Supporting Information

Transformations of *N*-Arylpropiolamides to Indoline-2,3-diones and Acids via Oxidative C≡C Bond Cleavage and C(sp^2)-H Functionalization

Ming-Bo Zhou[1,2], Yang Li[1*], Xuan-Hui Ouyang[1] & Jin-Heng Li[1,2,3*]

[1]*Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China*
[2]*Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, China*
[3]*State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*

E-mail: liyang8825490@126.com and jhli@hnu.edu.cn.

Supporting Information

List of Contents

(A) Typical Experimental Procedure

(a) Synthesis of *N*-Arylpropiolamides 1:

Substrates **1** were prepared according to the known procedures.[1]

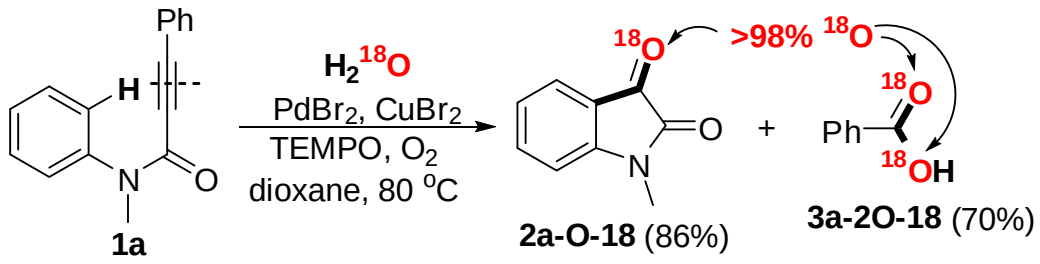
Typical Experimental Procedure: A mixture solution of arylamine (1.0 mmol) and propiolic acids (1.1 equiv) in CH_2Cl_2 was droped into the solution of DCC (1.1 equiv) in CH_2Cl_2 under ice-bath for 30 min until complete consumption of starting material as monitored by TLC. After completion, the reaction mixture was filtered and concentrated under vacuum. The residue was further purified by flash column chromatography on silica gel using ethyl acetate/petroleum ether as eluent to afford the desired *N*-arylpropiolamides (**1**).

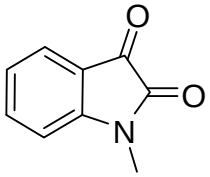
(b) Typical Experimental Procedure for Palladium-Catalyzed C≡C Bond Cleavage/C-H Bond Oxidation Cyclization of *N*-Arylpropiolamides:

To a Schlenk tube were added *N*-arylpropiolamides **1** (0.3 mmol), $PdBr_2$ (10 mol %), $CuBr_2$ (40 mol %), TEMPO (1.0 equiv) and H_2O/dioxane (v/v = 1/4, 3 mL) at 80 ^oC. Then the tube was recharged with O_2 (1 atm), and the mixture was stirred at 80 ^oC (oil bath temperature) for 48 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was diluted in ethyl acetate, and washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford indoline-2,3-diones.

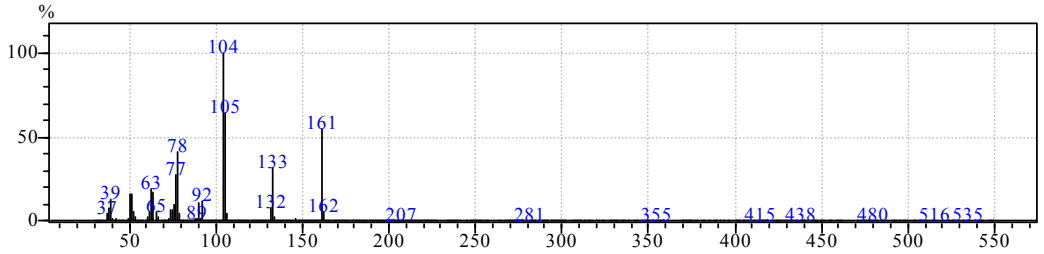
(c) Data of the ^{18}O-labeled Experiments Determined by GC-MS Analysis

Treatment of substrate **1a** (0.3 mmol) with $H_2{}^{18}O$, $PdBr_2$ (10 mol %), $CuBr_2$ (40 mol %), TEMPO (1.0 equiv) and O_2 (1 atm) in dioxane at 80 ^oC, afforded the corresponding ^{18}O-containing product **2a**-^{18}O, which was determined by GC-MS analysis.





Chemical Formula: $C_9H_7NO_2$
Molecular Weight: 161



30.05	2613	0.13
31.05	1689	0.08
32.00	73638	3.68
33.00	132	0.01
33.90	513	0.03
34.90	156	0.01
36.05	5134	0.26
37.05	100245	5.00
38.05	169438	8.46
49.05	37677	1.88
50.05	366340	18.29
51.10	376603	18.80
52.05	144486	7.21
53.05	53272	2.66
54.05	9234	0.46
55.05	14470	0.72
56.05	7305	0.36
65.55	145791	7.28
66.55	52552	2.62
67.55	1330	0.07
68.05	1655	0.08
69.05	4193	0.21
70.10	1920	0.10
71.15	4606	0.23
72.05	2634	0.13
73.05	33046	1.65

39.05	277258	13.84
40.05	30245	1.51
41.05	16338	0.82
42.05	27472	1.37
43.05	24609	1.23
44.05	9319	0.47
45.05	8003	0.40
46.10	235	0.01
48.05	3188	0.16

57.10	7408	0.37
58.10	2387	0.12
59.00	1692	0.08
60.00	6910	0.34
61.00	56070	2.80
62.00	120321	6.01
63.05	435166	21.72
64.05	356524	17.80

74.05	146956	7.34
75.05	132265	6.60
76.05	216101	10.79
77.10	562505	28.08
78.10	846380	42.25
79.10	88078	4.40
80.40	12083	0.60
81.35	2853	0.14
82.10	1012	0.05

83.10	1902	0.09
84.05	1901	0.09
85.10	6160	0.31
86.05	6989	0.35
87.05	14413	0.72
88.05	29403	1.47
89.05	26510	1.32
90.10	236289	11.79
91.10	28116	1.40
92.10	258398	12.90
93.10	18099	0.90
94.05	1772	0.09
95.15	1602	0.08
96.10	808	0.04
97.15	1707	0.09
98.10	1454	0.07
99.10	5419	0.27
100.10	2067	0.10
101.10	1641	0.08
102.10	11422	0.57
103.15	18800	0.94
104.10	2003438	100.00
105.10	1264244	63.10
106.10	114265	5.70

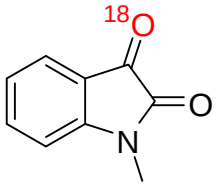
118.10	12409	0.62
119.10	3721	0.19
120.10	1720	0.09
121.10	665	0.03
122.20	896	0.04
123.10	678	0.03
124.10	352	0.02
125.15	888	0.04
126.15	581	0.03
127.25	1016	0.05
128.10	579	0.03
130.10	1427	0.07
131.15	1540	0.08
132.15	181969	9.08
133.15	612527	30.57
134.15	61500	3.07
135.15	5012	0.25
136.20	460	0.02
137.20	428	0.02
138.20	203	0.01
139.20	347	0.02
140.20	326	0.02
141.30	484	0.02
142.30	198	0.01

156.10	99	0.00
157.10	409	0.02
158.10	465	0.02
159.20	780	0.04
160.15	1886	0.09
161.10	974936	48.66
162.10	106563	5.32
163.15	9672	0.48

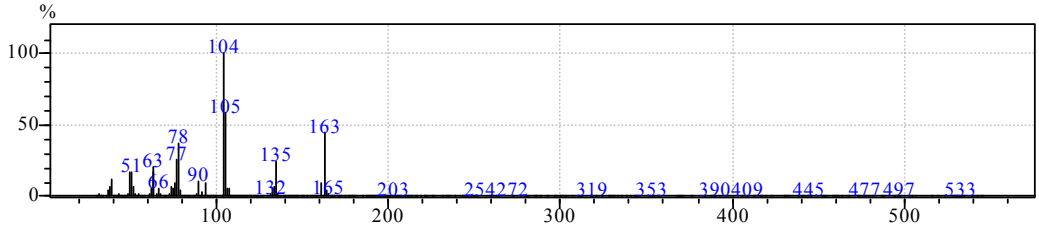
164.00	771	0.04
165.00	472	0.02
166.00	225	0.01
167.00	246	0.01
168.00	108	0.01
169.00	217	0.01
170.00	27	0.00
171.00	160	0.01

107.15	11981	0.60
108.25	1259	0.06
109.20	1019	0.05
110.20	702	0.04
111.25	1375	0.07
112.20	564	0.03
113.15	859	0.04
114.20	502	0.03
115.15	11090	0.06
116.10	1299	0.06
117.10	11518	0.57

143.30	262	0.01
145.15	802	0.04
146.10	31878	1.59
147.15	9939	0.50
148.15	19024	0.95
149.15	2522	0.13
150.20	388	0.02
151.15	819	0.04
152.10	640	0.03
153.10	307	0.02
154.10	300	0.01
155.10	313	0.02



Chemical Formula: $C_9H_7NO^{18}O$
Molecular Weight: 163



30.05	8223	0.63
31.05	2389	0.18
32.05	59228	4.57
33.00	348	0.03
34.00	280	0.02
36.05	3010	0.23
37.05	72105	5.57
38.05	118371	9.14
39.05	198233	15.31
40.05	22080	1.71
41.05	16602	1.28
42.05	18757	1.45
43.10	8328	0.64

49.05	27210	2.10
50.05	250976	19.38
51.10	251292	19.40
52.05	97183	7.50
53.05	37442	2.89
54.00	6777	0.52
55.05	11983	0.93
56.05	4241	0.33
57.10	3142	0.24
58.05	2695	0.21
59.05	1894	0.15
60.00	4841	0.37
51.05	41061	3.17

66.55	32767	2.53
68.10	3496	0.27
69.05	3998	0.31
70.10	1488	0.11
71.10	2073	0.16
72.05	1974	0.15
73.05	24020	1.85
74.05	100497	7.76
75.05	92297	7.13
76.05	143533	11.08
77.10	364180	28.12
78.10	576768	44.54
79.05	57755	4.46

44.05	7292	0.56
45.00	9473	0.73
46.00	937	0.07
48.00	2289	0.18

62.05	81199	6.27
63.05	288377	22.27
64.05	237004	18.30
65.55	89065	6.88

80.10	7705	0.59
81.15	5306	0.41
82.15	2070	0.16
83.10	1681	0.13

84.10	1585	0.12
85.10	36110.28	
86.05	4746	0.37
87.05	10571	0.82
88.05	19369	1.50
89.05	17092	1.32
90.10	157249	12.14
91.10	14011	1.08

92.10	160708	12.41
93.10	12192	0.94
94.10	11908	0.92
95.15	2233	0.17
96.15	1313	0.10
97.15	1343	0.10
98.05	865	0.07
99.10	3595	0.28

100.10	1214	0.09
101.10	1044	0.08
102.10	7164	0.55
103.15	11831	0.91
104.10	1295014	100.00
105.10	810020	62.55
106.10	62131	4.80
107.10	9331	0.72

108.15	11420.09	
109.10	971	0.07
110.10	404	0.03
111.10	11550.09	
112.10	310	0.02
113.15	1037	0.08
114.20	328	0.03
115.15	1022	0.08
116.15	610	0.05
117.10	7715	0.60

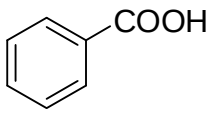
118.10	3587	0.28
119.15	2455	0.19
120.10	4139	0.32
121.10	852	0.07
122.10	454	0.04
123.20	504	0.04
124.20	1459	0.11
125.15	671	0.05
126.15	1856	0.14
127.10	395	0.03

128.10	380	0.03
129.10	235	0.02
130.15	932	0.07
131.15	844	0.07
132.15	114060	8.81
133.15	378981	29.26
134.15	38930	3.01
135.15	8202	0.63
136.10	611	0.05
137.10	315	0.02

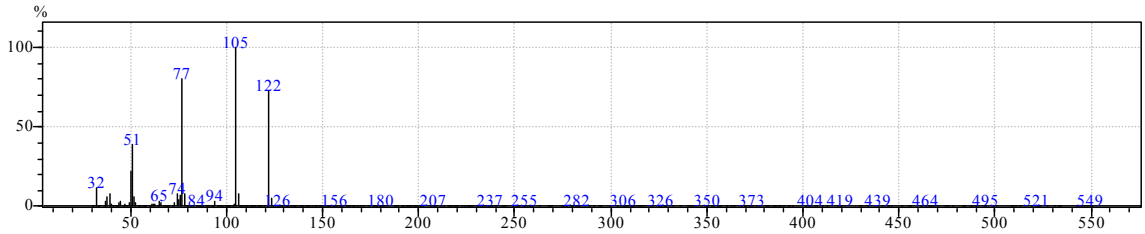
138.10	171	0.01
139.10	438	0.03
140.10	212	0.02
141.10	342	0.03
142.10	371	0.03
143.10	264	0.02
144.10	292	0.02
145.05	446	0.03
146.05	8312	0.64
147.10	1526	0.12
148.05	12591	0.97

149.05	1439	0.11
150.10	163	0.01
151.10	216	0.02
152.20	628	0.05
153.10	472	0.04
154.10	1803	0.14
155.10	416	0.03
156.10	409	0.03
157.10	222	0.02
158.10	56	0.00
159.10	142	0.01

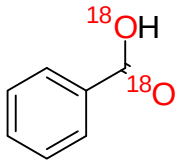
160.15	616	0.05
161.10	257072	19.85
162.10	28379	2.19
163.10	403296	31.14
164.10	43076	3.33
165.10	8401	0.65
166.15	828	0.06
167.10	129	0.01
168.10	40	0.00
169.10	51	0.00
170.10	112	0.01
171.10	73	0.01



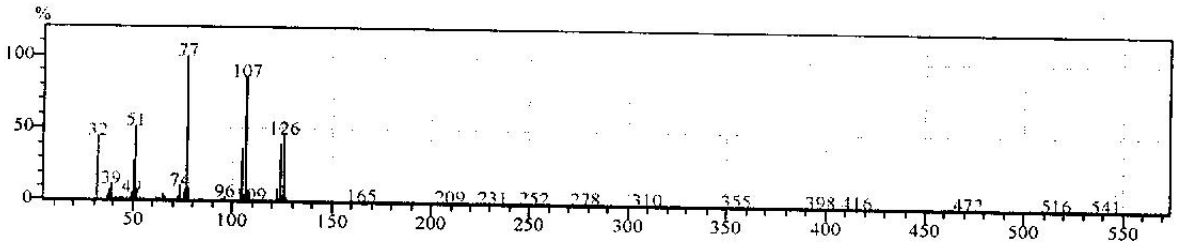
Chemical Formula: $C_7H_6O_2$
Molecular Weight: 122



32.05	102952	11.37	51.05	355867	39.31	52.10	77.10	730344	80.68
37.10	30369	3.35		57801	6.38		78.10	76352	8.43
38.10	53160	5.87	52.90	17014	1.88		94.15	29291	3.24
39.05	75355	8.32	63.05	13632	1.51		104.15	11525	1.27
40.05	15998	1.77	65.10	27464	3.03		105.15	905264	100.00
44.05	17155	1.90	66.10	22272	2.46		106.15	69048	7.63
45.05	30676	3.39	73.05	18790	2.08		**122.15**	**655657**	**72.43**
49.10	23683	2.62	74.05	74659	8.25		123.15	50816	5.61
50.05	200726	22.17	75.10	38198	4.22		124.15	46640	0.52
			76.10	65513	7.24				



Chemical Formula: $C_7H_6{}^{18}O_2$
Molecular Weight: 126



30.05	51161.00	
31.05	45110.89	
32.05	223544	43.87
33.10	1320	0.26
34.05	1034	0.20
35.00	75	0.01
36.00	1809	0.35
37.05	22924	4.50
38.05	38193	7.49
39.00	56232	11.03
40.00	21428	4.20
41.10	6972	1.37
42.10	3006	0.59
43.05	9269	1.82
44.05	11200	2.20
45.05	8429	1.65
46.05	2518	0.49
47.00	11771	2.31
48.05	7921	1.55
49.00	25809	5.06
50.00	142808	28.02
51.00	261168	51.25
52.05	41207	8.09
53.45	8156	1.60
55.05	10312	2.02
56.10	3640	0.71
57.05	3872	0.76
58.05	11170.22	
59.10	2636	0.52
60.00	2289	0.45
61.05	10354	2.03
62.05	7502	1.47
63.05	9605	1.88
64.10	2851	0.56
65.10	18780	3.69
66.10	14931	2.93
67.10	3520	0.69
68.10	2537	0.50
69.10	4996	0.98
70.10	1721	0.34
71.10	1395	0.27
72.05	1019	0.20
73.05	13938	2.74
74.00	48872	9.59
75.05	26375	5.18
76.05	41367	8.12
77.10	509592	100.00
78.10	46176	9.06
79.05	4212	0.83
80.10	761	0.15
81.10	1868	0.37
82.10	1396	0.27
83.15	1260	0.25
84.15	11570.23	
85.15	11870.23	
86.20	480	0.09
87.15	690	0.14
88.20	174	0.03
89.20	126	0.02
90.20	185	0.04
91.20	598	0.12
93.10	1238	0.24
94.10	6379	1.25
95.10	2880	0.57
96.10	13465	2.64
97.10	1760	0.35
98.10	1484	0.29
99.10	761	0.15
100.10	1036	0.20
101.15	660	0.13
102.20	422	0.08
103.15	721	0.14
104.10	2380	0.47
105.10	182417	35.80
106.10	19739	3.87
107.10	432638	84.90
108.10	33012	6.48
109.15	3406	0.67
110.20	344	0.07
111.20	348	0.07
112.20	144	0.03
113.20	347	0.07
114.20	217	0.04
115.20	414	0.08
116.20	198	0.04
117.20	270	0.05
118.20	120	0.02
119.20	192	0.04
120.20	99	0.02
121.15	592	0.12
122.15	43457	8.53
123.15	6148	1.21
124.15	203760	39.98
125.15	19318	3.79
126.15	239899	47.08
127.15	18002	3.53
128.15	906	0.18
129.10	380	0.07
130.10	104	0.02
131.10	49	0.01
132.10	137	0.03
133.10	251	0.05
134.10	115	0.02
135.10	91	0.02
136.10	3	0.00

(B) Analytical data for 2 and 3

***N*-Methylindoline-2,3-dione (2a):[2]**

Red solid, mp 121.7-123.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, DMSO-D_6) δ: 7.66 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 2H), 3.13 (s, 3H); ^{13}C NMR (125 MHz, DMSO-D_6) δ: 184.0, 158.7, 151.9, 138.7, 124.8, 123.7, 117.8, 111.1, 26.5; IR (KBr, cm^{-1}): 1749, 1615; LRMS (EI 70 ev) *m*/z (%): 161 (M^+, 55), 104 (100).

