Supporting Information

High Quantum Yield and pH sensitive Fluorescence dyes Based on Coumarin Derivatives：Fluorescence Characteristics and Theoretical Study

*Chao-jun Hua, Kan Zhang, Ming Xin, Ting Ying, Jian-rong Gao, Jian-hong Jia, Yu-jin Li**

College of Chemical Engineering , Zhejiang University of Technology, Hangzhou 310014, People's Republic of China.

E-mail: lyjzjut@zjut.edu.cn

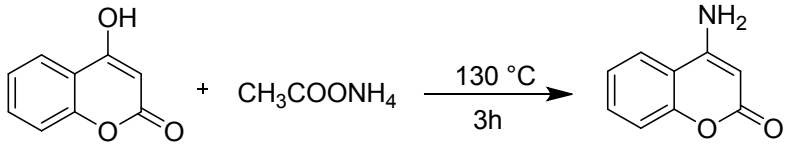
Table of Contents

1. General Information.

All of the chemicals used in the current study were purchased from commercial vendors and used as received without further

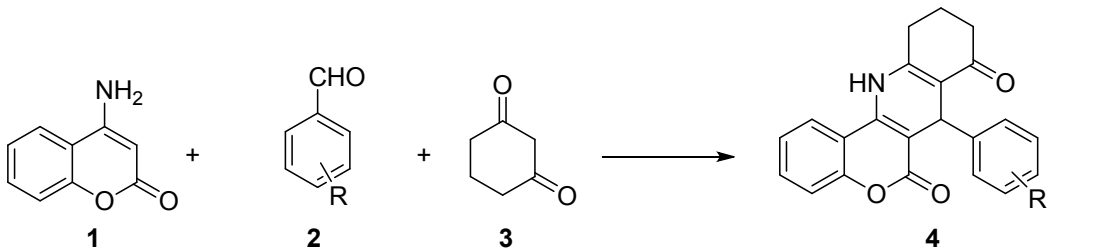
purification, unless otherwise noted. All solvents were purified and dried using standard methods prior to use. Nuclear magnetic resonance (^{1}H, ^{13}C) spectra were recorded on a Bruker AM 500 spectrometer with chemical shifts reported as ppm at 500, 125 MHz, respectively, (in DMSO and TMS as the internal standard). Fluorescence spectra were obtained with a F-7000 Fluorescence Spectrophotometer in a solution of 1.0×10^{-5} mol/L. UV-Vis absorption spectra were measured on a UV-2550. The absorption and emission studies at different pH were all measured in DMSO-water mixture(DMSO:H_2O=9:1).

2. General Procedure for the Synthesis of 4-aminocoumarin [a].



A mixture of well powdered 4-hydroxycoumarin (1.07 g, 0.0066 mol) and ammonium acetate (7.87 g, 0.100 mol) was melted in an oil bath (max. 130 ºC) and stirred for 3 h. After cooling to ambient temperature, water was added and the crude product was isolated as yellow crystals by simple filtration. 4-aminocoumarin was obtained by recrystallized from EtOH and water as yellow crystals (0.98 g, 92.2%).

General Procedure for the Synthesis of compound 4a-4e[b].



4a R=H **4d** R=3-Cl
4b R=4-NO_2 **4e** R=4-CH_3
4c R=4-OMe

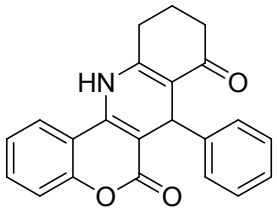
A mixture of benzaldehyde (0.106 g, 1.0 mmol), 1,3-cyclohexanedione (0.112 g , 1.0 mmol) and 4-aminocoumarin(0.161 g, 1.0 mmol) in acetic acid (6 mL) was stirred for 2-3 h at 110℃ and completed reaction by TLC detected. The mixture was cooled to room temperature and the crude was separated by filter. Then, the crude product was washed with H_2O (20 mL) and recrystallized from DMSO to give product **4a** (0.295 g, 86.3%) as light yellow solid.

Reference:

(a) Ahmed, N.; Babu, B. V.; Singh, S.; Mitrasinovic, P. M. Heterocycles 2012, 85, 1629.

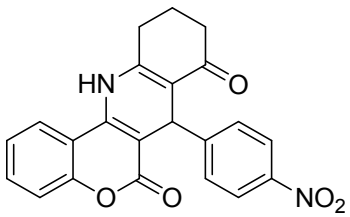
(b) Miri, R.; Motamedi, R.; Rezaei, M. R.; Firuzi, O.; Javidnia, A.; Shafiee, A. *Arch Pharm* **2011**, *344*, 111.

