Supplementary Material (ESI) for Chemical Communications

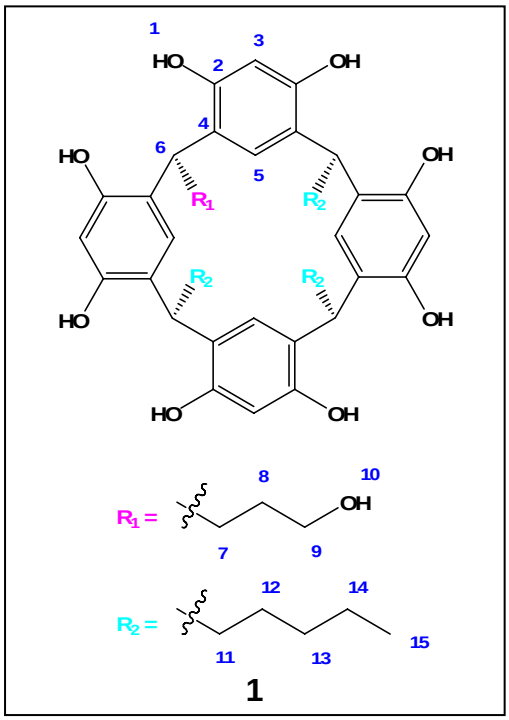
SUPORTING INFORMATION FOR MONO-FUNCTIONALIZATION OF RESORCINARENES

Experimental Section

General

^{1}H NMR and ^{13}C NMR were obtained using a Bruker DRX-600 or a Bruker AM-300 spectrometer. MALDI-FTMS experiments were performed on an IonSpec FTMS mass spectrometer. Electrospray MS experiments were performed on a single-quadrapole Perkin-Elmer API-100 Sciex mass spectrometer. All reagents were used as purchased from Aldrich unless otherwise indicated.

Monohydroxy Resorcinarene (1):



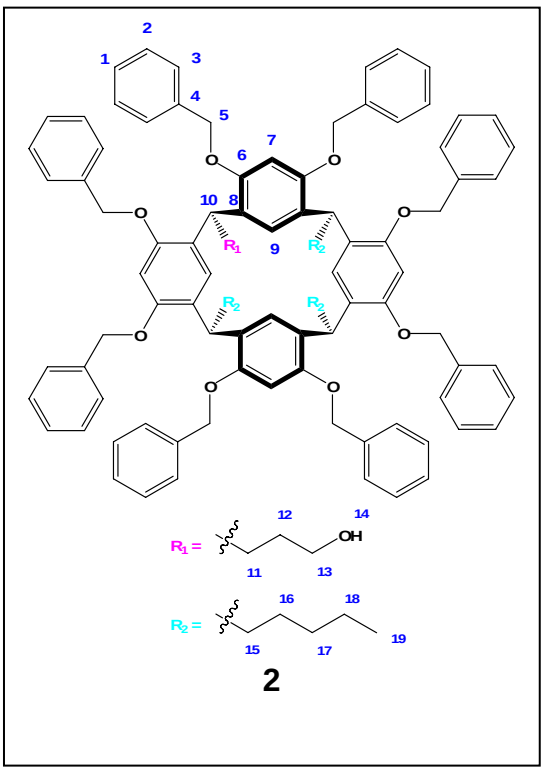
1

To a stirred solution of resorcinol (20.00 g, 181.6 mmol) in MeOH (150 ml) cooled to 0 °C was added 2,3-dehydro furan (3.44 ml, 45.41 mmol, 1.0 eq.) and hexanal (16.76 ml, 136.2 mmol, 3.0 eq.). HCl (conc.) (36 ml) was then added dropwise over 10 minutes. The reaction mixture was heated to 50 °C and stirred for 7 days. The red solution was poured into distilled water (1 l), stirred for 1 hour and the precipitate was collected by vacuum filtration. The solid was dissolved in acetone (200 ml), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of monohydroxy resorcinarene **1** was achieved by flash chromatography (silica) using a CH_2Cl_2/acetone 8:2 to 6:4 gradient.

- **Yield:** 8.45 g (24.6 %)
- **Symmetry:** C_V
- **^{1}H-NMR (Acetone-d_6, 600 MHz):** δ = 8.45 (*s*, 8 H, **1**), 7.58 (*s*, 4 H, **5**), 6.24 (*s*, 4 H, **3**), 4.31 (*t*, 4 H, ^{3}J = 8.1 Hz, **6**), 3.60 (d*t*, 2 H, ^{3}J = 5.2 Hz, ^{3}J = 6.4 Hz, **9**), 3.45 (*t*,1 H, ^{3}J = 5.2 Hz, **10**), 2.3 (*m*, 8 H, **7,11**), 1.52 (*m*, 2 H, **8**), 1.34 (*m*, 18 H, **12-14**), 0.90 (*m*, 9 H, **15**) ppm

- **^{13}C-NMR (Acetone-d_6, 150.9 MHz):** δ = 153.58/153.54 (8 C, **2**), 126.41/126.37/126.19/126.17/126.05 (12 C, **4,5**), 104.59 (4 C, **3**), 63.33 (1 C, **9**), 35.34, 35.27, 35.19, 35.11, 34.99, 33.69, 33.66, 33.591, 33.04, 31.57, 31.28, 29.67, 29.65, 29.60, 24.41, 24.39, 15.44 (3 C, **15**) ppm
- **MS (ESI-high acc.):** $^{m}/_{z}$ = 779.41 $[MNa]^+$

Octabenzylated Resorcinarene (2):



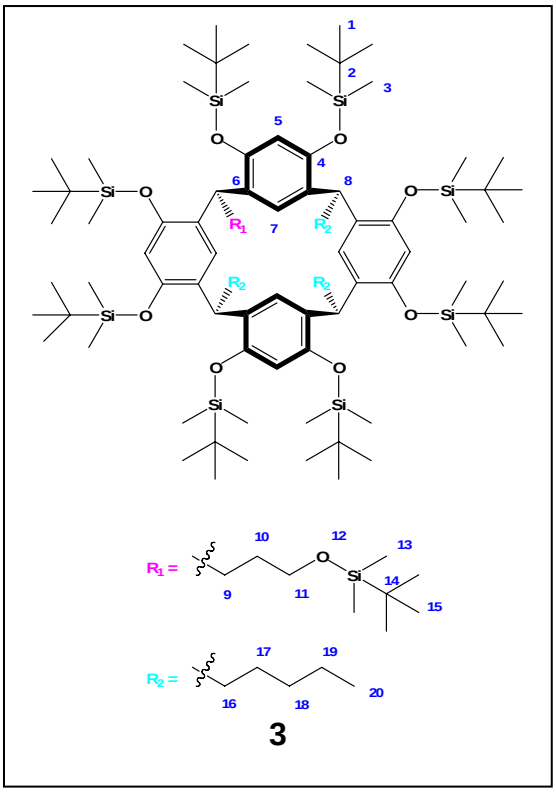
2

To a stirred solution of **1** (2.0 g, 2.64 mmol) in acetone (80 ml) under N_2 atmosphere was added K_2CO_3 (5.4 g, 39.1 mmol) and NaI (3.0 g, 20.0 mmol). The mixture was stirred for 2 hours at room temperature. Benzyl bromide (4.52 g, 3.12 ml, 26.4 mmol, 10 eq.) was added over 5 minutes and the reaction mixture was heated to reflux for 7 days.

To the cooled crude reaction mixture was added ethyl acetate (100 ml) and the precipitate was removed by vacuum filtration. The filtrate was concentrated *in vacuo*. Purification of benzylated monohydroxy resorcinarene **2** was achieved by flash chromatography (silica) using a hexanes/ethyl acetate 6:1 to 4:1 gradient.

- **Yield:** 2.0 g (51 %)
- **Symmetry: C_1**
- **^{1}H-NMR ($CDCl_3$, 300 MHz):** δ = 7.20 (br. *s*, 28 H, **1/2/3/9**), 6.81 („*d*“, 4 H, **7**), 5.0/4.8 (*m*, 20 H, **5/10**), 3.54 (*m*, 2 H, **13**), 3.29 (*t*, 1 H, ^{3}J = 5.1 Hz, **14**), 1.95 (*m*, 8 H, **11/15**), 1.61 (*m*, 2 H, **12**), 1.38 (*m*, 18 H, **16-18**), 0.80 (*m*, 9 H, **19**) ppm
- **^{13}C-NMR ($CDCl_3$, 150.9 MHz):** δ = 155.47, 141.41, 138.09, 137.90, 129.02, 128.69, 128.61, 128.09, 128.00, 127.89, 127.81, 127.64, 127.44, 126.85, 99.44, 71.25, 71.03, 65.79, 63.16, 36.77, 35.71, 35.04, 32.74, 32.70, 31.41, 30.64, 28.71, 26.17, 23.23, 14.65 ppm
- **MS (ESI):** $^{m}/_{z}$ = 1478.81 $[MH]^+$, 1499.79 $[MNa]^+$

TBDMS Resorcinarene (3):



