Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Materials

Visible light enabling regioselective chlorination of electron-deficient coumarins using $CuCl_2$ *via* LMCT excitation

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Contents

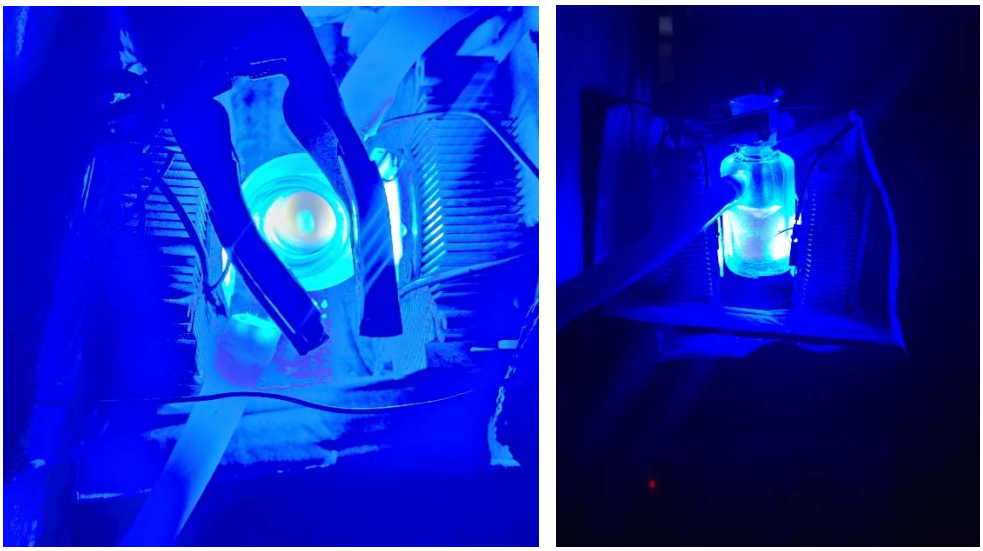
1. General information

All the commercially available coumarins are used without further purification. Thin-layer chromatography (TLC) was performed with silica gel GF254 plates. Column chromatography was performed on silica gel (300 ~ 400 mesh) with petroleum ether/ethyl acetate for the gradient elution. All melting points were measured without correction. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance III HD 600/500 spectrometer at 600/500 MHz (^{1}H NMR) and 151/125 MHz (^{13}C NMR) respectively. The chemical shifts are reported relative to $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.16 for ^{13}C NMR). The infrared spectra were recorded on a Nicolet iS 50 FT-IR spectrometer. HRMS spectra were acquired using an Agilent 6210 ESI/TOF mass spectrometer.

2. Typical procedure for 2a

A mixture of menadione (34.4 mg, 0.2 mmol)，$CuCl_2 \cdot 2H_2O$ (51.2 mg, 0.3 mmol), LiCl (25.4 mg, 0.6 mmol) and TFA (91.2 mg, 0.8 mmol) was dissolved in MeCN (2.0 mL) and put in a reaction vessel open to air as shown below and irradiated with two blue LEDs (460-465 nm, 20 W, ~1240 W/m^2) at 35 °C. The reaction vessel was open to air and the reaction process was monitored by TLC until completed. The reaction mixture was then diluted with 10 mL de-ionized water and extracted by 20 mL EtOAc for three times. The organic phase was combined, dried over Na_2SO_4 and the solvent was removed under vacuum. The crude product was then put on silica gel chromatography and eluted with EA/PE (0.5:100) to give **2a** as a yellow solid (34.1 mg, 82.6%).

The reaction temperature is controlled by a low temperature circulator and the apparatus is shown below:



Experimental Apparatus

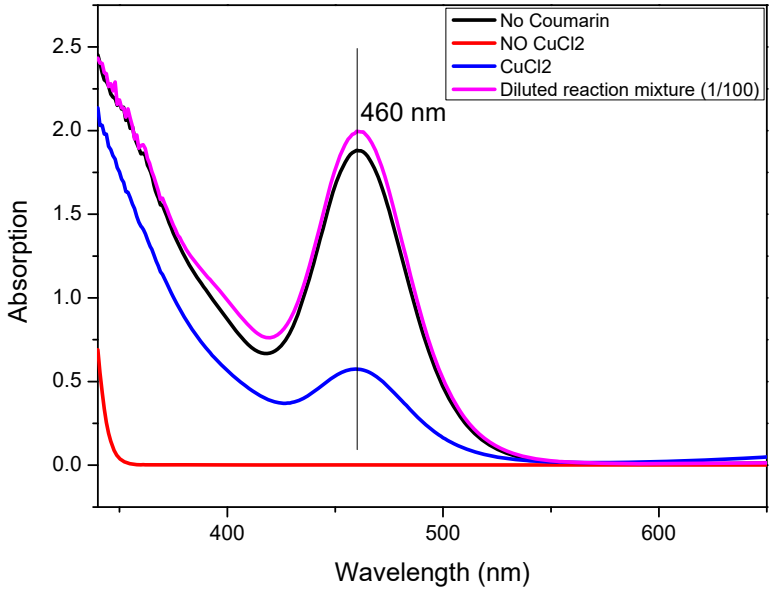
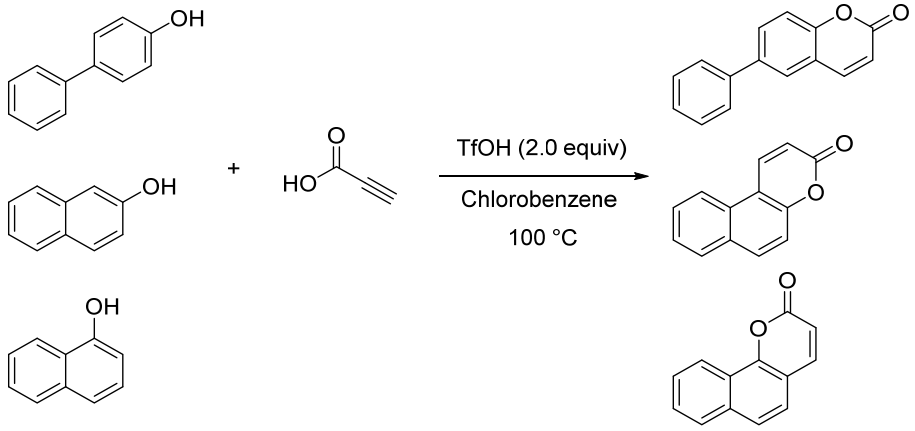


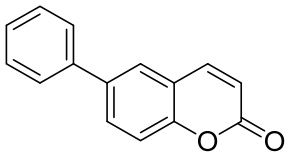
Figure S1 UV-vis spectra of $CuCl_2$ and other mixtures.

3. Syntheses of starting materials

3.1. Syntheses of 6-phenyl-2H-chromen-2-one, 3H-benzo[f]chromen-3-one and 2H-benzo[h]chromen-2-one. [1]



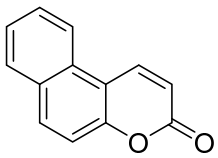
A mixture of Phenol derivatives (1.0 mmol), trifluoromethanesulfonic acid (1.0 mmol) and propionic acid (0.5 mmol) in chlorobenzene (3.0 mL) was stirred at 100 °C for 1 h. After completion of reaction as indicated by TLC, the reaction mixture was poured into H_2O, neutralized with $NaHCO_3$ solution and extracted CH_2Cl_2. The organic layer was washed with 2 M NaOH, dried over anhydrous $MgSO_4$. The solvent was removed in *vaccum*, and the products were purified by silica gel column chromatography (EtOAc-Hex) to give the desired product.



6-phenyl-2H-chromen-2-one (3o)

60 mg, 54%. Pale green solid, m.p. 108-110 ℃ (Acetone/PE, 1/2, V/V) (lit[1]. 118–120 °C) .^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 2H), 7.66 (d, *J* = 2.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 6.46 (dd, *J* = 9.5, 2.1 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 153.5, 143.6, 139.4, 137.9, 130.8, 129.1, 127.9, 127.1, 126.1, 119.1, 117.3, 117.1.

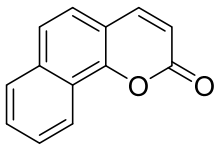
NMR spectra agree well with literature report.[1]



3H-benzo[f]chromen-3-one (3r)

78 mg, 80%. Light pink solid, m.p. 100-102 ℃(lit[1]. 109–112 °C) (Acetone/PE, 1/1, V/V) .^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 9.8 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.69 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 6.57 (d, *J* = 9.8 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 154.0, 139.2, 133.2, 130.4, 129.2, 128.4, 126.2, 121.5, 117.2, 115.8, 113.1.

NMR spectra agree well with literature report. [1]

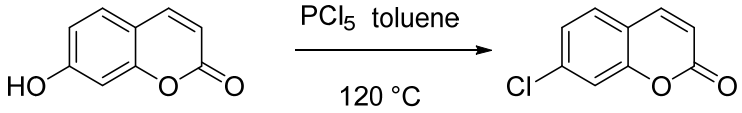


2H-benzo[h]chromen-2-one (3s)

80 mg, 81%. Light pink crystal, m.p. 136-138 ℃ (Acetone/PE, 1/2, V/V) (lit[1]. 100–102 °C).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.44 (m, 1H), 7.90 – 7.84 (m, 1H), 7.83 (d, *J* = 9.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.65-7.59 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 6.52 (d, *J* = 9.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 151.5, 144.3, 135.0, 128.9, 127.9, 127.4, 124.6, 123.7, 123.2, 122.5, 116.1, 114.4.

NMR spectra agree well with literature report.[1]

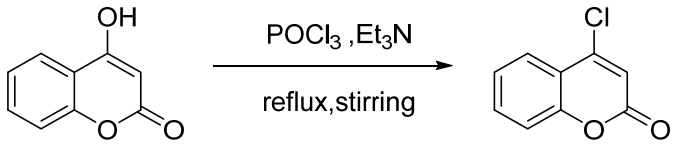
3.2 Synthesis of 7-chloro coumarin (**3e**).



To a three-neck flask, 7-hydroxycoumarin (3.24g 20 mmol) and phosphorus pentachloride (16.63g 80 mmol) and 50 mL toluene were added. The mixture was heated to 110 °C for about 6.5 h until the reaction is completed by TLC monitoring. The reaction mixture was cooled and then poured into ice water with stirring. The aqueous phase was extracted with dichloromethane twice and the organic phase was combined and dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel chromatography and recrystallized in ethyl acetate to give 7-

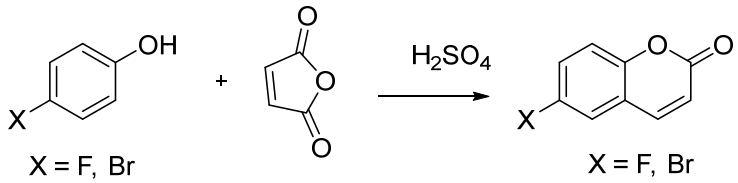
chlorocoumarin (2.88 g, 80%).

3.3 Synthesis of 4-chloro coumarin(**3b**).



4-Chlorocoumarin was synthesized as literature procedure.[2] To an oven-dried two-neck round-bottom flask, 4-hydroxycoumarin (100 mmol, 16.2 g) was charged in phosphorus oxychloride (50 mL). To this mixture, triethylamine (150 mmol, 20 mL) was added slowly in a period of 5–10 min and the mixture was refluxed for 3 h. After the completion of reaction, it was cooled to rt and quenched slowly by pouring into ice-cold water and extracted with dichloromethane. The organic extract was washed with water, brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude was purified by silica gel column chromatography ($CHCl_3$/EtOAc/PE = 7: 4: 100) to obtain 4-chlorocoumarin as white solid (14.5 g, 80% yield).

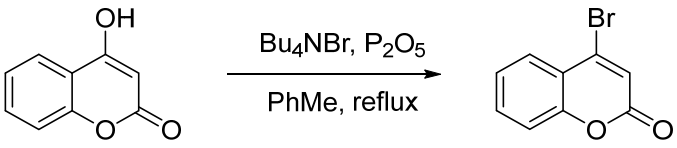
3.4 Synthesis of 6-fluoro coumarin and 6-brormo coumarin (**3h**, **3w**).



6-Fluoro coumarin was synthesized using literature procedure.[3] 4-Fluorophenol (0.01 mol), 0.01 mol of maleic anhydride and 1 mL of concentrated H_2SO_4 were mixed together. And the mixture was heated to 150 °C for 1.5 h. After cooling to room temperature, the reaction solution was diluted with 50 mL of water and extracted four times with 20 mL of ethyl acetate. The extracted liquid was dried with anhydrous magnesium sulfate, and then filtered and concentrated. The obtained crude product was further eluted and recrystallized from ethyl acetate for several times to give 6-fluoro coumarin (0.52 g, 32%).

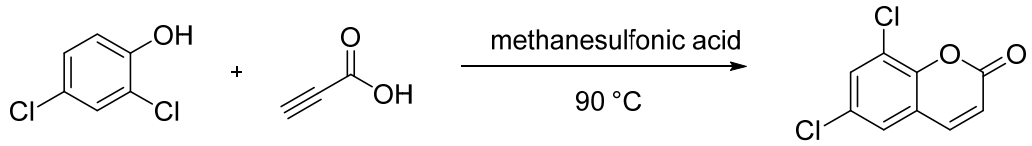
The 6-bromo coumarin was synthesized using the same protocol (0.17 g, 8%).

3.5 Synthesis of 4-bromocoumarin (**3v**)



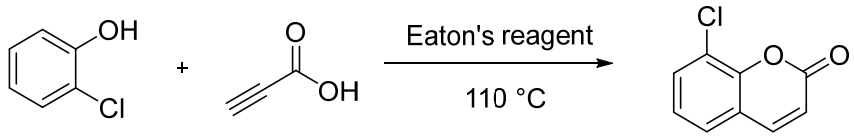
4-Bromo coumarin was synthesized using literature procedure.[4] 4-Hydroxycoumarin (1 g, 6.16 mmol) was added to toluene (12.4 mL, 0.5 M), under an Ar atmosphere and heated to 100 °C. Subsequently, Bu_4NBr (2.98 g, 9.26 mmol) was added, heating was continued until the Bu_4NBr was dissolved, then P_2O_5 (1.75 g,12.34 mmol) was added, and the mixture was further refluxed for 3 h. The hot organic layer was then poured out, and the lower layer was extracted with hot toluene (2 ×20 mL). The combined toluene layer was then successively washed with 5% $NaHCO_3$ (2 ×30 mL), water (50 mL), and saturated brine (50 mL). Subsequently, the organic layer was dried with anhydrous Na_2SO_4 (10 g) and concentrated in vacuum to obtain 4-bromocoumarin (1.34 g, 96%, m.p. 87−89 °C).

3.6 Synthesis of 6,8-dichlorocoumarin(**3g**).



6,8-Dichlorocoumarin coumarin was synthesized as literature procedure.[5] To a solution of phenol derivative (10 mmol) in methanesulfonic acid (20 mL) was added propiolic acid (12 mmol) at room temperature. After stirring at 80-90 ℃ under N_2 atmosphere for 4 h, the solution was diluted with 50 mL de-ionized water and extracted with ethyl acetate (20 mL*3). The ethyl acetate layer was washed with saturated Na_2CO_3 (10 mL*3), saturated NaCl, dried over $MgSO_4$ and concentrated to give 6,8-dichlorocoumarin (0.30 g, 14%) as a gray solid (m.p. 156-158 °C).