3. Spectroscopic Data for Products



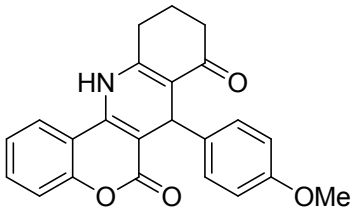
7-phenyl-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione (4a)

Light yellow solid. Yield 86%. Mp 296-298 ℃.^{1}H-NMR (DMSO, 500 MHz) δ (ppm): 9.76 (s,1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.62-7.65 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.11-7.24 (m, 4H), 7.09 (t, *J* = 7.2 Hz, 1H), 4.99 (s, 1H), 2.82-2.87 (m, 1H), 2.67-2.73 (m, 1H), 2.24-2.32 (m, 2H), 1.98-2.02 (m, 1H), 1.87-1.88 (m, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.93 (1C), 160.33 (1C), 152.02 (1C), 151.67 (1C), 145.90 (1C), 142.05 (1C), 131.92 (1C), 128.02 (2C), 127.65 (2C), 126.18 (1C), 123.97 (1C), 122.93 (1C), 116.85 (1C),113.03 (1C), 111.86 (1C), 101.78 (1C), 36.66 (1C), 34.12 (1C), 26.37 (1C), 20.71 (1C).



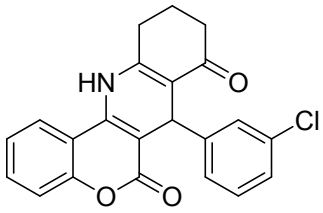
7-(4-nitrophenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione(*4b*)

Light yellow solid. Yield 90%. Mp 260-262 ℃. ^{1}H-NMR (DMSO,500 MHz) δ (ppm): 9.88 (s, 1H), 8.34-8.36 (m, 1H), 8.08-8.10 (m, 2H), 7.65-7.68 (m, 1H), 7.51-7.54 (m, 2H), 7.45-7.48 (m, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 5.11 (s, 1H), 2.87 (t, *J*=9.4Hz, 1H), 2.73 (t, *J* = 3.9 Hz, 1H), 2.27-2.33 (m, 2H), 1.98-2.02 (m, 1H), 1.88 (s, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.89 (1C), 160.21 (1C), 153.12 (1C), 152.31 (1C), 152.14 (1C), 145.94 (1C), 142.60 (1C), 132.22 (1C), 129.10 (2C), 124.06 (1C), 123.26 (2C), 123.12 (1C), 116.92 (1C), 112.83 (1C), 110.97 (1C), 100.63 (1C), 36.50 (1C), 34.96 (1C), 26.38 (1C), 20.61 (1C).



7-(4-methoxyphenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione(4c)

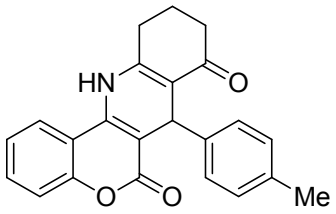
Light yellow solid. Yield 88%. Mp 276–278℃. ^{1}H-NMR (DMSO,500 MHz) δ (ppm): 9.72 (s, 1H), 8.30-8.32 (m, 1H), 7.61-7.65 (m, 1H), 7.42-7.45 (m, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.13-7.14 (m, 2H), 6.75-6.77 (m, 2H), 4.93 (s, 1H), 3.66 (s, 3H), 2.81-2.86 (m, 1H), 2.65-2.72 (m, 1H), 2.24-2.32 (m, 2H), 1.98-2.03 (m, 1H), 1.84-1.90 (m, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.90 (1C), 160.32 (1C), 151.98 (1C), 151.32 (1C), 141.74 (1C), 138.23 (1C), 131.80 (1C), 128.59 (3C), 123.91 (1C), 122.86 (1C), 116.79 (1C), 113.38 (2C), 113.05 (1C), 112.09 (1C), 102.06 (1C), 55.99 (1C), 36.67 (1C), 33.19 (1C), 26.33 (1C), 20.74 (1C).



7-(3-chlorophenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione (4d)

Light yellow solid. Yield 82% . Mp 267–269 ℃. ^{1}H-NMR (DMSO,500 MHz) δ (ppm): 9.82(s, 1H), 8.33-8.35 (m, 1H), 7.46 (s, 1H), 7.39-7.41 (m, 1H), 7.36-7.38 (m,

3H), 7.28(m, 1H), 5.26 (s, 1H), 2.85-2.88 (m, 1H), 2.68-2.72 (m, 1H), 2.29-2.33(m, 2H*)*, 2.00-2.02 (m, 1H), 1.83 (s, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.96 (1C), 160.30 (1C), 152.11 (1C), 149.12 (1C), 140.13 (1C), 133.39 (1C), 132.14 (1C), 131.21 (1C), 128.34 (1C), 126.83 (1C), 123.95 (1C), 121.08 (1C), 120.23 (1C), 116.82 (1C), 114.08 (1C), 113.04 (1C), 111.01 (1C), 101.09 (1C), 36.61 (1C), 33.93 (1C), 26.37 (1C), 20.65 (1C).



