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

Supporting Information

Visible-Light-Promoted Radical Acylation/Cyclization of Alkynoates with Aldehydes for the Synthesis of 3-Acylcoumarin

Qiumei Wang, Chao Yang, Chao Jiang*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

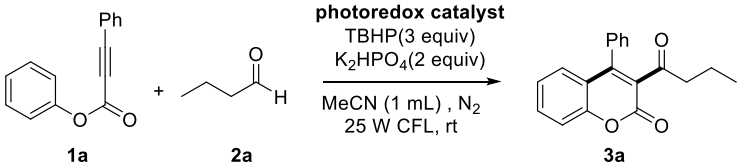
*E-mail: chaojiang@njust.edu.cn

Table of Contents

1. Detailed Optimization Studies of Reaction Conditions

A mixture of **1** (0.1 mmol), aldehyde and catalyst, TBHP, base in solvent was stirred in a sealed tube at room temperature (28-33 ºC) for 30 h. After completion of the reaction, the reaction mixture was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (30:1~10:1) as eluent to give the desired product. Full details of the optimization were listed below (Tables S1-S4).

Table S1. Effect of Different Photoredox catalysts[a]

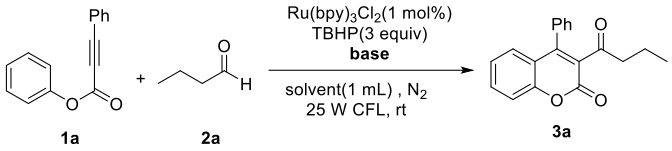


1a **2a** **3a**

entry	photoredox catalyst(1mol %)	yield(%)[b]
1	$Ru(bpy)_3Cl_2$	80
2	Eosin Y	0
3	$Ir(dtbpy)(ppy)_2PF_6$	0
4	fac-$Ir(ppy)_3$	47
5	no	0

[a]Reaction conditions: phenyl 3-phenylpropiolate (**1a**, 0.10 mmol), butyraldehyde (**2a**, 0.30 mmol), photoredox catalyst (1.0 mol %), TBHP (3.0 equiv), base (2.0 equiv), MeCN (1.0 mL) at room temperature under light irradiation in N_2 for 30 h. [b]Isolated yields.

Table S2. Effect of Different Bases[a]

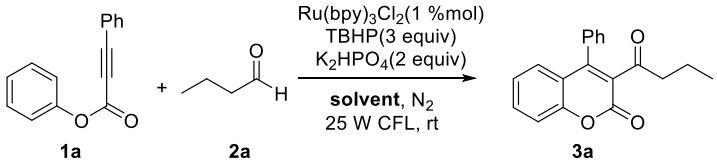


1a 2a 3a

entry	base (2 equiv)	yield(%)[b]
1	K_2HPO_4	80
2	KH_2PO_4	24
3	$NaHCO_3$	52
4	Cs_2CO_3	0
5	no	0

[a]Reaction conditions: phenyl 3-phenylpropiolate (**1a**, 0.10 mmol), butyraldehyde (**2a**, 0.30 mmol), $Ru(bpy)_3Cl_2$(1.0 mol %), TBHP (3.0 equiv), base (2.0 equiv), MeCN (1.0 mL) at room temperature under light irradiation in N_2 for 30 h. [b]Isolated yields.

Table S3. Effect of Different Solvents[a]

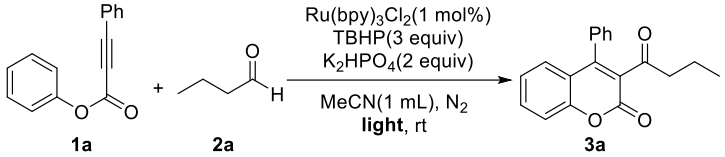


1a 2a 3a

entry	solvent(1 mL)	yield(%)[b]
1	THF	0
2	Toluene	35
3	DCE	0
4	DME	24
5	MeCN	80
6	MeCN(0.5 mL)	65
7	MeCN(2 mL)	57

[a]Reaction conditions: phenyl 3-phenylpropiolate (**1a**, 0.10 mmol), butyraldehyde (**2a**, 0.30 mmol), $Ru(bpy)_3Cl_2$(1.0 mol %), TBHP (3.0 equiv), K_2HPO_4 (2.0 equiv), solvent (1.0 mL) at room temperature under light irradiation in N_2 for 30 h. [b]Isolated yields.

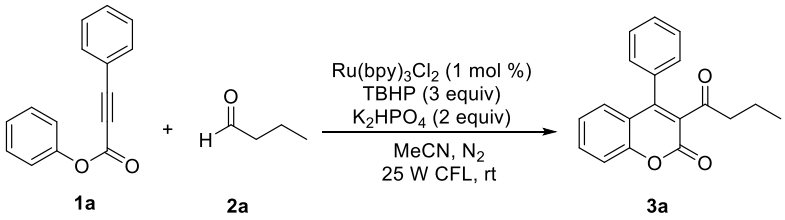
Table S4. Effect of Different Light Sources[a]



entry	light	yield(%)[b]
1	25 W CFL	80
2	13 W blue LED	75
3	36 W blue LED	65

[a]Reaction conditions: phenyl 3-phenylpropiolate (**1a**, 0.10 mmol), butyraldehyde (**2a**, 0.30 mmol), $Ru(bpy)_3Cl_2$(1.0 mol %), TBHP (3.0 equiv), K_2HPO_4 (2.0 equiv), solvent (1.0 mL) at room temperature under light irradiation in N_2 for 30 h. [b]Isolated yields.

2. Light/Dark Experiment



Set seven parallel reactions. A mixture of **1a** (0.1 mmol), **2a** (0.3 mmol) and $Ru(bpy)_3Cl_2$ (1 mol %), TBHP (0.3 mmol), K_2HPO_4 (0.2 mmol) in MeCN (1 mL) was stirred under 25 W CFL in atmosphere of N_2 in a sealed tube at room temperature for a certain time. After completion of the reaction, the reaction mixture was purified by a flash chromatography on silica gel with ethyl acetate as eluent to remove the solid impurities. The mixture was added 10 mg 1,3,5-trimethoxybenzene as the internal standard. After concentrating the mixture under vacuum, get its mixture ^1H NMR and its corresponding yield.

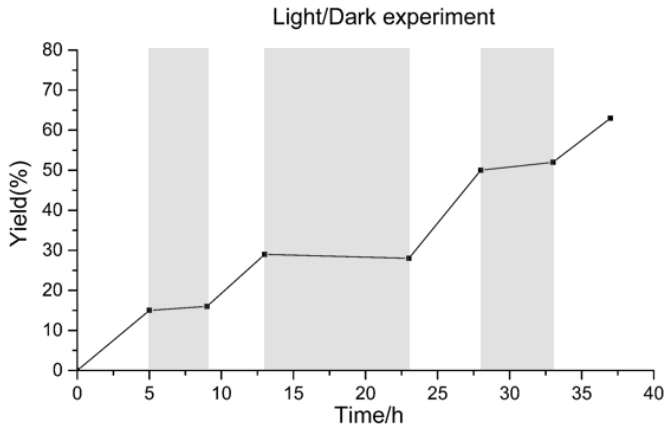
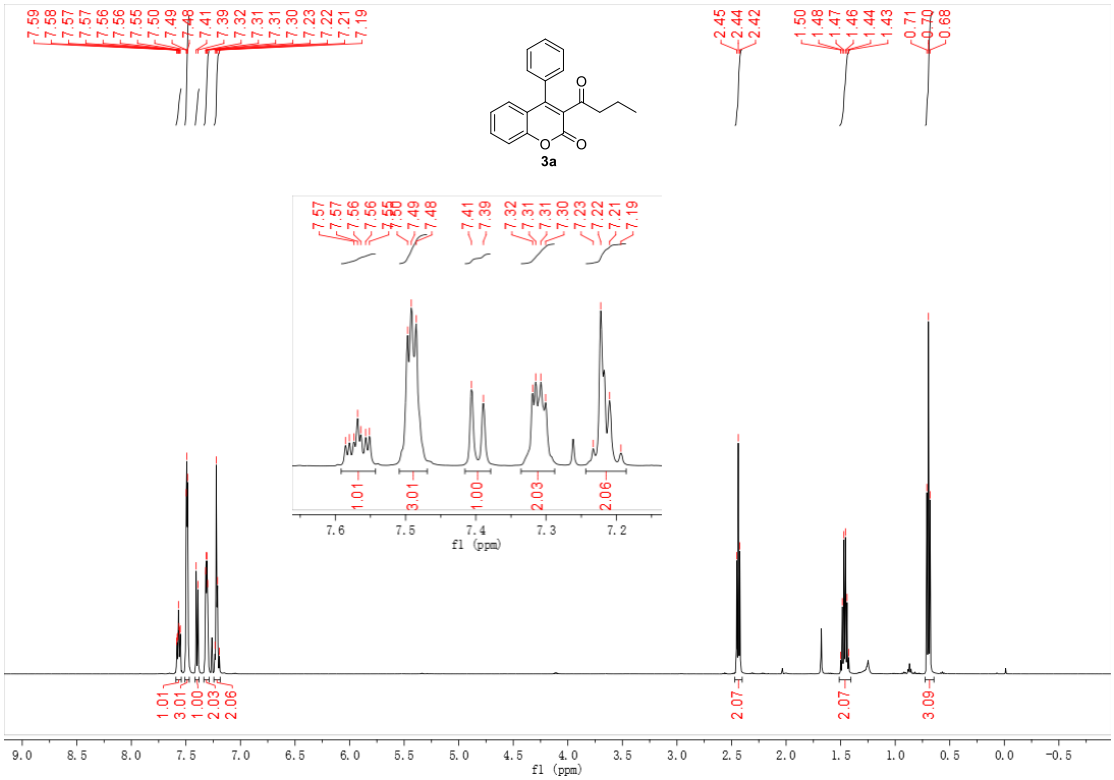
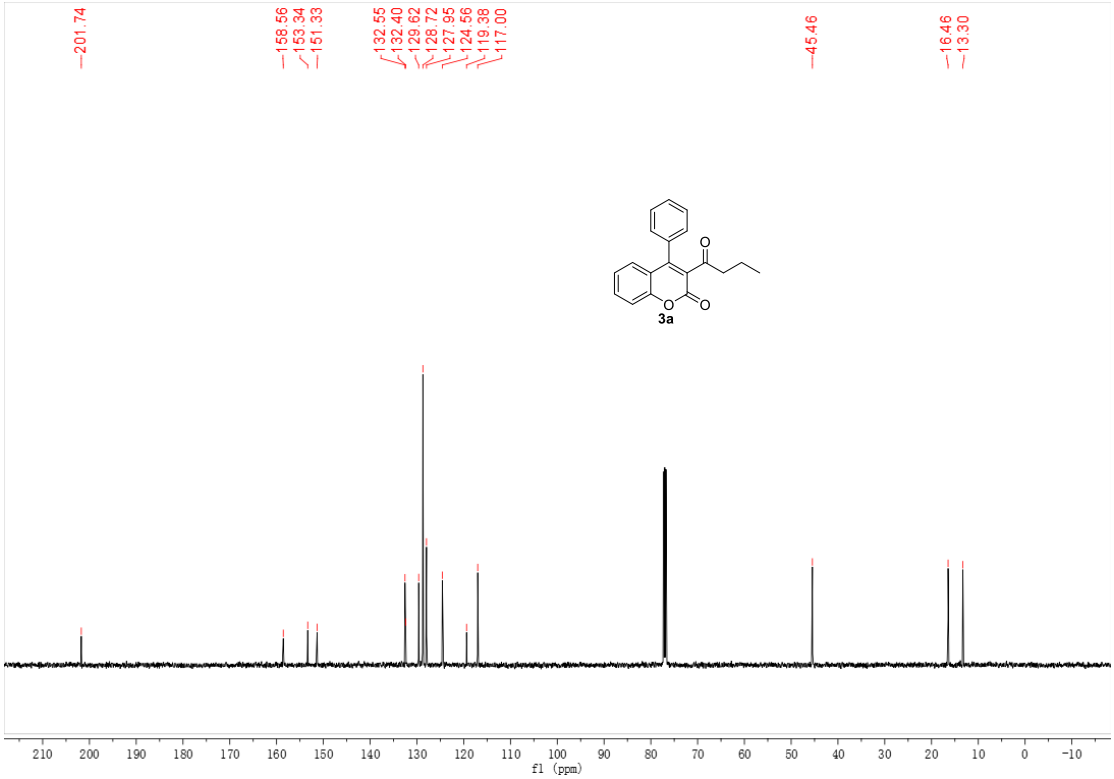
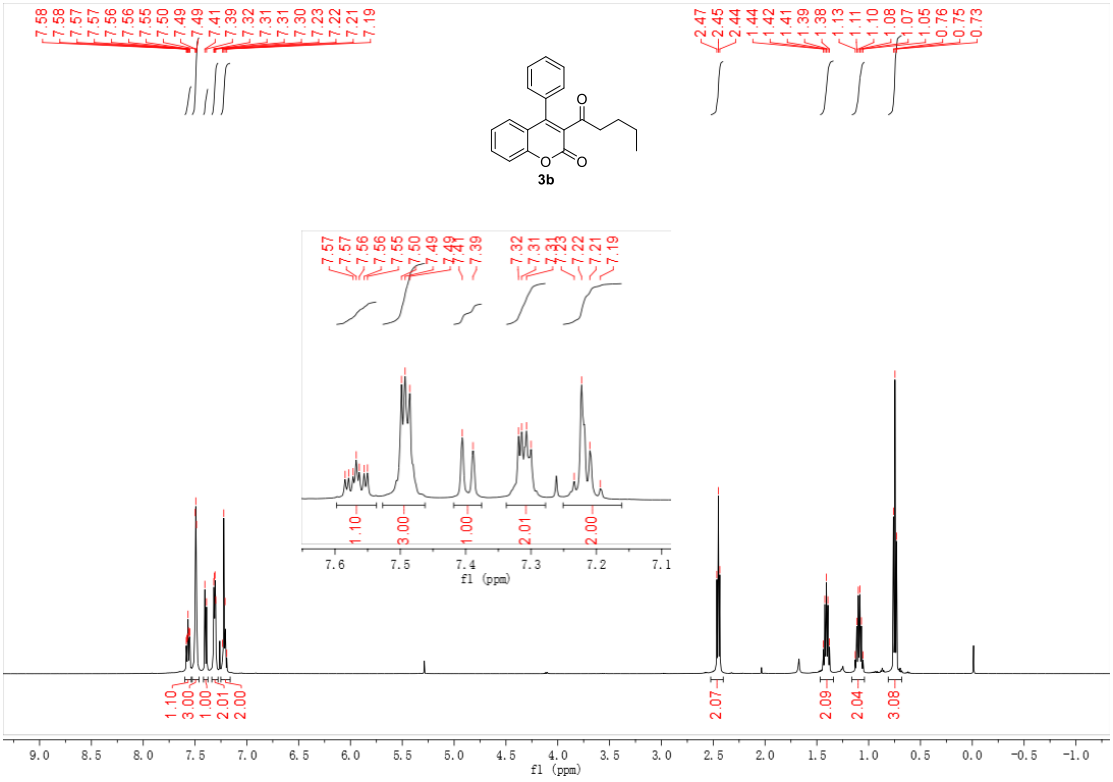


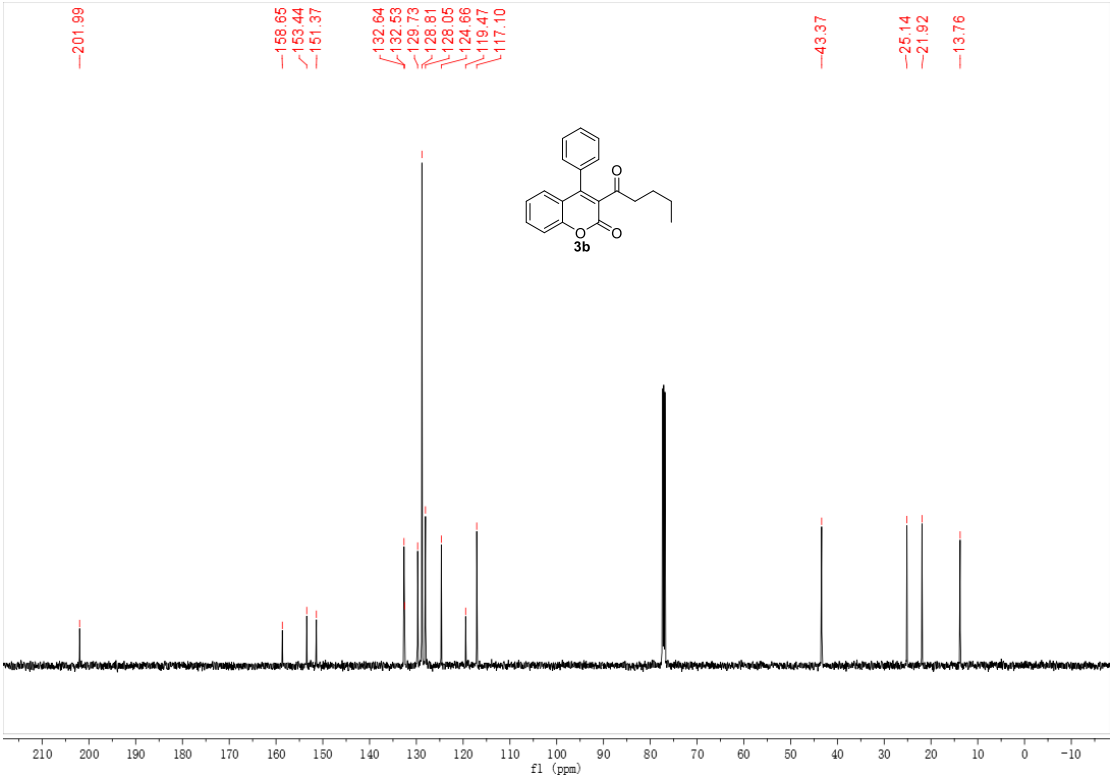
Figure S1. Light/Dark Experiment

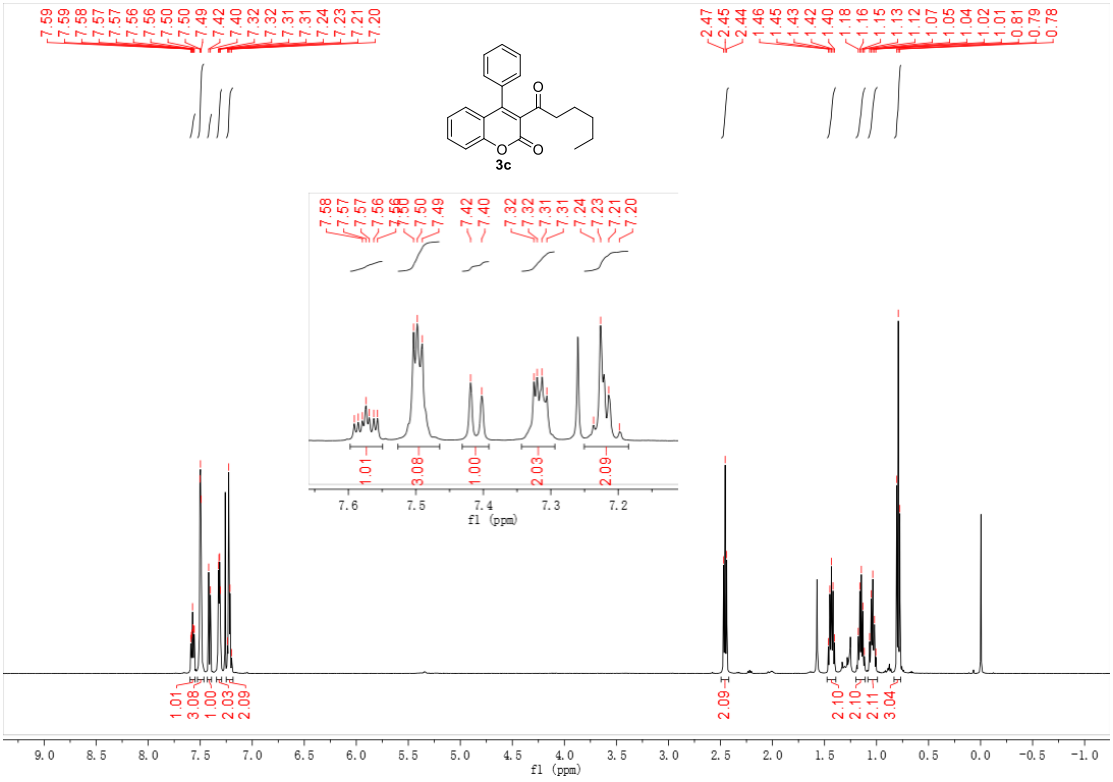
3. NMR spectra of compounds 3 and 4

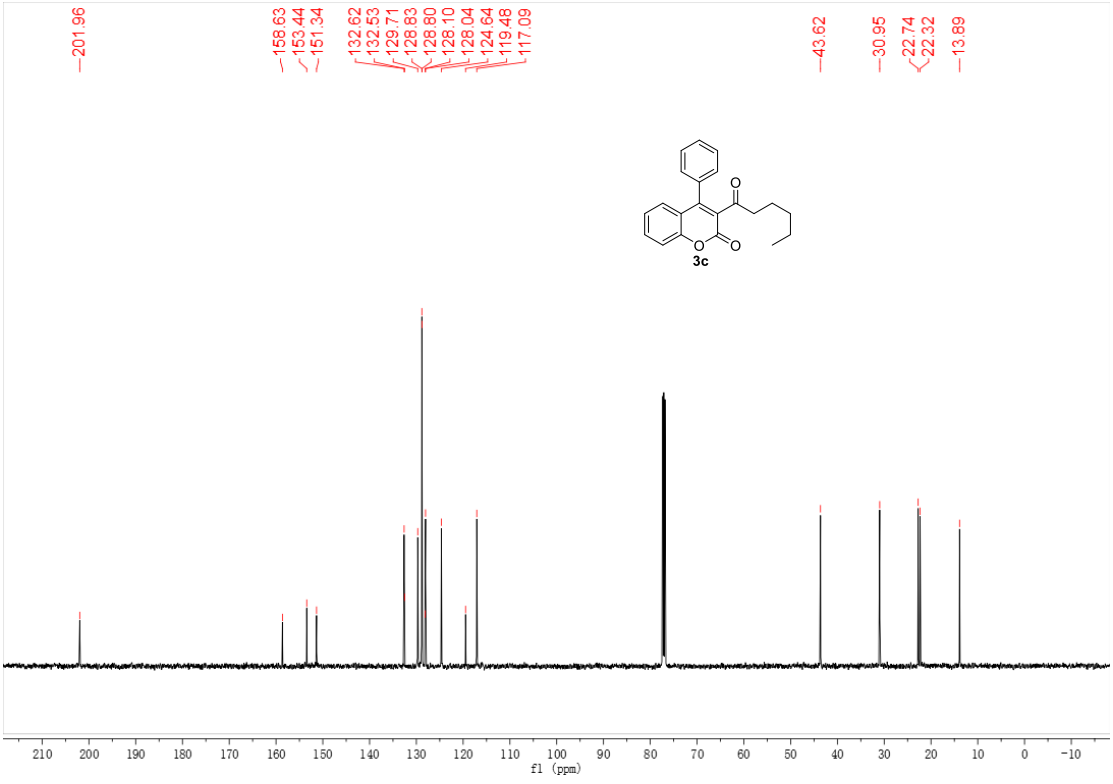


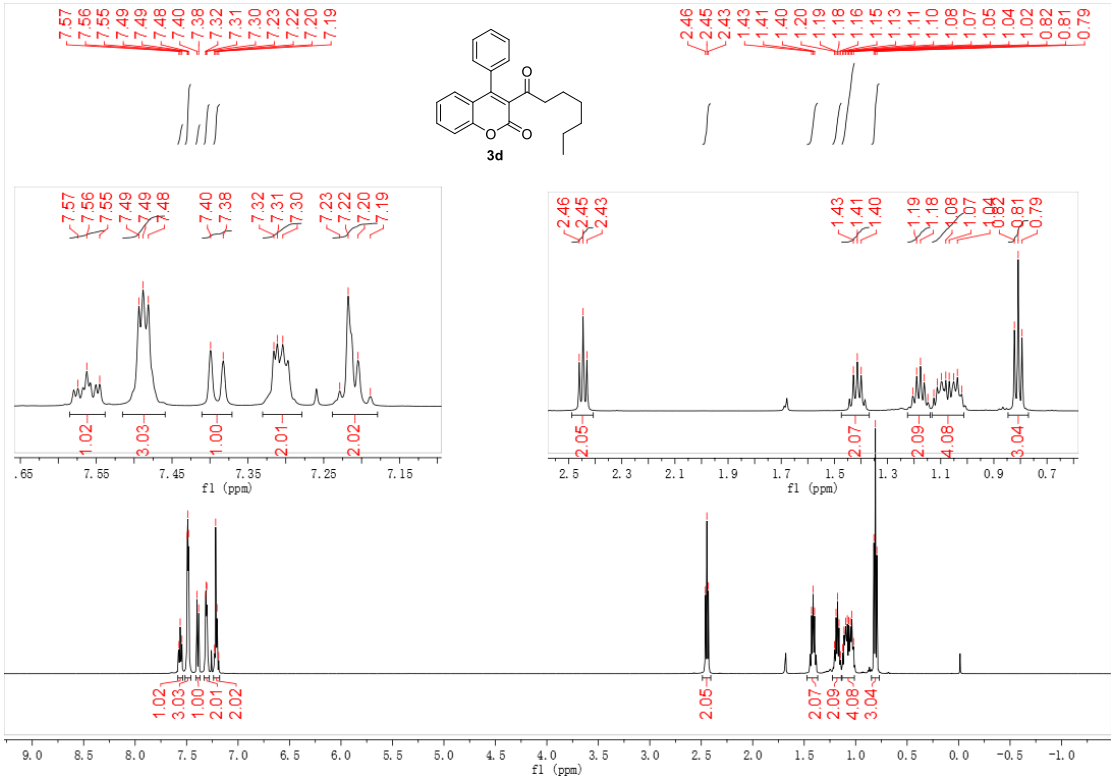


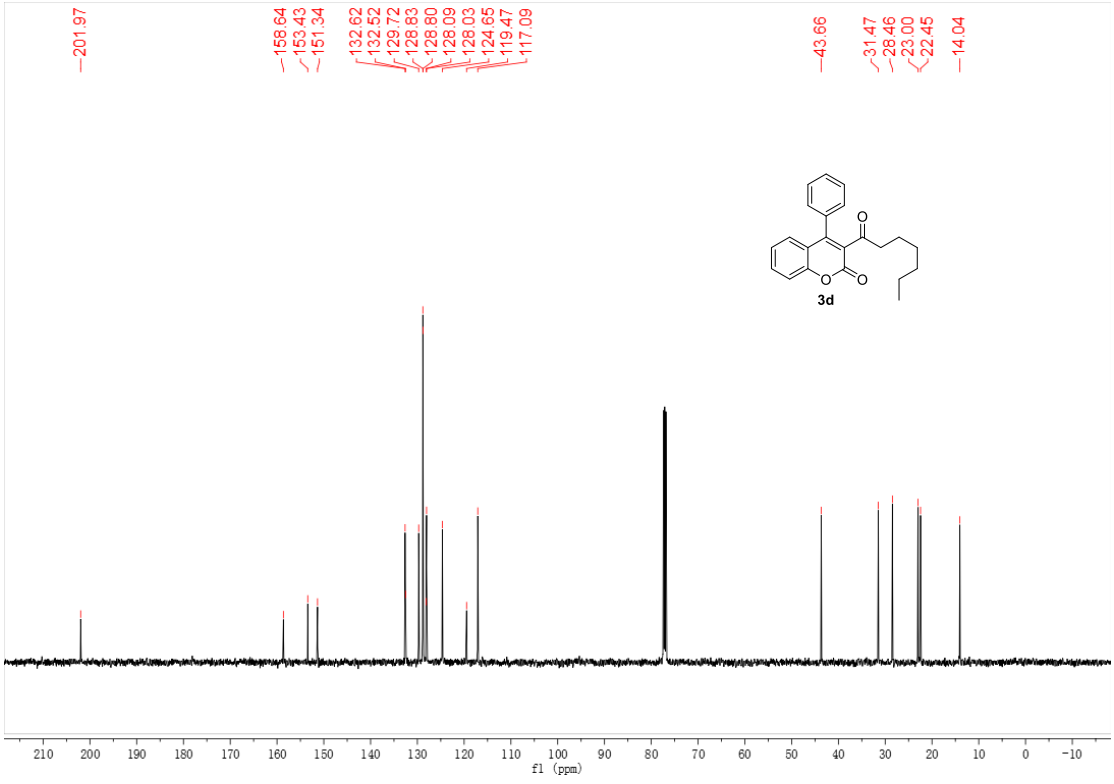

3b
f1 (ppm)