***N*-Benzylindoline-2,3-dione (2b):[2]**

Red solid, mp 127.8-129.2 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (d, J = 7.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.27-7.22 (m, 5H), 7.00 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 183.2, 158.2, 150.6, 138.3, 134.4, 129.0, 128.1, 127.4, 125.3, 123.8, 117.6, 111.0, 44.0; IR (KBr, cm^{-1}): 1731, 1611; LRMS (EI 70 ev) *m*/z (%): 237 (M^+, 79), 146 (100), 91 (66).

1-(2-Iodobenzyl)indoline-2,3-dione (2c):[3]

Red solid, mp 142.2-143.8 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.08-7.03 (m, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 4.90 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.9, 158.3, 150.4, 139.9, 138.5, 135.9, 129.7, 128.6, 127.1, 125.5, 124.1, 117.7, 111.3, 97.6, 49.1; IR (KBr, cm^{-1}): 1737, 1612; LRMS (EI 70 ev) *m*/z (%): 363 (M^+, 35), 272 (95), 91 (100).

***N*,7-Dimethylindoline-2,3-dione (2k):[2]**

Red solid, mp 162.3-164.8 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 3.50 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 183.6, 159.1, 148.8, 142.2, 123.8, 123.2, 121.8, 118.3, 29.6, 18.7; IR (KBr, cm^{-1}): 1732, 1716, 1699; LRMS (EI 70 ev) *m*/z (%): 175 (M^+, 69), 118 (100), 91 (43).

1-Methyl-7-phenylindoline-2,3-dione (2l):

Red solid, mp 175.3-177.4 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 8.5 Hz, 4H), 7.30 (s, 2H), 7.06 (t, J = 7.5 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ: 183.4, 159.4, 148.0, 141.2, 137.1, 129.5, 128.5, 128.2, 127.4, 124.4, 123.3, 118.6, 30.1; IR (KBr, cm^{-1}): 1736, 1615; LRMS (EI 70 ev) *m*/z (%): 237 (M^+, 90), 180 (100); HRMS (EI) $C_{15}H_{11}NO_2$ for (M^+) 237.0790, found 237.0794.

1,4-Dimethylindoline-2,3-dione (2m) and 1,6-dimethylindoline-2,3-dione (2m'):[2]

6-Me/4-Me = 1/1.7; Red solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39-7.34 (m, 1.8H), 6.84-6.80 (m, 1.8H), 6.62-6.61 (m, 1.8H), 3.14 (s, 4.9H), 2.47 (s, 3H), 2.37 (s, 1.8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 183.8, 182.6, 158.8, 158.1, 151.8, 151.5, 150.7, 141.1, 137.5, 126.1, 125.3, 124.4, 115.5, 115.2, 110.7, 107.1, 26.1, 22.9, 18.0; IR (KBr, cm^{-1}): 1730, 1615, 1558; LRMS (EI 70 ev) *m*/z (%): 175 (M^+, 100), 147 (37), 118 (78).

***N*,5-Dimethylindoline-2,3-dione (2n):[2]**

Red solid, mp 150.5-151.2 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (t, *J* = 7.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.15 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 183.6, 158.3, 149.2, 138.7, 133.6, 125.5, 117.3, 109.7, 26.1, 20.6; IR (KBr, cm^{-1}): 1736, 1723, 1622; LRMS (EI 70 ev) *m*/z (%): 175 (M^+, 45), 118 (100).

5-Butyl-1-methylindoline-2,3-dione (2o):

Red solid, mp 155.3-157.4 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.15 (s, 3H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.51-1.48 (m, 2H), 1.28-1.24 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 183.6, 158.3, 149.4, 138.7, 138.2, 124.9, 117.4, 109.7, 34.6, 33.2, 26.1, 22.0, 13.7; IR (KBr, cm^{-1}): 1734, 1623, 1615; LRMS (EI 70 ev) *m*/z (%): 217 (M^+, 32), 146 (50); HRMS (EI) $C_{13}H_{15}NO_2$ for (M^+) 217.1103, found 217.1107.

5-Fluoro-1-methylindoline-2,3-dione (2p):[4]

Red solid, mp 150.7-152.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29-7.23 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.7, 160.3, 158.2 (d, *J* = 52.6 Hz, 1C), 147.5, 124.6 (d, *J* = 23.8 Hz, 1C), 118.0 (d, *J* = 7.3 Hz, 1C), 112.3 (d, *J* = 24.1 Hz, 1C), 111.0 (d, *J* = 7.3 Hz, 1C), 26.3; IR (KBr, cm^{-1}): 1749, 1728, 1622; LRMS (EI 70 ev) *m*/z (%): 179 (M^+, 46), 122 (100).

5-Chloro-1-methylindoline-2,3-dione (2q):[4]

Red solid, mp 175.1-176.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.3, 157.6, 149.6, 137.7, 129.6, 125.1, 118.1, 111.2, 26.3; IR (KBr, cm^{-1}): 1741, 1720, 1603; LRMS (EI 70 ev) *m*/z (%): 195 (M^+, 63), 138 (100).

5-Bromo-1-methylindoline-2,3-dione (2r):[4]

Red solid, mp 170.1-171.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.1, 157.4, 150.1, 140.6, 128.0, 118.5, 116.6, 111.6, 26.3; IR (KBr, cm^{-1}): 1751, 1731, 1606; LRMS (EI 70 ev) *m*/z (%): 239 (M^+, 94), 184 (100).

5-Iodo-1-methylindoline-2,3-dione (2s):[5]

Red solid, mp 150.1-152.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 181.9, 157.2, 150.7, 146.4, 133.6, 118.9, 112.1, 86.0, 26.3; IR (KBr, cm^{-1}): 1749, 1628, 1612; LRMS (EI 70 ev) *m*/z (%): 287 (M^+, 100), 259 (61), 230 (50).

5-Acetyl-1-methylindoline-2,3-dione (2t):[2]

Red solid, mp 145.3-148.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.5 Hz, 1H), 8.10 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 3.25 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.3, 182.4, 158.3, 154.6, 138.7, 133.0, 125.4, 117.0, 110.0, 26.5, 26.4; IR (KBr, cm^{-1}): 1744, 1683, 1605; LRMS (EI 70 ev) *m*/z (%): 203 (M^+, 76), 160 (100).

***N*,4,7-Trimethylindoline-2,3-dione (2u):**

Red solid, mp 163.4-164.7 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.08 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.40 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 184.0, 159.0, 148.7, 141.5, 138.9, 126.1, 118.7, 116.3, 29.5, 18.5, 17.7; IR (KBr, cm^{-1}): 1733, 1684, 1602; LRMS (EI 70 ev) *m*/z (%): 189 (M^+, 100), 132 (87); HRMS (EI) $C_{11}H_{11}NO_2$ for (M^+) 189.0790, found 189.0794.

7-Chloro-1,5-dimethylindoline-2,3-dione (2v):

Red solid, mp 178.3-179.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (s, 2H), 3.53 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.7, 158.6, 144.4, 140.4, 135.1, 124.5, 120.1, 117.1, 31.9, 20.2 ; IR (KBr, cm^{-1}): 1743, 1722, 1607; LRMS (EI 70 ev) *m*/z (%): 209 (M^+, 100), 152 (99), 118 (84); HRMS (EI) $C_{10}H_8ClNO_2$ for (M^+) 209.0244, found 209.0247.

1-Methyl-6,7-dihydrocyclopenta[f]indole-2,3(1*H*,5*H*)-dione (2w) and 3-Methyl-7,8-dihdrocyclopenta[e]indole-1,2(3*H*,6*H*)-dione (2w'):[2]

1-Me/3-Me =1.2/1; Red solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (s, 0.5H), 7.30 (s, 0.4H), 6.67 (s, 0.5H), 6.55 (d, *J* = 8.0 Hz, 0.4H), 3.14 (s, 1.7H), 3.13 (s, 1.3H), 3.03 (t, *J* = 7.5 Hz, 0.9H), 2.88 (t, *J* = 7.5 Hz, 1.1H), 2.81-2.75 (m, 2.1H), 2.09-2.02 (m, 2.2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 183.9, 183.0, 159.0, 158.1, 156.9, 150.9, 150.0, 145.7, 141.4, 139.6, 132.9, 121.0, 116.2, 113.6, 107.3, 106.4, 34.2, 31.7, 31.2, 26.3, 26.1, 25.4, 25.1; IR (KBr, cm^{-1}): 1732, 1625; LRMS (EI 70 ev) *m*/z (%): 201 (M^+, 81), 144 (100), 115 (41).

Benzoic acid (3a):[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.0 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.4, 133.8, 130.2, 129.3, 128.5.

4-Methoxybenzoic acid (3e):[6]

^{1}H NMR (500 MHz, DMSO-D_6) δ:12.6 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, DMSO-D_6) δ: 167.1, 162.9, 131.4, 123.0, 113.8, 55.5.

4-Acetylbenzoic acid (3f):[6]

^{1}H NMR (500 MHz, DMSO-D_6) δ: 13.3 (s, 1H), 8.05 (s, 4H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, DMSO-D_6) δ: 197.7, 166.6, 139.8, 134.5, 129.5, 128.3, 27.0.

Thiophene-2-carboxylic acid (3g):[6]

^{1}H NMR (500 MHz, $CDCl_3$): 9.93 (s, 1H), 7.83 (s, 1H), 7.58 (d, *J* = 4.5 Hz, 1H), 7.07 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.8, 135.0, 134.0, 132.9, 128.1.

(C) References

(1) (a) Tang BX, Tang DJ, Tang S, Yu QF, Zhang YH, Liang Y, Zhong P, Li JH. *Org. Lett.* 2008, 10, 1063. (b) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927.

(2) Tang BX, Song RJ, Wu CY, Liu Y, Zhou MB, Wei WT, Deng GB, Yin DL, Li JH. *J. Am. Chem. Soc.* 2010, 132, 8900.

(3) Torres J, Pinto AC, Garden SJ. *Tetrahedron,* 2004, 60: 9889-9900.

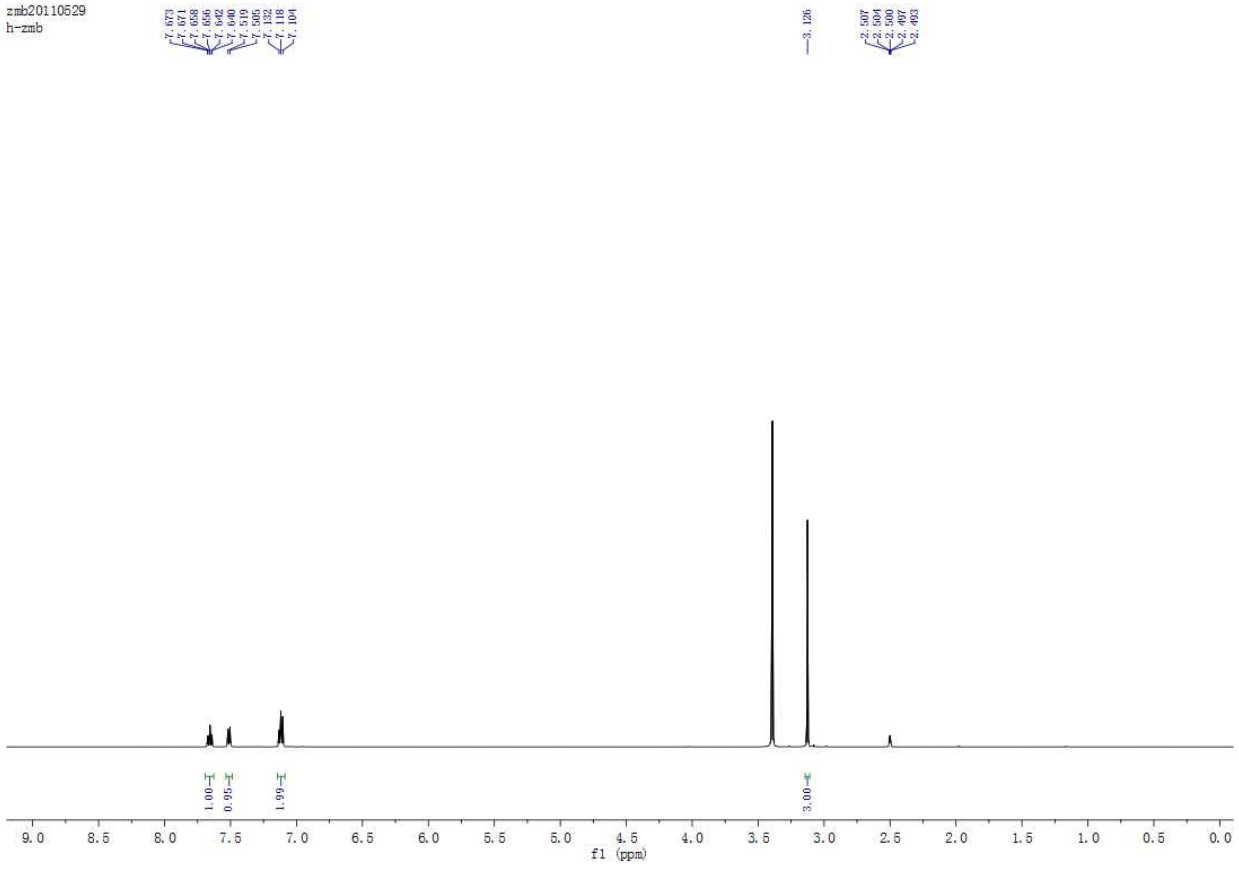
(4) Cheng Y, Ye HL, Zhan YH, Meth-Cohn O. *Synthesis,* 2001, 6: 904-908.

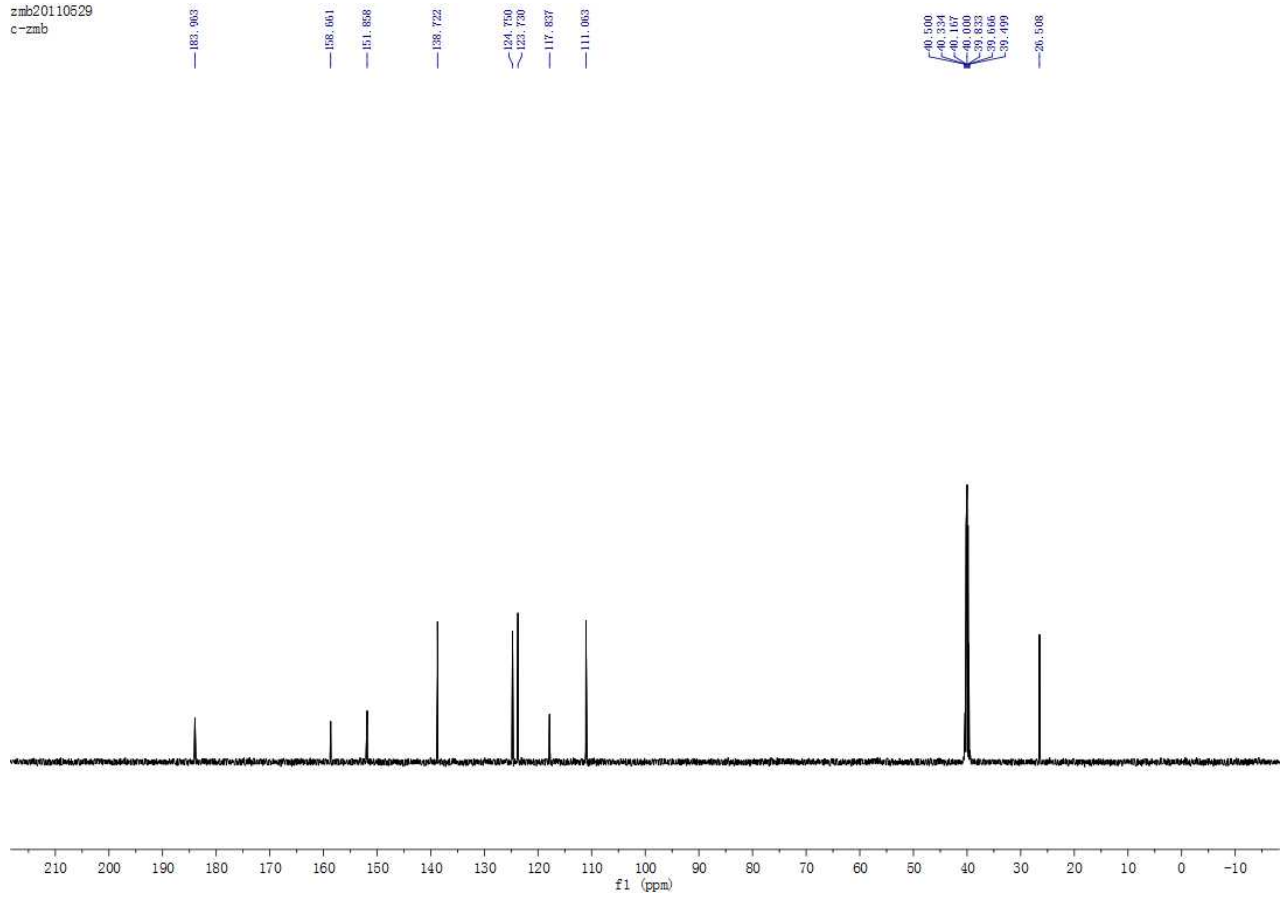
(5) Zhou L, Liu Y, Zhang W, Wei P, Huang C, Pei J, Yuan Y, Lai L. *J Med Chem,* 2006, 49: 3440-3443.

(6) (a) Song RJ, Liu Y, Hu RX, Liu YY, Wu JC, Yang XH, Li JH. *Advanced Synthesis & Catalysis,* 2011, 353: 1467-1473; (b) Sedelmeier J, Ley SV, Baumann I RBM. *Org Lett,* 2010, 12: 3618-3621.