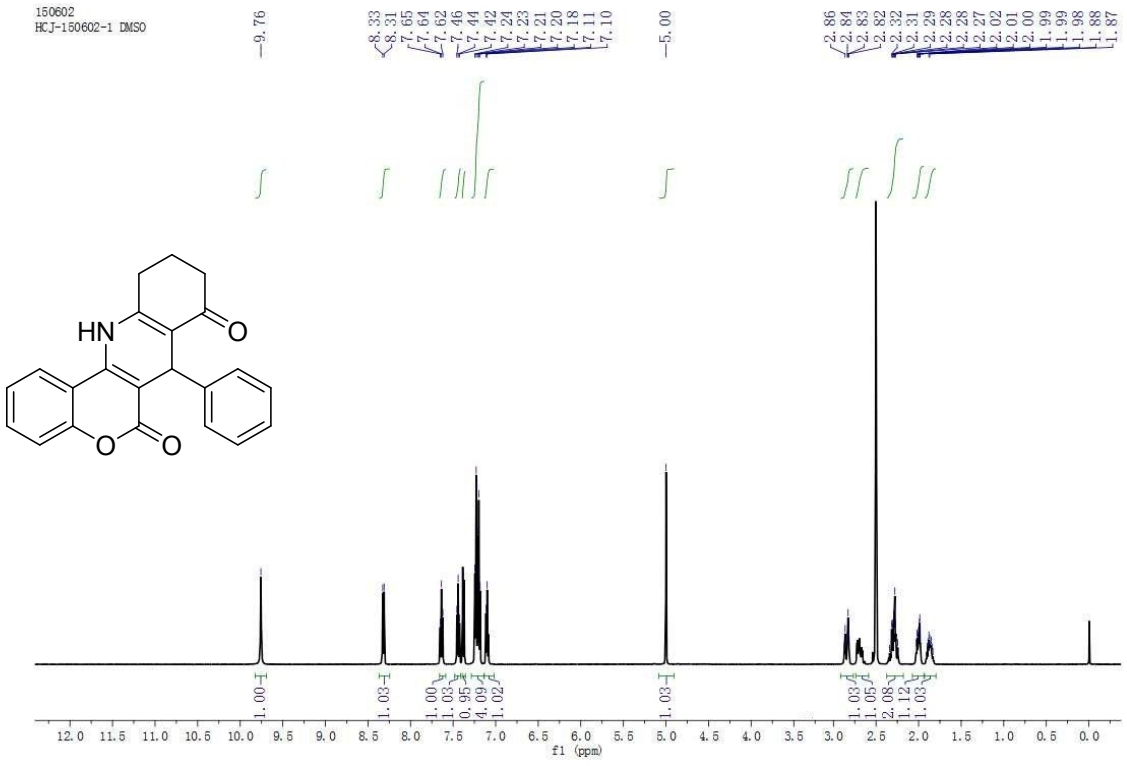
7-(p-tolyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)

-dione(4e)

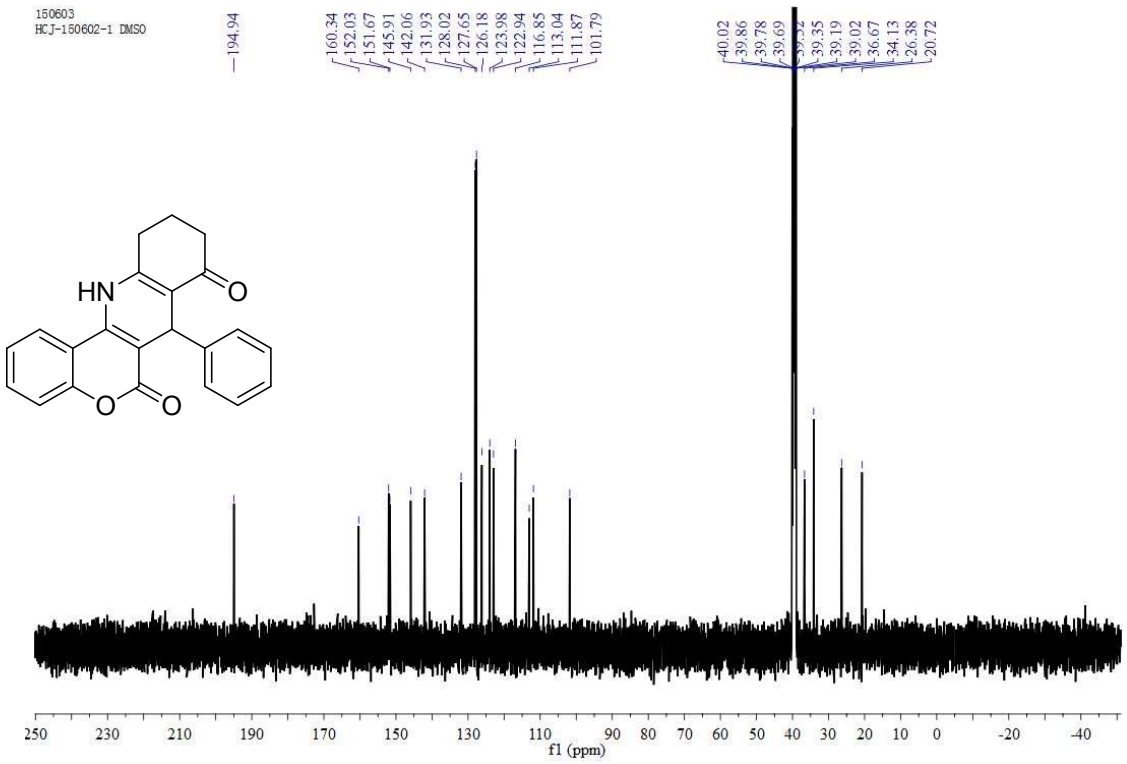
Light yellow solid. Yield 83%. Mp 304–305℃.^{1}H-NMR (DMSO,500 MHz) δ (ppm) : 9.72 (s, 1H), 8.30-8.32 (m, 1H*)*, 7.61-7.63 (m, 1H), 7.41-7.45 (m, 1H), 7.36 (t, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.05 Hz, 2H), 7.00 (d, *J* = 7.95 Hz, 2H), 4.95 (s, 1H), 2.82-2.86 (m, 1H), 2.69-2.71 (m, 1H), 2.18-2.31 (m, 2H), 2.19 (s, 3H), 2.0-2.02 (m, 1H), 1.82-1.89 (m, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.86 (1C), 160.28 (1C), 151.99 (1C), 151.40 (1C), 143.04 (1C), 141.87 (1C), 135.15 (1C), 131.81 (1C), 128.54 (2C), 127.52 (2C), 123.90 (1C), 122.87 (1C), 116.79 (1C), 113.02 (1C), 112.00 (1C), 101.91 (1C), 36.66 (1C), 33.66 (1C), 26.34 (1C), 20.72 (1C), 20.51 (1C).

