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Synthesis of 7-hydroxy-6*H*-naphtho[*2,3-c*]chromen-6-one via TsOH-Mediated Tandem reaction

Ding Wang, Zhishuang Ma, Nana Wang, Chenyu Li, Tao Wang, Yong Liang, Zunting Zhang*

Key Laboratory of the Ministry of Education for Medicinal Resources and Natural Pharmaceutical Chemistry, National Engineering Laboratory for Resource Development of Endangered Crude Drugs in Northwest of China, School of Chemistry and Chemical Engineering, and Basic Experimental Teaching Center, Shaanxi Normal University, Xi'an 710119, China

Supporting Information

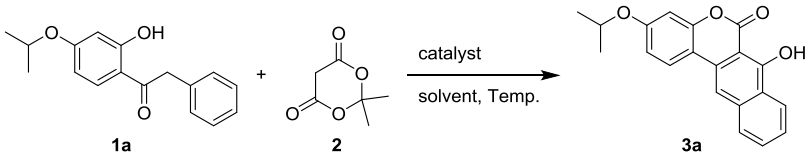
General information

Chemical reagents. Unless otherwise noted, materials and solvents were purchased from commercial suppliers and without further purification. *p*-Toluenesulfonic acid (TsOH) and 2,2-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) were purchased from Innochem. $CDCl_3$ and TFA-*d* were purchased from J&K and Cambridge Isotope Laboratories.

Instrumentation. NMR data were obtained on Bruker 400 M and JEOL 400 M nuclear resonance spectrometers. $CDCl_3$ as the deuterium solvent and tetramethylsilane (TMS) as the internal standard were employed. TFA-*d* was used as co-solvent when the compound is difficult to be dissolved by $CDCl_3$. The data of ^1H NMR was reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), coupling constants (Hz) and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Column chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. HRMS (ACPI) analysis was performed on the Bruker MAXIS mass spectrometer.

Optimization of reaction conditions

Table S1. Optimization of reaction conditions[a]



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

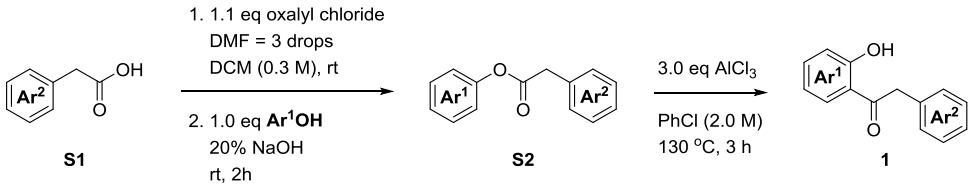
Entry	Meldrum's acid **2** (x equiv)	catalyst	solvent	Temp. (°C)	Yield[b]
1	**2.0**	**TsOH (20 mol%)**	***p*-xylene**	**150**	**17%**
2	2.0	$Yb(OTf)_3$ (20 mol%)	*p*-xylene	150	10%
3	2.0	MsOH (20 mol%)	*p*-xylene	150	ND
4	2.0	H_2SO_4 (20 mol%)	*p*-xylene	150	ND
5	2.0	TFA (20 mol%)	*p*-xylene	150	NR
6	2.0	$FeCl_3$ (20 mol%)	*p*-xylene	150	NR
7	2.0	$AlCl_3$ (20 mol%)	*p*-xylene	150	ND
8	2.0	TsOH (10 mol%)	*p*-xylene	150	6%
9	2.0	TsOH (30 mol%)	*p*-xylene	150	15%
10	2.0	TsOH (50 mol%)	*p*-xylene	150	16%
11	2.0	TsOH (1.0 eq)	*p*-xylene	150	NR
12	1.0	TsOH (20 mol%)	*p*-xylene	150	9%
13	3.0	TsOH (20 mol%)	*p*-xylene	150	18%
14	4.0	TsOH (20 mol%)	*p*-xylene	150	15%
15	**2.0**	**TsOH (20 mol%)**	**toluene**	**150**	**21%**
16	2.0	TsOH (20 mol%)	$PhCF_3$	150	7%
17	2.0	TsOH (20 mol%)	mesitylene	150	mess
18	2.0	TsOH (20 mol%)	PhCl	150	14%
19	2.0	TsOH (20 mol%)	DMF	150	NR
20	2.0	TsOH (20 mol%)	1,4-dioxane	150	NR
21	2.0	TsOH (20 mol%)	DCE	150	NR
22	**2.0**	**TsOH (20 mol%)**	***p*-xylene/toluene (1/1, v/v)**	**150**	**31%**
23	2.0	TsOH (20 mol%)	*p*-xylene/toluene (1/1, v/v)	170	17%
24	2.0	TsOH (20 mol%)	*p*-xylene/toluene (1/1, v/v)	120	trace
25	2.0	TsOH (20 mol%)	*p*-xylene/toluene (1/1, v/v)	100	NR
26[c]	2.0	TsOH (20 mol%)	*p*-xylene/toluene (1/1, v/v)	150	63%
27[d]	2.0	TsOH (20 mol%)	*p*-xylene/toluene (1/1, v/v)	150	72%[c]
28[e]	**2.0**	**TsOH (20 mol%)**	***p*-xylene/toluene (1/1, v/v)**	**150**	**73%(70%)[f]**

[a] The reactions were carried out on a 1.0 mmol scale of **1a**. [b] The yields were determined by ^{1}H NMR analysis with dibromomethane and 1,1,2,2-tetrachloroethane as the internal standard. [c] Another batch of TsOH (20 mmol%) and meldrum's acid (2.0 equiv.) was added when the reaction have been stirred for 1h. [d] The third batch of TsOH (20 mmol%) and meldrum's acid (2.0 equiv.) was added when the reaction have been stirred for 2h. [e] The third batch of TsOH (10 mmol%) and meldrum's acid (1.0 equiv.) was added when the reaction have been stirred for 2h. [f] Isolated yield. ND: no detected product.

Preparation and characterization of reaction substrates

All substrates were prepared according to literature's method. General procedure is illustrated as follows.

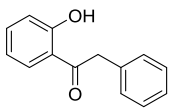
Method A: Fries rearrangement



To a solution of the carboxylic acid **S1** (20 mmol) in DCM (0.3M) was added oxalyl chloride (2.79 g, 22 mmol) dropwise. DMF (3 drops) was added. The mixture was stirred at room temperature until no more gas bubbles were observed (within 3-4 h). The crude acid chloride was obtained by removing the solvent under reduced pressure, which was used for the next step without further purification.[1]

The crude acid chloride was added to a solution of phenol (20 mmol, 1.0 equiv) dissolved in 10%aq. NaOH (10 mL) at 0 °C. After the reaction finished (ca. 2 h), 50 mL EtOAc was added, and the mixture was washed by 10% aq. NaOH (20 mL) twice to remove the residual phenol and carboxylic acid. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The organic solvent was removed under reduced pressure to give the ester product **S2**, which was usually pure and used without further purification.[2]

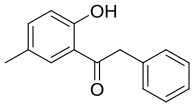
To the solvent of ester compound **S2** (10 mmol) in chlorobenzene (3.0 M) was added $AlCl_3$ (1.87 g, 14 mmol). The mixture was stirred at 130 °C for about 3 h. Then the reaction was poured into ice water, and extracted with EtOAc (20 mL) three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residual was further purified by silica gel chromatography to give compound **1**.[3]



1-(2-hydroxyphenyl)-2-phenylethan-1-one (1b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 7.86 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 3H), 6.98 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.90 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 4.30 (s, 2H).

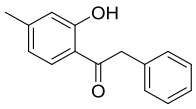
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.91, 162.94, 136.58, 133.95, 130.44, 129.46, 128.81, 127.23, 119.08, 119.02, 118.70, 45.17.



1-(2-hydroxy-5-methylphenyl)-2-phenylethan-1-one (1c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (s, 1H), 7.64 (d, *J* = 1.3 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 4H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.29 (s, 2H), 2.31 (s, 3H).

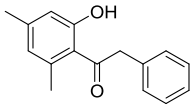
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.73, 160.84, 137.67, 134.04, 130.06, 129.51, 128.77, 128.09, 127.18, 118.76, 118.44, 45.03, 20.62.



1-(2-hydroxy-4-methylphenyl)-2-phenylethan-1-one (1d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.26 (M, 3H), 6.78 (s, 1H), 6.69 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.24 (s, 2H), 2.32 (s, 3H).

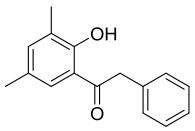
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.28, 163.09, 148.27, 134.23, 130.35, 129.43, 128.78, 127.15, 120.35, 118.67, 116.91, 45.04, 21.98.



1-(2-hydroxy-4,6-dimethylphenyl)-2-phenylethan-1-one (1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.93 (s, 1H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.26 – 7.19 (m, 2H), 6.69 (s, 1H), 6.59 (s, 1H), 4.28 (s, 2H), 2.62 (s, 3H), 2.30 (s, 3H).

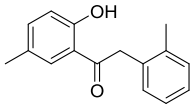
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.57, 162.76, 145.94, 138.87, 134.54, 129.68, 128.69, 127.12, 124.83, 119.83, 116.71, 50.51, 24.54, 21.68.



1-(2-hydroxy-3,5-dimethylphenyl)-2-phenylethan-1-one (1f)

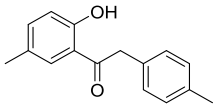
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 7.52 (s, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.19 (s, 1H), 4.31 (s, 2H), 2.30 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.97, 159.38, 138.59, 134.29, 129.53, 128.75, 127.57, 127.41, 127.28, 127.12, 118.08, 45.08, 20.63, 15.51.

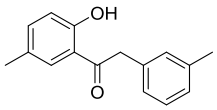


1-(2-hydroxy-5-methylphenyl)-2-(o-tolyl)ethan-1-one (1o)

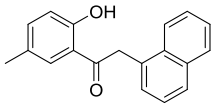
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 7.68 (d, *J* = 1.4 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 (d, *J* = 6.9 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 4.34 (s, 2H), 2.34 (s, 3H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.70, 160.64, 137.76, 137.07, 132.86, 130.49, 129.75, 128.24, 127.66, 126.31, 119.00, 118.56, 43.05, 20.73, 19.88.



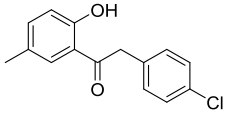
1-(2-hydroxy-5-methylphenyl)-2-(p-tolyl)ethan-1-one (1p)
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 7.64 (d, *J* = 1.5 Hz, 1H), 7.28 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.19 – 7.12 (m, 4H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.25 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.06, 160.87, 137.69, 136.92, 130.96, 130.14, 129.57, 129.45, 128.13, 118.81, 118.48, 44.73, 21.21, 20.72.



1-(2-hydroxy-5-methylphenyl)-2-(m-tolyl)ethan-1-one (1q)
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 7.64 (d, *J* = 1.5 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.08 (dd, *J* = 12.7, 8.4 Hz, 3H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.25 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.99, 160.88, 138.54, 137.74, 133.97, 130.30, 130.17, 128.74, 128.16, 128.05, 126.62, 118.84, 118.49, 45.05, 21.53, 20.73.



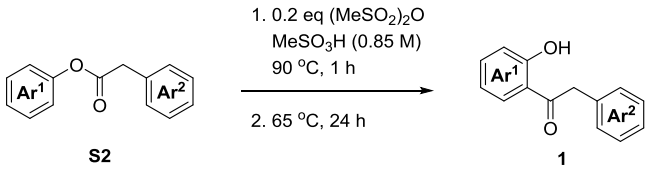
1-(2-hydroxy-5-methylphenyl)-2-(naphthalen-1-yl)ethan-1-one (1r)
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98 (s, 1H), 7.94 – 7.87 (m, 1H), 7.86 – 7.77 (m, 3H), 7.56 – 7.42 (m, 3H), 7.34 (m, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.77 (s, 2H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.73, 160.77, 137.89, 133.94, 132.28, 130.79, 129.83, 129.03, 128.33, 128.28, 128.27, 126.54, 125.96, 125.58, 123.78, 118.95, 118.64, 42.66, 20.74.



2-(4-chlorophenyl)-1-(2-hydroxy-5-methylphenyl)ethan-1-one (1s)
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 7.60 (d, *J* = 1.3 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 1H), 4.27 (s, 2H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.21, 160.87, 137.96, 133.26, 132.45, 131.01, 129.89, 128.98, 128.30, 118.61, 44.33, 20.72.

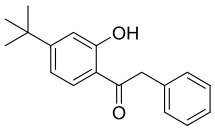
The preparation for compound **1g**, **1j**, **1m** and **1n** followed the **Method A** except the rearrangement of

the ester. The procedure of rearrangement was described as follows:[4]



S2 **1**

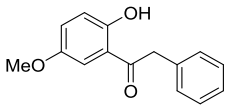
The methanesulfonic anhydride (175 mg, 1.0 mmol) was added to methanesulfonic acid (6.0 mL, ca. 0.83 M vs **S2**), and the mixture was stirred at 90 °C for 1 h. To the $(MeSO_2)_2O/MeSO_3H$ solution was added the ester (**S2**, 5.0 mmol) under nitrogen atmosphere. The mixture was stirred at 65 °C for 24 h. Then the reaction was poured into ice water, and extracted with EtOAc three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residual was further purified by silica gel chromatography to give compound **1**.



1-(4-(tert-butyl)-2-hydroxyphenyl)-2-phenylethan-1-one (1g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 3H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.93 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.26 (s, 2H), 1.29 (s, 9H).

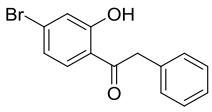
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.23, 163.00, 161.27, 134.25, 130.20, 129.50, 128.86, 127.22, 116.87, 116.83, 115.37, 45.14, 35.44, 30.84.



1-(2-hydroxy-5-methoxyphenyl)-2-phenylethan-1-one (1j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.25 (m, 4H), 7.10 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.93 (d, *J* = 9.1 Hz, 1H), 4.28 (s, 2H), 3.77 (s, 3H).

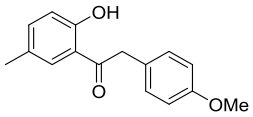
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.50, 157.39, 151.75, 134.02, 129.49, 128.94, 127.35, 124.49, 119.59, 118.54, 113.12, 56.03, 45.57.



1-(4-bromo-2-hydroxyphenyl)-2-phenylethan-1-one (1m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.27 – 7.22 (m, 2H), 7.18 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.25 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.51, 163.41, 133.60, 131.44, 131.07, 129.44, 128.99, 127.47, 122.67, 121.96, 117.95, 45.40.

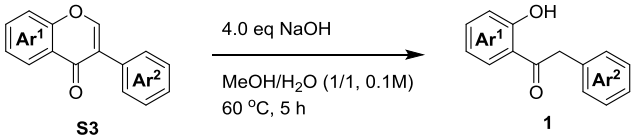


1-(2-hydroxy-5-methylphenyl)-2-(4-methoxyphenyl)ethan-1-one (1n)

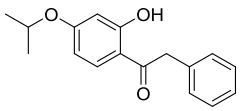
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, 1H), 7.64 (d, *J* = 1.5 Hz, 1H), 7.28 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.21 – 7.15 (m, 2H), 6.93 – 6.85 (m, 3H), 4.23 (s, 2H), 3.79 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.20, 160.87, 158.80, 137.71, 130.64, 130.13, 128.16, 125.99, 118.77, 118.48, 114.30, 55.36, 44.22, 20.73.

Method B: Alkaline hydrolysis of isoflavone.[5]



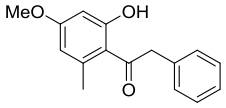
To a solution of isoflavone **S3** (5 mmol) in MeOH (20mL) was added 10% aq. NaOH (10 mL). The mixture was stirred at 60 ^{o}C for about 3 h, at this time TLC indicated completion. After reaction was cooled to room temperature, the organic solvent was removed under reduce pressure. The residue was dissolved in 30 mL EtOAc, and the solvent was acidified with 10% aq. HCl (ca. 15 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The solvent removed under reduced pressure and the residual was further purified by a short flash column chromatography to give compound **1**.



1-(2-hydroxy-4-isopropoxyphenyl)-2-phenylethan-1-one (1a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.71 (s, 1H), 7.77 – 7.70 (m, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.25 (m, 3H), 6.40 (m, 2H), 4.58 (hept, *J* = 6.1 Hz, 1H), 4.20 (s, 2H), 1.34 (d, *J* = 6.1 Hz, 6H).

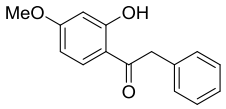
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.89, 165.93, 164.83, 134.57, 132.23, 129.44, 128.83, 127.16, 112.91, 109.01, 102.21, 70.51, 44.87, 21.94.



1-(2-hydroxy-4-methoxy-6-methylphenyl)-2-phenylethan-1-one (1h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.20 (s, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.30 (dd, *J* = 10.2, 2.5 Hz, 2H), 4.24 (s, 2H), 3.80 (s, 3H), 2.62 (s, 3H).

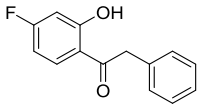
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.03, 167.16, 164.51, 141.38, 134.69, 129.68, 128.65, 127.08, 115.33, 112.24, 99.26, 55.49, 50.06, 25.39.



1-(2-hydroxy-4-methoxyphenyl)-2-phenylethan-1-one (1i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.72 (s, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 6.47 – 6.38 (m, 2H), 4.21 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.06, 166.27, 165.96, 134.48, 132.15, 129.44, 128.85, 127.18, 113.25, 107.95, 101.10, 55.69, 44.95.

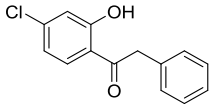


1-(4-fluoro-2-hydroxyphenyl)-2-phenylethan-1-one (1k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 7.86 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.32 – 7.25 (m, 3H), 6.72 – 6.53 (m, 2H), 4.25 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -98.85.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.74 (s), 167.47 (d, *J* = 257.2 Hz), 165.54 (d, *J* = 14.3 Hz), 133.74 (s), 132.82 (d, *J* = 11.8 Hz), 129.35 (s), 128.88 (s), 127.33 (s), 116.19 (d, *J* = 2.3 Hz), 107.35 (d, *J* = 22.9 Hz), 105.20 (d, *J* = 23.6 Hz), 45.28 (s).

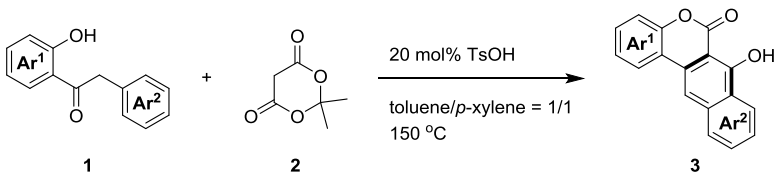


1-(4-chloro-2-hydroxyphenyl)-2-phenylethan-1-one (1l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.35 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.35 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.2 Hz, 1H), 4.26 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.29, 163.66, 142.41, 133.66, 131.51, 129.44, 128.98, 127.46, 119.81, 118.81, 117.67, 45.39.

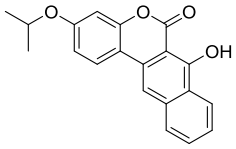
General procedure for TsOH-mediated tandem reaction



1 2 3

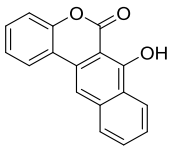
To a 25 mL round-bottomed flask with a condenser pipe was added 1-(2-hydroxyphenyl)-2-phenylethanone **1** (1.0 mmol), meldrum's acid **2** (288 mg, 2.0 mmol), TsOH (35 mg, 20 mol%), followed by the solvent of toluene (5.0 mL) and *p*-xylene (5.0 mL). The reaction mixture was heated at 150 °C for 1 h. Then, another batch of meldrum's acid **2** (288 mg,

2.0 mmol) and TsOH (35 mg, 20 mol%) was added to the above mixture. The reaction was stirred at 150 ^{o}C for another one hour. At the end, the third batch of meldrum's acid **2**(144 mg, 1.0 mmol) and TsOH (18 mg, 10 mol%) was added to the reaction, and the reaction was stirred another 1.5 h. The reaction was cooled to room temperature and then concentrated. The crude product was further purified by silica gel chromatography to give desired product **3**.



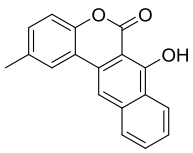
7-hydroxy-3-isopropoxy-6H-naphtho[2,3-c]chromen-6-one (3a)

Yellow solid. m.p. 156.2-157.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.55 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 4.61 (hept, *J* = 6.1 Hz, 1H), 1.40 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82, 162.60, 159.60, 151.30, 137.84, 130.65, 129.07, 127.57, 125.44, 124.20, 124.15, 122.99, 114.23, 111.36, 109.32, 103.24, 99.59, 70.58, 21.91. HRMS (APCI): m/z: calcd. for $C_{20}H_{17}O_4$ $[M + H]^+$ 321.1121; found 321.1132.



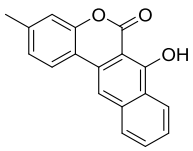
7-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3b)

Yellow solid. m.p. 202.8-203.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.67 – 7.59 (m, 1H), 7.52 – 7.45 (m, 1H), 7.44 – 7.36 (m, 1H), 7.34 – 7.28 (m, 1H), 7.27 – 7.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.47, 162.51, 150.09, 137.46, 130.69, 130.04, 128.50, 127.77, 125.97, 125.08, 124.09, 123.52, 123.11, 118.73, 117.72, 110.55, 99.94. HRMS (APCI): m/z: calcd. for $C_{17}H_{11}O_3$ $[M + H]^+$263.0703; found 263.0705.



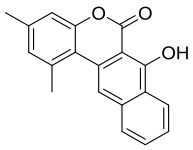
7-hydroxy-2-methyl-6H-naphtho[2,3-c]chromen-6-one (3c)

Yellow solid. m.p. 213.0-213.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.74 (m, 3H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.12 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 162.55, 148.20, 137.50, 134.72, 130.95, 130.64, 128.67, 127.76, 125.88, 124.12, 123.51, 123.11, 118.29, 117.43, 110.40, 100.04, 21.13. HRMS (APCI): m/z: calcd. for $C_{18}H_{13}O_3$ $[M + H]^+$ 277.0859; found 277.0863.



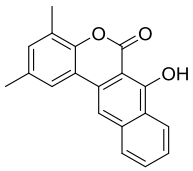
7-hydroxy-3-methyl-6H-naphtho[2,3-c]chromen-6-one (3d)

Yellow solid. m.p. 188.3-189.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.57 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.74 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.04 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.71, 162.50, 150.03, 140.86, 137.60, 130.61, 128.79, 127.69, 126.18, 125.71, 124.10, 123.32, 122.87, 117.81, 116.03, 110.03, 99.92, 21.34. HRMS (APCI): m/z: calcd. for $C_{18}H_{13}O_3$ $[M + H]^+$ 277.0859; found 277.0864.



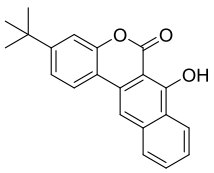
7-hydroxy-1,3-dimethyl-6H-naphtho[2,3-c]chromen-6-one (3e)

Yellow solid. m.p. 199.7-200.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.98 (s, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 7.99 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 2H), 2.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.81, 162.66, 151.02, 139.39, 137.25, 136.39, 130.52, 130.48, 130.02, 128.23, 125.98, 123.84, 122.84, 116.26, 115.78, 115.41, 100.36, 25.65, 20.93. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_3$ $[M + H]^+$ 291.1016; found 291.1019.



7-hydroxy-2,4-dimethyl-6H-naphtho[2,3-c]chromen-6-one (3f)

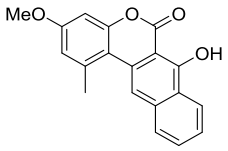
Yellow solid. m.p. 210.0-210.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.71 (s, 1H), 7.63 (dd, *J* = 11.6, 4.5 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.60, 162.38, 146.53, 137.49, 133.99, 132.44, 130.49, 129.03, 127.73, 126.60, 125.70, 124.02, 123.31, 120.66, 117.92, 110.42, 99.95, 21.04, 15.78. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_3$ $[M + H]^+$ 291.1016; found 291.1020.



3-(tert-butyl)-7-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3g)

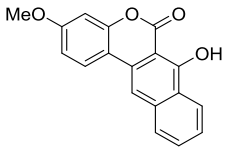
Yellow solid. m.p. 148.0-148.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.61 (s, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H),

7.37 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82, 162.54, 154.36, 150.06, 137.64, 130.63, 128.79, 127.73, 125.76, 124.14, 123.41, 122.81, 122.54, 116.05, 114.55, 110.18, 100.04, 35.01, 31.12. HRMS (APCI): m/z: calcd. for $C_{21}H_{19}O_3$ $[M + H]^+$ 319.1329; found 319.1342.



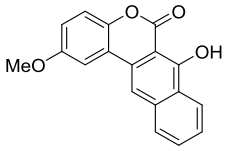
7-hydroxy-3-methoxy-1-methyl-6H-naphtho[2,3-c]chromen-6-one (3h)

Yellow solid. m.p. 213.1-213.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.90 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 6.57 (d, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 168.21, 162.83, 159.18, 151.67, 138.34, 137.77, 131.21, 129.71, 128.22, 126.19, 123.95, 122.29, 117.32, 115.40, 111.24, 100.07, 99.15, 55.64, 25.96. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_4$ $[M + H]^+$ 307.0965; found 307.0973.



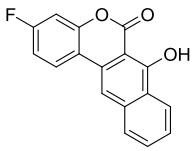
7-hydroxy-3-methoxy-6H-naphtho[2,3-c]chromen-6-one (3i)

Yellow solid. m.p. 191.1-191.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.70 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 162.61, 161.19, 151.26, 137.82, 130.68, 128.95, 127.58, 125.50, 124.17, 124.14, 123.03, 112.88, 111.67, 109.40, 101.69, 99.56, 55.67. HRMS (APCI): m/z: calcd. for $C_{18}H_{13}O_4$ $[M + H]^+$293.0808; found 293.0816.



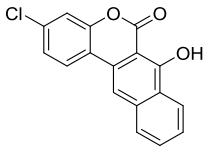
7-hydroxy-2-methoxy-6H-naphtho[2,3-c]chromen-6-one (3j)

Yellow solid. m.p. 214.3-215.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.57 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (s, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 168.07, 162.61, 156.61, 143.95, 137.66, 131.37, 127.97, 127.86, 126.48, 124.18, 123.34, 119.24, 118.76, 117.07, 111.13, 106.63, 98.93, 56.10. HRMS (APCI): m/z: calcd. for $C_{18}H_{13}O_4$ $[M + H]^+$ 293.0808; found 293.0815.



