Recyclable Dirhodium(II) Catalyst $Rh_2(esp)_2$ for the Allylic Oxidation of Δ^5-Steroids

Yi Wang,[†] Yi Kuang,[†] Hongyang Zhang,[†] Ruocheng Ma,[‡] and Yuanhua Wang*[,†]

[†]College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China

[‡]Jiaxiang Foreign Languages School Attached To Chengdu No.7 Middle School, Chengdu, 610023, P.R.China

E-mail: yhwang@scu.edu.cn

Supporting Information

1. The Pictures of the Oxidation Reaction of Dehydroepiandrosterone acetate 1a Catalyzed by $Rh_2(esp)_2$ (*gram scale*)

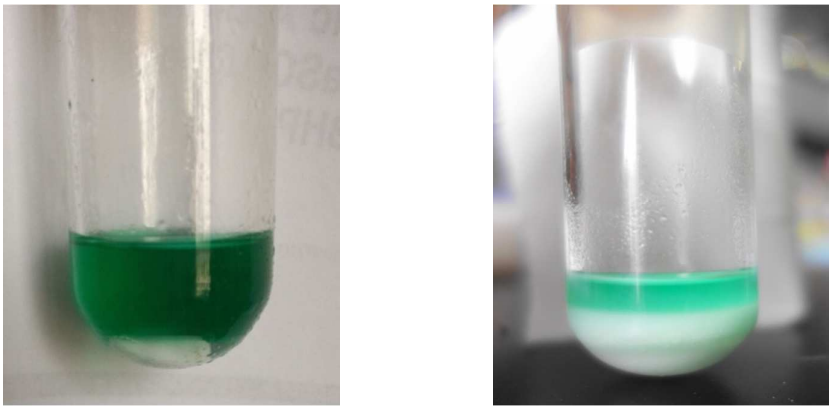


Figure S1 Homogenous reaction mixture when the reaction start (left) and the product **2a** was precipitated when the reaction was finished (right).

2. Catalyst Recycling Experiments.

After the EtOAc was removed 24 mg of $Rh_2(esp)_2$ (96% recovery rate) was obtained. Catalyst recovered from the first reaction was directly added to a 2 mL of **1a** (1.1 g, 3.3 mmol) in 2 mL heptane and 5 equiv T-HYDRO in order to initiate the second oxidation. After this second reaction, the solution was cooled to 0^oC, **2a** precipitated (78% yield) and 22 mg of $Rh_2(esp)_2$ complex (93% recovery rate) was recovered. This catalyst was cycled twice more according to the procedure of cycle 2. The stable $Rh_2(esp)_2$ catalytst system was found to maintain high activity and produce high yields after 5 cycles.

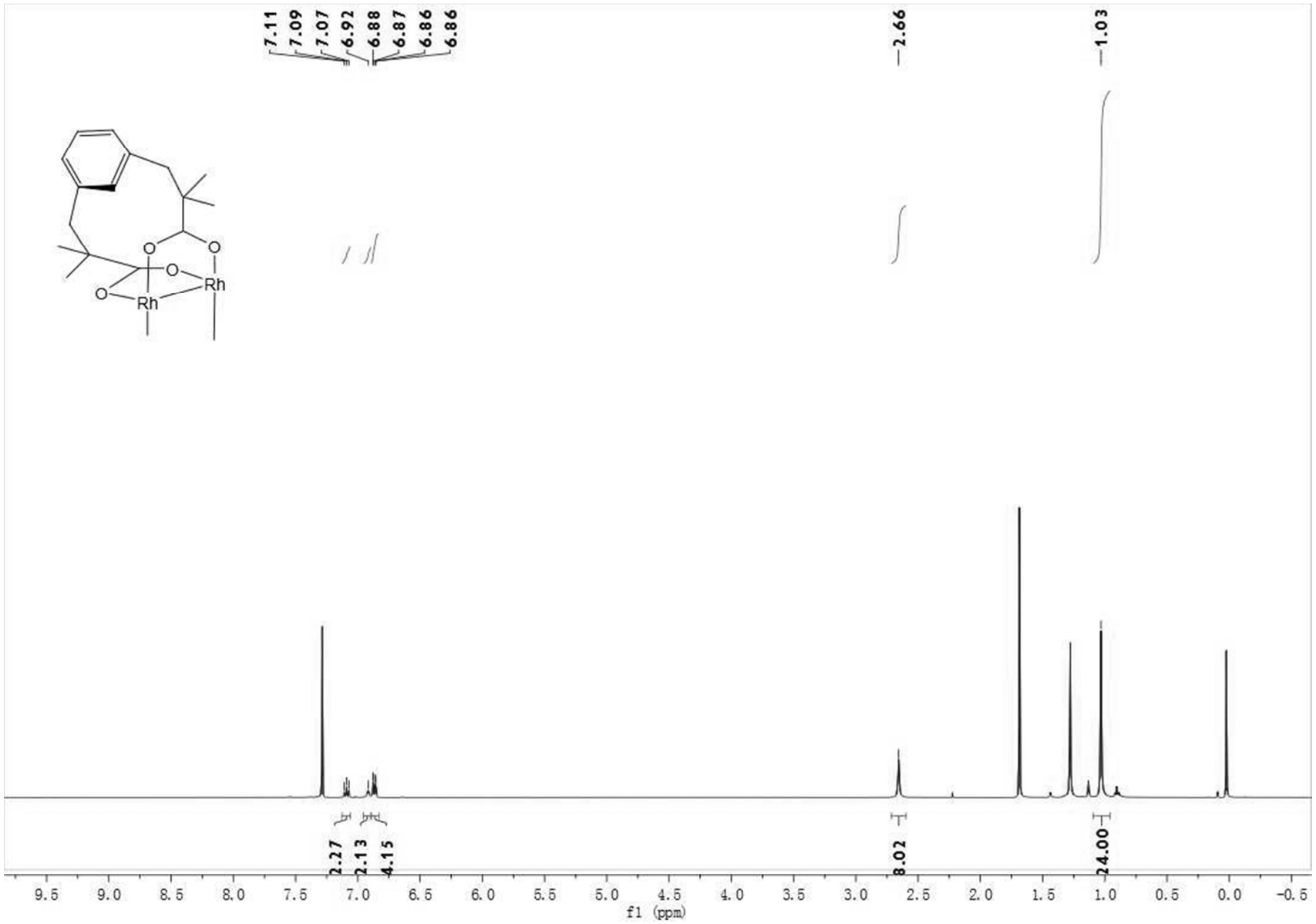
Table S1. Catalyst Recycling Experiments[a]

cycle	Precipitated yield (%)	$Rh_2(esp)_2$ recovery rate (%)
1	76	96
2	77	93
3	74	90
4	75	88
5	72	82

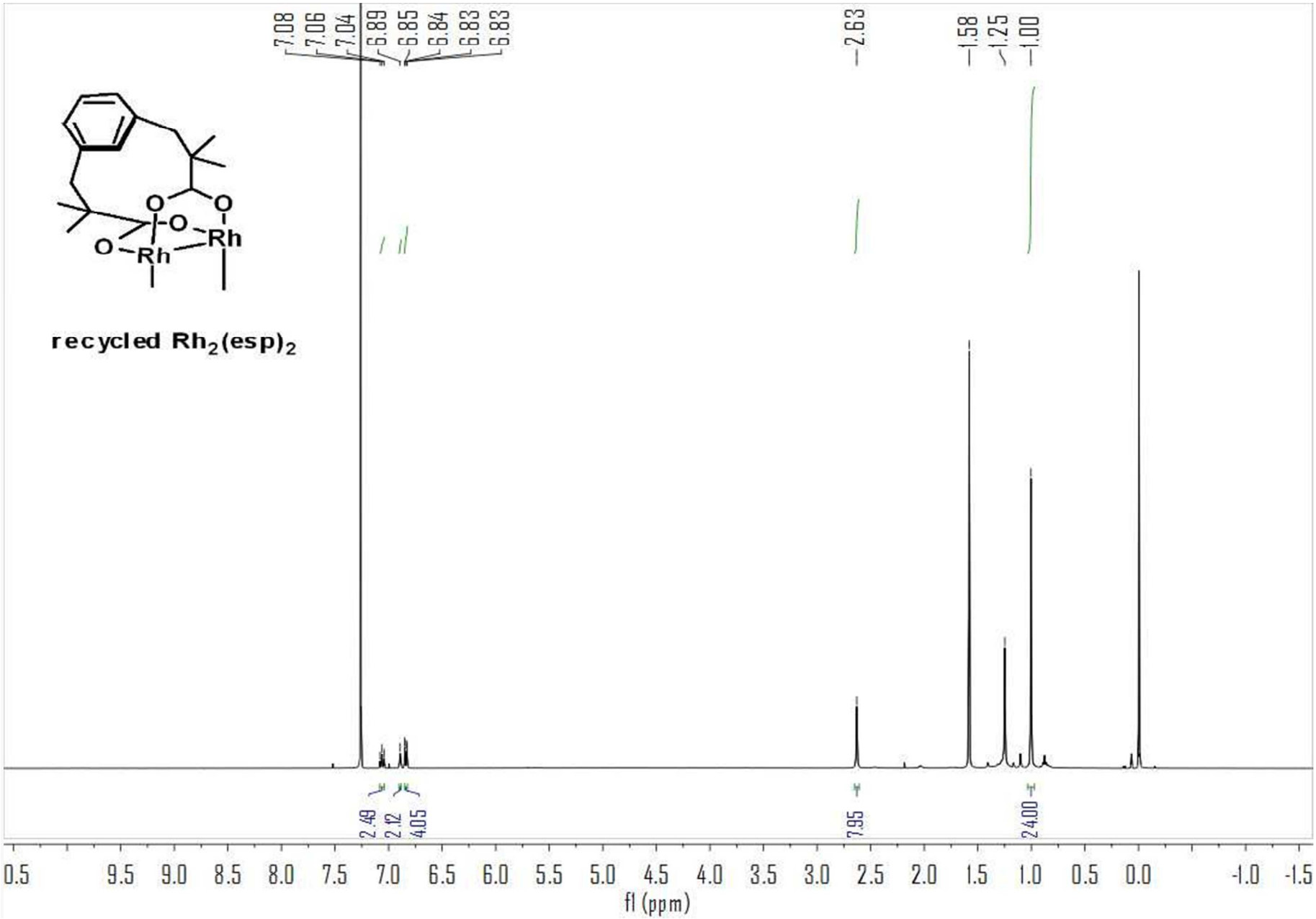
[a]All reactions were performed with **1a** (0.4 mmol), T-HYDRO (2 mmol), n-heptane (0.5 mL), $Rh_2(esp)_2$ (1.0 mol%).

