Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A new avenue to Dakin reaction in H_2O_2–WERSA

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Contents

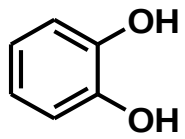
Materials and Methods

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 WERSA (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 (3:1 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]

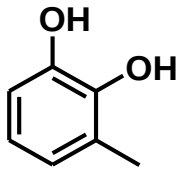


Catechol (Table 2; Entry 1)

^{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 (3:1 v/v).

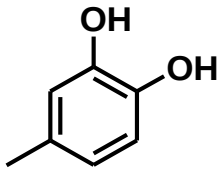
Hydroquinone (Table 2; Entry 2)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.63 (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 (3:1 v/v).



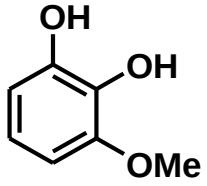
3-Methylcatechol (Table 2; Entry 3)

^{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 (3:1 v/v).



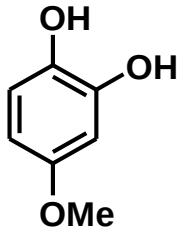
4-Methylbenzene-1,2-diol (Table 2; Entry 4)

^{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 (3:1 v/v).



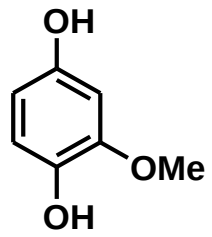
3-Methoxycatechol (Table 2; Entry 5)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.80 (s, 1 H), 8.19 (s, 1 H), 6.55 (t, *J* = 3.5 Hz, 1 H), 6.46 (d, *J* = 1.5 Hz, 1 H), 6.44 (d, *J* = 4.5 Hz, 1 H), 3.76 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 (3:1 v/v).



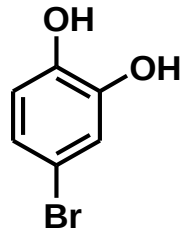
4-Methoxycatechol (Table 2; Entry 6)

^{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 (3:1 v/v).



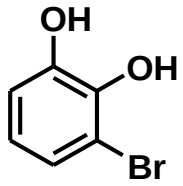
2-Methoxybenzene-1,4-diol (Table 2; Entry 7)

^{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 (3:1 v/v).



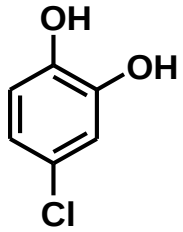
4-Bromocatechol (Table 2; Entry 8)

^{1}H NMR (500 MHz, DMSO-d6) δ 9.37 (brs, 1 H), 9.15 (brs, 1 H), 6.77 (d, *J* = 2.5 Hz, 1 H), 6.74–6.70 (m, 1 H), 6.60 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 (3:1 v/v).



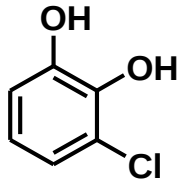
3-Bromocatechol (Table 2; Entry 9)

^{1}H NMR (500 MHz, DMSO-d6) δ 10.13 (brs, 1 H), 9.92 (brs, 1 H), 6.76 (d, *J* = 2.4 Hz, 1 H), 6.74–6.71 (m, 1 H), 6.60 ppm (d, *J* = 2.3 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d6) δ 147.8, 146.6, 125.8, 124.7, 116.9, 111.8 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (3:1 v/v).



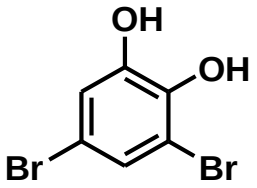
4-Chlorocatechol (Table 2; Entry 10)

^{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 (3:1 v/v).



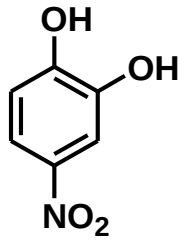
3-Chlorocatechol (Table 2; Entry 11)

^{1}H NMR (500 MHz, DMSO-d6) δ 9.28 (brs, 1 H), 9.12 (brs, 1 H), 6.77–6.71 (m, 1 H), 6.69–6.67 (m, 1 H), 6.62–6.59 ppm (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 144.1, 123.9, 122.9, 122.4, 115.2 ppm; Column chromatography on silica gel using *n*-hexane/ethyl acetate (3:1 v/v).



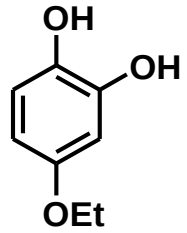
3,5-Dibromocatechol (Table 2; Entry 12)

^{1}H NMR (500 MHz, DMSO-d6) δ 10.31 (brs, 1 H), 9.45 (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 (3:1 v/v).



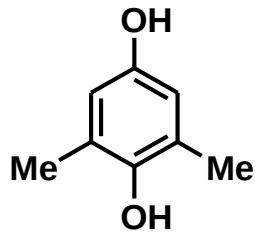
4-Nitrocatechol (Table 2; Entry 13)

^{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 (3:1 v/v).



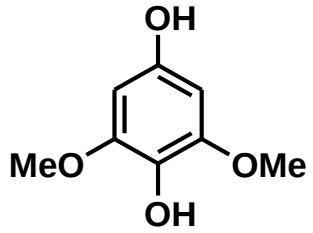
4-Ethoxycatechol (Table 2; Entry 14)

^{1}H NMR (500 MHz, DMSO-d6) δ 8.80 (s, 1 H), 8.02 (s, 1 H), 6.54–6.50 (m, 1 H), 6.43–6.39 (m, 2 H), 4.0 (q, *J* = 5 Hz, 2 H), 1.33 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 (3:1 v/v).



2,6-Dimethylhydroquinone (Table 2; Entry 15)

^{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 (3:1 v/v).



2,6-Dimethoxy-1,4-benzenediol (Table 2; Entry 16)

^{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 (3:1 v/v).

References

1. S. Chen, M. S. Hossain and F. W. Foss Jr., *Org. Lett*., 2012, **14**, 2806–2809.
2. S. Chen and F. W. Foss Jr., *Org. Lett*., 2012, **14**, 5150–5153.
3. R. S. Varma and K. P. Naicker, *Org. Lett*., 1999, **1**, 189–191.
4. R. Bernini, A. Coratti, G. Provenzano, G. Fabrizi and D. Tofani, *Tetrahedron*, 2005, **61**, 1821–1825.
5. A. Roy, K. R. Reddy, P. K. Mohanta, H. Ila and H. Junjappa, *Synth. Commun*., 1999, **29**, 3781–3791.
6. T. V. Hansen and L. Skattebol, *Tetrahedron Lett*., 2005, **46**, 3357–3358.
7. E. T. da Silva, C. A. Camara, O. A. C. Antunes, E. J. Barreiro and C. A. M. Fraga, *Synth. Commun*., 2008, **38**, 784–788.

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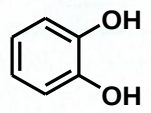

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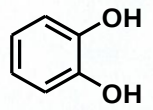

