Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Oxidative Transformations of Olefins Employing Persulfate/visible light Irradiation in Water

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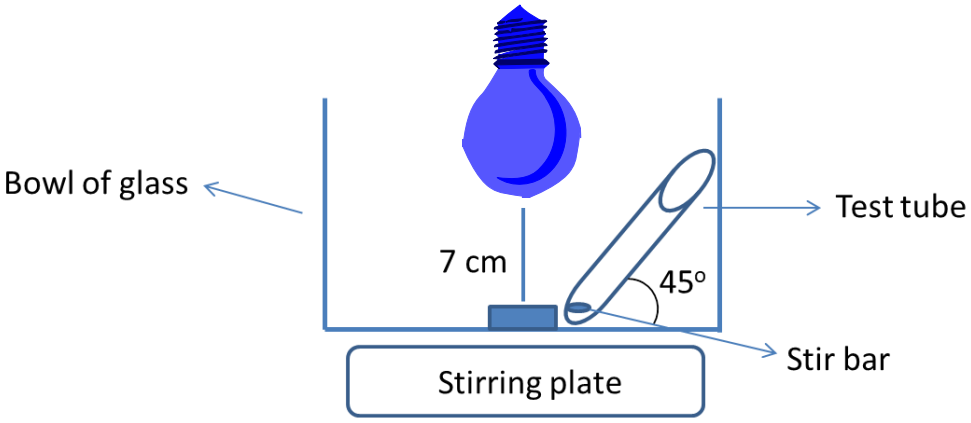
1. General Information

All reagents were purchased from commercial suppliers (Sigma-Aldrich, Oakwood and Combi-Blocks) and used without further purification, all solvents were analytical grade. Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness, visualization was accomplished with short wave UV light or $KMnO_4$ staining solution followed by heating. All melting points were determined using a Buchi micro melting point apparatus without correction. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 500 MHz in $CDCl_3$ solutions, at ambient temperature. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 125 MHz in $CDCl_3$ solutions, at ambient temperature. Chemicals shifts (δ) are given in ppm and the residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δH = 7.27 ppm, δC = 77.00 ppm. DMSO-d6: δH = 2.50 ppm, δC = 39.50 ppm). High resolution mass spectra were recorded on Q Exactive Orbitrap spectrometers working with electrospray ionization (ESI). The Gas Chromatography coupled to Mass Spectrometry (CG-MS) analyses were performed using a Network GC system 6890N (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with a HP-5MS 5% Phenyl Methyl Silox (25.0 m × 250 µm × 0.25 µ nominal) capillary column. The GC analyses were carried out in split mode (ratio 150:1) using helium as carrier gas at a flow rate of 504 mL/min (7.65 psi). The injection port temperature was 250 °C; the oven was maintained at an initial temperature of 50 °C for 3 minutes, then programmed at 40 °C/min to a temperature of 280 °C, where it was held, post-run, for 2 minutes. The MS detector was at 250 °C, using H_2 flow at 40.00 mL/min, air at 400 mL/min and He makeup flow at 45.0 mL/min.

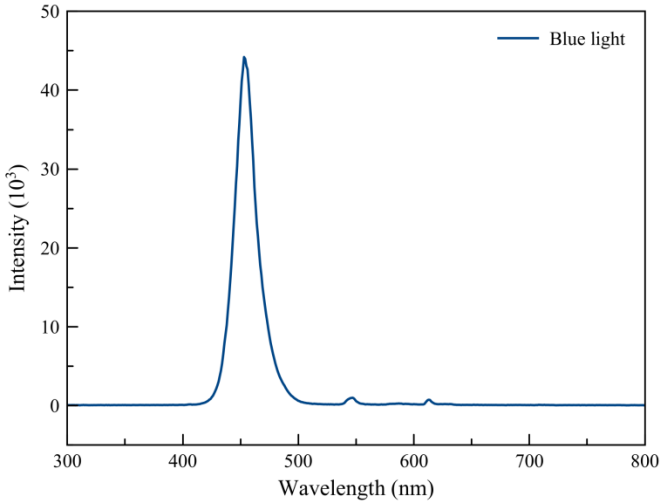
2. General Procedure

Styrenes, aliphatic olefins or α,β−unsaturated ketones (1.0 mmol, 1.0 equiv), were added to 0.8 ml of water containing $(NH_4)_2S_2O_8$ (3.0 mmol, 3.0 equiv) and TFA (1.5 mmol, 1.5 equiv). The reaction mixture was capped with a rubber septum and irradiated using blue LED (50 W) at room temperature under stirring (kept at around 35 °C using a fan) for 24 h. After completion of the reaction (followed by TLC), the suspension was extracted with ethyl acetate (3 × 2 mL) and the combined organic layers were concentrated. The crude mixture was filtered through a plug of silica (40 mm internal diameter, 7.5 g of SiO_2) using 55 mL of a mixture of ethyl acetate / n-hexane and followed by TLC to afford the desired pure product. For styrenes and aliphatic olefins, we have used a mixture of ethyl acetate / n-hexane (60:40). For acyclic α,β−unsaturated ketones, we have used a mixture of ethyl acetate / n-hexane (10:90). For cyclic α,β−unsaturated ketones, we have used a mixture of ethyl acetate / n-hexane (80:20)

A description of the apparatus for the photoreaction is shown below:



The emission spectrum of the blue LED is shown below:



3. Scheme 2, I and II in the main text

Styrene **1a** (0.25 mmol) and 4 equiv. of 2-propanol or tert-butanol were employed following the **General Procedure**. After the extraction, the crude mixture was diluted with ethyl acetate and analyzed by GC-MS (Figure S1). In another run, the crude mixture coming from the reaction in the presence of tert-butanol was purified according to the **General Procedure** to afford product **2a** in 85% yield as mentioned in the main text.

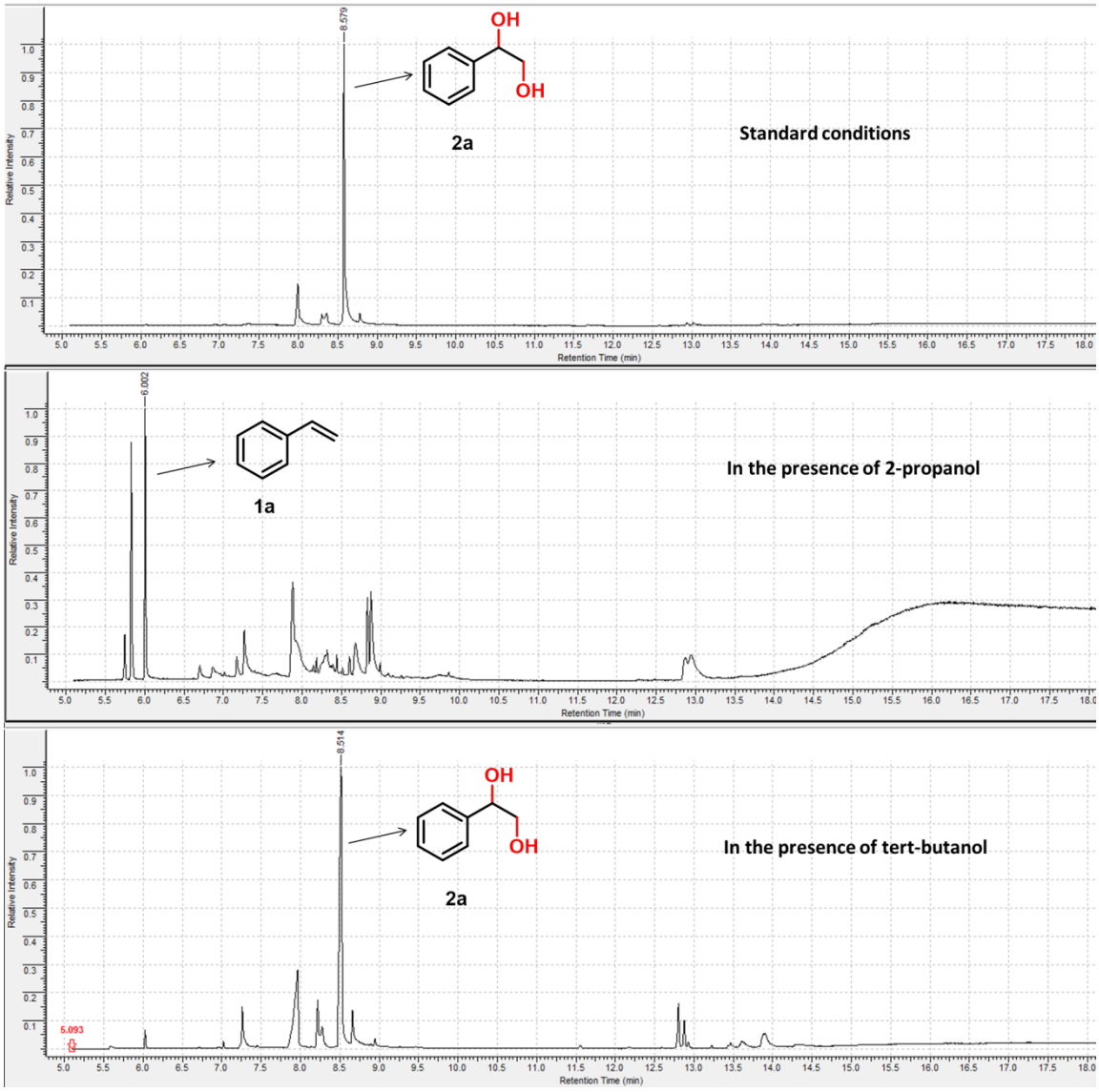
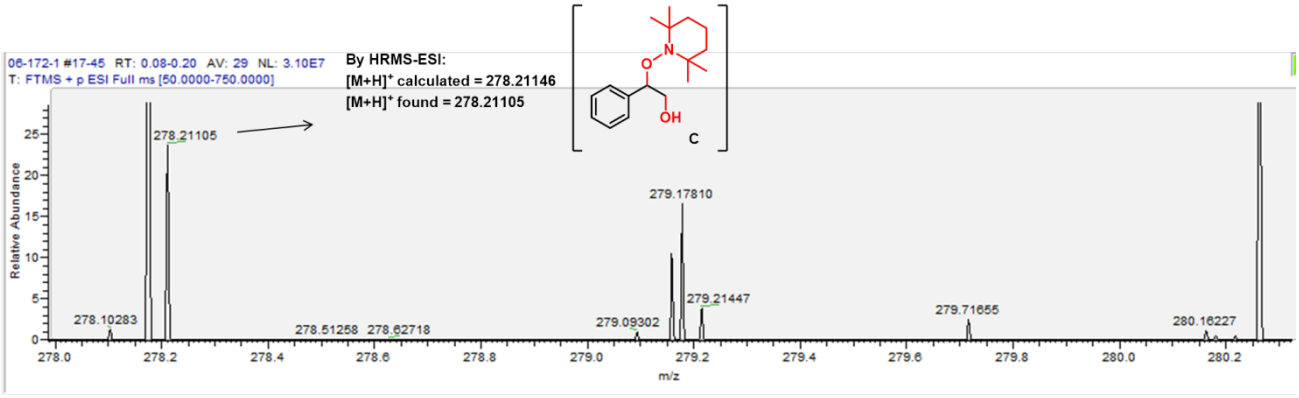


Figure S1. GC-MS of the reaction under standard conditions and in the presence of quenchers 2-propanol and tert-butanol.

4. Scheme 2, V in the main text

Styrene **1a** (0.25 mmol) and 3 equiv. of TEMPO were employed following the **General Procedure**. After the extraction, the crude mixture was evaporated, diluted with methanol and analyzed by HRMS-ESI positive mode (Figure S2).

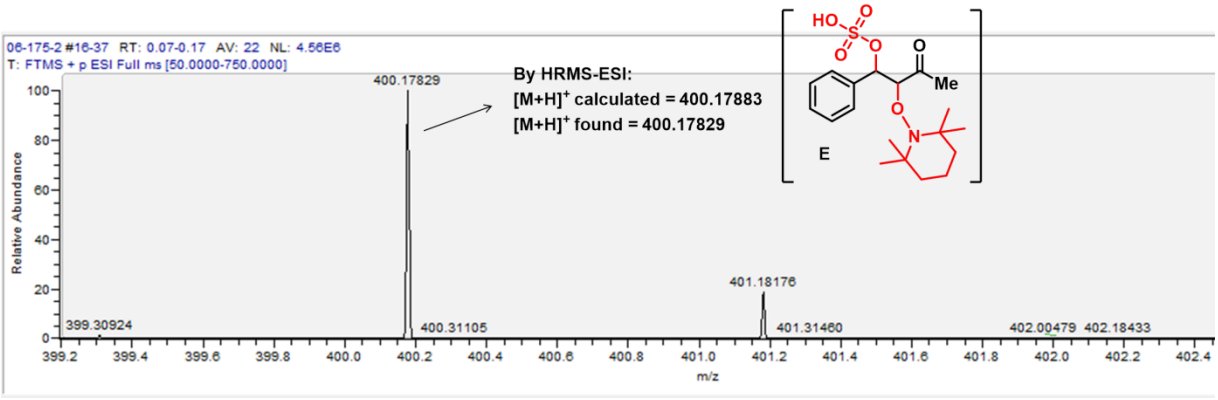


Analyzer: Orbitrap Thermo Qexactive
Column: no column (FIA)
Polarity: Positive
Flow: 200 uL/min of H_2O:MeOH 1:1 v/v with 0,1% v/v HCOOH
Resolution: 70 10E3
Range of m/z: 50 a 750
Injection volume: 20 uL
Cone: 3,5 KV e 50 V SLens

Figure S2. HRMS-ESI of the crude mixture evidencing the presence of adduct **C**.

5. Scheme 4, III in the main text

α,β–unsaturated ketone **3a** (0.25 mmol) and 3 equiv. of TEMPO were employed following the **General Procedure**. After the extraction, the crude mixture was evaporated, diluted with methanol and analyzed by HRMS-ESI positive mode (Figure S3).

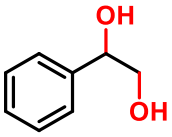


Analyzer: Orbitrap Thermo Qexactive
Column: no column (FIA)
Polarity: Positive

Flow: 200 uL/min of H_2O:MeOH 1:1 v/v with 0,1% v/v HCOOH
Resolution: 70 10E3
Range of m/z: 50 a 750
Injection volume: 20 uL
Cone: 3,5 KV e 50 V SLens

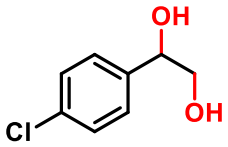
Figure S3. HRMS-ESI of the crude mixture evidencing the presence of adduct **E**.

6. Characterization of the products



2a

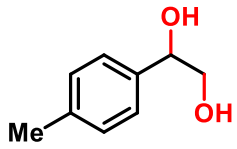
Prepared from styrene following the general procedure to give the product as colourless oil (91% yield). All data was consistent with that previously reported.[1]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.28 (m, 5H), 4.79 (dd, 1H, J = 8.31, 3.42 Hz), 3.72 (dd, 2H, J = 11.25, 3.42 Hz), 3.64 (dd, 2H, J = 11.25, 8.31 Hz), 3.29 (bs, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 140.38, 128.48, 127.94, 126.05, 74.67, 67.96.



2b

Prepared from 4-chlorostyrene following the general procedure to give the product as pale yellow oil (89% yield). All data was consistent with that previously reported.[1]
^{1}H NMR (500 MHz, DMSO-d6): δ 7.35 (bs, 4H), 5.32 (d, 1H, J = 4.40 Hz), 4.73 (t, 1H, J = 5.66 Hz), 4.52 (dt, 1H, J = 5.66, 5.03 Hz), 3.38–3.44 (m, 2H).
^{13}C NMR (125 MHz, DMSO-d6): δ 142.55, 131.24, 128.18, 127.74, 73.02, 67.18.

[1] K. M. Jones and N. C. O. Tomkinson, *J. Org. Chem.*, 2012, **77**, 921–928.

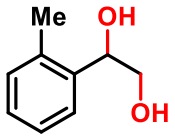


2c

Prepared from 4-methylstyrene following the general procedure to give the product as pale yellow oil (88% yield). All data was consistent with that previously reported.[1]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, 2H, J = 7.86 Hz), 7.17 (d, 2H, J = 7.86 Hz), 4.80 (dd, 1H, J = 8.17, 3.46 Hz), 3.74 (dd, 1H, J = 11.00, 2.83 Hz), 3.67 (dd, 1H, J = 11.30, 8.49 Hz), 2.77 (bs, 2H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.79, 137.36, 129.22, 126.01, 74.53, 67.98, 21.10.

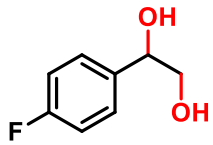


2d

Prepared from 2-methylstyrene following the general procedure to give the product as pale yellow oil (82% yield). All data was consistent with that previously reported.[1]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 1H, J = 7.55 Hz), 7.25–7.14 (m, 3H), 5.07 (bd, 1H, J = 8.17 Hz), 3.72 (bd, 1H, J = 11.32 Hz), 3.62 (apt t, 1H, J = 10.38 Hz), 3.10 (bs, 2H), 2.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.27, 134.74, 130.42, 127.74, 126.28, 125.62, 71.42, 66.80, 18.97.



2e

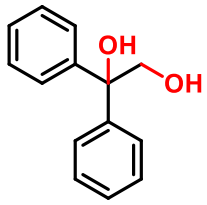
Prepared from 4-fluorostyrene following the general procedure to give the product as colourless oil (86% yield). All data was consistent with that previously reported.[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.03 (dt, 2H, J = 8.80, 1.96 Hz), 4.78 (dd, 1H, J = 8.31, 3.42 Hz), 3.70 (dd, 1H, J = 11.25, 2.93 Hz), 3.61 (dd, 1H, J = 11.25, 8.31 Hz), 3.15 (bs, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.65, 161.20, 136.13, 136.10, 127.77, 127.69, 115.48, 115.27, 74.01, 67.93.

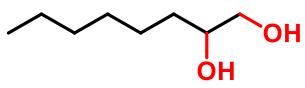
[2] R. Bag, D. Sar and T. Punniyamurthy, *Org. Biomol. Chem.*, 2016, **14**, 3246–3255.

^{19}F NMR (282 MHz, $CDCl_3$, decoupled): δ -114.35.
^{19}F NMR (282 MHz, $CDCl_3$, coupled): δ -114.41– -114.27 (m).



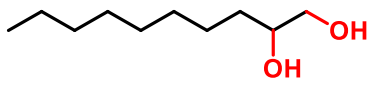
2f

Prepared from 1,1-diphenylethylene following the general procedure to give the product as pale yellow oil (84% yield). All data was consistent with that previously reported.[1]
^{1}H NMR (500 MHz, DMSO-d6): δ 7.43–7.41 (dd, 4H, J = 8.30, 1.47 Hz), 7.28–7.25 (t, 4H, J = 8.17 Hz), 7.19–7.16 (tt, 2H, J = 7.55, 1.26 Hz), 5.46 (s, 1H), 4.82 (t, 1H, J = 5.34 Hz), 3.94 (d, 2H, J = 5.34 Hz).
^{13}C NMR (125 MHz, DMSO-d6): δ 146.17, 127.61, 126.52, 126.28, 77.57, 68.30.



2g

Prepared from 1-octene following the general procedure to give the product as colourless oil (74% yield). All data was consistent with that previously reported.[3]
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.99 (bs, 2H), 3.64 (m, 1H), 3.57 (dd, 1H, J = 11.25, 2.45 Hz), 3.37 (dd, 1H, J = 11.25, 7.82 Hz), 1.39–1.26 (m, 10H), 0.86 (t, 3H, J = 6.85 Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 72.33, 66.63, 33.01, 31.72, 29.30, 25.53, 22.54, 13.98.

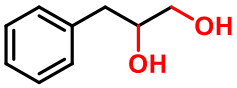


2h

Prepared from 1-decene following the general procedure to give the product as colourless oil (71% yield). All data was consistent with that previously reported.[4]

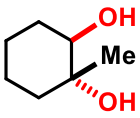
[3] V. Zubar, Y. Lebedev, L. M. Azofra, L. Cavallo, O. El-Sepelgy and M. Rueping, *Angew. Chemie - Int. Ed.*, 2018, **57**, 13439–13443.
[4] I. Prat, D. Font, A. Company, K. Junge, X. Ribas, M. Beller and M. Costas, *Adv. Synth. Catal.*, 2013, **355**, 947–956.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.77 (bs, 2H), 3.65 (m, 1H), 3.58 (dd, 1H, J = 11.25, 2.45 Hz), 3.38 (dd, 1H, J = 11.25, 7.83 Hz), 1.45–1.21 (m, 14H), 0.87 (t, 3H, J = 6.85 Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 72.35, 66.68, 33.06, 31.83, 29.67, 29.51, 29.24, 25.60, 22.60, 14.01.



