L-CYSTEINE CATALYZED ONE-POT SYNTHESIS OF BICYCLIC δ-LACTONES UNDER BALL-MILLING CONDITIONS

Ling Jiang,[1] Qingqing Lu,[1] Qianqian Tang,[1] Yue Cheng,[2] and Xiaohe Chu[1]*

[1]Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, 18 Chaowang Road, Hangzhou 310014, PR China. [2]Zhejiang Lvchuang Biotechnology Co., Ltd., 926 Changhong East Street, Huzhou 313200, PR China. *E-mail: chuxhe@zjut.edu.cn

1. General information

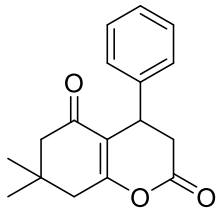
Unless otherwise noted, all the reagents were obtained from Aladdin Chemicals Reagent Co., Ltd. (Shanghai, China) and used without further purification.

Melting points were determined with an Optimelt MPA100 melting point apparatus, and uncorrected. NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) or Bruker AVANCE III 500 spectrometer (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR) using $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Mass spectra were measured by a Bruker micrOTOF-Q II spectrometer with ESI.

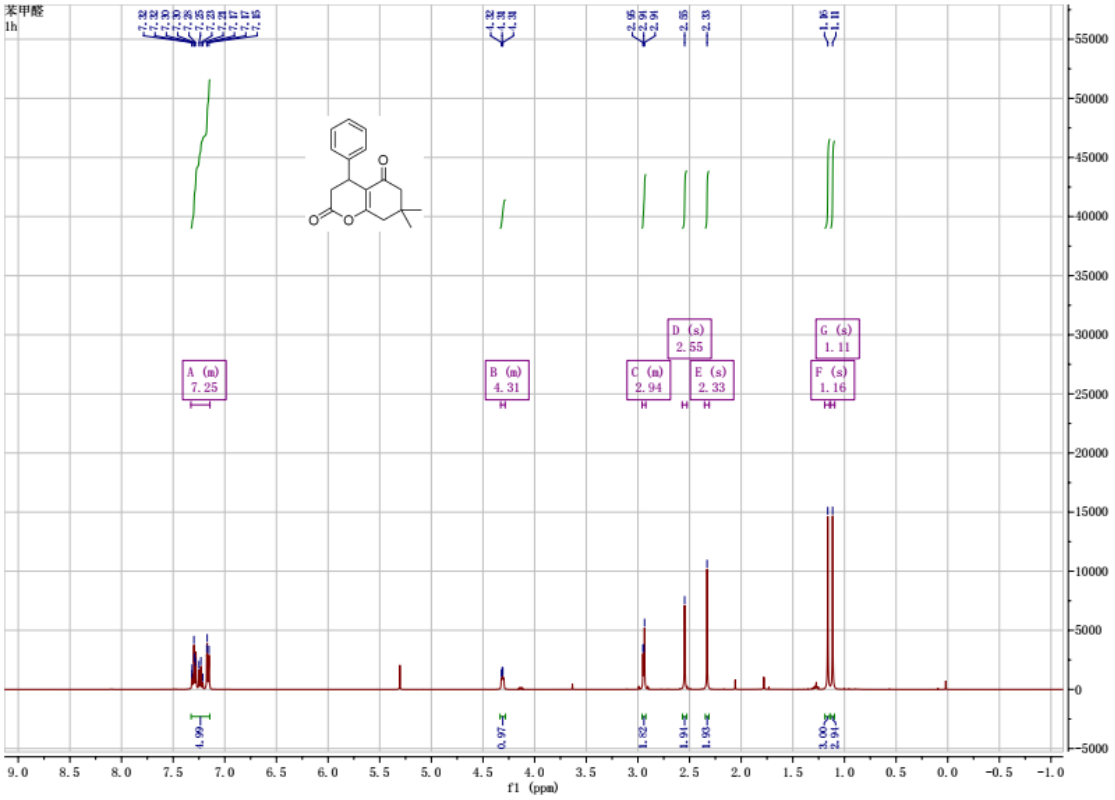
2. L-cysteine catalyzed rapid synthesis of bicyclic δ-lactones under ball-milling conditions

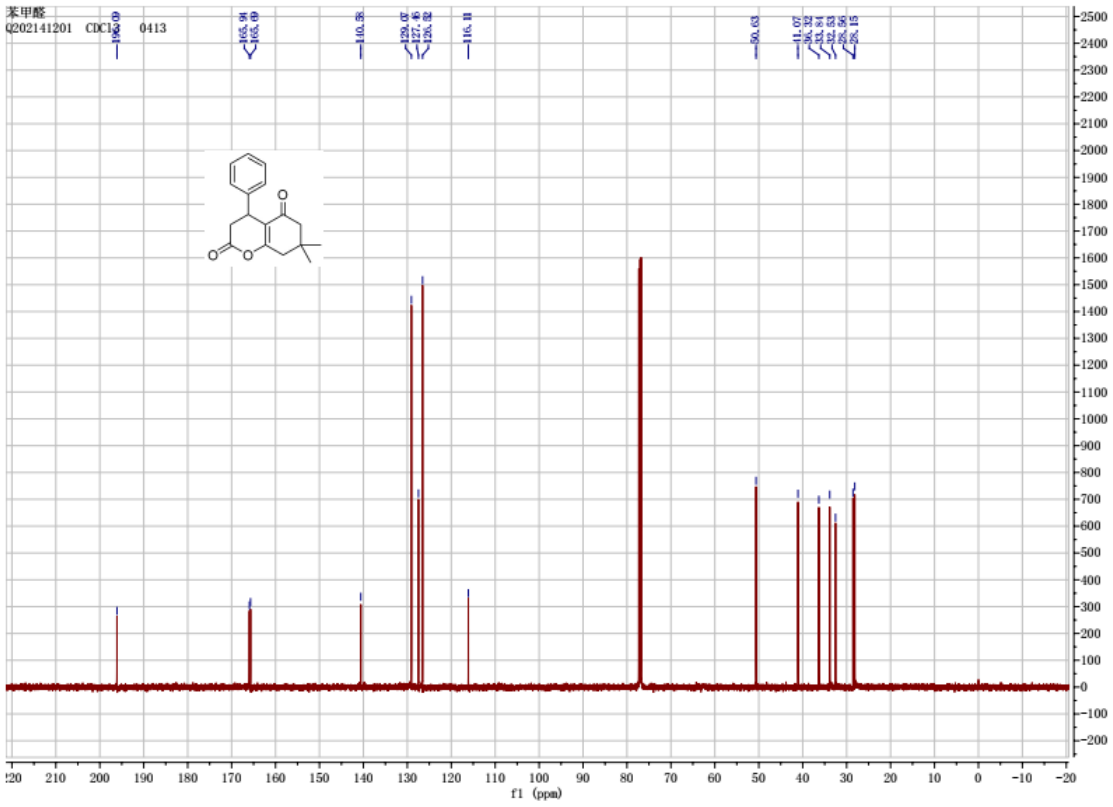
A mixture of aromatic aldehyde (1 mmol), Meldrum's acid (1 mmol), dimedone (1 mmol) or 1,3-cyclohexanedione (1 mmol), silica gel (600 mg) and L-cysteine (120 mg) was milled for 30 min at 30 Hz in a Retsch MM 400 Mixer Mill (MM 400, Retsch, Germany) using a 50 mL stainless steel grinding jar with three stainless steel grinding balls (diameter 10 mm). After the milling was stopped, the reaction mixture was diluted with CH_2Cl_2, filtered, the mixture of L-cysteine and silica gel was recovered and reused. The filtrate was concentrated in vacuo, and then purified by recrystallization from ethanol to afford the desired products (**4a**-**4t**). All title compounds were characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS.

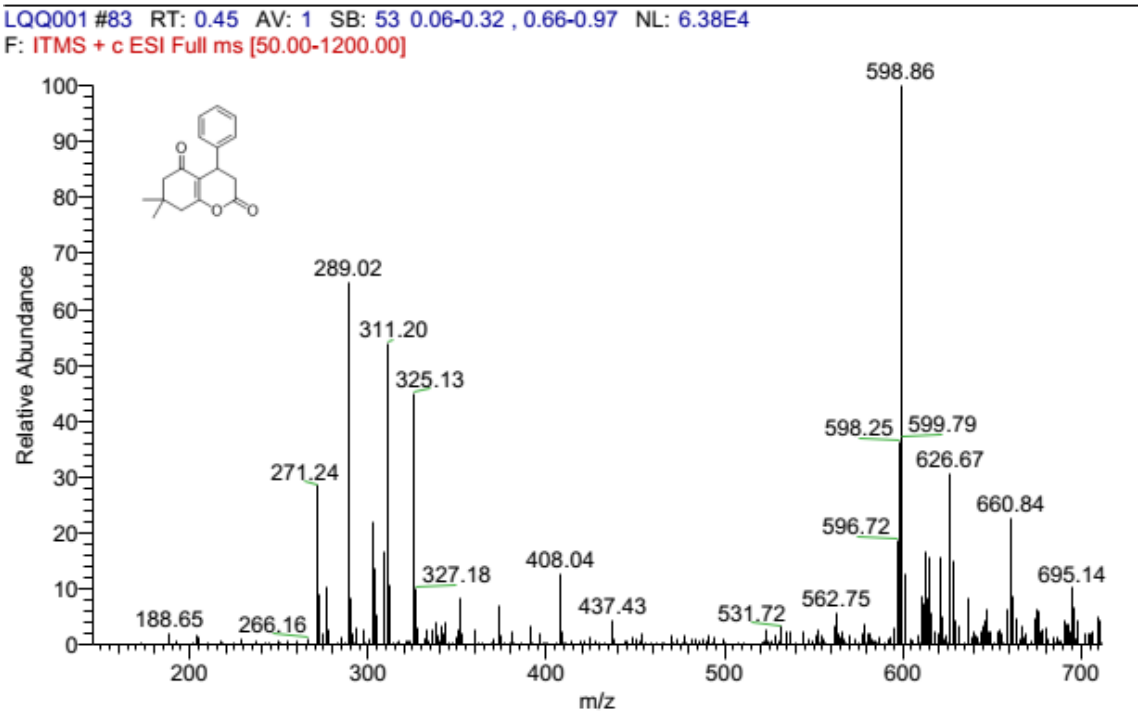
3. Data of the products

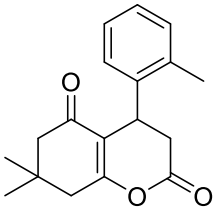


7,7-Dimethyl-4-phenyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4a**). White solid; mp 102-104 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 5H), 4.33 – 4.29 (m, 1H), 2.96 – 2.92 (m, 2H), 2.55 (s, 2H), 2.33 (s, 2H), 1.16 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.09, 165.94, 165.69, 140.58, 129.07, 127.46, 126.52, 116.11, 50.63, 41.07, 36.32, 33.84, 32.53, 28.56, 28.15. MS (ESI): $[M+H]^+$: 271.24.

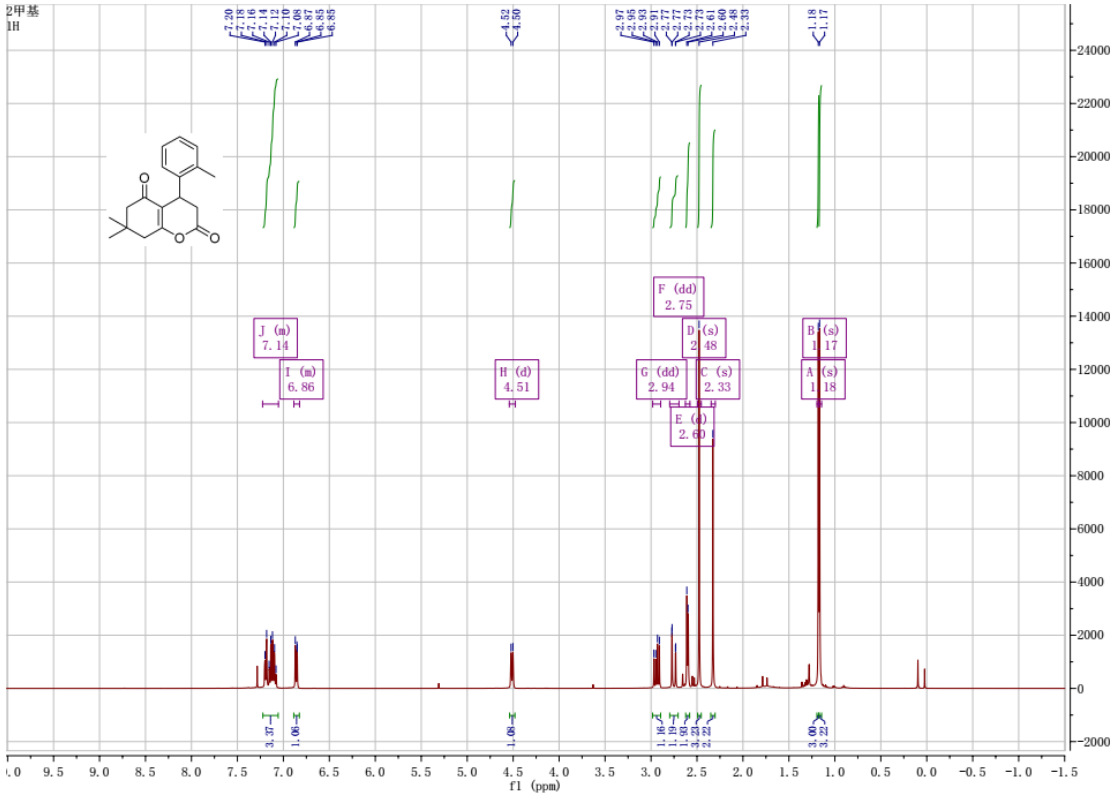


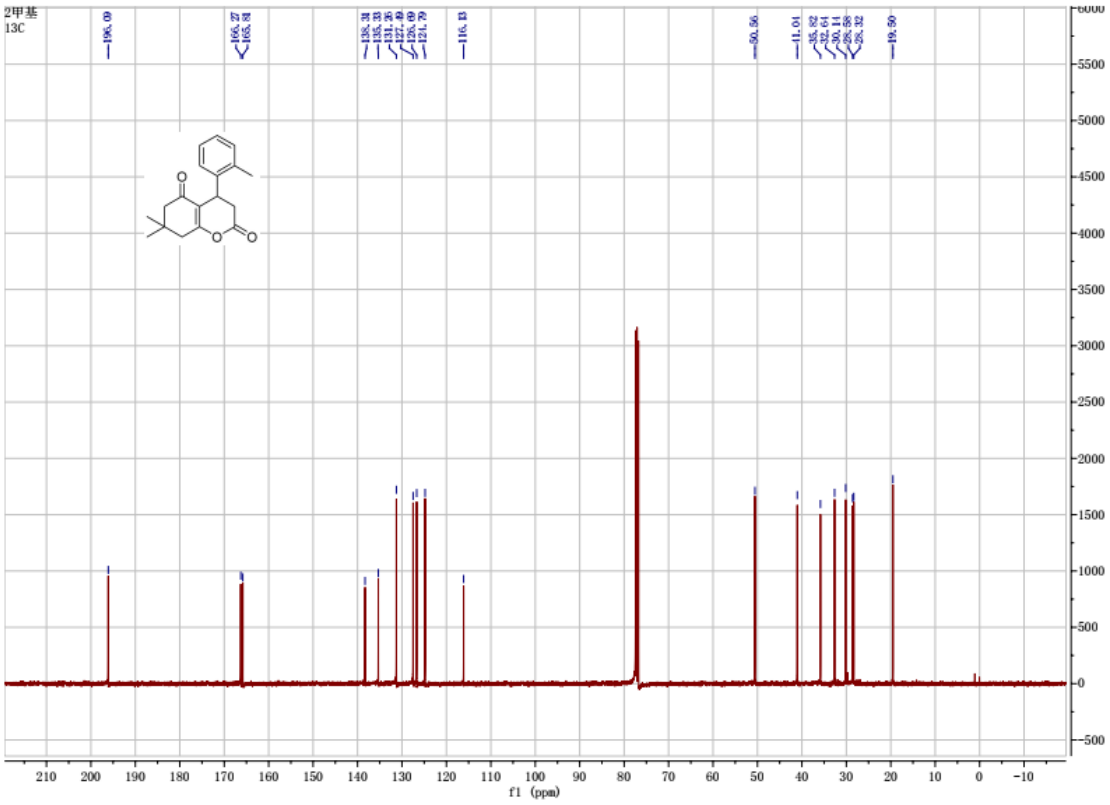

苯甲醛
Q202141201 CDCl3 0413
165.94
165.69
110.36
129.07
127.46
126.32
116.11
50.63
41.07
30.32
28.53
28.15
f1 (ppm)


LQQ001 #83 RT: 0.45 AV: 1 SB: 53 0.06-0.32 , 0.66-0.97 NL: 6.38E4
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
598.86
289.02
311.20
325.13
598.25
599.79
626.67
271.24
660.84
596.72
408.04
327.18
695.14
437.43
562.75
531.72
188.65
266.16

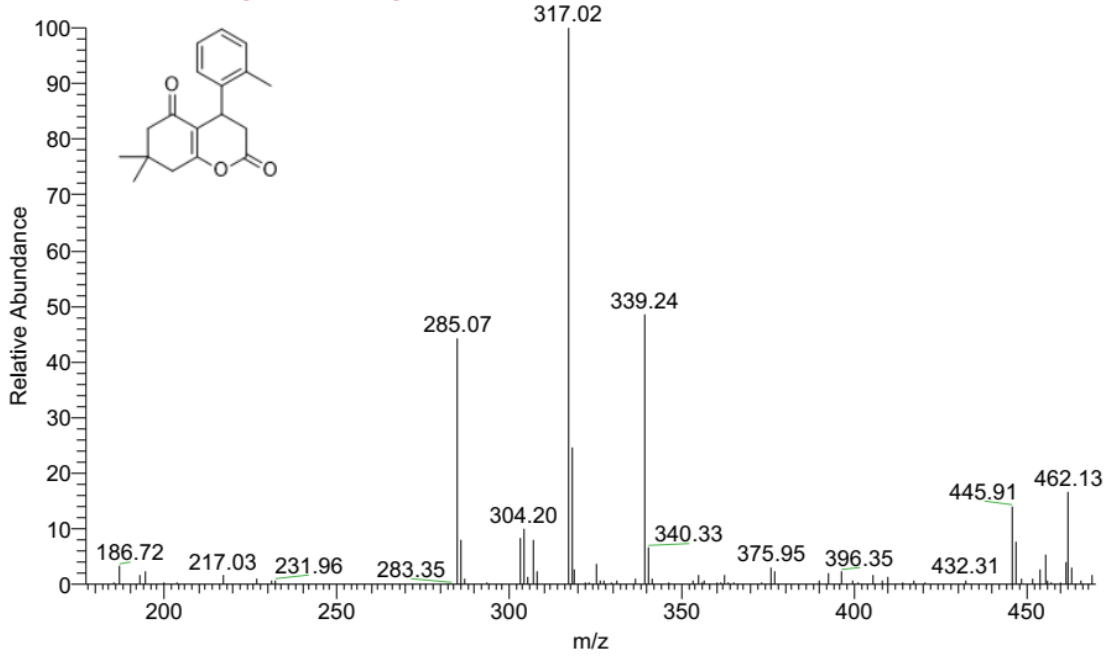


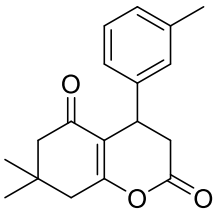
7,7-Dimethyl-4-(*o*-tolyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4b**). White solid, mp 101-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.05 (m, 3H), 6.89 – 6.82 (m, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 2.94 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.75 (dd, *J* = 15.8, 1.2 Hz, 1H), 2.60 (d, *J* = 5.3 Hz, 2H), 2.48 (s, 3H), 2.33 (s, 2H), 1.18 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.09, 166.27, 165.81, 138.31, 135.33, 131.26, 127.49, 126.69, 124.79, 116.13, 50.56, 41.04, 35.82, 32.64, 30.14, 28.58, 28.32, 19.50. MS (ESI): $[M+H+CH_3OH]^+$: 317.02.