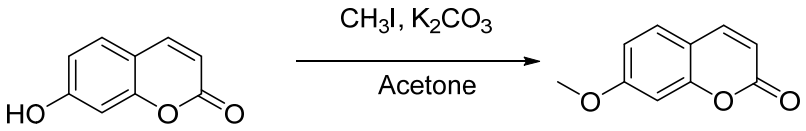
3.7 Synthesis of 8-chlorocoumarin (**3f**).



To a solution of *p*-chlorophenol (10 mmol) in Eaton's reagent (20 mL) was added propiolic acid (12 mmol) at room temperature. After stirring at 110 ℃ under N_2 atmosphere for 4 h, the solution was diluted with 50 mL de-ionized water and extracted with ethyl acetate (20 mL*3). The ethyl acetate layer was washed with saturated Na_2CO_3 (10 mL*3), saturated NaCl, dried over $MgSO_4$, concentrated and

chromatographed to give 8-chlorocoumarin (0.24 g, 13%) as a white solid with m.p. 140-142 °C.

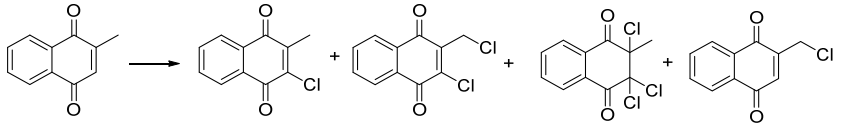
3.8 Synthesis of 7-methoxycoumarin (**3n**).



7-Methoxycoumarin was synthesized using literature procedure.[6] K_2CO_3 (2.0 g, 14.5 mmol) and MeI (3.42 g, 24.1 mmol) were added to a solution of 7-hydroxyl coumarin (2.0 g, 12.3 mmol) in acetone (100 mL) and the mixture was reacted for 5 h. After filtration and dilution with EtOAc, the resulting solution was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to afford compound 7-methoxycoumarin (2.1 g, 97%) as a crystalline solid.

4. Conditions optimization and reaction scope details

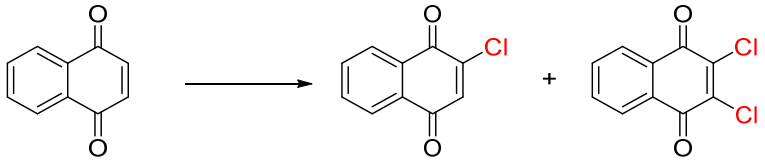
Table S1 Reaction conditions screening for chlorination of menadione (**1a**).



Entry	PC/Other	Lewis Acid	Cl Source	Acid	Time, h	Temp, °C	Conversion, %	Product and yield, % [a]		
								2a	**2a'**	**2a"**
1[c]	2% 4CzIPN	/	/	HCl 3eq	3.0	35	100	8.9		
2 [d]	2% 4CzIPN	$CuCl_2·2H_2O$ 0.1 eq	LiCl 2.8eq	HCl 3eq	8.5	35	92.7	17.8		
3	2% 4CzIPN	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	5.0	35	100	75.6	12.2	4.2
4	**N/A**	**$CuCl_2·2H_2O$ 1.5eq**	**/**	**HCl 3eq**	**4.3**	**35**	**100**	**81.0**	**13.3**	**5.1**
5	**N/A**	**$CuCl_2·2H_2O$ 1.5eq**	**LiCl 3eq**	**TFA 4eq**	**4.2**	**35**	**100**	**82.6**	**10.0**	**5.5**
6 [e]	N/A	$CuCl_2·2H_2O$ 1.5eq	LiCl 3eq	HOAc	5.5	35	91.4	11.8	/	/
7 [f]	Under O_2	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	4	35	100	85.5	7.1	5.3
8 [g]	Under Ar	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	8	35	84.1	42	3.1	5.1
9 [h]	No light	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	23	35	NR			
10	N/A	$FeCl_3·6H_2O$1.0 eq	LiCl 3eq	TFA 4eq	3	35	92.0	15.8	3.1	/
11	N/A	$CeCl_3$ 1.0 eq	LiCl 3eq	TFA 4eq	7.5	35	93.6	5.4		
12	N/A	$ZnCl_2$ 1.0 eq	LiCl 4eq	TFA 4eq	2.5	35	100	7.8		
13	N/A	$CuCl_2·2H_2O$ 1.0eq	NCS 2eq	/	8.5	35	100	61.5	2.7	5.7
14	N/A	$CuCl_2·2H_2O$ 1.5 eq	/	HCl 4eq	4.2	35	100	80.7	12.2	7.0
15	N/A	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	6.2	24	100	77.5	15.4	6.1
16	N/A	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	5.0	30	100	82.1	8.6	5.9
17	N/A	$CuCl_2·2H_2O$ 1.5eq	/	HCl 3eq	4.3	40	100	80.0	12.5	7.3
18	N/A	$CuCl_2·2H_2O$ 0.5eq	LiCl 5eq	TFA 4eq	10	35	82.3	39.0	/	7.6
19	N/A	$CuCl_2·2H_2O$ 1.0eq	LiCl 4eq	TFA 4eq	6.5	32	100	67.6	10.0	6.0
20	N/A	$CuCl_2·2H_2O$ 2.0eq	LiCl 2eq	TFA 4eq	3.8	35	100	80.7	9.7	3.2
21	N/A	CuCl2·2H2O 1.5eq	LiCl 2eq	TFA 4eq	5.4	40	100	82.8	10.9	5.0
22	N/A	$CuCl_2·2H_2O$ 1.5eq	LiCl 3eq	TFA 2 eq	5.4	38	100	75.8	11.2	6.2
23	N/A	CuCl2·2H2O 1.5eq	/	TFA 4eq	6	40	88.1	57.8	/	/
24	N/A	CuCl2·2H2O 1.5eq	LiCl 1eq	TFA 4eq	6	40	94.8	80.3	3.3	4.7
25	N/A	$CuCl_2·2H_2O$ 1.0eq	/	HCl 4eq	5.1	35	100	71.6	19.7	8.4

[a] Reagents and conditions：menadione (0.2 mmol), LiCl/TFA or HCl was mixed in 2 mL MeCN, irradiated between two blue LEDs (460-465 nm, 20 W, ~1240 W/m^2) open to air at 35 °C. NR= No reaction. [b] Isolated yield. [c] Methyl chlorinated naphthoquinone (2-(chloromethyl)naphthalene-1,4-dione, MCNQ) was obtained in 21% yield. [d] MCNQ (3.4%) was obtained. [e] Reacted in 2 mL acetic acid. The major product is 3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl acetate (42%). [f] Using O_2 balloon. [g] Using Ar balloon (1 atm). MCNQ was obtained in 12% yield. [h] In dark.

Table S2 Chlorination of naphthoquinone **1b**. [a]

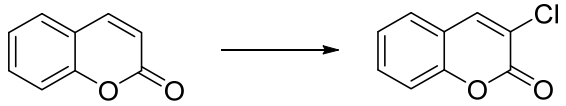


1b **2b** **2b'**

Lewis Acid/eq.	LiCl	TFA	Time, h	Conversion, %	Yield, % [b]	
					2b	**2b'**
$CuCl_2·2H_2O$ 2.5	1	2	9	100	37.6	40.0
$CuCl_2·2H_2O$ 1.5	0	0[c]	11.5	100	33.9	39.6
$CuCl_2·2H_2O$ 2.5	**1**	**2[d]**	**9.5**	**71.5**	**60.5**	**10.2**
$CuCl_2·2H_2O$ 1.5	3	4	62.5	89.8	7.4	44.1

[a] Reagents and conditions：naphthoquinone (0.2 mmol), LiCl/TFA or HCl was mixed in 2 mL MeCN, irradiated between two blue LEDs (460-465 nm, 20 W, ~1240 W/m^2) open to air at 35 °C. [b] Isolated yield. [c] 6 eq HCl. [d] 2.0 eq HOAc.

Table S3 Screening of halogenation for coumarin (**3a**). [a]



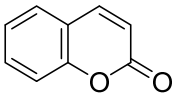
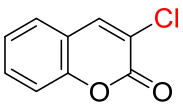
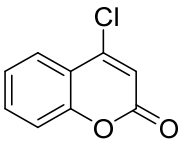
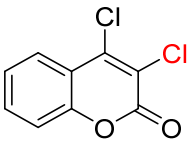
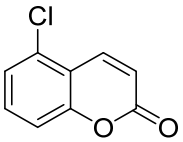
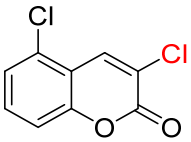
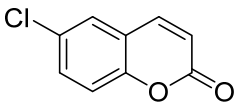
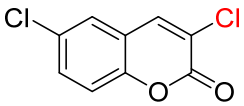
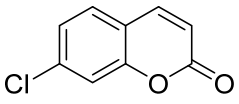
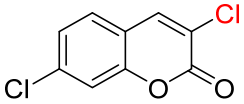
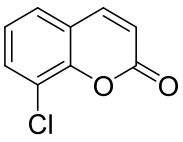
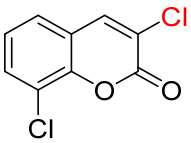
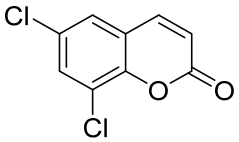
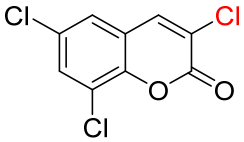
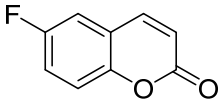
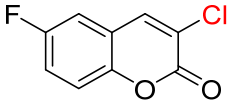
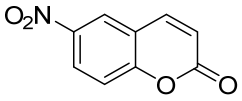
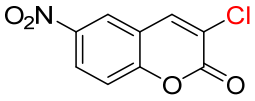
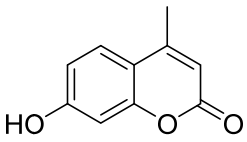
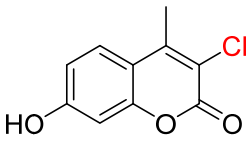
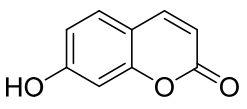
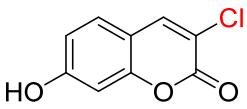
+ Ring opening product.

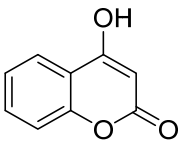
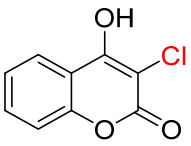
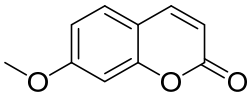
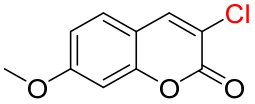
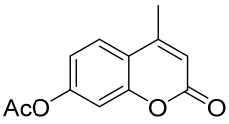
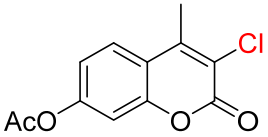
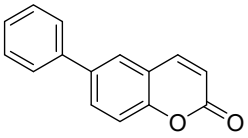
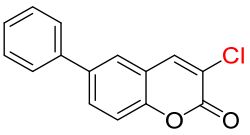
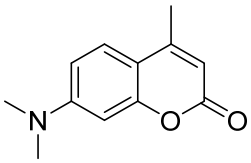
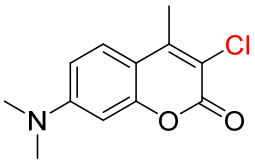
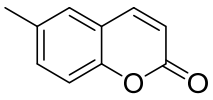
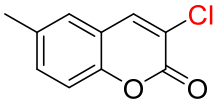
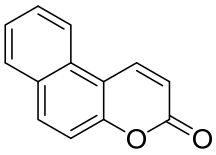
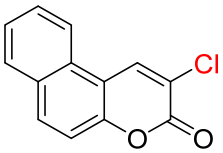
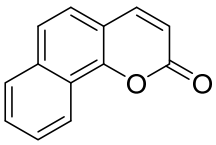
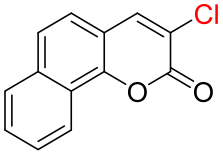
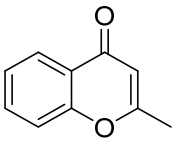
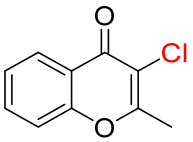
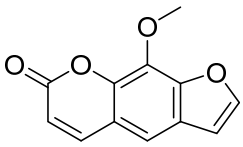
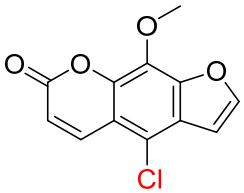
3a **4a**

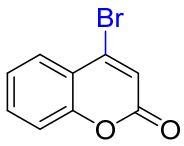
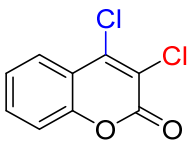
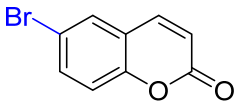
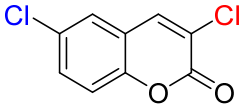
Entry	PC/2 mol%	Lewis Acid	LiCl	HCl	TFA	Time, h	Conv., %	Yield, % [b]
1	N/A	**$CuCl_2 \cdot 2H_2O$ 1.5 eq**	**3**	**0**	**3**	**9.5**	**100**	**67.6**
2	N/A	$CuCl_2 \cdot 2H_2O$ 1.5 eq	0	3	0	4.5	100	53.2
3	N/A	$CuCl_2 \cdot 2H_2O$ 1.5 eq	1	2.5	0	6.5	91.8	67.5
4	N/A	$CuCl_2 \cdot 2H_2O$ 2.0 eq	2	0	2	11.5	100	68.0
5	4CzIPN	$CuCl_2 \cdot 2H_2O$ 0.1 eq	4.3	1.5	0	3.2	100	56.6
6	4CzIPN	$CuCl_2 \cdot 2H_2O$ 0.1 eq	2	0	1.5	1.8	100	53.1
7	4CzIPN	N/A	2	0	1.5	1.8	64.0	0 [c]
8	N/A	$Cu(AcO)_2 \cdot H_2O$ 1.5 eq	5	0	3	15	100	65.0
9	N/A	CuCl 1.5 eq	5	0	3	14	100	69.4
10	N/A	$Cu(BF_4)_2 \cdot H_2O$ 1.5 eq	6	0	3	10	100	66.5

[a] Reagents and conditions: a mixture of coumarin (0.2 mmol)，Lewis Acid, LiCl or HCl was dissolved in MeCN (2 mL) and irradiated under two blue LEDs (460-465 nm, 20 W, ~1240 W/m^2) at 35 °C, open to air. NR= No reaction. [b] Isolated yield. [c] The conversion of coumarin is based on the recovery of starting materials (36.0%), complicated high polarized products was generated.

Table S4 Scope of the chlorination reactions.

