Chemical Communications

Hemicarceplex Formation Allows Ready Identification of the Isomers of the Metallofullerene $Sc_3N@C_{80}$ Using ^{1}H and ^{13}C NMR Spectroscopy

Min-Yan Gu, Shou-Ling Huang, Shing-Jong Huang, Yi-Hung Liu, Chien-Chen Lai, Shie-Ming Peng and Sheng-Hsien Chiu*

Supplementary Material

Page Number

Bis(4-bromobutyl) Succinate (4). A solution of succinic acid (1.88 g, 15.9 mmol), 4-bromobutan-1-ol (5.00 g, 32.7 mmol), and *p*-toluenesulfonic acid (33 mg, 0.18 mmol) in toluene (53 mL) was heated under reflux in a Dean–Stark apparatus for 16 h. After cooling to room temperature, the mixture was neutralized with saturated $NaHCO_{3(aq)}$ and then the solvents were evaporated under reduced pressure. The residue was partitioned between H_2O (50 mL) and CH_2Cl_2 (2 × 30 mL) and then the combined organic phases were dried ($MgSO_4$), concentrated, and purified (SiO_2; CH_2Cl_2/hexane, 2:1) to afford a yellow oil (5.83 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.75–1.82 (m, 4H), 1.89–1.96 (m, 4H), 2.61 (s, 4H), 3.42 (t, *J* = 6.8 Hz, 4H), 4.11 (t, *J* = 6.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 27.2, 29.0, 29.2, 33.0, 63.7, 172.2; HR-MS (ESI): calcd for $C_{12}H_{21}O_4Br_2^+$ $[M + H]^+$, *m*/*z* 386.9807; found, *m*/*z* 386.9806.

Macrocycle 5. A mixture of the alcohol **3** (7.25 g, 16.3 mmol), the dibromide **4** (6.33 g, 16.3 mmol), and K_2CO_3 (13.5 g, 97.8 mmol) in DMF (1630 mL) was stirred at 50 °C for 7 days and then the solvent was evaporated under reduced pressure. The residue was partitioned between H_2O (700 mL) and CH_2Cl_2 (3 × 300 mL) and then the combined organic phases were dried ($MgSO_4$), concentrated, and purified (SiO_2; CH_3OH/CH_2Cl_2, 1:99) to afford a white solid (4.03 g, 37%). Mp: 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.21–1.41 (m, 12H), 1.42–1.55 (m, 4H), 1.56–2.00 (m, 12H), 2.60 (s, 4H), 3.40–4.06 (m, 8H), 4.18–4.21 (m, 4H), 4.58 (s, 2H), 6.81–6.93 (m, 4H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.40 (dd, *J* = 8.4, 1.8 Hz, 1H), 9.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 26.2, 26.3, 29.2, 29.2, 29.4, 29.5, 29.5, 29.6, 29.6, 64.6, 64.7, 65.3, 68.7, 68.7, 69.0, 69.2, 110.9, 111.5, 113.1, 113.5, 119.8, 126.8, 129.6, 133.5, 148.7, 148.8, 149.0, 154.6, 171.9, 172.0, 190.7; HR-MS (ESI): calcd for $C_{38}H_{54}O_{10}Na^+$ $[M + Na]^+$, *m*/*z* 693.3615; found, *m*/*z* 693.3625.

Trialdehyde 6. $Sc(OTf)_3$ (0.40 g, 0.81 mmol) was added to a solution of the macrocycle **5** (10.9 g, 16.2 mmol) in CH_3NO_2 (71 mL) and $CHCl_3$ (91 mL) and then the mixture was stirred at 60 °C for 16 h. After cooling to room temperature, the organic solvents were evaporated under reduced pressure and the residue partitioned between H_2O (200 mL) and CH_2Cl_2 (2 × 150 mL). The combined organic phases were dried ($MgSO_4$), concentrated, and purified (SiO_2; acetone/CH_2Cl_2, 5:95) to afford a light-yellow oil (3.38 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.16–1.52 (m, 38H), 1.67–1.94 (m, 42H), 2.56 (s, 12H), 3.46 (d, *J* = 13.6 Hz, 3H), 3.78–4.00 (m, 12H),

4.00–4.09 (m, 12H), 4.09–4.24 (m, 12H), 4.67 (d, J = 13.6, 3H), 6.79 (s, 3H), 6.80 (s, 3H), 6.91 (d, J = 8.0 Hz, 3H), 7.35 (d, J = 1.6 Hz, 3H), 7.39 (dd, J = 8.2, 1.8 Hz, 3H), 9.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 25.6, 25.7, 26.0, 26.1, 29.0, 29.2, 29.3, 29.3, 29.4, 29.4, 29.5, 36.3, 64.5, 68.5, 68.9, 69.2, 69.3 (four aliphatic signals missing, possibly because of signal overlap), 110.8, 111.5, 115.6, 116.4, 126.9, 130.0, 132.0, 132.5, 147.5, 148.0, 149.1, 154.7, 172.1, 190.8; HR-MS (ESI): calcd for $C_{114}H_{156}O_{27}Na^+$ $[M + Na]^+$, m/z 1980.0732; found, m/z 1980.0764.

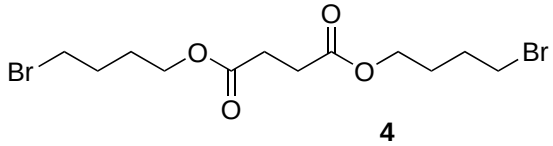
Host 2: $NaBH_4$ (82 mg, 2.22 mmol) was added to a solution of the trialdehyde **6** (1.45 g, 0.74 mmol) in MeOH (25 mL) and CH_2Cl_2 (50 mL) at –15 °C and then the mixture was stirred at that temperature for 2.5 h. After evaporating the solvent under reduced pressure, the residue was partitioned between H_2O (100 mL) and CH_2Cl_2 (2 × 75 mL). The combined organic phases were dried ($MgSO_4$), concentrated, and purified (SiO_2; acetone/CH_2Cl_2, 2:8) to afford the desired triol as a white solid, which was dissolved in $CHCl_3$ (40 mL) and added to a solution of trifluoroacetic acid (5%, 43 mL) in $CHCl_3$ (410 mL) and CH_3NO_2 (440 mL) at 0 °C. The mixture was slowly warmed to room temperature, stirred for 48 h, and then poured into an aqueous solution of Na_2CO_3 (2.0 M, 300 mL). The separated organic phase was washed with H_2O (500 mL), dried ($MgSO_4$), and concentrated. The residue was purified (SiO_2; EtOAc/hexane, 4:6) to afford a white solid (0.25 g, 18%). Mp: 217–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.13–1.45 (m, 42H), 1.59–1.89 (m, 42H), 2.56 (s, 12H), 3.45 (d, J = 13.6 Hz, 6H), 3.75–3.91 (m, 12H), 3.91–4.05 (m, 12H), 4.06–4.21 (br, 12H), 4.67 (d, J = 14.0, 6H), 6.78 (s, 6H), 6.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 25.7, 26.1, 26.1, 29.2, 29.5, 29.7, 29.7, 29.8, 36.4, 64.4, 69.0, 69.4, 115.9, 116.1, 132.2, 132.5, 147.7, 147.9, 172.0; HR-MS (ESI): calcd for $C_{114}H_{156}NaO_{24}^+$ $[M + Na]^+$, m/z 1932.0884; found, m/z 1931.9346.

