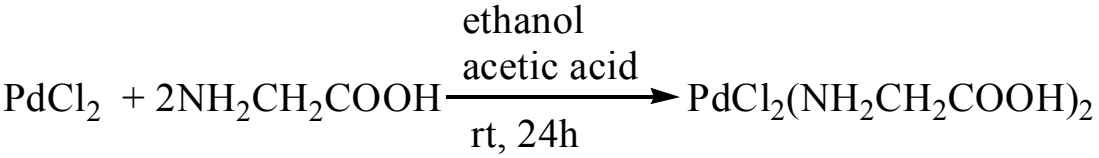
Supporting Information

A highly efficient catalyst of nitrogen-based ligand for the Suzuki coupling reaction at room temperature under air in neat water

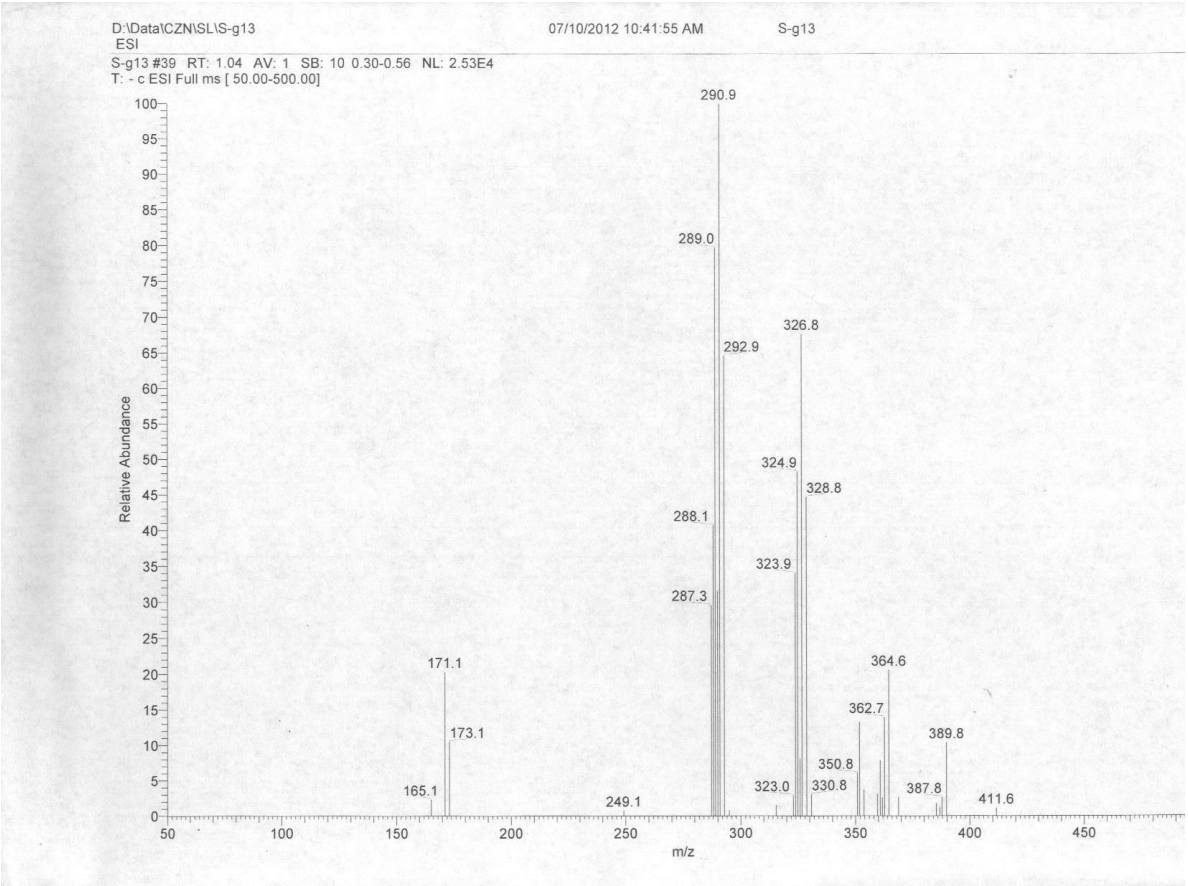
Experimental

All reagents employed in the reaction were analytical grade, obtained commercially from Aladdin or Alfa Aesar and used without further purification.

The complex ($[PdCl_2(NH_2CH_2COOH)_2]$) was synthesized in the lab by following the protocol as below. A mixture of glycine(10.2mmol), palladium chloride(5.0mmol), ethanol(30mL) and acetic acid(5mL) was stirred at room temperature under air for 24h in a round-bottomed flask. After 24h, large amounts of light brown precipitate emerged in the solution. Then, the precipitate was filtered and washed with cool ethanol. Lastly, a light brown compound was obtained after dried by vacuum. On the basis of elemental analysis, the complex was found to have the composition of C (14.90%), H (3.10%), N (8.56%); ESI-MS(m/z): 326.8[M+1]. Yield: 0.93g, 57%.



Synthesis of catalyst



Mass spectrum of catalyst

Instrumentation

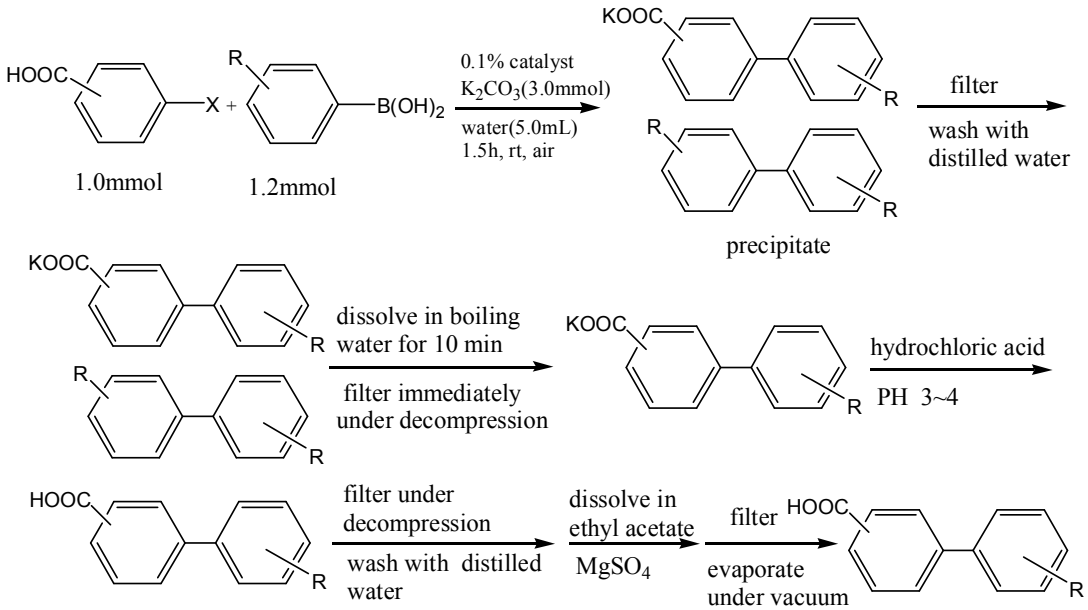
^{1}H NMR spectra was recorded on a Bruker Avance III (400MHz) spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent.

Elemental analyses (C, H, N) of catalyst were carried out on a Perkin Elmer model 240 C automatic instrument.

Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer.

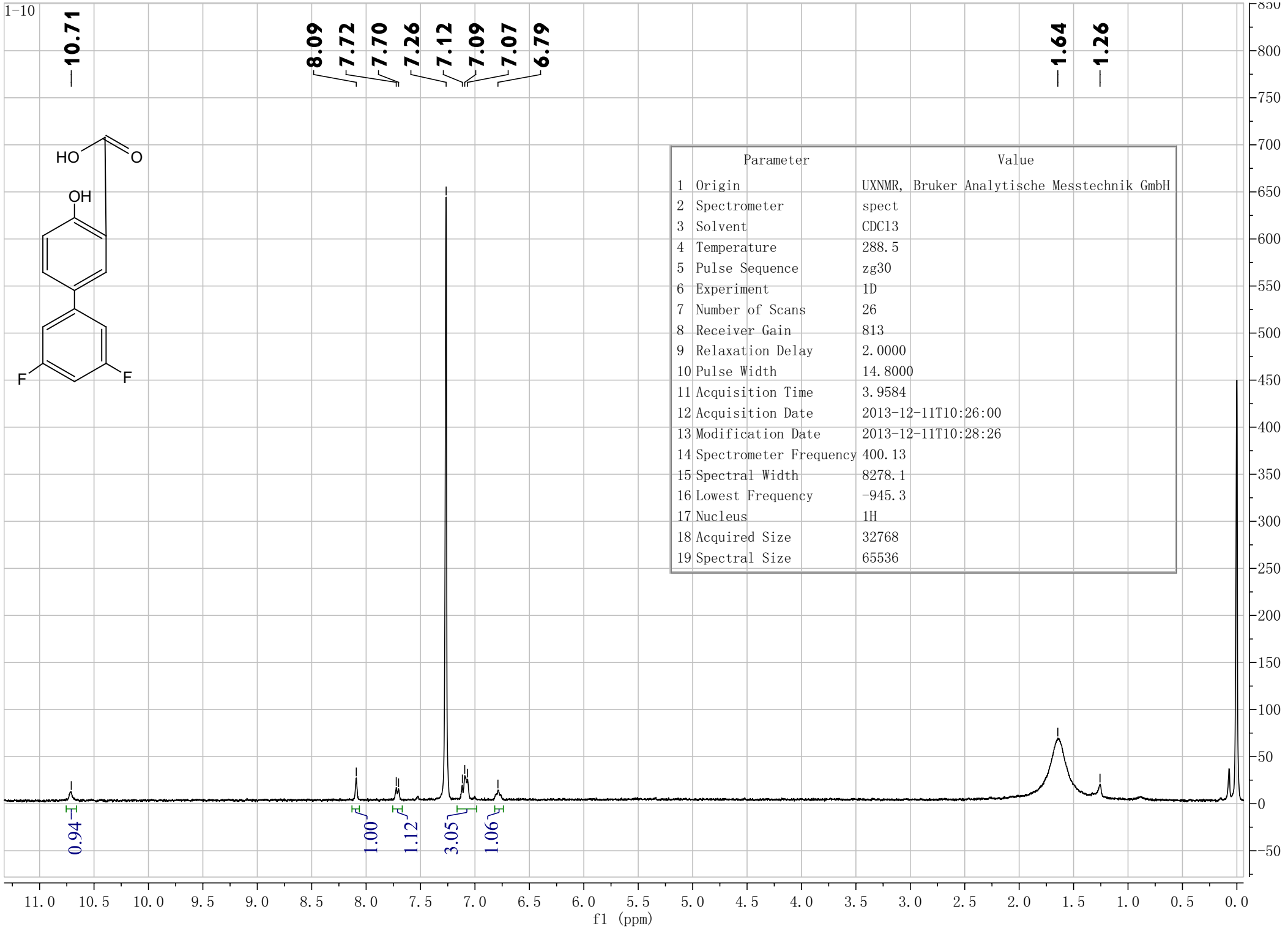
General procedure for Suzuki coupling of aryl halides with aryl boronic acids

