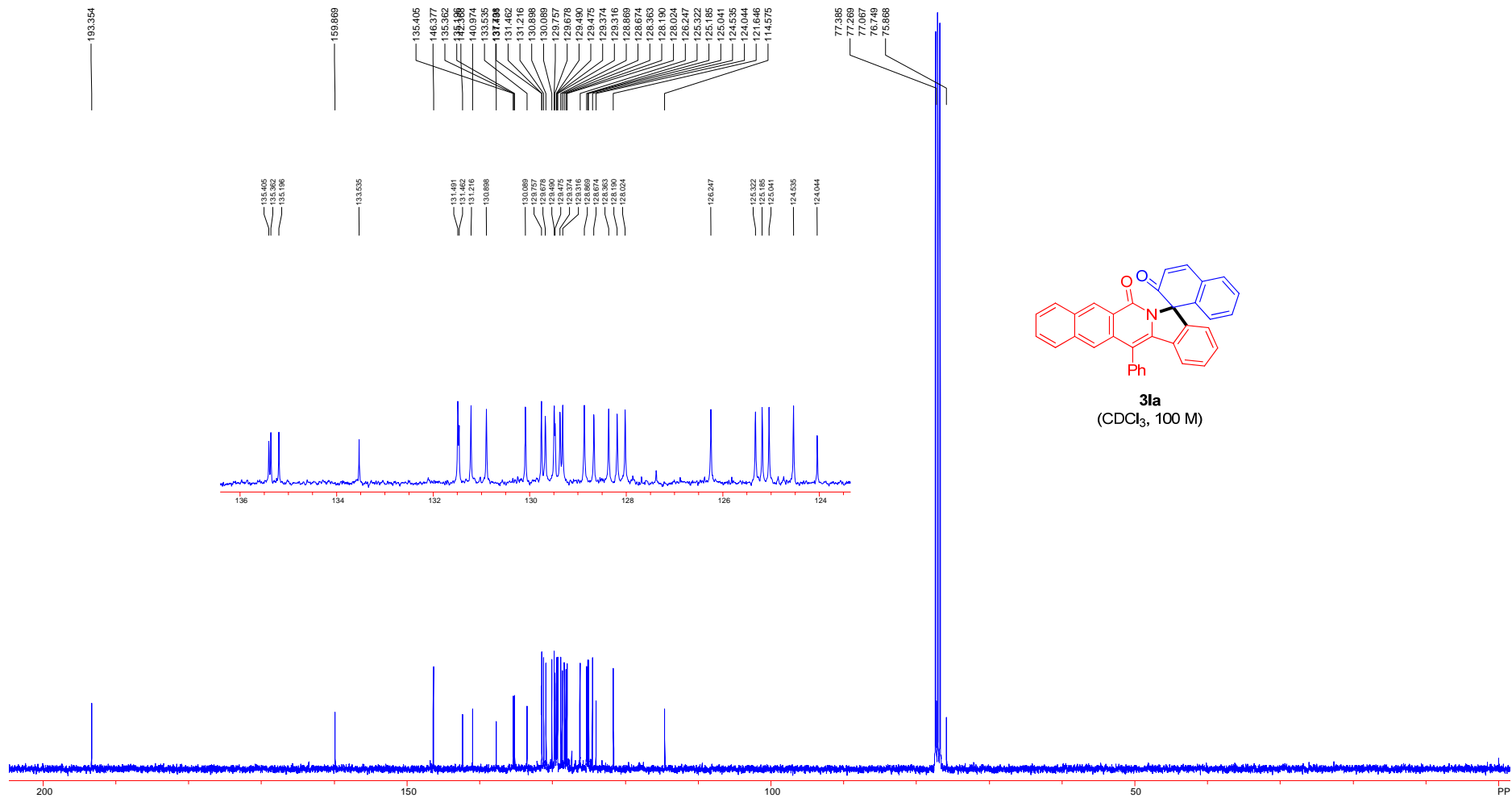


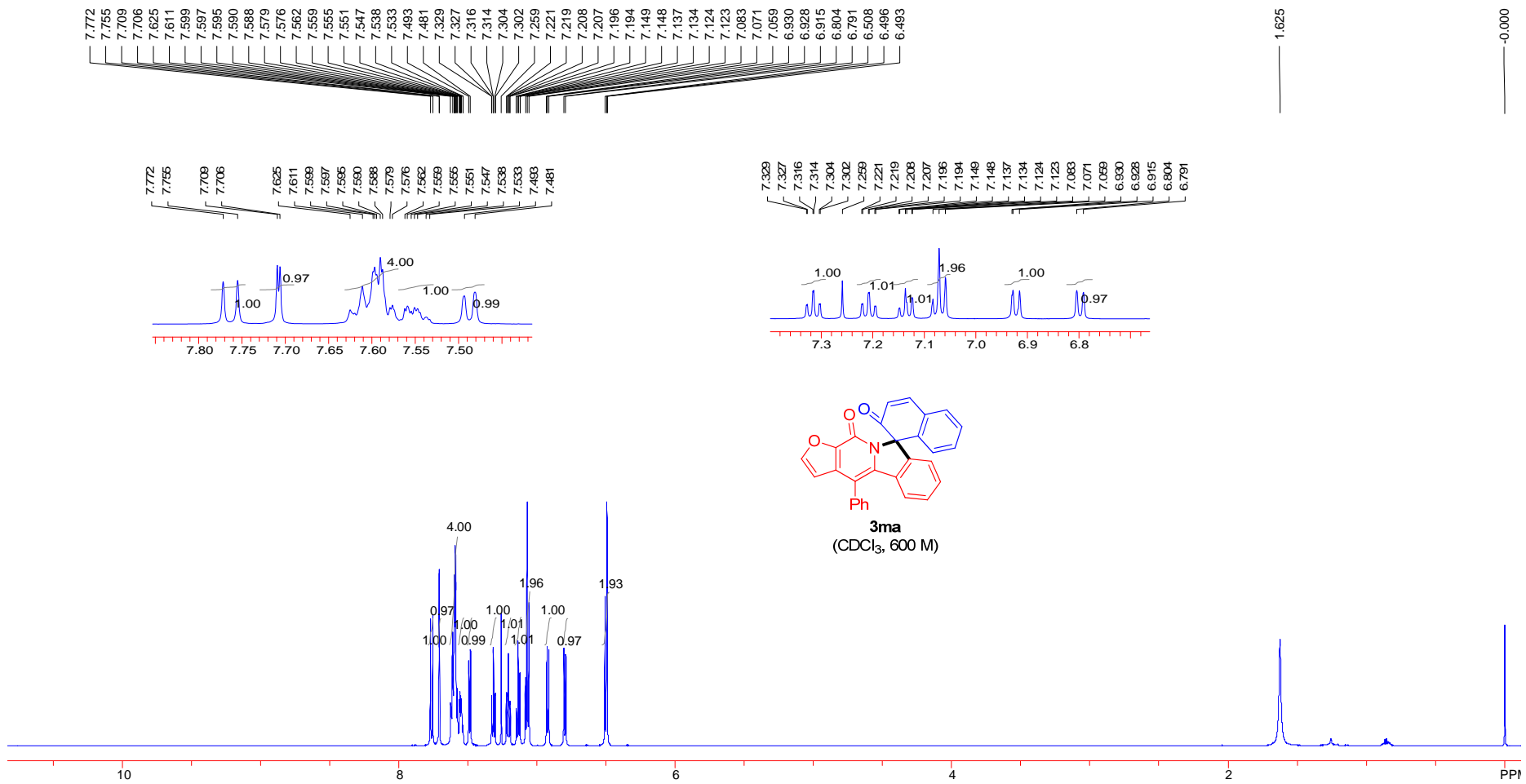


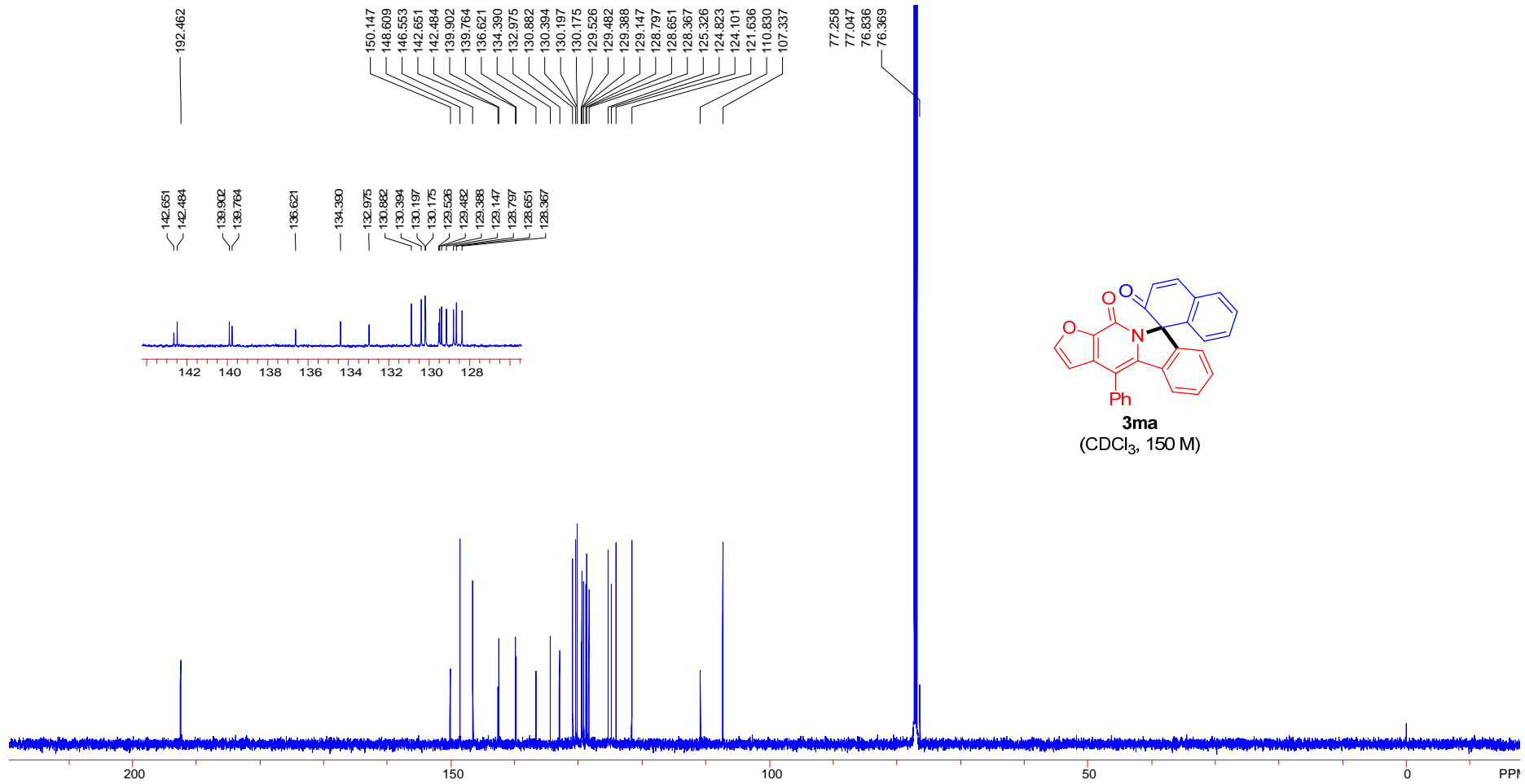


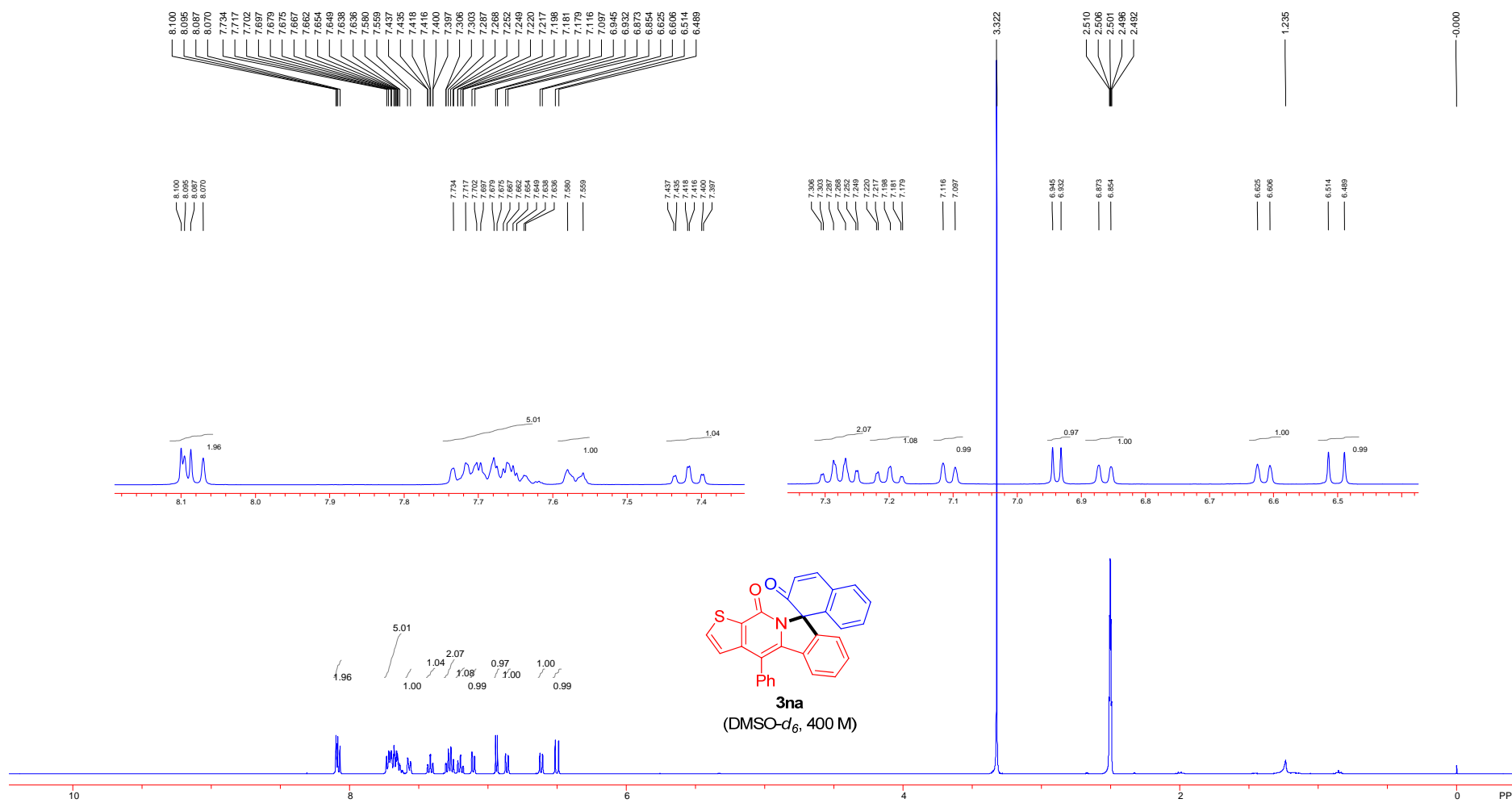


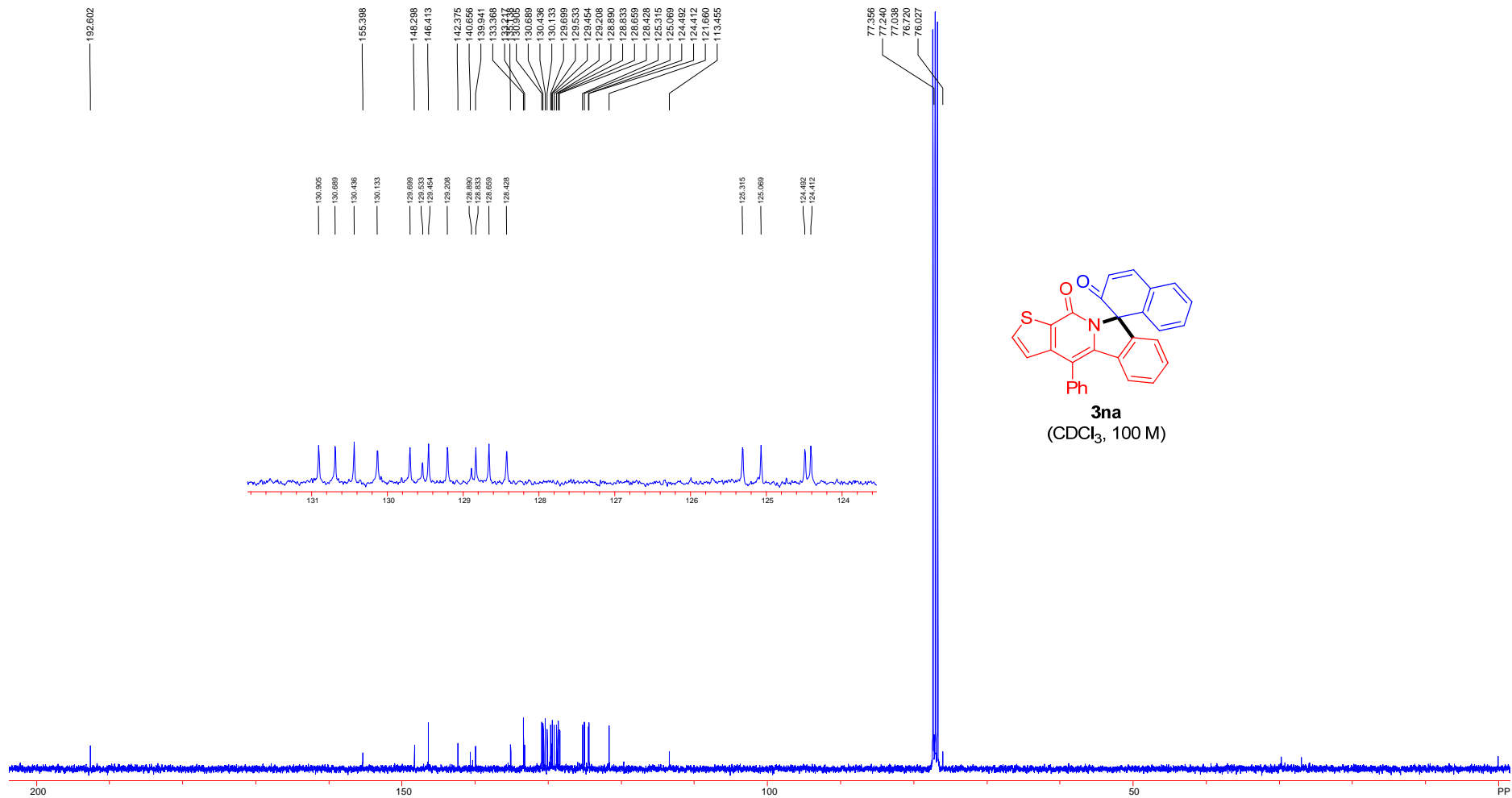


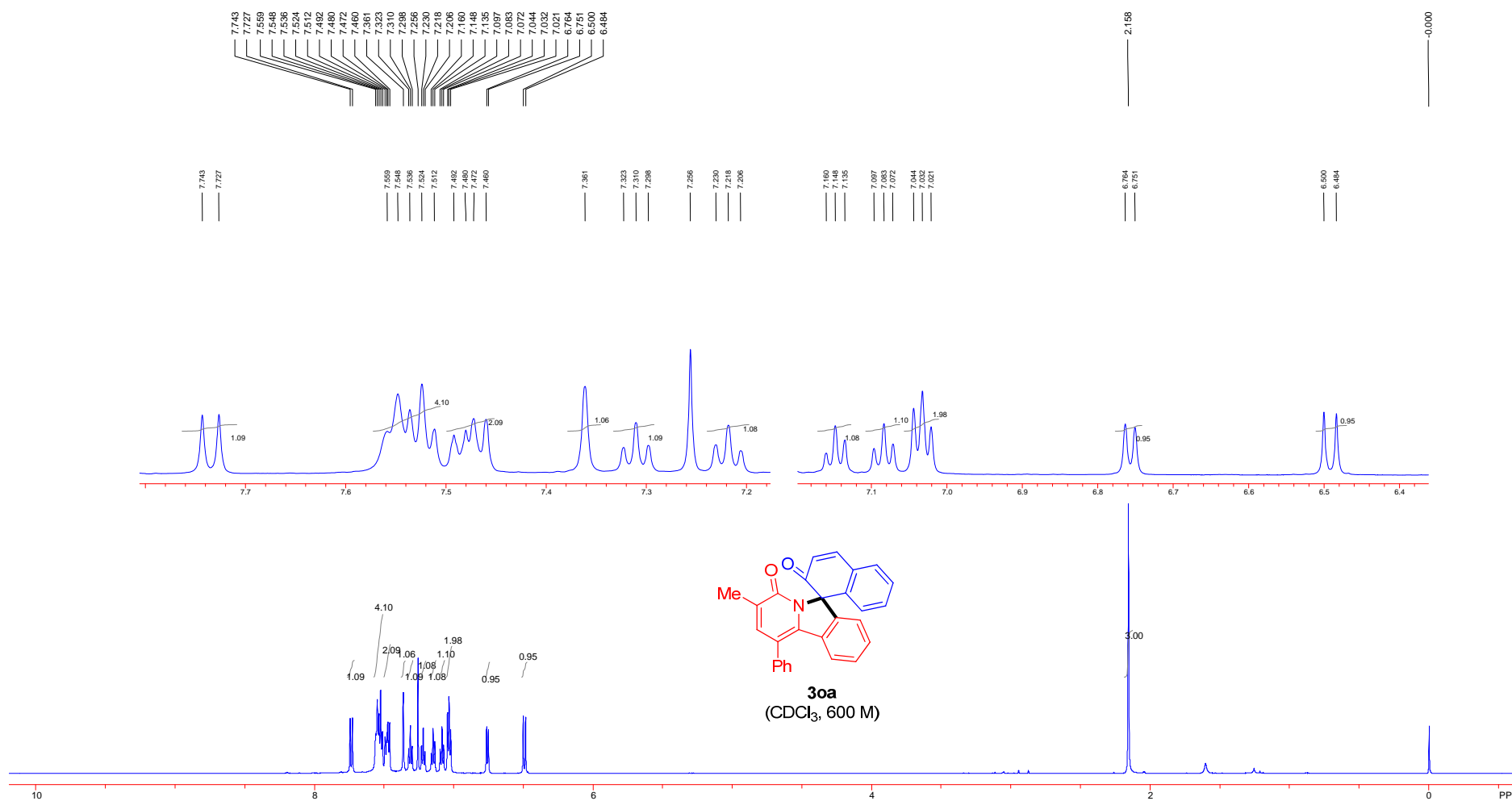


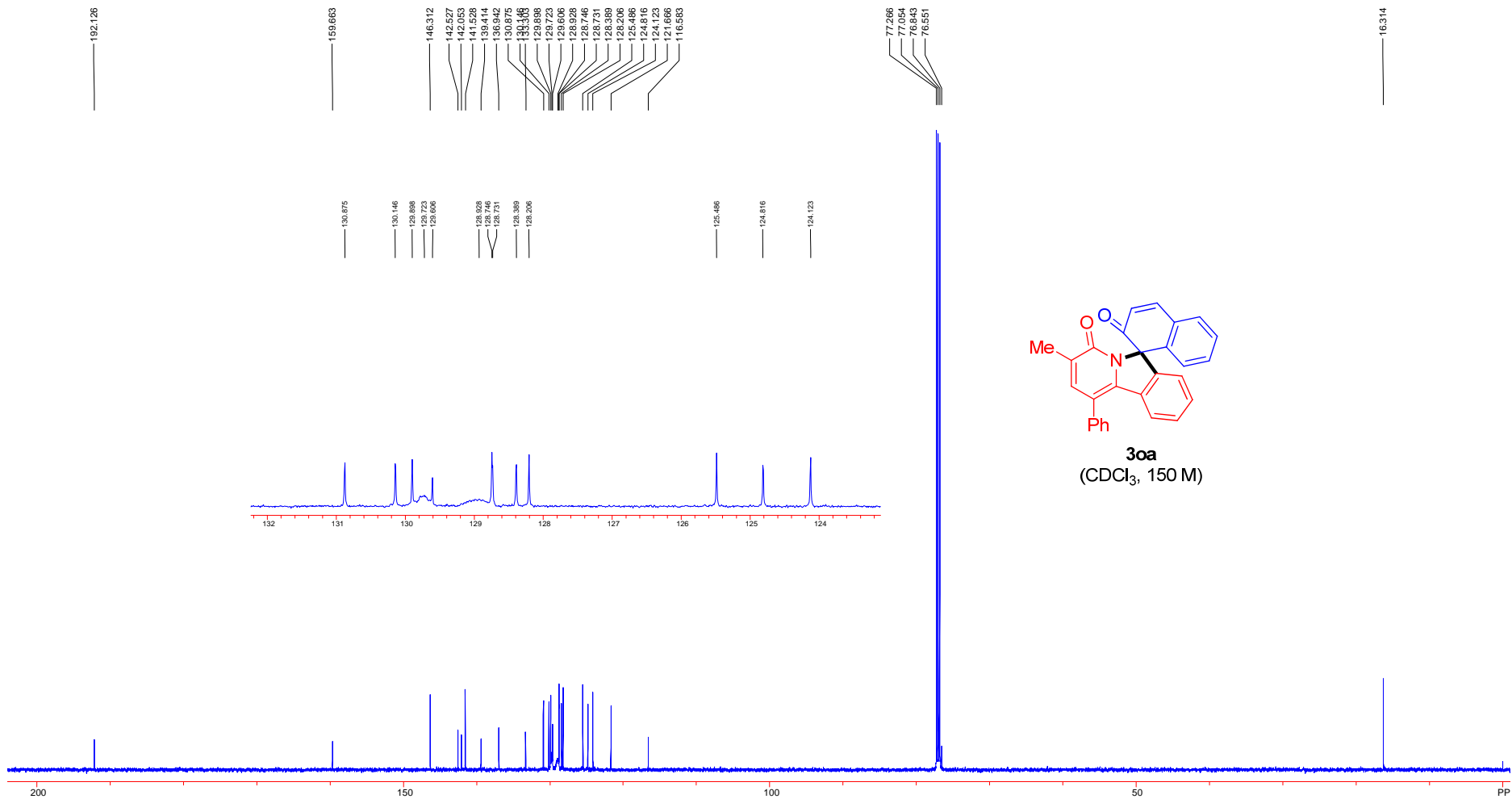


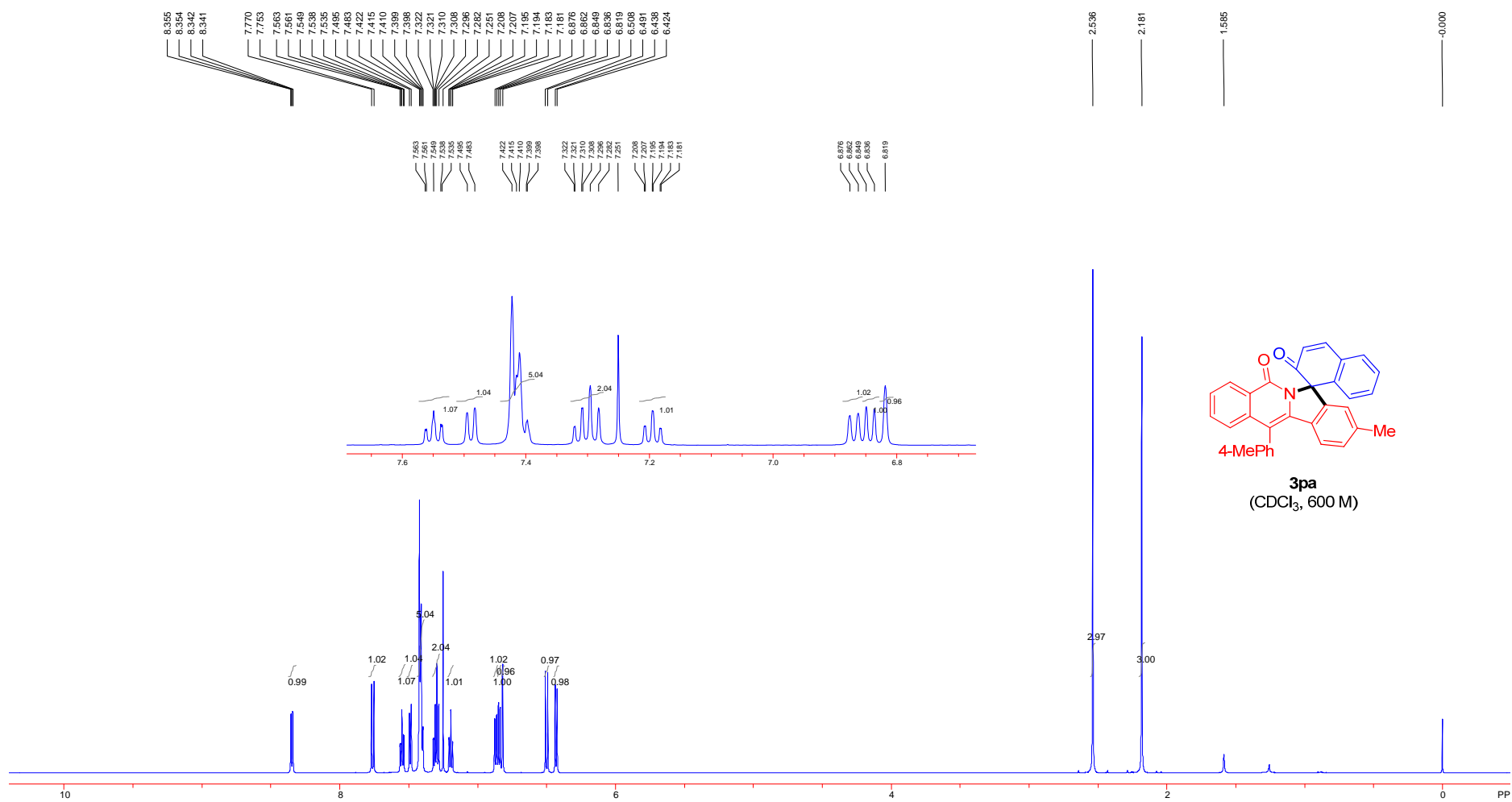


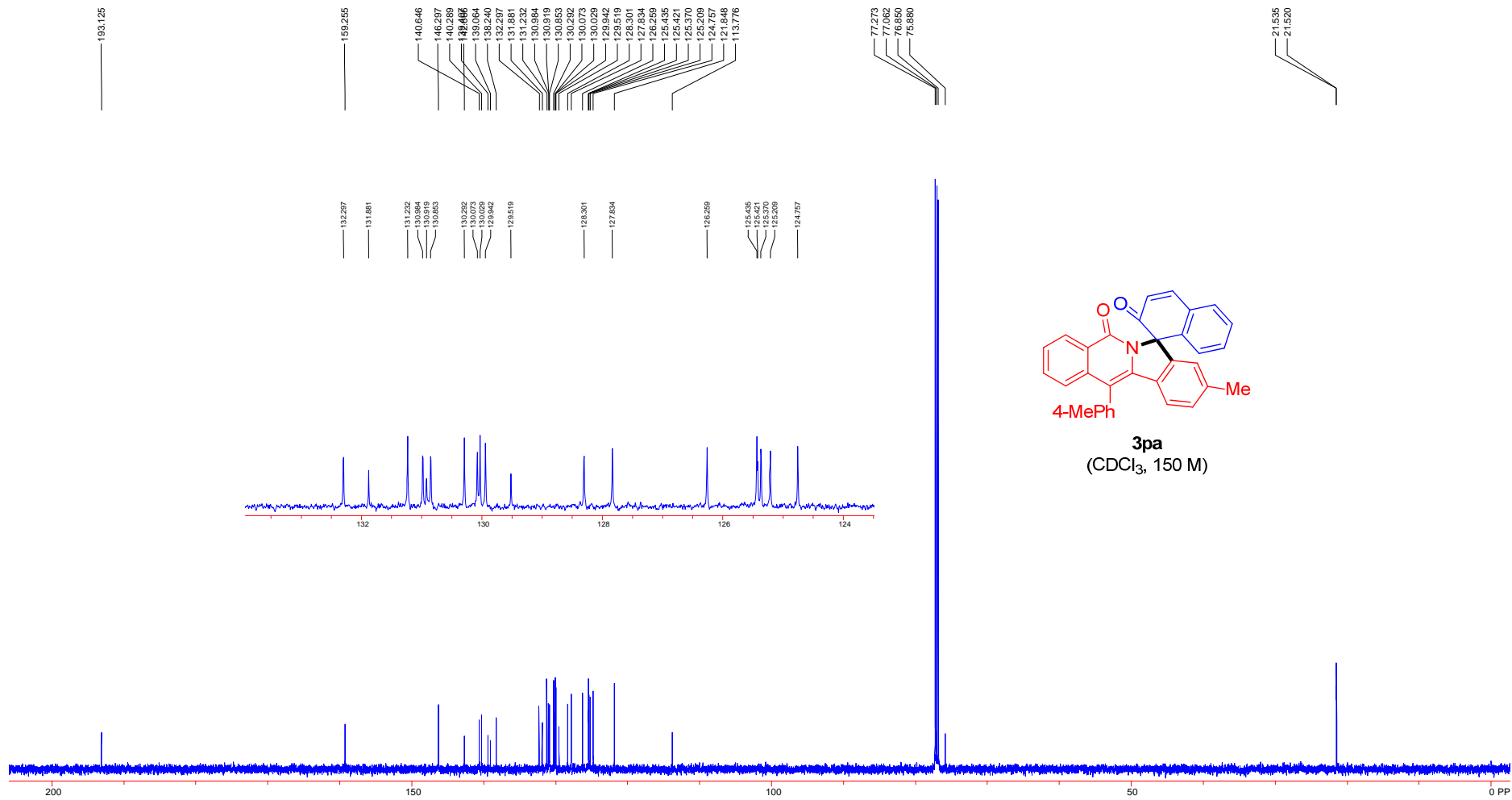


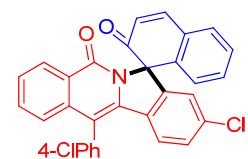
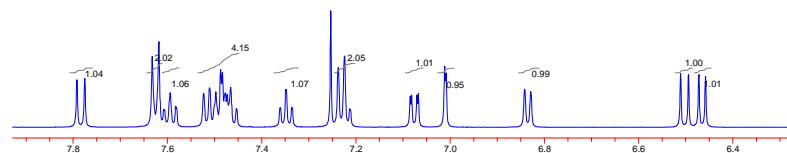
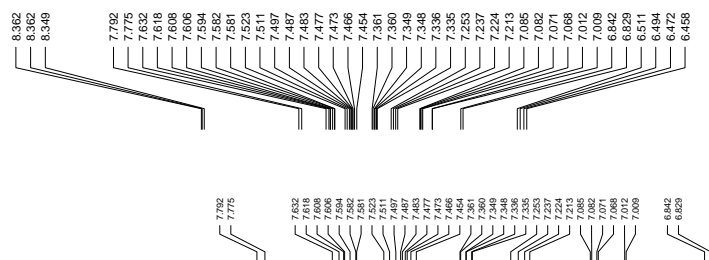