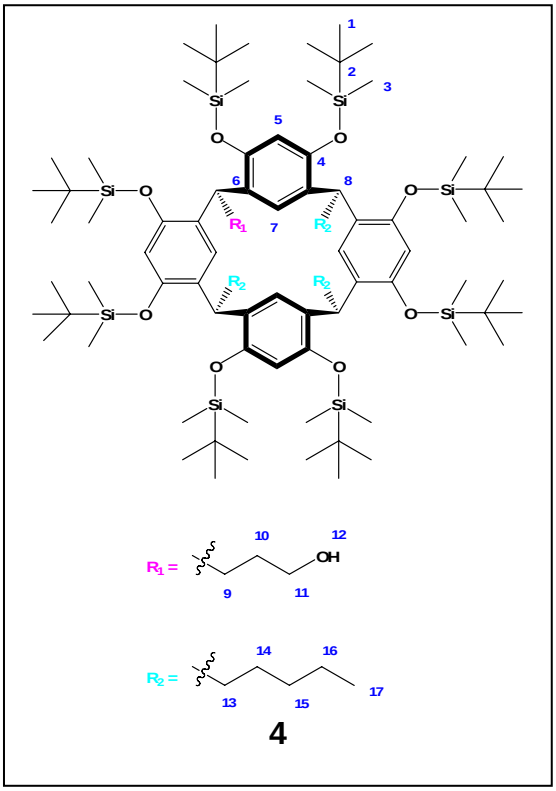
3

To a solution of **1** (3.0 g, 3.96 mmol) and *tert*-butyldimethylsilyl chloride (10.75 g, 71.34 mmol) in anhydrous DMF (100 ml) under N_2 atmosphere was added imidazole (9.71 g, 142.70 mmol). The solution changed from red to yellow immediately. The reaction mixture was heated to 75°C for 7 days. The solution was cooled to room temperature and poured into CH_2Cl_2 (500 ml) and $NaHCO_3$ (saturated aqueous) (500 ml). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 x 150 ml). The combined organic layers were washed with $NaHCO_3$ (saturated aqueous) (2 x 250 ml) and NaCl (saturated aqueous) (300 ml), dried over Na_2SO_4, filtered and concentrated *in vacuo*.

Purification of the globally protected TBDMS resorcinarene **3** was achieved by flash chromatography (silica) using a hexanes/ CH_2Cl_2 1:0 to 20:1 gradient.

- **Yield:** 3.6 g (50 %)
- **Symmetry:** C_1
- **^{1}H-NMR ($CDCl_3$, 600 MHz):** δ = 7.14/7.12 („*d*“, 2 H, **5**), 6.33 (*s*, 2 H, **7**), 6.24/6.23 („*d*“, 2 H, **5**), 6.10 (*s*, 2 H, **7**), 4.38 (*m*, 4 H, **8**), 3.52 (*m*, 2 H, **11**), 2.00/1.93 (*m*, 4 H, **9/16**), 1.74 (*m*, 4 H, **16**), 1.46 (*m*, 2 H, **10**), 1.22 (*m*, 18 H, **17-19**), 1.09 (*s*, 36 H, **1**), 0.86 (*s*, 36 H, **1**), 0.85 (*s*, 9 H, **15**), 0.83 (*m*, 9 H, **20**), 0.37 (*s*, 24 H, **3**), 0,06 (*s*, 12 H, **3**), -0.01 (*s*, 6 H, **13**), -0.14 (*s*, 12 H, **3**) ppm
- **^{13}C-NMR ($CDCl_3$, 150.9 MHz):** δ = 152.28, 152.23, 150.63, 150.61, 150.57, 129.16, 129.13, 129.11, 129.07, 129.04, 128.84, 126.28, 126.14, 123.82, 123.71, 123.49, 110.09, 110.02, 107.48, 107.38, 63.92, 37.62, 37.59, 36.97, 35.76, 32.59, 32.50, 28.78, 28.71, 26.25, 26.04, 22.92, 22.86, 18.49, 18.43, 18.39, 18.28, 14.25, -3.74, -3.85, -3.92, -4.01, -5.32 ppm
- **MS (ESI-high acc.):** $^m/_z$ = 1784.20 $[MH]^+$, 1806.22 $[MNa]^+$

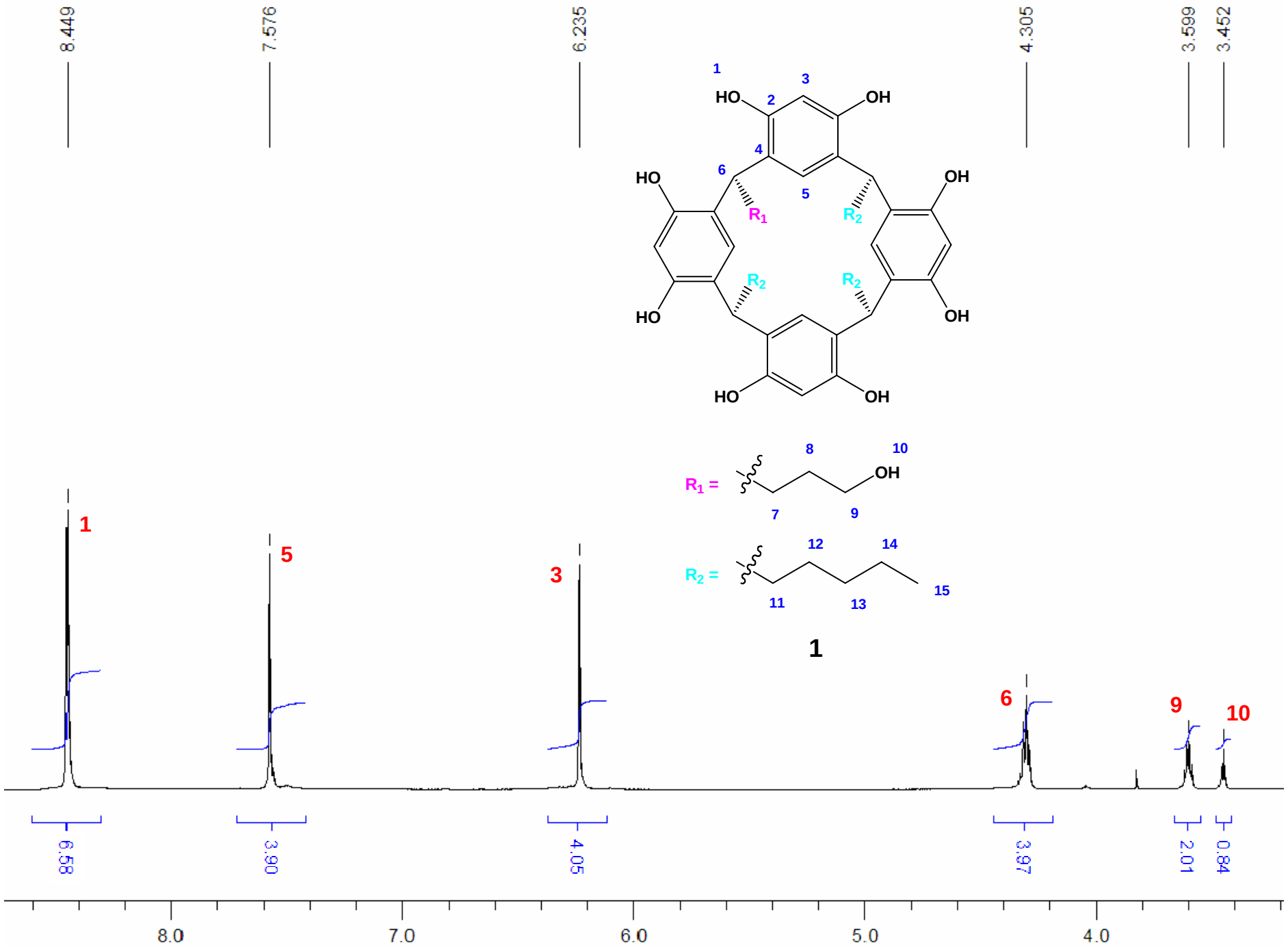
TBDMS Resorcinarene (4):

