Supplementary Information

A metal-free one-pot synthesis of benzo[*c*]chromen-6-ones from 3, 4- dichlorocoumarin and butadiene by tandem photo-thermal-photo reactions

Yan Zhang[†], Yan Tian[‡], Pei Xiang[†], Ning Huang[‡], Jianyi Wang[†], Jian-Hua Xu[§], Min Zhang[*, †]

[†]School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, China

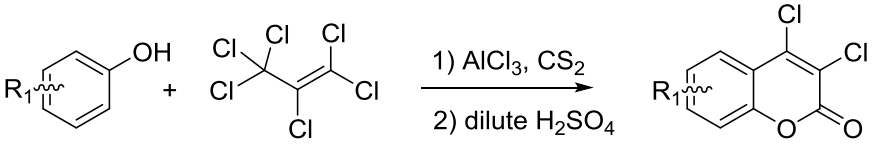
[‡]Guangxi Environmental Monitoring Center, Nanning, Guangxi 530028, China

[§]School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China

Contents

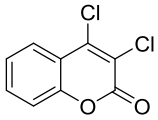
1. The synthesis details of starting materials.

a) The syntheses of 3, 4-dichlorocoumarins [1]



2

The syntheses of 3, 4-dichlorocoumarins are carried out as descripted in lit 1. The reaction started from phenols and hexachloropropene catalyzed by $AlCl_3$ in CS_2 and the solvent was removed. The residue was put in cold dilute H_2SO_4 and filtered, oven dried. The crude product was purified by silica gel chromatography. The proton NMR for the dichlorocoumarins are given below:

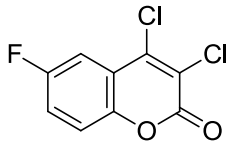


2a

3, 4-dichlorocoumarin (3, 4-dichloro-2H-chromen-2-one)

White needles, m.p. 106-108 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H).

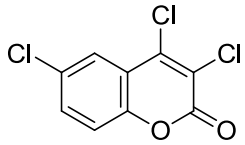


2b

3, 4-dichloro-6-fluoro-2H-chromen-2-one

White needle crystal m.p. 106-108 ºC (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.4, 2.9 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 (m, 1H).

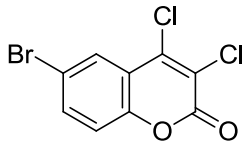


2c

3, 4, 6-trichloro-2H-chromen-2-one

White needles, m.p. 130-132 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 2.4 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.34 (d, J = 8.8 Hz, 1H).

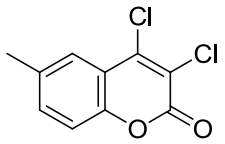


2d

6-bromo-3,4-dichloro-2H-chromen-2-one

Yellow needles, m.p. 144-146 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (t, *J* = 2.1 Hz, 1H), 7.70 (ddd, *J* = 8.8, 1.5, 0.6 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H).

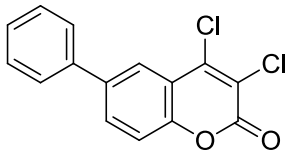


2e

3, 4-dichloro-6-methyl-2H-chromen-2-one

White needles, m.p. 160-164 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 2.47 (s, 4H).

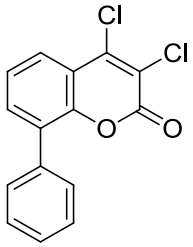


2f

3, 4-dichloro-6-phenyl-2H-chromen-2-one

White needles, m.p. 146-148 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.1 Hz, 1H), 7.84 (dd, *J* = 5.5, 3.8 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.52 – 7.48 (m, 2H), 7.47 (dd, *J* = 8.3, 4.0 Hz, 1H), 7.45 – 7.40 (m, 1H).

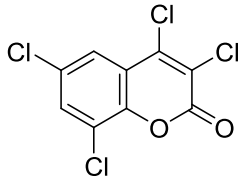


2g

3, 4-dichloro-8-phenyl-2H-chromen-2-one

White flocculent solid, m.p. 148-150 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.0, 1.6 Hz, 1H), 7.66 (dd, J = 7.6, 1.6 Hz, 1H), 7.56 (dt, J = 8.1, 1.7 Hz, 2H), 7.49 (ddd, J = 7.8, 6.0, 2.5 Hz, 3H), 7.46 – 7.41 (m, 1H).



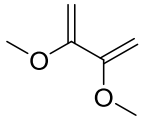
2h

3, 4, 6, 8-tetrachloro-2H-chromen-2-one

Yellow block crystals, m.p. 158-160 ℃ (Acetone/PE, 2/1, V/V)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H).

b) The synthesis of 2, 3-dimethoxy-1, 3-butadiene [2] (**3b**)



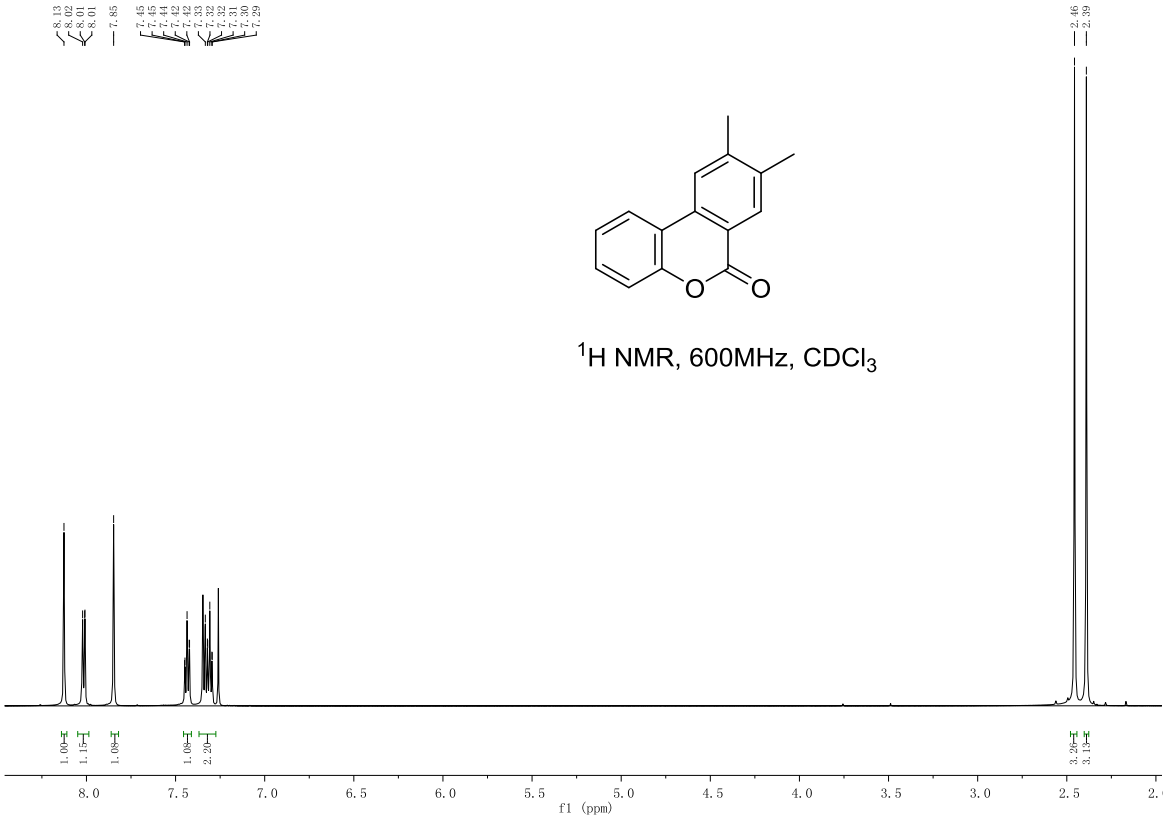
The synthesis of **3b** is carried out as descripted in the Supporting Information of lit 2: A mixture of biacetyl (17.20 g, 0.20 mol), absolute methanol (25 ml, 1.25 mol), trimethyl orthoformate (63.60 g, 0.60 mol) and concentrated sulfuric acid (5 drops) was refluxed for 10h. The excess of reagents were distilled of and the remaining liquid was vacuum-distilled. Ammonium dihydrogenphosphate (25 mg) and a few crystals of hydroquinone were added and the liquid was heated at 100°C to 110°C. Methanol slowly distilled over, together with some remaining orthoformate. The temperature was raised (160 °C to 170 °C) and the colorless oily liquid collected between 129°C and 132°C (17.30 g or 76% of crude diene). Redistillation gave 2, 3-dimethoxy-1, 3-butadiene (15.50 g, 68%), b. p. 132-132.5 °C.

References

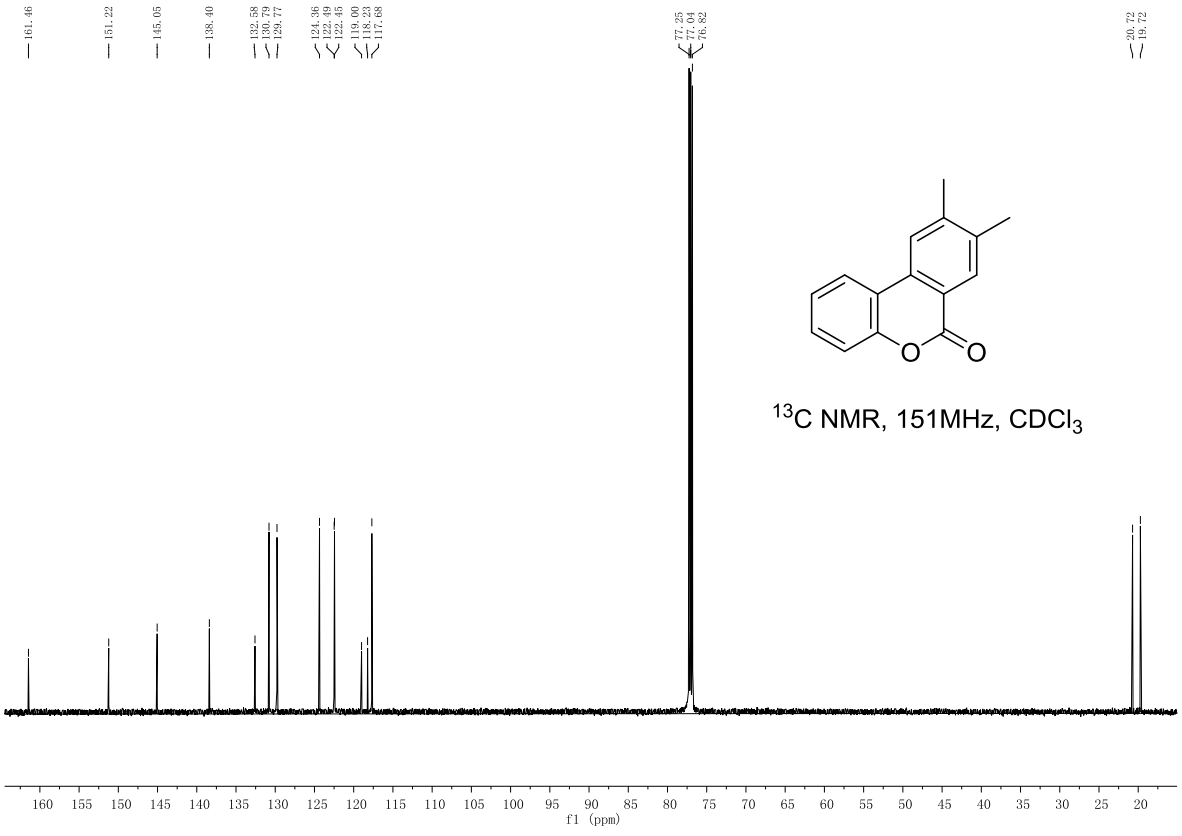
1. M. S. Newman and S. Schiff, *J. Am. Chem. Soc.*, 1959, **81**, 2266-2270.
2. J. Reichwagen, H. Hopf, A. Del Guerzo, C. Belin, H. Bouas-Laurent and J.-P. Desvergne, *Org. Lett.*, 2005, **7**, 971-974.

2. The NMR charts of compounds

1a

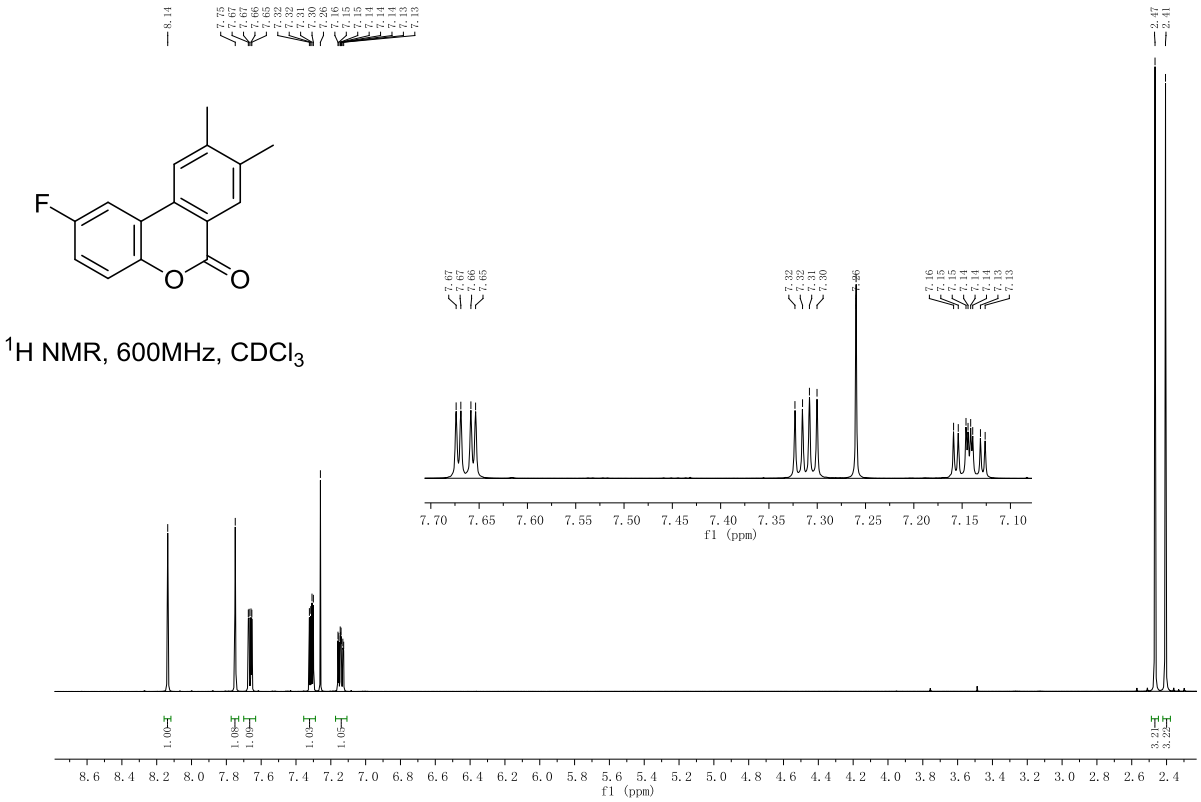


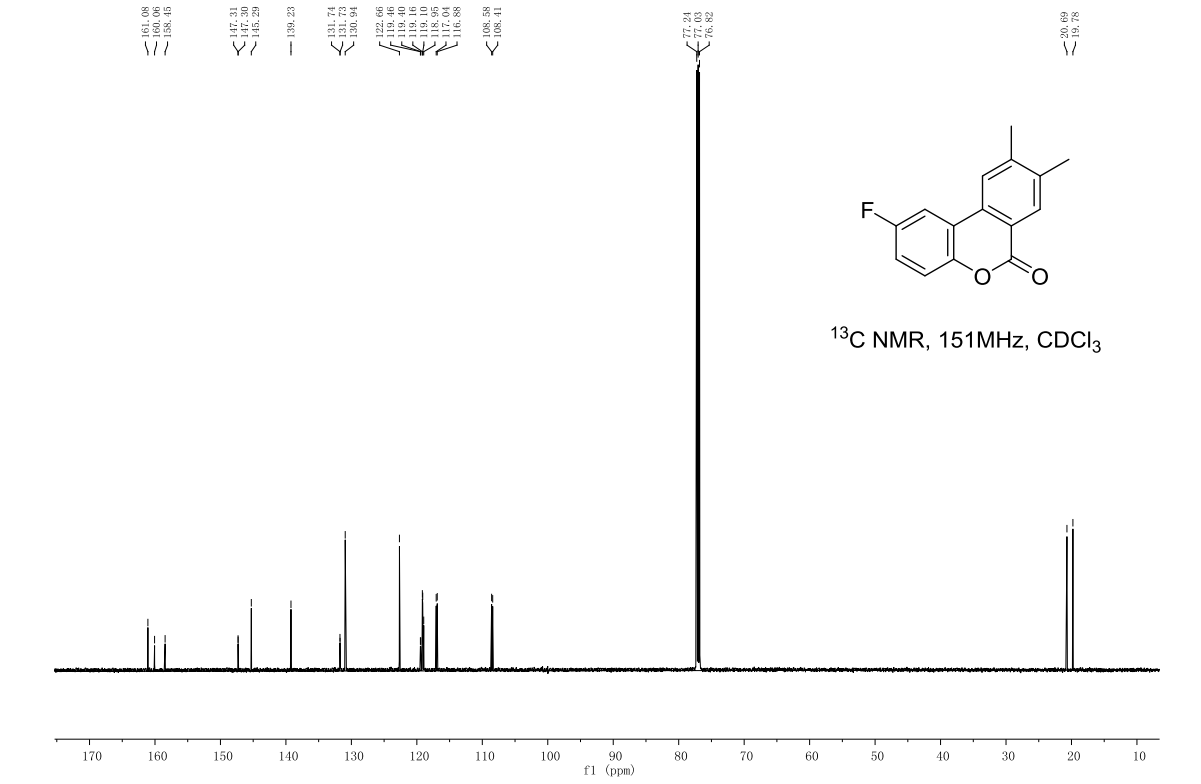
^{1}H NMR, 600MHz, $CDCl_3$

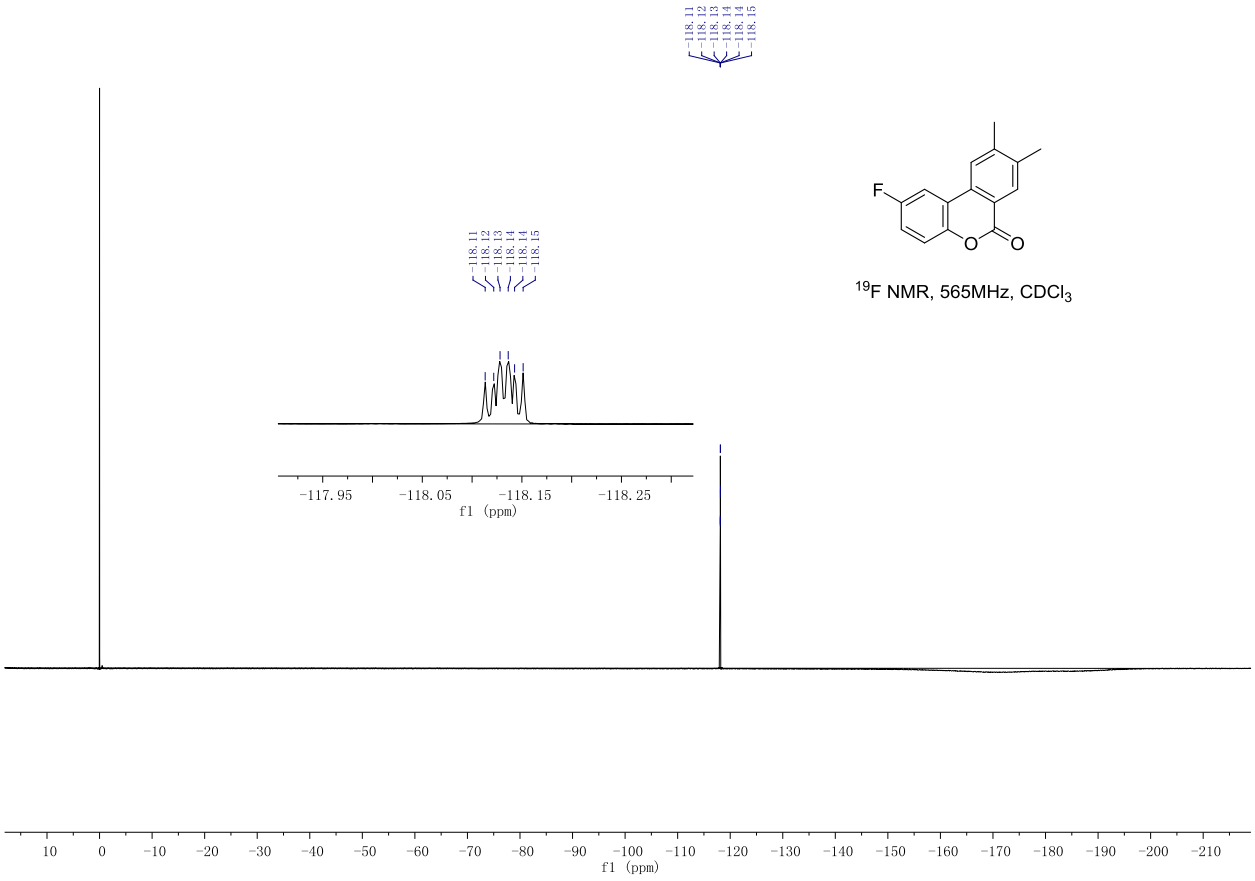


^{13}C NMR, 151MHz, $CDCl_3$

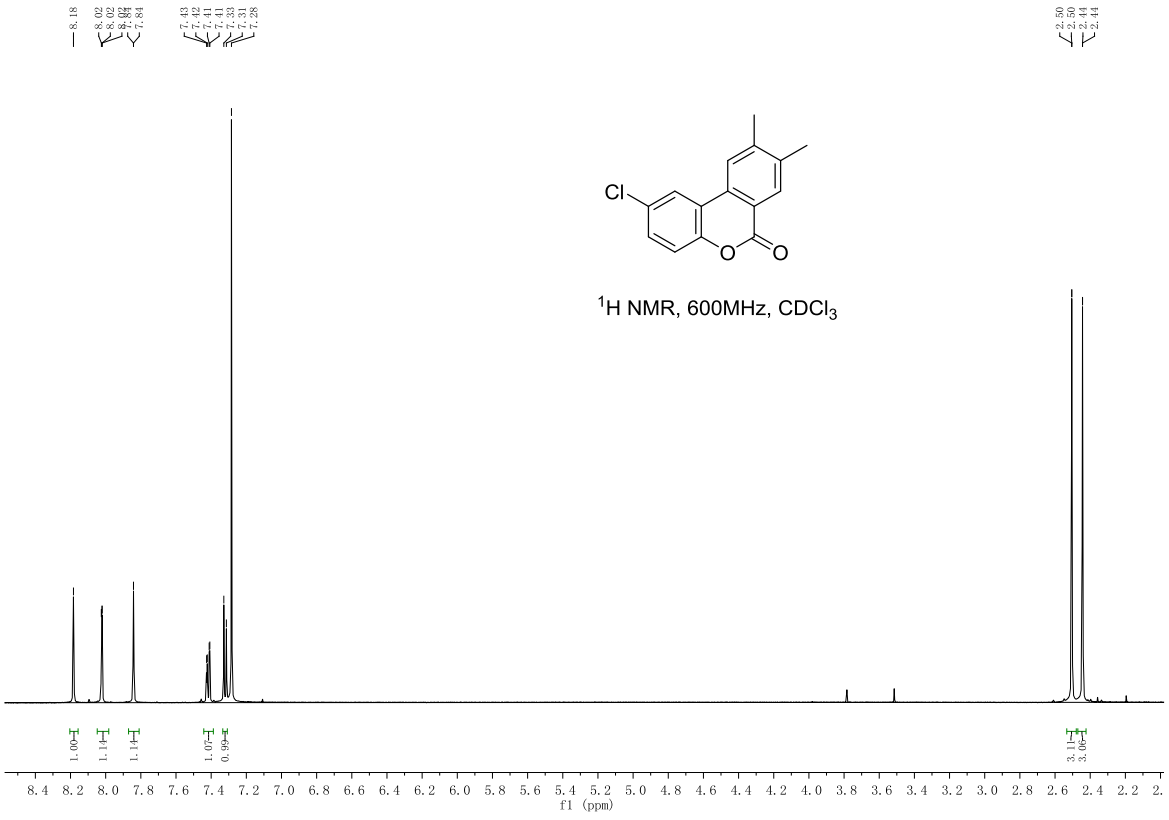
1b

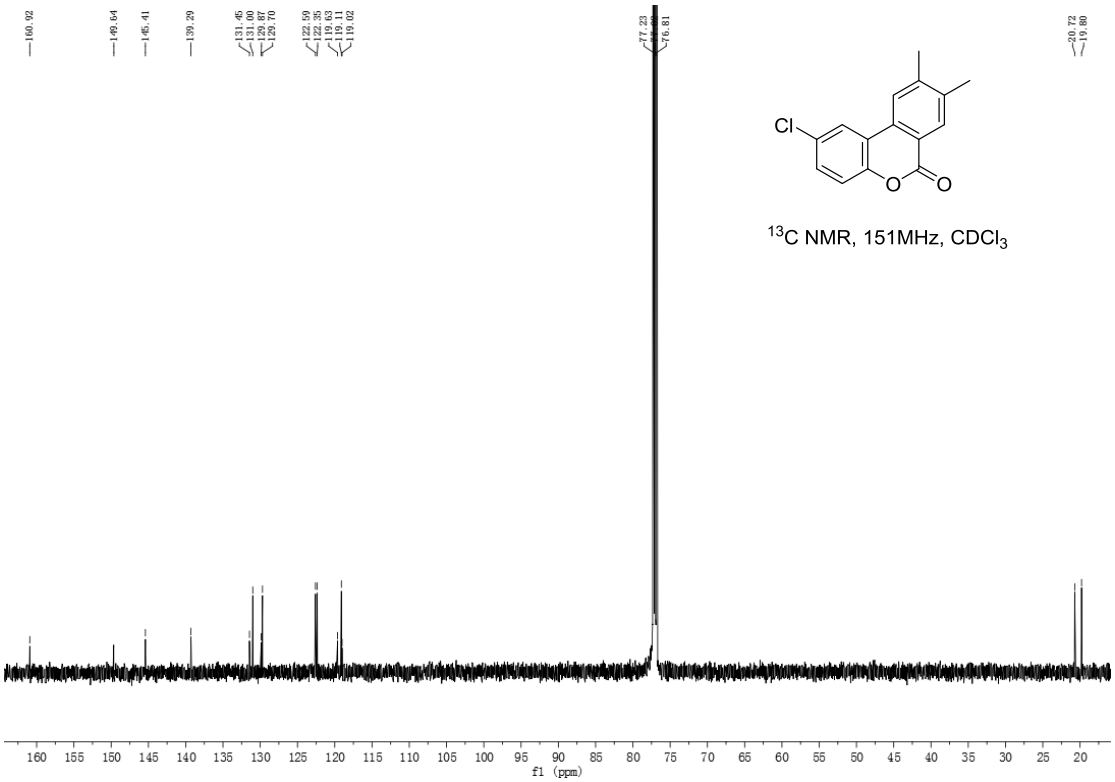





F
O
O
^{19}F NMR, 565MHz, CDCl$_3$
f1 (ppm)

