Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

2,7-Dinitrophenanthrene-9,10-dione as a Photosensitizer for Dehydrogenative Lactonization of 2-Arylbenzoic Acids

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1. General information

Unless otherwise specified, all reactions are performed in an air atmosphere. Solvents were purified by standard techniques without special instructions. All commercially available compounds were purchased from J&K, Across, Alfa, TCI, or Adamas. Thin-layer chromatography (TLC) was performed on SiO_2 (silica gel 60 F254, Merck) and spots were located with ultraviolet light (254 nm). Rapid chromatography on SiO_2 (silica gel 60, 200-300 mesh). The Bruker Avance II-400 Spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) and Bruker Avance NEO 600 M NMR Spectrometer (600 MHz for ^{1}H, 150 MHz for ^{13}C) recorded ^{1}H and ^{13}C NMR spectra; DMSO-d_6 (or $CDCl_3$), and tetramethylsilane (TMS) were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, and the coupling constants J are given in Hz. The peak patterns are shown as follows: s, single; d, double; t, triplet; m, multiplet; bs, broad singlet. High-resolution mass spectrometry was recorded on the G6224A (Agilent Technologies) mass spectrometer. UV-vis spectra were obtained on a Lambda 750S and Agilent 8453 UV-vis spectrophotometer. Cyclic voltammogram curves were obtained with a standard set of conditions to main internal consistency on a BAS 100 W electrochemical analyzer. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, saturated calomel electrode (SCE). The voltammograms were recorded at room temperature in MeCN at a photocatalyst concentration of 1×10^{-3} M and 0.1 M tetrabutylammonium hexafluorophosphate（NBu_4PF_6）as supporting electrolyte. All solutions were degassed with N_2 prior to the measurement. The scan rate for the CV measurements was 10 mV/s. Transient absorption spectrum and luminescence decay were carried out using Edinburgh LP 980. The samples for measurements were prepared using high purity MeCN in 1.0 cm quartz cuvettes, solutions were degassed with N_2 prior to the measurement.

The photocatalytic reactions are carried out on the reaction instrument of 455 nm CEL-LED100HA of China Education Jinyuan, the optical output power is 20 W, and the reaction temperature is controlled to room temperature by fan cooling.

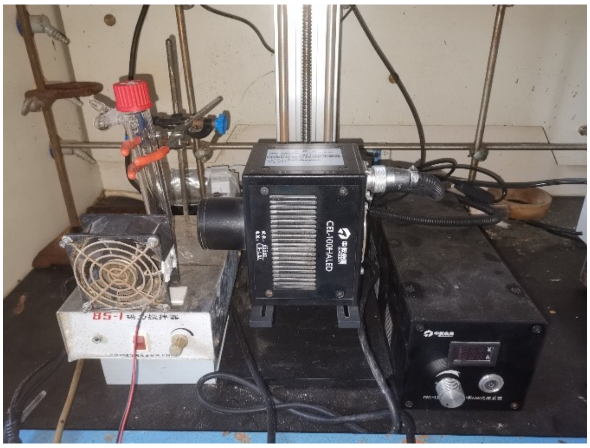
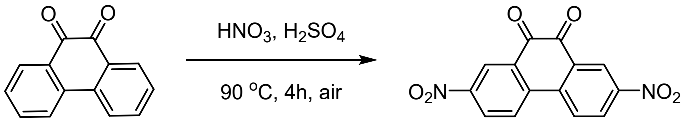


Figure S1. Devices for the photocatalytic reactions.

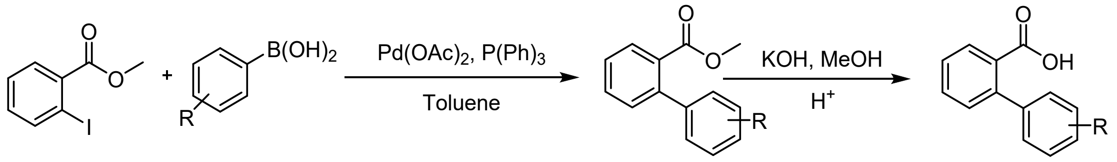
2. Synthesis of photocatalyst and starting materials

Synthesis of 2,7-dinitrophenanthrene-9,10-dione (**DNPO**)



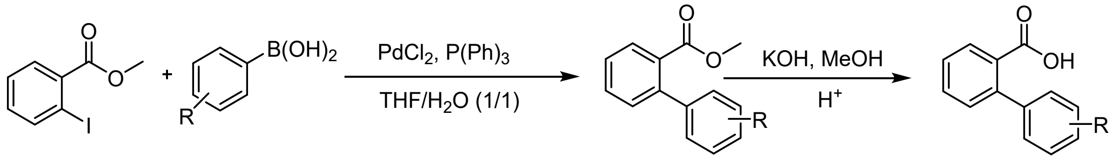
A mixture of 9, 10-phenquinone (15 mmol, 3.12 g), fuming nitric acid (40 mL) and concentrated sulfuric acid (4 mL) was refluxed with stirring for 4 hours. After cooling to room temperature, the resulting mixture was poured into ice water (200 mL) and then filtered. The solid was washed with water several times. The crude product was collected and recrystallized from AcOH to give compound **DNPO** in 53 % yield.

Staring materials **1b-1c**, **1f-1n**, and **1u** are synthesized by the following route:[1]



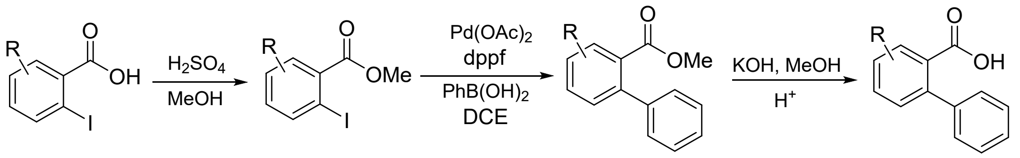
Methyl 2-iodobenzoate (0.65 g, 2.5 mmol), arylboronic acid (3.75 mmol), $Pd(OAc)_2$ (6 mg, 1 mol%), Ph_3P (13 mg, 2 mol%) and K_3PO_4 (1.06 g, 10 mmol) were added to the Schlenk tube (25 mL) and degassed three times with N_2. Then 5 mL toluene was added into the Schlenk tube. The mixture was subsequently stirred at 80 °C for 12 h. After the mixture cooled down to room temperature, the reaction mixture was then concentrated on a rotary evaporator and purified by column chromatography (PE/EtOAc = 30/1) to afford the desired esters. KOH (1.5 g, 37.5 mmol), MeOH (10 mL), and the desired ester were added to 25 mL Schlenk tube and the mixture was stirred at 80 °C. After 12 hours, the mixture was quenched with hydrochloric acid and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuo to give the corresponding 2-arylbenzoic acids.

Starting materials **1d** and **1e** are synthesized by the following route[2]



Methyl 2-iodobenzoate (0.65 g, 2.5 mmol), arylboronic acid (3.75 mmol), $PdCl_2$ (6 mg, 1 mol%), Ph_3P (13 mg, 2 mol%) and K_3PO_4 (1.06 g, 10 mmol) were added to the Schlenk tube (25 mL) and degassed three times with N_2. Then THF/H_2O (1/1, 5.0 mL) was added into the Schlenk tube. The mixture was subsequently stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was then concentrated on a rotary evaporator and purified by column chromatography (PE/EtOAc = 30/1) to afford the desired esters. KOH (1.5 g, 37.5 mmol), MeOH (10 mL), and the desired ester were added to 25 mL Schlenk tube and the mixture was stirred at 80 °C. After 12 hours, the mixture was quenched with hydrochloric acid and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuo to give the corresponding 2-arylbenzoic acids.

Starting materials **1o-1s**,**1t**, and **1v** are synthesized by the following route



2-Iodobenzoic acid (4 mmol), methanol (24 mL), and concentrated sulfuric acid (4 mL) were added to a 50 mL Schlenk tube and the reaction mixture was stired at 80 °C for 12 h. After cooling to room temperature, the resulting mixture was concentrated on a rotary evaporator. The concentrated reaction solution was added to the potassium carbonate solution and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and then removed solvent with a rotary evaporator to afford the corresponding esters. The corresponding ester (2.5 mmol), aryl arylboronic acid (3.75 mmol), $Pd(OAc)_2$ (56 mg, 10 mol%), bis(diphenylphosphino)ferrocene (dppf, 169 mg) and K_3PO_4 (2.12 g 10 mmol) were added into the 25 mL drying Schlenk tube. The Schlenk tube was degassed three times with N_2 3 times. After addition dichloromethane (DCE, 10 mL), the reaction mixture was heated to 80 °C for 12 h. The reaction mixture was then concentrated on a rotary evaporator and purified by column chromatography (PE/EtOAc = 30/1) to afford the desired esters. KOH (1.5 g, 37.5 mmol), MeOH (10 mL), and the desired ester were added to 25 mL Schlenk tube and the mixture was stirred at 80 °C. After 12 hours, the mixture was quenched with hydrochloric acid and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuo to give the corresponding 2-arylbenzoic acids.

3. UV- vis absorption spectroscopy

UV/Vis spectrum was recorded a on a Lambda 750S and Agilent 8453 UV-vis spectrophotometer. The sample was measured in 1 cm High Precision Cell made of quartz.

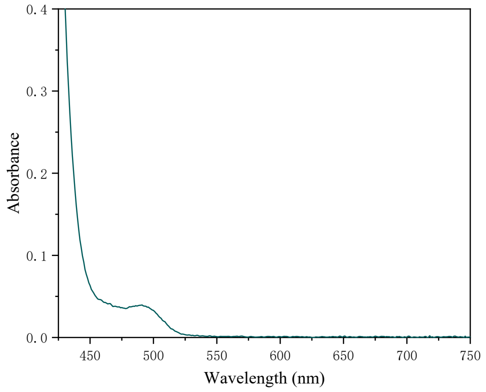


Figure S2. UV-vis absorption spectrum of **DNPO** in MeCN (1 mmol/L).

4. Cyclic voltammogram

Cyclic voltammogram curves were obtained with a standard set of conditions to main internal consistency on a BAS 100W electrochemical analyzer. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, saturated calomel electrode (SCE). The voltammograms were recorded at room temperature in MeCN at a photocatalyst concentration of 1 × 10^{-3} M and 0.1 M tetrabutylammonium hexafluorophosphate（NBu_4PF_6）as supporting electrolyte. All solutions were degassed with N_2 prior to the measurement. The scan rate for the CV measurements was 10 mV/s. The excited state reduction potential is calculated by formula 4.1. $E_{red}(\mathbf{P}^*/\mathbf{P}^{\bullet-})$ is the excited state reduction potential, $E_{red}(\mathbf{P}/\mathbf{P}^{\bullet-})$ is the ground state reduction potential, $E_{0,0}$ is the energy level band gap, and λmax is the maximum wavelength of absorption.

$$E_{0,0} = \frac{1240}{\lambda_{max}}$$

$$E_{red}(P^*\ /P^{\bullet -}\ ) = E_{red}(P/P^{\bullet -}) + E_{0,0} \qquad (4.1)$$

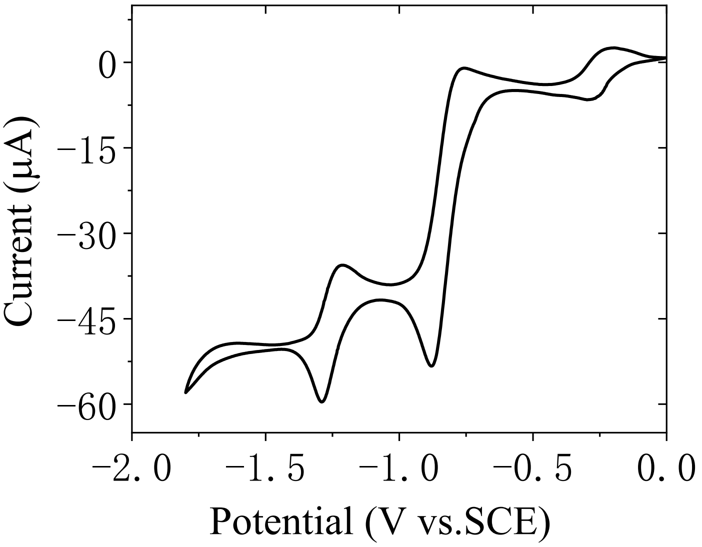


Figure S3. Cyclic voltammetry of **DNPO** in MeCN.

It can be seen from the figure that the first reduction potential of **DNPO** is -0.253 V. Because the fluorescence spectrum cannot be obtained, λ_{max} is regarded as the maximum wavelength, which is 420 nm. According to formula 4.1, $E_{0,0}$ = 2.38 eV. Further, $E_{red}(\mathbf{P}^*/\mathbf{P}^{\bullet-})$= - 0.25 + 2.38 = 2.13 V vs. SCE.

5. Nanosecond transient absorption spectroscopy

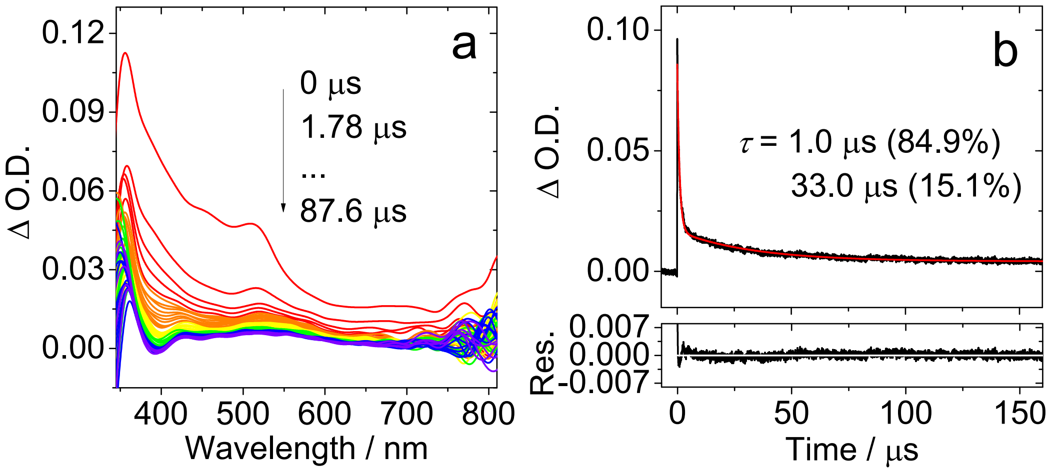
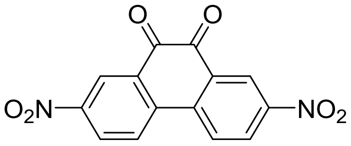
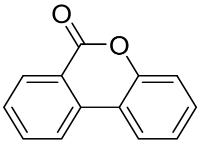


Figure S4. (a) Nanosecond transient absorption spectra of the compound and (b) the corresponding decay traces at 540 nm in deaerated MeCN. λ_{ex} = 355 nm, $c = 2.0 \times 10^{-5}$ M, 20 °C.

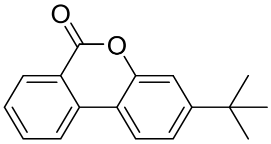
6. Characterization of products



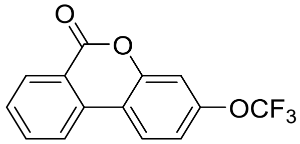
2,7-dinitrophenanthrene-9,10-dione (**DNPO**)[3]: Yellow solid, mp >200 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 – 8.65 (m, 4H), 8.58 (dd, J = 8.8, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.2, 148.8, 138.9, 134.0, 128.9, 128.1, 123.1 .



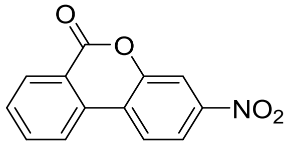
6H-benzo[c]chromen-6-one (**2a**)[1]: White solid, mp 94−95 °C, ^{1}H NMR (400 MHz, Chloroform-d) δ 8.34 (d, J = 9.3 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.56 – 7.52 (m, 1H), 7.50 – 7.42 (m, 1H), 7.32 – 7.26 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-d) δ 161.1, 151.3, 134.8, 134.7, 130.5, 130.4, 128.9, 124.5, 122.8, 121.7, 121.2, 118.0, 117.7.



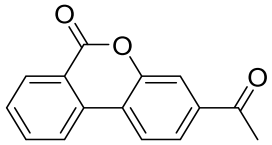
3-($tert$-butyl)-6H-benzo[c]chromen-6-one (**2b**)[4]: White solid, mp 157−159 °C, ^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.82 – 7.73 (m, 1H), 7.56 – 7.49 (m, 1H), 7.41 – 7.33 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 154.7, 151.2, 134.9, 134.7, 130.5, 128.4, 122.4, 122.0, 121.5, 121.0, 115.4, 114.5, 35.0, 31.1.



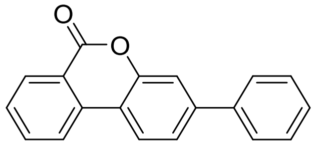
3-(trifluoromethoxy)-6*H*-benzo[c]chromen-6-one (**2c**)[5]: White solid, mp 77−79 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, J = 7.9 Hz, 1H), 8.04 – 8.01 (m, 2H), 7.83 – 7.79 (m, 1H), 7.59 – 7.55 (m, 1H), 7.18 – 7.17 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.4, 151.7, 150.1 (q, $J_{C\text{-}F}$ = 1.9 Hz), 135.1, 133.7, 130.7, 129.3, 124.2,121.7, 120.8, 119.1 (q, $J_{C\text{-}F}$ = 257.2 Hz), 116.9, 116.7, 110.0; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.87.



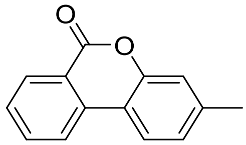
3-nitro-6*H*-benzo[c]chromen-6-one (**2d**) [2]: Yellow solid, mp > 200 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.61 (d, J = 8.1 Hz, 1H), 8.52 (d, J = 8.1 Hz, 1H), 8.28 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 8.2 Hz, 2H), 8.06 – 7.99 (m, 1H), 7.83 – 7.79 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.9, 151.0, 148.3, 136.1, 132.9, 131.6, 130.4, 125.6, 124.4, 124.3, 121.8, 119.5, 113.1.



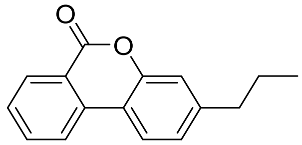
3-acetyl-6*H*-benzo[c]chromen-6-one (**2e**)[6]: Yellow solid, mp 188−190 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 – 8.35 (m, 1H), 8.12 (dd, J = 10.3, 7.7 Hz, 2H), 7.92 – 7.81 (m, 3H), 7.67 – 7.61 (m, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.4, 160.5, 151.1, 138.4, 135.1, 133.6, 130.8, 130.1, 123.9, 123.1, 122.4, 121.9, 121.7, 117.8, 26.7.



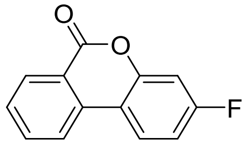
3-phenyl-6*H*-benzo[c]chromen-6-one (**2f**)[1]: White solid, mp 125−127 °C ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, J = 7.9 Hz, 1H), 8.05 (dd, J = 11.7, 8.1 Hz, 2H), 7.80 – 7.77 (m, 1H), 7.62 (d, J = 7.4 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.49 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.2, 151.6, 143.4, 139.2, 134.8, 134.6, 130.6, 129.0, 128.8, 128.3, 127.1, 123.3, 123.2, 121.7, 121.1, 116.9, 115.7.



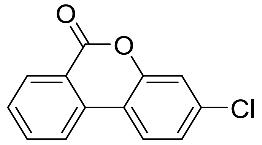
3-methyl-6*H*-benzo[c]chromen-6-one (**2g**)[1]: White solid, mp 133−135 °C, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.35 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.53 – 7.51 (m, 1H), 7.13 – 7.11 (m, 2H), 2.43 (s, 3H).; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 161.4, 151.2, 141.3, 135.0, 134.8, 130.5, 128.3, 125.7, 122.5, 121.4, 120.9, 117.9, 115.4, 21.4.



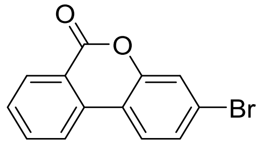
3-propyl-6*H*-benzo[c]chromen-6-one (**2h**) : White solid, mp 59−61 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, J = 7.9 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.52 – 7.49 (m, 1H), 7.13 – 7.11 (m, 2H), 2.67 – 2.63 (m, 2H), 1.73 – 1.63 (m, 2H), 0.99 – 0.94 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 151.3, 146.1, 135.0, 134.7, 130.5, 128.3, 125.0, 122.5, 121.4, 120.9, 117.2, 115.6, 37.7, 24.2, 13.7; HRMS (ESI) m/z $C_{16}H_{15}O_2$ $[M+H]^+$ Calcd for 239.1072; found 239.1067.