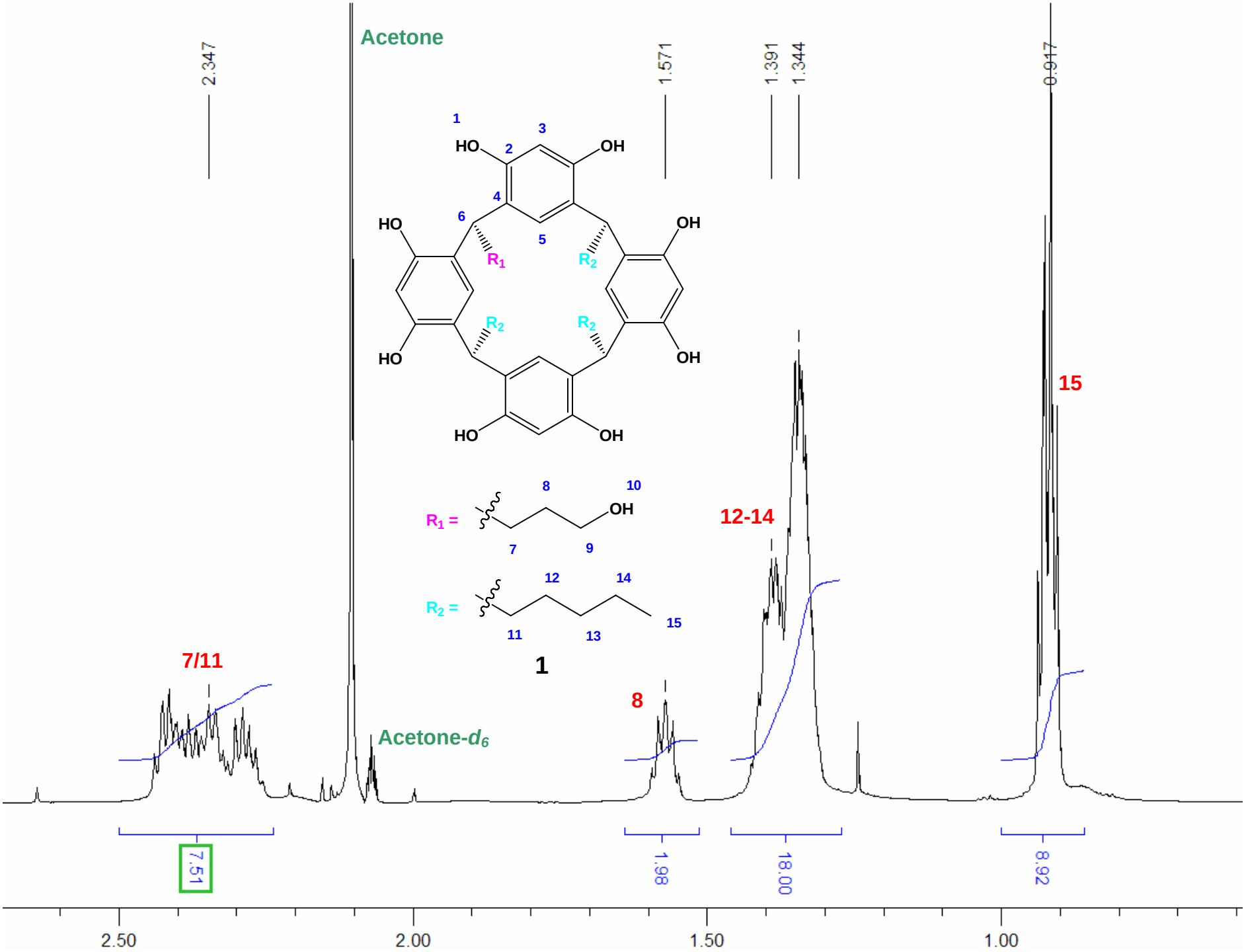


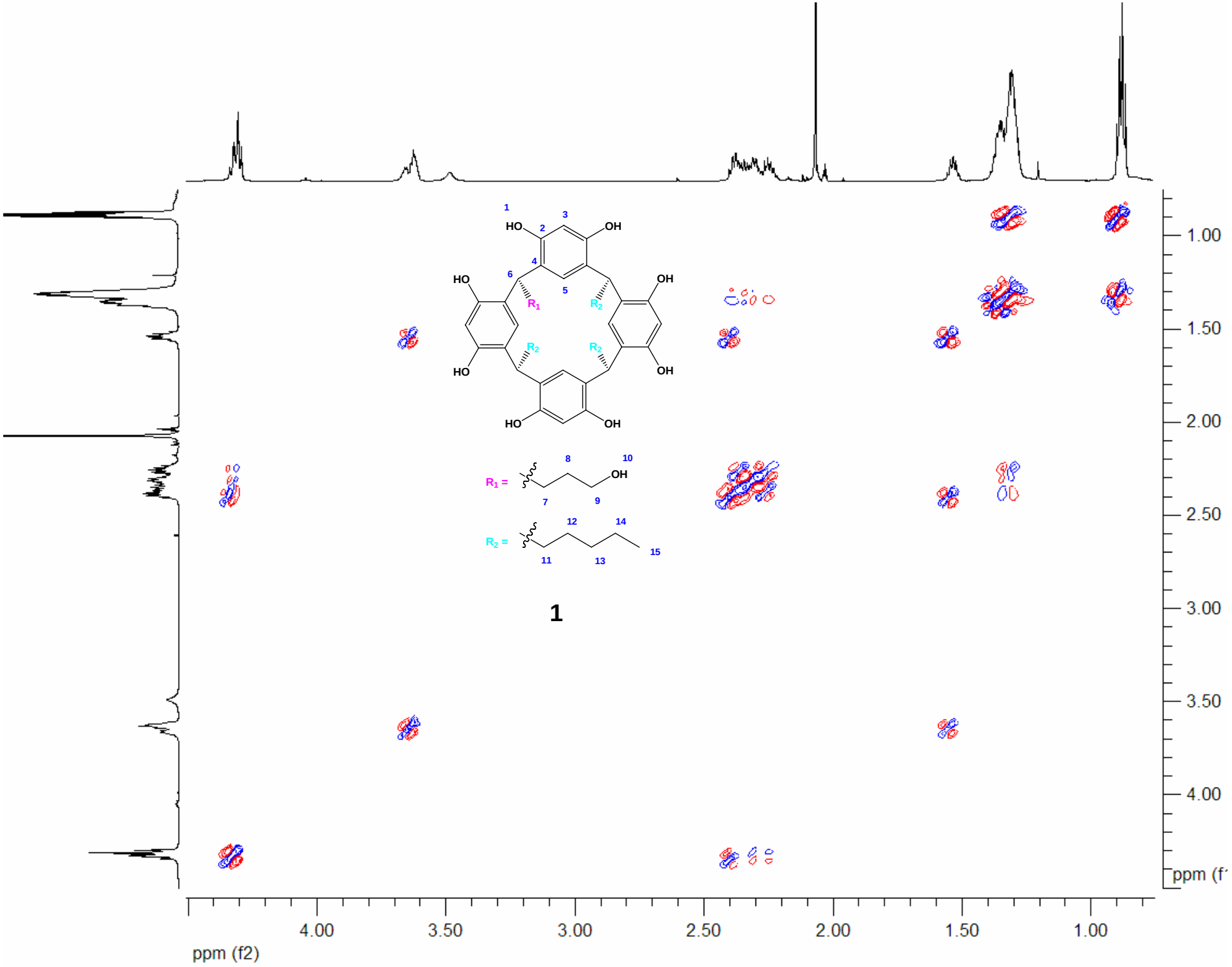
To a solution of **3** (2.21 g, 1.23 mmol) in CH_2Cl_2 (50 ml) and MeOH (50 ml) was added a solution of I_2 (60 mg, 0.24 mmol) in MeOH (6 ml). The reaction mixture was stirred for 5 hours at room temperature, after which $Na_2S_2O_3$ (300 mg) was added resulting in a colorless solution. CH_2Cl_2 (100 ml) was added, the mixture was filtered and the filtrate was concentrated *in vacuo*.

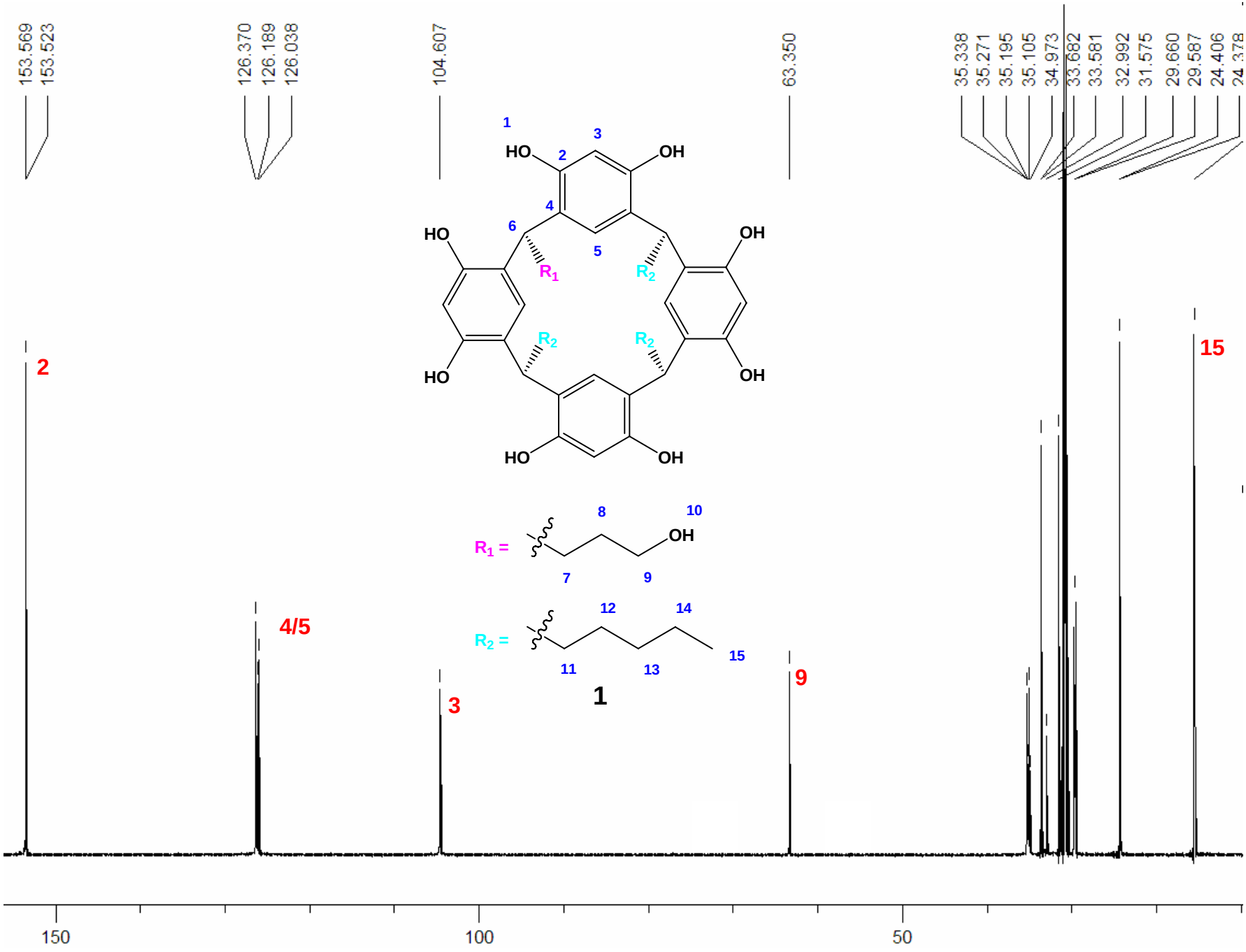
Purification of the mono hydroxy TBDMS resorcinarene **4** was achieved by flash chromatography (silica) using a hexanes/ CH_2Cl_2 1:0 to 2:1 gradient.

