Supporting Information

Persulfate-Promoted Synthesis of Biphenyl Compounds in Water from Biomass-Derived Triacetic Acid Lactone

Gilberto G. Duarte Ortin and Airton G. Salles, Jr[a]

[a] Department of Organic Chemistry, Institute of Chemistry, University of Campinas, P.O. Box 6154, Campinas, SP 13084-862, Brazil

Table of contents

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. 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-d: δH = 2.50 ppm, δC = 39.50 ppm). High resolution mass spectra were recorded on Q Exactive Orbitrap spectrometers working with an 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

Phenylacetylenes (1.0 mmol, 1.0 equiv), triacetic acid lactone (1.0 mmol, 1.0 equiv) and $(NH_4)_2S_2O_8$ (2.0 mmol, 2.0 equiv) were added to 4 ml of water. The resulting suspension was capped with a rubber septum and stirred at 85 ^{o}C for 24 h. The stirring speed of the reaction mixture was kept at 1150 rpm to ensure a proper diffusion of reaction components. Then, the suspension was extracted with ethyl acetate (2 × 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 (10:90) and followed by TLC to afford the desired pure product. For **3k** and **3l**, we have used a mixture of ethyl acetate / n-hexane (20:80).

3. Scheme 4, I

Phenylacetylene (0.25 mmol), triacetic acid lactone (0.25 mmol), $(NH_4)_2S_2O_8$ (0.50 mmol) and 1 mL of water were employed following the **General Procedure**. The tube was purged for 1 minute using a gentle flow of N_2. It was capped with a rubber septum and constant supply of N_2 was allowed using a balloon. After the extraction, the crude mixture was diluted with ethyl acetate and analyzed by GC-MS (Figure S1).

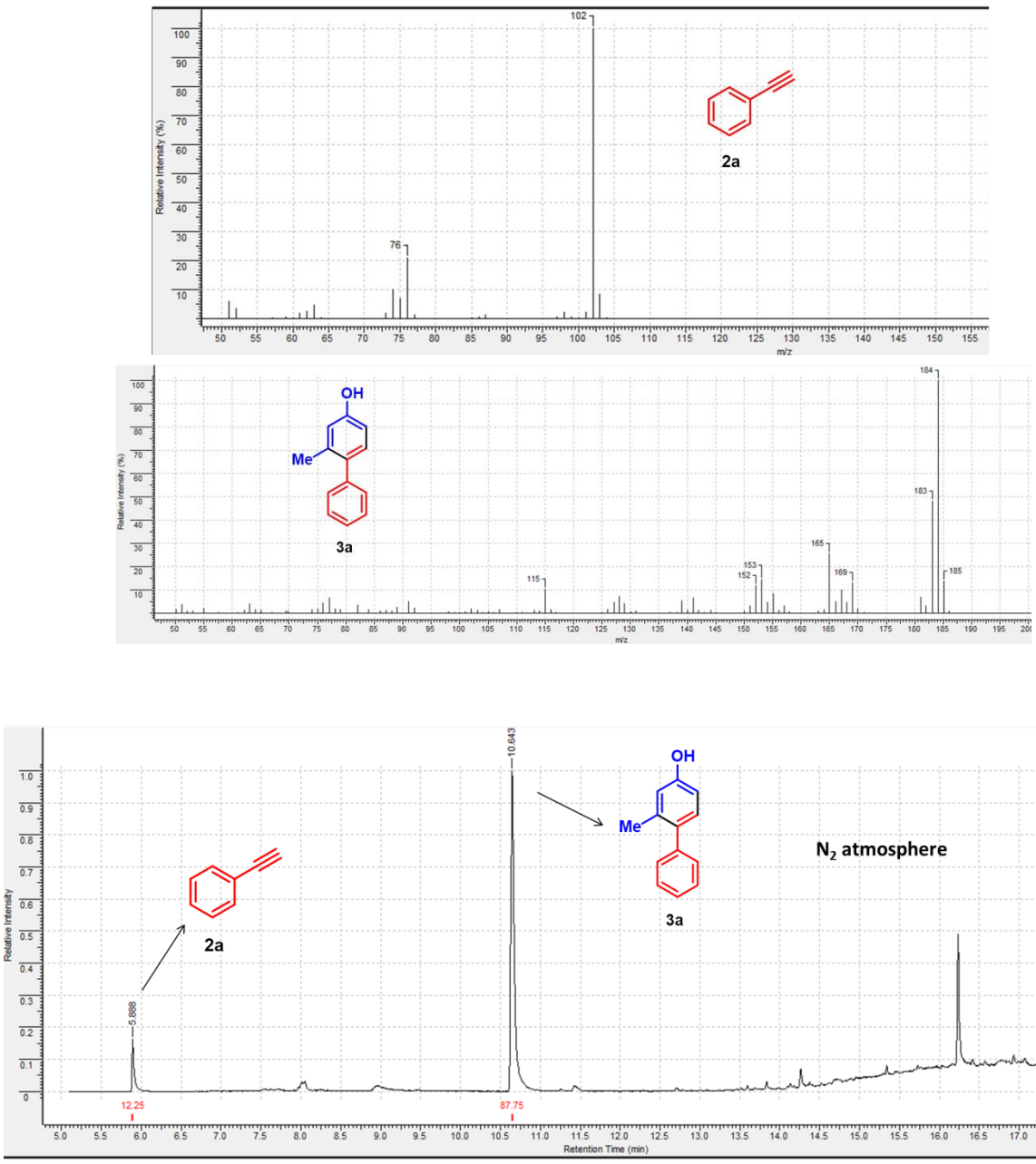
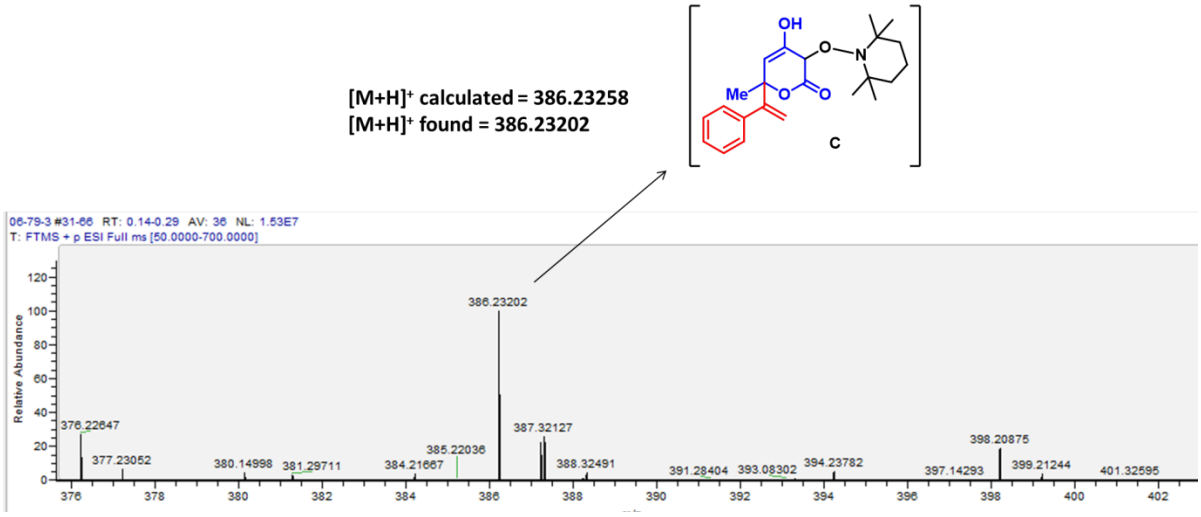


Figure S1. EI spectra of **2a** and **3a** observed in the experiment. GC-MS of the reaction under nitrogen atmosphere.

4. Scheme 4, III

Phenylacetylene (0.25 mmol), triacetic acid lactone (0.25 mmol), TEMPO (0.50 mmol), $(NH_4)_2S_2O_8$ (0.50 mmol) and 1 mL of water 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 5

Phenylacetylenes (0.08 mmol of **2a** + 0.08 mmol of **2b** + 0.08 mmol of **2c**), triacetic acid lactone (0.25 mmol), $(NH_4)_2S_2O_8$ (0.50 mmol) and 1 mL of water were employed following the **General Procedure** during 6 h reaction time. After the extraction, the crude mixture was diluted with ethyl acetate and analyzed by GC-MS (Figure S3).

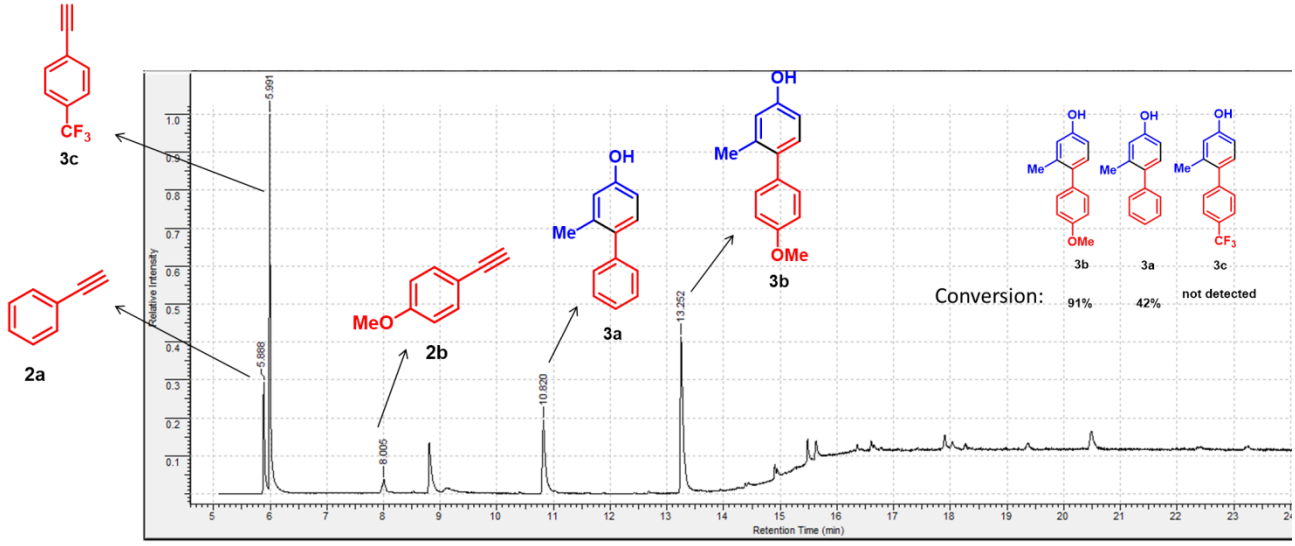
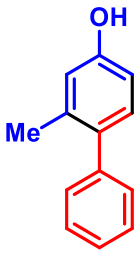


Figure S3. Competition experiment employing different phenylacetylenes.

6. Characterization of the products



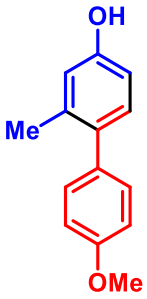
3a

Prepared from phenylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (84% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42–7.39 (m, 2H), 7.34–7.29 (m, 3H), 7.11 (d, 1H, *J* = 8.17 Hz), 6.76 (d, 1H, *J* = 2.83 Hz), 6.71 (dd, 1H, *J* = 8.17, 2.83 Hz), 4.69 (s, 1H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.60, 141.55, 137.04, 134.81, 131.04, 129.39, 128.02, 126.50, 116.89, 112.61, 20.56.

HRMS m/z (ESI): calcd. for $C_{13}H_{13}O$ $[M+H]^+$ 185.09609, found 185.09602.



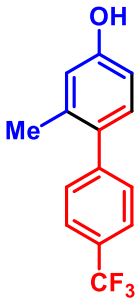
3b

Prepared from 4-methoxyphenylacetylene and triacetic acid lactone following the general procedure to give the product as colourless oil (92% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.22 (dt, 2H, *J* = 8.80, 2.20 Hz), 7.09 (d, 1H, *J* = 8.17 Hz), 6.94 (dt, 2H, *J* = 8.80, 2.20 Hz), 6.75 (d, 1H, *J* = 2.83 Hz), 6.71 (dd, 1H, *J* = 8.17, 2.83 Hz), 4.78 (s, 1H), 3.86 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 158.29, 154.40, 137.14, 134.39, 133.99, 131.07, 130.39, 116.85, 113.46, 112.58, 55.28, 20.61.

HRMS m/z (ESI): calcd. for $C_{14}H_{15}O_2$ $[M+H]^+$ 215.10666, found 215.10646.



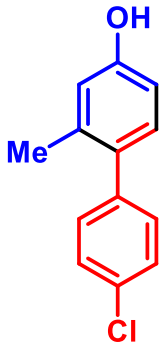
3c

Prepared from 4-(trifluoromethyl)phenylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (74% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.65 (d, 2H, *J* = 7.86 Hz), 7.41 (d, 2H, *J* = 7.86 Hz), 7.09 (d, 1H, *J* = 8.17 Hz), 6.78 (d, 1H, *J* = 2.83 Hz), 6.74 (dd, 1H, *J* = 8.17, 2.52 Hz), 4.79 (s, 1H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 155.15, 145.25, 137.00, 133.33, 130.94, 129.70, 126.85, 125.42, 124.99 (q, ^{3}J = 4.02 Hz), 123.26, 117.13, 112.88, 20.45.

HRMS m/z (ESI): calcd. for $C_{14}H_{12}F_3O$ $[M+H]^+$ 253.08348, found 253.08334.



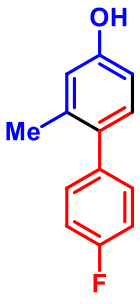
3d

Prepared from 4-chlorophenylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (81% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.36 (dt, 2H, *J* = 8.49, 2.52 Hz), 7.22 (dt, 2H, *J* = 8.49, 2.20 Hz), 7.07 (d, 1H, *J* = 8.17 Hz), 6.76 (d, 1H, *J* = 2.83 Hz), 6.72 (dd, 1H, *J* = 8.17, 2.20 Hz), 4.86 (s, 1H), 2.23 (s, 3H).

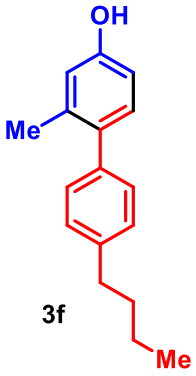
^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.84, 139.95, 137.00, 133.50, 132.52, 130.93, 130.69, 128.21, 117.02, 112.76, 20.49.

HRMS m/z (ESI): calcd. for $C_{13}H_{12}ClO$ $[M+H]^+$ 219.05712, found 219.05719.



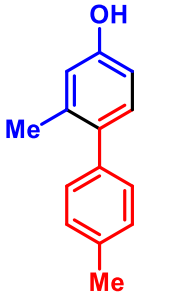
3e

Prepared from 4-fluorophenylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (76% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.27–7.23 (m, 2H), 7.10–7.07 (m, 3H), 6.76 (d, 1H, *J* = 2.52 Hz), 6.72 (dd, 1H, *J* = 7.55, 2.52 Hz), 4.69 (s, 1H), 2.22 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 161.77 (d, ^{1}J = 245 Hz), 154.69, 137.43 (d, ^{4}J = 3.01 Hz), 137.09, 133.77, 131.04, 130.86 (d, ^{3}J = 8.03 Hz), 116.93, 114.89 (d, ^{2}J = 21.1 Hz), 112.67, 20.52.
HRMS m/z (ESI): calcd. for $C_{13}H_{12}FO$ $[M+H]^+$ 203.08667, found 203.08614.



3f

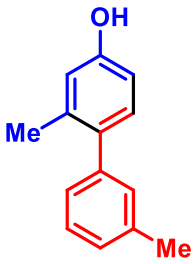
Prepared from 4-butylphenylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (86% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.21 (s, 4H), 7.11 (d, 1H, *J* = 8.17 Hz), 6.75 (d, 1H, *J* = 2.83 Hz), 6.70 (dd, 1H, *J* = 8.17, 2.20 Hz), 4.88 (s, 1H), 2.66 (app t, 2H, *J* = 7.55 Hz), 2.25 (s, 3H), 1.66 (m, 2H), 1.41 (sext, 2H, *J* = 7.55 Hz), 0.97 (t, 3H, J = 7.23 Hz).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.42, 141.11, 138.74, 137.08, 134.80, 131.08, 129.21, 128.04, 116.85, 112.56, 35.33, 33.62, 22.45, 20.61, 13.98.
HRMS m/z (ESI): calcd. for $C_{17}H_{21}O$ $[M+H]^+$ 241.15869, found 241.15847.



3g

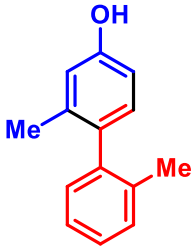
Prepared from 4-methylphenylacetylene and triacetic acid lactone following the general procedure to give the product as colourless oil (88% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.21 (m, 4H), 7.11 (d, 1H, *J* = 8.17 Hz), 6.76 (d, 1H, *J* = 2.83 Hz), 6.72 (dd, 1H, *J* = 8.17, 2.83 Hz), 4.80 (s, 1H), 2.42 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.42, 138.58, 137.06, 136.09, 134.73, 131.05, 129.24, 128.73, 116.87, 112.59, 21.11, 20.58.
HRMS m/z (ESI): calcd. for $C_{14}H_{15}O$ $[M+H]^+$ 199.11174, found 199.11155.



