Supporting Information

I_2-DMSO mediated dual C(sp^2)-H functionalization/bicyclization of *o*-hydroxyphenyl enaminones to construct C2, C3-disubstituted chromone derivatives: chromeno[2,3-*b*]pyrrol-4(*1H*)-ones

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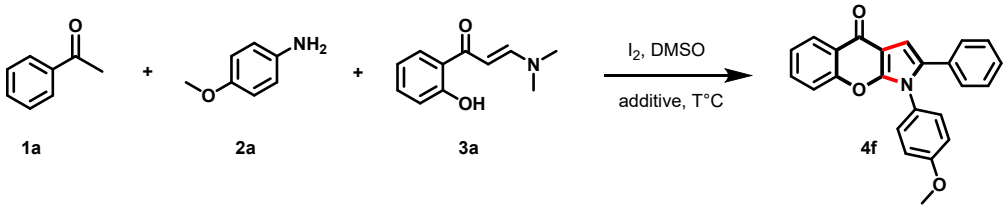
1. General

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H, ^{13}C, ^{19}F spectra were recorded in $CDCl_3$ and DMSO-d_6 on Bruker 400 MHz NMR (AVANCE III HD 400) spectrometers and chemical shifts of ^{1}H NMR are reported in ppm, relative to the internal standard of tetramethylsilane (TMS, δ = 0.00 ppm). Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$, δ = 77.0 ppm, DMSO-$_{d6}$, δ = 39.5 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ on 100 MHz NMR spectrometers and resonances (δ) are given in ppm. ^{19}F spectra were recorded in $CDCl_3$ on 376 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on an Agilent LC1290-TOF 6224 equipped with an electrospray source. The *X-ray* crystal-structure determinations of **4d** were obtained on a D8 Venture diffractometer system. Melting points were determined using XT-4 apparatus and not corrected. UV/Vis spectra were recorded using an Agilent Cary-60 UV/Vis spectrophotometer. Fluorescence spectra were recorded using an Ocean Optics QEpro fluorescence spectrophotometer.

2. Screening of the reaction conditions[a]

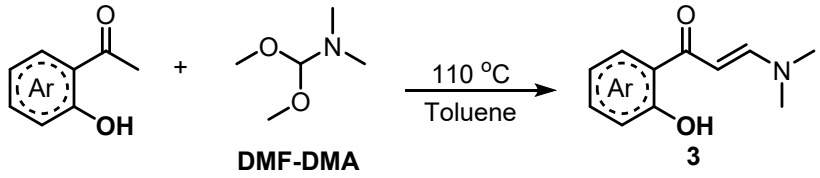


Entry	I_2 (equiv)	Additives (equiv)	Temp (°C)	Yield (%)[b]
1	1.0	-	100	42%
2	1.0	AcOH(1.0)	100	37%
3	1.0	HI(1.0)	100	40%
4	1.0	TsOH(1.0)	100	29%
5	1.0	TfOH(1.0)	100	25%
6	1.0	Na_2CO_3(1.0)	100	21%
7	1.0	K_3PO_4 (1.0)	100	15%
8	1.0	DABCO (1.0)	100	17%
9	1.0	$FeCl_3$(1.0)	100	38%
10	1.0	$CuCl_2$(1.0)	100	36%
11	1.0	$NiCl_2$(1.0)	100	31%
12	1.0	$ZnCl_2$(1.0)	100	28%
13	1.0	TBHP(1.0)	100	37%
14	1.0	DTBP(1.0)	100	35%
15	1.0	KHS_2O_5(1.0)	100	40%
16	1.0	$K_2S_2O_8$(1.0)	100	34%
17	0.5	-	100	21%
18	1.5	-	100	54%
19	2.0	-	100	51%
20[c]	1.5	-	100	49%
21[d]	**1.5**	**-**	**100**	**70%**
22[e]	1.5	-	100	43%
23[f]	1.5	-	100	52%
24[g]	1.5	-	100	45%
25[h]	1.5	-	100	48%
26[i]	1.5	-	100	66%
27[d]	1.5	-	90	65%
28[d]	1.5	-	110	63%
29[d]	1.5	-	120	57%

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), **3a** (0.5 mmol), I_2 (equiv), additive (equiv), indicated temperature, DMSO 2.5 mL, 4 h. [b]Isolated yields. [c]**1a**: **2a**: **3a** = 2: 1: 1. [d]**1a**: **2a**: **3a** = 1: 2: 1. [e]**1a**: **2a**: **3a** = 1: 1: 2. [f]**1a**: **2a**: **3a** = 2: 2: 1. [g]**1a**: **2a**: **3a** = 2: 1: 2. [h]**1a**: **2a**: **3a** = 1: 2: 2. [i]**1a**: **2a**: **3a** = 1: 3: 1

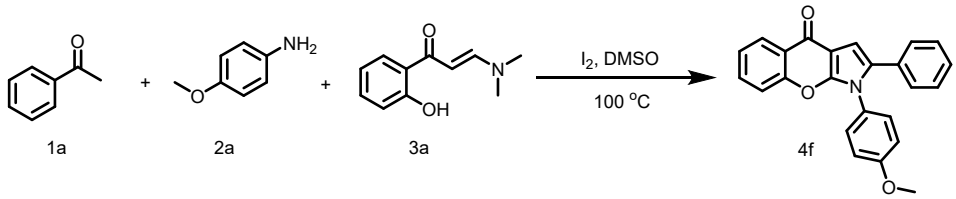
3. Operation methods for synthesis compounds

Synthetic method of *o*-hydroxyphenyl enaminone



To a stirred solution of *o*-hydroxy aryl methyl ketone (5.0 mmol, 1.0 eq.) in toluene (5.0 mL), 1,1-dimethoxy-*N,N*-dimethylmethanamine (7.0 mmol, 1.4 eq.) was added and stirred at 110 ℃ (metal heating block). After completion of the reaction (monitored by TLC), use ethyl acetate to transfer the reaction solution to the eggplant shaped bottle, rotate and evaporate under vacuum and pressure at 60 ℃ to obtain the product, which turns into yellow solid after cooling. Wash the solid with petroleum ether with the aid of ultrasound and discard the supernatant. In this way, pure yellow solid **3** can be obtained after three times of washing.[1]

General procedure for the synthesis of 4 and 5 (4f as example)



1.0 mmol scale: The reactions did not require the protection of inert gases. In a 35 mL sealed tube were added acetophenone (**1a**) (120 mg, 1.0 mmol), iodine (381 mg, 1.5 mmol) and dimethyl sulfoxide (5 mL) and the resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 1 hour. Then add (**2a**) (246 mg, 2.0 mmol), (**3a**) (191 mg, 1.0 mmol). The resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 4 hour until substrate conversion was almost complete by TLC analysis. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (50 mL) and NaCl solution (150 mL), then the mixture was extracted with EtOAc (150 mL x 2), the organic layers were separated and combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 8:1) to afford the product **4f** (257 mg, 70% yield).

10.0 mmol scale: The reactions did not require the protection of inert gases. In a 100 mL round flask were added acetophenone (**1a**) (1200 mg, 10 mmol), iodine (3810 mg, 15 mmol) and dimethyl sulfoxide (50 mL) and the resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 1 hour. Then add (**2a**) (2460 mg, 20.0 mmol), (**3a**) (1910 mg, 10.0 mmol), and the resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 4 hour until substrate conversion was almost complete by TLC analysis. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (150 mL) and NaCl solution

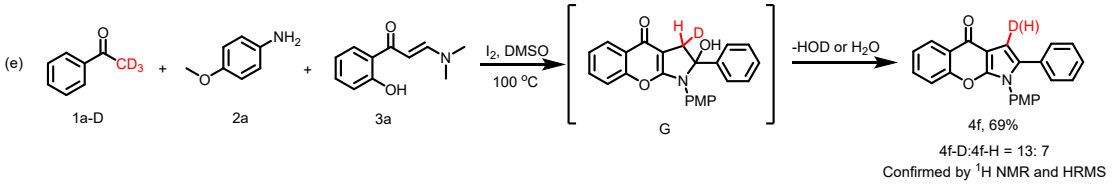
(300 mL), then the mixture was extracted with EtOAc (300 mL x 2), the organic layers were separated and combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 8:1) to afford the product **4f** (2060 mg, 56% yield).

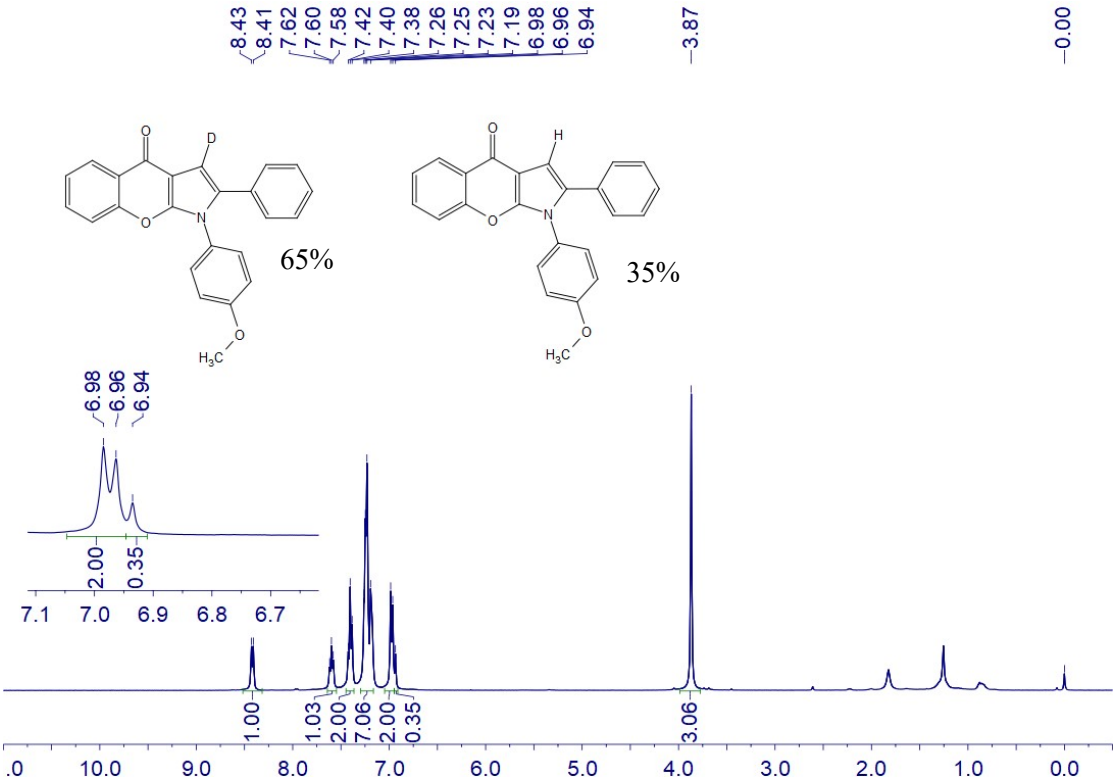
1. (a) Wang, F.; Sun, W.; Wang, Y.; Jiang, Y.; Loh, T. P. *Org. Lett.* 2018, **20**, 1256-1260. (b) Ni, M.; Zhang, J.; Liang, X.; Jiang, Y.; Loh, T. P. *Chem. Commun.* 2017, **53**, 12286-12289.

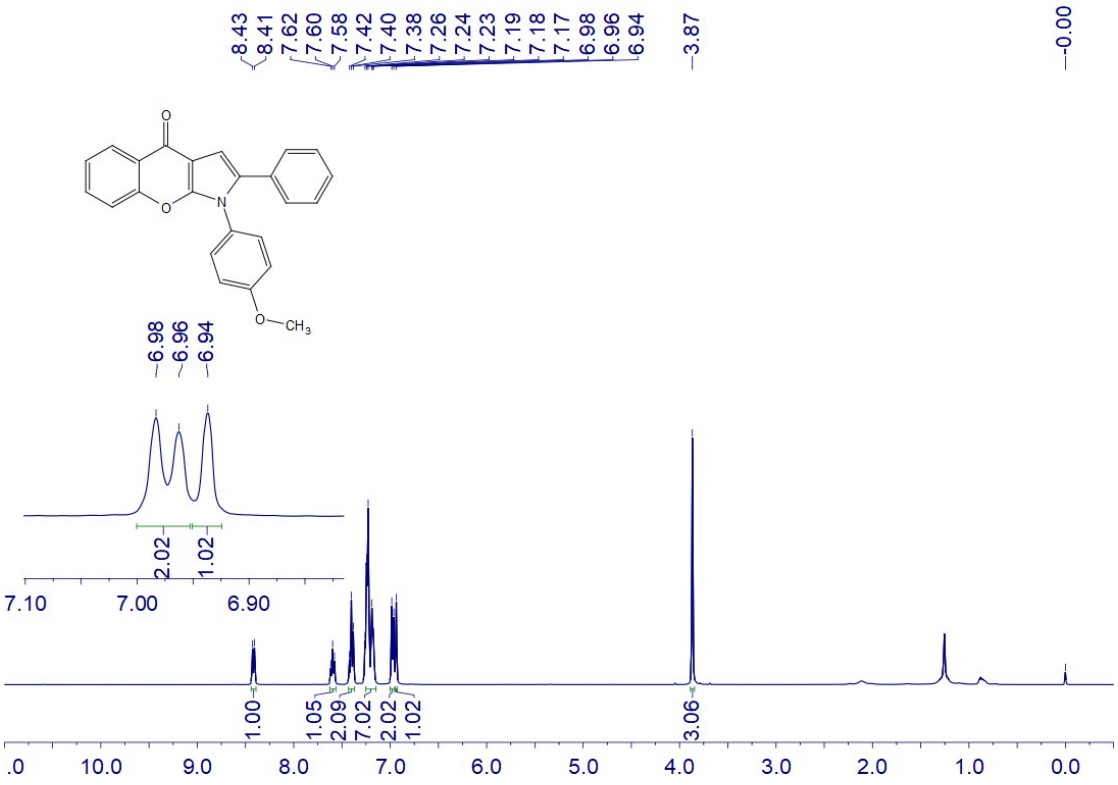
2. Mechanistic studies

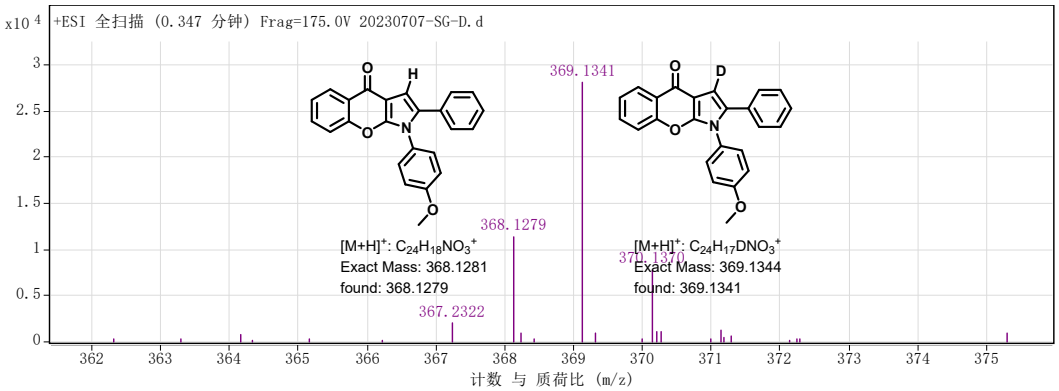
Isotope labeling experiment

In a 35 mL sealed tube were added CD_3-labeled acetophenone (**1a-D,** 123 mg, 1.0 mmol), iodine (381 mg, 1.5 mmol) and dimethyl sulfoxide (5 mL) and the resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 1 hour. Then add (**2a**) (246mg, 2.0 mmol), (**3a**) (191 mg, 1.0 mmol). The resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 4 hour until substrate conversion was almost complete by TLC analysis. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (50 mL) and NaCl solution (150 mL), then the mixture was extracted with EtOAc (150 mL x 2), the organic layers were separated and combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 8:1) to afford the product (254 mg, 69% yield).

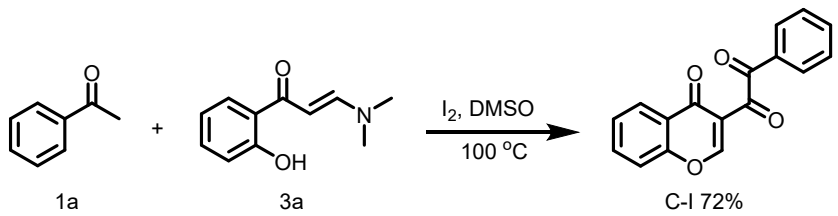








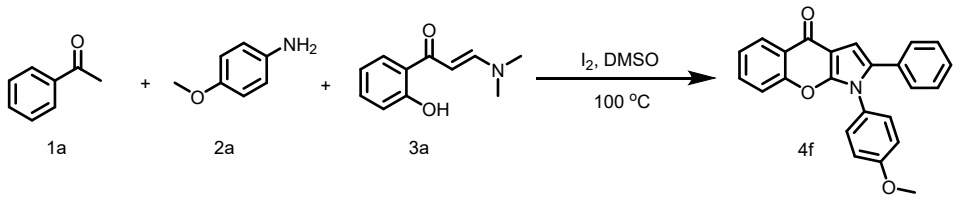
The synthesis of C-I



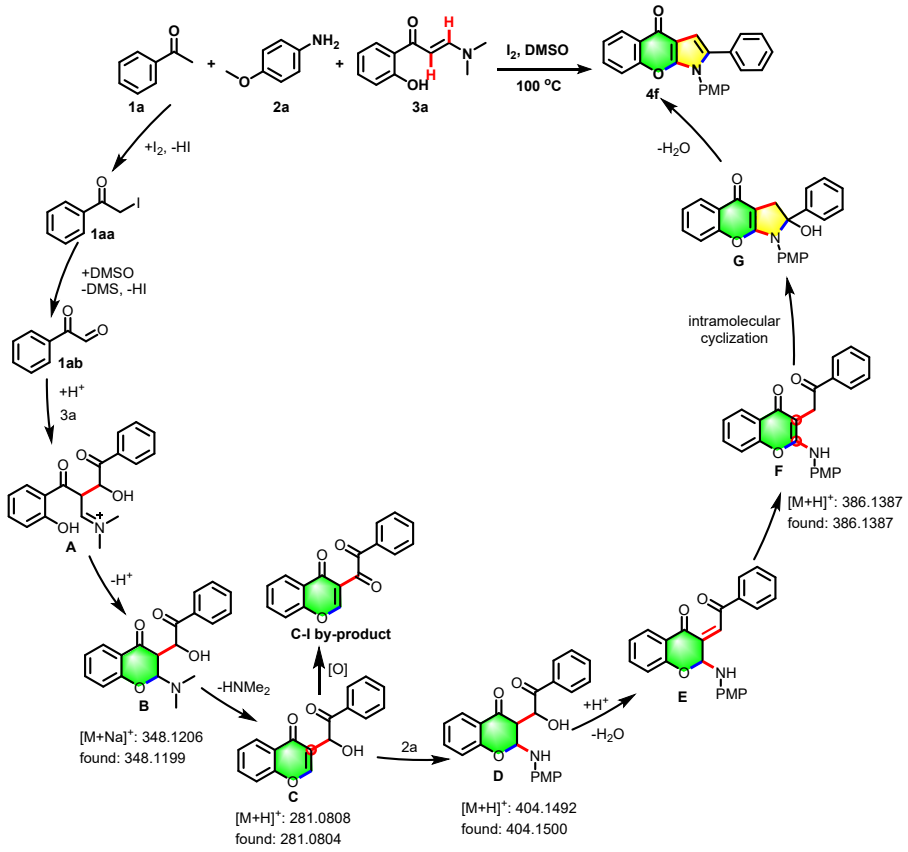
In a 35 mL sealed tube were added acetophenone (**1a**) (120 mg, 1.0 mmol), iodine (381 mg, 1.5 mmol) and dimethyl sulfoxide (5 mL) and the resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 1 hour. Then add (**3a**) (191 mg, 1.0 mmol), the resulting mixture was stirred at 100 ℃ (metal heating block), the reaction tube was removed after about 3 hour until substrate conversion was almost complete by TLC analysis. The reaction mixture was

quenched with saturated $Na_2S_2O_3$ solution (50 mL) and NaCl solution (150 mL), then the mixture was extracted with EtOAc (150 mL x 2), the organic layers were separated and combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 15:1) to afford the product (200mg, 72% yield).

The HRMS date of mechanistic studies



In a 35 mL sealed tube were added acetophenone (**1a**) (120 mg, 1.0 mmol), iodine (381 mg, 1.5 mmol) and dimethyl sulfoxide (5 mL) and the resulting mixture was stirred at 100 ℃ (heating block), the reaction tube was removed after about 1 hour. Then add (**2a**) (246mg, 2.0 mmol), (**3a**) (191 mg, 1.0 mmol), and the resulting mixture was stirred at 100 ℃, the reaction tube was removed after about 4 hour. Then, the 1 mL of the reaction solution was quenched with 4 mL of saturation $Na_2S_2O_3$ solution, and then extracted with 3 mL of EtOAc. Then 1.0 mL of the extraction solution was added into the test bottle and diluted with 0.5 mL of EtOAc. Take samples every 15 minutes, 30 minutes and 45 minutes, the samples were immediately monitored by HRMS.


1a
2a
3a
I2, DMSO
100 °C
4f
PMP
+I2, -HI
1aa
+DMSO
-DMS, -HI
1ab
+H+
3a
A
-H+
B
[M+Na]+: 348.1206
found: 348.1199
-HNMe2
[O]
C-I by-product
C
[M+H]+: 281.0808
found: 281.0804
2a
D
[M+H]+: 404.1492
found: 404.1500
+H+
-H2O
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PMP
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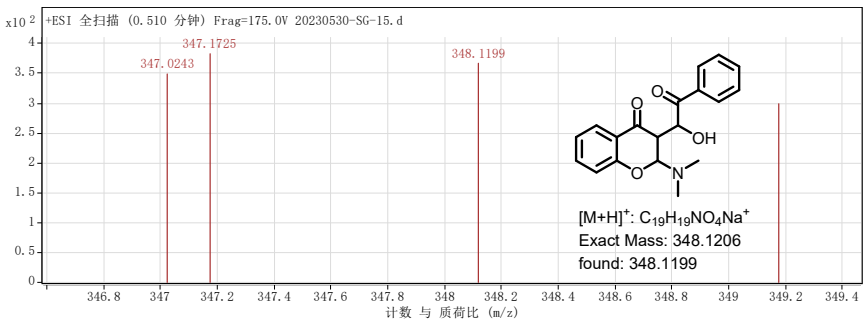
found: 386.1387
intramolecular
cyclization
F
G
-H2O

HRMS: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347.0243
348.1199
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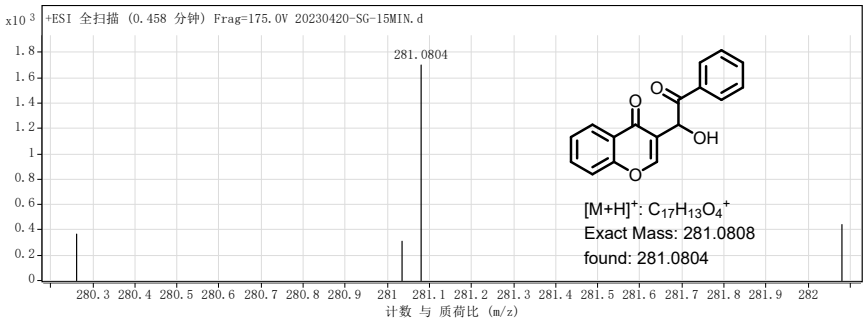
Exact Mass: 348.1206
found: 348.1199
计数 与 质荷比 (m/z)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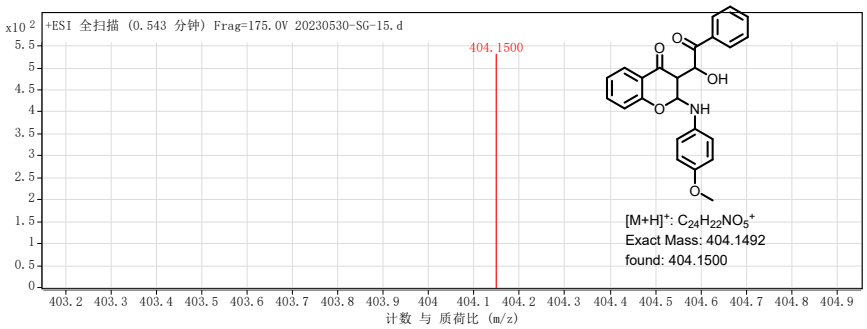
计数 与 质荷比 (m/z)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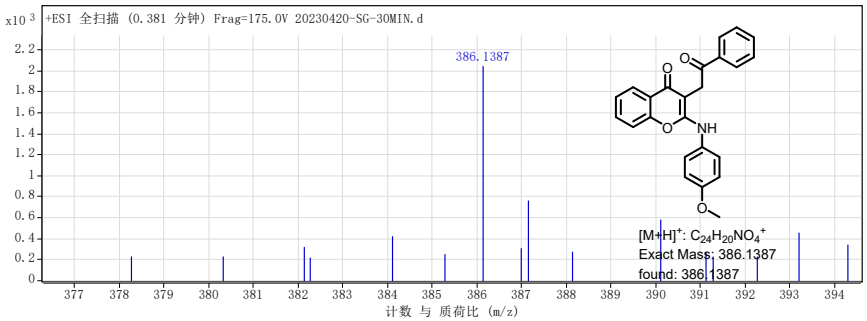
found: 404.1500
计数 与 质荷比 (m/z)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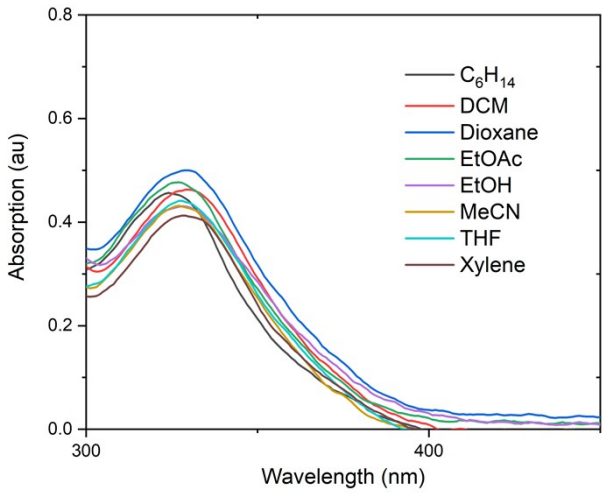
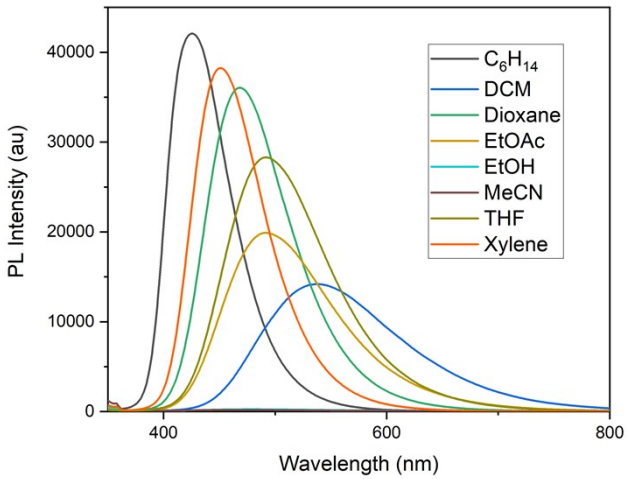
386.1387
[M+H]+: C24H20NO4+
Exact Mass: 386.1387
found: 386.1387
计数 与 质荷比 (m/z)

3. Photophysical Properties

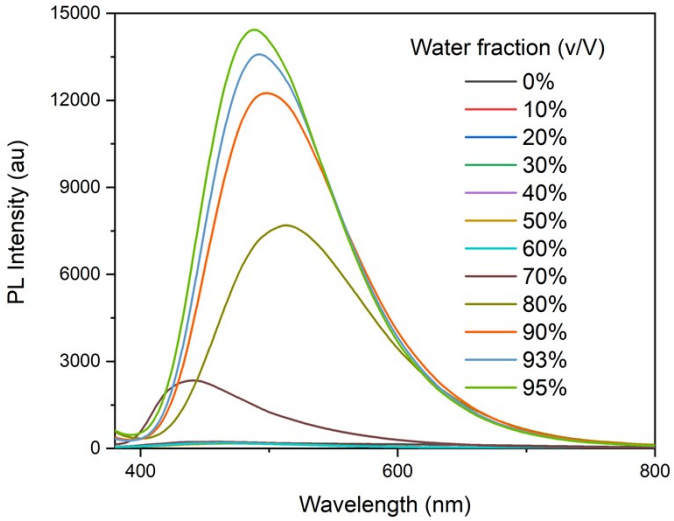
Solvatochromic effect of 4p-PXZ:The test solution of 4p-PXZ is diluted with stock solution (2.0 x 10^{-4} mol/L), and the solution of equal concentration (10^{-5} mol/L) is prepared by eight different polarity solvents. The excitation wavelength of the fluorescence test is 328 nm and is tested with a quartz cuvette.



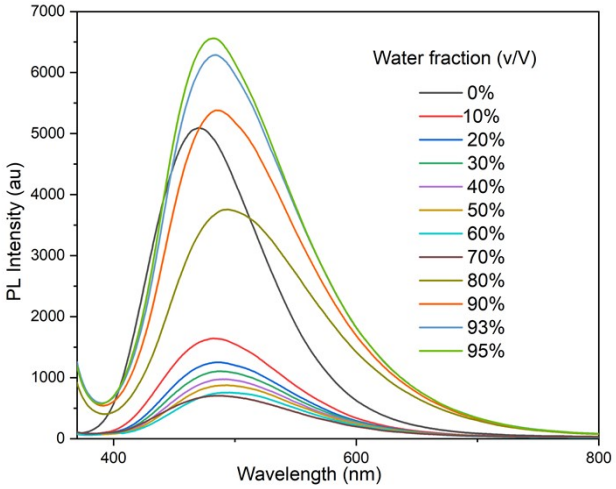


Fluorescence emission spectrum of AIE:

The test solution of 4p-PXZ and 5d-PXZ are diluted with stock solution (2.0 x 10^{-4} mol/L), and the solution of equal concentration (10^{-5} mol/L) with different water fractions is prepared by MeCN/H_2O mixed solvent system. The excitation wavelength of the fluorescence test is 328 nm, and the AIE solution is tested with a quartz cuvette.