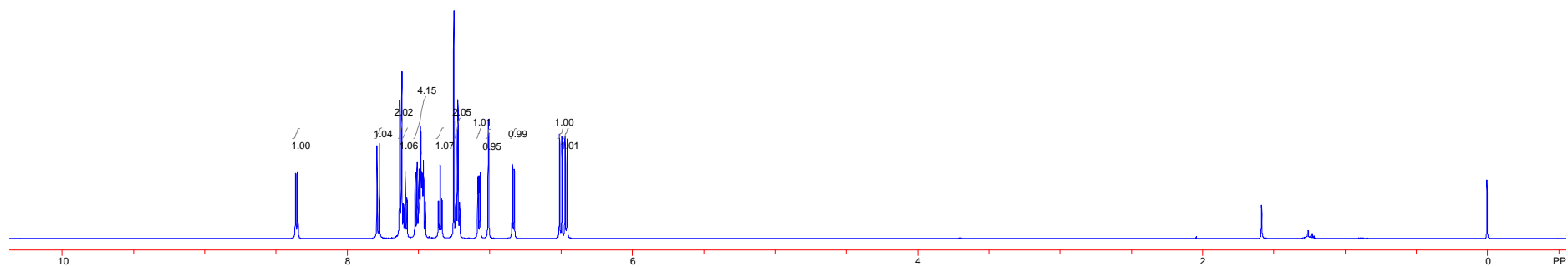


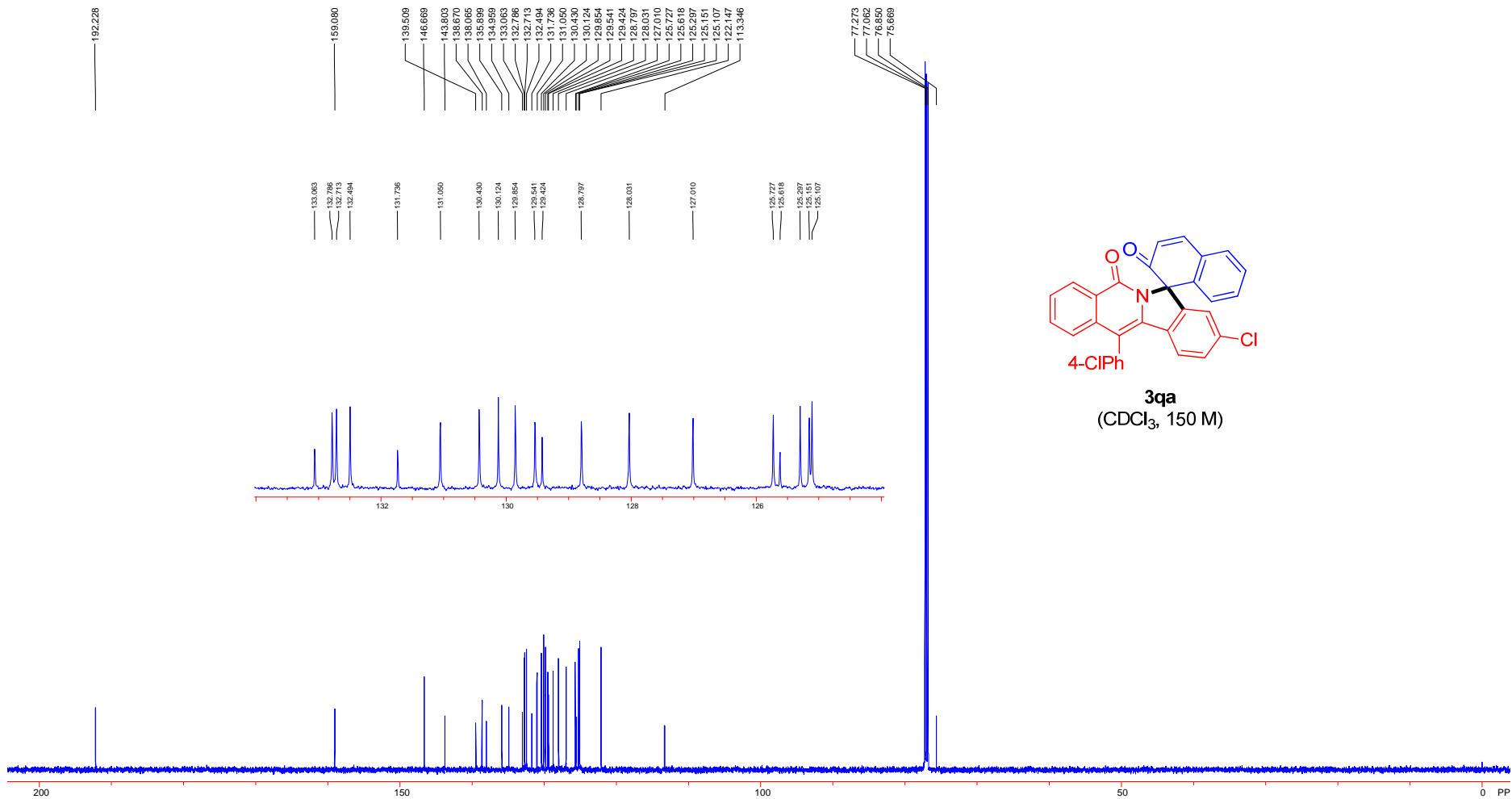


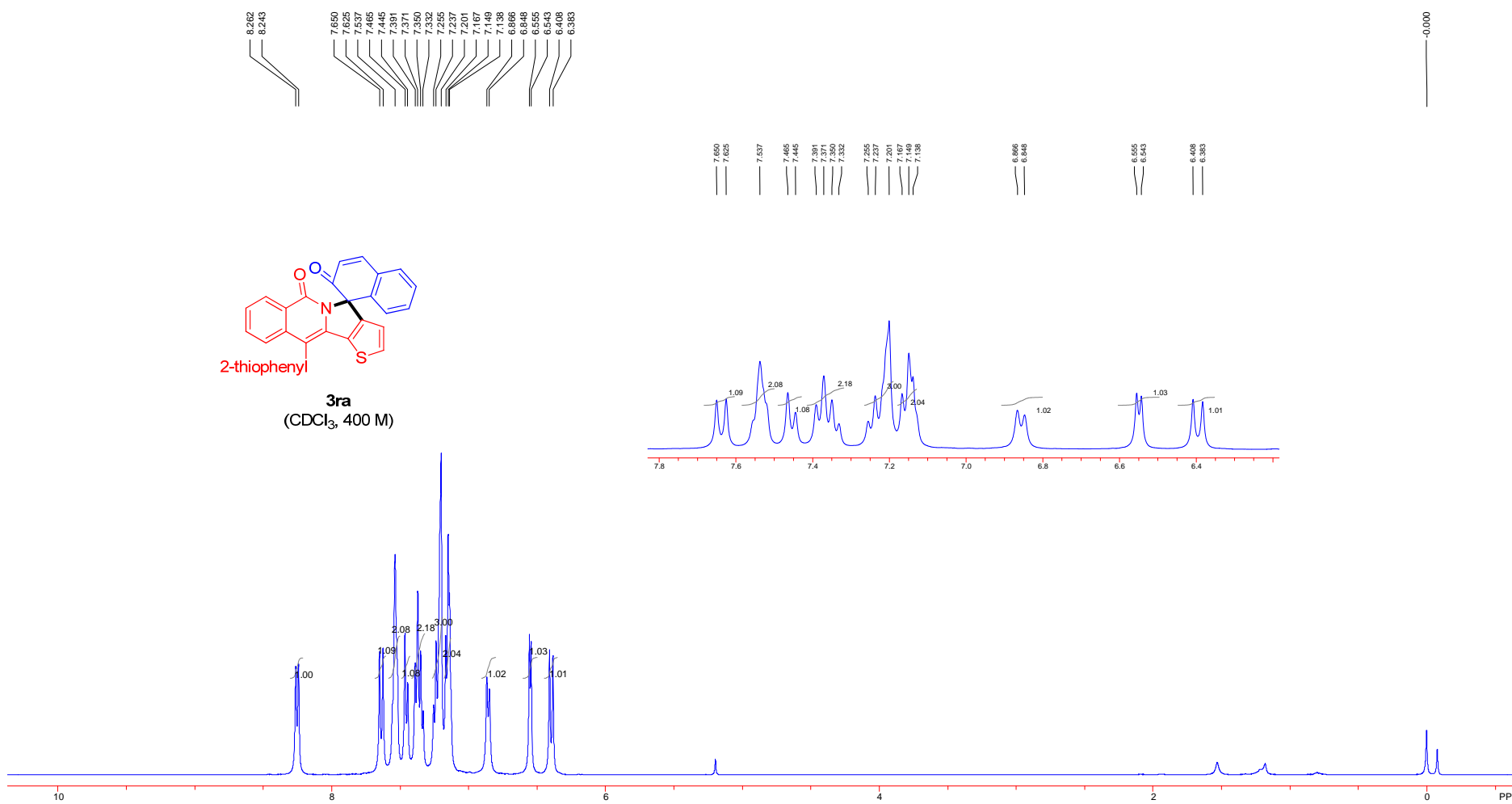


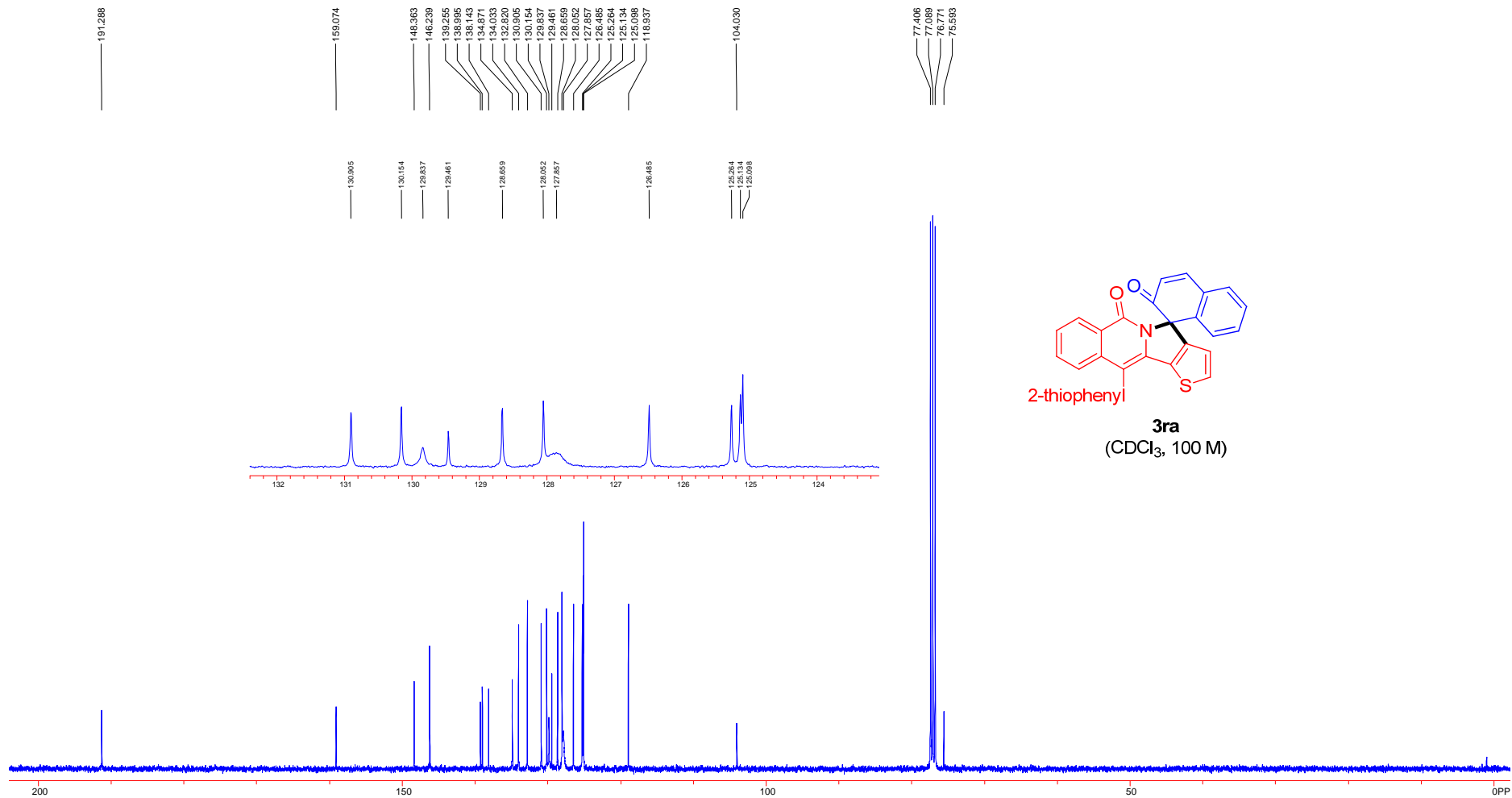


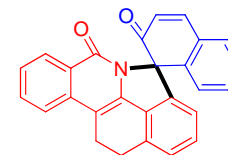
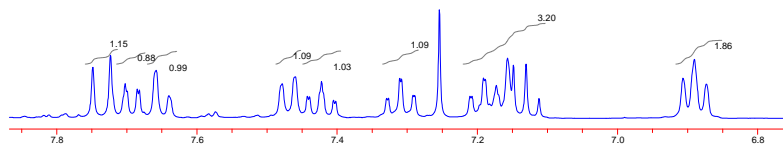
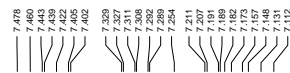
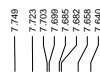
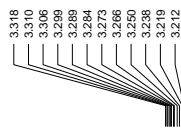
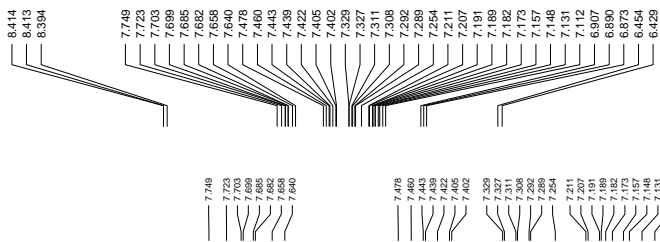
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(CDCl₃, 600 M)



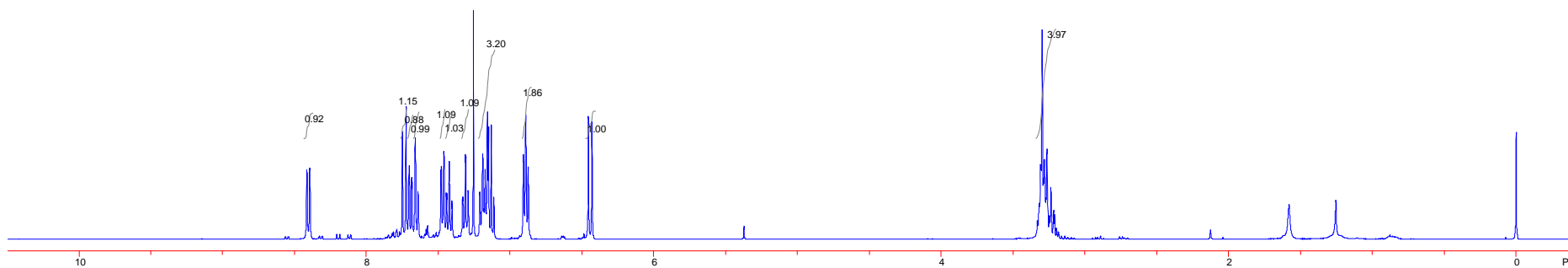


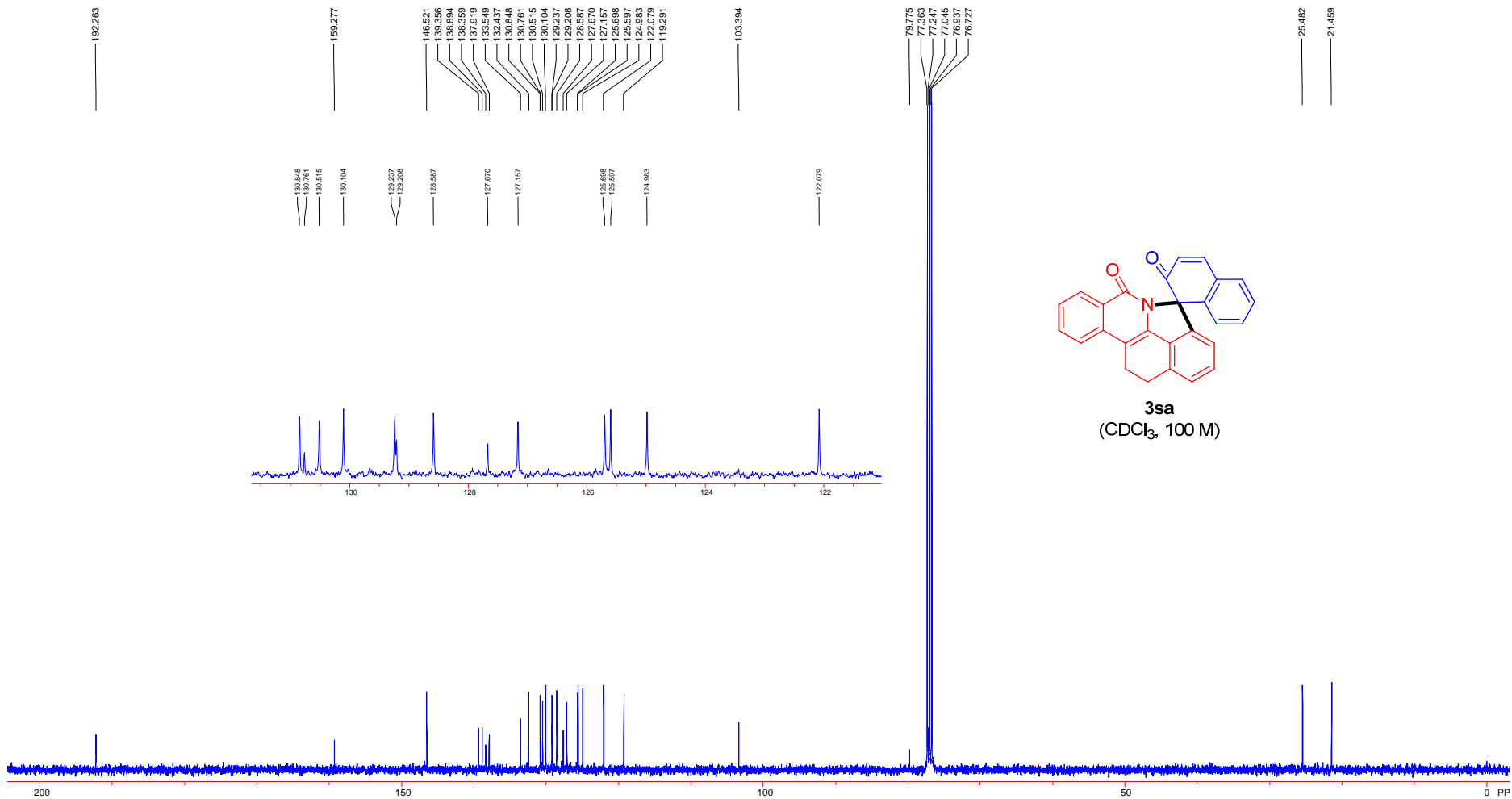


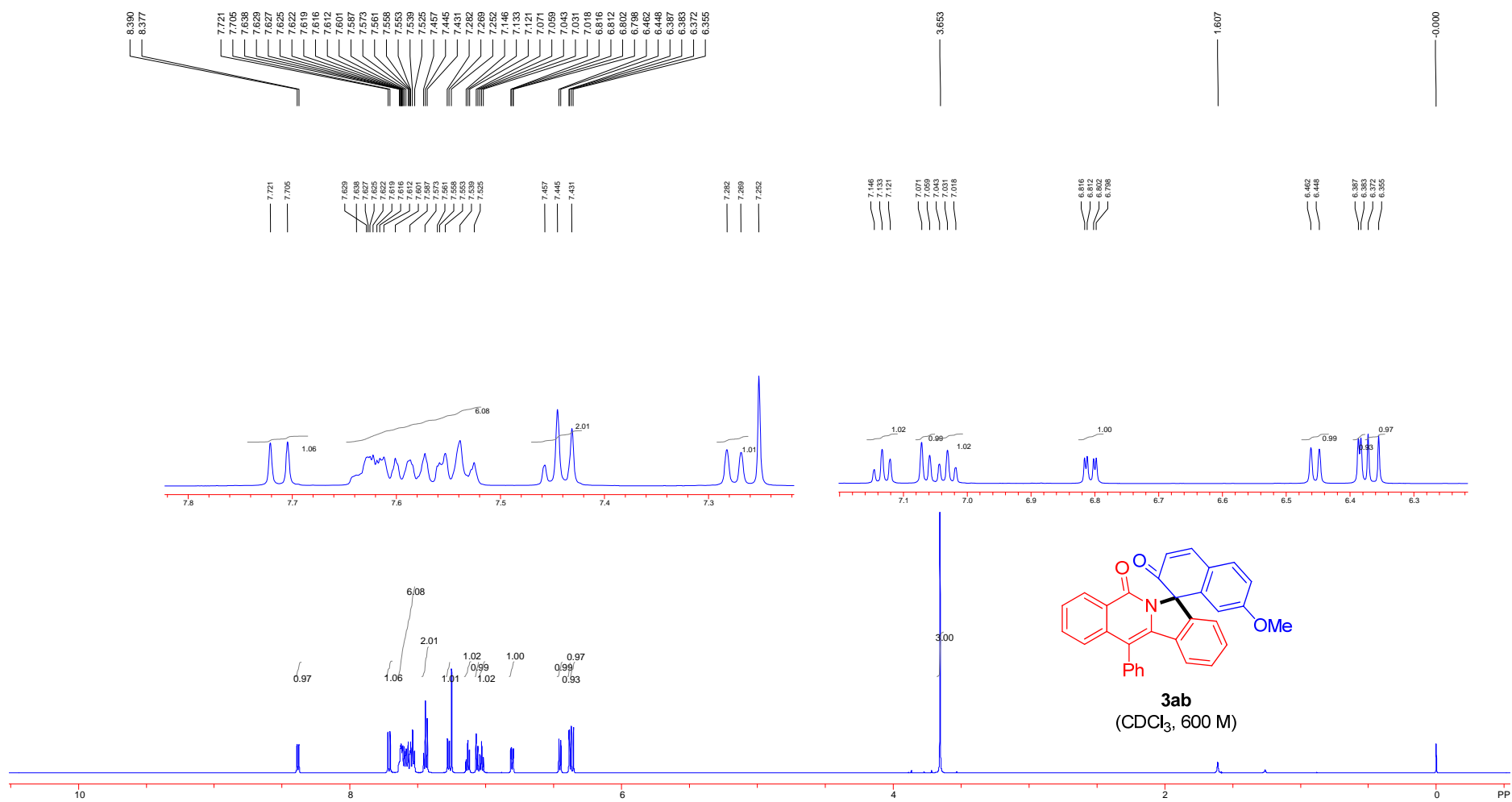


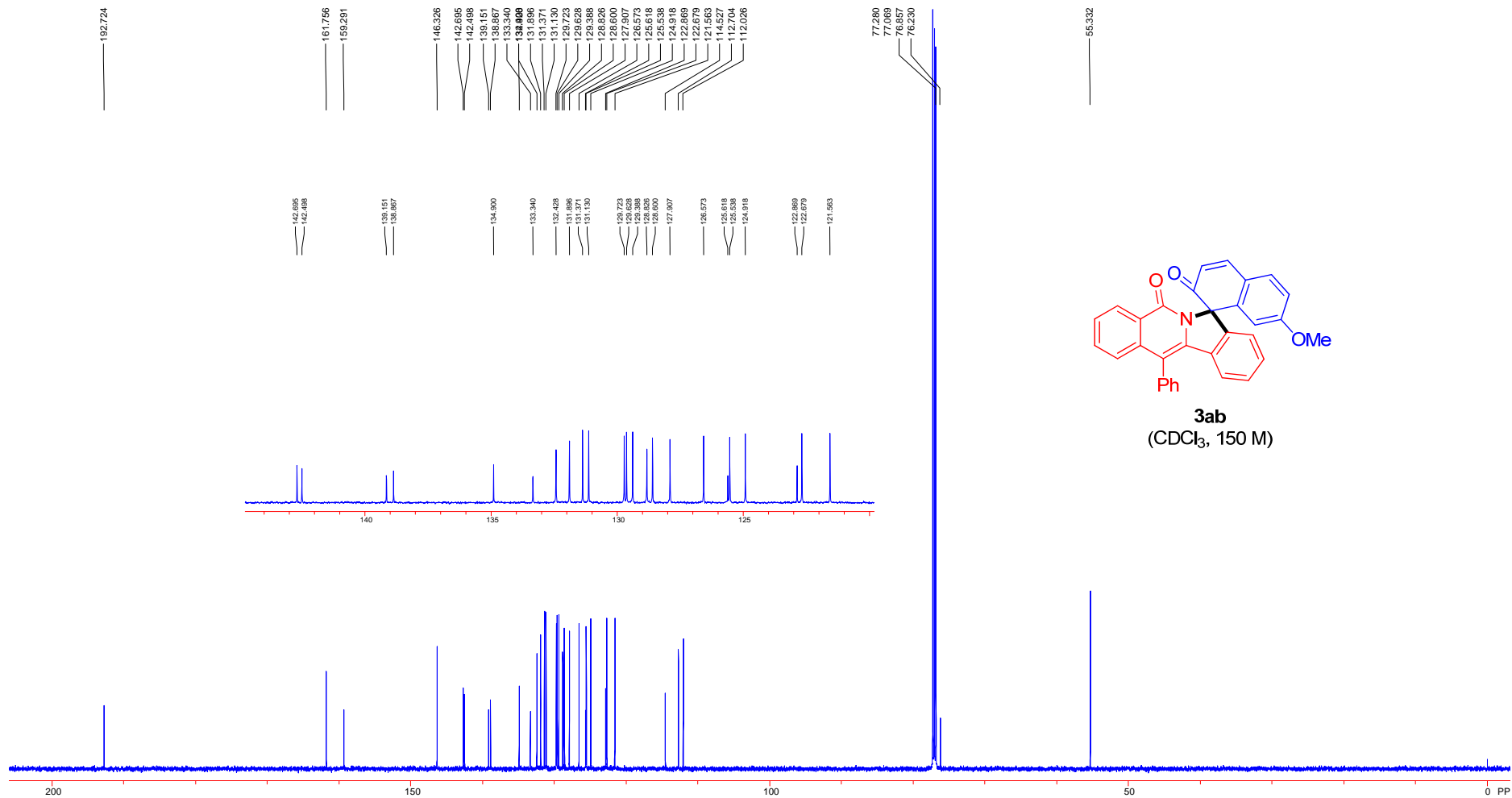


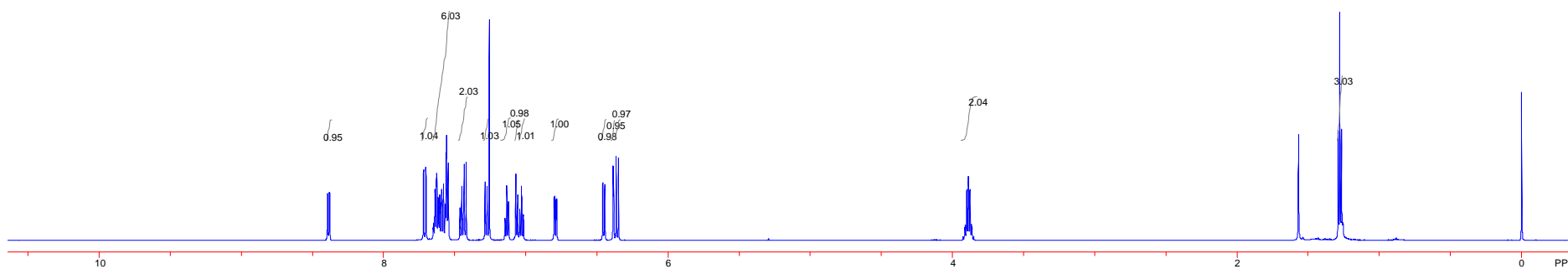
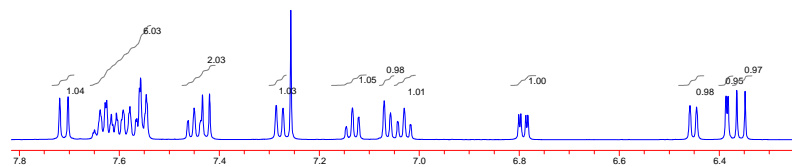
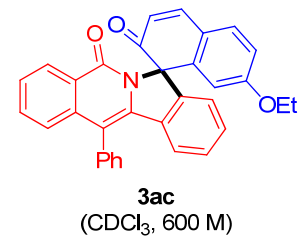
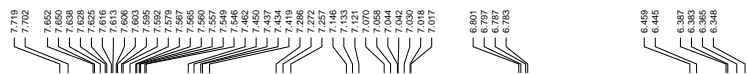
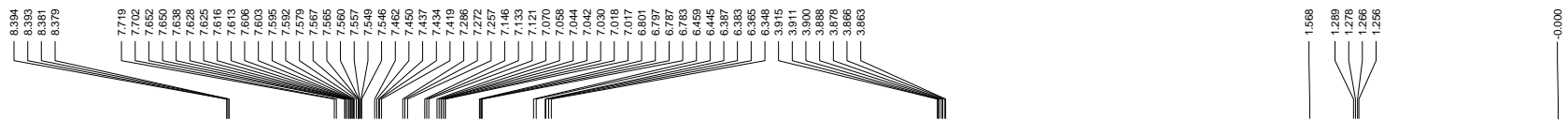
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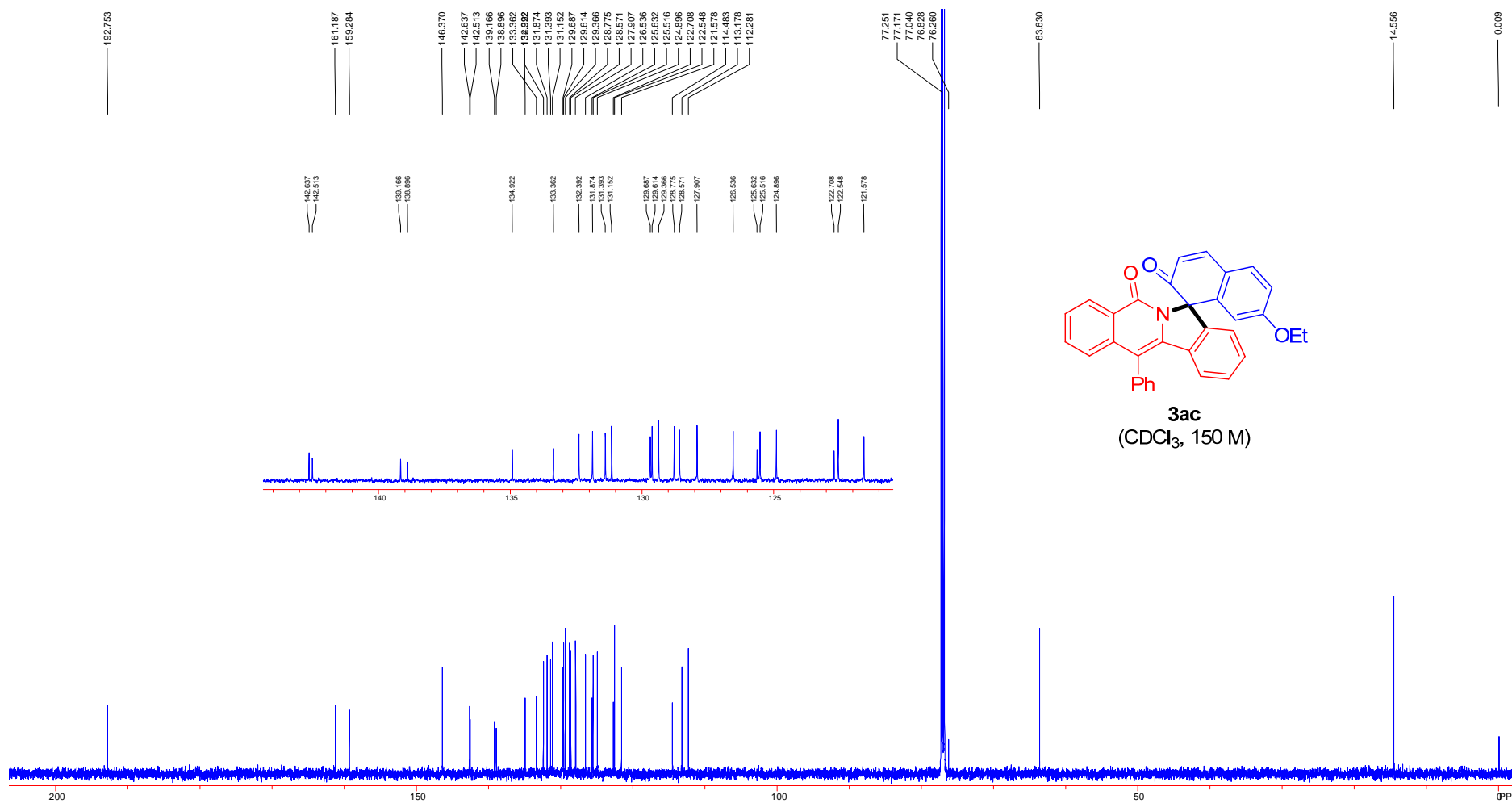