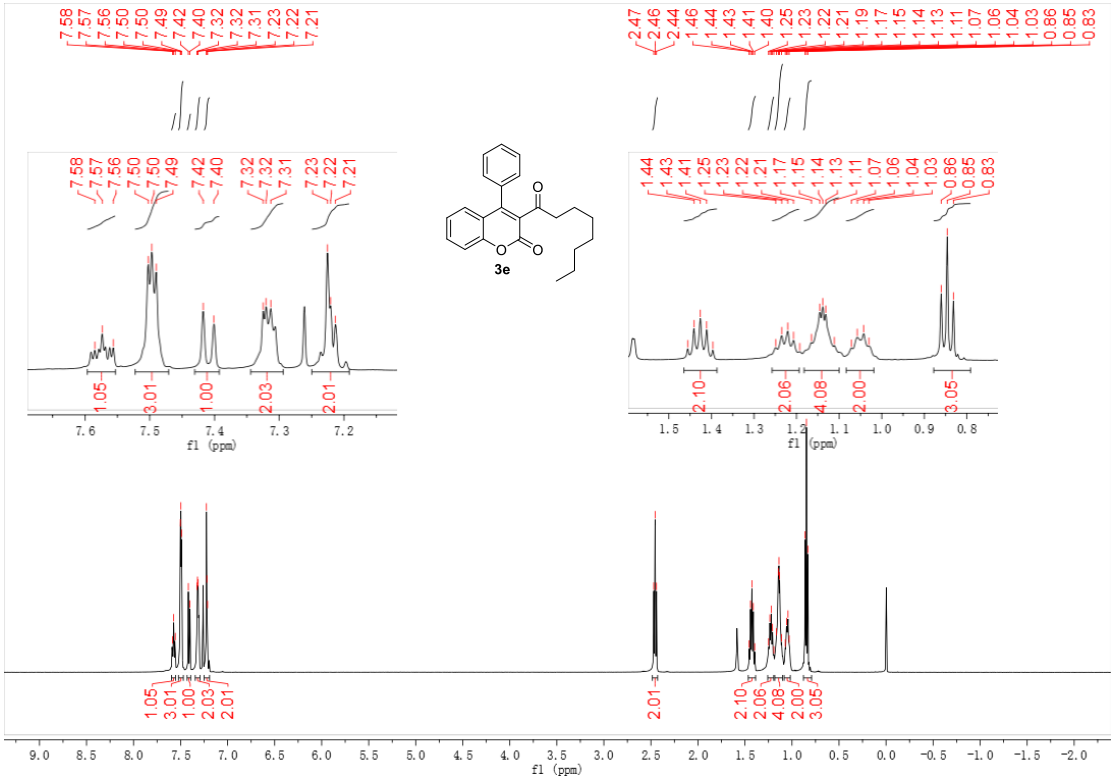

3b
f1 (ppm)

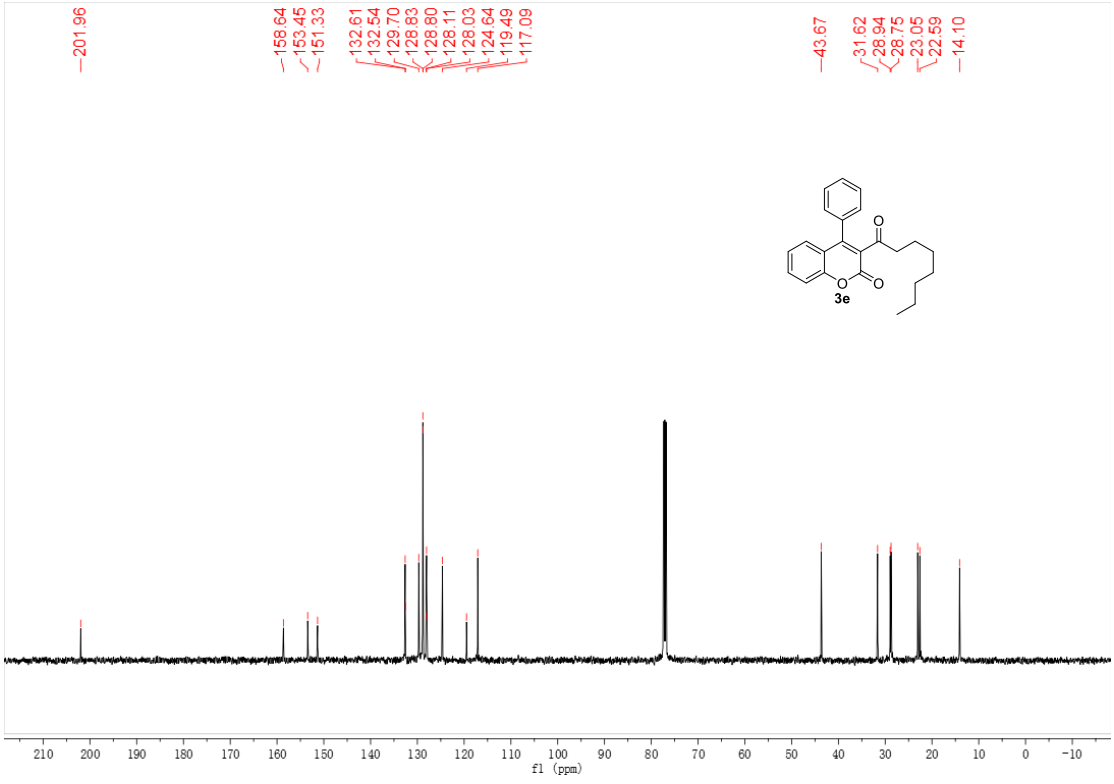

7.59
7.59
7.58
7.57
7.57
7.56
7.56
7.50
7.49
7.42
7.40
7.32
7.32
7.31
7.31
7.24
7.23
7.21
7.20
2.47
2.45
2.44
1.46
1.45
1.43
1.42
1.40
1.18
1.16
1.15
1.13
1.12
1.07
1.05
1.04
1.02
1.01
0.81
0.79
0.78
3c
1.01
3.08
1.00
2.03
2.09
f1 (ppm)
2.09
2.10
2.10
2.11
3.04
f1 (ppm)

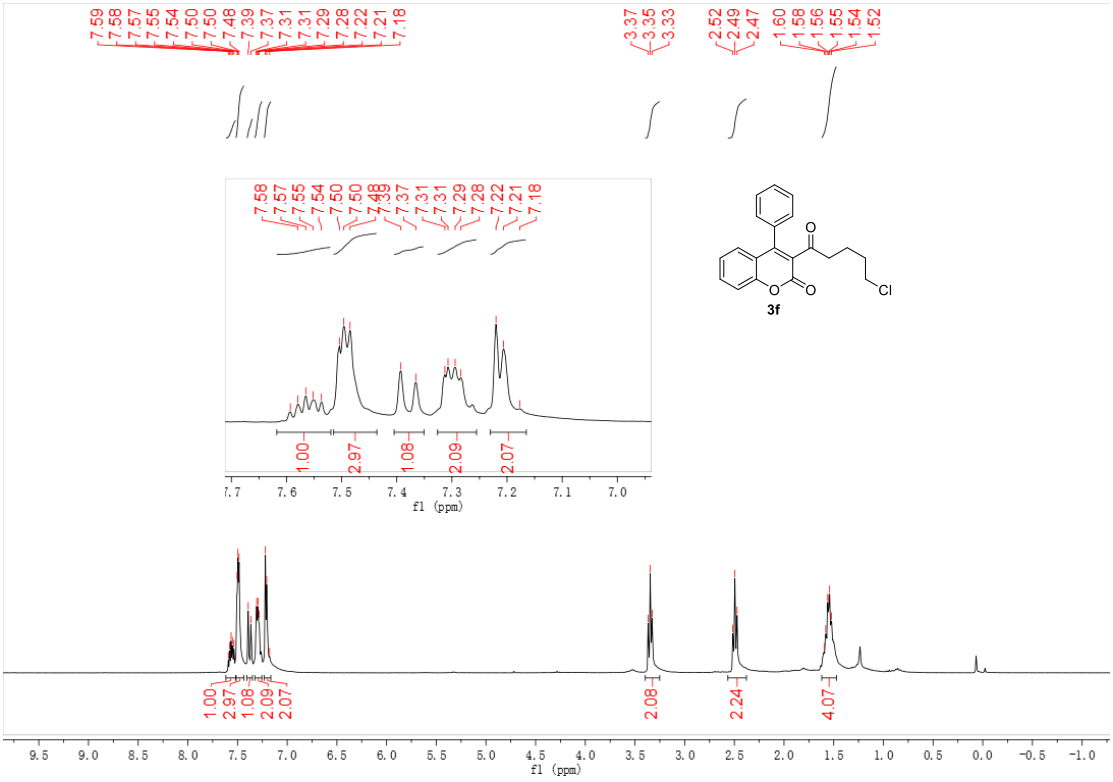

201.96
158.63
153.44
151.34
132.62
132.53
129.71
128.83
128.80
128.10
128.04
124.64
119.48
117.09
43.62
30.95
22.74
22.32
13.89
3c
f1 (ppm)

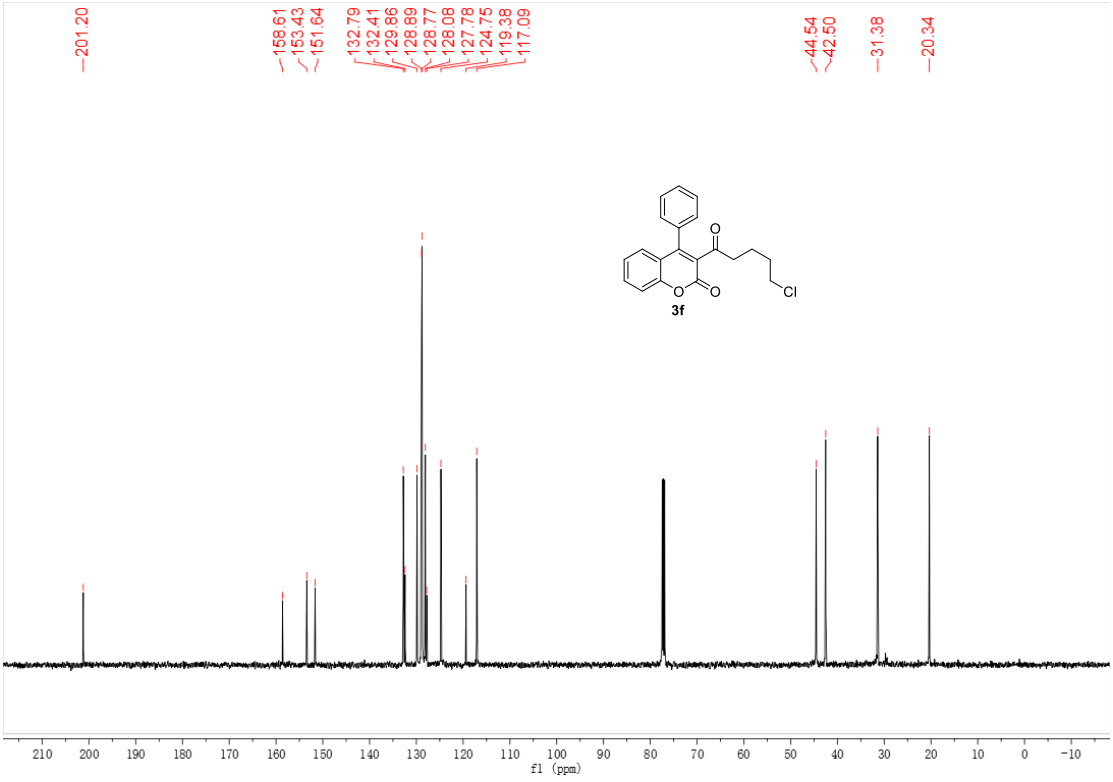

7.57
7.56
7.55
7.49
7.49
7.48
7.40
7.38
7.32
7.31
7.30
7.23
7.22
7.20
7.19
2.46
2.45
2.43
1.43
1.41
1.40
1.20
1.19
1.18
1.16
1.15
1.13
1.11
1.10
1.08
1.07
1.05
1.04
1.02
0.82
0.81
0.79
3d
1.02
3.03
1.00
2.01
2.02
2.05
2.07
2.09
4.08
3.04
f1 (ppm)

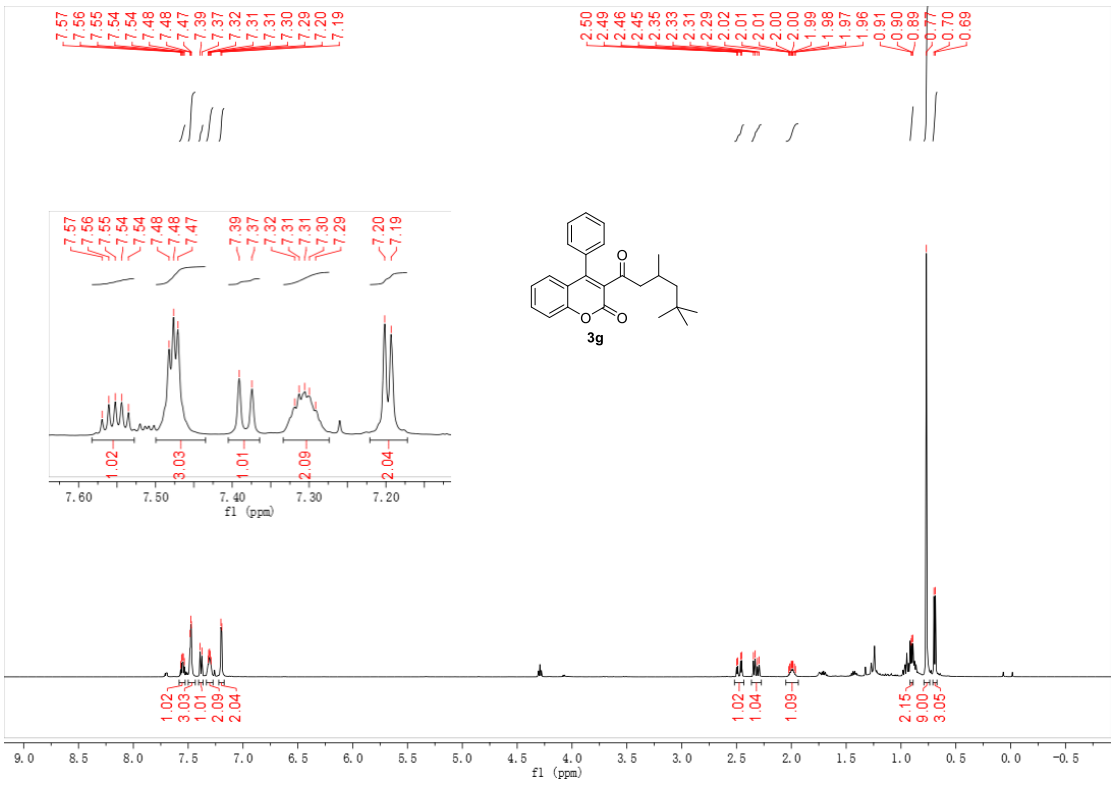

201.97
158.64
153.43
151.34
132.62
132.52
129.72
128.83
128.80
128.09
128.03
124.65
119.47
117.09
43.66
31.47
28.46
23.00
22.45
14.04
3d
f1 (ppm)

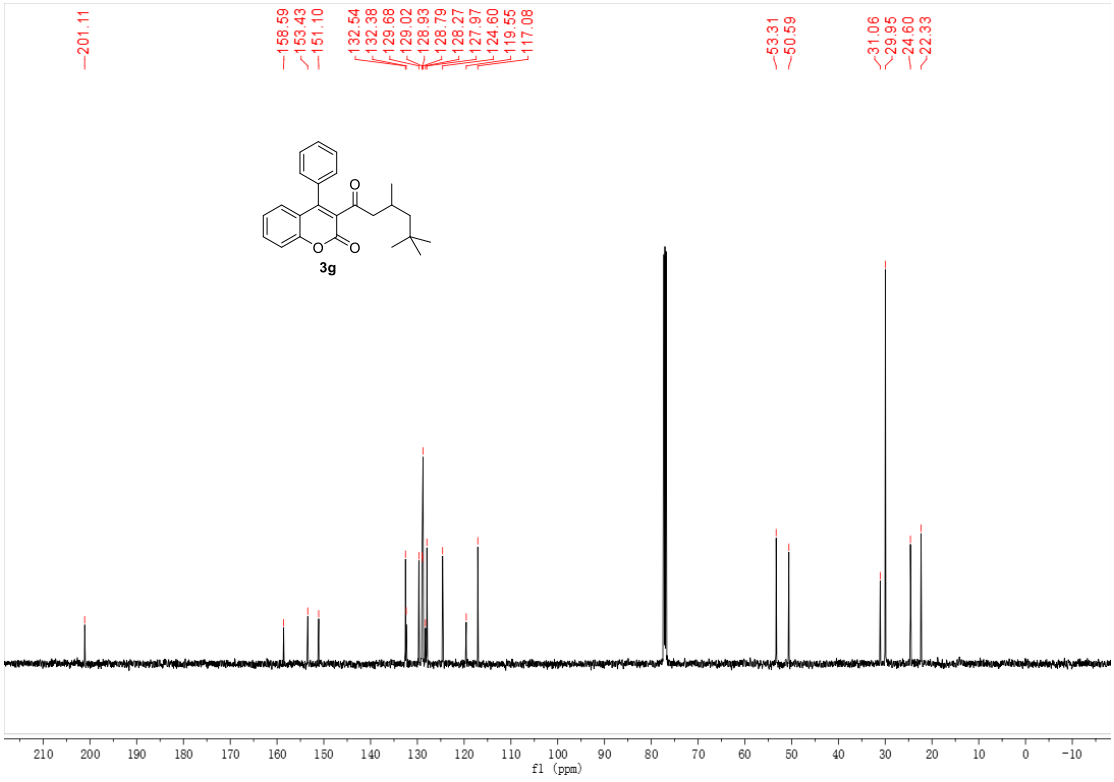

7.58 7.57 7.56 7.50 7.50 7.49 7.42 7.40 7.32 7.32 7.31 7.23 7.22 7.21
2.47 2.46 2.44 1.46 1.44 1.43 1.41 1.40 1.25 1.23 1.22 1.21 1.19 1.17 1.15 1.14 1.13 1.11 1.07 1.06 1.04 1.03 0.86 0.85 0.83
3e
1.05 3.01 1.00 2.03 2.01
2.10 2.06 4.08 2.00 3.05
f1 (ppm)

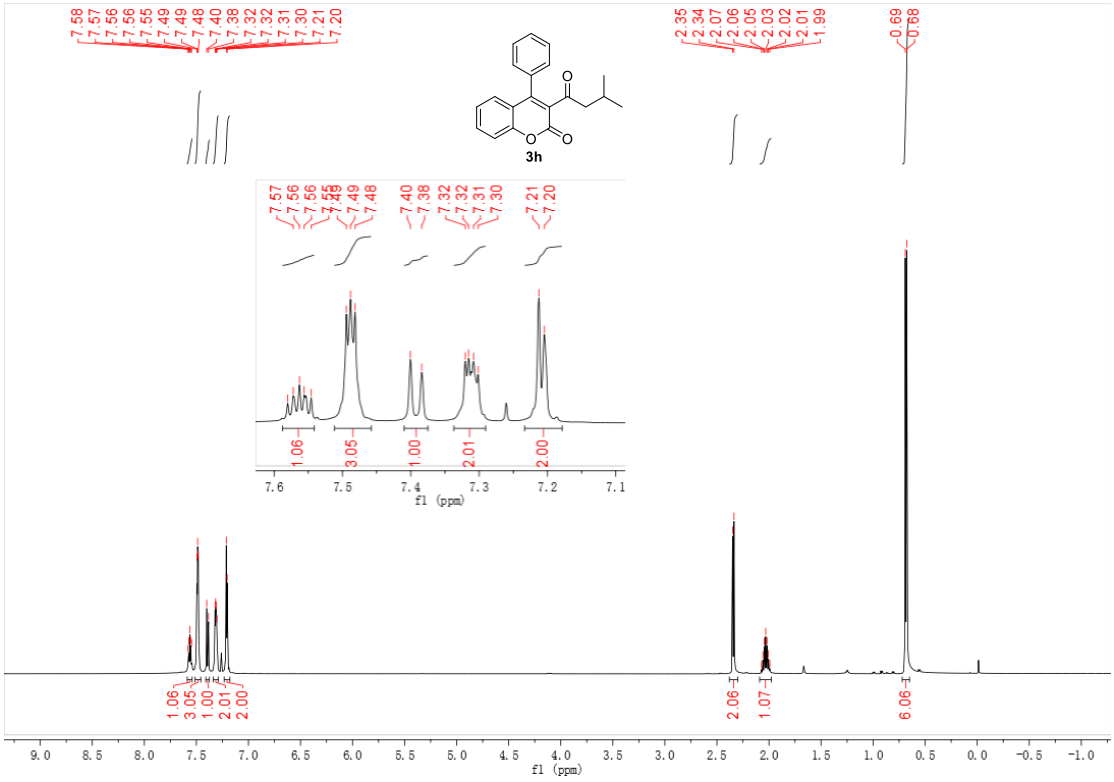

201.96
158.64 153.45 151.33 132.61 132.54 129.70 128.83 128.80 128.11 128.03 124.64 119.49 117.09
43.67 31.62 28.94 28.75 23.05 22.59 14.10
3e
f1 (ppm)

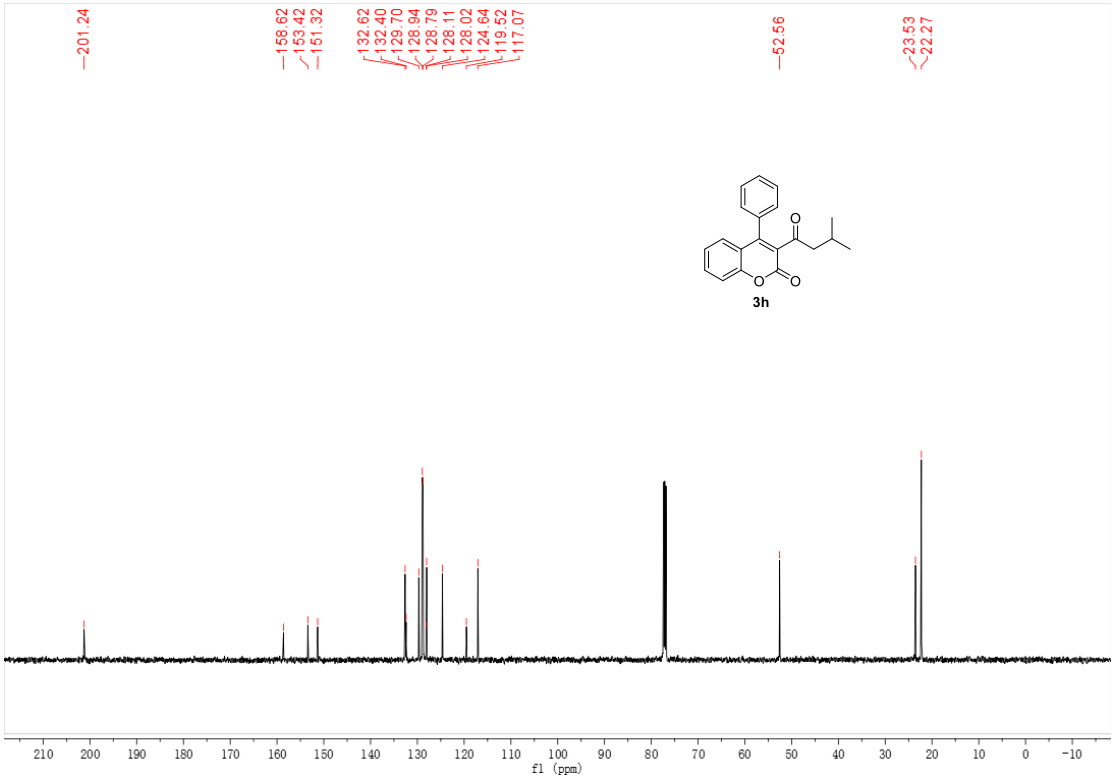

7.59 7.58 7.57 7.55 7.54 7.50 7.50 7.48 7.39 7.37 7.31 7.31 7.29 7.28 7.22 7.21 7.18
3.37 3.35 3.33
2.52 2.49 2.47
1.60 1.58 1.56 1.55 1.54 1.52
1.00 2.97 1.08 2.09 2.07
f1 (ppm)
2.08 2.24 4.07
3f

