Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry


*Supporting Information*

# Direct arylation of phenanthroline derivatives *via* oxidative C–H/C–H cross-coupling: synthesis and discovery of excellent ligands

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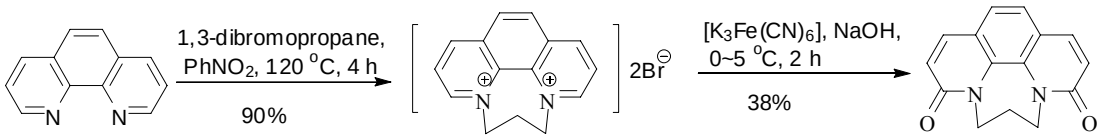
## I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz, a Varian Inova 400 MHz or a Bruker AMX-600. The $^{1}H$ NMR (400 MHz or 600 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: $\delta$ = 7.26 ppm). The $^{13}C$ NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: $\delta$ = 77.16 ppm). High resolution mass spectra (HRMS) were recorded by ESI-TOF. Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by refluxing for at least 24 h over $CaH_2$ (DMF), sodium (THF), and freshly distilled prior to use. All syntheses and manipulations were carried out under $N_2$ atmosphere.

## II. Preparation and characterization of starting materials

### (1) 6,7-Dihydro-3*H*-1,4-diazepino[1,2,3,4-*lmn*][1,10]phenanhroline-3,9(5*H*)-dione (1a)[1]



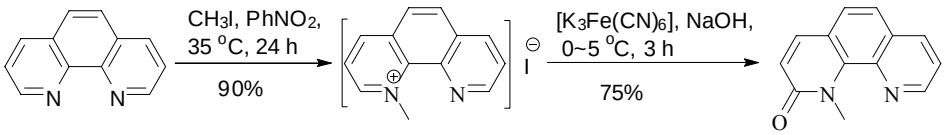

**1a**

1,10-Phenanthroline monohydrate (10.0 g, 50.4 mmol) was dissolved in nitrobenzene (80.0 mL). 1,3-dibromopropane (26.0 mL, 253 mmol, 5.0 equiv) was then slowly added and the mixture was heated to 120 ºC with stirring. During the reaction, a crystalline product precipitated from the reaction mixture. After 4 h, the mixture was allowed to cool to room temperature and the crystalline product was collected by filtration. The mother liquor was concentrated by evaporating the solvent under reduced pressure, producing a second crop of crystalline material. The products were combined, washed with small amounts of toluene, and dried under vacuum for 24 h. The product was then dissolved in water (ca. 50.0 mL), the solution obtained was warmed to 80 ºC, and ethanol (ca. 300.0 mL) was slowly added with stirring until the precipitated material no longer dissolved in the mixture upon heating and stirring.

The mixture was left to cool overnight and the crystals were collected to yield 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium dibromide (16.9 g, 88%).

$[K_3Fe(CN)_6]$ (123.5 g, 375.0 mmol, 10.0 equiv) was dissolved in water (200.0 mL) and NaOH (56.4 g, 1.4 mol, 34 equiv) was gradually added with stirring. The flask was then placed in an ice/water bath. A solution of 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium dibromide (16.0 g, 41.9 mmol) in water (25.0 mL) was added dropwise, maintaining the temperature in the range 0–5 °C. The mixture was allowed to react for 2 h. It was then neutralised with 4 M HCl to pH 7–8 with simultaneous cooling and concentrated under reduced pressure. The resulting brown solid was crushed and subjected to Soxhlet extraction with refluxing $CHCl_3$ (4×500 mL). The solvent was evaporated from the combined organic layers to give 5.7 g of a brown crude product, which was adsorbed on silica (40 g) and subjected to chromatography (440 g of silica, prepared in $CH_2Cl_2$). Gradient elution from $CH_2Cl_2$ to $CH_2Cl_2$/2% MeOH gave **1a** as pale yellow needles (4.0 g, 38%), multi-gram batches of **1a** could be prepared relatively easily. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.43-2.49 (m, 2H), 4.39 (s, 4H), 6.81 (d, $J$ = 9.2 Hz, 2H), 7.37 (s, 2H), 7.72 (d, $J$ = 9.6 Hz, 2H) ppm.

**(2) 1-methyl-1,10-phenanthrolin-2(1*H*)-one (1b)**[2]




**1b**

Under a stream of $N_2$, 1,10-phenanthroline (4.6 g, 25.5 mmol) was dissolved in nitrobenzene (70.0 mL). To the reaction mixture, methyl iodide (9.6 g, 63.8 mmol) was added dropwise at 35 ºC for 24 h. The reaction mixture was cooled in an ice bath, filtered out. The resulting solids were sequentially washed with nitrobenzene, benzene, and ethanol, and evaporated under reduced pressure to give 7.4 g (yield: 90%) of the compound 1-methyl-1,10-phenanthrolinium iodide.

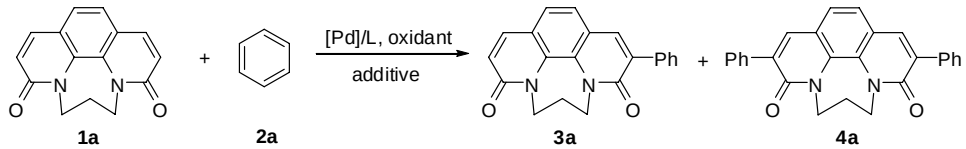
To a stirred aqueous solution of potassium ferricyanide (184.4 g, 140 mmol) ($H_2O$,

224.0 mL), 1-methyl-1,10-phenanthrolinium iodide (7.4 g, 23 mmol) and an aqueous solution of sodium hydroxide (13.9 g, 346 mmol NaOH was dissolved in 40.0 mL water) were alternately added in an ice bath (0-5 ºC) over 20 minutes. The resulting reaction mixture was stirred at room temperature for 3 h, filtered out. The resulting residue was washed with isopropyl ethyl acetate, and then dried to give 4.7 g (yield: 75%) of the compound **1b**. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.49 (s, 3H), 6.91 (d, $J$ = 9.6 Hz, 1H), 7.48-7.52 (m, 1H), 7.54-7.59 (m, 2H), 7.78 (d, $J$ = 9.2 Hz, 1H), 8.18 (dd, $J$ = 8.0 Hz, 1.6 Hz, 1H ), 8.95 (dd, $J$ = 4.0 Hz, 1.6 Hz, 1H ) ppm.

## III. Optimization of the oxidative cross-coupling of 6,7-dihydro-3*H*-1,4-diazepino [1,2,3,4-*lmn*][1,10]phenanhroline-3,9(5*H*)-dione with benzene

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with palladium species (10-20 mol%), the oxidant (3-6 equiv), **1a** (63.5 mg, 0.25 mmol), and the additive under $N_2$ atmosphere. The reaction mixture was stirred for 5 min at room temperature, and then heated at indicated temperature for the indicated time. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc, which was washed with brine. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel to provide the desired product.

Table S1. Optimization of arylation reaction.[a]




**1a** **2a** **3a** **4a**

| Entry | [Pd] | Time (h) | Additive | Oxidant | ratio[b] **3a**/**4a** | yield (%)[c] (**3a**+**4a**) |
|---|---|---|---|---|---|---|
| 1[d] | $Pd(OAc)_2$ | 24 | PivOH | AgOAc | 37/16 | 53 |
| 2[d] | $Pd(PPh_3)_4$ | 24 | PivOH | AgOAc | 35/8 | 43 |
| 3[d] | $PdCl_2$ | 24 | PivOH | AgOAc | 30/9 | 39 |
| 4[d] | $Pd(PhCN)Cl_2$ | 24 | PivOH | AgOAc | 32/12 | 44 |
| 5[d] | $Pd(acac)_2$ | 24 | PivOH | AgOAc | 27/7.6 | 34.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 6[d] | $Pd(PPh_3)_2Cl_2$ | 24 | PivOH | AgOAc | 32/14 | 46 |
| 7[d] | $Pd(TFA)_2$ | 24 | PivOH | AgOAc | 40/25 | 65 |
| 8 | - | 24 | PivOH | AgOAc | | n.r |
| 9 | $Pd(TFA)_2$ | 48 | PivOH | AgOAc | 43/40 | 83 |
| 10 | $Pd(TFA)_2$ | 48 | PivOH | $Ag_2CO_3$ | 40/47 | 87 |
| 11 | $Pd(TFA)_2$ | 48 | PivOH | $Na_2S_2O_8$ | 39/19 | 58 |
| 12 | $Pd(TFA)_2$ | 48 | PivOH | $O_2$ +TEMPO | - | n.r |
| 13 | $Pd(TFA)_2$ | 48 | PivOH | $Cu(OAc)_2$ | - | trace |
| 14 | $Pd(TFA)_2$ | 48 | PivOH | BQ + $Ag_2CO_3$ | - | trace |
| 15 | $Pd(TFA)_2$ | 48 | TFA | $Ag_2CO_3$ | 40/20 | 60 |
| 16 | $Pd(TFA)_2$ | 48 | EtCOOH | $Ag_2CO_3$ | 41/17 | 58 |
| 17 | $Pd(TFA)_2$ | 48 | PivOH (DMSO) | $Ag_2CO_3$ | 42/32 | 74 |
| 18[e] | $Pd(TFA)_2$ | 48 | PivOH | $Ag_2CO_3$ | 40/39 | 79 |
| 19[f] | $Pd(TFA)_2$ | 48 | PivOH | $Ag_2CO_3$ | 32/48 | 80 |
| 20 | $Pd(TFA)_2$ | 96 | PivOH | $Ag_2CO_3$ | 26/57 | 83 |

[a] Reactions were carried out by using **1a** (0.25 mmol), [Pd] (20 mol%), oxidant (3.0 equiv), additive (4.0 equiv), in benzene (**2a**, 2.0 mL, 15~23 mmol, 60~90 equiv) under $N_2$ at 130 ºC. [b] Ratio was determined after isolation and purification by flash silica gel chromatography. [c] Sum of the isolated yields of **3a** and **4a**. [d] [Pd] (10 mol%). [e] 110 °C. [f] 150 °C. n.r.: no reaction. PivOH = pivalic acid. TFA = trifluoroacetic acid. BQ = benzoquinone. DMSO = dimethyl sulfoxide. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

## IV. General procedure for the oxidative cross-coupling of phenanthroline derivatives with simple arenes

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1** (0.25 mmol), $Pd(TFA)_2$ (16.6 mg, 0.05 mmol), $Ag_2CO_3$ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in arenes (2.0 mL, 15~23 mmol, 60~90 equiv). A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with $N_2$. The reaction mixture was stirred for 5 min at room temperature, and then heated at 130 ºC for 48 h. The reaction mixture was then cooled to ambient temperature, diluted with 20.0 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc, which was washed with brine. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (100-200 mesh) to provide the desired product **3**

and **4**, respectively.

**V. General procedure for the synthesis of unsymmetrical diarylated Phens**

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **3** $Pd(TFA)_2$, $Ag_2CO_3$, PivOH, in arenes. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with $N_2$. The reaction mixture was stirred for 5 min at room temperature, and then heated 130 ºC for 48 h. The reaction mixture was then cooled to ambient temperature, diluted with 20.0 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc, which was washed with brine. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (100-200 mesh) to provide the desired product **5**.

**VI. General procedure for the preparation 2,9-dichloro-3,8-diaryl-1,10-phenanthrolines**

Compound **4** (0.25 mmol) was suspended in $POCl_3$ (1.0 mL) and $PCl_5$ (104.1 mg, 0.5 mmol, 2 equiv) was added. The mixture was degassed and refluxed (120 ºC) under $N_2$ for 12 h. The excess $POCl_3$ was then distilled off under reduced pressure and the remaining material was decomposed with ice. The resulting suspension was neutralised with aqueous ammonia solution (30%) with simultaneous cooling. The brown precipitate was collected and dried under vacuum, and the mother liquor was extracted with $CH_2Cl_2$ (2×4 mL). Purification via silica gel column chromatography (Petroleum ether/$CH_2Cl_2$/EtOAc = 4/1/0.05-3/1/0.1, v/v/v) afforded the desired product **6**.

**VII. General procedure for the preparation 3,8-diaryl-1,10-phenanthrolines**[3]

A mixture of the **6** (0.25 mmol) in anhydrous THF (4.0 mL) was degassed by bubbling $N_2$ for few minutes. Then, $PdCl_2$(dppf) ( 18.3 mg, 0.025 mmol, 10 mol %), TMEDA (98.5 mg, 0.85 mmol, 3.4 equiv) and finally $NaBH_4$ (32.1 mg, 0.85 mmol, 3.4 equiv) were introduced in sequence. The mixture was stirred at heated at 70 ºC

under $N_2$ for 16 h. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried by anhydrous $Na_2SO_4$, the solvent was evaporated. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product **7**.

**VIII. General procedure for the preparation 2,3,8,9-tetraaryl-1,10-phenanthrolines**

A mixture of the **6** (0.25 mmol) and aryl boronic acid (0.65 mmol, 2.6 equiv), $K_2CO_3$ (207.3 mg, 1.5 mmol, 6.0 equiv) were dissolved in toluene (2.0 mL)/DMF (2.0 mL) . The solution was degassed and then $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol, 10 mol%) was rapidly added under a flow of $N_2$. The mixture was heated at 120 ºC with vigorous stirring for 20 h. It was then allowed to cool to room temperature. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried by anhydrous $Na_2SO_4$, the solvent was evaporated. Purification via silica gel column chromatography (Petroleum ether/$CH_2Cl_2$/EtOAc = 4/1/0.05-3/1/0.1, v/v/v) afforded the desired product **8**.

**IX. General procedure for direct arylation of benzene with aryl halides in the presence of a catalytic amount of Phens.**

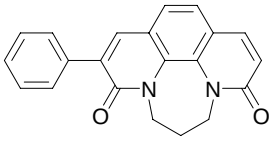
A mixture aryl substituted Phen (10 mol% or 20 mol%), potassium *t*-butoxide ( 67.3 mg, 0.6 mmol), aryl halides (0.2 mmol) and benzene (2.4 mL, 27 mmol) in a 35 mL oven-dried pressure-resistant tube was stirred at 100 ºC for 24 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product **9**.

**X. General procedure for the Heck coupling reaction**

A mixture of a iodobenzene (168.0 uL, 1.5 mmol), *n*-butylacrylate (427.5 uL, 3.0 mmol), $2.0\times10^{-4}$ mmol/mL $Pd(OAc)_2$ (0.05 mL, $1.0\times10^{-5}$ mmol), $1.0\times10^{-4}$ mmol/mL ligand (0.1 mL, $1.0\times10^{-5}$ mmol) and $K_2CO_3$ (414.5 mg, 3.0 mmol) in DMF (2.0 mL)

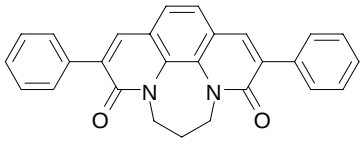
were allowed to react in a sealed tube at 130 ºC for 10 h. After reaction, the volatiles were removed under reduced pressure. The residue was then dispersed in 20.0 mL $CH_2Cl_2$ and filtered. The organic phase was concentrated and passed through a silica gel column to afford the desired coupling product **10**.

## XI. Experimental data for the described substances



**2-Phenyl-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3a)**

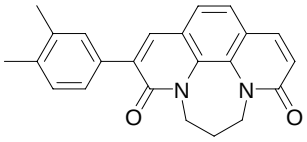
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (33 mg, 40% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.50 (t, $J$ = 6.0 Hz, 2H), 4.38 (s, 4H), 6.83 (d, $J$ = 8.8 Hz, 1H), 7.37-7.47 (m, 5H), 7.76 (t, $J$ = 8.4 Hz, 3H), 7.85 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.9, 45.9, 46.5, 122.6, 122.9, 123.0, 123.2, 128.4, 128.7, 129.0, 131.6, 132.0, 133.9, 135.9, 136.2, 139.1, 162.0, 162.9 ppm. HRMS ($ESI^+$): calcd for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1290, found 329.1302.



**2,10-Diphenyl-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4a)**

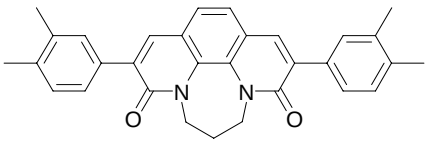
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 ºC for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (47 mg, 47% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$

= 2.51-2.57 (m, 2H), 4.45 (s, 4H), 7.40-7.49 (m, 8H), 7.78 (d, $J$ = 7.6 Hz, 4H), 7.87 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.1, 45.5, 121.9, 122.0, 127.5, 127.7, 128.1, 130.4, 132.7, 135.1, 135.3, 161.1 ppm. HRMS ($ESI^+$): calcd for $C_{27}H_{21}N_2O_2$ $[M+H]^+$ 405.1603, found 405.1602.



**2-(3,4-Dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3b)**

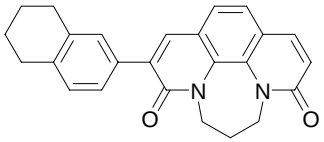
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (35 mg, 39% yield). M.p.: 224-226 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.32 (s, 3H), 2.34 (s, 3H), 2.49 (t, $J$ = 6.2 Hz, 2H), 4.38 (s, 4H), 6.80 (d, $J$ = 8.8 Hz, 1H), 7.23 (d, $J$ = 8.0 Hz, 1H), 7.35-7.42 (m, 2H), 7.49 (d, $J$ = 8.0 Hz, 1H), 7.57 (s, 1H), 7.73 (d, $J$ = 8.8 Hz, 1H), 7.82 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.8, 20.0, 26.0, 45.9, 46.6, 122.5, 122.86, 122.89, 123.0, 123.3, 126.4, 129.8, 130.2, 131.4, 132.1, 133.5, 134.0, 135.5, 136.6, 137.5, 139.1, 162.1 ppm. HRMS ($ESI^+$): calcd for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ 357.1603, found 357.1609.



**2,10-Bis(3,4-dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4b)**

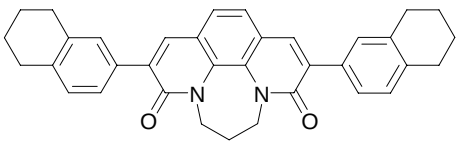
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (53 mg, 46% yield) . M.p.: 220-222 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.32 (s, 6H), 2.35 (s, 6H), 2.50-2.56 (m, 2H), 4.43 (s, 4H), 7.23 (d, $J$ = 8.0 Hz,

2H), 7.41 (s, 2H), 7.51 (d, $J$ = 8.0 Hz, 2H), 7.58 (s, 2H), 7.83 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.8, 20.0, 26.0, 46.4, 122.76, 122.83, 126.4, 129.7, 130.1, 131.1, 133.55, 133.58, 135.7, 136.6, 137.3, 162.1 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{29}N_2O_2$ $[M+H]^+$ 461.2229, found 461.2233.



**2-(5,6,7,8-Tetrahydronaphthalen-2-yl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3c)**

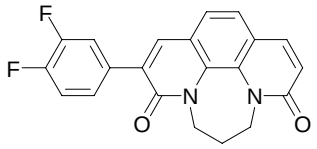
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (38 mg, 40% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.84 (t, $J$ = 3.0 Hz, 2H), 2.24-2.31 (m, 2H), 2.76 (t, $J$ = 7.0 Hz, 2H), 2.82-2.85 (m, 2H), 2.98-2.99 (m, 2H), 4.44 (s, 4H), 7.07 (d, $J$ = 7.6 Hz, 1H), 7.15 (d, $J$ = 8.0 Hz, 1H), 7.26-7.28 (m, 3H), 7.43 (d, $J$ = 8.0 Hz, 1H), 7.45 (s, 1H), 7.70 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 23.3, 26.0, 27.3, 29.5, 29.6, 45.9, 46.5, 122.5, 122.75, 122.82, 122.9, 123.3, 126.1, 129.2, 129.7, 131.4, 132.0, 133.1, 134.1, 135.5, 137.2, 138.1, 139.1, 162.1, 162.9 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{23}N_2O_2$ $[M+H]^+$ 383.1760, found 383.1754.



**2,10-Bis(5,6,7,8-tetrahydronaphthalen-2-yl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4c)**

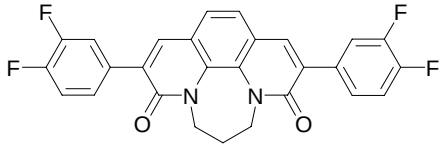
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (41 mg, 32% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$

= 1.85 (s, 8H), 2.49-2.56 (m, 2H), 2.82-2.86 (m, 8H), 4.42 (s, 4H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.40 (s, 2H), 7.48 (d, $J$ = 9.6 Hz, 2H), 7.51 (s, 2H), 7.82 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 23.3, 23.4, 26.1, 29.5, 29.7, 46.4, 122.81, 122.83, 126.1, 129.2, 129.7, 131.2, 133.2, 133.7, 135.6, 137.2, 138.0, 162.2 ppm. HRMS (ESI$^+$): calcd for $C_{35}H_{33}N_2O_2$ $[M+H]^+$ 513.2542, found 513.2365.




**2-(3,4-Difluorophenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3d)**

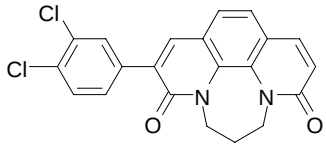
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (34 mg, 37% yield). M.p.: 219-221 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.47-2.53 (m, 2H), 4.38 (s, 4H), 6.82 (dd, $J$ = 9.2 Hz, 3.2 Hz, 1H), 7.16-7.23 (m, 1H), 7.37-7.43 (m, 3H), 7.50-7.52 (m, 1H), 7.74 (d, $J$ = 9.6 Hz, 1H), 7.86 (d, $J$ = 17.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.8 (d, $J$ = 3.0 Hz), 45.8, 46.6 (d, $J$ = 6.0 Hz), 117.1, 117.3-117.6 (m), 118.2-118.4 (m), 122.5, 122.8, 122.9-123.1 (m), 123.3, 123.4, 123.9-124.0 (m), 125.2-125.3 (m), 126.36-126.40 (m), 127.9, 131.6, 132.0-132.1 (m), 136.5, 138.9-139.0 (m), 161.1 (d, $J$ = 48 Hz), 162.8 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{15}F_2N_2O_2$ $[M+H]^+$ 365.1102, found 365.1104.




**2,10-Bis(3,4-difluorophenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4d)**

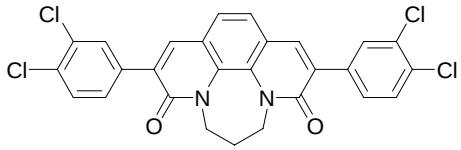
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product

as a yellow solid (35 mg, 29% yield). M.p.: 220-222 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.54 (s, 2H), 4.44 (s, 4H), 7.10-7.22 (m, 2H), 7.45 (s, 2H), 7.55-7.57 (m, 2H), 7.69-7.78 (m, 2H), 7.85-7.90 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.9, 46.6 (d, $J$ = 4.0 Hz), 117.2-117.6 (m), 118.3, 118.5, 122.5-122.8(m), 123.0-123.4 (m), 123.9-124.1 (m), 125.2-125.3 (m), 126.40, 131.6-131.9 (m), 136.5, 139.0, 161.2 (d, $J$ = 47 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{17}F_4N_2O_2$ $[M+H]^+$ 477.1226, found 477.1262.




**2-(3,4-Dichlorophenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3e)**

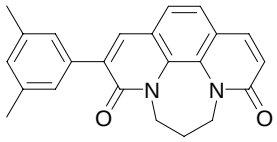
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (38 mg, 38% yield). M.p.: > 250 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.46-2.53 (m, 2H), 4.37 (s, 4H), 6.83 (d, $J$ = 9.6 Hz, 1H), 7.38-7.44 (m, 2H), 7.52 (d, $J$ = 8.4 Hz, 1H), 7.65 (d, $J$ = 8.4 Hz, 1H), 7.74 (d, $J$ = 9.2 Hz, 1H), 7.86 (s, 1H), 7.91 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.9, 45.8, 46.6, 122.8, 123.01, 123.04, 123.2, 123.4, 128.3, 130.3, 130.8, 131.3, 131.8, 132.1, 132.6, 132.8, 135.8, 136.7, 138.9, 161.5, 162.8 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{15}Cl_2N_2O_2$ $[M+H]^+$ 397.0511, found 397.0541.




**2,10-Bis(3,4-dichlorophenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4e)**

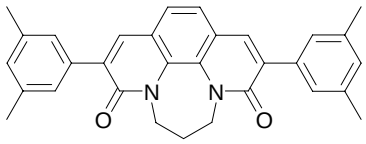
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column

chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (35 mg, 26% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.50-2.57 (m, 2H), 4.43 (s, 4H), 7.46 (s, 2H), 7.53 (d, $J$ = 8.4 Hz, 2H), 7.66 (d, $J$ = 8.0 Hz, 2H), 7.88 (s, 2H), 7.93 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.9, 46.6, 122.8, 123.4, 128.4, 130.4, 130.9, 131.4, 131.6, 132.7, 132.9, 135.8, 136.6, 161.5 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{17}Cl_4N_2O_2$ $[M+H]^+$ 543.0015, found 543.0053.



**2-(3,5-Dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3f)**

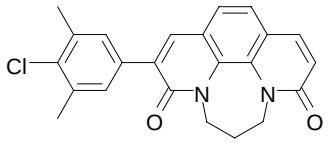
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (32 mg, 36% yield) . M.p.: 203-205 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.39 (s, 6H), 2.46-2.53 (m, 2H), 4.37 (s, 4H), 6.80 (d, $J$ = 9.6 Hz, 1H), 7.06 (s, 1H), 7.35-7.42 (m, 4H), 7.72 (d, $J$ = 9.6 Hz, 1H), 7.82 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.5, 26.0, 45.9, 46.5, 122.6, 122.8, 122.86, 122.94, 123.3, 126.8, 130.5, 131.5, 132.0, 134.3, 135.8, 136.0, 137.9, 139.1, 162.1, 162.9 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ 357.1603, found 357.1618.



**2,10-Bis(3,5-dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4f)**

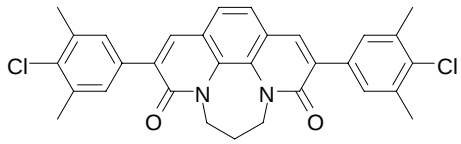
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product

as a yellow solid (44 mg, 38% yield). M.p.: > 250 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.40 (s, 12H), 2.51 (t, $J$ = 6.4 Hz, 2H), 4.43 (s, 4H), 7.06 (s, 2H), 7.38(s, 4H), 7.42 (s, 2H), 7.83 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.5, 26.0, 46.5, 122.8, 122.9, 126.8, 130.4, 131.3, 133.9, 136.0, 136.1, 137.9, 162.1 ppm. HRMS ($ESI^+$): calcd for $C_{31}H_{29}N_2O_2$ $[M+H]^+$ 461.2229, found 461.2241.