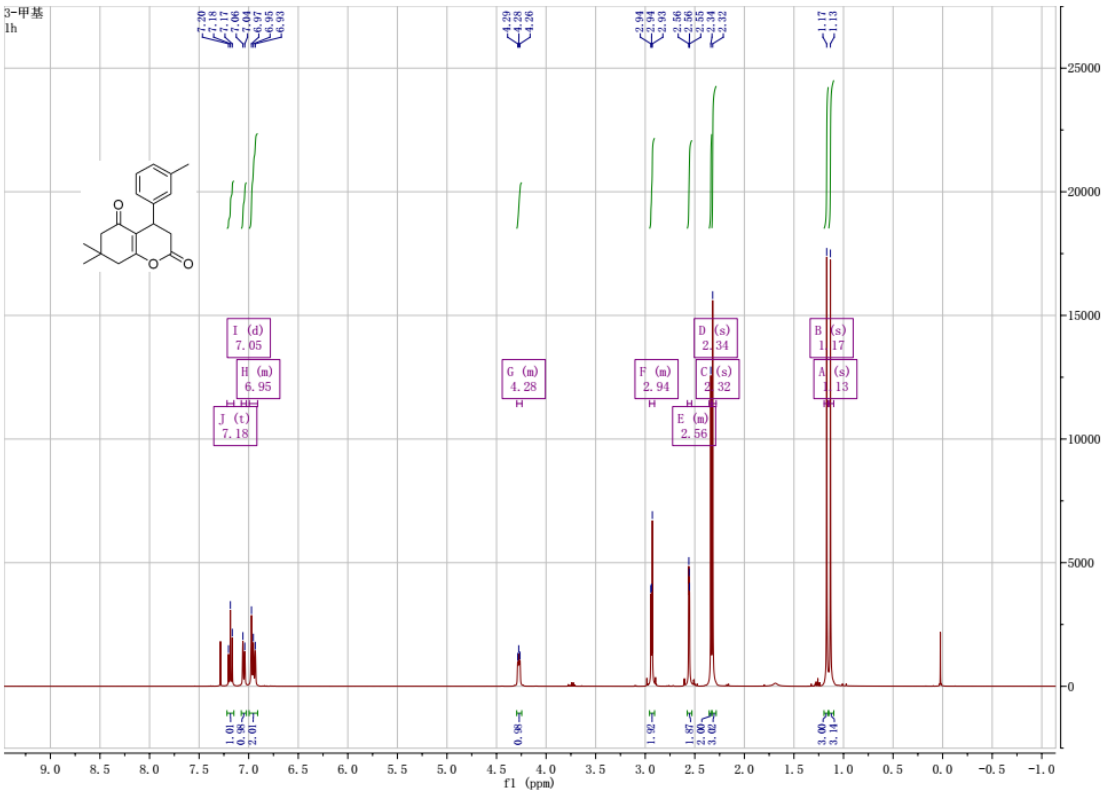


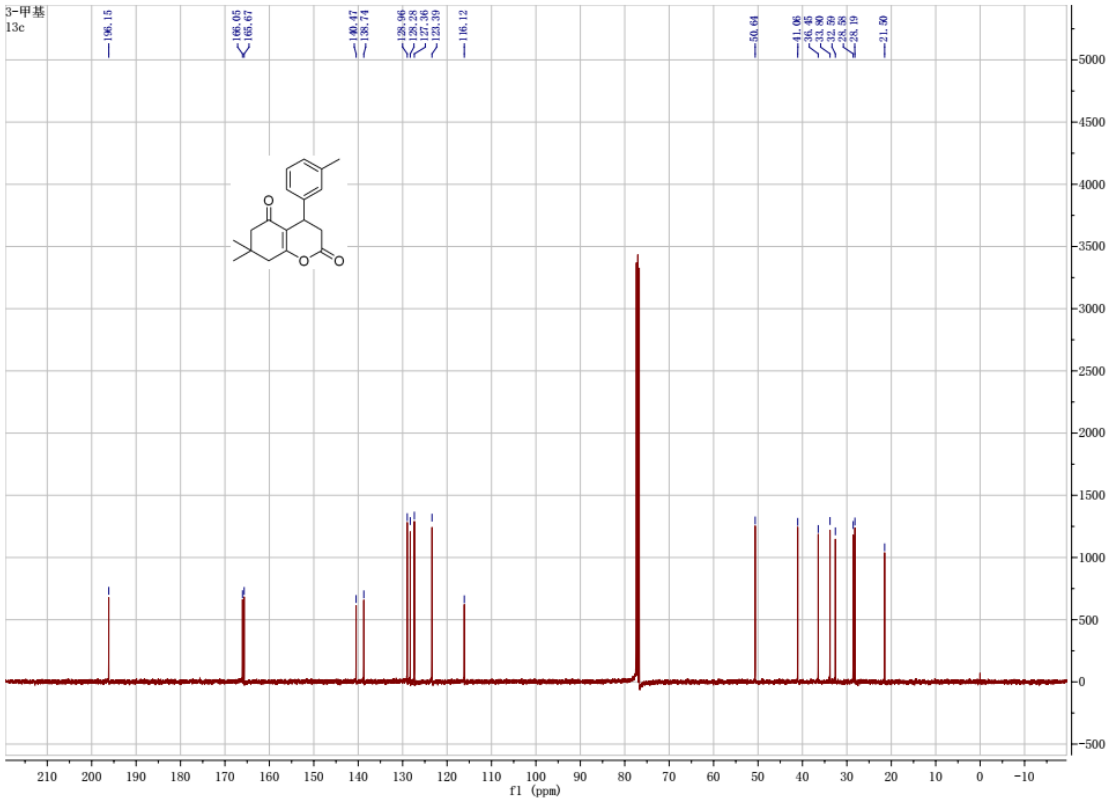
LQQ013_210522113322 #77 RT: 0.41 AV: 1 SB: 59 0.05-0.28 , 0.66-1.07 NL: 1.44E5
F: ITMS + c ESI Full ms [50.00-1200.00]

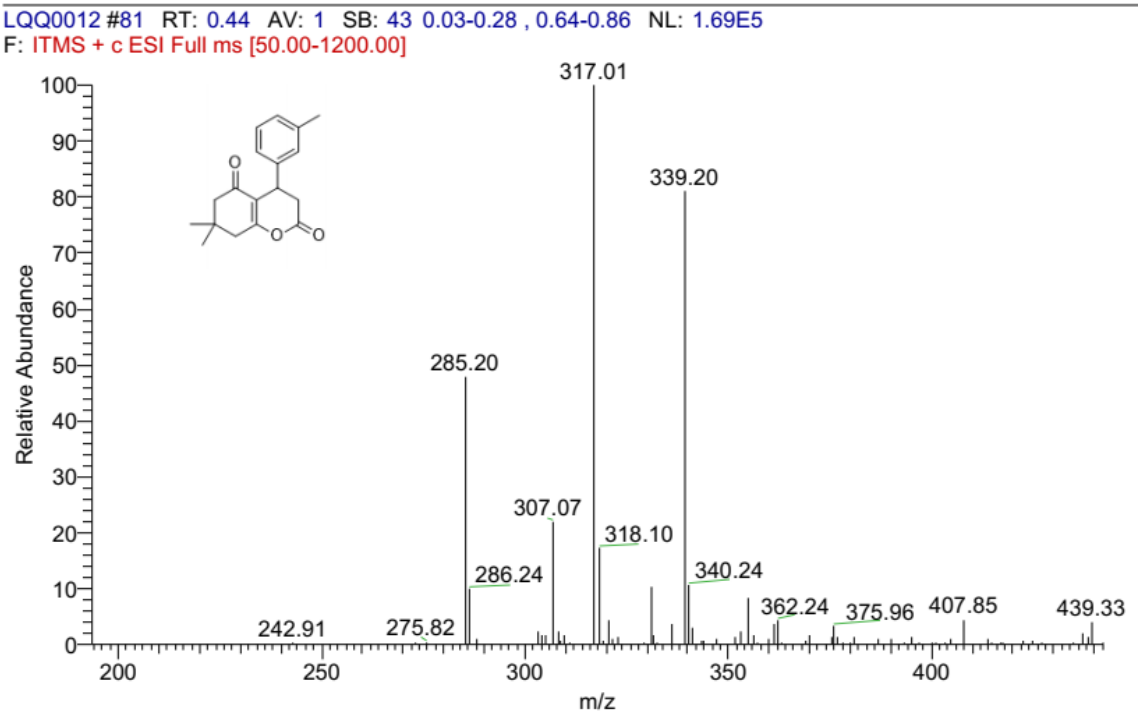


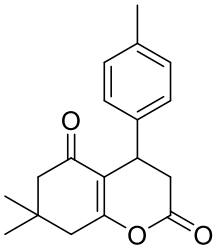


7,7-Dimethyl-4-(*m*-tolyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4c**). White solid, mp 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.91 (m, 2H), 4.30 – 4.24 (m, 1H), 2.96 – 2.91 (m, 2H), 2.57 – 2.53 (m, 2H), 2.34 (s, 2H), 2.32 (s, 3H), 1.17 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.15, 166.05, 165.67, 140.47, 138.74, 128.96, 128.28, 127.36, 123.39, 116.12, 50.64, 41.06, 36.45, 33.80, 32.59, 28.58, 28.19, 21.50. MS (ESI): $[M+H+CH_3OH]^+$: 317.01.

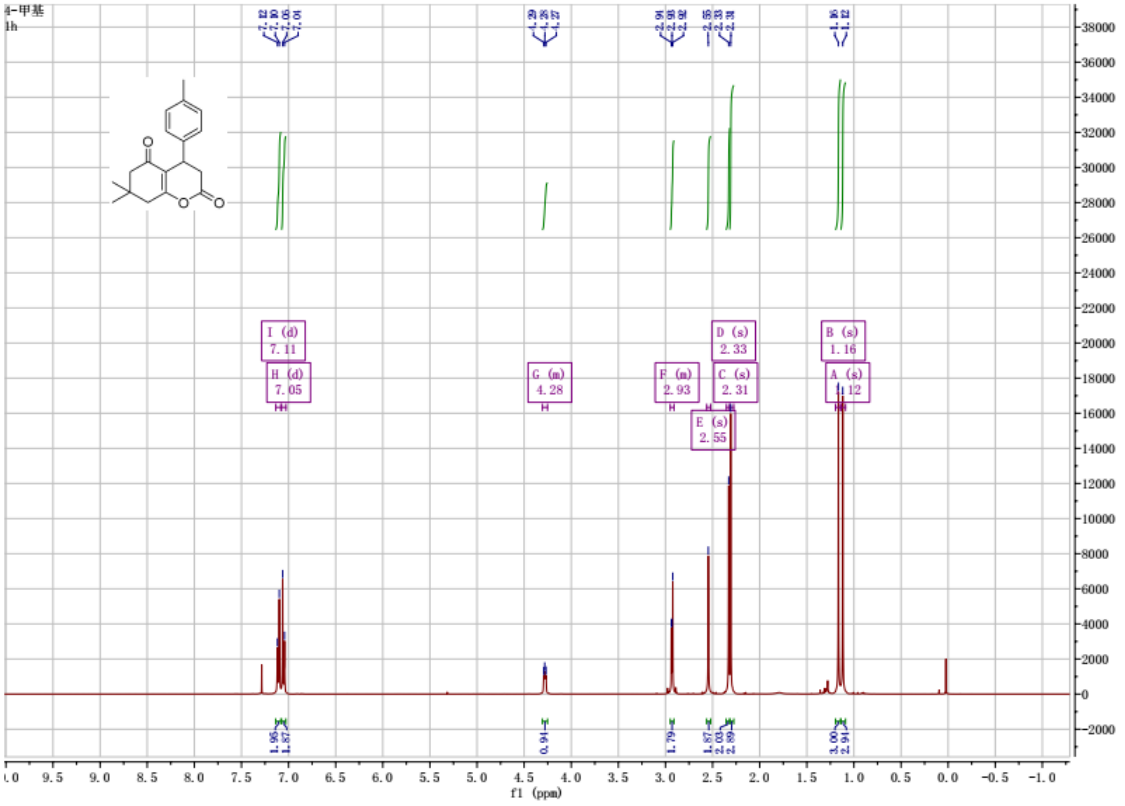


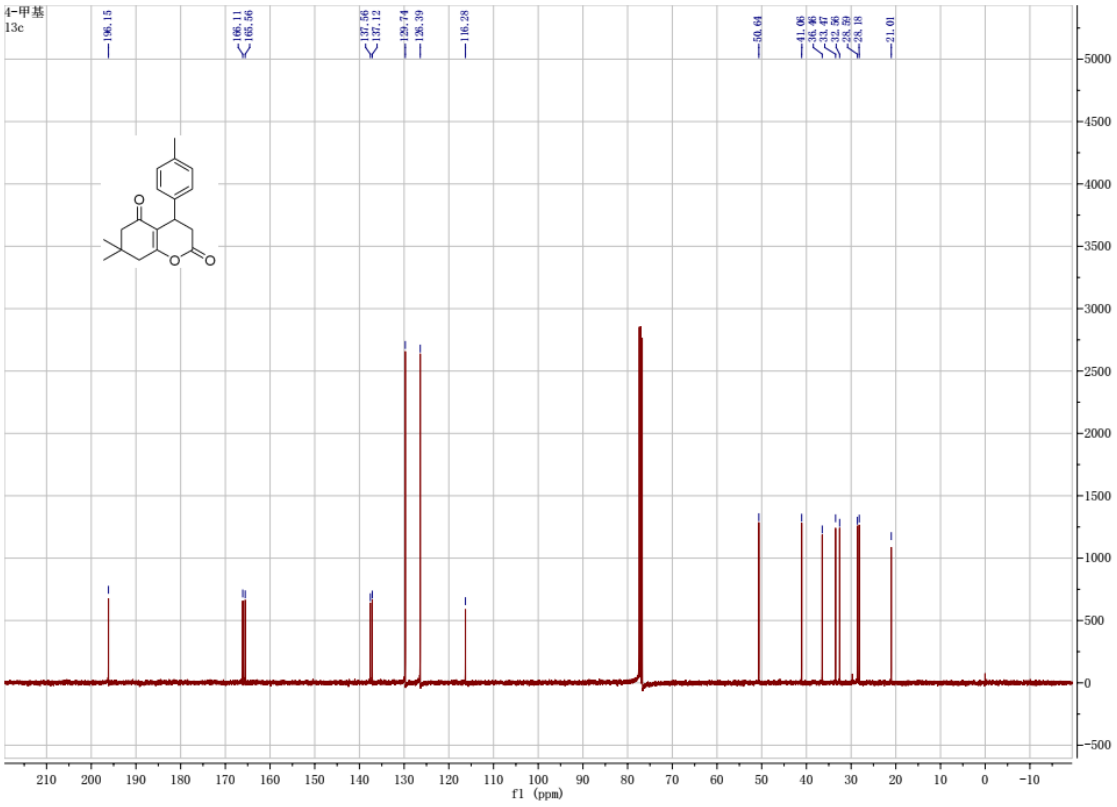

3-甲基
13c
196.15
166.05
165.67
140.47
138.74
128.96
128.38
127.36
123.39
116.12
50.64
41.06
36.45
31.49
32.59
28.58
28.19
21.50
f1 (ppm)

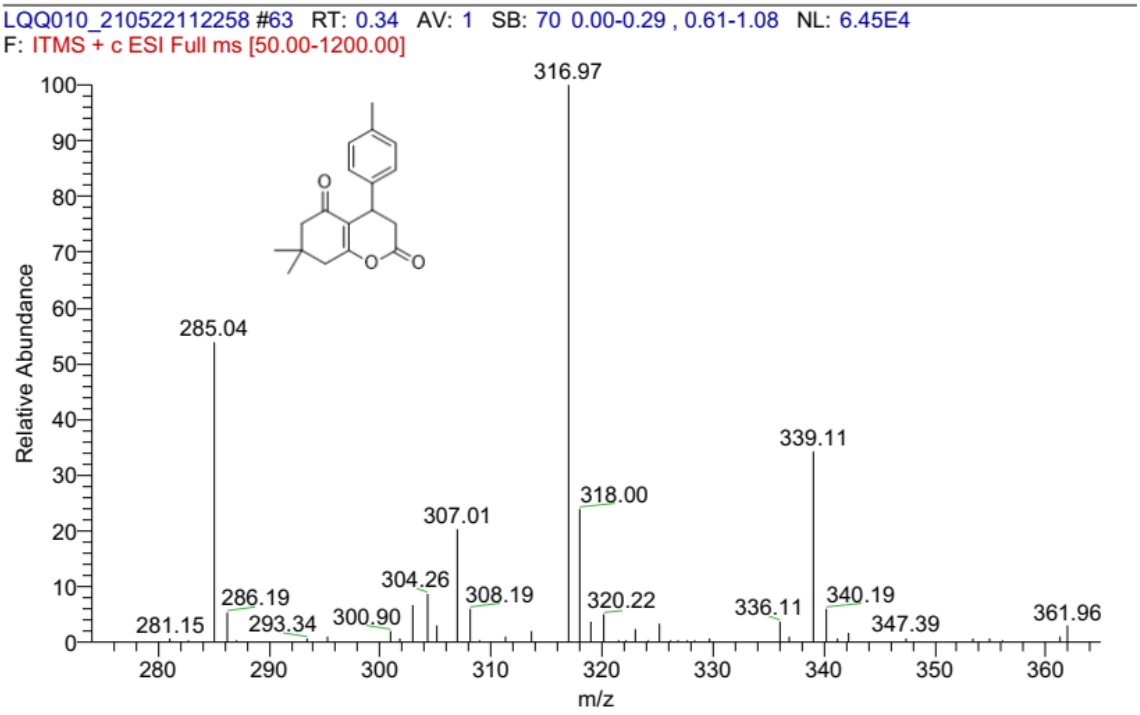

LQQ0012 #81 RT: 0.44 AV: 1 SB: 43 0.03-0.28 , 0.64-0.86 NL: 1.69E5
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
317.01
339.20
285.20
307.07
318.10
286.24
340.24
362.24
375.96
407.85
439.33
242.91
275.82

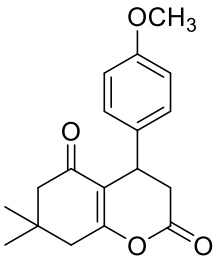


7,7-Dimethyl-4-(*p*-tolyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4d**). White solid, mp 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 4.31 – 4.25 (m, 1H), 2.95 – 2.91 (m, 2H), 2.55 (s, 2H), 2.33 (s, 2H), 2.31 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.15, 166.11, 165.56, 137.56, 137.12, 129.74, 126.39, 116.28, 50.64, 41.06, 36.46, 33.47, 32.56, 28.59, 28.18, 21.01. MS (ESI): $[M+H+CH_3OH]^+$: 316.97.

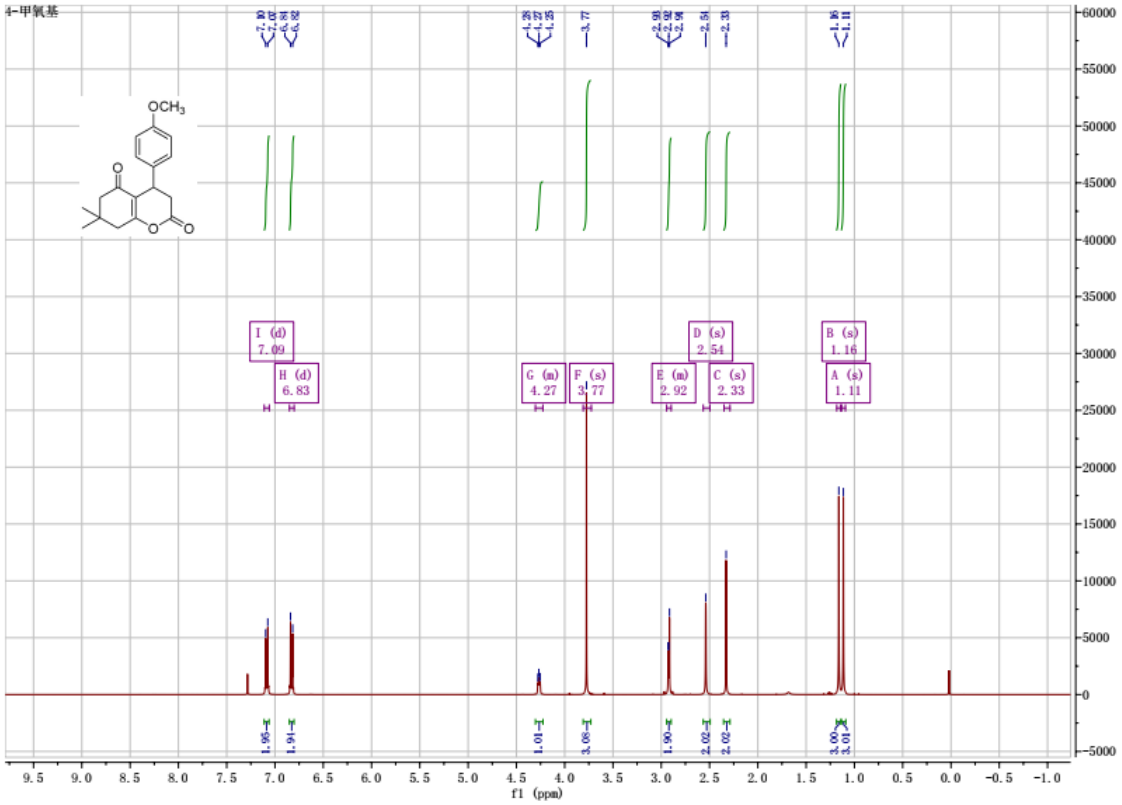


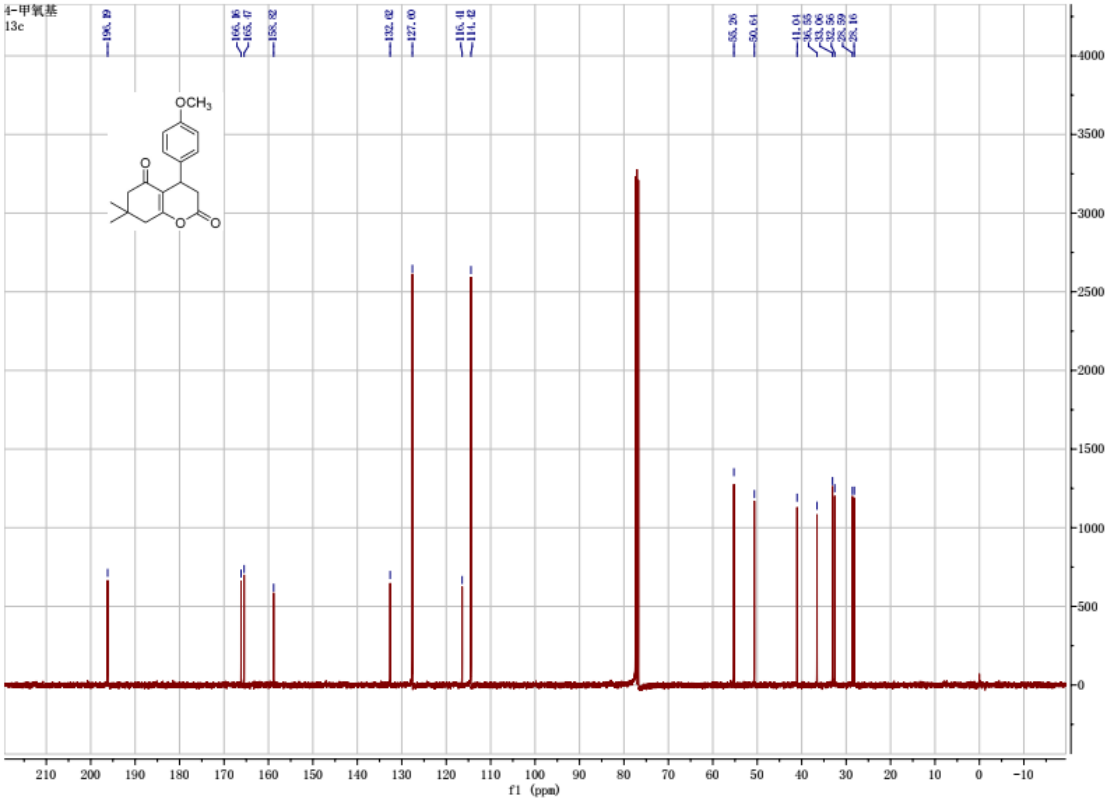

4-甲基
13c
196.15
166.11
165.56
137.56
137.12
129.74
126.39
116.28
50.64
41.06
36.46
33.47
32.56
28.39
28.18
21.01
f1 (ppm)


LQQ010_210522112258 #63 RT: 0.34 AV: 1 SB: 70 0.00-0.29 , 0.61-1.08 NL: 6.45E4
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
316.97
285.04
339.11
318.00
307.01
304.26
308.19
320.22
286.19
281.15
293.34
300.90
336.11
340.19
347.39
361.96

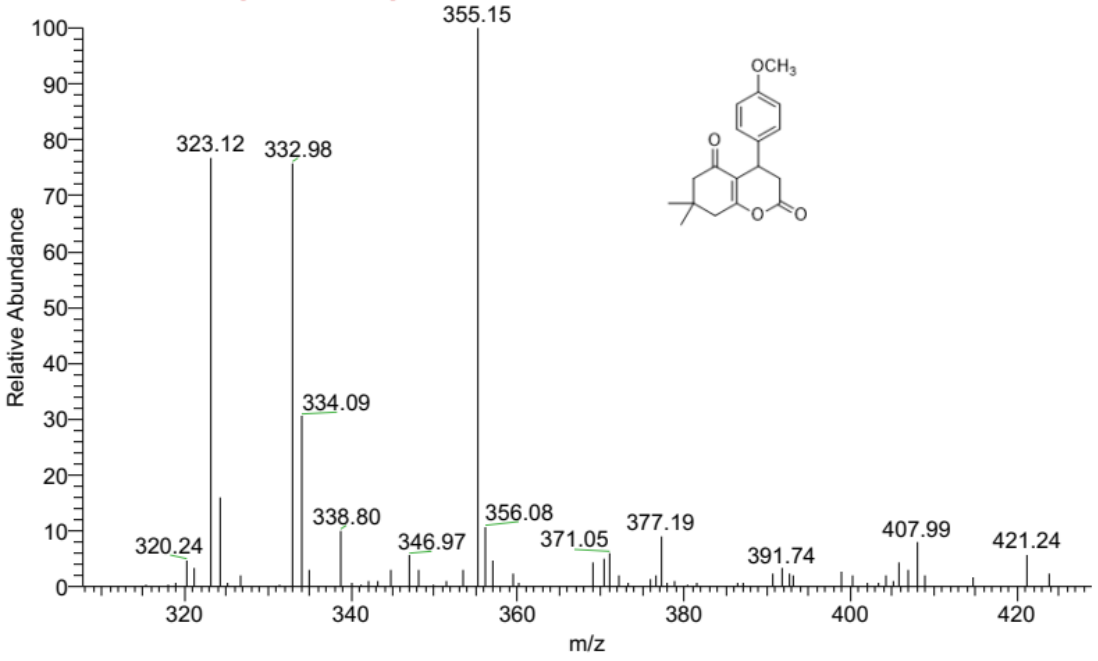


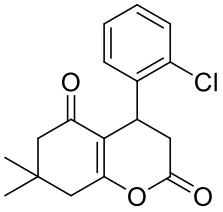
4-(4-Methoxyphenyl)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4e**). Yellow solid, mp 134-137 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.30 – 4.23 (m, 1H), 3.77 (s, 3H), 2.94 – 2.90 (m, 2H), 2.54 (s, 2H), 2.33 (s, 2H), 1.16 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.19, 166.16, 165.47, 158.82, 132.62, 127.60, 116.41, 114.42, 55.26, 50.64, 41.04, 36.55, 33.06, 32.56, 28.59, 28.16. MS (ESI): $[M+Na]^+$: 323.12.