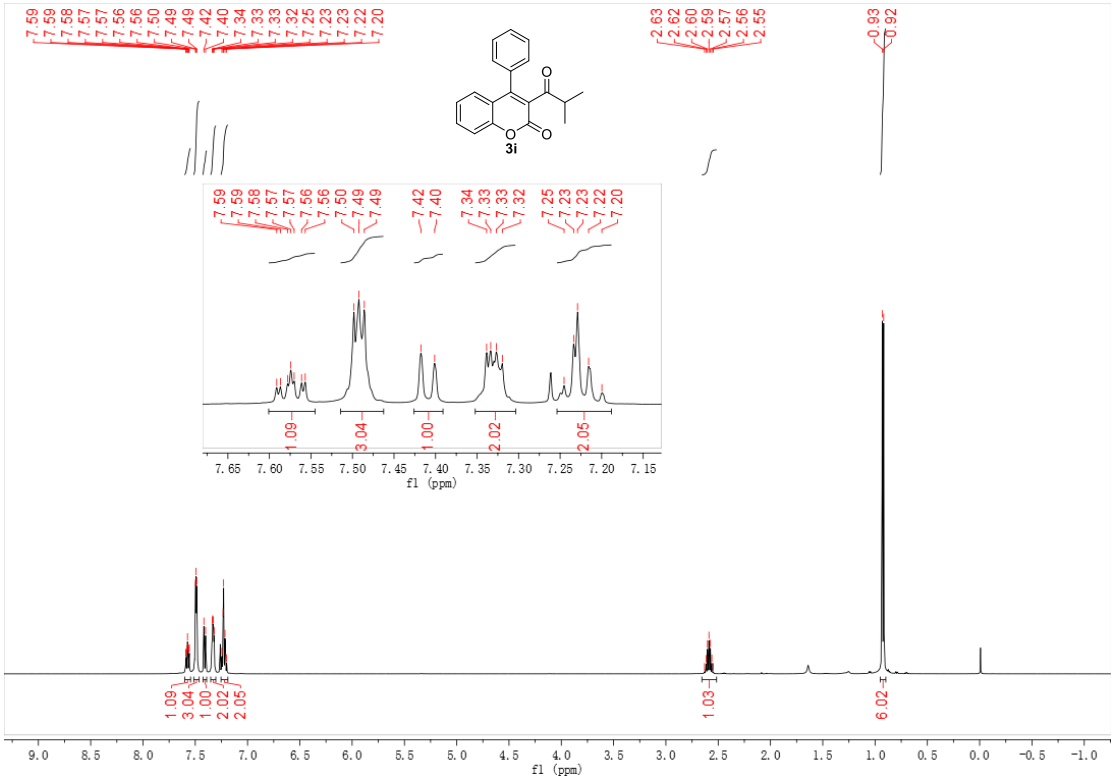

201.20
158.61 153.43 151.64
132.79 132.41 129.86 128.89 128.77 128.08 127.78 124.75 119.38 117.09
44.54 42.50
31.38
20.34
f1 (ppm)
3f

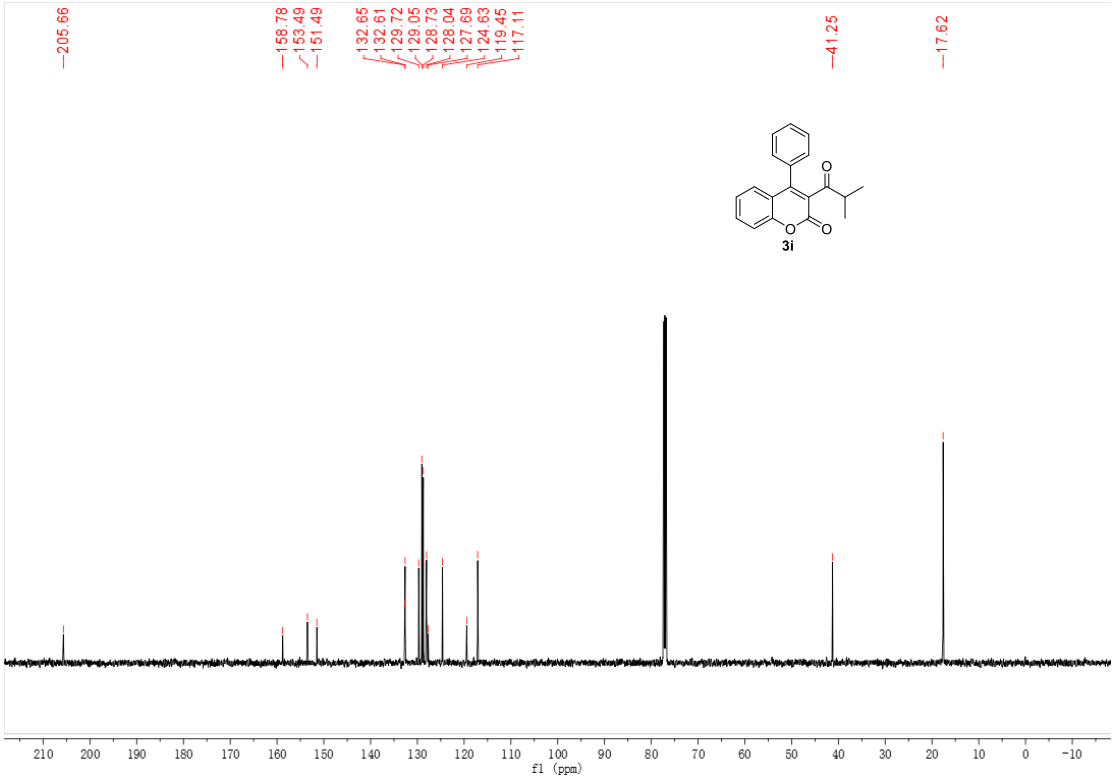

7.57
7.56
7.55
7.54
7.54
7.48
7.48
7.47
7.39
7.37
7.32
7.31
7.31
7.30
7.29
7.20
7.19
2.50
2.49
2.46
2.45
2.35
2.33
2.31
2.29
2.02
2.01
2.01
2.00
2.00
1.99
1.98
1.97
1.96
0.91
0.90
0.89
0.77
0.70
0.69
3g
1.02
3.03
1.01
2.09
2.04
f1 (ppm)
1.02
1.04
1.09
2.15
9.00
3.05

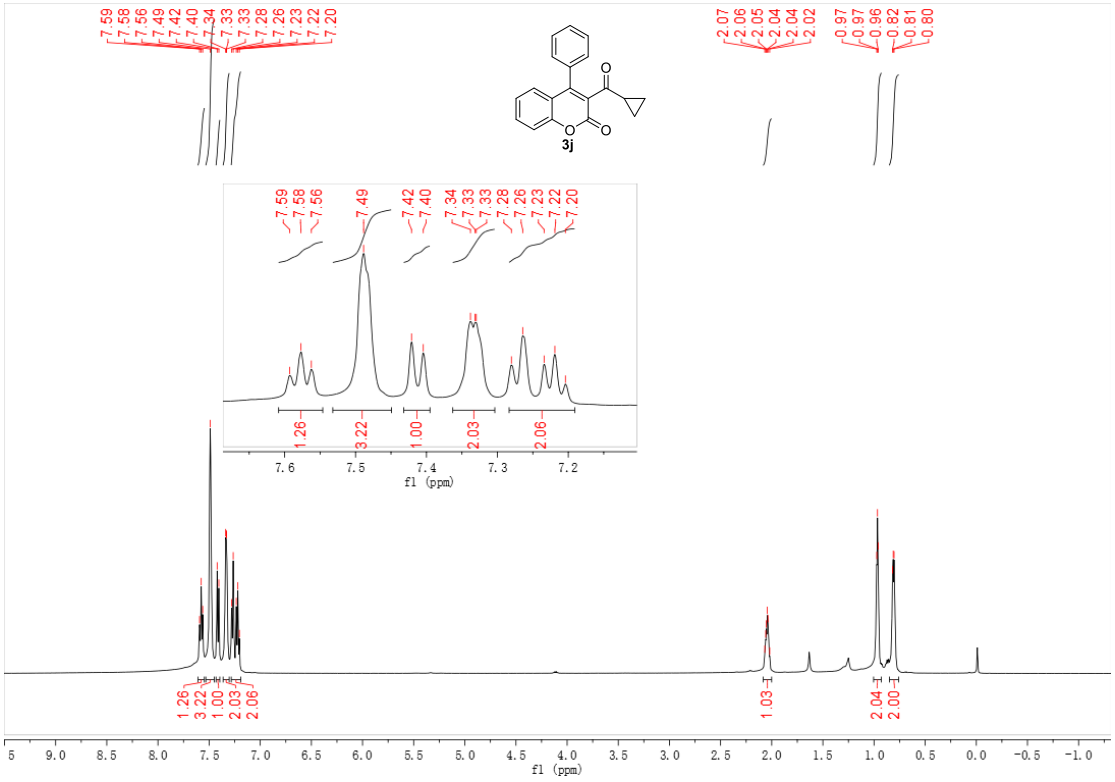

201.11
158.59
153.43
151.10
132.54
132.38
129.68
129.02
128.93
128.79
128.27
127.97
124.60
119.55
117.08
53.31
50.59
31.06
29.95
24.60
22.33
3g
f1 (ppm)

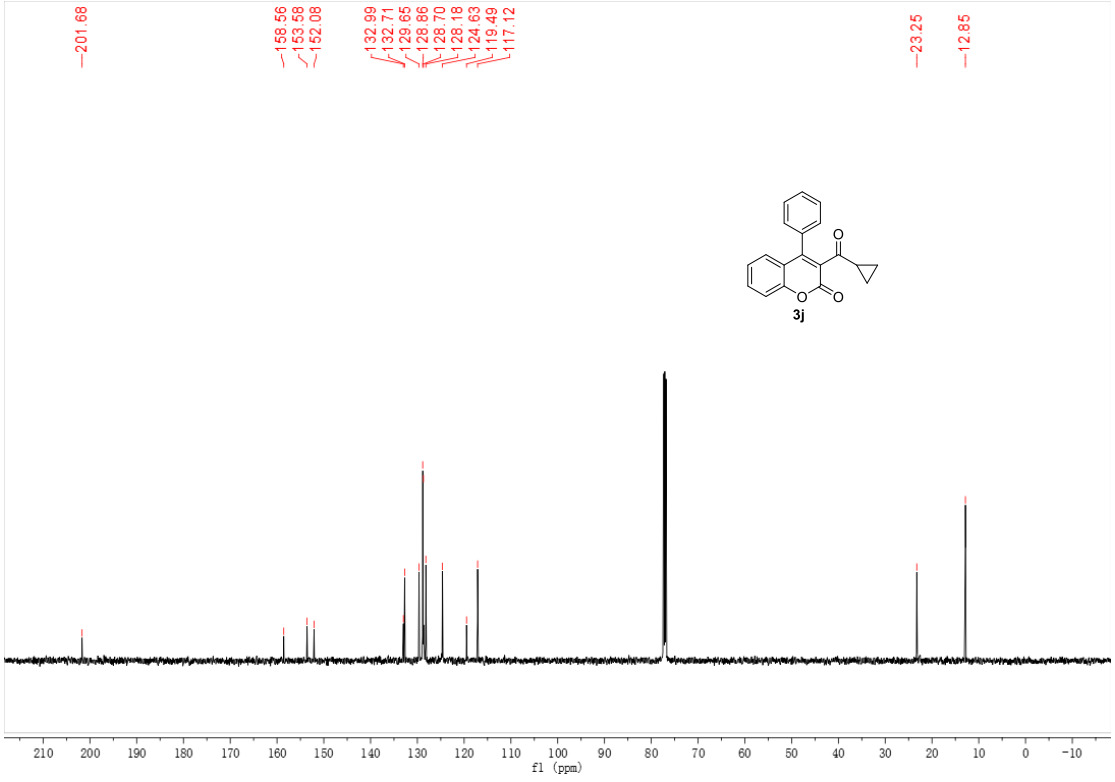

7.58
7.57
7.56
7.56
7.55
7.49
7.49
7.48
7.40
7.38
7.32
7.32
7.31
7.30
7.21
7.20
2.35
2.34
2.07
2.06
2.05
2.03
2.02
2.01
1.99
0.69
0.68
3h
1.06
3.05
1.00
2.01
2.00
2.06
1.07
6.06
f1 (ppm)

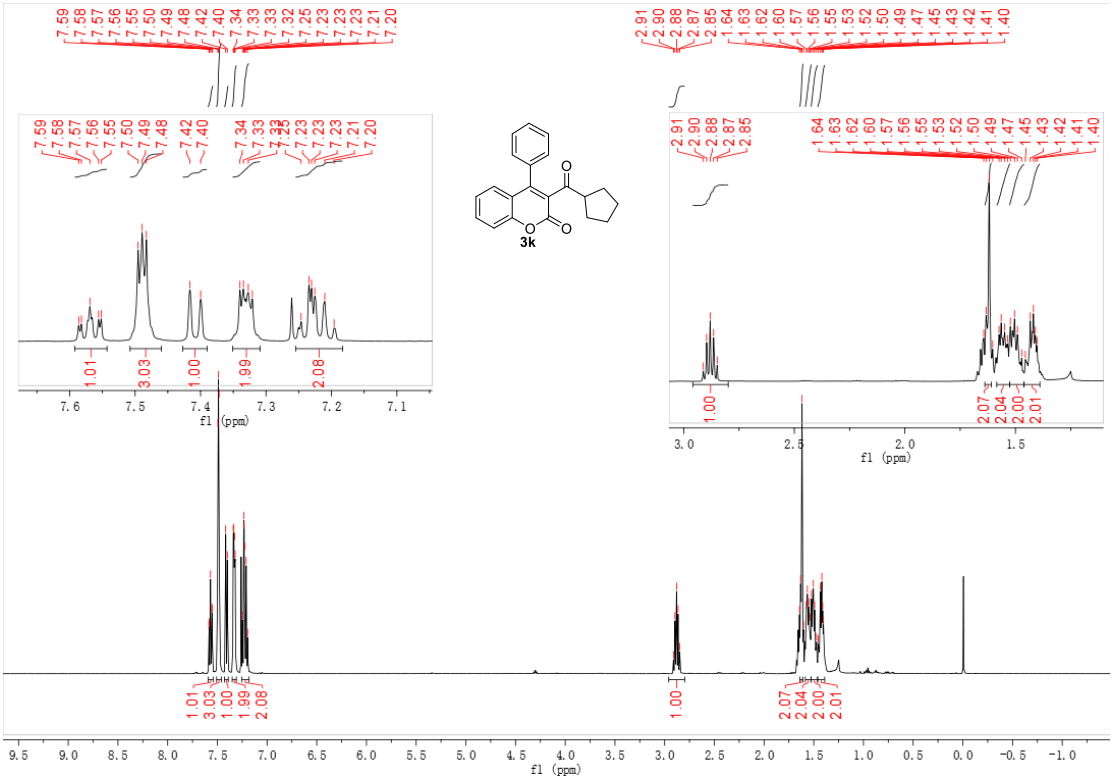

201.24
158.62
153.42
151.32
132.62
132.40
129.70
128.94
128.79
128.11
128.02
124.64
119.52
117.07
52.56
23.53
22.27
3h
f1 (ppm)

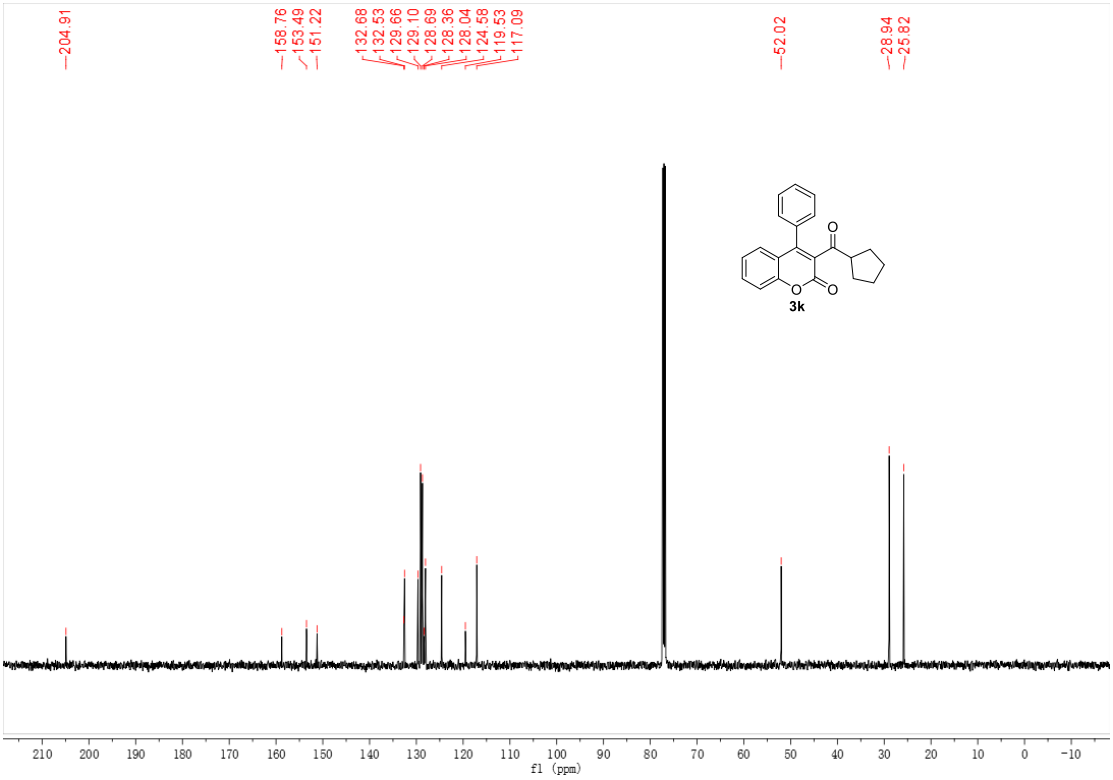

7.59
7.59
7.58
7.57
7.57
7.56
7.56
7.50
7.49
7.49
7.42
7.40
7.34
7.33
7.33
7.32
7.25
7.23
7.23
7.22
7.20
2.63
2.62
2.60
2.59
2.57
2.56
2.55
0.93
0.92
3i
1.09
3.04
1.00
2.02
2.05
1.03
6.02
f1 (ppm)

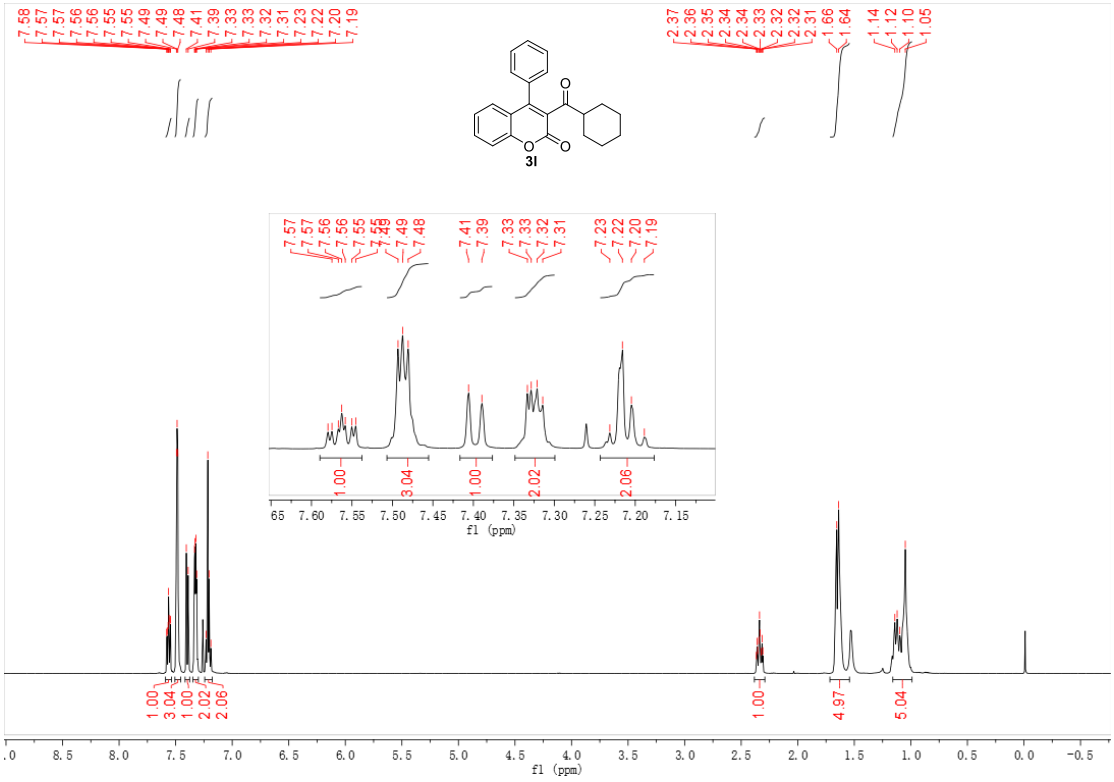

205.66
158.78
153.49
151.49
132.65
132.61
129.72
129.05
128.73
128.04
127.69
124.63
119.45
117.11
41.25
17.62
3i
f1 (ppm)

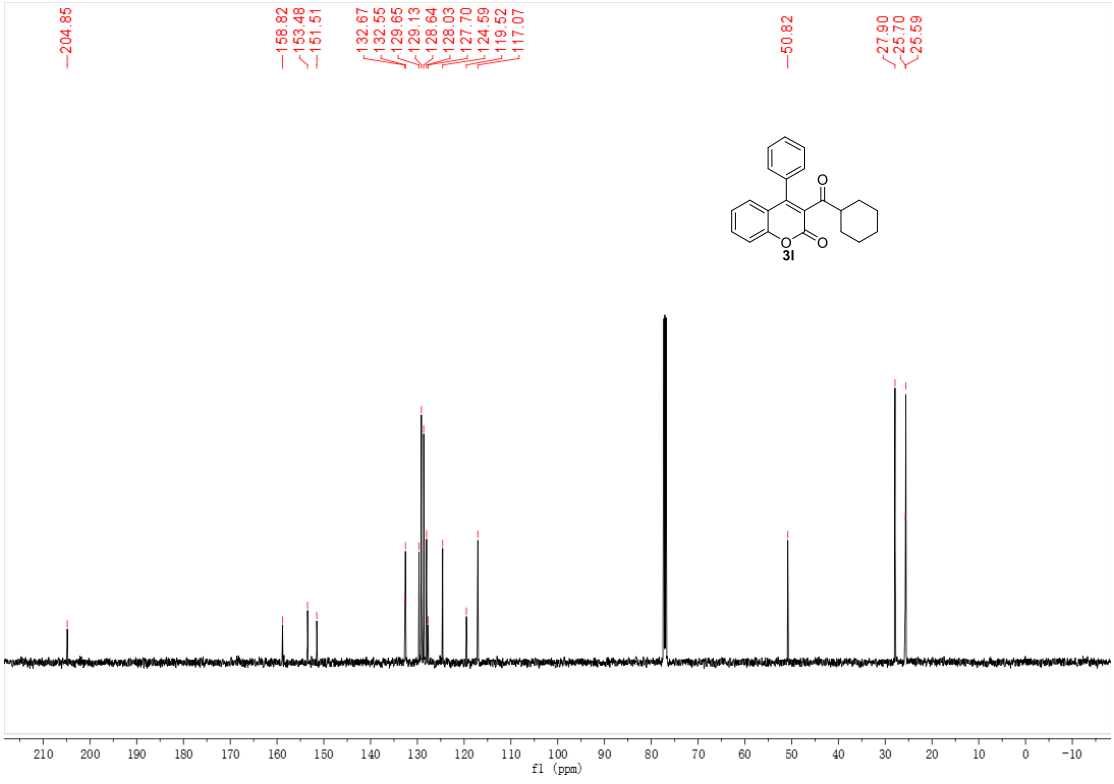

7.59
7.58
7.56
7.49
7.42
7.40
7.34
7.33
7.33
7.28
7.26
7.23
7.22
7.20
2.07
2.06
2.05
2.04
2.04
2.02
0.97
0.97
0.96
0.82
0.81
0.80
3j
1.26
3.22
1.00
2.03
2.06
f1 (ppm)
1.03
2.04
2.00

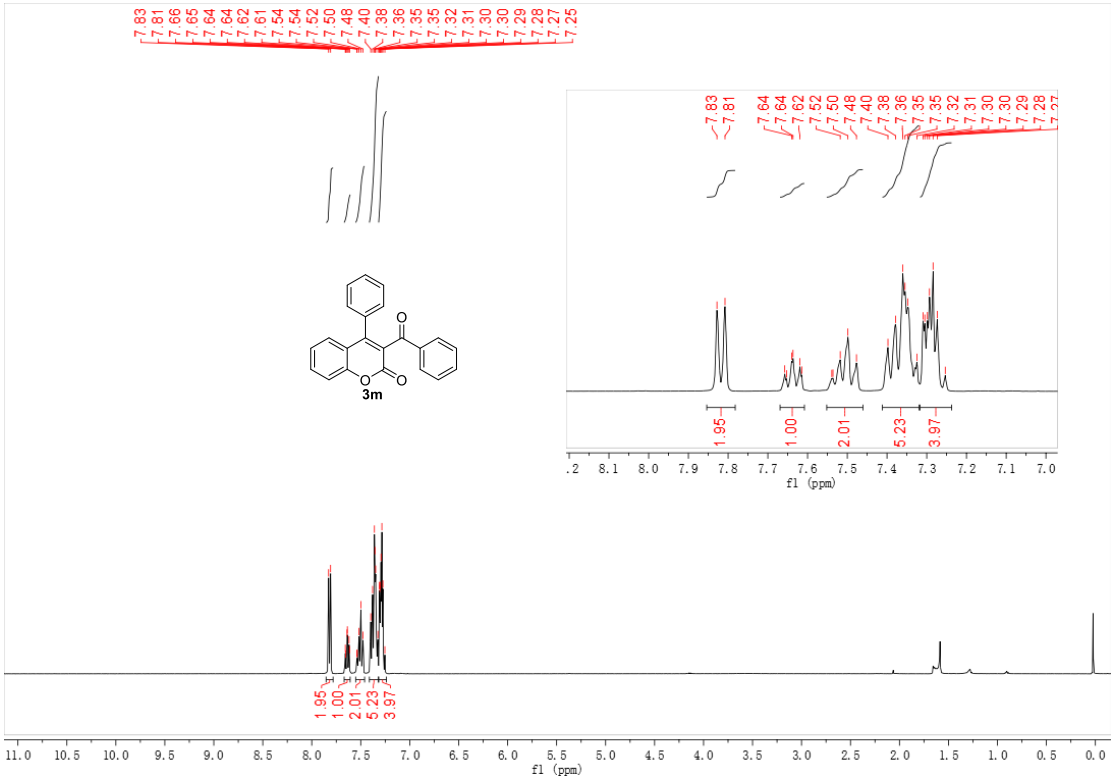

201.68
158.56
153.58
152.08
132.99
132.71
129.65
128.86
128.70
128.18
124.63
119.49
117.12
23.25
12.85
3j
f1 (ppm)