**2-(4-Chloro-3,5-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3g)**

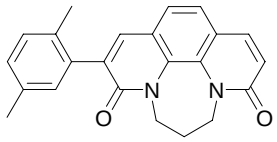
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (36 mg, 37% yield). M.p.: 200-202 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 6H), 2.50 (t, $J$ = 6.4 Hz, 2H), 4.37 (s, 4H), 6.82 (d, $J$ = 9.6 Hz, 1H), 7.37-7.43 (m, 2H), 7.49 (s, 2H), 7.73 (d, $J$ = 9.6 Hz, 1H), 7.82 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.0, 25.9, 45.8, 46.6, 122.7, 122.9, 123.0, 123.08, 123.13, 129.0, 131.5, 132.1, 133.1, 133.7, 135.4, 136.0, 136.3, 139.0, 161.9, 162.9 ppm. HRMS ($ESI^+$): calcd for $C_{23}H_{20}ClN_2O_2$ $[M+H]^+$ 391.1213, found 391.1214.




**2,10-Bis(4-chloro-3,5-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4g)**

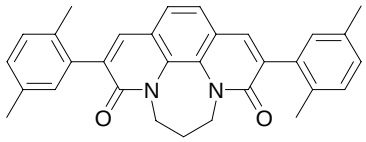
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (57 mg, 43% yield). M.p.: > 250 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 12H), 2.50-2.56 (m, 2H), 4.42 (s, 4H), 7.43 (s, 2H), 7.50 (s, 4H), 7.83 (s,

2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.0, 26.0, 46.5, 122.8, 123.0, 128.9, 131.3, 132.9, 133.8, 135.3, 136.1, 136.3, 161.9 ppm. HRMS ($ESI^+$): calcd for $C_{31}H_{27}Cl_2N_2O_2$ $[M+H]^+$ 529.1450, found 529.1453.



**2-(2,5-Dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3h)**

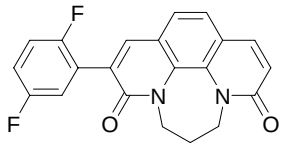
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (33 mg, 37% yield). M.p.: 158-160 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.24 (s, 3H), 2.35 (s, 3H), 2.46-2.52 (m, 2H), 4.38 (s, 4H), 6.85 (d, $J$ = 9.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.18 (d, $J$ = 7.6 Hz, 1H), 7.39 (s, 2H), 7.67 (s, 1H), 7.75 (d, $J$ = 9.2 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.7, 21.0, 25.9, 45.9, 46.4, 122.6, 122.8, 122.9, 123.0, 129.4, 130.3, 130.4, 131.9, 132.1, 133.8, 135.3, 135.8, 135.9, 137.6, 139.0, 161.8, 162.9 ppm. HRMS ($ESI^+$): calcd for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ 357.1603, found 357.1608.



**2,10-Bis(2,5-dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4h)**

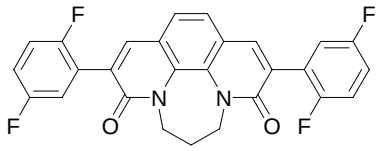
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (31 mg, 27% yield). M.p.: 98-100 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.25 (s, 6H), 2.36 (s, 6H), 2.51 (t, $J$ = 6.4 Hz, 2H), 4.44 (s, 4H), 7.13 (d, $J$ = 9.6 Hz, 4H), 7.19 (d, $J$ = 7.6 Hz, 2H), 7.40 (s, 2H), 7.69 (s, 2H) ppm. $^{13}$C NMR (100

MHz, $CDCl_3$): $\delta$ = 19.7, 21.1, 26.0, 27.0, 46.4, 122.6, 122.8, 129.3, 130.3, 130.5, 131.7, 133.9, 135.3, 135.6, 136.0, 137.6, 161.9 ppm. HRMS ($ESI^+$): calcd for $C_{31}H_{29}N_2O_2$ $[M+H]^+$ 461.2229, found 461.2242.




**2-(2,5-Difluorophenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (3i)**

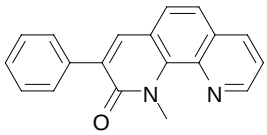
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (38 mg, 42% yield). M.p.: 219-221 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.46-2.53 (m, 2H), 4.38 (s, 4H), 6.84 (d, $J$ = 9.2 Hz, 1H), 7.07-7.17 (m, 2H), 7.36-7.41 (m, 3H), 7.74 (d, $J$ = 9.2 Hz, 1H), 7.89 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.8, 46.0, 46.6, 116.7-118.4 (m), 121.4, 122.3, 122.7, 123.1, 124.1, 128.1, 132.1, 132.3, 138.89, 138.92, 144.4, 155.1, 156.7, 157.3, 157.6, 161.1, 161.9 ppm. HRMS ($ESI^+$): calcd for $C_{21}H_{15}F_2N_2O_2$ $[M+H]^+$ 365.1102, found 365.1105.




**2,10-Bis(2,5-difluorophenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (4i)**

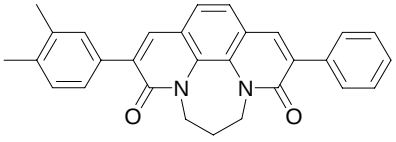
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (35 mg, 29% yield). M.p.: 230-232 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.51-2.57 (m, 2H), 4.44 (s, 4H), 7.06-7.17 (m, 4H), 7.40 (s, 2H), 7.45 (s, 2H), 7.92 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 25.9, 46.6, 116.7-117.2 (m), 118.1-118.4 (m), 122.7, 123.4, 124.7-125.0 (m), 127.9, 131.9, 139.0 (d, $J$ = 4.0 Hz),

155.2 (d, $J$ = 3.0 Hz), 157.3-157.6 (m), 159.7 (d, $J$ = 2.0 Hz), 161.1 ppm. HRMS ($ESI^+$): calcd for $C_{27}H_{17}F_4N_2O_2$ $[M+H]^+$ 477.1226, found 477.1266.



**1-Methyl-3-phenyl-1,10-phenanthrolin-2(1*H*)-one (3j)**

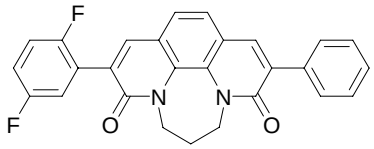
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 100 °C for 48 h. Purification via silica gel column chromatography (Petroleum ether/$CH_2Cl_2$/EtOAc = 30/10/1, v/v/v) afforded the desired product as a yellow solid (45 mg, 63% yield). M.p.: 145-147 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.56 (s, 3H), 7.40 (t, $J$ = 7.2 Hz, 1H), 7.45-7.53 (m, 3H), 7.58 (d, $J$ = 8.4 Hz, 1H), 7.65 (d, $J$ = 8.4 Hz, 1H), 7.82 (d, $J$ = 7.2 Hz, 2H), 7.94 (s, 1H), 8.20 (dd, $J$ = 8.0, 1.2 Hz, 1H), 8.97 (d, $J$ = 2.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 38.6, 120.7, 121.9, 122.6, 127.1, 128.4, 129.1, 130.2, 132.9, 136.3, 136.8, 137.0, 137.5, 140.3, 147.4 ppm. HRMS ($ESI^+$): calcd for $C_{19}H_{15}N_2O$ $[M+H]^+$ 287.1184, found 287.1183.



**2-(3,4-Dimethylphenyl)-10-phenyl-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (5a)**

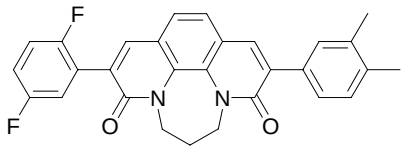
Following the general procedure, **3b** (89.0 mg, 0.25 mmol), $Pd(TFA)_2$ (16.6 mg, 0.05 mmol), $Ag_2CO_3$ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in benzeen (2.0 mL, 22 mmol, 88 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (73 mg, 68% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.33 (s, 3H), 2.35 (s, 3H), 2.50-2.57 (m, 2H), 4.44 (s, 4H), 7.23 (d, $J$ = 7.6 Hz, 1H), 7.42-7.43 (m, 3H), 7.45-7.52 (m, 3H), 7.59 (s, 1H), 7.78 (d, $J$ = 8.0 Hz, 2H), 7.83 (s,

1H), 7.86 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 18.7, 19.0, 25.0, 45.39, 45.40, 121.6, 121.9, 122.0, 125.4, 127.4, 127.6, 128.0, 128.7, 129.1, 130.2, 130.3, 132.4, 132.6, 132.7, 134.6, 135.1, 135.3, 135.5, 136.4, 161.0, 161.1 ppm. HRMS ($ESI^+$): calcd for $C_{29}H_{25}N_2O_2$ $[M+H]^+$ 433.1916, found 433.1930.



**2-(2,5-Difluorophenyl)-10-phenyl-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (5b)**

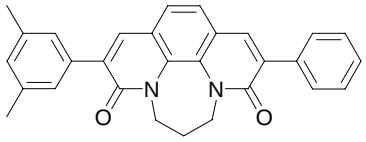
Following the general procedure, **3i** (36.4 mg, 0.1 mmol), $Pd(TFA)_2$ (6.6 mg, 0.02 mmol), $Ag_2CO_3$ (82.7 mg, 0.3 mmol), PivOH (40.8 mg, 0.4 mmol), in benzeen (1.0 mL, 11 mmol, 110 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (29.5 mg, 67% yield). M.p.: 226-228 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.51-2.57 (m, 2H), 4.45 (s, 4H), 7.05-7.08 (m, 1H), 7.10-7.18 (m, 1H), 7.38-7.49 (m, 6H), 7.79 (d, $J$ = 7.2 Hz, 2H), 7.87 (s, 1H), 7.91 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.0, 46.5, 46.6, 116.6, 116.7, 116.8-116.9 (m), 117.1, 117.2, 118.1 (d, $J$ = 3.0 Hz), 118.40 (d, $J$ = 3.0 Hz), 122.2, 123.2 (d, $J$ = 4.0 Hz), 123.4, 127.5, 128.5, 128.8, 129.1, 131.5, 131.9, 134.1, 136.0, 136.2, 139.2 (d, $J$ = 4.0 Hz), 161.2, 162.0 ppm. HRMS ($ESI^+$): calcd for $C_{27}H_{19}F_2N_2O_2$ $[M+H]^+$ 441.1415, found 441.1452.



**2-(2,5-Difluorophenyl)-10-(3,4-dimethylphenyl)-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9(5*H*)-dione (5c)**

Following the general procedure, **3i** (91 mg, 0.25 mmol), $Pd(TFA)_2$ (16.6 mg, 0.05 mmol), $Ag_2CO_3$ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in

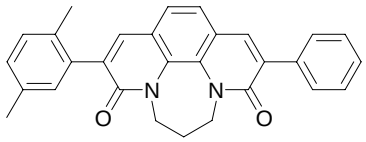
1,2-dimethylbenzene (2.0 mL, 16.6 mmol, 66 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (70 mg, 60% yield). M.p.: 106-108 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.33 (s, 3H), 2.35 (s, 3H), 2.49-2.56 (m, 2H), 4.44 (s, 4H), 7.05-7.18 (m, 3H), 7.24 (d, $J$ = 8.0 Hz, 1H), 7.39-7.43 (m, 2H), 7.51 (d, $J$ = 8.0 Hz, 1H), 7.59 (s, 1H), 7.84 (s, 1H), 7.90 (s, 1H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$, except for C-F carbons because of the low solubility of **6c** in $CDCl_3$): $\delta$ = 19.8, 20.0, 29.8, 46.4, 46.6, 116.8-117.0 (m), 117.1 (d, $J$ = 2.0 Hz), 117.2 (d, $J$ = 2.0 Hz), 118.0, 118.1 (d, $J$ = 3.0 Hz), 118.4 (d, $J$ = 3.0 Hz), 122.0, 123.1 (d, $J$ = 4.0 Hz), 123.5, 126.5, 127.3, 129.8, 130.2, 131.3, 131.8, 133.5, 134.2, 135.5, 136.6, 137.6, 139.18, 139.22, 161.2, 162.1 ppm. HRMS ($ESI^+$): calcd for $C_{29}H_{23}F_2N_2O_2$ $[M+H]^+$ 469.1728, found 469.1727.




**2-(3,5-Dimethylphenyl)-10-phenyl-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1, 10]phenanthroline-3,9(5*H*)-dione (5d)**

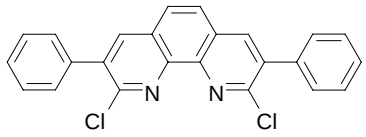
Following the general procedure, **3f** (35.6 mg, 0.1 mmol), $Pd(TFA)_2$ (6.6 mg, 0.02 mmol), $Ag_2CO_3$ (82.7 mg, 0.3 mmol), PivOH (40.8 mg, 0.4 mmol), in benzeen (1.0 mL, 11 mmol, 110 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (28 mg, 65% yield). M.p.: > 119-121 °C. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.40 (s, 6H), 2.50-2.57 (m, 2H), 4.44 (s, 4H), 7.06 (s, 1H), 7.39 (s, 2H), 7.41-7.42 (m, 3H), 7.47 (t, $J$ = 7.2 Hz, 2H), 7.78 (d, $J$ = 6.8 Hz, 2H), 7.84 (s, 1H), 7.86 (s, 1H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 21.5, 26.0, 46.4, 122.7, 122.91, 122.94, 126.8, 128.4, 128.7, 129.1, 129.8, 130.4, 131.3, 131.4, 133.6, 134.0, 135.9, 136.06, 136.09, 136.3, 137.9, 162.0, 162.1 ppm. HRMS ($ESI^+$): calcd for $C_{29}H_{25}N_2O_2$

$[M+H]^+$ 433.1916, found 433.1912.



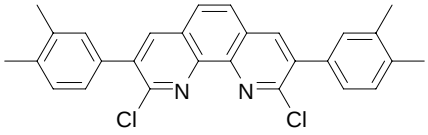
**2-(2,5-Dimethylphenyl)-10-phenyl-6,7-dihydro-3*H*-[1,4]diazepino[1,2,3,4-*lmn*][1, 10]phenanthroline-3,9(5*H*)-dione (5e)**

Following the general procedure, **3h** (89.0 mg, 0.25 mmol), $Pd(TFA)_2$ (16.6 mg, 0.05 mmol), $Ag_2CO_3$ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in benzeen (2.0 mL, 22 mmol, 88 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (76.7 mg, 71% yield). M.p.:170-172 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.26 (s, 3H), 2.36 (s, 3H), 2.50-2.56 (m, 2H), 4.44 (s, 4H), 7.13 (d, $J$ = 9.6 Hz, 2H), 7.19 (d, $J$ = 7.6 Hz, 1H), 7.38-7.49 (m, 5H), 7.69 (s, 1H), 7.79 (d, $J$ = 7.2 Hz, 2H), 7.88 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.7, 21.1, 26.1, 46.4, 46.5, 122.6, 122.85, 122.90, 122.93, 128.4, 128.7, 129.1, 129.4, 130.3, 130.5, 131.5, 131.7, 133.7, 133.9, 135.3, 135.6, 136.0, 136.1, 136.3, 137.7, 161.9, 162.1 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{25}N_2O_2$ $[M+H]^+$ 433.1916, found 433.1930 ppm.



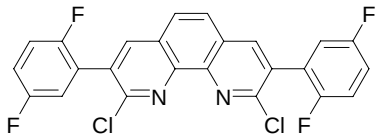
**2,9-Dichloro-3,8-diphenyl-1,10-phenanthroline (6a)**

Following the general procedure, the mixture was degassed and refluxed (120 ºC) under $N_2$ for 12 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a white solid (76 mg, 76% yield). M.p.: 233-235 °C. $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 7.49-7.55 (m, 6H), 7.60 (d, $J$ = 7.2 Hz, 4H), 7.86 (s, 2H), 8.22 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 126.7, 128.1, 128.5, 128.7, 129.8, 137.4, 139.1, 143.7, 150.8 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{15}Cl_2N_2$ $[M+H]^+$ 401.0612, found 401.0644.



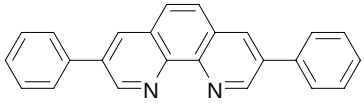

**2,9-Dichloro-3,8-bis(3,4-dimethylphenyl)-1,10-phenanthroline (6b)**

Following the general procedure, compound **4b** (130 mg, 0.28 mmol) was suspended in $POCl_3$ (1.1 mL) and $PCl_5$ (116.6 mg, 0.56 mmol, 2.0 equiv) was added. the mixture was degassed and refluxed (120 ºC) under $N_2$ for 12 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (93mg, 73% yield). M.p.: 240-242 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.27 (s, 12H), 7.18 (d, $J$ = 9.2 Hz, 4H), 7.24 (s, 2H), 7.74 (s, 2H), 8.09 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.8, 20.0, 126.6, 127.2, 128.1, 129.8, 130.8, 134.9, 136.9, 137.4, 138.9, 143.6, 150.9 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{23}Cl_2N_2$ $[M+H]^+$ 457.1238, found 457.1241.



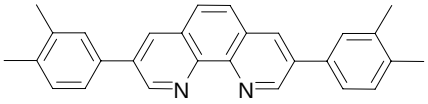

**2,9-Dichloro-3,8-bis(2,5-difluorophenyl)-1,10-phenanthroline (6c)**

Following the general procedure, compound **4i** (140 mg, 0.29 mmol) was suspended in $POCl_3$ (1.2 mL) and $PCl_5$ (120.7 mg, 0.58 mmol, 2.0 equiv) was added. the mixture was degassed and refluxed (120 ºC) under $N_2$ for 12 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a white solid (94 mg, 69% yield). M.p.: 217-219 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.18-7.23 (m, 6H), 7.89 (s, 2H), 8.26 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, except for C-F carbons because of the low solubility of **6c** in $CDCl_3$): $\delta$ = 117.2-118.3 (m), 125.8, 126.4, 127.7, 130.5, 131.6, 137.3, 139.0, 143.4, 144.7, 151.5, 152.3 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{11}Cl_2F_4N_2$ $[M+H]^+$ 473.0235, found 473.0263.



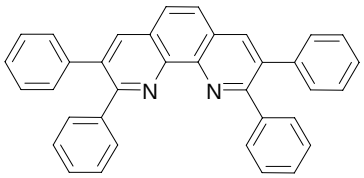
**3,8-Diphenyl-1,10-phenanthroline (7a)**

Following the general procedure, the mixture was stirred at heated at 70 ºC under $N_2$ for 16 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a white solid (71 mg, 86% yield). M.p.: 189-191 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.46 (t, $J$ = 7.4 Hz, 2H), 7.55 (t, $J$ = 7.6 Hz, 4H), 7.78 (d, $J$ = 7.2 Hz, 4H), 7.86 (s, 2H), 8.38 (d, $J$ = 2.4 Hz, 2H), 9.44 (d, $J$ = 2.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 127.2, 127.7, 128.5, 128.6, 129.4, 133.5, 135.9, 137.7, 145.3, 149.7 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{17}N_2$ $[M+H]^+$ 333.1392, found 333.1390.



**3,8-Bis(3,4-dimethylphenyl)-1,10-phenanthroline (7b)**

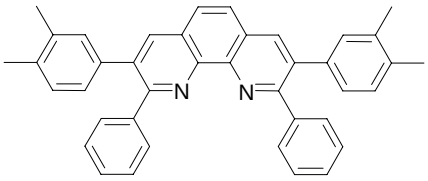
Following the general procedure, the mixture was stirred at heated at 70 ºC under $N_2$ for 16 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a white solid (82 mg, 85% yield). M.p.: 140-142 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.35 (s, 6H), 2.39 (s, 6H), 7.31 (d, $J$ = 7.6 Hz, 2H), 7.53 (d, $J$ = 7.6 Hz, 2H), 7.56 (s, 2H), 7.95 (s, 2H), 8.51 (s, 2H), 9.55 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.7, 20.1, 125.0, 127.5, 128.7, 129.0, 130.9, 134.0, 134.6, 136.8, 137.99, 138.01, 148.6 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{25}N_2$ $[M+H]^+$ 389.2018, found 389.2011.



**2,3,8,9-Tetraphenyl-1,10-phenanthroline (8a)**

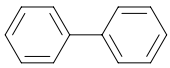
Following the general procedure, the mixture was heated at 120 ºC with vigorous stirring for 20 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a white solid (111 mg, 92% yield). M.p.: 212-214 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.27 (s, 6H),

7.33 (s, 10H), 7.61 (d, $J$ = 6.8 Hz, 4H), 7.89 (s, 2H), 8.31 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 126.8, 127.6, 127.9, 128.1, 128.3, 128.6, 129.9, 130.8, 136.3, 138.5, 140.0, 144.4, 157.8 ppm. HRMS ($ESI^+$): calcd for $C_{36}H_{25}N_2$ $[M+H]^+$ 485.2018, found 485.2029.



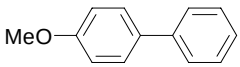

**3,8-Bis(3,4-dimethylphenyl)-2,9-diphenyl-1,10-phenanthroline (8b)**

Following the general procedure, the mixture was heated at 120 ºC with vigorous stirring for 20 h. Purification via silica gel column chromatography ($CH_2Cl_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (126 mg, 93% yield). M.p.: 124-126 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.22 (s, 6H), 2.26 (s, 6H), 6.90 (d, $J$ = 8.0 Hz, 2H), 7.02 (d, $J$ = 8.0 Hz, 2H), 7.06-7.09 (m, 6H), 7.17 (t, $J$ = 7.2 Hz, 2H), 7.40 (d, $J$ = 4.4 Hz, 4H), 7.91 (d, $J$ = 6.0 Hz, 2H), 8.31 (d, $J$ = 7.2 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.6, 19.9, 126.9, 127.3, 127.7, 128.2, 128.3, 129.7, 130.4, 130.9, 136.2, 136.3, 136.66, 136.72, 136.8, 136.9, 138.8, 157.4 ppm. HRMS ($ESI^+$): calcd for $C_{40}H_{33}N_2$$[M+H]^+$ 541.2644, found 541.2642.



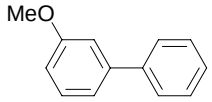
**Biphenyl (9a)**

Following the general procedure, the mixture was stirred at heated at 100 ºC for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a white solid (28.6 mg, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.43 (t, $J$ = 6.8 Hz, 2H), 7.53 (t, $J$ = 7.2 Hz, 4H), 7.69 (d, $J$ = 7.6 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 127.3, 127.4, 128.9, 141.4 ppm.



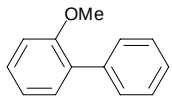
**4-Methoxybiphenyl (9b)**

Following the general procedure, the mixture was stirred at heated at 100 ºC for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a white solid (34.2 mg, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.86 (s, 3H), 6.99 (d, $J$ = 8.4 Hz, 2H), 7.31 (t, $J$ = 7.4 Hz, 1H), 7.43 (t, $J$ = 7.6 Hz, 2H), 7.55 (t, $J$ = 8.4 Hz, 4H) ppm.



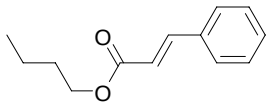

**3-Methoxybiphenyl (9c)**

Following the general procedure, the mixture was stirred at heated at 100 ºC for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as yellow oil (32.7 mg, 89% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.89 (s, 3H), 6.93 (d, $J$ = 8.0 Hz, 1H), 7.16 (s, 1H), 7.21 (d, $J$ = 8.0 Hz, 1H), 7.36-7.40 (m, 2H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.62 (d, $J$ = 7.6 Hz, 2H) ppm.




**2-Methoxybiphenyl (9d)**

Following the general procedure, the mixture was stirred at heated at 100 ºC for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as colorless oil (30.5 mg, 83% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.82 (s, 3H), 6.99-7.06 (m, 2H), 7.34 (m, 3H), 7.42 (t, $J$ = 7.6 Hz, 2H), 7.54 (d, $J$ = 7.6 Hz, 2H) ppm.




***n*-Butyl cinnamate (10a)**

A mixture of a iodobenzene (168.0 ul, 1.5 mmol), *n*-butylacrylate (427.5 ul, 3.0 mmol), $2.0\times10^{-4}$ mmol/mL $Pd(OAc)_2$ (0.05 mL, $1.0\times10^{-5}$ mmol), $1.0\times10^{-4}$ mmol/mL 2,3,8,9-Tetraphenyl-1,10-phenanthroline (0.1 mL, $1.0\times10^{-5}$ mmol) and $K_2CO_3$ (414.5

mg, 3.0 mmol) in DMF (2.0 mL) were allowed to react in a sealed tube at 130 ºC for 10 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as colorless liquid. (302.9 mg, 99% yield). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.97 (t, $J$ = 7.4 Hz, 3H), 1.40-1.47 (m, 2H), 1.66-1.73 (m, 2H), 4.21 (t, $J$ = 6.6 Hz, 2H), 6.45 (d, $J$ = 16.0 Hz, 1H), 7.38 (m, 3H), 7.53 (m, 2H), 7.69 (d, $J$ = 16.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.9, 19.3, 30.9, 64.6, 118.4, 128.2, 129.0, 130.3, 134.6, 144.7, 167.2 ppm.