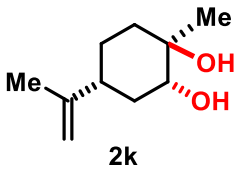
2i

Prepared from allylbenzene following the general procedure to give the product as pale yellow oil (80% yield). All data was consistent with that previously reported.[5]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.28 (m, 2H), 7.25–7.19 (m, 3H), 3.86 (m, 1H), 3.67 (bs, 2H), 3.56 (dd, 1H, J = 11.25, 2.93 Hz), 3.41(dd, 1H, J = 11.25, 7.34 Hz), 2.70 (d, 2H, J = 6.85 Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 137.87, 129.22, 128.38, 126.34, 73.02, 65.74, 39.55.



***(rac)*- 2j**

Prepared from 1-methylcyclohex-1-ene following the general procedure to give the product as colourless oil (88% yield). All data was consistent with that previously reported.[6]
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.46 (dd, 1H, J = 10.76, 4.40 Hz), 3.07 (bs, 2H), 1.85–1.81 (m, 1H), 1.74–1.66 (m, 2H), 1.60–1.57 (m, 1H), 1.41–1.25(m, 4H), 1.17 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 77.12, 74.11, 38.61, 31.07, 24.13, 23.19, 19.35.

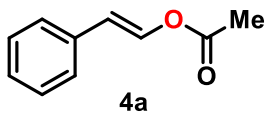


2k

Prepared from (*R*)-(+)-limonene following the general procedure to give the product as colourless oil (79% yield). All data was consistent with that previously reported. [7]

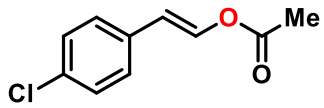
[5] S. Fang, X. Wang, F. Yin, P. Cai, H. Yang and L. Kong, *Org. Lett.*, 2019, **21**, 1841–1844.
[6] Y. Masuda, D. Ikeshita and M. Murakami, *Helv. Chim. Acta*, 2021, 104.
[7] A. E. Leung, R. Rubbiani, G. Gasser and K. L. Tuck, *Org. Biomol. Chem.*, 2014, **12**, 8239–8246.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.72 (s, 2H), 3.58 (dd, 1H, J = 11.74, 4.40 Hz), 2.08 (tt, 1H, J = 12.20, 3.40 Hz), 1.90–1.96 (m, 1H), 1.79 (dt, 1H, J = 12.72, 3.40 Hz), 1.73–1.68 (s+m, 4H), 1.49 (td, 1H, J = 19.60, 3.91 Hz), 1.36–1.27 (m, 2H), 1.28 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 148.46, 109.07, 77.19, 74.01, 43.61, 38.50, 36.06, 28.63, 20.91, 18.87.



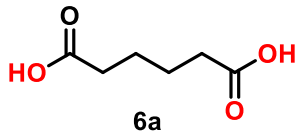
4a

Prepared from (*E*)-4-phenylbut-3-en-2-one following the general procedure to give the product as pale yellow oil (77% yield). All data was consistent with that previously reported.[8]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, 1H, J = 12.72 Hz), 7.37–7.23 (m, 5H), 6.39 (d, 1H, J = 12.72 Hz), 2.21 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 168.02, 136.23, 134.11, 128.70, 127.41, 126.22, 115.29, 20.74.



4b

Prepared from (*E*)-4-(4-chlorophenyl)but-3-en-2-one following the general procedure to give the product as pale yellow oil (78% yield). All data was consistent with that previously reported.[8]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, 1H, J = 12.89 Hz), 7.29–7.24 (m, 4H), 6.33 (d, 1H, J = 12.89 Hz), 2.20 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 167.79, 136.52, 132.92, 132.60, 128.79, 127.32, 114.06, 20.60.

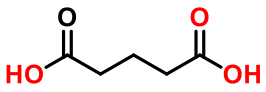


6a

Prepared from 2-cyclohexen-1-one following the general procedure to give the product as a white solid (92% yield, mp = 153 ^{o}C). All data was consistent with that previously reported.[9]

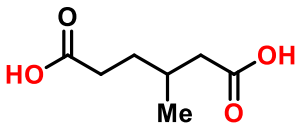
[8] B. Poladura, Á. Martínez-Castañeda, H. Rodríguez-Solla, R. Llavona, C. Concellón and V. Del Amo, *Org. Lett.*, 2013, **15**, 2810–2813.

^{1}H NMR (500 MHz, DMSO-d6): δ 11.98 (s, 2H), 2.20 (m, 4H), 1.49 (m, 4H).
^{13}C NMR (125 MHz, DMSO-d6): δ 174.42, 33.45, 24.10.



6b

Prepared from 2-cyclopenten-1-one following the general procedure to give the product as a white solid (90% yield, mp = 95 ^{o}C). All data was consistent with that previously reported.[9]
^{1}H NMR (500 MHz, DMSO-d6): δ 12.06 (bs, 1H), 3.42 (bs, 1H), 2.23 (t, 4H, J = 7.55 Hz), 1.69 (quint, 2H, J = 7.55 Hz).
^{13}C NMR (125 MHz, DMSO-d6): δ 174.21, 32.84, 20.05.

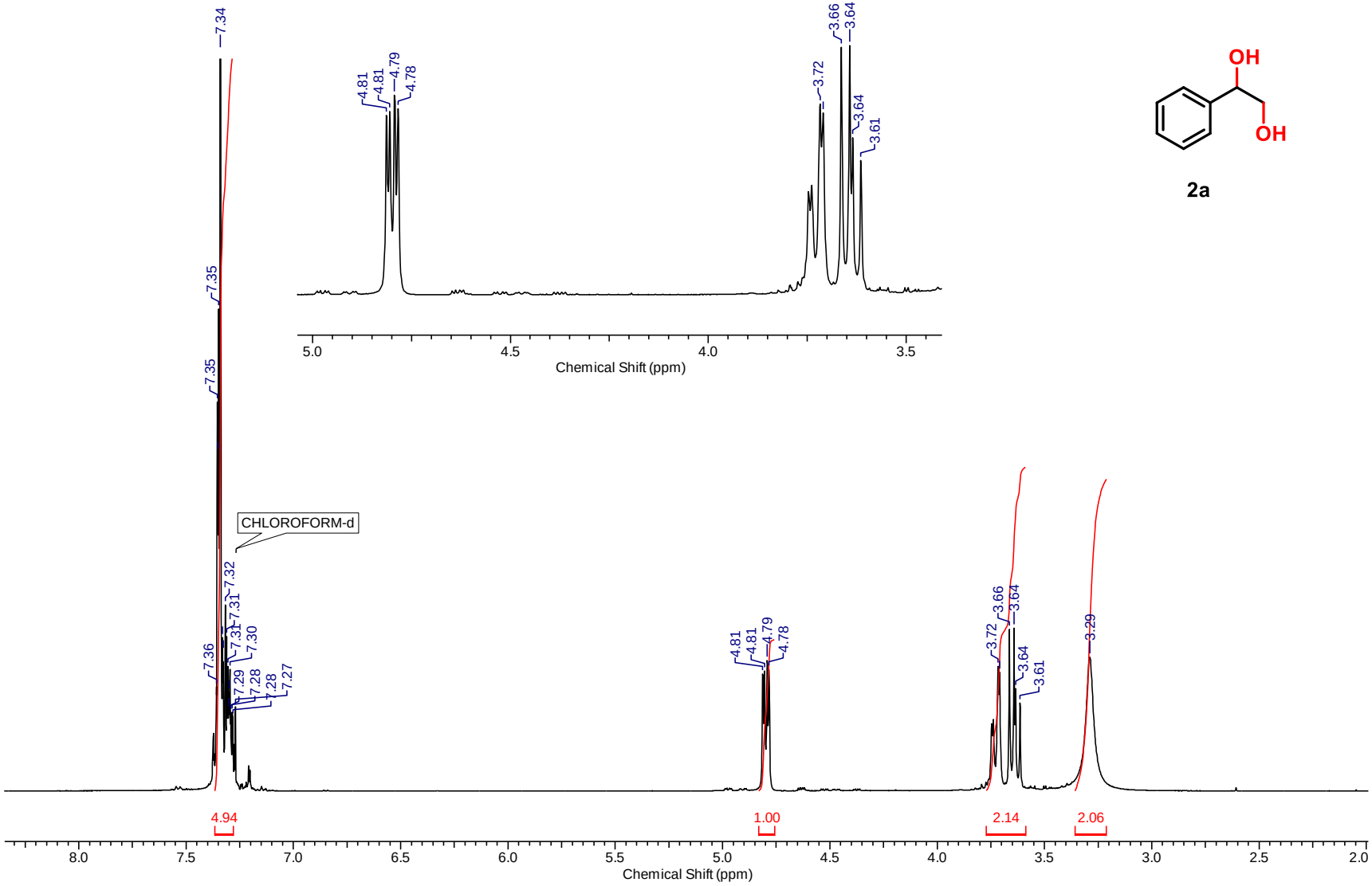


6c

Prepared from 4-methyl-2-cyclohexen-1-one following the general procedure to give the product as colourless oil (87% yield). All data was consistent with that previously reported.[10]
^{1}H NMR (500 MHz, DMSO-d6): δ 10.35 (bs, 2H), 2.46-2.34 (m, 3H), 2.22 (dd, 1H, J = 15.41, 7.86 Hz), 2.02 (octet, 1H, J = 6.60 Hz), 1.79–1.72 (m, 1H), 1.60–1.54 (m, 1H), 1.00 (d, 3H, J = 6.60 Hz).
^{13}C NMR (125 MHz, DMSO-d6): δ 180.00, 179.29, 41.17, 31.65, 31.03, 29.52, 19.26.

[9] Y. Matsumoto, M. Kuriyama, K. Yamamoto, K. Nishida and O. Onomura, *Org. Process Res. Dev.*, 2018, **22**, 1312–1317.
[10] C. H. Lee, C. L. Wu, S. A. Hua, Y. H. Liu, S. M. Peng and S. T. Liu, *Eur. J. Inorg. Chem.*, 2015, **2015**, 1417–1423.

7. Spectral Data


7.34
7.35
7.35
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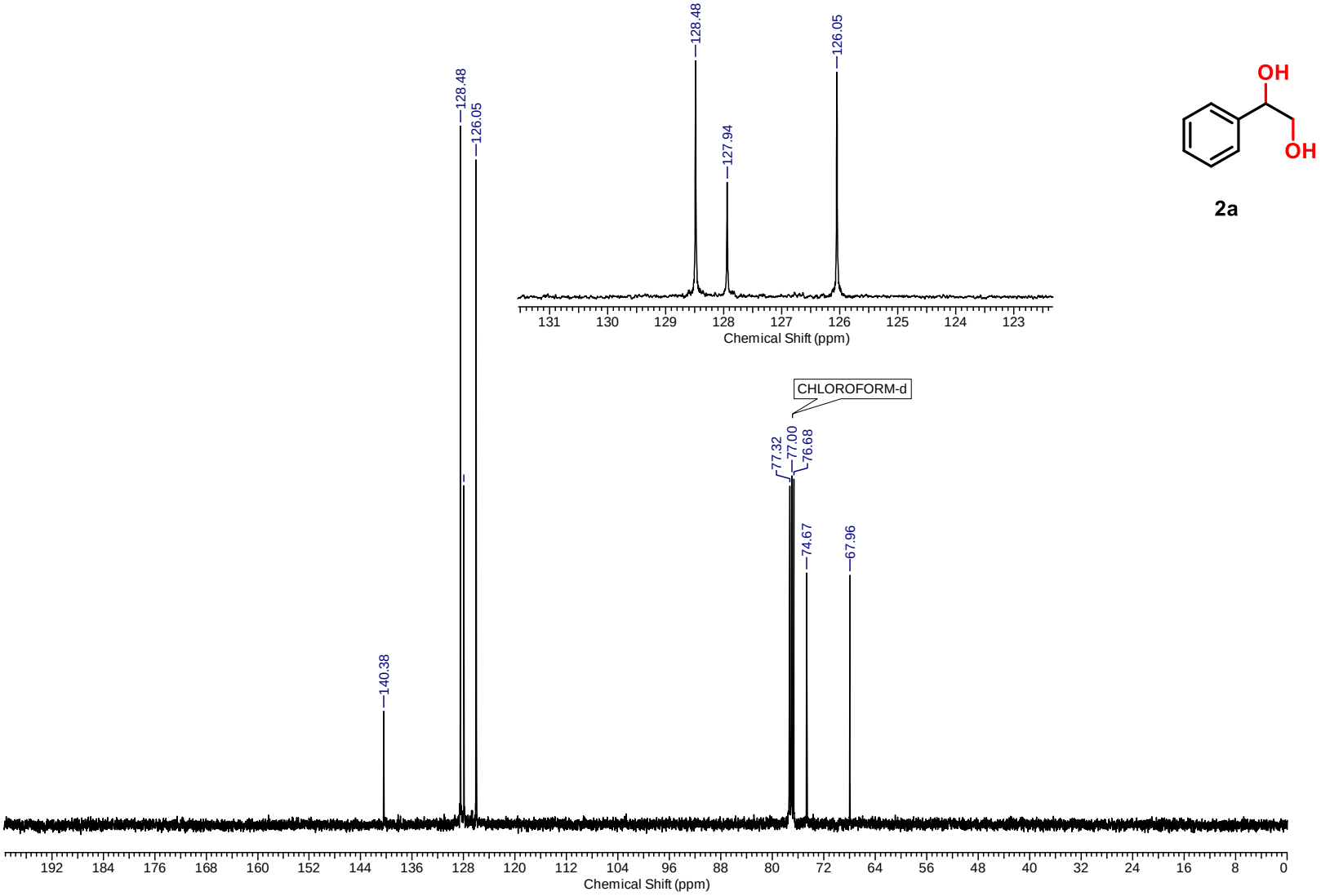
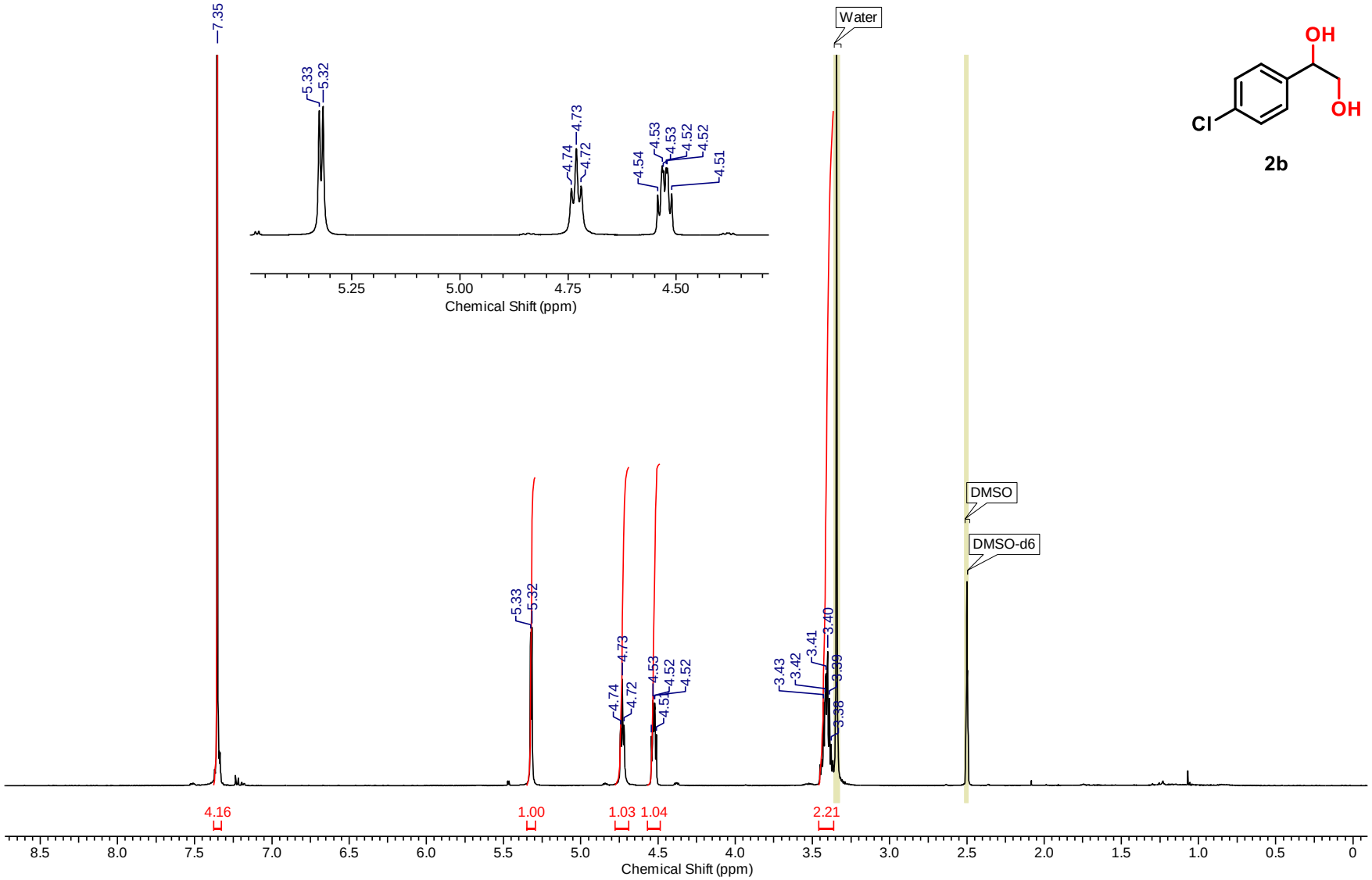
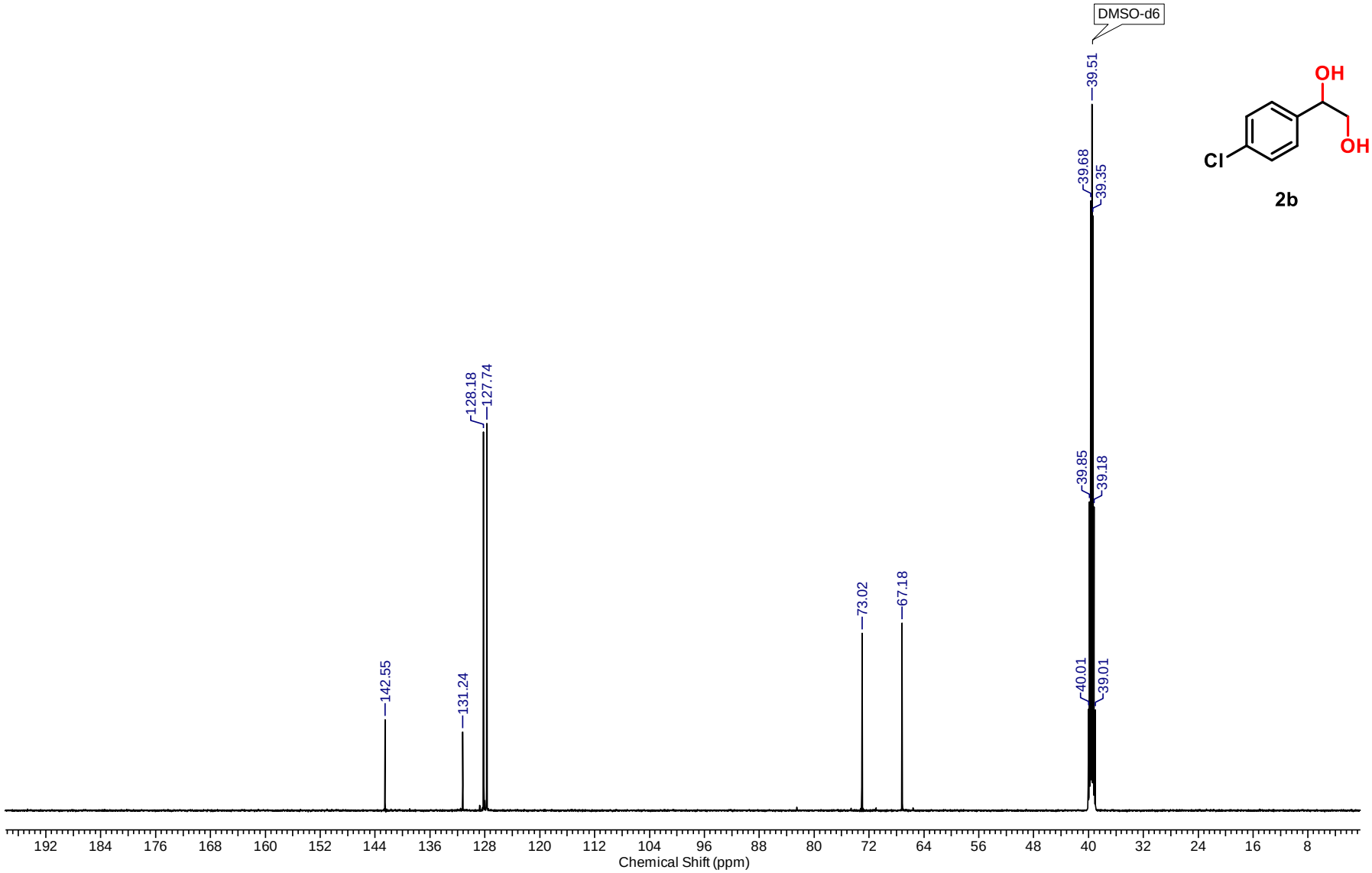
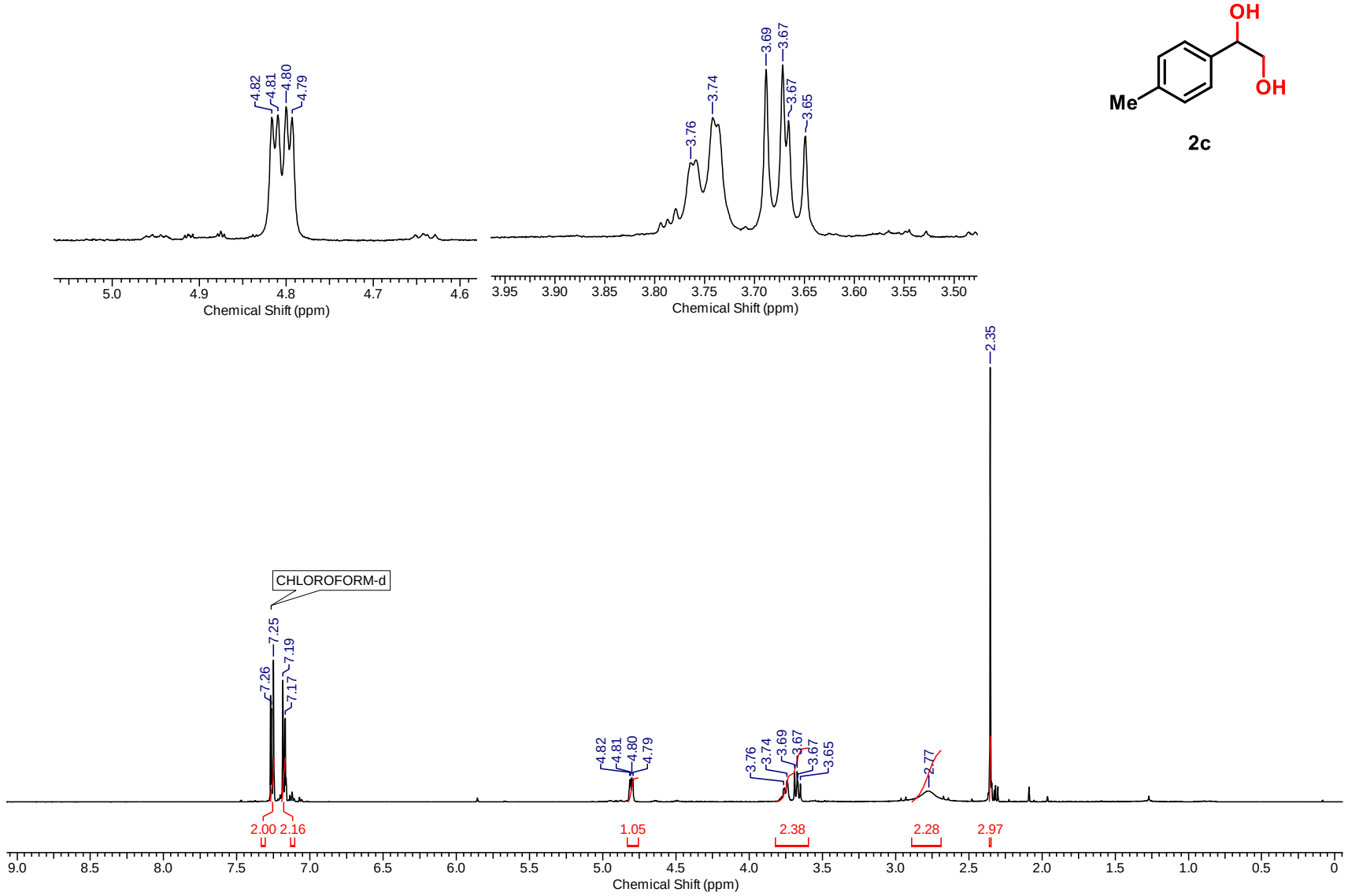
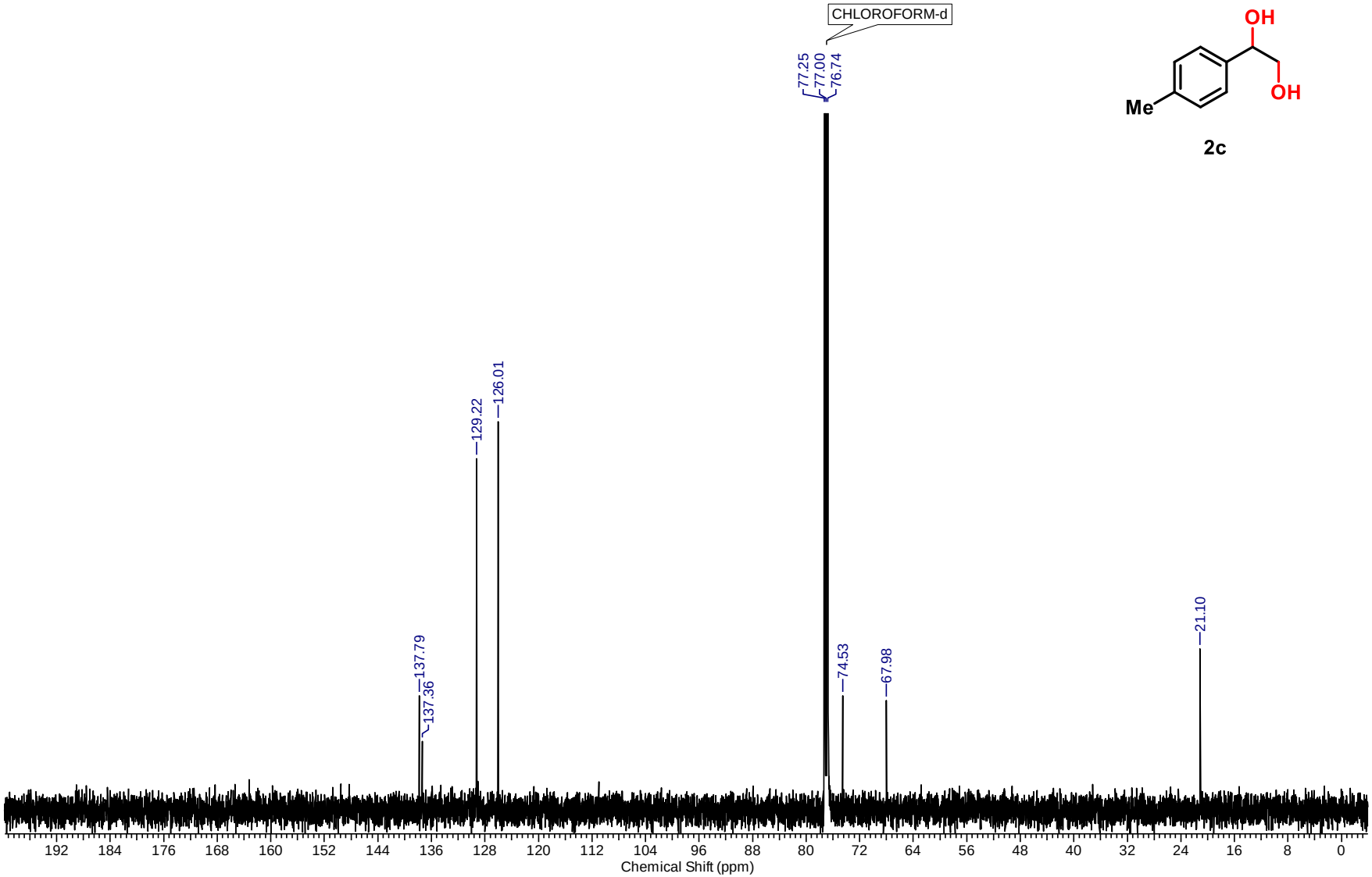
7.27
4.81
4.81
4.79
4.78
3.72
3.66
3.64
3.64
3.61
3.29
4.94
1.00
2.14
2.06
Chemical Shift (ppm)
Chemical Shift (ppm)
OH
OH
2a