4. Copies of Product NMR Spectra

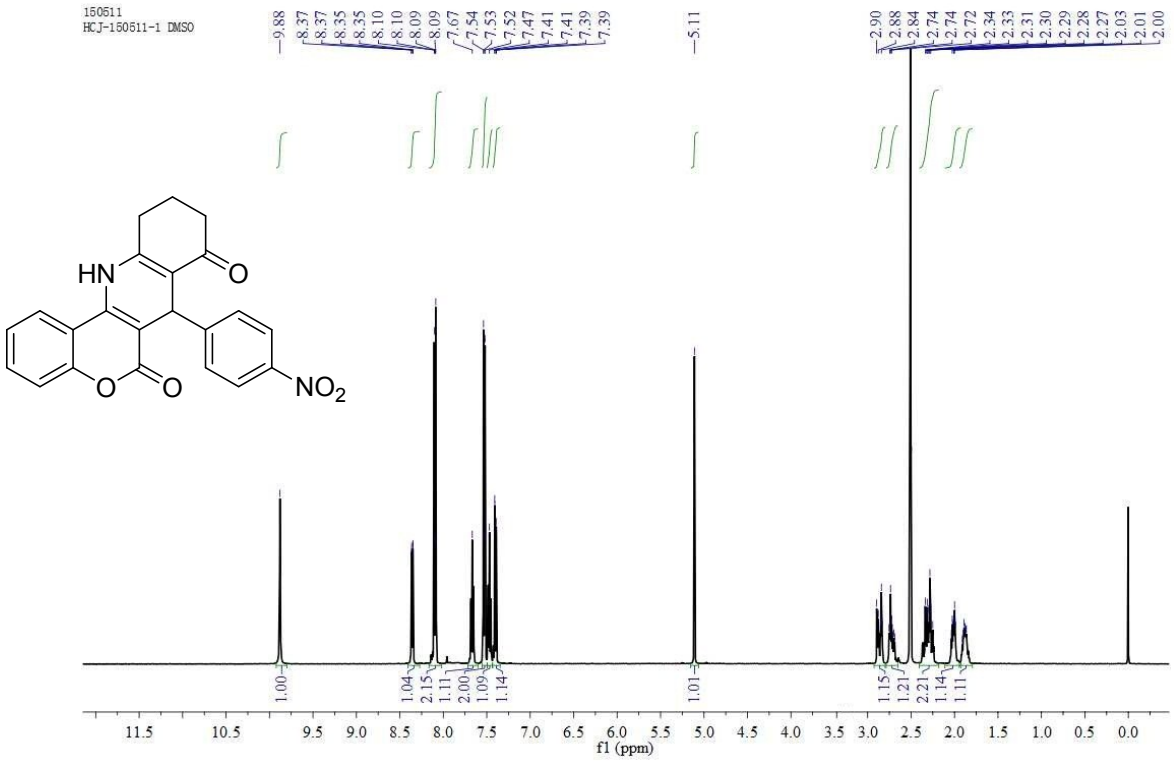
4a ^{1}H NMR (500 MHz, DMSO)