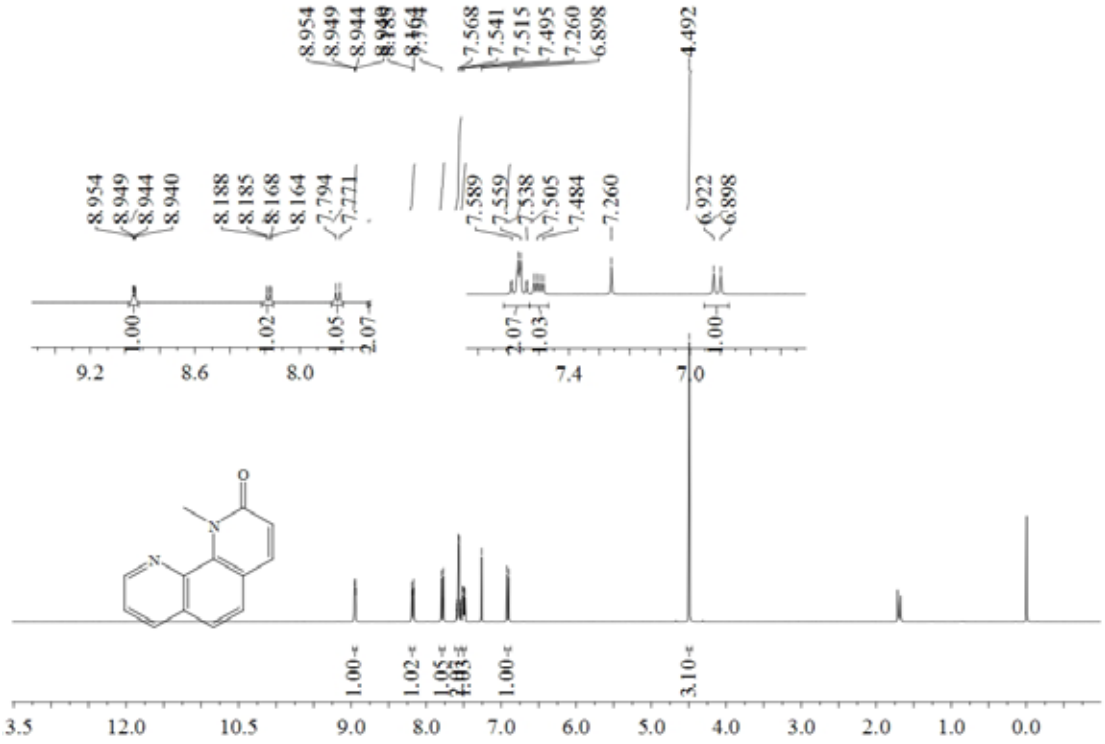
## XII. References

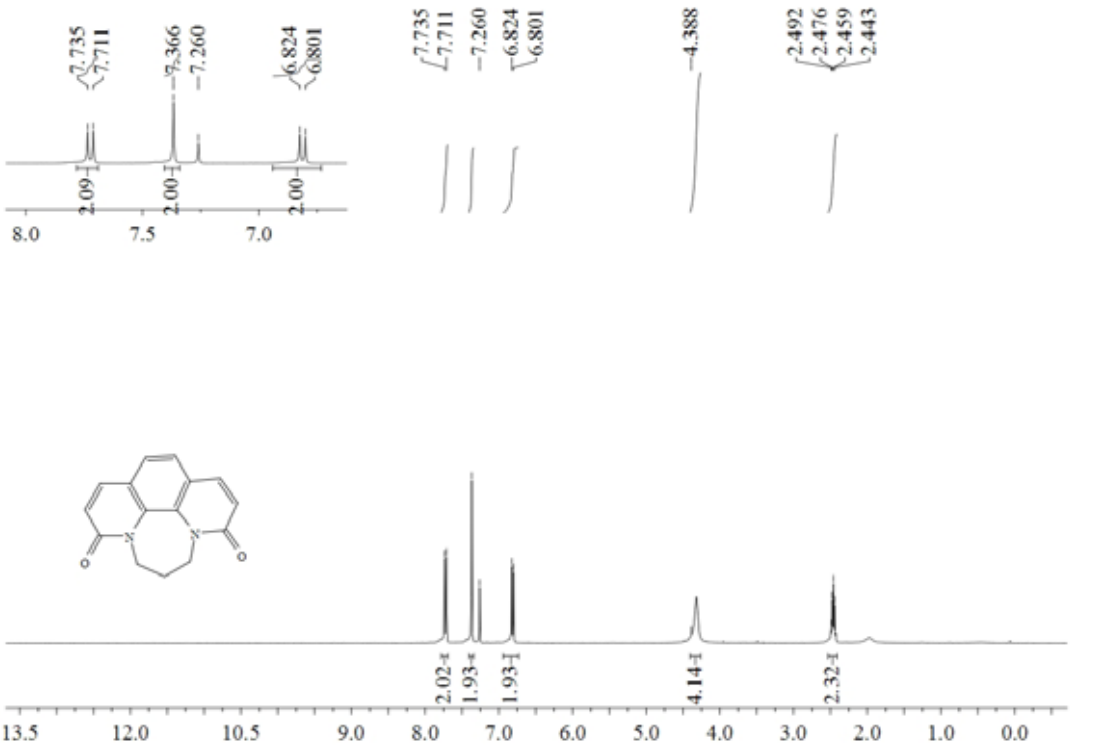
1. J. Frey, T. Kraus, V. Heitz and J.-P. Sauvage, *Chem. Eur. J.*, 2007, **13**, 7584.

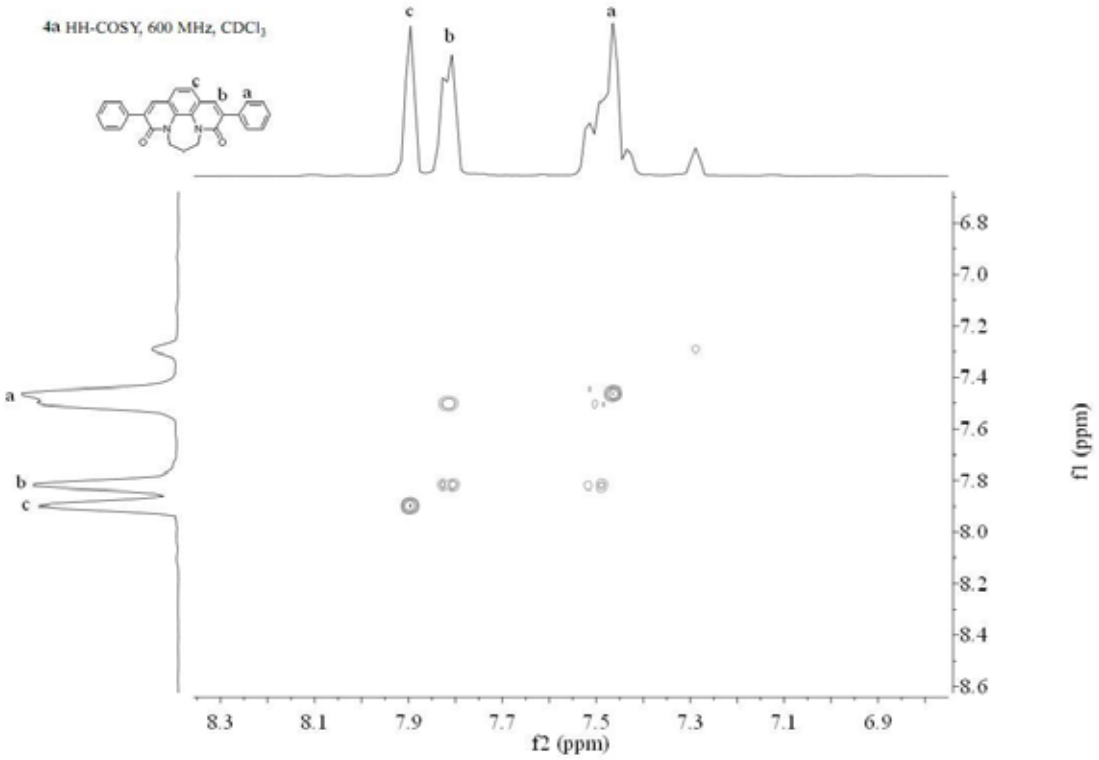
2. F. Eggers and U. Lüning, *Eur. J. Org. Chem.,* 2009, 2328.

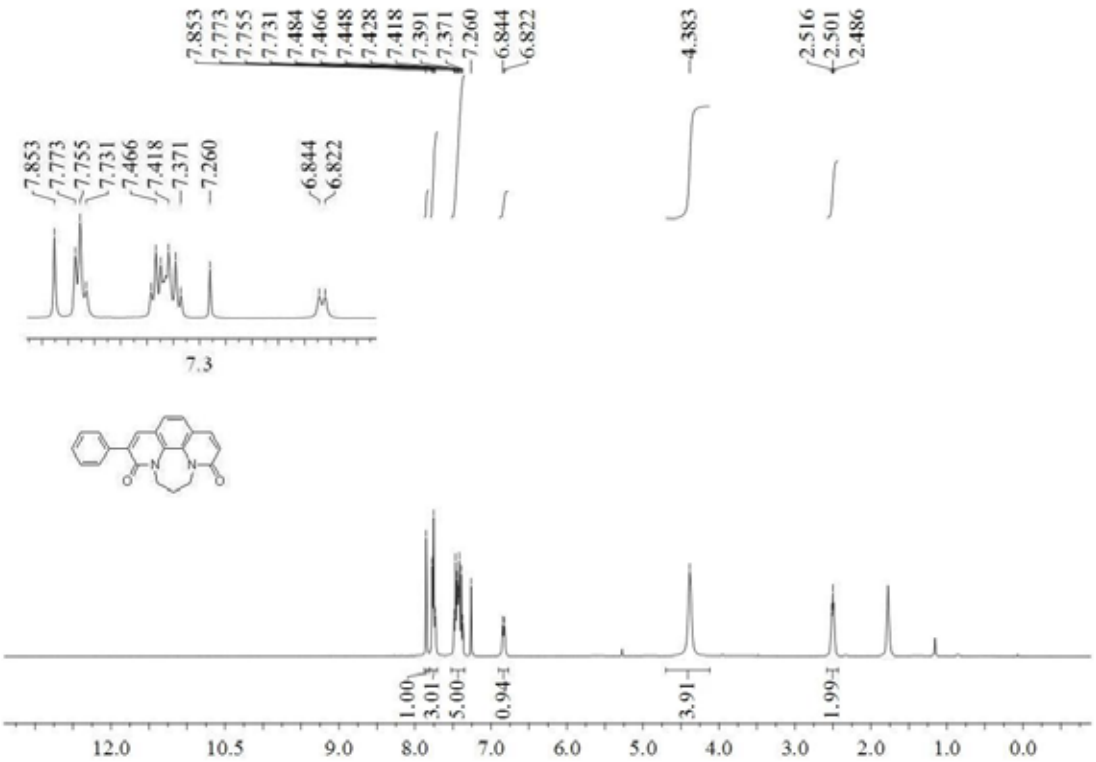
3. G. Chelucci, *Tetrahedron Lett.,* 2010, **51,** 1562.

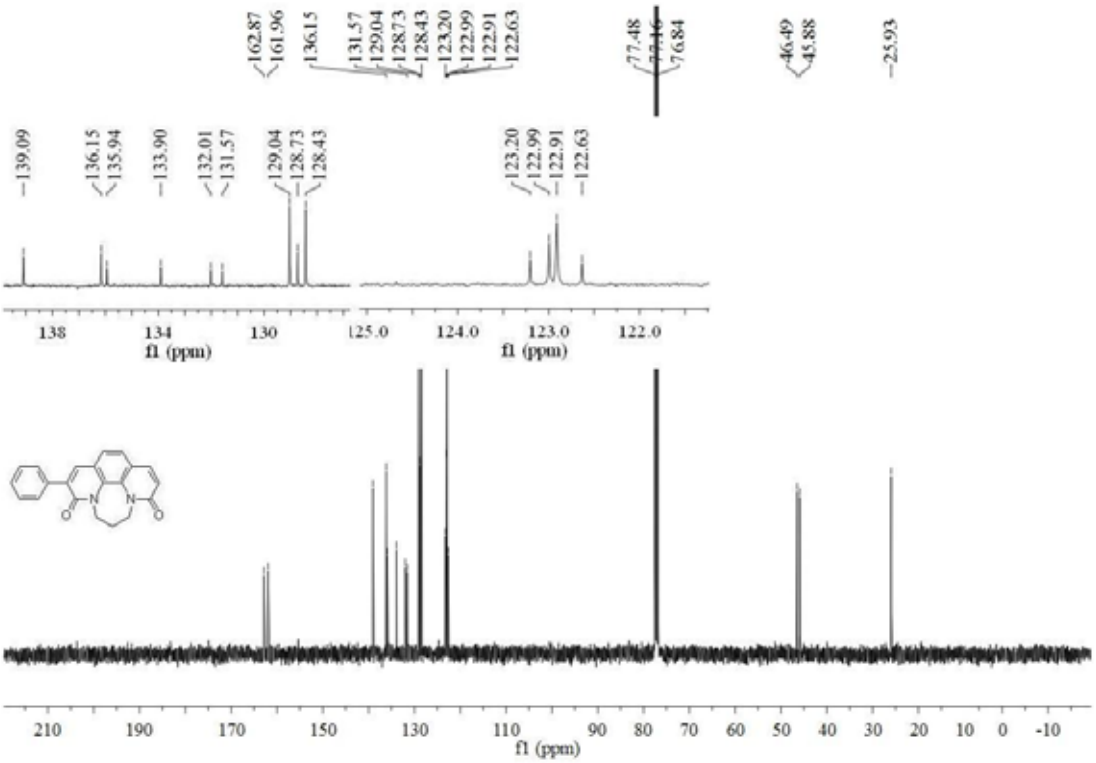
## XIII. Copies of NMR spectra

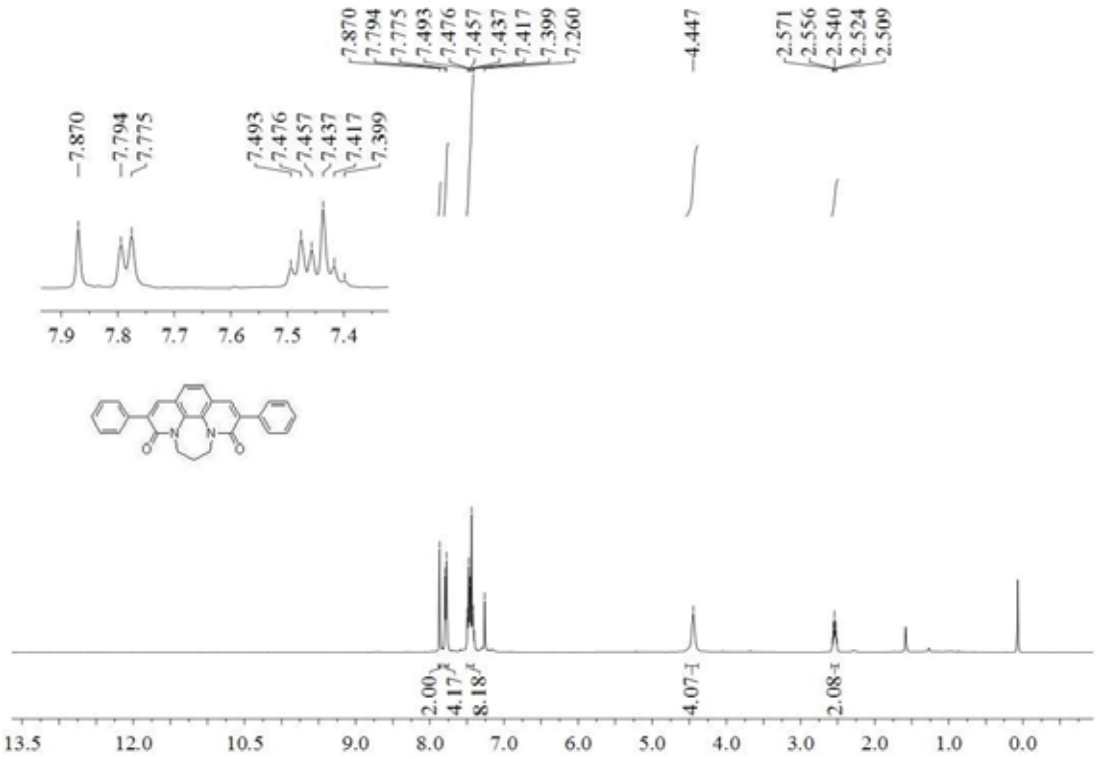




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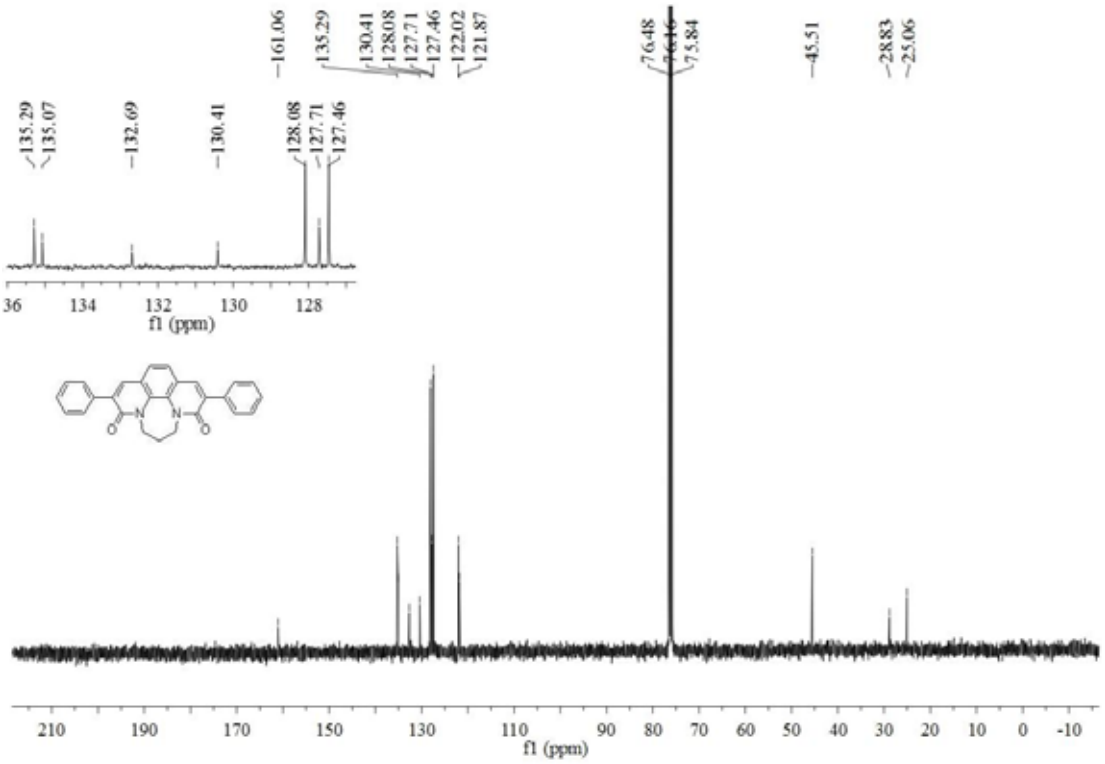
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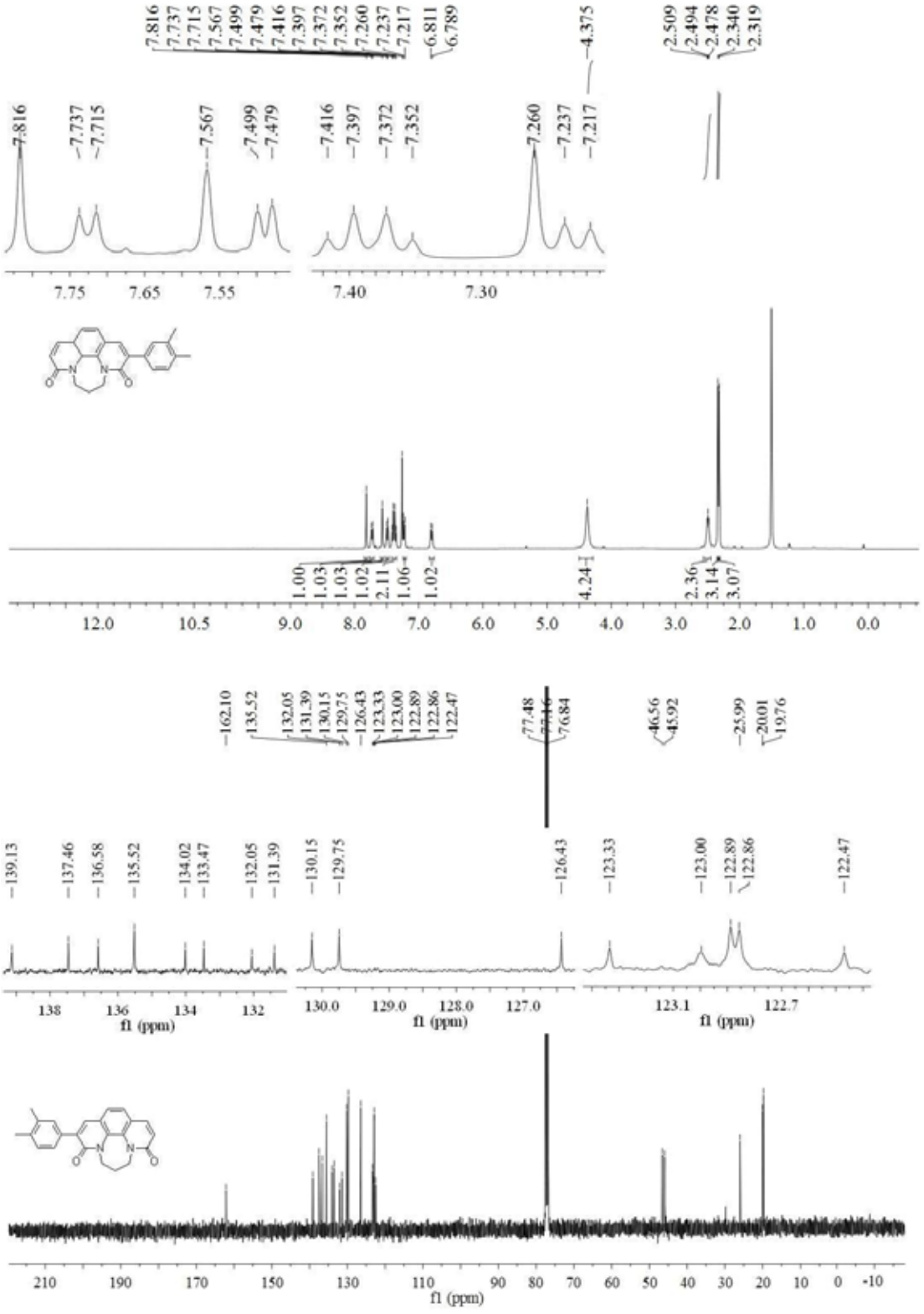