3 ^{1}H and ^{13}C NMR Spectrum of Compounds

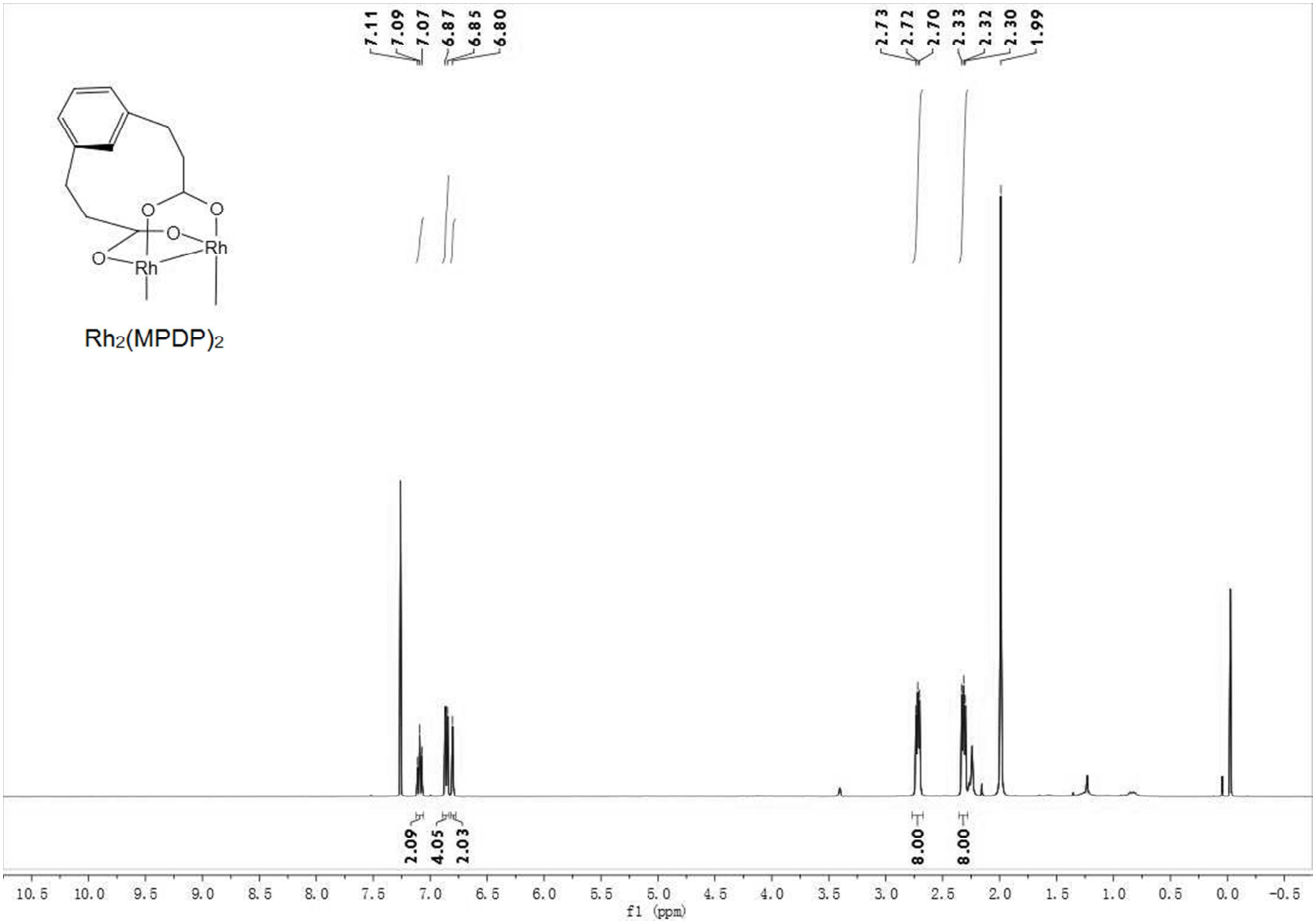
^{1}H NMR of $Rh_2(esp)_2$



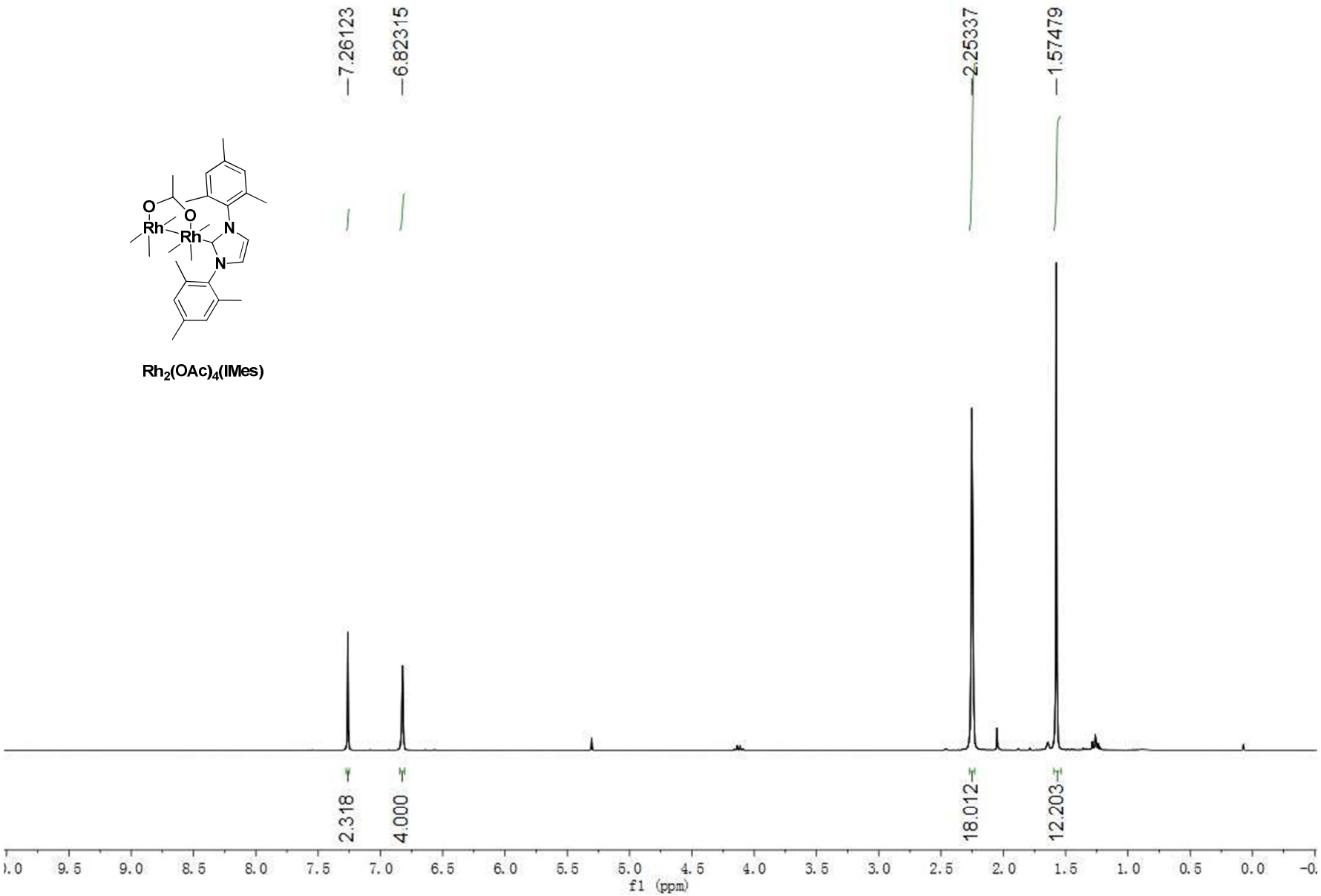
^{1}H NMR of $Rh_2(esp)_2$ recovered by Merrifield-pyridine resin.



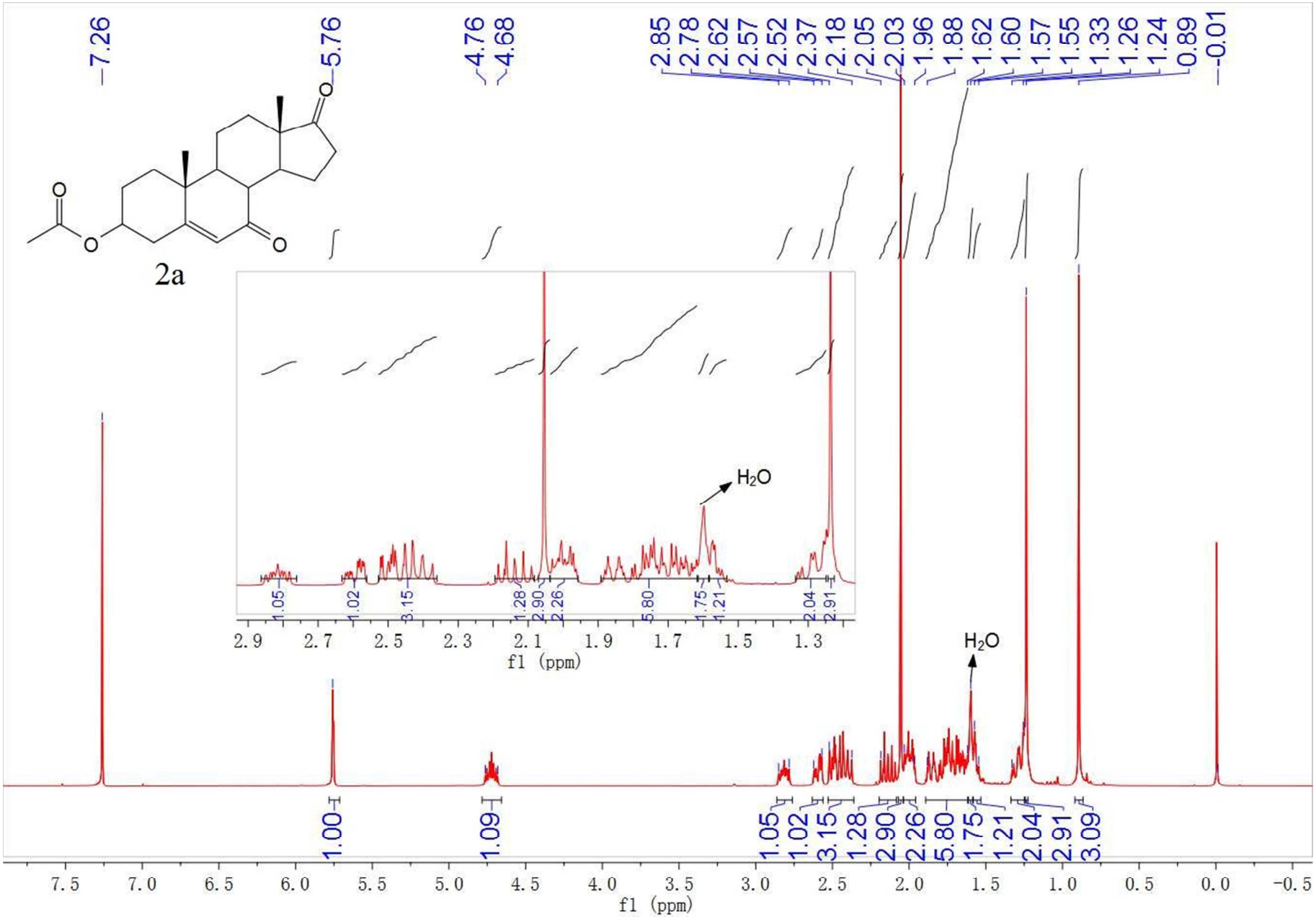
^{1}H NMR of $Rh_2(MPDP)_2$

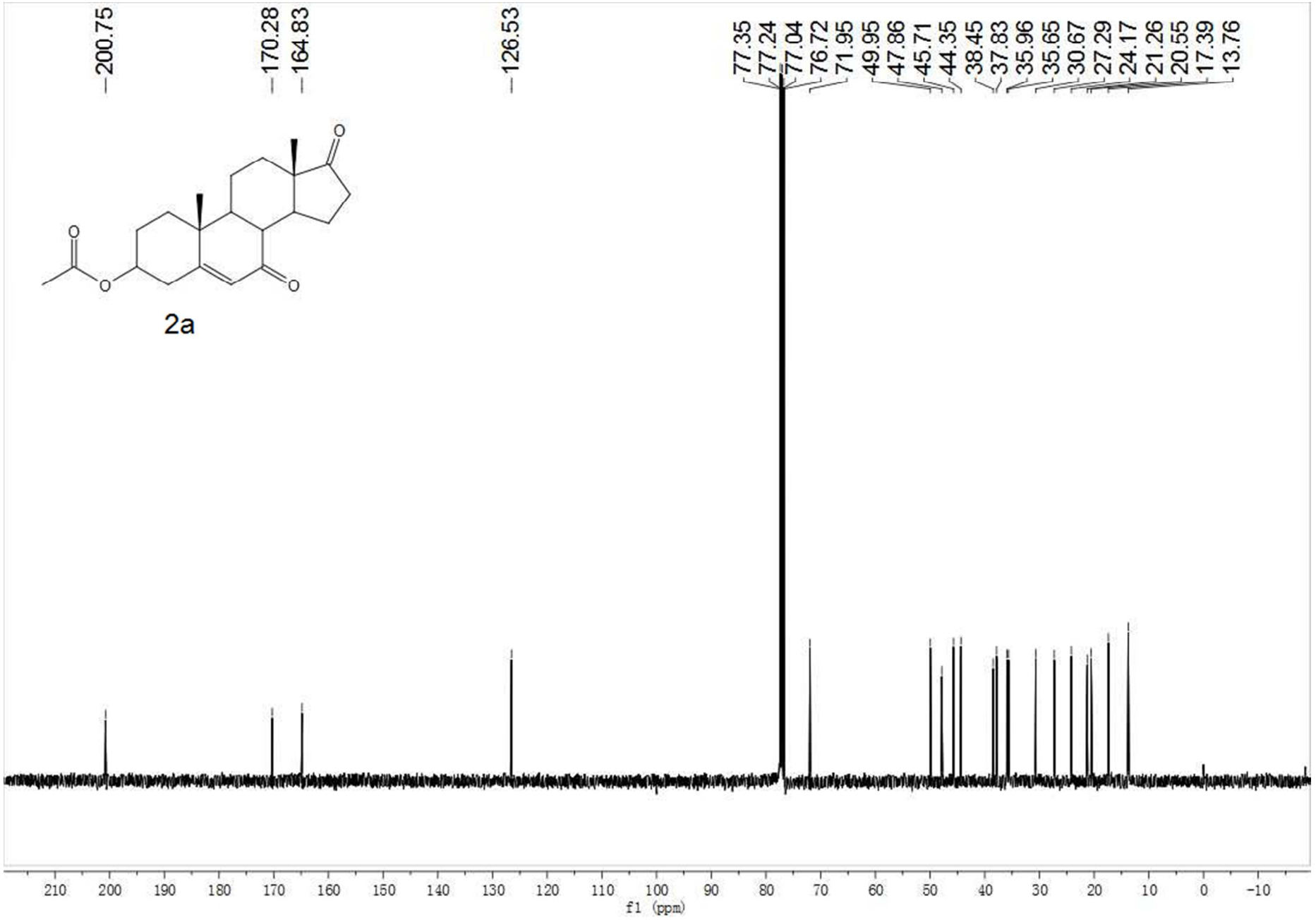


^{1}H NMR of $Rh_2(OAc)_4(IMes)$

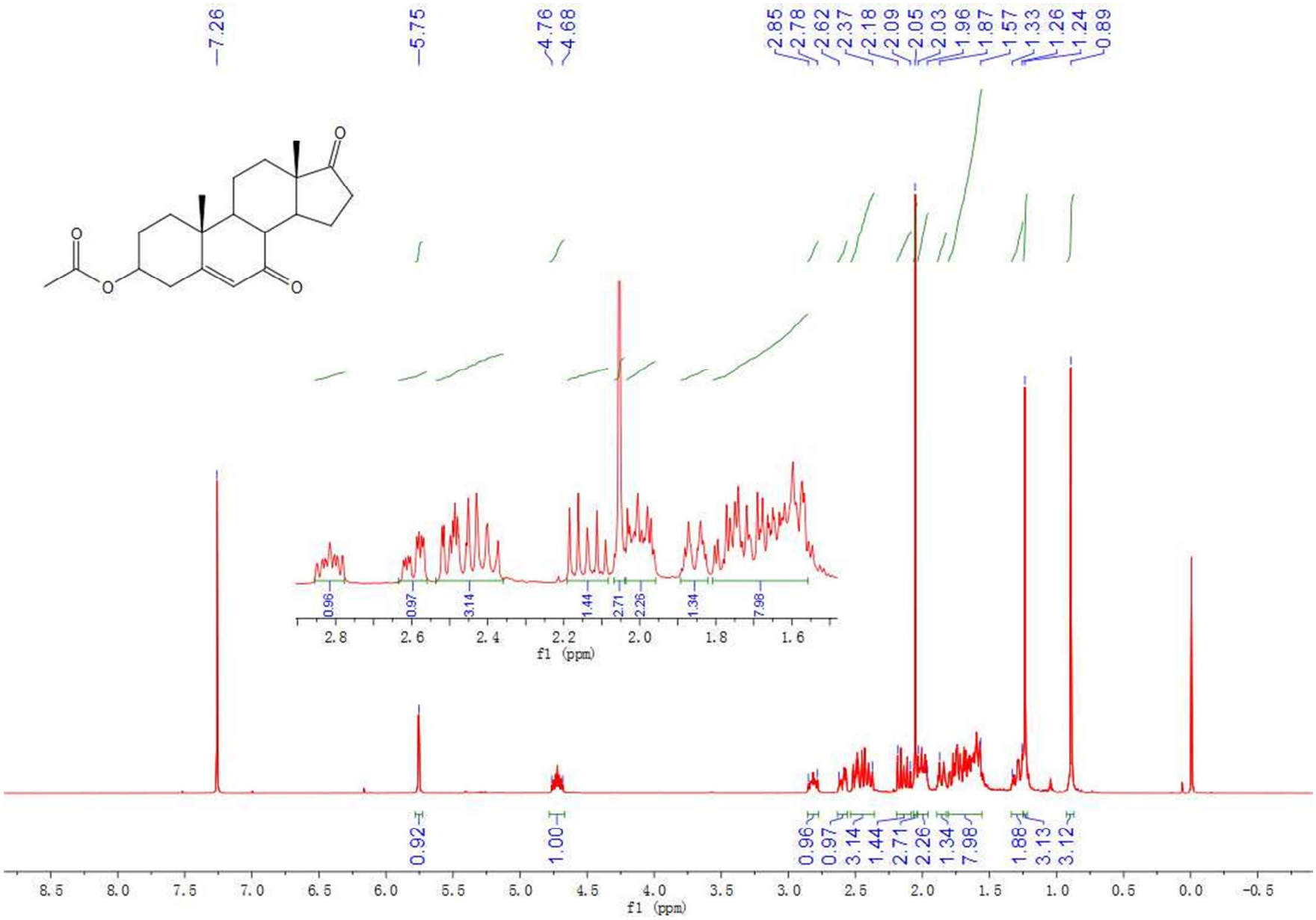


^{1}H NMR and ^{13}C NMR of **2a** which was purified by column.