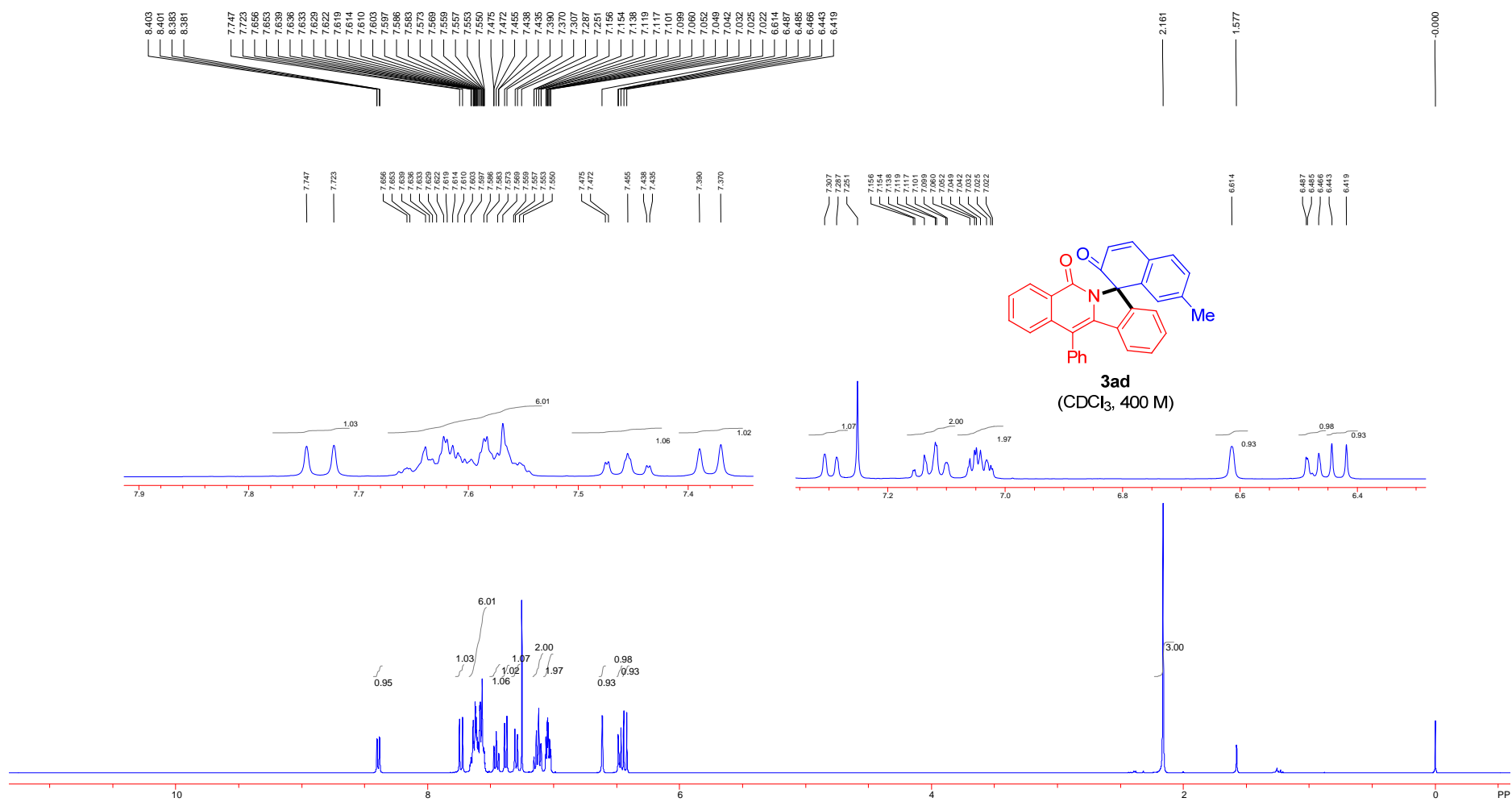


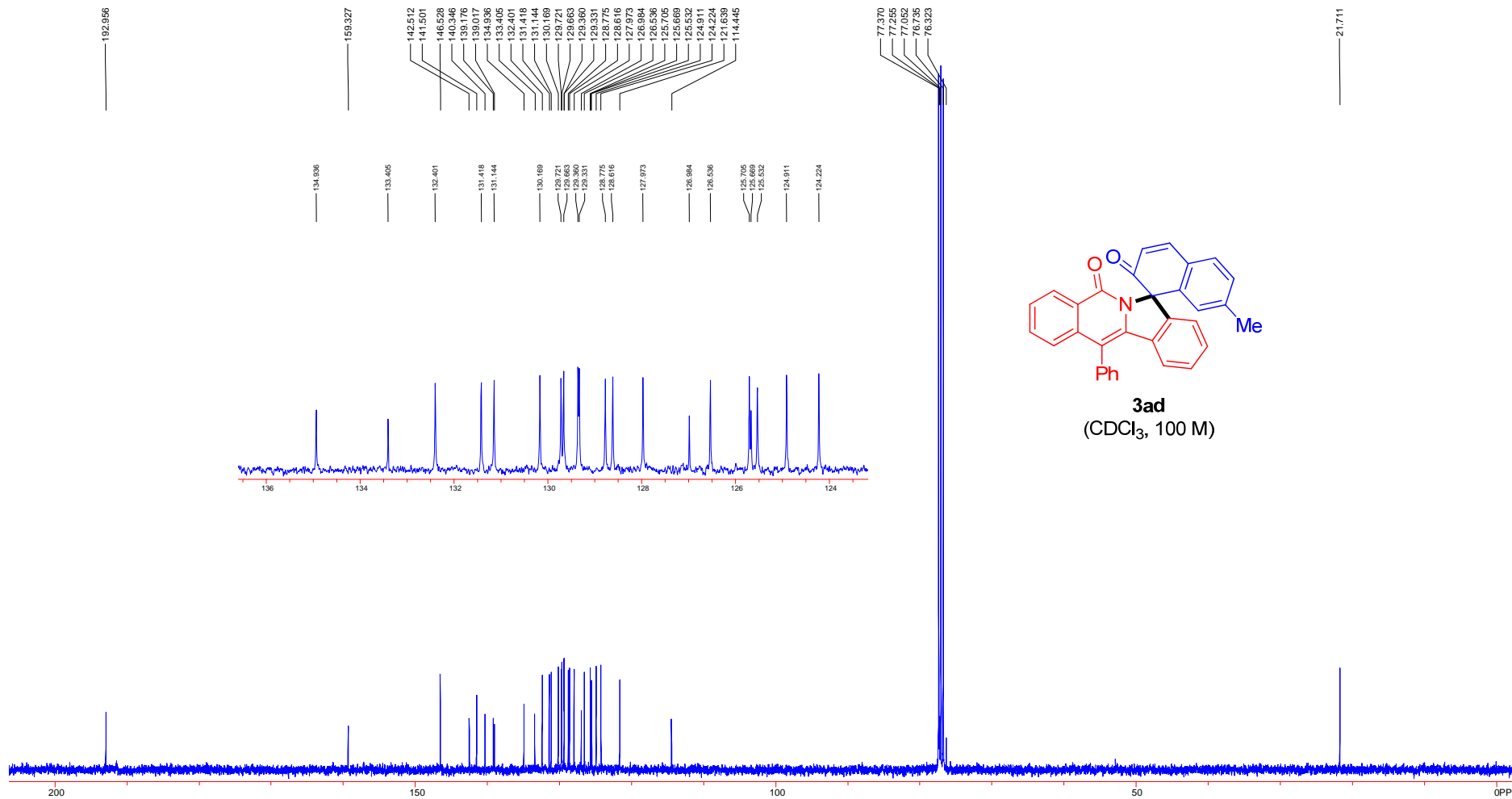


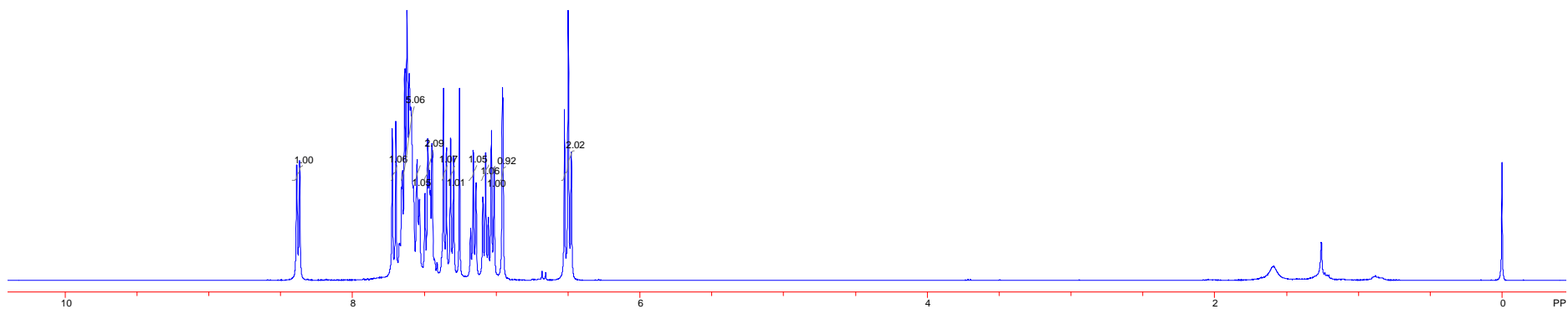
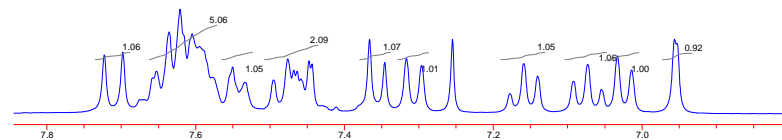
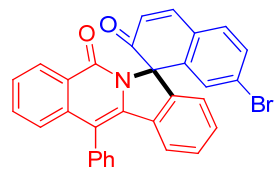
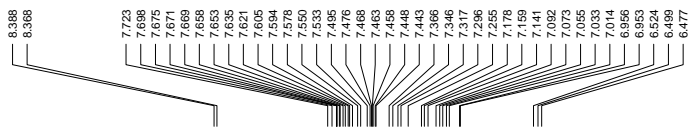


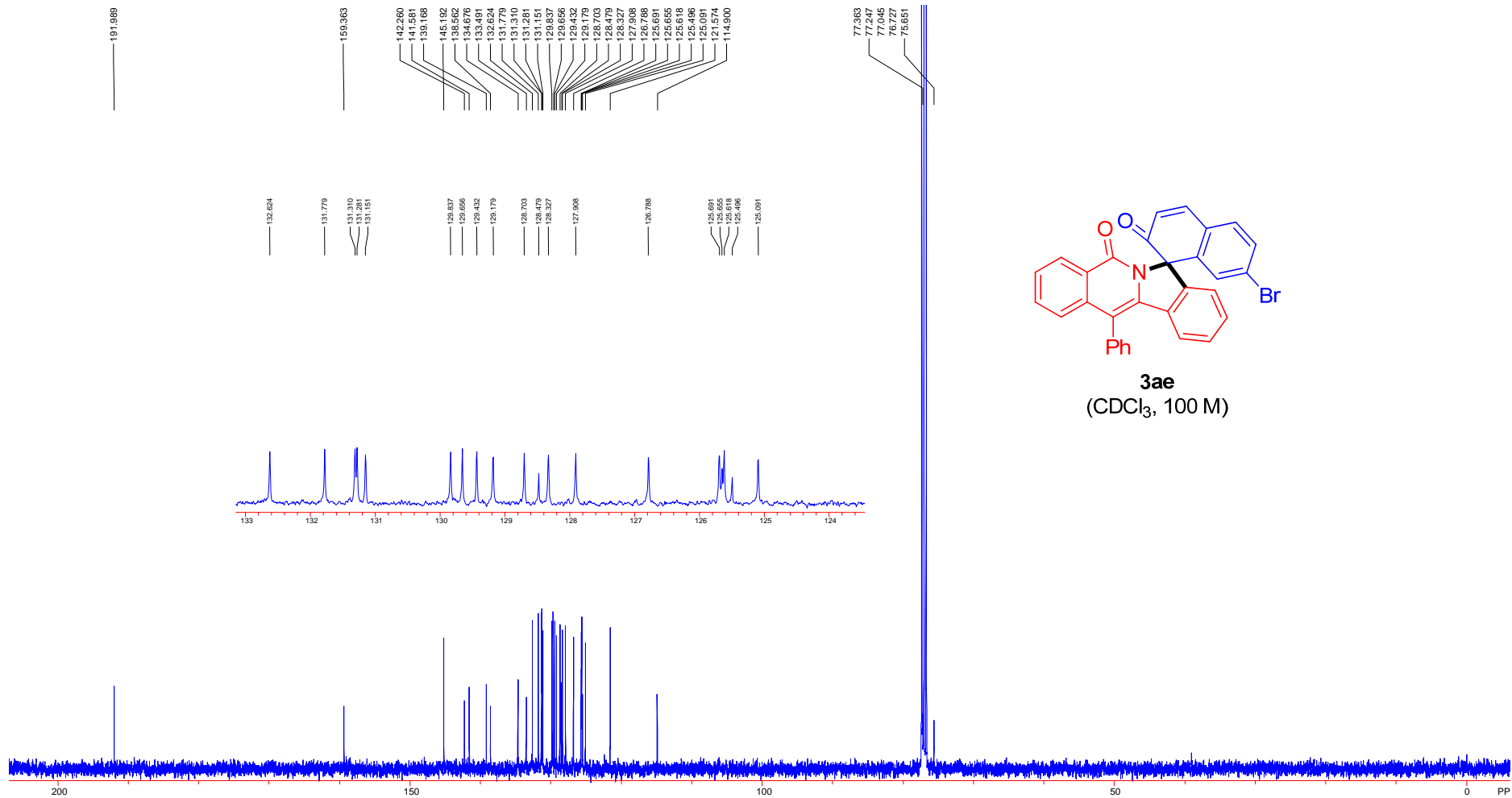


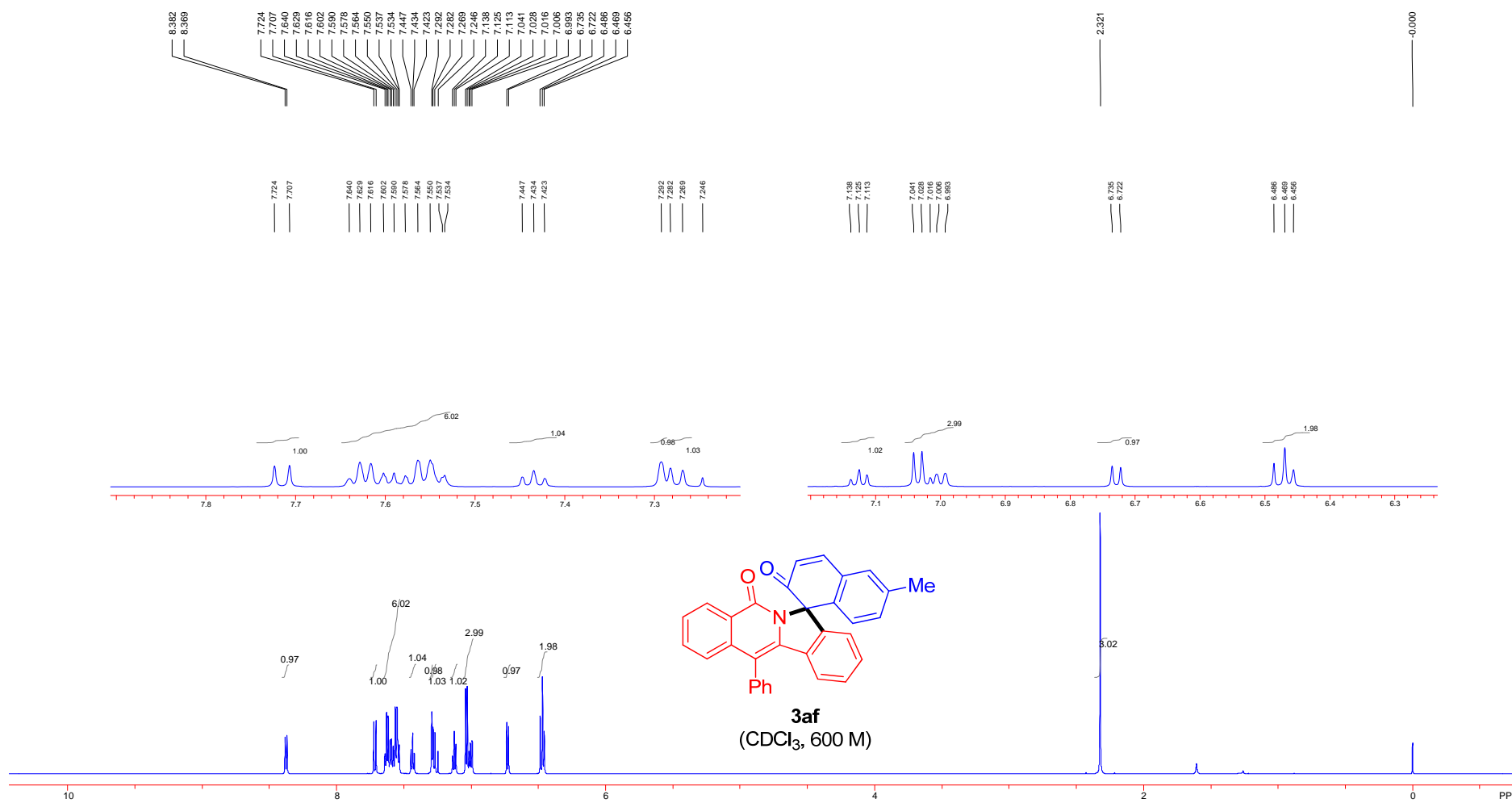


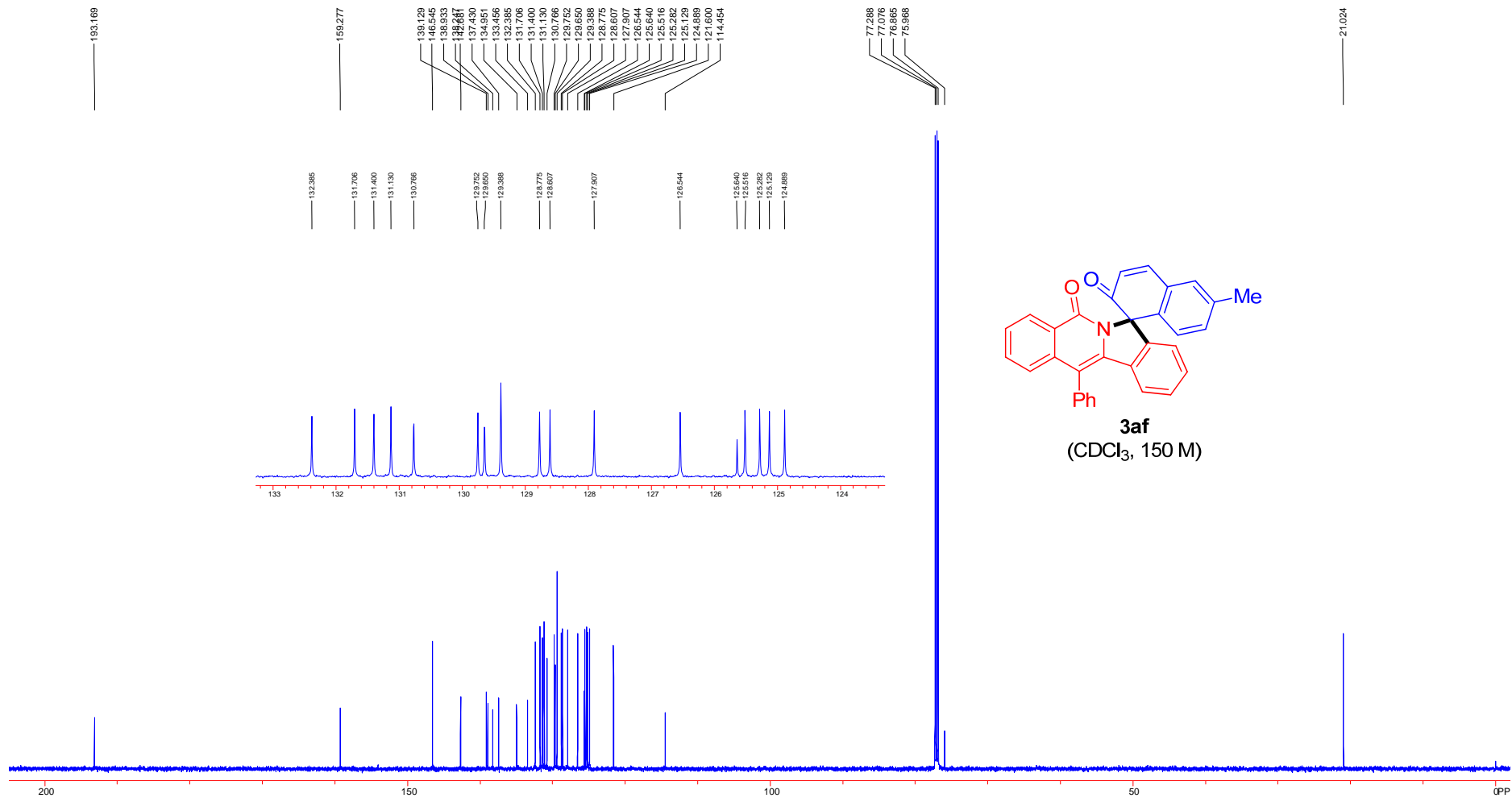


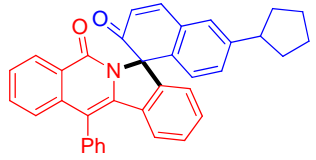
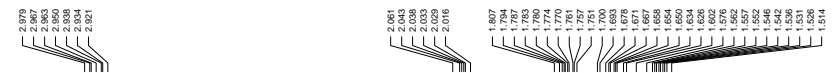
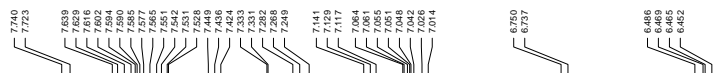
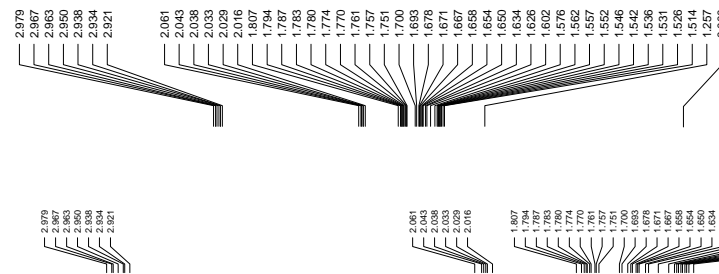
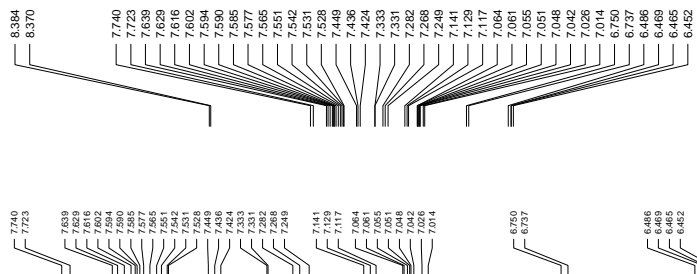




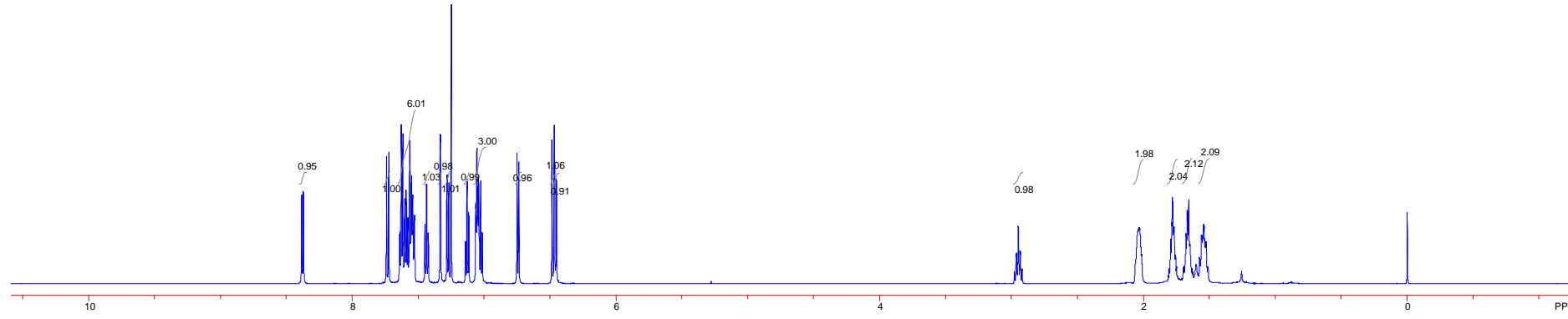
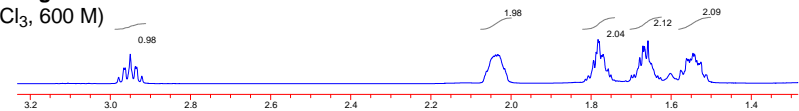
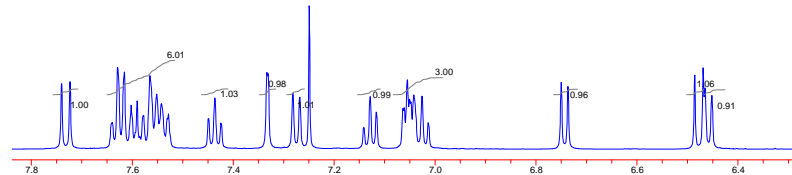


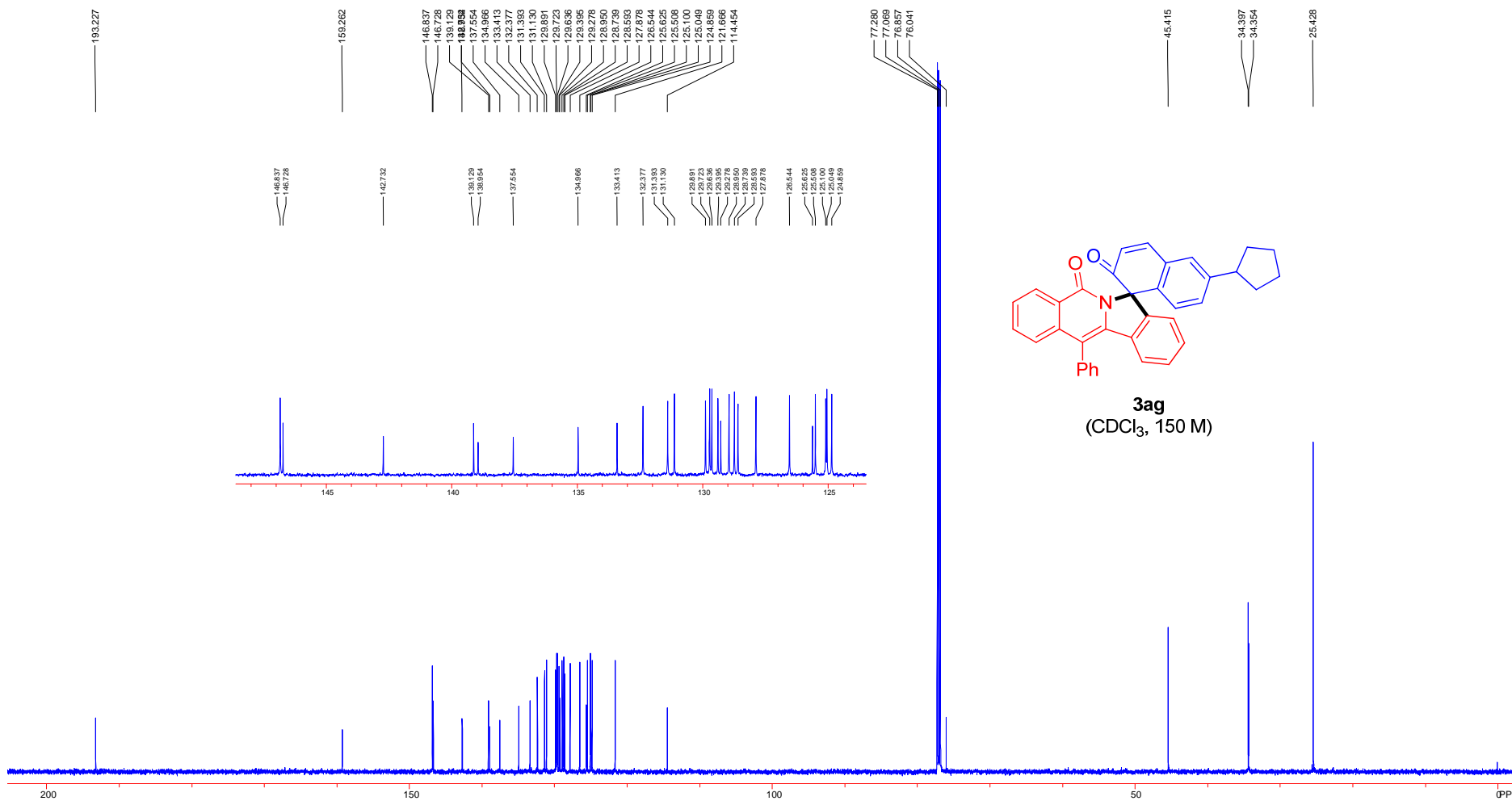


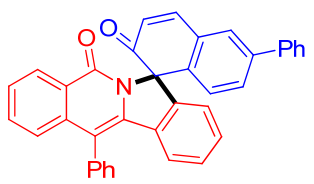
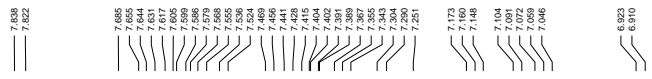
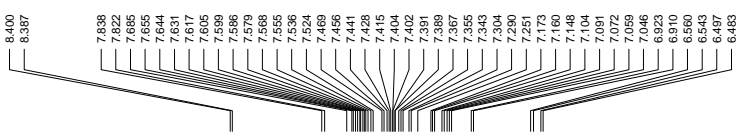




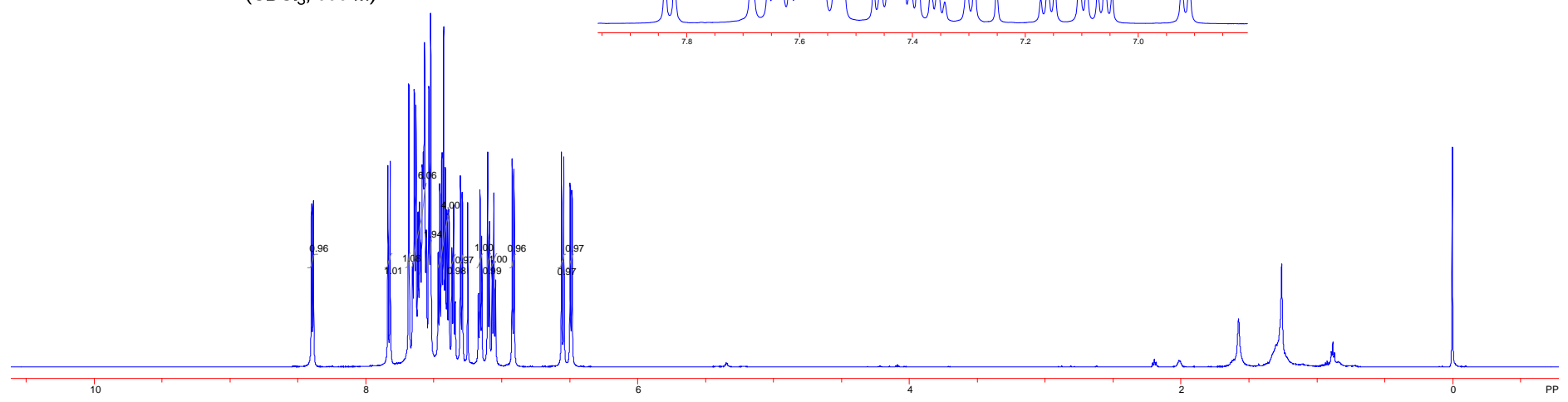
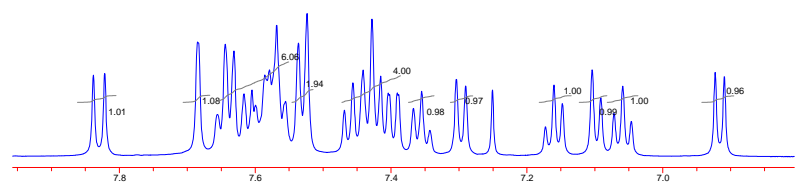
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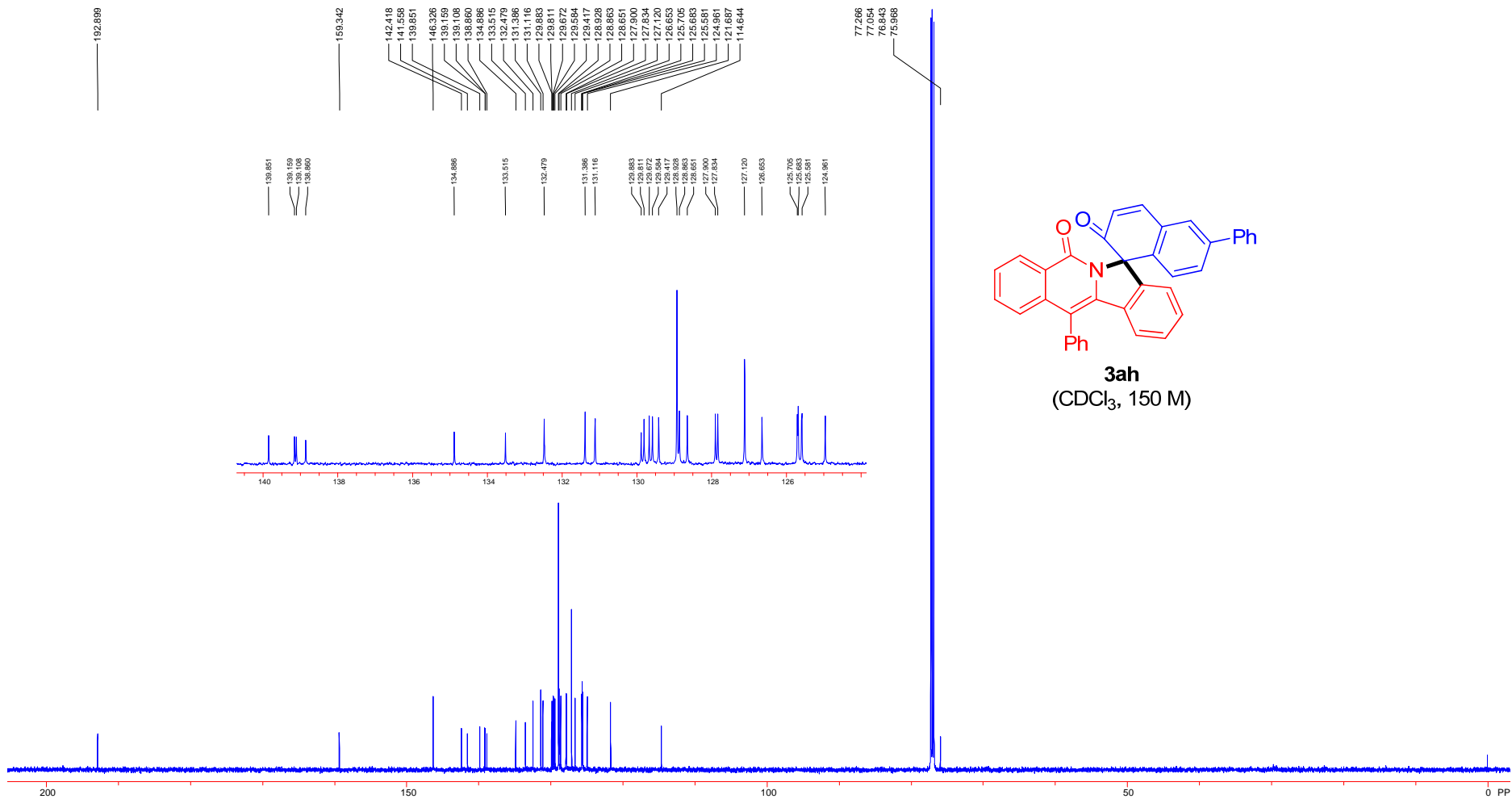


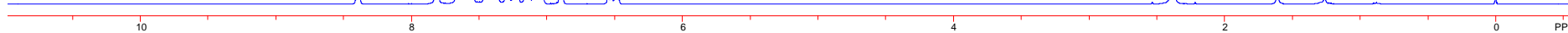
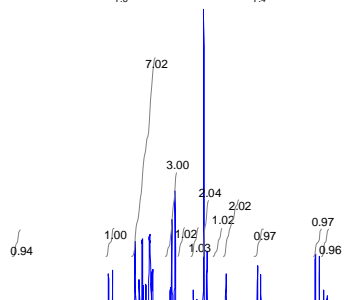
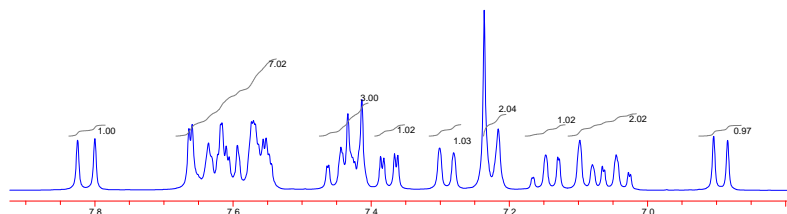
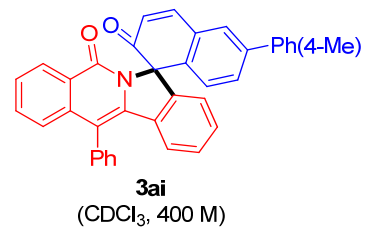
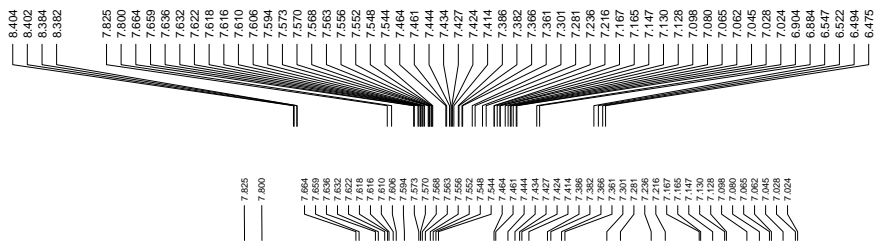