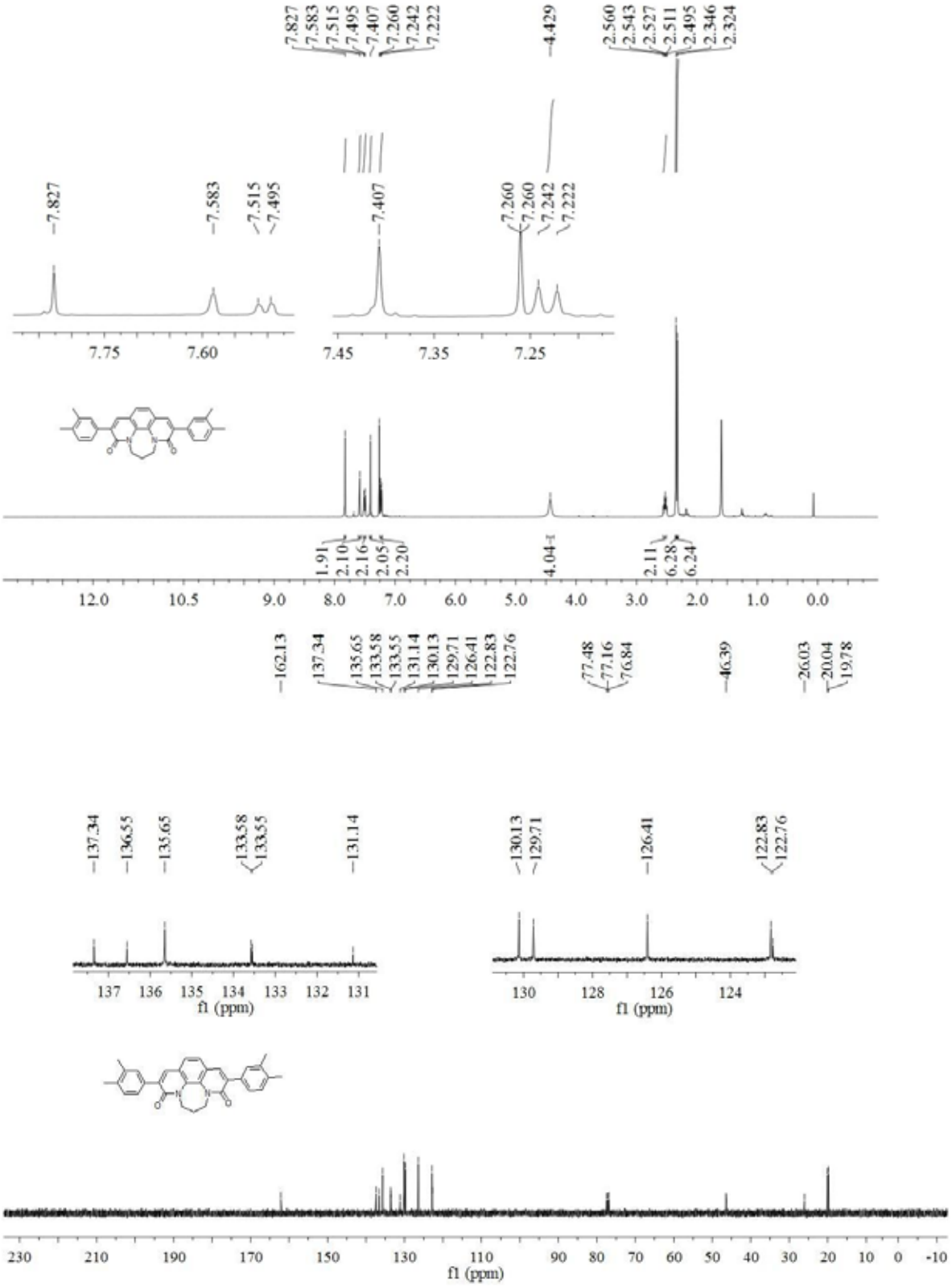

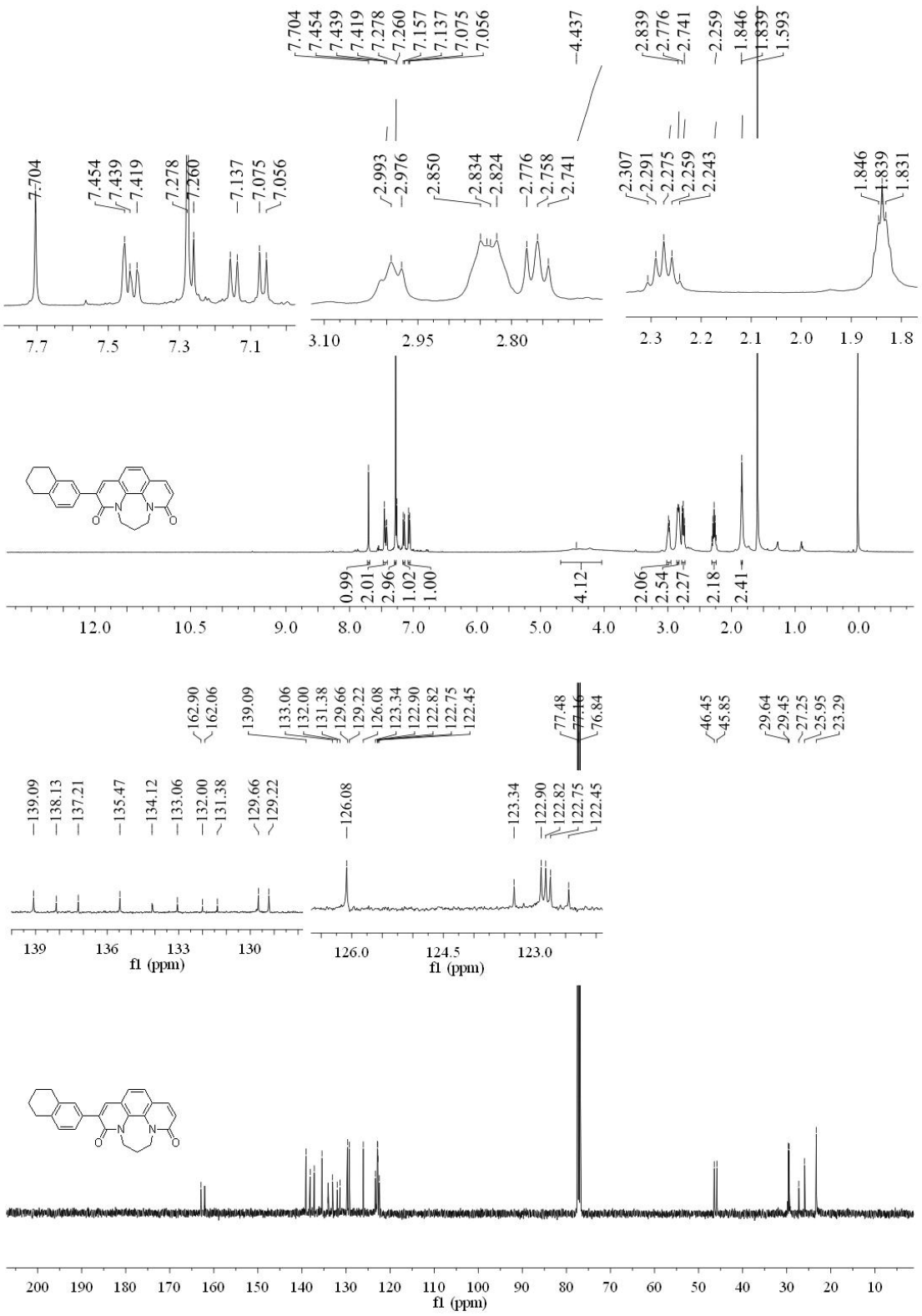
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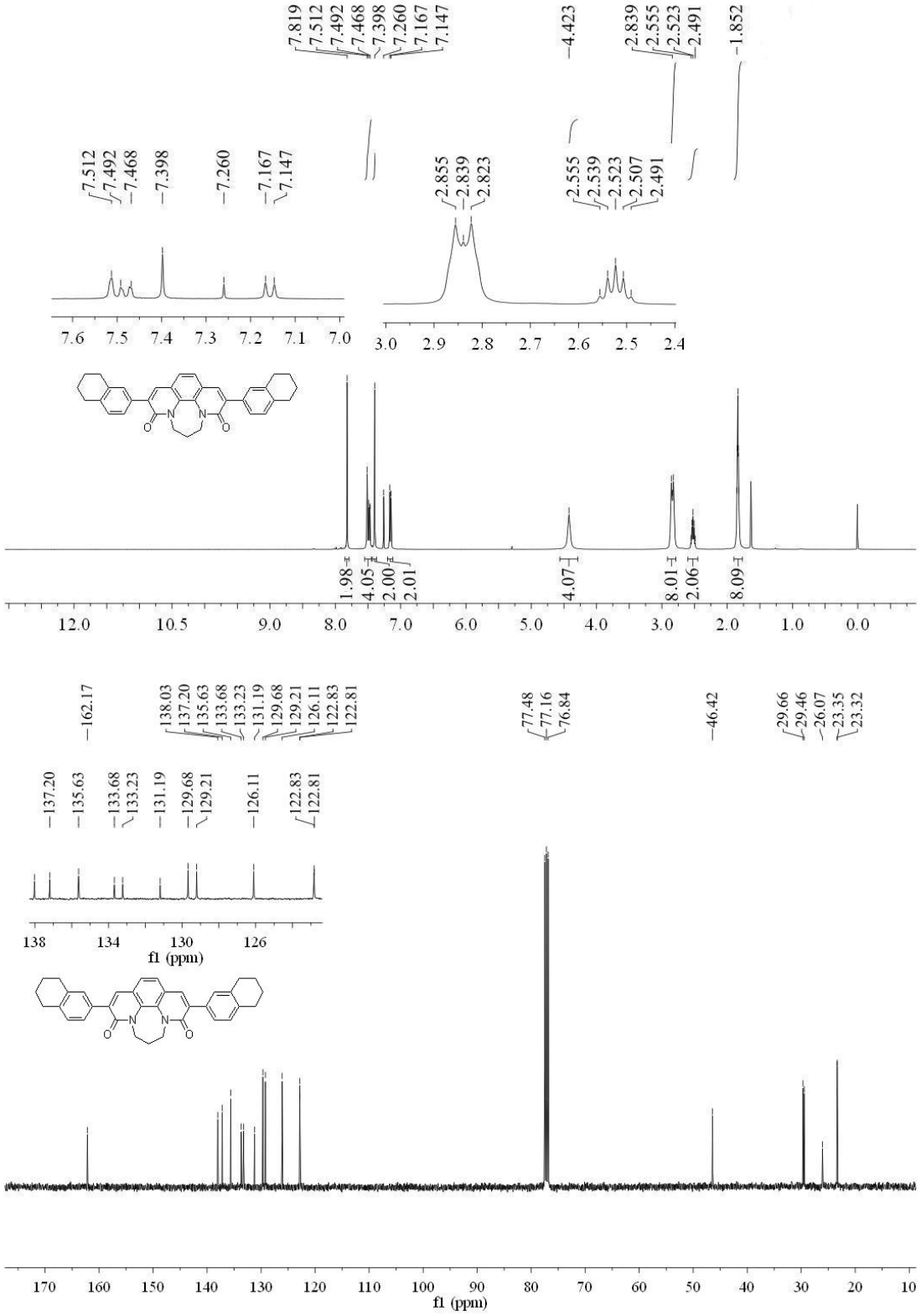
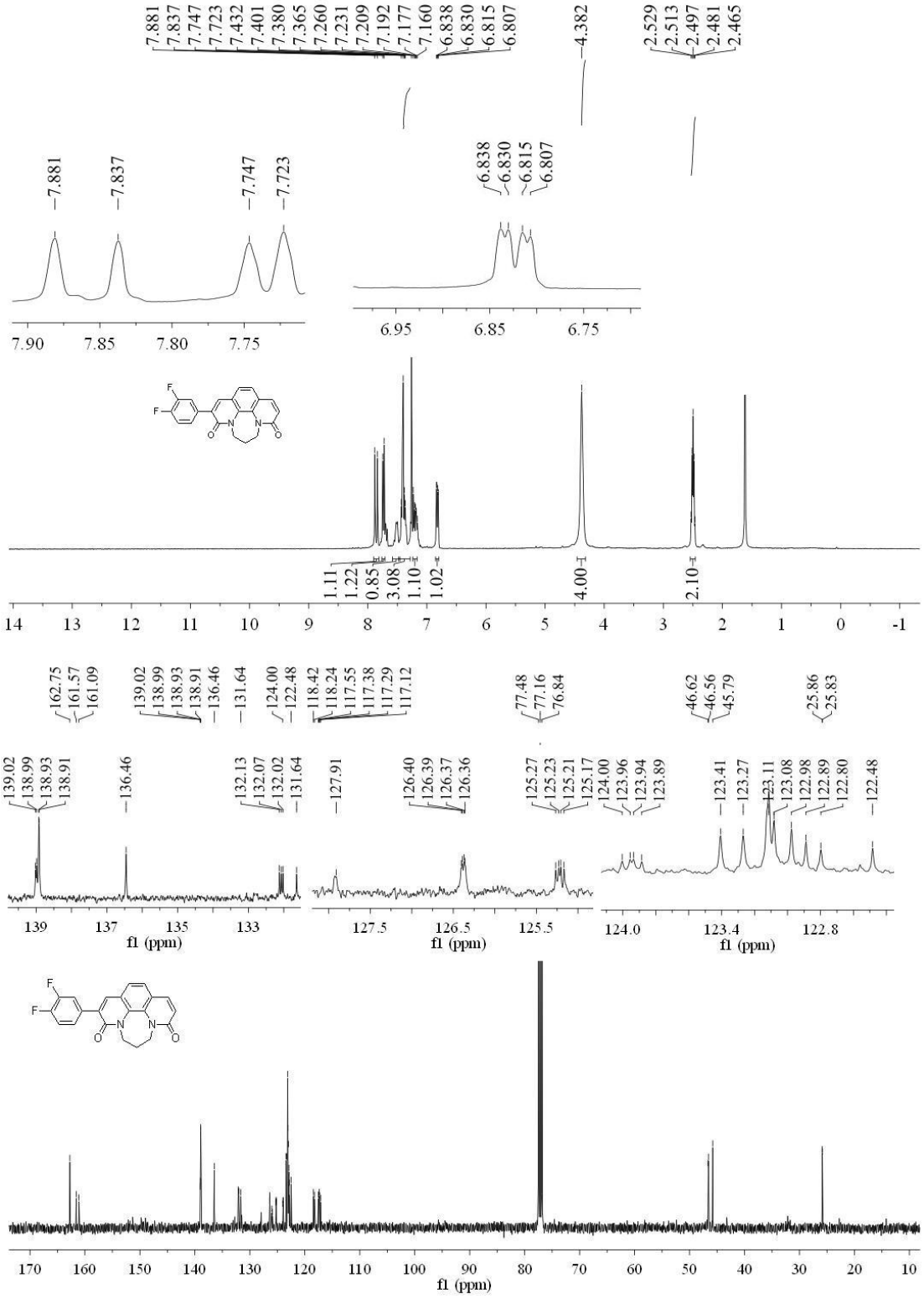
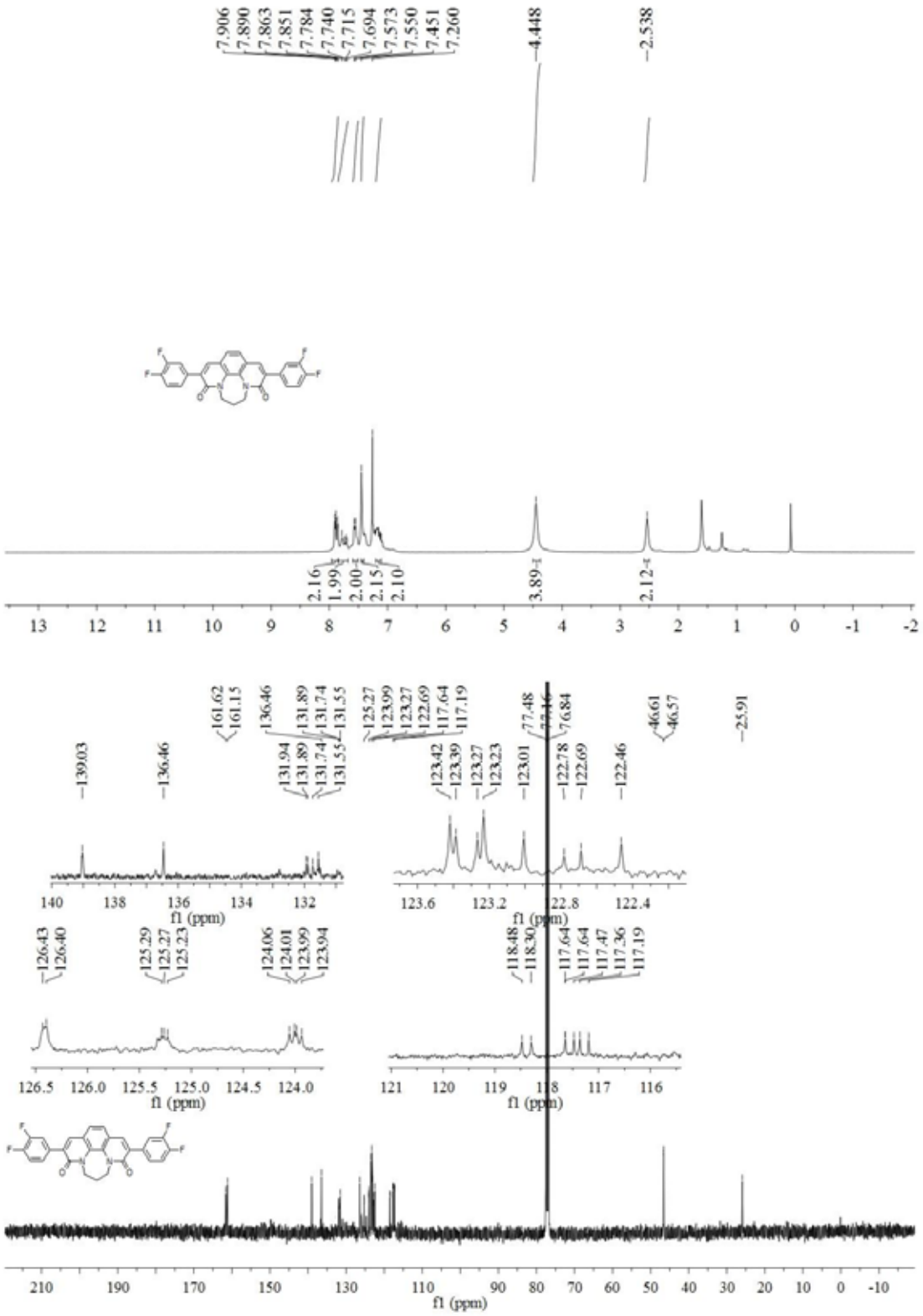
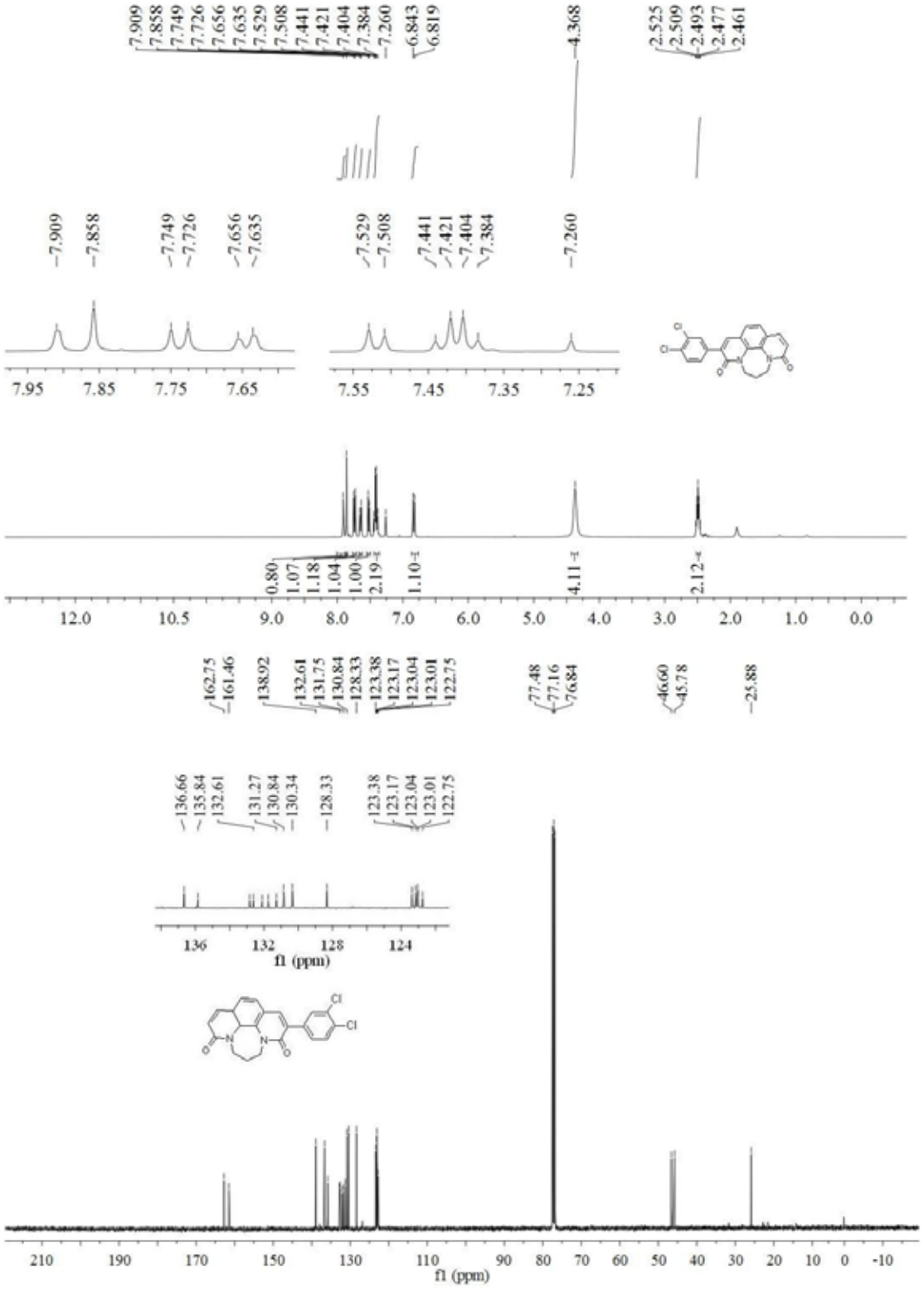
f1 (ppm)





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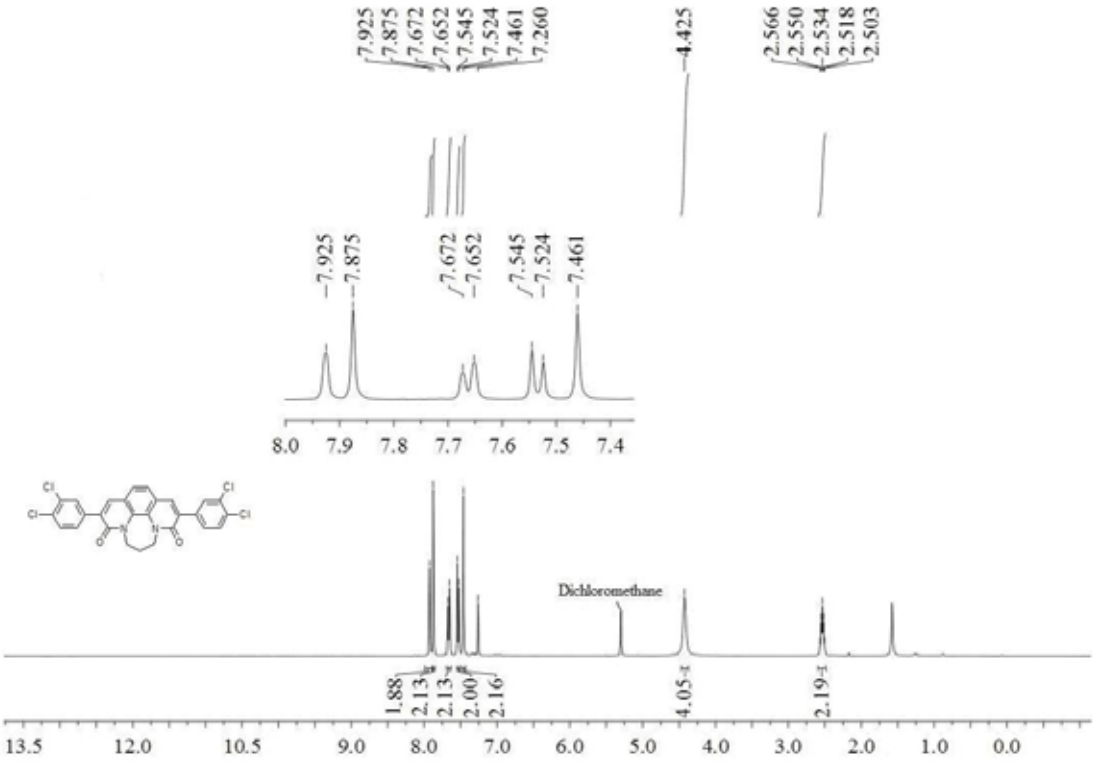


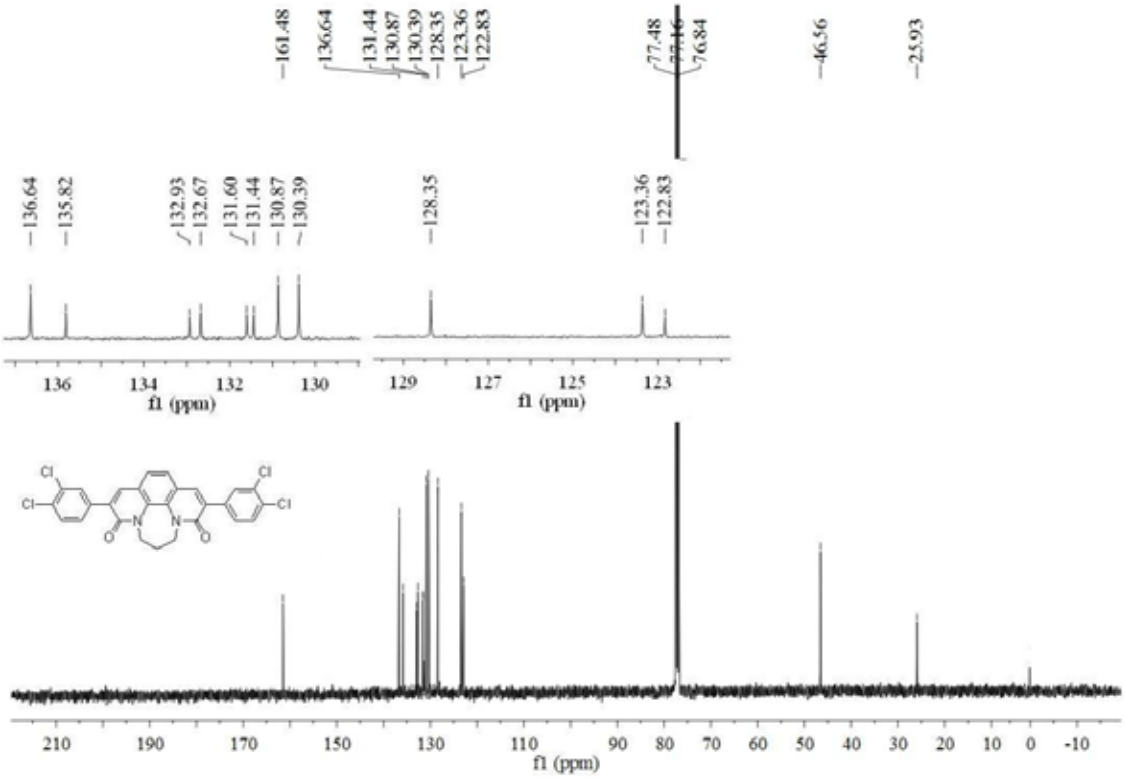

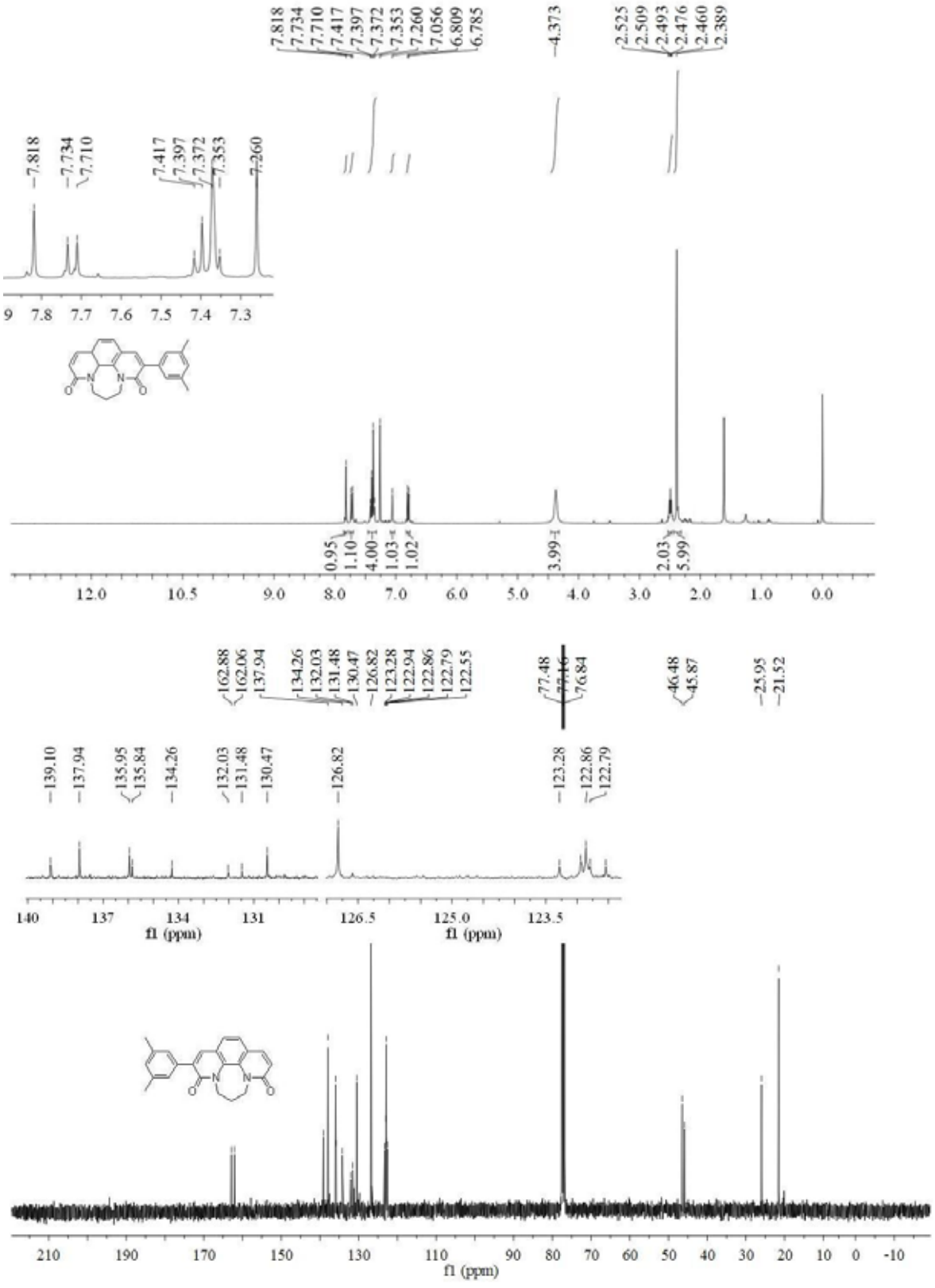
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f1 (ppm)
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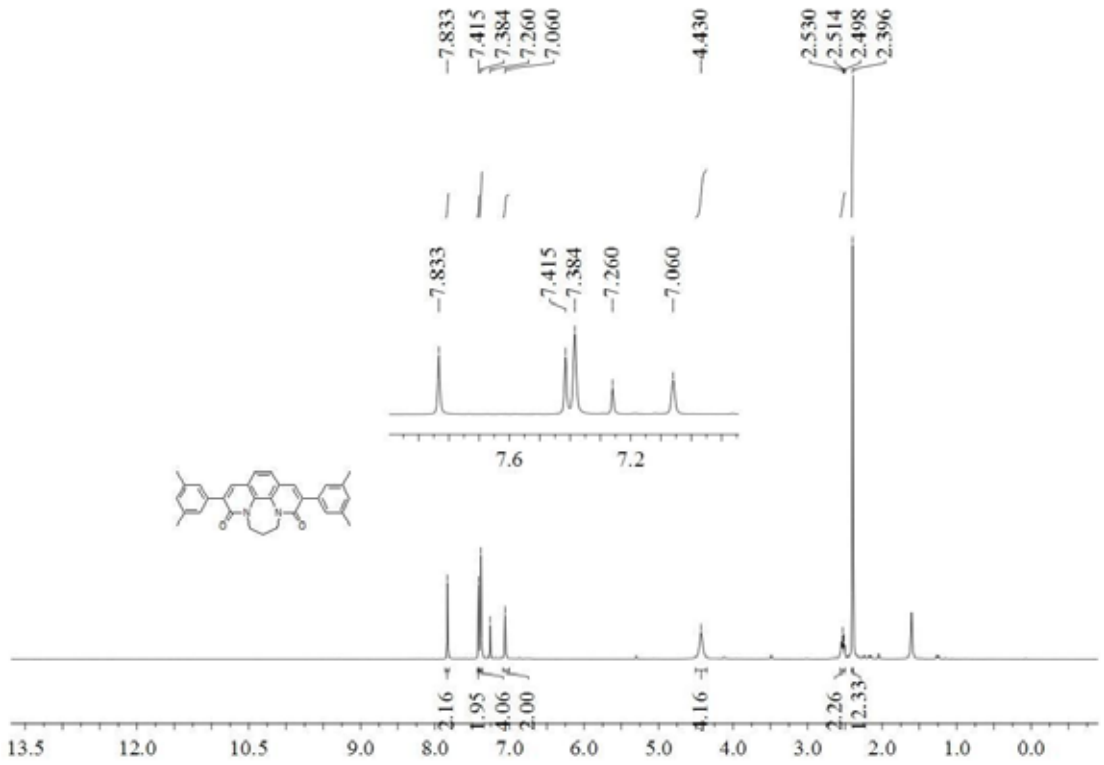