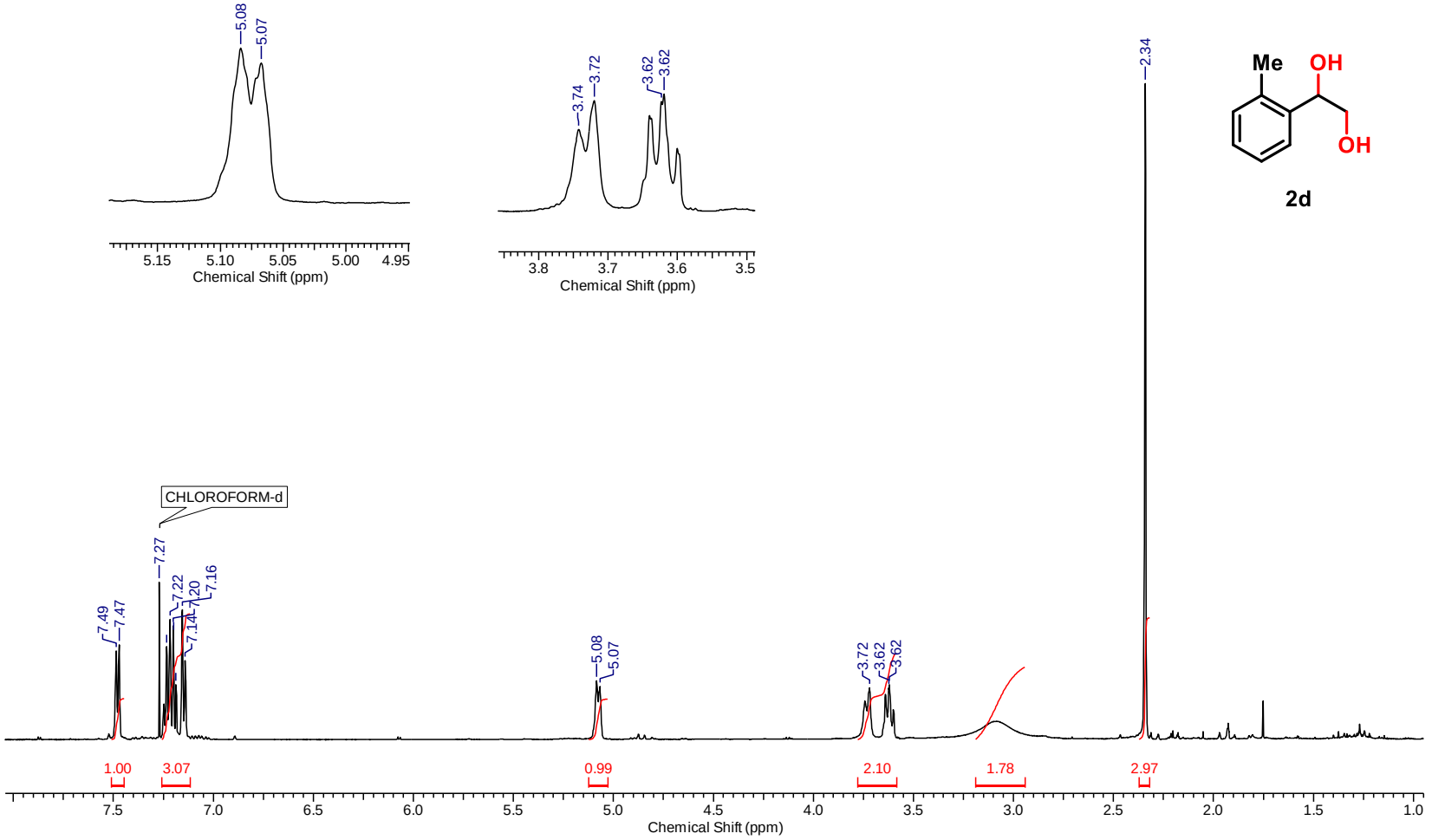

128.48
126.05
127.94
131
130
129
128
127
126
125
124
123
Chemical Shift (ppm)
OH
OH
2a
CHLOROFORM-d
77.32
77.00
76.68
74.67
67.96
140.38
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

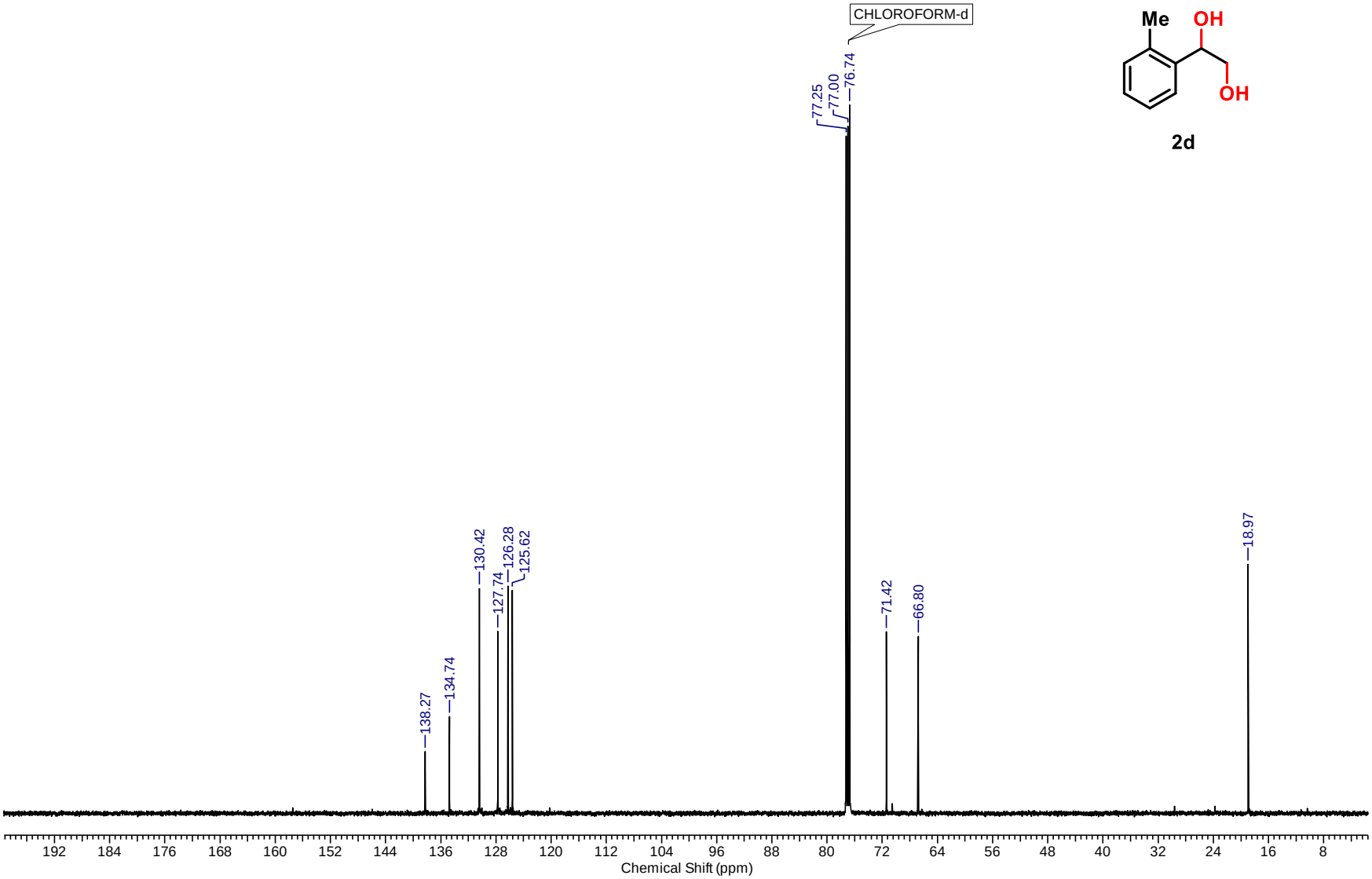

7.35
5.33
5.32
4.74
4.73
4.72
4.54
4.53
4.53
4.52
4.52
4.51
5.25
5.00
4.75
4.50
Chemical Shift (ppm)
Water
DMSO
DMSO-d6
3.43
3.42
3.41
3.40
3.39
3.38
4.16
1.00
1.03
1.04
2.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
OH
OH
Cl
2b

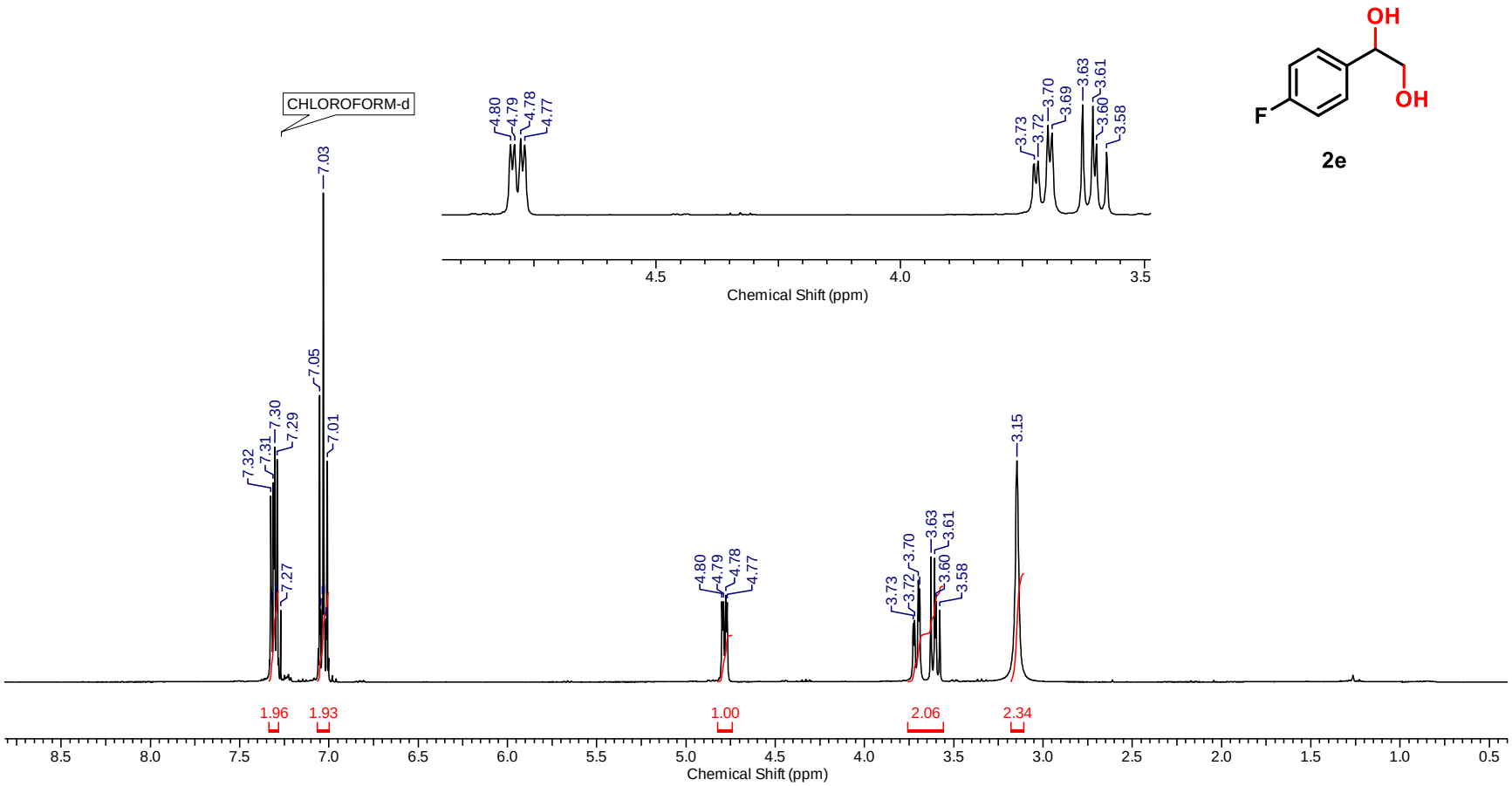

DMSO-d6
39.51
39.68
39.35
39.85
39.18
40.01
39.01
128.18
127.74
142.55
131.24
73.02
67.18
OH
OH
Cl
2b
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

