Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

H_2O_2 in WEB: a highly efficient catalyst system for the Dakin reaction

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Contents

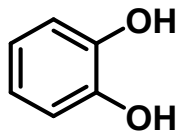
Materials and Methods

Compounds were purchased from Aldrich and Alfa Aesar. All other chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz using TMS as internal standard. Chemical shifts are recorded in reference to residual solvent peaks (DMSO-d6 = 2.50 ppm, $CDCl_3$ = 7.26 ppm). TLC experiments were performed on EMD Merck F_{254}, 250 mm thickness. Column chromatography was performed with Merck silica gel (100–200 mesh).

General experimental procedure

In a round bottomed flask, hydroxylated benzaldehyde (1 mmol) in WEB (3 mL) was taken and H_2O_2 (2 equiv.) was added to the same and stirred at room temperature for a time period as mentioned in **Table 2** in the manuscript. The progress of the reaction was monitored by TLC. After completion of the reaction it was extracted with ethyl acetate (3 x 10 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by column chromatography over silica gel using *n*-hexane/ethyl acetate (4:1 v/v) to get the desired coupling product. The products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Characterization data of the product of the Dakin reaction[1–7]

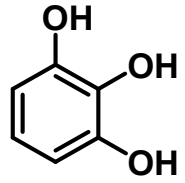


Catechol (Table 2; Entry 1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90–6.84 (m, 2 H), 6.84–6.78 (m, 2 H), 5.38–5.29 ppm (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 121.1, 115.4 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).

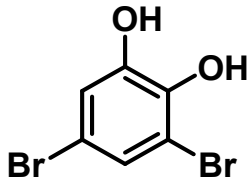
Hydroquinone (Table 2; Entry 2)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.64 (s, 2 H), 6.56 ppm (s, 4 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 150.06, 116.05 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



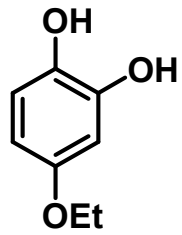
3-Hydroxycatechol (Table 2; Entry 3)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.75 (brs, 2 H), 8.03 (brs, 1 H), 6.43–6.39 (m, 1 H), 6.27–6.23 ppm (m, 2 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 146.5, 133.4, 118.7, 107.3 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



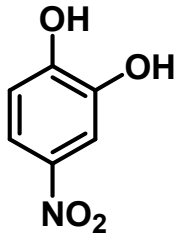
3,5-Dibromocatechol (Table 2; Entry 4)

^{1}H NMR (500 MHz, DMSO-d6) δ 10.36 (brs, 1 H), 9.48 (brs, 1 H), 7.09 (s, 1 H), 6.91 ppm (s, 1 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 147.7, 143.1, 124.6, 117.4, 110.7, 110.1 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



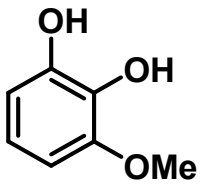
4-Ethoxycatechol (Table 2; Entry 5)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.84 (s, 1 H), 8.05 (s, 1 H), 6.53–6.48 (m, 1 H), 6.42–6.38 (m, 2 H), 3.99 (q, *J* = 5 Hz, 2 H), 1.34 ppm (t, *J* = 10 Hz, 3 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 147.9, 146.3, 134.8, 118.6, 109.3, 105.2, 64.3, 15.1 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



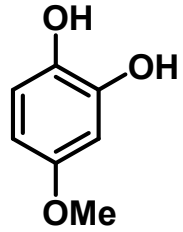
4-Nitrocatechol (Table 2; Entry 6)

^{1}H NMR (500 MHz, DMSO-d6) δ 10.29 (brs, 2 H), 7.67 (d, *J* = 8.5 Hz, 1 H), 7.60 (s, 1 H), 6.9 ppm (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 153.2, 145.7, 139.8, 116.8, 115.3, 110.7 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



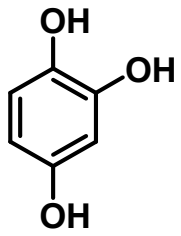
3-Methoxycatechol (Table 2; Entry 7)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.82 (s, 1 H), 8.20 (s, 1 H), 6.59 (t, *J* = 3.5 Hz, 1 H), 6.44 (d, *J* = 1.5 Hz, 1 H), 6.43 (d, *J* = 4.5 Hz, 1 H), 3.73 ppm (s, 3 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 148.8, 146.2, 134.4, 118.6, 109.3, 103.8, 50.09 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



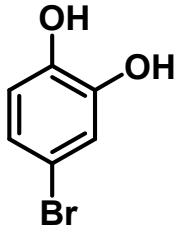
4-Methoxycatechol (Table 2; Entry 8)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.80 (s, 1 H), 8.20 (s, 1 H), 6.58–6.54 (m, 1 H), 6.41 (d, *J* = 4.0 Hz, 1 H), 6.39 (s, 1 H), 3.73 ppm (s, 3 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 150.09, 148.2, 135.1, 118.7, 109.7, 103.7, 56.2 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



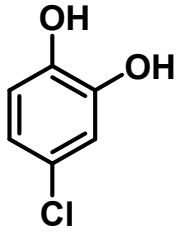
4-Hydroxycatechol (Table 2; Entry 9)

^{1}H NMR (500 MHz, DMSO-d6) δ 10.67 (s, 1 H), 10.32 (s, 1 H), 9.84 (s, 1 H), 7.1 (d, *J* = 8.5 Hz, 1 H), 6.49 (d, *J* = 8.5 Hz, 1 H), 6.35 ppm (s, 1 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 153.6, 151.3, 137.3, 118.5, 108.7, 103.3 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



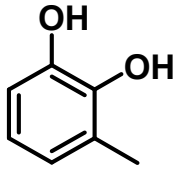
4-Bromocatechol (Table 2; Entry 10)

^{1}H NMR (500 MHz, DMSO-d6) δ 9.41 (brs, 1 H), 9.21 (brs, 1 H), 6.90 (d, *J* = 2.5 Hz, 1 H), 6.79–6.75 (m, 1 H), 6.72 ppm (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 147.07, 145.31, 122.04, 118.4, 117.5, 109.9 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



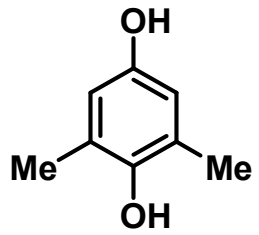
4-Chlorocatechol (Table 2; Entry 11)

^{1}H NMR (500 MHz, DMSO-d6) δ 9.38 (brs, 1 H), 9.16 (brs, 1 H), 6.75–6.73 (m, 1 H), 6.71–6.69 (m, 1 H), 6.62–6.60 ppm (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 144.8, 122.4, 119.06, 116.8, 115.7 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



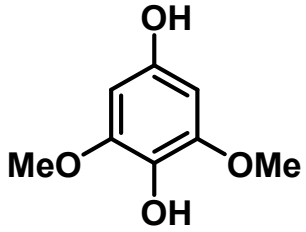
3-Methylcatechol (Table 2; Entry 12)

^{1}H NMR (500MHz, DMSO-d6) δ 8.82 (s, 1 H), 8.2 (s, 1 H), 6.58 (t, J = 8 Hz, 1 H), 6.44 (d, J = 6 Hz, 1 H), 6.42 (d, J = 3.5 Hz, 1 H), 2.37 ppm (s, 3 H); ^{13}C NMR (125MHz, DMSO-d6) δ 144.8, 142.2, 125.8, 123.2, 120.6, 113.3, 15.09 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



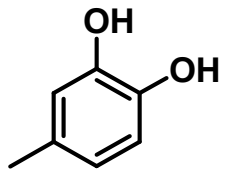
2,6-Dimethylhydroquinone (Table 2; Entry 13)

^{1}H NMR (500MHz, DMSO-d6) δ 8.43 (s, 1 H), 7.38 (s, 1 H), 6.27 (s, 2 H), 2.03 ppm (s, 6 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 150.2, 145.8, 125.9, 115.07, 17.3 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



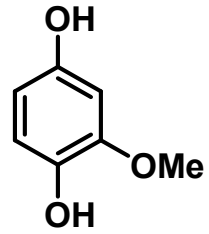
2,6-Dimethoxy-1,4-benzenediol (Table 2; Entry 14)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (s, 2 H), 3.81 ppm (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 141.1, 124.1, 122.05, 119.2, 113.4, 56.7 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



4-Methylbenzene-1,2-diol (Table 2; Entry 15)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.70 (s, 1 H), 8.56 (s, 1 H), 6.59 (d, J = 1.0 Hz, 1 H), 6.52 (s, 1 H), 6.40 (d, J = 8 Hz, 1 H), 2.12 ppm (s, 3 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 145.2, 143.2, 128.2, 119.8, 116.7, 115.7, 20.6 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).



2-Methoxybenzene-1,4-diol (Table 2; Entry 16)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (d, *J* = 2.5 Hz, 1 H), 6.43–6.40 (m, 1 H), 6.34 (s, 1 H), 5.23 (s, 1 H), 5.02 (s, 1 H), 3.84 ppm (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 147.8, 139.6, 114.4, 106.9, 99.8, 56.4 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (4:1 v/v).

References

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5. A. Roy, K. R. Reddy, P. K. Mohanta, H. Ila and H. Junjappa, *Synth. Commun*., 1999, **29**, 3781–3791.
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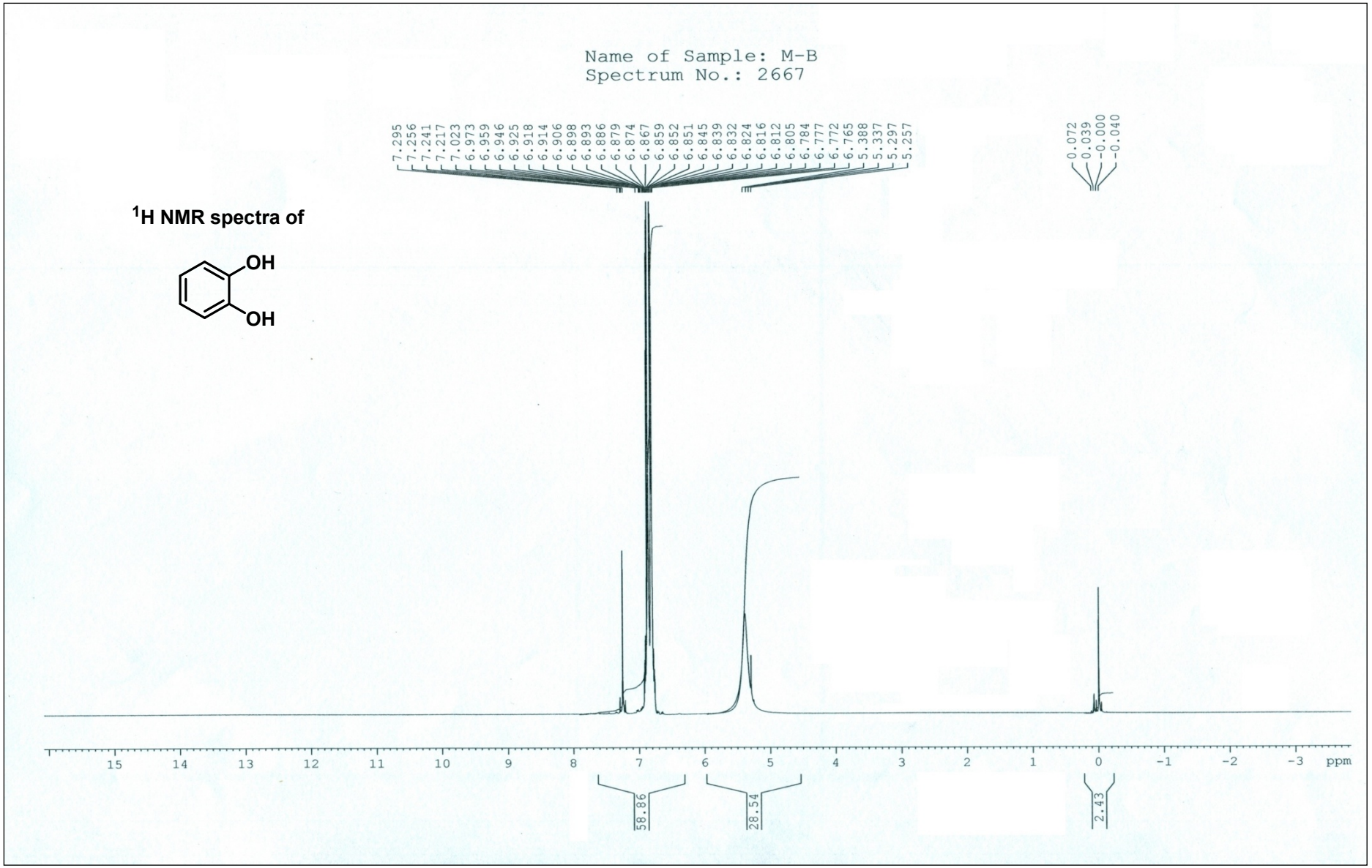