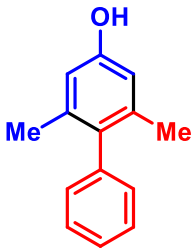
3h

Prepared from 3-methylphenylacetylene and triacetic acid lactone following the general procedure to give the product as colourless oil (87% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.30 (t, 1H, *J* = 7.55 Hz), 7.16–7.10 (m, 4H), 6.76 (d, 1H, *J* = 2.52 Hz), 6.71 (dd, 1H, *J* = 8.17, 2.83 Hz), 4.74 (s, 1H), 2.41 (s, 3H), 2.25 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.49, 141.48, 137.59, 137.02, 134.92, 130.99, 130.14, 127.88, 127.22, 126.45, 116.85, 112.56, 21.45, 20.57.
HRMS m/z (ESI): calcd. for $C_{14}H_{15}O$ $[M+H]^+$ 199.11174, found 199.11157.



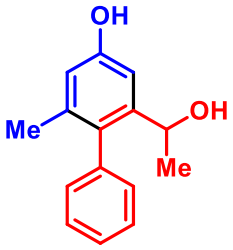
3i

Prepared from 2-methylphenylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (82% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.29–7.27 (m, 2H), 7.26–7.22 (m, 1H), 7.11 (d, 1H, *J* = 6.92 Hz), 6.99 (d, 1H, *J* = 8.17 Hz), 6.78 (d, 1H, *J* = 2.83 Hz), 6.72 (dd, 1H, *J* = 8.17, 2.20 Hz), 4.82 (s, 1H), 2.09 (s, 3H), 2.04 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.42, 141.15, 137.51, 136.29, 134.31, 130.44, 129.75, 127.04, 125.49, 116.44, 112.37, 19.91, 19.83.
HRMS m/z (ESI): calcd. for $C_{14}H_{15}O$ $[M+H]^+$ 199.11174, found 199.11159.



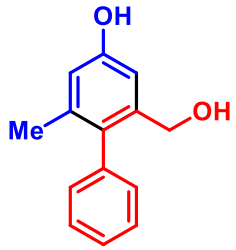
3j

Prepared from 1-phenyl-1-propyne and triacetic acid lactone following the general procedure to give the product as pale yellow oil (80% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.41 (app t, 2H, *J* = 7.34 Hz), 7.33 (dt, 1H, *J* = 7.34, 1.47 Hz), 7.12 (dd, 2H, *J* = 8.31, 1.47 Hz), 6.61 (s, 2H), 4.58 (s, 1H), 2.00 (s, 6H).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.11, 140.76, 137.76, 134.74, 129.65, 128.34, 126.51, 113.91, 20.89.
HRMS m/z (ESI): calcd. for $C_{14}H_{15}O$ $[M+H]^+$ 199.11174, found 199.11179.



3k

Prepared from 4-phenyl-3-butyn-2-ol and triacetic acid lactone following the general procedure to give the product as colourless oil (79% yield).
^{1}H NMR (500 MHz, DMSO-*d*): δ 9.20 (s, 1H), 7.41 (d, 1H, *J* = 7.55 Hz), 7.40 (d, 1H, *J* = 7.86 Hz), 7.32 (dt, 1H, *J* = 7.55, 1.26 Hz), 7.12 (app d, 1H, *J* = 7.23 Hz), 7.06 (app d, 1H, *J* = 7.23 Hz), 6.88 (d, 1H, *J* = 2.83 Hz), 6.55 (dd, 1H, *J* = 2.52, 0.63 Hz), 4.82 (s, 1H), 4.33 (q, 1H, *J* = 6.29 Hz), 1.84 (s, 3H), 1.04 (d, 3H, *J* = 6.29 Hz).
^{13}C NMR (125 MHz, DMSO-*d*): δ 156.37, 146.60, 139.85, 135.98, 130.23, 129.89, 129.47, 128.27, 128.13, 126.49, 114.78, 109.32, 65.04, 25.60, 20.58.
HRMS m/z (ESI): calcd. for $C_{15}H_{17}O_2$ $[M+H]^+$ 229.12231, found 229.12240.



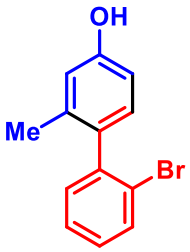
3l

Prepared from 3-phenylprop-2-yn-1-ol and triacetic acid lactone following the general procedure to give the product as colourless oil (85% yield).

^{1}H NMR (500 MHz, DMSO-*d*): δ 9.21 (s, 1H), 7.40 (app t, 2H, *J* = 7.34 Hz), 7.31 (dt, 1H, *J* = 7.34, 1.96 Hz), 7.10–7.07 (m, 2H), 6.84 (d, 1H, *J* = 2.45 Hz), 6.55 (d, 1H, *J* = 2.45 Hz), 4.90 (t, 1H, *J* = 5.38 Hz), 4.03 (d, 2H, *J* = 5.38 Hz), 1.87 (s, 3H).

^{13}C NMR (125 MHz, DMSO-*d*): δ 156.23, 141.19, 139.45, 135.95, 130.13, 129.56, 128.23, 126.53, 114.54, 110.87, 61.02, 20.27.

HRMS m/z (ESI): calcd. for $C_{14}H_{15}O_2$ $[M+H]^+$ 215.10666, found 215.10670.



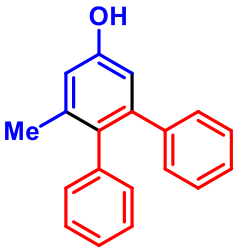
3m

Prepared from 1-bromo-2-ethynylbenzene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (84% yield).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.69–7.65 (m, 1H), 7.35 (td, 1H, *J* = 6.80, 1.32 Hz), 7.24–7.20 (m, 2H), 6.99 (d, 1H, *J* = 8.12 Hz), 6.77 (d, 1H, *J* = 2.64 Hz), 6.72 (dd, 1H, *J* = 8.12, 2.64 Hz), 4.95 (s, 1H), 2.08 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.99, 142.24, 137.76, 133.99, 132.48, 131.34, 130.51, 128.60, 127.14, 124.36, 116.48, 112.36, 19.96.

HRMS m/z (ESI): calcd. for $C_{13}H_{12}BrO$ $[M+H]^+$ 263.00660, found 263.00650.

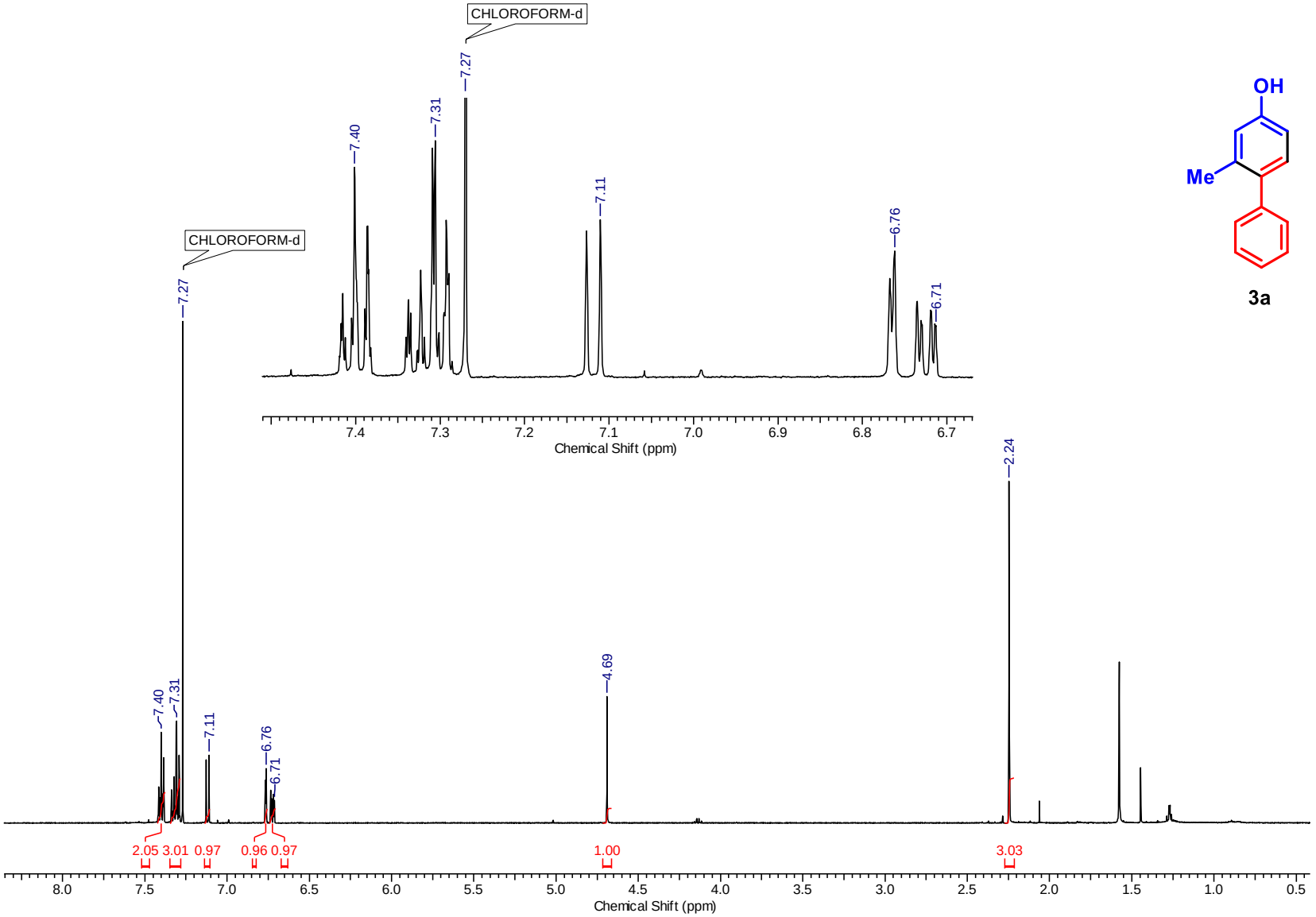


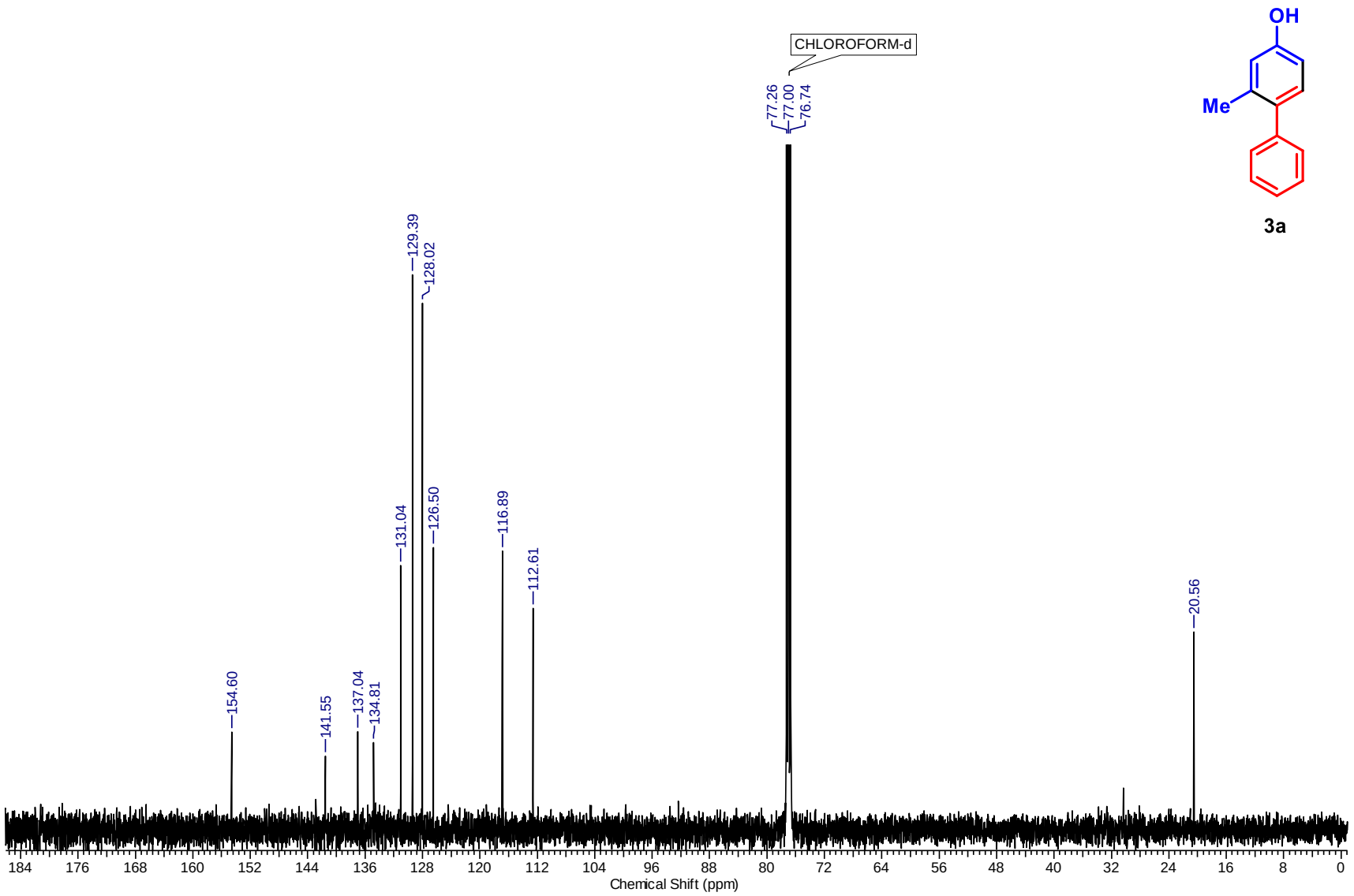
3n

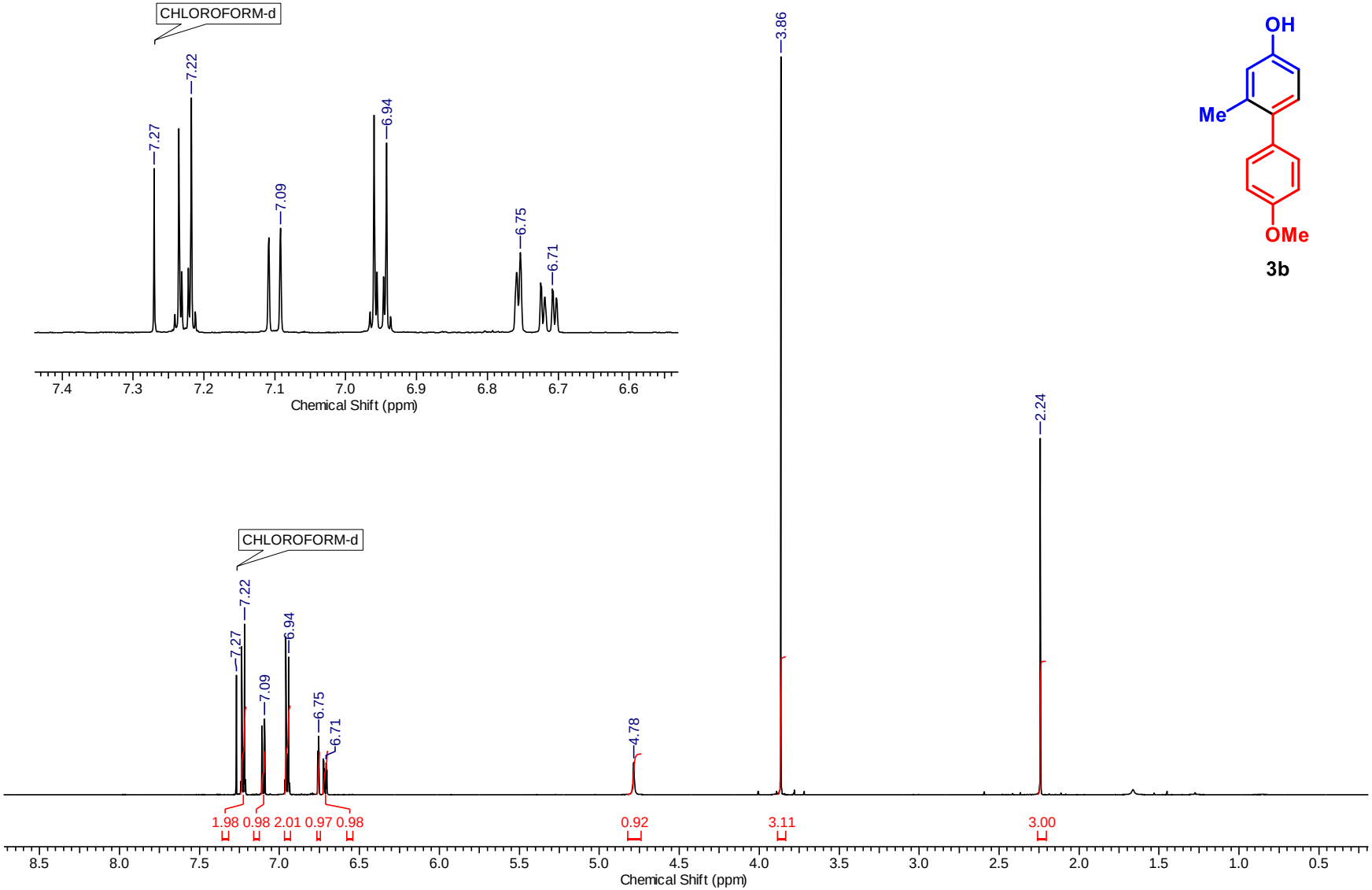
Prepared from dipheylacetylene and triacetic acid lactone following the general procedure to give the product as pale yellow oil (73% yield).

