Supporting Information

Cu-Catalyzed tandem *N*-arylation of dihydrazides with cyclic iodoniums to yield dihydrobenzo[*c*]cinnoline derivatives

Rongrong Xie[#], Hongxu Lv[#], Xiuqing Ye, Xiangfei Kong, and Shiqing Li**

Guangxi Key Laboratory of Electrochemical and Magneto-Chemical Function Materia, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China.
E-mail: lisq@glut.edu.cn; xiangfei.kong@glut.edu.cn

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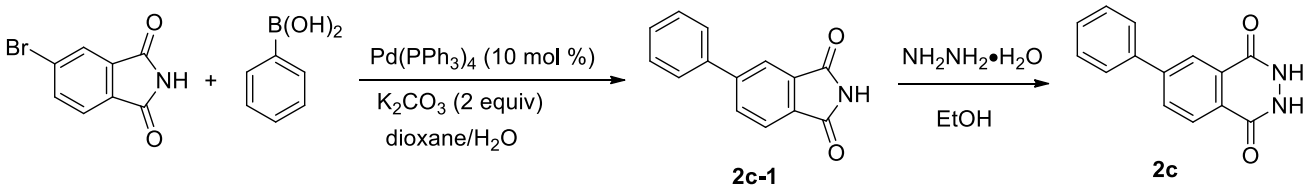
I. General remarks

NMR spectra were obtained on a BRUKER Ascend400 and Ascend500. The ^{1}H NMR (400 and 500 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm;). The ^{13}C NMR (100 and 125 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+). Melting points were determined with SGW® X-4 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Hydrazdes were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd. Cu salts were purchased from Adamas-beta Ltd. Cyclic iodonium salts[1] were prepared according to the literature procedures.

II. General procedure for synthesis of substituted hydrazides



Synthesis 2c-1: The mixture of 5-bromoisoindoline-1,3-dione (226 mg, 1 mmol), phenylboronic acid (1.5 mmol), $Pd(PPh_3)_4$ (10 mol %), K_2CO_3 (276 mg, 2mmol), dioxane (3 mL) and H_2O (1 mL) was reacted at 100 ℃ for 10 h. The reaction mixture was extracted with EtOAc, and dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1, v/v) to give pure **2c-1**.

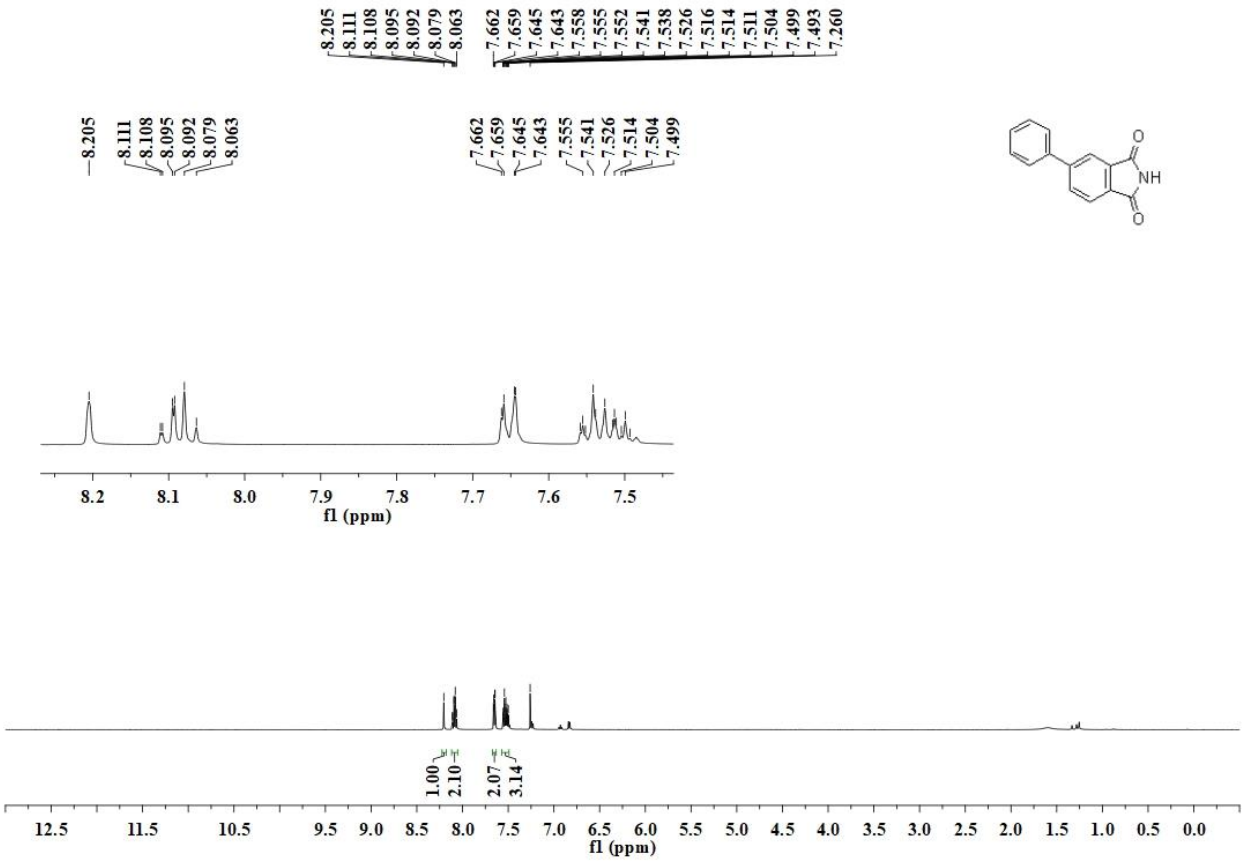
Synthesis of 2c: The mixture of **2c-1** (0.4 mmol), hydrazine hydrate (0.4 mmol), and EtOH (2 mL) was reacted at 100 ℃ for 10 h. The reaction mixture was extracted with EtOAc, and dried over anhydrous Na_2SO_4, concentrated by rotary evaporation and recrystallized by EtOH to give **2c**.

5-Phenylisoindoline-1,3-dione (2c-1): A white solid (89 mg, 40% yield). M.p.: 135–137 ℃. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 8.11–8.06 (m, 2H), 7.66–7.64 (m, 2H), 7.56–7.49 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.04, 162.84, 149.91, 138.27, 134.88, 132.42, 129.73, 129.59, 127.64, 126.25, 124.13, 115.42 ppm. HRMS (ESI) *m/z*: calcd for $C_{14}H_{10}NO_2$ (M+H) 224.0712, found 224.0717.

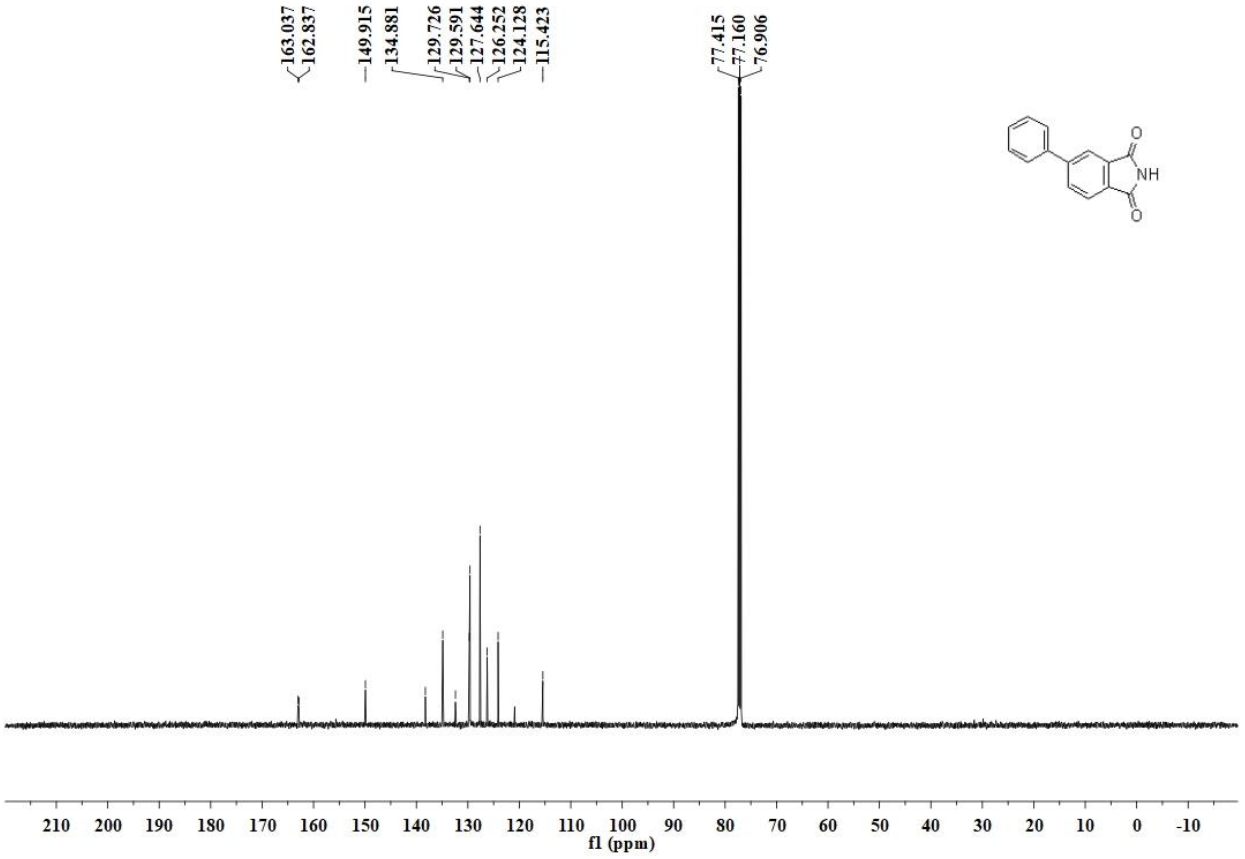
6-Phenyl-2,3-dihydrophthalazine-1,4-dione (2c): A white solid (90 mg, 95% yield). M.p.: 247–249 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.30 (s, 1H), 8.16–8.11 (m, 2H), 7.79 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.05, 155.75, 143.38, 138.87, 130.33, 129.21, 128.82, 128.44, 127.12, 126.25, 122.89, 115.25 ppm. HRMS (ESI) *m/z*: calcd for $C_{14}H_{11}N_2O_2$ (M+H) 239.0821, found 239.0825.

III. Copies of ^{1}H and ^{13}C spectra

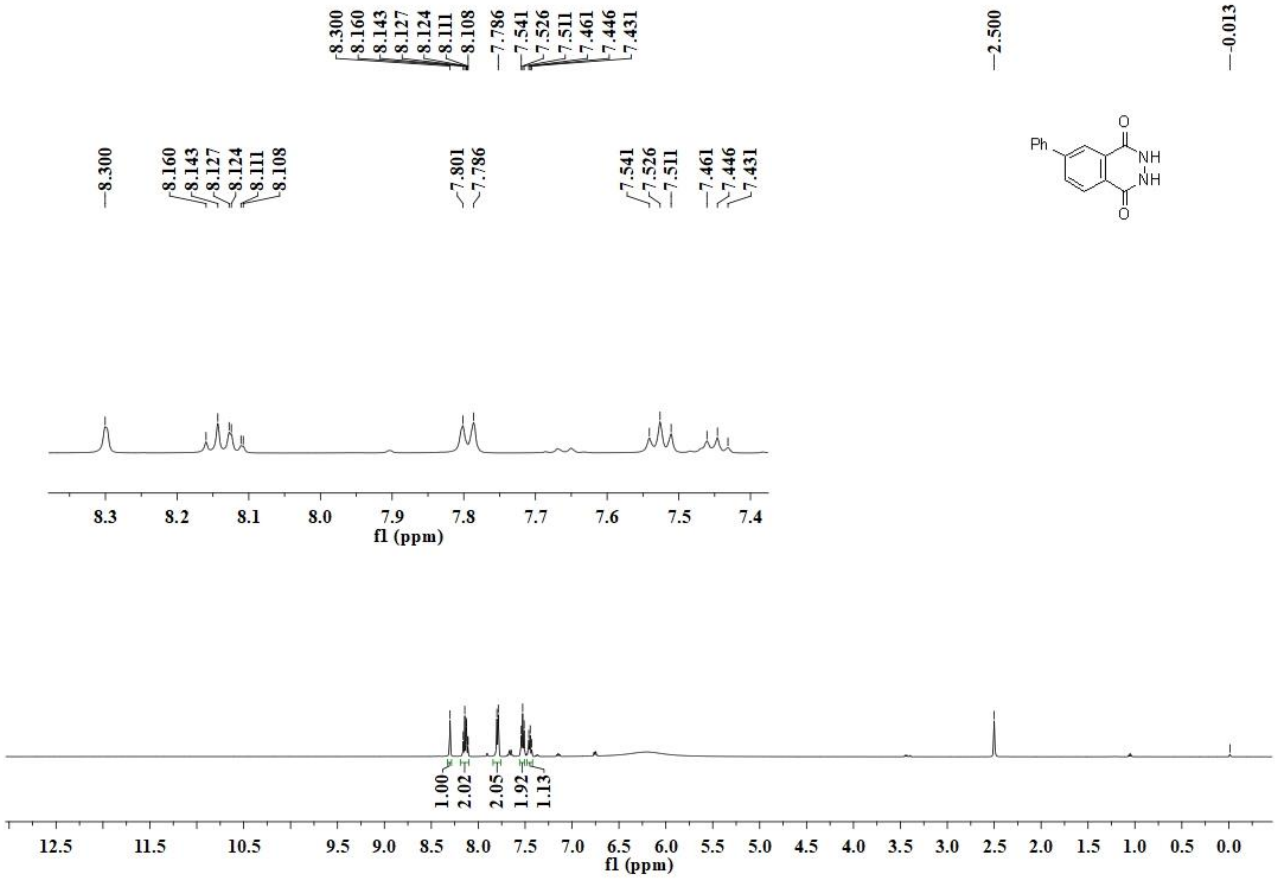
^{1}H NMR (500 MHz, $CDCl_3$) of **2c-1**



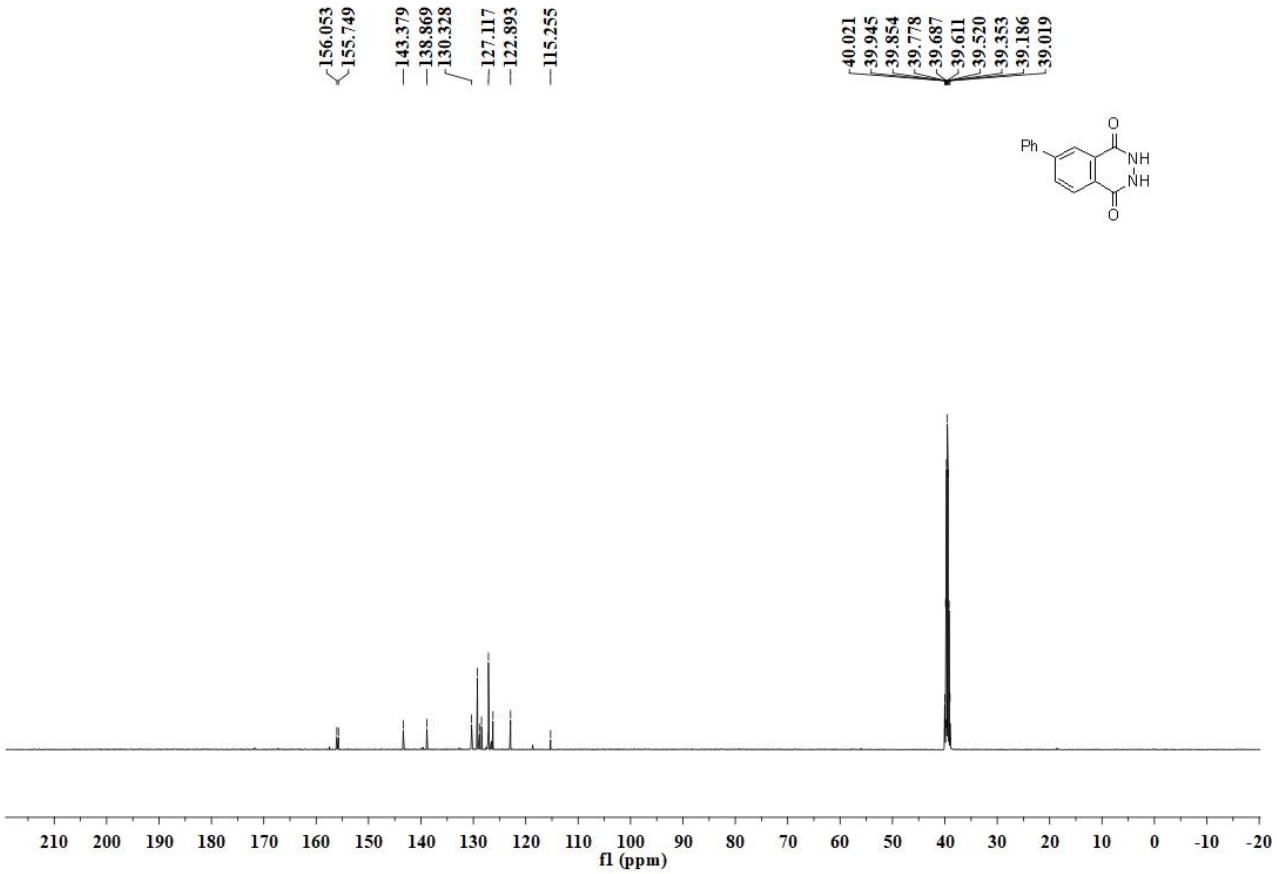
^{13}C NMR (125 MHz, $CDCl_3$) of **2c-1**