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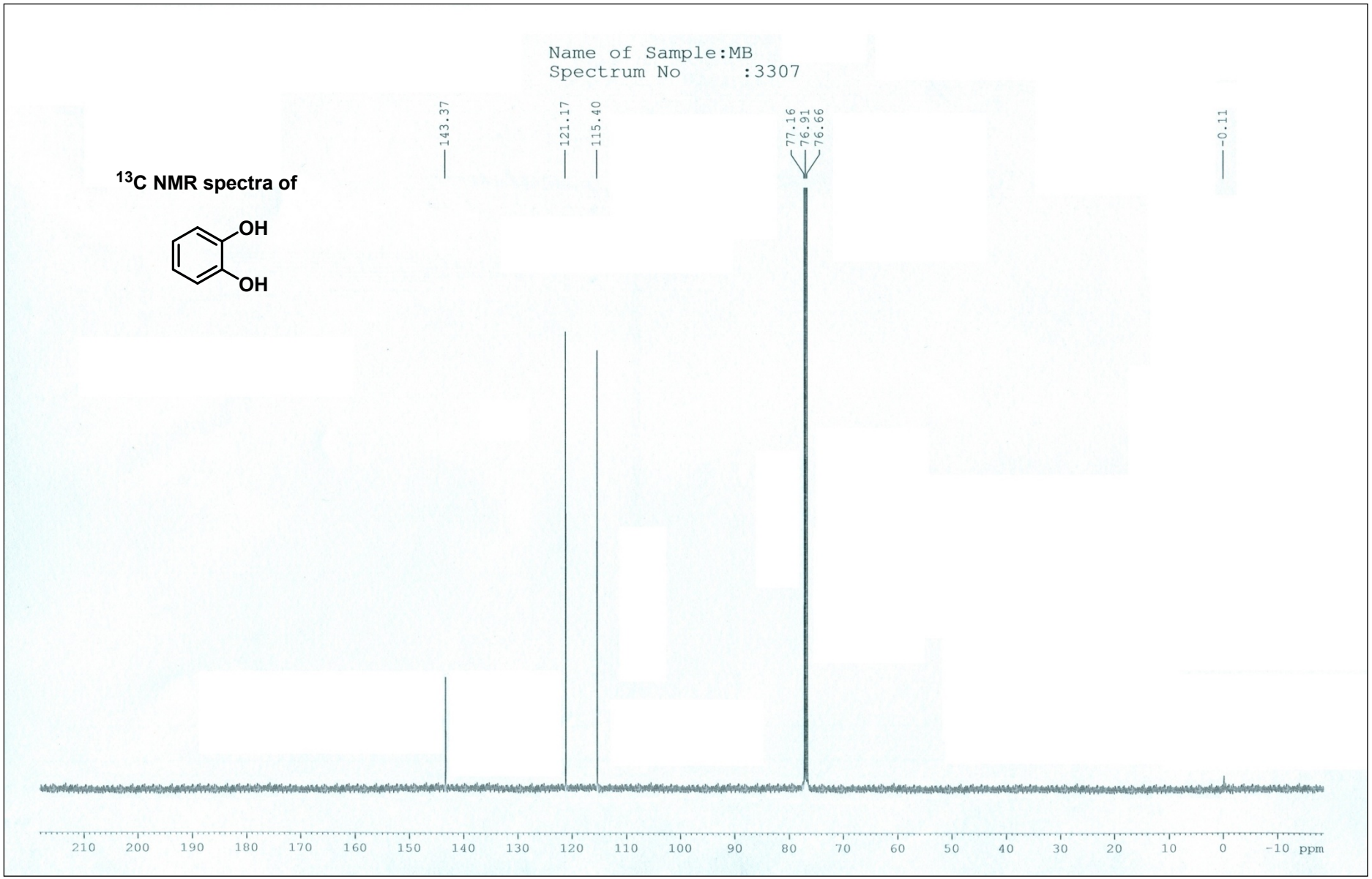
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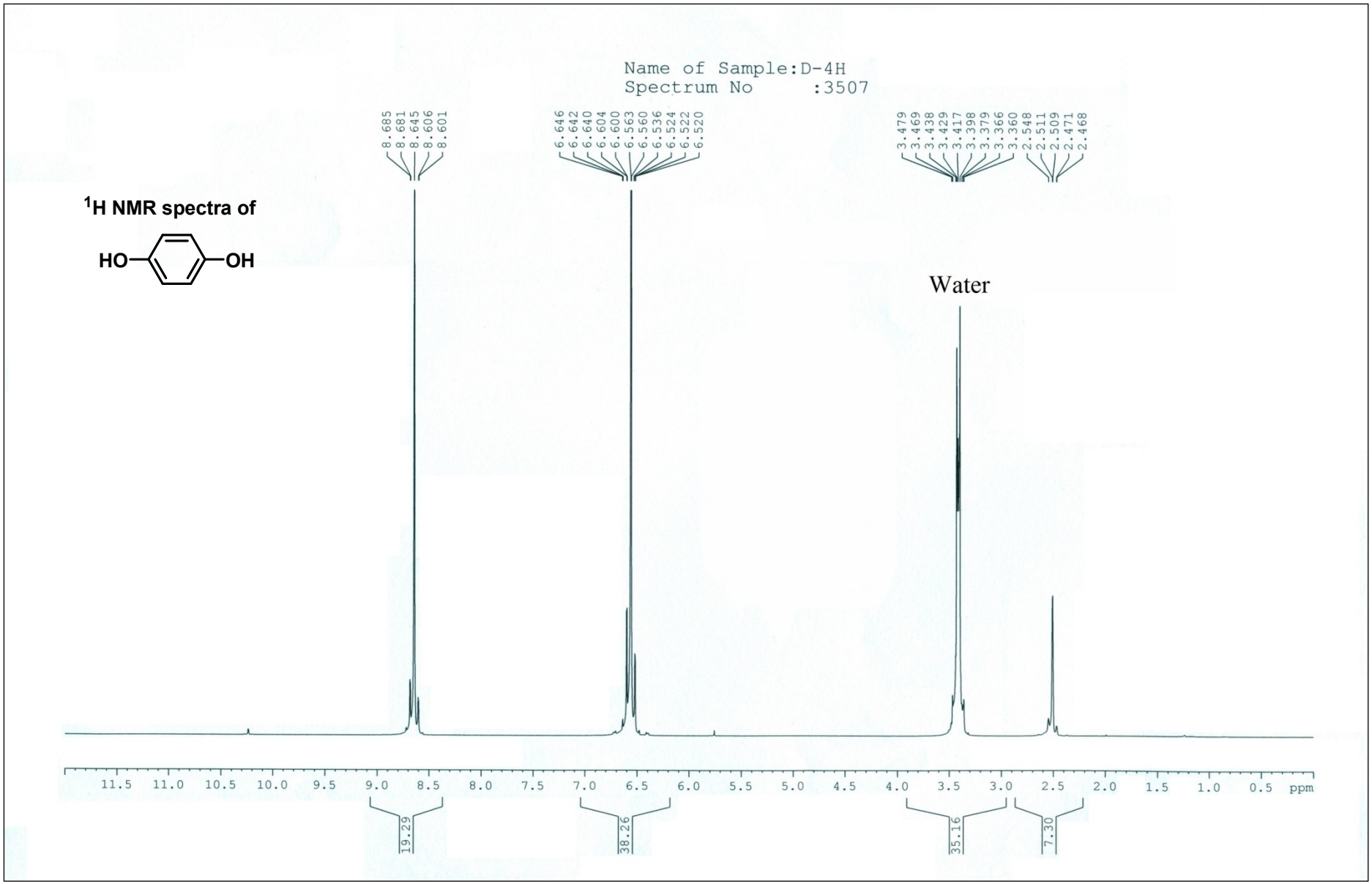
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3.360
2.548
2.511
2.509
2.471
2.468
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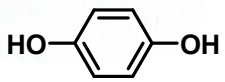

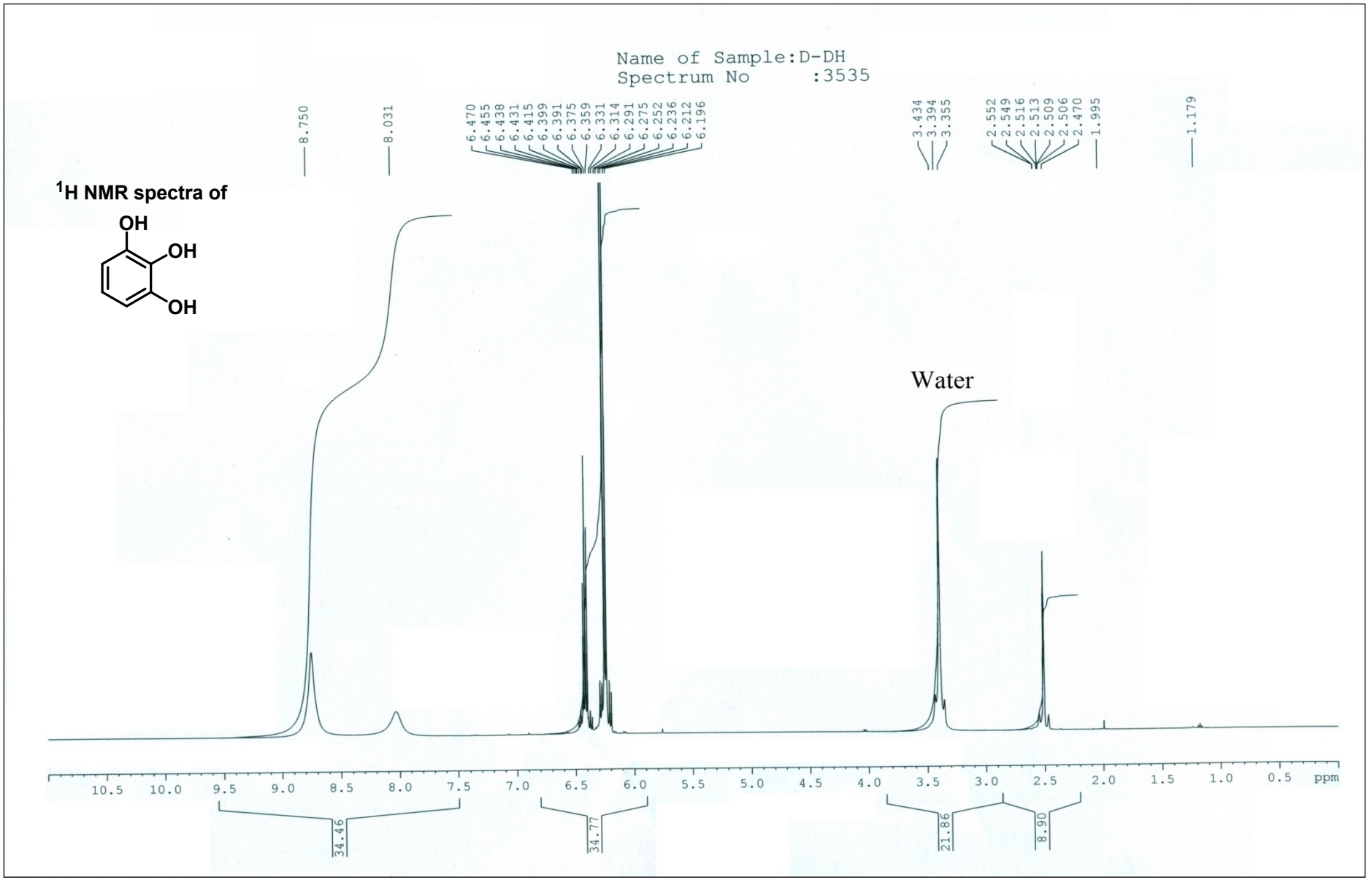
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6.196
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2.549
2.516
2.513
2.509
2.506
2.470
1.995
1.179
Water
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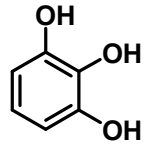
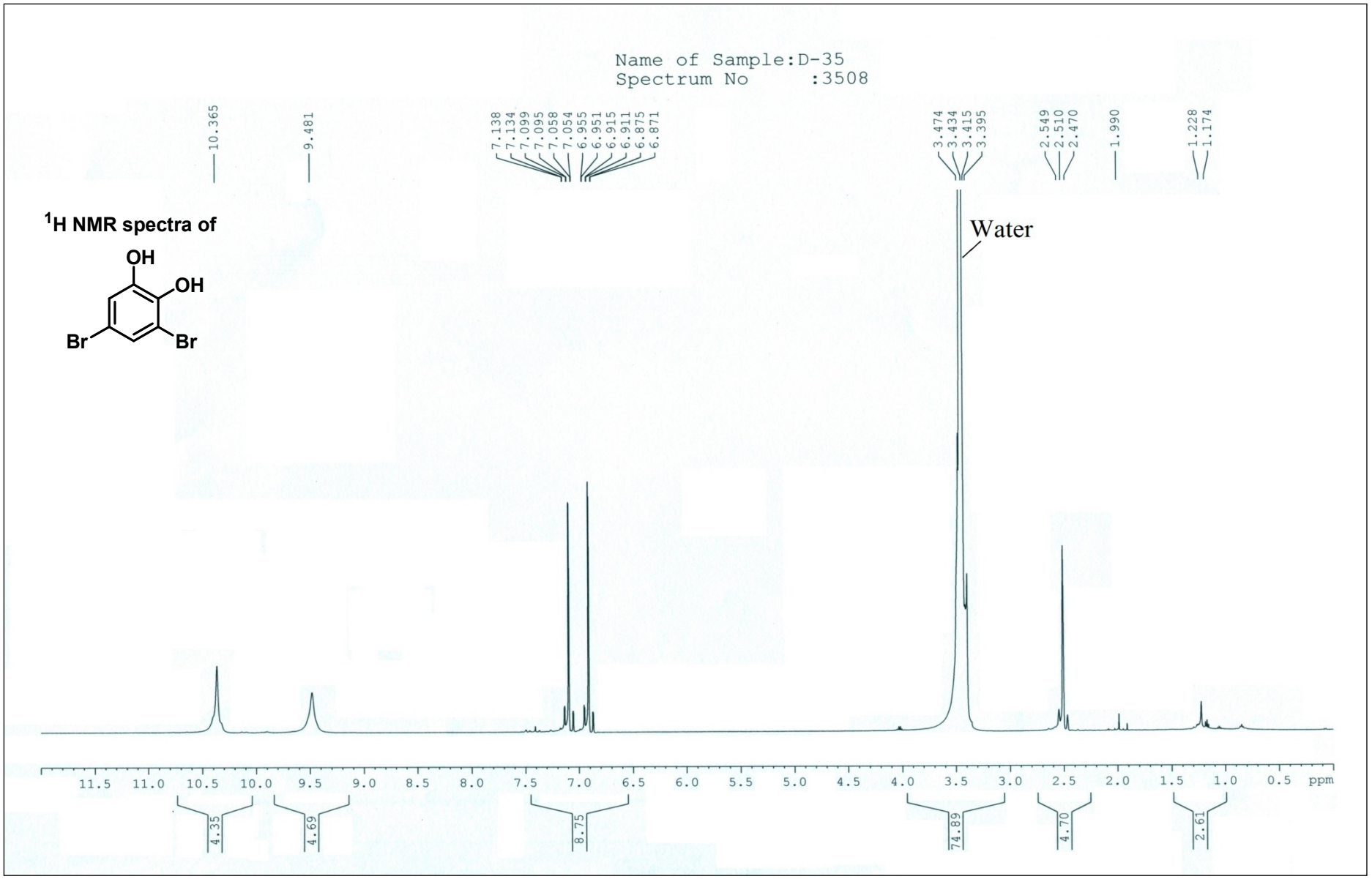
^{13}C NMR spectra of