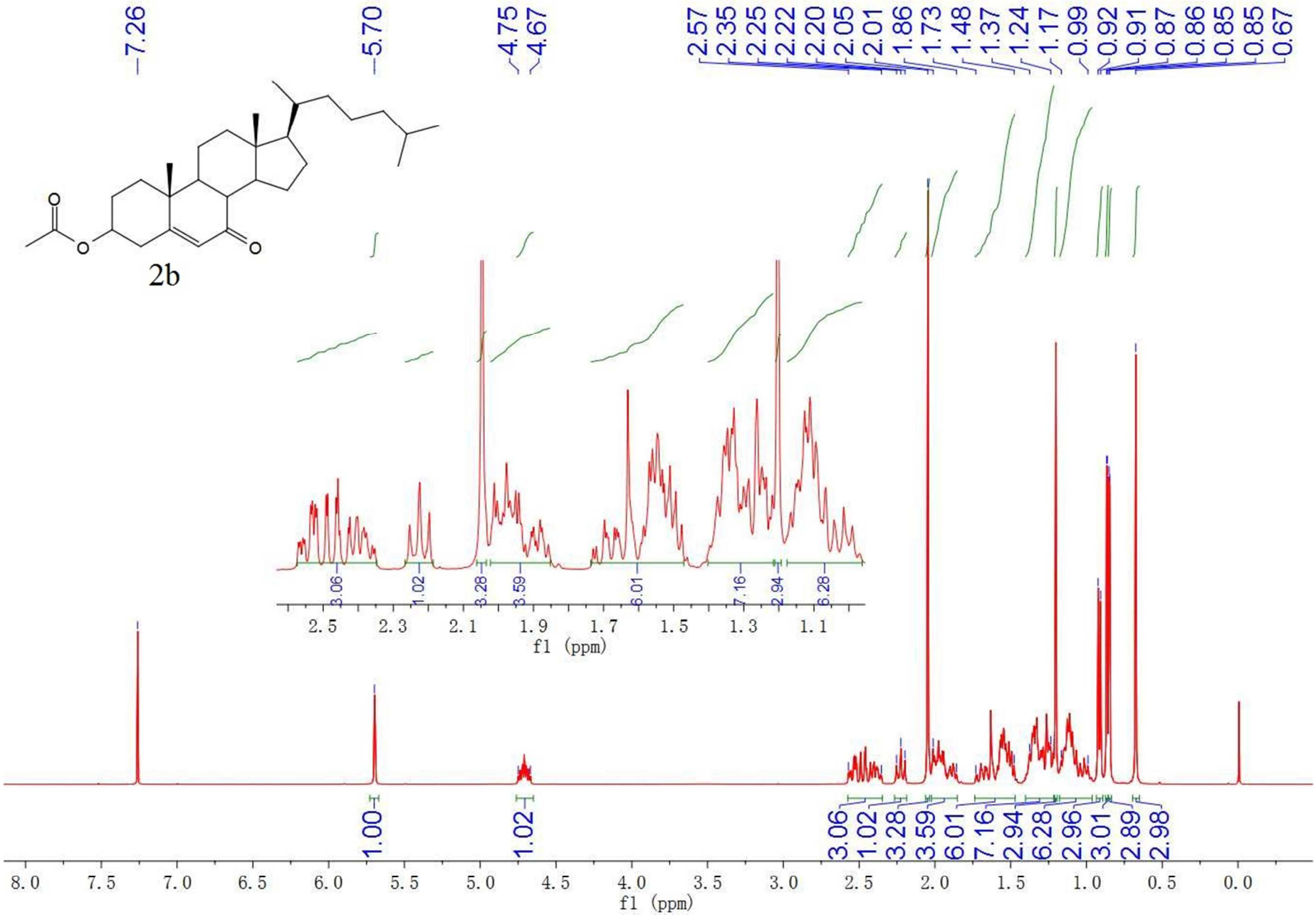


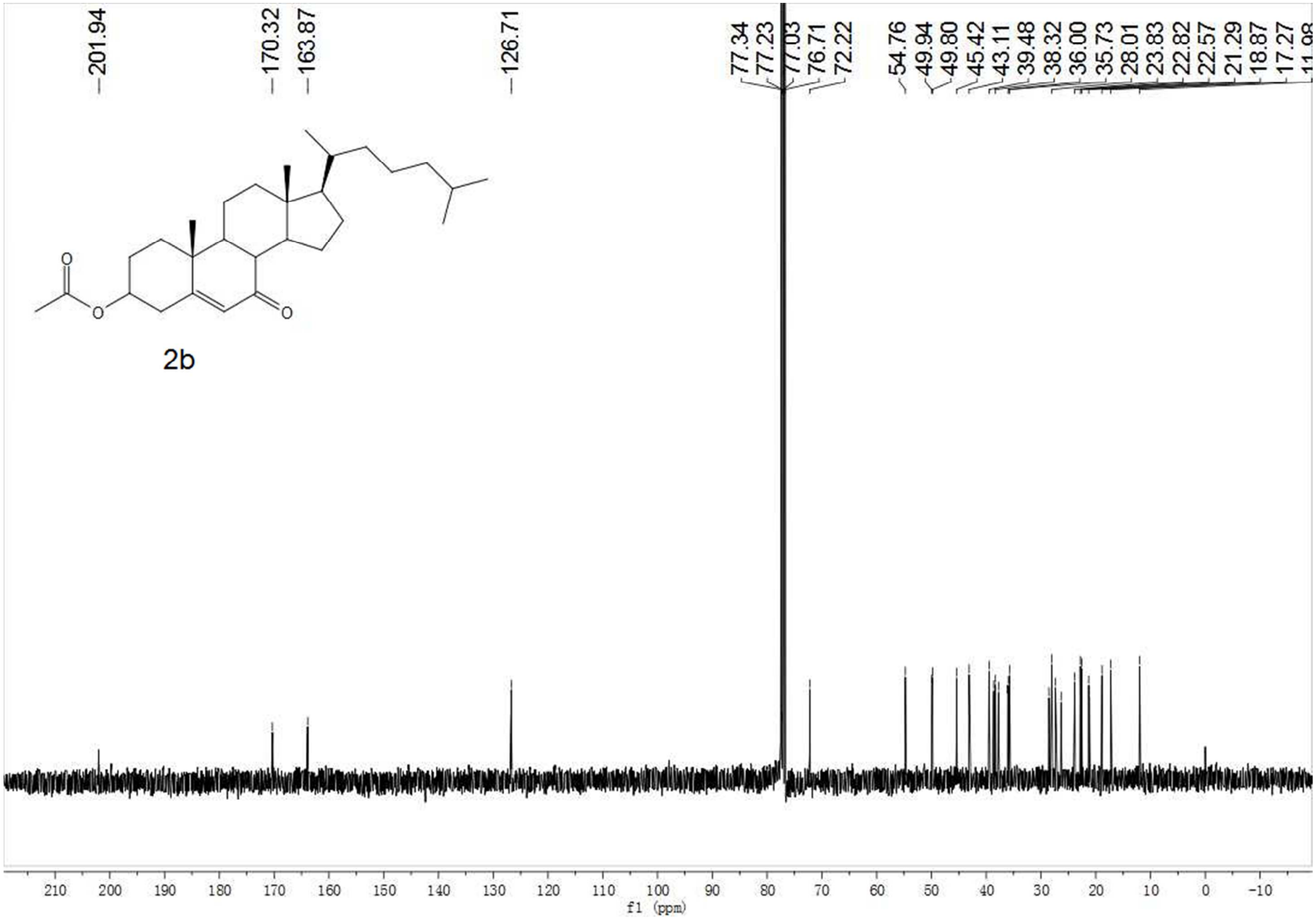

200.75
170.28
164.83
126.53
77.35
77.24
77.04
76.72
71.95
49.95
47.86
45.71
44.35
38.45
37.83
35.96
35.65
30.67
27.29
24.17
21.26
20.55
17.39
13.76
2a
f1 (ppm)

^{1}H NMR of **2a** which was directly precipitated from the reaction mixture.

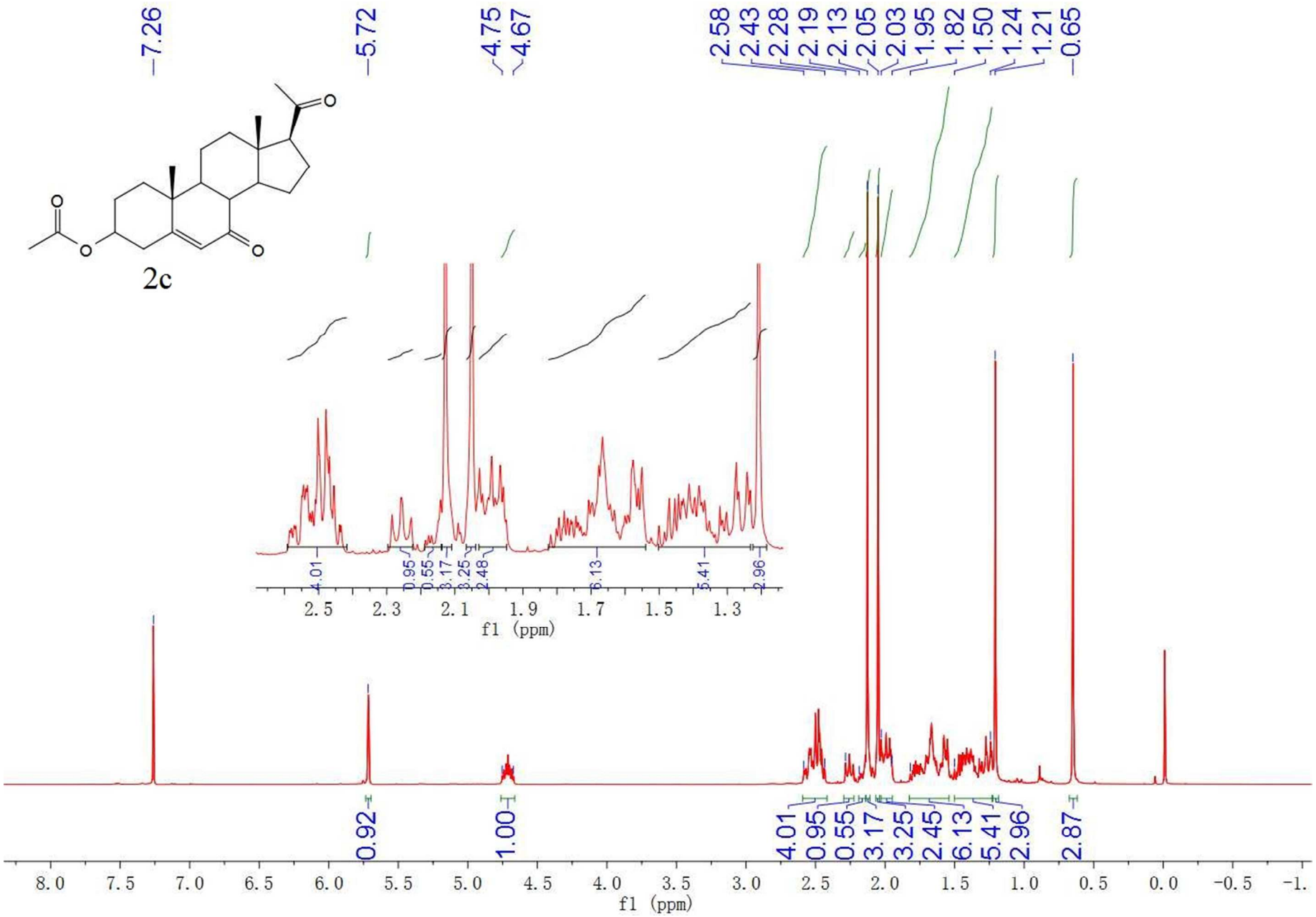


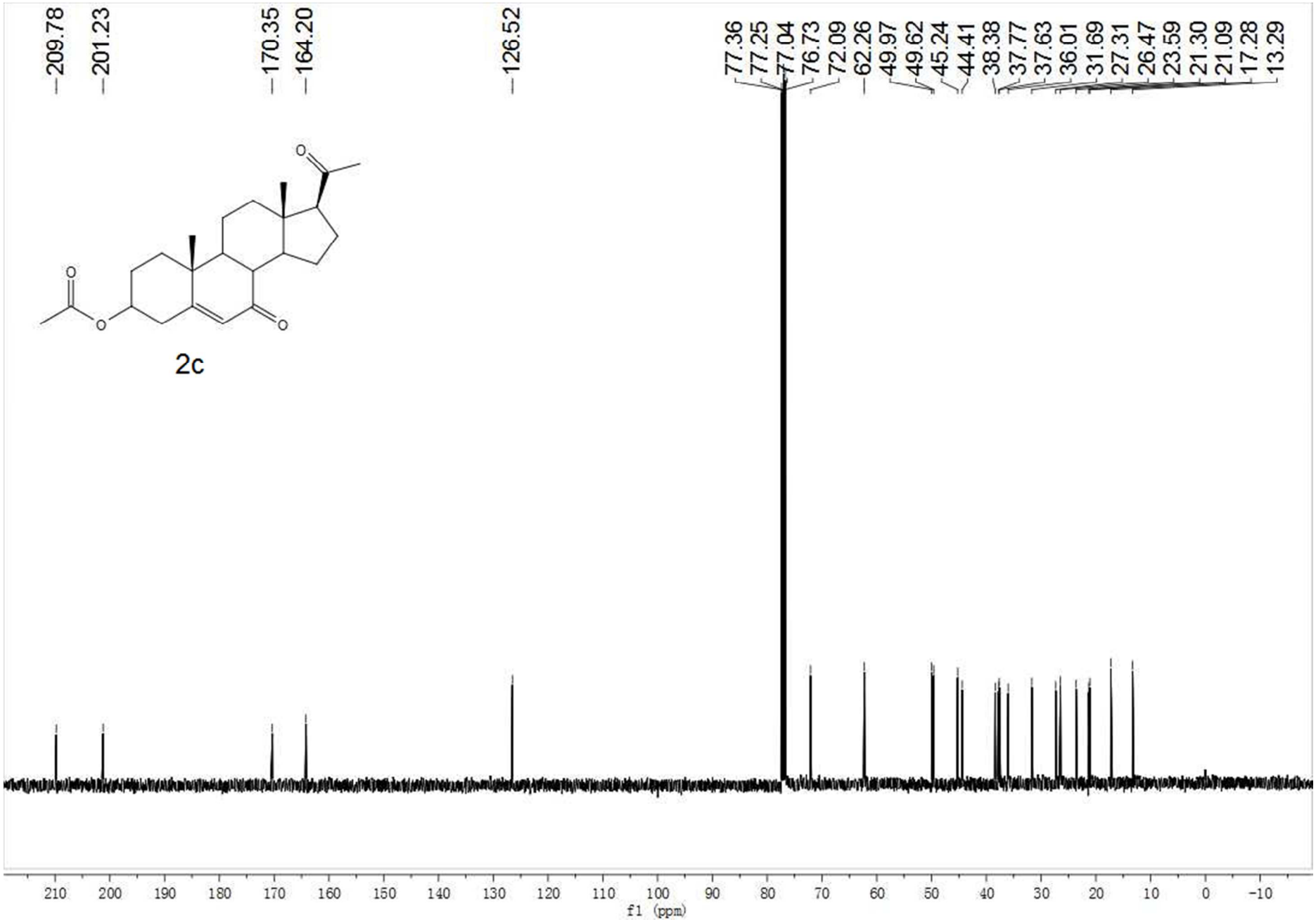
^{1}H NMR and ^{13}C NMR of **2b**.



