

Supporting Information

Visible-Light-Induced Acylation/Cyclization of Alkynoates with Acyl Oximes for the Construction of 3- Acylcoumarins

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List of Contents

1. General Information	S1
2. Experimental Section	S1-S3
2.1 General Procedure for the Synthesis of Substrates	S1
2.2 Typical Experimental Procedure	S1-S2
2.3 Figure S1: Profile of 3aa with Light on or off over Time	S2
2.4 Radical trapping Experiments	S3-S7
3. Reference	S7
4. ¹H and ¹³C spectra	S8-S49

1. General Information

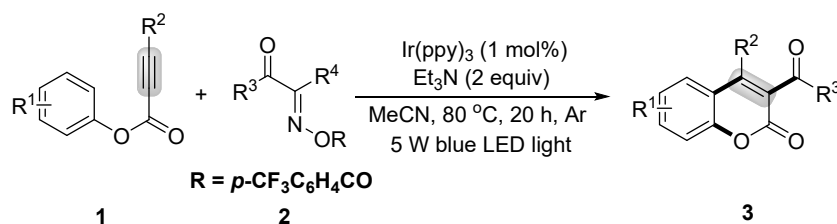
Unless otherwise stated, all commercial reagents were used as received. Acetylenic acid (BK, 99%), ketones (Innochem, >98%) and phenol (Innochem, >98%) were used without further treatment. All reagents and solvents were commercially available and used without any further purification unless specified. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (0.25mm, 300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25mm 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). All reactions were carried out with magnetic stirring and in dried glassware. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. The solvent peak was used as a reference value, for ^1H NMR: TMS = 0.00 ppm, for ^{13}C NMR: CDCl_3 = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experiment Section

2.1 General Procedure for the Synthesis of Substrates

All alkynoates **1** and acyl oxime esters **2**²⁻³ were synthesized according to the known methods.

2.2 Typical Experimental Procedure



To a Schlenk tube were added alkynoates **1** (0.2 mmol, 0.1 M), acyl oxime esters **2** (0.3 mmol, 1.5 equiv), Ir(ppy)₃ (1 mol%), Et₃N (0.4 mmol, 2 equiv) and MeCN (2 mL) at 80 °C under irradiation of 5 W blue light for 20 h. Until complete consumption of the starting material was observed by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 10 : 1) to provide the desired products **3**. A scaled-up experiment conducted in the presence of **1a** (5 mmol), **2a** (7.5 mmol, 1.5 equiv), Ir(ppy)₃ (0.05 mmol, 1 mol%), Et₃N (10 mmol, 2 equiv) and MeCN (50 mL) at 80 °C under irradiation of 5 W blue light for 120 h gave the target product **3aa** in 73% yield.

2.3 Figure S1: Profile of **3aa** with Light on or off over Time

Alternatively, a light on/off experiment was conducted between alkynoate **1a** and acyl oxime ester **2a** under the standard conditions. However, this reaction stopped when the light irradiation was turned off. These results verified the necessity of continuous irradiation of visible light (Figure S1).

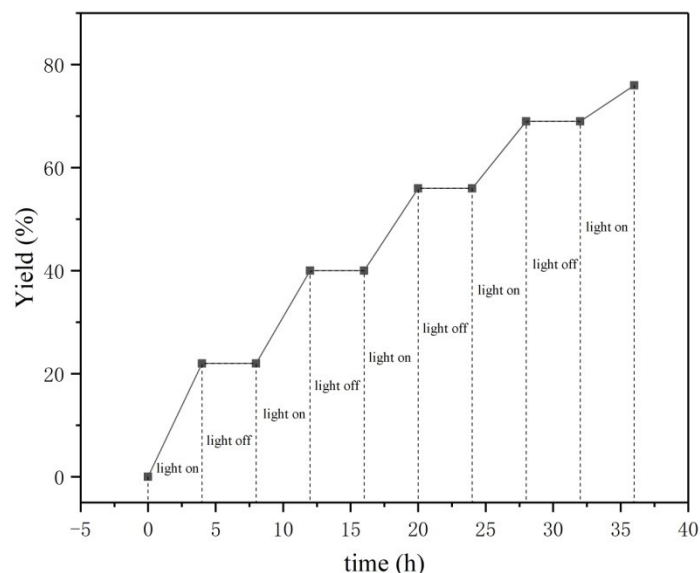
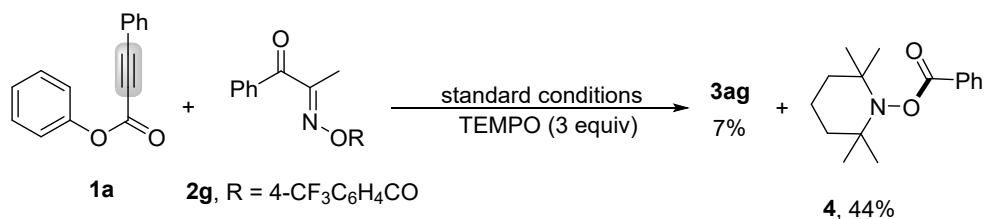


Figure S1. Profile of **3aa** with Light on or off over Time. GC yield using biphenyl as an internal standard.

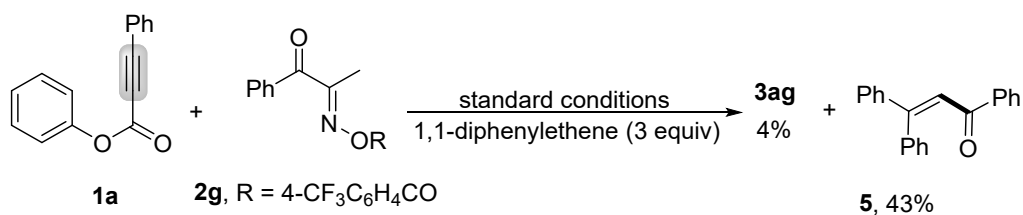
2.4 Radical Trapping Experiments

2.4.1 Using TEMPO as Radical Inhibitor



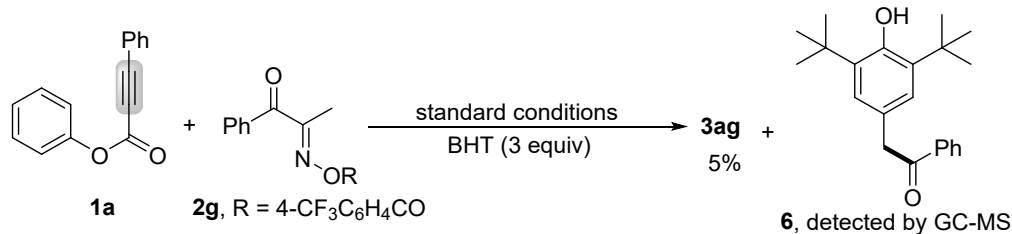
To a Schlenk tube were added alkynoate **1a** (0.2 mmol, 0.1 M), acyl oxime esters compounds **2g** (1.5 equiv), Ir(ppy)₃ (1 mol%), Et₃N (2 equiv), TEMPO (3 equiv) and MeCN (2 mL) at 80 °C under irradiation of 5 W blue light for 20 h. The GC-MS analysis of raw reaction mixture showed that onyl 7% yield of target product **3ag** was detected. The benzoyl-trapping products **4** could be obtained in 44% yield.

2.4.2 Using 1,1-diphenylethene as Radical Inhibitor



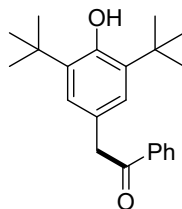
To a Schlenk tube were added alkynoate **1a** (0.2 mmol, 0.1 M), acyl oxime esters compounds **2g** (1.5 equiv), Ir(ppy)₃ (1 mol%), Et₃N (2 equiv), 1,1-diphenylethene (3 equiv) and MeCN (2 mL) at 80 °C under irradiation of 5 W blue light for 20 h. The GC-MS analysis of raw reaction mixture showed that onyl 4% yield of target product **3ag** was detected. The benzoyl-trapping products **5** could be obtained in 43% yield.

2.4.3 Using BHT as Radical Inhibitor



To a Schlenk tube were added alkynoate **1a** (0.2 mmol, 0.1 M), acyl oxime esters compounds **2g** (1.5 equiv), Ir(ppy)₃ (1 mol%), Et₃N (2 equiv), BHT (3 equiv) and MeCN (2 mL) at 80 °C under irradiation of 5 W blue light for 20 h. The GC-MS

analysis of raw reaction mixture showed that only 5% yield of target product **3ag** was detected. Additionally, the benzoyl-trapping products **6** could be detected by GC-MS analysis of raw reaction mixture.



6, detected by GC-MS

Chemical Formula: $C_{22}H_{28}O_2$

Exact Mass: 324.21

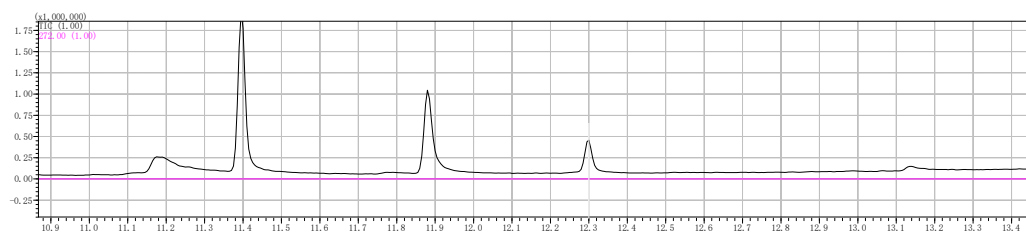
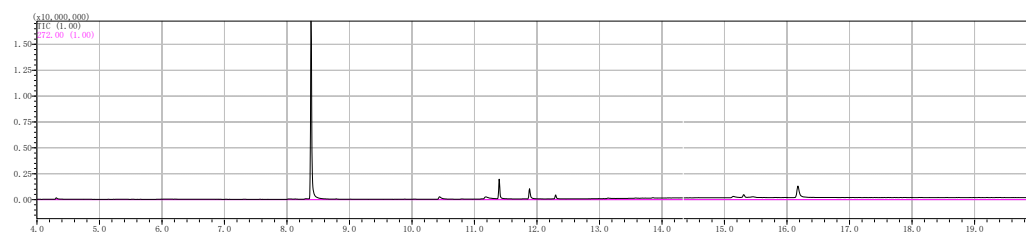
Molecular Weight: 324.46

m/z: 324.21 (100.0%), 325.21 (23.9%), 326.22 (2.8%)

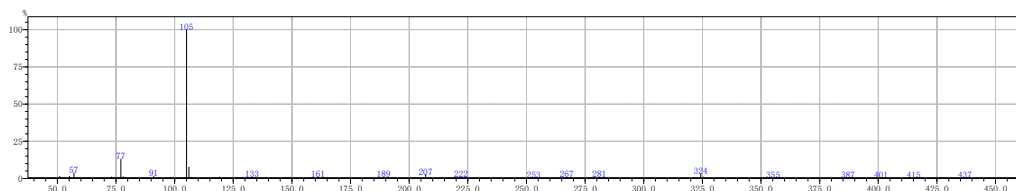
Elemental Analysis: C, 81.44; H, 8.70; O, 9.86

GC-MS analysis of raw reaction mixture by using BHT as radical inhibitor

GC spectra



MS spectra of the peak at 12.300 min



[MS Spectrum]	92.10	334	0.13	144.10	213	0.08
# of Peaks	273	93.10	476	0.19	145.10	10640.42
Raw Spectrum	12.300 (scan : 1661)	94.95	259	0.10	146.15	460 0.18
		97.10	41	0.02	147.15	316 0.13
Background	12.250 (scan : 1651)	100.10	36	0.01	148.10	437 0.17
		101.10	18	0.01	149.10	847 0.34
Base Peak	m/z 105.10 (Inten : 250,674)	102.10	165	0.07	150.10	40 0.02
		103.15	369	0.15	152.10	12 0.00
Event#	1	104.15	1432	0.57	153.10	208 0.08
m/z	Absolute Intensity	105.10	250674	100.00	154.10	91 0.04
	Relative Intensity	106.10	18755	7.48	155.15	284 0.11
50.00	590 0.24	107.10	1917	0.76	156.10	229 0.09
51.05	2994 1.19	108.10	138	0.06	157.10	64 0.03
52.05	172 0.07	109.10	110	0.04	158.10	116 0.05
53.00	762 0.30	110.10	107	0.04	159.00	242 0.10
55.05	2840 1.13	112.10	216	0.09	160.10	44 0.02
56.05	194 0.08	113.10	8	0.00	161.15	2691 1.07
57.05	8621 3.44	114.15	127	0.05	162.10	230 0.09
58.05	361 0.14	115.05	1253	0.50	163.20	386 0.15
59.00	957 0.38	116.15	596	0.24	164.15	51 0.02
62.00	18 0.01	117.10	642	0.26	165.05	319 0.13
62.90	164 0.07	118.15	300	0.12	167.10	19 0.01
65.05	665 0.27	119.15	20200.81		169.10	70 0.03
66.10	125 0.05	120.20	199	0.08	170.10	59 0.02
67.05	696 0.28	121.20	1270	0.51	171.10	122 0.05
68.05	112 0.04	122.10	234	0.09	172.10	67 0.03
69.05	709 0.28	123.30	409	0.16	173.20	381 0.15
70.10	256 0.10	124.30	28	0.01	174.10	95 0.04
71.05	107 0.04	125.30	32	0.01	175.10	353 0.14
72.05	369 0.15	126.10	61	0.02	176.00	111 0.04
75.00	134 0.05	127.10	350	0.14	177.00	399 0.16
76.15	1029 0.41	128.15	1402	0.56	180.00	2 0.00
77.05	32019 12.77	129.15	1209	0.48	181.00	35 0.01
78.05	2542 1.01	130.15	383	0.15	182.00	21 0.01
79.05	1491 0.59	131.10	831	0.33	183.00	54 0.02
80.00	1 0.00	132.10	198	0.08	184.00	1 0.00
81.05	37 0.01	133.10	1384	0.55	185.00	58 0.02
82.05	262 0.10	134.00	310	0.12	186.00	59 0.02
83.00	611 0.24	135.20	661	0.26	187.20	565 0.23
86.90	19 0.01	137.20	22	0.01	188.20	69 0.03
87.90	112 0.04	138.20	103	0.04	189.20	2136 0.85
88.90	118 0.05	141.10	907	0.36	190.15	482 0.19
90.10	54 0.02	142.10	295	0.12	192.05	328 0.13
91.10	2912 1.16	143.25	276	0.11	193.00	3 0.00

194.10	118	0.05	259.10	9	0.00	332.10	27	0.01
195.10	4	0.00	260.10	39	0.02	333.10	105	0.04
196.10	3	0.00	264.10	22	0.01	335.10	10	0.00
200.10	50	0.02	265.10	86	0.03	336.10	2	0.00
201.10	17	0.01	266.20	243	0.10	339.10	32	0.01
202.10	220	0.09	267.20	1012	0.40	340.10	10	0.00
203.15	442	0.18	268.25	268	0.11	341.20	321	0.13
204.10	488	0.19	269.20	2	0.00	343.20	70	0.03
205.20	555	0.22	270.20	28	0.01	345.20	78	0.03
206.10	51	0.02	272.20	46	0.02	346.20	29	0.01
207.05	840	0.34	273.20	60	0.02	348.20	13	0.01
209.00	30	0.01	275.20	5	0.00	349.20	66	0.03
210.00	21	0.01	276.20	5	0.00	351.20	4	0.00
211.00	141	0.06	277.20	53	0.02	353.20	90	0.04
212.00	46	0.02	278.20	36	0.01	354.20	47	0.02
215.00	40	0.02	279.20	34	0.01	355.25	65	0.03
217.00	94	0.04	281.10	236	0.09	358.30	107	0.04
218.00	36	0.01	282.20	317	0.13	359.30	10	0.00
219.10	372	0.15	287.00	23	0.01	360.30	3	0.00
220.10	204	0.08	289.00	83	0.03	362.30	8	0.00
221.15	218	0.09	291.00	150	0.06	363.30	25	0.01
222.10	13	0.01	297.00	61	0.02	367.30	10	0.00
223.10	182	0.07	298.00	32	0.01	368.30	16	0.01
224.10	51	0.02	299.00	3	0.00	369.30	96	0.04
230.10	46	0.02	300.00	5	0.00	372.30	106	0.04
232.10	61	0.02	303.00	4	0.00	374.30	5	0.00
235.10	72	0.03	305.00	8	0.00	376.30	19	0.01
236.10	106	0.04	307.00	52	0.02	381.30	6	0.00
237.10	72	0.03	309.00	58	0.02	387.10	212	0.08
239.10	60	0.02	317.00	15	0.01	390.10	1	0.00
243.10	26	0.01	318.00	32	0.01	391.10	51	0.02
244.10	16	0.01	319.00	10	0.00	395.10	9	0.00
245.10	13	0.01	320.00	3	0.00	397.10	30	0.01
246.10	36	0.01	321.00	31	0.01	399.10	61	0.02
247.10	68	0.03	322.00	1	0.00	402.20	17	0.01
248.10	56	0.02	323.30	79	0.03	403.20	10	0.00
250.10	107	0.04	324.30	69122.76		404.20	1	0.00
251.10	98	0.04	325.30	21250.85		405.20	39	0.02
252.10	116	0.05	326.15	235	0.09	406.20	21	0.01
253.15	388	0.15	327.10	110	0.04	408.20	8	0.00
254.10	99	0.04	328.10	15	0.01	409.20	14	0.01
255.10	15	0.01	329.10	42	0.02	410.20	19	0.01
256.10	76	0.03	330.10	24	0.01	411.20	53	0.02
257.10	25	0.01	331.10	9	0.00	412.20	3	0.00

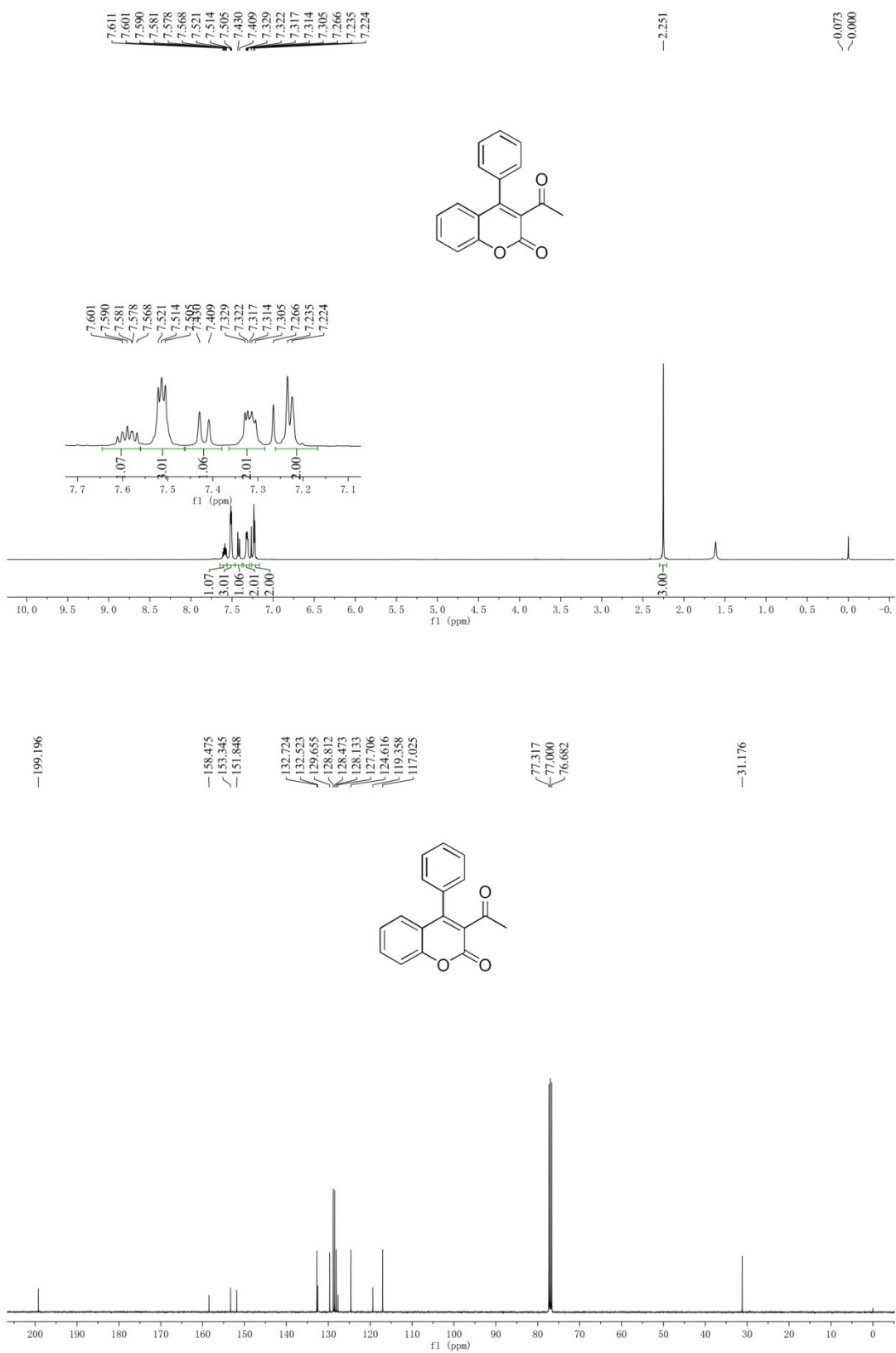
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415.10	40	0.02	431.00	27	0.01	439.00	3	0.00
416.10	26	0.01	432.00	17	0.01	445.00	24	0.01
417.00	248	0.10	433.00	52	0.02	446.00	23	0.01
418.00	1	0.00	434.00	5	0.00	447.00	39	0.02
420.00	7	0.00	435.00	25	0.01	448.0	14	0.01
421.00	11	0.00	436.00	30	0.01			

3. References

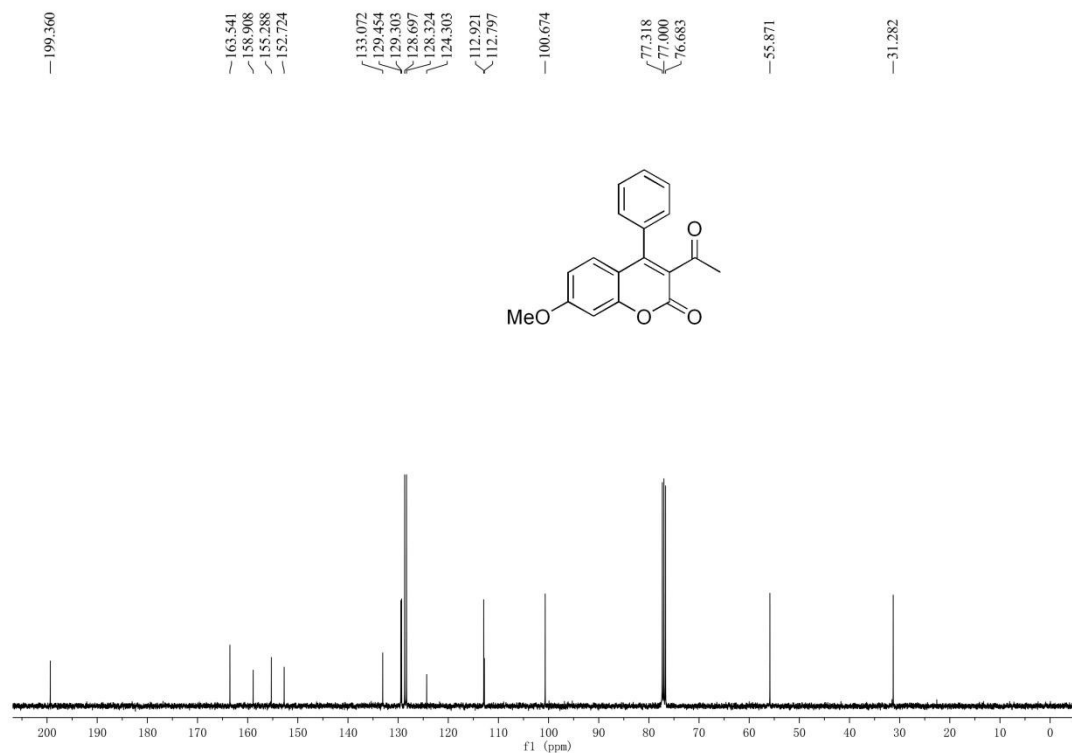
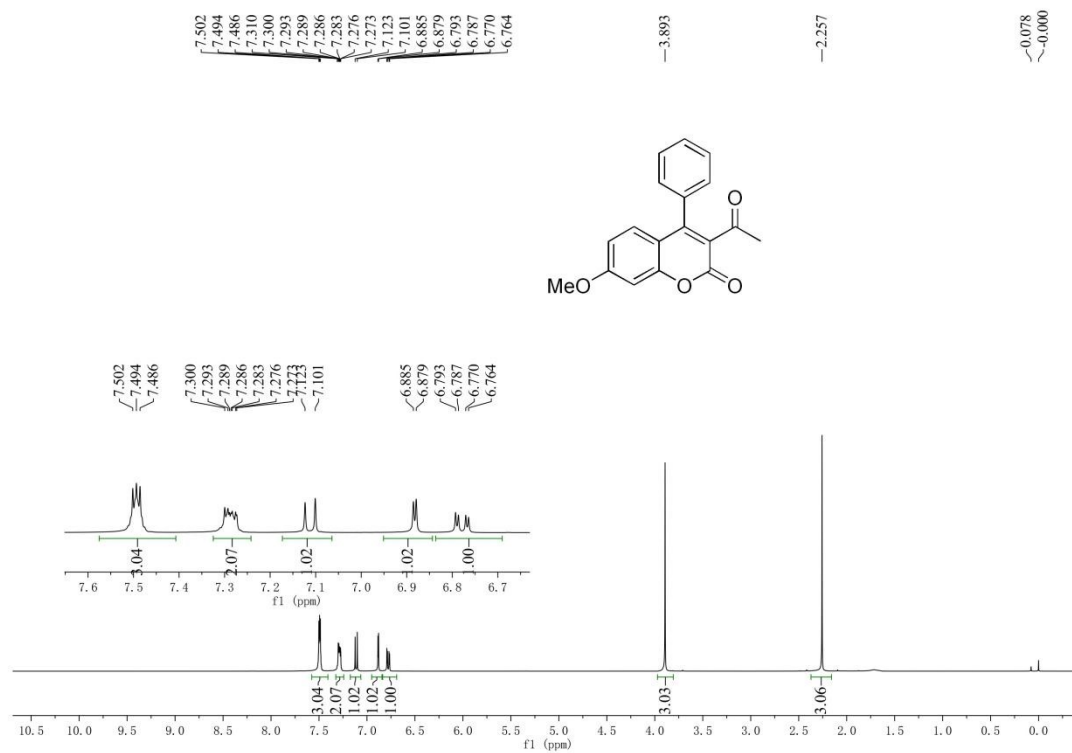
- [1] H. Li, S. Liu, Y.-G. Huang, X.-H. Xu, F.-L. Qing. Tang, *Chem. Commun.*, 2017, **53**, 10136.
- [2] P. Chen, J. Xie, Z. Chen, B.-Q. Xiong, Y. Liu, C.-A. Yang and K.-W. Tang, *Adv. Synth. Catal.*, 2021, doi: 10.1002/adsc.202100852.
- [3] X. Fan, T. Lei, B. Chen, C.-H. Tung and L.-Z. Wu, *Org. Lett.*, 2019, **21**, 4153.