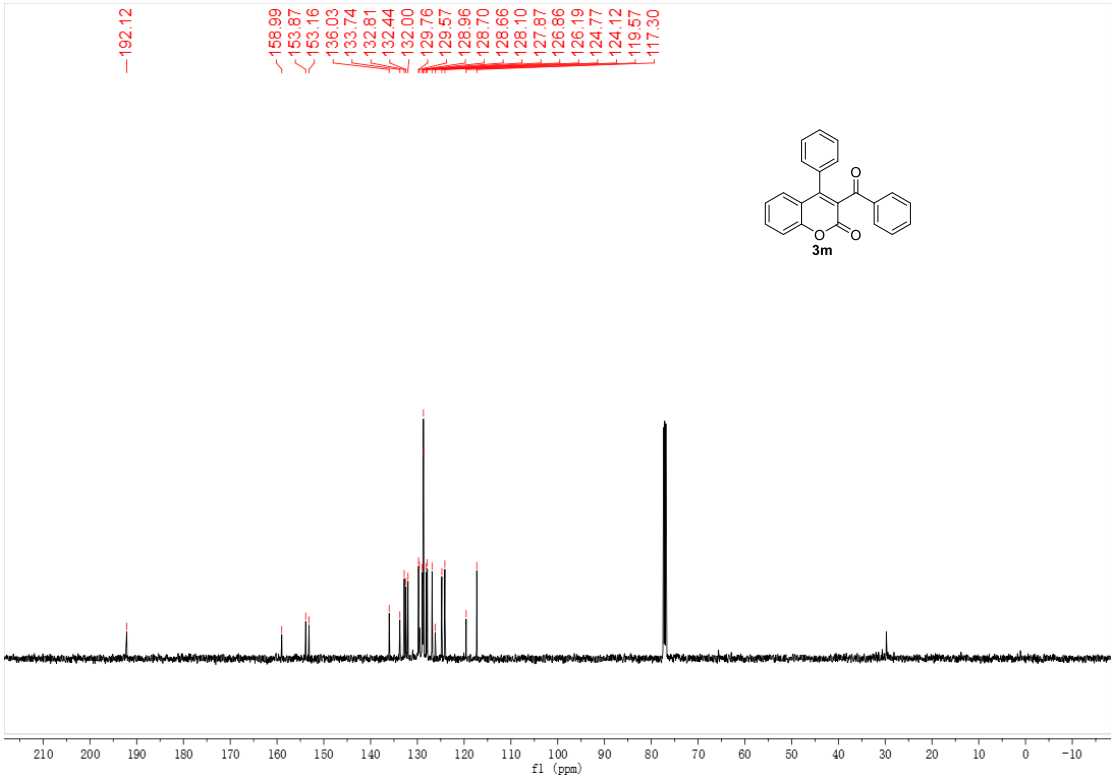

3k
f1 (ppm)

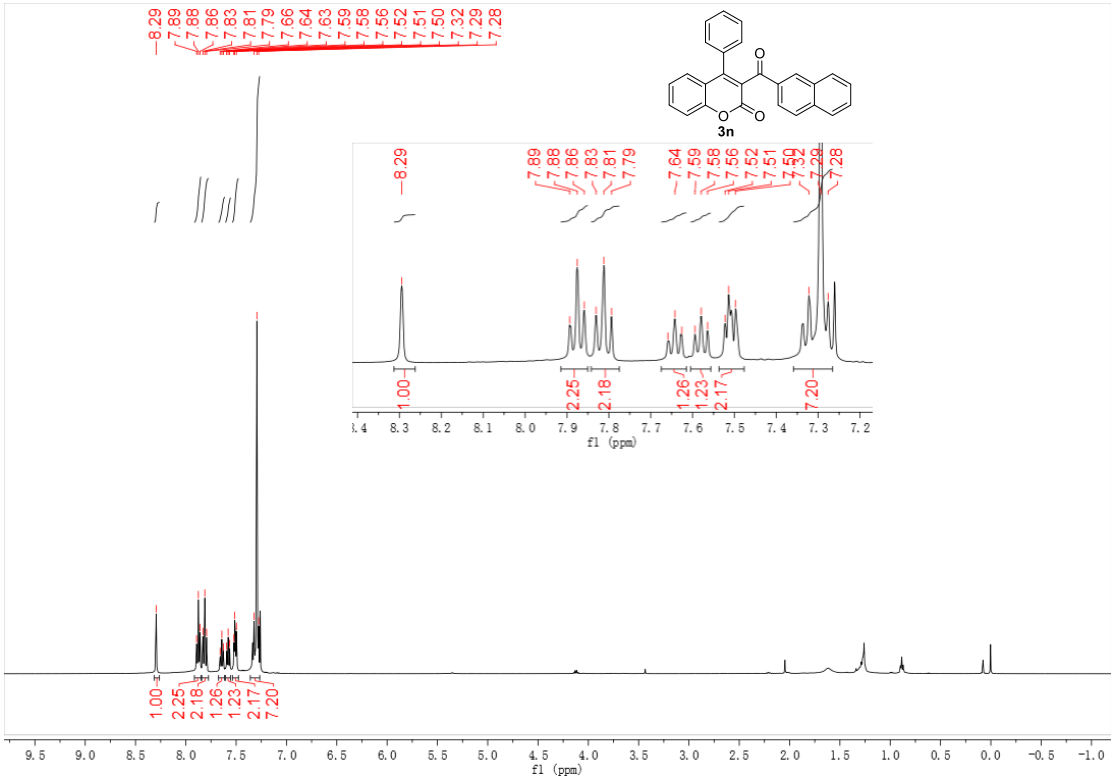

3k
f1 (ppm)

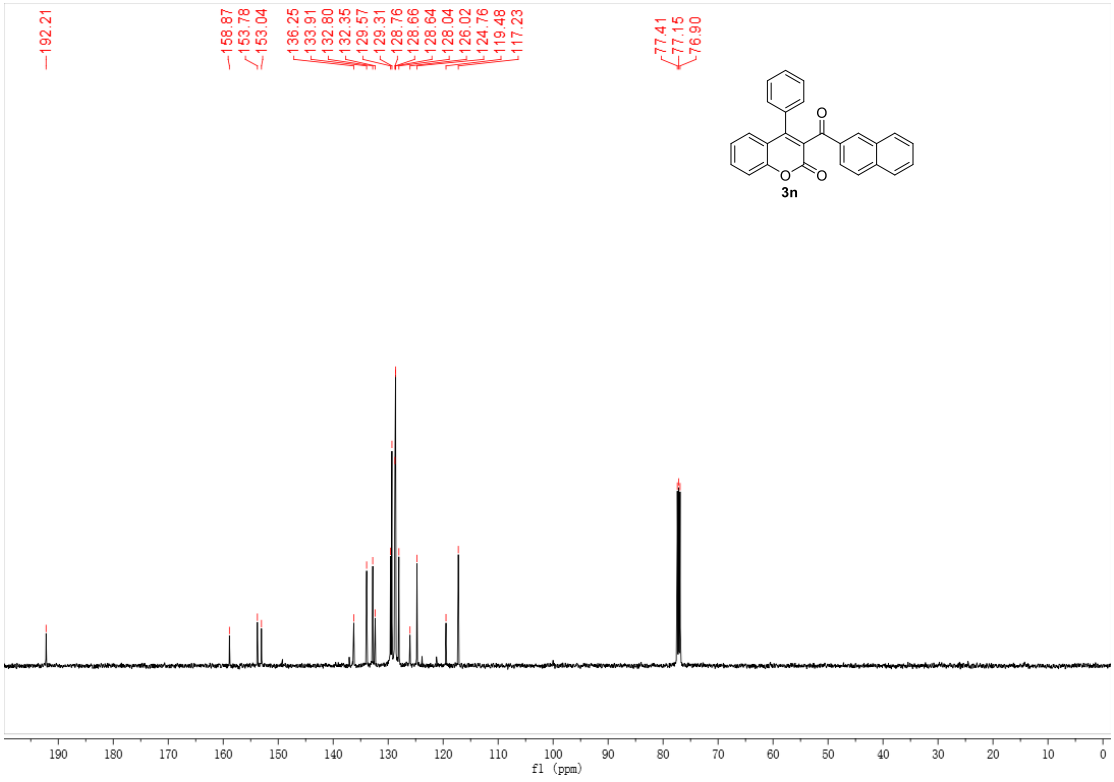

7.58 7.57 7.57 7.56 7.56 7.55 7.55 7.49 7.48 7.41 7.39 7.33 7.32 7.31 7.23 7.22 7.20 7.19
2.37 2.36 2.35 2.34 2.34 2.33 2.32 2.32 2.31 1.66 1.64 1.14 1.12 1.10 1.05
3l
1.00 3.04 1.00 2.02 2.06 1.00 4.97 5.04
f1 (ppm)

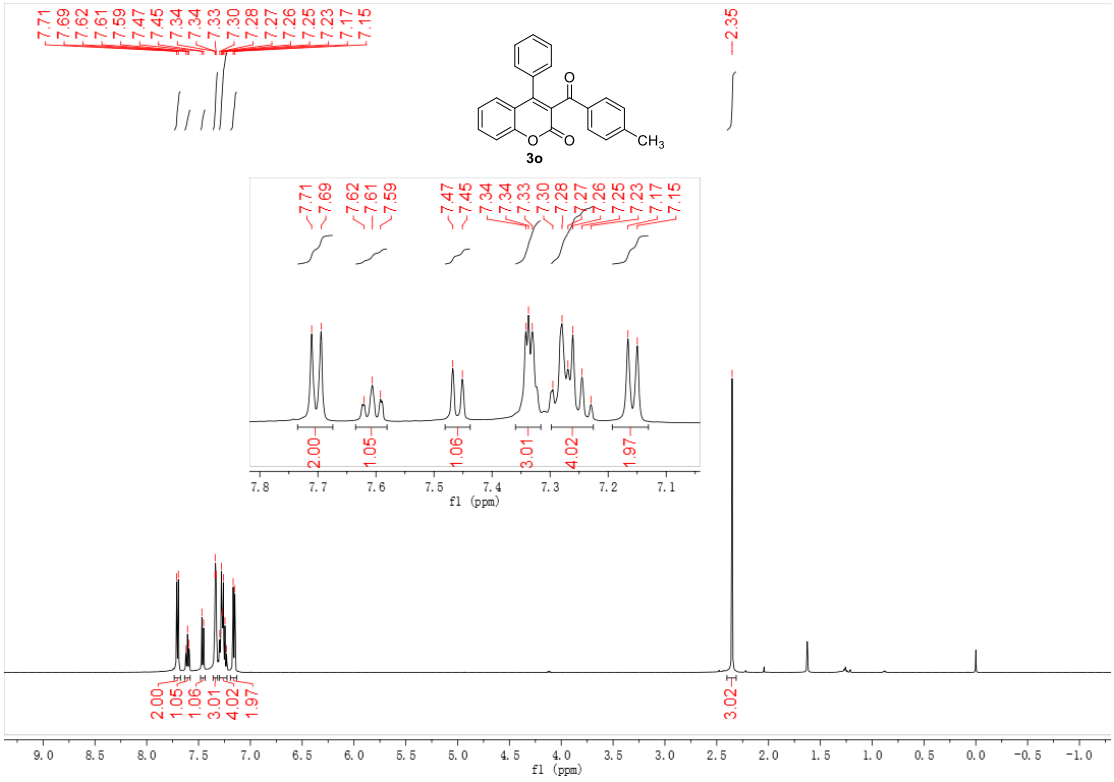

204.85 158.82 153.48 151.51 132.67 132.55 129.65 129.13 128.64 128.03 127.70 124.59 119.52 117.07 50.82 27.90 25.70 25.59
3l
f1 (ppm)

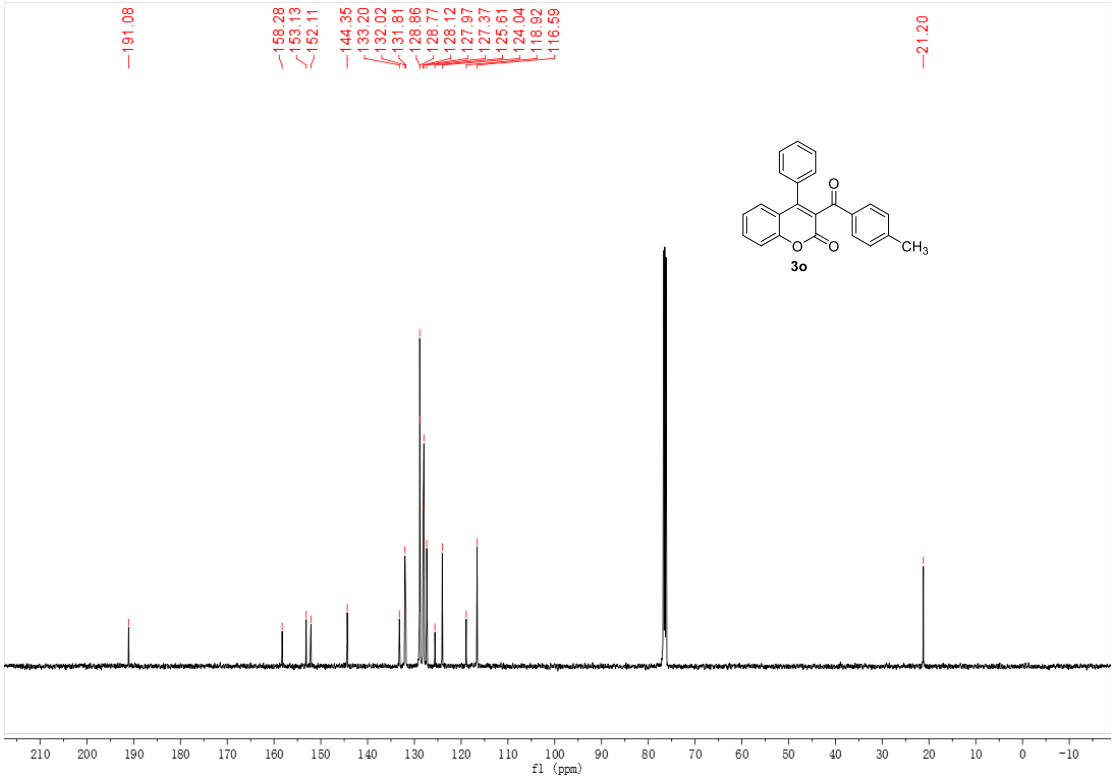

7.83
7.81
7.66
7.65
7.64
7.64
7.62
7.61
7.54
7.54
7.52
7.50
7.48
7.40
7.38
7.36
7.35
7.35
7.32
7.31
7.30
7.29
7.28
7.27
7.25
3m
1.95
1.00
2.01
5.23
3.97
f1 (ppm)

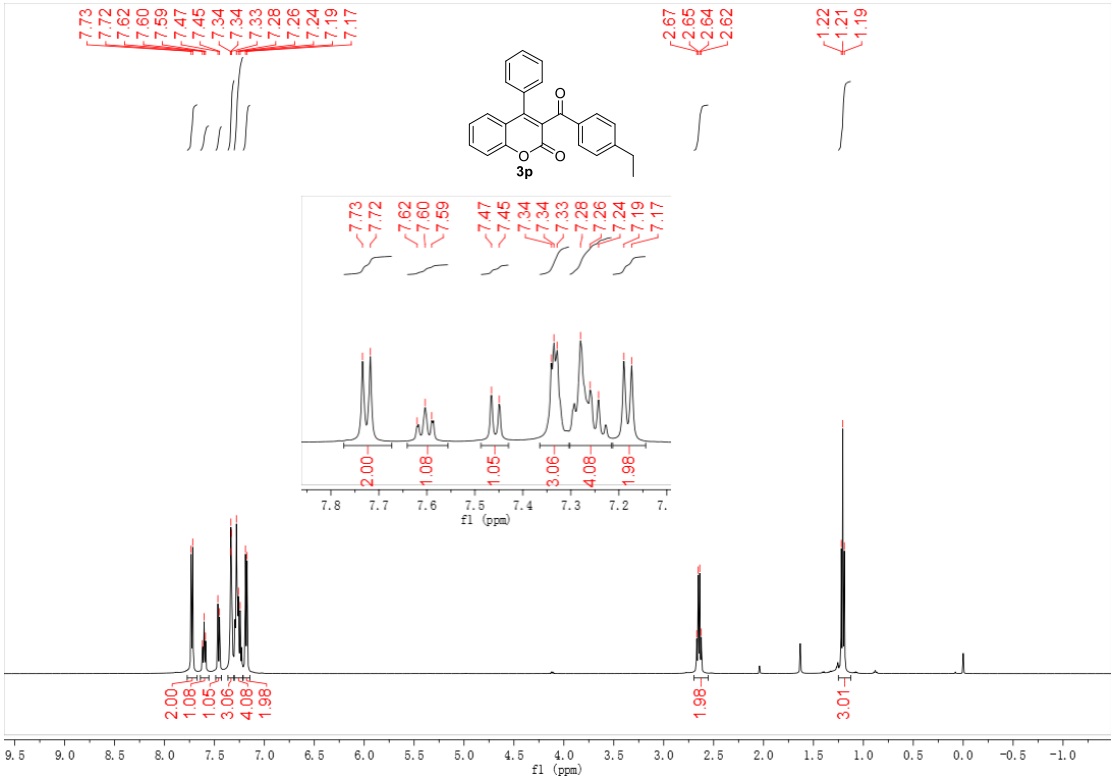

192.12
158.99
153.87
153.16
136.03
133.74
132.81
132.44
132.00
129.76
129.57
128.96
128.70
128.66
128.10
127.87
126.86
126.19
124.77
124.12
119.57
117.30
3m
f1 (ppm)

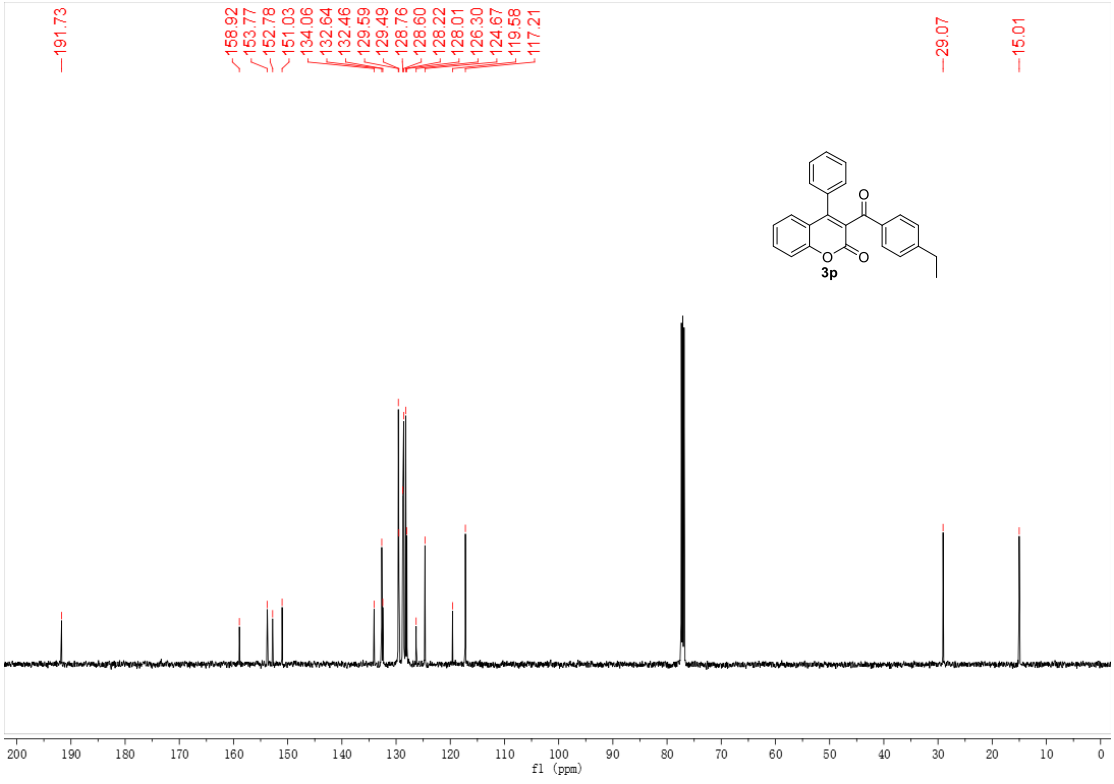

8.29
7.89
7.88
7.86
7.83
7.81
7.79
7.66
7.64
7.63
7.59
7.58
7.56
7.52
7.51
7.50
7.32
7.29
7.28
3n
1.00
2.25
2.18
1.26
1.23
2.17
7.20
f1 (ppm)

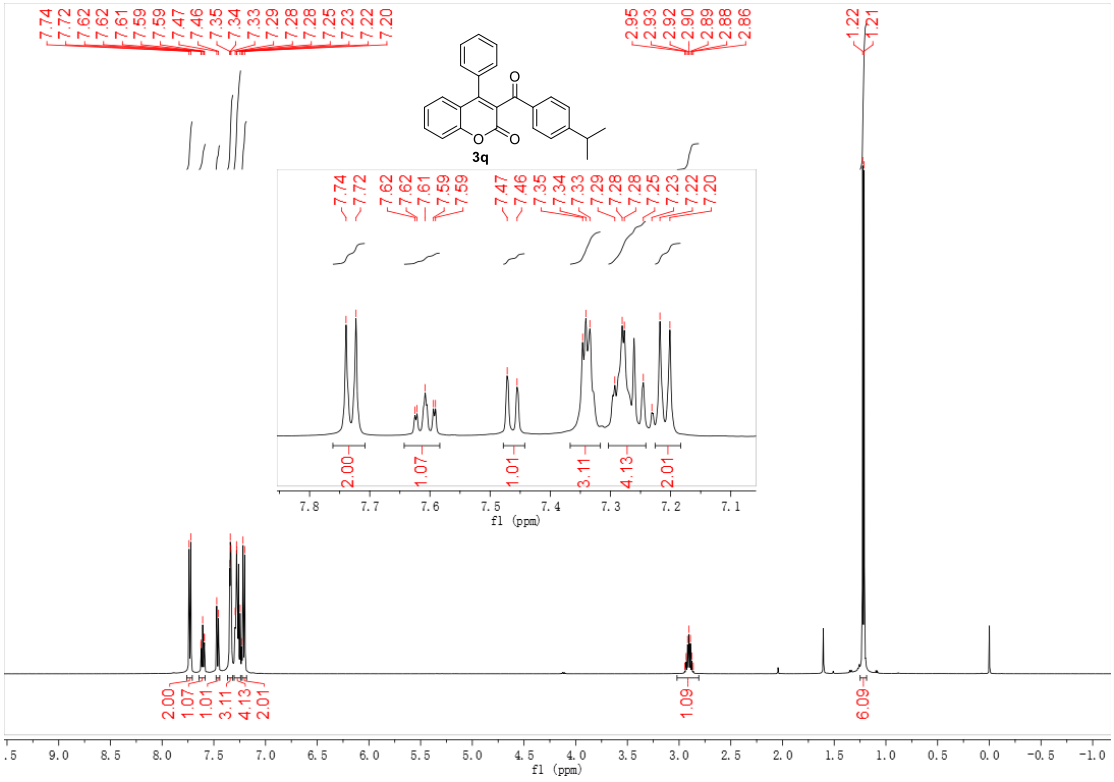

192.21
158.87
153.78
153.04
136.25
133.91
132.80
132.35
129.57
129.31
128.76
128.66
128.64
128.04
126.02
124.76
119.48
117.23
77.41
77.15
76.90
3n
f1 (ppm)

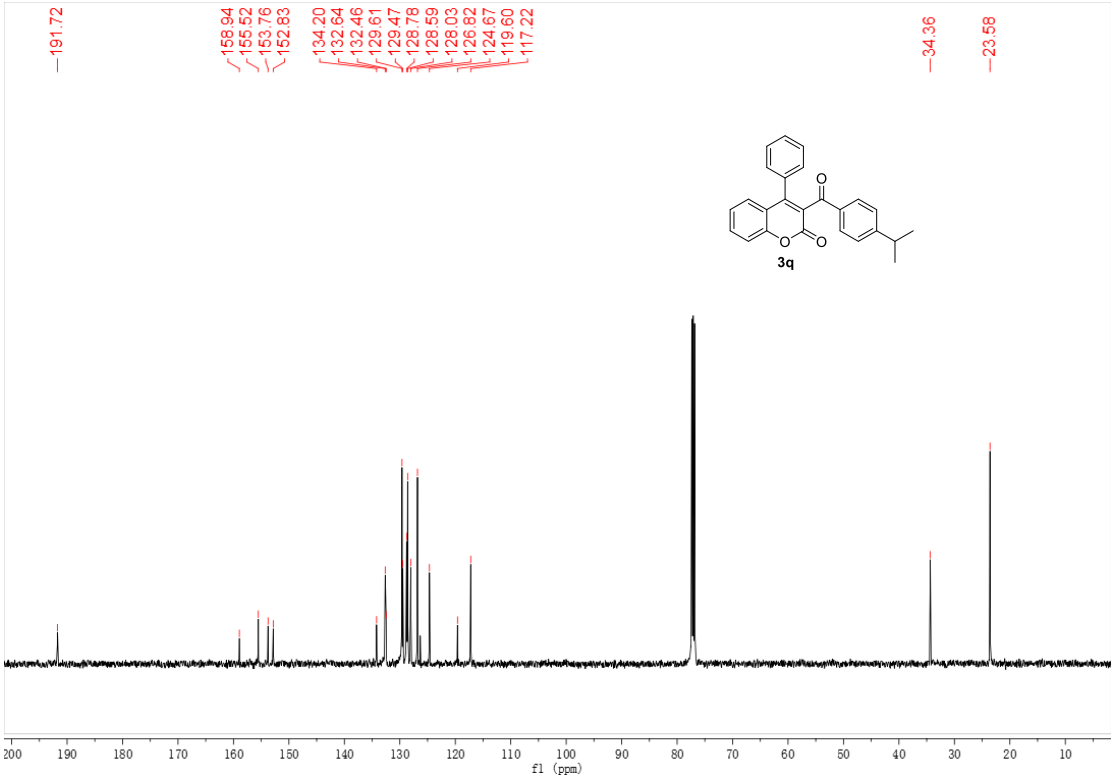

7.71
7.69
7.62
7.61
7.59
7.47
7.45
7.34
7.34
7.33
7.30
7.28
7.27
7.26
7.25
7.23
7.17
7.15
2.35
3o
2.00
1.05
1.06
3.01
4.02
1.97
3.02
f1 (ppm)