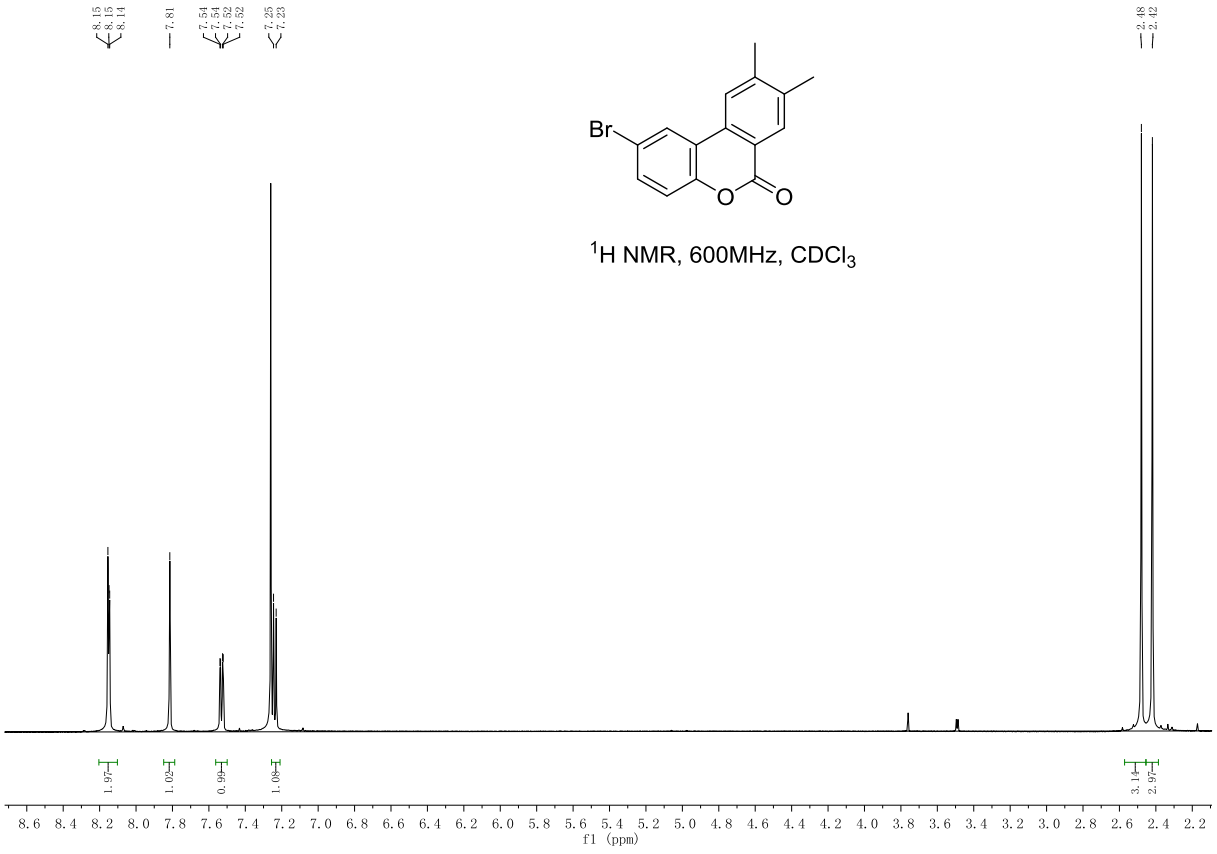
1c


Cl
O
O
^{1}H NMR, 600MHz, CDCl$_3$
f1 (ppm)

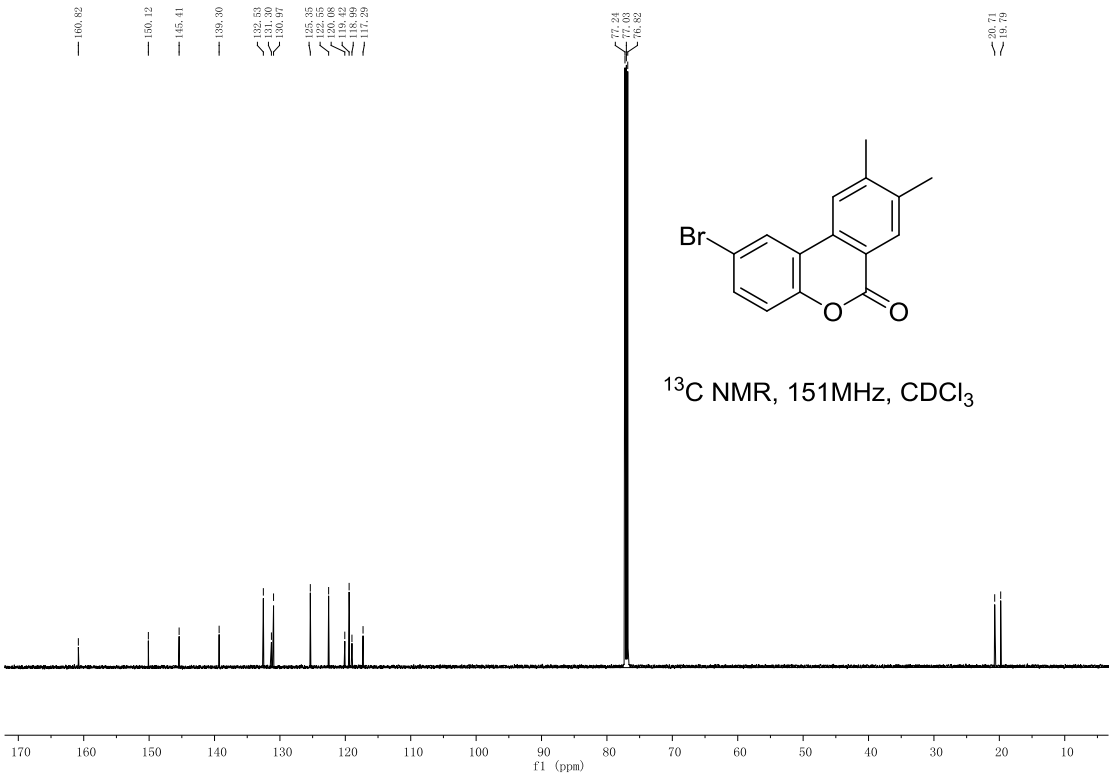


^{13}C NMR, 151MHz, $CDCl_3$

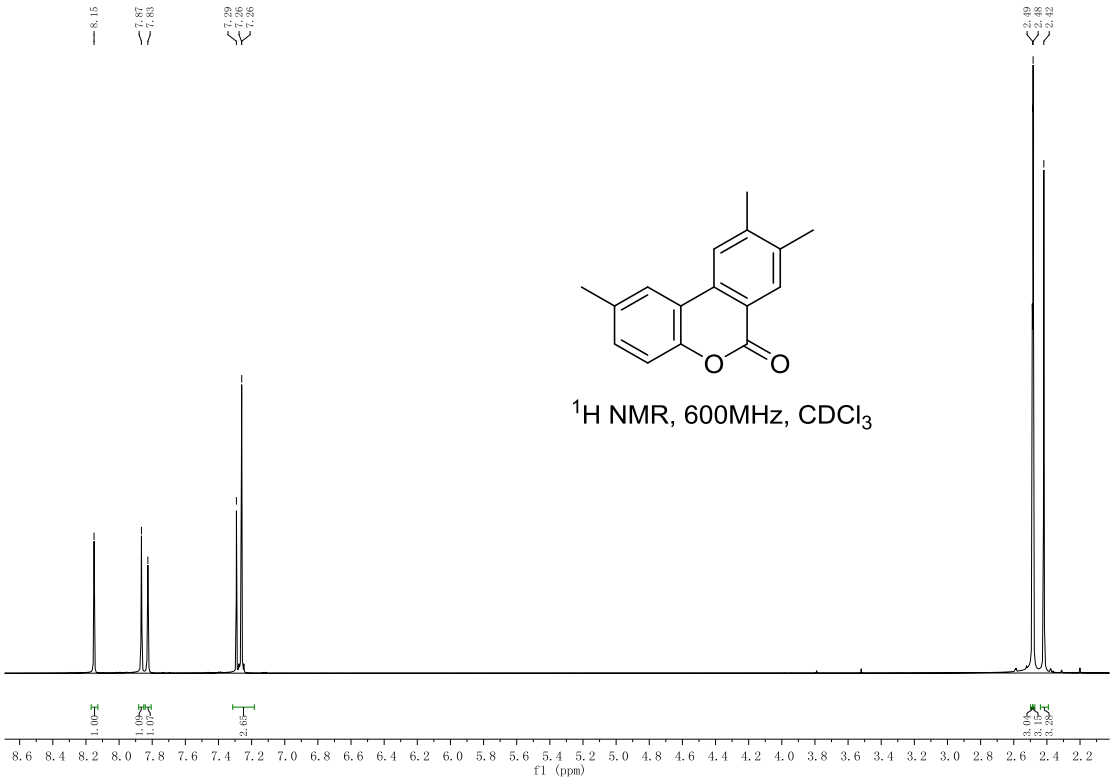
1d

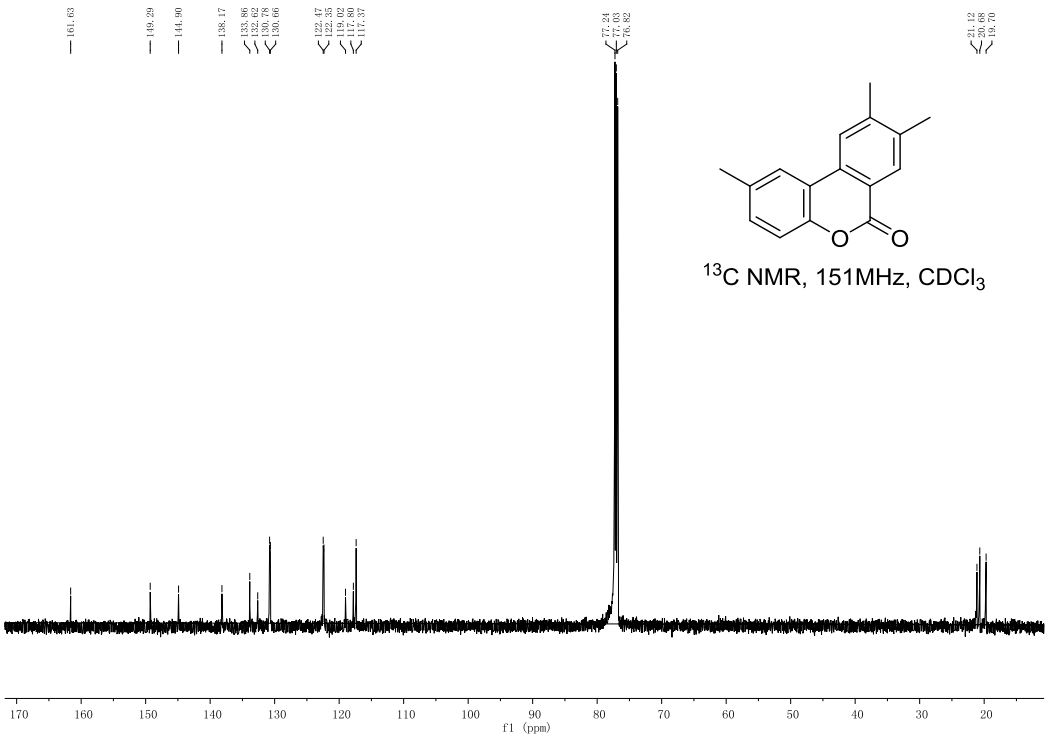


^{1}H NMR, 600MHz, $CDCl_3$

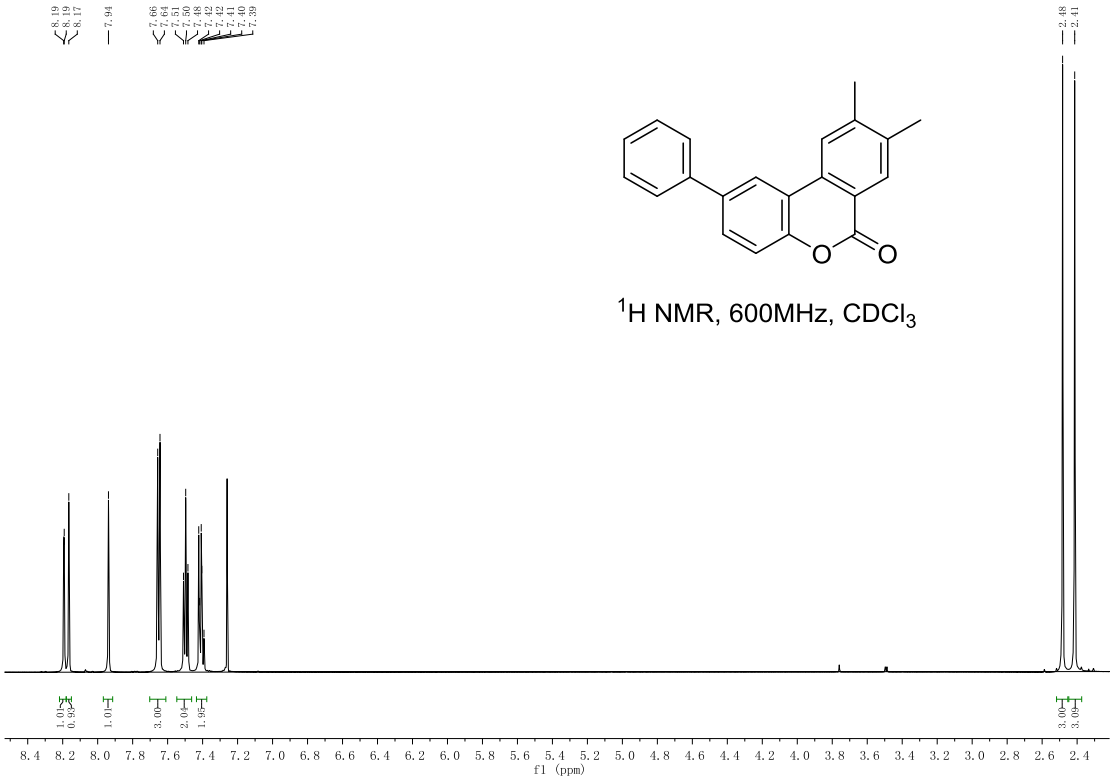

160.82
150.12
145.41
139.30
132.53
131.90
130.97
125.35
122.55
120.08
119.42
118.99
117.29
77.24
77.03
76.82
20.71
19.79
Br
O
O
13C NMR, 151MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

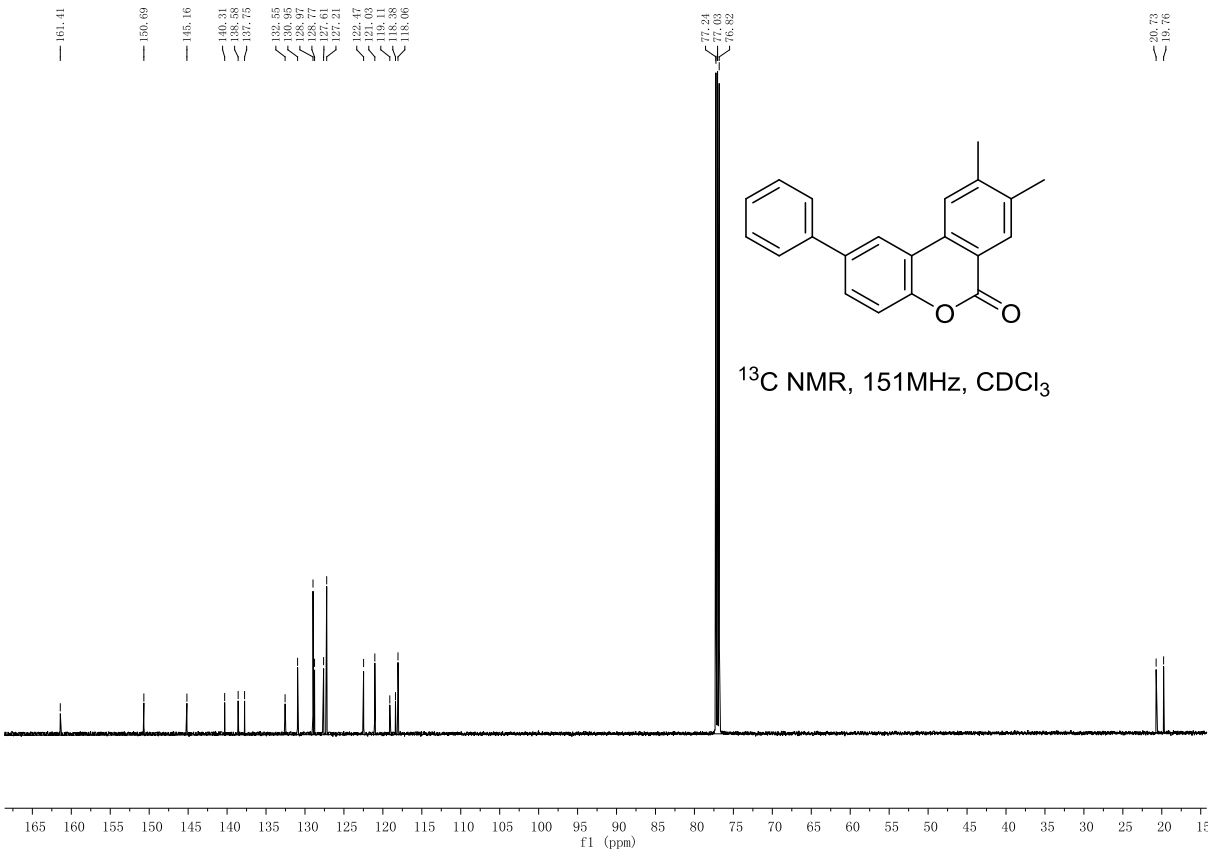
1e


8.15
7.87
7.83
7.29
7.26
7.25
2.49
2.48
2.42
O
O
1H NMR, 600MHz, CDCl3
1.00
1.09
1.07
2.68
3.05
3.00
3.20
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
f1 (ppm)


161.63
149.29
144.90
138.17
133.86
132.02
130.74
130.66
122.47
122.35
119.02
117.60
117.37
77.24
77.00
76.82
21.12
20.68
19.70
O
O
13C NMR, 151MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

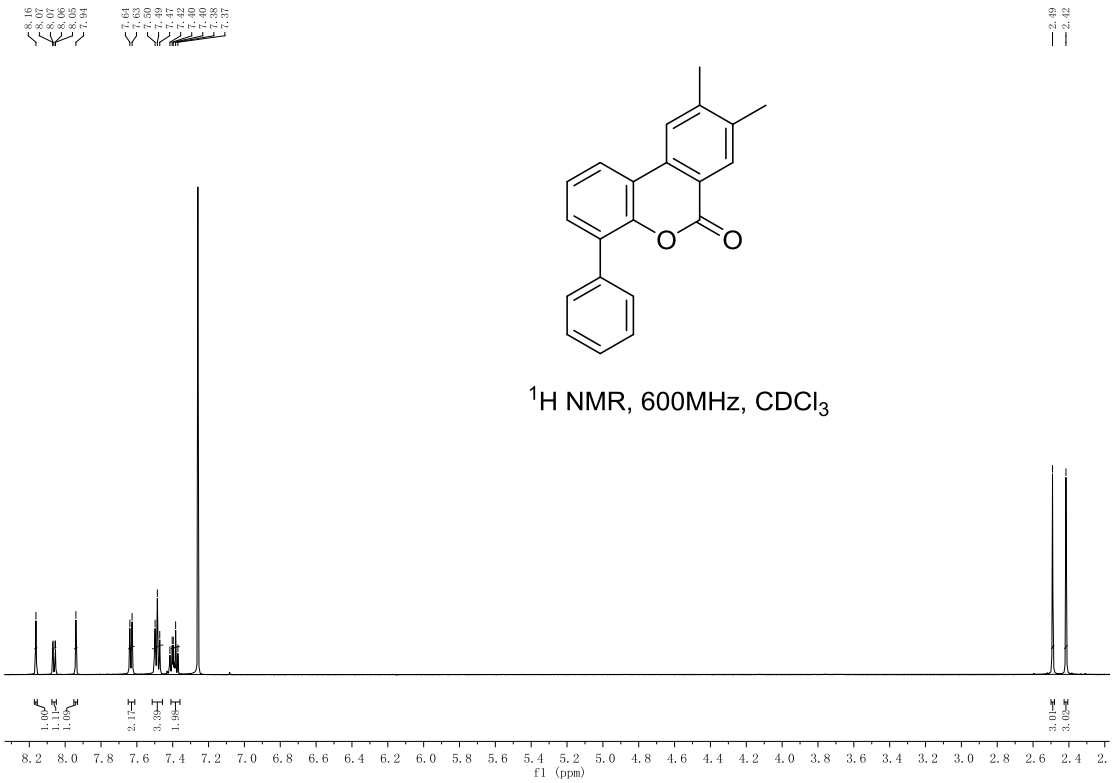
1f


8.19
8.19
8.17
7.94
7.66
7.64
7.51
7.50
7.48
7.42
7.42
7.41
7.40
7.39
2.48
2.41
O
O
1H NMR, 600MHz, CDCl3
1.01
0.99
1.01
3.00
2.04
1.95
3.01
3.00
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
f1 (ppm)