4. Spectra

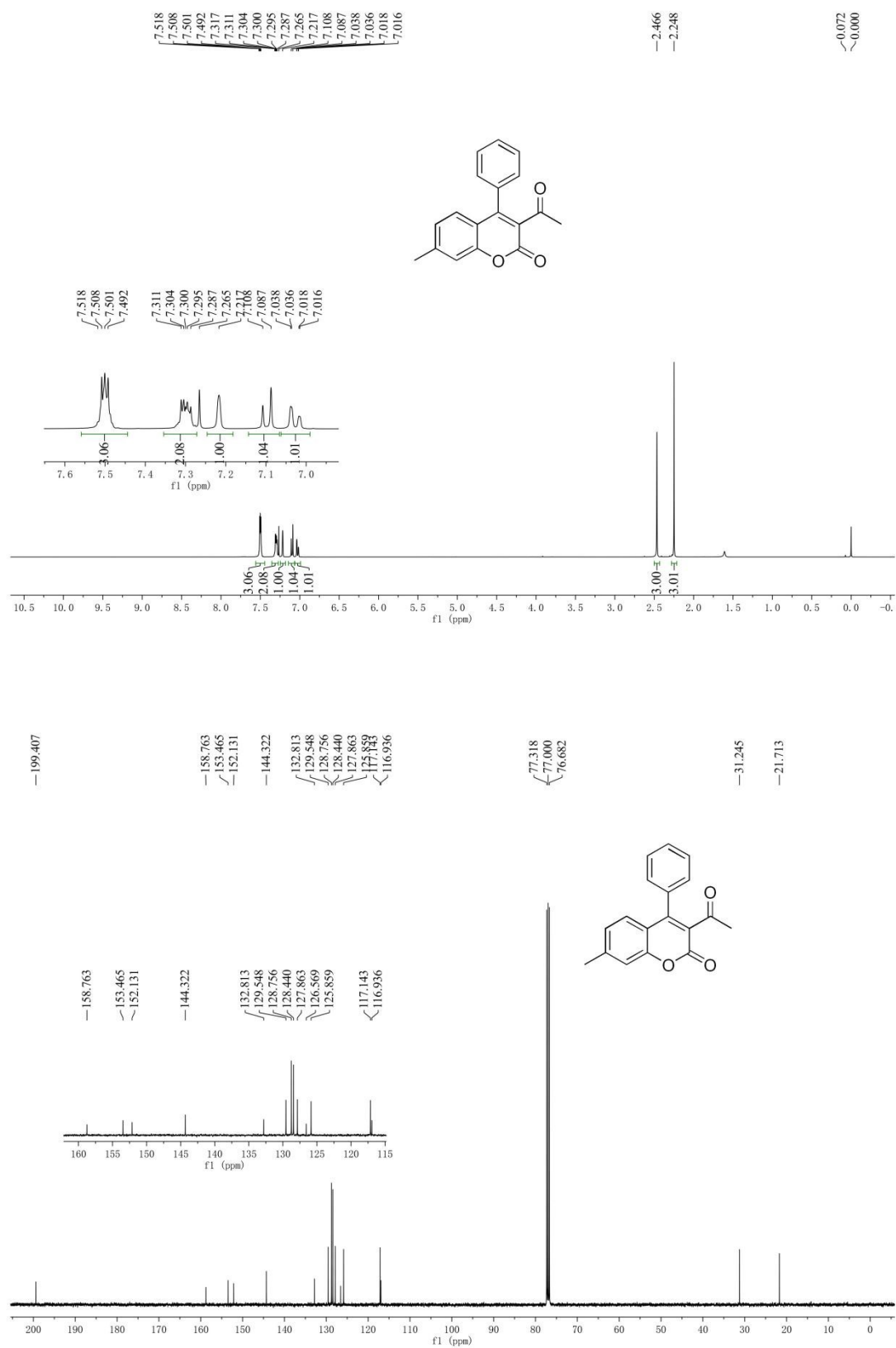
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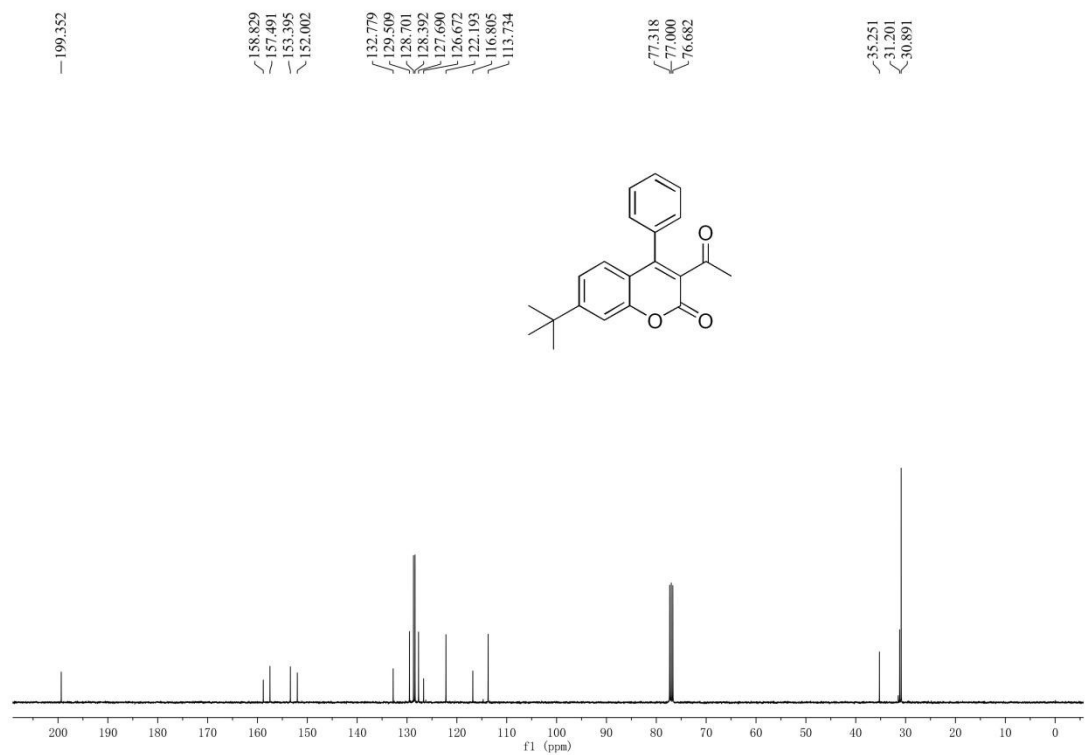
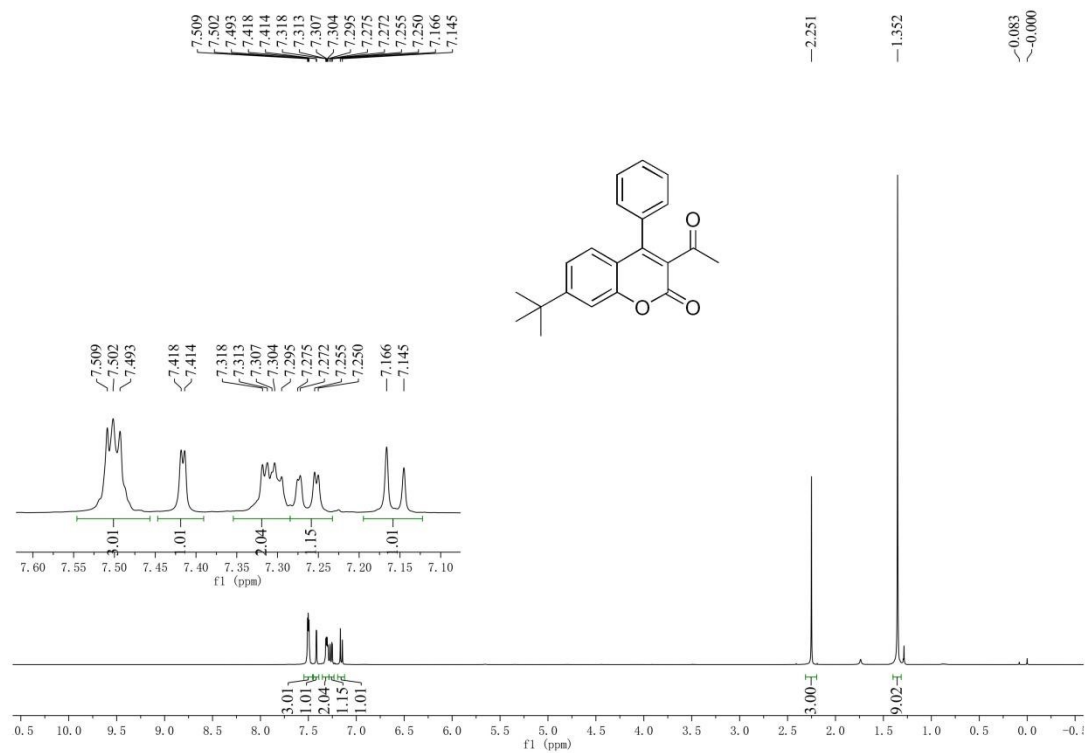
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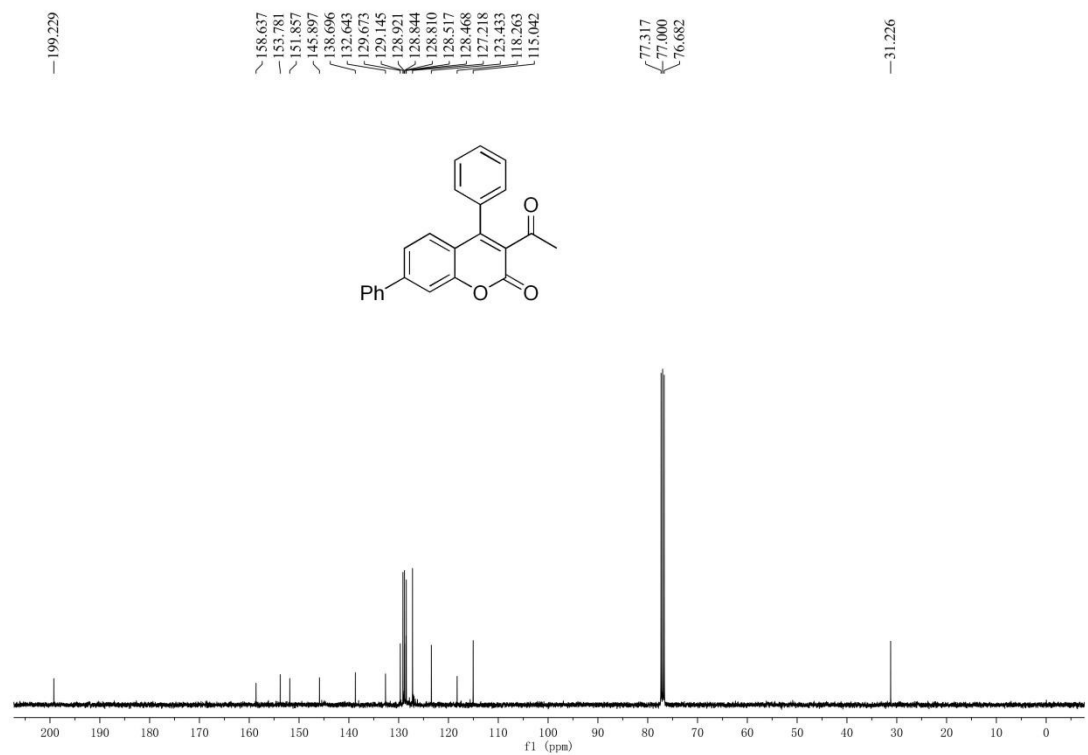
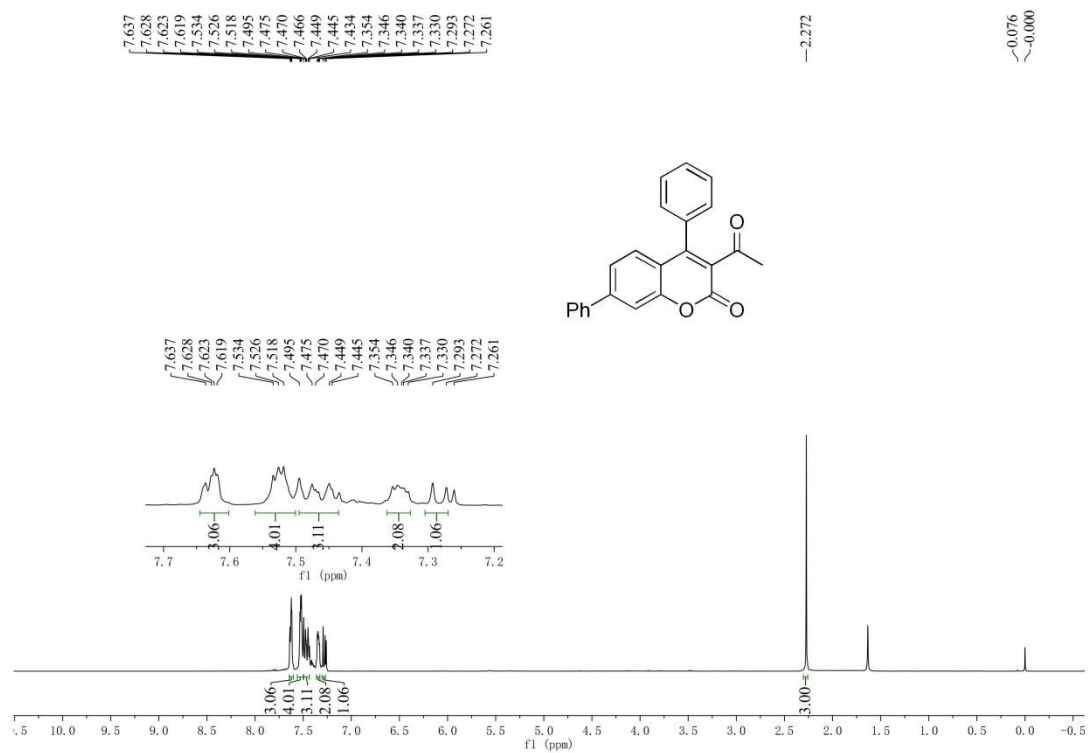
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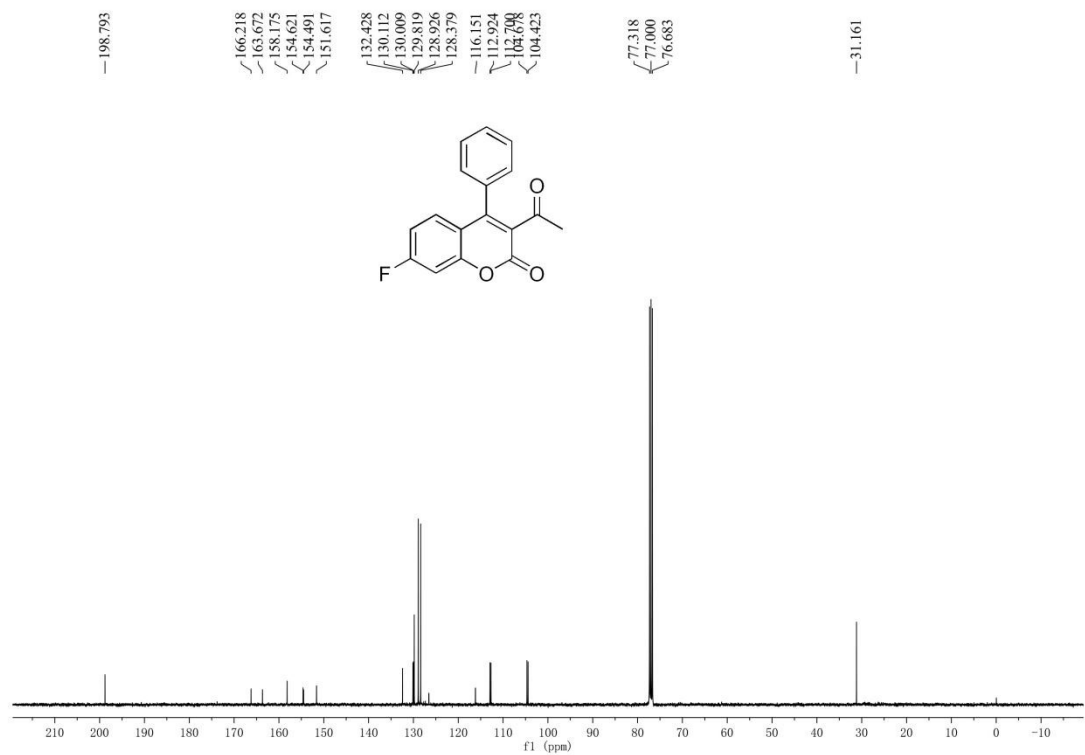
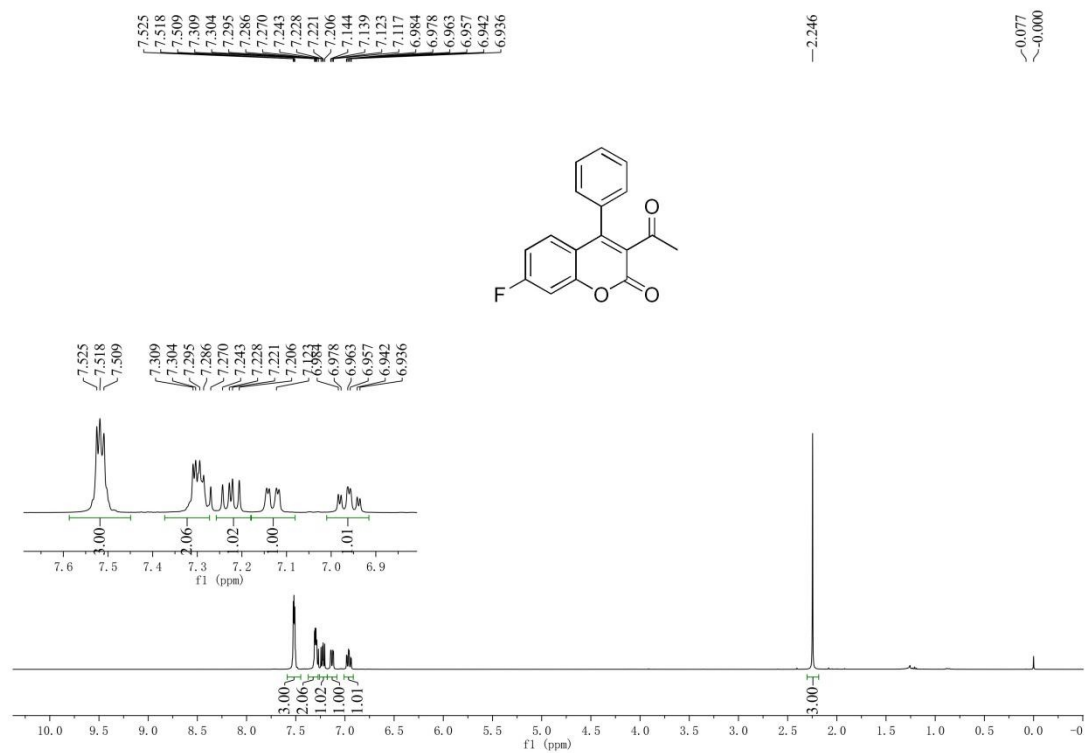
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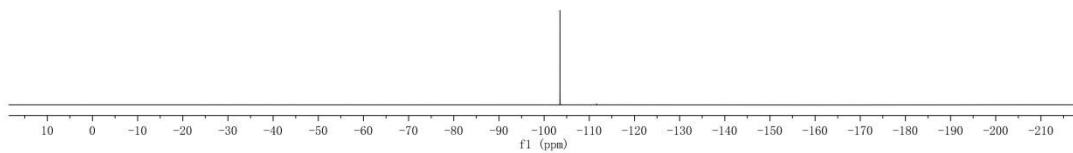
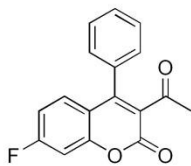
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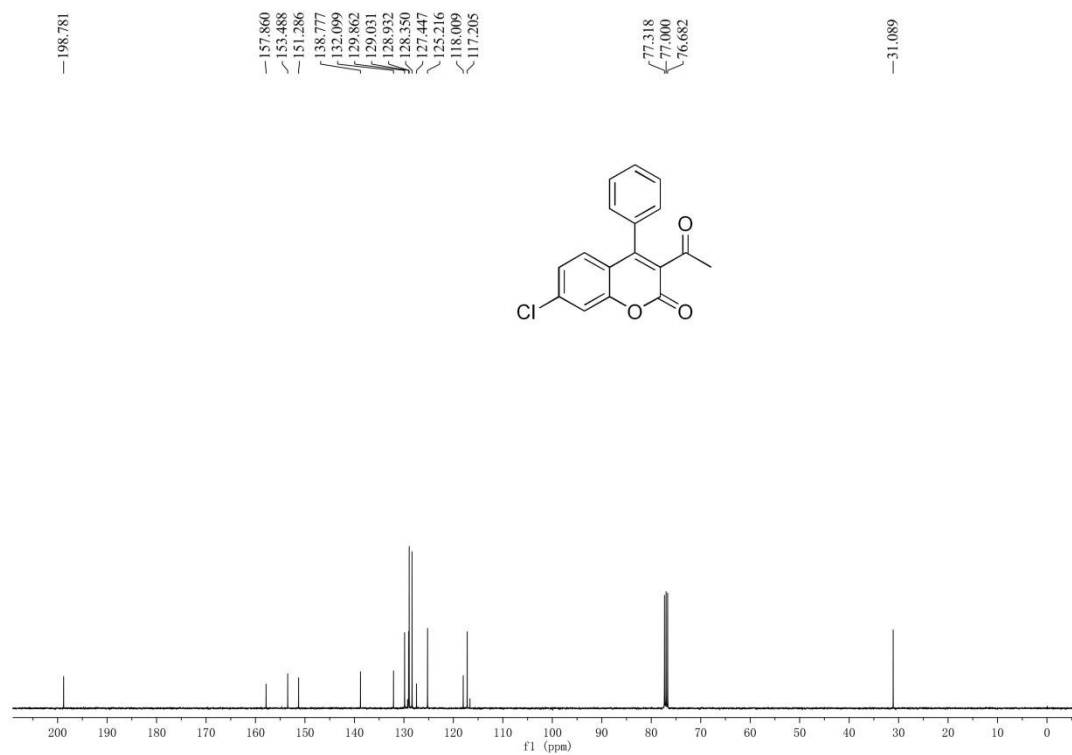
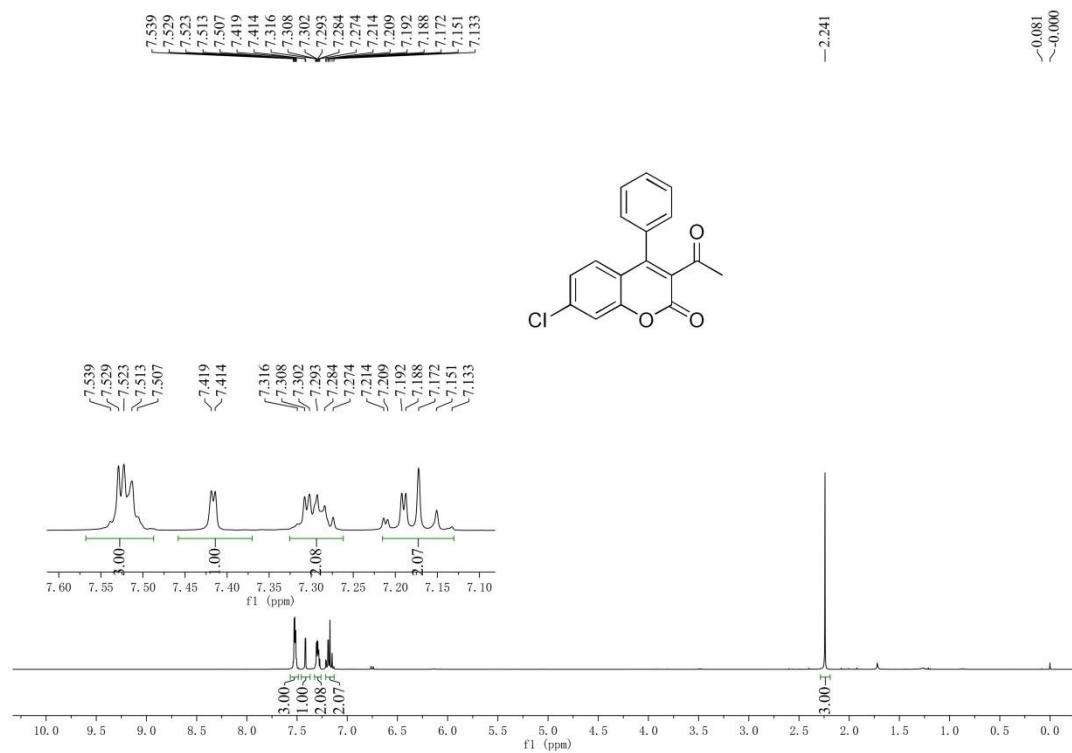
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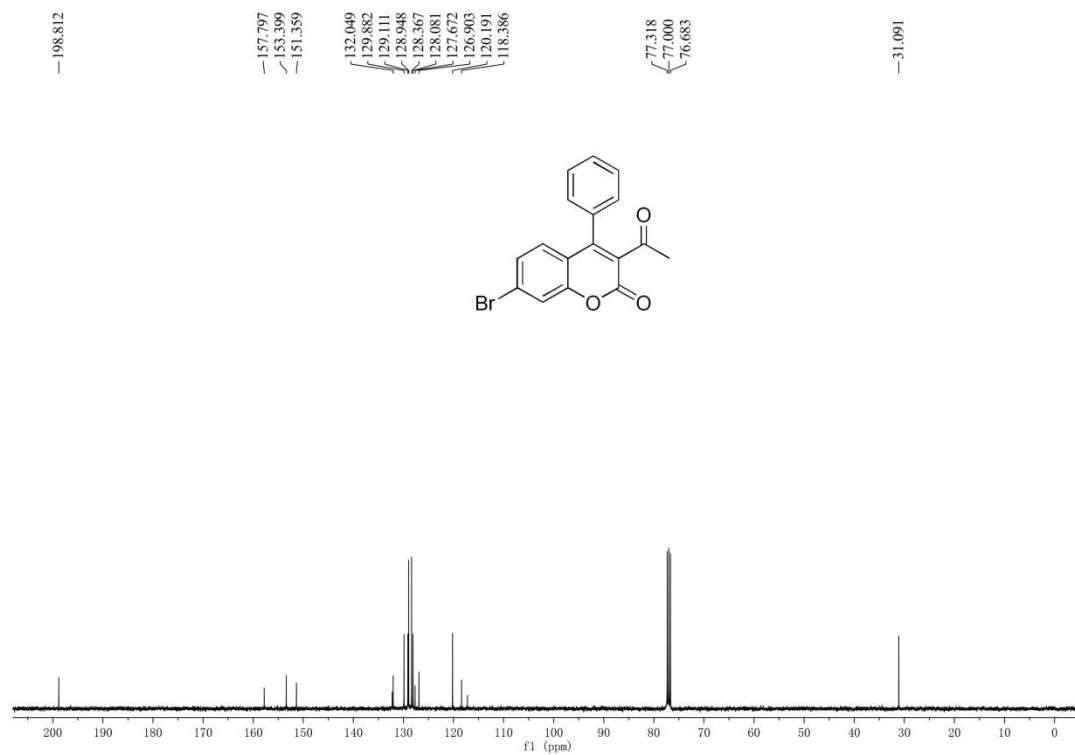
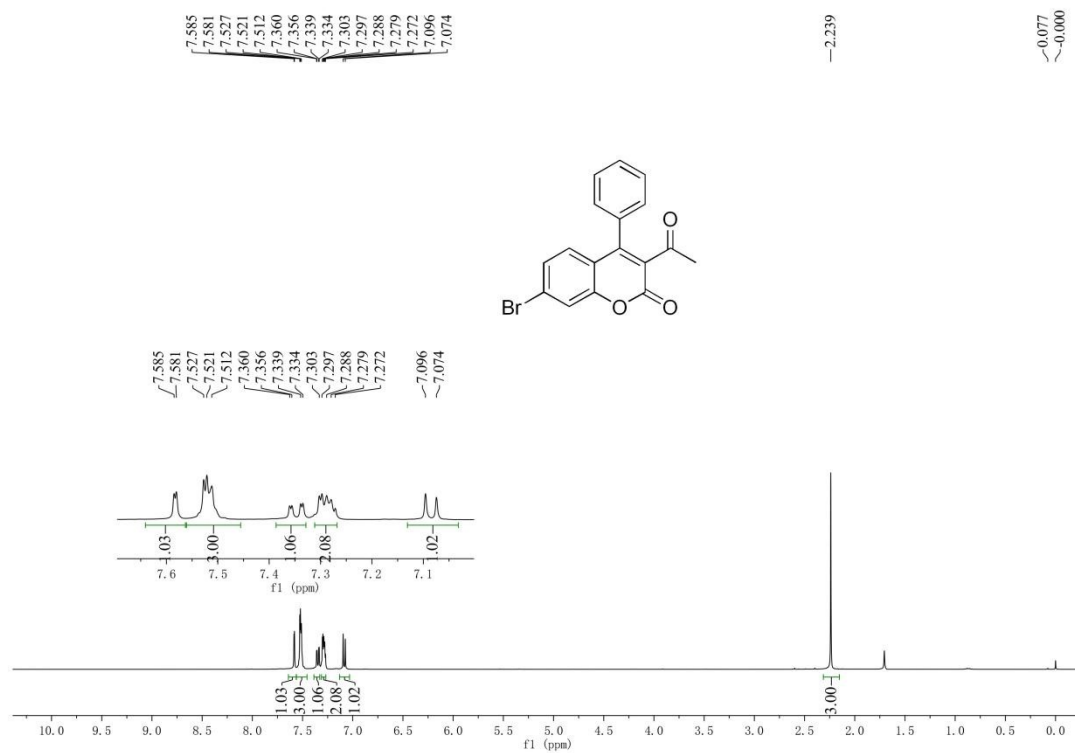