- **Yield:** 1.41 g (69 %)
- **Symmetry:** C_1
- **^{1}H-NMR ($CDCl_3$, 600 MHz):** δ = 7.13/7.12 („*d*“, 2 H, **7**), 6.34/6.33 („*d*“, 2 H, **7**), 6.24/6.22 („*d*“, 2 H, **5**), 6.11/6.10 (“*d*“, 2 H, **5**), 4.40 (*m*, 4 H, **8**), 3.56 (*m*, 2 H, **11**), 2.04 („*t*“, 1 H, **12**), 1.93 (*m*, 4 H, **10**), 1.73 (*m*, 4 H, **9/13**), 1.50 (*m*, 4 H, **9/13**), 1.21 (*m*, 18 H, **14-16**), 1.09 (*s*, 36 H, **1**), 0.83 (*m*, 9 H, **17**), 0.37 (*s*, 24 H, **3**), 0,06 (*s*, 12 H, **3**), -0.14 (*s*, 12 H, **3**) ppm
- **^{13}C-NMR ($CDCl_3$, 150.9 MHz):** δ = 152.89, 152.73, 152.70, 151.22, 151.10, 151.04, 129.81, 129.56, 129.54, 129.43, 129.40, 128.98, 126.66, 126.55, 124.34, 124.15, 124.12, 123.58, 110.62, 110.50, 107.90, 107.86, 64.03, 53.83, 38.10, 38.02, 37.56, 36.21, 36.11, 33.04, 32.99, 32.50, 31.89, 29.23, 26.55, 23.40, 23.36, 18.91, 18.89, 18.87, 18.73, 14.69, -3.27, -3.28, -3.31, -3.46, -3.48, -3.55, -3.57 ppm
- **MS (ESI-high acc.):** $^m/_z$ = 1670.12 $[MH]^+$, 1692.10 $[MNa]^+$


8.449
7.576
6.235
4.305
3.599
3.452
1
3
HO
2
OH
4
6
5
HO
OH
R1
R2
R2
R2
HO
OH
HO
OH
R1 =
8
10
OH
7
9
R2 =
12
14
15
11
13
1
1
5
3
6
9
10
6.58
3.90
4.05
3.97
2.01
0.84
8.0
7.0
6.0
5.0
4.0


Acetone
2.347
1.571
1.391
1.344
0.917
HO
OH
R1
R2
R1 =
R2 =
1
7/11
8
12-14
15
Acetone-d6
7.51
1.98
18.00
8.92
2.50
2.00
1.50
1.00


HO
OH
R1
R2
R1 =
R2 =
1
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f2)
ppm (f


153.569
153.523
126.370
126.189
126.038
104.607
63.350
35.338
35.271
35.195
35.105
34.973
33.682
33.581
32.992
31.575
29.660
29.587
24.406
24.378
2
4/5
3
9
15
1
HO
OH
R1 =
R2 =
150
100
50

*ESI-TOF
Sample Name: rkam7901
Printing Time: 09:16:17 AM
Polarity/Scan Type: Positive
Printing Date: 04/8/2005
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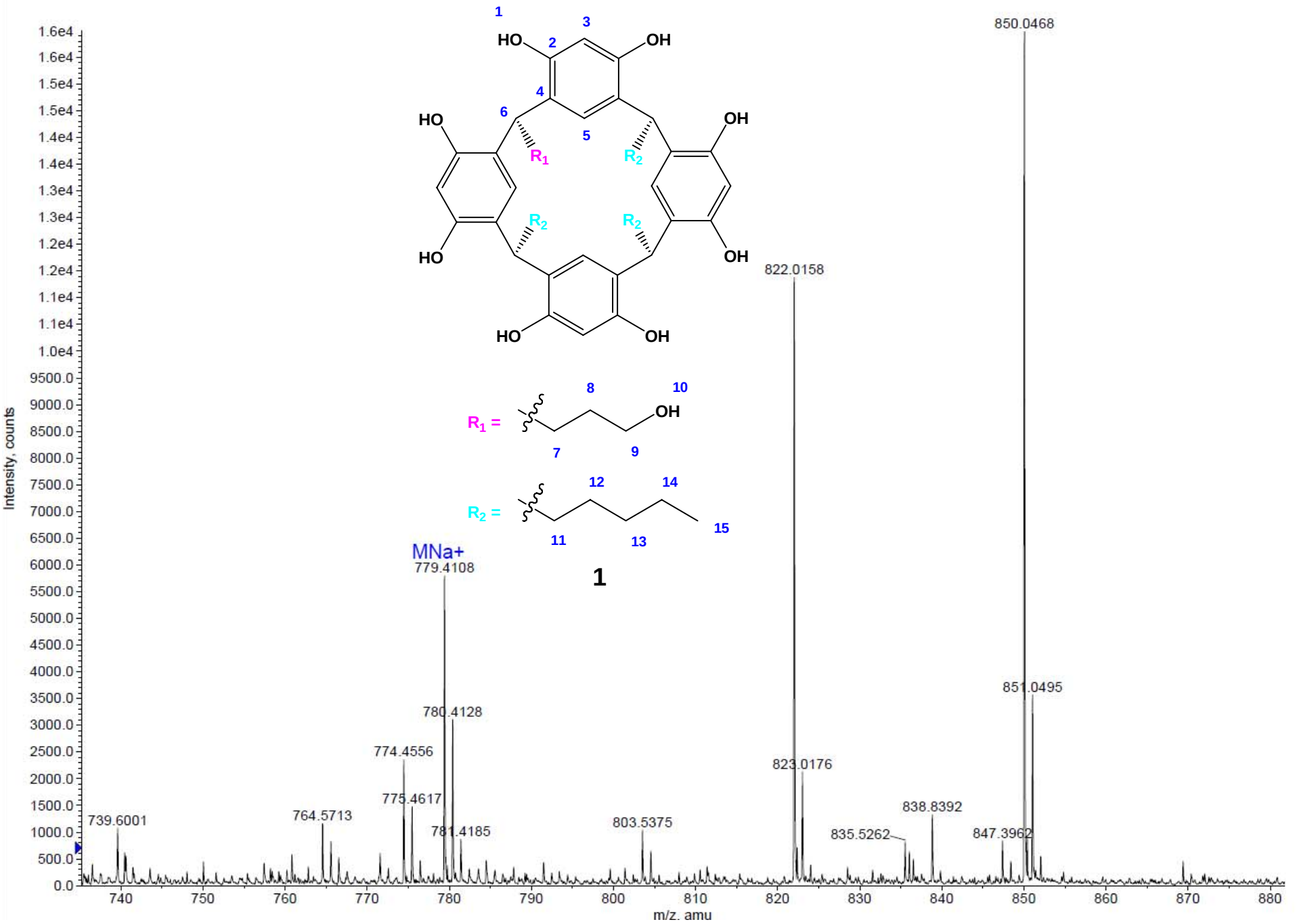
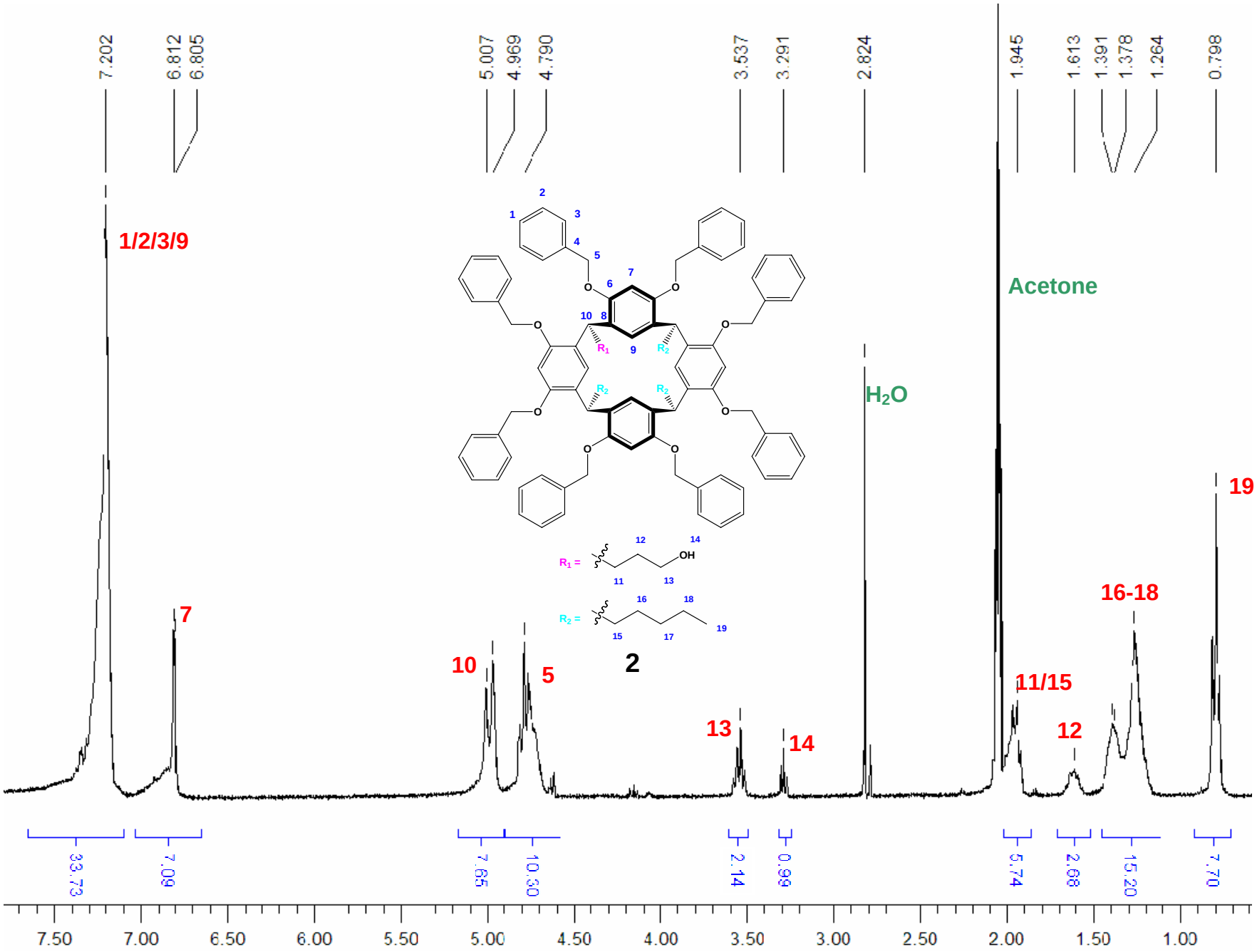
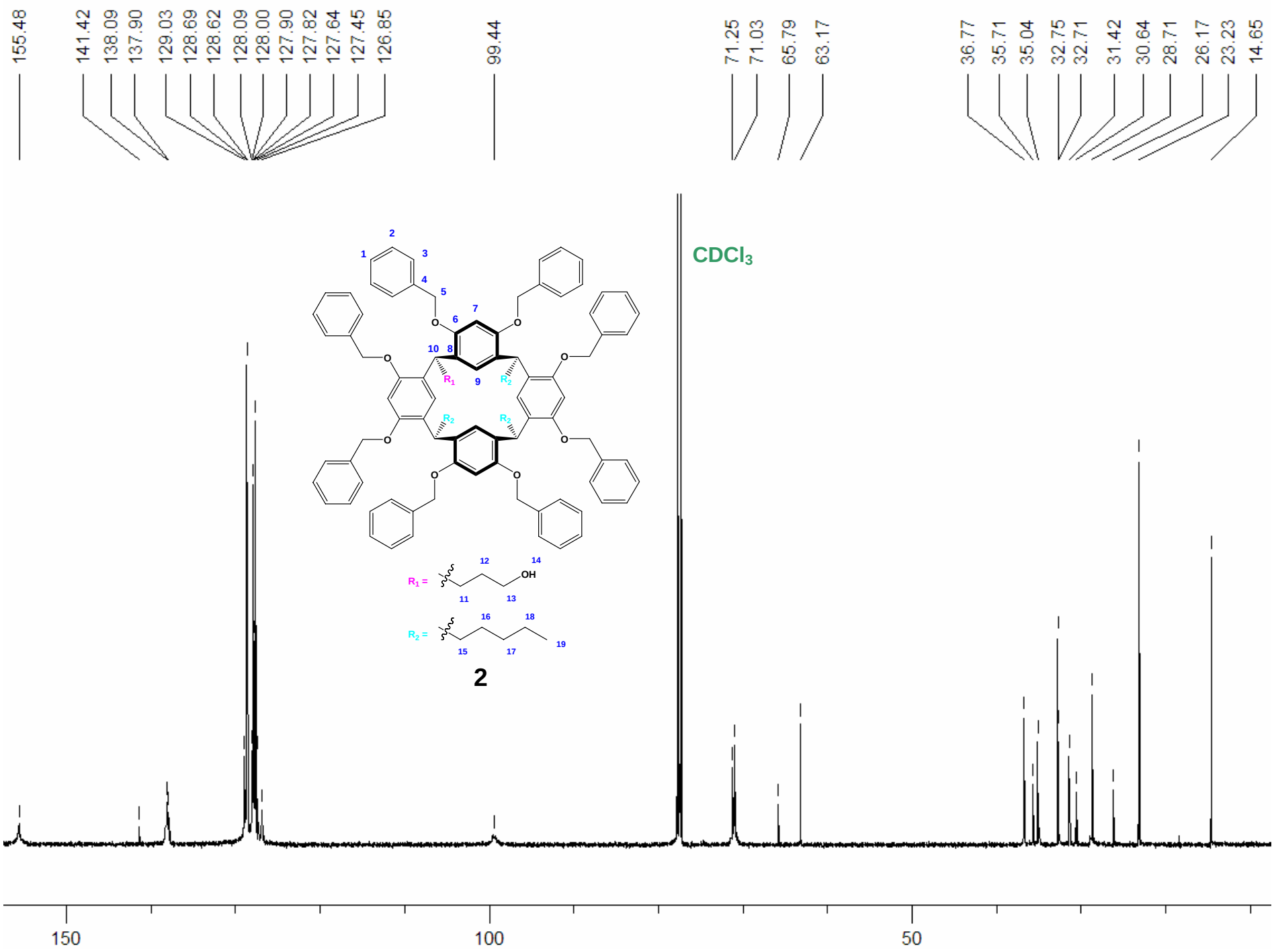
Max. 7.2e5 counts.