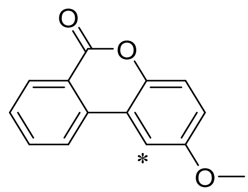
3-fluoro-6*H*-benzo[c]chromen-6-one (**2i**)[1]: White solid, mp 157−159 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, J = 8.0 Hz, 1H), 8.01 – 7.97 (m, 2H), 7.82 – 7.78 (m, 1H), 7.56 – 7.52 (m, 1H), 7.07 – 7.03 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.5 (d, J_{C-F} = 249.8 Hz), 160.7, 152.1(d, J_{C-F} = 12.1 Hz), 135.1, 134.2, 130.6, 128.7, 124.4(d, J_{C-F} = 9.8 Hz), 121.5, 120.4, 114.6(d, J_{C-F} = 3.0 Hz), 112.4(d, J_{C-F} =22.2 Hz), 105.1 (d, J_{C-F}= 25.1 Hz); ^{19}F NMR (376 MHz, Chloroform-d) δ -108.39.



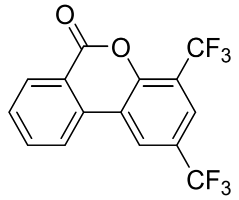
3-chloro-6*H*-benzo[c]chromen-6-one (**2j**)[1]: White solid, mp 153−155 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.59 – 7.55 (m, 1H), 7.29 – 7.27 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.5, 151.4, 135.9, 135.1, 133.9, 130.6, 129.2, 125.0, 123.8, 121.6, 120.8, 117.8, 116.6.



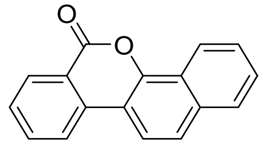
3-bromo-6*H*-benzo[c]chromen-6-one (**2k**)[1]: White solid, mp 149−151 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.57 – 7.54 (m, 1H), 7.46 – 7.36 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.4, 151.4, 135.1, 133.9, 130.7, 129.2, 127.8, 123.9, 123.7, 121.6, 120.9, 120.8, 117.0.



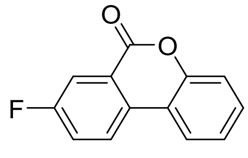
2-methoxy-6*H*-benzo[c]chromen-6-one (**2l**)[1]: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (dd, J = 7.9, 1.4 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.54 – 7.49 (m, 1H), 7.37 (d, J = 2.9 Hz, 1H), 7.20 (d, J = 9.0 Hz, 1H), 6.97 (dd, J = 9.0, 2.9 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.2, 156.3, 145.5, 134.7, 134.5, 130.5, 128.9, 121.6, 121.2, 118.5, 118.4, 117.1, 106.2, 55.8



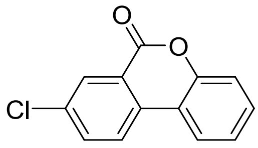
2,4-bis(trifluoromethyl)-6*H*-benzo[c]chromen-6-one (**2m**)[7]: White solid, mp 174−175 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, J = 2.1 Hz, 1H), 8.44 (dd, J = 8.0, 1.4 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.76 – 7.69 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.2, 150.6, 135.6, 132.5,131.0, 130.8, 126.5(q, $J_{C\text{-}F}$ = 33.9 Hz), 124.6 (br), 124.0 (br), 123.1 (d, $J_{C\text{-}F}$ = 270.7 Hz),122.1, 121.9(d, $J_{C\text{-}F}$ = 271.9 Hz), 121.1, 120.3(d, $J_{C\text{-}F}$ = 33.1 Hz), 120.0; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.16, -62.33.



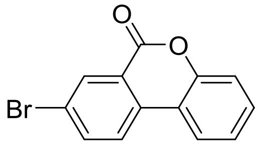
6*H*-dibenzo[c,h]chromen-6-one (**2n**)[8]: Yellow solid, mp 193−195 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 – 8.42 (m, 1H), 8.35 (dd, J = 7.9, 1.4 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.58 – 7.46 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.0, 147.1, 135.2, 134.8, 134.1, 130.5, 128.5, 127.8, 127.6, 127.0, 124.4, 123.7, 122.2, 121.9, 121.0, 119.0, 112.9.



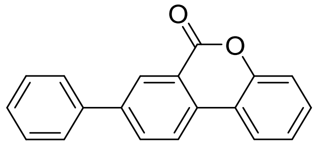
8-fluoro-6*H*-benzo[c]chromen-6-one (**2o**)[4]: White solid, mp 145−147 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, J = 8.9, 4.8 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.54 – 7.46 (m, 1H), 7.46 – 7.40 (m, 1H), 7.35 – 7.27 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.4 (d, $J_{C\text{-}F}$ = 249.3 Hz), 160.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 150.7, 131.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.4, 124.8, 124.2(d, $J_{C\text{-}F}$ = 7.8 Hz), 123.0 (d, $J_{C\text{-}F}$ =22.8 Hz), 123.1 (d, $J_{C\text{-}F}$ = 8.1 Hz),122.6, 117.7, 117.3, 116.1(d, $J_{C\text{-}F}$ = 23.0 Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.16.



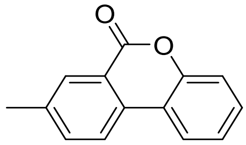
8-chloro-6*H*-benzo[c]chromen-6-one (**2p**)[4]: Yellow solid, mp 170−172 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, J = 2.3 Hz, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.72 (dd, J = 8.6, 2.3 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.34 – 7.29 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.9, 151.1, 135.1, 135.0, 133.2, 130.80, 130.0, 124.8, 123.4, 122.7, 122.5, 117.8, 117.2.



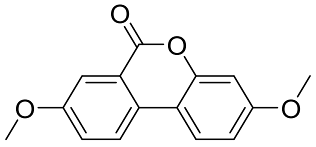
8-bromo-6*H*-benzo[c]chromen-6-one (**2q**)[9]: White solid, mp 173−175 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, J = 2.1 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.85 (dd, J = 8.6, 2.1 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.34 – 7.28 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.7, 151.0, 137.9, 133.5, 133.0, 130.9, 124.8, 123.0, 122.7, 122.7, 122.6, 117.8, 117.2.



8-phenyl-6*H*-benzo[c]chromen-6-one (**2r**)[1]: Yellow solid, mp 176−178 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, J = 1.6 Hz ,1H), 8.10 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 6.2 Hz, 2H), 7.67 – 7.63 (m, 2H), 7.50 – 7.37 (m, 4H), 7.31 (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.2, 151.2, 141.7, 138.8, 133.4, 133.4, 130.3, 129.1, 128.4, 128.3, 127.0, 124.6, 122.8, 122.3, 121.6, 117.9, 117.7.

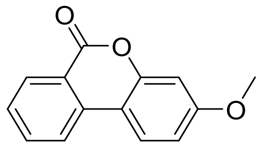


8-methyl-6*H*-benzo[c]chromen-6-one (**2s**)[4]: White solid, mp 120−122 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.97 – 7.92 (m, 2H), 7.57 (dd, J = 8.2, 2.0 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.33 – 7.26 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.3, 151.0, 139.2, 136.0, 132.1, 130.3, 129.9, 124.4, 122.5, 121.6, 121.0, 118.1, 117.6, 21.2.

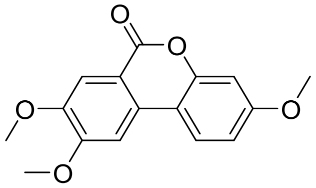


3,8-dimethoxy-6*H*-benzo[c]chromen-6-one (**2t**)[5] : Yellow solid, mp 149−151 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.65 (d, J = 5.2 Hz, 1H), 7.30 (dd, J = 8.9, 2.8 Hz, 1H), 6.84 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 5.0 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ

161.5, 160.6, 159.1, 151.5, 128.5, 124.3, 123.0, 122.7, 120.8, 112.3, 111.2, 110.9, 101.4, 55.7, 55.6.



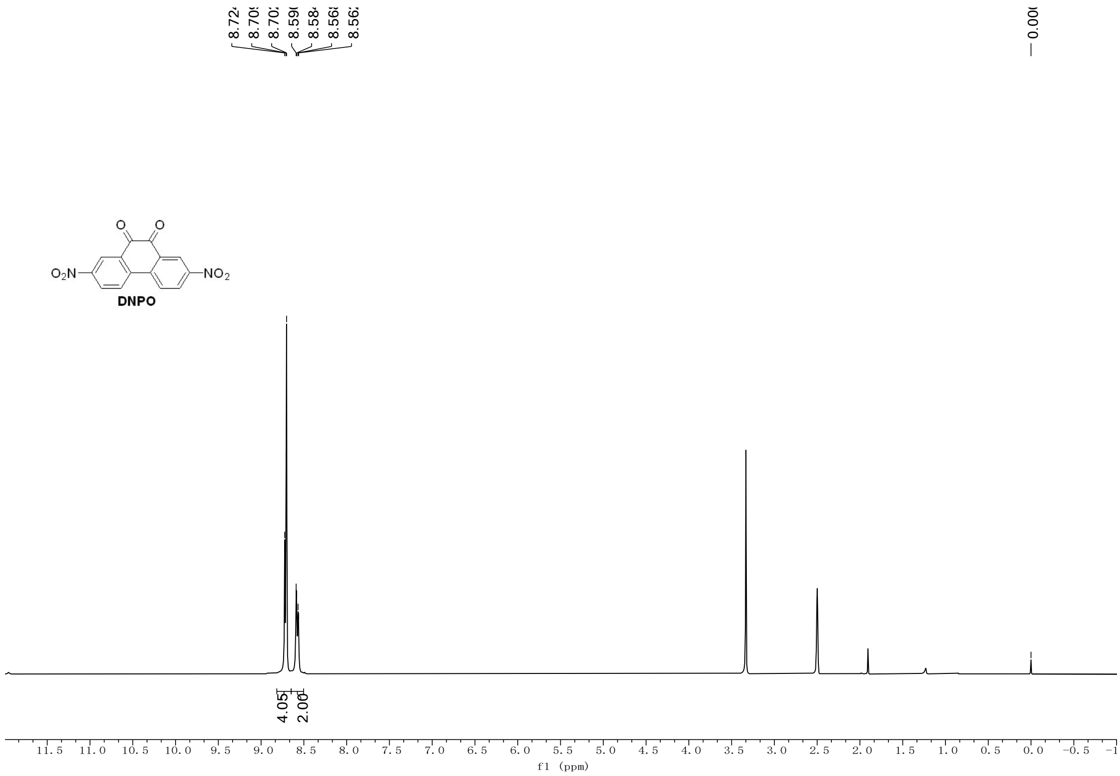
3-methoxy-6*H*-benzo[c]chromen-6-one (**2u**)[4]: White solid, mp 143−145 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.28 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.47 – 7.41 (m, 1H), 6.84 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100MHz, Chloroform-*d*) *δ* 161.4 , 152.5, 135.1, 134.8, 130.4, 127.7, 123.7, 121.0, 119.9, 112.3, 111.1, 101.6, 55.7.



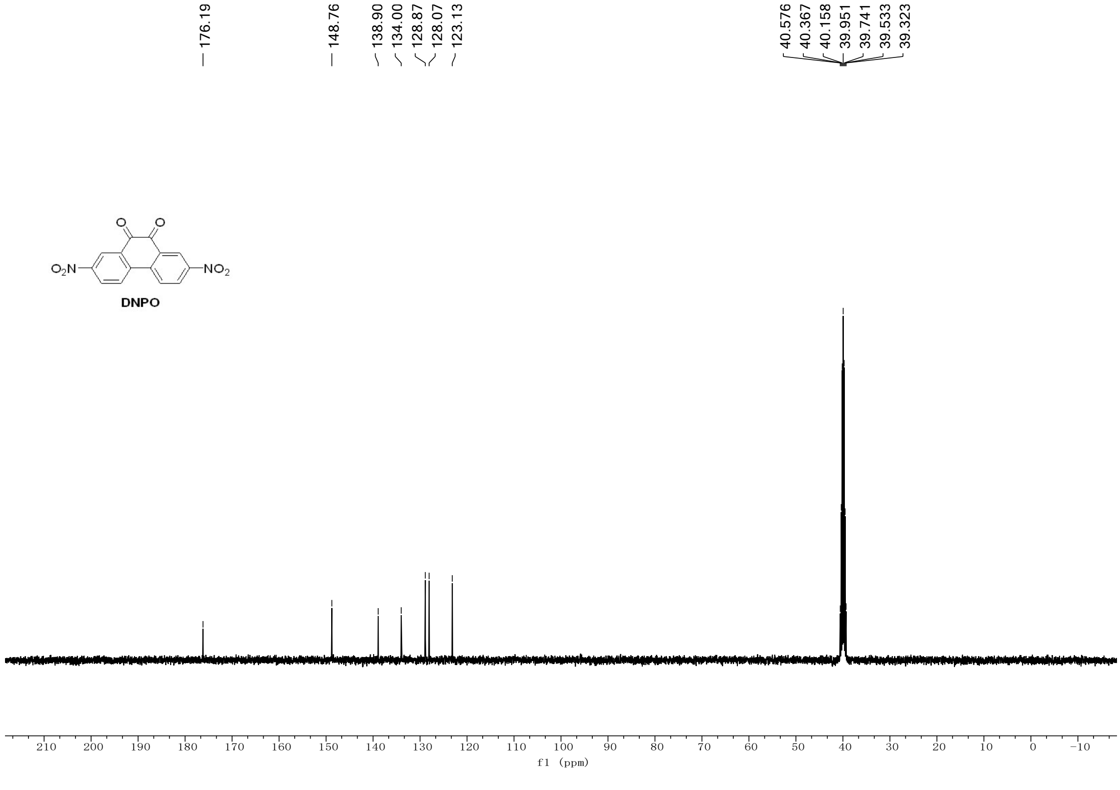
3,8,9-trimethoxy-6*H*-benzo[c]chromen-6-one (**2v**)[5]: Yellow solid, mp 177−179 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.73 (d, *J* = 8.7 Hz, 1H), 7.57 (s, 1H), 7.21 (s, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.73 (s, 1H), 4.05 (s, 3H), 3.94 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 161.3, 160.8, 155.1, 152.2, 149.2, 130.3, 123.0, 112.9, 112.2, 111.1, 110.3, 102.0, 101.4, 56.2, 56.2, 55.6.