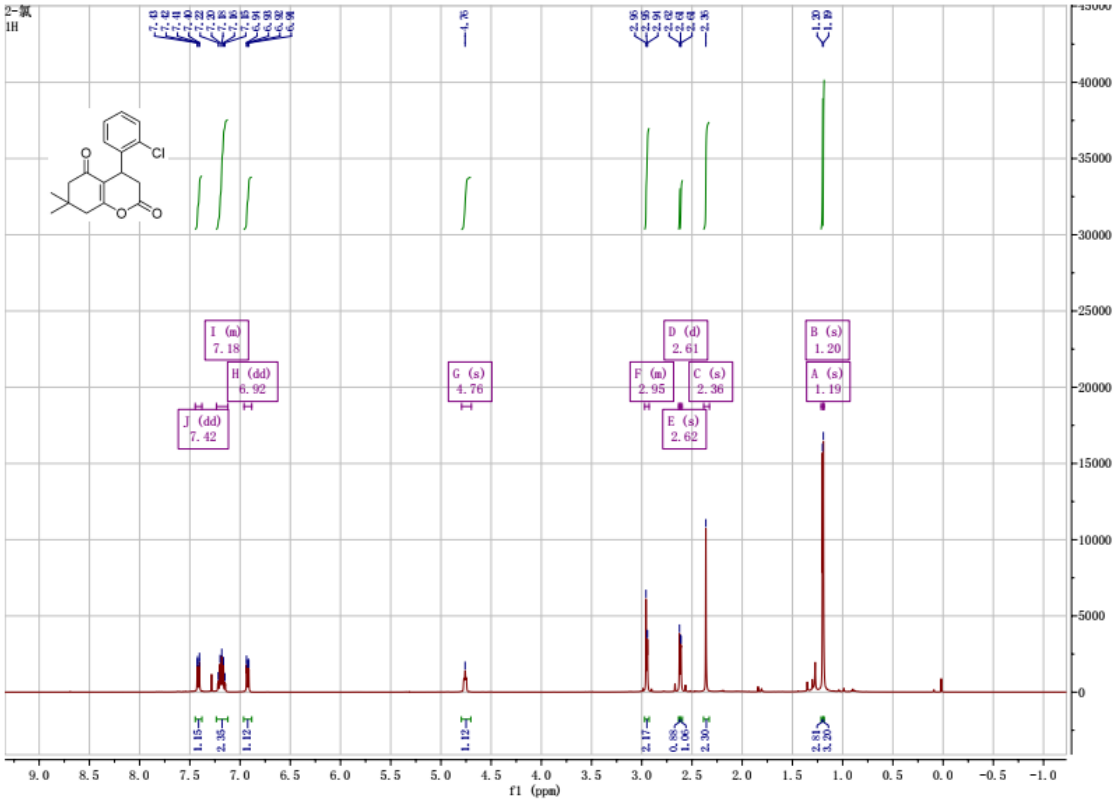


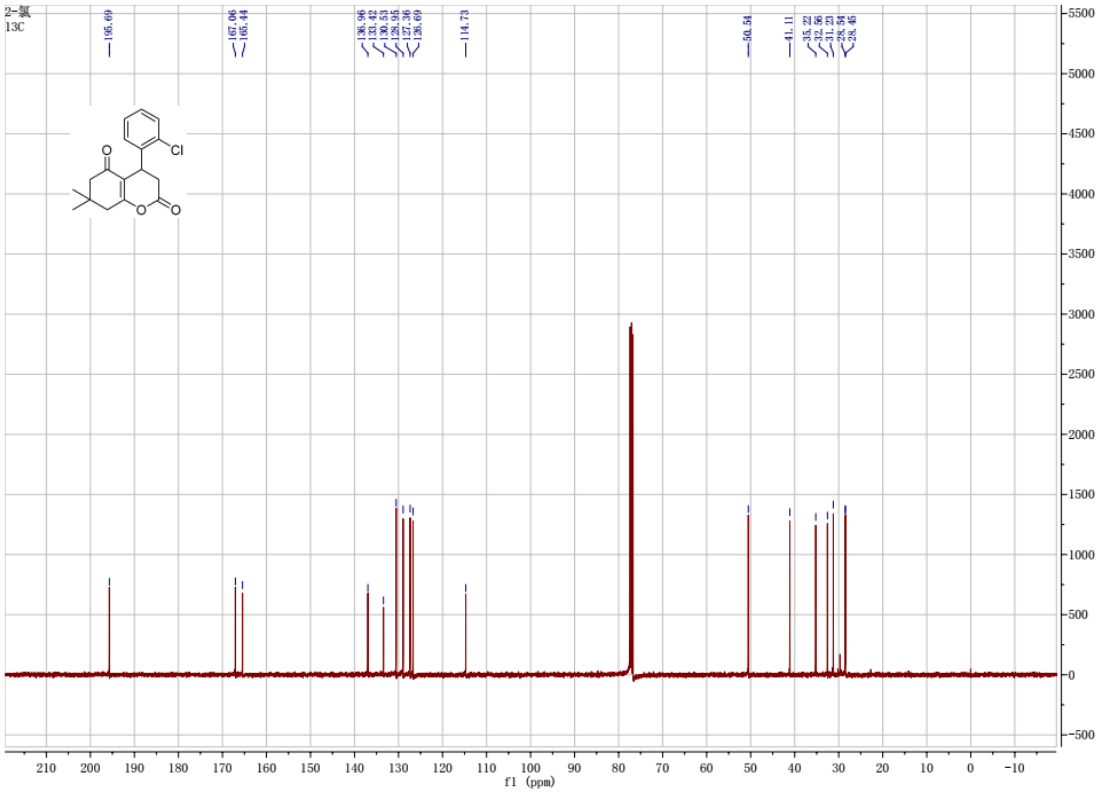
LQQ009 #79 RT: 0.43 AV: 1 SB: 66 0.03-0.28 , 0.72-1.19 NL: 1.07E5
F: ITMS + c ESI Full ms [50.00-1200.00]



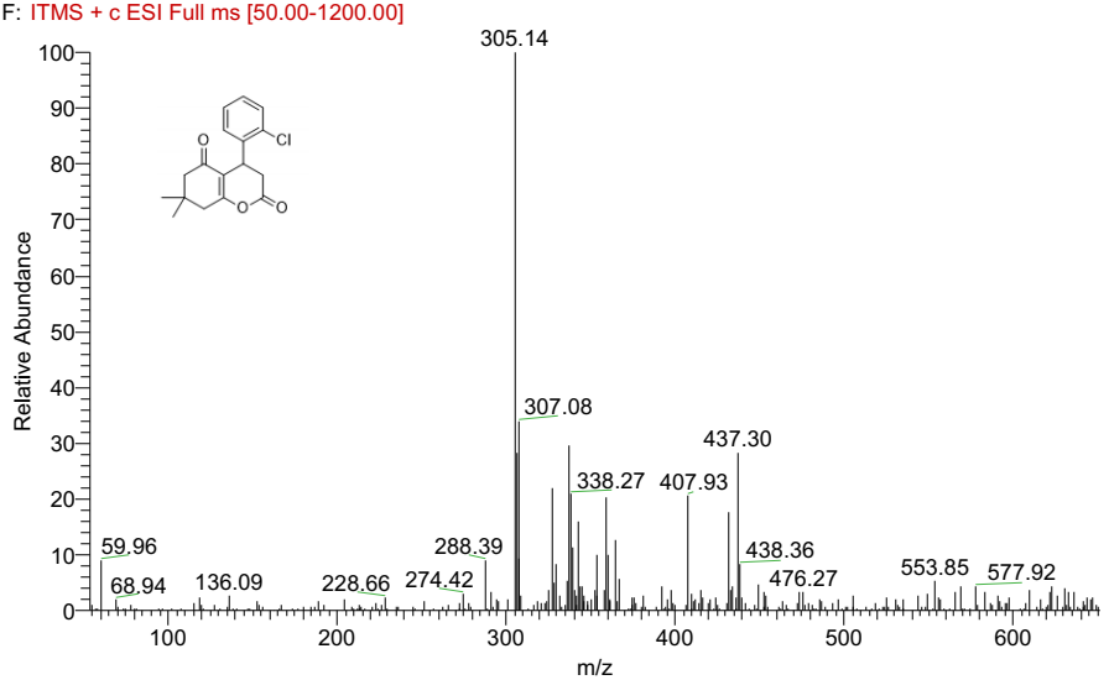


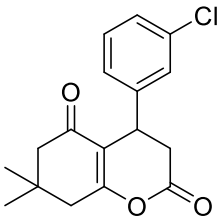
4-(2-Chlorophenyl)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4f**). White solid, mp 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 – 7.12 (m, 2H), 6.92 (dd, *J* = 7.2, 2.0 Hz, 1H), 4.76 (s, 1H), 2.97 – 2.93 (m, 2H), 2.62 (s, 1H), 2.61 (d, *J* = 1.3 Hz, 1H), 2.36 (s, 2H), 1.20 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.69, 167.06, 165.44, 136.96, 133.42, 130.53, 128.95, 127.36, 126.69, 114.73, 50.54, 41.11, 35.22, 32.56, 31.23, 28.54, 28.45. MS (ESI): $[M+H]^+$: 305.14.



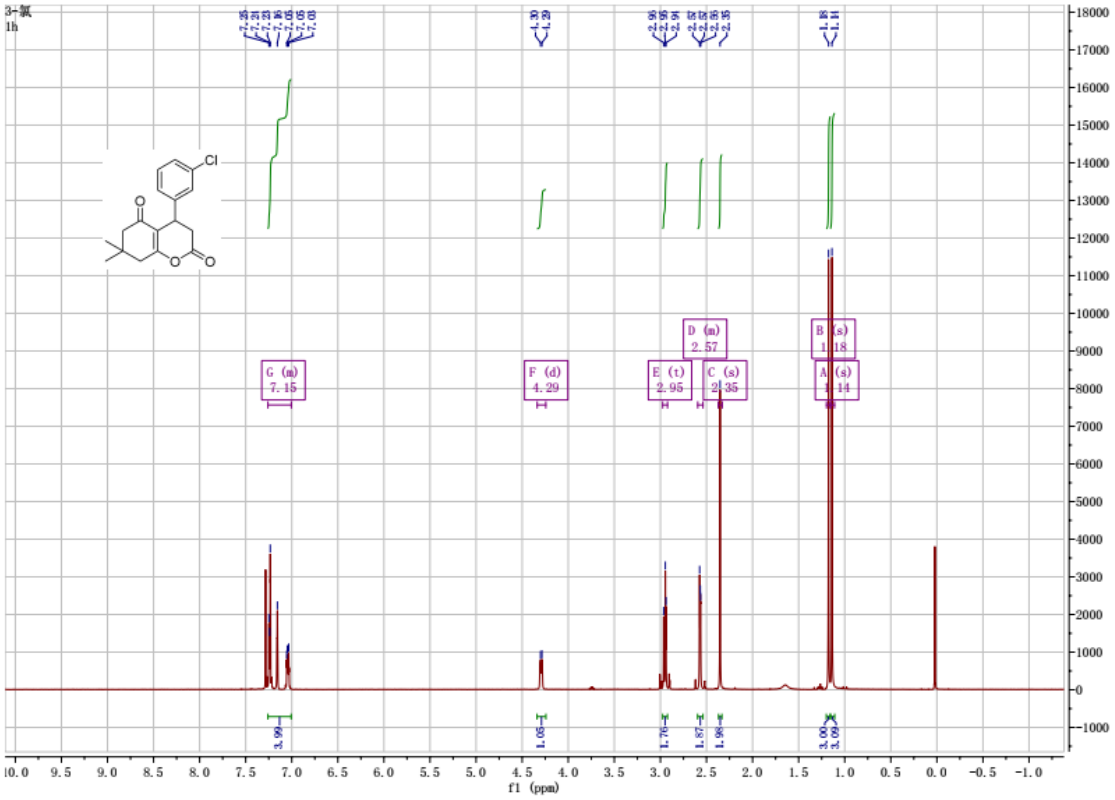


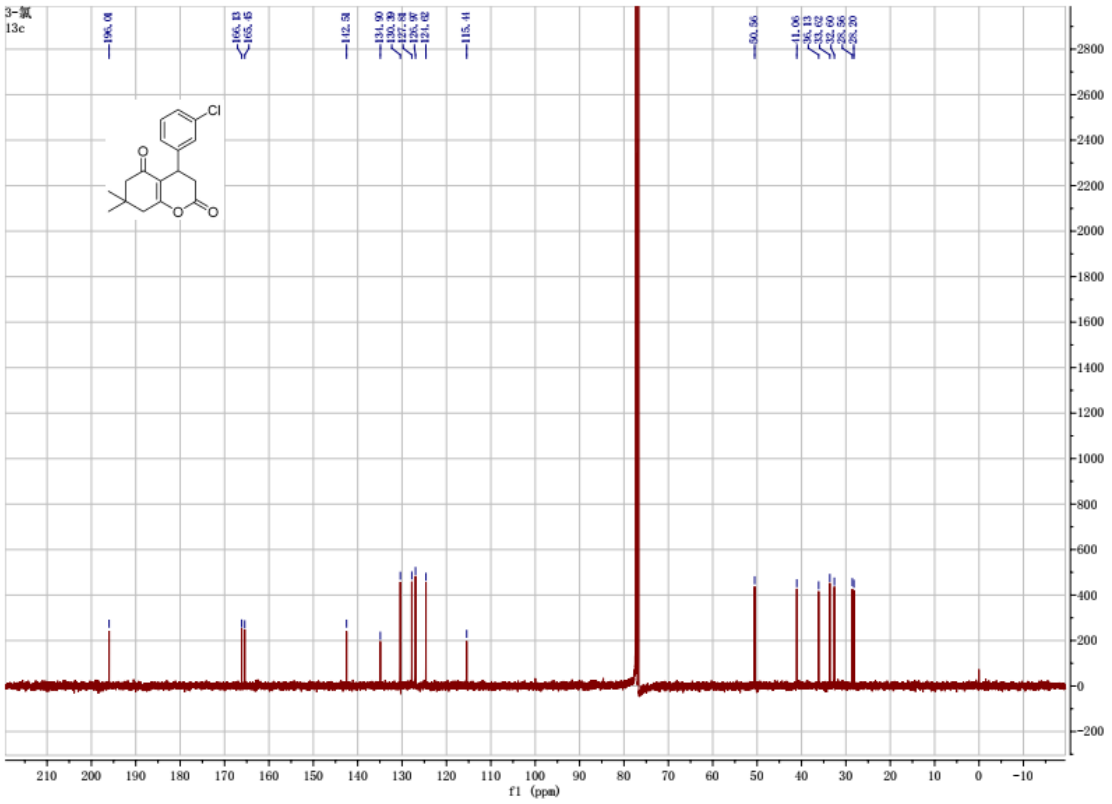
LQQ002 #79 RT: 0.43 AV: 1 SB: 49 0.11-0.29 , 0.65-0.99 NL: 1.99E4
F: ITMS + c ESI Full ms [50.00-1200.00]



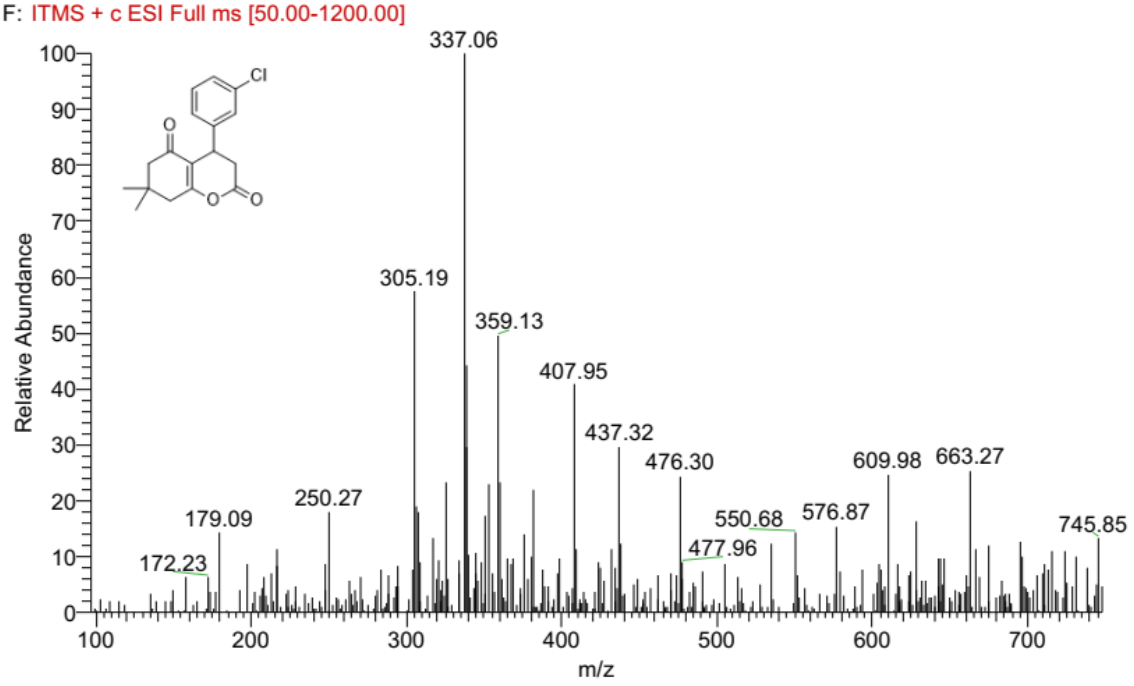


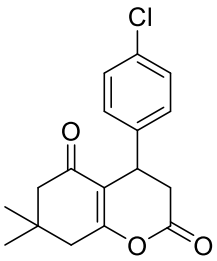
4-(3-Chlorophenyl)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4g**). White solid, mp 122-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.01 (m, 4H), 4.29 (d, *J* = 5.9 Hz, 1H), 2.95 (t, *J* = 5.1 Hz, 2H), 2.59 – 2.54 (m, 2H), 2.35 (s, 2H), 1.18 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.01, 166.13, 165.45, 142.51, 134.90, 130.39, 127.81, 126.97, 124.62, 115.44, 50.56, 41.06, 36.13, 33.62, 32.60, 28.56, 28.20. MS (ESI): $[M+H]^+$: 305.19.