($Sc_3N@C_{80}$)@1 (Solvent-Free Synthesis). A solid mixture of **1** (20.4 mg, 11.8 μmol) and $Sc_3N@C_{80}$ (5.00 mg, 4.51 μmol) was ball-milled at room temperature for 30 min and then the resulting solid was heated at 250 °C under Ar for 16 h. The resulting solid was purified chromatographically (SiO_2; CS_2 then CH_2Cl_2/hexane, 1:1) to afford a black solid (4.4 mg, 34%). Mp: >300 °C; ^{1}H NMR (800 MHz, $CDCl_3$, 298 K): δ = 1.20–1.47 (m, 84H, I_h + D_{5h}), 1.59–1.67 (m, 12H, I_h + D_{5h}), 1.68–1.76 (m, 12H, I_h + D_{5h}), 1.77–1.87 (m, 12H, I_h + D_{5h}), 3.46 (d, J = 13.6 Hz, 1.08H, D_{5h}), 3.49 (d, J = 14.4 Hz, 4.92H, I_h), 3.72–3.81 (m, 12H, I_h + D_{5h}), 3.98–4.07 (m, 12H, I_h + D_{5h}), 4.70 (d, J = 13.6 Hz, 1.08H, D_{5h}), 4.73 (d, J = 14.4 Hz, 4.92H, I_h), 6.73 (s, 2.16H,

D_{5h}), 6.75 (s, 9.84H, I_h); HR-MS (ESI): calcd for $C_{194}H_{169}NO_{12}Sc_3^+$ $[M + H]^+$, *m*/*z* 2839.1322; found, *m*/*z* 2839.1317.

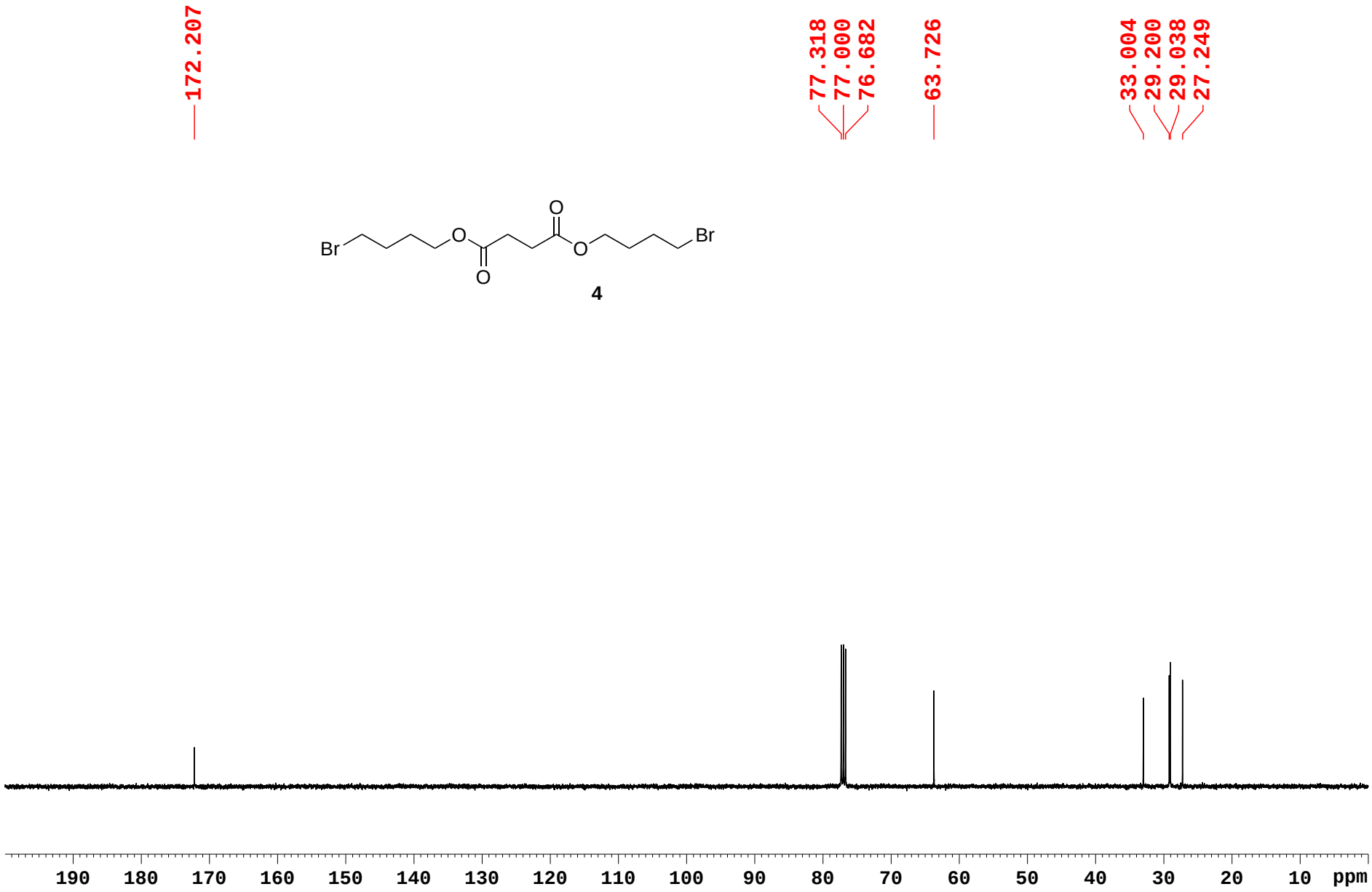
($Sc_3N@C_{80}$)@2 (Synthesis in Solution). A solution of the host **2** (11.6 mg, 6.07 μmol) and $Sc_3N@C_{80}$ (11.6 mg, 10.5 μmol) in $CHCl_2CHCl_2$ (2 mL) was stirred at 50 °C for 50 h and then the organic solvent was evaporated under reduced pressure. The residue was purified chromatographically (SiO_2; CS_2 then EtOAc/hexane, 3:7) to afford a black solid (3.0 mg, 16%).