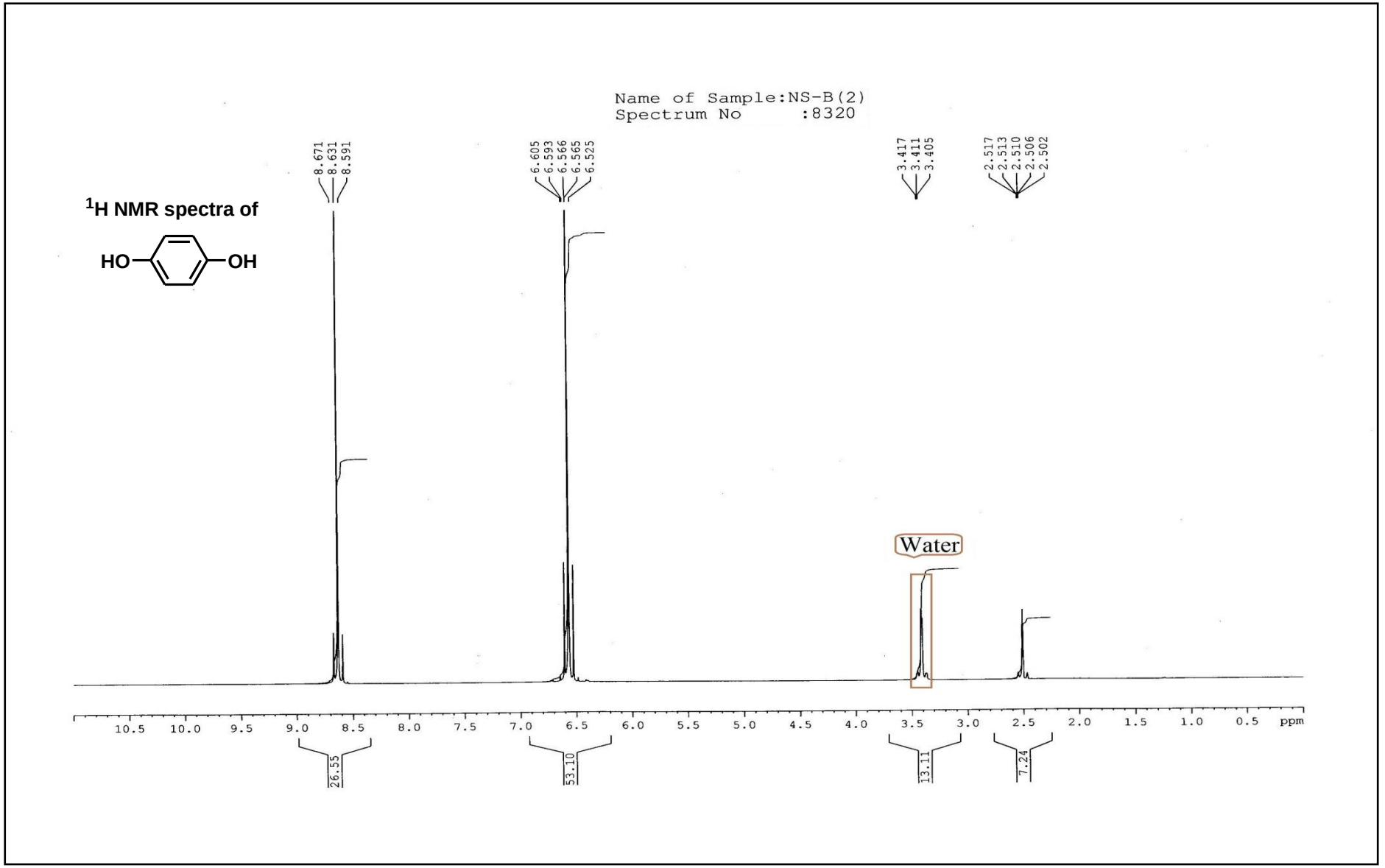
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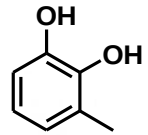
^{13}C NMR spectra of

^{1}H NMR spectra of



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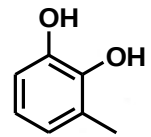

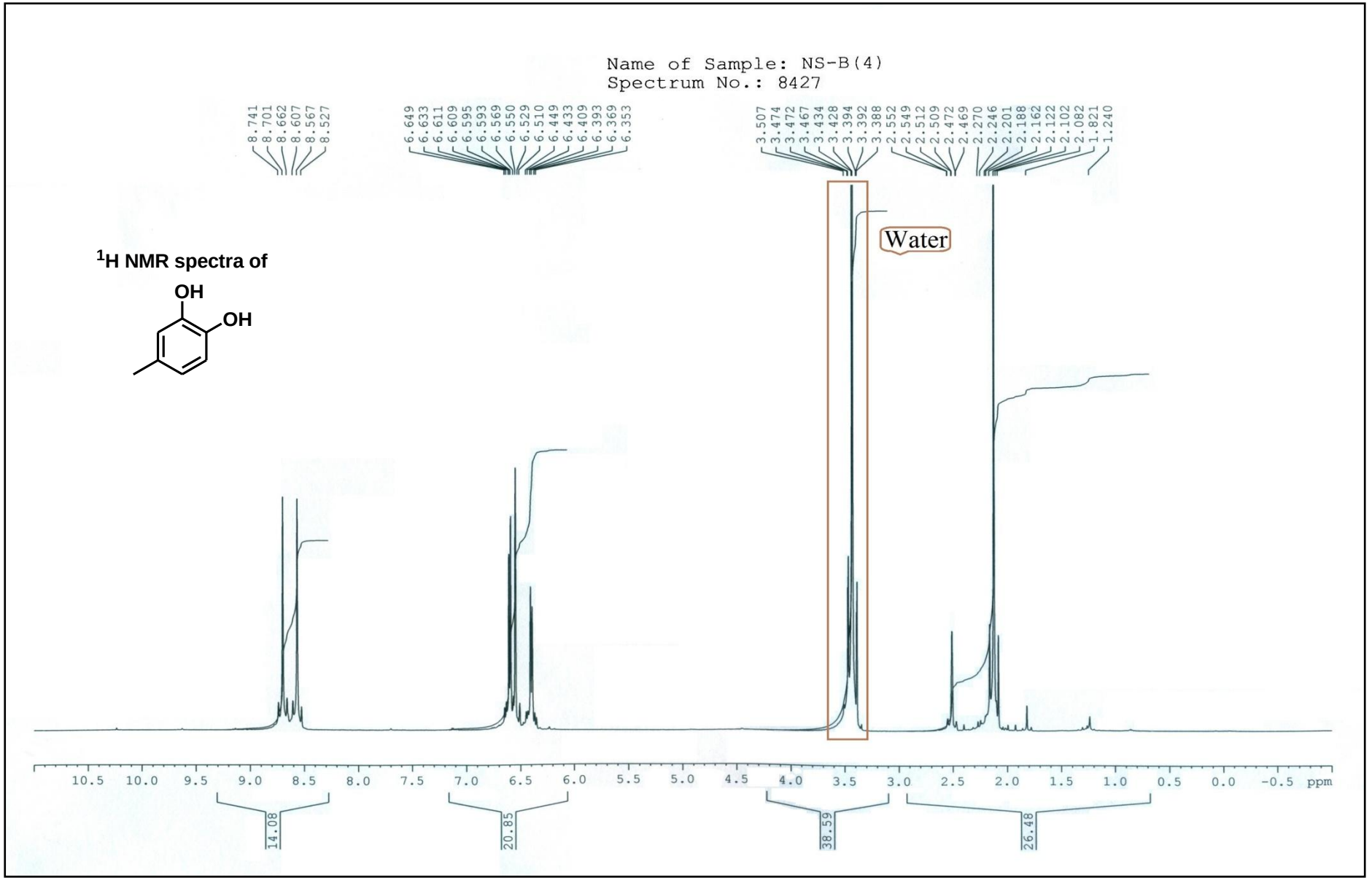
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6.369
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3.467
3.434
3.428
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3.388
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2.549
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2.472
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2.082
1.821
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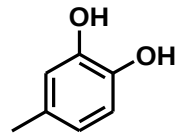

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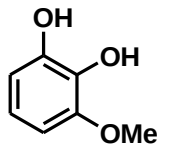