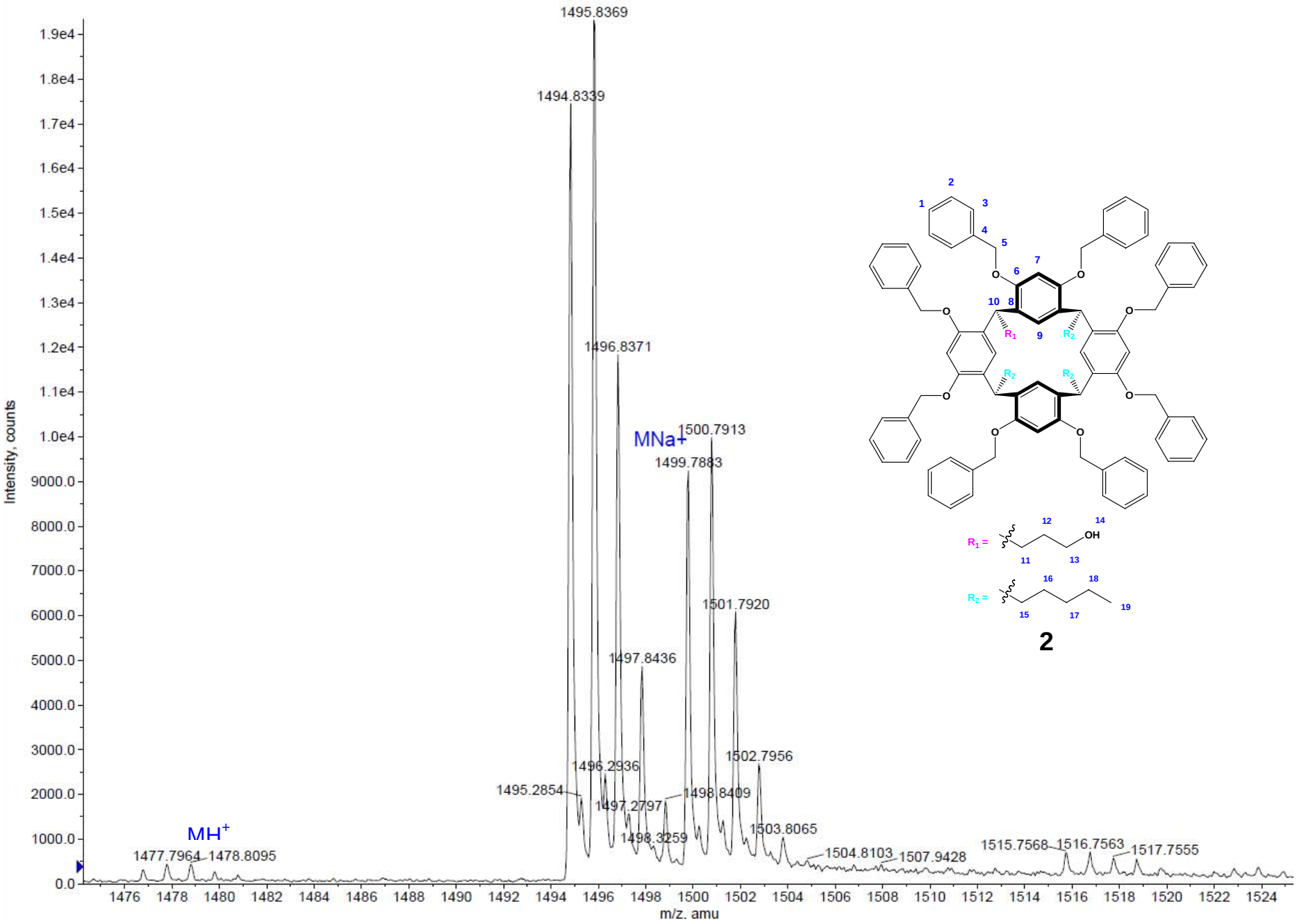

7.202
6.812
6.805
5.007
4.969
4.790
3.537
3.291
2.824
1.945
1.613
1.391
1.378
1.264
0.798
1/2/3/9
7
10
5
13
14
H2O
Acetone
11/15
12
16-18
19
R1 =
R2 =
OH
2
33.73
7.09
7.65
10.30
2.14
0.99
5.74
2.68
15.20
7.70
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00


155.48
141.42
138.09
137.90
129.03
128.69
128.62
128.09
128.00
127.90
127.82
127.64
127.45
126.85
99.44
71.25
71.03
65.79
63.17
36.77
35.71
35.04
32.75
32.71
31.42
30.64
28.71
26.17
23.23
14.65
CDCl3
R1 =
OH
R2 =
2
150
100
50