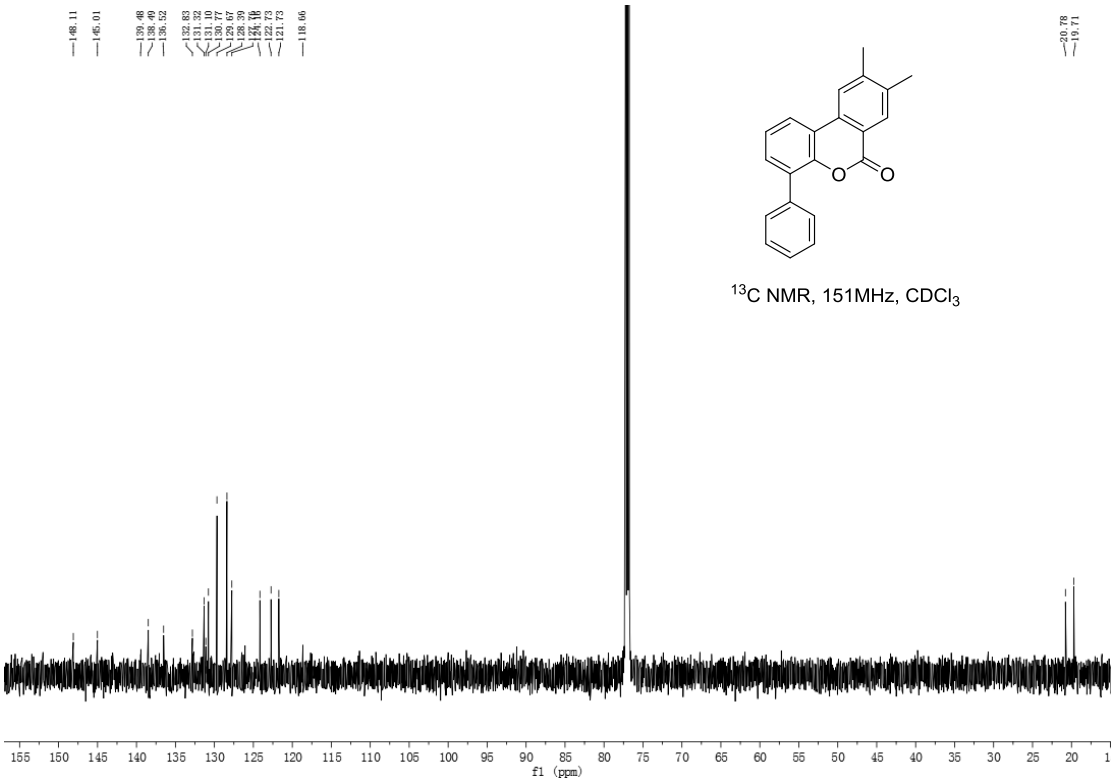


^{13}C NMR, 151MHz, $CDCl_3$

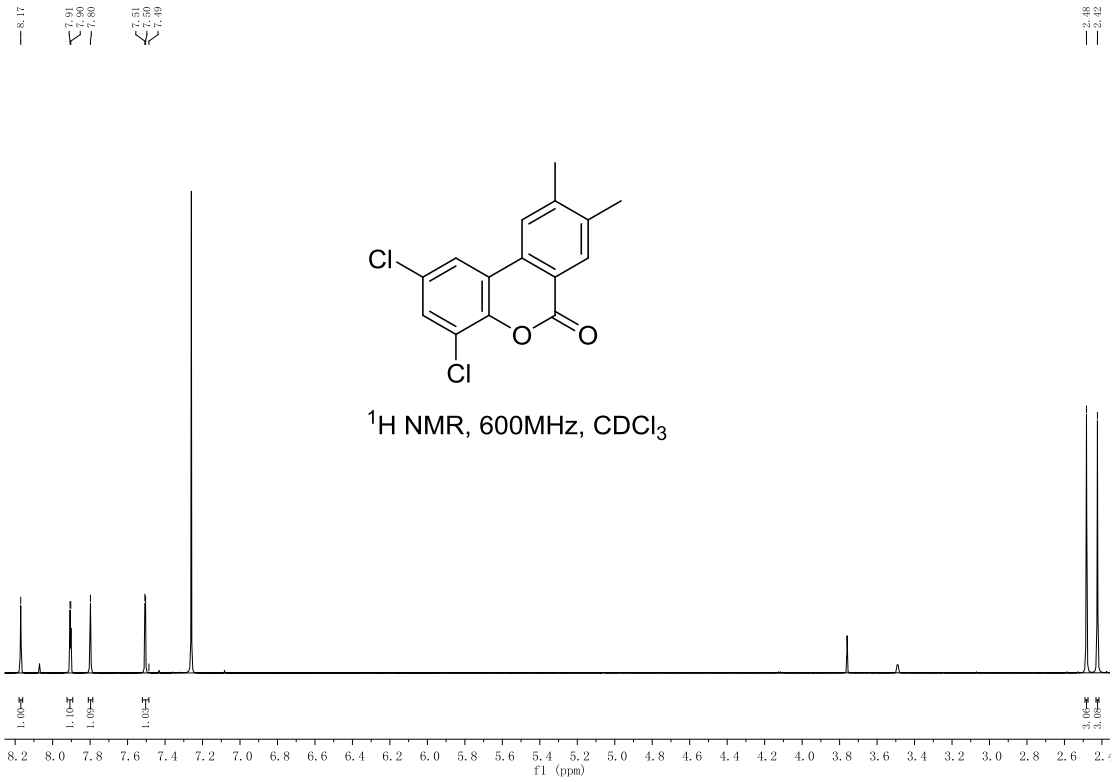
1g

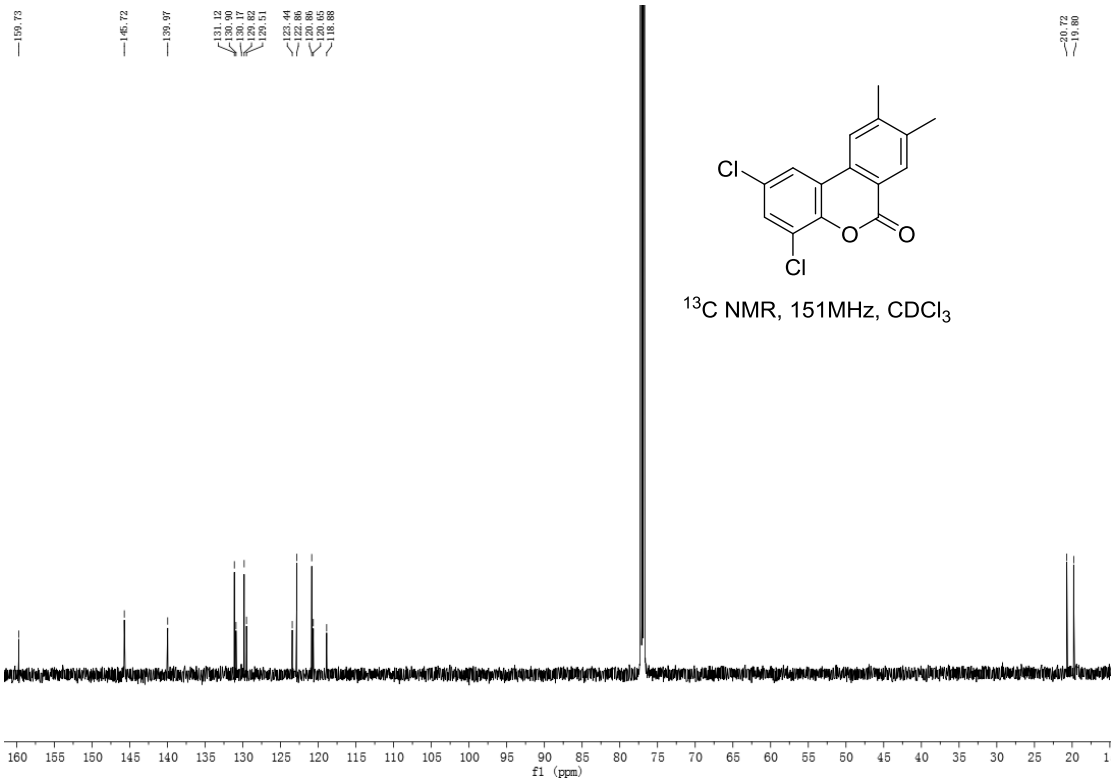


^{1}H NMR, 600MHz, $CDCl_3$


O
O
^{13}C NMR, 151MHz, $CDCl_3$
f1 (ppm)

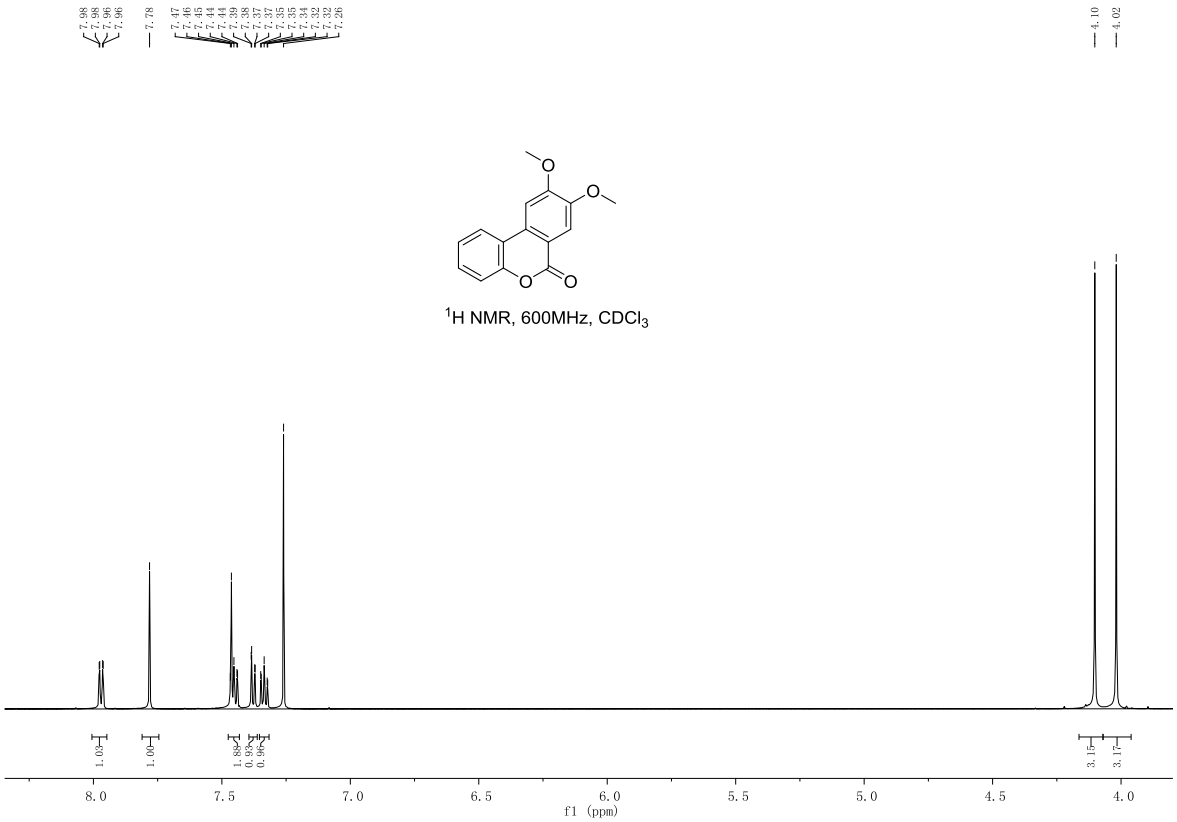
1h


Cl
O
O
Cl
^{1}H NMR, 600MHz, $CDCl_3$
f1 (ppm)

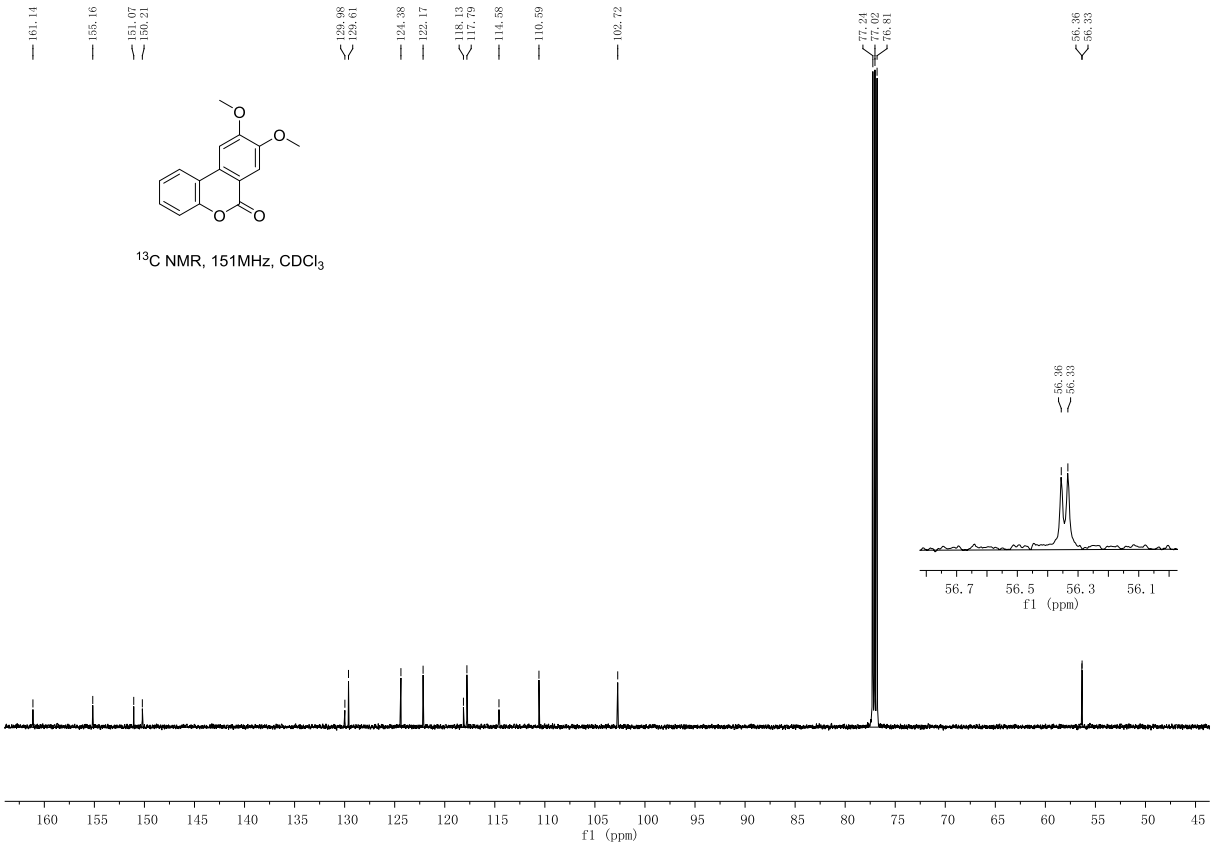


^{13}C NMR, 151MHz, $CDCl_3$

1i



^{1}H NMR, 600MHz, $CDCl_3$



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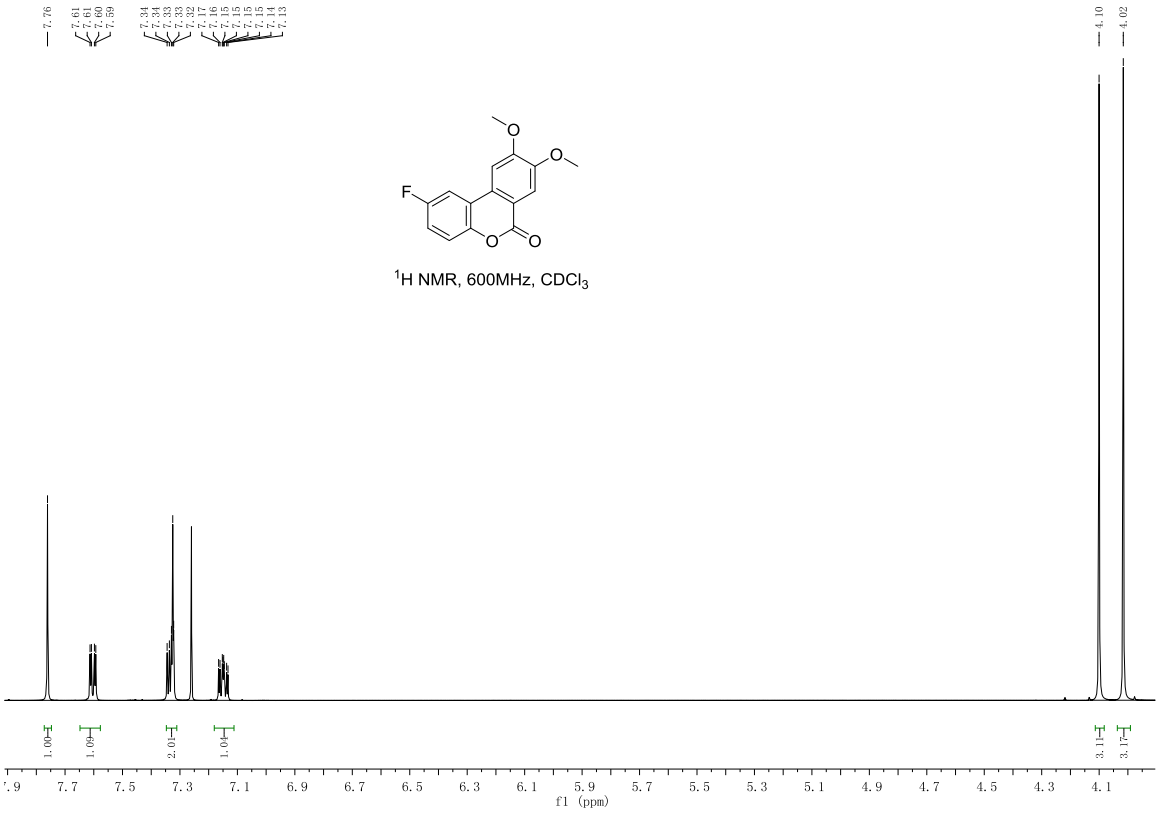
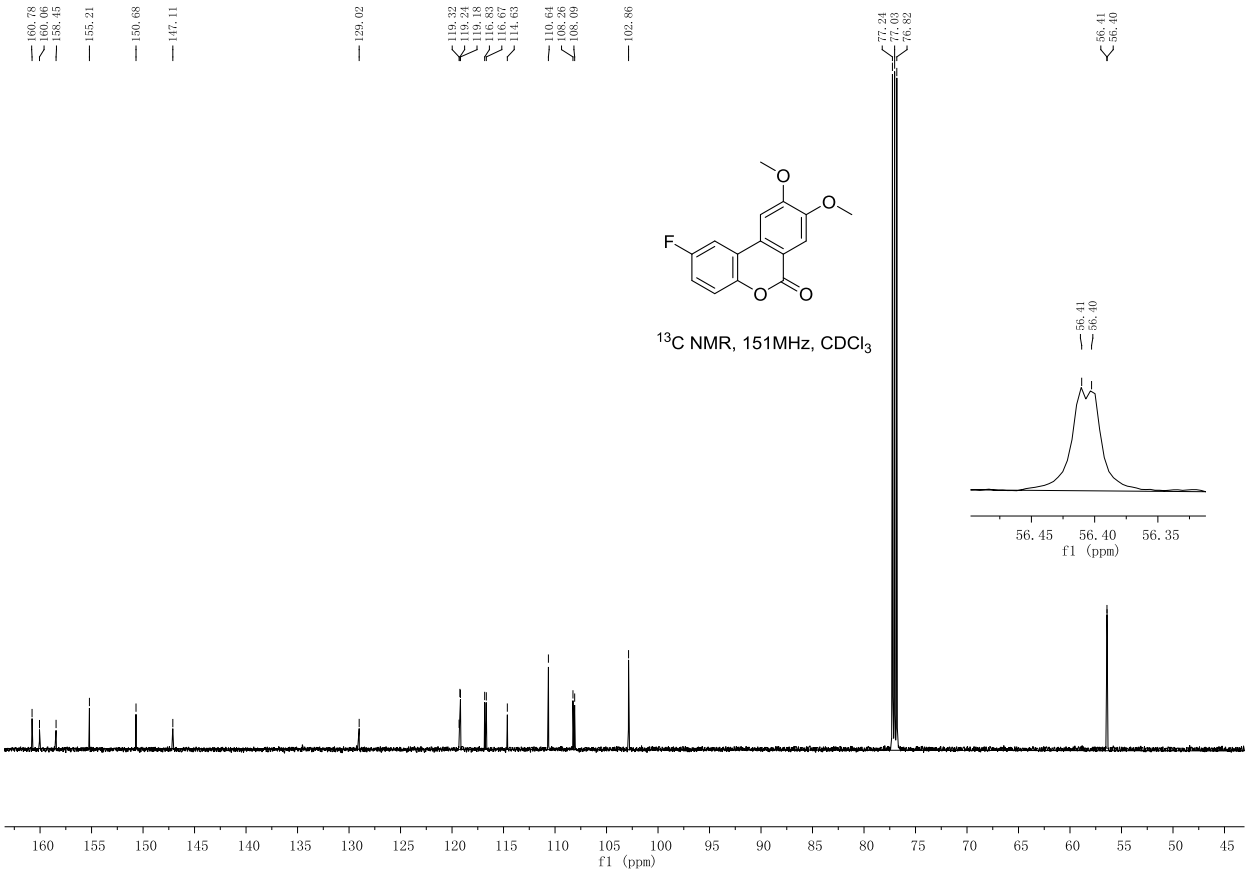
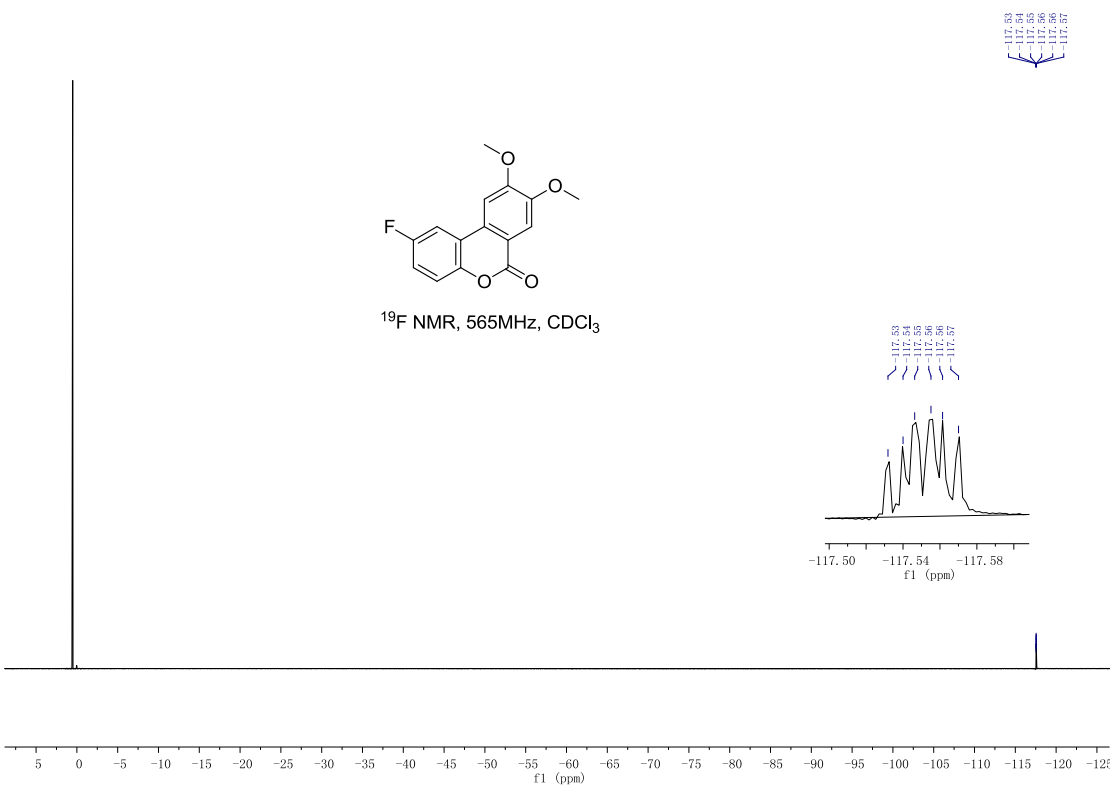
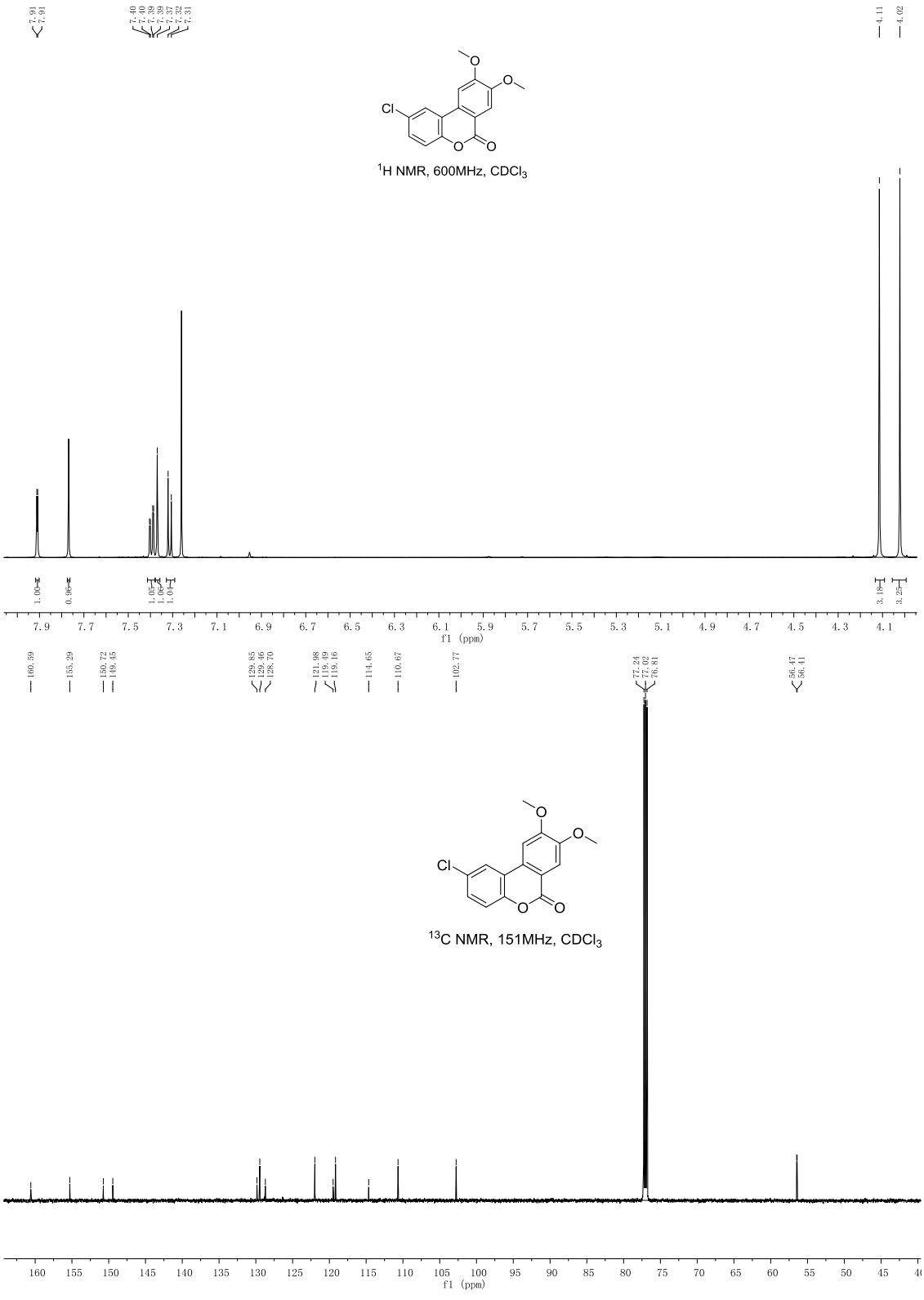