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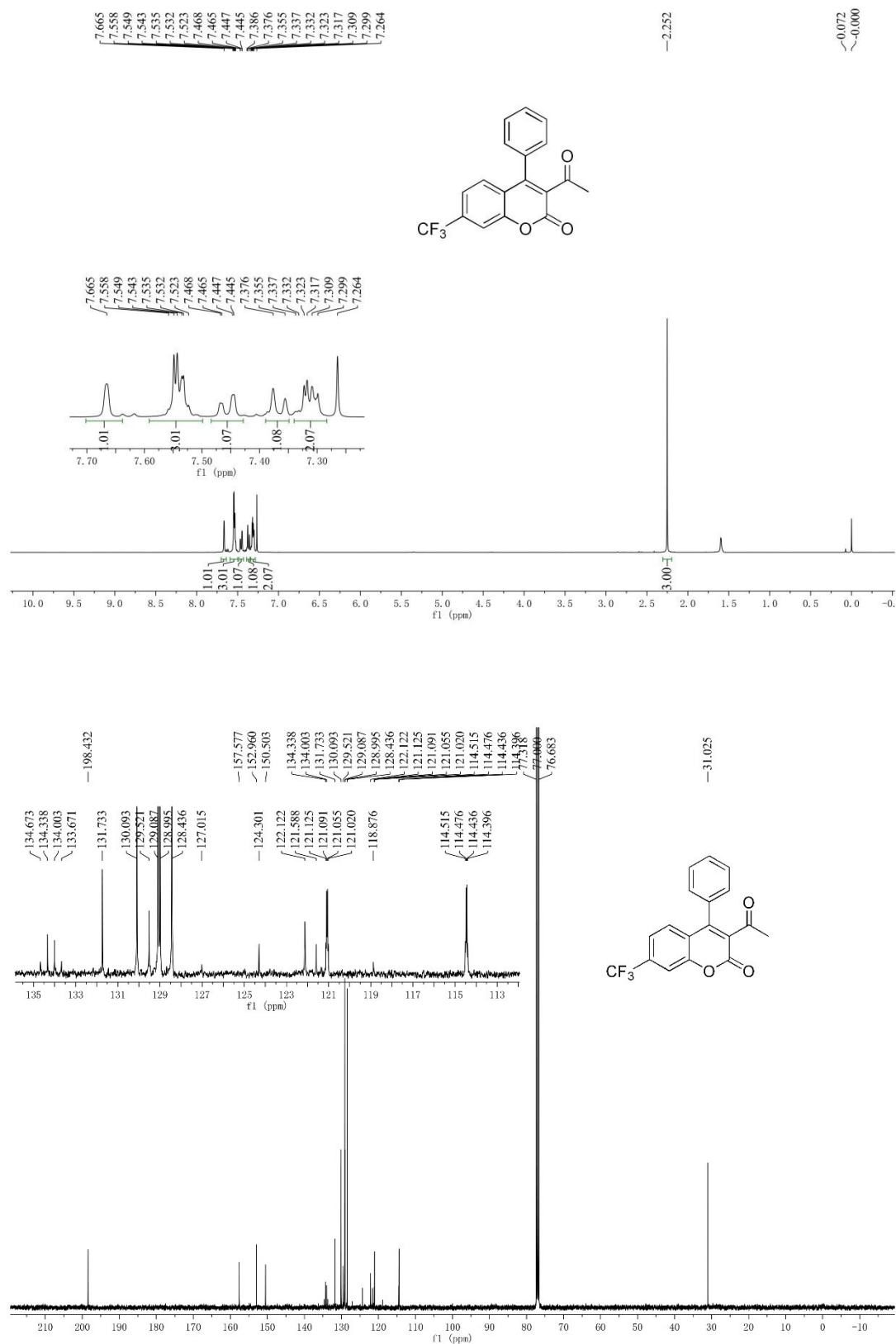
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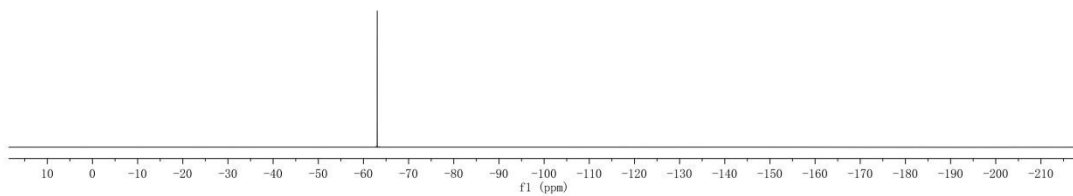
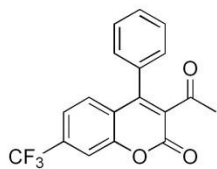
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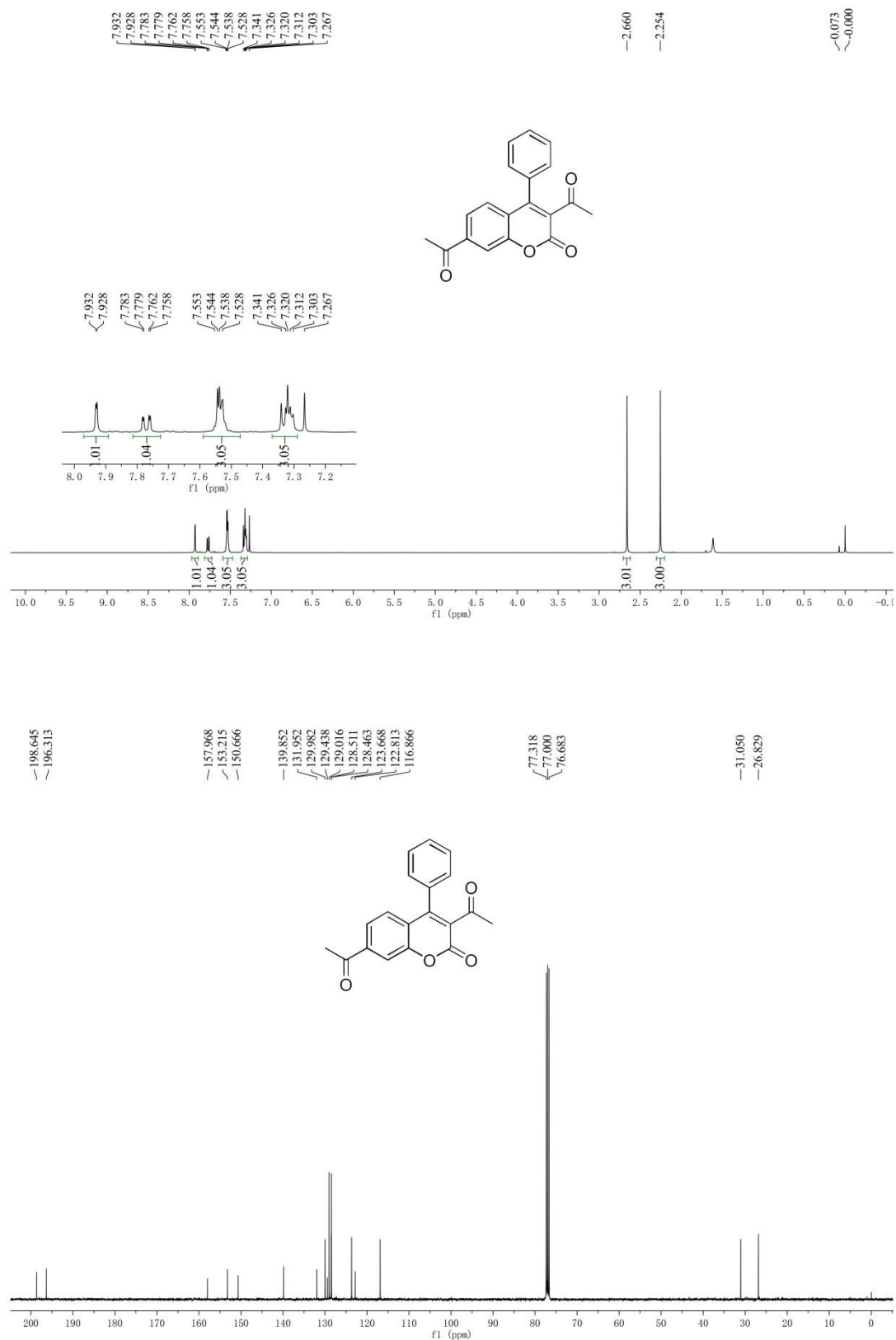
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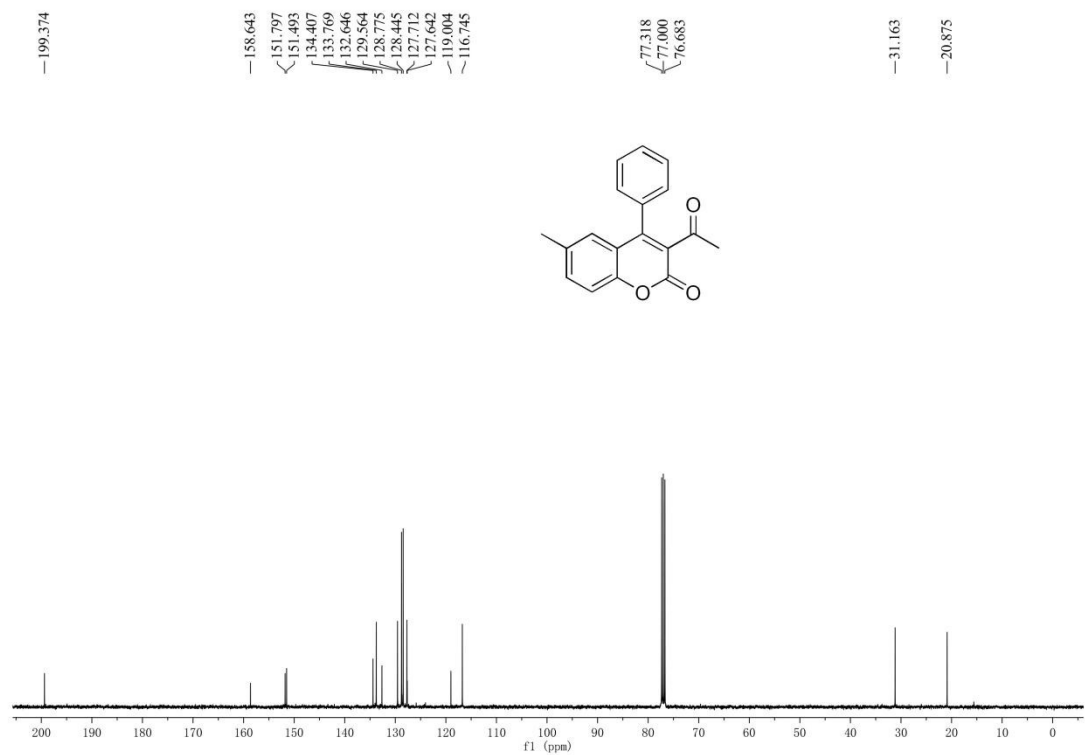
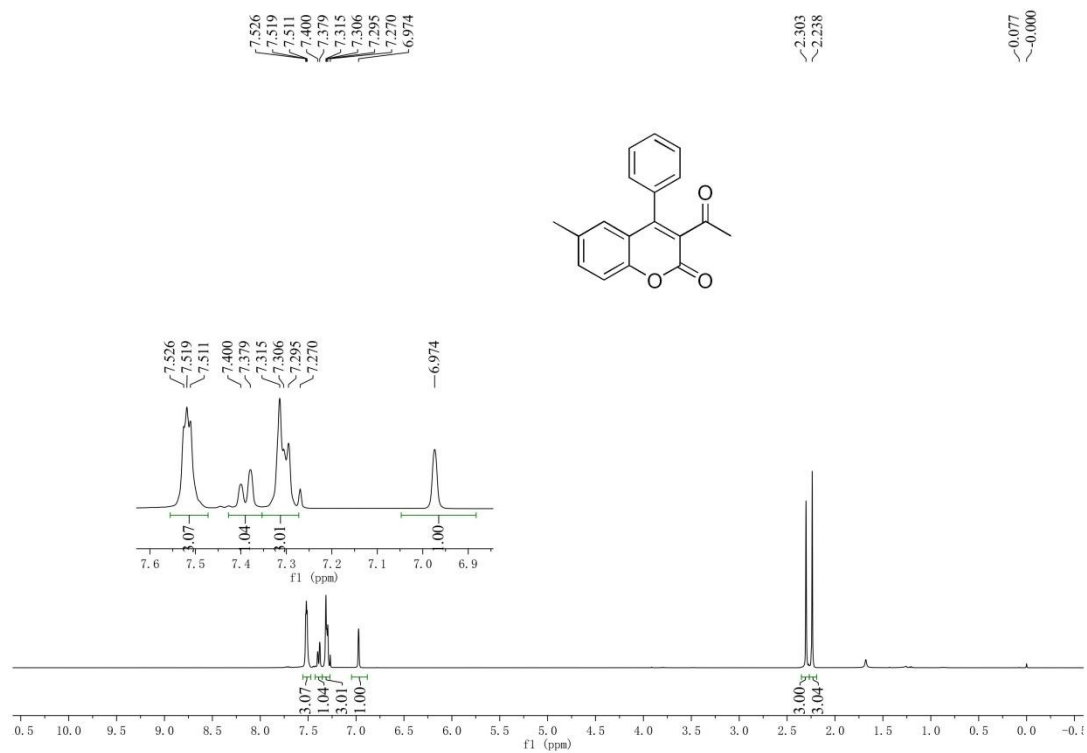
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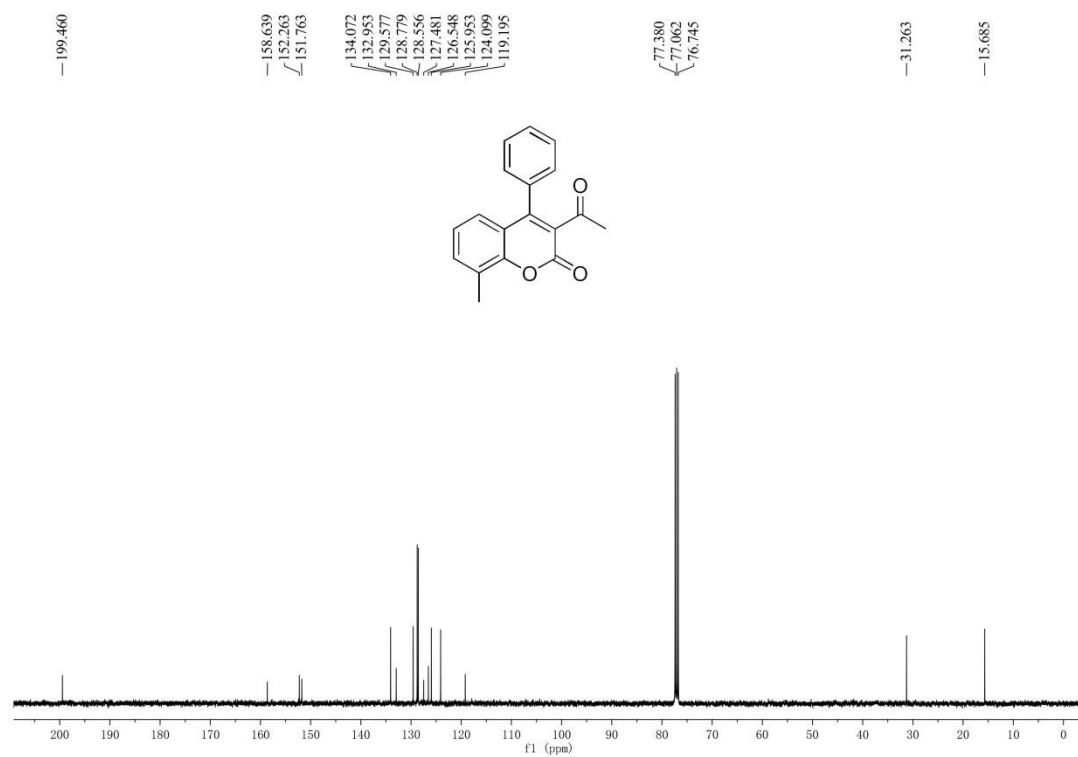
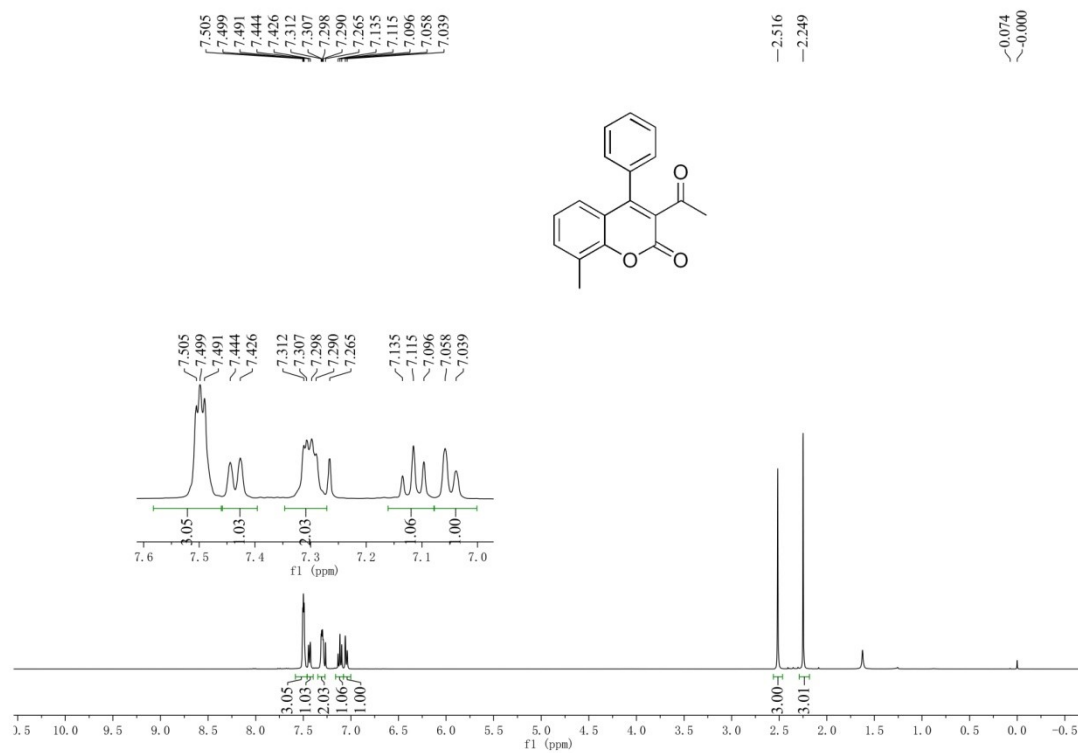
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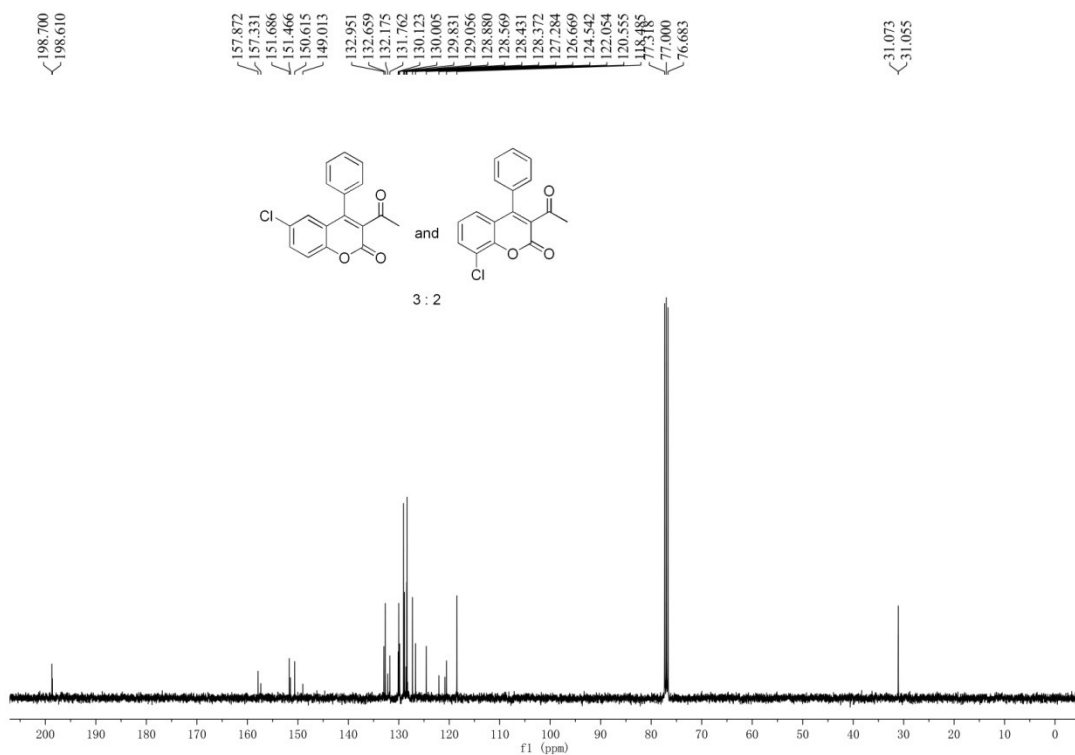
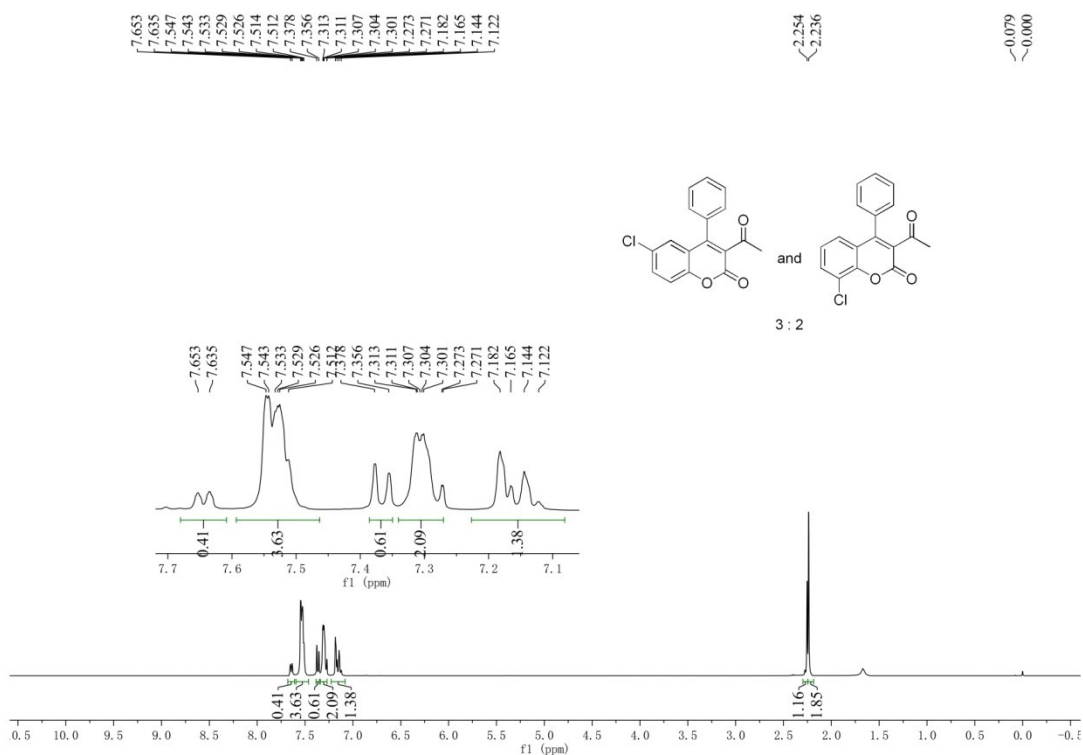
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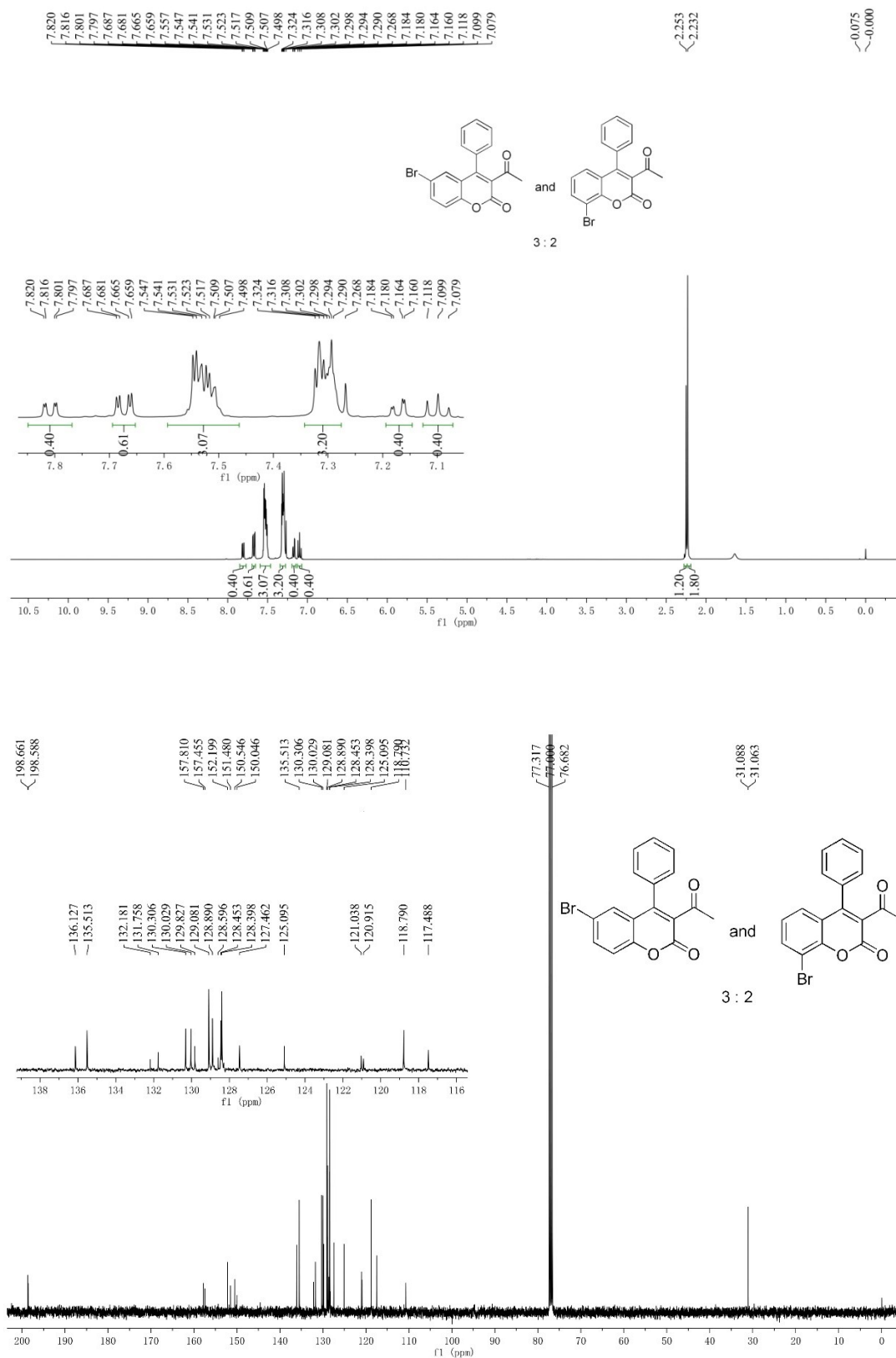
3-Acetyl-8-methyl-4-phenyl-2H-chromen-2-one (3ka')