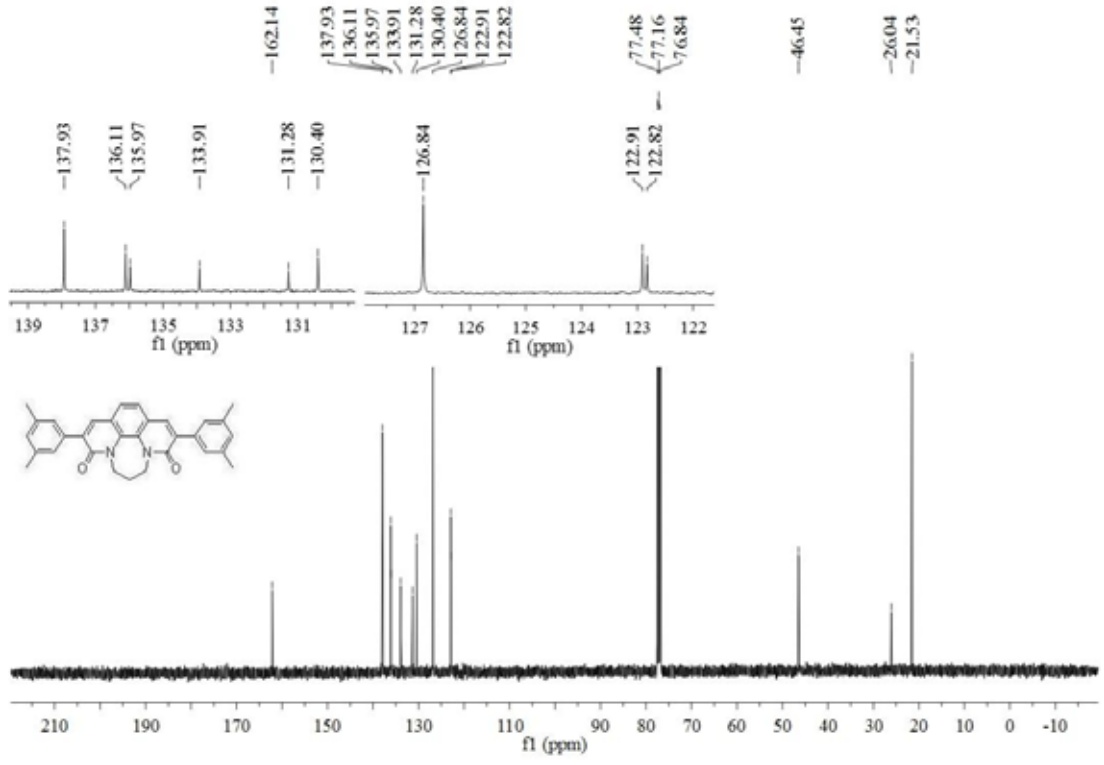

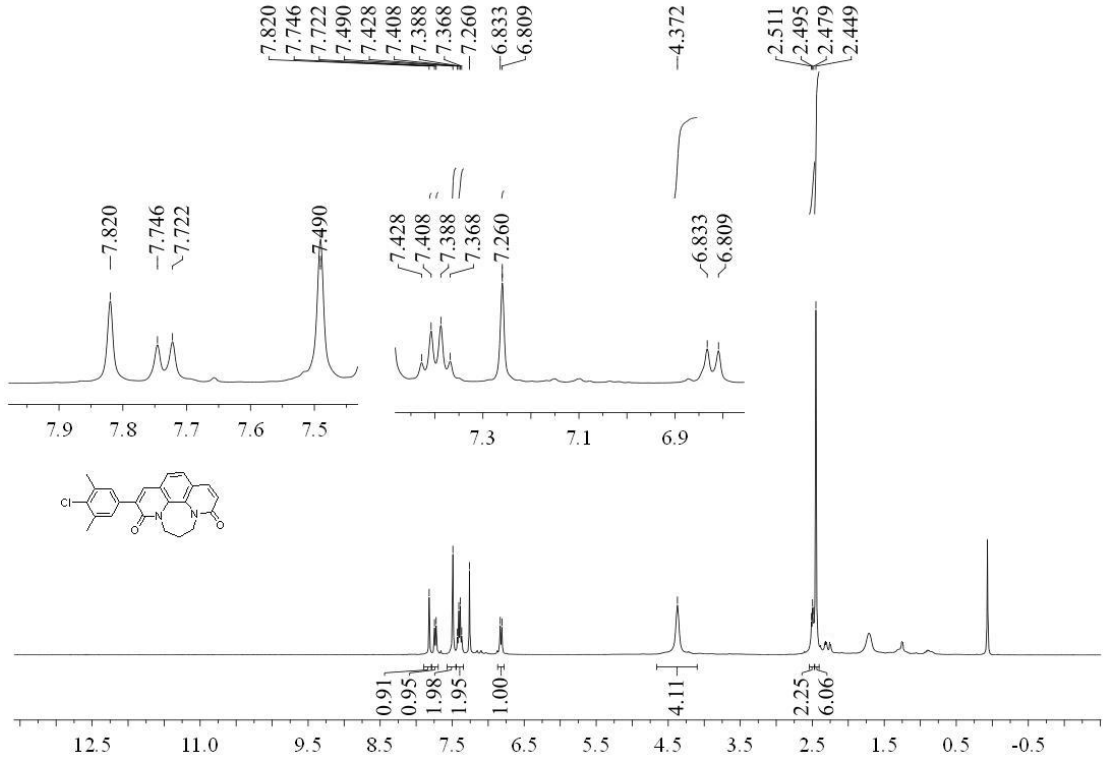
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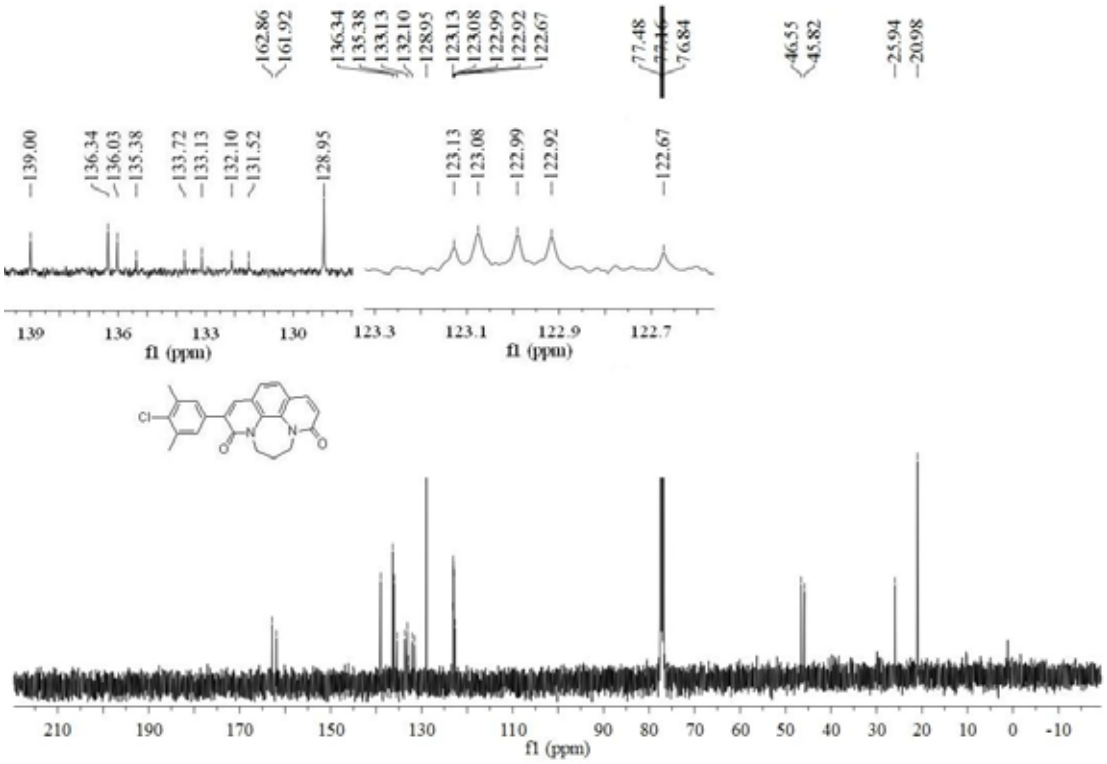
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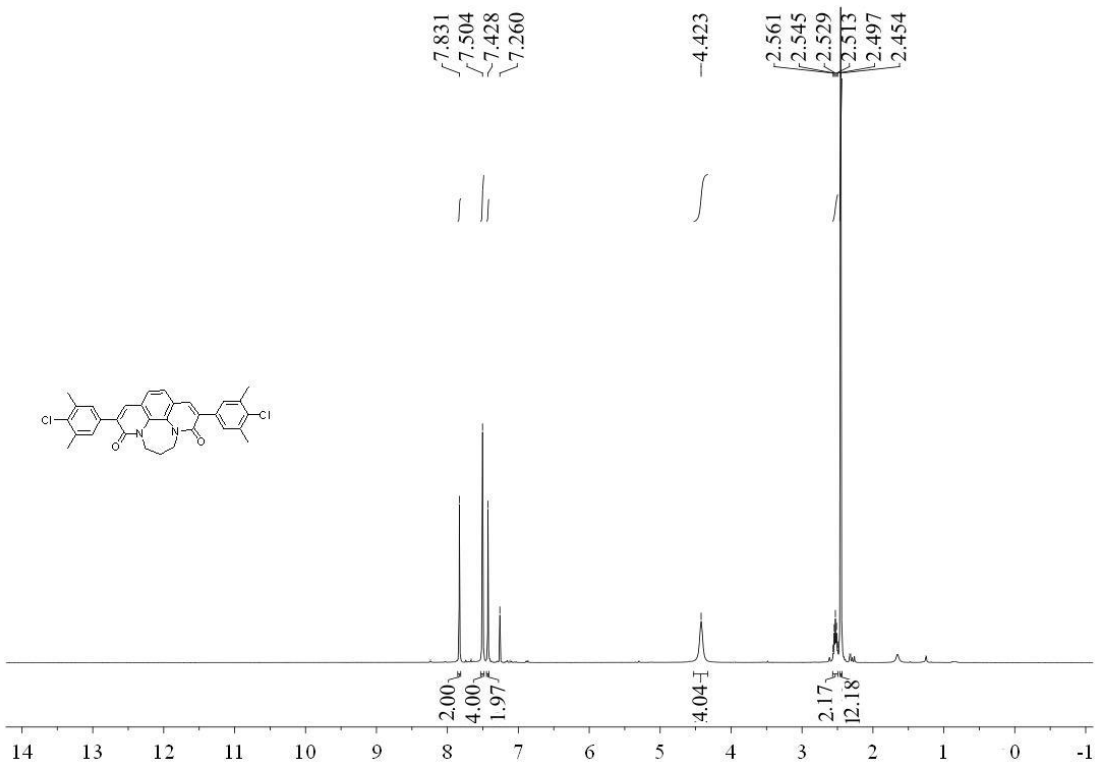
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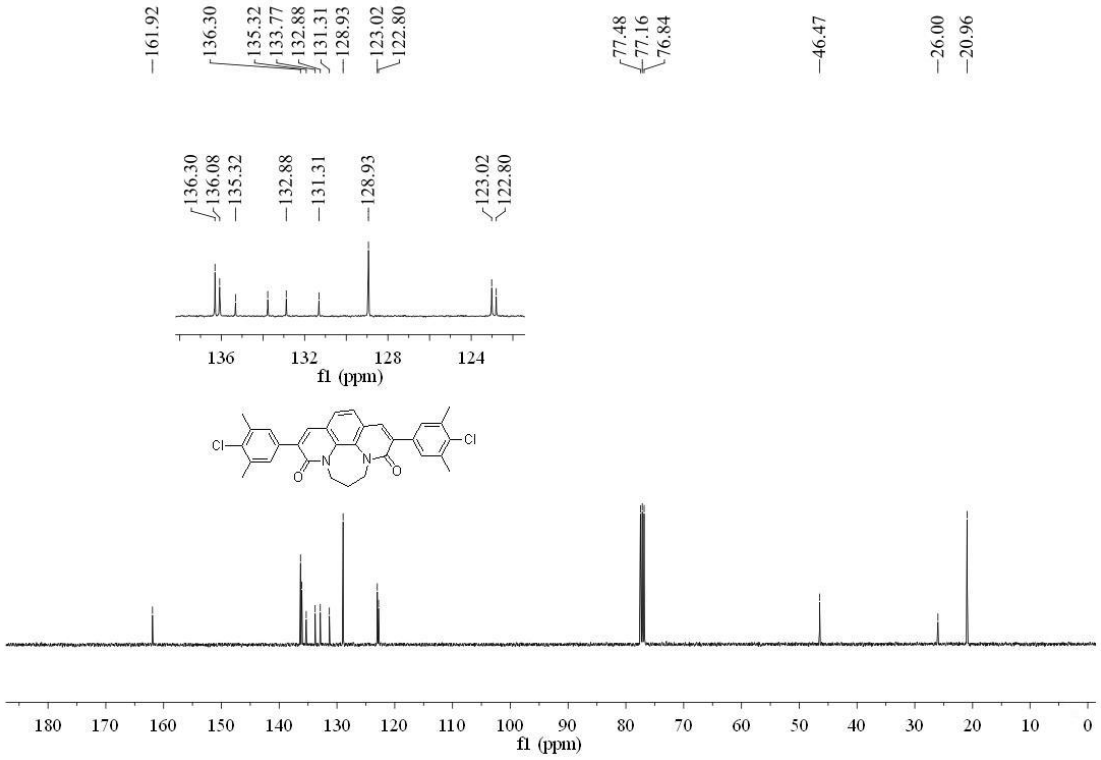
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f1 (ppm)
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O
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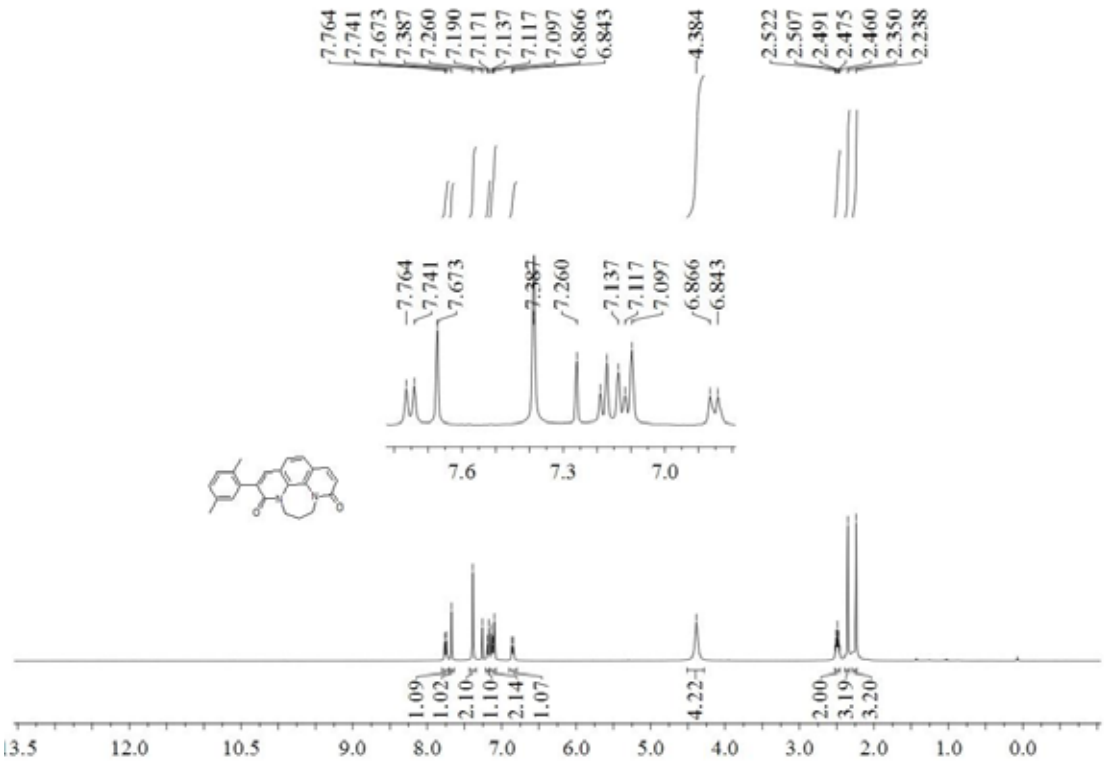