Substrate	Substrate's Structure	Product	Deviation from standard condition [a]	Time, h	Yield, %
3a			None	9.5	68
3b			None	12	87
3c			None	7.5	66
3d			None	8.5	70
3e			None	6	62
3f			None	10.5	62
3g			None	9.5	75
3h			None	16	61
3i			None	10.5	62
3j			None	37	69
3k			2.5 eq $CuCl_2.2H_2O$	11.5	87

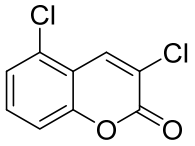
3l			None	9.5	89
3m			None	3.5	57
3n			None	11.5	78
3o			2.5 eq $CuCl_2.2H_2O$	26	74
3p			None	6	18
3q			2.5 eq $CuCl_2.2H_2O$, 1.5 eq HOAc	1.5	29
3r			4 eq TFA	13.5	74
3s			2.5 eq $CuCl_2.2H_2O$	36	58
5a			None	16	37
5b			None	10	25

3v		 **3b**	None	9	93
3w		 **3d**	None	8	67

[a] Standard condition: Substrate (0.2 mmol), $CuCl_2 \cdot 2H_2O$ (0.3 mmol), LiCl (0.6 mmol), TFA (0.4 mmol) in 2 mL MeCN. The reaction mixture was irradiated under two blue LEDs (460-465 nm, 20 W, ~1240 W/m^2) at 35 °C until the reaction is completed by TLC monitoring.

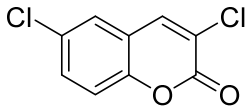
5. The spectral data

The unreported compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS the details are given below. All the known compounds' spectral data (^{1}H NMR, ^{13}C NMR, IR, MS) agree with the reported references. The spectral data of the compounds reported in previous paper of *Synlett*, 2019, 30, 630–634 (DOI: 10.1055/s-0037-1612080) are not shown here.



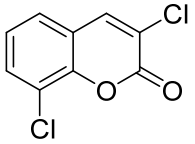
3,5-dichloro-2H-chromen-2-one (4c)

Yield: 28.3 mg, 66%. White solid, m.p. 164-166 ℃ (Acetone/PE, 2/1, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.48 (t, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 153.5, 136.6, 132.0, 131.7, 125.7, 123.8, 117.6, 115.7. IR(KBr) υ_{max}: 3089, 1743, 1730, 1609, 1591, 1446, 1314, 1247, 1228, 1201, 1157, 1137, 991, 964, 914, 789, 752, 722, 679, 605, 582, 475. HRMS calcd for $C_9H_5Cl_2O_2^+$ $(M+H)^+(Cl^{35})$:214.9661, found: 214.9662.



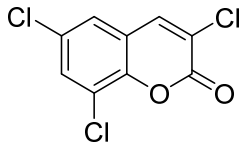
3,6-dichloro-2H-chromen-2-one (4d)

Yield: 29.5 mg, 70%. White solid, m.p. 166-168 ℃(Acetone/PE, 2/1, V/V) (lit[7]124-126 ℃).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 151.2, 138.9, 132.0, 130.6, 126. 6, 124.0, 119.9, 118.4.IR(KBr) υ_{max}: 3099, 3062, 3045, 1732, 1601, 1557, 1475, 1409, 1336, 1266, 1241, 1145, 1081, 998, 945, 925, 893, 865, 819, 755, 651, 638, 571, 530, 461 cm^{-1}. HRMS calcd for $C_9H_5Cl_2O_2^+$ $(M+H)^+(Cl^{35})$: 214.9661, found: 214.9668.



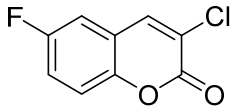
3,8-dichloro-2H-chromen-2-one (4f)

Yield: 26.5 mg, 62%.White solid, m.p.164-166 ℃ (Acetone/PE, 2/1, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 148.5, 139.7, 132.4, 125.8, 125.5, 123.4, 122.0, 120.2. IR(KBr) υ_{max}: 2924, 2855, 1756, 1738, 1600, 1489, 1442, 1354, 1253, 1225, 1143, 10036, 948, 932, 779, 748, 725, 658cm^{-1}. HRMS calcd for $C_9H_5Cl_2O_2^+$ $(M+H)^+(Cl^{35})$: 214.9661, found: 214.9657.



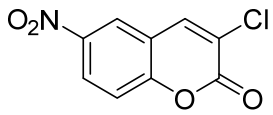
3,6,8-trichloro-2H-chromen-2-one (4g)

Yield: 37.2 mg, 75%. White solid, m.p. 126-128℃ (Acetone/PE, 2/1, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 147.1, 138.6, 131.9, 130.4, 125.2, 124.7, 122.8, 120.6. IR(KBr) υ_{max}:3075, 2924, 2853, 1754, 1553, 1458, 1449, 1439, 1416, 1341, 1243, 1229, 1149, 1100, 1013, 966, 931, 885, 866, 837, 752, 688, 641, 573, 539cm^{-1}. HRMS calcd for $C_9H_4Cl_3O_2^+$ $(M+H)^+(Cl^{35})$: 248.9271, found: 248.9267.



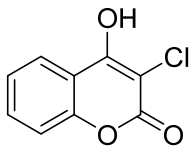
3-chloro-6-fluoro-2H-chromen-2-one (4h)

Yield: 24.2 mg, 61%. White solid, m.p. 148-150 ℃ (Acetone/PE, 2/1, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.35 (dd, *J* = 9.1, 4.4 Hz, 1H), 7.28 (ddd, *J* = 10.9, 8.1, 2.9 Hz, 1H), 7.17 (dd, *J* = 7.7, 2.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.16 (d, *J* = 245.6 Hz), 156.95 (s), 148.98 (d, *J* = 2.1 Hz), 139.17 (d, *J* = 2.8 Hz), 124.05 (s), 119.65 (d, *J* = 9.3 Hz), 119.46 (d, *J* = 24.6 Hz), 118.55 (d, *J* = 8.5 Hz), 112.73 (d, *J* = 24.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.79. IR(KBr) υ_{max}: 3054, 1741, 1568, 1486, 1431, 1346, 1260, 1149, 1001, 933, 890, 876, 822, 750, 696, 588, 463 cm^{-1}. HRMS calcd for $C_9H_5ClFO_2^+$ $(M+H)^+(Cl^{35})$: 198.9957, found:198.9954.



3-chloro-6-nitro-2H-chromen-2-one (4i)

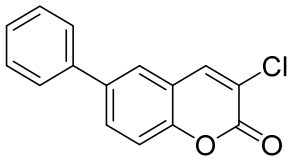
Yield: 28.3 mg, 62%. Yellow solid, m.p. 186-188 °C (Acetone/PE, 2/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 – 8.40 (m, 1H), 8.41 (s, 1H), 7.96 (s, 1H), 7.53 – 7.48 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 155. 8, 144.7, 138.7, 126.7, 125.2, 123.2, 119.0, 118.2. IR（KBr）：3056, 1741, 1609, 1528, 1475, 1350, 1261, 1244, 1155, 1121, 1086, 990, 949, 930, 841, 821, 756, 748, 722, 650 cm^{-1}. HRMS calcd for $C_9H_4ClNNaO_4^+$ $(M+Na)^+(Cl^{35})$: 247.9721, found: 247.9726.



3-chloro-4-hydroxy-2H-chromen-2-one (4l)

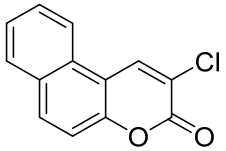
Yield: 34.9 mg, 89%. White solid, m.p. 206-208 ℃ (lit[8] 206-207℃) (CH_2Cl_2/PE, 1/1, V/V). ^{1}H NMR (500 MHz, Acetone-*d*$_6$) δ 7.94 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.8, 7.4, 1.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, Acetone-*d*$_6$) δ 160.4, 158.8, 152.6, 133.5, 125.3, 124.2, 117.3, 116.5, 100.4.

NMR spectra agree well with literature report.[8]



3-chloro-6-phenyl-2H-chromen-2-one (4o)

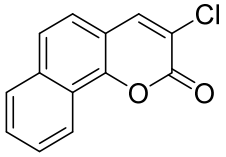
Yield: 38.5 mg, 74%. White solid, m.p. 162-164 ℃ (CH_2Cl_2/PE, 1/2, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.76 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.57 (dt, *J* = 3.1, 1.9 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 152.2, 140.2, 139.2, 138.6, 131.0, 129.2, 128.2, 127.2, 125.5, 122.9, 119.2, 117.3. IR(KBr) υ_{max}: 1730, 1708, 1569, 1480, 996, 754, 693, 645, 607 cm^{-1}. HRMS calcd for $C_{15}H_{10}ClO_2^+$ $(M+H)^+(Cl^{35})$: 257.0364 , found: 257.0360.



2-chloro-3H-benzo[f]chromen-3-one (4r)

Yield: 34.7 mg, 75%.White solid, m.p.160-162 ℃ (lit[9] 164-165 ℃)(CH_2Cl_2/PE, 1/2, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ8.57 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.60 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 152.5, 136.4, 133.3, 130.5, 129.2, 128.7, 128.4, 126.6, 121.9, 121.5, 116.7, 113.2. IR(KBr) υ_{max}: 3063, 2924, 1732, 1697, 1626, 1586, 1562, 1509, 1457, 1435, 1330, 1277, 1208, 1001, 985, 916, 903, 812, 776, 745, 588, 539 cm^{-1}.

NMR spectra agree well with literature report.[9]

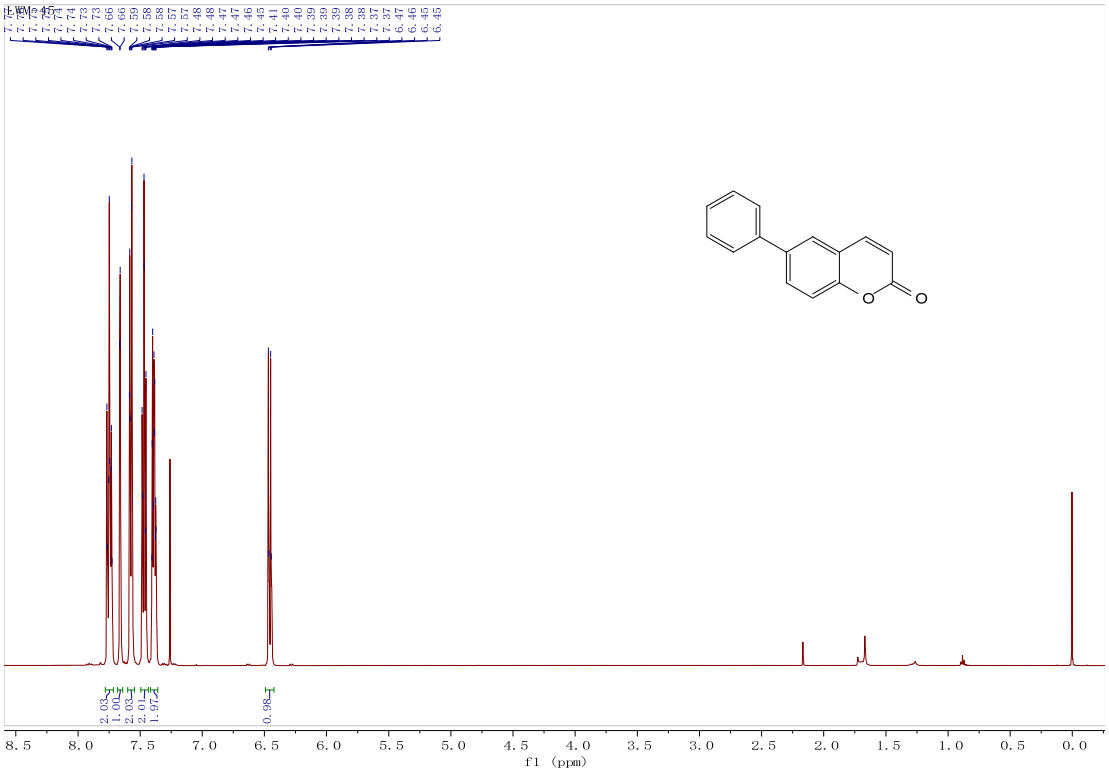


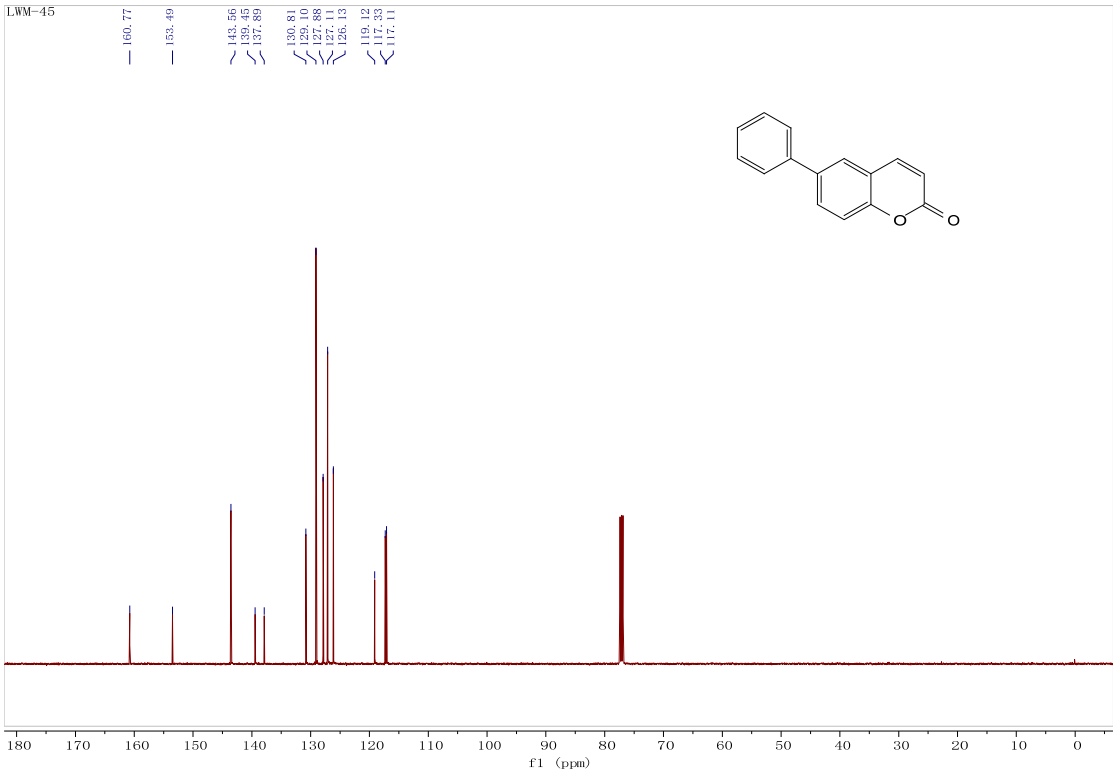
3-chloro-2H-benzo[h]chromen-2-one (4s)

Yield: 27.6 mg, 58%. White solid, m.p.146-148 ℃ (CH_2Cl_2/PE, 1/2, V/V). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 – 8.42 (m, 1H), 7.92 (s, 1H), 7.85 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 149.9, 140.8, 134.7, 129.0, 127.9, 127.6, 125.2, 122.8, 122.7, 122.2, 121.8, 114.3. IR(KBr) υ_{max}:1739, 1721, 1635, 1601, 1556, 1542, 1471, 1373, 1340, 1278, 1128, 1049, 941, 918, 807, 754, 671, 619, 569 cm^{-1}. HRMS calcd for $C_{13}H_8ClO_2^+$ $(M+H)^+(Cl^{35})$: 231.0207, found:231.0204.