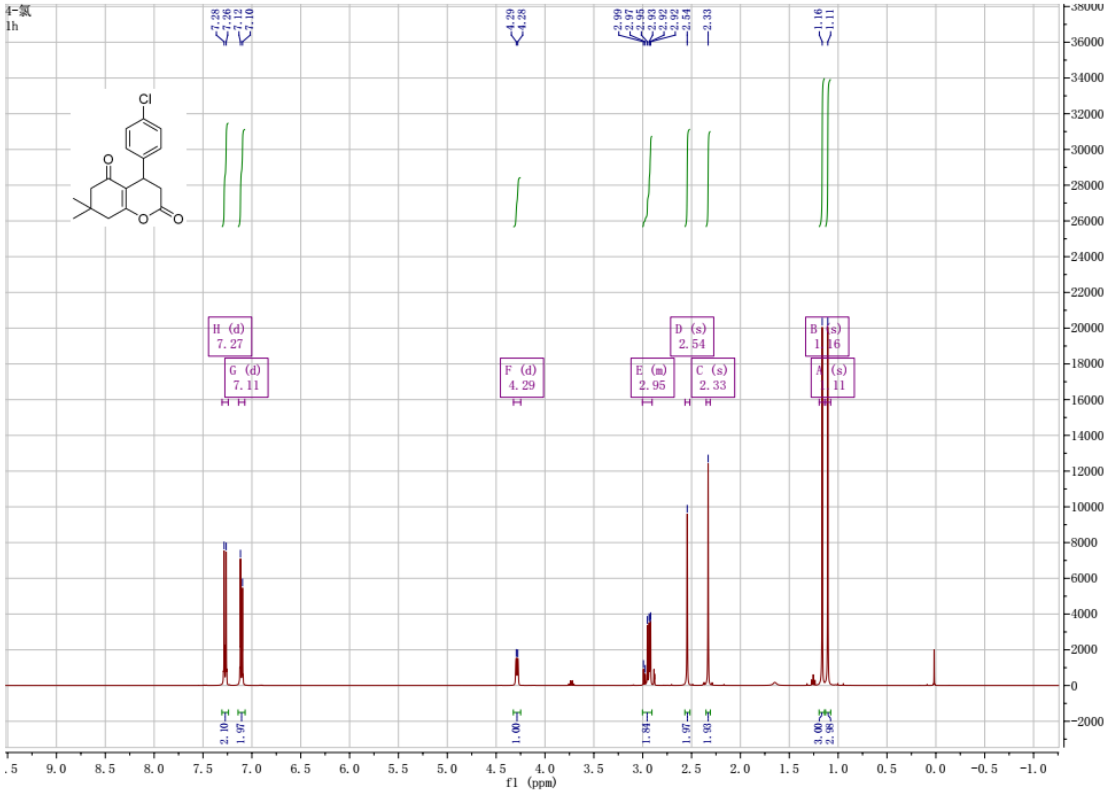


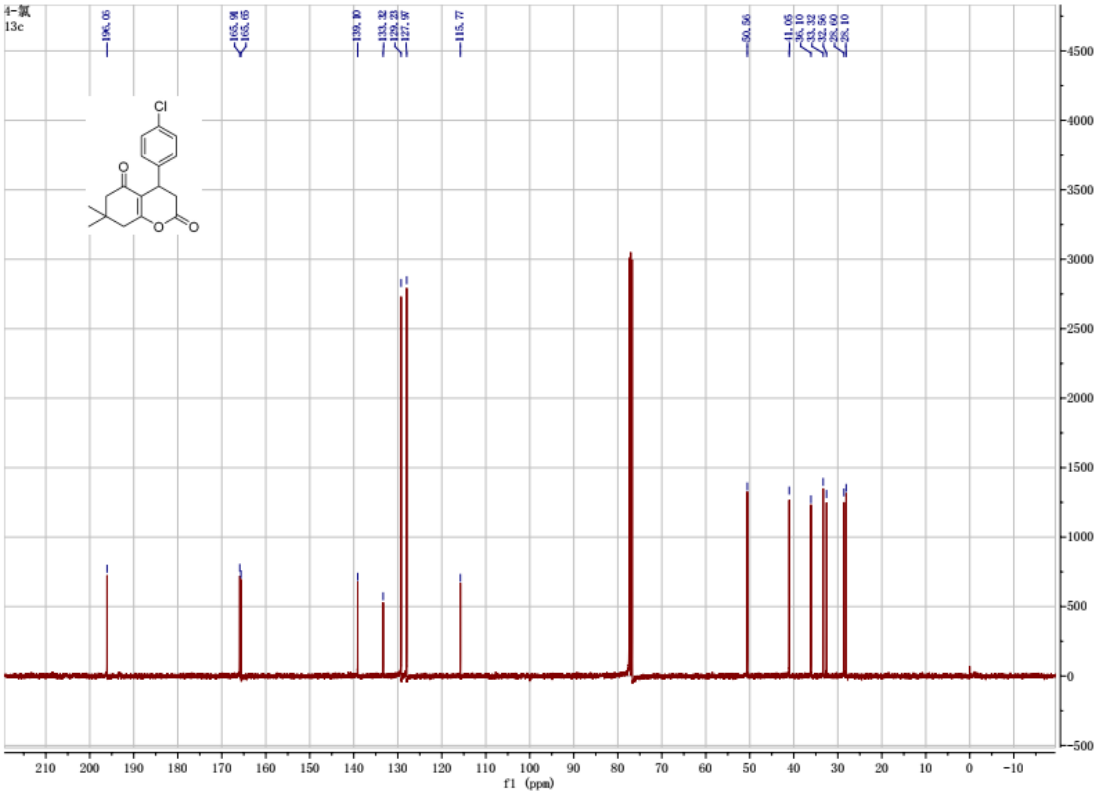
LQQ003 #79 RT: 0.43 AV: 1 SB: 43 0.07-0.28 , 0.62-0.87 NL: 7.62E3
F: ITMS + c ESI Full ms [50.00-1200.00]

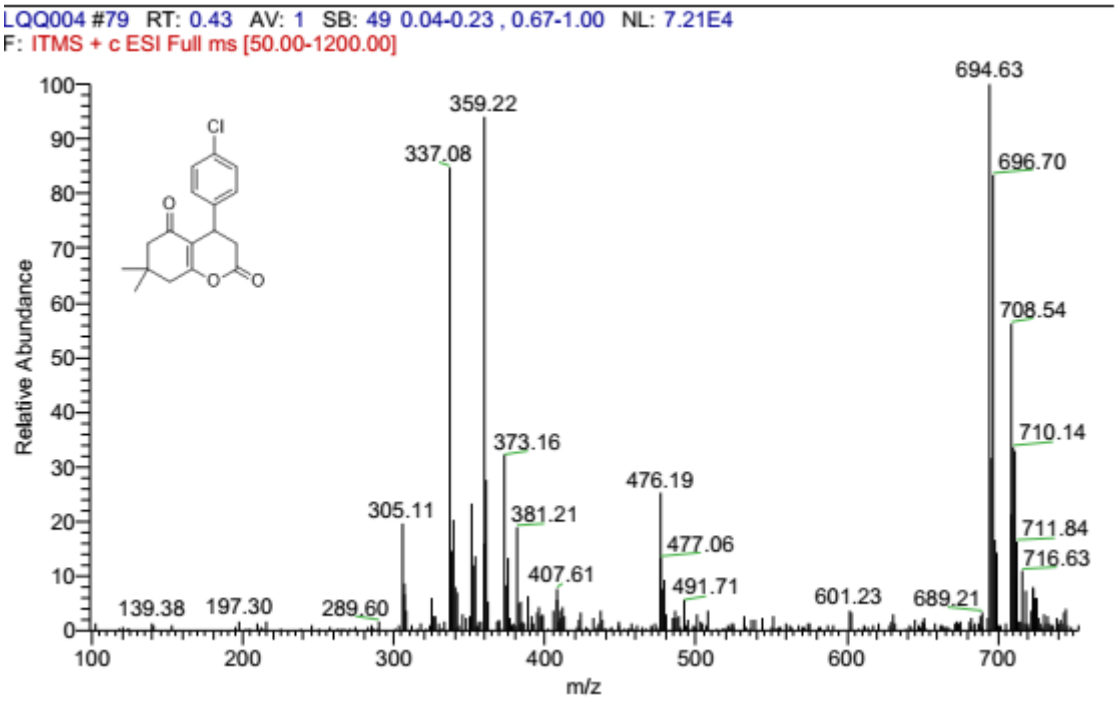


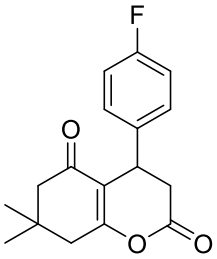


4-(4-Chlorophenyl)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4h**). White solid, mp 166-168 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 4.29 (d, J = 6.1 Hz, 1H), 3.00 – 2.90 (m, 2H), 2.54 (s, 2H), 2.33 (s, 2H), 1.16 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.06, 165.91, 165.65, 139.10, 133.32, 129.23, 127.97, 115.77, 50.56, 41.05, 36.10, 33.32, 32.56, 28.60, 28.10. MS (ESI): $[M+H+CH_3OH]^+$: 337.08.

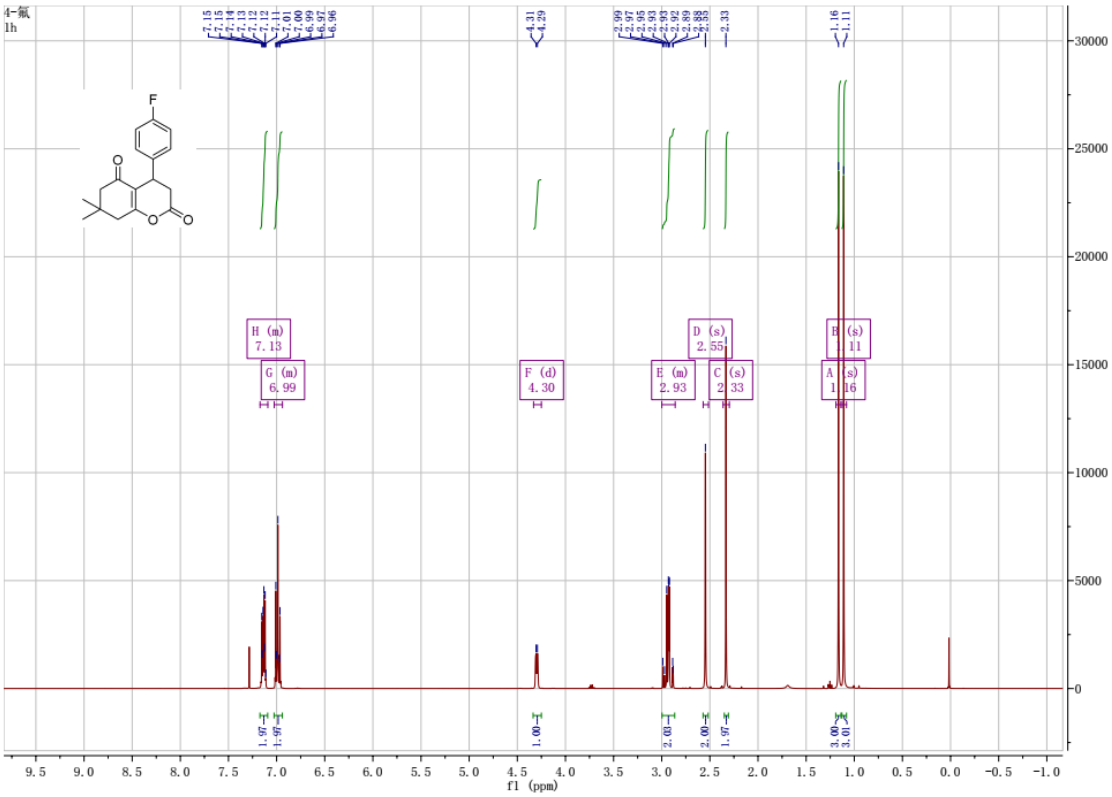


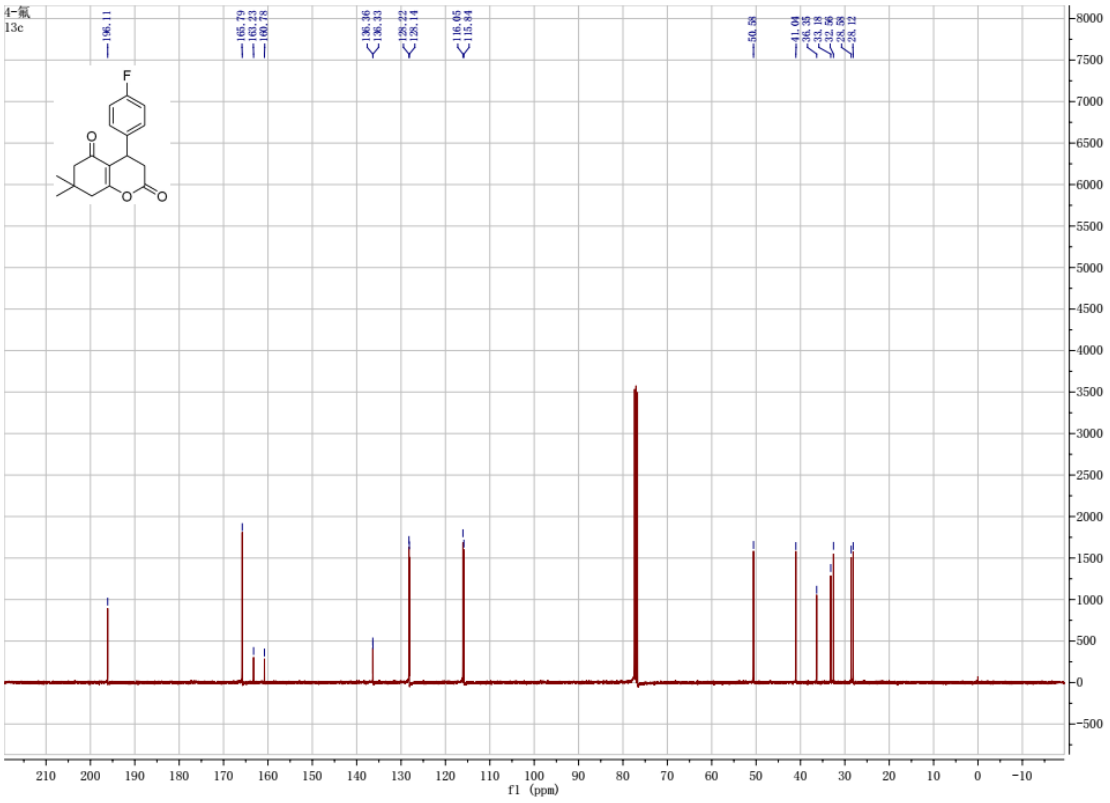

4-氯
13c
196.05
165.98
165.65
139.97
133.32
129.23
127.97
115.77
50.56
41.05
36.10
33.32
32.56
28.60
28.10
Cl
O
O
O
f1 (ppm)


LQQ004 #79 RT: 0.43 AV: 1 SB: 49 0.04-0.23 , 0.67-1.00 NL: 7.21E4
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
694.63
359.22
337.08
696.70
708.54
710.14
373.16
476.19
305.11
381.21
477.06
711.84
716.63
407.61
491.71
139.38
197.30
289.60
601.23
689.21
Cl
O
O
O

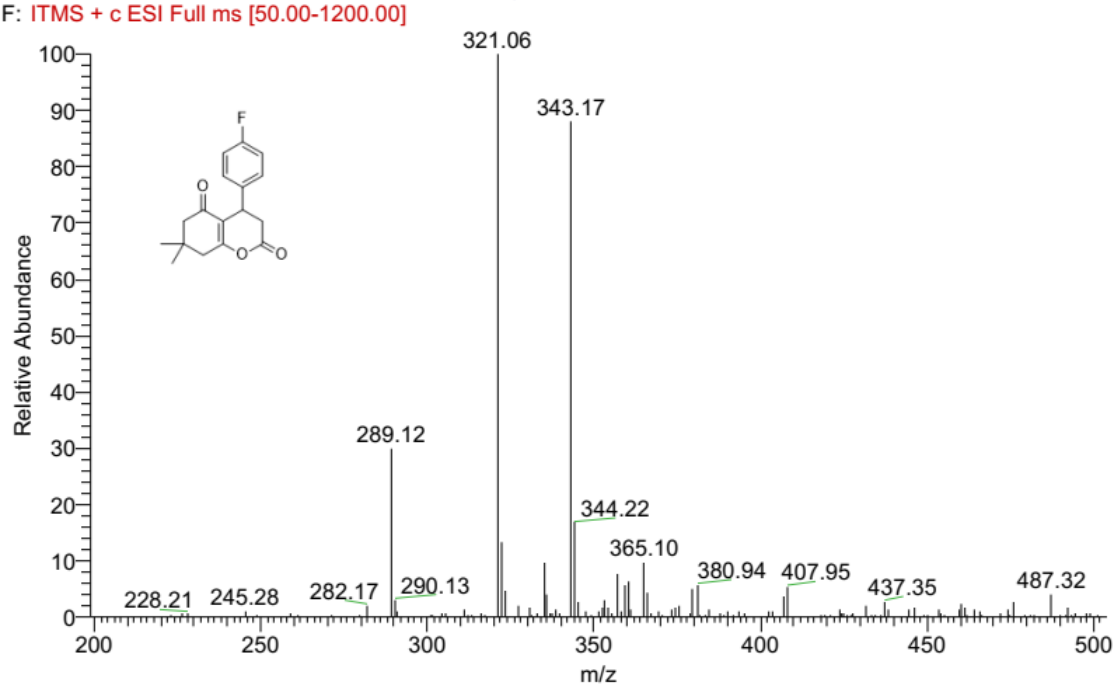


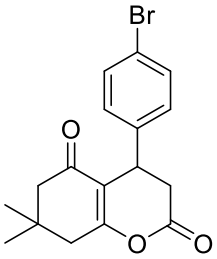
4-(4-Fluorophenyl)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4i**). White solid, mp 171-173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 2H), 7.03 – 6.94 (m, 2H), 4.30 (d, *J* = 5.6 Hz, 1H), 3.00 – 2.86 (m, 2H), 2.55 (s, 2H), 2.33 (s, 2H), 1.16 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.11, 165.79, 163.23, 160.78, 136.36, 136.33, 128.22, 128.14, 116.05, 115.84, 50.58, 41.04, 36.35, 33.18, 32.56, 28.58, 28.12. MS (ESI): $[M+H+CH_3OH]^+$: 321.06.





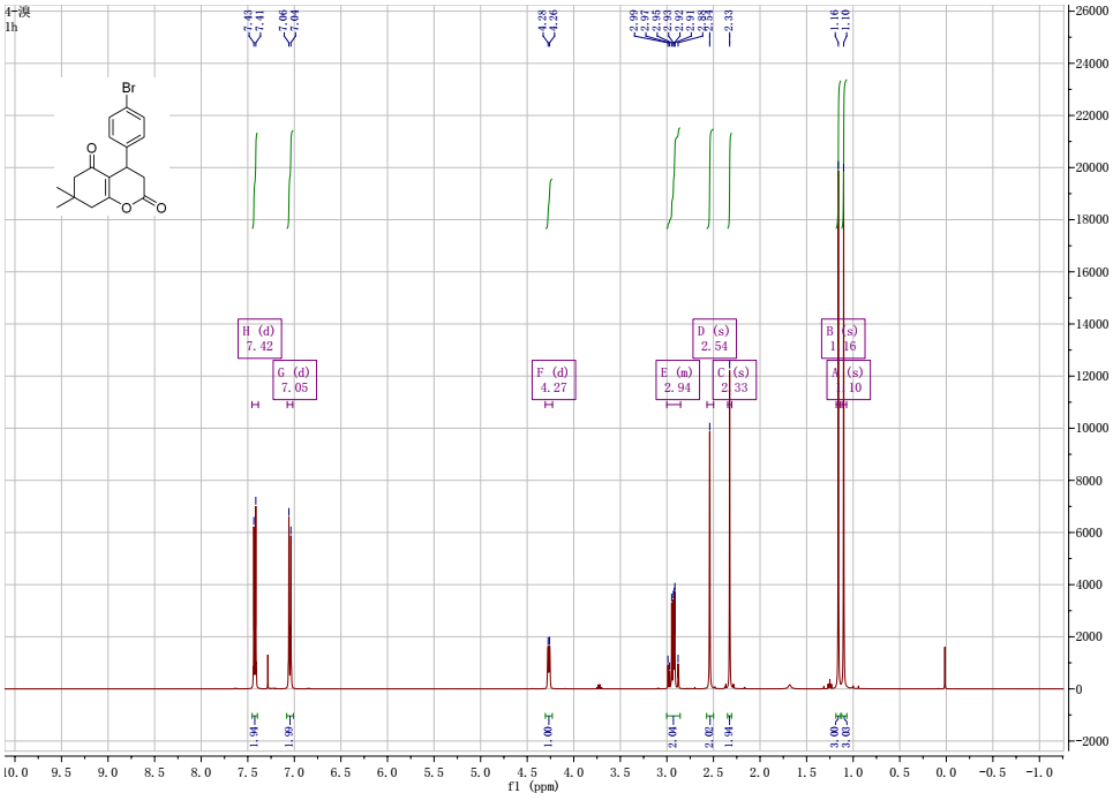
LQQ005 #87 RT: 0.47 AV: 1 SB: 63 0.08-0.24 , 0.71-1.22 NL: 9.53E4
F: ITMS + c ESI Full ms [50.00-1200.00]

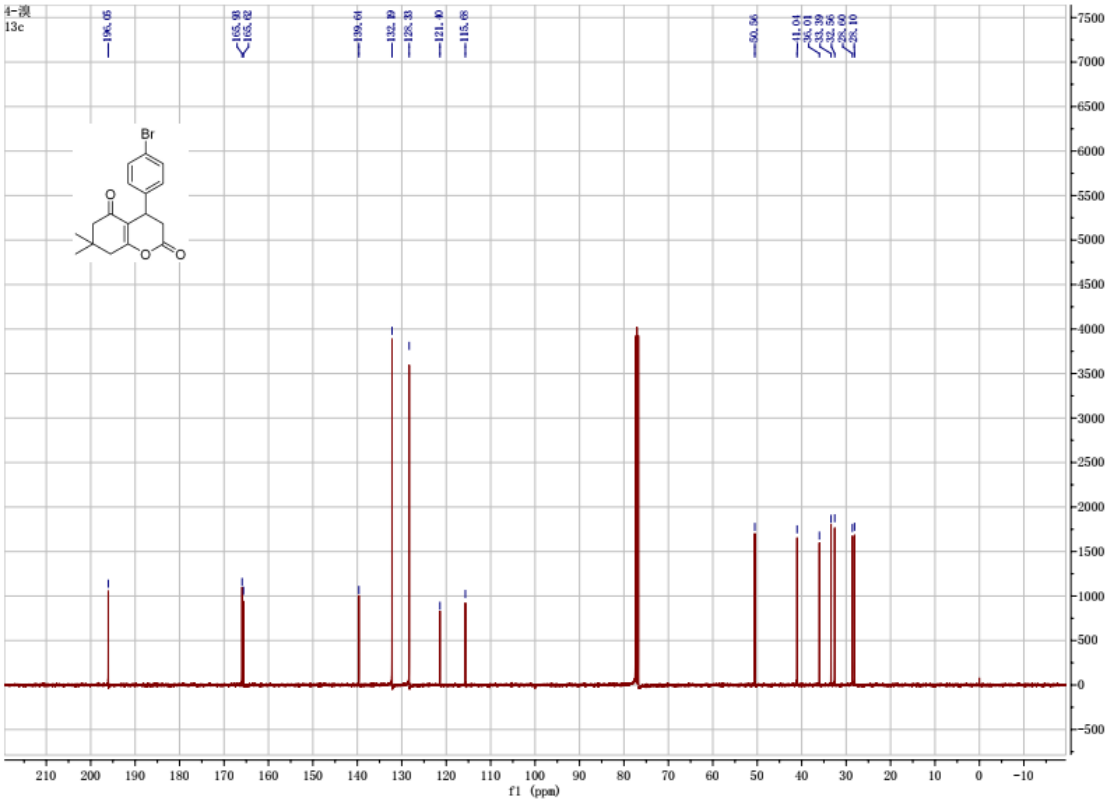


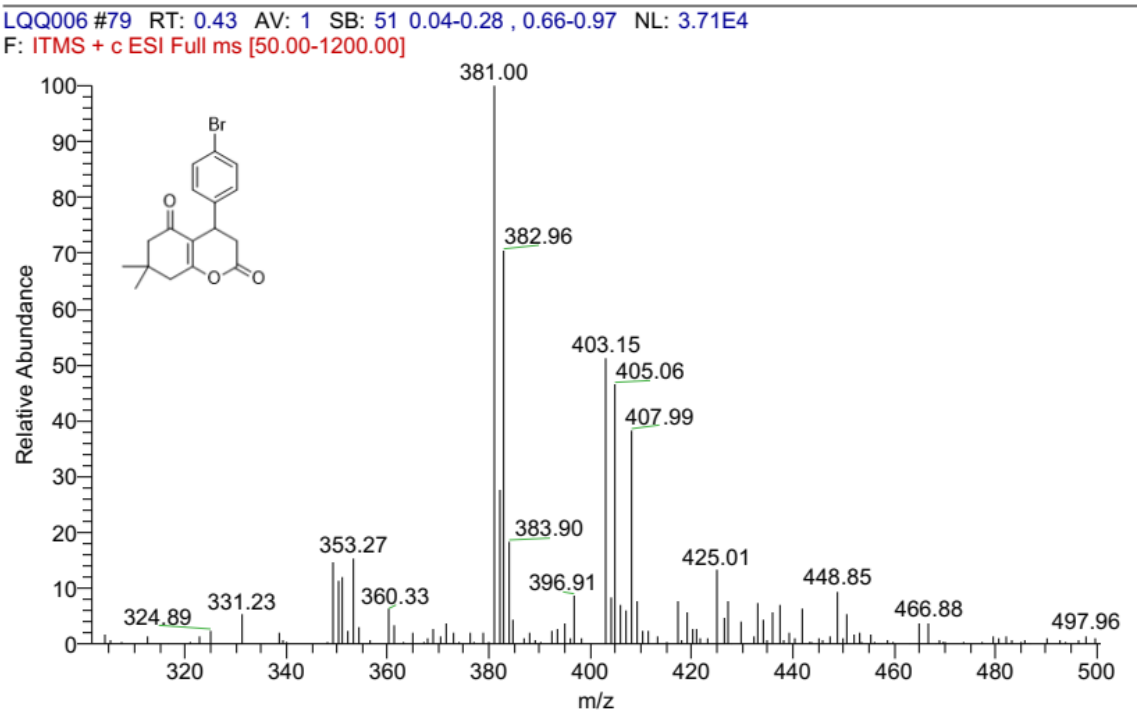


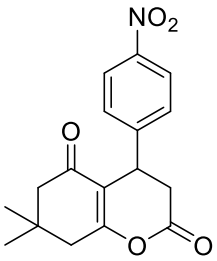
4-(4-Bromophenyl)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4j**). White solid, mp 157-159 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.27 (d, *J* = 6.4 Hz, 1H), 3.00 – 2.85 (m, 2H), 2.54 (s, 2H), 2.33 (s, 2H), 1.16 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.05, 165.93, 165.62, 139.64, 132.19, 128.33, 121.40, 115.68, 50.56, 41.04, 36.01, 33.39, 32.56, 28.60, 28.10.