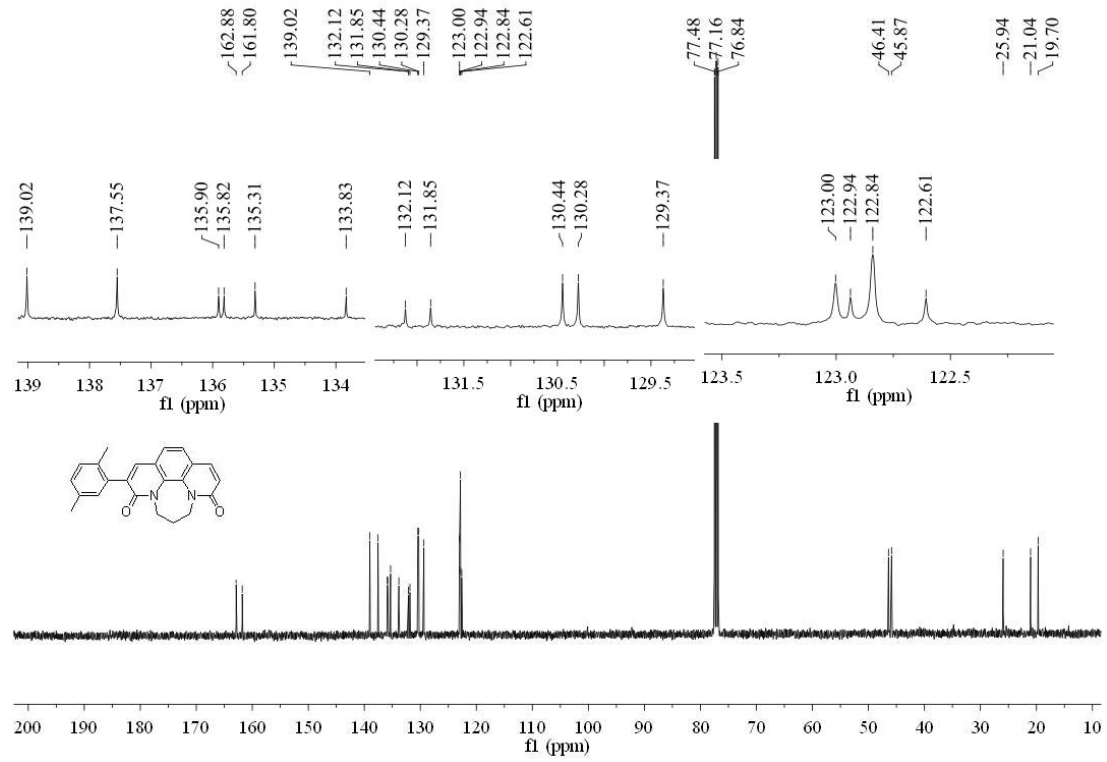

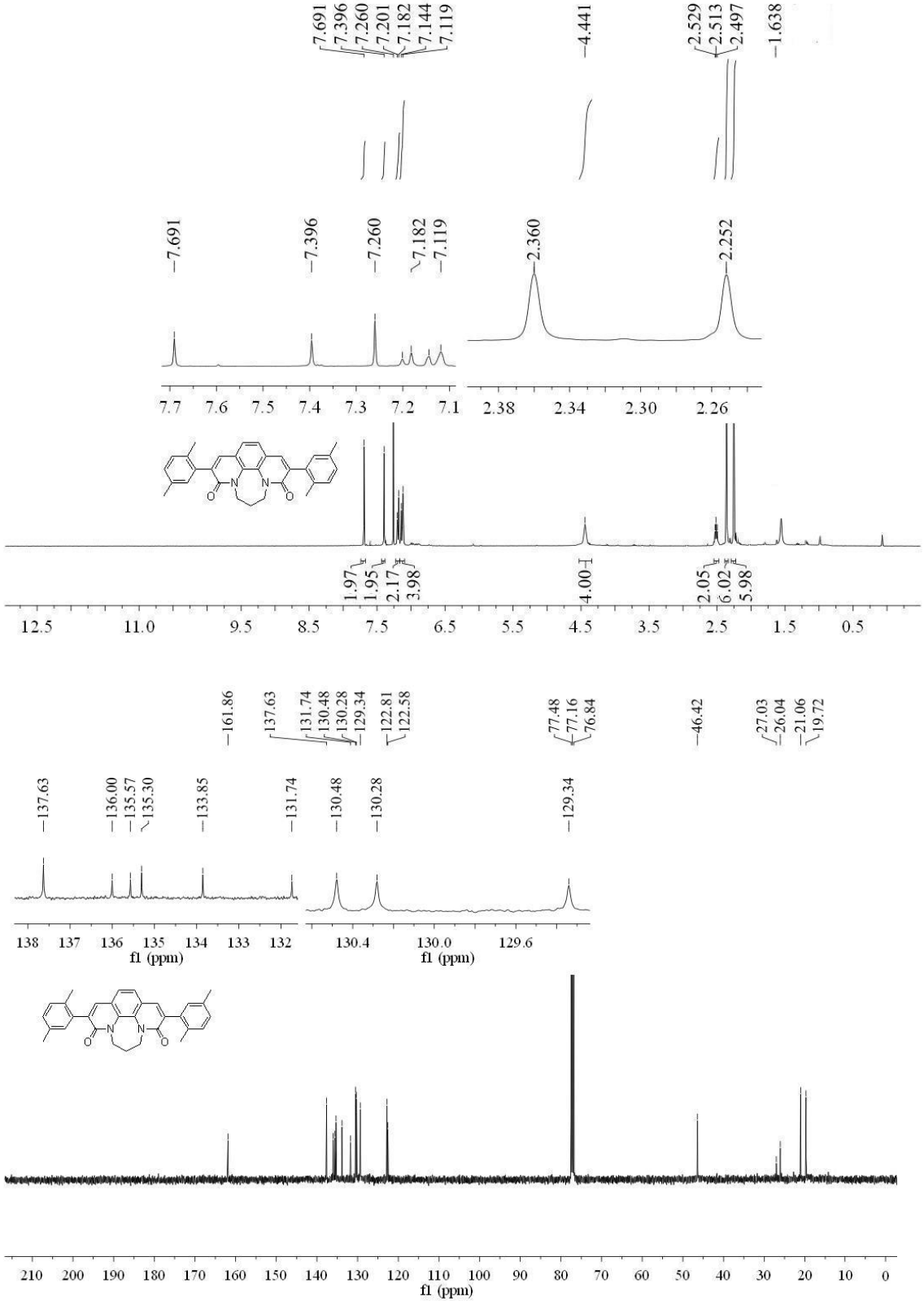

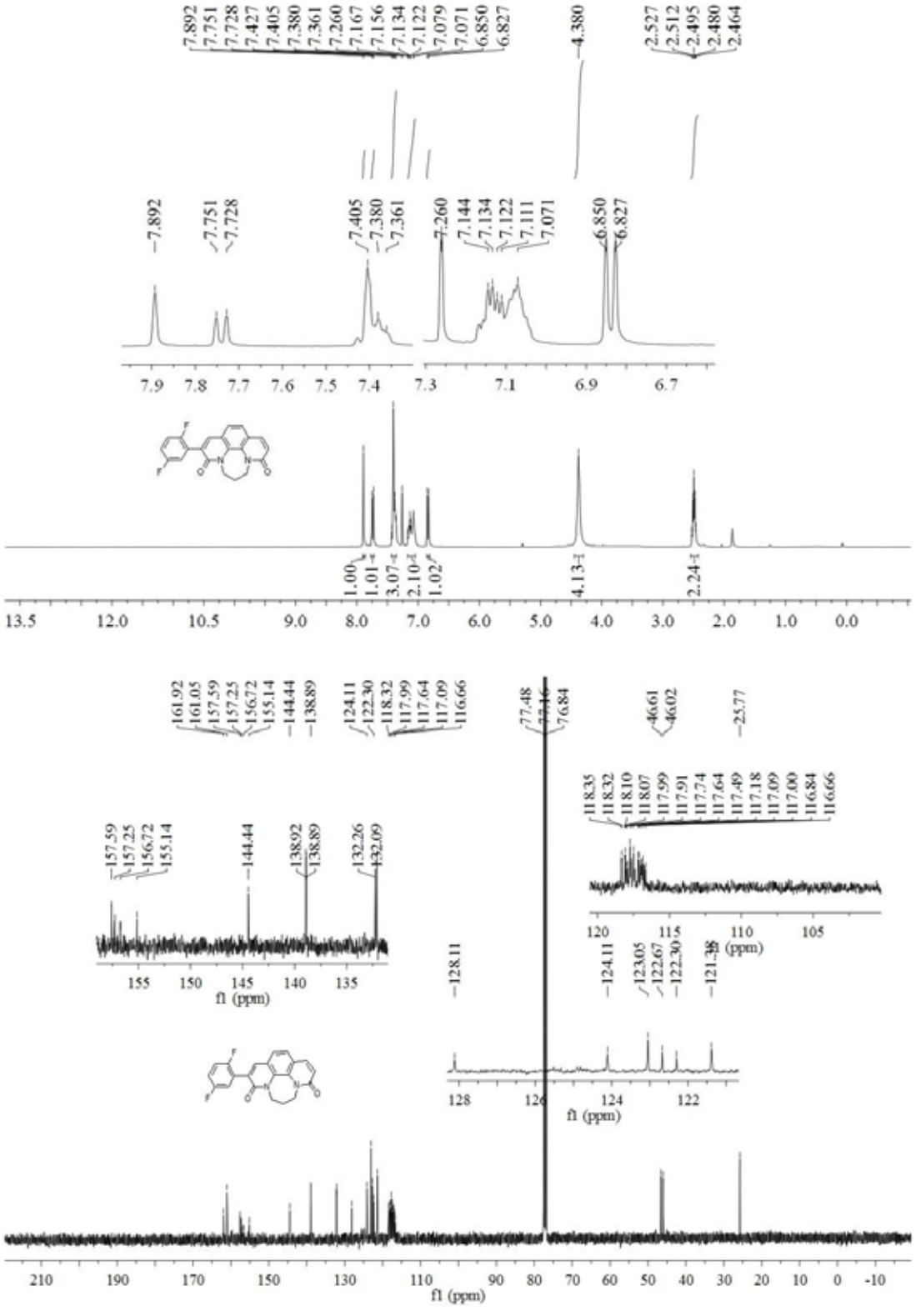

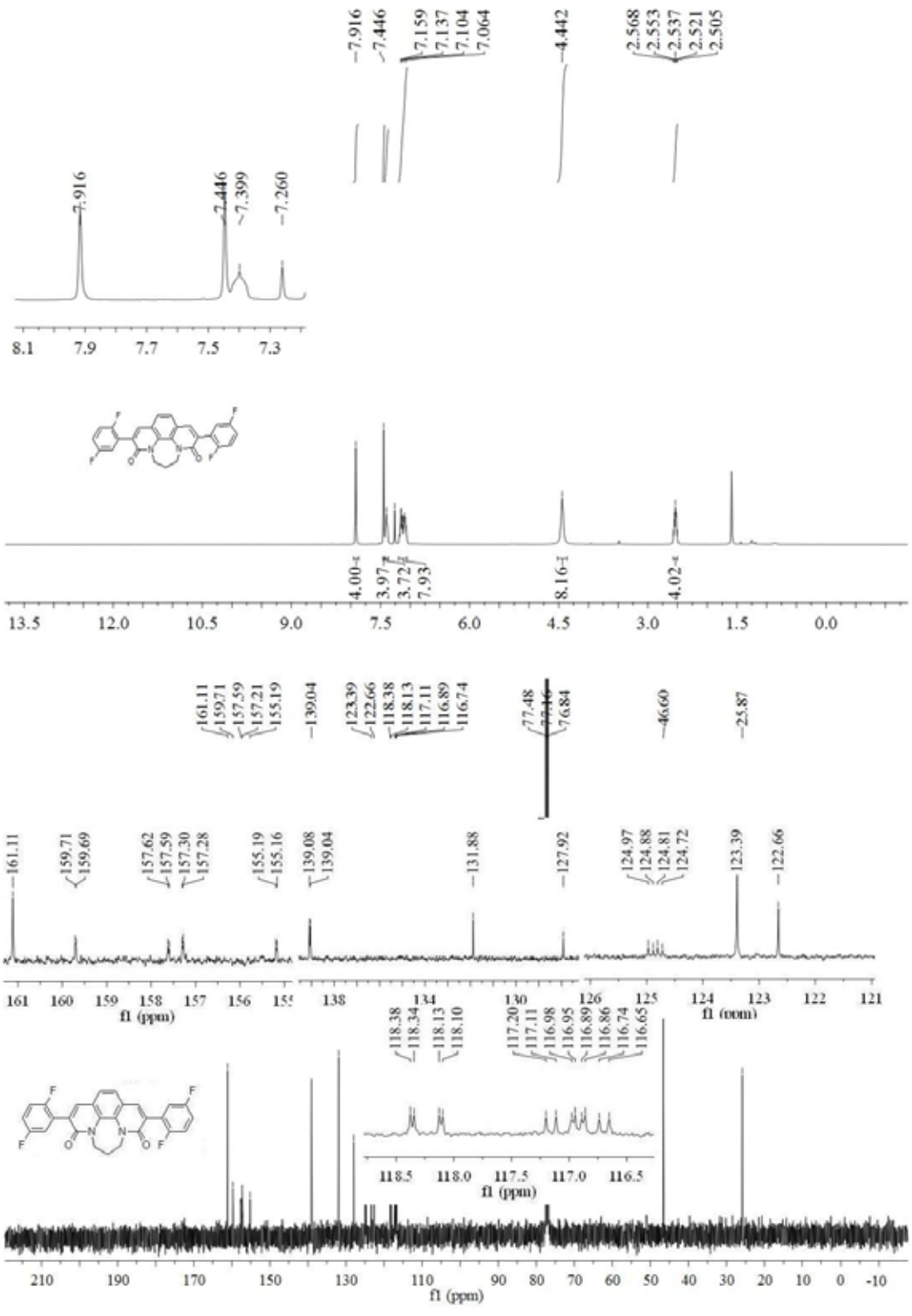

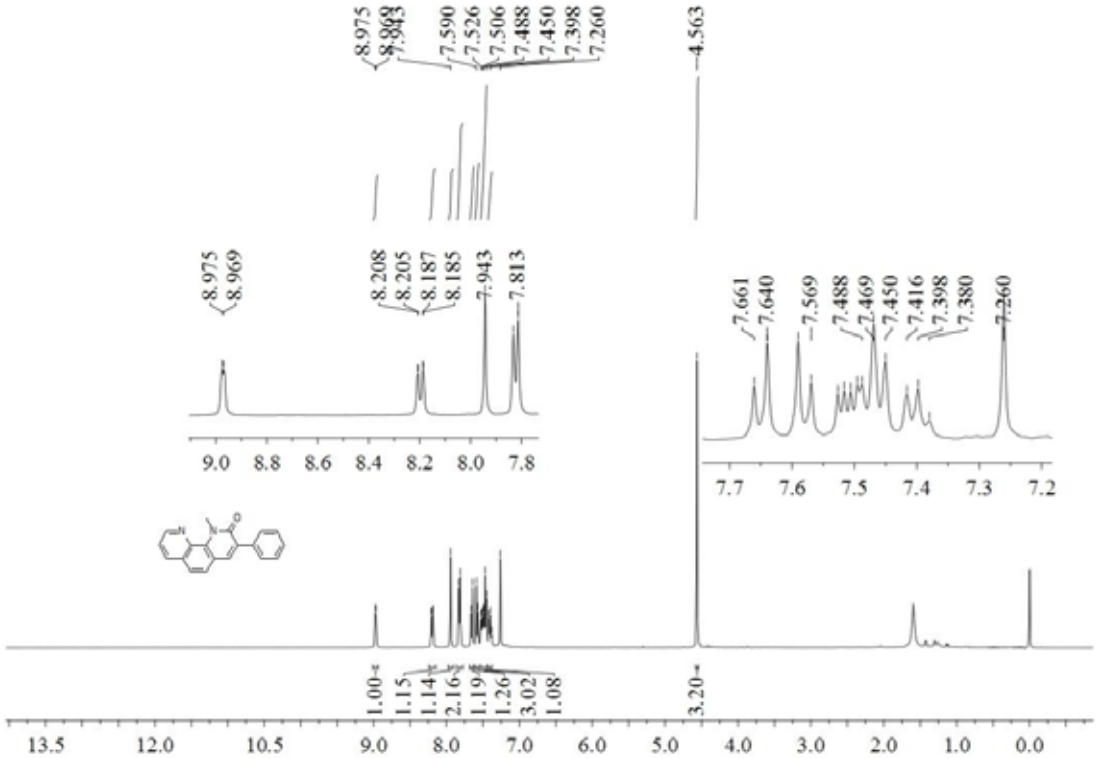
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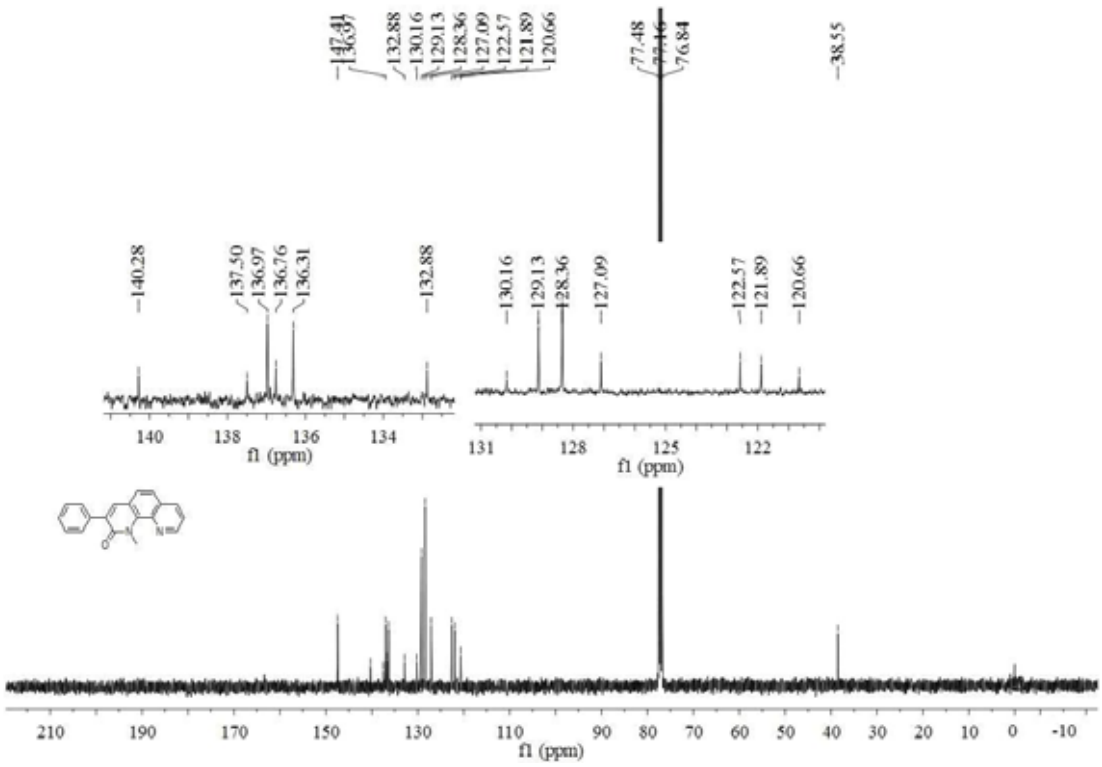
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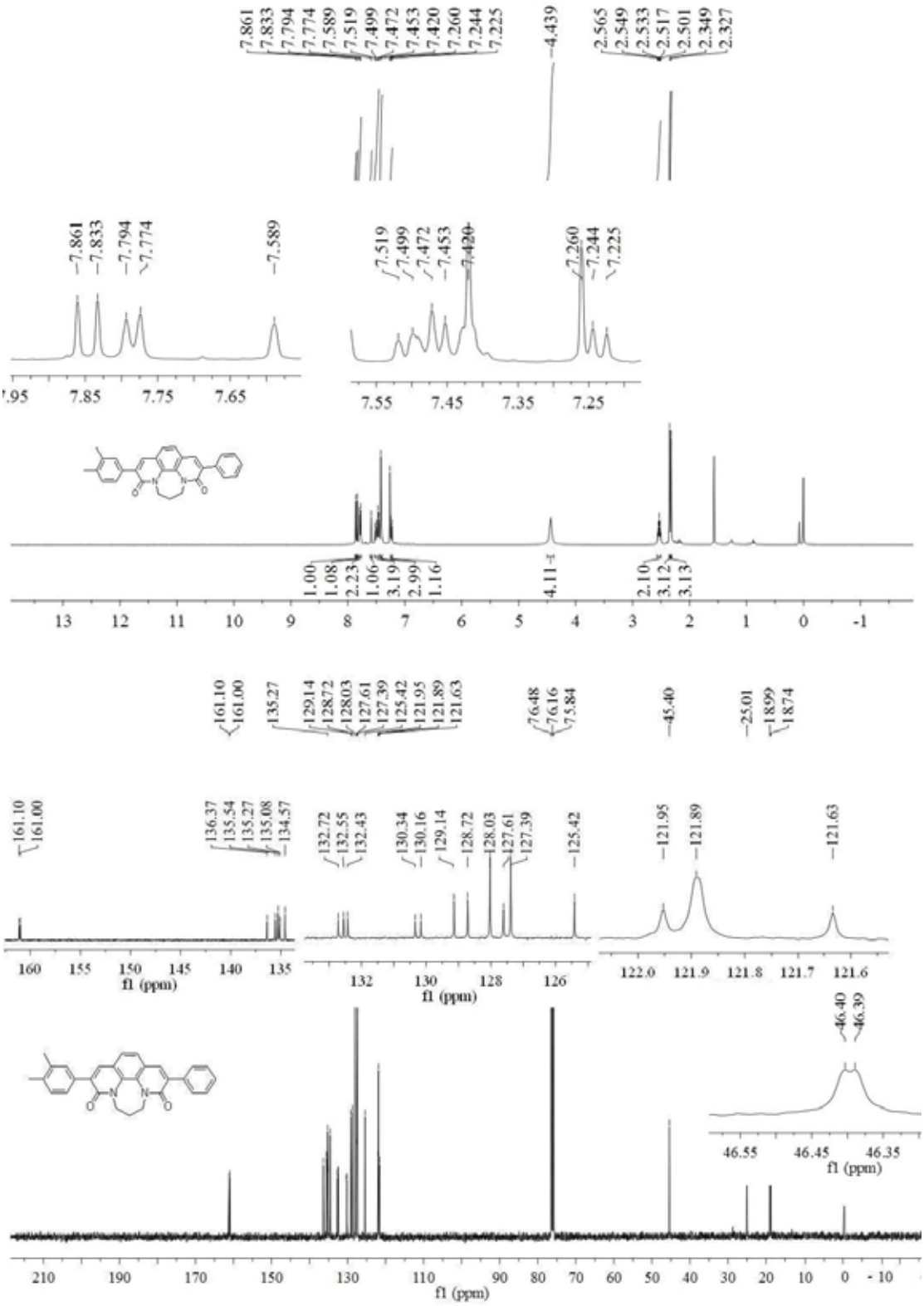
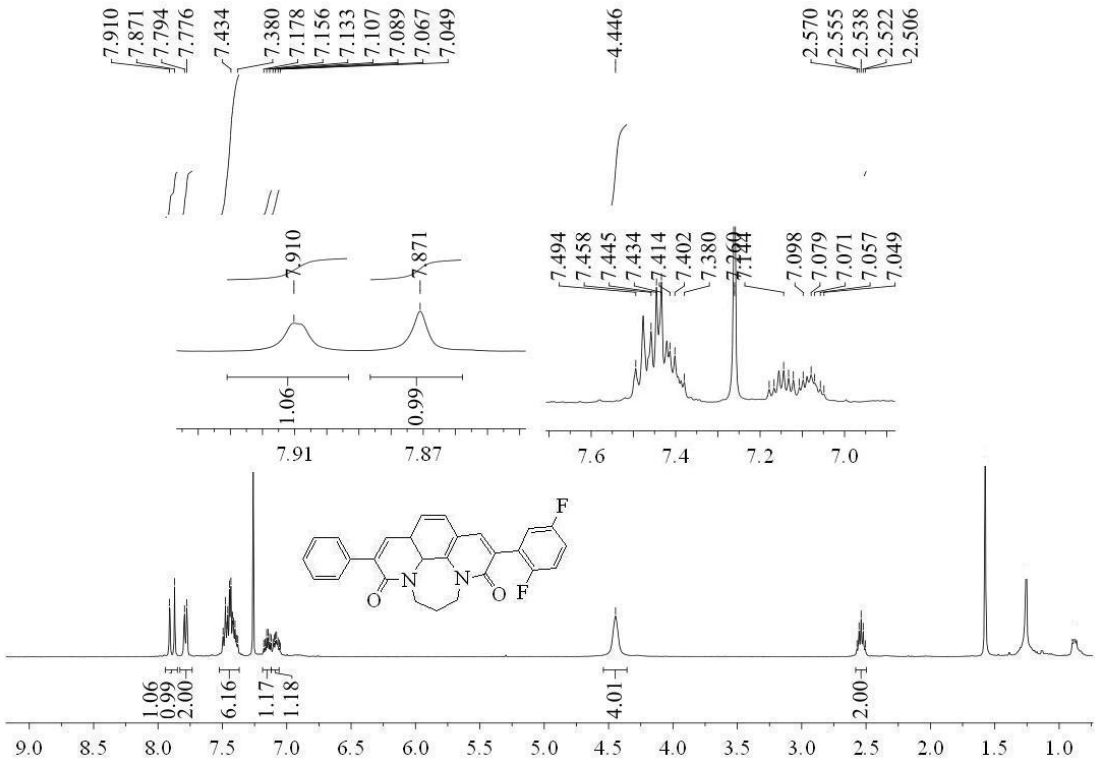
f1 (ppm)
f1 (ppm)

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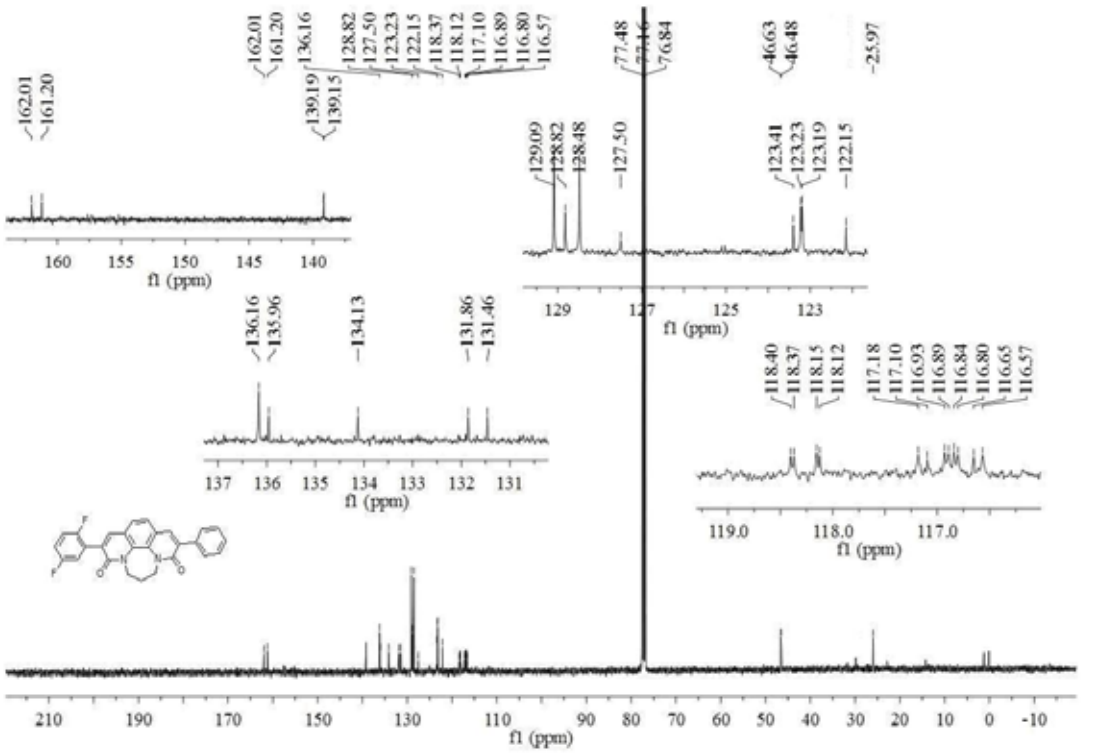
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116.80
116.57
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139.15
77.48
77.16
76.84
46.63
46.48
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128.48
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117.18
117.10
116.93
116.89
116.84
116.80
116.65
116.57
160
155
150
145
140
f1 (ppm)
129
127
125
123
f1 (ppm)
137
136
135
134
133
132
131
f1 (ppm)
119.0
118.0
117.0
f1 (ppm)
F
O
N
O
F
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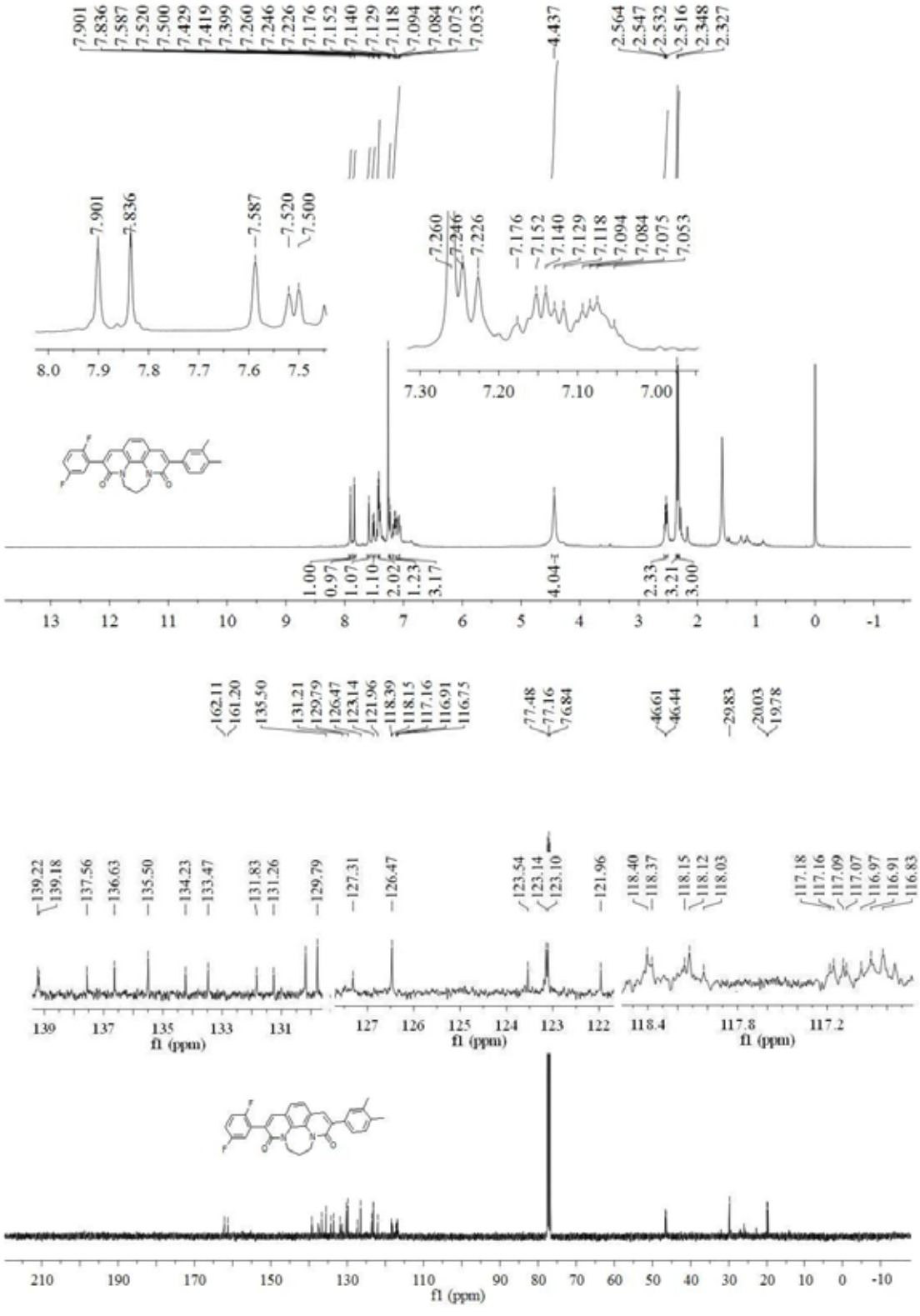
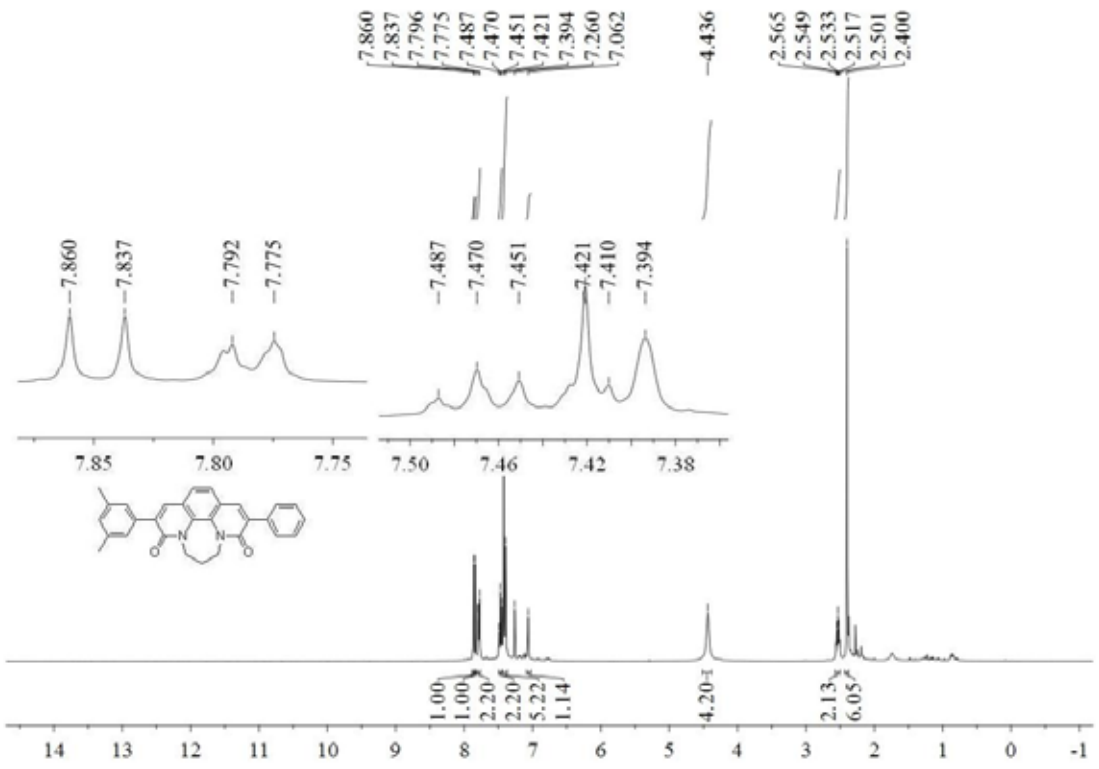
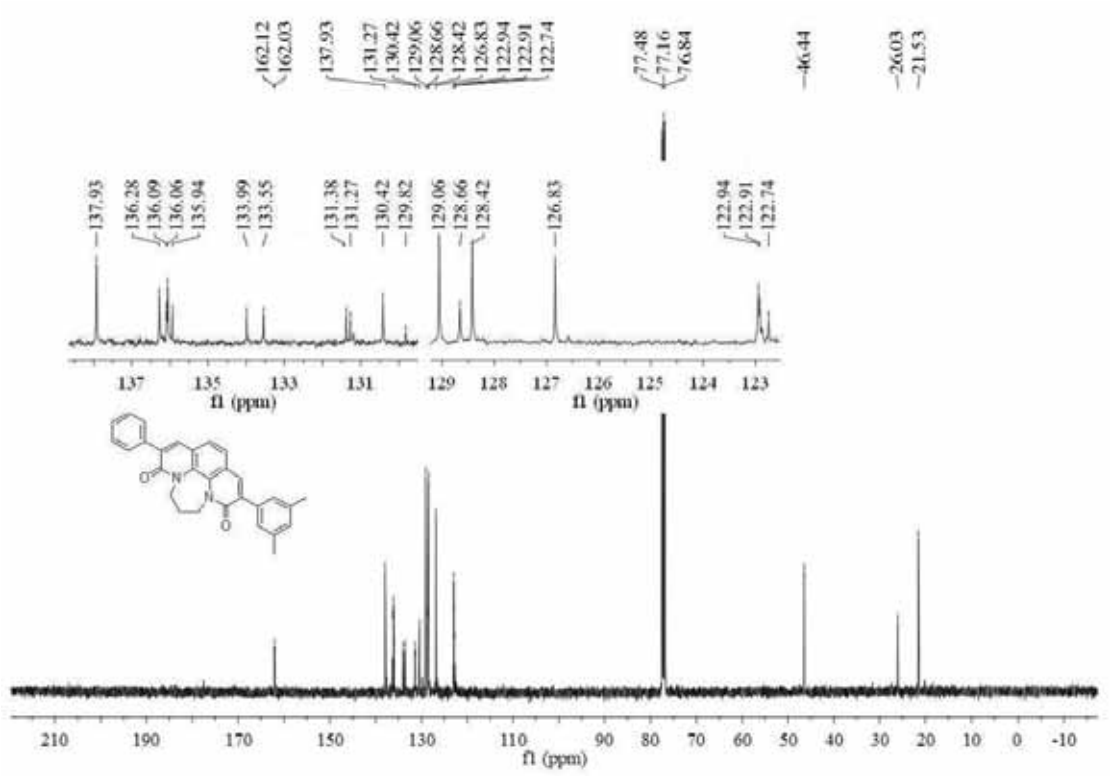
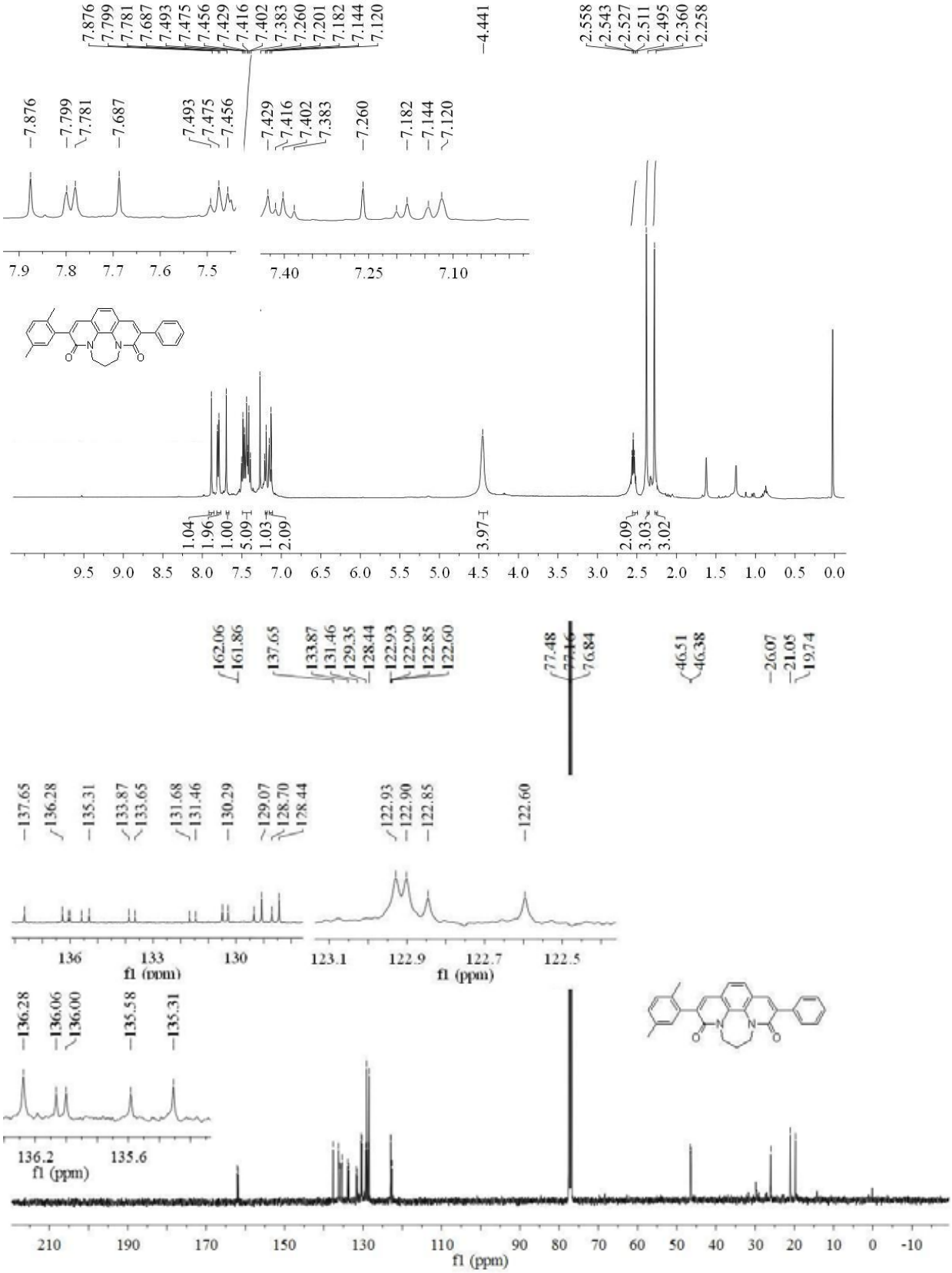
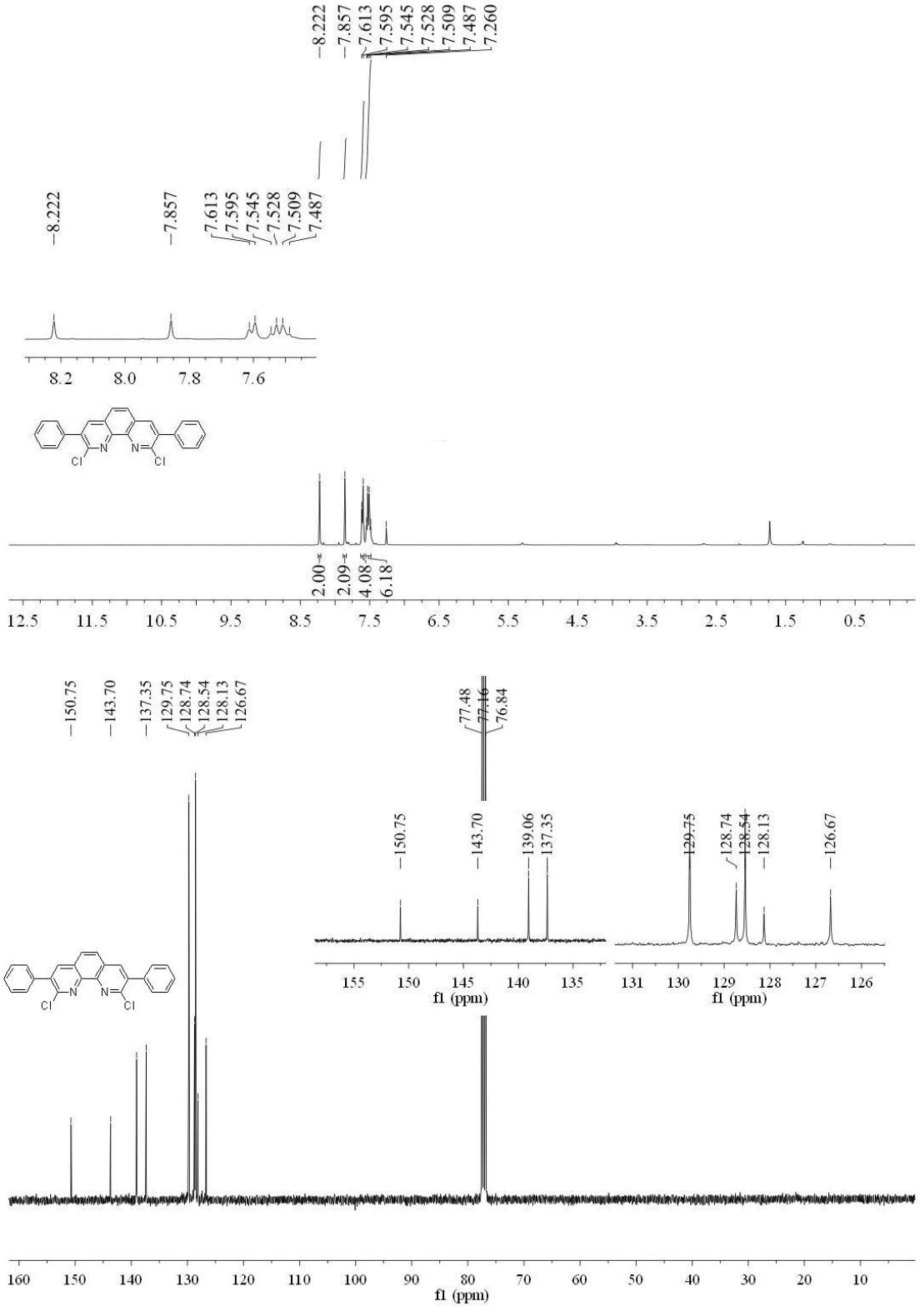
-10
f1 (ppm)