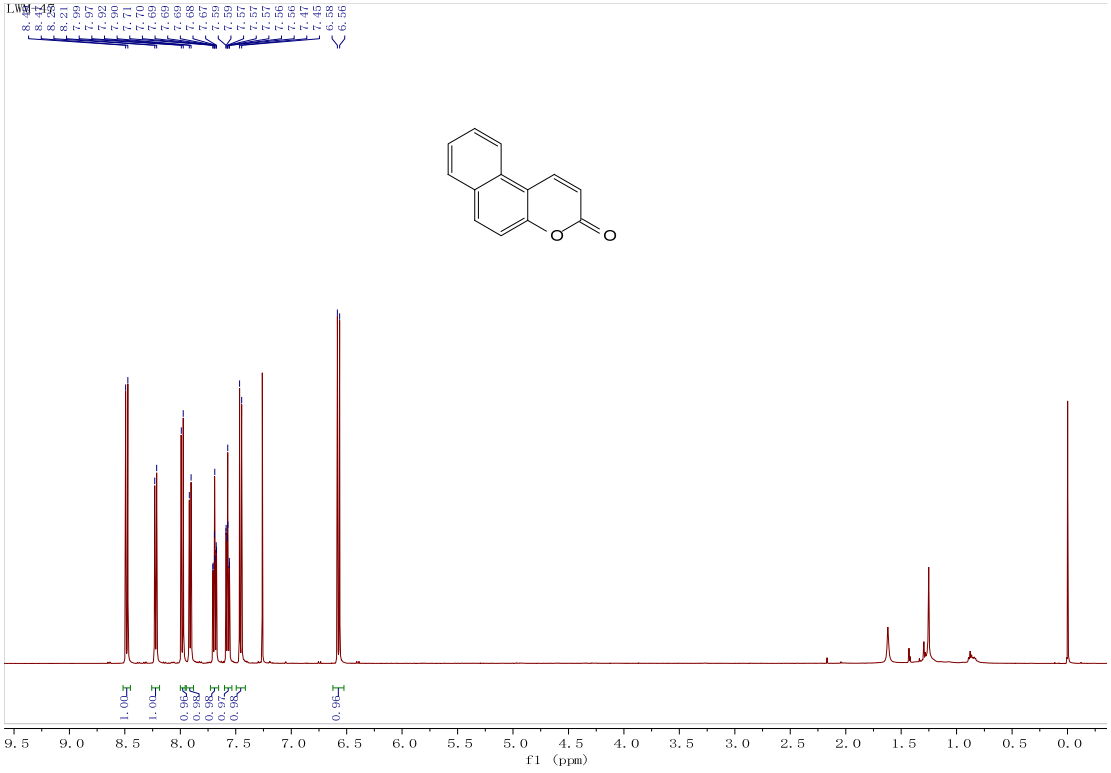
6. The NMR Charts

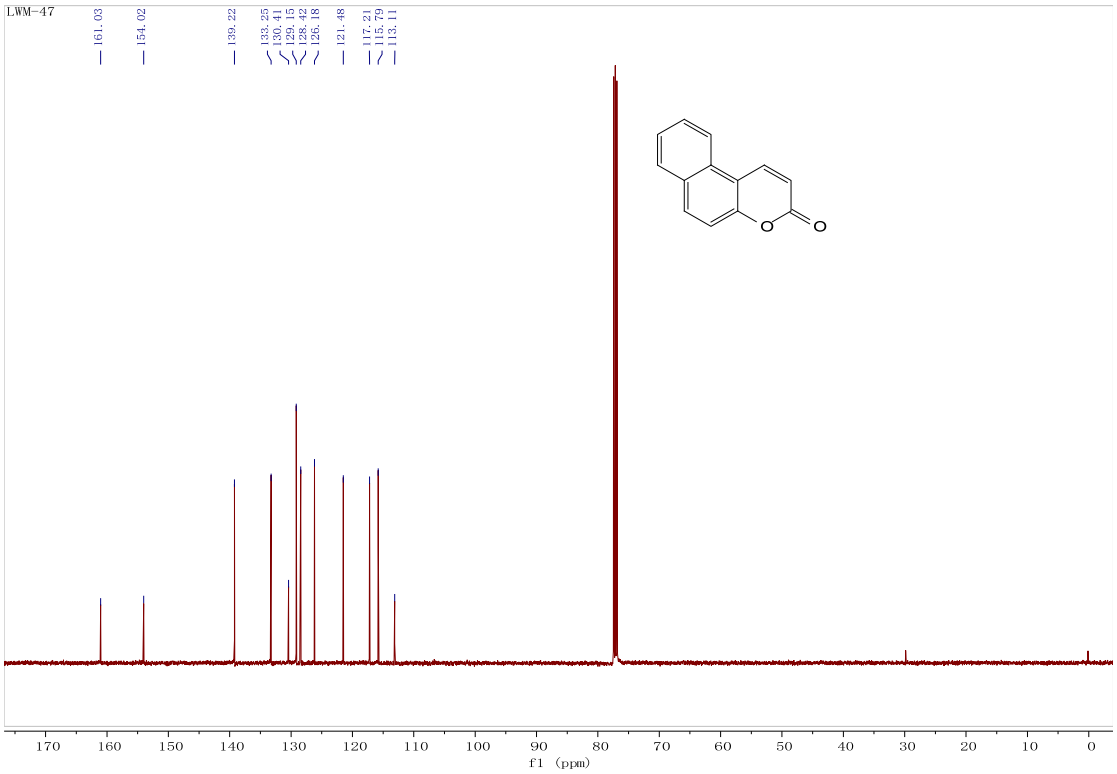
3o



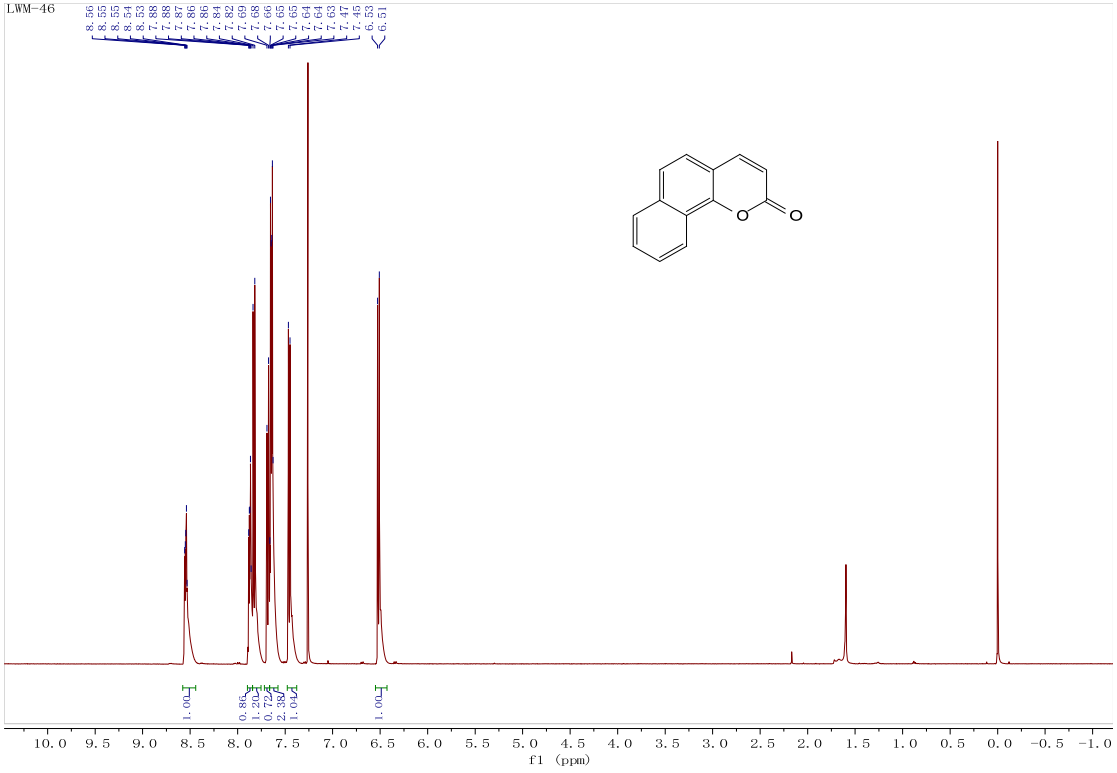


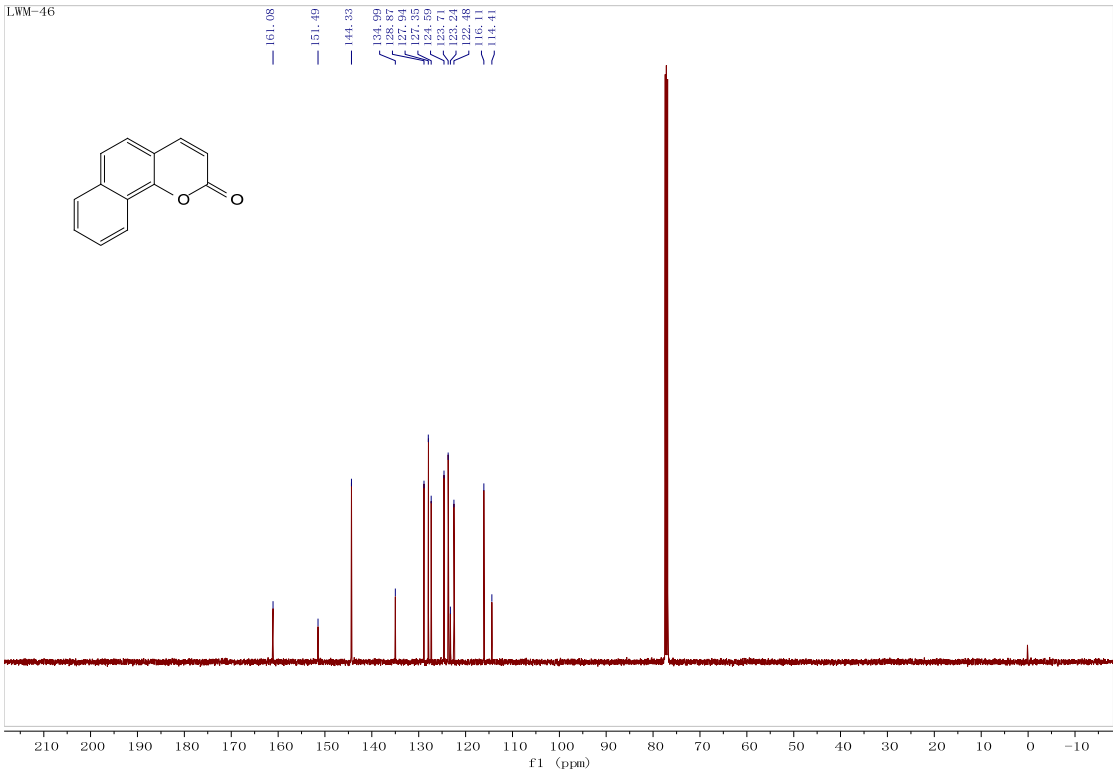
3r


LWM-47
8.44
8.43
8.25
8.21
7.99
7.97
7.92
7.90
7.71
7.70
7.69
7.69
7.68
7.67
7.59
7.59
7.57
7.57
7.57
7.56
7.56
7.47
7.45
6.58
6.56
1.00
1.00
0.96
0.98
0.98
0.97
0.98
0.96
f1 (ppm)

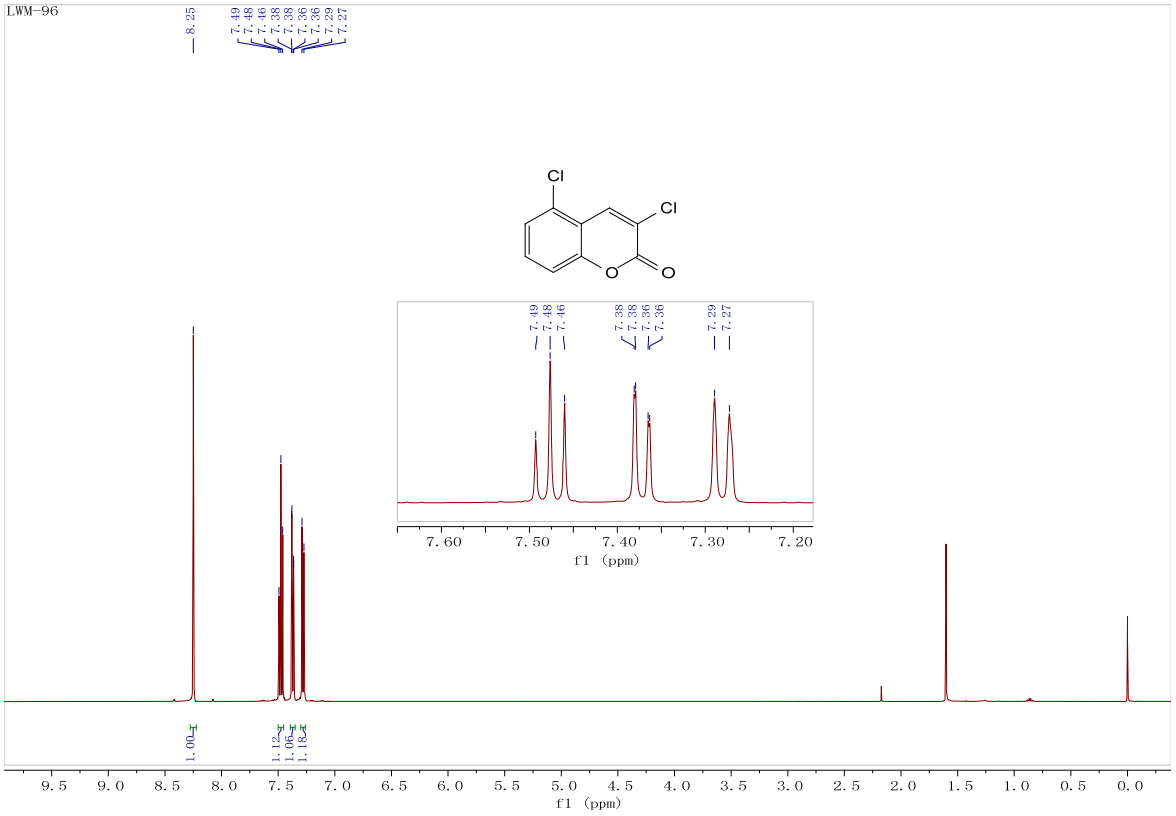

LWM-47
161.03
154.02
139.22
133.25
130.41
129.15
128.42
126.18
121.48
117.21
115.79
113.11
f1 (ppm)