($Sc_3N@C_{80}$)@2 (Solvent-Free Synthesis). A solution of $Sc_3N@C_{80}$ (5.20 mg, 4.69 μmol) in CS_2 (2 mL) was added to a solution of the host **2** (20.1 mg, 10.5 μmol) in CH_2Cl_2 (2 mL) and then the mixture was concentrated under reduced pressure. The resulting solid was heated under vacuum at 180 °C for 12 h and then purified chromatographically (SiO_2; CS_2 then EtOAc/hexane, 3:7) to afford a black solid (3.9 mg, 28%). Mp: >300 °C; ^{1}H NMR (800 MHz, $CDCl_3$, 298 K): δ = 1.20–1.42 (m, 42H, I_h + D_{5h}), 1.51–1.58 (m, 6H, I_h + D_{5h}), 1.67–1.74 (m, 6H, I_h + D_{5h}), 1.77–1.87 (m, 24H, I_h + D_{5h}), 1.87–1.96 (m, 6H, I_h + D_{5h}), 2.57–2.66 (m, 12H, I_h + D_{5h}), 3.47 (d, *J* = 14.4 Hz, 1.20H, D_{5h}), 3.49 (d, *J* = 13.6 Hz, 4.80H, I_h), 3.72–3.78 (m, 6H), 3.85–3.90 (m, 6H), 3.95–4.03 (m, 12H), 4.22–4.29 (m, 6H), 4.29–4.35 (m, 6H), 4.71 (d, *J* = 14.4 Hz, 1.20H, D_{5h}), 4.74 (d, *J* = 13.6 Hz, 4.80H, I_h), 6.72 (s, 1.20H, D_{5h}), 6.72 (s, 1.20H, D_{5h}) 6.74 (s, 9.60H, I_h); ^{13}C NMR (200 MHz, $CDCl_3$, 298 K): δ = 25.8, 26.7, 27.1, 27.1, 29.9, 29.9, 30.4, 30.5, 30.7, 36.9, 37.0, 64.9, 68.7, 68.8, 114.0, 114.0, 114.3, 114.4, 131.5, 131.5, 132.0, 132.0, 134.2 (D_{5h}), 136.1 (I_h), 137.4 (D_{5h}), 138.1 (D_{5h}), 142.7 (D_{5h}), 143.3 (I_h), 143.6 (D_{5h}), 147.1, 147.2, 147.4 (D_{5h}), 147.6, 147.7, 171.9 (one aromatic and ten aliphatic signals were missing, possibly because of signal overlap); HR-MS (ESI): calcd for $C_{194}H_{156}NO_{24}Sc_3^+$ $[M]^+$, *m*/*z* 3017.9695; found, *m*/*z* 3018.0253.

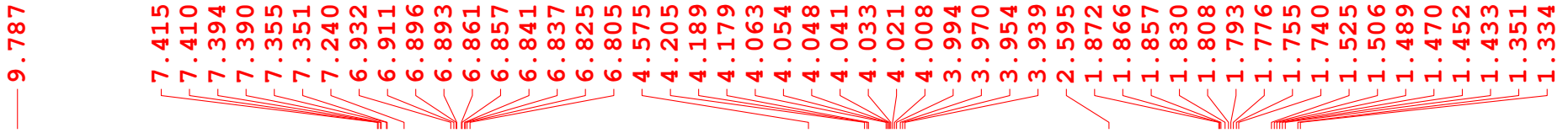

Br
O
O
O
O
Br

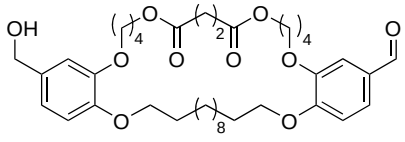
4

7.240
4.127
4.111
4.095
3.434
3.417
3.401
2.611
1.959
1.942
1.935
1.927
1.925
1.918
1.911
1.906
1.889
1.821
1.805
1.800
1.792
1.784
1.777
1.769
1.767
1.751
9
8
7
6
5
4
3
2
1
0
ppm
4.000
4.036
4.033
4.214
4.417

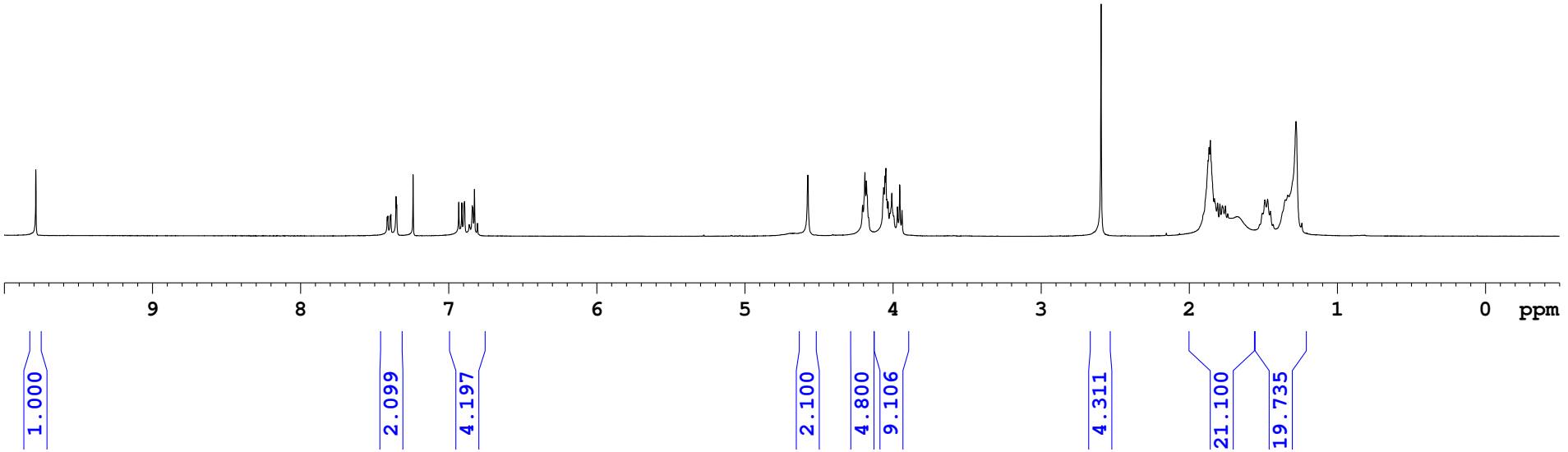

172.207
77.318
77.000
76.682
63.726
33.004
29.200
29.038
27.249
Br
O
O
O
O
Br
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