MS (ESI): $[M+H+CH_3OH]^+$: 381.00.

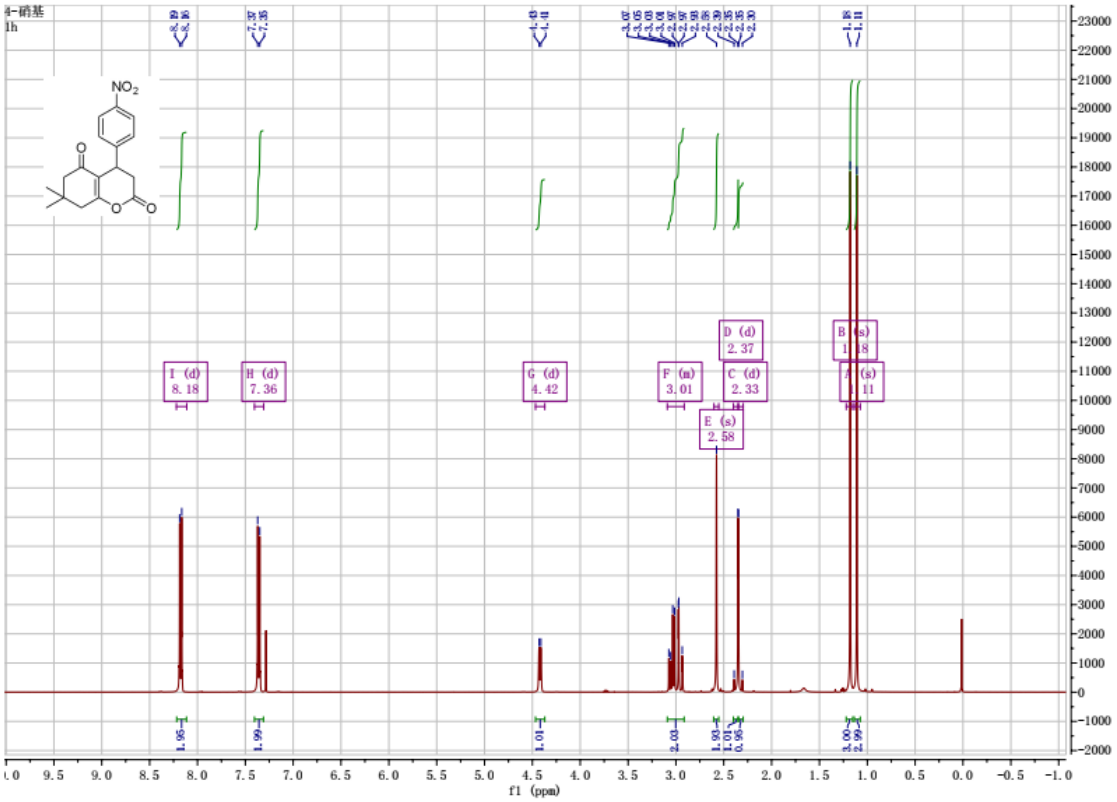


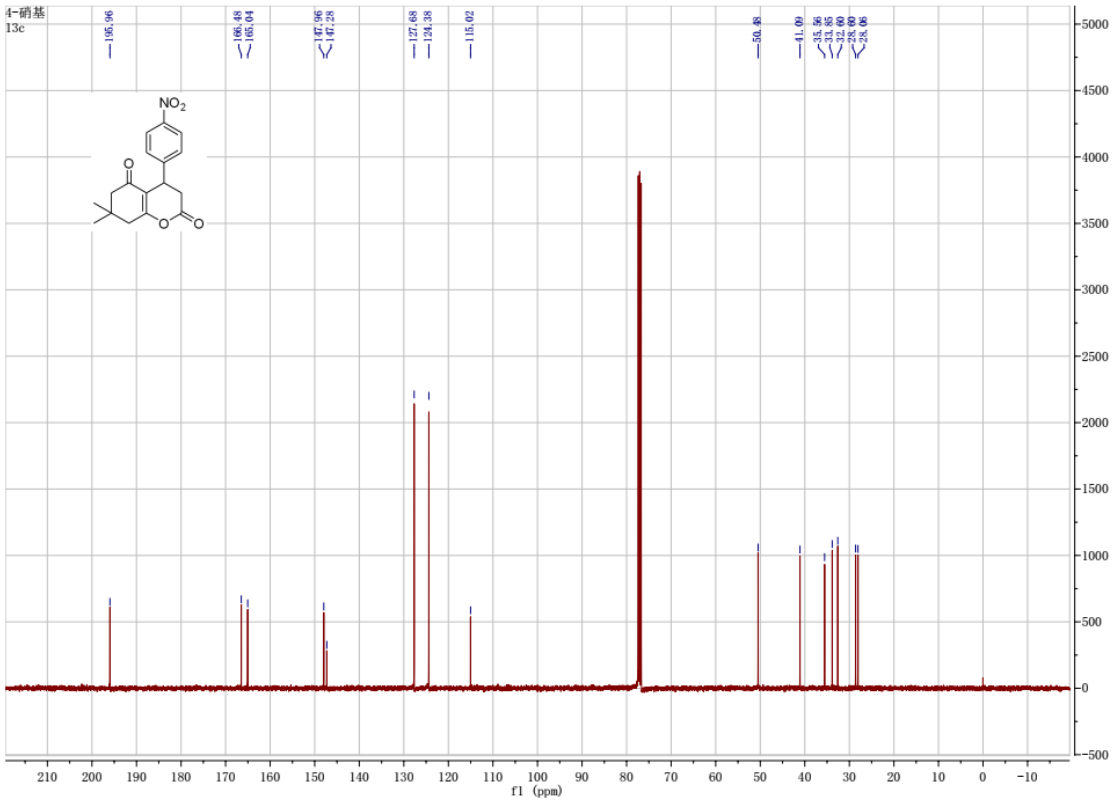

4-溴
13c
196.05
165.90
165.62
139.64
132.89
128.33
121.40
115.66
50.56
41.04
36.01
33.39
32.56
28.00
26.10
Br
O
O
O
f1 (ppm)


LQQ006 #79 RT: 0.43 AV: 1 SB: 51 0.04-0.28 , 0.66-0.97 NL: 3.71E4
F: ITMS + c ESI Full ms [50.00-1200.00]
Br
O
O
O
Relative Abundance
m/z
381.00
382.96
403.15
405.06
407.99
383.90
353.27
425.01
448.85
396.91
331.23
360.33
466.88
324.89
497.96

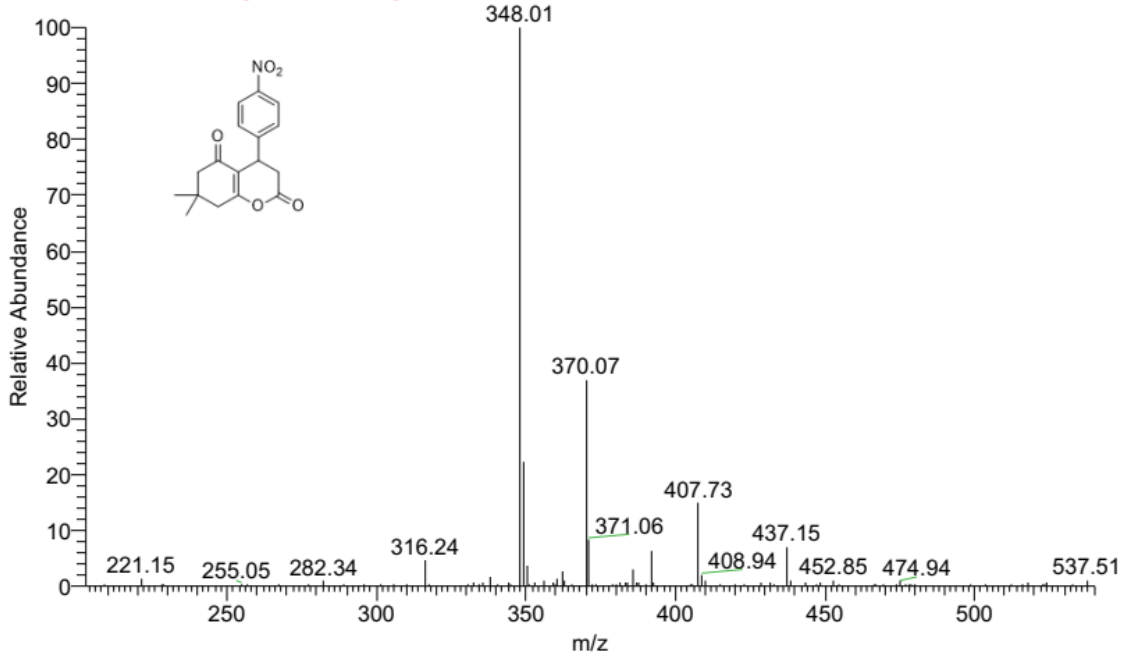


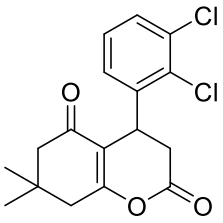
7,7-Dimethyl-4-(4-nitrophenyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4k**). Yellow solid, mp 141-143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.42 (d, *J* = 7.3 Hz, 1H), 3.09 – 2.91 (m, 2H), 2.58 (s, 2H), 2.37 (d, *J* = 16.4 Hz, 1H), 2.33 (d, *J* = 16.5 Hz, 1H), 1.18 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.96, 166.48, 165.04, 147.96, 147.28, 127.68, 124.38, 115.02, 50.48, 41.09, 35.56, 33.85, 32.60, 28.60, 28.06. MS (ESI): $[M+H+CH_3OH]^+$: 348.01.



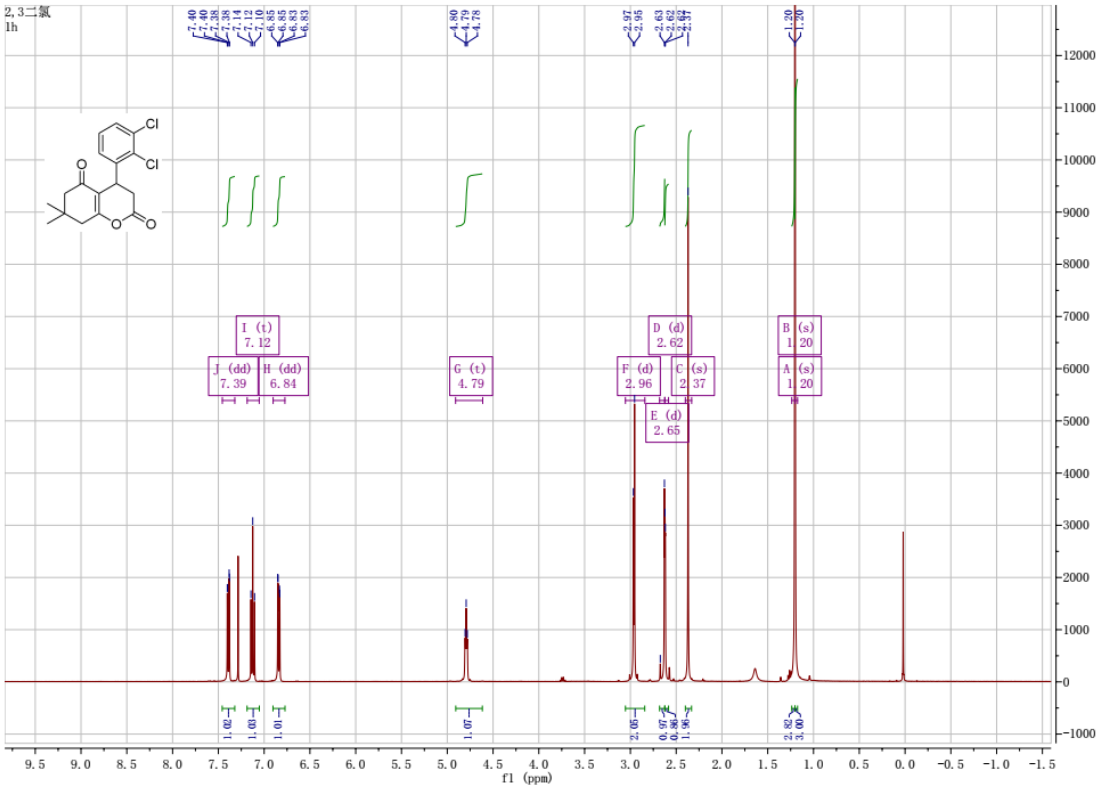


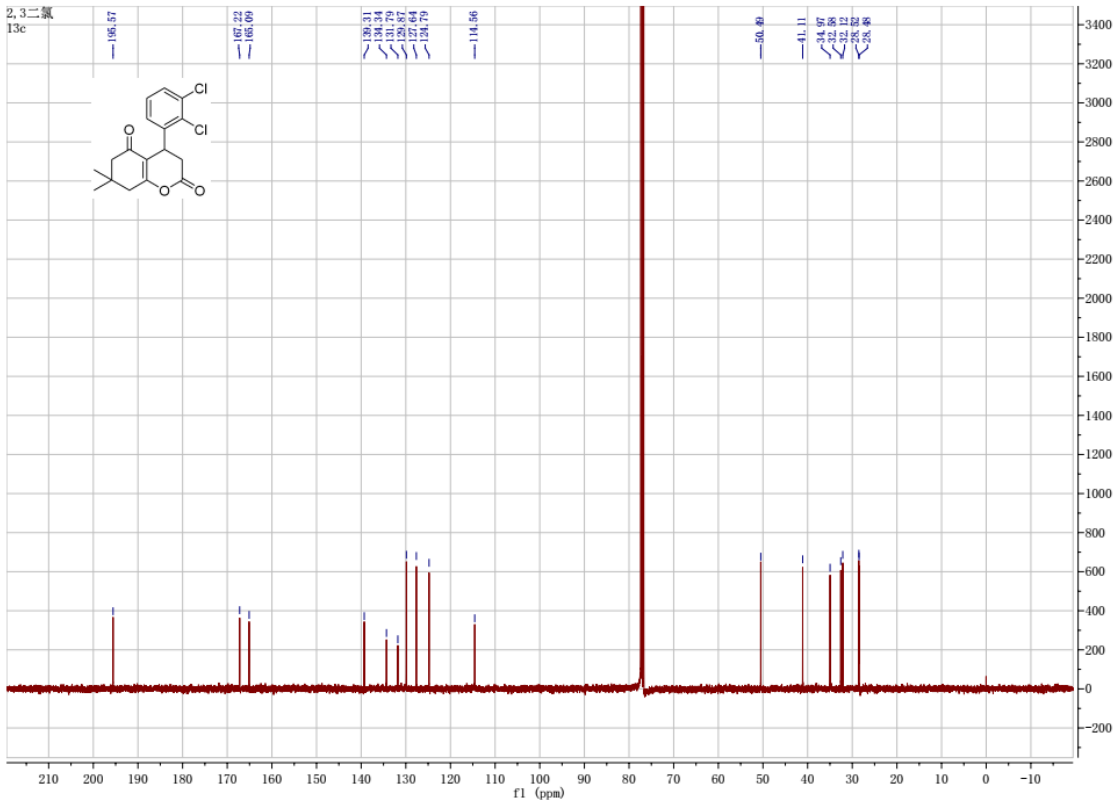
LQQ007 #83 RT: 0.44 AV: 1 SB: 66 0.04-0.27 , 0.69-1.17 NL: 1.62E5
F: ITMS + c ESI Full ms [50.00-1200.00]

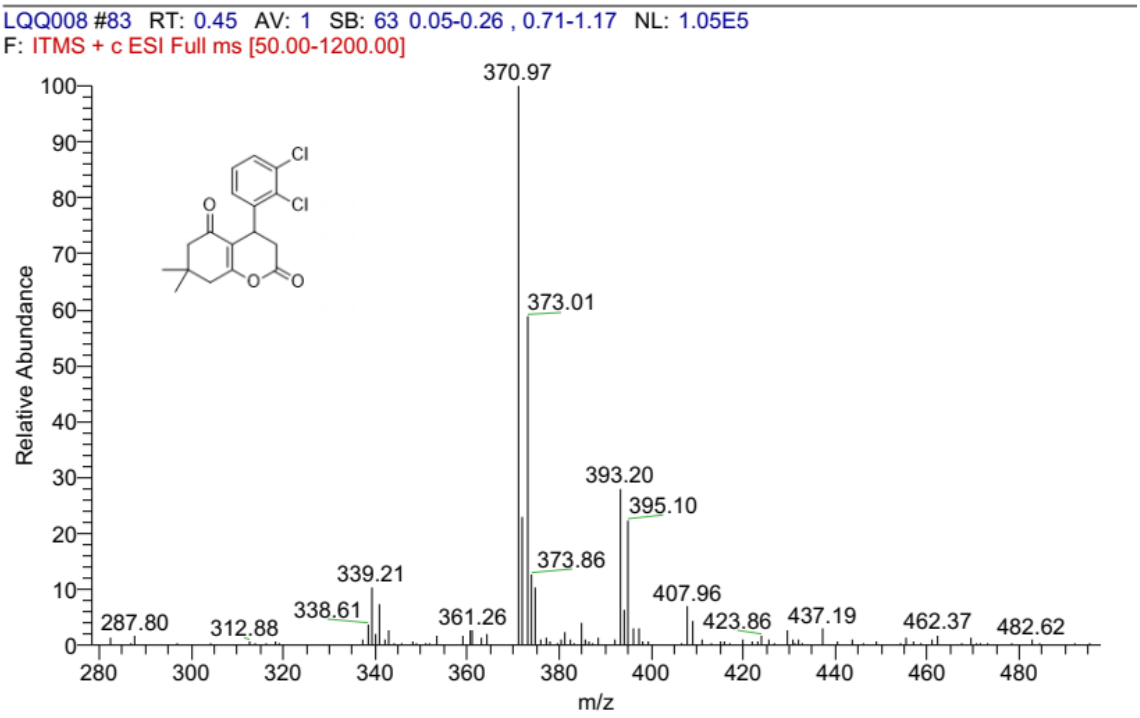


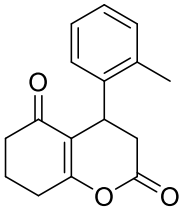


4-(2,3-Dichloropheny)-7,7-dimethyl-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4l**). White solid, mp 190-192 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.79 (t, *J* = 4.8 Hz, 1H), 2.96 (d, *J* = 5.3 Hz, 2H), 2.65 (d, *J* = 18.1 Hz, 1H), 2.62 (d, *J* = 1.3 Hz, 1H), 2.37 (s, 2H), 1.20 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.57, 167.22, 165.09, 139.31, 134.34, 131.79, 129.87, 127.64, 124.79, 114.56, 50.49, 41.11, 34.97, 32.58, 32.12, 28.52, 28.48. MS (ESI): $[M+H+CH_3OH]^+$: 370.97.

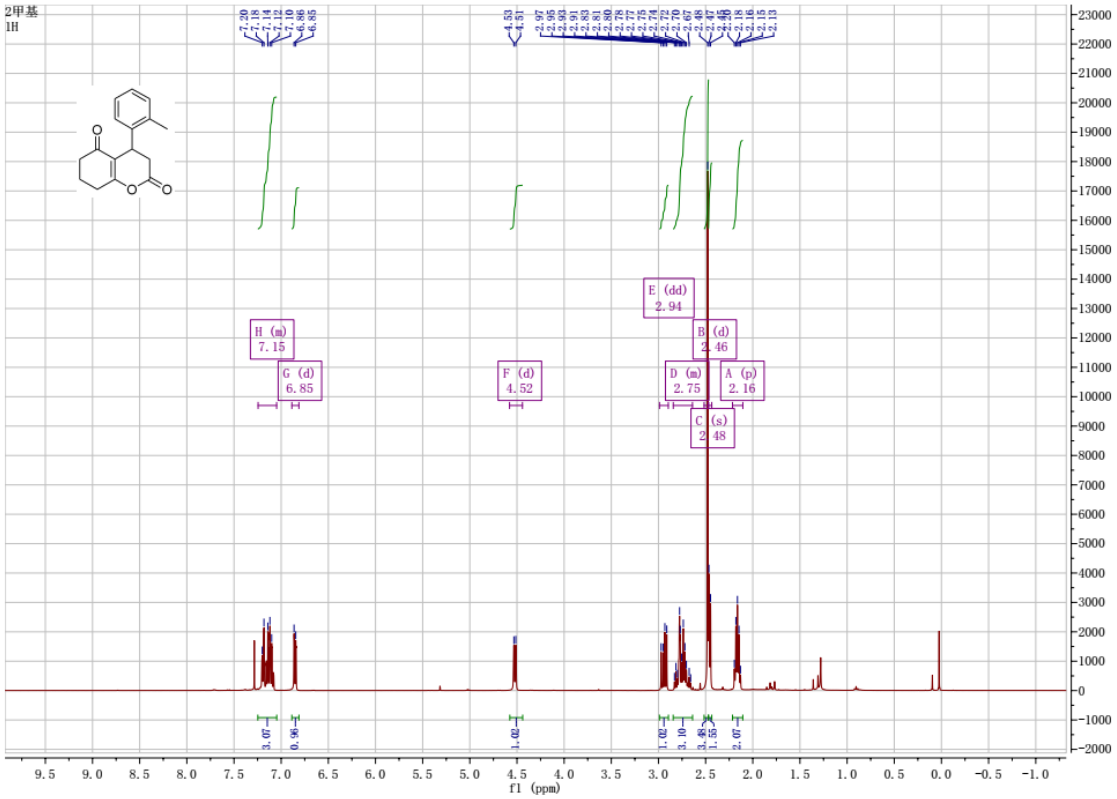


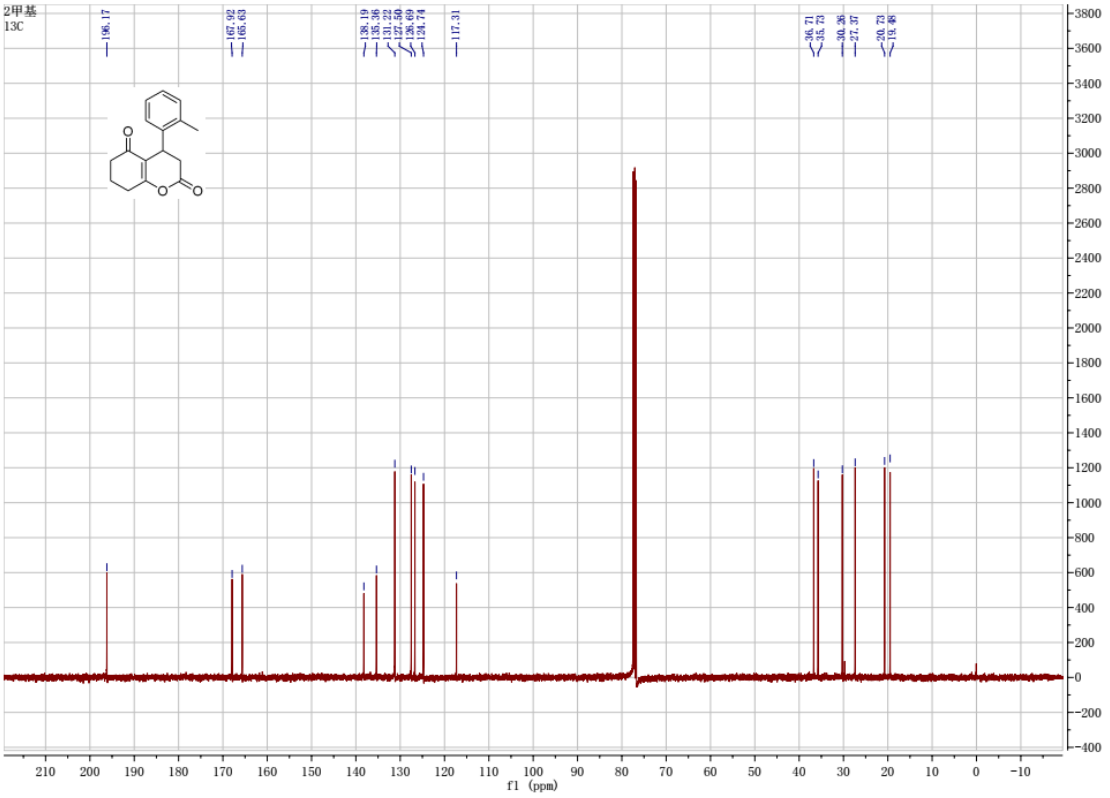

2, 3二氯
13c
195.57
167.22
165.69
139.31
134.34
131.79
129.87
127.64
124.79
114.56
50.89
41.11
34.97
32.58
32.12
28.82
28.48
Cl
Cl
O
O
O
f1 (ppm)