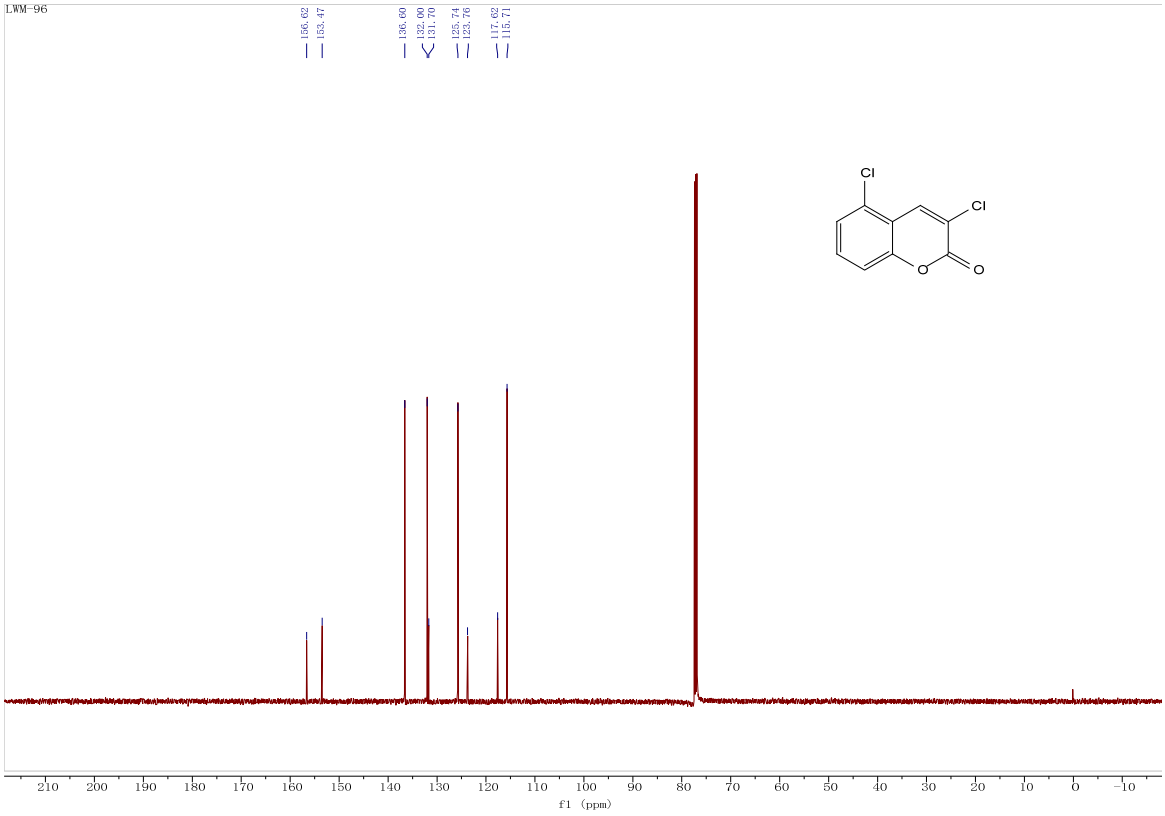
3s


LWM-46
8.56
8.55
8.55
8.54
8.54
7.88
7.88
7.87
7.86
7.86
7.84
7.82
7.69
7.68
7.66
7.65
7.65
7.64
7.64
7.63
7.47
7.45
6.53
6.51
1.00
0.85
1.20
0.72
2.38
1.04
1.00
f1 (ppm)

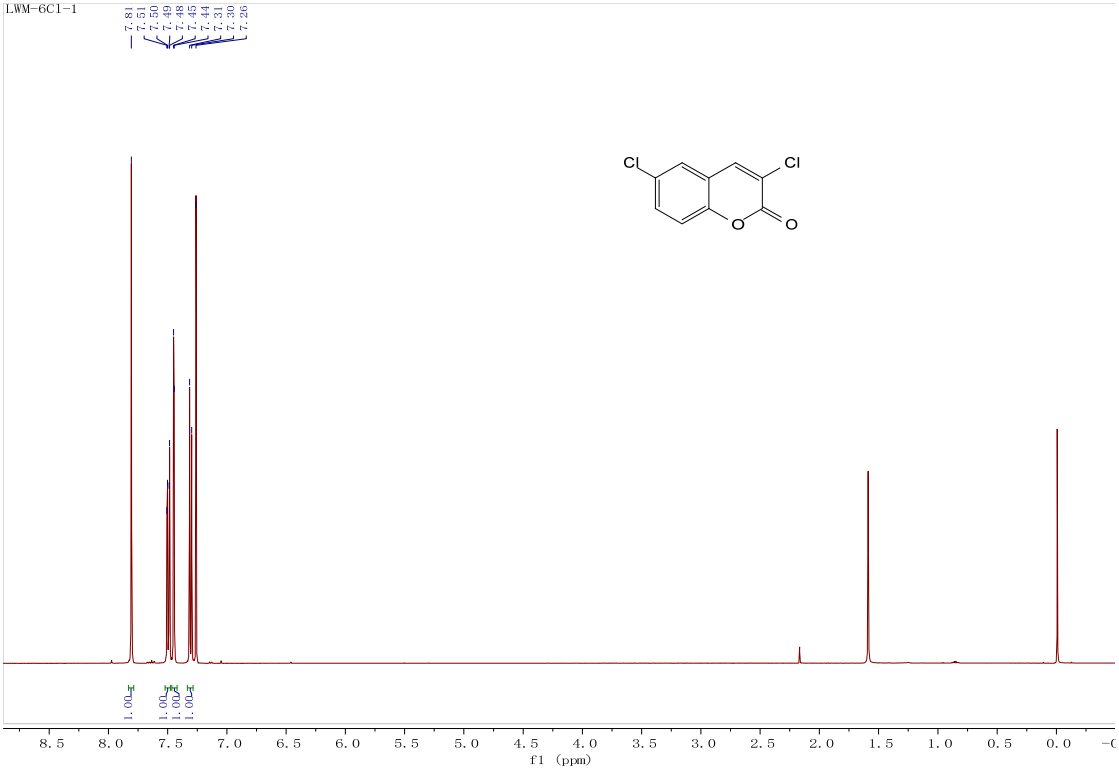

LWM-46
161.08
151.49
144.33
134.99
128.87
127.94
127.35
124.59
123.71
123.24
122.48
116.11
114.41
f1 (ppm)

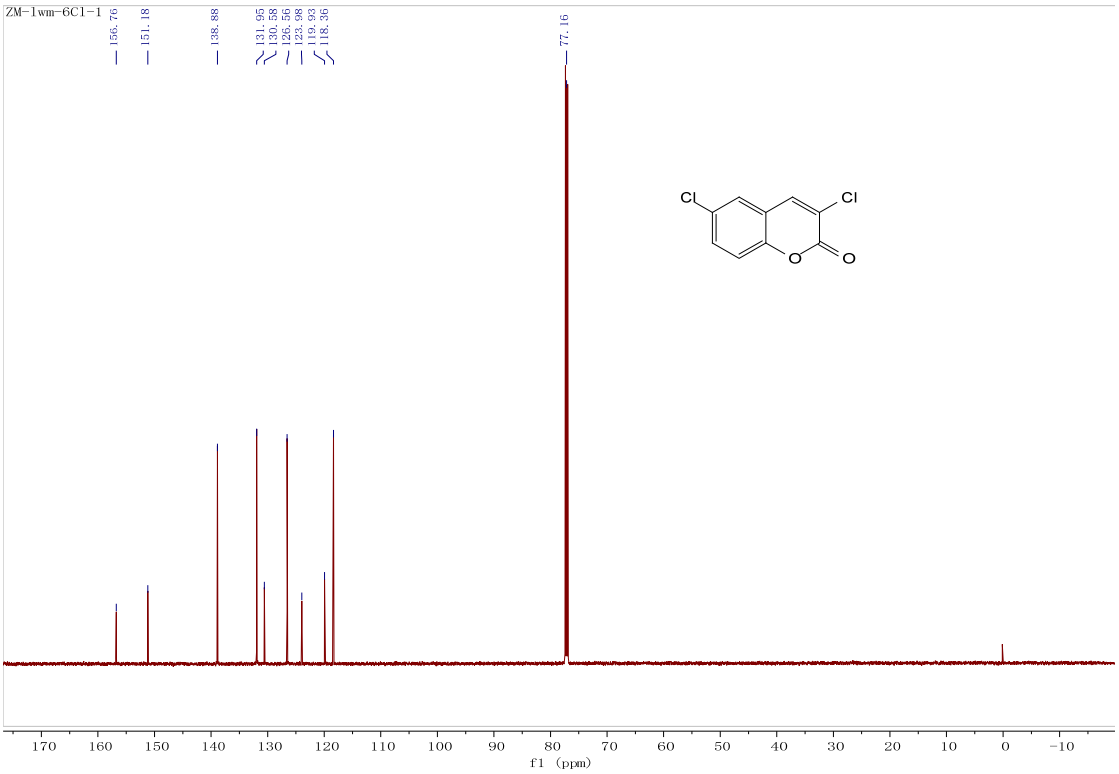
4c


LWM-96
8.25
7.49
7.48
7.46
7.38
7.38
7.36
7.36
7.29
7.27
Cl
Cl
O
O
1.00
1.12
1.06
1.18
f1 (ppm)

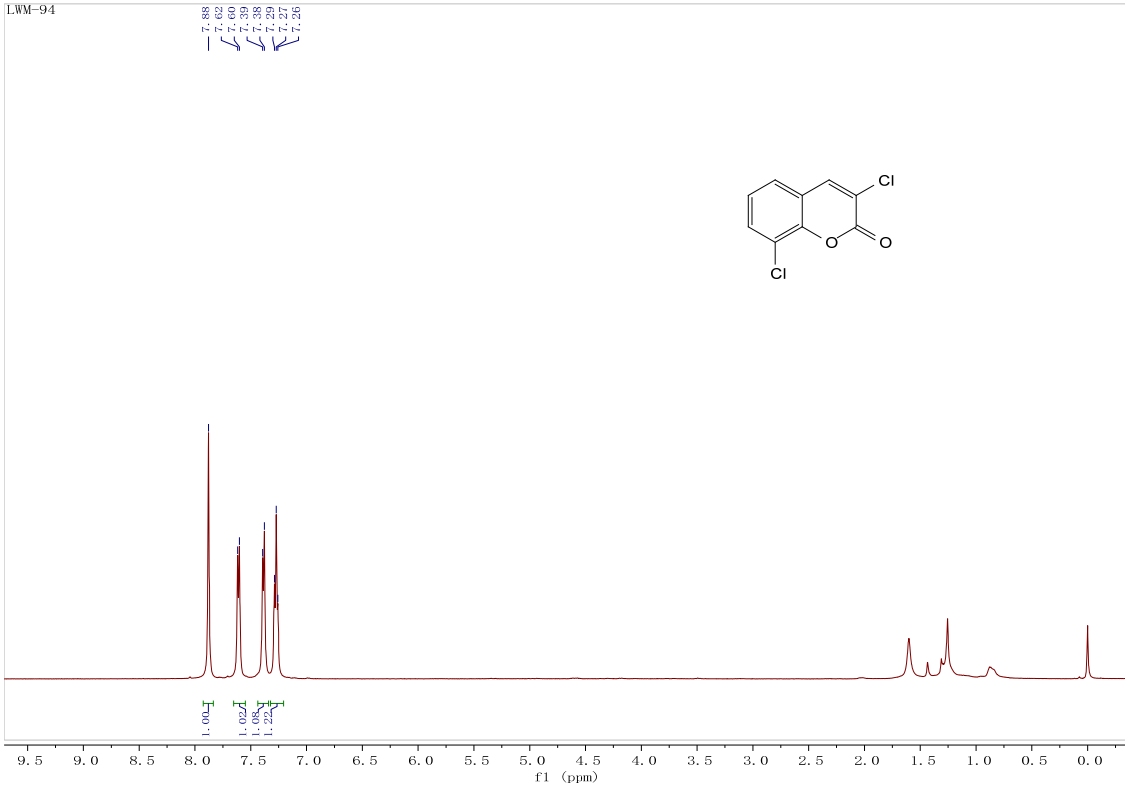

LWM-96
156.62
153.47
136.60
132.00
131.70
125.74
123.76
117.62
115.71
Cl
Cl
O
O
f1 (ppm)

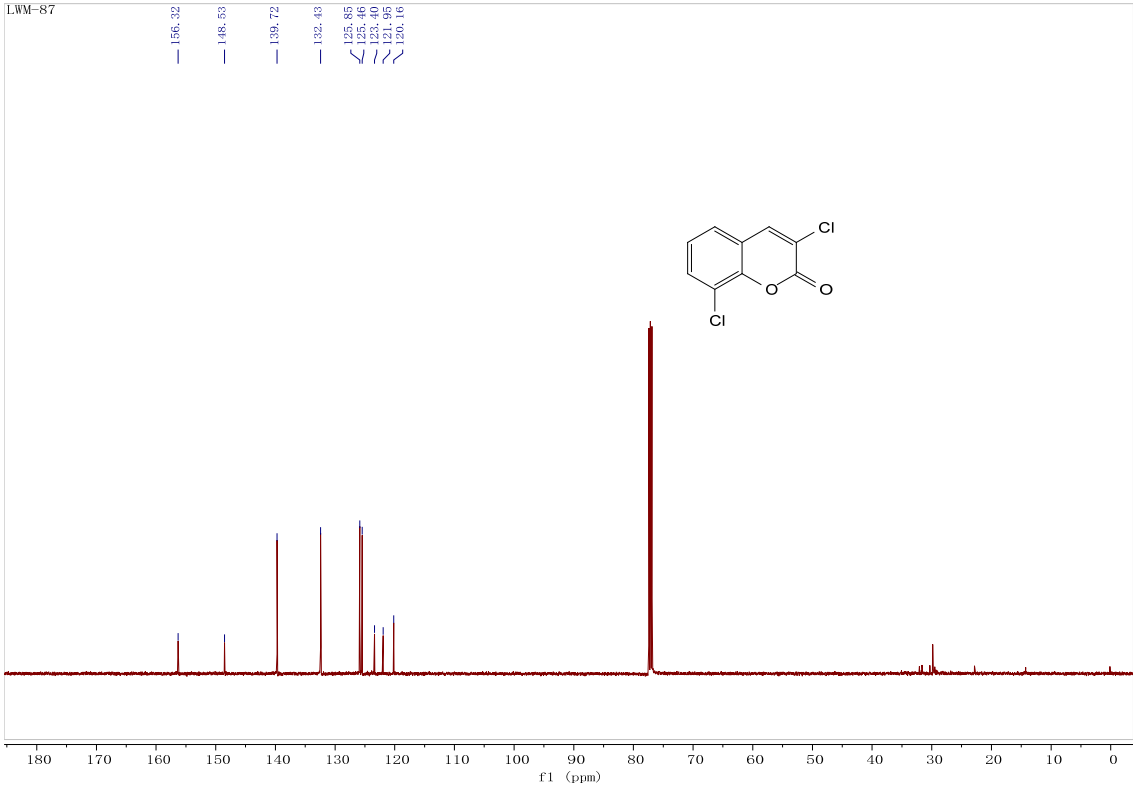
4d


LWM-6C1-1
7.81
7.51
7.50
7.49
7.48
7.45
7.44
7.31
7.30
7.26
Cl
Cl
O
O
1.00
1.00
1.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ZM-1wm-6C1-1
156.76
151.18
138.88
131.95
130.58
126.56
123.98
119.93
118.36
77.16
Cl
Cl
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4f


LWM-94
7.88
7.62
7.60
7.39
7.38
7.29
7.27
7.25
Cl
O
O
Cl
1.00
1.02
1.08
1.22
f1 (ppm)