ANDARD 1H OBSER

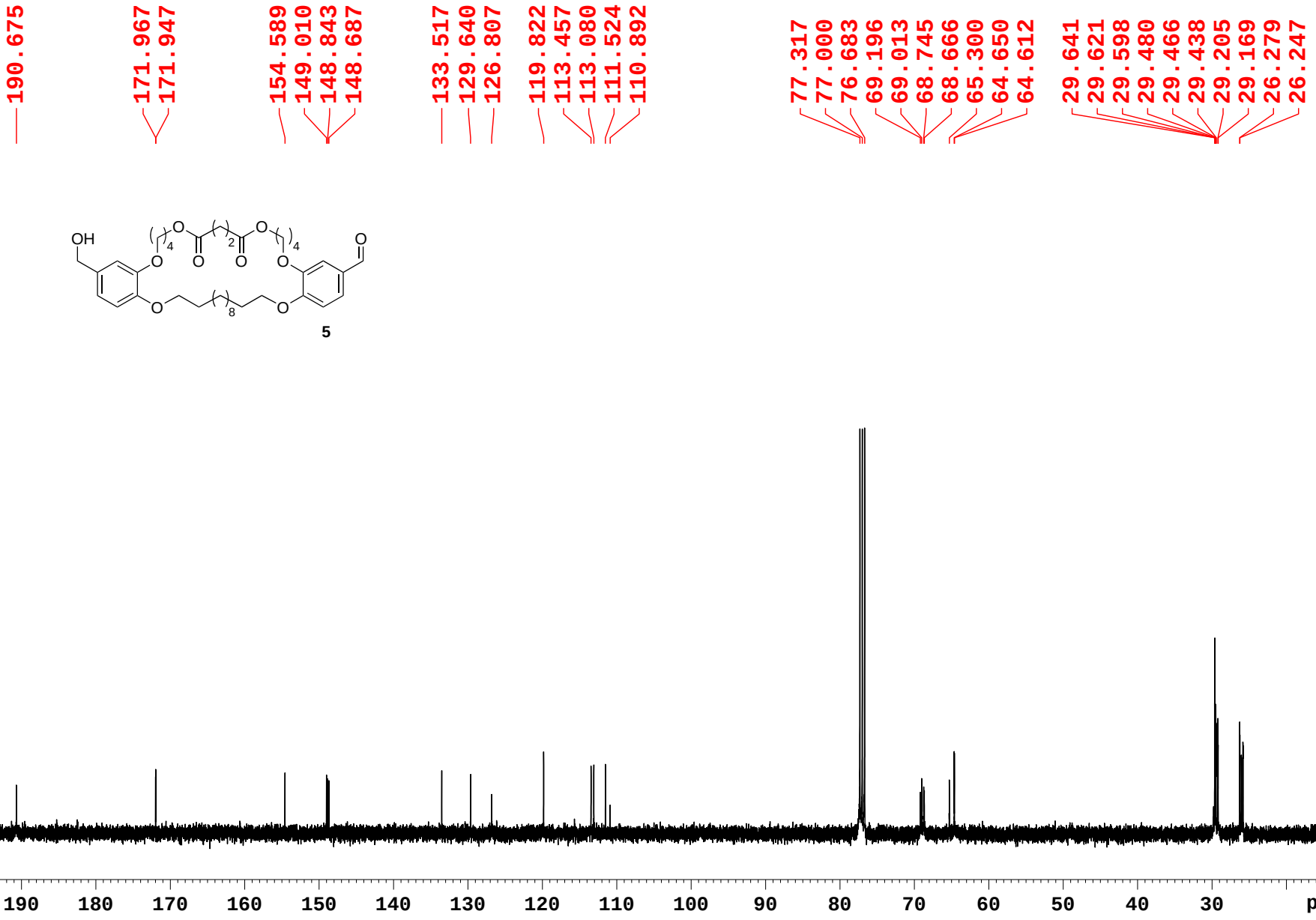


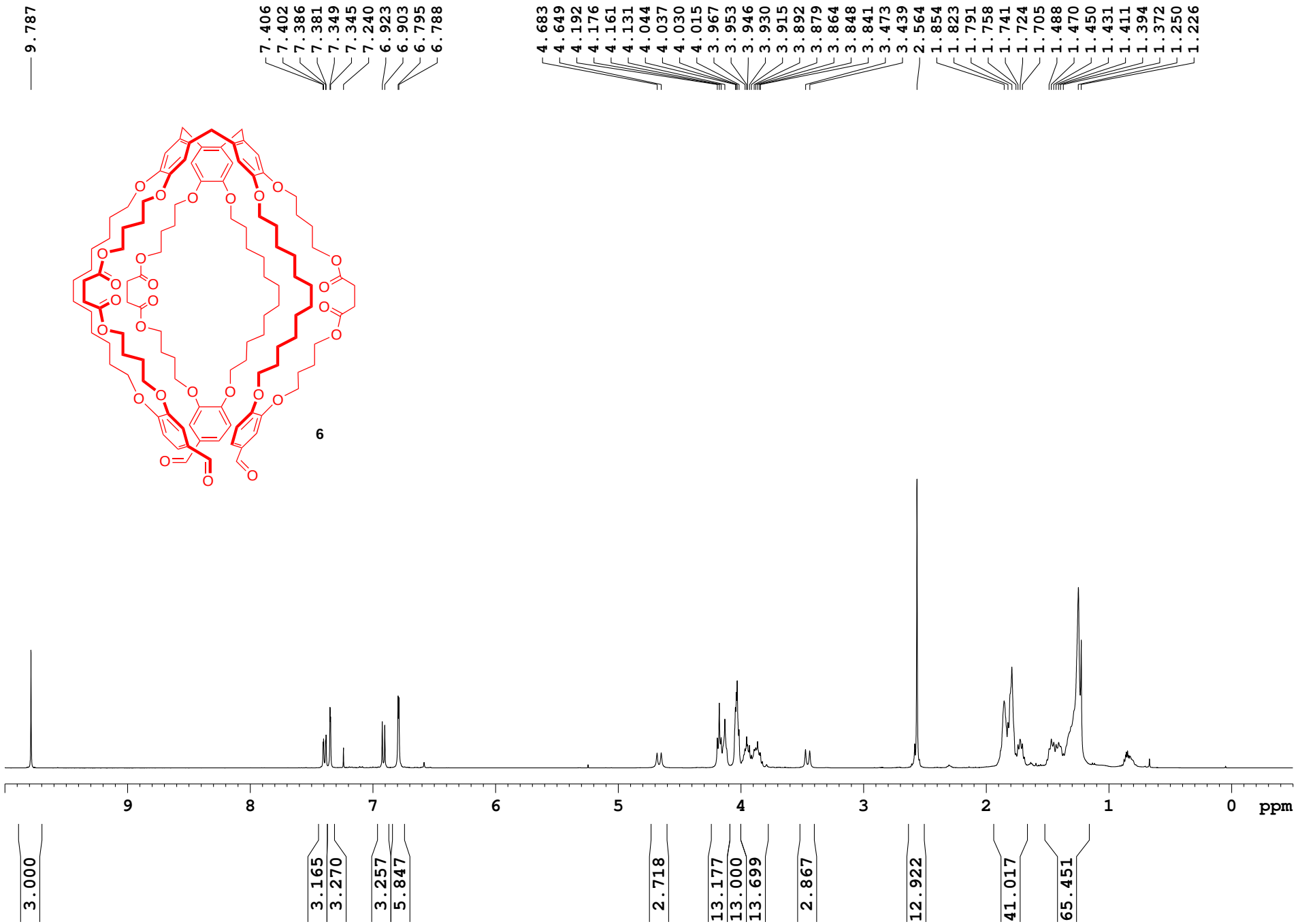


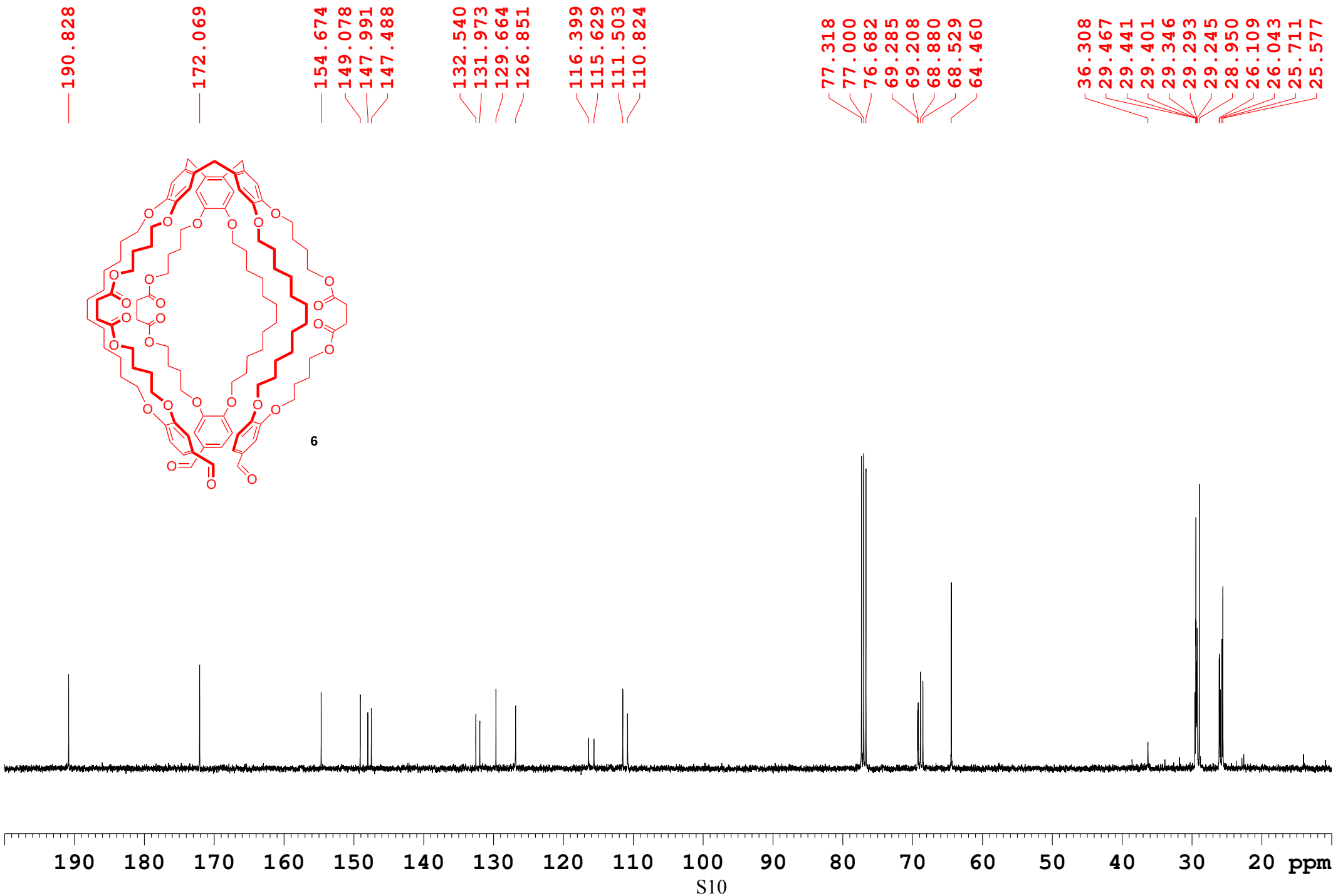
5

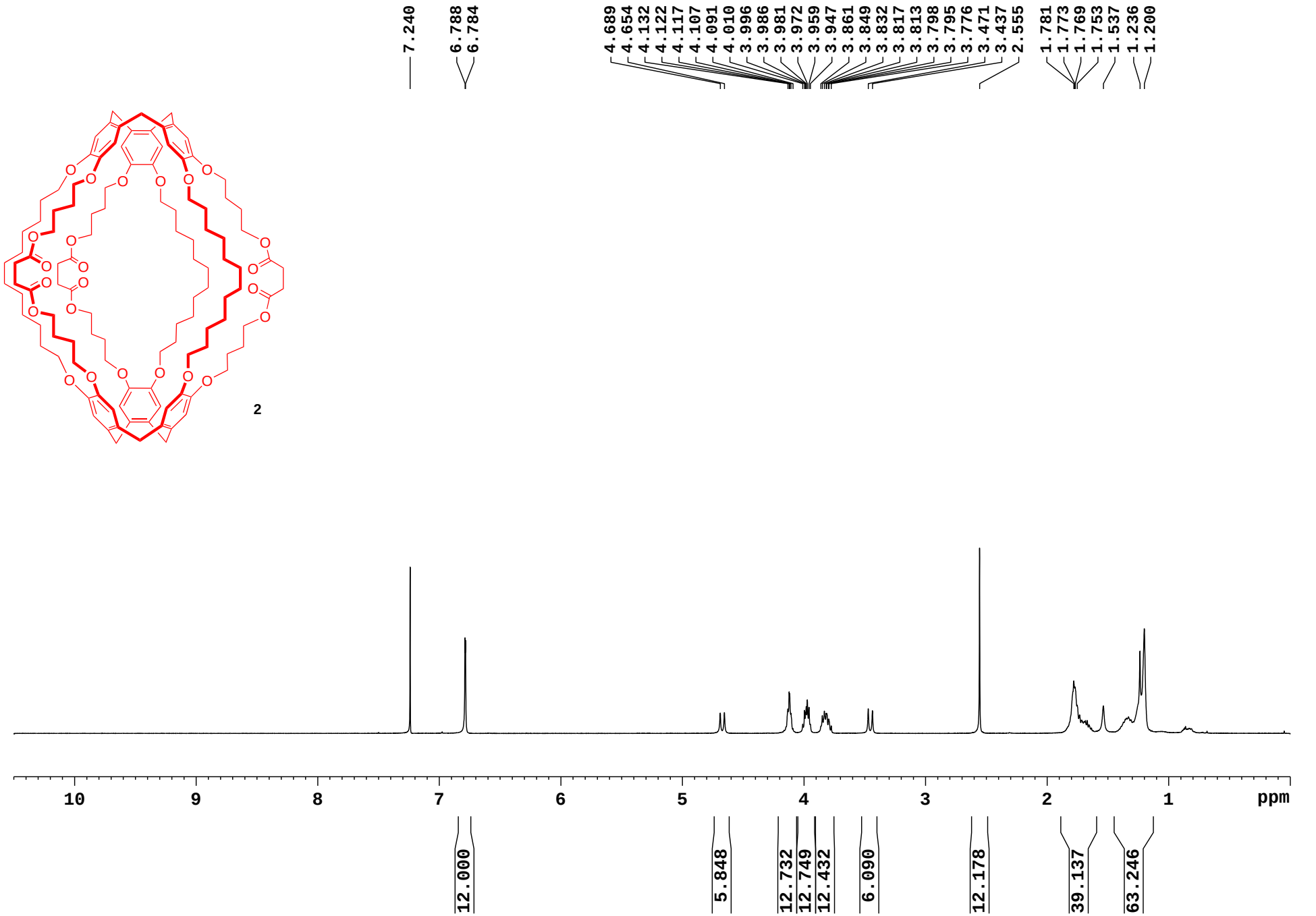


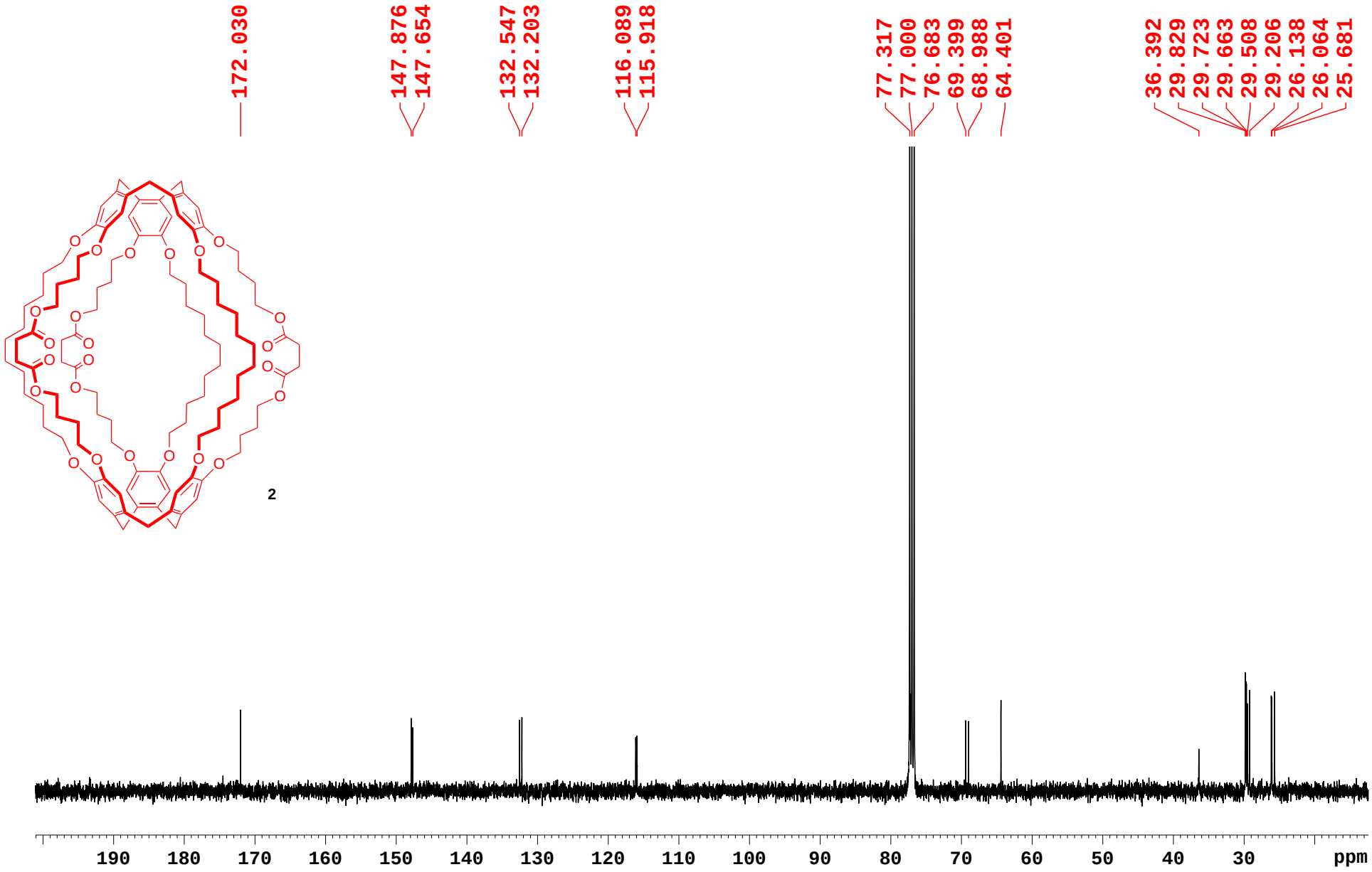
13C OBSERVE

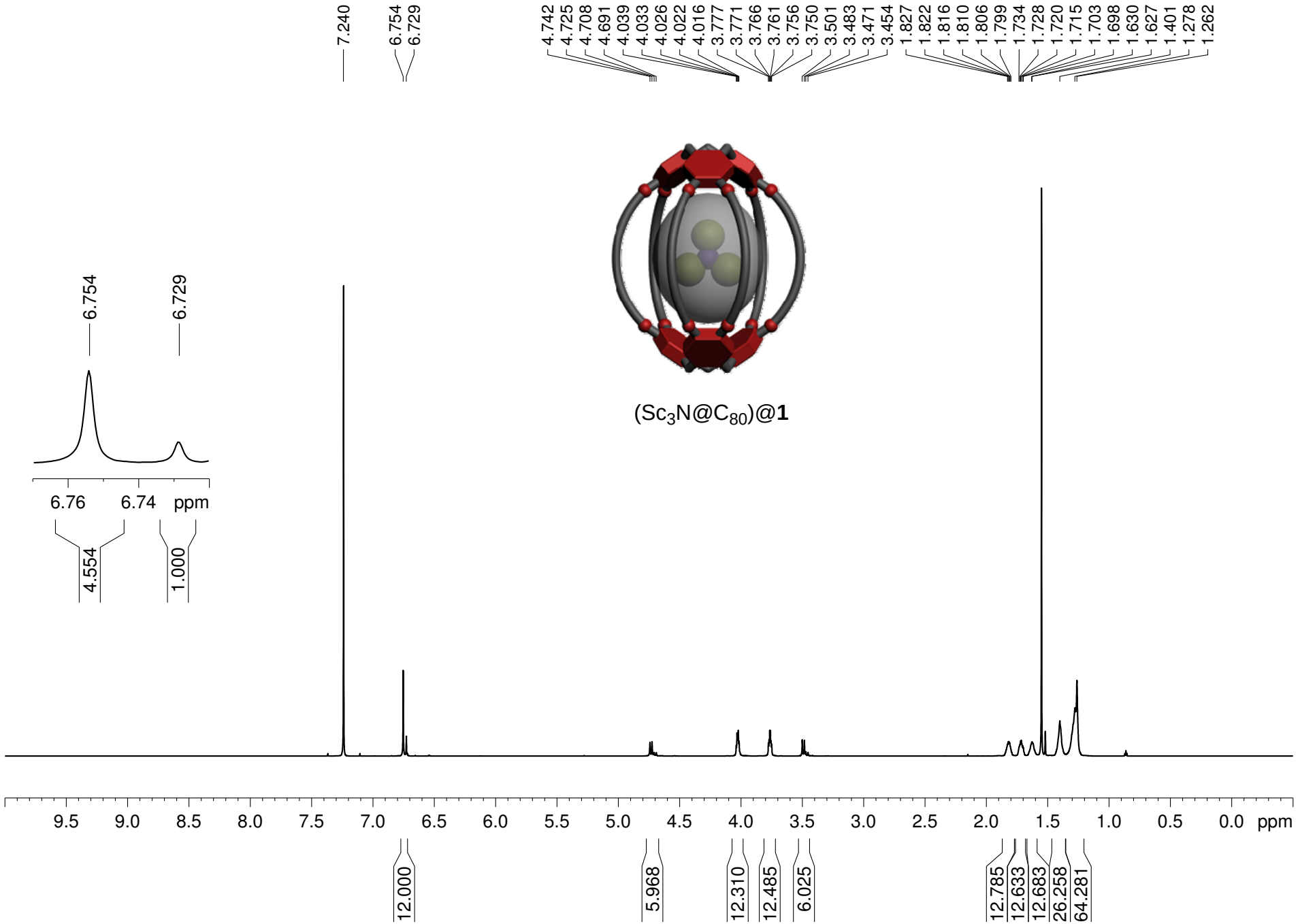

190.675
171.967
171.947
154.589
149.010
148.843
148.687
133.517
129.640
126.807
119.822
113.457
113.080
111.524
110.892
77.317
77.000
76.683