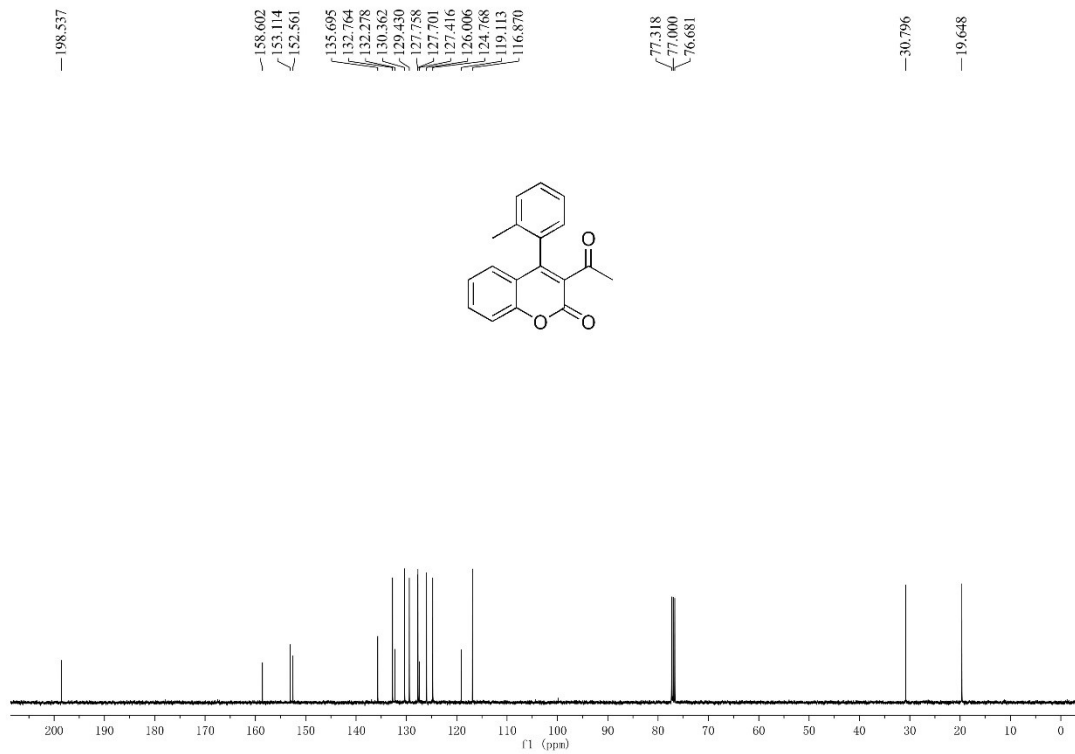
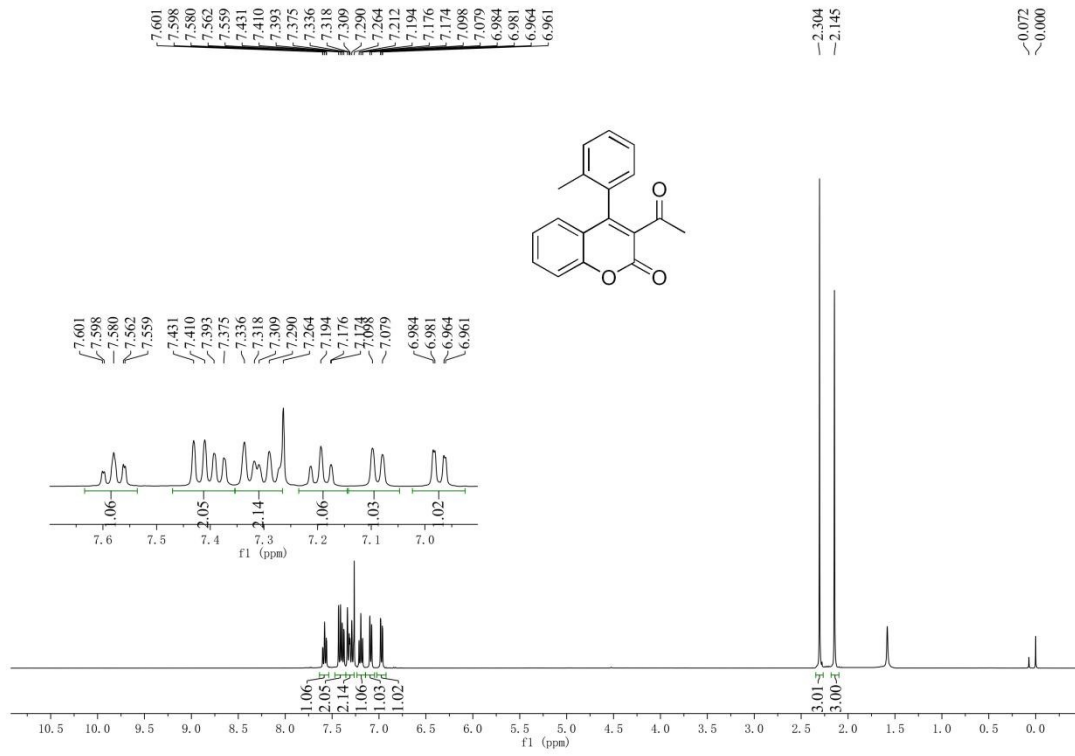
3-Acetyl-6-chloro-4-phenyl-2H-chromen-2-one (3la) and 3-Acetyl-8-chloro-4-phenyl-2H-chromen-2-one (3la')



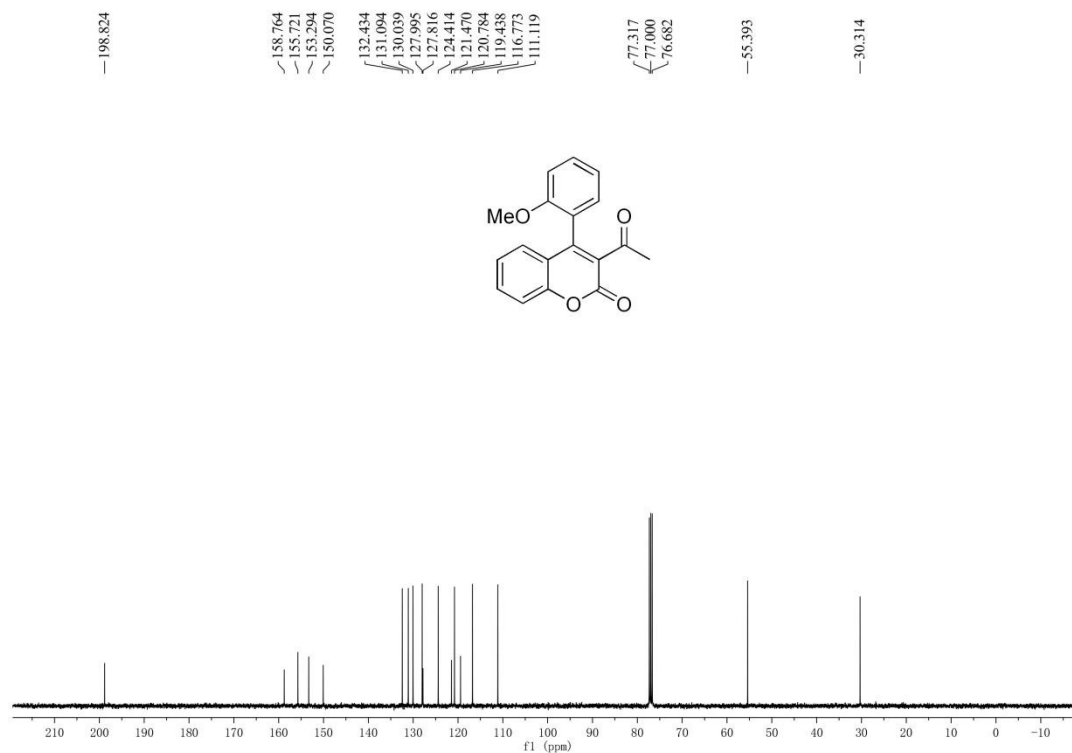
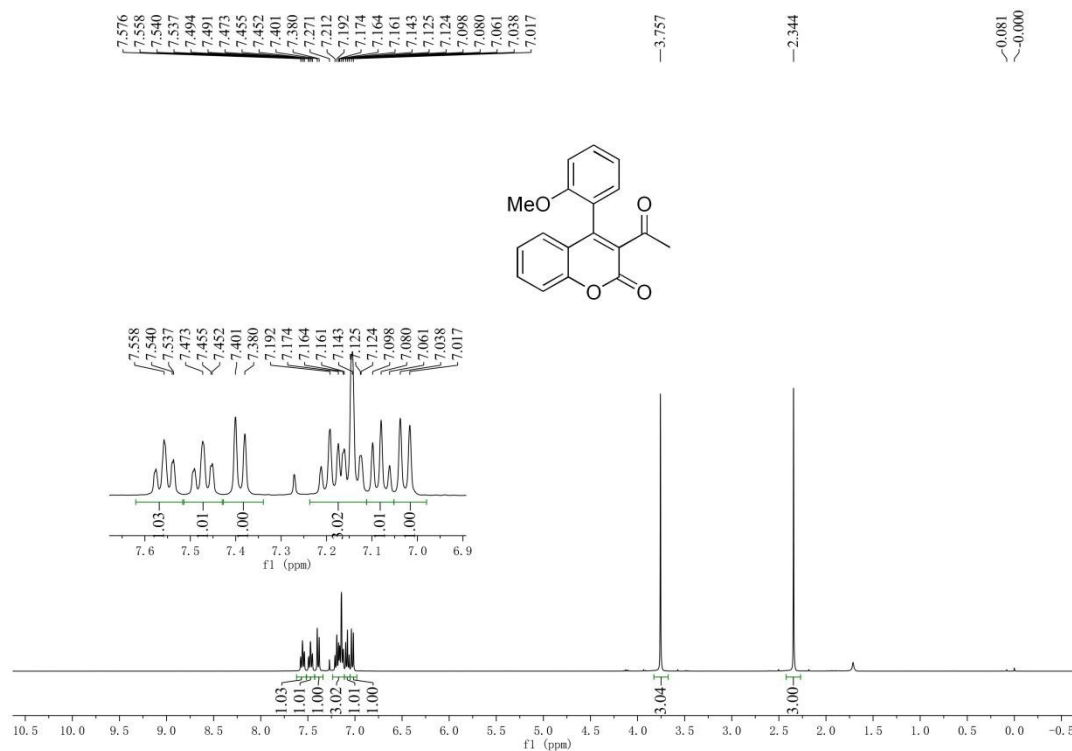
3-Acetyl-6-bromo-4-phenyl-2H-chromen-2-one (3ma) and 3-Acetyl-8-bromo-4-phenyl-2H-chromen-2-one (3ma')