LWM-87
156.32
148.53
139.72
132.43
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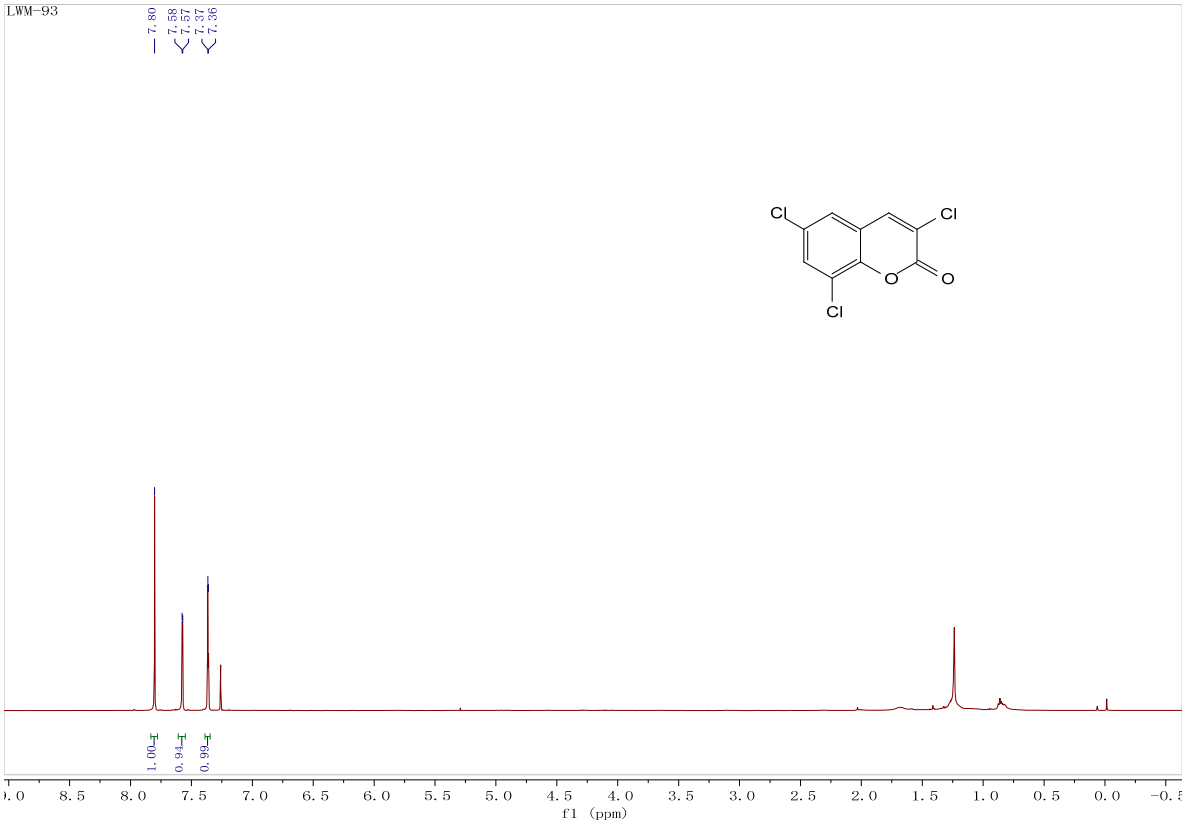
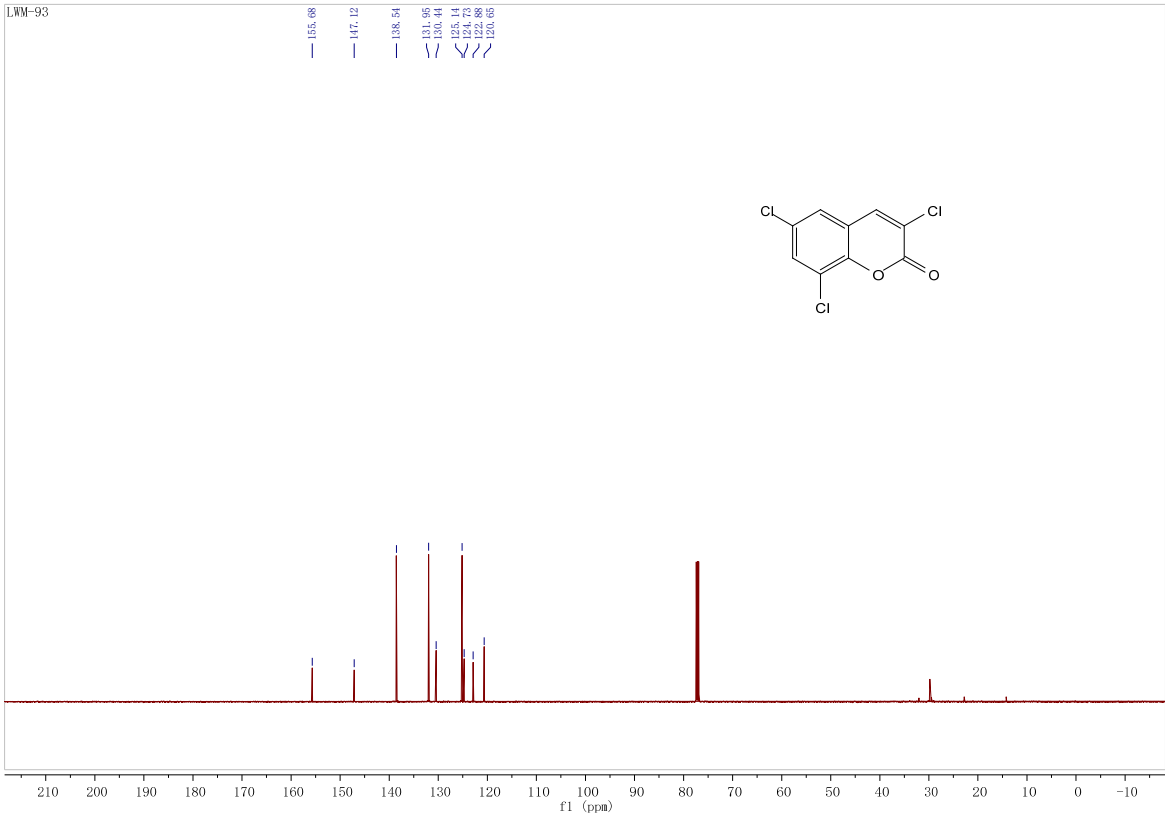
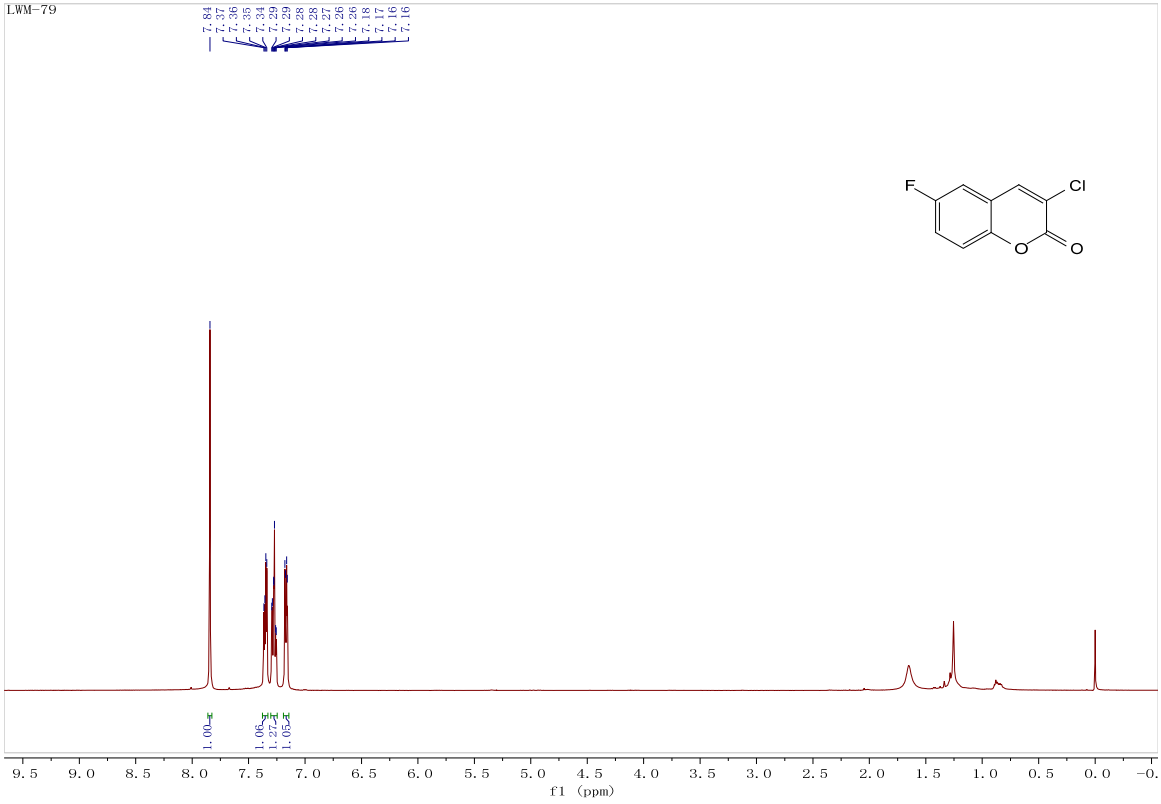
125.46
123.40
121.95
120.16
Cl
O
O
Cl
f1 (ppm)

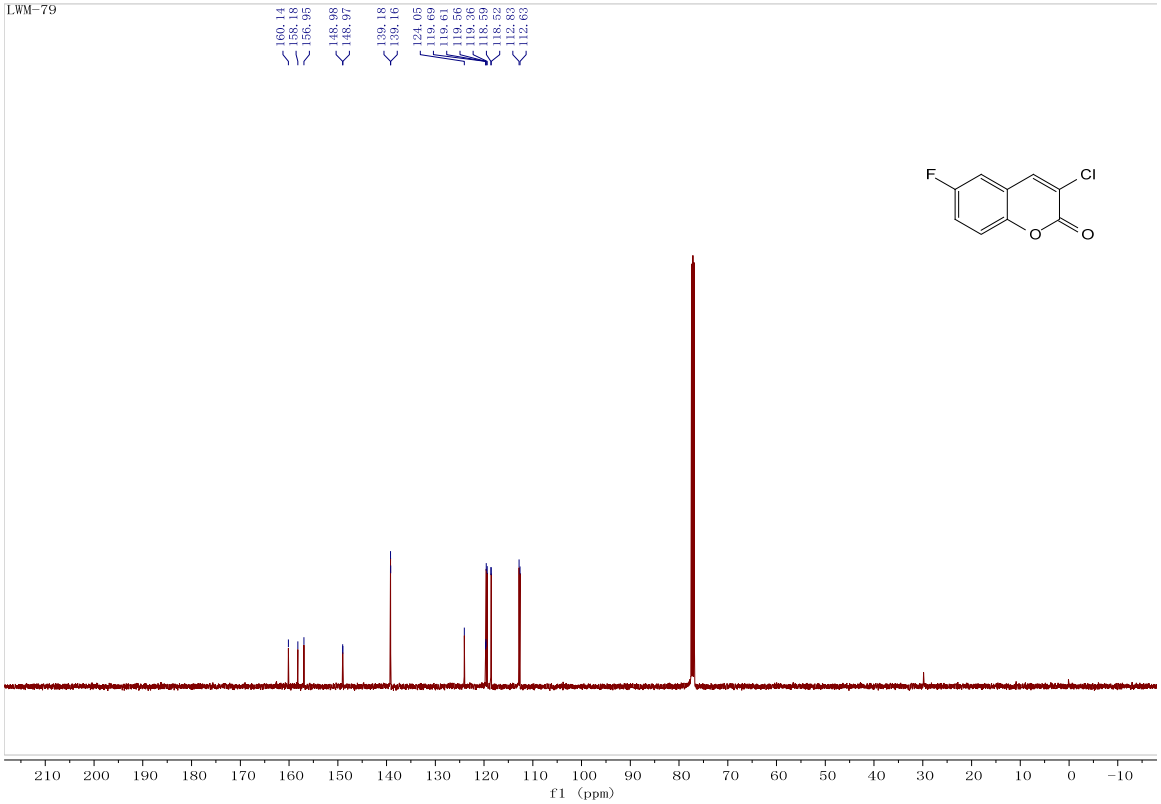
4g


LWM-93
7.80
7.58
7.57
7.37
7.36
Cl
Cl
O
O
Cl
1.00
0.94
0.99
f1 (ppm)


LWM-93
155.68
147.12
138.54
131.95
130.44
125.14
124.73
122.88
120.65
Cl
Cl
O
O
Cl
f1 (ppm)

4h


LWM-79
7.84
7.37
7.36
7.35
7.34
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.18
7.17
7.16
7.16
F
Cl
O
O
1.00
1.06
1.27
1.05
f1 (ppm)