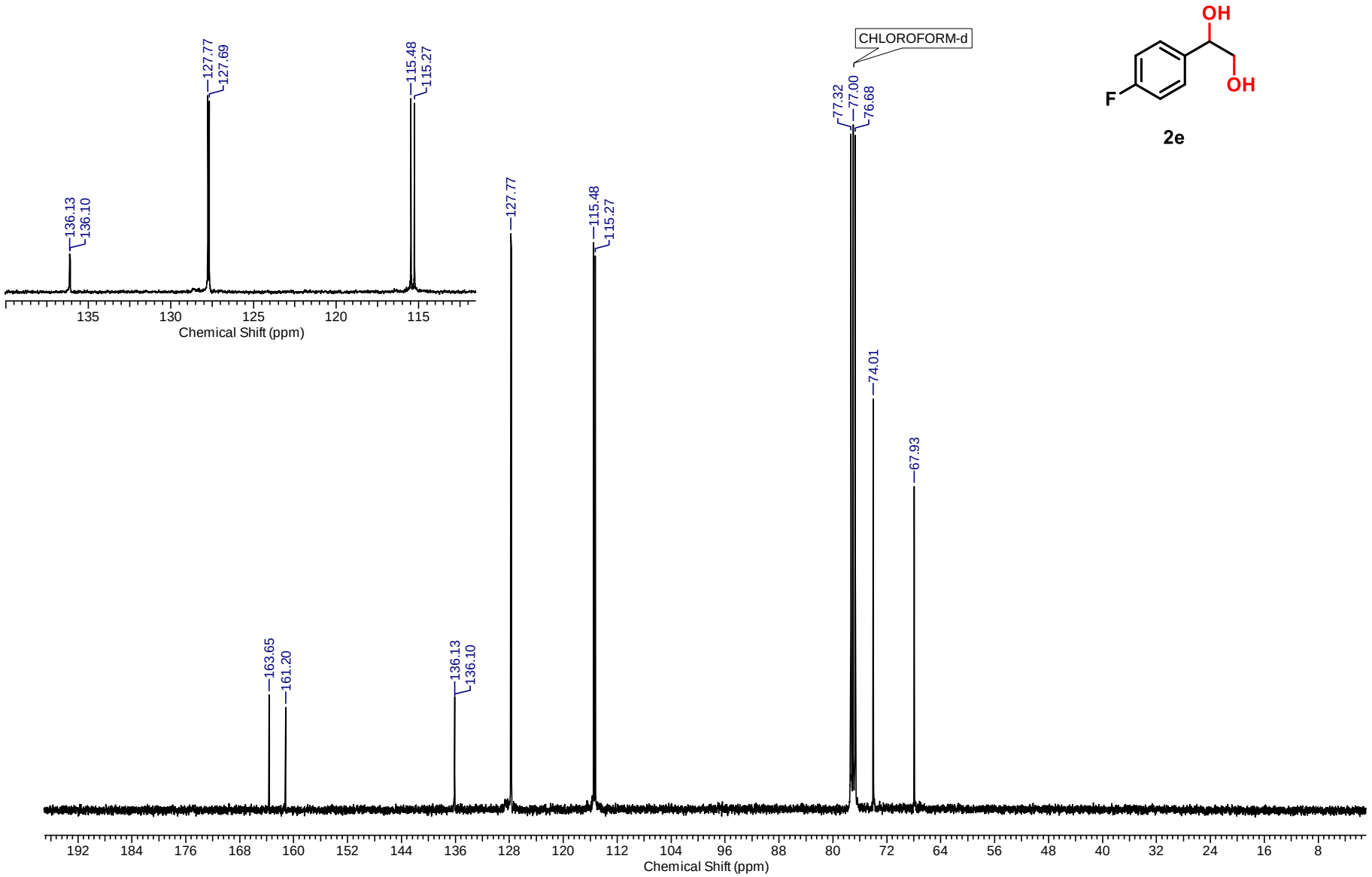

OH
OH
Me
2c
4.82
4.81
4.80
4.79
3.76
3.74
3.69
3.67
3.67
3.65
Chemical Shift (ppm)
Chemical Shift (ppm)
CHLOROFORM-d
7.26
7.25
7.19
7.17
2.35
2.77
2.00
2.16
1.05
2.38
2.28
2.97
Chemical Shift (ppm)

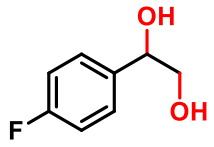

CHLOROFORM-d
77.25
77.00
76.74
137.79
137.36
129.22
126.01
74.53
67.98
21.10
OH
OH
Me
2c
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


5.08
5.07
5.15
5.10
5.05
5.00
4.95
Chemical Shift (ppm)
3.74
3.72
3.62
3.62
3.8
3.7
3.6
3.5
Chemical Shift (ppm)
2.34
Me
OH
OH
2d
CHLOROFORM-d
7.27
7.49
7.47
7.22
7.20
7.16
7.14
5.08
5.07
3.72
3.62
3.62
1.00
3.07
0.99
2.10
1.78
2.97
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
Chemical Shift (ppm)

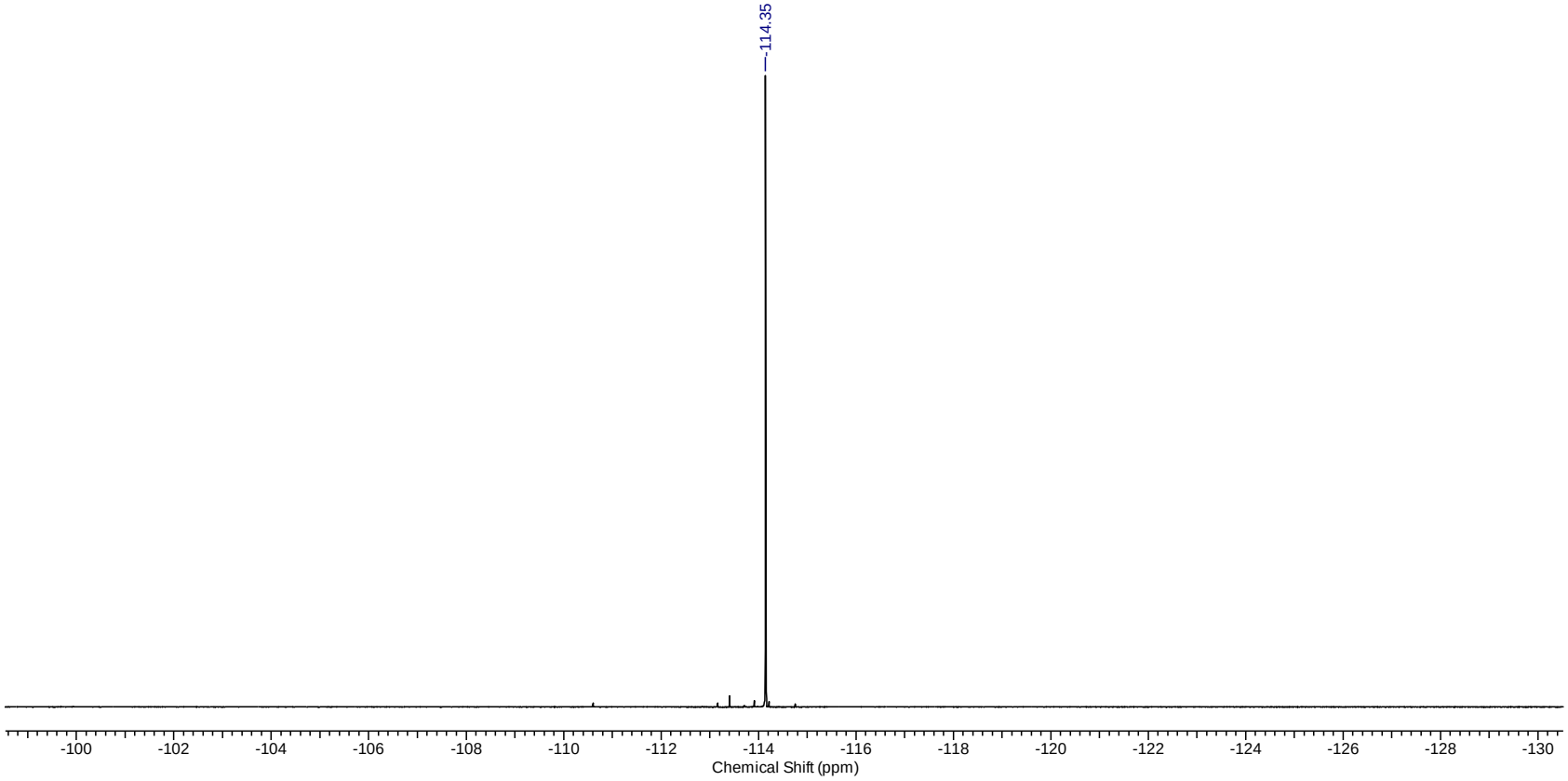

CHLOROFORM-d
77.25
77.00
76.74
Me
OH
OH
2d
138.27
134.74
130.42
127.74
126.28
125.62
71.42
66.80
18.97
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

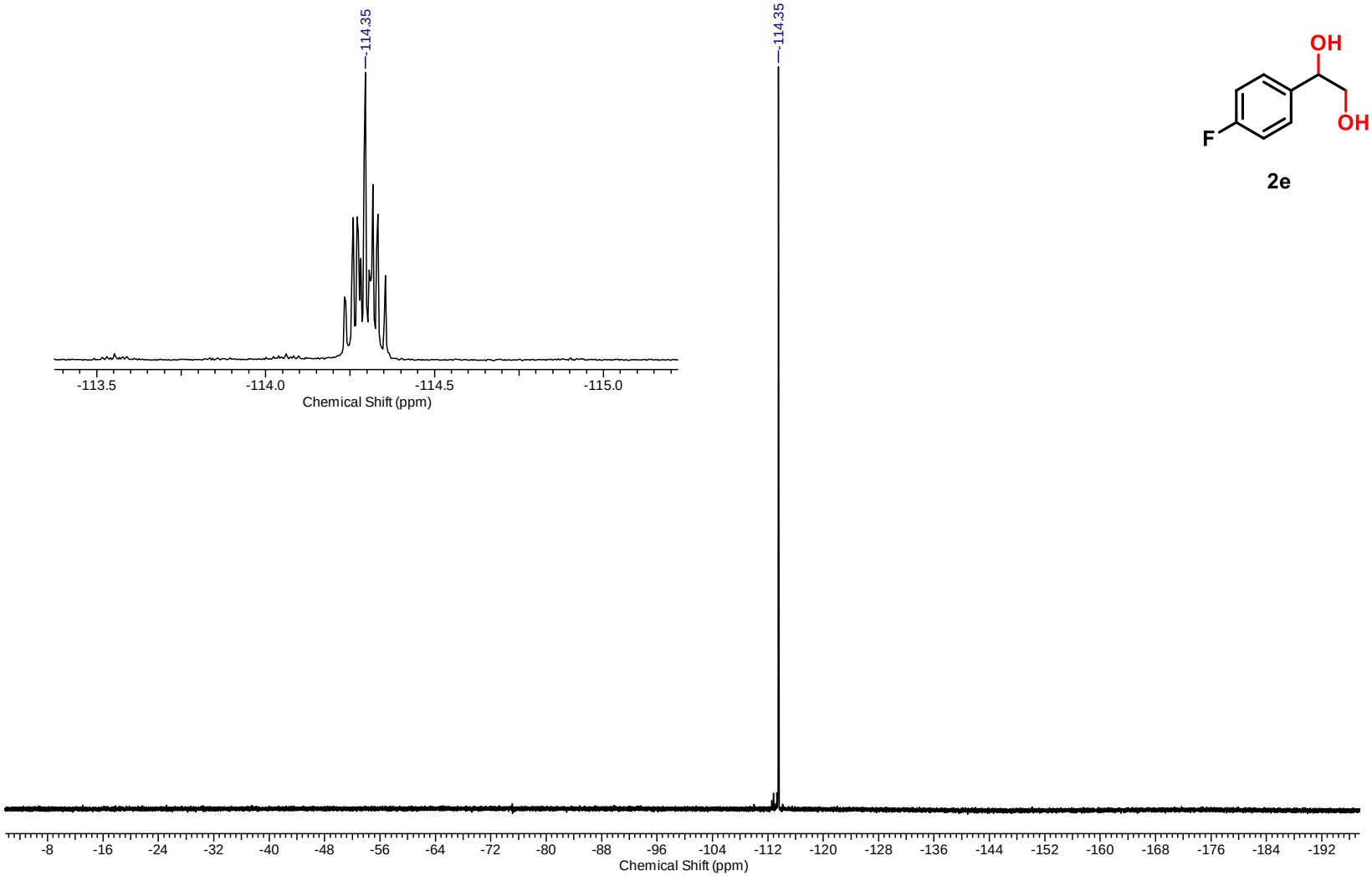

CHLOROFORM-d
7.32
7.31
7.30
7.29
7.27
7.05
7.03
7.01
4.80
4.79
4.78
4.77
3.73
3.72
3.70
3.69
3.63
3.61
3.60
3.58
3.15
1.96
1.93
1.00
2.06
2.34
Chemical Shift (ppm)
OH
OH
F
2e


OH
OH
F
2e
CHLOROFORM-d
77.32
77.00
76.68
127.77
127.69
115.48
115.27
136.13
136.10
74.01
67.93
163.65
161.20
Chemical Shift (ppm)
Chemical Shift (ppm)


OH
OH
F

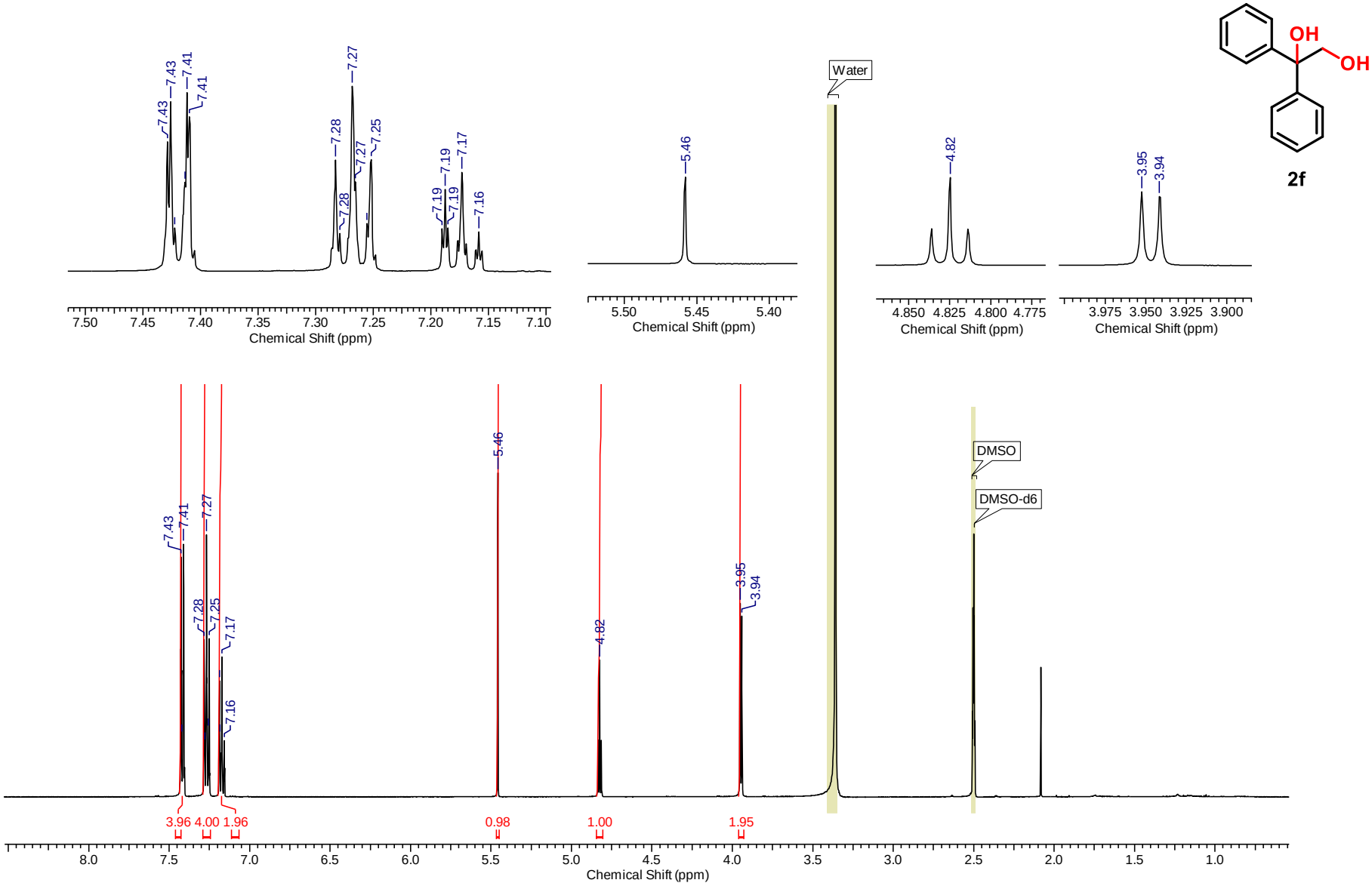
2e

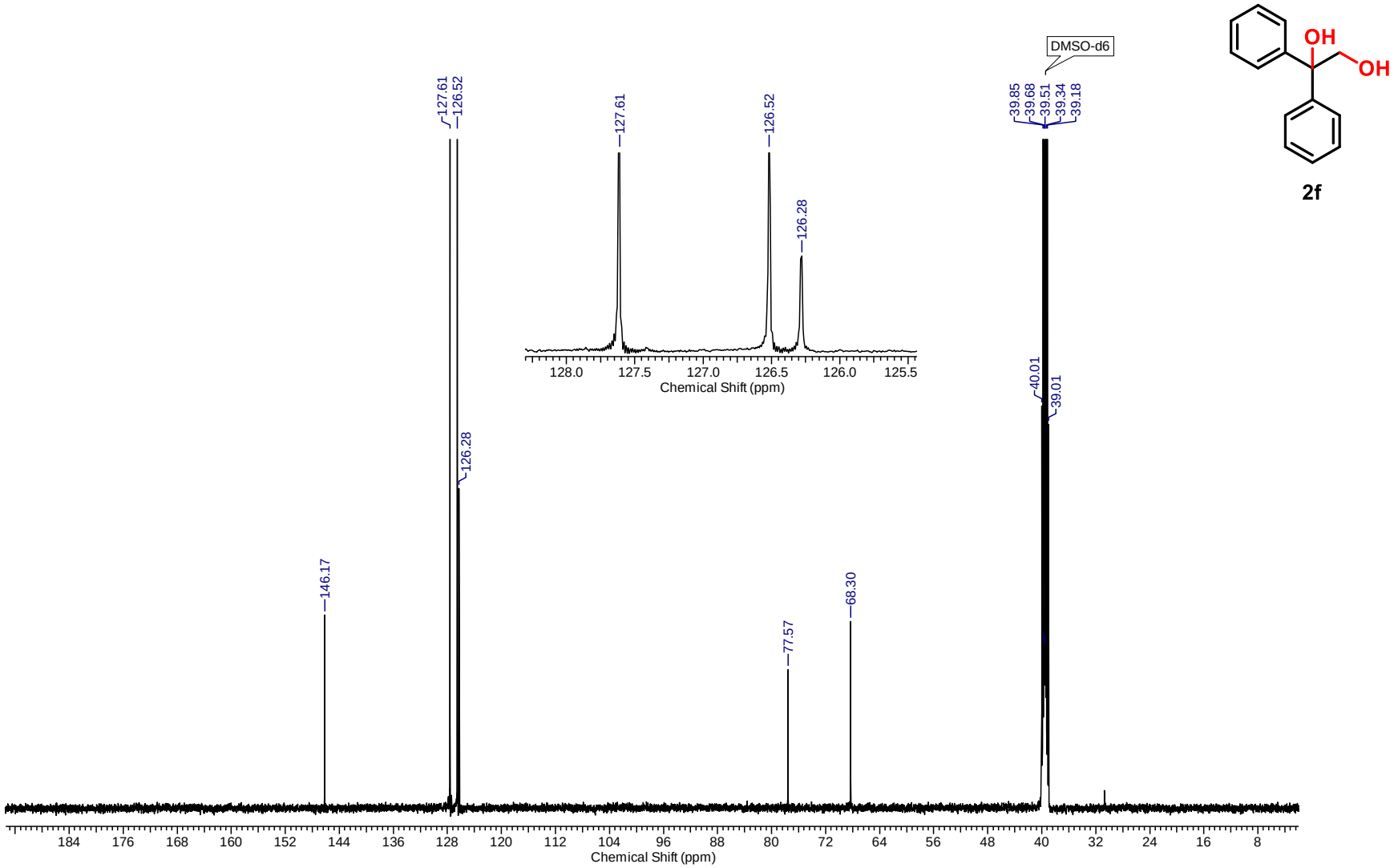

-114.35
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
Chemical Shift (ppm)