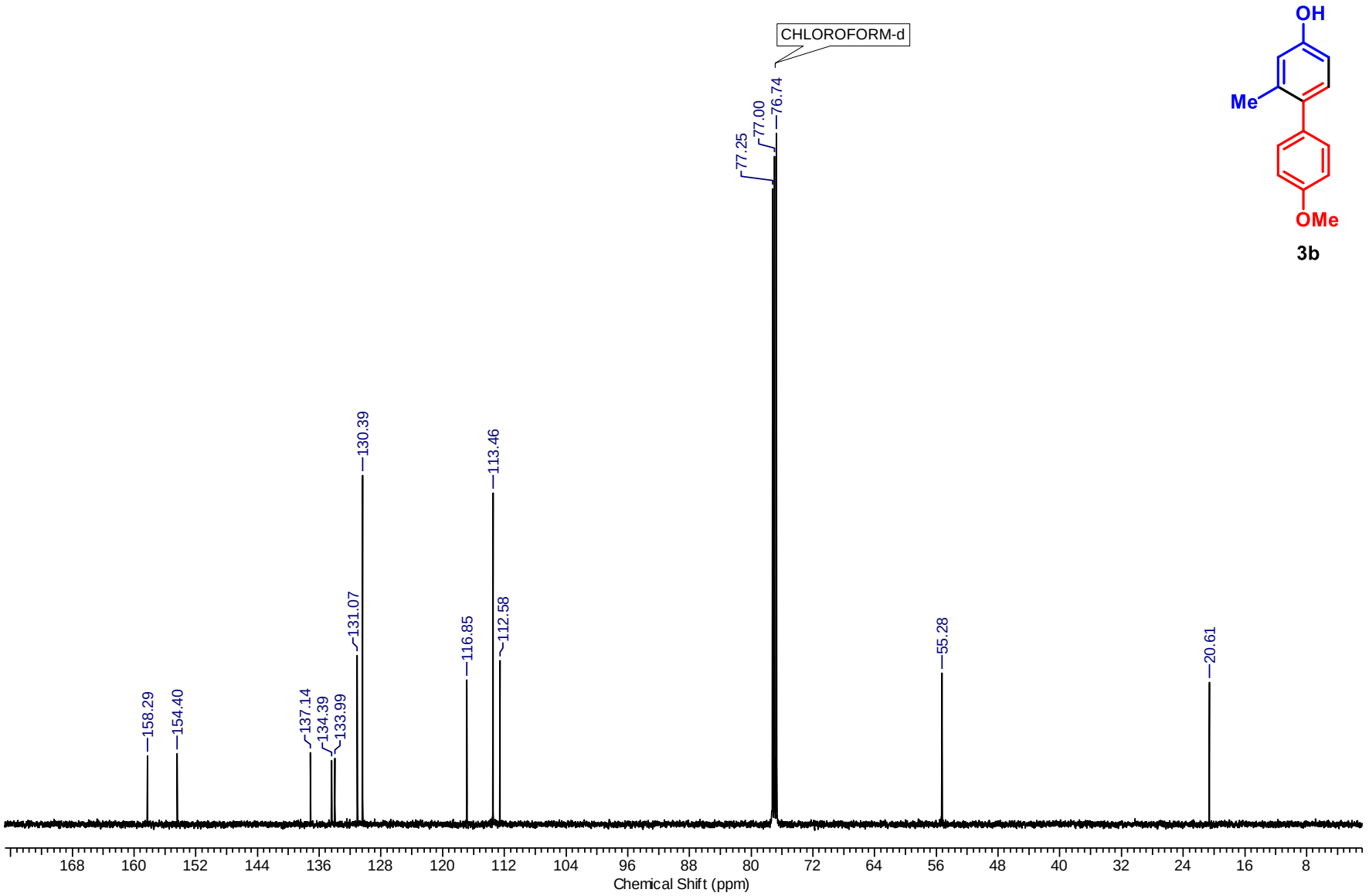
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.23–7.12 (m, 6H), 7.07–7.01 (m, 4H), 6.80 (dd, 1H, *J* = 2.64, 0.76 Hz), 6.76 (dd, 1H, *J* = 2.64, 0.38 Hz), 4.83 (s, 1H), 2.15 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 154.13, 143.03, 141.62, 139.96, 138.32, 133.46, 130.85, 129.65, 127.64, 127.42, 126.18, 126.10, 115.81, 114.39, 21.28.
HRMS m/z (ESI): calcd. for $C_{19}H_{17}O$ $[M+H]^+$ 261.12739, found 261.12748.

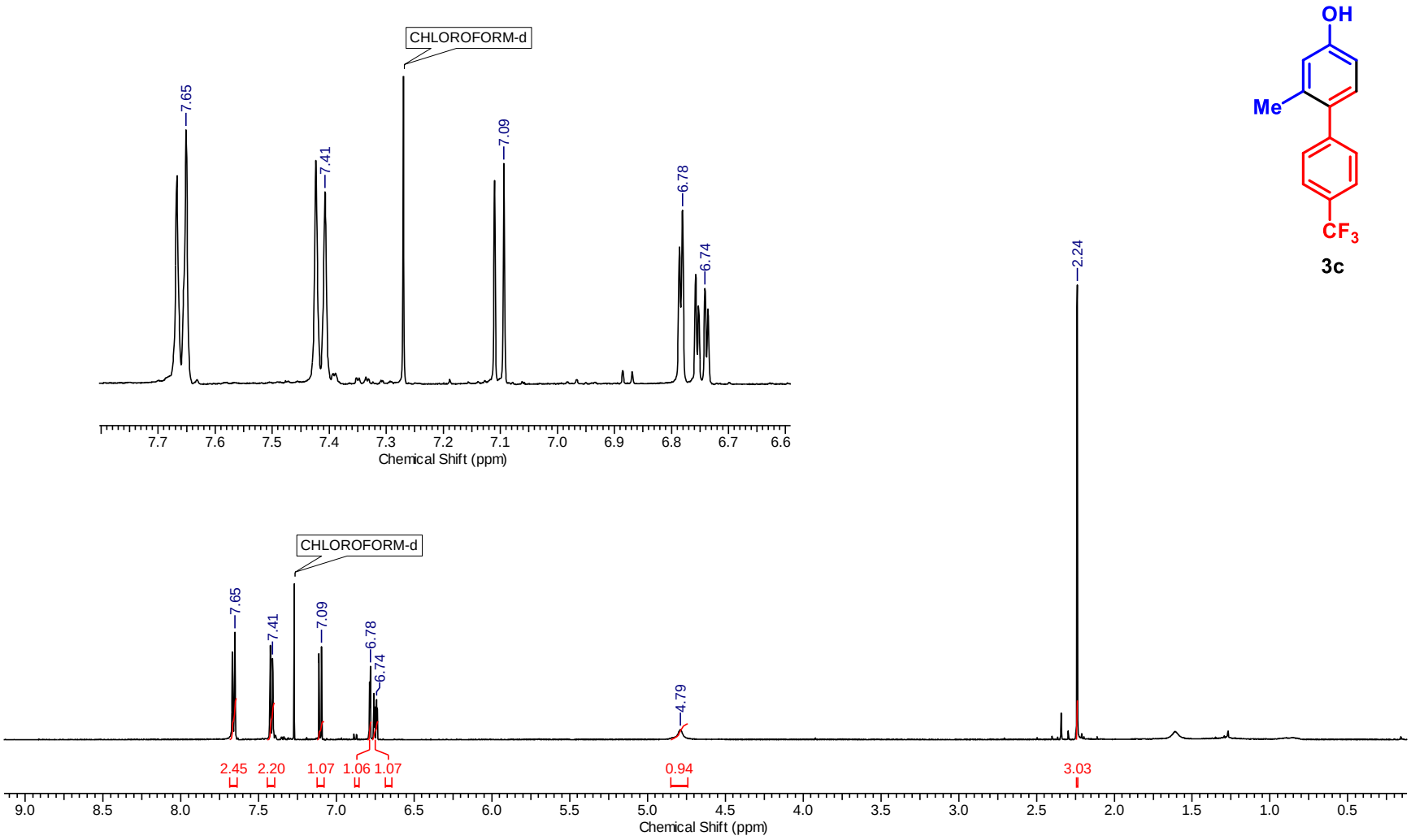
7. Spectral Data

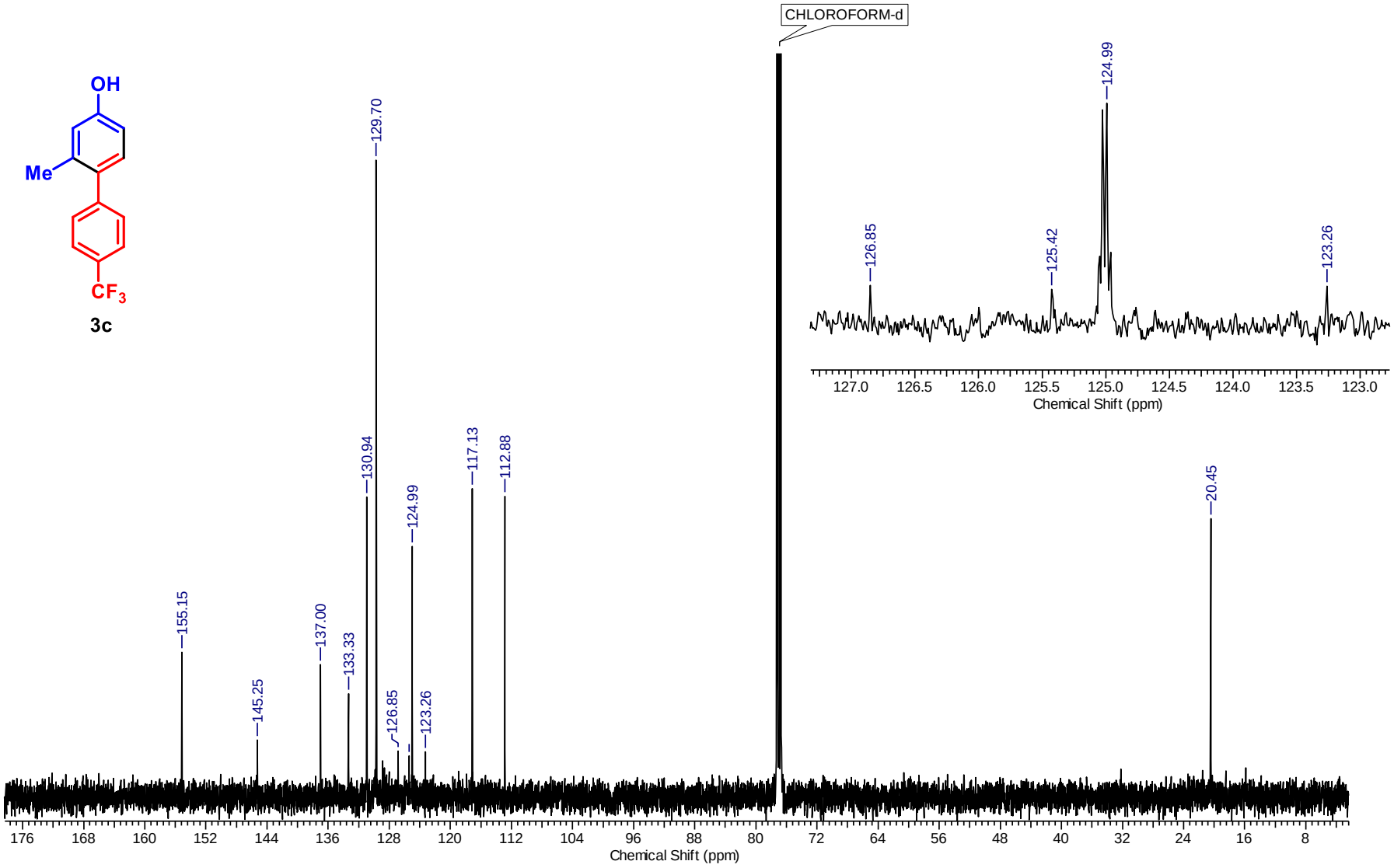

CHLOROFORM-d
7.27
7.40
7.31
7.11
6.76
6.71
Chemical Shift (ppm)
CHLOROFORM-d
7.27
7.40
7.31
7.11
6.76
6.71
4.69
2.24
2.05
3.01
0.97
0.96
0.97
1.00
3.03
Chemical Shift (ppm)
OH
Me
3a

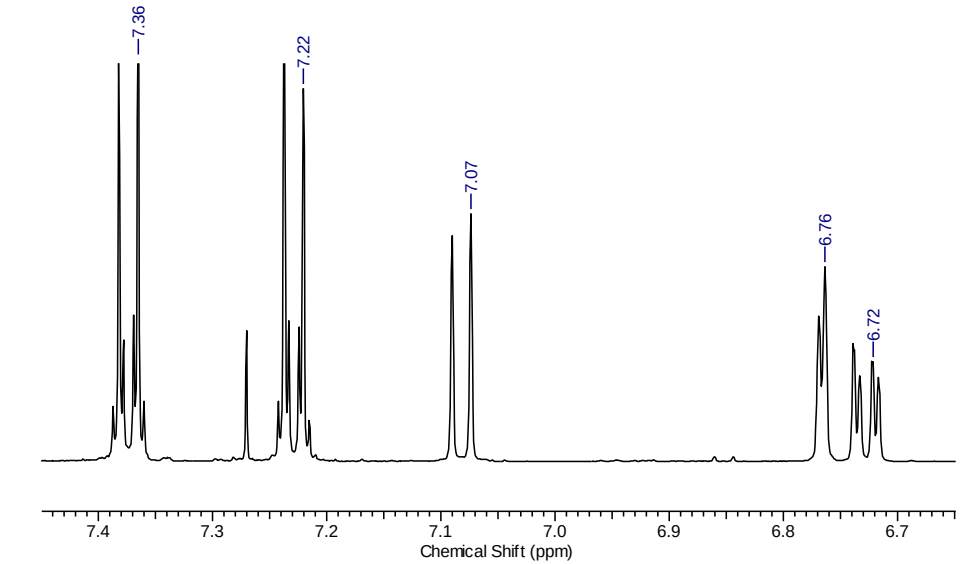

CHLOROFORM-d
77.26
77.00
76.74
129.39
128.02
131.04
126.50
116.89
112.61
154.60
141.55
137.04
134.81
20.56
OH
Me
3a
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

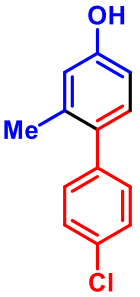

CHLOROFORM-d
7.27
7.22
7.09
6.94
6.75
6.71
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
Chemical Shift (ppm)
OH
Me
OMe
3b
3.86
2.24
CHLOROFORM-d
7.22
7.27
6.94
7.09
6.75
6.71
4.78
1.98
0.98
2.01
0.97
0.98
0.92
3.11
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


CHLOROFORM-d
77.25
77.00
76.74
158.29
154.40
137.14
134.39
133.99
131.07
130.39
116.85
113.46
112.58
55.28
20.61
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
OMe
3b

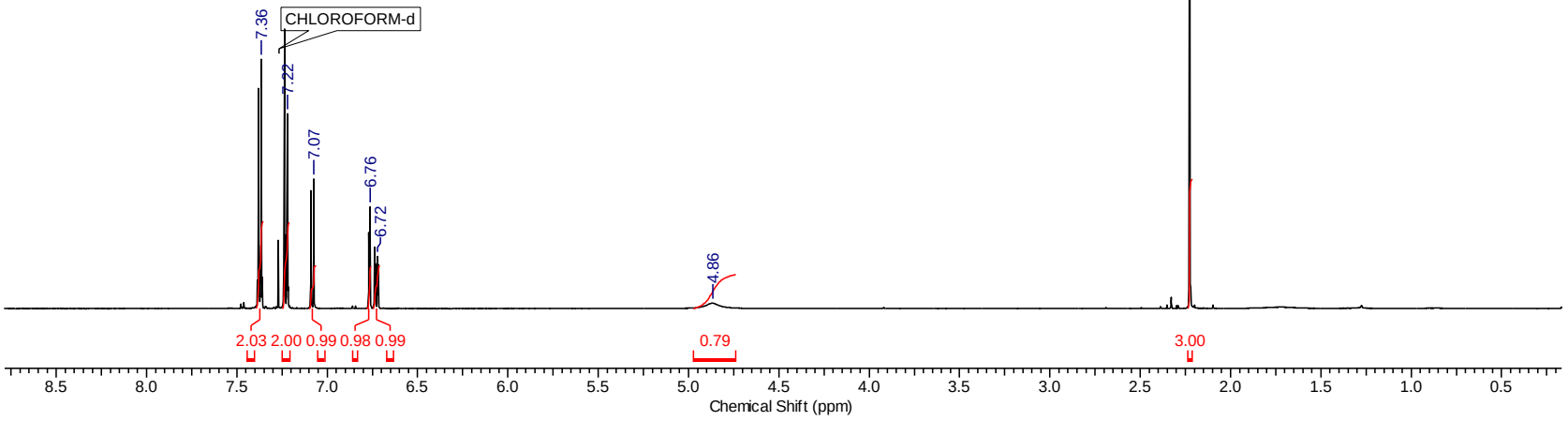

CHLOROFORM-d
7.65
7.41
7.09
6.78
6.74
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
Chemical Shift (ppm)
OH
Me
CF3
3c
CHLOROFORM-d
7.65
7.41
7.09
6.78
6.74
4.79
2.24
2.45 2.20 1.07 1.06 1.07 0.94 3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