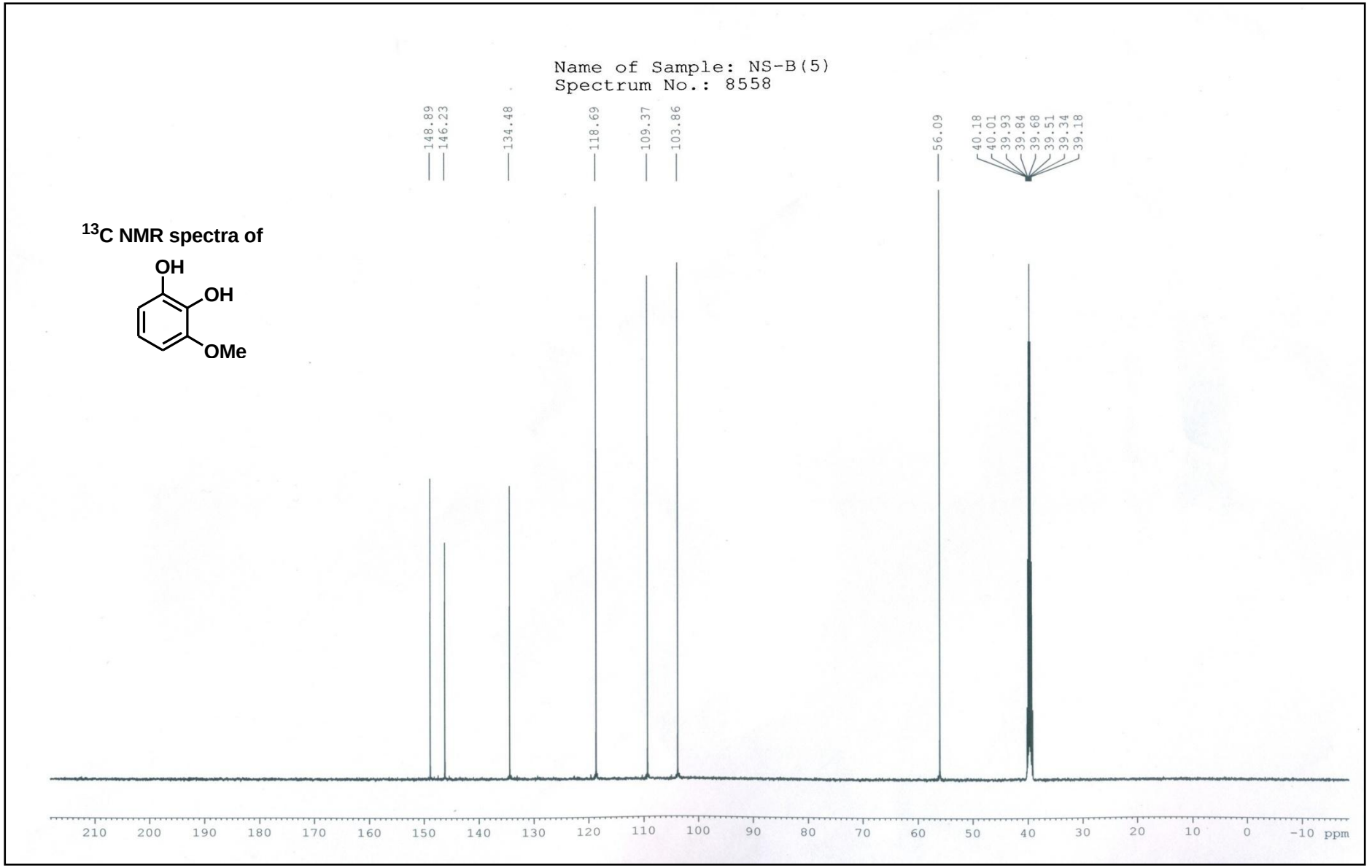

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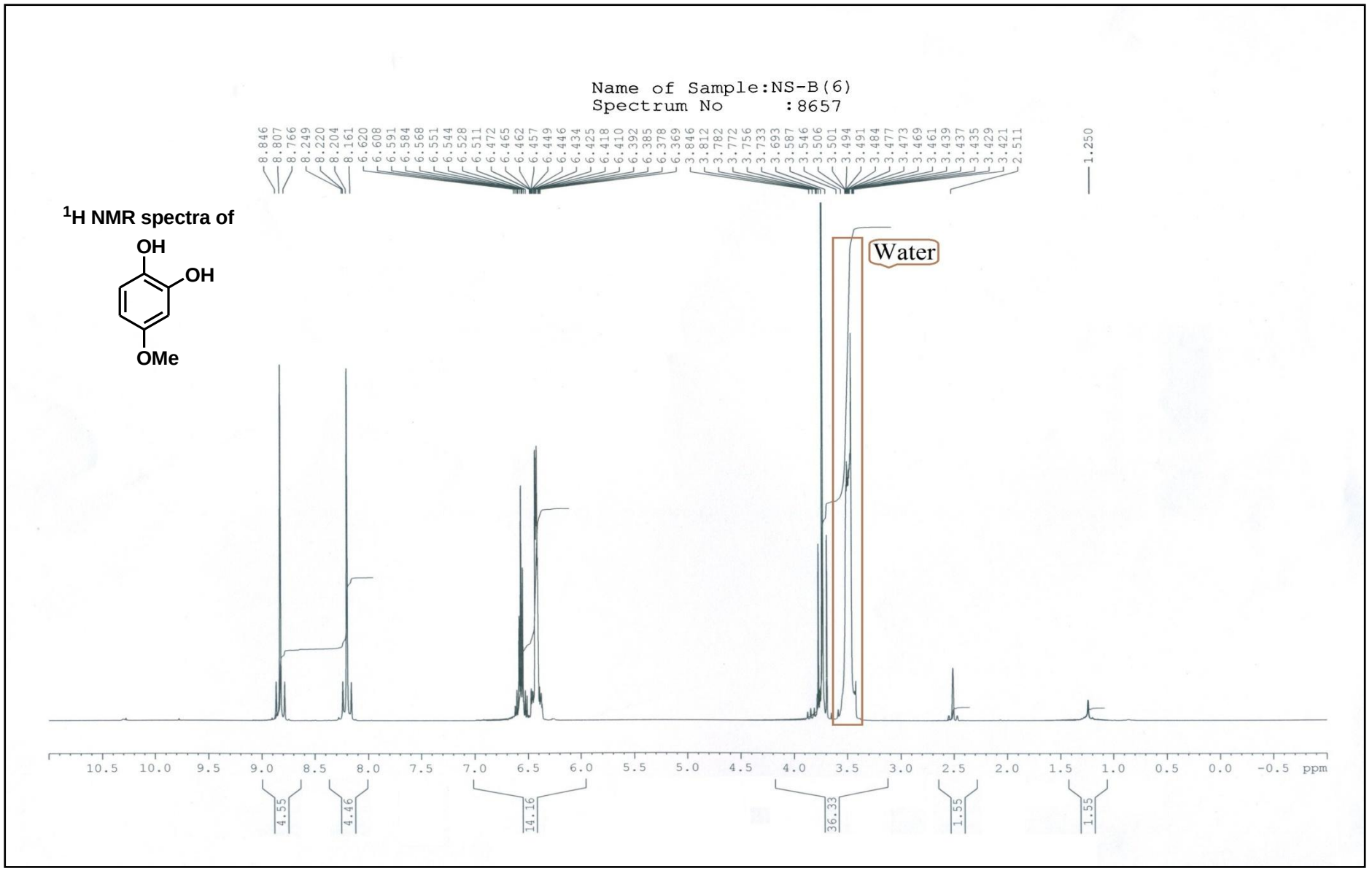
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1.55