Fluorescence emission curve of AIE (4p-PXZ, c = 10^{-5} mol/L)



Fluorescence emission curve of AIE (5d-PXZ, c = 10^{-5} mol/L)

4. Crystallographic data and molecular structure of 4d

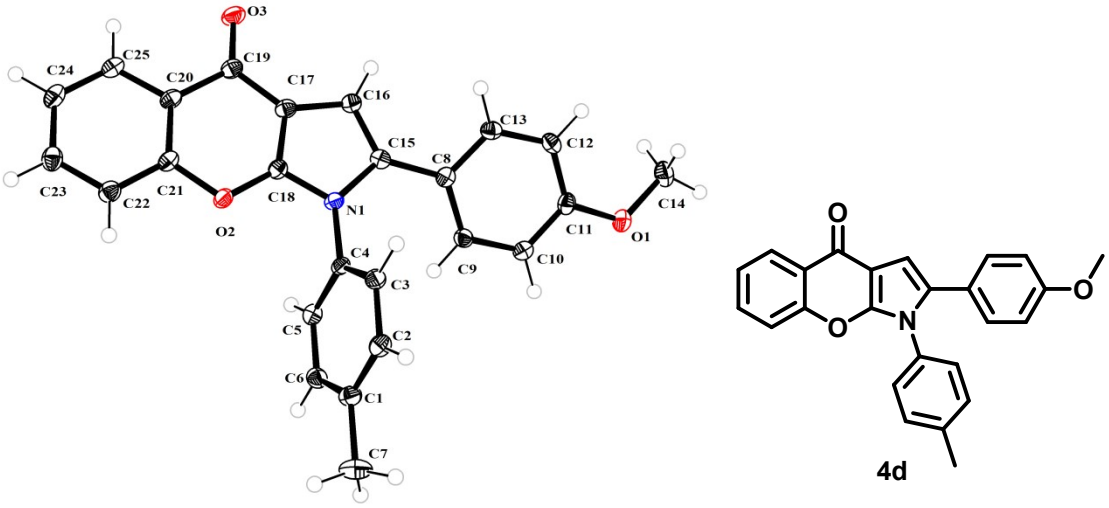


Figure 1. Molecular structure of **4d** with 50% probability ellipsoids

Crystal Data for Compound **4d**: CCDC 2265550 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