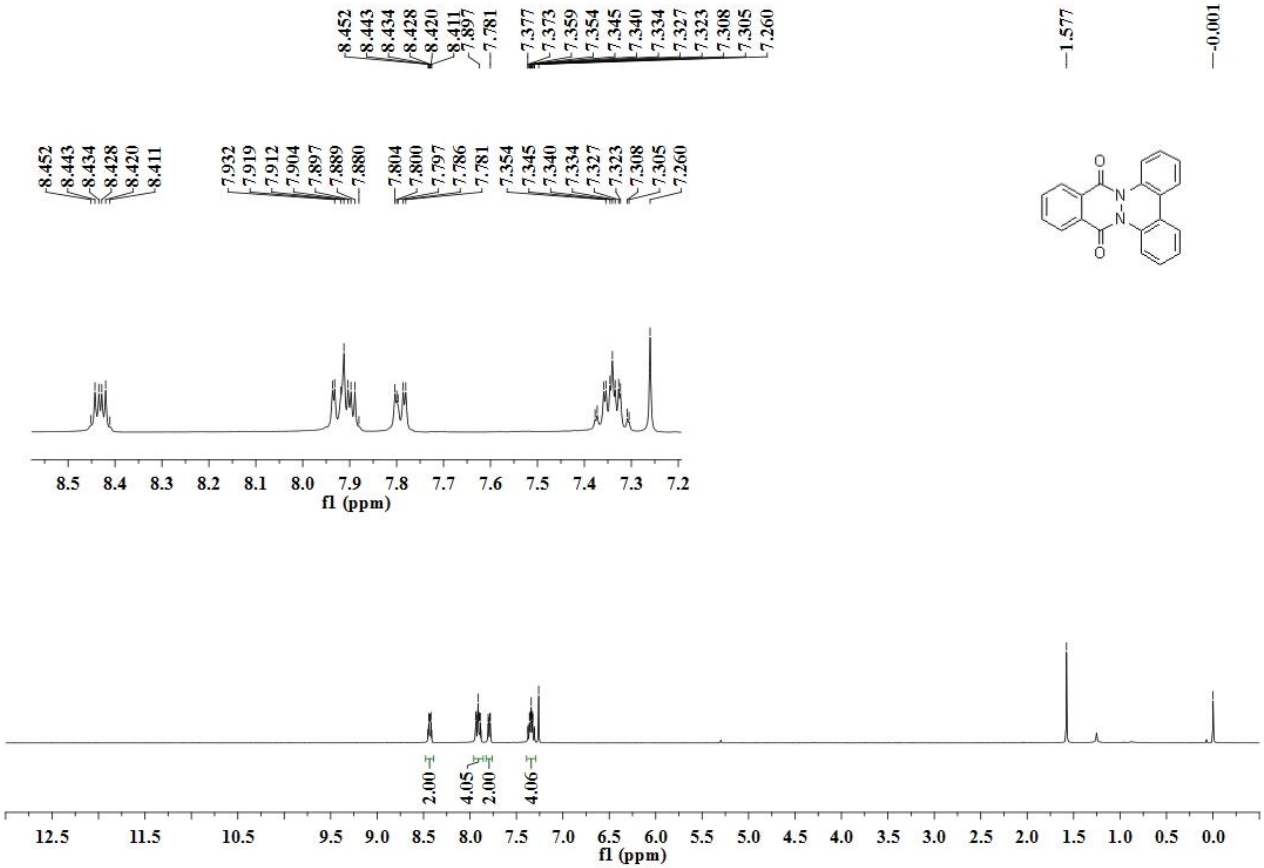
^{1}H NMR (500 MHz, DMSO-d_6) of **2c**



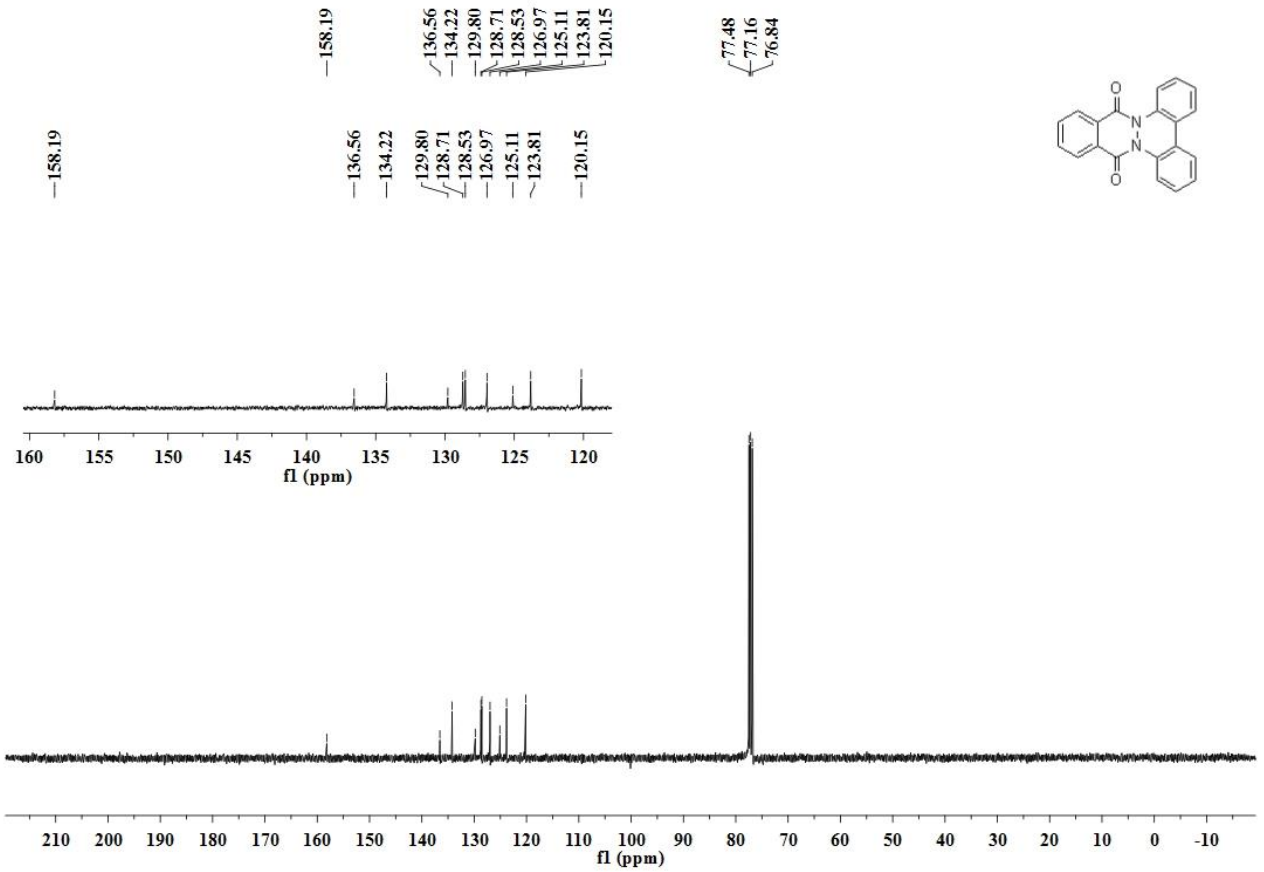
^{13}C NMR (125 MHz, DMSO-d_6) of **2c**



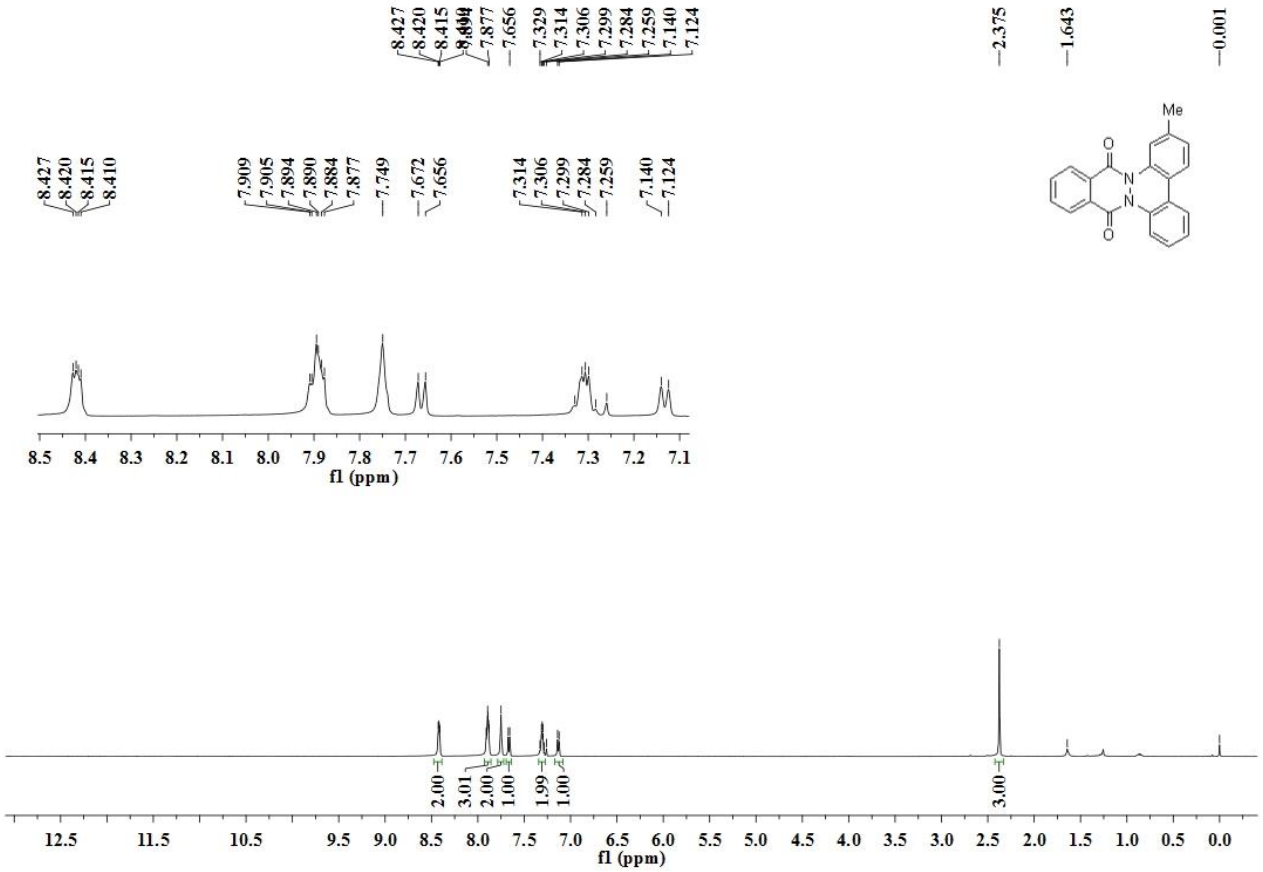
^{1}H NMR (400 MHz,$CDCl_3$) of **3a**



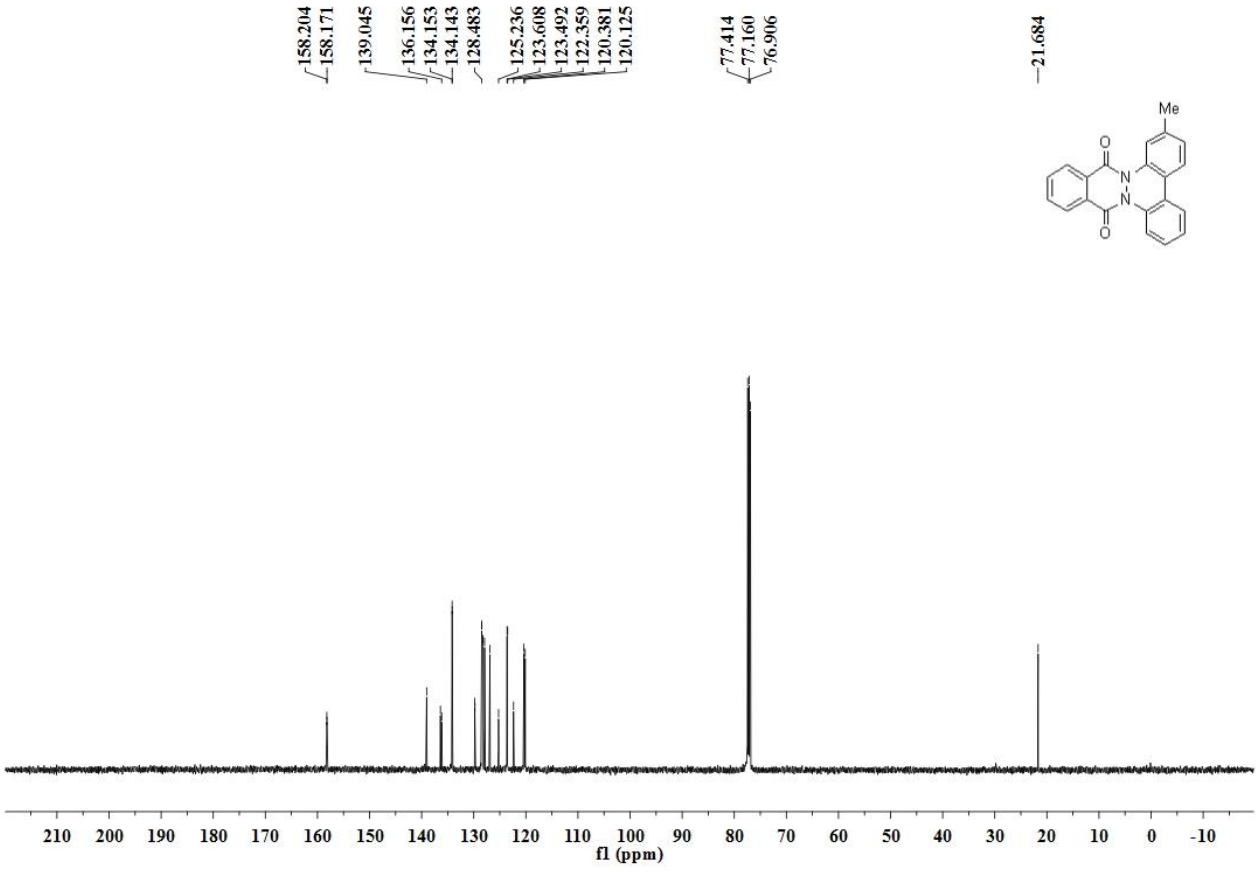
^{13}C NMR (100 MHz, $CDCl_3$) of **3a**



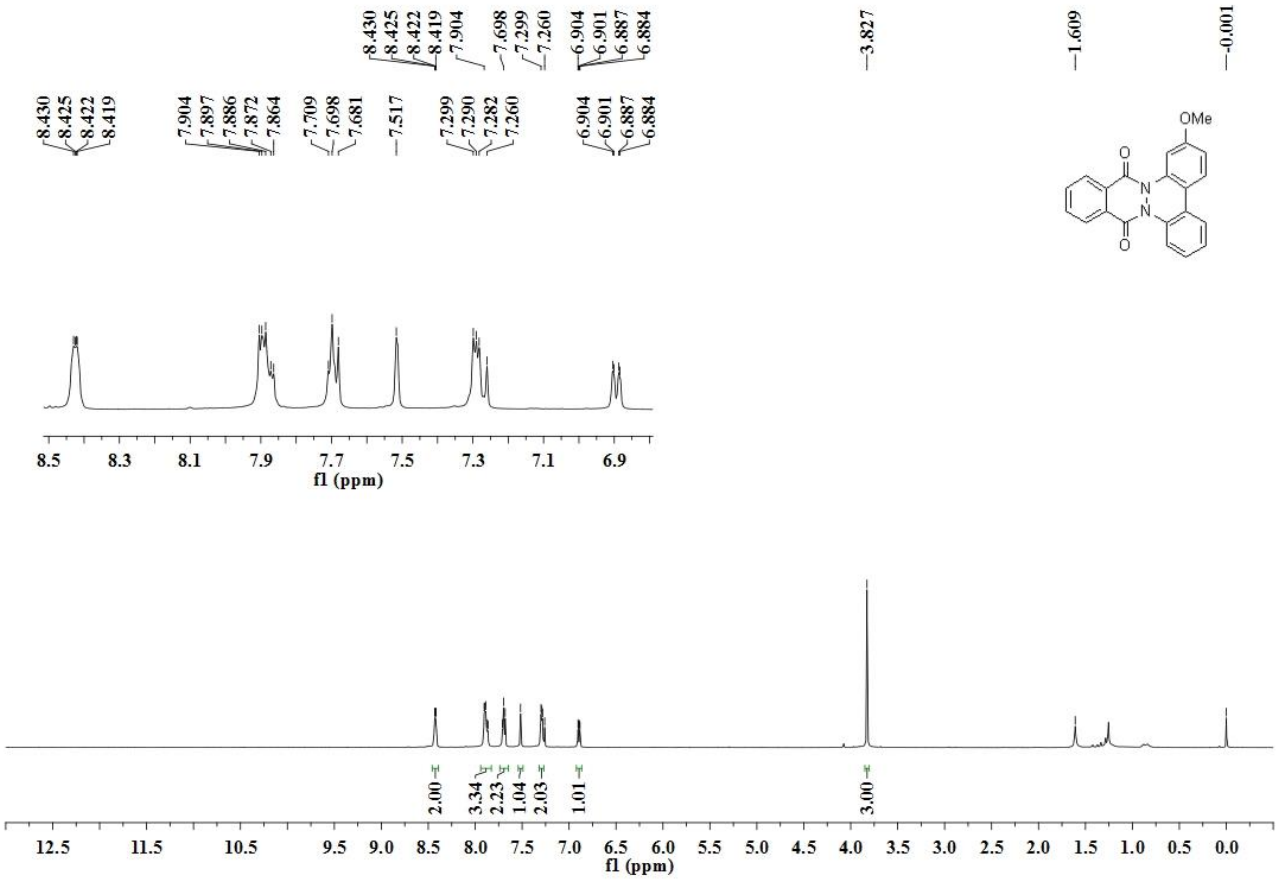
^{1}H NMR (500 MHz,$CDCl_3$) of **3b**



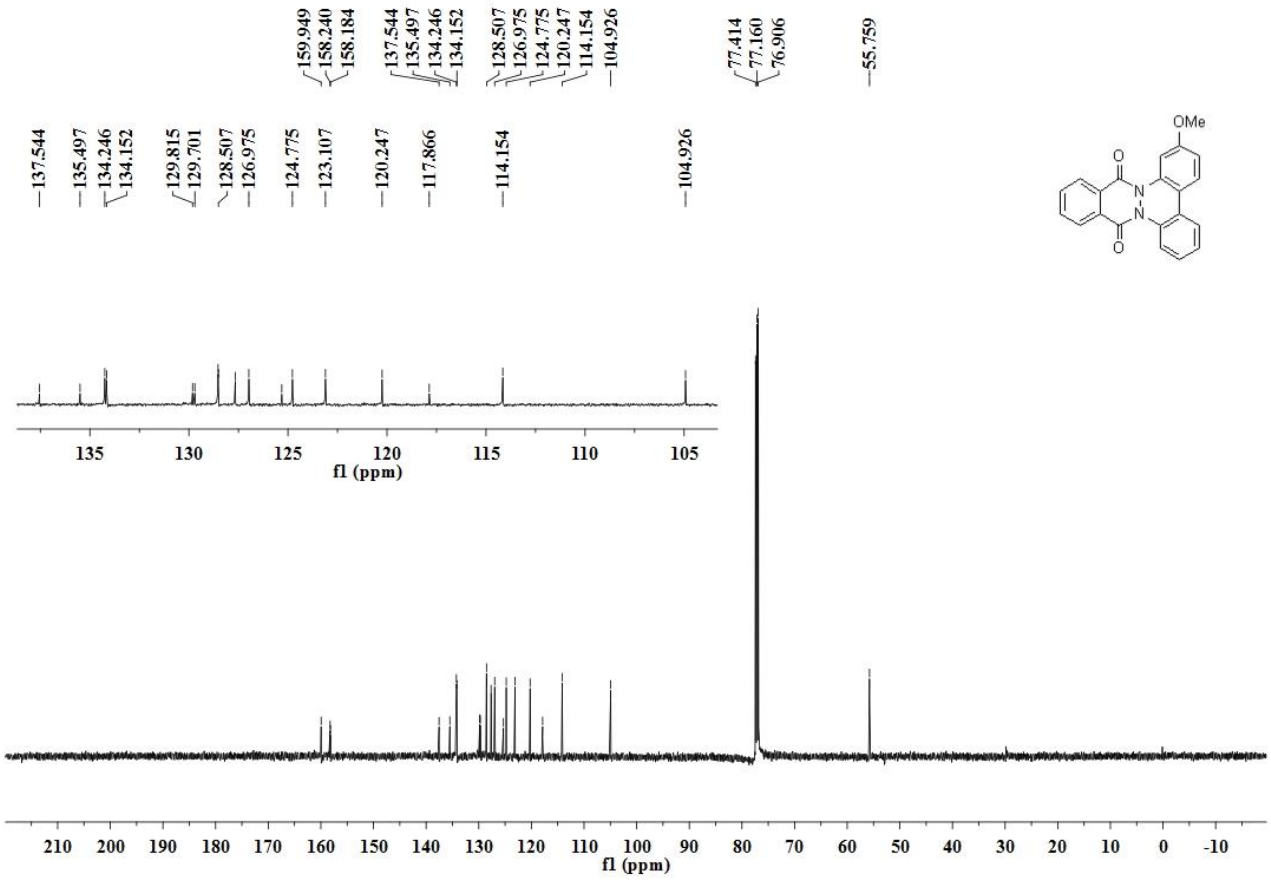
^{13}C NMR (125 MHz, $CDCl_3$) of **3b**