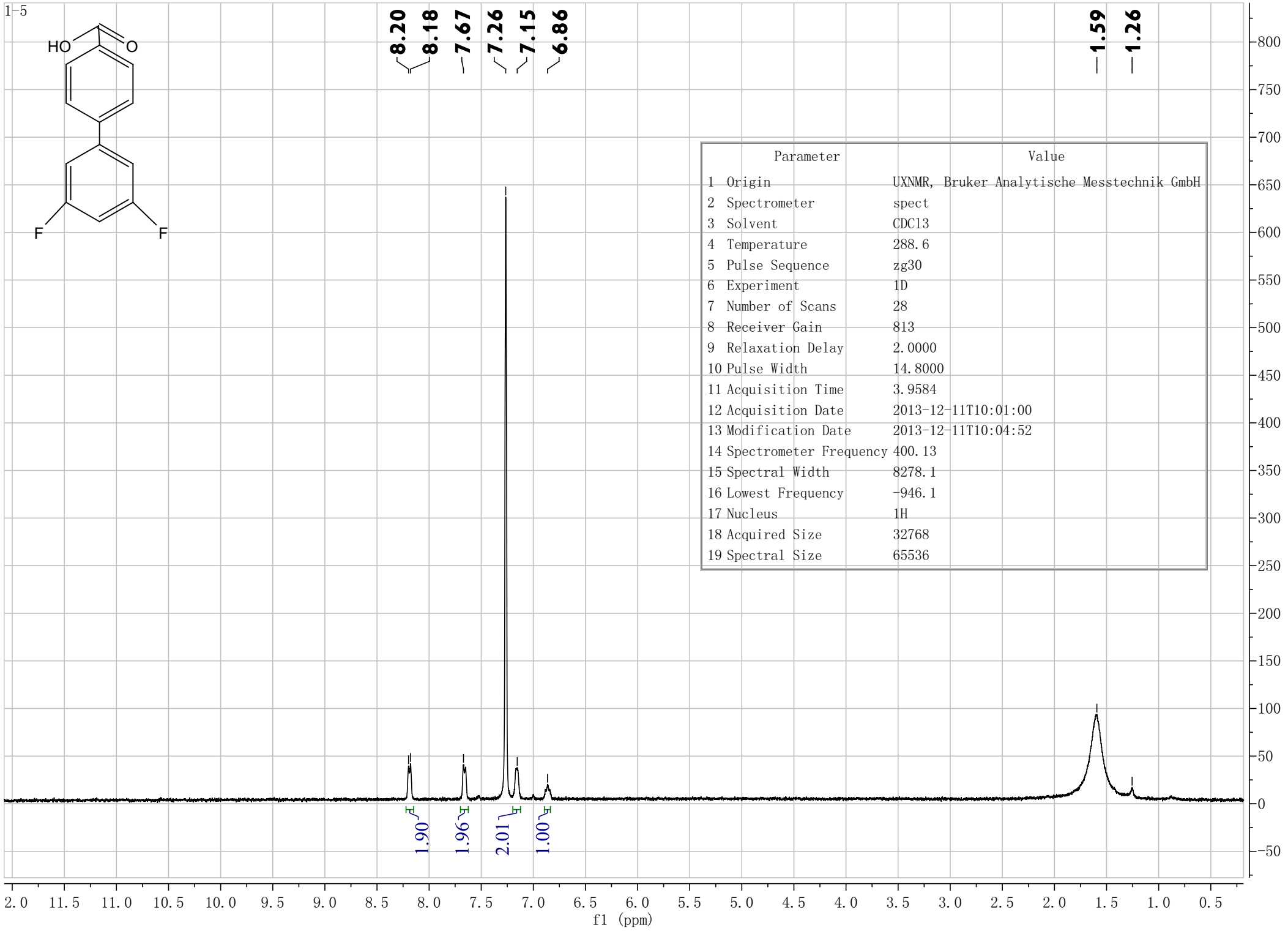
A mixture of aryl halides (1.0 mmol), aryl boronic acid (1.2 mmol), catalyst (0.1% mmol), K_2CO_3 (3.0mmol), distilled water (5.0 mL) was stirred at room temperature under air for 1.5h in a round-bottomed flask. After 1.5h, the precipitate in the mixture was filtered and washed with distilled water so that the product was separated from the mixture. Then, the precipitate was dissolved in boiling water (100 mL) for 10 min and filtered immediately under decompression to remove the by-product deriving from homo-coupling of aryl boronic acids. Next, the solution was acidized with dilute hydrochloric acid under stirring for 0.5h until the PH was up to 3~4 so that the precipitate would formed completely. Following, the white precipitate was filtered under decompression again and washed with 20mL distilled water. After that, the white solid was dissolved in 10mL ethyl acetate and two tablespoons of desiccant (Na_2SO_4 or $MgSO_4$) were added into the ethyl acetate to get rid of water from product. Finally, the solution was filtered and evaporated under vacuum, leaving the product, which is confirmed by ^{1}HNMR Spectroscopy.



experimental procedure

^{1}H NMR of products


1-10
10.71
8.09
7.72
7.70
7.26
7.12
7.09
7.07
6.79
1.64
1.26
HO
O
OH
F
F
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 288.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 26
8 Receiver Gain 813
9 Relaxation Delay 2.0000
10 Pulse Width 14.8000
11 Acquisition Time 3.9584
12 Acquisition Date 2013-12-11T10:26:00
13 Modification Date 2013-12-11T10:28:26
14 Spectrometer Frequency 400.13
15 Spectral Width 8278.1
16 Lowest Frequency -945.3
17 Nucleus 1H
18 Acquired Size 32768
19 Spectral Size 65536
0.94
1.00
1.12
3.05
1.06
f1 (ppm)



Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	288.6
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	28
8 Receiver Gain	813
9 Relaxation Delay	2.0000
10 Pulse Width	14.8000
11 Acquisition Time	3.9584
12 Acquisition Date	2013-12-11T10:01:00
13 Modification Date	2013-12-11T10:04:52
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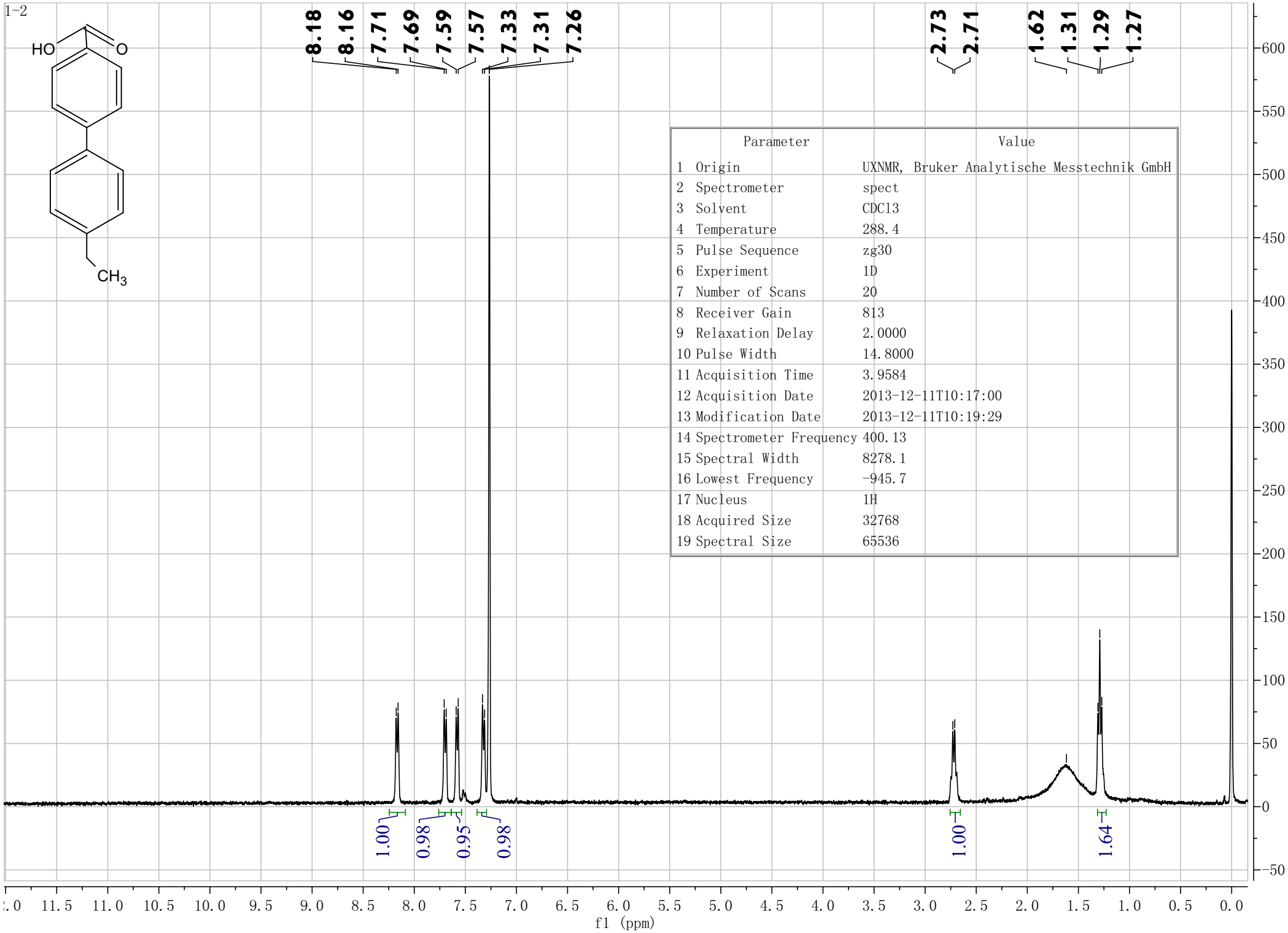
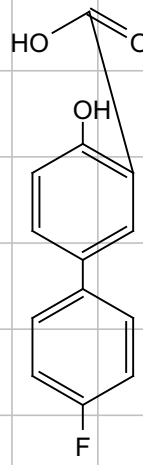
15 Spectral Width	8278.1
16 Lowest Frequency	-946.1
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	65536