LWM-79
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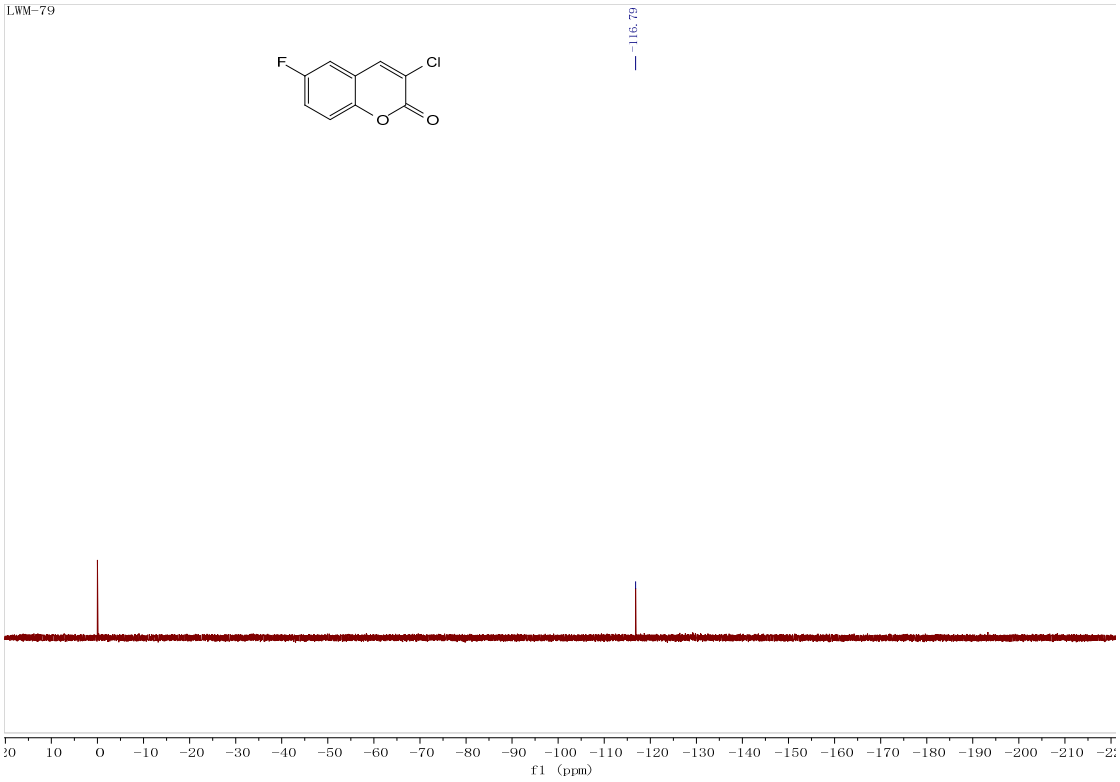
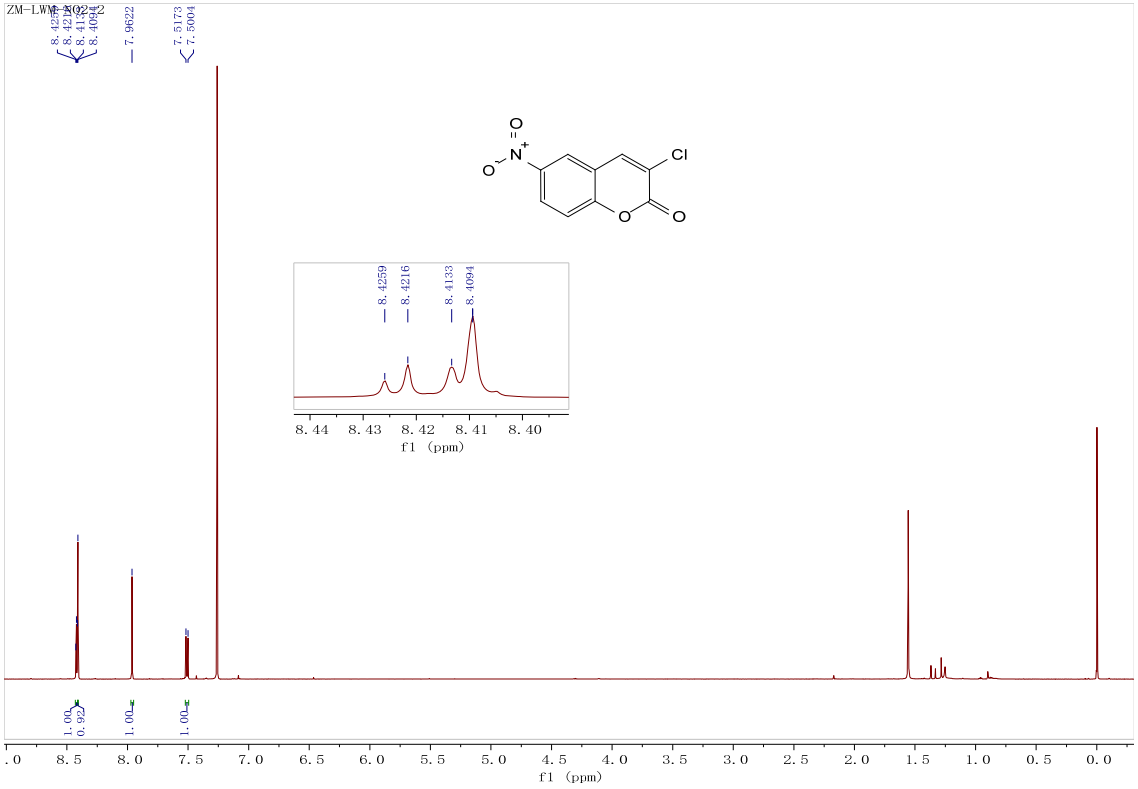
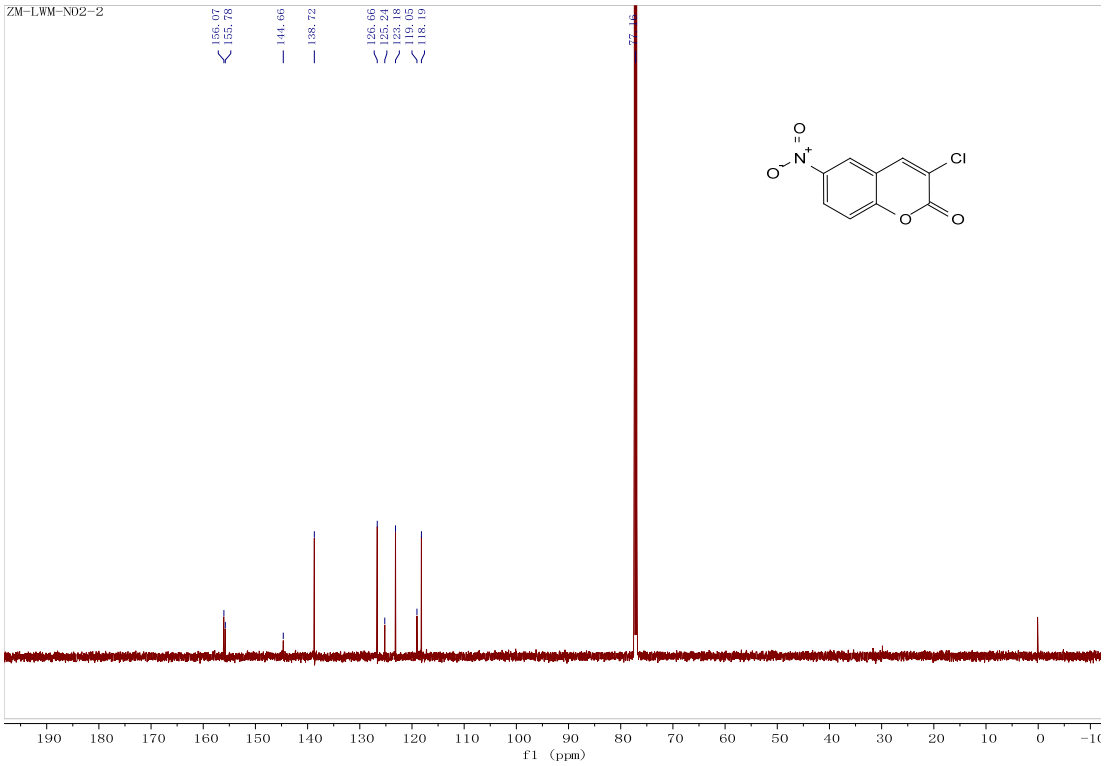
158.18
156.95
148.98
148.97
139.18
139.16
124.05
119.69
119.61
119.56
119.36
118.59
118.52
112.83
112.63
F
Cl
O
O
f1 (ppm)


LWM-79
F
Cl
O
O
-116.79
f1 (ppm)

4i


ZM-LWM-NO2-2
8.4259
8.4216
8.4133
8.4094
7.9622
7.5173
7.5004
O
N+
O
Cl
O
O
8.4259
8.4216
8.4133
8.4094
8.44 8.43 8.42 8.41 8.40
f1 (ppm)
1.00
0.92
1.00
1.00
f1 (ppm)


ZM-LWM-NO2-2
156.07
155.78
144.66
138.72
126.66
125.24
123.18
119.05
118.19
77.16
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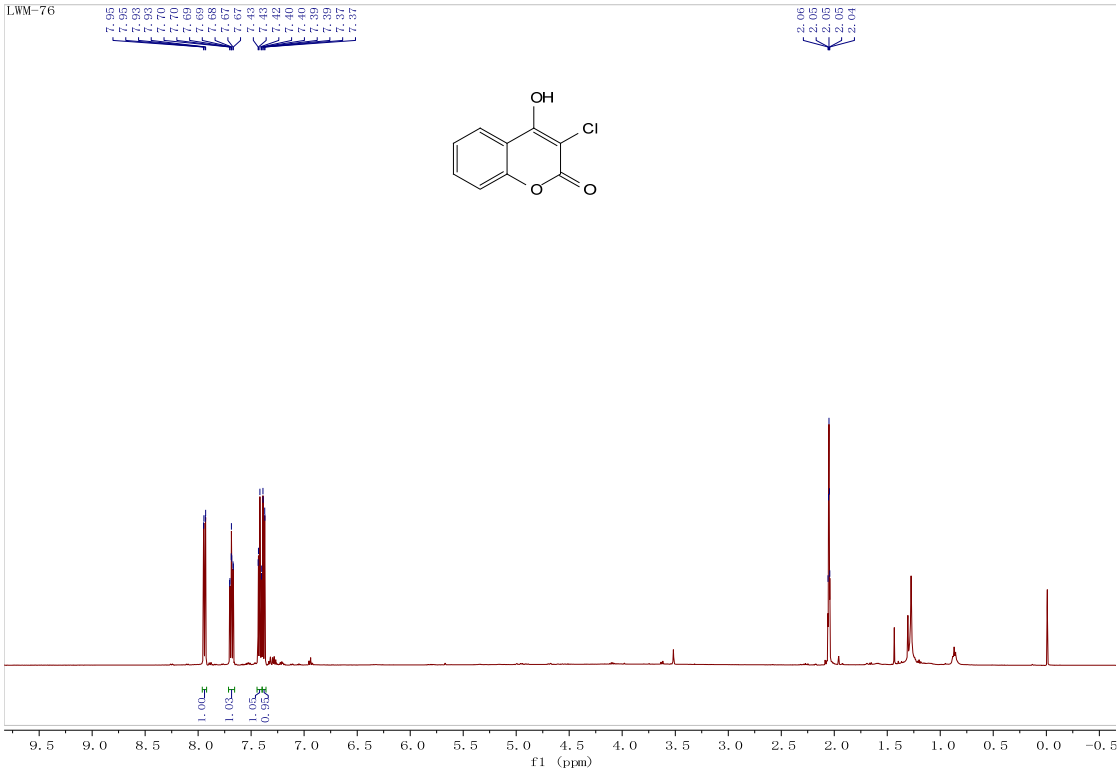
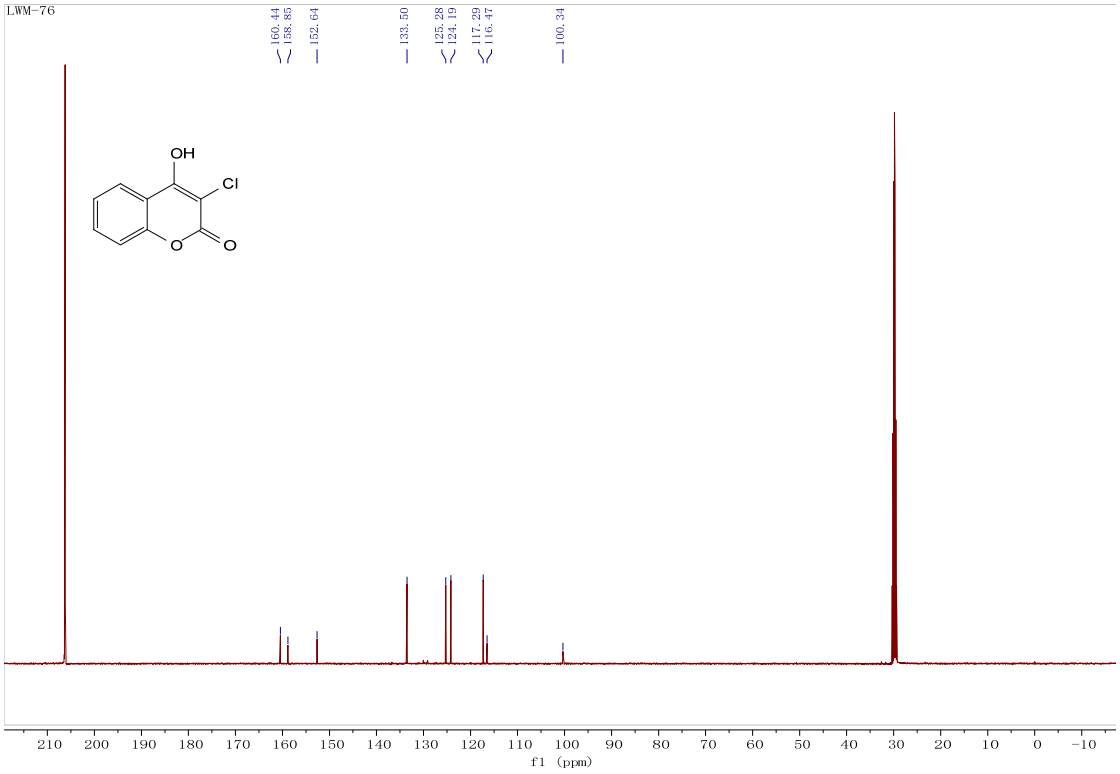
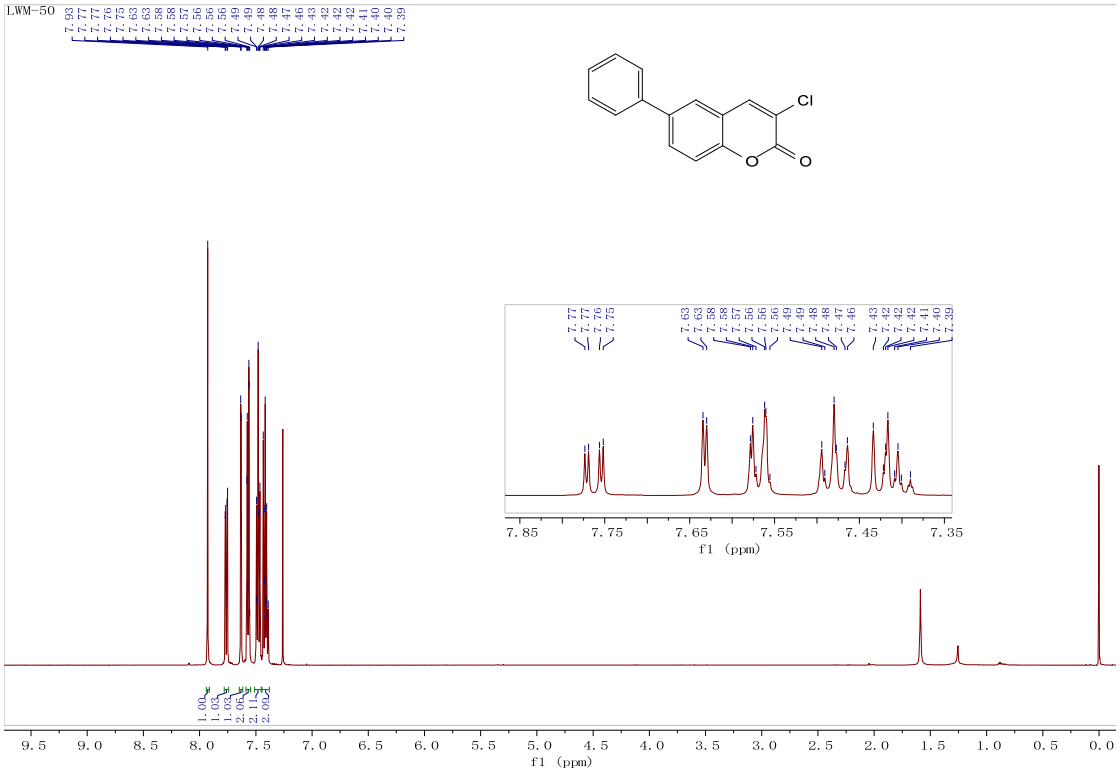
O
N
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