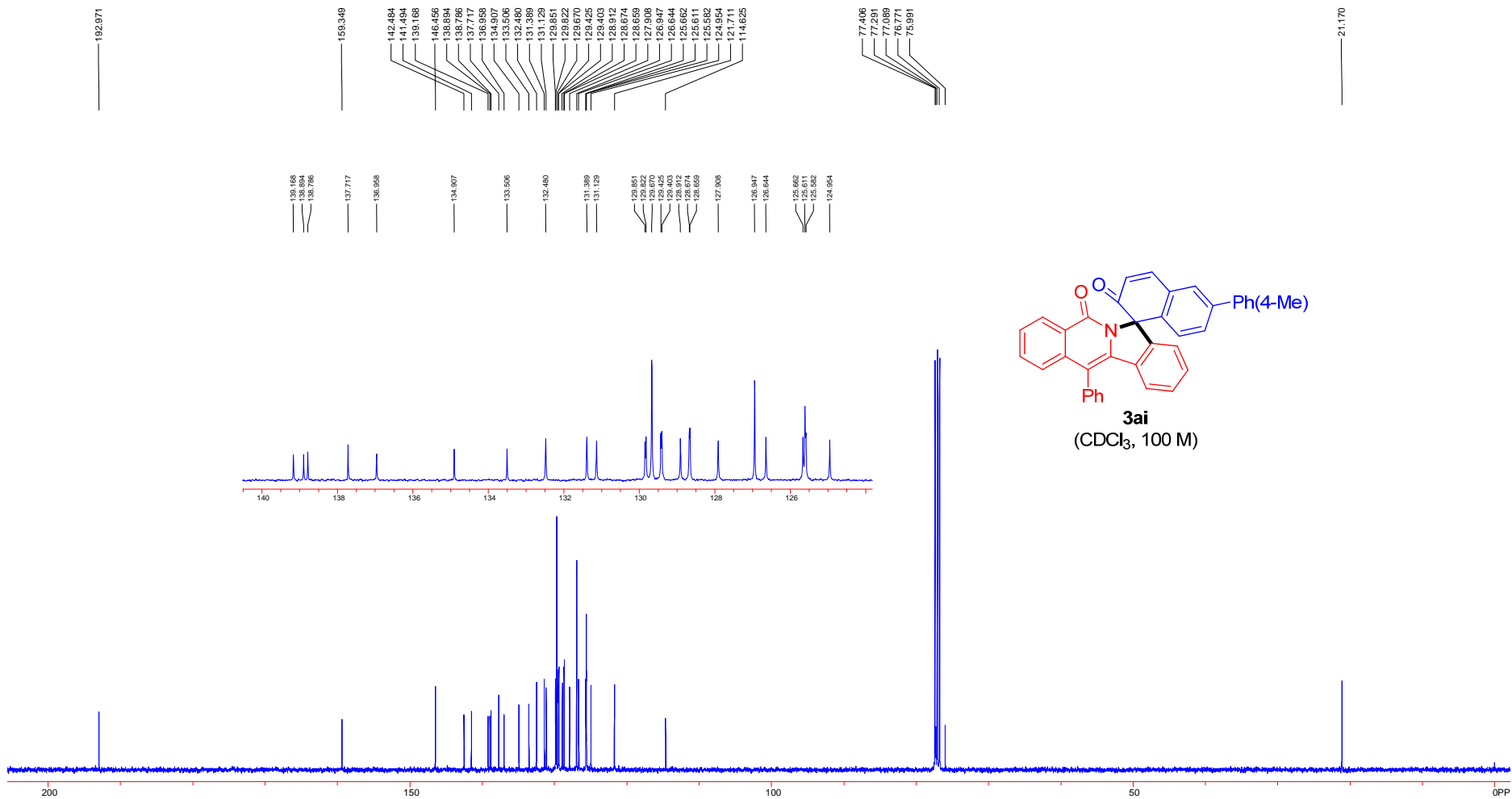


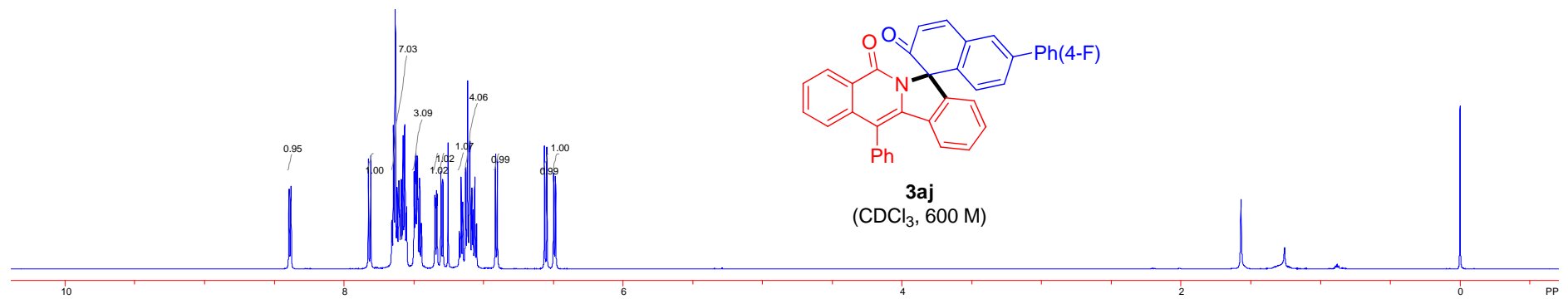
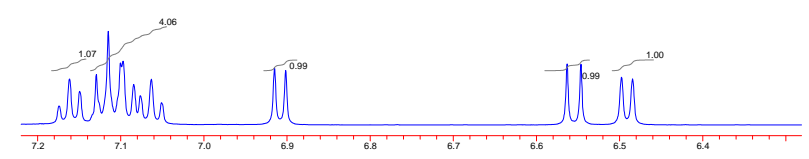
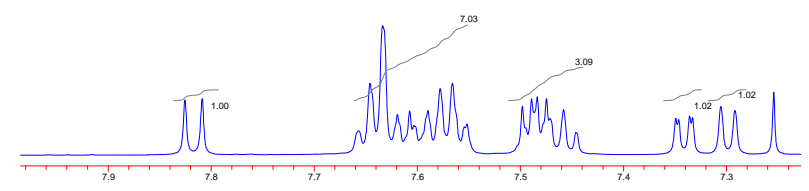
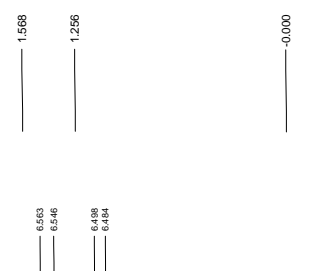
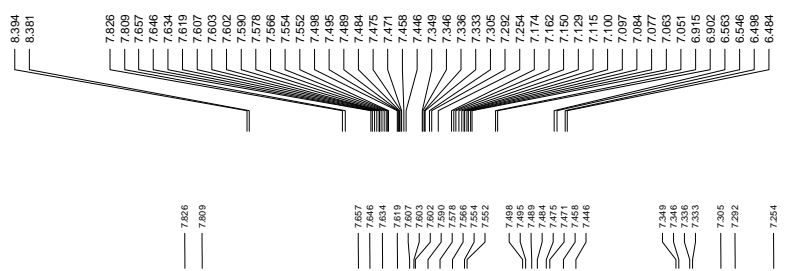
3ah
(CDCl₃, 600 M)

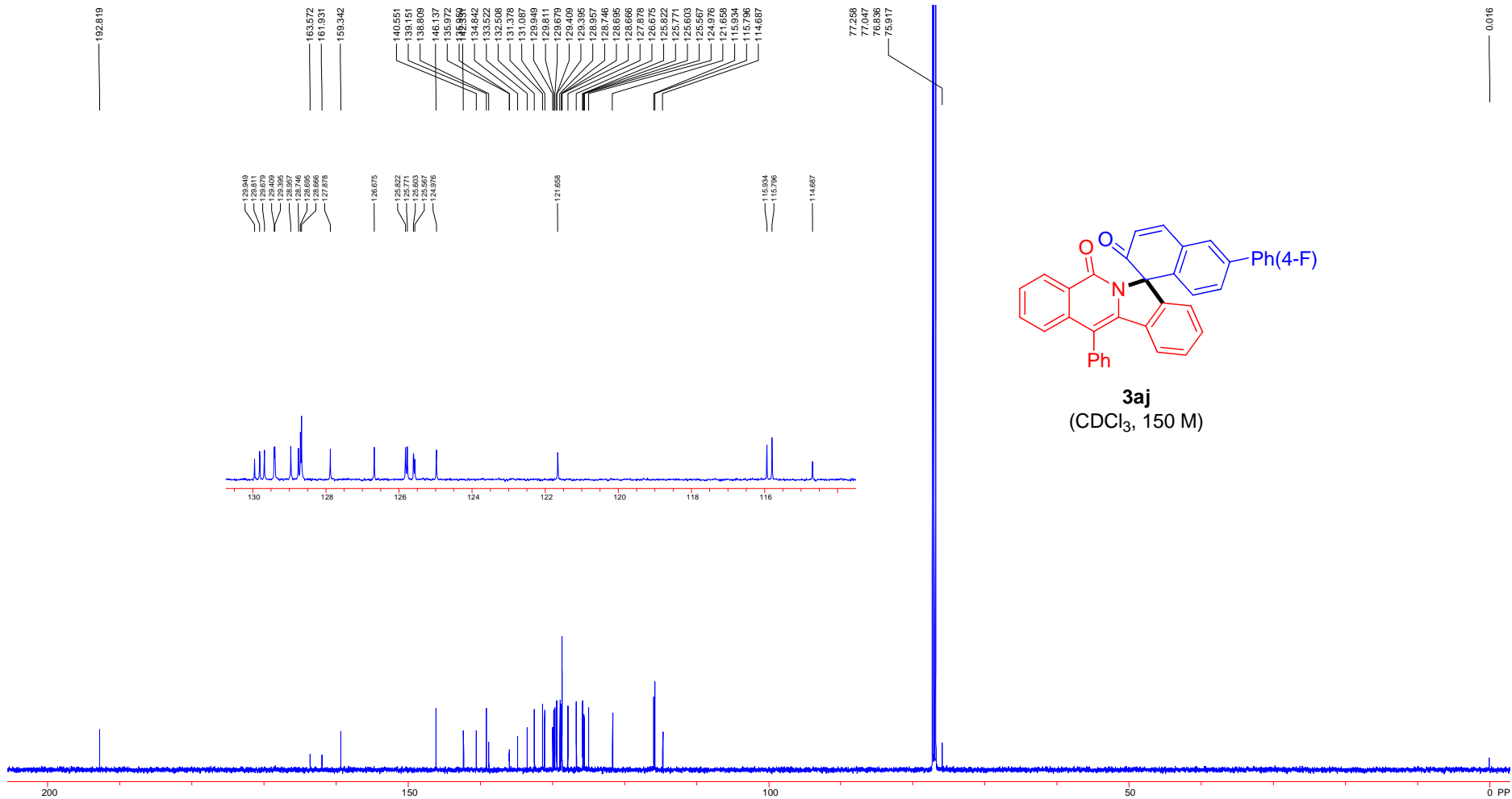


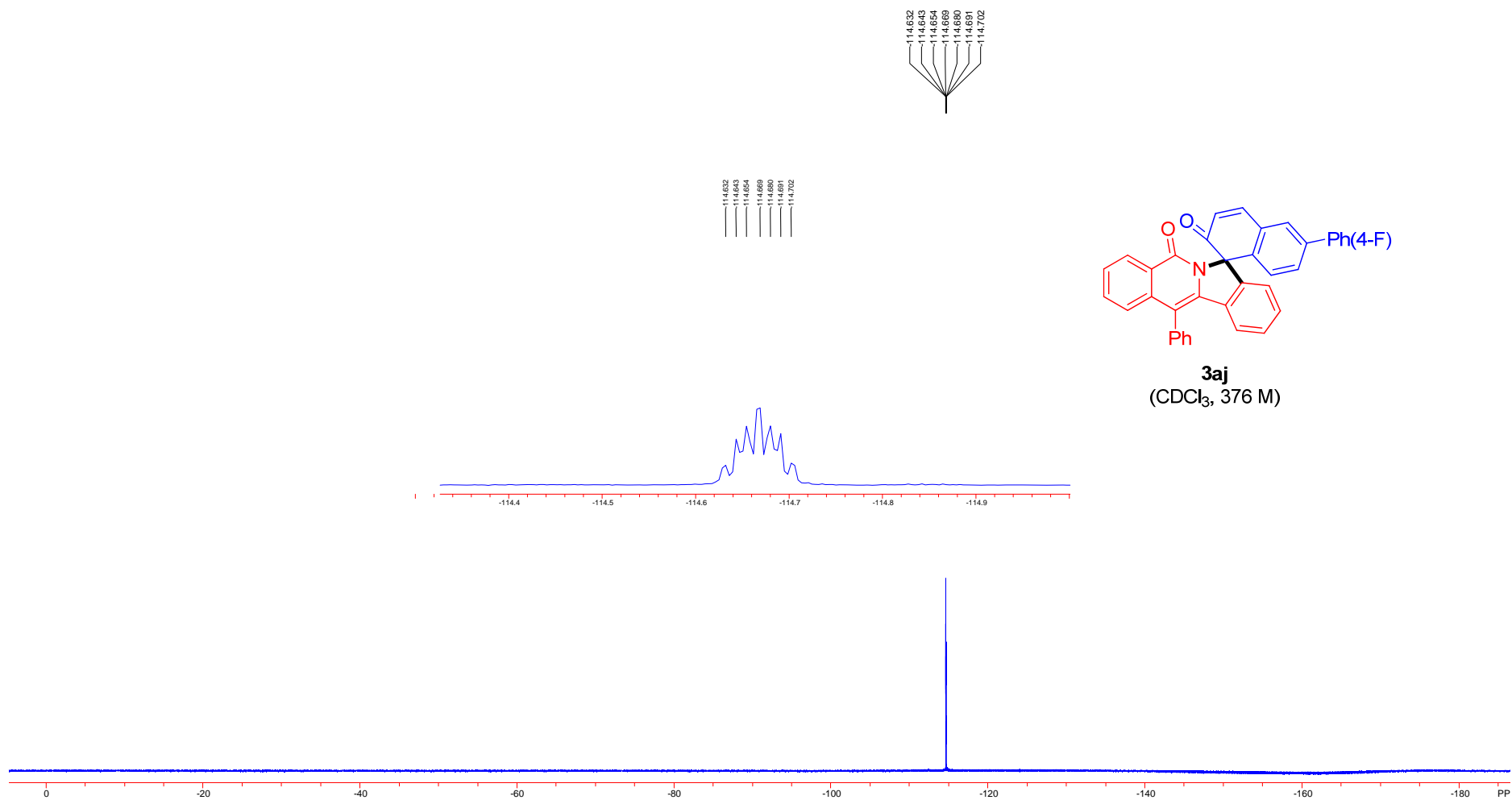


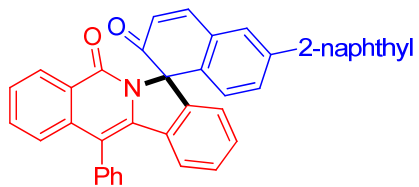
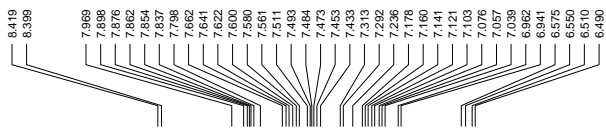




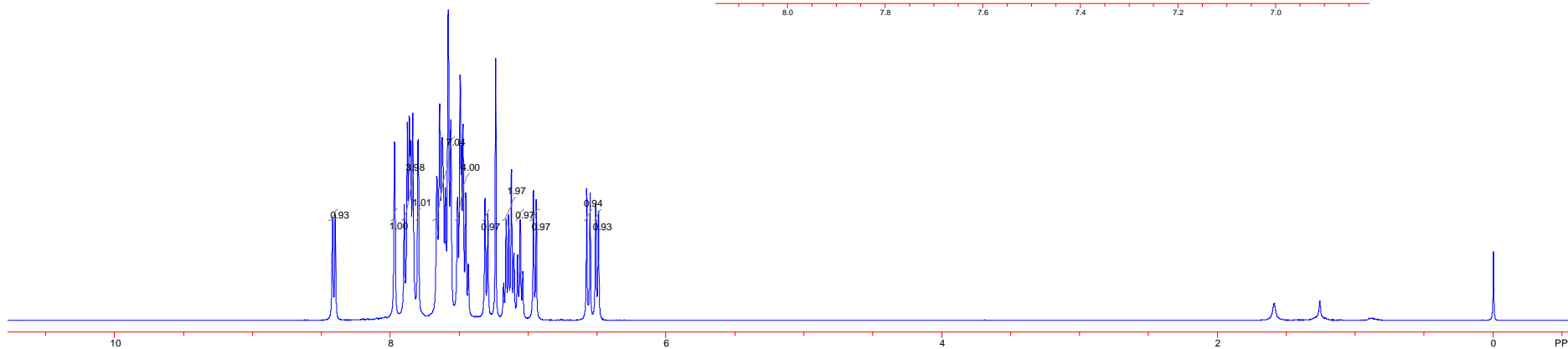
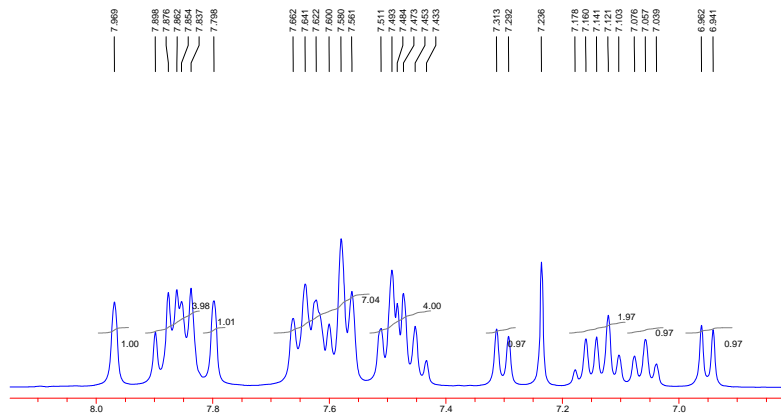


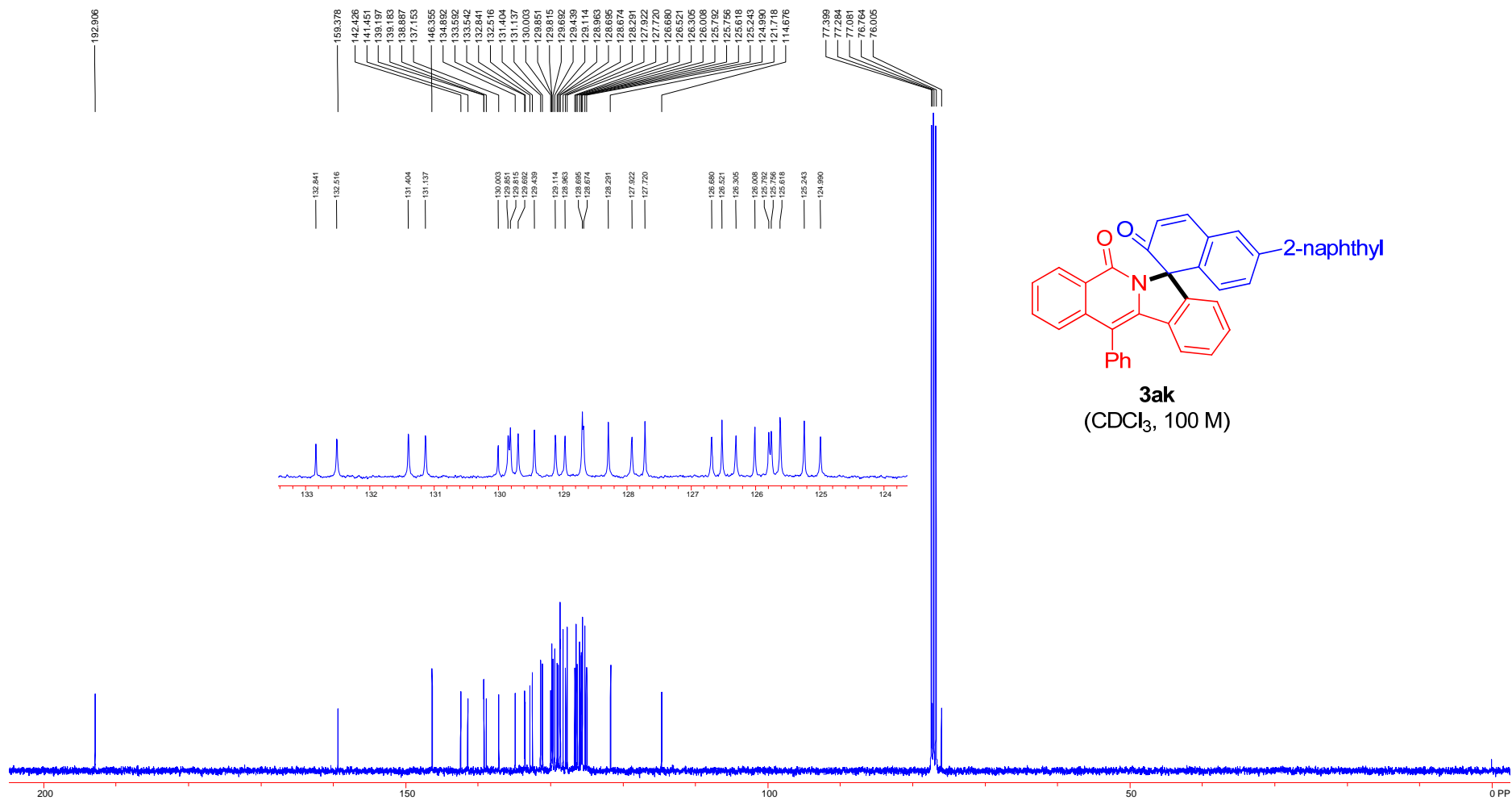


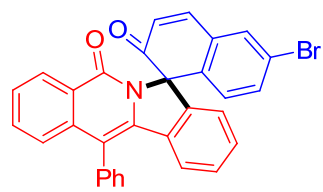
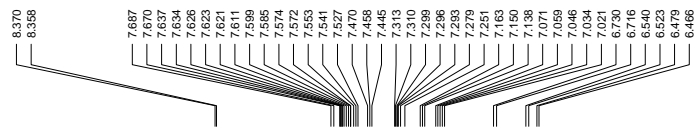




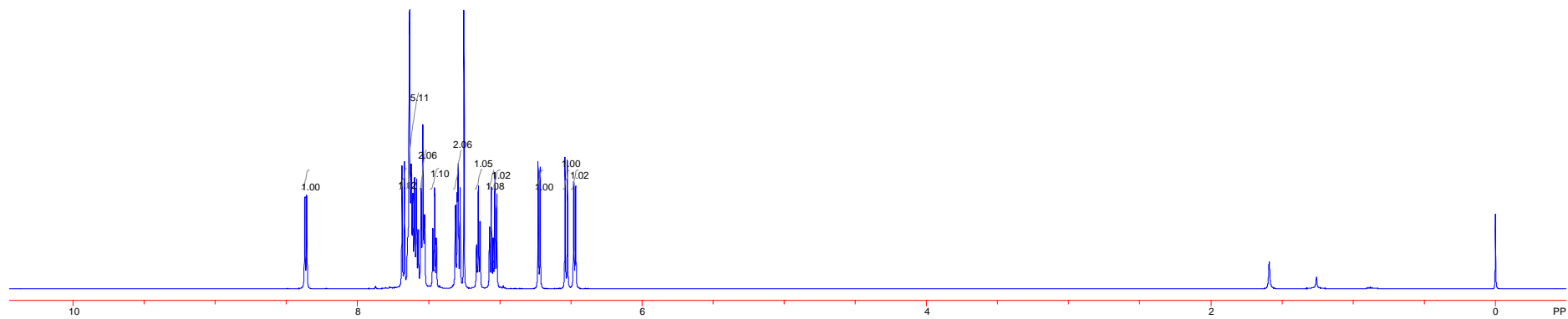
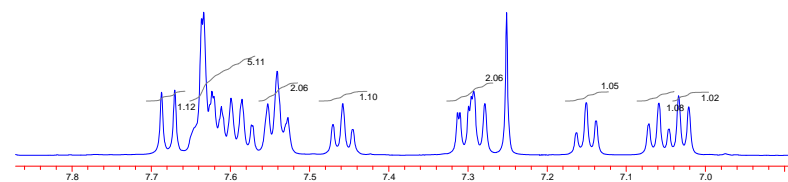
3ak
(CDCl₃, 400 M)

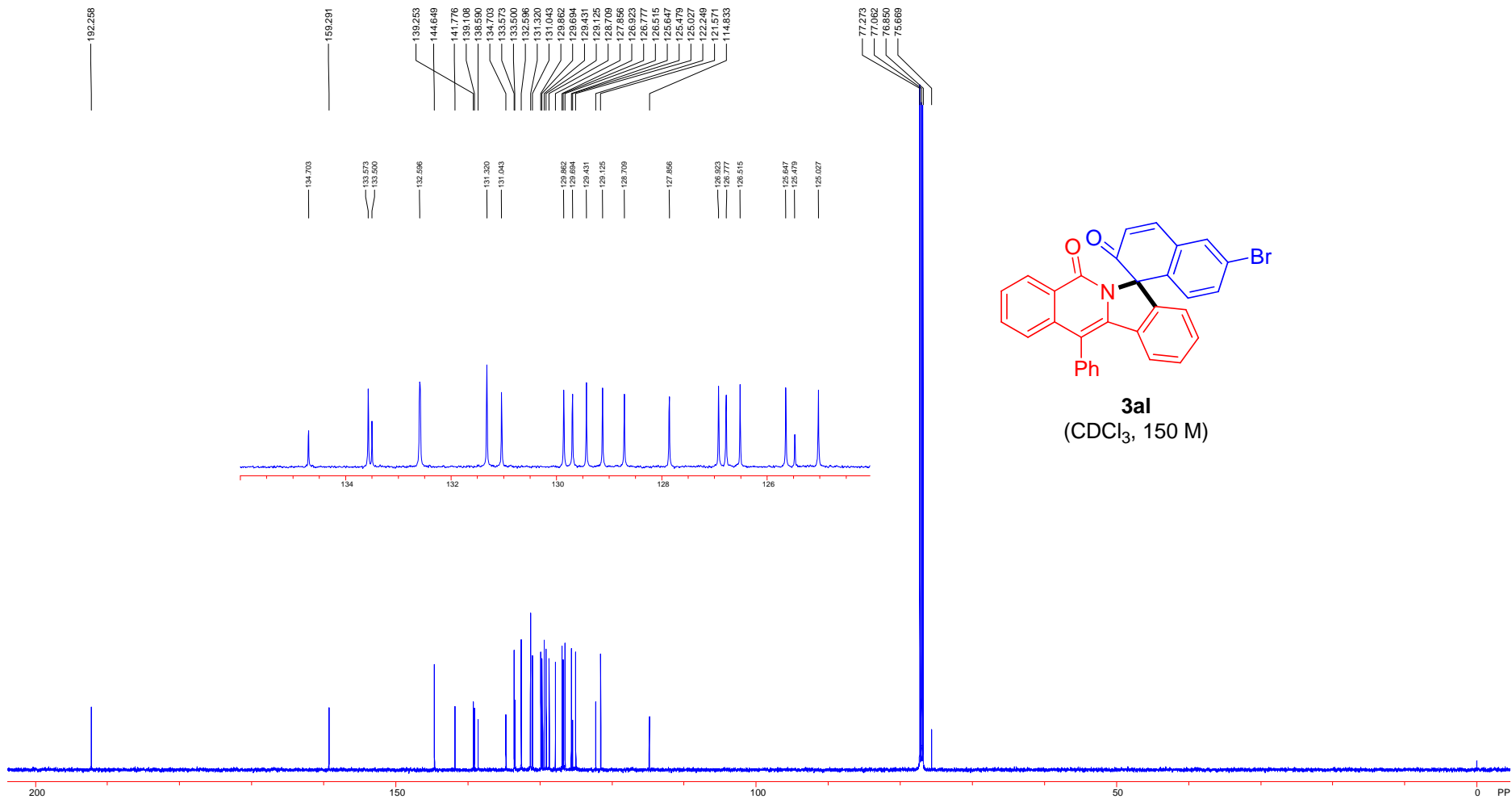


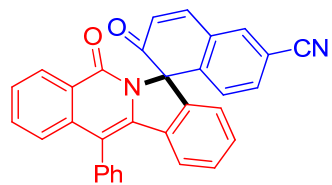
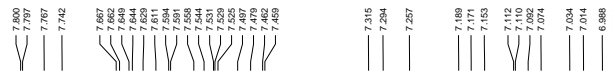
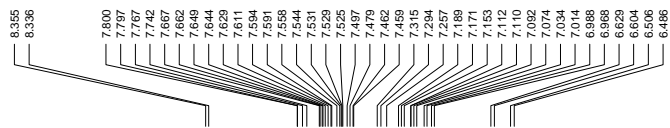




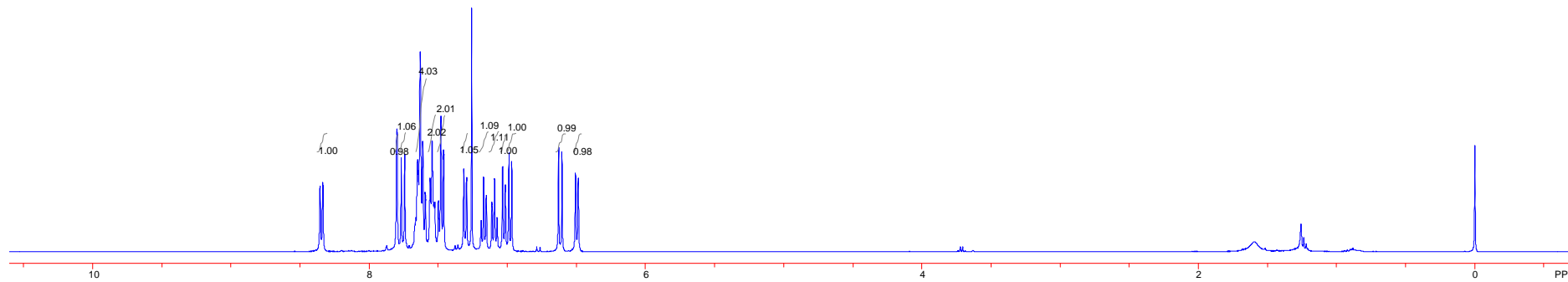
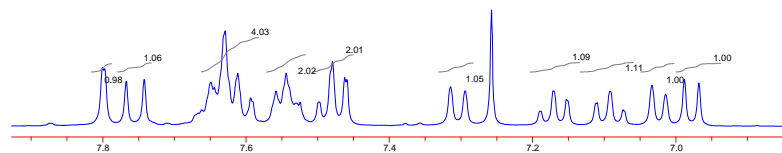
3aI
(CDCl₃, 600 M)

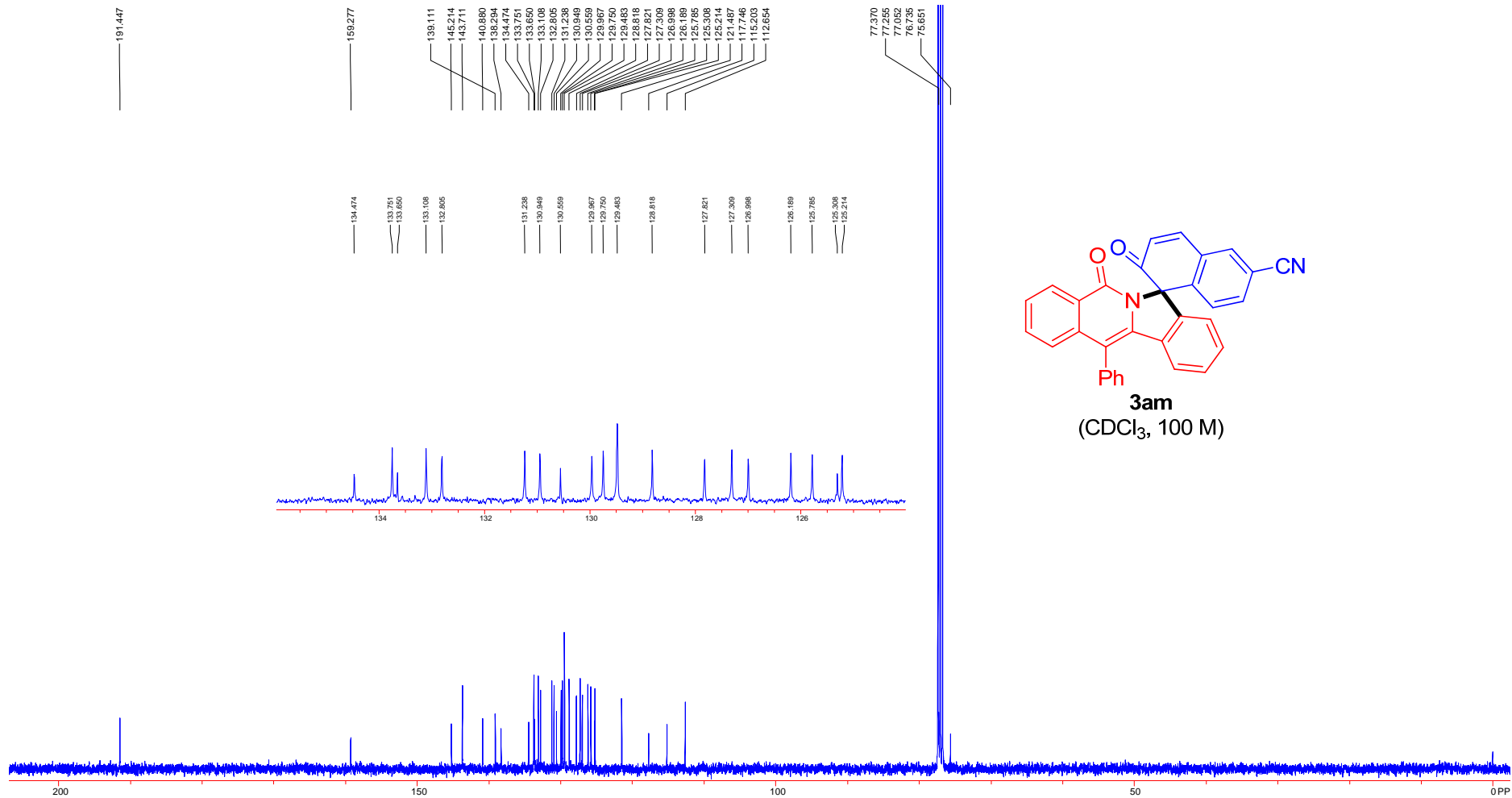


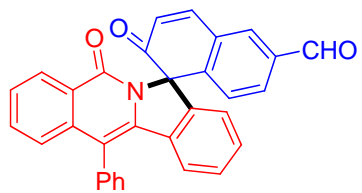
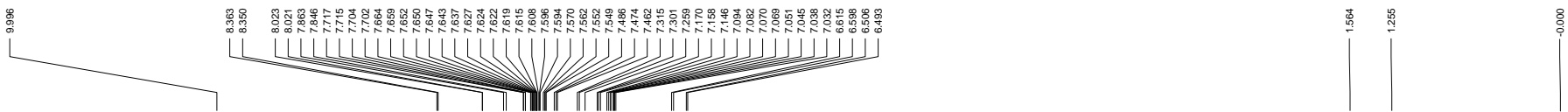