^{1}H NMR, 600MHz, $CDCl_3$


160.78
160.66
158.45
155.21
150.68
147.11
129.02
119.32
119.24
119.18
116.83
116.67
114.63
110.64
108.86
108.69
102.86
77.24
77.03
76.82
56.41
56.40
O
O
F
O
O
13C NMR, 151MHz, CDCl3
56.45
56.40
56.35
f1 (ppm)
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)


-117.53
-117.54
-117.55
-117.56
-117.56
-117.57
O
O
F
O
O
19F NMR, 565MHz, CDCl3
-117.50
-117.54
-117.58
f1 (ppm)
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

1k


7.91
7.91
7.40
7.40
7.39
7.39
7.37
7.32
7.31
4.11
4.02
Cl
O
O
O
O
^{1}H NMR, 600MHz, CDCl$_3$
1.00
0.96
1.07
1.06
1.04
3.18
3.25
f1 (ppm)
160.59
155.29
150.72
149.45
128.85
128.46
128.70
121.98
119.49
119.16
114.65
110.67
102.77
77.24
77.02
76.81
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56.41
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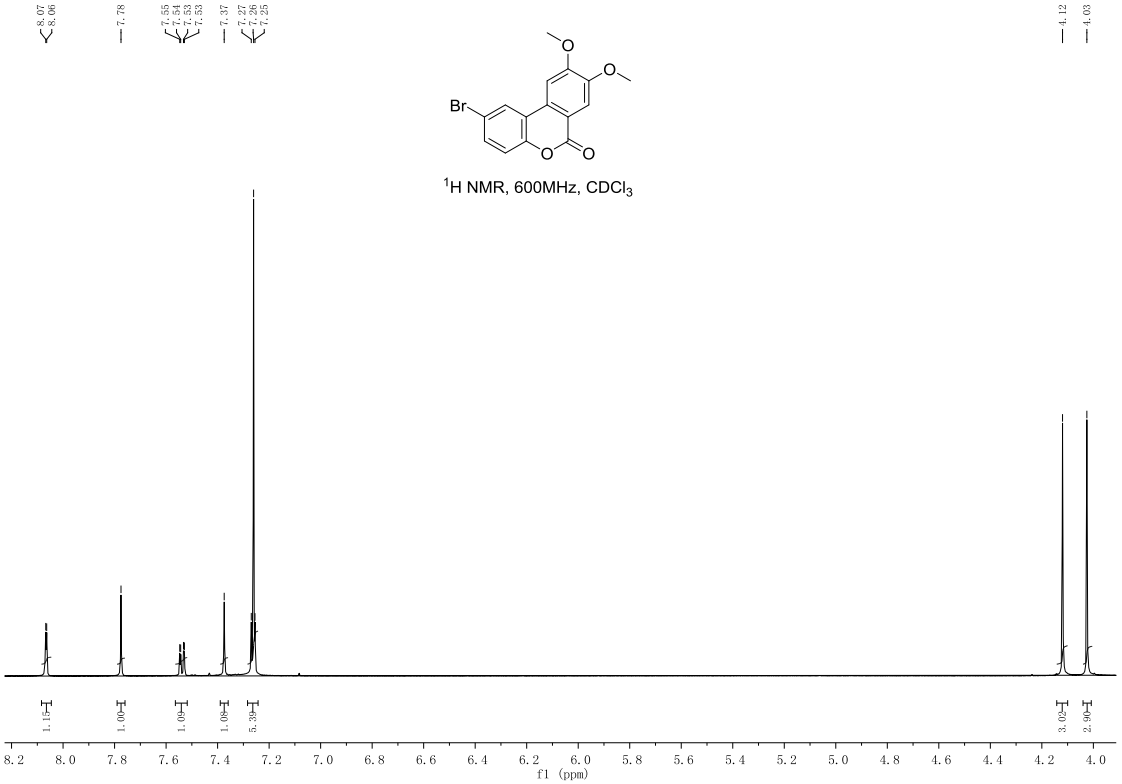
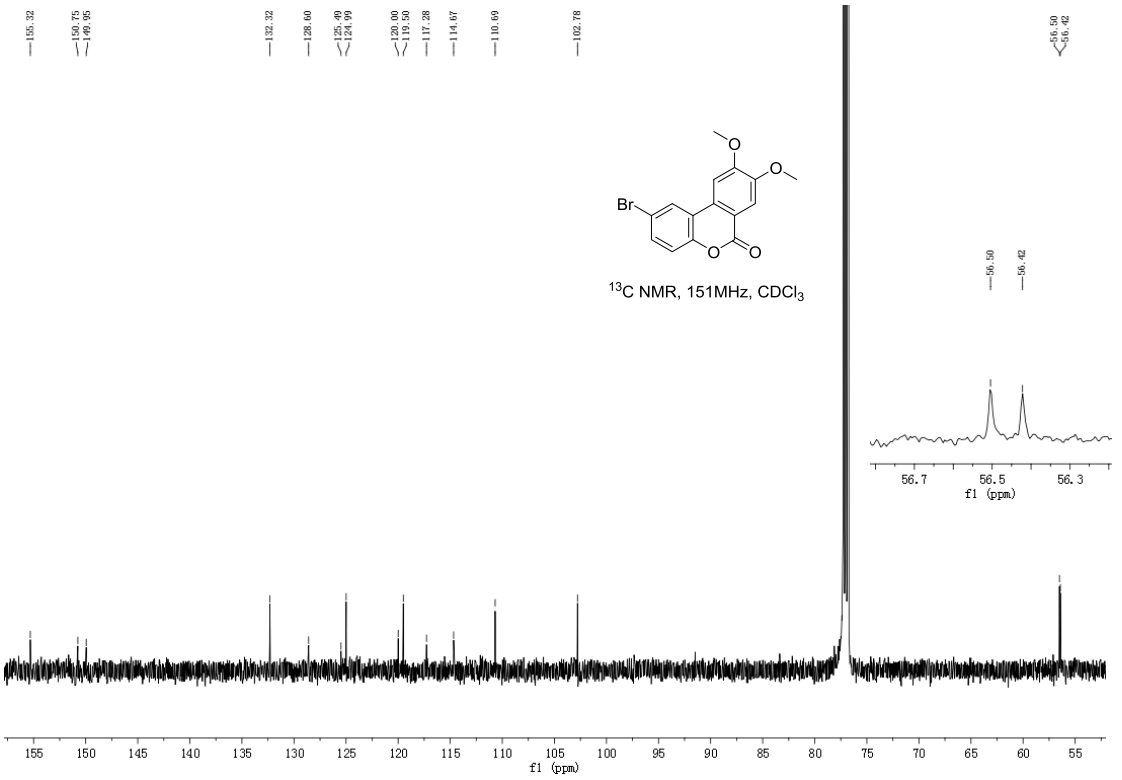
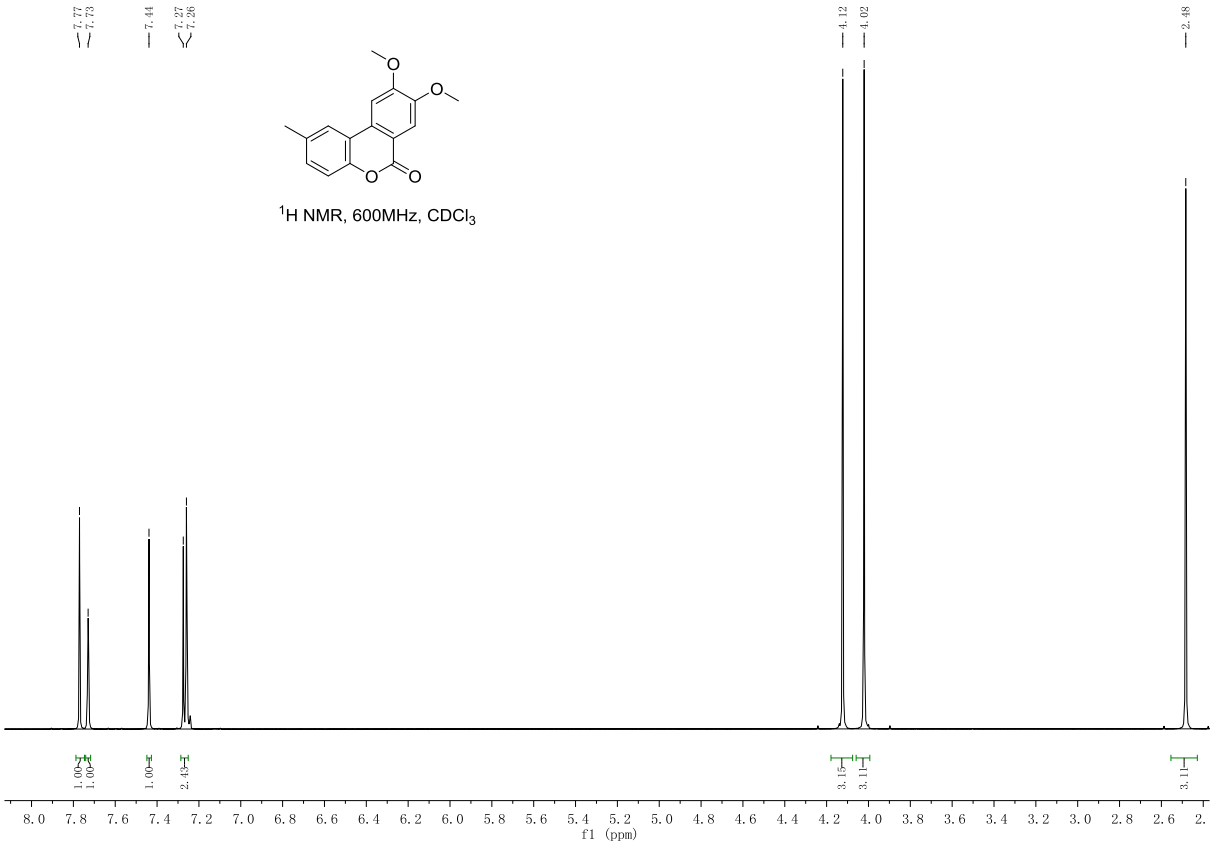
O
O
O
O
^{13}C NMR, 151MHz, CDCl$_3$
f1 (ppm)

1l

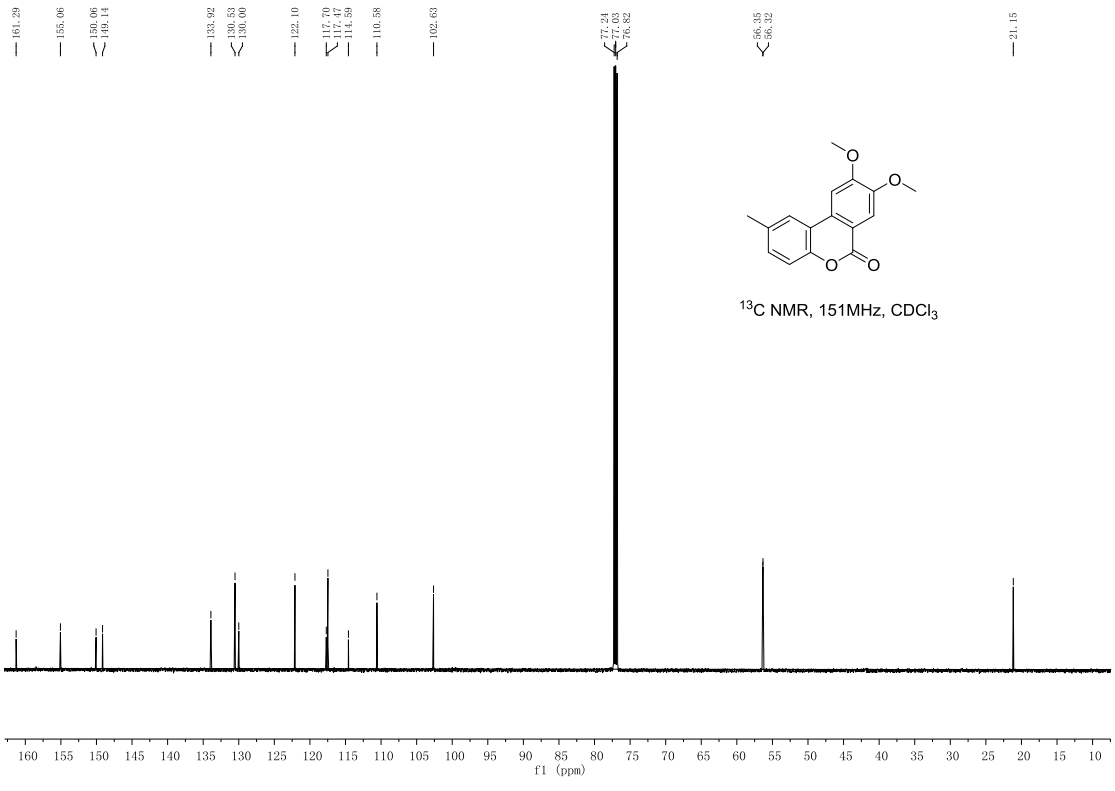

8.07
8.06
7.78
7.55
7.54
7.53
7.53
7.37
7.27
7.26
7.25
4.12
4.03
Br
O
O
O
O
^{1}H NMR, 600MHz, CDCl$_3$
1.15
1.00
1.09
1.08
5.39
3.02
2.90
f1 (ppm)


155.32
150.75
149.95
132.32
128.60
125.49
124.99
120.00
119.59
117.28
114.67
110.69
102.78
56.50
56.42
Br
O
O
O
O
^{13}C NMR, 151MHz, CDCl$_3$
56.50
56.42
56.7
56.5
56.3
f1 (ppm)
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

1m

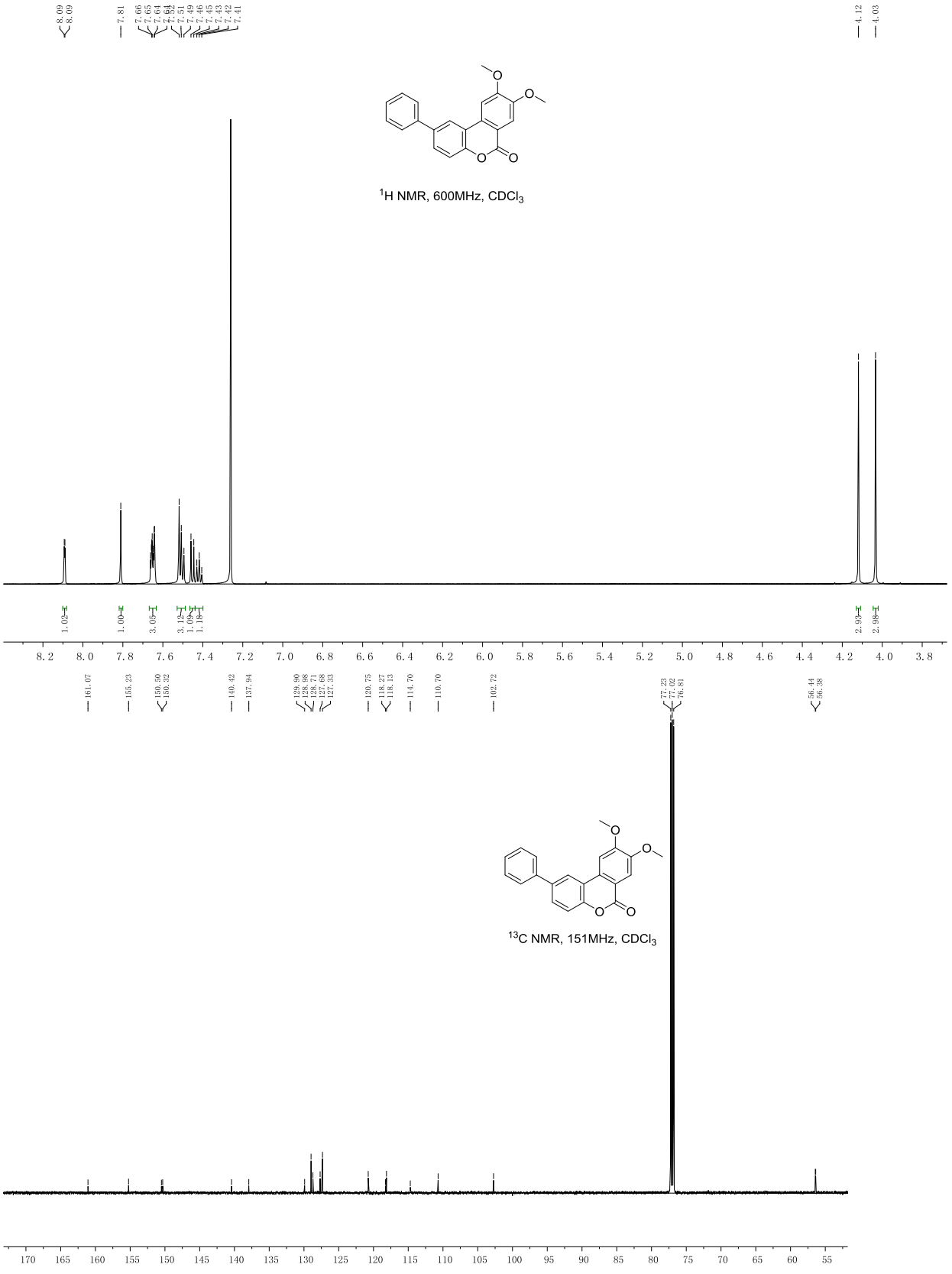


^{1}H NMR, 600MHz, $CDCl_3$

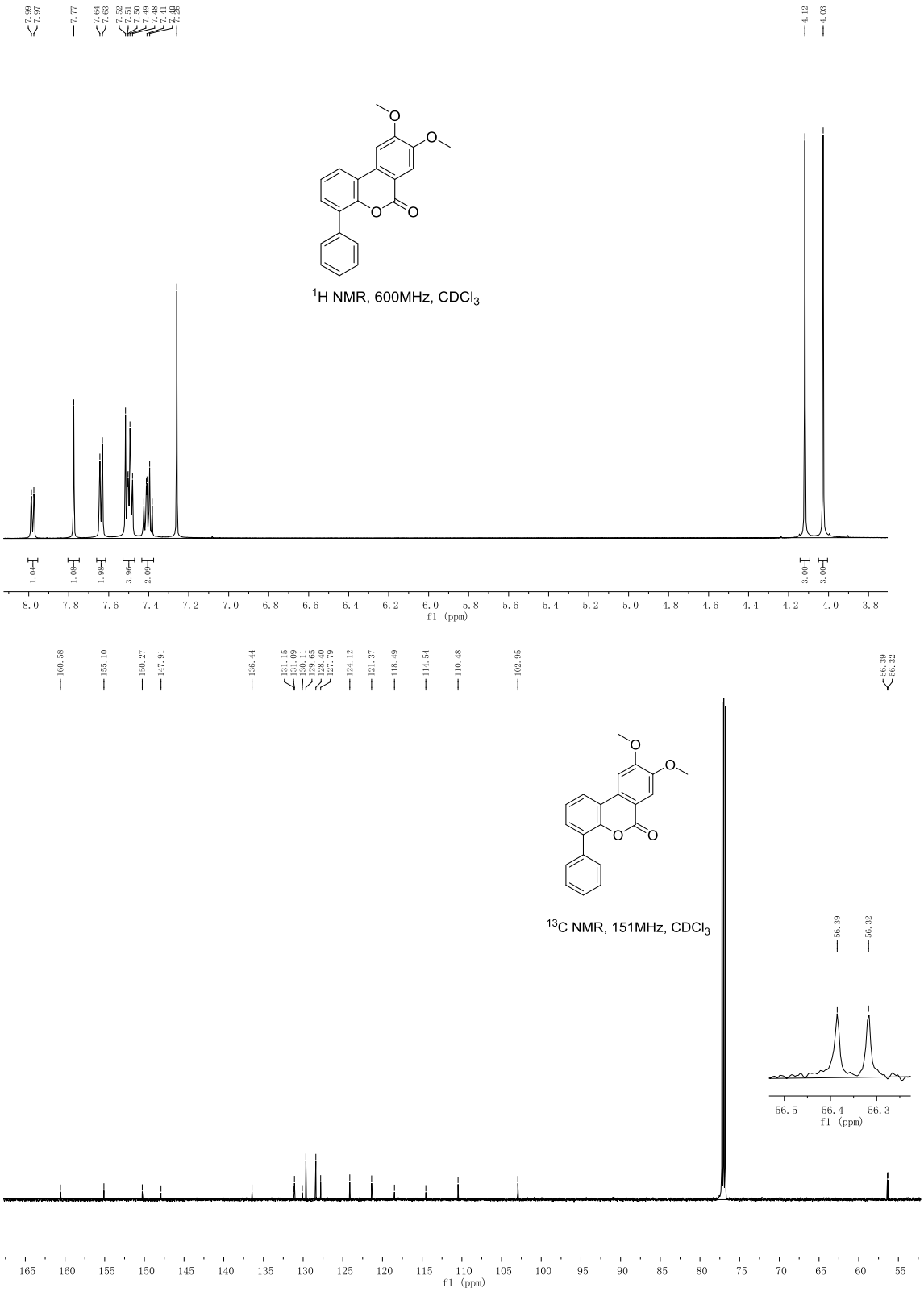


^{13}C NMR, 151MHz, $CDCl_3$

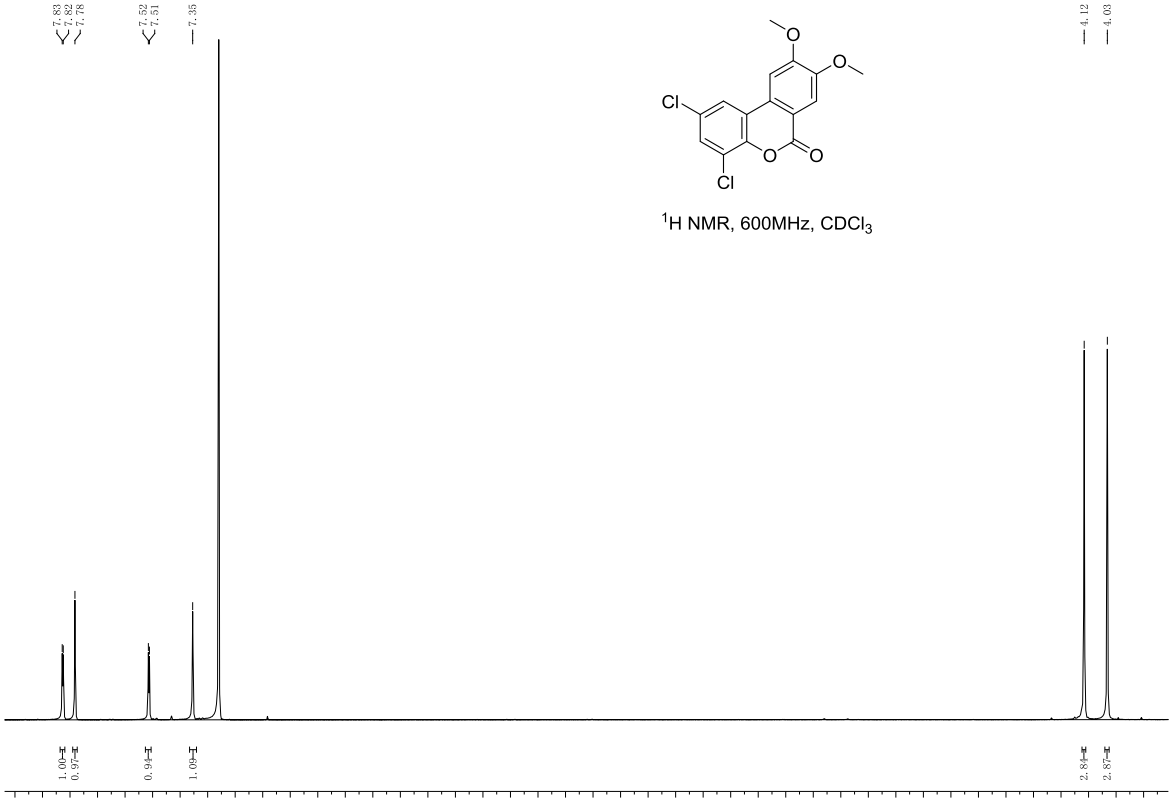
1n


8.09
8.09
7.81
7.66
7.65
7.64
7.51
7.49
7.46
7.45
7.43
7.42
7.41
4.12
4.03
O
O
O
O
1H NMR, 600MHz, CDCl3
1.02
1.00
3.05
3.12
1.09
1.18
2.93
2.98
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
161.07
155.23
150.50
150.32
140.42
137.94
129.90
128.98
128.71
127.68
127.33
120.75
118.27
118.13
114.70
110.70
102.72
77.23
77.02
76.81
56.44
56.38
O
O
O
O
13C NMR, 151MHz, CDCl3
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55