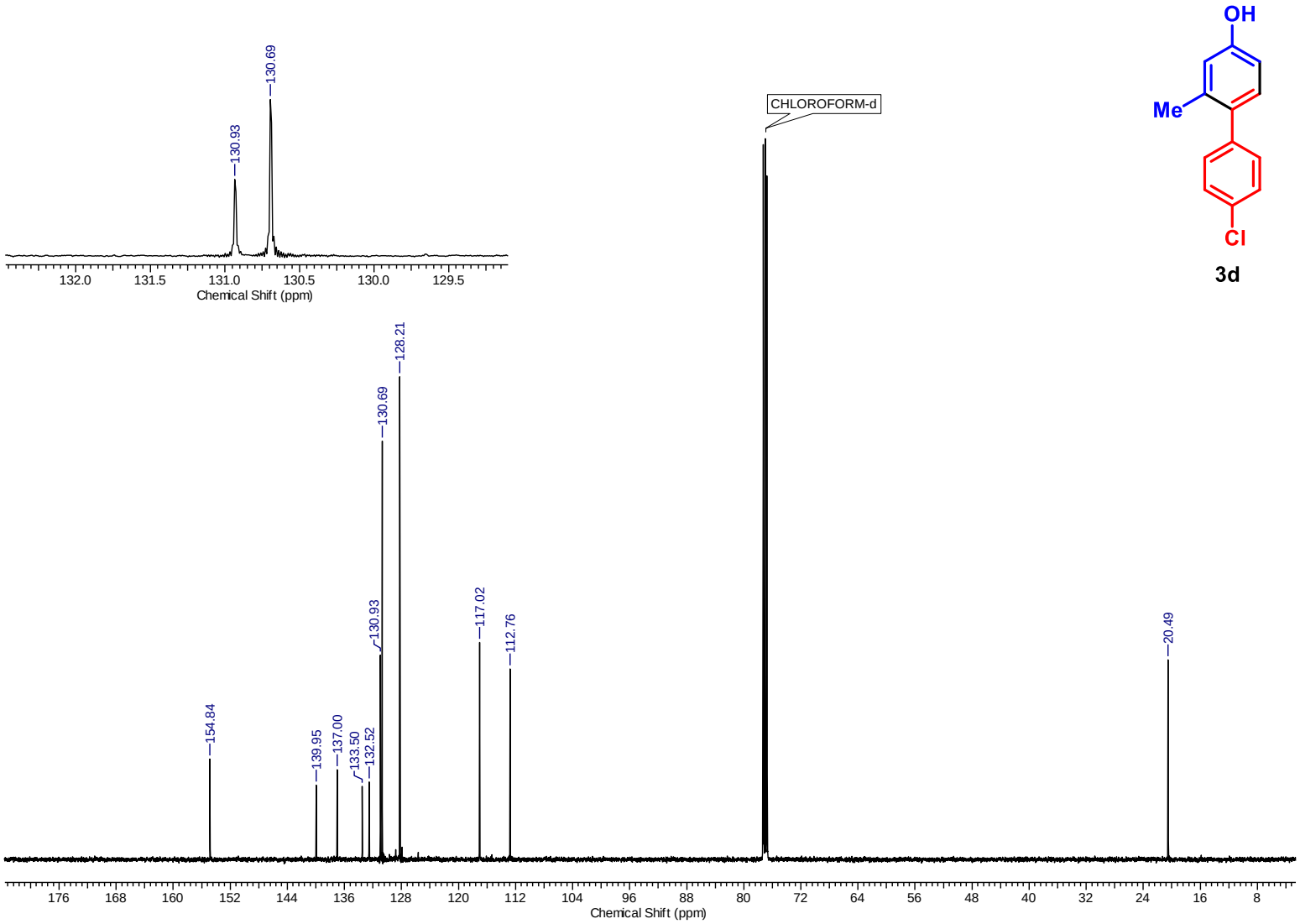

OH
Me
CF3
3c
CHLOROFORM-d
155.15
145.25
137.00
133.33
129.70
130.94
126.85
124.99
123.26
117.13
112.88
20.45
126.85
125.42
124.99
123.26
Chemical Shift (ppm)
Chemical Shift (ppm)

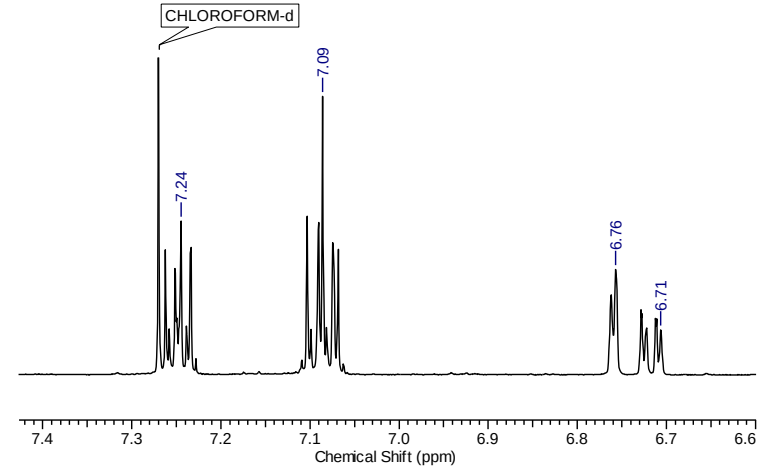

7.36
7.22
7.07
6.76
6.72
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
Chemical Shift (ppm)

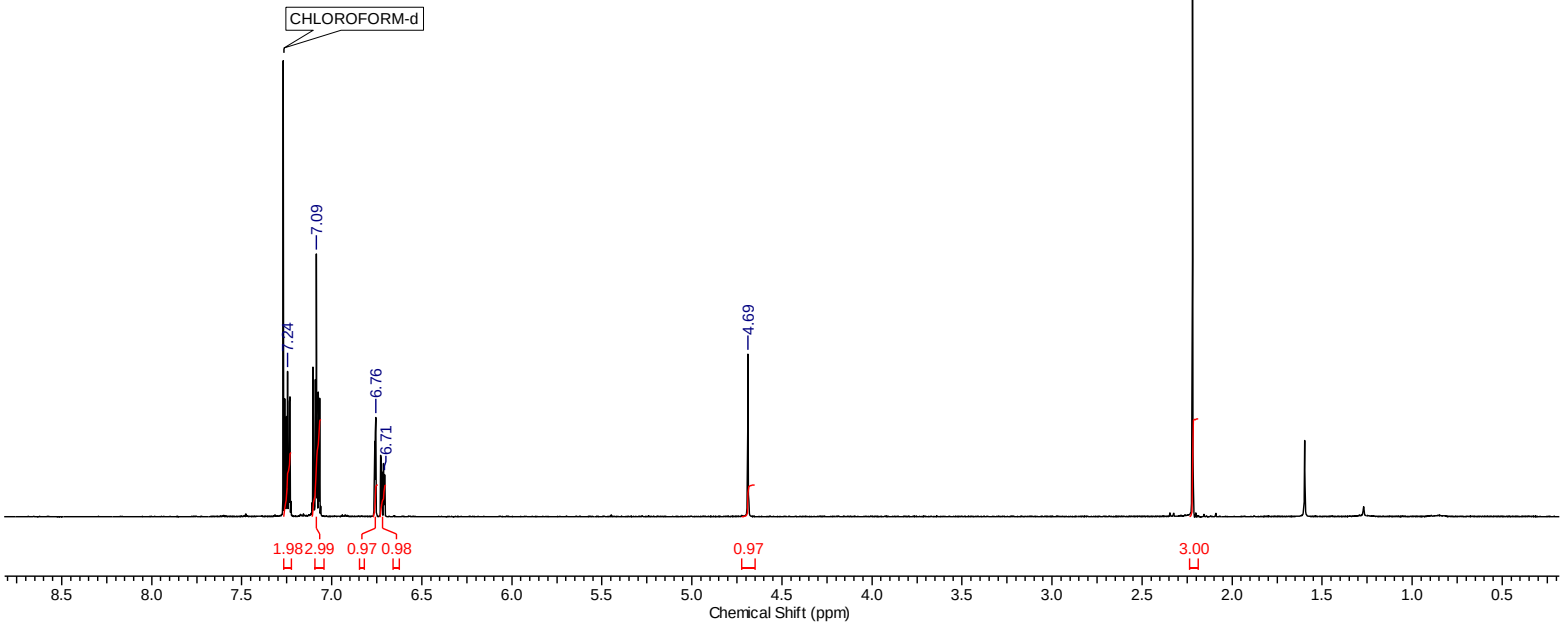

OH
Me
Cl

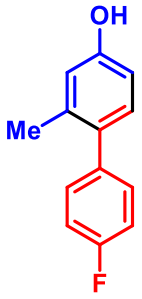
3d


7.36
CHLOROFORM-d
7.22
7.07
6.76
6.72
4.86
2.23
2.03
2.00
0.99
0.98
0.99
0.79
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
Chemical Shift (ppm)

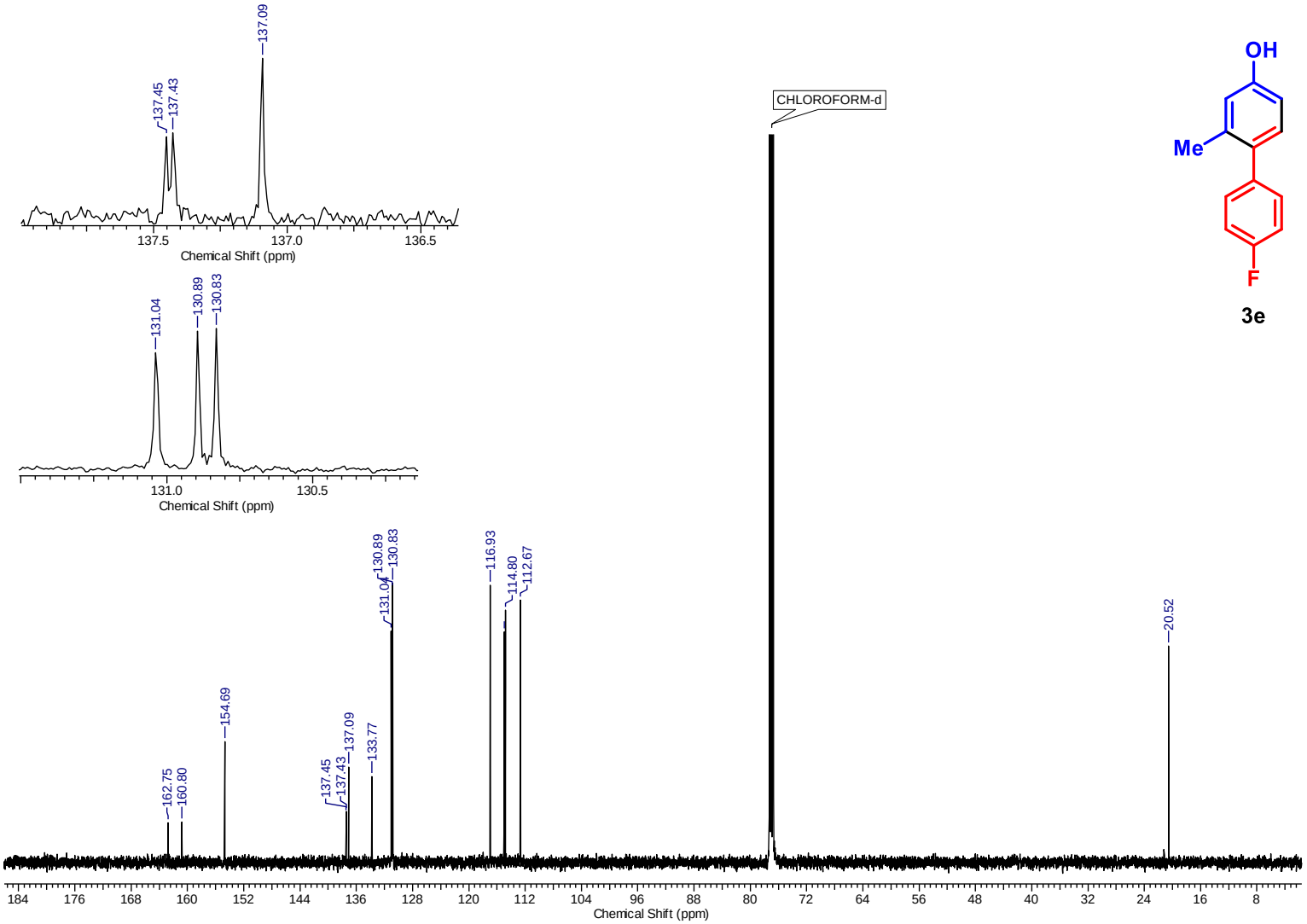

OH
Me
Cl
3d
CHLOROFORM-d
130.93
130.69
132.0
131.5
131.0
130.5
130.0
129.5
Chemical Shift (ppm)
154.84
139.95
137.00
133.50
132.52
130.93
130.69
128.21
117.02
112.76
20.49
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

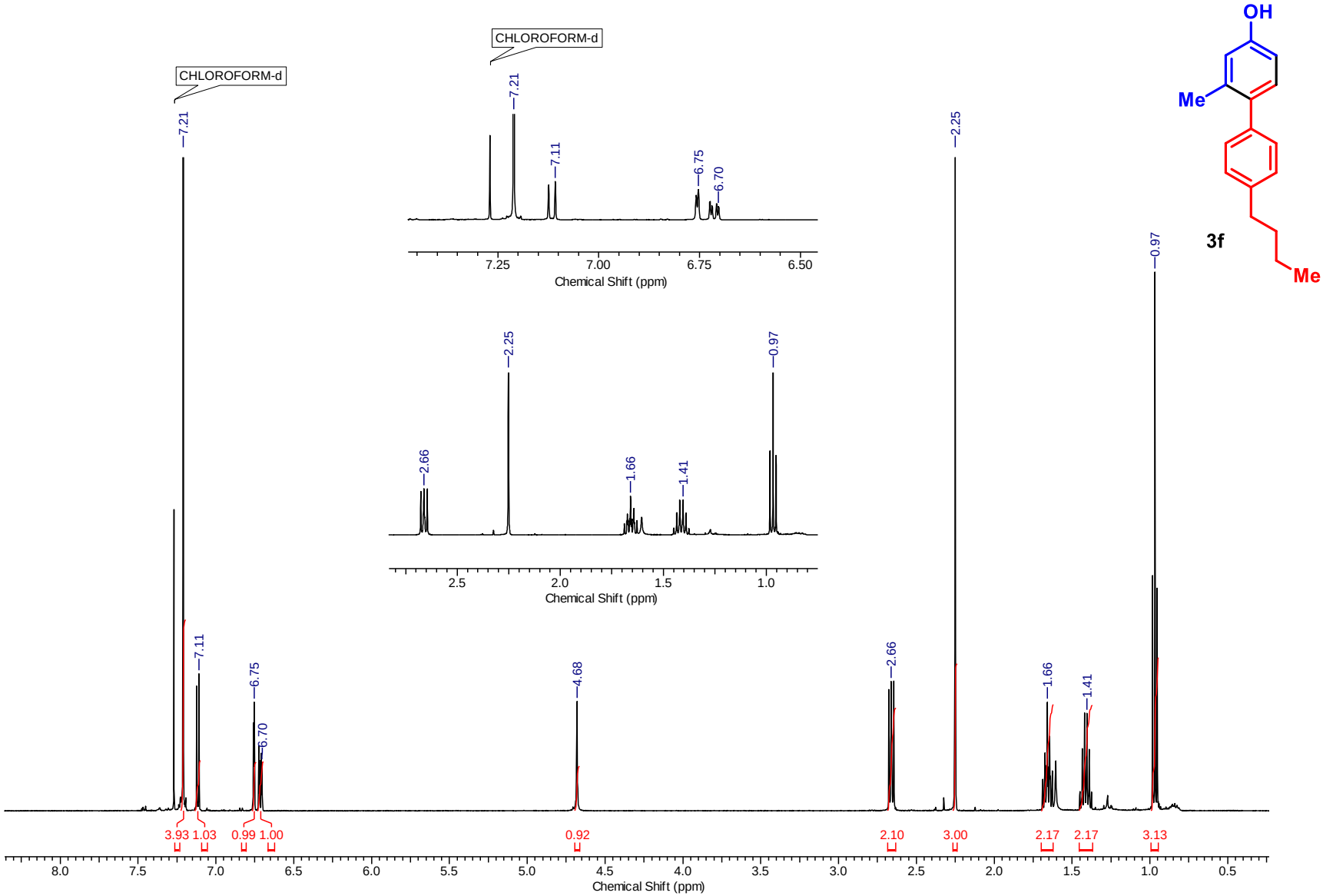

CHLOROFORM-d
7.09
7.24
6.76
6.71
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
Chemical Shift (ppm)