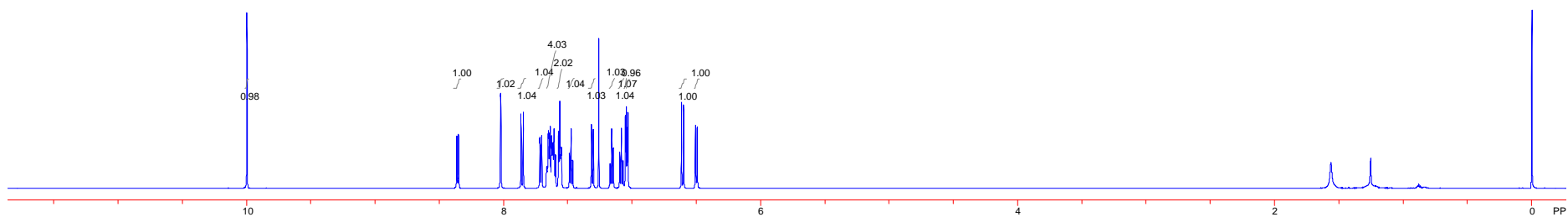
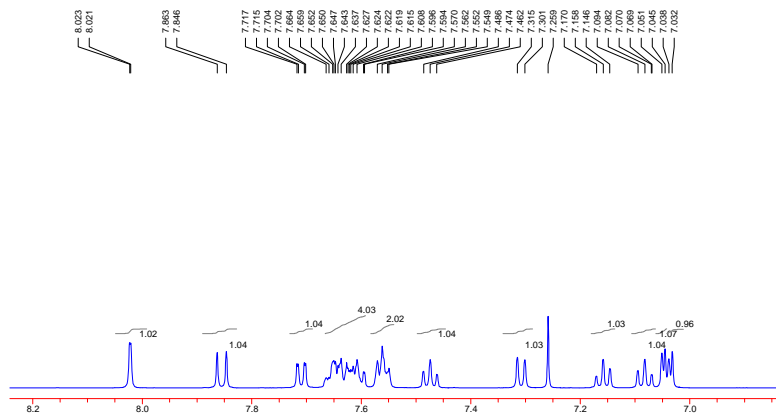
3am
(CDCl₃, 400 M)

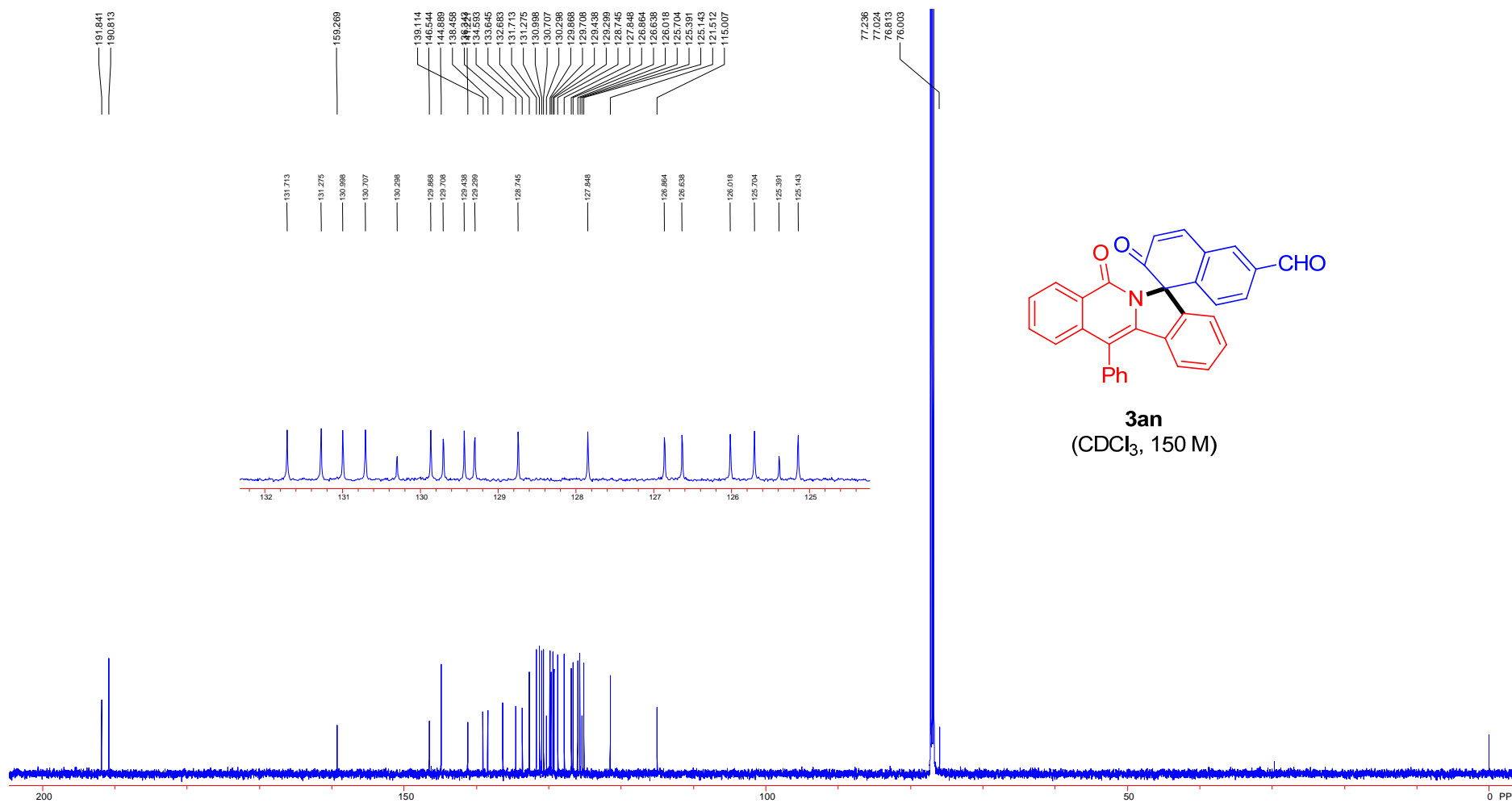


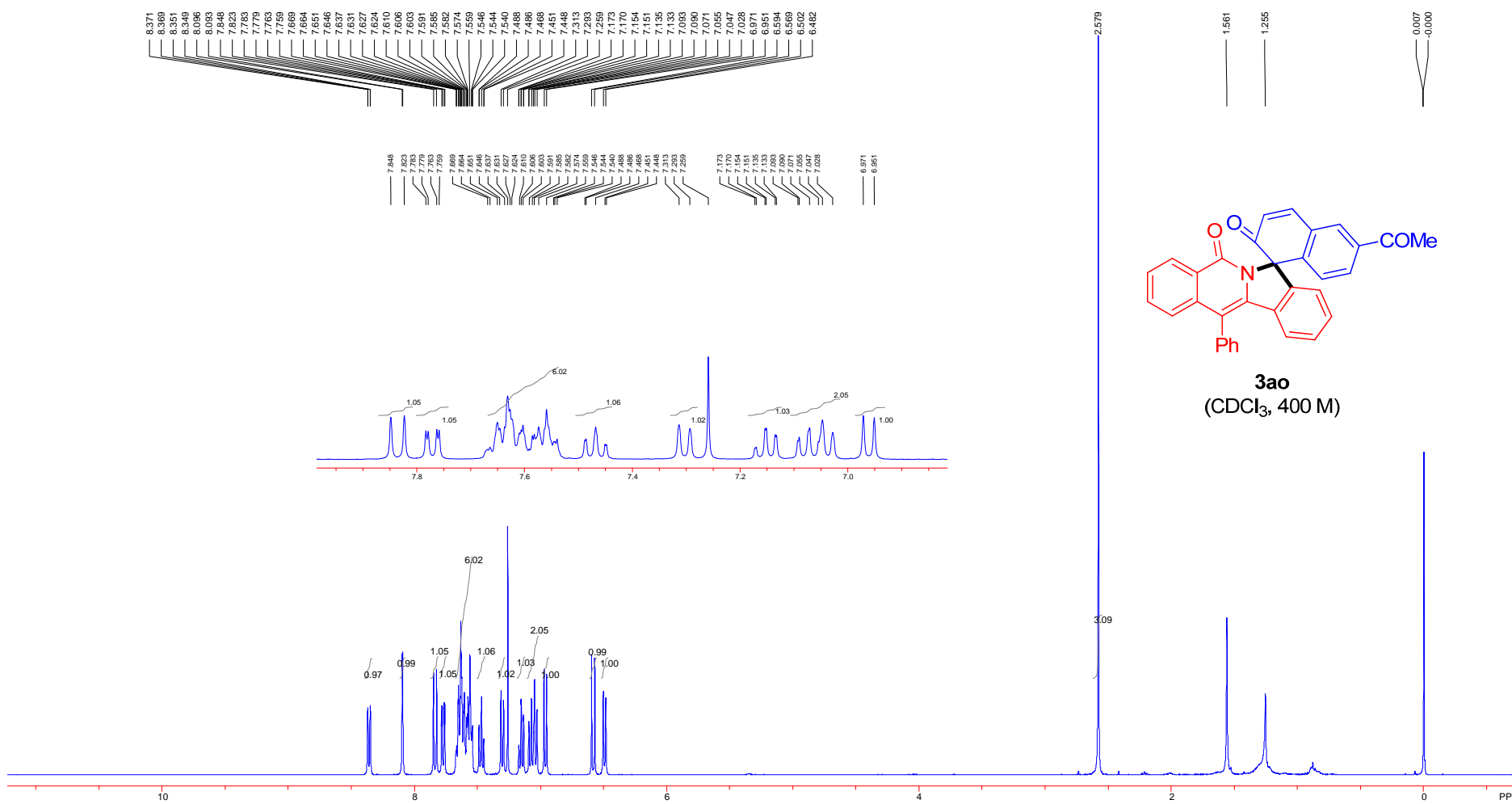


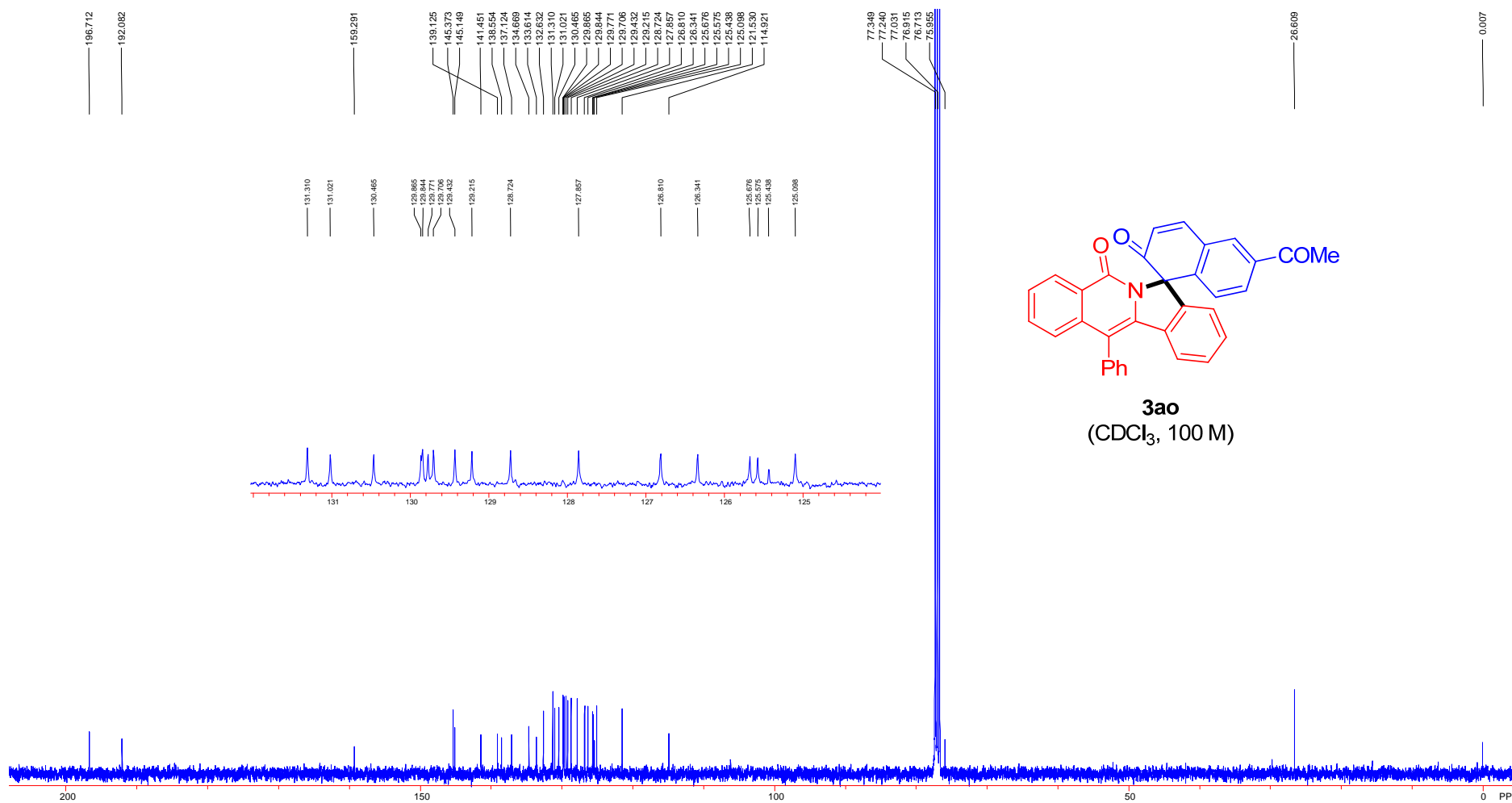


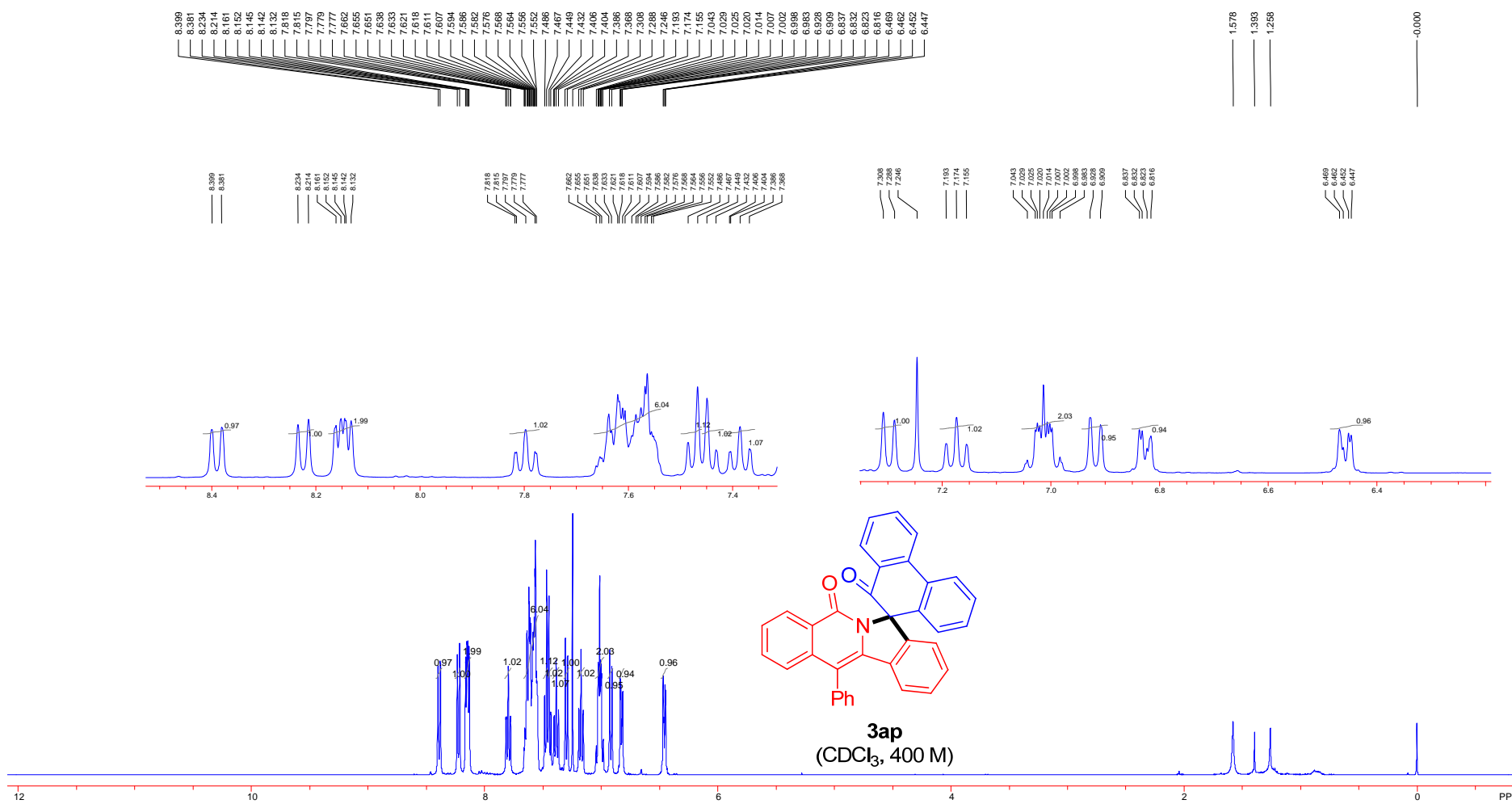
3an
(CDCl₃, 600 M)

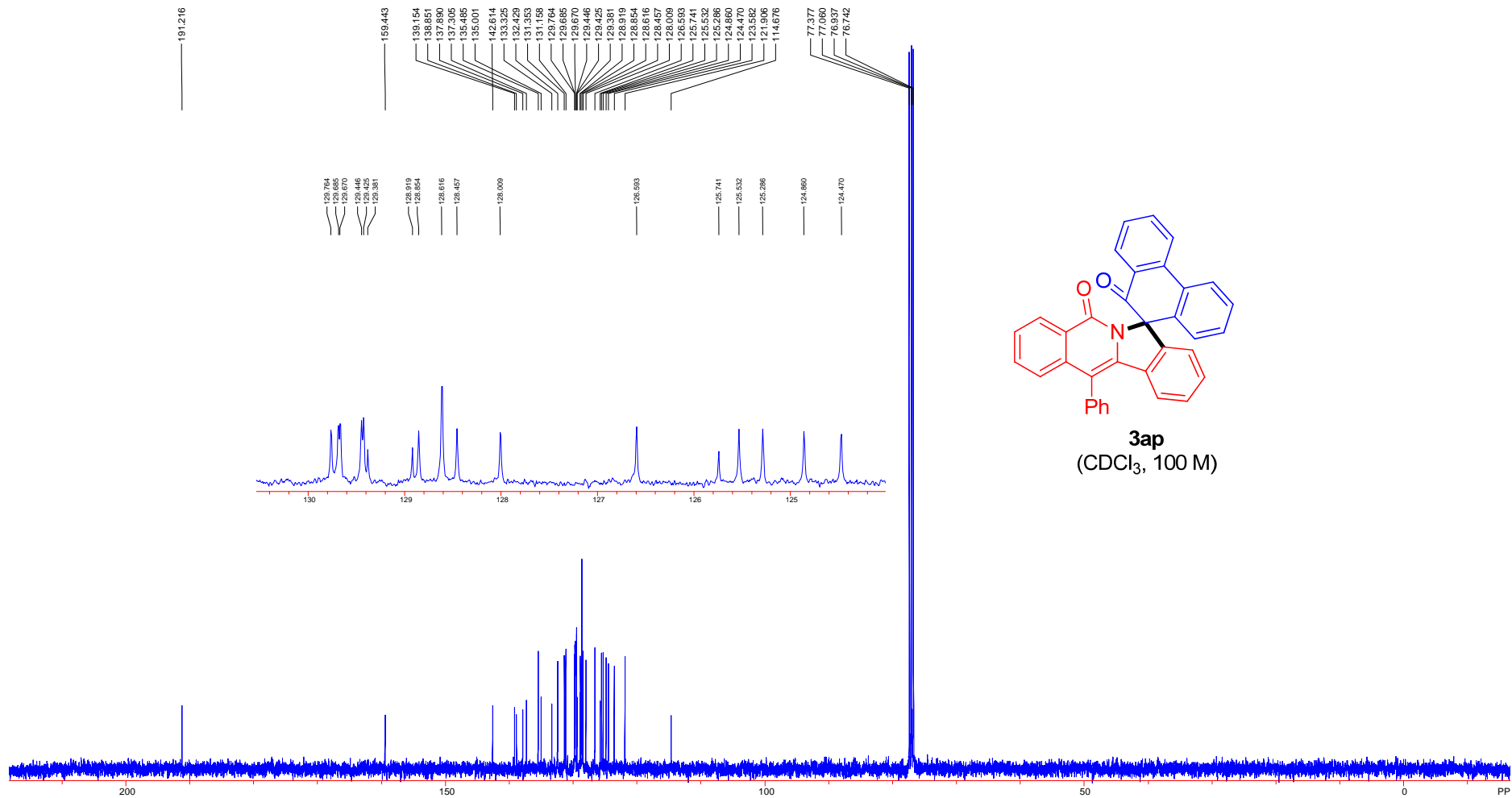


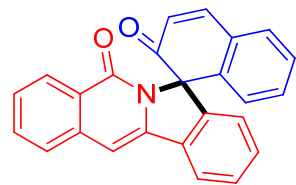
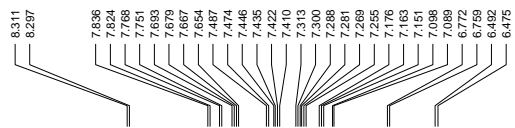




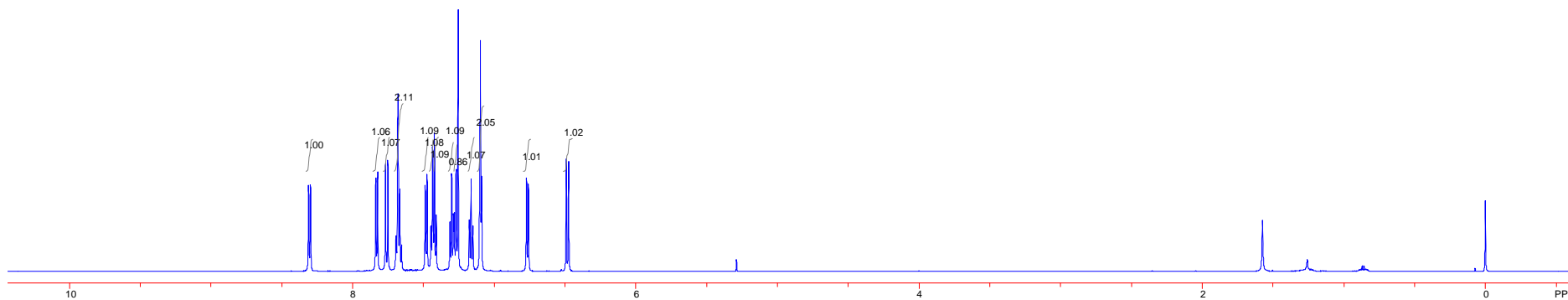
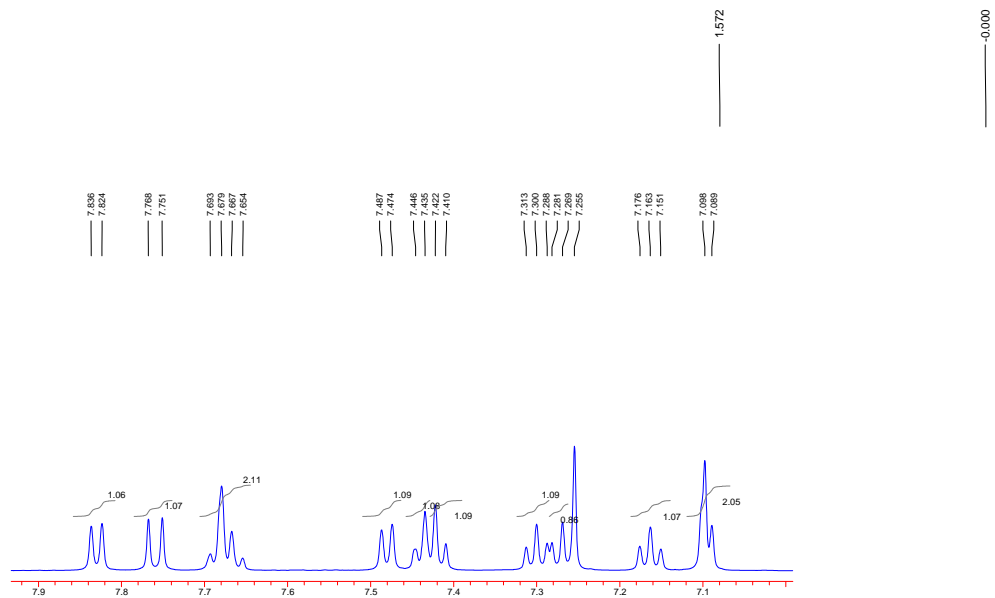


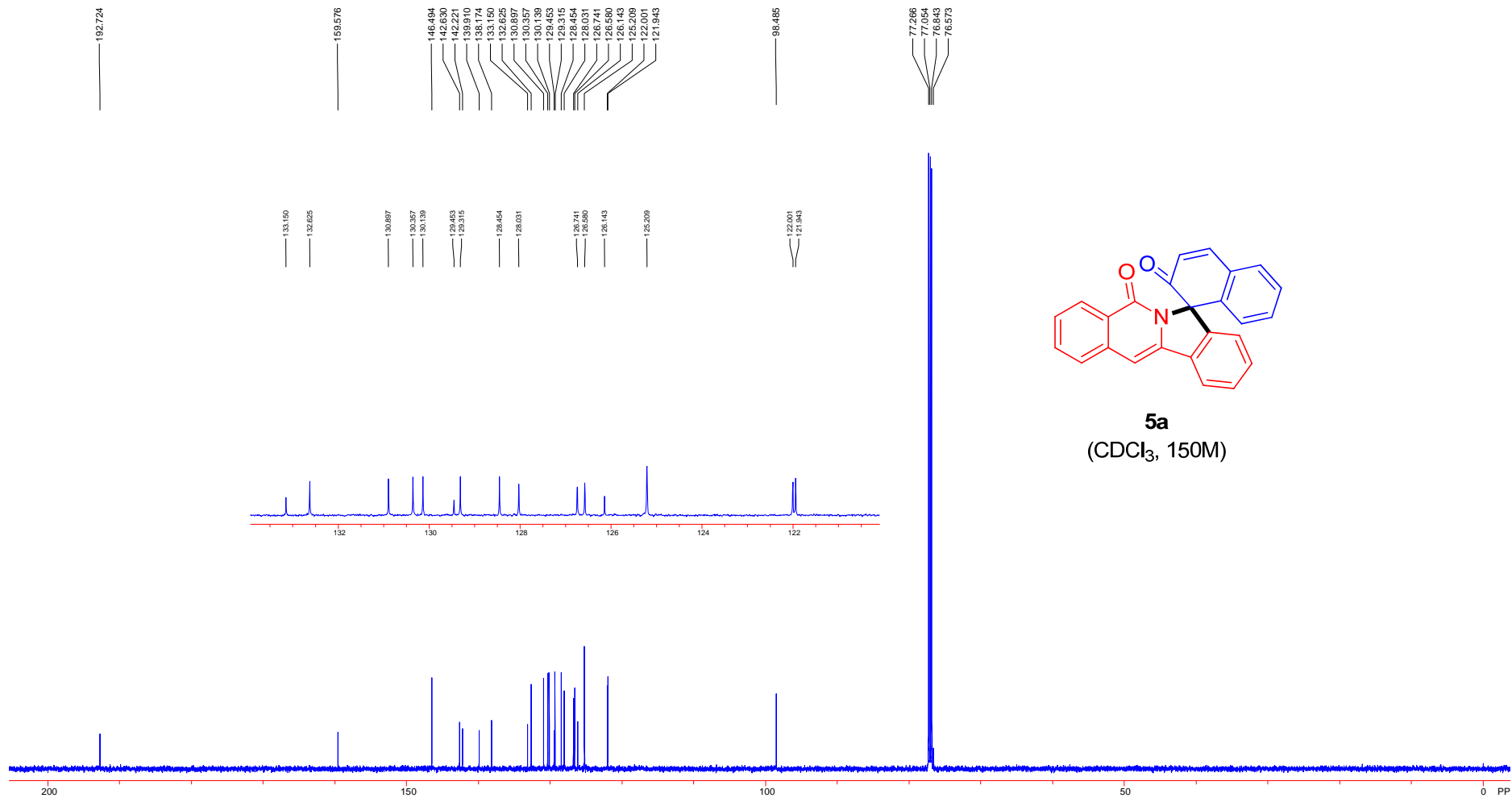


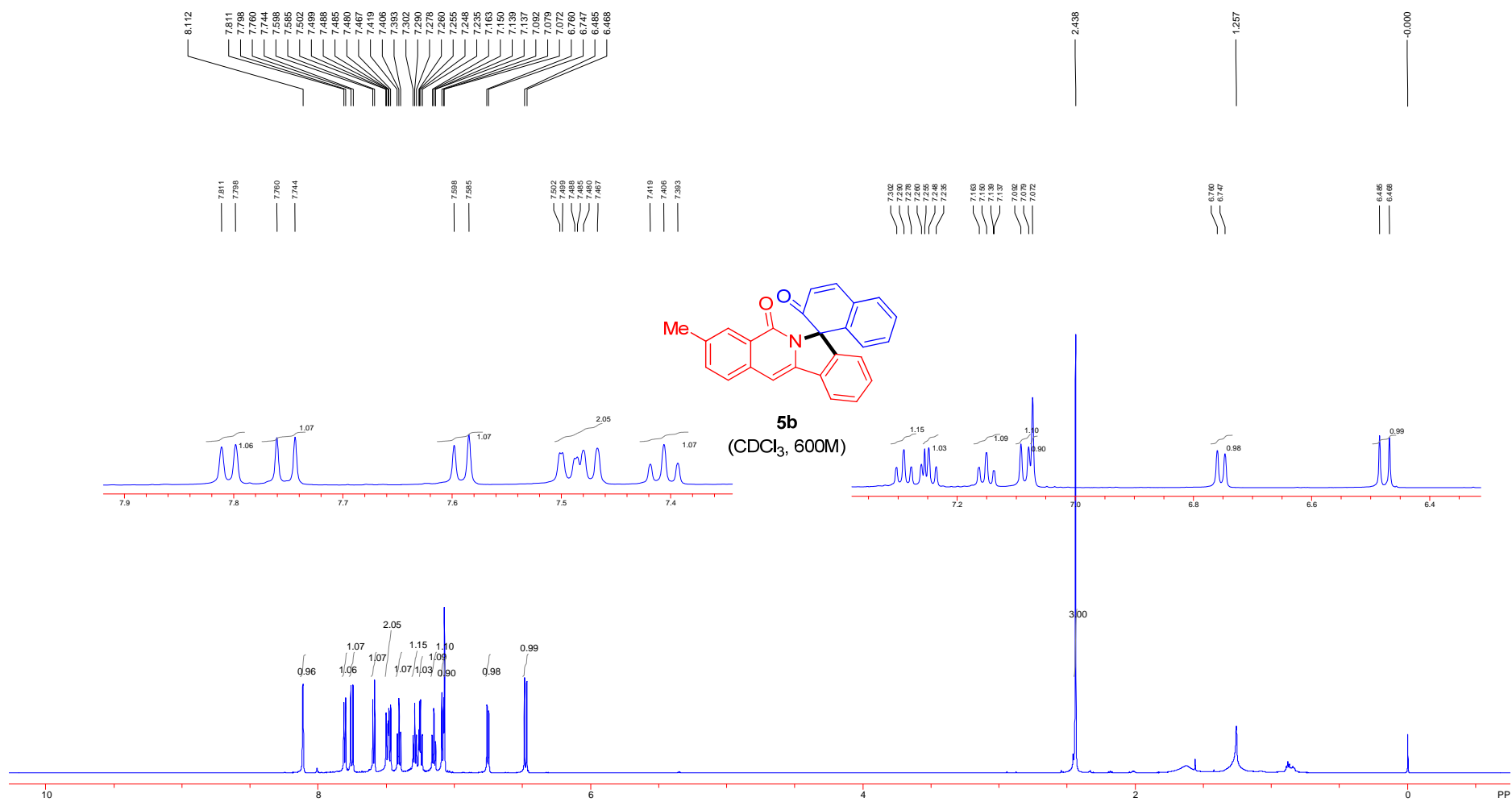


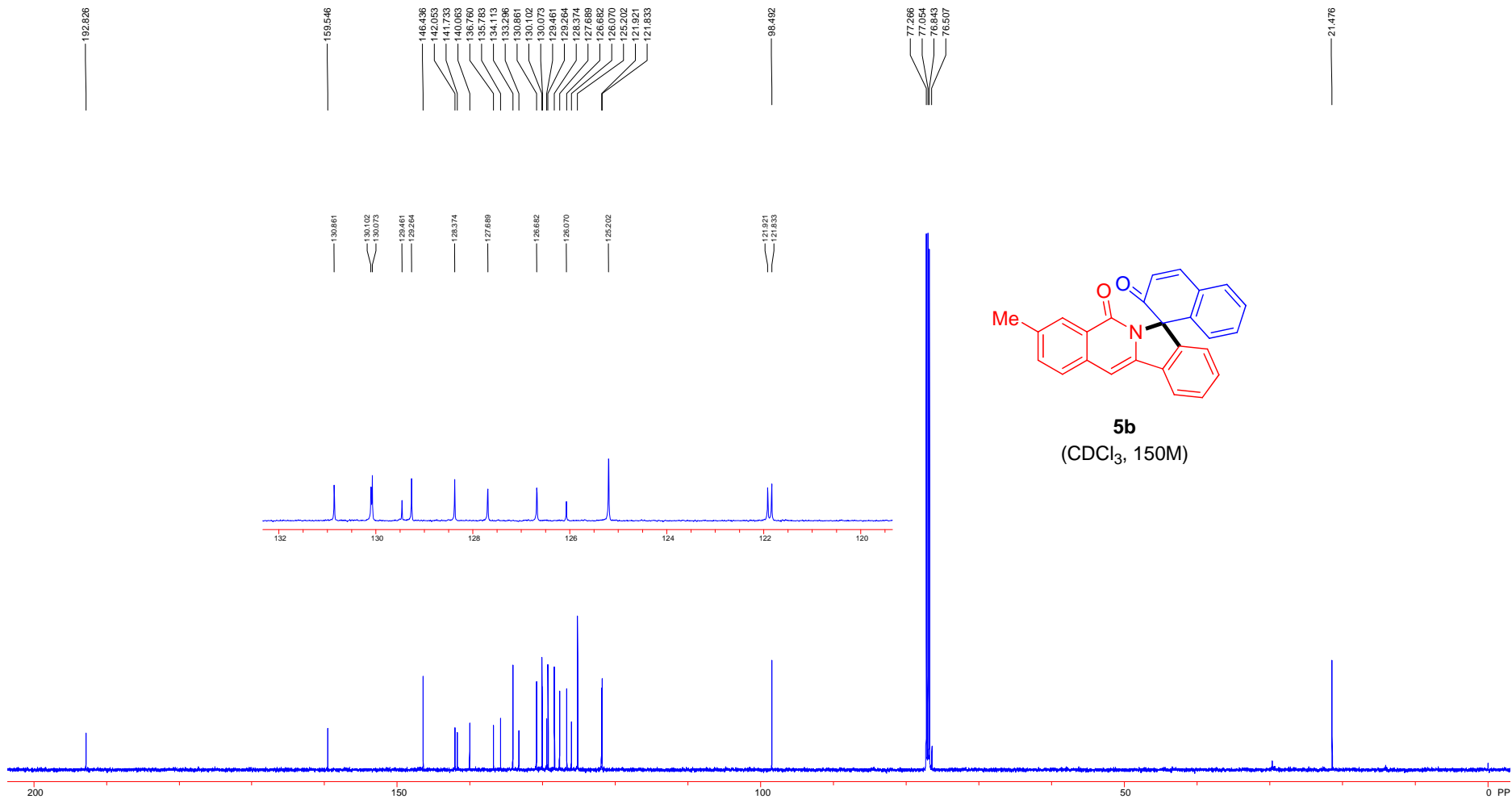


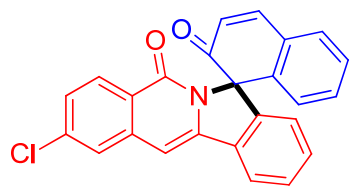
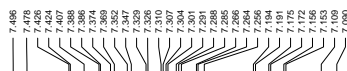
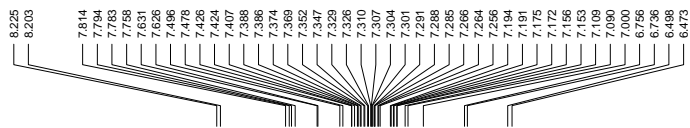
5a
(CDCl₃, 600M)