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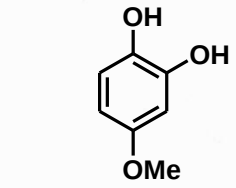
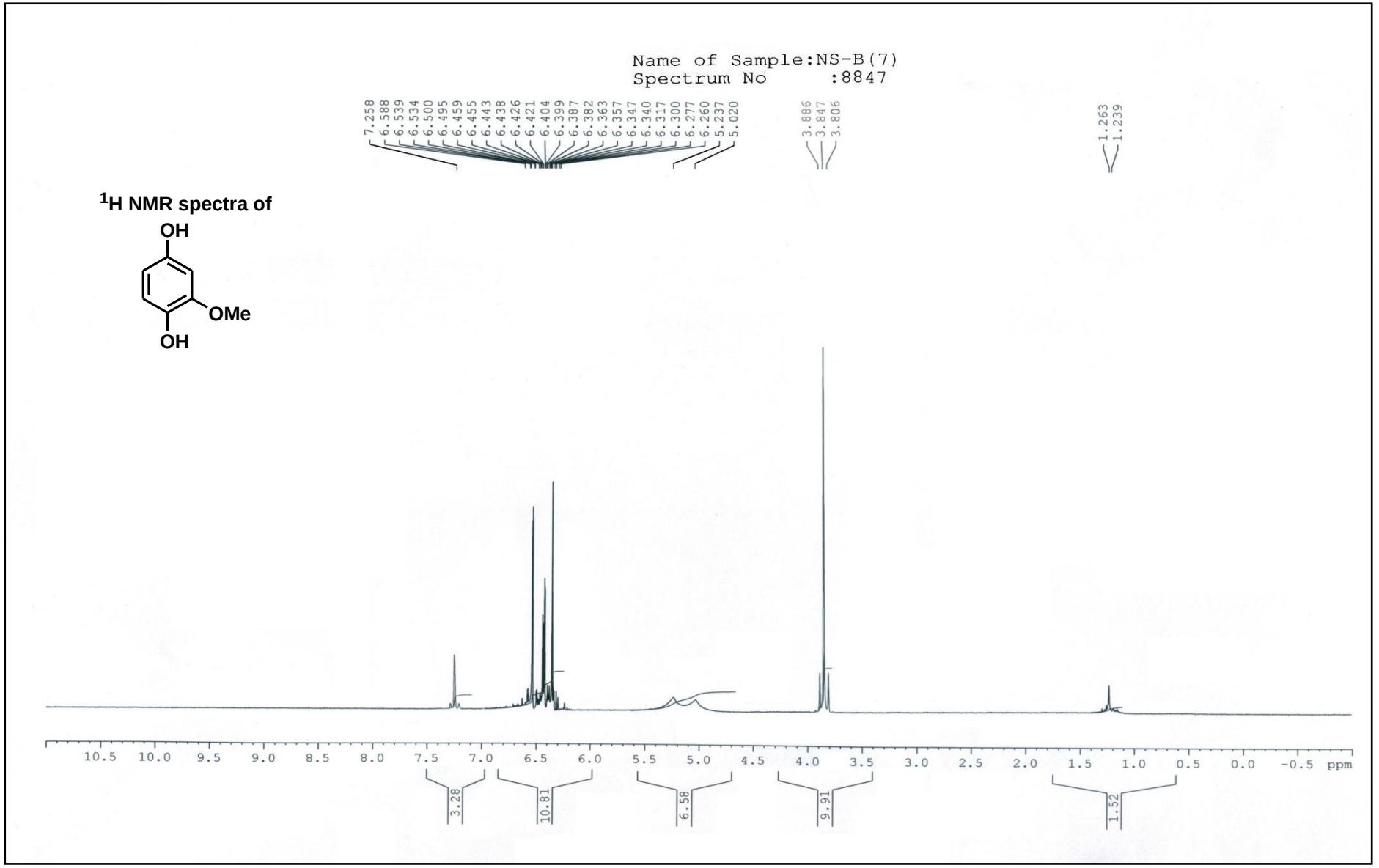
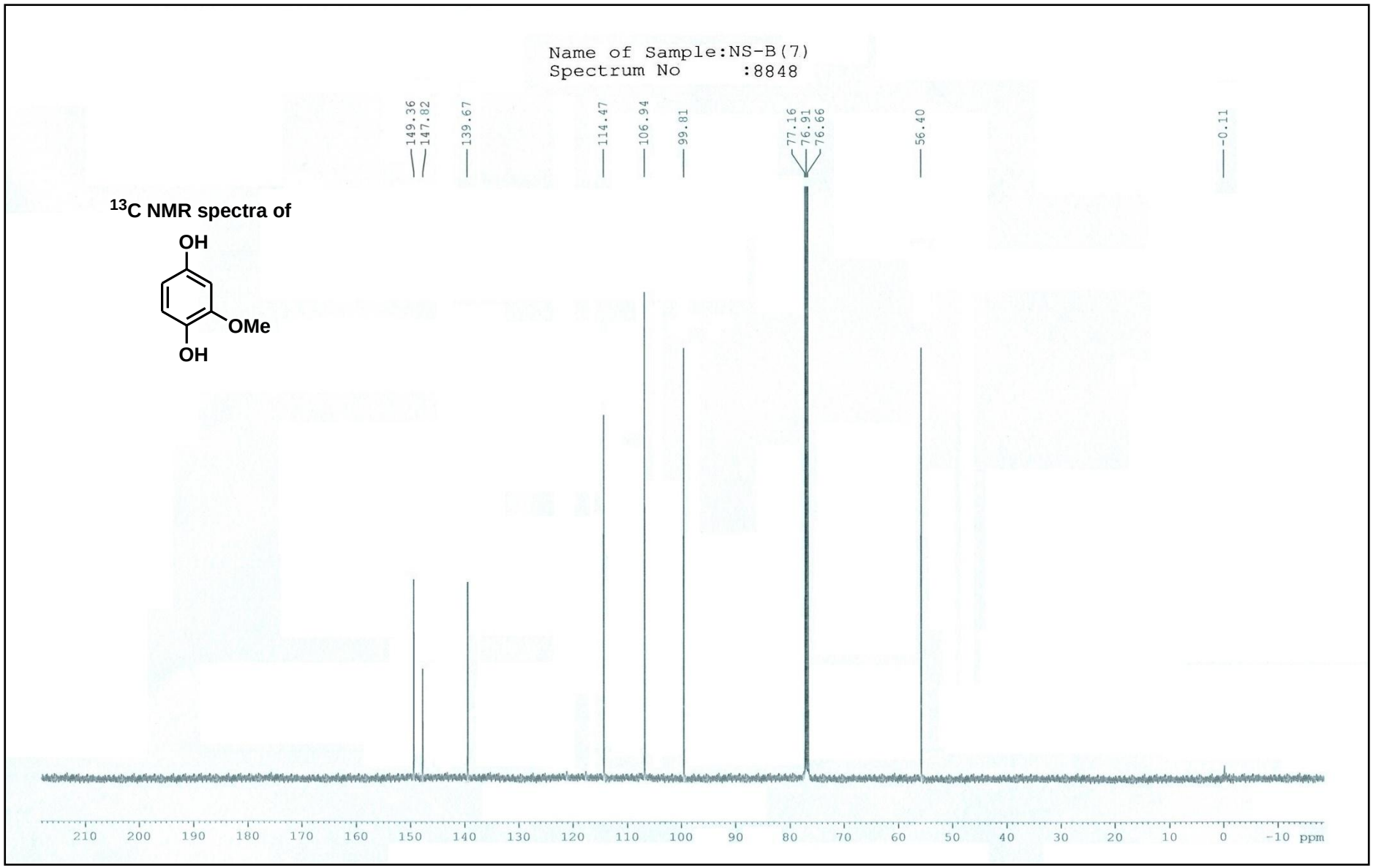




^{1}H NMR spectra of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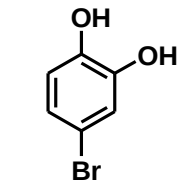
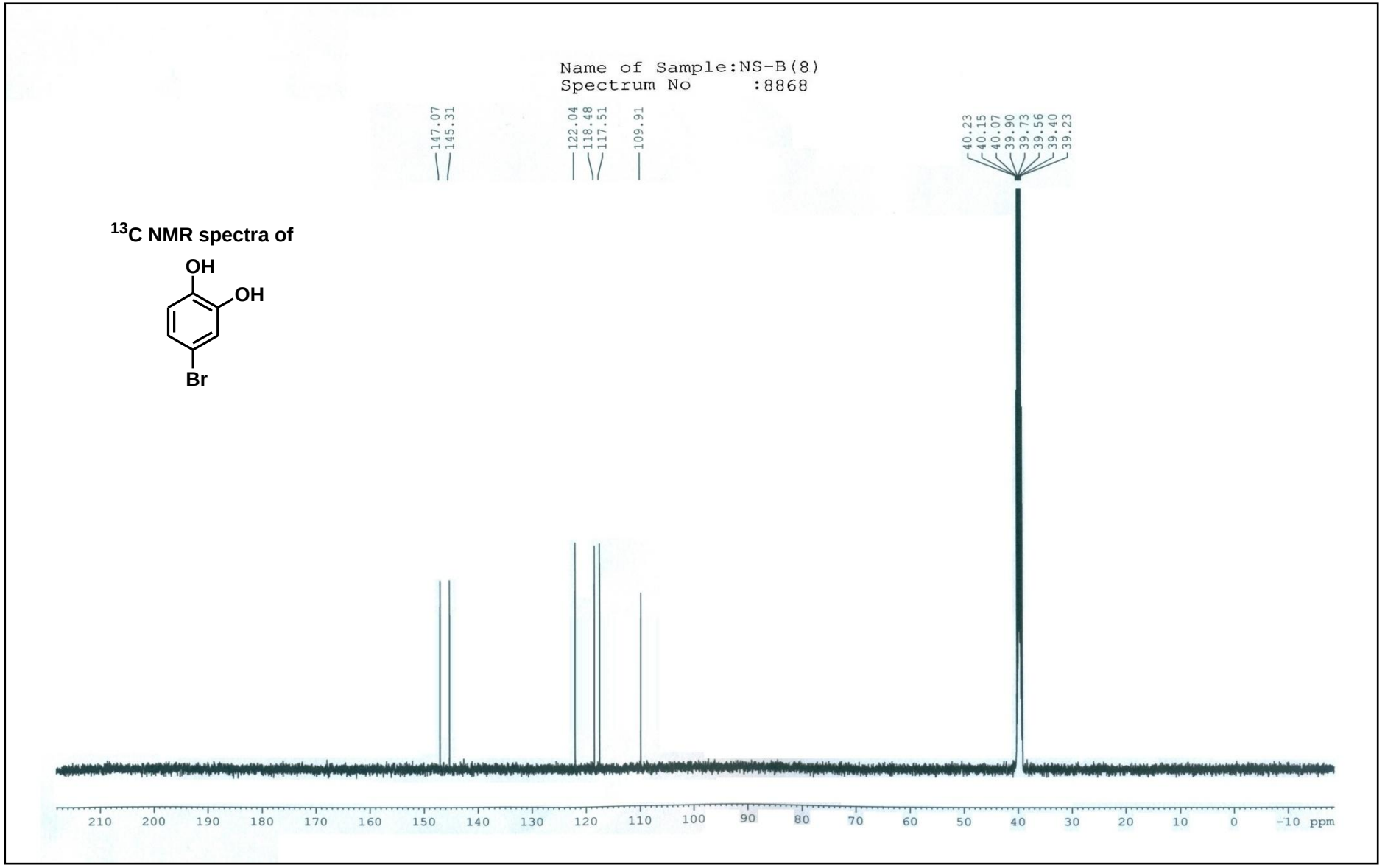
OH
OMe
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