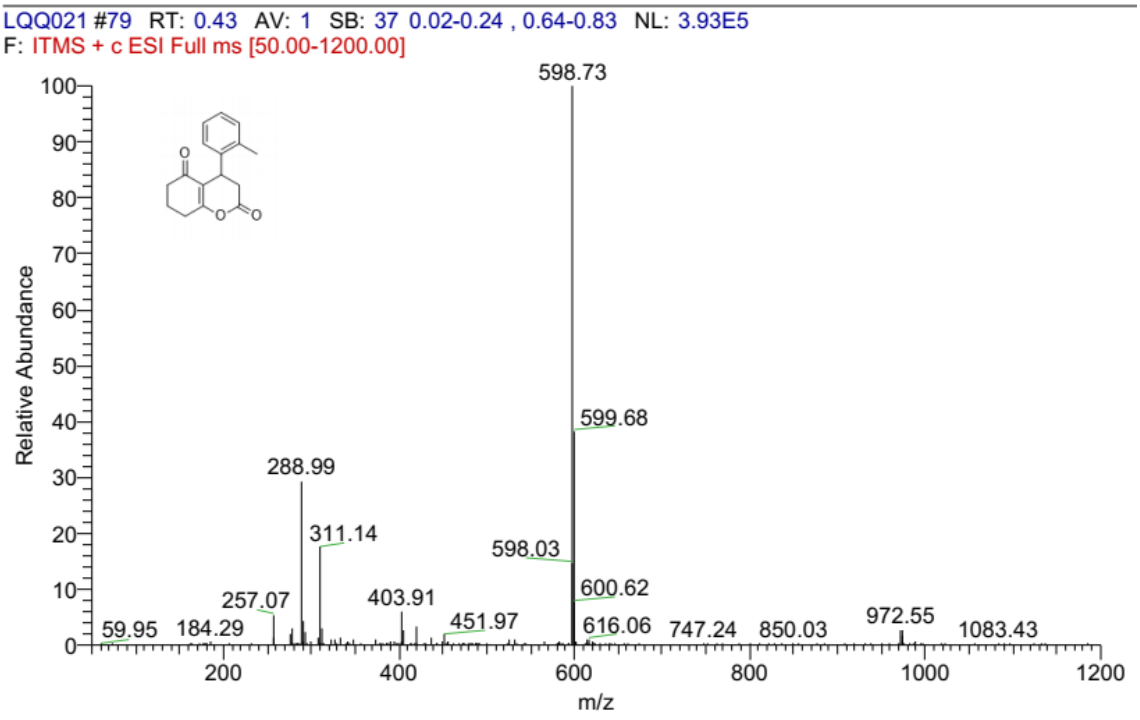

LQQ008 #83 RT: 0.45 AV: 1 SB: 63 0.05-0.26 , 0.71-1.17 NL: 1.05E5
F: ITMS + c ESI Full ms [50.00-1200.00]
370.97
373.01
393.20
395.10
373.86
339.21
338.61
407.96
287.80
312.88
361.26
423.86
437.19
462.37
482.62
Cl
Cl
O
O
O
Relative Abundance
m/z

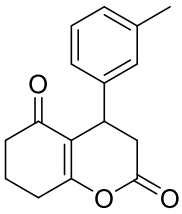


4-(*o*-Tolyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4m**): White solid, mp 151-153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.05 (m, 3H), 6.85 (d, *J* = 7.3 Hz, 1H), 4.52 (d, *J* = 8.1 Hz, 1H), 2.94 (dd, *J* = 15.8, 8.1 Hz, 1H), 2.84 – 2.64 (m, 3H), 2.48 (s, 3H), 2.46 (d, *J* = 6.9 Hz, 2H), 2.16 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.17, 167.92, 165.63, 138.19, 135.36, 131.22, 127.50, 126.69, 124.74, 117.31, 36.71, 35.73, 30.26, 27.37, 20.73, 19.48. MS (ESI): $[M+H+CH_3OH]^+$: 288.99.

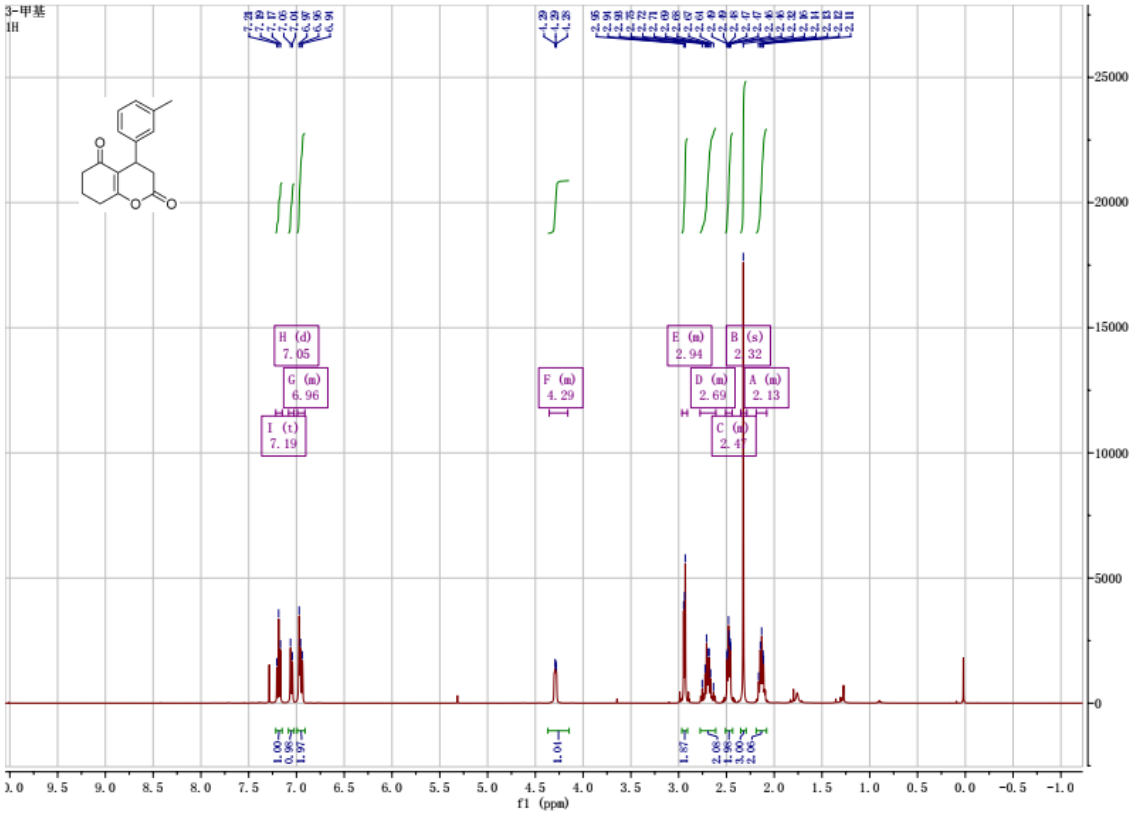


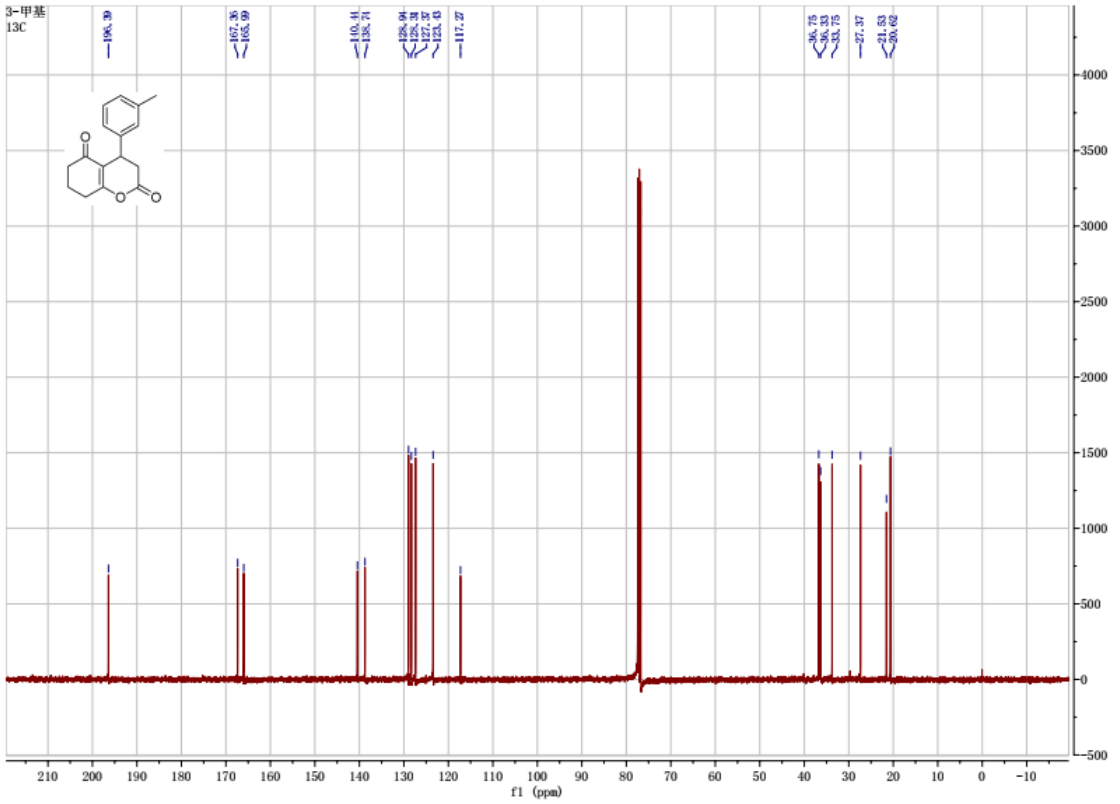

2甲基
13C
196.17
167.92
165.63
138.19
135.36
131.22
127.59
126.69
124.74
117.31
36.71
35.73
30.36
27.47
20.73
19.48
f1 (ppm)

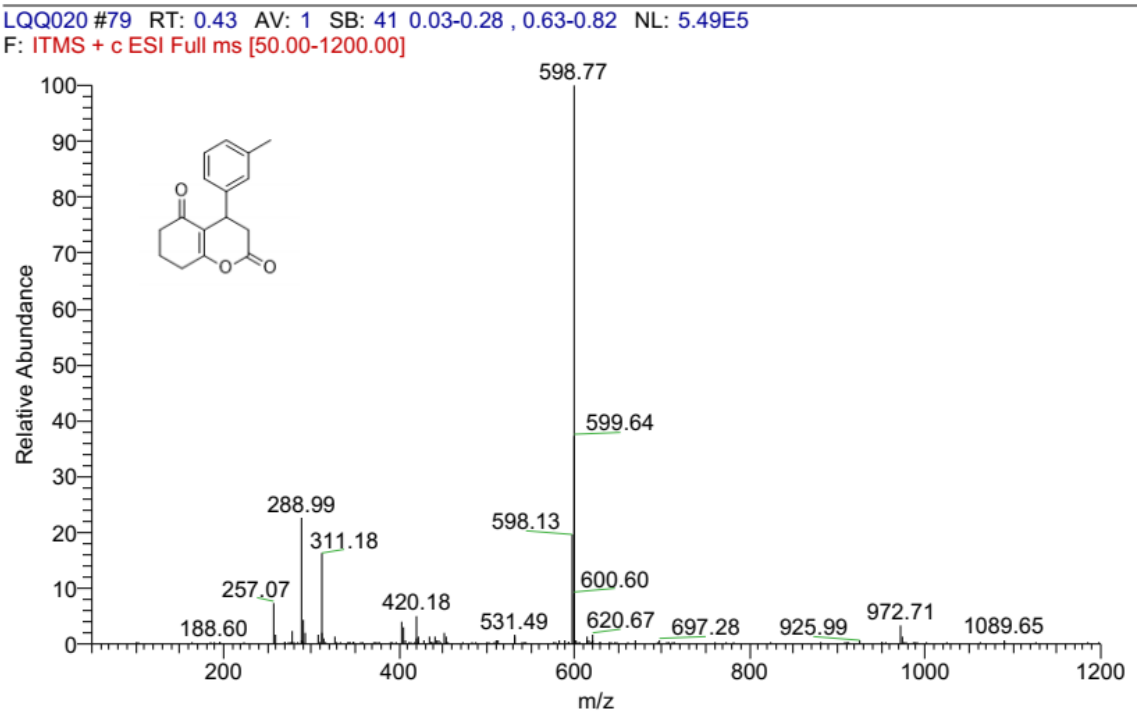

LQQ021 #79 RT: 0.43 AV: 1 SB: 37 0.02-0.24 , 0.64-0.83 NL: 3.93E5
F: ITMS + c ESI Full ms [50.00-1200.00]
598.73
599.68
288.99
311.14
598.03
600.62
257.07
403.91
451.97
59.95
184.29
616.06
747.24
850.03
972.55
1083.43
Relative Abundance
m/z

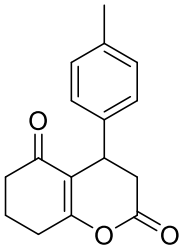


4-(*m*-Tolyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4n**): White solid, mp 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.99 – 6.91 (m, 2H), 4.35 – 4.16 (m, 1H), 2.96 – 2.91 (m, 2H), 2.78 – 2.61 (m, 2H), 2.51 – 2.44 (m, 2H), 2.32 (s, 3H), 2.19 – 2.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.39, 167.36, 165.99, 140.44, 138.74, 128.94, 128.31, 127.37, 123.43, 117.27, 36.75, 36.33, 33.75, 27.37, 21.53, 20.62. MS (ESI): $[M+H+CH_3OH]^+$: 288.99.

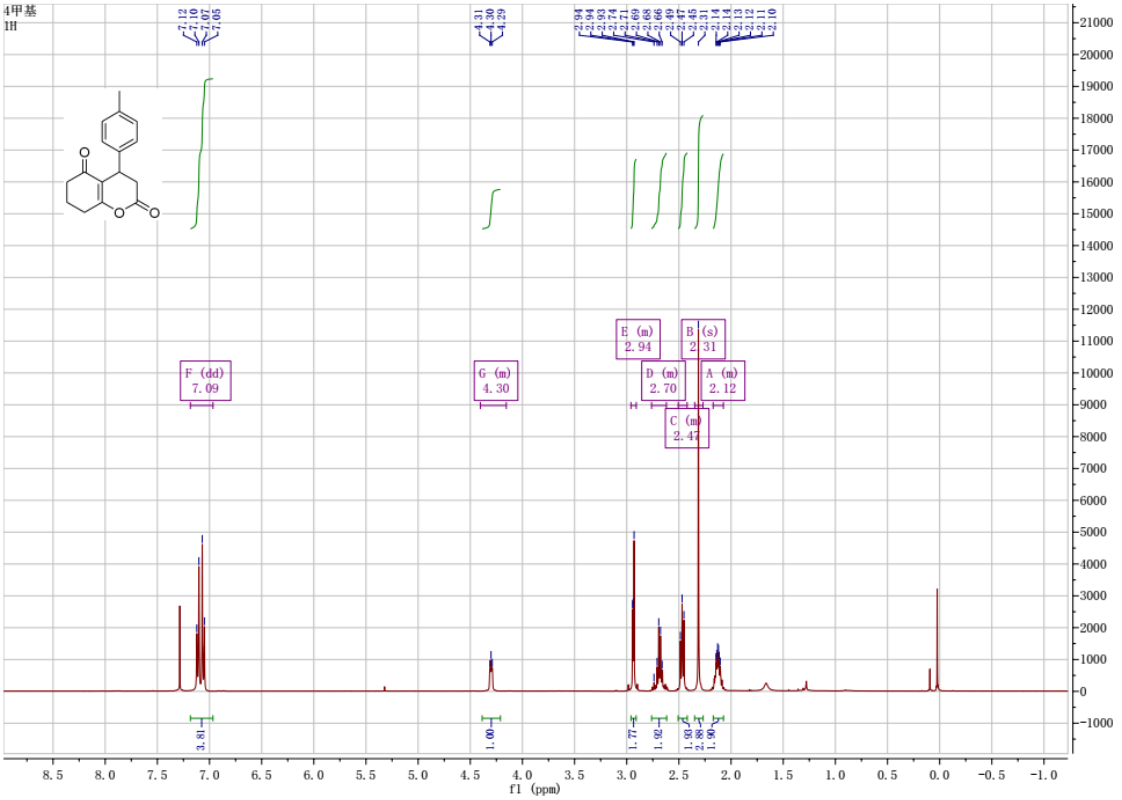


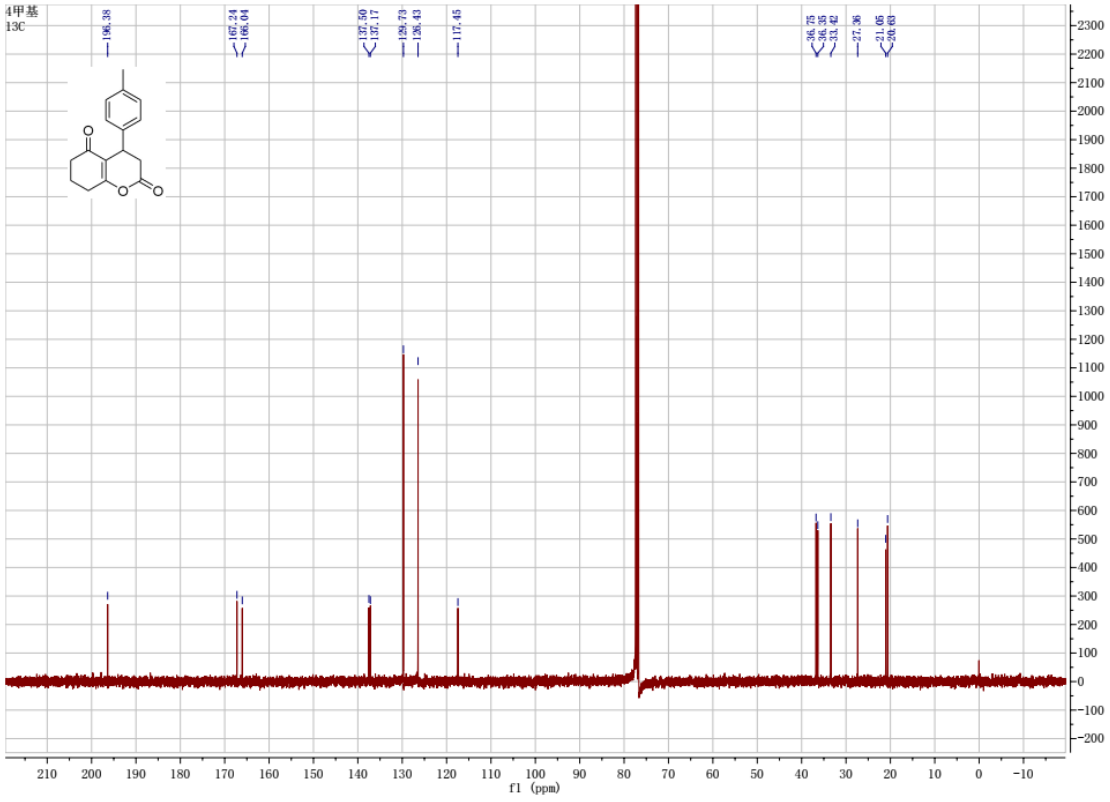

3-甲基
13C
196.39
167.36
165.99
140.44
138.74
128.94
128.78
127.39
123.43
117.27
36.75
36.33
33.75
27.37
21.53
20.62
f1 (ppm)

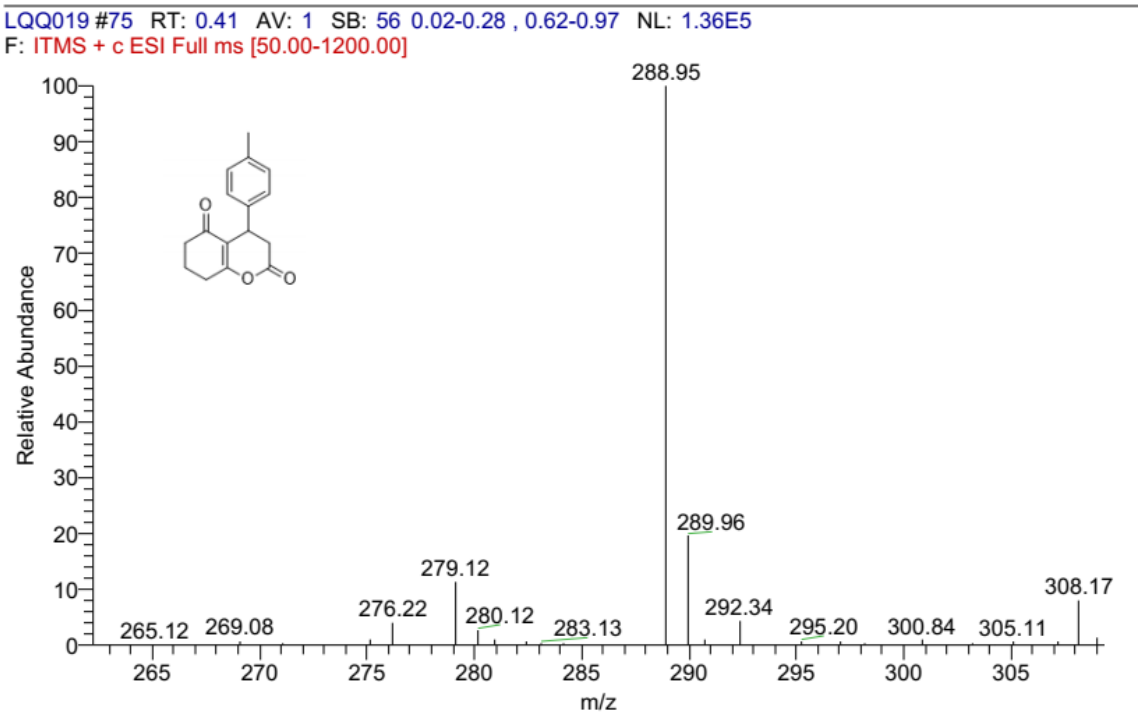

LQQ020 #79 RT: 0.43 AV: 1 SB: 41 0.03-0.28 , 0.63-0.82 NL: 5.49E5
F: ITMS + c ESI Full ms [50.00-1200.00]
598.77
599.64
288.99
311.18
598.13
600.60
257.07
420.18
188.60
531.49
620.67
697.28
925.99
972.71
1089.65
Relative Abundance
m/z

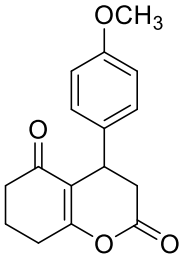


4-(*p*-Tolyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4o**). White solid, mp 105-106 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 21.0, 8.1 Hz, 4H), 4.40 – 4.16 (m, 1H), 2.96 – 2.91 (m, 2H), 2.76 – 2.62 (m, 2H), 2.51 – 2.42 (m, 2H), 2.31 (s, 3H), 2.17 – 2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.38, 167.24, 166.04, 137.50, 137.17, 129.73, 126.43, 117.45, 36.75, 36.35, 33.42, 27.36, 21.05, 20.63. MS (ESI): $[M+H+CH_3OH]^+$: 288.95.