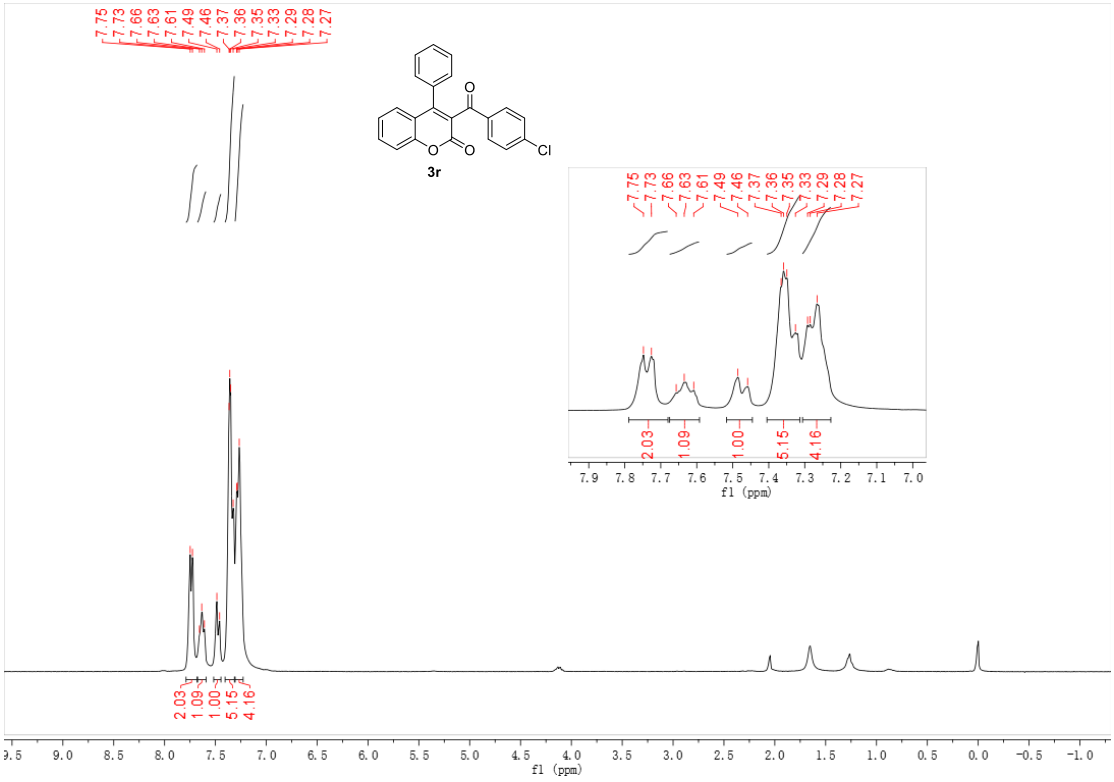

191.08
158.28
153.13
152.11
144.35
133.20
132.02
131.81
128.86
128.77
128.12
127.97
127.37
125.61
124.04
118.92
116.59
21.20
3o
f1 (ppm)

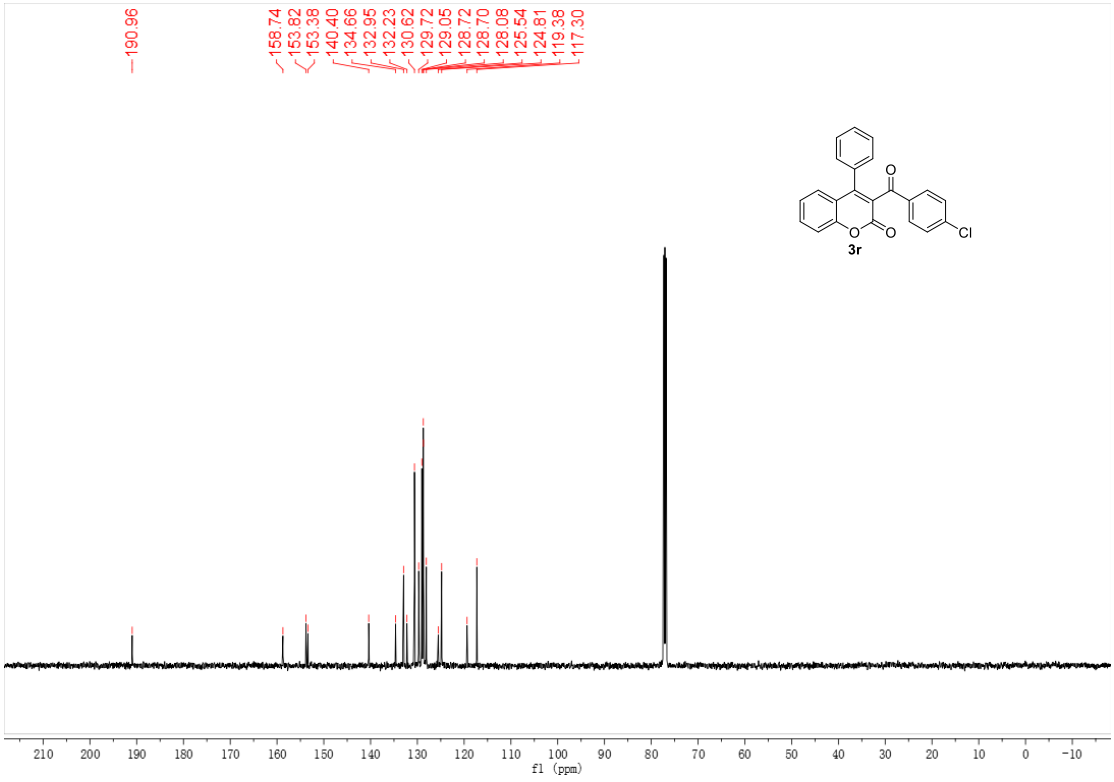

7.73
7.72
7.62
7.60
7.59
7.47
7.45
7.34
7.33
7.28
7.26
7.24
7.19
7.17
2.67
2.65
2.64
2.62
1.22
1.21
1.19
3p
2.00
1.08
1.05
3.06
4.08
1.98
1.98
3.01
f1 (ppm)

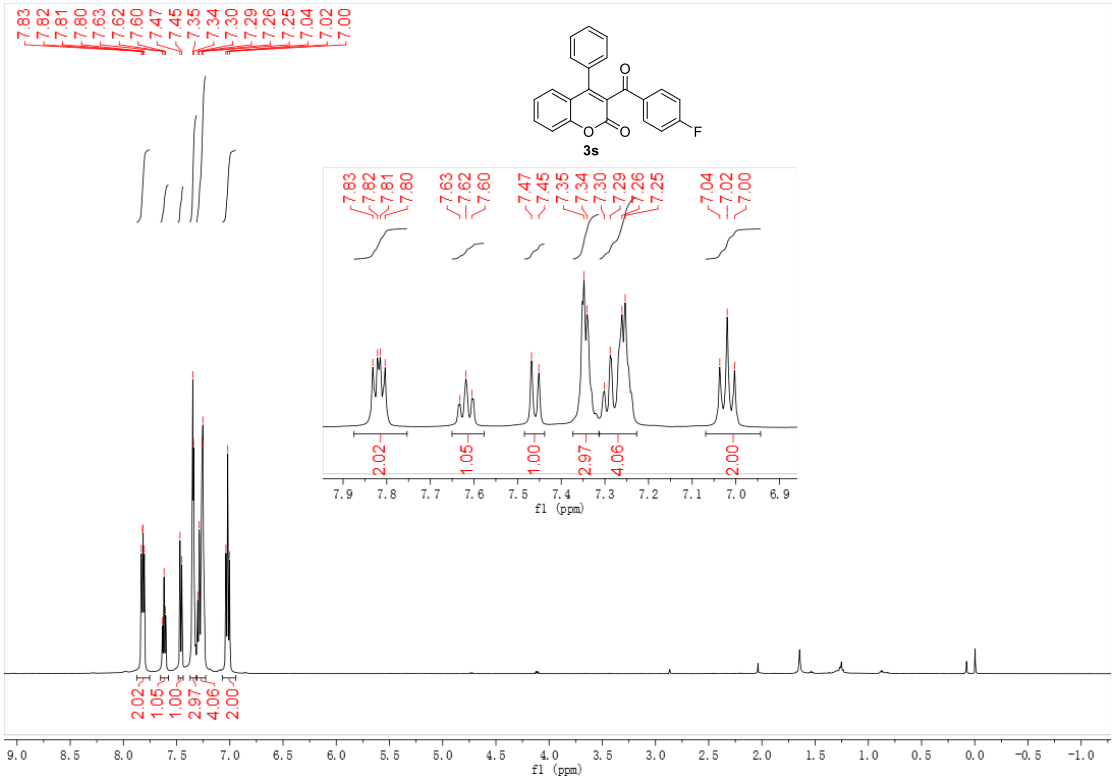

191.73
158.92
153.77
152.78
151.03
134.06
132.64
132.46
129.59
129.49
128.76
128.60
128.22
128.01
126.30
124.67
119.58
117.21
29.07
15.01
3p
f1 (ppm)

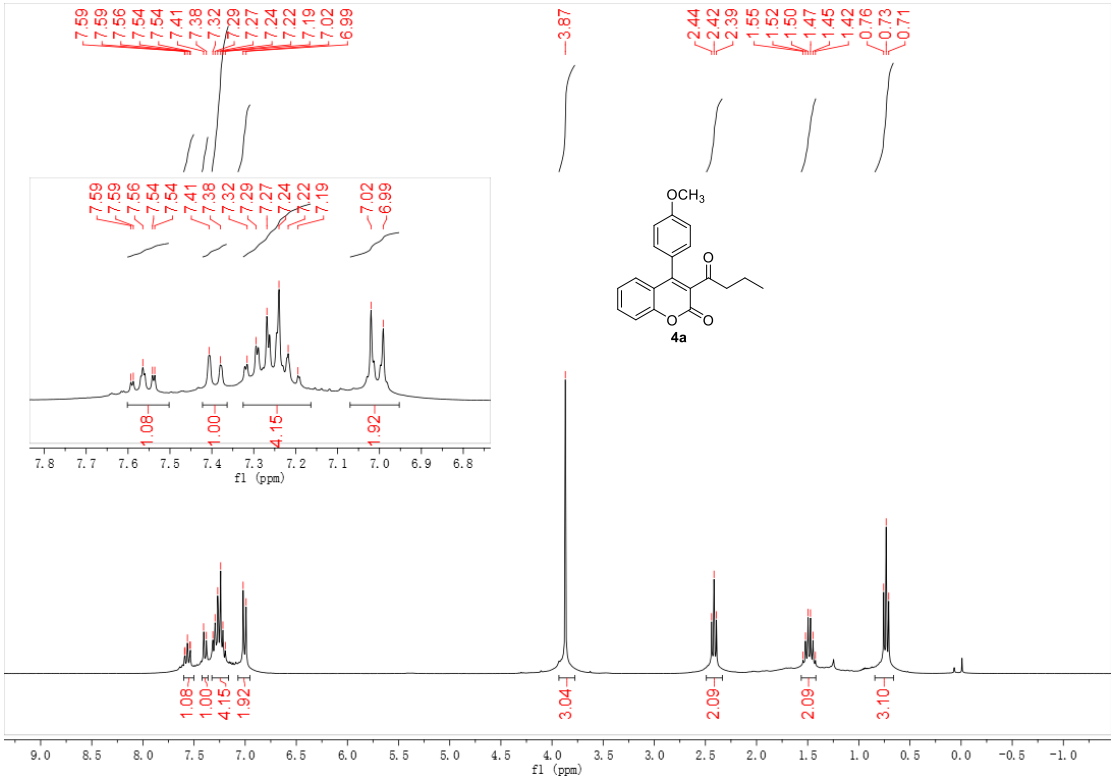

7.74
7.72
7.62
7.62
7.61
7.59
7.59
7.47
7.46
7.35
7.34
7.33
7.29
7.28
7.28
7.25
7.23
7.22
7.20
2.95
2.93
2.92
2.90
2.89
2.88
2.86
1.22
1.21
3q
2.00
1.07
1.01
3.11
4.13
2.01
1.09
6.09
f1 (ppm)

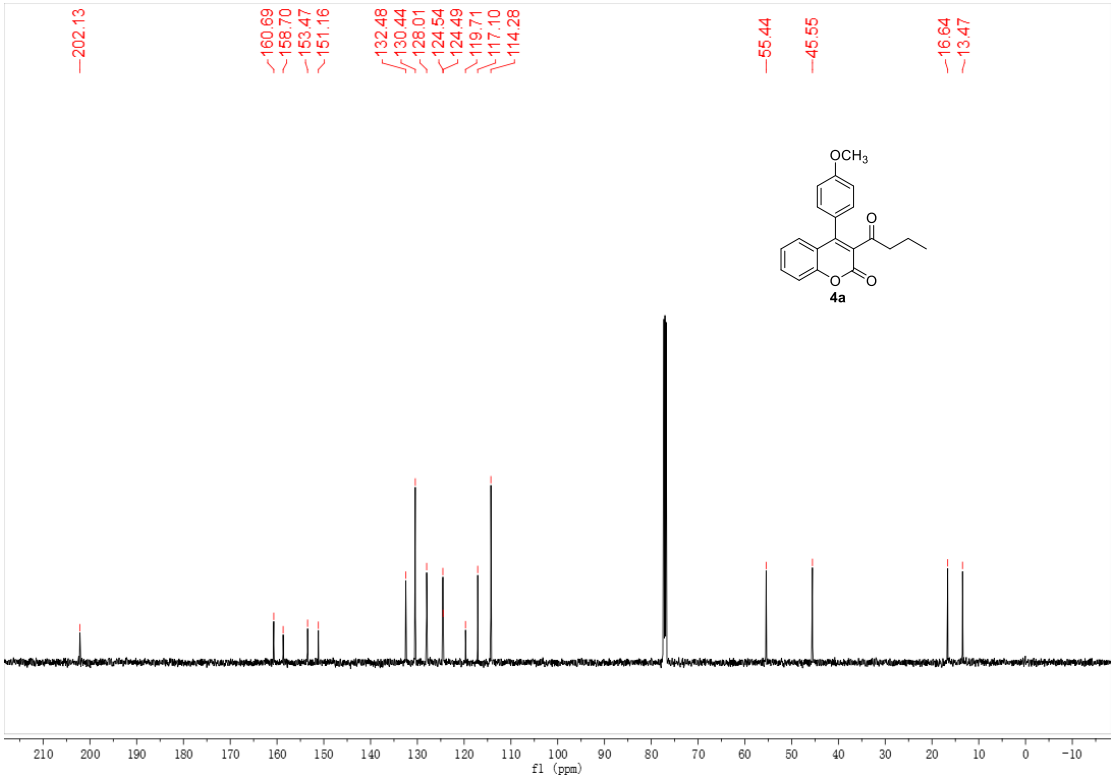

191.72
158.94
155.52
153.76
152.83
134.20
132.64
132.46
129.61
129.47
128.78
128.59
128.03
126.82
124.67
119.60
117.22
34.36
23.58
3q
f1 (ppm)

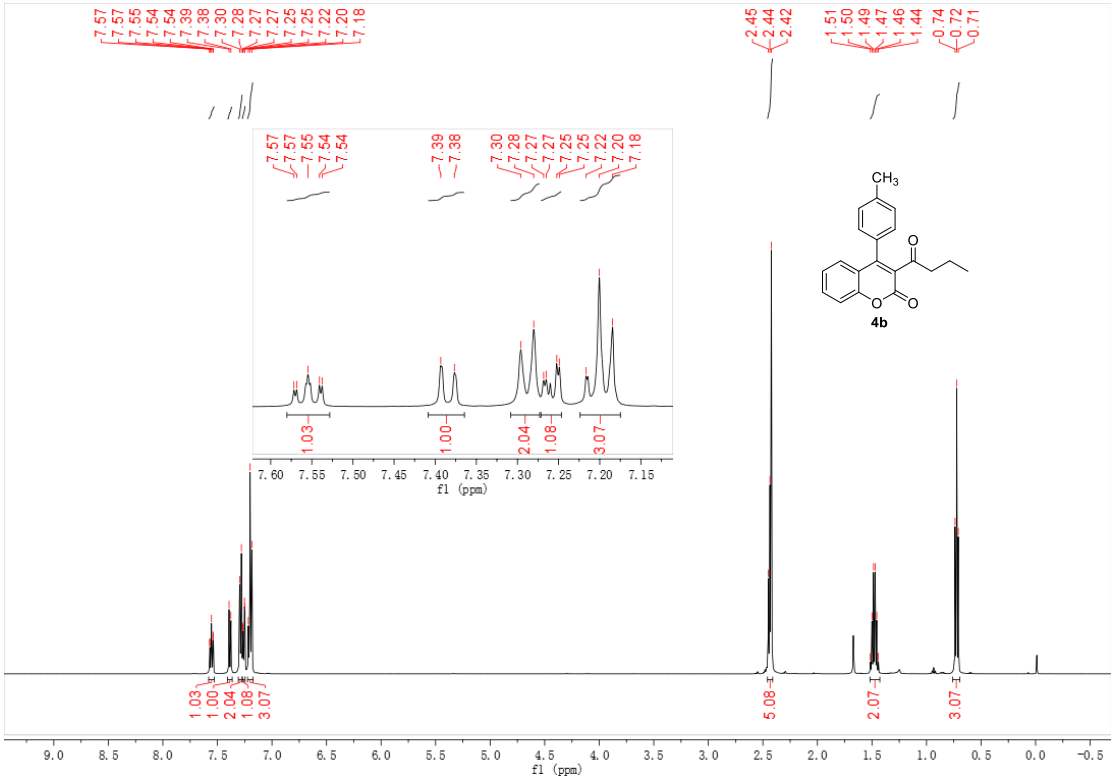

7.75
7.73
7.66
7.63
7.61
7.49
7.46
7.37
7.36
7.35
7.33
7.29
7.28
7.27
O
O
O
Cl
3r
2.03
1.09
1.00
5.15
4.16
f1 (ppm)

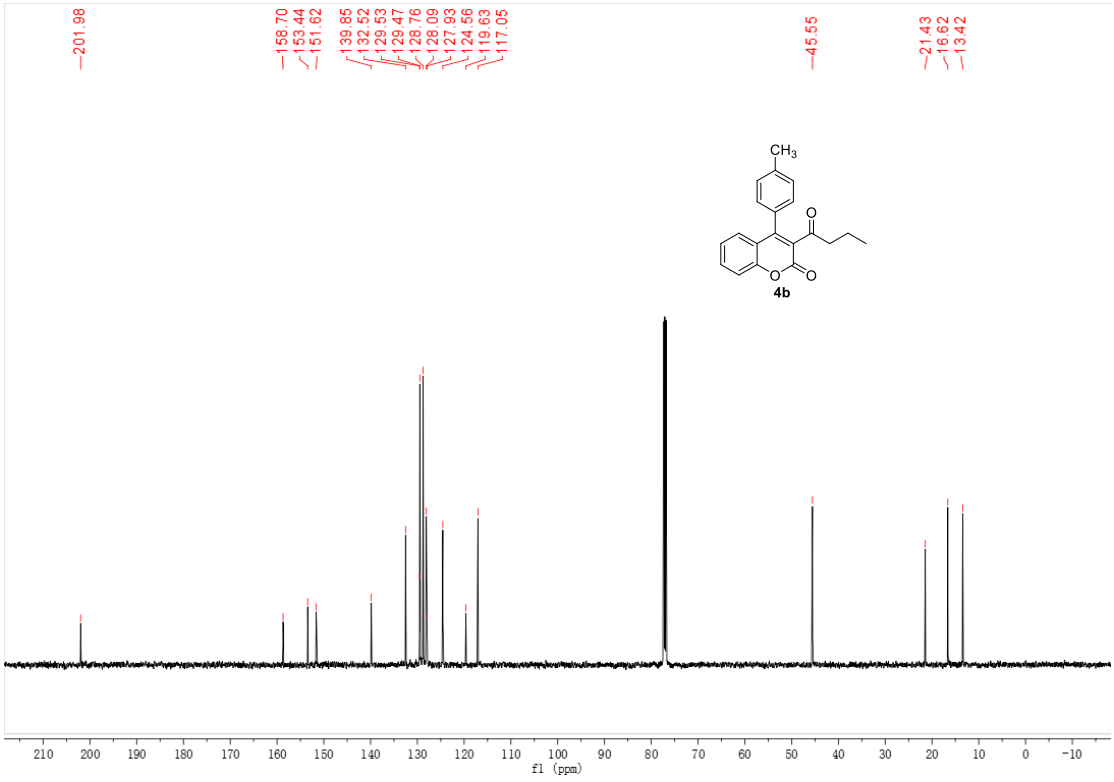

190.96
158.74
153.82
153.38
140.40
134.66
132.95
132.23
130.62
129.72
129.05
128.72
128.70
128.08
125.54
124.81
119.38
117.30
O
O
O
Cl
3r
f1 (ppm)

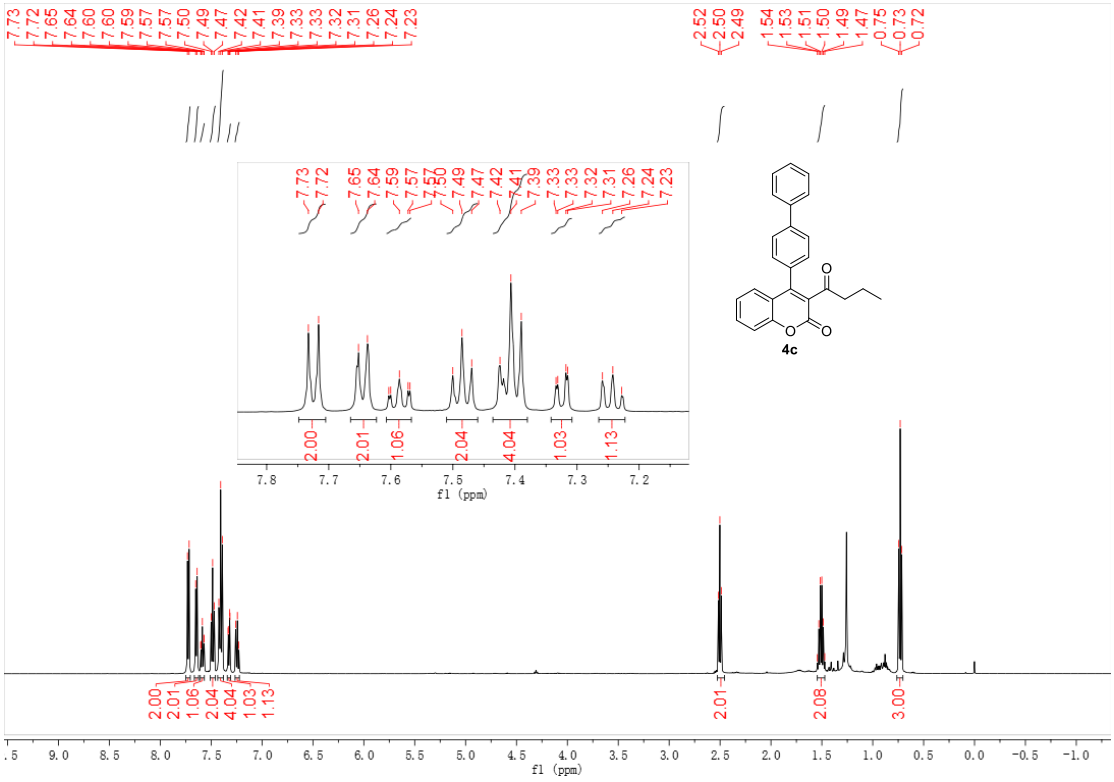

7.83
7.82
7.81
7.80
7.63
7.62
7.60
7.47
7.45
7.35
7.34
7.30
7.29
7.26
7.25
7.04
7.02
7.00
O
O
O
F
3s
2.02
1.05
1.00
2.97
4.06
2.00
f1 (ppm)

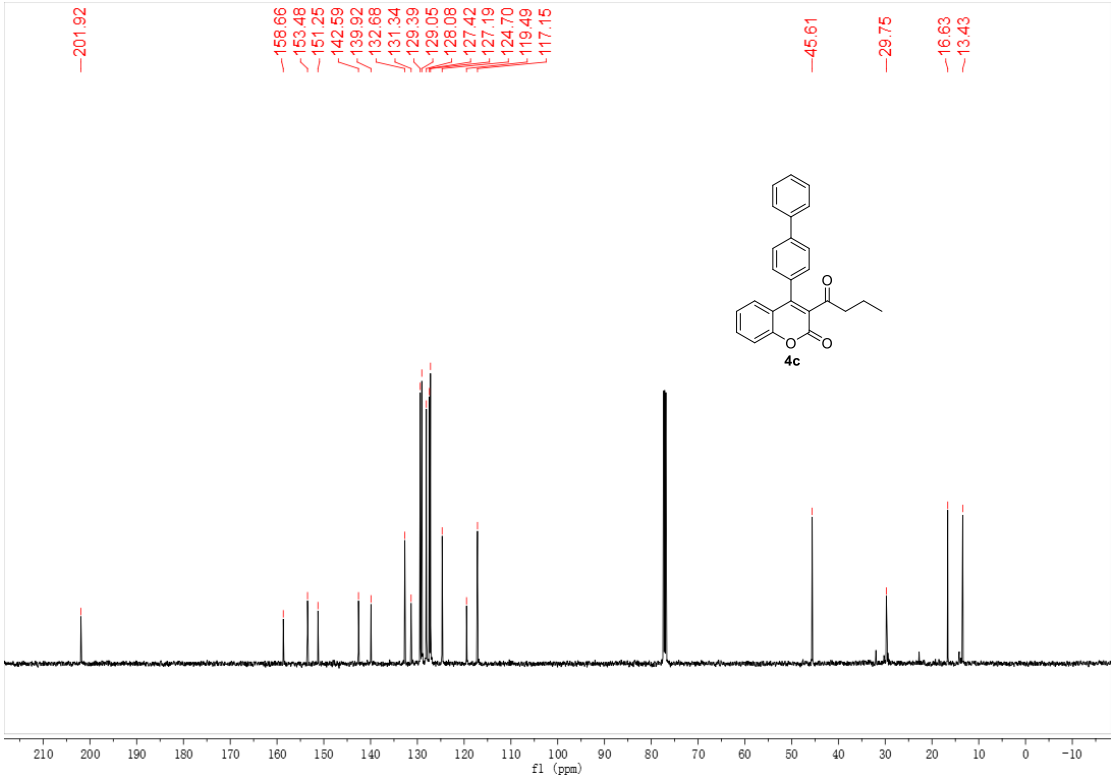

7.59
7.59
7.56
7.54
7.54
7.41
7.38
7.32
7.29
7.27
7.24
7.22
7.19
7.02
6.99
3.87
2.44
2.42
2.39
1.55
1.52
1.50
1.47
1.45
1.42
0.76
0.73
0.71
OCH3
O
O
O
4a
1.08
1.00
4.15
1.92
3.04
2.09
2.09
3.10
f1 (ppm)