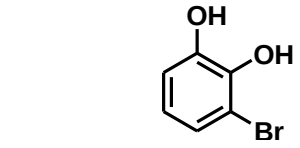
^{1}H NMR spectra of



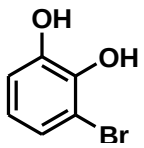


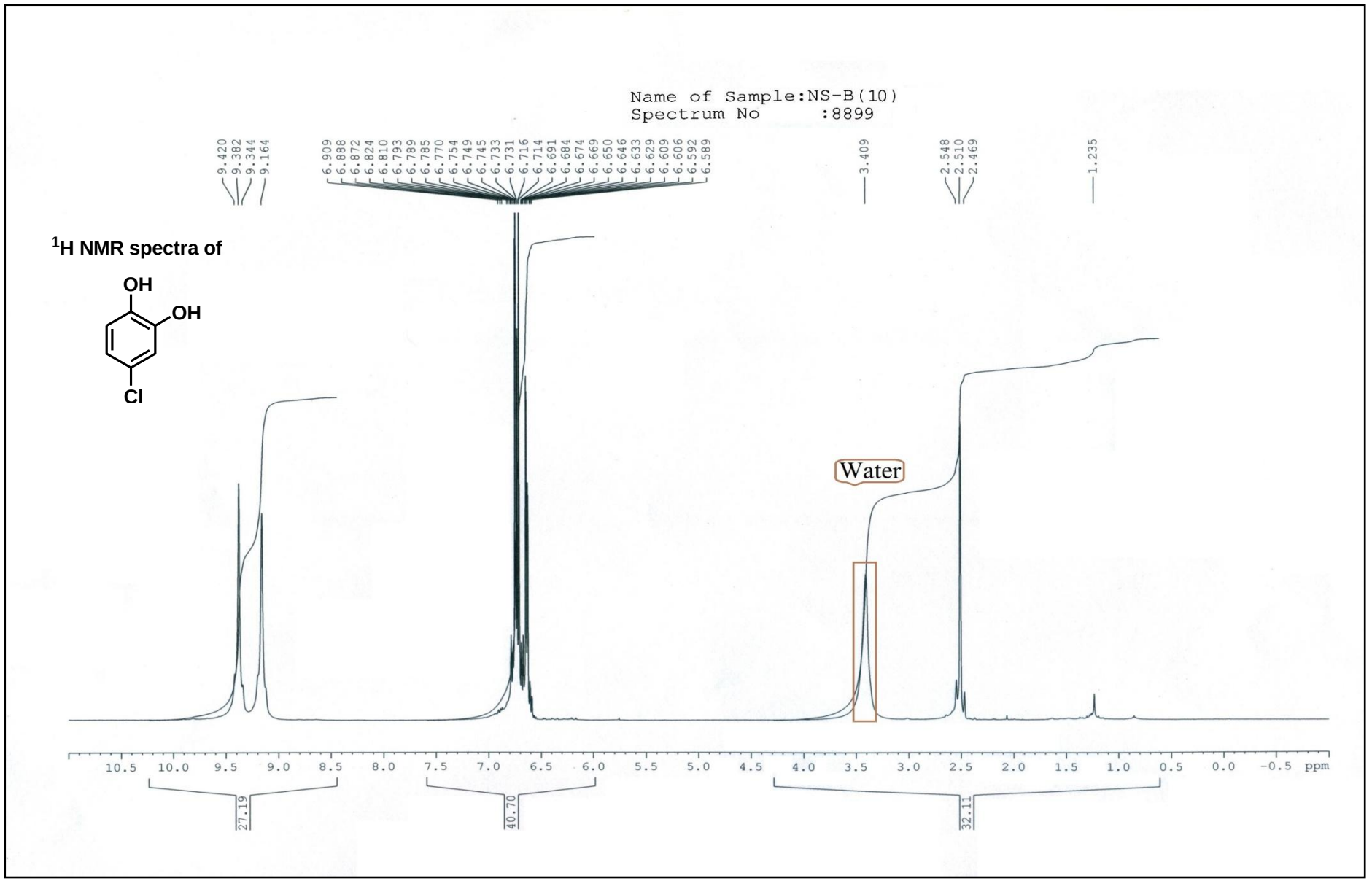
^{13}C NMR spectra of

^{1}H NMR spectra of



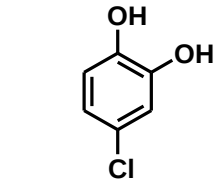
^{13}C NMR spectra of

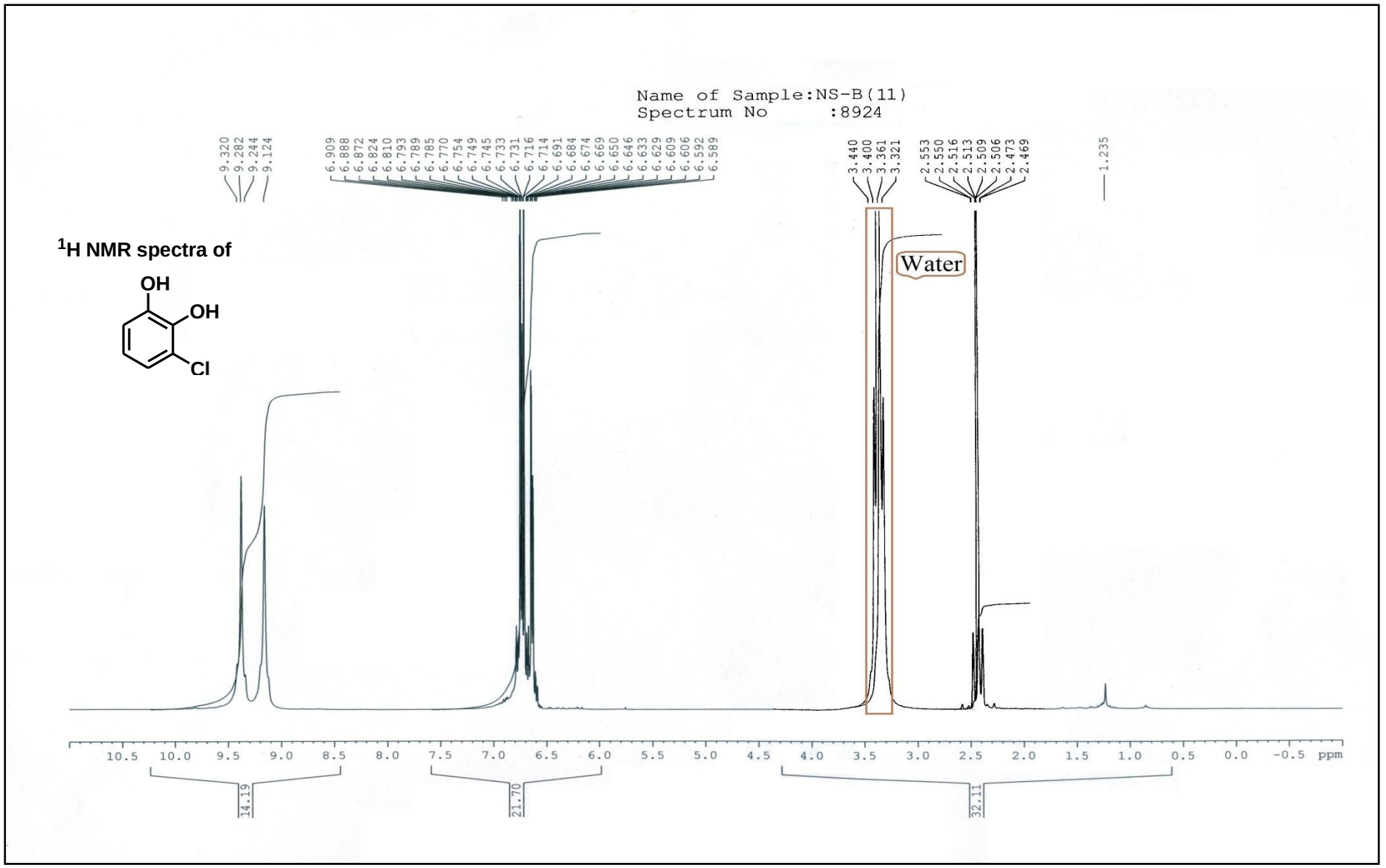




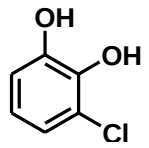
^{1}H NMR spectra of

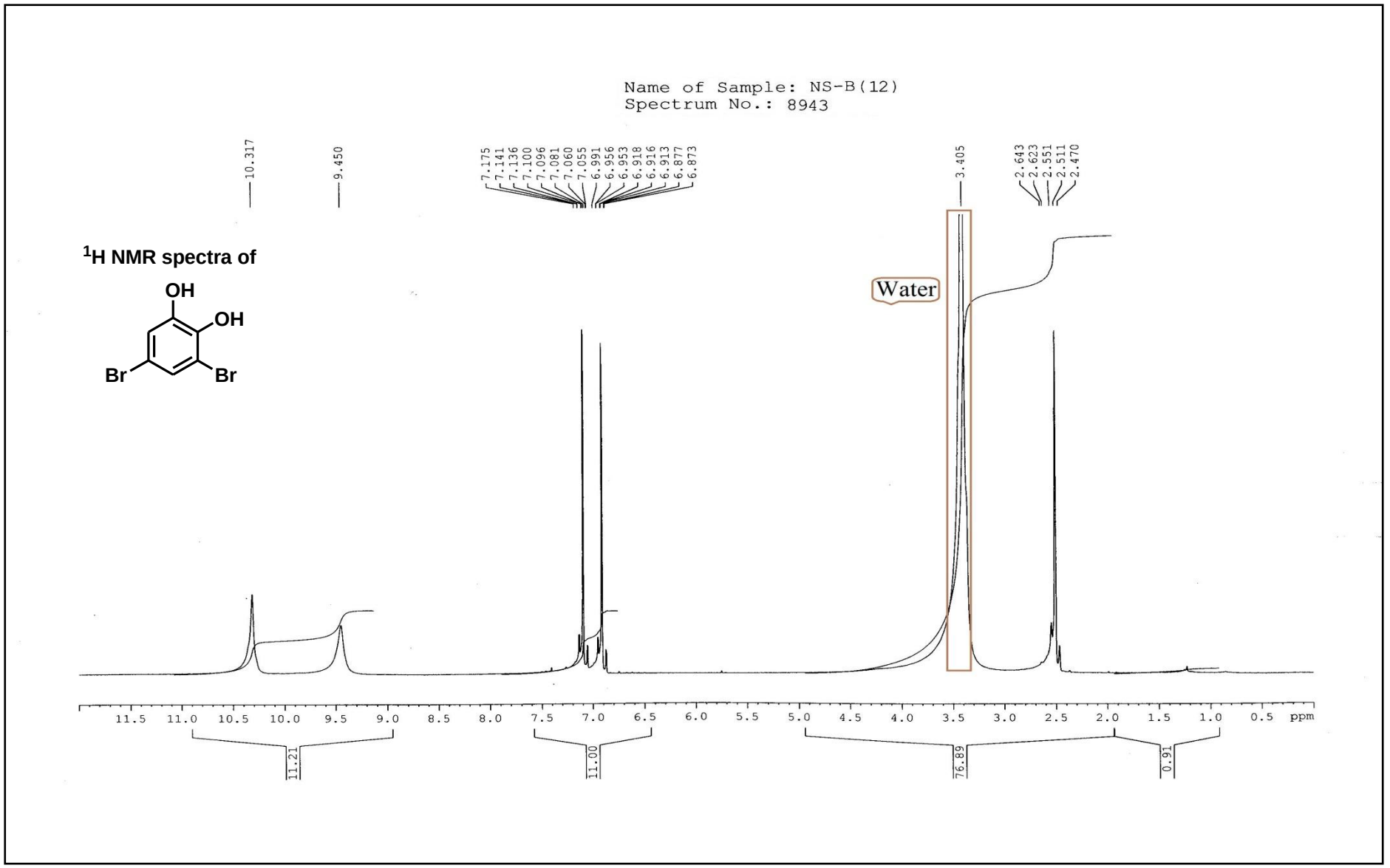
^{13}C NMR spectra of



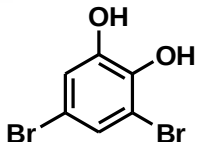

Name of Sample:NS-B(11)
Spectrum No :8924
1H NMR spectra of
OH
OH
Cl
Water
9.320
9.282
9.244
9.124
6.909
6.888
6.872
6.824
6.810
6.793
6.789
6.785
6.770
6.754
6.749
6.745
6.733
6.731
6.716
6.714
6.691
6.684
6.674
6.669
6.650
6.646
6.633
6.629
6.609
6.606
6.592
6.589
3.440
3.400
3.361
3.321
2.553
2.550
2.516
2.513
2.509
2.506
2.473
2.469
1.235
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
14.19
21.70
32.11