Sample preparation: In a 10 mL glass bottle, 15 mg of pure **4d** was completely dissolved in the mixed solvent of 3 mL $CHCl_3$, and then 2 mL of n-hexane was added slowly. After a week of solvent evaporation, some white transparent crystals were obtained. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a D8 Venture diffractometer with Ga Kα radiation (1.34139 Å) at room temperature.

```
Bond precision:   C-C = 0.0020 A          Wavelength=1.34139

Cell:             a=5.5560(3)     b=21.2465(12)      c=19.5024(11)
                  alpha=90        beta=96.515(2)     gamma=90
Temperature:      100 K

                  Calculated                  Reported
Volume            2287.3(2)                   2287.3(2)
Space group       P 21/c                      P 21/c
Hall group        -P 2ybc                     -P 2ybc
Moiety formula    C25 H19 N O3, C H Cl3       ?
Sum formula       C26 H20 Cl3 N O3            C26 H20 Cl3 N O3
Mr                500.78                      500.78
Dx,g cm-3         1.454                       1.454
Z                 4                           4
Mu (mm-1)         2.566                       2.566
F000              1032.0                      1032.0
F000'             1037.84
h,k,lmax          7,28,26                     7,28,26
Nref              5701                        5657
Tmin,Tmax         0.831,0.902                 0.748,0.904
Tmin'             0.735

Correction method= # Reported T Limits: Tmin=0.748 Tmax=0.904
AbsCorr = MULTI-SCAN

Data completeness= 0.992           Theta(max)= 63.503

R(reflections)= 0.0401( 4584)                wR2(reflections)=
                                             0.1057( 5657)
S = 1.058                  Npar= 300
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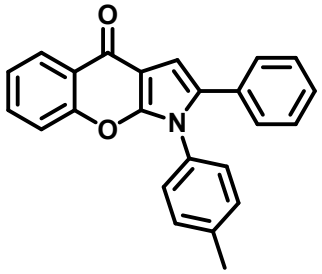
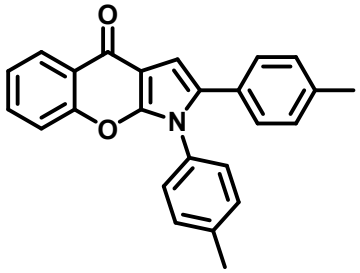
6. Characterization data for compounds



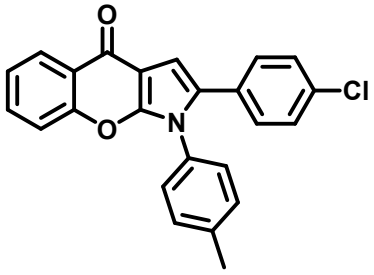
2-phenyl-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (4a):

Yield 65%; 228 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 208-210 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.28-7.19 (m, 9H), 6.94 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 154.0, 150.6, 138.6, 132.4, 132.1, 131.9, 131.1, 130.0, 128.3, 128.2, 127.4, 127.3, 126.7, 124.4, 123.5, 117.5, 107.0, 102.4, 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{18}N_1O_2^+$: 352.1332; found: 352.1335.



1,2-di-*p*-tolylchromeno[2,3-*b*]pyrrol-4(*1H*)-one (4b):

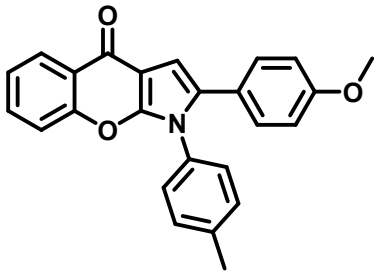
Yield 63%; 238 mg; white solid column chromatography, silica gel (PE:EA, 8:1); mp 210-212 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.8 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 8.8 Hz, 4H), 6.90 (s, 1H), 2.44 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 154.1, 150.5, 138.5, 137.3, 132.3, 132.2, 132.1, 130.0, 129.1, 128.3, 128.2, 127.4, 126.7, 124.4, 123.6, 117.5, 107.0, 101.9, 21.3, 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{20}NO_2^+$:366.1489; found: 366.1487.



2-(4-chlorophenyl)-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4c):

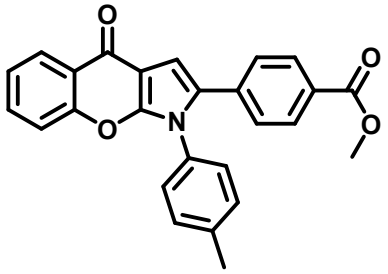
Yield 68%; 262 mg; yellowish white solid; column chromatography, silica gel (PE:EA, 8:1); mp 216-218 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 4H), 7.08 (d, J = 8.0 Hz, 2H), 6.92 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 154.0, 150.6, 138.8, 133.3, 132.4, 131.8, 130.6, 130.1, 129.6, 129.3, 128.6, 127.3, 126.6, 124.4, 123.4,

117.4, 106.9, 102.7, 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{17}ClNO_2^+$: 386.0942; found: 386.0941.



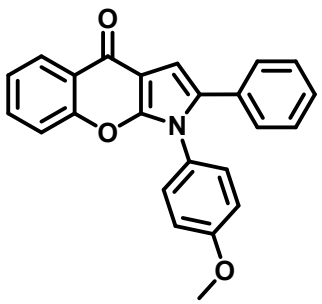
2-(4-methoxyphenyl)-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4d):

Yield 66%; 251 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 220-222 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.86 (s, 1H), 6.77 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.0, 154.0, 150.4, 138.5, 132.3, 132.1, 131.9, 130.0, 129.6, 127.4, 126.7, 124.3, 123.6, 123.5, 117.4, 113.8, 106.9, 101.3, 55.2, 21.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{20}NO_3^+$: 382.1438; found: 382.1439.



methyl 4-(4-oxo-1-(*p*-tolyl)-1,4-dihydrochromeno[2,3-*b*]pyrrol-2-yl)benzoate (4e):

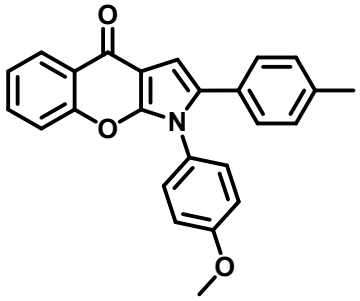
Yield 64%; 262 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 222-224 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 8.4 Hz, 2H), 7.30-7.28 (m, 2H), 7.24-7.19 (m, 4H), 7.05 (s, 1H), 3.89 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 166.7, 154.1, 151.0, 138.9, 135.5, 132.6, 131.9, 130.7, 130.2, 129.6, 128.6, 127.7, 127.3, 126.7, 124.5, 117.5, 103.9, 52.1, 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{20}NO_4^+$: 410.1387; found: 410.1385.



1-(4-methoxyphenyl)-2-phenylchromeno[2,3-*b*]pyrrol-4(*1H*)-one (4f):

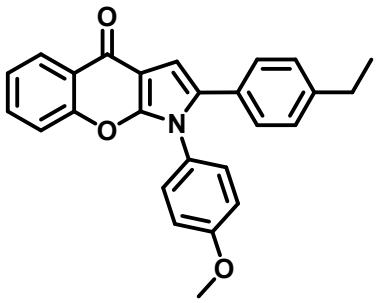
Yield 70%; 257 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 256-258 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.40

(t, J = 8.0 Hz, 2H), 7.24-7.15 (m, 7H), 6.97 (t, J = 8.0 Hz, 2H), 8.64 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.4, 154.0, 150.7, 132.4, 132.0, 131.1, 128.8, 128.3, 128.2, 127.39, 127.36, 126.7, 124.4, 123.5, 117.4, 114.5, 106.9, 102.1, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{18}NO_3^+$:368.1281; found: 368.1282.



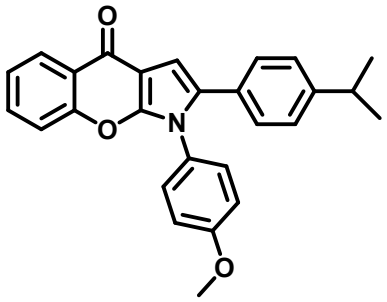
1-(4-methoxyphenyl)-2-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4g):

Yield 69%; 263 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 236-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 2H), 7.08-7.03 (m, 4H), 6.97 (d, J = 8.4 Hz, 2H), 6.89 (s, 1H), 3.87 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.4, 154.0, 150.6, 137.2, 132.3, 132.1, 129.1, 128.8, 128.2, 128.1, 127.5, 126.6, 124.3, 123.5, 117.4, 114.5, 106.8, 101.5, 55.5, 21.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{20}NO_3^+$: 382.1438; found: 382.1439.