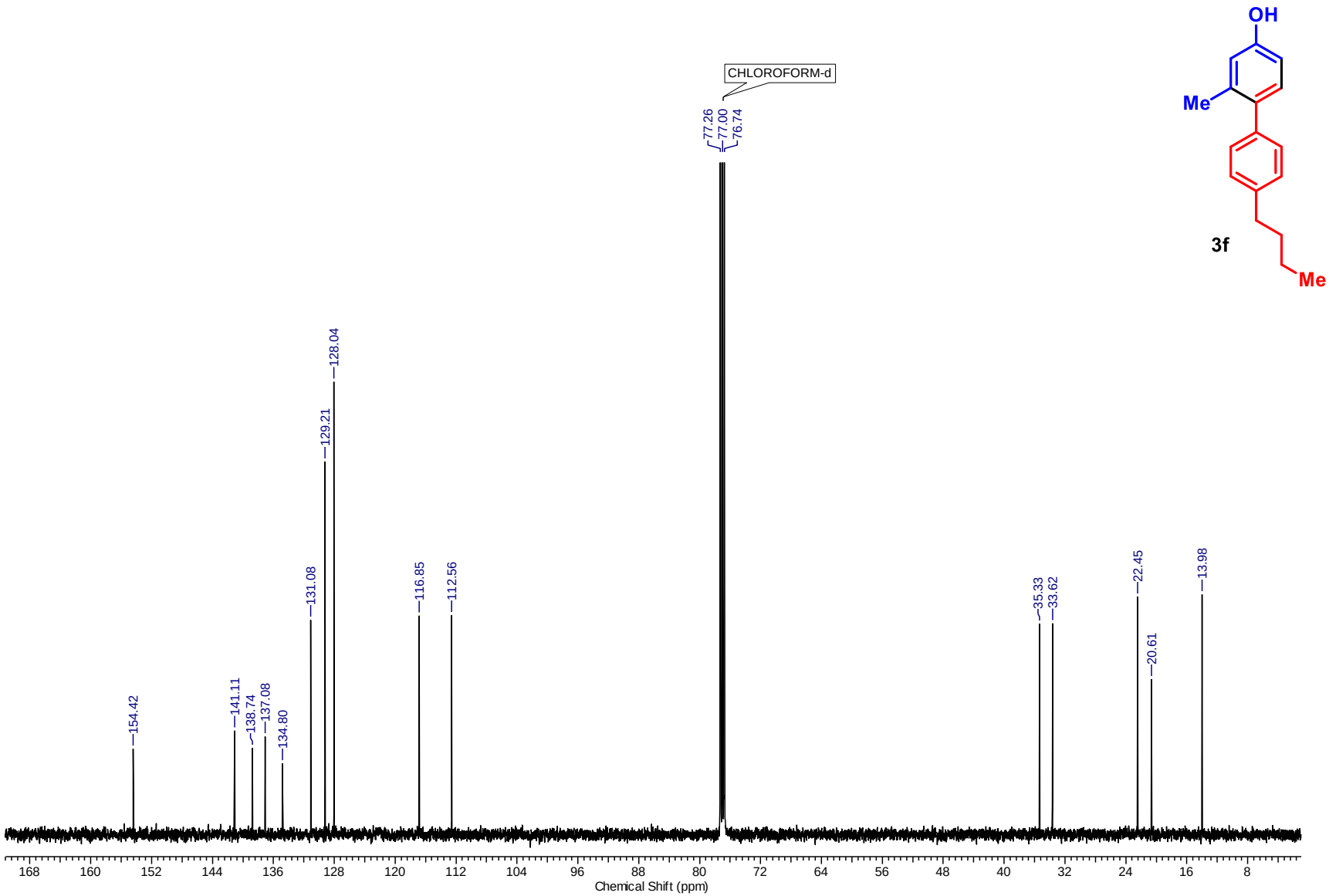

CHLOROFORM-d
7.09
7.24
6.76
6.71
4.69
2.22
1.98
2.99
0.97
0.98
0.97
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

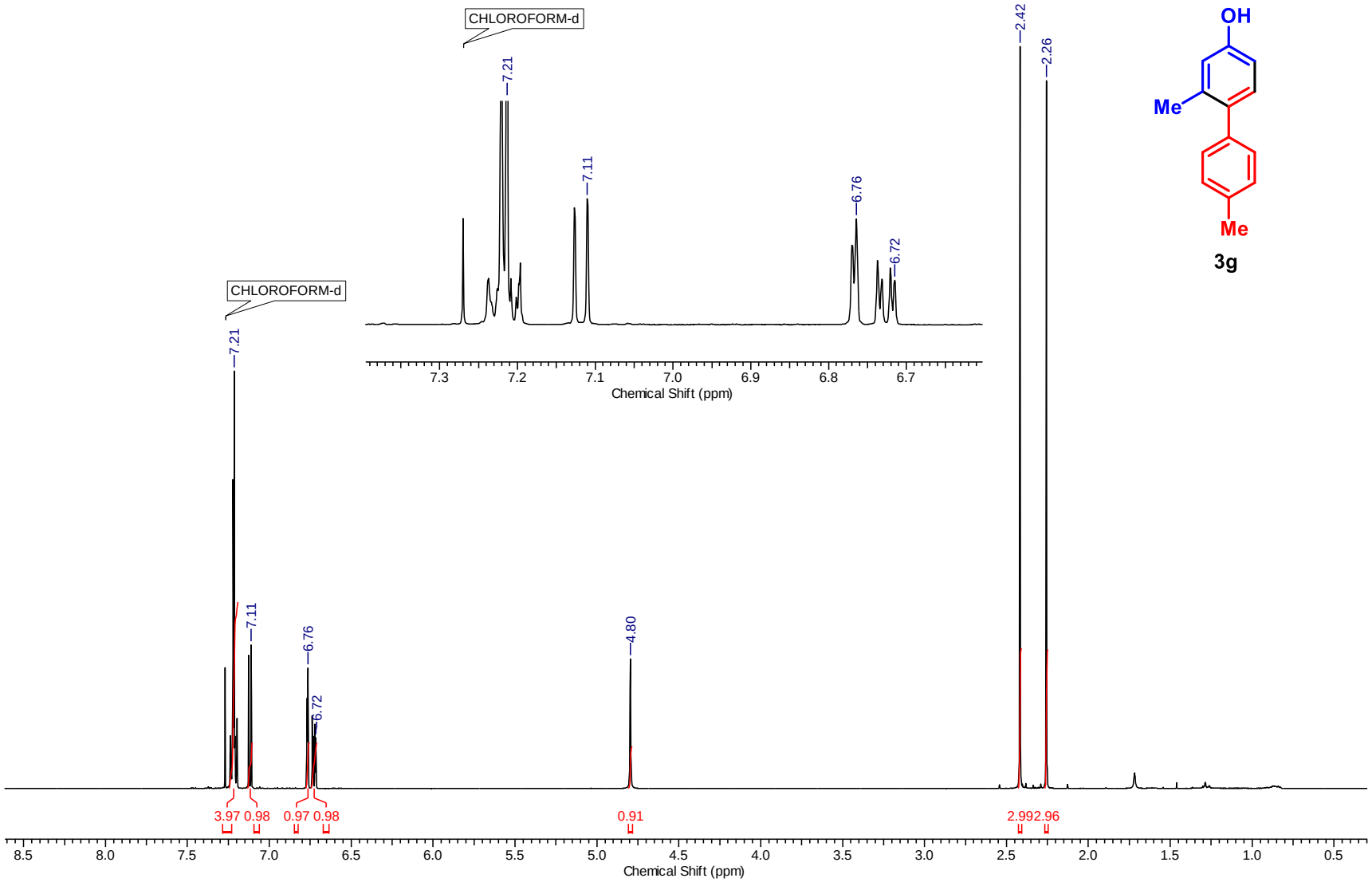

OH
Me
F

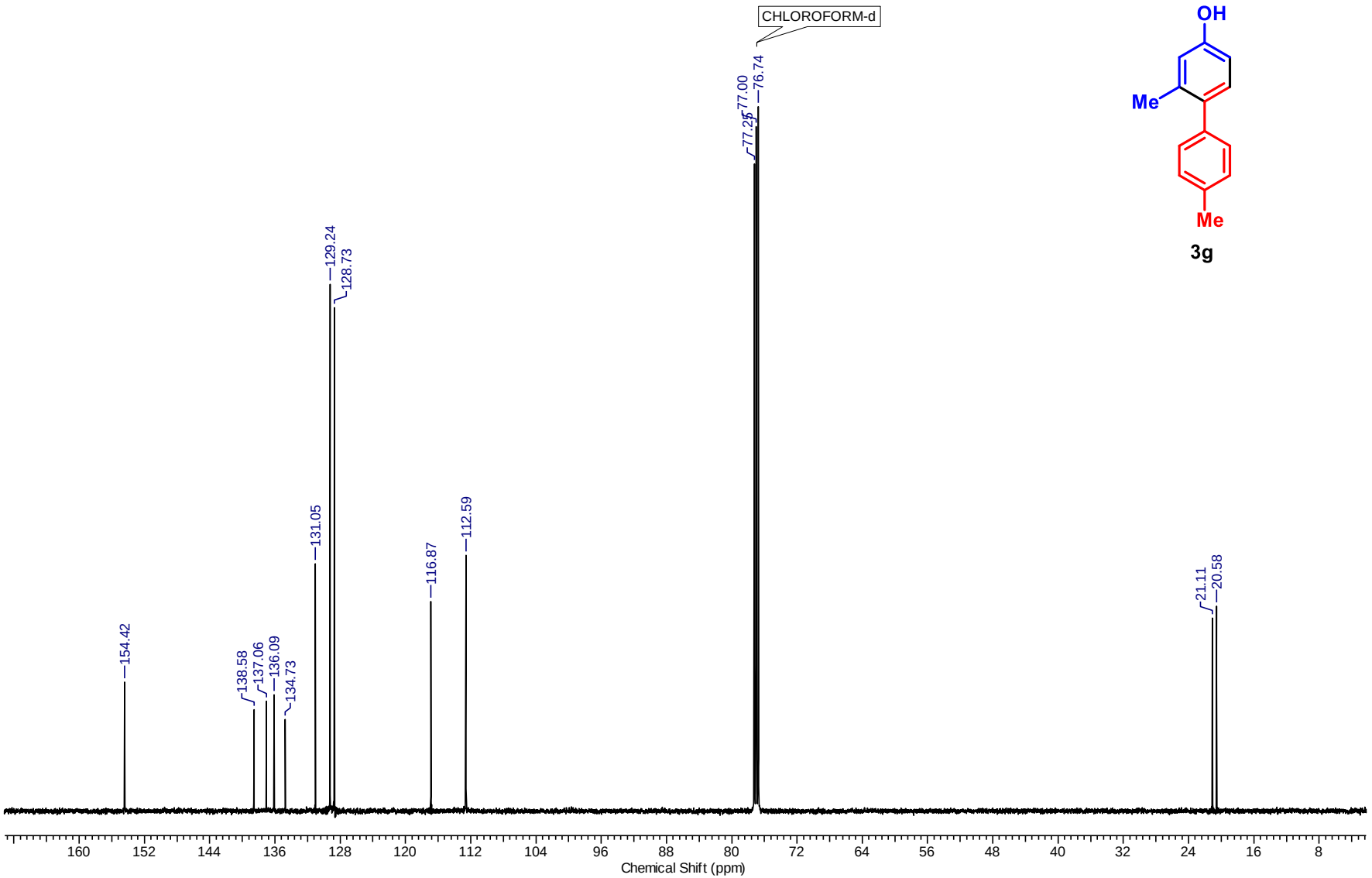
3e

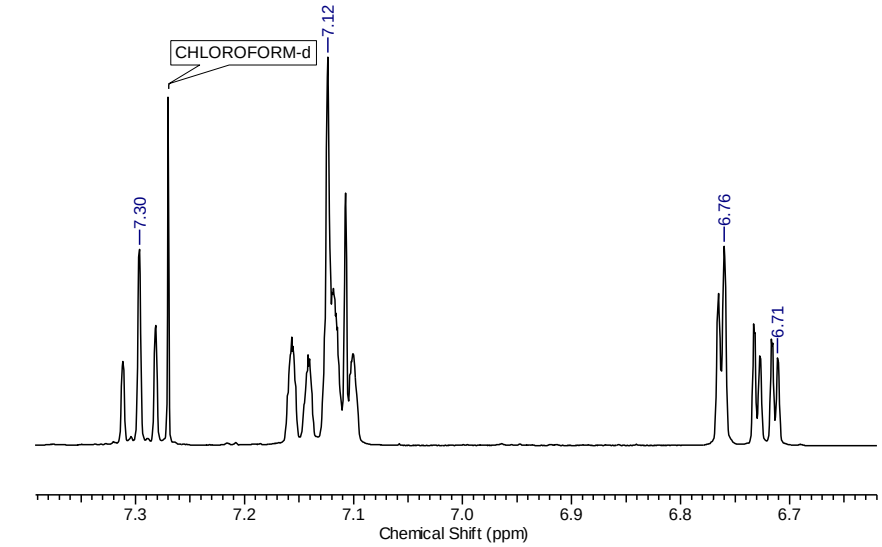

137.09
137.45
137.43
137.5
137.0
136.5
Chemical Shift (ppm)
131.04
130.89
130.83
131.0
130.5
Chemical Shift (ppm)
CHLOROFORM-d
OH
Me
F
3e
130.89
130.83
131.04
116.93
114.80
112.67
20.52
154.69
137.09
137.45
137.43
133.77
162.75
160.80
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

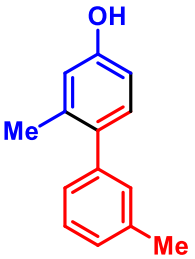

CHLOROFORM-d
7.21
7.11
6.75
6.70
2.25
0.97
2.66
1.66
1.41
4.68
3.93
1.03
0.99
1.00
0.92
2.10
3.00
2.17
2.17
3.13
Chemical Shift (ppm)
OH
Me
3f
Me


OH
Me
3f
Me
CHLOROFORM-d
77.26
77.00
76.74
154.42
141.11
138.74
137.08
134.80
131.08
129.21
128.04
116.85
112.56
35.33
33.62
22.45
20.61
13.98
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

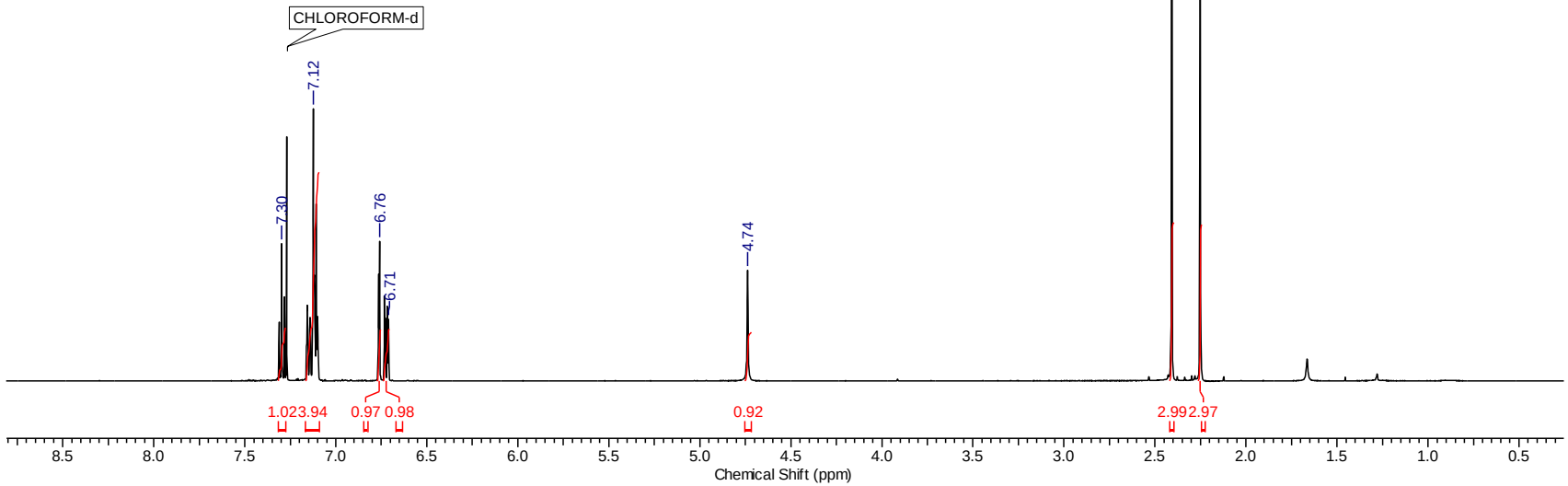

CHLOROFORM-d
7.21
7.11
6.76
6.72
7.3
7.2
7.1
7.0
6.9
6.8
6.7
Chemical Shift (ppm)
CHLOROFORM-d
7.21
7.11
6.76
6.72
4.80
2.42
2.26
3.97 0.98 0.97 0.98
0.91
2.99 2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)
OH
Me
Me
3g

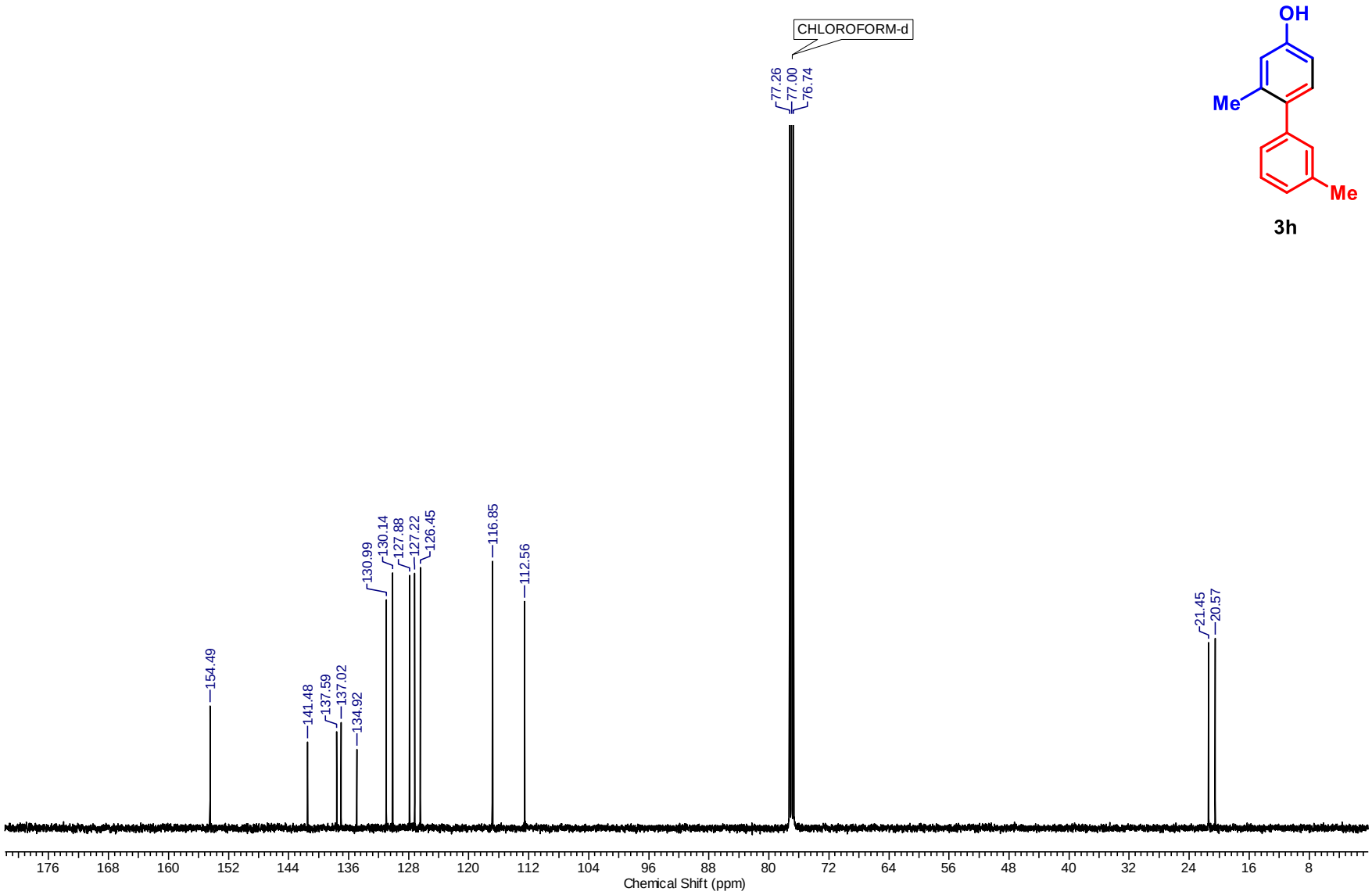

CHLOROFORM-d
OH
Me
Me
3g
154.42
138.58
137.06
136.09
134.73
131.05
129.24
128.73
116.87
112.59
77.00
76.74
21.11
20.58
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

