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Supporting Information

Regioselective Iridium(III)-Catalyzed C–H Cyclization Using Acetylene Surrogate: Direct Access to Hydroxylated Polycyclic Phthalazinones

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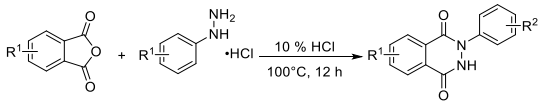
1. General Methods

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. NMR data were obtained for ^{1}H at 400 MHz, ^{13}C at 151 MHz. Chemicl shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, sep: septet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. TLC was performed on glass-backed silica plates. UV detection was monitored at 254 nm. Column chromatography was performed on silica gel (300-400 mesh), eluting with ethyl acetate and petroleum ether. Commercially available 2-chloroacetaldehyde (50 wt% in water) was utilized as the starting material. phthalazine/pyridazine dione and 2-chloro-2-phenylacetaldehyde were obtained according to the literature procedures.[1-9]

2. General Procedure for the Synthesis of Substrates

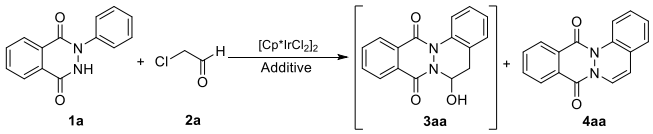
2.1 General procedure for the synthesis of phthalazine/pyridazine dione (1) [1-5]



The appropriate phenylhydrazine (1.1equiv) was added in one portion to a stirred mixture of phthalic/malonic anhydride (1.0 equiv) in 10% HCl at room temperature. The mixture was heated to 100 °C for 9 h after it was cooled, the resulting solid was collected by filtration washed with water and recrystallized by using ethanol. Yield (50-85%).

3. Optimization of the reaction conditions

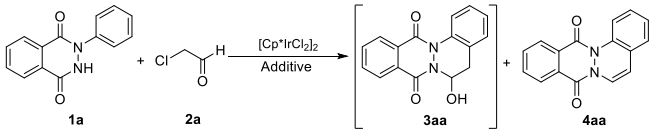
Table 1 Evaluation of acids[a]



Entry	**2a** (equiv)	Catalyst	Additive (eq.)	Solvent	T/°C	Yield **3aa**[b]	Yield **4aa**[c]
1[c]	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/MsOH (1)	DCE/THF(0.5:0.5mL)	100	NR	NR
2[d]	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/AcOH (1)	DCE/THF(0.5:0.5mL)	100	11%	35%
3	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/TFA (1)	DCE/THF(0.5:0.5mL)	100	55%	64%
4	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/CA (1)	DCE/THF(0.5:0.5mL)	100	56%	68%
5	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/HCOOH (1)	DCE/THF(0.5:0.5mL)	100	27%	41%

[a] Unless otherwise stated, reaction conditions are as follows: **1a** (0.05 mmol), **2a** (10 equiv) and $[Cp^*IrCl_2]_2$ (5 mol %) in solvent (1.0 mL) at 100 °C under Ar atmosphere for 3 h-15 h in a sealed tube. [b] The reaction was carried out for 3 h. [c] The reaction was carried out for 15 h.

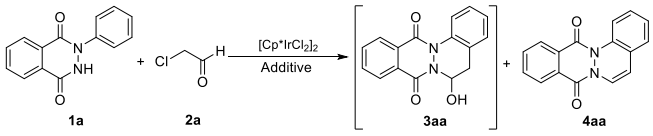
Table 2 Evaluation of oxidants[a]



Entry	**2a** (equiv)	Catalyst	Additive (eq.)	Solvent	T/°C	Yield **3aa**[b]	Yield **4aa**[c]
1[c]	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/$AgSbF_6$ (1)	DCE/MeOH(0.5:0.5mL)	100	26%	31%
2[d]	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/AgTFA (1)	DCE/THF(0.5:0.5mL)	100	60%	66%
3	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2)/Ag_2CO_3 (1)	DCE/THF(0.5:0.5mL)	100	36%	44%
4	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (2) (2)/Ag_2CO_3 (1)	DCE/THF(0.5:0.5mL)	100	18%	34%
5	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2{\cdot}H_2O$ (2)	DCE/THF(0.5:0.5mL)	100	58%	67%
6	10	$[IrCp^*Cl_2]_2$	$CuSO_4$ (2)	DCE/THF(0.5:0.5mL)	100	trace	trace
7	10	$[IrCp^*Cl_2]_2$	CuOTf (2)	DCE/THF(0.5:0.5mL)	100	trace	trace

[a] Unless otherwise stated, reaction conditions are as follows: **1a** (0.05 mmol), **2a** (10 equiv) and $[Cp^*IrCl_2]_2$ (5 mol %) in solvent (1.0 mL) at 100 °C under Ar atmosphere for 3 h-15 h in a sealed tube. [b] The reaction was carried out for 3 h. [c] The reaction was carried out for 15 h.

Table 3 Evaluation for equivalent of copper acetate[a]

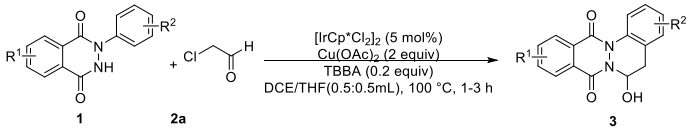


Entry	**2a** (equiv)	Catalyst	Additive (eq.)	Solvent	T/°C	Yield **3aa**[b]	Yield **4aa**[c]
1[c]	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (0.5)	DCE/THF(0.5:0.5mL)	100	trace	trace
2[d]	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (1)	DCE/THF(0.5:0.5mL)	100	13%	21%
3	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (3)	DCE/THF(0.5:0.5mL)	100	31%	38%
4	10	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2$ (4)	DCE/THF(0.5:0.5mL)	100	trace	trace

[a] Unless otherwise stated, reaction conditions are as follows: **1a** (0.05 mmol), **2a** (10 equiv) and $[Cp^*IrCl_2]_2$ (5 mol %) in solvent (1.0 mL) at 100 °C under Ar atmosphere for 3 h-15 h in a sealed tube. [b] The reaction was carried out for 3 h. [c] The reaction was carried out for 15 h.

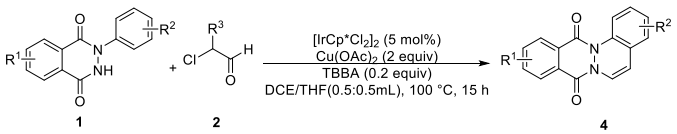
4. General Procedure for the Synthesis of Tetracyclic Phthalazine Derivatives

3.1 General procedure for the synthesis of 3



N-aryl phthalazinones **1a** (0.05 mmol, 1.0 equiv), 2-chloroacetaldehyde **2a** (0.5 mmol, 10 equiv), $[Cp^*IrCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.1 mmol, 2.0 equiv) and TBBA (0.01 mmol, 0.2 equiv) were stirred in DCE/THF (0.5:0.5 mL) in preheated oil bath at 100 °C for 1-3 h. After completion of the reaction, the mixture was then cooled to room temperature, the reaction mixture was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to give product **3** as white solid.

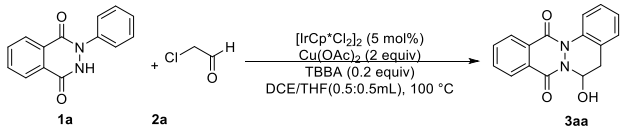
3.2 General procedure for the synthesis of 4



N-aryl phthalazinones **1a** (0.05 mmol, 1.0 equiv), 2-chloroacetaldehyde **2a** (0.5 mmol, 10 equiv) or 2-chloro-2-phenylacetaldehyde (0.1 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.1 mmol, 2.0 equiv) and TBBA (0.01 mmol, 0.2 equiv) were stirred in DCE/THF (0.5:0.5 mL) in preheated oil bath at 100 °C for 15 h. After completion of the reaction, the mixture was then cooled

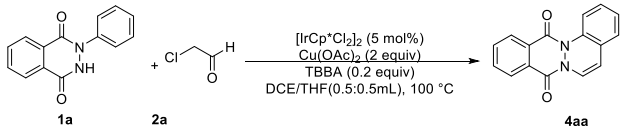
to room temperature, the reaction mixture was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to give product **4** as yellow solid.

3.3 Gram-scale reaction for the synthesis of 3aa



N-aryl phthalazinones **1a** (4.2 mmol, 1.0 equiv), 2-chloroacetaldehyde **2a** (42 mmol, 10 equiv), $[Cp^*IrCl_2]_2$ (0.21 mmol, 5 mol %), $Cu(OAc)_2$ (8.4 mmol, 2.0 equiv) and TBBA (0.84 mmol, 0.2 equiv) were stirred in DCE/THF (10:10 mL) in preheated oil bath at 100 °C for 3 h. After completion of the reaction, the mixture was then cooled to room temperature, the reaction mixture was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to give product **3aa** in 61% yield as white solid.

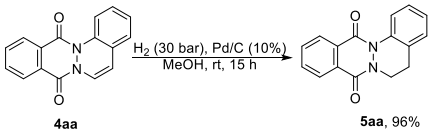
3.4 Gram-scale reaction for the synthesis of 4aa



N-aryl phthalazinones **1a** (4.2 mmol, 1.0 equiv), 2-chloroacetaldehyde **2a** (42 mmol, 10 equiv), $[Cp^*IrCl_2]_2$ (0.21 mmol, 5 mol %), $Cu(OAc)_2$ (8.4 mmol, 2.0 equiv) and TBBA (0.84 mmol, 0.2 equiv) were stirred in DCE/THF (10:10 mL) in preheated oil bath at 100 °C for 15 h. After completion of the reaction, the mixture was then cooled to room temperature, the reaction mixture was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to give product **4aa** in 73% yield as yellow solid.

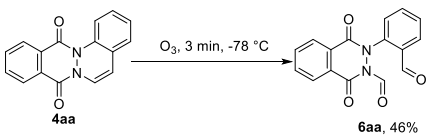
4. Synthetic Applications of 3aa

4.1 Procedure for the synthesis of compound 4aa and 7aa:



Pd/C (10%) was added to a stirred solution of **3aa** (0.05 mmol, 1.0 equiv) in MeOH (1.0 mL) at room temperature under 30 bar H_2 atmosphere. The mixture was stirred in room temperature for 15 h. Filter the reaction mixture through Celite. Wash the reaction mixture with MeOH. Distill off the solvent under reduced pressure. And the crude product was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to obtain the corresponding product **5aa** as white solid.

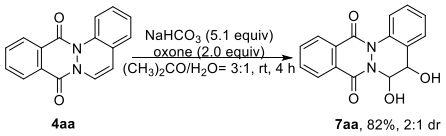
4.2 Procedure for the synthesis of compound 6aa:



3aa (0.2 mmol, 1.0 equiv) was dissolved in DCM (3.0 mL) and cooled down to -78 °C. Ozone was bubbled through the solution for 3 min. ozone was then replaced with argon until excess ozone

was removed at -78 ºC. The reaction mixture was returned to room temperature. the crude product was purified by column chromatography (eluent: petroleum ether /EtOAc/AcOH = 3:1:0.5%, v/v/v) to obtain the **6aa** as white solid.

4.3 Procedure for the synthesis of compound 7aa:

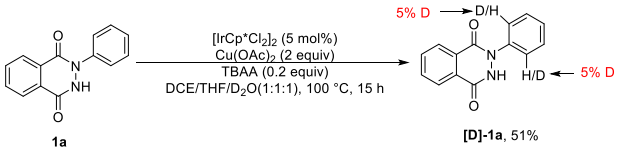


4aa **7aa**, 82%, 2:1 dr

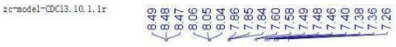
4aa (0.1 mmol, 1.0 equiv), $NaHCO_3$ (0.51 mmol, 5.1 equiv) and oxone (0.2 mmol, 2.0 equiv) were stirred in $(CH_3)_2CO/H_2O$ (1.5:0.5 mL) at rt for 4 h. After completion of the reaction, the reaction mixture was purified by column chromatography (eluent: petroleum ether /EtOAc = 1:1, v/v) to give product **7aa** as white solid.

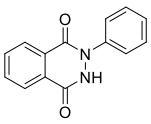
5. Mechanistic Studies

5.1 *H/D* exchange experiments

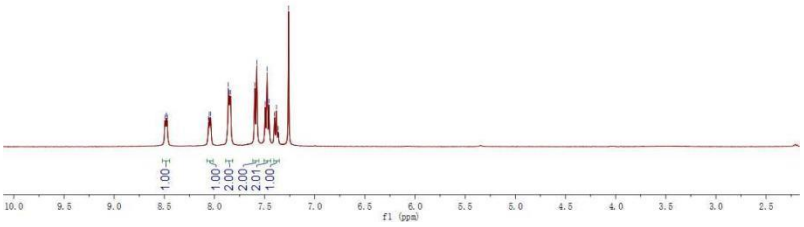


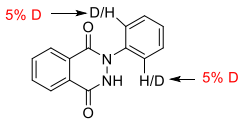
1a **[D]-1a**, 51%



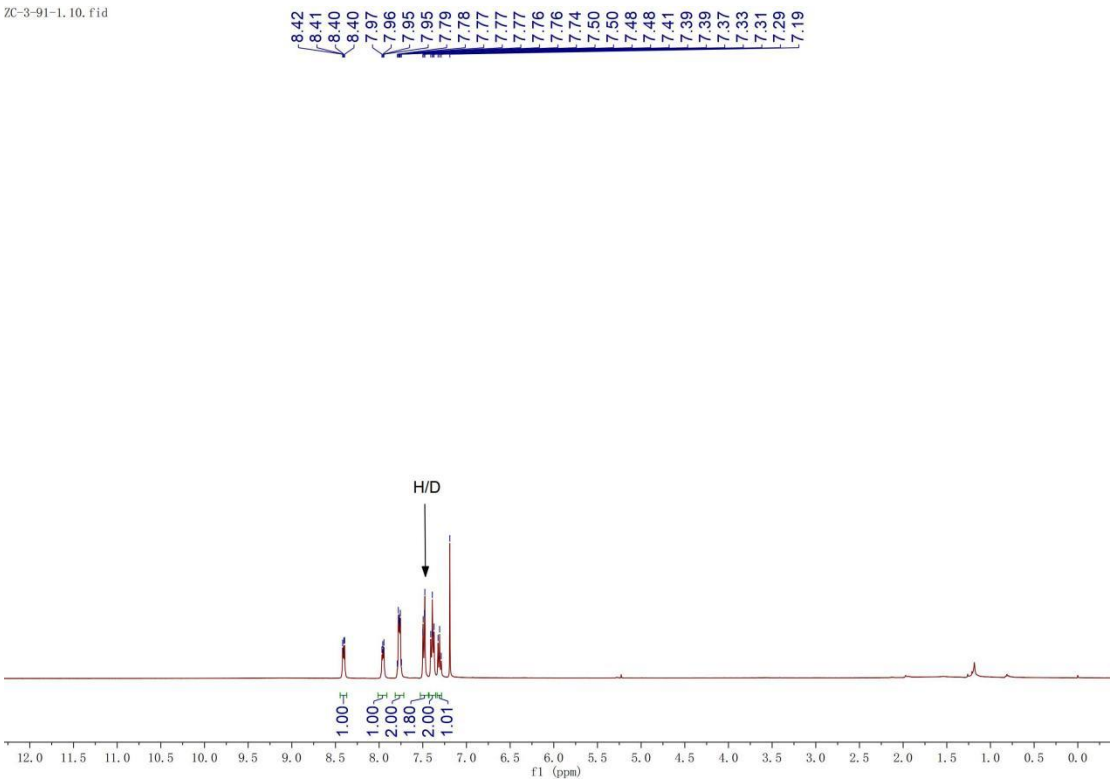


1a



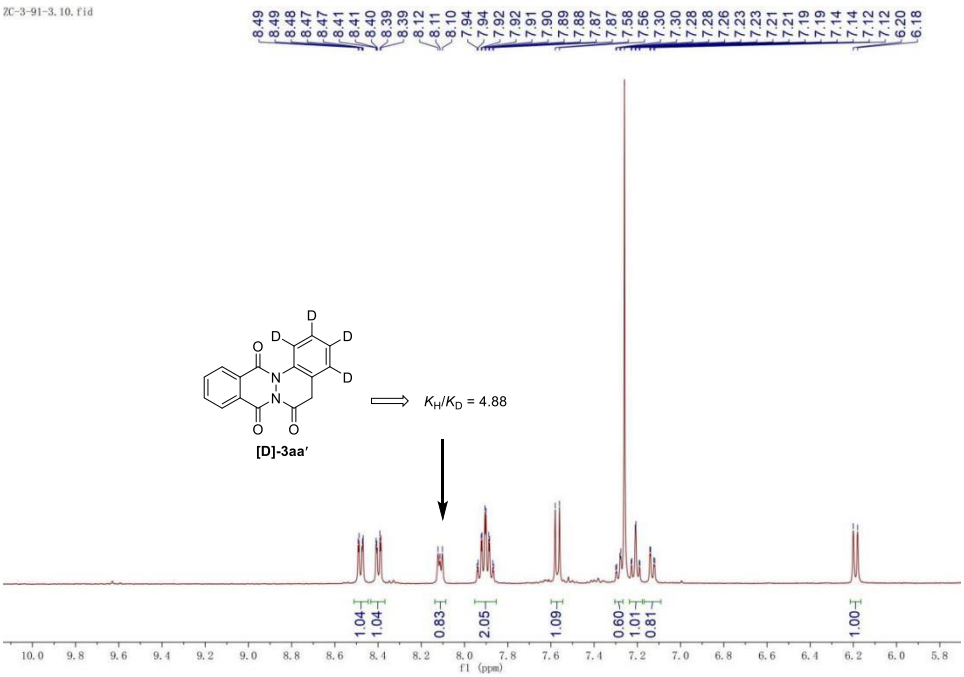


[D]-1a



To an oven dried sealed tube was equipped with a stir bar were charged with 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (0.05 mmol, 1.0 equiv), $[Cp^*IrCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.1 mmol, 2.0 equiv) and TBBA (0.01 mmol, 0.2 equiv) were stirred in DCE/THF/D_2O (0.5:0.5:0.5 mL) in preheated oil bath at 100 °C for 15 h under Ar atmosphere. After completion of the reaction, the mixture was then cooled to room temperature. The residue was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to afford **[D]-1a**. The deuterium content product was 51%. The content was determined by the ^1H NMR.

5.2 Kinetic isotope effect (KIE) studies



To an oven dried sealed tube was equipped with a stir bar were charged with 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (0.05 mmol, 1.0 equiv), **[D]-1a'** (0.05 mmol, 1.0 equiv) were added under the optimized conditions. The resulting mixture was stirred at 100 °C for 15 h and then concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether /EtOAc = 3:1, v/v) to get the desired product, which was determined by ^{1}H NMR. The calculated k_H/k_D =0.83/0.17=4.88.

6. References

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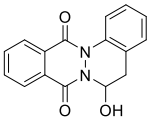
7. Characterization Data and NMR Spectra of Tetracyclic Phthalazine Derivatives

6-hydroxy-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (3aa)

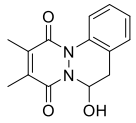


3aa

11.6 mg, 83% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, J = 6.9, 2.1 Hz, 1H), 8.31 (dd, J = 6.8, 2.2 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.86 (tt, J = 7.4, 5.6 Hz, 2H), 7.37 (ddd, J = 9.5, 7.2, 1.7 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 3.4 Hz, 1H), 4.36 (s, 1H), 3.19 (d, J = 3.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.7, 135.2, 134.18, 133.9,

130.0, 129.2, 128.6, 128.6, 127.7, 127.6, 127.4, 126.5, 123.1, 78.6, 33.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_3^+$ 281.0921; Found 281.0917.

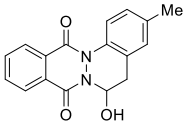
6-hydroxy-2,3-dimethyl-6,7-dihydropyridazino[1,2-a]cinnoline-1,4-dione (3ba)



3ba

11.0 mg, 85% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.28 – 7.16 (m, 3H), 6.38 (s, 1H), 4.35 (s, 1H), 3.04 (d, J = 2.6 Hz, 2H), 2.14 (d, J = 22.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 156.6, 141.1, 138.7, 134.8, 129.1, 127.4, 127.2, 125.8, 122.5, 77.2, 33.2, 14.1, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2O_3^+$ 259.1077; Found 259.1076.

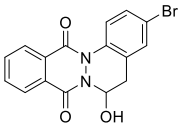
6-hydroxy-3-methyl-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (3ca)



3ca

11.8 mg, 80% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 – 8.18 (m, 2H), 7.97 (q, J = 5.2, 4.2 Hz, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.25 – 7.03 (m, 2H), 6.74 (d, J = 4.2 Hz, 1H), 6.55 (d, J = 4.1 Hz, 1H), 3.17 (d, J = 15.0 Hz, 1H), 3.02 – 2.88 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.2, 156.1, 136.1, 134.4, 134.2, 132.4, 130.1, 129.9, 128.9, 128.1, 127.8, 127.6, 127.2, 123.4, 76.1, 34.2, 21.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_3^+$ 295.1077; Found 295.1072.

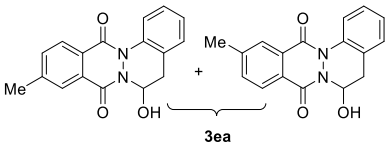
3-bromo-6-hydroxy-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (3da)



3da

15.0 mg, 84% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (dt, J = 15.8, 3.8 Hz, 2H), 8.02 – 7.87 (m, 3H), 7.62 (d, J = 2.3 Hz, 1H), 7.52 (dd, J = 8.8, 2.4 Hz, 1H), 6.86 (d, J = 4.2 Hz, 1H), 6.57 (q, J = 3.1 Hz, 1H), 3.21 (d, J = 14.9 Hz, 1H), 3.05 (dd, J = 15.2, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.3, 156.1, 134.5, 134.1, 132.2, 130.8, 129.7, 129.4, 128.9, 128.1, 127.7, 125.7, 118.9, 75.8, 34.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrN_2O_3^+$ 359.0026; Found 359.0020.

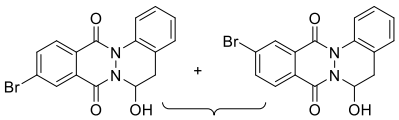
6-hydroxy-10-methyl-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione and **6-hydroxy-11-methyl-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (3ea)**



3ea

11.5 mg, 78% yield; White solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.11 (m, 2H), 7.92 (d, J = 8.1 Hz, 1H), 7.65 (dd, J = 8.0, 1.7 Hz, 1H), 7.39 – 7.27 (m, 3H), 6.52 (s, 1H), 4.12 (d, J = 6.6 Hz, 1H), 3.19 (d, J = 3.3 Hz, 2H), 2.57 (d, J = 3.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 156.9, 145.7, 145.5, 135.4, 135.0, 129.2, 128.6, 127.7, 127.6, 127.4, 126.5, 126.1, 123.1, 78.7, 33.3, 22.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_3^+$ 295.1077; Found 295.1073.

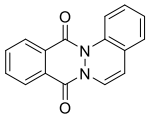
10-bromo-6-hydroxy-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (3fa) and **11-bromo-6-hydroxy-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (3fa)**



3fa

14.7mg, 82% yield; White solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 2.0 Hz, 0.5H), 8.45 (d, J = 2.0 Hz, 0.5H), 8.29 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.97 (td, J = 8.5, 2.0 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.39 – 7.28 (m, 3H), 6.52 (d, J = 3.3 Hz, 1H), 4.19 (s, 1H), 3.19 (d, J = 3.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 156.7, 156.1, 155.5, 137.4, 137.2, 135.0, 131.5, 131.3, 130.5, 130.3, 129.9, 129.6, 129.4, 129.3, 129.3, 127.7, 127.7, 127.7, 127.6, 127.3, 126.4, 123.1, 78.8, 78.6, 33.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrN_2O_3^+$ 359.0026; Found 359.0021.

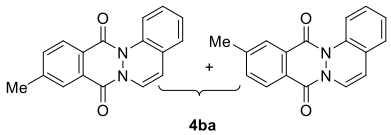
Phthalazino[2,3-a]cinnoline-8,13-dione (4aa)



4aa

12.6 mg, 96% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.45 (m, 1H), 8.44 – 8.35 (m, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.57 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H), 7.13 (d, J = 6.7 Hz, 1H), 6.19 (d, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 154.3, 134.3, 134.0, 133.9, 129.2, 128.4, 128.1, 128.0, 127.6, 127.2, 125.7, 125.6, 125.2, 121.5, 110.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}N_2O_2^+$ 263.0815; Found 263.0813.

10-methylphthalazino[2,3-a]cinnoline-8,13-dione (3ga) and **11-methylphthalazino[2,3-a]cinnoline-8,13-dione (4ba)**

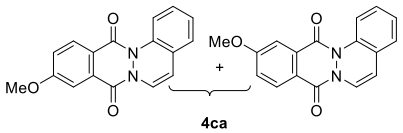


4ba

12.6 mg, 91% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.19 (m, 2H), 8.09 (d, J = 8.2

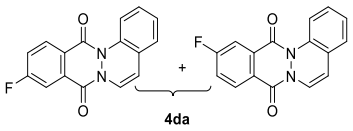
Hz, 1H), 7.69 (t, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.26 (dd, *J* = 10.2, 5.4 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.16 (d, *J* = 7.9 Hz, 1H), 2.59 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 156.9, 154.4, 145.7, 135.4, 135.0, 134.0, 129.1, 128.5, 128.4, 128.0, 128.0, 127.9, 127.5, 127.2, 127.1, 125.7, 125.6, 125.3, 125.1, 121.5, 121.4, 110.3, 110.0, 22.1, 22.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2^+$ 277.0972; Found 277.0966.

10-methoxyphthalazino[2,3-a]cinnoline-8,13-dione and **11-methoxyphthalazino[2,3-a]cinnoline-8,13-d-ione (4ca)**



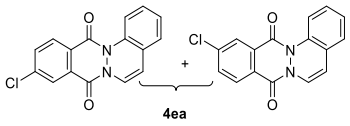
12.9mg, 88% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.34 (dd, *J* = 30.6, 8.8 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 20.0 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.17 (dd, *J* = 15.3, 7.9 Hz, 1H), 4.00 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 164.6, 156.6, 154.2, 133.9, 131.4, 130.6, 130.1, 128.1, 127.9, 127.2, 126.9, 125.8, 125.5, 125.5, 123.0, 122.6, 121.6, 121.3, 120.7, 110.6, 109.8, 109.6, 109.2, 56.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3^+$ 293.0921; Found 293.0915.

10-fluorophthalazino[2,3-a]cinnoline-8,13-dione and **11-fluorophthalazino[2,3-a]cinnoline-8,13-11-di-one (4da)**



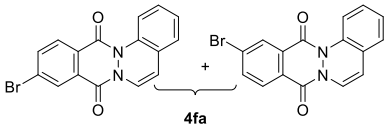
13.3 mg, 95% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.46 (ddd, *J* = 32.0, 8.7, 5.1 Hz, 1H), 8.16 – 7.98 (m, 2H), 7.56 (dt, *J* = 8.1, 5.1 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.22 (td, *J* = 7.3, 3.4 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 6.20 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 166.2, 165.9, 164.5, 164.2, 155.0, 154.8, 154.7, 152.5, 152.3, 152.3, 132.9, 132.7, 131.0, 130.9, 130.9, 130.8, 130.4, 130.3, 129.2, 127.2, 127.2, 126.5, 126.3, 124.8, 124.7, 124.4, 124.3, 124.1, 123.9, 123.1, 121.4, 121.3, 121.1, 121.0, 120.5, 120.4, 113.7, 113.6, 113.2, 113.0, 109.8, 109.3. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -100.93, -100.94, -100.95, -100.97, -100.97, -100.99, -101.80, -101.81, -101.82. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 281.0721; Found 281.0717.

10-chlorophthalazino[2,3-a]cinnoline-8,13-dione and **11-chlorophthalazino[2,3-a]cinnoline-8,13-d-ione (4ea).**



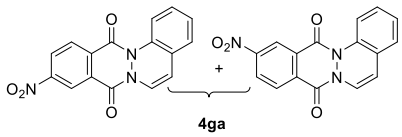
11.5 mg, 78% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, J = 12.4, 5.0 Hz, 1H), 8.34 (dd, J = 9.9, 5.1 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.83 (dd, J = 14.0, 5.6 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.14 (d, J = 7.1 Hz, 1H), 6.20 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 155.7, 153.6, 153.2, 141.3, 140.9, 134.6, 134.3, 133.9, 133.8, 130.6, 130.3, 129.7, 128.3, 128.2, 127.7, 127.5, 127.5, 127.4, 125.9, 125.8, 125.8, 125.4, 125.3, 125.1, 124.9, 121.5, 121.4, 110.8, 110.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 297.0425; Found 297.0412.

10-bromophthalazino[2,3-a]cinnoline-8,13-dione and **11-bromophthalazino[2,3-a]cinnoline-8,13-dione (4fa).**



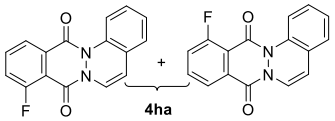
11.9 mg, 70% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 2.0 Hz, 1H), 8.46 (d, J = 1.9 Hz, 0H), 8.26 (d, J = 8.4 Hz, 0H), 8.18 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.92 (dd, J = 8.4, 2.0 Hz, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.22 (td, J = 7.8, 1.8 Hz, 1H), 7.16 (td, J = 7.5, 1.3 Hz, 1H), 7.07 (dd, J = 7.5, 1.7 Hz, 1H), 6.13 (d, J = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 153.7, 137.5, 137.2, 133.8, 131.3, 130.8, 130.5, 130.2, 129.7, 129.7, 128.2, 127.5, 127.4, 126.3, 125.8, 125.8, 125.3, 125.3, 125.0, 124.9, 121.5, 110.8, 110.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}BrN_2O_2^+$ 340.9920; Found 340.9914.

10-nitrophthalazino[2,3-a]cinnoline-8,13-dione and **11-nitrophthalazino[2,3-a]cinnoline-8,13-dione (4ga).**



9.4 mg, 61% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (m, 1H), 8.64 (ddd, J = 26.4, 14.2, 4.9 Hz, 2H), 8.14 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.28 (s, 1H), 7.18 (dd, J = 7.4, 1.4 Hz, 1H), 6.27 (dd, J = 7.8, 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 154.0, 152.5, 151.3, 133.6, 131.7, 131.6, 130.7, 130.6, 130.2, 129.2, 128.6, 128.5, 128.0, 127.9, 127.8, 127.8, 126.2, 126.0, 125.0, 124.9, 124.7, 124.2, 123.7, 121.5, 121.4, 111.5, 111.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}N_3O_4^+$ 308.0666; Found 308.0664.

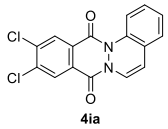
9-fluorophthalazino[2,3-a]cinnoline-8,13-dione and 12-fluorophthalazino[2,3-a]cinnoline-8,13-dione (4ha)



4ha

12.6 mg, 90% yield; Yellow solid (the product was obtained as mixtures of two regioisomers in varying ratio, as its starting substrates itself was prepared as an inseparable regioisomeric mixture); eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 30.9, 7.9 Hz, 1H), 8.04 (dd, J = 14.7, 8.2 Hz, 1H), 7.88 (dt, J = 12.7, 6.1 Hz, 1H), 7.70 – 7.35 (m, 3H), 7.17 (dd, J = 29.2, 7.2 Hz, 2H), 6.20 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 160.8, 155.7, 151.3, 135.6, 135.5, 133.6, 131.1, 129.7, 129.0, 128.2, 128.1, 127.5, 127.3, 125.8, 125.7, 125.4, 125.3, 124.6, 124.3, 122.5, 121.9, 121.7, 121.5, 116.1, 111.0, 110.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.66, -108.67, -108.69, -108.70, -109.16, -109.17, -109.19, -109.20. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 281.0721; Found 281.0716.

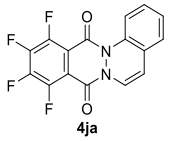
10,11-dichlorophthalazino[2,3-a]cinnoline-8,13-dione (4ia)



4ia

8.4 mg, 51% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 33.4 Hz, 2H), 8.09 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.22 (d, J = 7.3 Hz, 1H), 7.15 (d, J = 7.1 Hz, 1H), 6.22 (d, J = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 152.8, 139.8, 139.5, 133.8, 130.5, 129.9, 128.5, 127.7, 126.9, 126.0, 125.3, 125.0, 121.5, 110.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_9Cl_2N_2O_2^+$ 331.0036; Found 331.0030.