1-2
HO
O
CH3
8.18
8.16
7.71
7.69
7.59
7.57
7.33
7.31
7.26
2.73
2.71
1.62
1.31
1.29
1.27
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 288.4
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 20
8 Receiver Gain 813
9 Relaxation Delay 2.0000
10 Pulse Width 14.8000
11 Acquisition Time 3.9584
12 Acquisition Date 2013-12-11T10:17:00
13 Modification Date 2013-12-11T10:19:29
14 Spectrometer Frequency 400.13
15 Spectral Width 8278.1
16 Lowest Frequency -945.7
17 Nucleus 1H
18 Acquired Size 32768
19 Spectral Size 65536
1.00
0.98
0.95
0.98
1.00
1.64
f1 (ppm)

1-9



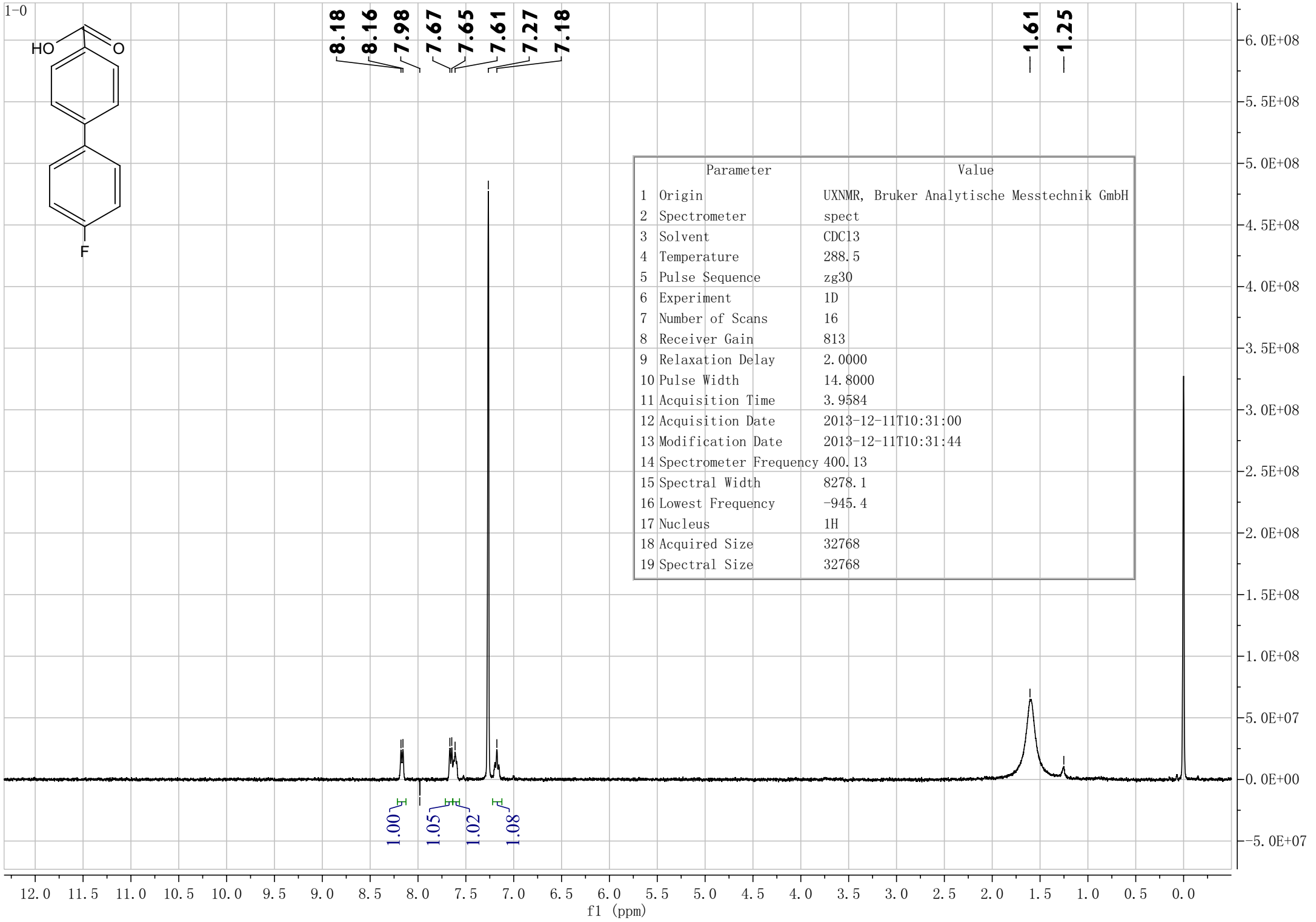
10.59 | 8.08 | 7.72 | 7.70 | 7.52 | 7.27 | 7.16 | 7.14 | 7.11 | 7.08 | 2.70 | 1.69 | 1.26

Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	288.5
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	20
8 Receiver Gain	813
9 Relaxation Delay	2.0000
10 Pulse Width	14.8000
11 Acquisition Time	3.9584
12 Acquisition Date	2013-12-11T10:22:00
13 Modification Date	2013-12-11T10:23:01
14 Spectrometer Frequency	400.13
15 Spectral Width	8278.1
16 Lowest Frequency	-945.1
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	65536

1.00 | 1.11 | 1.03 | 1.98 | 2.80

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)



	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	288.5
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	813
9	Relaxation Delay	2.0000
10	Pulse Width	14.8000
11	Acquisition Time	3.9584
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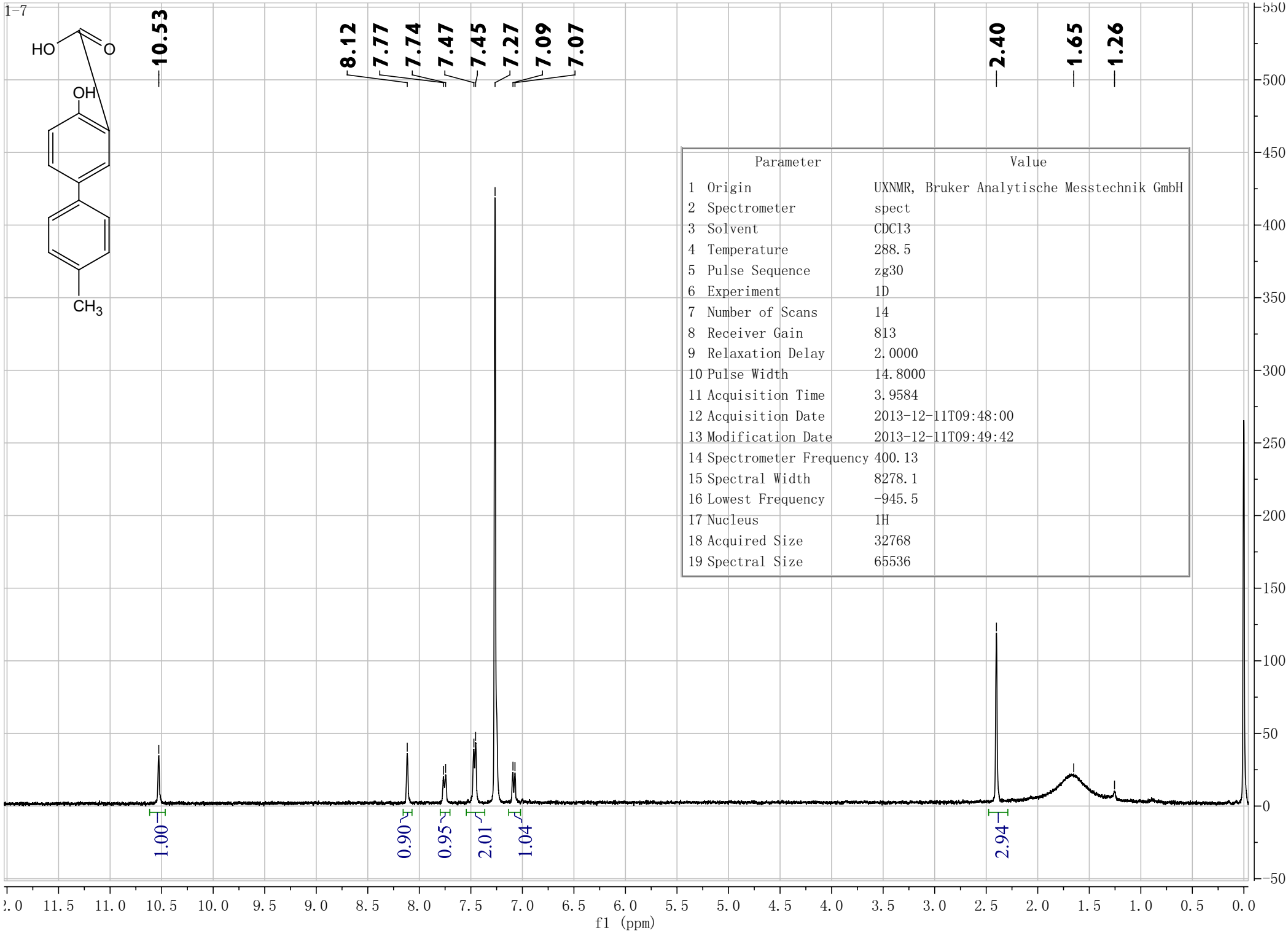
14	Spectrometer Frequency	400.13
15	Spectral Width	8278.1
16	Lowest Frequency	-945.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	32768



Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	288.5
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	14
8 Receiver Gain	813
9 Relaxation Delay	2.0000
10 Pulse Width	14.8000
11 Acquisition Time	3.9584
12 Acquisition Date	2013-12-11T09:48:00
13 Modification Date	2013-12-11T09:49:42
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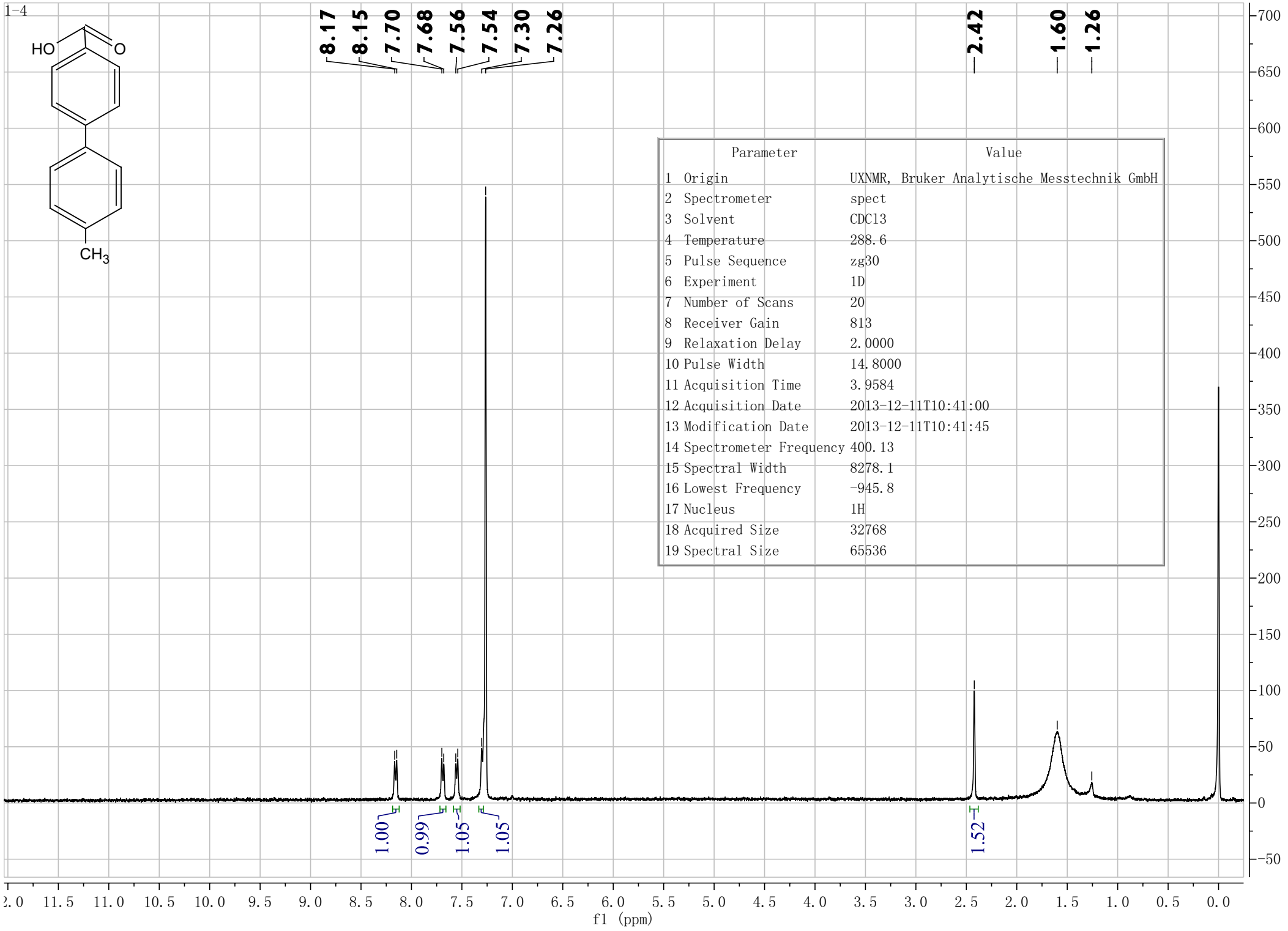
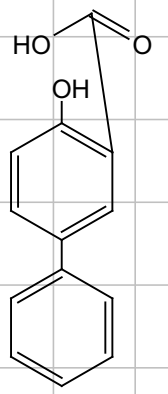
15 Spectral Width	8278.1
16 Lowest Frequency	-945.5
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	65536


1-4
HO
O
CH3
8.17
8.15
7.70
7.68
7.56
7.54
7.30
7.26
2.42
1.60
1.26
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 288.6
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 20
8 Receiver Gain 813
9 Relaxation Delay 2.0000
10 Pulse Width 14.8000
11 Acquisition Time 3.9584
12 Acquisition Date 2013-12-11T10:41:00
13 Modification Date 2013-12-11T10:41:45
14 Spectrometer Frequency 400.13
15 Spectral Width 8278.1
16 Lowest Frequency -945.8
17 Nucleus 1H
18 Acquired Size 32768
19 Spectral Size 65536
1.00
0.99
1.05
1.05
1.52
f1 (ppm)

1-6

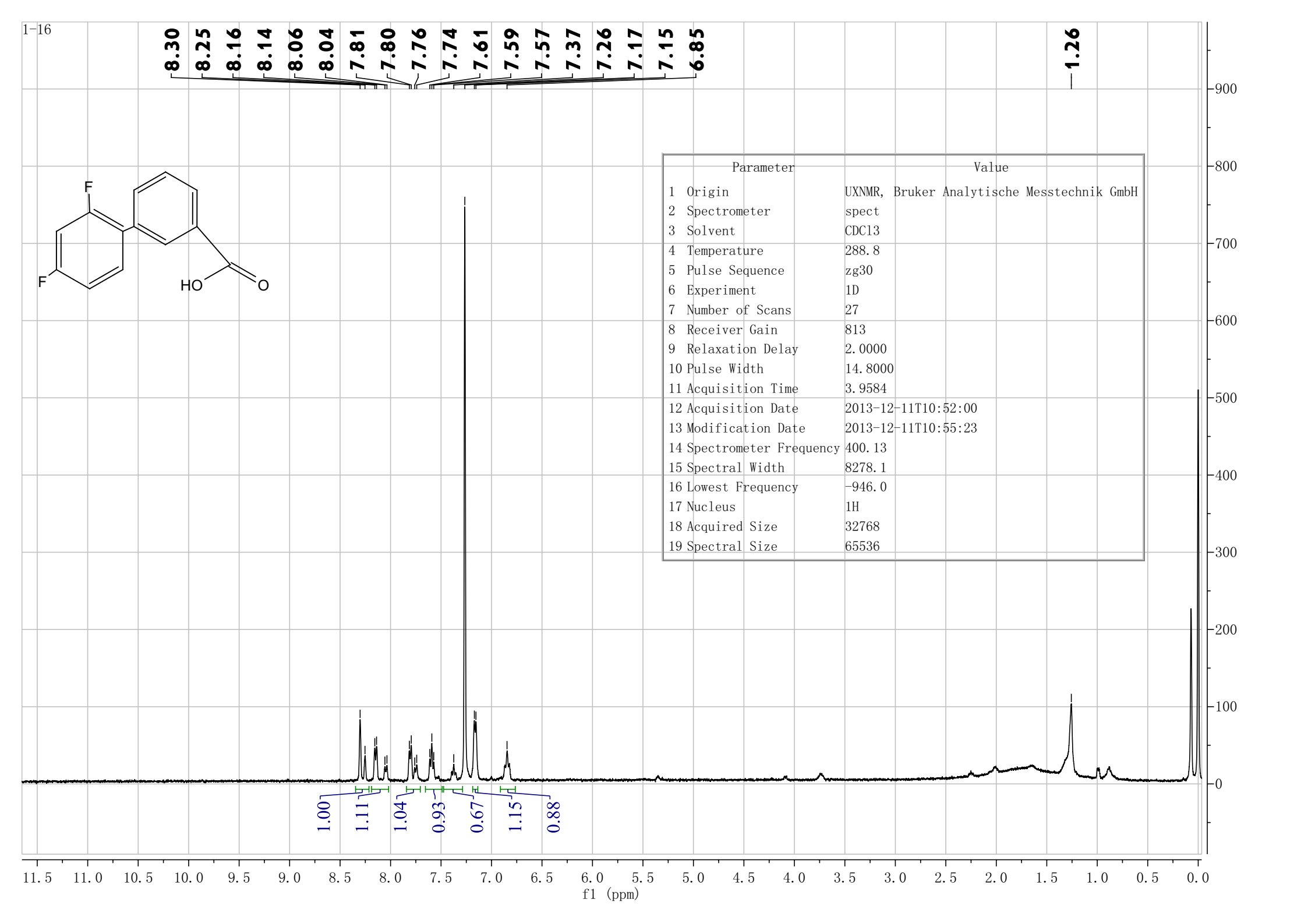


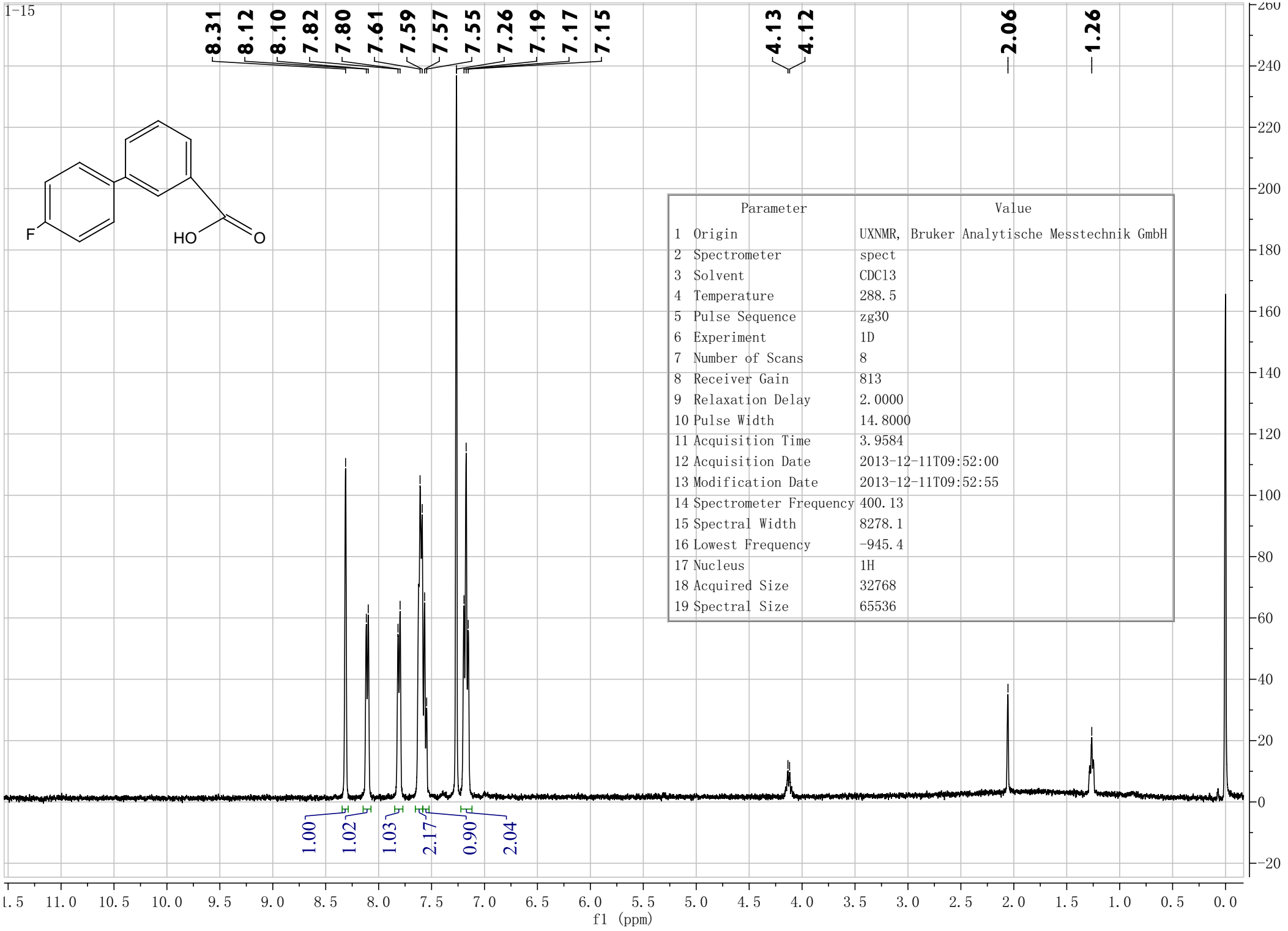
10.52 | 8.15 | 7.79 | 7.77 | 7.58 | 7.56 | 7.47 | 7.45 | 7.43 | 7.37 | 7.35 | 7.26 | 7.11 | 7.09 | 1.96 | 1.26