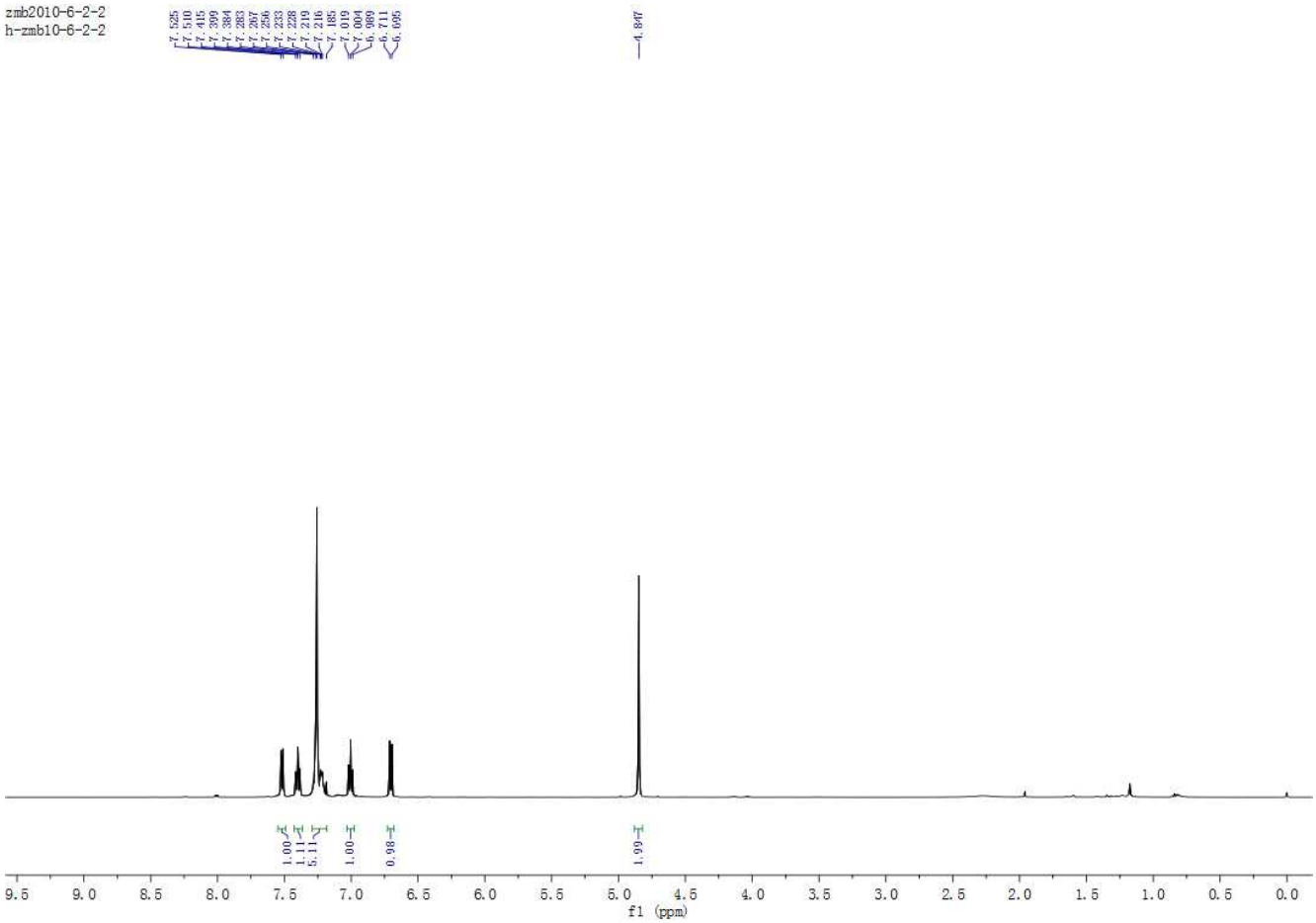
(D) Spectra

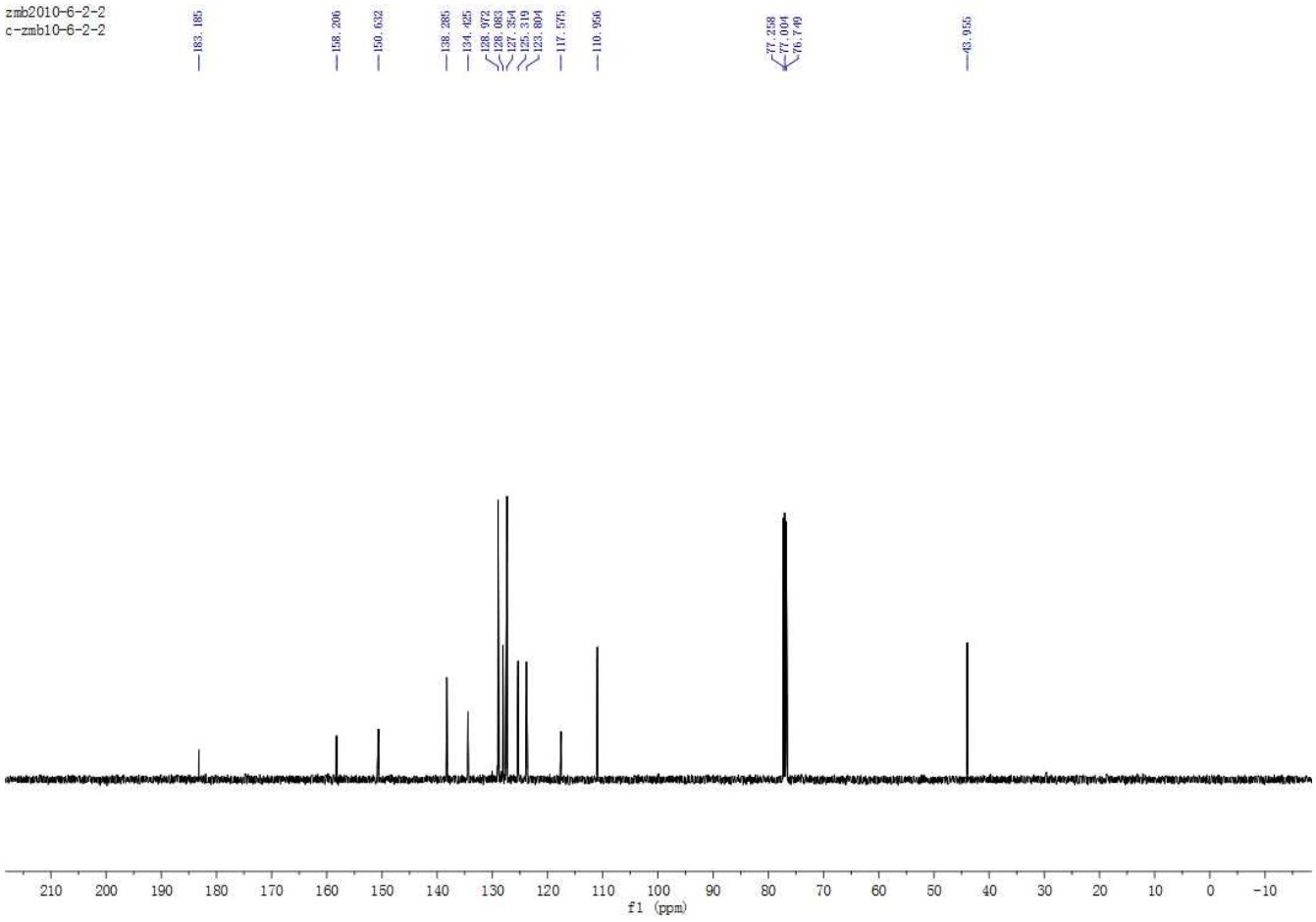
_N_-Methylindoline-2,3-dione (2a)



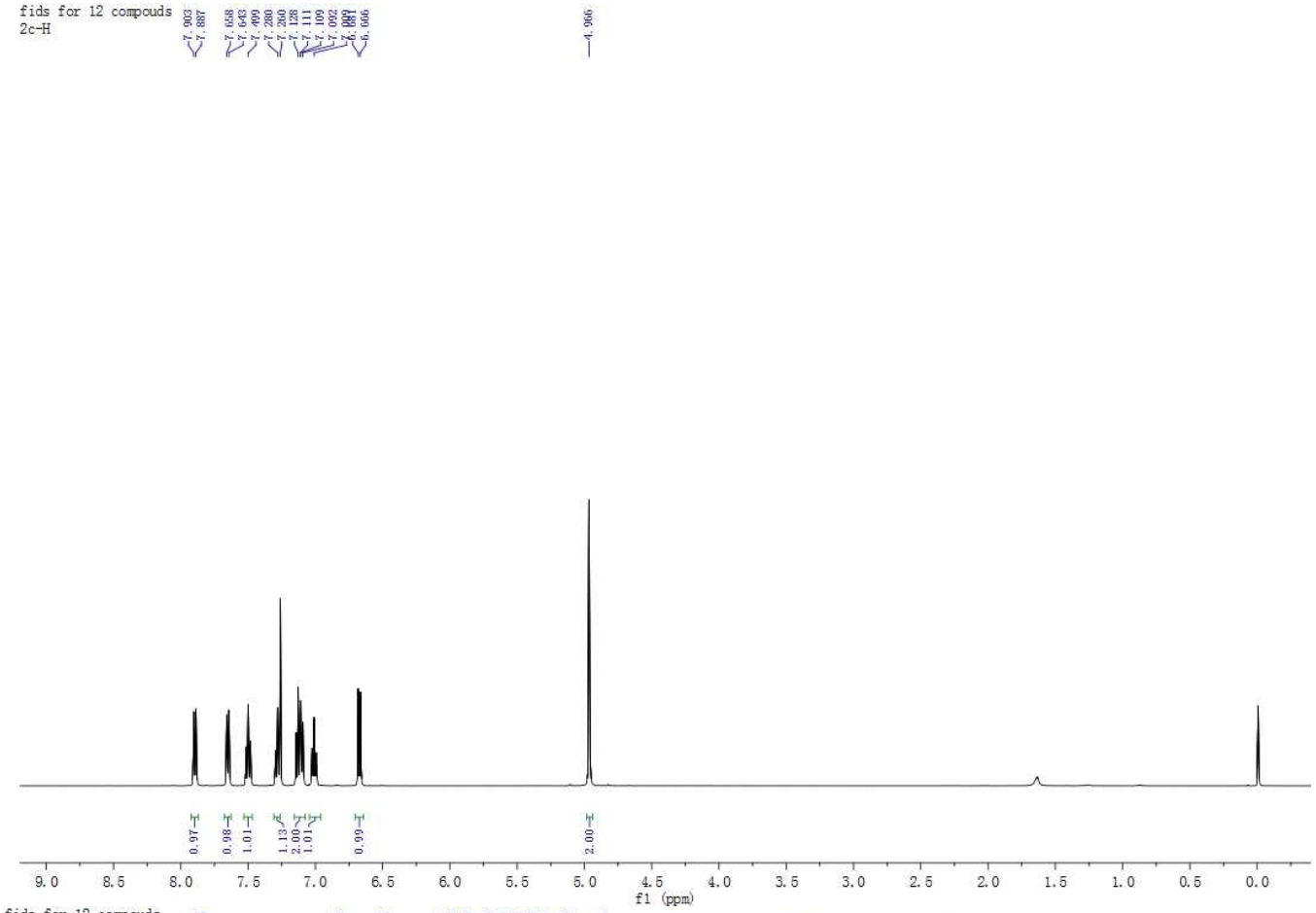


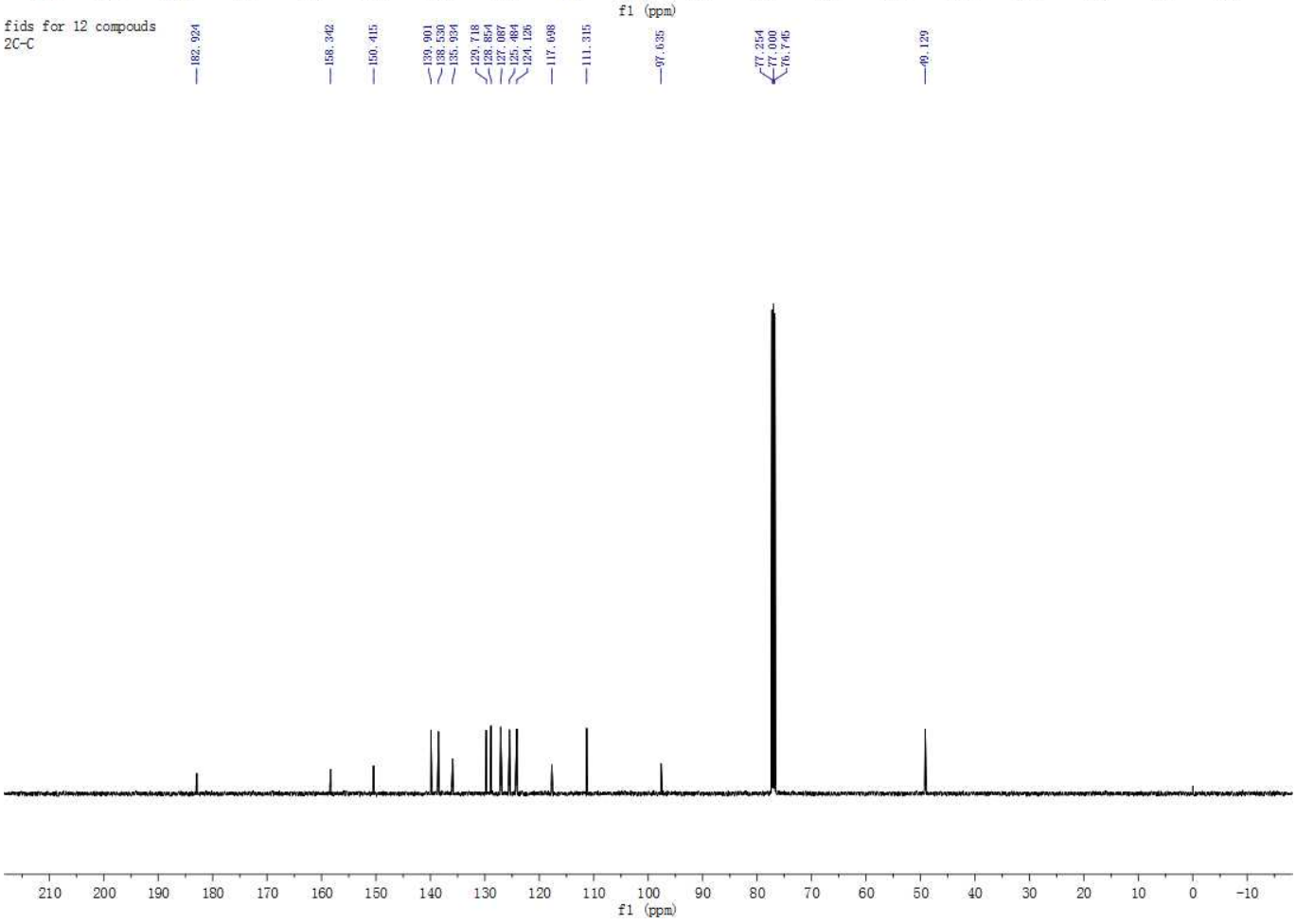
***N*-Benzylindoline-2,3-dione (2b)**



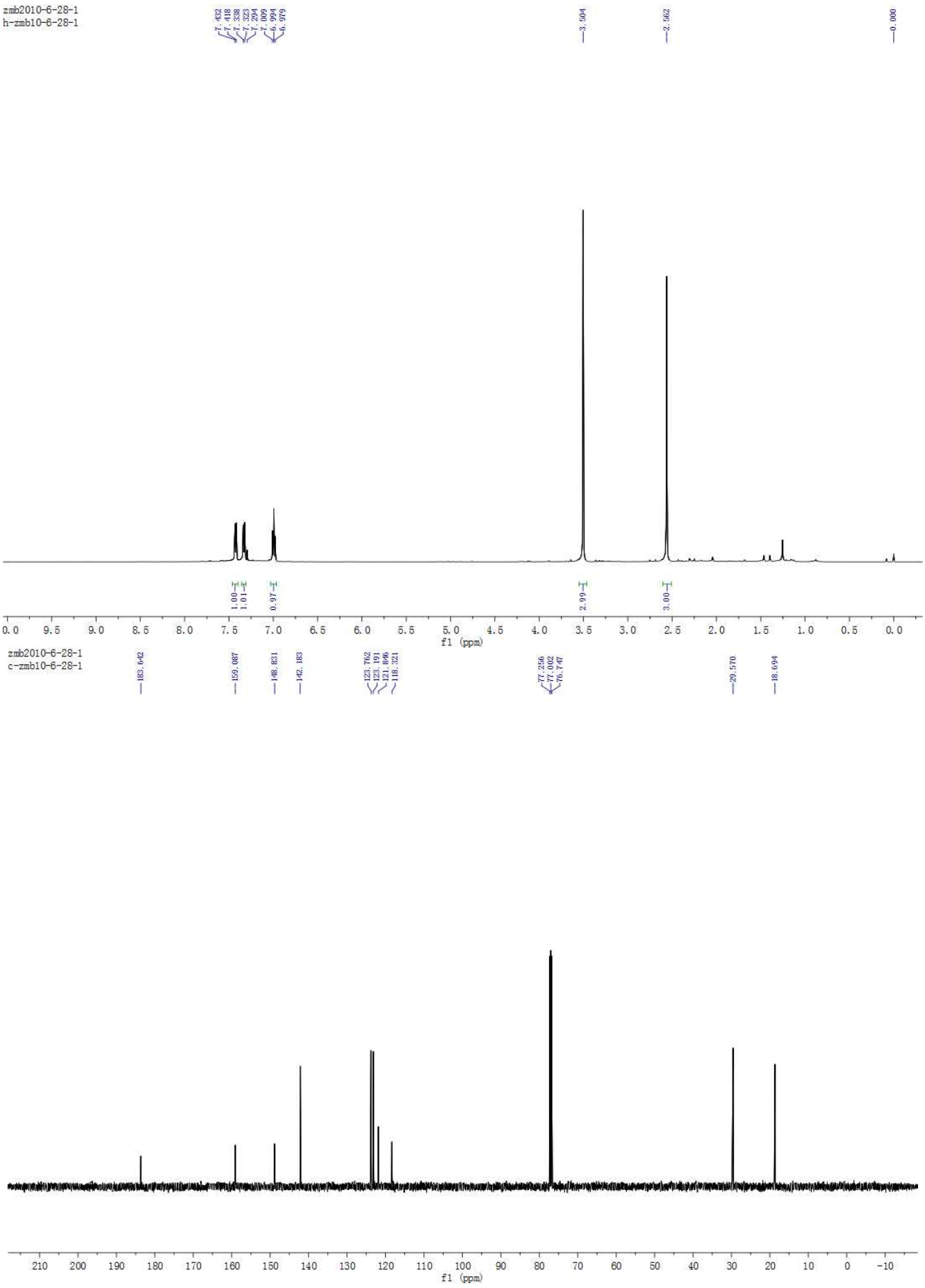


1-(2-Iodobenzyl)indoline-2,3-dione (2c)