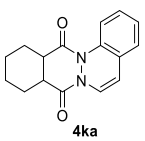
9,10,11,12-tetrafluorophthalazino[2,3-a]cinnoline-8,13-dione (4ja)



4ja

9.0 mg, 54% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.26 (d, J = 7.4 Hz, 1H), 7.18 (d, J = 7.1 Hz, 1H), 6.27 (d, J = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 149.4, 133.0, 129.0, 128.4, 127.8, 126.0, 125.5, 124.9, 124.6, 121.6, 114.2, 113.0, 111.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.27, -134.30, -134.31, -134.33, -134.34, -134.35, -134.37, -134.39, -134.51, -134.54, -134.55, -134.57, -134.58, -134.59, -134.61, -134.63, -143.05, -143.07, -143.10, -143.13, -143.15, -143.18, -143.68, -143.71, -143.73, -143.76, -143.78, -143.81. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_7F_4N_2O_2^+$ 335.0438; Found 335.0420.

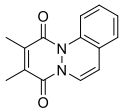
8a,9,10,11,12,12a-hexahydrophthalazino[2,3-a]cinnoline-8,13-dione (4ka)



4ka

9.4 mg, 70% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.12 (dd, J = 7.5, 6.8 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 5.93 (d, J = 7.7 Hz, 1H), 2.43 – 2.32 (m, 2H), 2.31 – 2.20 (m, 2H), 1.96 – 1.85 (m, 2H), 1.49 – 1.37 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 166.9, 133.9, 128.0, 126.8, 126.2, 125.7, 125.3, 122.5, 110.1, 40.4, 40.0, 27.0, 26.0, 24.6, 24.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O_2^+$ 269.1285; Found 269.1277.

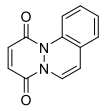
2,3-dimethylpyridazino[1,2-a]cinnoline-1,4-dione (4la)



4la

11.6 mg, 97% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.16 (dt, J = 14.5, 6.5 Hz, 2H), 7.05 (d, J = 7.1 Hz, 1H), 6.11 (d, J = 7.9 Hz, 1H), 2.20 (d, J = 12.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 154.1, 140.3, 137.5, 133.9, 128.0, 127.2, 125.6, 124.7, 124.6, 120.8, 110.2, 14.4, 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}N_2O_2^+$ 241.0972; Found 241.0967.

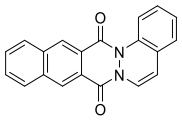
Pyridazino[1,2-a]cinnoline-1,4-dione (4ma)



4ma

9.1 mg, 86% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.23 (td, J = 8.0, 1.7 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.10 – 7.03 (m, 2H), 6.98 (d, J = 10.1 Hz, 1H), 6.17 (d, J = 8.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 152.8, 135.5, 133.7, 132.2, 128.3, 127.7, 125.9, 124.2, 124.1, 120.6, 110.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_9N_2O_2^+$ 213.0659; Found 213.0656.

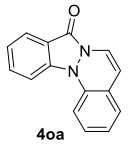
Benzo[6,7]phthalazino[2,3-a]cinnoline-8,15-dione (4na)



4na

11.1 mg, 71% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.96 (s, 1H), 8.17 (td, J = 6.7, 3.4 Hz, 2H), 8.04 (d, J = 8.2 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.55 (d, J = 7.8 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.20 (td, J = 7.5, 1.0 Hz, 1H), 7.12 (dd, J = 7.5, 1.5 Hz, 1H), 6.17 (d, J = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 155.1, 135.4, 135.1, 134.2, 130.4, 130.0, 129.8, 129.7, 129.6, 128.1, 127.1, 126.1, 125.6, 125.5, 124.8, 123.5, 121.8, 110.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{13}N_2O_2^+$ 313.0972; Found 313.0965.

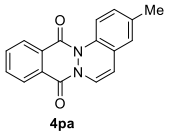
8H-indazolo[1,2-a]cinnolin-8-one (4oa)



4oa

10.4 mg, 89% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.52 (d, J = 7.9 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 6.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.12 (d, J = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 137.1, 136.3, 132.5, 129.3, 127.3, 124.7, 124.3, 122.0, 121.8, 121.0, 115.0, 112.0, 111.9, 108.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}N_2O^+$ 235.0866; Found 235.0862.

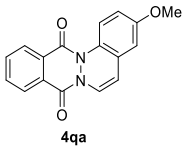
3-methylphthalazino[2,3-a]cinnoline-8,13-dione (4pa)



4pa

12.8 mg, 93% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.45 (m, 1H), 8.44 – 8.30 (m, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.89 (pd, J = 7.3, 1.6 Hz, 2H), 7.57 (d, J = 7.9 Hz, 1H), 7.08 (dd, J = 8.5, 2.0 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 6.15 (d, J = 7.9 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 154.3, 137.1, 134.2, 133.7, 131.6, 129.3, 128.6, 128.3, 127.9, 127.5, 126.1, 125.3, 124.9, 121.3, 110.3, 21.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2^+$ 277.0972; Found 277.0965.

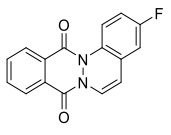
3-methoxyphthalazino[2,3-a]cinnoline-8,13-dione (4qa)



4qa

13.1 mg, 90% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, J = 7.4, 1.7 Hz, 1H), 8.39 (dd, J = 7.4, 1.7 Hz, 1H), 8.09 (d, J = 9.2 Hz, 1H), 7.94 – 7.84 (m, 2H), 7.60 (d, J = 7.9 Hz, 1H), 6.80 (dd, J = 9.1, 2.9 Hz, 1H), 6.65 (d, J = 2.9 Hz, 1H), 6.14 (d, J = 7.9 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 156.3, 154.4, 134.3, 133.7, 129.3, 128.3, 127.9, 127.4, 127.1, 126.6, 125.8, 122.9, 112.9, 110.5, 110.1, 55.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3^+$ 293.0921; Found 293.0913.

3-fluorophthalazino[2,3-a]cinnoline-8,13-dione (4ra)

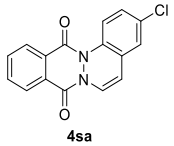


4ra

10.7 mg, 76% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.45 (m, 1H), 8.45 – 8.33 (m, 1H), 8.11 (dd, J = 9.2, 4.9 Hz, 1H), 7.91 (pd, J = 7.4, 1.6 Hz, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.02 – 6.92 (m, 1H), 6.83 (dd, J = 8.2, 3.0 Hz, 1H), 6.12 (d, J = 7.9

Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 156.6, 154.4, 134.5, 134.0, 129.2, 128.5, 128.1, 127.5, 126.8, 123.6, 123.5, 114.5, 114.3, 112.2, 111.9, 109.3, 109.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.03, -114.04, -114.05, -114.06, -114.07, -114.09. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 281.0721; Found 281.0714.

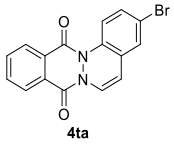
3-chlorophthalazino[2,3-a]cinnoline-8,13-dione (4sa)



4sa

7.6 mg, 51% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.44 (m, 1H), 8.39 (dd, J = 7.0, 2.0 Hz, 1H), 8.07 (d, J = 8.9 Hz, 1H), 7.92 (qt, J = 7.9, 3.9 Hz, 2H), 7.60 (d, J = 7.9 Hz, 1H), 7.22 (dd, J = 8.9, 2.5 Hz, 1H), 7.10 (d, J = 2.5 Hz, 1H), 6.11 (d, J = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 154.3, 134.5, 134.1, 132.5, 132.4, 129.1, 128.5, 128.1, 127.7, 127.5, 127.0, 126.8, 125.2, 122.9, 109.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}ClN_2O_2^+$ 297.0425; Found 297.0418.

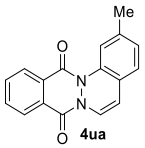
3-bromophthalazino[2,3-a]cinnoline-8,13-dione (4ta)



4ta

6.1 mg, 36% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, J = 7.1, 2.0 Hz, 1H), 8.39 (dd, J = 7.0, 2.1 Hz, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.59 (d, J = 7.9 Hz, 1H), 7.37 (dd, J = 8.9, 2.3 Hz, 1H), 7.25 (d, J = 2.2 Hz, 1H), 6.10 (d, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 154.3, 134.5, 134.1, 133.0, 130.7, 129.1, 128.5, 128.1, 127.5, 127.3, 126.8, 125.6, 123.1, 120.3, 109.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}BrN_2O_2^+$ 340.9920; Found 340.9916.

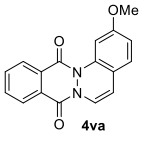
2-methylphthalazino[2,3-a]cinnoline-8,13-dione (4ua)



4ua

9.9 mg, 72% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.44 (m, 1H), 8.43 – 8.36 (m, 1H), 7.96 (s, 1H), 7.90 (qt, J = 7.9, 4.0 Hz, 2H), 7.52 (d, J = 7.9 Hz, 1H), 7.02 (s, 2H), 6.17 (d, J = 7.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 154.3, 138.4, 134.2, 133.9, 133.8, 129.2, 128.4, 128.0, 127.9, 127.6, 125.5, 124.6, 122.4, 122.0, 110.4, 21.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2^+$ 277.0972; Found 277.0967.

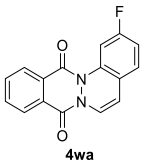
2-methoxyphthalazino[2,3-a]cinnoline-8,13-dione (4va)



4va

8.2 mg, 56% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.45 (m, 1H), 8.41 – 8.37 (m, 1H), 7.90 (ddd, J = 6.6, 4.1, 1.9 Hz, 2H), 7.79 (d, J = 2.4 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.77 (dd, J = 8.4, 2.5 Hz, 1H), 6.17 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 156.9, 154.2, 135.1, 134.1, 133.9, 129.1, 128.4, 127.9, 127.7, 126.5, 123.3, 117.9, 113.4, 110.4, 107.4, 55.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3^+$ 293.0921; Found 293.0915.

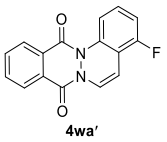
2-fluorophthalazino[2,3-a]cinnoline-8,13-dione (4wa)



4wa

2.4 mg, 17% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.45 (m, 1H), 8.44 – 8.32 (m, 1H), 8.00 – 7.87 (m, 3H), 7.54 (d, J = 7.9 Hz, 1H), 7.08 (dd, J = 8.4, 6.1 Hz, 1H), 6.92 (td, J = 8.2, 2.5 Hz, 1H), 6.16 (d, J = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 160.8, 156.8, 154.2, 135.2, 135.2, 134.4, 134.2, 128.9, 128.5, 128.0, 127.6, 126.7, 126.6, 124.8, 124.8, 121.3, 121.2, 114.3, 114.1, 109.9, 109.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.90, -109.91, -109.92, -109.93, -109.93, -109.94, -109.95, -109.96. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 281.0721; Found 281.0715.

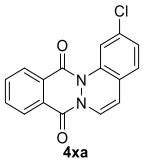
4-fluorophthalazino[2,3-a]cinnoline-8,13-dione (4wa')



4wa′

4.8 mg, 34% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H), 8.33 (dd, J = 7.4, 1.8 Hz, 1H), 7.89 – 7.79 (m, 3H), 7.51 (d, J = 8.0 Hz, 1H), 7.18 – 7.11 (m, 1H), 6.88 (t, J = 8.6 Hz, 1H), 6.34 (d, J = 8.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9, 156.8, 156.3, 154.4, 135.1, 135.0, 134.5, 134.1, 129.1, 128.6, 128.6, 128.5, 128.1, 127.6, 126.2, 117.2, 117.2, 114.4, 114.3, 113.7, 113.6, 103.1, 103.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.57, -121.59, -121.61. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 281.0721; Found 281.0714.

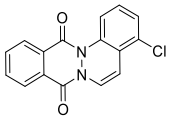
2-chlorophthalazino[2,3-a]cinnoline-8,13-dione (4xa)



4xa

5.2 mg, 35% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.45 (m, 1H), 8.39 (dd, J = 7.5, 1.7 Hz, 1H), 8.18 (d, J = 2.0 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.56 (d, J = 7.9 Hz, 1H), 7.18 (dd, J = 8.1, 2.0 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.14 (d, J = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 154.2, 134.8, 134.5, 134.2, 133.5, 129.0, 128.5, 128.1, 127.6, 127.3, 126.3, 125.8, 123.7, 121.8, 109.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}ClN_2O_2^+$ 297.0425; Found 297.0418.

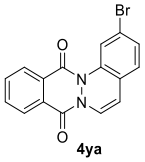
4-chlorophthalazino[2,3-a]cinnoline-8,13-dione (4xa')



4xa′

1.9 mg, 13% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.44 (m, 1H), 8.40 (dd, J = 7.5, 1.8 Hz, 1H), 7.98 – 7.87 (m, 3H), 7.60 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 1.2 Hz, 1H), 7.19 (t, J = 8.2 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 154.3, 135.1, 134.5, 134.1, 130.2, 129.1, 128.6, 128.2, 128.1, 127.8, 127.7, 127.1, 123.9, 120.1, 106.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}ClN_2O_2^+$ 297.0425; Found 297.0418.

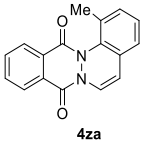
2-bromophthalazino[2,3-a]cinnoline-8,13-dione (4ya)



4ya

4.9 mg, 29% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.45 (m, 1H), 8.40 (dd, J = 7.5, 1.7 Hz, 1H), 8.37 – 8.30 (m, 1H), 7.95 – 7.88 (m, 2H), 7.58 (d, J = 7.9 Hz, 1H), 7.34 (dd, J = 8.1, 1.8 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.13 (d, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 154.2, 134.5, 134.5, 134.2, 132.9, 130.3, 128.6, 128.1, 127.6, 127.0, 126.5, 126.0, 124.6, 121.3, 109.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}BrN_2O_2^+$ 340.9920; Found 340.9918.

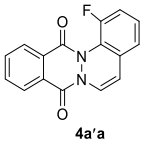
1-methylphthalazino[2,3-a]cinnoline-8,13-dione (4za)



4za

8.3 mg, 60% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.31 (m, 2H), 7.93 – 7.83 (m, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.18 (dt, J = 14.9, 7.6 Hz, 2H), 6.97 (d, J = 7.1 Hz, 1H), 6.13 (d, J = 7.8 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 155.5, 134.5, 133.7, 132.8, 131.2, 130.7, 129.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.1, 122.6, 109.6, 20.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_2^+$ 277.0972; Found 277.0967.

1-fluorophthalazino[2,3-a]cinnoline-8,13-dione (4a'a)

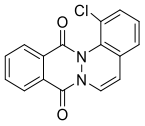


4a′a

4.5 mg, 32% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.33 (m, 1H), 8.30 (dd, J = 7.0, 1.9 Hz, 1H), 7.83 (pd, J = 7.4, 1.6 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.17 (dd, J = 8.0, 4.9 Hz, 1H), 7.05 – 6.95 (m, 1H), 6.85 (d, J = 7.3 Hz, 1H), 6.06 (dd, J = 7.9, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 155.0, 134.5, 133.8, 129.1, 129.0, 128.9, 128.3, 128.1,

128.0, 127.5, 120.4, 120.3, 116.9, 116.7, 108.5, 108.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.48, -107.49, -107.49, -107.51, -107.52, -107.52. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}FN_2O_2^+$ 281.0721; Found 281.0716.

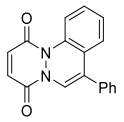
1-chlorophthalazino[2,3-a]cinnoline-8,13-dione (4b'a)



4b'a

3.3 mg, 22% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, J = 7.1, 1.9 Hz, 1H), 8.35 (dd, J = 7.1, 1.9 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.32 (dd, J = 8.2, 1.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.03 (dd, J = 7.5, 1.3 Hz, 1H), 6.10 (d, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 159.4, 134.8, 134.7, 134.4, 133.9, 130.4, 130.1, 129.3, 128.9, 128.5, 128.4, 128.4, 128.2, 123.2, 108.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}ClN_2O_2^+$ 297.0425; Found 297.0421.

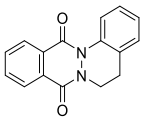
7-phenylpyridazino[1,2-a]cinnoline-1,4-dione (4mb)



4mb

7.7 mg, 53% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.49 – 7.42 (m, 5H), 7.37 – 7.32 (m, 1H), 7.23 – 7.14 (m, 3H), 7.08 (d, J = 10.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 153.0, 135.5, 134.4, 134.0, 132.5, 129.1, 129.1, 128.8, 128.4, 127.5, 125.6, 125.2, 124.4, 122.4, 120.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}N_2O_2^+$ 289.0972; Found 289.0969.

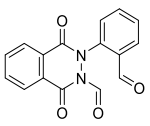
5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (5aa)



5aa

12.7 mg, 96% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.39 (m, 1H), 8.39 – 8.32 (m, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.35 (ddd, J = 8.5, 6.9, 2.2 Hz, 1H), 7.29 – 7.21 (m, 2H), 4.42 – 4.32 (m, 2H), 3.03 (t, J = 5.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 156.2, 135.0, 133.8, 133.5, 130.7, 129.5, 128.9, 128.3, 127.7, 127.6, 127.2, 126.9, 124.3, 44.8, 27.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_2^+$ 265.0972; Found 265.0967.

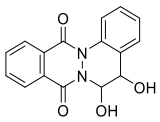
3-(2-formylphenyl)-1,4-dioxo-3,4-dihydrophthalazine-2(1H)-carbaldehyde (6aa)



6aa

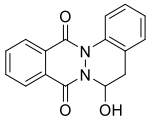
6.8 mg, 46% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 9.05 (s, 1H), 8.37 – 8.26 (m, 2H), 7.94 – 7.82 (m, 3H), 7.63 (td, J = 7.7, 1.7 Hz, 1H), 7.54 – 7.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 161.4, 157.0, 139.7, 136.1, 134.6, 134.4, 133.9, 131.6, 131.6, 131.4, 129.4, 129.4, 128.6, 128.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}N_2O_4^+$ 295.0713; Found 295.0719.

5,6-dihydroxy-5,6-dihydrophthalazino[2,3-a]cinnoline-8,13-dione (7aa)



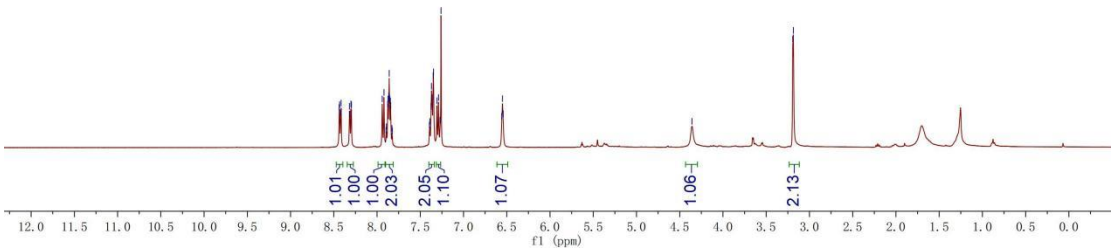
7aa

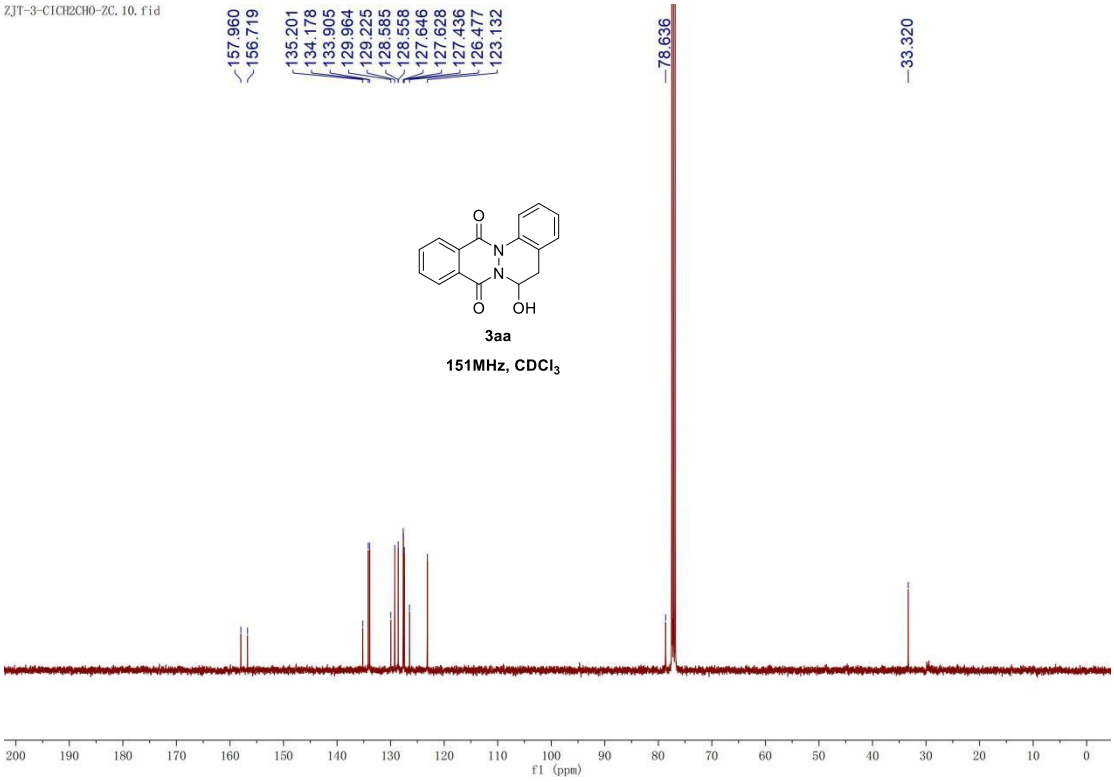
12.1 mg, 82% yield; White solid; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 – 8.22 (m, 3H), 8.14 (d, J = 8.3 Hz, 1H), 7.98 (ddt, J = 7.4, 5.8, 4.0 Hz, 3.5H), 7.65 – 7.56 (m, 0.5H), 7.50 – 7.40 (m, 2H), 7.40 – 7.19 (m, 2H), 6.99 (d, J = 4.6 Hz, 1H), 6.87 (d, J = 4.8 Hz, 0.5H), 6.49 (dd, J = 4.6, 3.0 Hz, 1H), 6.42 (dd, J = 4.8, 3.1 Hz, 0.5H), 5.96 (d, J = 6.9 Hz, 0.5H), 5.88 (d, J = 5.1 Hz, 1H), 4.95 (dd, J = 6.9, 2.9 Hz, 0.5H), 4.65 (dd, J = 5.1, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.2, 156.4, 156.1, 155.9, 134.9, 134.6, 134.6, 134.4, 134.3, 134.2, 130.6, 130.0, 129.7, 129.0, 128.9, 128.7, 128.3, 128.2, 128.1, 127.7, 126.7, 126.4, 126.3, 125.4, 123.6, 123.1, 78.4, 77.4, 67.6, 66.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_4^+$ 297.0870; Found 297.0863.



3aa

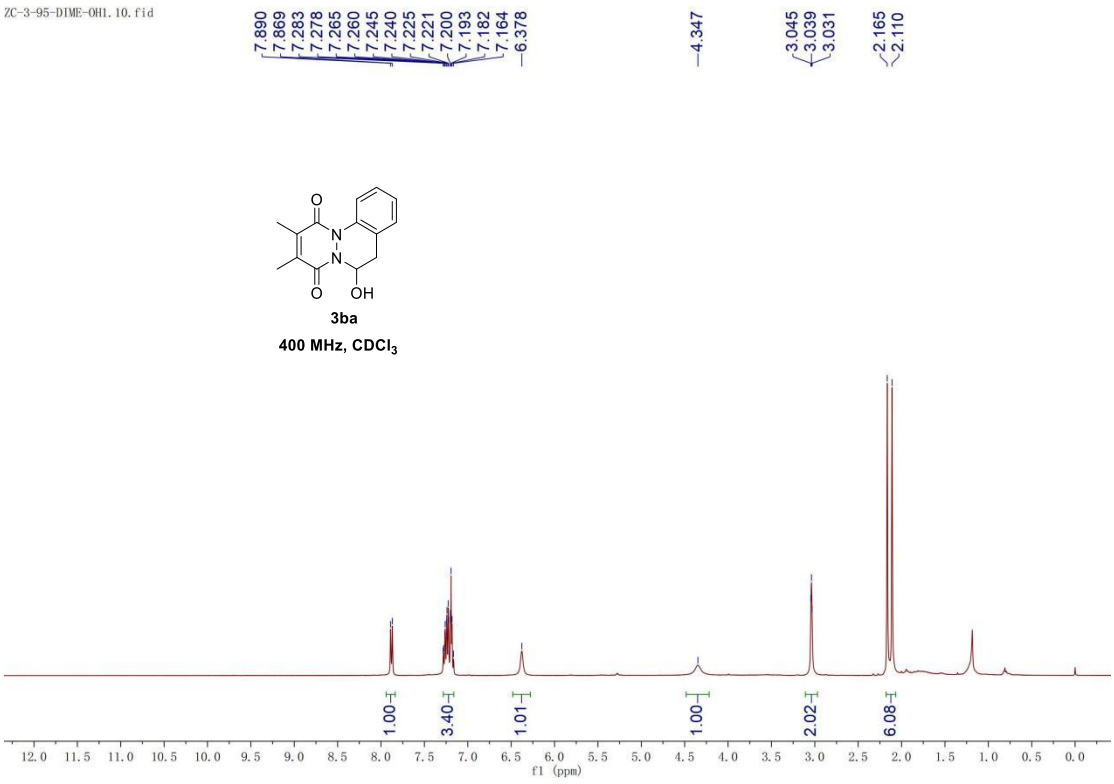
400 MHz, $CDCl_3$





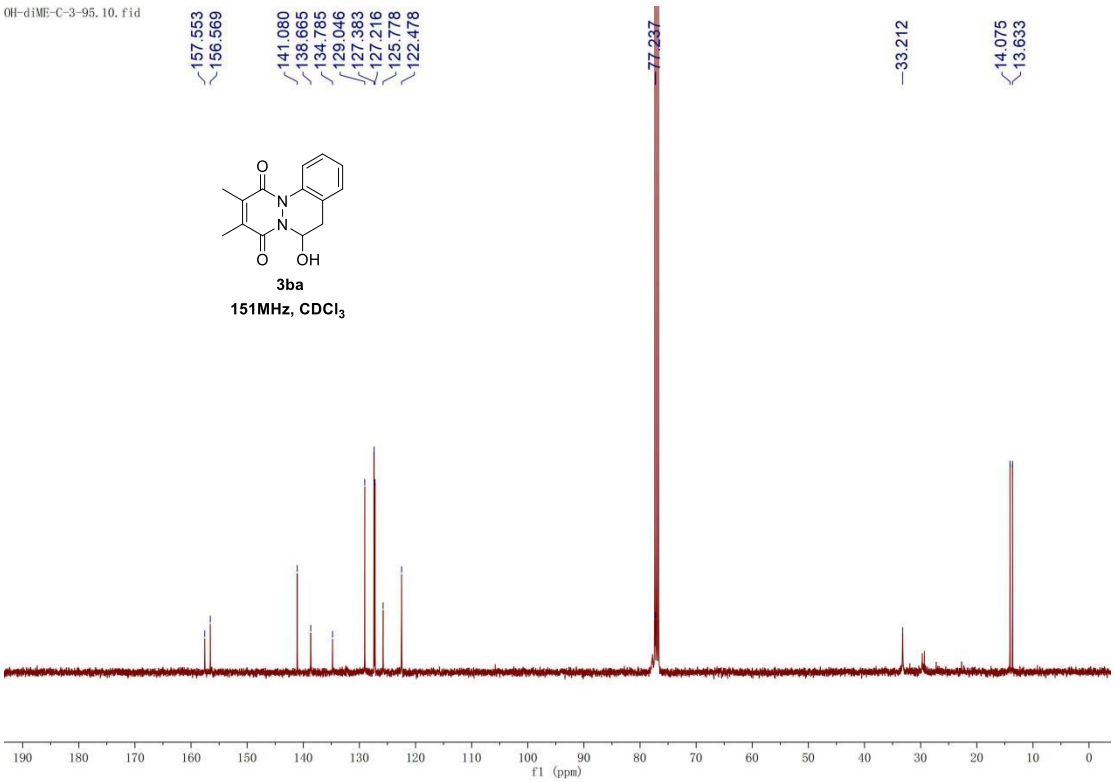
3aa

151MHz, $CDCl_3$



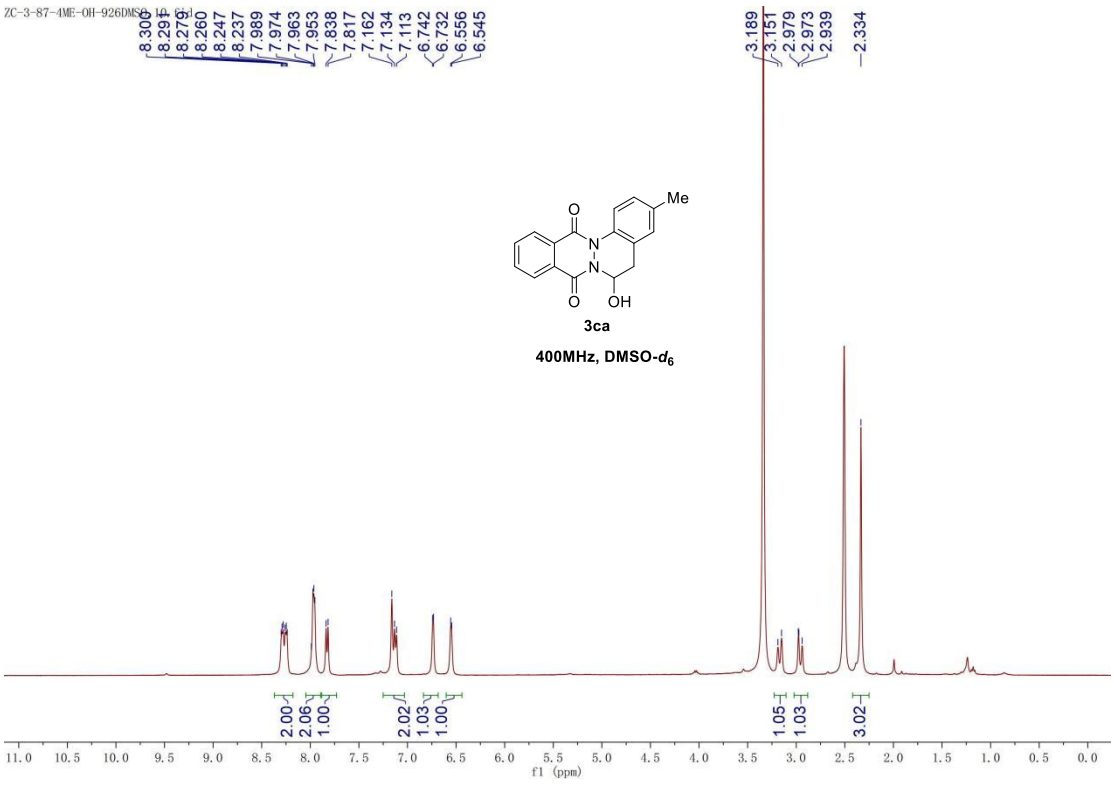
3ba

400 MHz, $CDCl_3$



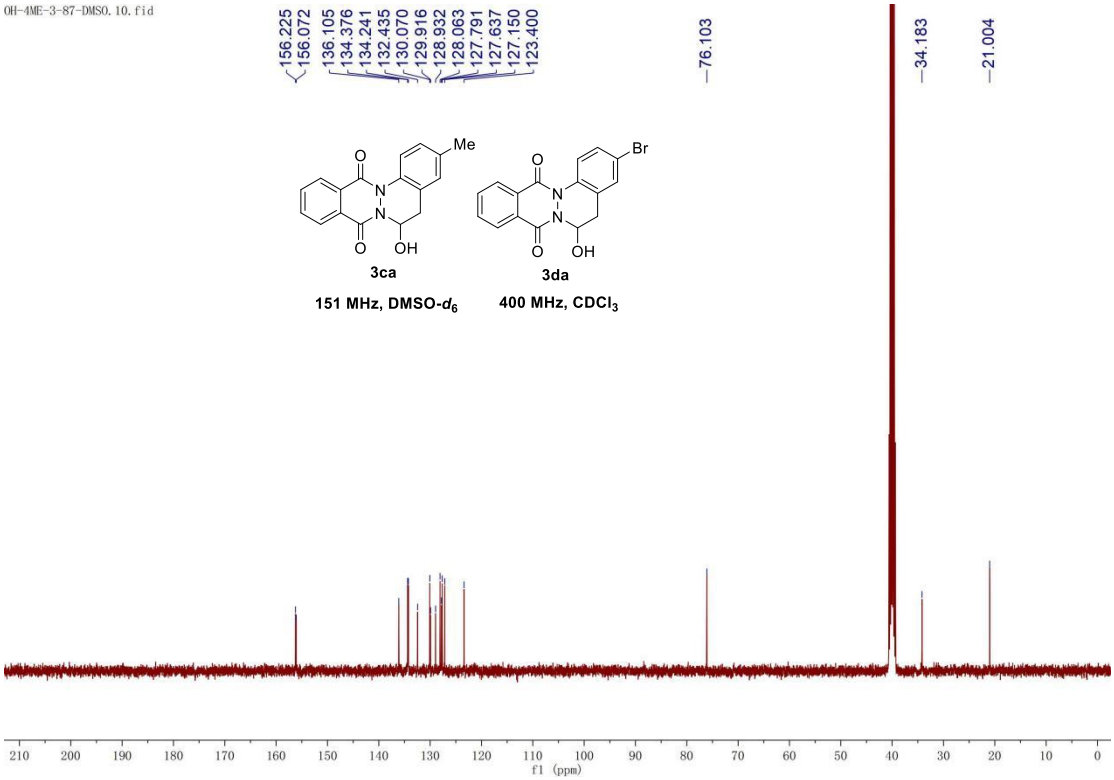
3ba

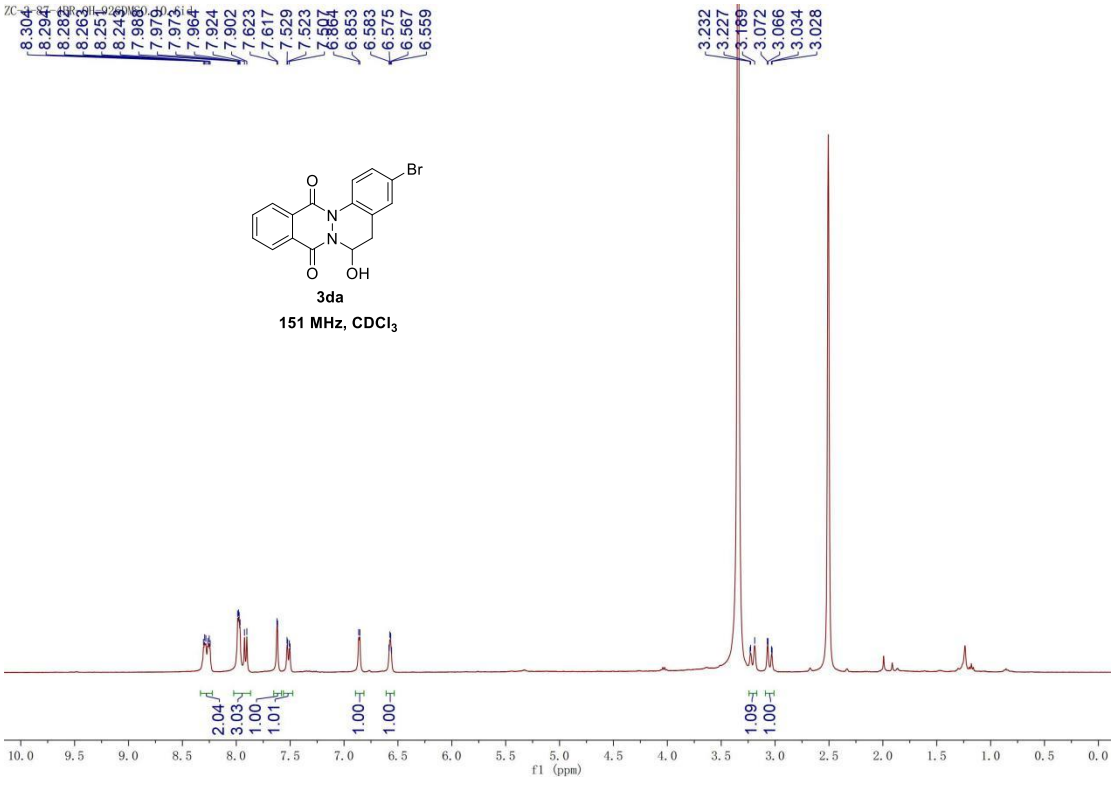
151MHz, $CDCl_3$

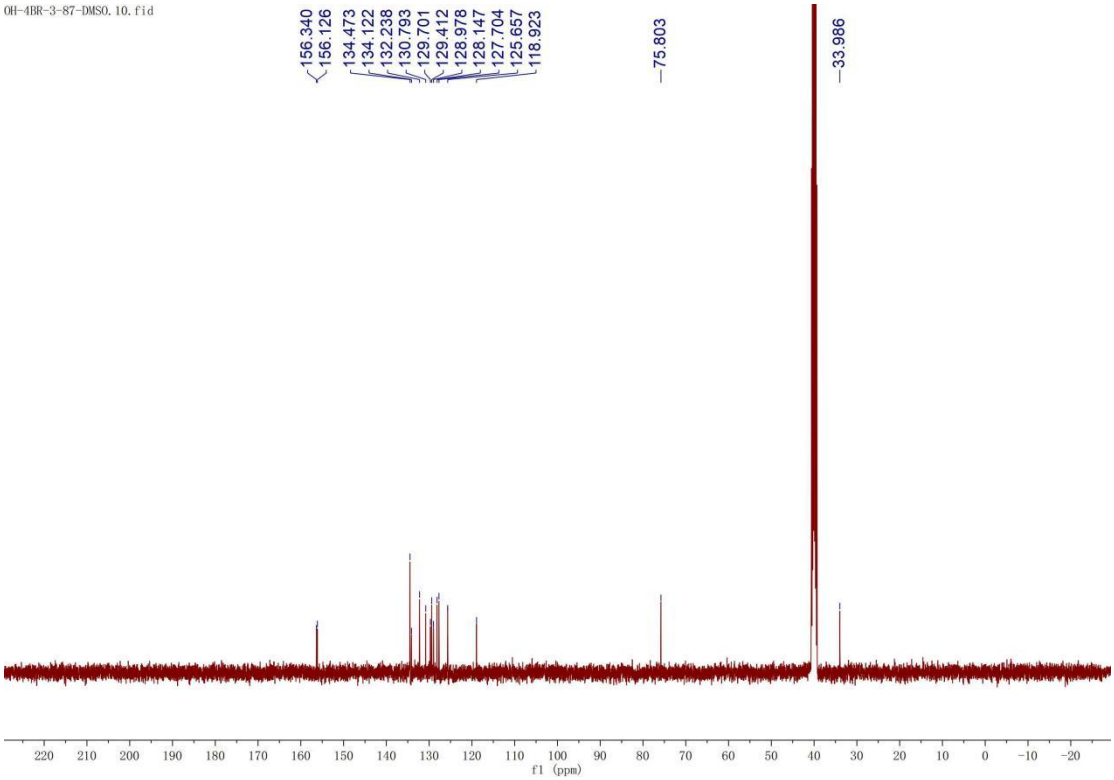


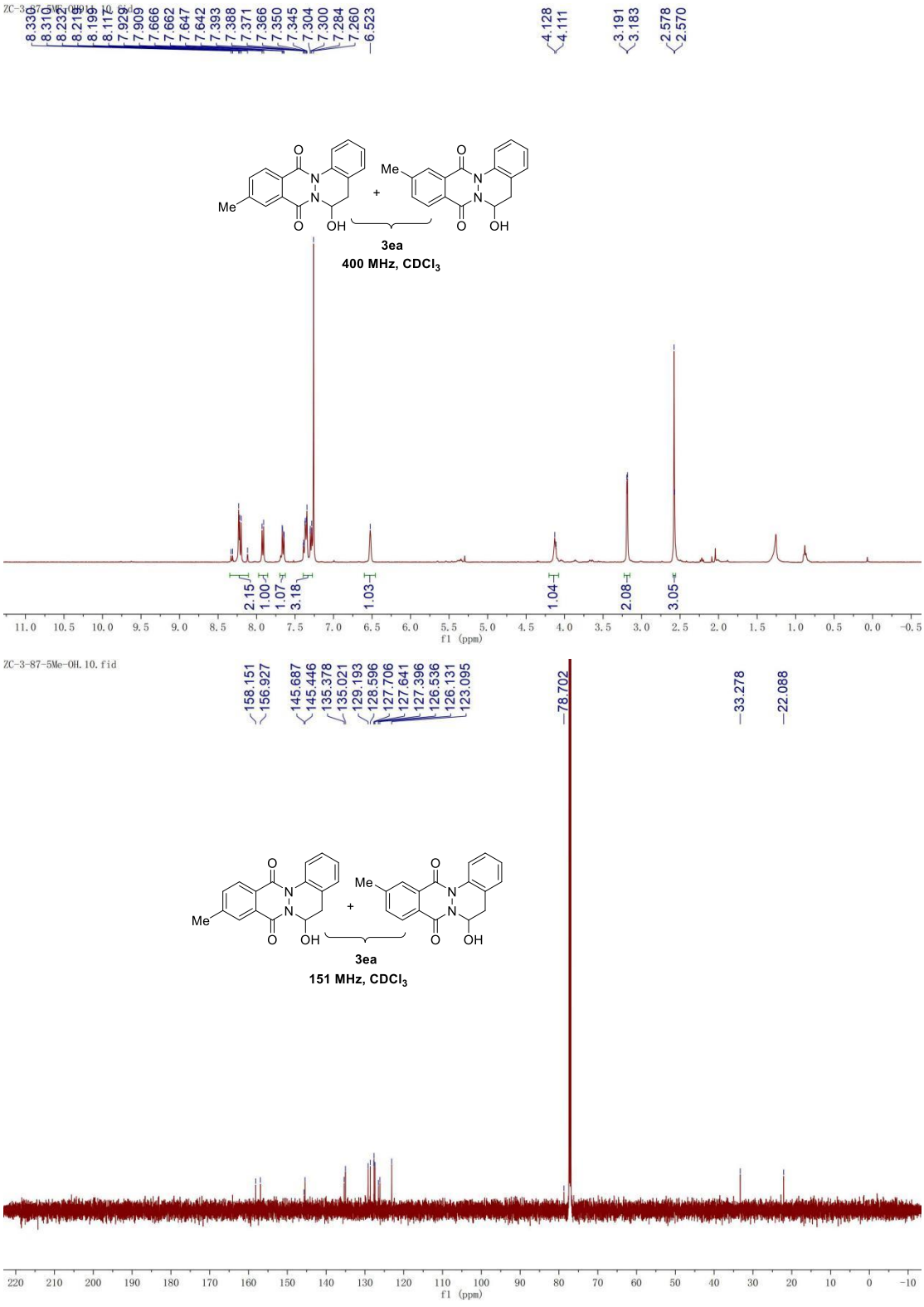
3ca

400MHz, DMSO-d_6


OH-4ME-3-87-DMSO.10.fid
156.225
156.072
136.105
134.376
134.241
132.435
130.070
129.916
128.932
128.063
127.791
127.637
127.150
123.400
76.103
34.183
21.004
Me
OH
3ca
151 MHz, DMSO-d_6
Br
OH
3da
400 MHz, CDCl$_3$
f1 (ppm)


8.304
8.294
8.282
8.263
8.251
8.245
7.988
7.977
7.975
7.964
7.924
7.902
7.623
7.617
7.529
7.523
7.507
7.504
6.853
6.583
6.575
6.567
6.559
3.232
3.227
3.189
3.072
3.066
3.034
3.028
Br
OH
3da
151 MHz, CDCl$_3$
2.04
3.03
1.00
1.01
1.00
1.00
1.09
1.00
f1 (ppm)


OH-4BR-3-87-DMSO.10.fid
156.340
156.126
134.473
134.122
132.238
130.793
129.701
129.412
128.978
128.147
127.704
125.657
118.923
75.803
33.986
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.330
8.310
8.232
8.219
8.199
8.117
7.929
7.909
7.666
7.662
7.647
7.642
7.393
7.388
7.371
7.366
7.350
7.345
7.304
7.300
7.284
7.260
6.523
4.128
4.111
3.191
3.183
2.578
2.570
Me
OH
3ea
400 MHz, CDCl3
2.15
1.00
1.07
3.18
1.03
1.04
2.08
3.05
f1 (ppm)
158.151
156.927
145.687
145.446
135.378
135.021
129.193
128.596
127.706
127.641
127.396
126.536
126.131
123.095
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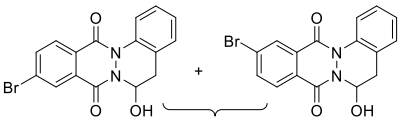
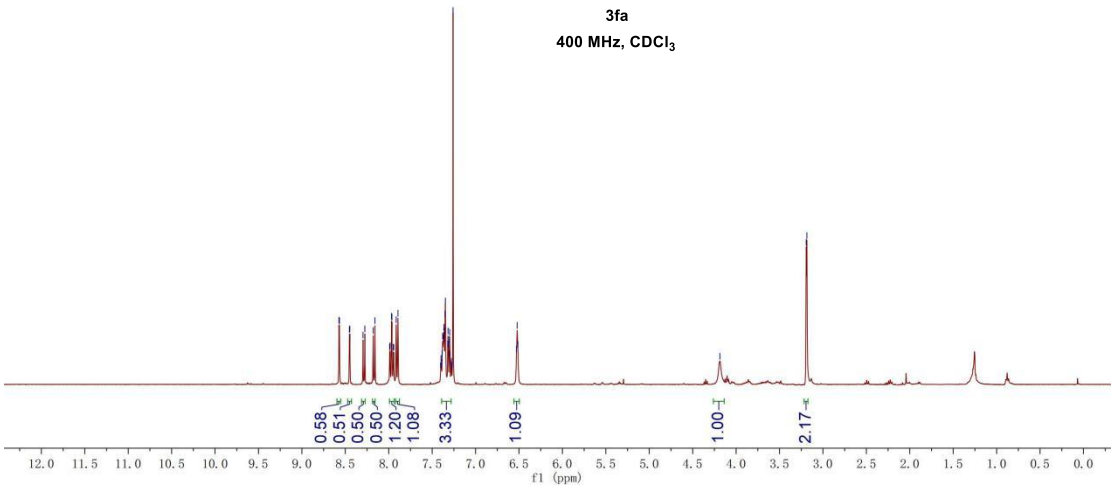
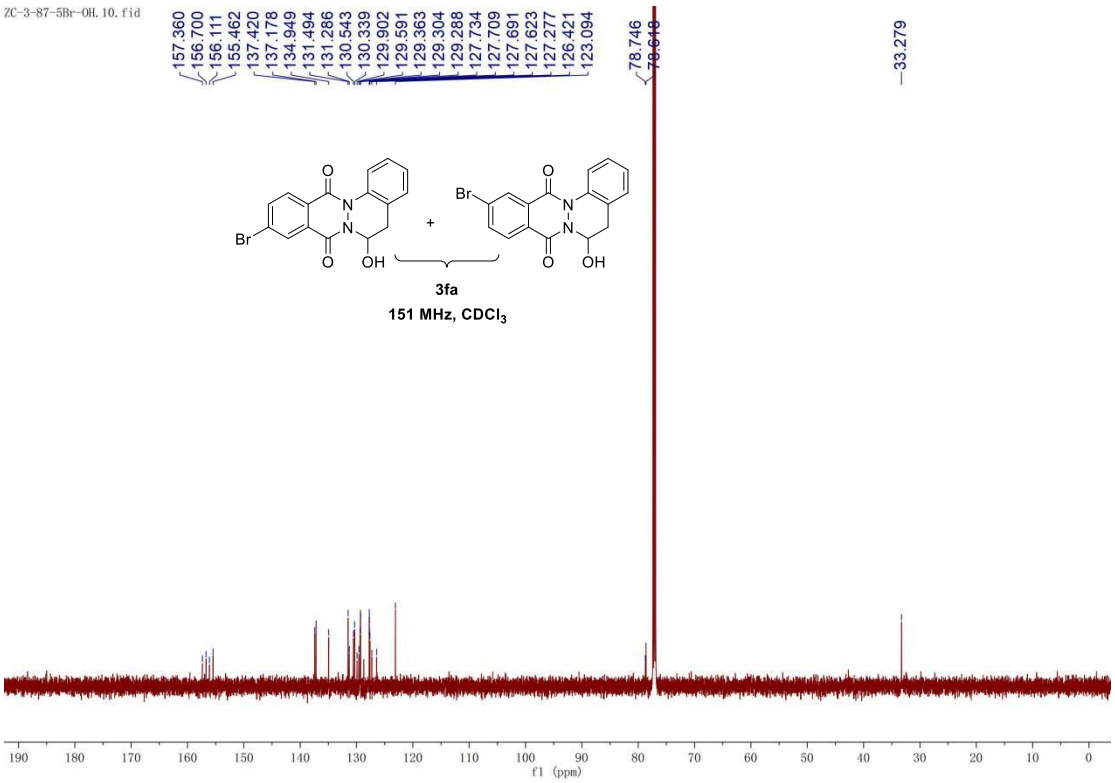
33.278
22.088
3ea
151 MHz, CDCl3
f1 (ppm)



3fa

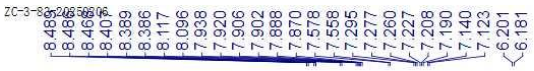
400 MHz, $CDCl_3$

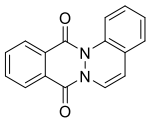




3fa

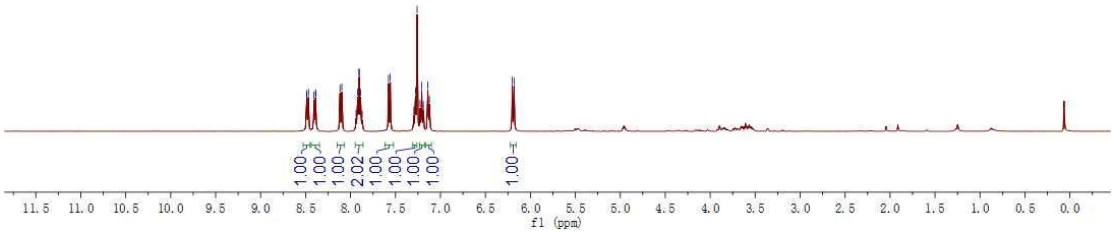
151 MHz, $CDCl_3$

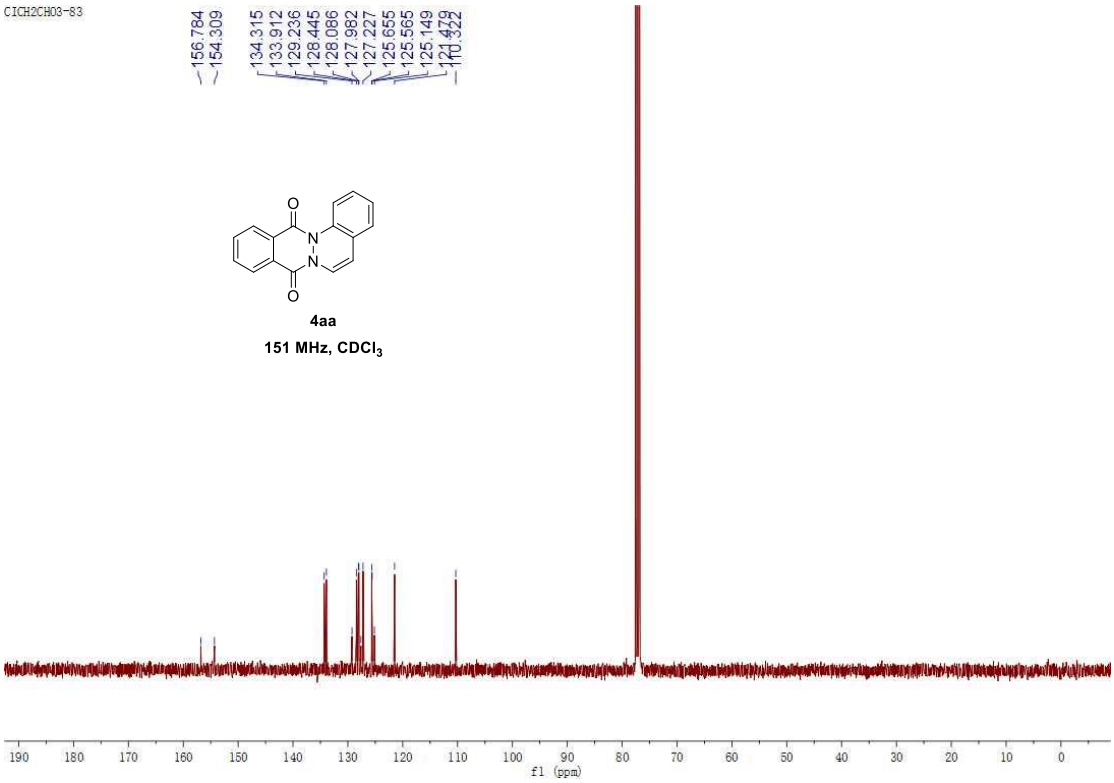




4aa

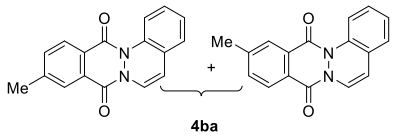
400 MHz, $CDCl_3$





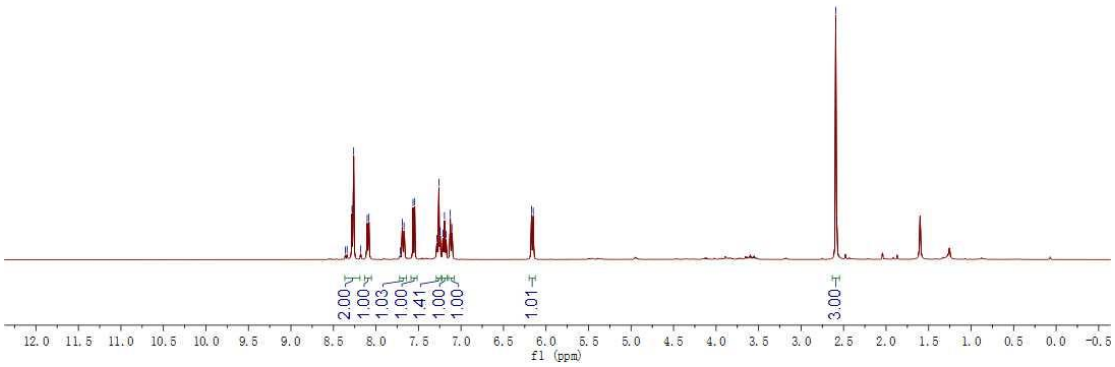
4aa

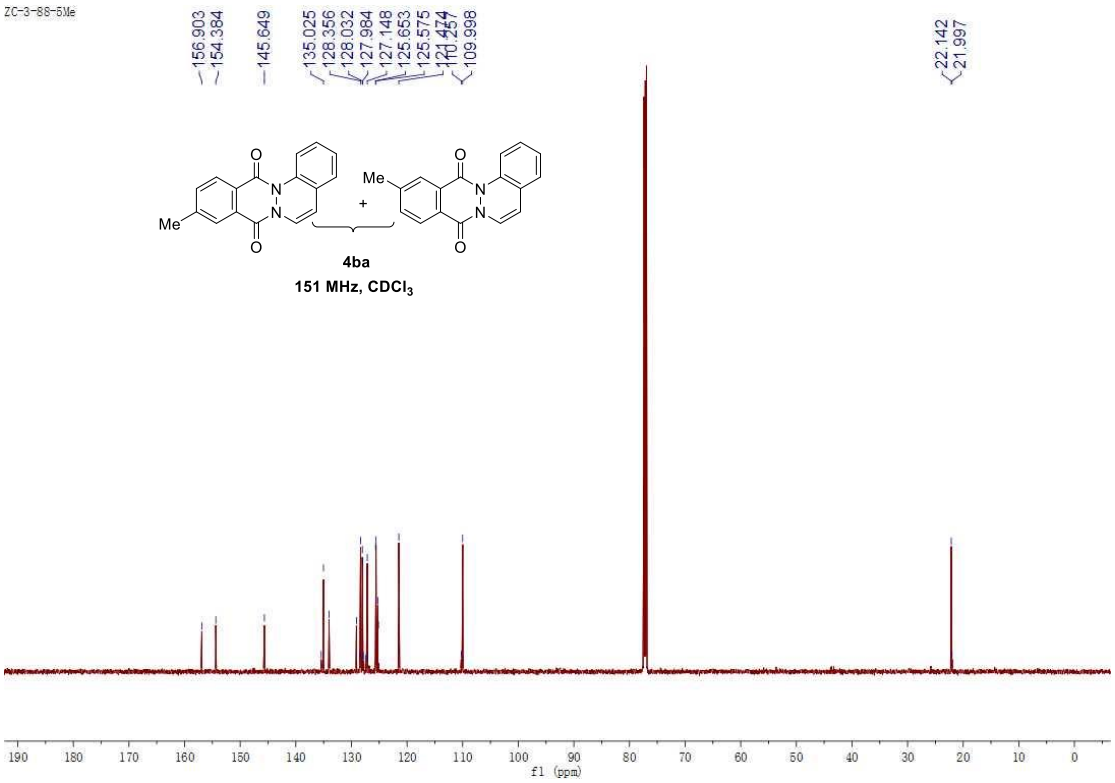
151 MHz, $CDCl_3$



4ba

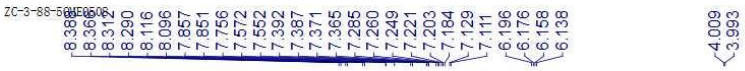
400 MHz, $CDCl_3$

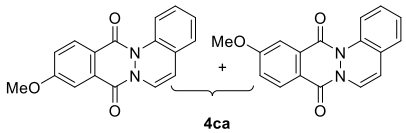




4ba

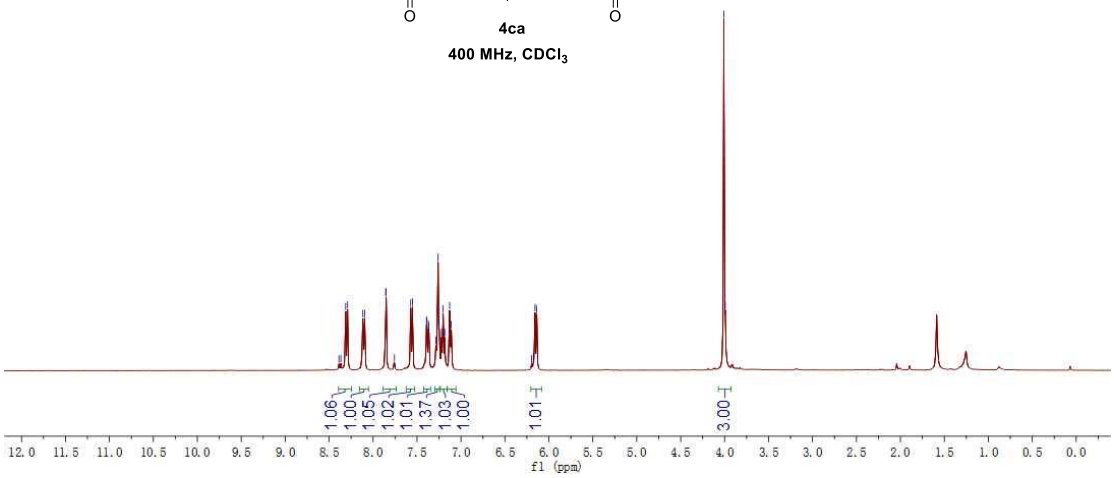
151 MHz, $CDCl_3$

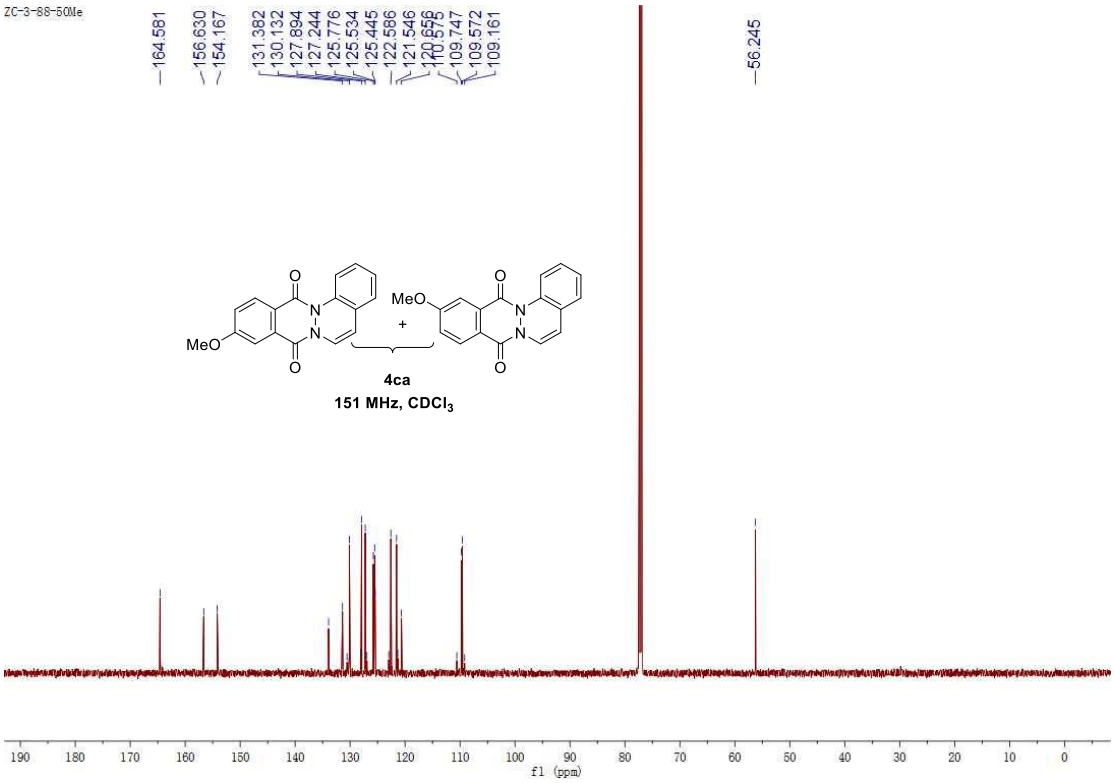




4ca

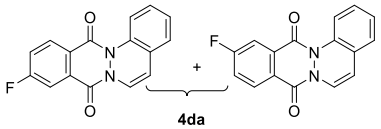
400 MHz, $CDCl_3$





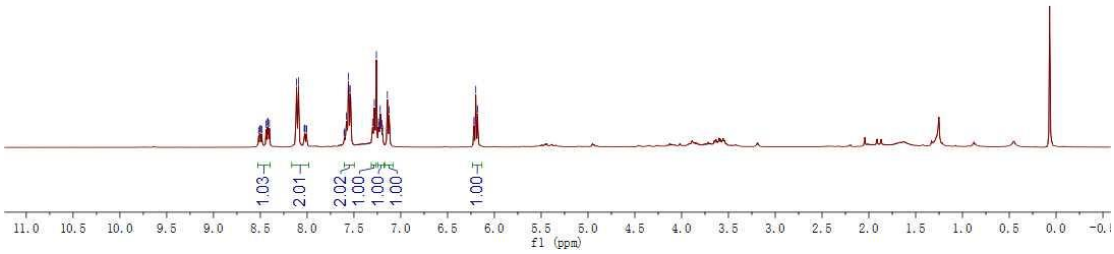
4ca

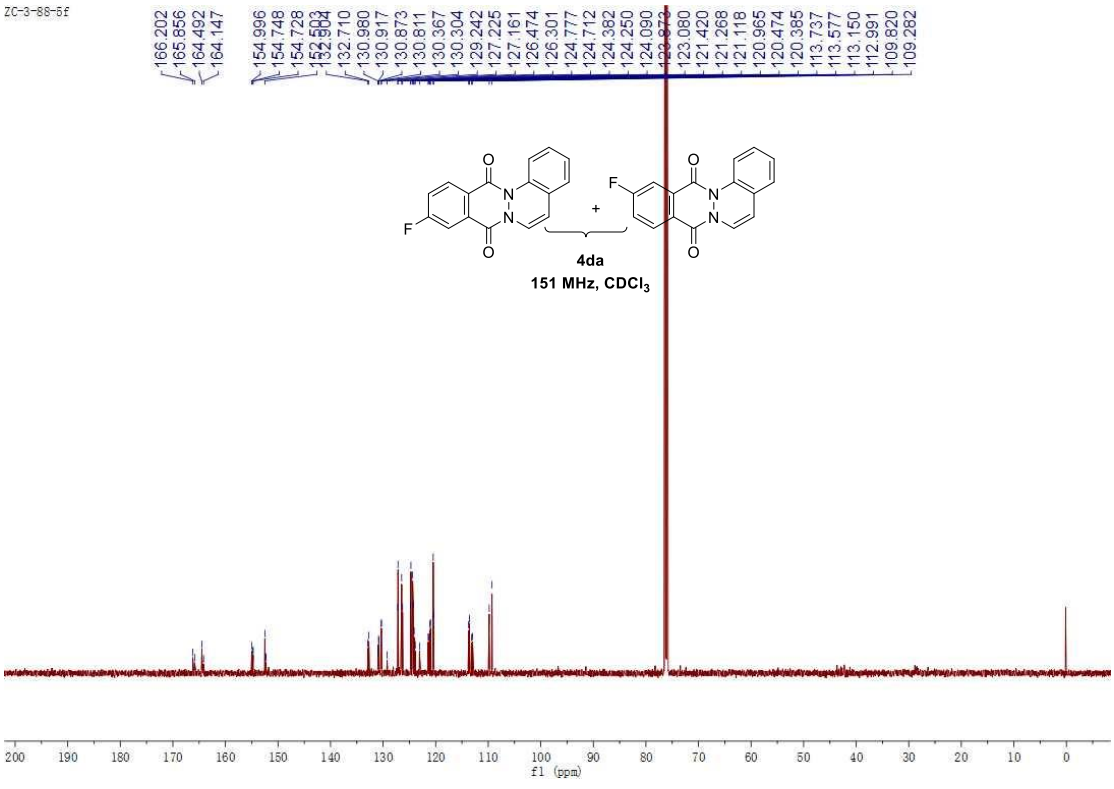
151 MHz, $CDCl_3$



4da

400 MHz, $CDCl_3$



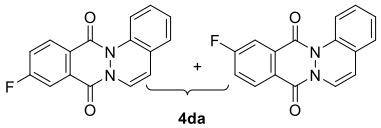


4da

151 MHz, $CDCl_3$

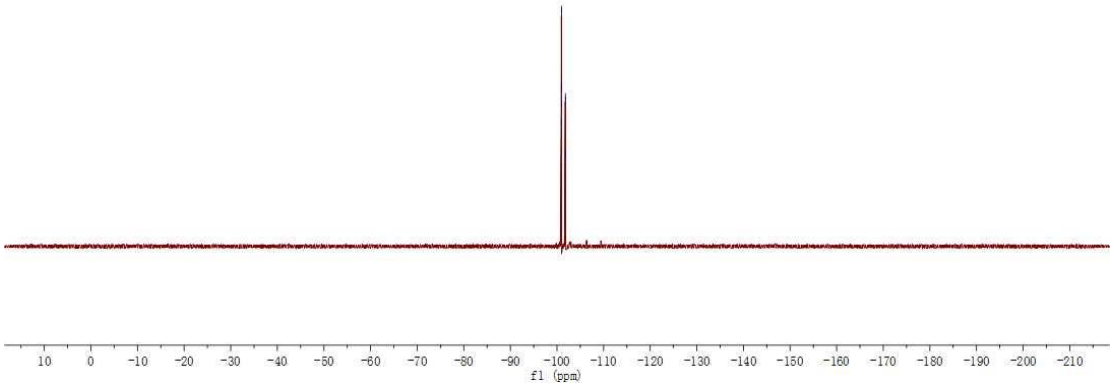
ZC-3-8S-5F-F20250427

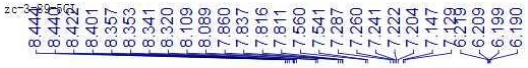
100.930
100.945
100.952
100.966
100.973
100.988
101.800
101.814
101.822