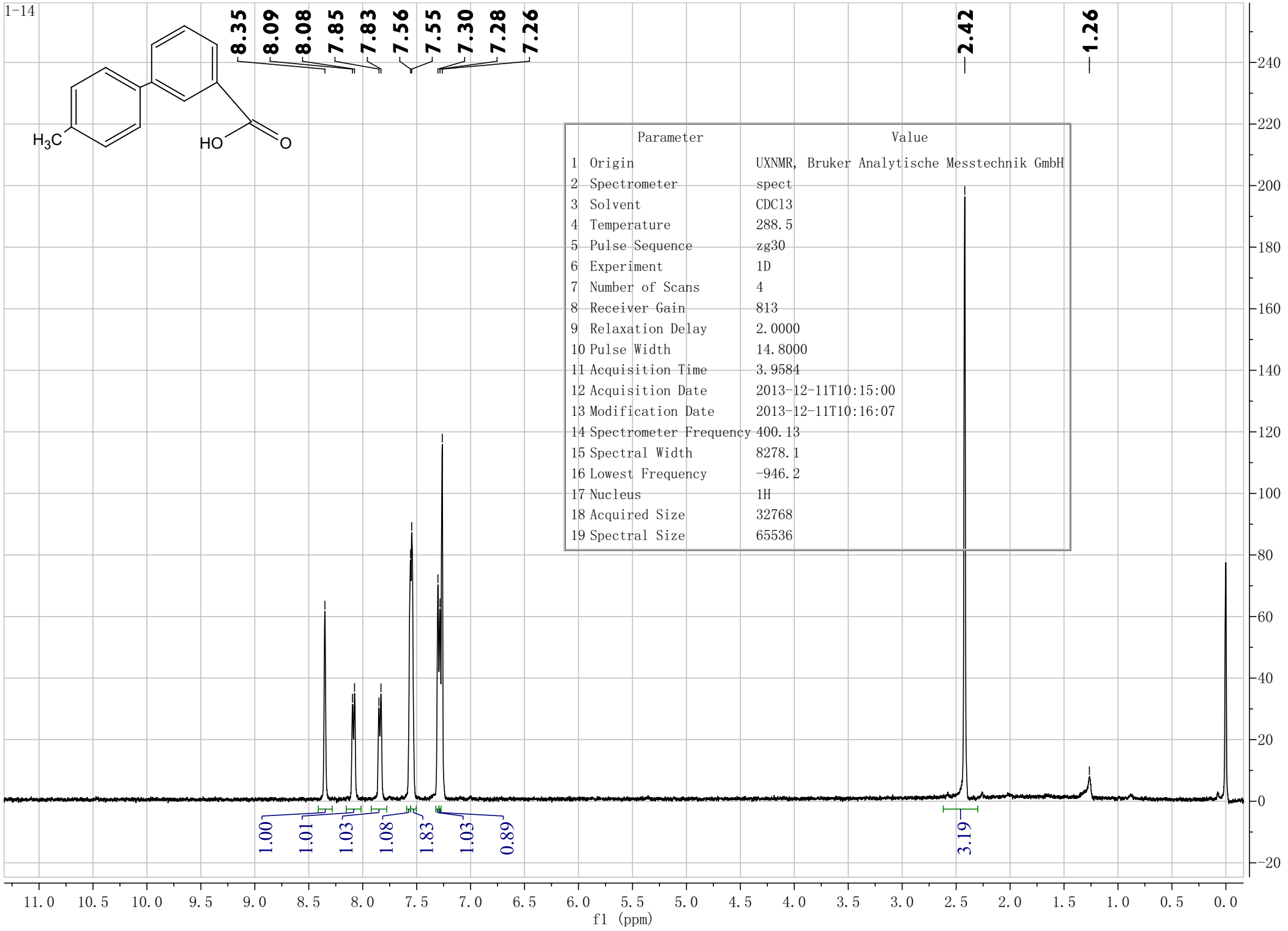
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	288.7
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	20
8 Receiver Gain	813
9 Relaxation Delay	2.0000
10 Pulse Width	14.8000
11 Acquisition Time	3.9584
12 Acquisition Date	2013-12-11T10:47:00
13 Modification Date	2013-12-11T10:47:55
14 Spectrometer Frequency	400.13
15 Spectral Width	8278.1
16 Lowest Frequency	-946.0
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	65536

1.09 | 1.00 | 1.02 | 1.89 | 1.97 | 1.10 | 1.06

f1 (ppm)


1-16
8.30
8.25
8.16
8.14
8.06
8.04
7.81
7.80
7.76
7.74
7.61
7.59
7.57
7.37
7.26
7.17
7.15
6.85
1.26
F
F
HO
O
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 288.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 27
8 Receiver Gain 813
9 Relaxation Delay 2.0000
10 Pulse Width 14.8000
11 Acquisition Time 3.9584
12 Acquisition Date 2013-12-11T10:52:00
13 Modification Date 2013-12-11T10:55:23
14 Spectrometer Frequency 400.13
15 Spectral Width 8278.1
16 Lowest Frequency -946.0
17 Nucleus 1H
18 Acquired Size 32768
19 Spectral Size 65536
1.00
1.11
1.04
0.93
0.67
1.15
0.88
f1 (ppm)


1-15
8.31
8.12
8.10
7.82
7.80
7.61
7.59
7.57
7.55
7.26
7.19
7.17
7.15
4.13
4.12
2.06
1.26
F
HO
O
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 288.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 8
8 Receiver Gain 813
9 Relaxation Delay 2.0000
10 Pulse Width 14.8000
11 Acquisition Time 3.9584
12 Acquisition Date 2013-12-11T09:52:00
13 Modification Date 2013-12-11T09:52:55
14 Spectrometer Frequency 400.13
15 Spectral Width 8278.1
16 Lowest Frequency -945.4
17 Nucleus 1H
18 Acquired Size 32768
19 Spectral Size 65536
1.00
1.02
1.03
2.17
0.90
2.04
f1 (ppm)


1-14
8.35
8.09
8.08
7.85
7.83
7.56
7.55
7.30
7.28
7.26
2.42
1.26
H3C
HO
O
Parameter Value
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2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 288.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 4
8 Receiver Gain 813
9 Relaxation Delay 2.0000
10 Pulse Width 14.8000
11 Acquisition Time 3.9584
12 Acquisition Date 2013-12-11T10:15:00
13 Modification Date 2013-12-11T10:16:07
14 Spectrometer Frequency 400.13
15 Spectral Width 8278.1
16 Lowest Frequency -946.2
17 Nucleus 1H
18 Acquired Size 32768
19 Spectral Size 65536
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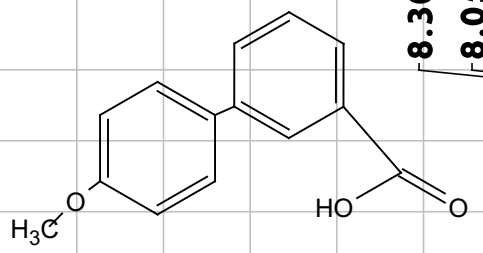
1.01
1.03
1.08
1.83
1.03
0.89
3.19
f1 (ppm)