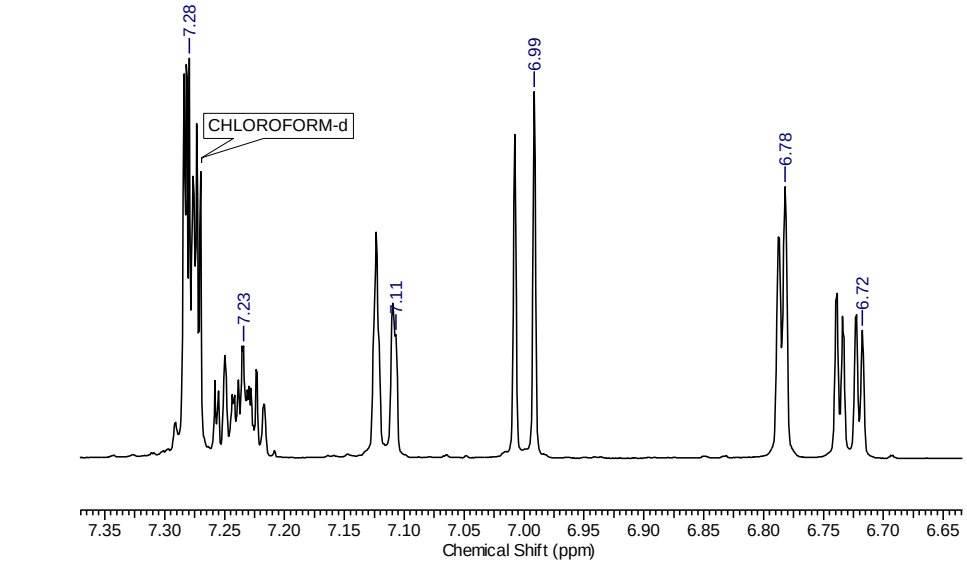

CHLOROFORM-d
7.12
7.30
6.76
6.71
7.3
7.2
7.1
7.0
6.9
6.8
6.7
Chemical Shift (ppm)

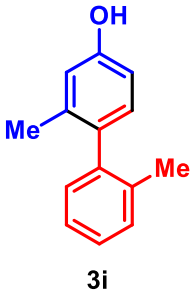

OH
Me
Me

3h

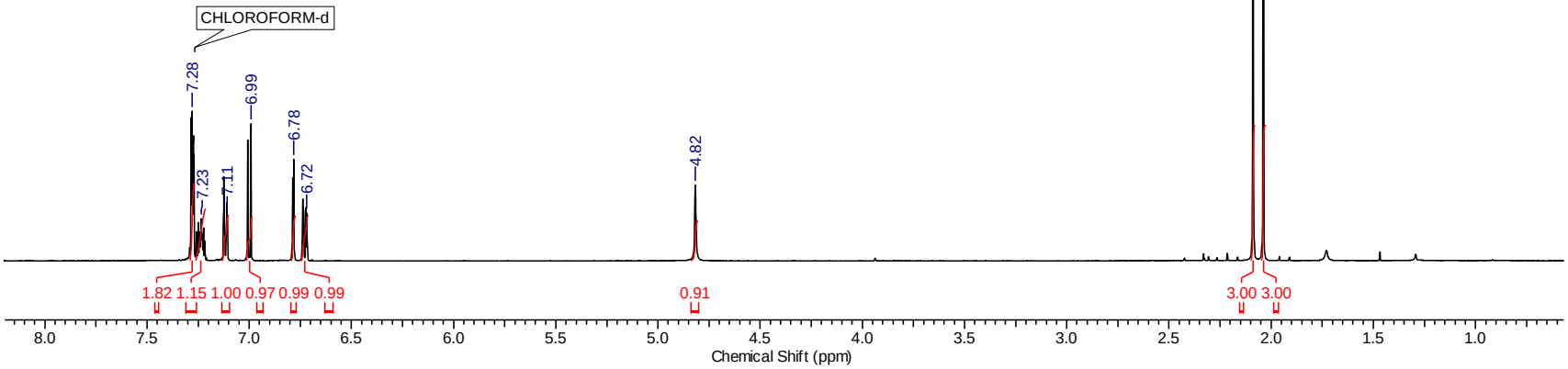

CHLOROFORM-d
7.12
7.30
6.76
6.71
4.74
2.41
2.25
1.02
3.94
0.97
0.98
0.92
2.99
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

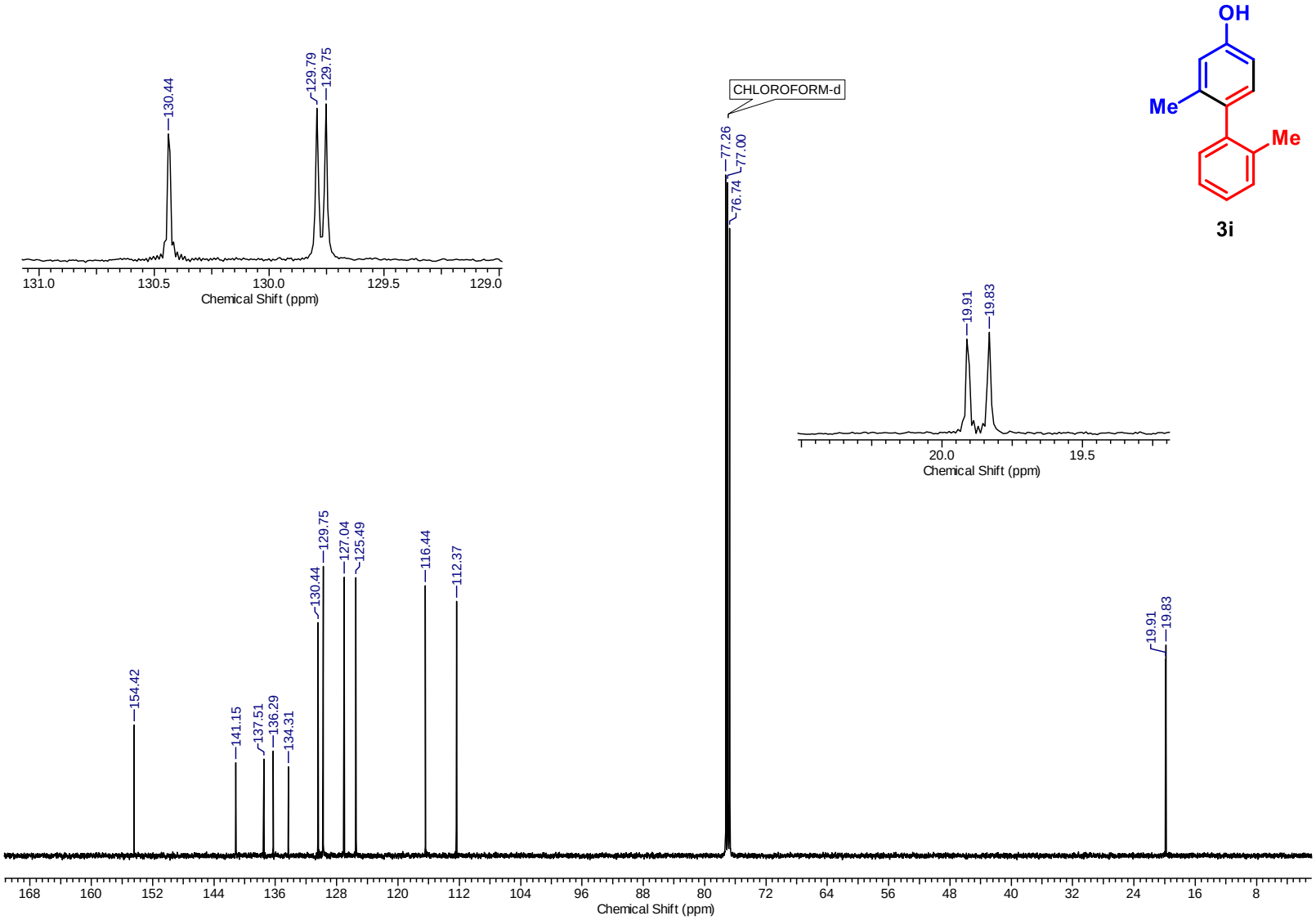

CHLOROFORM-d
77.26
77.00
76.74
154.49
141.48
137.59
137.02
134.92
130.99
130.14
127.88
127.22
126.45
116.85
112.56
21.45
20.57
OH
Me
Me
3h
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

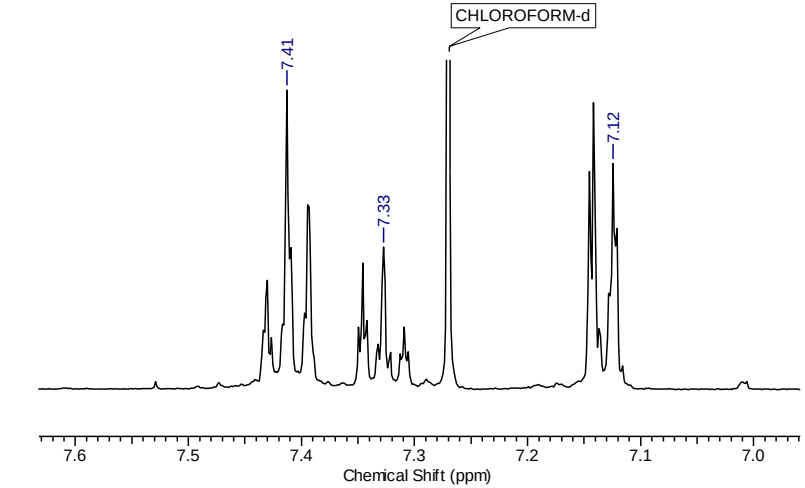

7.28
CHLOROFORM-d
7.23
7.11
6.99
6.78
6.72
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65
Chemical Shift (ppm)

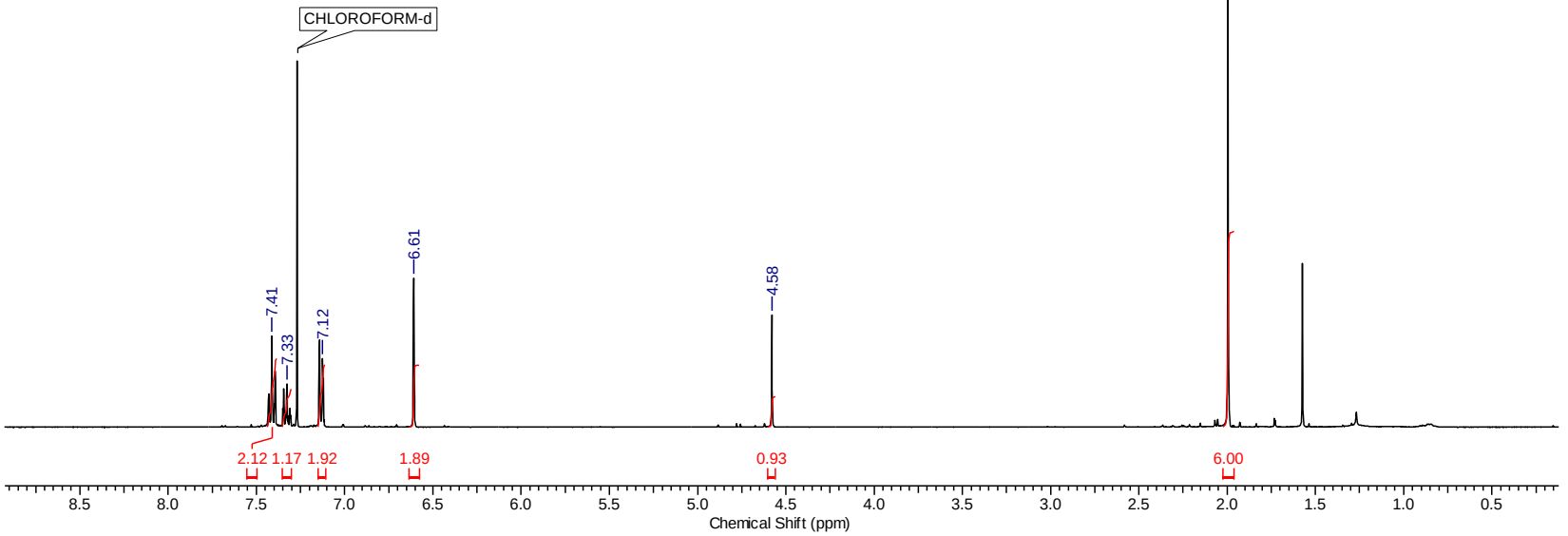

OH
Me
Me

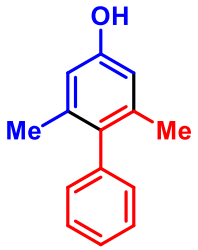
3i


CHLOROFORM-d
7.28
7.23
7.11
6.99
6.78
6.72
4.82
2.09
2.04
1.82 1.15 1.00 0.97 0.99 0.99
0.91
3.00 3.00
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
Chemical Shift (ppm)

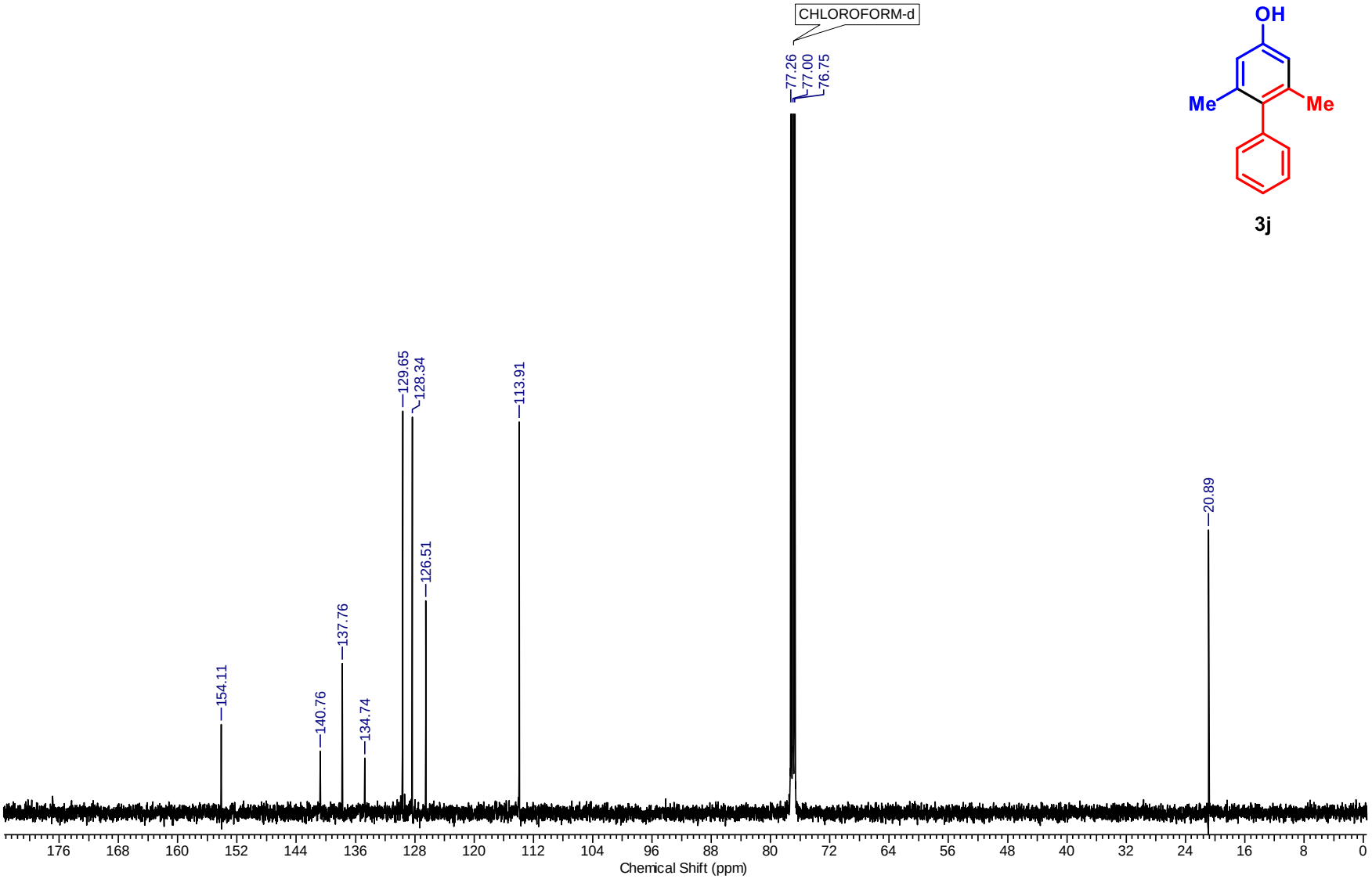

OH
Me
Me
3i
CHLOROFORM-d
77.26
77.00
76.74
130.44
129.79
129.75
19.91
19.83
154.42
141.15
137.51
136.29
134.31
130.44
129.75
127.04
125.49
116.44
112.37
19.91
19.83
Chemical Shift (ppm)