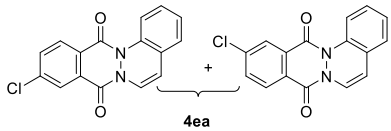
4da

376 MHz, $CDCl_3$



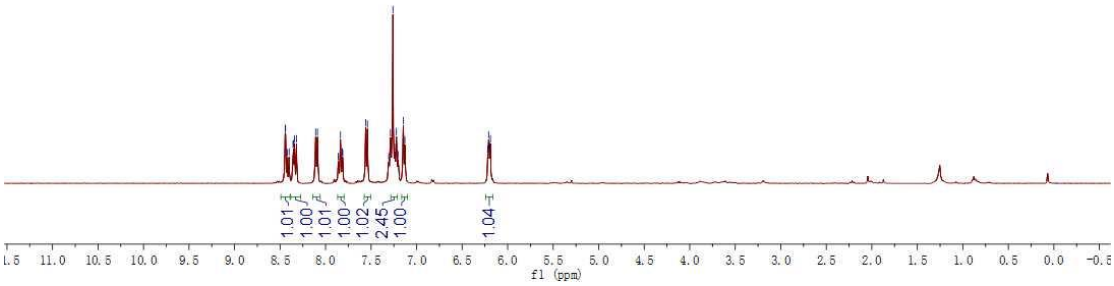


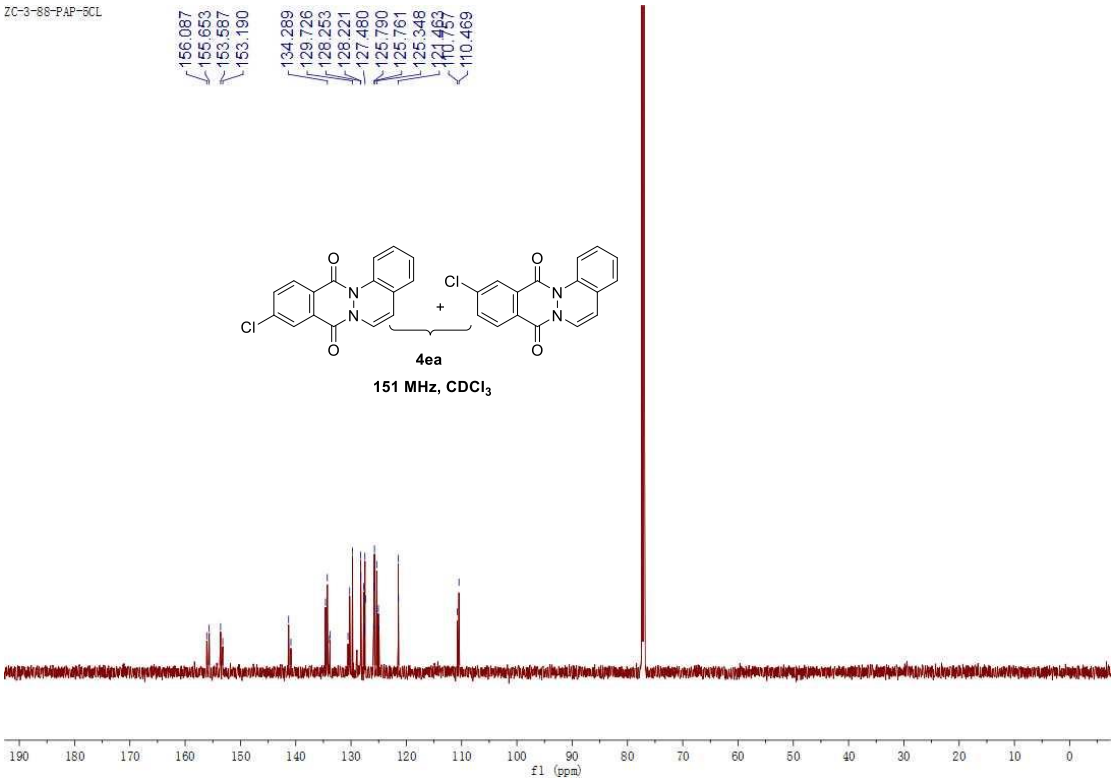
8.444
8.440
8.422
8.401
8.357
8.353
8.341
8.320
8.109
8.089
7.860
7.837
7.816
7.811
7.560
7.541
7.287
7.260
7.241
7.222
7.204
7.147
7.129
6.209
6.199
6.190



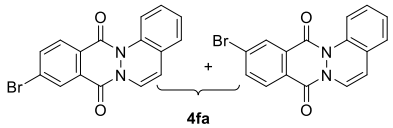
4ea

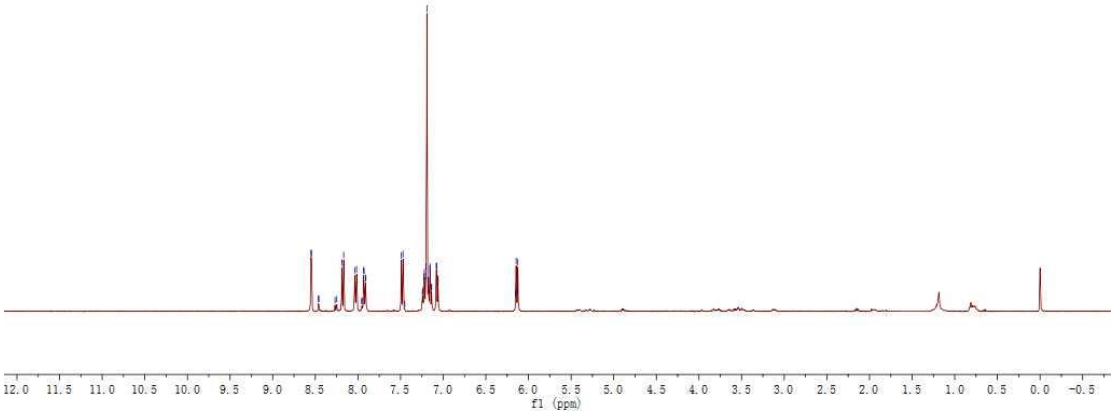
400 MHz, $CDCl_3$

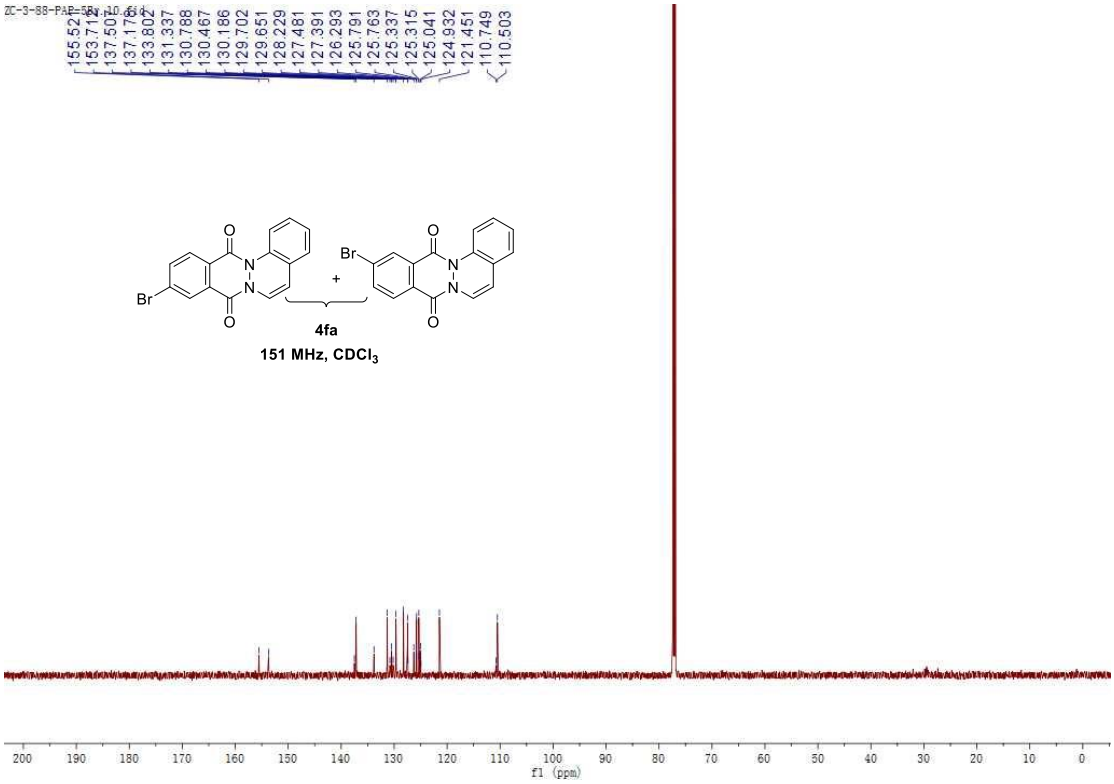


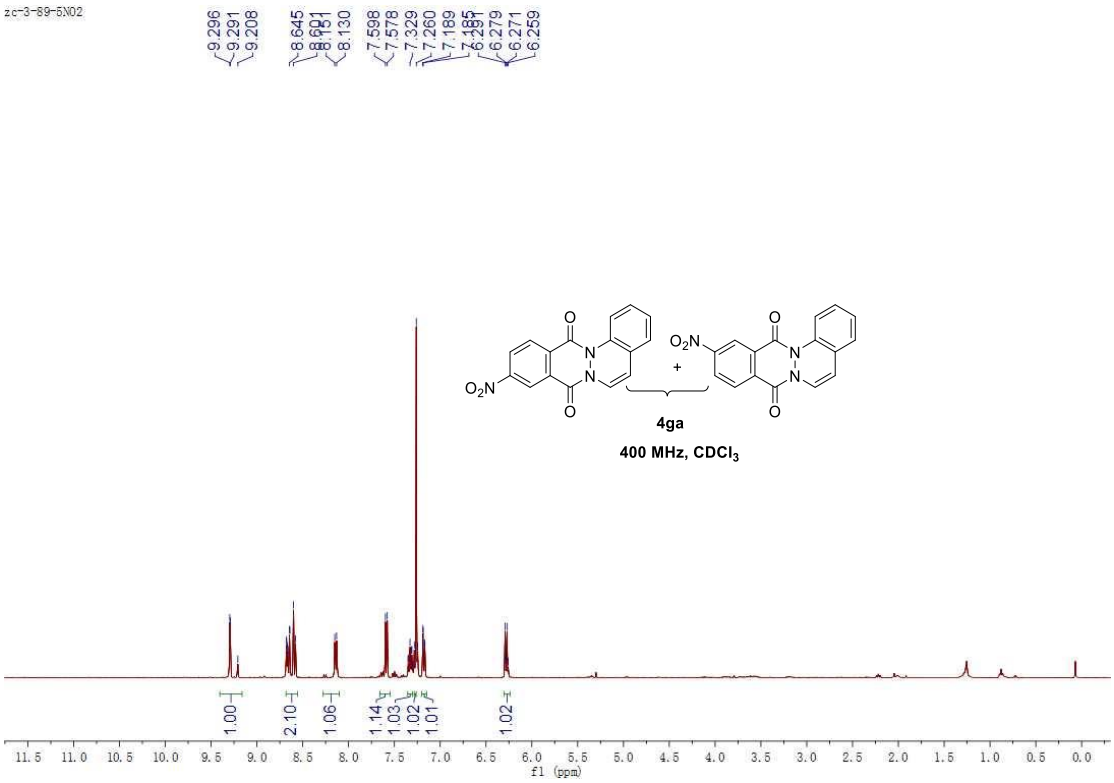

ZC-3-88-PAP-5CL
156.087
155.653
153.587
153.190
134.289
129.726
128.253
128.221
127.480
125.790
125.761
125.348
121.463
111.457
110.469
Cl
Cl
4ea
151 MHz, CDCl3
f1 (ppm)

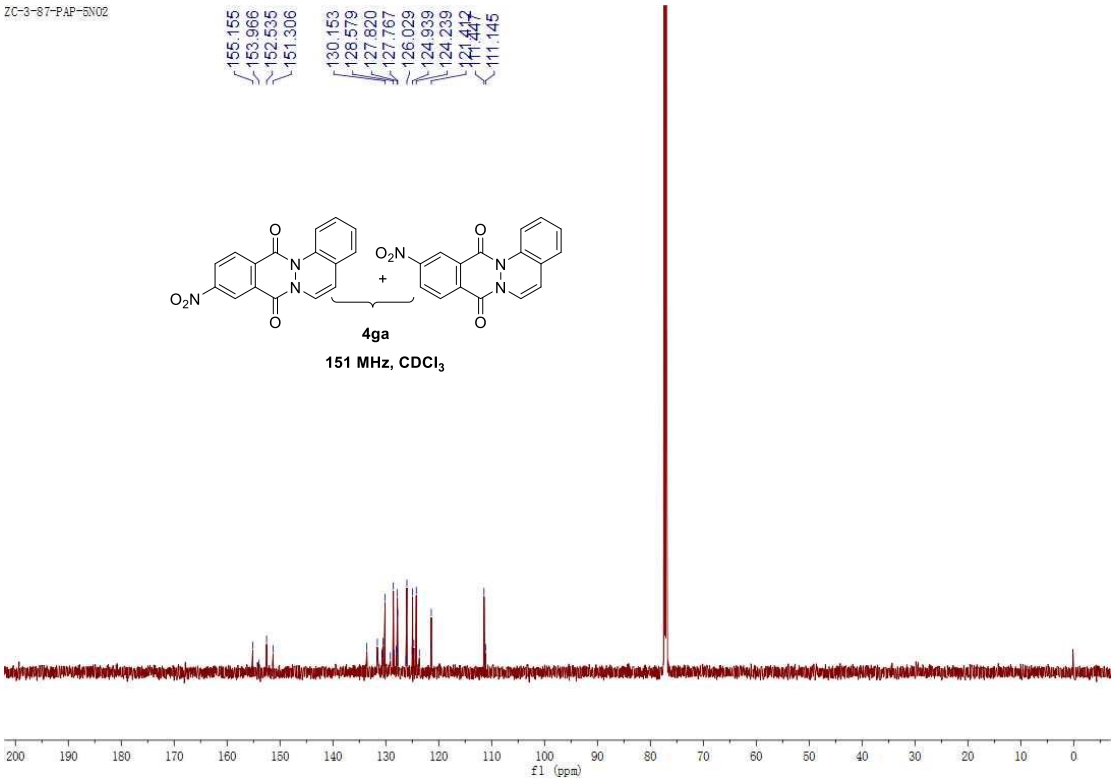

8.551
8.546
8.188
8.167
8.036
8.016
7.933
7.928
7.912
7.907
7.491
7.471
7.225
7.221
7.205
7.201
7.191
7.176
7.173
7.157
7.154
7.082
7.077
7.063
6.145
6.131
6.125


Br
Br
4fa
400 MHz, CDCl3

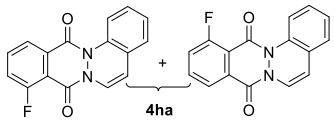

f1 (ppm)

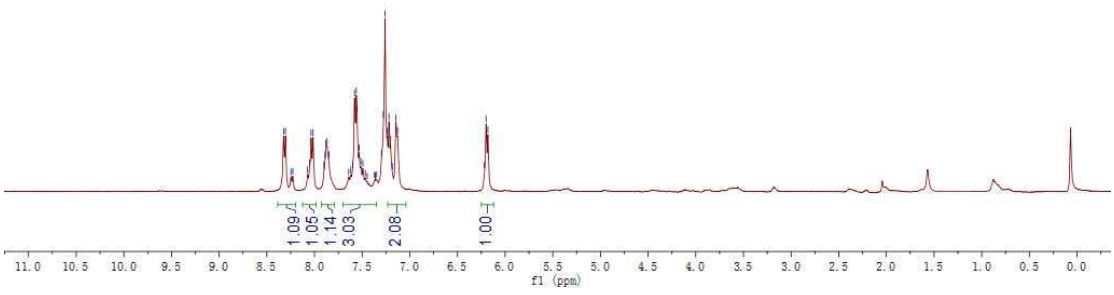

155.521
153.712
137.507
137.176
133.802
131.337
130.788
130.467
130.186
129.702
129.651
128.229
127.481
127.391
126.293
125.791
125.763
125.337
125.315
125.041
124.932
121.451
110.749
110.503
Br
Br
4fa
151 MHz, CDCl3
f1 (ppm)

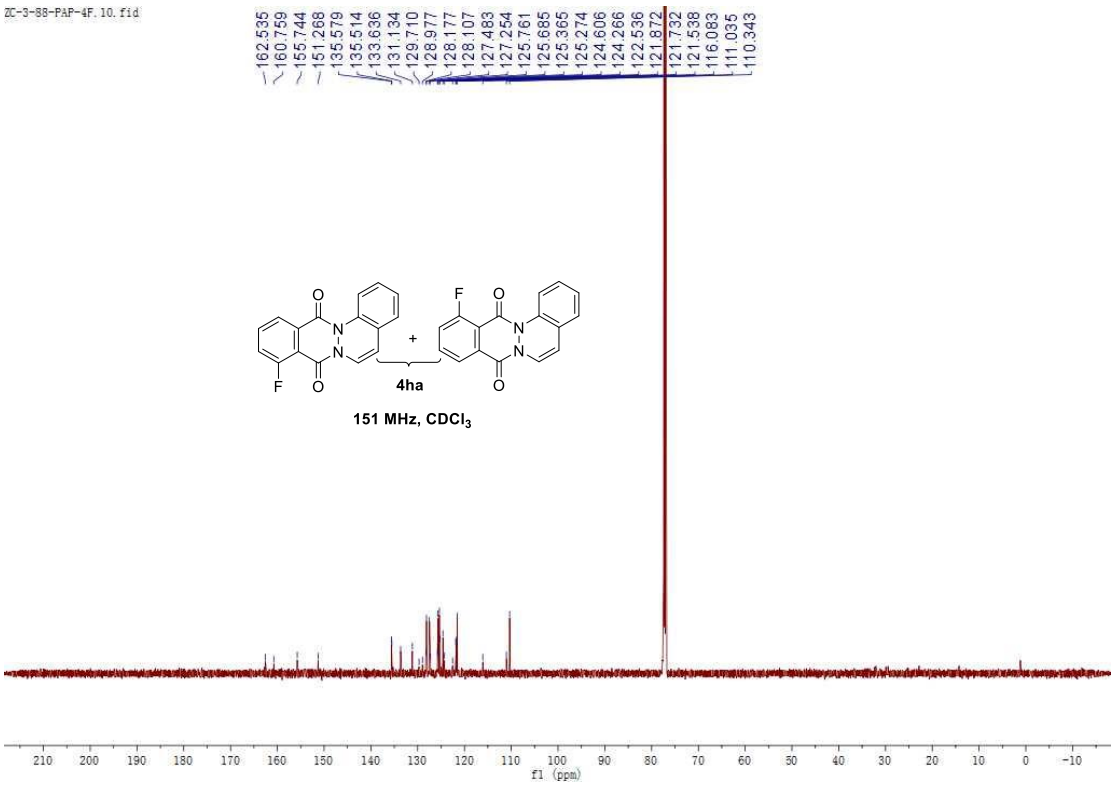

zc-3-89-5N02
9.296
9.291
9.208
8.645
8.130
7.598
7.578
7.329
7.260
7.189
6.279
6.271
6.259
O2N
O2N
4ga
400 MHz, CDCl3
1.00
2.10
1.06
1.14
1.03
1.02
1.01
1.02
f1 (ppm)

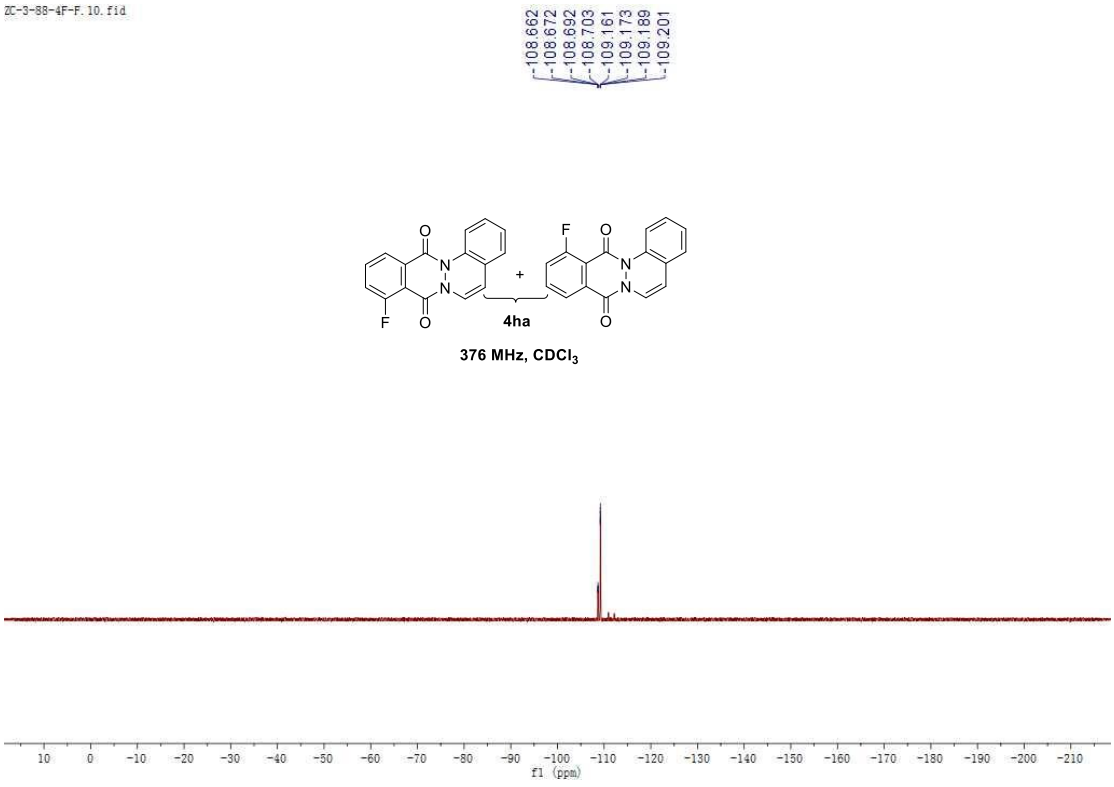

ZC-3-87-PAP-5N02
155.155
153.966
152.535
151.306
130.153
128.579
127.820
127.767
126.029
124.939
124.239
121.412
121.447
111.145
4ga
151 MHz, CDCl3
f1 (ppm)

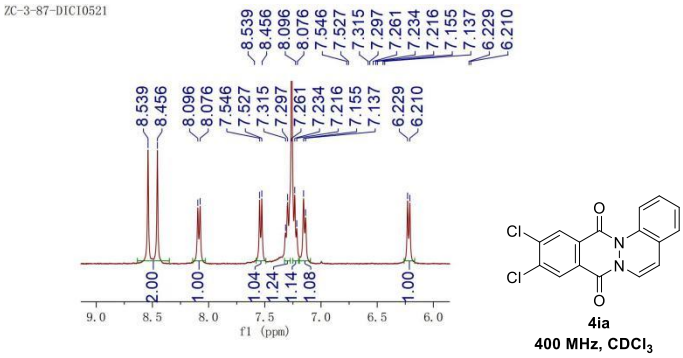

8.324
8.304
8.247
8.227
8.072
8.052
8.036
8.015
7.901
7.889
7.881
7.868
7.849
7.641
7.620
7.601
7.580
7.561
7.552
7.530
7.513
7.492
7.467
7.447
7.370
7.361
7.347
7.297
7.278
7.259
7.238
7.219
7.201
7.185
7.146
7.128
6.218
6.200
6.181


4ha
400 MHz, CDCl3

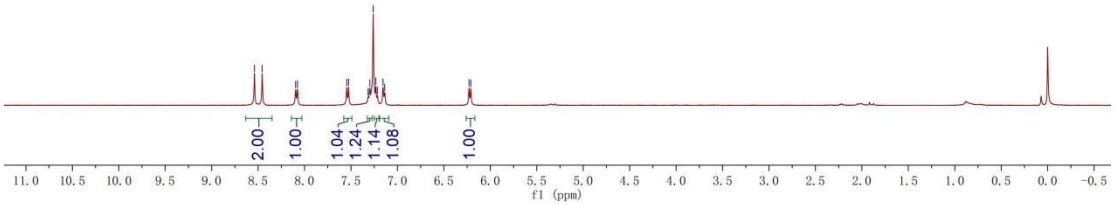

1.09
1.05
1.14
3.03
2.08
1.00
f1 (ppm)

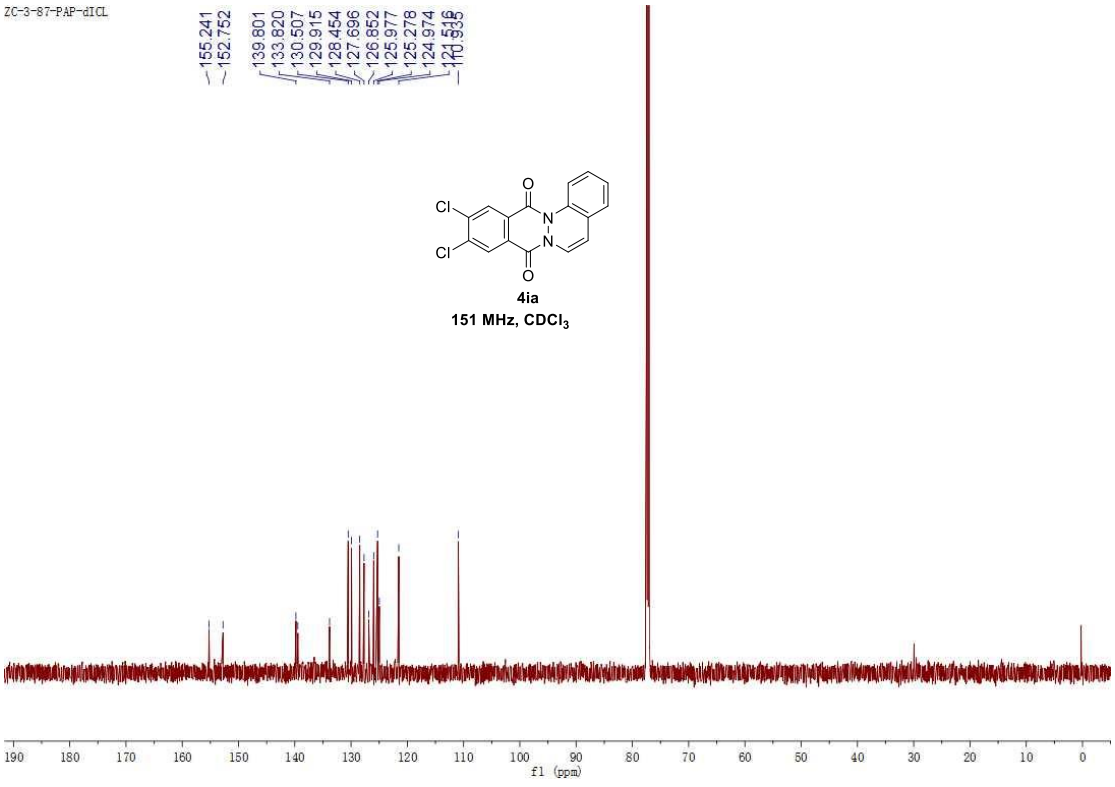

ZC-3-88-PAP-4F.10.fid
162.535
160.759
155.744
151.268
135.579
135.514
133.636
131.134
129.710
128.977
128.177
128.107
127.483
127.254
125.761
125.685
125.365
125.274
124.606
124.266
122.536
121.872
121.732
121.538
116.083
111.035
110.343
4ha
151 MHz, CDCl3
f1 (ppm)


ZC-3-88-4F-F.10.fid
-108.662
-108.672
-108.692
-108.703
-109.161
-109.173
-109.189
-109.201
4ha
376 MHz, CDCl3
f1 (ppm)