1-13



8.30 8.05 8.03 7.80 7.59 7.57 7.53 7.26 7.02 7.00

3.87

1.59 1.26

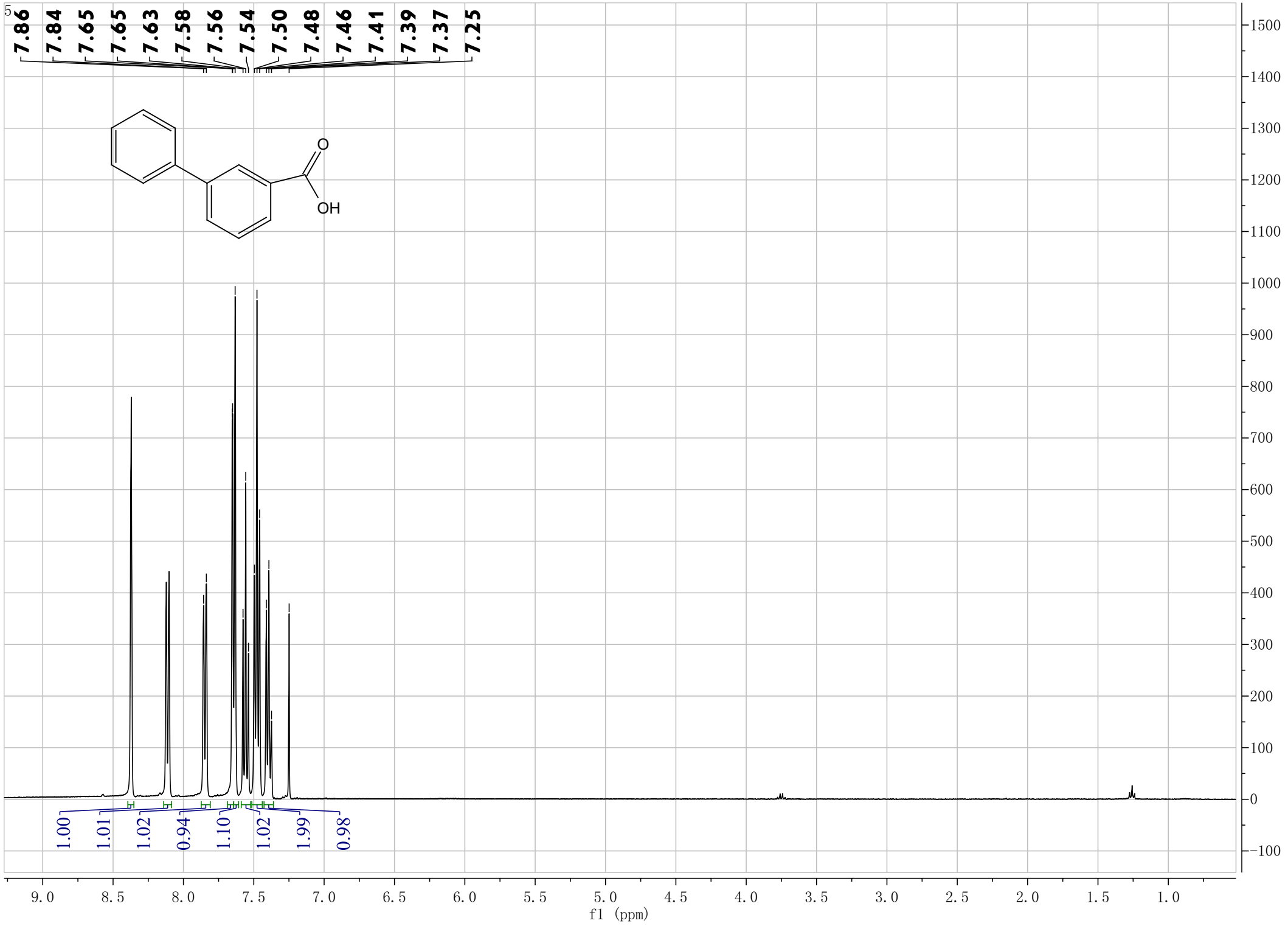
Parameter	Value
1 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	288.6
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	2
8 Receiver Gain	813
9 Relaxation Delay	2.0000
10 Pulse Width	14.8000
11 Acquisition Time	3.9584
12 Acquisition Date	2013-12-11T10:43:00
13 Modification Date	2013-12-11T10:43:34
14 Spectrometer Frequency	400.13
15 Spectral Width	8278.1
16 Lowest Frequency	-945.7
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	65536