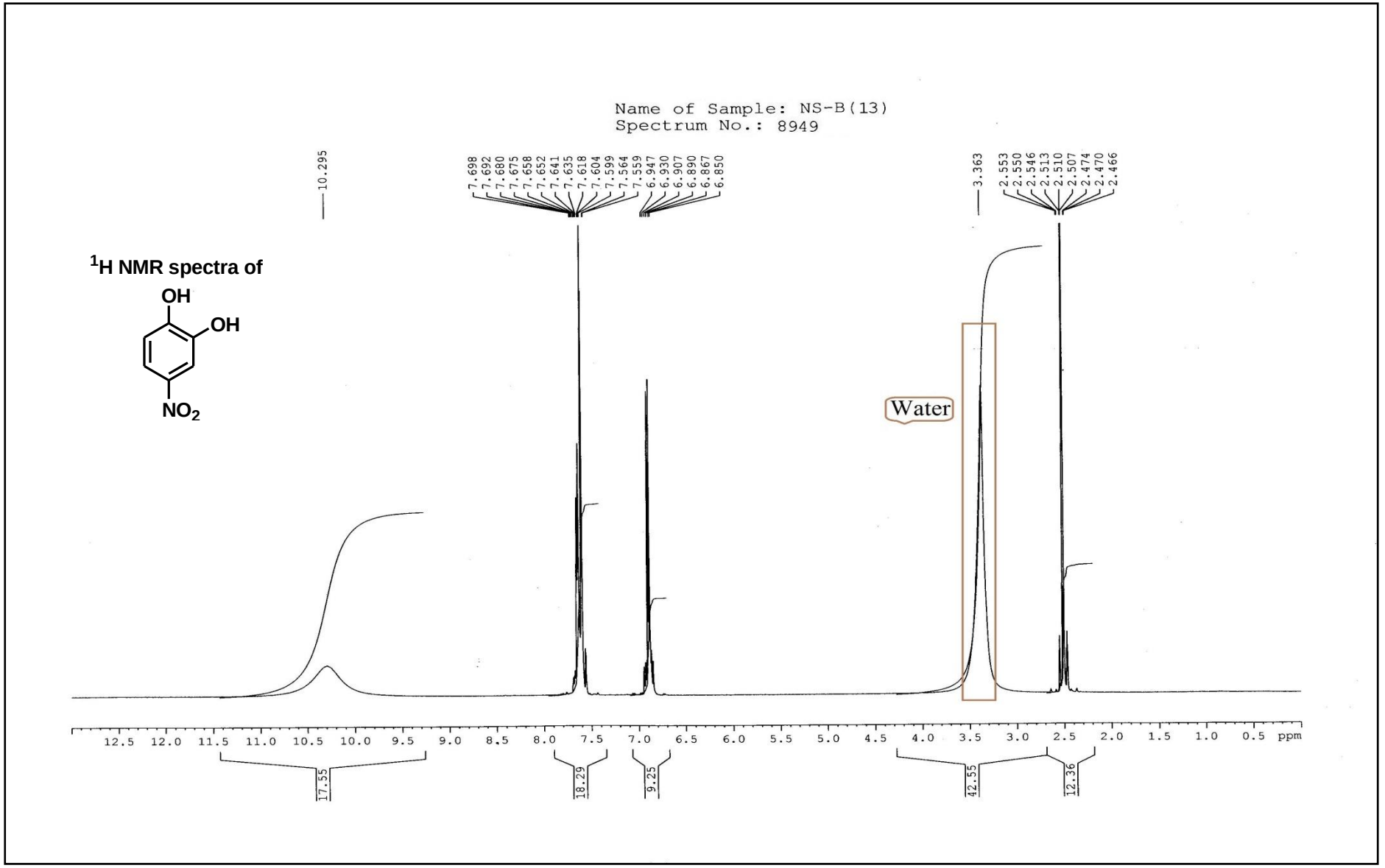
^{13}C NMR spectra of

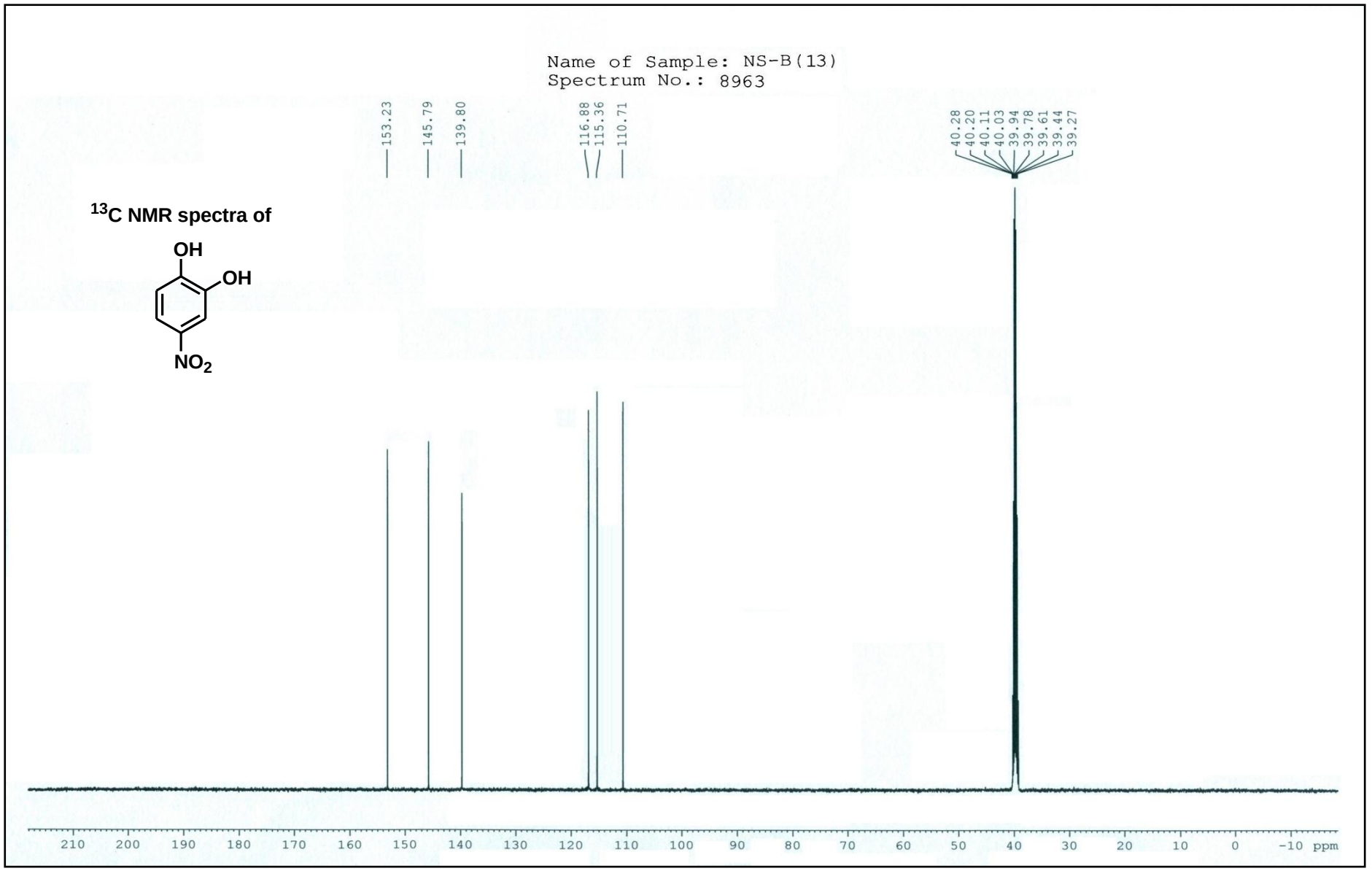


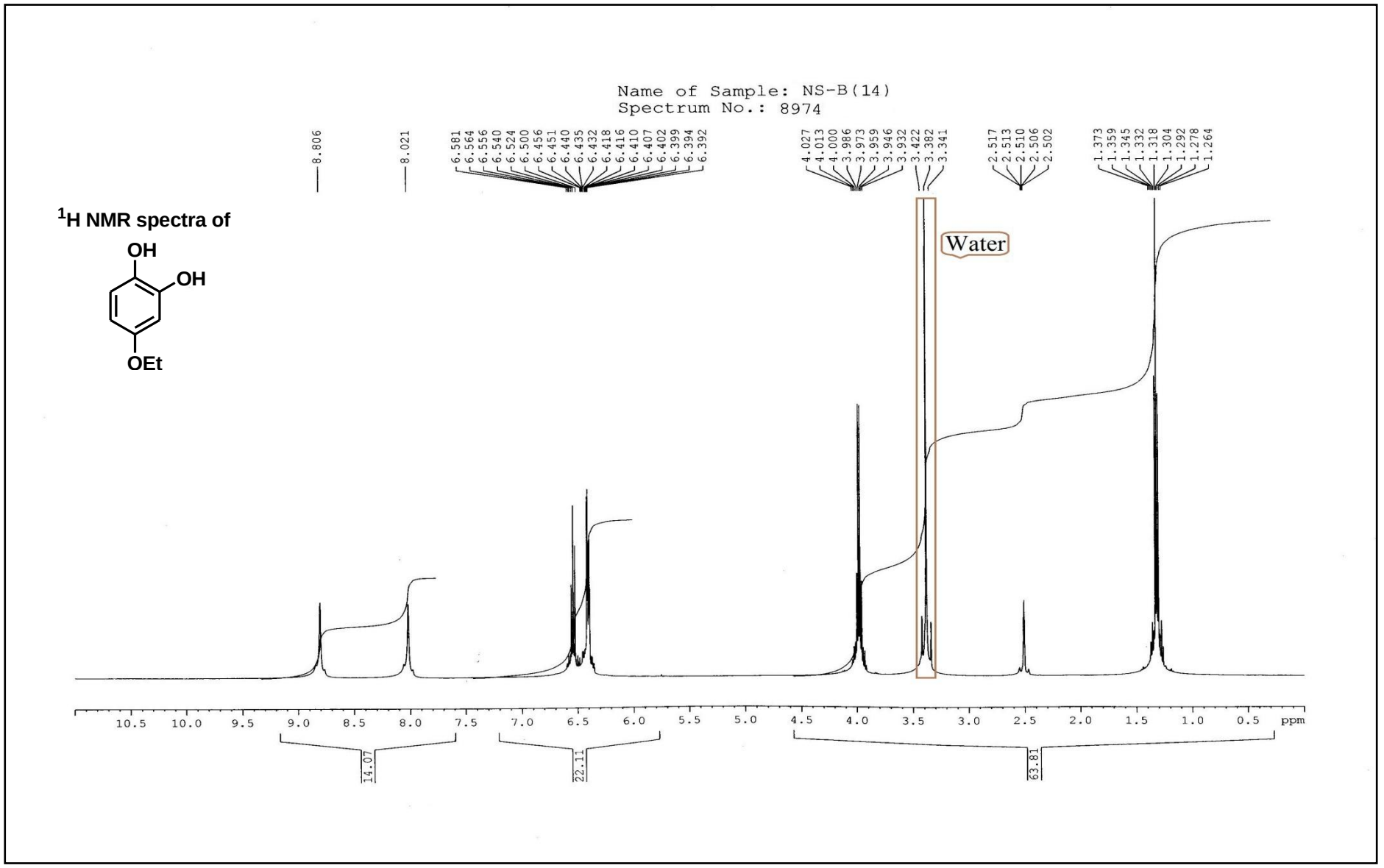

Name of Sample: NS-B(12)
Spectrum No.: 8943
1H NMR spectra of
OH
OH
Br
Br
Water
10.317
9.450
7.175
7.141
7.136
7.100
7.096
7.081
7.060
7.055
6.991
6.956
6.953
6.918
6.916
6.913
6.877
6.873
3.405
2.643
2.623
2.551
2.511
2.470
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
11.21
11.00
76.89
0.91