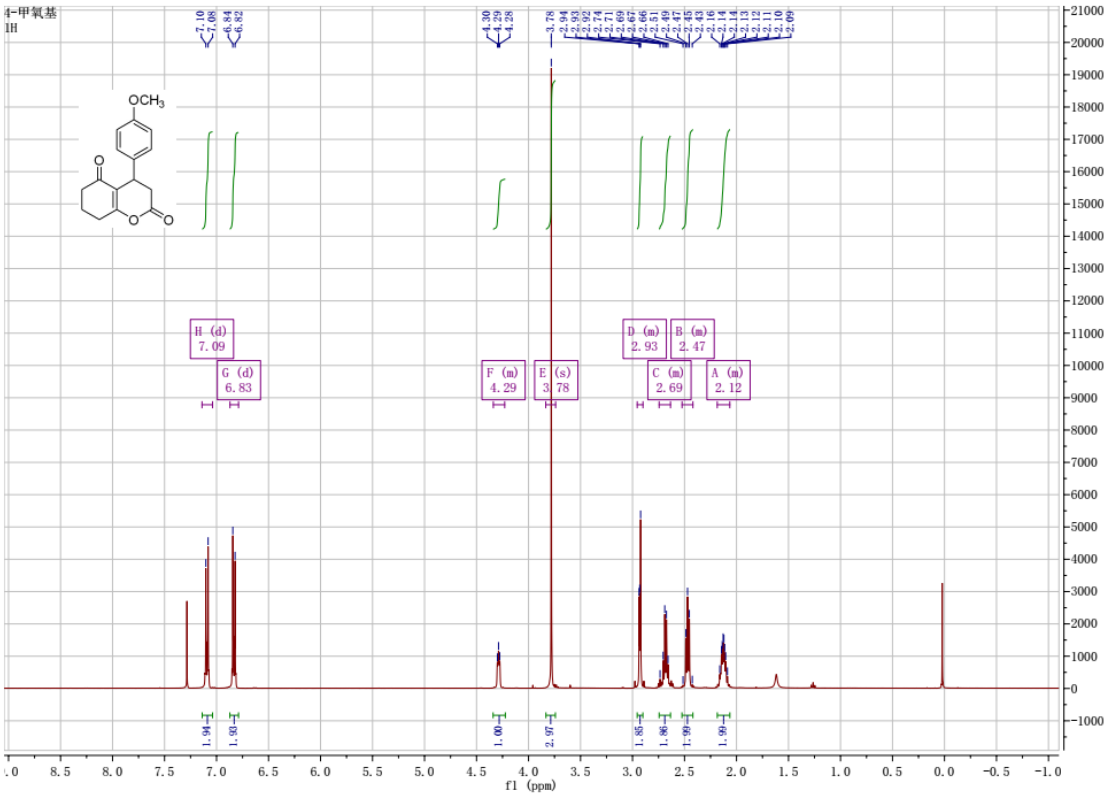


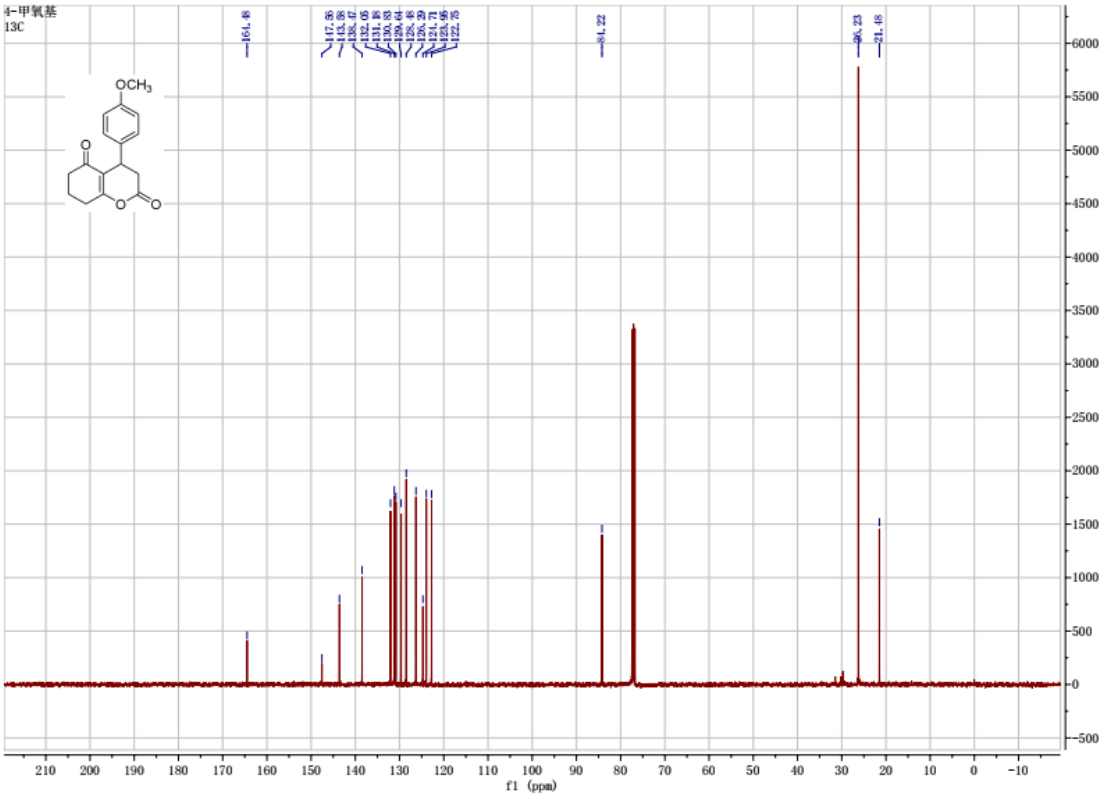

4甲基
13C
196.38
167.24
166.04
137.50
137.17
129.73
126.43
117.45
36.75
36.35
33.42
27.36
21.65
20.63
f1 (ppm)


LQQ019 #75 RT: 0.41 AV: 1 SB: 56 0.02-0.28 , 0.62-0.97 NL: 1.36E5
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
288.95
289.96
279.12
276.22
280.12
283.13
265.12
269.08
292.34
295.20
300.84
305.11
308.17

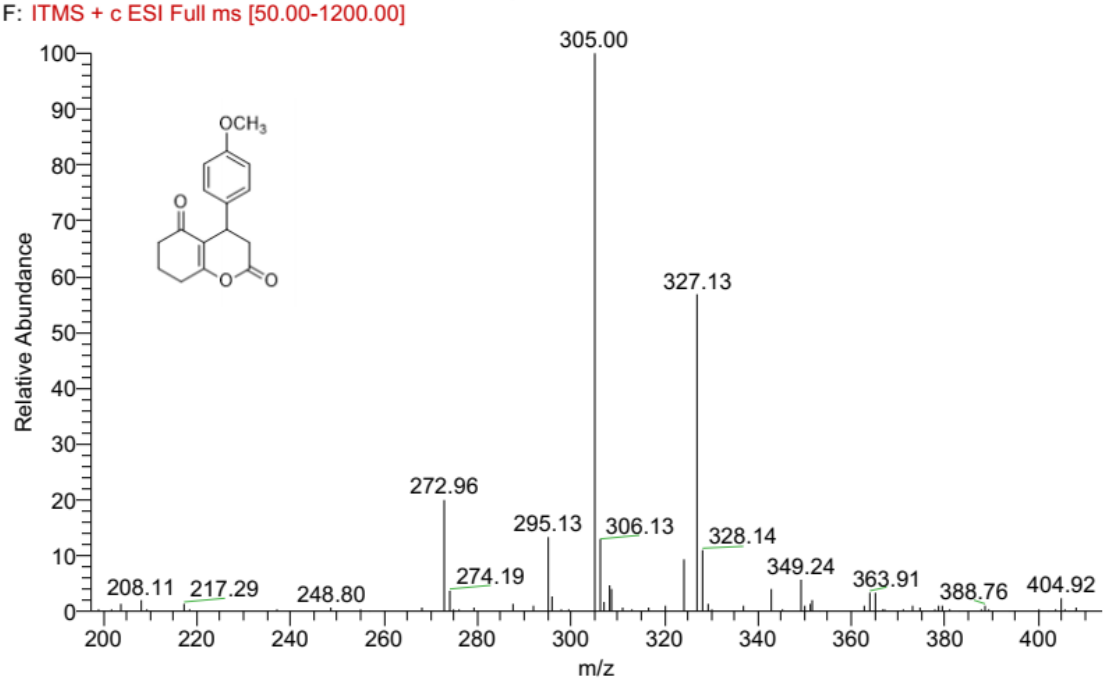


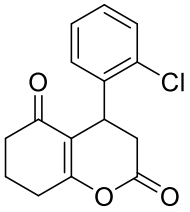
4-(4-Methoxypheny)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione **(4p)**: White solid, mp 134-136 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.34 – 4.23 (m, 1H), 3.78 (s, 3H), 2.95 – 2.90 (m, 2H), 2.74 – 2.63 (m, 2H), 2.52 – 2.42 (m, 2H), 2.19 – 2.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.48, 147.56, 143.58, 138.47, 132.05, 131.18, 130.83, 129.64, 128.48, 126.29, 124.71, 123.95, 122.75, 84.22, 26.23, 21.48. MS (ESI): $[M+H+CH_3OH]^+$: 305.00.



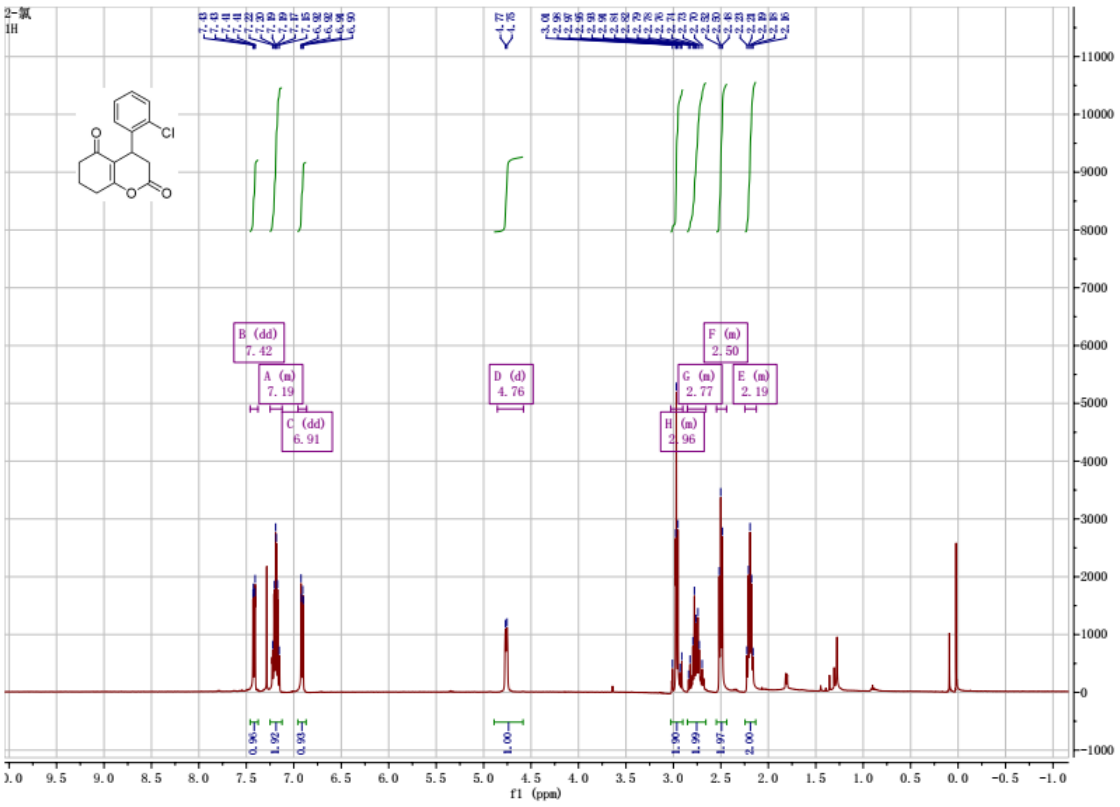


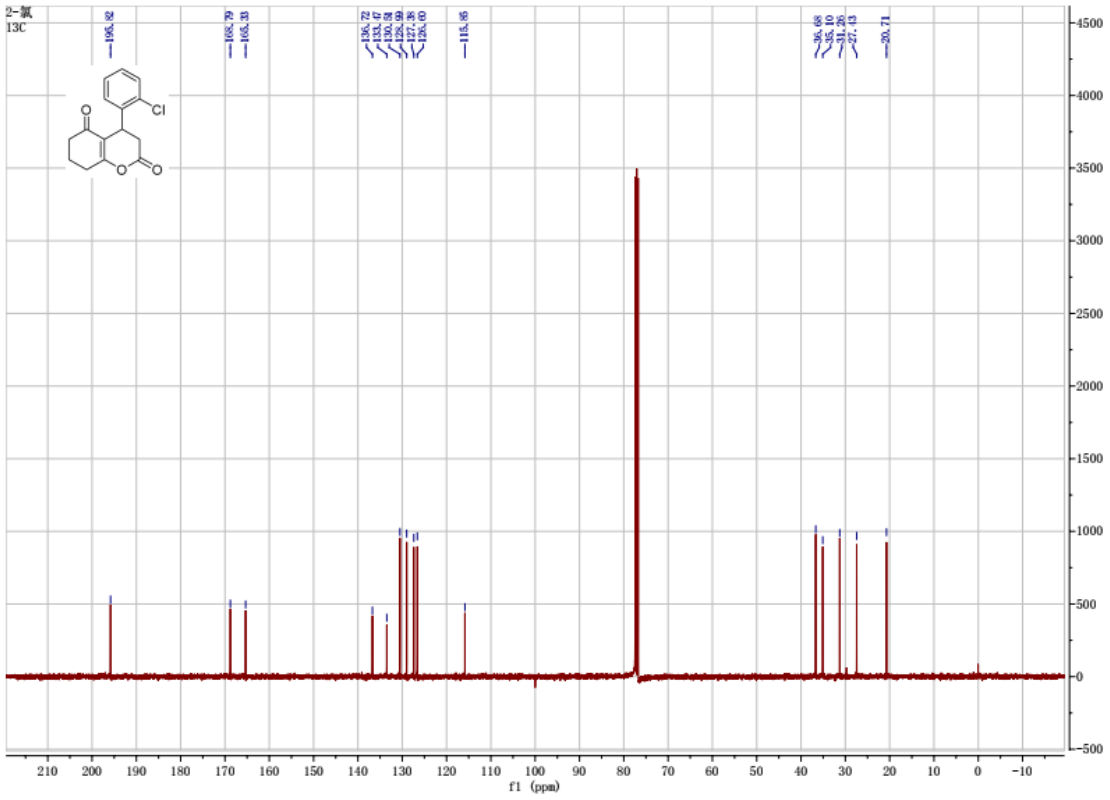
LQQ018 #79 RT: 0.43 AV: 1 SB: 53 0.01-0.28 , 0.60-0.89 NL: 1.12E5
F: ITMS + c ESI Full ms [50.00-1200.00]

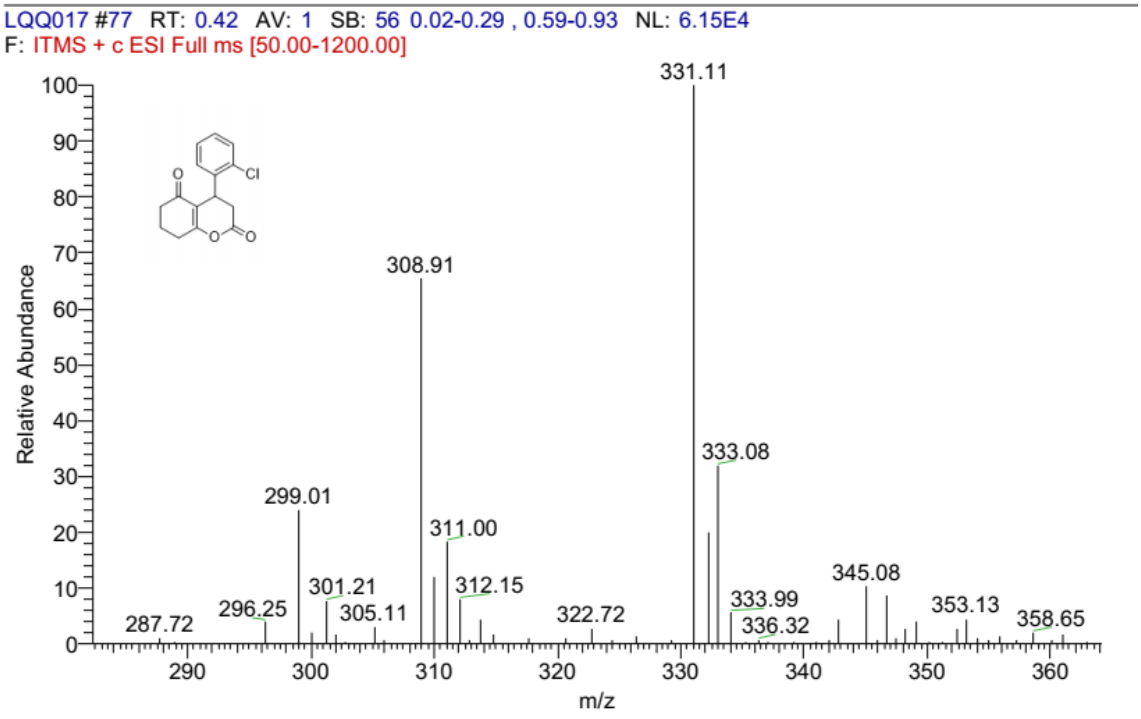


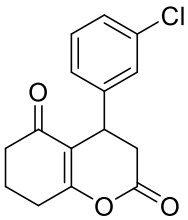


4-(2-Chlorophenyll)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4q**). White solid, mp 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.25 – 7.12 (m, 2H), 6.91 (dd, *J* = 7.3, 2.0 Hz, 1H), 4.76 (d, *J* = 6.8 Hz, 1H), 3.03 – 2.90 (m, 2H), 2.85 – 2.66 (m, 2H), 2.55 – 2.44 (m, 2H), 2.25 – 2.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.82, 168.79, 165.33, 136.72, 133.47, 130.51, 128.99, 127.38, 126.60, 115.85, 36.68, 35.10, 31.26, 27.43, 20.71. MS (ESI): $[M+H+CH_3OH]^+$: 308.91.