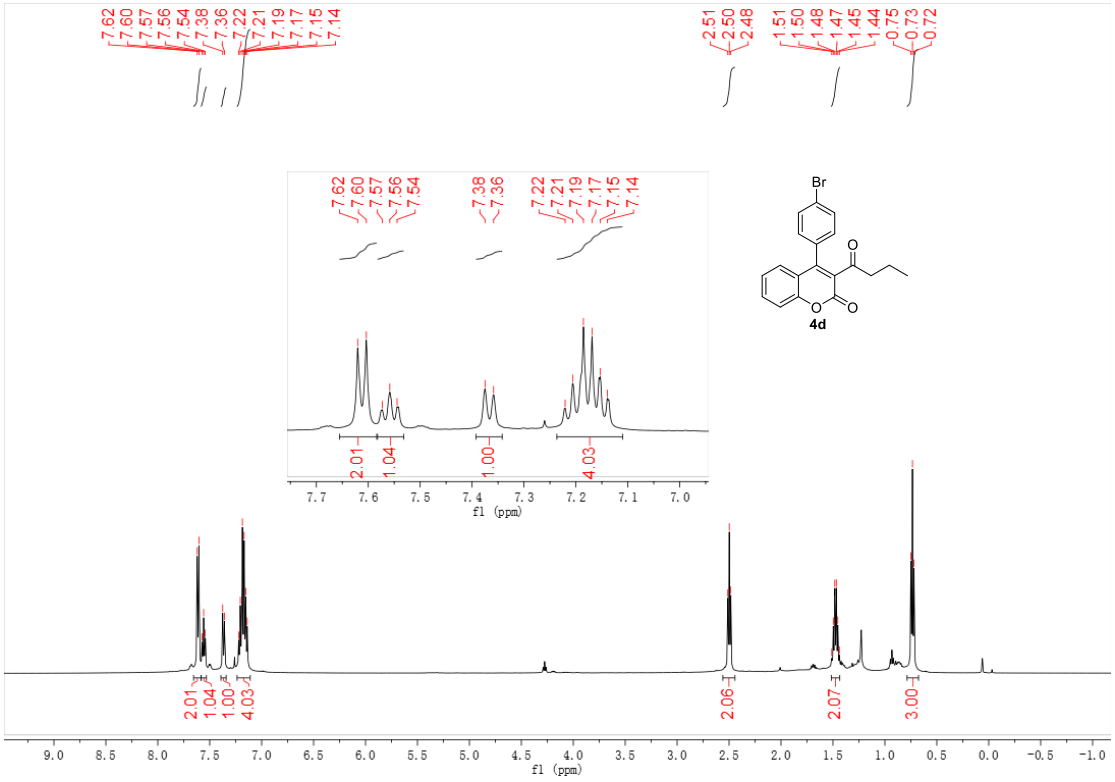

202.13
160.69
158.70
153.47
151.16
132.48
130.44
128.01
124.54
124.49
119.71
117.10
114.28
55.44
45.55
16.64
13.47
OCH3
O
O
O
4a
f1 (ppm)

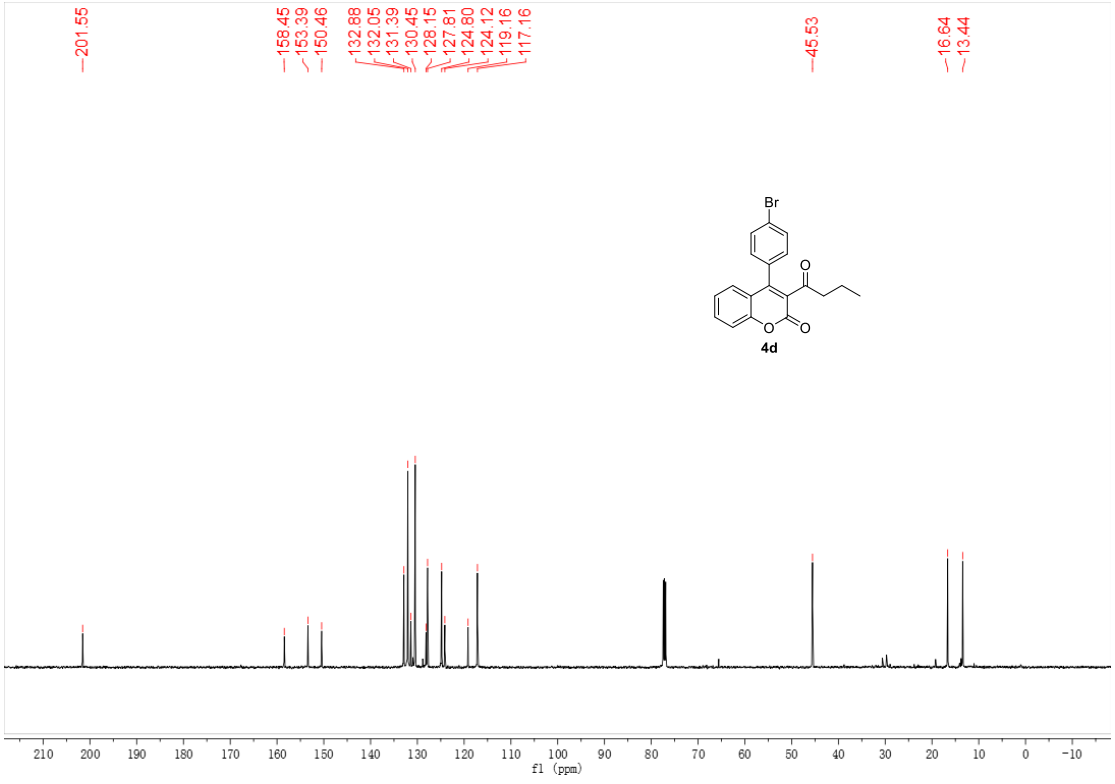

7.57
7.57
7.55
7.54
7.54
7.39
7.38
7.30
7.28
7.27
7.27
7.25
7.22
7.20
7.18
2.45
2.44
2.42
1.51
1.50
1.49
1.47
1.46
1.44
0.74
0.72
0.71
CH3
O
O
O
4b
1.03
1.00
2.04
1.08
3.07
5.08
2.07
3.07
f1 (ppm)

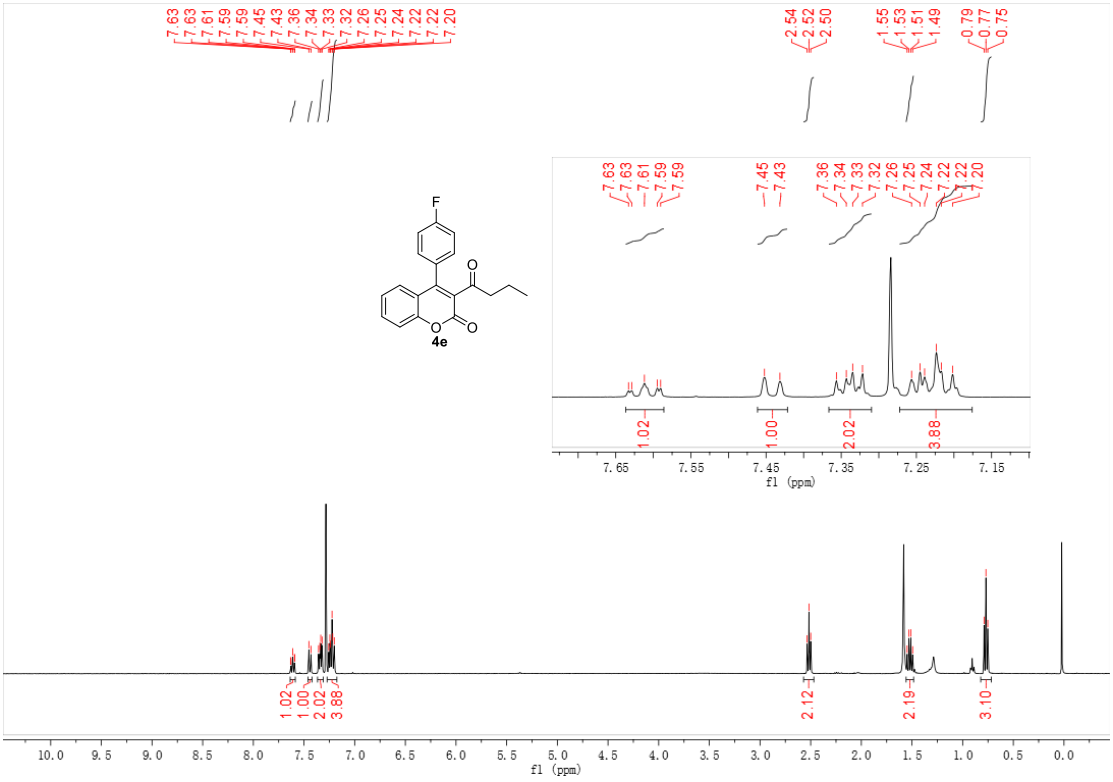

201.98
158.70
153.44
151.62
139.85
132.52
129.53
129.47
128.76
128.09
127.93
124.56
119.63
117.05
45.55
21.43
16.62
13.42
CH3
O
O
O
4b
f1 (ppm)

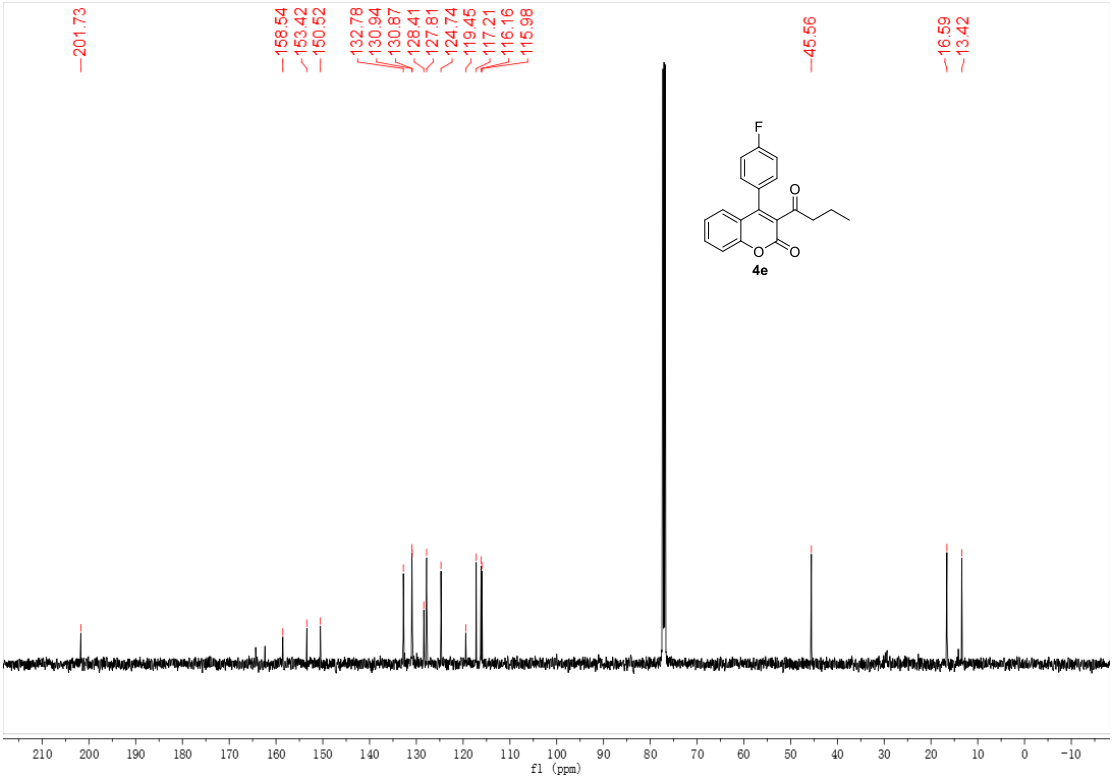

7.73
7.72
7.65
7.64
7.60
7.60
7.59
7.57
7.57
7.50
7.49
7.47
7.42
7.41
7.39
7.33
7.33
7.32
7.31
7.26
7.24
7.23
2.52
2.50
2.49
1.54
1.53
1.51
1.50
1.49
1.47
0.75
0.73
0.72
2.00
2.01
1.06
2.04
4.04
1.03
1.13
f1 (ppm)
4c

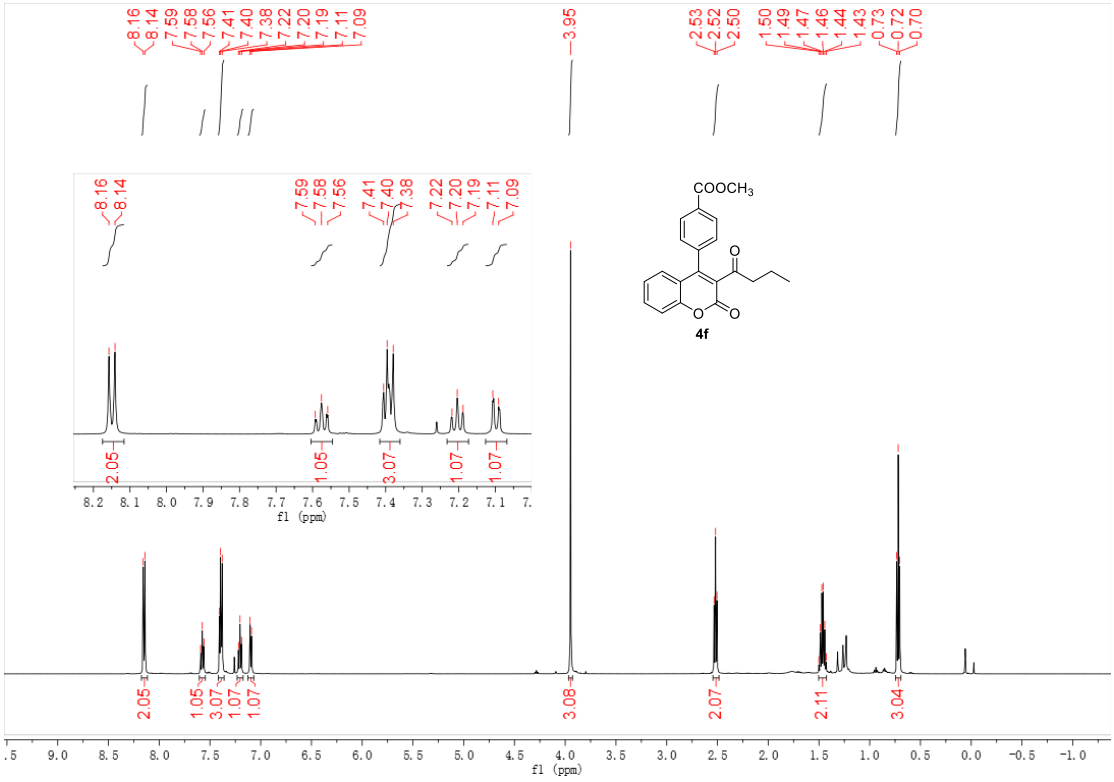

201.92
158.66
153.48
151.25
142.59
139.92
132.68
131.34
129.39
129.05
128.08
127.42
127.19
124.70
119.49
117.15
45.61
29.75
16.63
13.43
f1 (ppm)
4c

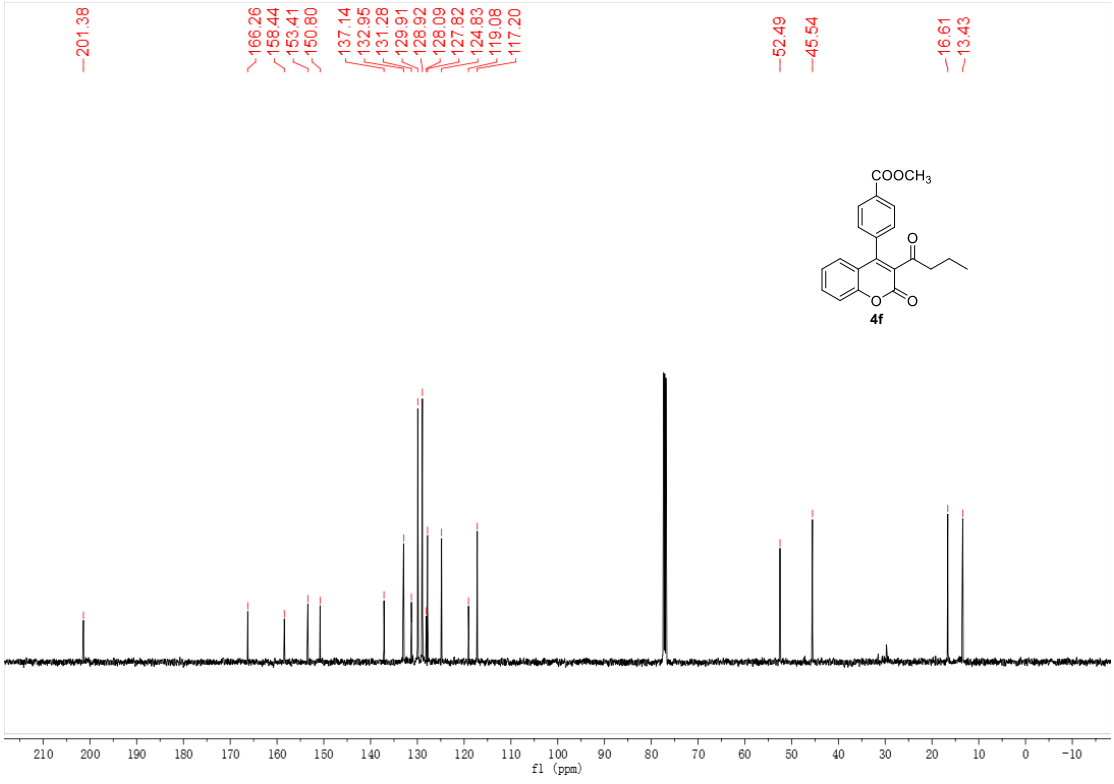

7.62
7.60
7.57
7.56
7.54
7.38
7.36
7.22
7.21
7.19
7.17
7.15
7.14
2.51
2.50
2.48
1.51
1.50
1.48
1.47
1.45
1.44
0.75
0.73
0.72
Br
O
O
O
4d
2.01
1.04
1.00
4.03
f1 (ppm)
2.06
2.07
3.00

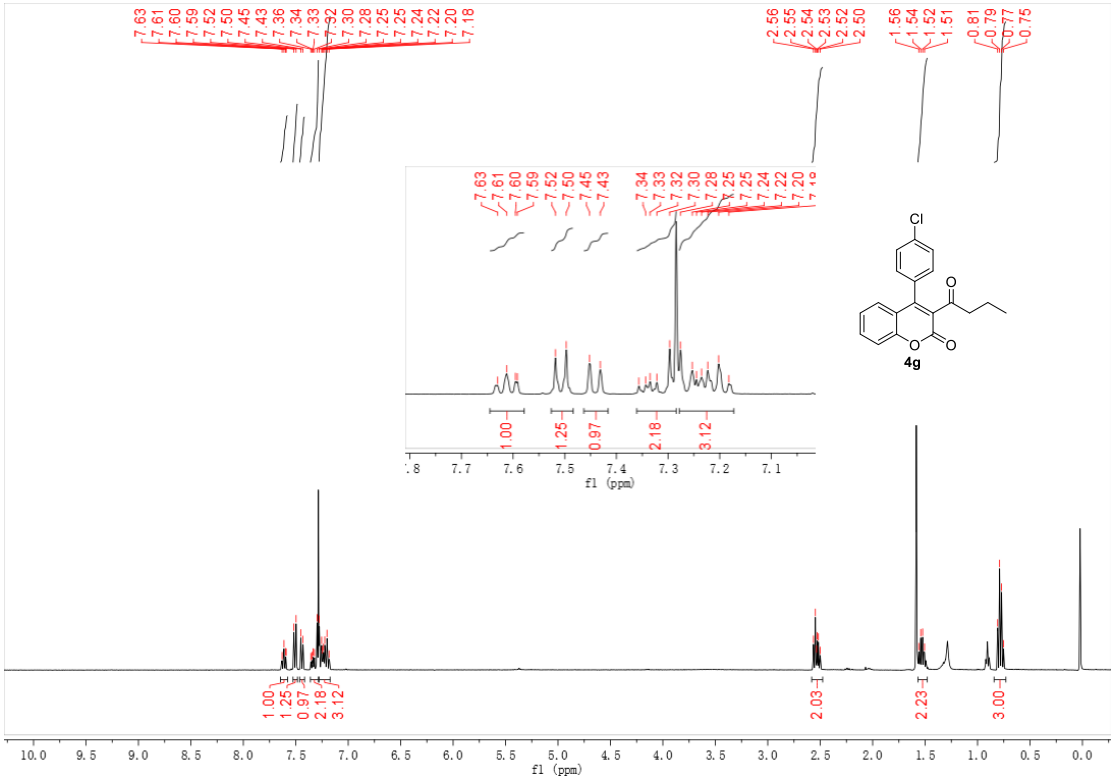

201.55
158.45
153.39
150.46
132.88
132.05
131.39
130.45
128.15
127.81
124.80
124.12
119.16
117.16
45.53
16.64
13.44
Br
O
O
O
4d
f1 (ppm)

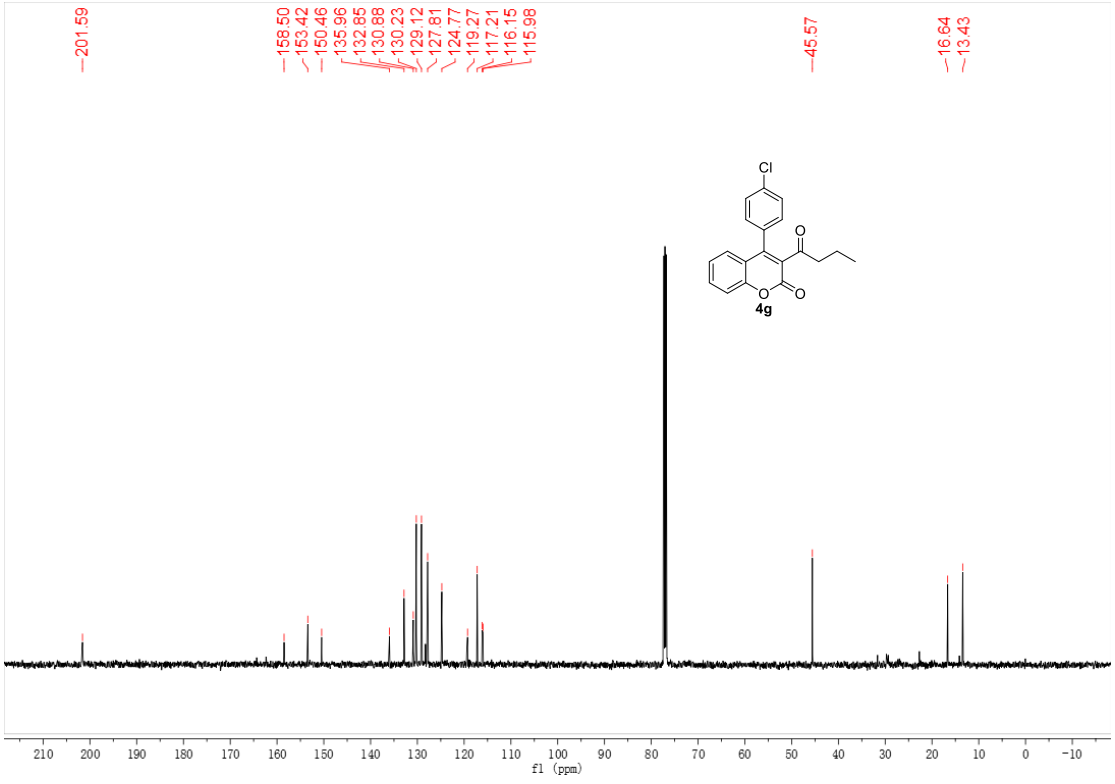

7.63
7.63
7.61
7.59
7.59
7.45
7.43
7.36
7.34
7.33
7.32
7.26
7.25
7.24
7.22
7.22
7.20
2.54
2.52
2.50
1.55
1.53
1.51
1.49
0.79
0.77
0.75
F
O
O
O
4e
1.02
1.00
2.02
3.88
7.65
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
1.02
1.00
2.02
3.88
2.12
2.19
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

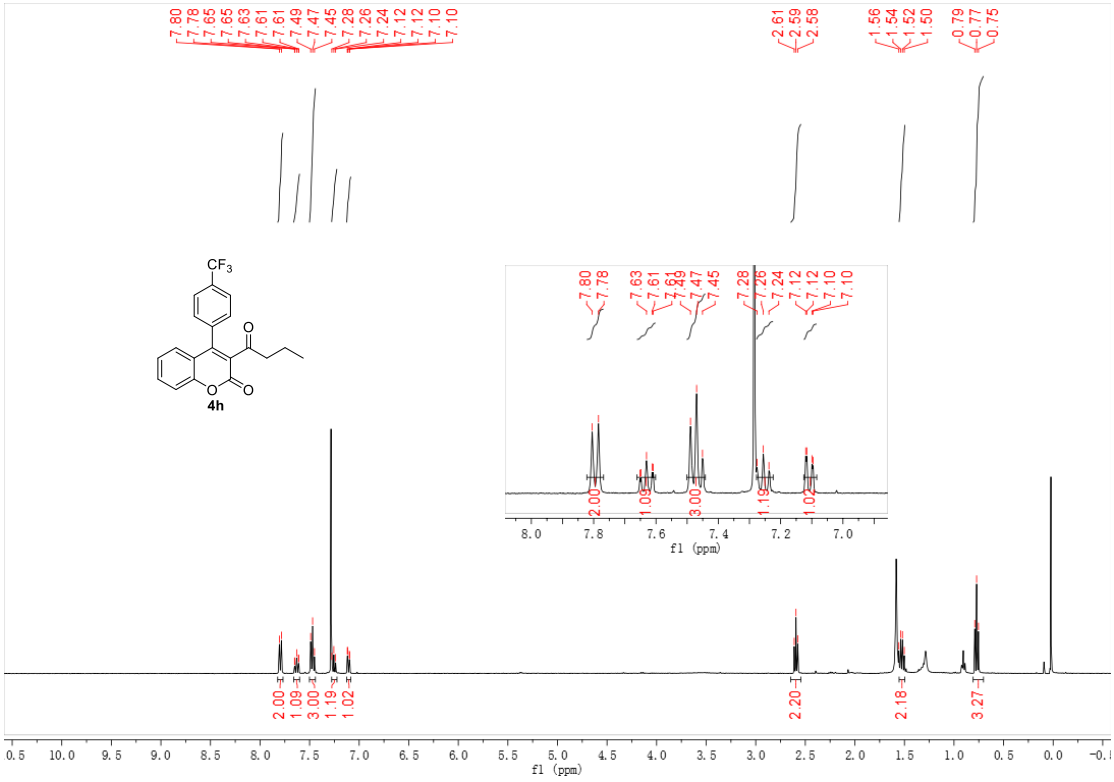

201.73
158.54
153.42
150.52
132.78
130.94
130.87
128.41
127.81
124.74
119.45
117.21
116.16
115.98
45.56
16.59
13.42
F
O
O
O
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