7. NMR Spectra

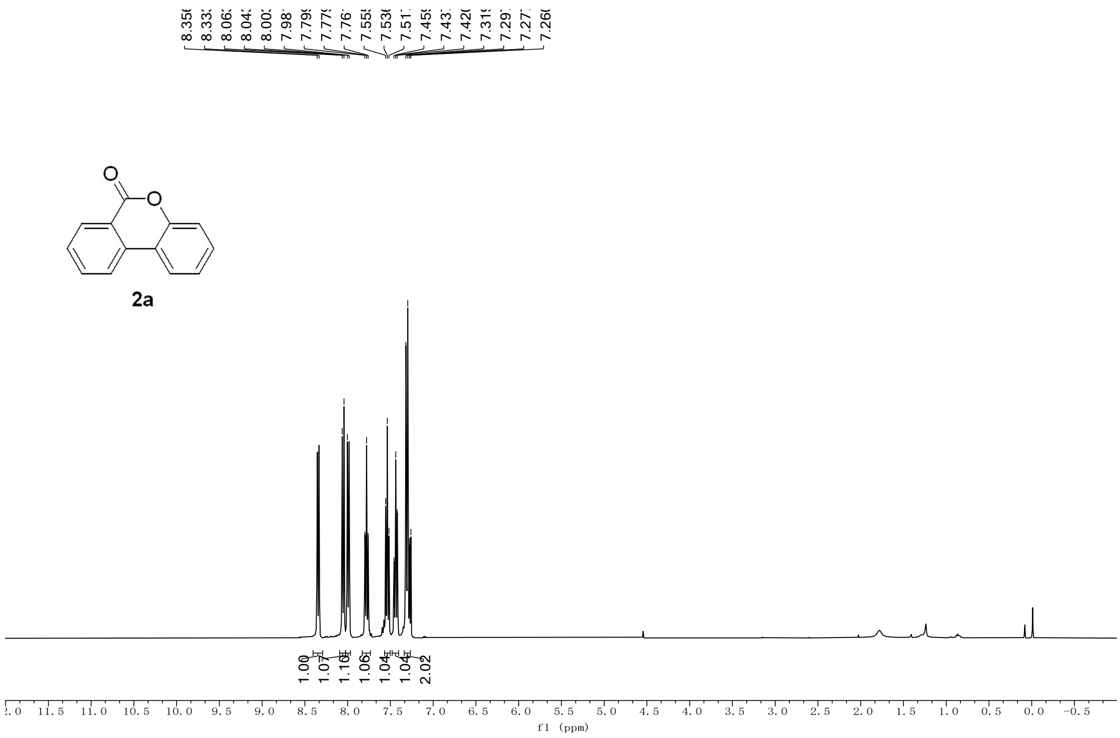
^1H NMR, 400 MHz, DMSO-d_6



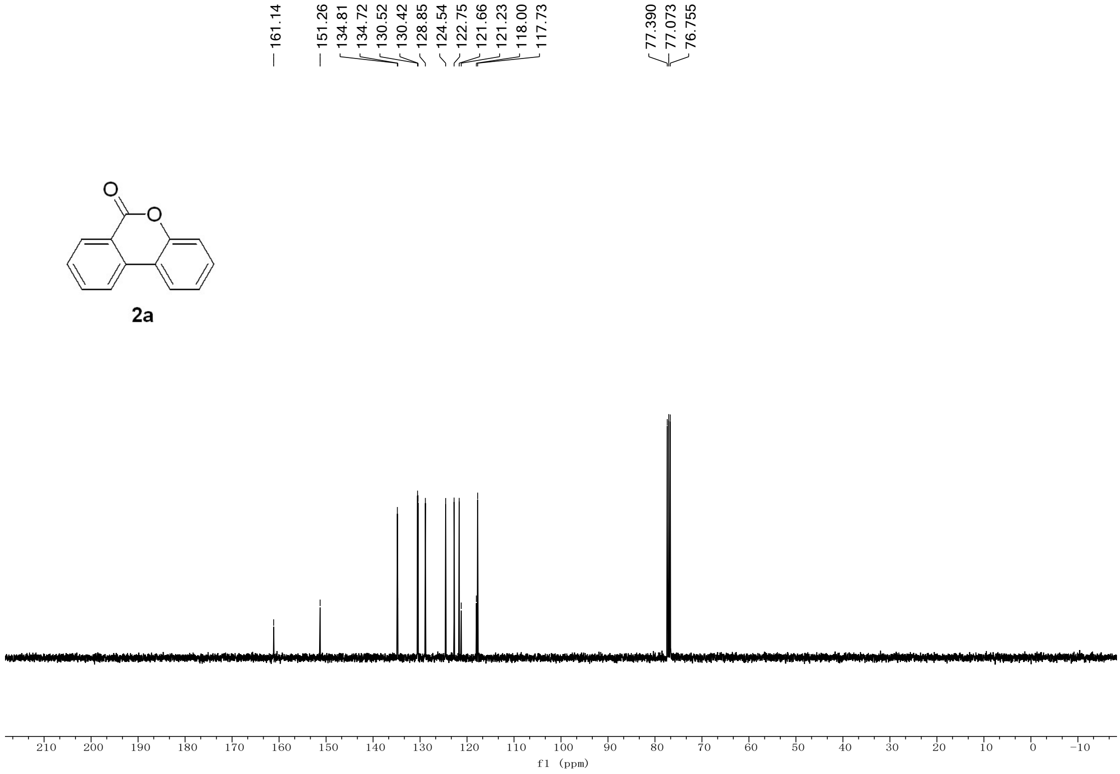
^{13}C NMR, 100 MHz, DMSO-d_6



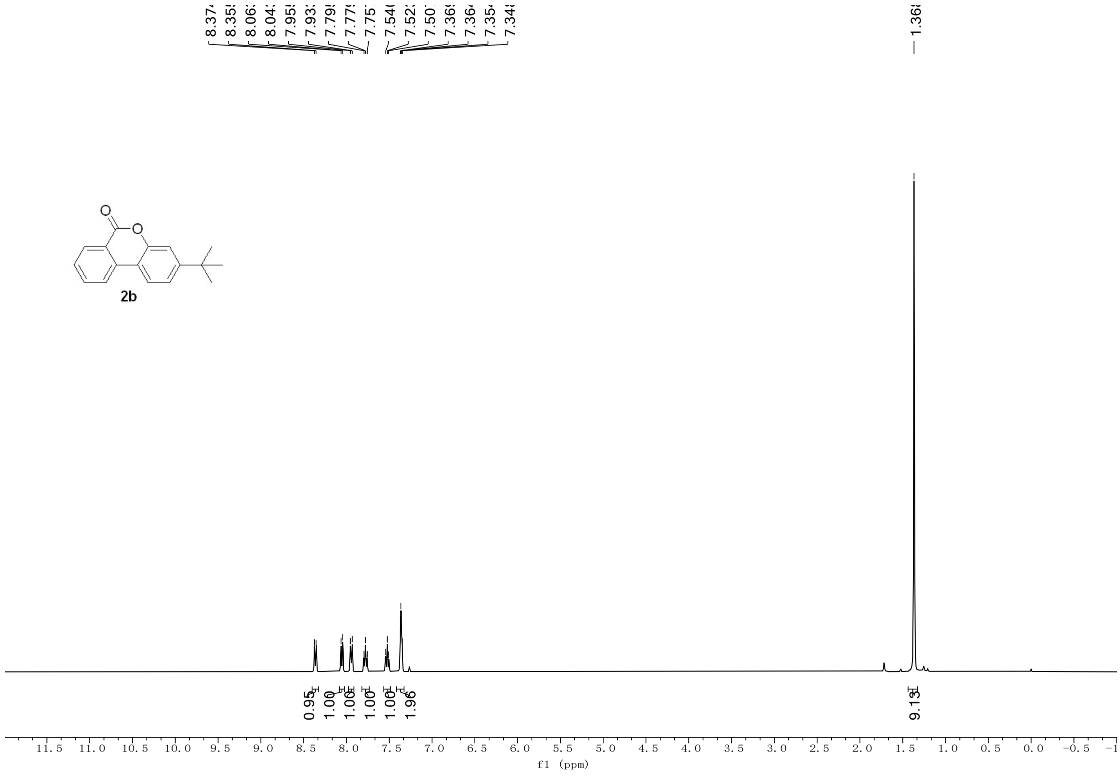
^{1}H NMR, 400 MHz, Chloroform-*d*



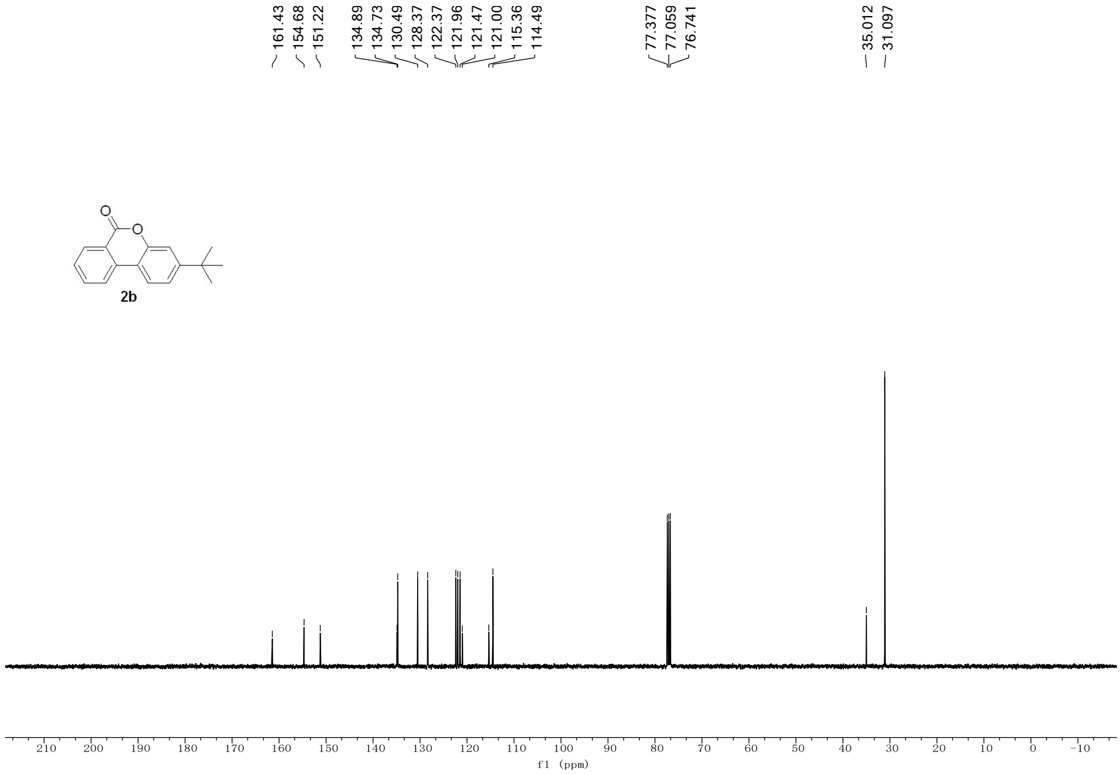
^{13}C NMR, 100 MHz, Chloroform-*d*



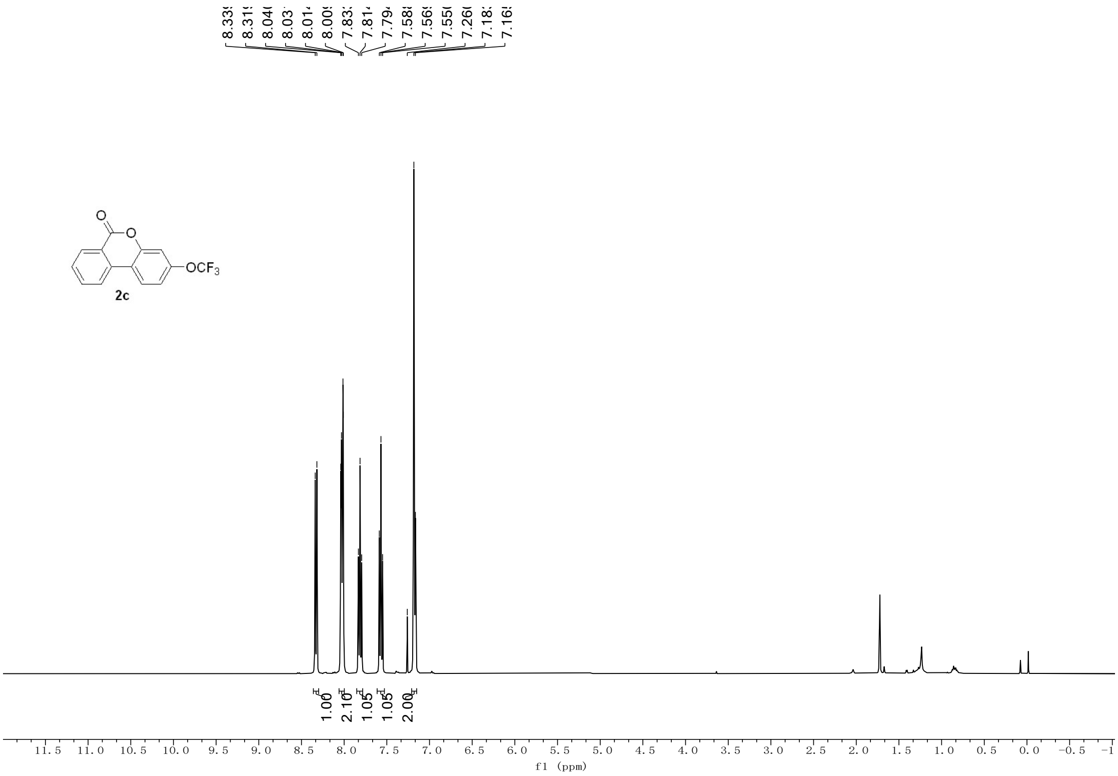
^{1}H NMR ,400 MHz, Chloroform-*d*



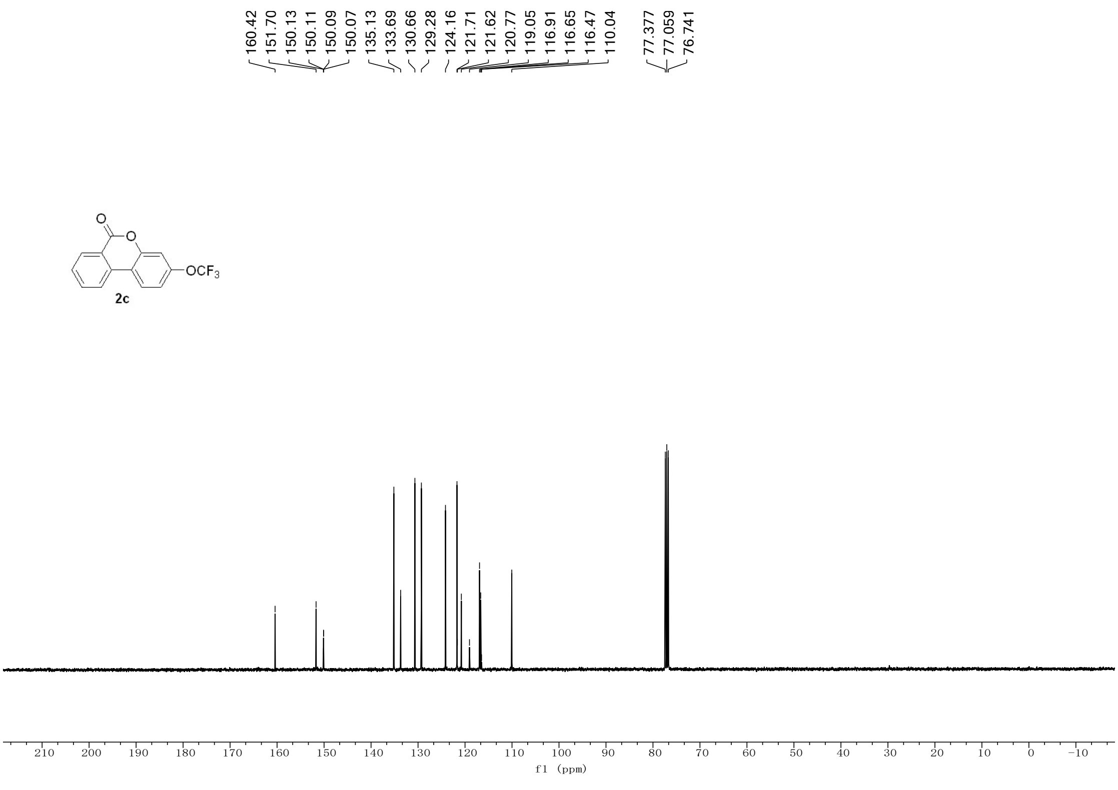
^{13}C NMR ,100 MHz, Chloroform-*d*



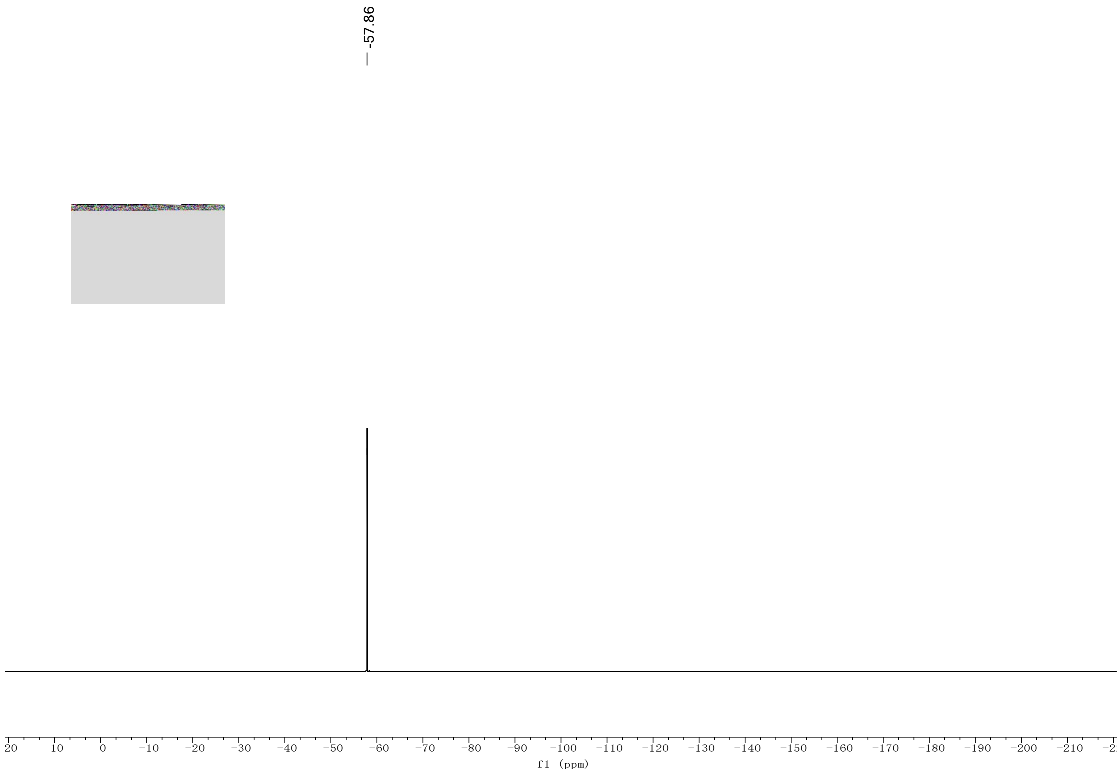
^{1}H NMR ,400 MHz, Chloroform-*d*



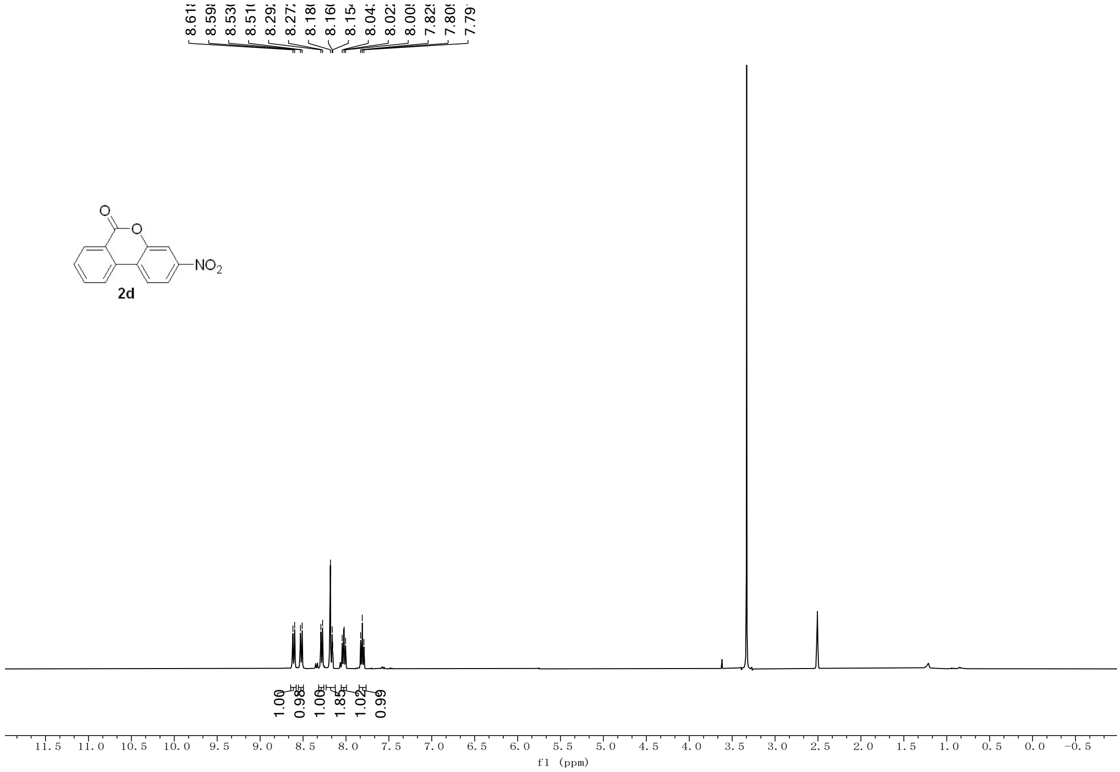
^{13}C NMR ,100 MHz, Chloroform-*d*