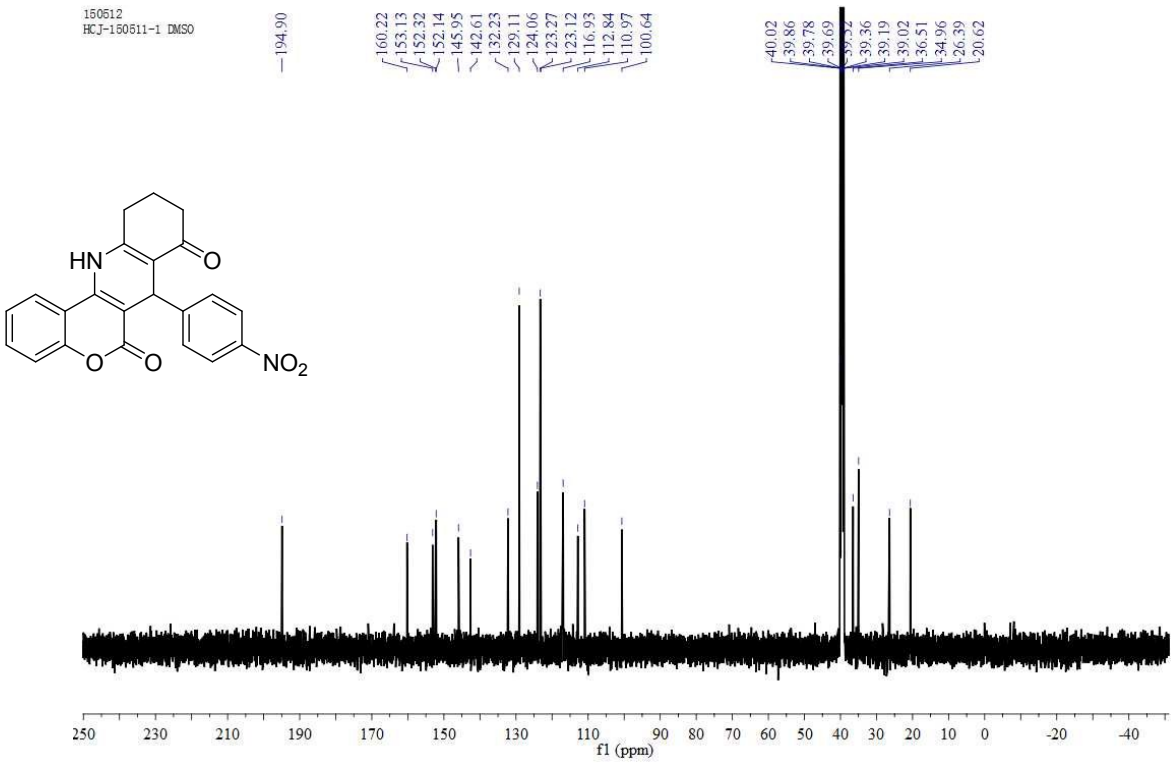
4a ^{13}C NMR (125MHz, DMSO)



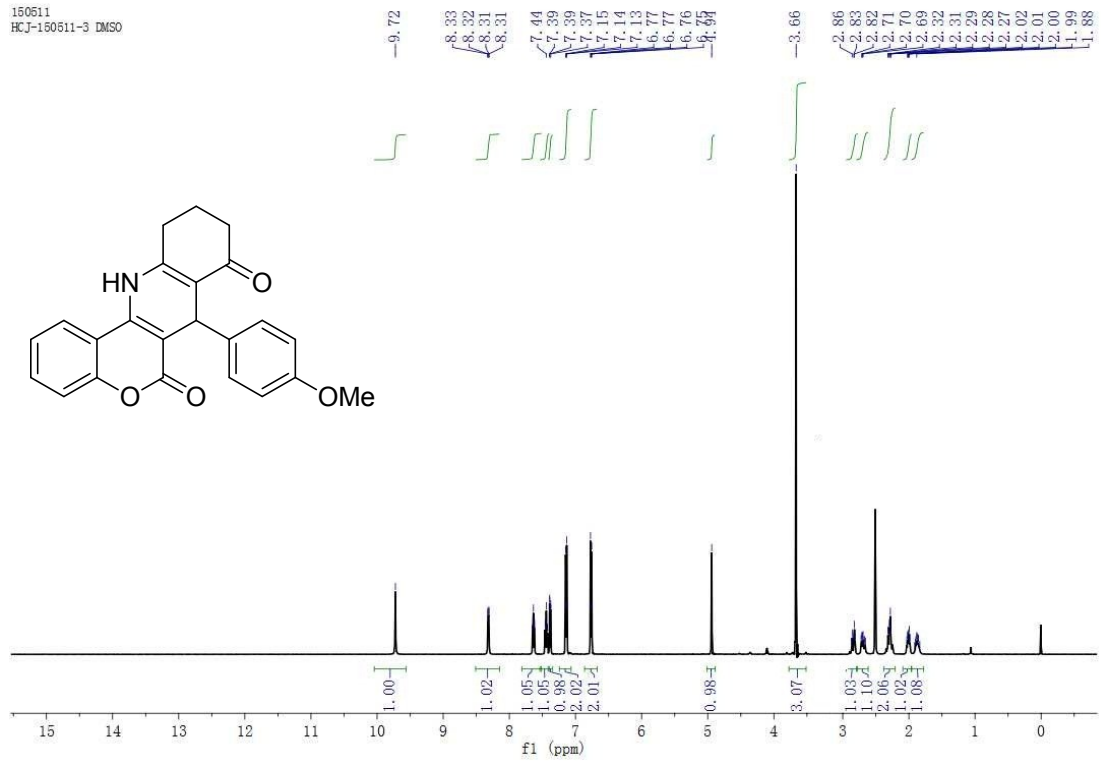
4b ^{1}H NMR (500 MHz, DMSO)