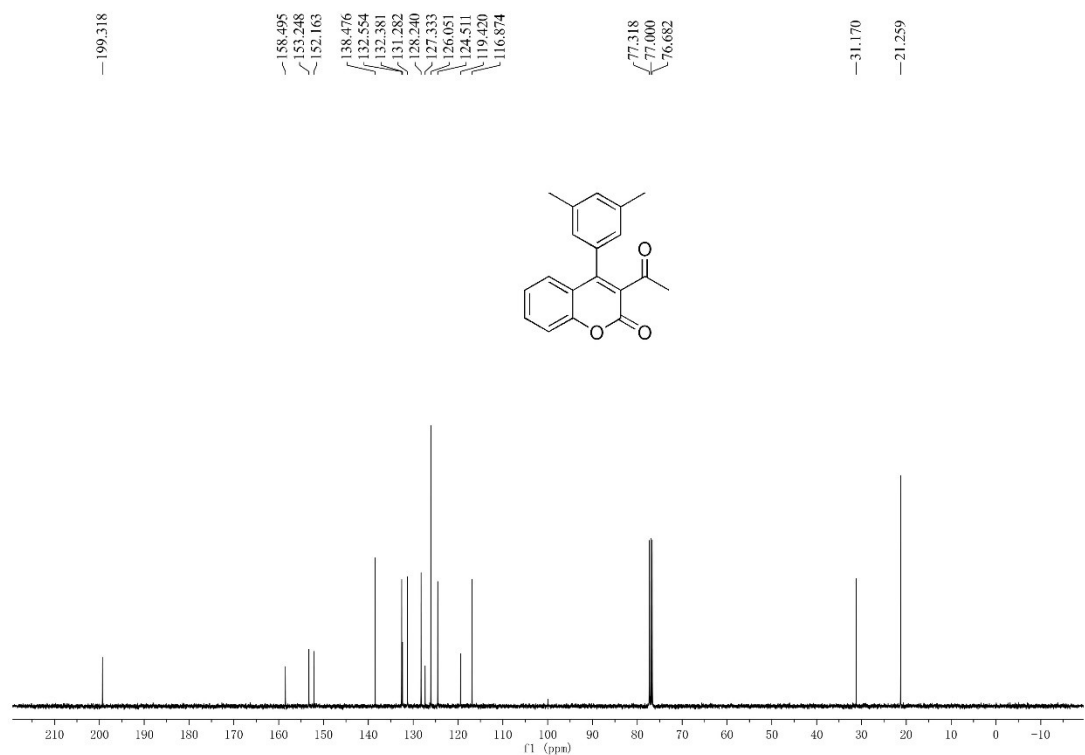
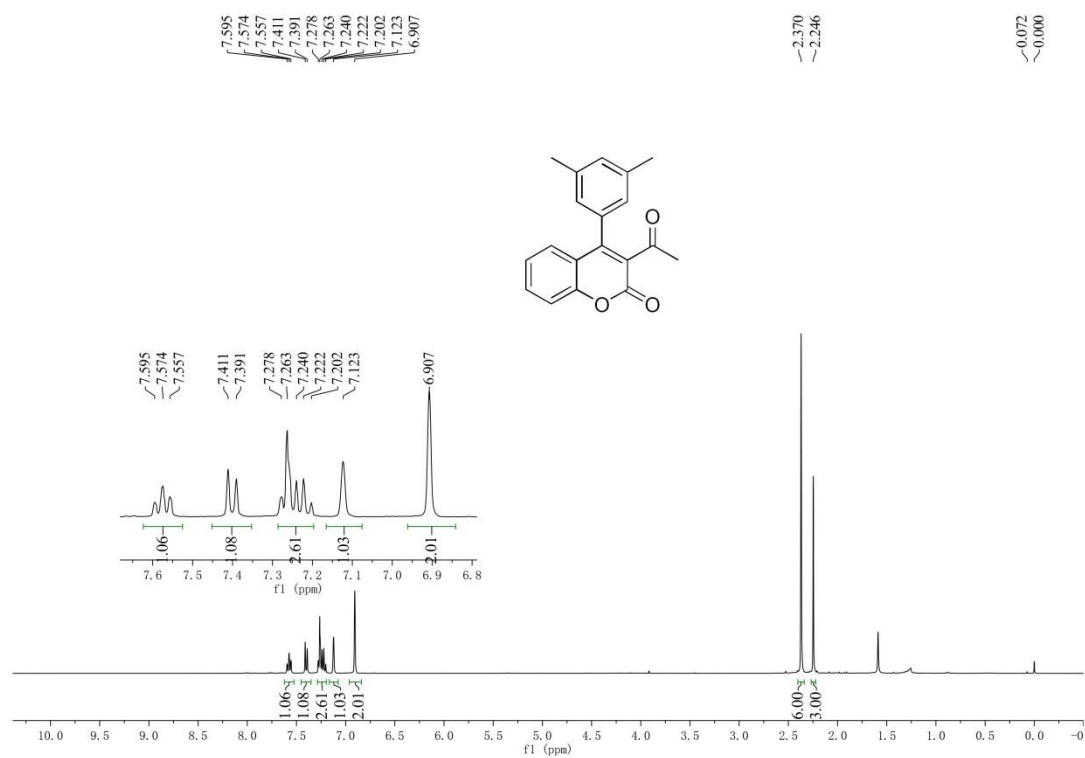
3-Acetyl-4-(*o*-tolyl)-2*H*-chromen-2-one (30a)



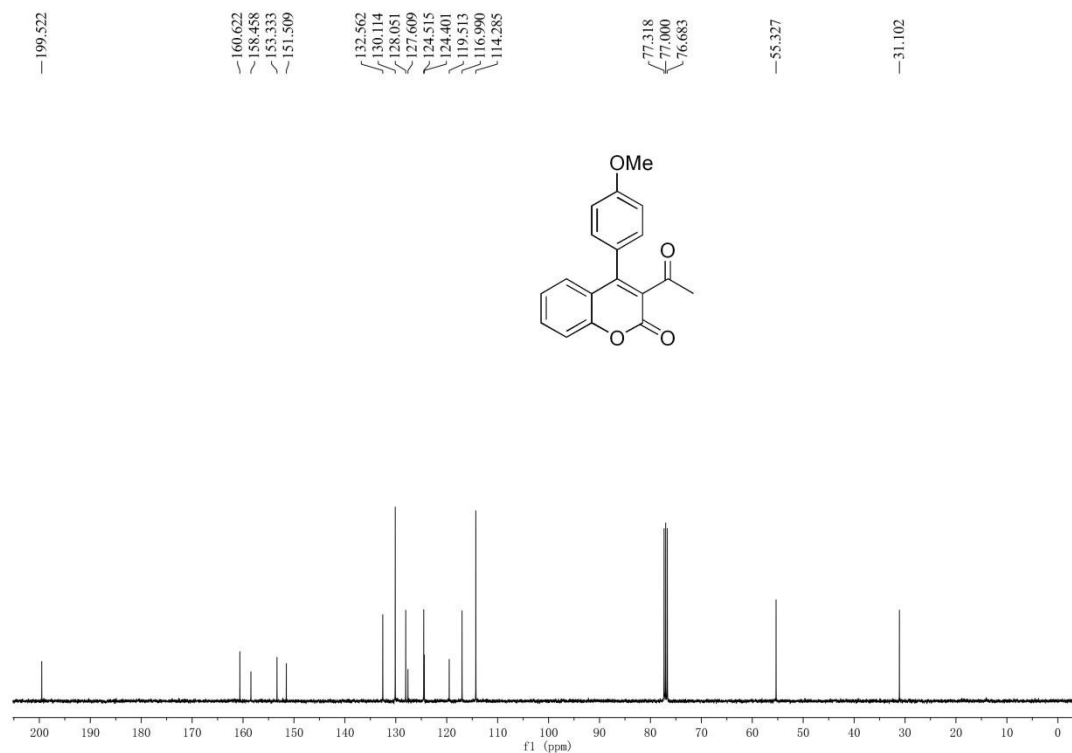
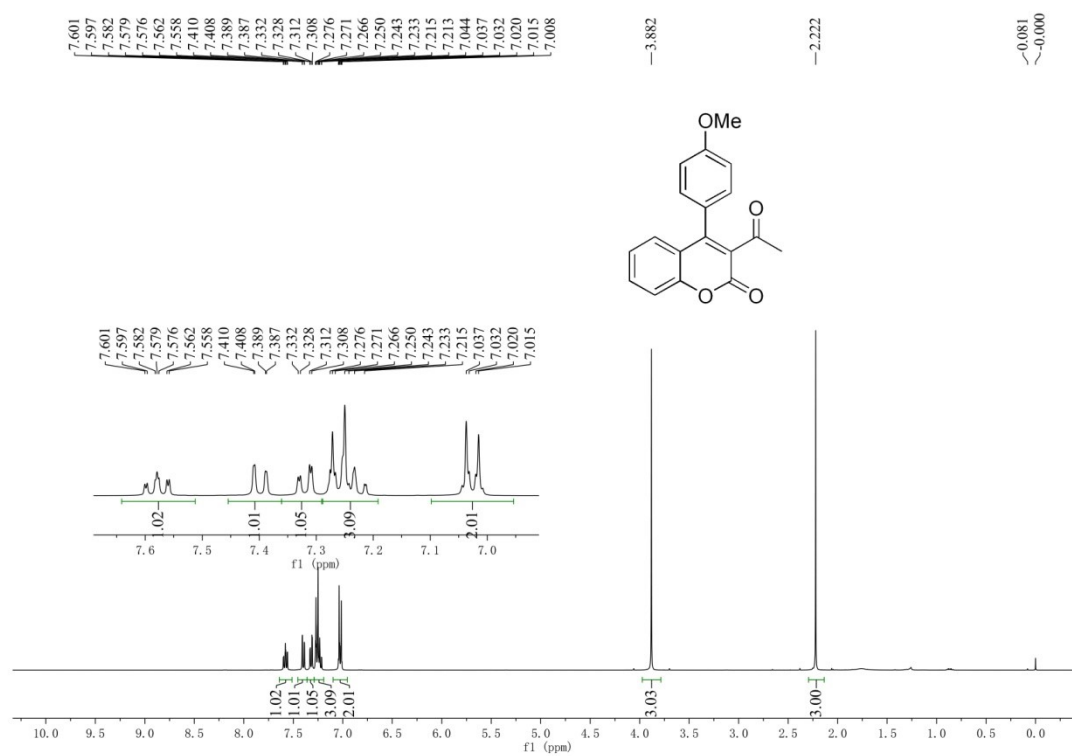
3-Acetyl-4-(2-methoxyphenyl)-2H-chromen-2-one (3pa)



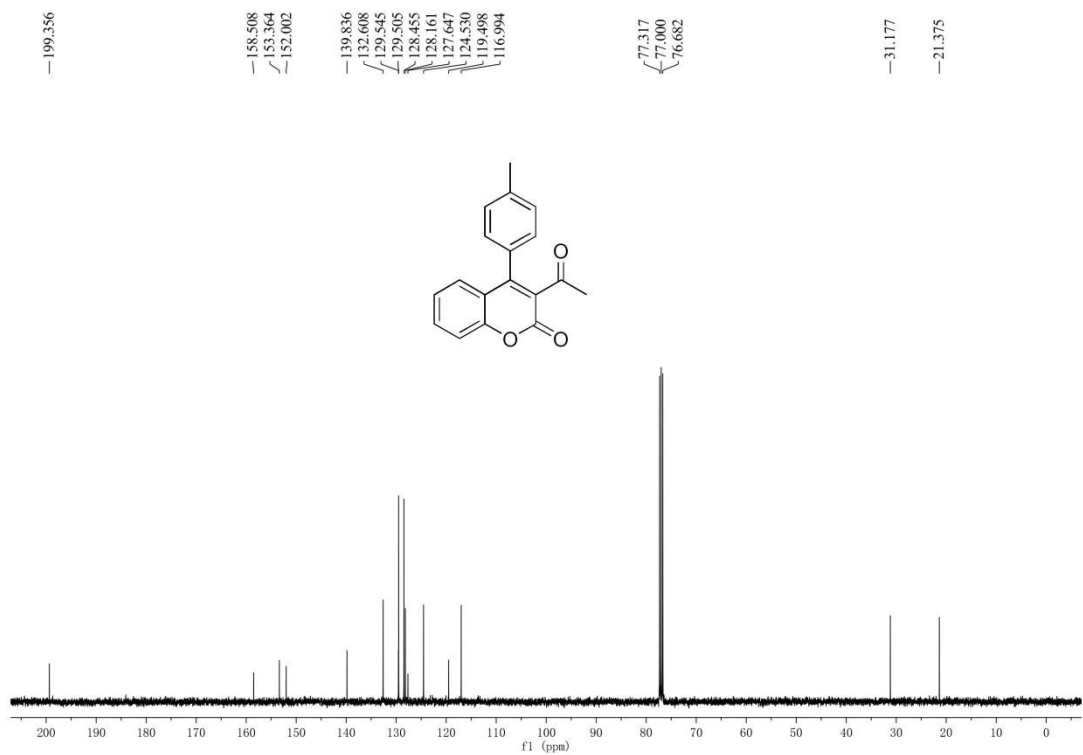
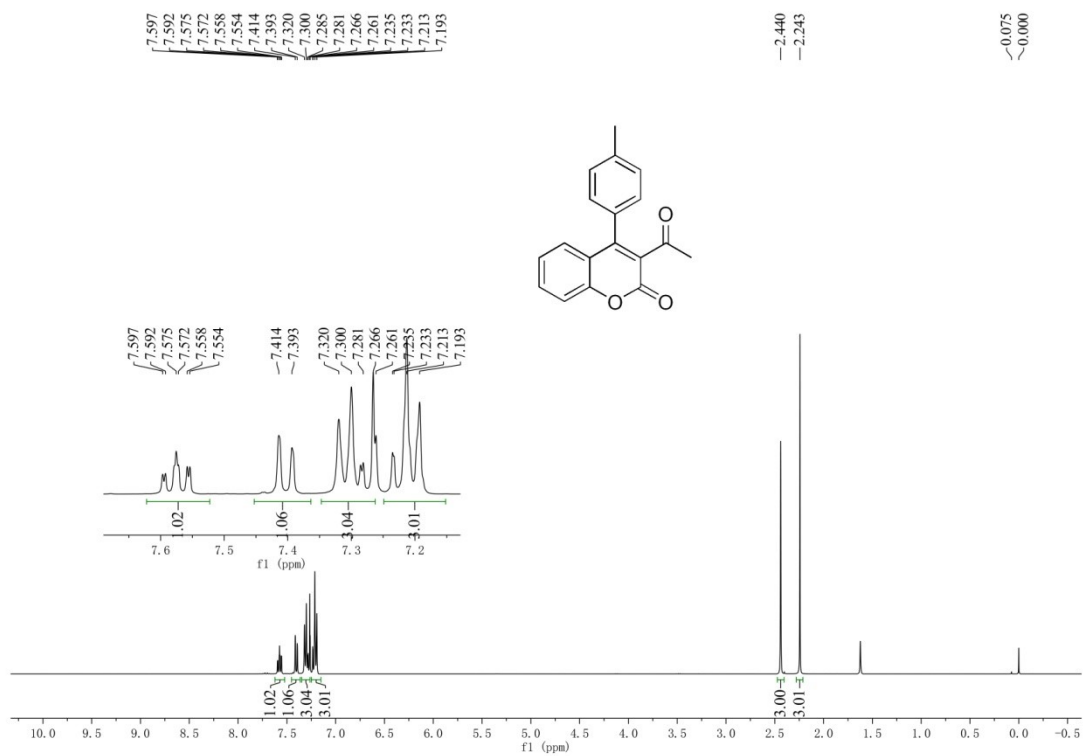
3-Acetyl-4-(3,5-dimethylphenyl)-2H-chromen-2-one (3qa)



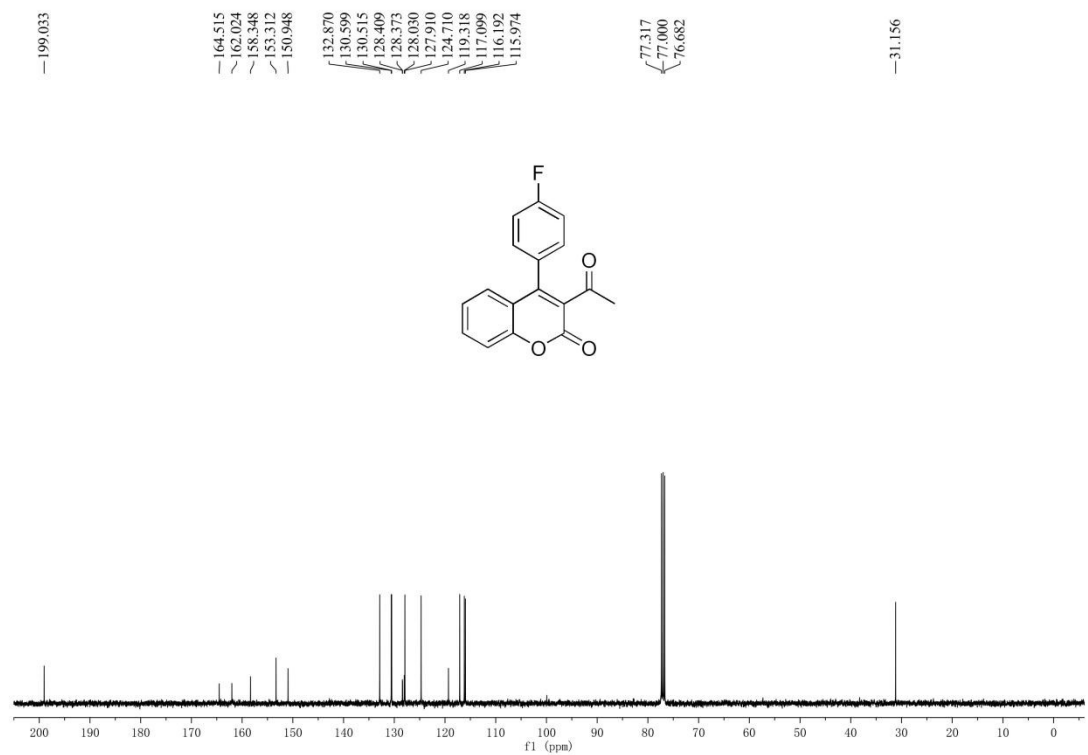
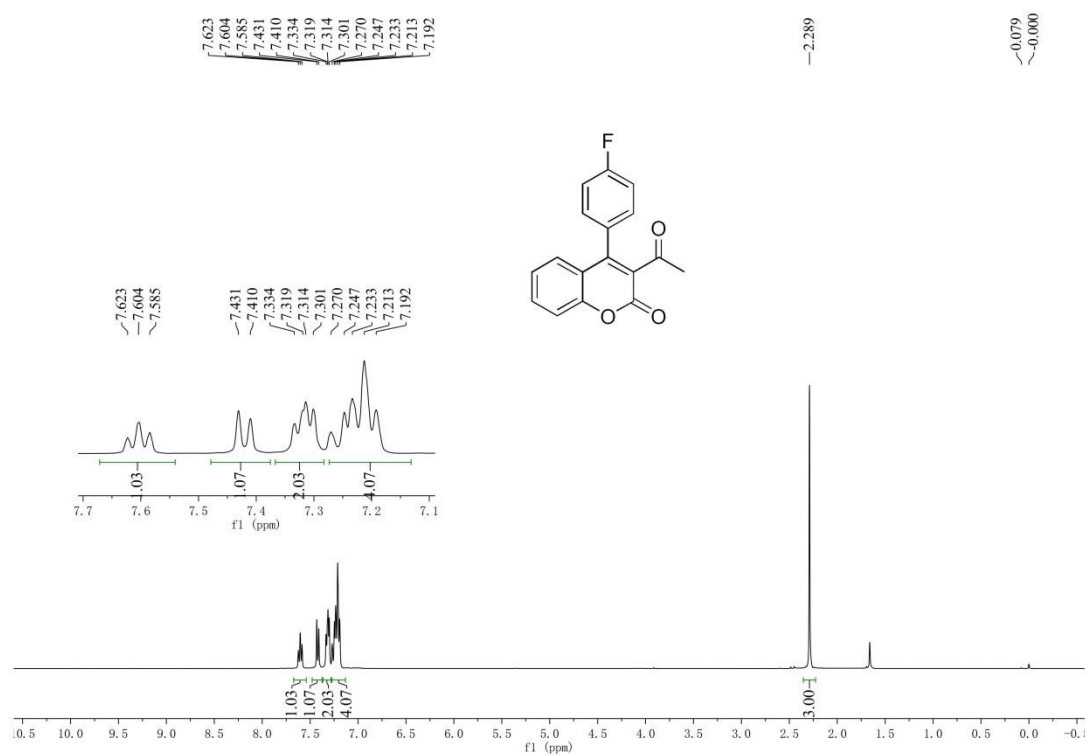
3-Acetyl-4-(4-methoxyphenyl)-2H-chromen-2-one (3ra)



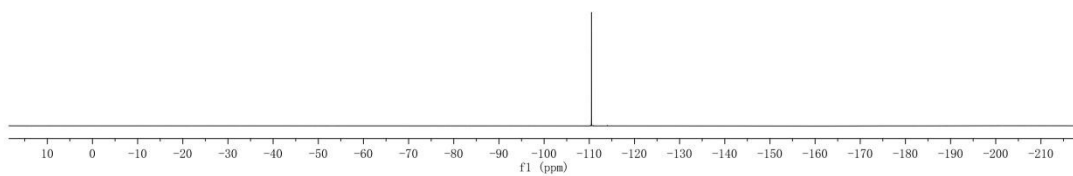
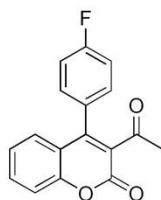
3-Acetyl-4-(p-tolyl)-2H-chromen-2-one (3sa)



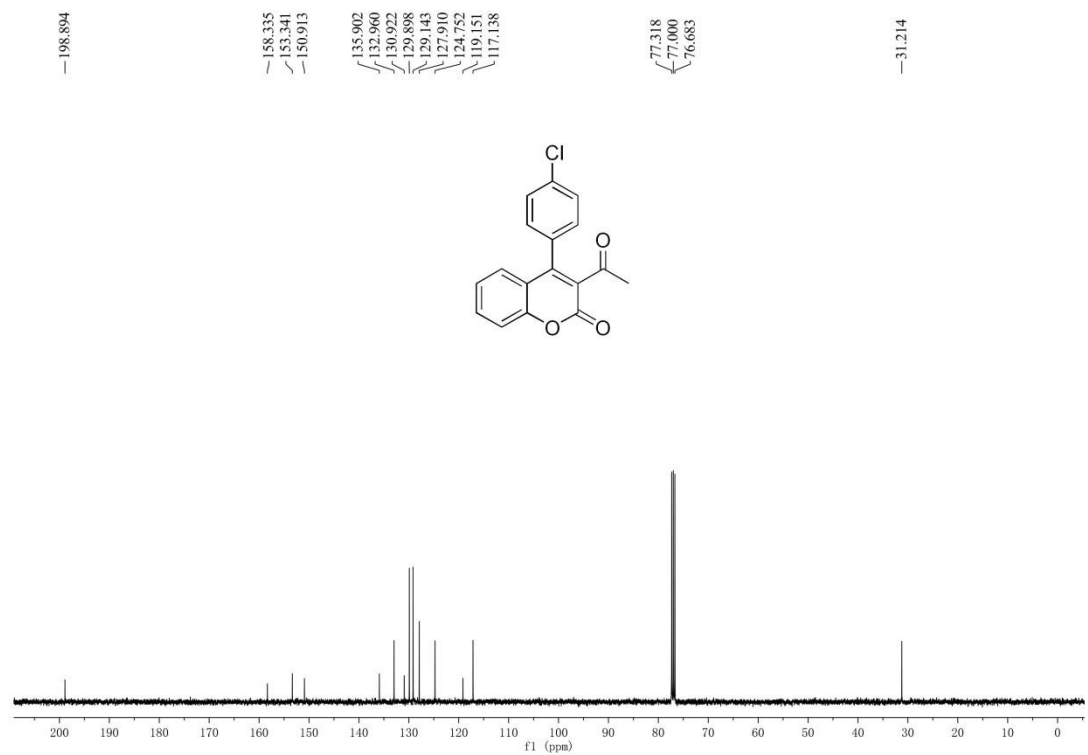
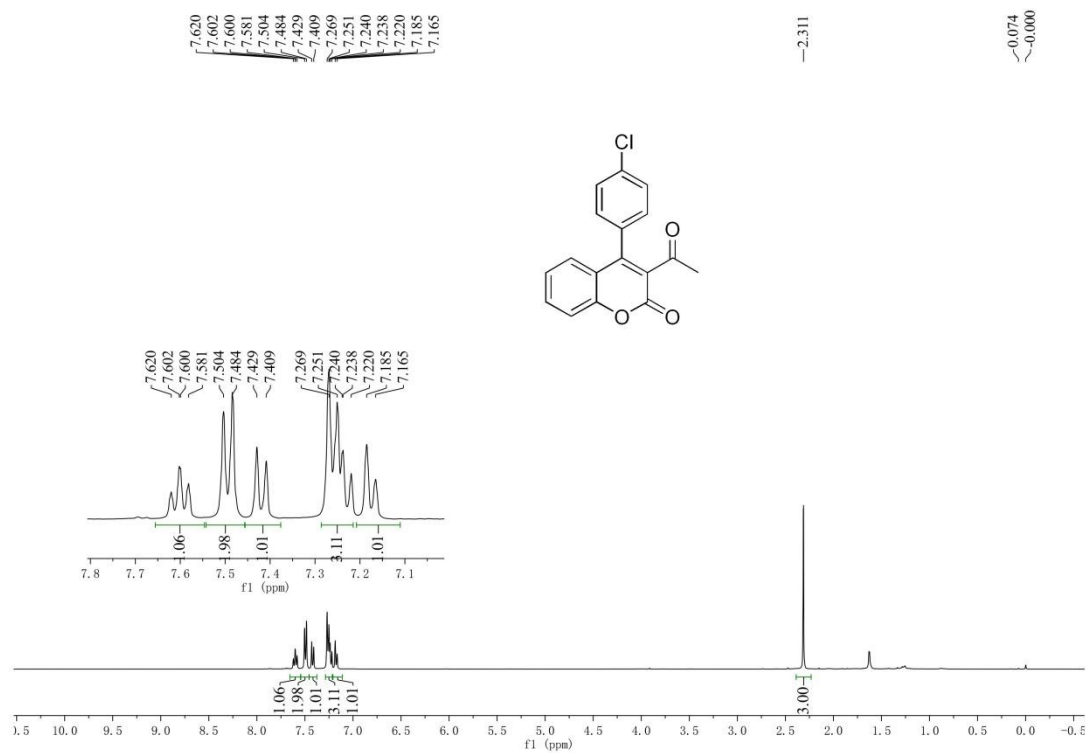
3-Acetyl-4-(4-fluorophenyl)-2H-chromen-2-one (3ta)