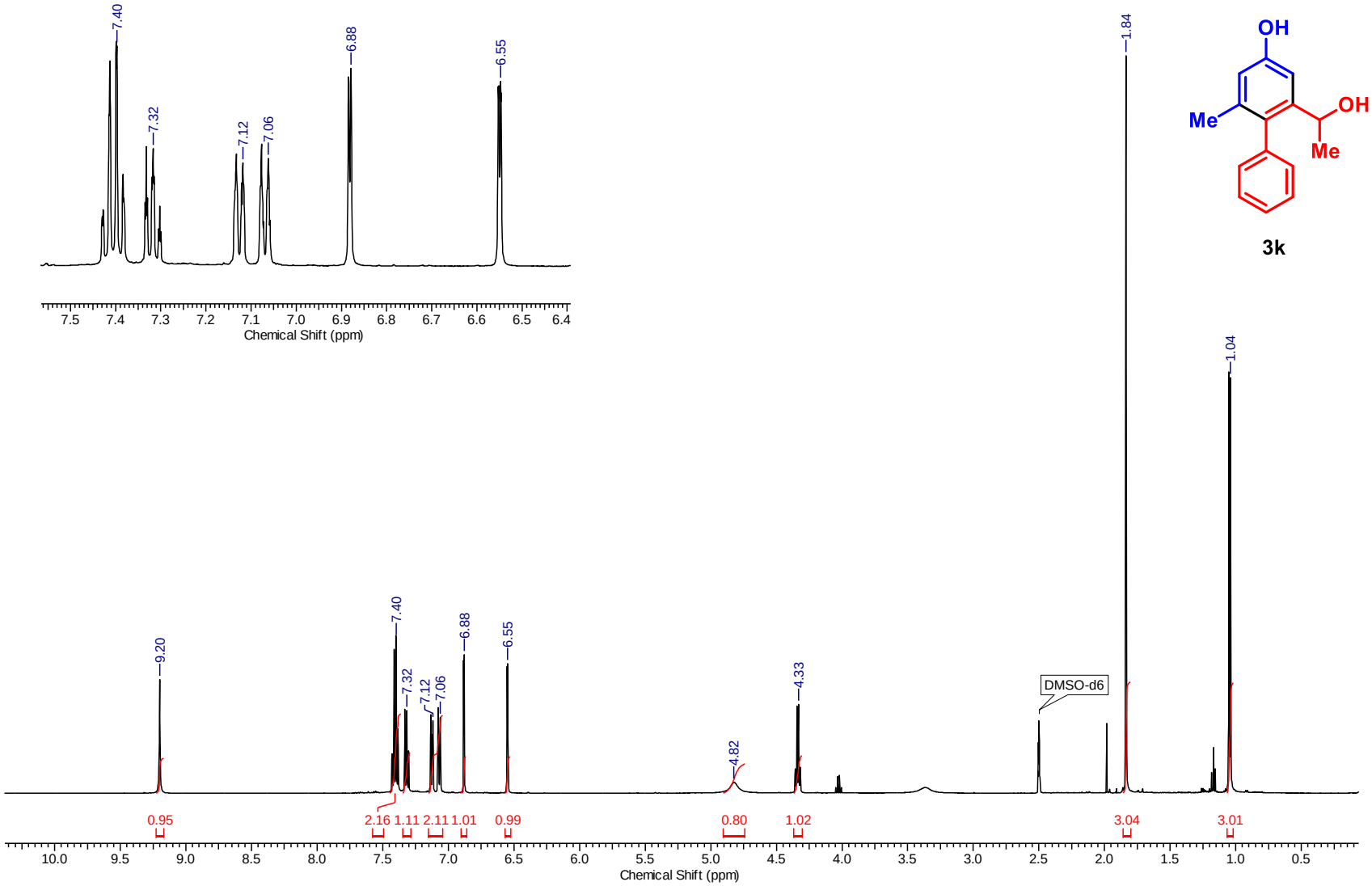

CHLOROFORM-d
7.41
7.33
7.12
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)

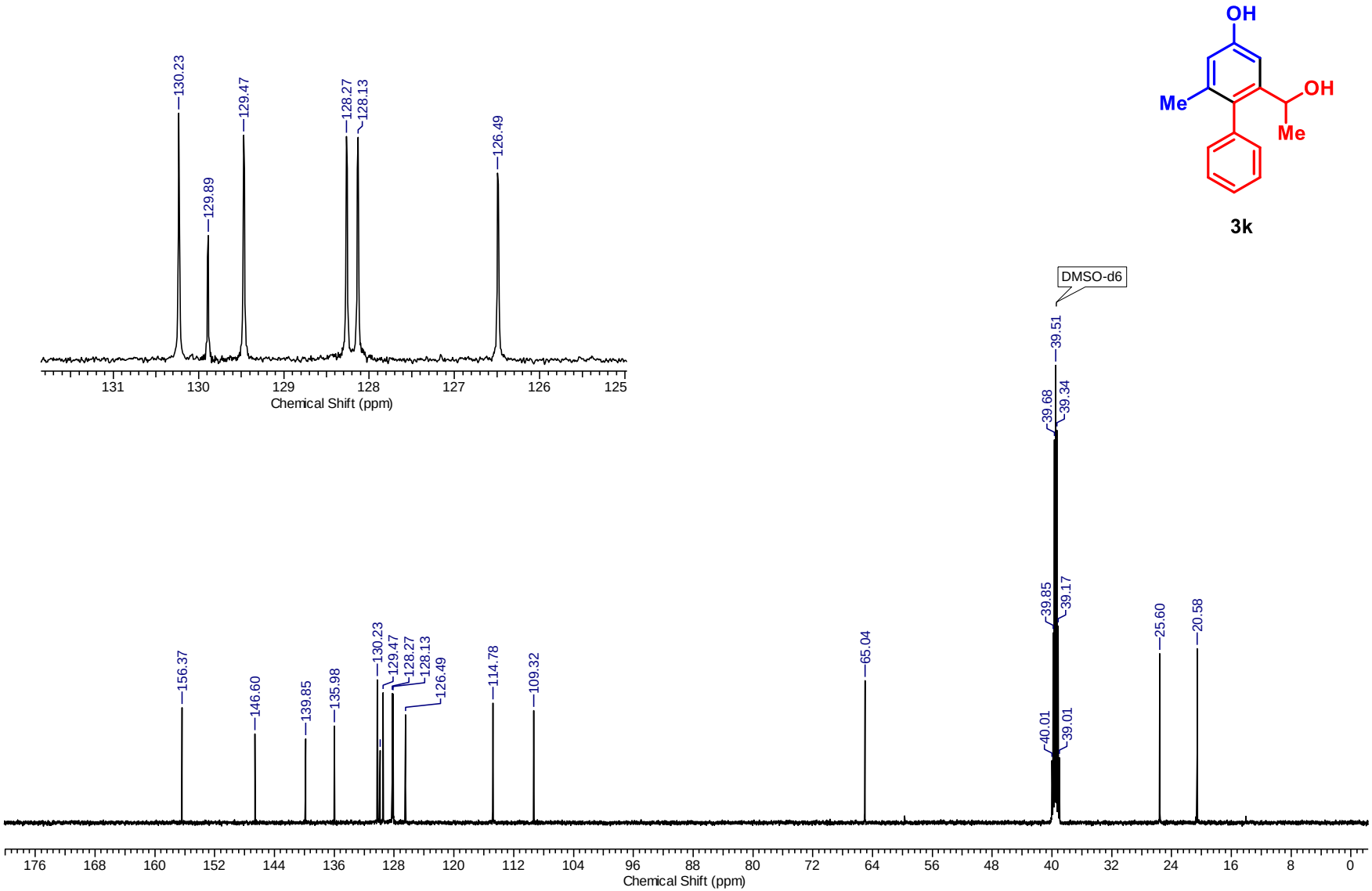

CHLOROFORM-d
7.41
7.33
7.12
6.61
4.58
2.00
2.12
1.17
1.92
1.89
0.93
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