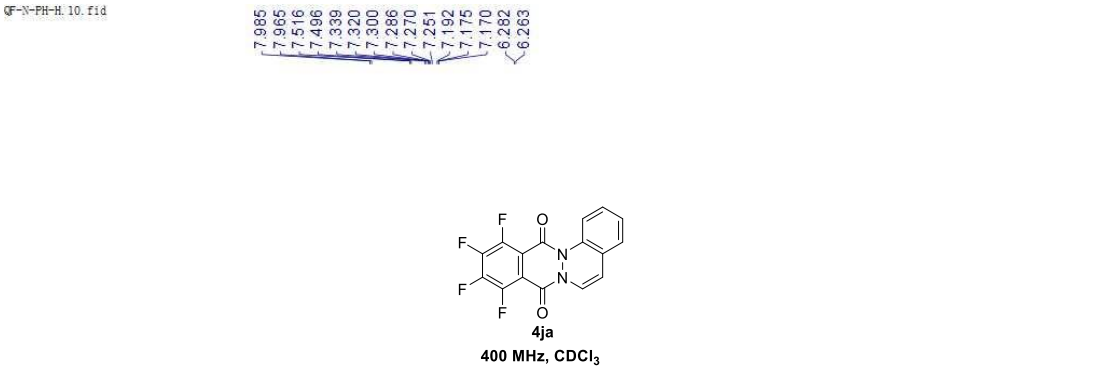


4ia
400 MHz, $CDCl_3$



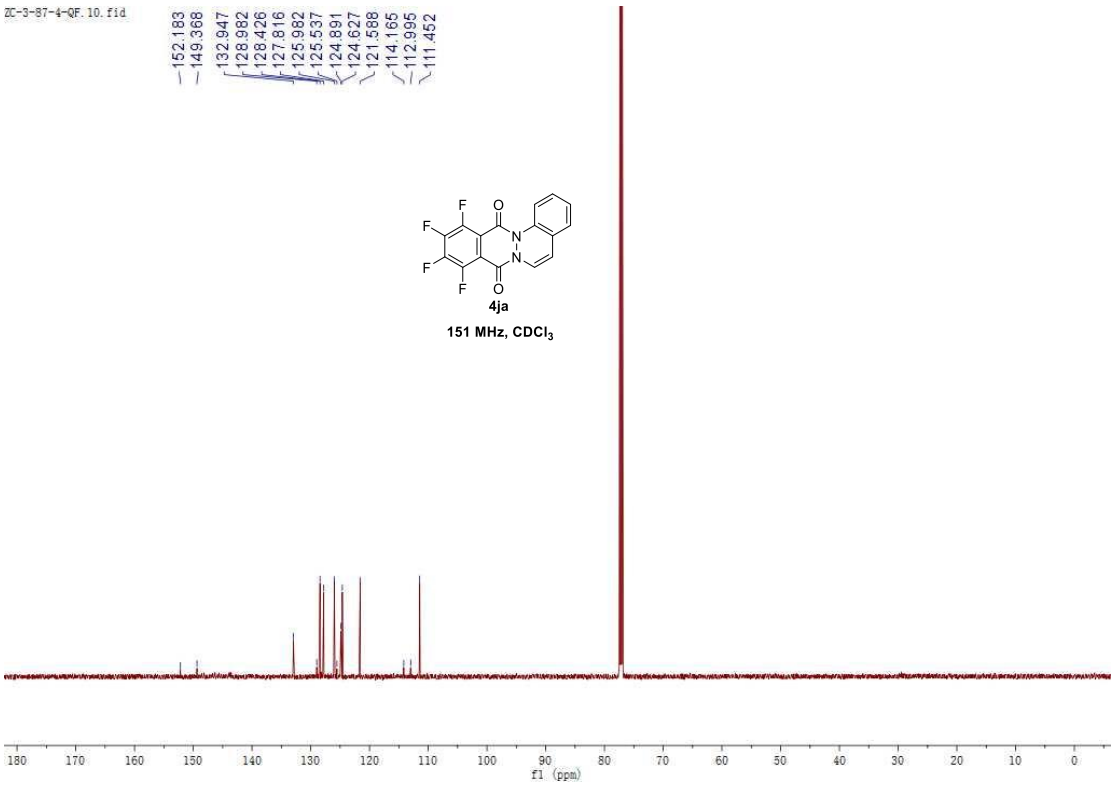


4ia
151 MHz, $CDCl_3$



4ja

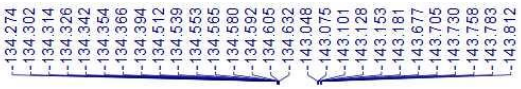
400 MHz, $CDCl_3$

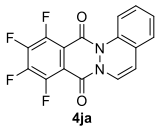


4ja

151 MHz, $CDCl_3$

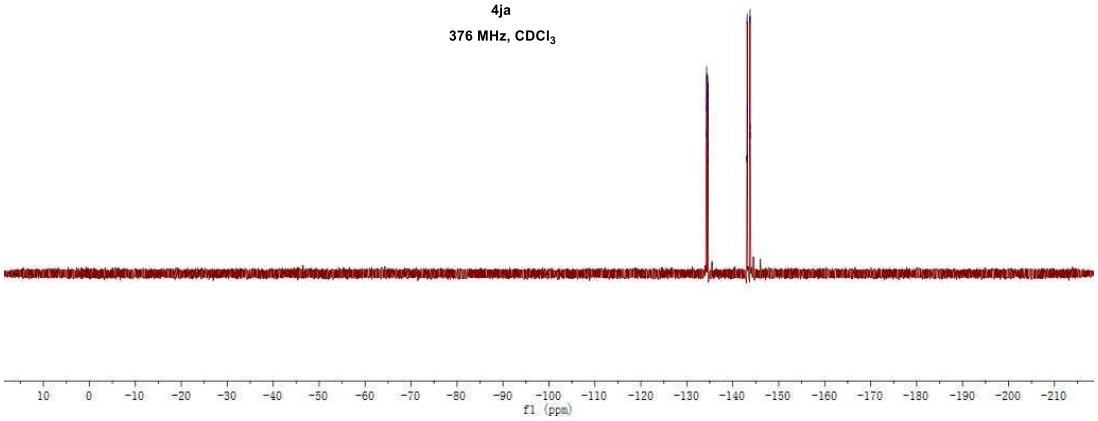
QF-N-PH-H-F.10.fid



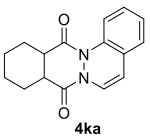


4ja

376 MHz, $CDCl_3$

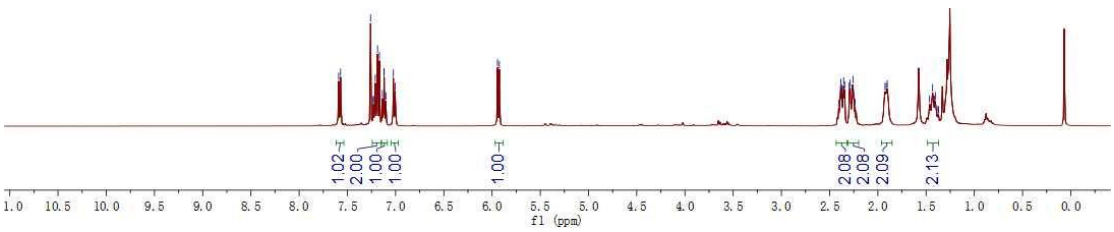


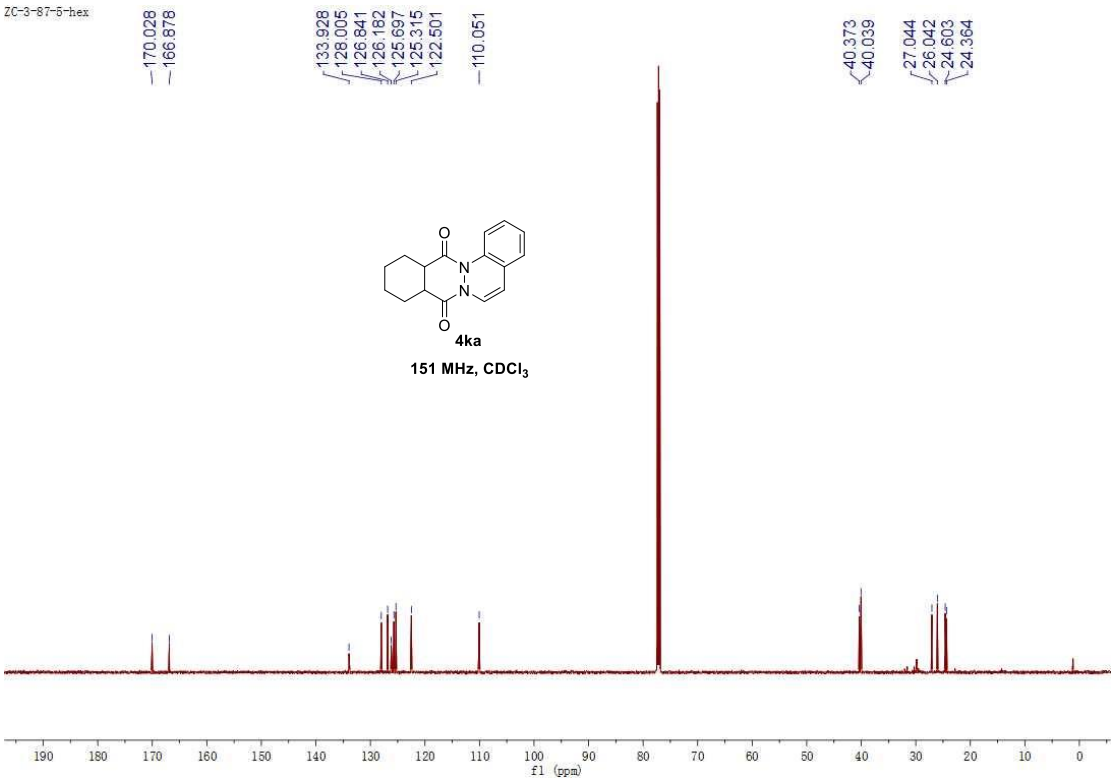
ZC-3-87-5HEX0506

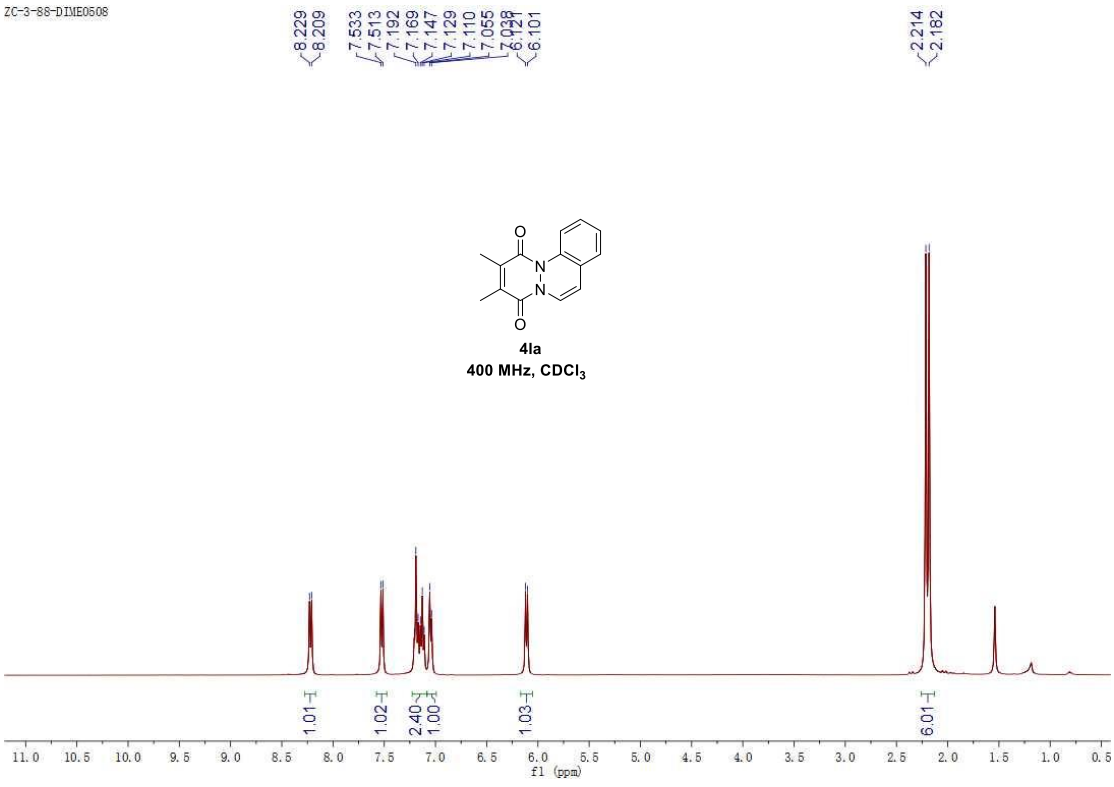


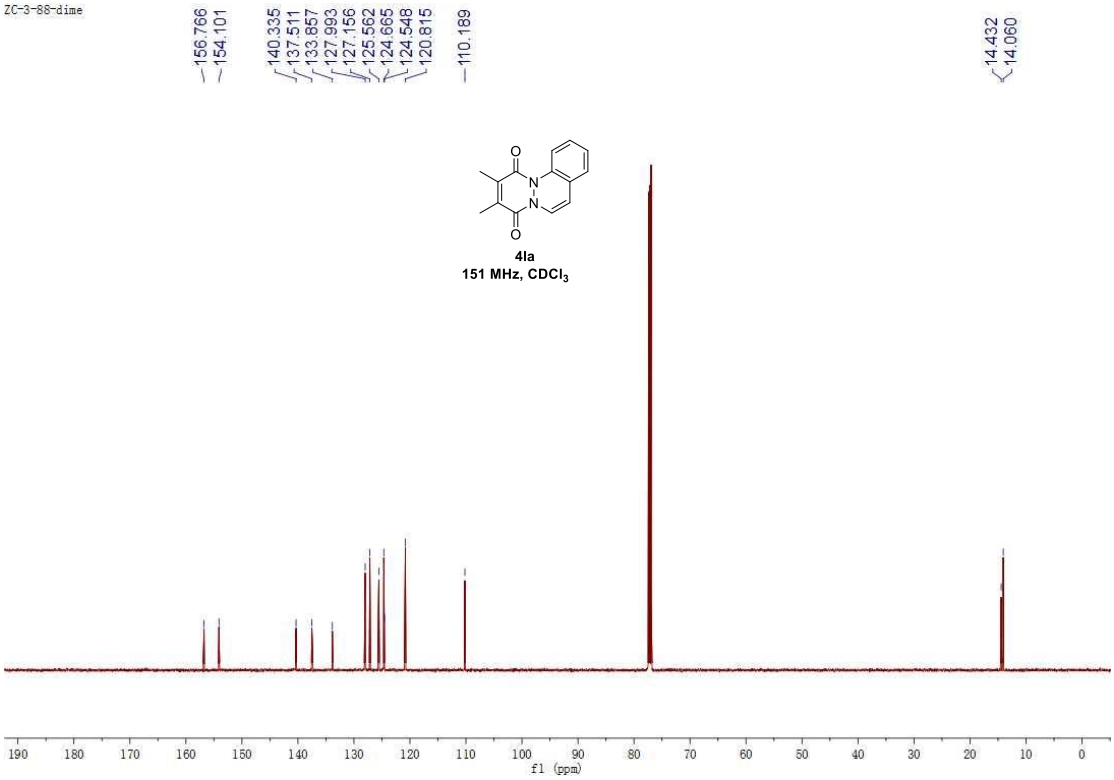
4ka

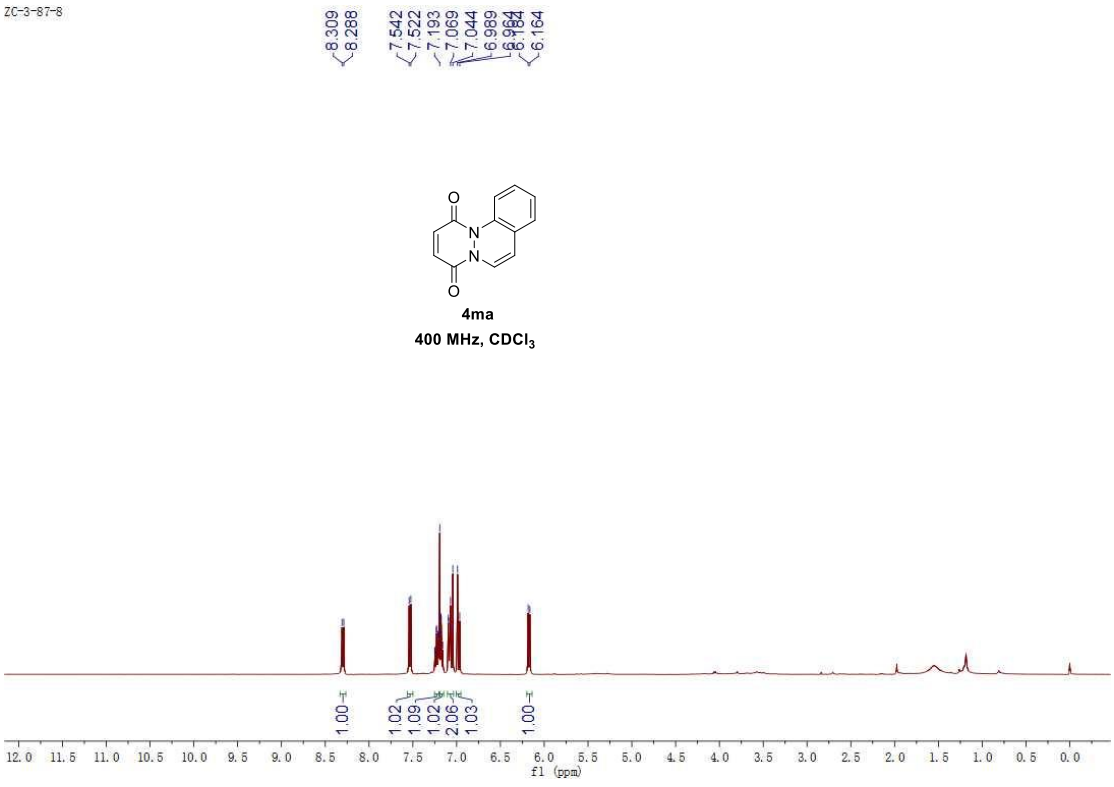
400 MHz, $CDCl_3$

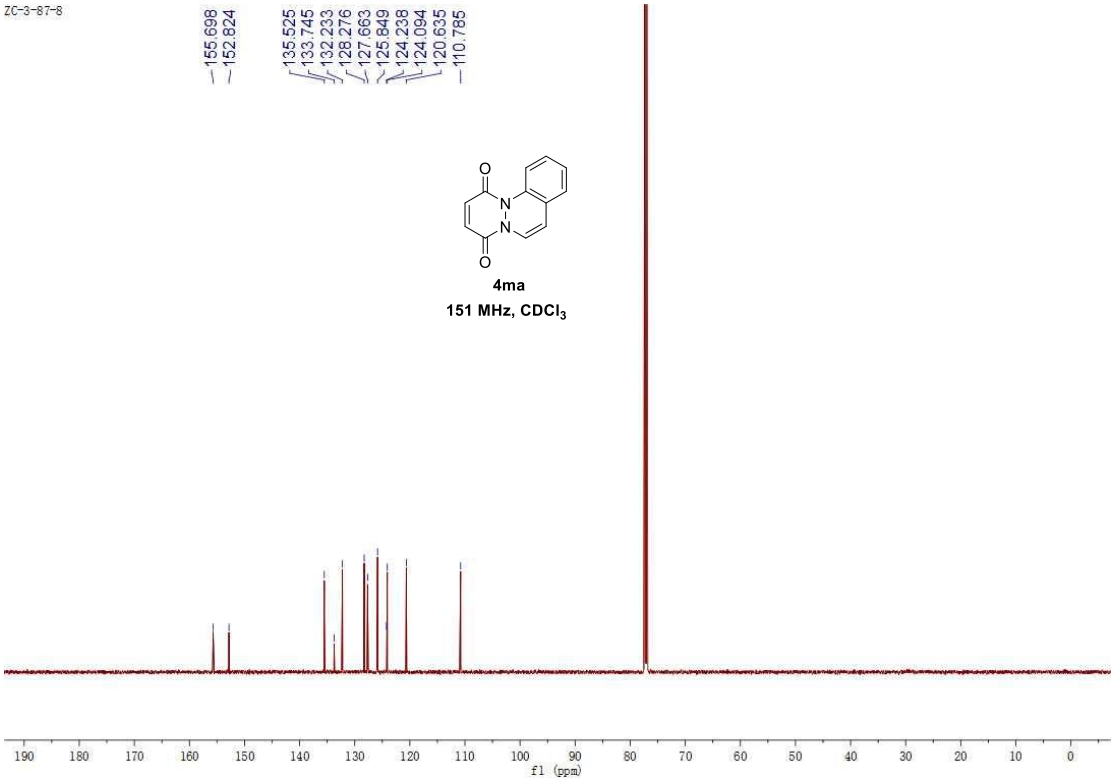


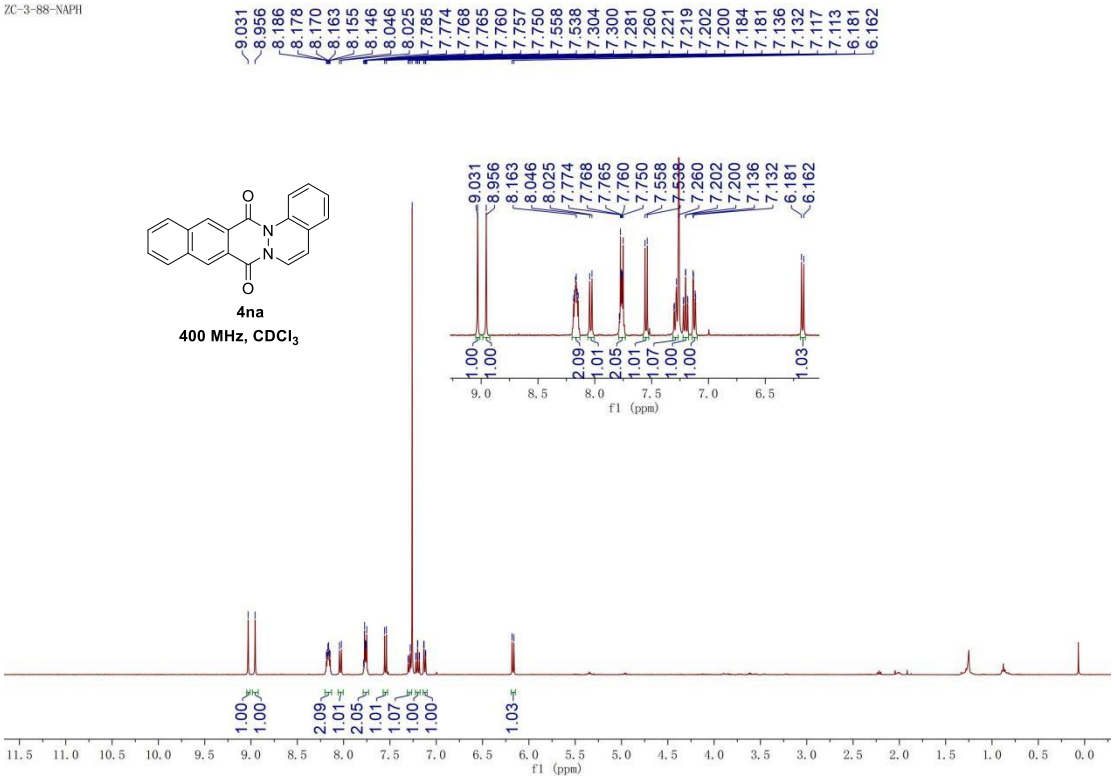

ZC-3-87-5-hex
170.028
166.878
133.928
128.005
126.841
126.182
125.697
125.315
122.501
110.051
40.373
40.039
27.044
26.042
24.603
24.364
O
N
N
O
4ka
151 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

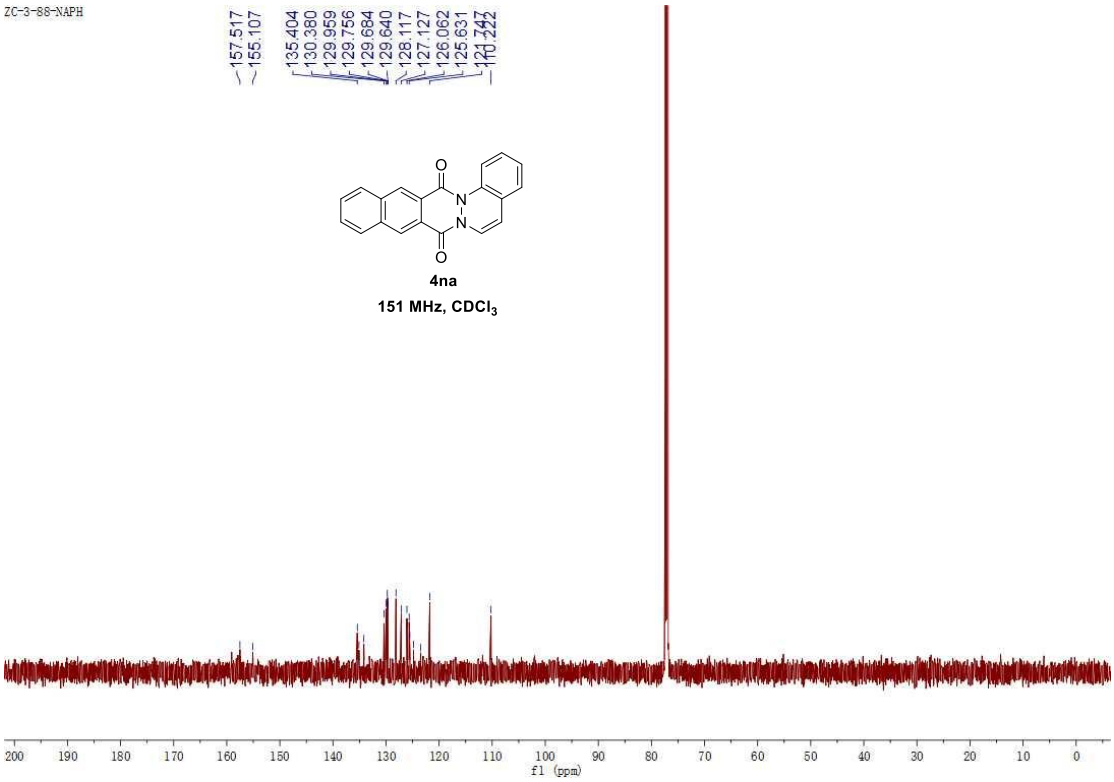

ZC-3-88-DIME0508
8.229
8.209
7.533
7.513
7.192
7.169
7.147
7.129
7.110
7.055
6.101
2.214
2.182
O
N
N
O
4la
400 MHz, CDCl3
1.01
1.02
2.40
1.00
1.03
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


ZC-3-88-dime
156.766
154.101
140.335
137.511
133.857
127.993
127.156
125.562
124.665
124.548
120.815
110.189
14.432
14.060
4la
151 MHz, CDCl3
f1 (ppm)


ZC-3-87-8
8.309
8.288
7.542
7.522
7.193
7.069
7.044
6.989
6.164
4ma
400 MHz, CDCl3
1.00
1.02
1.09
1.02
2.06
1.03
1.00
f1 (ppm)

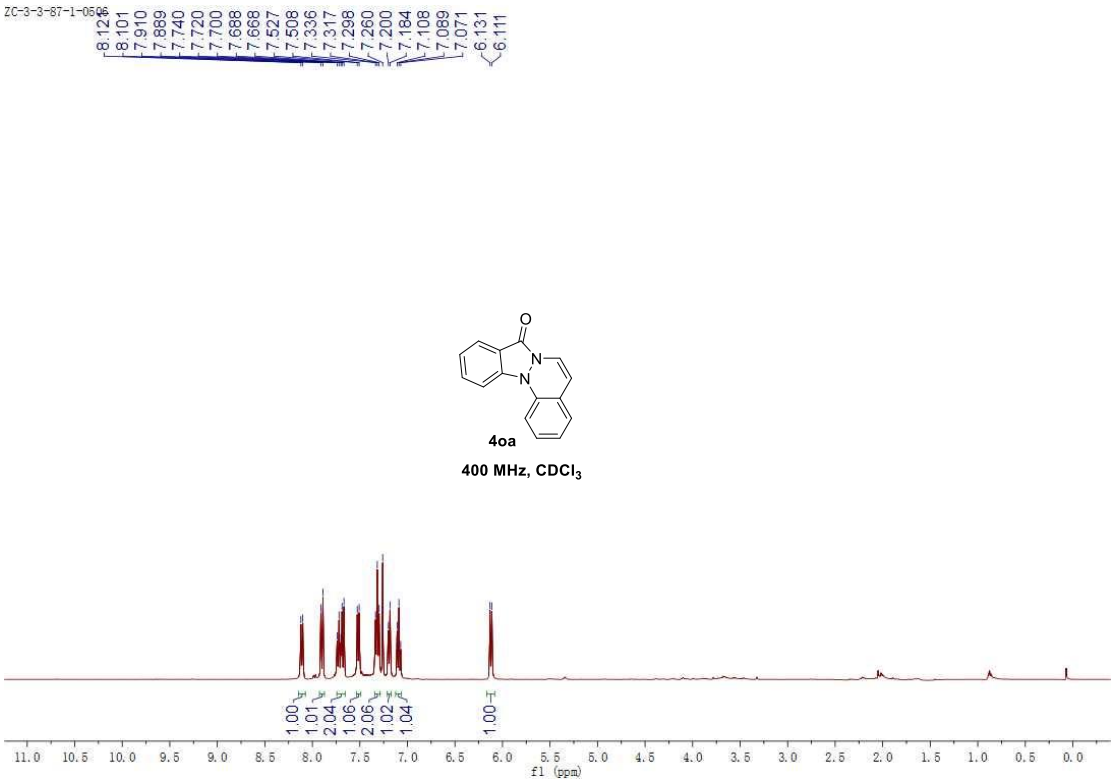

ZC-3-87-8
155.698
152.824
135.525
133.745
132.233
128.276
127.663
125.849
124.238
124.094
120.635
110.785
4ma
151 MHz, CDCl3
f1 (ppm)


ZC-3-88-NAPH
9.031
8.956
8.186
8.178
8.170
8.163
8.155
8.146
8.046
8.025
7.785
7.774
7.768
7.765
7.760
7.757
7.750
7.558
7.538
7.304
7.300
7.281
7.260
7.221
7.219
7.202
7.200
7.184
7.181
7.136
7.132
7.117
7.113
6.181
6.162
4na
400 MHz, CDCl3
1.00
1.00
2.09
1.01
2.05
1.01
1.07
1.00
1.00
1.03
f1 (ppm)