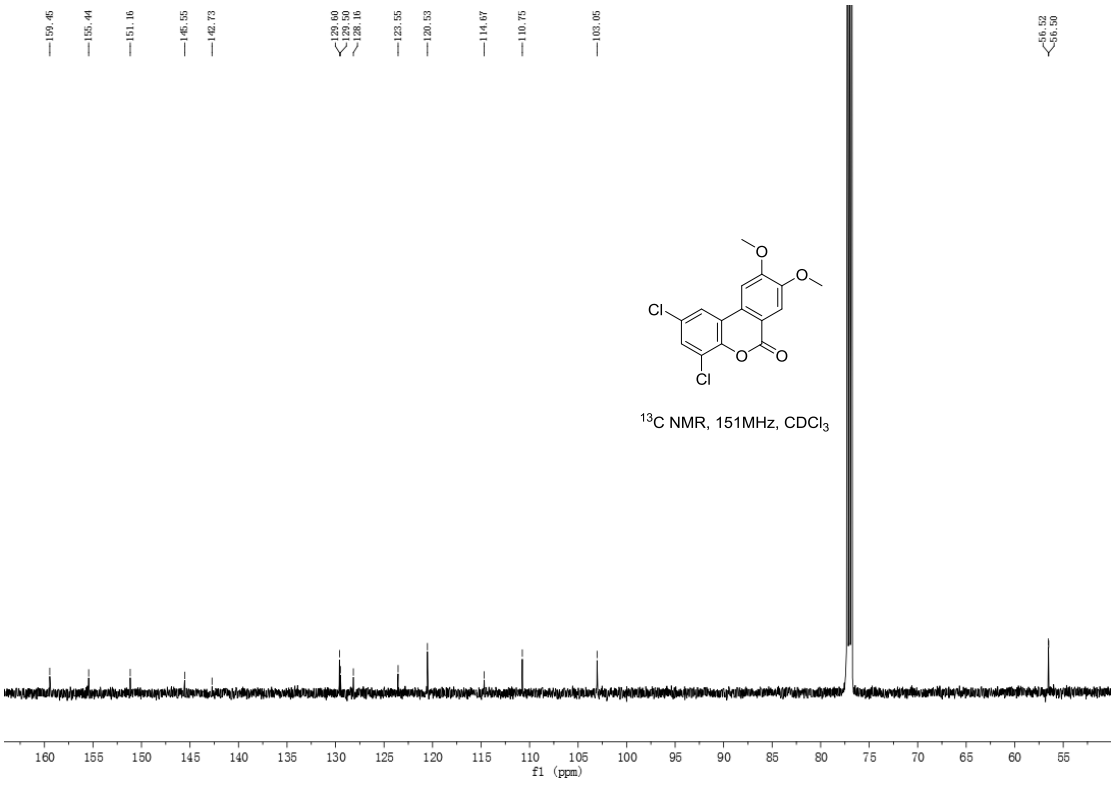
1o


7.99
7.97
7.77
7.64
7.63
7.52
7.51
7.50
7.49
7.48
7.41
7.40
7.38
4.12
4.03
1.04
1.08
1.99
3.96
2.00
3.00
3.00
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
f1 (ppm)
O
O
O
O
^{1}H NMR, 600MHz, CDCl$_3$
160.58
155.10
150.27
147.91
136.44
131.15
131.09
130.11
129.65
128.40
127.79
124.12
121.37
118.49
114.54
110.48
102.95
56.39
56.32
^{13}C NMR, 151MHz, CDCl$_3$
56.5 56.4 56.3
f1 (ppm)
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
f1 (ppm)

1p

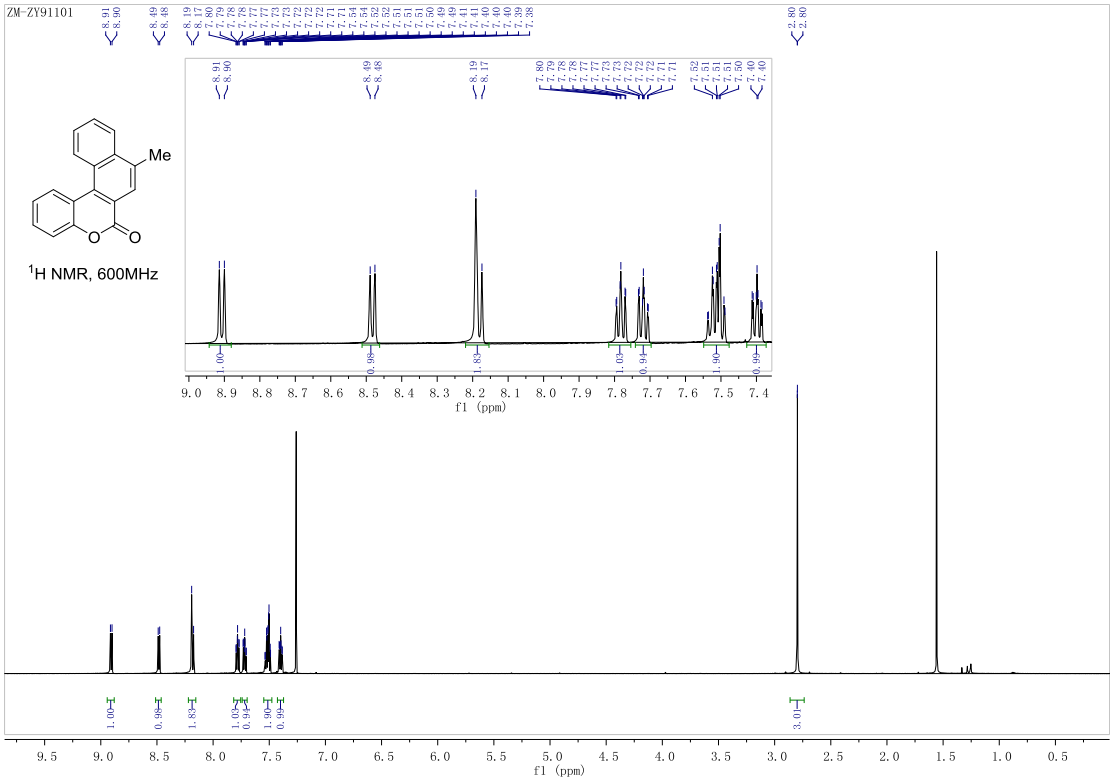


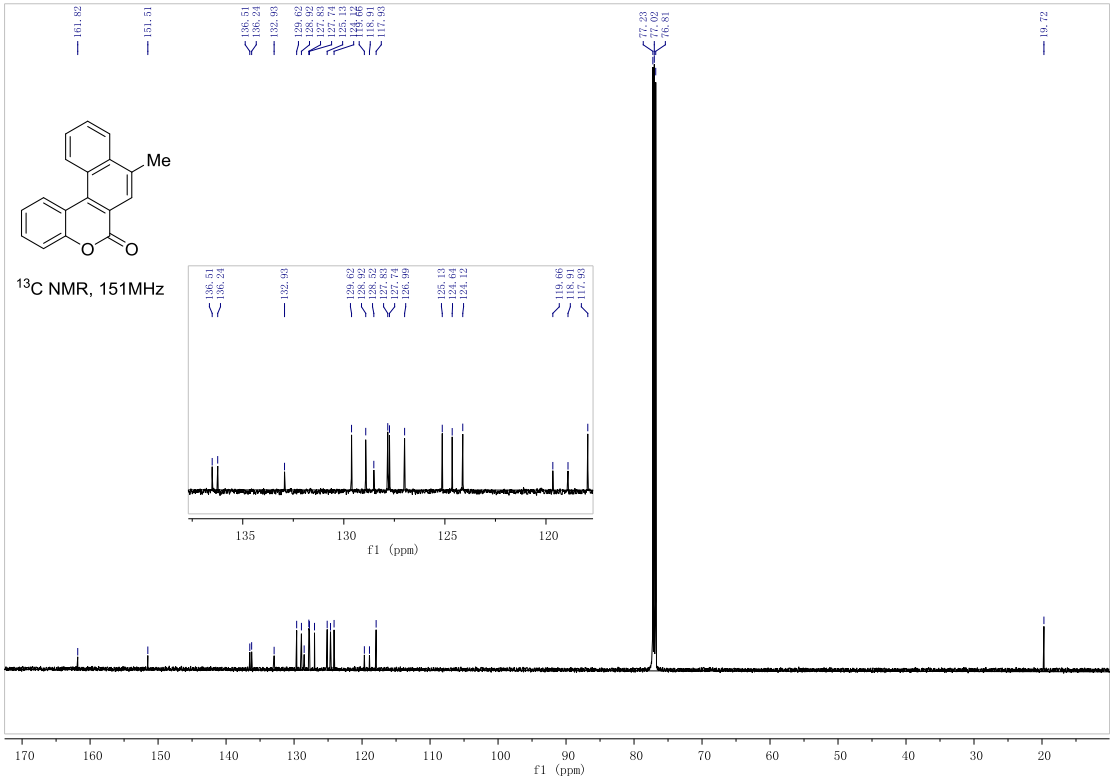
^{1}H NMR, 600MHz, $CDCl_3$



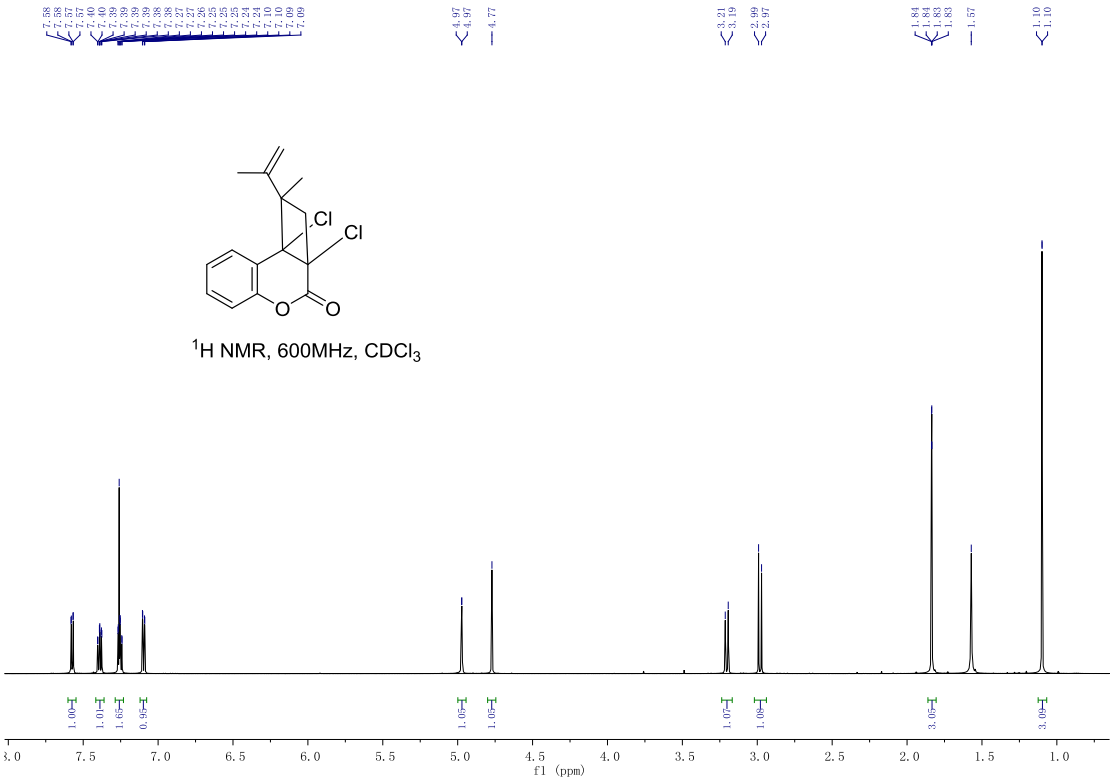
^{13}C NMR, 151MHz, $CDCl_3$

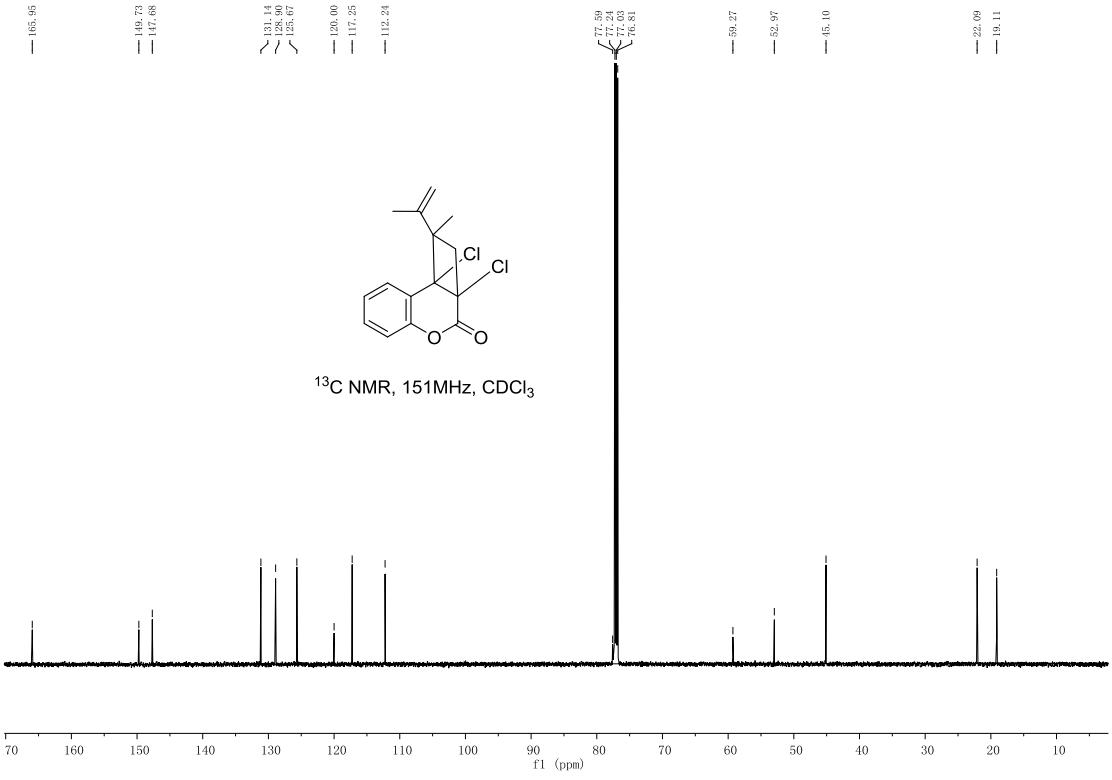
1q


ZM-ZY91101
Me
O
O
^{1}H NMR, 600MHz
f1 (ppm)

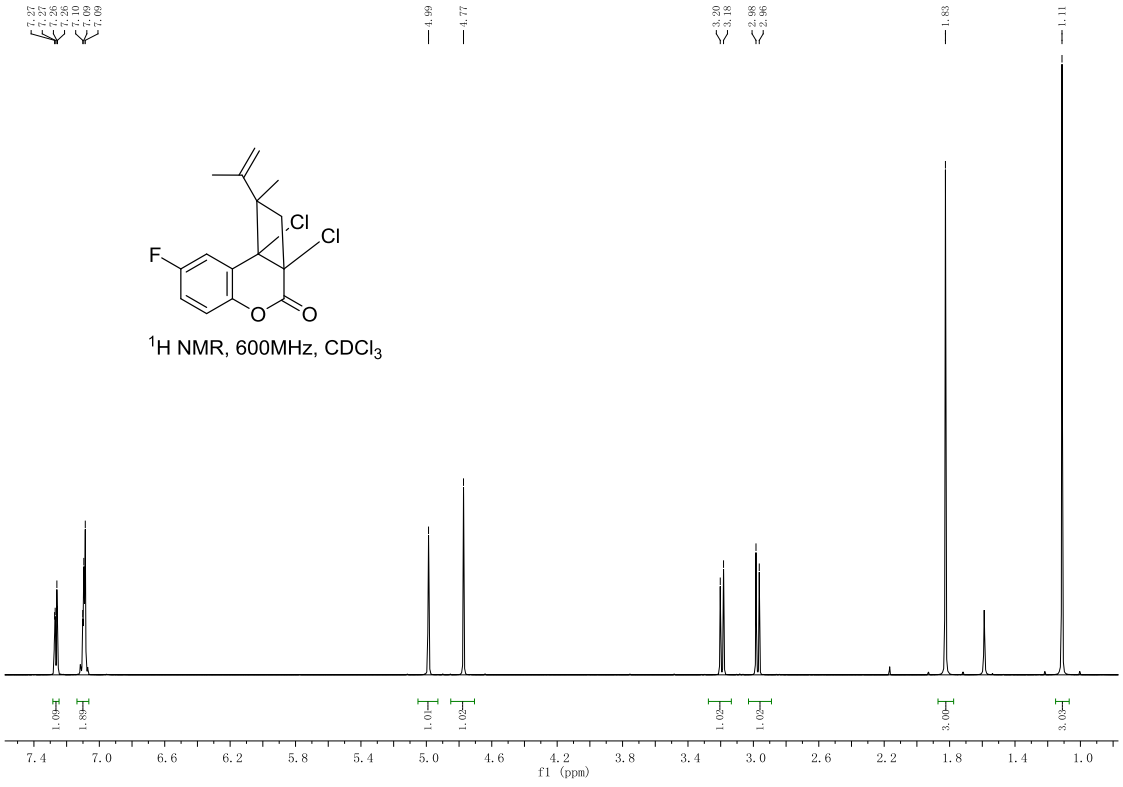

Me
O
O
^{13}C NMR, 151MHz
f1 (ppm)

4a


Cl
Cl
O
O
1H NMR, 600MHz, CDCl3
f1 (ppm)

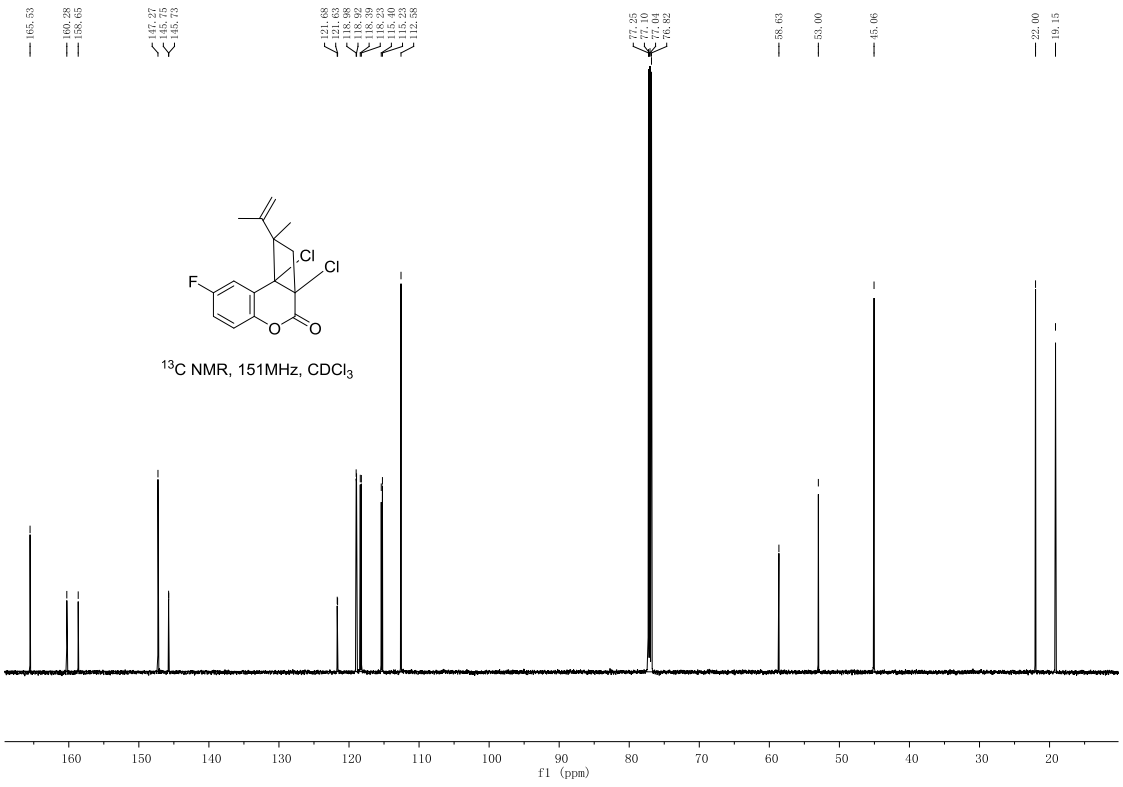

Cl
Cl
O
O
13C NMR, 151MHz, CDCl3
f1 (ppm)