69.196
69.013
68.745
68.666
65.300
64.650
64.612
29.641
29.621
29.598
29.480
29.466
29.438
29.205
29.169
26.279
26.247
OH
O
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

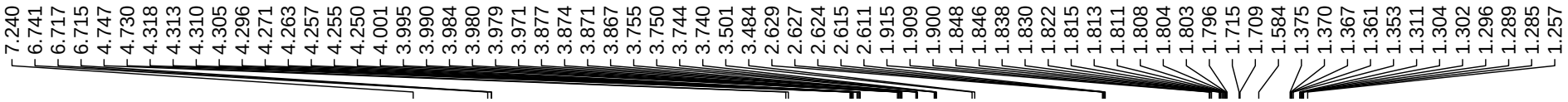

9.787
7.406
7.402
7.386
7.381
7.349
7.345
7.240
6.923
6.903
6.795
6.788
4.683
4.649
4.192
4.176
4.161
4.131
4.044
4.037
4.030
4.015
3.967
3.953
3.946
3.930
3.915
3.892
3.879
3.864
3.848
3.841
3.473
3.439
2.564
1.854
1.823
1.791
1.758
1.741
1.724
1.705
1.488
1.470
1.450
1.431
1.411
1.394
1.372
1.250
1.226
6
9
8
7
6
5
4
3
2
1
0
ppm
3.000
3.165
3.270
3.257
5.847
2.718
13.177
13.000
13.699
2.867
12.922
41.017
65.451

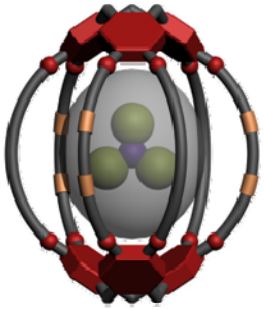

190.828
172.069
154.674
149.078
147.991
147.488
132.540
131.973
129.664
126.851
116.399
115.629
111.503
110.824
77.318
77.000
76.682
69.285
69.208
68.880
68.529
64.460
36.308
29.467
29.441
29.401
29.346
29.293
29.245
28.950
26.109
26.043
25.711
25.577
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.240
6.788
6.784
4.689
4.654
4.132
4.122
4.117
4.107
4.091
4.010
3.996
3.986
3.981
3.972
3.959
3.947
3.861
3.849
3.832
3.817
3.813
3.798
3.795
3.776
3.471
3.437
2.555
1.781
1.773
1.769
1.753
1.537
1.236
1.200
2
10
9
8
7
6
5
4
3
2
1
ppm
12.000
5.848
12.732
12.749
12.432
6.090
12.178
39.137
63.246