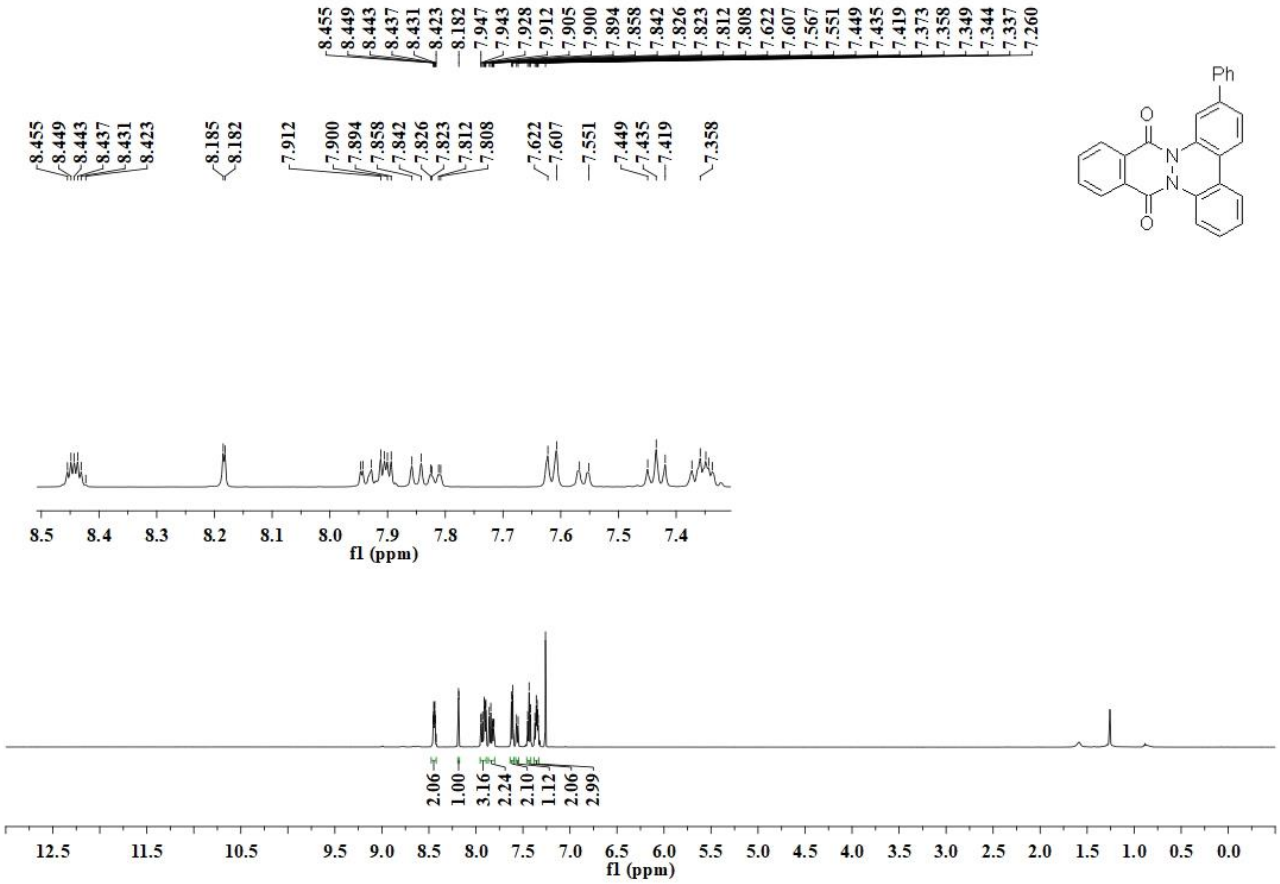
^{1}H NMR (500 MHz, $CDCl_3$) of **3c**



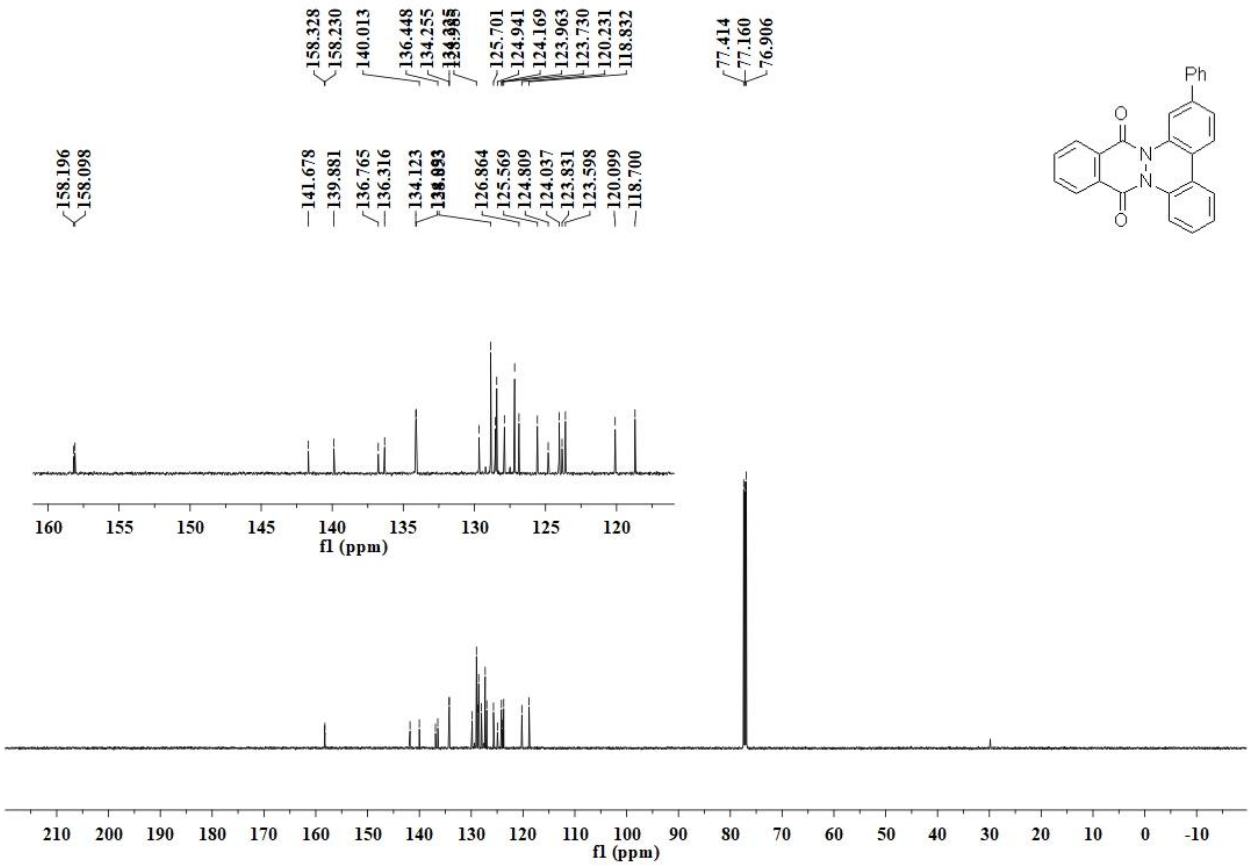
^{13}C NMR (125 MHz, $CDCl_3$) of **3c**



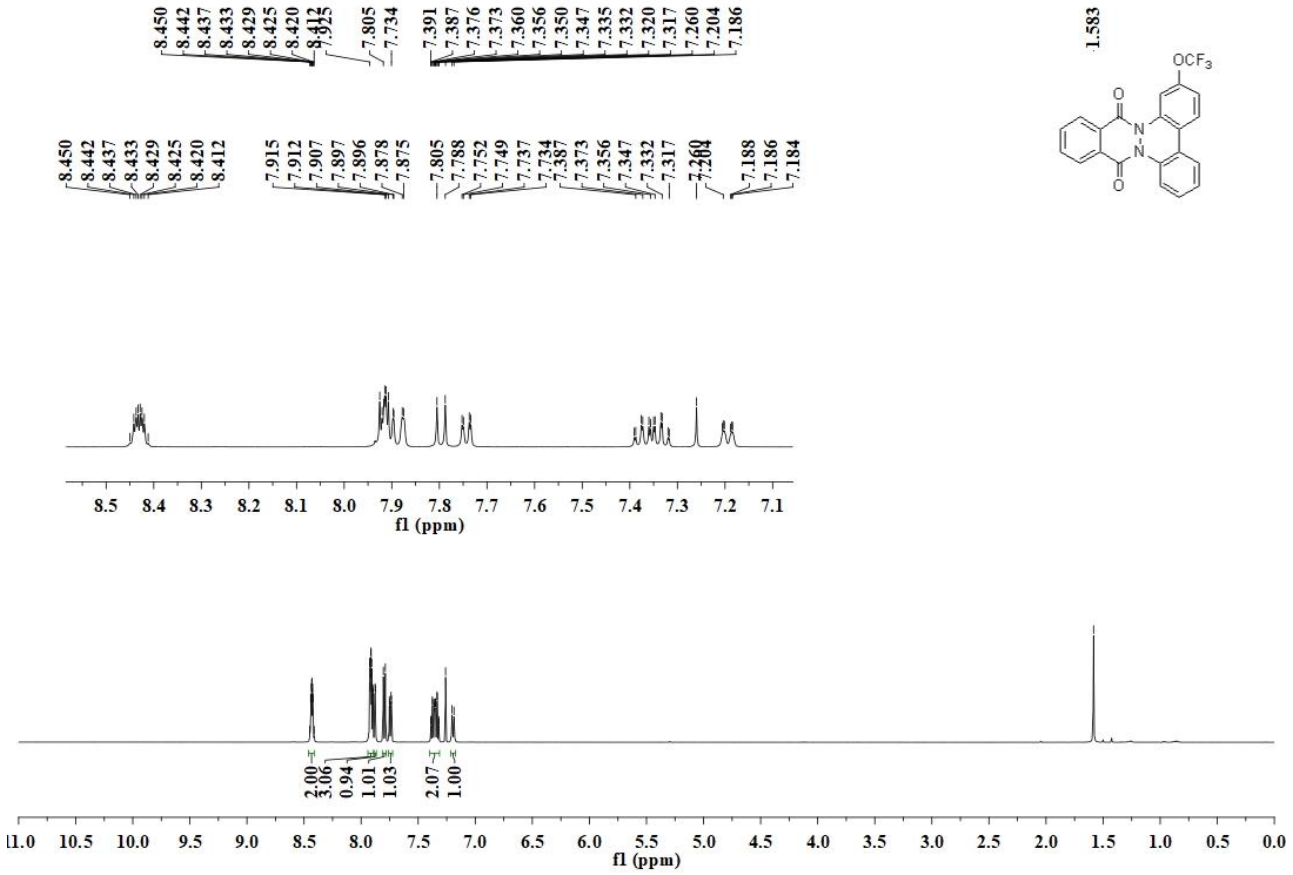
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



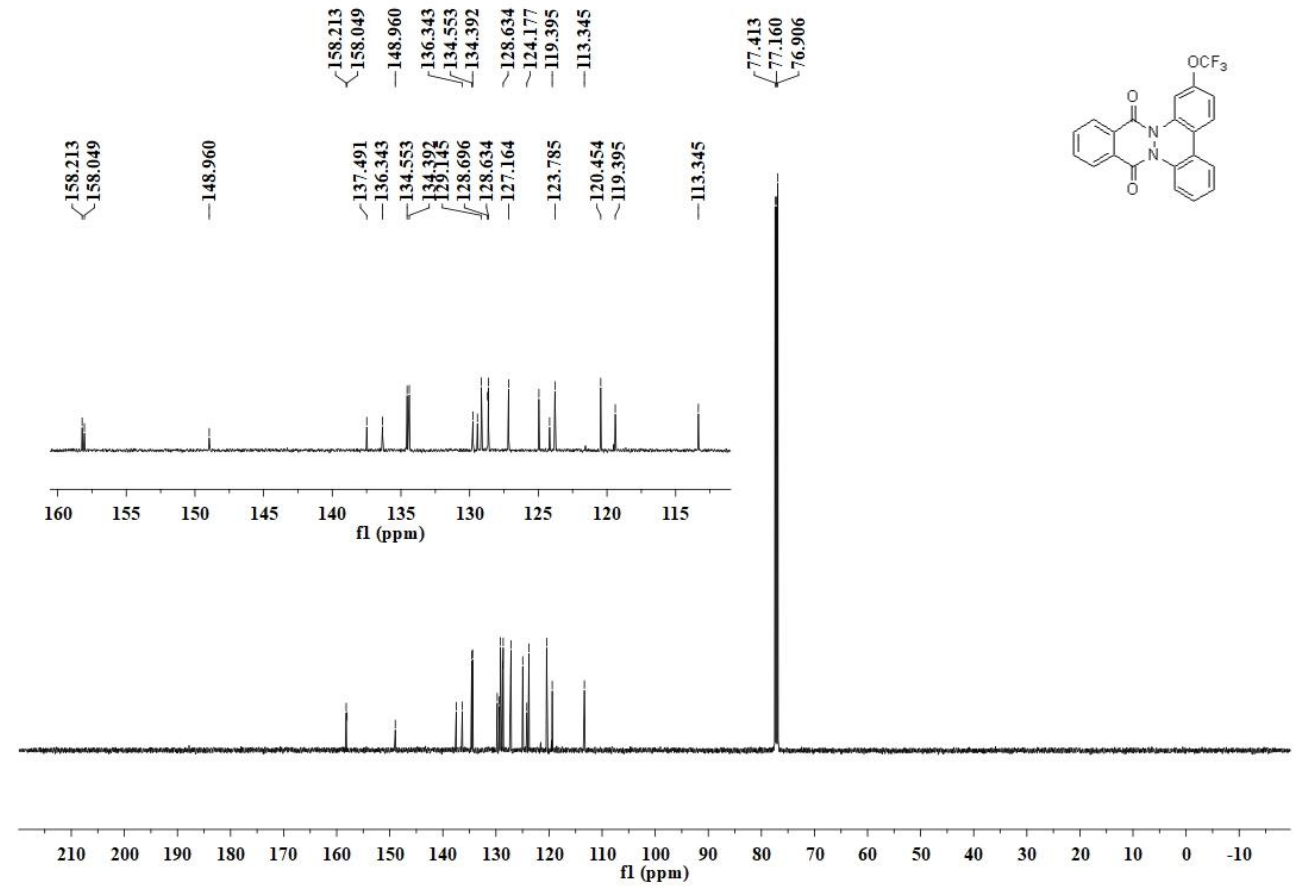
^{13}C NMR (125 MHz, $CDCl_3$) of **3d**



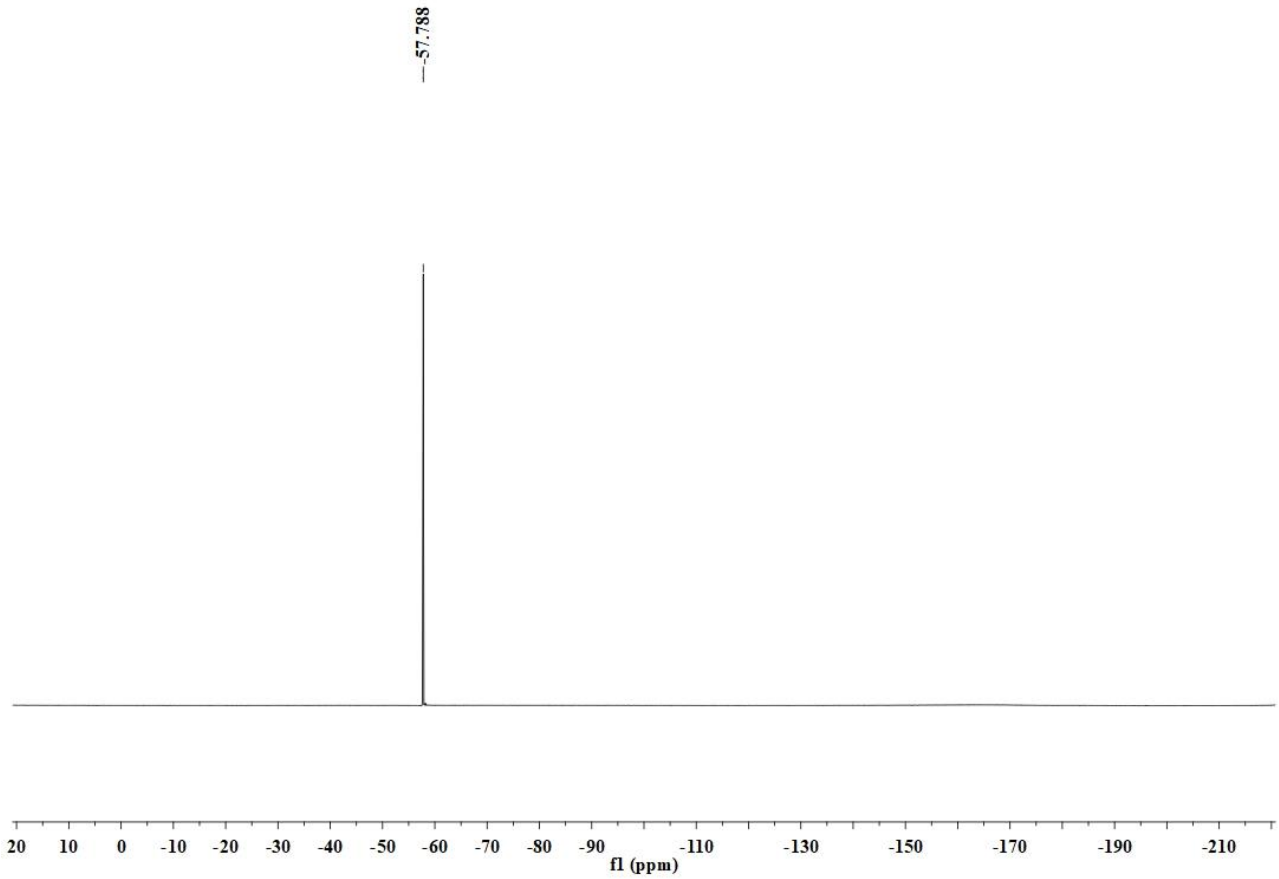
^{1}H NMR (500 MHz, $CDCl_3$) of **3e**



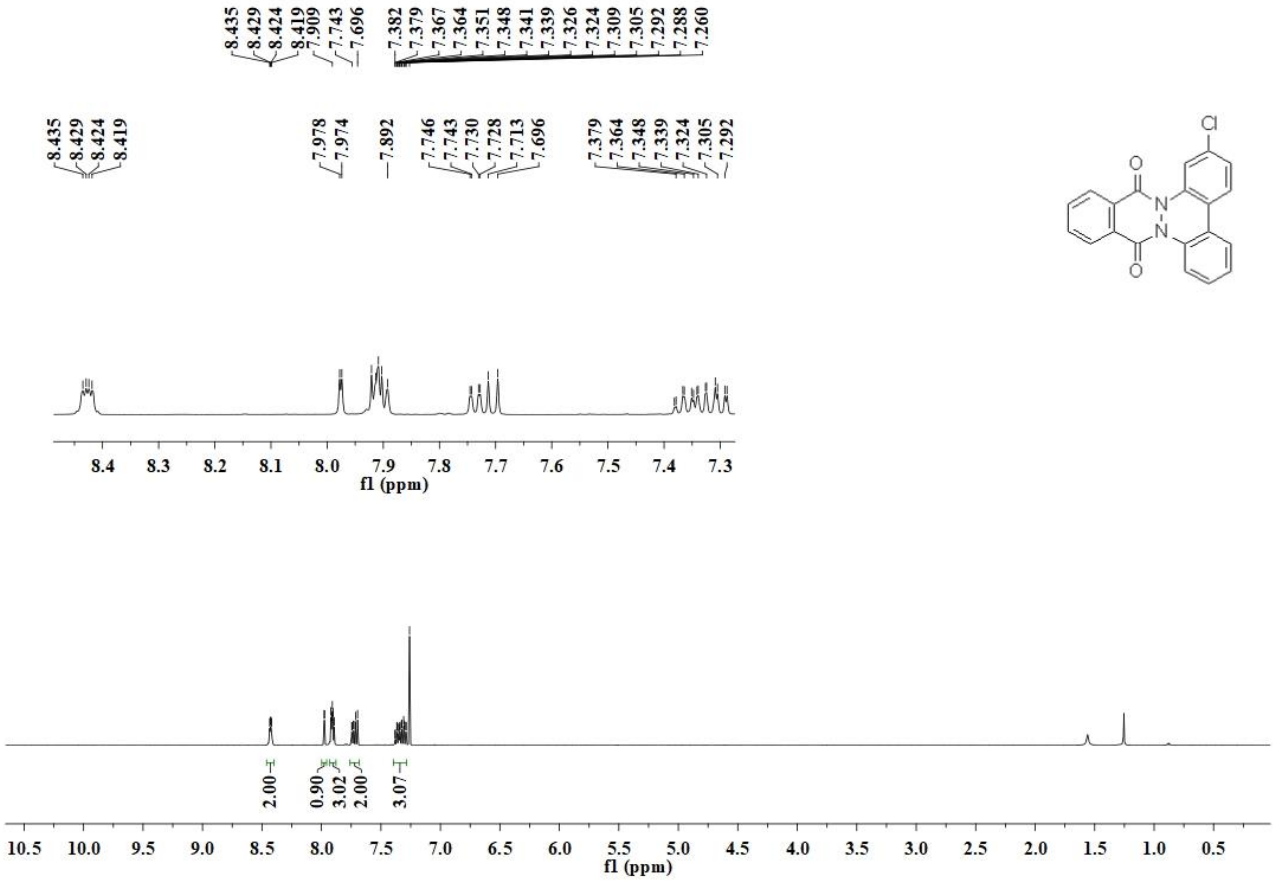
^{13}C NMR (125 MHz, $CDCl_3$) of **3e**