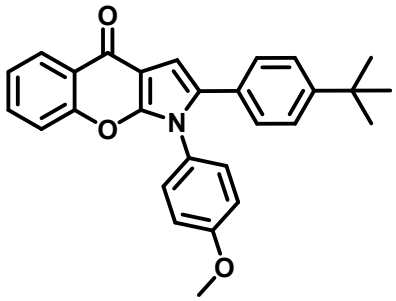
2-(4-ethylphenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4h):

Yield 67%; 265 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 192-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 2H), 7.10-7.05 (m, 4H), 6.97 (d, J = 7.6 Hz, 2H), 6.89 (s, 1H), 3.87 (s, 3H), 2.60 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.4, 154.0, 150.6, 143.5, 132.3, 132.2, 128.8, 128.4, 128.1, 127.8, 127.5, 126.6, 124.3, 123.5, 117.4, 114.5, 106.8, 101.6, 55.5, 28.4, 15.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{22}NO_3^+$: 396.1594; found: 396.1595.



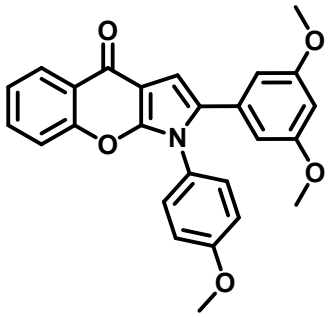
2-(4-isopropylphenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4i):

Yield 72%; 294 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 170-172 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 8.4 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 7.02 (s, 4H), 6.90 (d, J = 8.8 Hz, 2H), 6.82 (s, 1H), 3.80 (s, 3H), 2.81-2.74 (m, 1H), 1.14 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.4, 154.0, 150.6, 148.1, 132.3, 132.2, 128.8, 128.5, 128.1, 127.5, 126.7, 126.4, 124.3, 123.6, 117.4, 114.5, 106.9, 101.6, 55.5, 33.7, 23.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{24}NO_3^+$: 410.1751; found: 410.1749.



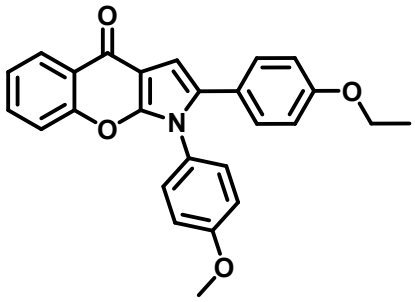
2-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4j):

Yield 68%; 288 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 198-200 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 5.2 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.29-7.23 (m, 2H), 7.16-7.09 (m, 2H), 7.02-6.97 (m, 2H), 6.91 (s, 1H), 3.89 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.4, 154.0, 150.7, 150.4, 132.3, 132.1, 128.8, 128.1, 127.7, 126.7, 125.3, 124.3, 123.5, 117.4, 114.5, 106.9, 101.6, 55.5, 34.5, 31.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{26}NO_3^+$: 424.1907; found: 424.1908.



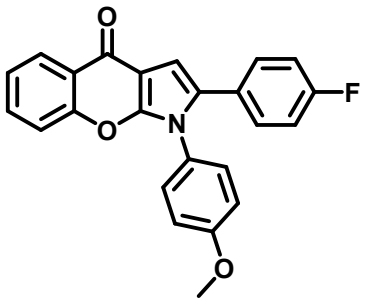
2-(3,5-dimethoxyphenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (4k):

Yield 67%; 286 mg; white solid; column chromatography, silica gel (PE:EA, 3:1); mp 161-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.60 (d, J = 5.6 Hz, 1H), 7.41 (d, J = 6.0 Hz, 2H), 7.28-7.23 (m, 2H), 7.02-6.97 (m, 2H), 6.91-6.88 (m, 1H), 6.80-6.75 (m, 2H), 6.64 (s, 1H), 3.86 (s, 6H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.5, 154.0, 150.5, 148.4, 132.3, 132.0, 128.9, 127.5, 126.7, 124.4, 123.7, 120.9, 117.4, 114.5, 111.4, 110.9, 106.8, 101.1, 55.8, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{22}NO_5^+$: 428.1492; found: 428.1492.



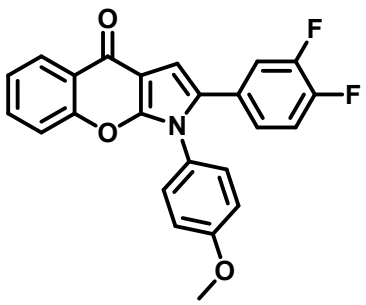
2-(4-ethoxyphenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4l):

Yield 65%; 267 mg; white solid; column chromatography, silica gel (PE:EA, 6:1); mp 185-187 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.85 (s, 1H), 6.77 (d, J = 8.4 Hz, 2H), 4.00 (q, J = 6.8 Hz, 2H), 3.87 (s, 3H), 1.39 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.4, 158.4, 154.0, 150.5, 132.3, 132.1, 129.6, 128.8, 127.5, 126.7, 124.3, 123.6, 123.4, 117.4, 114.5, 114.3, 106.8, 101.0, 63.4, 55.5, 14.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{22}NO_4^+$: 412.1543; found: 412.1542.



2-(4-fluorophenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4m):

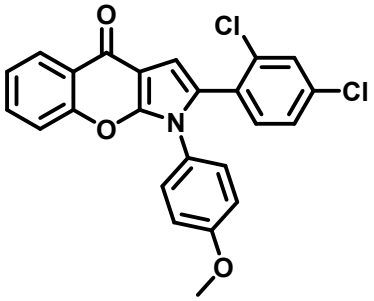
Yield 70%; 270 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 248-250 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz ,1H), 7.60 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.8 Hz, 2H), 7.22 (d, J = 6.0 Hz, 2H), 7.17-7.11 (m, 2H), 6.99-6.95 (m, 4H), 6.88 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 162.0 (d, J_{CF} = 247.0 Hz, $^{1}J_{CF}$), 159.5, 154.0, 150.6, 132.4, 131.0, 130.0 (d, J_{CF} =8.0 Hz, $^{3}J_{CF}$), 128.8, 127.2, 127.1, 126.7, 124.4, 123.5, 117.4, 115.4 (d, J_{CF} = 21.0 Hz, $^{2}J_{CF}$), 114.6, 106.8, 102.0, 99.9, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.90. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{17}N_1O_3F^+$: 386.1187; found: 386.1185.



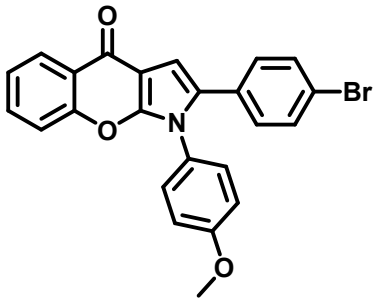
2-(3,4-difluorophenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4n):

Yield 74%; 298 mg; yellowish white solid; column chromatography, silica gel (PE:EA, 8:1); mp 214-216 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz,

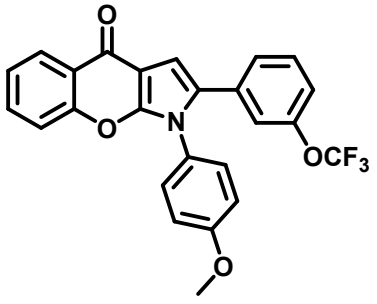
1H), 7.39 (t, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.07-7.00 (m, 3H), 6.97-6.89 (m, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.7, 154.0, 149.9 (dd, J_{CF} =247.0, 13.0 Hz), 150.7, 149.6 (dd, J_{CF} =249.0, 12.0 Hz), 132.5, 129.7, 128.7, 128.1 (dd, J_{CF} =6.0, 4.0 Hz), 126.8, 126.6, 124.5, 124.3 (dd, J_{CF} =6.0, 4.0 Hz), 124.2, 123.4, 117.4, 117.2 (dd, J_{CF} =31.0, 18.0 Hz), 116.9, 114.7, 106.7, 102.7, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.96, -138.59. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{16}NO_3F_2^+$: 404.1093; found: 404.1090.



2-(2,4-dichlorophenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4o):
Yield 71%; 309 mg; yellowih solid; column chromatography, silica gel (PE:EA, 8:1); mp 204-206 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 6.4 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 2H), 7.35 (s, 1H), 7.21-7.14 (m, 4H), 6.91 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.3, 154.0, 150.0, 135.3, 134.9, 133.5, 132.5, 129.6, 128.9, 128.2, 127.4, 126.9, 126.8, 126.7, 124.4, 123.4, 117.4, 114.3, 106.6, 104.6, 55.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{16}NO_3Cl_2^+$: 436.0502; found: 436.0501.