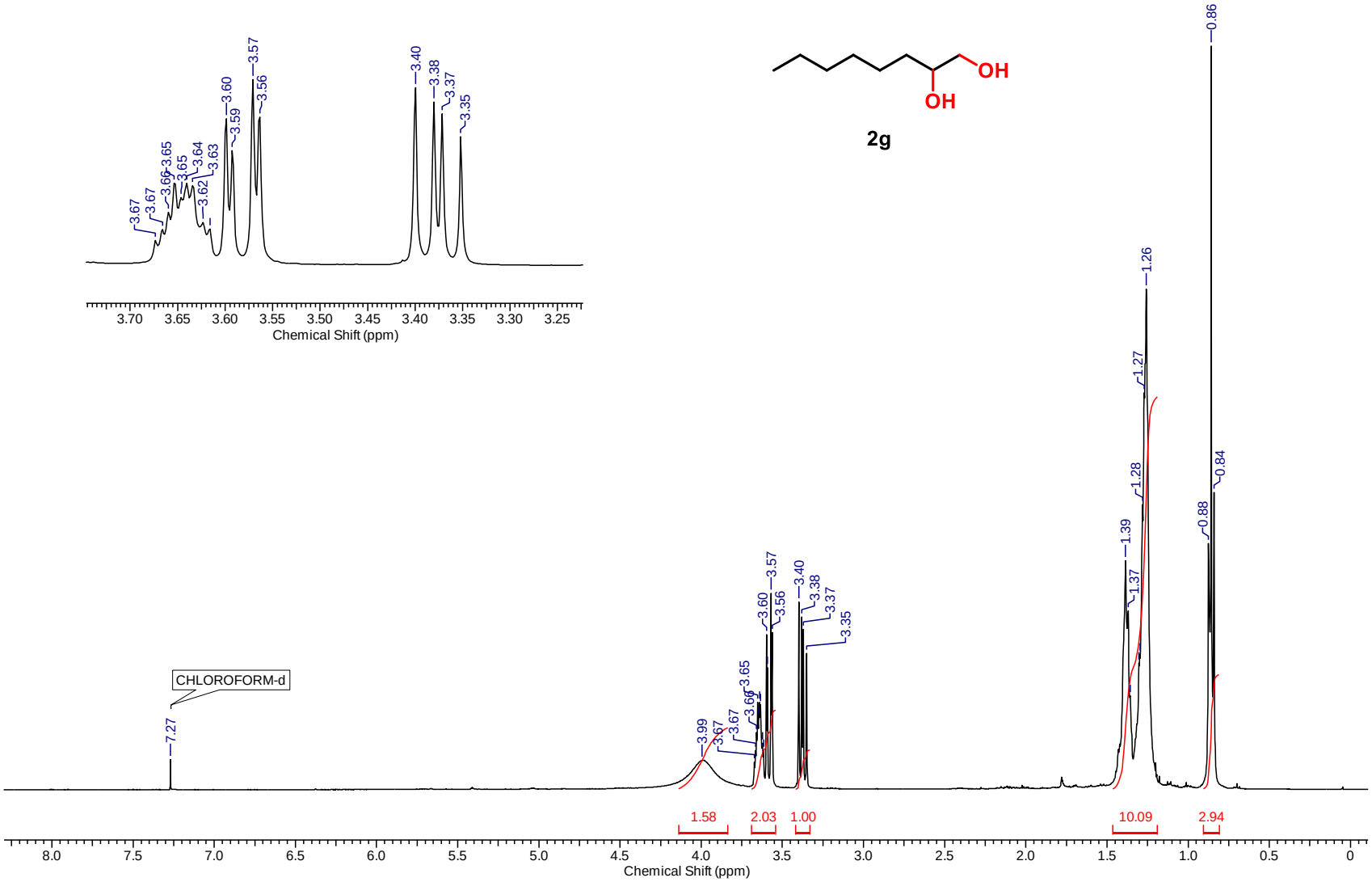

-114.35
-114.35
-113.5
-114.0
-114.5
-115.0
Chemical Shift (ppm)
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

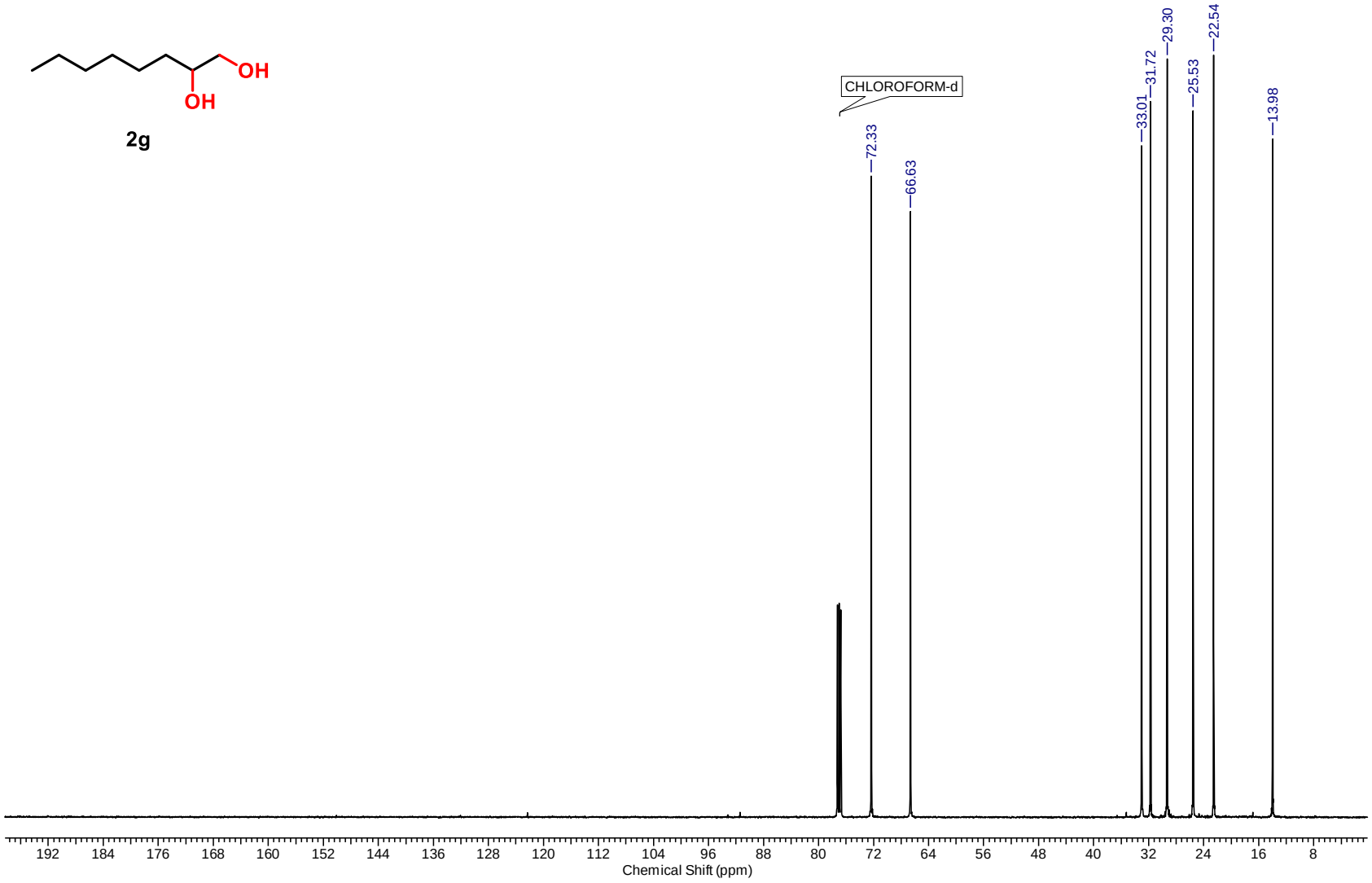
OH
OH
F

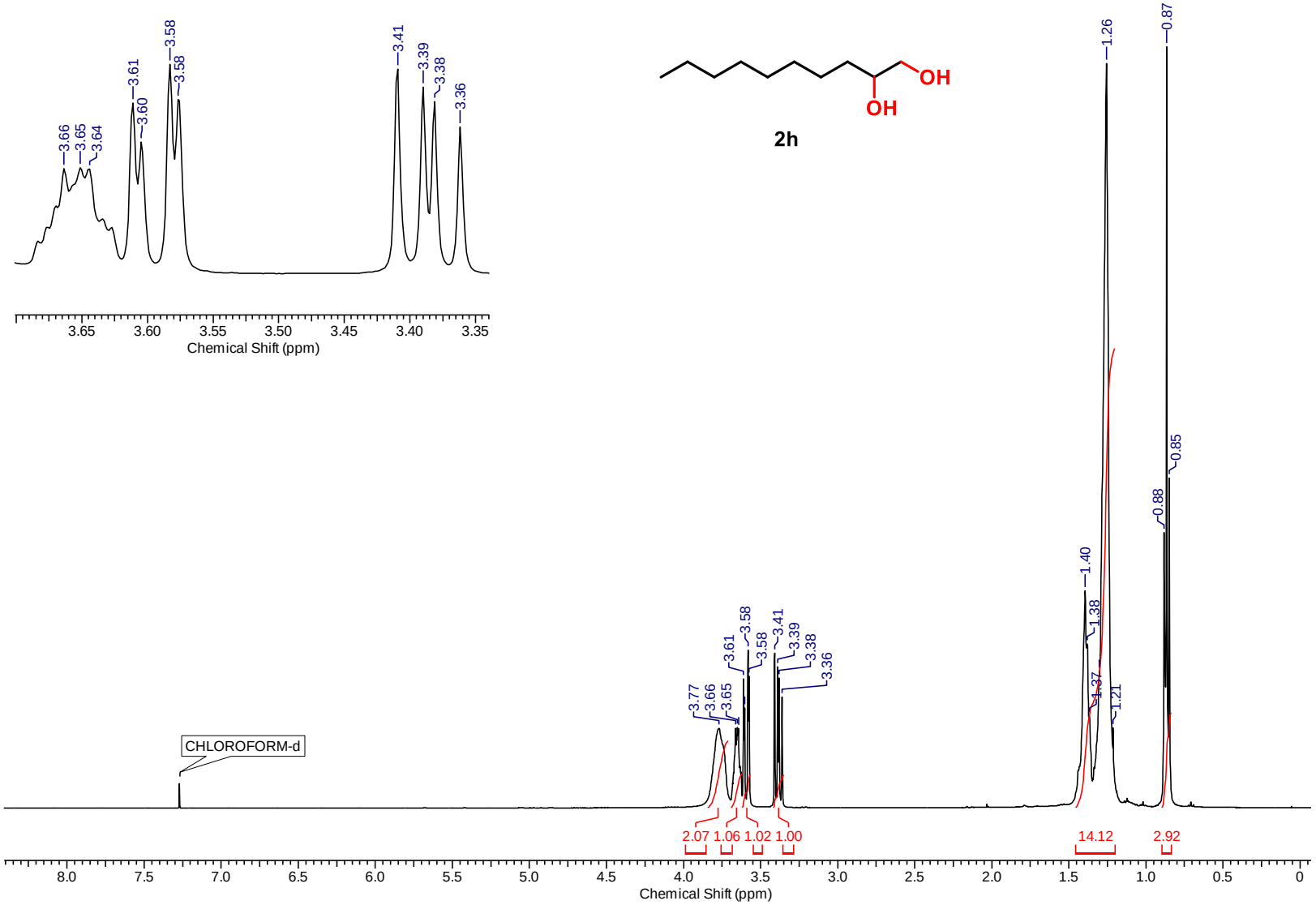
2e

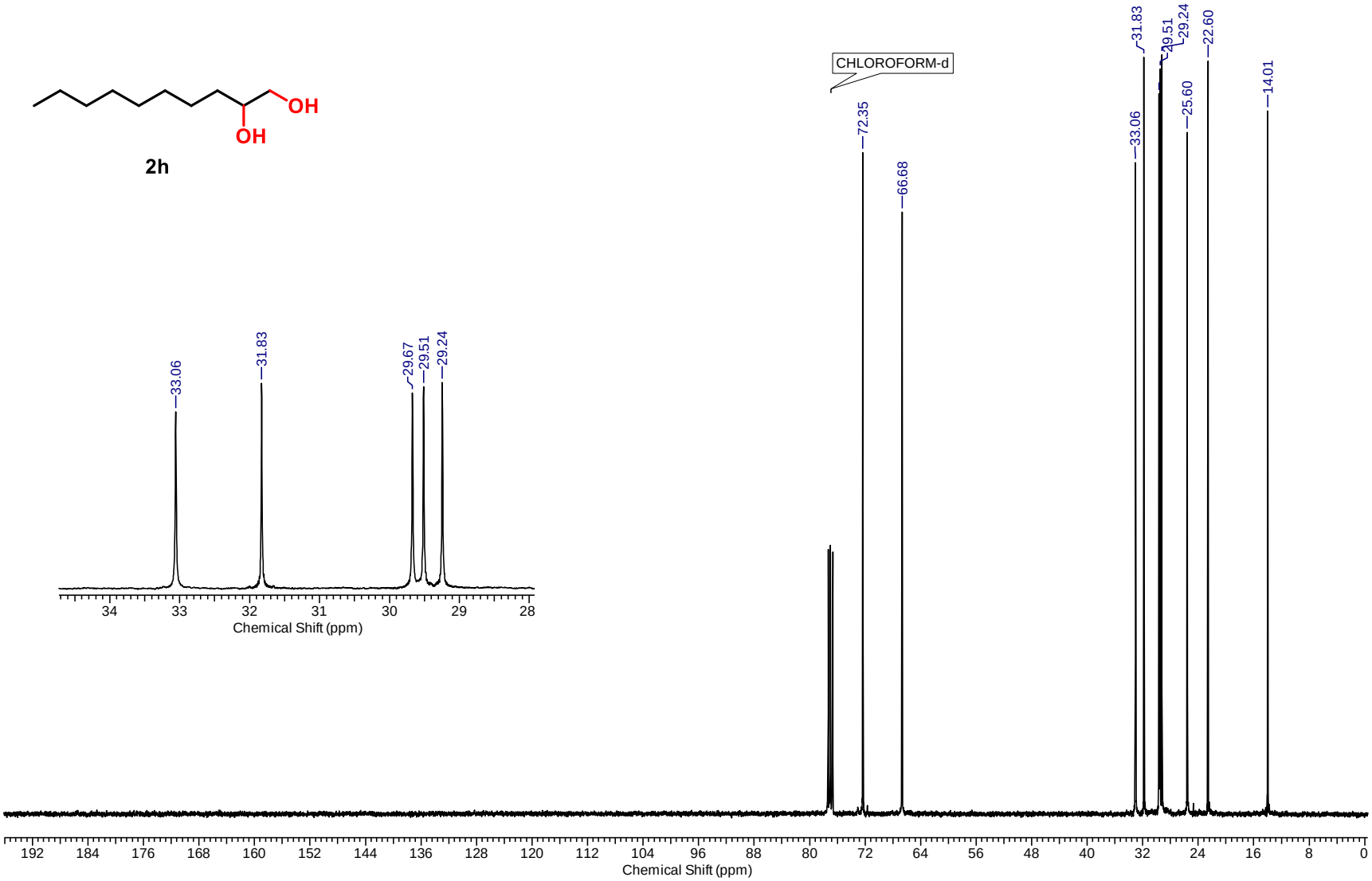

OH
OH
2f
Water
DMSO
DMSO-d6
7.43
7.41
7.27
7.28
7.25
7.17
7.16
7.19
5.46
4.82
3.95
3.94
3.96
4.00
1.96
0.98
1.00
1.95
Chemical Shift (ppm)

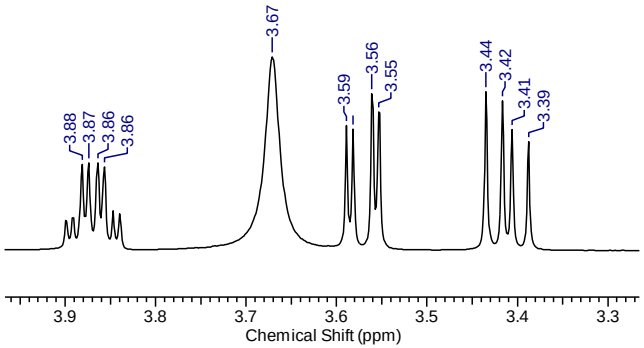

OH
OH
2f
DMSO-d6
127.61
126.52
126.28
146.17
77.57
68.30
40.01
39.01
39.85
39.68
39.51
39.34
39.18
Chemical Shift (ppm)
Chemical Shift (ppm)

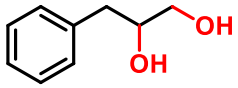

OH
OH
2g
CHLOROFORM-d
Chemical Shift (ppm)
Chemical Shift (ppm)


OH
OH
2g
CHLOROFORM-d
72.33
66.63
33.01
31.72
29.30
25.53
22.54
13.98
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

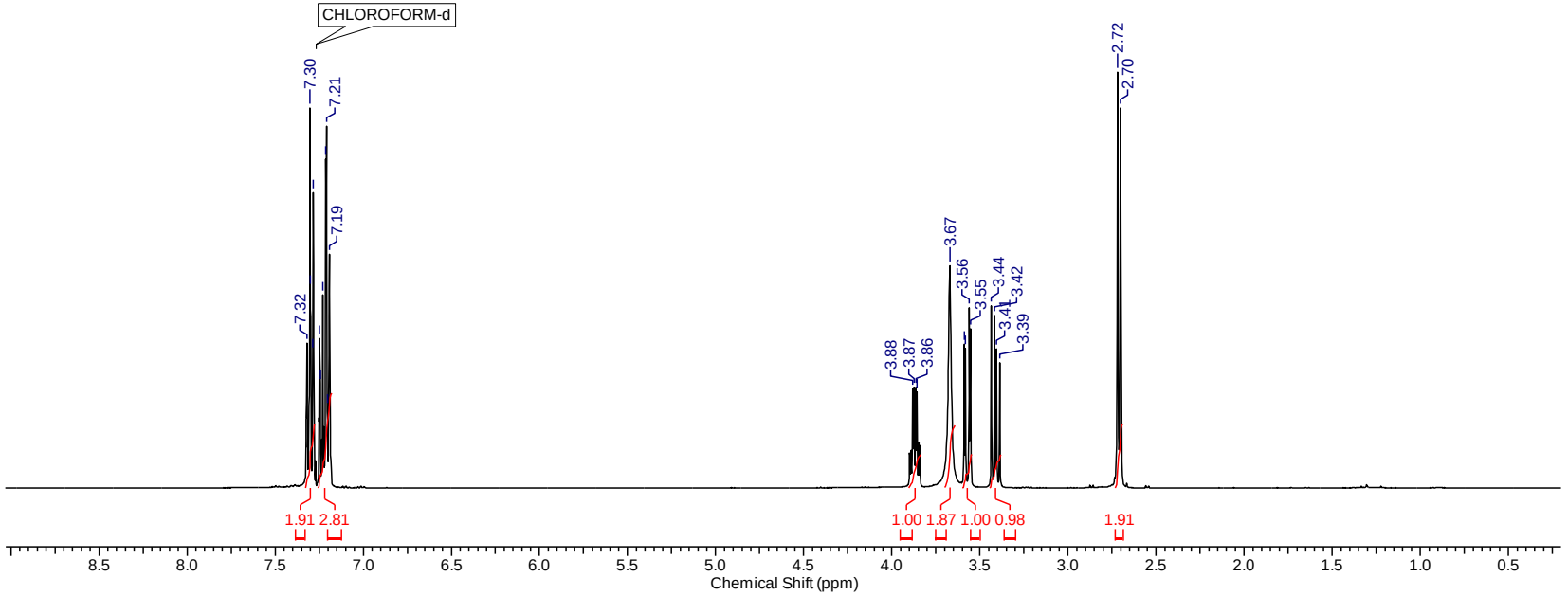

3.66
3.65
3.64
3.61
3.60
3.58
3.58
3.41
3.39
3.38
3.36
3.65 3.60 3.55 3.50 3.45 3.40 3.35
Chemical Shift (ppm)
OH
OH
2h
1.26
0.87
0.88
0.85
1.40
1.38
1.37
1.21
3.77
3.66
3.65
3.61
3.58
3.58
3.41
3.39
3.38
3.36
CHLOROFORM-d
2.07 1.06 1.02 1.00
14.12
2.92
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