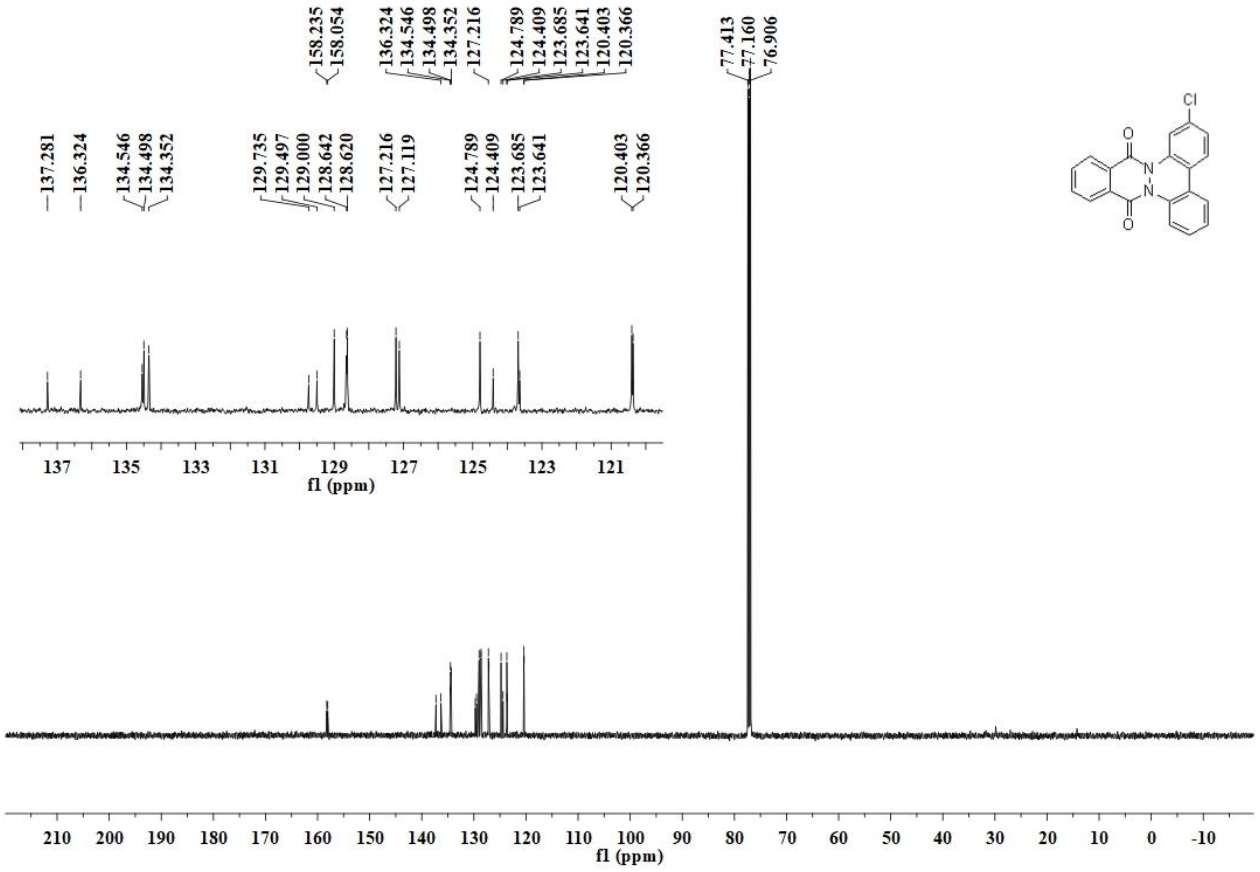
^{19}F NMR (470 MHz, $CDCl_3$) of **3e**



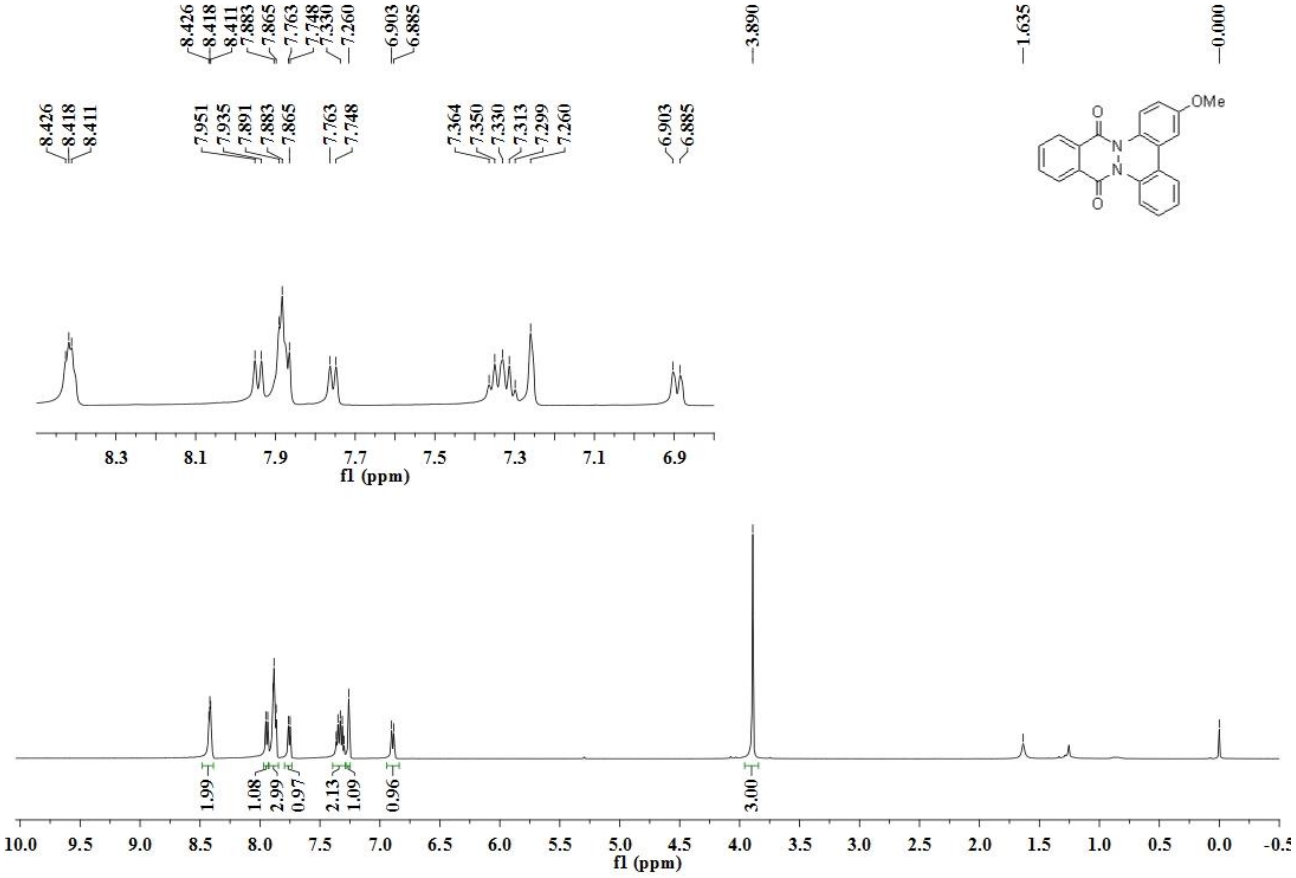
^{1}H NMR (500 MHz, $CDCl_3$) of **3f**



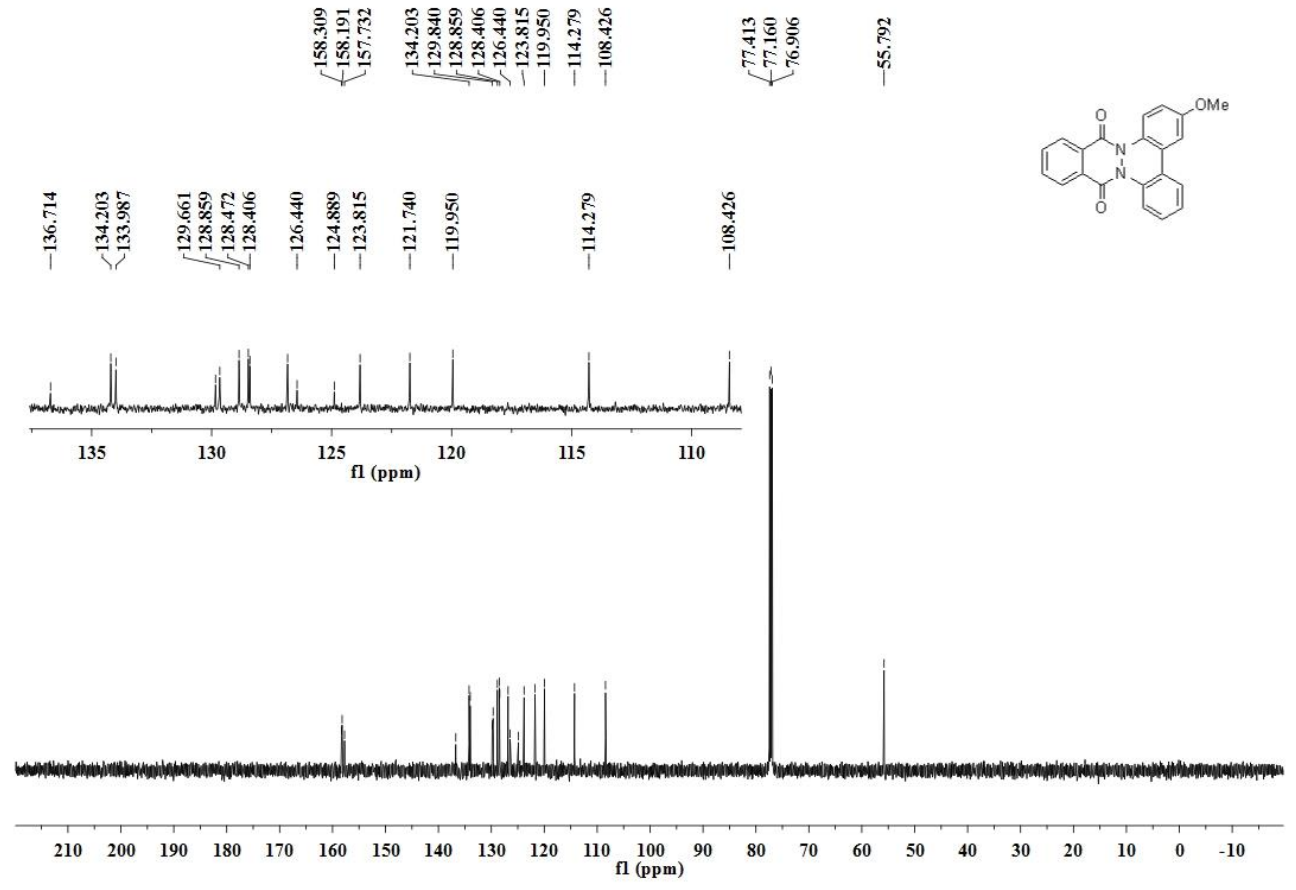
^{13}C NMR (125 MHz, $CDCl_3$) of **3f**



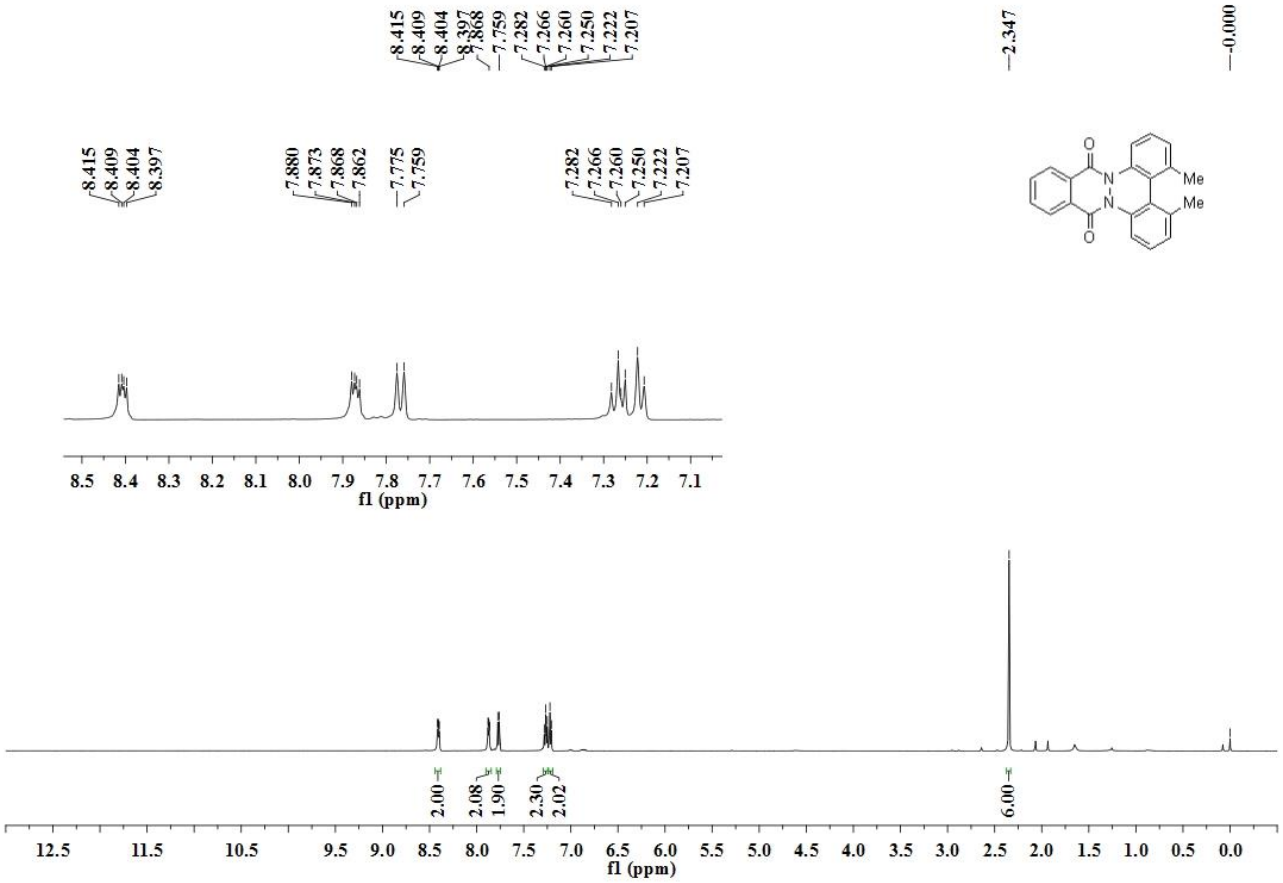
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



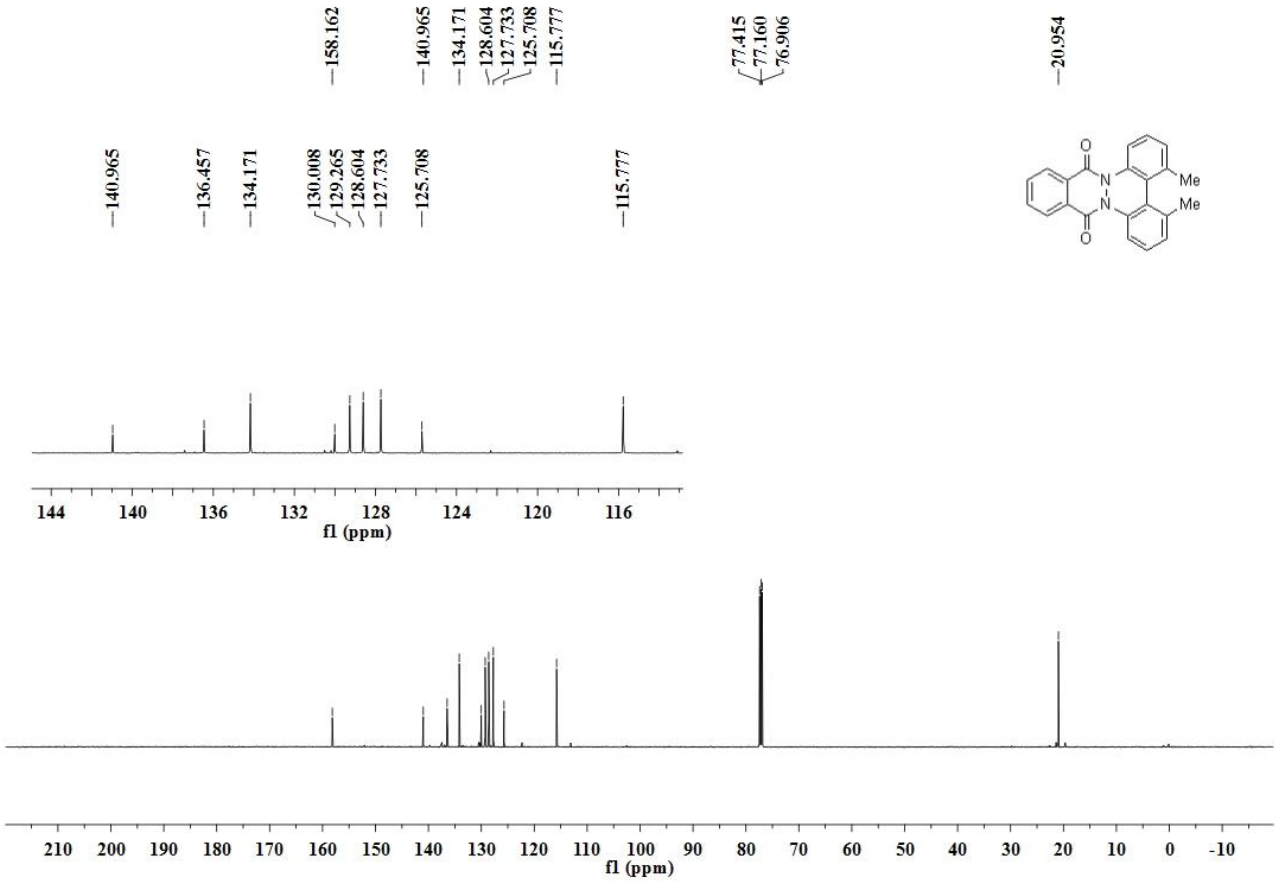
^{13}C NMR (125 MHz, $CDCl_3$) of **3g**



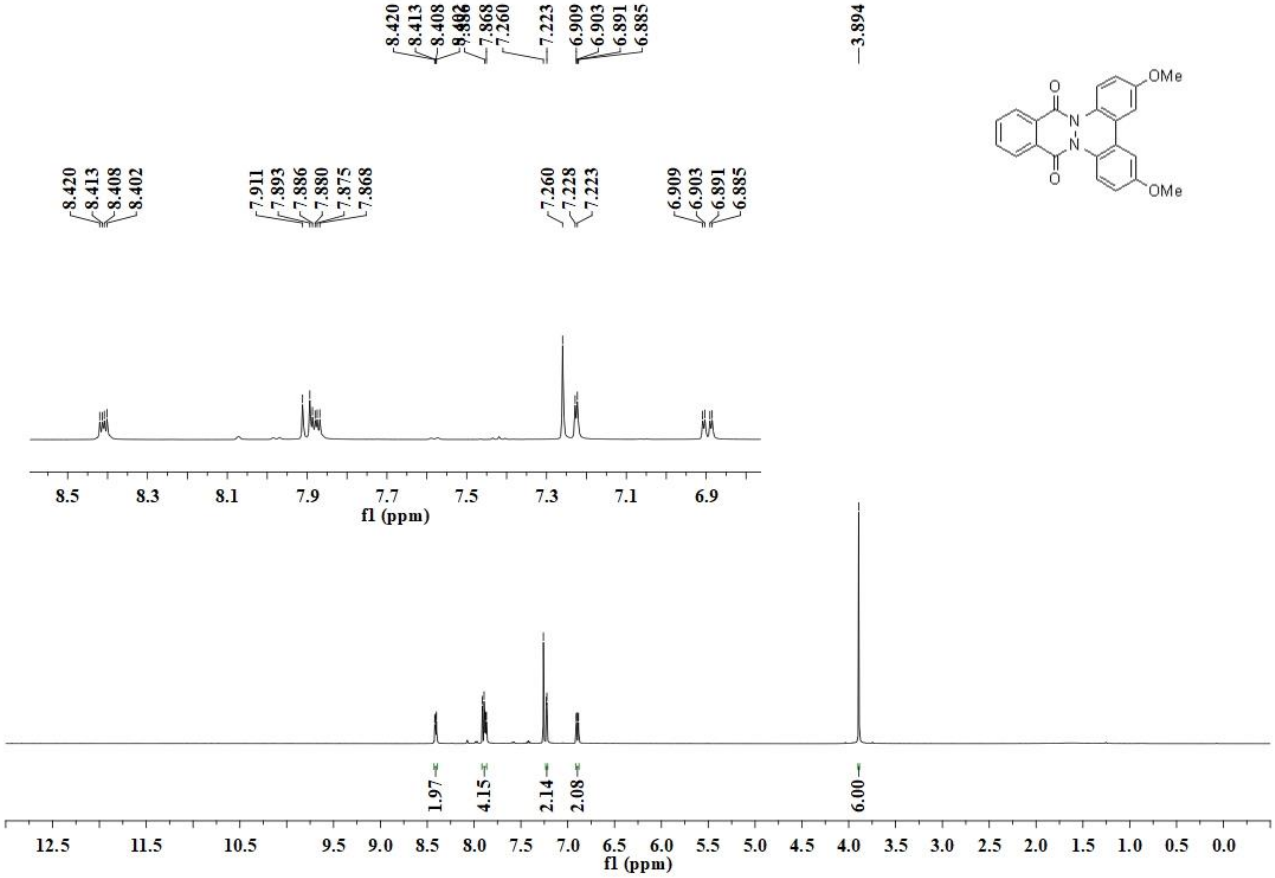
^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