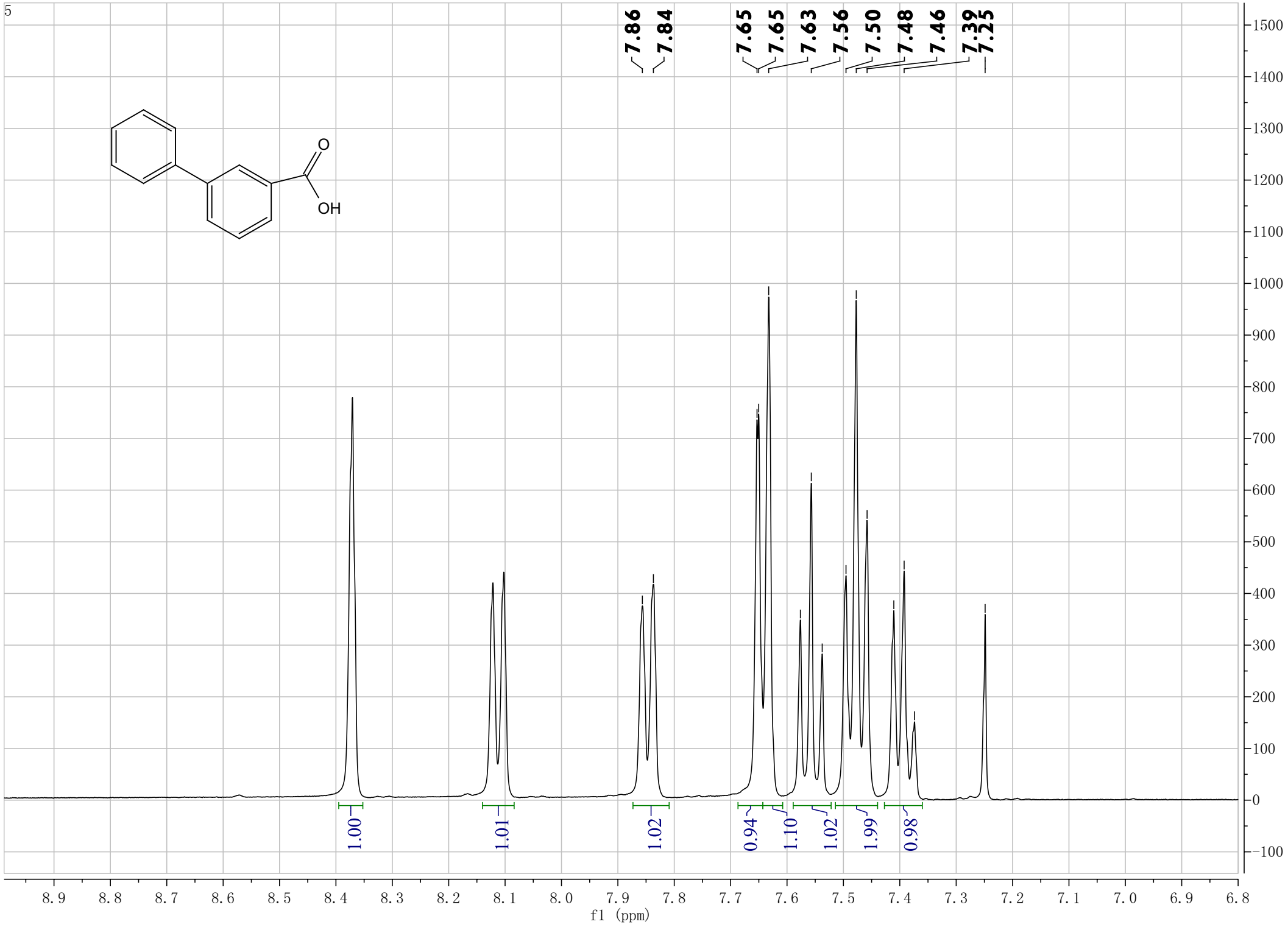
1.00 1.06 1.00 1.90 0.90 2.00

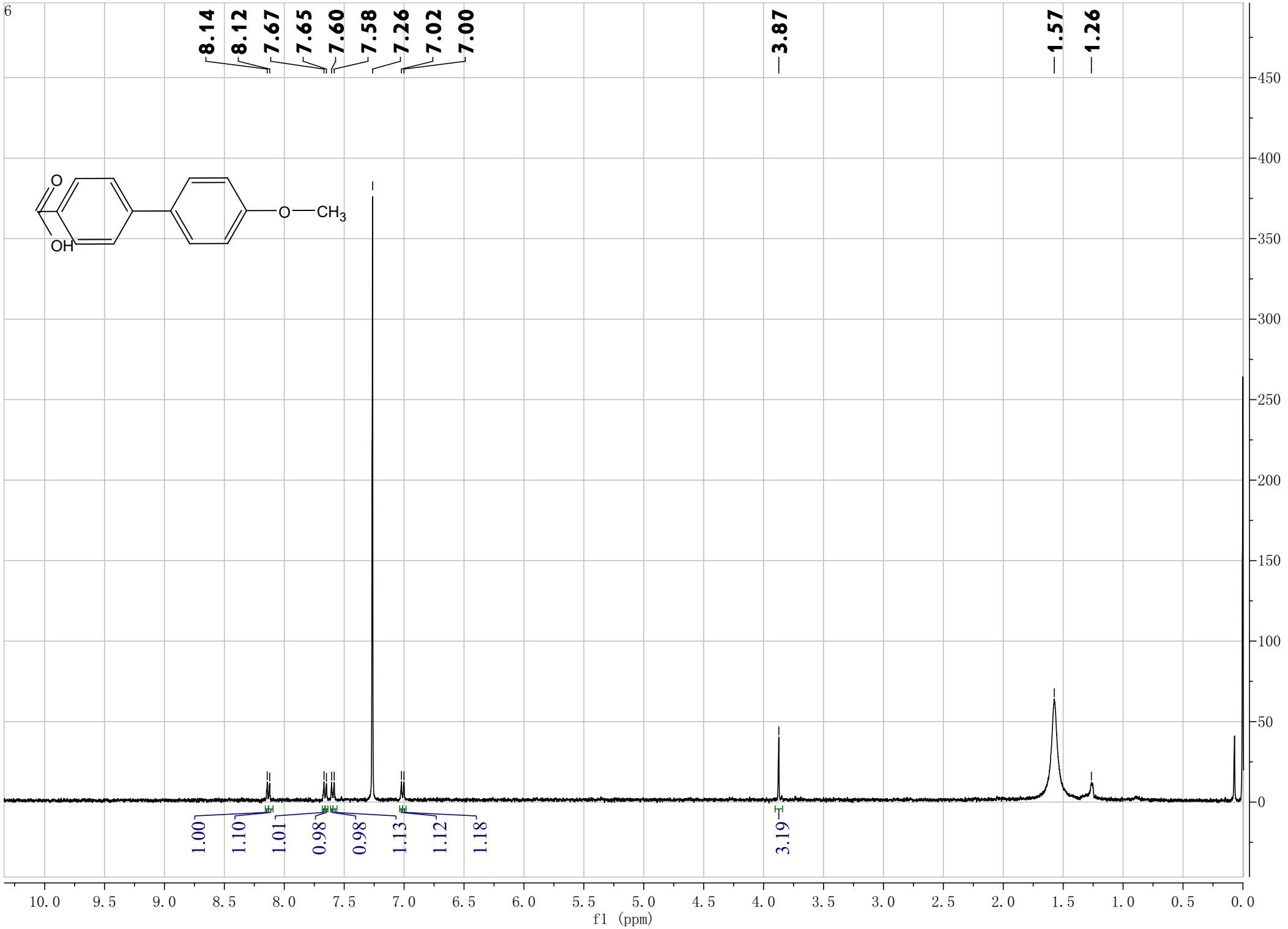
2.89

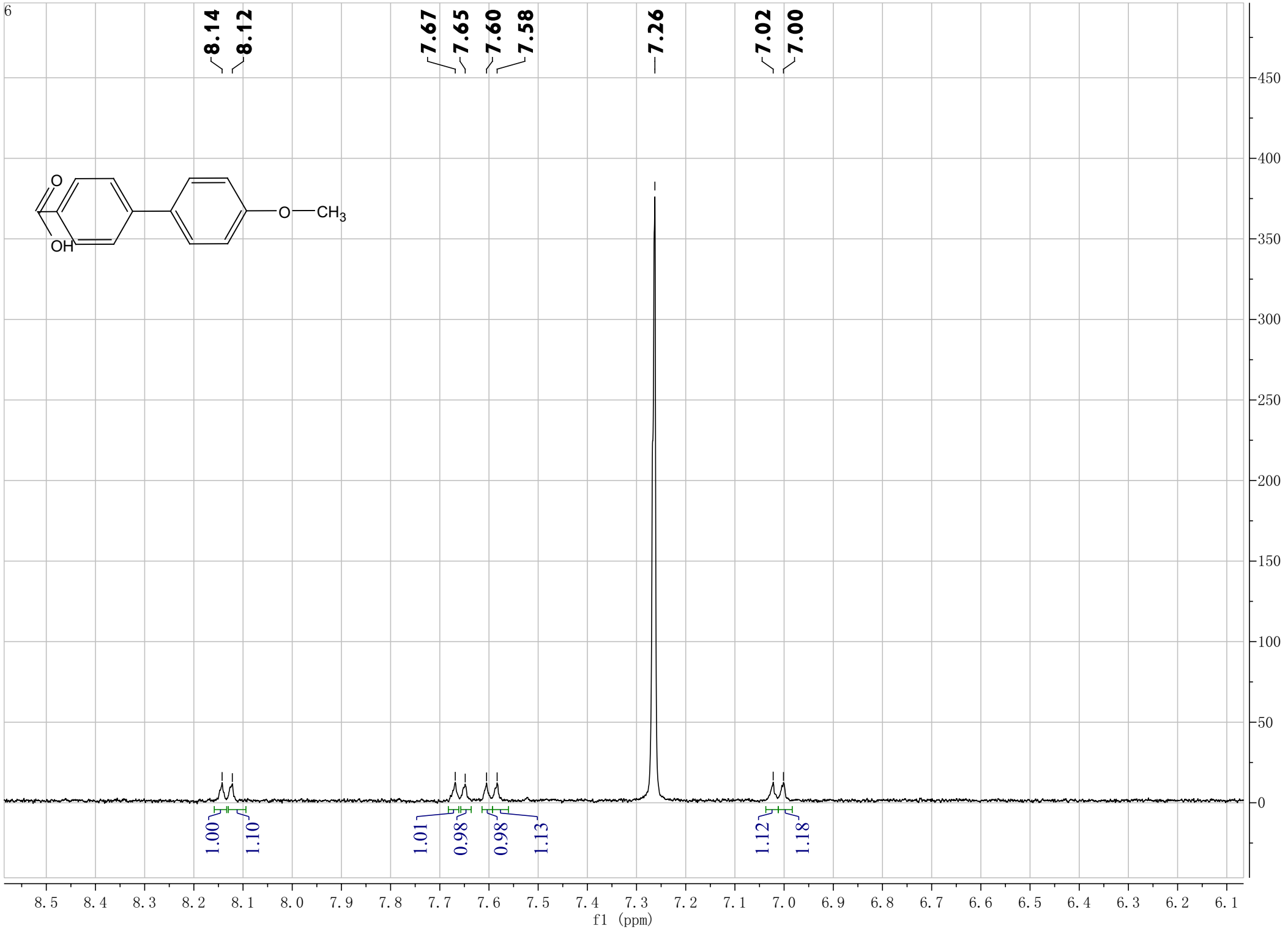
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

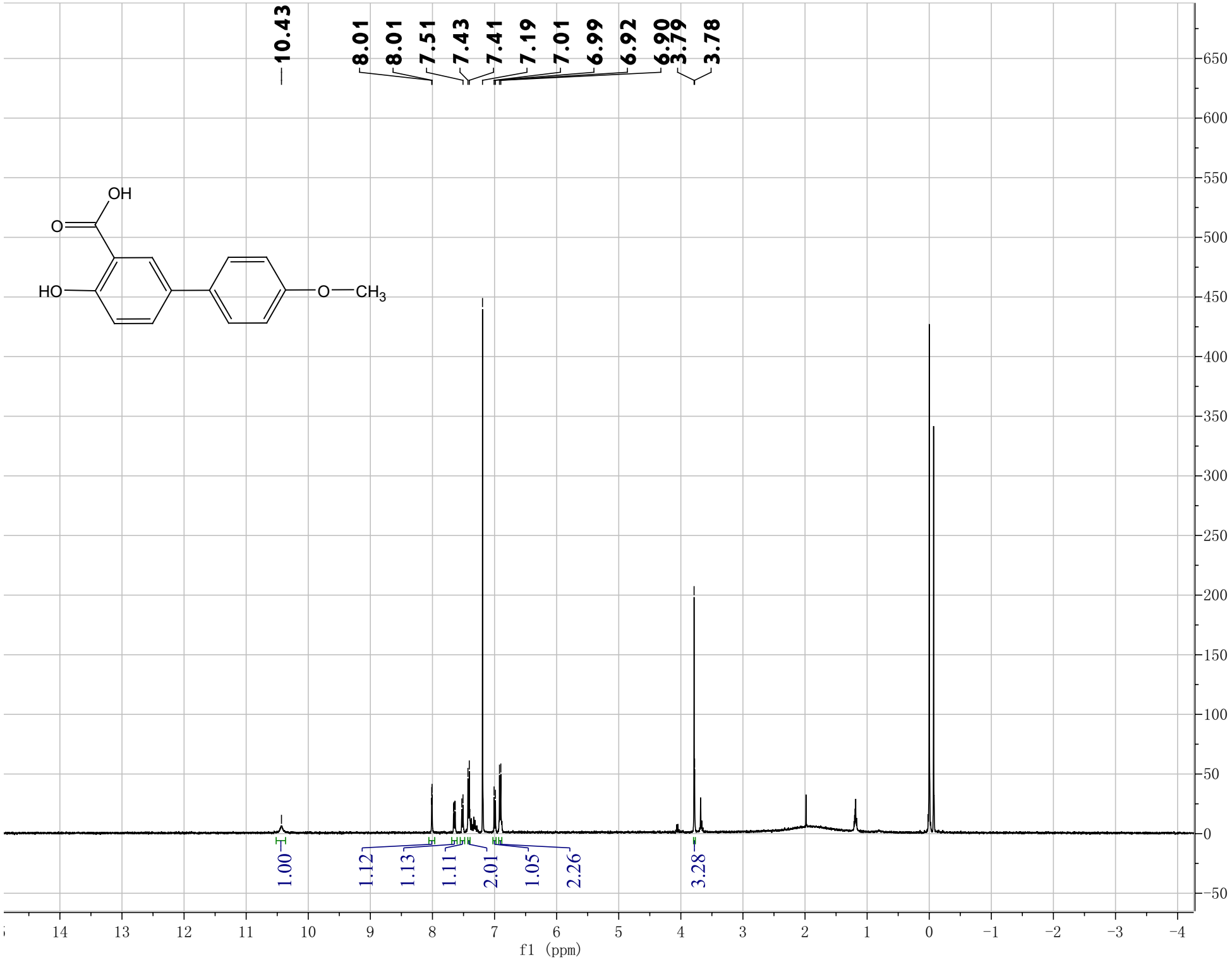
f1 (ppm)

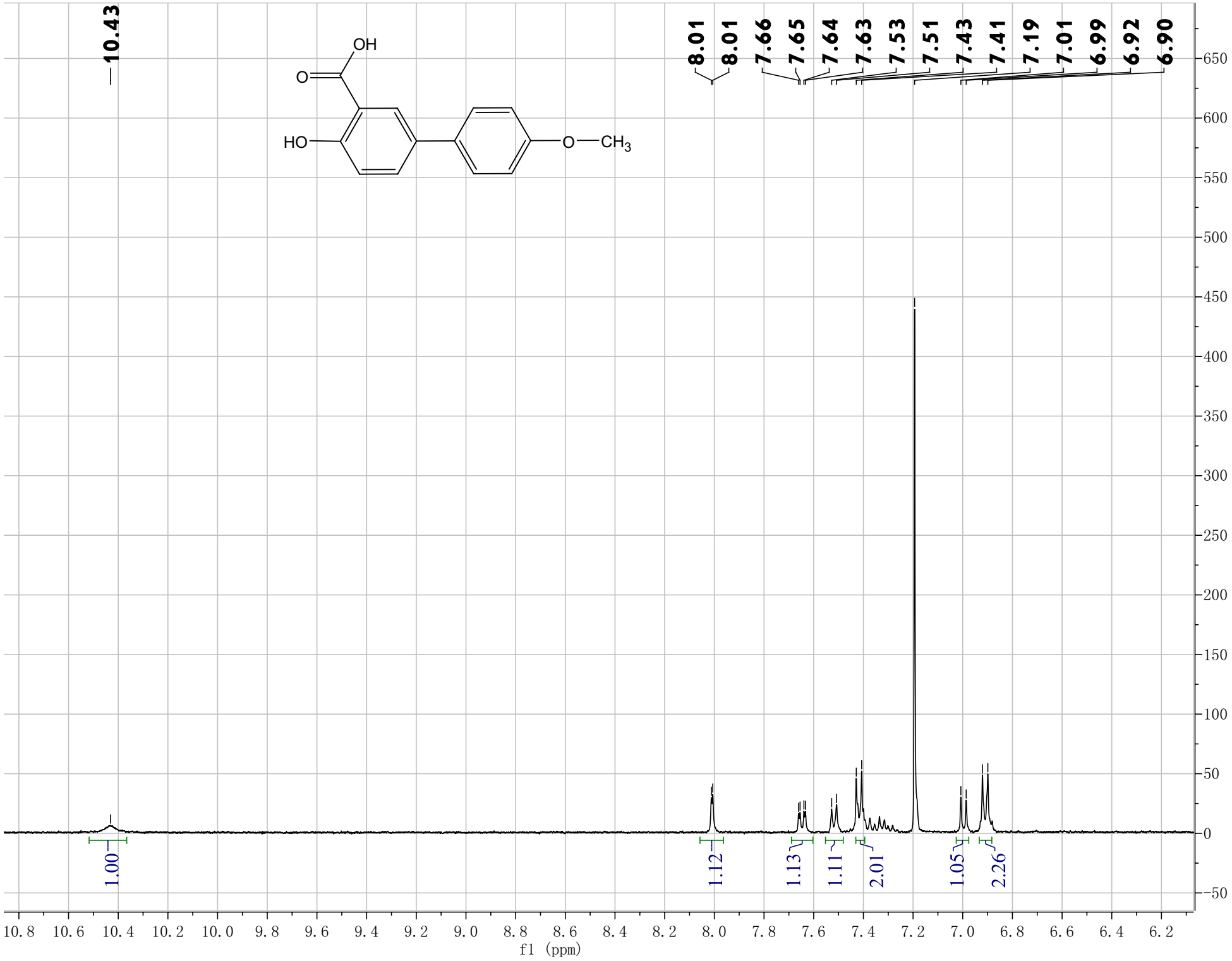

7.86
7.84
7.65
7.65
7.63
7.58
7.56
7.54
7.50
7.48
7.46
7.41
7.39
7.37
7.25
O
OH
1.00
1.01
1.02
0.94
1.10
1.02
1.99
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