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1H NMR spectra of
OH
OH
Br
Br
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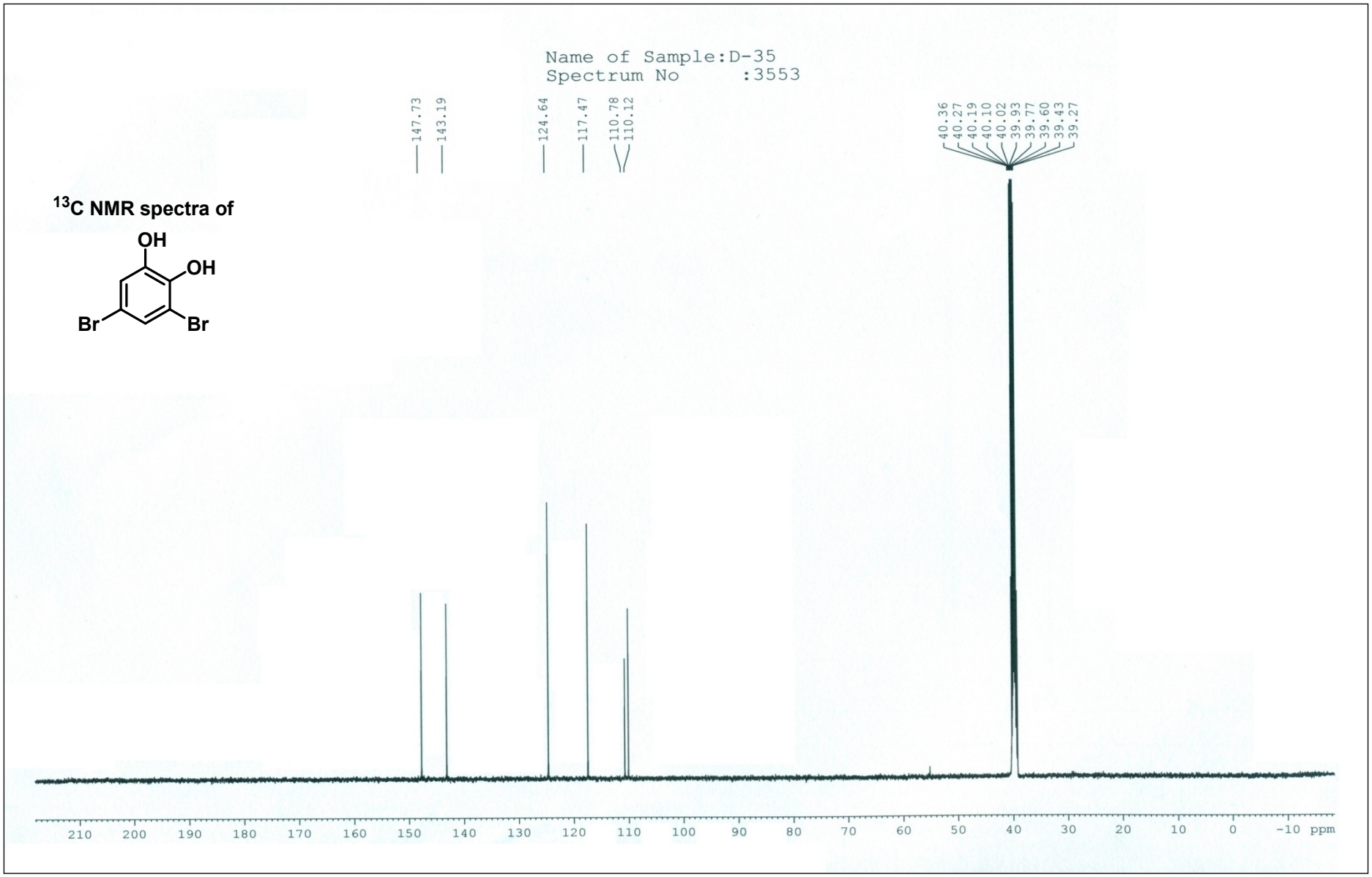

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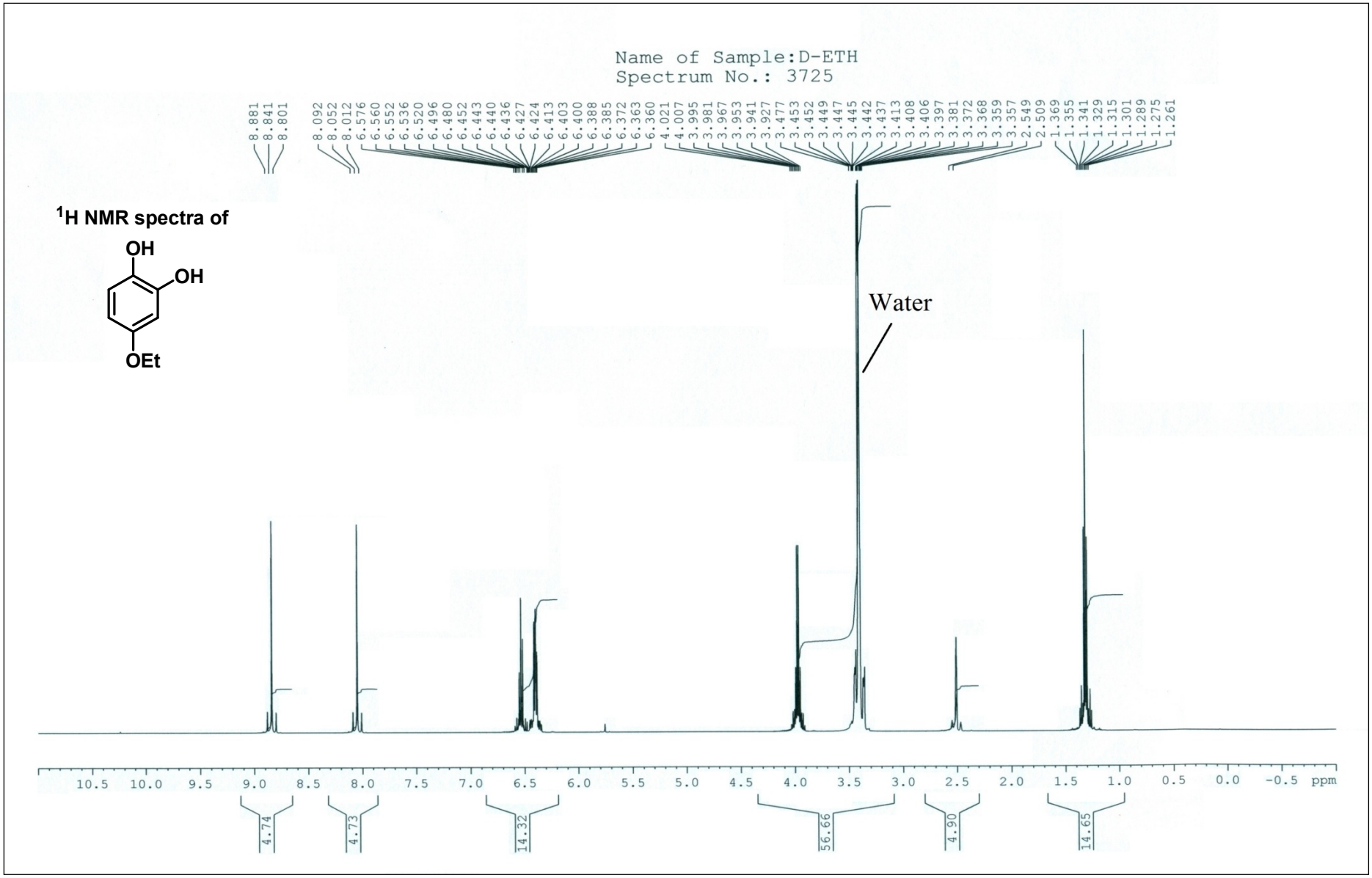
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1H NMR spectra of
OH
OH
OEt
Water
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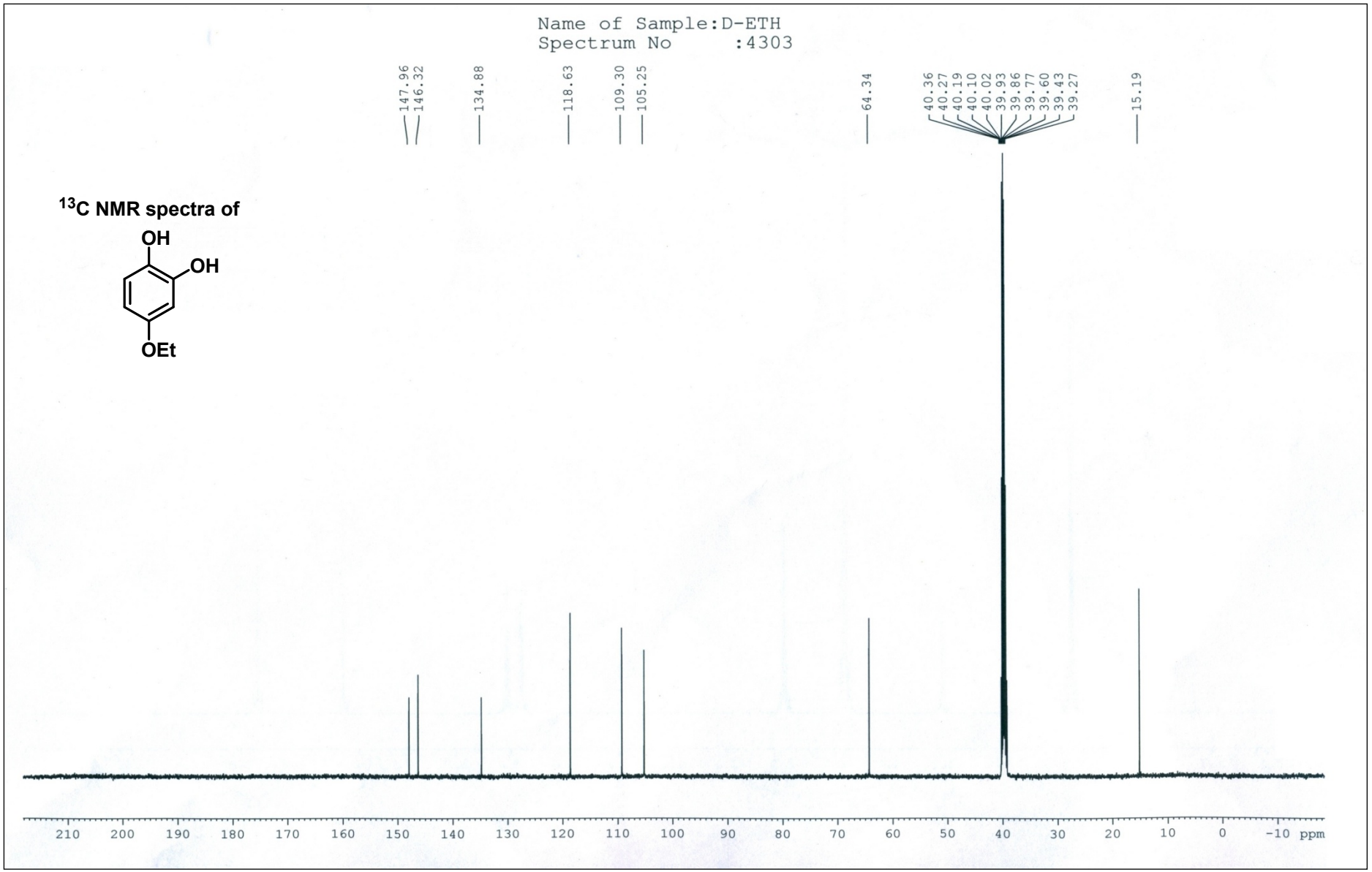
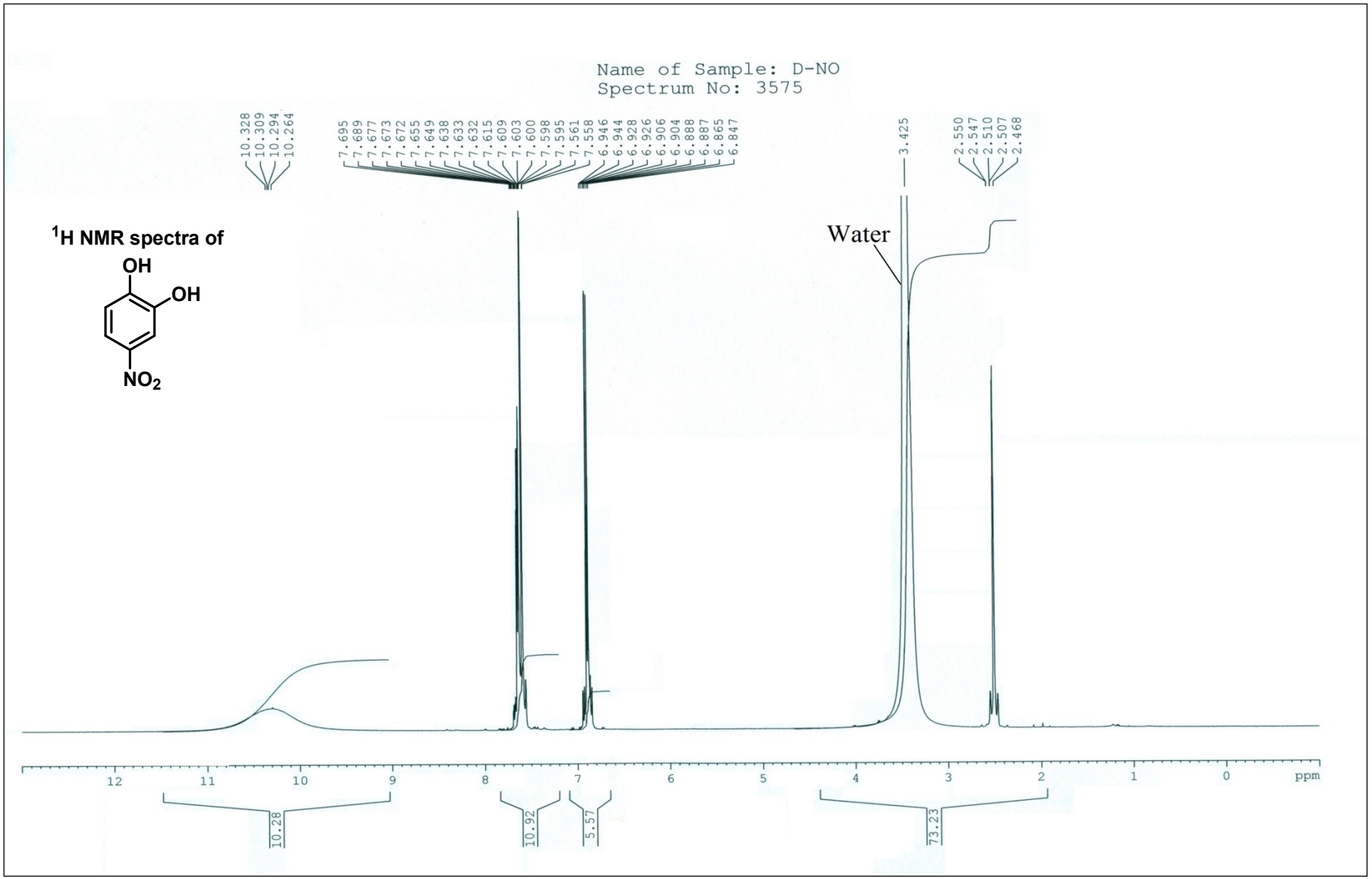
56.66
4.90
14.65