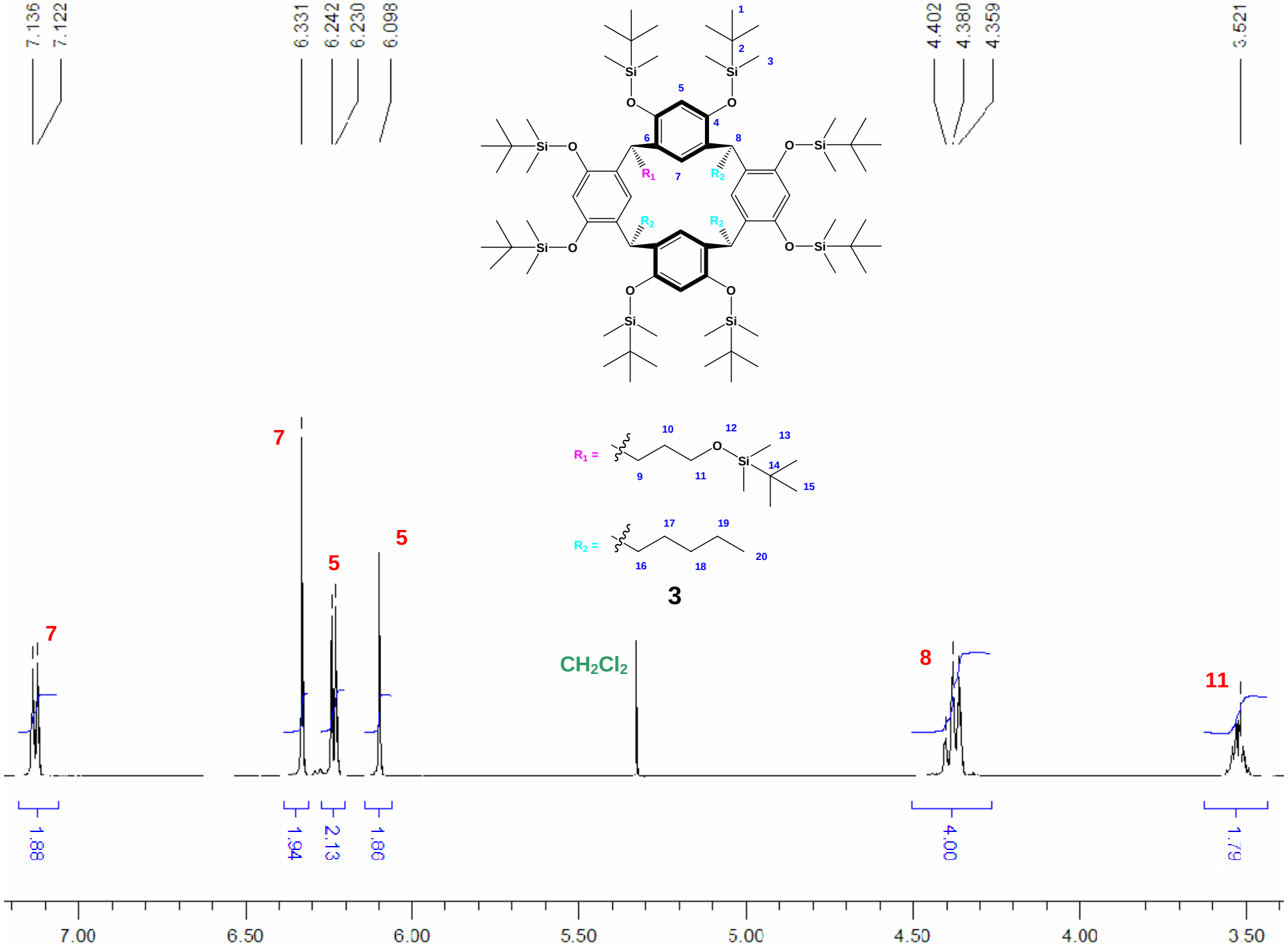
*ESI-TOF Sample Name: rkam5238 Printing Time: 04:28:04

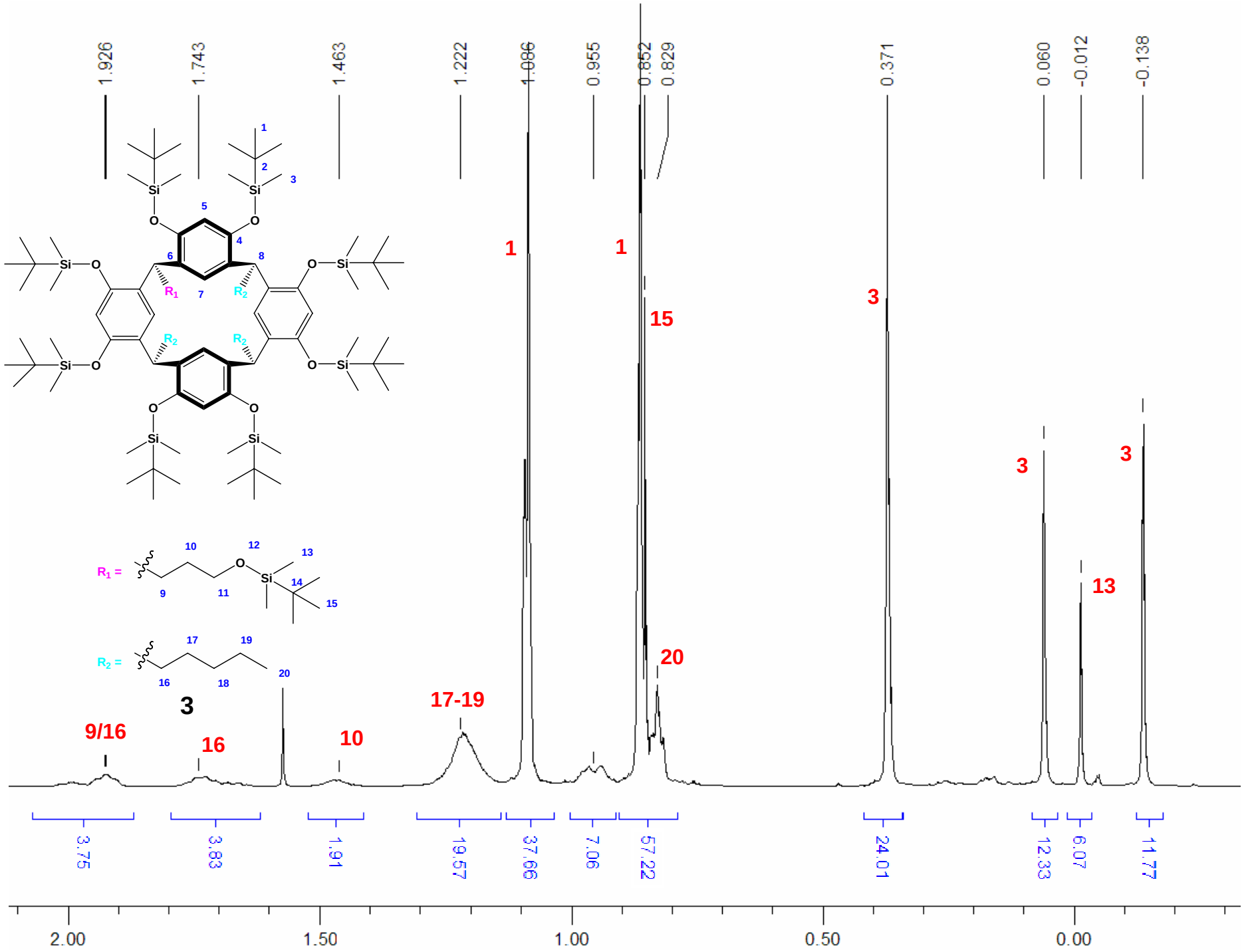
Polarity/Scan Type: Positive Printing Date: 01/18/2(

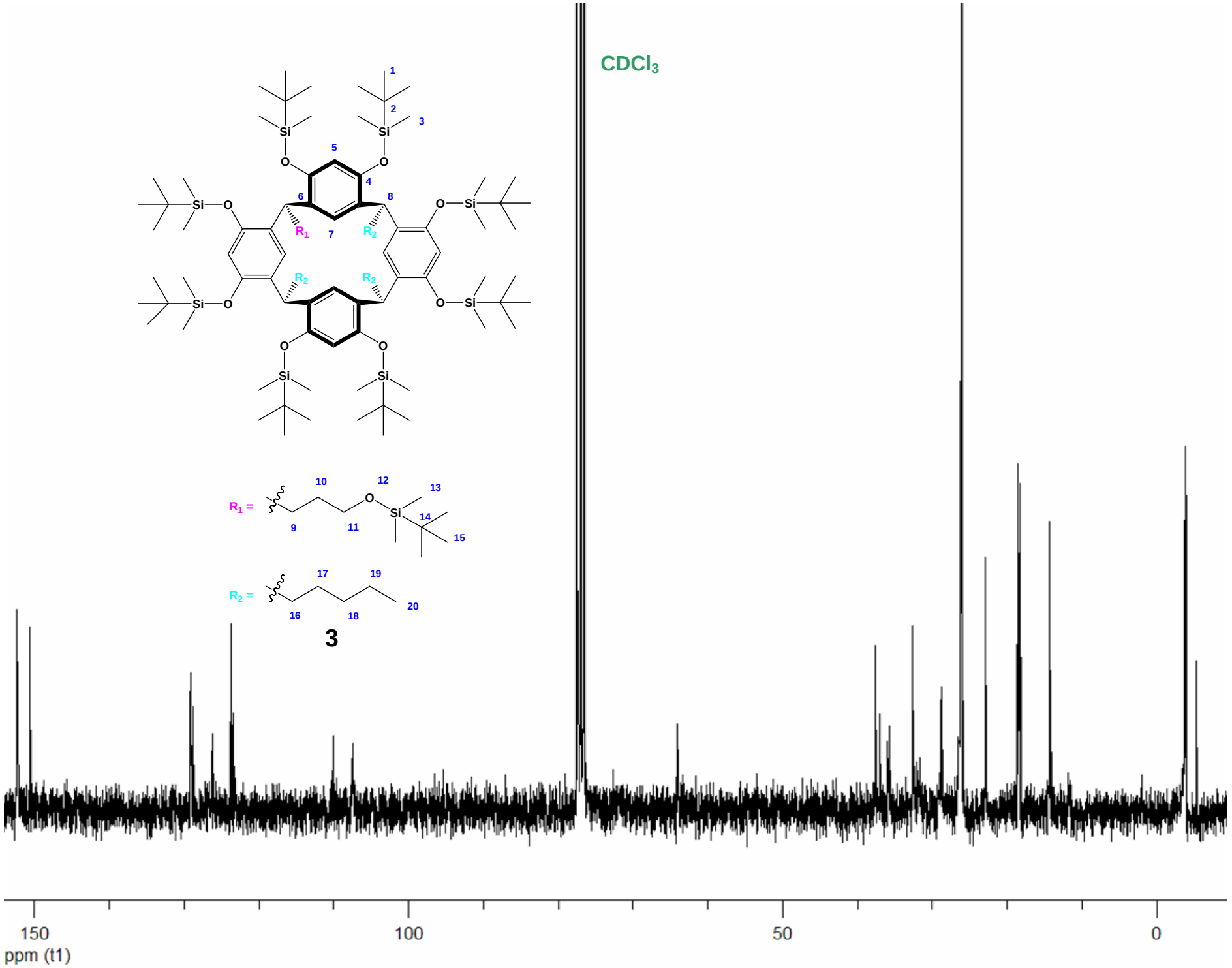
+TOF MS: 0.100 to 0.335 min from 011805069.wiff Agilent Max. 1.9e5 cou