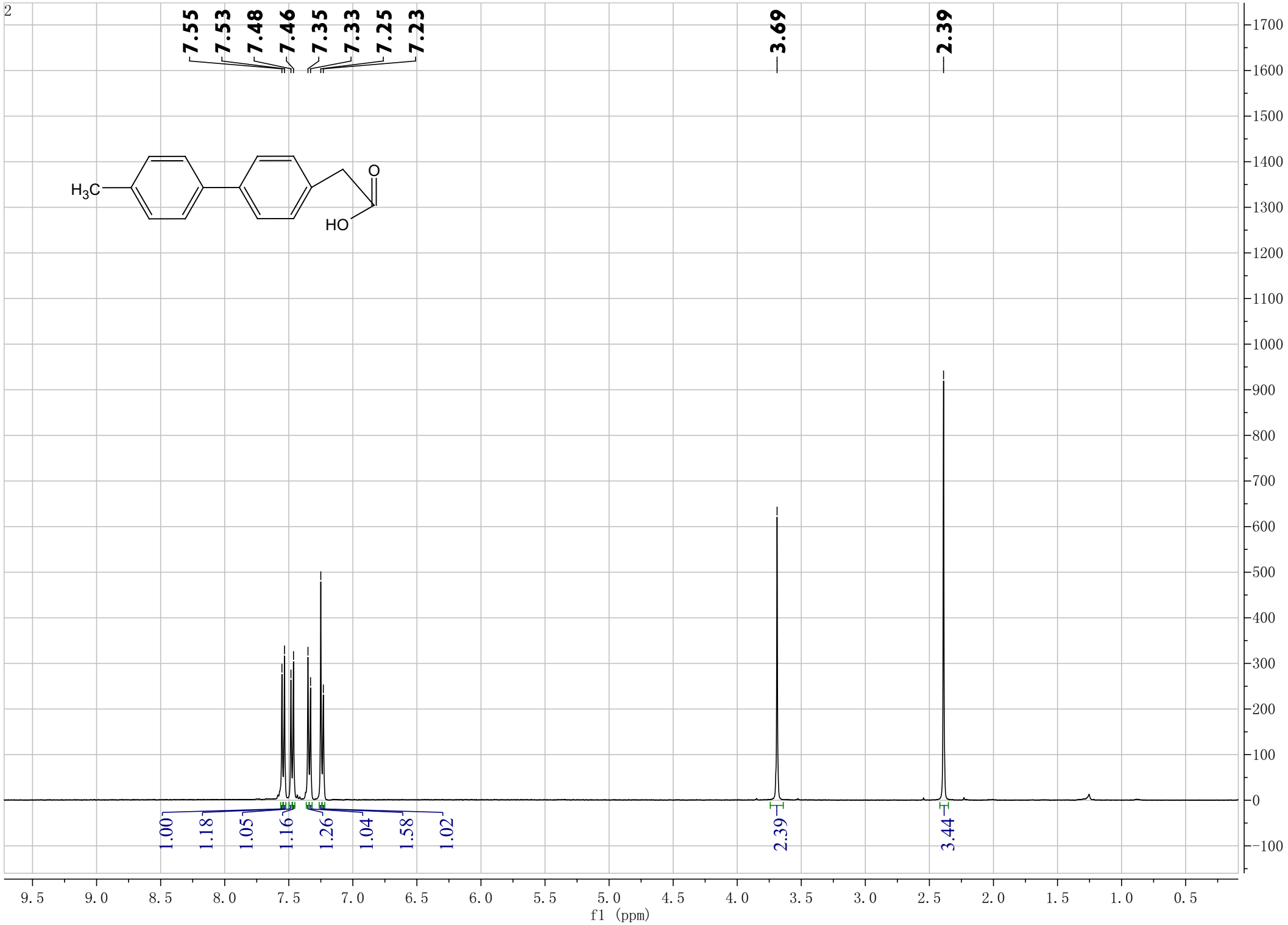

5
7.86
7.84
7.65
7.65
7.63
7.56
7.50
7.48
7.46
7.39
7.25
O
OH
1.00
1.01
1.02
0.94
1.10
1.02
1.99
0.98
f1 (ppm)

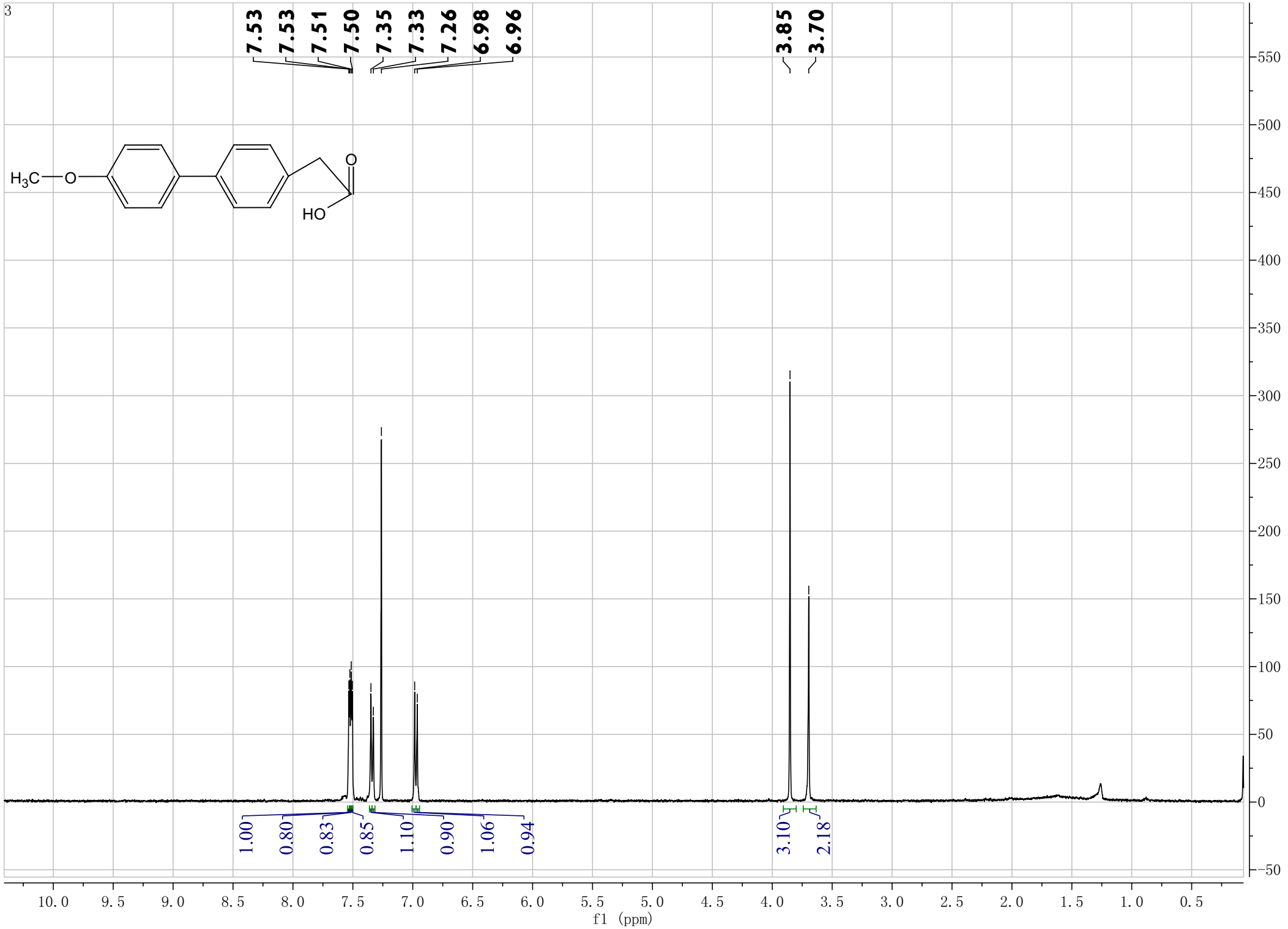

6
8.14
8.12
7.67
7.65
7.60
7.58
7.26
7.02
7.00
3.87
1.57
1.26
O
OH
O—CH3
1.00
1.10
1.01
0.98
0.98
1.13
1.12
1.18
3.19
450
400
350
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


6
8.14
8.12
7.67
7.65
7.60
7.58
7.26
7.02
7.00
O
OH
O—CH3
1.00
1.10
1.01
0.98
0.98
1.13
1.12
1.18
450
400
350
300
250
200
150
100
50
0
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1
f1 (ppm)


10.43
8.01
8.01
7.51
7.43
7.41
7.19
7.01
6.99
6.92
6.90
3.79
3.78
OH
O
HO
O—CH3
1.00
1.12
1.13
1.11
2.01
1.05
2.26
3.28
f1 (ppm)


10.43
OH
O
HO
O—CH3
8.01
8.01
7.66
7.65
7.64
7.63
7.53
7.51
7.43
7.41
7.19
7.01
6.99
6.92
6.90
1.00
1.12
1.13
1.11
2.01
1.05
2.26
f1 (ppm)


2
7.55
7.53
7.48
7.46
7.35
7.33
7.25
7.23
3.69
2.39
H3C
O
HO
1.00
1.18
1.05
1.16
1.26
1.04
1.58
1.02
2.39
3.44
f1 (ppm)


3
7.53
7.53
7.51
7.50
7.35
7.33
7.26
6.98
6.96
3.85
3.70
H3C—O
O
HO
1.00
0.80
0.83
0.85
1.10
0.90
1.06
0.94
3.10
2.18
f1 (ppm)