4b



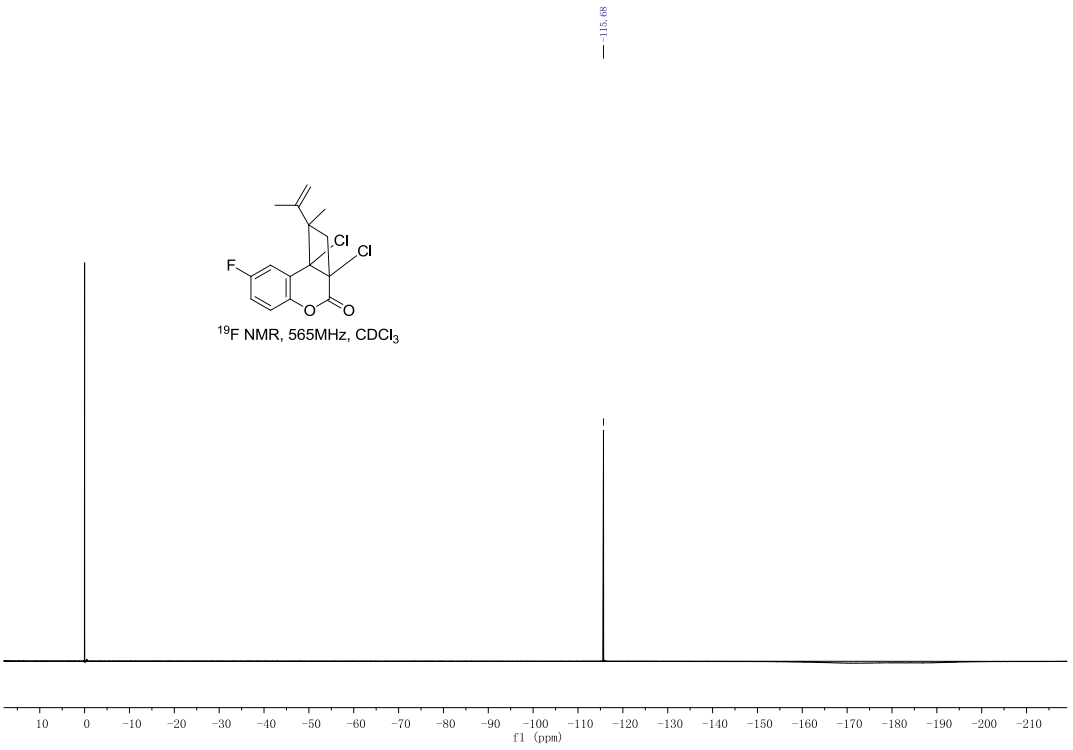
^{1}H NMR, 600MHz, $CDCl_3$

^{13}C NMR



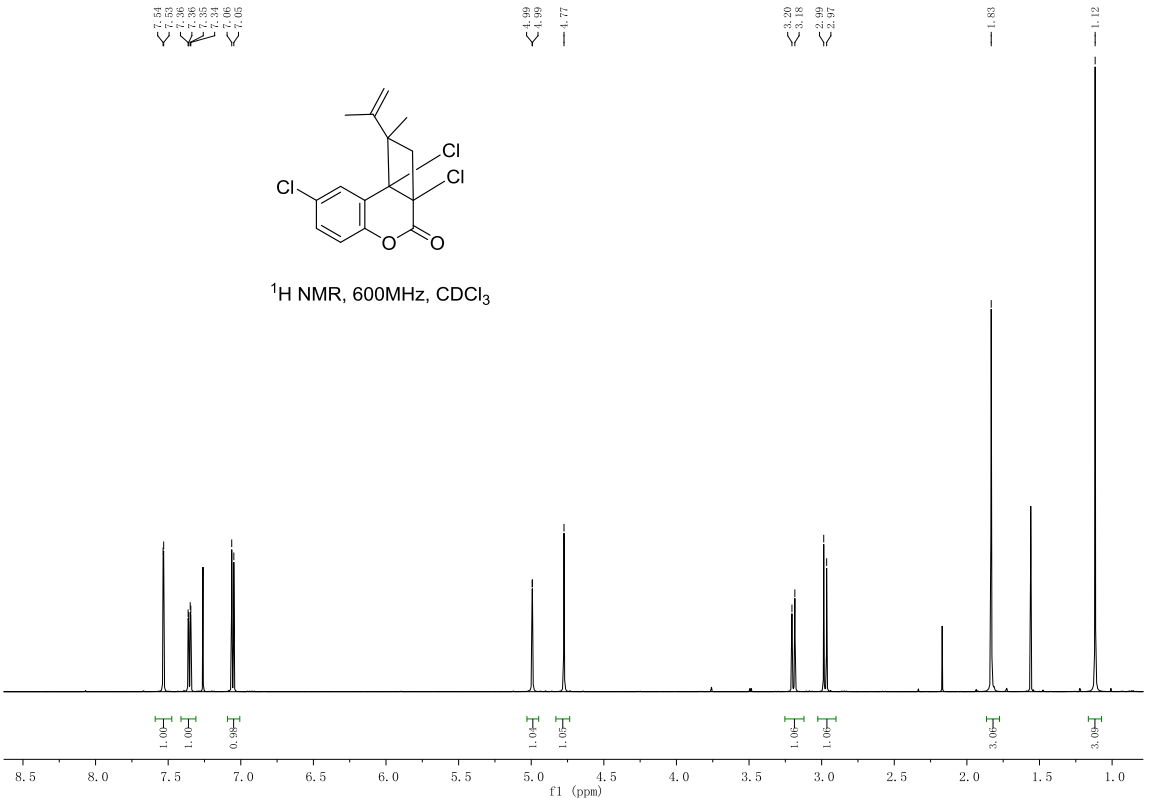
^{13}C NMR, 151MHz, $CDCl_3$

^{19}F NMR

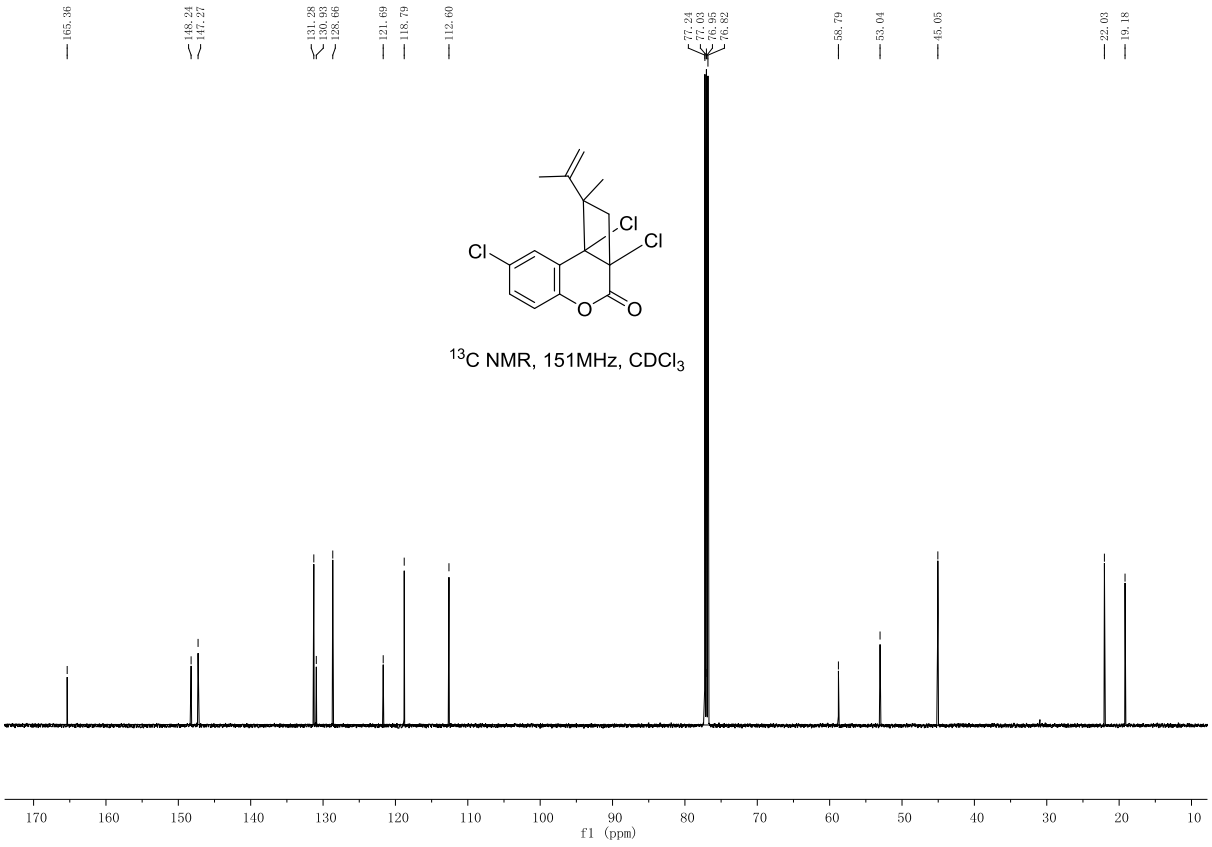


^{19}F NMR, 565MHz, $CDCl_3$

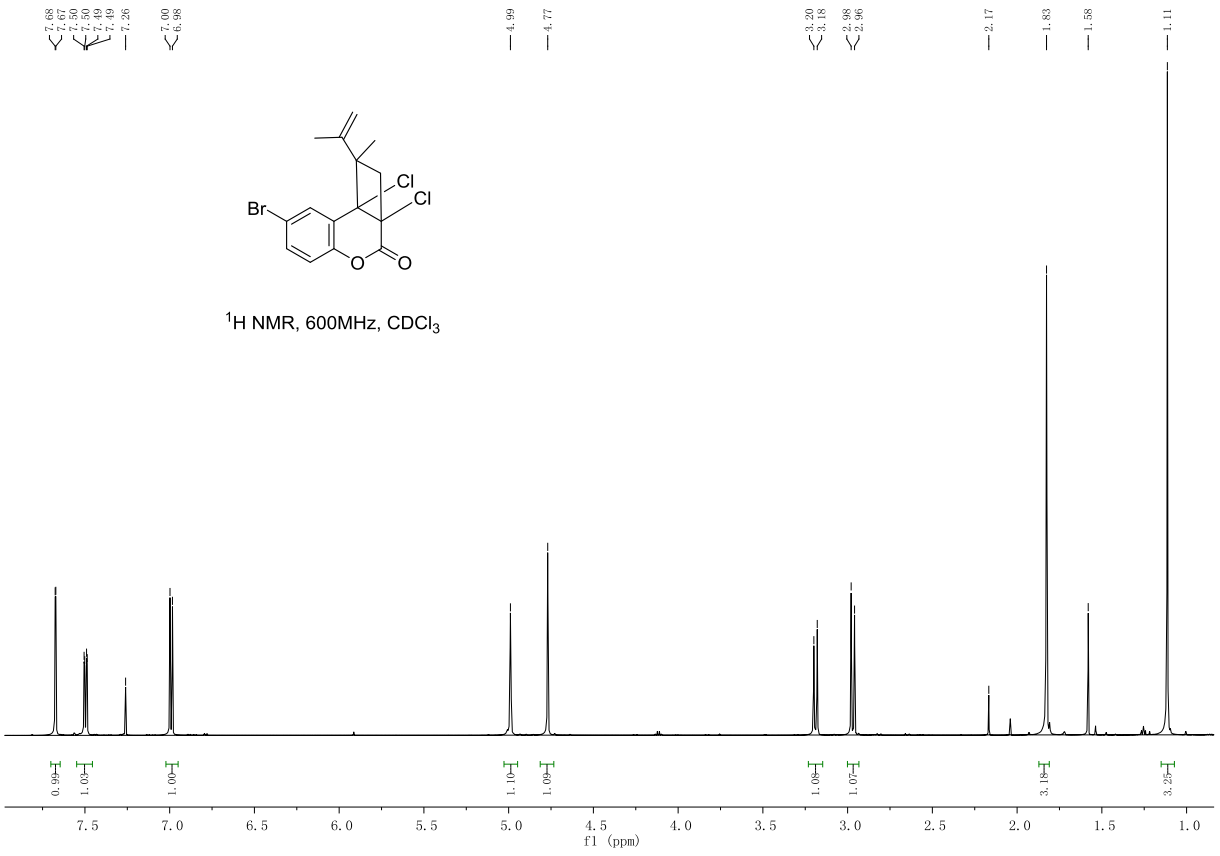
4c

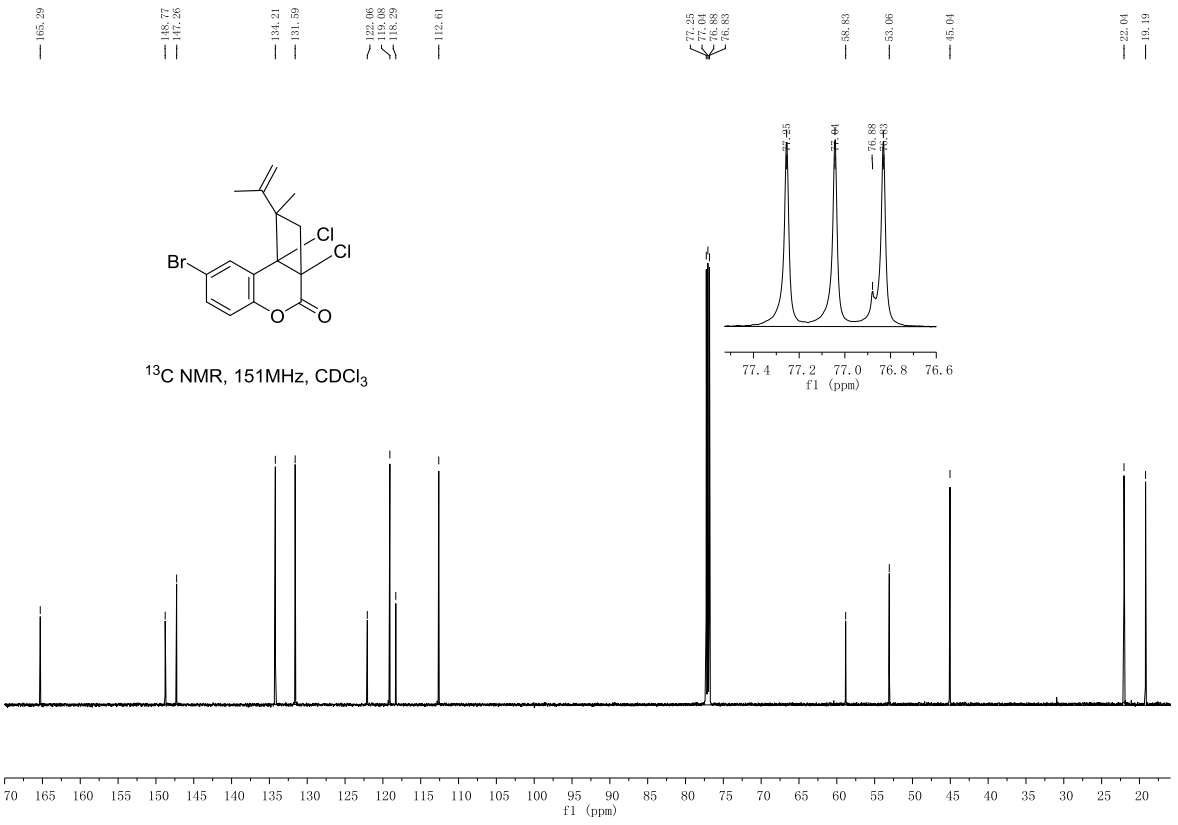


^{1}H NMR, 600MHz, $CDCl_3$

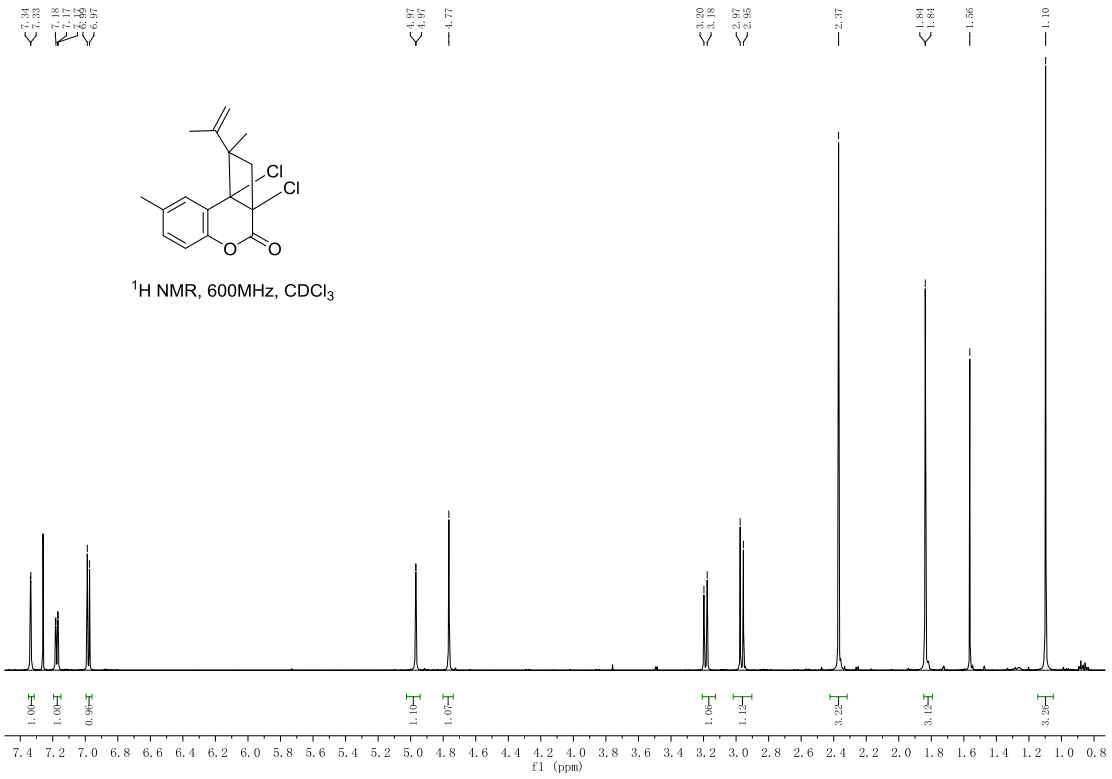

165.36
148.24
147.27
131.98
130.83
128.66
121.69
118.79
112.60
77.24
77.03
76.95
76.82
58.79
53.04
45.05
22.03
19.18
Cl
Cl
Cl
O
O
13C NMR, 151MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

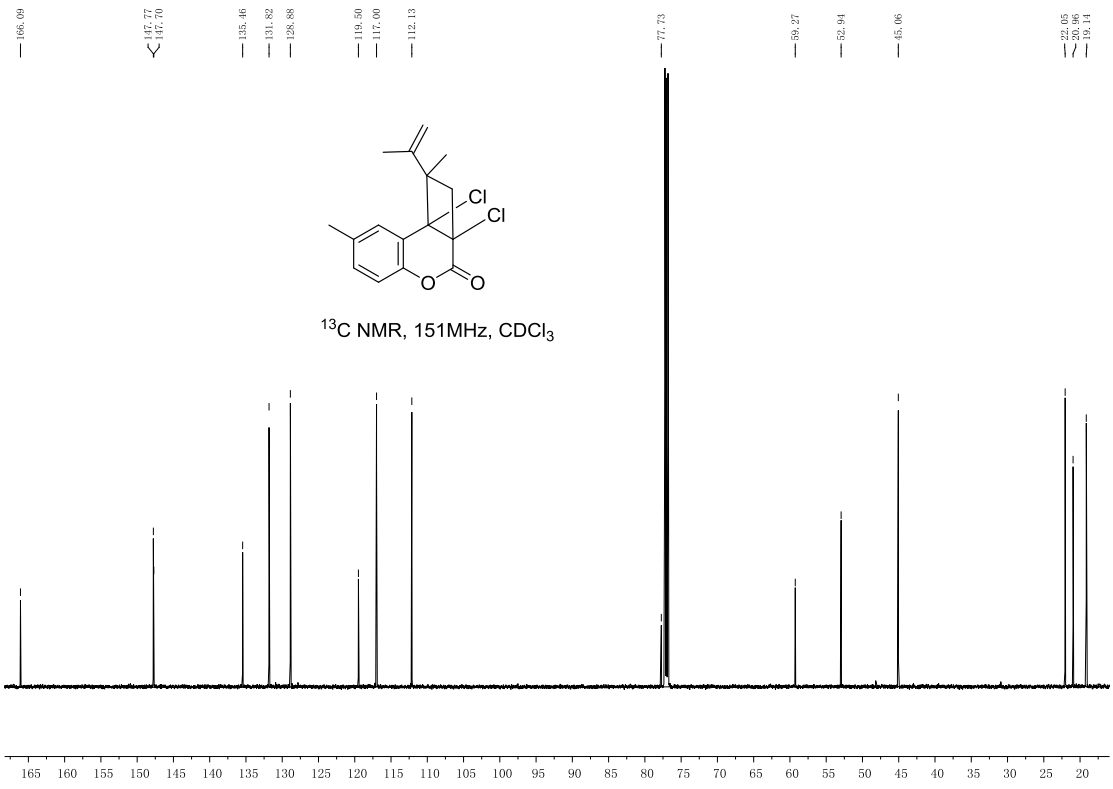
4d


7.68
7.67
7.50
7.50
7.49
7.49
7.26
7.00
6.98
4.99
4.77
3.20
3.18
2.98
2.96
2.17
1.83
1.58
1.11
Br
Cl
Cl
O
O
1H NMR, 600MHz, CDCl3
0.99
1.03
1.00
1.10
1.09
1.08
1.07
3.18
3.25
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
f1 (ppm)


165.29
148.77
147.26
134.21
131.59
122.06
119.08
116.29
112.61
77.25
77.04
76.88
76.83
58.83
53.06
45.04
22.04
19.19
Cl
Cl
Br
O
O
^{13}C NMR, 151MHz, CDCl$_3$
f1 (ppm)

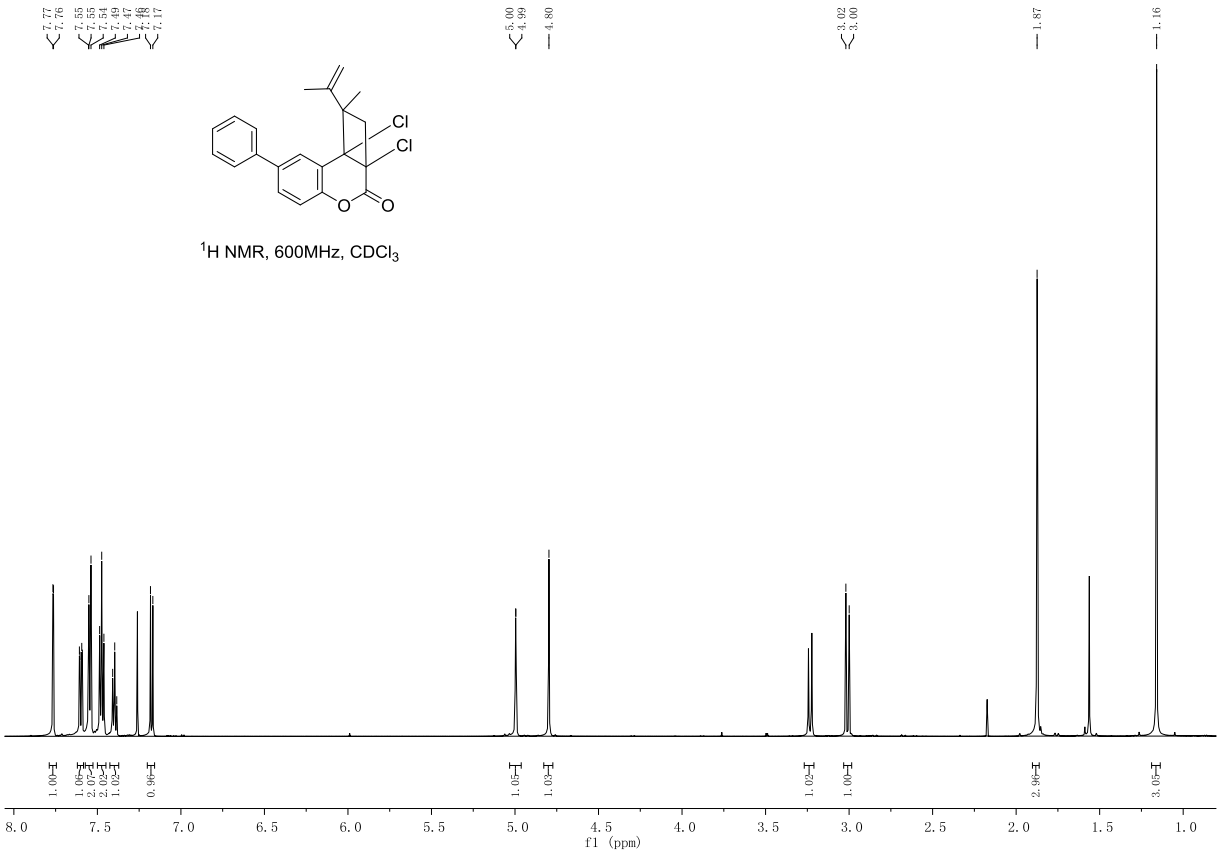
4e


7.34
7.33
7.18
7.17
6.97
4.97
4.77
3.20
3.18
2.97
2.95
2.37
1.84
1.56
1.10
Cl
Cl
O
O
^{1}H NMR, 600MHz, CDCl$_3$
f1 (ppm)