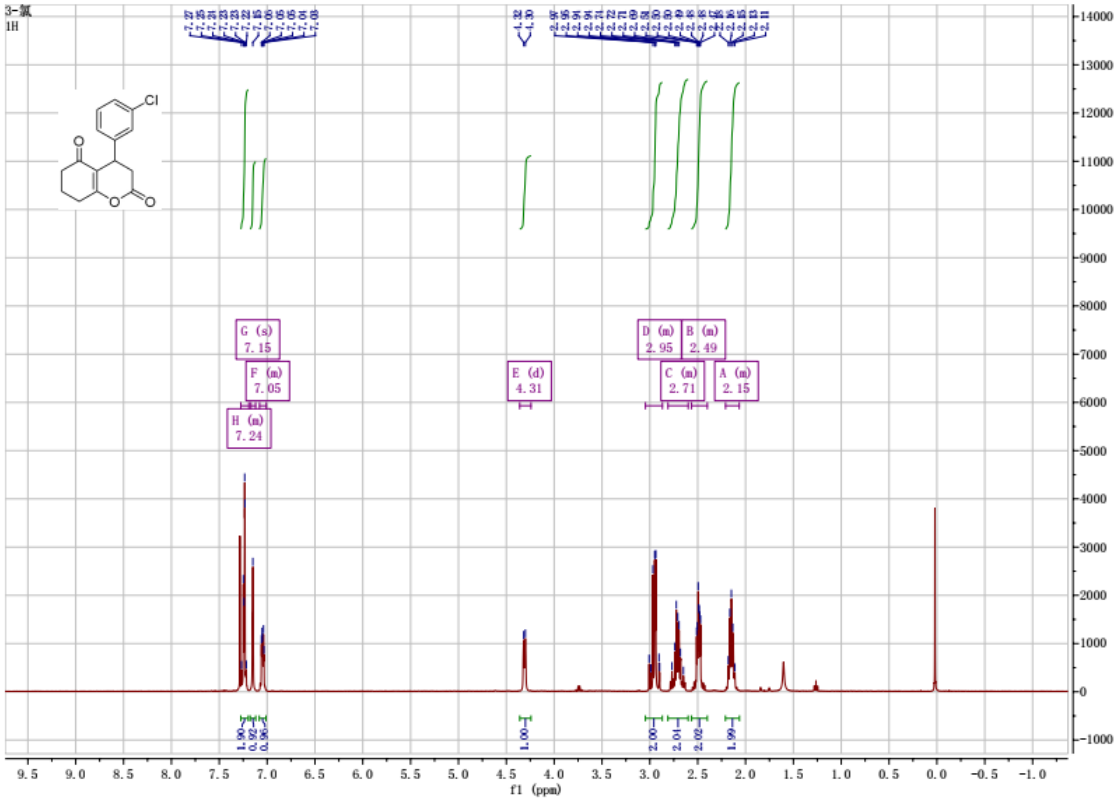


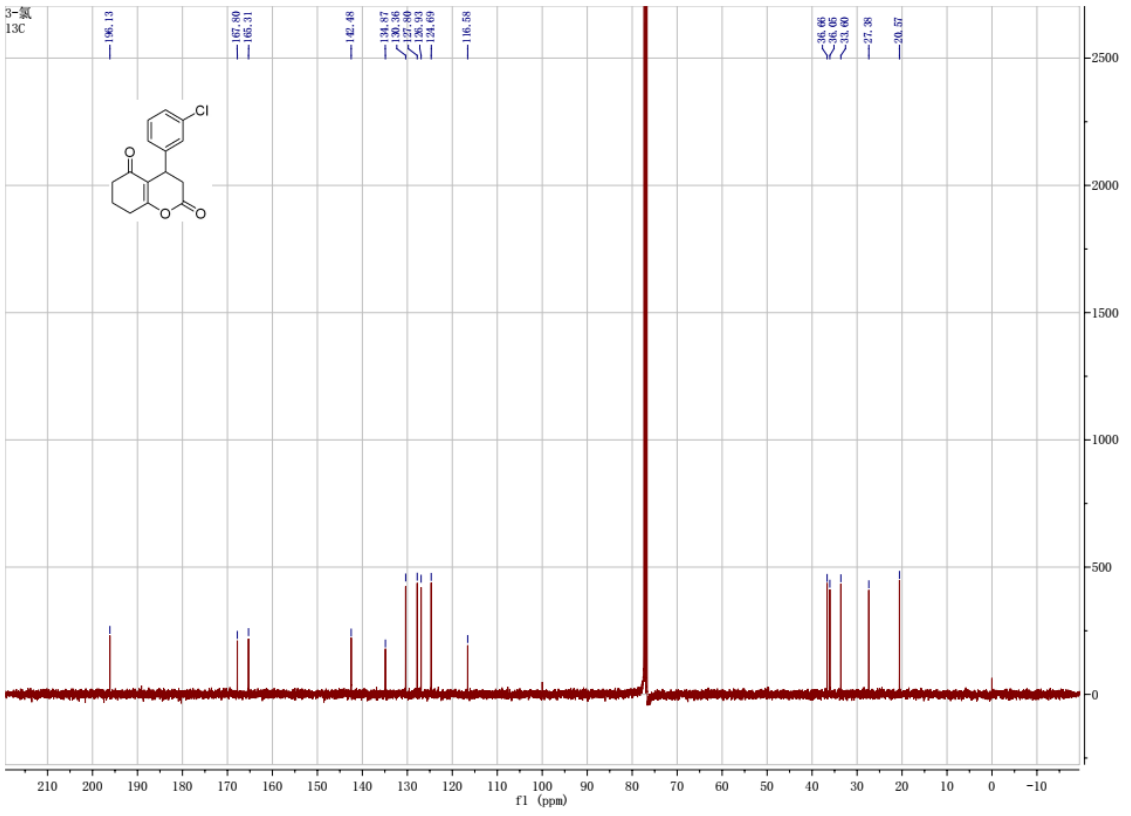

2-氯
13C
196.92
168.79
165.33
136.72
133.47
130.58
129.39
127.36
126.00
115.95
36.68
35.10
31.26
27.13
20.71
f1 (ppm)

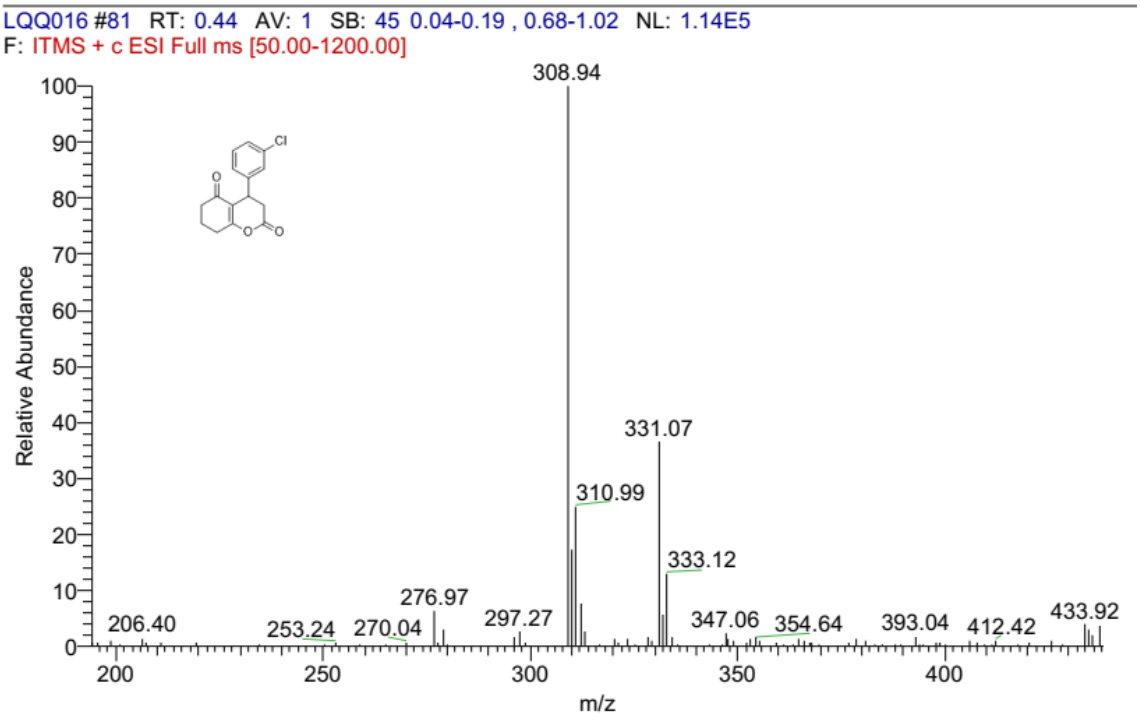

LQQ017 #77 RT: 0.42 AV: 1 SB: 56 0.02-0.29 , 0.59-0.93 NL: 6.15E4
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
331.11
308.91
333.08
299.01
311.00
345.08
301.21
312.15
333.99
353.13
296.25
305.11
322.72
336.32
358.65
287.72



4-(3-Chlorophenyll)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4r**). White solid, mp 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 7.15 (s, 1H), 7.08 – 7.01 (m, 1H), 4.31 (d, *J* = 6.9 Hz, 1H), 3.05 – 2.87 (m, 2H), 2.81 – 2.60 (m, 2H), 2.56 – 2.40 (m, 2H), 2.21 – 2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.13, 167.80, 165.31, 142.48, 134.87, 130.36, 127.80, 126.93, 124.69, 116.58, 36.66, 36.05, 33.60, 27.38, 20.57. MS (ESI): $[M+H+CH_3OH]^+$: 308.94.




3-氯
13C
196.13
167.80
165.31
142.48
134.87
130.36
127.60
126.93
124.69
116.58
36.66
36.05
33.60
27.38
20.57
Cl
O
O
O
2500
2000
1500
1000
500
0
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)


LQQ016 #81 RT: 0.44 AV: 1 SB: 45 0.04-0.19 , 0.68-1.02 NL: 1.14E5
F: ITMS + c ESI Full ms [50.00-1200.00]
Relative Abundance
m/z
Cl
O
O
O
308.94
331.07
310.99
333.12
276.97
206.40
253.24
270.04
297.27
347.06
354.64
393.04
412.42
433.92
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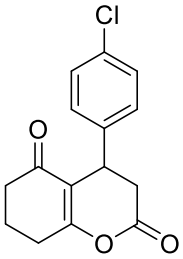
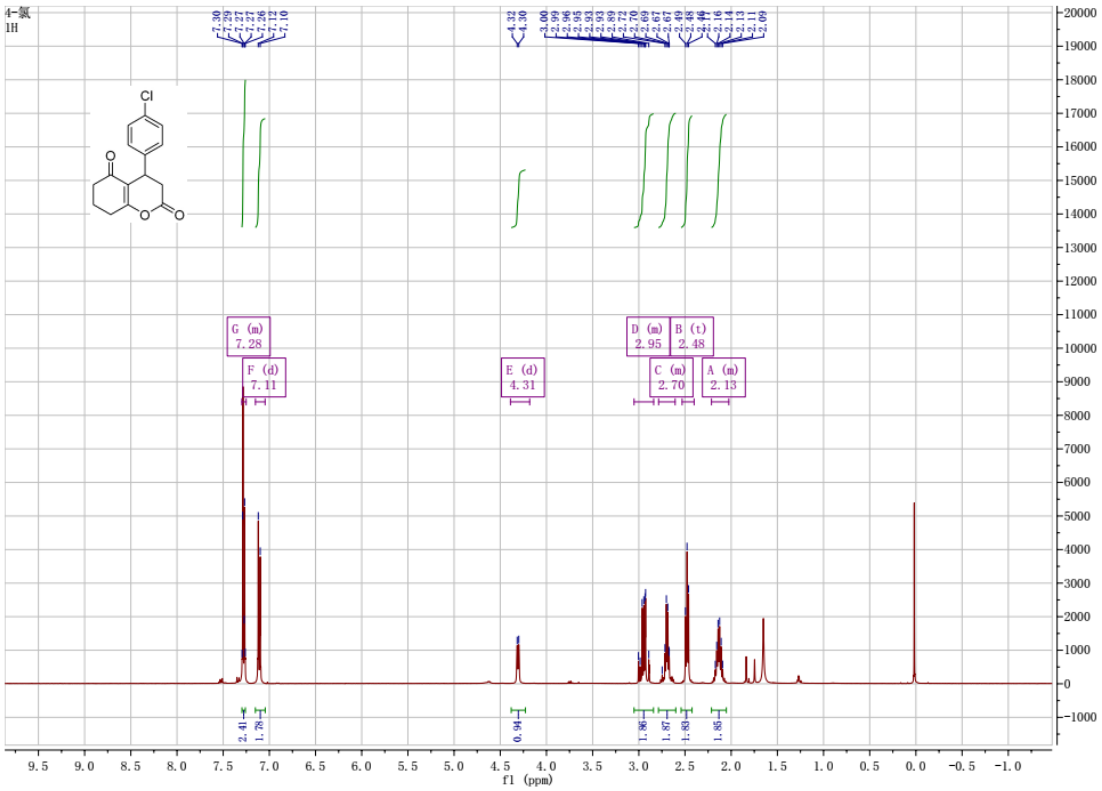
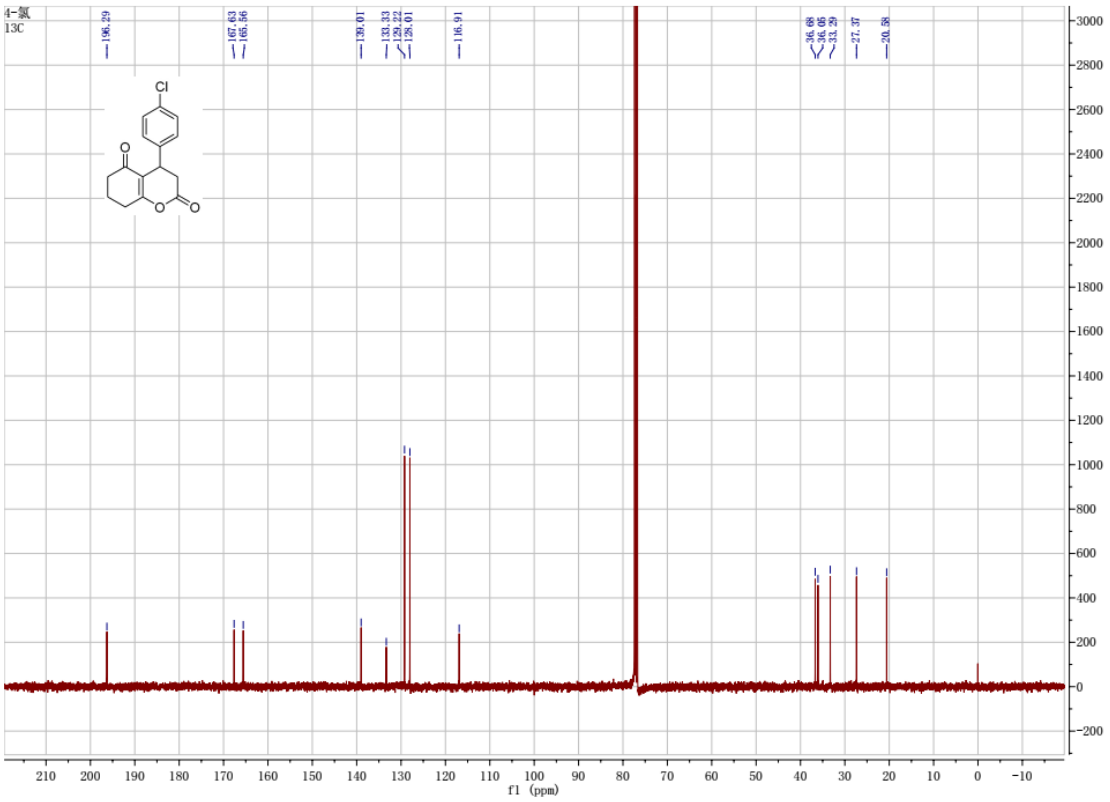
50
40
30
20
10
0
200
250
300
350
400

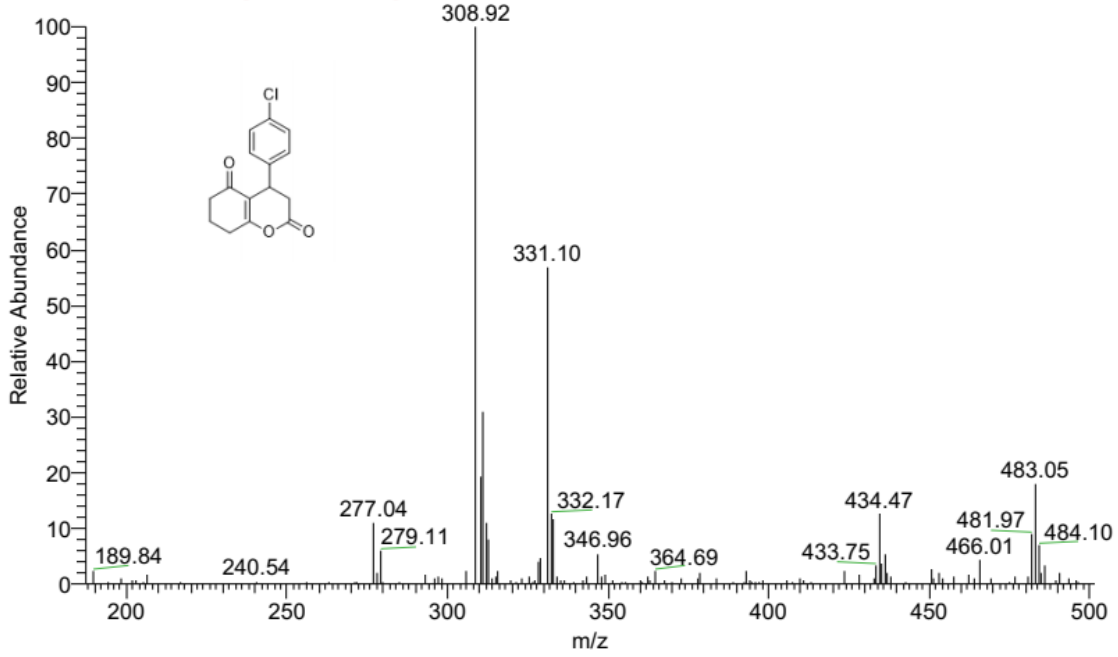


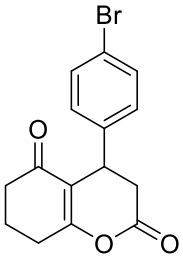
4-(4-Chlorophenyll)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione (**4s**): White solid, mp 135-137 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 4.31 (d, *J* = 7.0 Hz, 1H), 3.05 – 2.84 (m, 2H), 2.79 – 2.61 (m, 2H), 2.48 (t, *J* = 6.7 Hz, 2H), 2.21 – 2.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.29, 167.63, 165.56, 139.01, 133.33, 129.22, 128.01, 116.91, 36.68, 36.05, 33.29, 27.37, 20.58. MS (ESI): $[M+H+CH_3OH]^+$: 308.92.



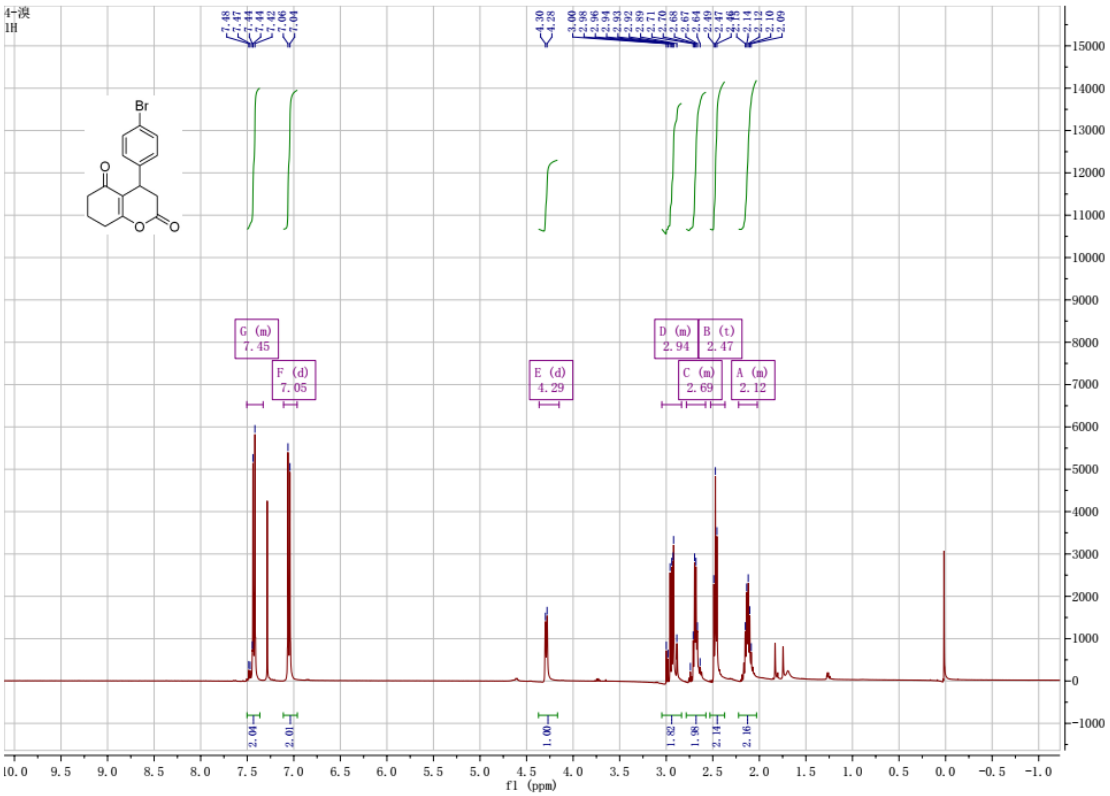


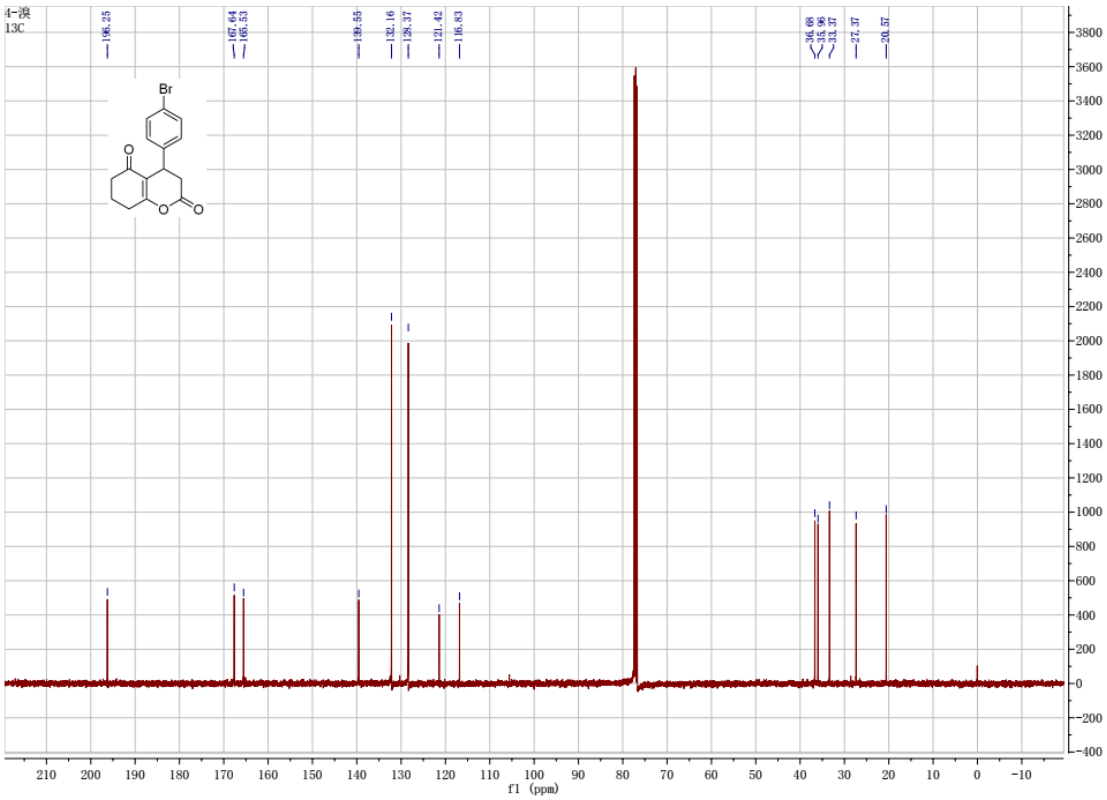
LQQ015_210522114125 #81 RT: 0.44 AV: 1 SB: 84 0.04-0.35 , 0.72-1.32 NL: 9.37E4
F: ITMS + c ESI Full ms [50.00-1200.00]





4-(4-Bromophenyl)-4,6,7,8-tetrahydro-2*H*-chromene-2,5(3*H*)-dione(**4t**). White solid, mp 144-146 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.33 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.29 (d, *J* = 7.0 Hz, 1H), 3.05 – 2.84 (m, 2H), 2.78 – 2.58 (m, 2H), 2.47 (t, *J* = 6.7 Hz, 2H), 2.22 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.25, 167.64, 165.53, 139.55, 132.16, 128.37, 121.42, 116.83, 36.68, 35.96, 33.37, 27.37, 20.57. MS (ESI): $[M+H+CH_3OH]^+$: 352.92.





LQQ014_210522113724 #81 RT: 0.44 AV: 1 SB: 21 0.45 , 0.08-0.30 NL: 4.98E4
F: ITMS + c ESI Full ms [50.00-1200.00]