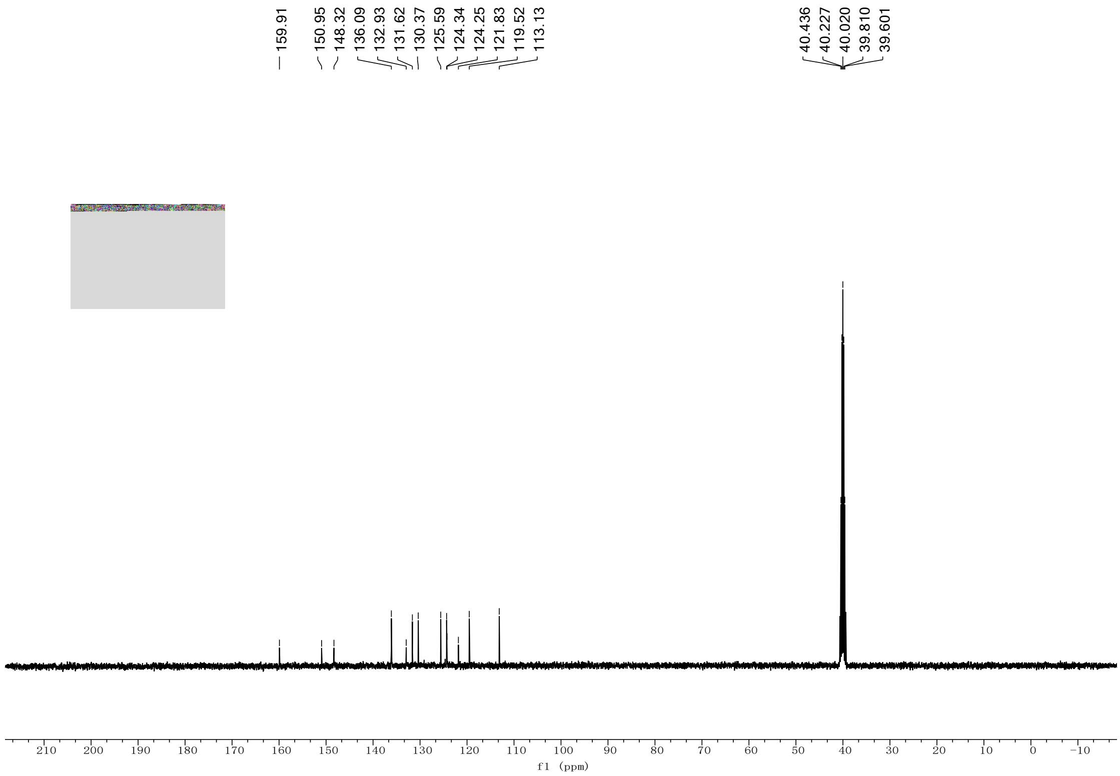
^{19}F NMR ,376 MHz, Chloroform-*d*



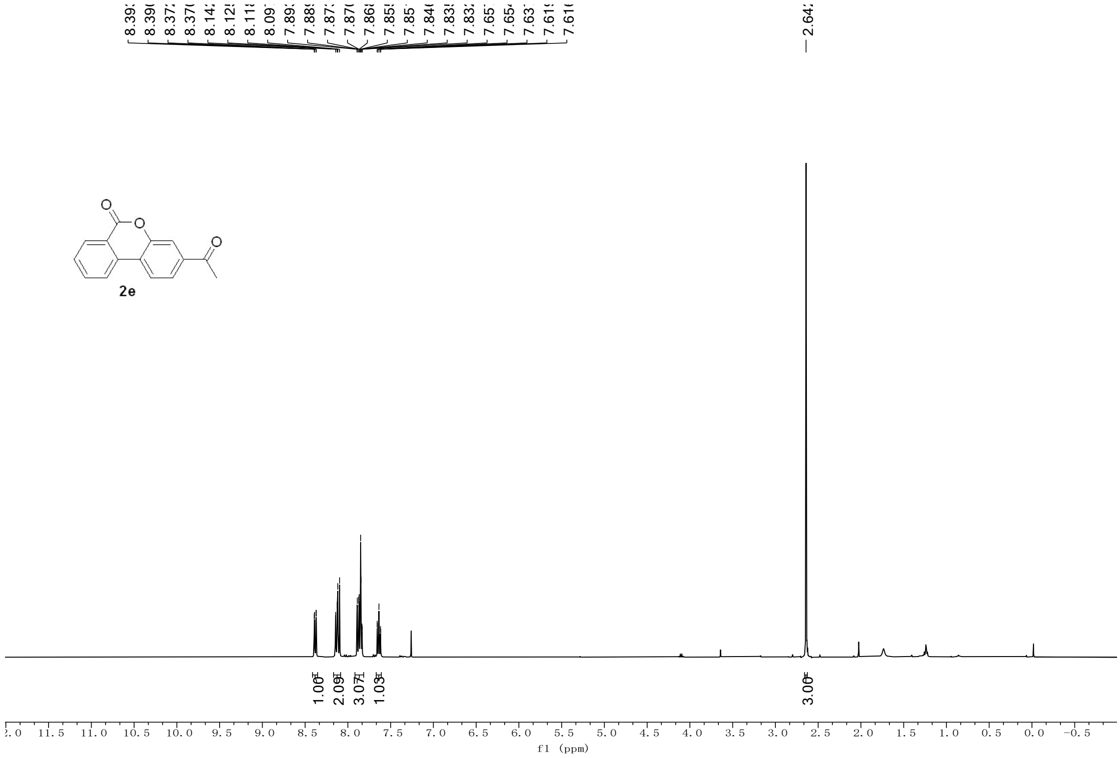
^{1}H NMR, 400 MHz, DMSO-d_6



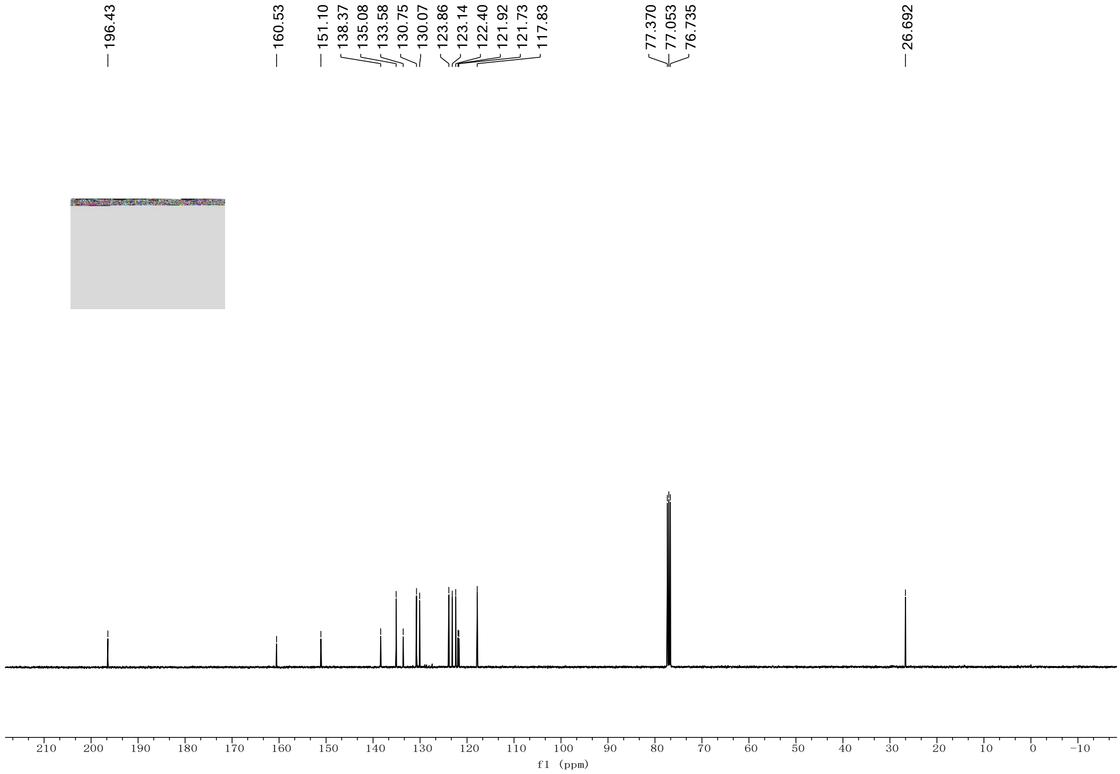
^{13}C NMR, 100 MHz, DMSO-d_6



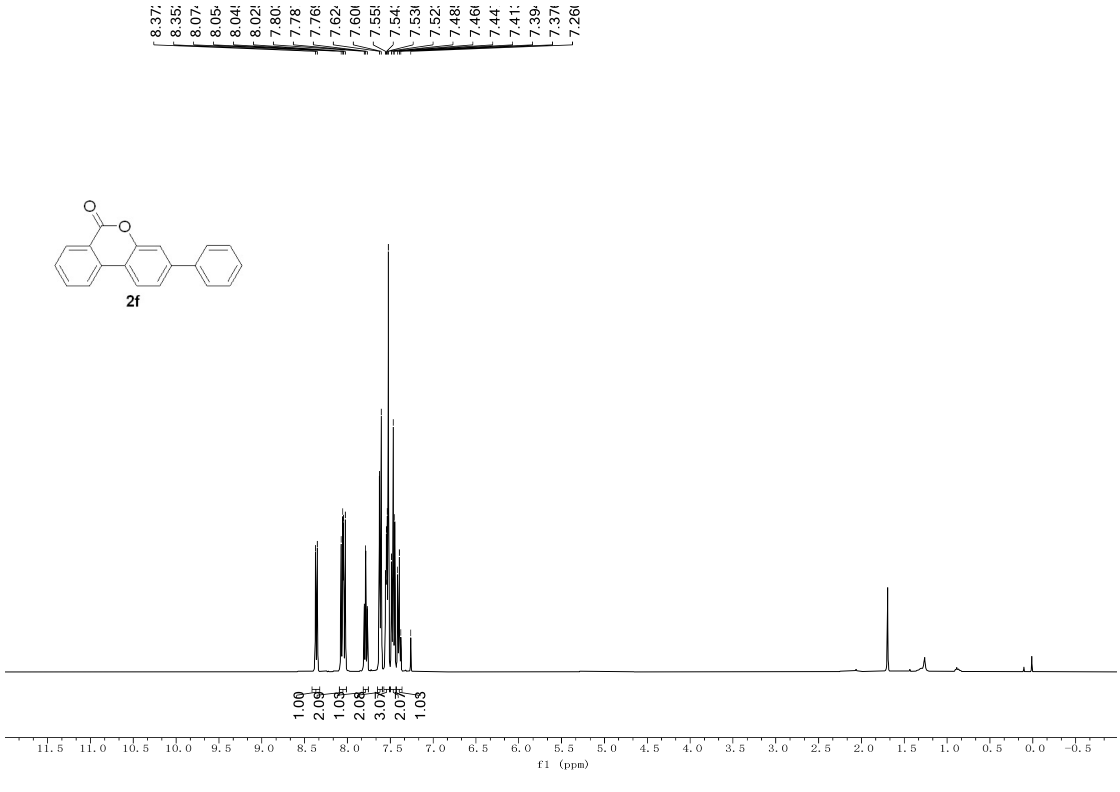
^{1}H NMR ,400 MHz, Chloroform-d



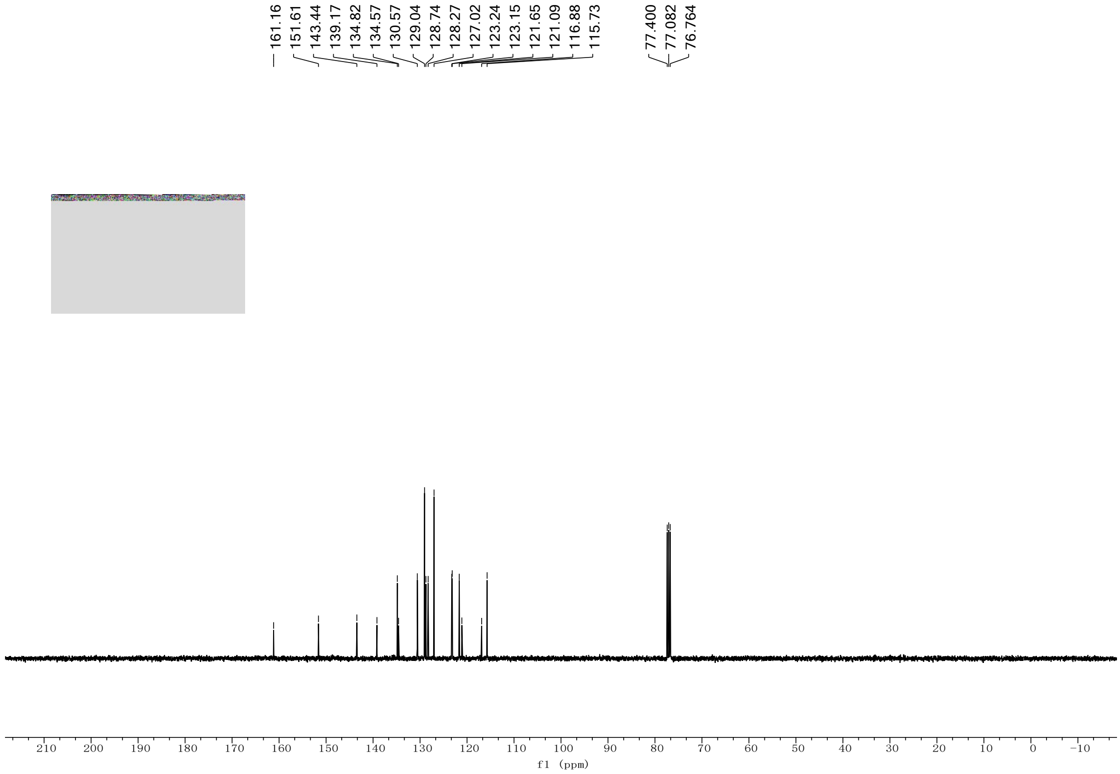
^{13}C NMR, 100 MHz, Chloroform-*d*



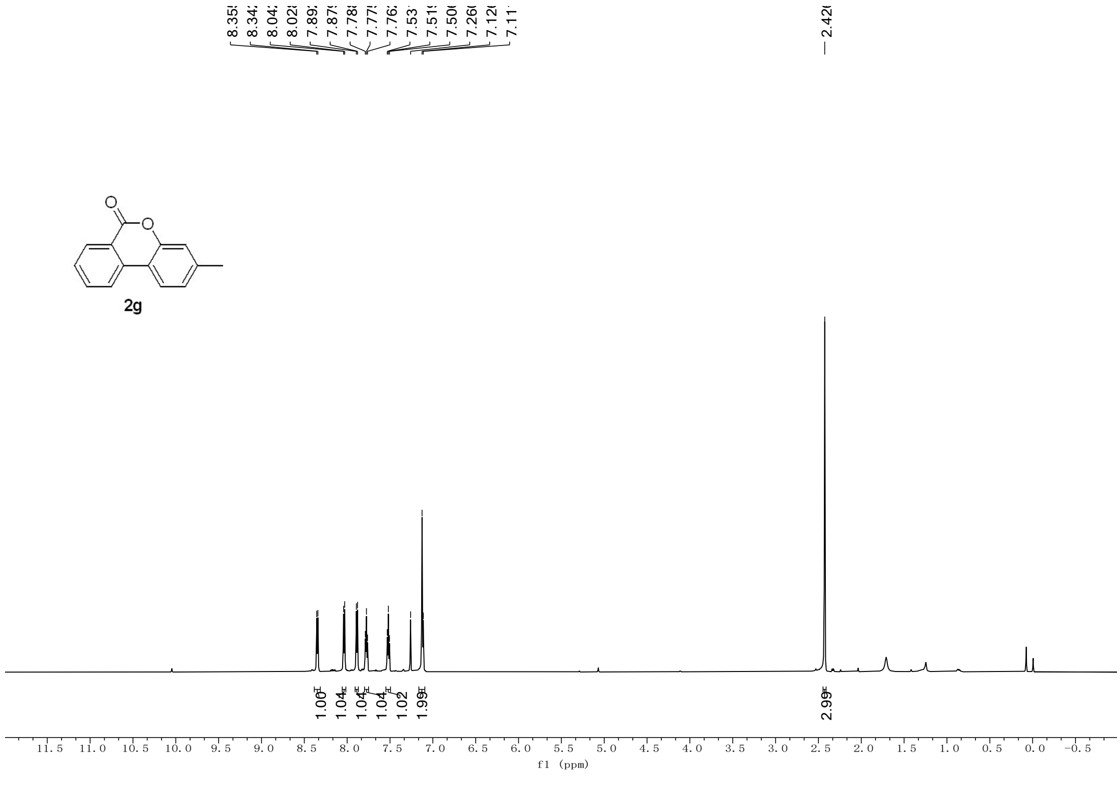
^{1}H NMR, 400 MHz, Chloroform-*d*



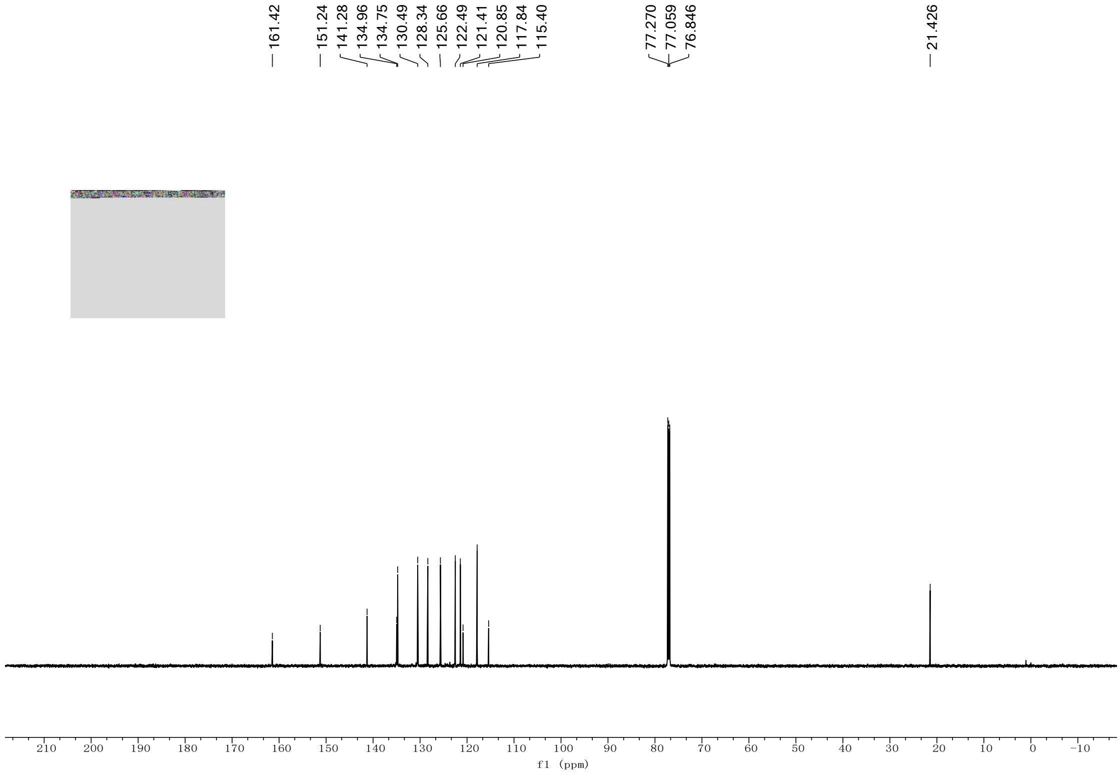
^{13}C NMR, 100 MHz, Chloroform-*d*



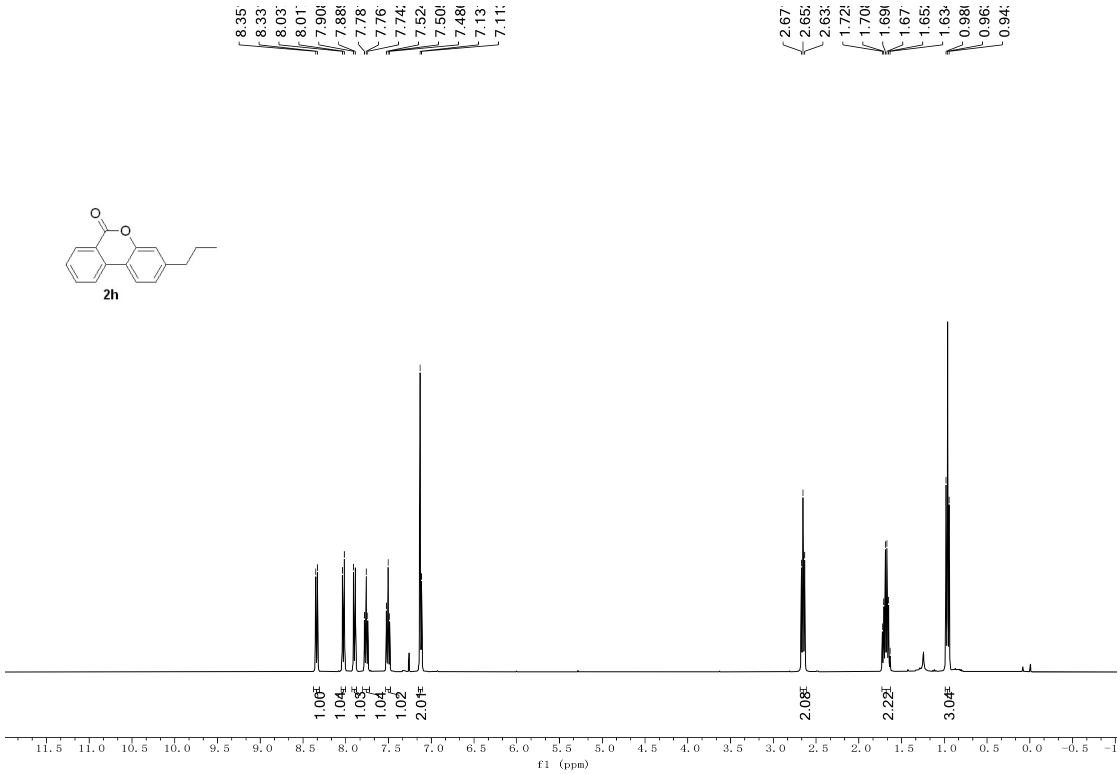
^{1}H NMR, 600 MHz, Chloroform-*d*