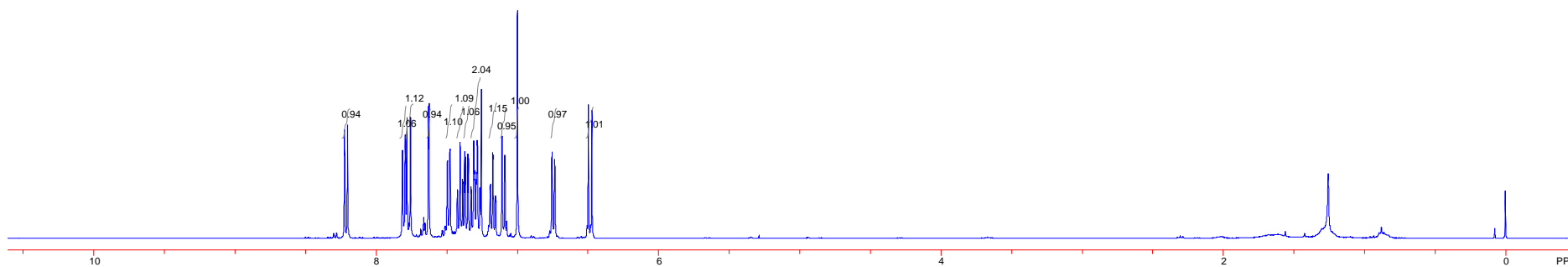
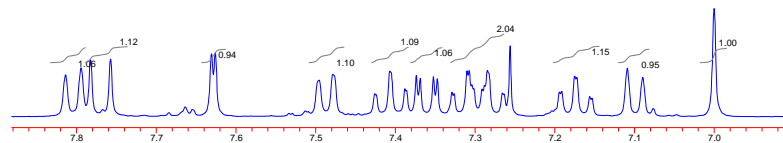


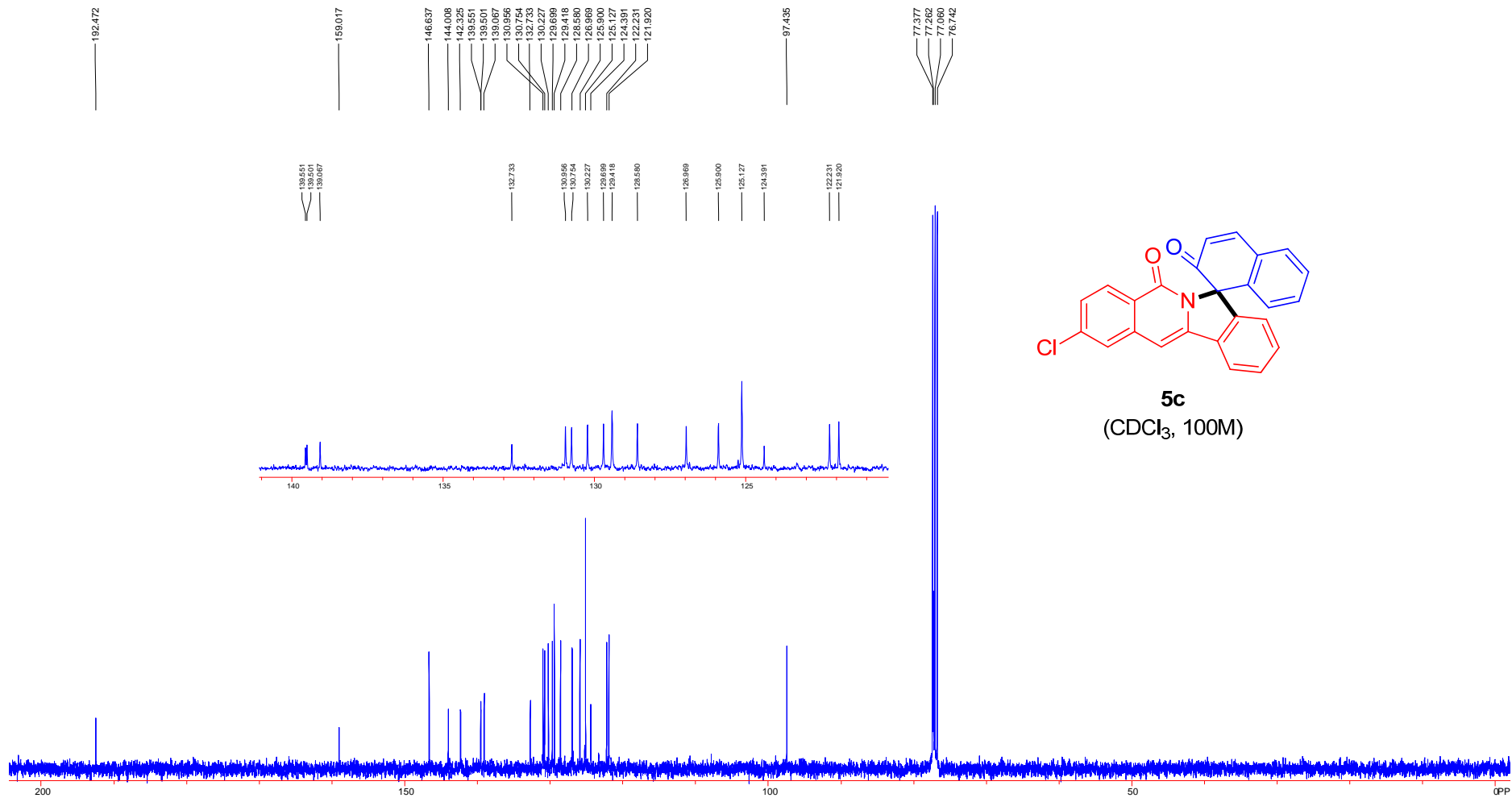


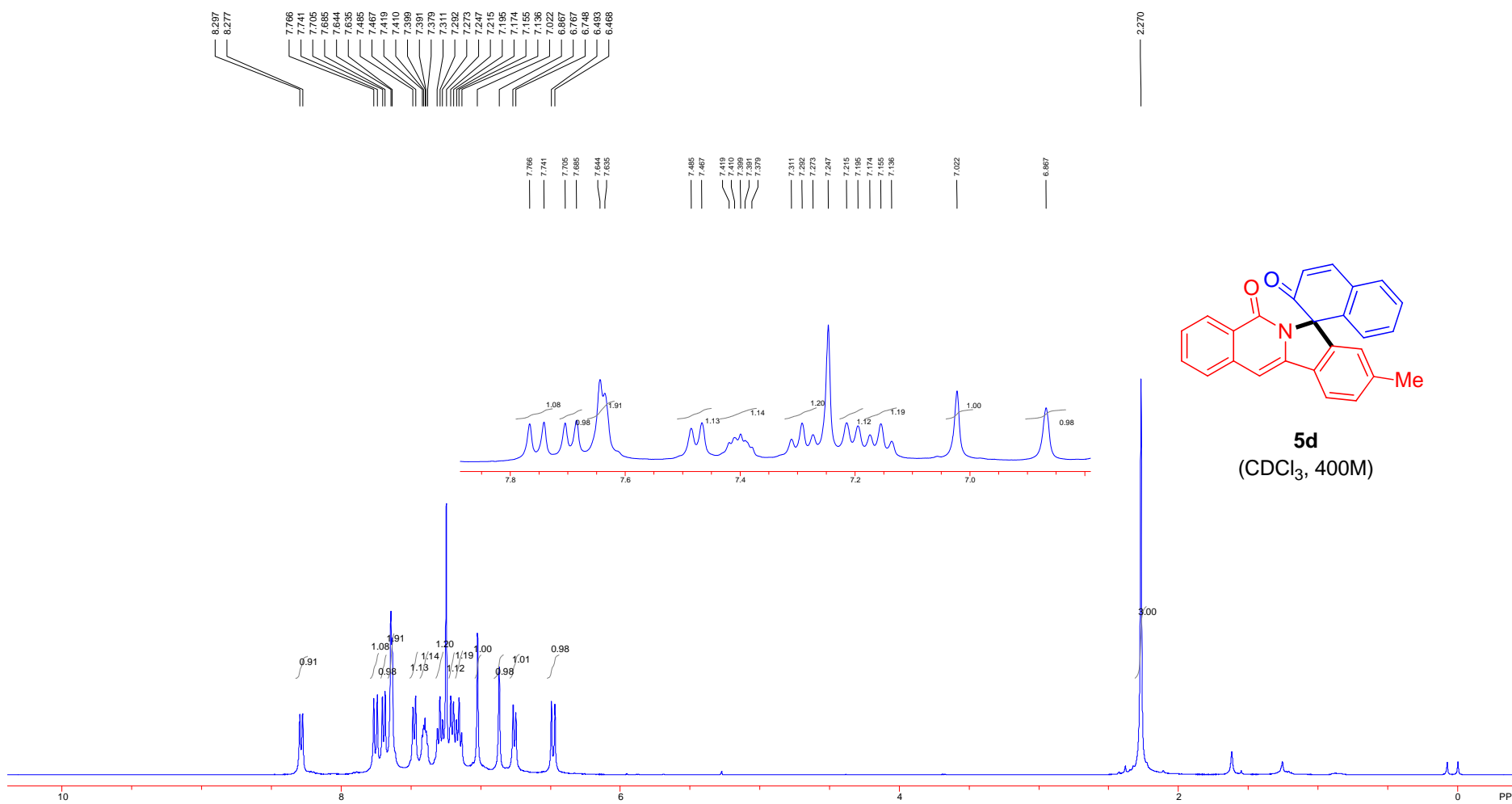


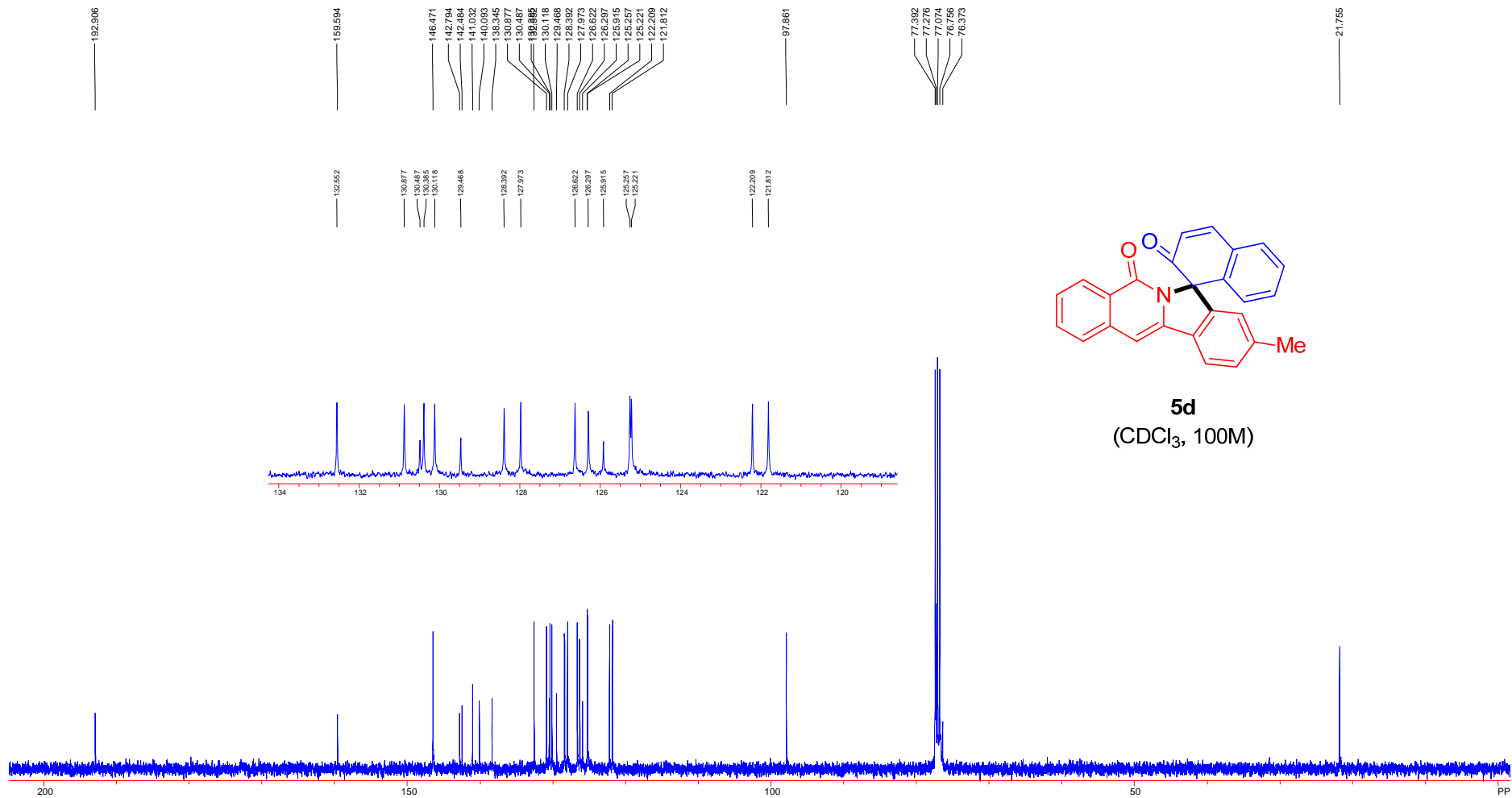


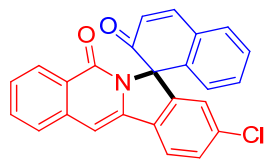
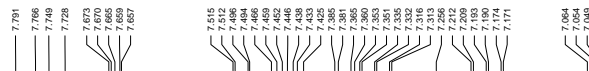
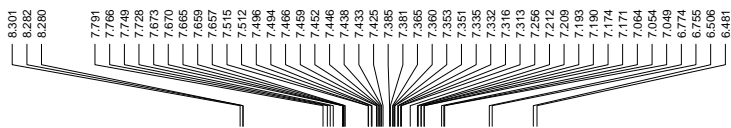
5c
(CDCl₃, 400M)



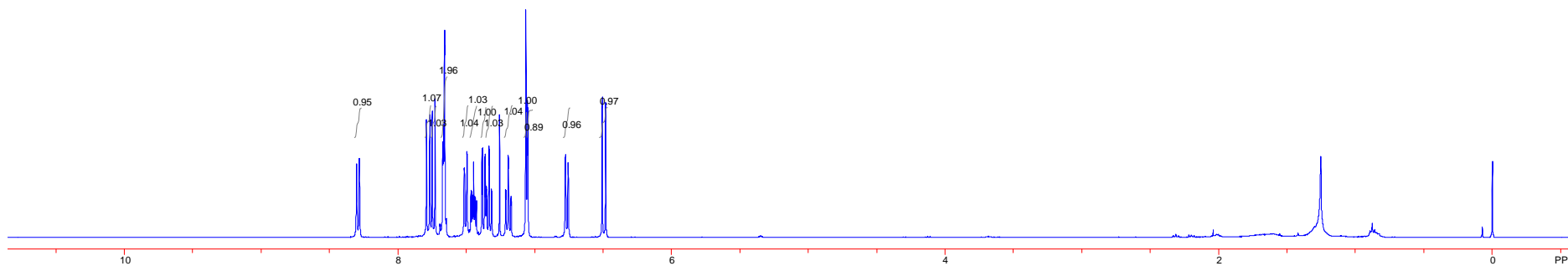
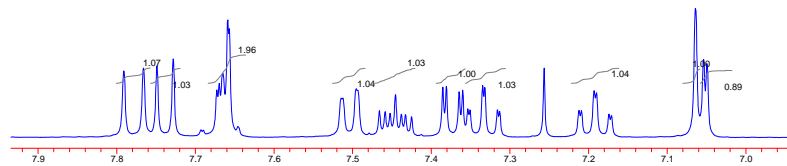


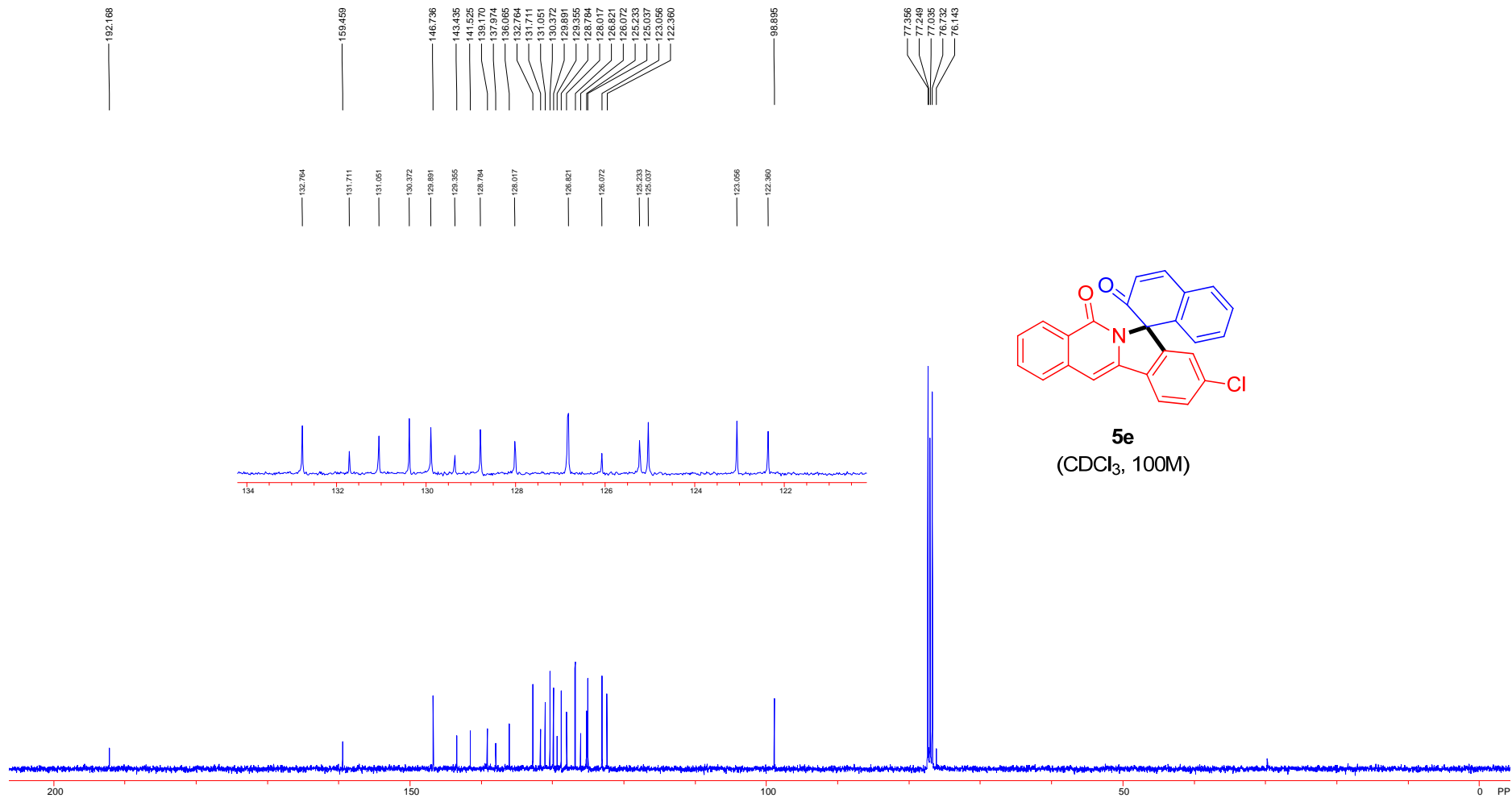


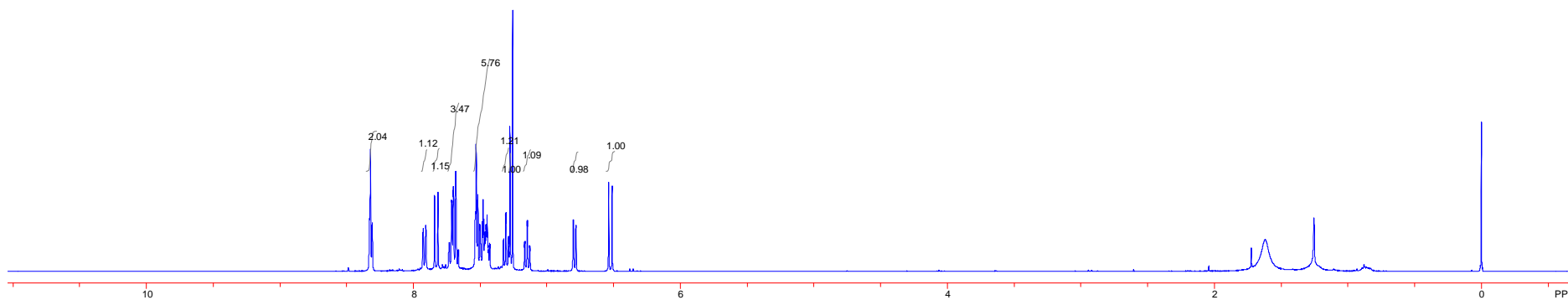
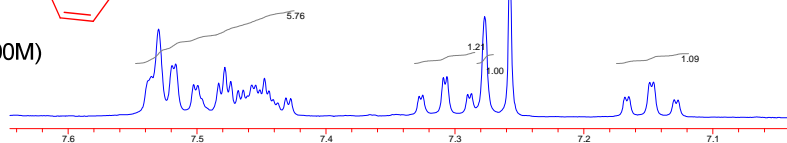
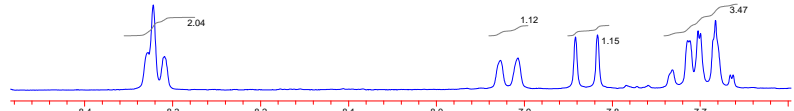
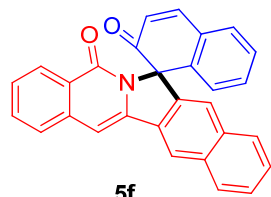
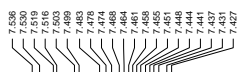
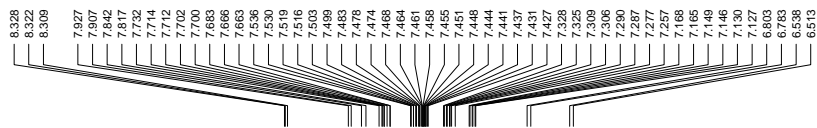


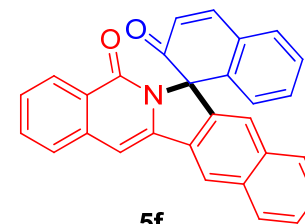
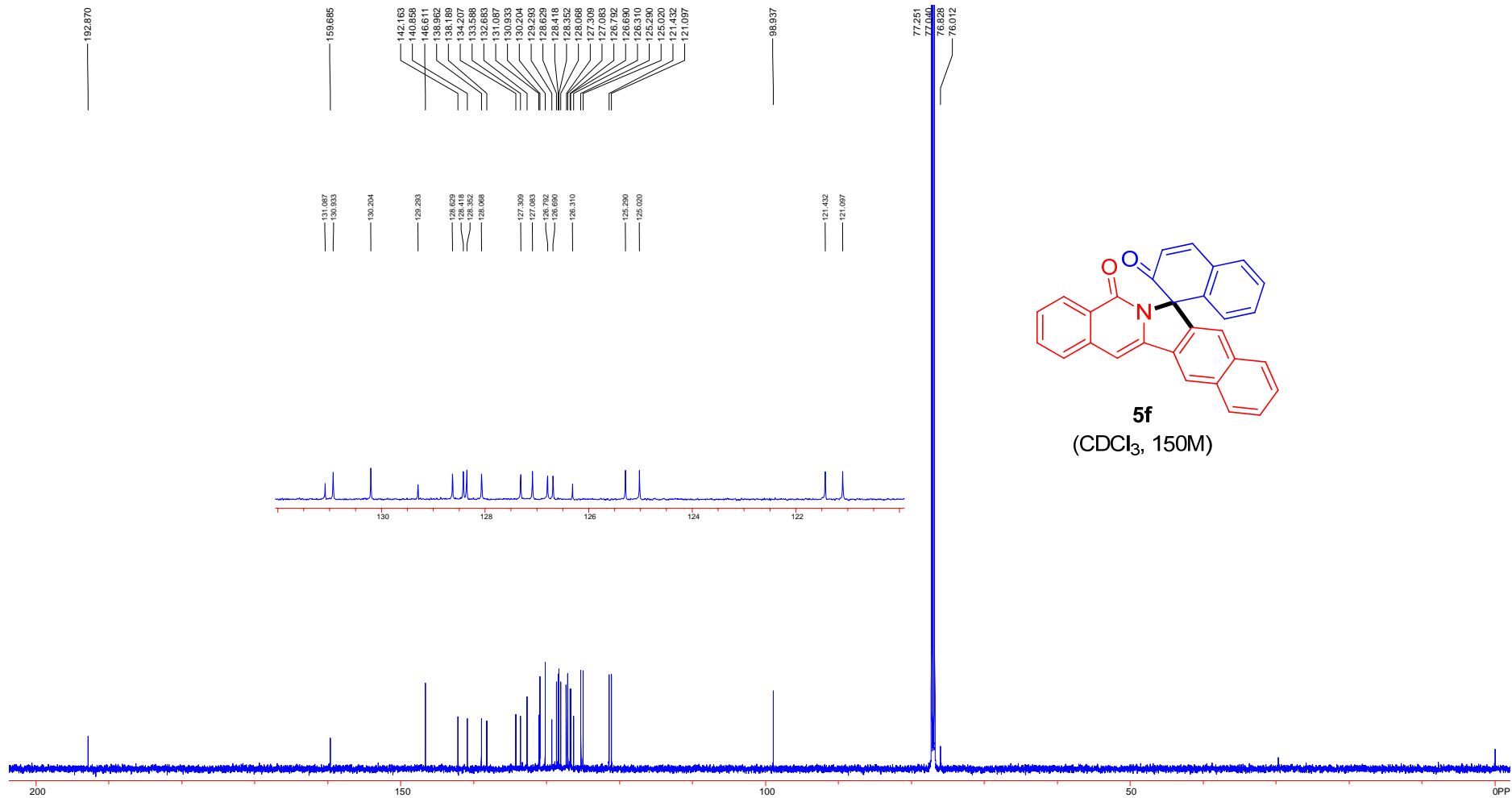


5e
(CDCl₃, 400M)

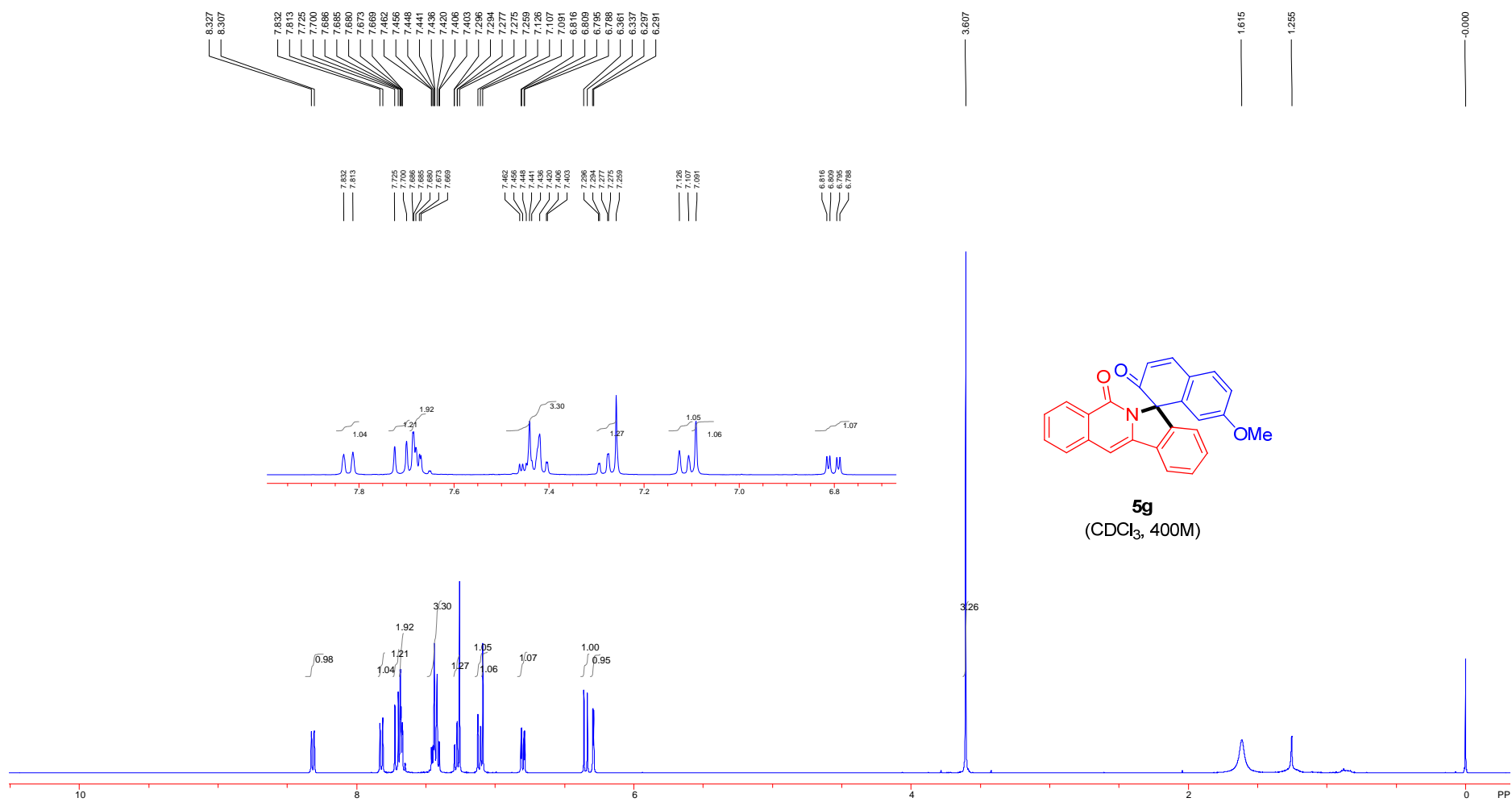


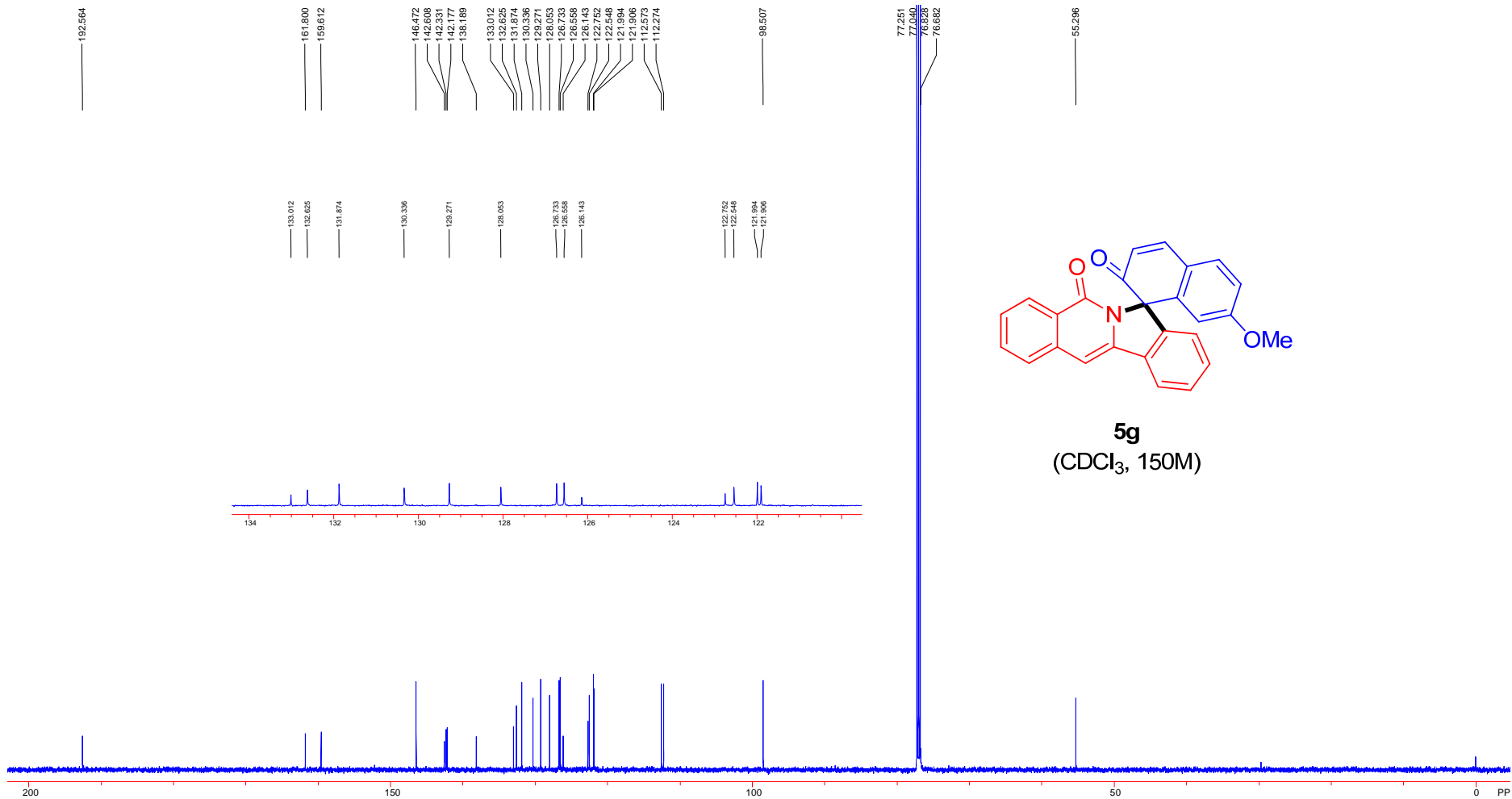


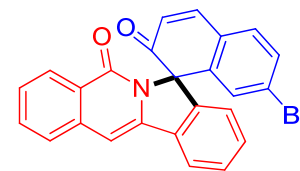
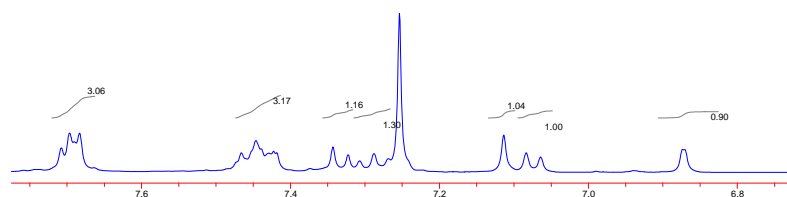
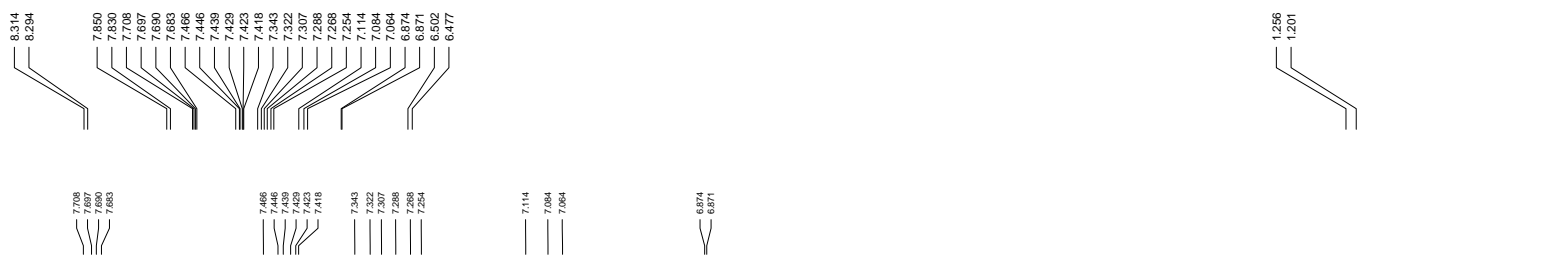