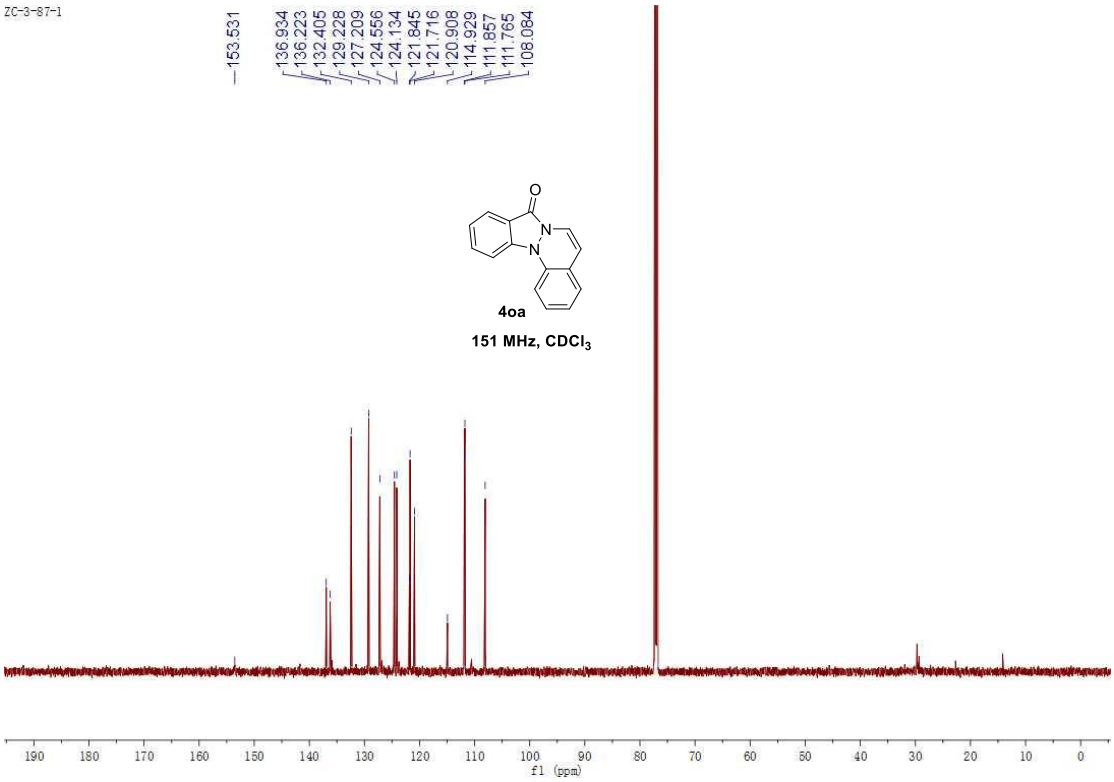
4na

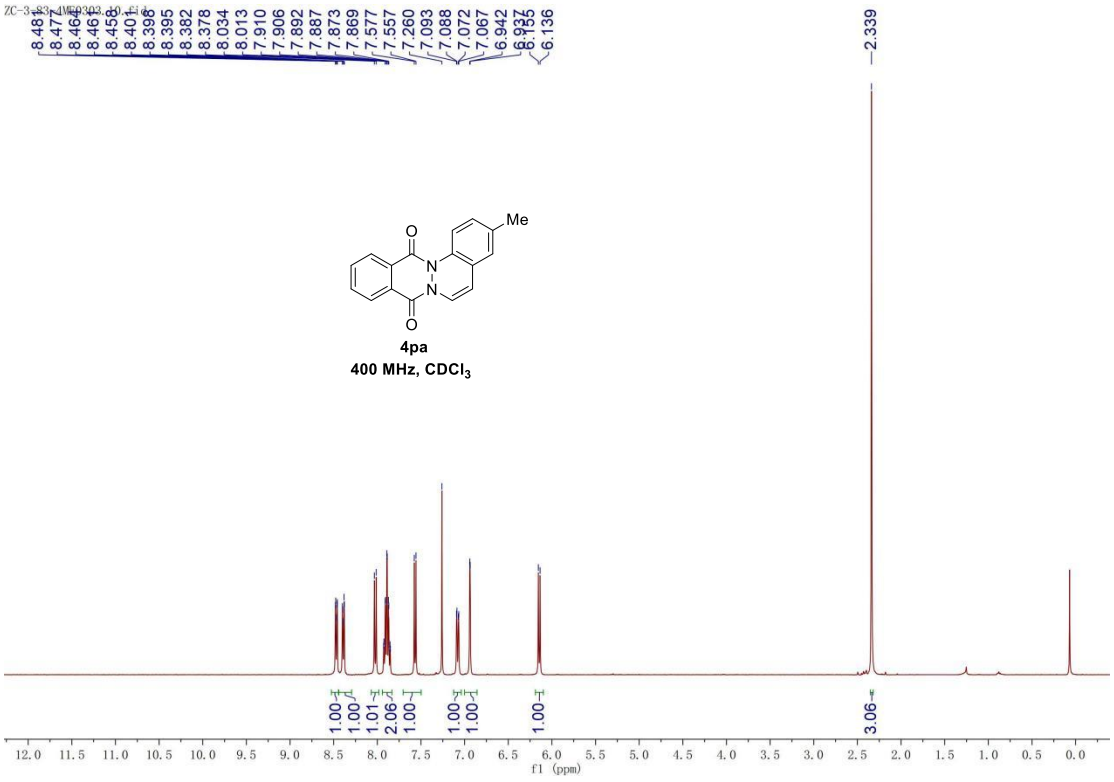
151 MHz, $CDCl_3$

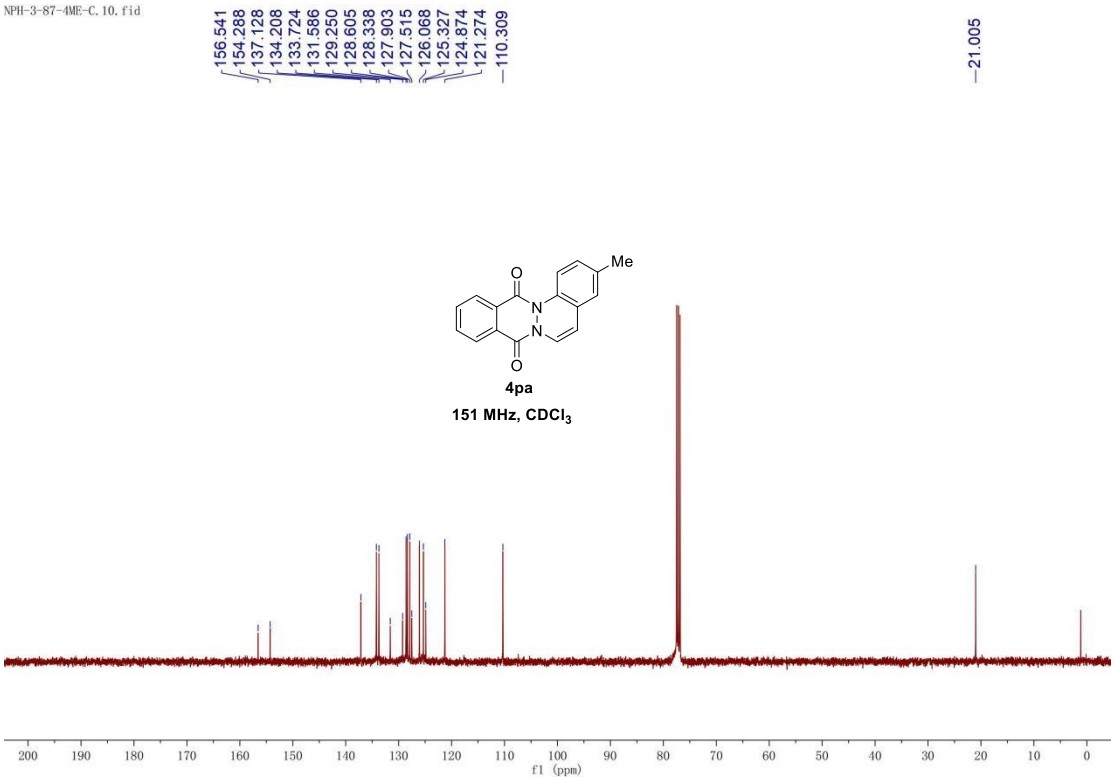


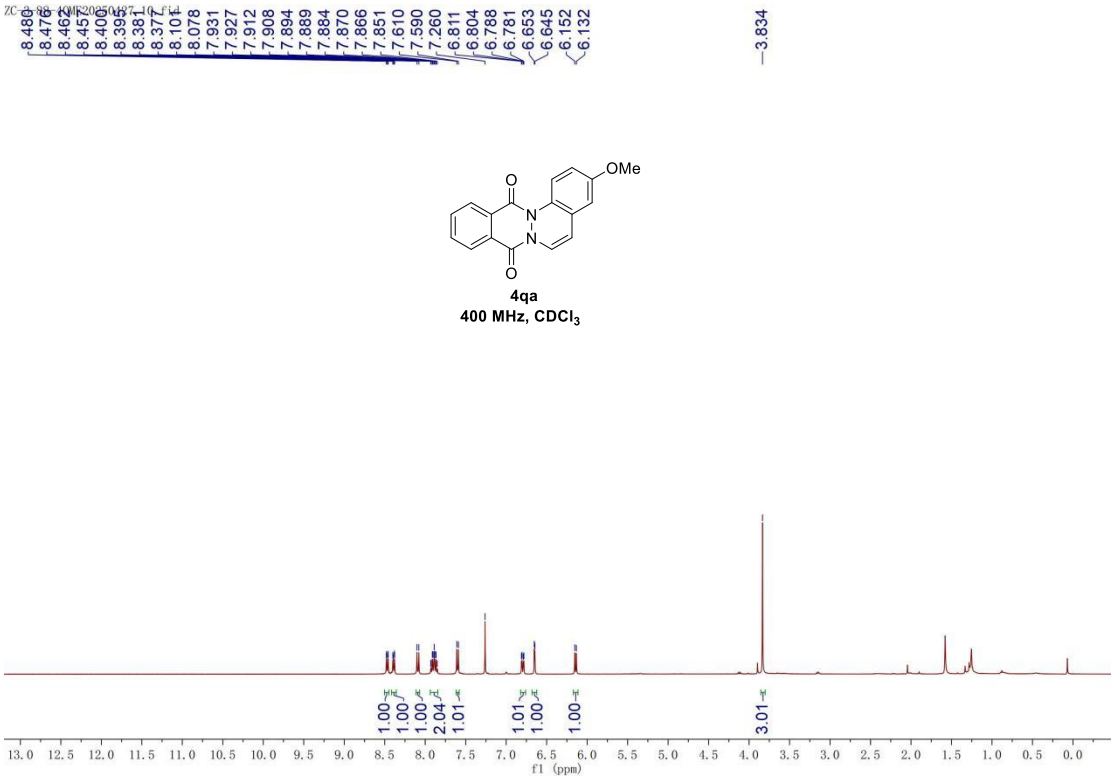
4oa

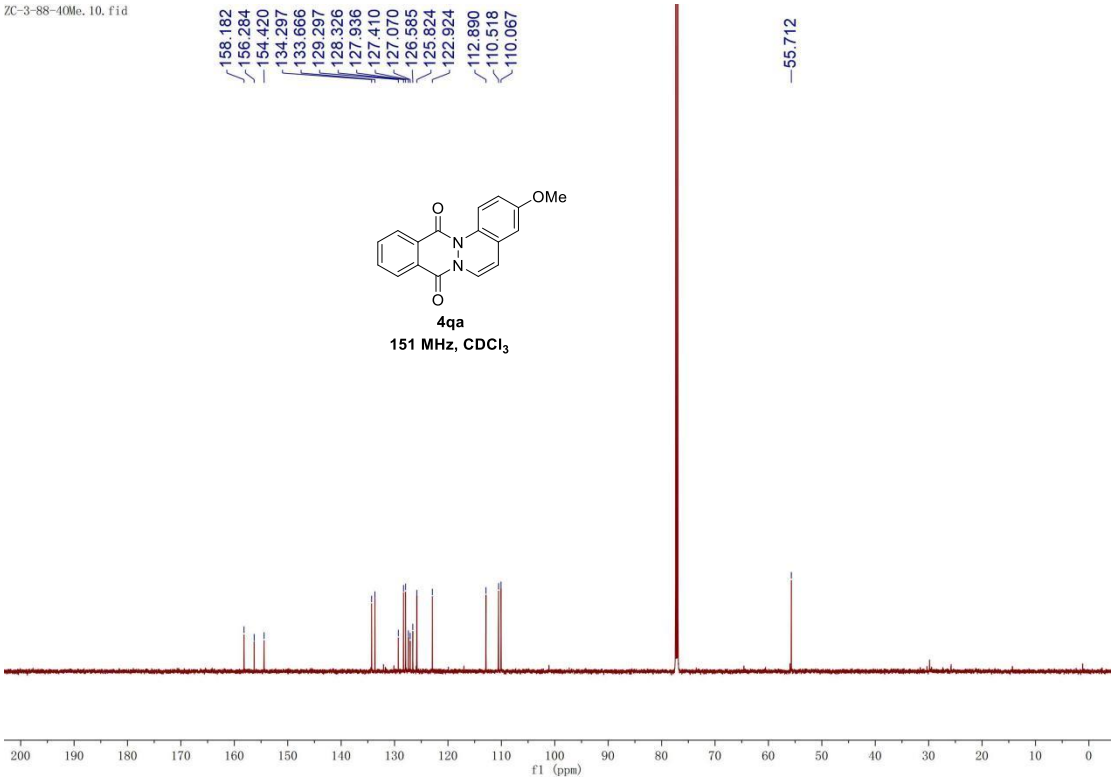
400 MHz, $CDCl_3$


ZC-3-87-1
153.531
136.934
136.223
132.405
129.228
127.209
124.556
124.134
121.845
121.716
120.908
114.929
111.857
111.765
108.084
O
N
N
4oa
151 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

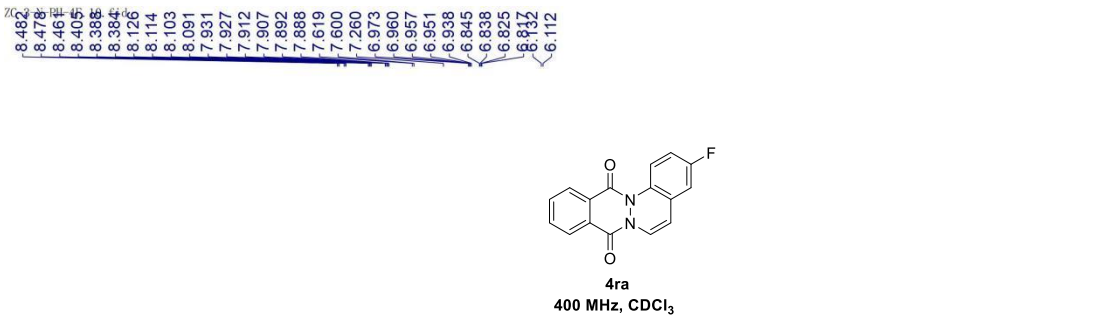

8.484
8.477
8.463
8.461
8.458
8.401
8.398
8.395
8.382
8.378
8.034
8.013
7.910
7.906
7.892
7.887
7.873
7.869
7.577
7.557
7.260
7.093
7.088
7.072
7.067
6.942
6.937
6.136
2.339
O
N
N
O
Me
4pa
400 MHz, CDCl3
1.00
1.00
1.01
2.06
1.00
1.00
1.00
1.00
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NPH-3-87-4ME-C.10.fid
156.541
154.288
137.128
134.208
133.724
131.586
129.250
128.605
128.338
127.903
127.515
126.068
125.327
124.874
121.274
110.309
21.005
Me
O
N
N
O
4pa
151 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

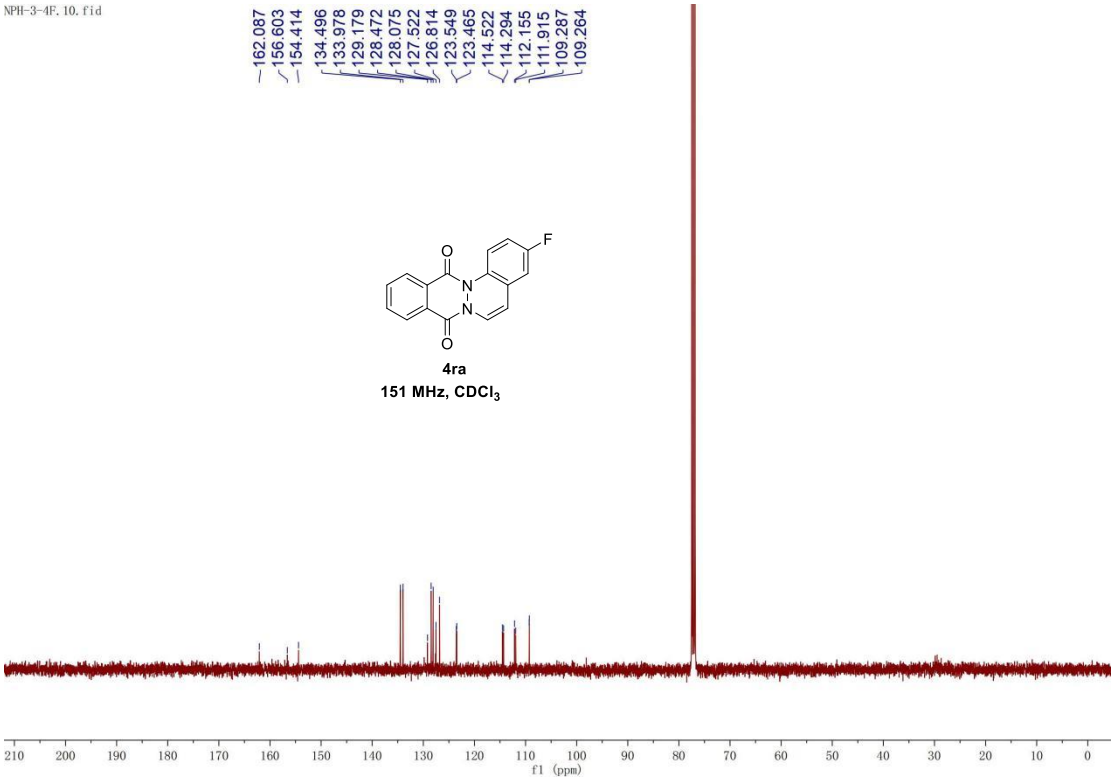

8.480
8.476
8.462
8.457
8.400
8.395
8.381
8.377
8.101
8.078
7.931
7.927
7.912
7.908
7.894
7.889
7.884
7.870
7.866
7.851
7.610
7.590
7.260
6.811
6.804
6.788
6.781
6.653
6.645
6.152
6.132
3.834
OMe
O
N
N
O
4qa
400 MHz, CDCl3
1.00
1.00
1.00
2.04
1.01
1.01
1.00
1.00
3.01
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



4qa
151 MHz, $CDCl_3$

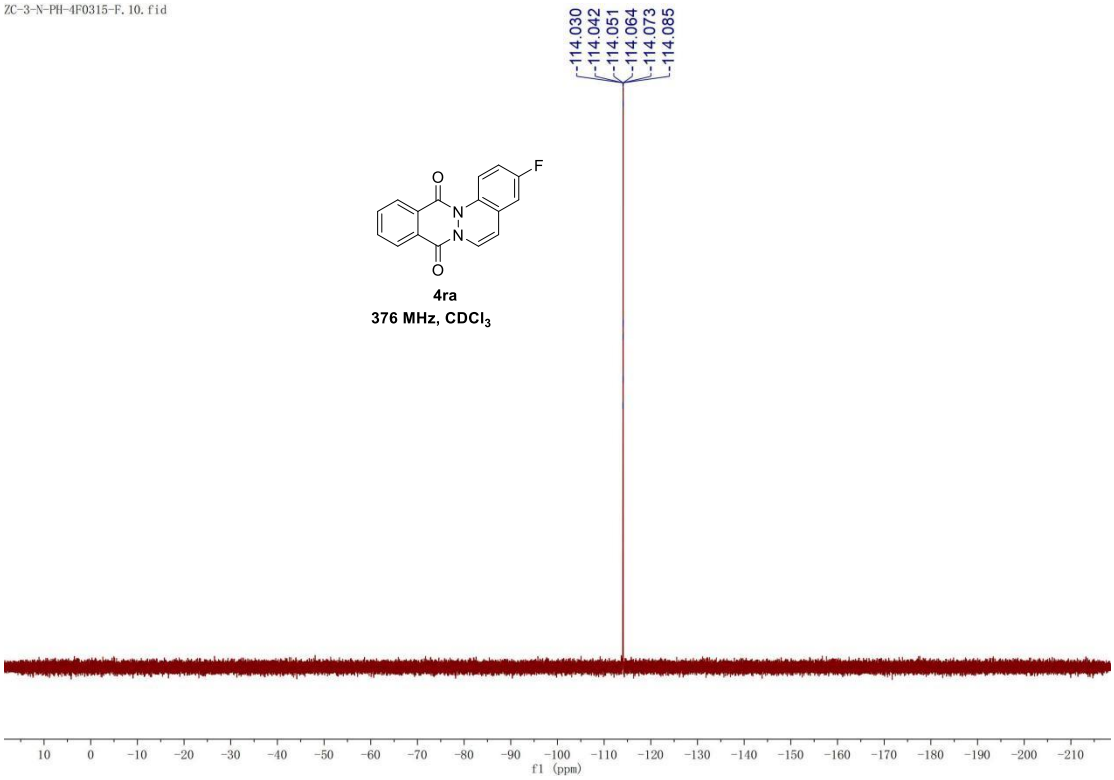


4ra
400 MHz, $CDCl_3$



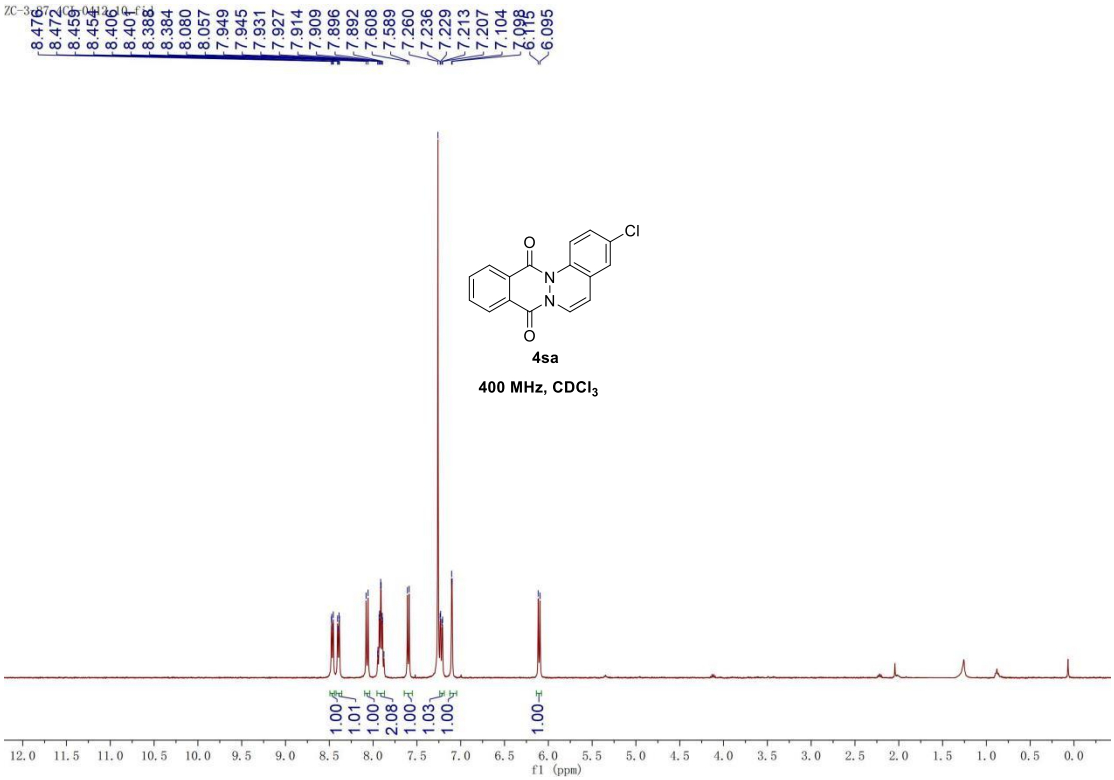
4ra

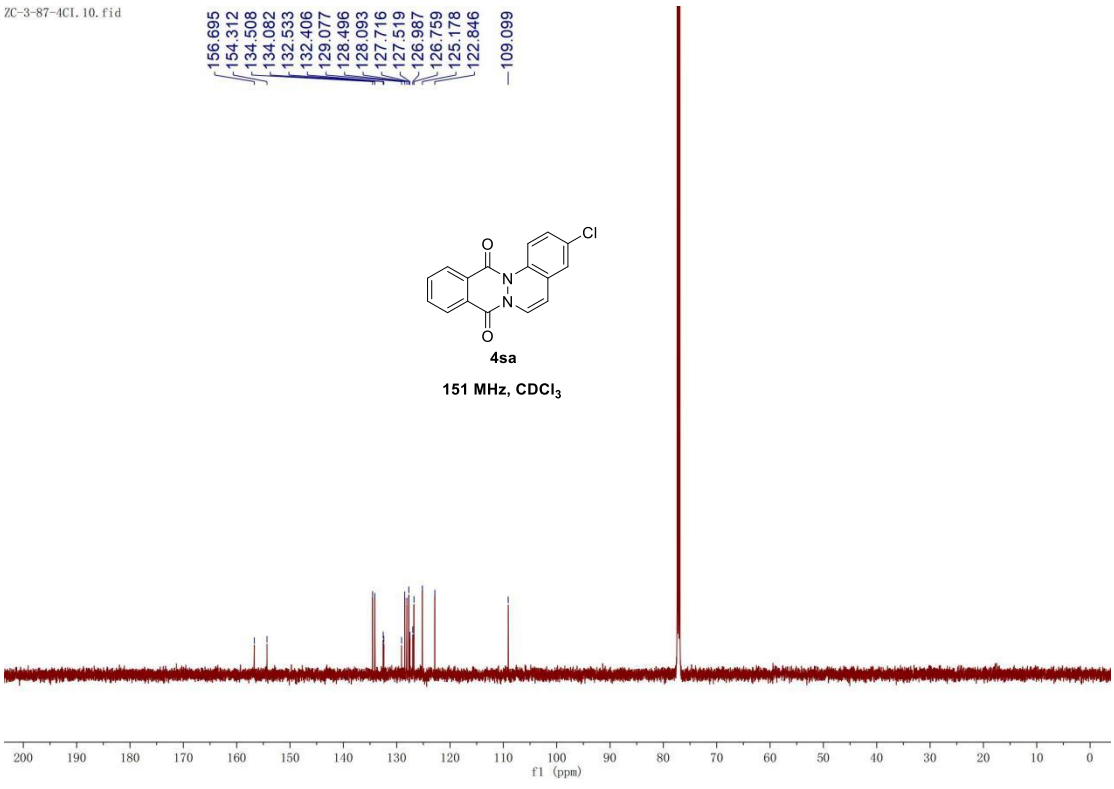
151 MHz, $CDCl_3$

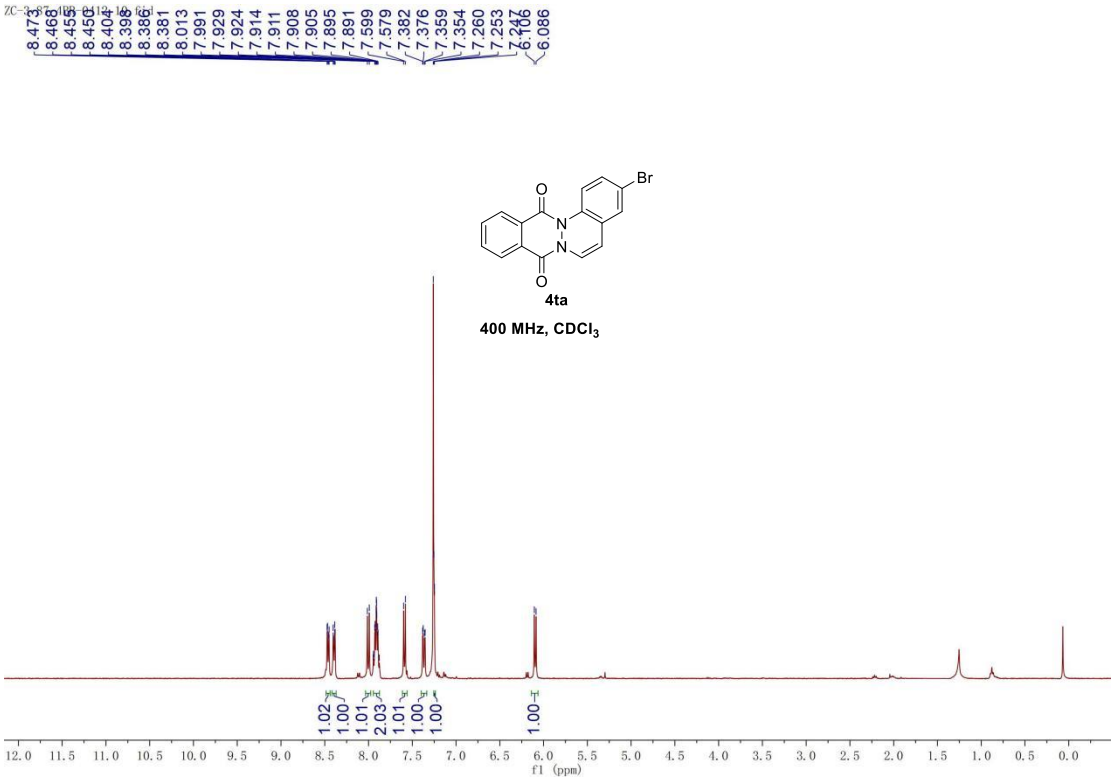


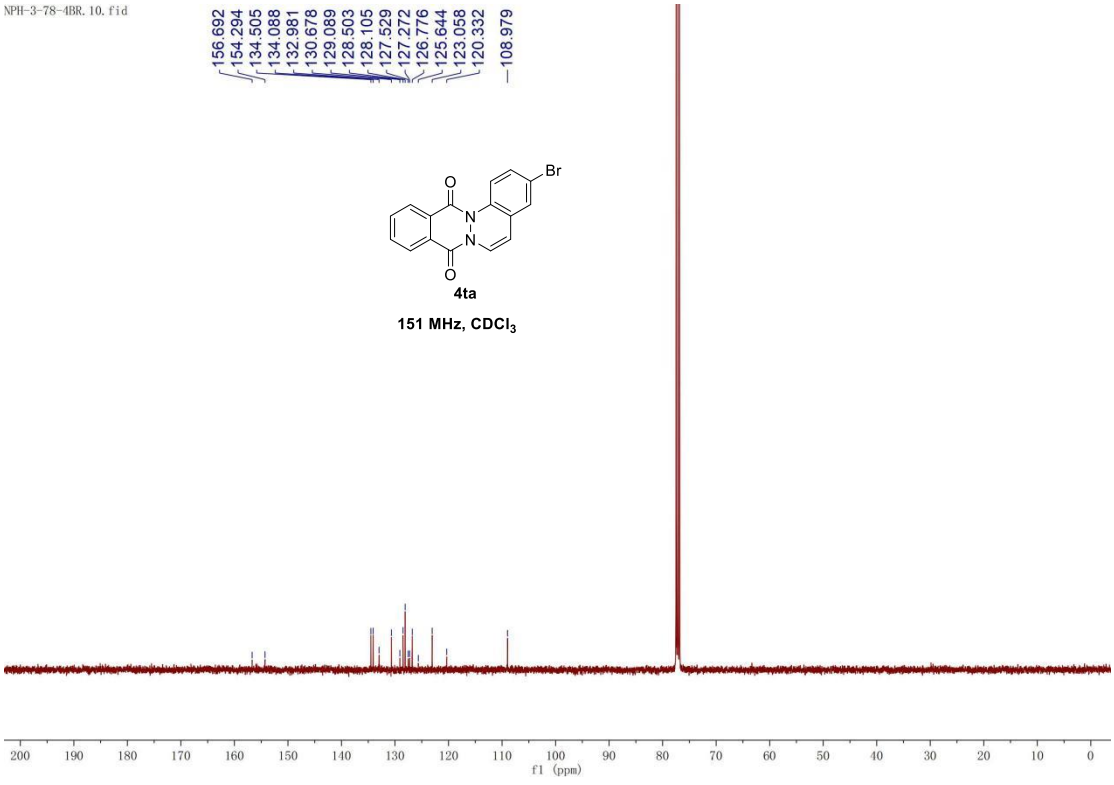
4ra

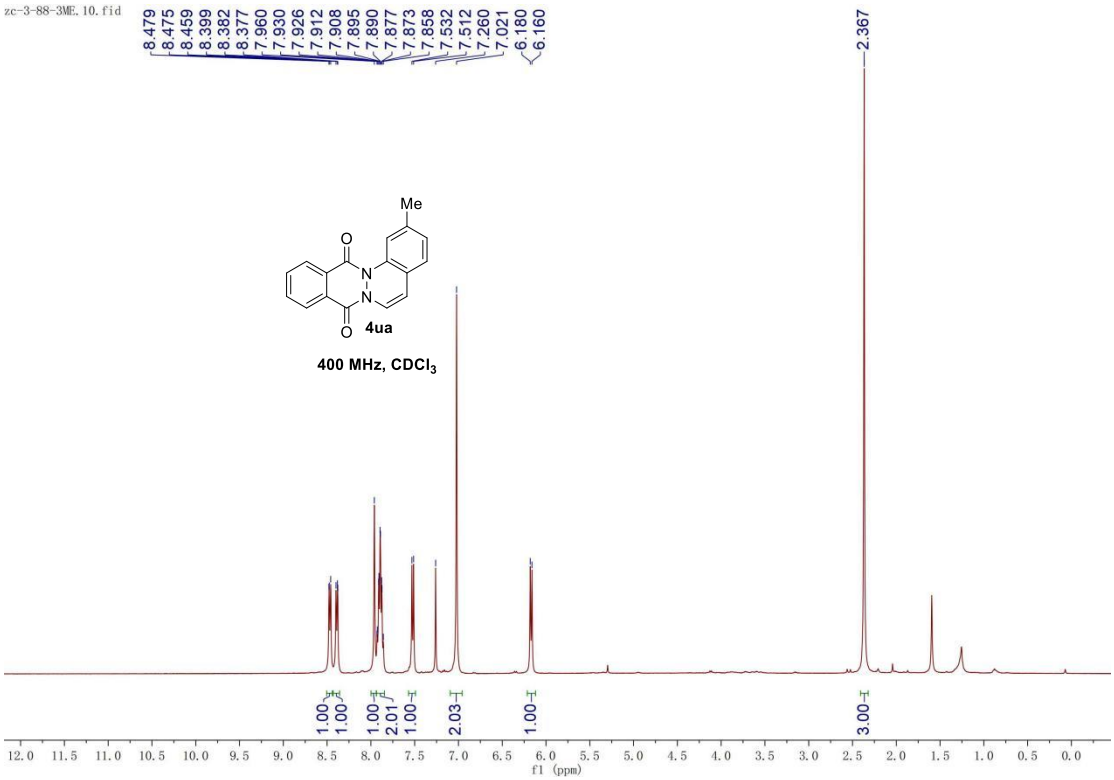
376 MHz, $CDCl_3$

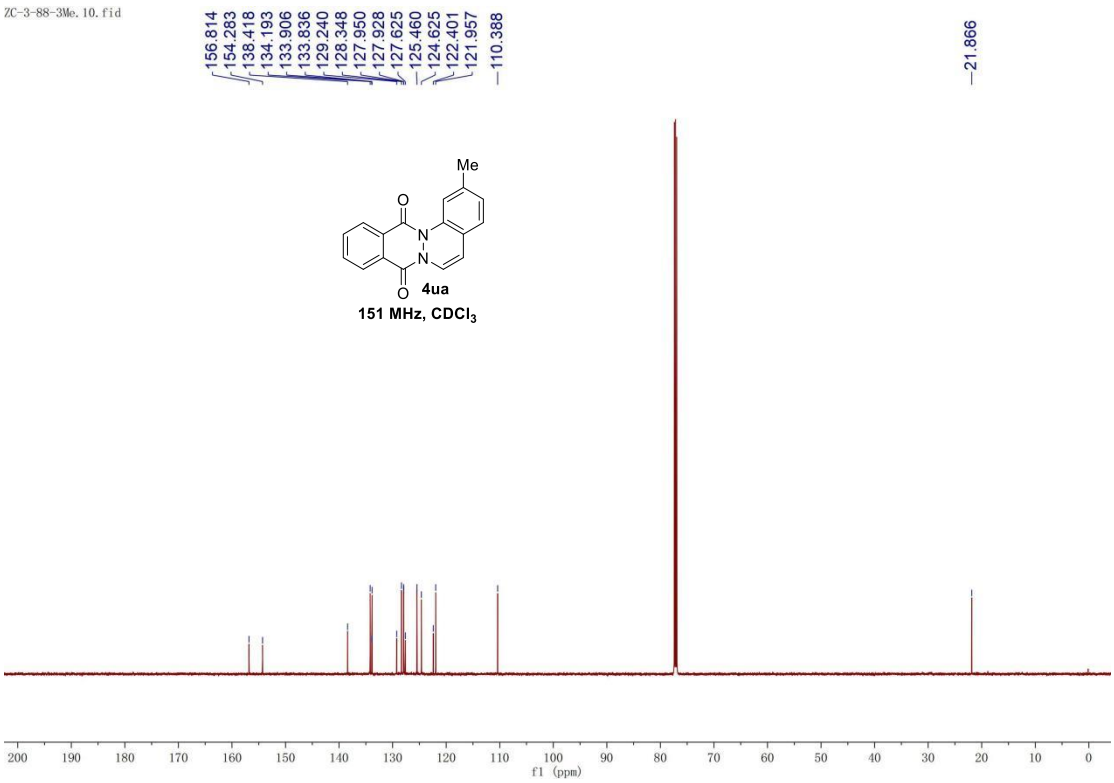

8.476
8.472
8.459
8.454
8.406
8.401
8.388
8.384
8.080
8.057
7.949
7.945
7.931
7.927
7.914
7.909
7.896
7.892
7.608
7.589
7.260
7.236
7.229
7.213
7.207
7.104
6.095
Cl
O
N
N
O
4sa
400 MHz, CDCl3
1.00
1.01
1.00
2.08
1.00
1.03
1.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