^{13}C NMR spectra of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2.547
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2.507
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Water
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NO2
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11
10
9
8
7
6
5
4
3
2
1
0
ppm
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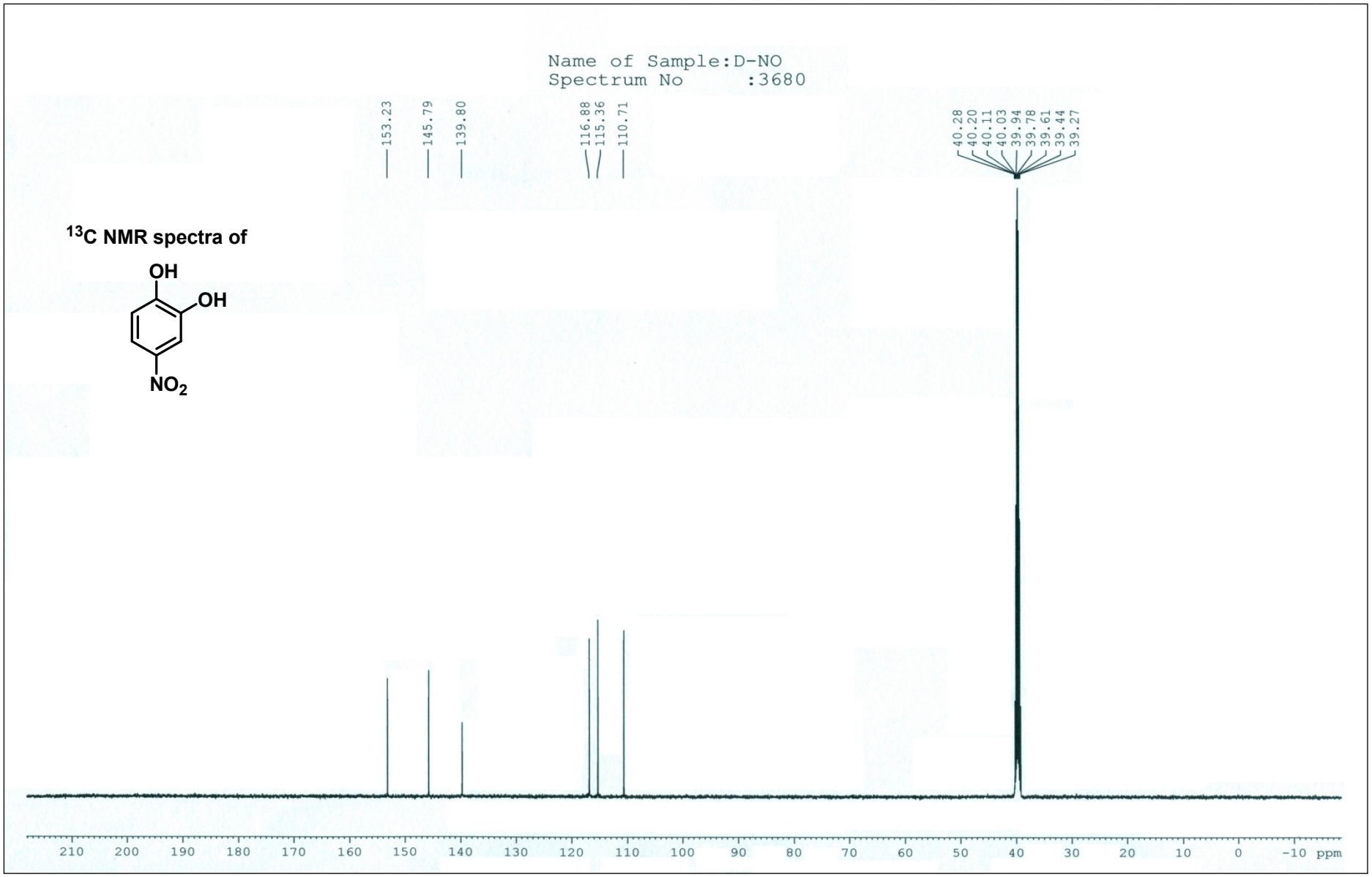
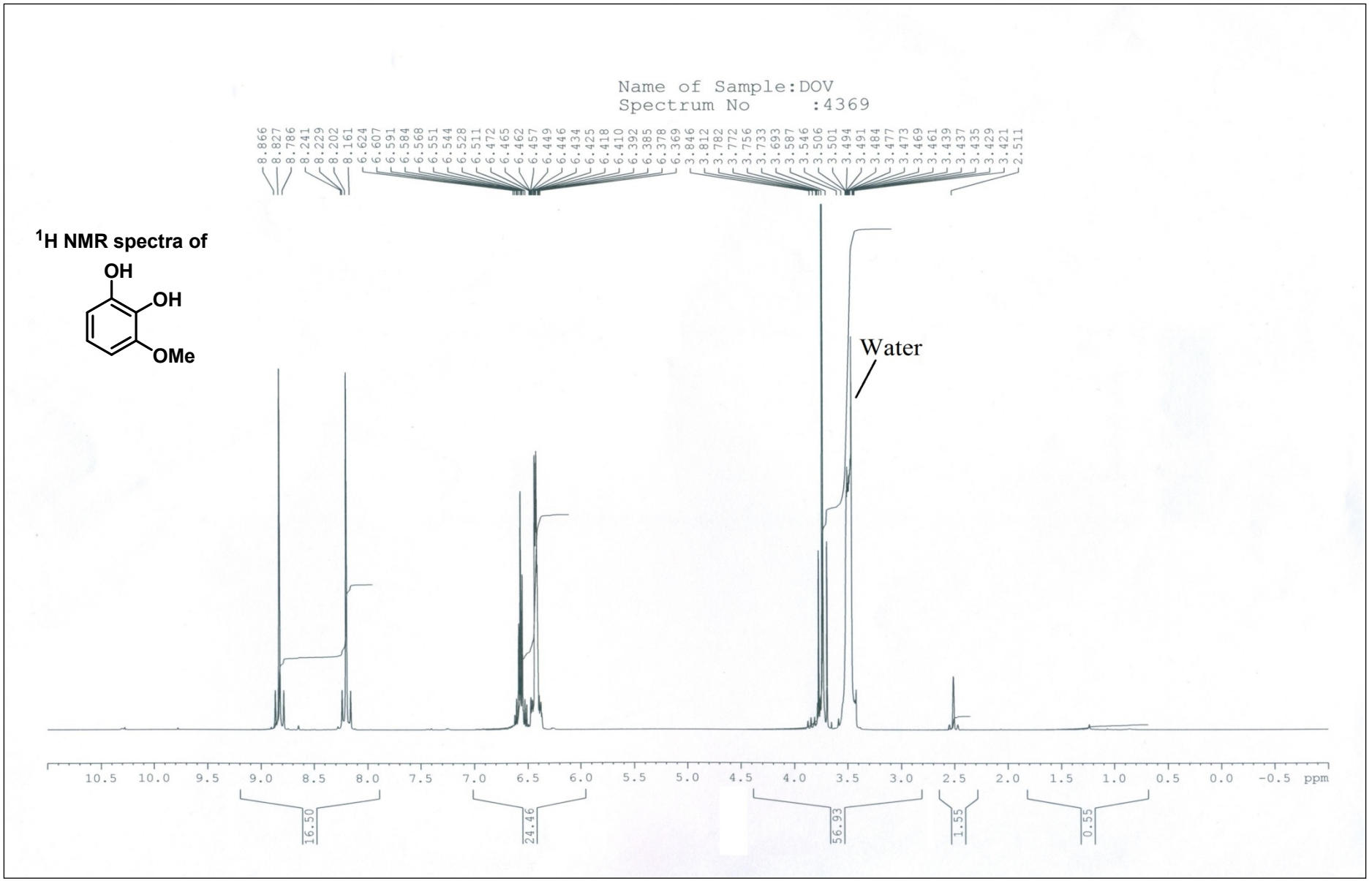
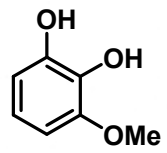
5.57
73.23