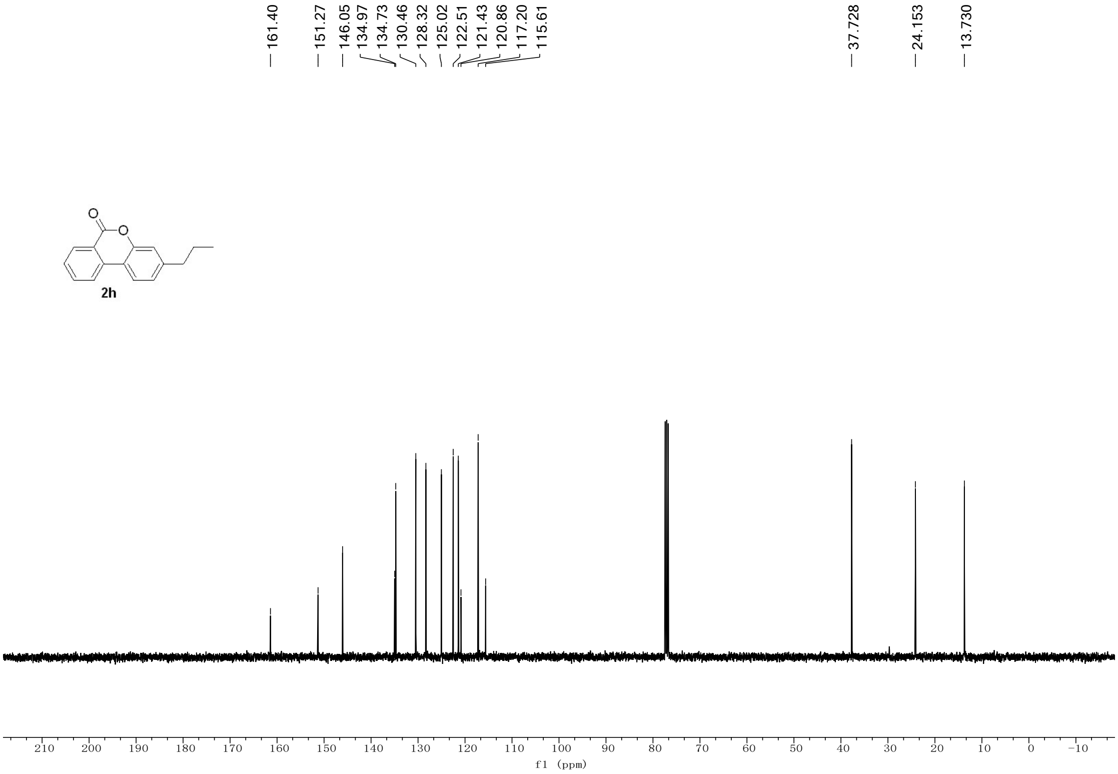
^{13}C NMR, 150 MHz, Chloroform-*d*



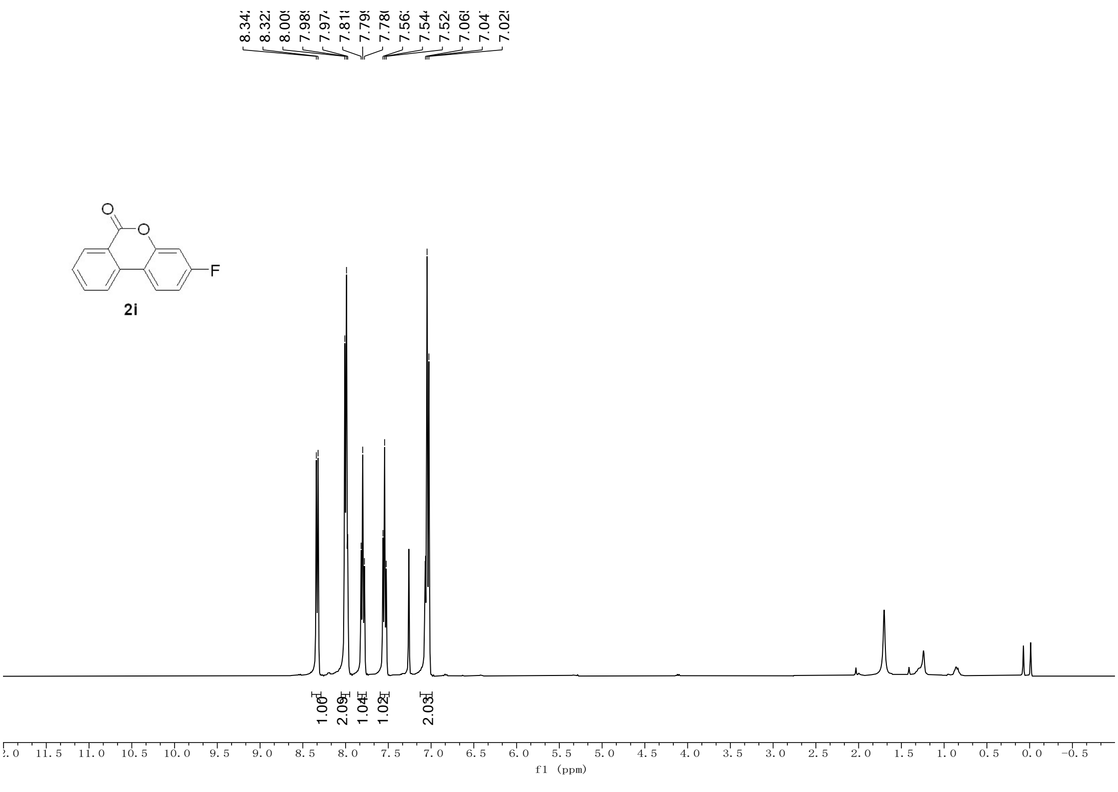
^{1}H NMR, 400 MHz, Chloroform-*d*



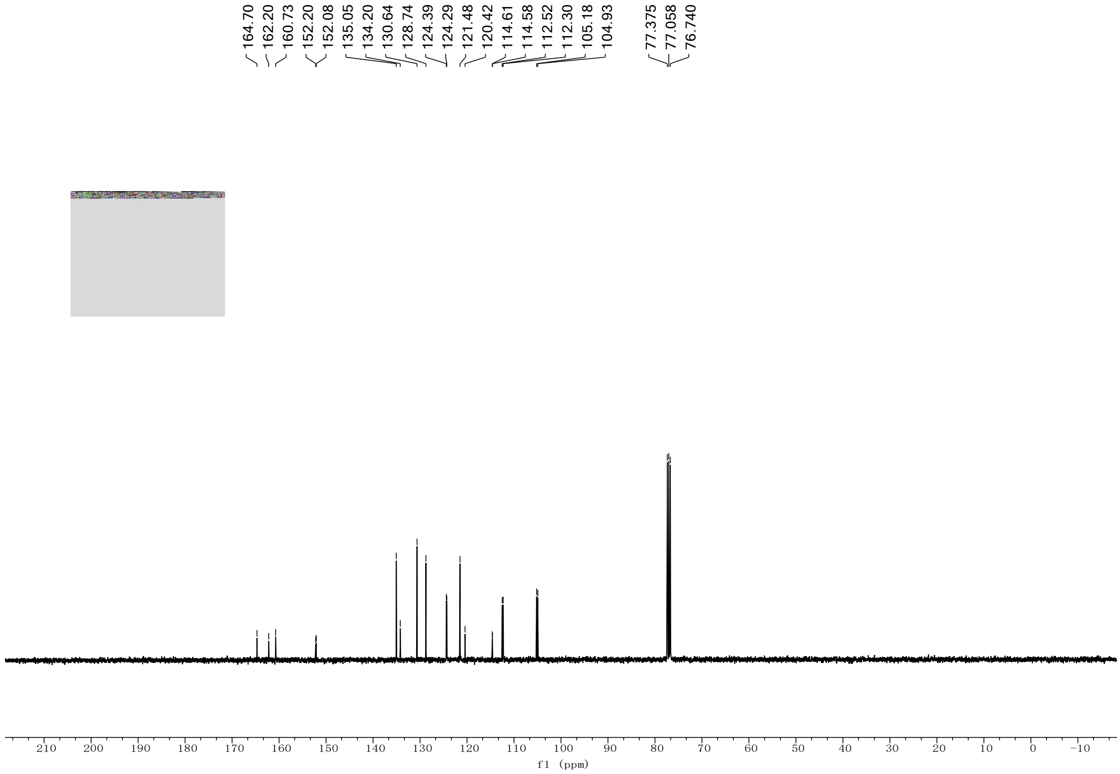
^{13}C NMR, 100 MHz, Chloroform-*d*



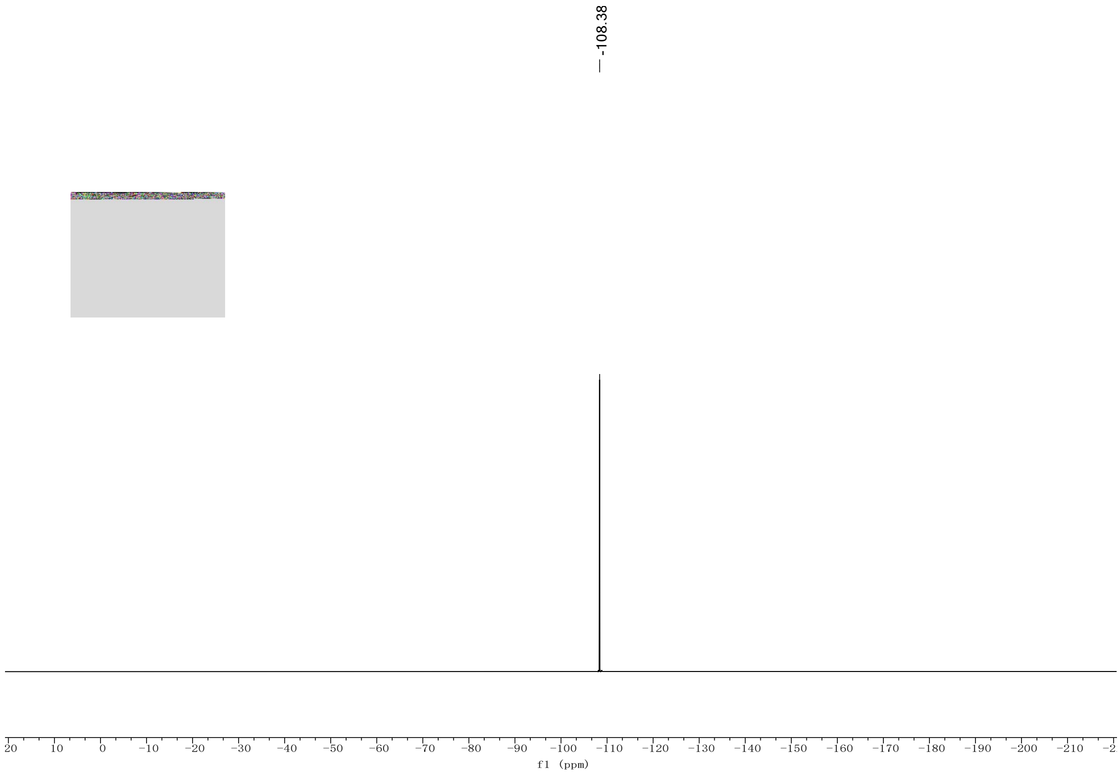
^{1}H NMR, 400 MHz, Chloroform-*d*



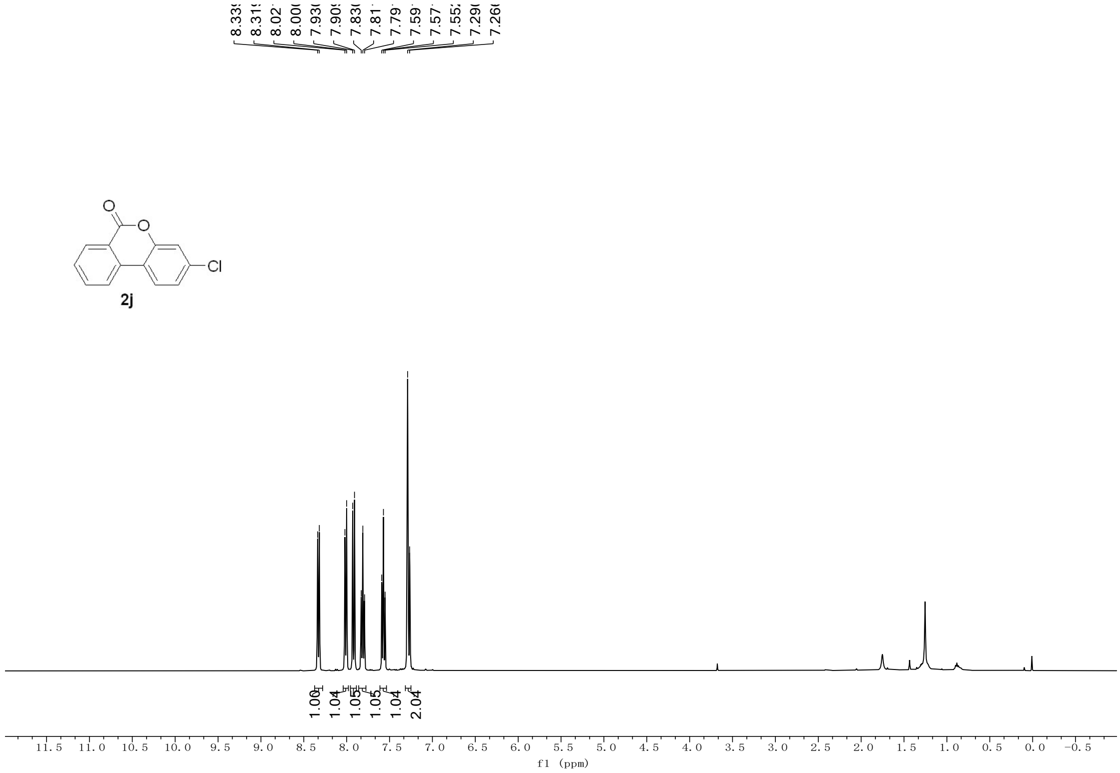
^{1}H NMR, 100 MHz, Chloroform-*d*



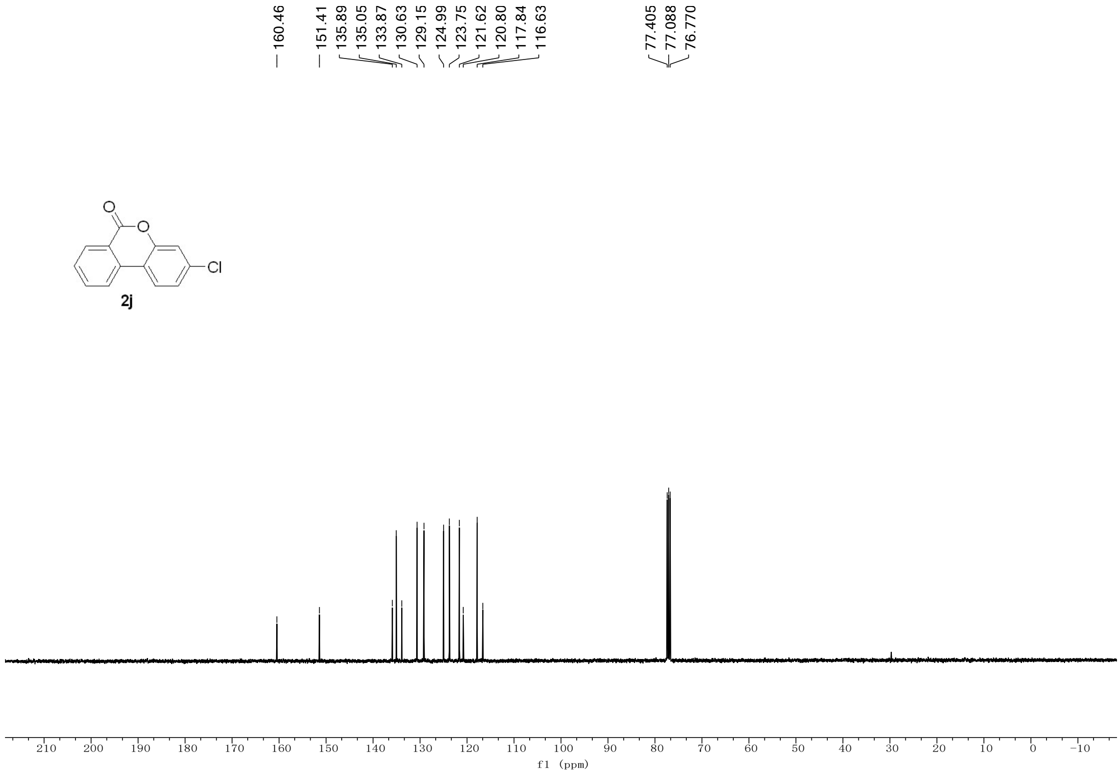
^{19}F NMR, 376 MHz, Chloroform-*d*



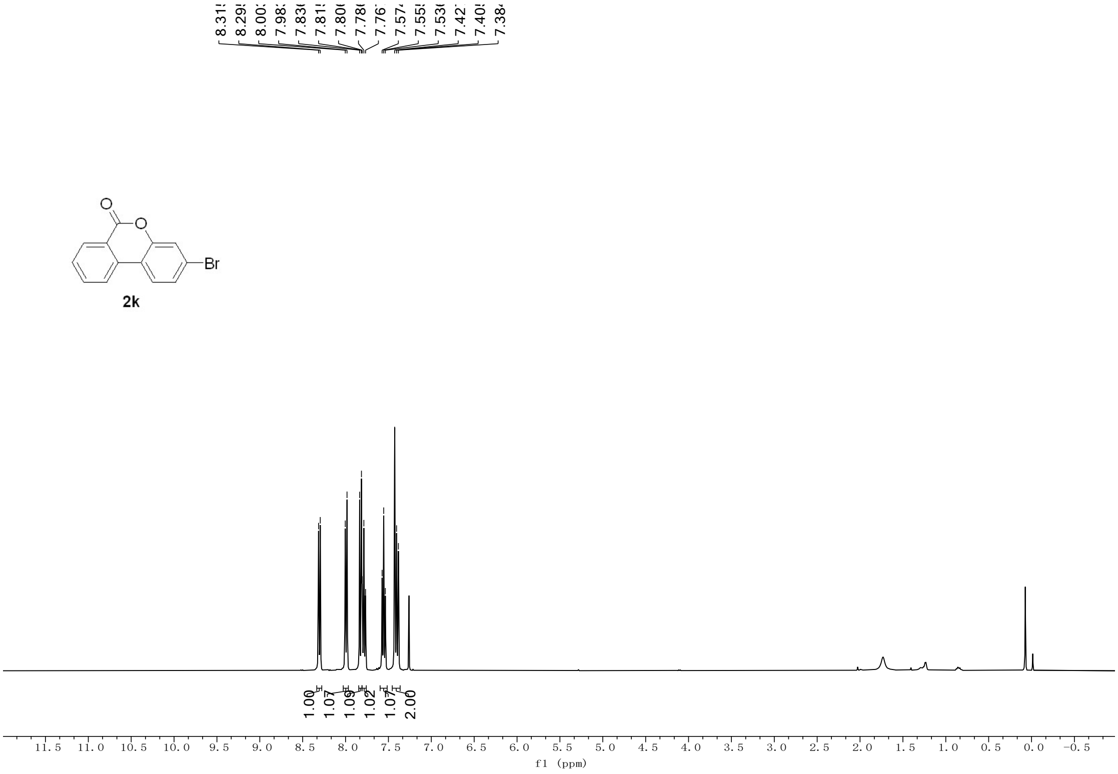
^{1}H NMR, 400 MHz, Chloroform-*d*



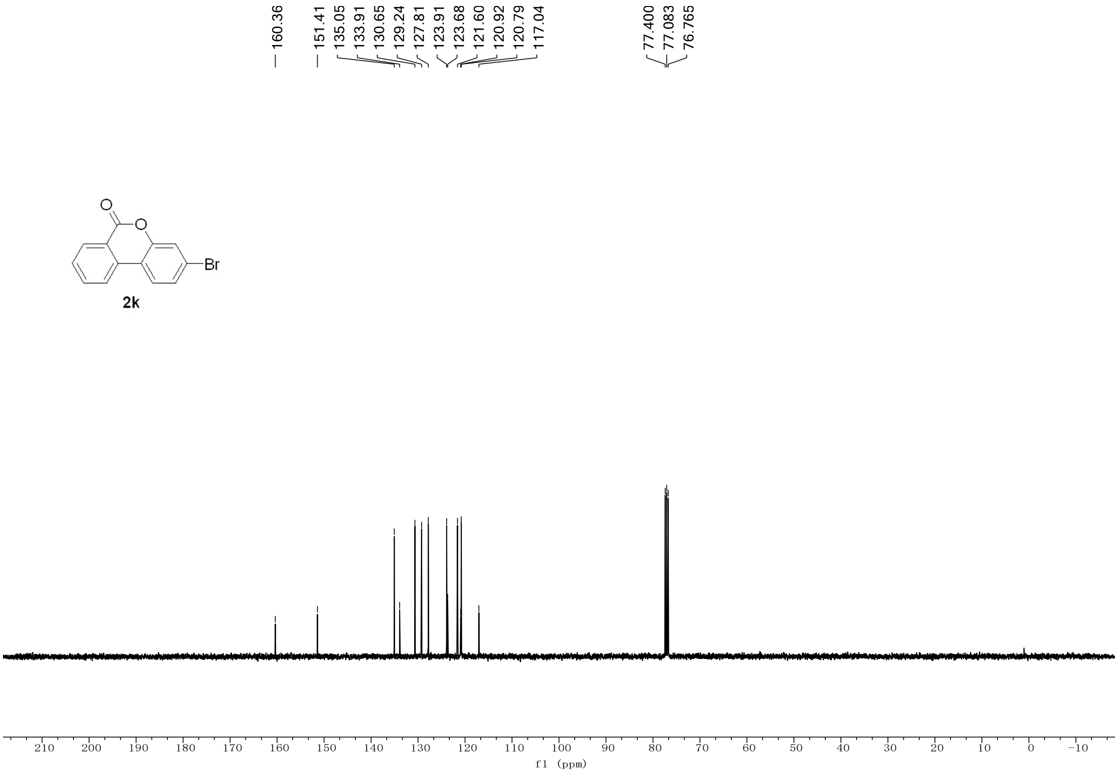
^{13}C NMR, 100 MHz, Chloroform-*d*