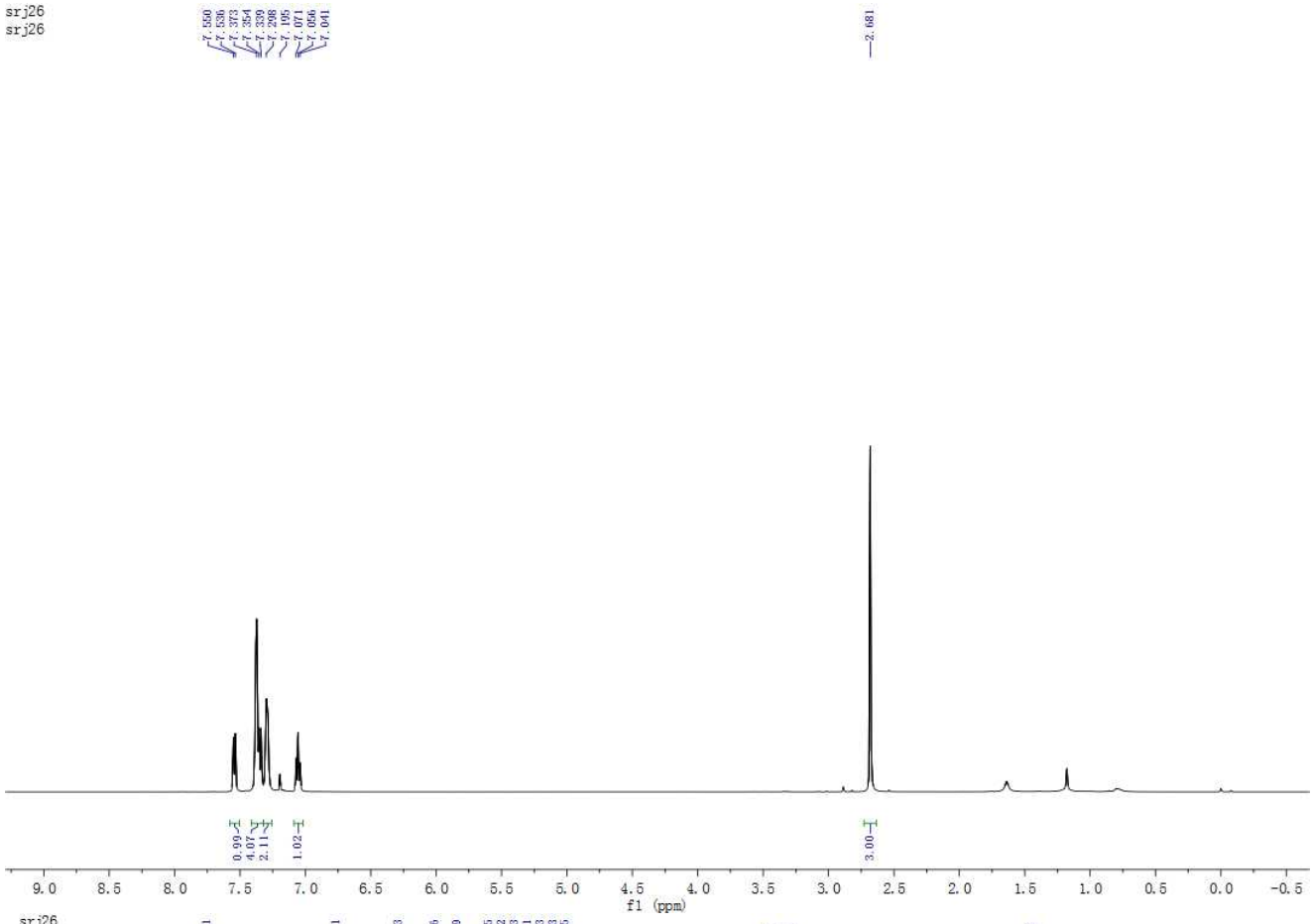


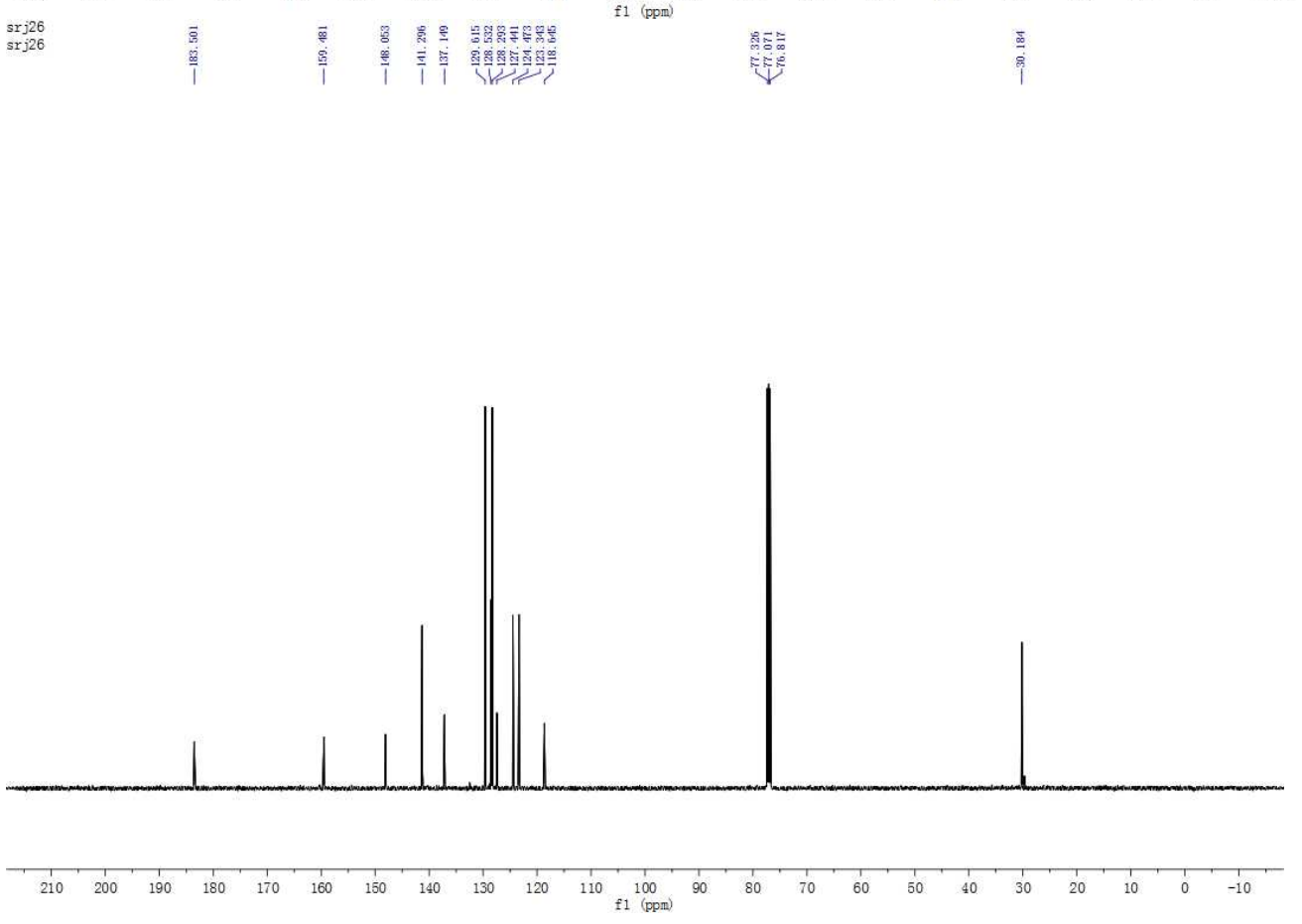


***N*,7-Dimethylindoline-2,3-dione (2k)**

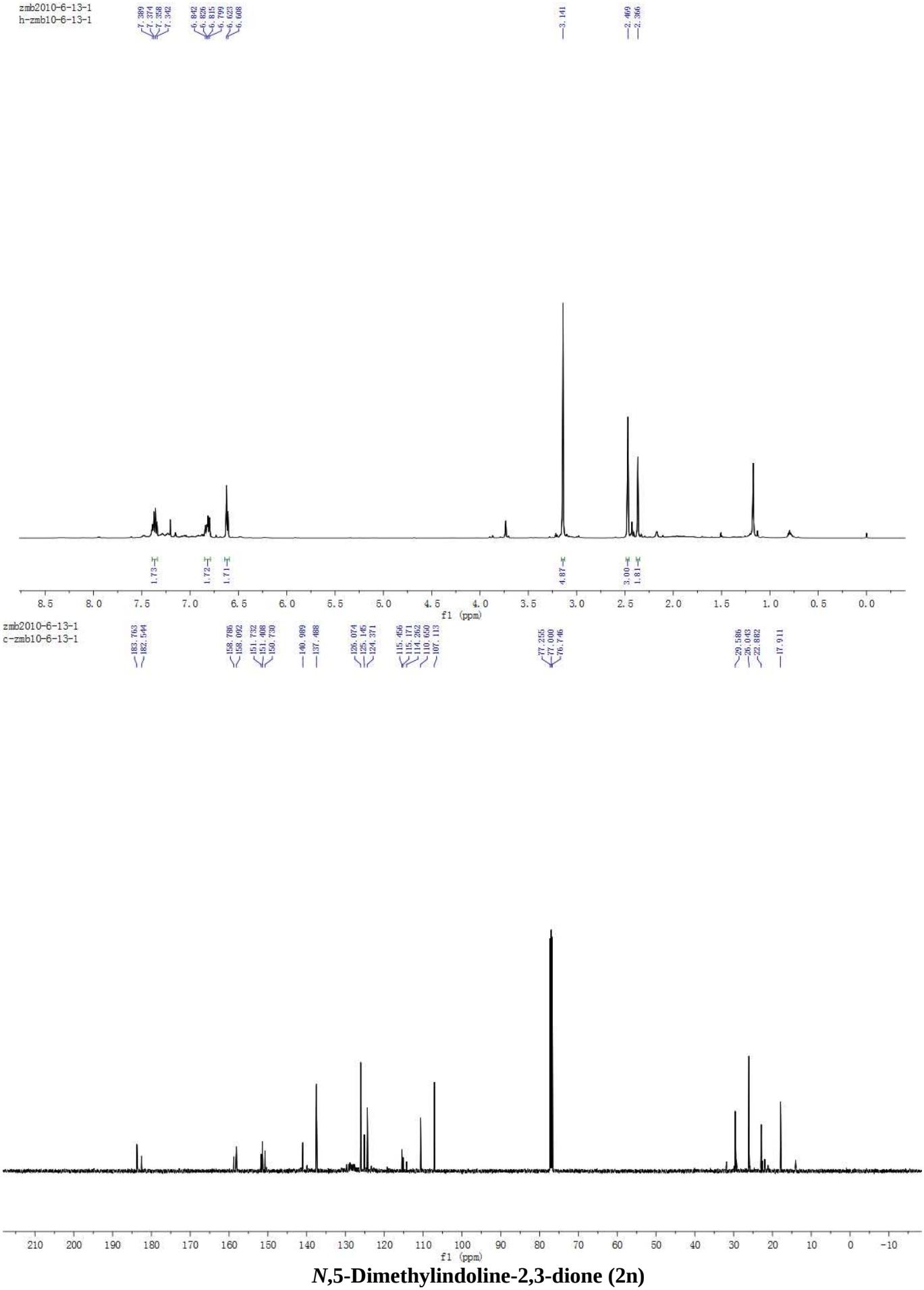


1-Methyl-7-phenylindoline-2,3-dione (2l)

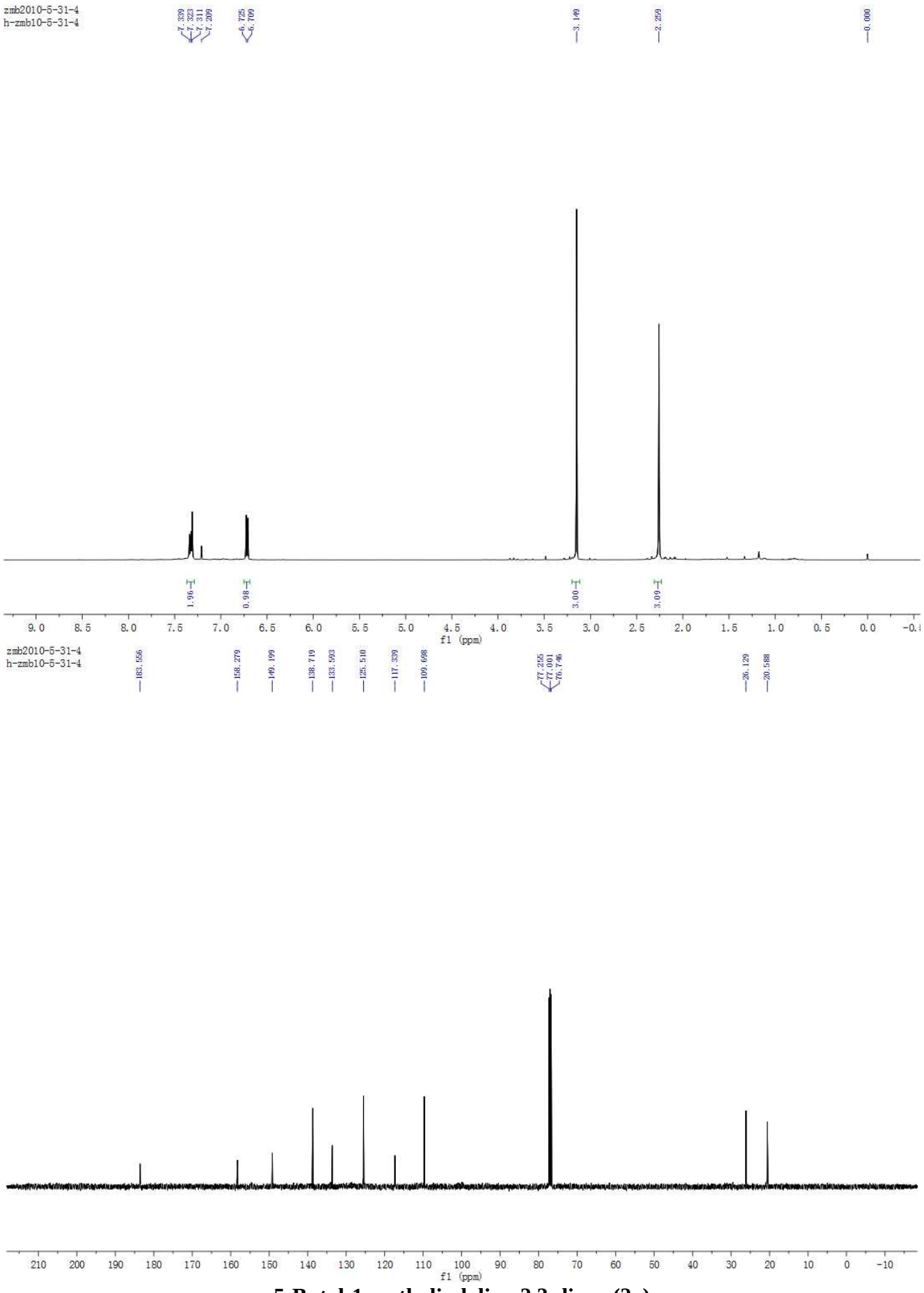




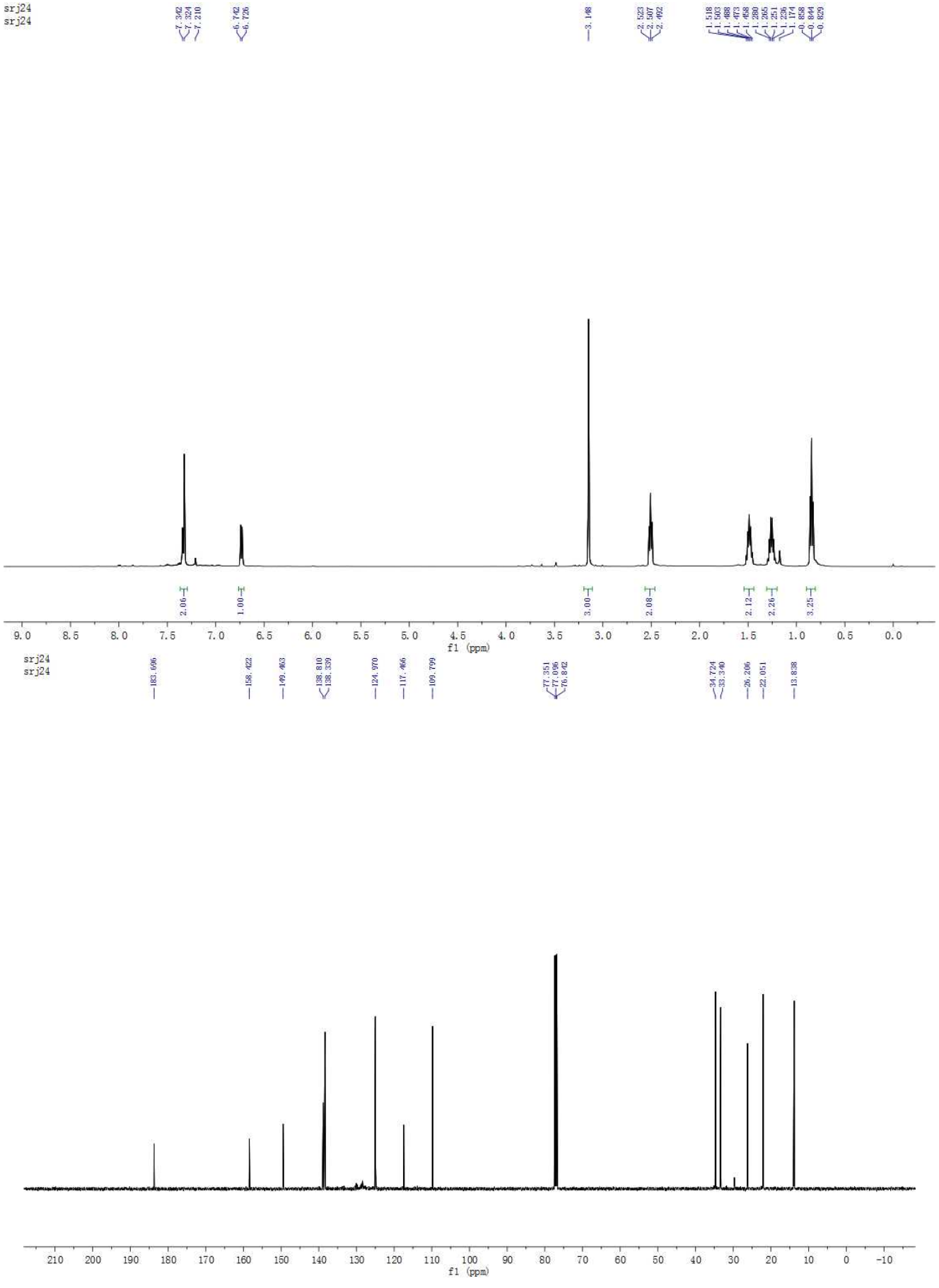
1,4-Dimethylindoline-2,3-dione (2m) and 1,6-dimethylindoline-2,3-dione (2m')