2


7.136
7.122
6.331
6.242
6.230
6.098
4.402
4.380
4.359
3.521
R1 =
R2 =
3
7
5
5
7
CH2Cl2
8
11
1.88
1.94
2.13
1.86
4.00
1.79
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50


1.926
1.743
1.463
1.222
1.086
0.955
0.852
0.829
0.371
0.060
-0.012
-0.138
1
1
15
3
3
3
13
20
17-19
9/16
16
10
3
R1 =
R2 =
3.75
3.83
1.91
19.57
37.66
7.06
57.22
24.01
12.33
6.07
11.77
2.00
1.50
1.00
0.50
0.00


CDCl3
R1 =
R2 =
3
150
100
50
0
ppm (t1)

*ESI-TOF Sample Name: rkfh6075 Printing Time: 03:09:05 PM

Polarity/Scan Type: Positive Printing Date: 02/10/2005

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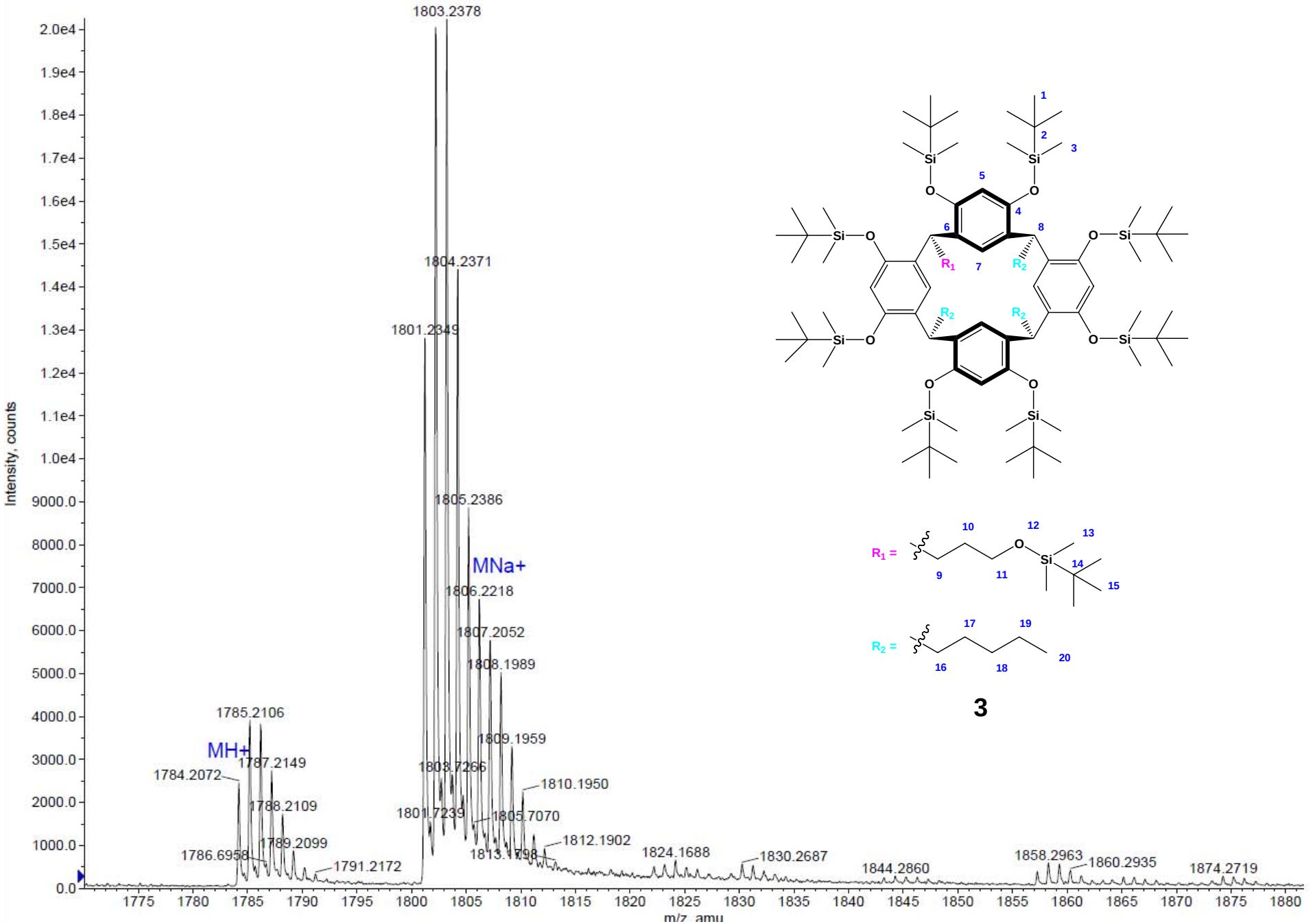
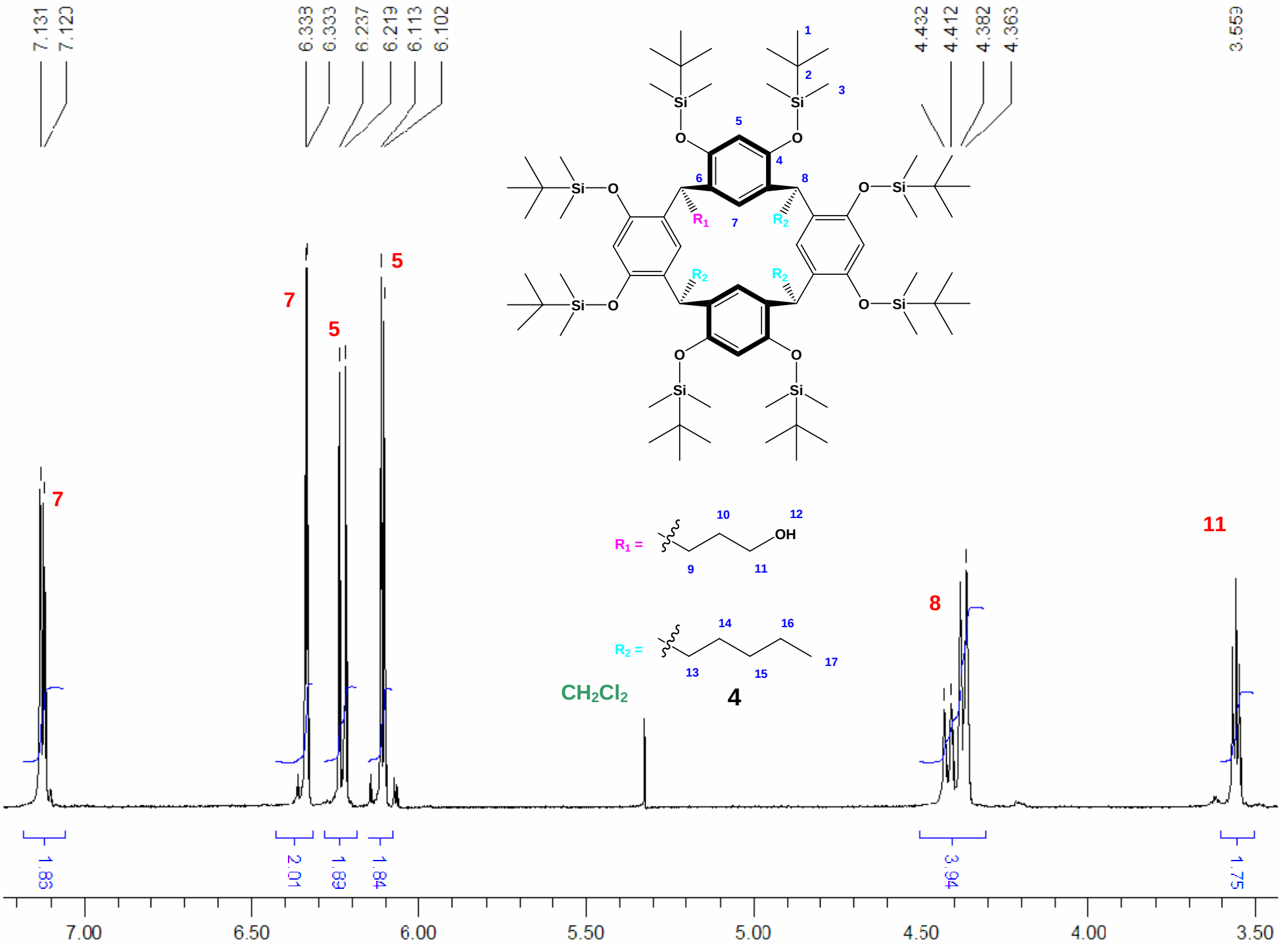