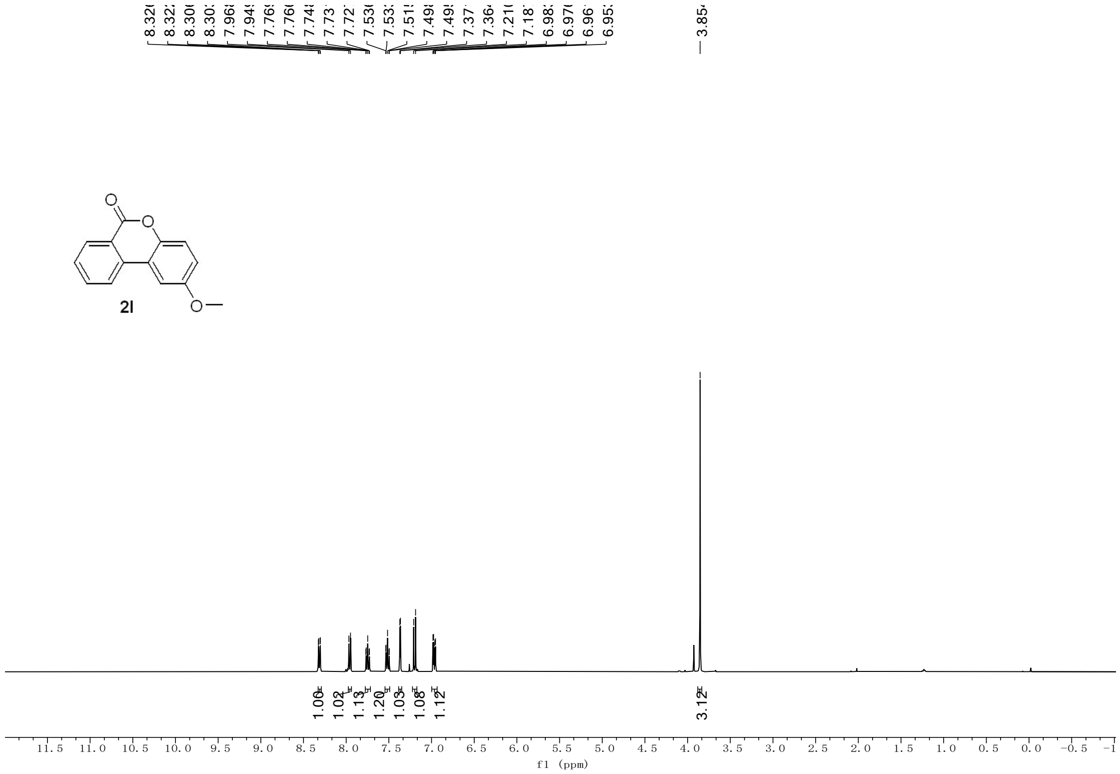
^{1}H NMR, 400 MHz, Chloroform-*d*



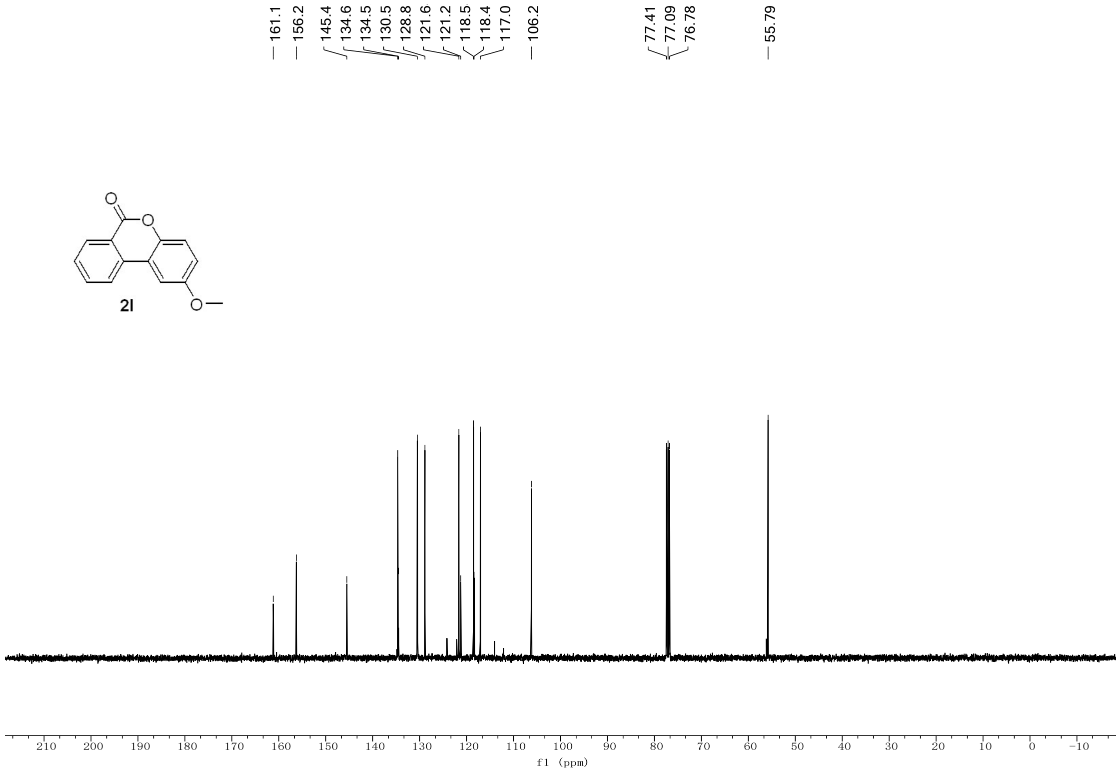
^{13}C NMR, 100 MHz, Chloroform-*d*



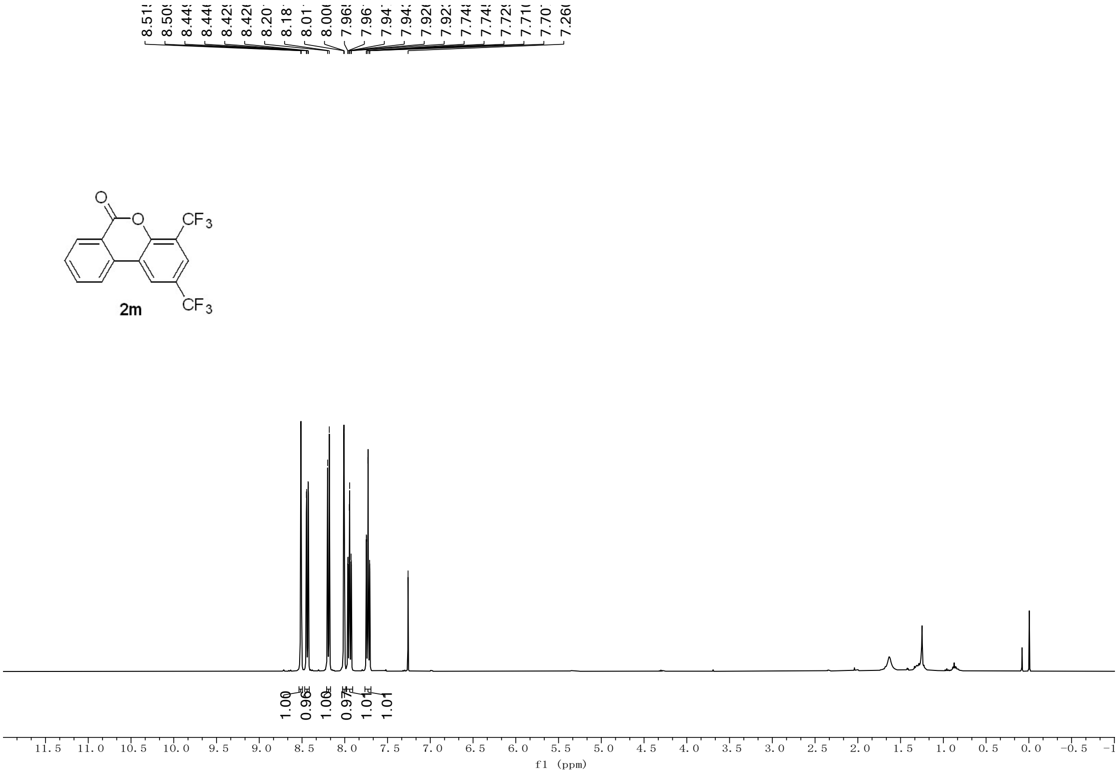
^{1}H NMR, 400 MHz, Chloroform-*d*



^{13}C NMR, 100 MHz, Chloroform-*d*



^{1}H NMR, 400 MHz, Chloroform-*d*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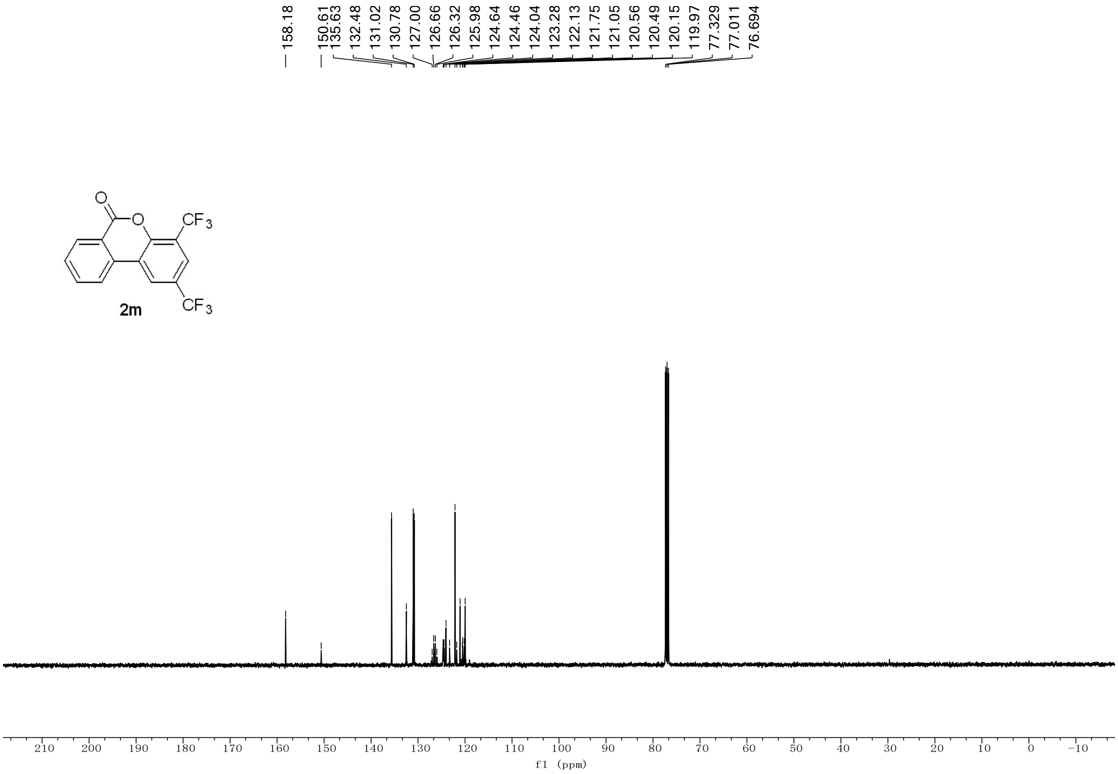
^{13}C NMR, 100 MHz, Chloroform-*d*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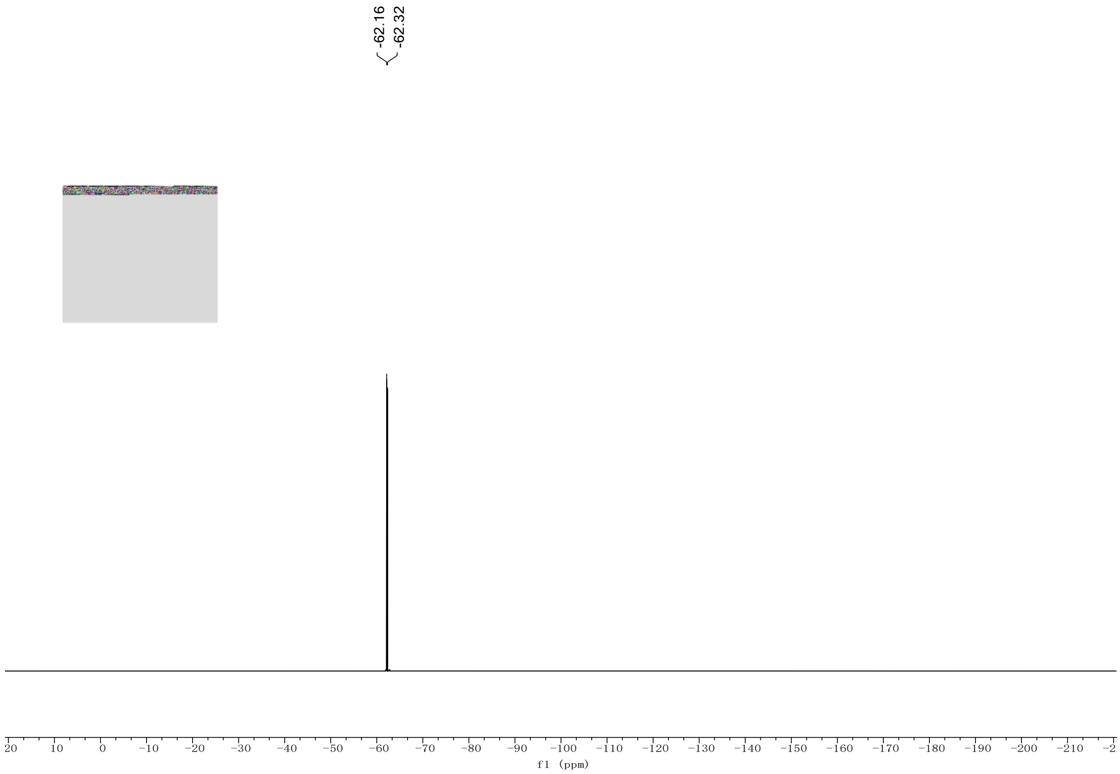
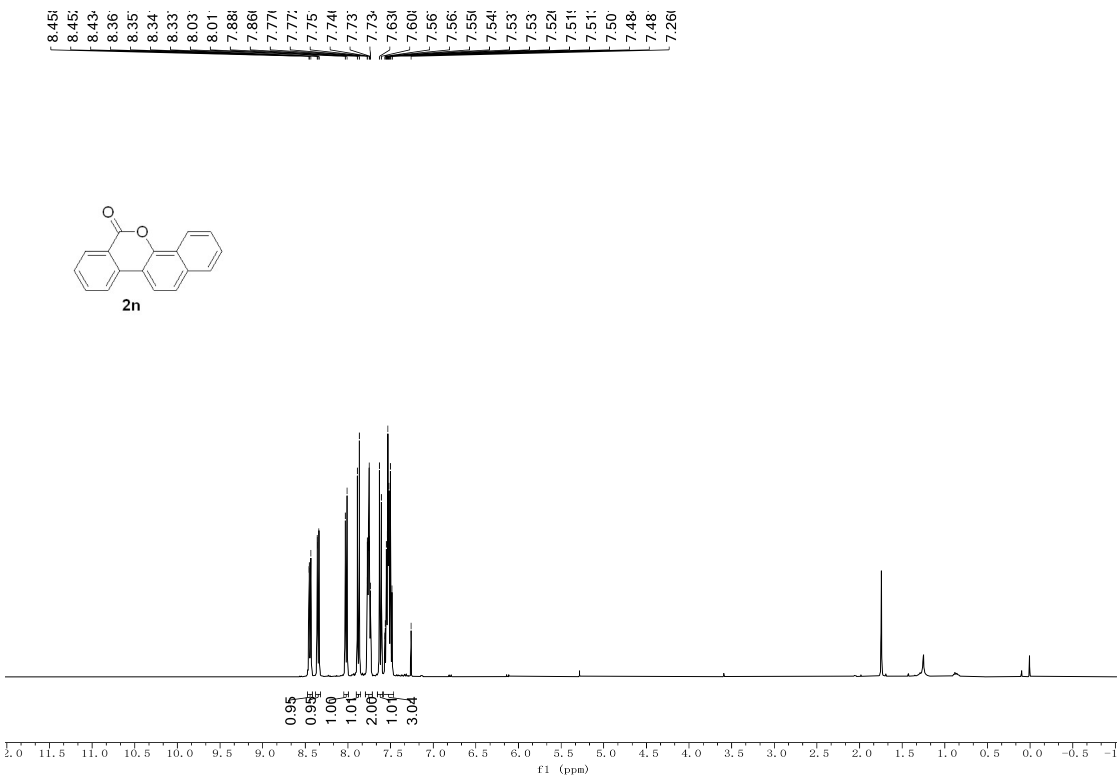
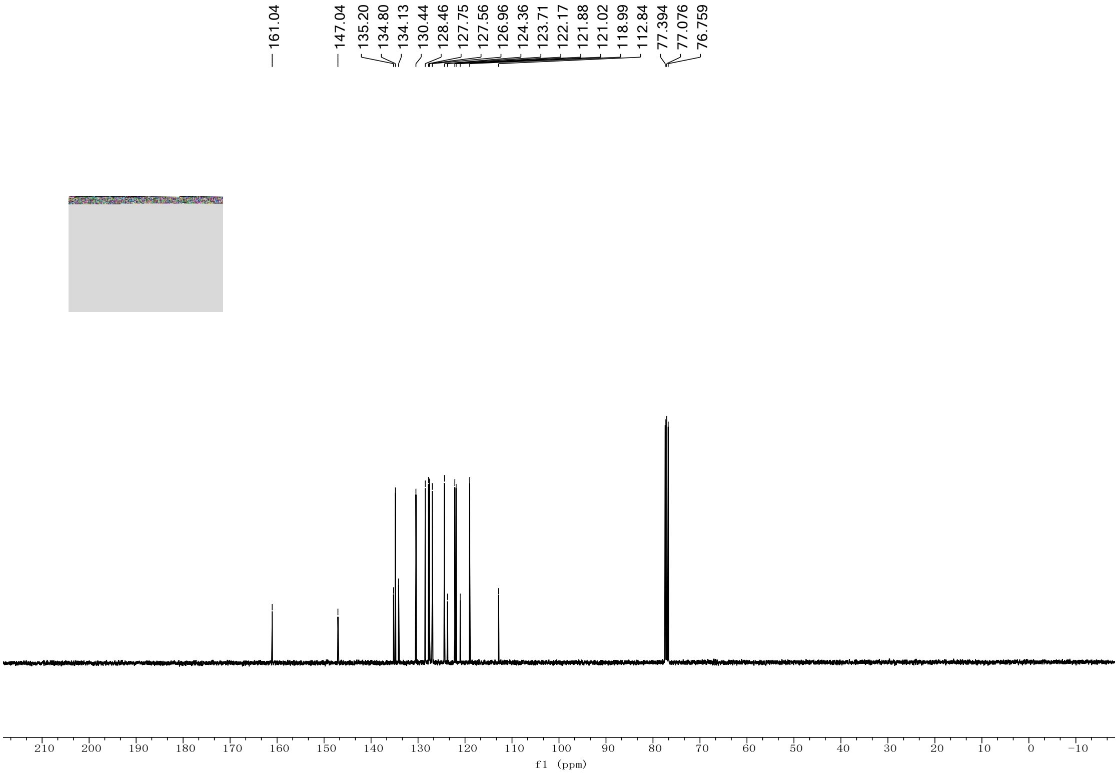
^{19}F NMR, 376 MHz, Chloroform-*d*