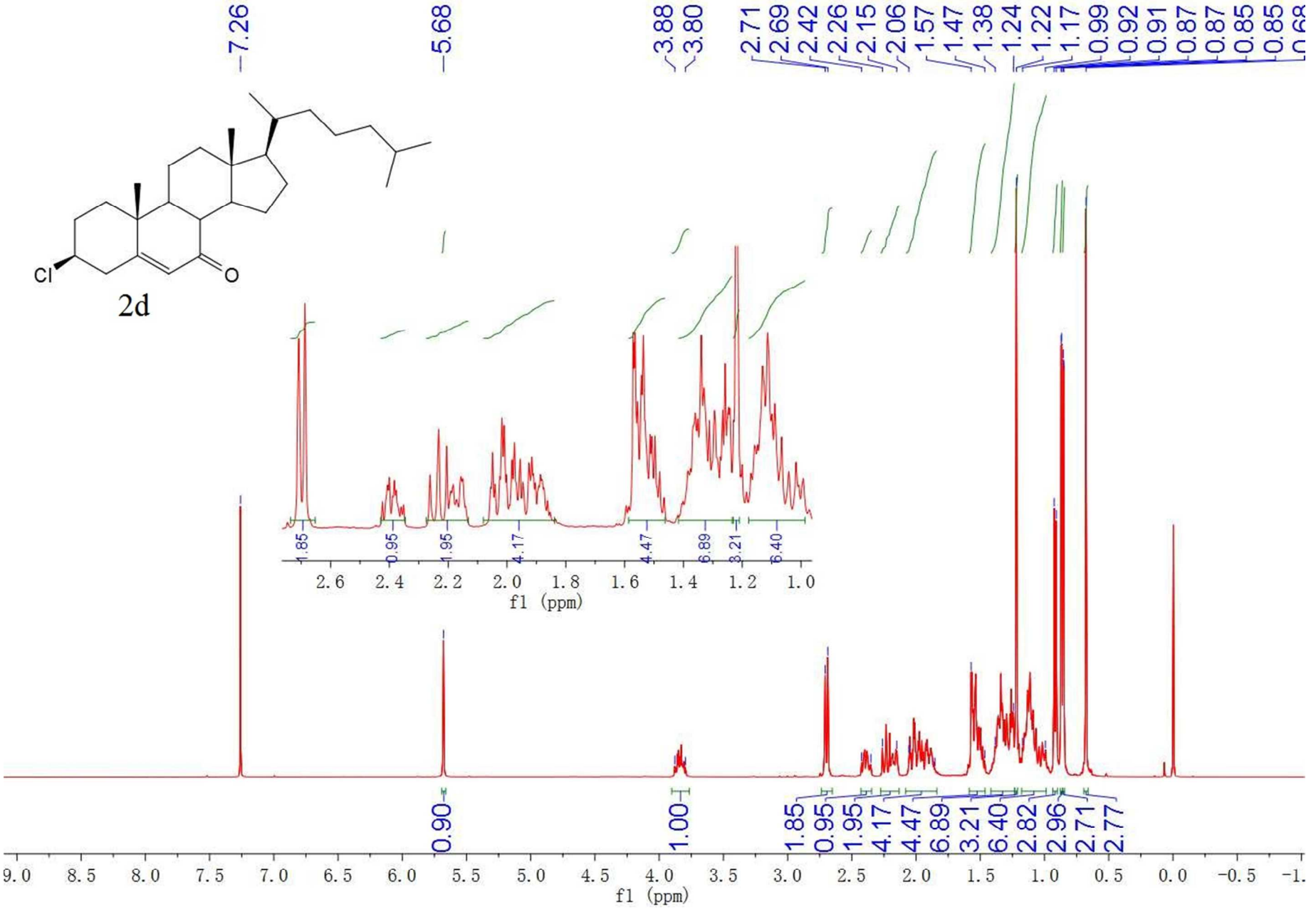

201.94
170.32
163.87
126.71
77.34
77.23
77.03
76.71
72.22
54.76
49.94
49.80
45.42
43.11
39.48
38.32
36.00
35.73
28.01
23.83
22.82
22.57
21.29
18.87
17.27
2b
f1 (ppm)

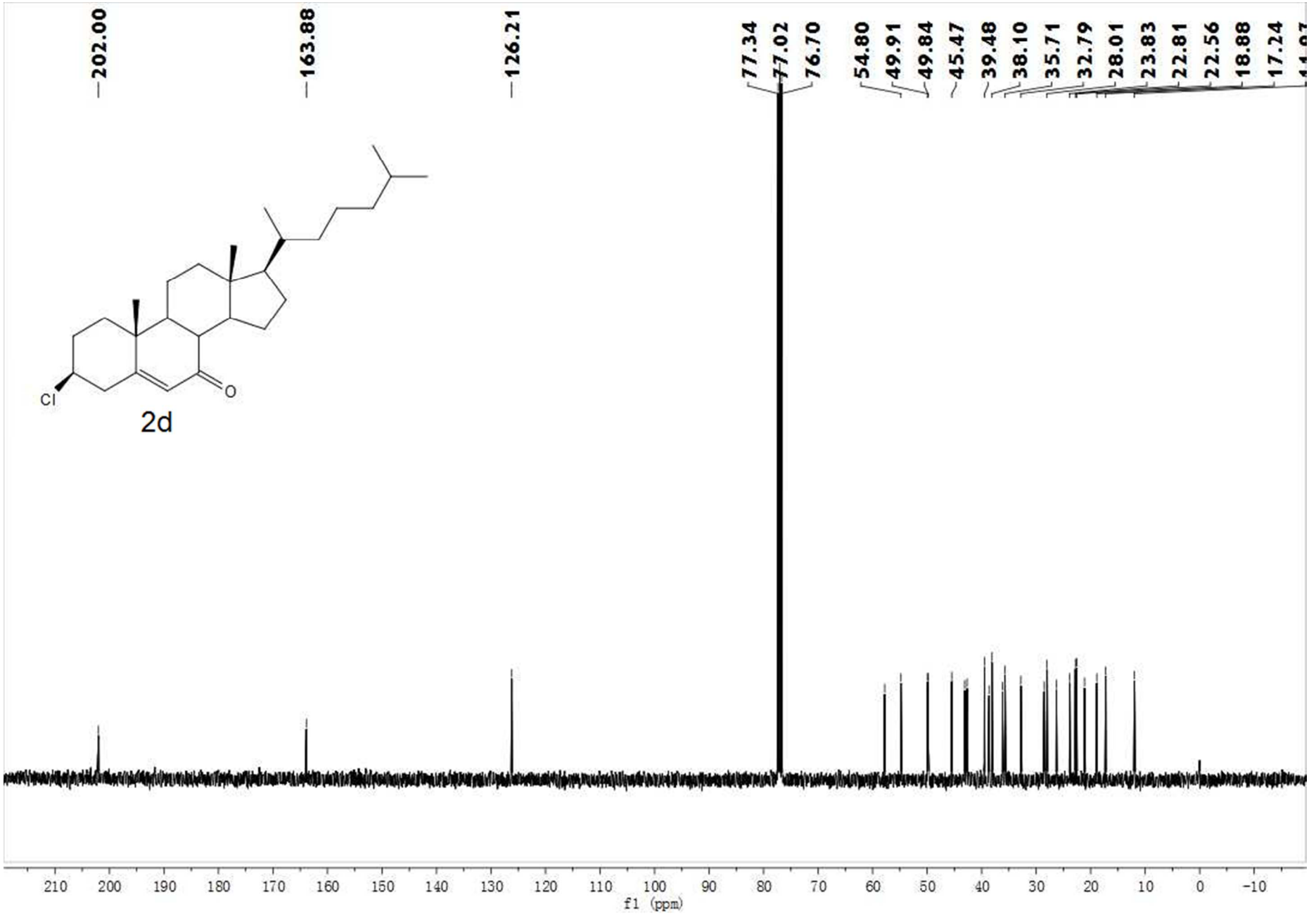
^{1}H NMR and ^{13}C NMR of **2c**.



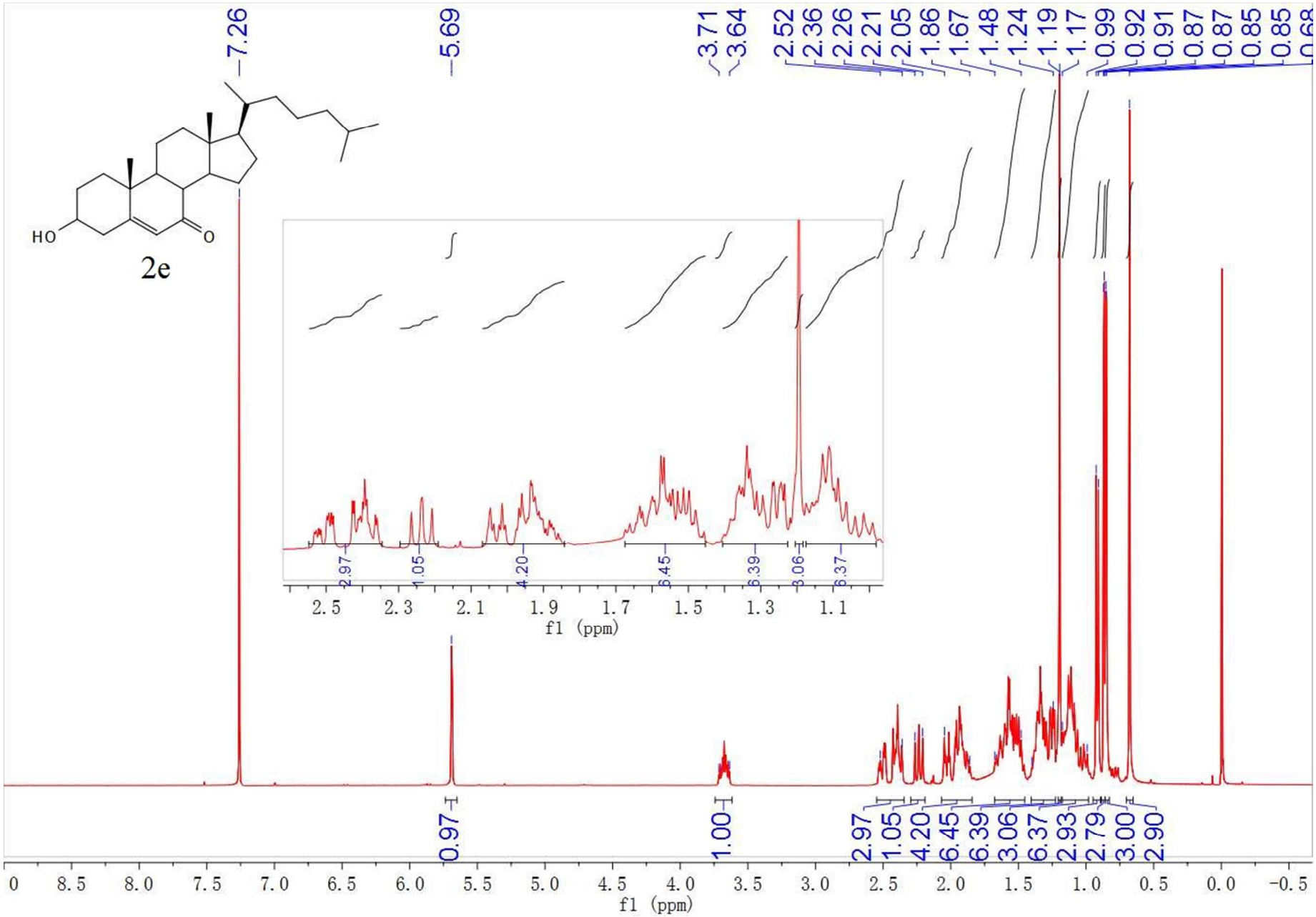

209.78
201.23
170.35
164.20
126.52
77.36
77.25
77.04
76.73
72.09
62.26
49.97
49.62
45.24
44.41
38.38
37.77
37.63
36.01
31.69
27.31
26.47
23.59
21.30
21.09
17.28
13.29
O
O
O
O
O
2c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

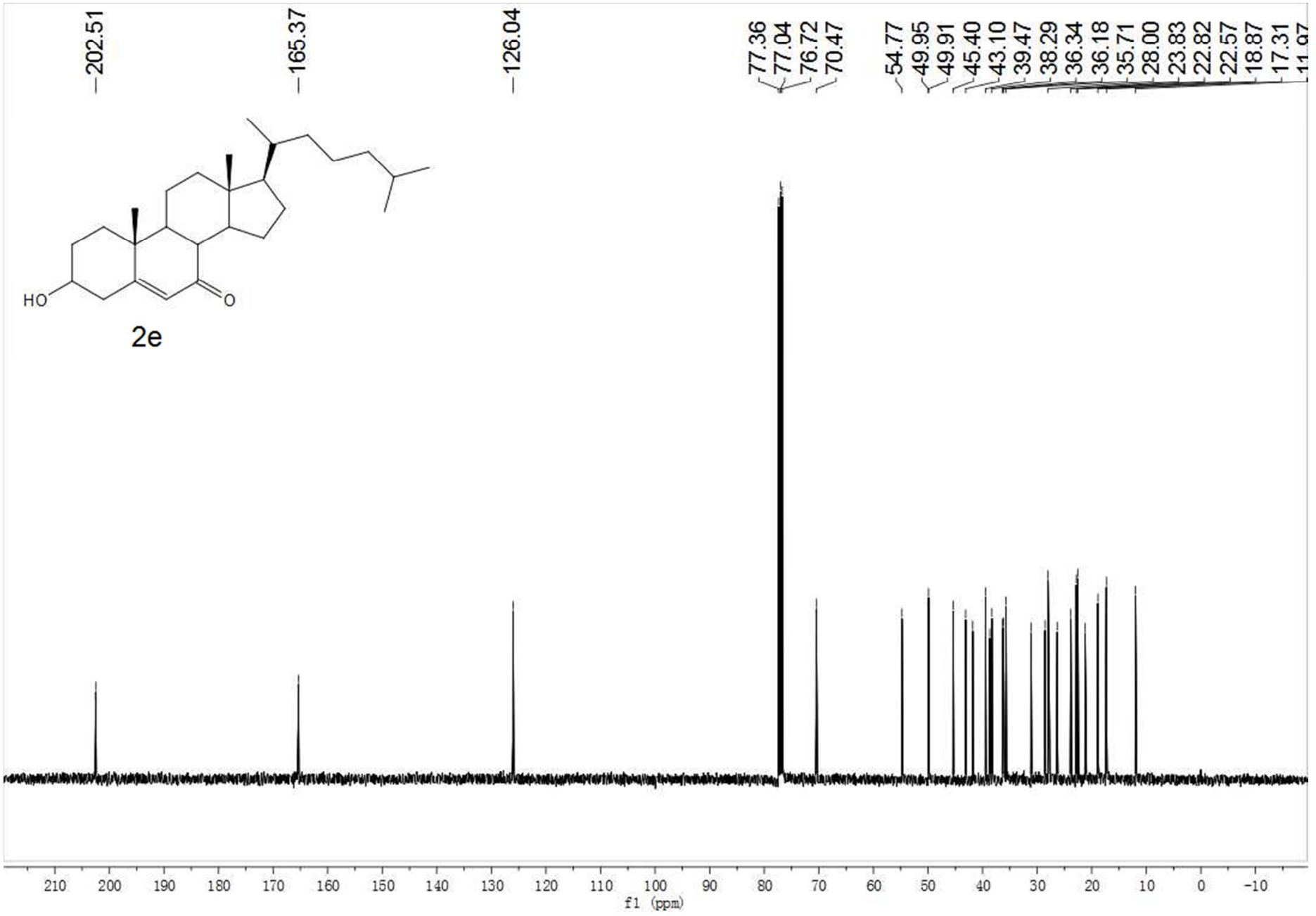
^{1}H NMR and ^{13}C NMR of **2d**.