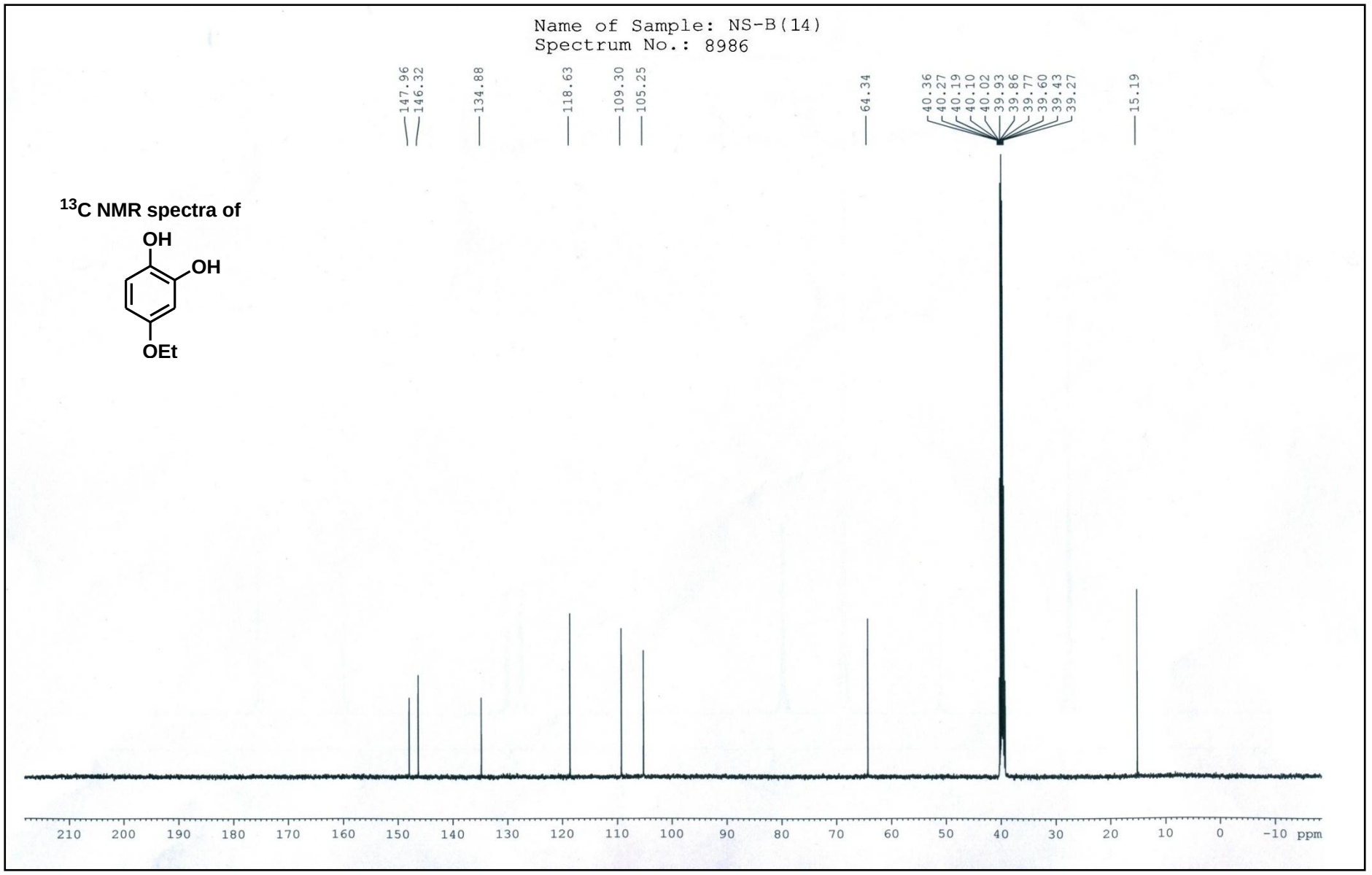
^{13}C NMR spectra of



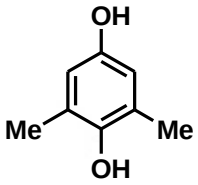

Name of Sample: NS-B(13)
Spectrum No.: 8949
1H NMR spectra of
OH
OH
NO2
Water
10.295
7.698
7.692
7.680
7.675
7.658
7.652
7.641
7.635
7.618
7.604
7.599
7.564
7.559
6.947
6.930
6.907
6.890
6.867
6.850
3.363
2.553
2.550
2.546
2.513
2.510
2.507
2.474
2.470
2.466
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 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 ppm
17.55
18.29
9.25
42.55
12.36


Name of Sample: NS-B(13)
Spectrum No.: 8963
153.23
145.79
139.80
116.88
115.36
110.71
40.28
40.20
40.11
40.03
39.94
39.78
39.61
39.44
39.27
^{13}C NMR spectra of
OH
OH
NO_2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

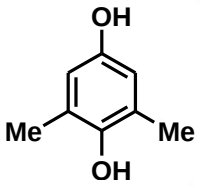

Name of Sample: NS-B(14)
Spectrum No.: 8974
1H NMR spectra of
OH
OH
OEt
Water
8.806
8.021
6.581
6.564
6.556
6.540
6.524
6.500
6.456
6.451
6.440
6.435
6.432
6.418
6.416
6.410
6.407
6.402
6.399
6.394
6.392
4.027
4.013
4.000
3.986
3.973
3.959
3.946
3.932
3.422
3.382
3.341
2.517
2.513
2.510
2.506
2.502
1.373
1.359
1.345
1.332
1.318
1.304
1.292
1.278
1.264
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
ppm
14.07
22.11
63.81


Name of Sample: NS-B(14)
Spectrum No.: 8986
147.96
146.32
134.88
118.63
109.30
105.25
64.34
40.36
40.27
40.19
40.10
40.02
39.93
39.86
39.77
39.60
39.43
39.27
15.19
^{13}C NMR spectra of
OH
OH
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

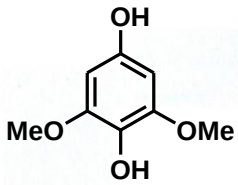
^{1}H NMR spectra of

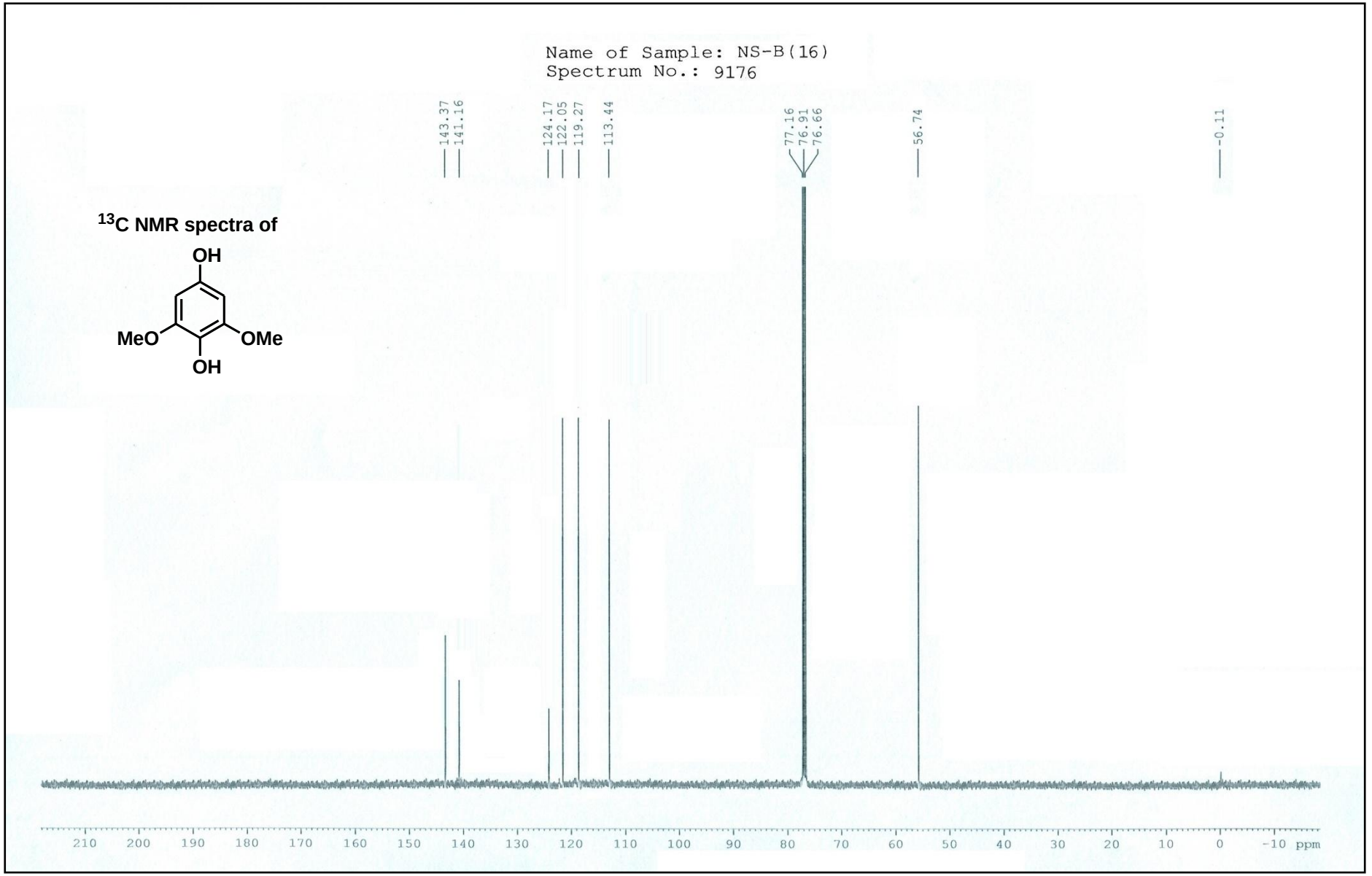


^{13}C NMR spectra of



^{1}H NMR spectra of





^{13}C NMR spectra of