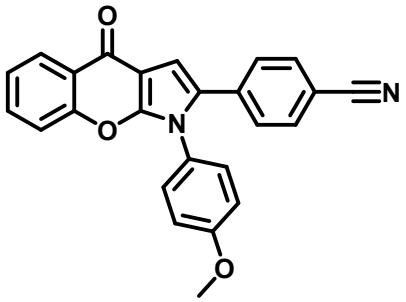


2-(4-bromophenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4p):
Yield 72%; 320 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 260-262 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.42-7.36 (m, 4H), 7.23 (d, J = 8.4 Hz, 2H), 7.01 (dd, J = 16.4, 8.4 Hz, 4H), 6.93 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.6, 154.1, 150.8, 132.5, 131.6, 130.8, 130.0, 129.6, 128.7, 127.1, 126.7, 124.5, 123.5, 121.5, 117.5, 114.7, 106.9, 102.5, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{17}NO_3Br^+$: 446.0386; found: 446.0387.



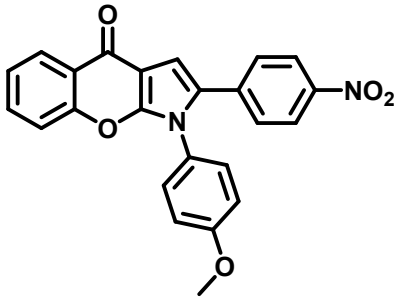
1-(4-methoxyphenyl)-2-(3-(trifluoromethoxy)phenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4q)：

Yield 75%; 338 mg; yellowish white solid; column chromatography, silica gel (PE:EA, 8:1); mp 151-153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.31-7.23 (m, 3H), 7.17 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.02-6.98 (m, 3H), 6.95 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.8, 154.1, 150.9, 149.0, 133.0, 132.6, 130.3, 129.8, 128.7, 126.9, 126.7, 126.3, 124.5, 123.5, 121.5 (q, J_{CF} = 256.0 Hz, $^1J_{CF}$), 120.3, 119.7, 117.5, 114.8, 106.9, 103.1, 55.5, 29.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87 HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{17}NO_4F_3^+$: 452.1104; found: 452.1103.



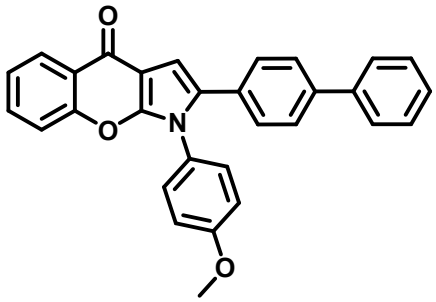
4-(1-(4-methoxyphenyl)-4-oxo-1,4-dihydrochromeno[2,3-*b*]pyrrol-2-yl)benzonitrile (4r):

Yield 69%; 270 mg; white solid; column chromatography, silica gel (PE:EA, 5:1); mp > 300 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 5.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 4.4 Hz, 4H), 7.35 (d, J = 5.6 Hz, 2H), 7.30-7.24 (m, 3H), 7.09 (s, 2H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 160.4, 153.9, 153.6, 135.3, 134.7, 133.8, 132.7, 128.8, 128.6, 126.7, 126.3, 125.6, 118.7, 117.5, 115.9, 115.4, 110.8, 105.8, 104.2, 55.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{17}N_2O_3^+$: 393.1234; found: 393.1233.

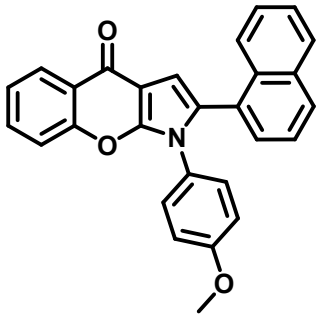


1-(4-methoxyphenyl)-2-(4-nitrophenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4s):

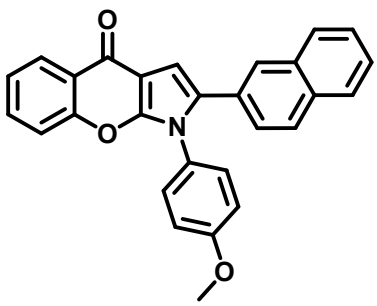
Yield 66%; 272 mg; yellow solid; column chromatography, silica gel (PE:EA, 5:1); mp 233-235 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.43 (dd, J = 14.0, 8.0 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 2.8 Hz, 2H), 7.13 (s, 1H), 7.03 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.9, 154.2, 151.5, 146.3, 137.5, 132.9, 129.4, 128.7, 128.0, 126.8, 124.8, 123.8, 123.4, 117.5, 115.0, 107.2, 105.1, 55.6. HRMS (ESI): m/z [M+H]+ calcd for $C_{24}H_{17}N_2O_5^+$: 413.1132; found: 413.1133.



2-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4t):
Yield 57%; 253 mg; yellowish brown solid; column chromatography, silica gel (PE:EA, 8:1); mp 205-207 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.56 (t, J =7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.43-7.40 (m, 4H), 7.34 (d, J = 7.2 Hz, 1H), 7.29 (s, 1H), 7.29-7.23 (t, J = 6.8 Hz, 3H), 7.03–6.97 (m, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.5, 154.0, 150.8, 140.2, 139.9, 132.4, 131.7, 130.0, 128.82, 128.77, 128.4, 127.4, 127.0, 126.8, 126.7, 124.4, 123.5, 117.5, 114.6, 107.0, 102.2, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{22}NO_3^+$: 444.1594; found: 444.1593.

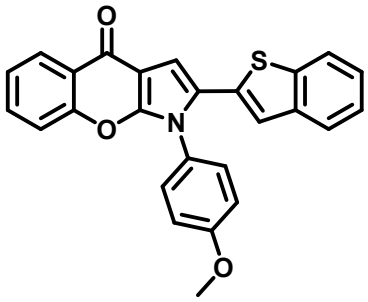


1-(4-methoxyphenyl)-2-(naphthalen-1-yl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4u):
Yield 62%; 259 mg; yellowish white solid; column chromatography, silica gel (PE:EA, 8:1); mp 124-126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.79 (dd, J = 13.2, 8.0 Hz, 2H), 7.63-7.60 (m, 1H), 7.47-7.41 (m, 4H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 7.11 (d, J = 8.8 Hz, 2H), 6.98 (s, 1H), 6.74 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.0, 154.1, 150.1, 133.5, 132.6, 132.4, 129.7, 129.4, 128.7, 128.6, 128.2, 128.1, 127.2, 126.8, 126.5, 126.0, 125.7, 124.8, 124.4, 123.7, 117.4, 114.2, 106.8, 104.5, 55.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{20}NO_3^+$: 418.1438; found: 418.1435.

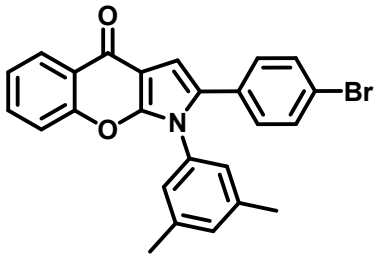


1-(4-methoxyphenyl)-2-(naphthalen-2-yl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4v):
Yield 60%; 250 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 206-208 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 7.6 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.70-

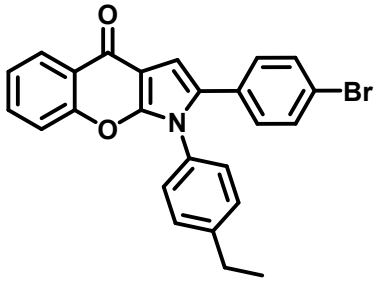
7.66 (m, 3H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.44 (dd, J = 9.2, 4.0 Hz, 3H), 7.40 (s, 1H), 7.29-7.26 (m, 2H), 7.23 (s, 1H), 7.06 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.5, 154.1, 150.8, 133.1, 132.4, 132.3, 132.0, 128.8, 128.5, 128.1, 127.9, 127.5, 127.4, 127.2, 126.7, 126.3, 126.2, 126.0, 124.4, 123.5, 117.5, 114.6, 107.0, 102.7, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{20}NO_3^+$: 418.1438; found: 418.1439.



2-(benzo[b]thiophen-2-yl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4w):
Yield 67%; 283 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 240-242 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.40 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 6.8 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.41-7.36 (m, 4H), 7.26 (t, *J* = 3.2 Hz, 2H), 7.10 (s, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 160.3, 154.1, 151.2, 139.7, 139.2, 133.1, 132.5, 129.6, 126.7, 126.6, 126.0, 124.5, 124.4, 123.5, 123.4, 121.8, 121.4, 117.5, 114.8, 106.9, 103.4, 55.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{18}NO_3S^+$: 424.1002; found: 424.1001.