3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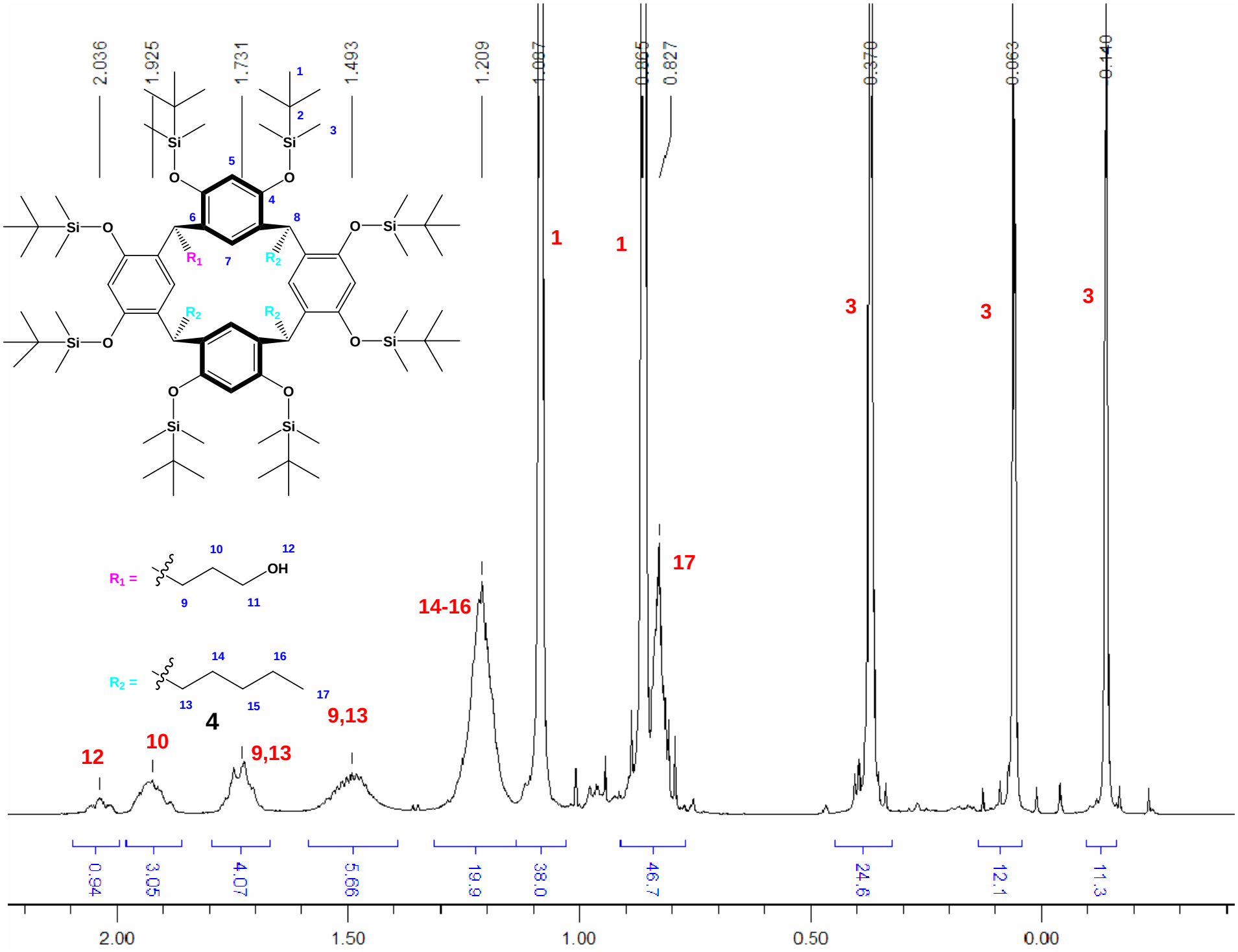
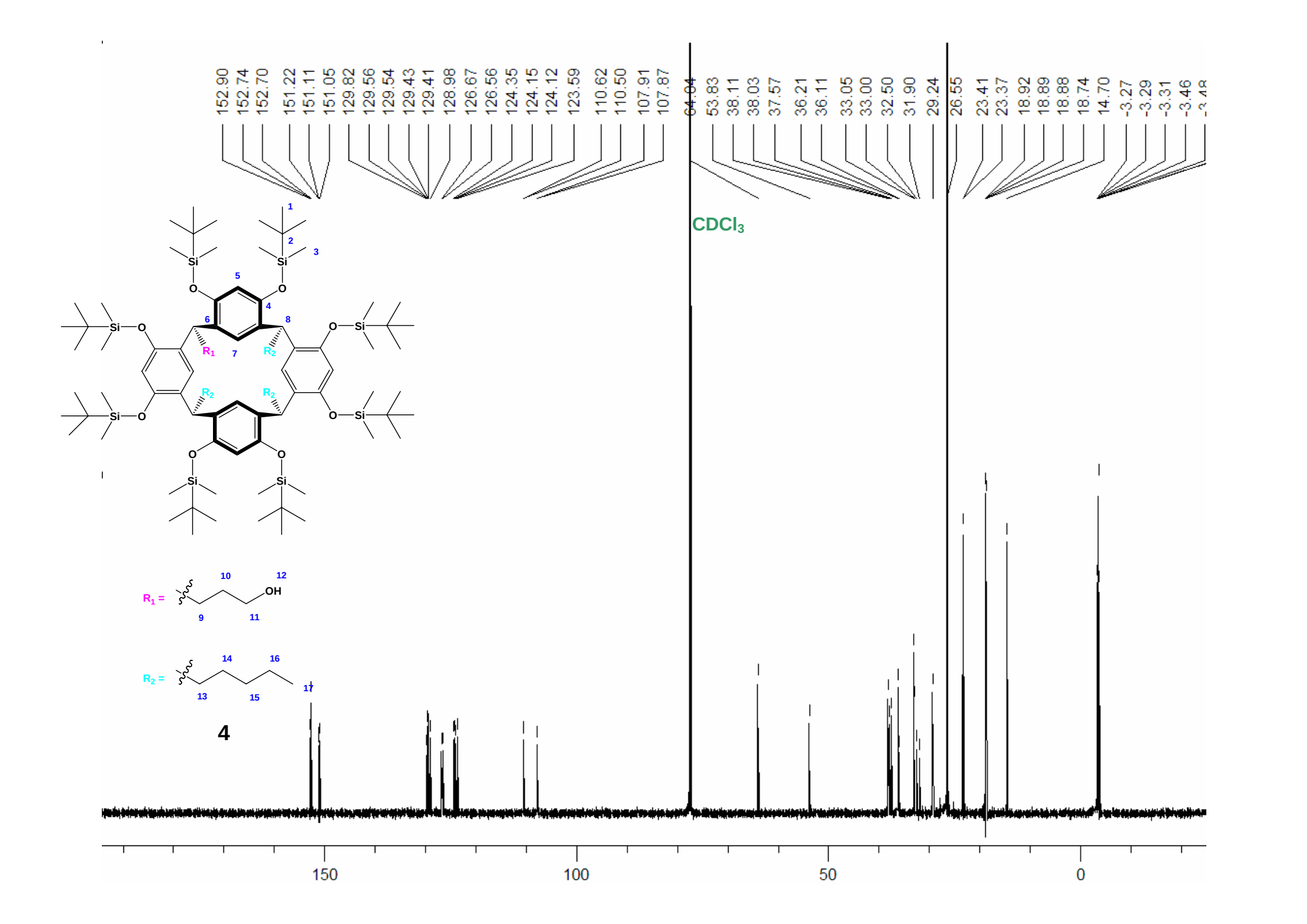
7.120
6.333
6.333
6.237
6.219
6.113
6.102
4.432
4.412
4.382
4.363
3.559
7
5
7
5
7
8
11
CH2Cl2
4
R1 =
R2 =
OH
1.85
2.01
1.89
1.84
3.94
1.75
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50


2.036
1.925
1.731
1.493
1.209
1.087
0.865
0.827
0.370
0.063
0.140
1
1
3
3
3
17
14-16
9,13
12
10
9,13
4
R1 =
R2 =
OH
0.94
3.05
4.07
5.66
19.9
38.0
46.7
24.6
12.1
11.3
2.00
1.50
1.00
0.50
0.00


152.90
152.74
152.70
151.22
151.11
151.05
129.82
129.56
129.54
129.43
129.41
128.98
126.67
126.56
124.35
124.15
124.12
123.59
110.62
110.50
107.91
107.87
64.04
53.83
38.11
38.03
37.57
36.21
36.11
33.05
33.00
32.50
31.90
29.24
26.55
23.41
23.37
18.92
18.89
18.88
18.74
14.70
-3.27
-3.29
-3.31
-3.46
CDCl3
R1 =
R2 =
OH
4
150
100
50
0

*ESI-TOF
Sample Name: rkfh6076
Printing Time: 03:19:21 PM
Polarity/Scan Type: Positive
Printing Date: 02/10/2005
+TOF MS: 0.227 to 0.245 min from 021005055.wiff Agilent
Max. 4.4e5 counts.