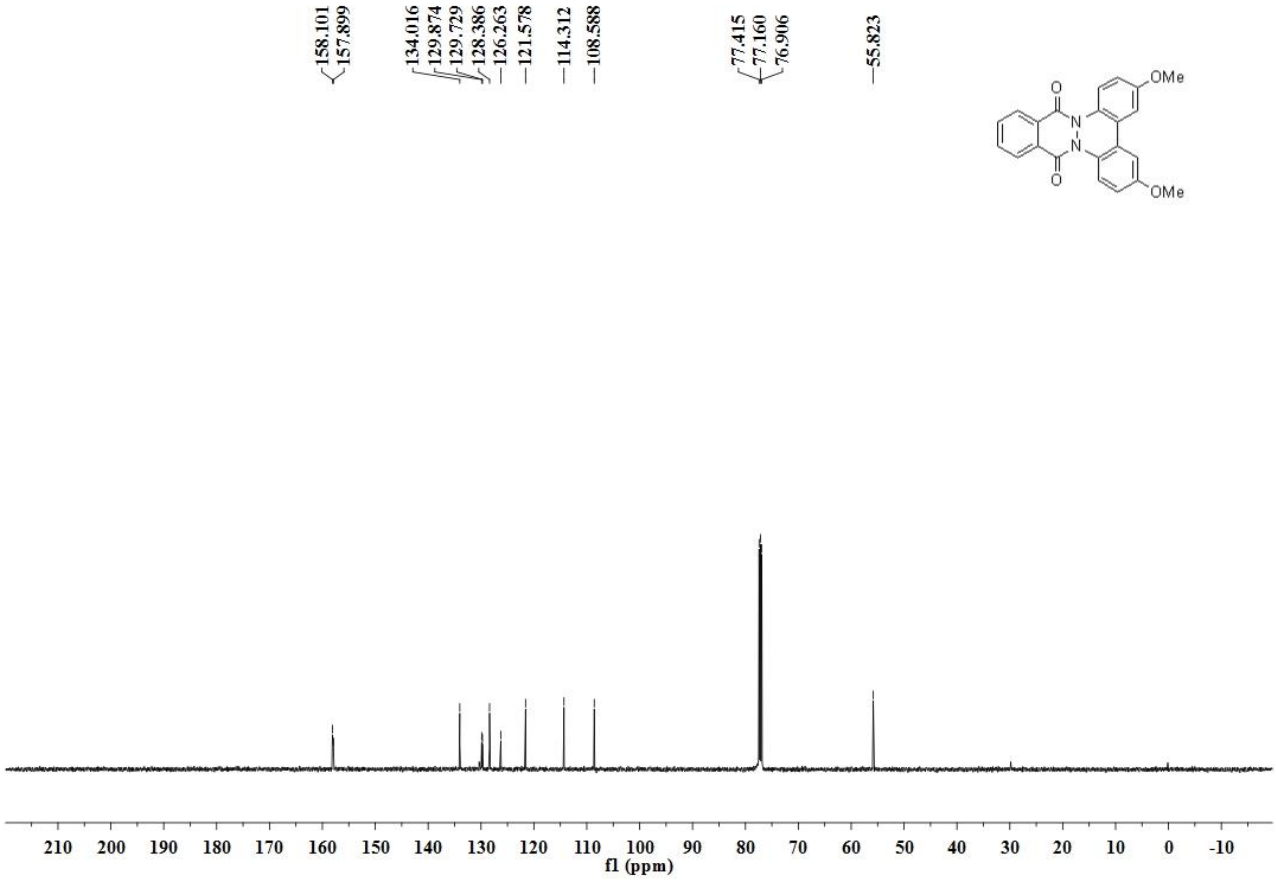
^{13}C NMR (125 MHz, $CDCl_3$) of **3h**



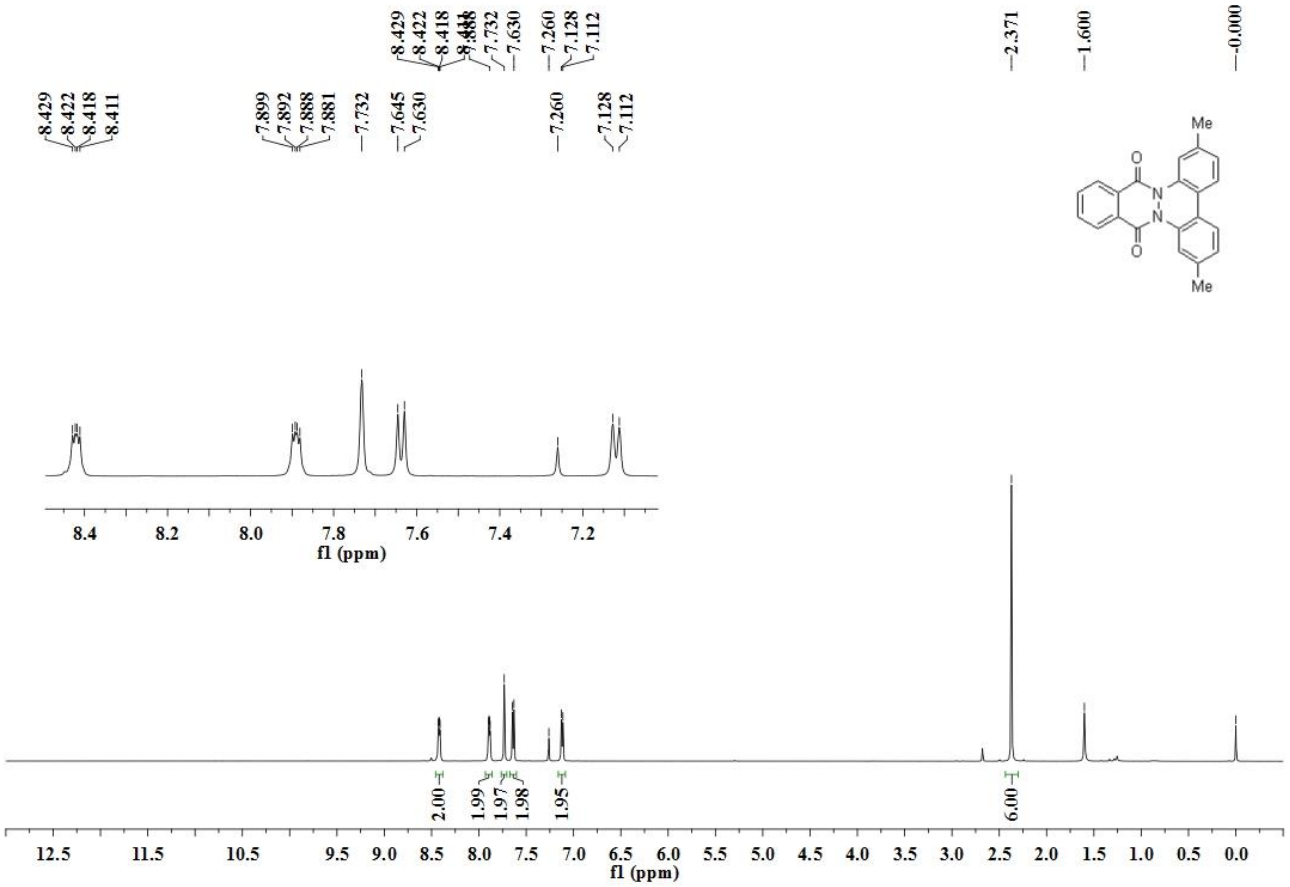
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**



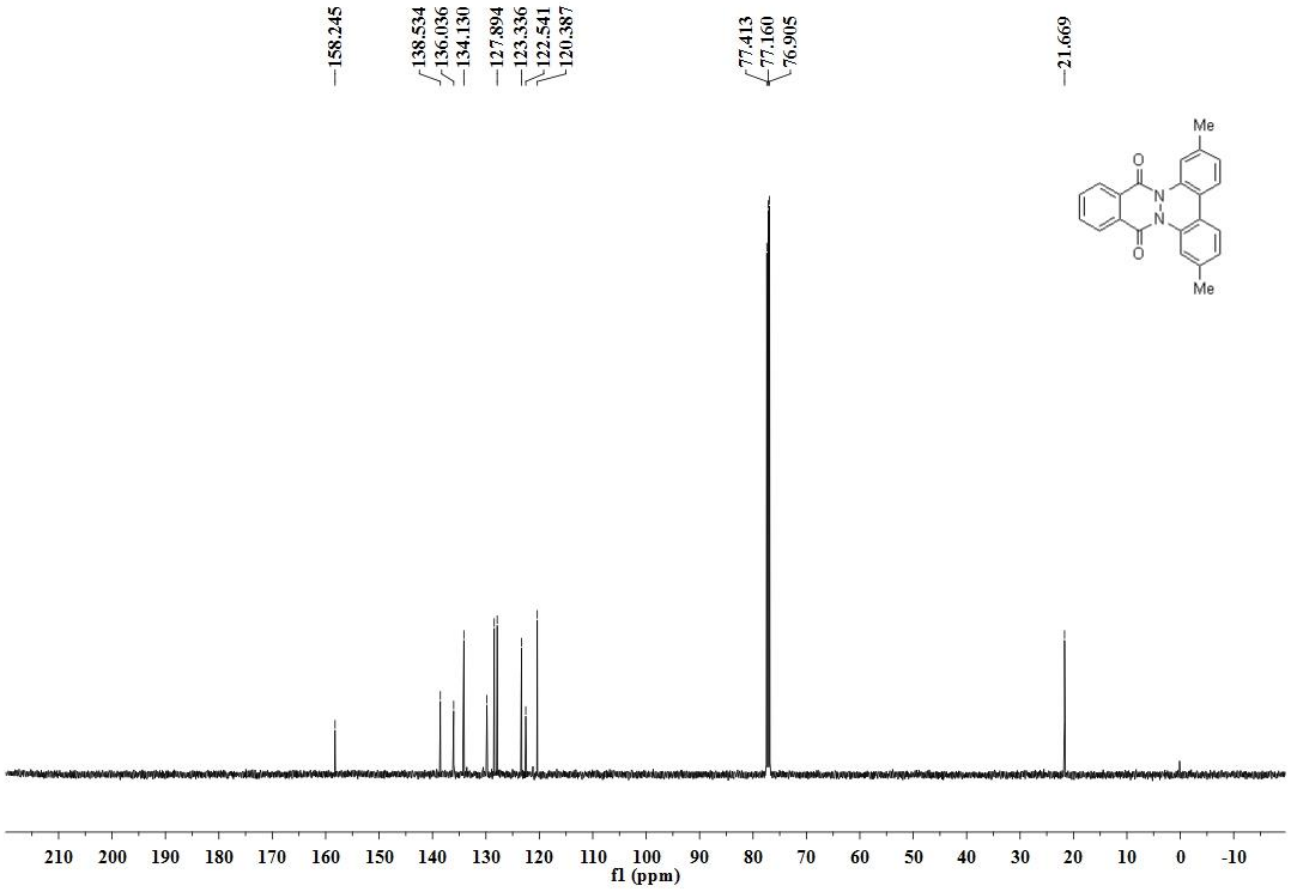
^{13}C NMR (125 MHz, $CDCl_3$) of **3i**



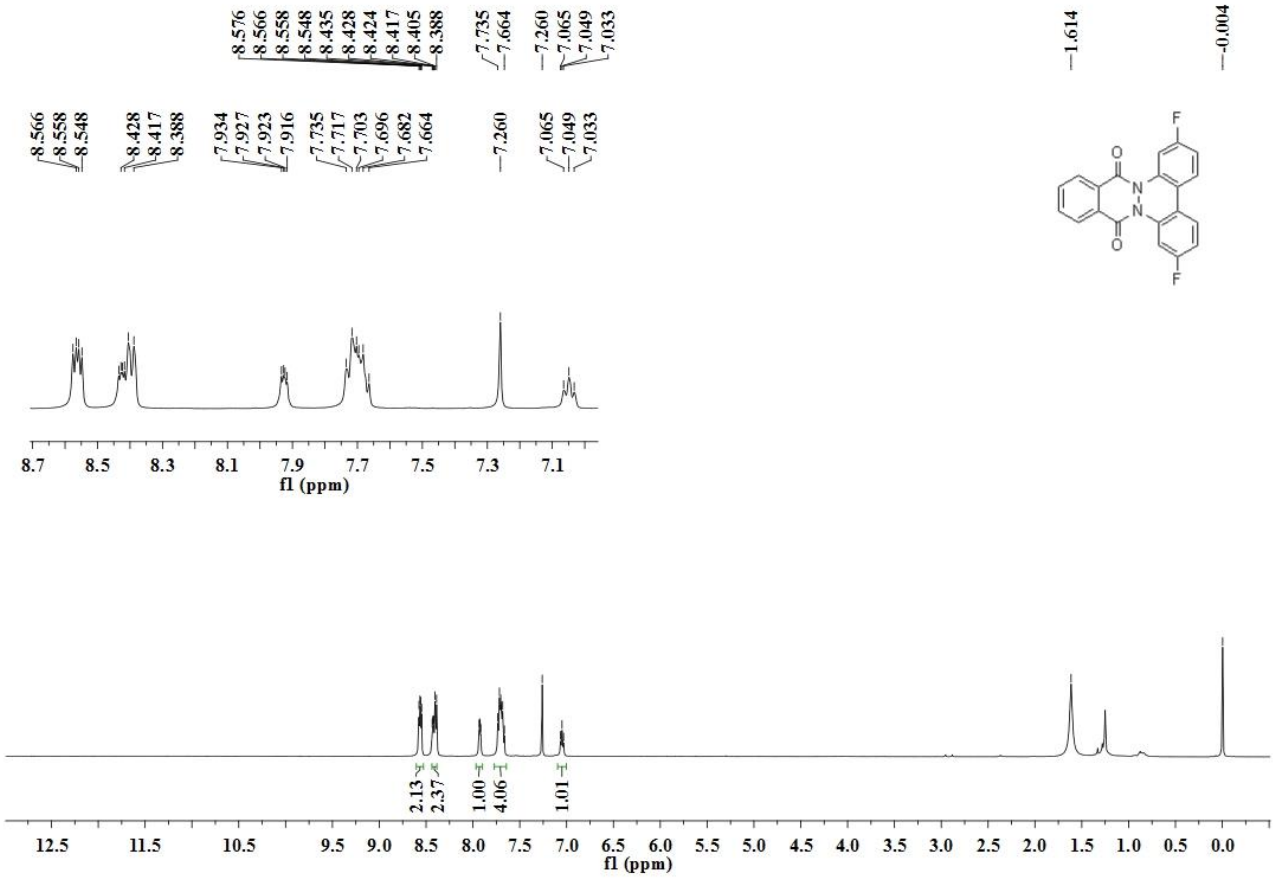
^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



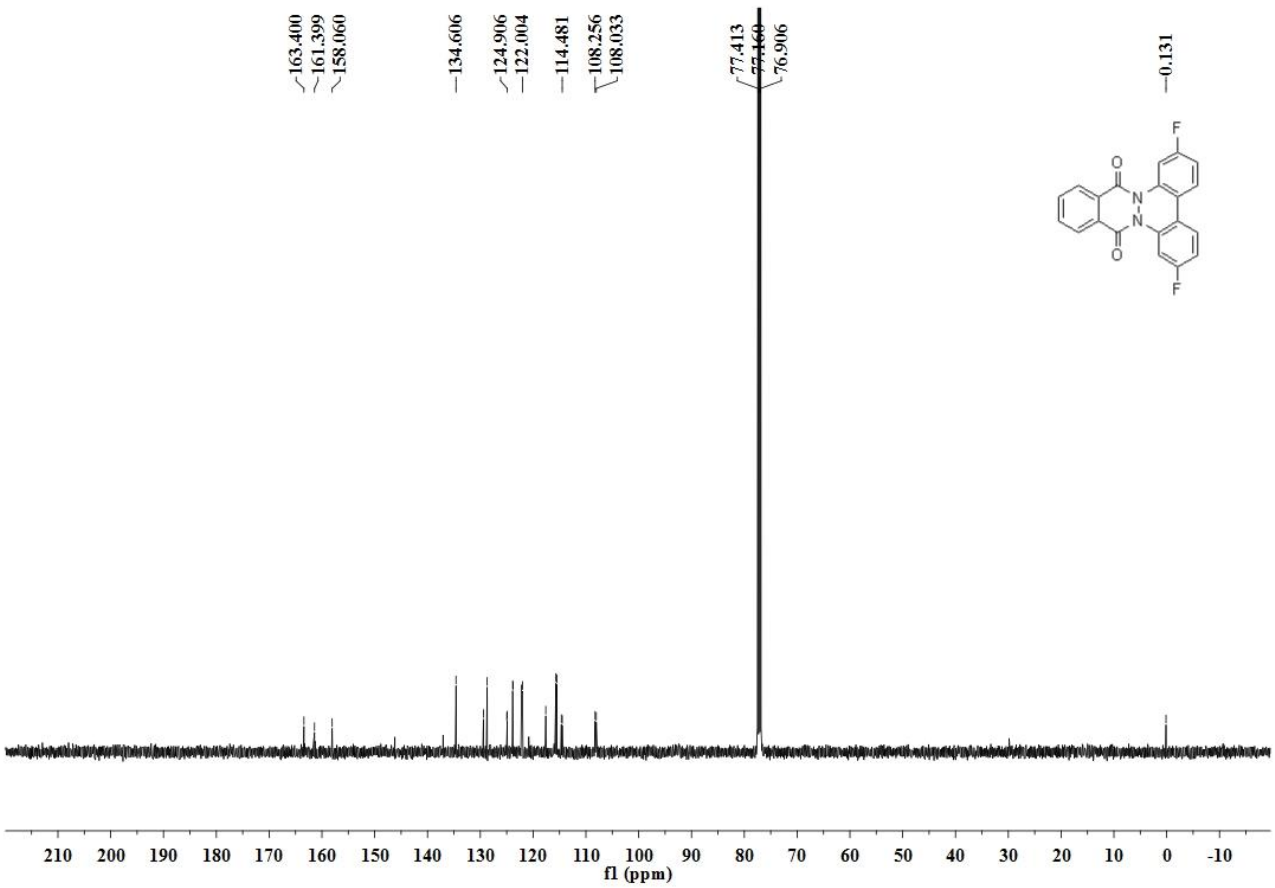
^{13}C NMR (125 MHz, $CDCl_3$) of **3j**