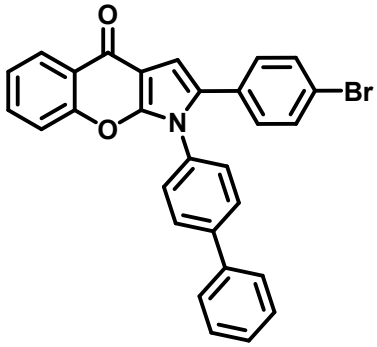


2-(4-bromophenyl)-1-(3,5-dimethylphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4x):
Yield 56%; 248 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 239-241 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.41 (s, 1H), 7.60 (d, *J* = 5.2 Hz, 1H), 7.44-7.34 (m, 4H), 7.11 (s, 1H), 7.06-7.02 (m, 2H), 6.95-6.90 (m, 3H), 2.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 154.1, 150.8, 139.4, 134.3, 132.5, 131.5, 130.7, 130.6, 130.1, 129.4, 126.7, 125.3, 124.5, 123.5, 121.5, 117.5, 107.0, 102.7, 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{19}NO_2Br^+$: 444.0594; found: 444.0593.



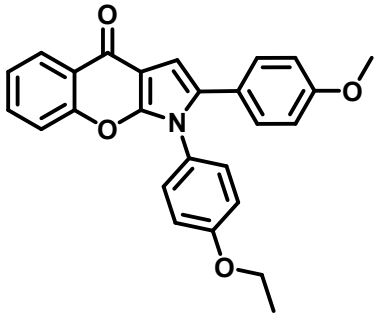
2-(4-bromophenyl)-1-(4-ethylphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4y):

Yield 59%; 261 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 193-195 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.2 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.95 (s, 1H), 2.75 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 154.1, 150.7, 145.0, 132.5, 132.0, 131.5, 130.7, 130.1, 129.6, 128.9, 127.3, 126.7, 124.5, 123.5, 121.5, 117.5, 107.0, 102.8, 28.5, 15.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{19}NO_2Br^+$: 444.0594; found: 444.0592.



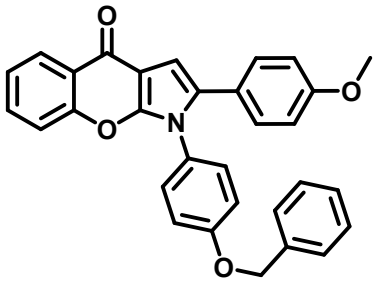
1-([1,1'-biphenyl]-4-yl)-2-(4-bromophenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4z):

Yield 57%; 280 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 223-225℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.43-7.37 (m, 7H), 7.07 (d, J = 8.4 Hz, 2H), 6.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 154.1, 150.7, 141.5, 139.5, 139.0, 133.5, 132.6, 131.6, 130.6, 130.0, 129.7, 129.0, 128.1, 127.8, 127.1, 126.7, 124.6, 123.5, 121.7, 117.5, 107.2, 103.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{20}NO_2Br^+$: 492.0594; found: 492.0595.

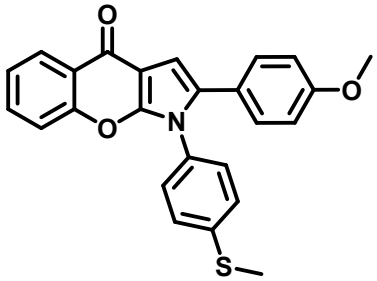


1-(4-ethoxyphenyl)-2-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5a):

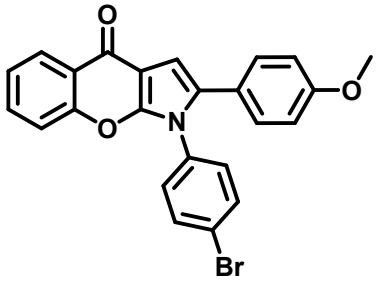
Yield 61%; 251 mg; yellow solid; column chromatography, silica gel (PE:EA, 6:1); mp 194-196 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.0 Hz, 1H), 7.61-7.56 (m, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.84 (s, 1H), 6.77 (d, J = 8.8 Hz, 2H), 4.09 (q, J = 8.0 Hz, 2H), 3.77 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 158.9, 158.8, 154.0, 150.5, 132.2, 132.0, 129.6, 128.8, 127.2, 126.6, 124.3, 123.5, 117.4, 114.9, 113.8, 106.8, 101.0, 63.7, 55.1, 14.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{22}NO_4^+$: 412.1543; found: 412.1545.



1-(4-(benzyloxy)phenyl)-2-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5b):
Yield 58%; 274 mg; yellowish white solid; column chromatography, silica gel (PE:EA, 5:1); mp 125-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.47-7.44 (m, 2H), 7.39 (dd, J = 15.6, 7.2 Hz, 5H), 7.24 (d, J = 6.8 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.85 (s, 1H), 6.78 (d, J = 8.4 Hz, 2H), 5.11 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.0, 158.6, 154.0, 150.5, 136.3, 132.3, 132.0, 129.7, 128.8, 128.7, 128.2, 127.7, 127.6, 126.7, 124.3, 123.6, 117.4, 115.4, 113.8, 106.8, 101.1, 70.3, 55.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{24}NO_4^+$: 474.1700; found: 474.1697.

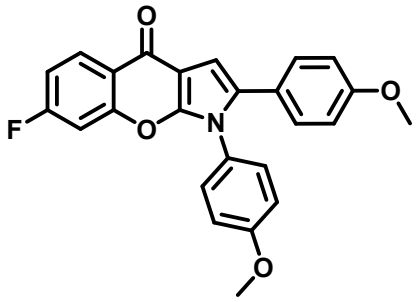


2-(4-methoxyphenyl)-1-(4-(methylthio)phenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5c):
Yield 53%; 219 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 202-204 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.0 Hz, 1H), 7.62-7.57 (m, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.85 (s, 1H), 6.79 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.1, 154.0, 150.3, 139.5, 132.4, 131.8, 131.5, 129.7, 127.9, 126.7, 126.5, 124.4, 123.6, 123.4, 117.4, 113.9, 107.0, 101.5, 55.2, 15.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{20}NO_3S^+$: 414.1158; found: 414.1155.



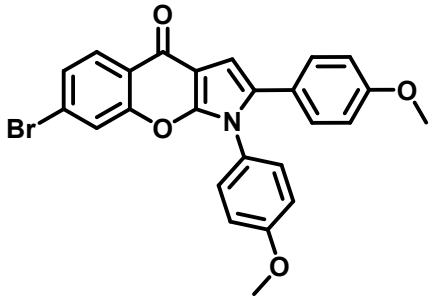
1-(4-bromophenyl)-2-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5d):
Yield 50%; 223 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 221-223 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 3H), 7.42 (t, J = 10.0 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 6.86 (s, 1H), 6.81 (d, J = 7.6 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.2, 153.9, 150.2, 133.8,

132.6, 132.5, 131.7, 129.8, 129.1, 126.8, 124.6, 123.1, 122.3, 117.4, 114.0, 107.1, 101.9, 55.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{17}NO_3Br^+$: 446.0386; found: 446.0384.



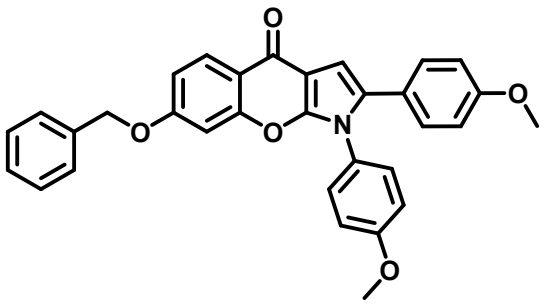
7-fluoro-1,2-bis(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5e):

Yield 63%; 261 mg; white solid; column chromatography, silica gel (PE:EA, 6:1); mp 191-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.8, 2.8 Hz, 1H), 7.38 (dd, J = 9.2, 4.0 Hz, 1H), 7.33-7.27 (m, 1H), 7.22 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.82 (s, 1H), 6.78 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.5, 159.1 (d, J_{CF}= 244.0 Hz, $^1J_{CF}$), 150.7, 150.0, 132.4, 129.7, 128.8, 127.3,124.9 (d, J_{CF}= 8.0 Hz, $^3J_{CF}$), 123.4, 120.0 (d, J_{CF}= 26.0 Hz, $^2J_{CF}$), 119.2 (d, J_{CF}= 8.0 Hz, $^3J_{CF}$), 114.6, 114.2, 113.9, 111.8 (d, J_{CF}= 24 Hz, $^2J_{CF}$), 106.4, 100.8, 55.5, 55.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.91. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{19}NO_4F^+$: 416.1293; found: 416.1292.



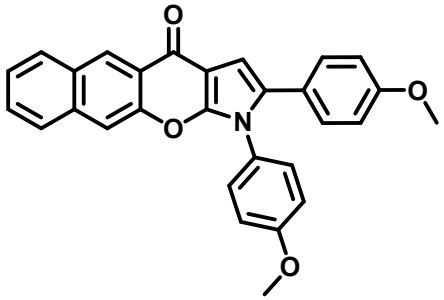
7-bromo-1,2-bis(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5f):