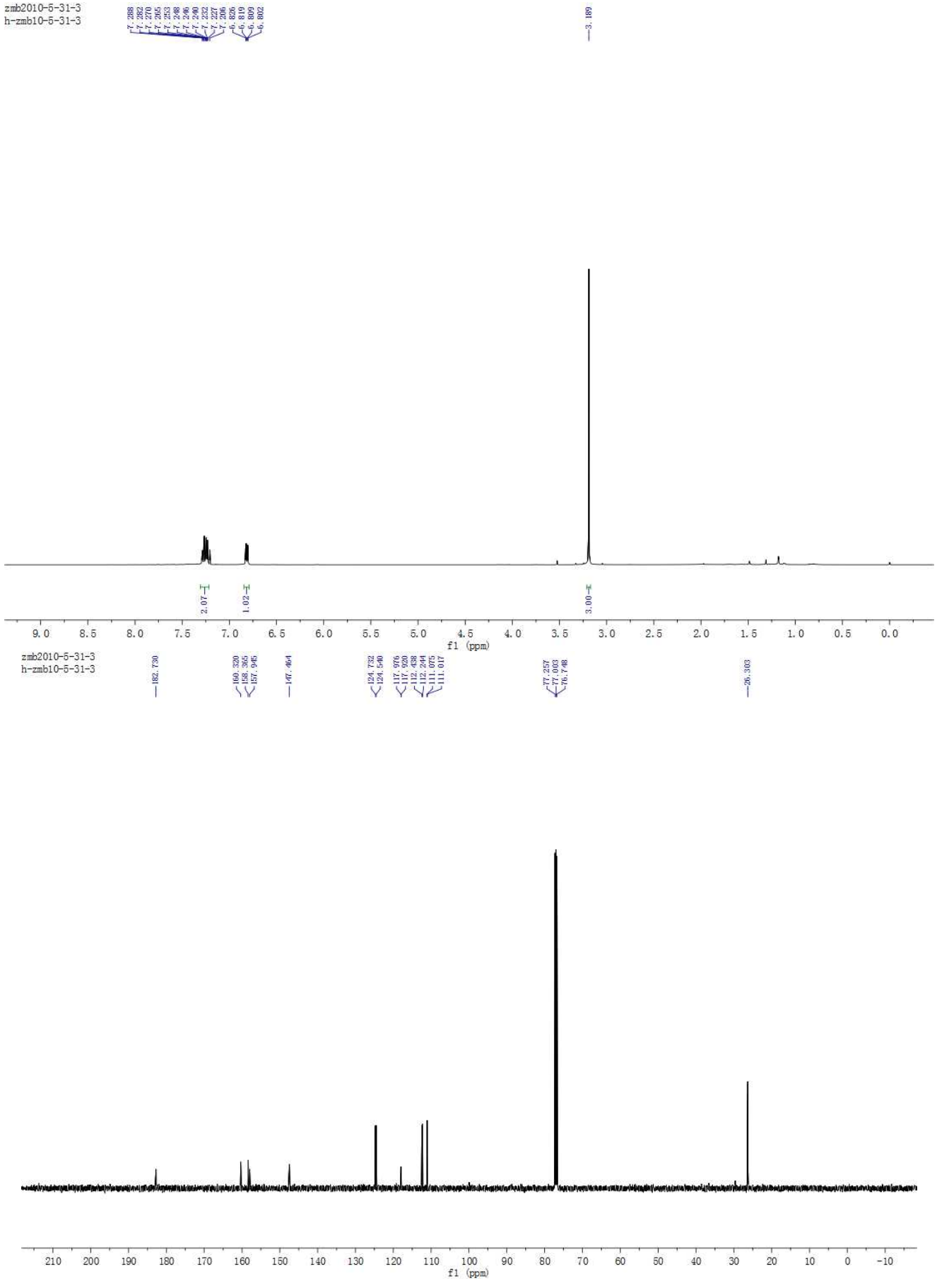
***N*,5-Dimethylindoline-2,3-dione (2n)**



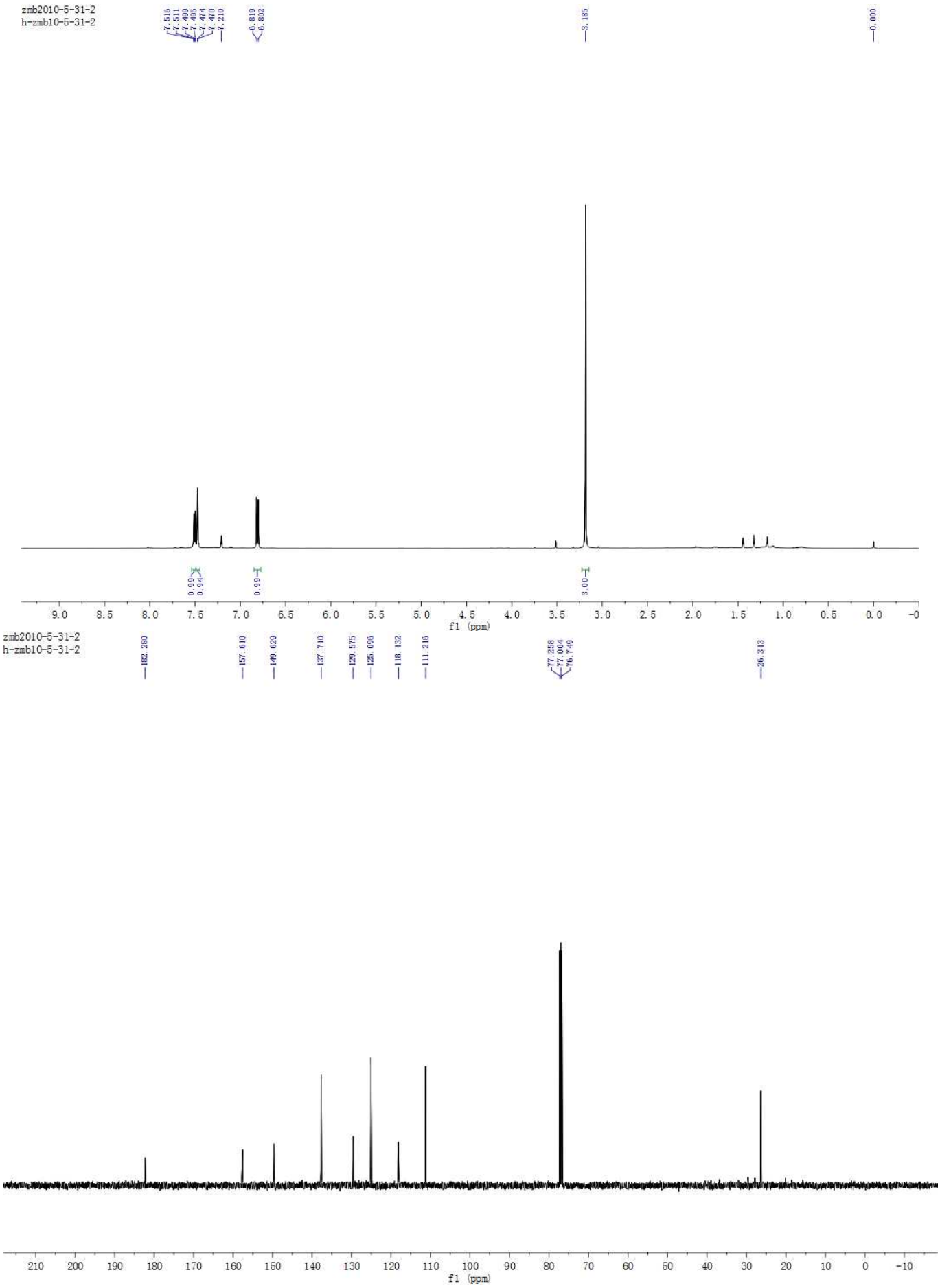
5-Butyl-1-methylindoline-2,3-dione (2o)



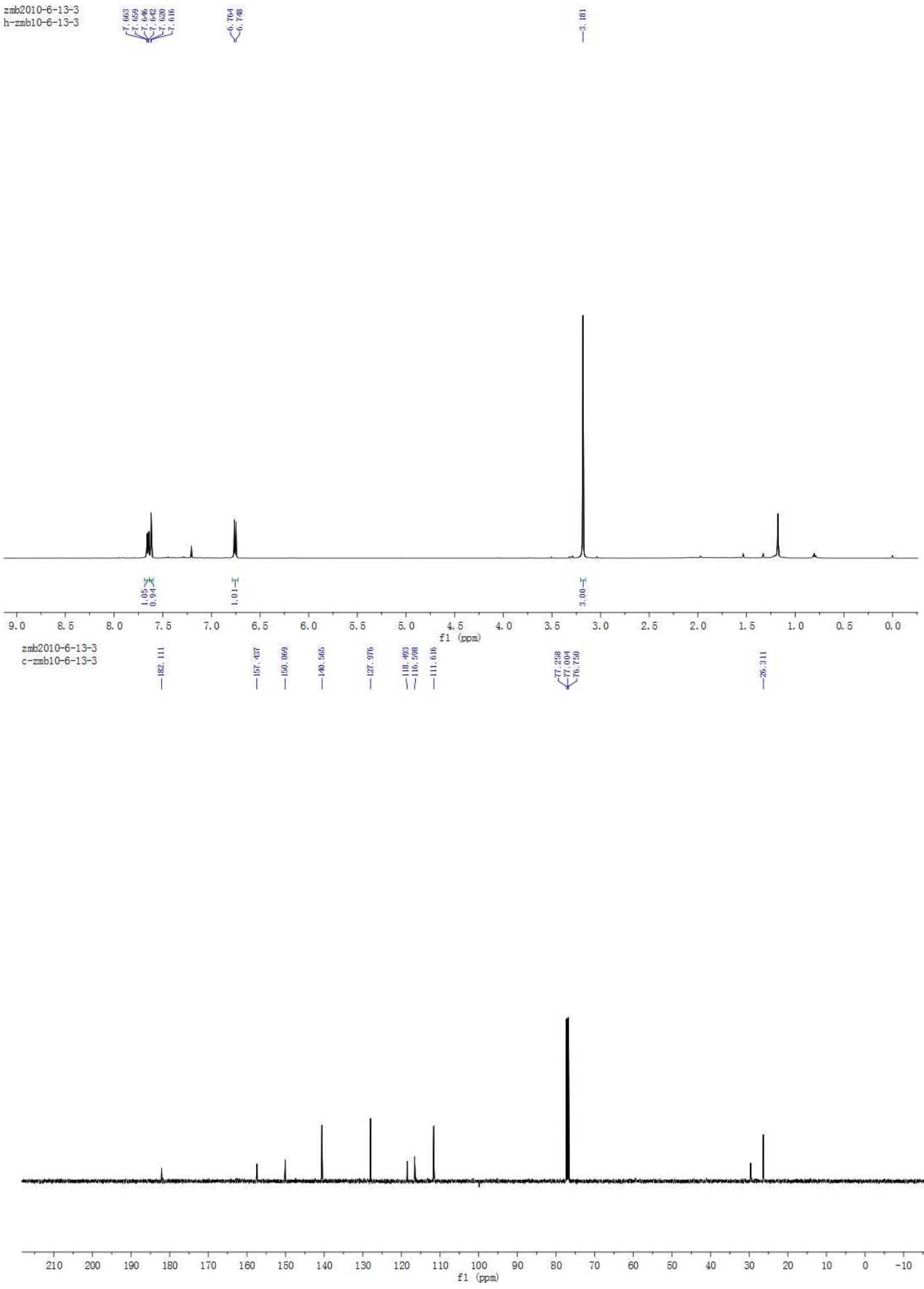
5-Fluoro-1-methylindoline-2,3-dione (2p)



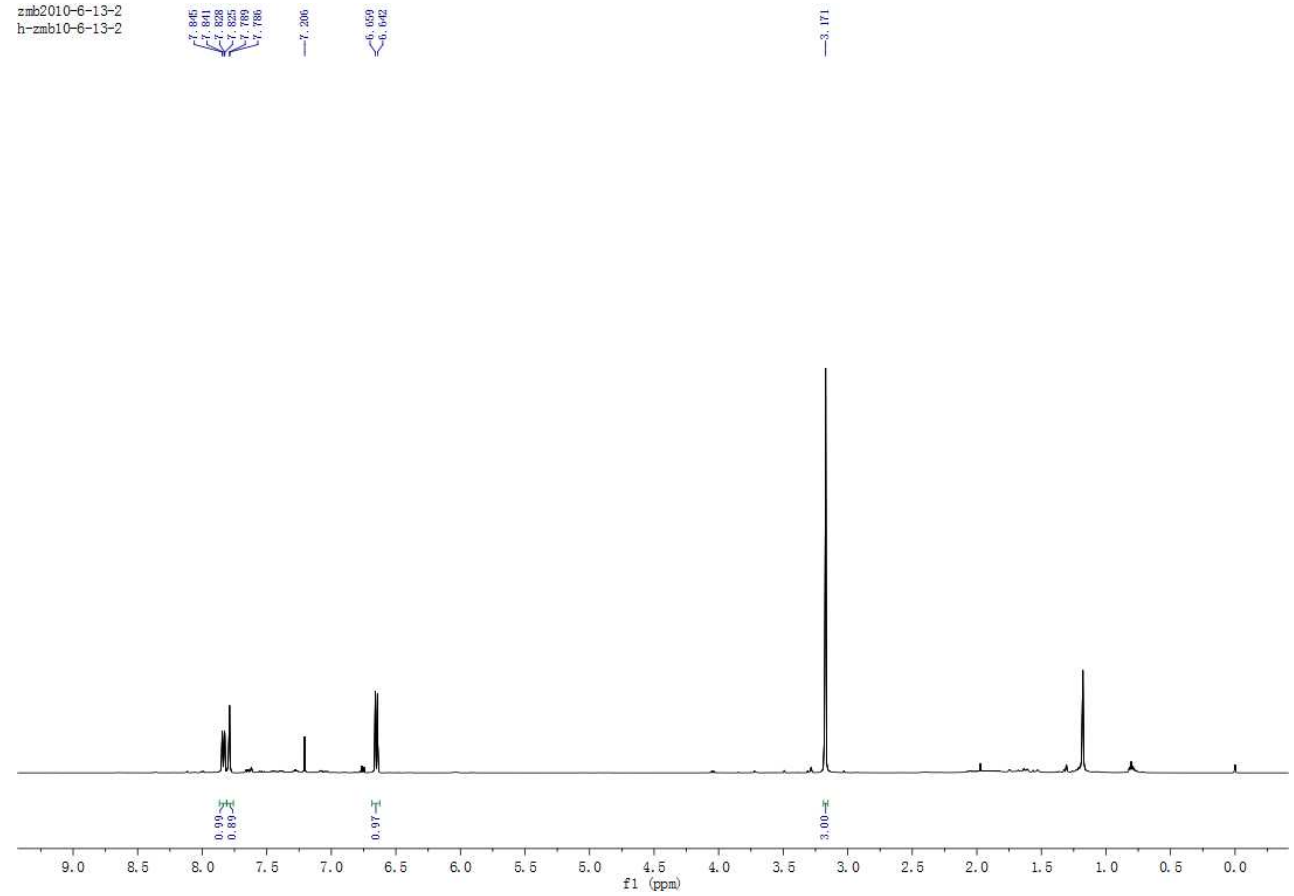
5-Chloro-1-methylindoline-2,3-dione (2q)

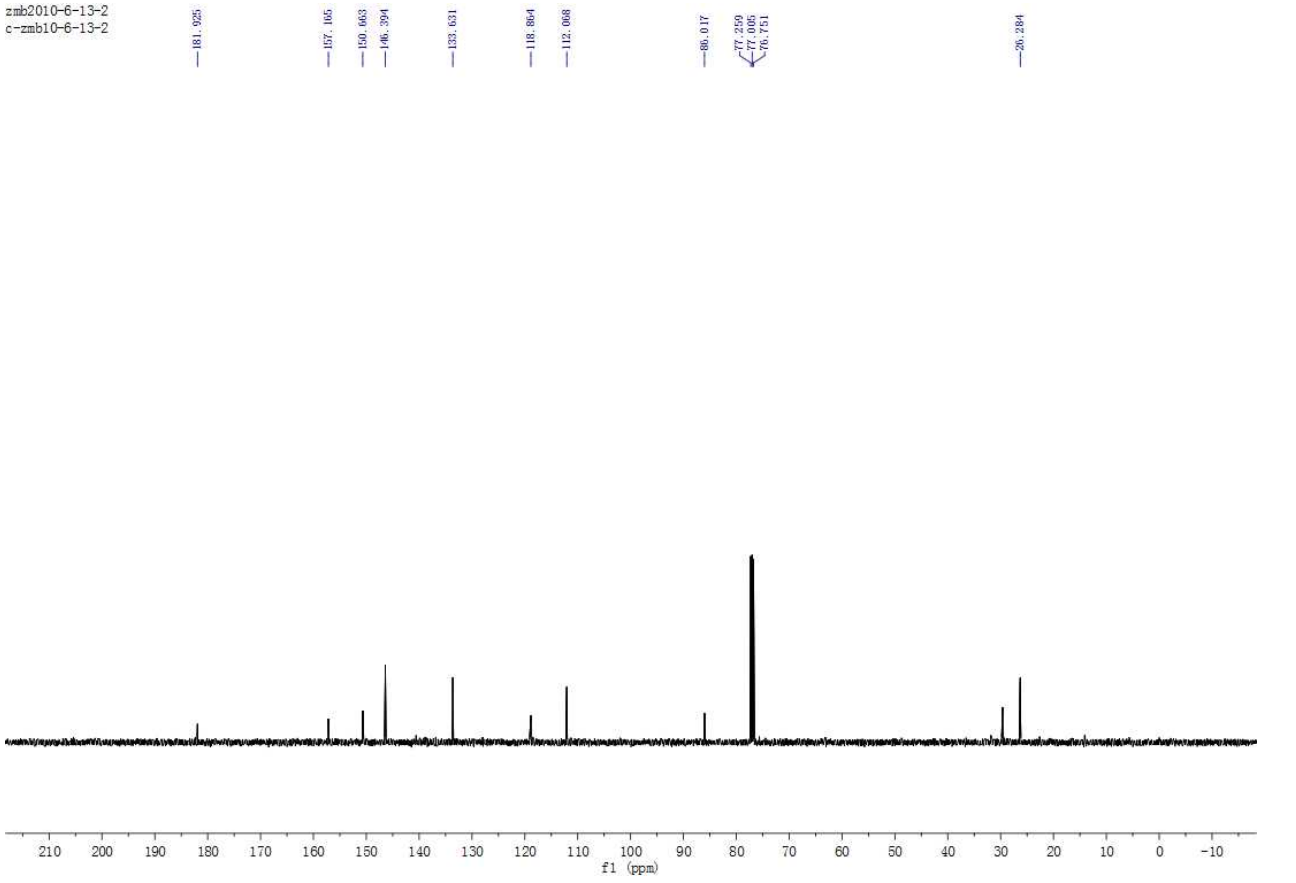


5-Bromo-1-methylindoline-2,3-dione (2r)

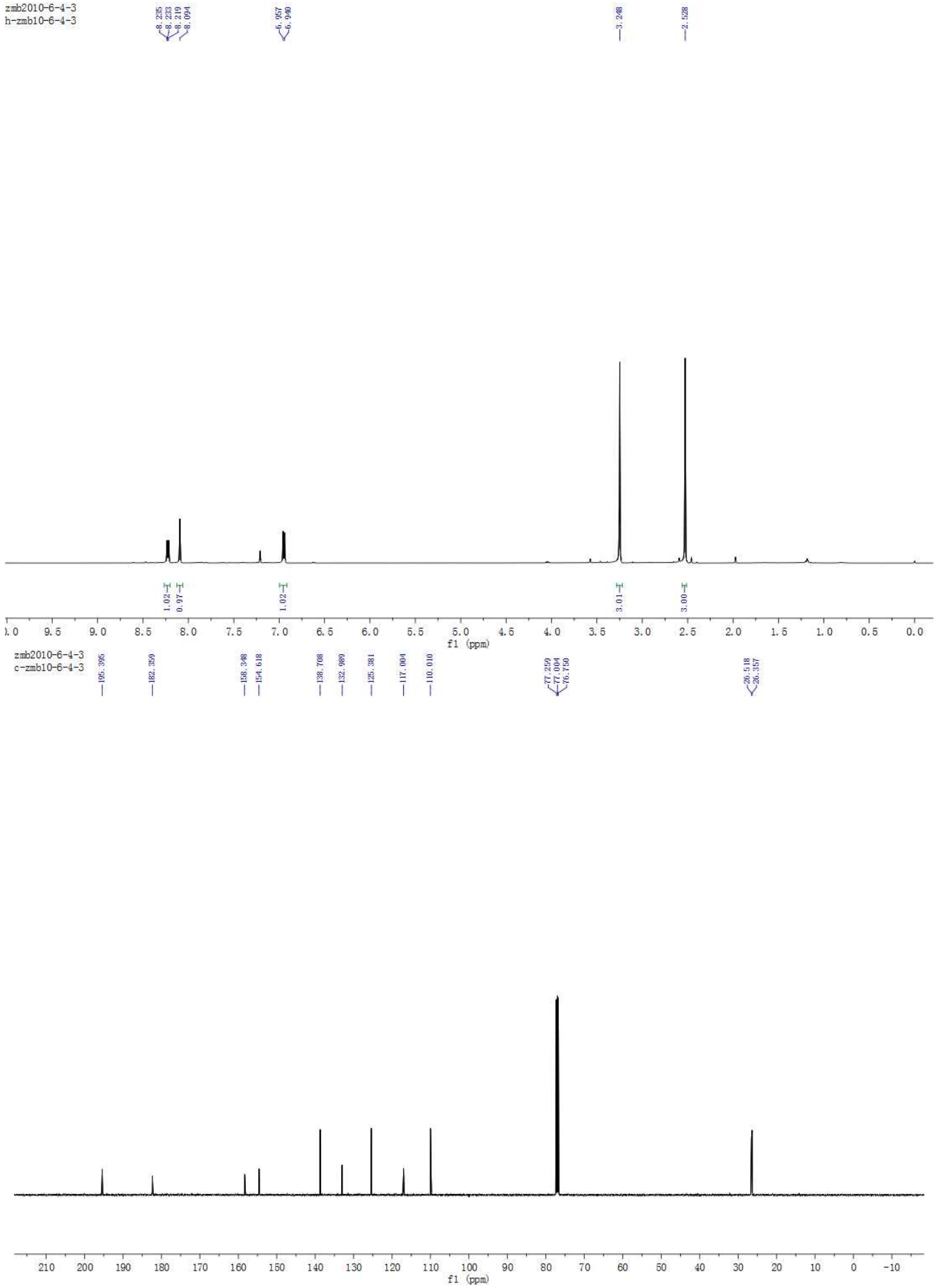


5-Iodo-1-methylindoline-2,3-dione (2s)

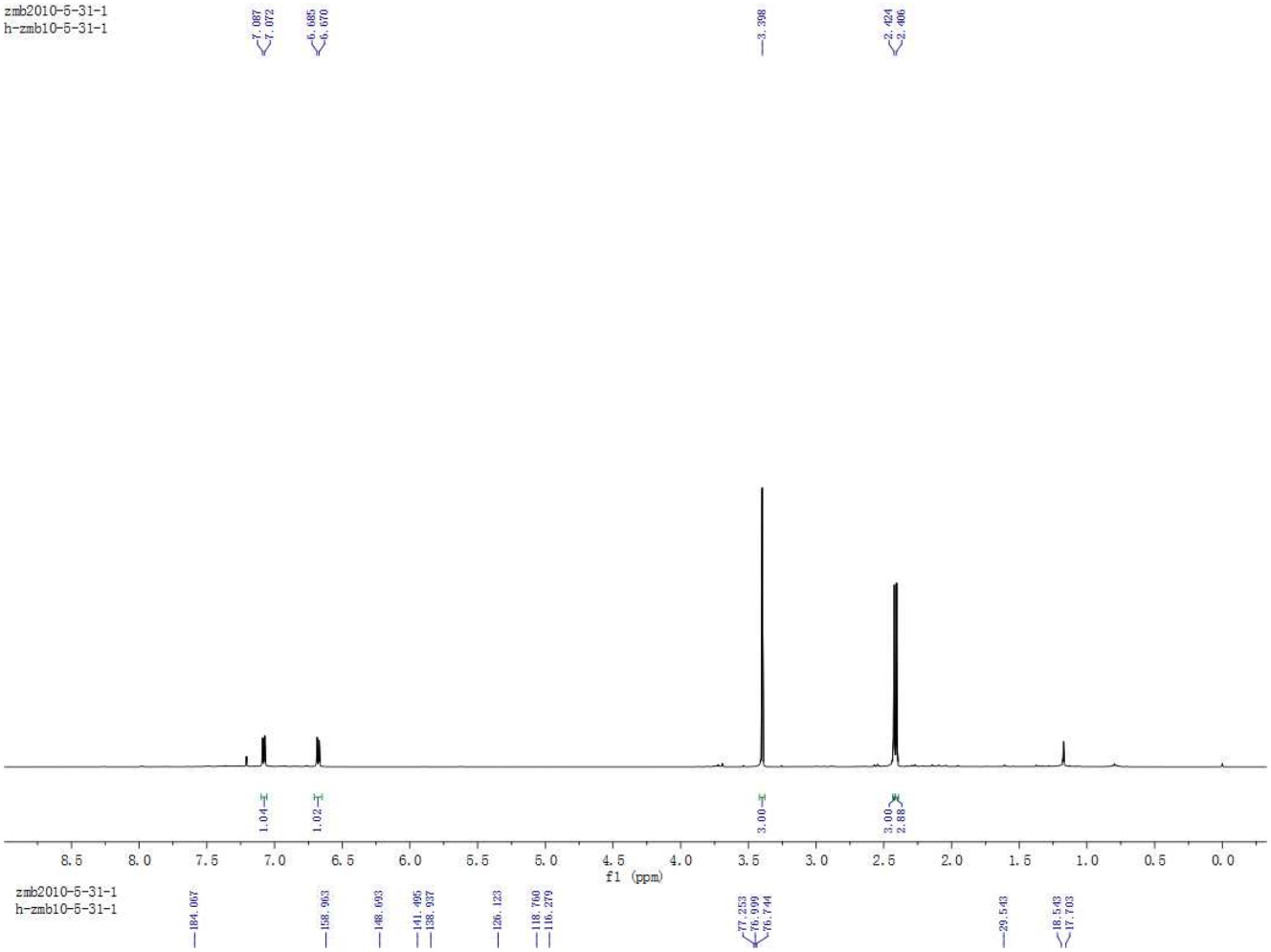




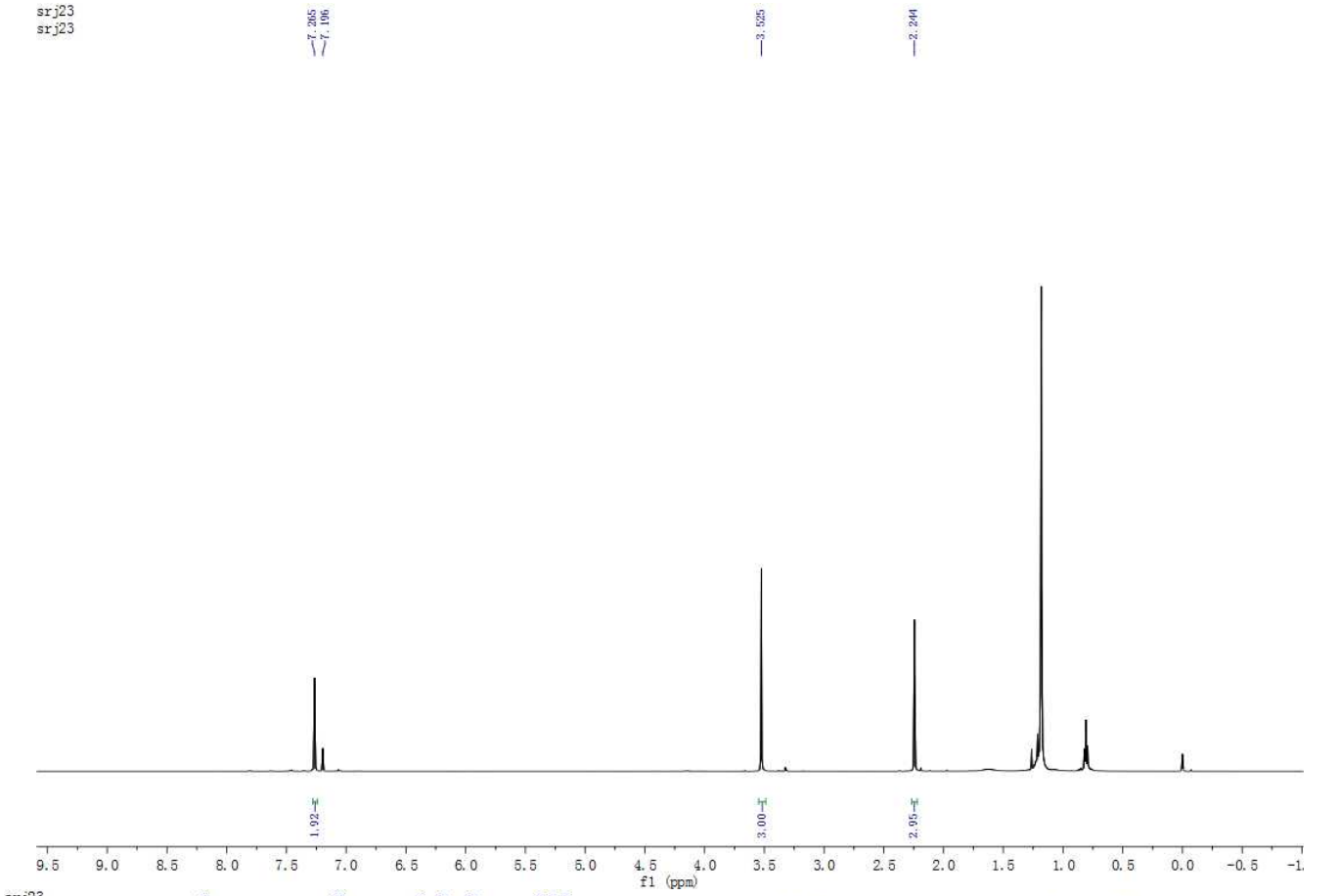
5-Acetyl-1-methylindoline-2,3-dione (2t)

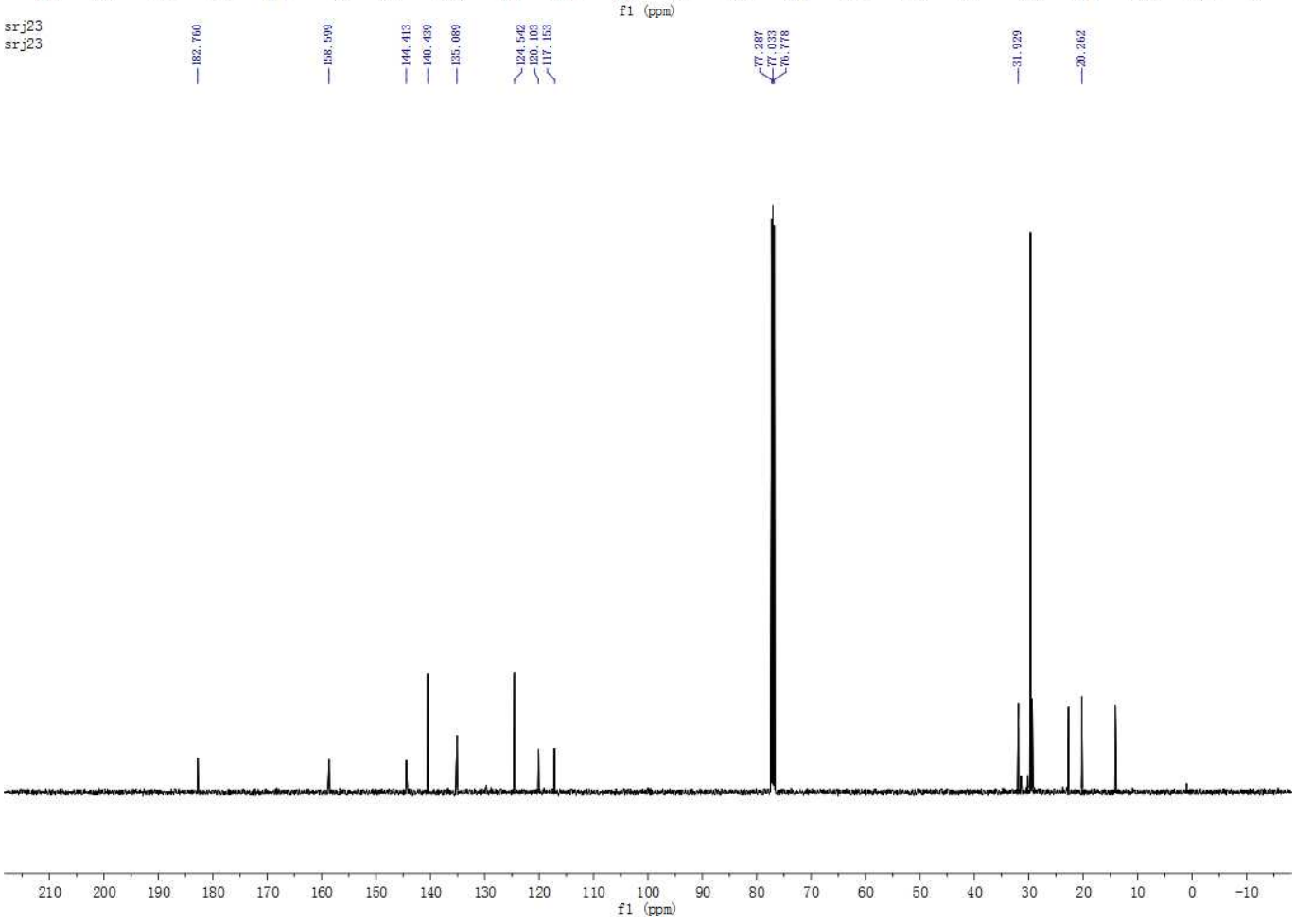


***N*,4,7-Trimethylindoline-2,3-dione (2u)**

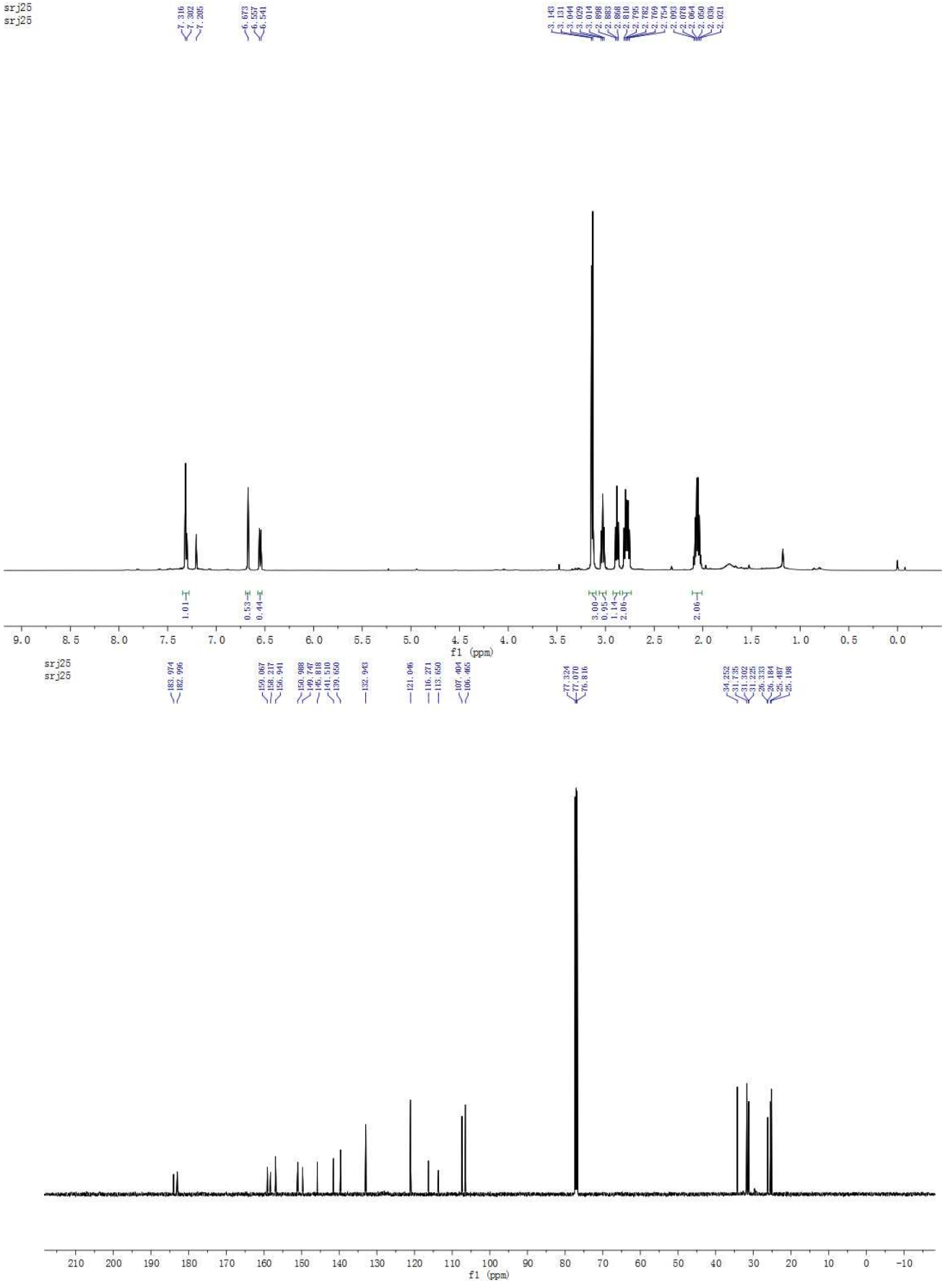


7-Chloro-1,5-dimethylindoline-2,3-dione (2v)

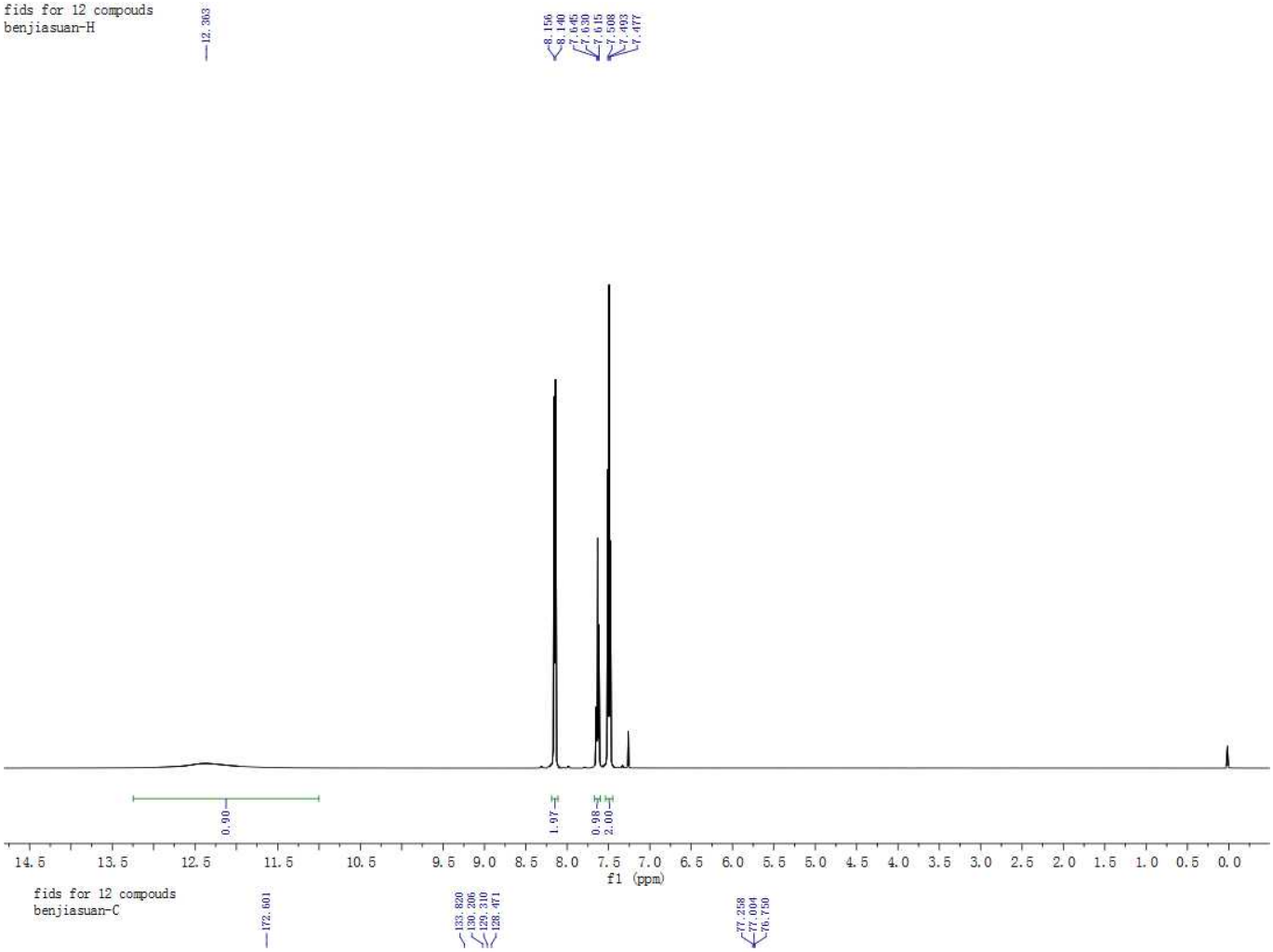

srj23
srj23
7.265
7.196
3.525
2.244
1.92
3.00
2.95
f1 (ppm)

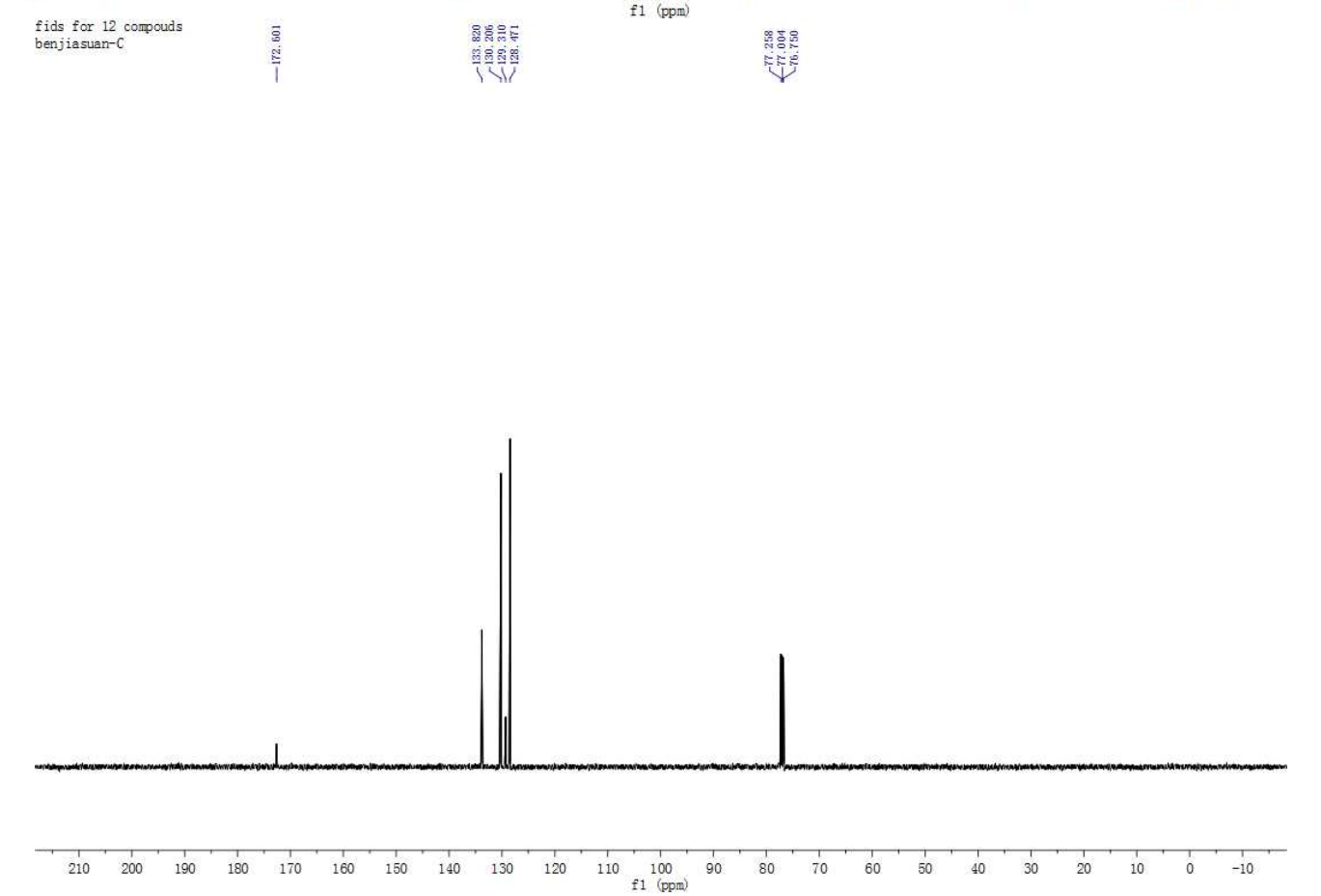

srj23
srj23
182.760
158.599
144.413
140.439
135.089
124.542
120.103
117.153
77.287
77.033
76.778
31.929
20.262
f1 (ppm)

1-Methyl-6,7-dihydrocyclopenta[f]indole-2,3(1*H*,5*H*)-dione (2w) and 3-Methyl-7,8-dihdrocyclopenta[e]indole-1,2(3*H*,6*H*)-dione (2w')

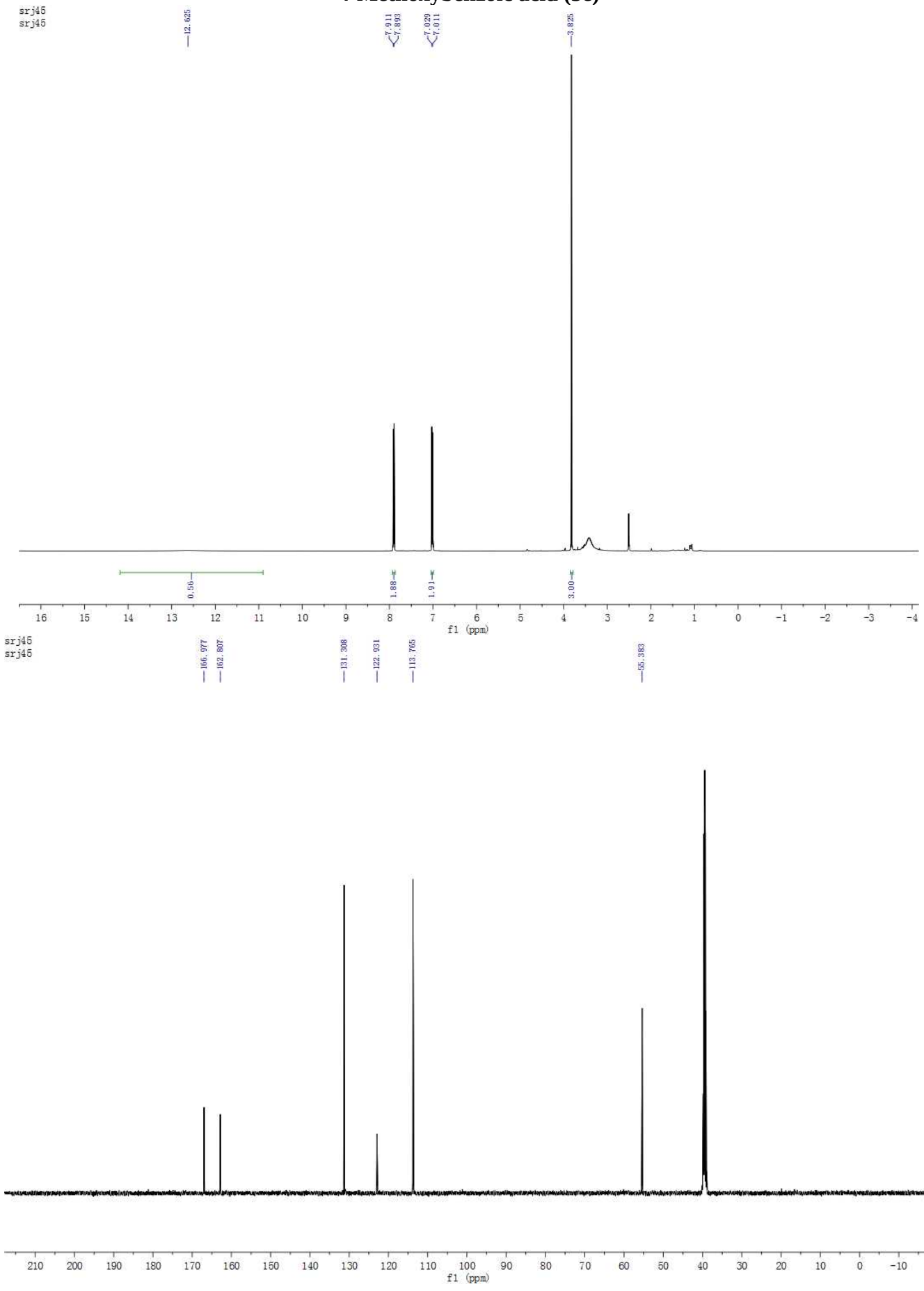


Benzoic acid (3a)

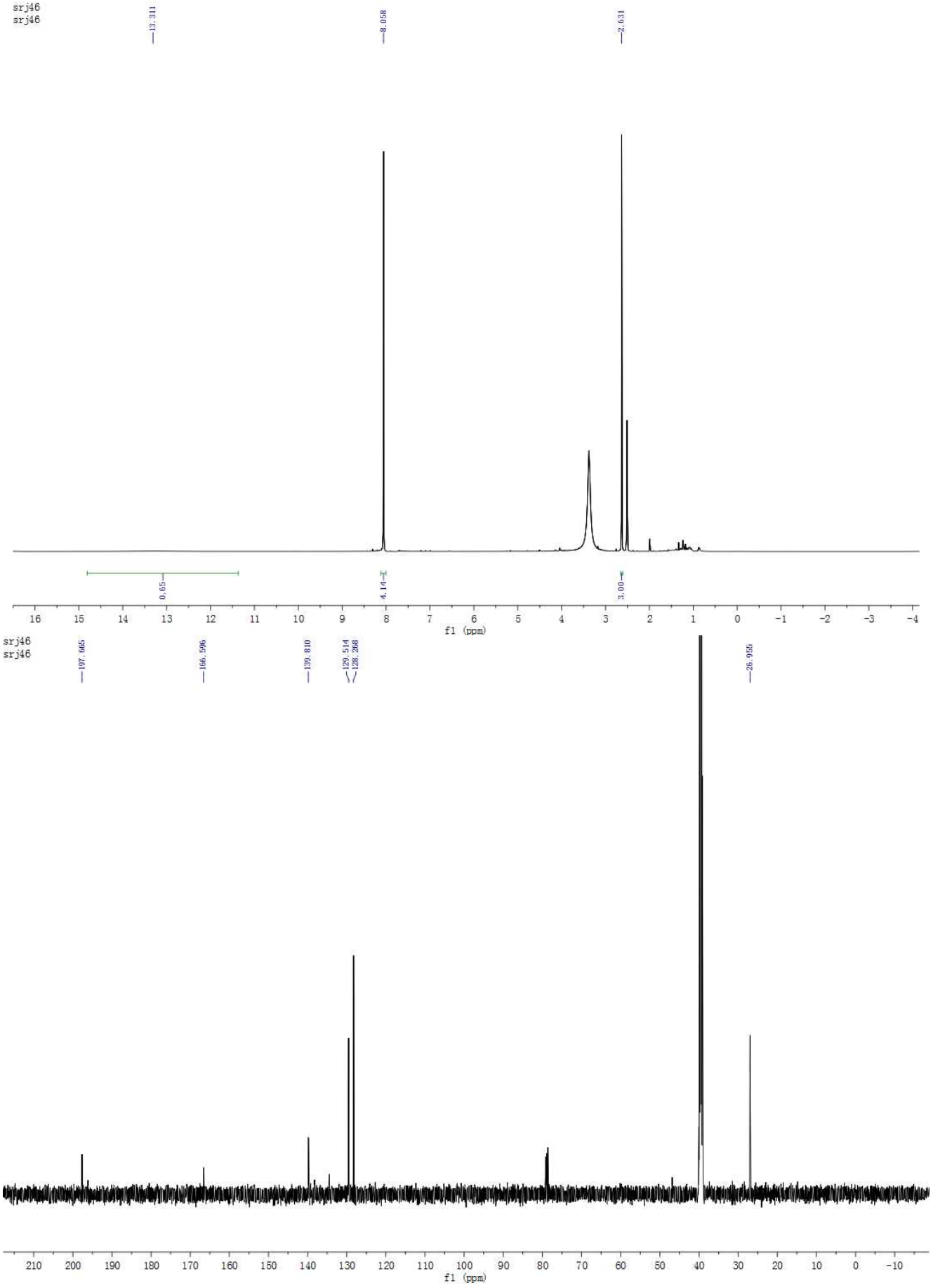




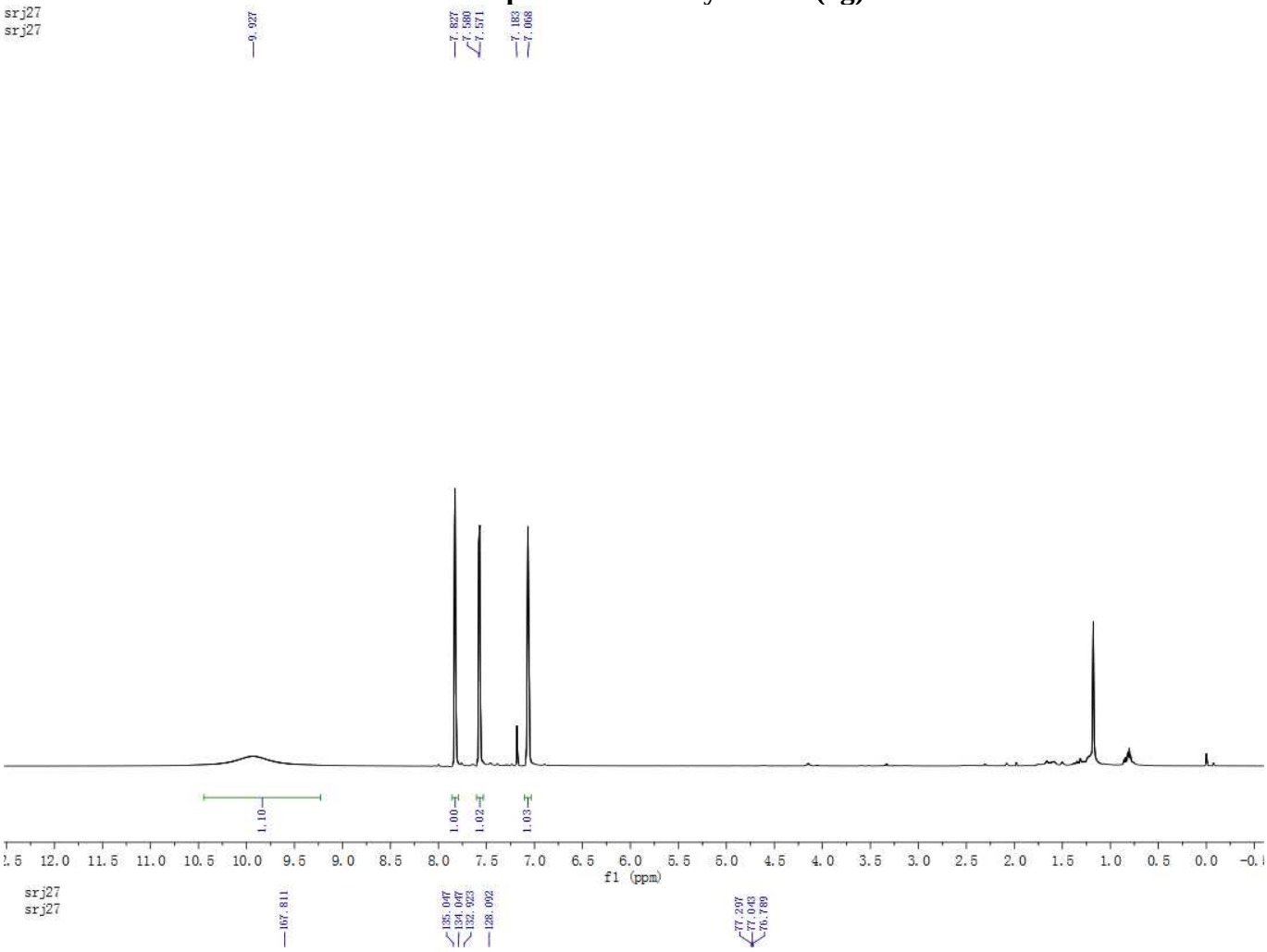
4-Methoxybenzoic acid (3e)

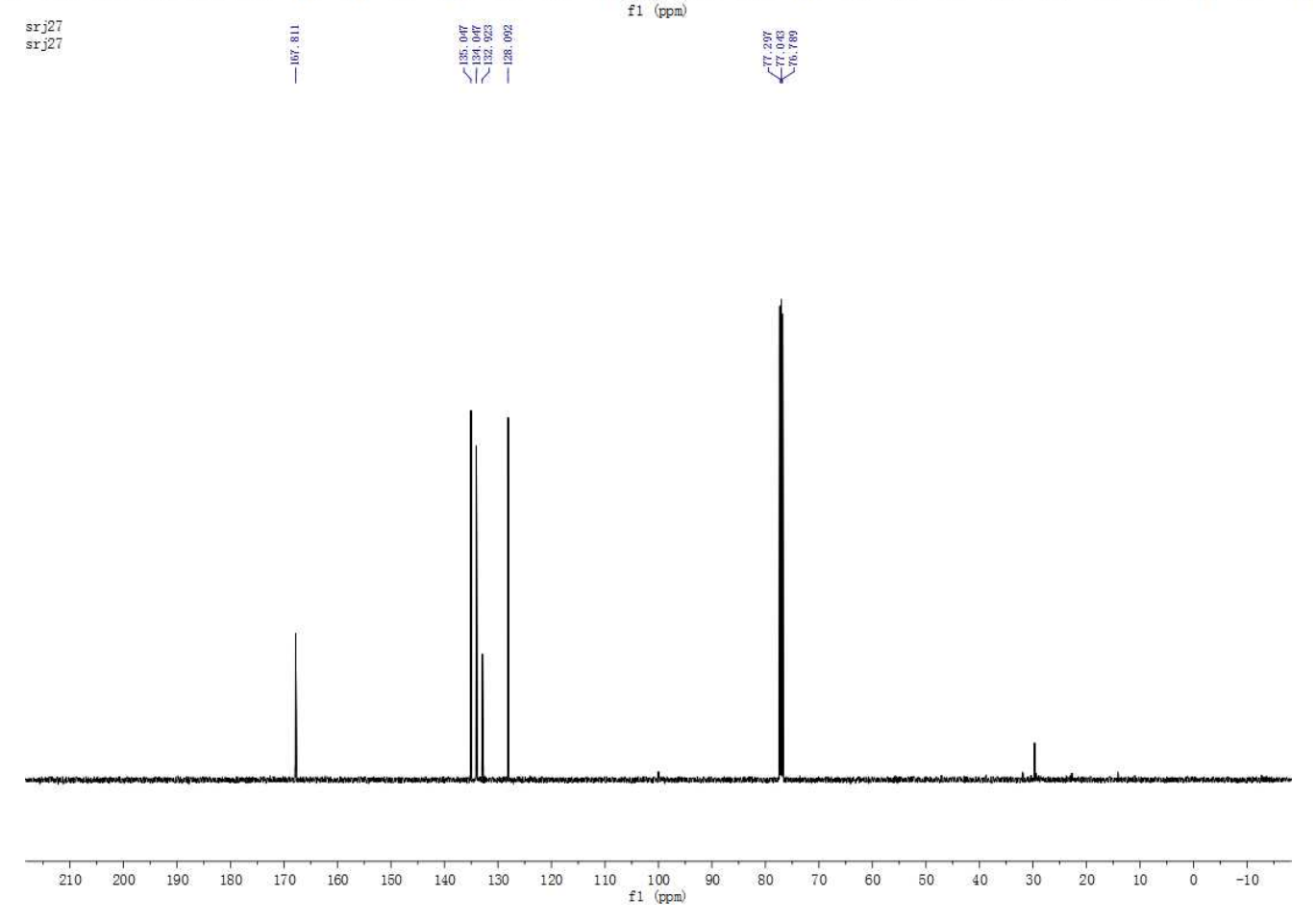


4-Acetylbenzoic acid (3f)



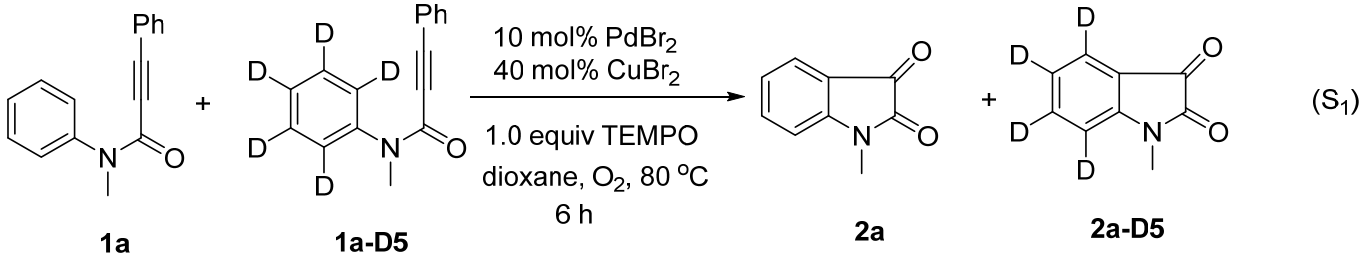
Thiophene-2-carboxylic acid (3g)





(D) The Kinetic Isotope Experiments

To elucidate the mechanism, the kinetic isotope effect of this reaction was examined. It was found that the intermolecular K_H/K_D value of competitive experiment of **1a** and **1a-D$_5$** was 1 (Figure S1). The results showed that the C-H functionalization is not the rate-determining step.[1b] Subsequently, the reaction of **1a-D$_1$** was also conducted, and it provided an intramolecular isotope effect of 1.9 (Figure S2). The results indicated that the mechanism of C-H activation was not compatible with the S_EAr mechanism ((a) Hennessy, E. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 12084. (b) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581.).



(S$_1$)

A mixture of aniline **1a** (0.1 mmol), **1-D5** (0.1 mmol), $PdBr_2$ (10 mol%) $CuBr_2$ (40 mol%) and TEMPO (1.0 equiv) in H_2O/dioxane(v/v = 1/4, 3 mL) with O_2 (1 atm) was stirred at 80 ^oC for about 6 h. After the reaction was cooled, the mixture was poured into ethyl acetate, which was washed with brine. The aqueous layer was extracted with ethyl acetate and the combined organic layers was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude material was determined by GC-MS analysis and ^1H NMR (500 MHZ) (Figure S1).

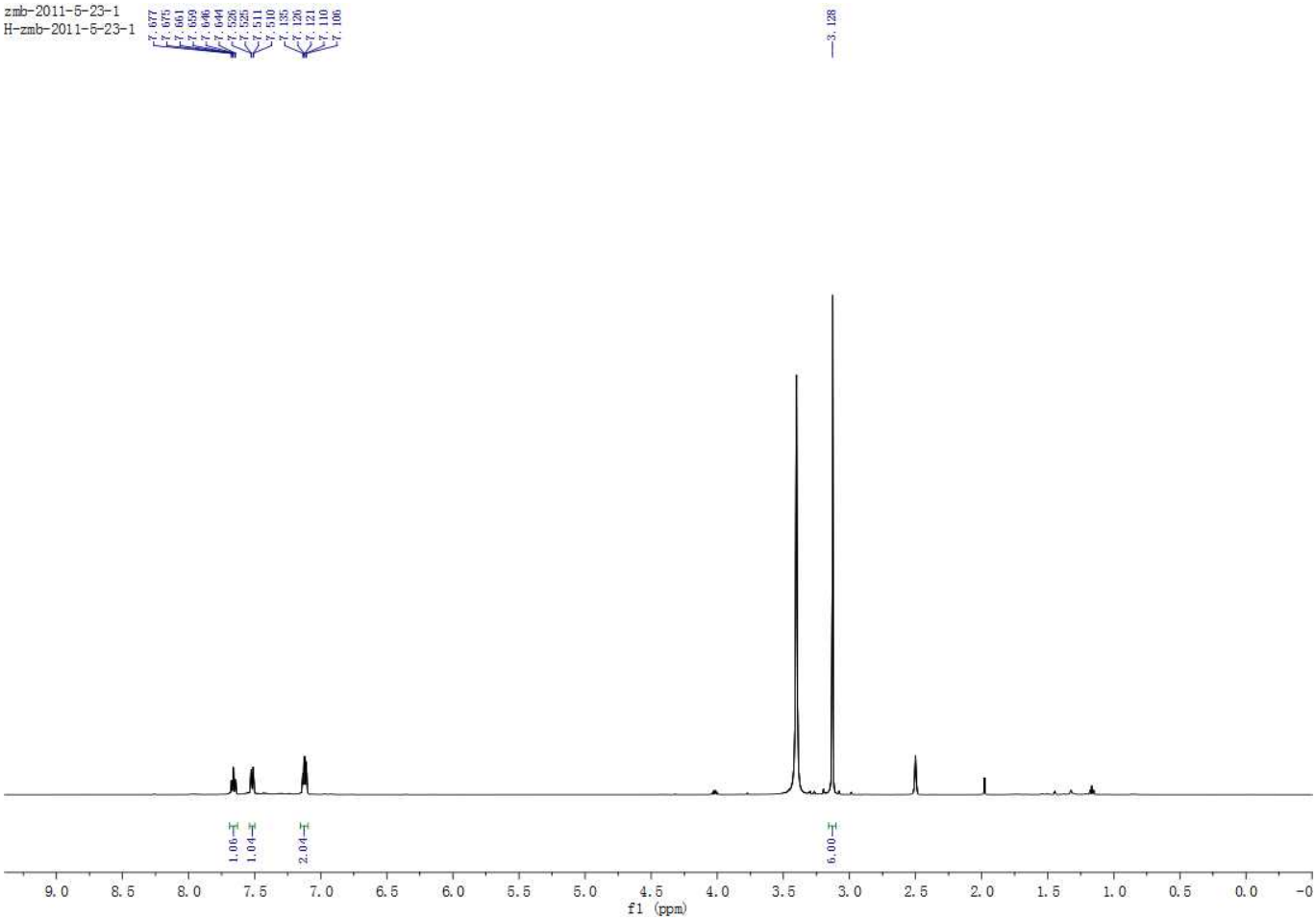
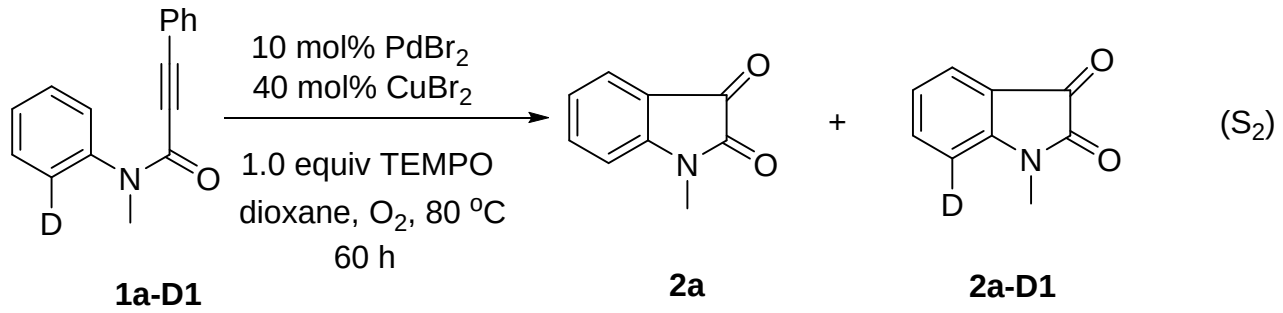


Figure S1. The intermolecular competition experiment between amides **1a** and **1a-D5**.



1a-D1 **2a** **2a-D1**

A mixture of aniline **1a-D1** (0.2 mmol), $PdBr_2$ (10 mol%) $CuBr_2$ (40 mol%) and TEMPO (1.0 equiv) in H_2O/dioxane(v/v = 1/4, 3 mL) with O_2 (1 atm) was stirred at 80 ^oC for about 60 h as monitored by TLC. After the reaction was finished, the mixture was poured into ethyl acetate, which was washed with brine. The aqueous layer was extracted with ethyl acetate and the combined organic layers was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product (Figure S2).

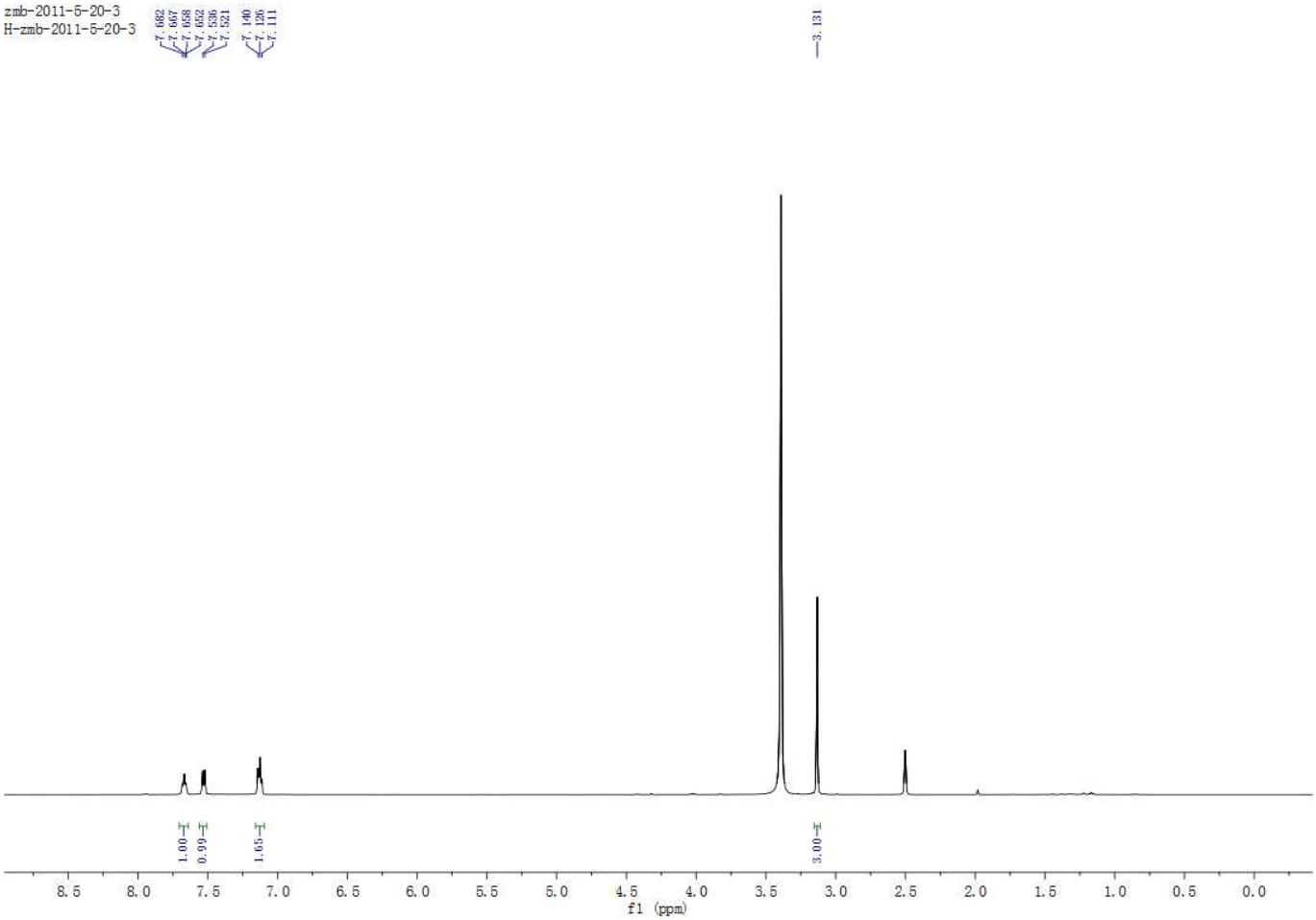
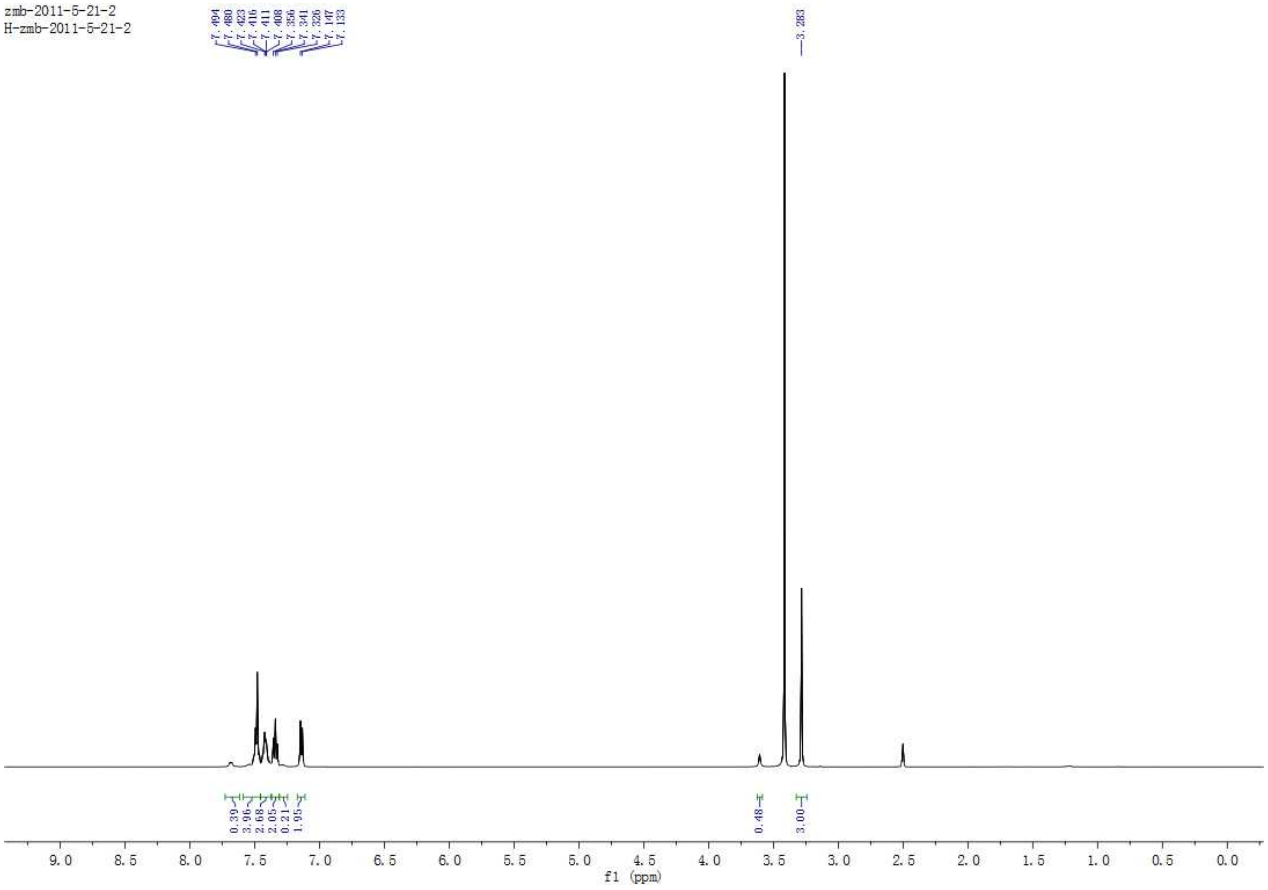


Figure S2. The intramolecular competition experiment of **1a-D1**.

1a-D1



1a-D5