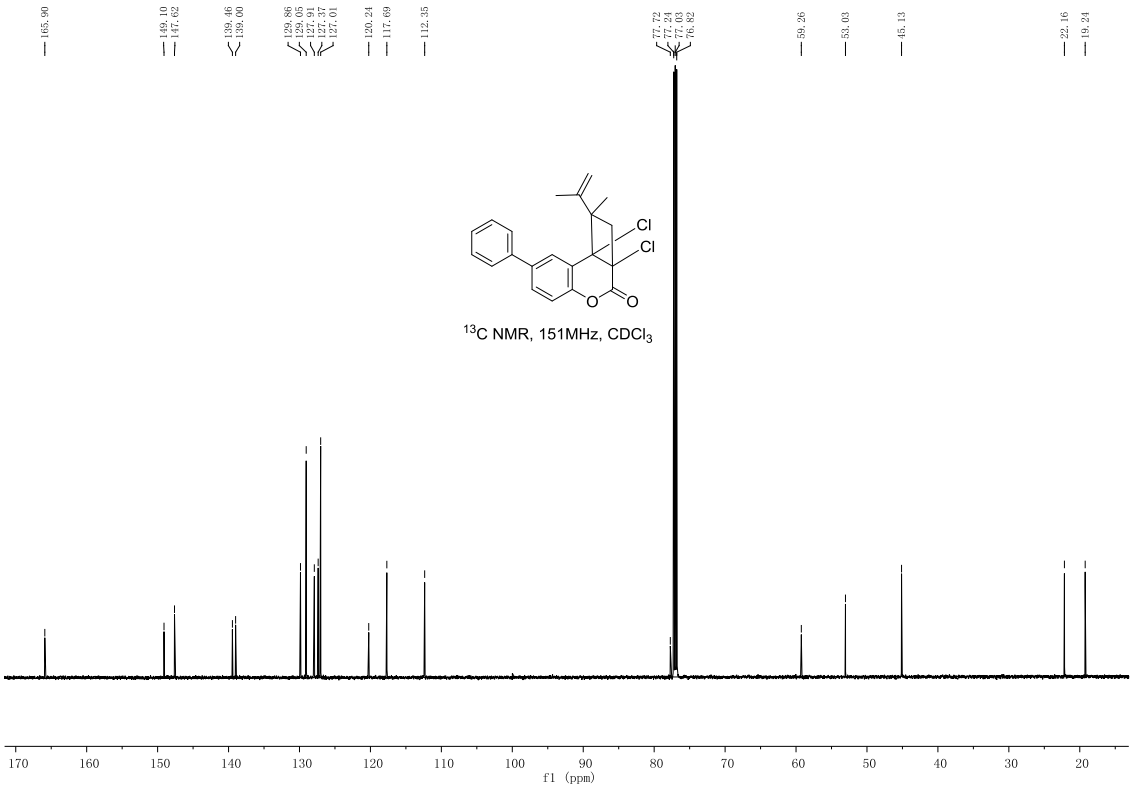


^{13}C NMR, 151MHz, $CDCl_3$

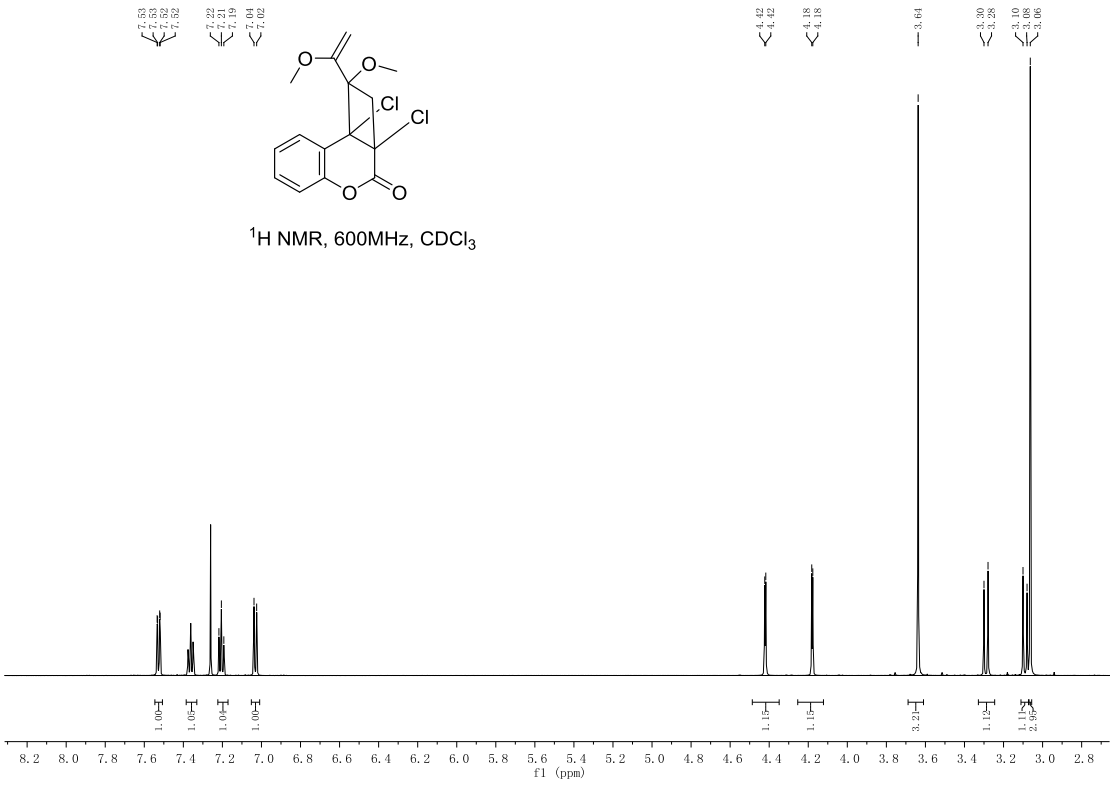
4f

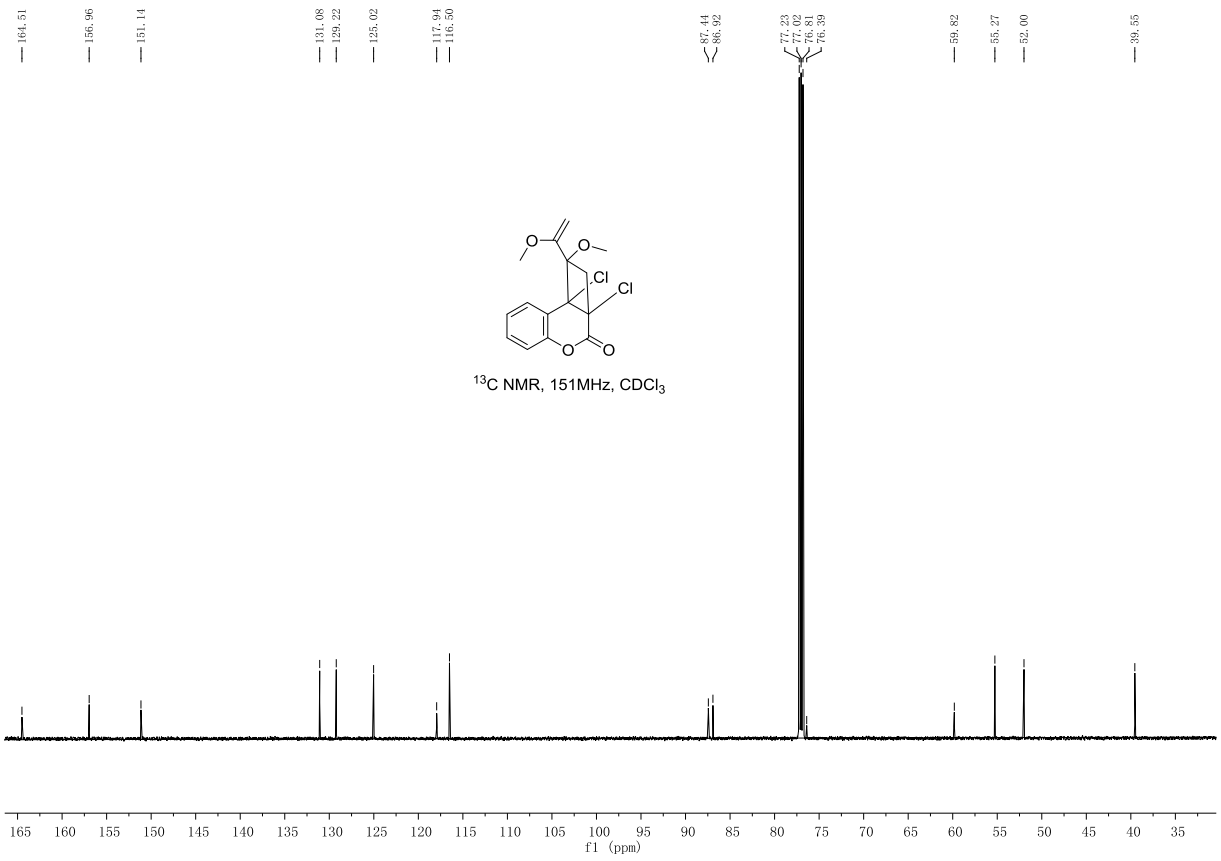


^{1}H NMR, 600MHz, $CDCl_3$


165.90
149.10
147.62
139.46
139.00
129.86
129.05
127.94
127.37
127.01
120.24
117.69
112.35
77.72
77.24
77.03
76.82
59.26
53.03
45.13
22.16
19.24
Cl
Cl
O
O
^{13}C NMR, 151MHz, CDCl$_3$
f1 (ppm)

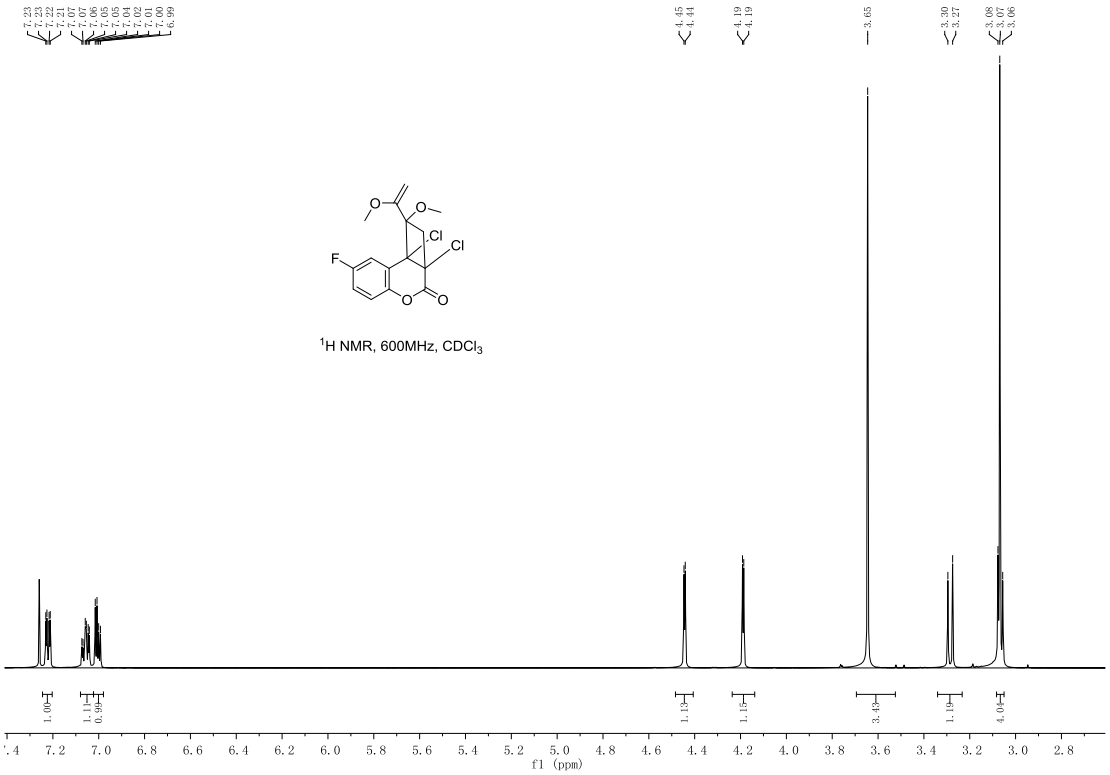
4i


7.53
7.53
7.52
7.52
7.22
7.21
7.19
7.04
7.02
4.42
4.42
4.18
4.18
3.64
3.30
3.28
3.10
3.08
3.06
O
O
Cl
Cl
O
O
^{1}H NMR, 600MHz, CDCl$_3$
1.00
1.05
1.04
1.00
1.15
1.15
3.21
1.12
1.11
2.95
f1 (ppm)