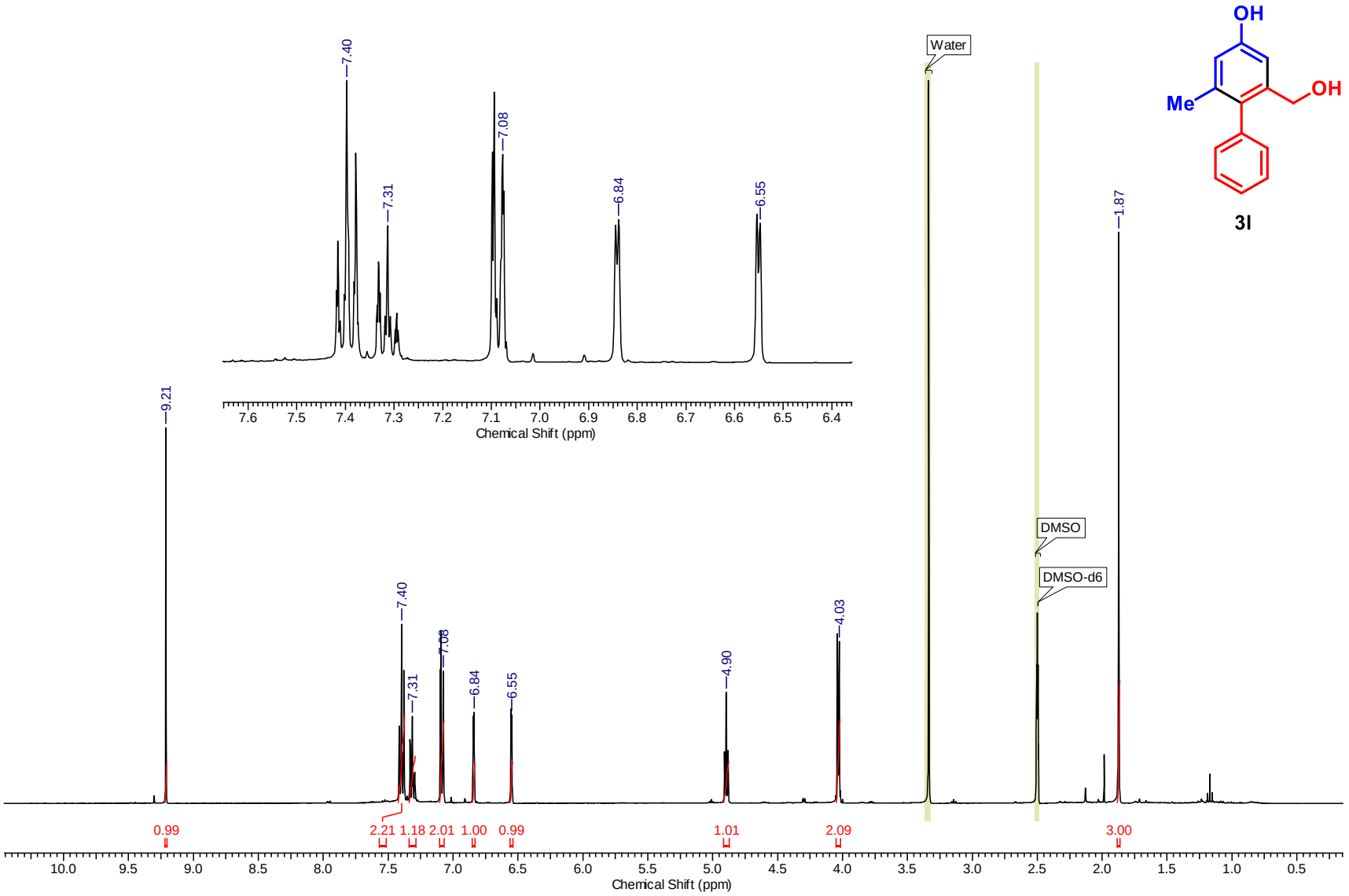

OH
Me
Me

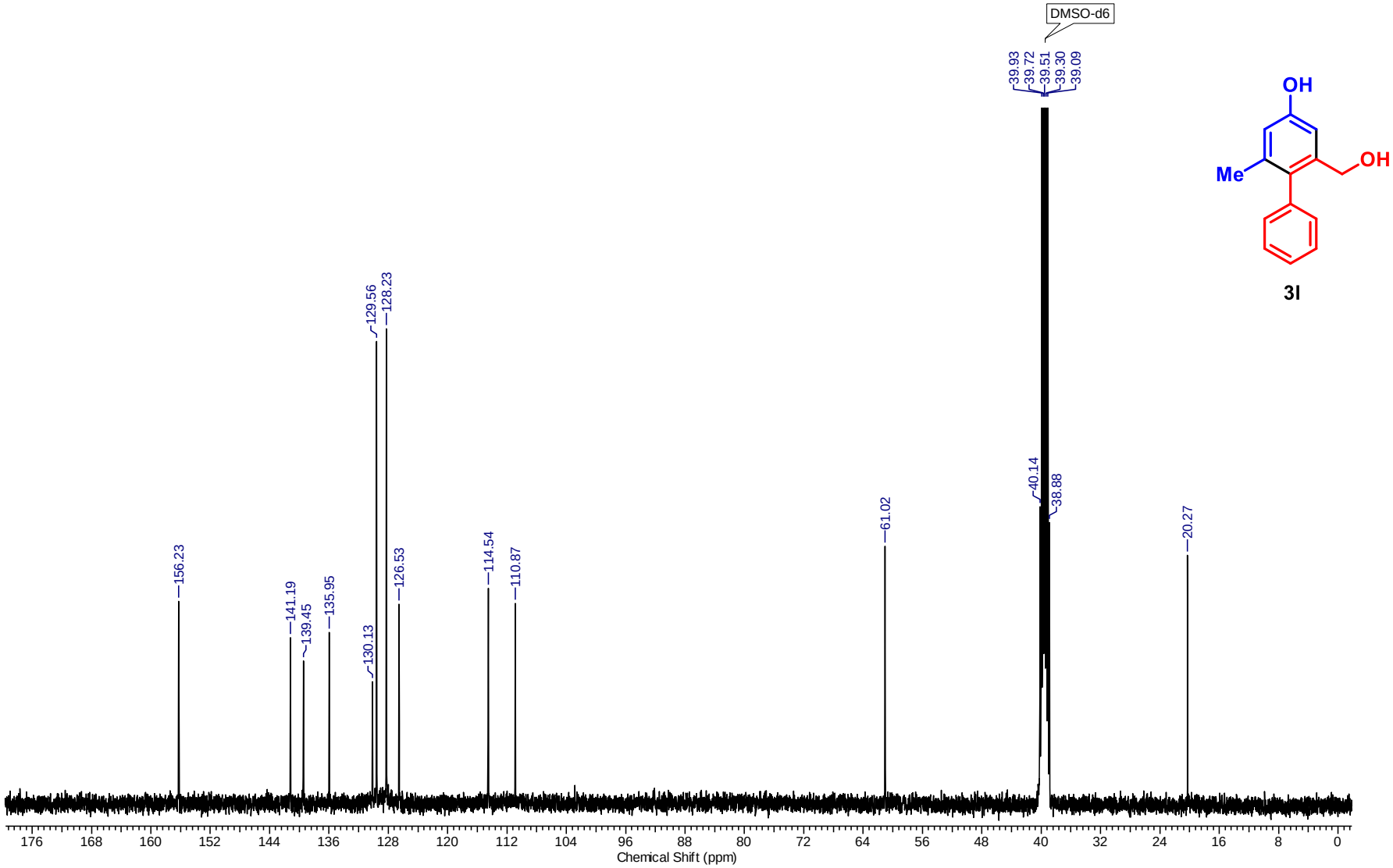
3j

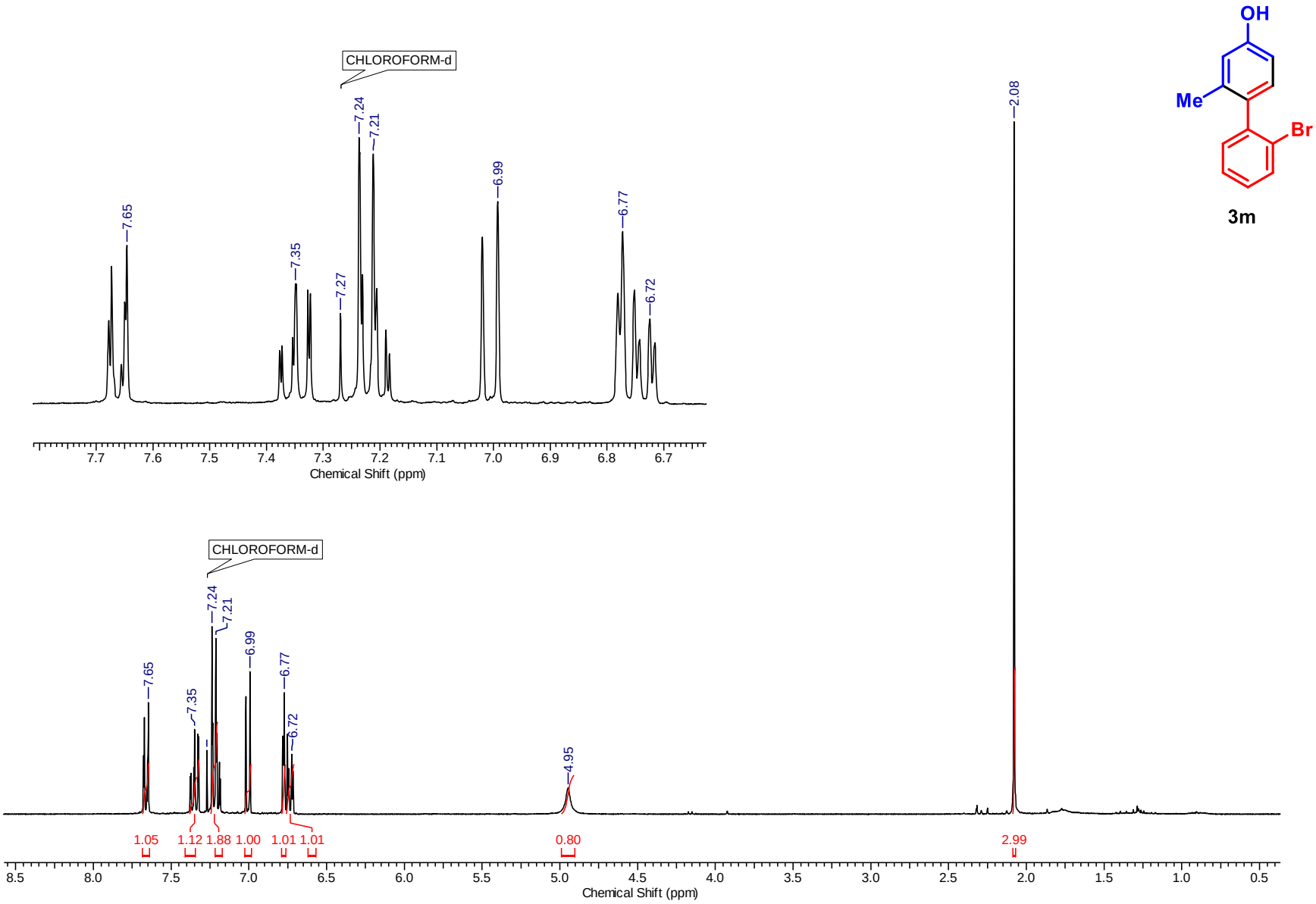

CHLOROFORM-d
77.26
77.00
76.75
154.11
140.76
137.76
134.74
129.65
128.34
126.51
113.91
20.89
OH
Me
Me
3j
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

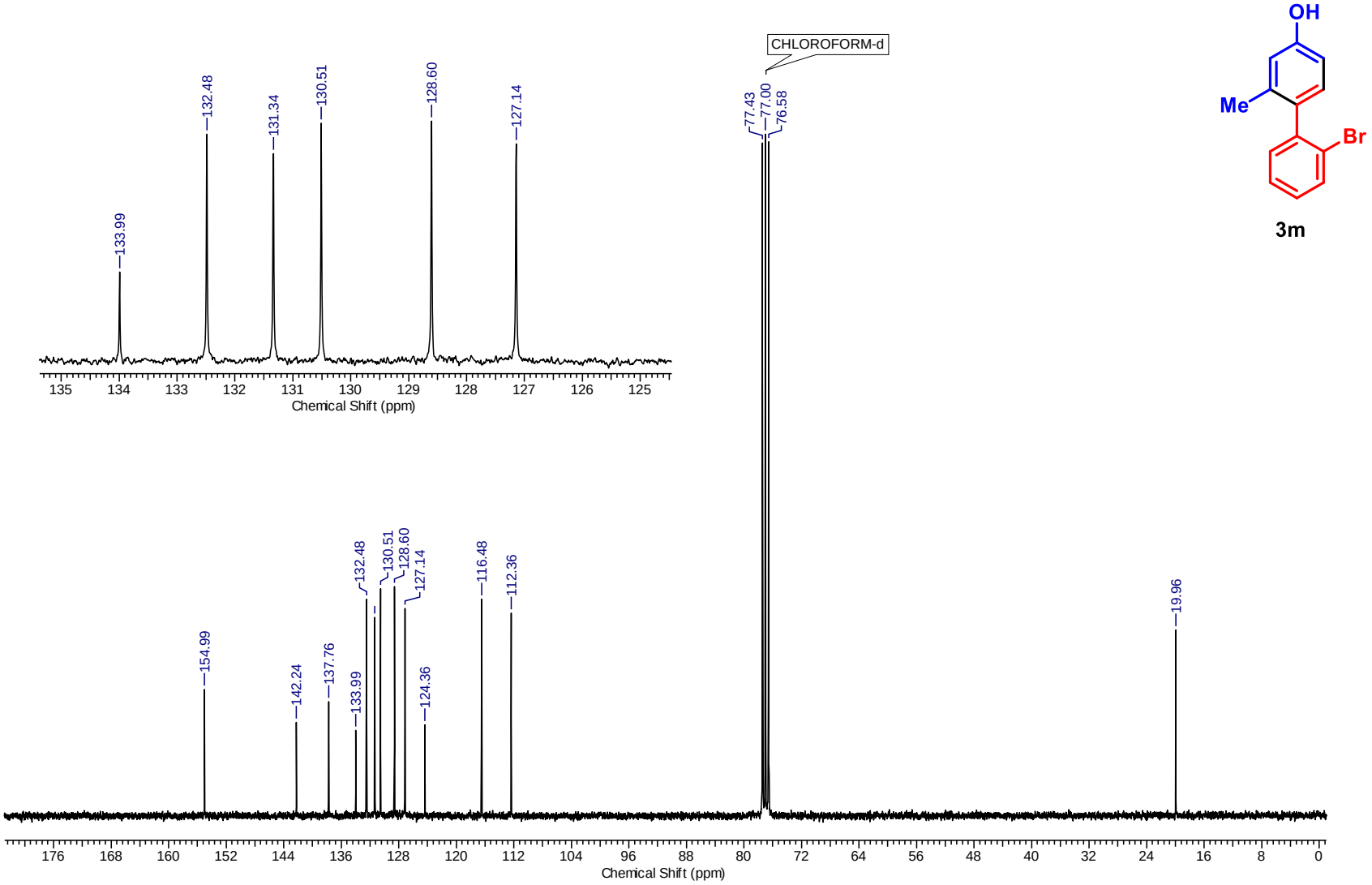

7.40
7.32
7.12
7.06
6.88
6.55
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
Chemical Shift (ppm)
OH
Me
OH
Me
3k
1.84
1.04
9.20
7.40
7.32
7.12
7.06
6.88
6.55
4.82
4.33
DMSO-d6
0.95
2.16
1.11
2.11
1.01
0.99
0.80
1.02
3.04
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

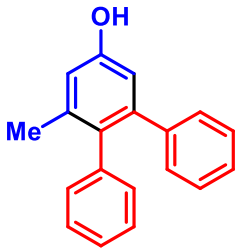

OH
Me
OH
Me
3k
DMSO-d6
130.23
129.89
129.47
128.27
128.13
126.49
39.51
39.68
39.34
39.85
39.17
40.01
39.01
156.37
146.60
139.85
135.98
114.78
109.32
65.04
25.60
20.58
Chemical Shift (ppm)
Chemical Shift (ppm)


OH
Me
OH
3l
Water
DMSO
DMSO-d6
9.21
7.40
7.31
7.08
6.84
6.55
4.90
4.03
1.87
0.99
2.21
1.18
2.01
1.00
0.99
1.01
2.09
3.00
Chemical Shift (ppm)

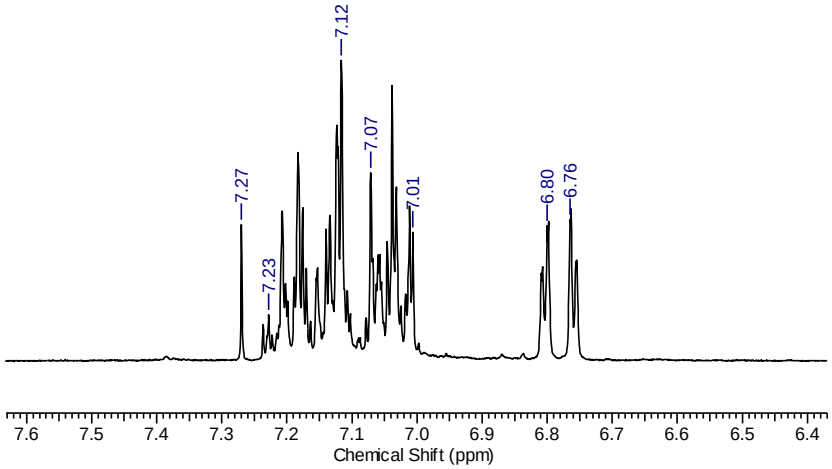

DMSO-d6
39.93
39.72
39.51
39.30
39.09
OH
Me
OH
3l
129.56
128.23
156.23
141.19
139.45
135.95
130.13
126.53
114.54
110.87
61.02
40.14
38.88
20.27
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

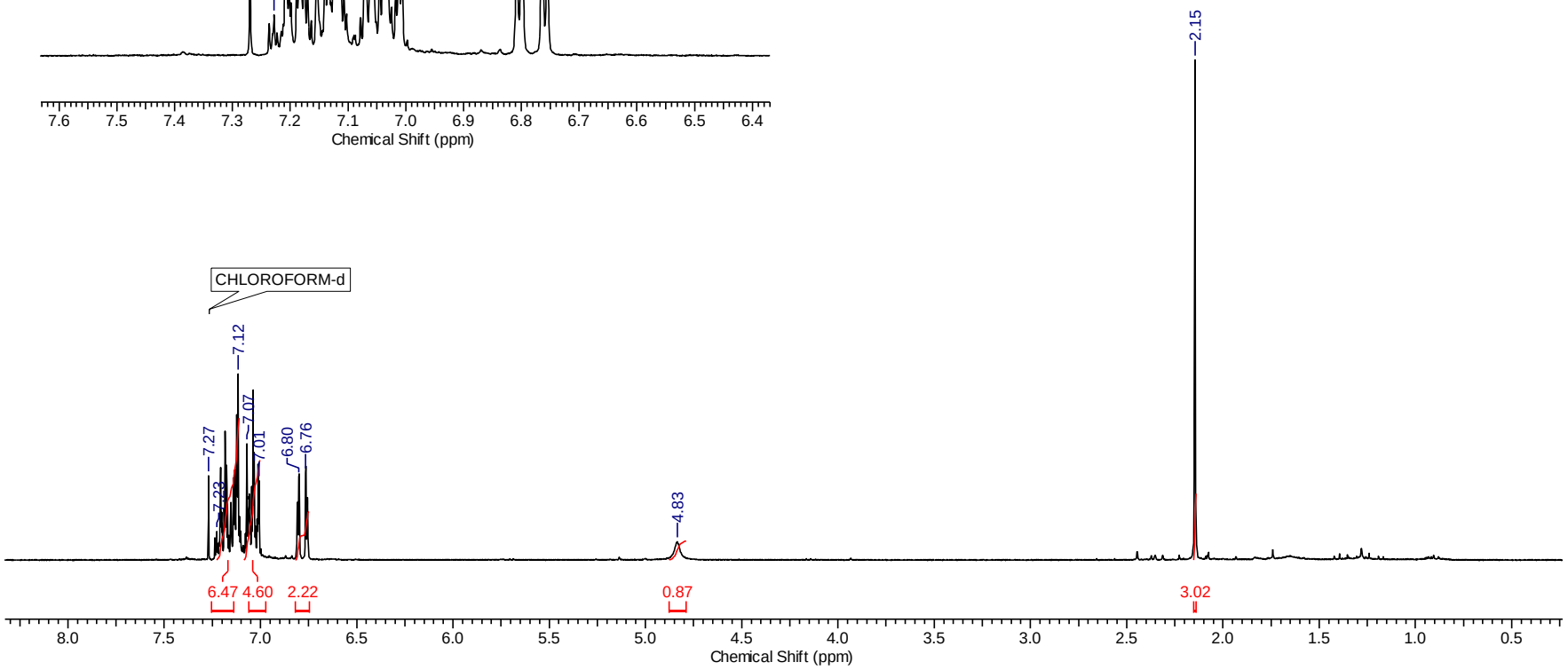

OH
Me
Br
3m
CHLOROFORM-d
7.65
7.35
7.27
7.24
7.21
6.99
6.77
6.72
2.08
4.95
1.05
1.12
1.88
1.00
1.01
1.01
0.80
2.99
Chemical Shift (ppm)

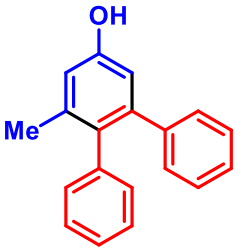

CHLOROFORM-d
77.43
77.00
76.58
132.48
131.34
130.51
128.60
127.14
133.99
154.99
142.24
137.76
133.99
132.48
130.51
128.60
127.14
124.36
116.48
112.36
19.96
Chemical Shift (ppm)
OH
Me
Br
3m


OH
Me

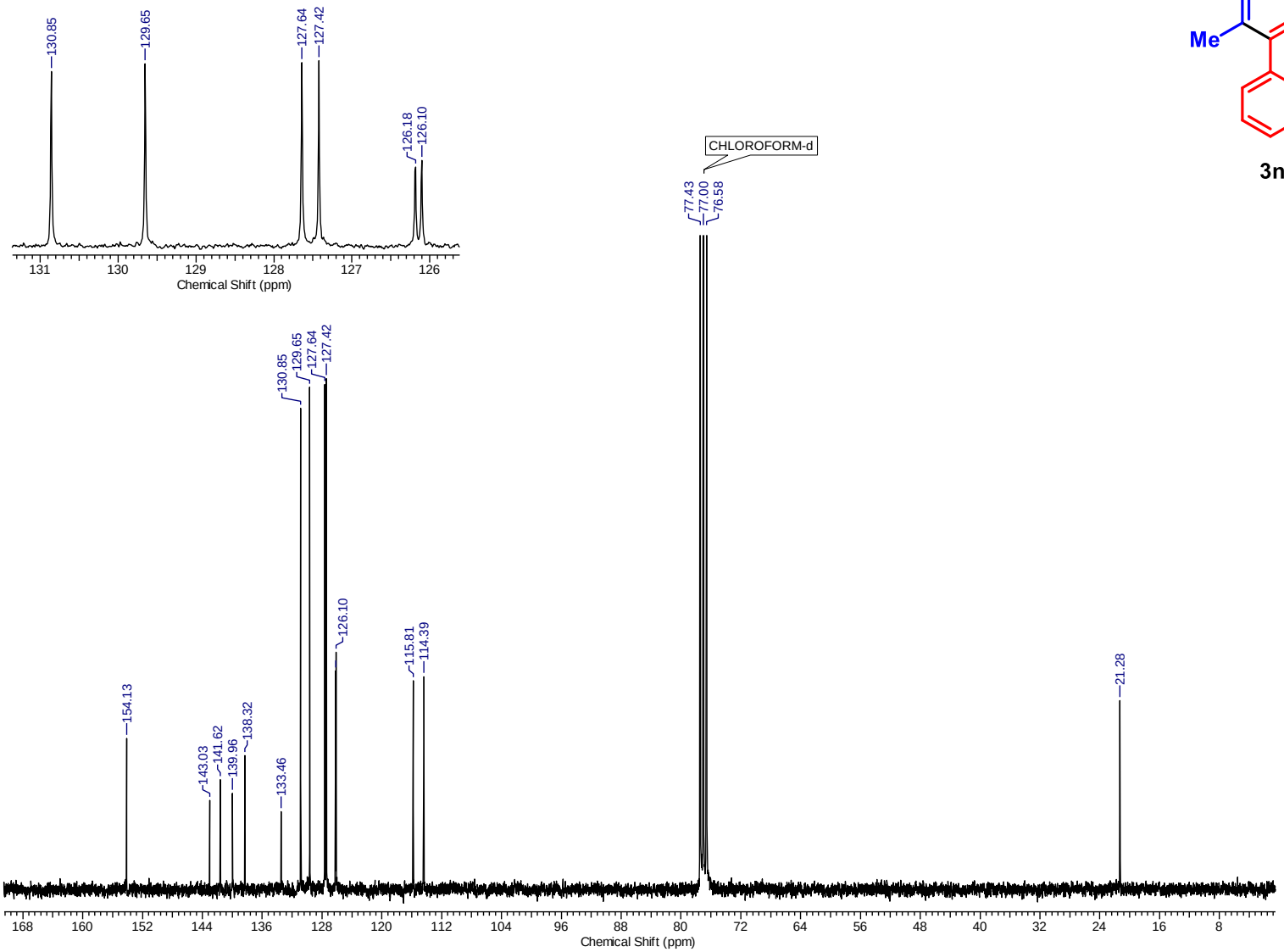
3n


7.27
7.23
7.12
7.07
7.01
6.80
6.76
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
Chemical Shift (ppm)


CHLOROFORM-d
7.27
7.23
7.12
7.07
7.01
6.80
6.76
4.83
2.15
6.47
4.60
2.22
0.87
3.02
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
Me

3n


130.85
129.65
127.64
127.42
126.18
126.10
131
130
129
128
127
126
Chemical Shift (ppm)
CHLOROFORM-d
77.43
77.00
76.58
154.13
143.03
141.62
139.96
138.32
133.46
130.85
129.65
127.64
127.42
126.10
115.81
114.39
21.28
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)