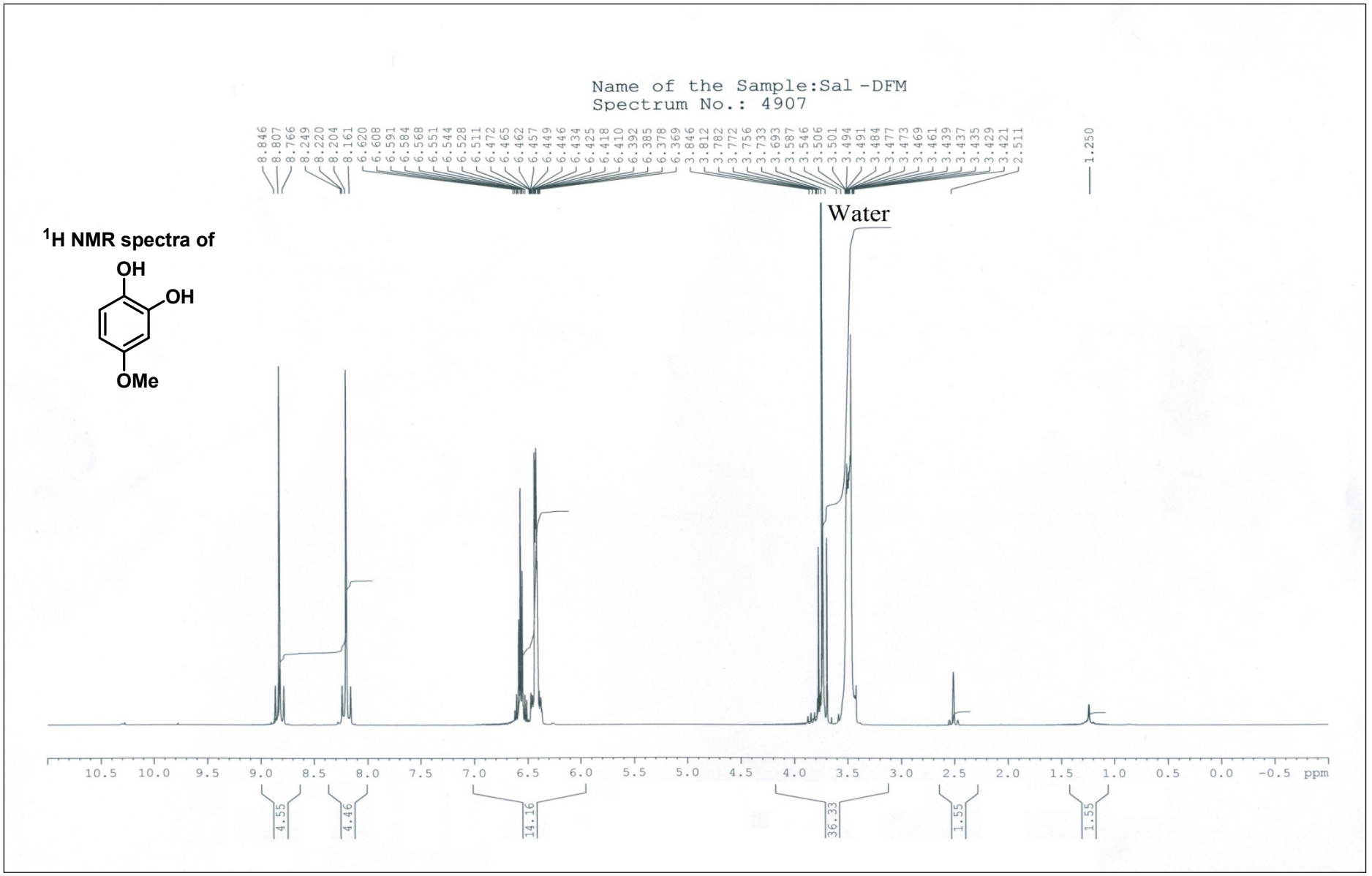


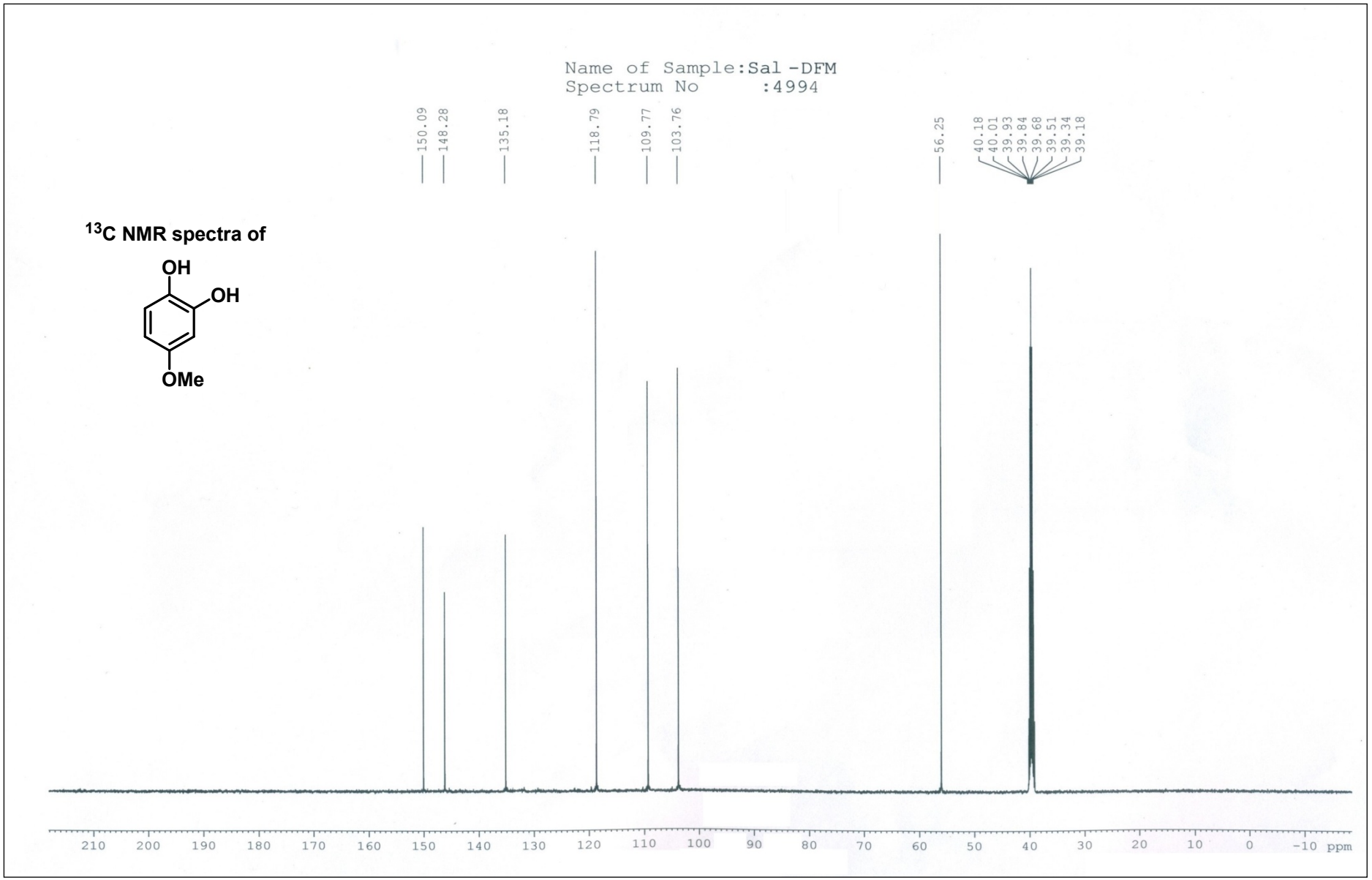
^{13}C NMR spectra of

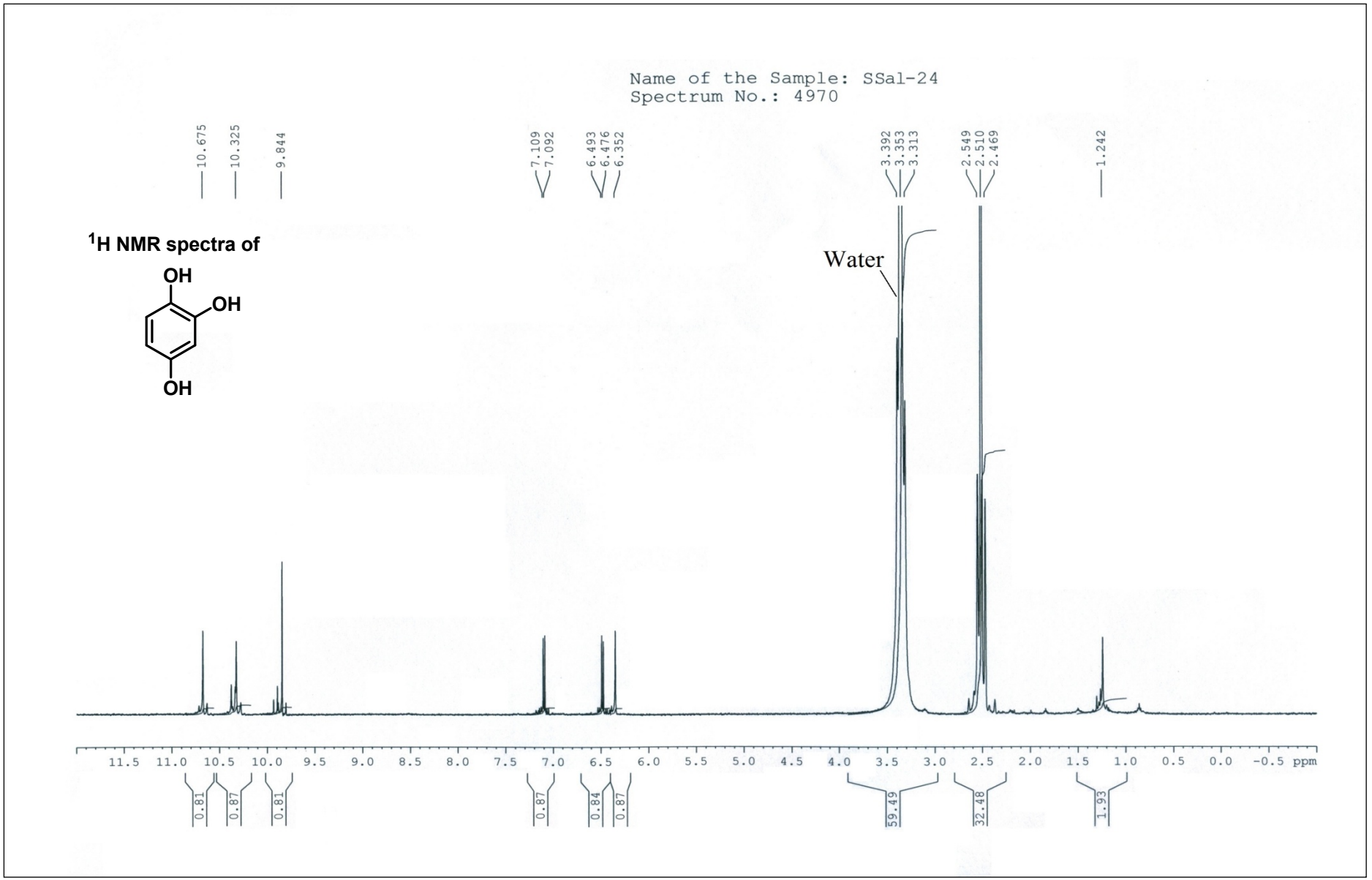

Name of Sample:DOV
Spectrum No :4369
8.866 8.827 8.786 8.241 8.229 8.202 8.161 6.624 6.607 6.591 6.584 6.568 6.551 6.544 6.528 6.511 6.472 6.465 6.462 6.457 6.449 6.446 6.434 6.425 6.418 6.410 6.392 6.385 6.378 6.369 3.846 3.812 3.782 3.772 3.756 3.733 3.693 3.587 3.546 3.506 3.501 3.494 3.491 3.484 3.477 3.473 3.469 3.461 3.439 3.437 3.435 3.429 3.421 2.511
1H NMR spectra of
OH
OH
OMe
Water
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 -0.5 ppm
16.50
24.46
56.93
1.55
0.55