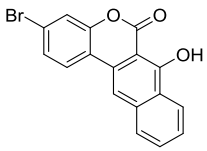
3-fluoro-7-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3k)

Yellow solid. m.p. 250.3-251.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.35 (d, J = 8.4 Hz, 1H), 8.08 (dd, J = 8.4, 6.1 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.78 (s, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 168.22, 163.27 (d, $^{1}J_{C\text{-}F}$ = 251.7 Hz), 162.92, 150.04 (d, $^{3}J_{C\text{-}F}$ = 12.2 Hz), 137.99, 131.68, 127.77, 127.53, 126.52, 124.79 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 124.27, 123.22, 115.17, 113.74 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 109.96, 105.16 (d, $^{2}J_{C\text{-}F}$ = 25.7 Hz), 98.57.^{19}F NMR (376 MHz, $CDCl_3$) δ -109.42. HRMS (APCI): m/z: calcd. for $C_{17}H_{10}FO_3$ $[M + H]^+$ 281.0608; found 281.0617.



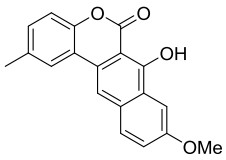
3-chloro-7-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3l)

Yellow solid. m.p. 228.0-228.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.30 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.74 (s, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.30 (dd, J = 8.6, 2.1 Hz, 1H), 7.20 (d, J = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 167.84, 162.84, 149.49, 137.85, 135.83, 131.67, 127.86, 127.31, 126.69, 126.25, 124.26, 124.09, 123.37, 117.92, 117.26, 111.28, 98.66. HRMS (APCI): m/z: calcd. for $C_{17}H_{10}ClO_3$ $[M + H]^+$ 297.0313; found 297.0325.



3-bromo-7-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3m)

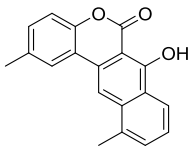
Yellow solid. m.p. 214.9-215.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.29 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.73 (s, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.34 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 167.54, 162.77, 149.51, 137.76, 131.64, 129.02, 127.87, 127.34, 126.70, 124.26, 124.23, 123.46, 123.40, 120.85, 117.66, 111.23, 98.73. HRMS (APCI): m/z: calcd. for $C_{17}H_{10}BrO_3$ $[M + H]^+$ 340.9808; found 340.9823.



7-hydroxy-9-methoxy-2-methyl-6H-naphtho[2,3-c]chromen-6-one (3n)

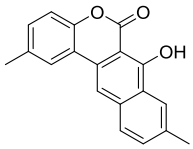
Yellow solid. m.p. 217.4-218.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.52 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 2.5 Hz, 1H), 7.29 (dd, J = 8.9, 2.6 Hz, 1H), 7.20 – 7.11 (m,

2H), 3.94 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.78, 160.86, 157.86, 147.94, 134.64, 132.93, 130.39, 129.34, 126.50, 124.44, 123.68, 122.82, 118.51, 117.33, 110.35, 101.61, 100.33, 55.53, 21.14. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_4$ $[M + H]^+$ 307.0965; found 307.0973.



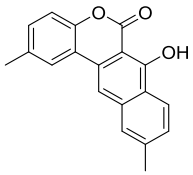
7-hydroxy-2,11-dimethyl-6H-naphtho[2,3-c]chromen-6-one (3o)

Yellow solid. m.p.190.1-191.4^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.72 (s, 1H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.33 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.14 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 2.66 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 162.57, 148.10, 136.55, 134.64, 134.17, 131.21, 130.82, 128.09, 125.49, 123.48, 122.79, 122.12, 118.39, 117.34, 106.47, 99.63, 21.13, 19.67. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_3$ $[M + H]^+$ 291.1016; found 291.1026.



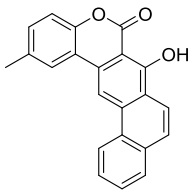
7-hydroxy-2,9-dimethyl-6H-naphtho[2,3-c]chromen-6-one (3p)

Yellow solid. m.p. 193.9-194.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 8.11 (s, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.08 (m, 2H), 2.51 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 161.89, 148.05, 135.95, 135.69, 134.62, 132.87, 130.63, 127.71, 127.61, 123.52, 122.99, 122.91, 118.43, 117.35, 110.25, 100.00, 21.79, 21.14. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_3$ $[M + H]^+$ 291.1016; found 291.1026.



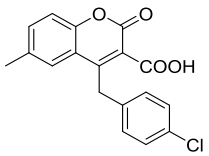
7-hydroxy-2,10-dimethyl-6H-naphtho[2,3-c]chromen-6-one (3q')

Yellow solid. m.p. 194.5-194.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.61 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 7.85 (s, 1H), 7.73 (s, 1H), 7.59 (s, 1H), 7.34 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.23 – 7.18 (m, 2H), 2.54 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.84, 162.62, 148.31, 141.29, 137.98, 134.73, 130.95, 128.87, 128.29, 126.98, 124.07, 123.21, 121.75, 118.53, 117.54, 109.96, 99.60, 22.19, 21.27. HRMS (APCI): m/z: calcd. for $C_{19}H_{15}O_3$ $[M + H]^+$ 291.1016; found 291.1026.



7-hydroxy-2-methyl-6H-phenanthro[2,3-c]chromen-6-one (3r)

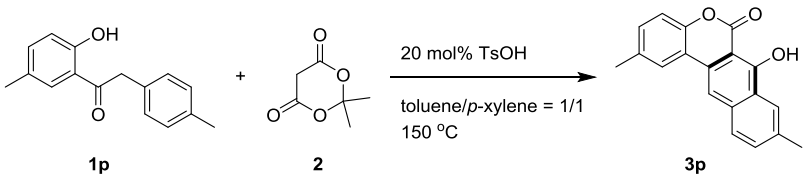
Yellow solid. m.p. 228.4-229.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.23 (s, 1H), 8.50 – 8.45 (m, 1H), 8.26 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.62 – 7.53 (m, 3H), 7.17 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 161.15, 148.34, 135.80, 134.70, 133.77, 131.05, 129.75, 129.13, 128.79, 128.41, 126.85, 126.77, 123.52, 122.91, 121.16, 120.51, 118.30, 117.43, 105.22, 101.26, 21.17. HRMS (APCI): m/z: calcd. for $C_{22}H_{15}O_3$ $[M + H]^+$327.1016; found 327.1027.



4-(4-chlorobenzyl)-6-methyl-2-oxo-2H-chromene-3-carboxylic acid (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.52 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.36 (d, *J* = 8.5 Hz,1H), 7.25 – 7.21 (m, 2H), 7.15 – 7.07 (m, 2H), 4.96 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.72, 164.17, 163.36, 150.87, 136.59, 136.19, 135.38, 132.81, 129.68, 129.14, 127.25, 119.52, 117.39, 113.67, 34.30, 21.40.

Gram-scale synthesis



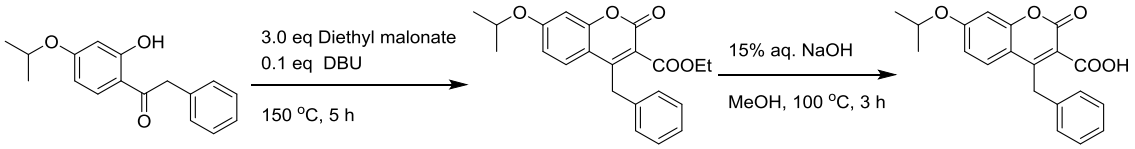
1p **2** **3p**

To a 100 mL round-bottomed flask with a condenser pipe was added 1-(2-hydroxy-5-methylphenyl)-2-(p-tolyl)ethan-1-one **1p** (4.5 mmol, 1.08 g), meldrum's acid **2** (9.0 mmol, 1.3 g), TsOH (20 mol%, 155 mg), followed by the solvent of toluene (22.5 mL) and *p*-xylene (22.5 mL). The reaction mixture was heated at 150 ^{o}C for 1 h. Then, another batch of meldrum's acid **2** (9.0 mmol, 1.3 g) and TsOH (20 mol%, 155 mg) was added to the above mixture. The reaction was stirred at 150 ^{o}C for another one hour. At the end, the third batch of meldrum's acid **2** (4.5 mmol, 650 mg) and TsOH (10 mol%, 78 mg) was added to the reaction, and the reaction was stirred another 1.5 h. The reaction was cooled to room temperature and then concentrated. The crude product was further purified by silica gel chromatography to give desired

product **3p** (0.915 g, 70% isolated yield).

Mechanistic studies

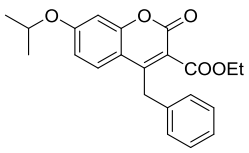
Procedure for the synthesis of intermediate (4)



1a **S4** **4**

To a 25 mL tube were added 1-(2-hydroxy-4-isopropoxyphenyl)-2-phenylethan-1-one (**1a**, 1.35 g, 5.0 mmol), Diethyl malonate (2.4 g, 15 mmol), and DBU (76 mg, 0.5 mmol). The reaction was stirred at 150 ^{o}C for 5 h. And the crude product was purified by flash chromatography to give the desired product **S4** (0.89 g yellow oil, 48%).

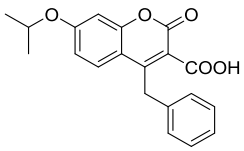
Then the compound **S4** (0.73 g, 2.0 mmol) was dissolved in MeOH (6.0 mL, 0.33 M), and 15% aq. NaOH (6.0 mL) was added to the reaction. The mixture was stirred at 100 ^{o}C for 3 h. After reaction was cooled to room temperature, the organic solvent was removed under reduce pressure. The residuewas dissolved in 20 mL EtOAc, and the solvent was acidified with 10% aq. HCl (ca. 10 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residual was further purified by a short flash column chromatography to give compound **4** (0.53 g white solid, 78%).



ethyl 4-benzyl-7-isopropoxy-2-oxo-2H-chromene-3-carboxylate (S4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.9 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.15 (m, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.71 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.64 – 4.49 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.18 (s, 2H), 1.34 (d, *J* = 6.1 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16, 161.78, 158.54, 155.40, 151.80, 136.67, 128.89, 128.35, 127.56, 127.00, 119.02, 114.05, 111.37, 102.13, 70.83, 62.06, 35.73, 21.76, 14.05.



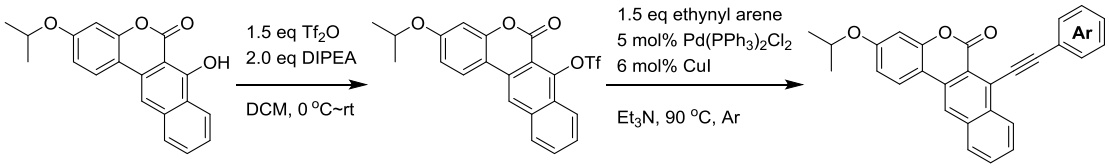
4-benzyl-7-isopropoxy-2-oxo-2H-chromene-3-carboxylic acid (4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.21 (s, 1H), 7.81 (d, *J* = 9.1 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.23 – 7.14 (m, 3H), 6.88 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 5.05 (s, 2H), 4.71 – 4.59 (m, 1H), 1.39 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.60, 165.45, 164.03, 163.74, 155.01, 137.22, 129.42, 128.94, 128.37, 126.86, 116.08, 113.33, 109.68, 101.60, 71.67, 34.90, 21.80.

Transformation of the 7-hydroxy-6H-naphtho[2,3-c]chromen-6-one

Procedure for the synthesis of 7-(phenylethynyl)-6H-naphtho[2,3-c]chromen-6-one (10a-d)

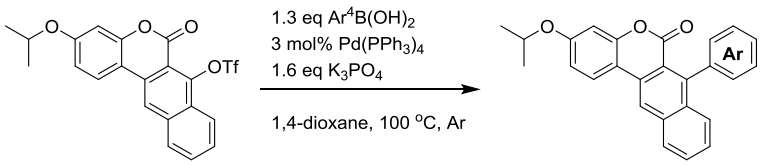


3a **5** **6a-d**

Compound **3a** (0.5 mmol) and DIPEA (130 mg, 1.0 mmol) was dissolved in 4.0 mL DCM, and the solution of Tf_2O (212 mg, 1.5 equiv) in 1.0 mL DCM was added dropwise at 0 °C. Then the mixture was warmed up to room temperature and stirred 1 h. The crude product **5** was obtained by removing the solvent under reduced pressure, which was used for the next step without further purification.[6]

The alkynylation of **5** followed reported literature.[7] To a 50 mL tube containing **5** were added ethynyl arene (1.5 equiv), $Pd(PPh_3)_2Cl_2$(3 mol%), and CuI (6 mol%). The tube was filled with argon, then the Et_3N (10 mL) was added to the tube. The mixture was heated at 90 °C for 12 h. The reaction was cooled to room temperature and then concentrated. The crude product was further purified by silica gel chromatography to give desired product **6a-d**.

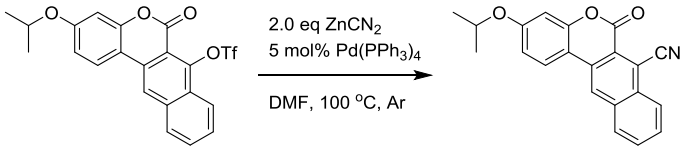
Procedure for the synthesis of 7-aryl-6H-naphtho[2,3-c]chromen-6-one (6e-i)



5 **6e-i**

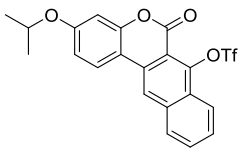
The compound **5** was prepared according to above procedure. The arylation of **5** followed reported literature.[8] Then to a 50 mL tube containing **5** were added arylboronic acid (1.3 equiv), $Pd(PPh_3)_4$ (3 mol%), and K_3PO_4 (1.6 equiv). The tube was filled with argon, then the 1,4-dioxane (5.0 mL) was added to the tube. The mixture was heated at 100 ^oC for 12 h. The reaction was cooled to room temperature and then concentrated. The crude product was further purified by silica gel chromatography to give desired product **6e-i**.

Procedure for the synthesis of 7-cyano-6H-naphtho[2,3-c]chromen-6-one (6j)



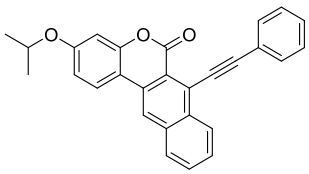
5 **6j**

The compound **5** was prepared according to above procedure. The cyanation of **5** followed reported literature.[9] Then to a 50 mL tube containing **5** were added $ZnCN_2$ (2.0 mmol) and $Pd(PPh_3)_4$ (5 mol%). The tube was filled with argon, and then the DMF (3.0 mL) was added to the tube. The mixture was heated at 100 ^oC for 12 h. The reaction was cooled to room temperature and then concentrated. The crude product was further purified by silica gel chromatography to give desired product **6j.**



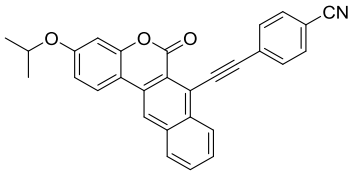
3-isopropoxy-6-oxo-6H-naphtho[2,3-c]chromen-7-yl trifluoromethanesulfonate (5)

m.p. 150.0-150.8 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.66 – 7.60 (m, 1H), 6.88 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 4.61 (hept, *J* = 6.0 Hz, 1H), 1.39 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.38, 158.21, 151.87, 147.55, 137.25, 131.15, 130.54, 128.11, 128.02, 125.43, 124.23, 122.75, 119.84, 118.768 (d, *J* = 320.9 Hz), 114.31, 111.39, 109.58, 102.92, 70.74, 21.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.12. HRMS (APCI): m/z: calcd. for $C_{21}H_{16}FO_6S$ $[M + H]^+$ 453.0614; found 453.0612.



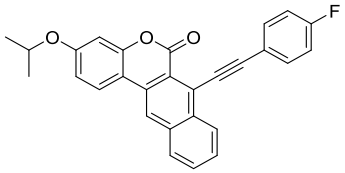
3-isopropoxy-7-(phenylethynyl)-6H-naphtho[2,3-c]chromen-6-one (6a)

m.p. 125.3-126.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.25 (s, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.64 – 7.57 (m, 2H), 7.47 – 7.40 (m, 3H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 4.64 – 4.57 (m, 1H), 1.40 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.79, 159.59, 152.09, 135.31, 133.07, 132.22, 130.83, 129.45, 129.10, 128.50, 128.20, 127.94, 127.33, 126.10, 123.97, 123.44, 119.55, 119.25, 113.58, 110.62, 104.44, 102.85, 87.11, 70.50, 21.95.HRMS (APCI): m/z: calcd. for $C_{28}H_{21}O_3$ $[M + H]^+$405.1485; found 405.1478.



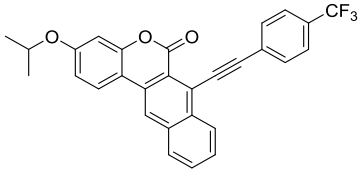
3-isopropoxy-7-((4-cyanophenyl)ethynyl)- 6H-naphtho[2,3-c]chromen-6-one (6b)

m.p. 235.8-236.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.0 Hz, 1H), 8.36 (s, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.61 (m, 2H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 4.62 (hept, *J* = 6.1 Hz, 1H), 1.40 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 162.12, 159.96, 135.54, 132.91, 132.64, 132.34, 130.76, 130.08, 128.40, 127.99, 127.51, 125.03, 124.03, 120.72, 118.39, 118.05, 114.51, 111.50, 110.39, 102.84, 102.28, 90.72, 70.98, 21.93.HRMS (APCI): m/z: calcd. for $C_{29}H_{20}NO_3$ $[M + H]^+$ 430.1438; found 430.1435.



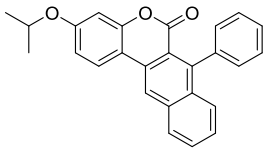
3-isopropoxy-7-((4-fluorophenyl)ethynyl)-6H-naphtho[2,3-c]chromen-6-one (6c)

m.p. 163.3-164.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.26 (s, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.80 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.60 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 4.67 – 4.54 (m, 1H), 1.40 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.12 (d, $^{1}J_{C\text{-}F}$ = 250.8 Hz), 159.82, 159.59, 152.09, 135.32, 134.19 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 132.96, 130.88, 129.45, 128.20, 127.83, 127.33, 125.94, 123.95, 119.55, 119.44 (d, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 115.94, 115.72, 113.62, 110.60, 103.27, 102.86, 86.90, 70.53, 21.93.^{19}F NMR (376 MHz, $CDCl_3$) δ -109.52.HRMS (APCI): m/z: calcd. for $C_{28}H_{20}FO_3$ $[M + H]^+$ 423.1391; found 423.1381.



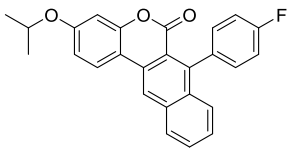
3-isopropoxy-7-((4-(trifluoromethyl)phenyl)ethynyl)-6H-naphtho[2,3-c]chromen-6-one (6d)

m.p. 168.2-169.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.2 Hz, 1H), 8.19 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.56 – 7.52 (m, 1H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.72 (d, *J* = 2.3 Hz, 1H), 4.63 – 4.55 (m, 1H), 1.40 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.83, 159.38, 151.99, 135.18, 132.89, 132.33, 130.79, 130.50 (q, *J* = 32.4 Hz), 129.45, 128.20, 127.55, 127.48, 127.21, 125.34 (q, *J* = 3.4 Hz), 125.00, 123.98 (q, *J* = 272.3 Hz), 123.90, 120.09, 119.53, 113.58, 110.39, 102.78, 102.18, 89.11, 70.50, 21.92.^{19}F NMR (376 MHz, $CDCl_3$) δ -62.72.HRMS (APCI): m/z: calcd. for $C_{29}H_{20}F_3O_3$ $[M + H]^+$ 473.1359; found 473.1351.



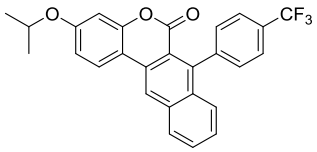
3-isopropoxy-7-phenyl-6H-naphtho[2,3-c]chromen-6-one (6e)

m.p. 208.7-209.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.61 (ddd, *J* = 8.0, 6.7, 1.0 Hz, 1H), 7.56 – 7.45 (m, 4H), 7.40 – 7.35 (m, 1H), 7.28 – 7.26 (m, 2H), 6.89 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 4.70 – 4.54 (m, 1H), 1.39 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.75, 159.69, 152.23, 147.01, 139.79, 135.84, 132.68, 130.75, 129.09, 128.61, 128.59, 128.11, 127.78, 127.25, 126.36, 124.09, 119.72, 116.18, 113.75, 111.05, 102.77, 70.49, 21.94.HRMS (APCI): m/z: calcd. for $C_{26}H_{21}O_3$ $[M + H]^+$ 381.1485; found 381.1474.



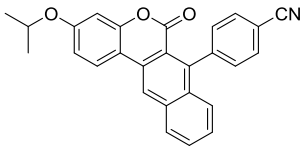
3-isopropoxy-7-(4-fluorophenyl)-6H-naphtho[2,3-c]chromen-6-one (6f)

m.p. 223.7-224.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.23 (s, 2H), 7.21 (s, 2H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 4.67 – 4.55 (m, 1H), 1.39 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.24 (d, *J* = 245.7 Hz), 159.78, 159.76, 152.17, 145.86, 135.84, 135.50 (d, *J* = 3.7 Hz), 132.72, 130.78, 130.23 (d, *J* = 7.9 Hz), 129.15, 128.32, 127.86, 126.51, 124.09, 119.94, 116.40, 115.22 (d, *J* = 21.4 Hz), 113.80, 110.95, 102.77, 70.52, 21.92.^{19}F NMR (376 MHz, $CDCl_3$) δ -115.26.HRMS (APCI): m/z: calcd. for $C_{26}H_{20}FO_3$ $[M + H]^+$ 399.1391; found 399.1386.



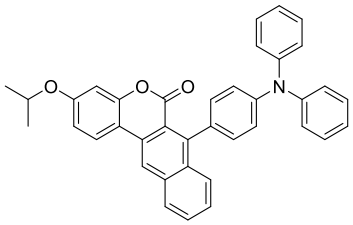
3-isopropoxy-7-(4-(trifluoromethyl)phenyl)-6H-naphtho[2,3-c]chromen-6-one (6g)

m.p. 224.7-225.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.44 – 7.32 (m, 4H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.78 (s, 1H), 4.65 – 4.56 (m, 1H), 1.39 (d, *J* = 5.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.83, 159.81, 152.11, 145.09, 143.79, 135.85, 132.14, 130.75, 129.41 (d, *J* = 32.1 Hz), 129.29, 129.03, 128.01, 127.95, 126.74, 125.14 (q, *J* = 3.2 Hz), 124.43 (q, *J* = 272.0 Hz), 124.10, 120.26, 116.13, 113.88, 110.77, 102.78, 70.53, 21.90.^{19}F NMR (376 MHz, $CDCl_3$) δ -62.19.HRMS (APCI): m/z: calcd. for $C_{27}H_{20}F_3O_3$ $[M + H]^+$ 449.1359; found 449.1359.



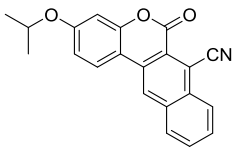
3-isopropoxy-7-(4-cyanophenyl)-6H-naphtho[2,3-c]chromen-6-one (6h)

m.p. 270.7-271.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.43 – 7.39 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 4.62 (hept, *J* = 6.1 Hz, 1H), 1.39 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.95, 152.11, 145.29, 144.43, 135.95, 132.11, 131.82, 130.84, 129.61, 129.52, 128.17, 127.79, 127.03, 124.22, 120.65, 119.23, 116.07, 114.06, 111.27, 110.69, 102.81, 70.62, 21.99.HRMS (APCI): m/z: calcd. for $C_{27}H_{20}NO_3$ $[M + H]^+$ 406.1438; found 406.1439.



3-isopropoxy-7-(4-(diphenylamino)phenyl)-6H-naphtho[2,3-c]chromen-6-one (6i)

m.p. 210.0-210.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.34 – 7.27 (m, 4H), 7.27 – 7.25 (m, 3H), 7.24 – 7.21 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.04 (t, *J* = 7.1 Hz, 2H), 6.89 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 4.67 – 4.57 (m, 1H), 1.39 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.87, 159.68, 152.22, 147.90, 147.06, 146.88, 135.87, 133.70, 132.80, 130.81, 129.55, 129.29, 129.09, 128.69, 127.82, 126.38, 124.51, 124.10, 123.30, 122.79, 119.58, 116.43, 113.60, 111.13, 102.84, 70.50, 21.93.HRMS (APCI): m/z: calcd. for $C_{38}H_{30}NO_3$ $[M + H]^+$ 548.2220; found 548.2227.



3-isopropoxy-6-oxo-6H-naphtho[2,3-c]chromene-7-carbonitrile (6j)

m.p. 257.2-258.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TFA-d_1) δ 8.68 (s, 1H), 8.40 (d, J = 7.9 Hz, 1H), 8.12 – 8.02 (m, 2H), 7.83 – 7.71 (m, 2H), 6.98 (dd, J = 8.7, 2.5 Hz, 1H), 6.82 (d, J = 2.5 Hz, 1H), 4.65 (hept, J = 6.0 Hz, 1H), 1.41 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, TFA-d_1) δ 160.62, 160.56, 151.23, 135.58, 132.91, 131.11, 130.78, 130.08, 128.84, 126.23, 125.21, 124.12, 120.21, 115.01, 111.96, 109.16, 103.18, 71.30, 21.83. HRMS (APCI): m/z: calcd. for $C_{21}H_{16}NO_3$ $[M + H]^+$ 330.1125; found 330.1116.

Table S2. Spectral properties of **3a**, **5** and **6** in dichloromethane solution (10^{-5} mol/L)

No.	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Stokes shift (nm)	ΦF (%)
3a	390	389	459	70	17
5	394	392	483	91	19
6a	413	415	496	81	78
6b	419	420	511	91	77
6c	412	414	496	82	78
6d	415	417	502	85	74
6e	384	386	463	77	28
6f	385	386	464	78	31
6g	386	387	472	85	36
6h	388	387	480	93	39
6i	392	390	563	173	14
6j	413	412	514	102	39

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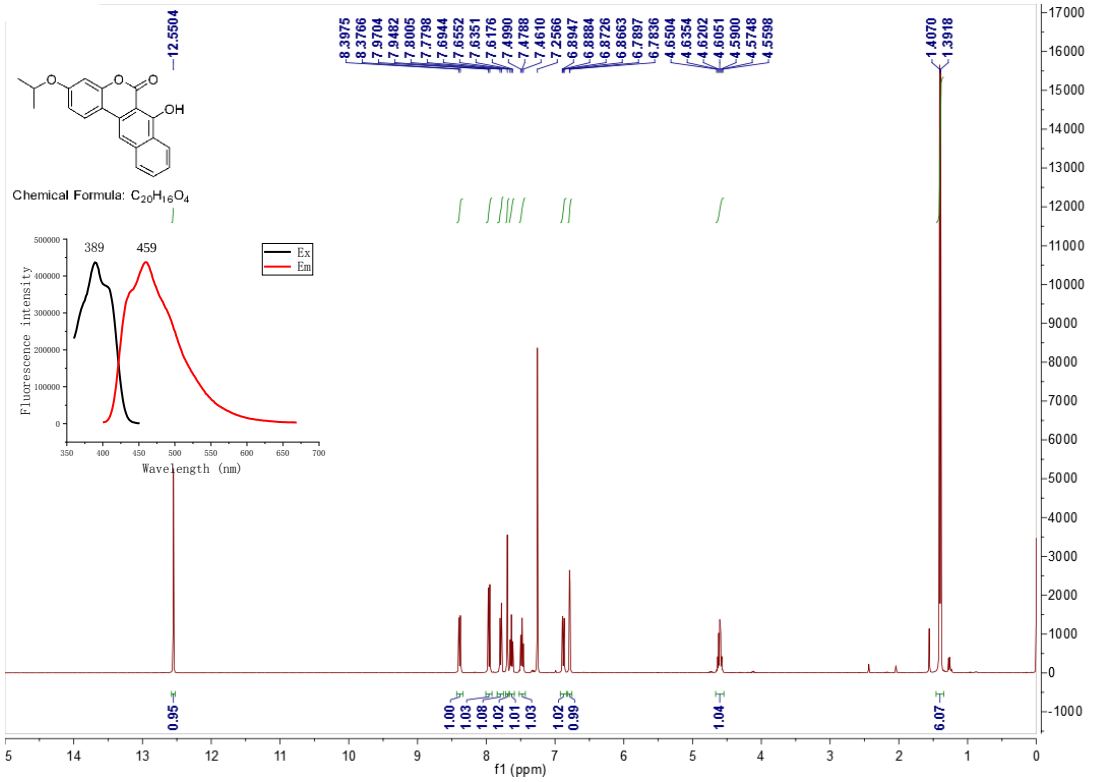
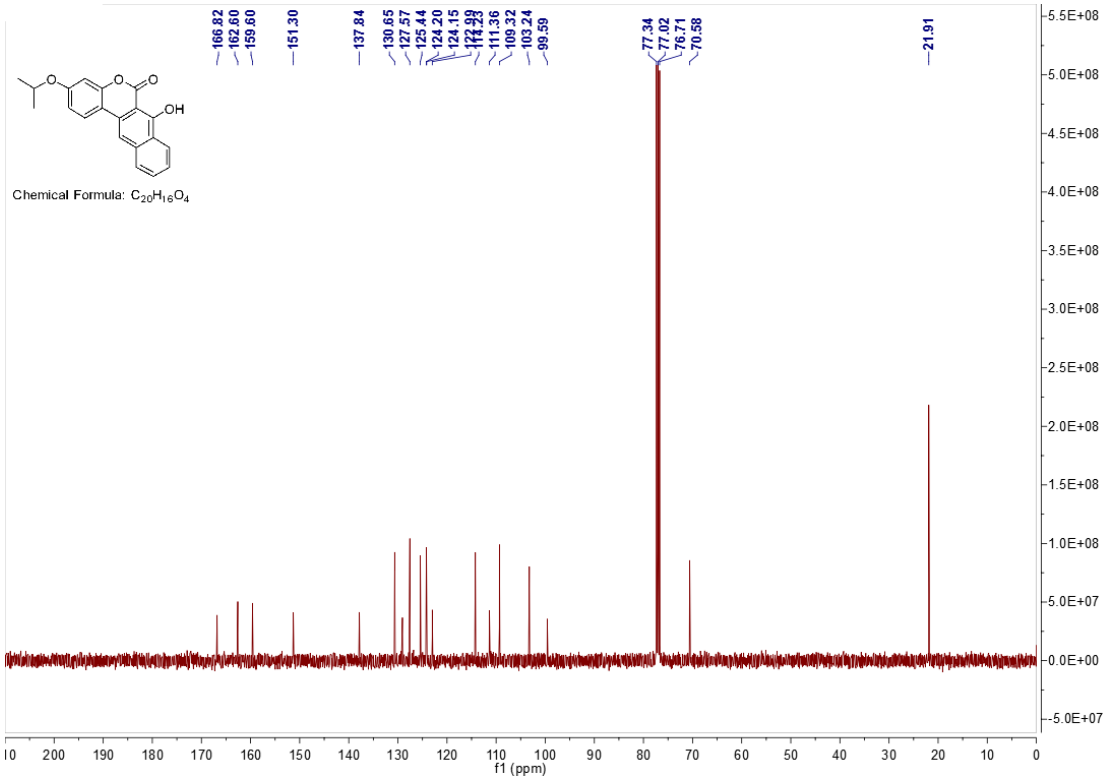
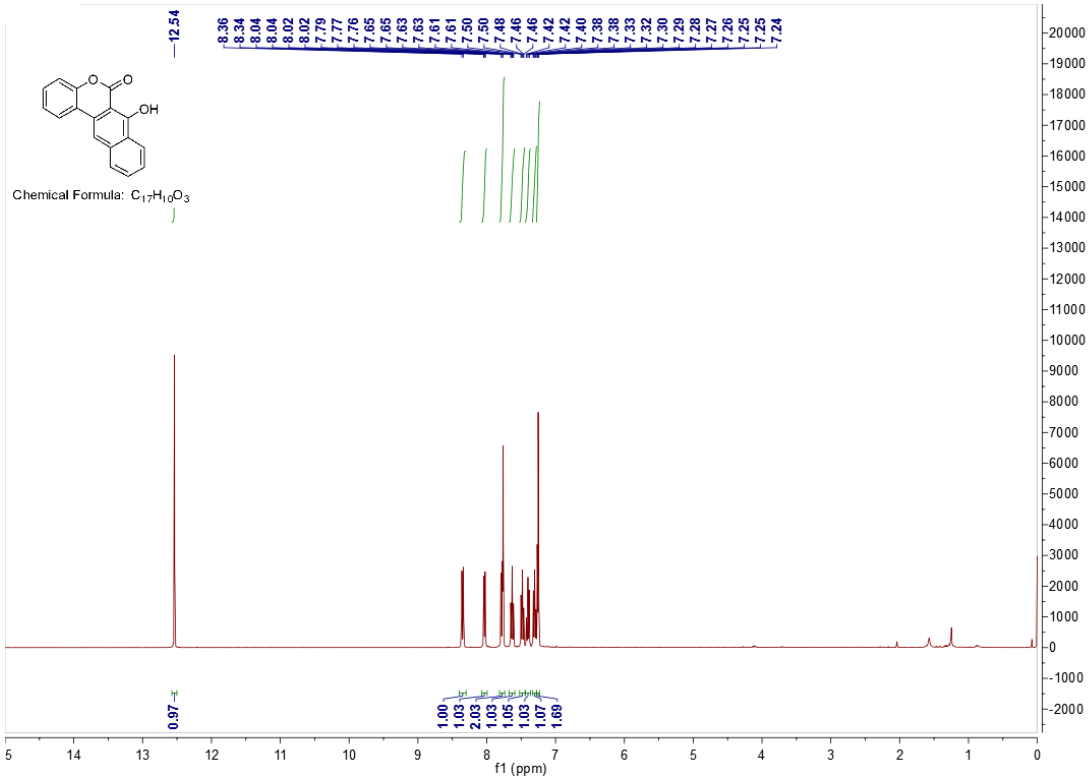
NMR Spectra



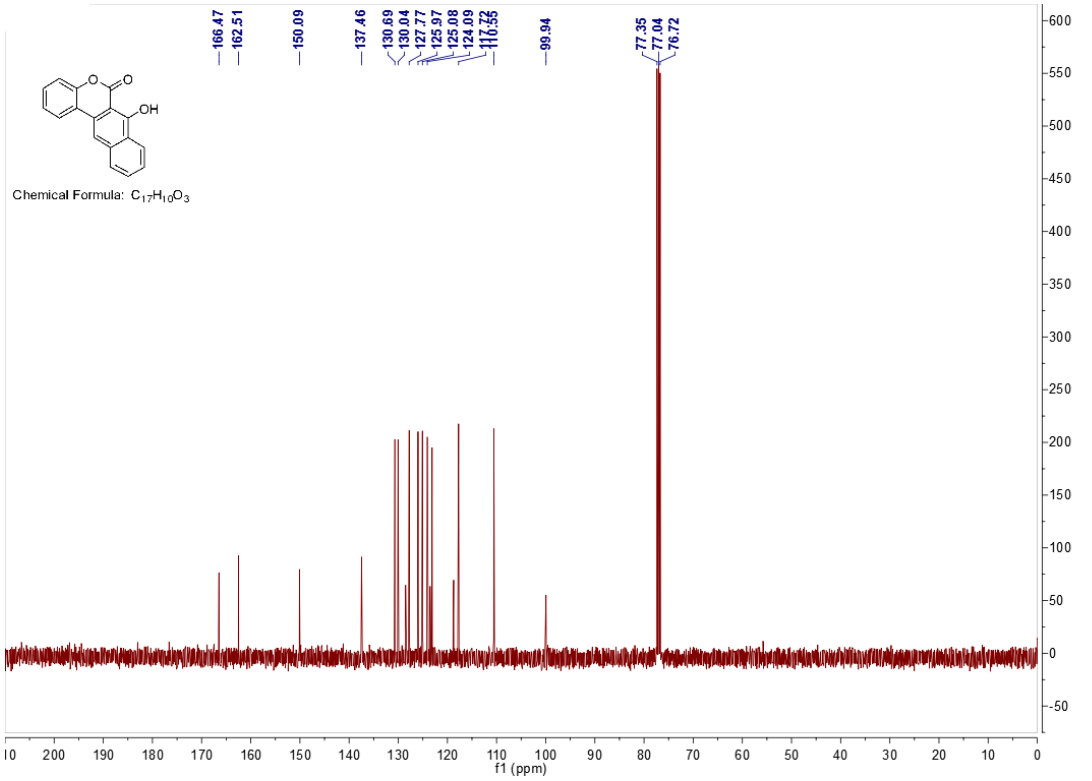
^{1}H NMR of **3a** in $CDCl_3$



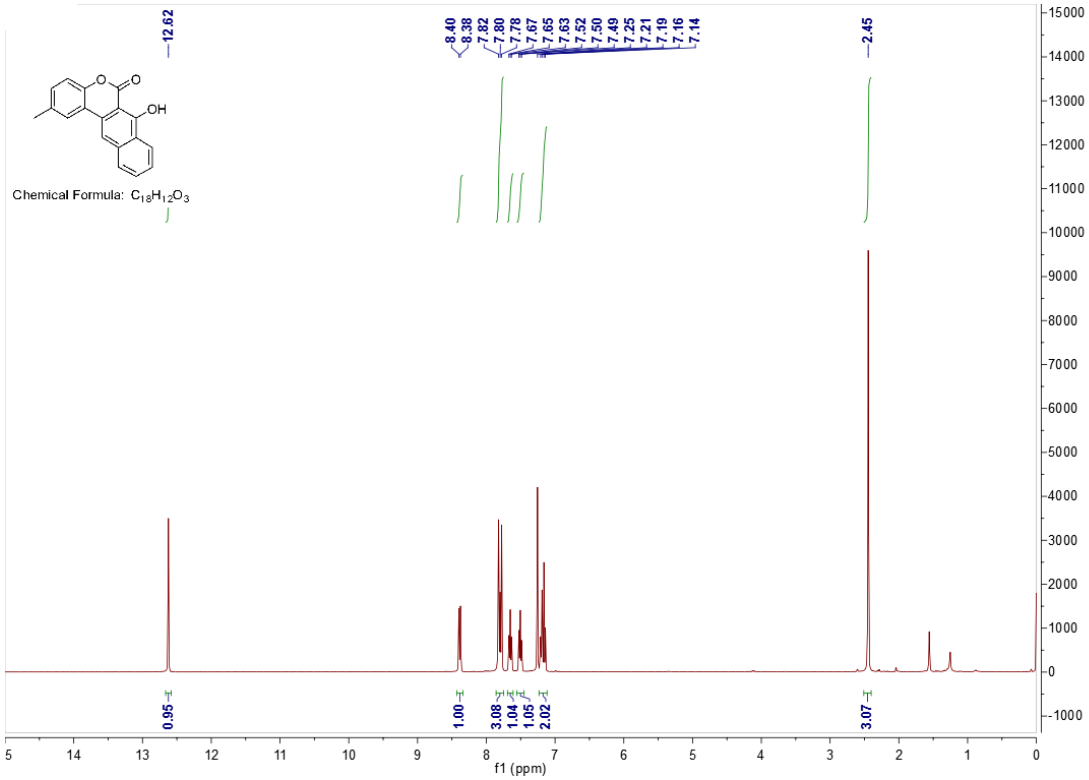
^{13}C NMR of **3a** in $CDCl_3$



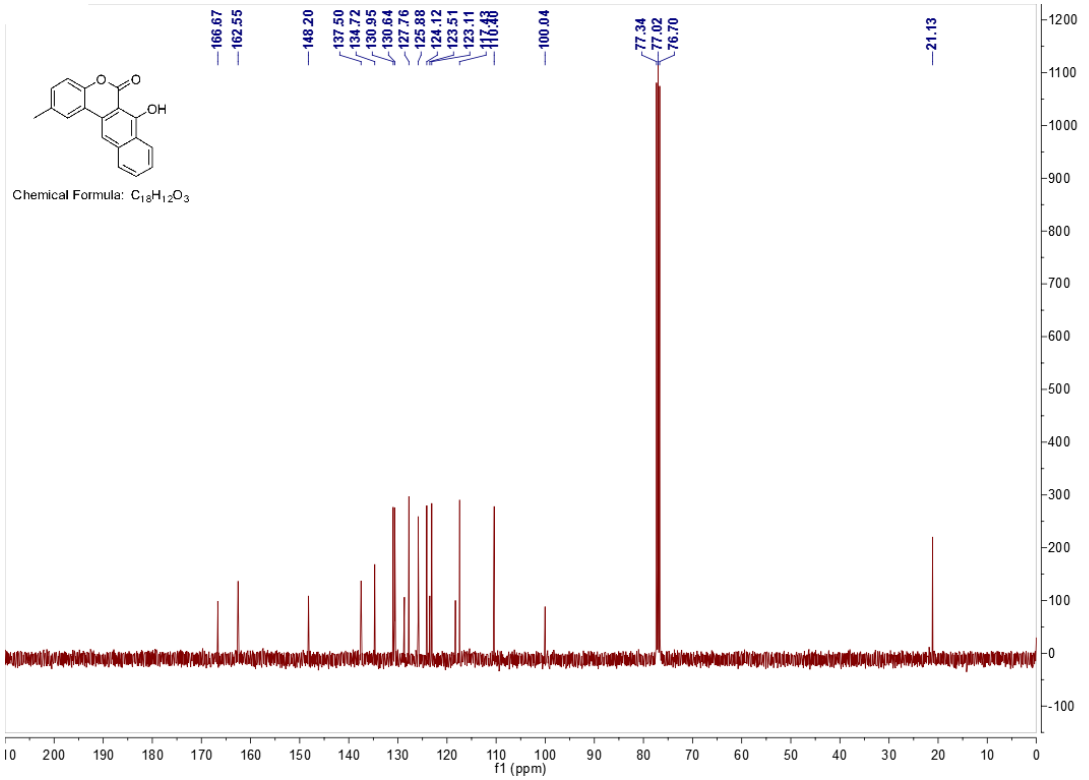
^{1}H NMR of **3b** in $CDCl_3$



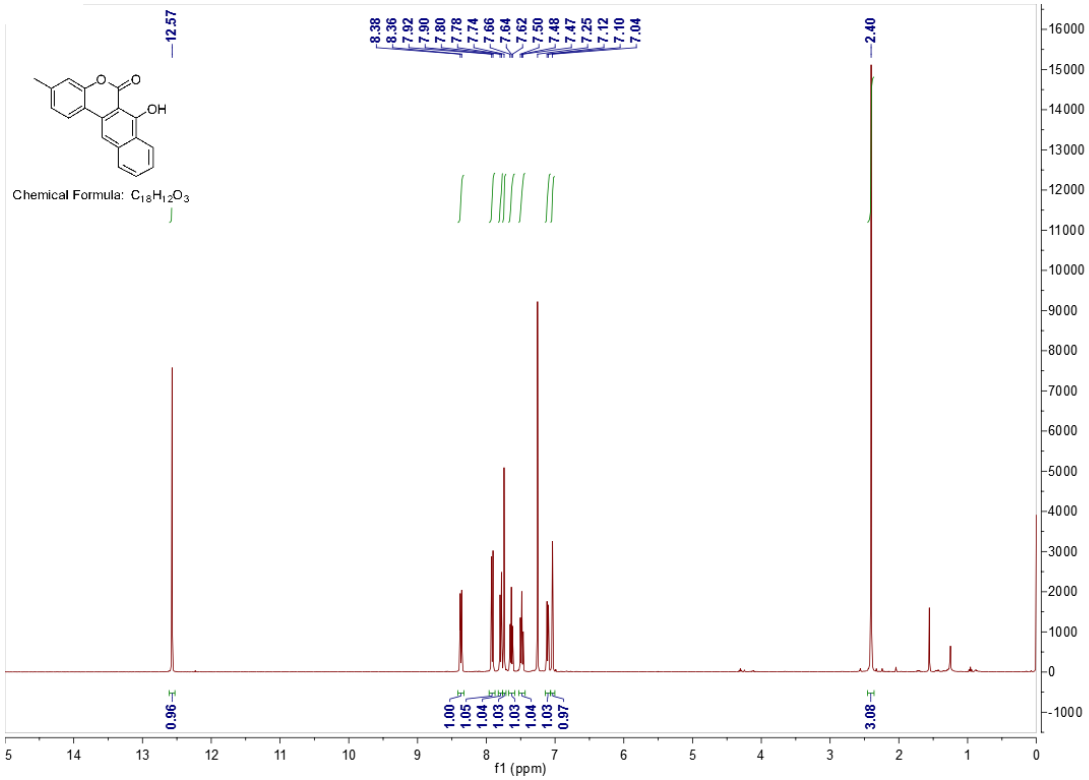
^{13}C NMR of **3b** in $CDCl_3$



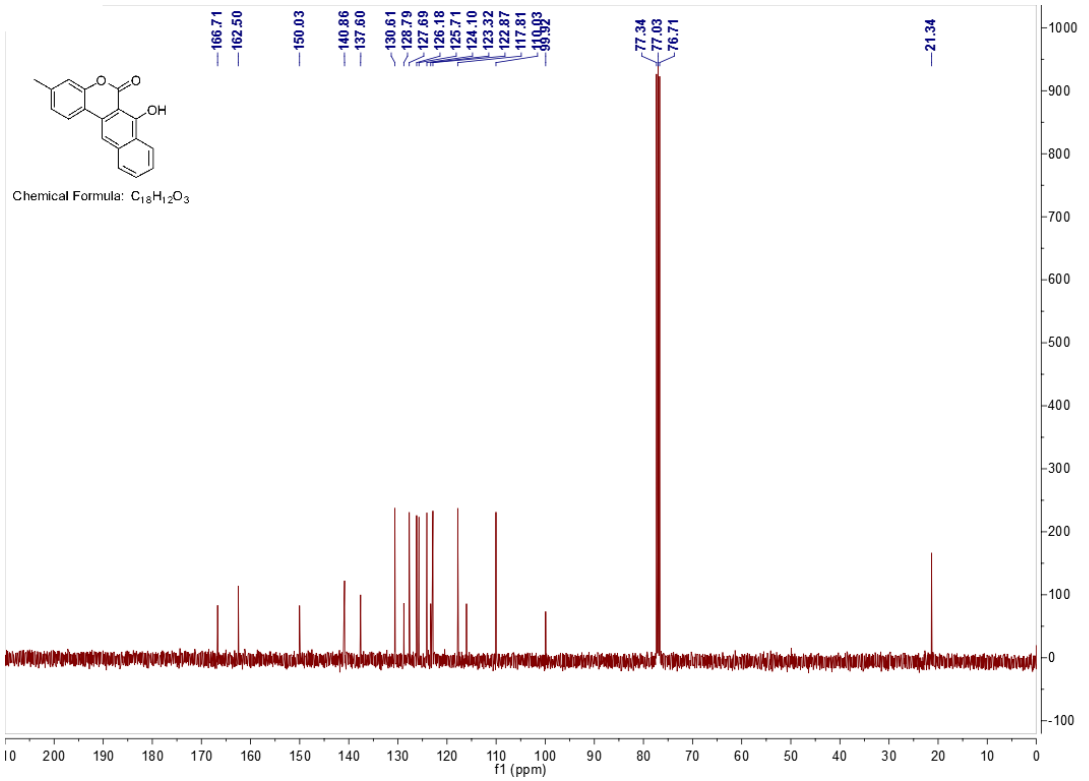
^{1}H NMR of **3c** in $CDCl_3$



^{13}C NMR of **3c** in $CDCl_3$



^{1}H NMR of **3d** in $CDCl_3$



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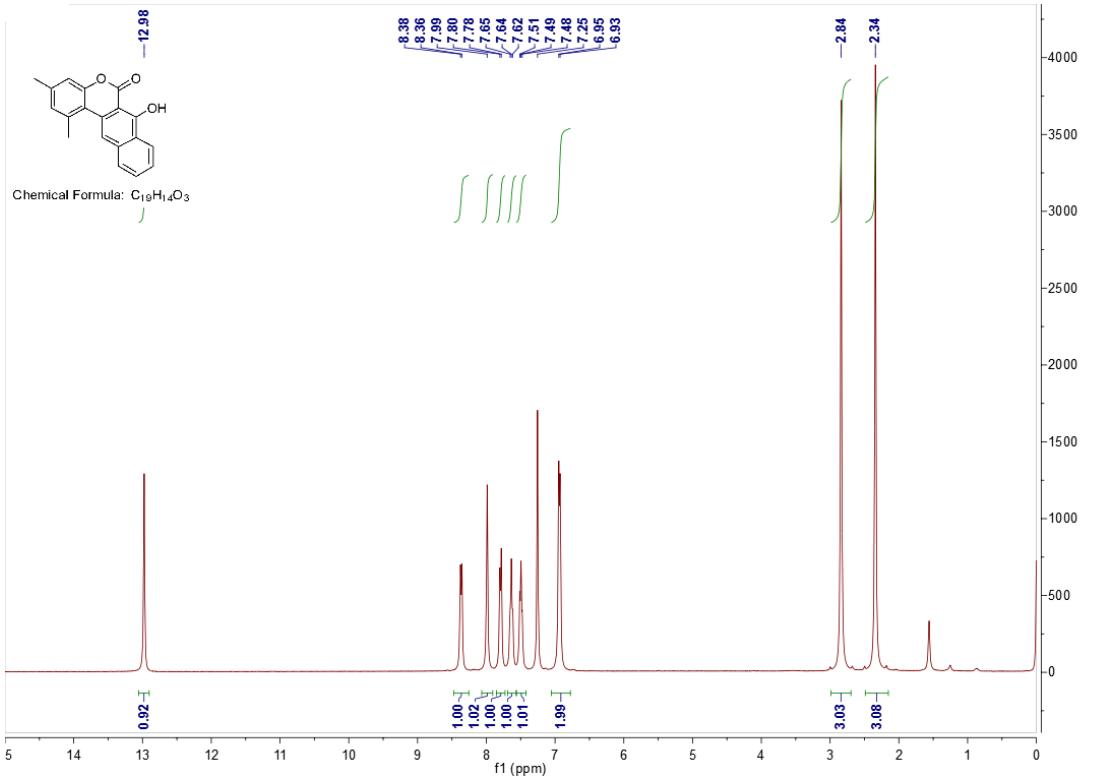

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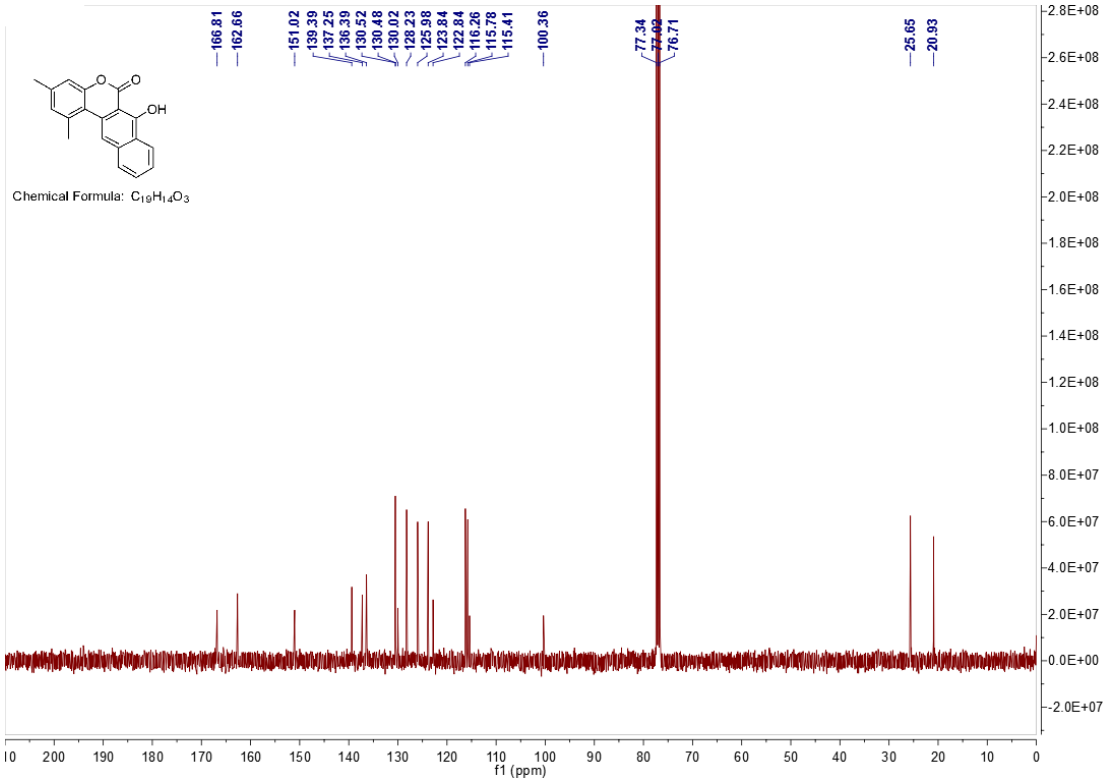

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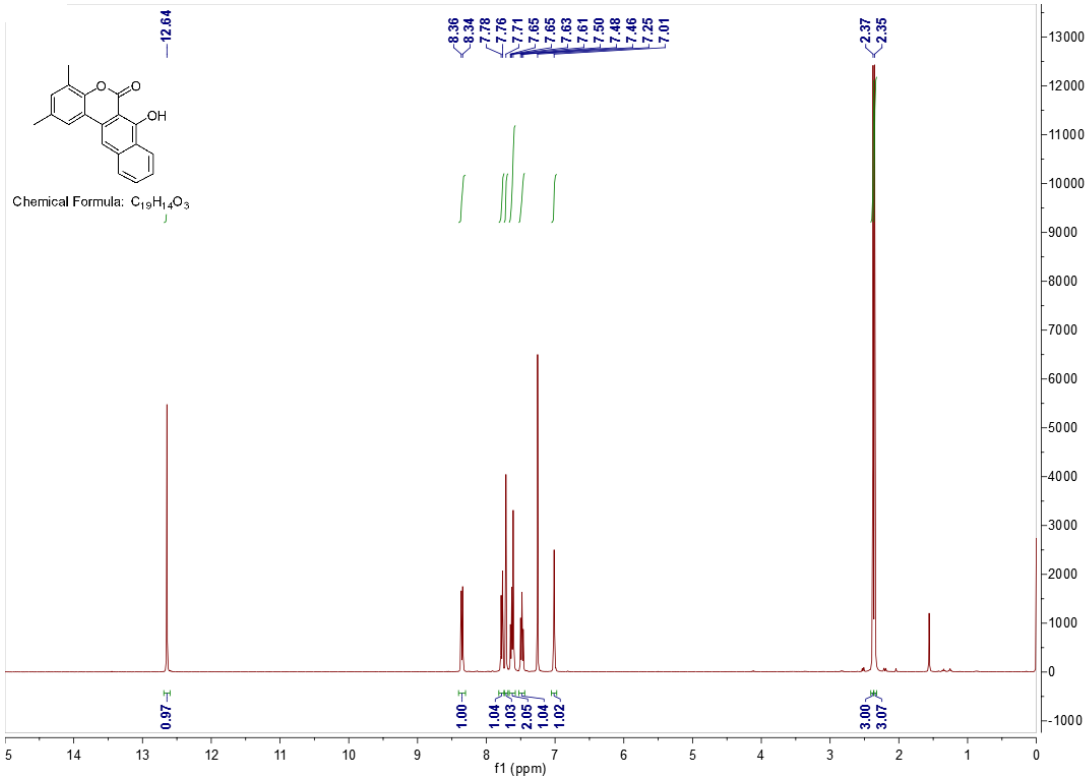
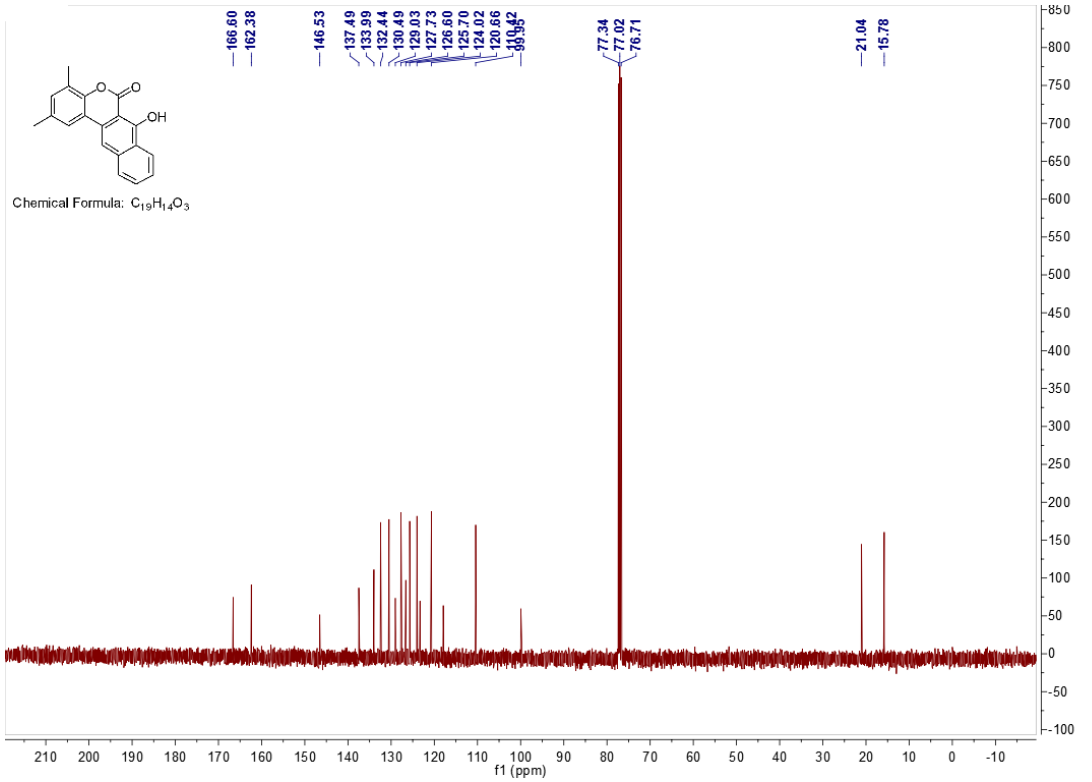
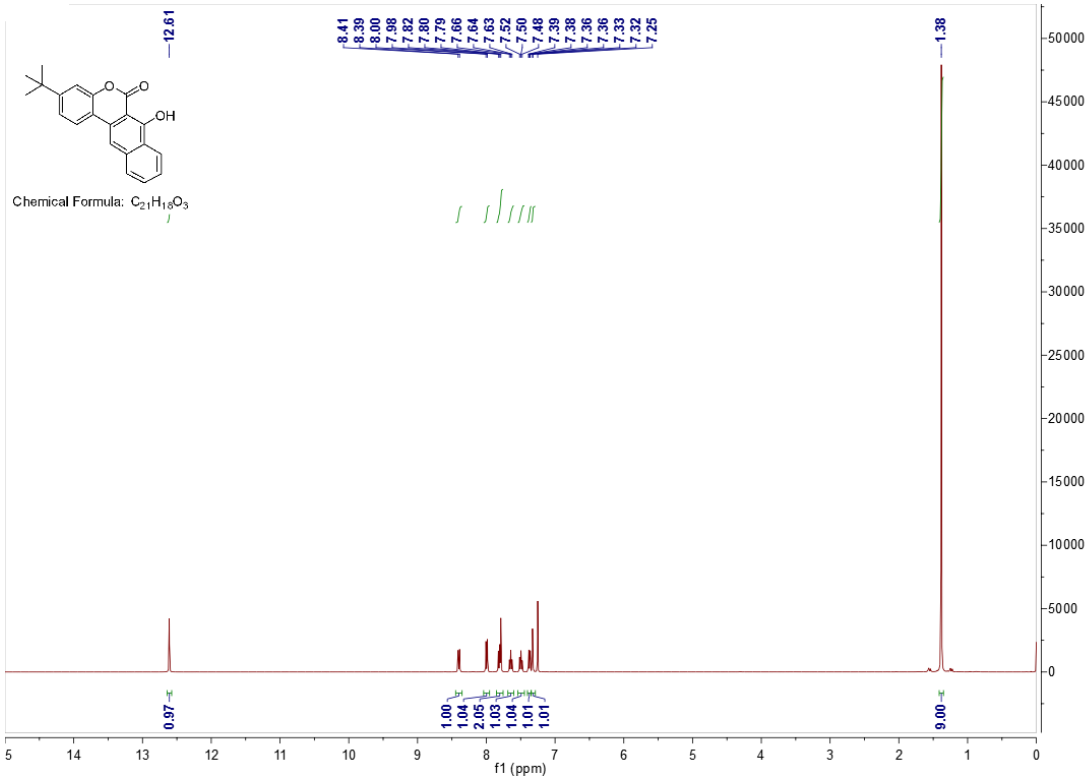


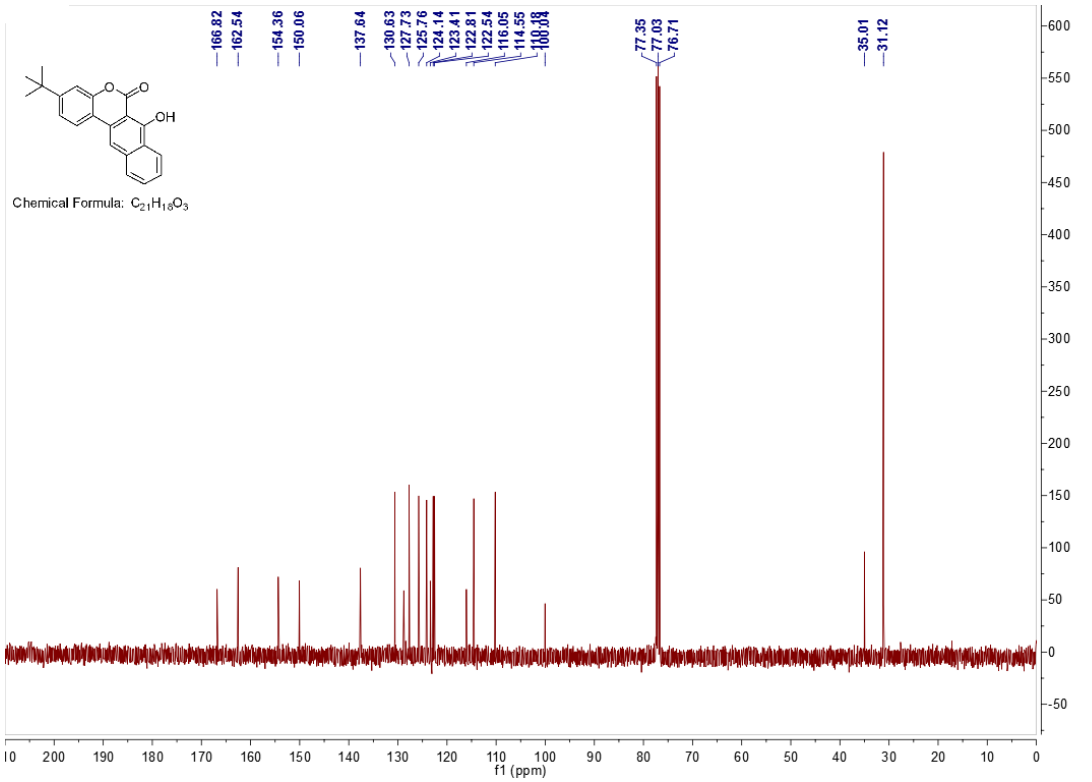
^{1}H NMR of **3f** in $CDCl_3$



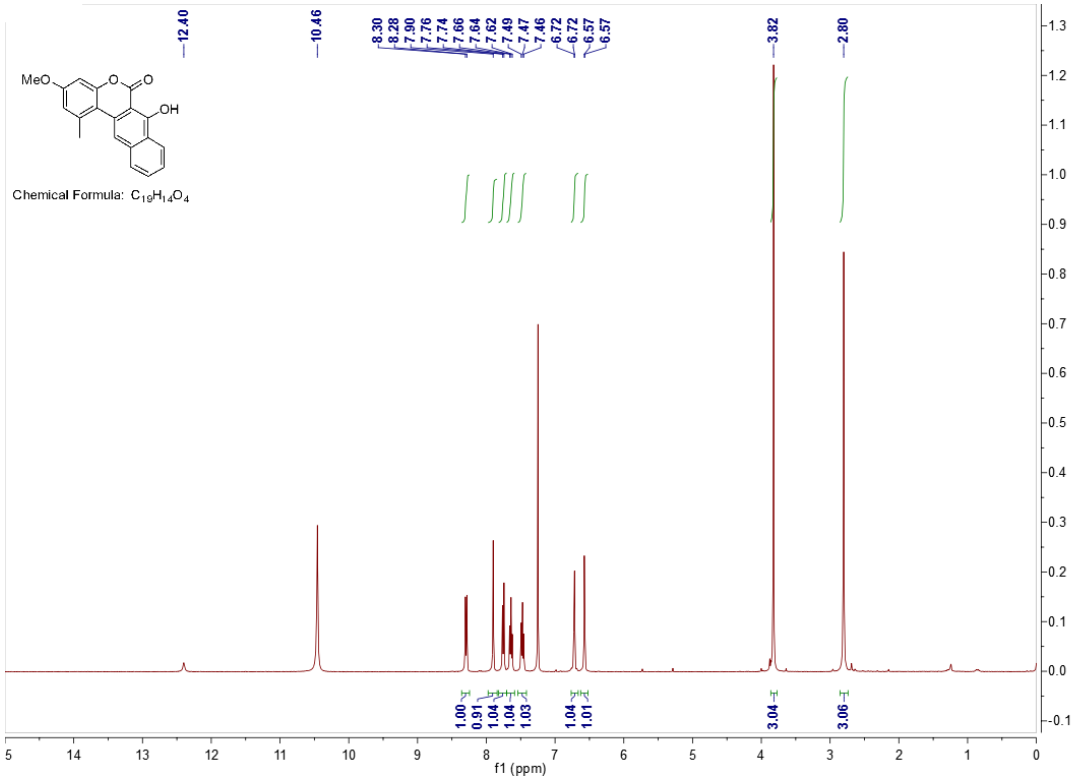
^{13}C NMR of **3f** in $CDCl_3$



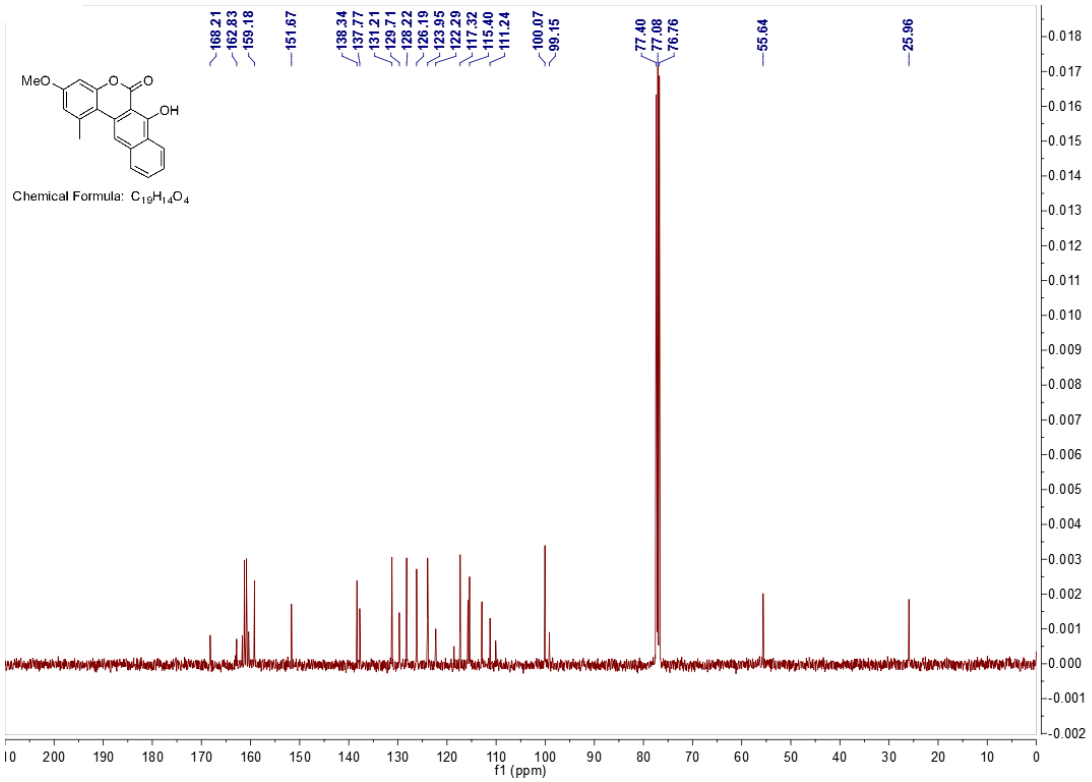
^{1}H NMR of **3g** in $CDCl_3$



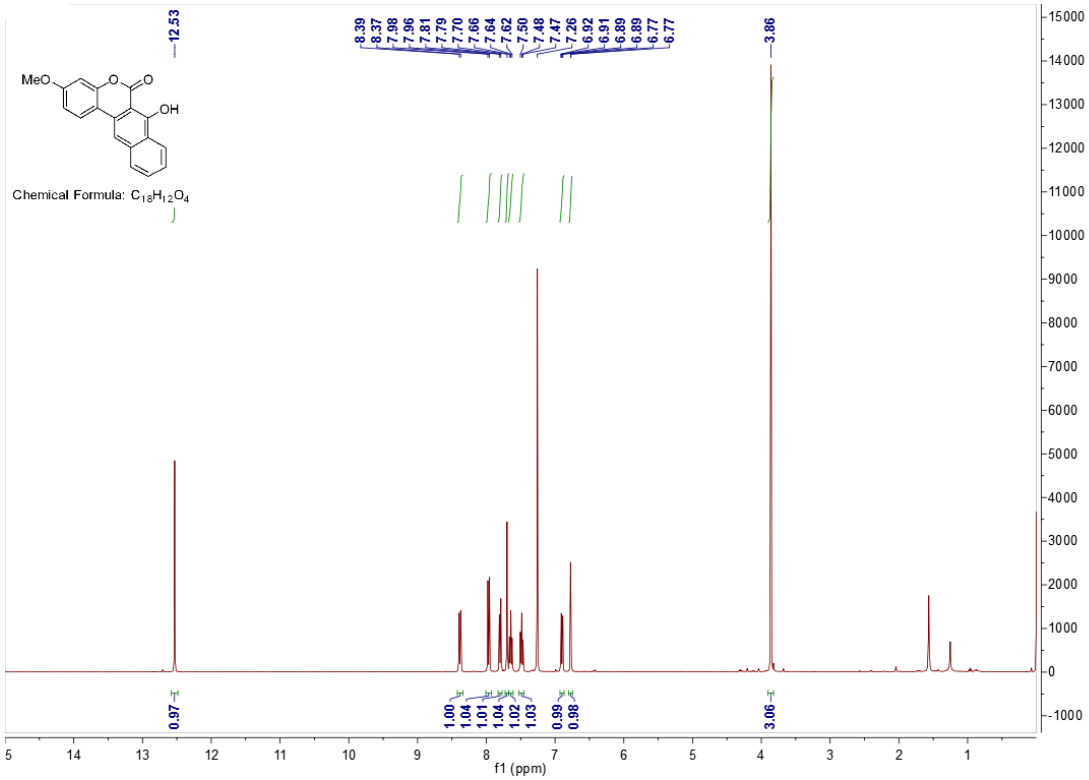
^{13}C NMR of **3g** in $CDCl_3$



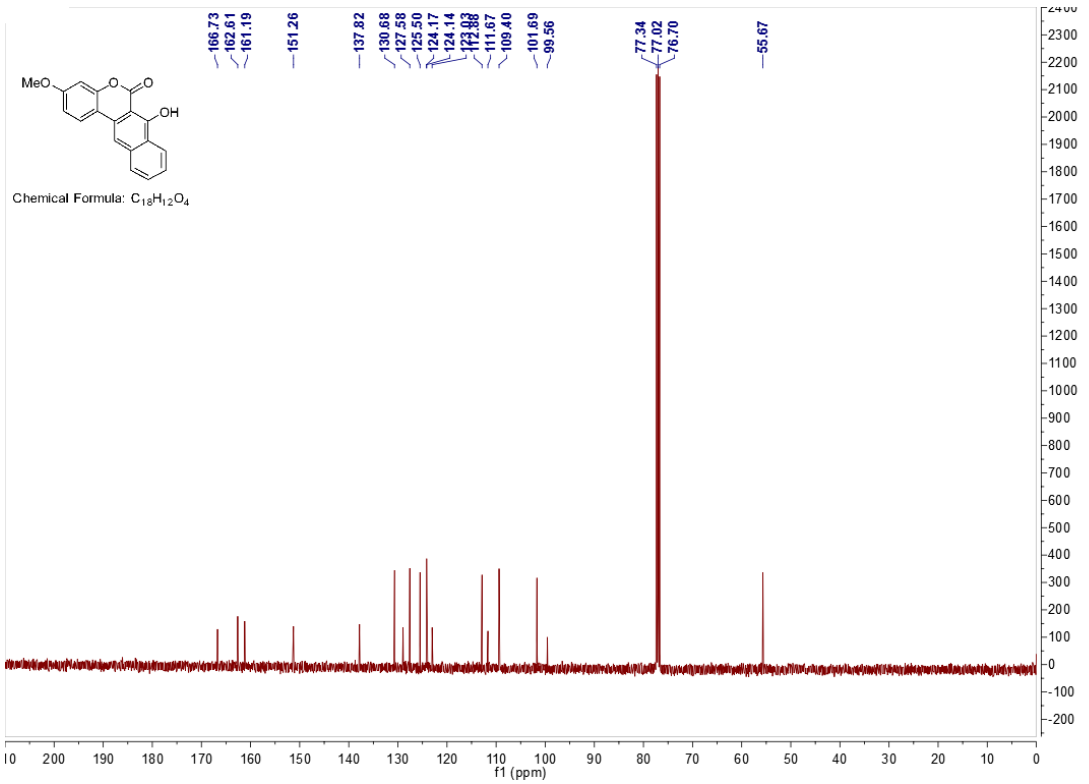
^{1}H NMR of **3h** in $CDCl_3$ & TFA-d_1



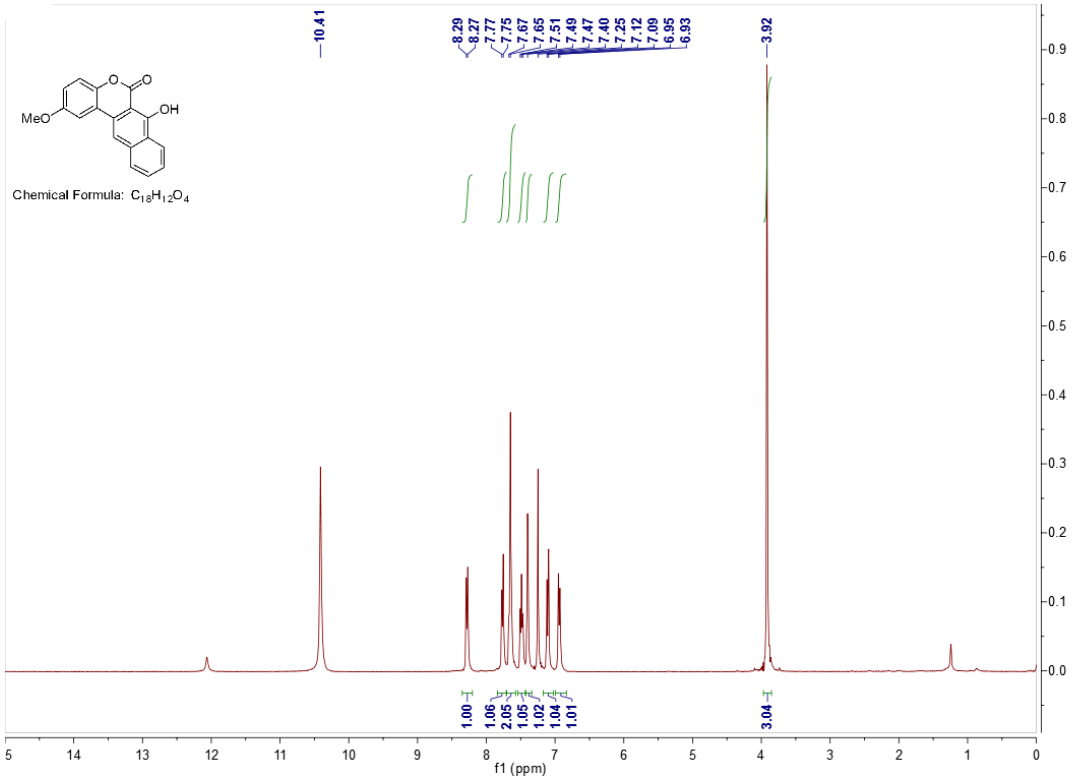
^{13}C NMR of **3h** in $CDCl_3$ & TFA-d_1



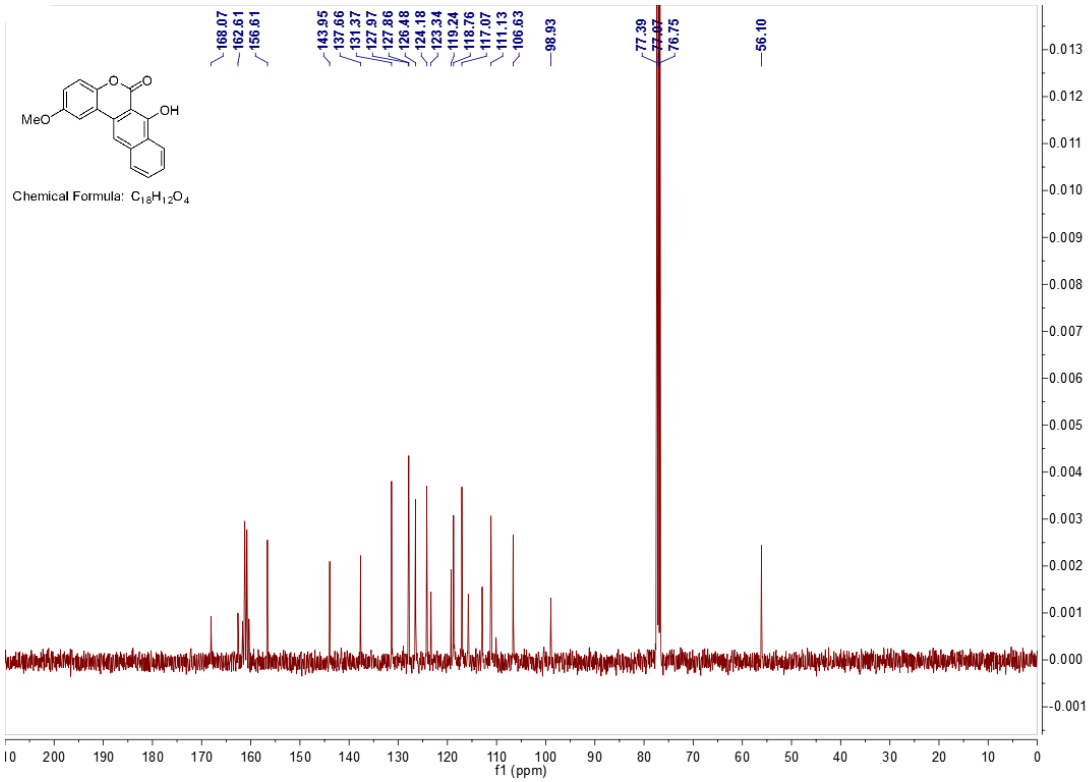
^{1}H NMR of **3i** in $CDCl_3$



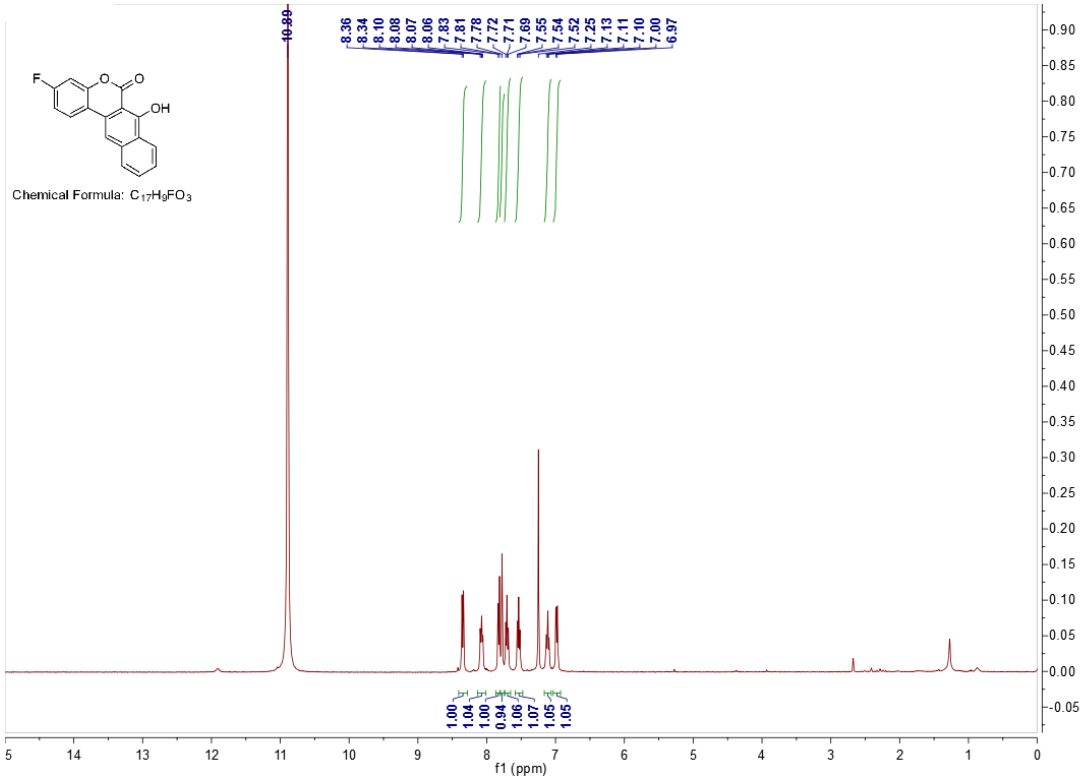
^{13}C NMR of **3i** in $CDCl_3$



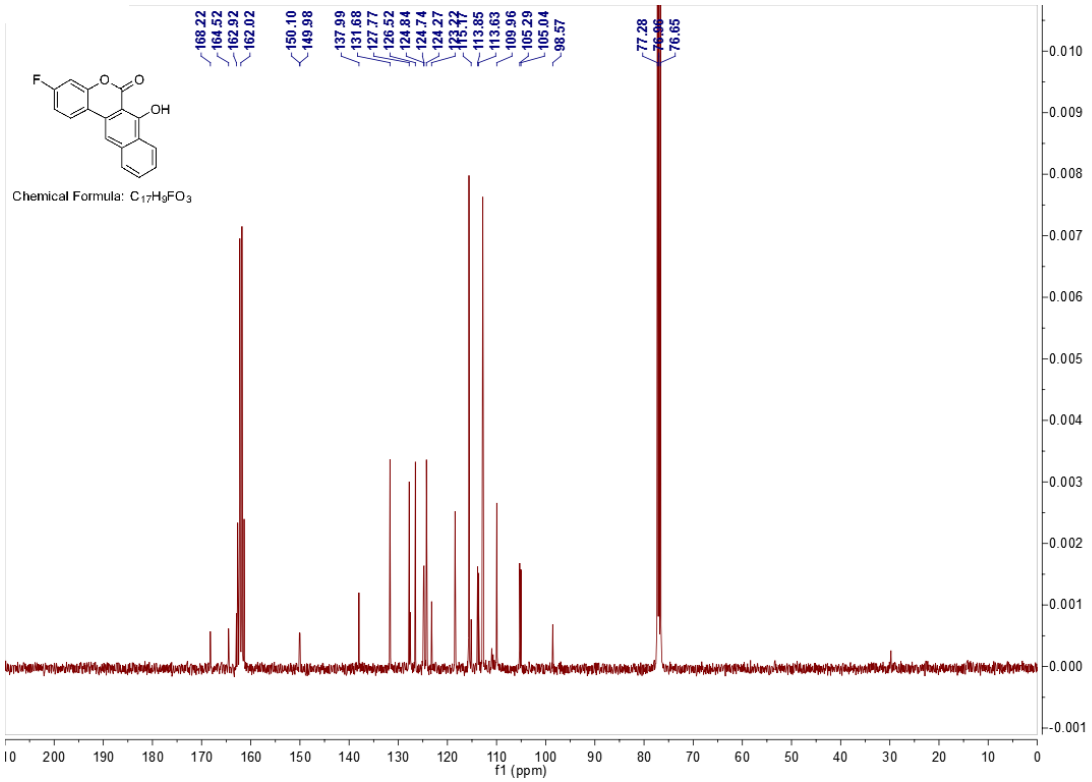
^{1}H NMR of **3j** in $CDCl_3$ & TFA-d_1



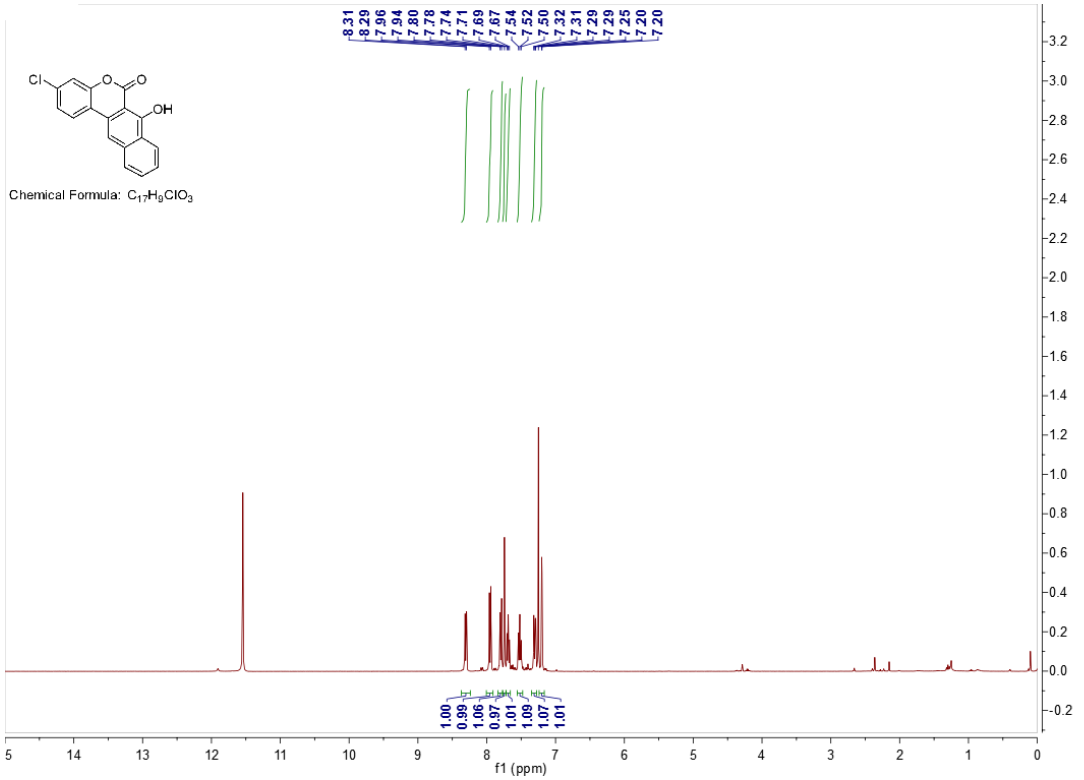
^{13}C NMR of **3j** in $CDCl_3$ & TFA-d_1



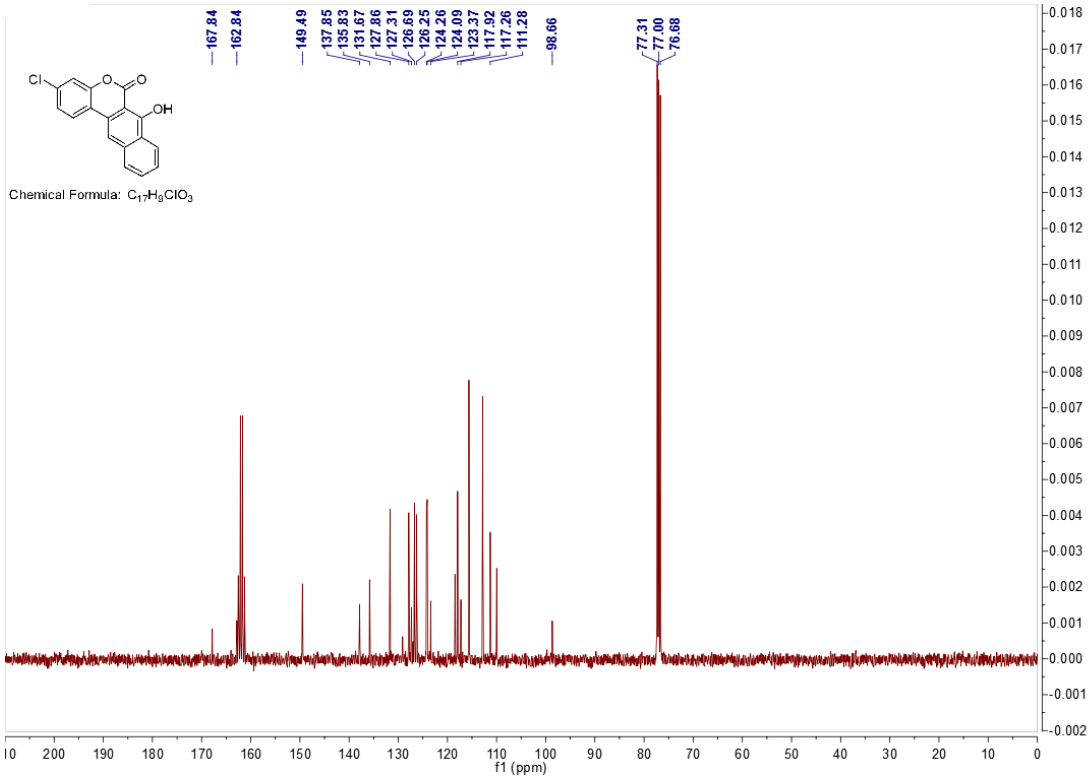
^{1}H NMR of **3k** in $CDCl_3$ & TFA-d_1



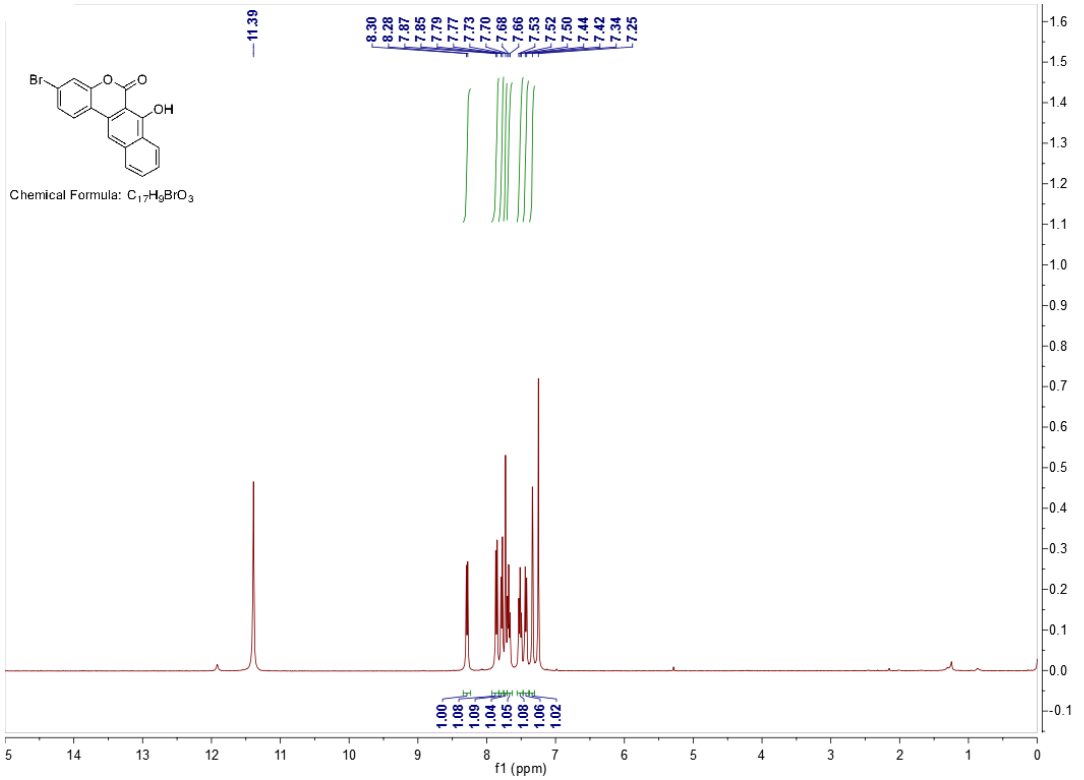
^{13}C NMR of **3k** in $CDCl_3$ & TFA-d_1



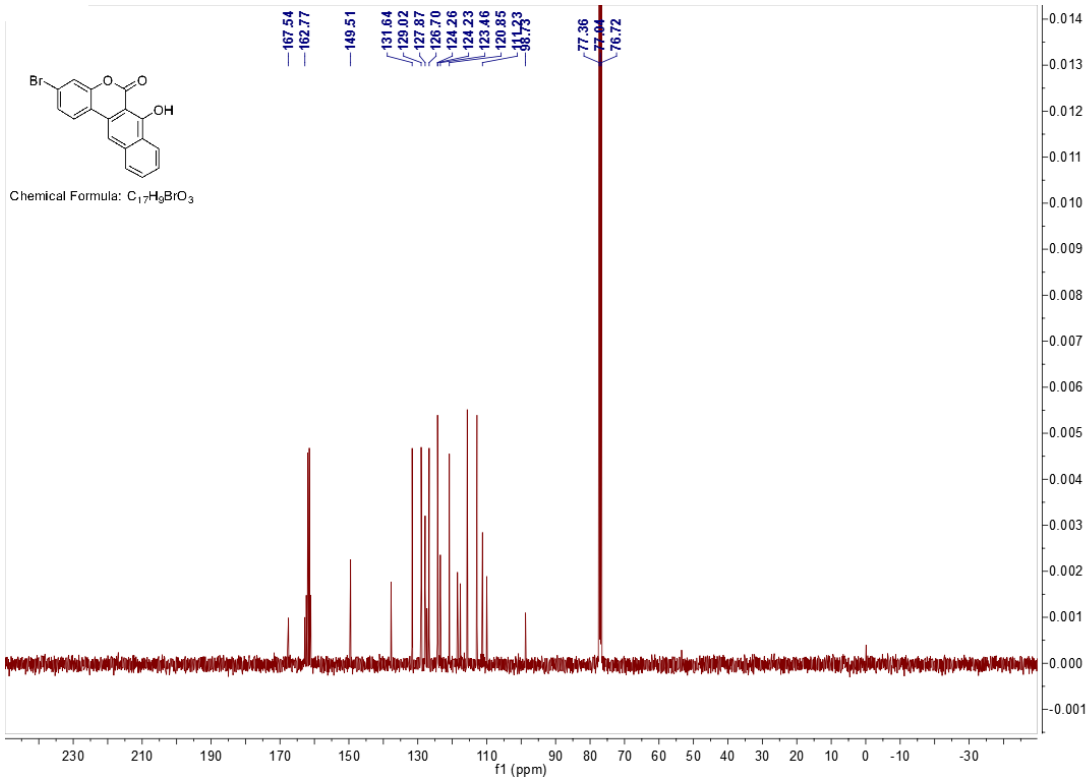
^{1}H NMR of **3l** in $CDCl_3$ & TFA-d_1



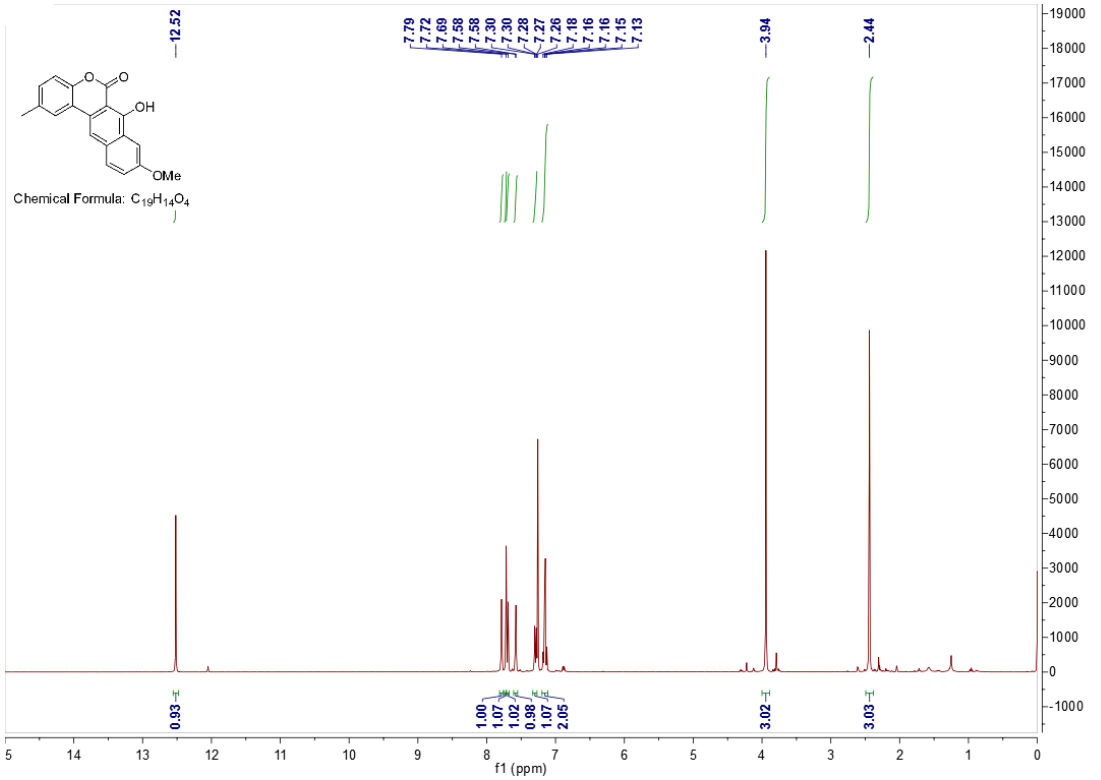
^{13}C NMR of **3l** in $CDCl_3$ & TFA-d_1



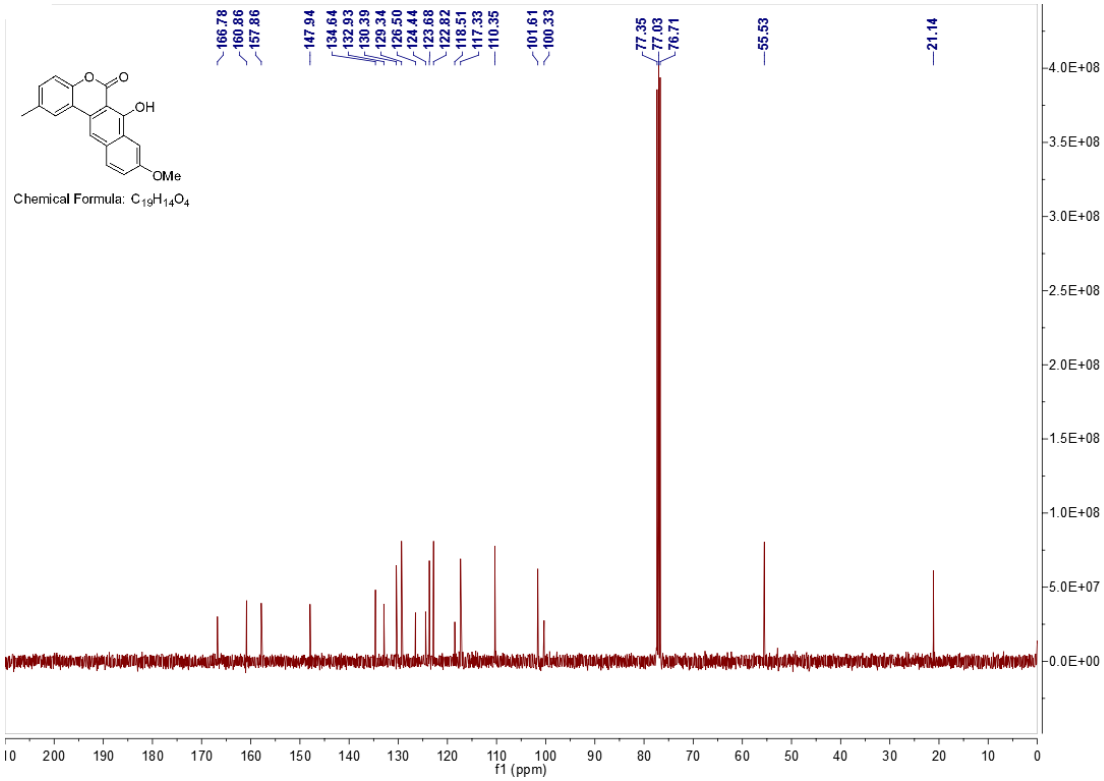
^{1}H NMR of **3m** in $CDCl_3$ & TFA-d_1



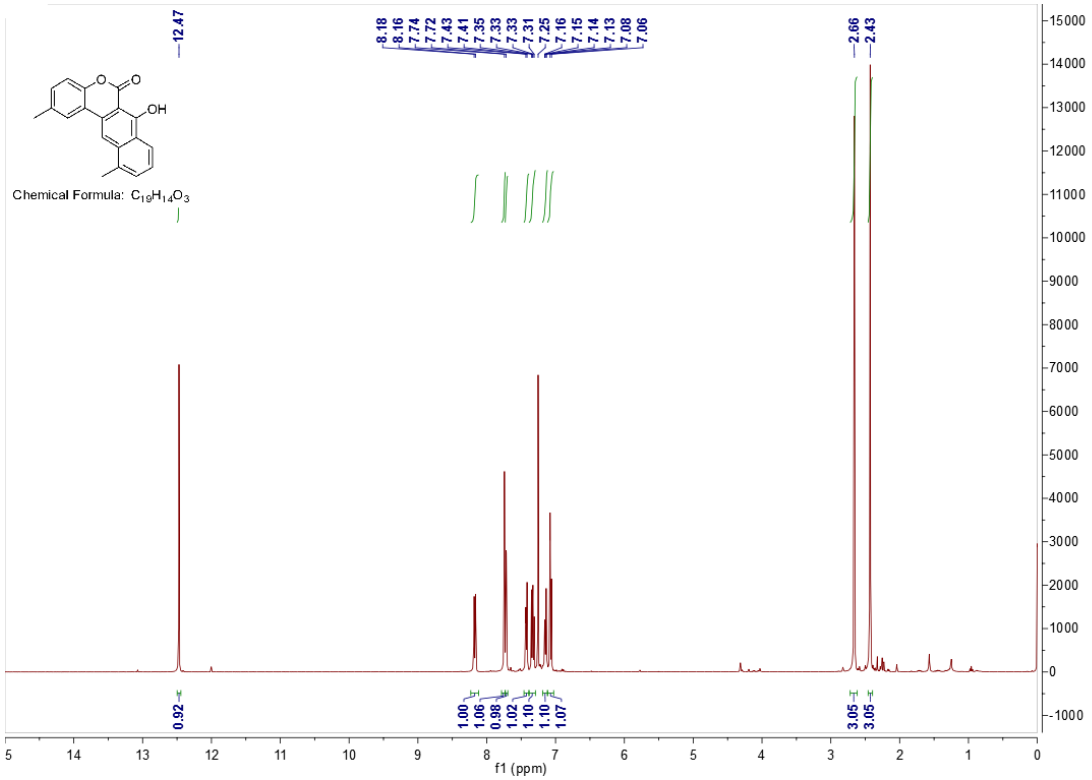
^{13}C NMR of **3m** in $CDCl_3$ & TFA-d_1



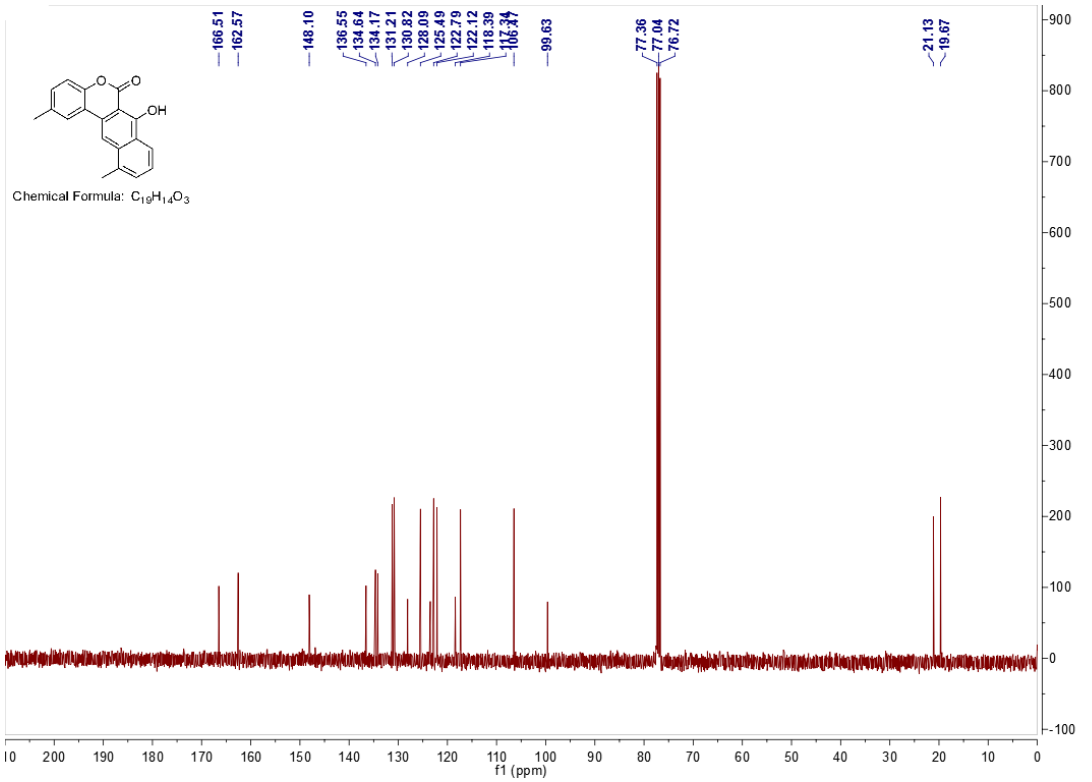
^{1}H NMR of **3n** in $CDCl_3$



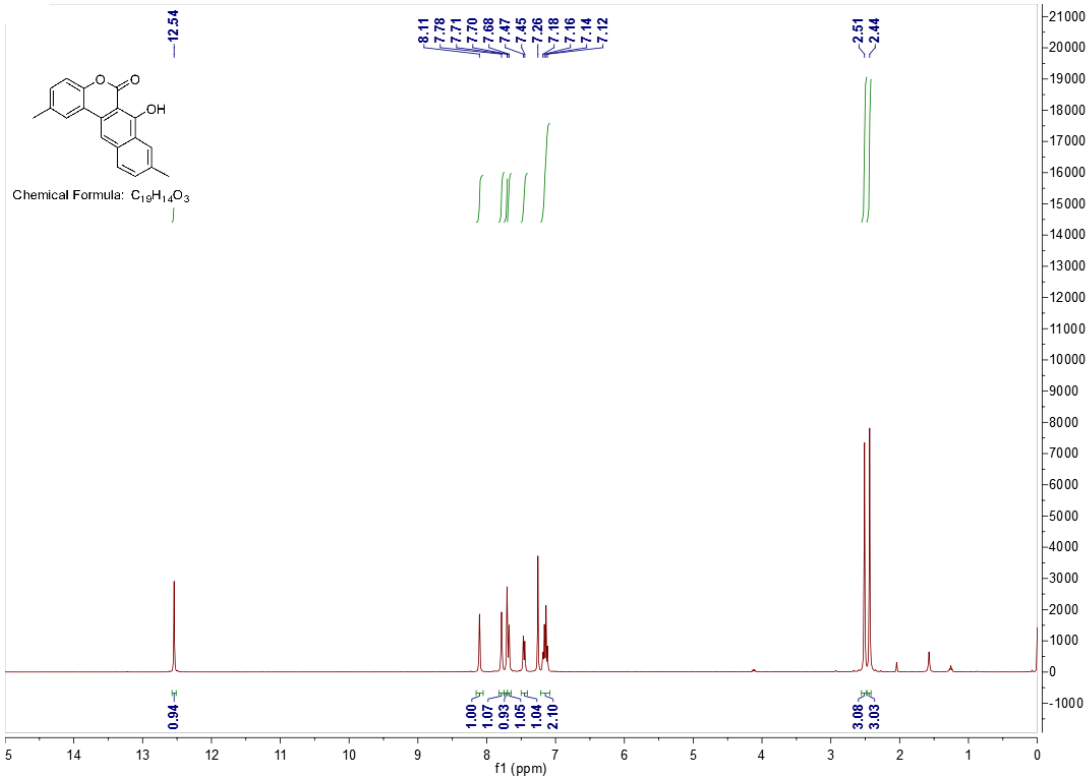
^{13}C NMR of **3n** in $CDCl_3$



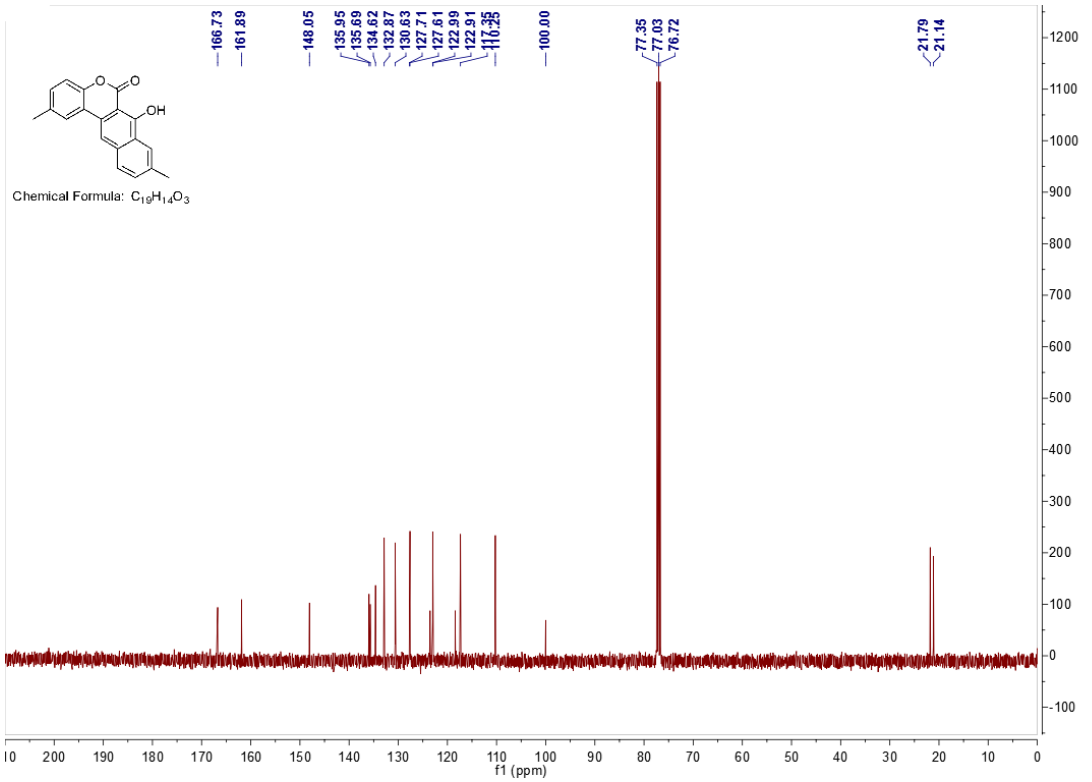
^{1}H NMR of **3o** in $CDCl_3$



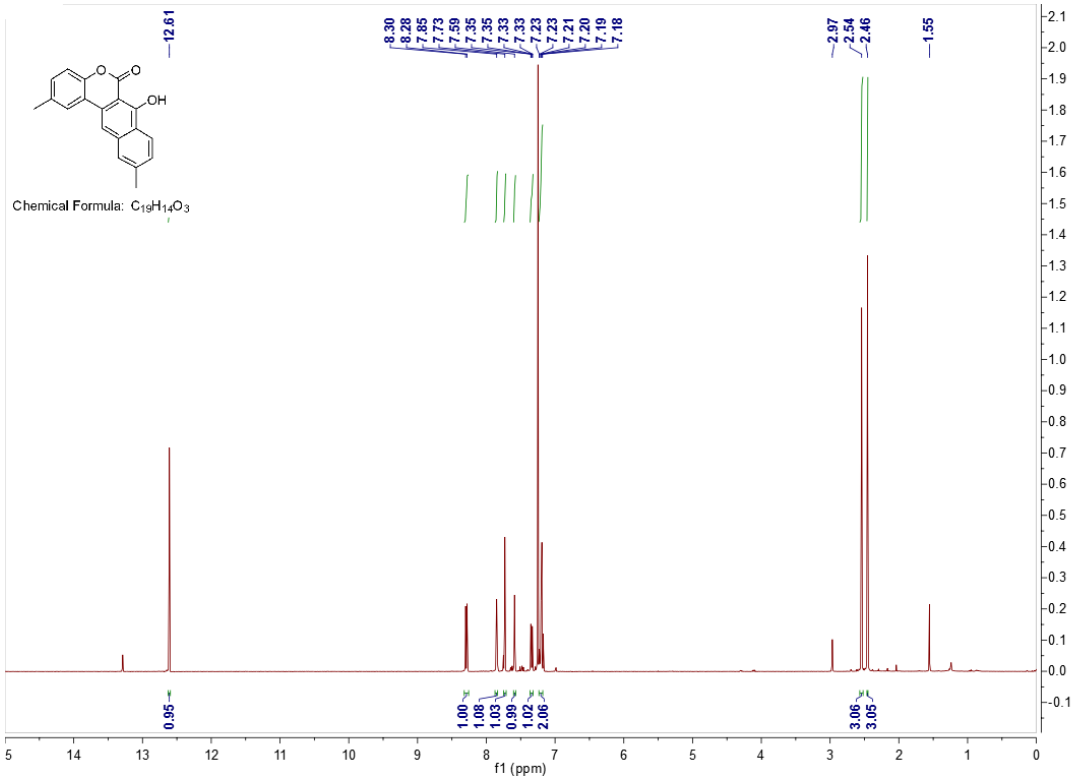
^{13}C NMR of **3o** in $CDCl_3$



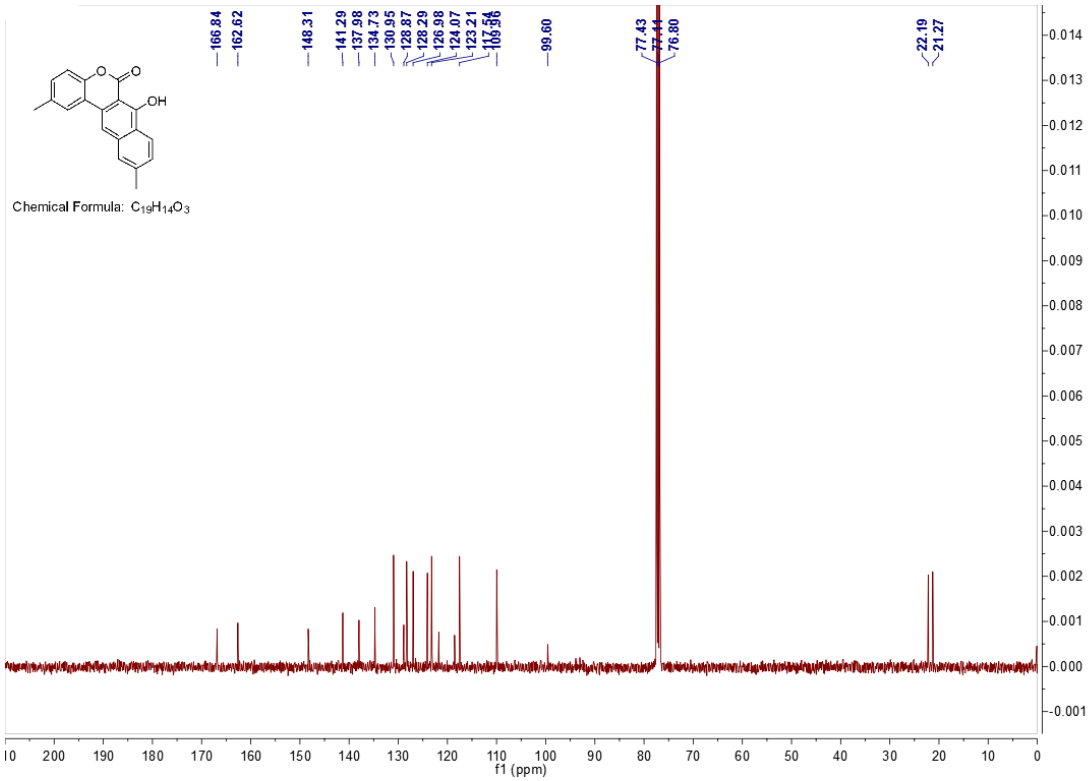
^{1}H NMR of **3p** in $CDCl_3$



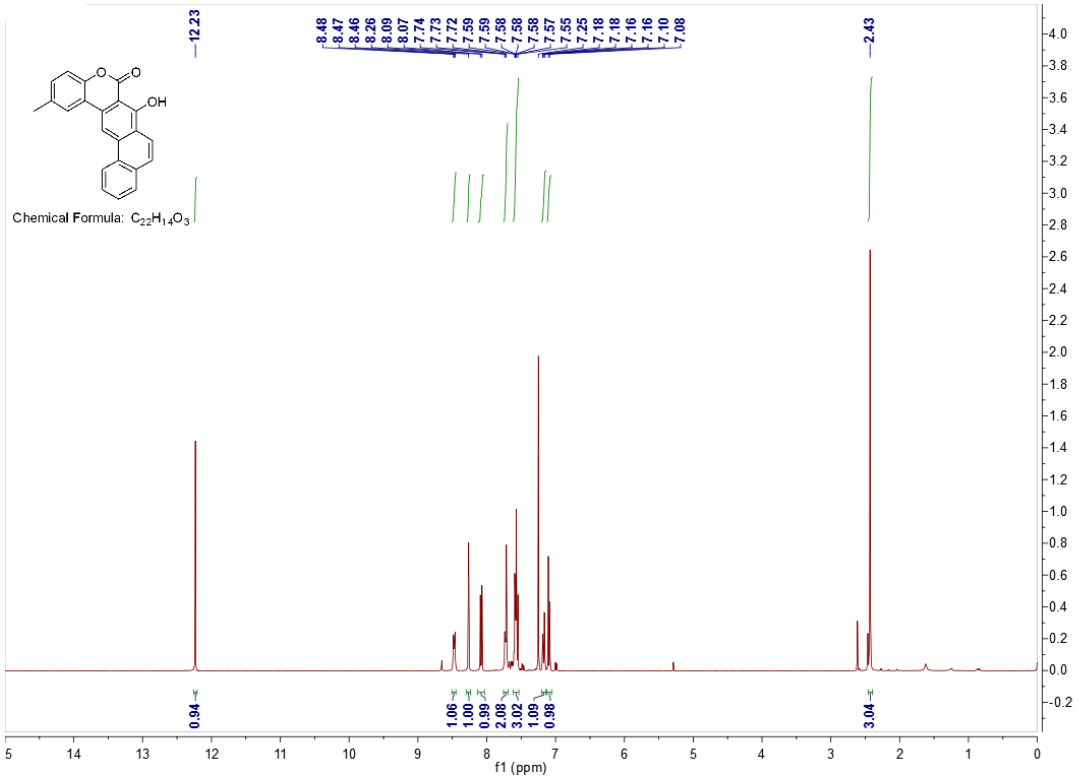
^{13}C NMR of **3p** in $CDCl_3$



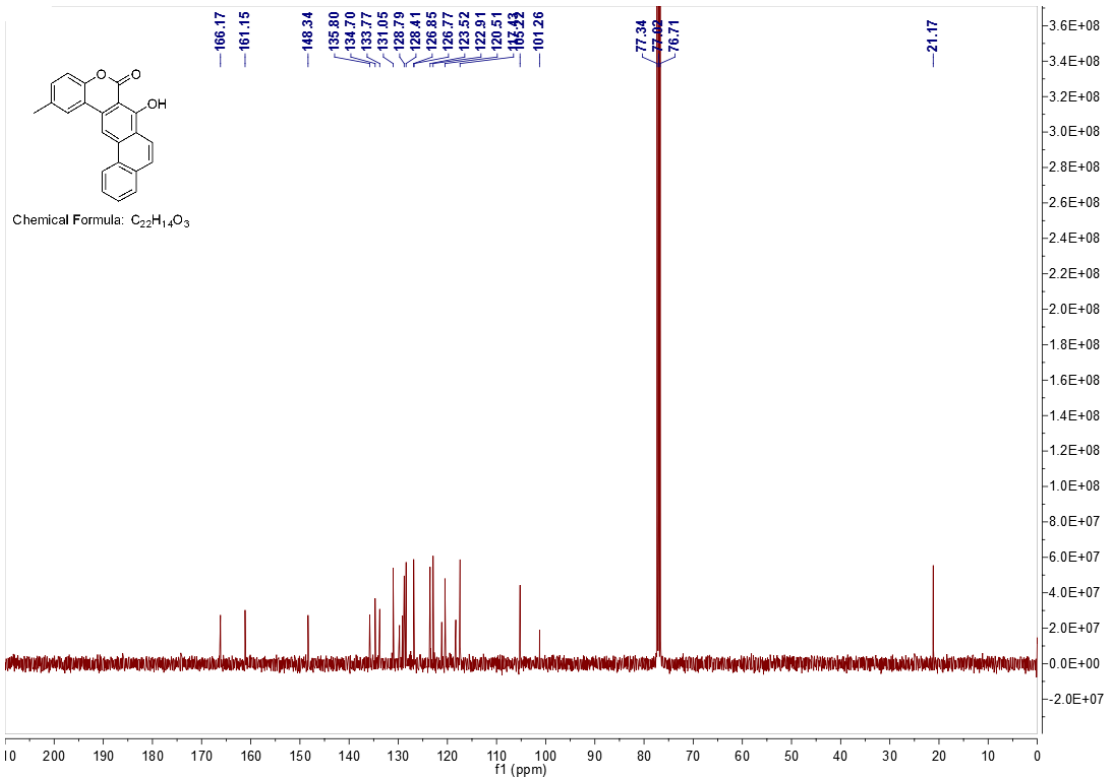
^{1}H NMR of **3q'** in $CDCl_3$



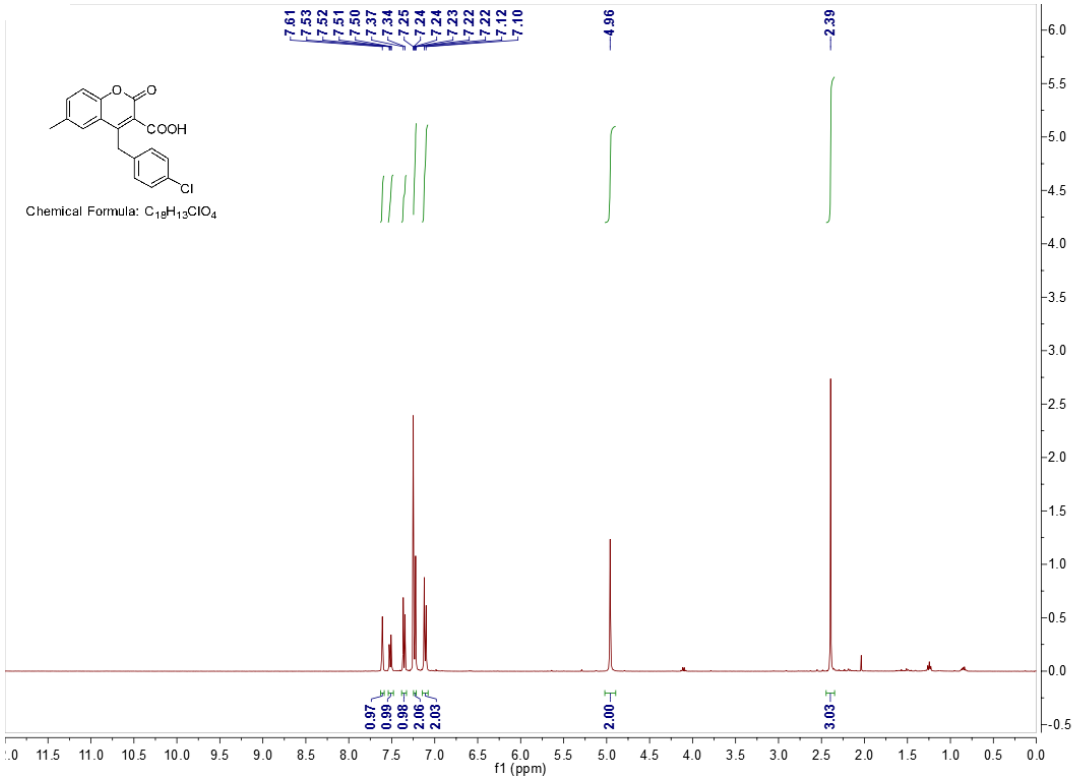
^{13}C NMR of **3q'** in $CDCl_3$



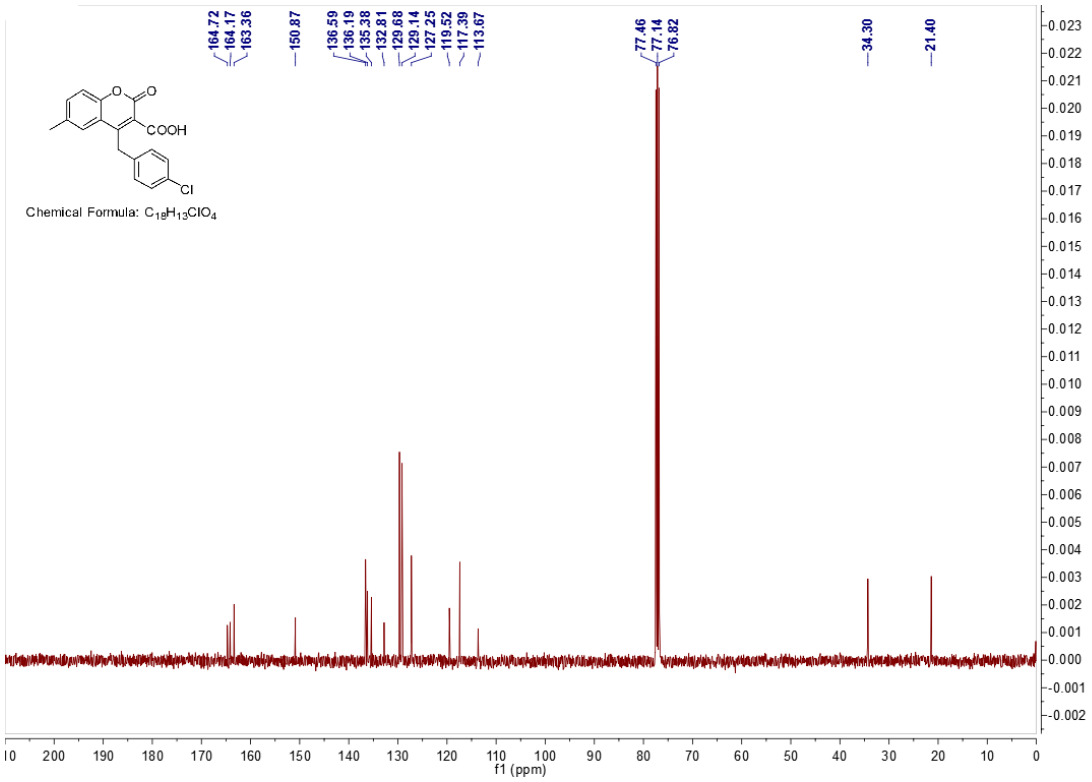
^{1}H NMR of **3r** in $CDCl_3$



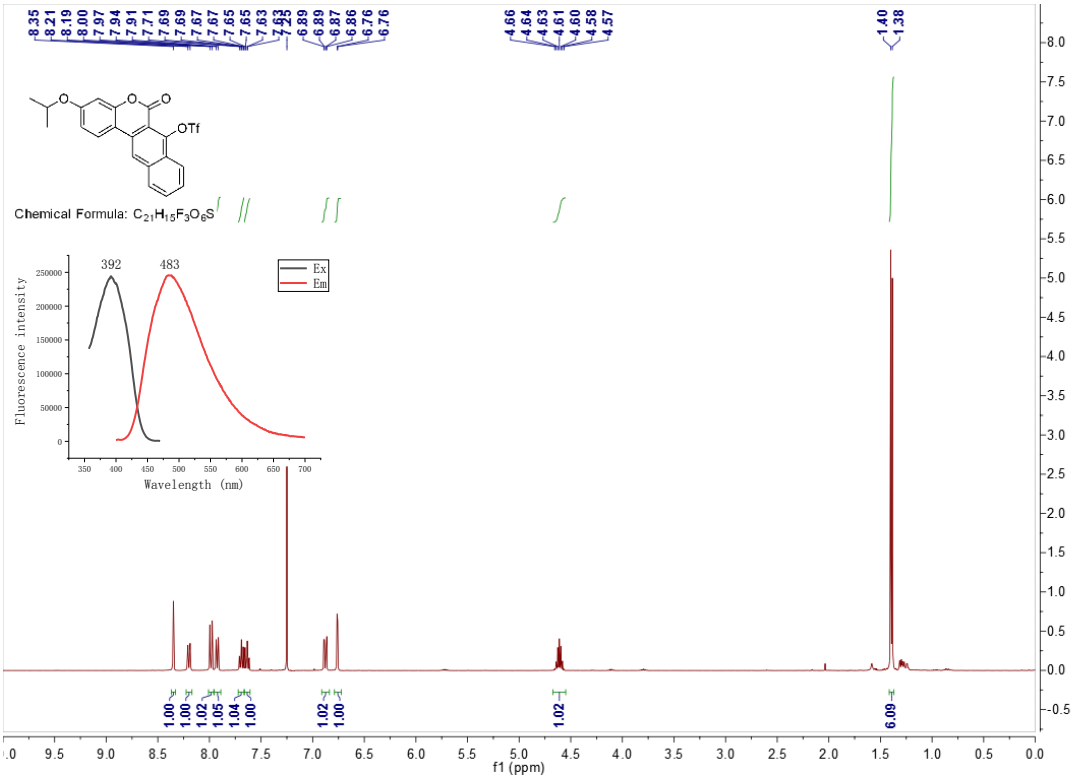
^{13}C NMR of **3r** in $CDCl_3$



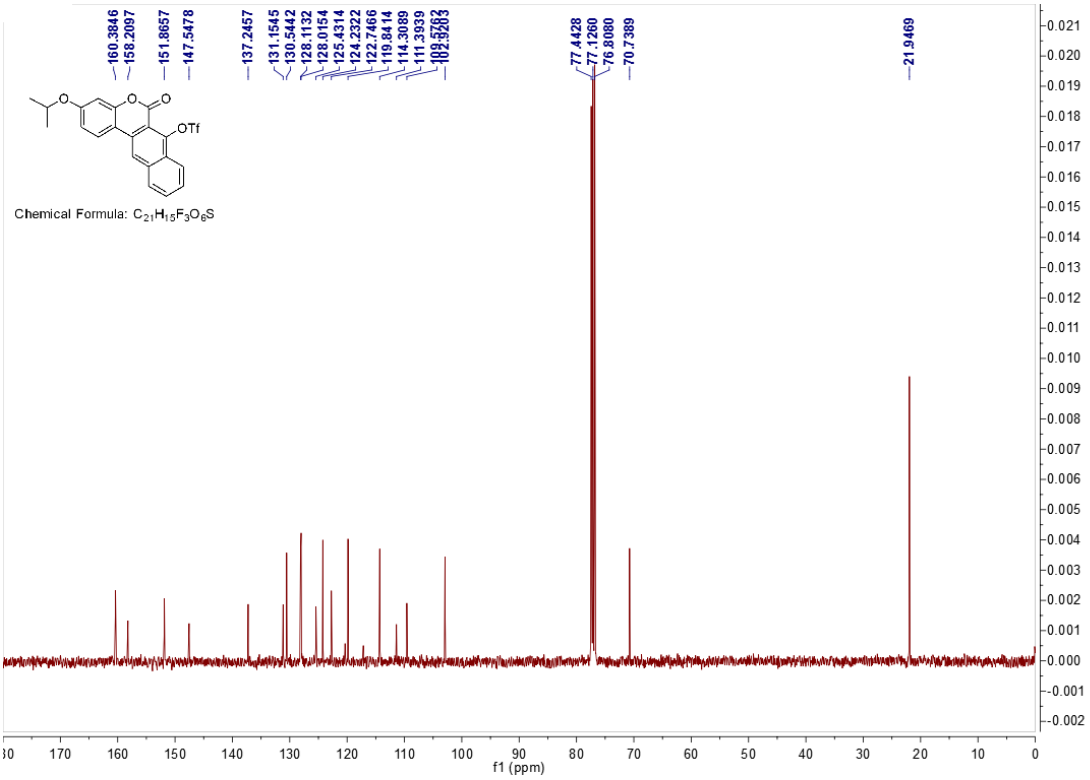
^{1}H NMR of **3s** in $CDCl_3$



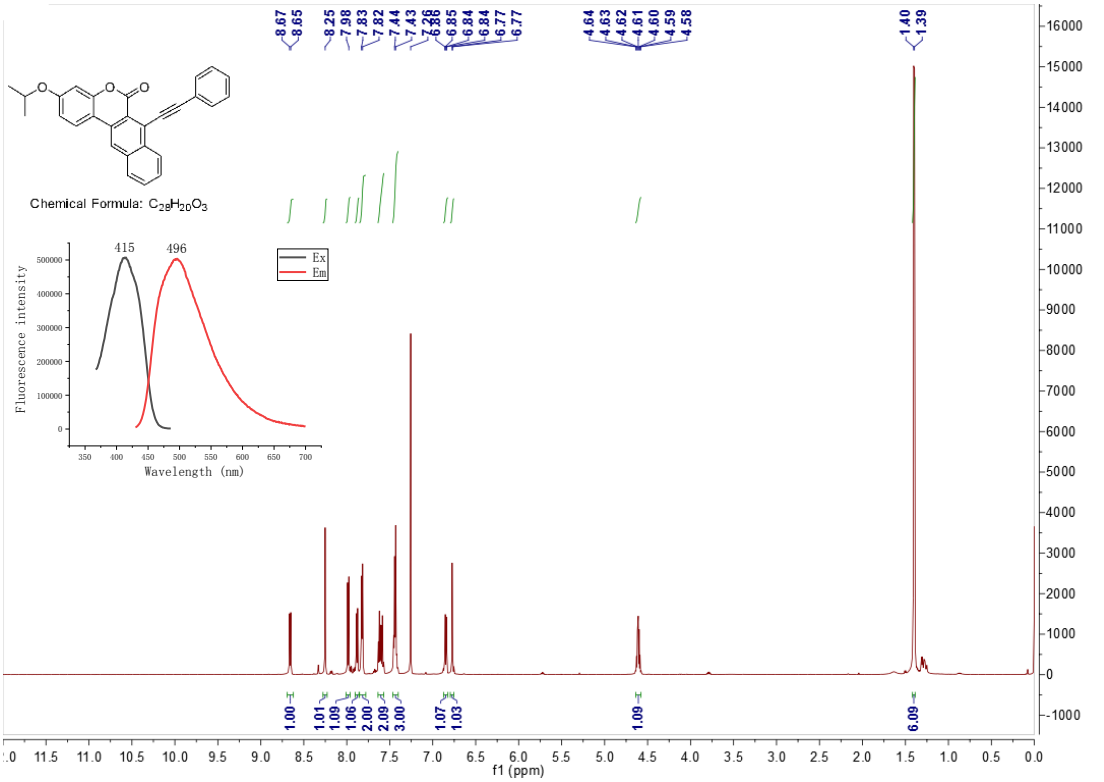
^{13}C NMR of **3s** in $CDCl_3$



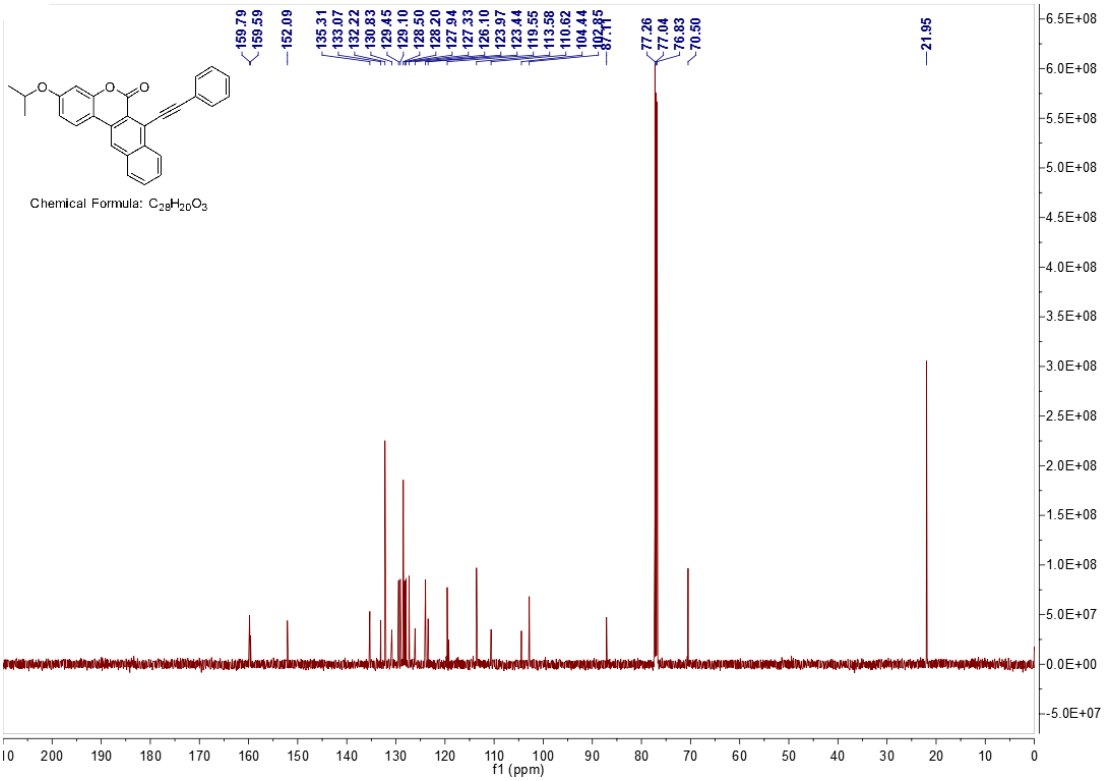
^{1}H NMR of **5** in $CDCl_3$



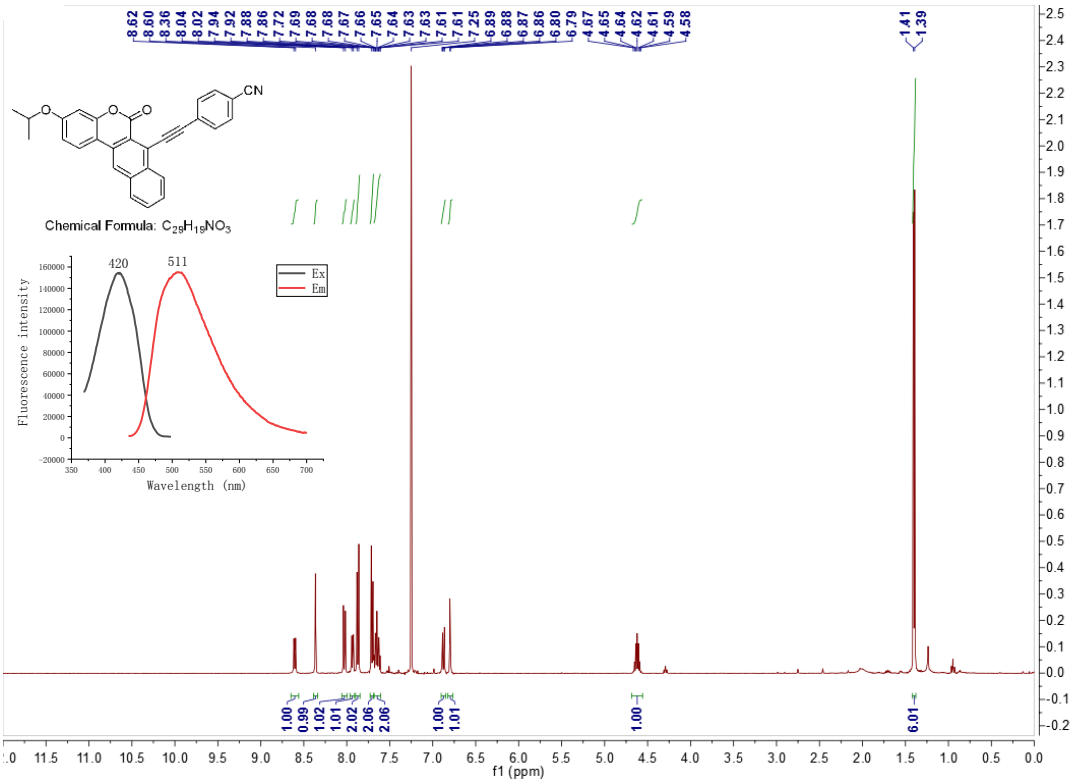
^{13}C NMR of **5** in $CDCl_3$



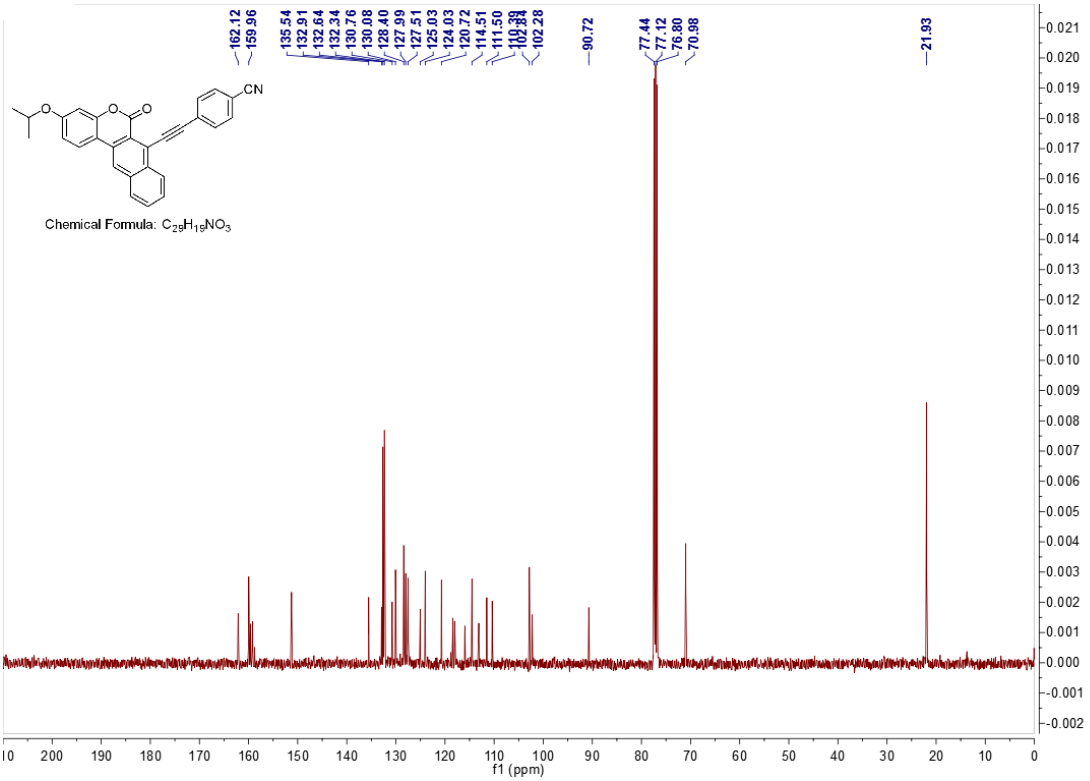
^{1}H NMR of **6a** in $CDCl_3$



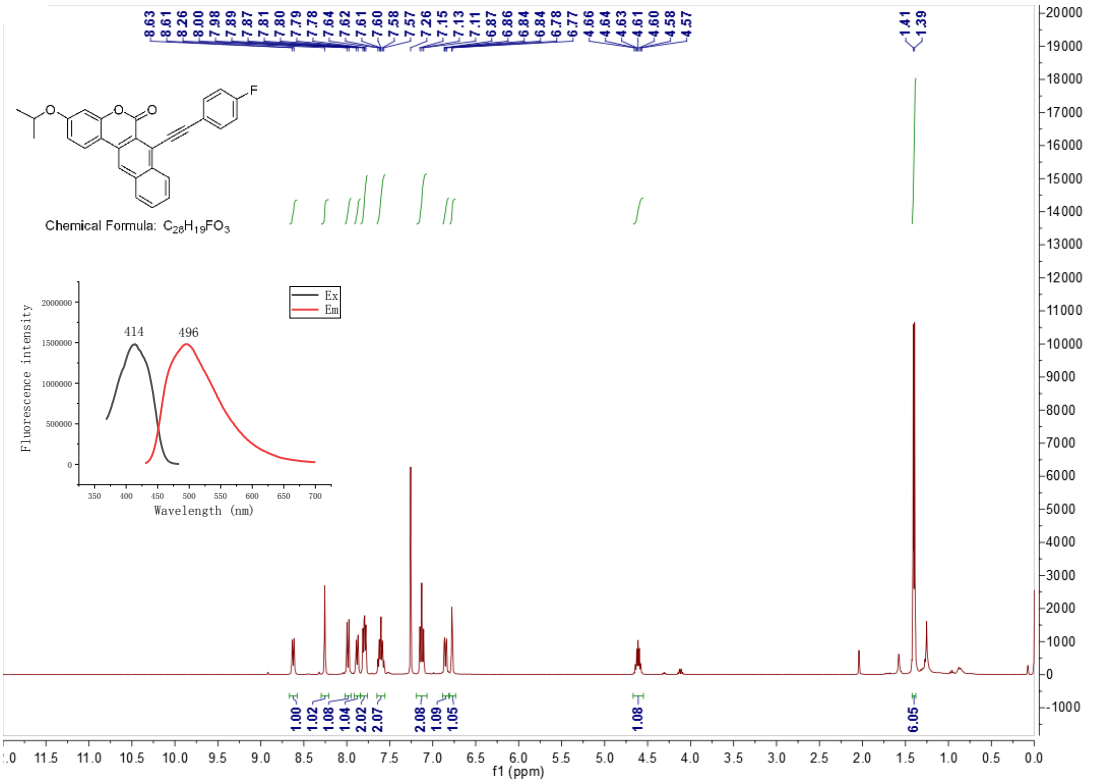
^{13}C NMR of **6a** in $CDCl_3$



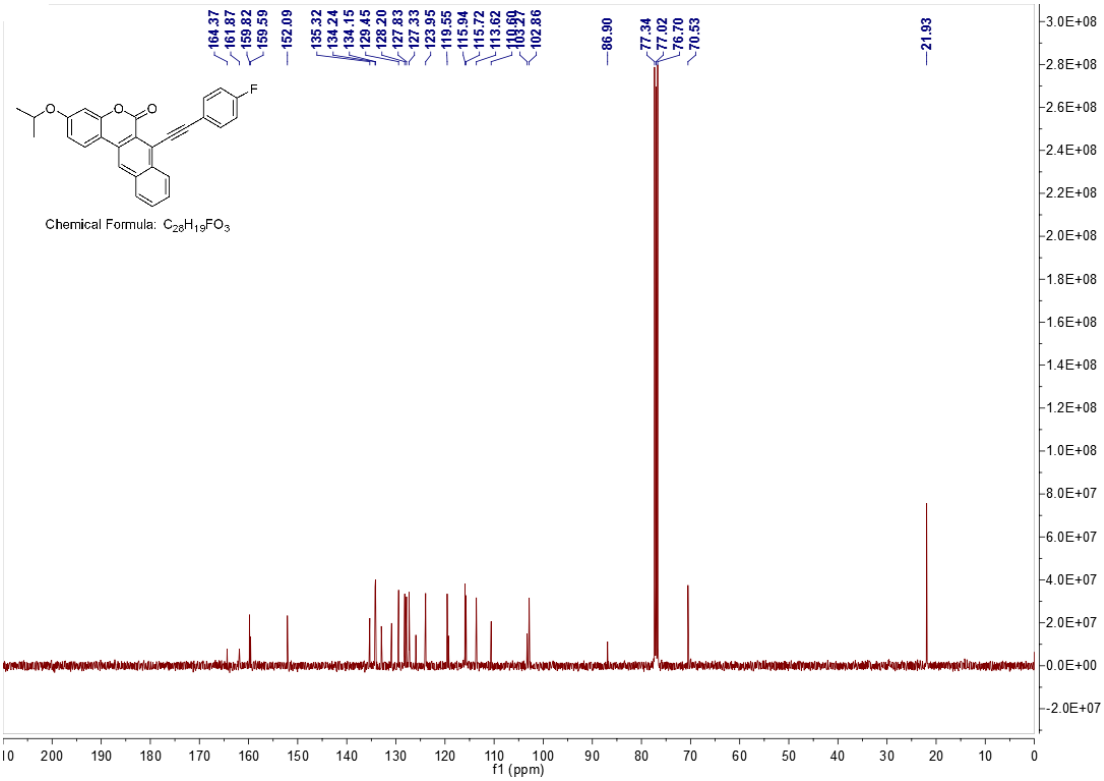
^{1}H NMR of **6b** in $CDCl_3$



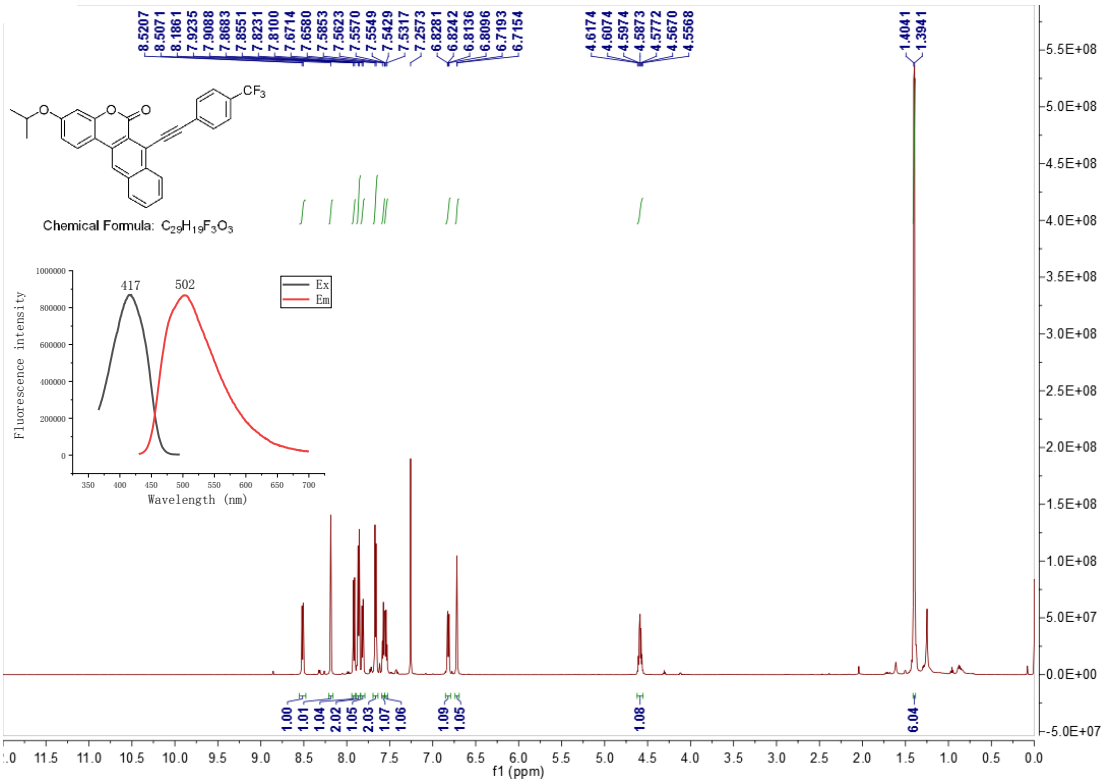
^{13}C NMR of **6b** in $CDCl_3$ & TFA-d_1



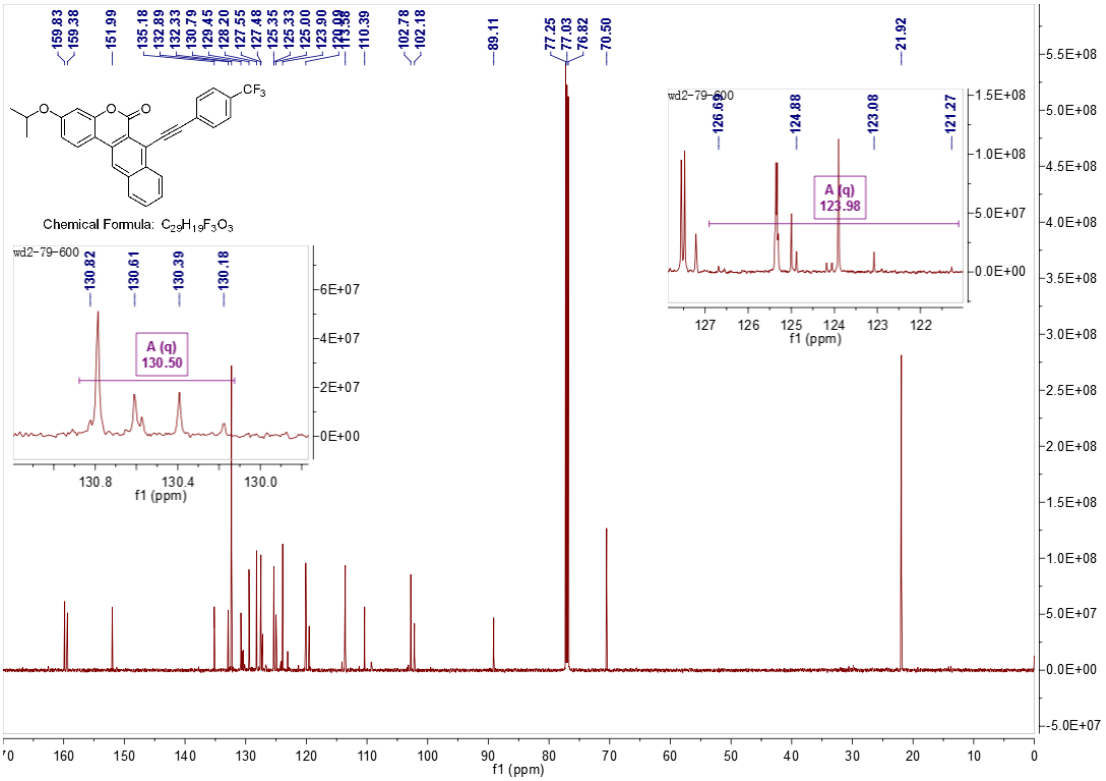
^{1}H NMR of **6c** in $CDCl_3$



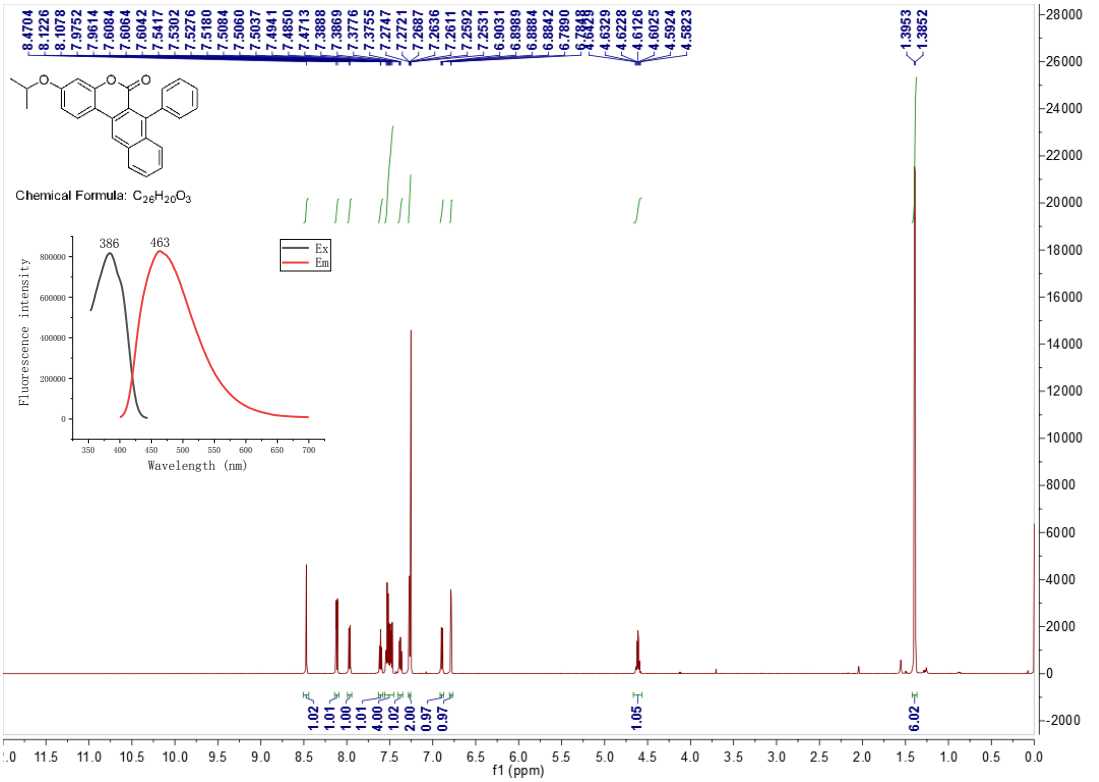
^{13}C NMR of **6c** in $CDCl_3$



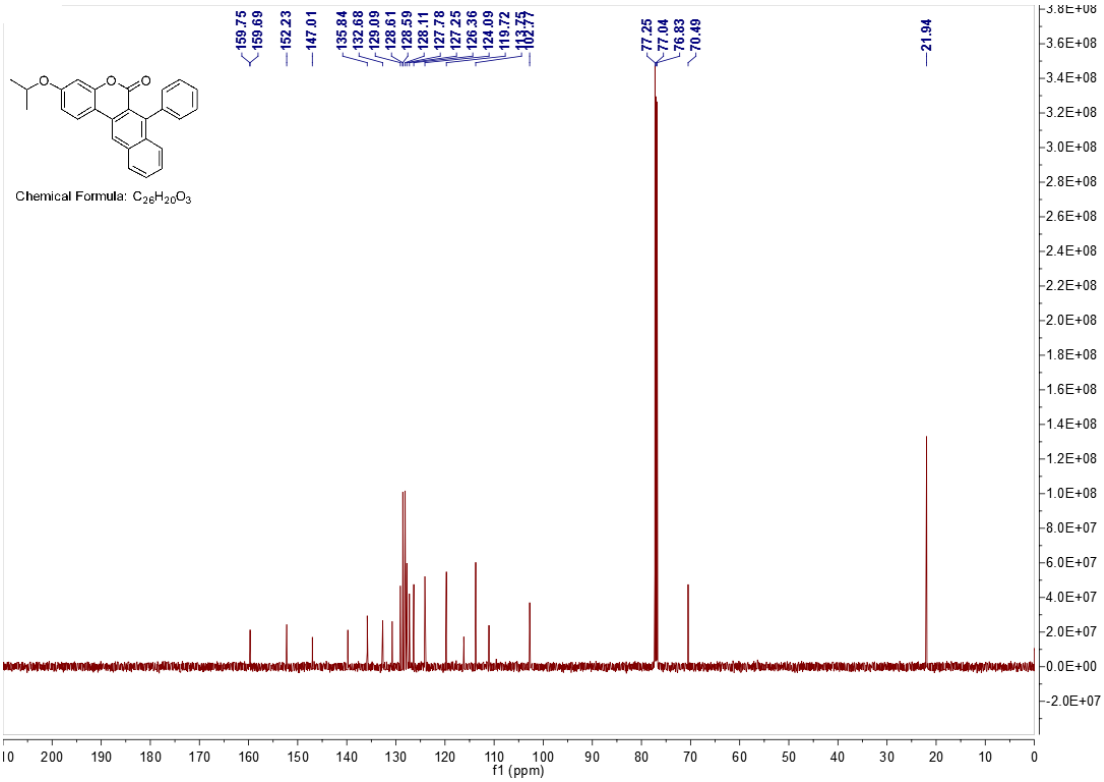
^{1}H NMR of **6d** in $CDCl_3$



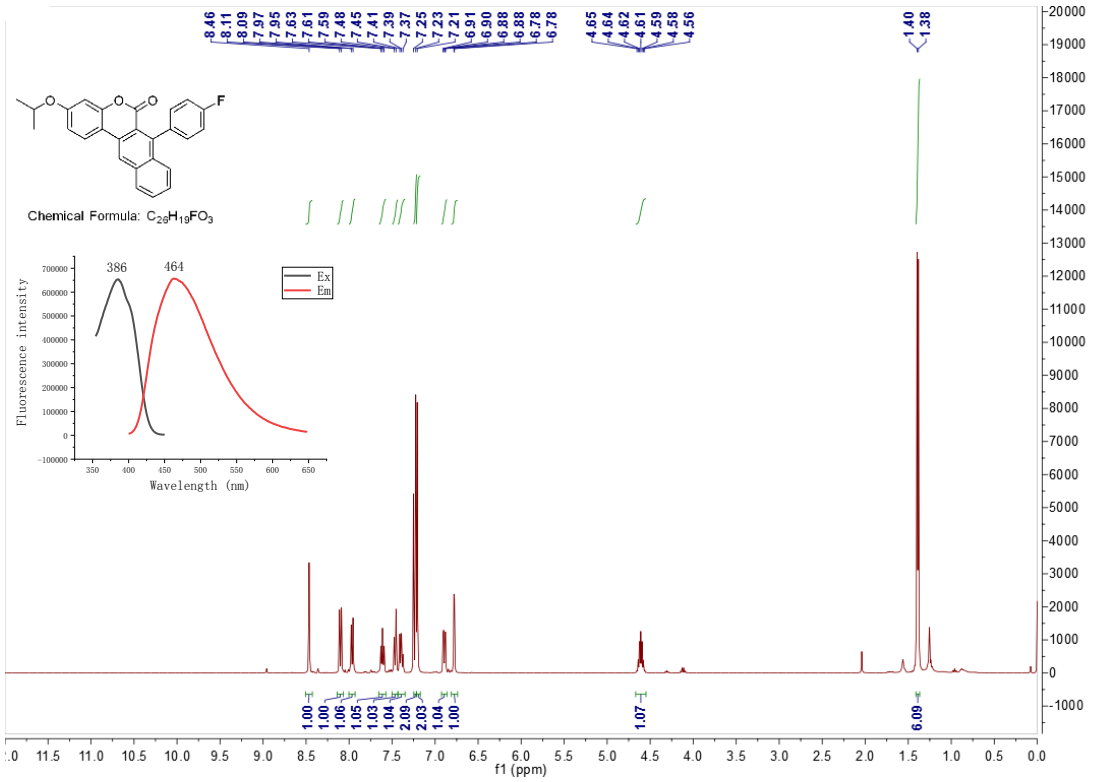
^{13}C NMR of **6d** in $CDCl_3$



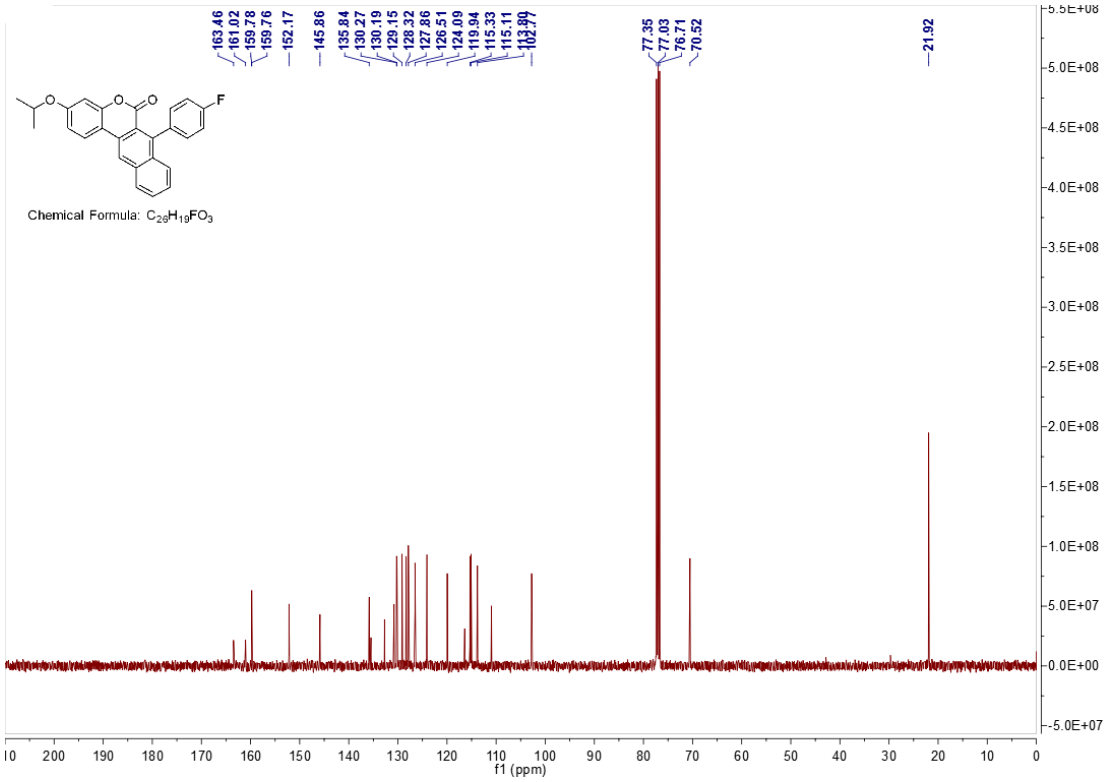
^{1}H NMR of **6e** in $CDCl_3$



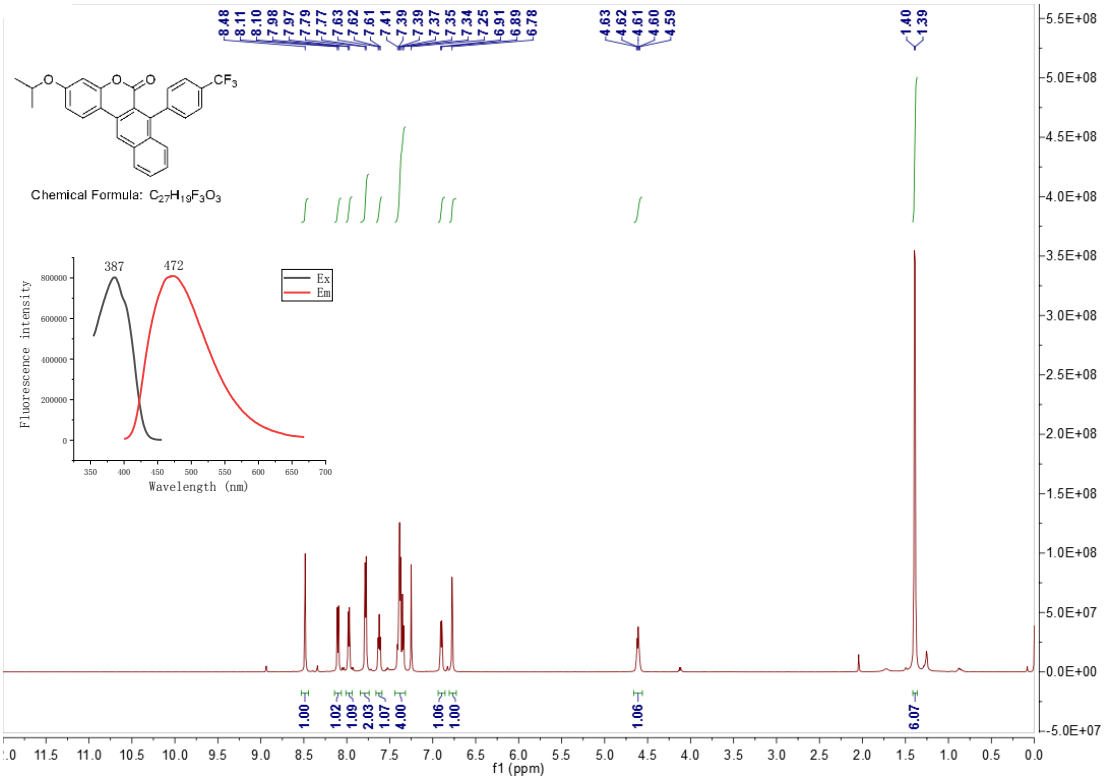
^{13}C NMR of **6e** in $CDCl_3$



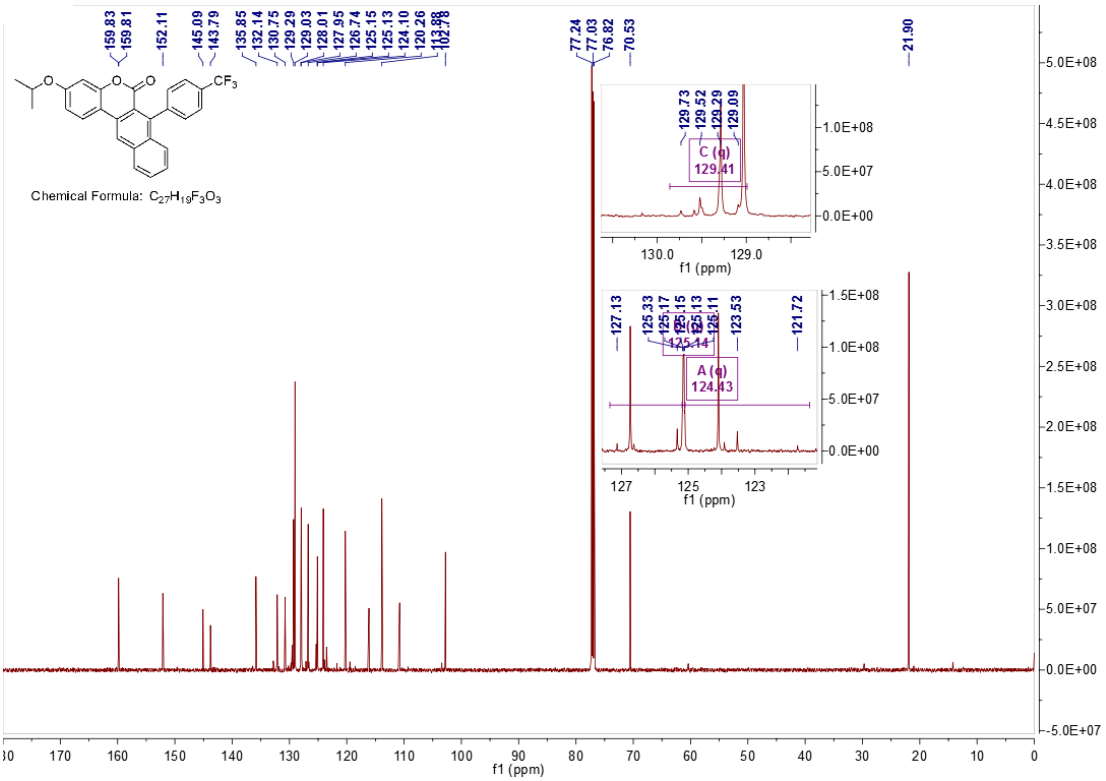
^{1}H NMR of **6f** in $CDCl_3$



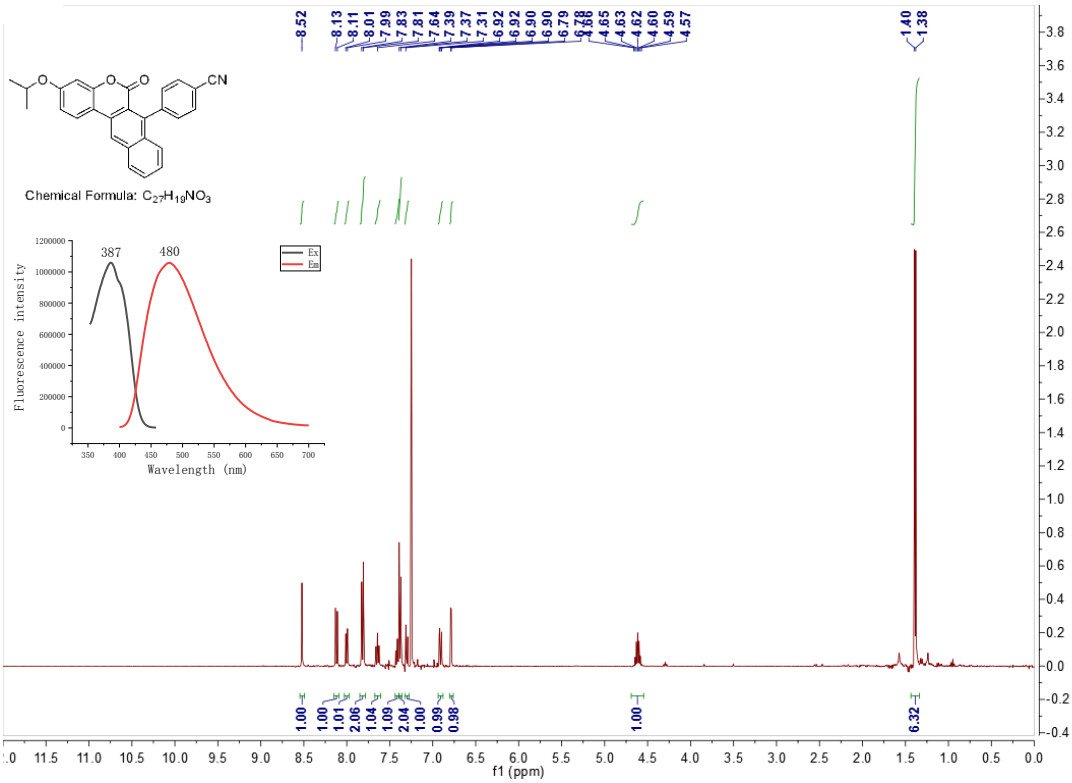
^{13}C NMR of **6f** in $CDCl_3$



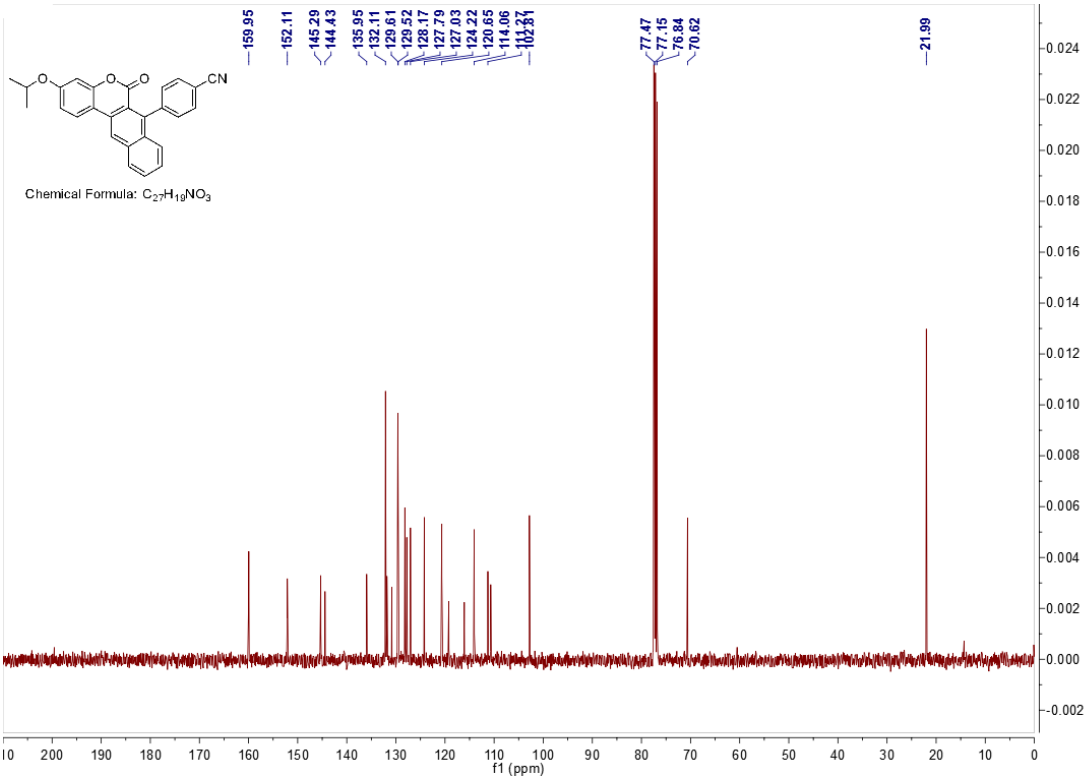
^{1}H NMR of **6g** in $CDCl_3$



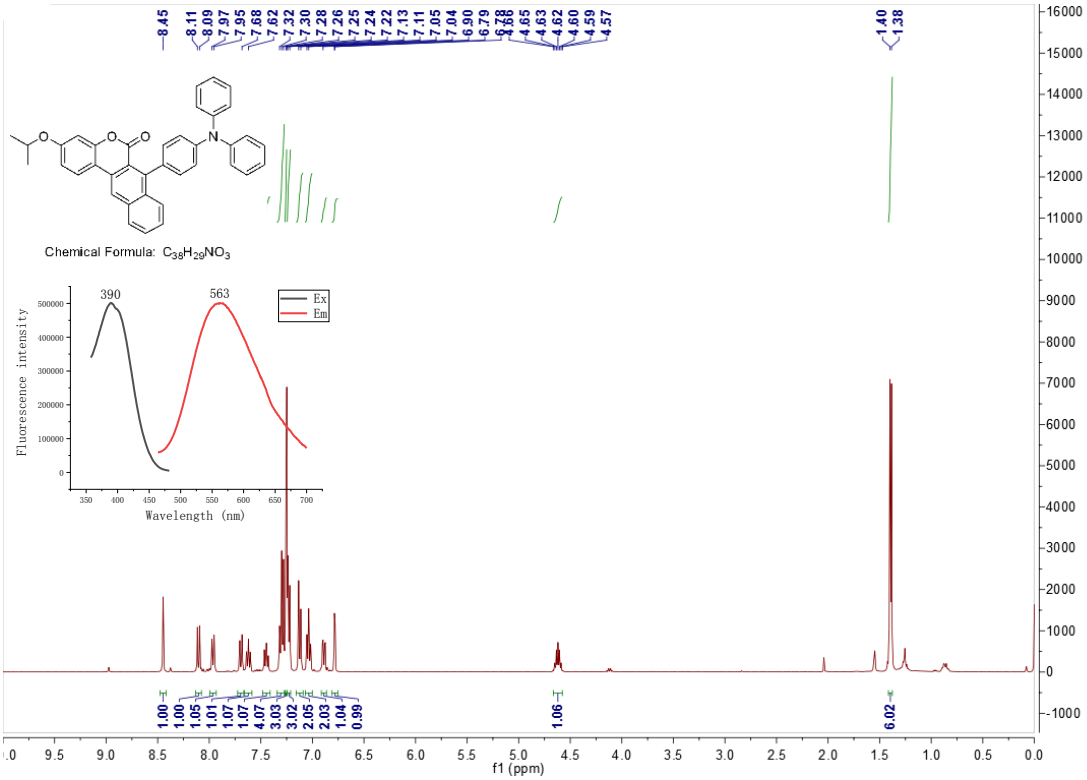
^{13}C NMR of **6g** in $CDCl_3$



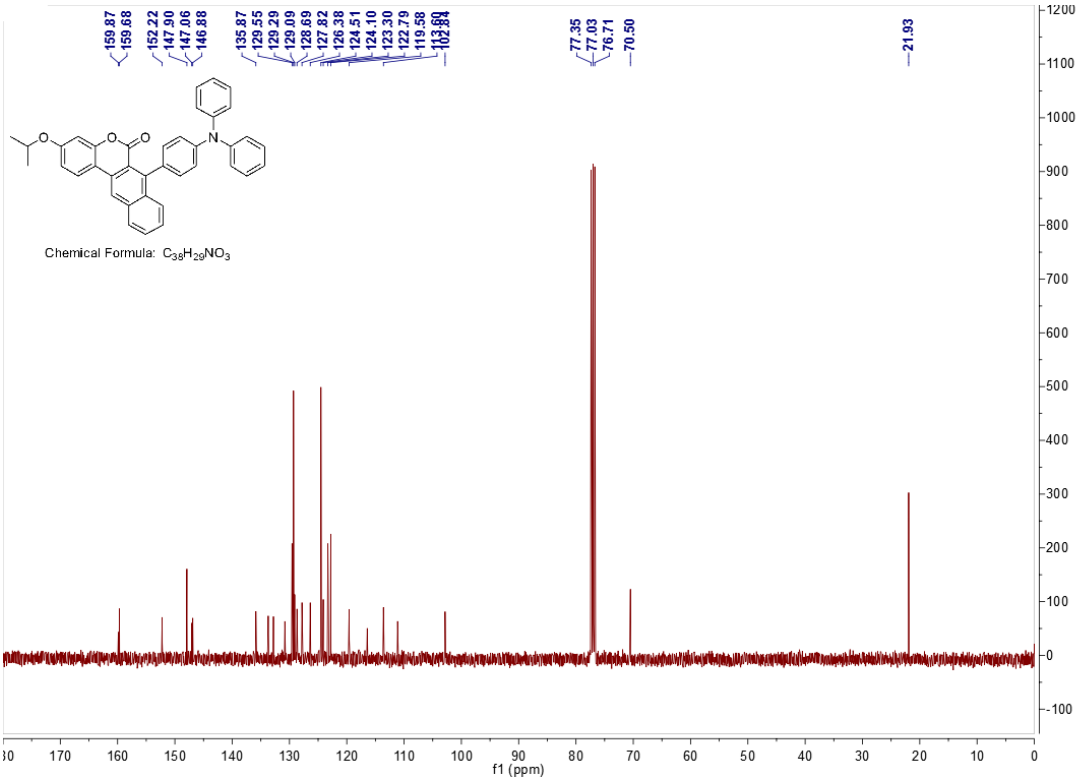
^{1}H NMR of **6h** in $CDCl_3$



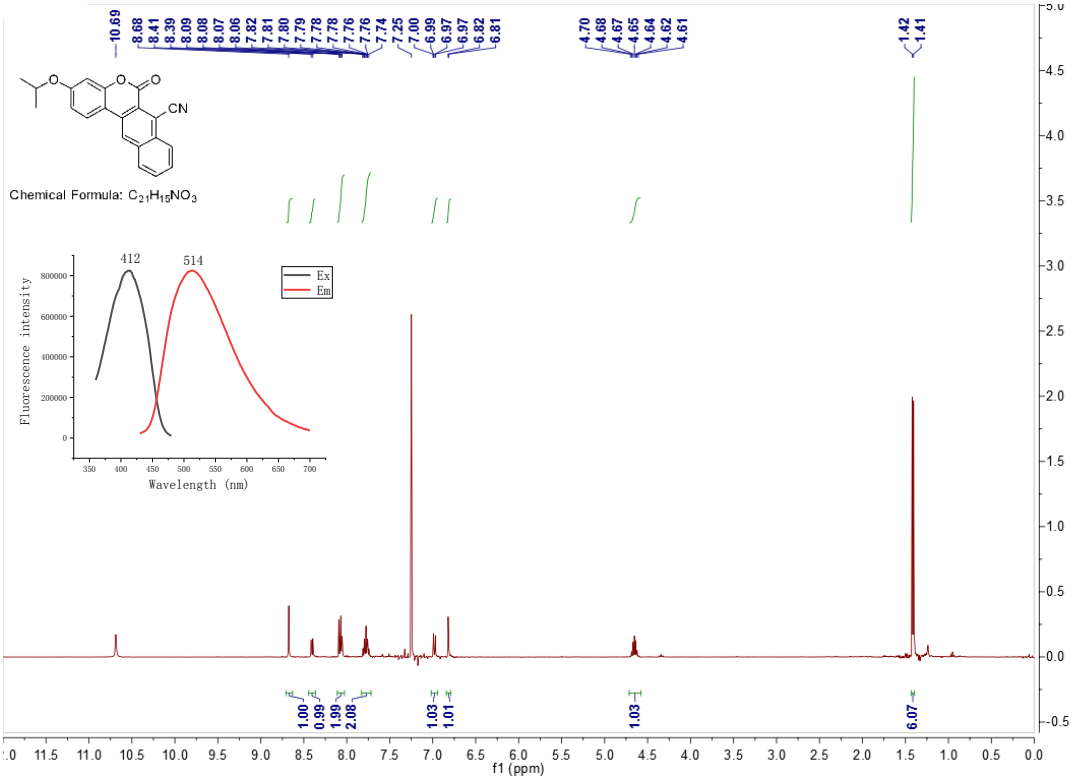
^{13}C NMR of **6h** in $CDCl_3$



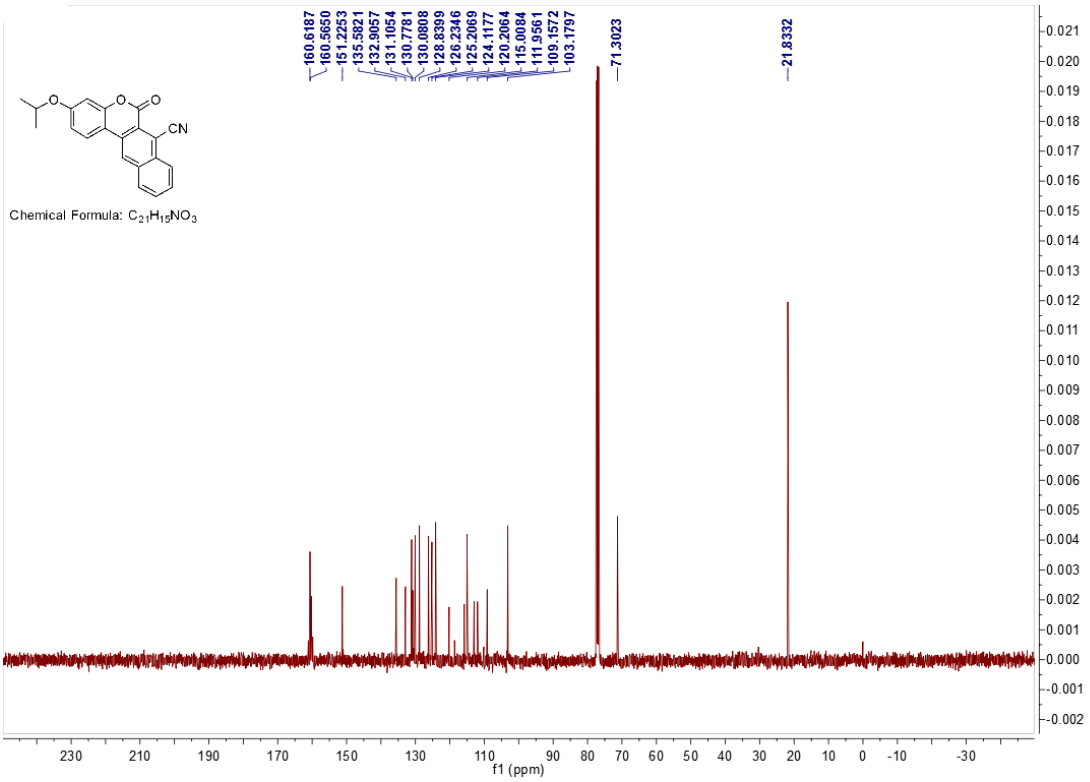
^{1}H NMR of **6i** in $CDCl_3$



^{13}C NMR of **6i** in $CDCl_3$



^{1}H NMR of **6j** in $CDCl_3$ & TFA-d_1



^{13}C NMR of **6j** in $CDCl_3$ & TFA-d_1