Yield 57%; 271 mg; yellowish white solid; column chromatography, silica gel (PE:EA, 6:1); mp 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.29 (s, 1H), 7.21 (d, J = 7.2 Hz, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 7.2 Hz, 2H), 6.82 (s, 1H), 6.78 (d, J = 7.2 Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 159.5, 159.1, 152.7, 150.4, 135.1, 132.5, 129.7, 129.3, 128.8, 127.2, 125.1, 123.3, 119.3, 117.6, 114.6, 113.9, 106.8, 101.0, 55.5, 55.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{19}NO_4Br^+$: 476.0492; found: 476.0490.



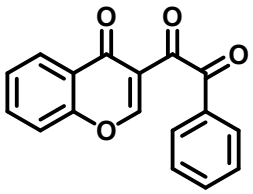
7-(benzyloxy)-1,2-bis(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5g):

Yield 51%; 257 mg; white solid; column chromatography, silica gel (PE:EA, 5:1); mp 114-116 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.8 Hz, 1H), 7.43-7.38 (m, 5H), 7.22 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 9.2 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 6.91 (s, 1H), 6.82 (s, 1H), 6.77 (d, J = 8.4 Hz, 2H), 5.11 (s, 2H), 3.87 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 164.3, 162.2, 159.4, 159.0, 155.6, 150.5, 135.9, 131.6, 131.5, 129.7, 128.9, 128.7, 128.3, 128.0, 127.5, 123.8, 117.6, 114.5, 113.8, 113.5, 101.6, 101.2, 70.4, 55.5, 55.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{26}NO_5^+$: 504.1805; found: 504.1802.



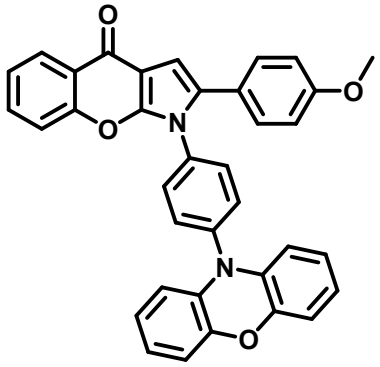
1,2-bis(4-methoxyphenyl)benzo[6,7]chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5h):

Yield 53%; 237 mg; white solid; column chromatography, silica gel (PE:EA, 6:1); mp 120-122 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.91 (s, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.4, 159.0, 150.7, 150.1, 135.5, 132.2, 129.7, 128.6, 128.5, 128.0, 127.6, 126.8, 124.2, 123.9, 123.6, 122.0, 121.9, 119.3, 114.6, 113.9, 107.5, 101.1, 55.5, 55.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{22}NO_4^+$: 448.1543; found:448.1540.



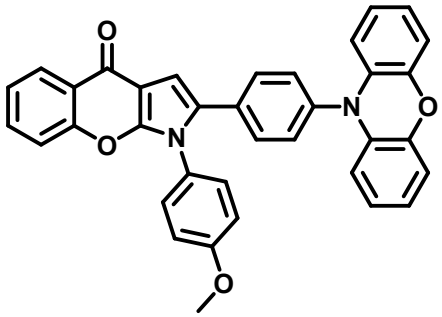
1-(4-oxo-4H-chromen-3-yl)-2-phenylethane-1,2-dione (C-I):

Yield 72%; 200 mg; white solid; column chromatography, silica gel (PE:EA, 15:1); mp 186-188 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.58-7.51 (m, 3H), 7.47 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 192.1, 174.9, 162.0, 156.2, 135.0, 134.3, 132.3, 129.7, 128.9, 126.8, 126.3, 124.7, 121.3, 118.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{11}NO_4^+$: 279.0652; found:279.0651.



1-(4-(*10H*-phenoxazin-10-yl)phenyl)-2-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (5d-PXZ):

Yield 86%; 471 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 292-294 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.49 (m, 6H), 7.18-7.10 (m, 2H), 6.91 (s, 1H), 6.86-6.80(m, 2H), 6.72 (s, 6H), 5.97 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 159.3, 154.0, 144.0, 139.0, 134.8, 133.9, 132.5, 132.0, 131.8, 130.4, 129.9, 126.8, 124.6, 123.6, 123.31, 123.25, 121.8, 117.5, 115.7, 113.9, 113.1, 107.2, 102.0, 55.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{25}N_2O_4^+$: 549.1809; found:549.1809.

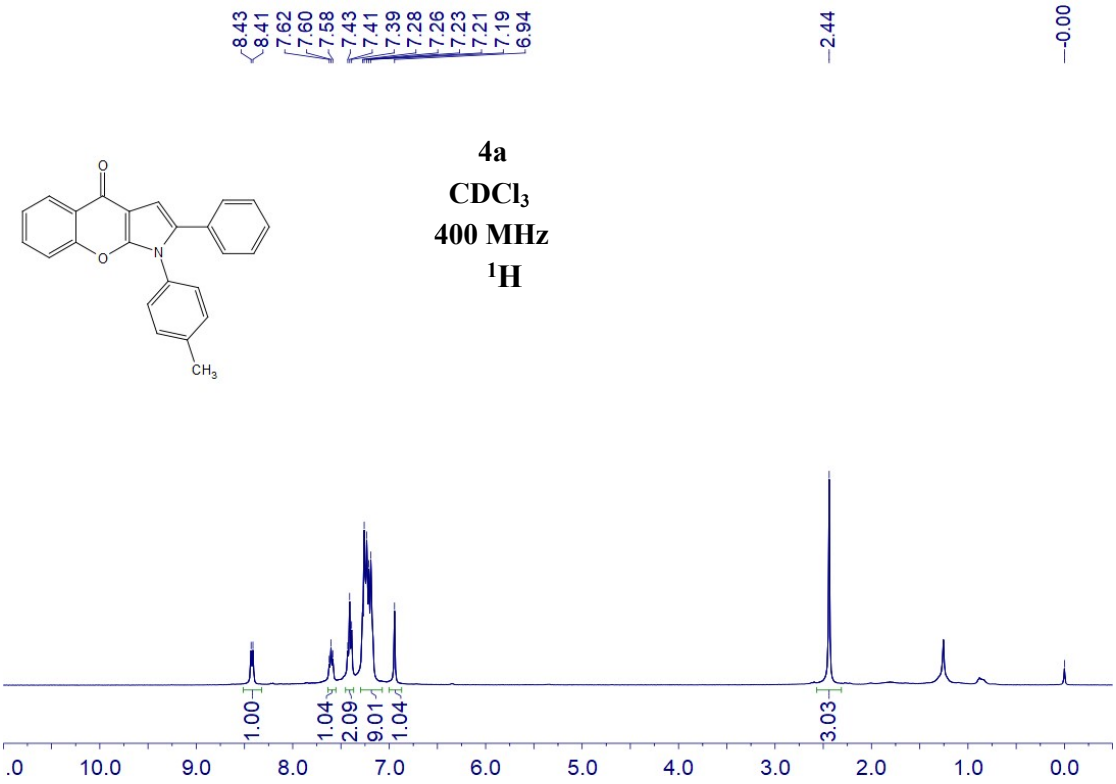


2-(4-(*10H*-phenoxazin-10-yl)phenyl)-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(*1H*)-one (4p-PXZ):

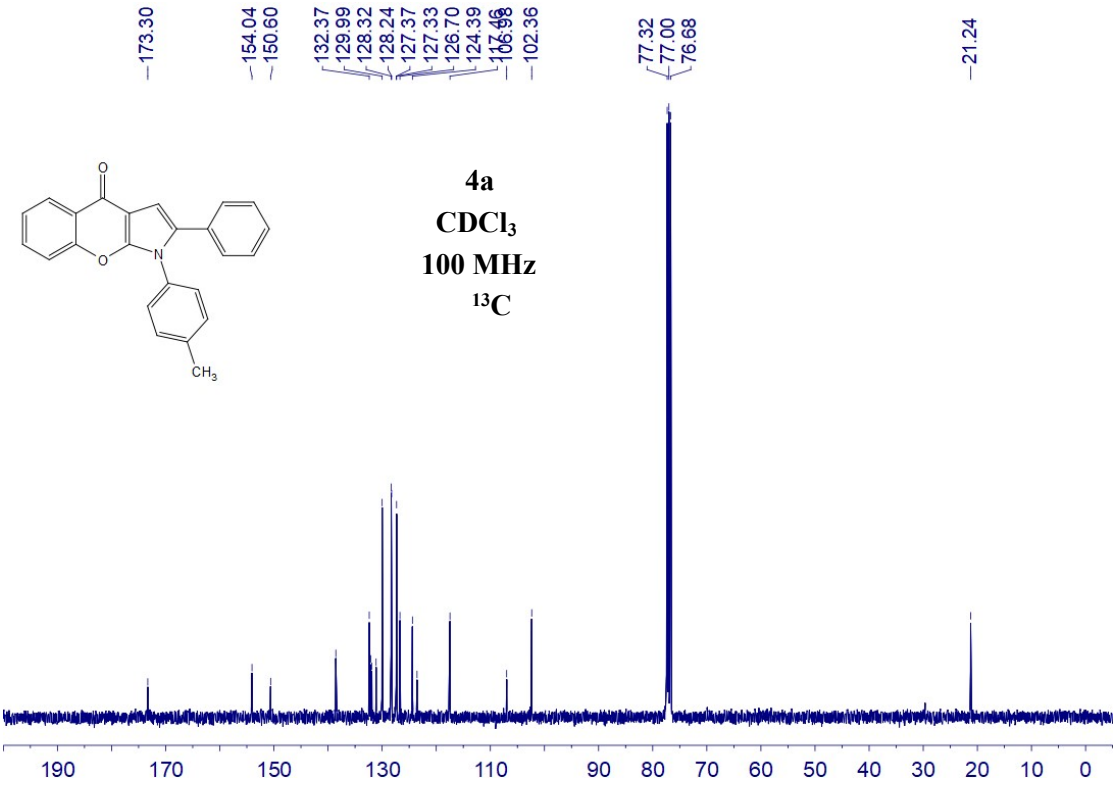
Yield 95%; 521 mg; white solid; column chromatography, silica gel (PE:EA, 8:1); mp 280-282 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.39 (dd, J = 15.6, 7.6 Hz, 4H), 7.29 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 6.0 Hz, 3H), 6.69-6.55 (m, 6H), 5.89 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.6, 154.0, 150.8, 143.8, 137.8, 134.0, 132.5, 131.3, 130.8, 130.5, 128.8, 127.2, 126.7, 124.4, 123.5, 123.1, 121.3, 117.4, 115.4, 114.6, 113.1, 106.9, 102.8, 95.5, 55.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{25}N_2O_4^+$: 549.1809; found:549.1799.

5. ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds

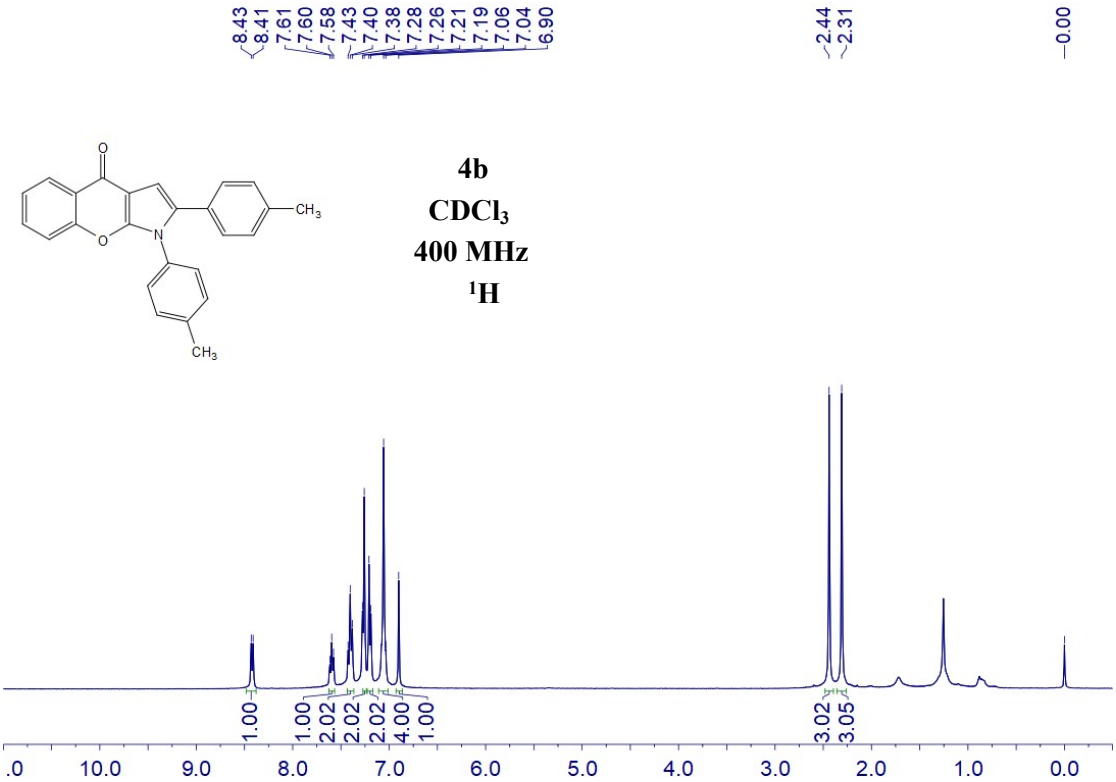
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4a



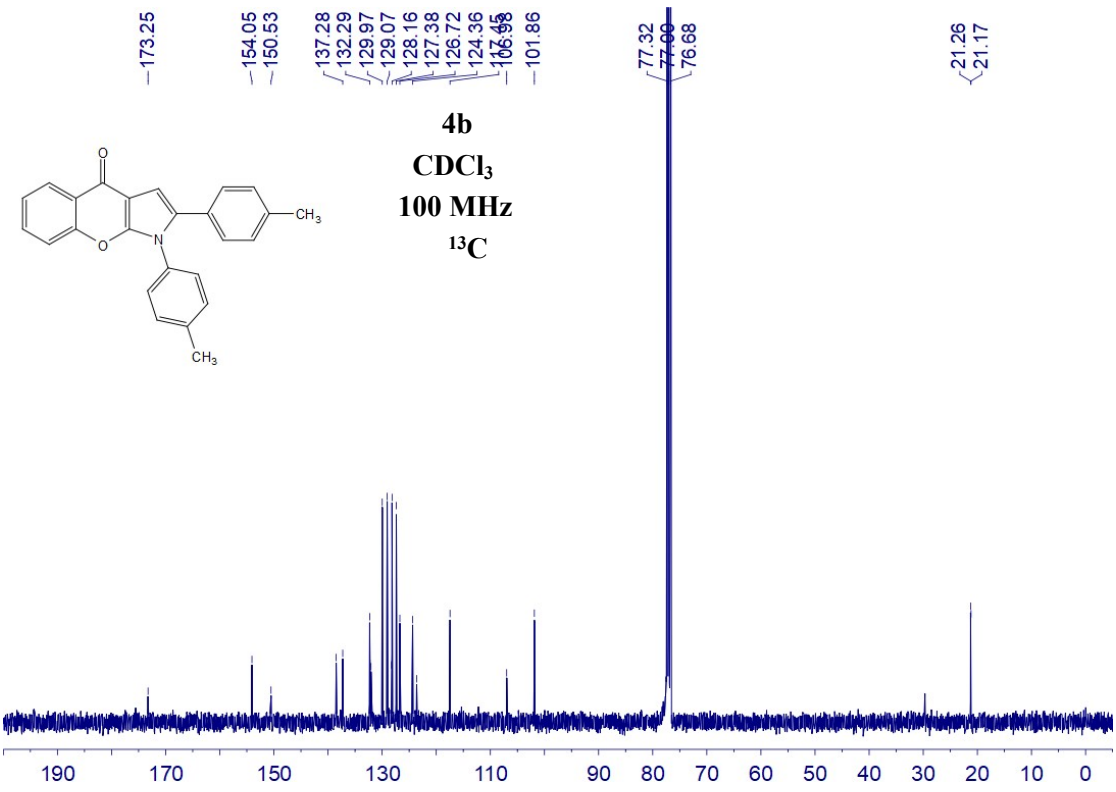
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound 4a



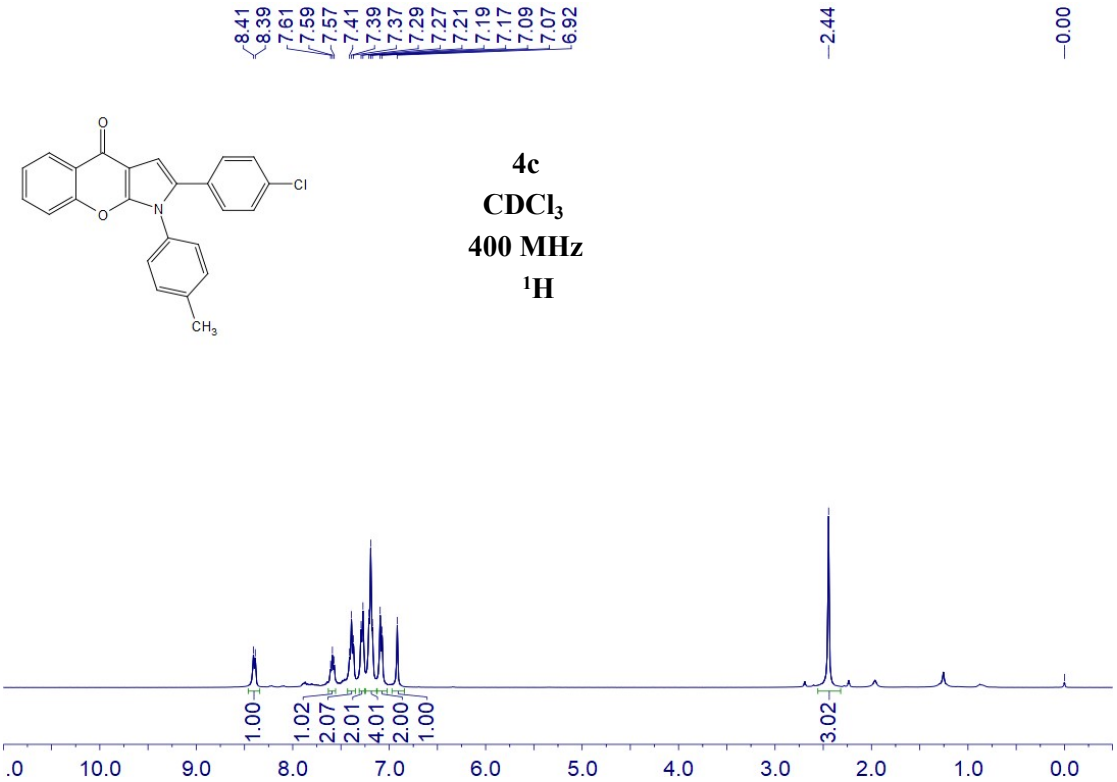
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4b



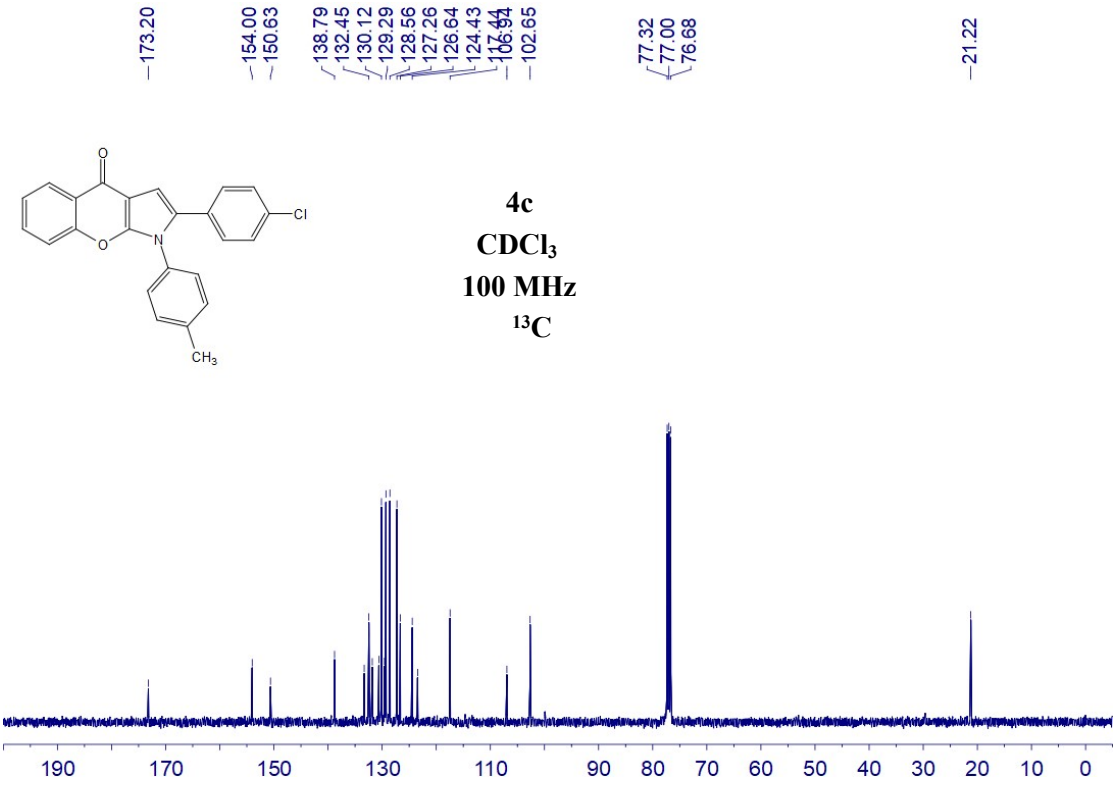
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of compound 4b



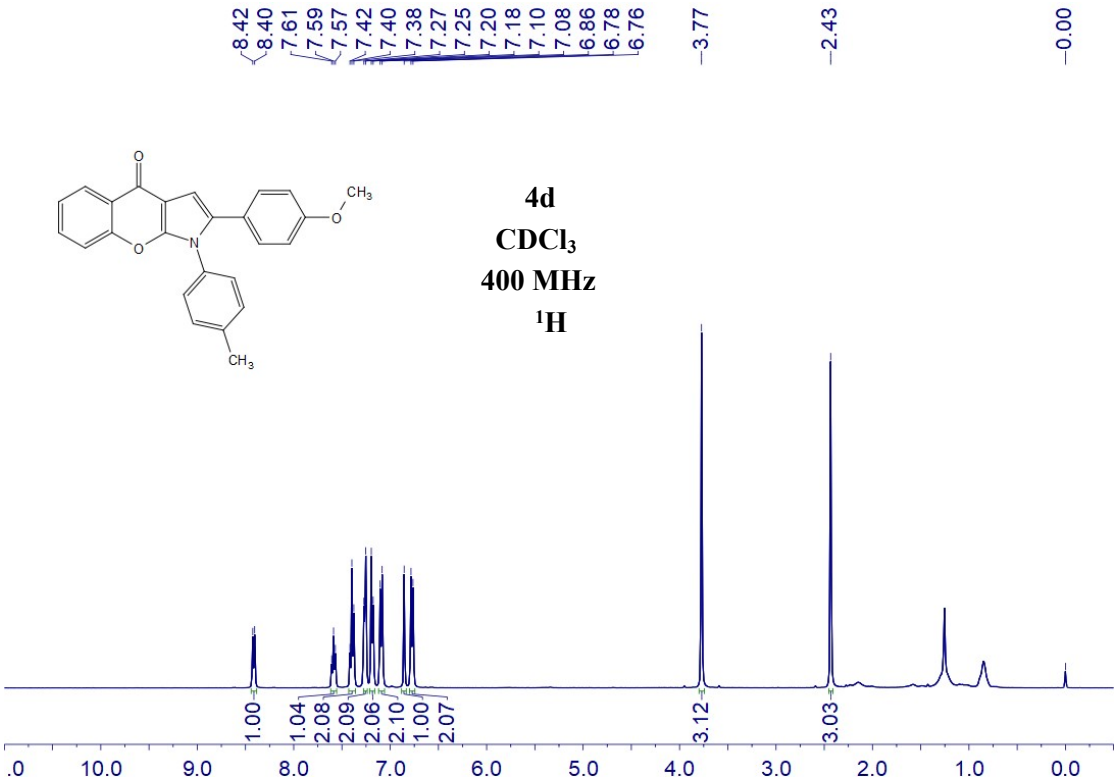
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4c



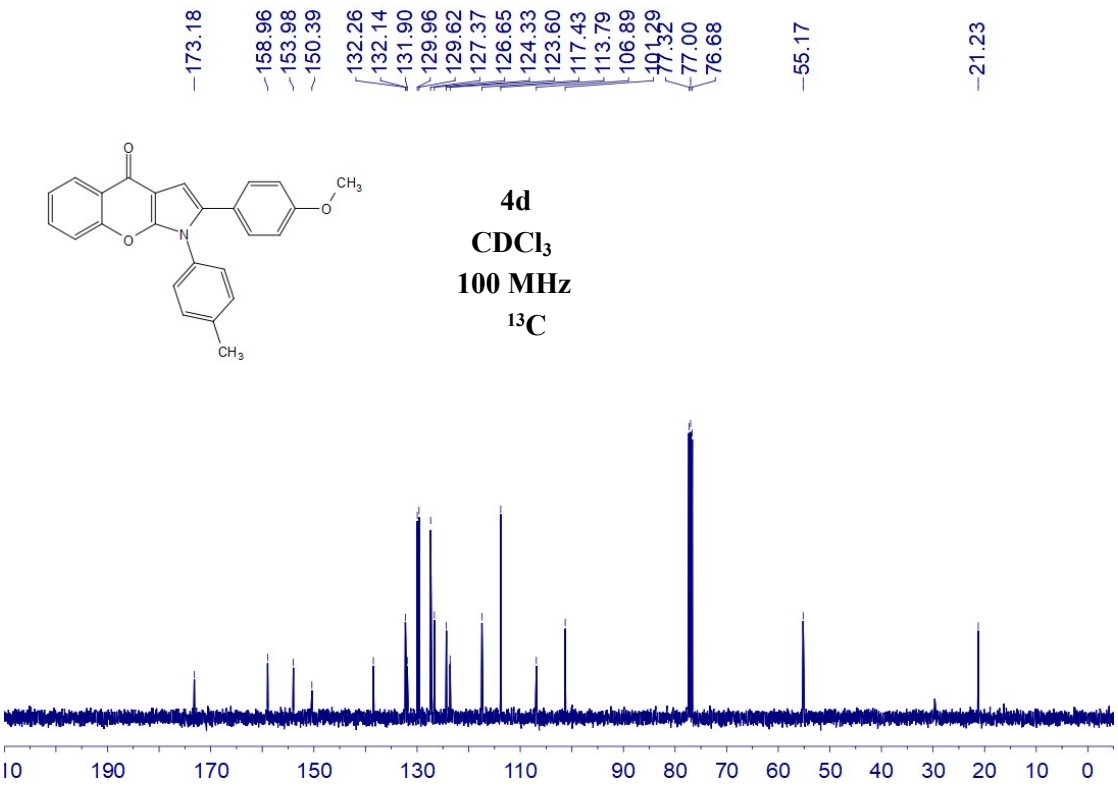
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of compound 4c



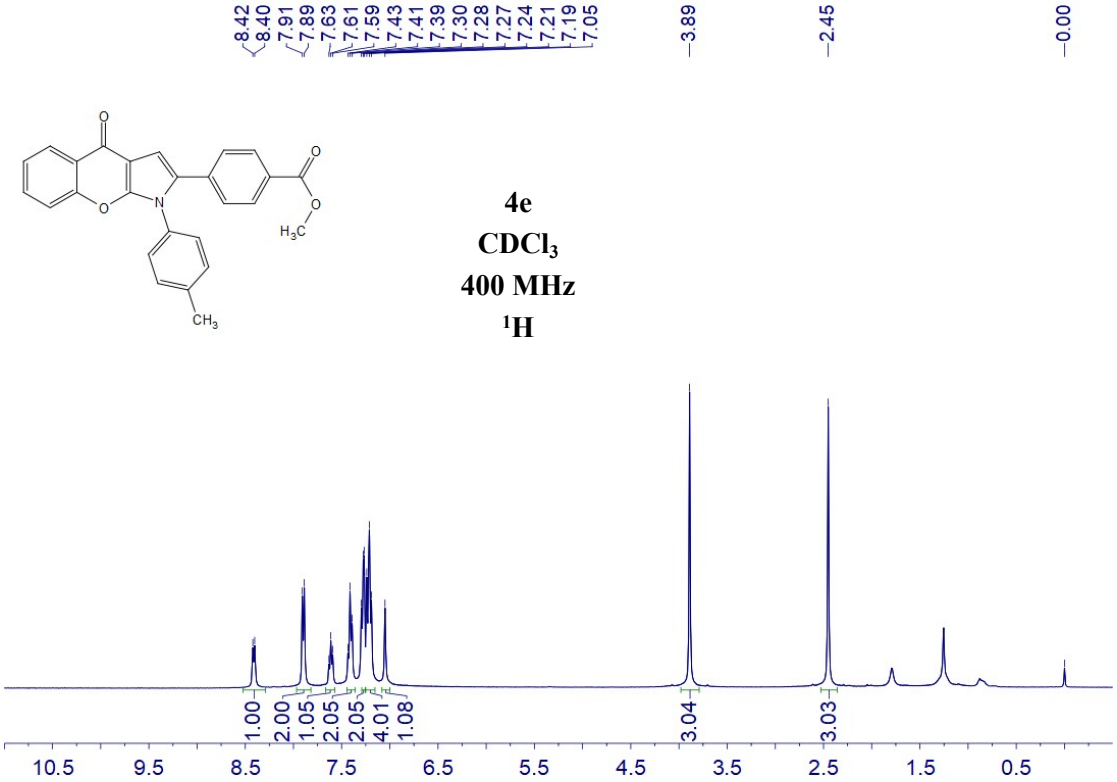
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4d



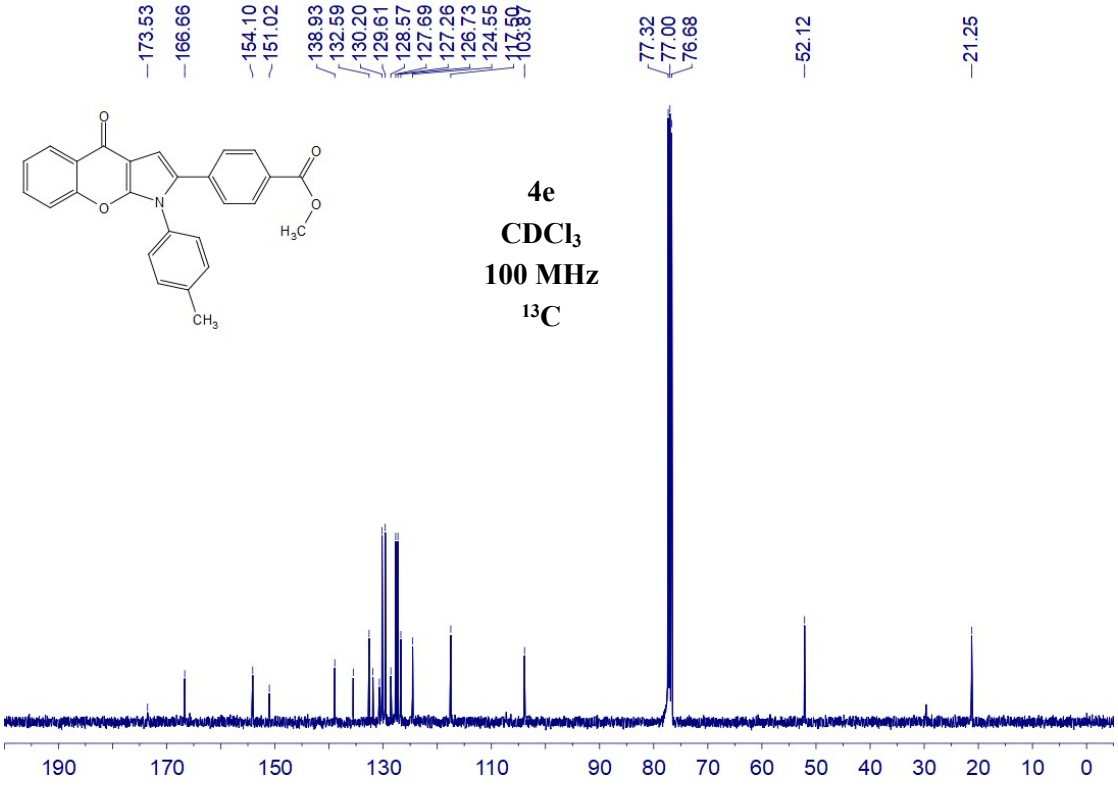
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of compound 4d



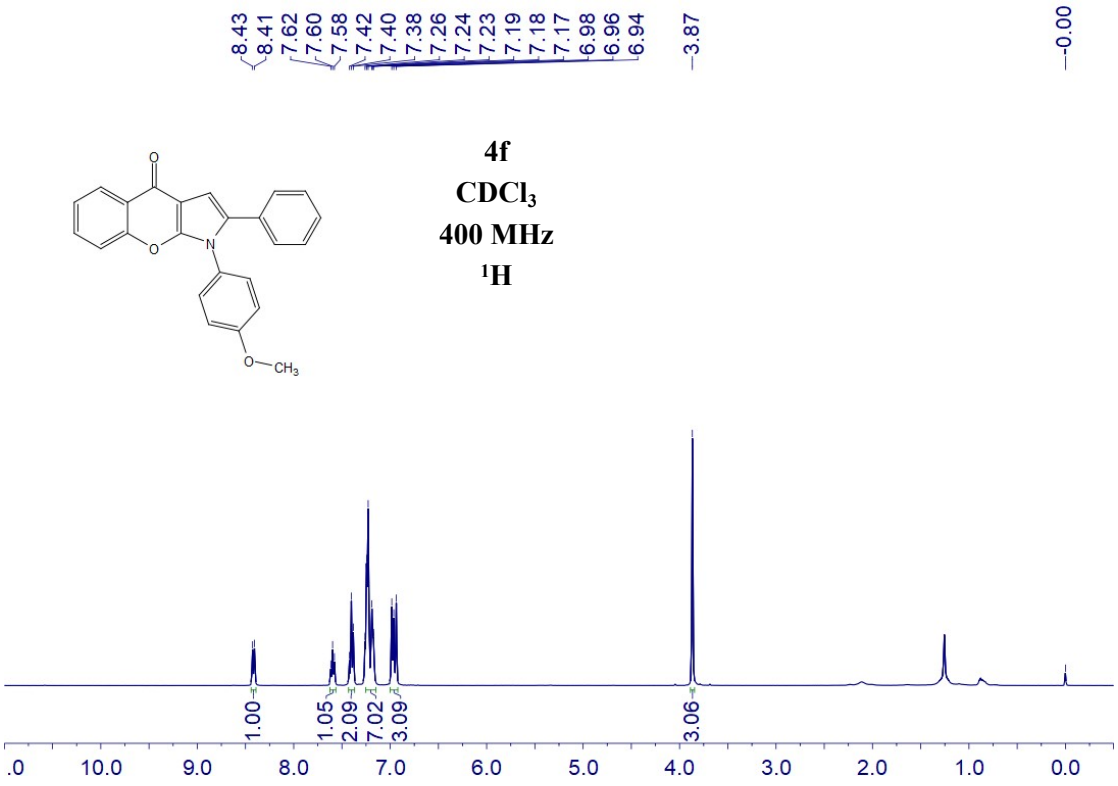
^{1}H NMR (400 MHz, $CDCl_3$) of 4e



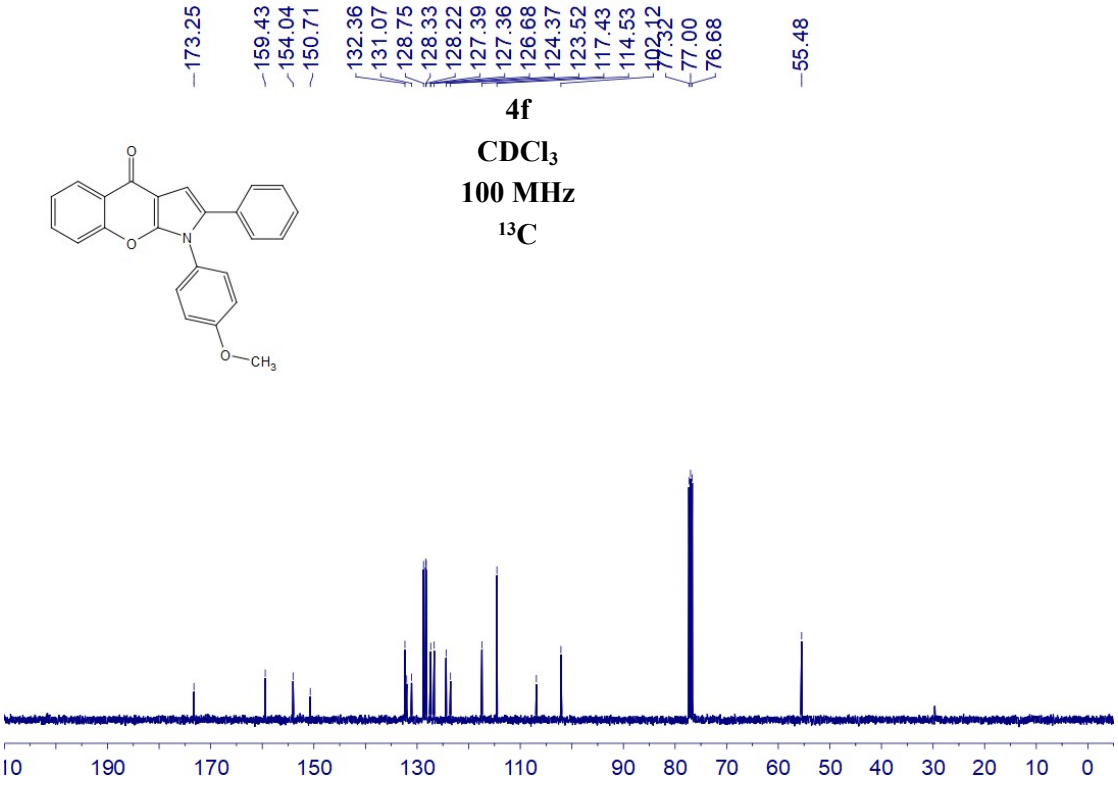
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4e



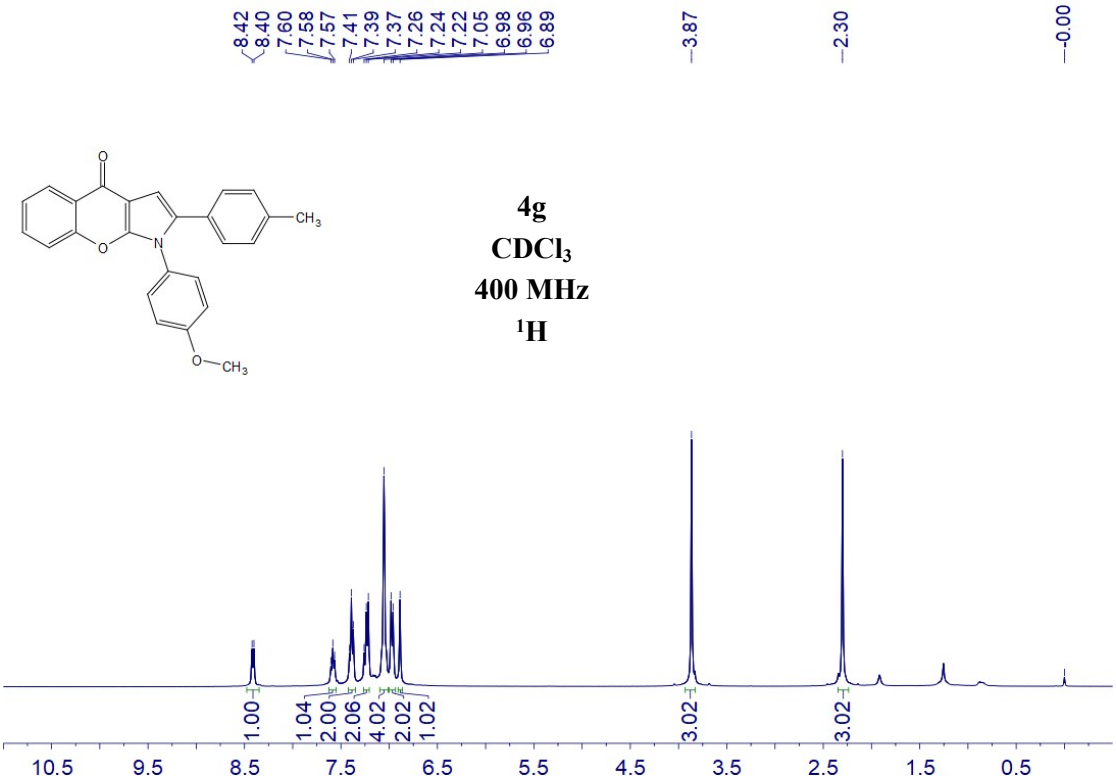
^{1}H NMR (400 MHz, $CDCl_3$) of 4f



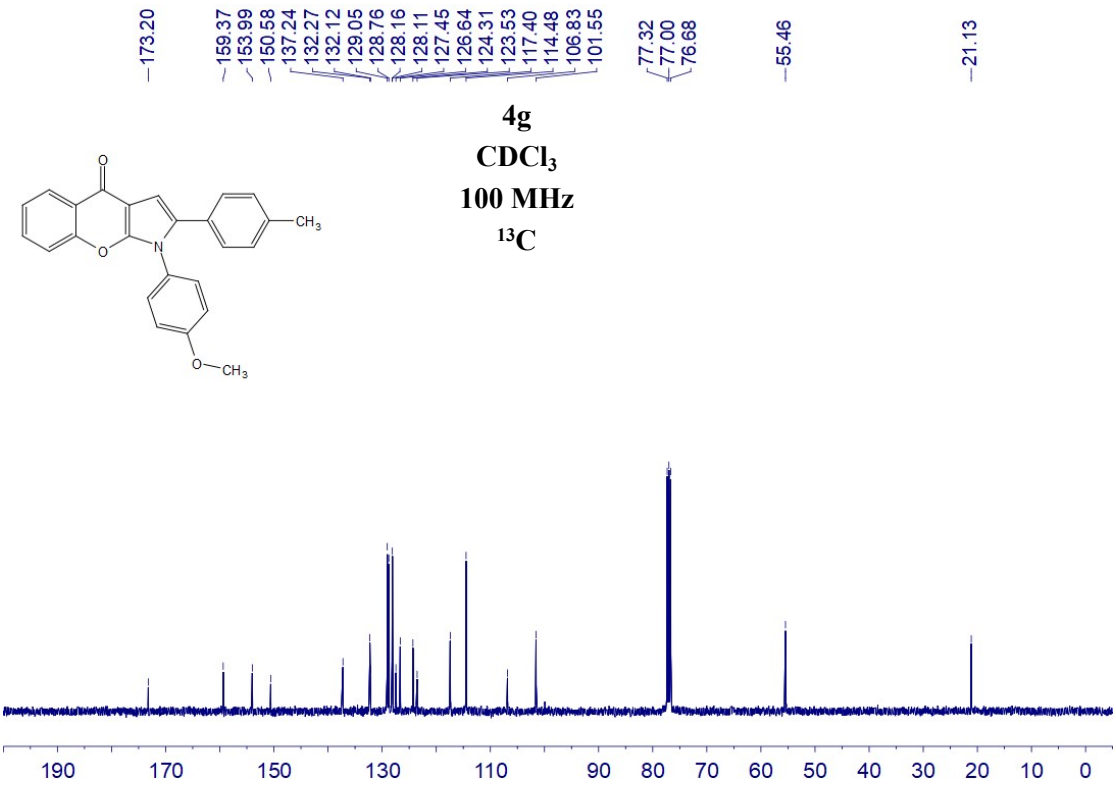
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4f



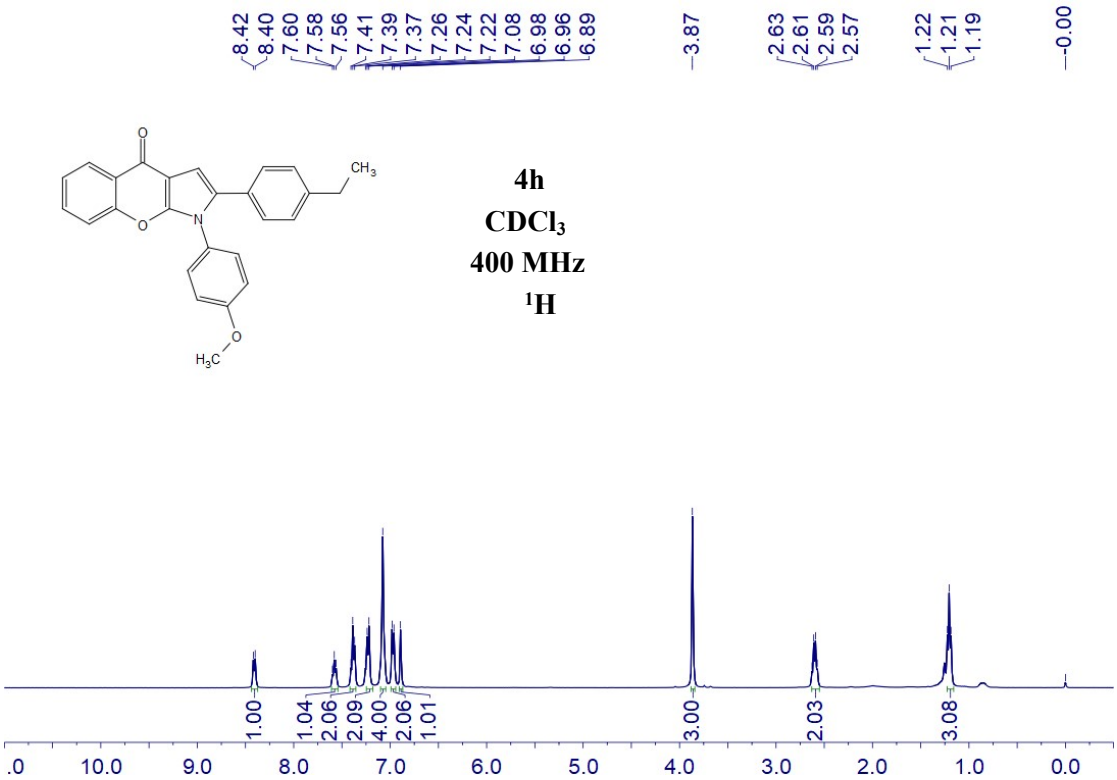
^{1}H NMR (400 MHz, $CDCl_3$) of 4g



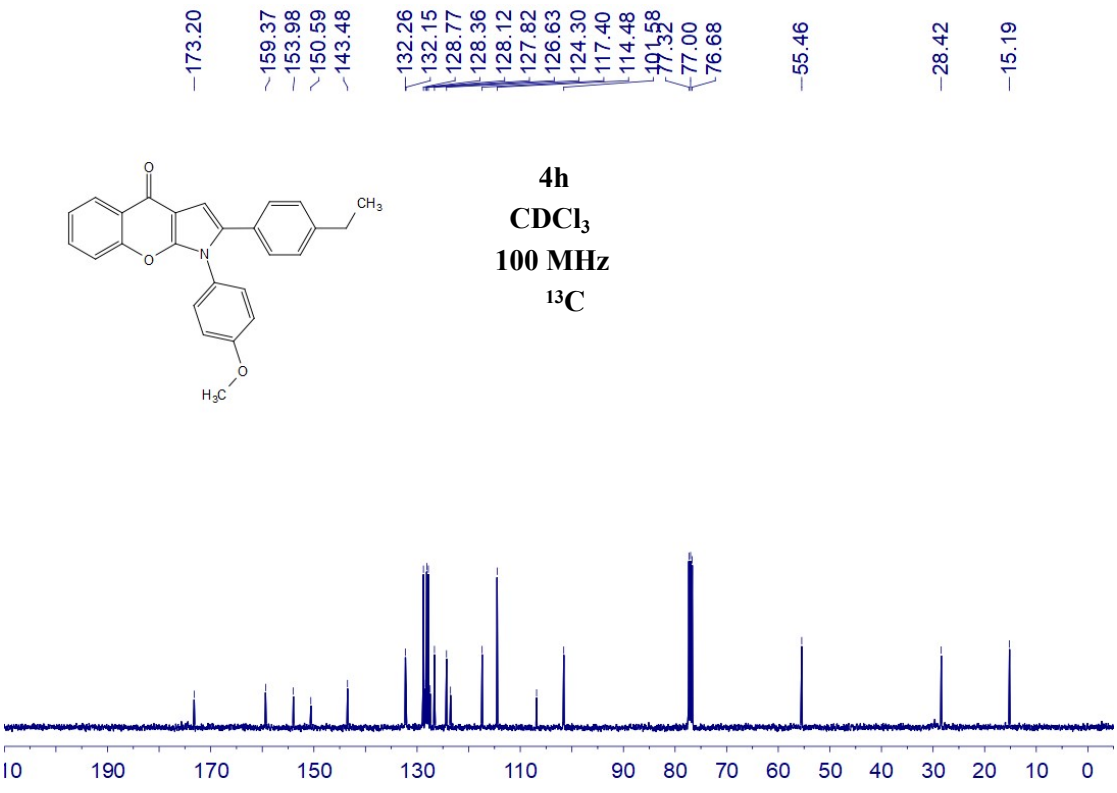
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4g



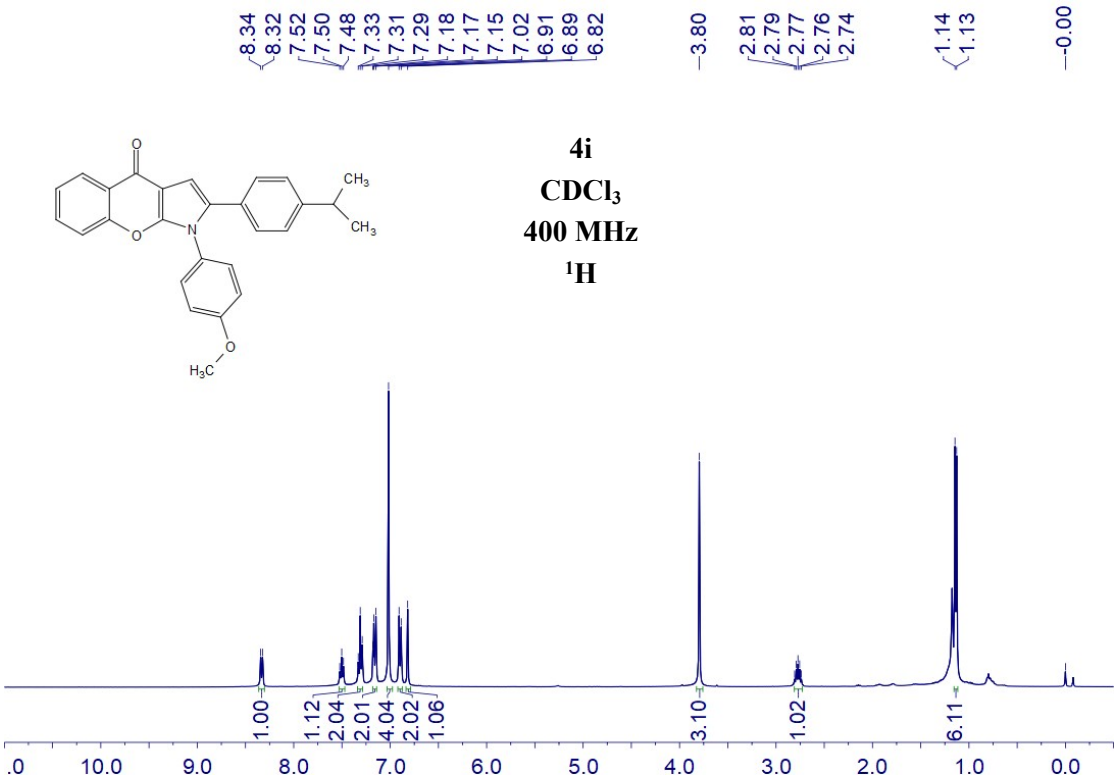
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4h



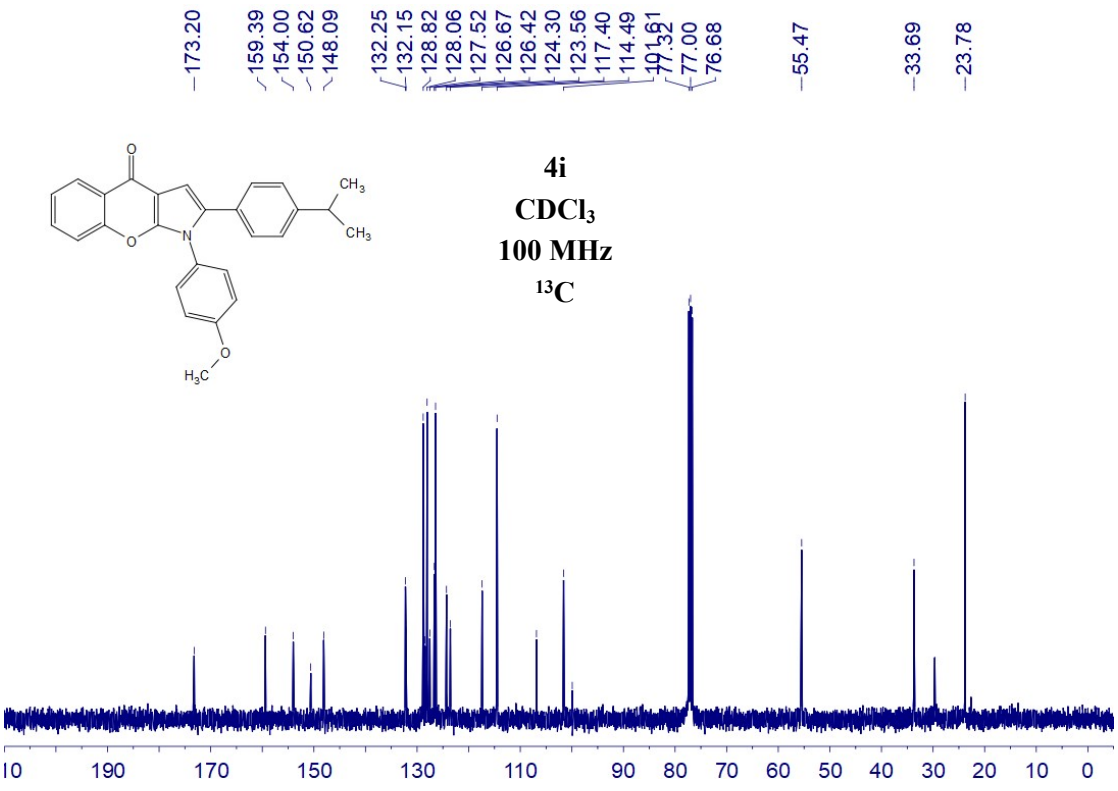
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4h



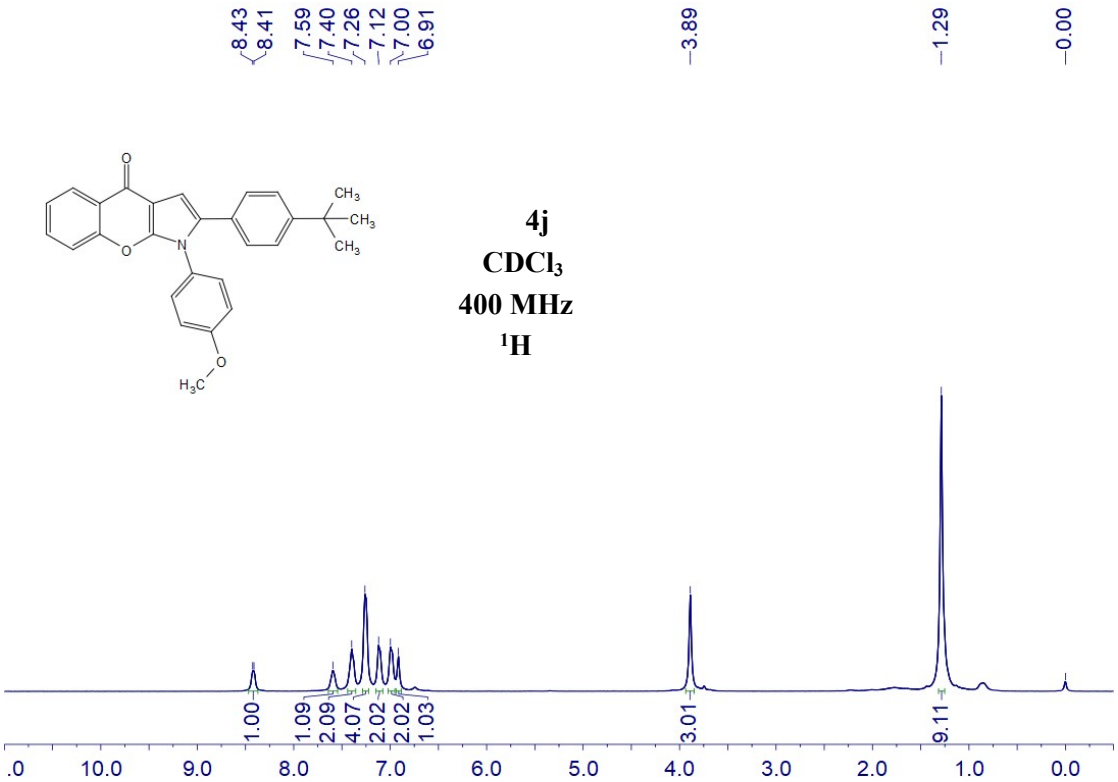
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4i



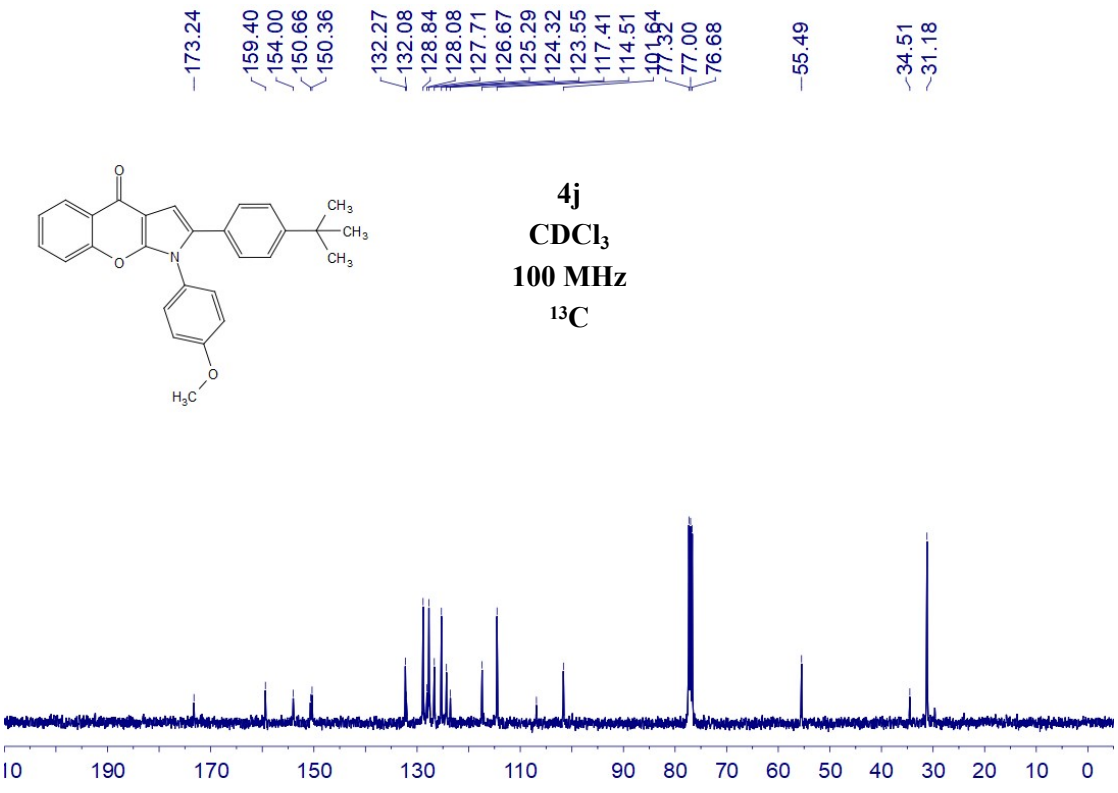
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4i



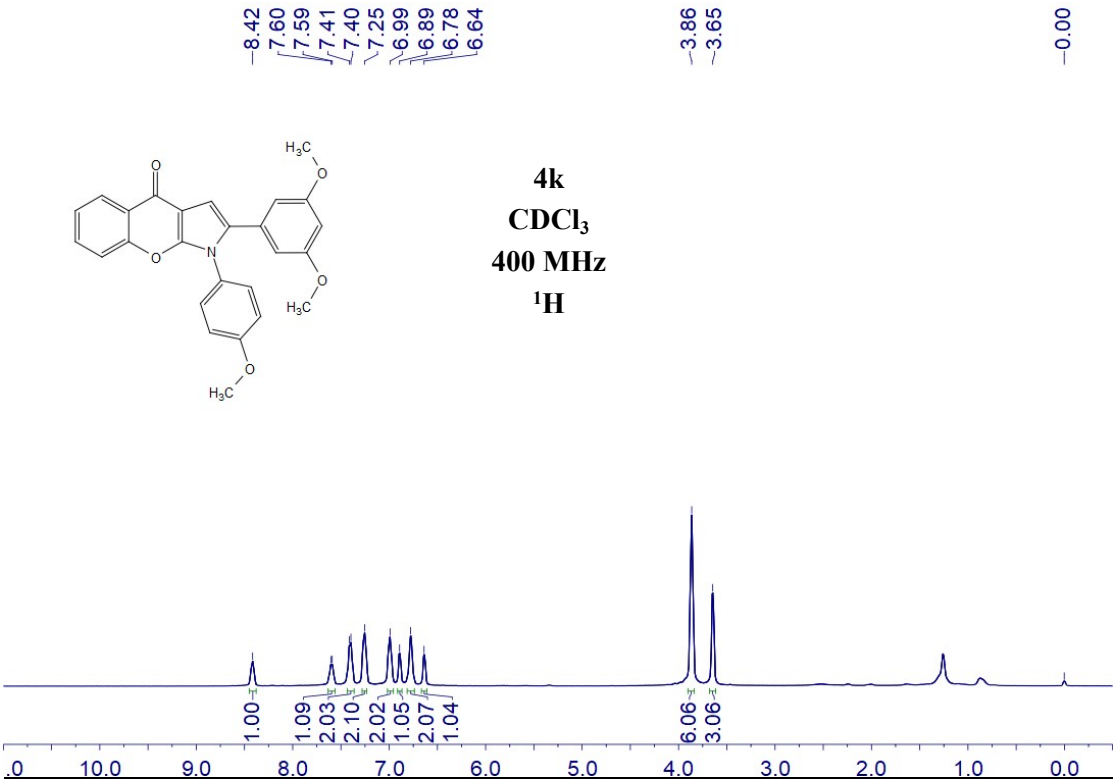
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4j



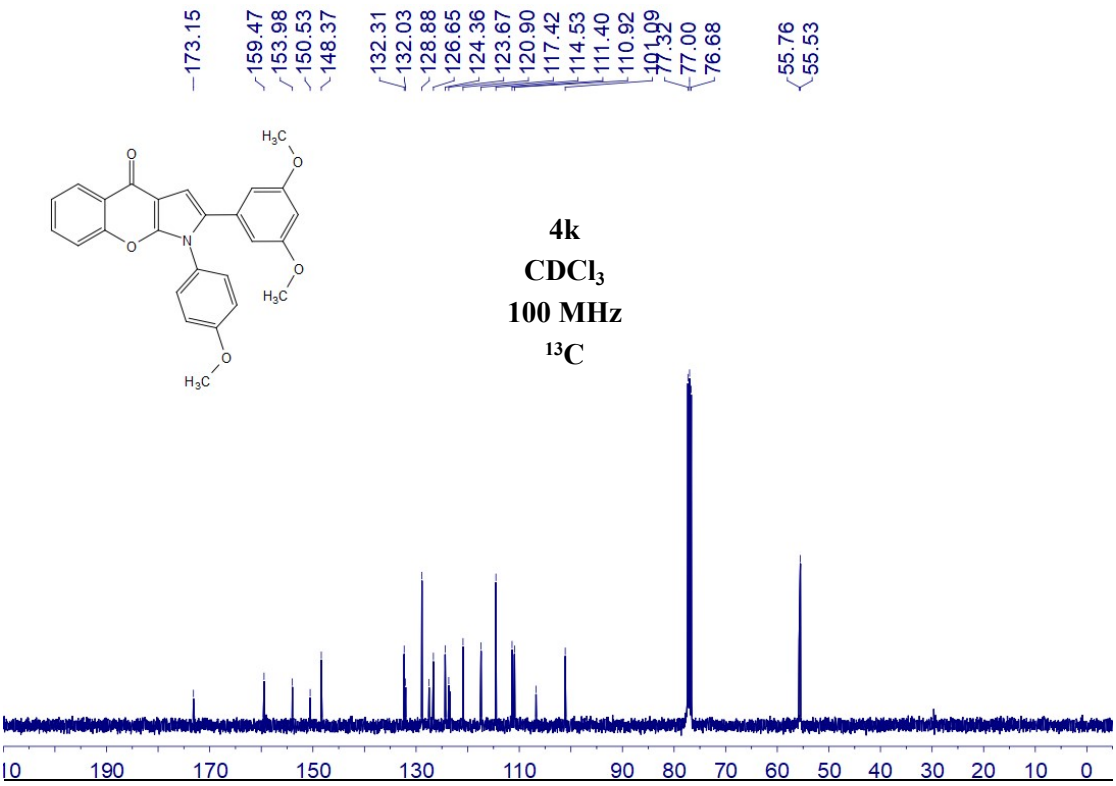
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4j