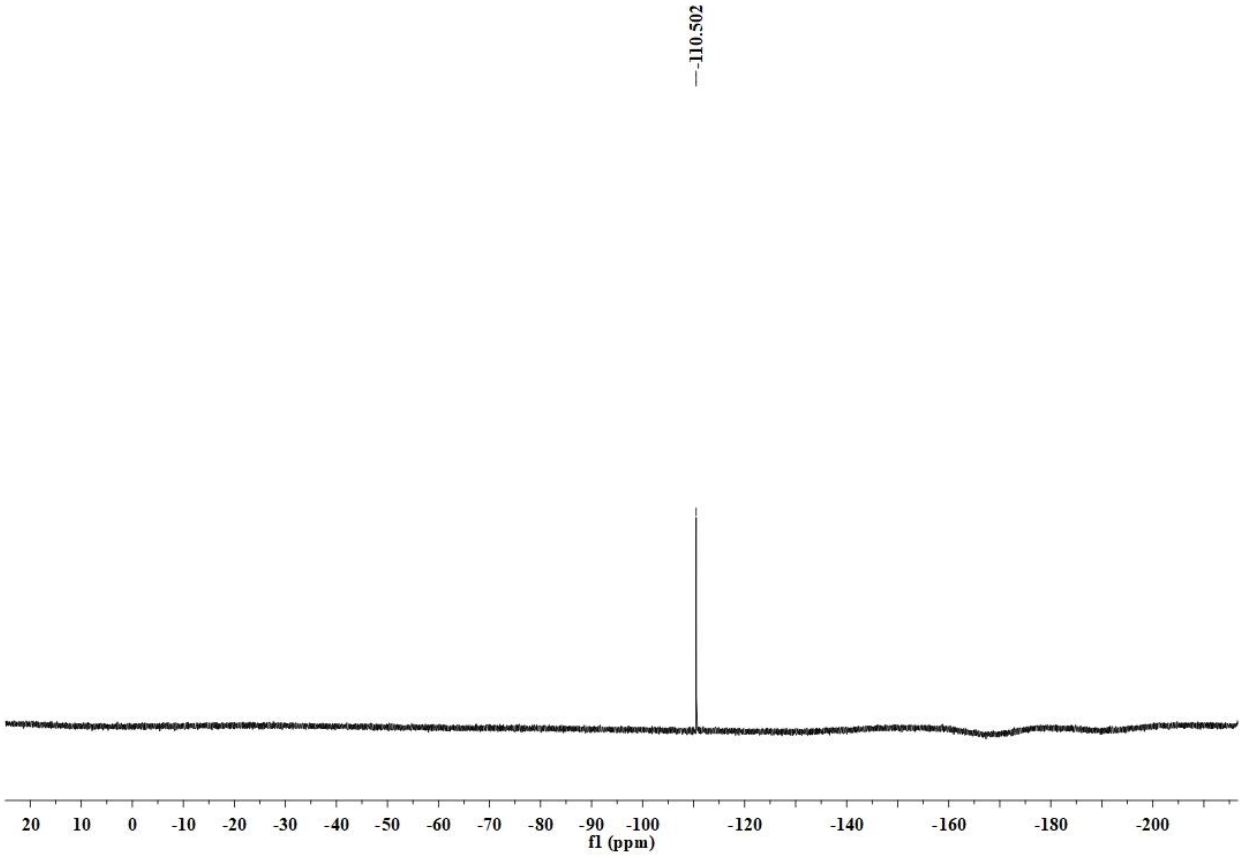
^{1}H NMR (500 MHz, $CDCl_3$) of **3k**



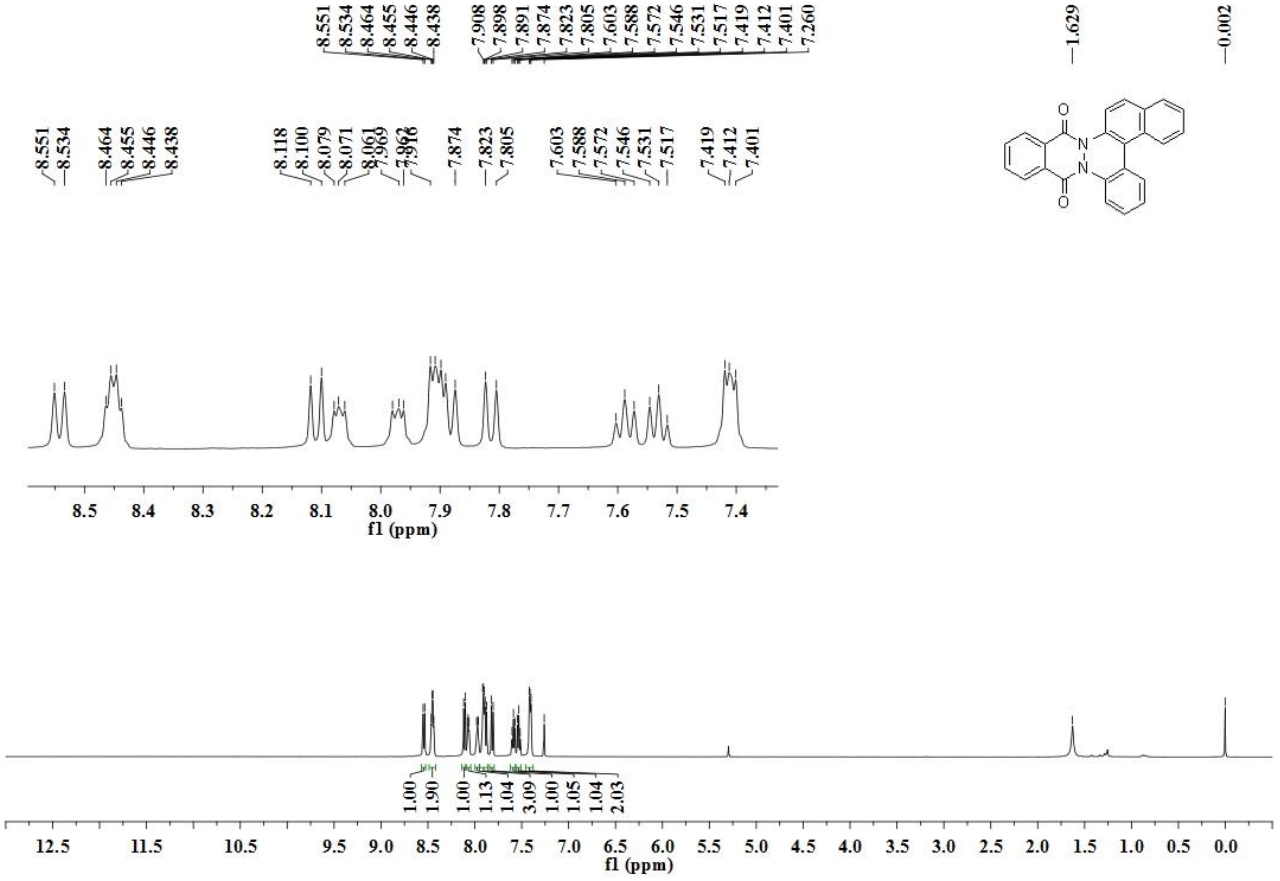
^{13}C NMR (125 MHz, $CDCl_3$) of **3k**



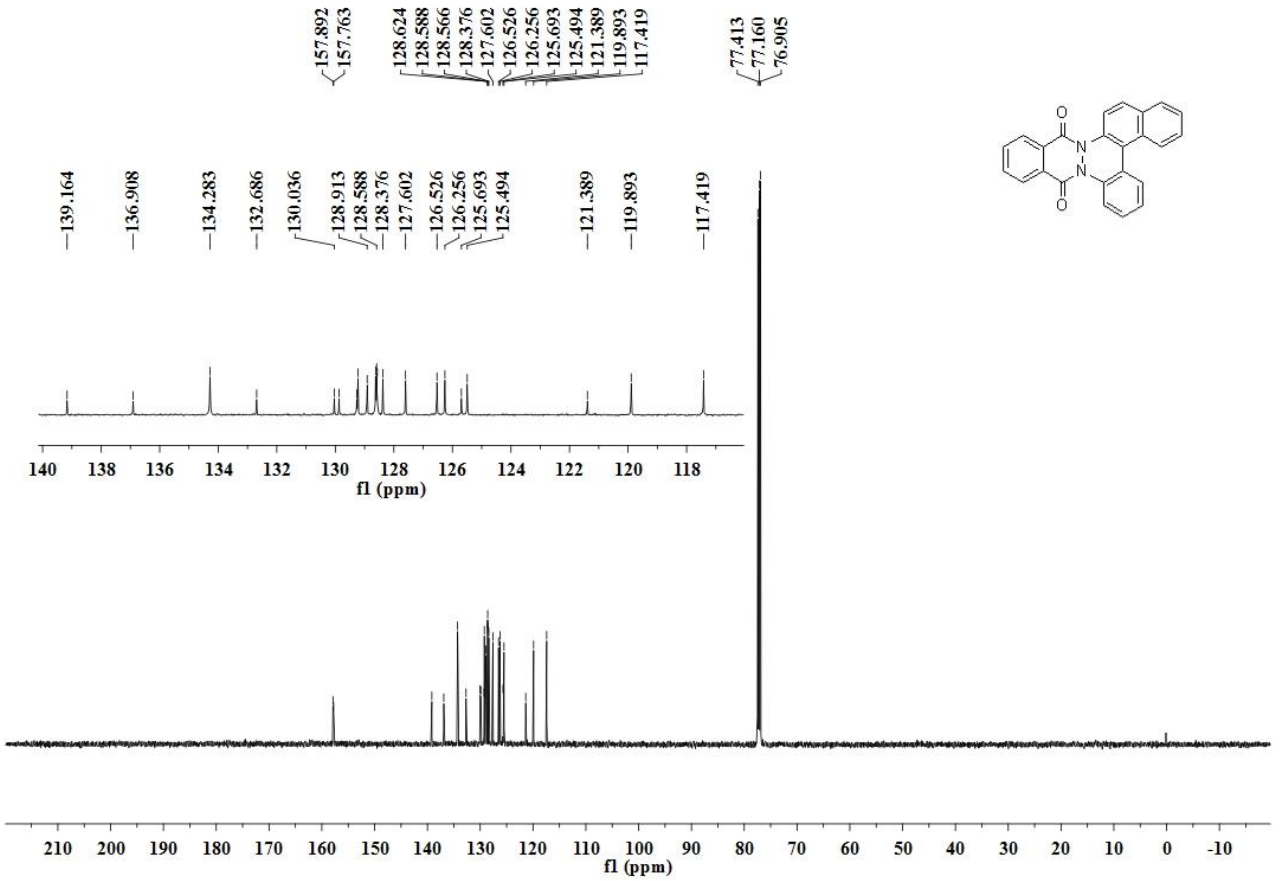
^{19}F NMR (470 MHz, $CDCl_3$) of **3k**



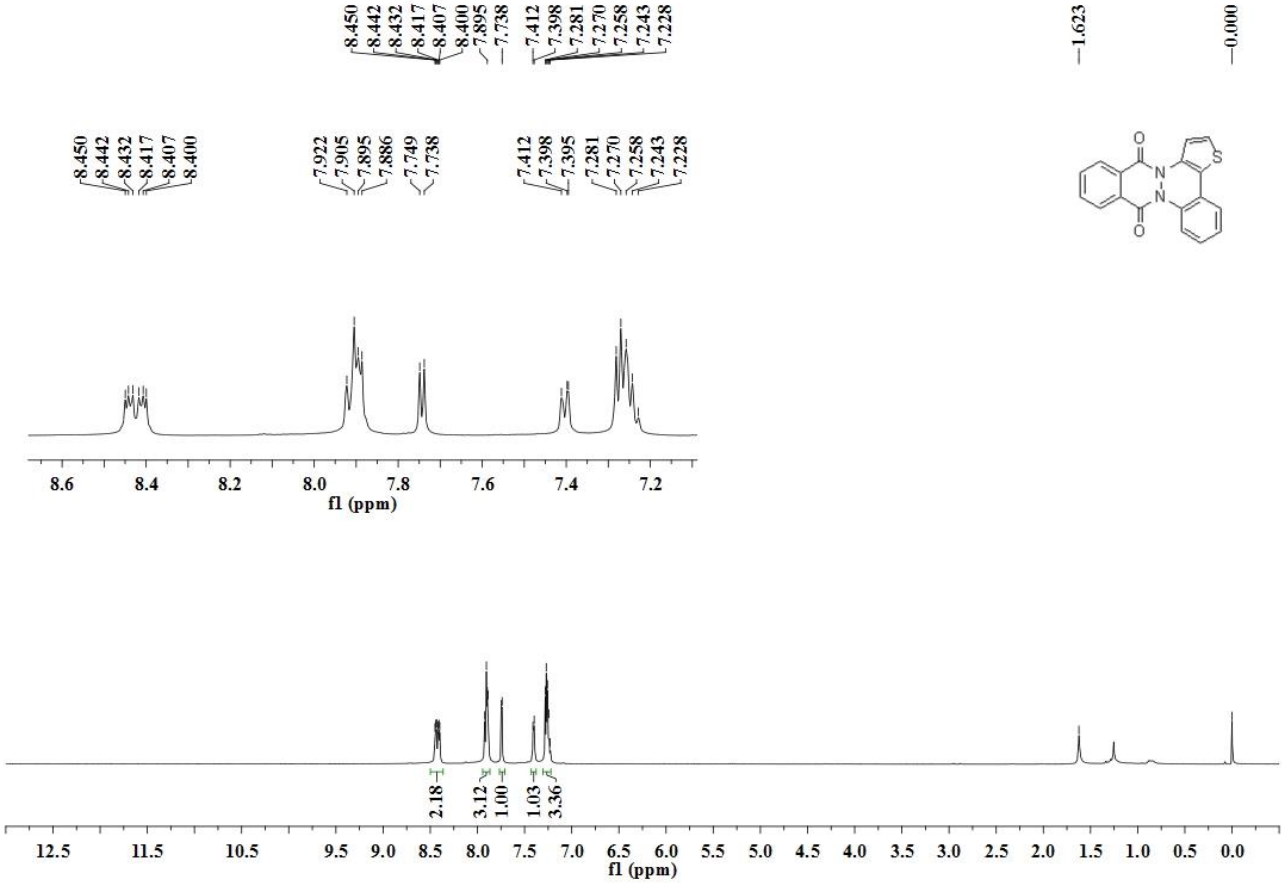
^{1}H NMR (500 MHz, $CDCl_3$) of **3l**



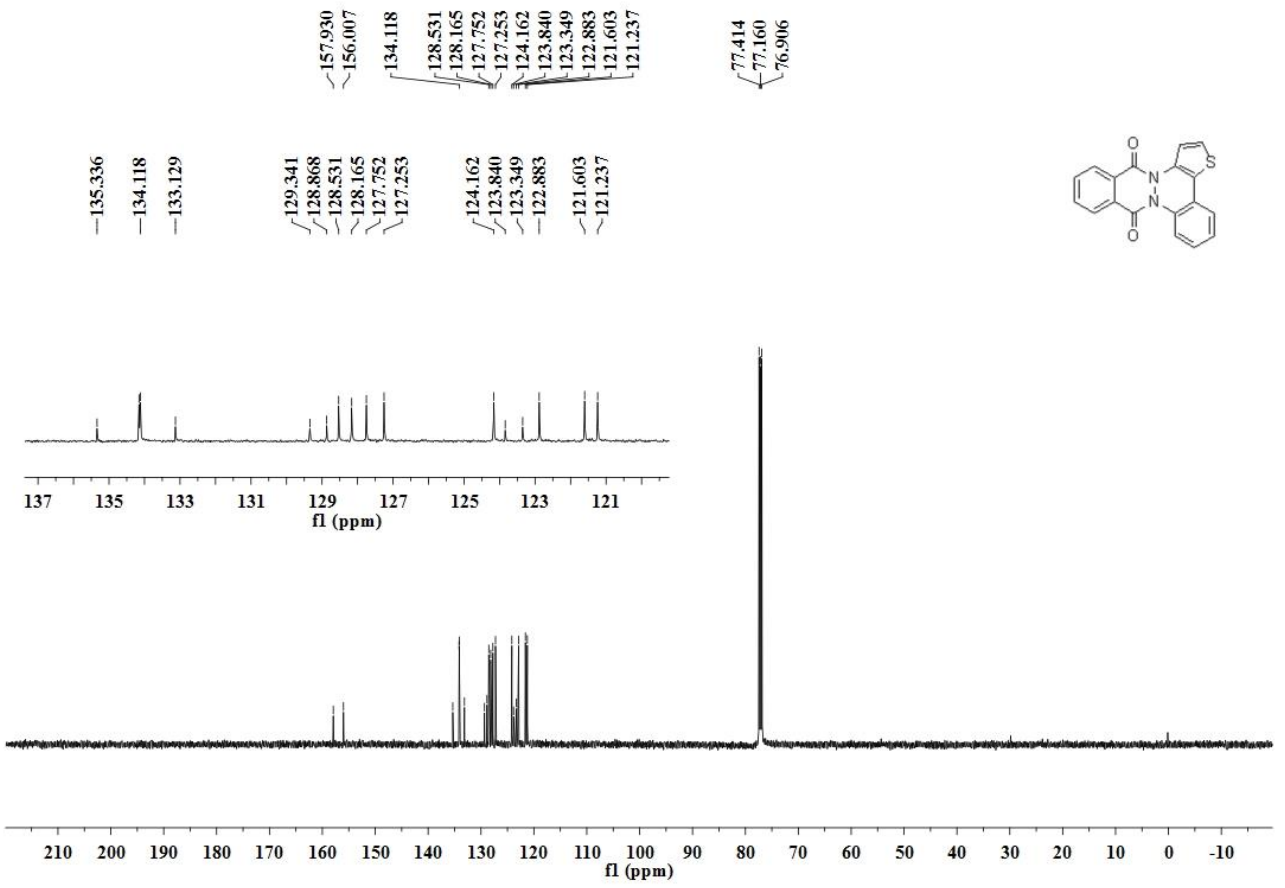
^{13}C NMR (125 MHz, $CDCl_3$) of **3l**



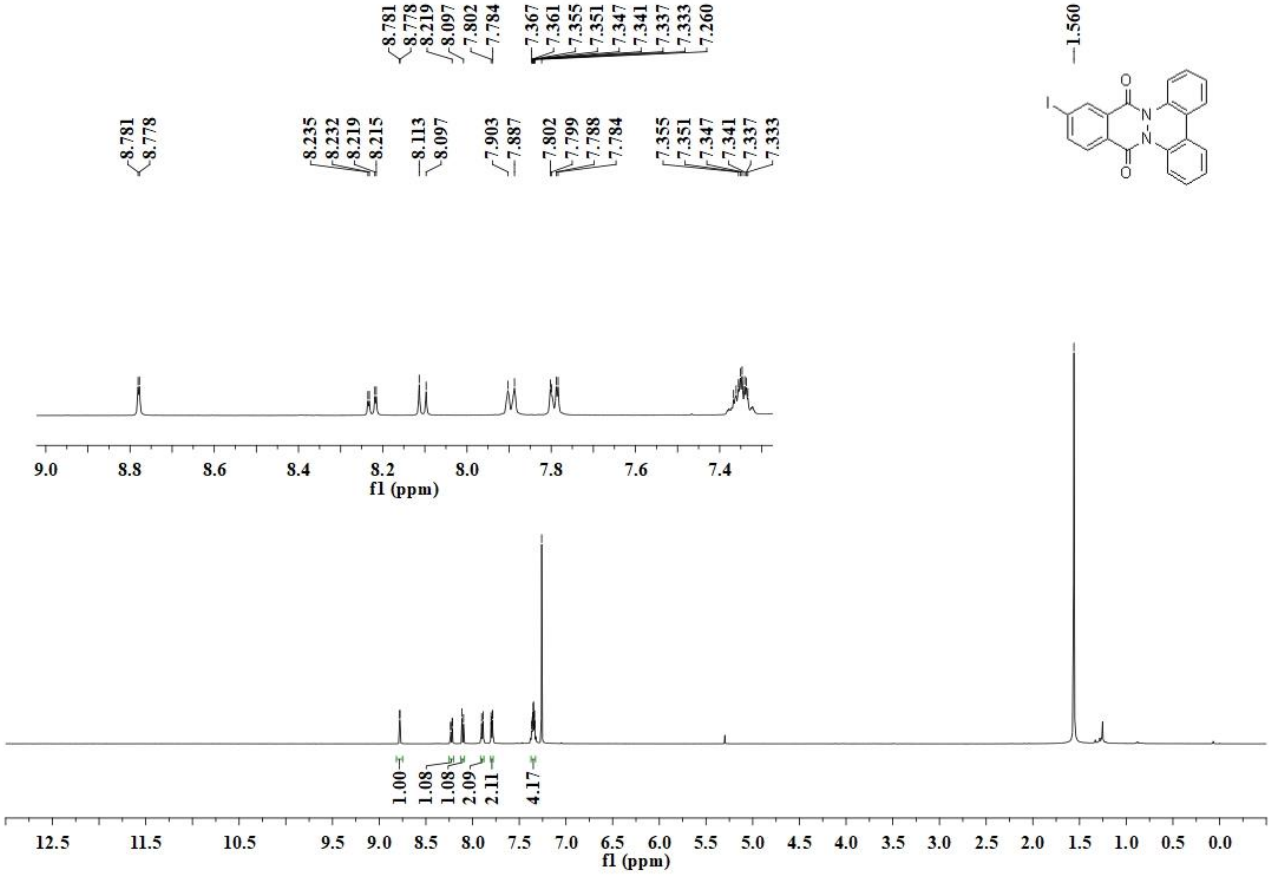
^{1}H NMR (500 MHz, $CDCl_3$) of **3m**



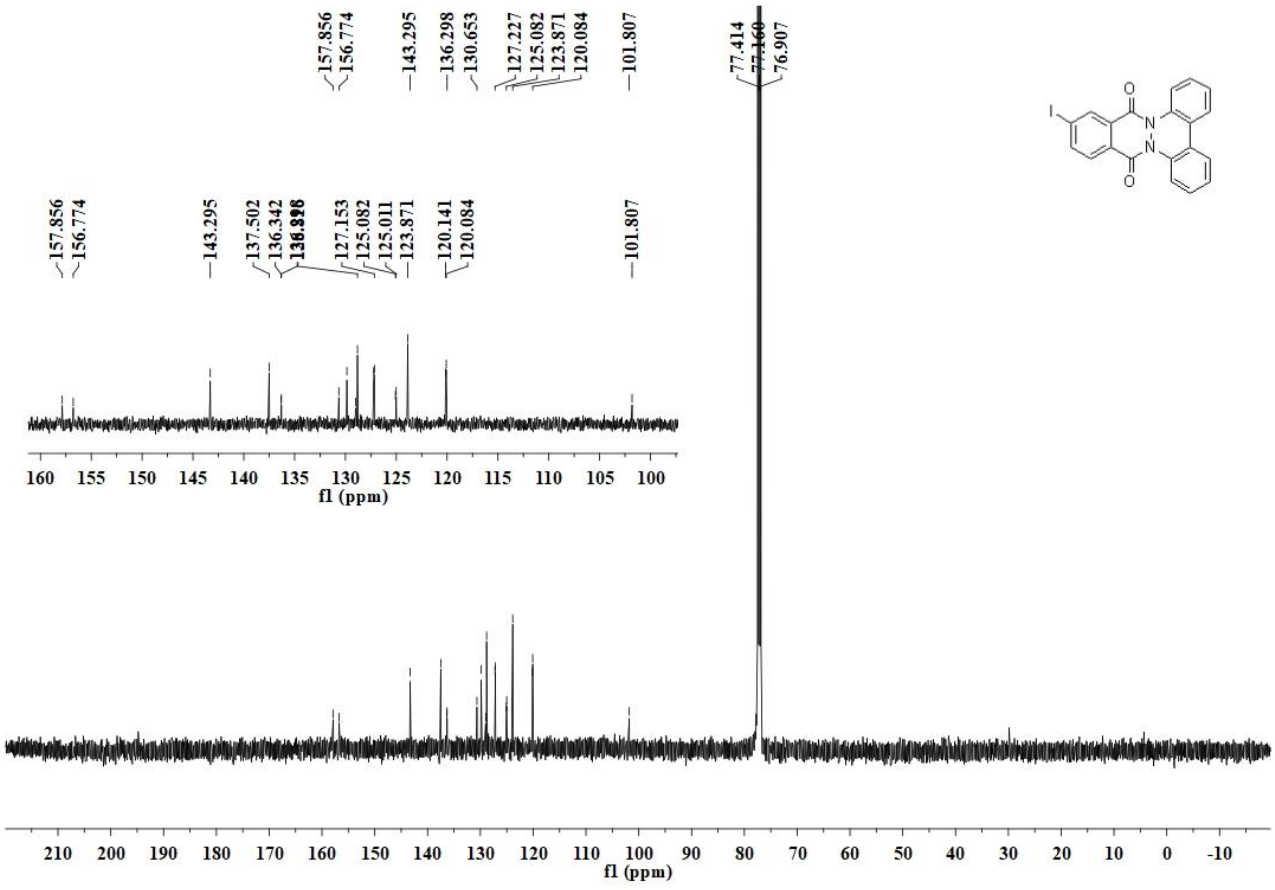
^{13}C NMR (125 MHz, $CDCl_3$) of **3m**