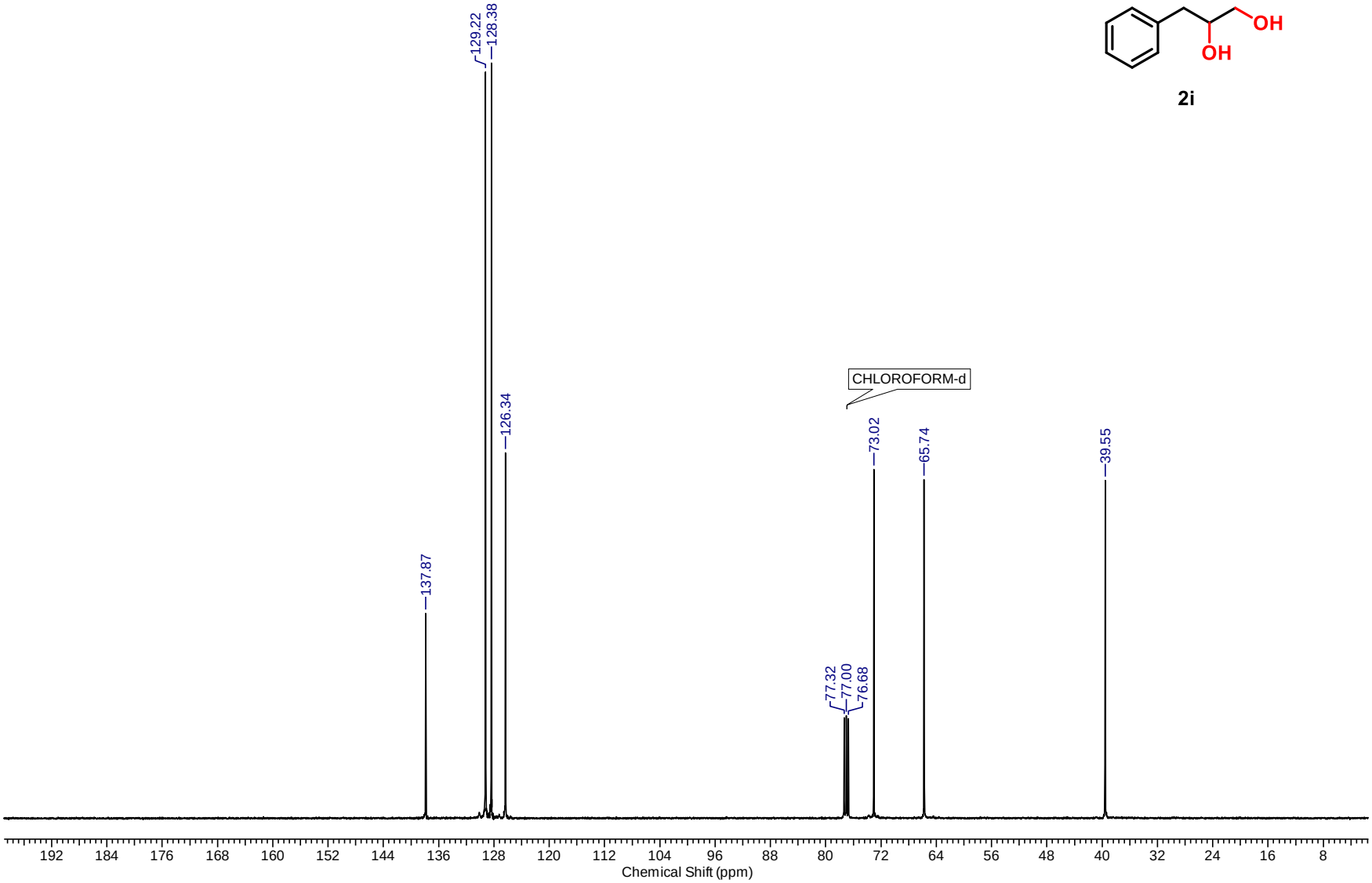

OH
OH
2h
CHLOROFORM-d
72.35
66.68
33.06
31.83
29.51
29.24
25.60
22.60
14.01
29.67
Chemical Shift (ppm)
Chemical Shift (ppm)

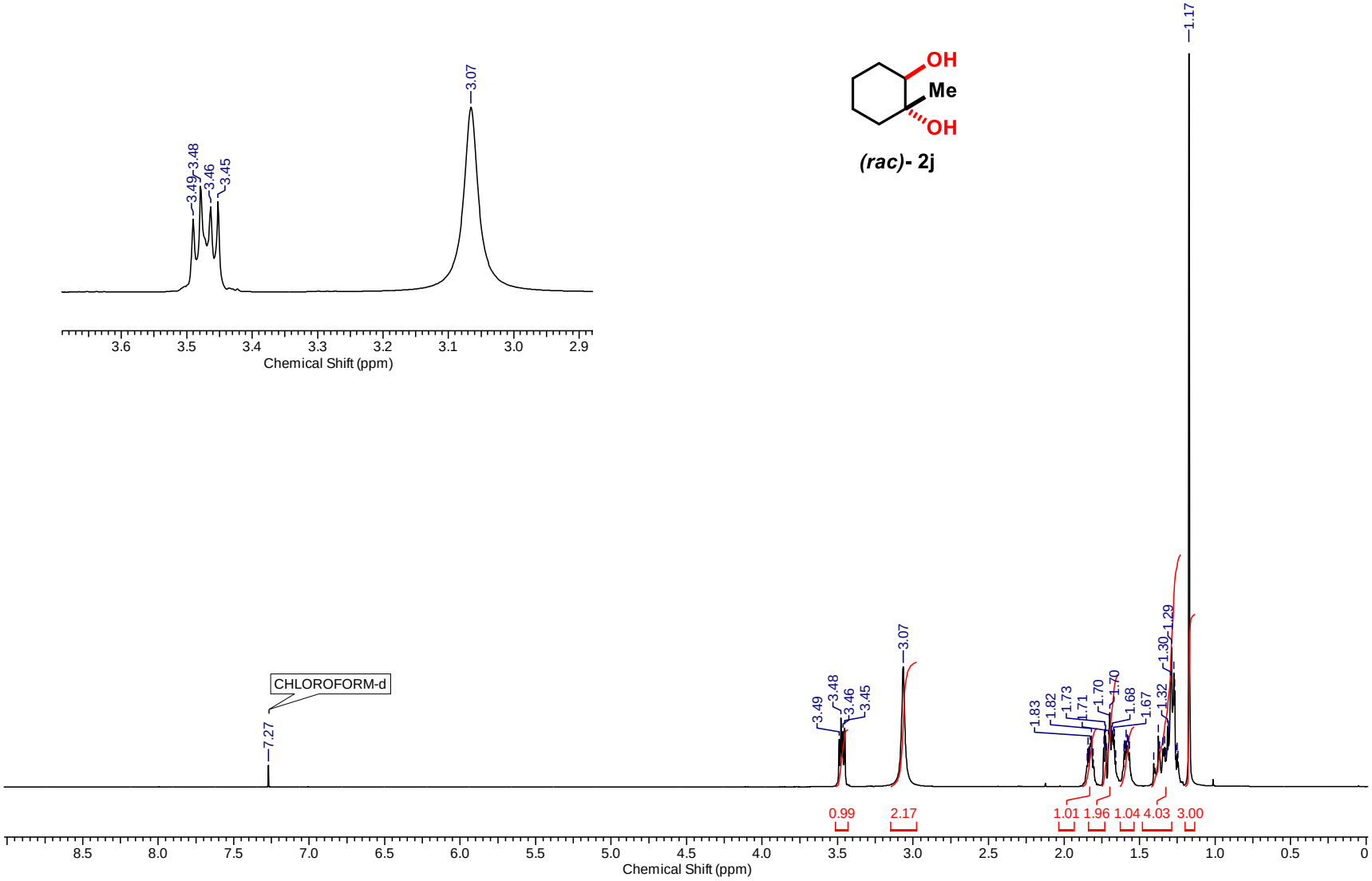

3.88
3.87
3.86
3.86
3.67
3.59
3.56
3.55
3.44
3.42
3.41
3.39
3.9
3.8
3.7
3.6
3.5
3.4
3.3
Chemical Shift (ppm)

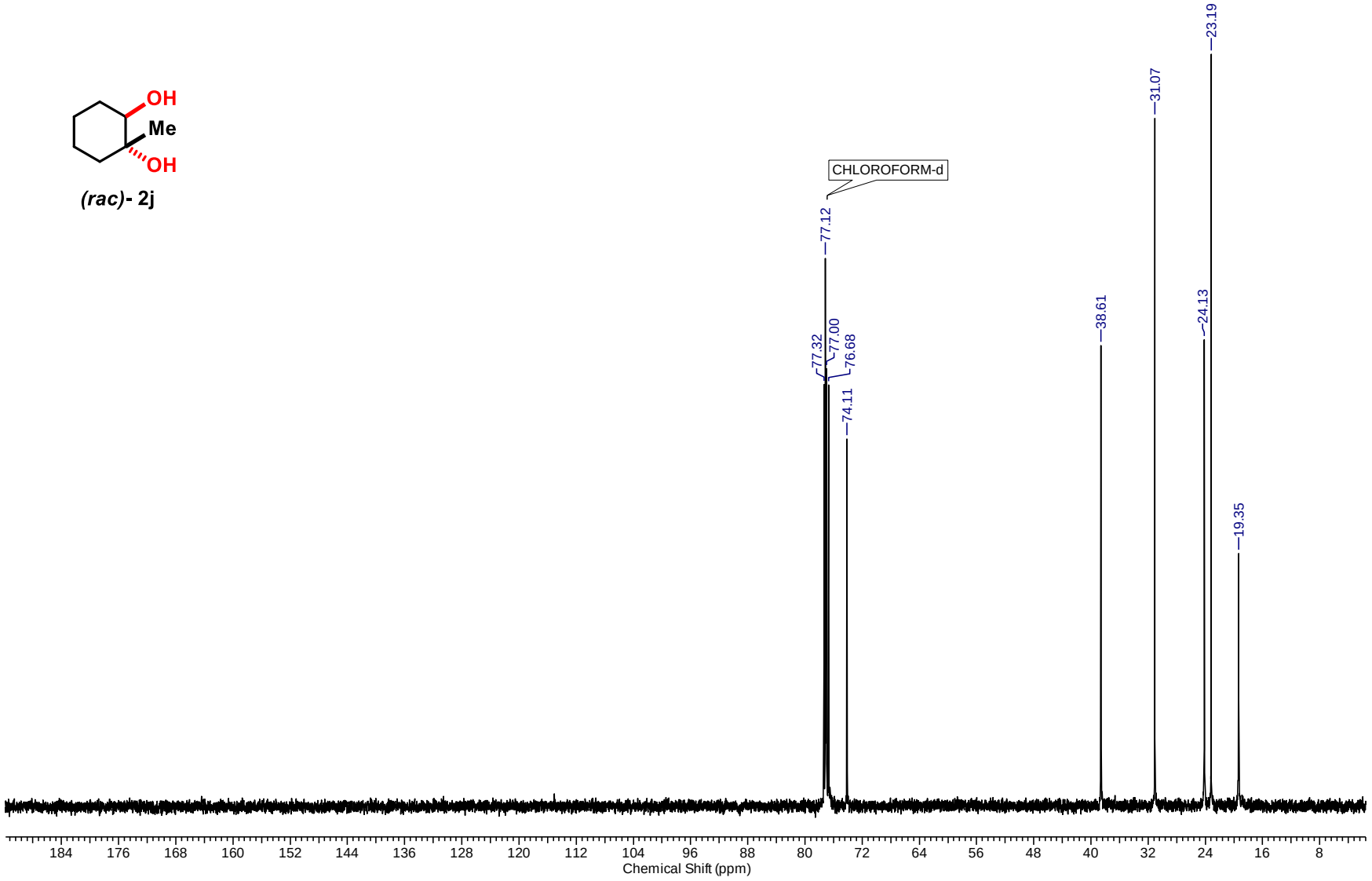

OH
OH

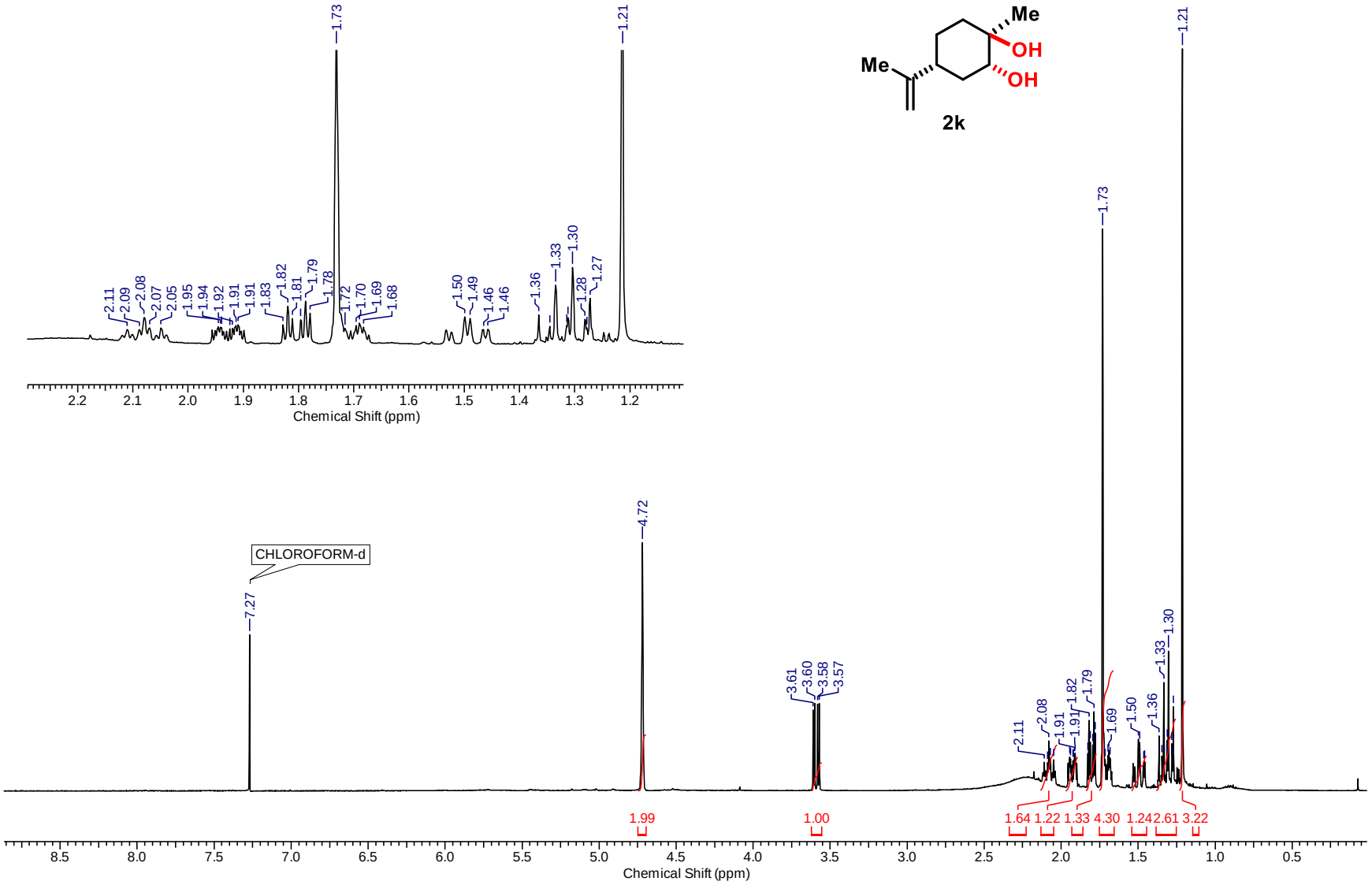
2i

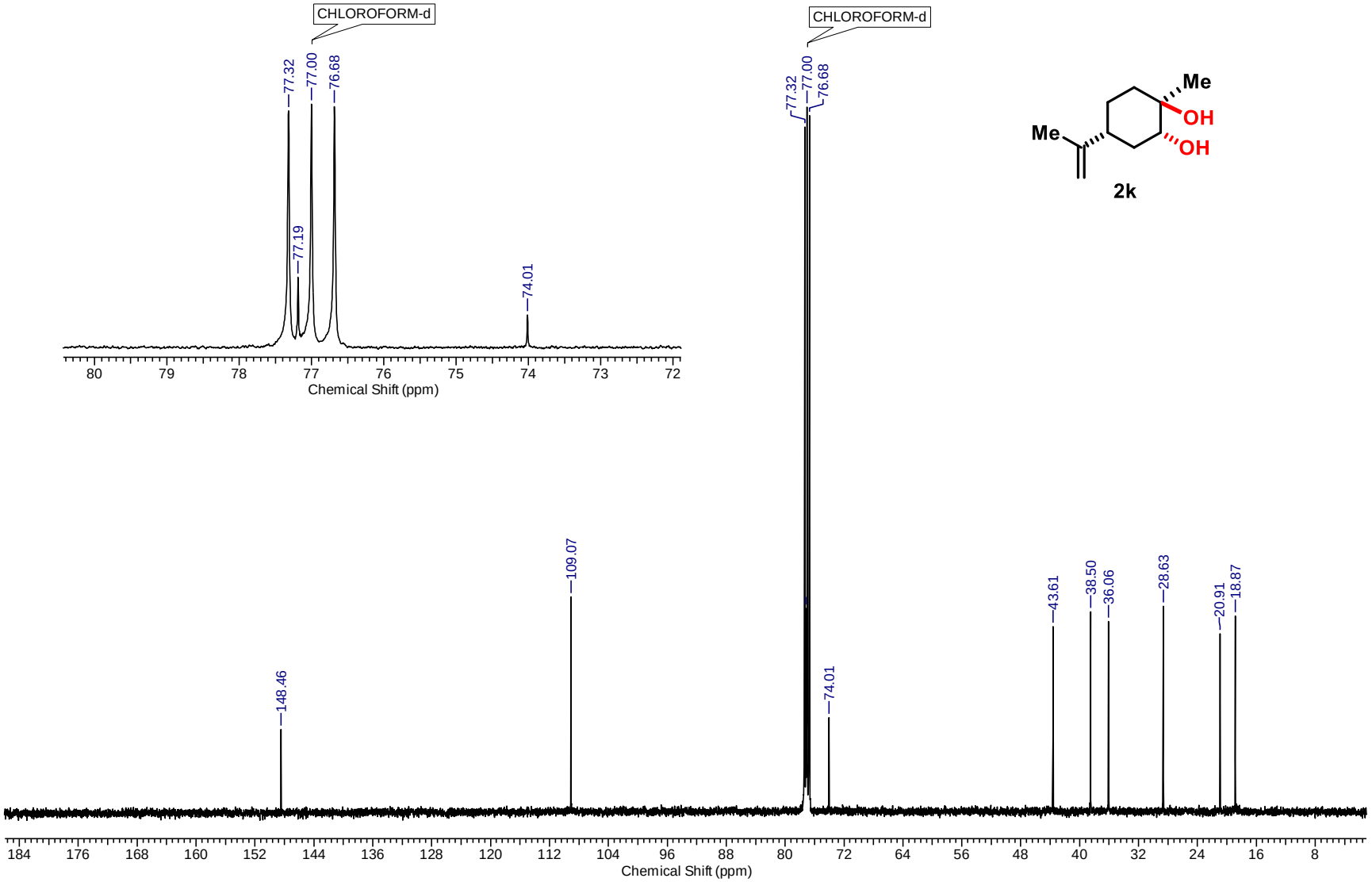

CHLOROFORM-d
7.30
7.21
7.19
7.32
3.88
3.87
3.86
3.67
3.56
3.55
3.44
3.42
3.41
3.39
2.72
2.70
1.91
2.81
1.00
1.87
1.00
0.98
1.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