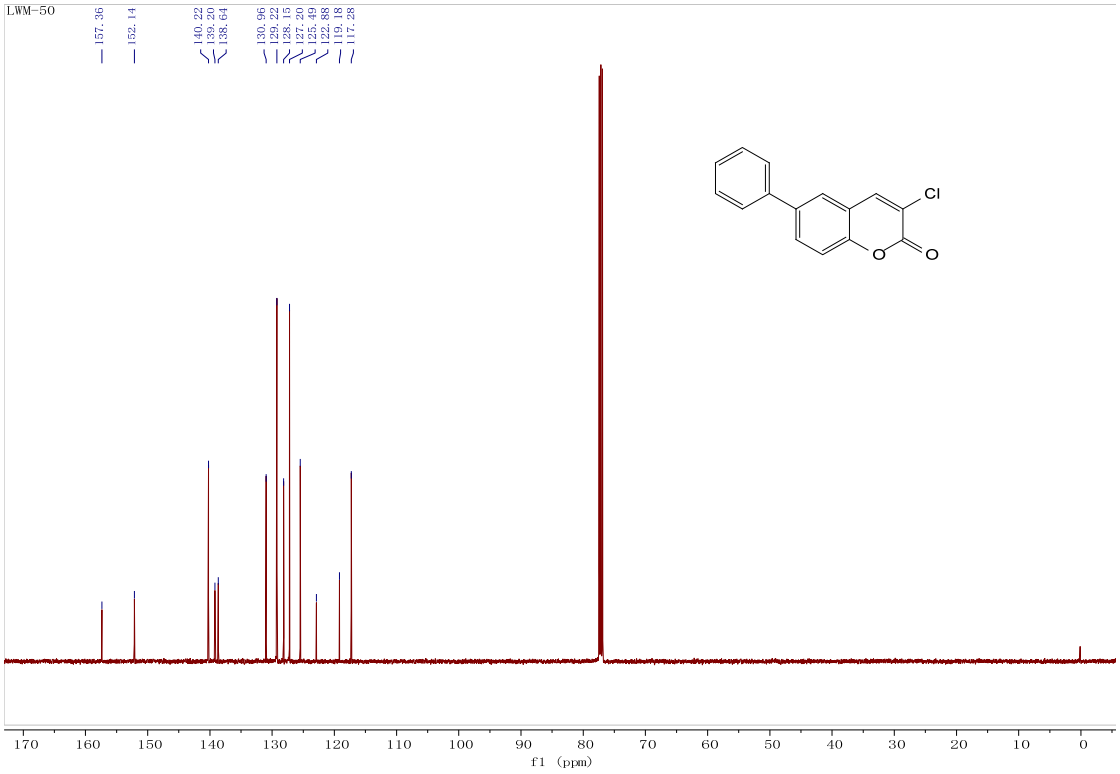
4l


LWM-76
7.95
7.95
7.93
7.93
7.70
7.70
7.69
7.68
7.67
7.67
7.43
7.42
7.40
7.39
7.39
7.37
7.37
2.06
2.05
2.05
2.05
2.04
OH
Cl
O
O
1.00
1.03
1.05
0.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

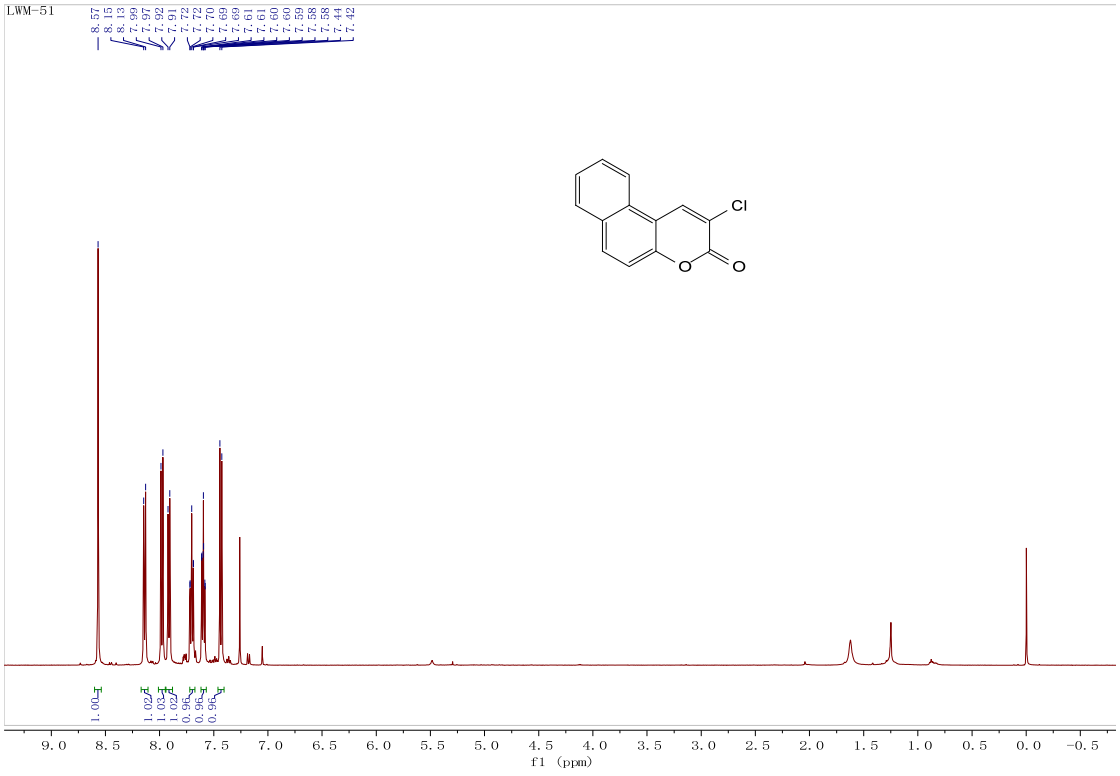

LWM-76
160.44
158.85
152.64
133.50
125.28
124.19
117.29
116.47
100.34
OH
Cl
O
O
f1 (ppm)

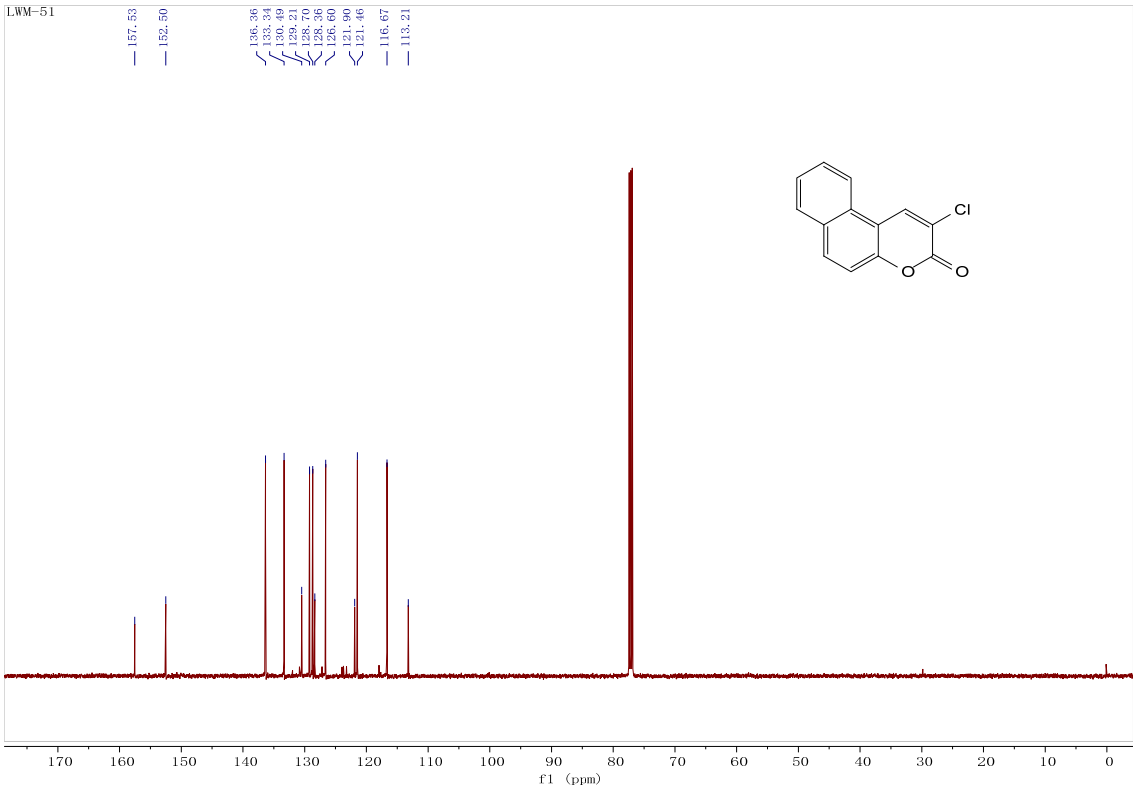
4o


LWM-50
Cl
O
O
f1 (ppm)

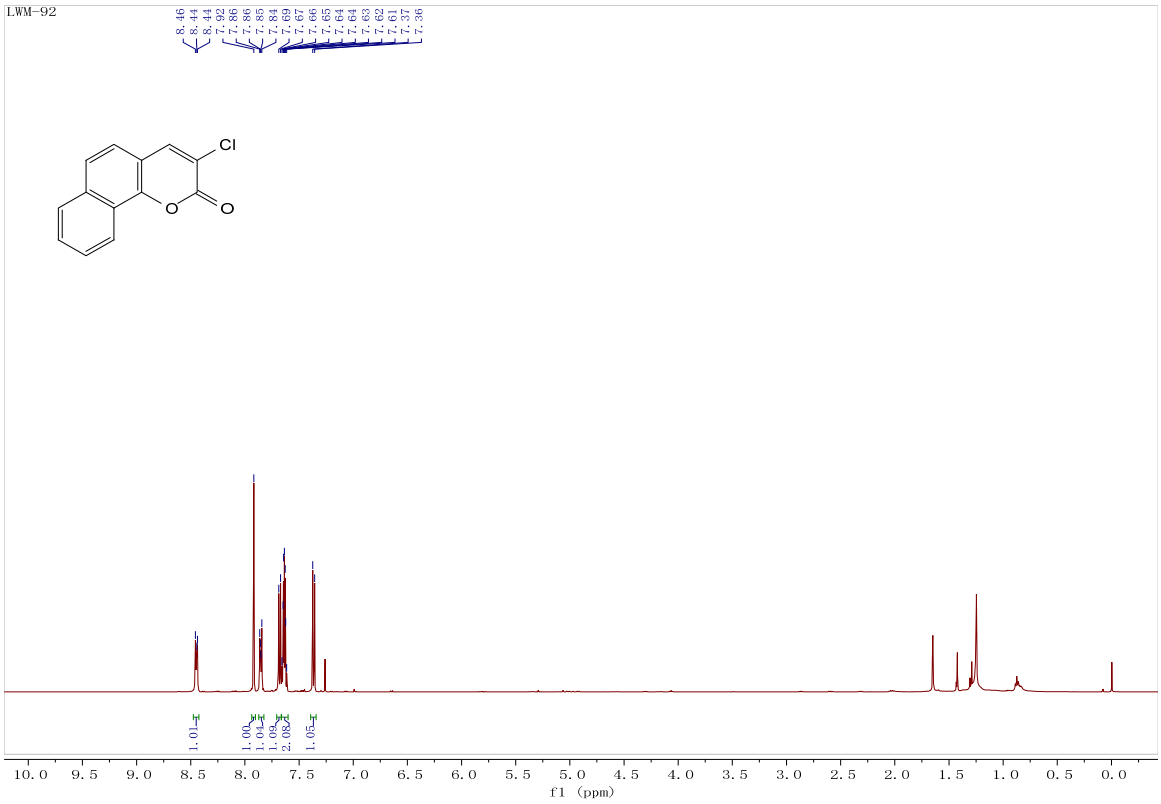

LWM-50
157.36
152.14
140.22
139.20
138.64
130.96
129.22
128.15
127.20
125.49
122.88
119.18
117.28
Cl
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

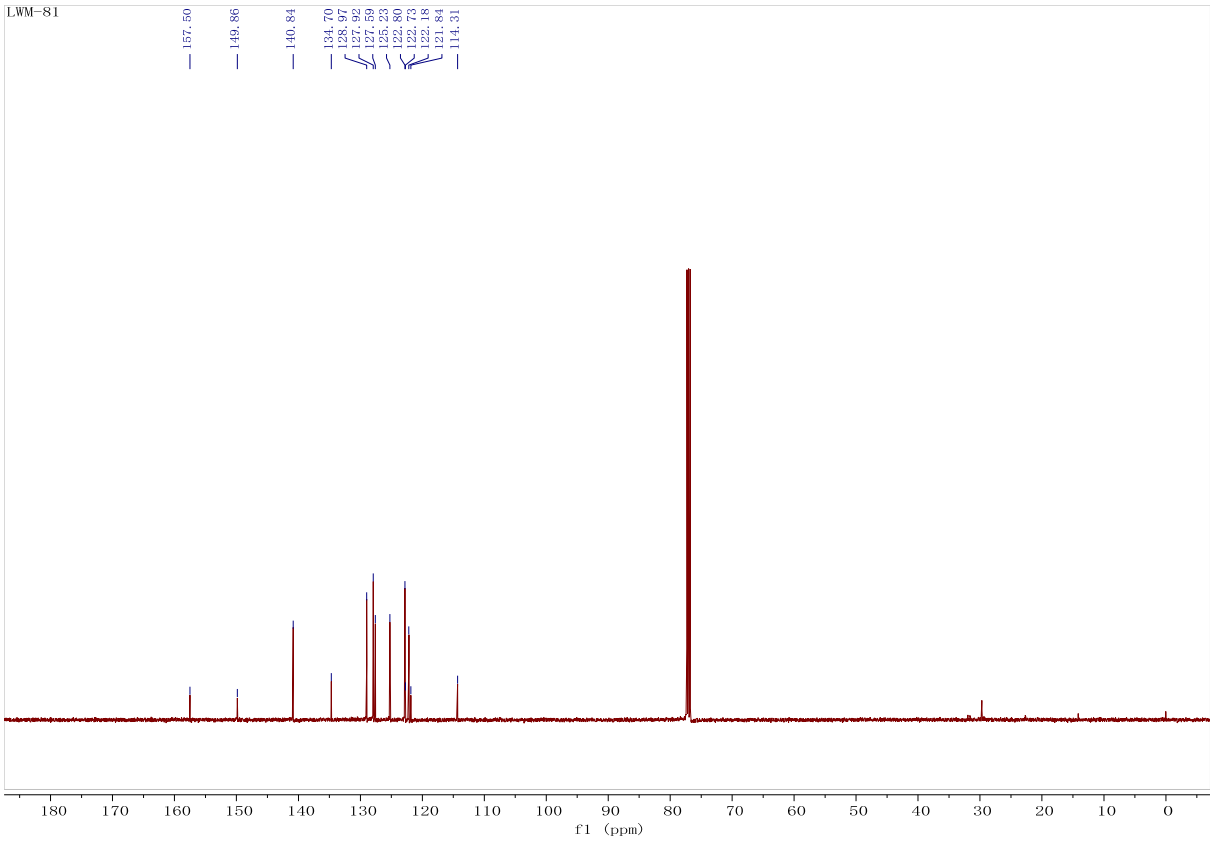
4r


LWM-51
8.57
8.15
8.13
7.99
7.97
7.92
7.91
7.72
7.72
7.70
7.69
7.69
7.61
7.61
7.60
7.60
7.59
7.58
7.58
7.44
7.42
Cl
O
O
1.00
1.02
1.03
1.02
0.96
0.96
0.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


LWM-51
157.53
152.50
136.36
133.34
130.49
129.21
128.70
128.36
126.60
121.90
121.46
116.67
113.21
Cl
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4s


LWM-92
8.46
8.44
8.44
7.92
7.86
7.86
7.85
7.84
7.69
7.67
7.66
7.65
7.64
7.64
7.63
7.62
7.61
7.37
7.36
Cl
O
O
1.01
1.00
1.04
1.09
2.08
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LWM-81
157.50
149.86
140.84
134.70
128.97
127.92
127.59
125.23
122.80
122.73
122.18
121.84
114.31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7. References

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