^{13}C NMR spectra of

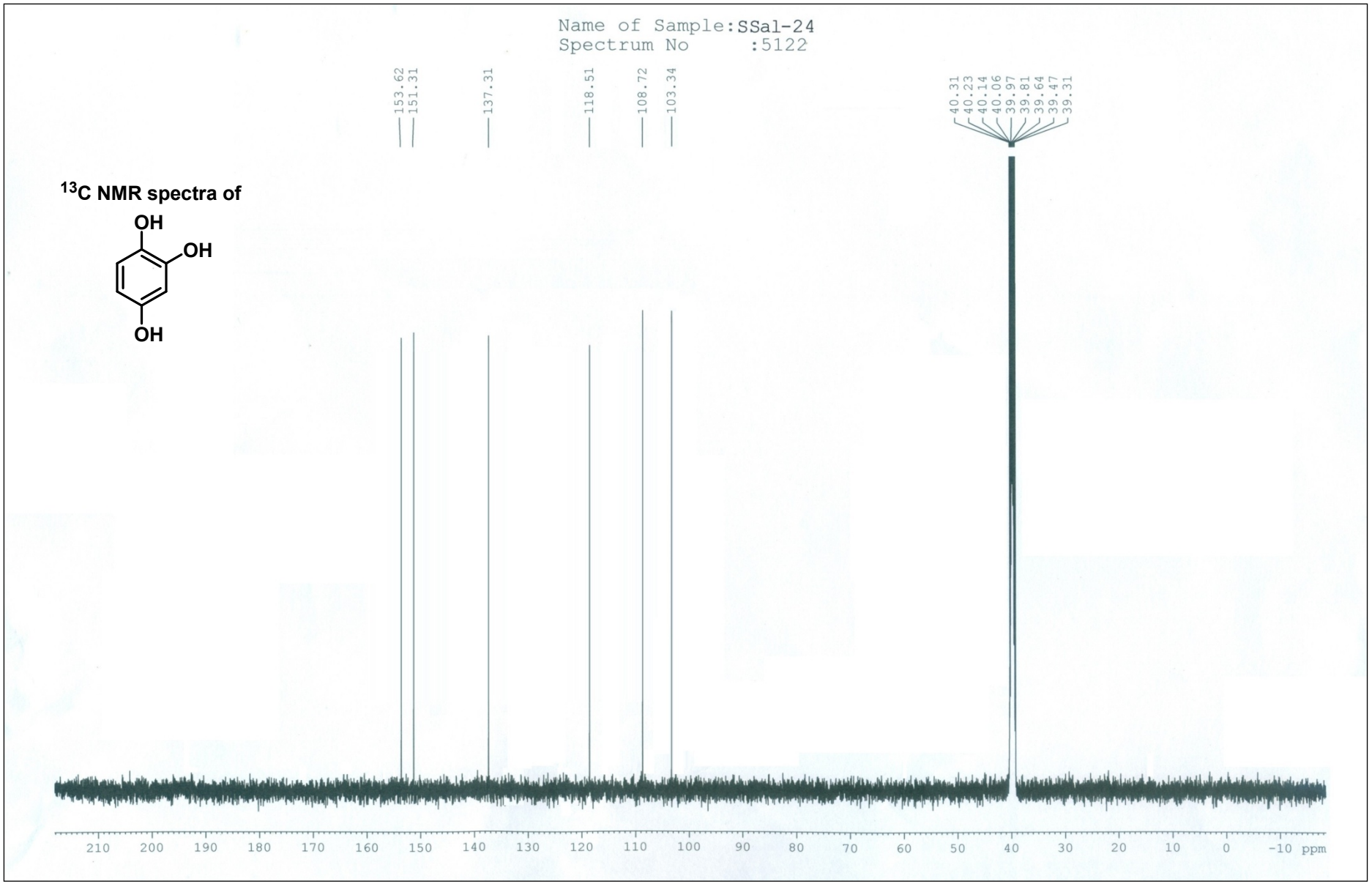



Name of the Sample:Sal -DFM
Spectrum No.: 4907
Water
^{1}H NMR spectra of
OH
OH
OMe
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
4.55
4.46
14.16
36.33
1.55
1.55

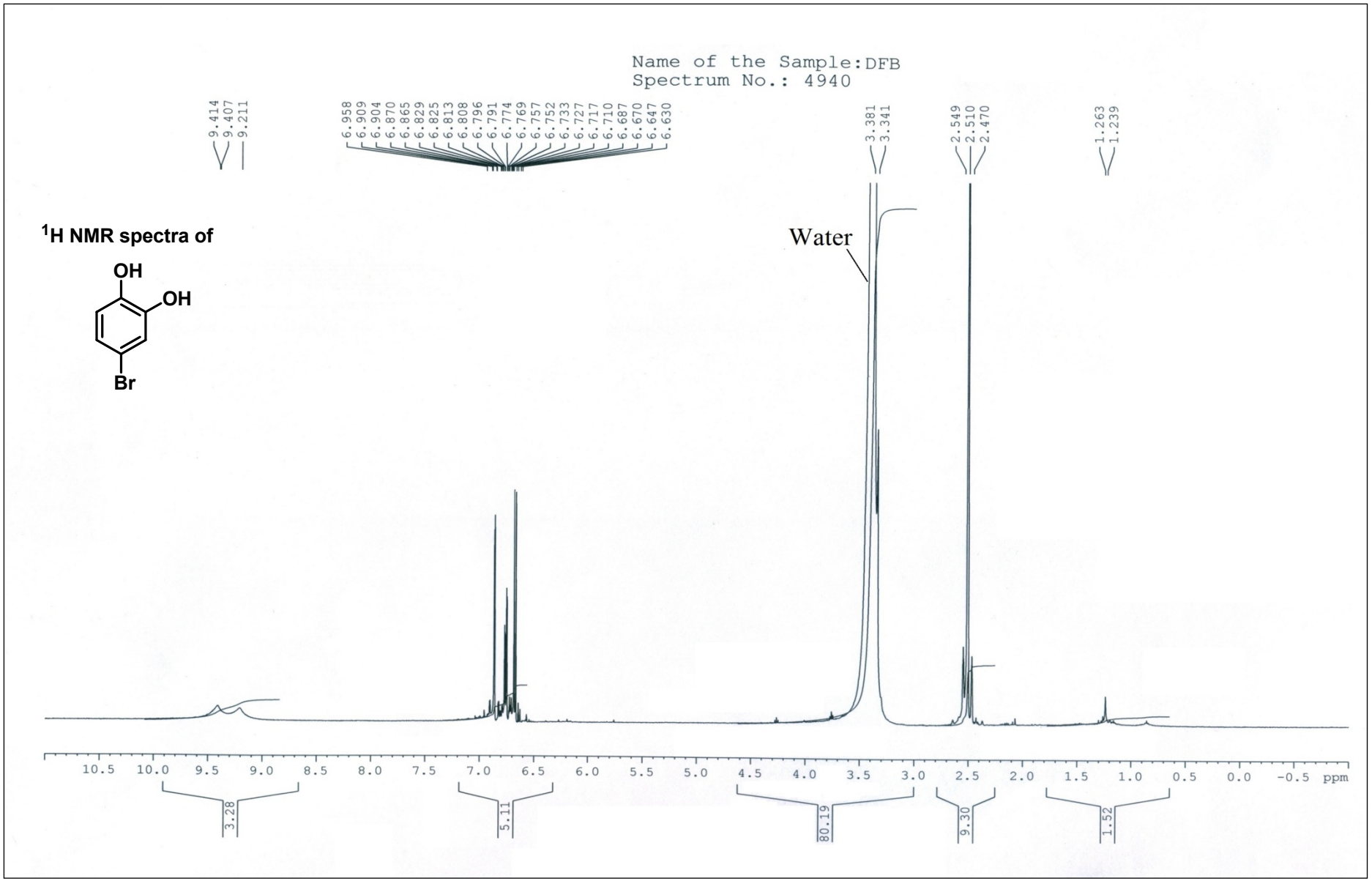

Name of Sample:Sal -DFM
Spectrum No :4994
150.09
148.28
135.18
118.79
109.77
103.76
56.25
40.18
40.01
39.93
39.84
39.68
39.51
39.34
39.18
13C NMR spectra of
OH
OH
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