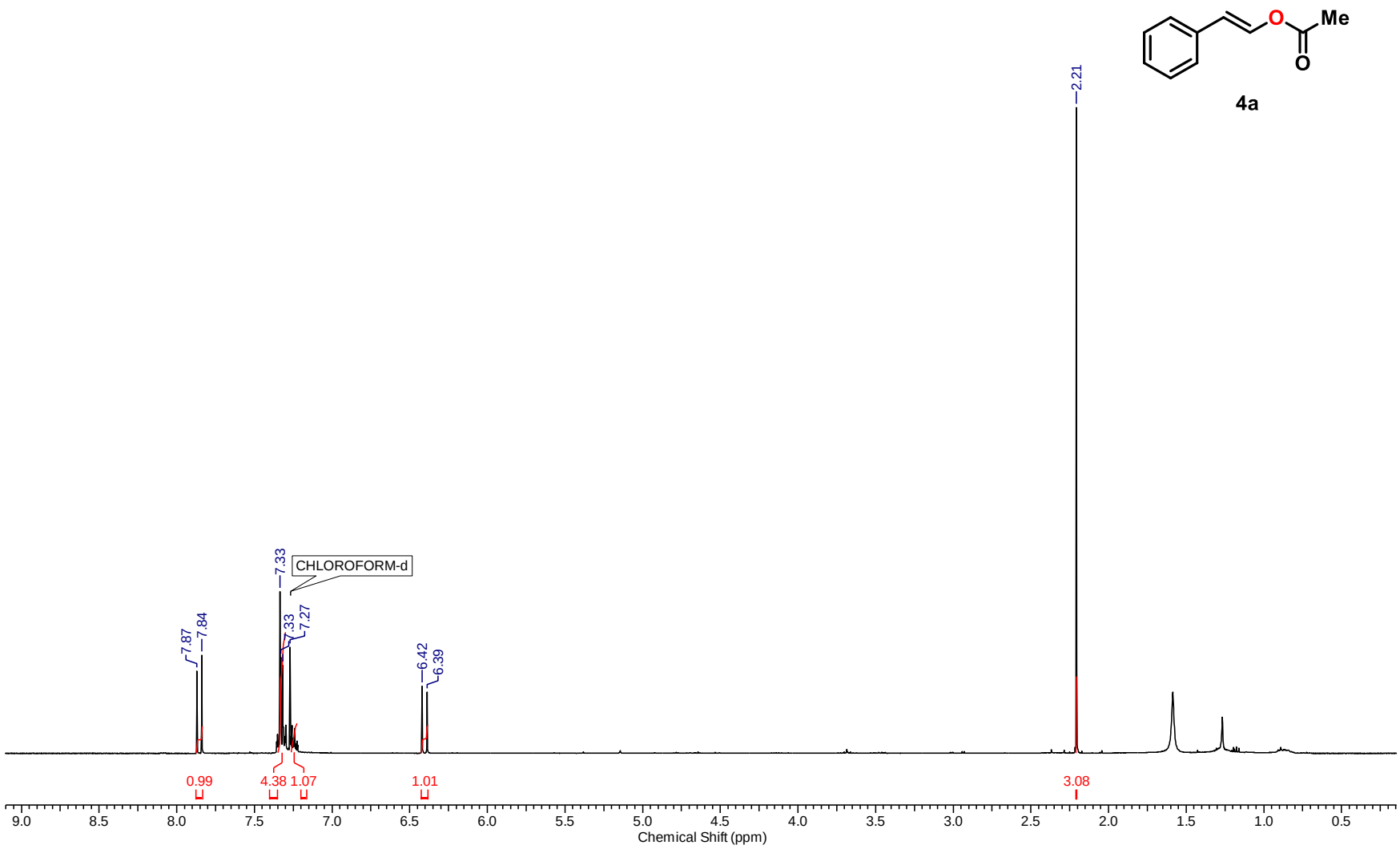

OH
OH
2i
129.22
128.38
126.34
137.87
CHLOROFORM-d
73.02
65.74
39.55
77.32
77.00
76.68
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

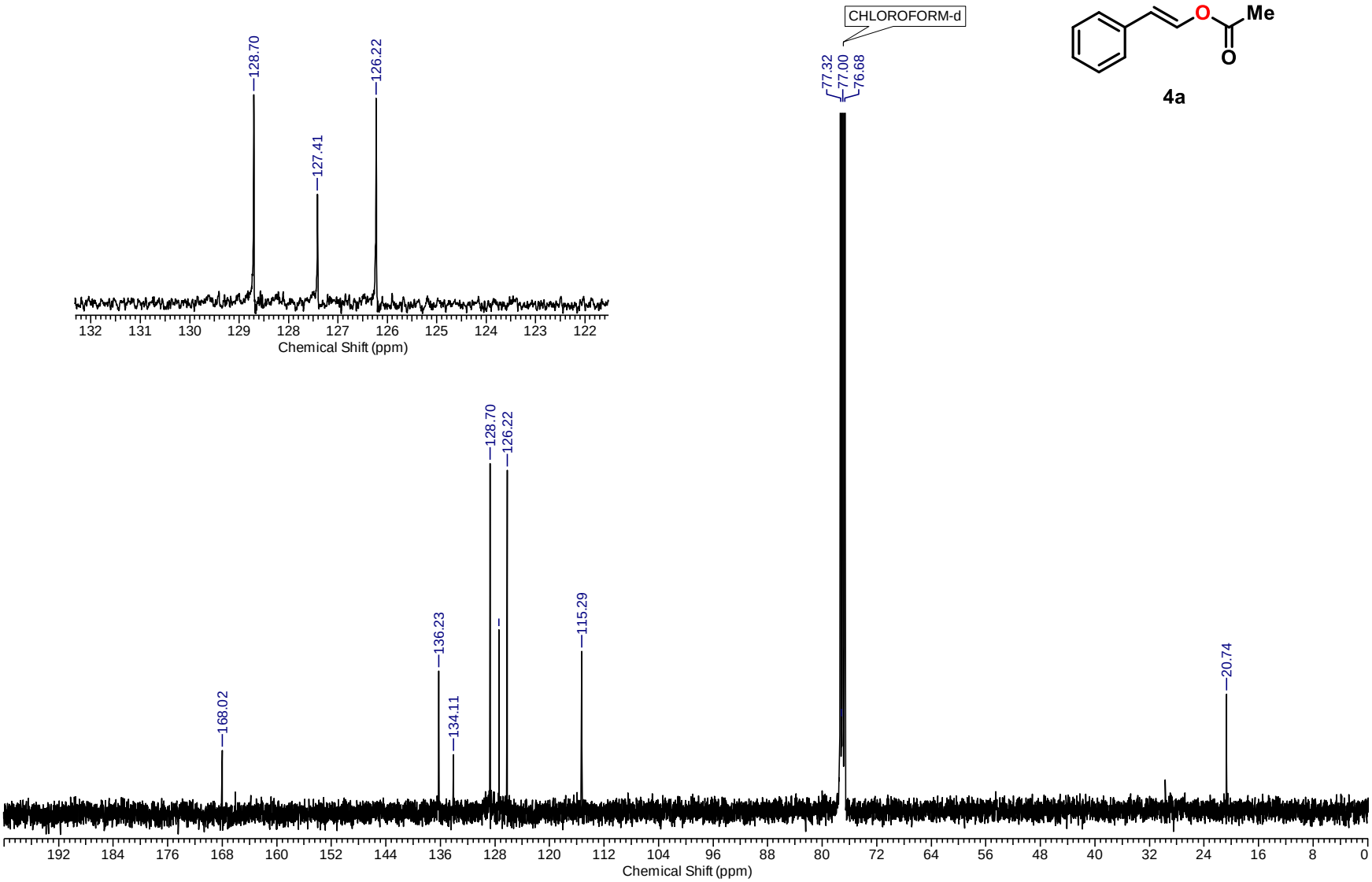

OH
Me
OH
(rac)- 2j
3.07
3.49
3.48
3.46
3.45
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
Chemical Shift (ppm)
1.17
CHLOROFORM-d
7.27
3.49
3.48
3.46
3.45
3.07
1.83
1.82
1.73
1.71
1.70
1.70
1.68
1.67
1.32
1.30
1.29
0.99
2.17
1.01
1.96
1.04
4.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

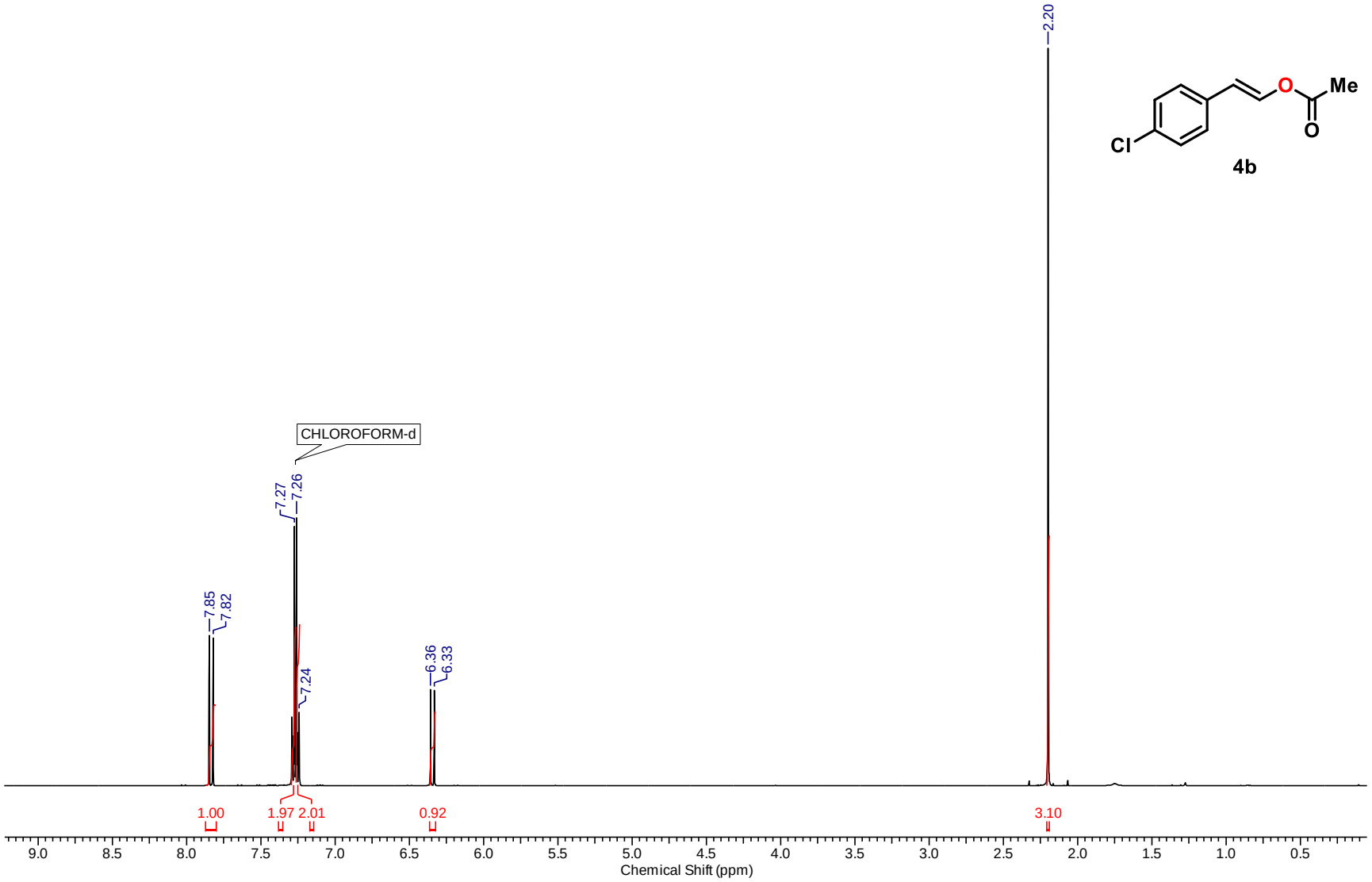

OH
Me
OH
(rac)- 2j
CHLOROFORM-d
77.12
77.32
77.00
76.68
74.11
38.61
31.07
24.13
23.19
19.35
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

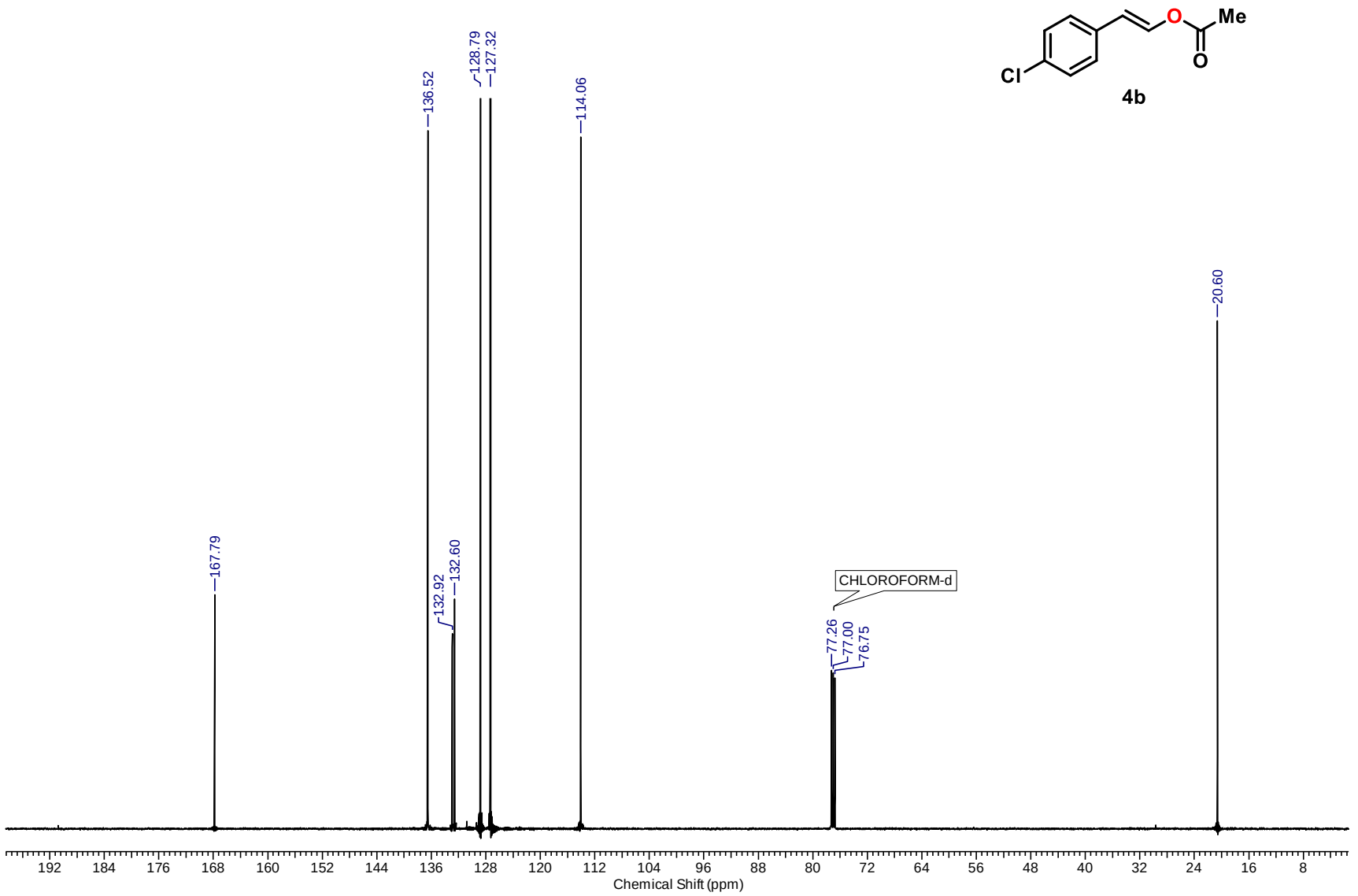

Me
OH
OH
Me
2k
CHLOROFORM-d
Chemical Shift (ppm)
Chemical Shift (ppm)

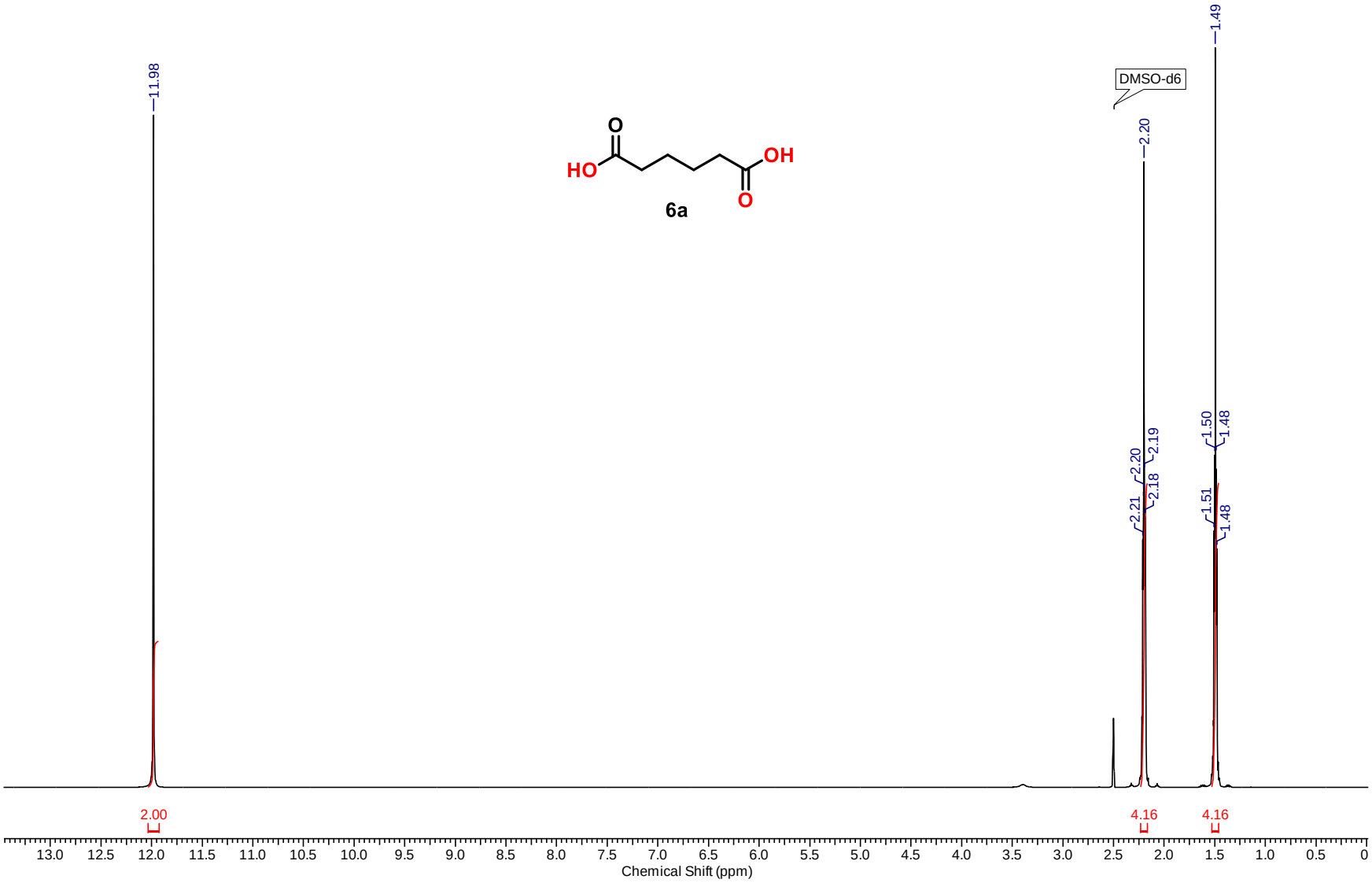

CHLOROFORM-d
77.32
77.00
76.68
77.19
74.01
80
79
78
77
76
75
74
73
72
Chemical Shift (ppm)
CHLOROFORM-d
77.32
77.00
76.68
Me
OH
OH
Me
2k
148.46
109.07
74.01
43.61
38.50
36.06
28.63
20.91
18.87
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