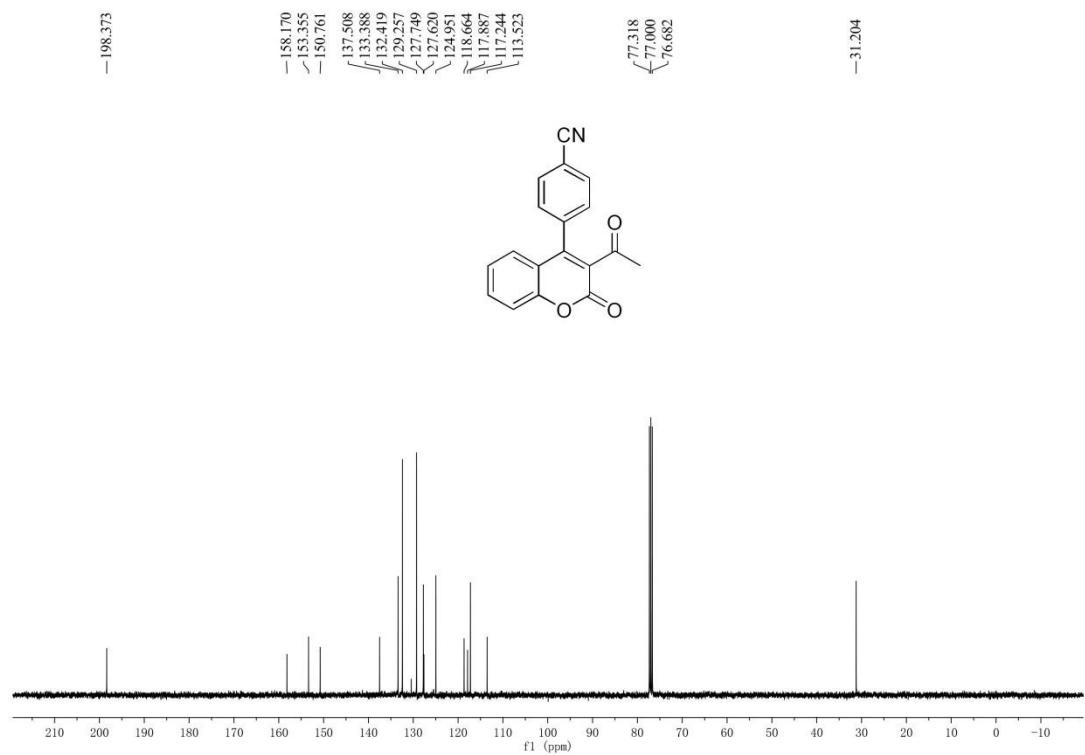
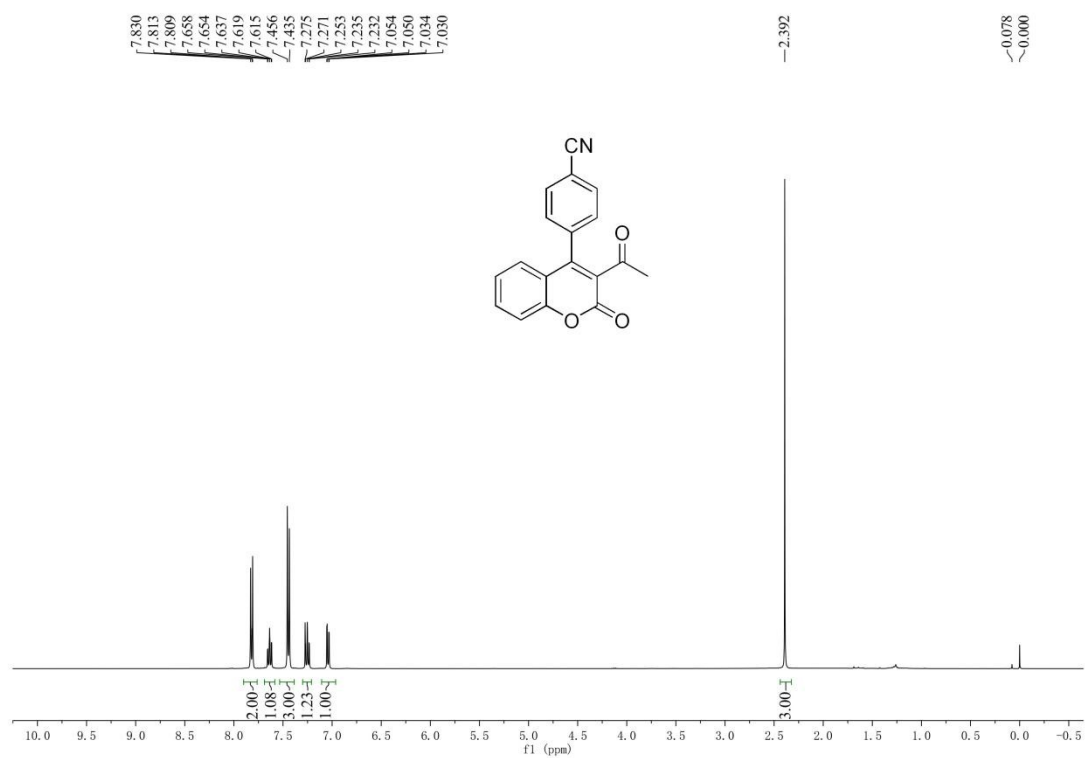
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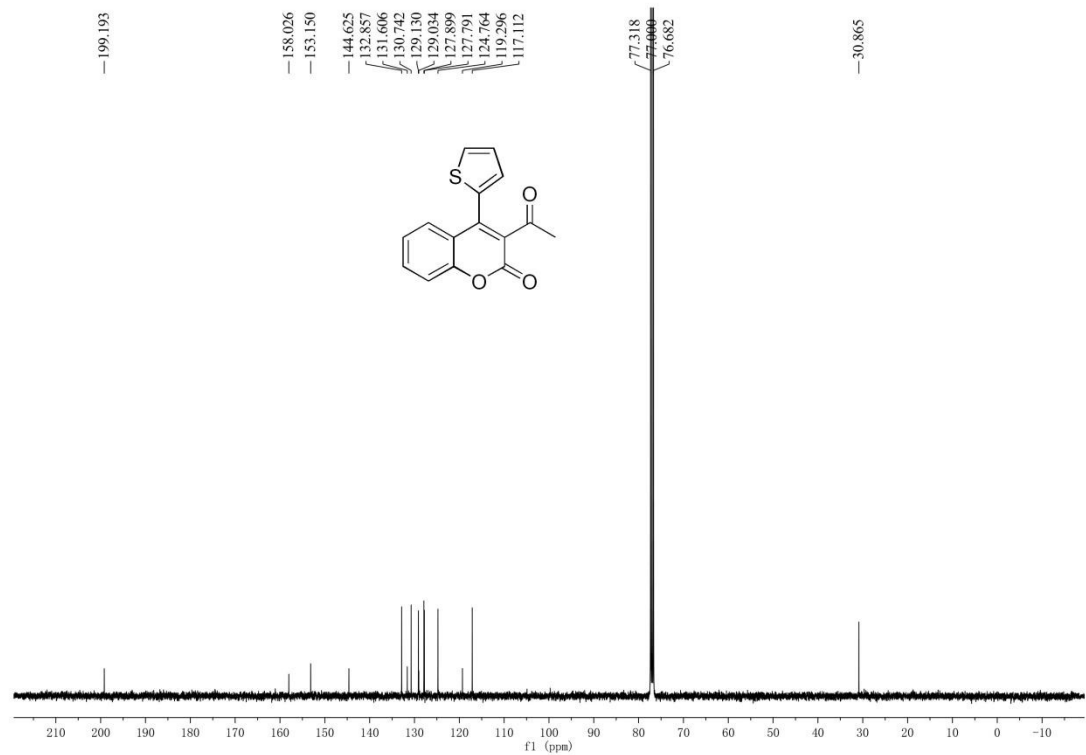
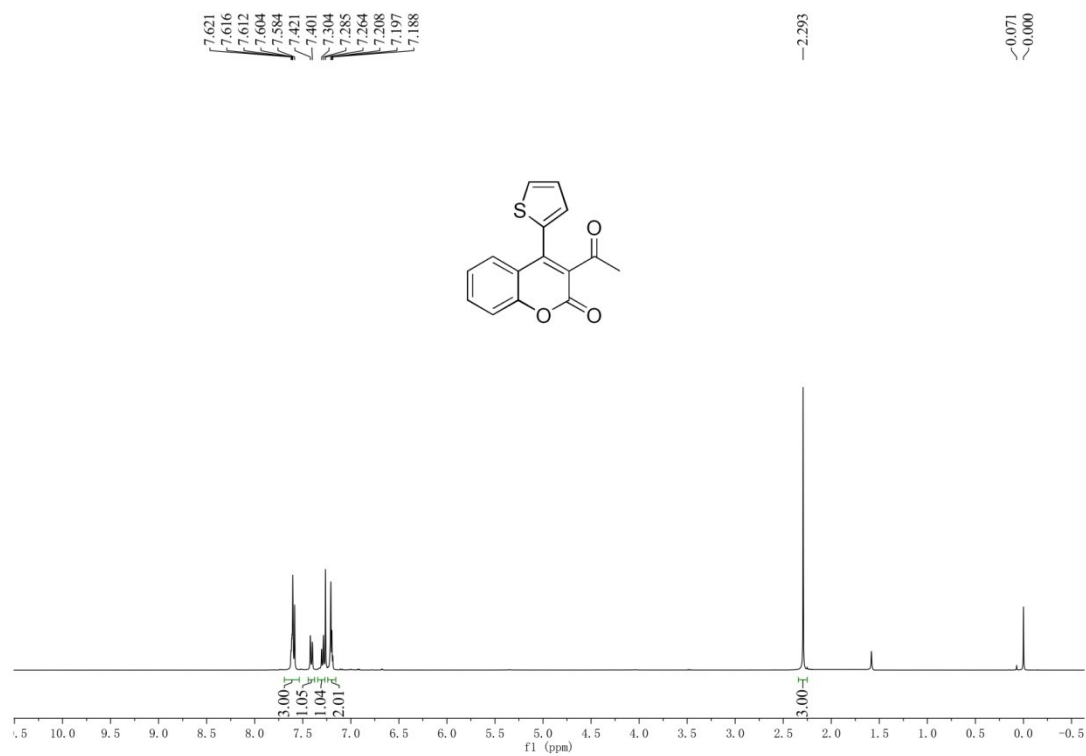
3-Acetyl-4-(4-chlorophenyl)-2H-chromen-2-one (3ua)



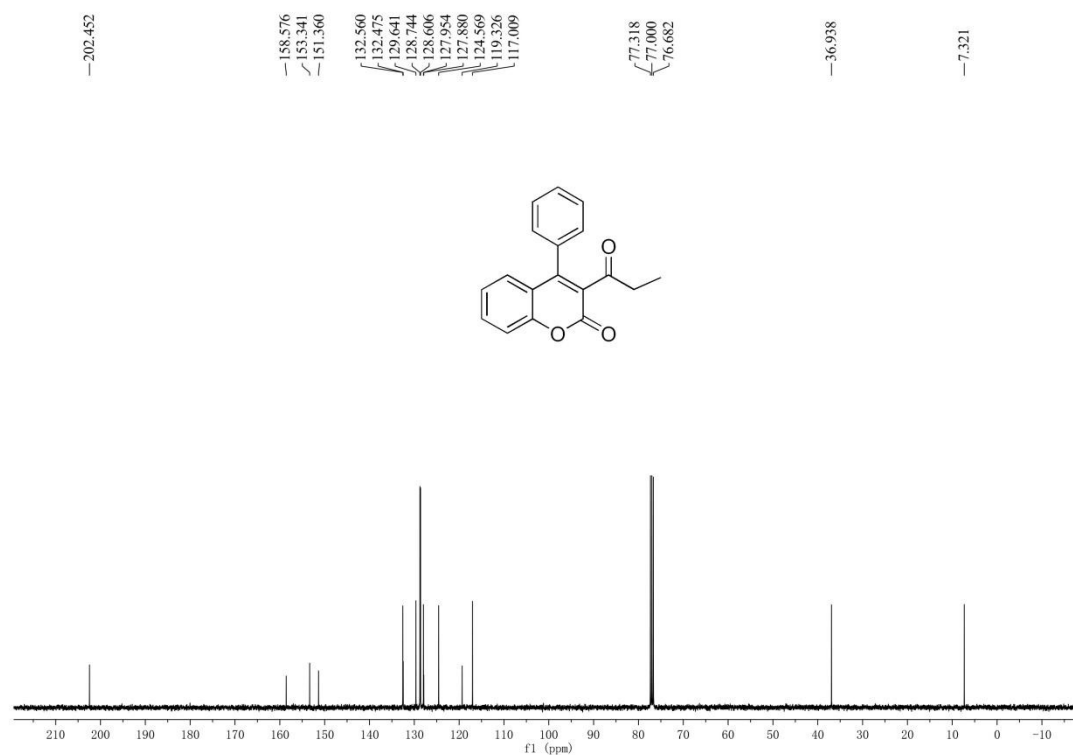
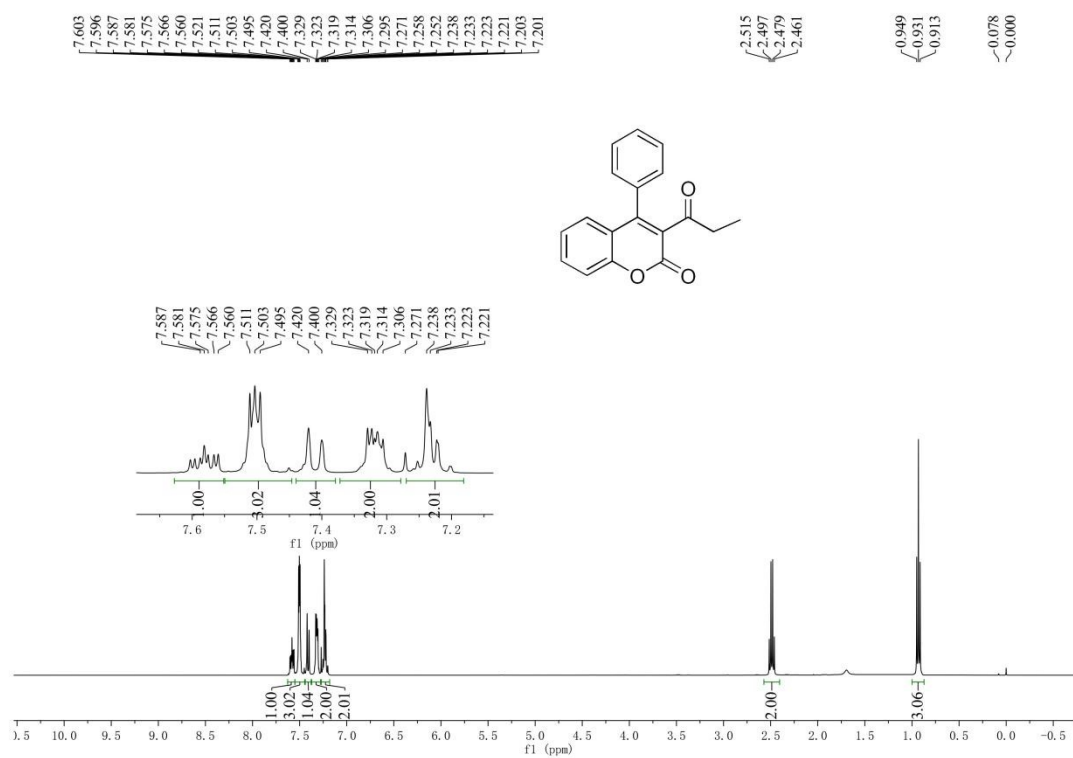
4-(3-Acetyl-2-oxo-2H-chromen-4-yl)benzonitrile (3va)



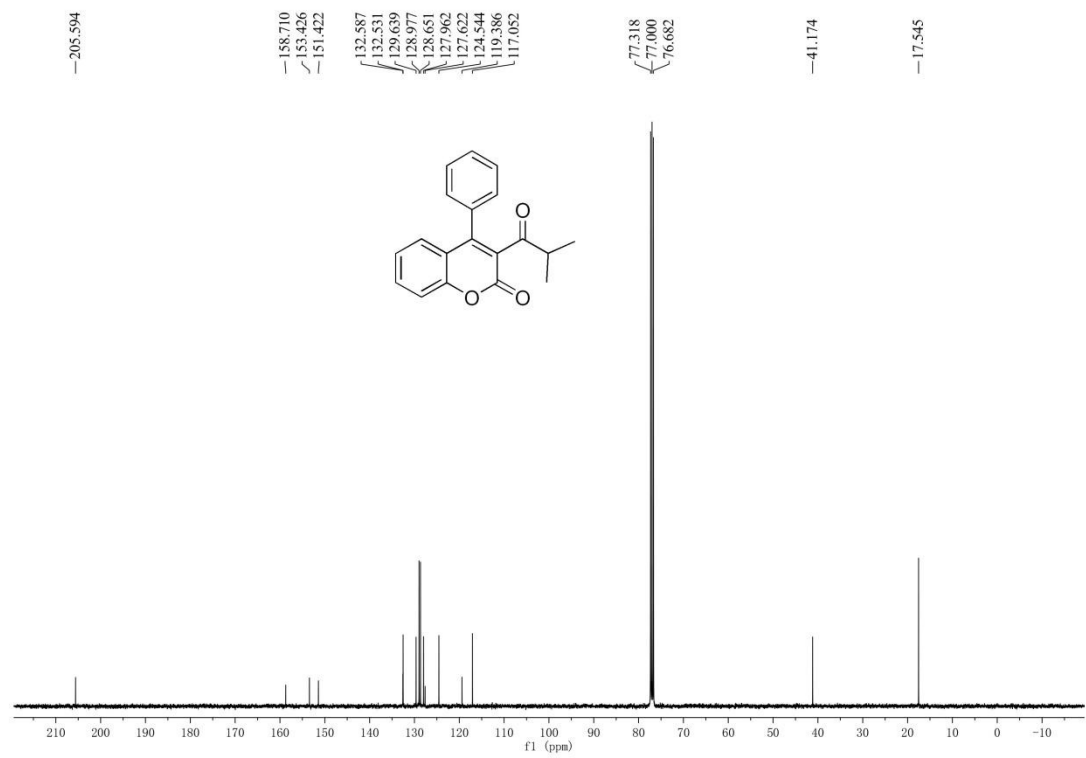
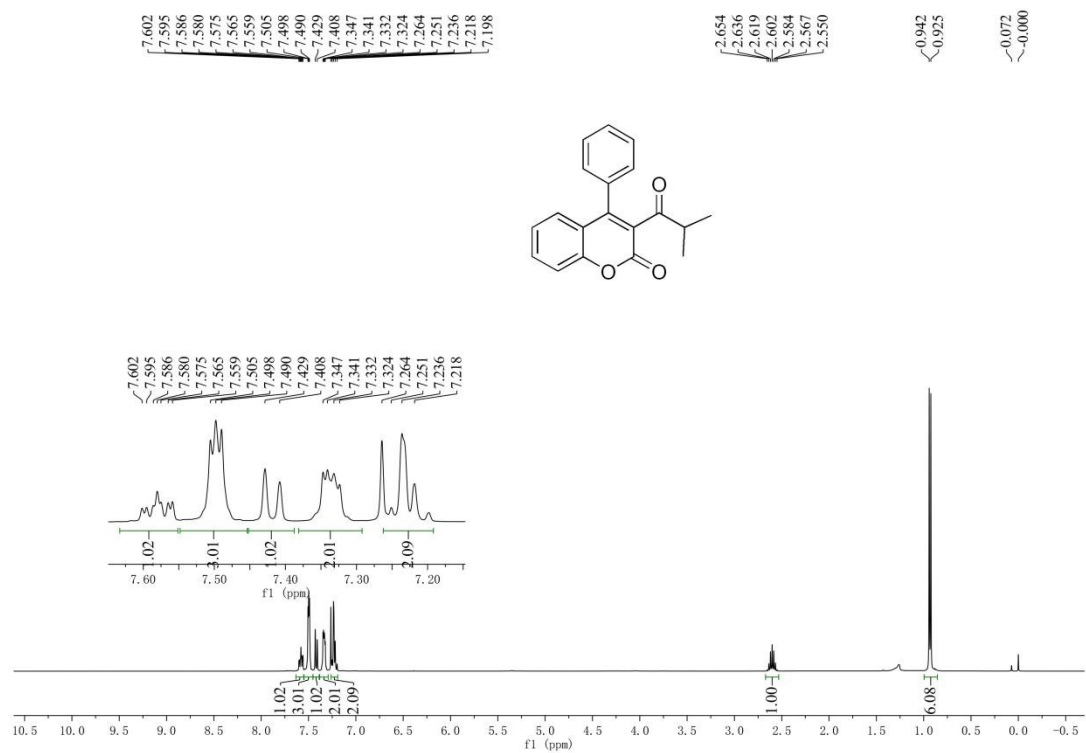
3-Acetyl-4-(thiophen-2-yl)-2H-chromen-2-one (3wa)



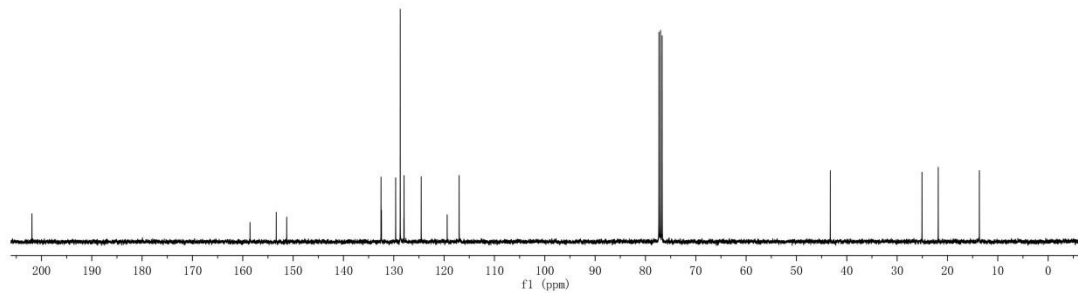
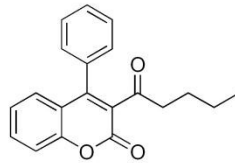
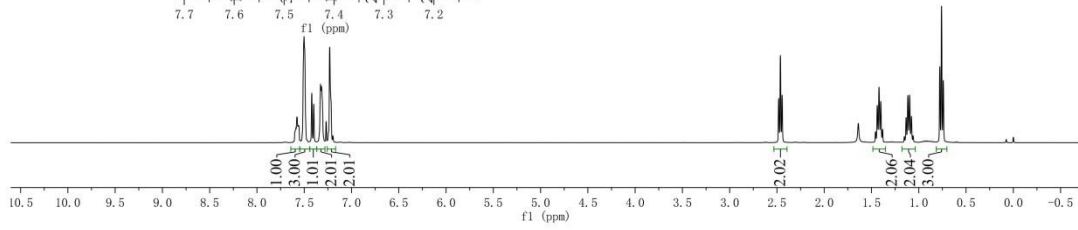
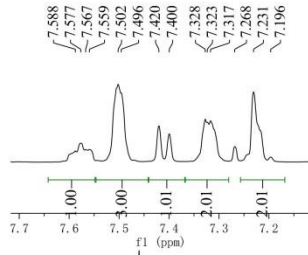
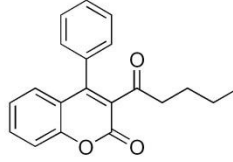
4-Phenyl-3-propionyl-2H-chromen-2-one (3ab)



3-Isobutyryl-4-phenyl-2H-chromen-2-one (3a)

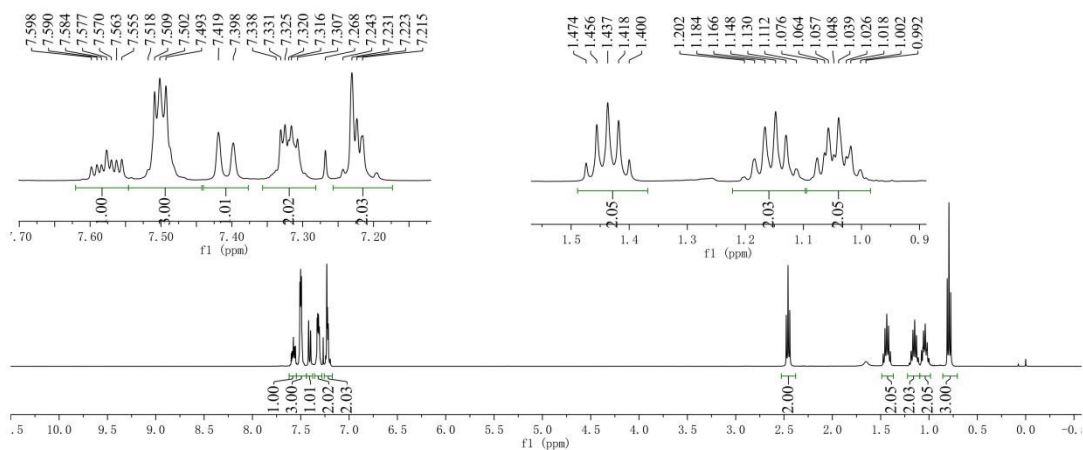
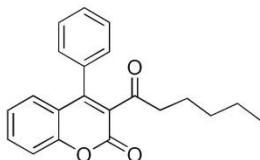