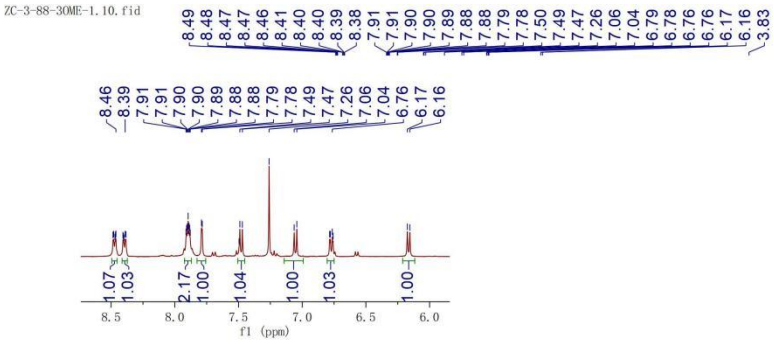

ZC-3-87-4Cl. 10. fid
156.695
154.312
134.508
134.082
132.533
132.406
129.077
128.496
128.093
127.716
127.519
126.987
126.759
125.178
122.846
109.099
Cl
O
N
N
O
4sa
151 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

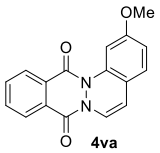

8.473
8.468
8.455
8.450
8.404
8.396
8.386
8.381
8.013
7.991
7.929
7.924
7.914
7.911
7.908
7.905
7.895
7.891
7.599
7.579
7.382
7.376
7.359
7.354
7.260
7.253
7.247
6.106
6.086
Br
O
N
N
O
4ta
400 MHz, CDCl3
1.02
1.00
1.01
2.03
1.01
1.00
1.00
1.00
f1 (ppm)


NPH-3-78-4BR.10.fid
156.692
154.294
134.505
134.088
132.981
130.678
129.089
128.503
128.105
127.529
127.272
126.776
125.644
123.058
120.332
108.979
Br
O
N
N
O
4ta
151 MHz, CDCl3
f1 (ppm)


zc-3-88-3ME.10.fid
8.479
8.475
8.459
8.399
8.382
8.377
7.960
7.930
7.926
7.912
7.908
7.895
7.890
7.877
7.873
7.858
7.532
7.512
7.260
7.021
6.180
6.160
2.367
Me
O
N
N
O
4ua
400 MHz, CDCl3
1.00
1.00
1.00
2.01
1.00
2.03
1.00
3.00
f1 (ppm)

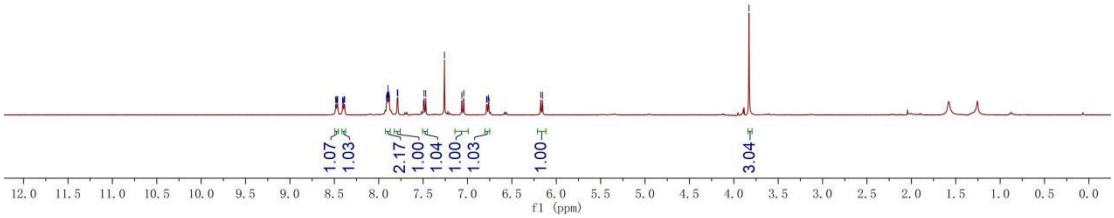

ZC-3-88-3Me.10.fid
156.814
154.283
138.418
134.193
133.906
133.836
129.240
128.348
127.950
127.928
127.625
125.460
124.625
122.401
121.957
110.388
21.866
Me
O
N
N
O
4ua
151 MHz, CDCl3
f1 (ppm)

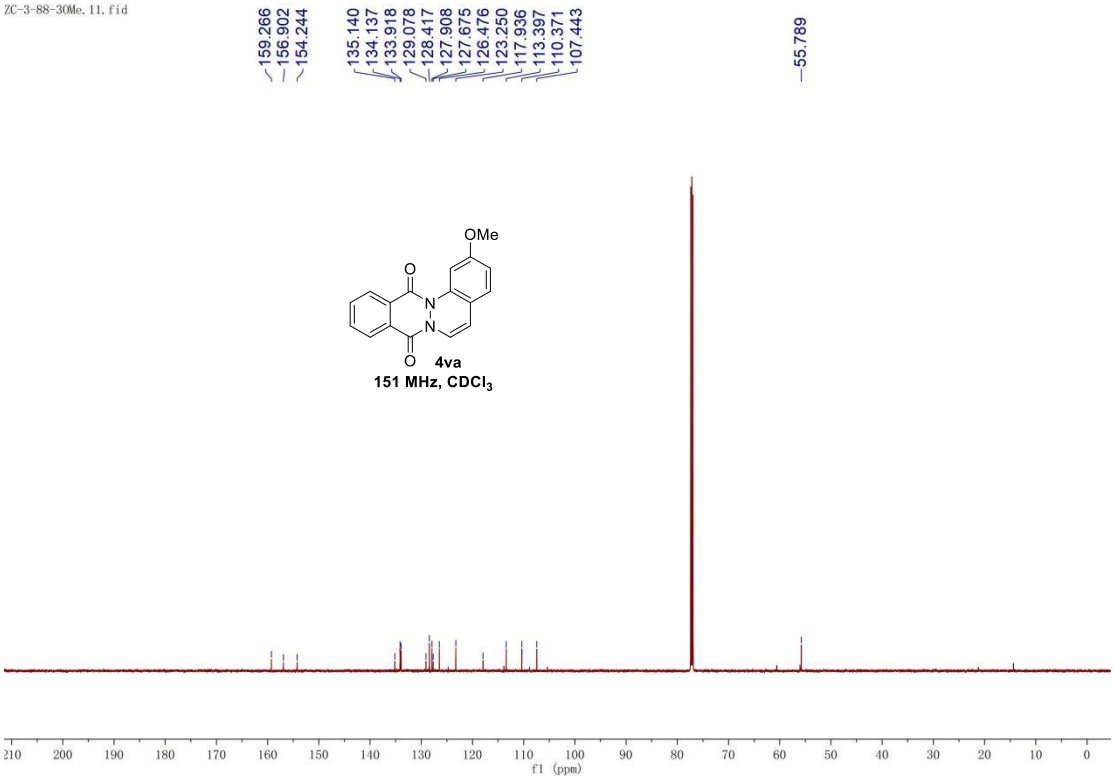




4va

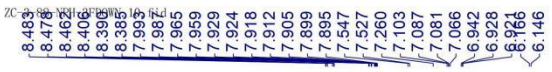
400 MHz, $CDCl_3$

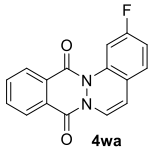




4va

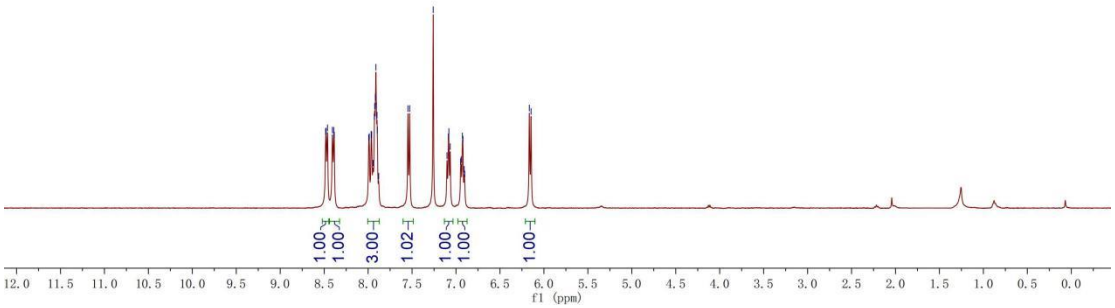
151 MHz, $CDCl_3$

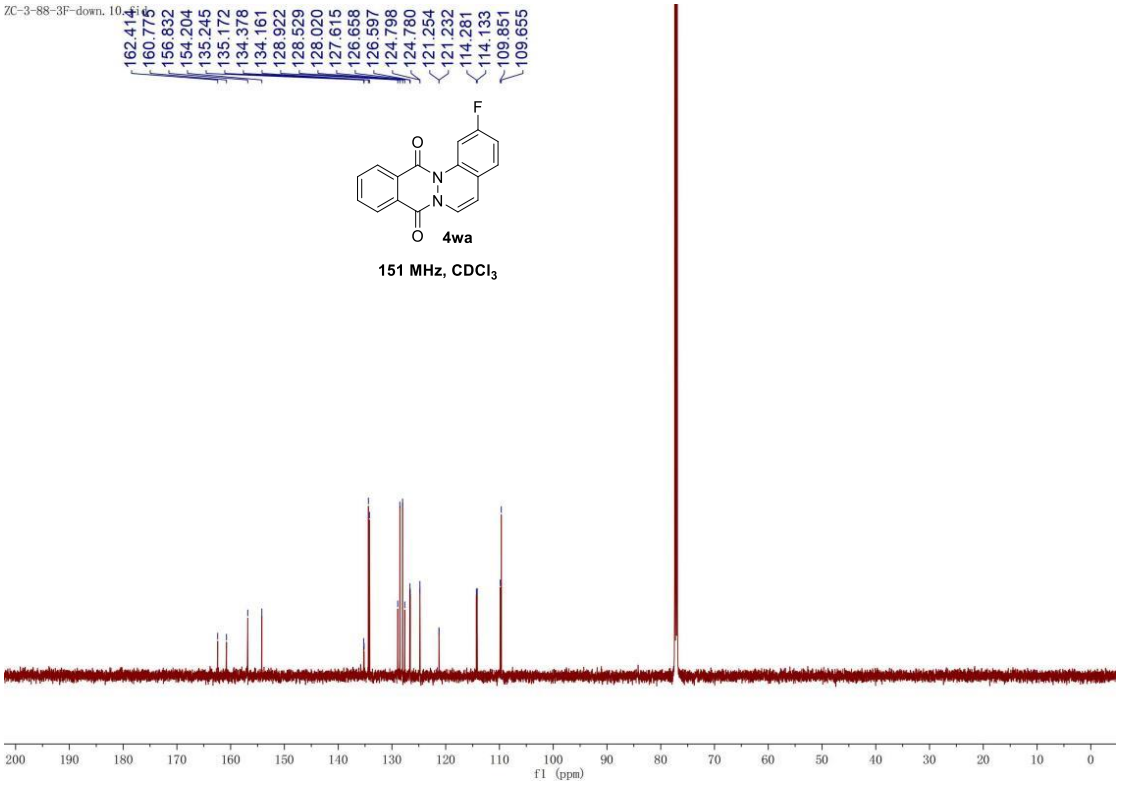




4wa

400 MHz, $CDCl_3$

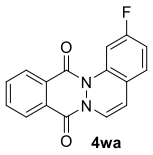




4wa

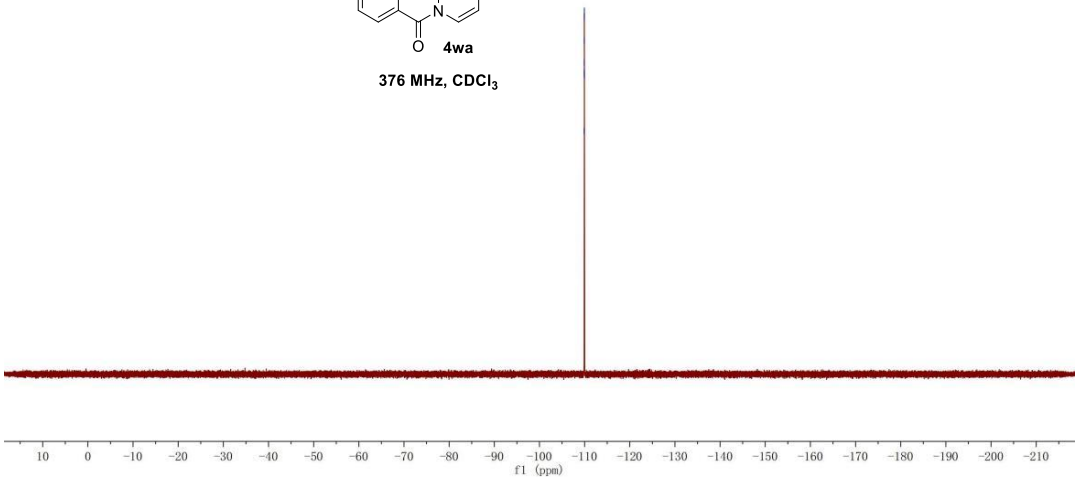
151 MHz, $CDCl_3$

zc-3-88-PAP-3F-down.10.fid

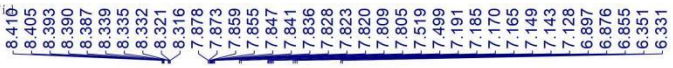


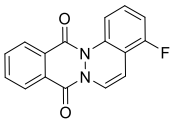
4wa

376 MHz, $CDCl_3$



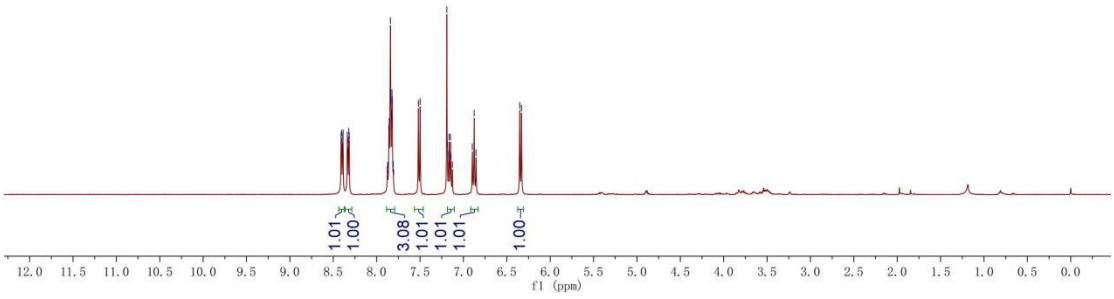
ZC-3-88-NPH-3F-UP-0509.10.fid

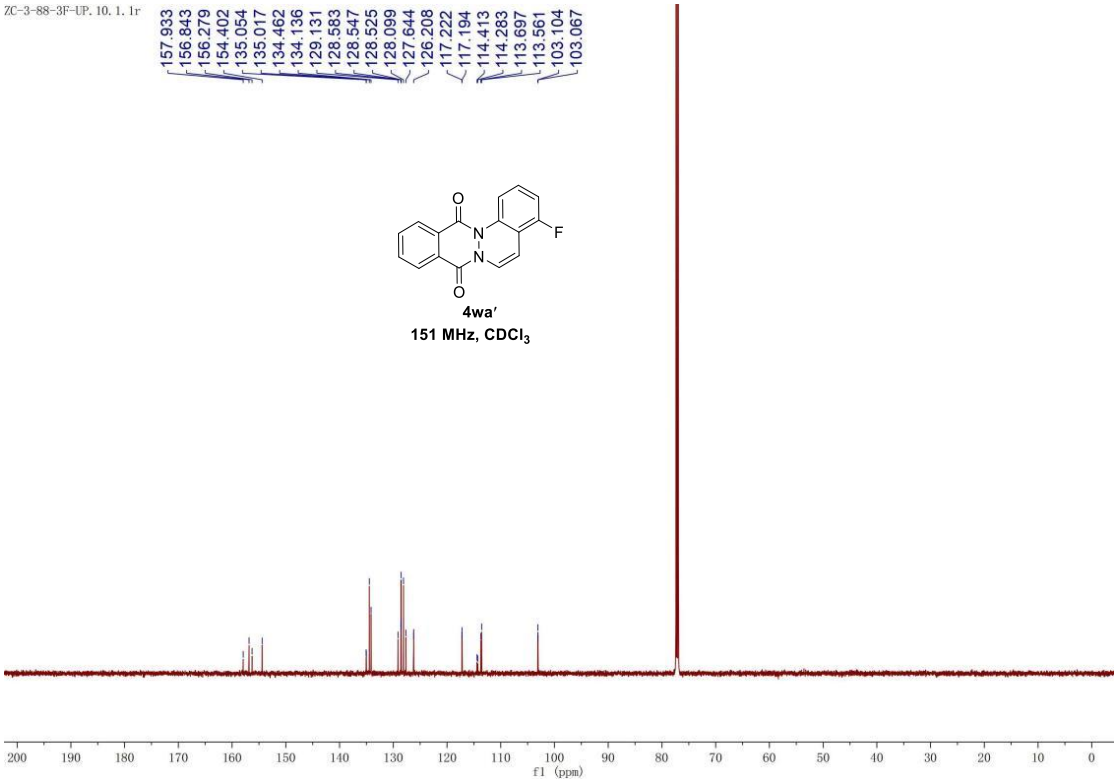




4wa′

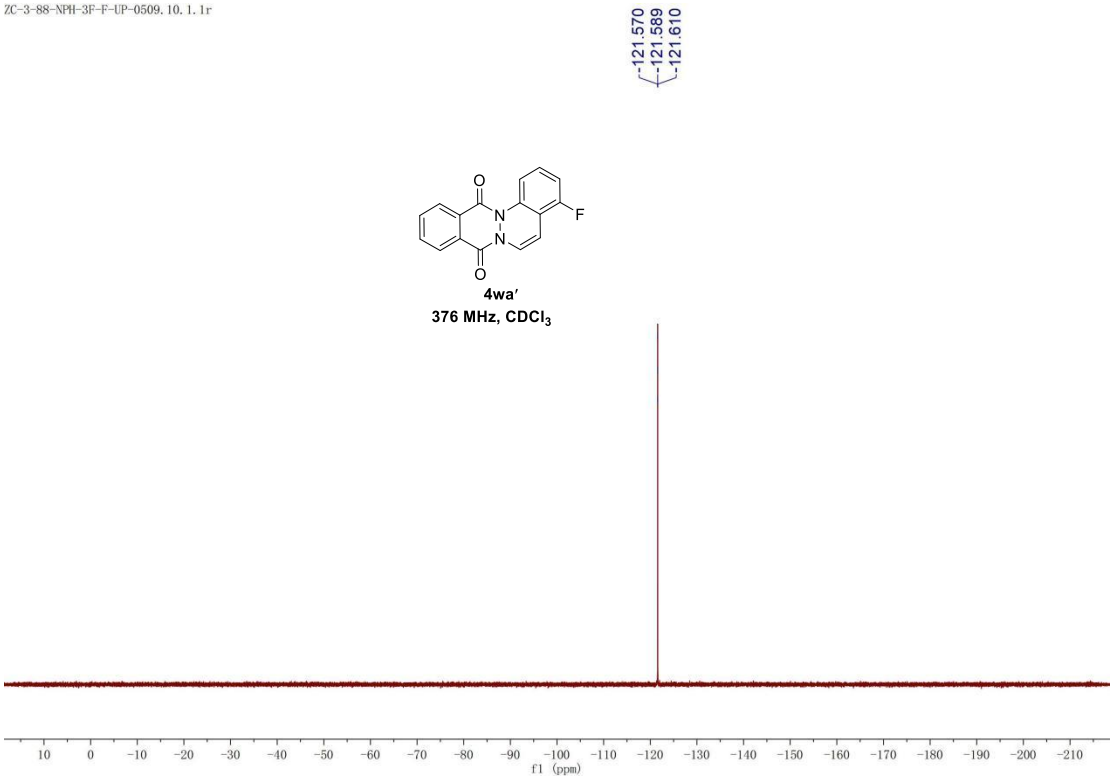
400 MHz, $CDCl_3$





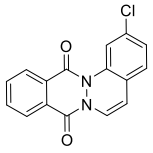
4wa′

151 MHz, $CDCl_3$

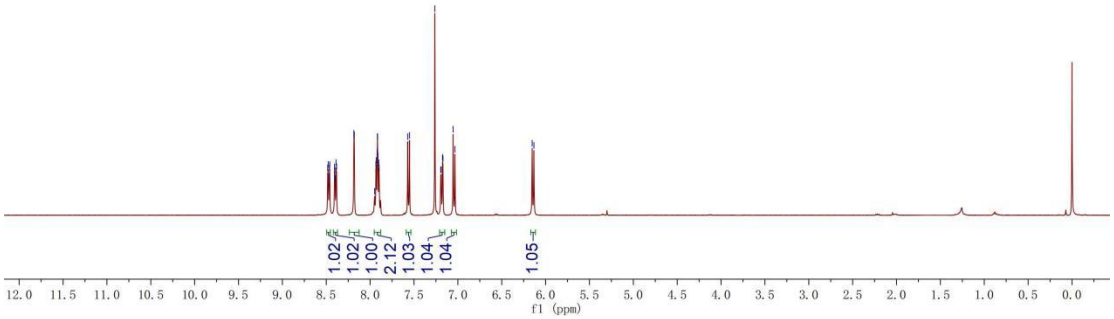


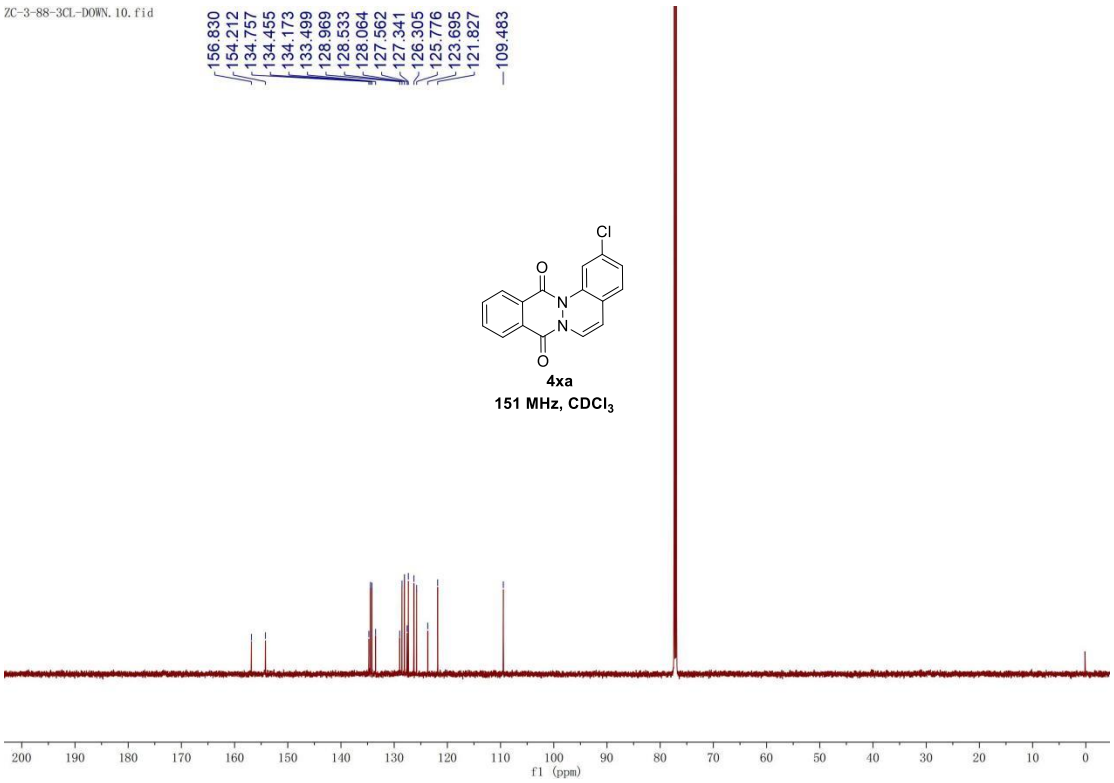
4wa′

376 MHz, $CDCl_3$

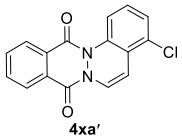


4xa
400 MHz, $CDCl_3$



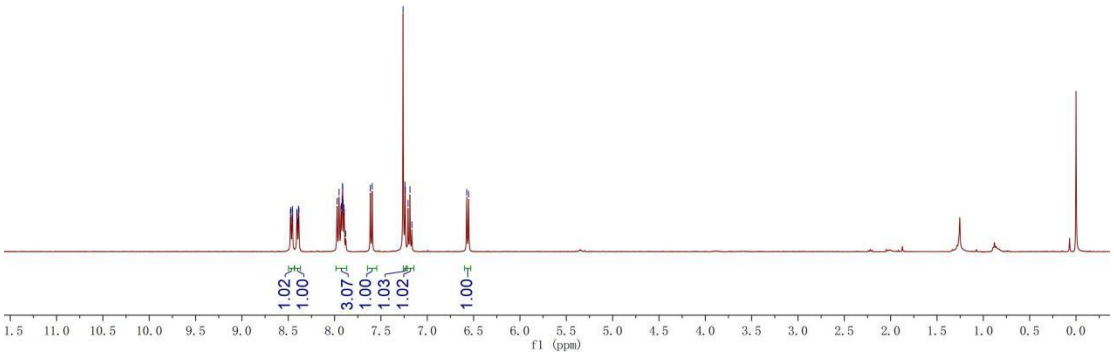


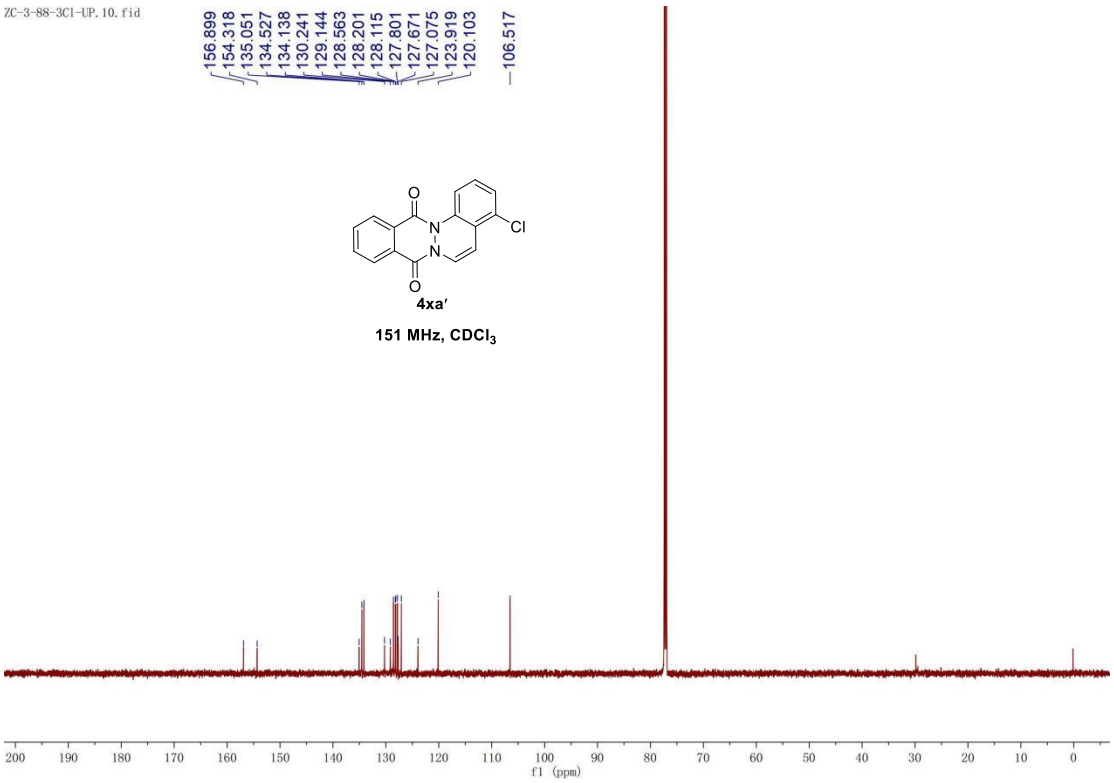
4xa
151 MHz, $CDCl_3$



4xa′

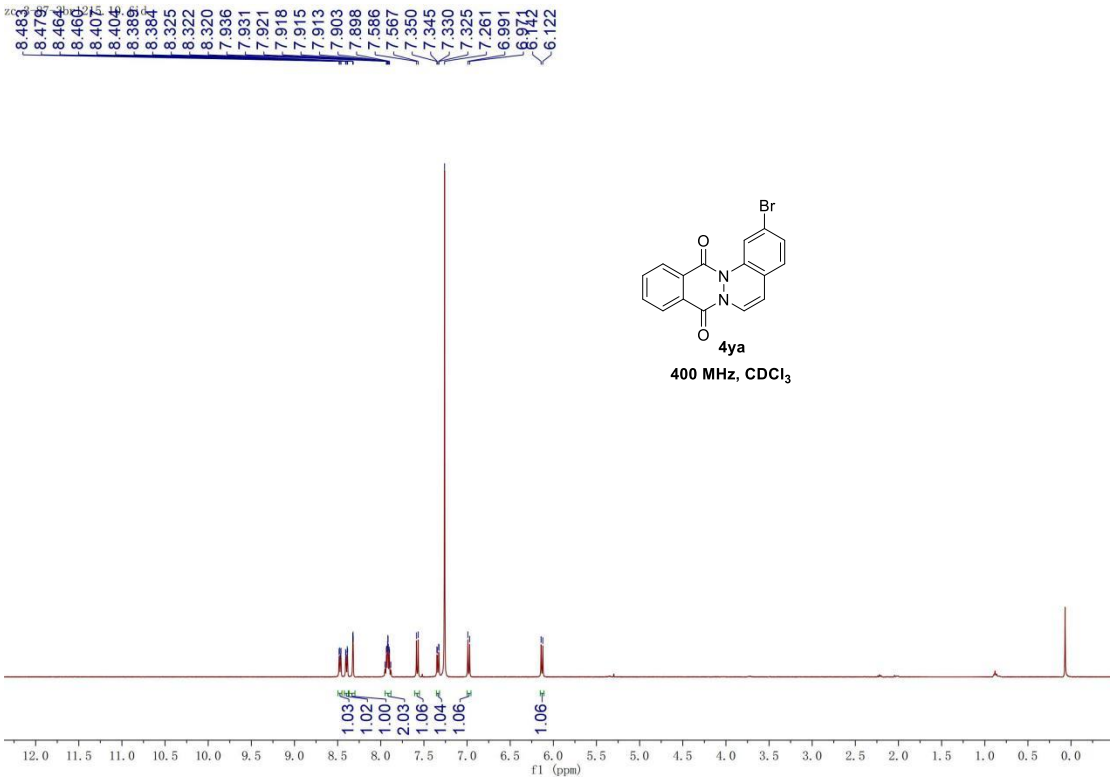
400 MHz, $CDCl_3$

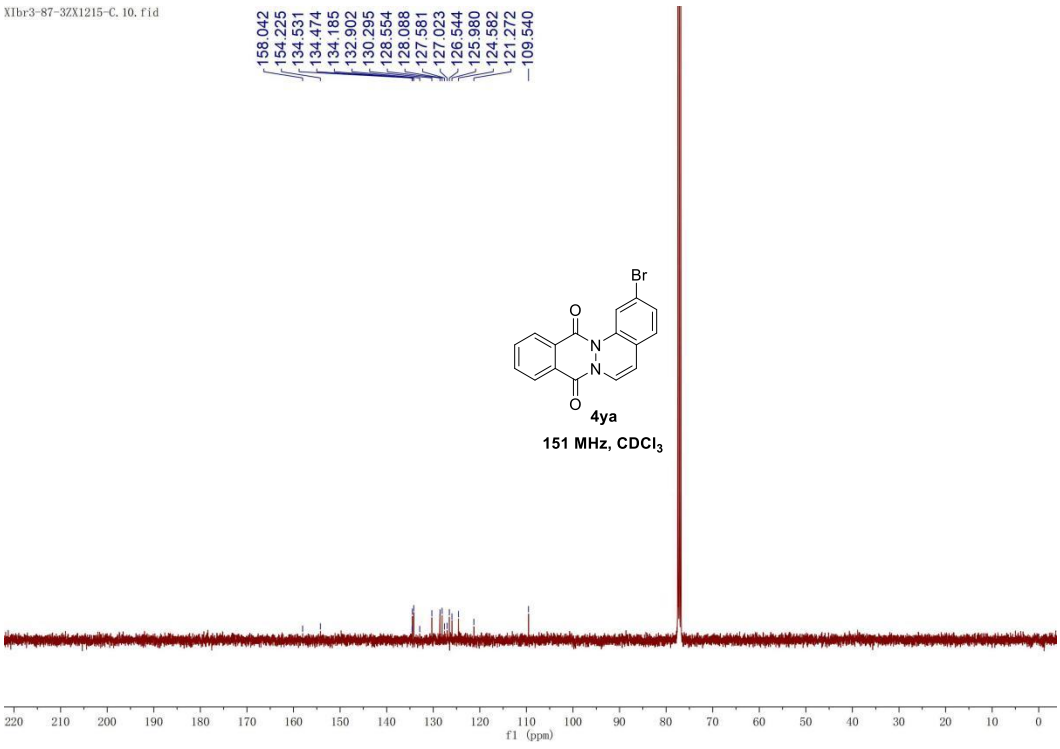


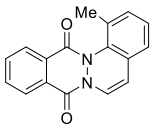


4xa′

151 MHz, $CDCl_3$

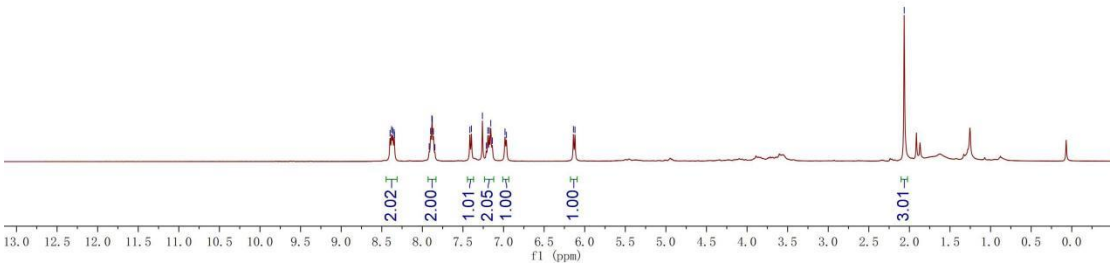

8.483
8.479
8.464
8.460
8.407
8.404
8.389
8.384
8.325
8.322
8.320
7.936
7.931
7.921
7.918
7.915
7.913
7.903
7.898
7.586
7.567
7.350
7.345
7.330
7.325
7.261
6.991
6.942
6.122
Br
O
N
N
O
4ya
400 MHz, CDCl3
1.03
1.02
1.00
2.03
1.06
1.04
1.06
1.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