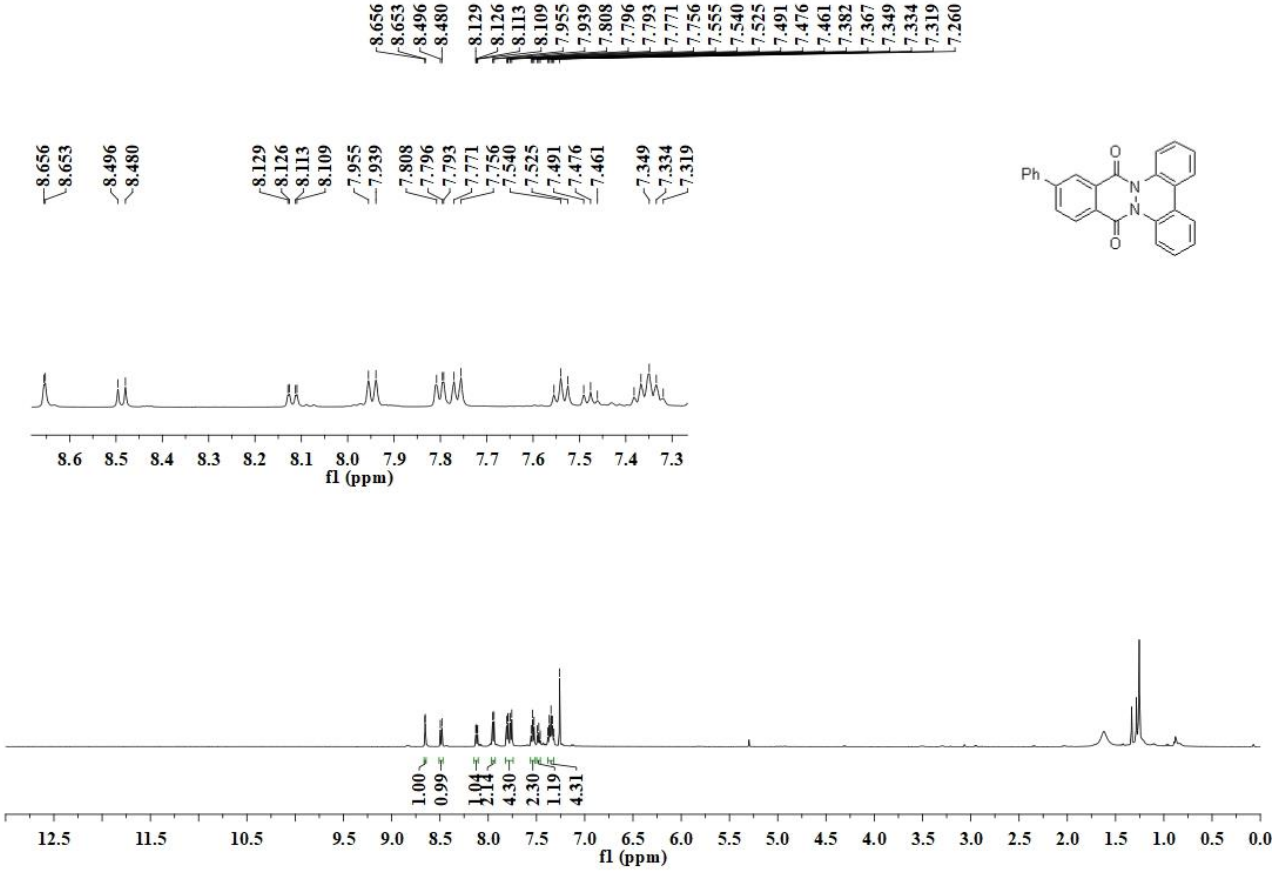
^{1}H NMR (500 MHz, $CDCl_3$) of **3n**



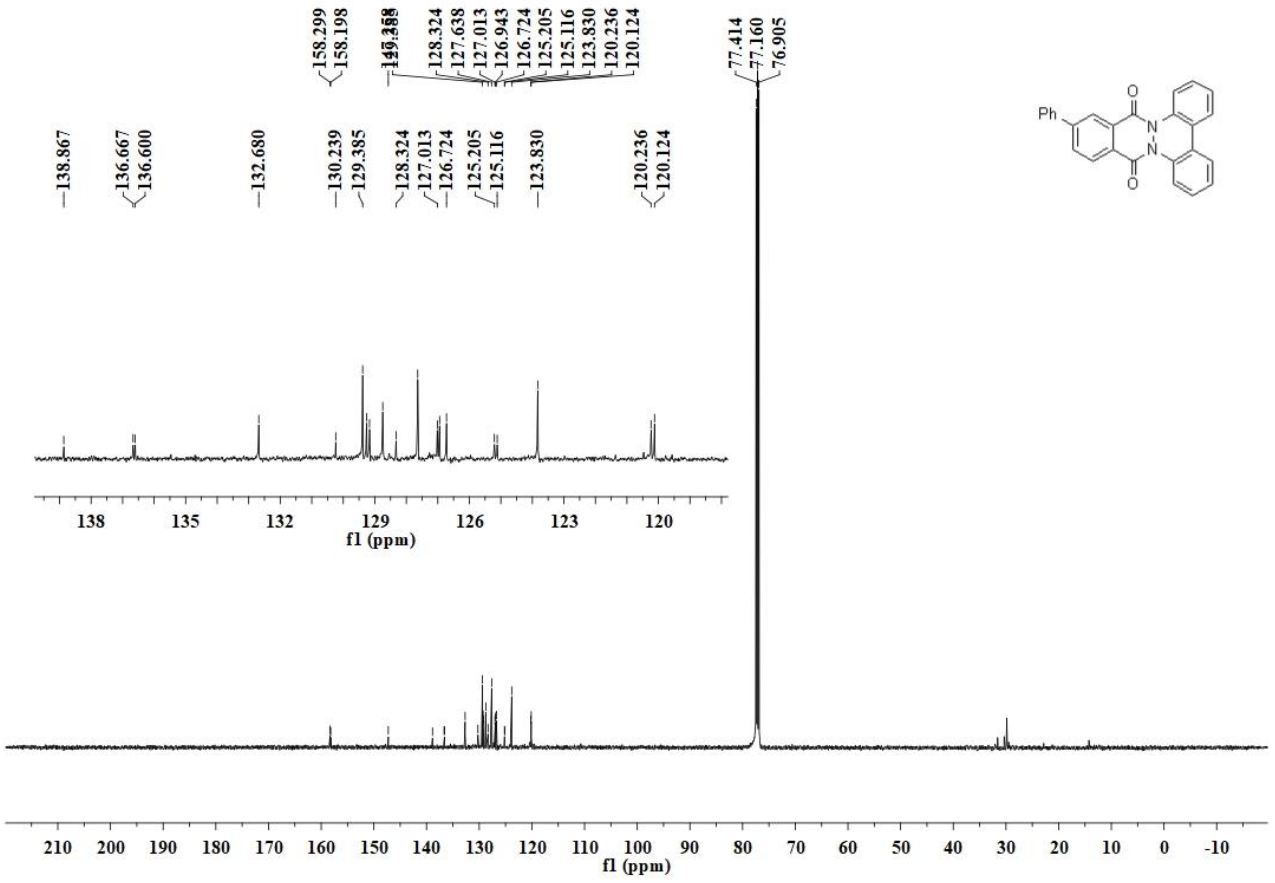
^{13}C NMR (125 MHz, $CDCl_3$) of **3n**



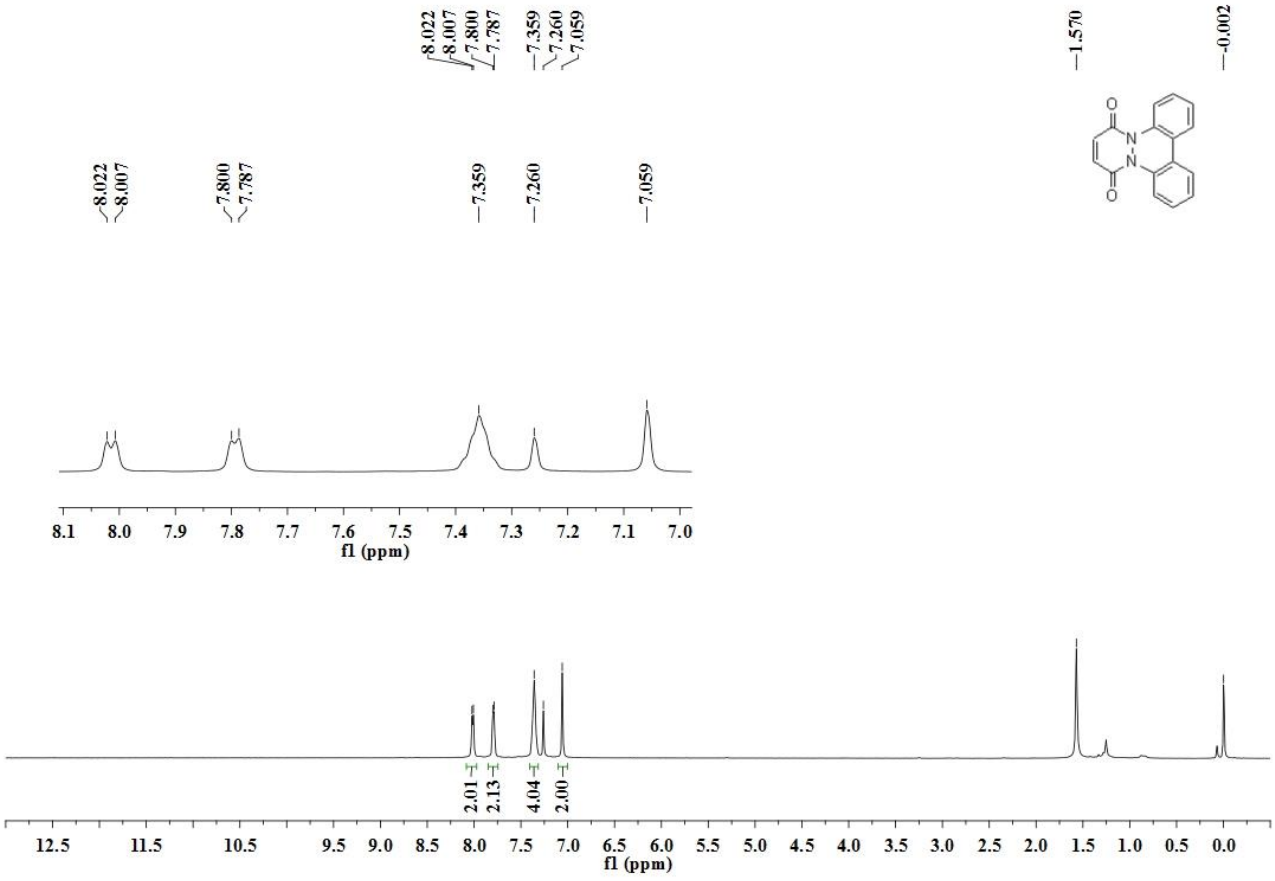
^{1}H NMR (500 MHz, $CDCl_3$) of **3o**



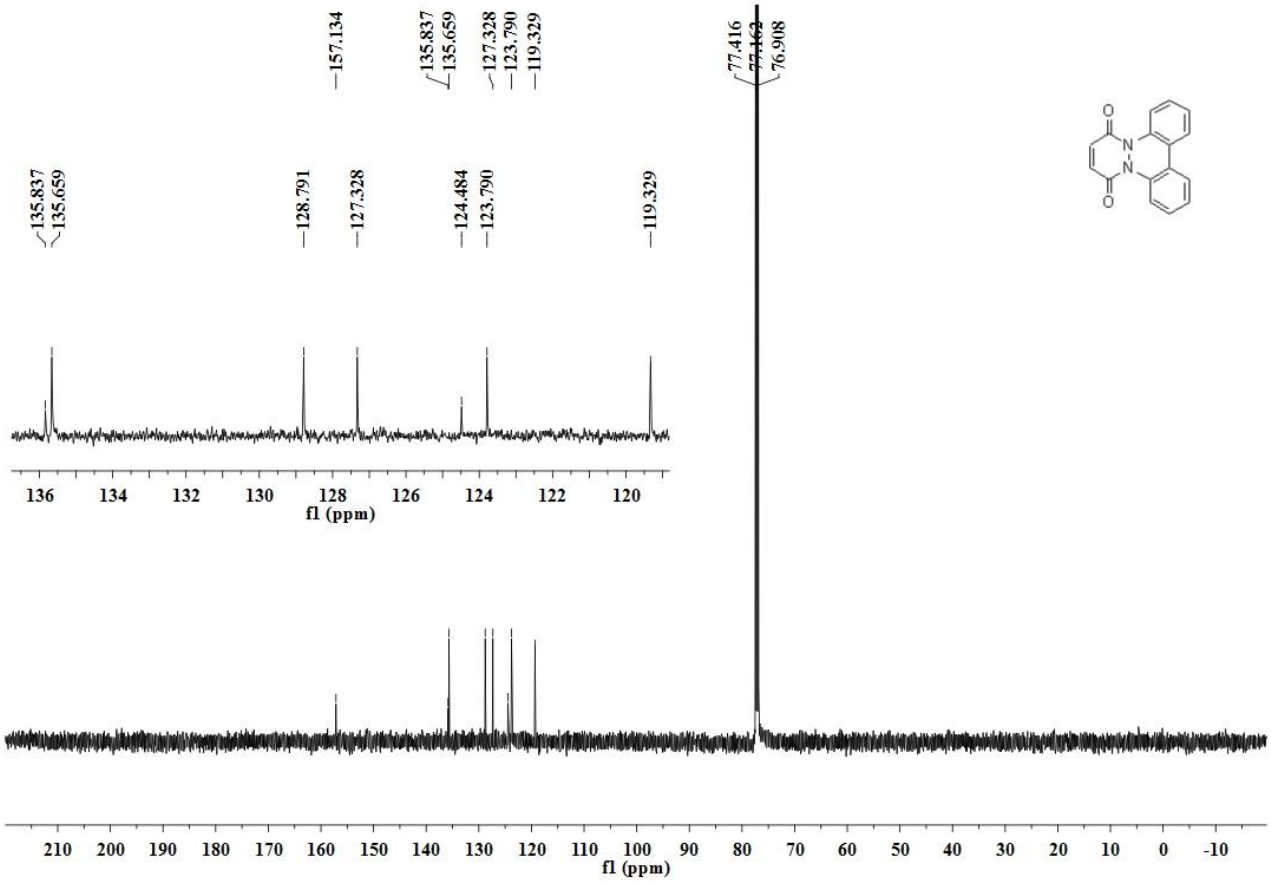
^{13}C NMR (125 MHz, $CDCl_3$) of **3o**



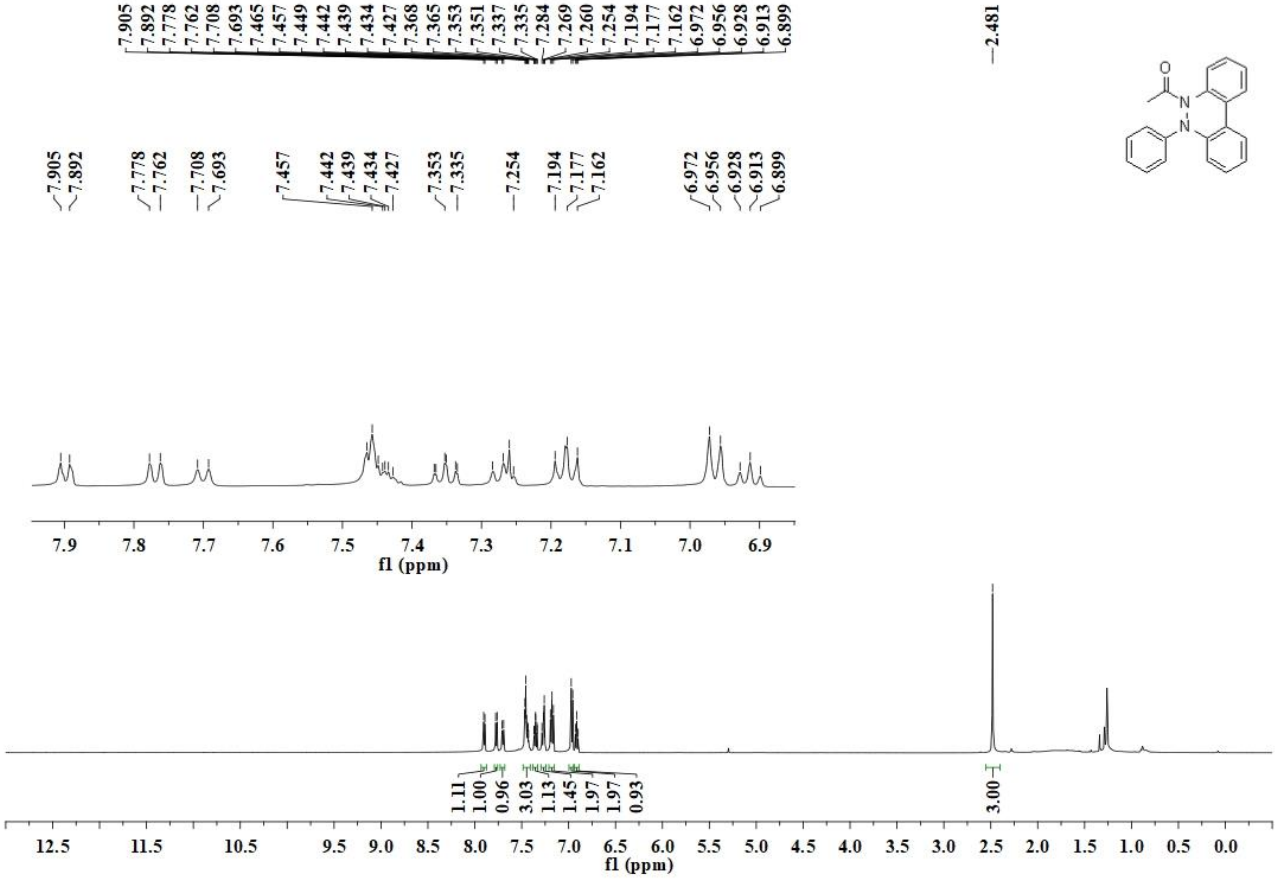
^{1}H NMR (500 MHz, $CDCl_3$) of **3p**



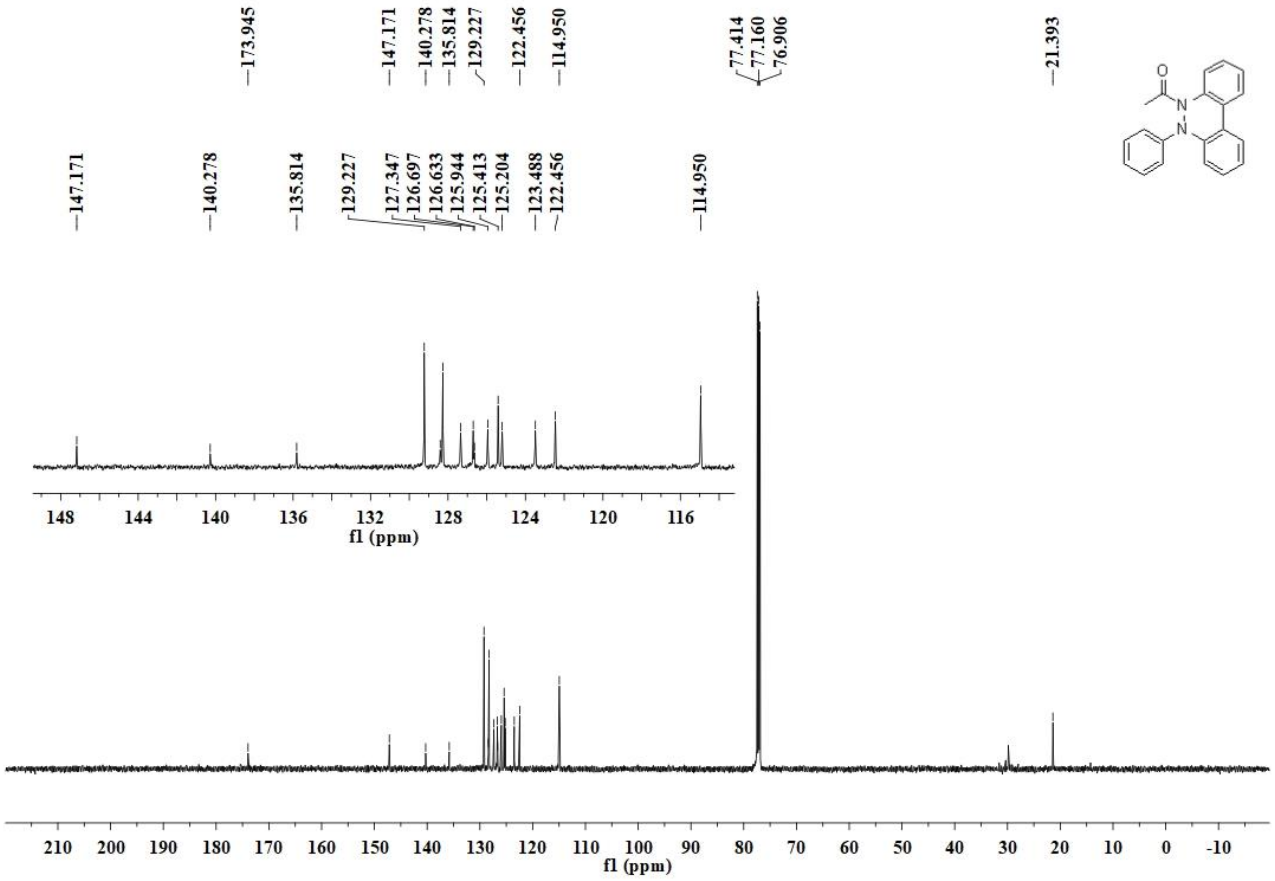
^{13}C NMR (125 MHz, $CDCl_3$) of **3p**