3-Pentanoyl-4-phenyl-2H-chromen-2-one (3ad)

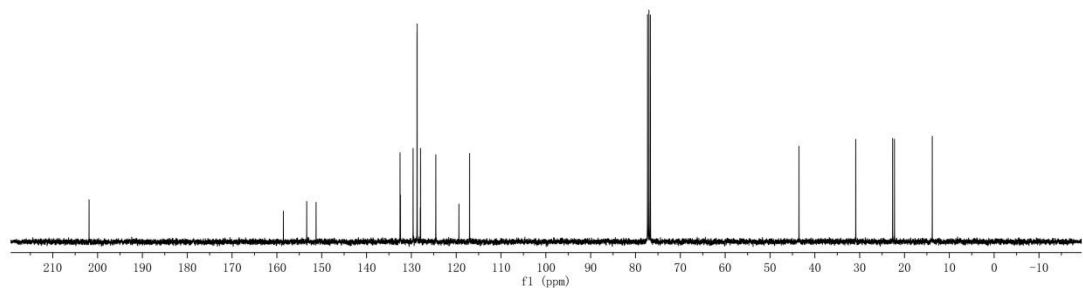
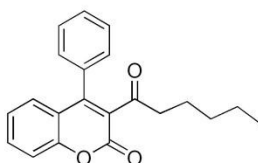


3-Hexanoyl-4-phenyl-2H-chromen-2-one (3ae)

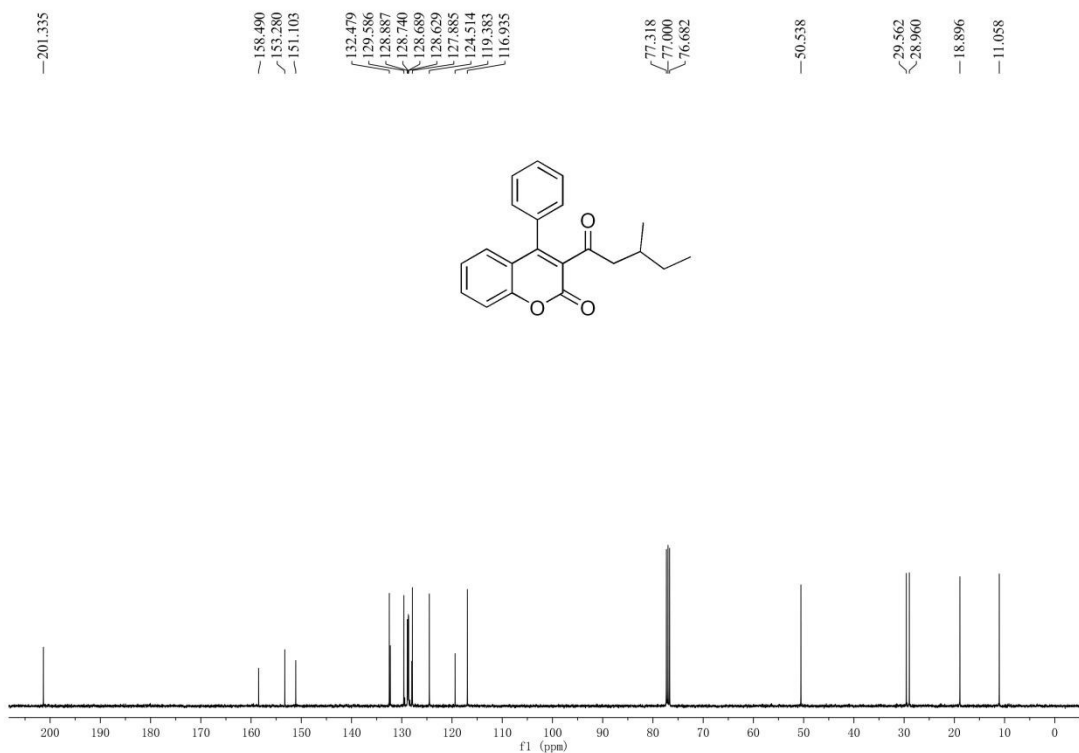
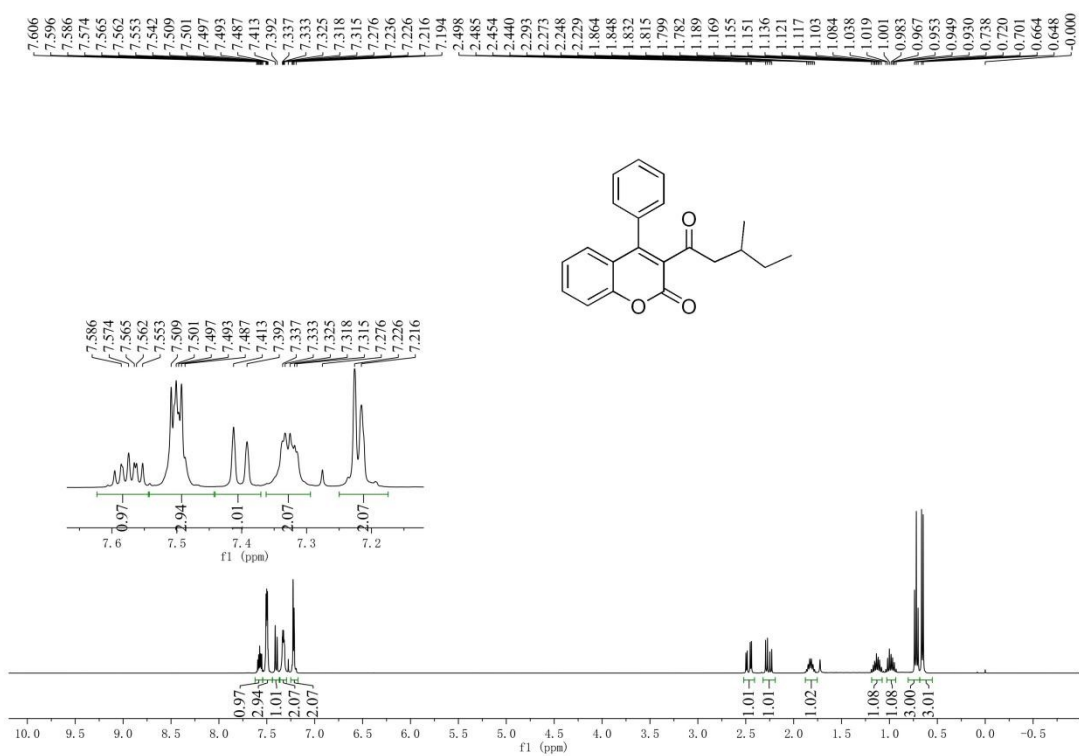
7.598, 7.590, 7.584, 7.577, 7.570, 7.563, 7.555, 7.518, 7.509, 7.502, 7.493, 7.419, 7.398, 7.338, 7.331, 7.325, 7.320, 7.316, 7.307, 7.297, 7.268, 7.243, 7.231, 7.223, 7.215, 7.195, 2.477, 2.459, 2.441, 1.456, 1.437, 1.418, 1.166, 1.148, 1.130, 1.112, 1.076, 1.064, 1.057, 1.048, 1.039, 1.026, 1.018, 1.002, 0.992, 0.812, 0.794, 0.076, 0.000



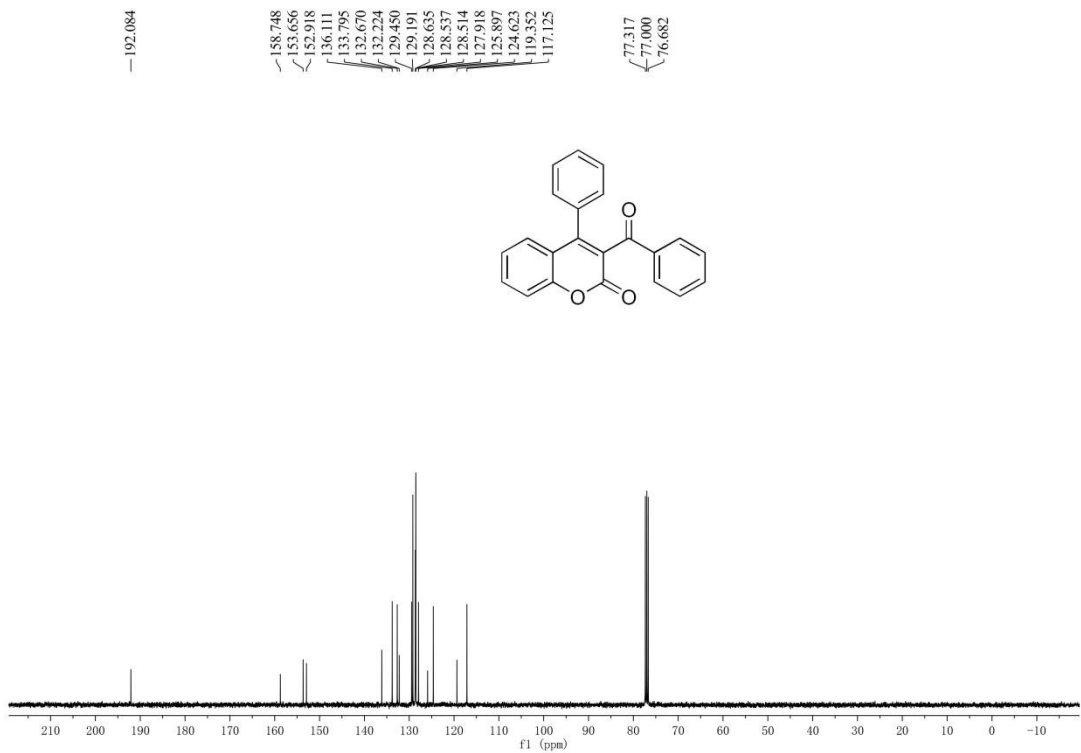
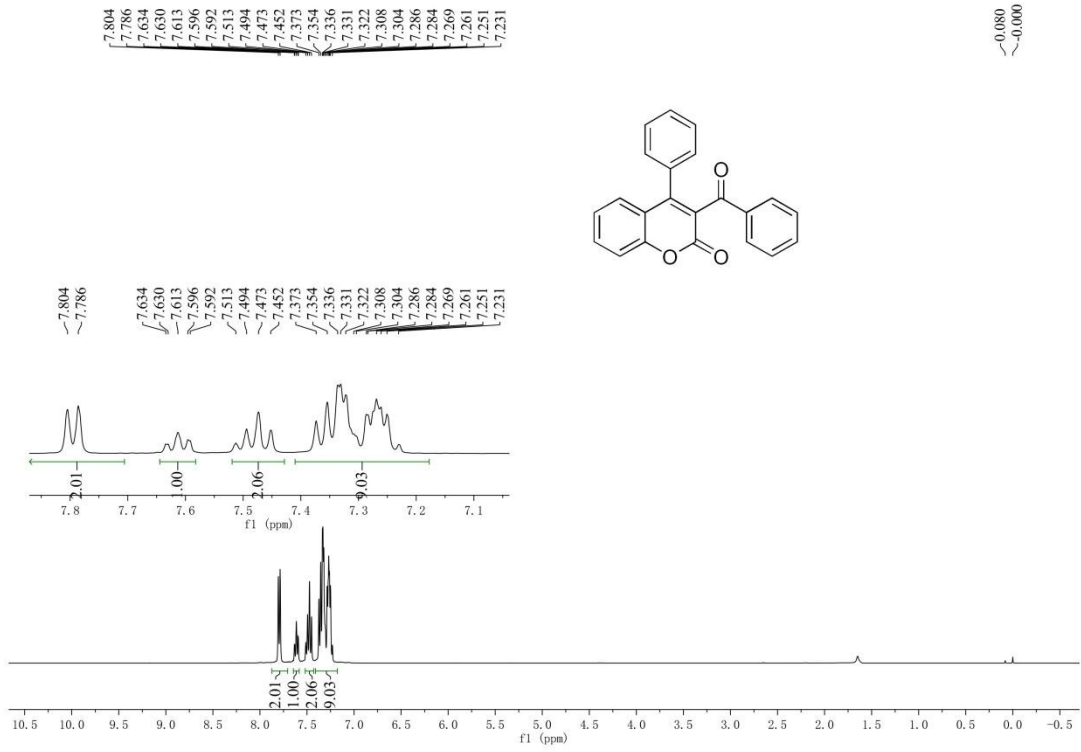
201.897, 158.557, 153.346, 151.255, 132.525, 132.432, 129.616, 128.737, 128.711, 128.007, 127.944, 124.549, 119.391, 117.008, 77.317, 77.000, 76.682, 43.532, 30.864, 22.646, 22.231, 13.800



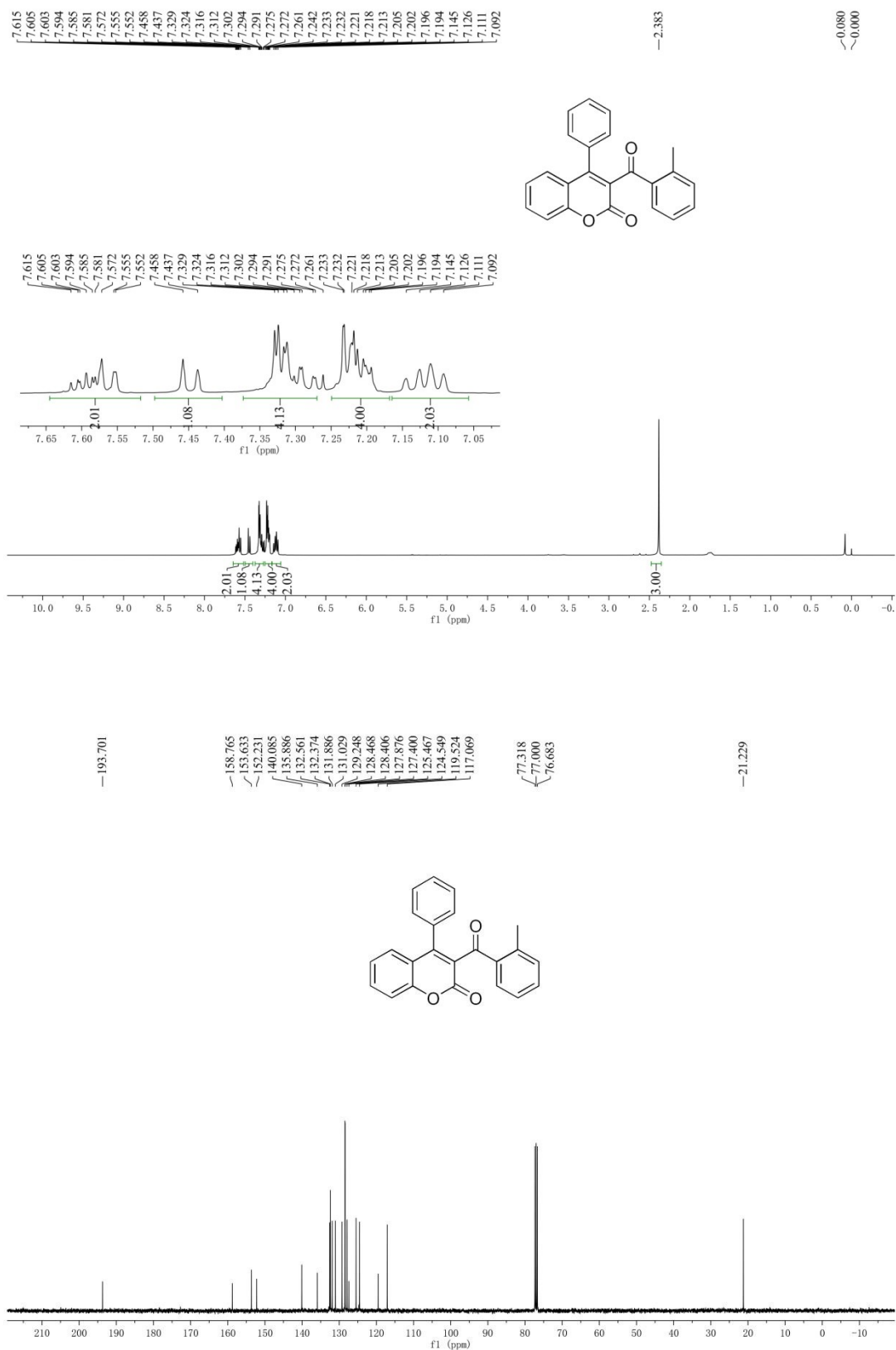
3-(3-Methylpentanoyl)-4-phenyl-2H-chromen-2-one (3af)



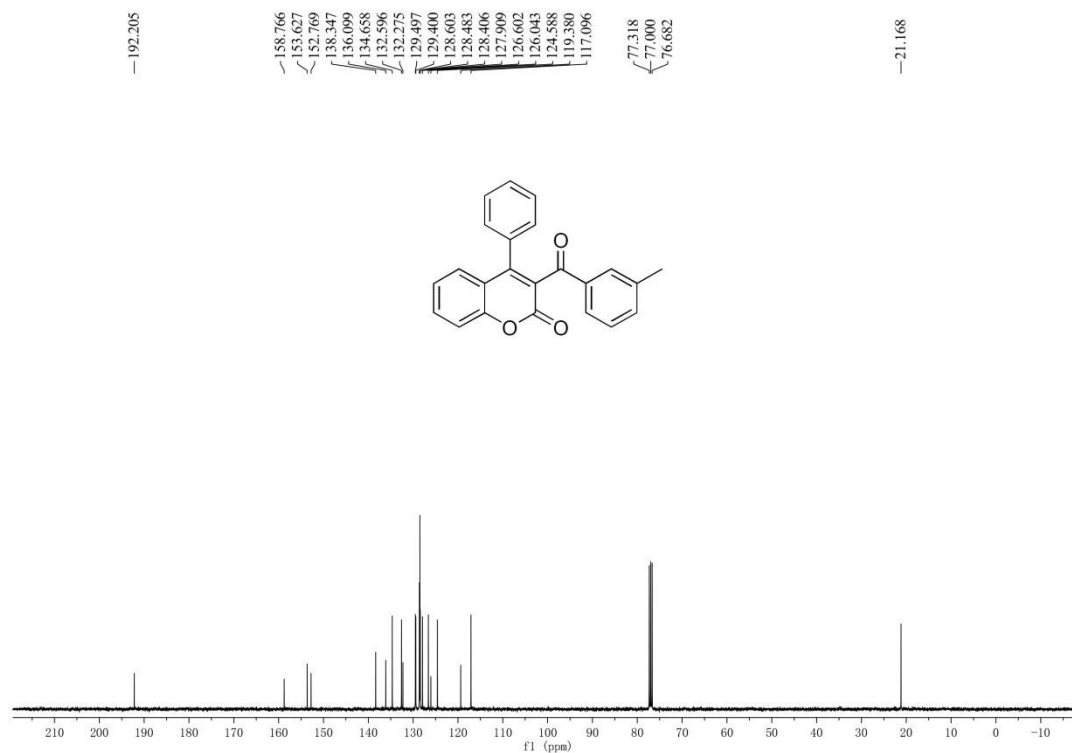
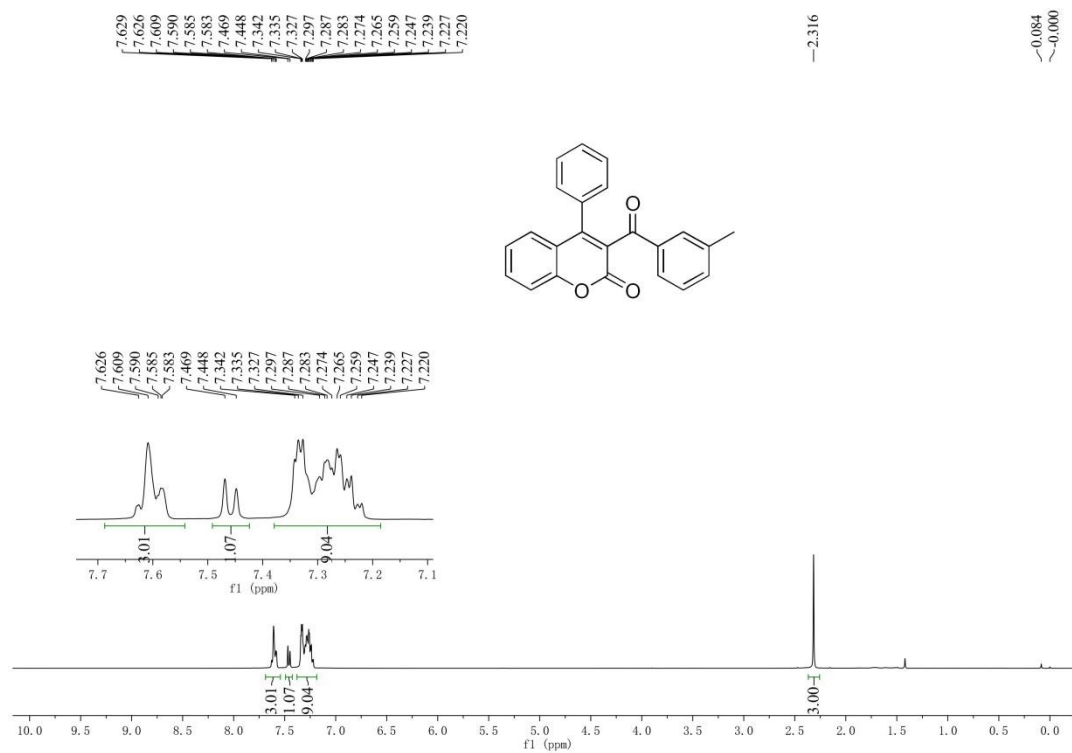
3-Benzoyl-4-phenyl-2H-chromen-2-one (3ag)



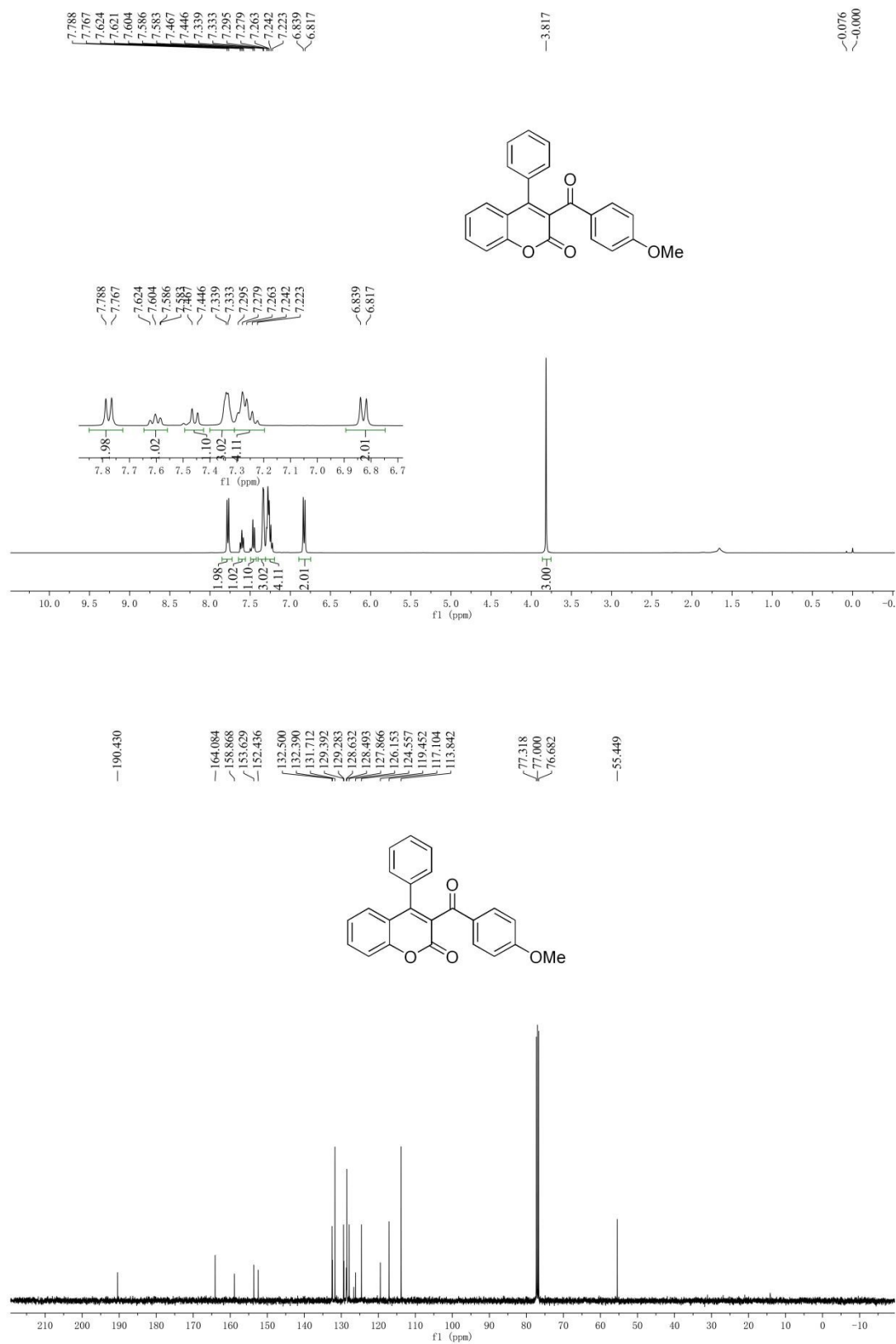
3-(2-Methylbenzoyl)-4-phenyl-2H-chromen-2-one (3ah)