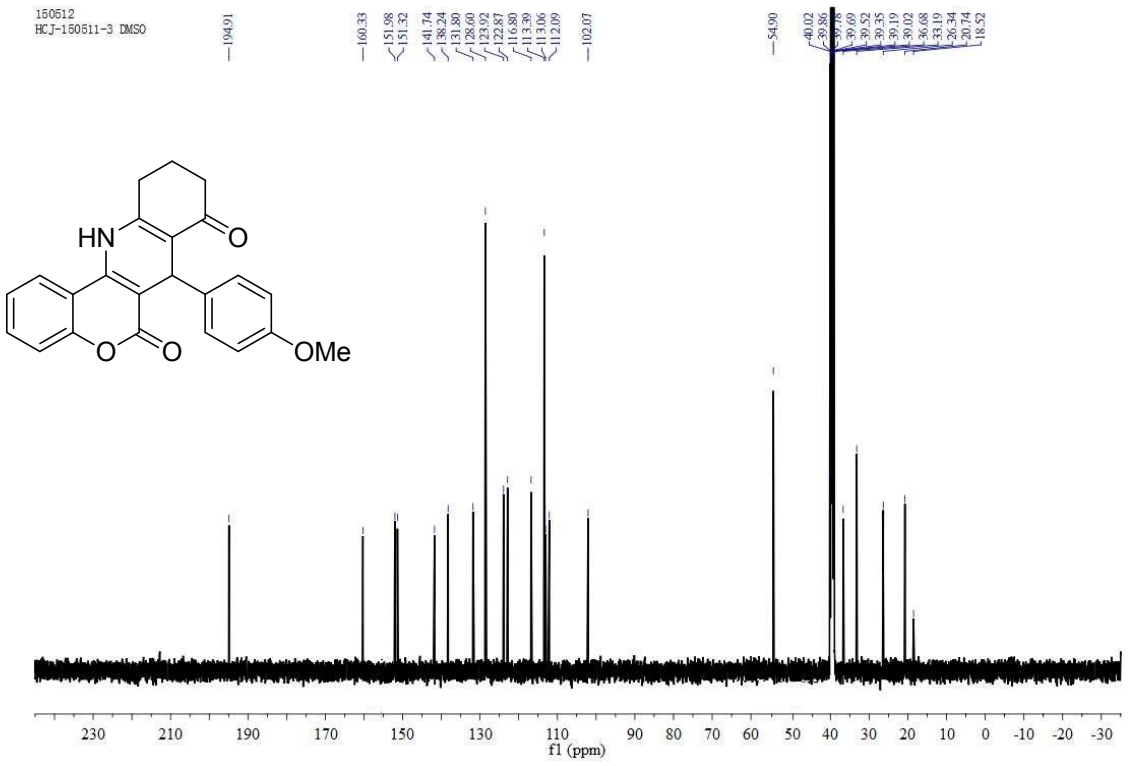
4b ^{13}C NMR (125MHz, DMSO)



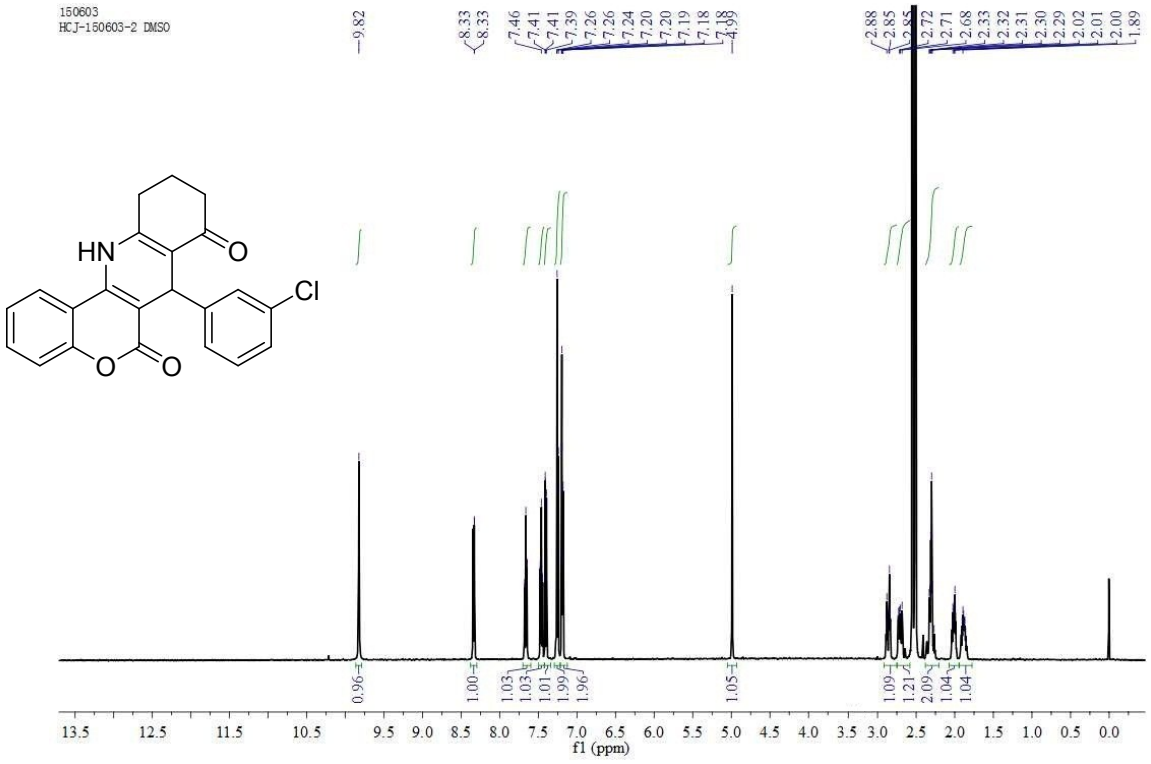
4c ^{1}H NMR (500 MHz, DMSO)