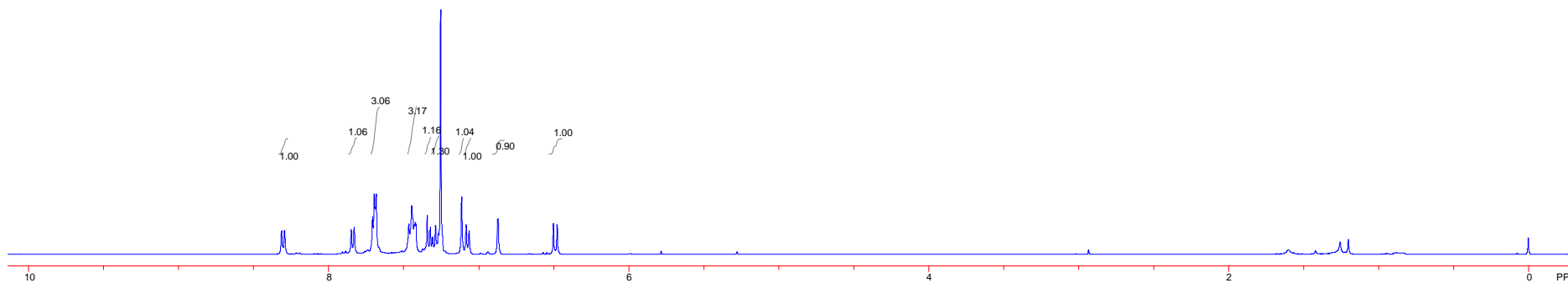
5f
(CDCl₃, 150M)

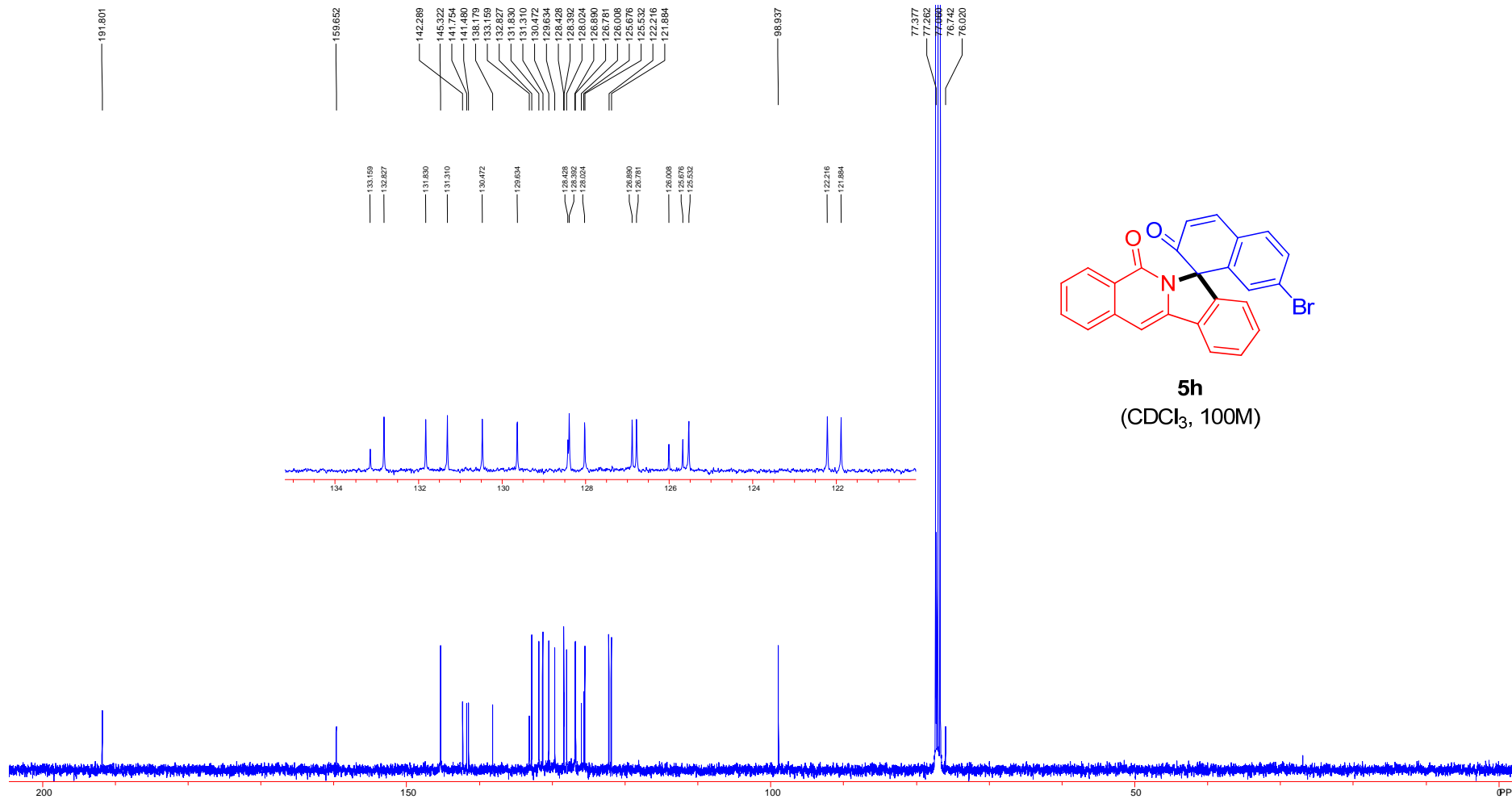


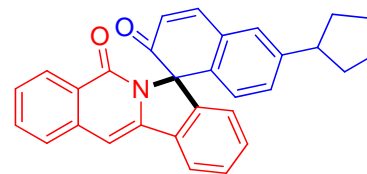
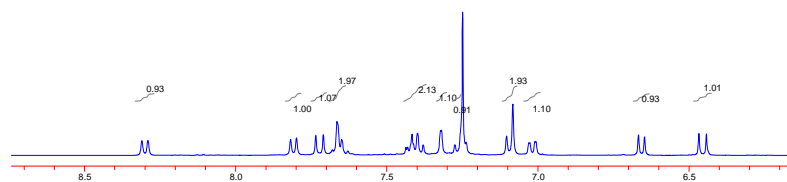
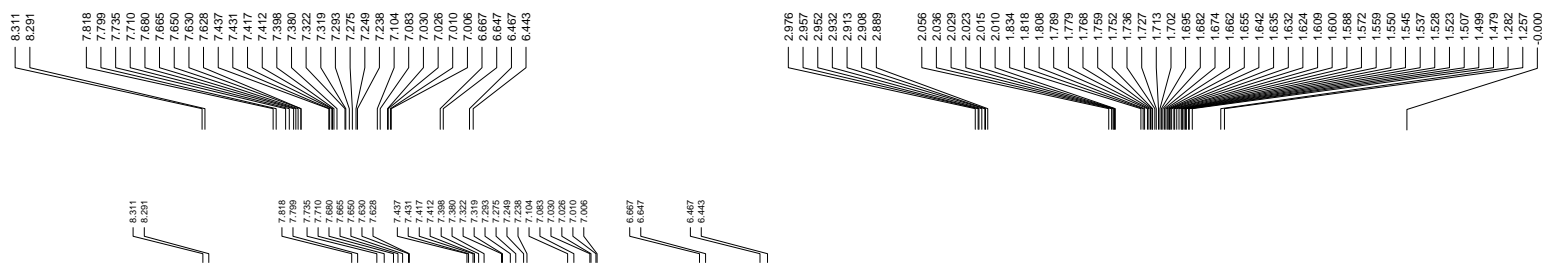




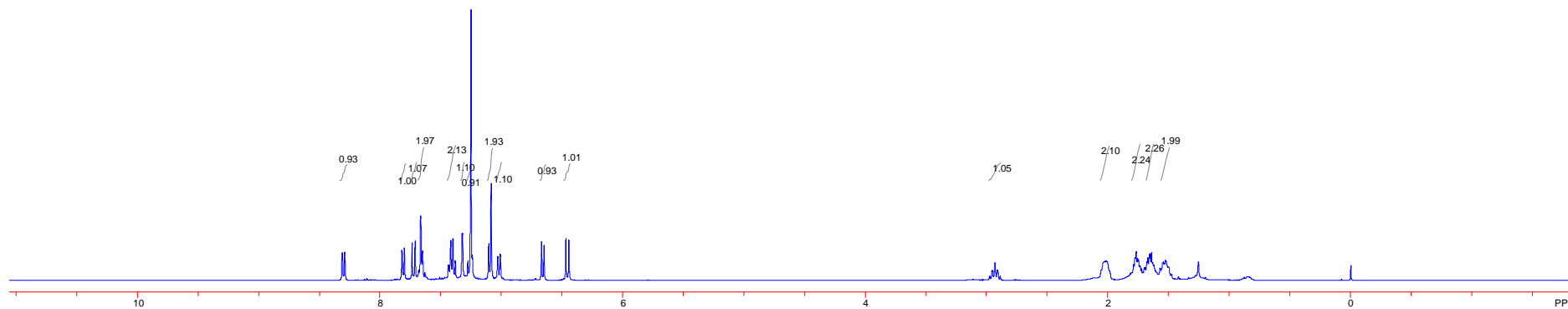
5h
(CDCl₃, 400M)

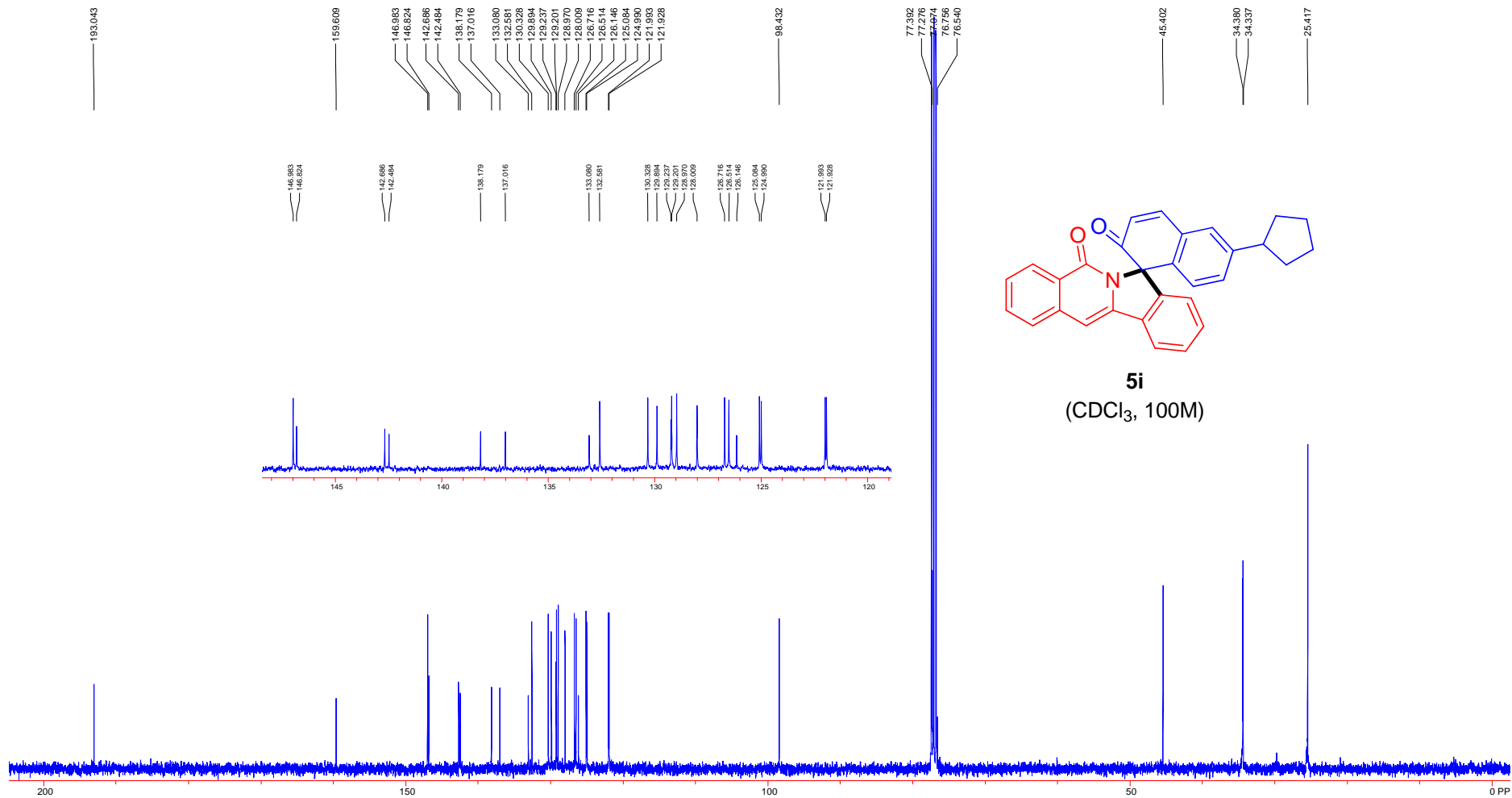


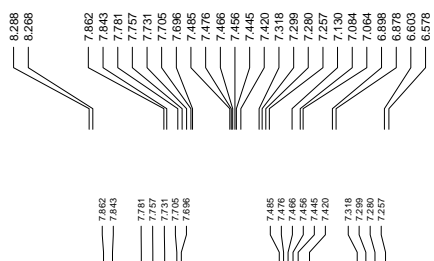




5i
(CDCl₃, 400M)

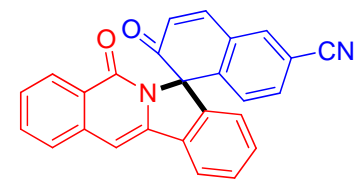
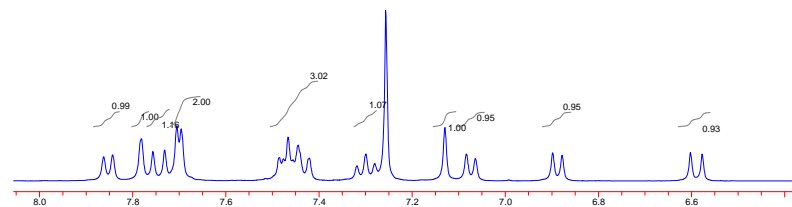




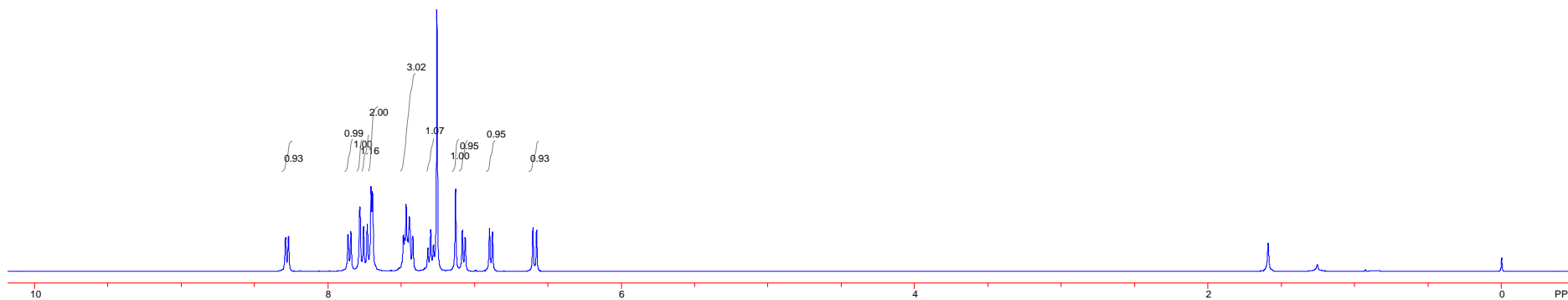


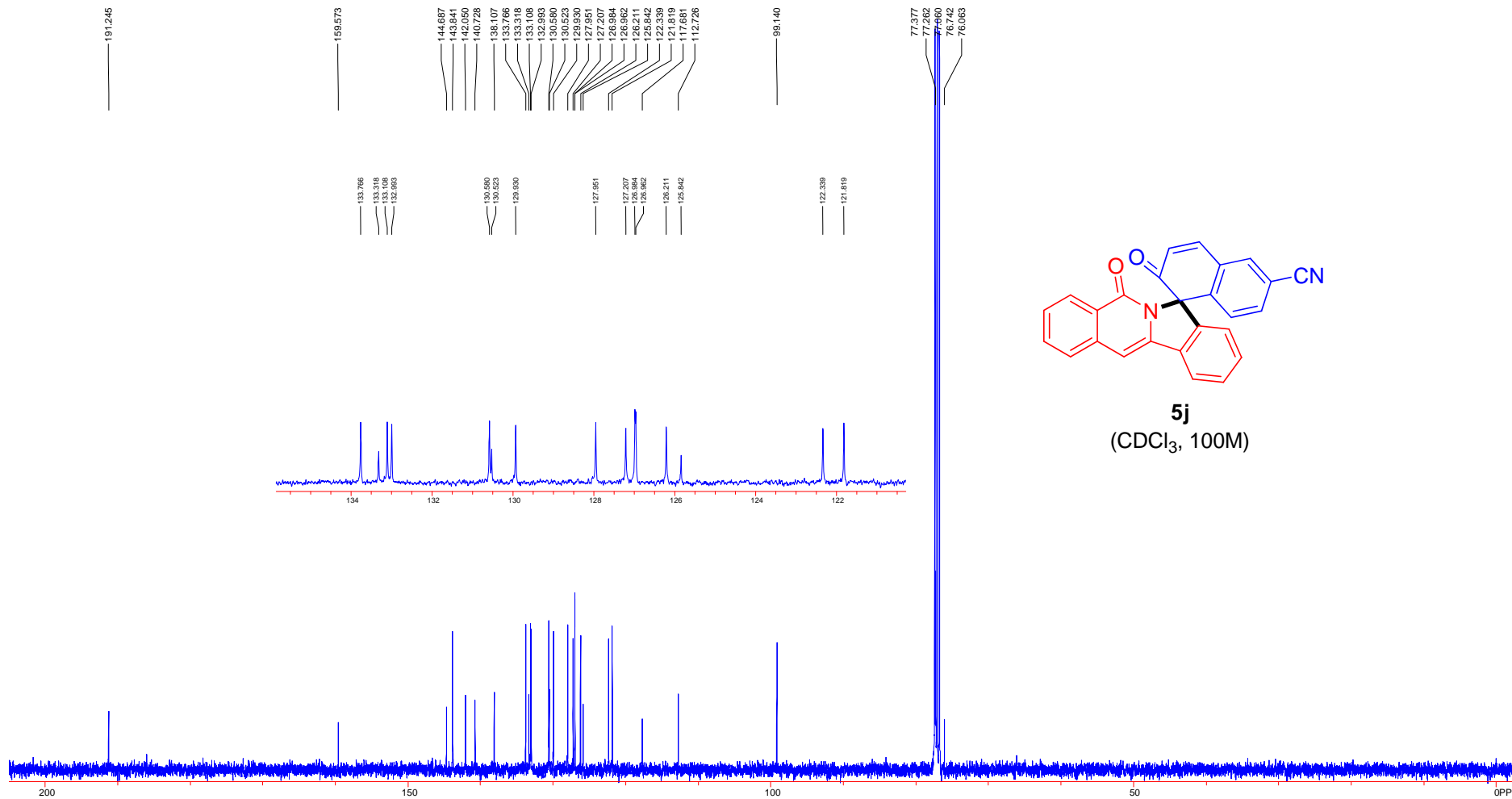
1.591

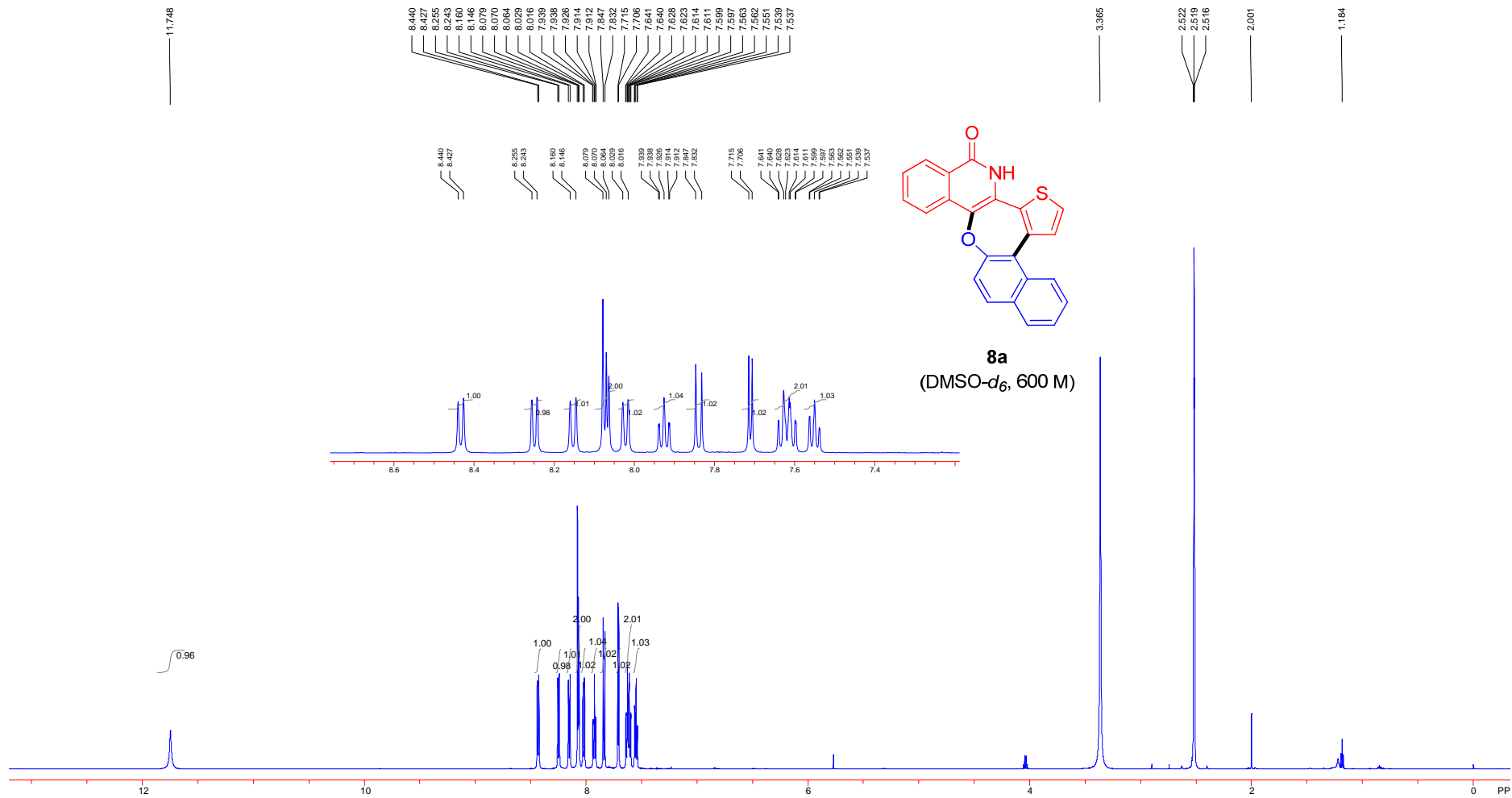
-0.000

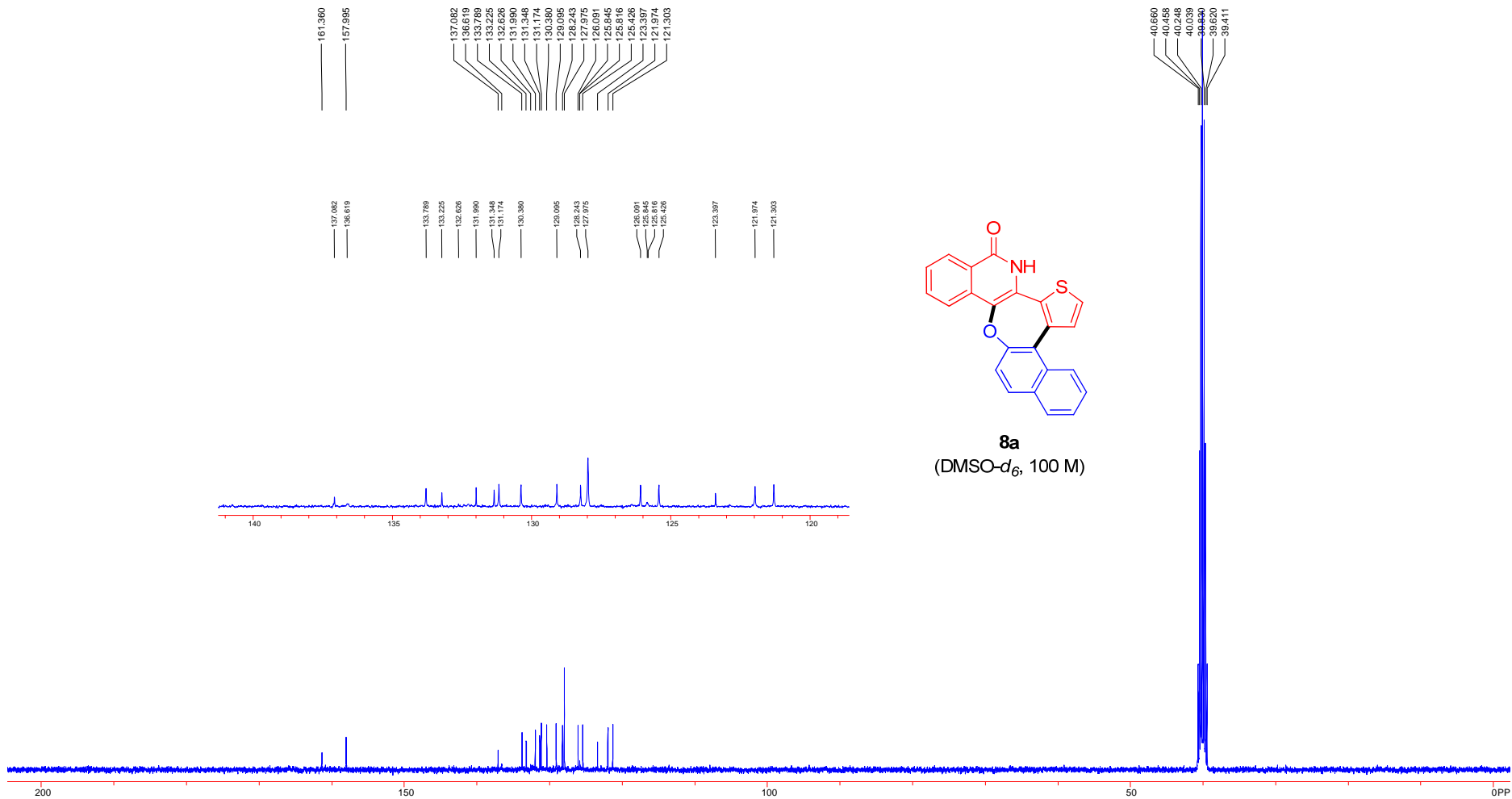


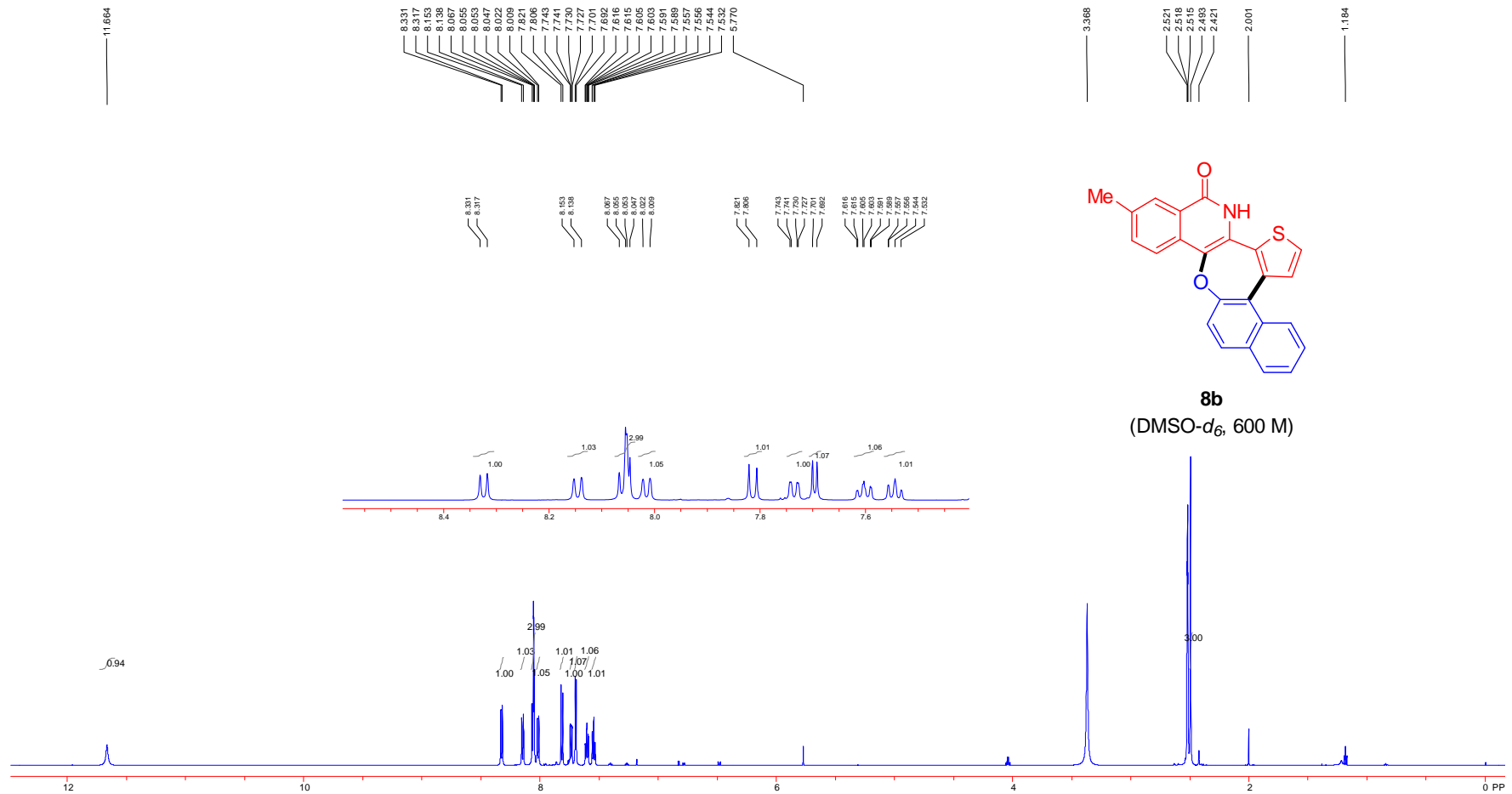
5j
(CDCl₃, 400M)