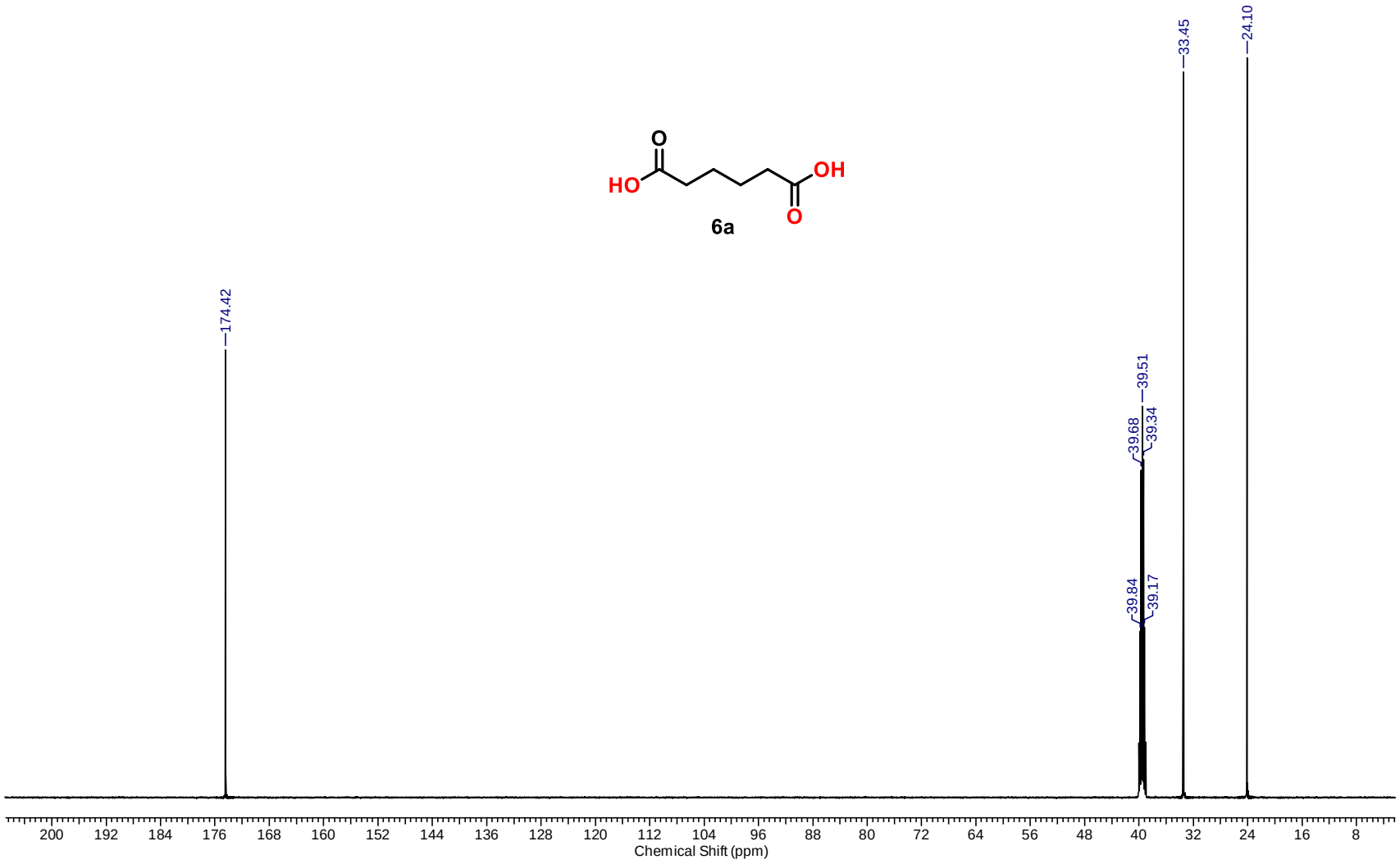

O
Me
O
4a
2.21
7.87
7.84
7.33
CHLOROFORM-d
7.33
7.27
6.42
6.39
0.99
4.38
1.07
1.01
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

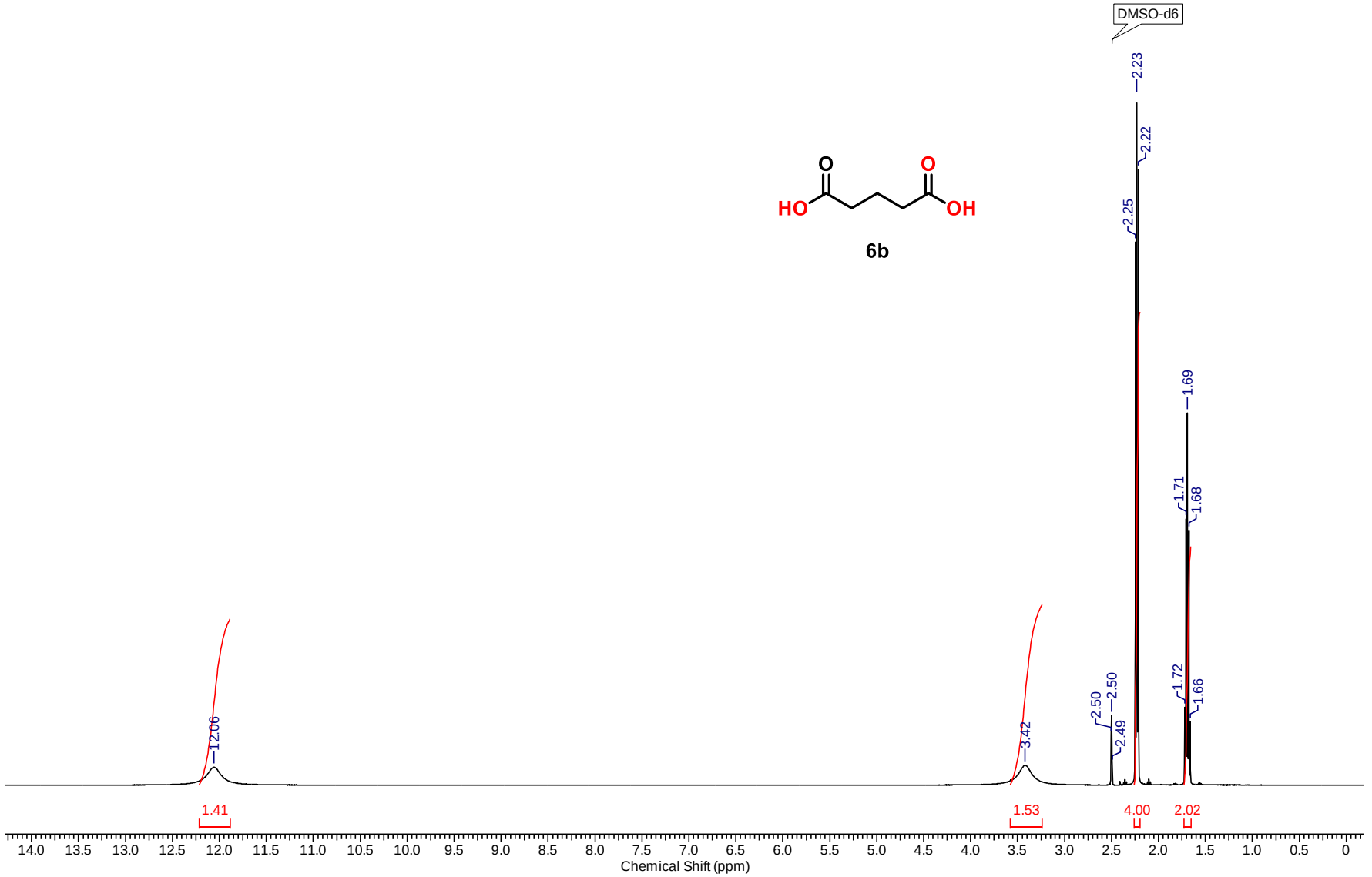

CHLOROFORM-d
77.32
77.00
76.68
128.70
127.41
126.22
132 131 130 129 128 127 126 125 124 123 122
Chemical Shift (ppm)
O
Me
O
4a
128.70
126.22
136.23
134.11
115.29
168.02
20.74
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

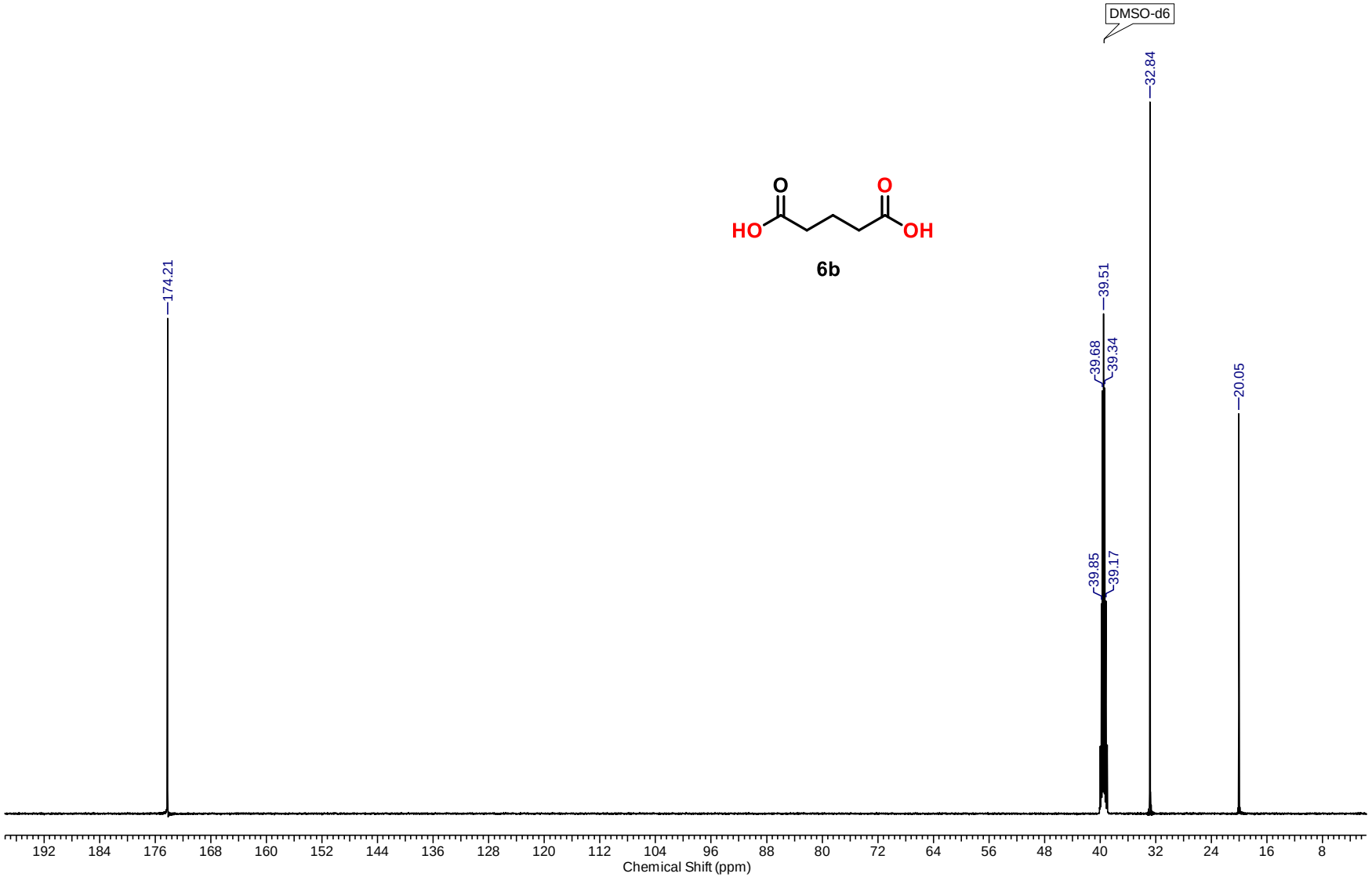

2.20
Cl
O
Me
O
4b
CHLOROFORM-d
7.27
7.26
7.85
7.82
7.24
6.36
6.33
1.00
1.97
2.01
0.92
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

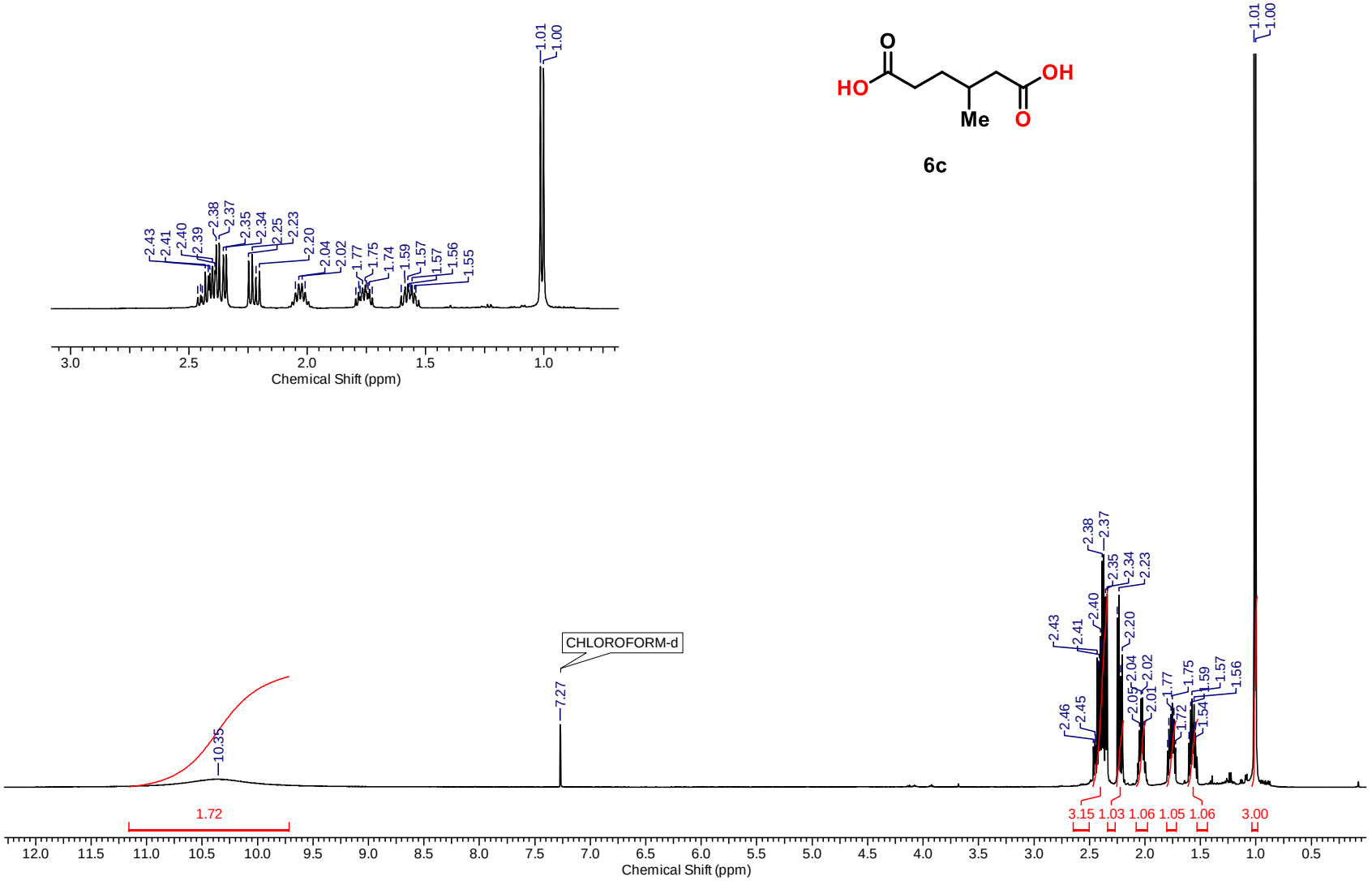

Cl
O
Me
O
4b
167.79
136.52
132.92
132.60
128.79
127.32
114.06
77.26
77.00
76.75
CHLOROFORM-d
20.60
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

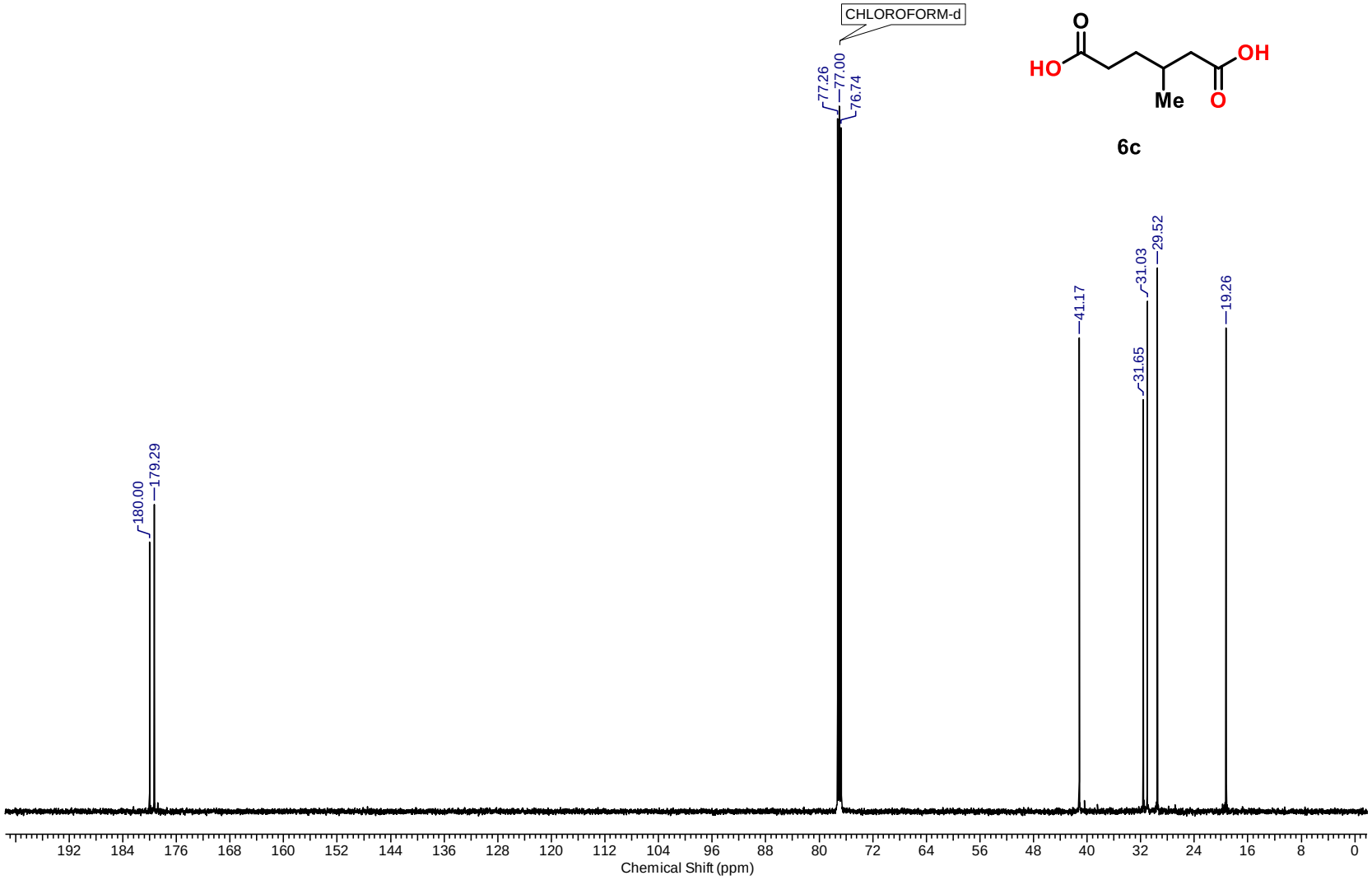

11.98
1.49
DMSO-d6
2.20
2.20
2.19
2.21
2.18
1.50
1.48
1.51
1.48
HO
O
OH
O
6a
2.00
4.16
4.16
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


O
HO
OH
O
6a
174.42
39.84
39.68
39.51
39.34
39.17
33.45
24.10
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


DMSO-d6
2.23
2.22
2.25
1.69
1.71
1.68
1.72
1.66
2.50
2.50
2.49
3.42
12.06
HO
O
O
OH
6b
1.41
1.53
4.00
2.02
14.0 13.5 13.0 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 0
Chemical Shift (ppm)


DMSO-d6
32.84
174.21
39.51
39.68
39.34
20.05
39.85
39.17
O
O
HO
OH
6b
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


6c
CHLOROFORM-d
Chemical Shift (ppm)
Chemical Shift (ppm)


CHLOROFORM-d
77.26
77.00
76.74
180.00
179.29
41.17
31.65
31.03
29.52
19.26
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)
O
HO
OH
Me
O
6c