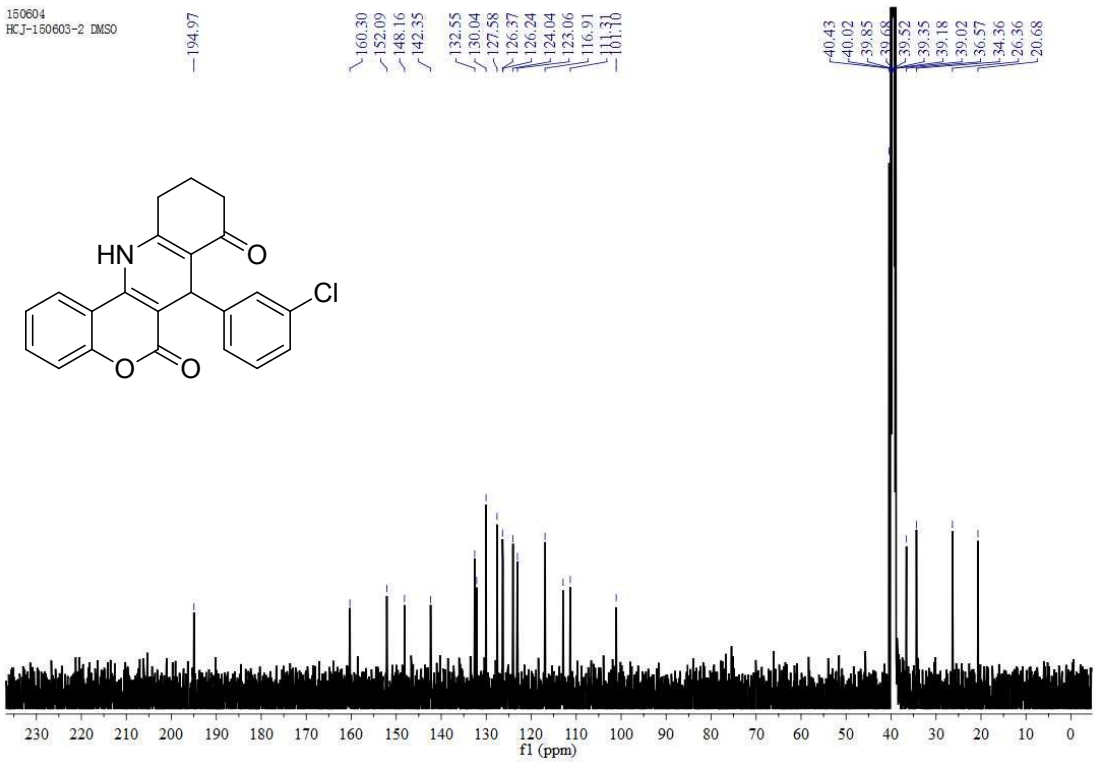
4c ^{13}C NMR (125MHz, DMSO)



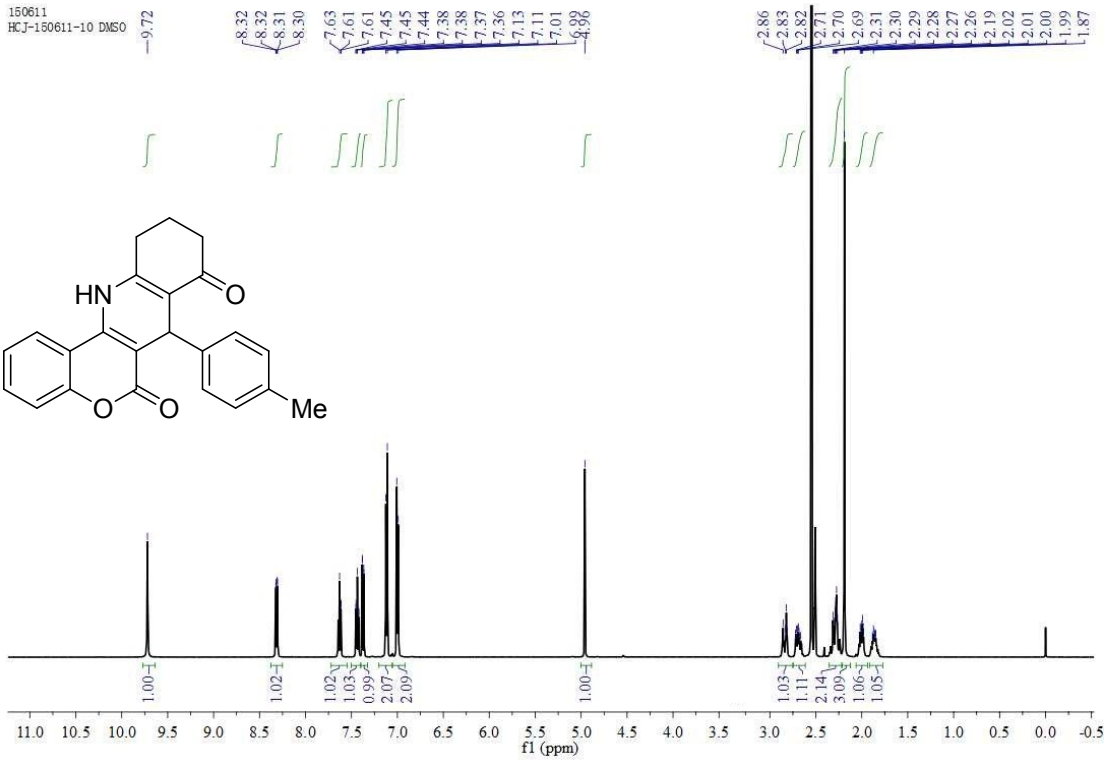
4d ^{1}H NMR (500 MHz, DMSO)



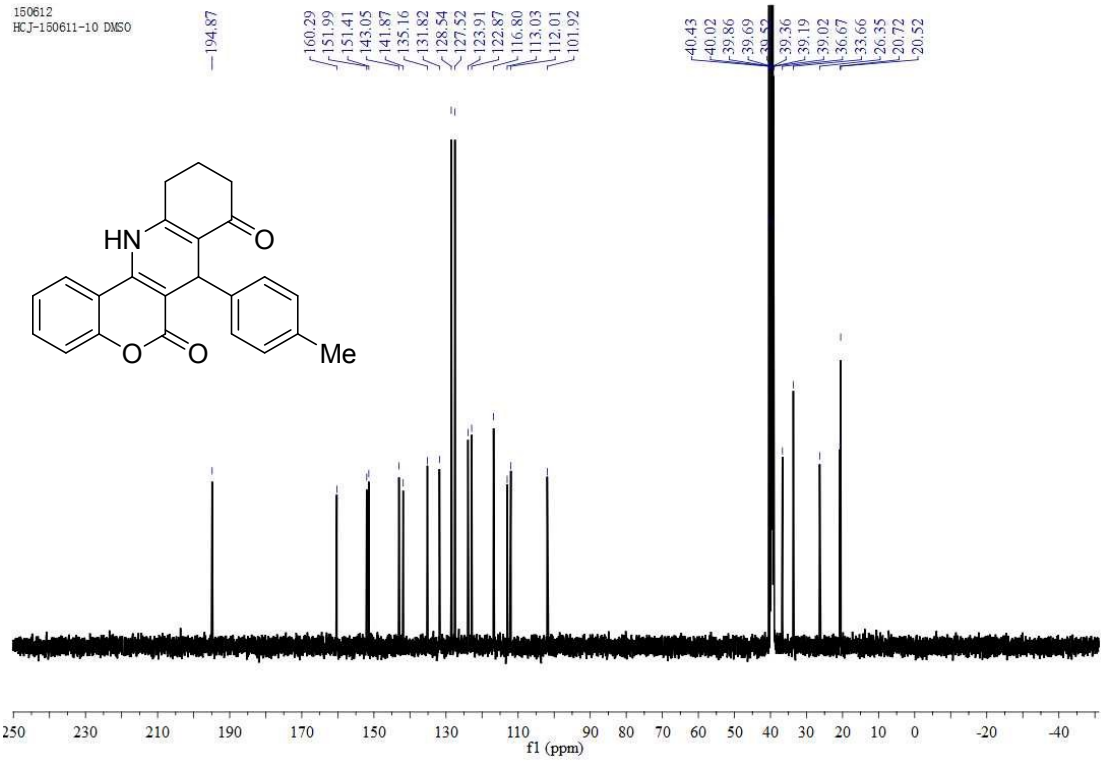
4d ^{13}C NMR (125MHz, DMSO)



4e ^{1}H NMR (500 MHz, DMSO)



4e ^{13}C NMR (125MHz, DMSO)


150612
HCJ-160611-10 DMSO
194.87
160.29
151.99
151.41
143.05
141.87
135.16
131.82
128.54
127.52
123.91
122.87
116.80
113.03
112.01
101.92
40.43
40.02
39.86
39.69
39.52
39.36
39.19
39.02
36.67
33.66
26.35
20.72
20.52
HN
O
O
O
Me
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
f1 (ppm)