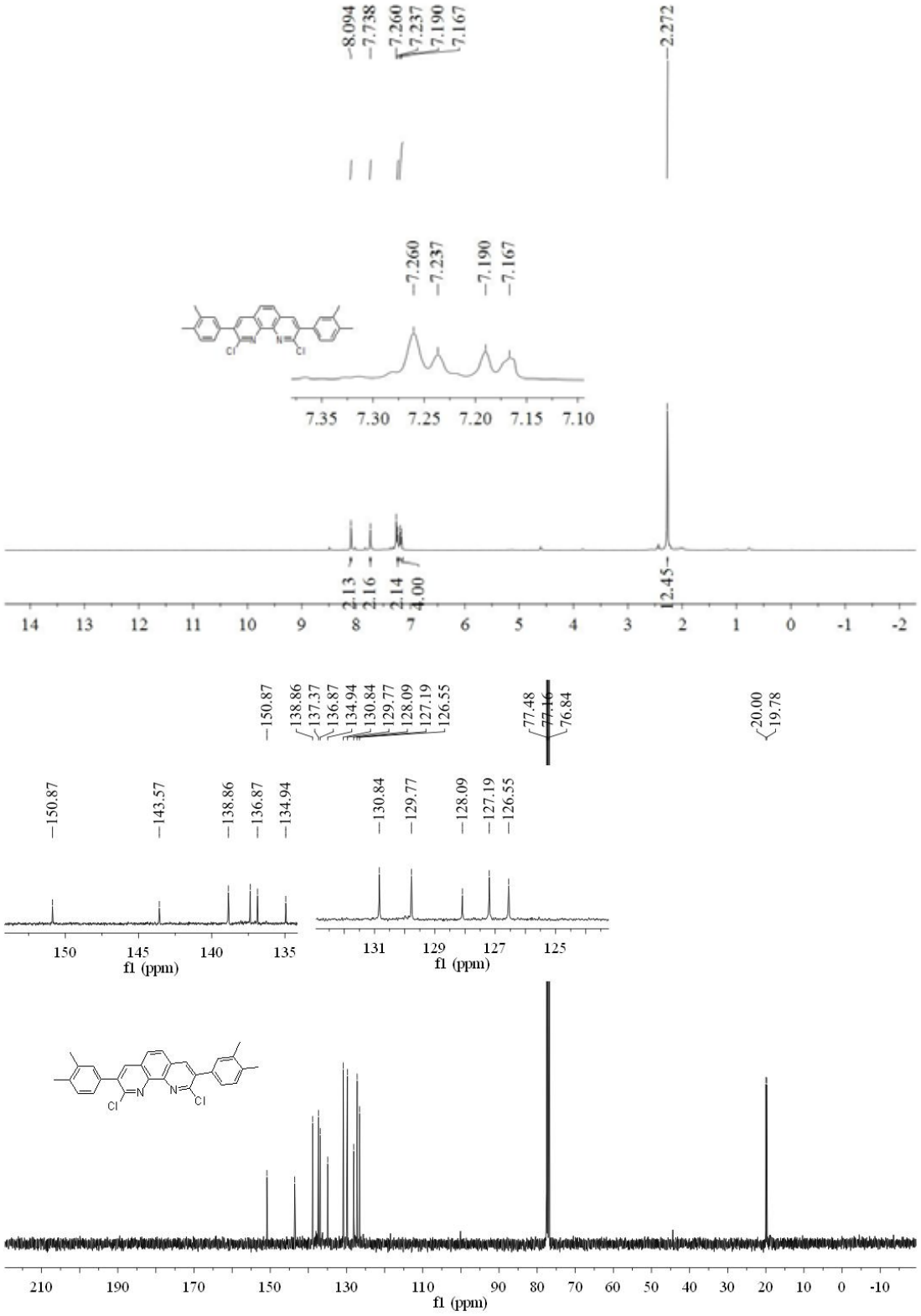


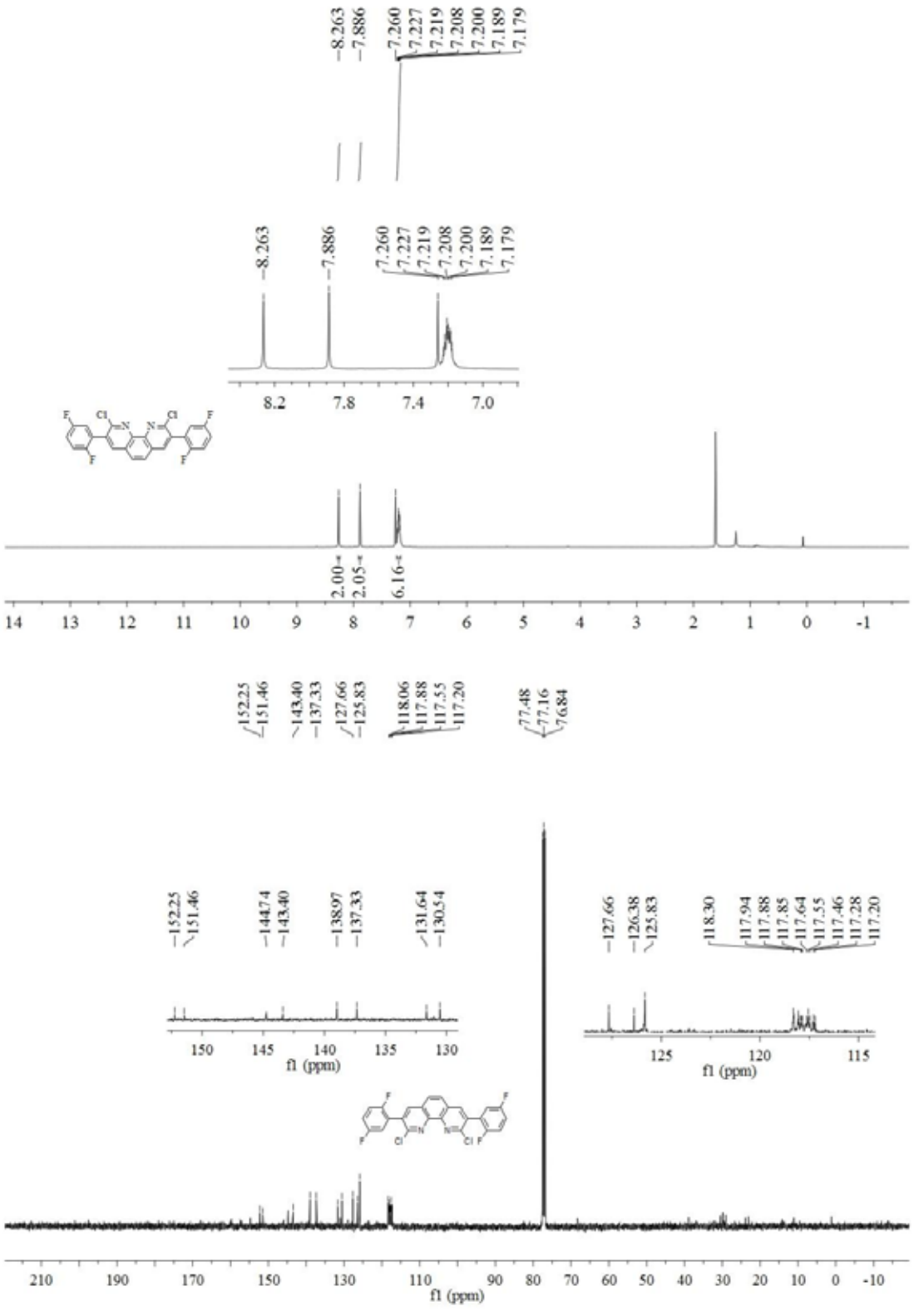


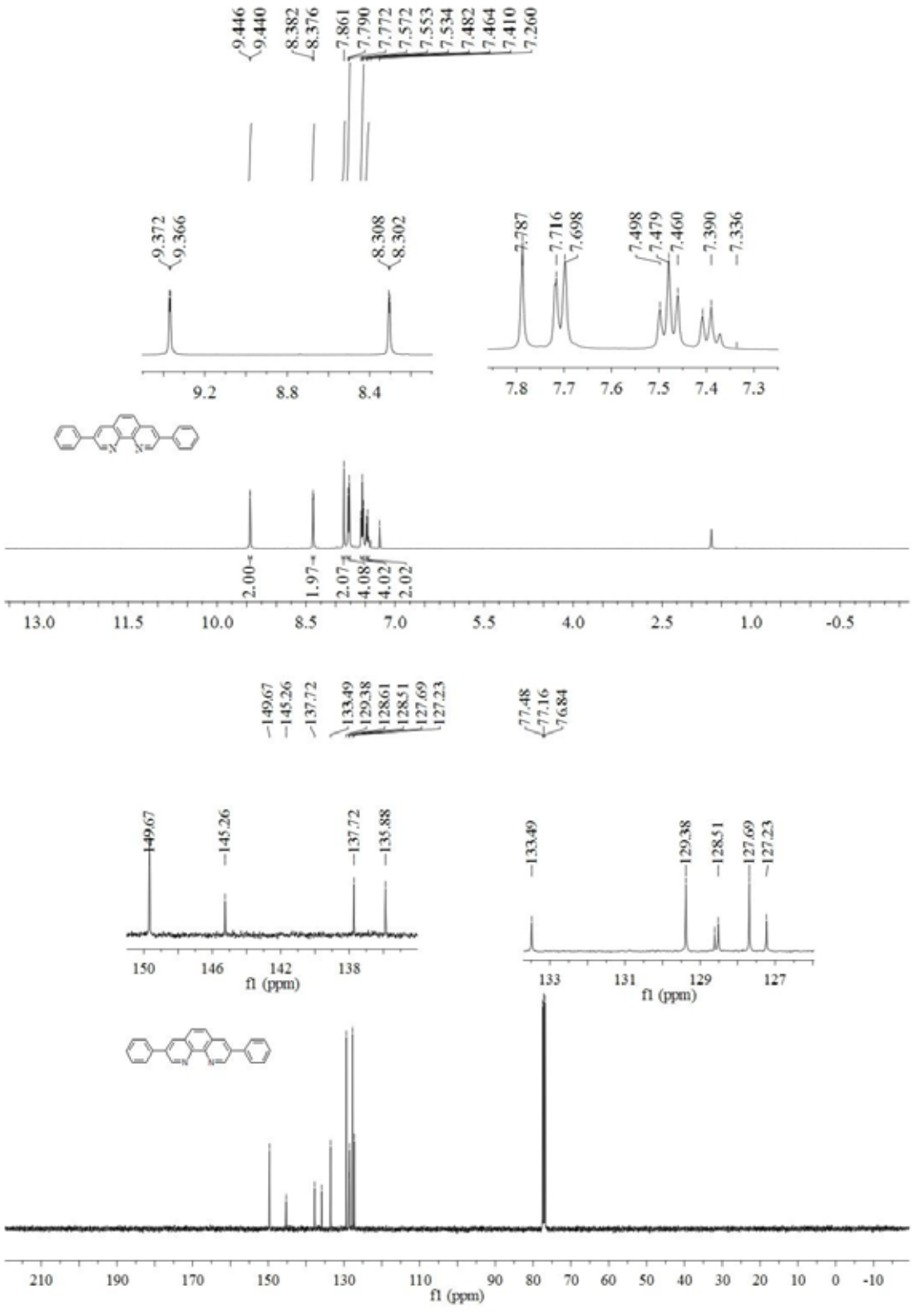



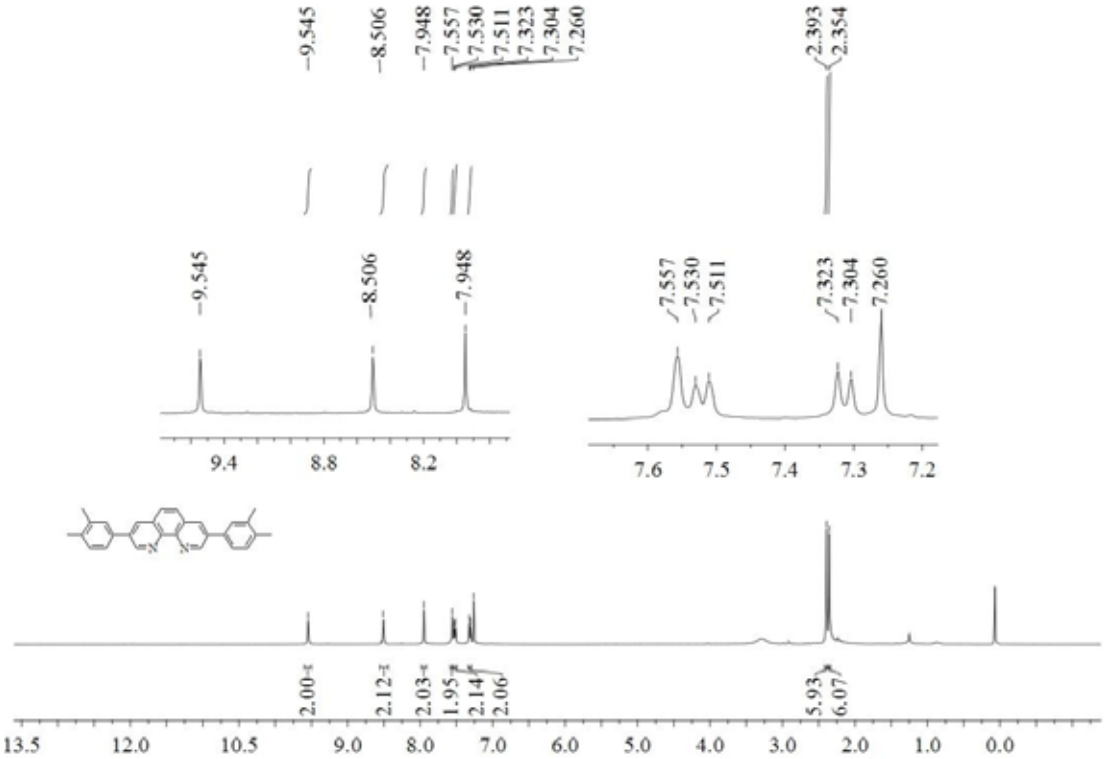


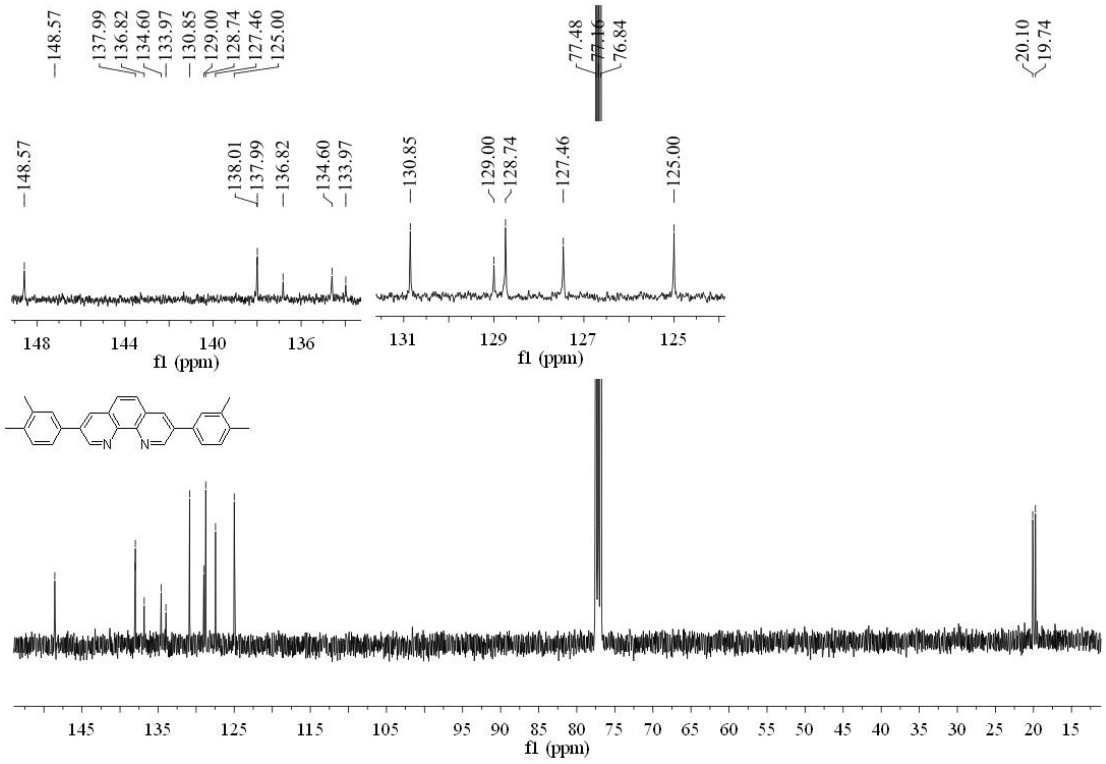


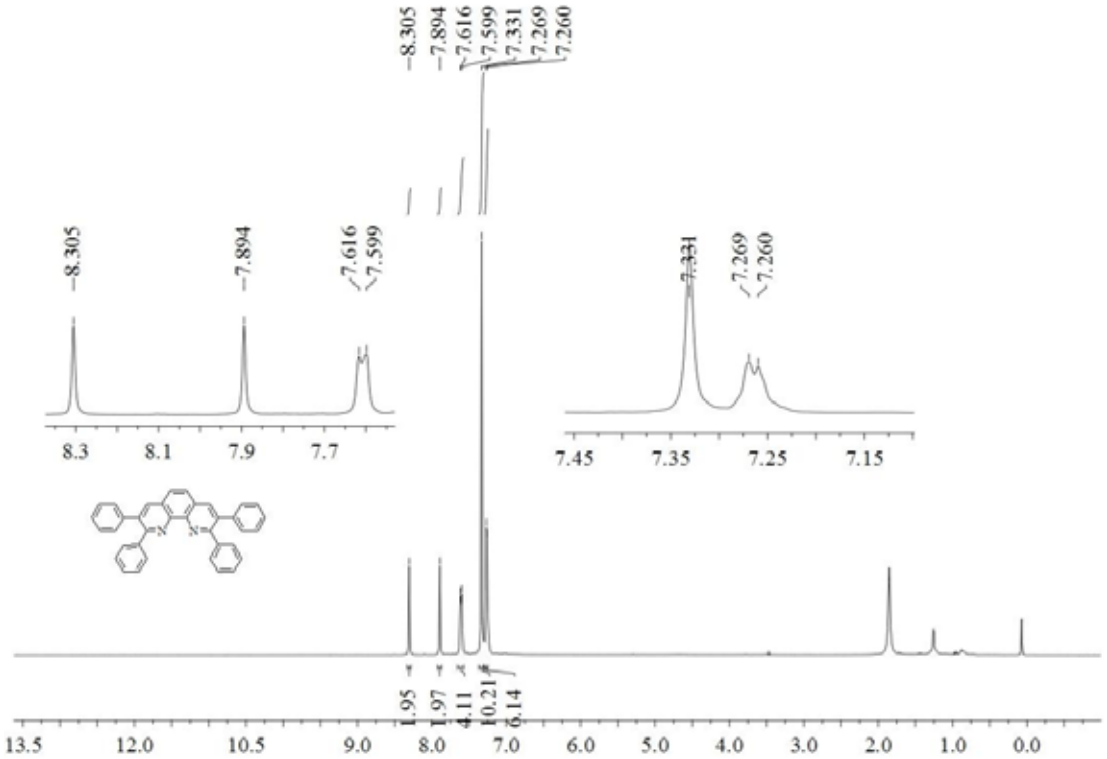


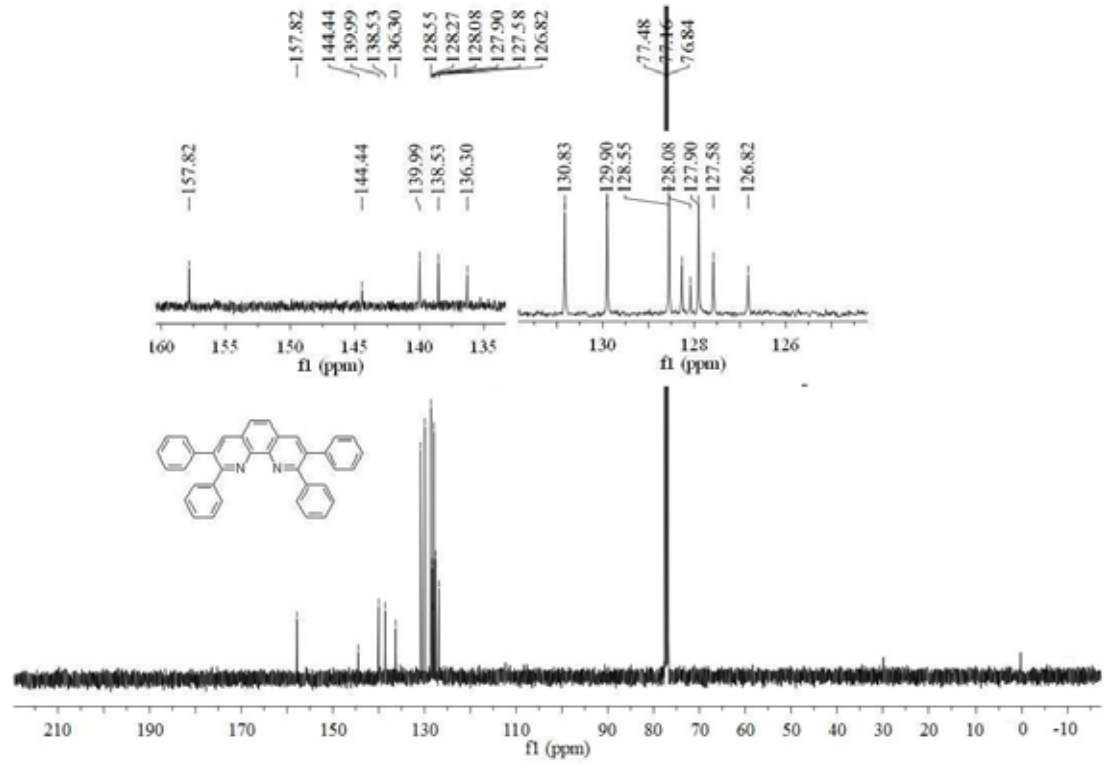


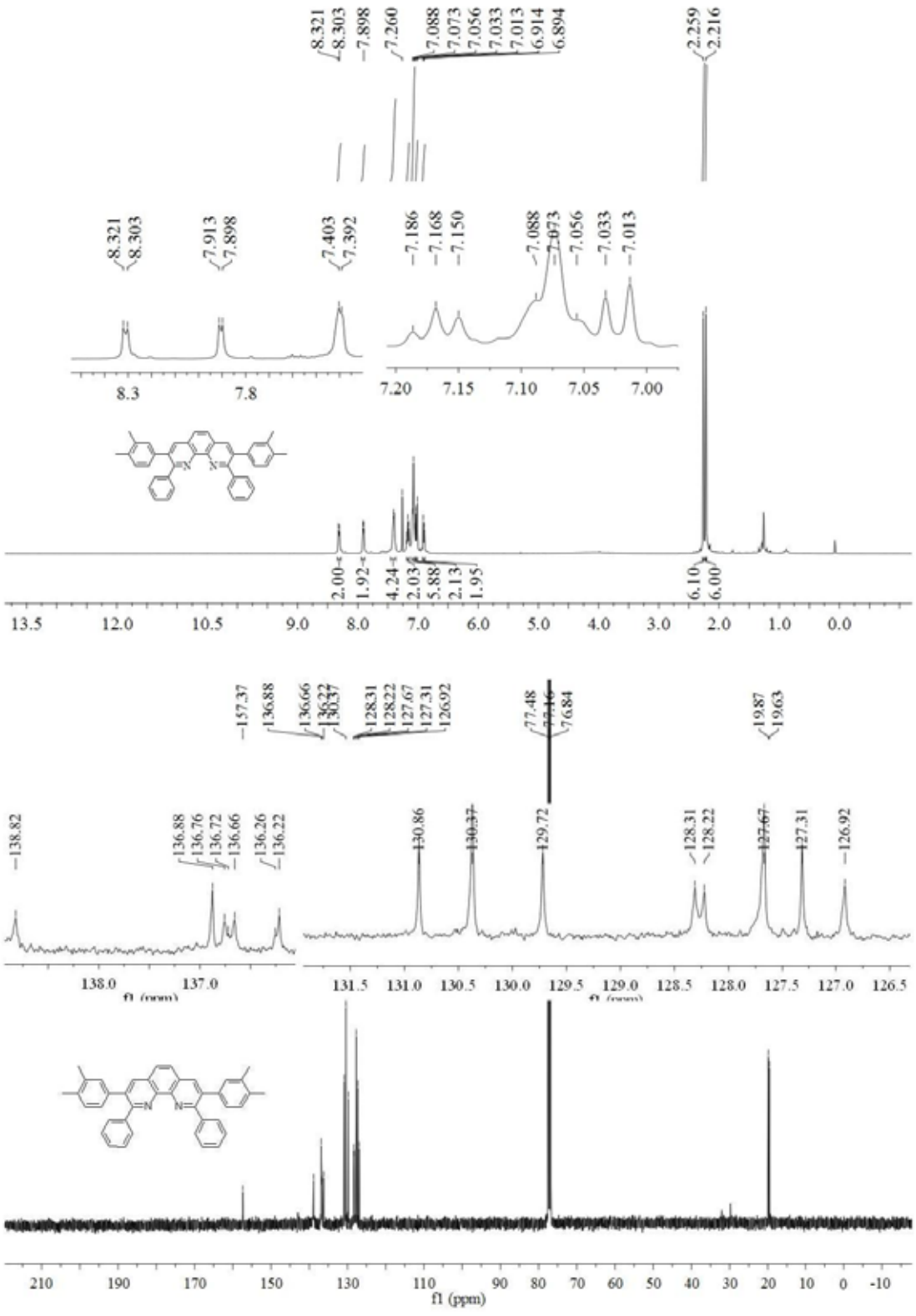


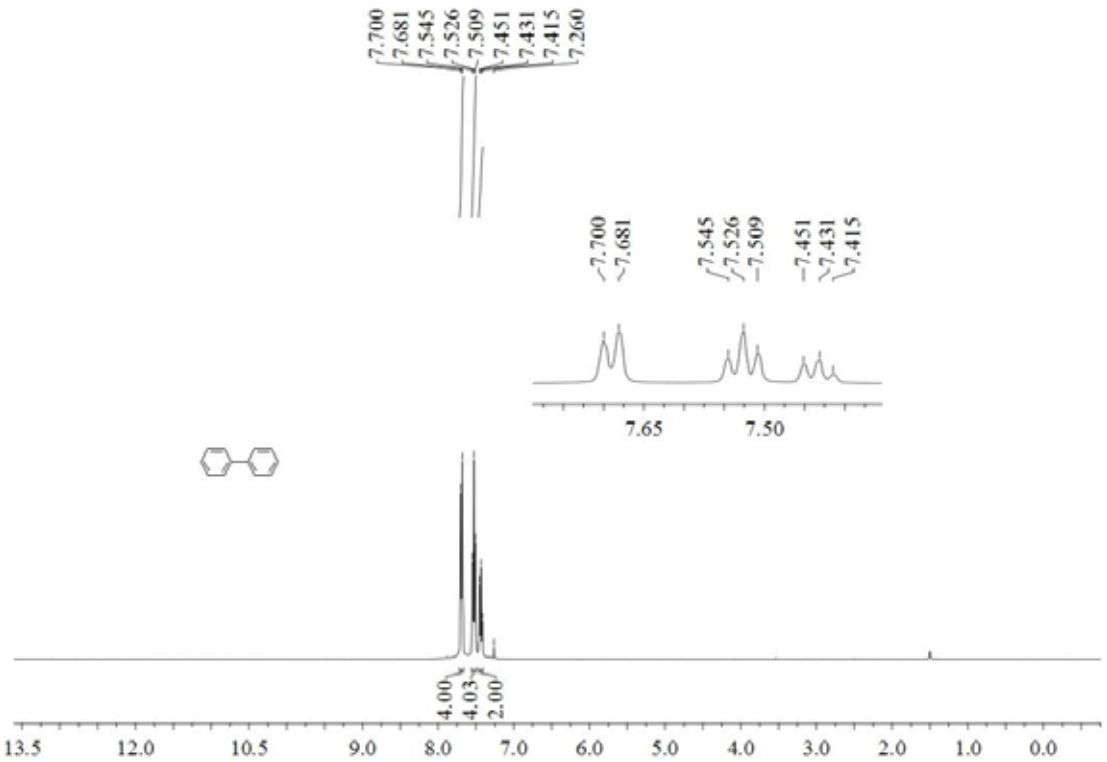


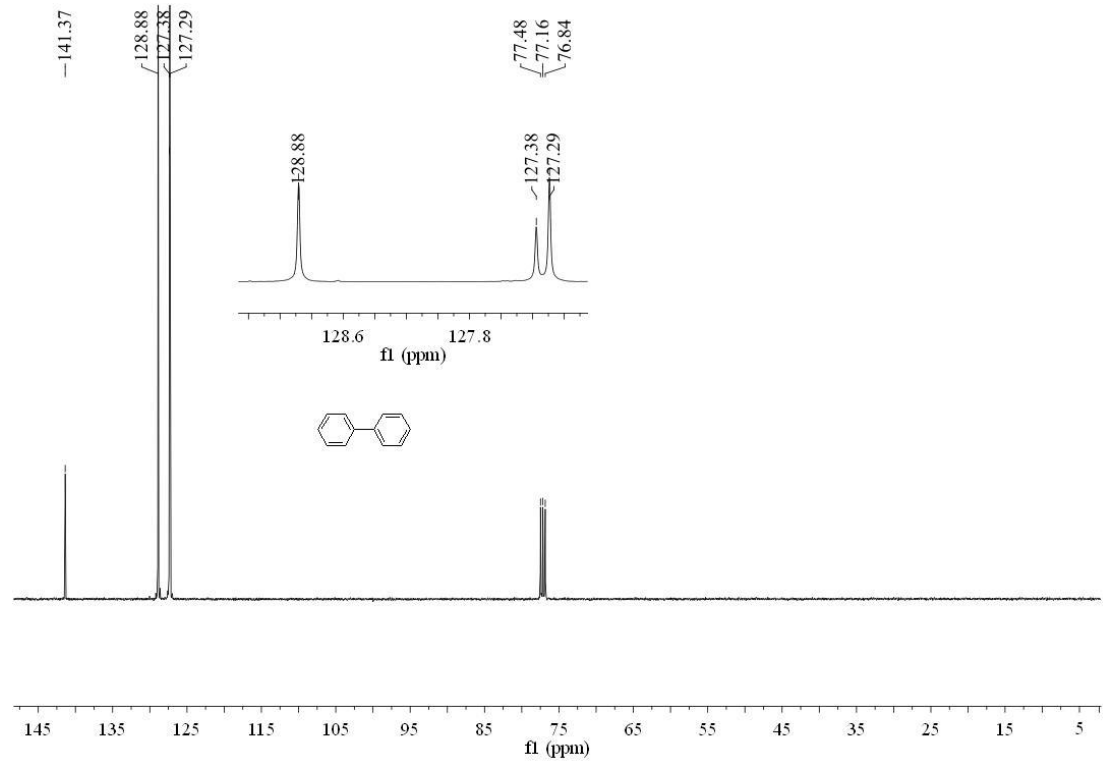



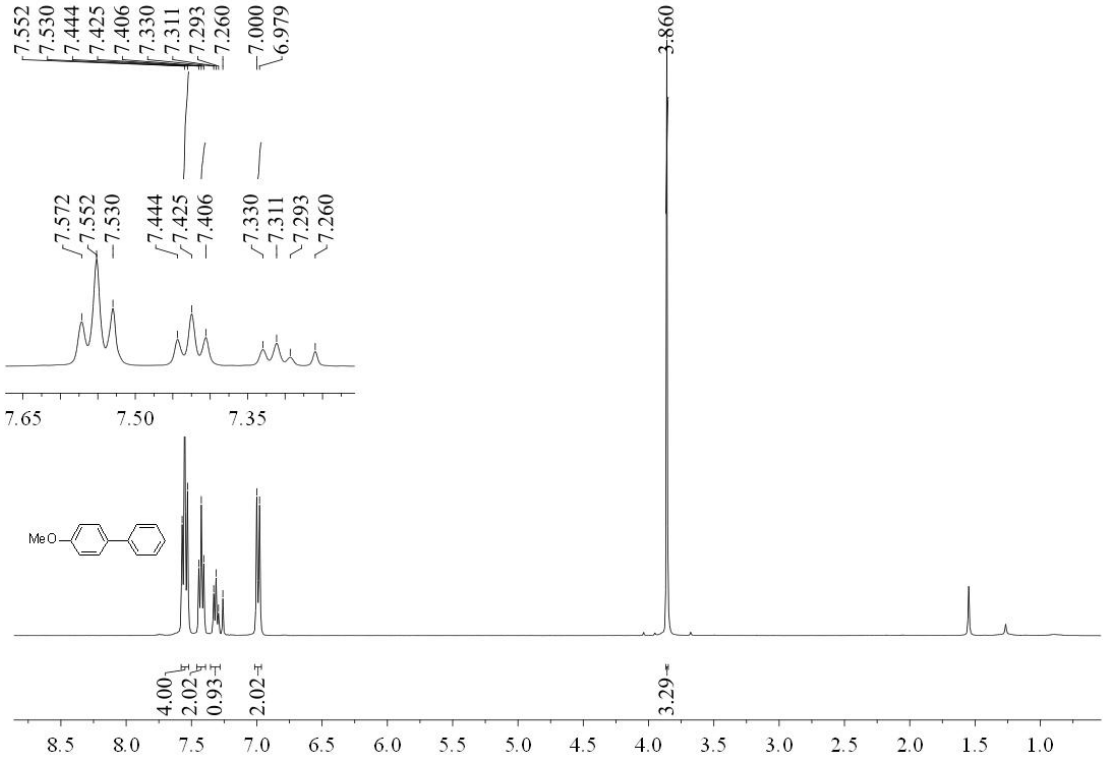




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7.000
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7.552
7.530
7.444
7.425
7.406
7.330
7.311
7.293
7.260
7.65
7.50
7.35
MeO
4.00
2.02
0.93
2.02
3.29
8.5
8.0
7.5
7.0
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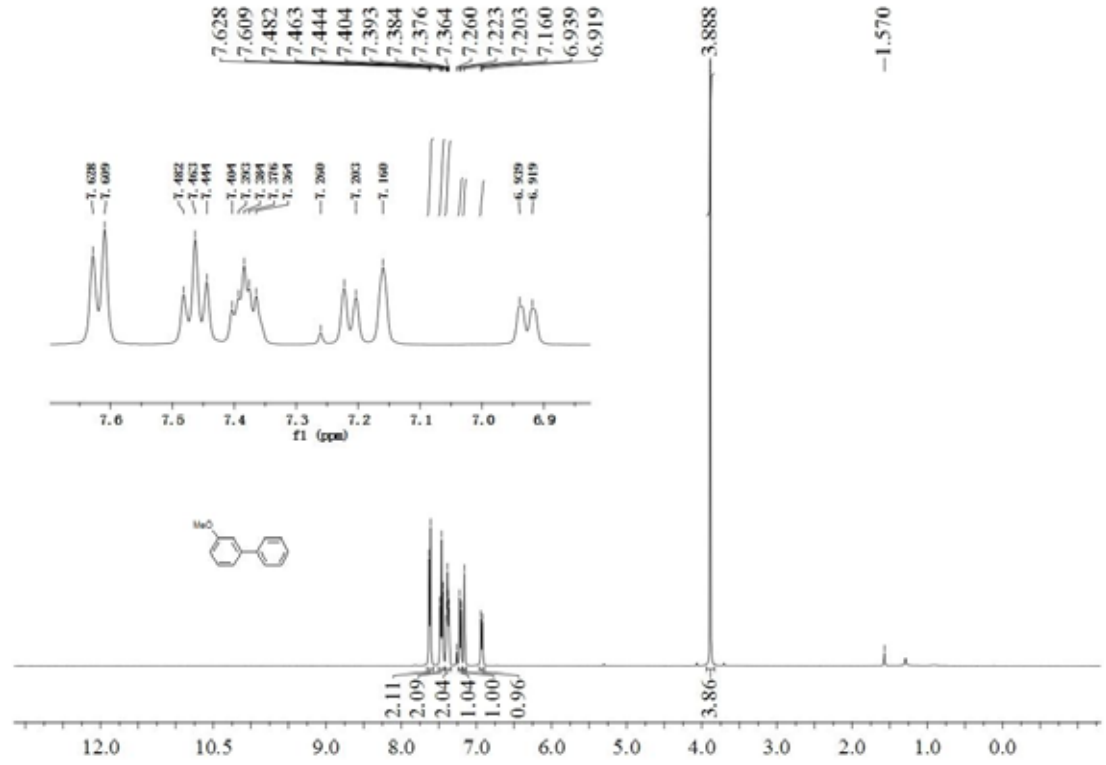