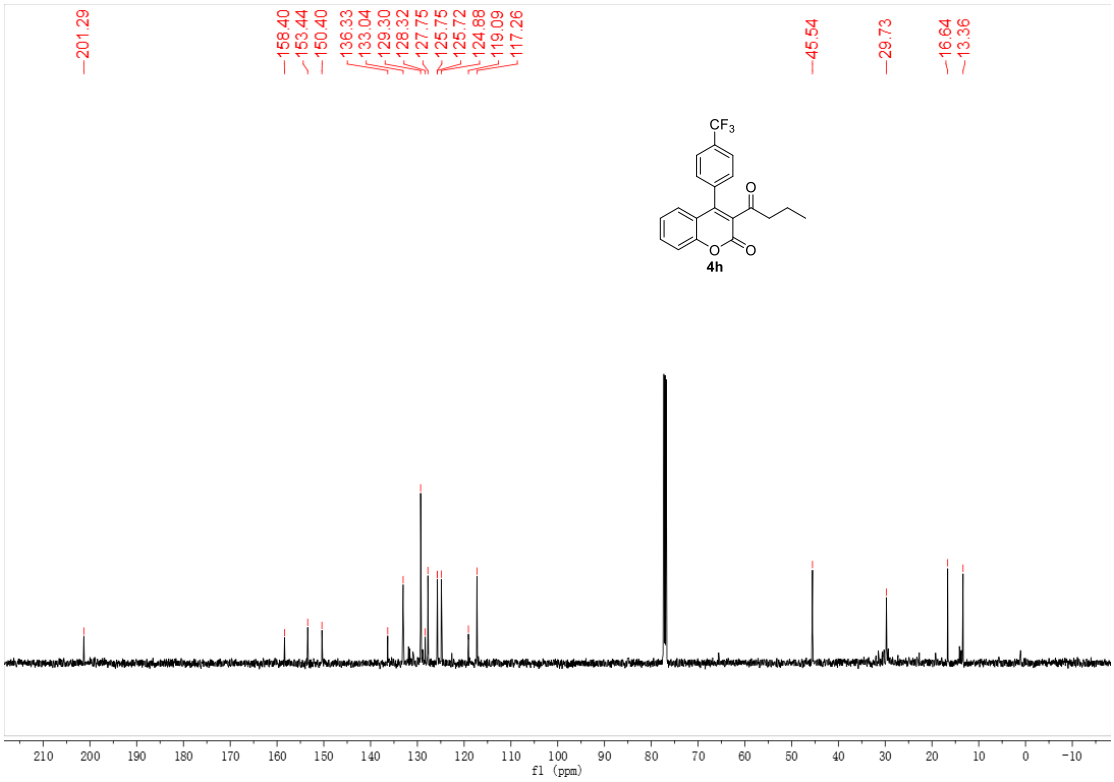

8.16
8.14
7.59
7.58
7.56
7.41
7.40
7.38
7.22
7.20
7.19
7.11
7.09
3.95
2.53
2.52
2.50
1.50
1.49
1.47
1.46
1.44
1.43
0.73
0.72
0.70
COOCH3
O
O
O
4f
2.05
1.05
3.07
1.07
1.07
3.08
2.07
2.11
3.04
f1 (ppm)

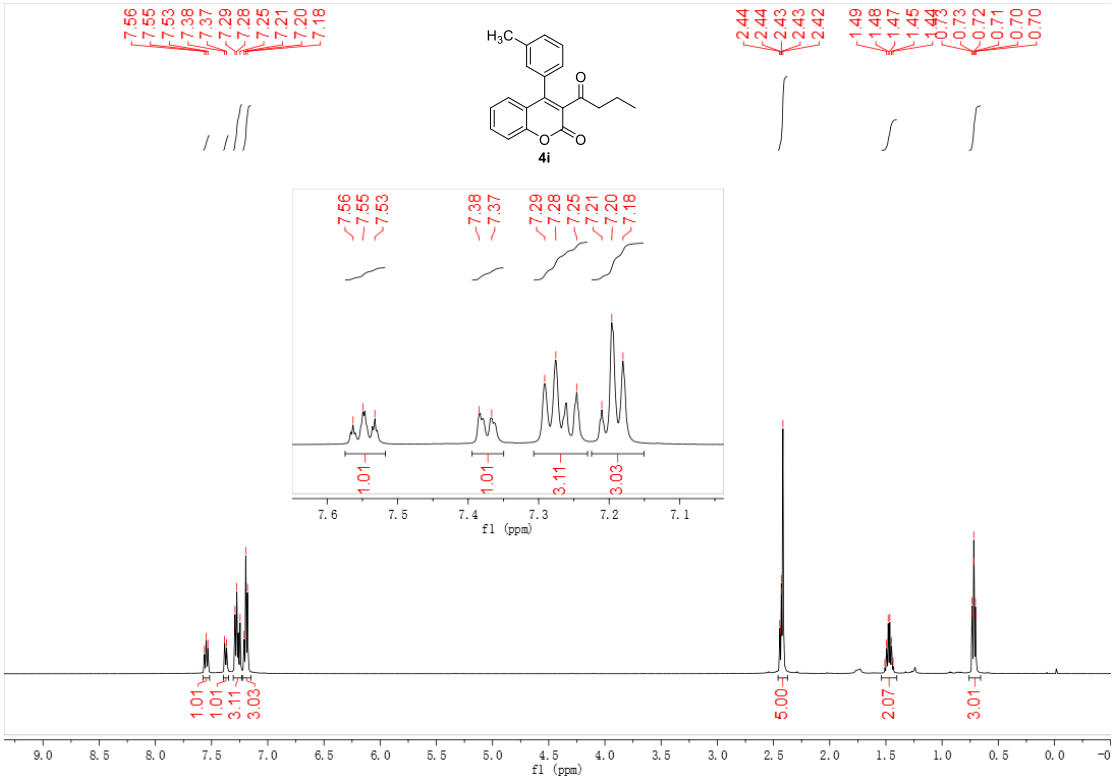

201.38
166.26
158.44
153.41
150.80
137.14
132.95
131.28
129.91
128.92
128.09
127.82
124.83
119.08
117.20
52.49
45.54
16.61
13.43
COOCH3
O
O
O
4f
f1 (ppm)

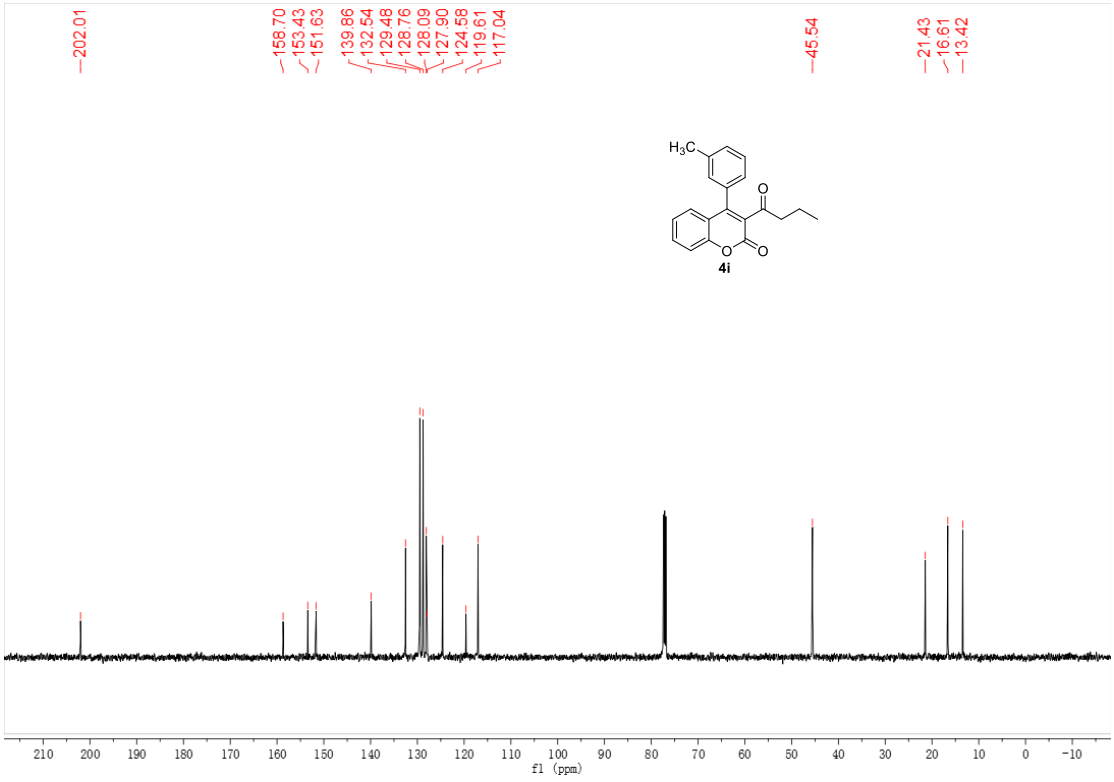

7.63
7.61
7.60
7.59
7.52
7.50
7.45
7.43
7.36
7.34
7.33
7.32
7.30
7.28
7.25
7.24
7.22
7.20
7.18
2.56
2.55
2.54
2.53
2.52
2.50
1.56
1.54
1.52
1.51
0.81
0.79
0.77
0.75
Cl
O
O
O
4g
1.00
1.25
0.97
2.18
3.12
2.03
2.23
3.00
f1 (ppm)

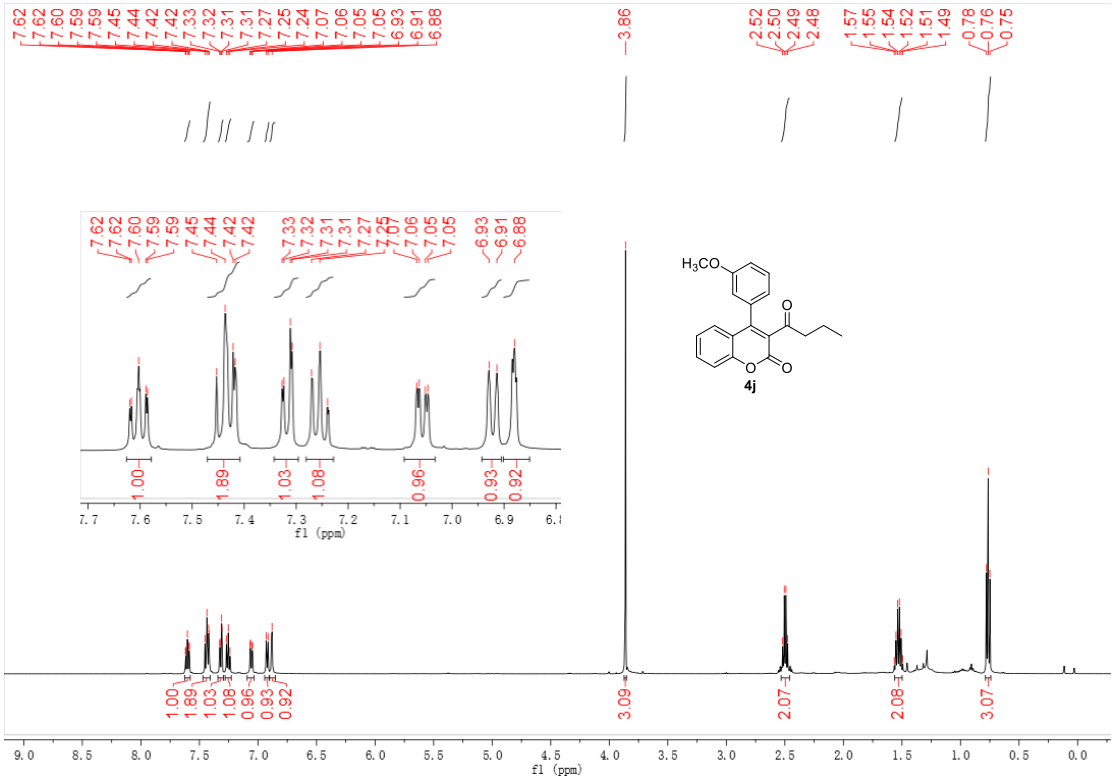

201.59
158.50
153.42
150.46
135.96
132.85
130.88
130.23
129.12
127.81
124.77
119.27
117.21
116.15
115.98
45.57
16.64
13.43
Cl
O
O
O
4g
f1 (ppm)

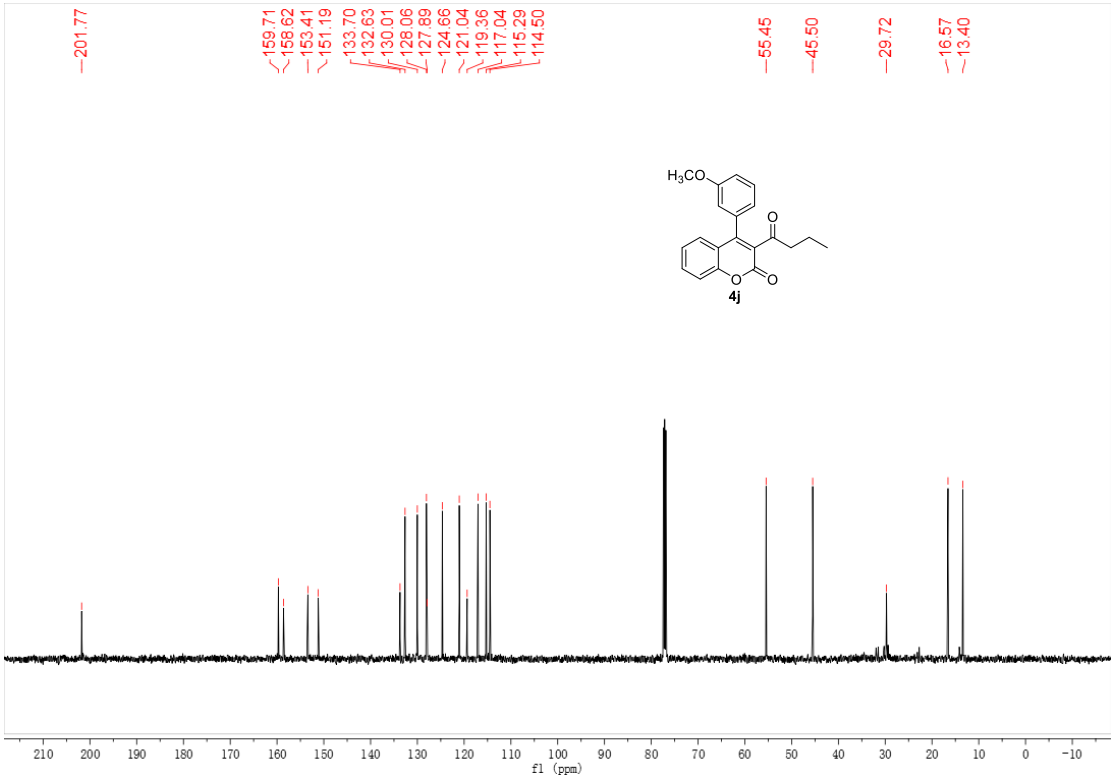

7.80
7.78
7.65
7.63
7.61
7.49
7.47
7.45
7.28
7.26
7.24
7.12
7.10
2.61
2.59
2.58
1.56
1.54
1.52
1.50
0.79
0.77
0.75
CF3
O
O
O
4h
2.00
1.09
3.00
1.19
1.02
2.20
2.18
3.27
f1 (ppm)

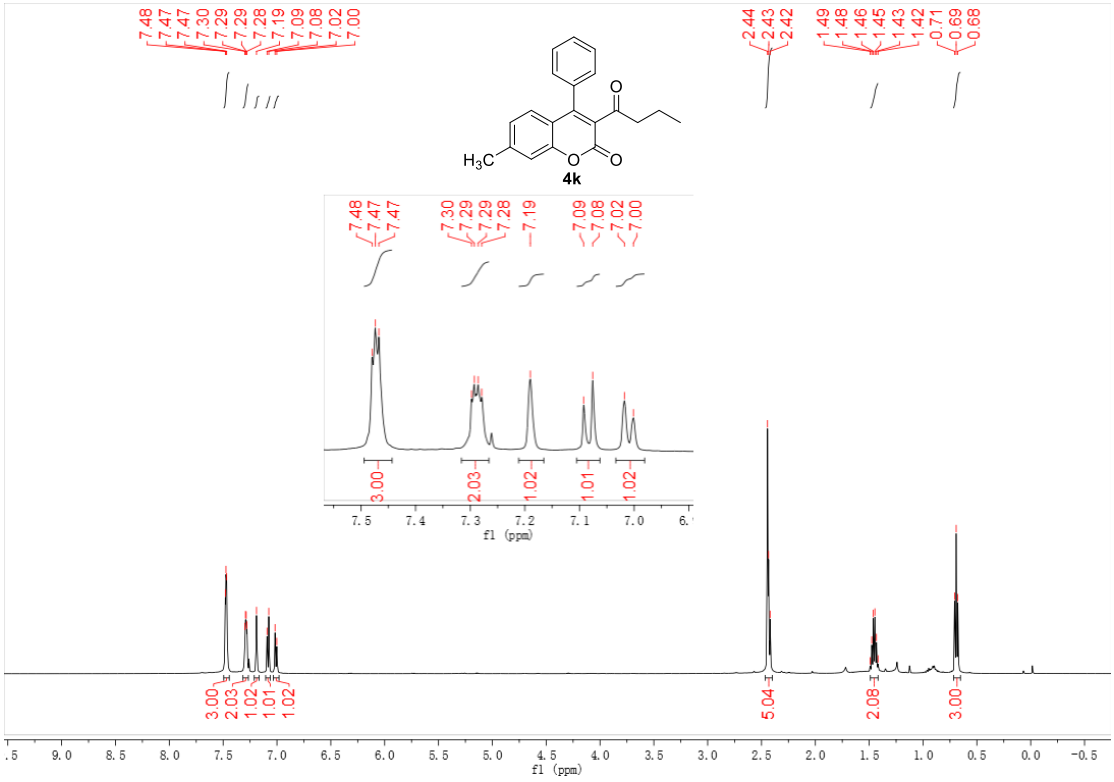

201.29
158.40
153.44
150.40
136.33
133.04
129.30
128.32
127.75
125.75
125.72
124.88
119.09
117.26
45.54
29.73
16.64
13.36
CF3
O
O
O
4h
f1 (ppm)

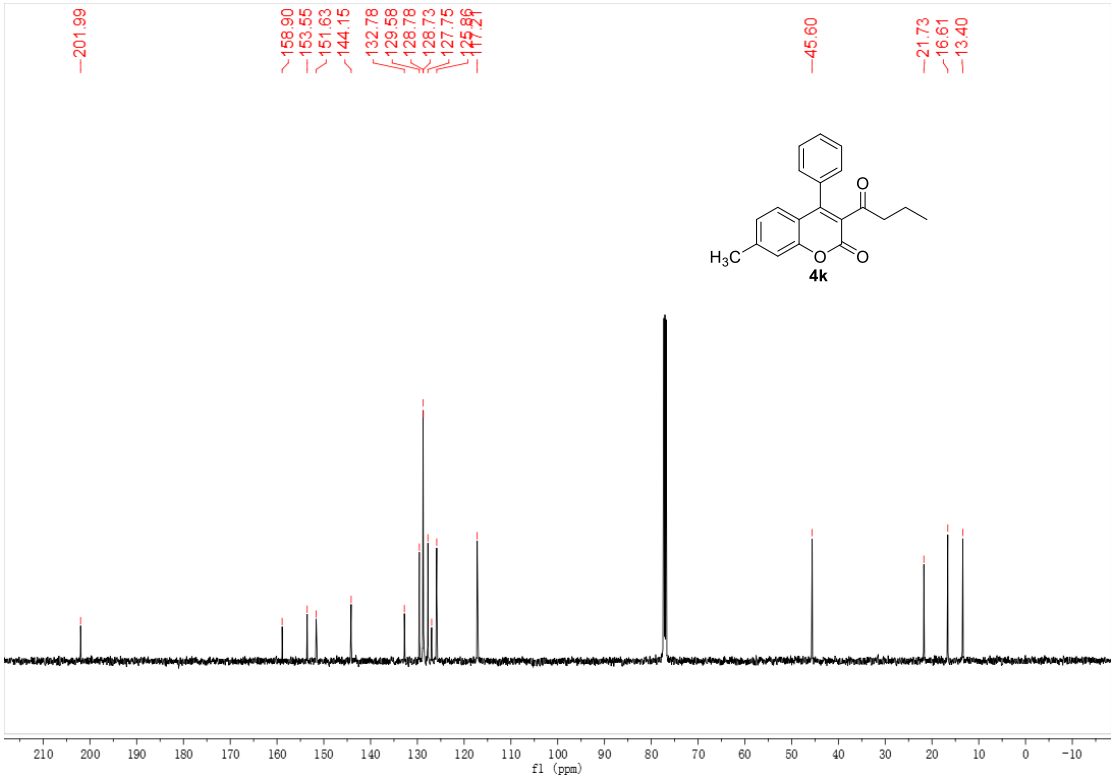

7.56
7.55
7.53
7.38
7.37
7.29
7.28
7.25
7.21
7.20
7.18
2.44
2.44
2.43
2.43
2.42
1.49
1.48
1.47
1.45
1.44
0.73
0.72
0.71
0.70
0.70
H3C
O
O
O
4i
1.01
1.01
3.11
3.03
5.00
2.07
3.01
f1 (ppm)

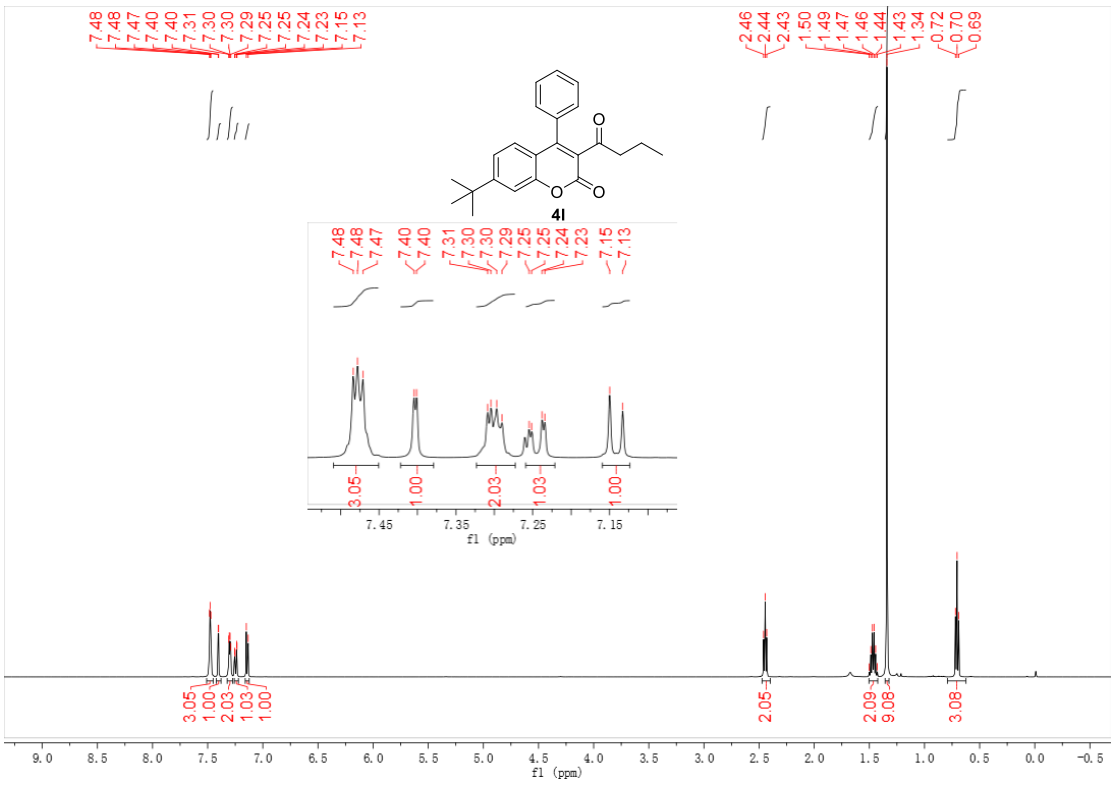

202.01
158.70
153.43
151.63
139.86
132.54
129.48
128.76
128.09
127.90
124.58
119.61
117.04
45.54
21.43
16.61
13.42
H3C
O
O
O
4i
f1 (ppm)

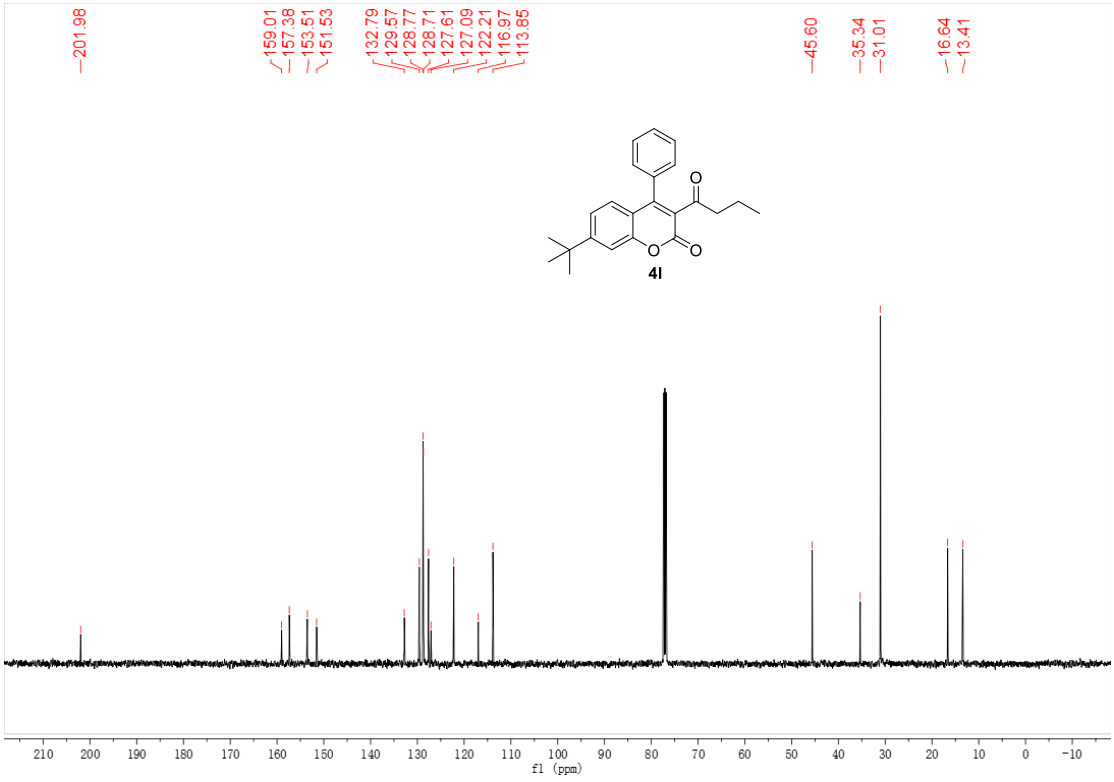

7.62
7.62
7.60
7.59
7.59
7.45
7.44
7.42
7.42
7.33
7.32
7.31
7.31
7.27
7.25
7.24
7.07
7.06
7.05
7.05
6.93
6.91
6.88
3.86
2.52
2.50
2.49
2.48
1.57
1.55
1.54
1.52
1.51
1.49
0.78
0.76
0.75
H3CO
O
O
O
4j
1.00
1.89
1.03
1.08
0.96
0.93
0.92
3.09
2.07
2.08
3.07
f1 (ppm)