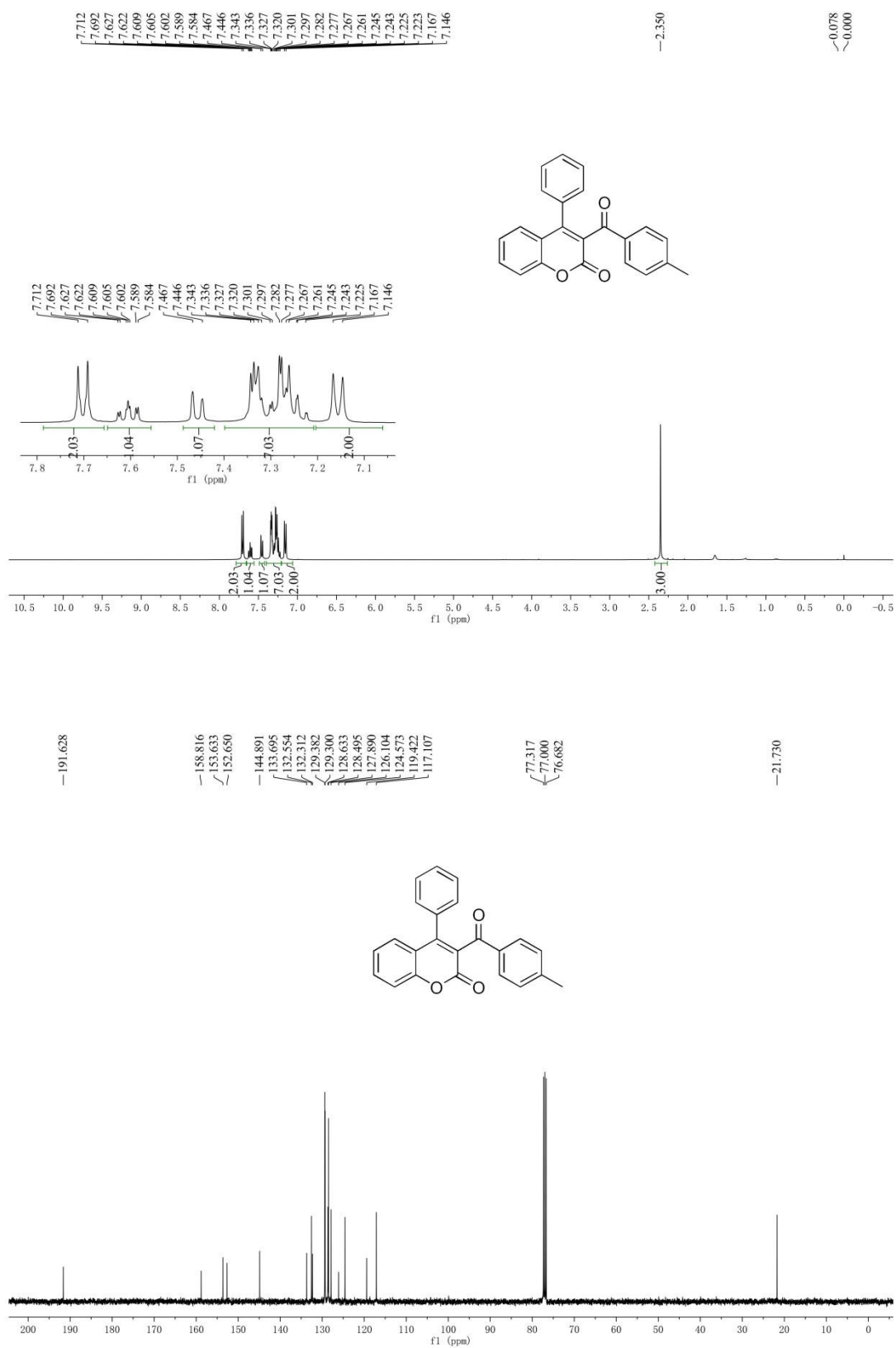
3-(3-Methylbenzoyl)-4-phenyl-2H-chromen-2-one (3ai)



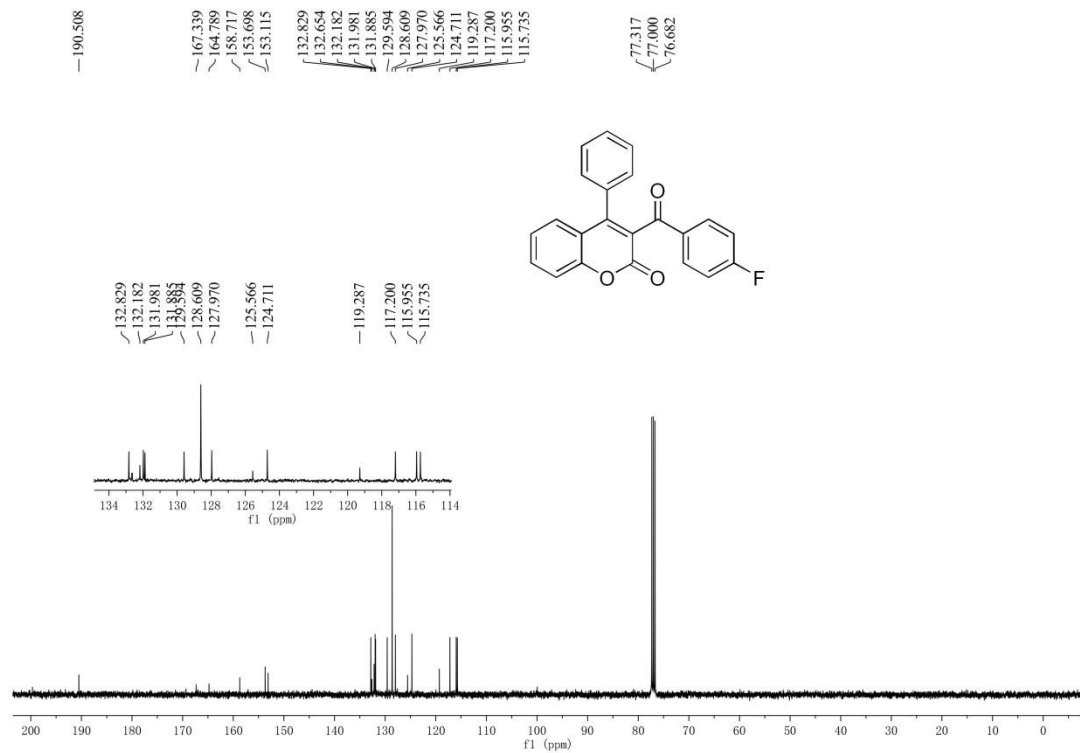
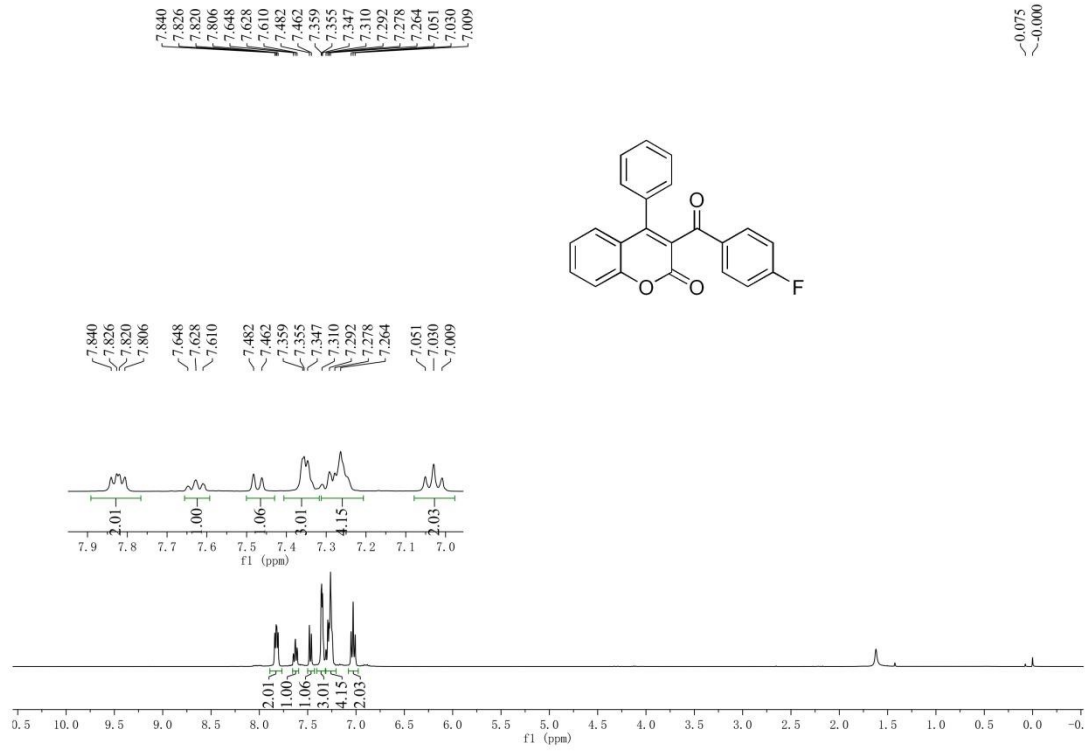
3-(4-Methoxybenzoyl)-4-phenyl-2H-chromen-2-one (3aj)



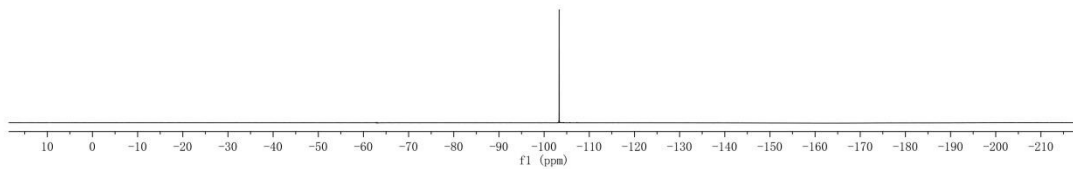
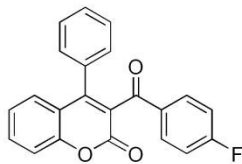
3-(4-Methylbenzoyl)-4-phenyl-2H-chromen-2-one (3ak)



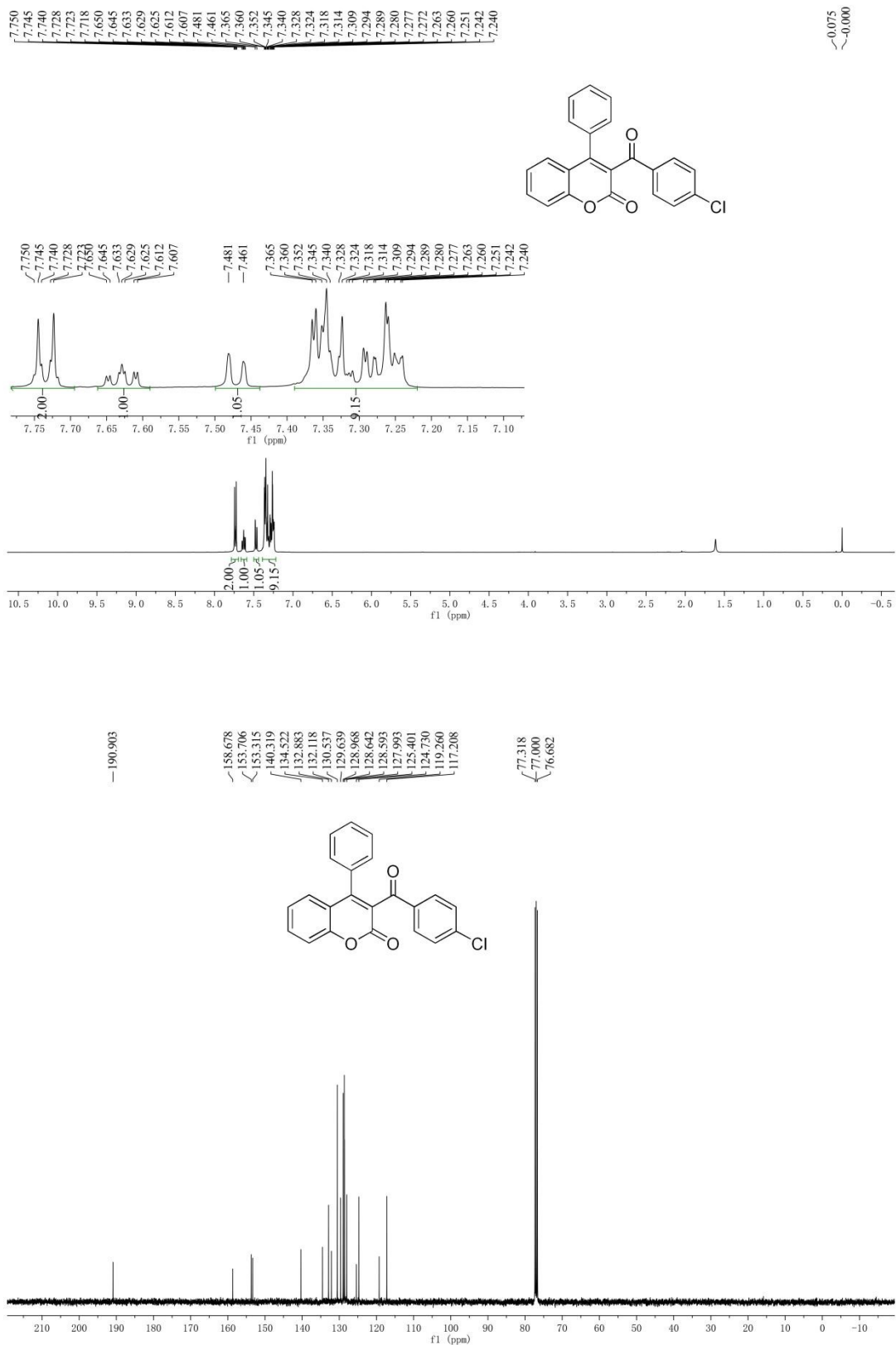
3-(4-Fluorobenzoyl)-4-phenyl-2H-chromen-2-one (3a)



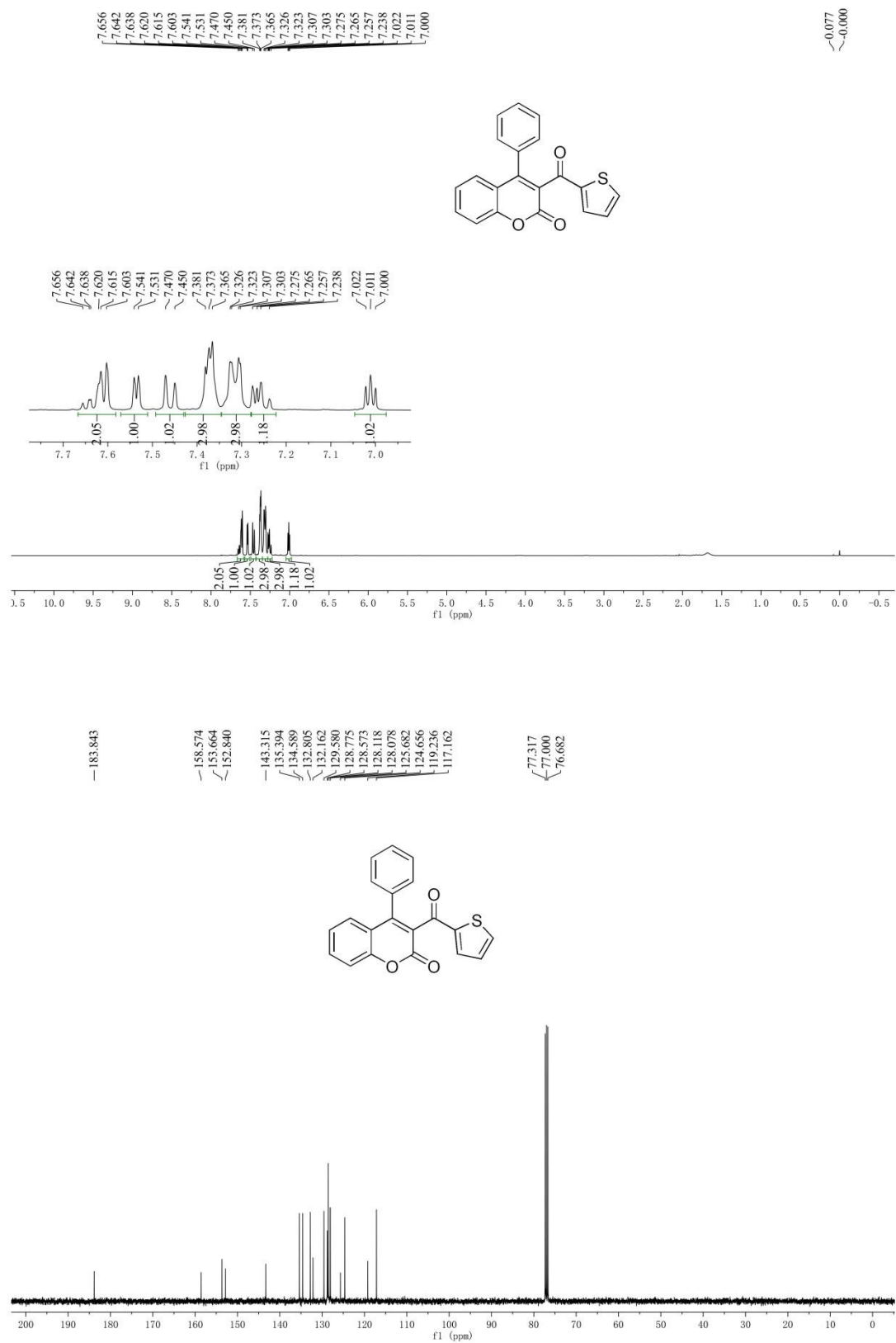
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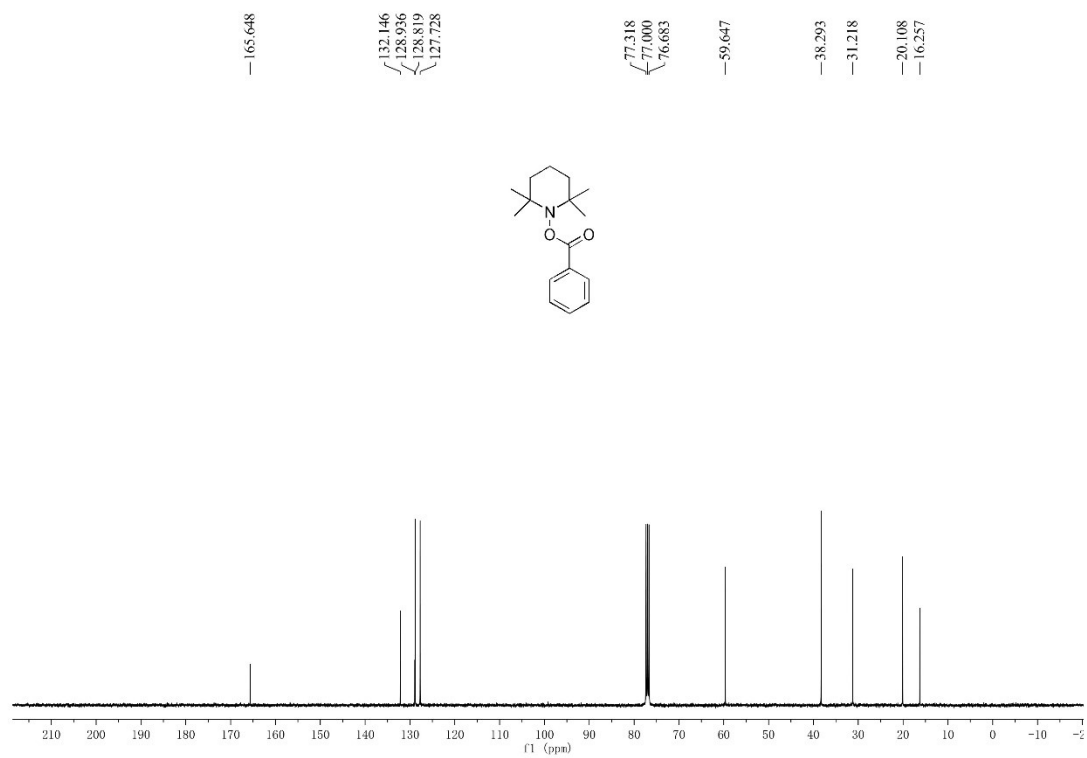
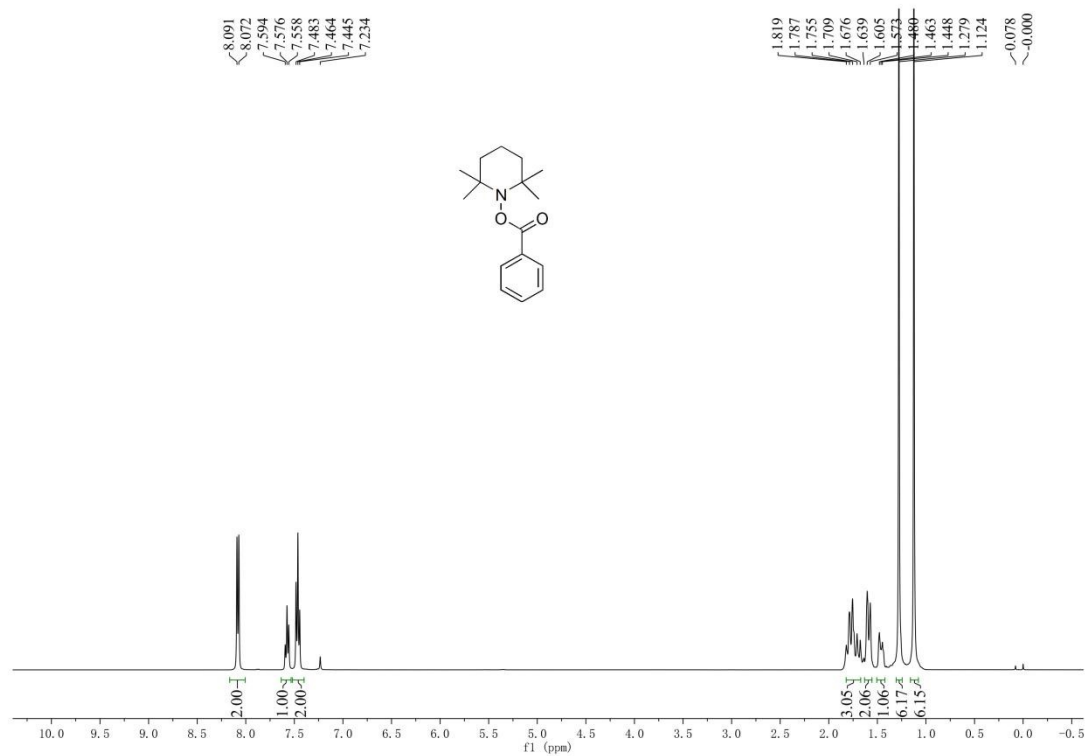
3-(4-Chlorobenzoyl)-4-phenyl-2H-chromen-2-one (3am)



4-Phenyl-3-(thiophene-2-carbonyl)-2H-chromen-2-one (3an)



2,2,6,6-Tetramethylpiperidin-1-yl benzoate (4)



1,3,3-Triphenylprop-2-en-1-one (5)