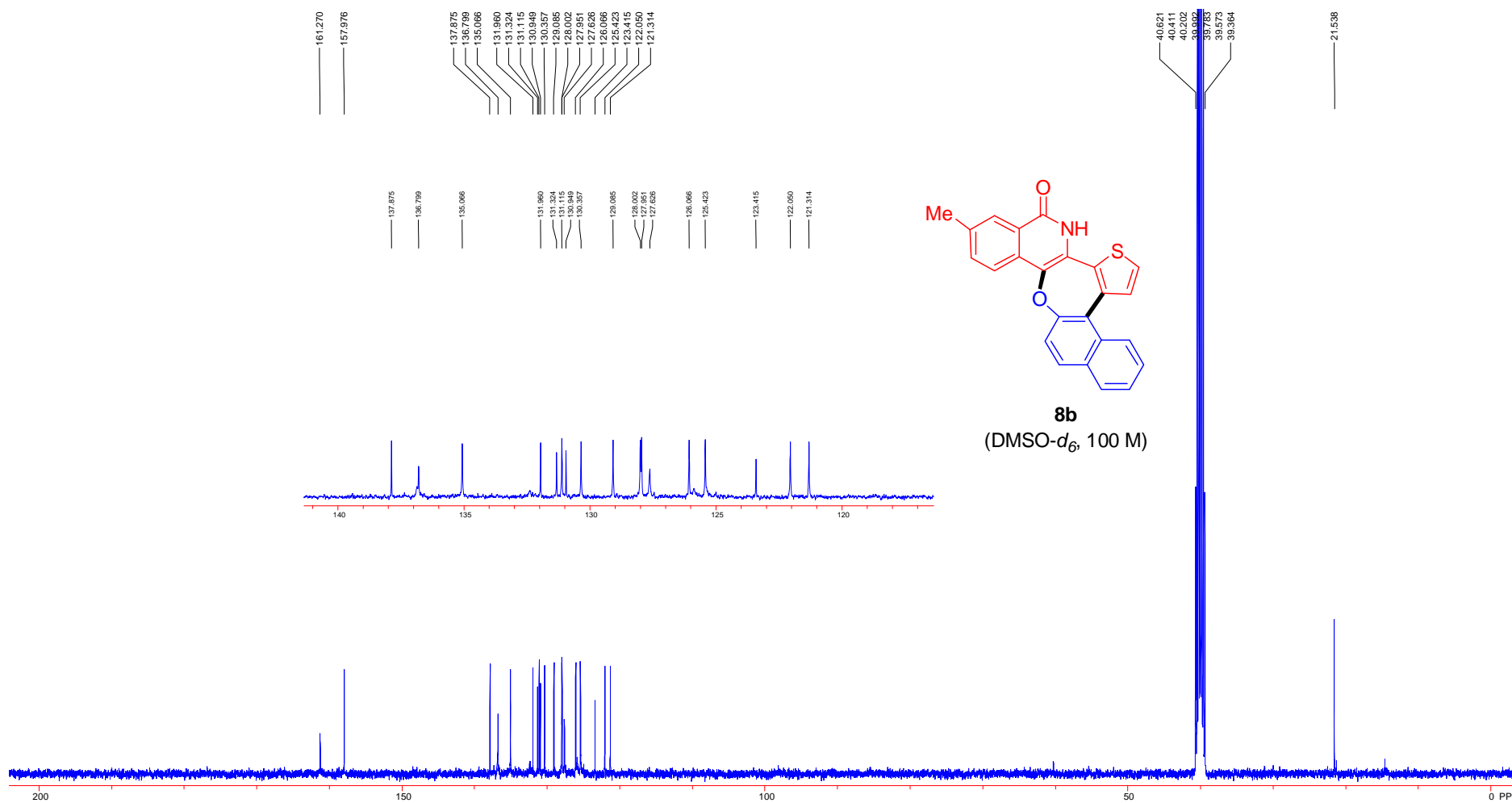


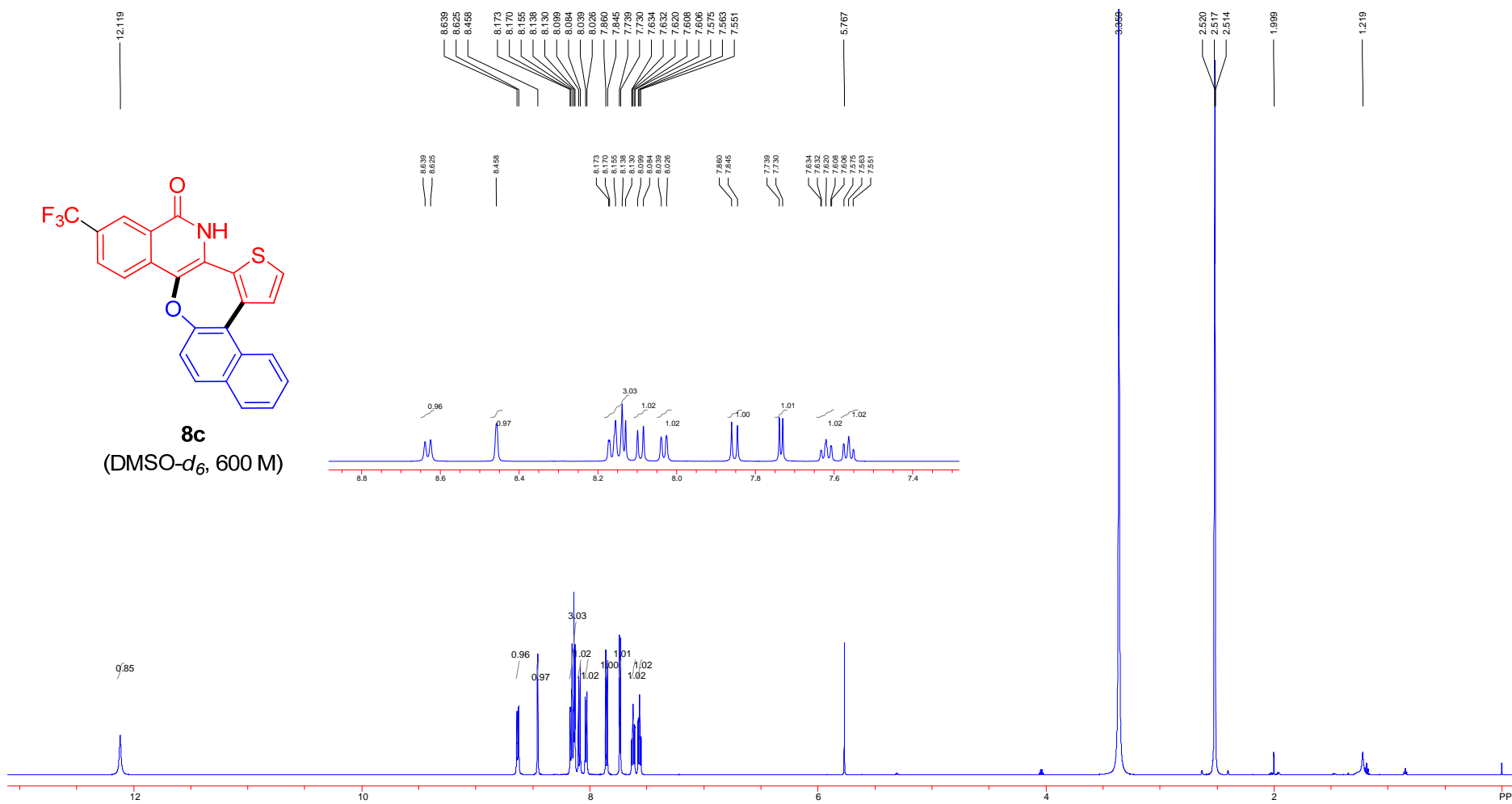


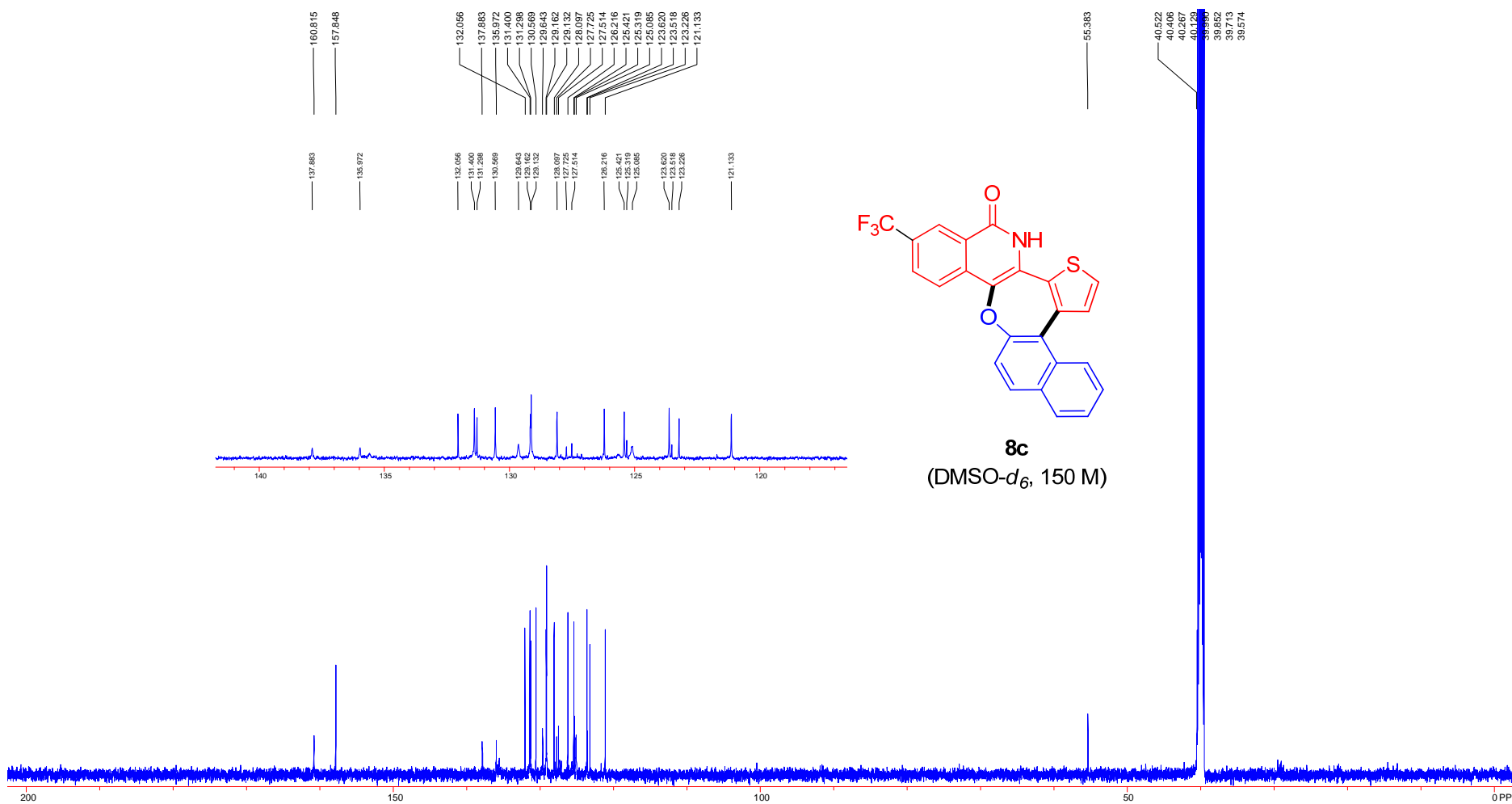


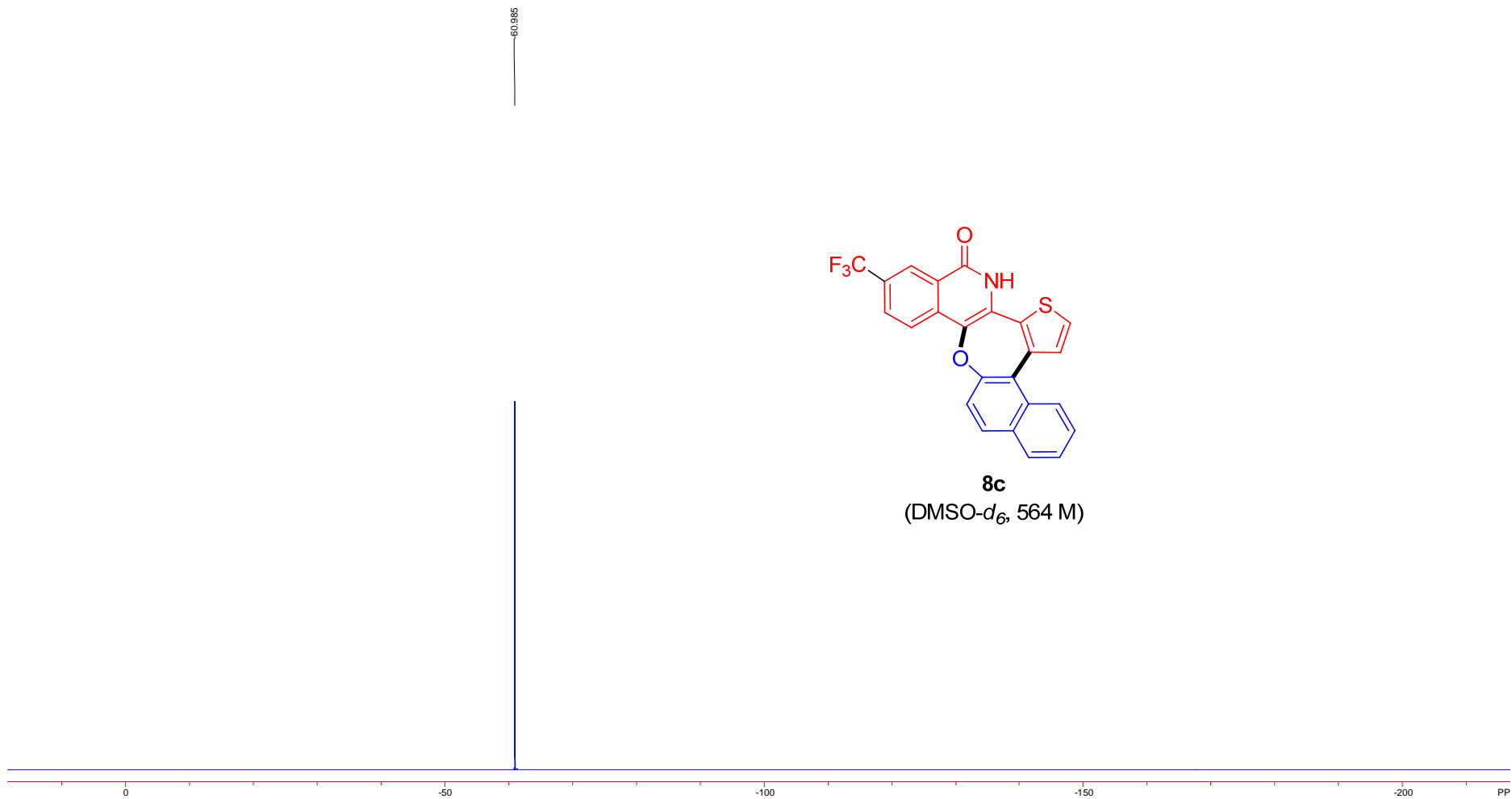


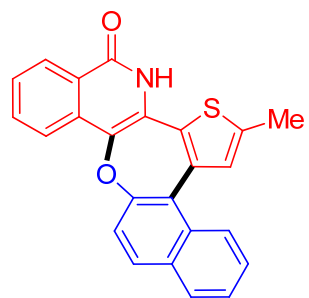




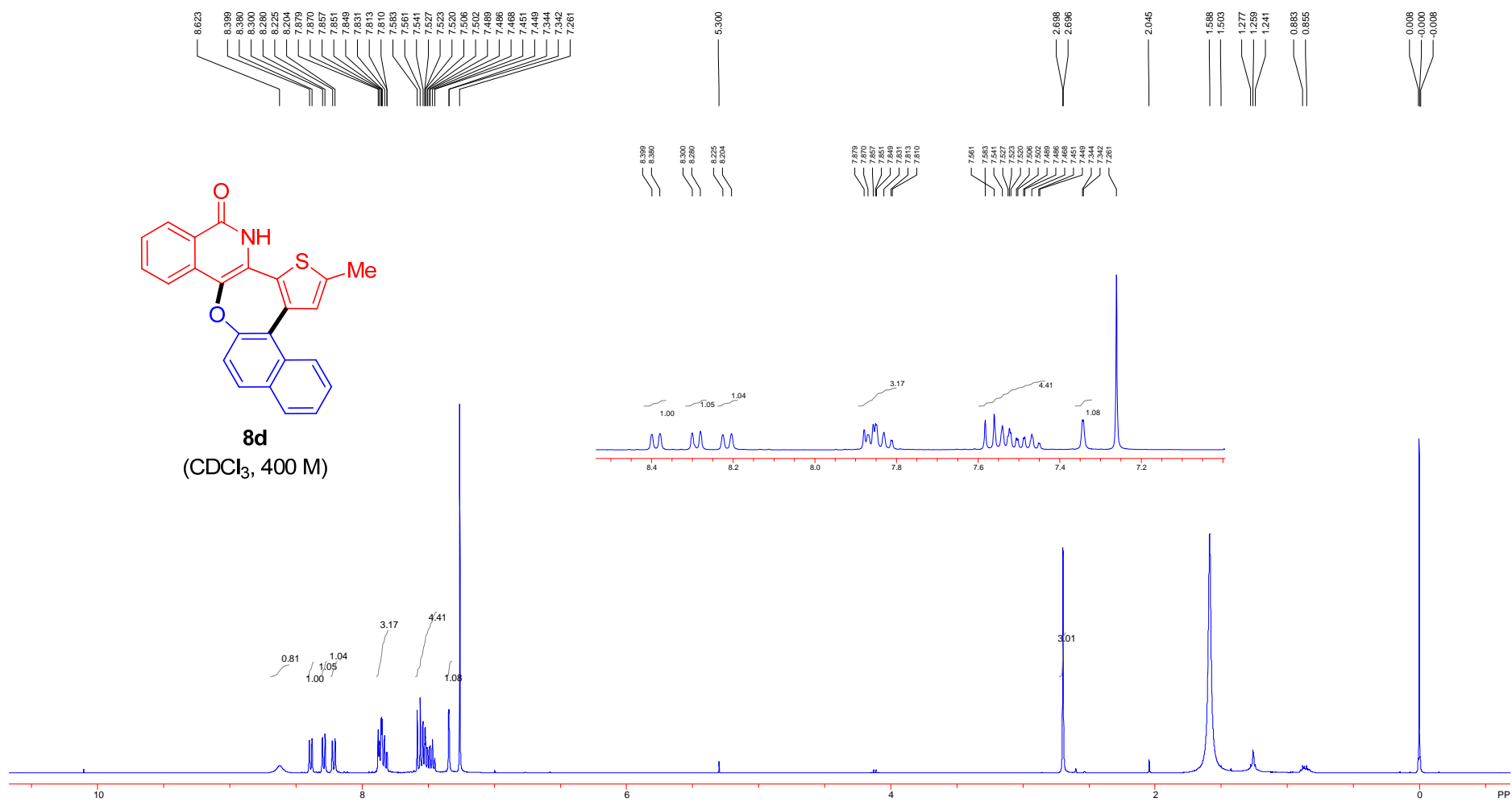


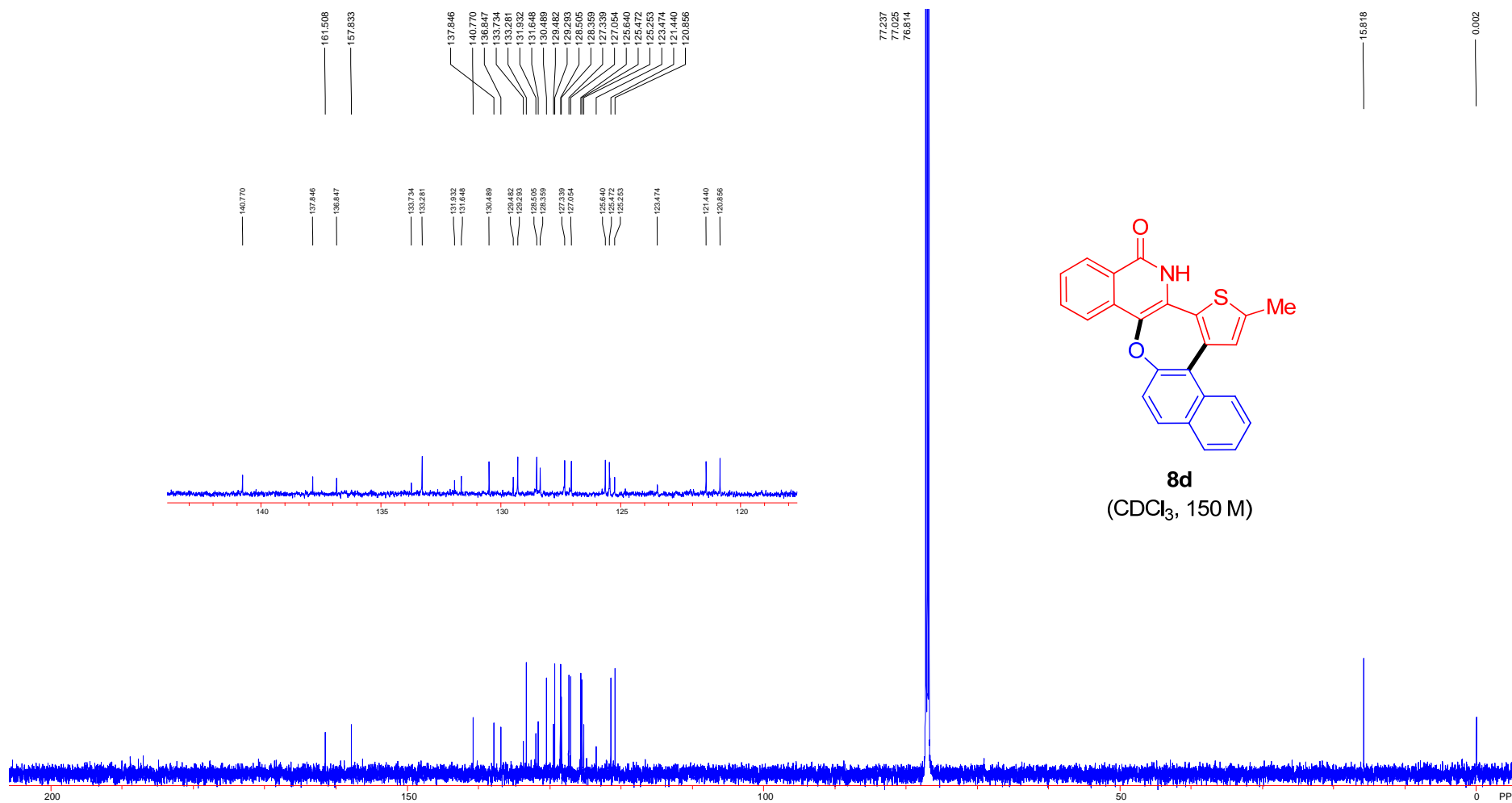


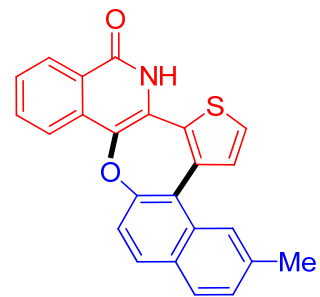
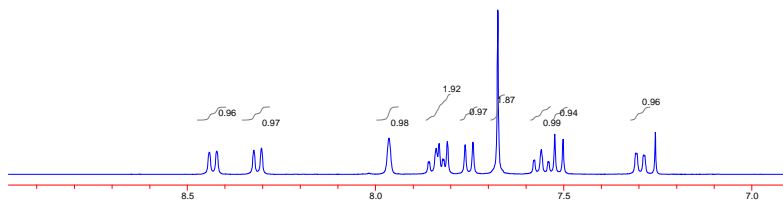
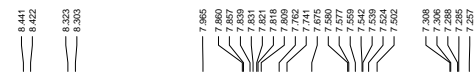
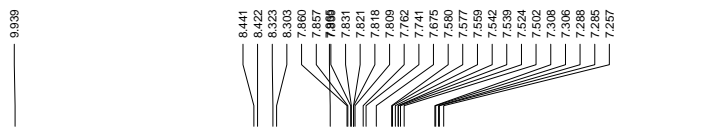




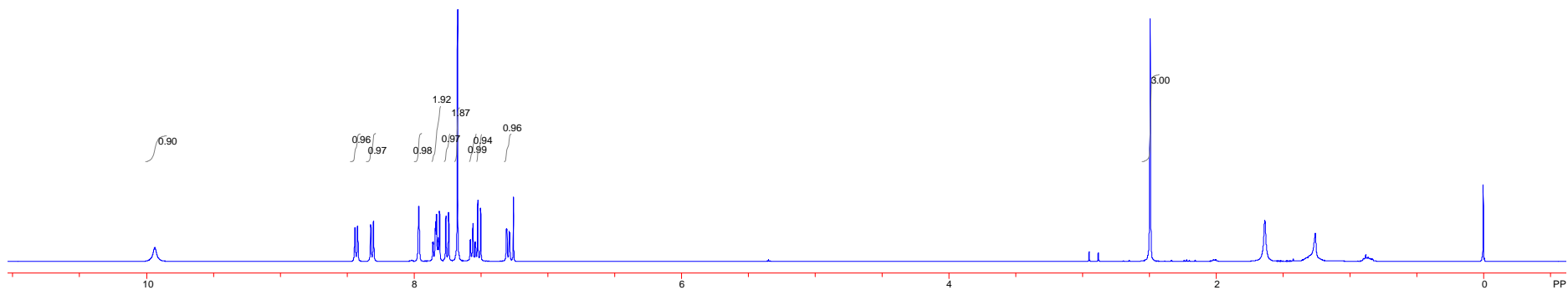
8d
(CDCl₃, 400 M)

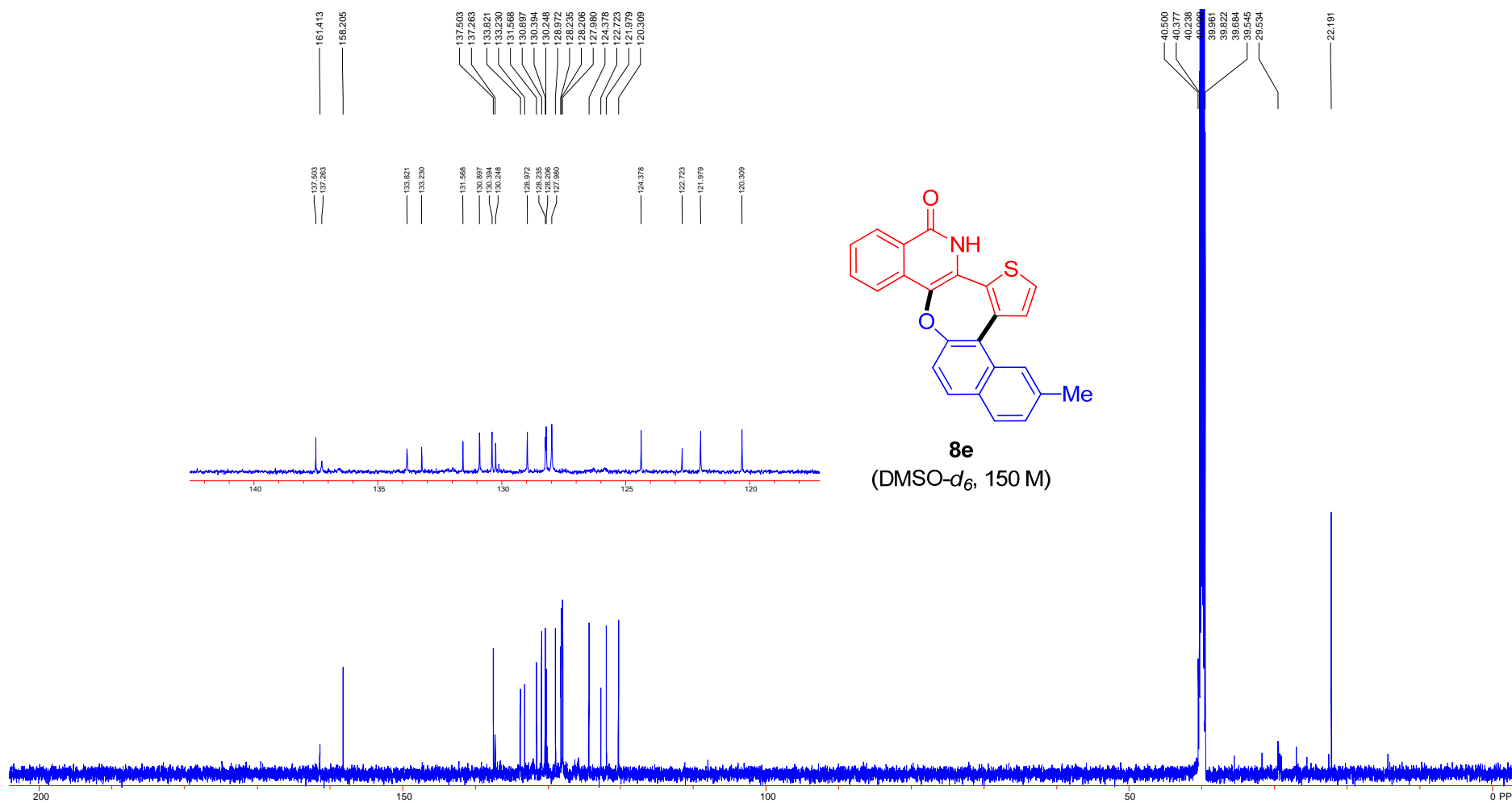


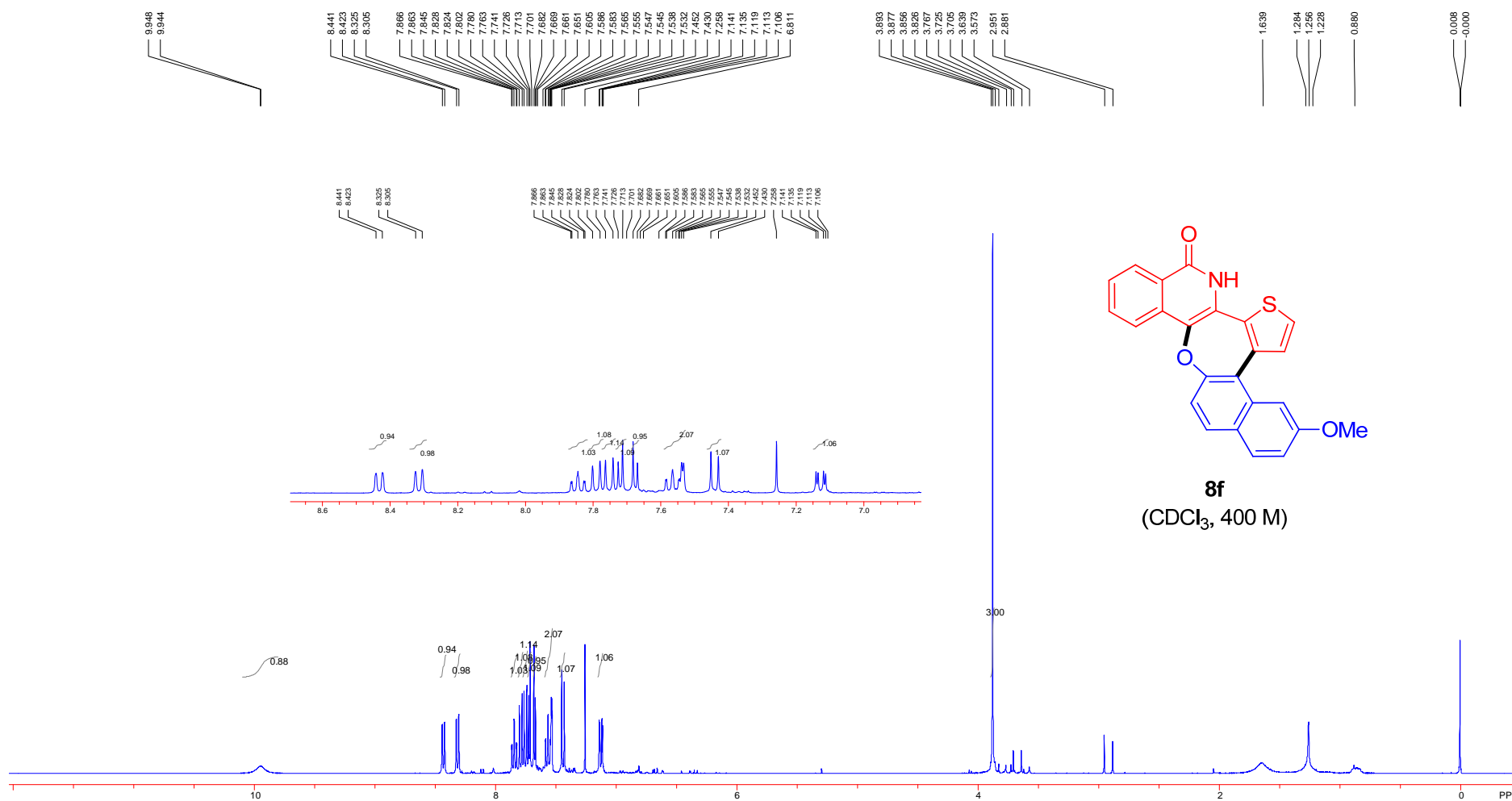


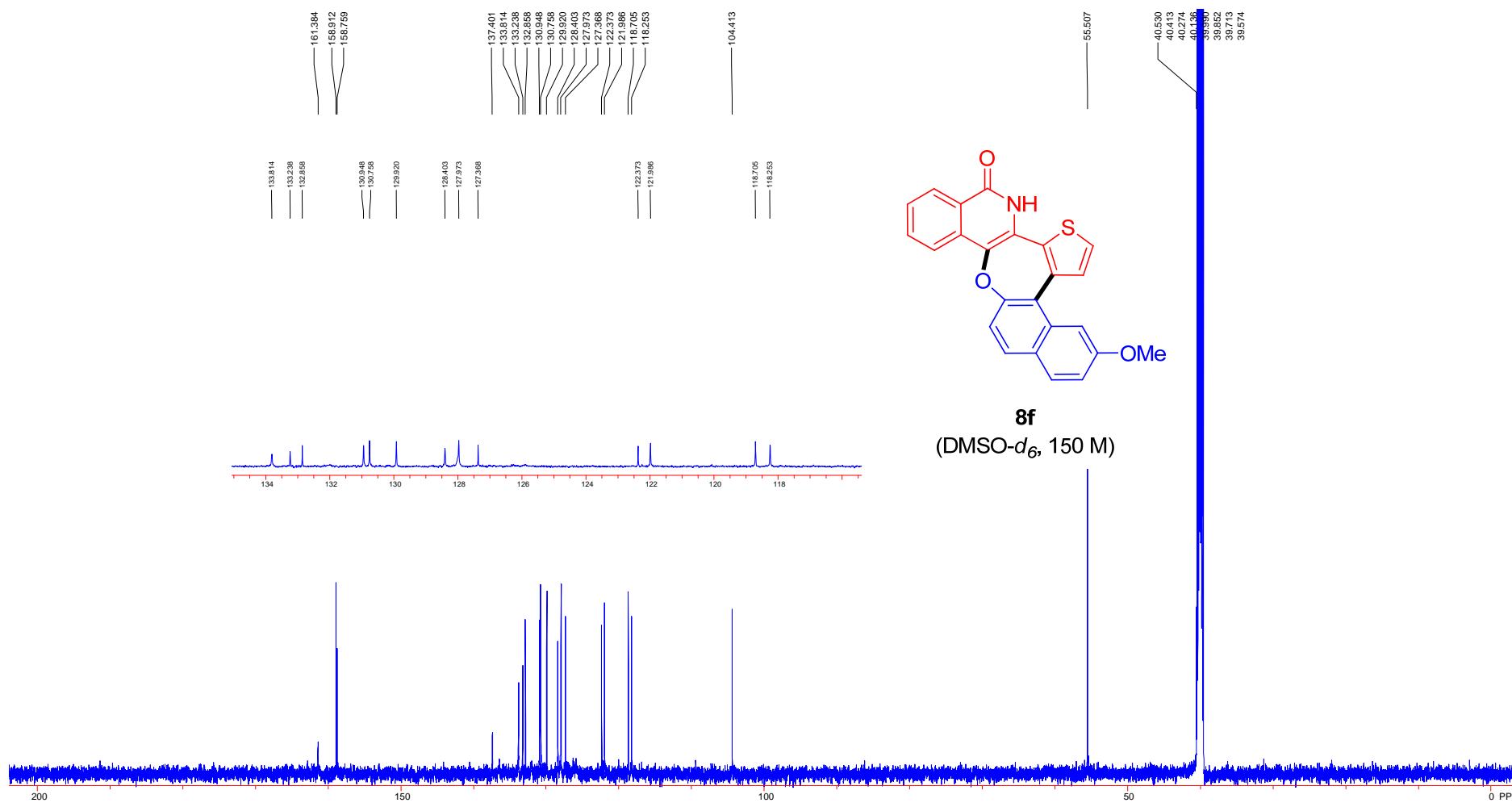


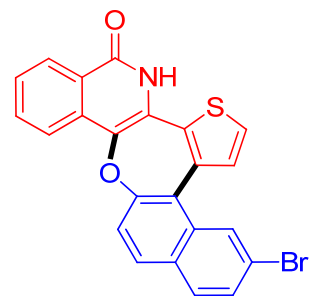
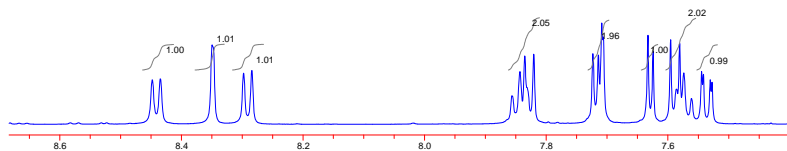
8e
(CDCl₃, 400 M)











8g
(CDCl₃, 600 M)