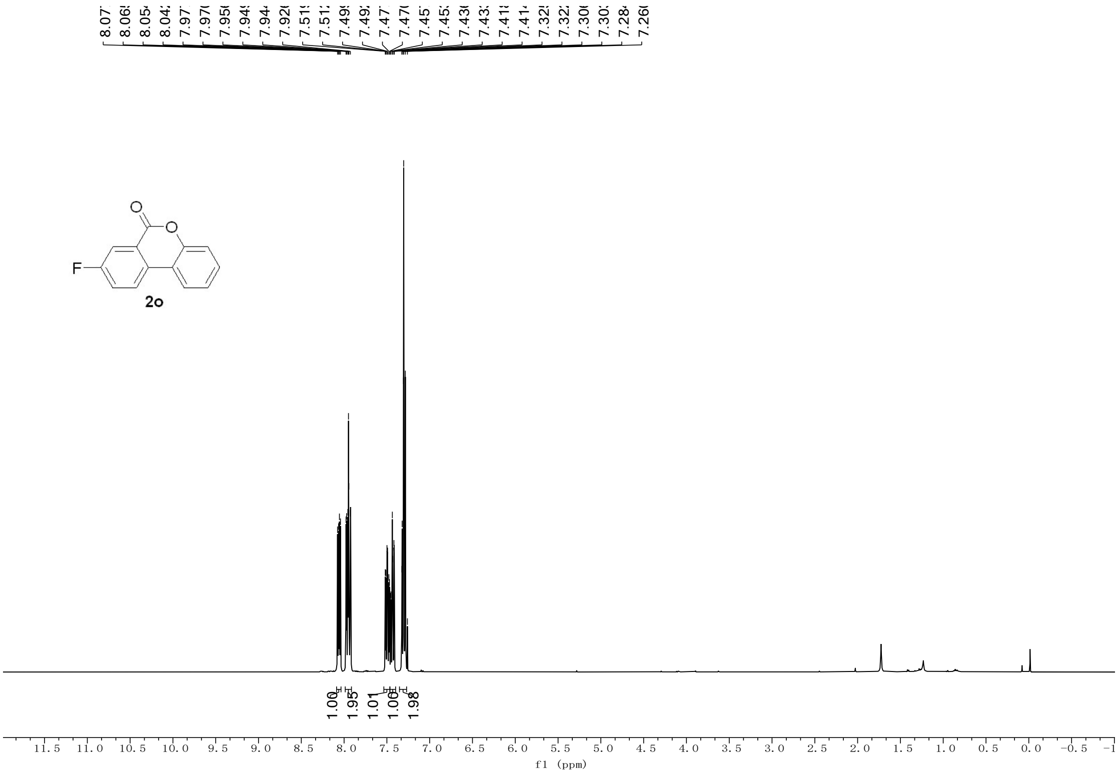
^{1}H NMR, 400 MHz, Chloroform-*d*



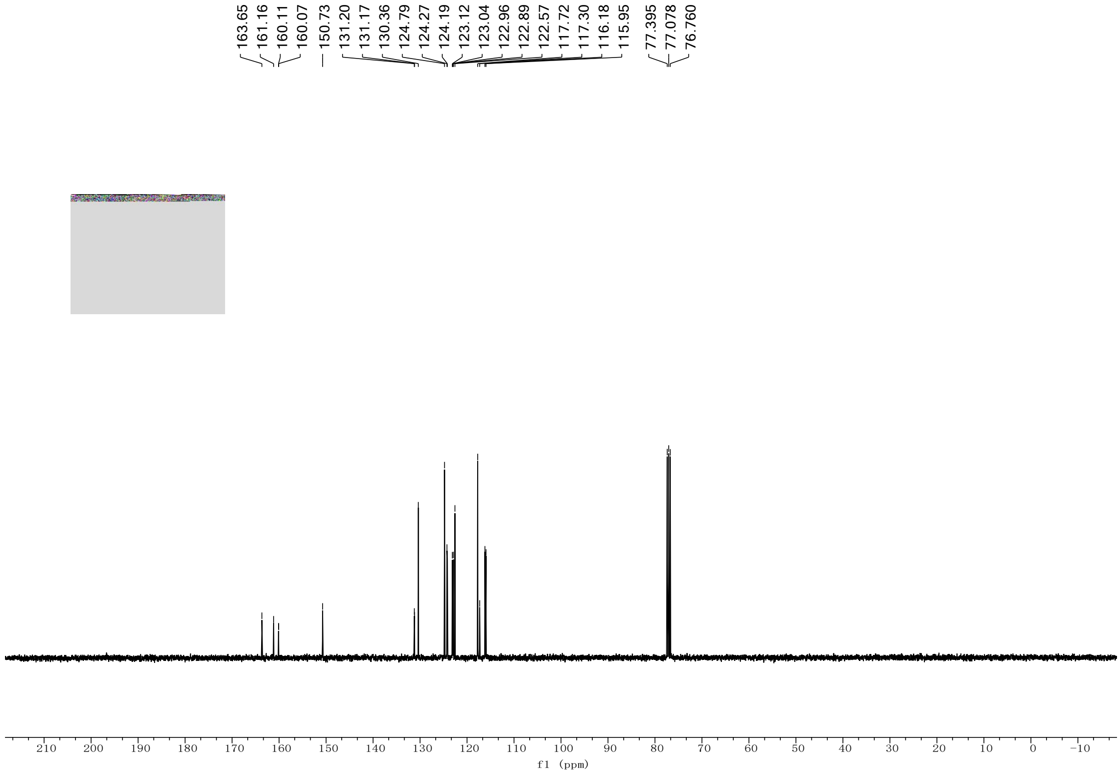
^{13}C NMR, 100 MHz, Chloroform-*d*



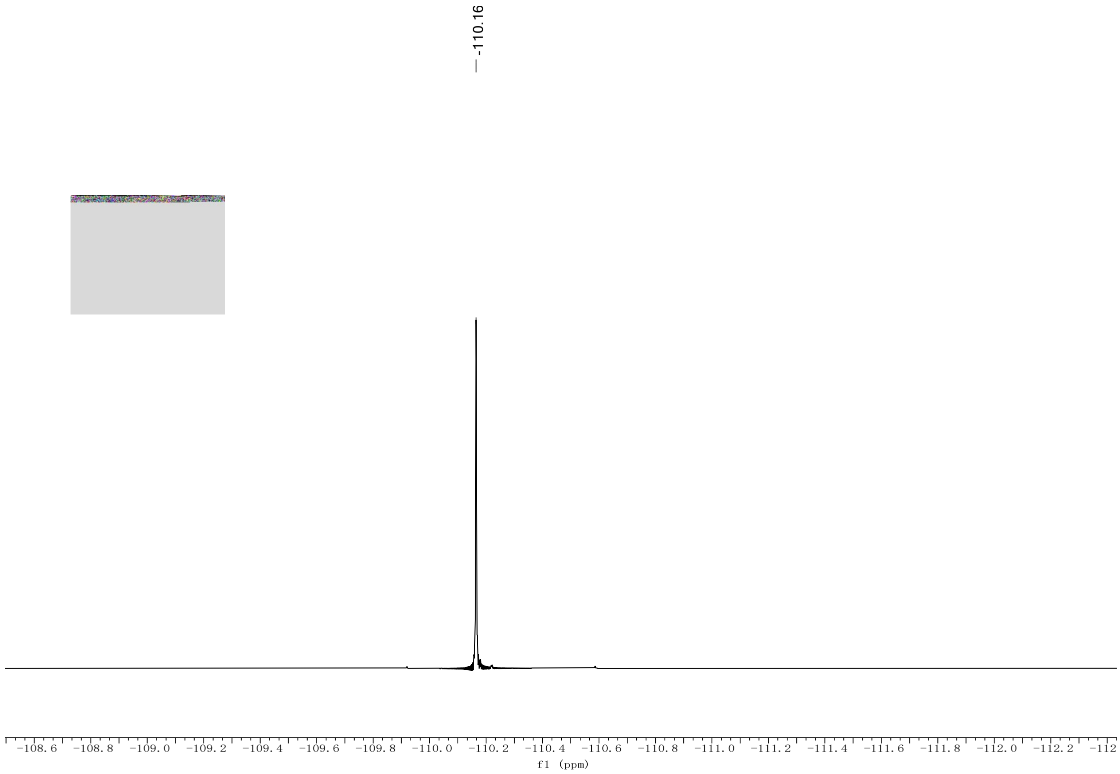
^{1}H NMR, 400 MHz, Chloroform-*d*



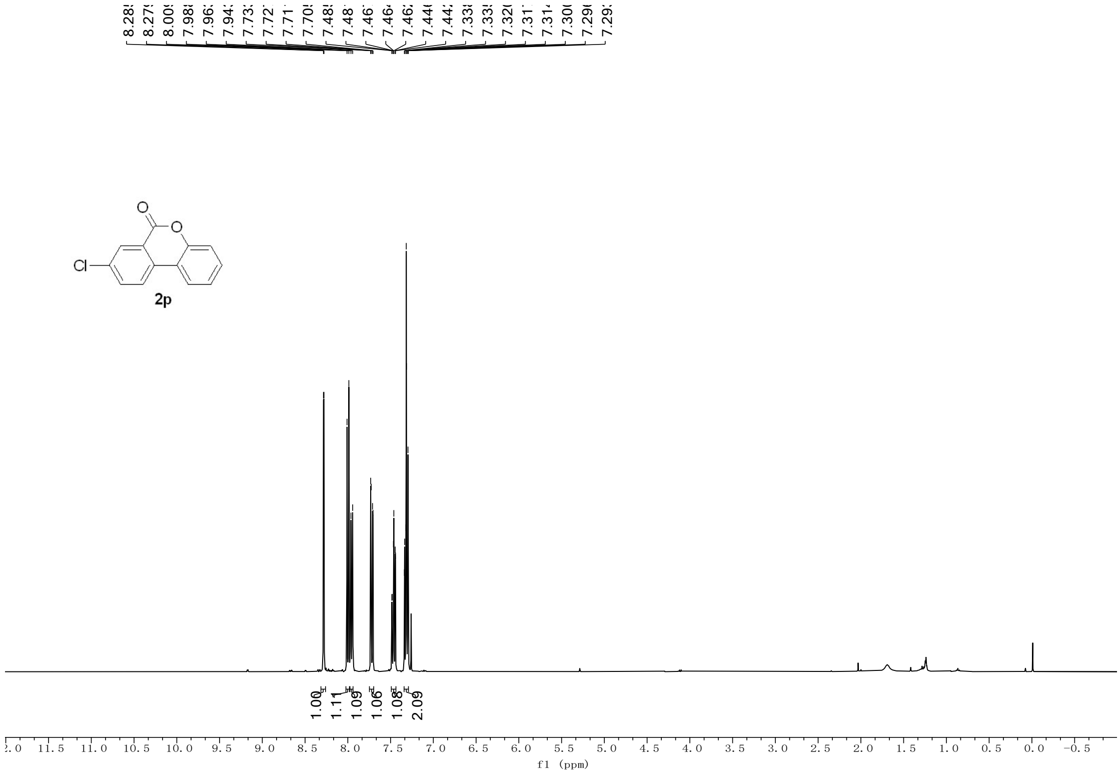
^{13}C NMR, 100 MHz, Chloroform-*d*



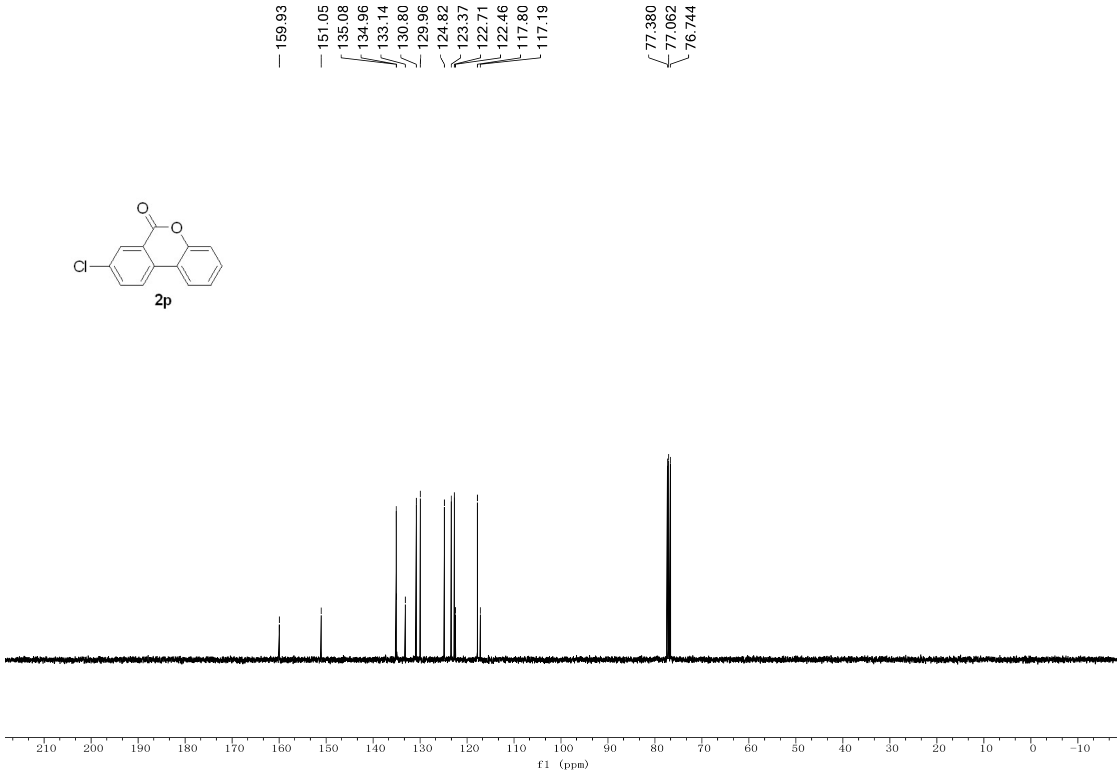
^{19}F NMR, 376 MHz, Chloroform-*d*



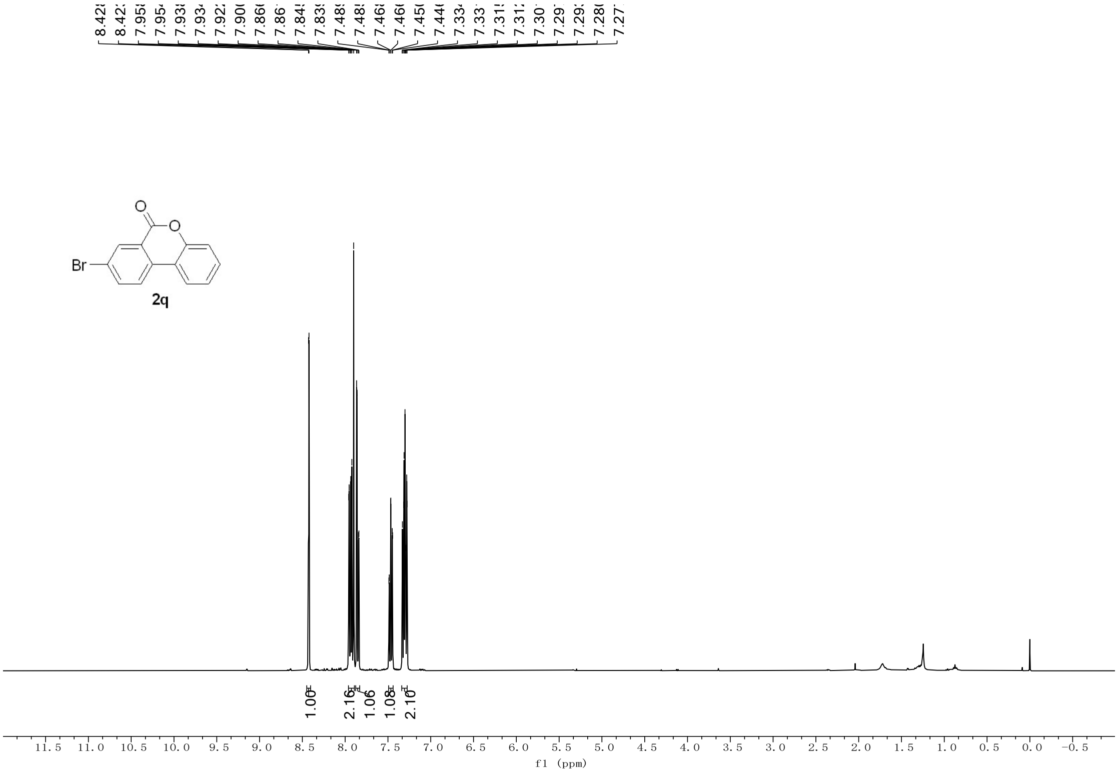
^{1}H NMR, 400 MHz, Chloroform-*d*



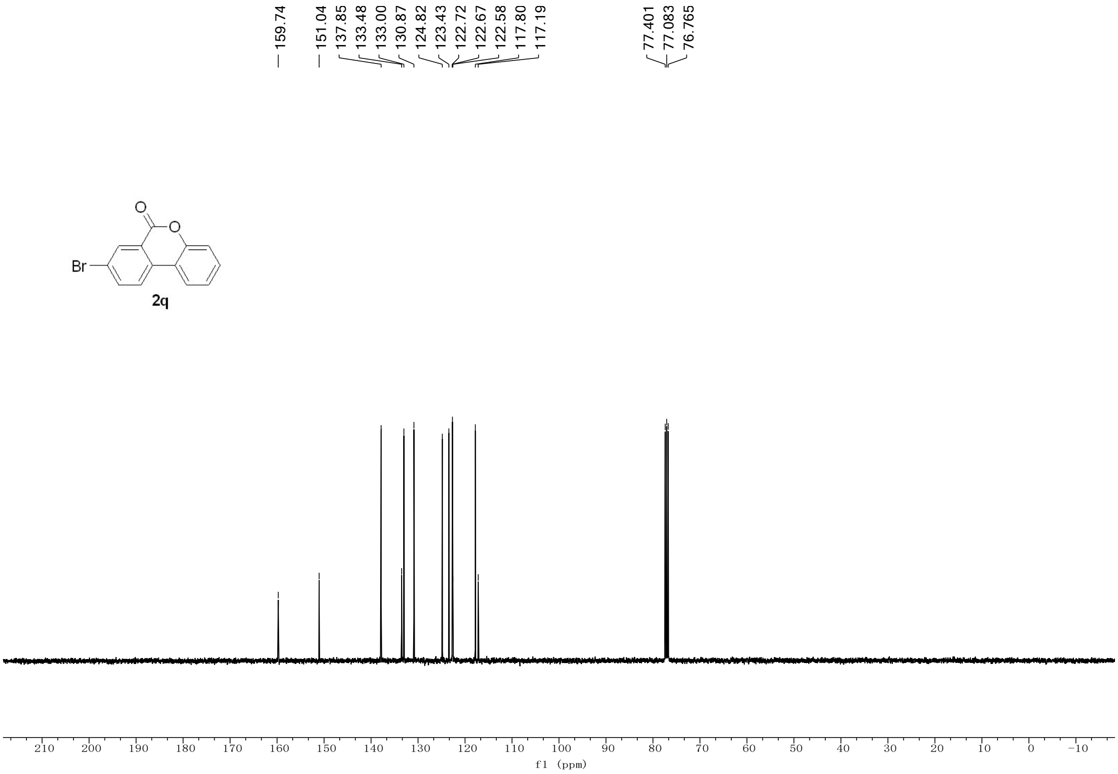
^{13}C NMR, 100 MHz, Chloroform-*d*



^{1}H NMR, 400 MHz, Chloroform-*d*



^{13}C NMR, 100 MHz, Chloroform-*d*



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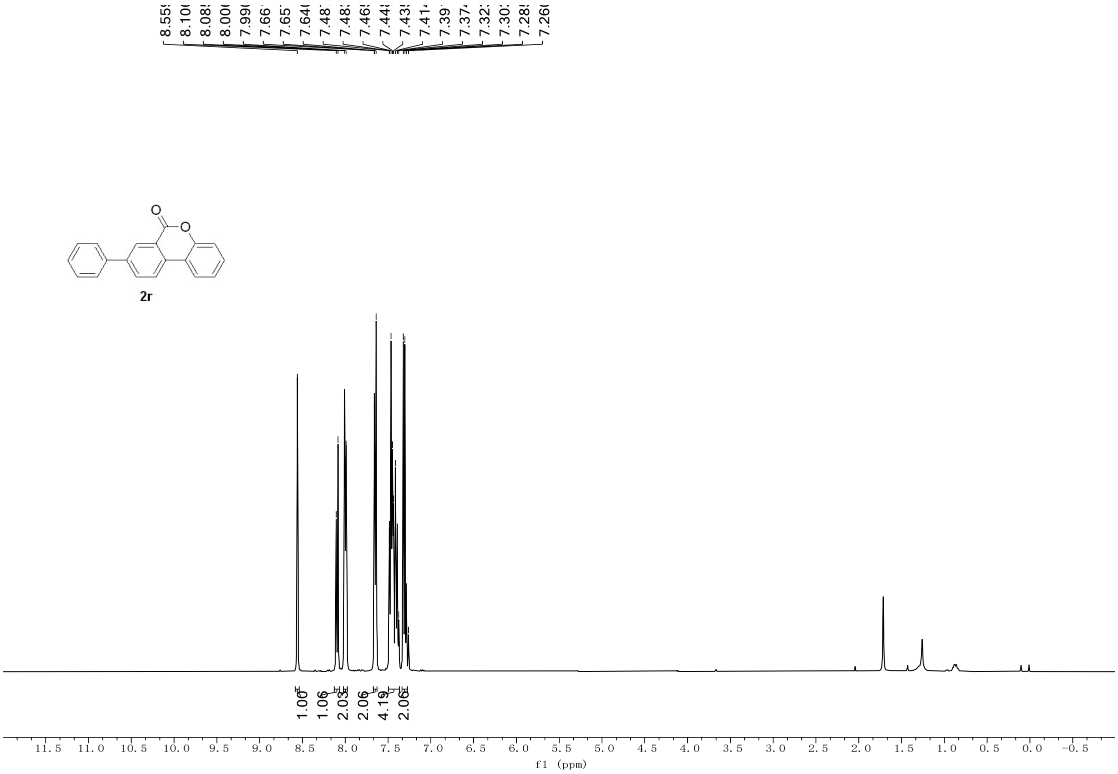

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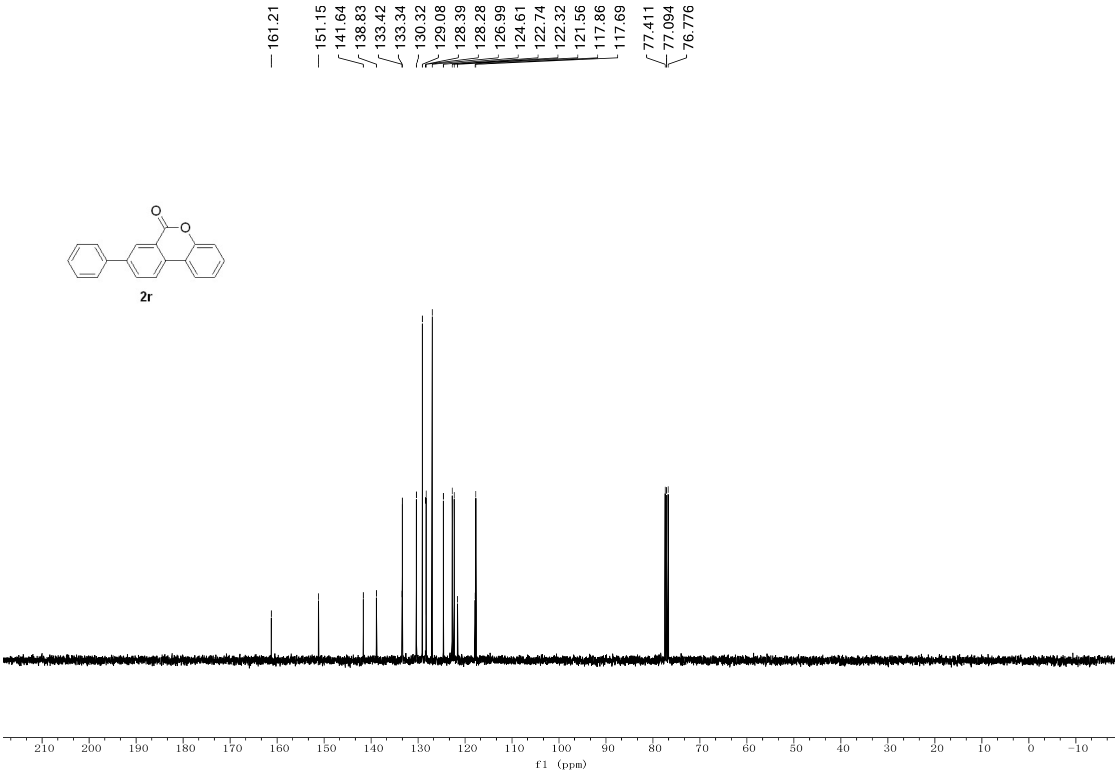