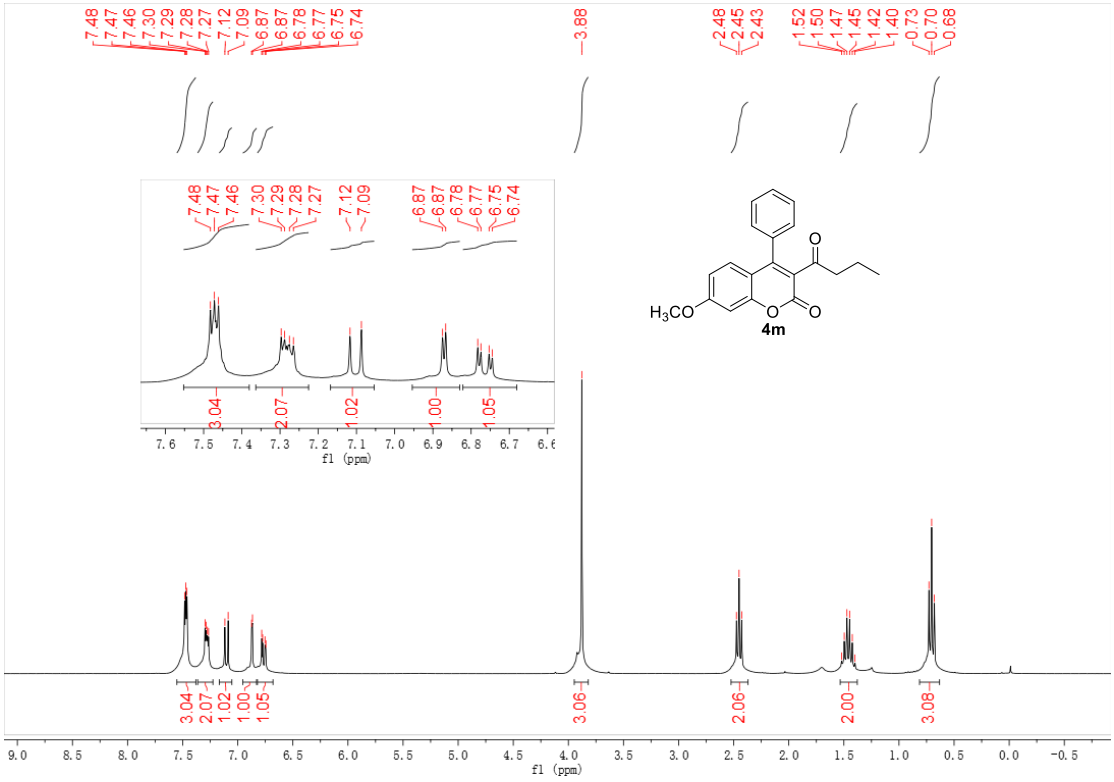

201.77
159.71
158.62
153.41
151.19
133.70
132.63
130.01
128.06
127.89
124.66
121.04
119.36
117.04
115.29
114.50
55.45
45.50
29.72
16.57
13.40
H3CO
O
O
O
4j
f1 (ppm)

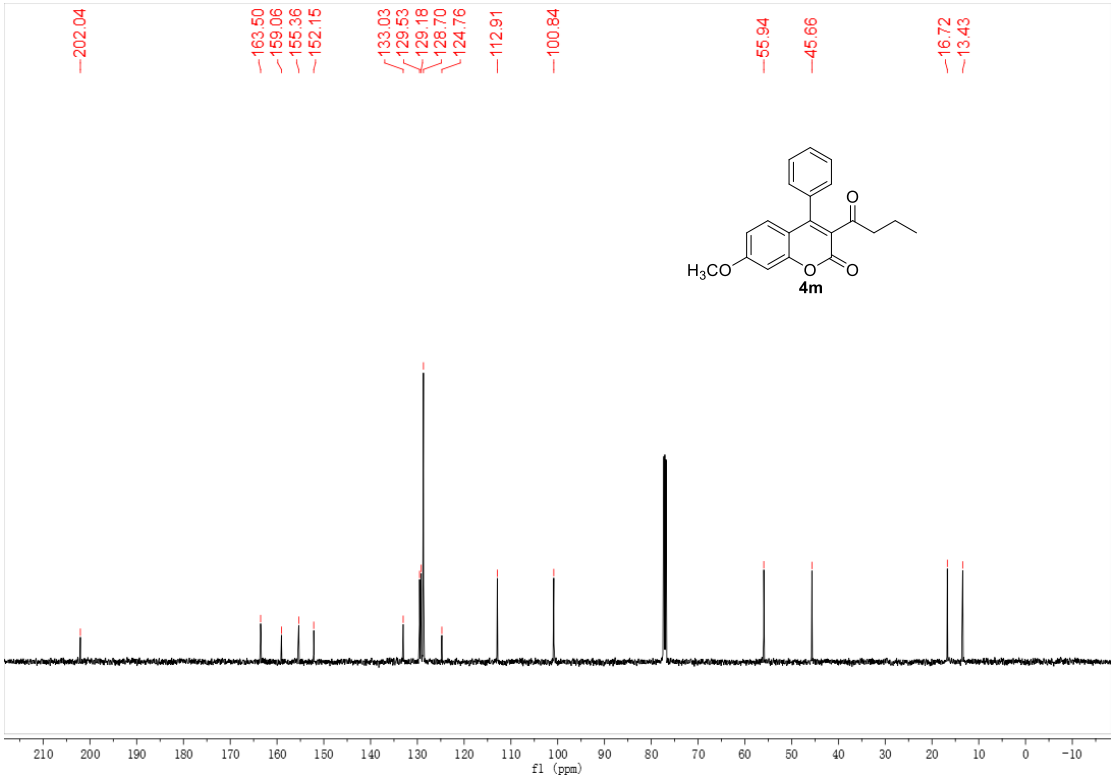

7.48
7.47
7.47
7.30
7.29
7.29
7.28
7.19
7.09
7.08
7.02
7.00
2.44
2.43
2.42
1.49
1.48
1.46
1.45
1.43
1.42
0.71
0.69
0.68
H3C
O
O
O
4k
3.00
2.03
1.02
1.01
1.02
5.04
2.08
3.00
f1 (ppm)

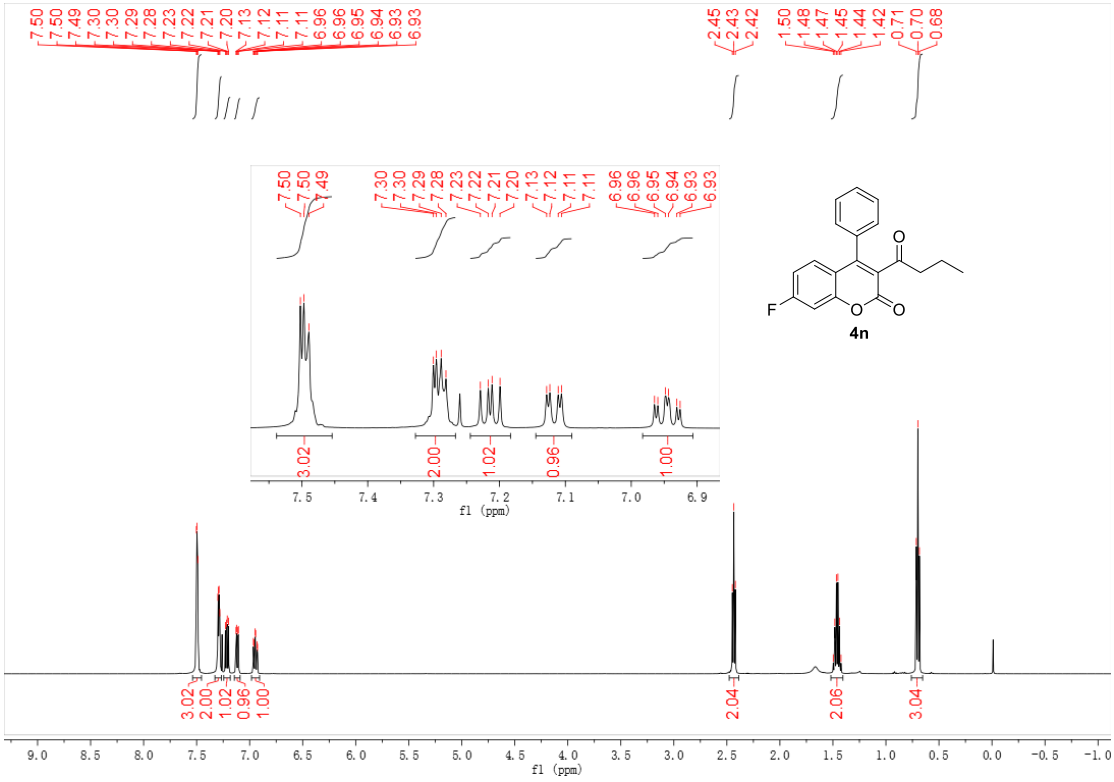

201.99
158.90
153.55
151.63
144.15
132.78
129.58
128.78
128.73
127.75
117.21
45.60
21.73
16.61
13.40
H3C
O
O
O
4k
f1 (ppm)

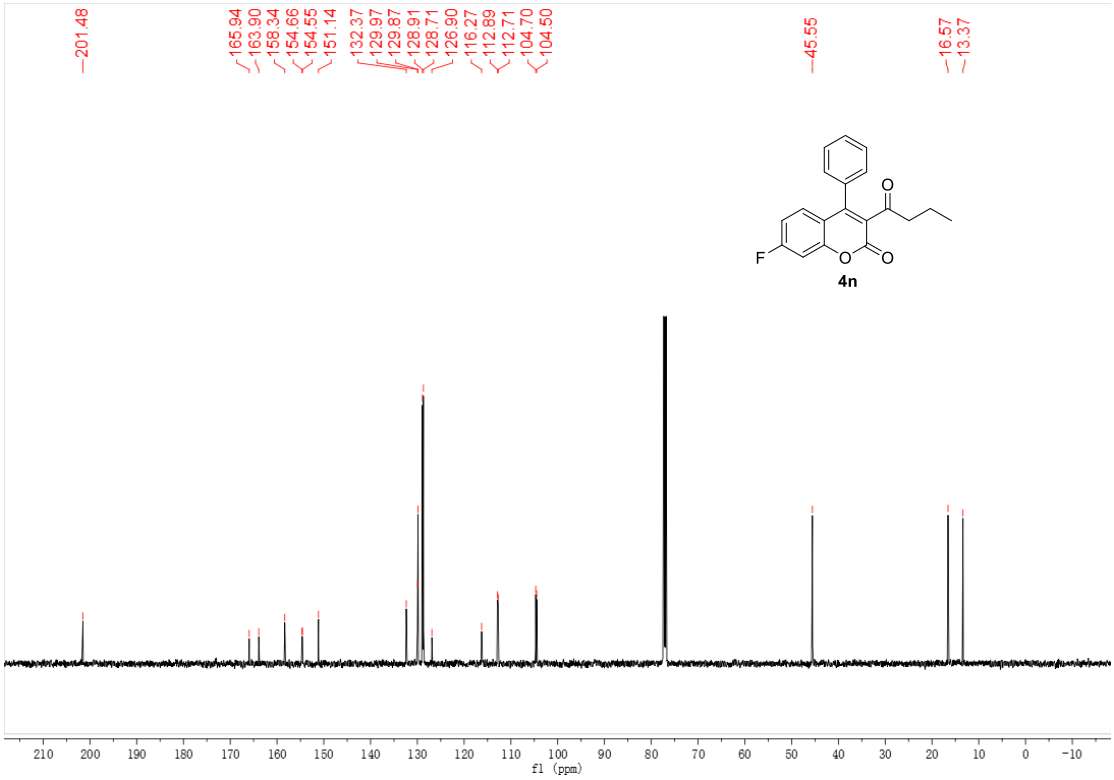

7.48
7.48
7.47
7.40
7.40
7.31
7.30
7.30
7.29
7.25
7.25
7.24
7.23
7.15
7.13
2.46
2.44
2.43
1.50
1.49
1.47
1.46
1.44
1.43
1.34
0.72
0.70
0.69
O
O
O
4l
3.05
1.00
2.03
1.03
1.00
7.45
7.35
7.25
7.15
f1 (ppm)
3.05
1.00
2.03
1.03
1.00
2.05
2.09
9.08
3.08
f1 (ppm)

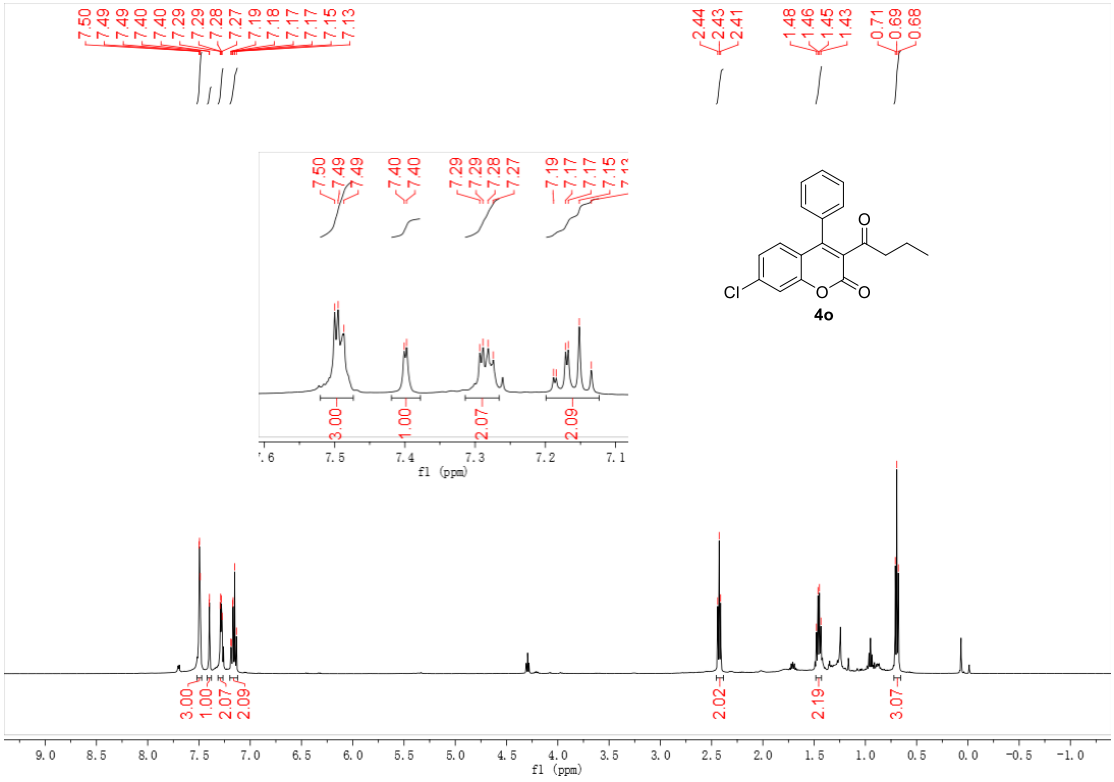

201.98
159.01
157.38
153.51
151.53
132.79
129.57
128.77
128.71
127.61
127.09
122.21
116.97
113.85
45.60
35.34
31.01
16.64
13.41
O
O
O
4l
f1 (ppm)

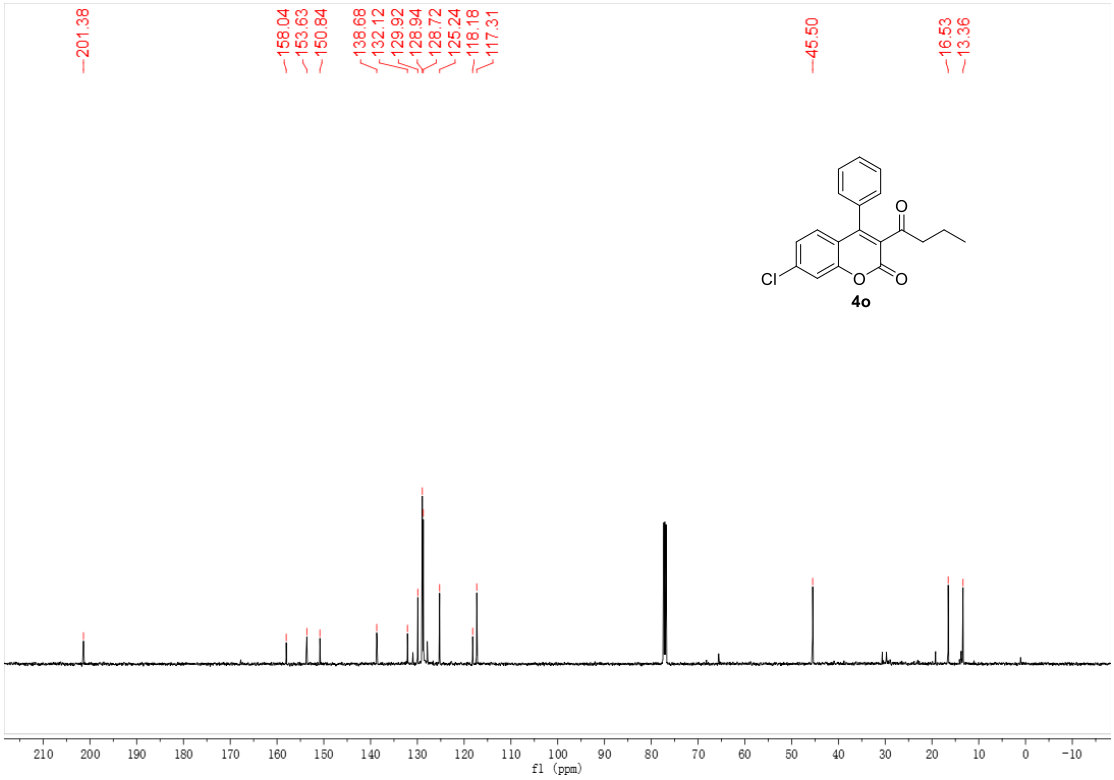

7.48
7.47
7.46
7.30
7.29
7.28
7.27
7.12
7.09
6.87
6.87
6.78
6.77
6.75
6.74
3.88
2.48
2.45
2.43
1.52
1.50
1.47
1.45
1.42
1.40
0.73
0.70
0.68
3.04
2.07
1.02
1.00
1.05
f1 (ppm)
H3CO
O
O
O
4m
3.04
2.07
1.02
1.00
1.05
3.06
2.06
2.00
3.08
f1 (ppm)

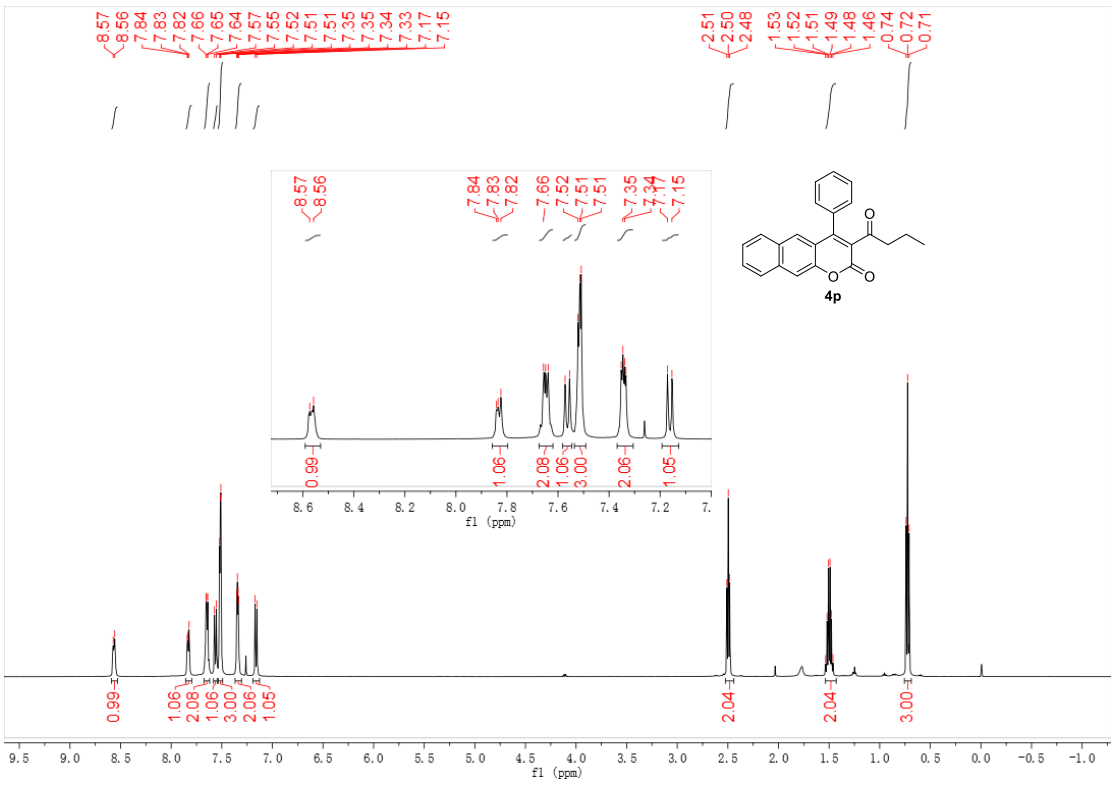

202.04
163.50
159.06
155.36
152.15
133.03
129.53
129.18
128.70
124.76
112.91
100.84
55.94
45.66
16.72
13.43
H3CO
O
O
O
4m
f1 (ppm)

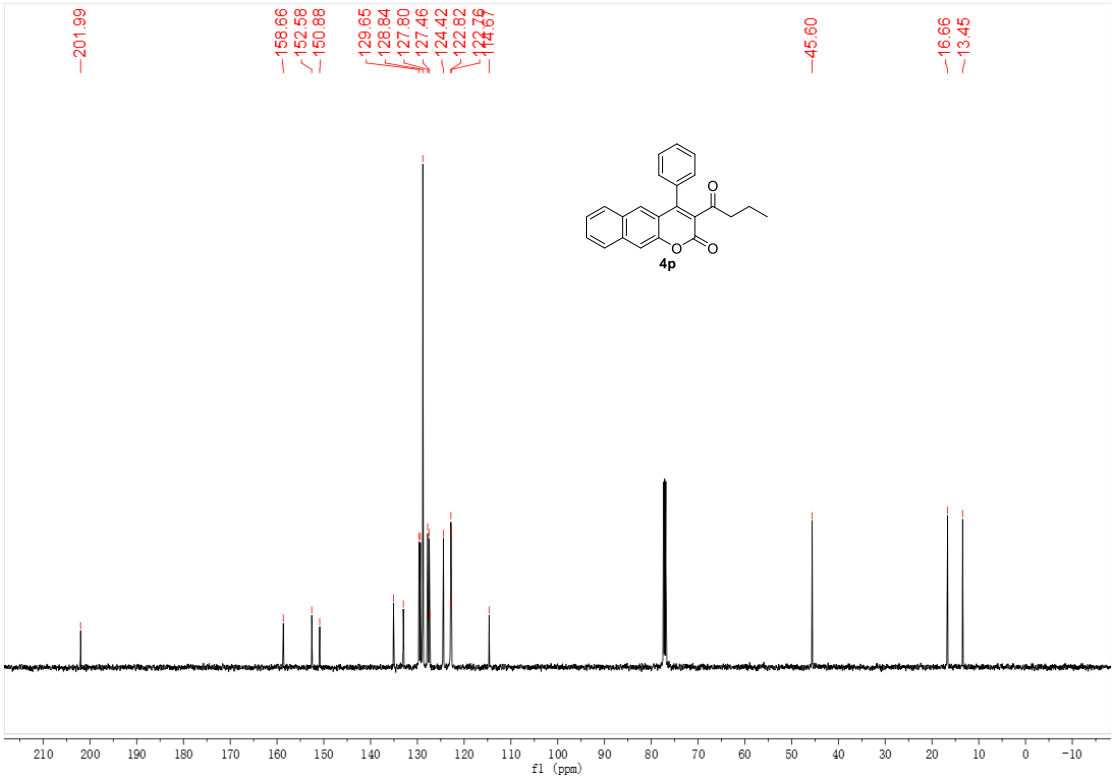

7.50 7.50 7.49 7.30 7.30 7.29 7.28 7.23 7.22 7.21 7.20 7.13 7.12 7.11 7.11 6.96 6.96 6.95 6.94 6.93 6.93
2.45 2.43 2.42
1.50 1.48 1.47 1.45 1.44 1.42
0.71 0.70 0.68
3.02 2.00 1.02 0.96 1.00
f1 (ppm)
4n
3.02 2.00 1.02 0.96 1.00
2.04 2.06 3.04
f1 (ppm)


201.48
165.94 163.90 158.34 154.66 154.55 151.14 132.37 129.97 129.87 128.91 128.71 126.90 116.27 112.89 112.71 104.70 104.50
45.55
16.57 13.37
4n
f1 (ppm)


7.50
7.49
7.49
7.40
7.40
7.29
7.29
7.28
7.27
7.19
7.18
7.17
7.17
7.15
7.13
2.44
2.43
2.41
1.48
1.46
1.45
1.43
0.71
0.69
0.68
3.00
1.00
2.07
2.09
f1 (ppm)
Cl
O
O
O
4o
3.00
1.00
2.07
2.09
2.02
2.19
3.07
f1 (ppm)


201.38
158.04
153.63
150.84
138.68
132.12
129.92
128.94
128.72
125.24
118.18
117.31
45.50
16.53
13.36
Cl
O
O
O
4o
f1 (ppm)


8.57
8.56
7.84
7.83
7.82
7.66
7.65
7.64
7.57
7.55
7.52
7.51
7.51
7.35
7.35
7.34
7.33
7.17
7.15
2.51
2.50
2.48
1.53
1.52
1.51
1.49
1.48
1.46
0.74
0.72
0.71
4p
0.99
1.06
2.08
1.06
3.00
2.06
1.05
2.04
2.04
3.00
f1 (ppm)


201.99
158.66
152.58
150.88
129.65
128.84
127.80
127.46
124.42
122.82
122.76
114.97
45.60
16.66
13.45
4p
f1 (ppm)