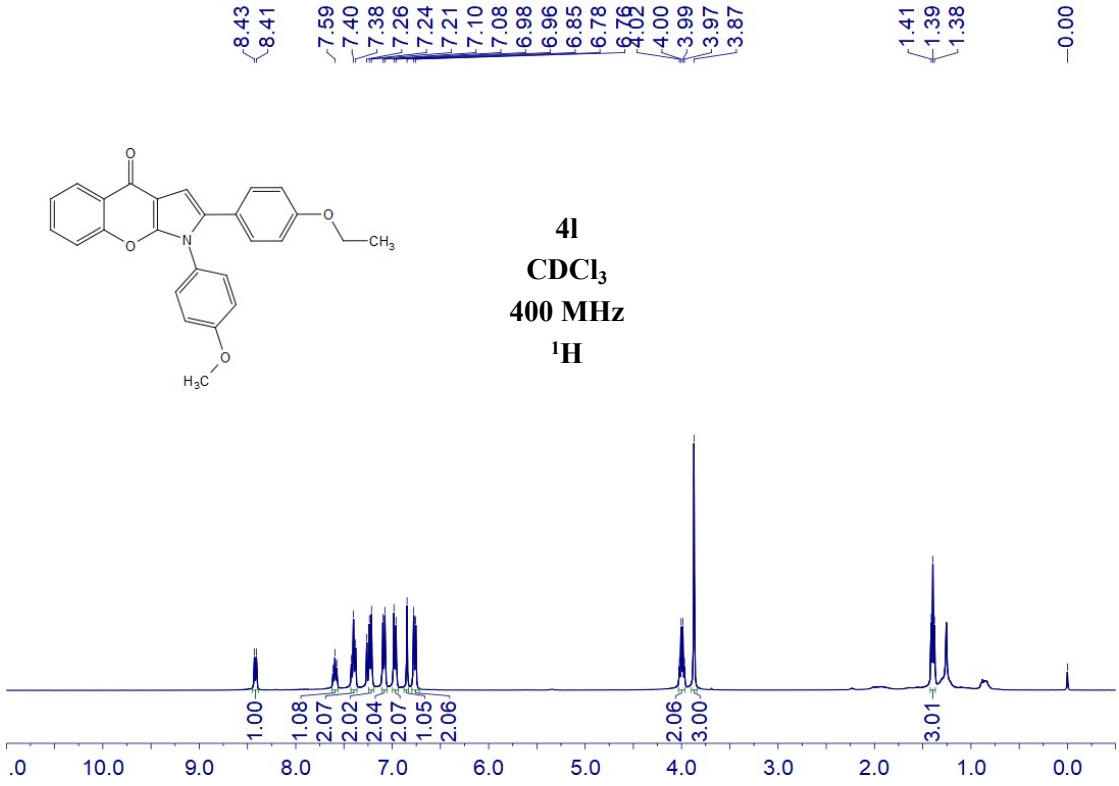
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4k



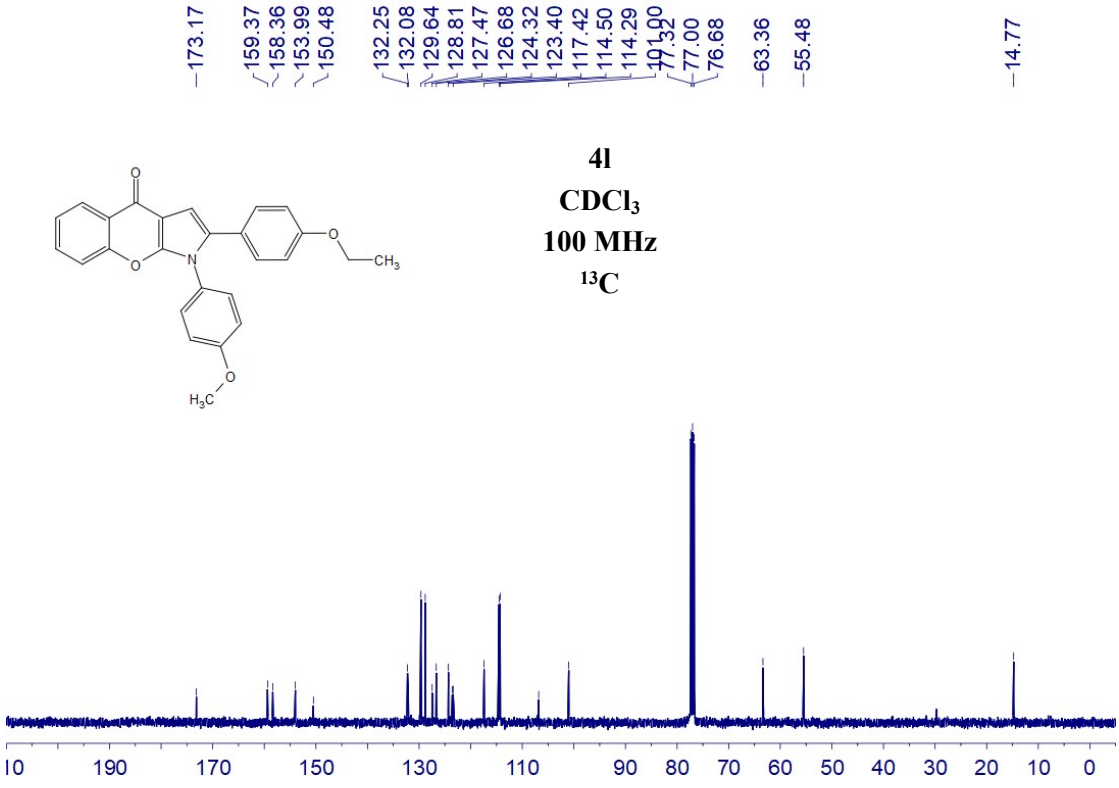
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4k



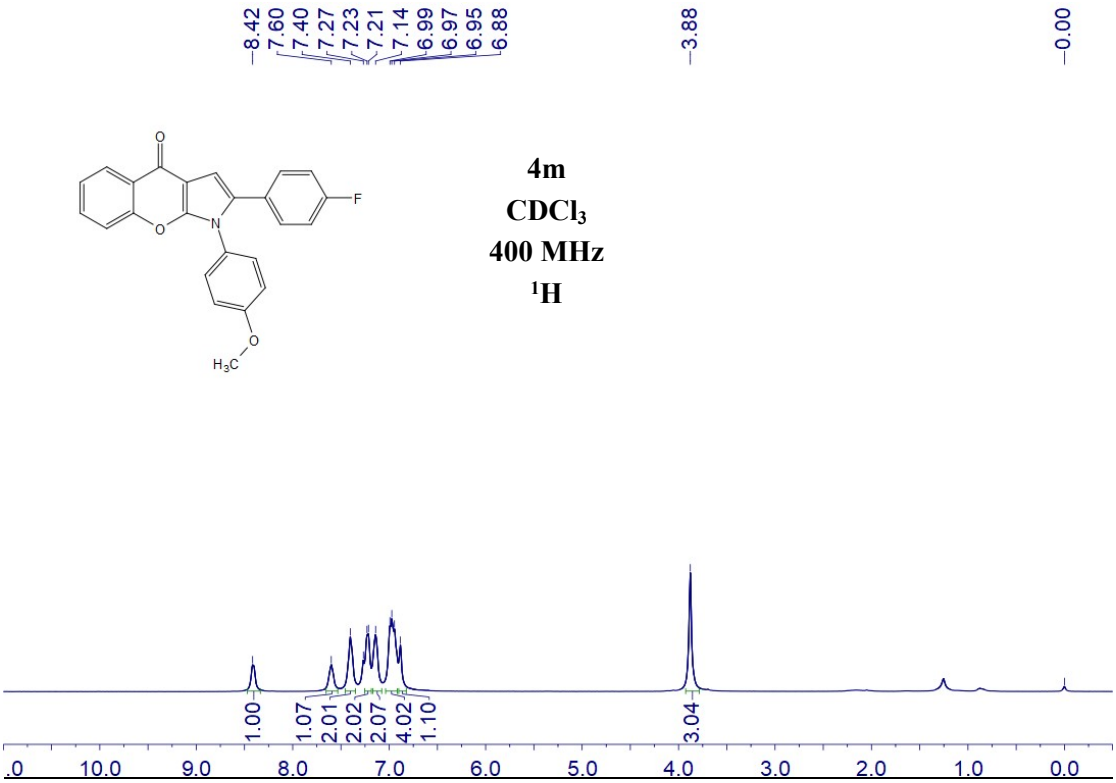
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4l



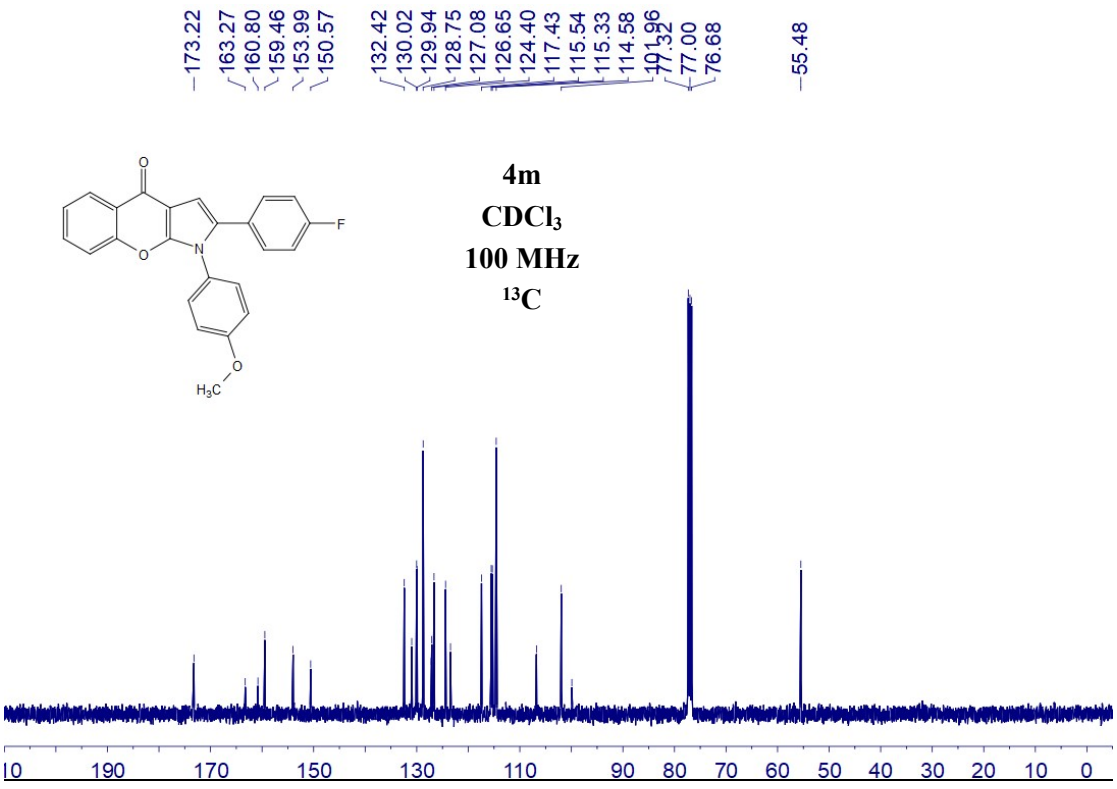
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4l



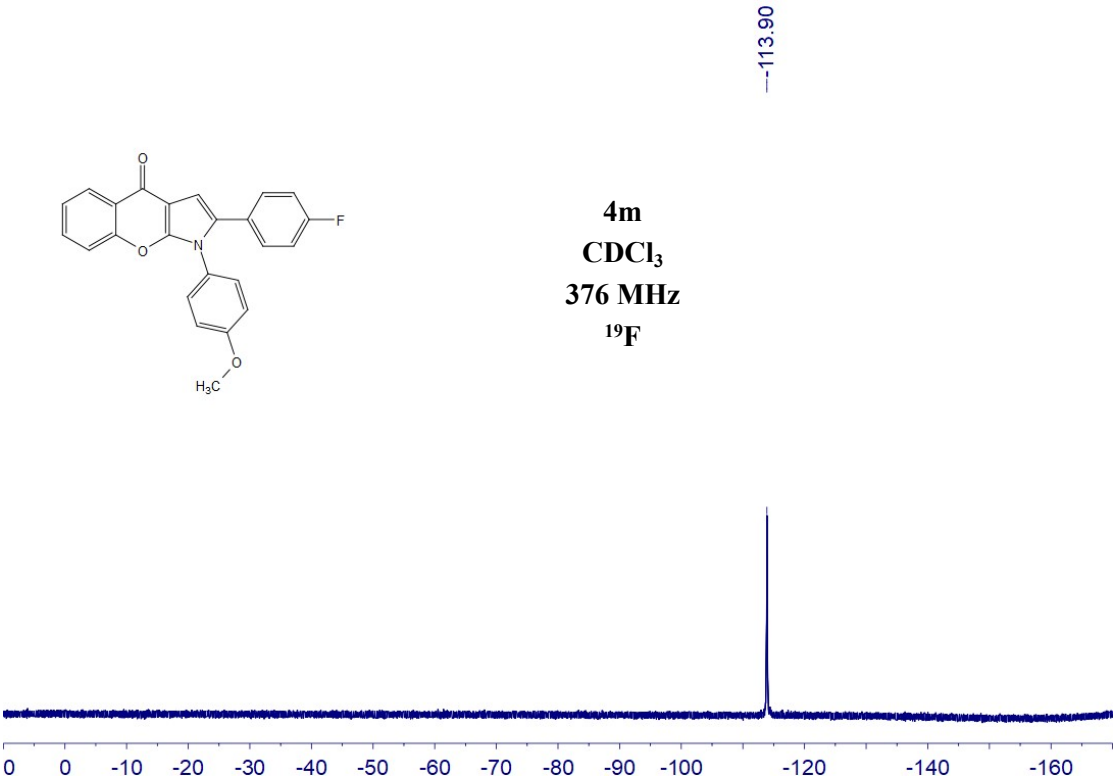
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4m



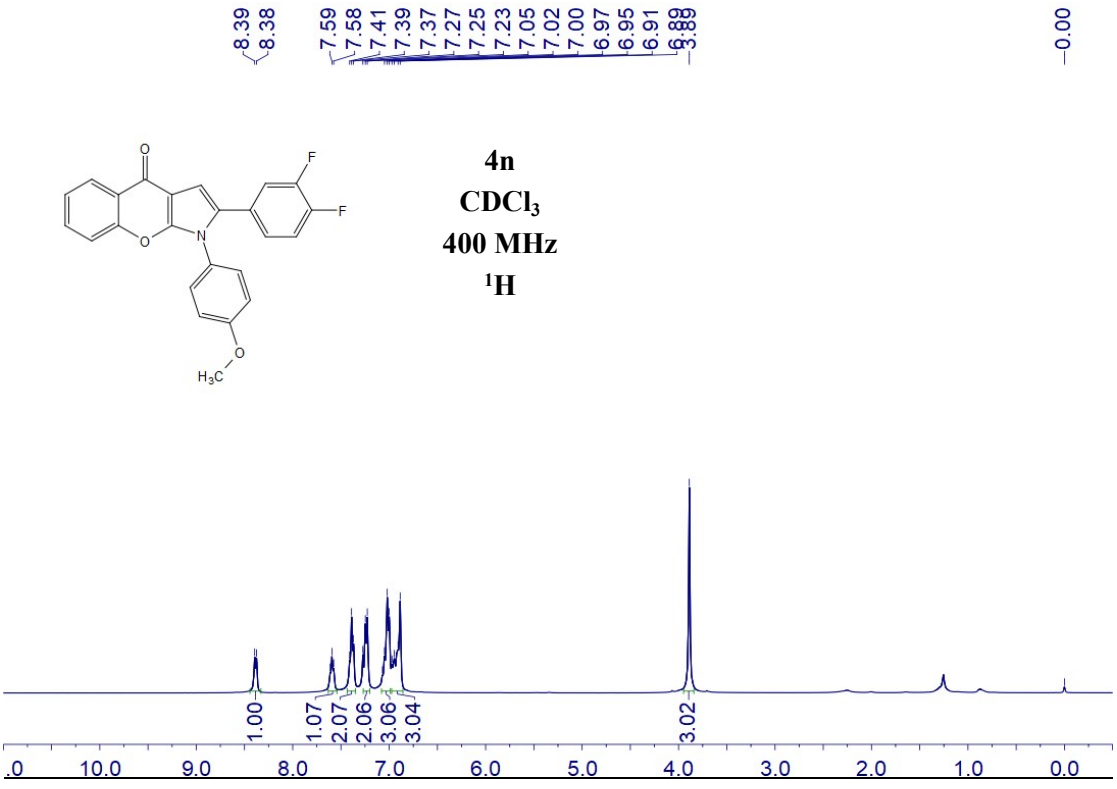
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4m



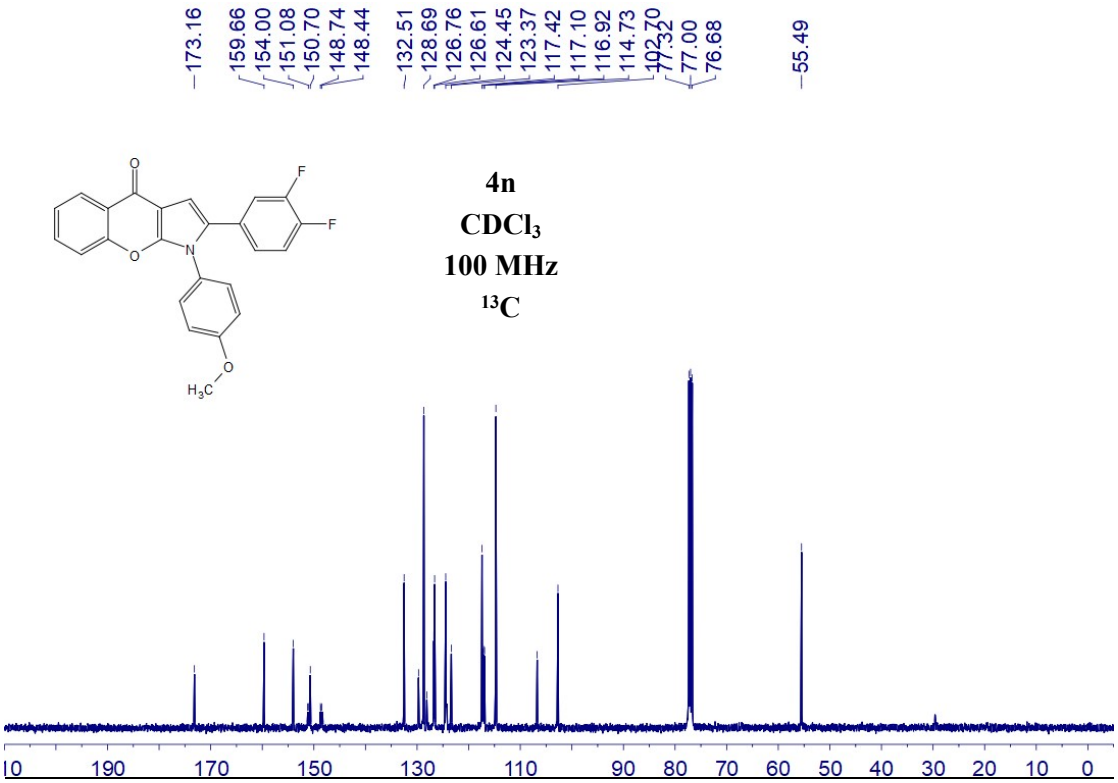
^{19}F NMR (376 MHz, $CDCl_3$)of compound 4m



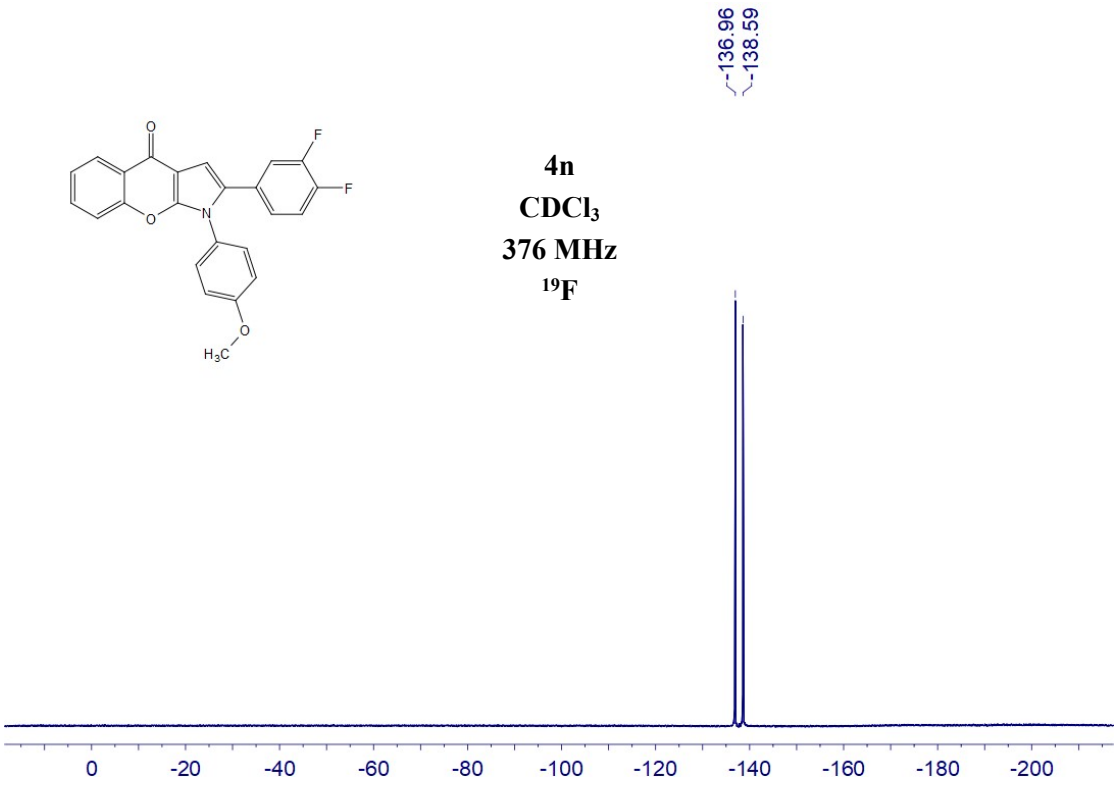
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4n



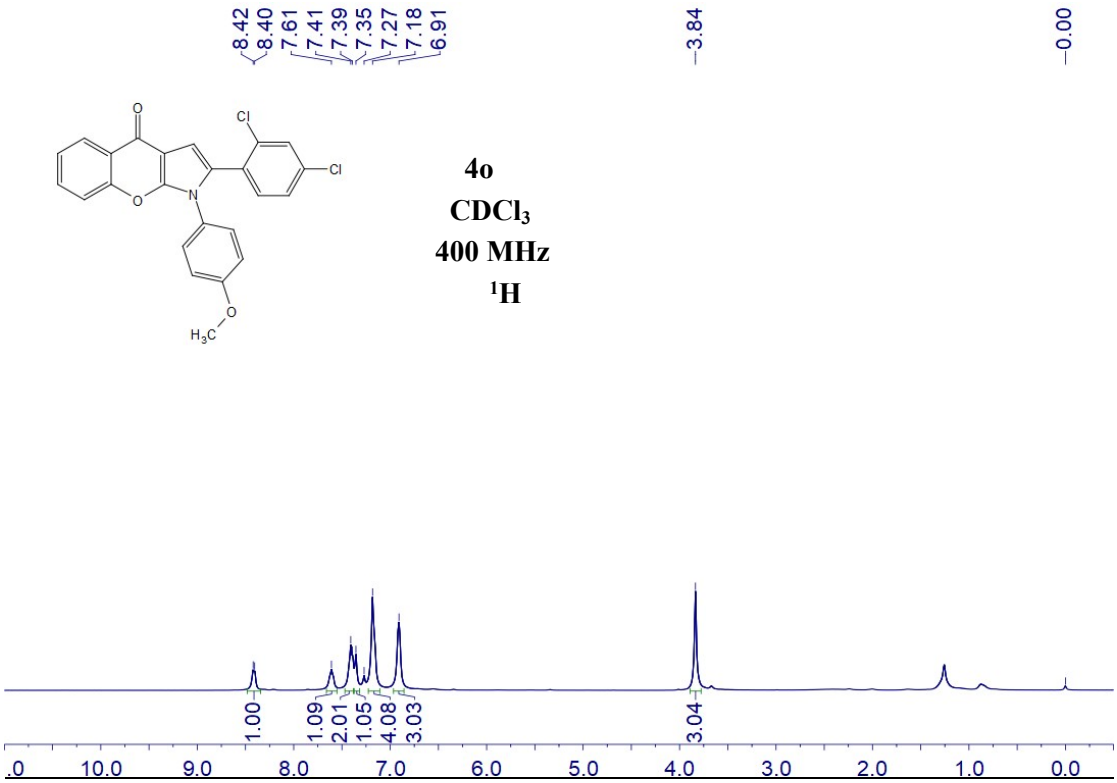
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4n



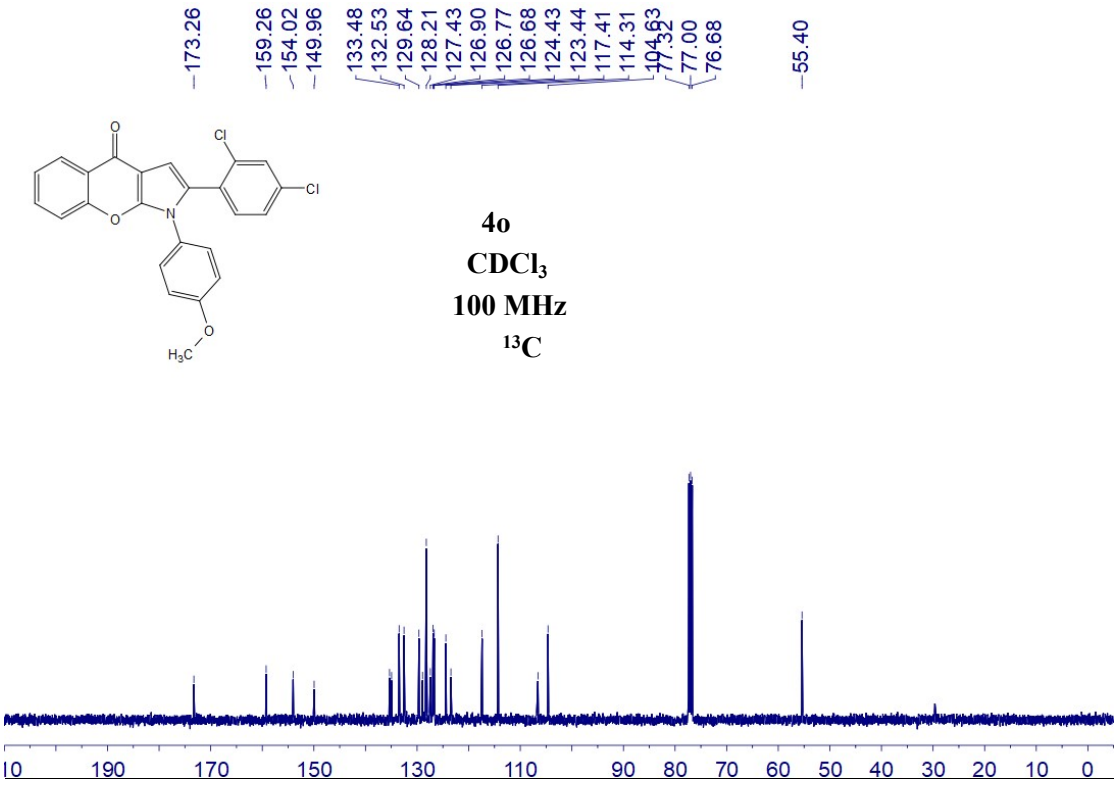
^{19}F NMR (376 MHz, $CDCl_3$)of compound 4n



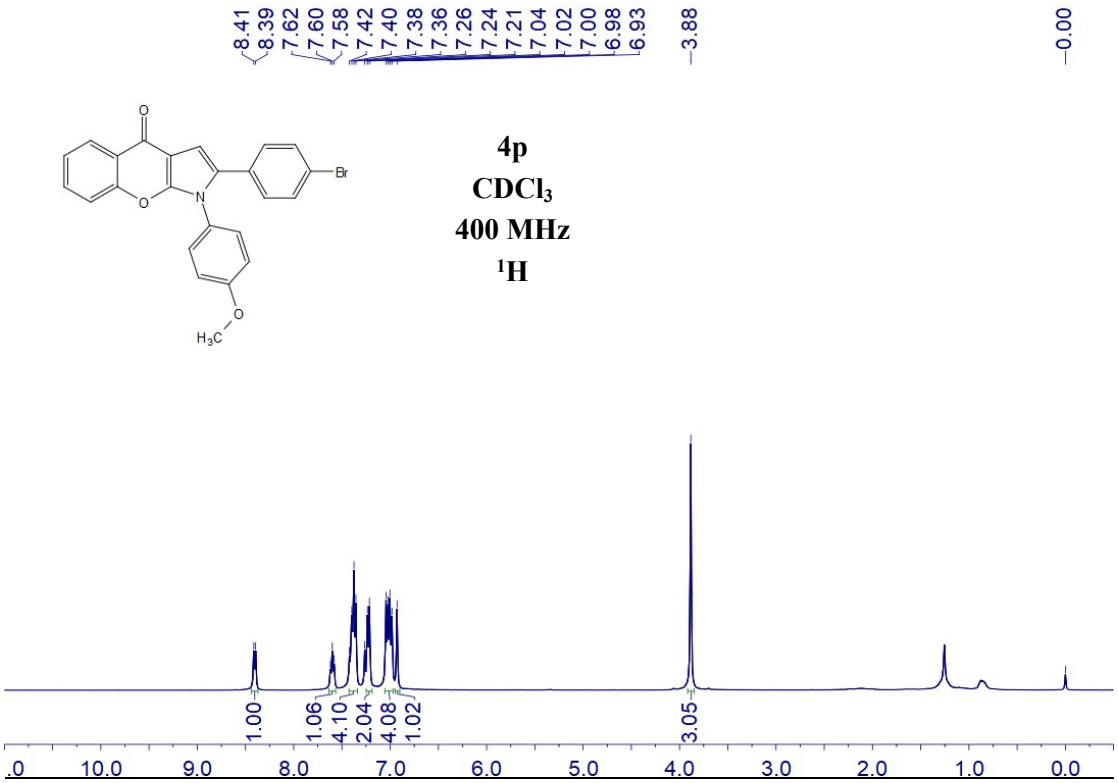
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4o



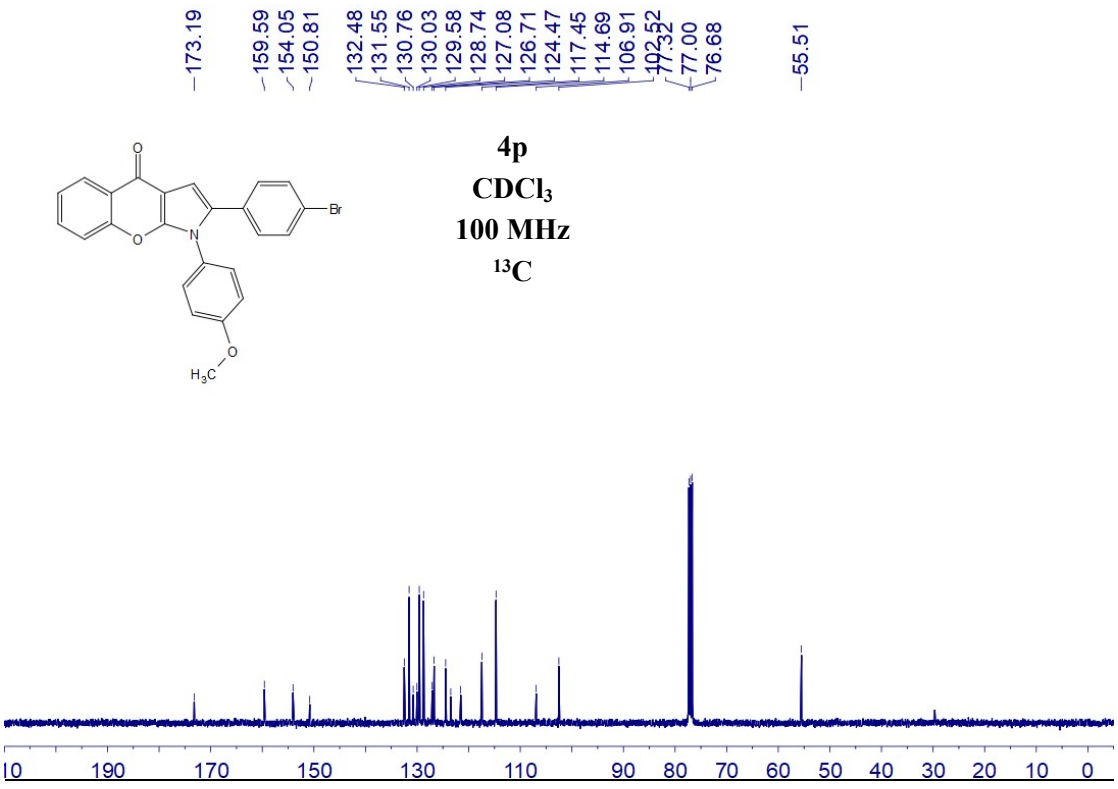
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4o



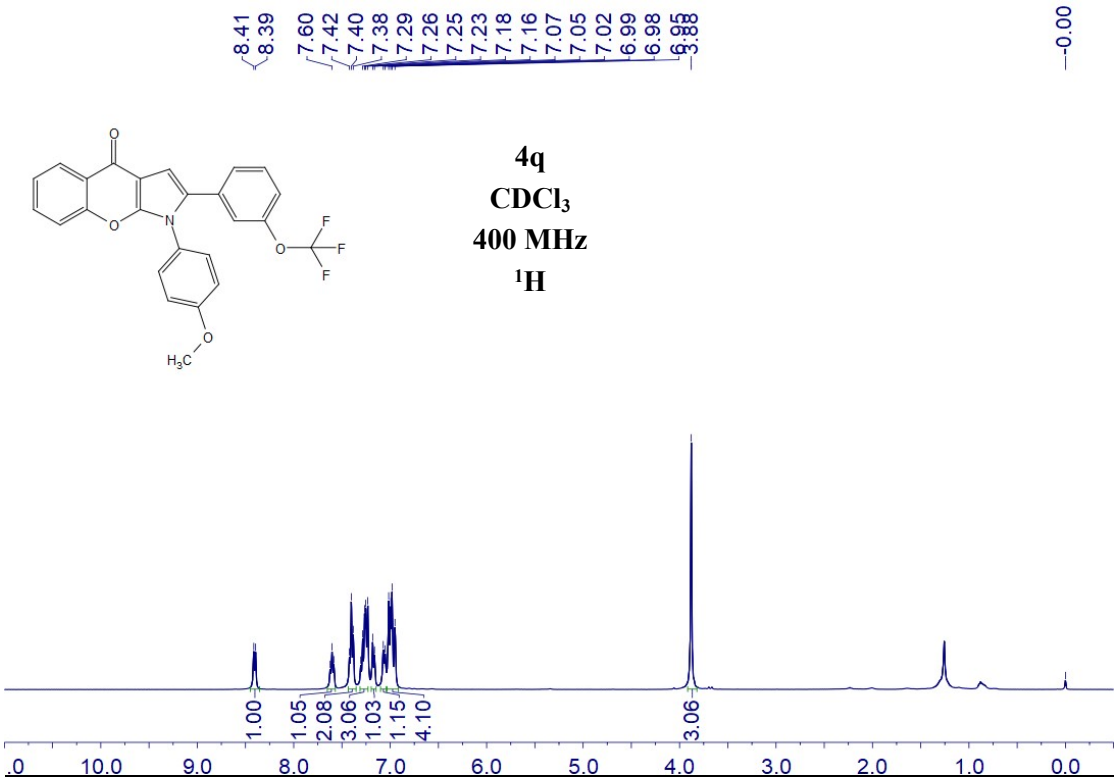
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4p



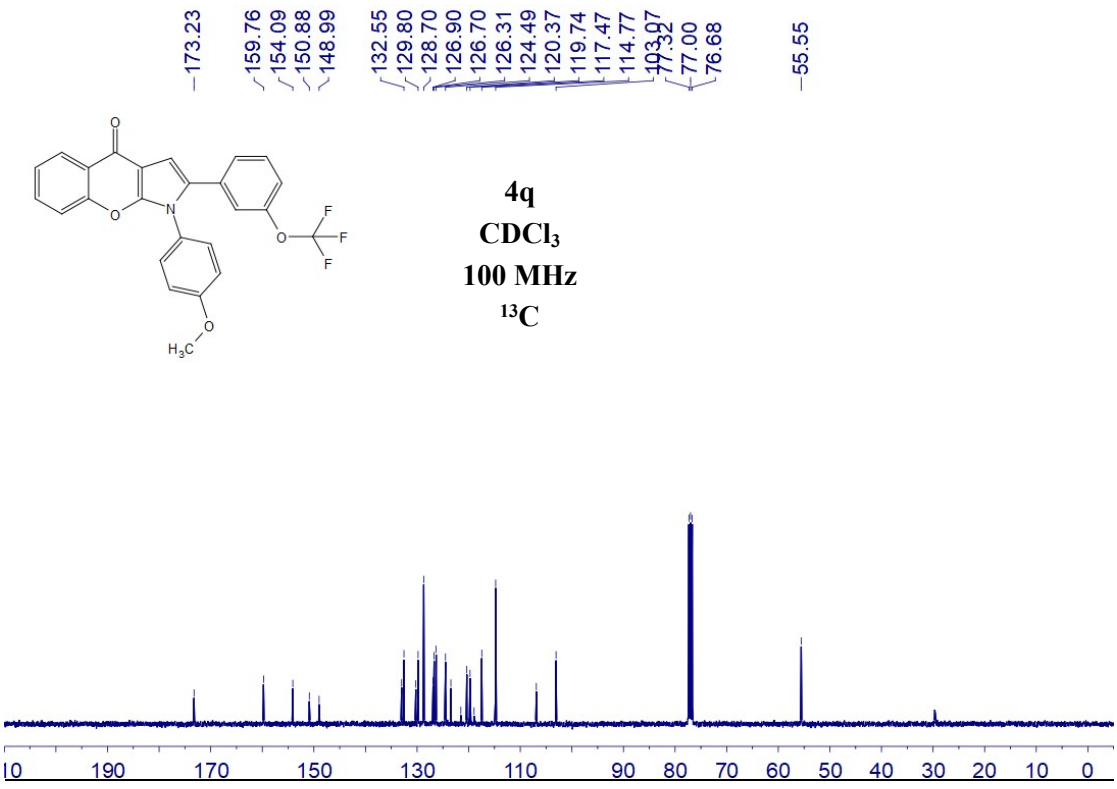
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4p



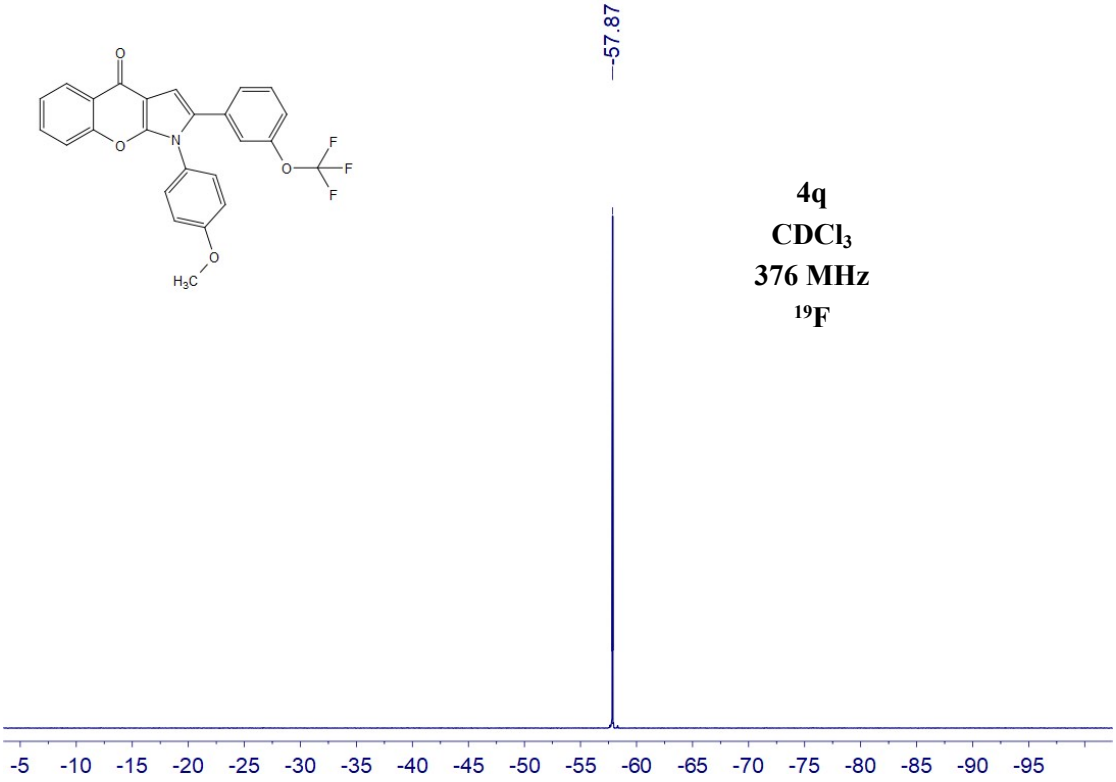
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4q



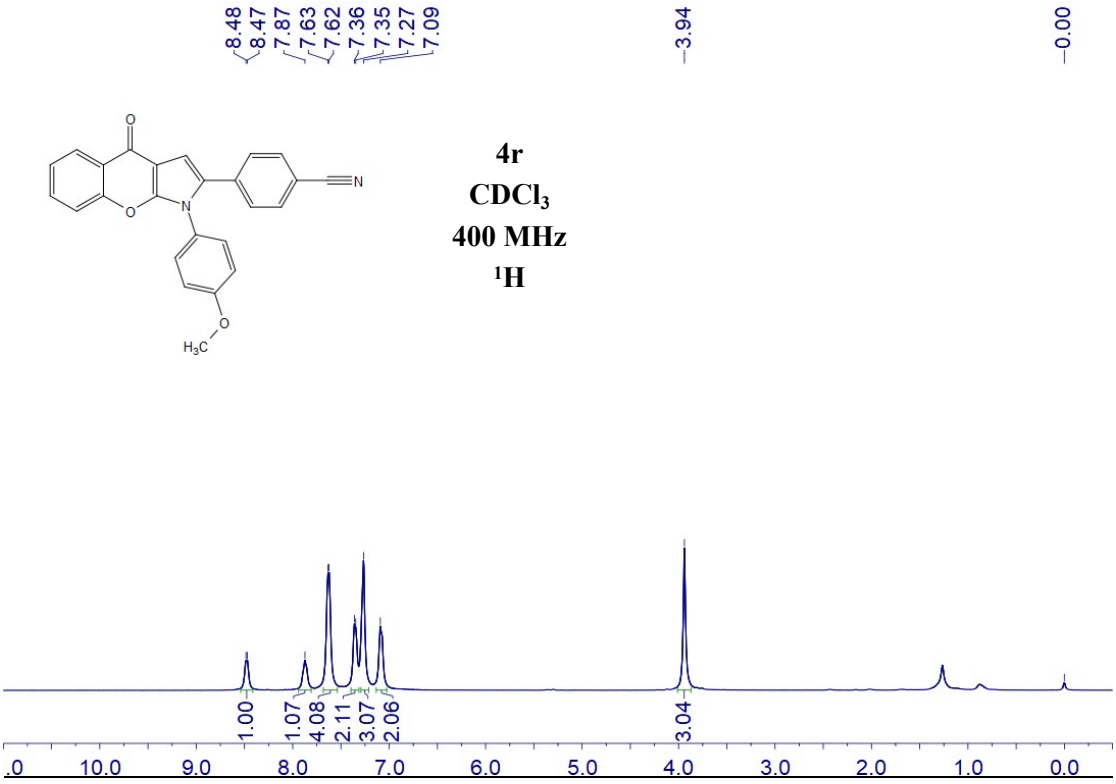
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4q



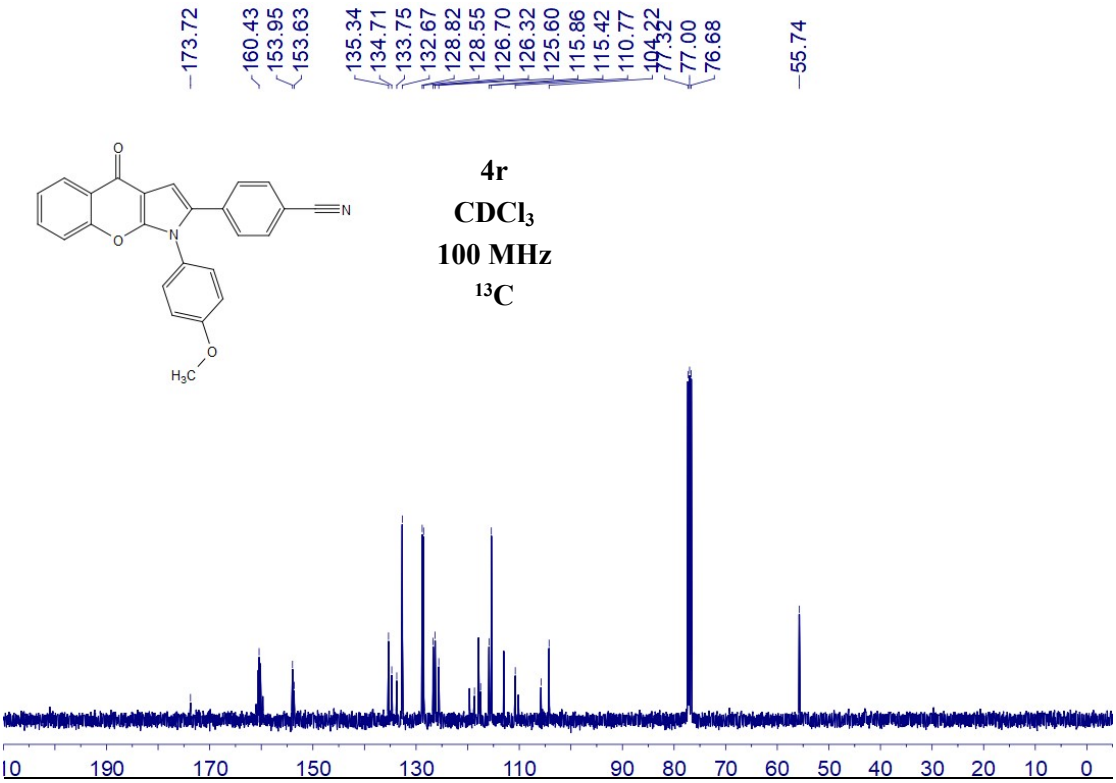
^{19}F NMR (376 MHz, $CDCl_3$)of compound 4q



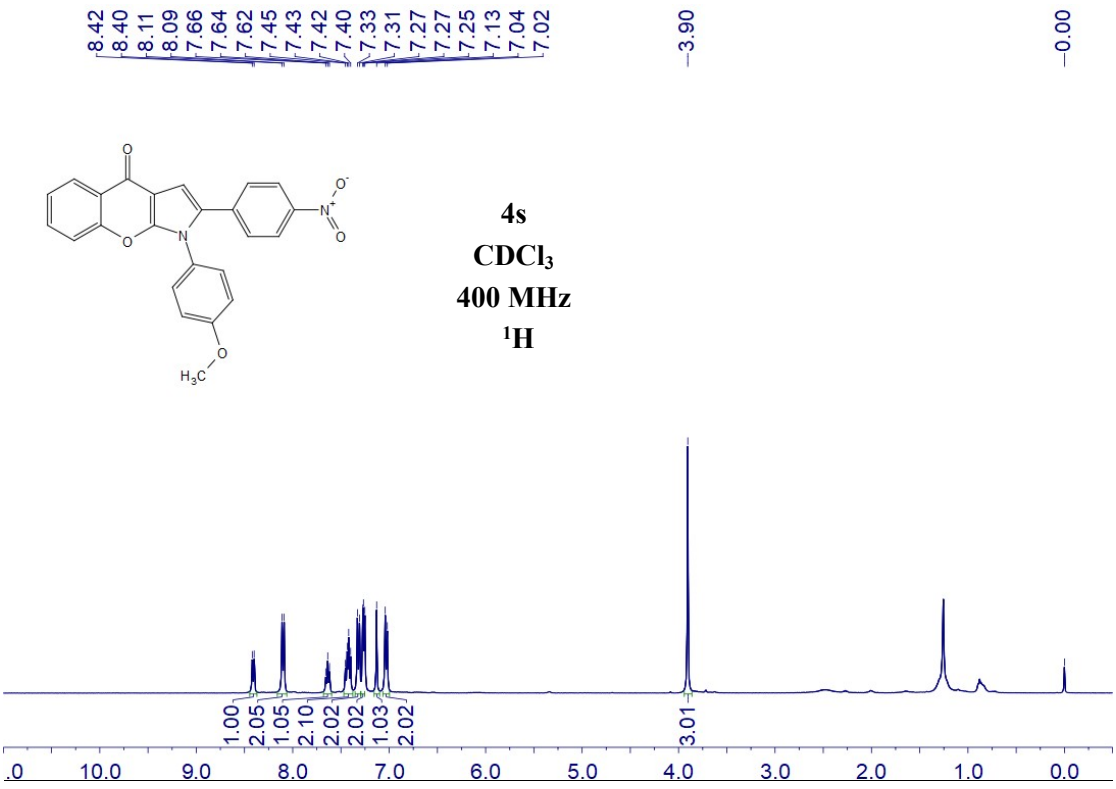
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4r



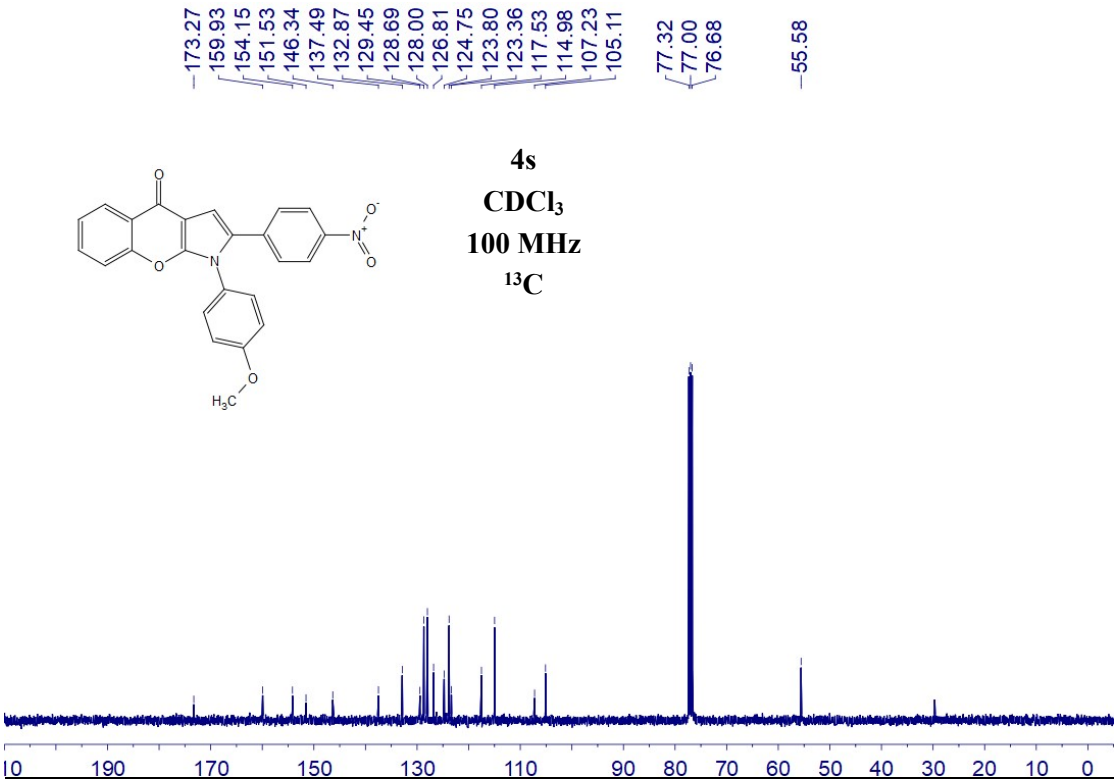
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4r



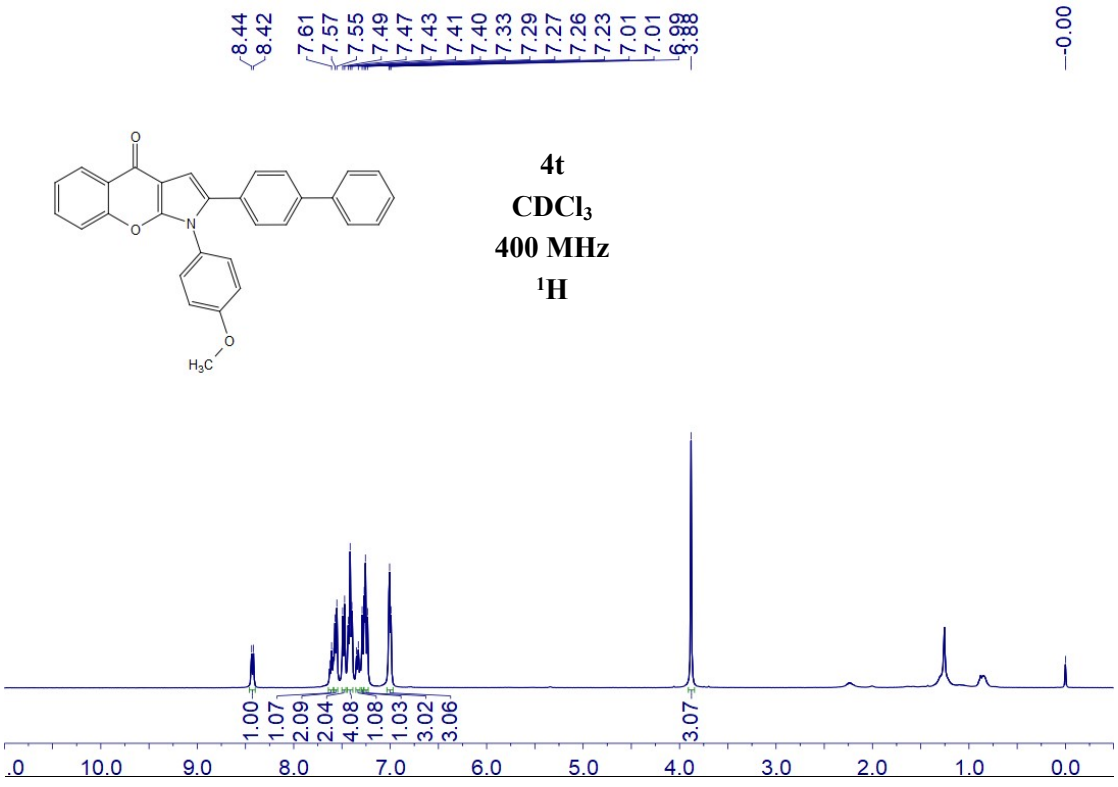
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4s



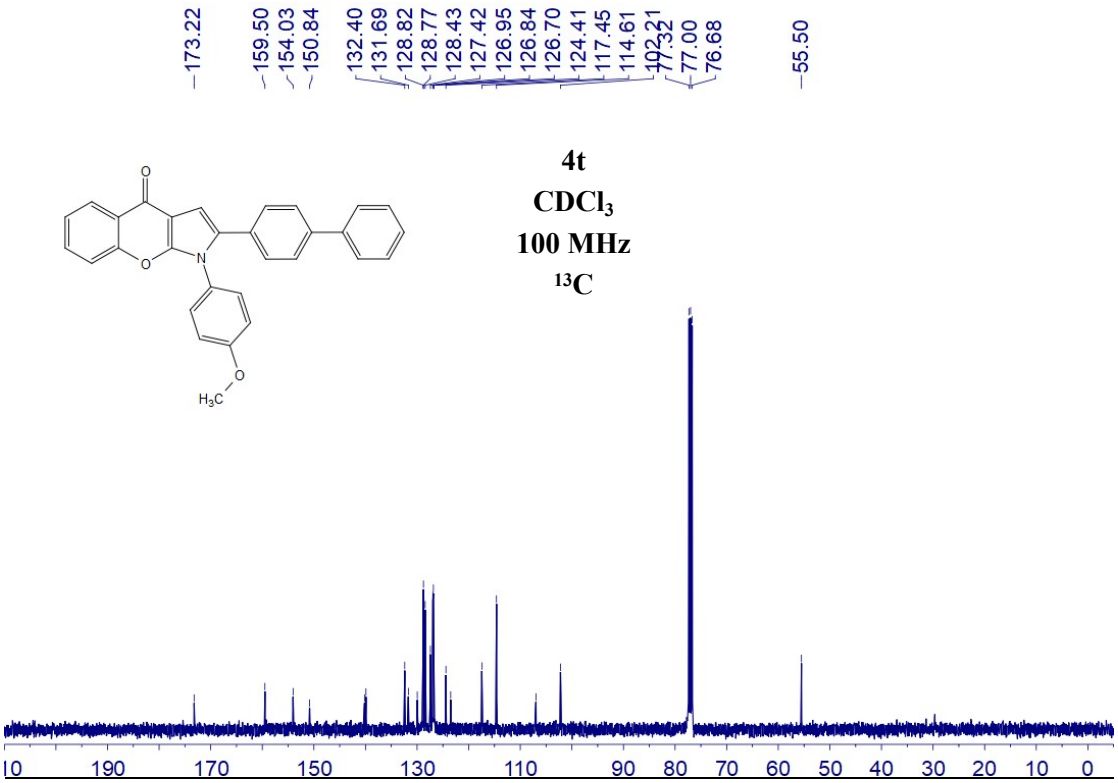
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4s



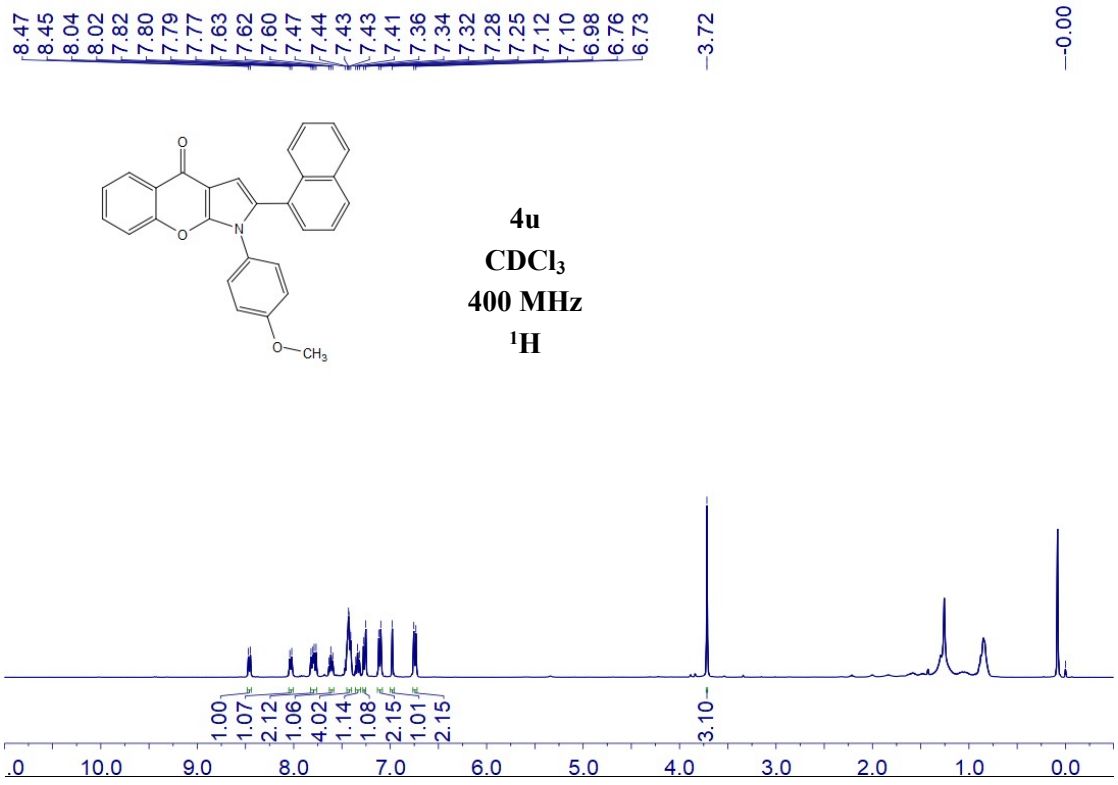
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4t



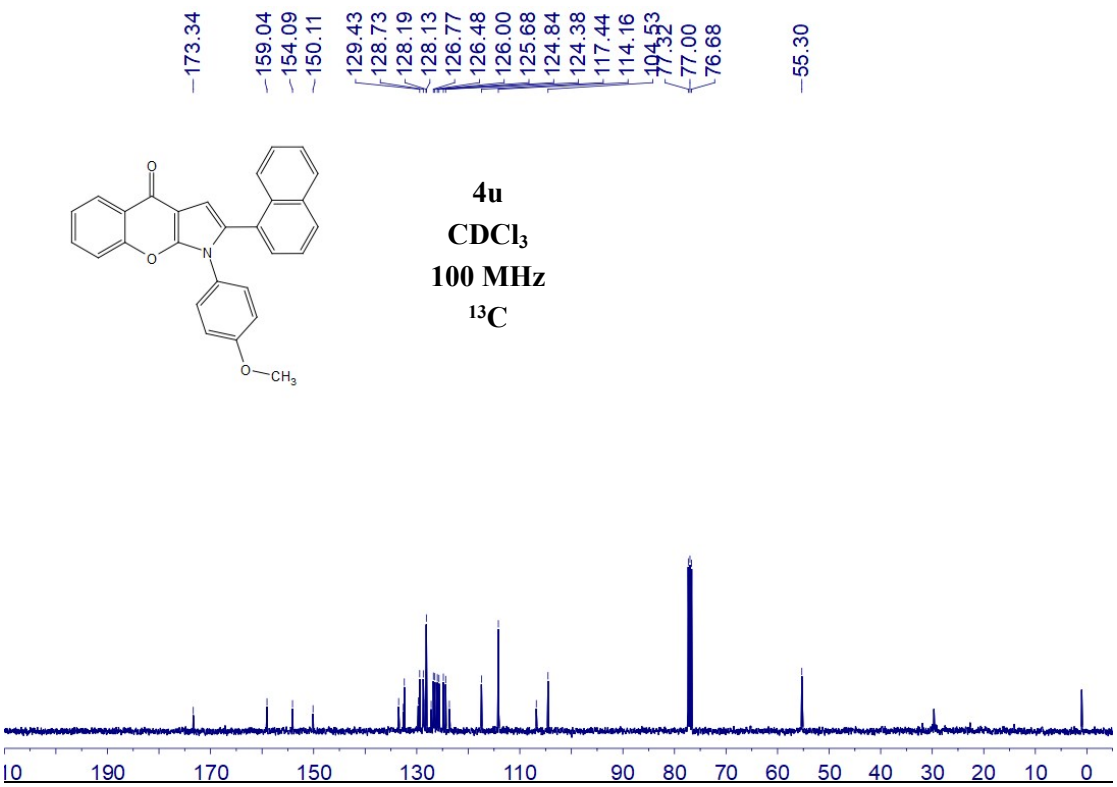
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4t



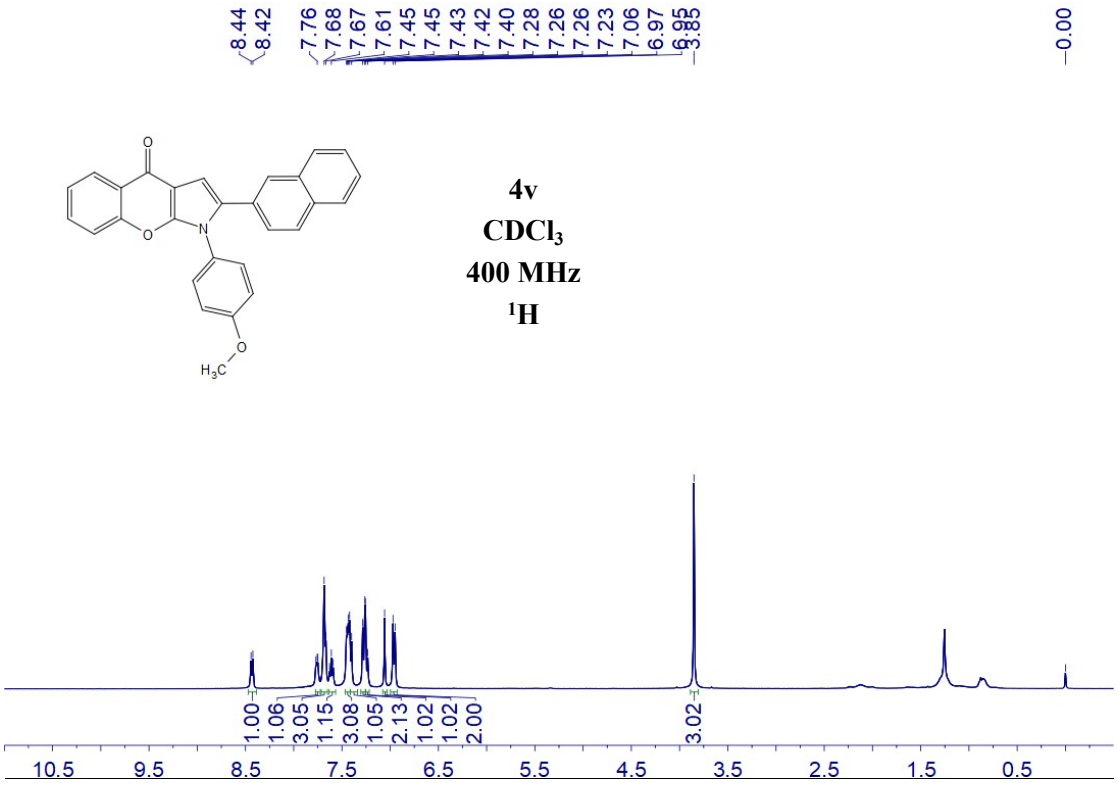
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4u



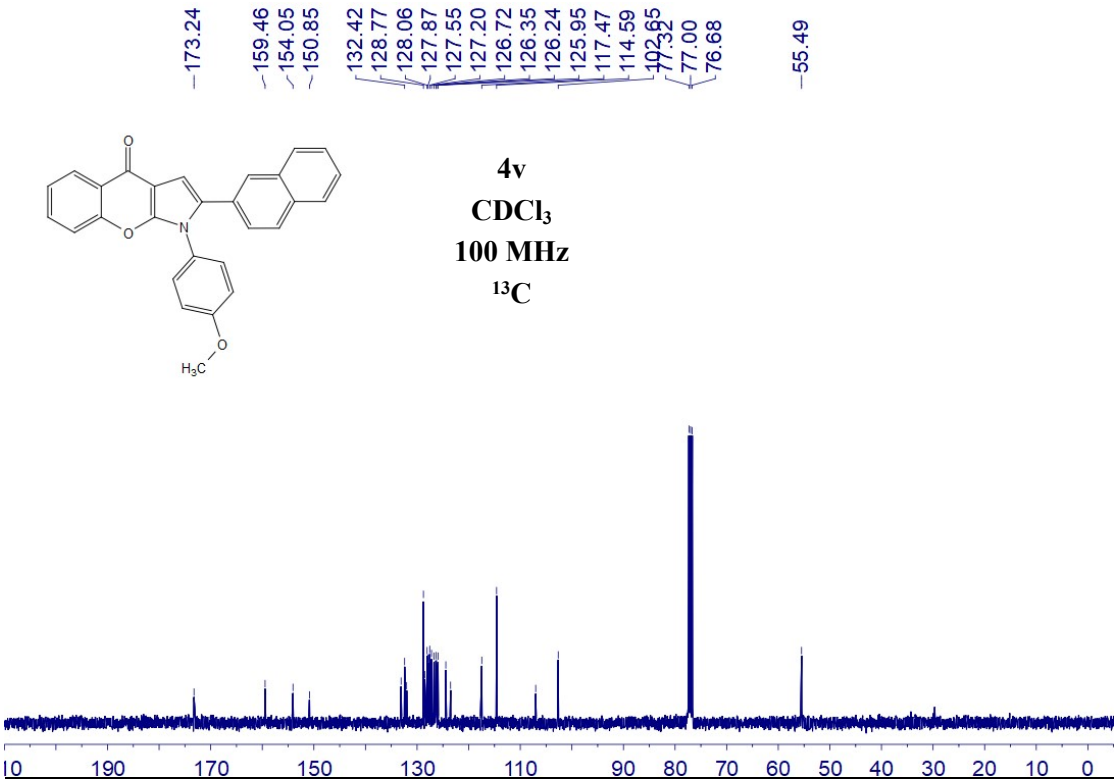
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4u



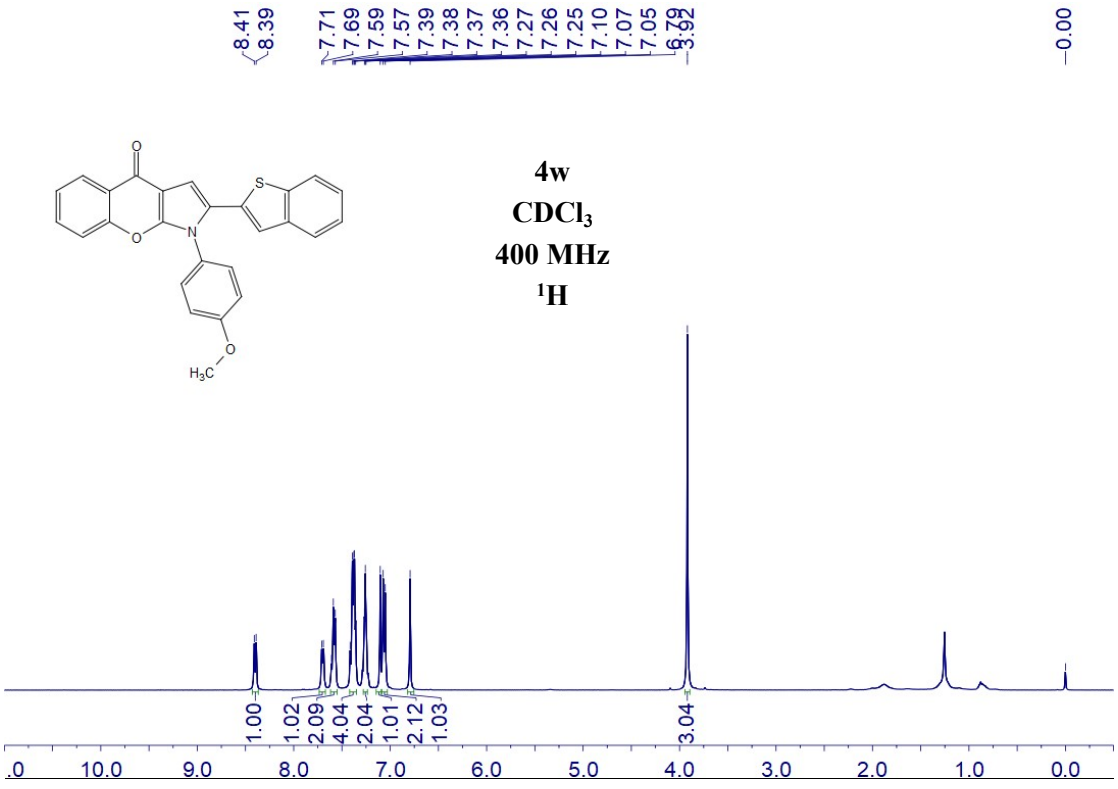
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4v



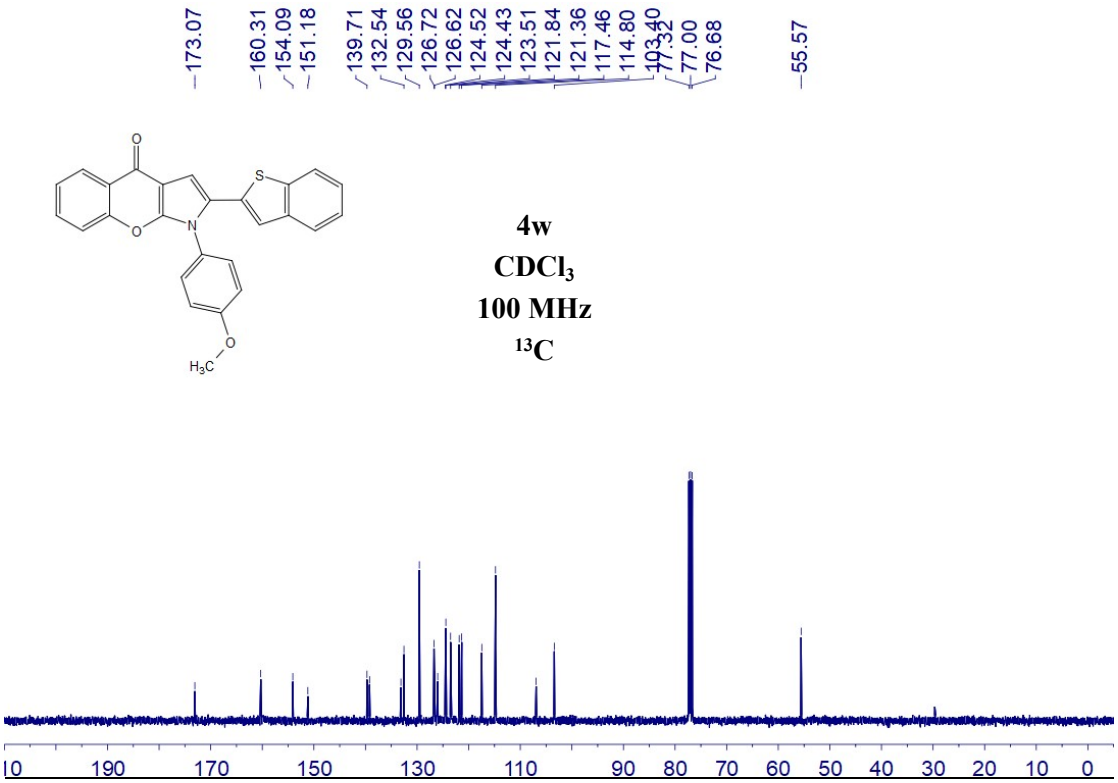
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4v



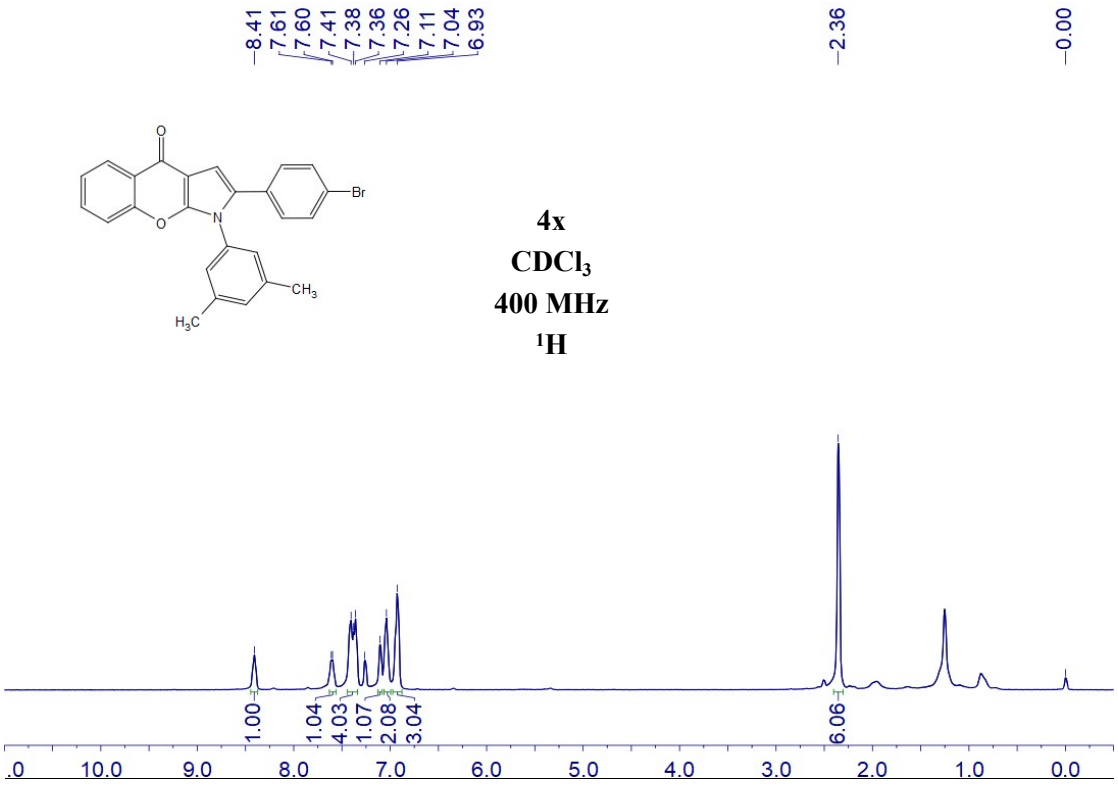
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4w



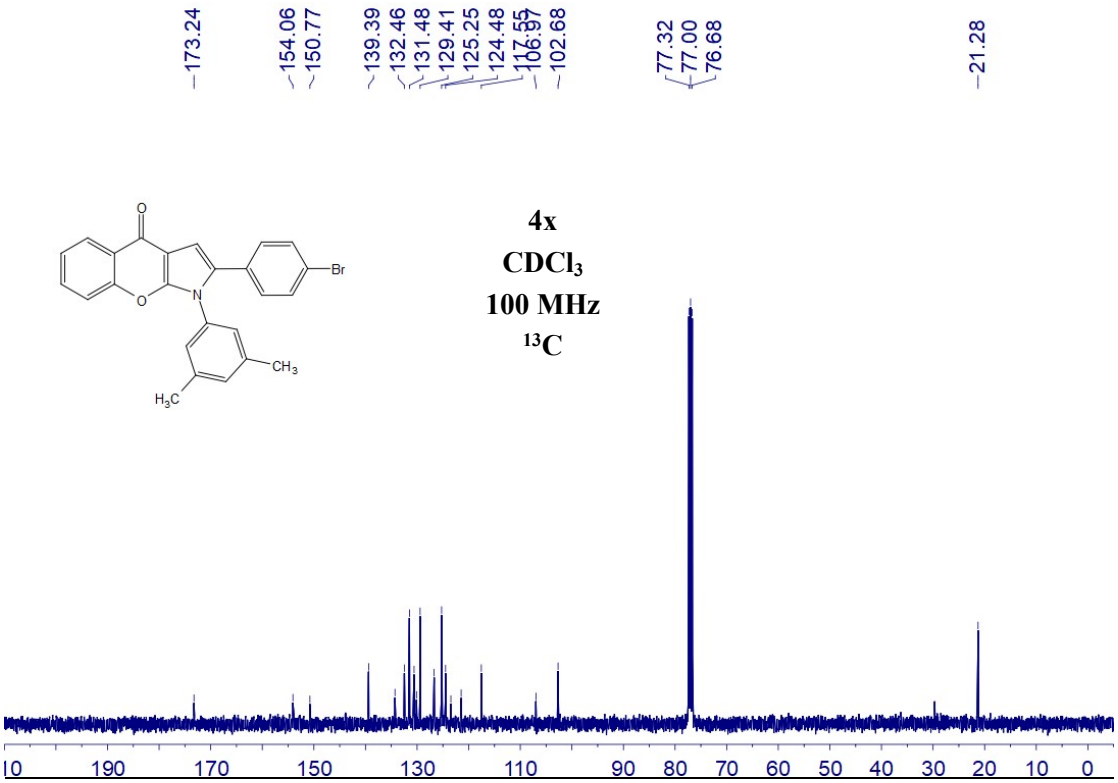
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4w



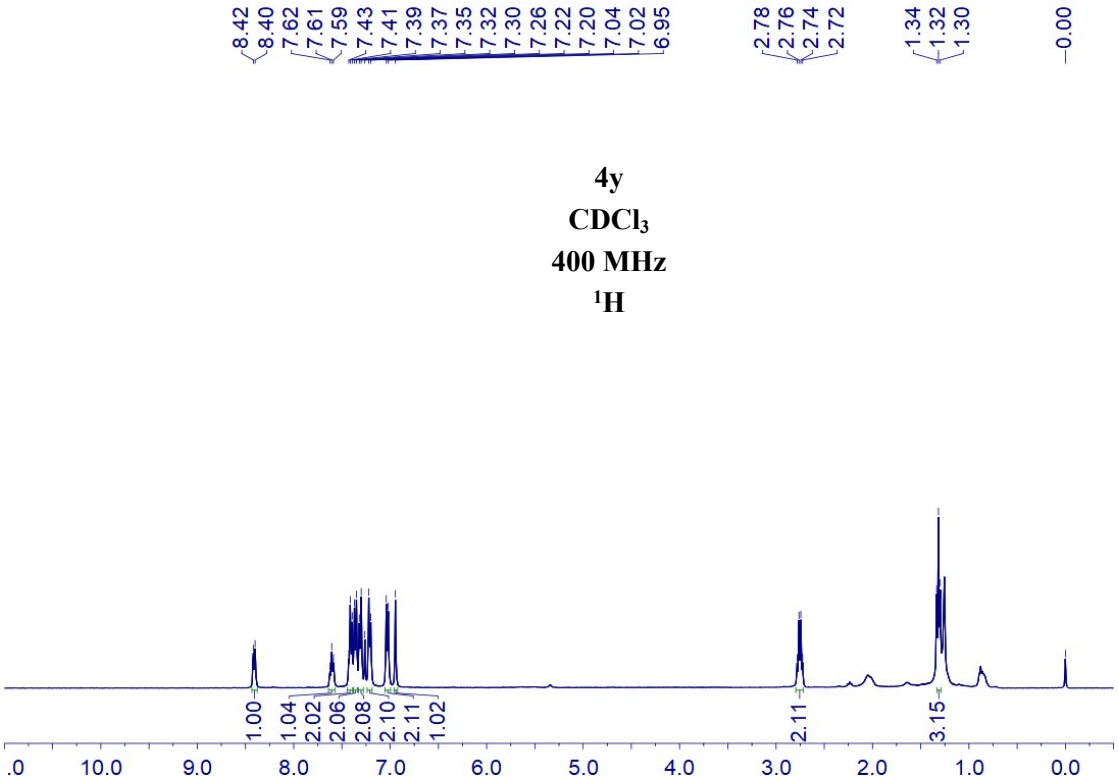
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4x



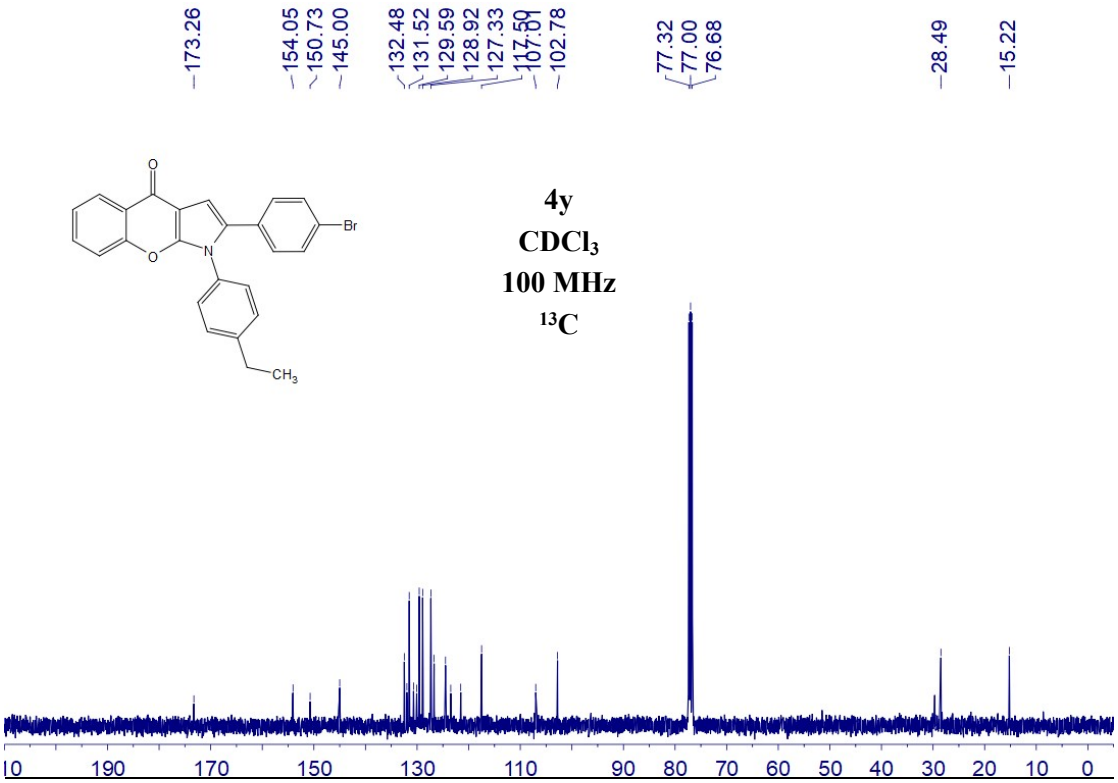
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4x



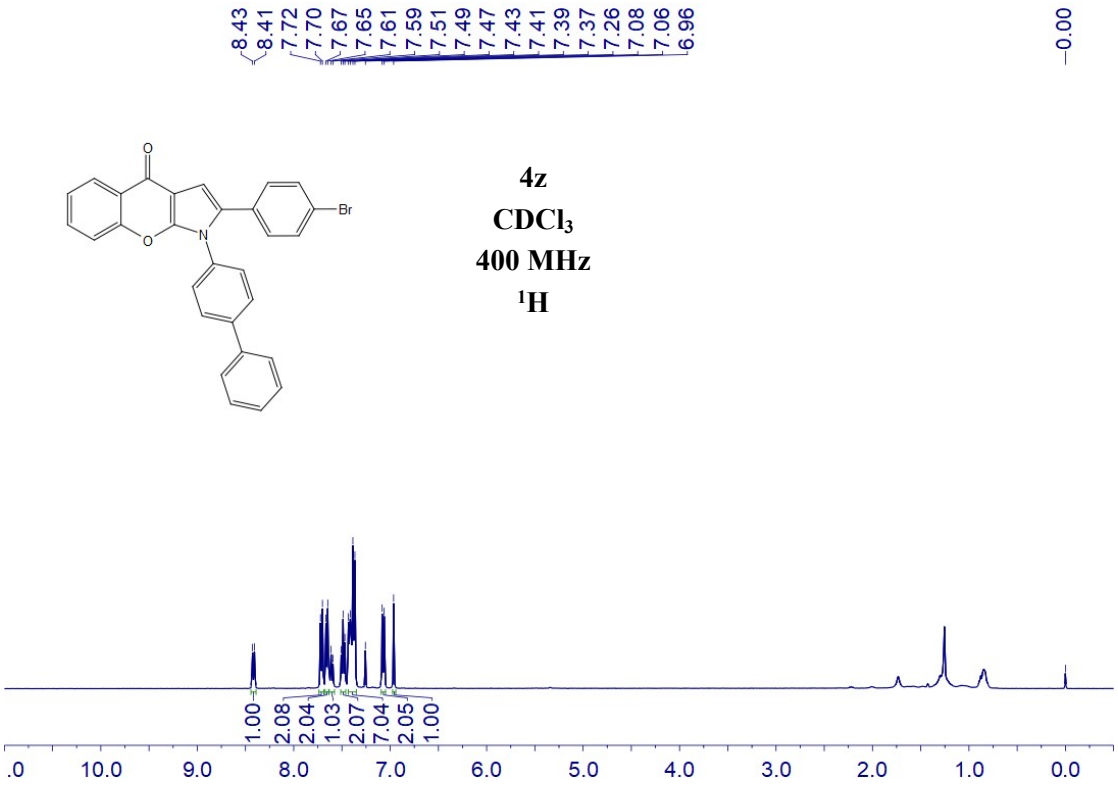
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4y



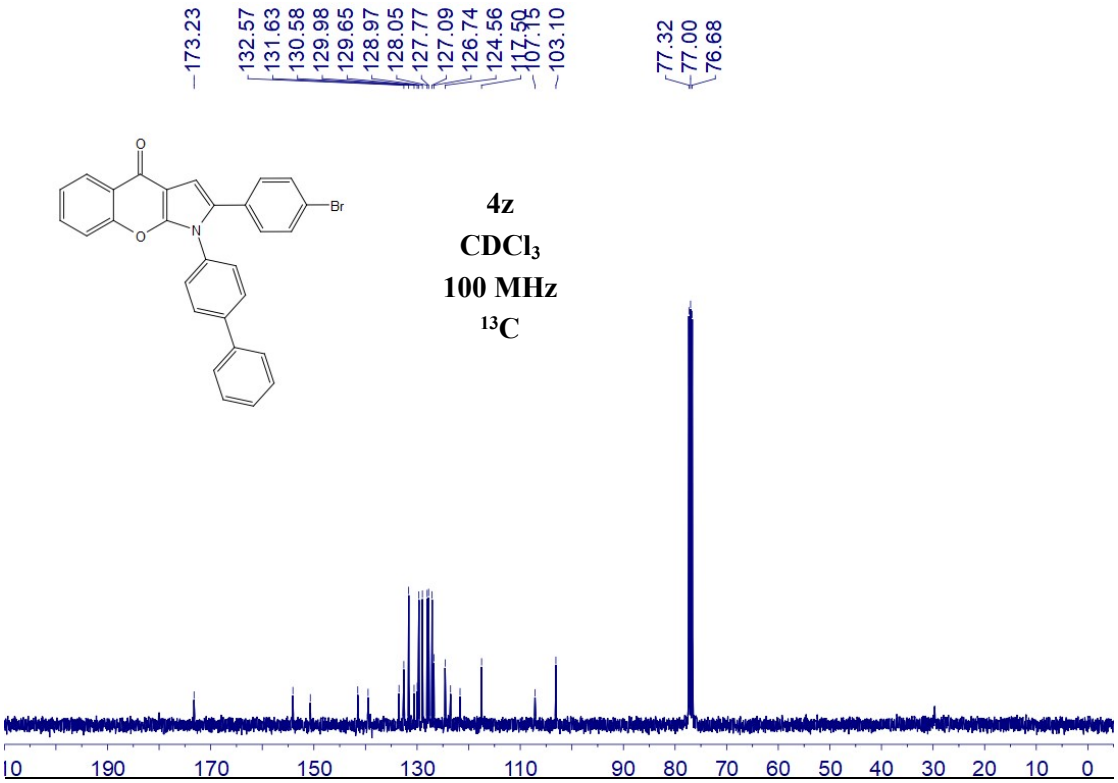
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4y



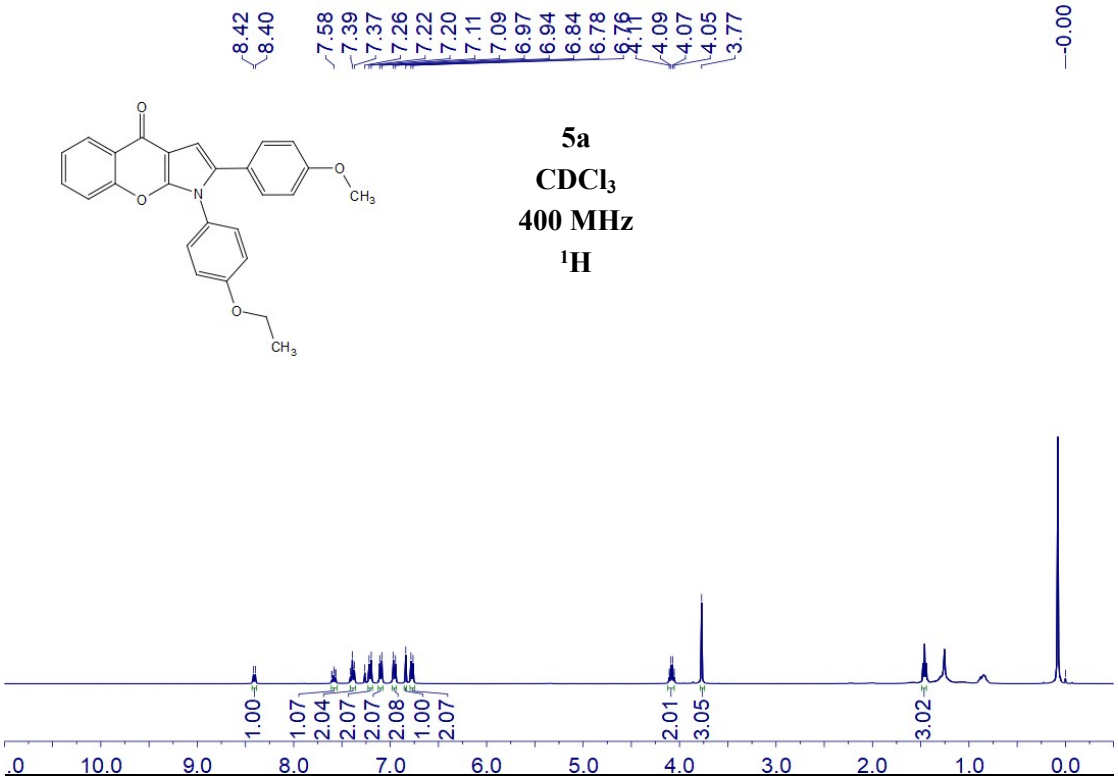
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4z



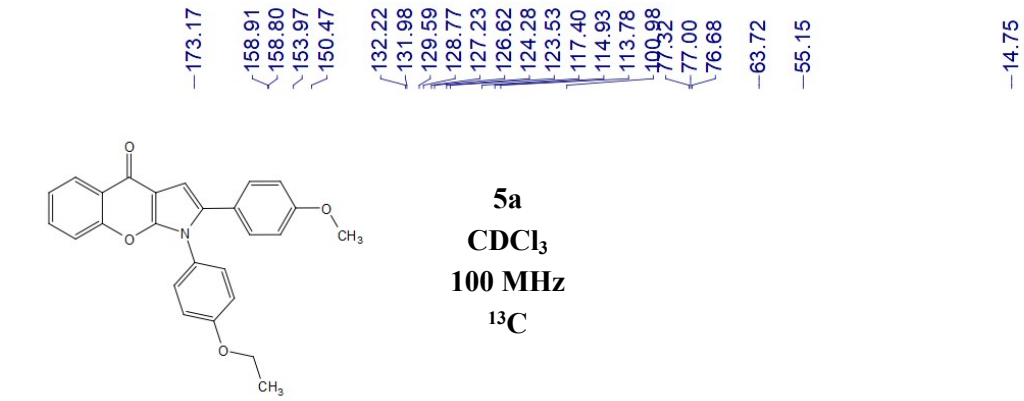
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4z



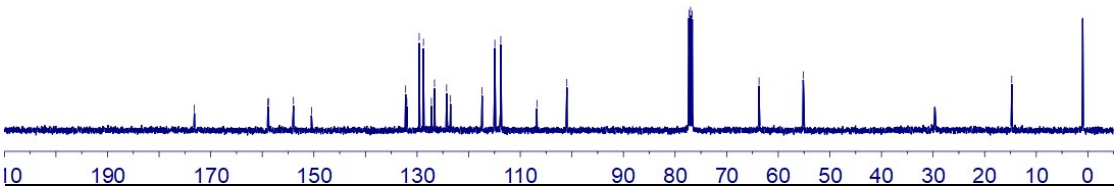
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5a



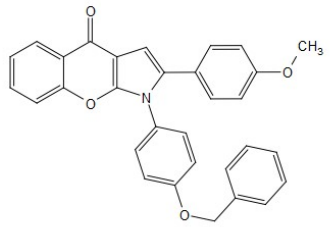
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5a



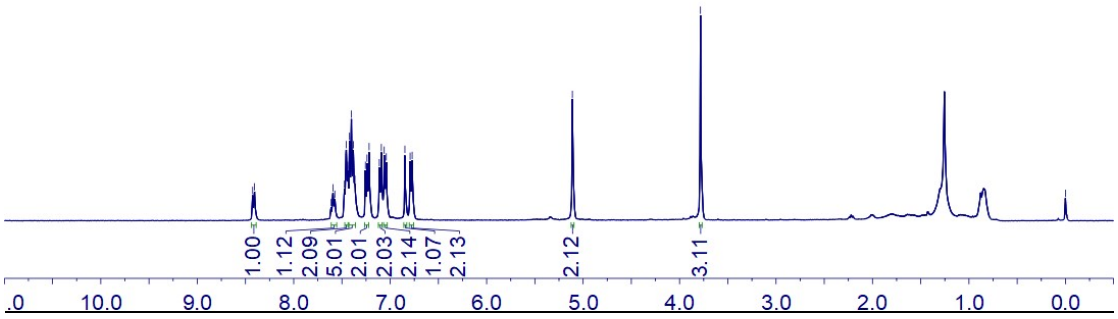
5a
$CDCl_3$
100 MHz
^{13}C



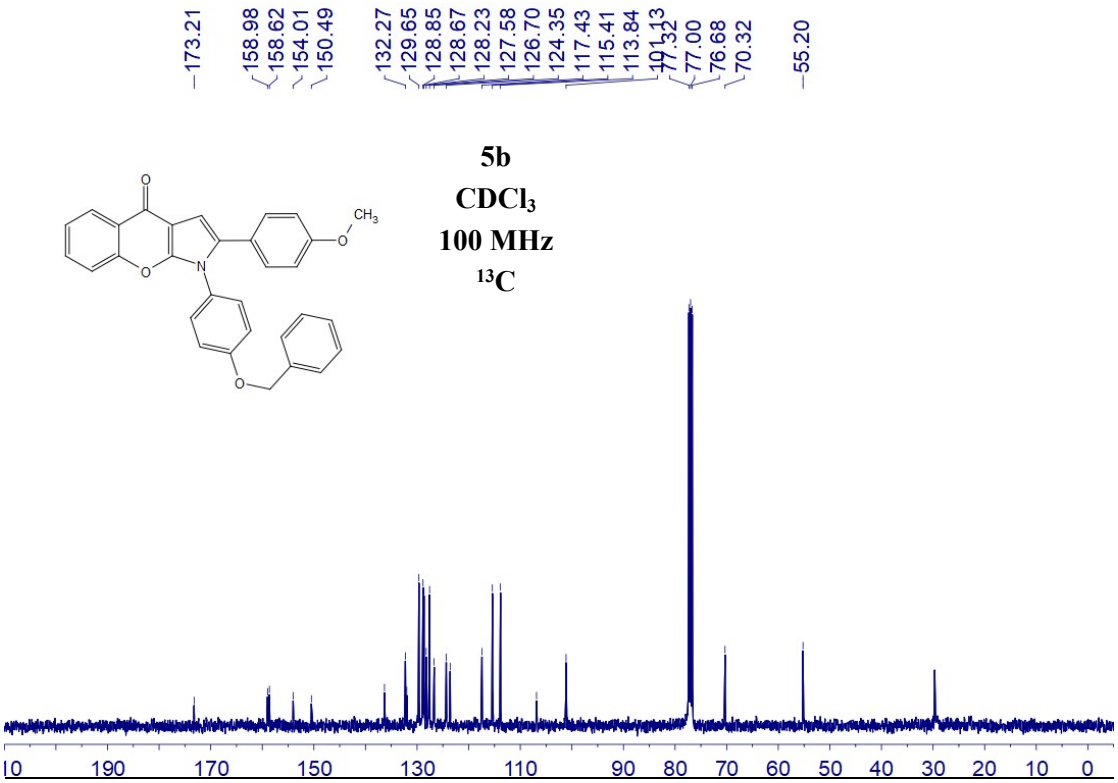
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5b



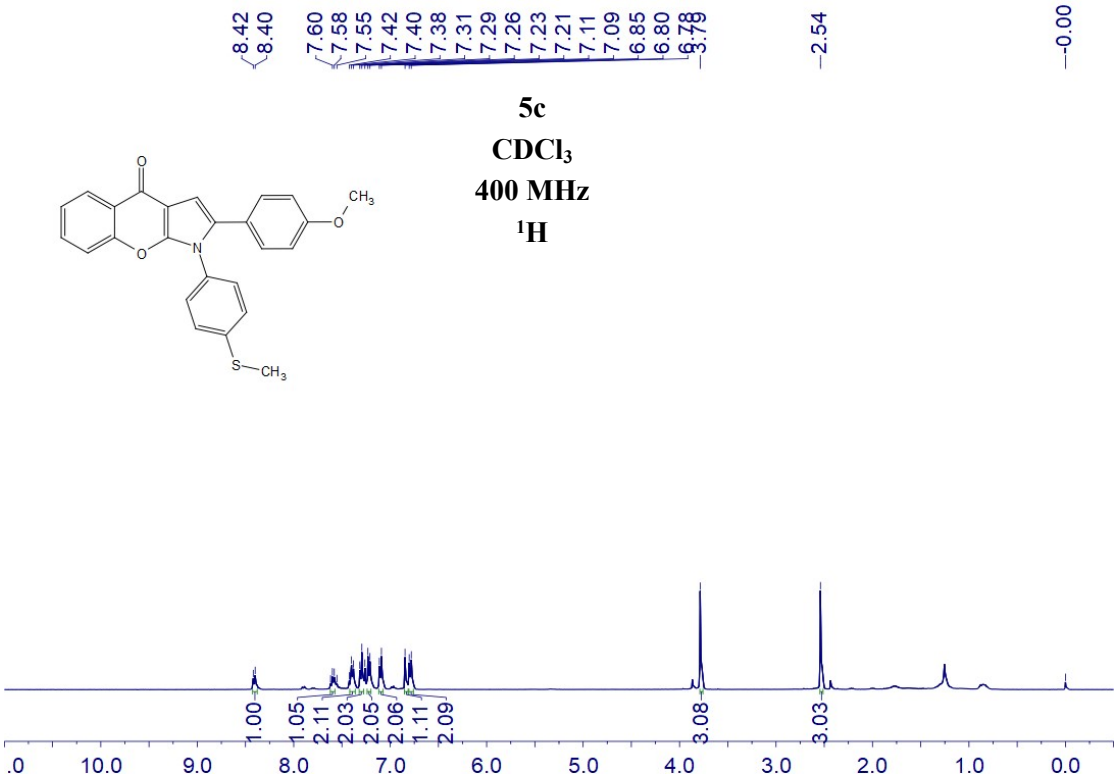
5b
$CDCl_3$
400 MHz
^{1}H



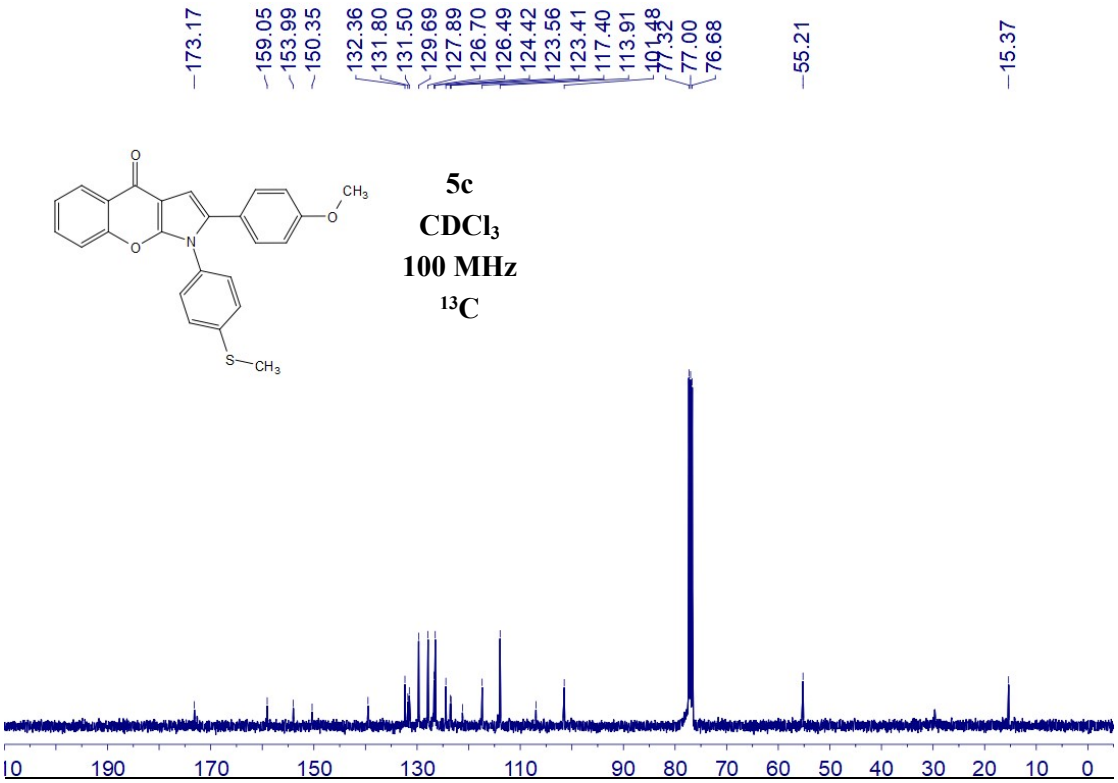
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5b



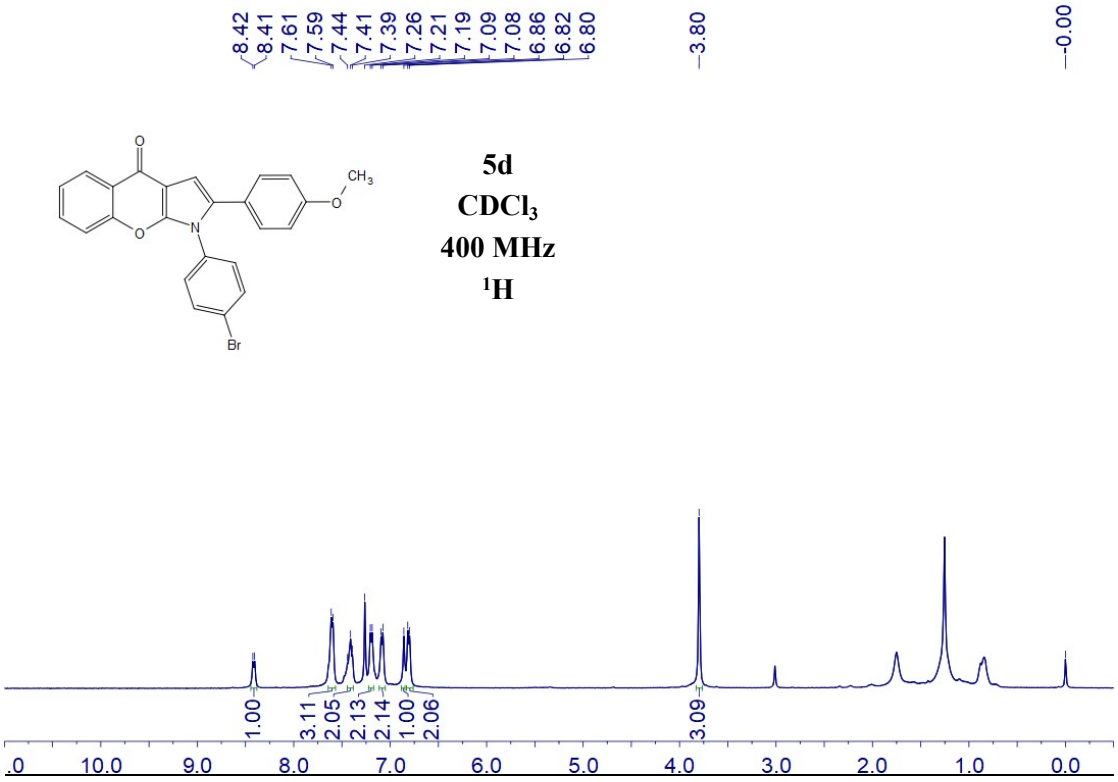
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5c



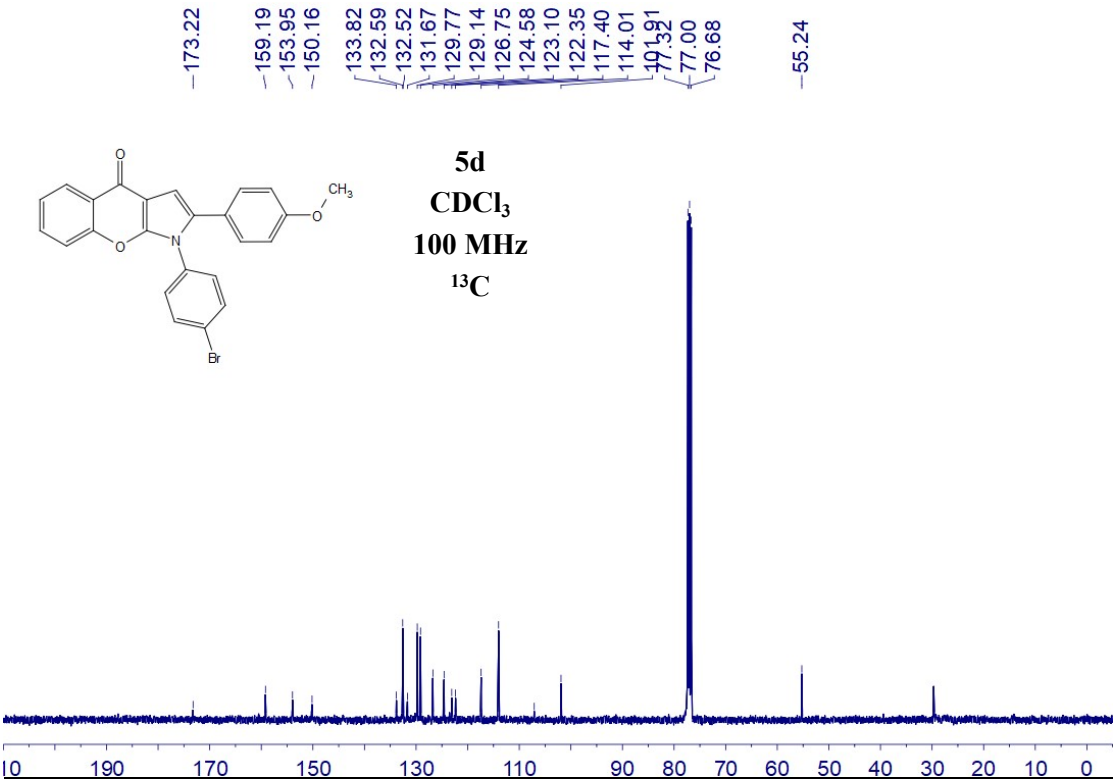
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5c



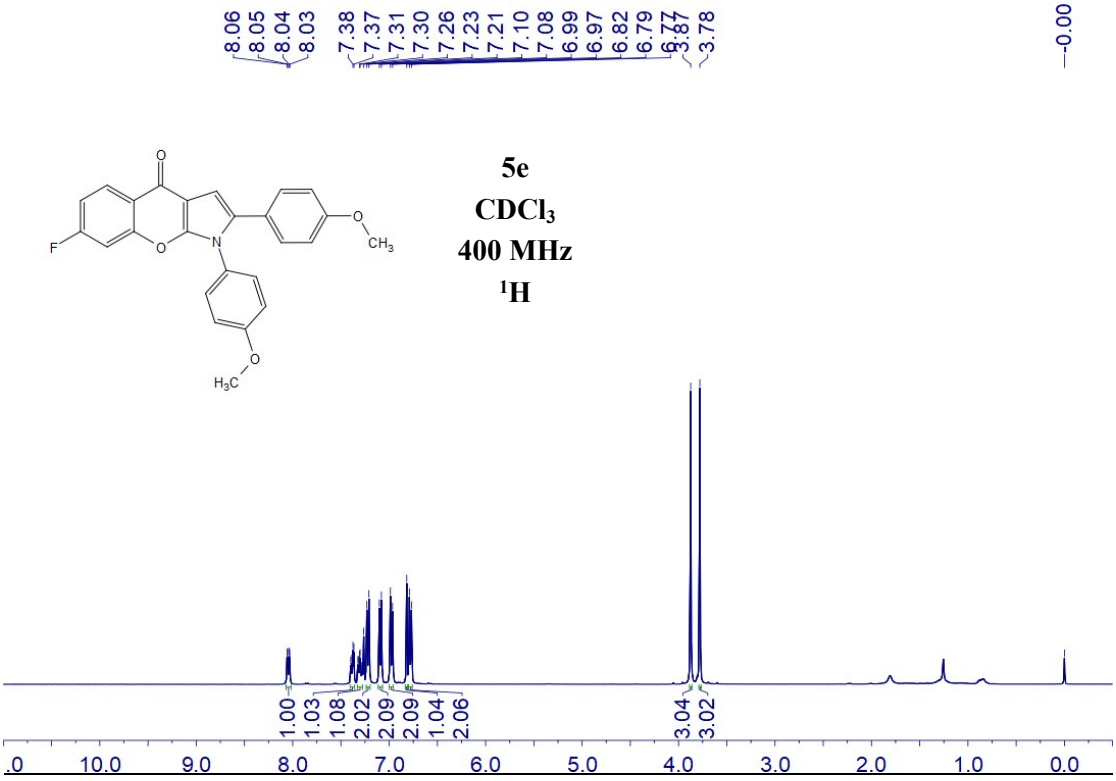
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5d



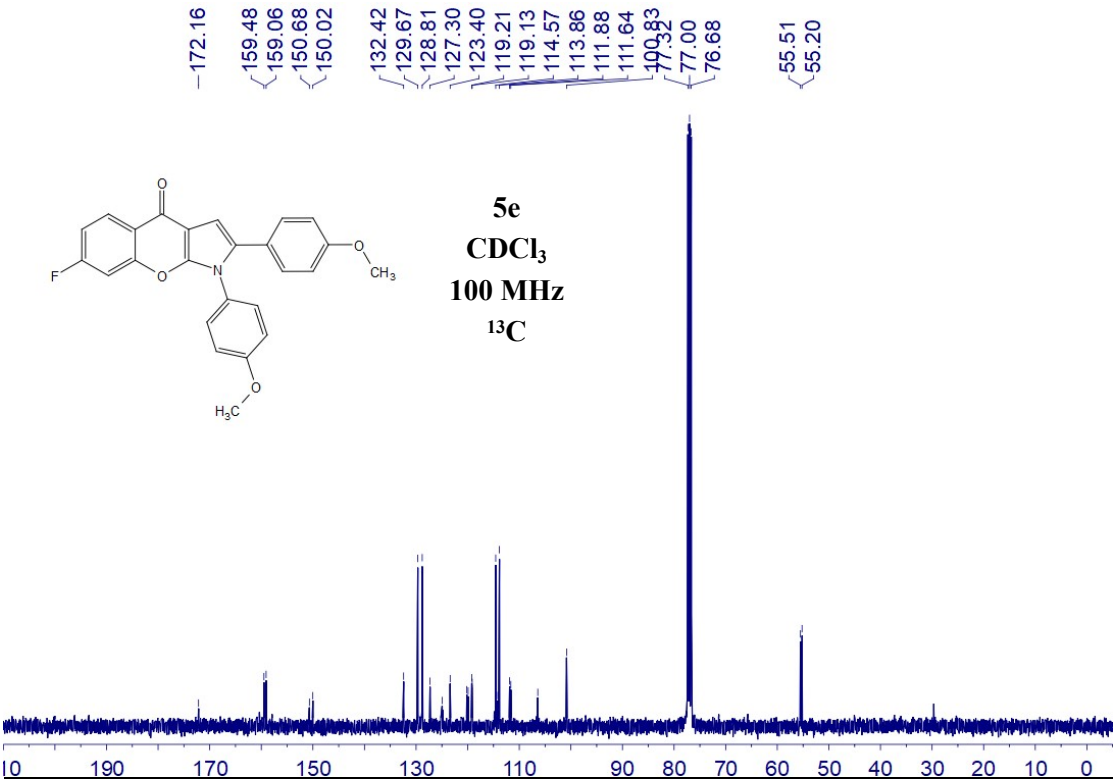
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5d



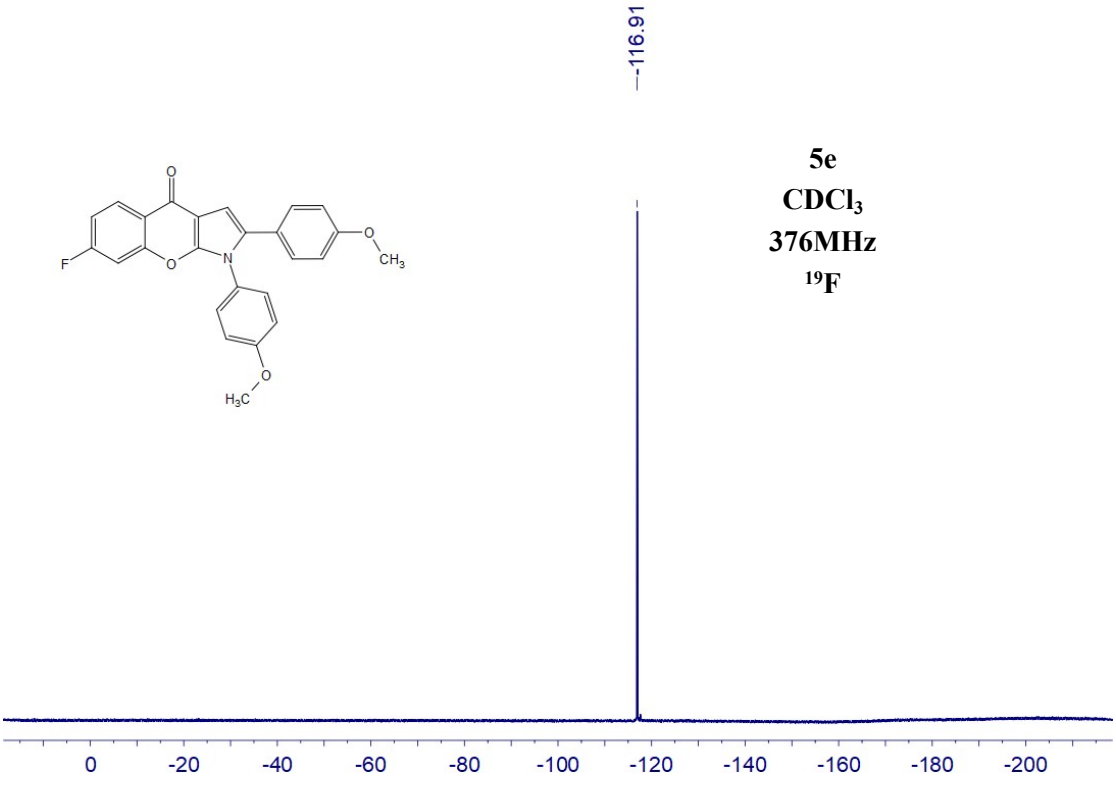
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5e



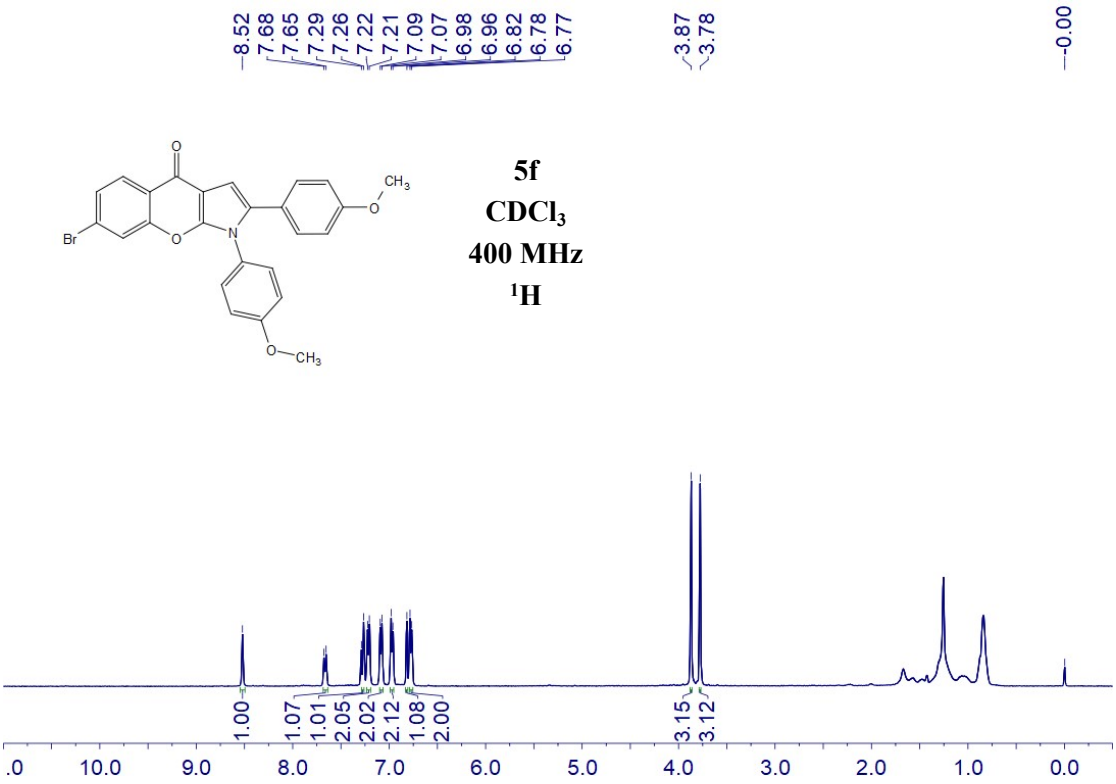
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5e



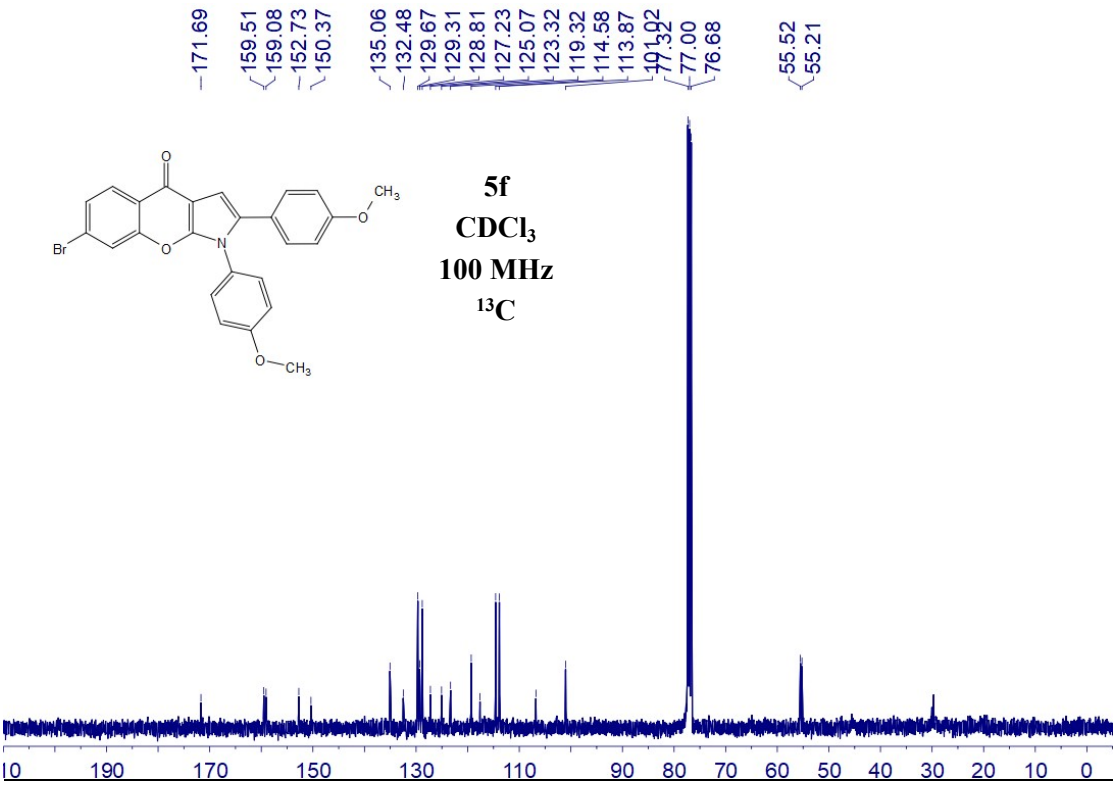
^{19}F NMR (376 MHz, $CDCl_3$)of compound 5e



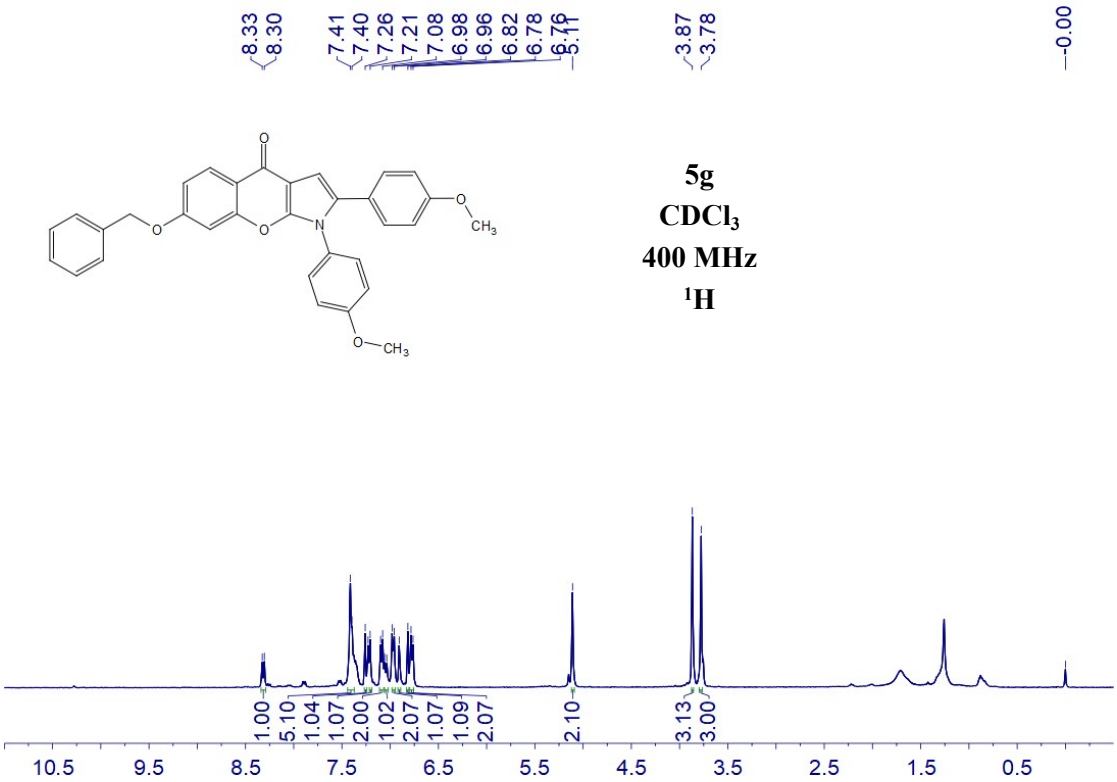
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5f



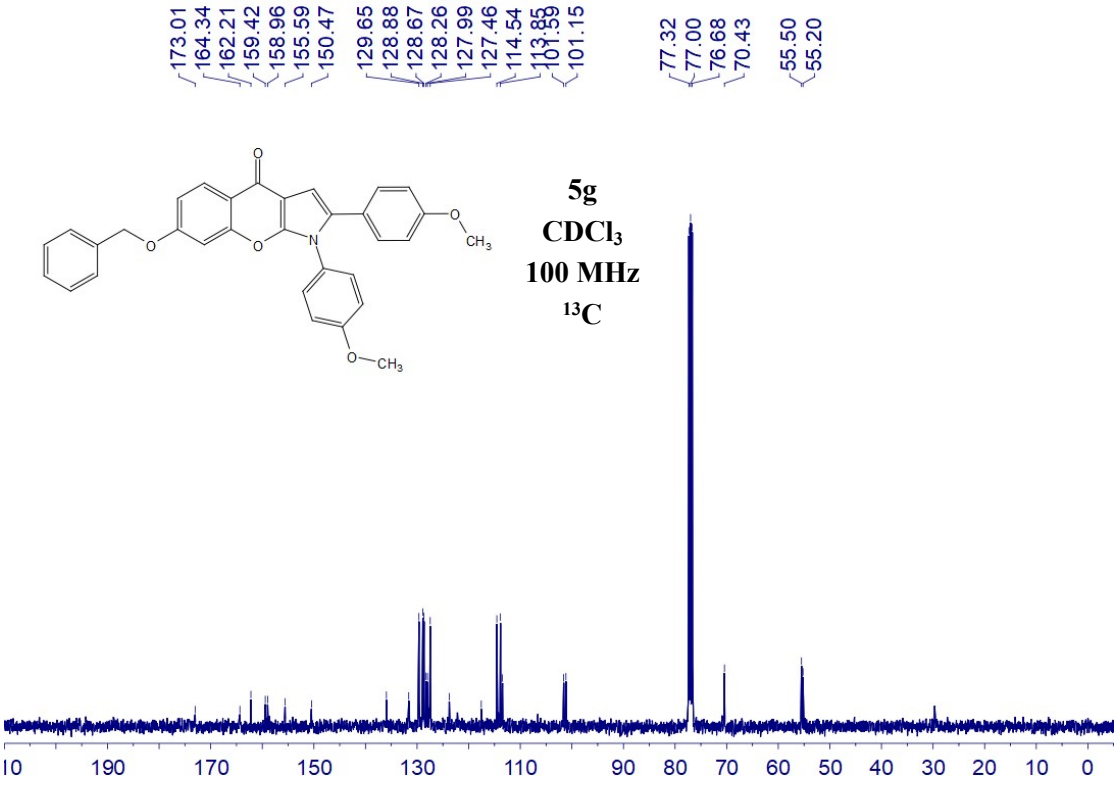
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5f



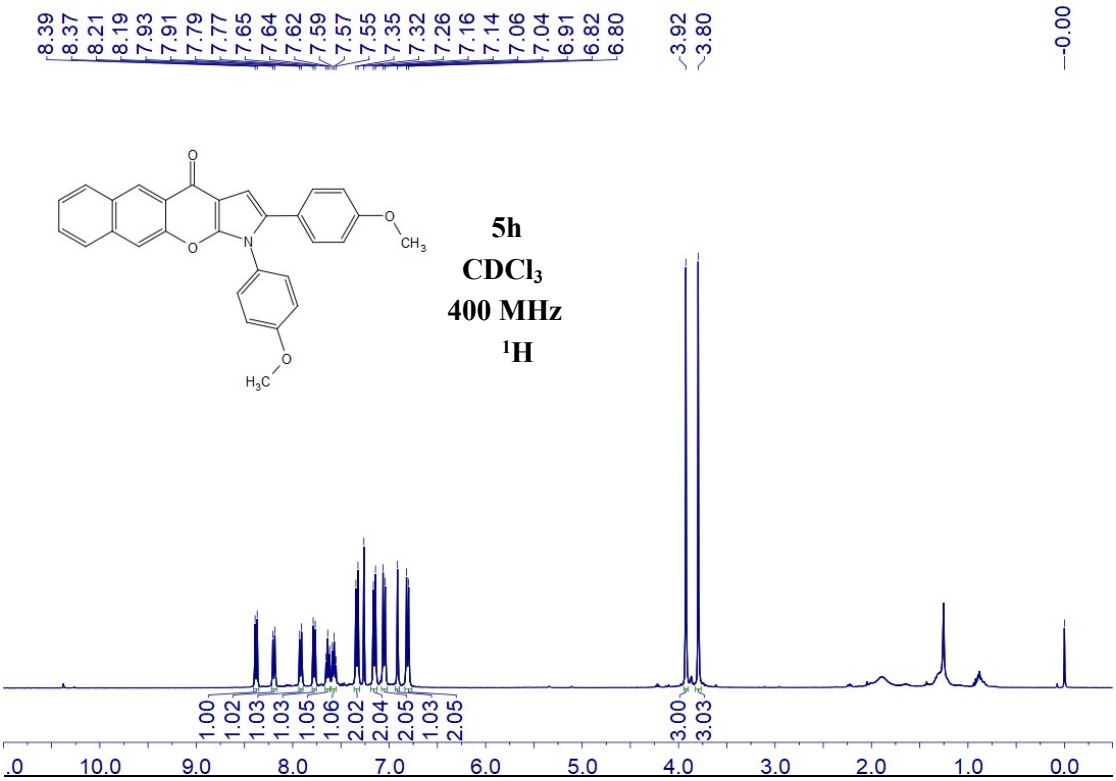
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5g



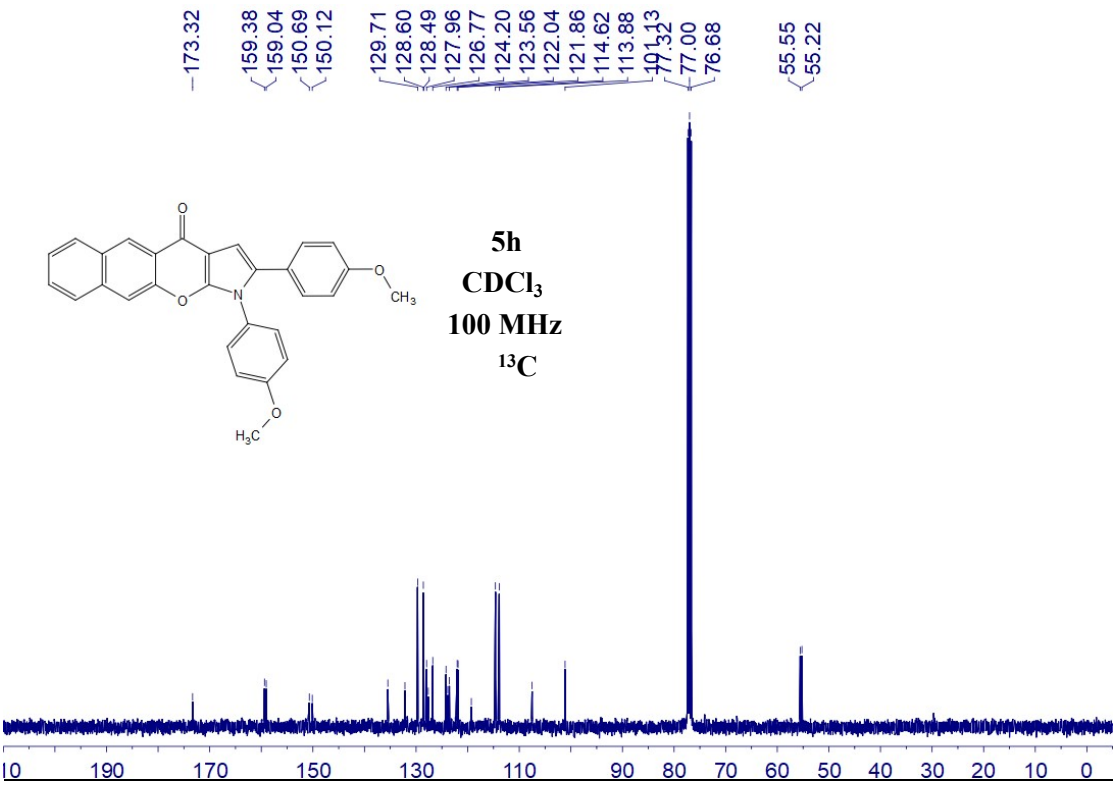
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5g



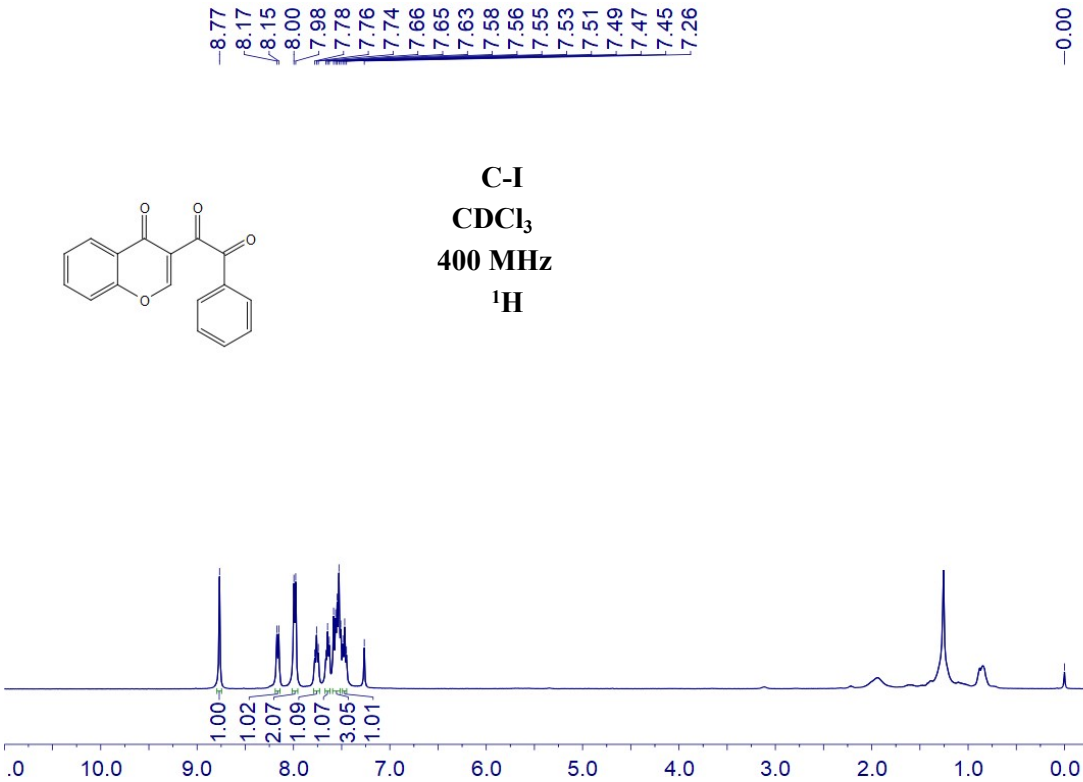
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5h



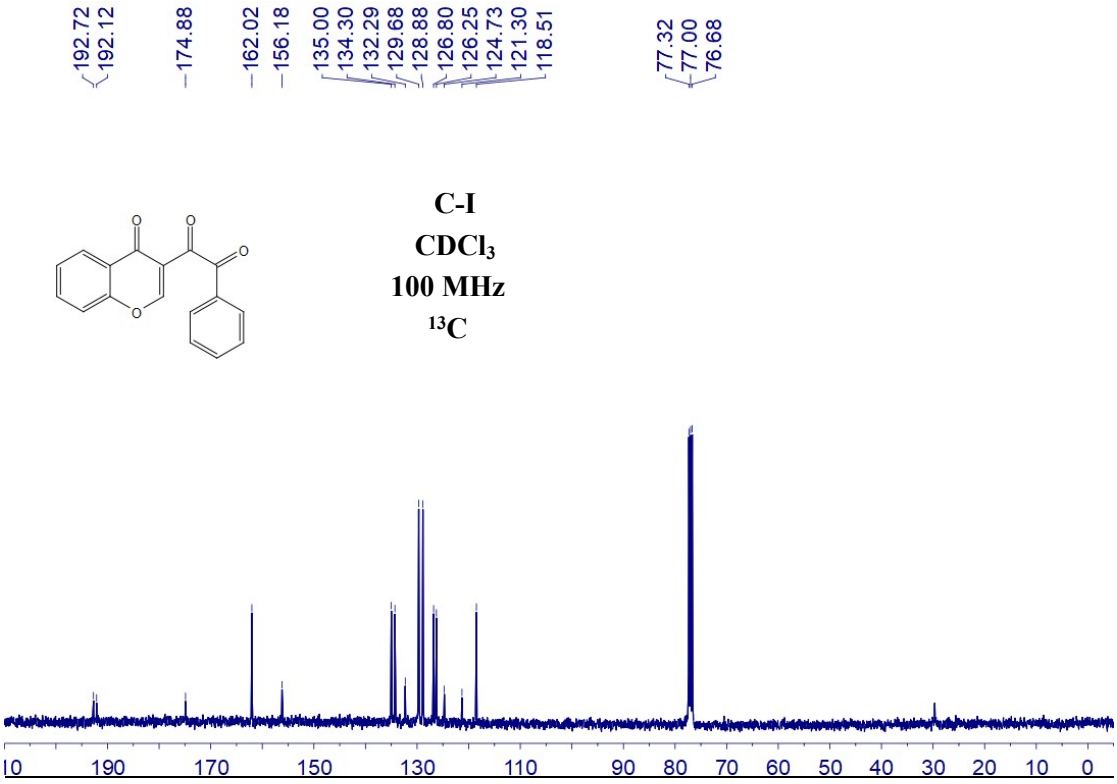
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5h



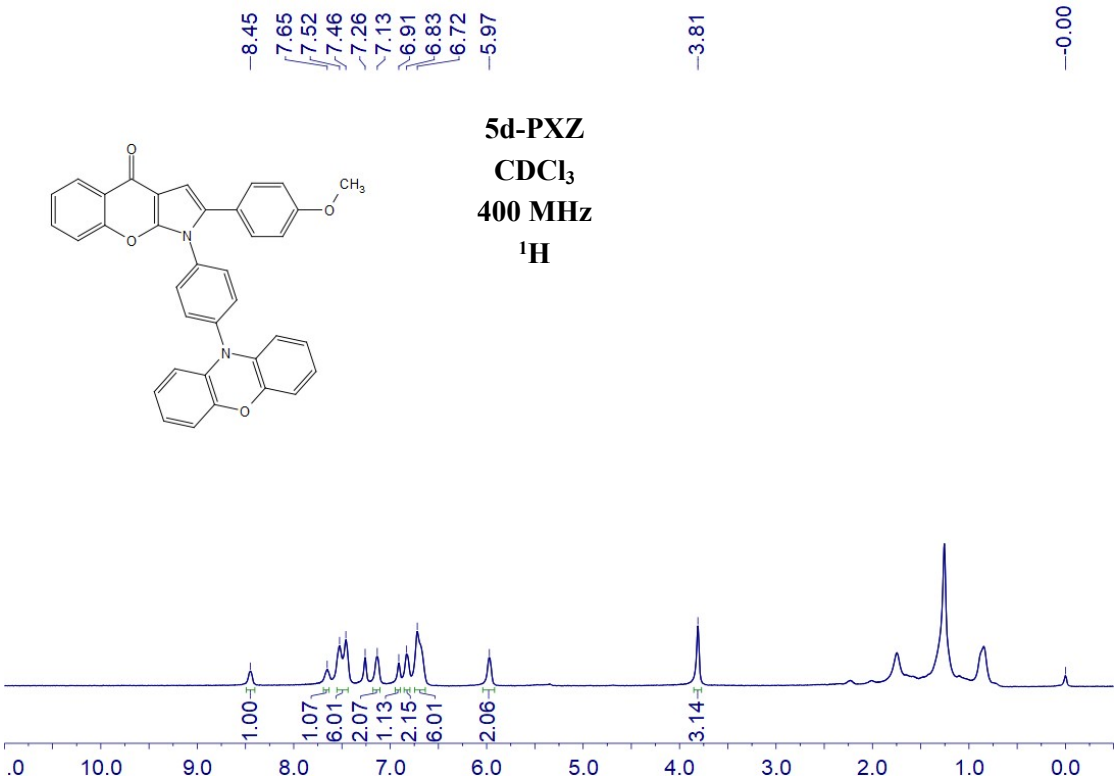
^{1}H NMR (400 MHz, $CDCl_3$) of compound C-I



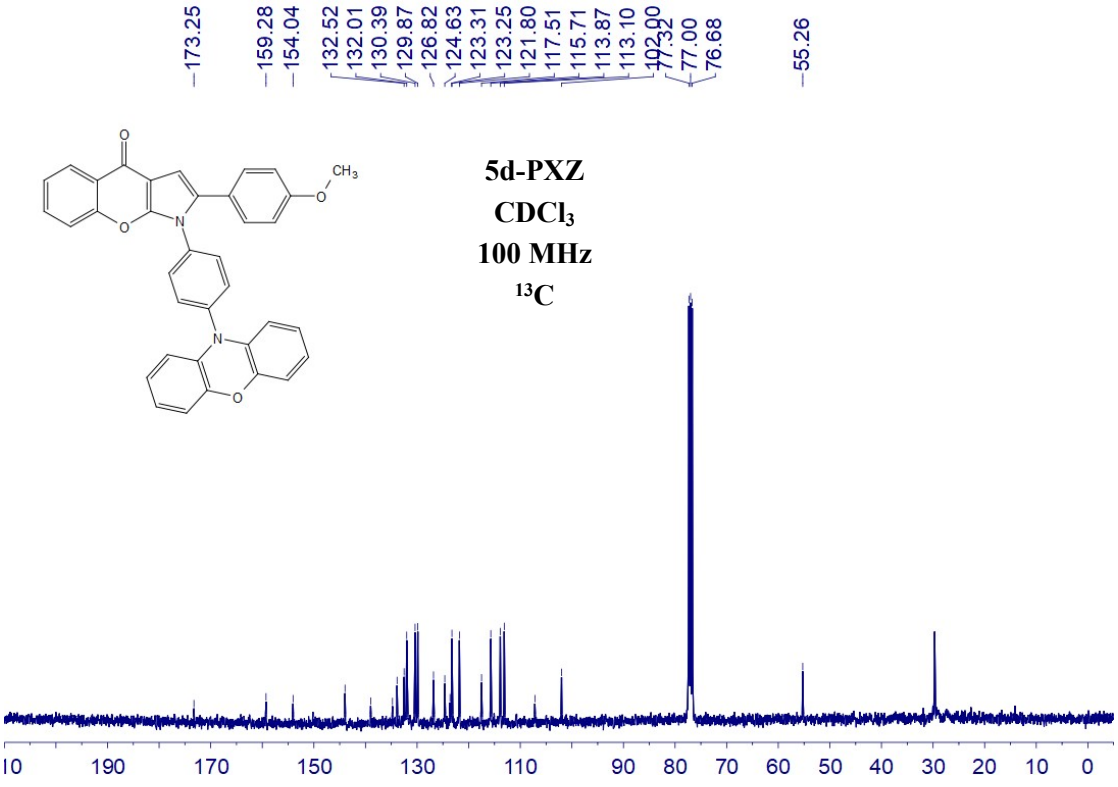
^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of C-I



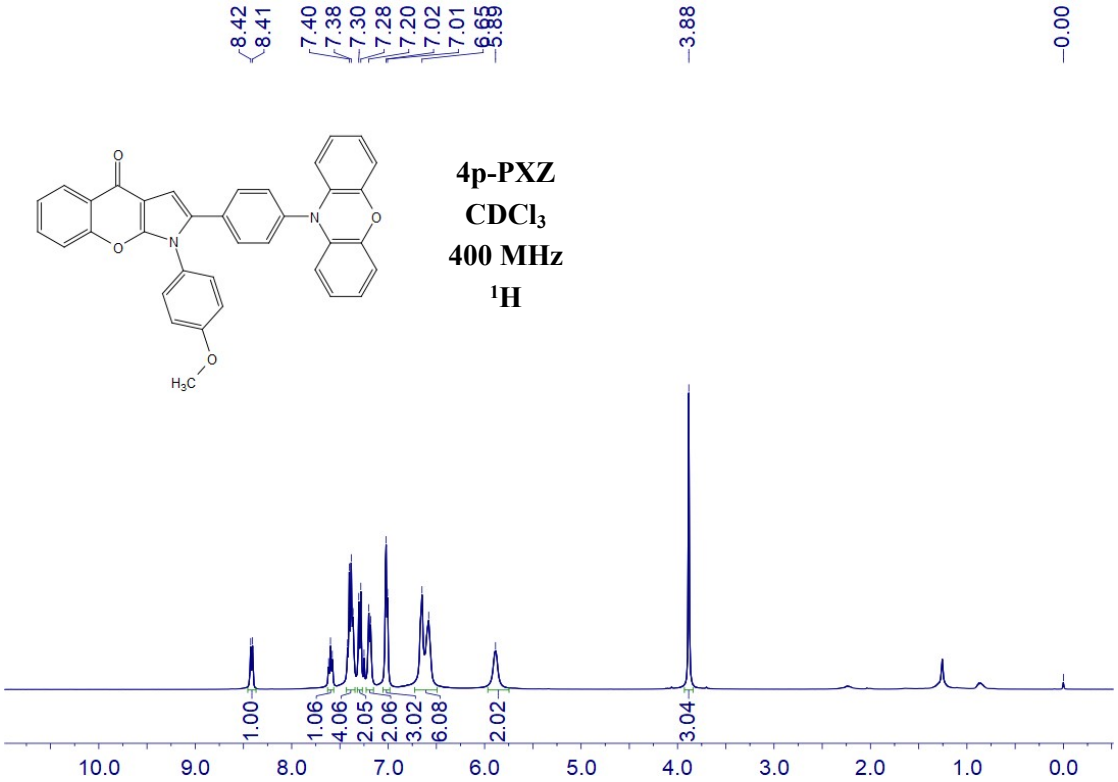
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5d-PXZ



^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 5d-PXZ



^{1}H NMR (400 MHz, $CDCl_3$) of compound 4p-PXZ



^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) of 4p-PXZ