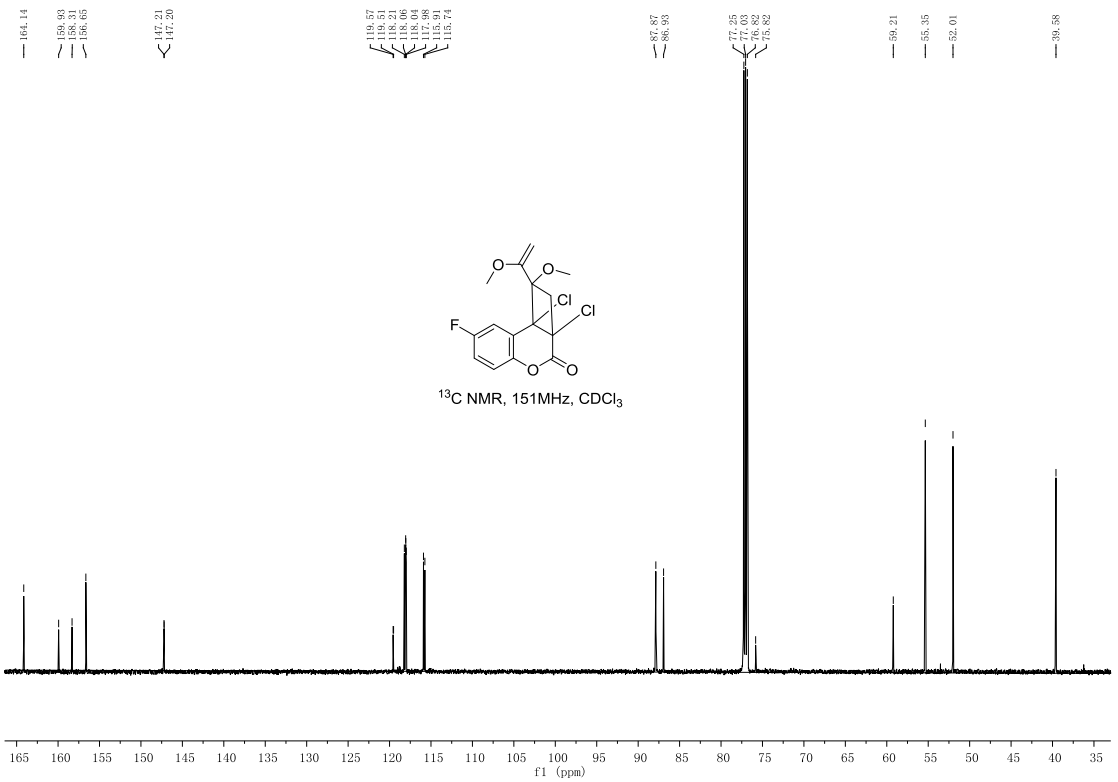


^{13}C NMR, 151MHz, $CDCl_3$

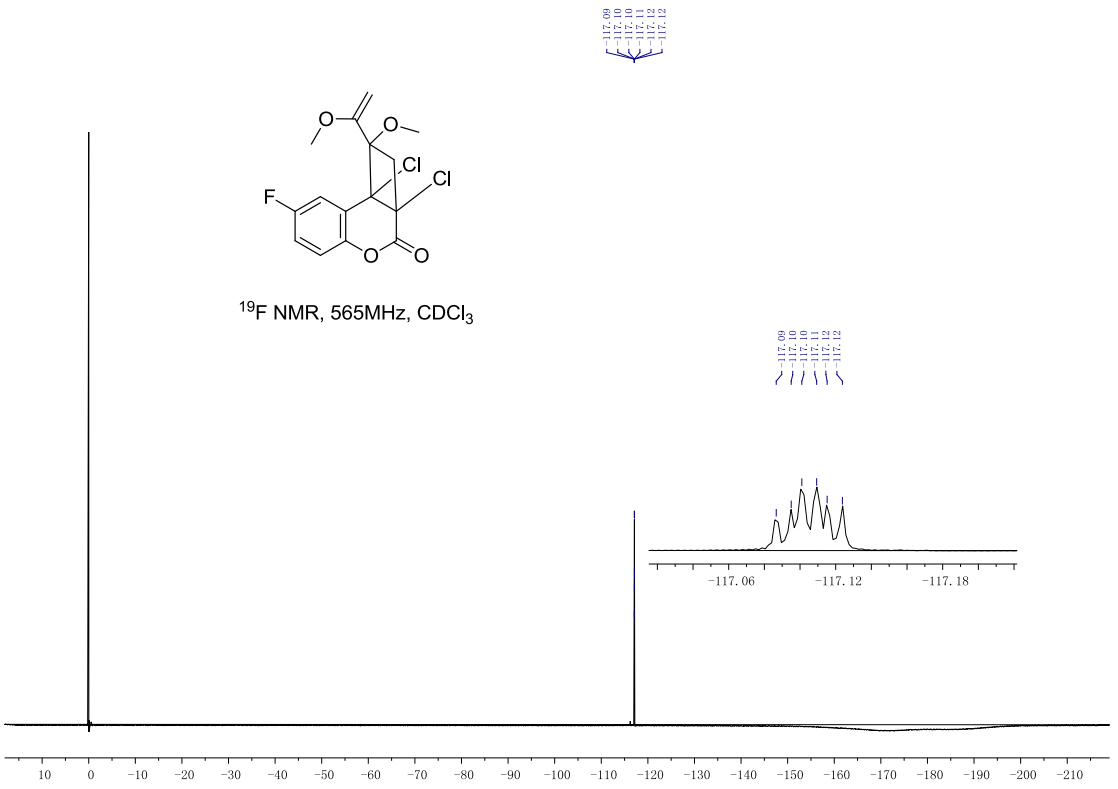
4j



^{1}H NMR, 600MHz, $CDCl_3$

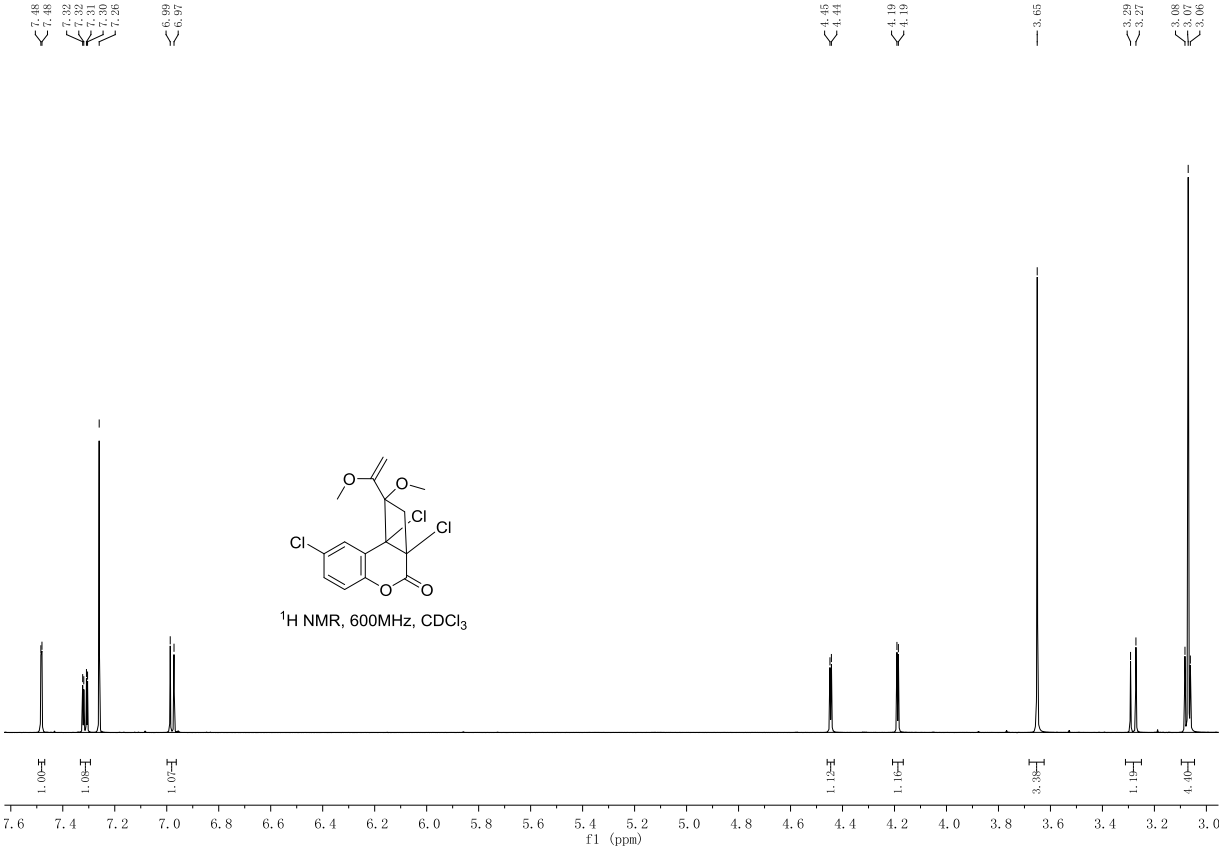


^{13}C NMR, 151MHz, $CDCl_3$

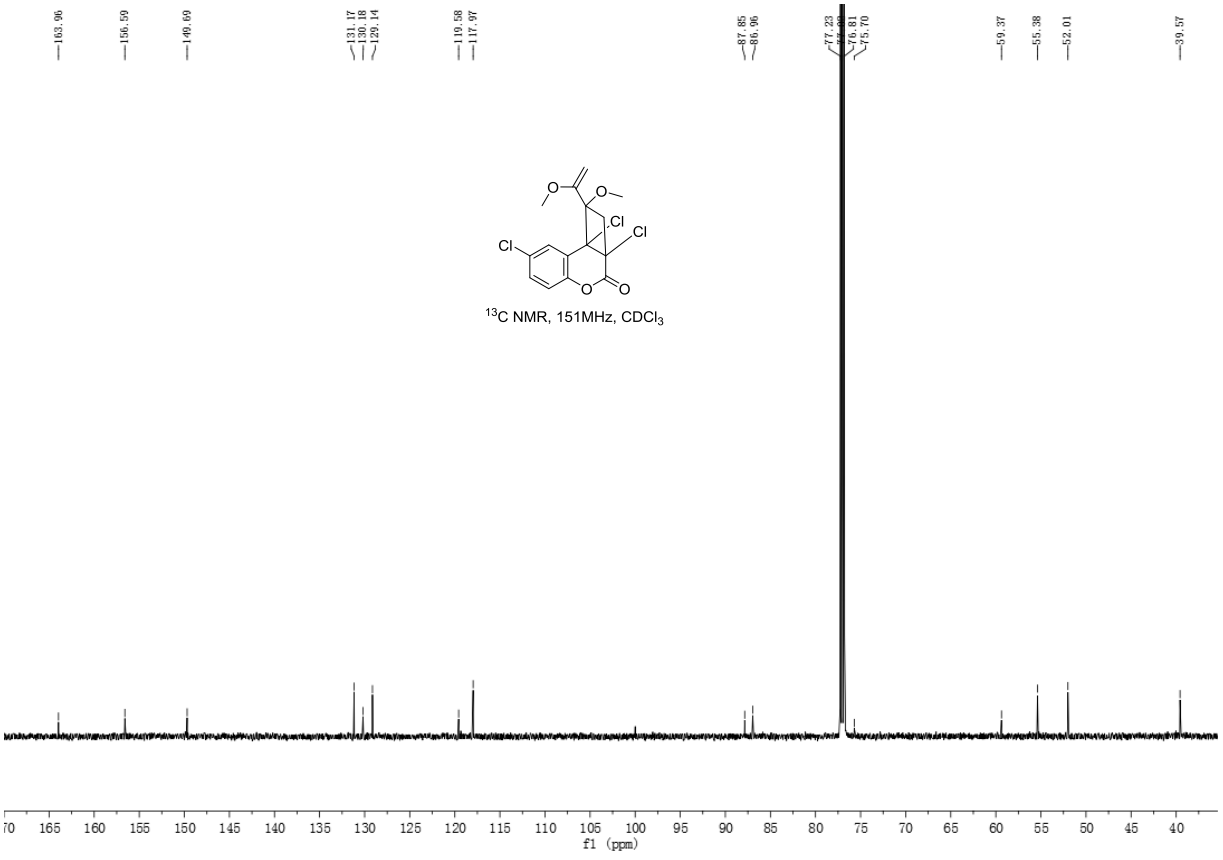


^{19}F NMR, 565MHz, $CDCl_3$

4k

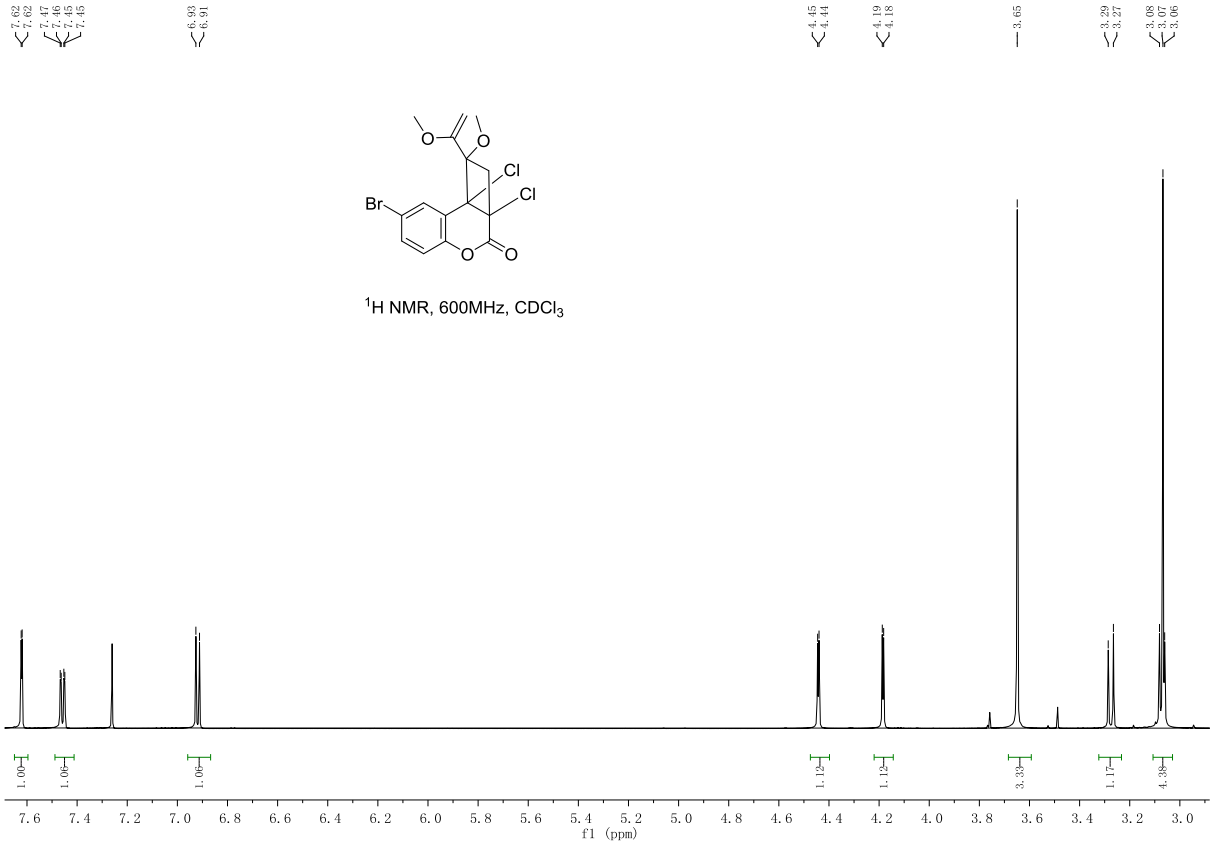


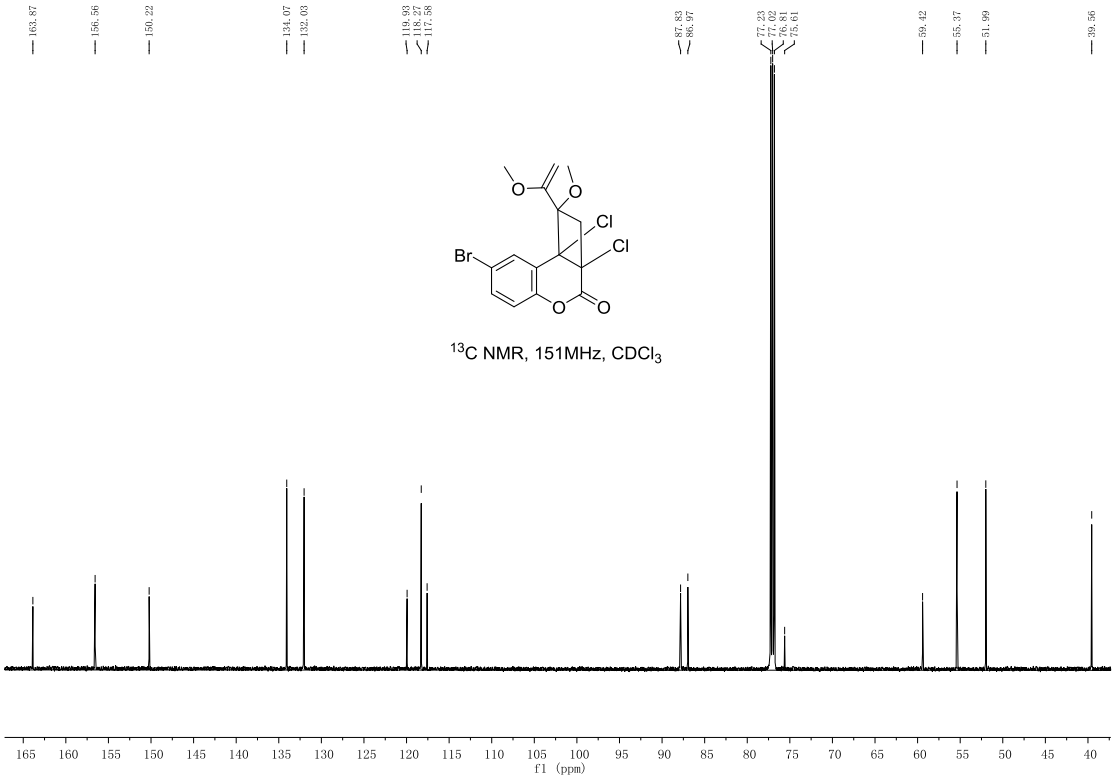
^{1}H NMR, 600MHz, $CDCl_3$



^{13}C NMR, 151MHz, $CDCl_3$

4l


7.62
7.62
7.47
7.46
7.45
7.45
6.93
6.91
4.45
4.44
4.19
4.18
3.65
3.29
3.27
3.08
3.07
3.06
O
O
Cl
Cl
Br
O
O
1H NMR, 600MHz, CDCl3
1.00
1.06
1.06
1.12
1.12
3.33
1.17
4.38
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
f1 (ppm)


163.87
156.56
150.22
134.07
132.03
119.93
118.27
117.58
87.83
86.97
77.23
77.02
76.81
75.61
59.42
55.37
51.99
39.56
O
O
Cl
Cl
Br
O
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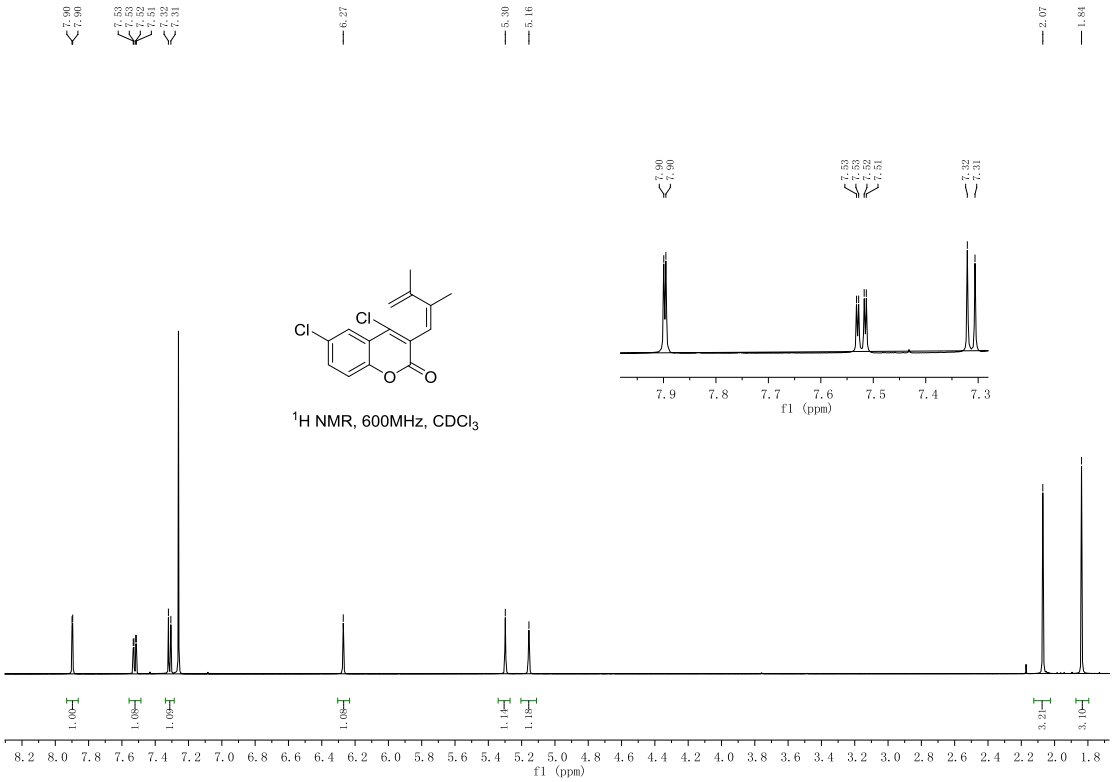
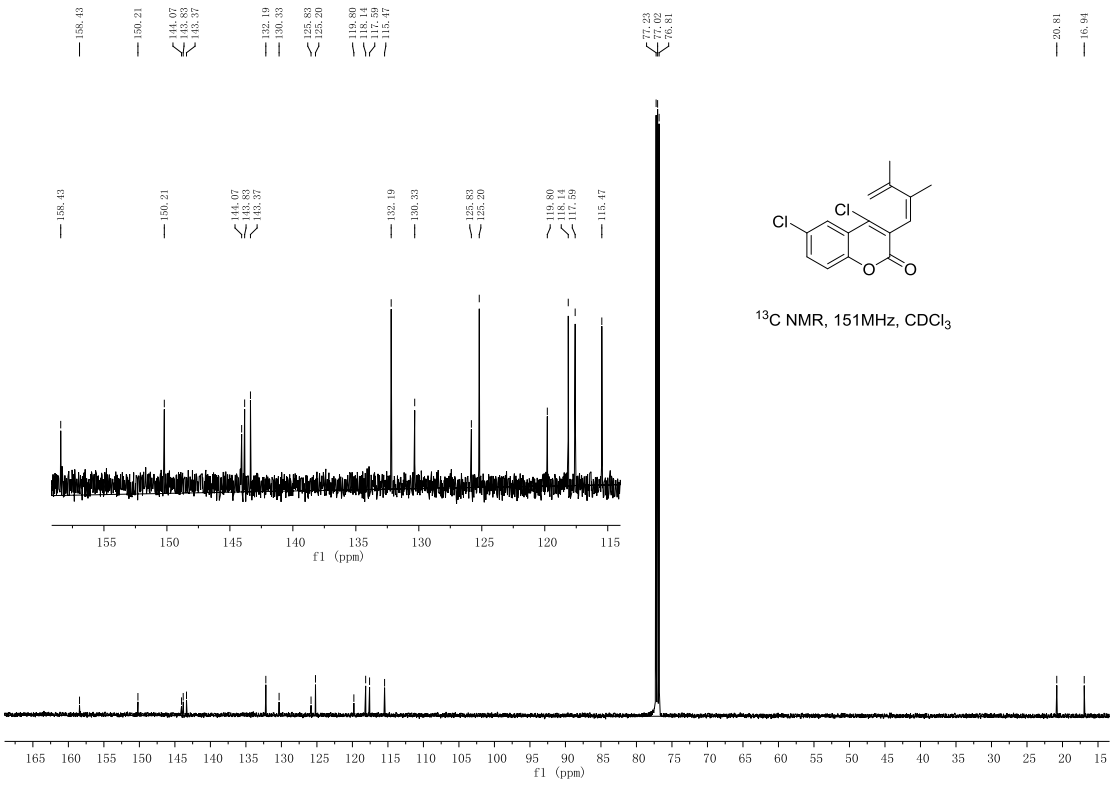
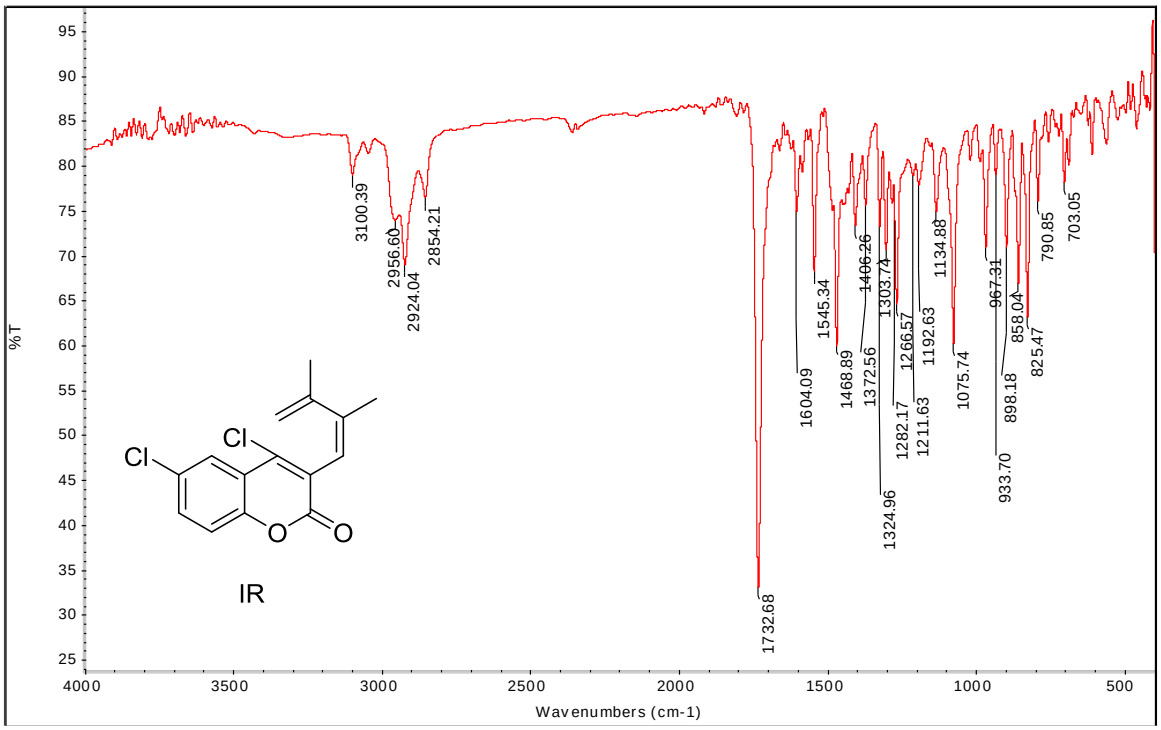
13C NMR, 151MHz, CDCl3
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

5c


7.90
7.90
7.53
7.53
7.52
7.51
7.32
7.31
6.27
5.30
5.16
2.07
1.84
Cl
Cl
O
O
^{1}H NMR, 600MHz, CDCl$_3$
f1 (ppm)


158.43
150.21
144.07
143.83
143.37
132.19
130.33
125.83
125.20
119.80
118.14
117.59
115.47
77.23
77.02
76.81
20.81
16.94
Cl
Cl
O
O
^{13}C NMR, 151MHz, CDCl$_3$
f1 (ppm)



IR

Elemental composition search on mass 295.03

m/z= 290.03-300.03

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
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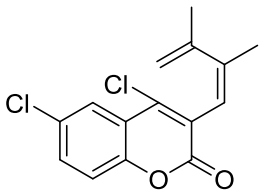
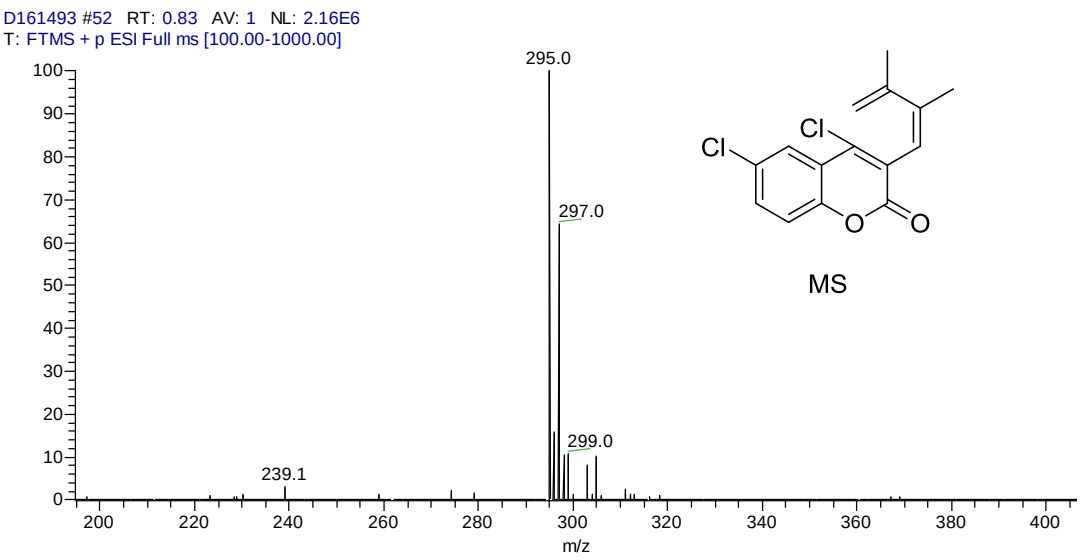
	295.0291	-1.71	22.5	$C_{22}H_3N_2$
	295.0274	4.07	9.0	$C_{13}H_{11}ON_3Cl_2$



HRMS


D161493 #52 RT: 0.83 AV: 1 NL: 2.16E6
T: FTMS + p ESI Full ms [100.00-1000.00]
295.0
297.0
299.0
239.1
m/z
Cl
Cl
O
O
MS

3. The crystal data

Crystal data for **1d** (Fig. 2): C15H11BrO2, M = 303.15, yellow needle, Bruker CCD diffractometer, Mo-Kα radiation (λ= 0.71073 Å), 0.32 × 0.26 × 0.14mm, T = 293(2) K. Triclinic, space group *P*-1, a = 7.8650(11) Å, b = 8.6070(11) Å, c = 10.2615(15) Å, α = 92.788(6)º, β = 112.186(6)º, γ = 105.046(4)º, V = 612.75(15) $Å^3$, Z = 2, Dc = 1.643 g cm^{-3}, μ = 3.344 mm^{-1}, F(000) = 304. The structure was solved by direct method (SHELXL 97) and refined on F2 by full-matrix least-squares method. A total of 2718 independent reflections [R (int) = 0.0366] were used in the refinement, which converged with R1 = 0.0564 and wR2 = 0.1076 (GOF = 1.020).

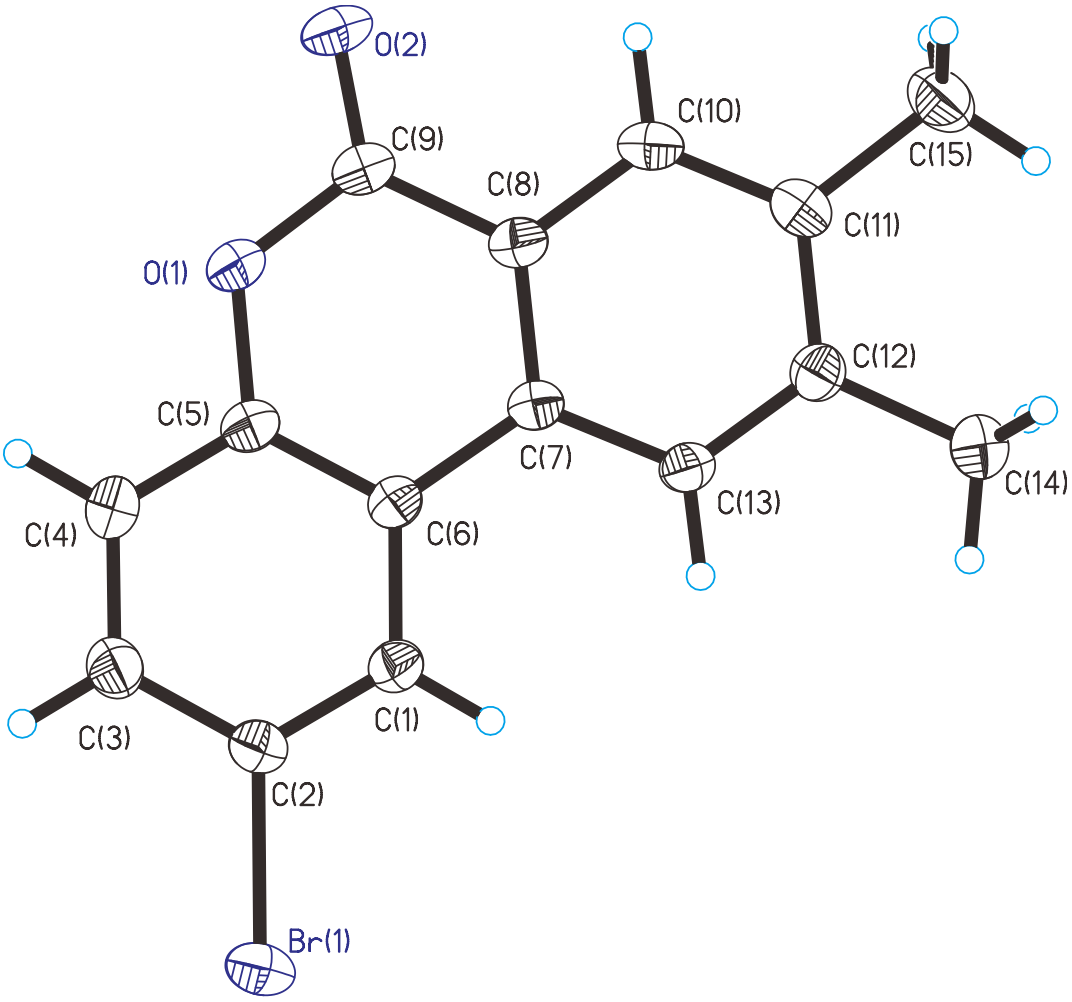


Fig. 1 ORTEP drawing of **1d**, ellipsoids are drawn at 30 % probability level.

Crystal data for **4i** (Fig. 1): C15H14Cl2O4, M = 329.16, colorless blocks, Bruker CCD diffractometer, Mo-Kα radiation (λ= 0.71073 Å), 0.32 × 0.28 × 0.26mm, T = 296(2) K. Monoclinic, space group *P*21/*c*, a = 13.0766(3) Å, b = 8.0857(2) Å, c = 14.0760(4) Å, α = 90.00º, β = 90.350(2)º, γ = 90.00º, V = 1488.28(7) $Å^3$, Z = 4, Dc = 1.478 g cm^{-3}, μ = 0.448 mm^{-1}, F(000) = 688. The structure was solved by direct method (SHELXL 97) and refined on F2 by full-matrix least-squares method. A total of 3393 independent reflections [R (int) = 0.0389] were used in the refinement, which converged with R1 = 0.0442 and wR2 = 0.1007 (GOF = 1.046).

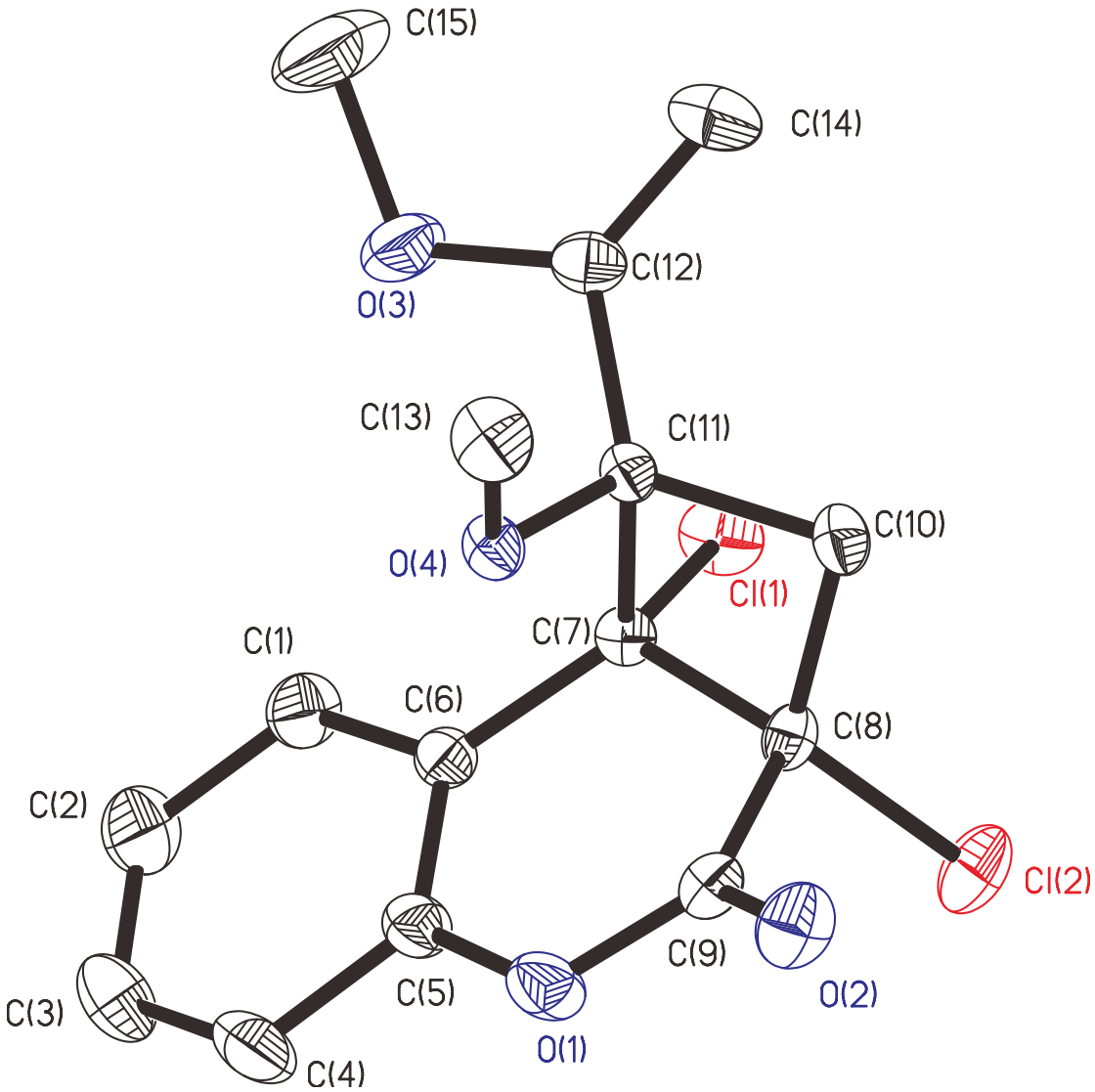


Fig. 2 ORTEP drawing of **4i**, ellipsoids are drawn at 30 % probability level.