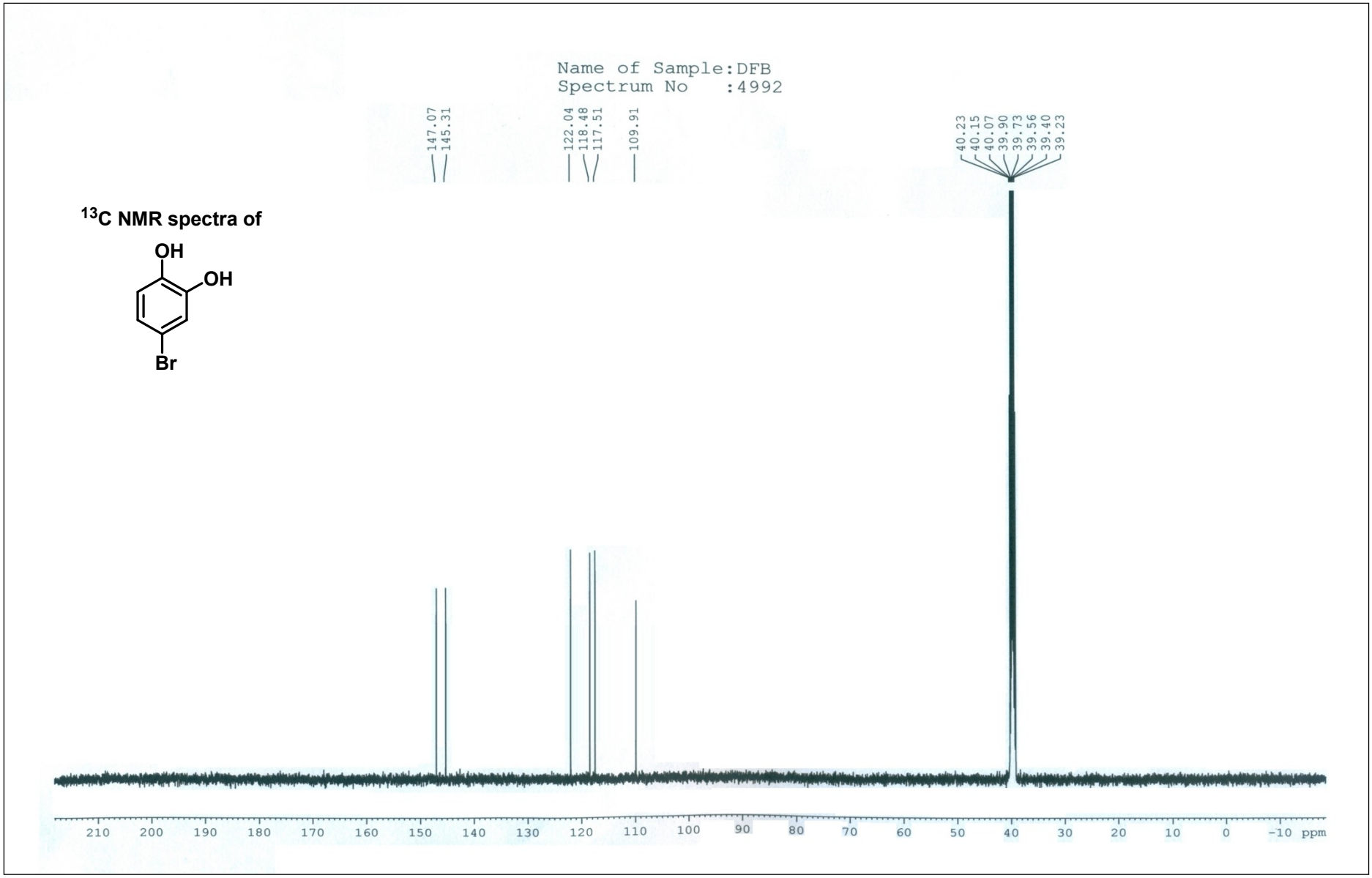


^{1}H NMR spectra of

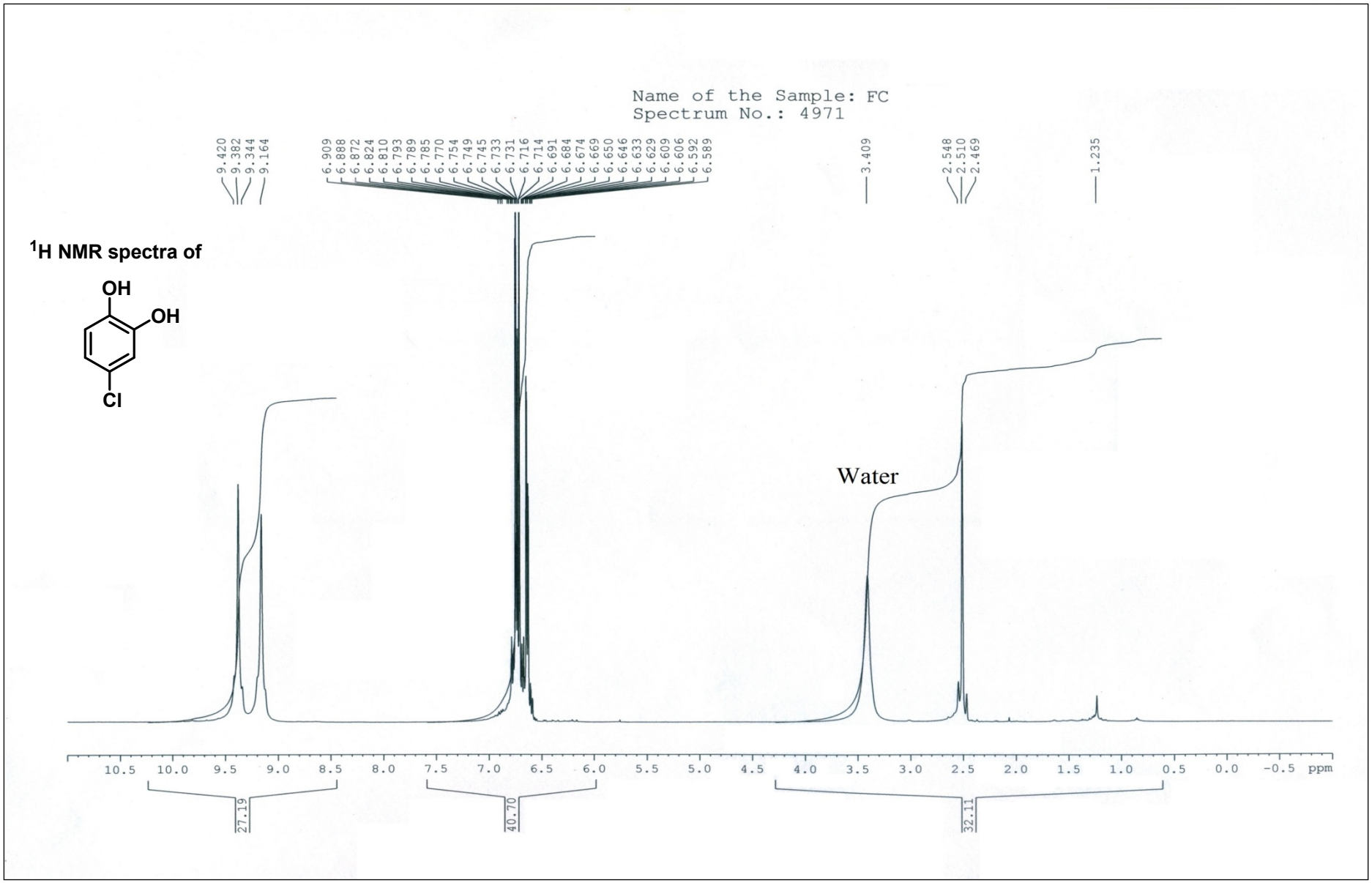


^{13}C NMR spectra of


Name of the Sample:DFB
Spectrum No.: 4940
9.414
9.407
9.211
6.958
6.909
6.904
6.870
6.865
6.829
6.825
6.813
6.808
6.796
6.791
6.774
6.769
6.757
6.752
6.733
6.727
6.717
6.710
6.687
6.670
6.647
6.630
3.381
3.341
2.549
2.510
2.470
1.263
1.239
Water
1H NMR spectra of
OH
OH
Br
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 -0.5 ppm
3.28
5.11
80.19
9.30
1.52