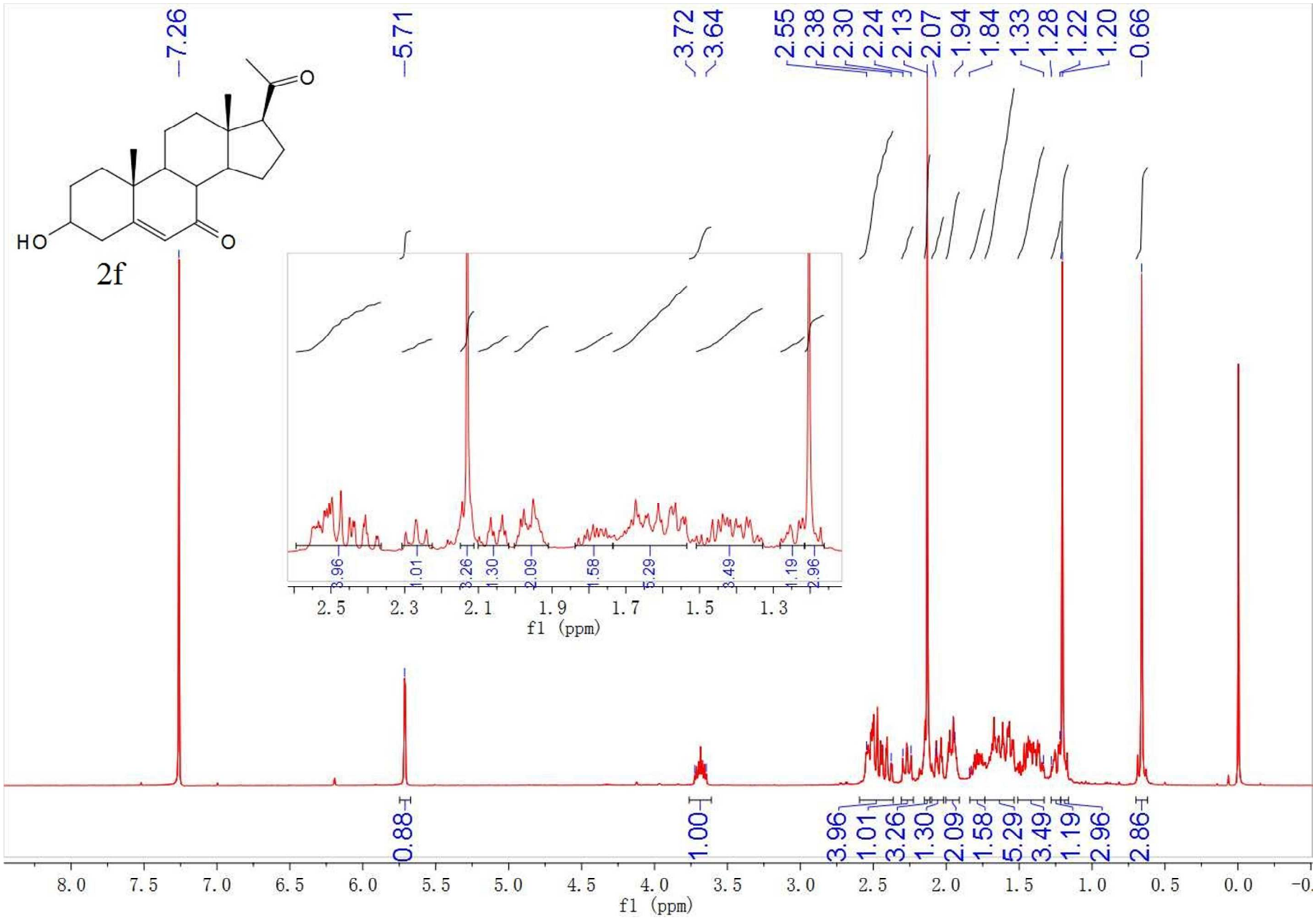

202.00
163.88
126.21
77.34
77.02
76.70
54.80
49.91
49.84
45.47
39.48
38.10
35.71
32.79
28.01
23.83
22.81
22.56
18.88
17.24
Cl
O
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

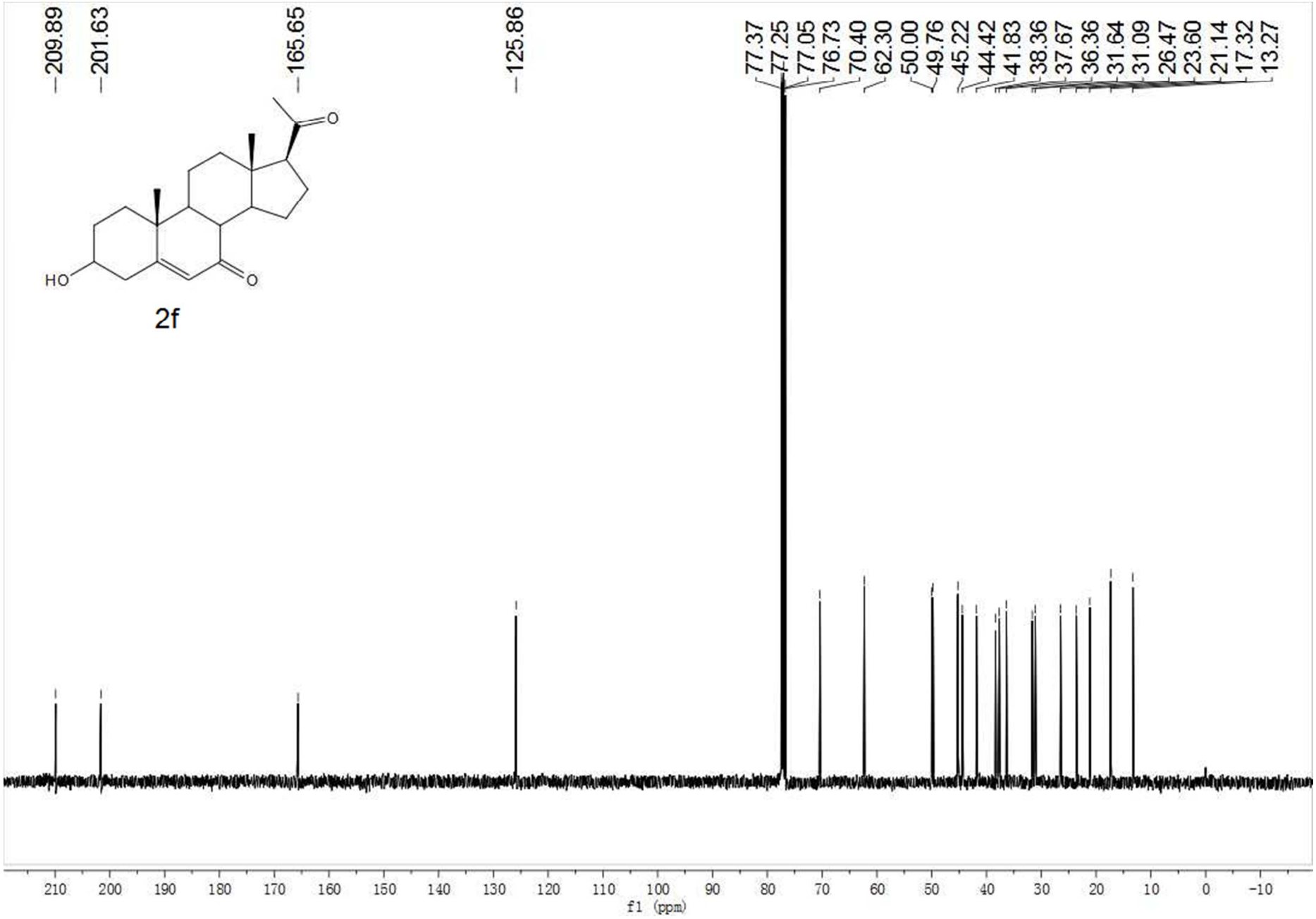
^{1}H NMR and ^{13}C NMR of **2e**.



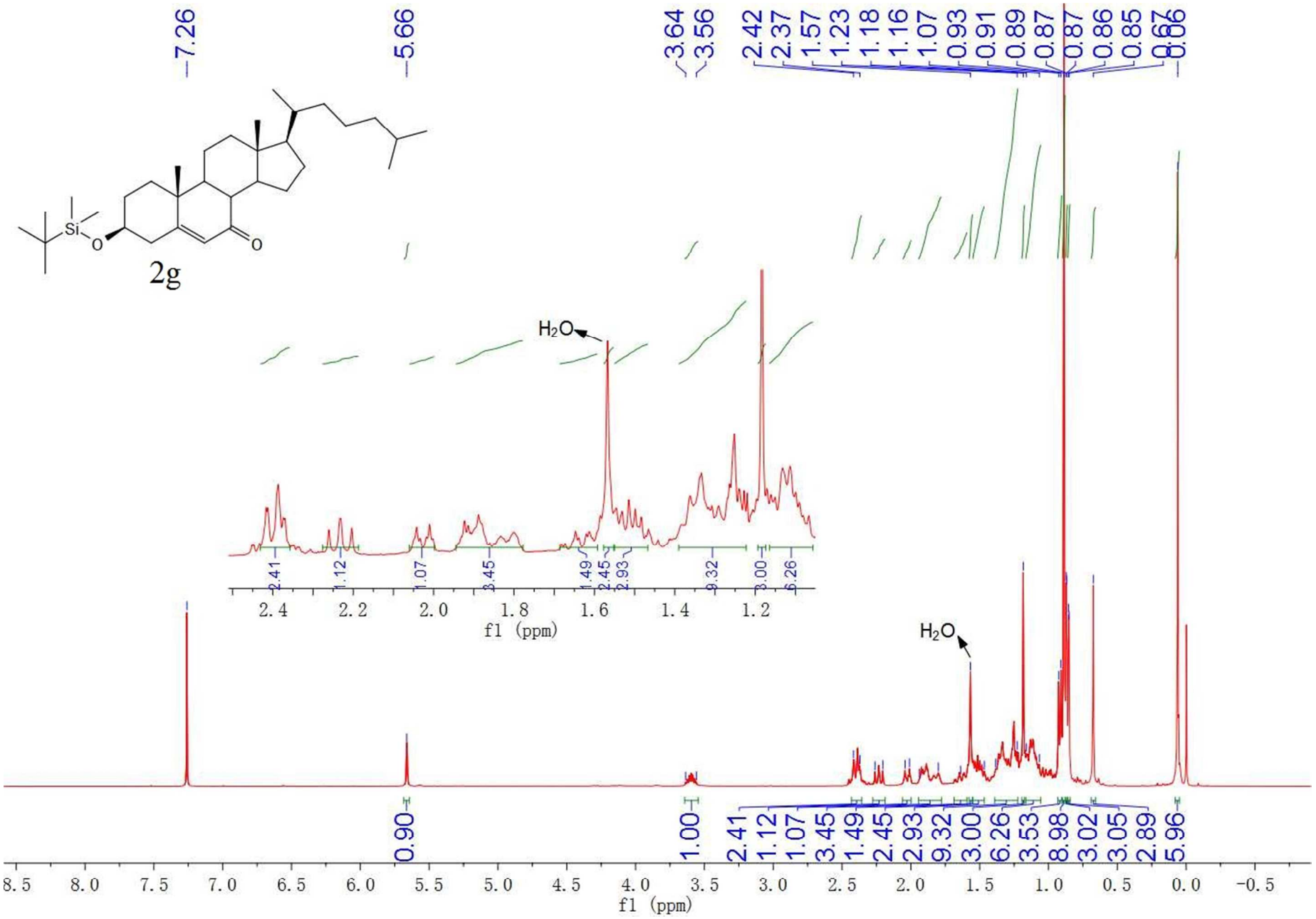

202.51
165.37
126.04
77.36
77.04
76.72
70.47
54.77
49.95
49.91
45.40
43.10
39.47
38.29
36.34
36.18
35.71
28.00
23.83
22.82
22.57
18.87
17.31
HO
O
2e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

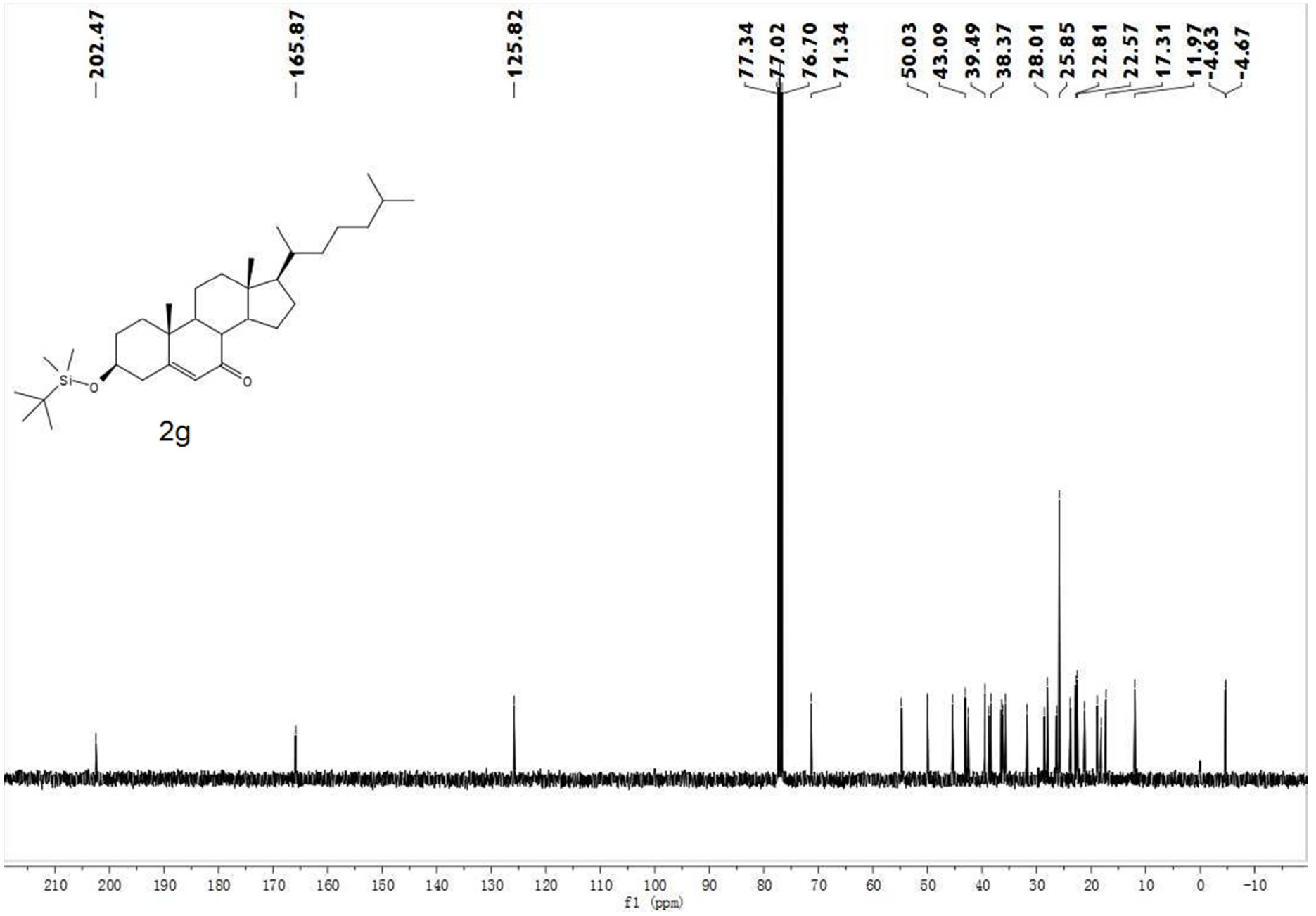
^{1}H NMR and ^{13}C NMR of **2f**.



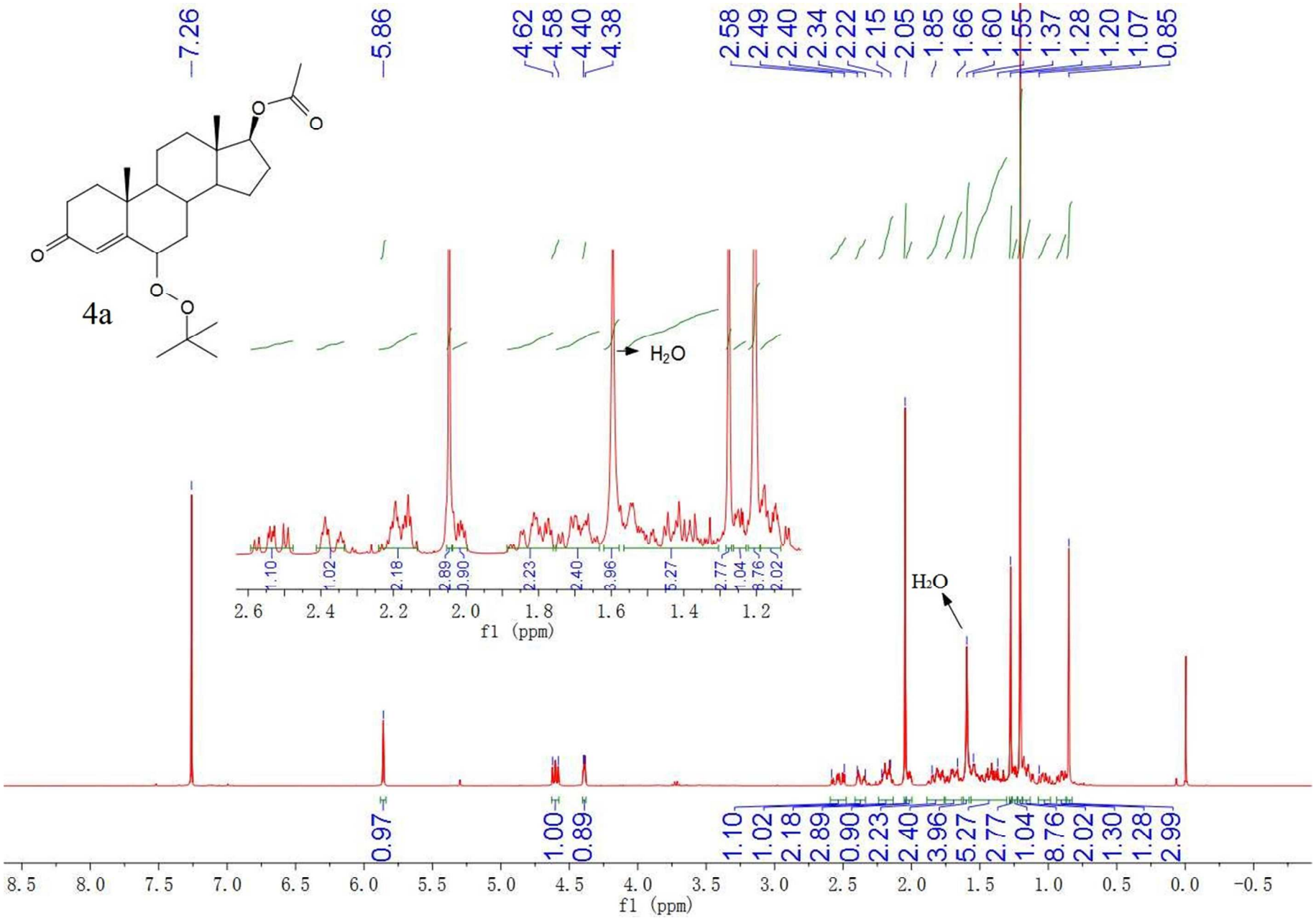

209.89
201.63
165.65
125.86
77.37
77.25
77.05
76.73
70.40
62.30
50.00
49.76
45.22
44.42
41.83
38.36
37.67
36.36
31.64
31.09
26.47
23.60
21.14
17.32
13.27
HO
O
O
2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

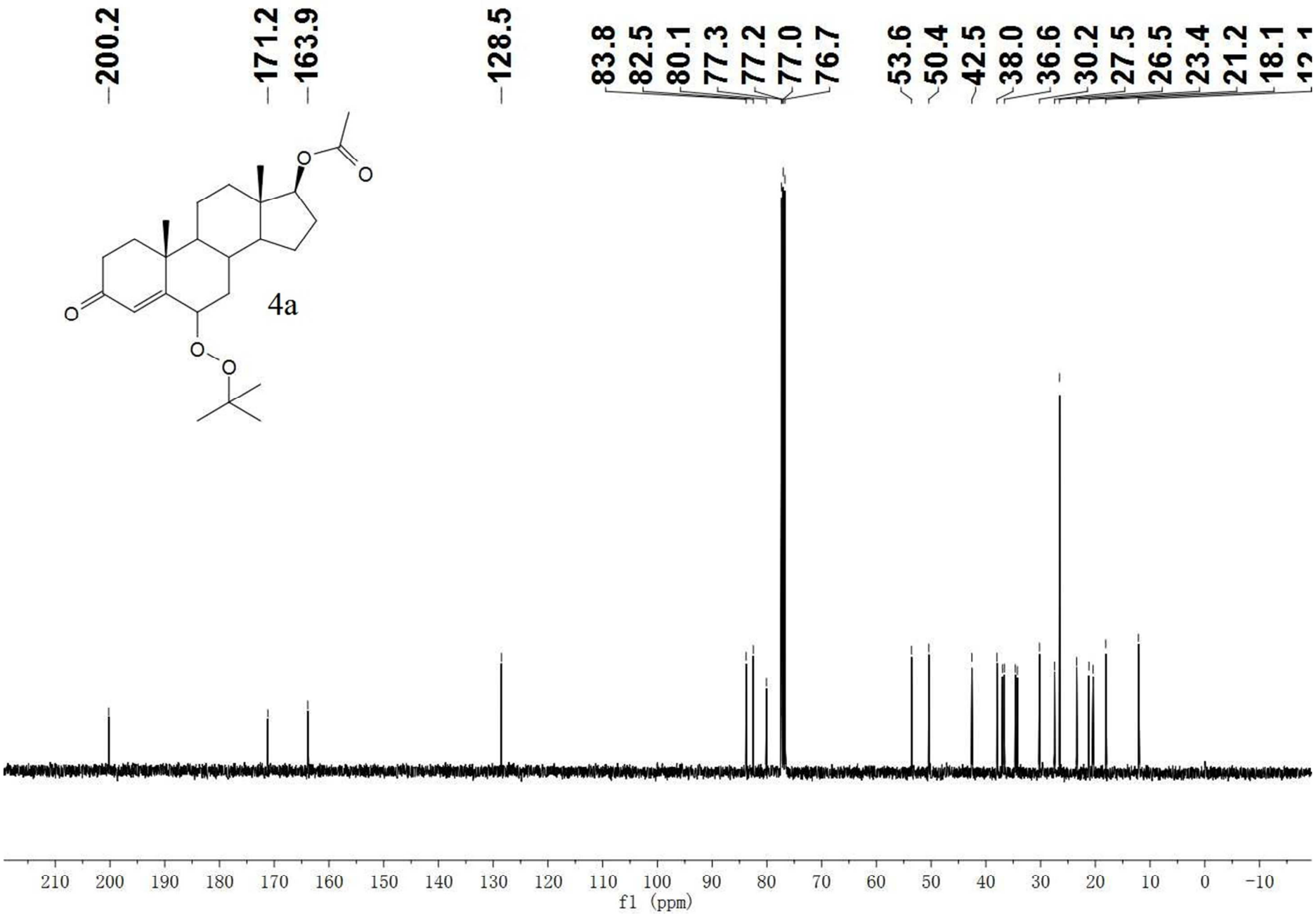
^{1}H NMR and ^{13}C NMR of **2g**.



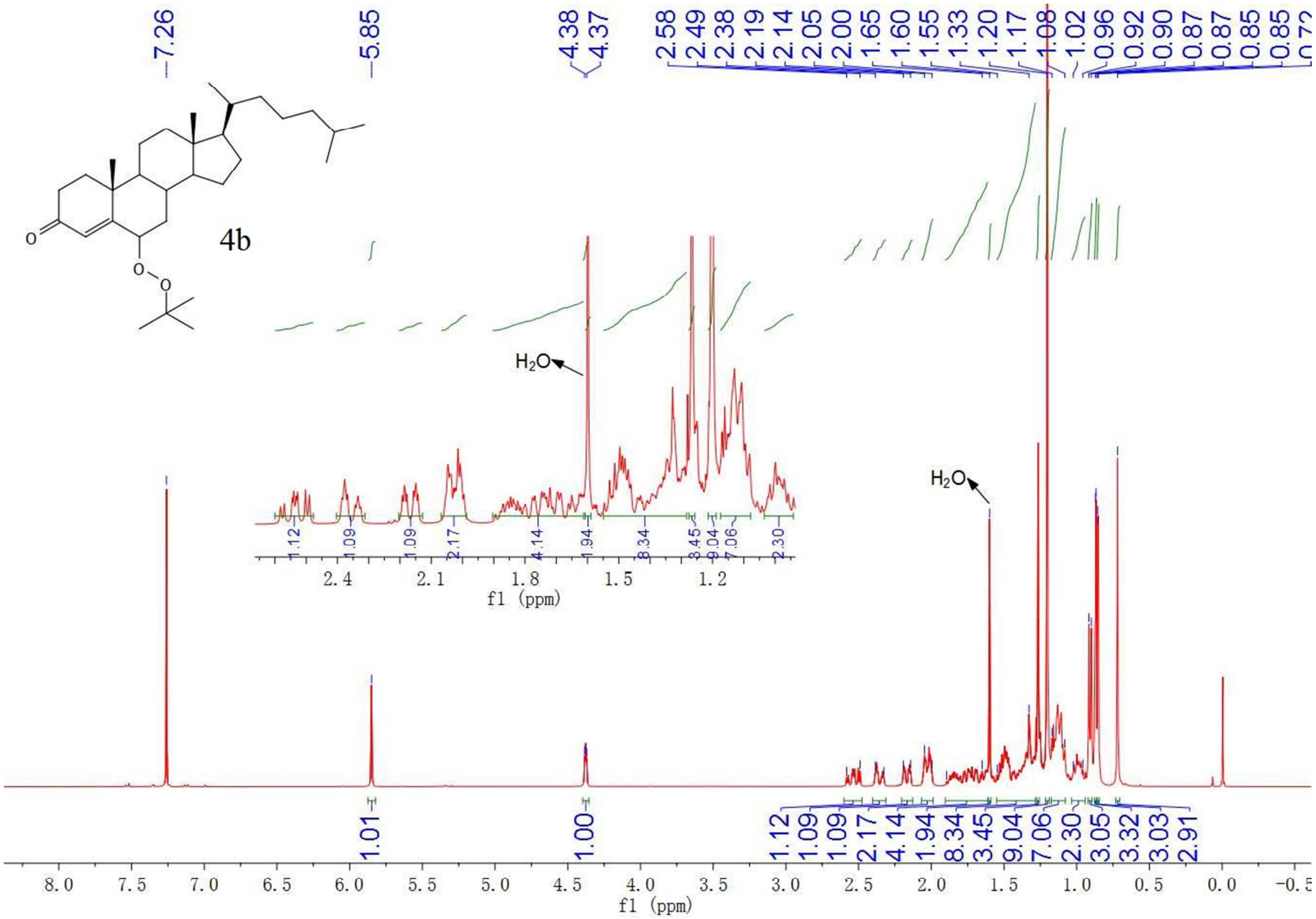

202.47
165.87
125.82
77.34
77.02
76.70
71.34
50.03
43.09
39.49
38.37
28.01
25.85
22.81
22.57
17.31
11.97
-4.63
-4.67
Si
O
O
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

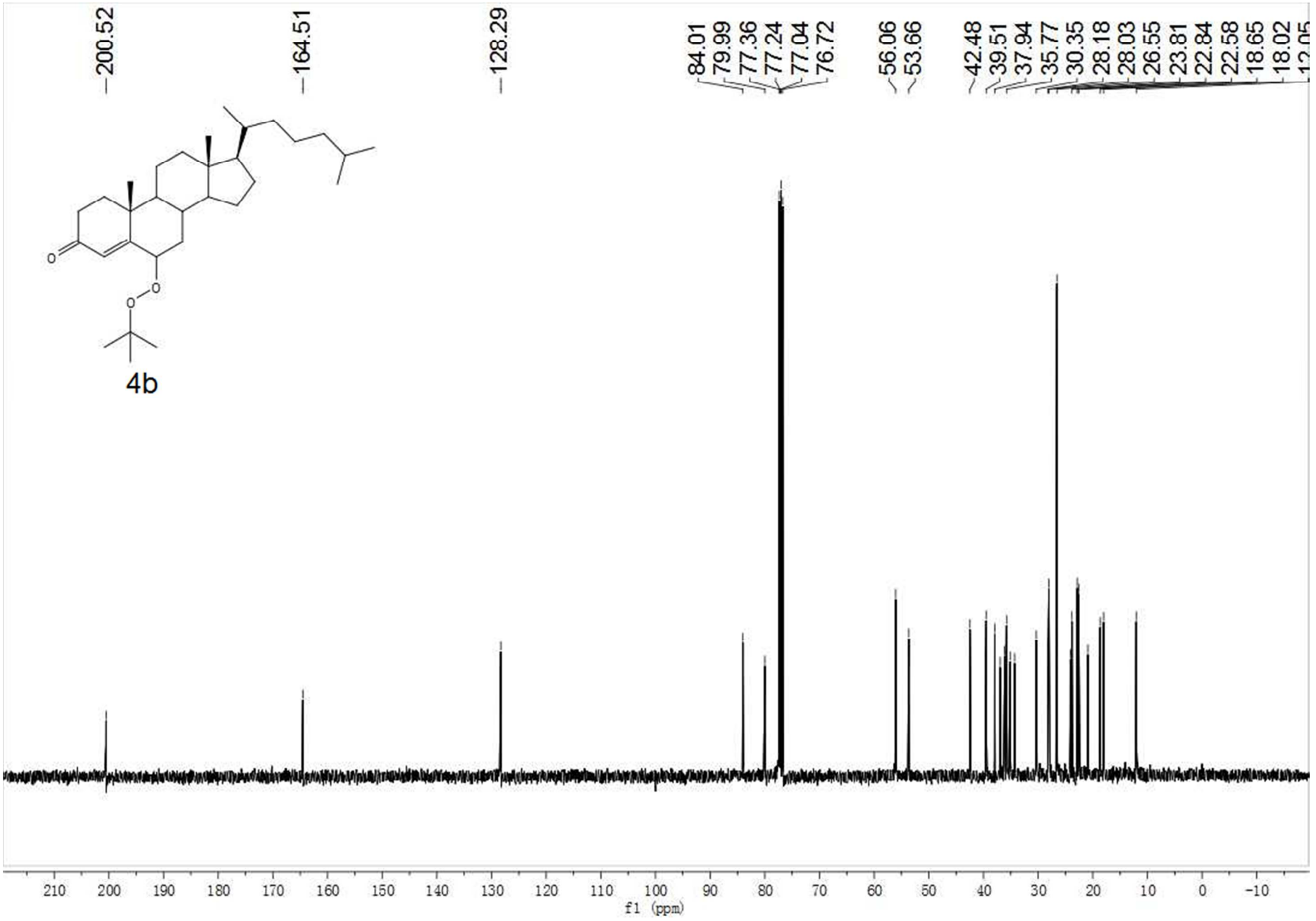
^{1}H NMR and ^{13}C NMR of **4a**.



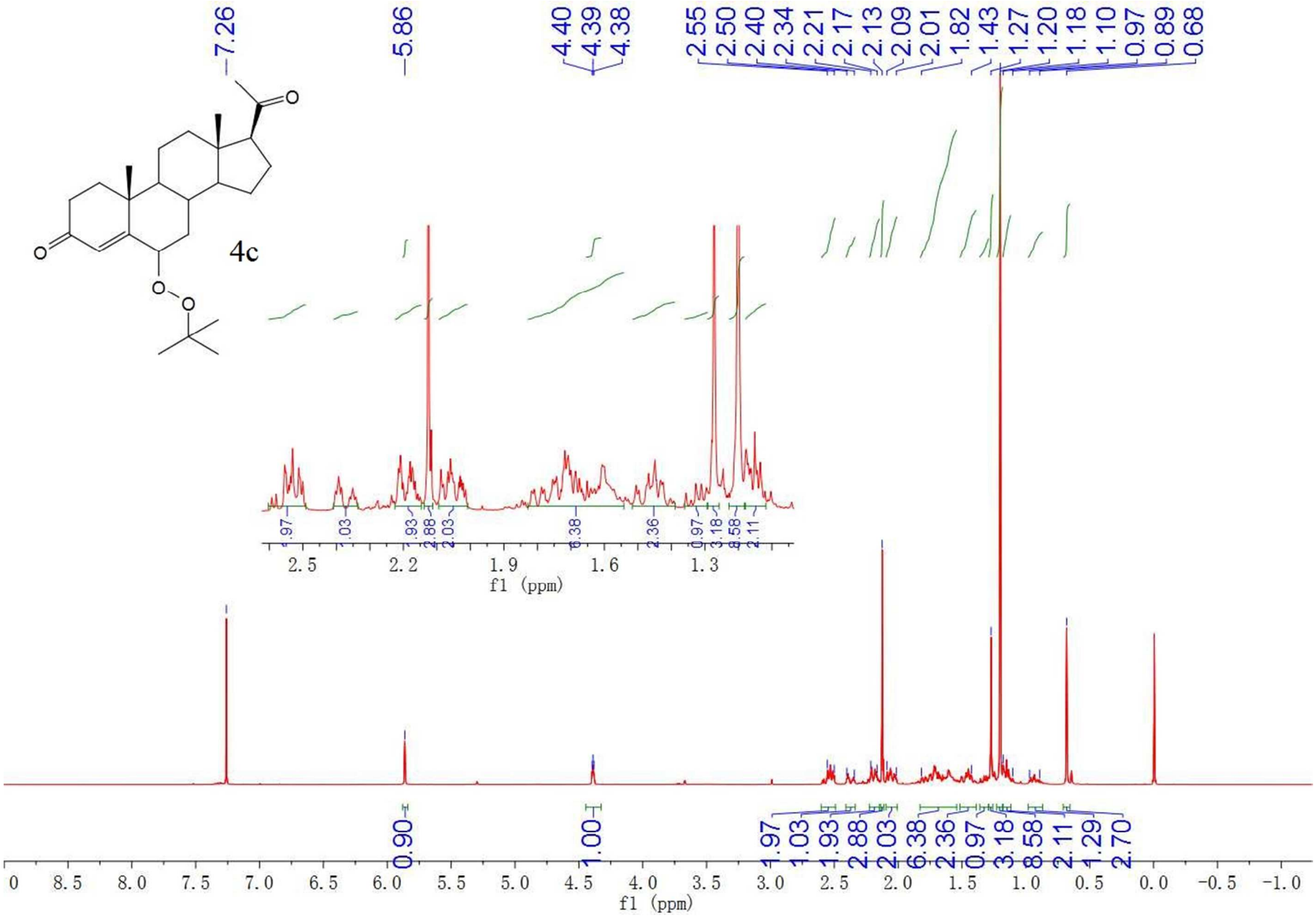

200.2
171.2
163.9
128.5
83.8
82.5
80.1
77.3
77.2
77.0
76.7
53.6
50.4
42.5
38.0
36.6
30.2
27.5
26.5
23.4
21.2
18.1
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

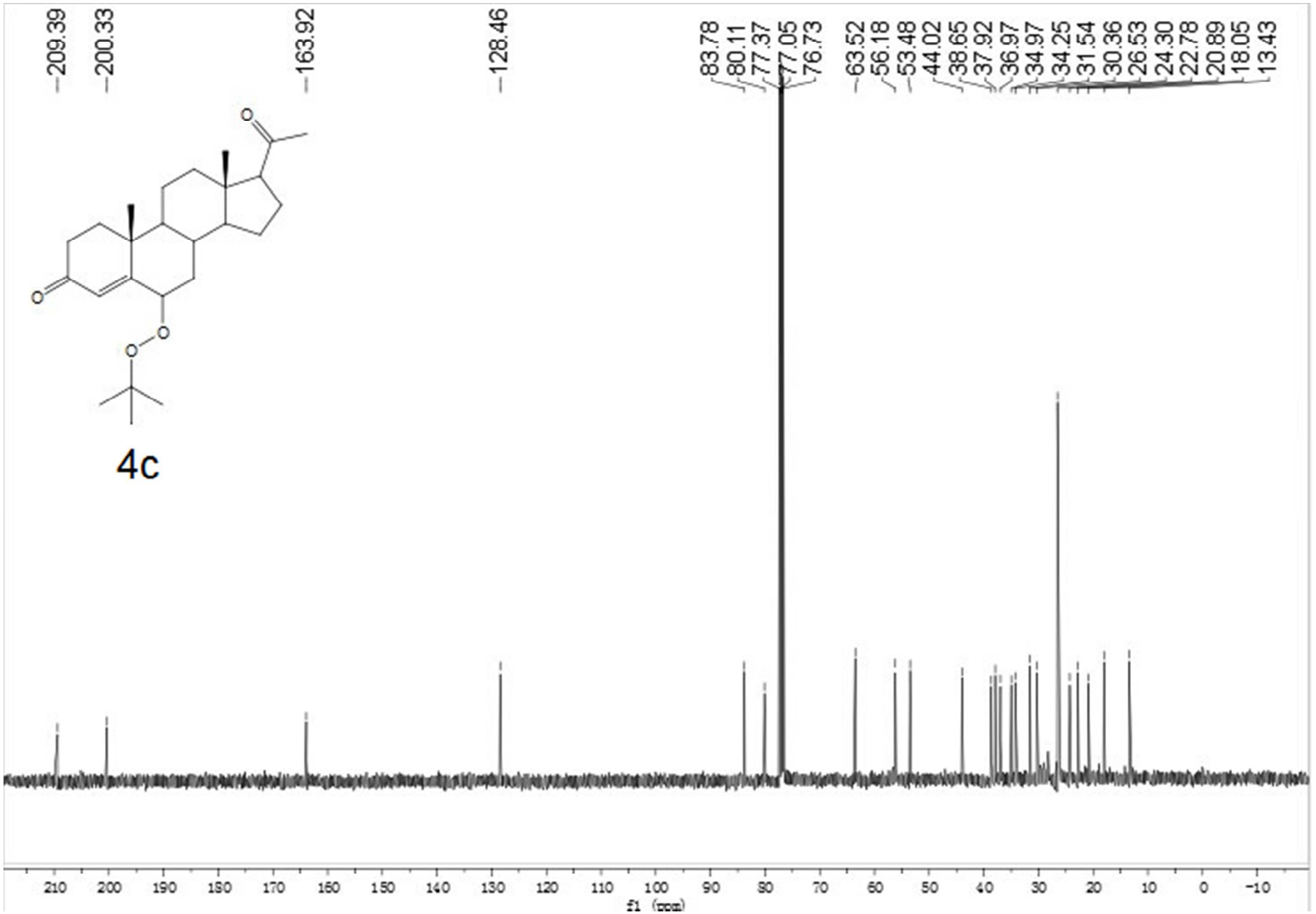
^{1}H NMR and ^{13}C NMR of **4b**.



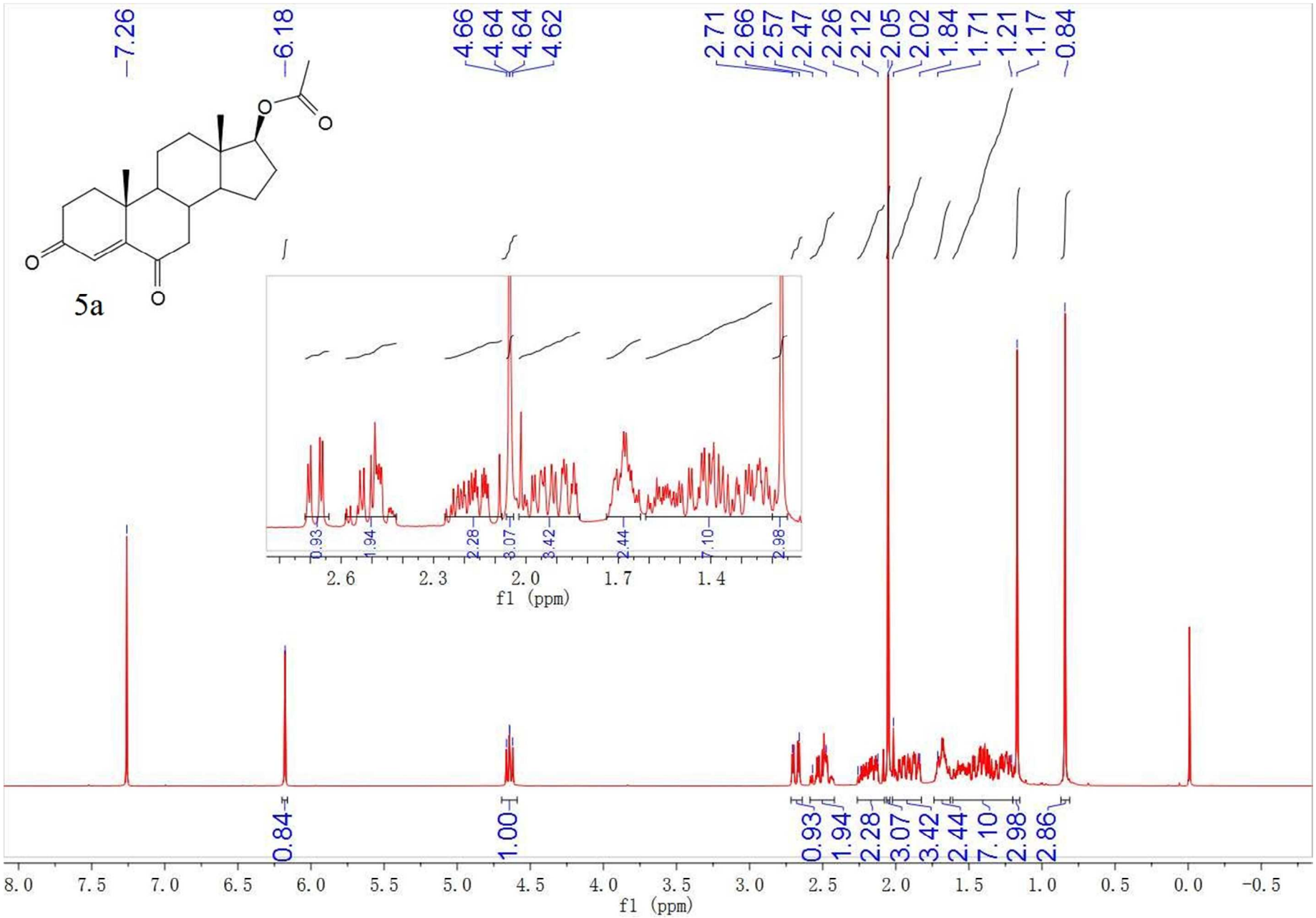

200.52
164.51
128.29
84.01
79.99
77.36
77.24
77.04
76.72
56.06
53.66
42.48
39.51
37.94
35.77
30.35
28.18
28.03
26.55
23.81
22.84
22.58
18.65
18.02
O
O
O
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

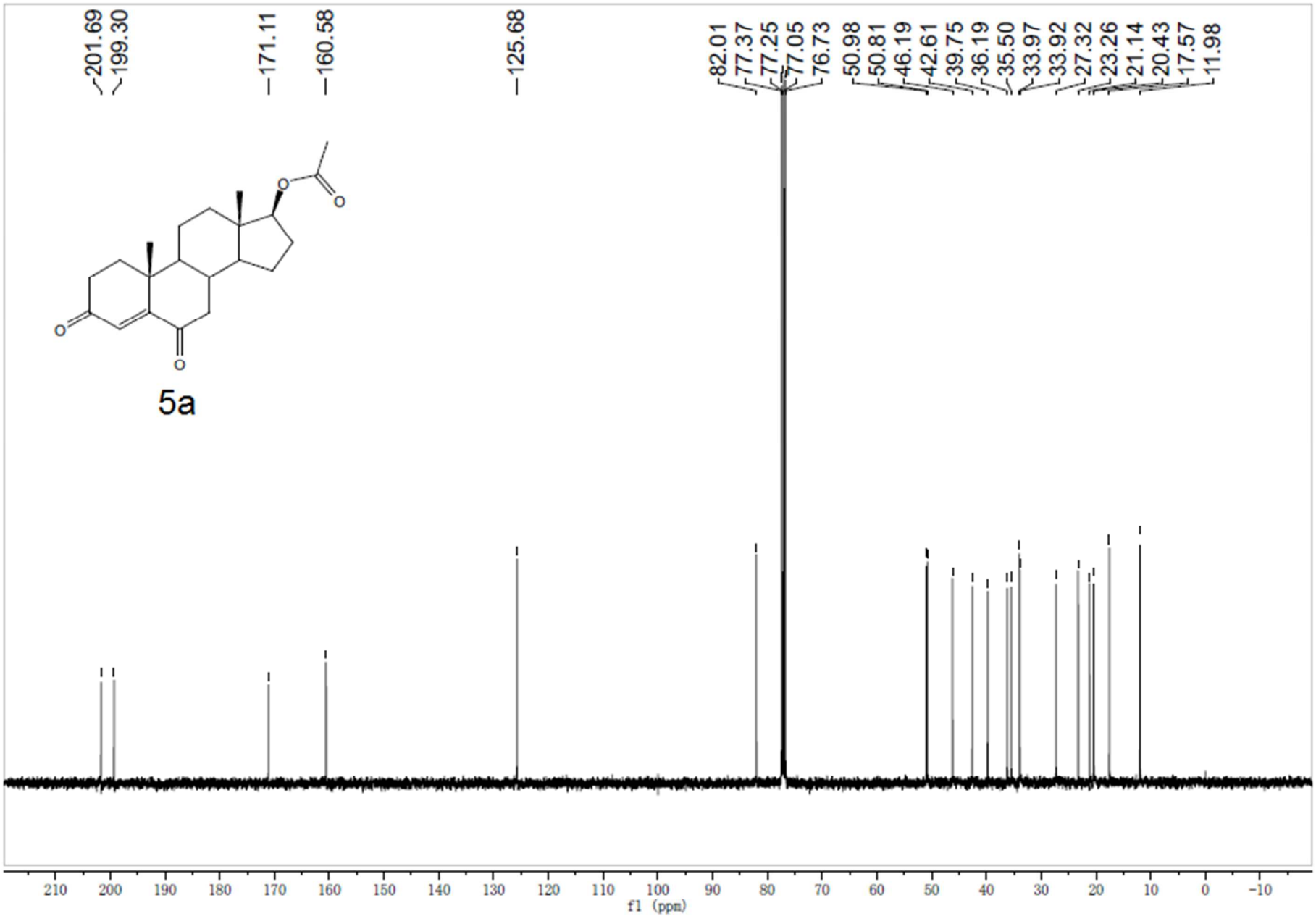
^{1}H NMR and ^{13}C NMR of **4c**.



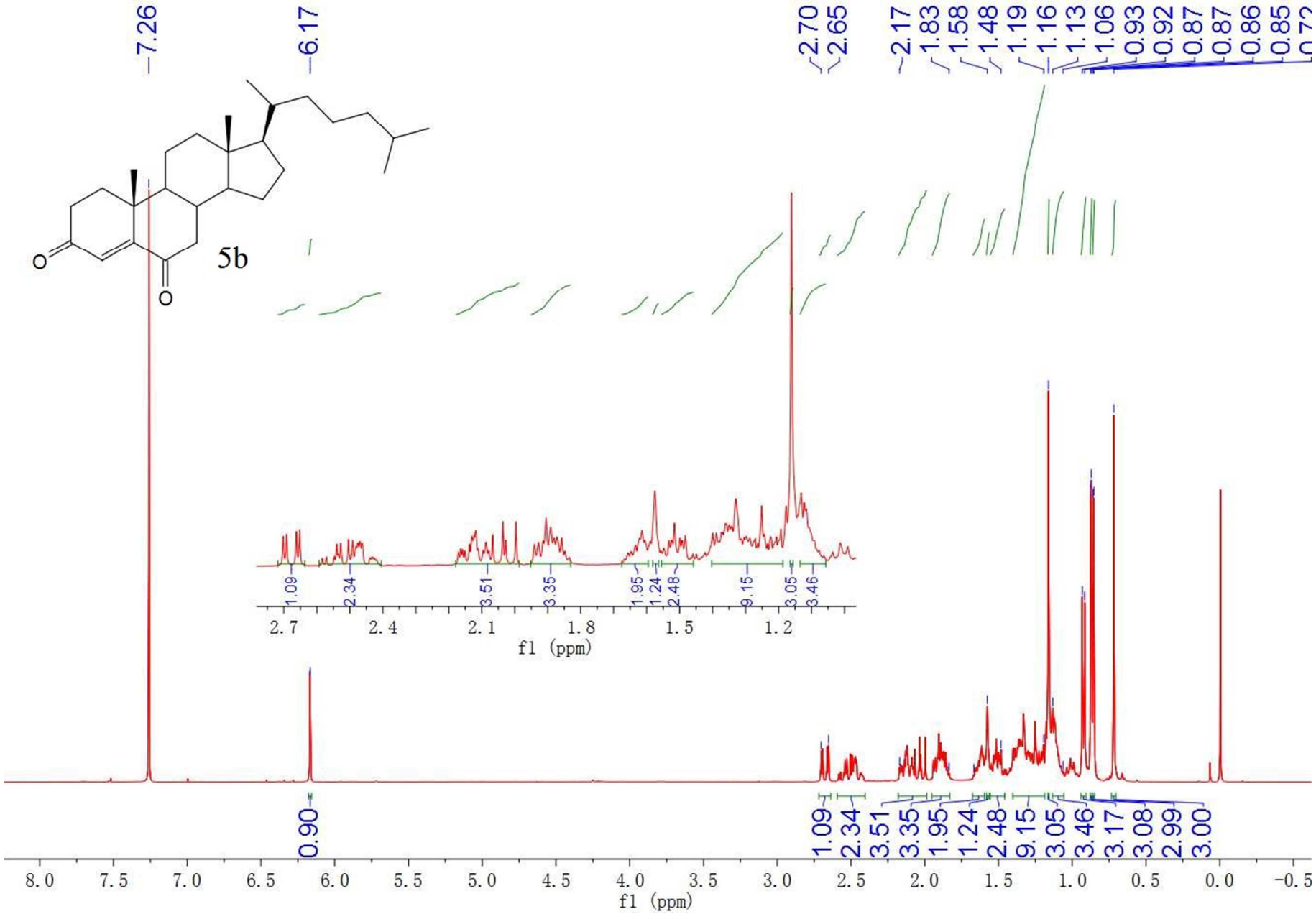

209.39
200.33
163.92
128.46
83.78
80.11
77.37
77.05
76.73
63.52
56.18
53.48
44.02
38.65
37.92
36.97
34.97
34.25
31.54
30.36
26.53
24.30
22.78
20.89
18.05
13.43
4c
f1 (ppm)

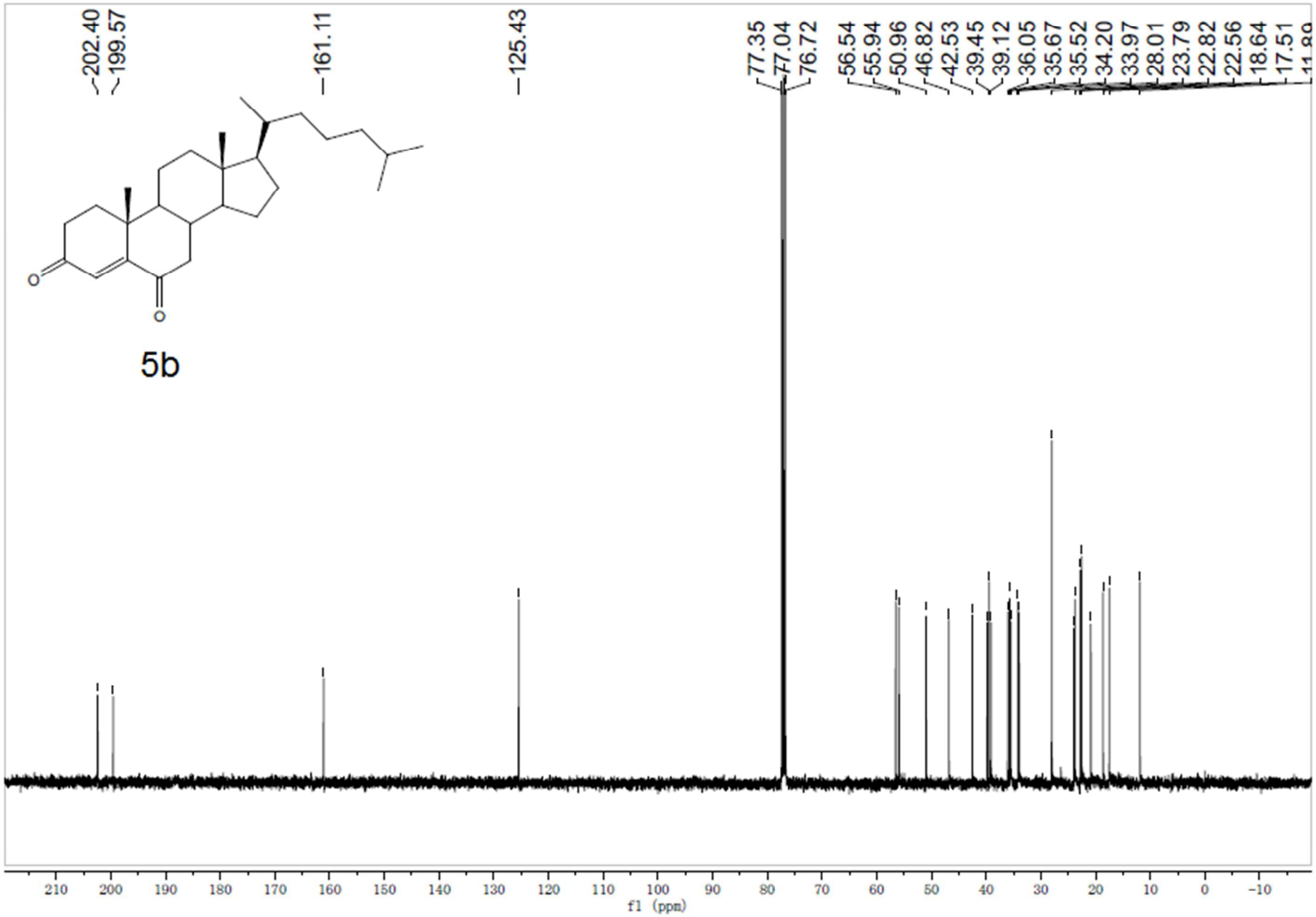
^{1}H NMR and ^{13}C NMR of **5a**.



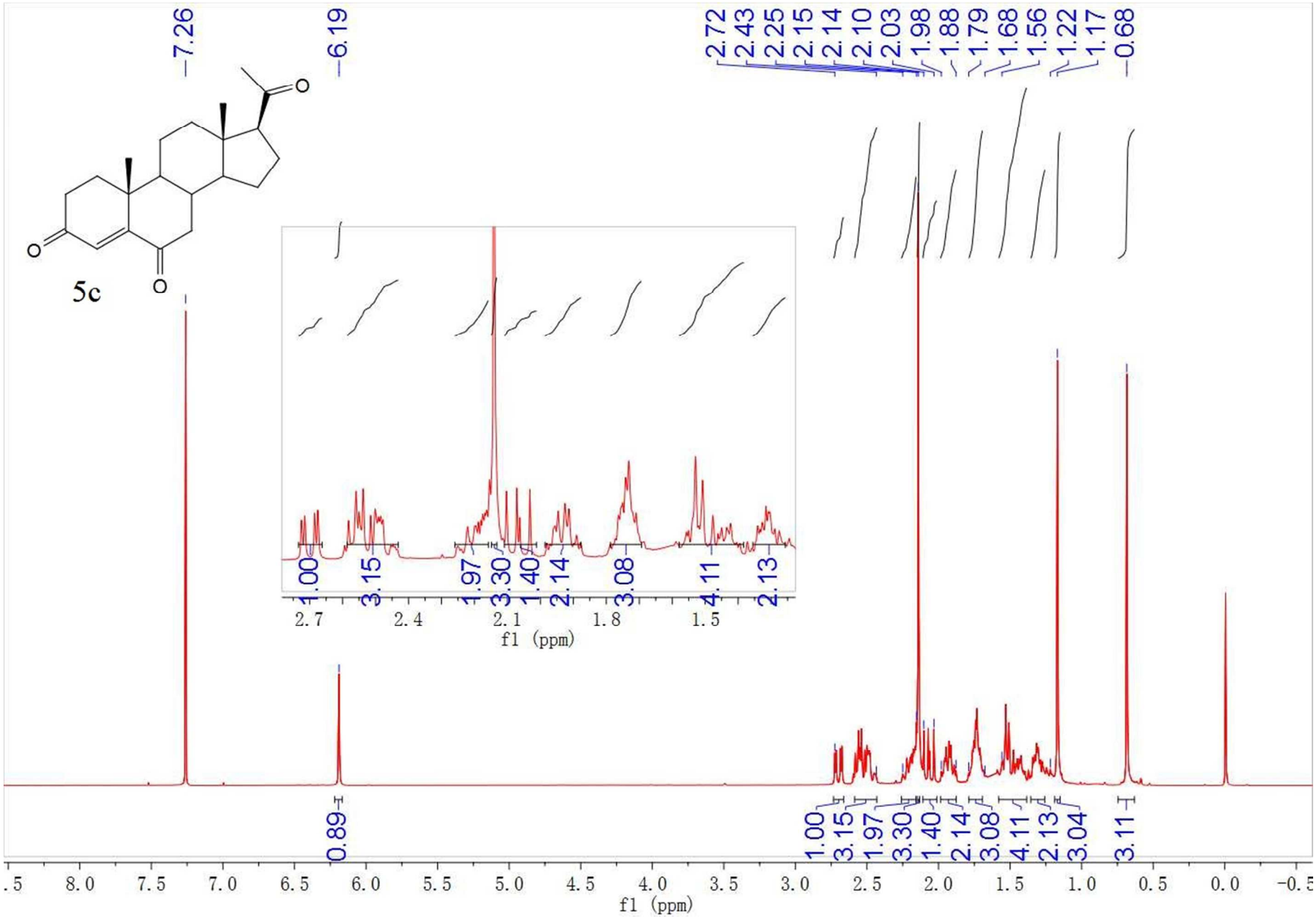

201.69
199.30
171.11
160.58
125.68
82.01
77.37
77.25
77.05
76.73
50.98
50.81
46.19
42.61
39.75
36.19
35.50
33.97
33.92
27.32
23.26
21.14
20.43
17.57
11.98
5a
f1 (ppm)

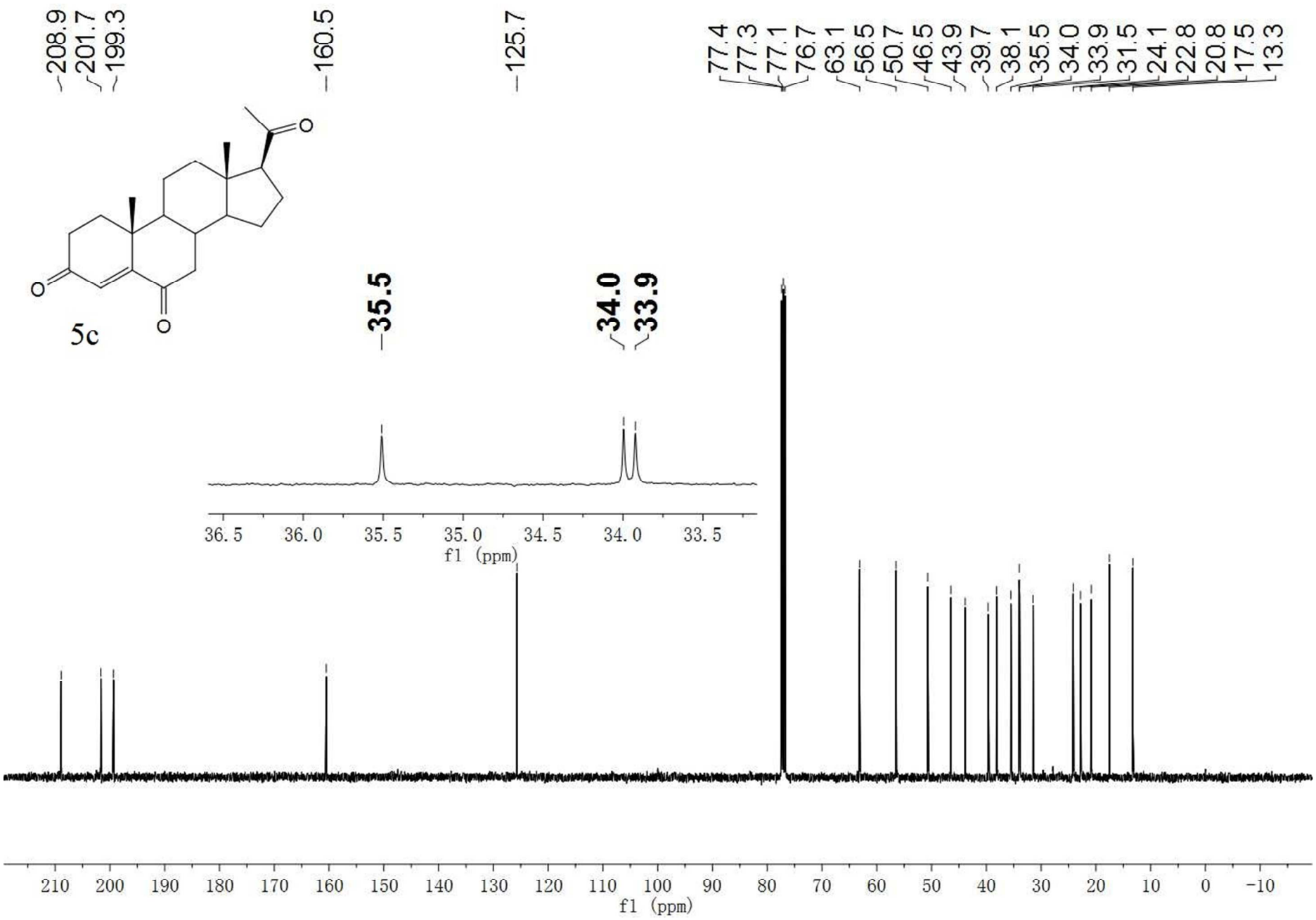
^{1}H NMR and ^{13}C NMR of **5b**.




202.40
199.57
161.11
125.43
77.35
77.04
76.72
56.54
55.94
50.96
46.82
42.53
39.45
39.12
36.05
35.67
35.52
34.20
33.97
28.01
23.79
22.82
22.56
18.64
17.51
5b
f1 (ppm)

^{1}H NMR and ^{13}C NMR of **5c**.




208.9
201.7
199.3
160.5
125.7
77.4
77.3
77.1
76.7
63.1
56.5
50.7
46.5
43.9
39.7
38.1
35.5
34.0
33.9
31.5
24.1
22.8
20.8
17.5
13.3
5c
35.5
34.0
33.9
36.5 36.0 35.5 35.0 34.5 34.0 33.5
f1 (ppm)
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)