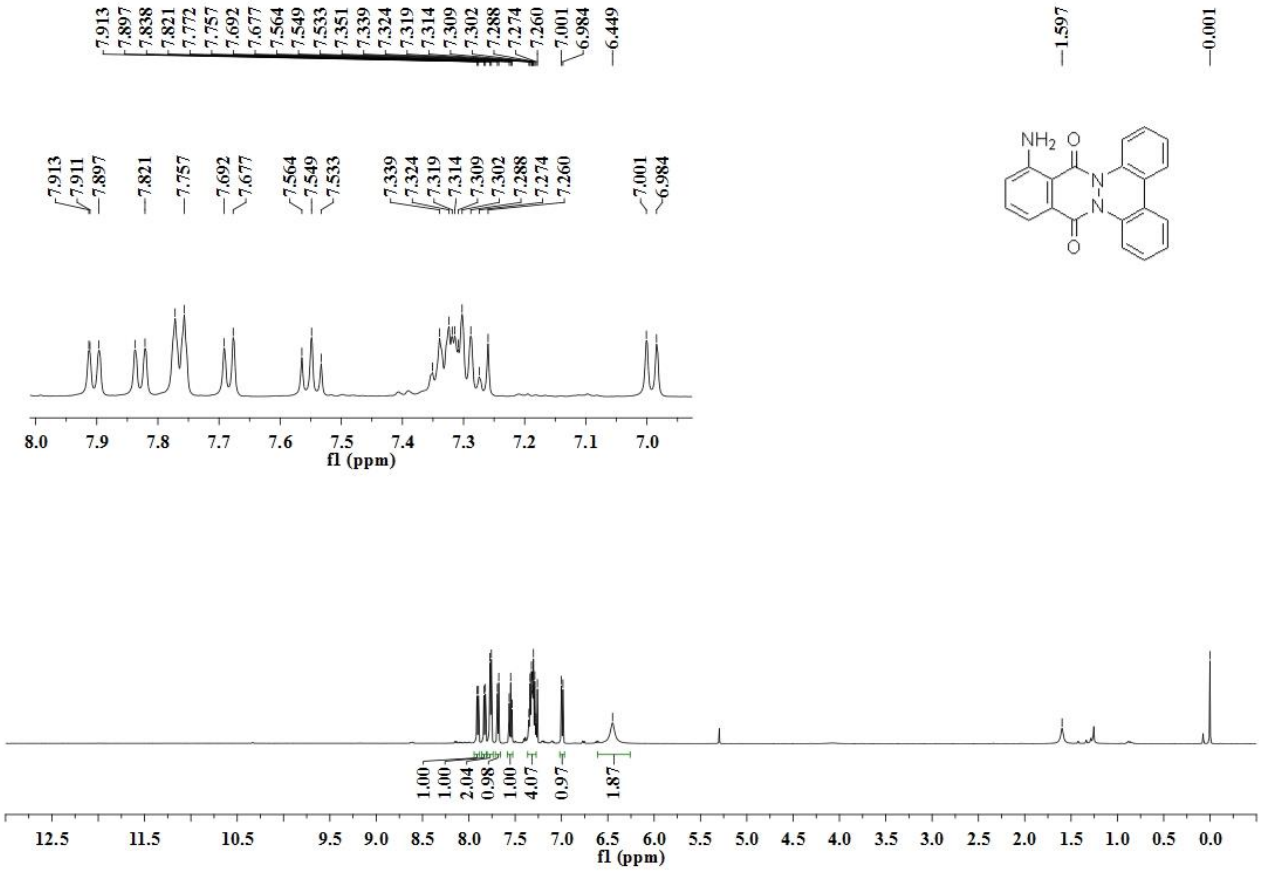
^{1}H NMR (500 MHz, $CDCl_3$) of **3q**



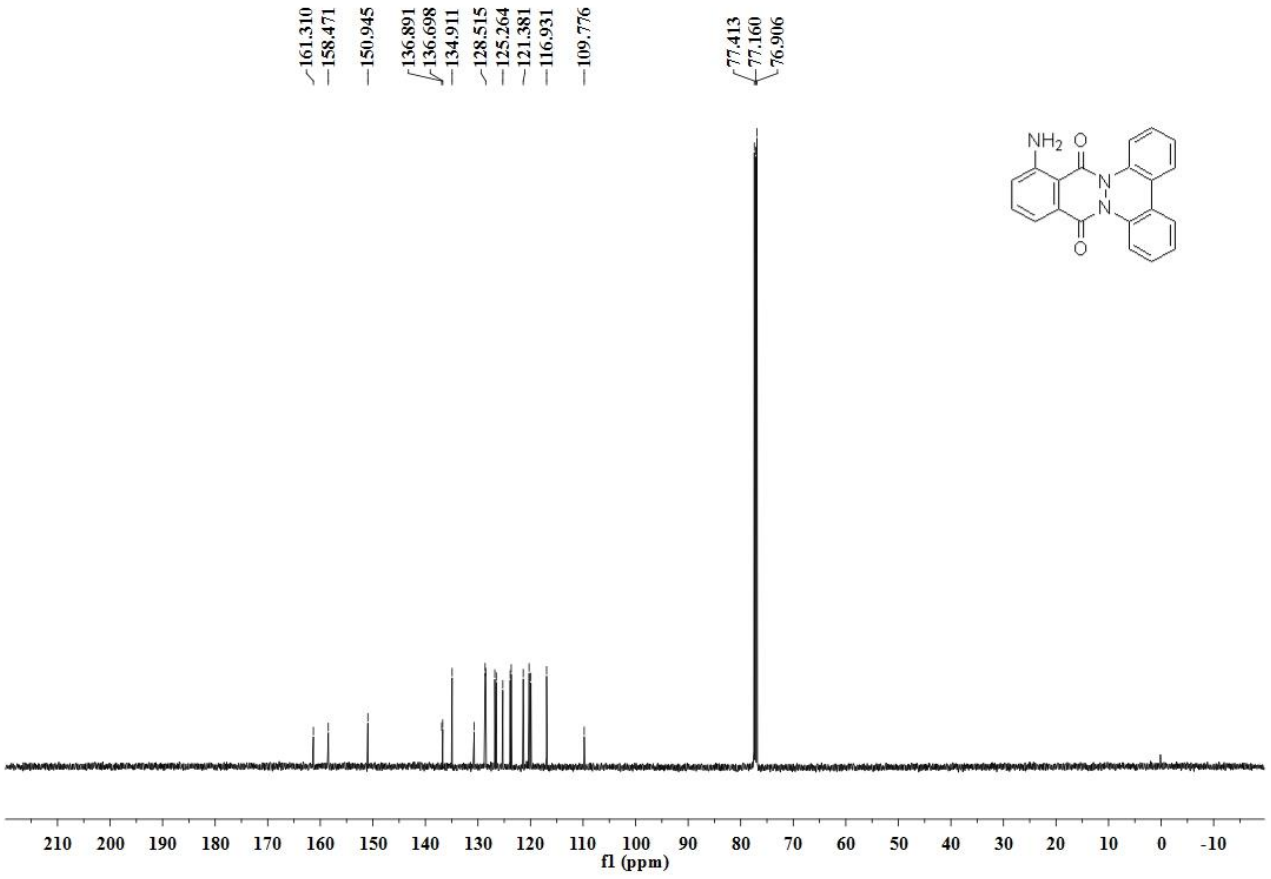
^{13}C NMR (125 MHz, $CDCl_3$) of **3q**



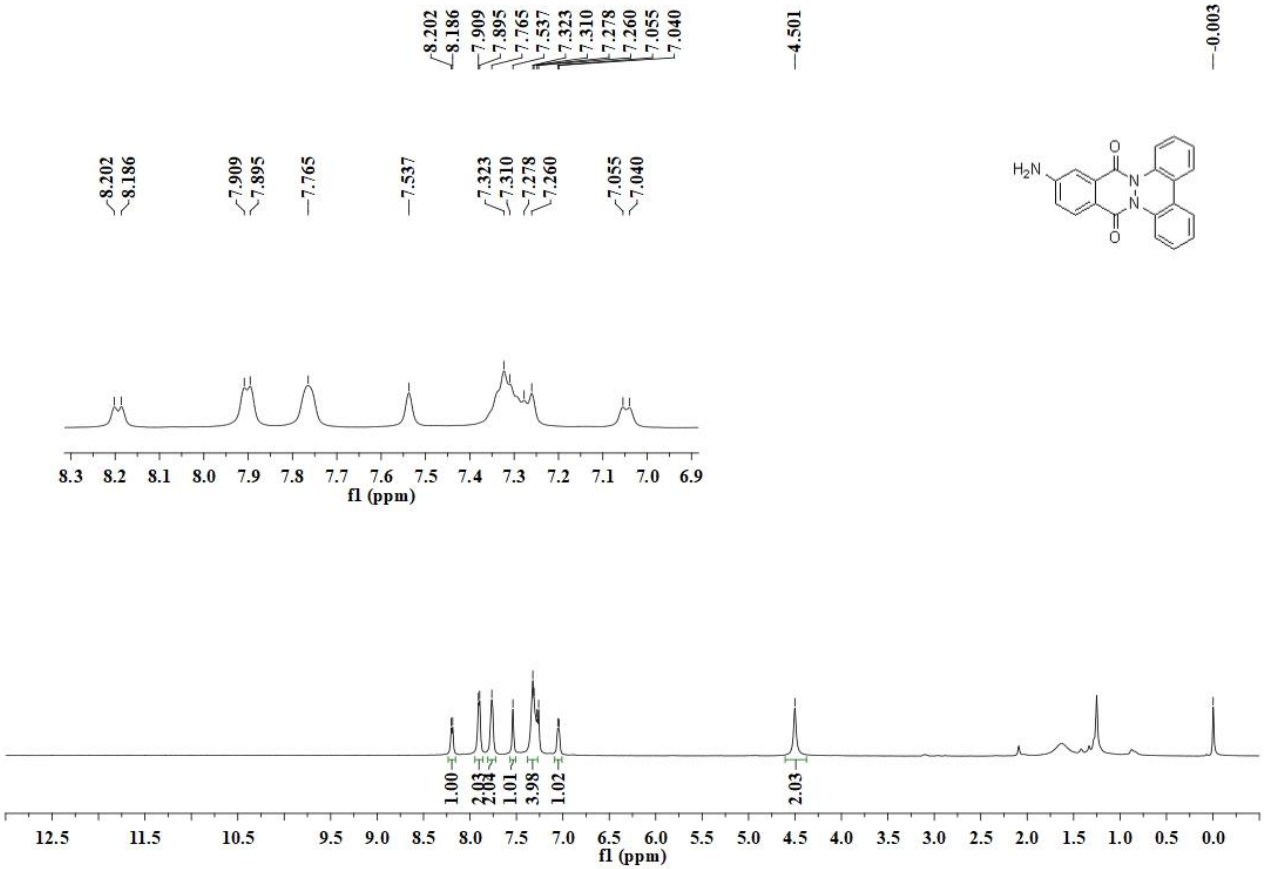
^{1}H NMR (500 MHz, $CDCl_3$) of **5**



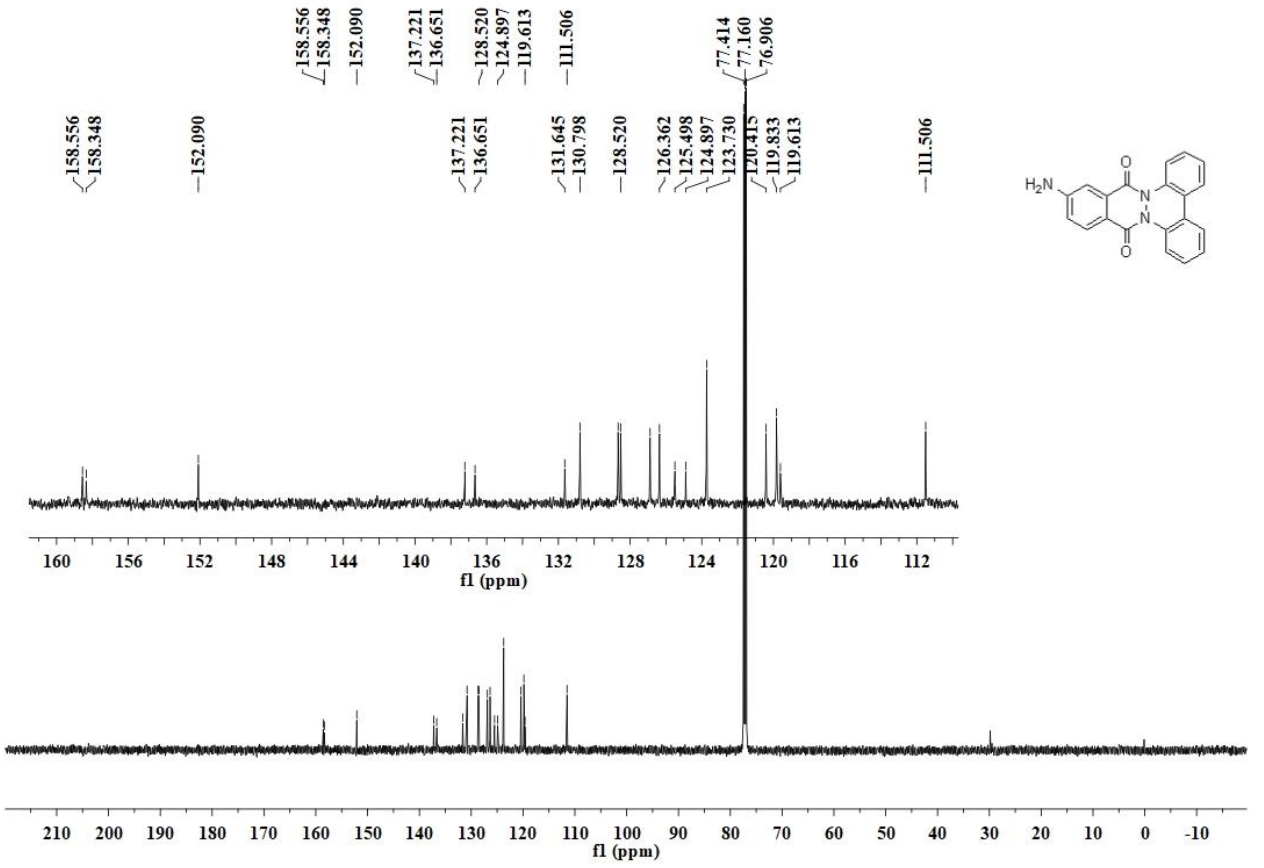
^{13}C NMR (125 MHz, $CDCl_3$) of **5**



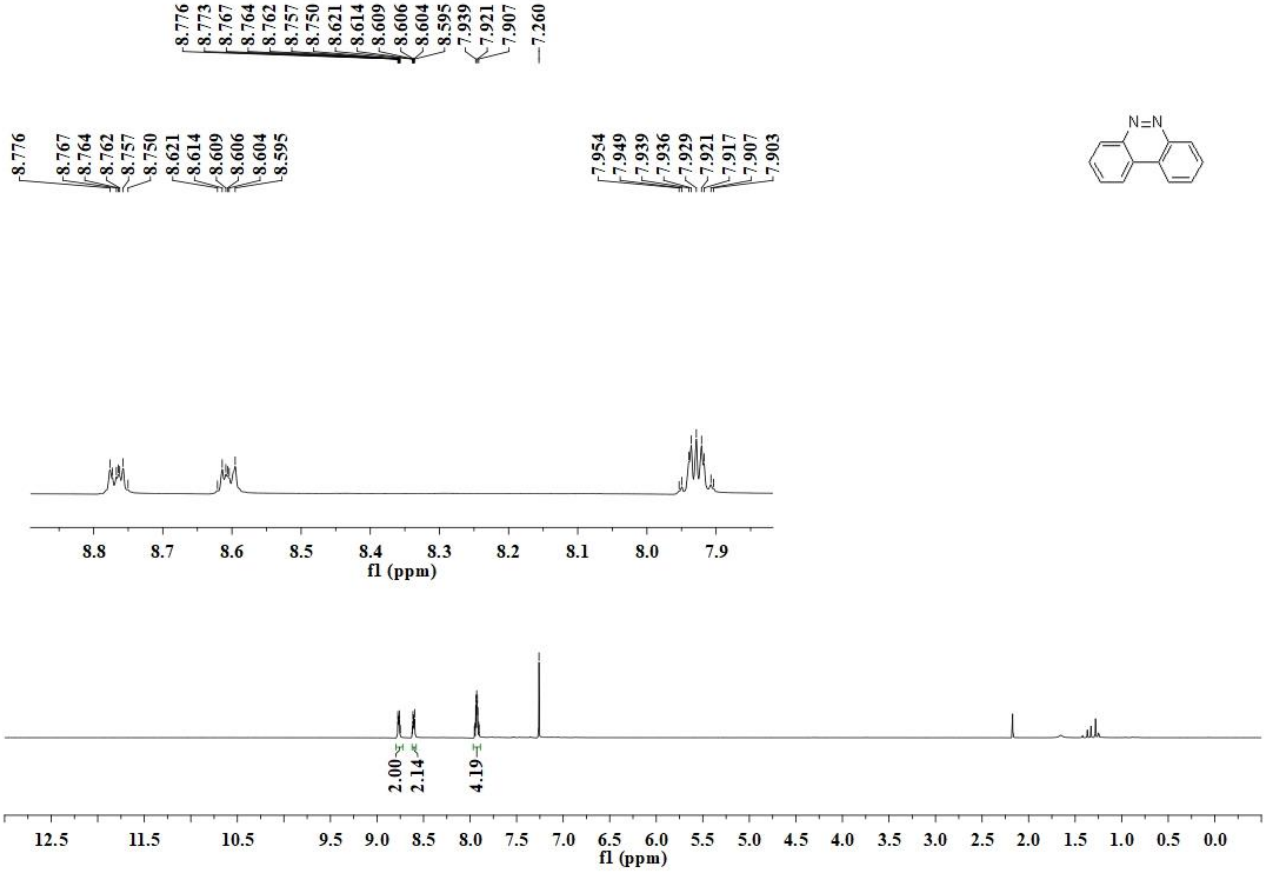
^{1}H NMR (500 MHz, $CDCl_3$) of **6**



^{13}C NMR (125 MHz, $CDCl_3$) of **6**



^{1}H NMR (500 MHz, $CDCl_3$) of benzo[*c*]cinnoline **7**



^{13}C NMR (125 MHz, $CDCl_3$) of benzo[*c*]cinnoline **7**