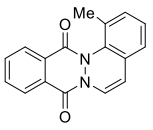

XIbr3-87-3ZX1215-C.10.fid
158.042
154.225
134.531
134.474
134.185
132.902
130.295
128.554
128.088
127.581
127.023
126.544
125.980
124.582
121.272
109.540
Br
O
N
N
O
4ya
151 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



4za

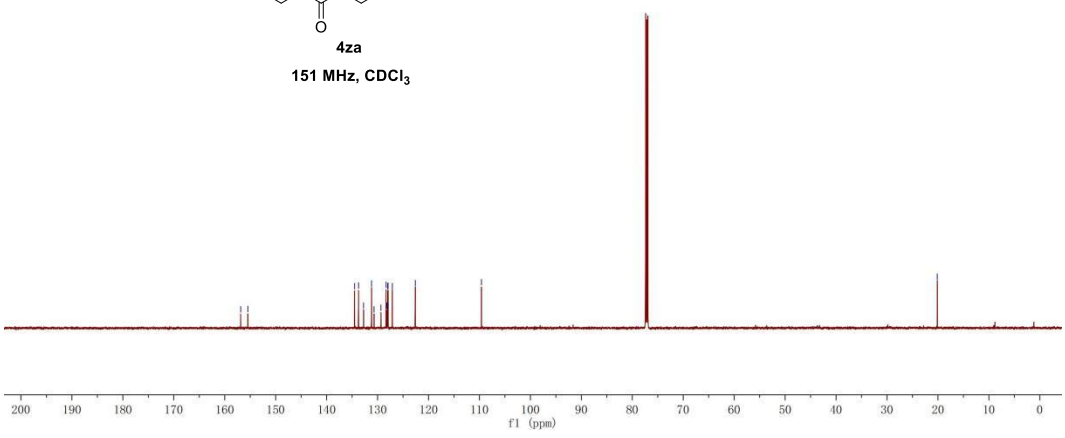
400 MHz, $CDCl_3$

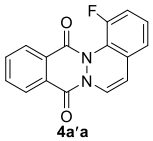




4za

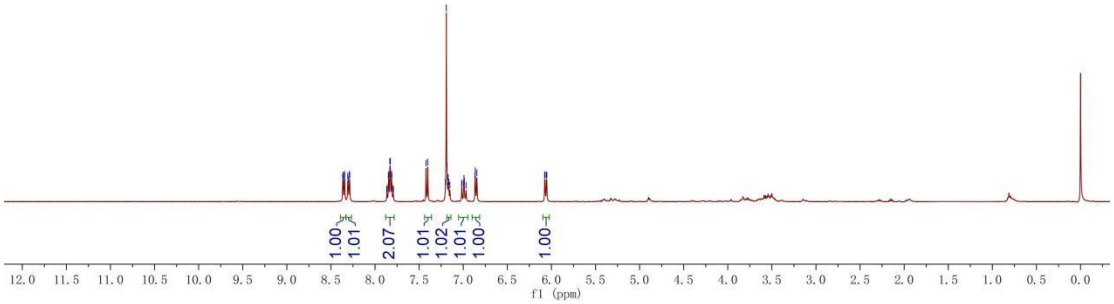
151 MHz, $CDCl_3$

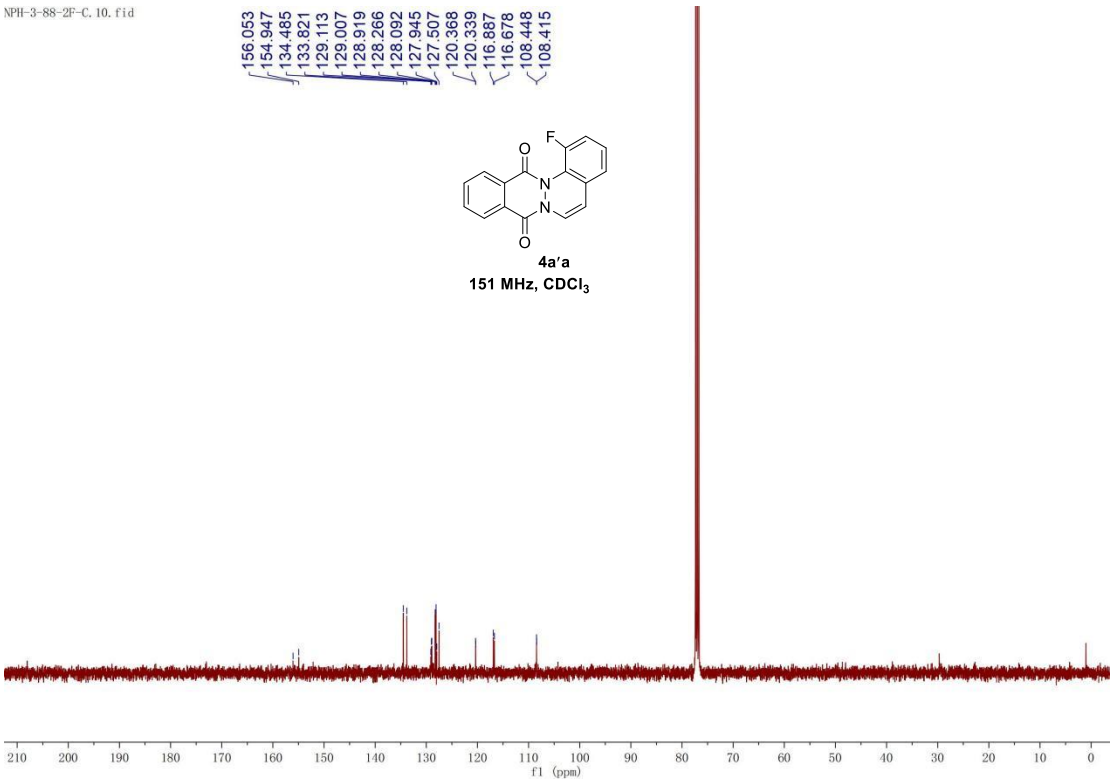




4a′a

400 MHz, $CDCl_3$



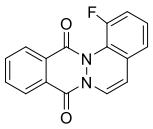


4a′a

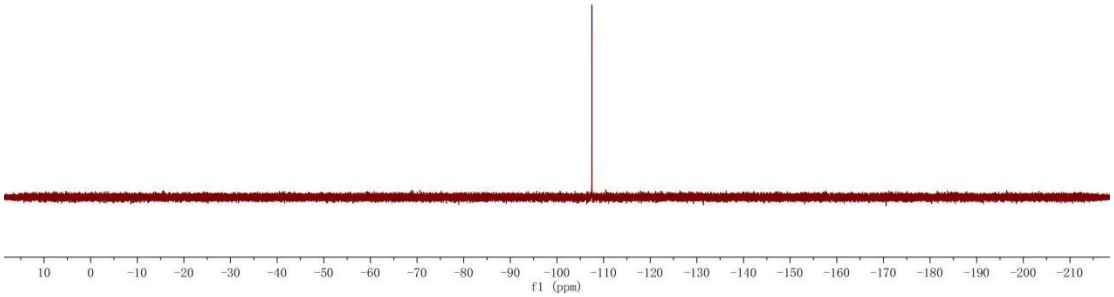
151 MHz, $CDCl_3$

N-PH-2F0424.11.fid

107.477
107.489
107.494
107.506
107.517
107.522



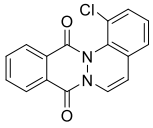
4a′a
376 MHz, $CDCl_3$



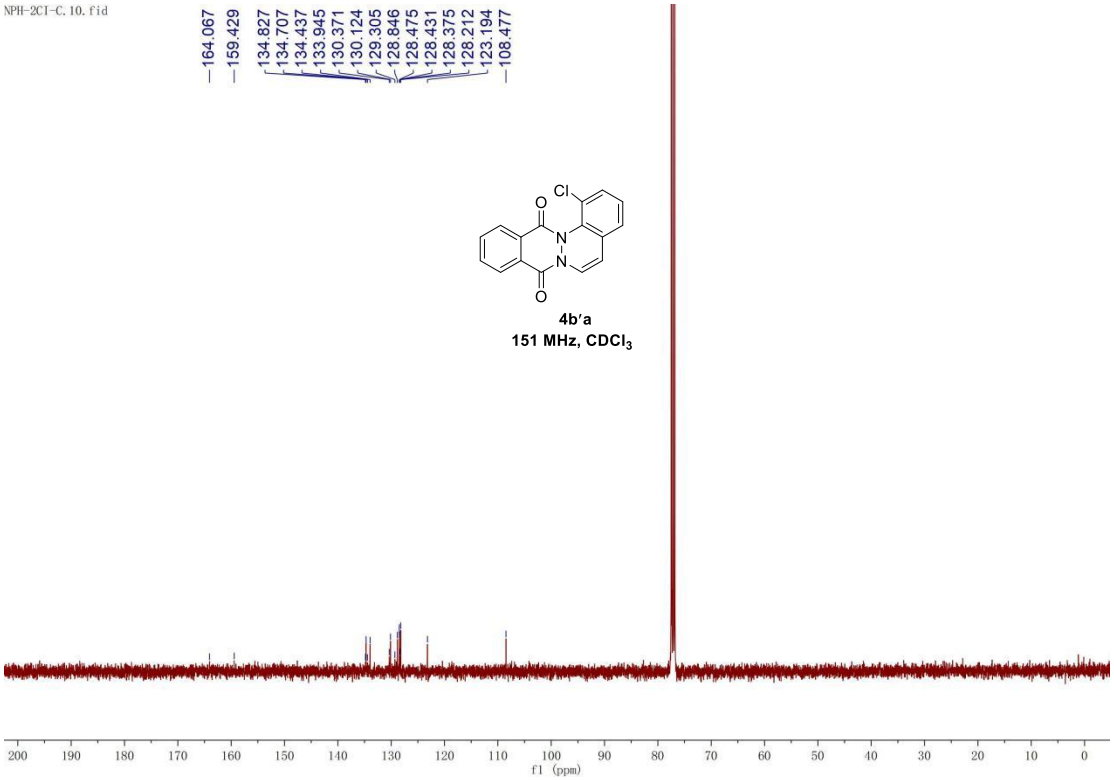
ZC-3-87-2CI.10.fid

8.414
8.409
8.396
8.391
8.360
8.355
8.342
8.337

6.109
6.089

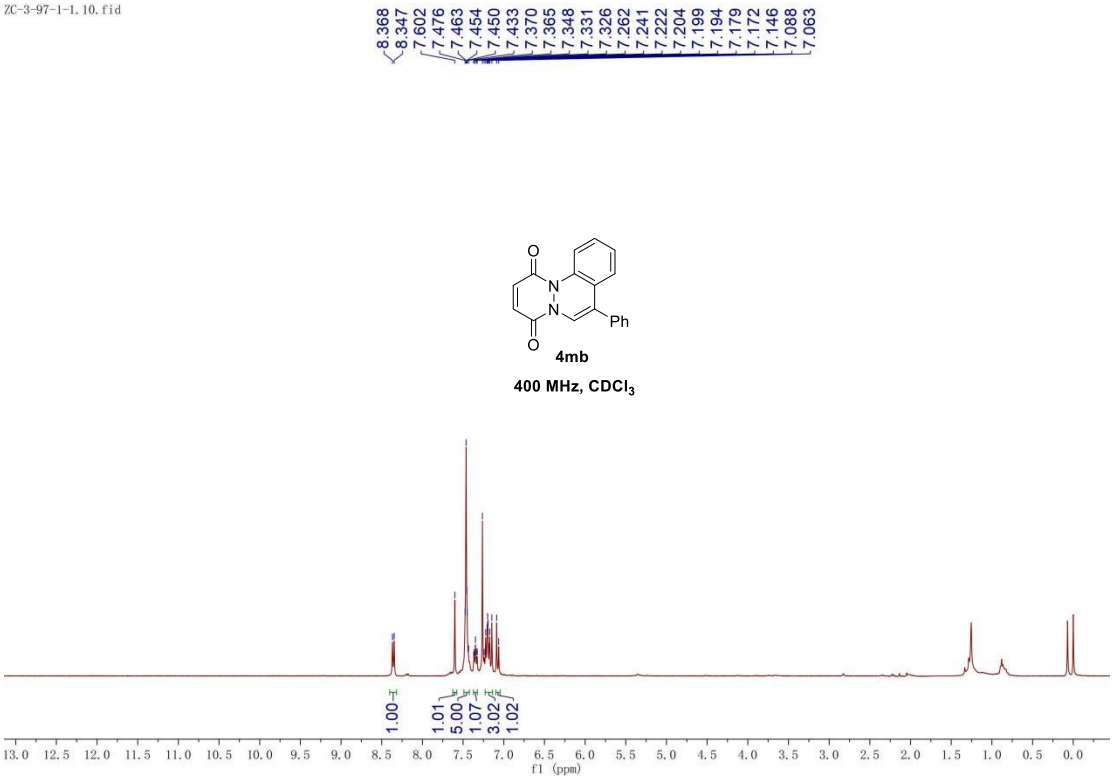


4b′a
400 MHz, $CDCl_3$



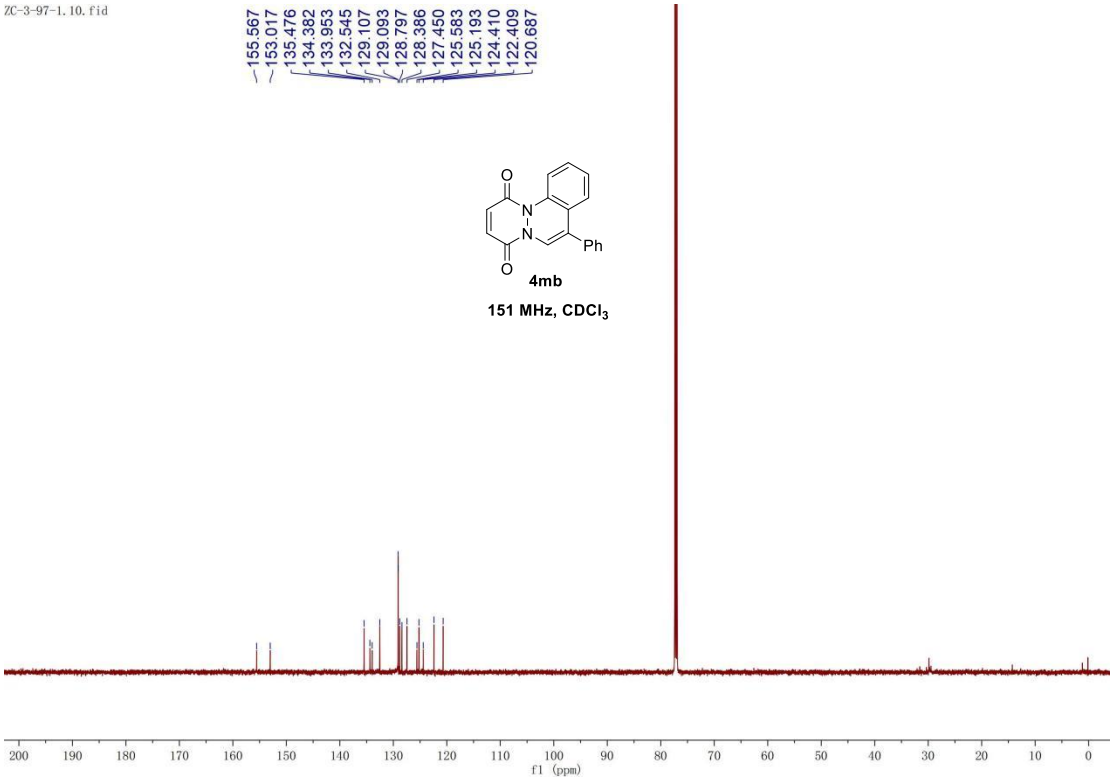
4b′a

151 MHz, $CDCl_3$



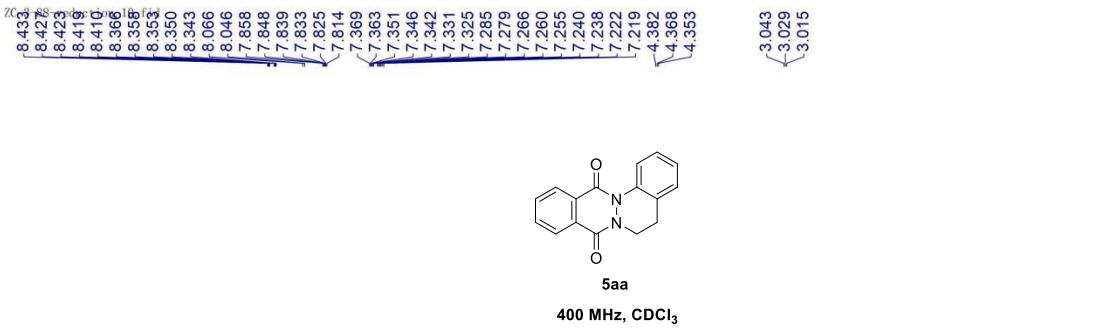
4mb

400 MHz, $CDCl_3$



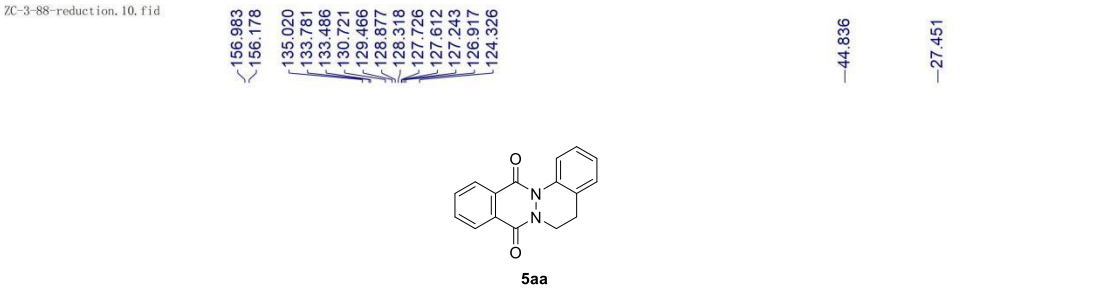
4mb

151 MHz, $CDCl_3$



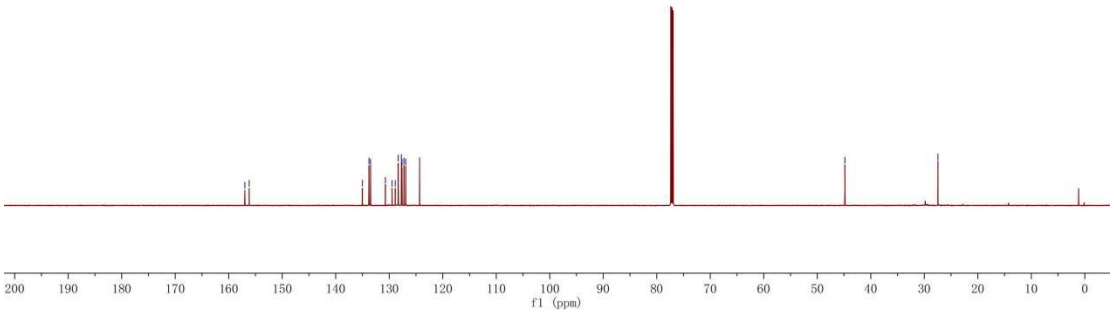
5aa

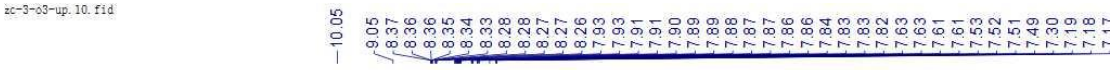
400 MHz, $CDCl_3$

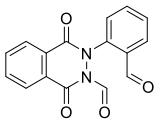


5aa

151 MHz, $CDCl_3$

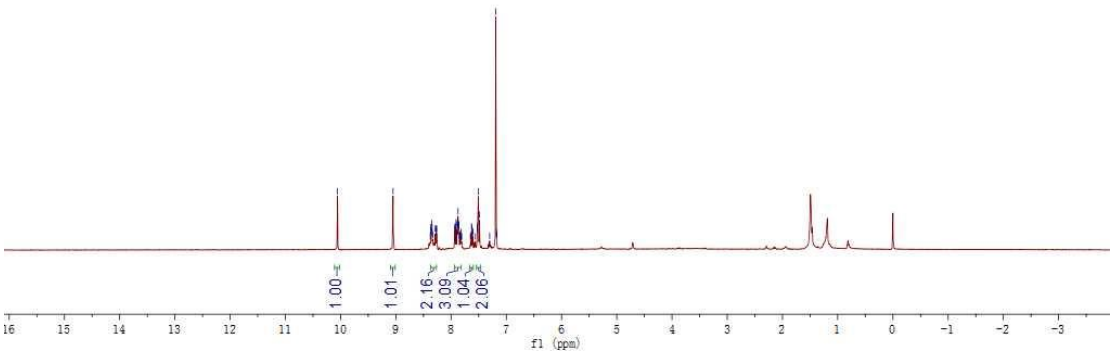


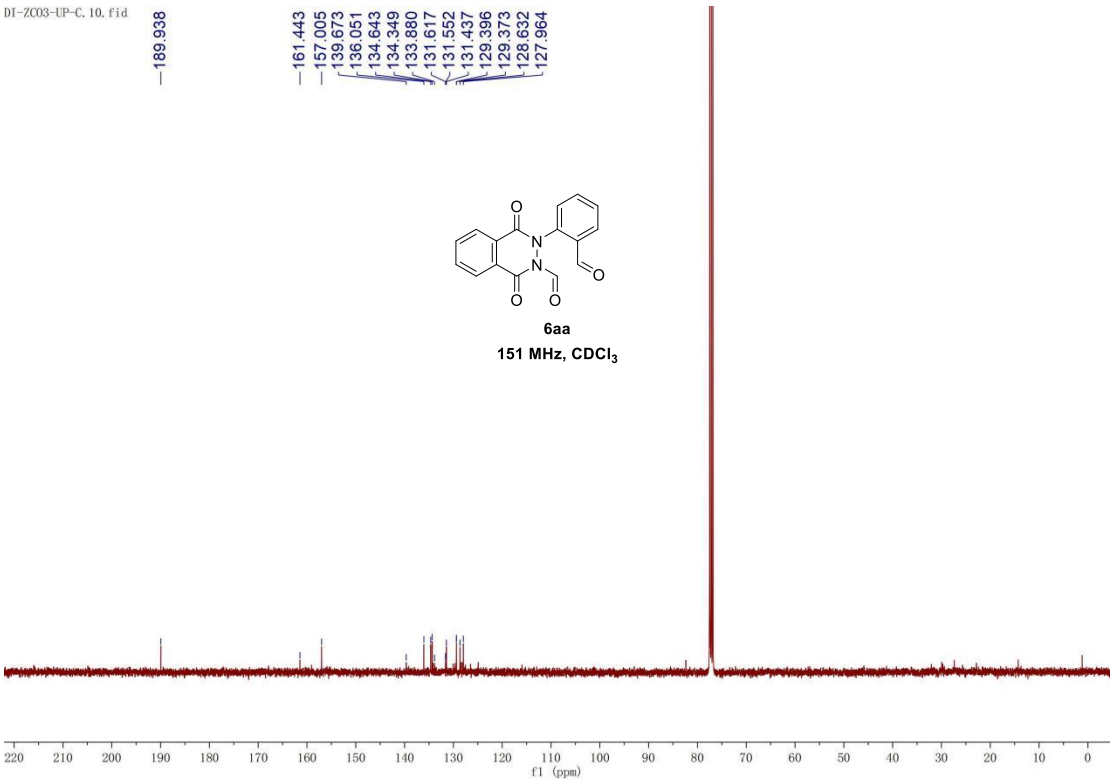




6aa

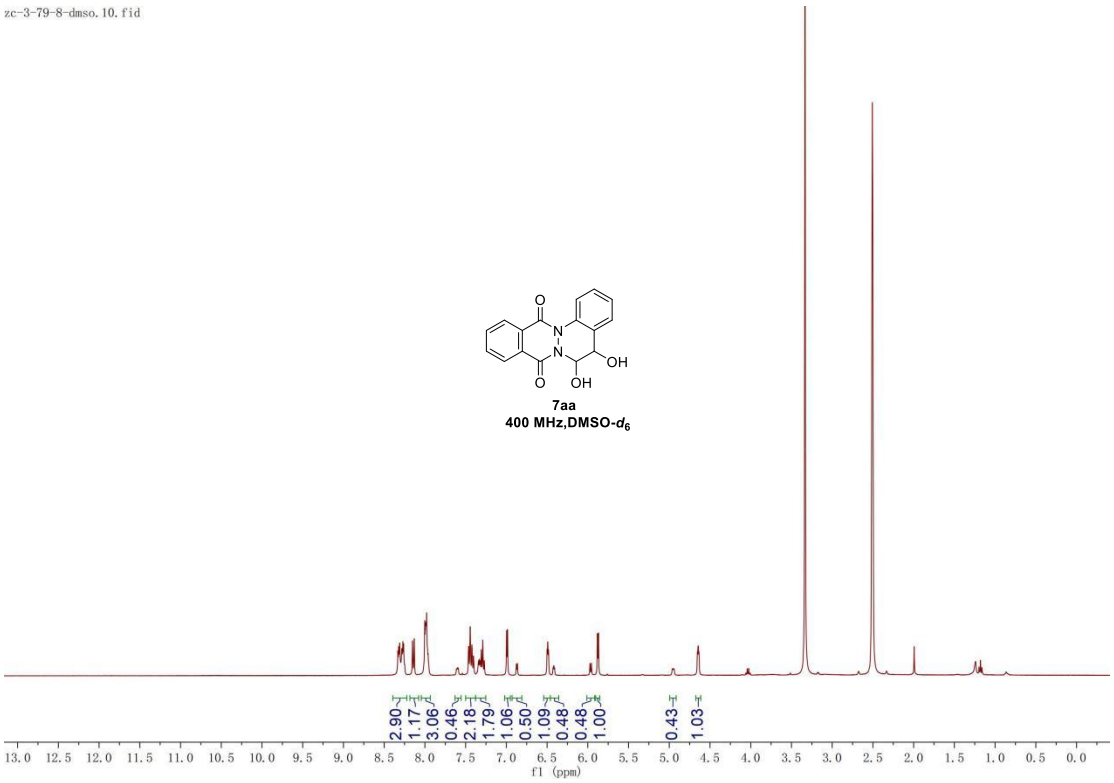
400 MHz, $CDCl_3$





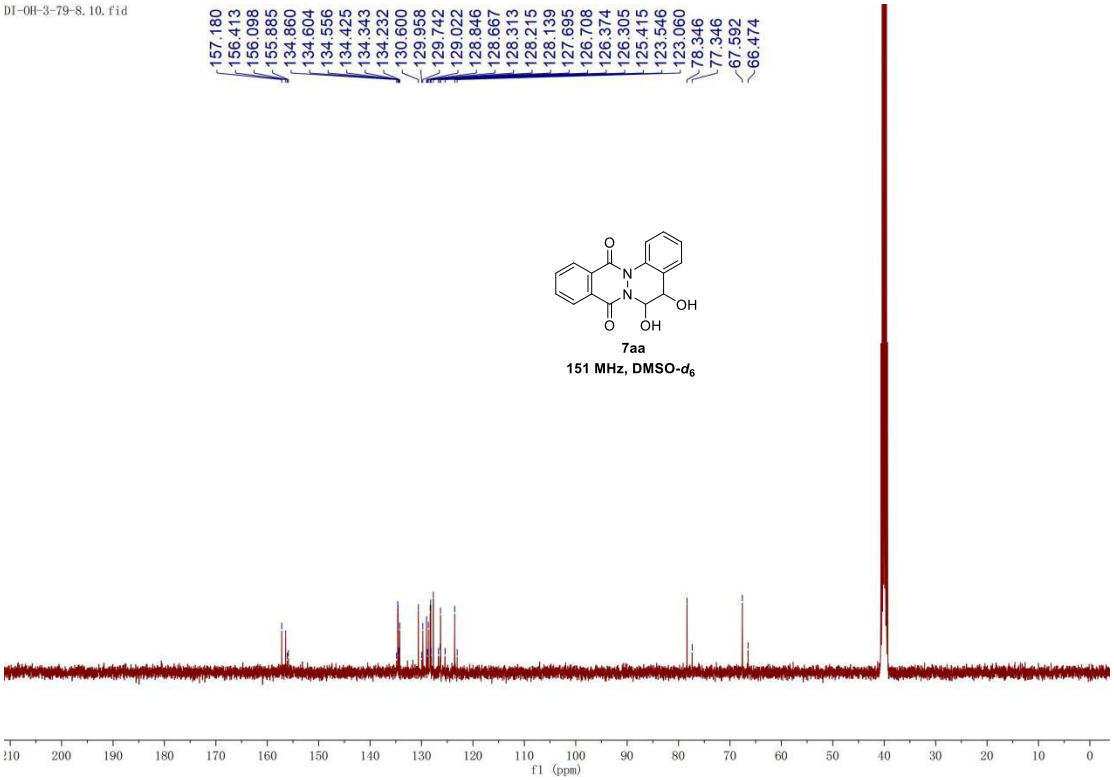
6aa

151 MHz, $CDCl_3$



7aa

400 MHz,DMSO-d_6



7aa

151 MHz, DMSO-d_6