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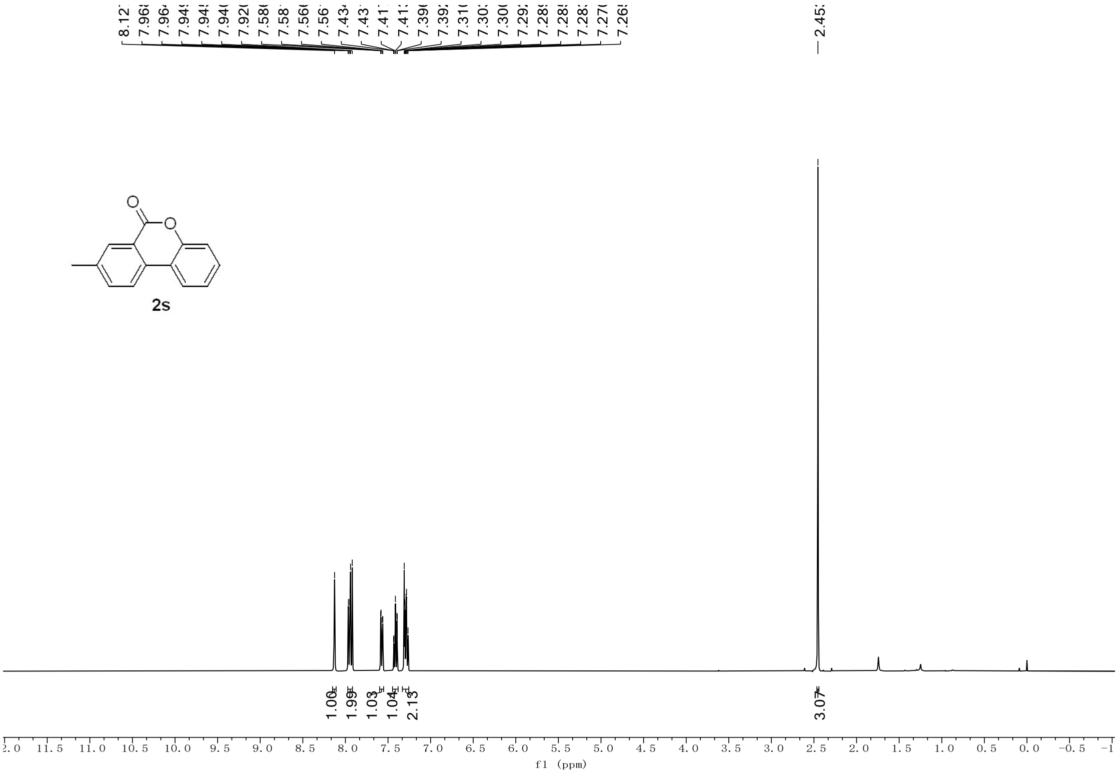

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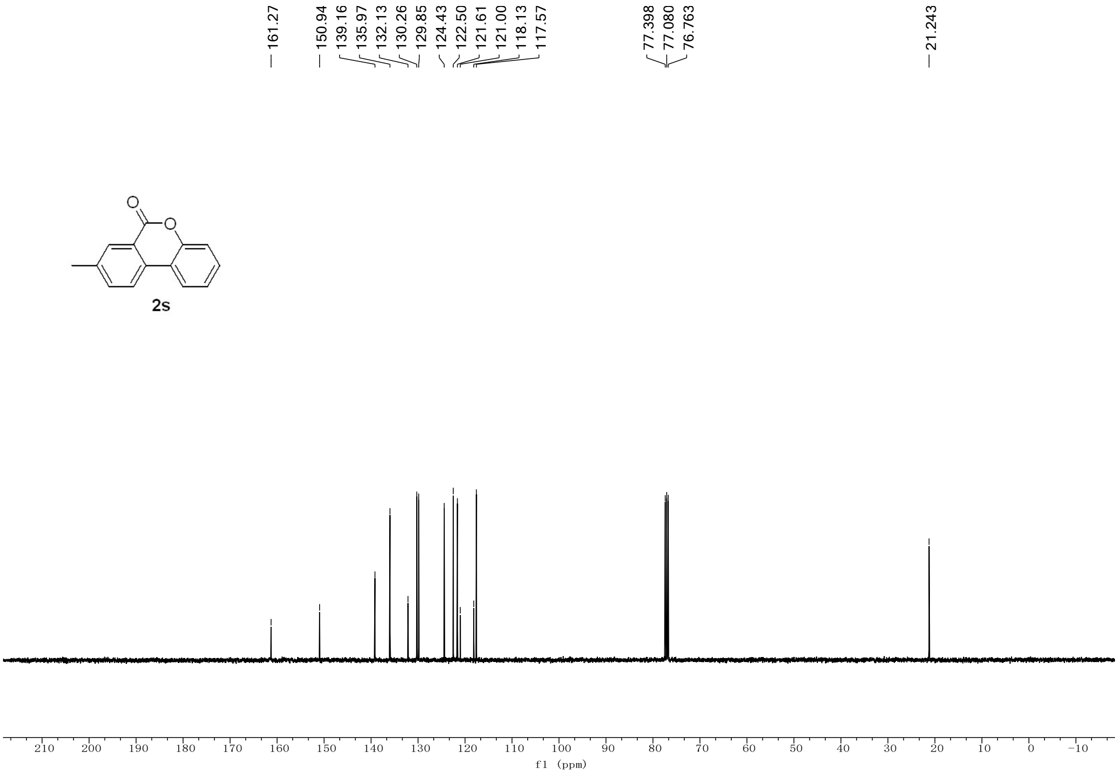

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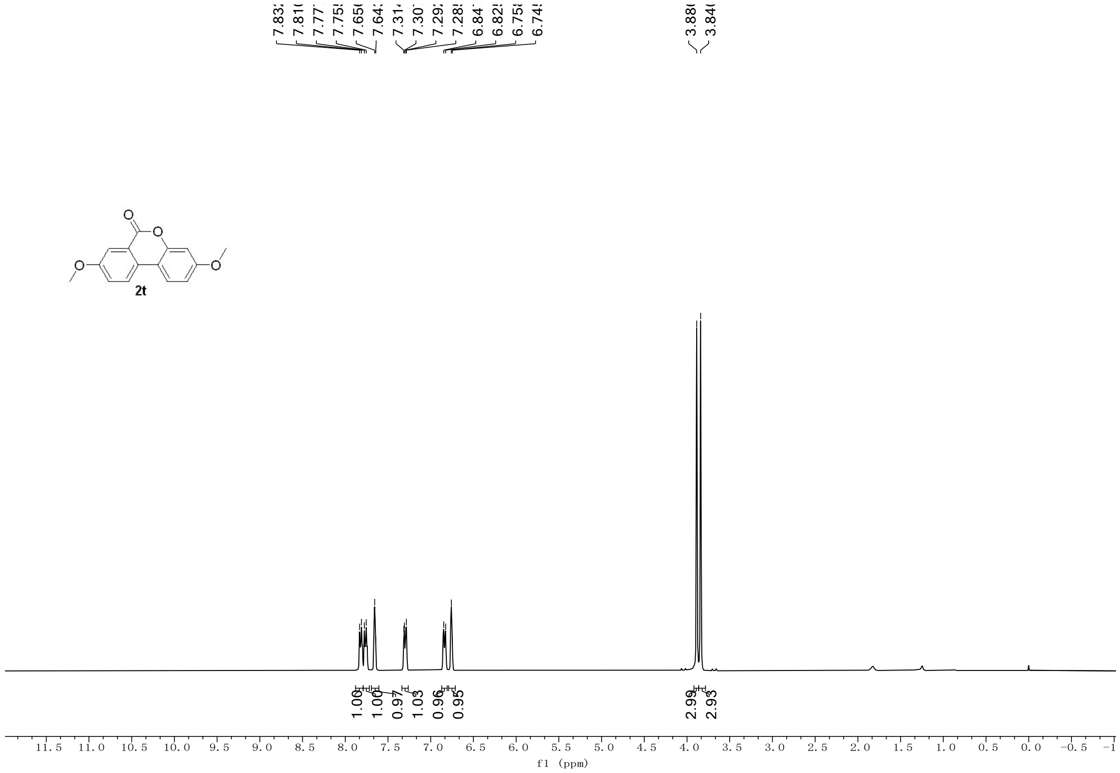

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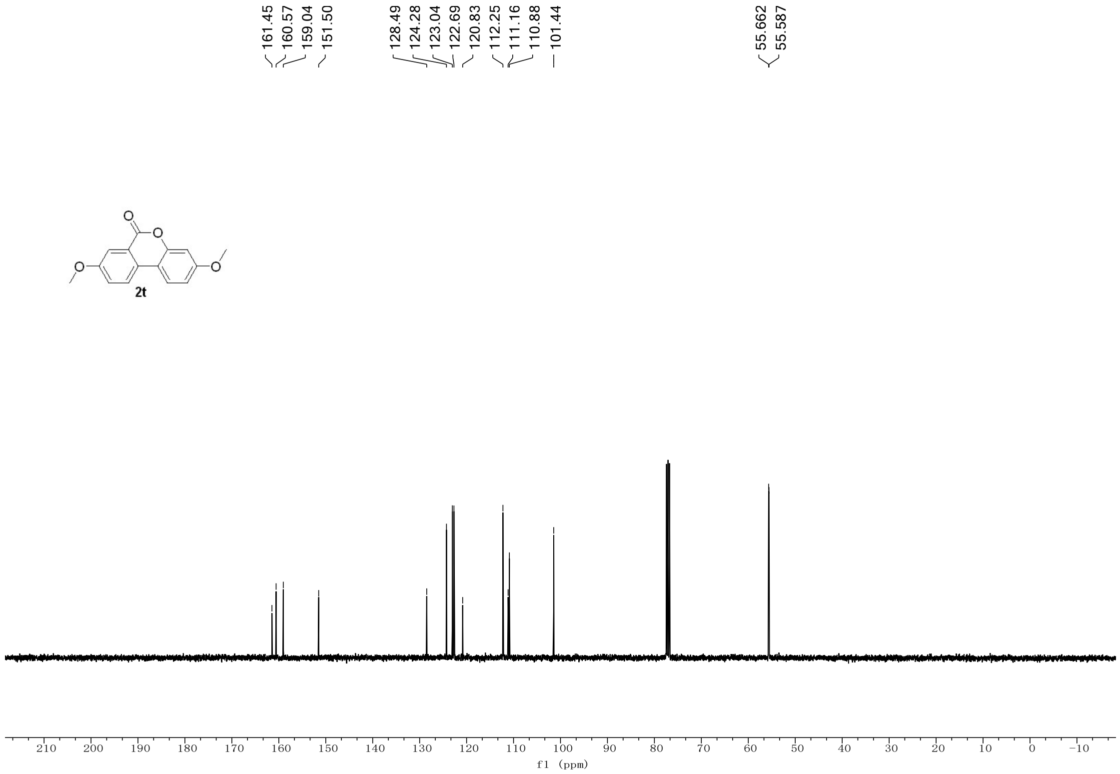

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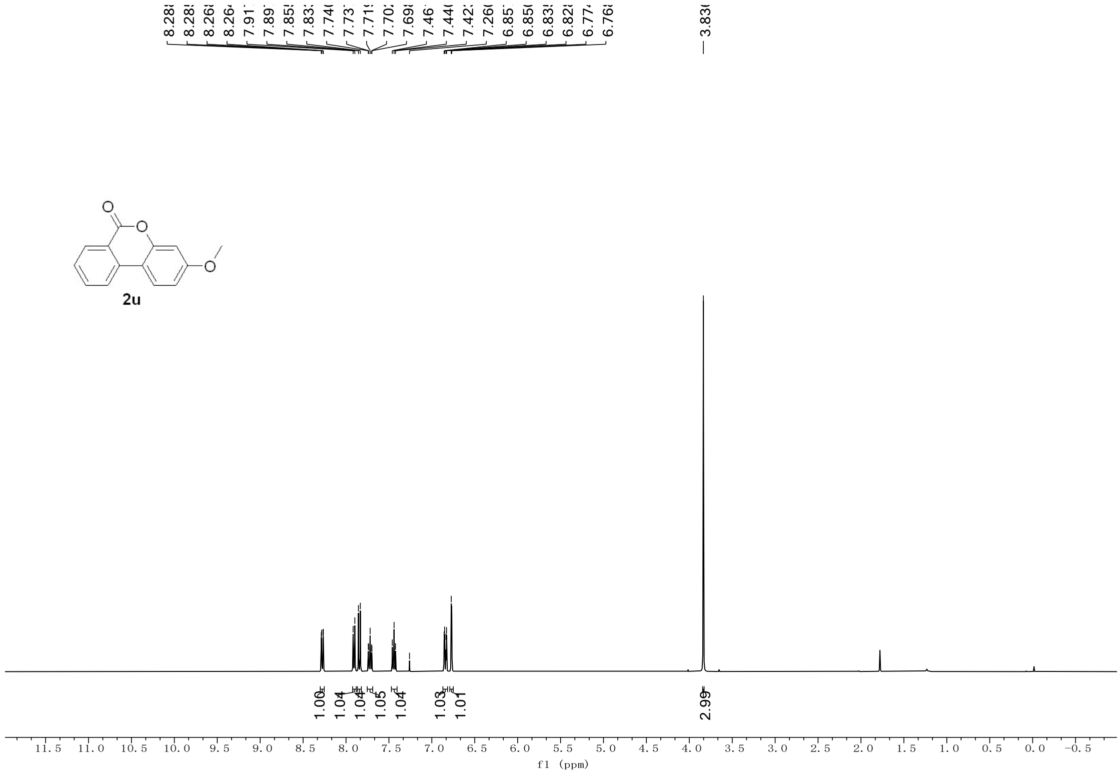

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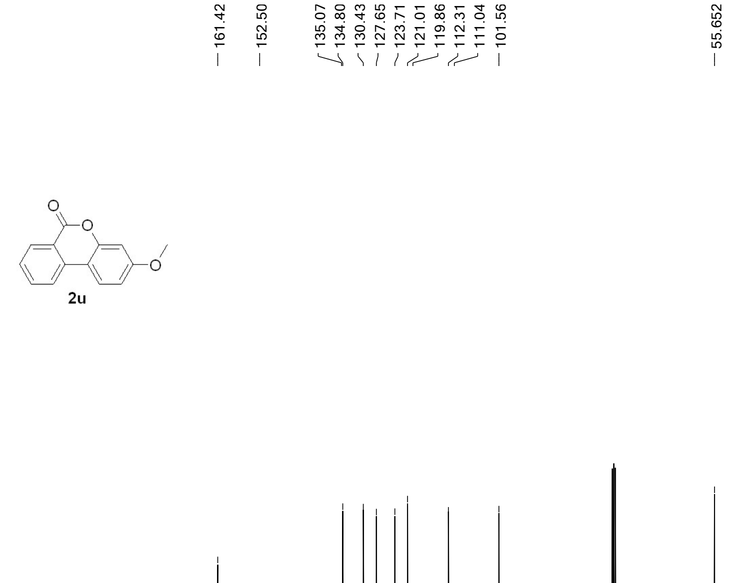

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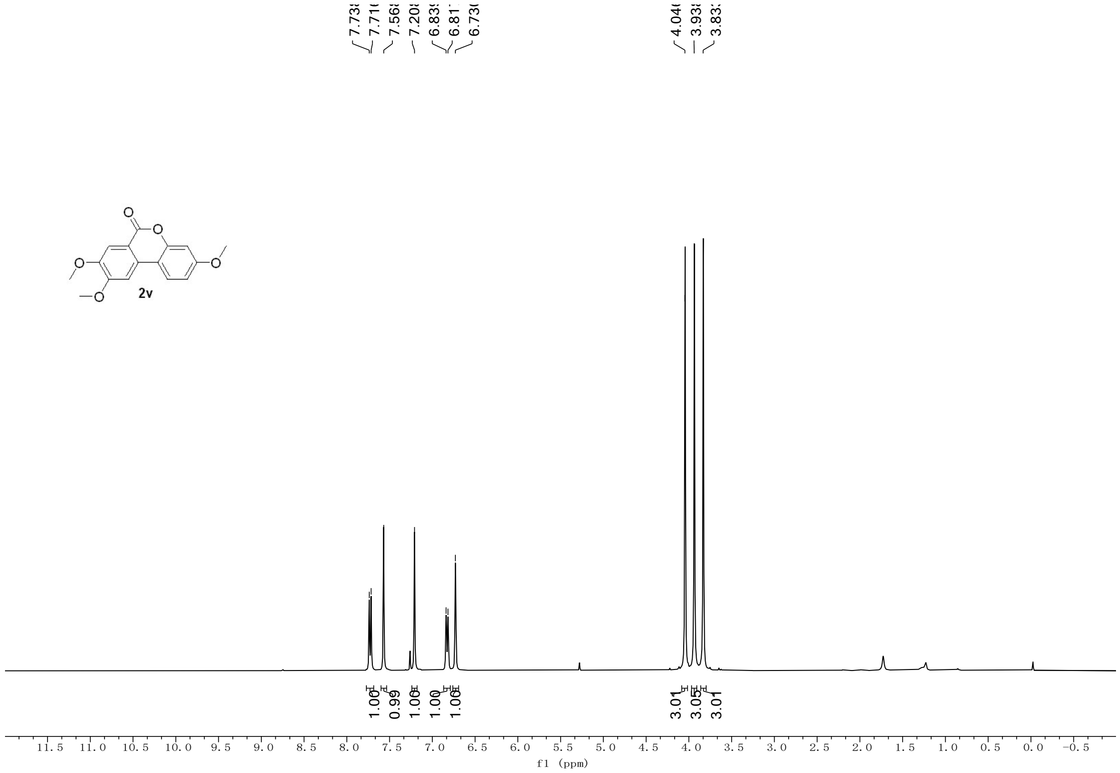

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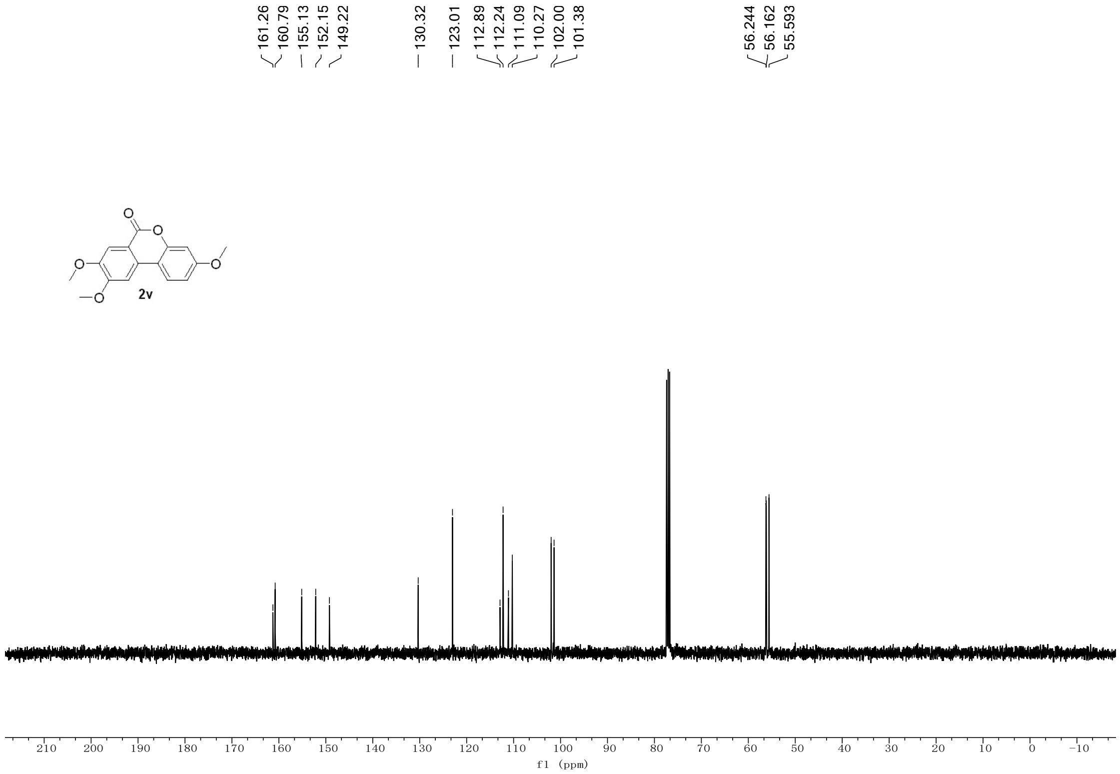

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