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7.160
6.939
6.919
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7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
MeO
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2.09
2.04
1.04
1.00
0.96
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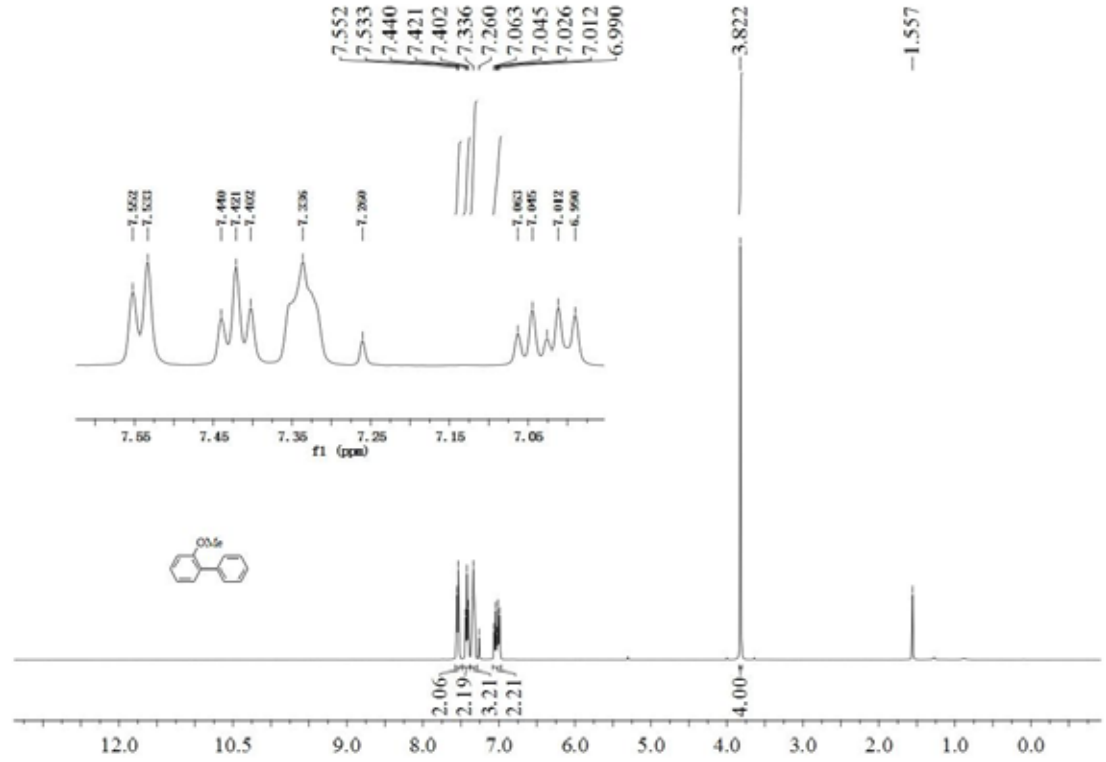


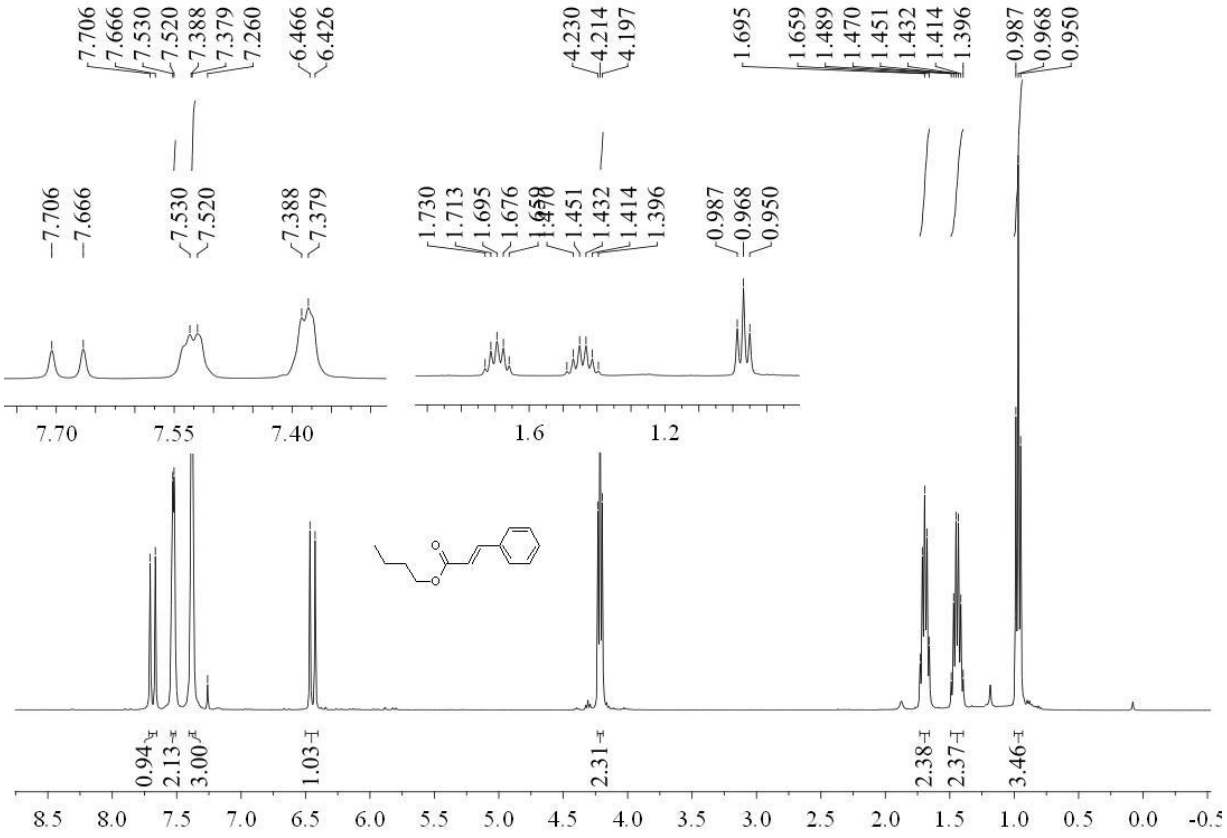

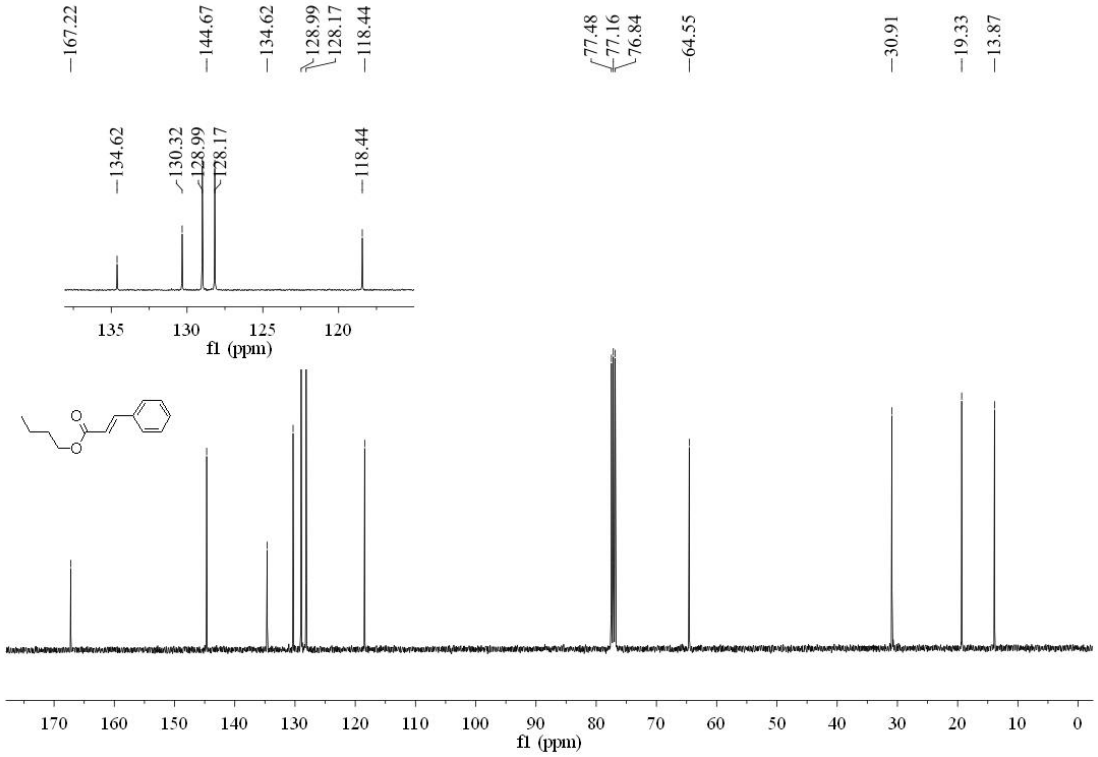
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128.99
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77.16
76.84
64.55
30.91
19.33
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134.62
130.32
128.99
128.17
118.44
135
130
125
120
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)