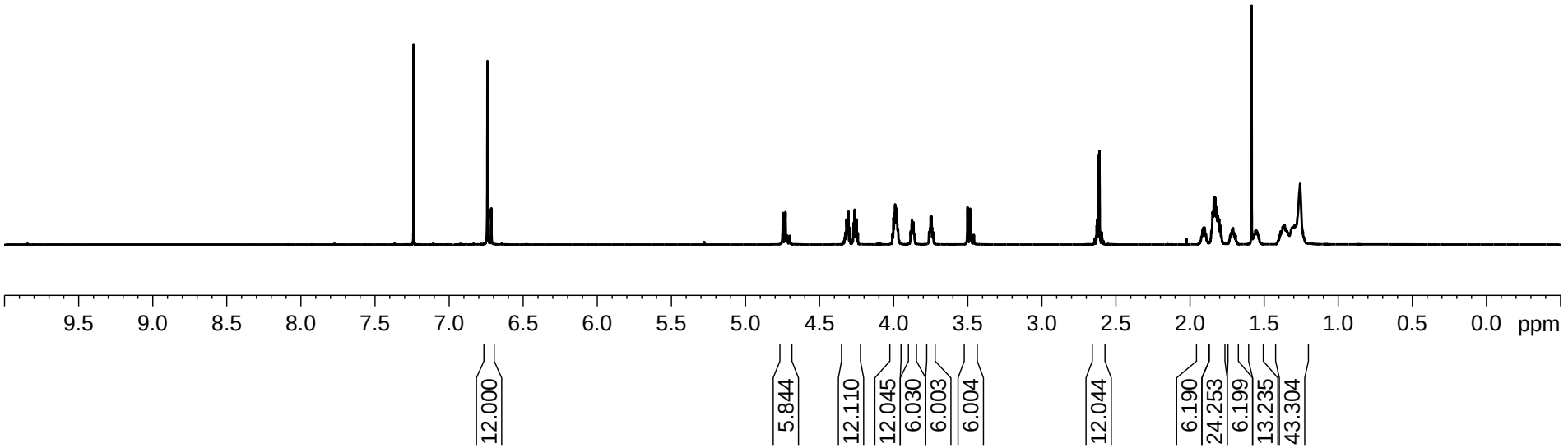

172.030
147.876
147.654
132.547
132.203
116.089
115.918
77.317
77.000
76.683
69.399
68.988
64.401
36.392
29.829
29.723
29.663
29.508
29.206
26.138
26.064
25.681
2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

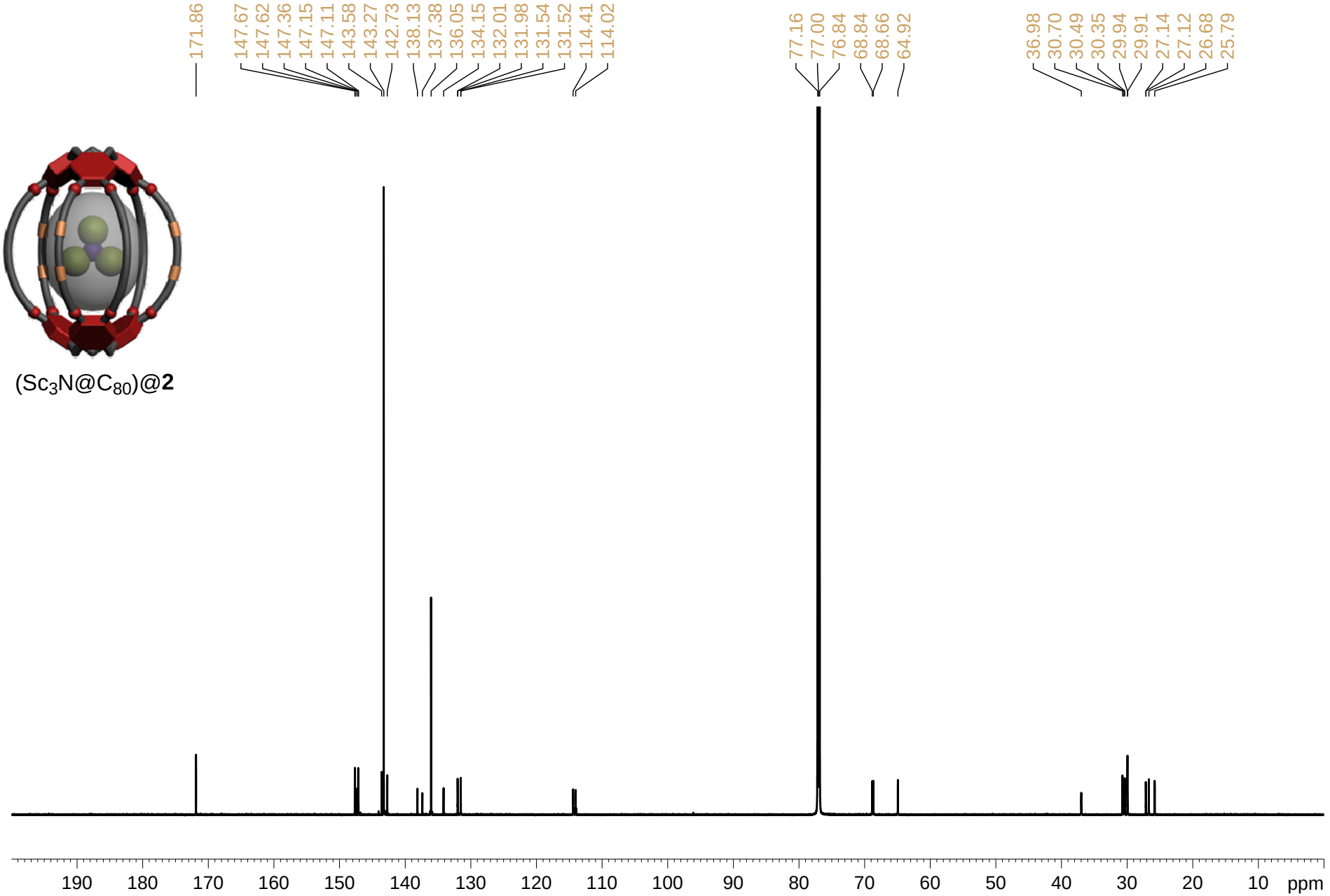

7.240
6.754
6.729
4.742
4.725
4.708
4.691
4.039
4.033
4.026
4.022
4.016
3.777
3.771
3.766
3.761
3.756
3.750
3.501
3.483
3.471
3.454
1.827
1.822
1.816
1.810
1.806
1.799
1.734
1.728
1.720
1.715
1.703
1.698
1.630
1.627
1.401
1.278
1.262
6.754
6.729
6.76
6.74
ppm
4.554
1.000
(Sc3N@C80)@1
9.5
9.0
8.5
8.0
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
ppm
12.000
5.968
12.310
12.485
6.025
12.785
12.633
12.683
26.258
64.281


7.240
6.741
6.717
6.715
4.747
4.730
4.318
4.313
4.310
4.305
4.296
4.271
4.263
4.257
4.255
4.250
4.001
3.995
3.990
3.984
3.980
3.979
3.971
3.877
3.874
3.871
3.867
3.755
3.750
3.744
3.740
3.501
3.484
2.629
2.627
2.624
2.615
2.611
1.915
1.909
1.900
1.848
1.846
1.838
1.830
1.822
1.815
1.813
1.811
1.808
1.804
1.803
1.796
1.715
1.709
1.584
1.375
1.370
1.367
1.361
1.353
1.311
1.304
1.302
1.296
1.289
1.285
1.257



($Sc_3N@C_{80}$)@**2**


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
ppm
12.000
5.844
12.110
12.045
6.030
6.003
6.004
12.044
6.190
24.253
6.199
13.235
43.304


171.86
147.67
147.62
147.36
147.15
147.11
143.58
143.27
142.73
138.13
137.38
136.05
134.15
132.01
131.98
131.54
131.52
114.41
114.02
77.16
77.00
76.84
68.84
68.66
64.92
36.98
30.70
30.49
30.35
29.94
29.91
27.14
27.12
26.68
25.79
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

$(Sc_3N@C_{80})@$**2**