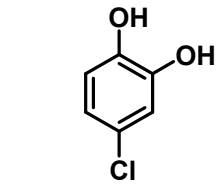


^{13}C NMR spectra of

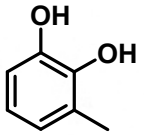


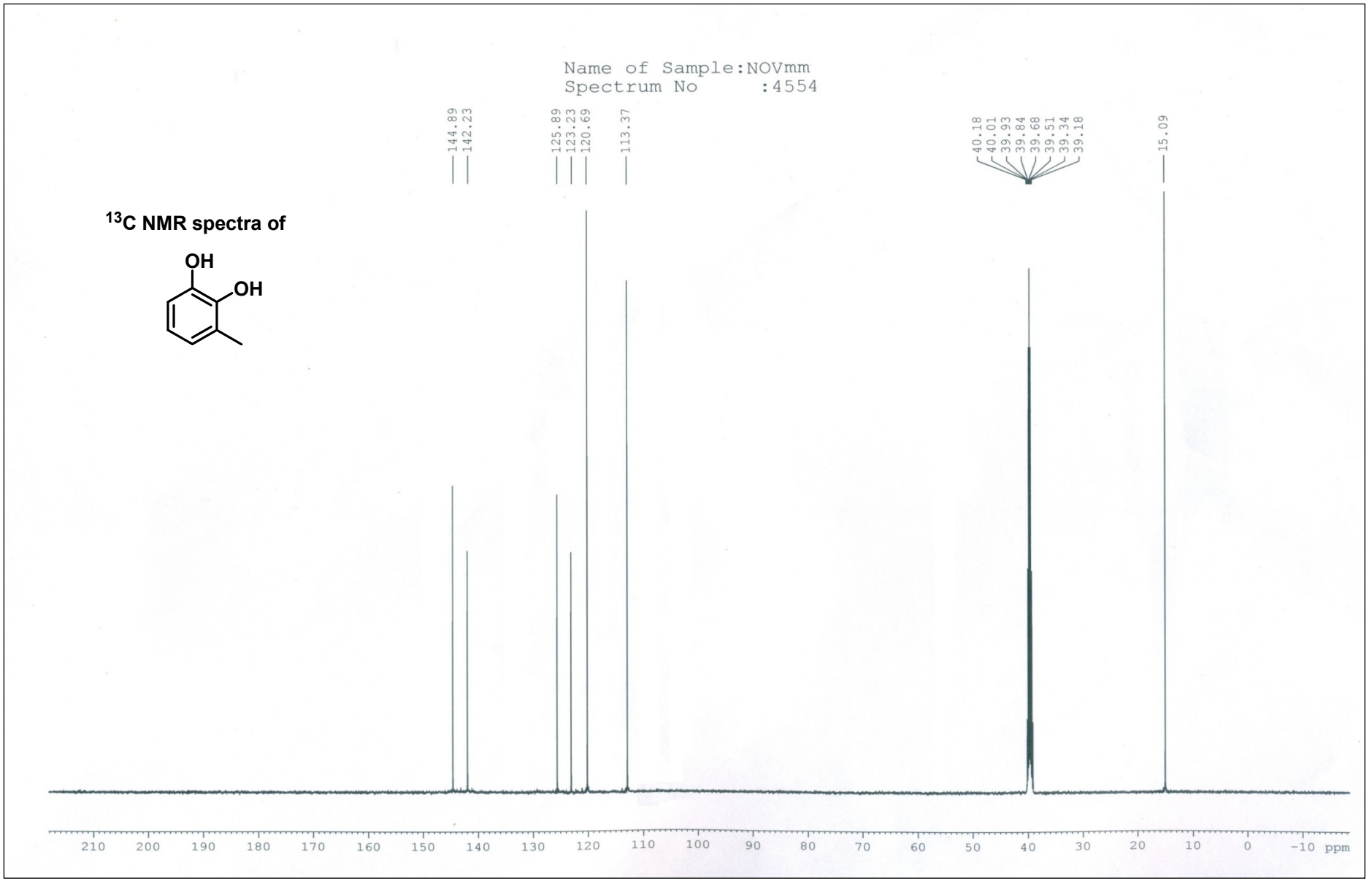
^{1}H NMR spectra of

^{13}C NMR spectra of



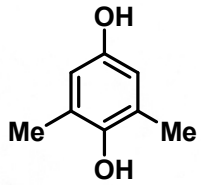
^{1}H NMR spectra of



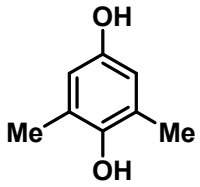


^{13}C NMR spectra of

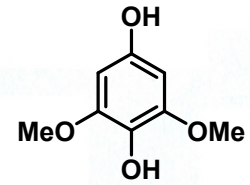
^{1}H NMR spectra of

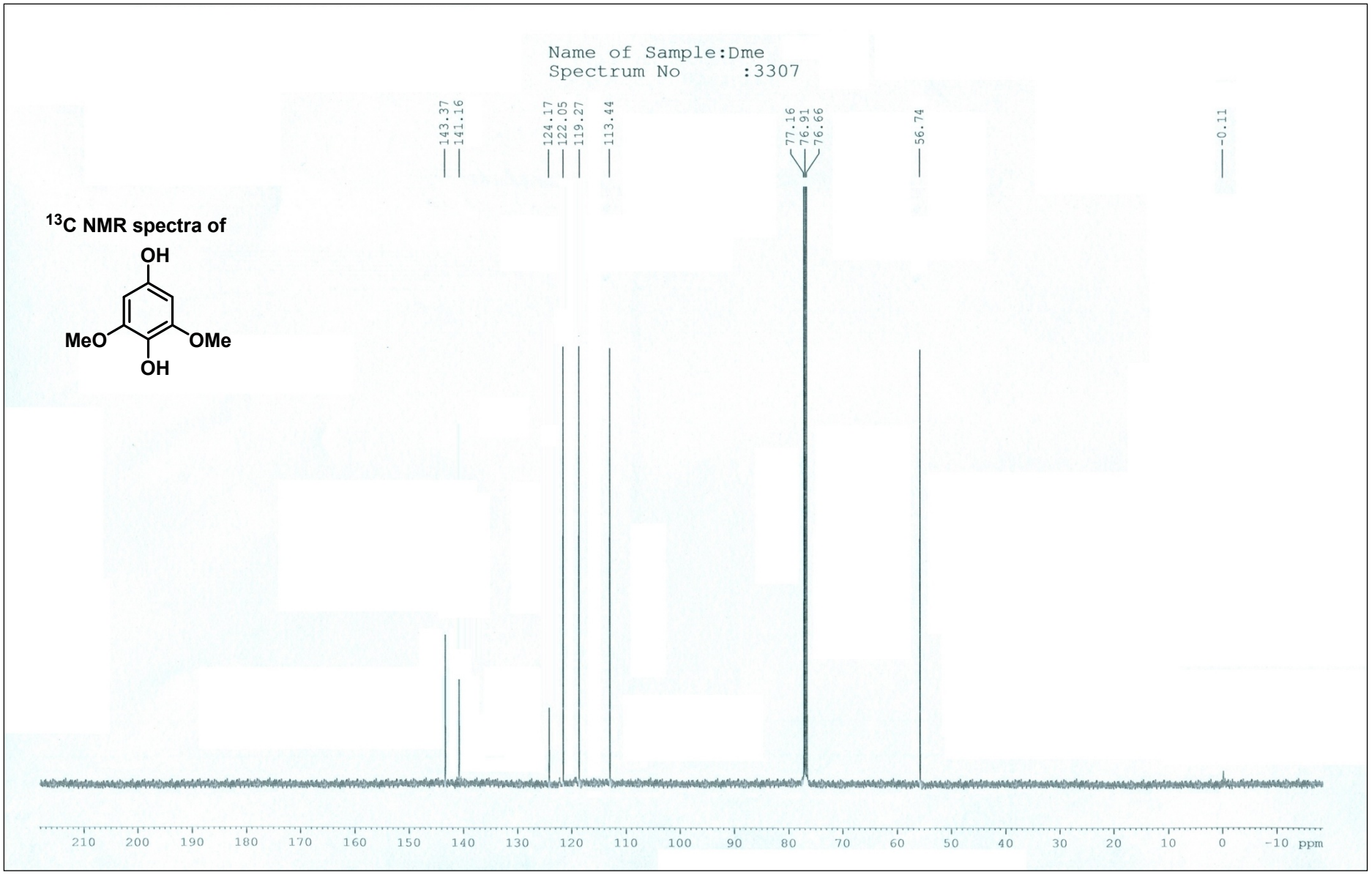


^{13}C NMR spectra of

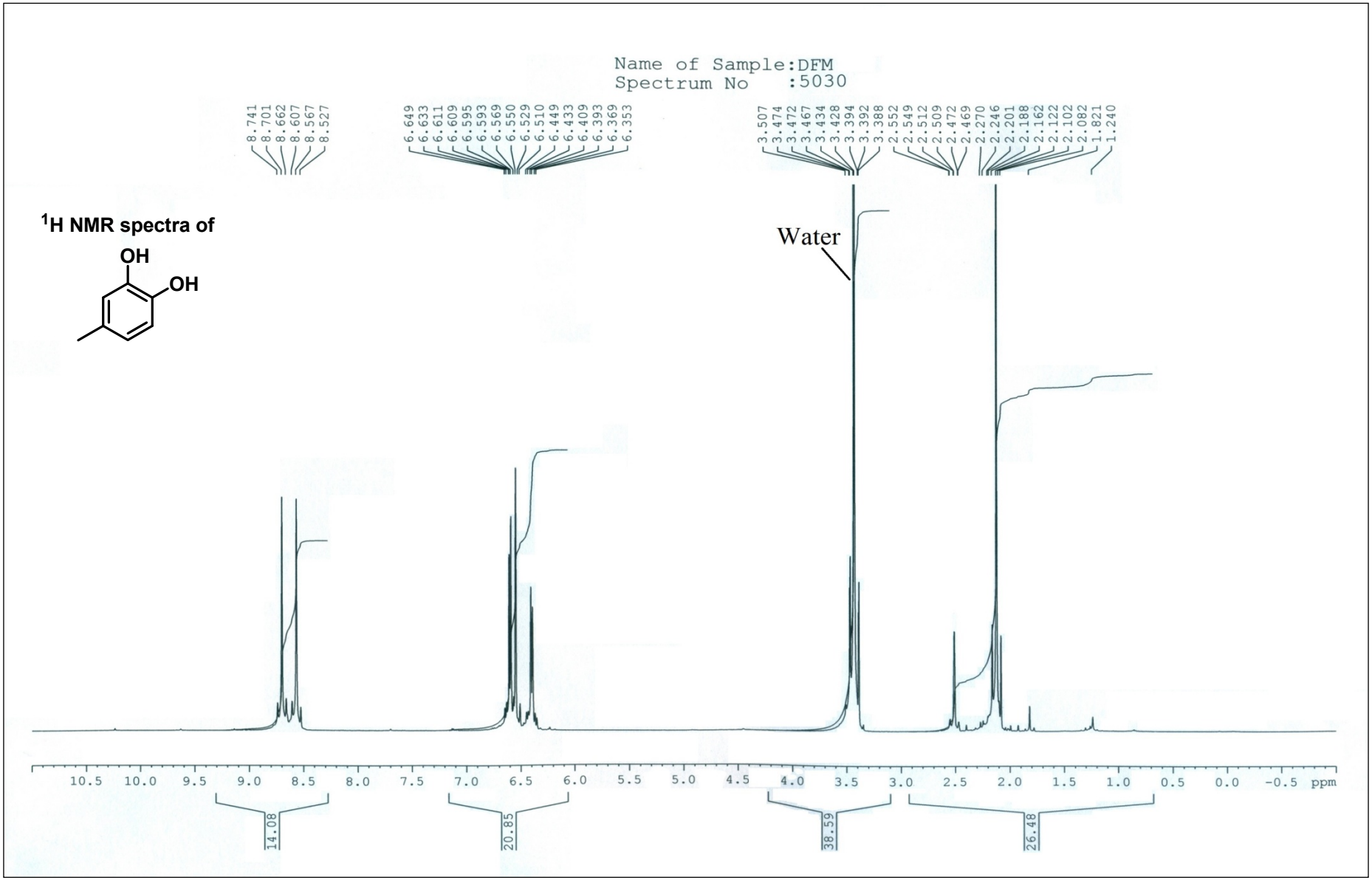


^{1}H NMR spectra of

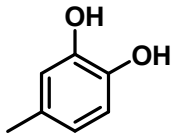


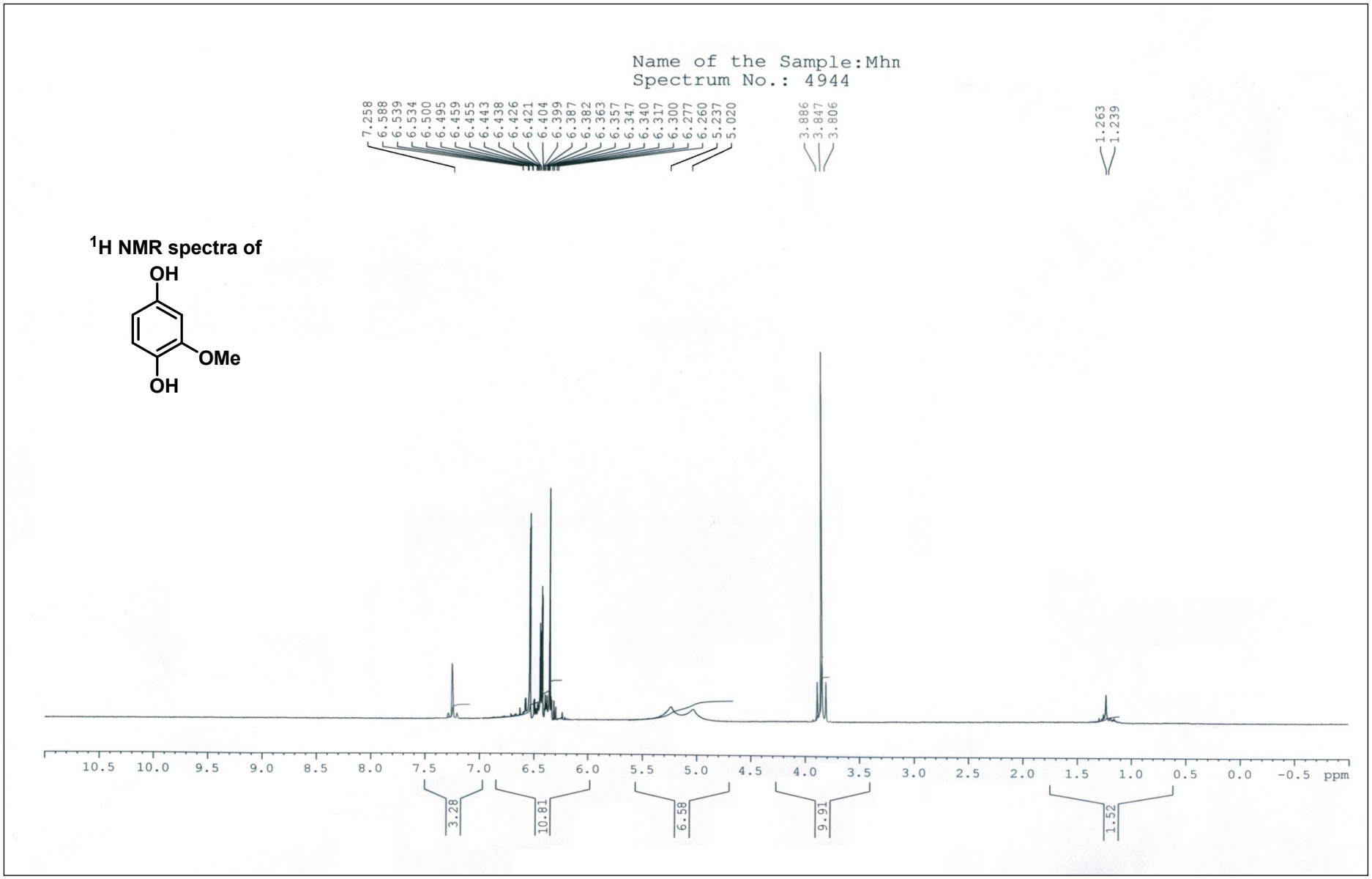


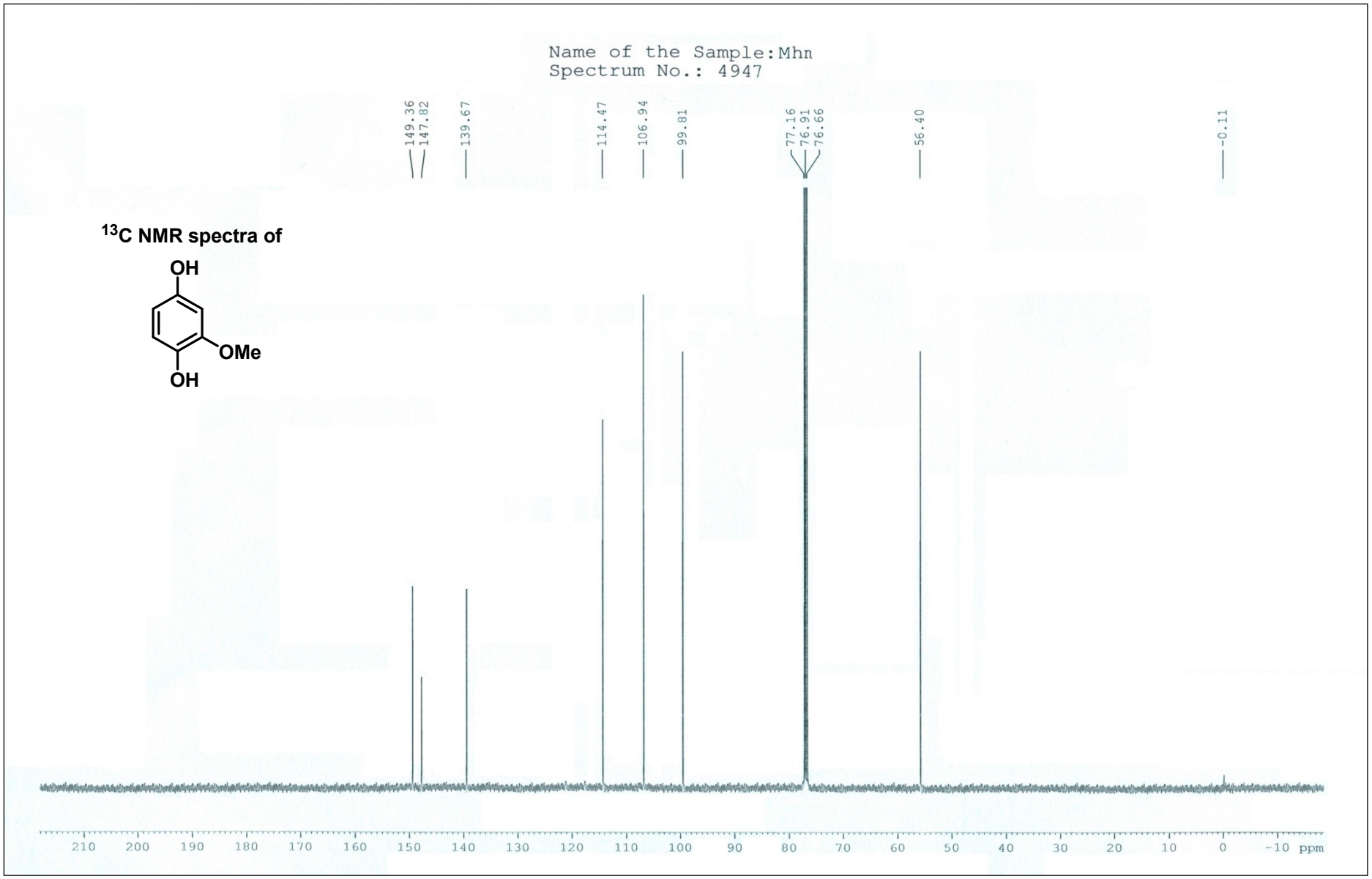
^{13}C NMR spectra of


Name of Sample:DFM
Spectrum No :5030
8.741
8.701
8.662
8.607
8.567
8.527
6.649
6.633
6.611
6.609
6.595
6.593
6.569
6.550
6.529
6.510
6.449
6.433
6.409
6.393
6.369
6.353
3.507
3.474
3.472
3.467
3.434
3.428
3.394
3.392
3.388
2.552
2.549
2.512
2.509
2.472
2.469
2.270
2.246
2.201
2.188
2.162
2.122
2.102
2.082
1.821
1.240
Water
1H NMR spectra of
OH
OH
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 -0.5 ppm
14.08
20.85
38.59
26.48

^{13}C NMR spectra of




Name of the Sample:Mhn
Spectrum No.: 4944
7.258
6.588
6.539
6.534
6.500
6.495
6.459
6.455
6.443
6.438
6.426
6.421
6.404
6.399
6.387
6.382
6.363
6.357
6.347
6.340
6.317
6.300
6.277
6.260
5.237
5.020
3.886
3.847
3.806
1.263
1.239
1H NMR spectra of
OH
OMe
OH
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 -0.5 ppm
3.28
10.81
6.58
9.91
1.52


Name of the Sample:Mhn
Spectrum No.: 4947
149.36
147.82
139.67
114.47
106.94
99.81
77.16
76.91
76.66
56.40
-0.11
13C NMR spectra of
OH
OMe
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm