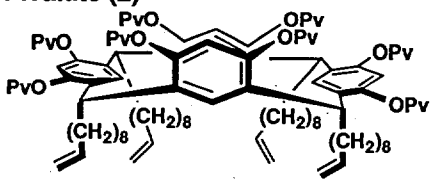
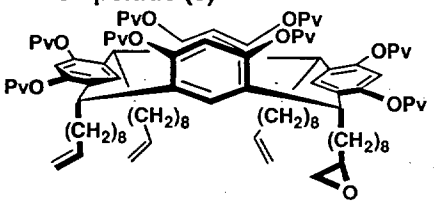
General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 and a Bruker DRX-600 spectrometers. The chemical shifts were measured relative to residual non-deuterated solvent resonances or TMS. Fast Atom Bombardment (FAB) mass-spectra were obtained with a VG ZAB-VSE double focusing high resolution mass spectrometer equipped with a cesium ion gun; m-nitrobenzyl alcohol (NBA) was used as a matrix. For high-resolution mass spectral data (HRMS-FAB), for compounds with molecular weight < 500, the measured masses always agreed to < 5 ppm with the calculated values. For compounds with significantly higher molecular weight (> 2000), lower resolution was achieved. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry experiments were performed on a PerSeptive Biosystems Voyager-Elite mass spectrometer with delayed extraction, using 2,5-dihydroxybenzoic acid (DHB) as a matrix. FTIR spectra were recorded on a Perkin Elmer Paragon 1000 PC FT-IR spectrometer. Silica gel chromatography was performed with Silica Gel 60 (EM Science or Bodman, 230-400 mesh). All experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under a nitrogen atmosphere.

Pivalate (2)



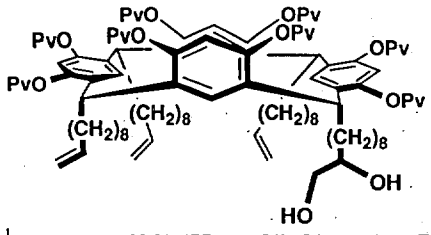
^{1}H-NMR (600MHz, $CDCl_3$, δ): 7.31(s, 2H), 7.01(s, 2H), 6.78(s, 2H), 6.05(s, 2H), 5,80(m, 4H), 5.00(d, 4H, J=18Hz), 4.94(d, 4H, J=18Hz), 4.12(brd, 4H, J-7.2Hz), 2.02(m, 8H), 1.87(m, 4H), 1.73(m, 4H), 1.35(s, 36H), 1.16(s, 36H), 1.4~1.2(m, 48H); ^{13}C-NMR(150MHz, $CDCl_3$, δ): 176.6, 176.2, 149.0, 146.2, 139.5, 134.8, 129.2, 127.7, 126.3, 117.0, 116.5, 114.5, 39.7, 39.4, 38.8, 35.0, 34.1, 30.6, 30.0, 29.9, 29.5, 29.3, 29.1, 27.6, 27.4; IR(cm^{-1}): 3075.7, 2974.5, 2927.7, 2854.6, 1754.5, 1480.0, 1463.0, 1396.5, 1367.7, 1271.1, 906.32, 733.36

mono epoxide (3)



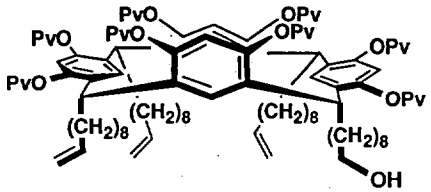
^{1}H-NMR(600MHz, CDCl3, δ): 7.34(s, 2H), 6.97(s, 2H), 6.63(s, 2H), 6.04(s, 2H), 5.91(m, 3H), 4.97(m, 3H), 4.92(brd, 3H, J= 10Hz), 4.19(brd, 4H, J=12Hz), 2.88(m, 1H), 2.73(brt, 1H, J=5.0Hz), 2.45(dd, 1H, J=2.8, 5.0 Hz), 2.04(m, 8H), 1.88 (m, 4H), 1.72(m, 4H), 1.39(s, 36H), 1.16(s,36H), 1.4~1.1(m, 48H); IR(cm^{-1}): 2974.6, 2928.5, 2855.0 1754.2, 1480.0, 1463.3, 1396.7, 1367.8, 1271.1, 1113.7 1028.5, 906.1, 757.5; MS(HRMS-FAB) m/Z 1862.0896 ([M+Cs]+, calcd. For C108H160O17Cs = 1862.0710 error 10.0 ppm)

Diol



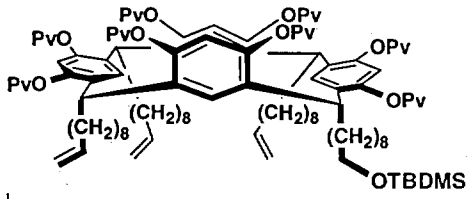
^{1}H-NMR(600MHz, $CDCl_3$, δ); 7.31(s, 2H), 6.96(s, 1H), 6.95(s, 1H), 6.64(s,1H), 6.63(s,1H), 6.05(s, 1H), 6.04(s, 1H), 4.17(m, 4H), 3.61(m, 2H), 3.37(m, 1H), 1.88(m, 4H), 1.72(m, 4H), 1.38(s, 36H), 1.15(s, 36H), 1.3~1.1(m, 62H), 0.86(t, 9H, J=7.0Hz); IR(cm^{-1}): 2927.1, 2854.5, 1754.4, 1480.0, 1464.4, 1396.6, 1271.0, 1113.7, 757.3; MS(HRMS-FAB) m/Z 1886.1481 ([M+Cs]+, calcd. For $C_{108}H_{168}O_{18}Cs$, 1886.1285, error 10.4 ppm)

Mono-ol



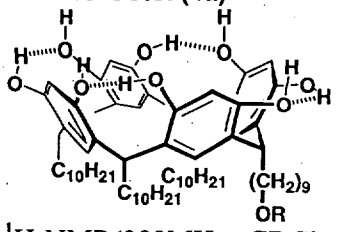
^{1}H-NMR(600MHz, $CDCl_3$, δ): 7.31(brs, 2H), 6.97(s, 1H), 6.96(s, 1H), 6.64(s, 1H), 6.63(s, 1H), 6.05(brs, 2H), 4.18(brd, 4H, J= 11.5Hz), 3.58(t, 2H, J=6.7Hz), 1.87(m, 4H), 1.72(m, 4H), 1.51(m, 2H), 1.38(s, 36H), 1.3~1.1(m, 60H), 1.20(s, 36H), 0.86(t, 9H, J=7.0Hz); IR(cm^{-1}): 2959.1, 2928.1, 2855.0, 2256.5, 1753.4, 1479.9, 1463.3, 1397.1, 1368.6, 1271.3, 1116.8, 1028.6, 909.0, 734.6; MS(HRMS-FAB): m/Z 1856.1043 ([M+Cs]+, calcd. For $C_{107}H_{166}O_{17}Cs$, 1856.1179, error 7.3 ppm)

TBDMS-ether



^{1}H-NMR(600MHz, $CDCl_3$, δ); 7.31(s, 2H), 6.97(s, 2H), 6.64(s, 2H), 6.05(s, 2H), 4.19(brd, 4H, J=5.6Hz), 3.57(t, 2H, J=6.4Hz), 1.87(m, 4H), 1.73(m, 4H), 1.48(m, 2H), 1.38(s, 36H), 1.3~1.1(m, 60H), 1.15(s, 36H), 0.86(m, 18H), 0.0(s, 6H); IR(cm^{-1}): 2958.1, 2928.6, 2855.4, 1752.5, 1479.9, 1463.7, 1397.0, 1368.7, 1271.2, 1117.3, 1028.5, 908.9, 734.7, 648.2; MS(HRMS-FAB) m/Z 1970.2245 ([M+Cs]+, calcd. For $C_{113}H_{180}O_{17}SiCs$, 1970.2044, error 10.2 ppm)

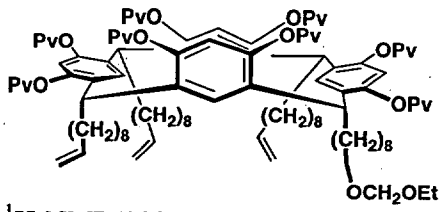
TBDMS-Octol (4a)



4a R = TBDMS

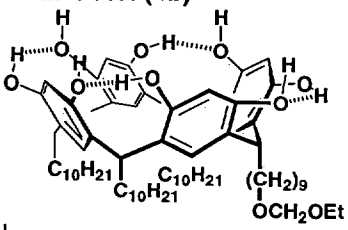
^{1}H-NMR(300MHz, $CDCl_3$, δ); 9.8~9.2 (br, 8H), 7.15(s, 4H), 6.06(s, 4H), 4.28(br, 4H), 3.58(br, 2H), 2.6~0.7(m, 88H), 0.02(s, 6H)

EOM-ether



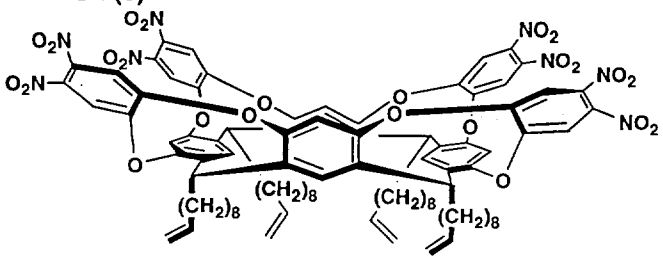
^{1}H-NMR(300MHz, $CDCl_3$, δ); 7.28(s, 2H), 6.92(s, 2H), 6.62(s, 2H), 6.01(s, 2H), 4.63(s, 2H), 4.15(br, 4H), 3.7~3.4(m, 4H), 2.0~0.8(m, 82H)

EOM-Octol (4b)



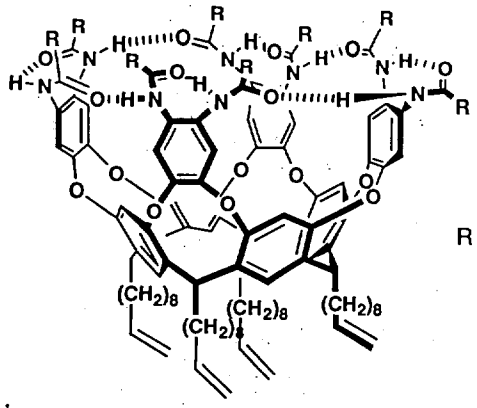
^{1}H-NMR(300MHz, $CDCl_3$, δ); 9.7~9.2(br, 8H), 7.14(s, 4H), 6.03(s, 4H), 4.61(s, 2H), 4.22(s, 4H), 3.6~3.35(m, 4H), 2.4~0.7(m, 82H)

Oct-NO2 (8)



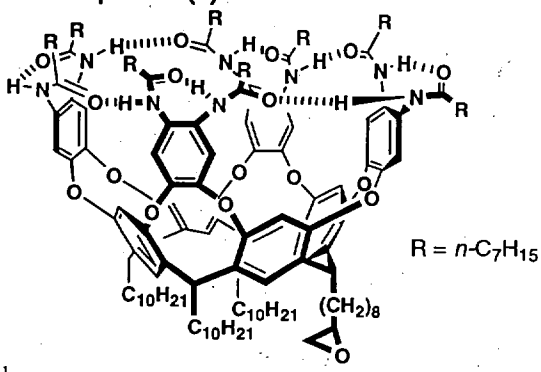
^{1}H-NMR(300MHz, $CDCl_3$, δ); 7.71(s, 4H), 7.63(s, 4H), 7.20~6.85(m, 6H), 6.19(s, 2H), 5.86~5.71(m, 4H), 5.00~4.90(m, 8H), 4.00~3.85(m, 4H), 2.20~1.80(m, 16H), 1.60~1.05(m, 48H)

oct-amide



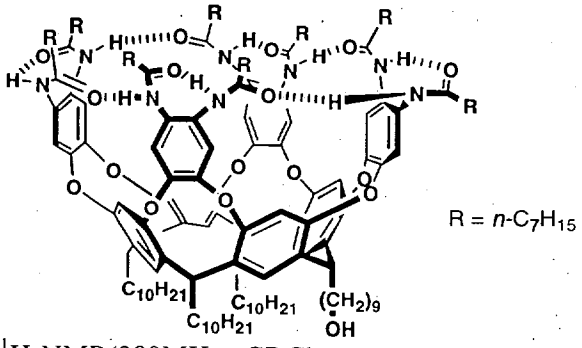
^{1}H-NMR(300MHz, $CDCl_3$, δ); 9.88(s, 4H), 9.06(s, 4H), 7.74(s, 4H), 7.4~7.1(m, 12H), 5.7(m, 8H), 4.90(m, 8H), 2.5~0.6(m, 184H)

mono-epoxide (9)



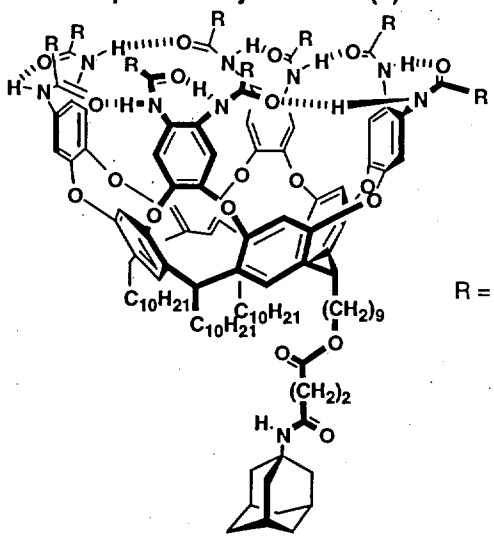
^{1}H-NMR(300MHz, $CDCl_3$, δ); 9.89(s, 4H), 9.06(s, 4H), 7.74(s, 4H), 7.4~7.1(m, 12H), 5.72(m, 7H), 4.94(m, 6H), 2.90(m, 1H), 2.74(brt, 1H, J=4.6Hz), 2.5~0.8(m, 200H)

Mono-primary alcohol (5)

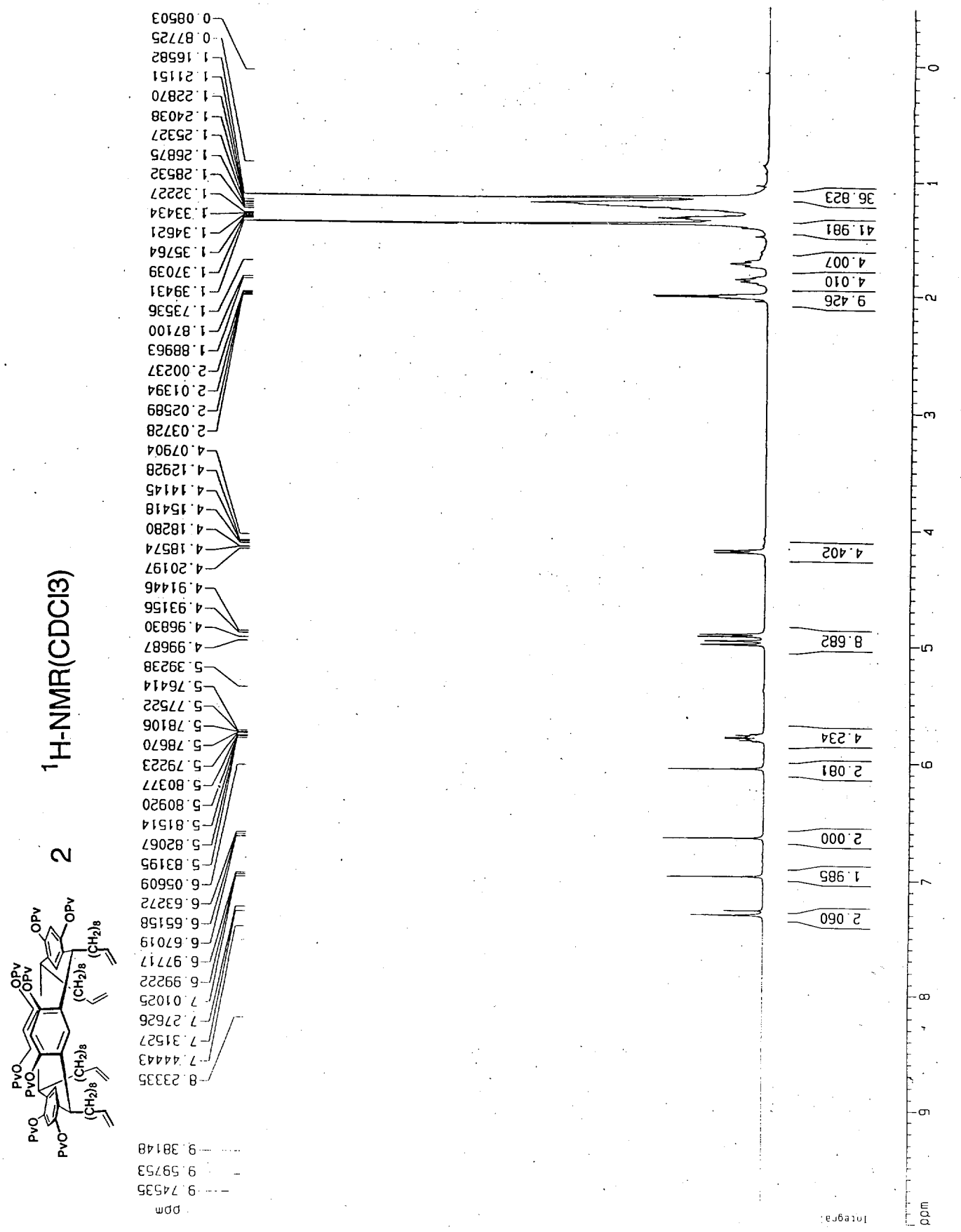


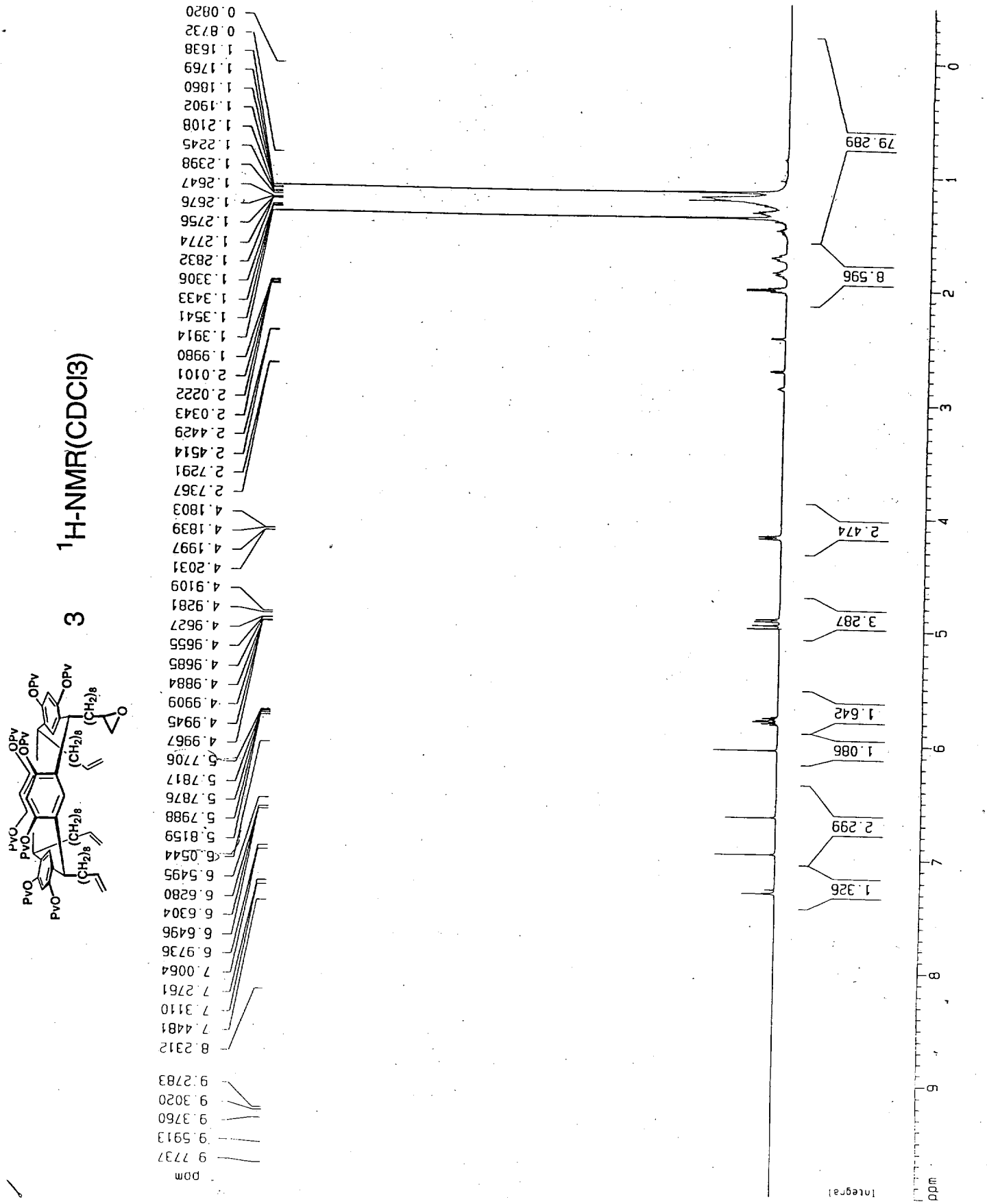
^{1}H-NMR(300MHz, $CDCl_3$, δ); 9.88(s, 4H), 9.05(s, 4H), 7.74(s, 4H), 7.3~7.2(m, 12H), 5.74(m, 4H), 3.65(brt, 2H, J=7.0Hz), 2.6~0.8(m, 199H)

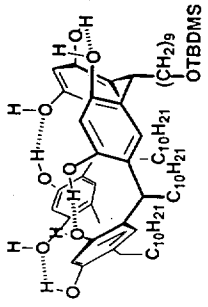
Self complementary cavitand (7)



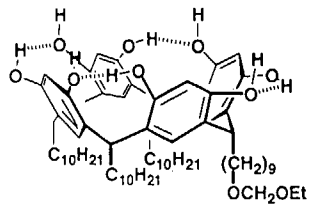
^{1}H-NMR(600MHz, $CDCl_3$, δ); 9.90(s, 4H), 9.08(s, 4H), 7.72(s, 4H), 7.30(s, 4H), 7.24(s, 4H), 7.23(s, 4H), 5.77(m, 4H), 5.32(br, 1H), 4.08(t, 2H, J=6.7Hz), 2.6~0.8(m, 218H); MALDI-HRMS m/Z 2731.8798 ($[M+Na]^+$, calcd. For $C_{169}H_{249}N_9O_{19}Na$, 2731.8692, error 3.9 ppm)


^{1}H-NMR(CDCl3)
2
OPv
OPv
OPv
OPv
PvO
PvO
PvO
PvO
(CH2)8
(CH2)8
(CH2)8
(CH2)8
0.08503
0.87725
1.16582
1.21151
1.22870
1.24038
1.25327
1.26875
1.28532
1.32227
1.33434
1.34621
1.35764
1.37039
1.39431
1.73536
1.87100
1.88963
2.00237
2.01394
2.02589
2.03728
4.07904
4.12928
4.14145
4.15418
4.18280
4.18574
4.20197
4.91446
4.93156
4.96830
4.99687
5.39238
5.76414
5.77522
5.78106
5.78670
5.79223
5.80377
5.80920
5.81514
5.82067
5.83195
6.05609
6.63272
6.65158
6.67019
6.97717
6.99222
7.01025
7.27626
7.31527
7.44443
8.23335
9.38148
9.59753
9.74535
ppm
36.823
41.981
4.007
4.010
9.426
4.402
8.682
4.234
2.081
2.000
1.985
2.060
Integra
ppm

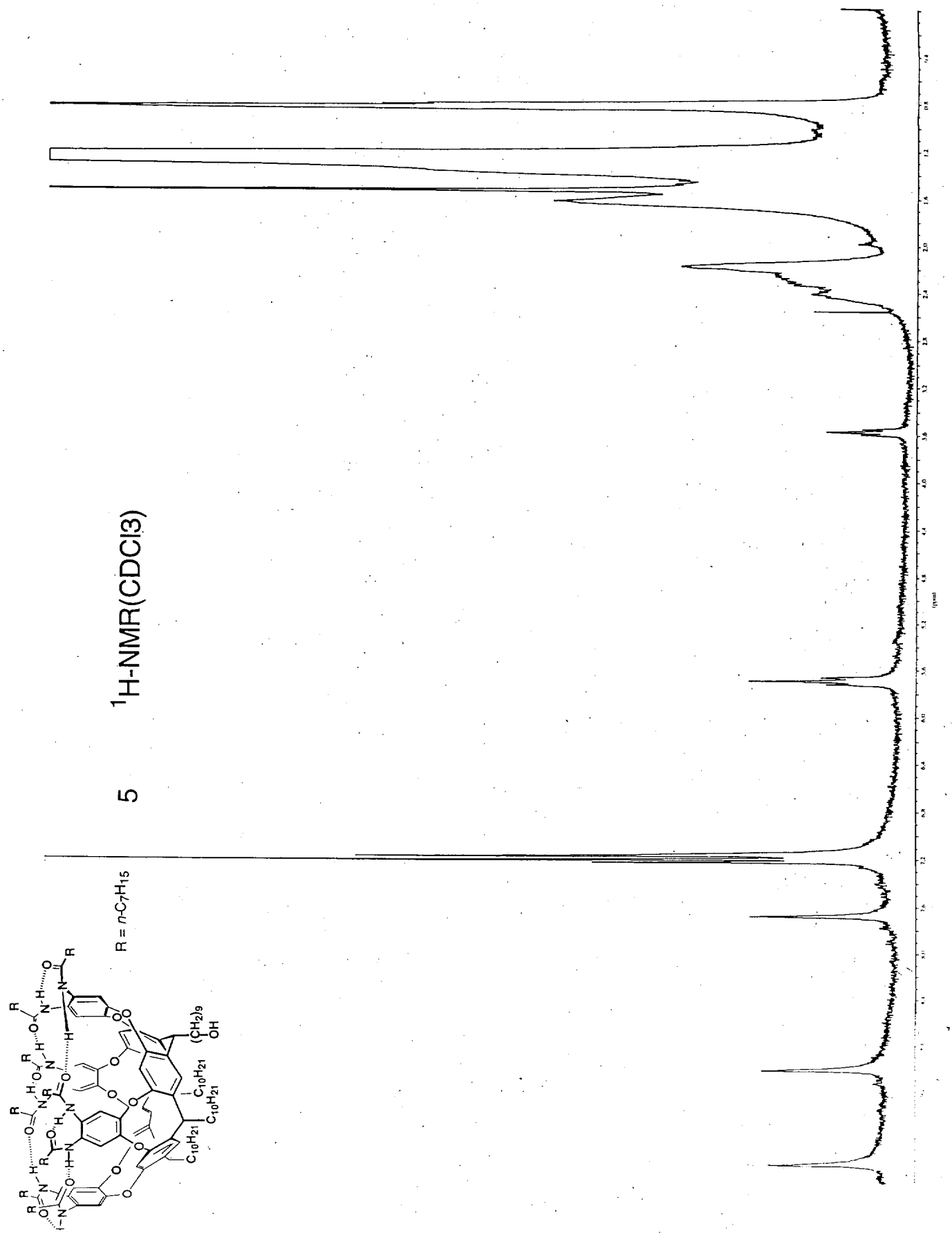

1H-NMR(CDCl3)
3
OPv
OPv
OPv
OPv
PvO
PvO
PvO
PvO
(CH2)8
(CH2)8
(CH2)8
(CH2)8
O
0.0820
0.8732
1.1638
1.1769
1.1860
1.1902
1.2108
1.2245
1.2398
1.2647
1.2676
1.2756
1.2774
1.2832
1.3306
1.3433
1.3541
1.3914
1.9980
2.0101
2.0222
2.0343
2.4429
2.4514
2.7291
2.7367
4.1803
4.1839
4.1997
4.2031
4.9109
4.9281
4.9627
4.9655
4.9685
4.9884
4.9909
4.9945
4.9967
5.7706
5.7817
5.7876
5.7988
5.8159
6.0544
6.5495
6.6280
6.6304
6.6496
6.9736
7.0064
7.2761
7.3110
7.4481
8.2312
9.2783
9.3020
9.3760
9.5913
9.7737
ppm
79.289
8.596
2.474
3.287
1.642
1.086
2.299
1.326
Integral
0
1
2
3
4
5
6
7
8
9
ppm

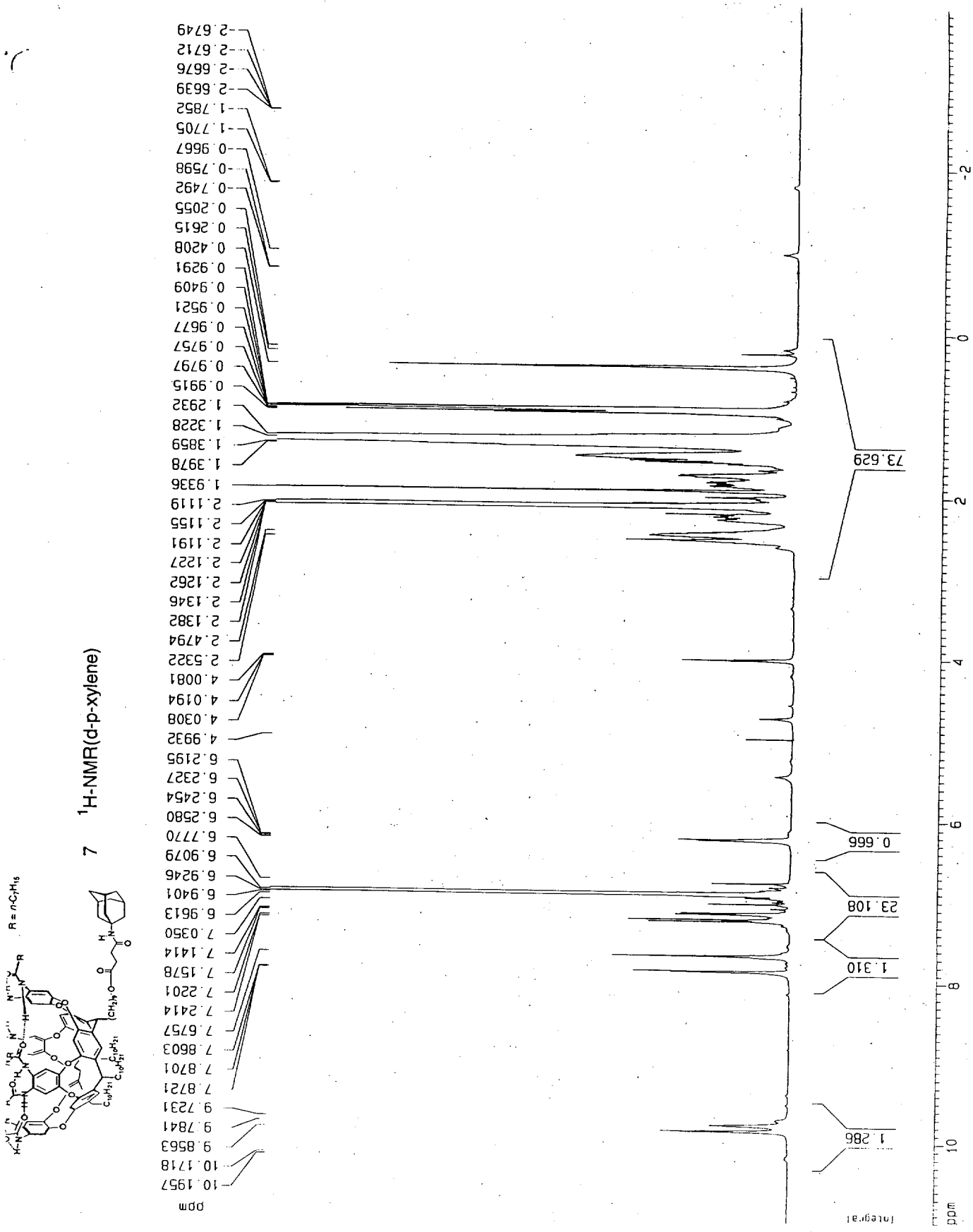


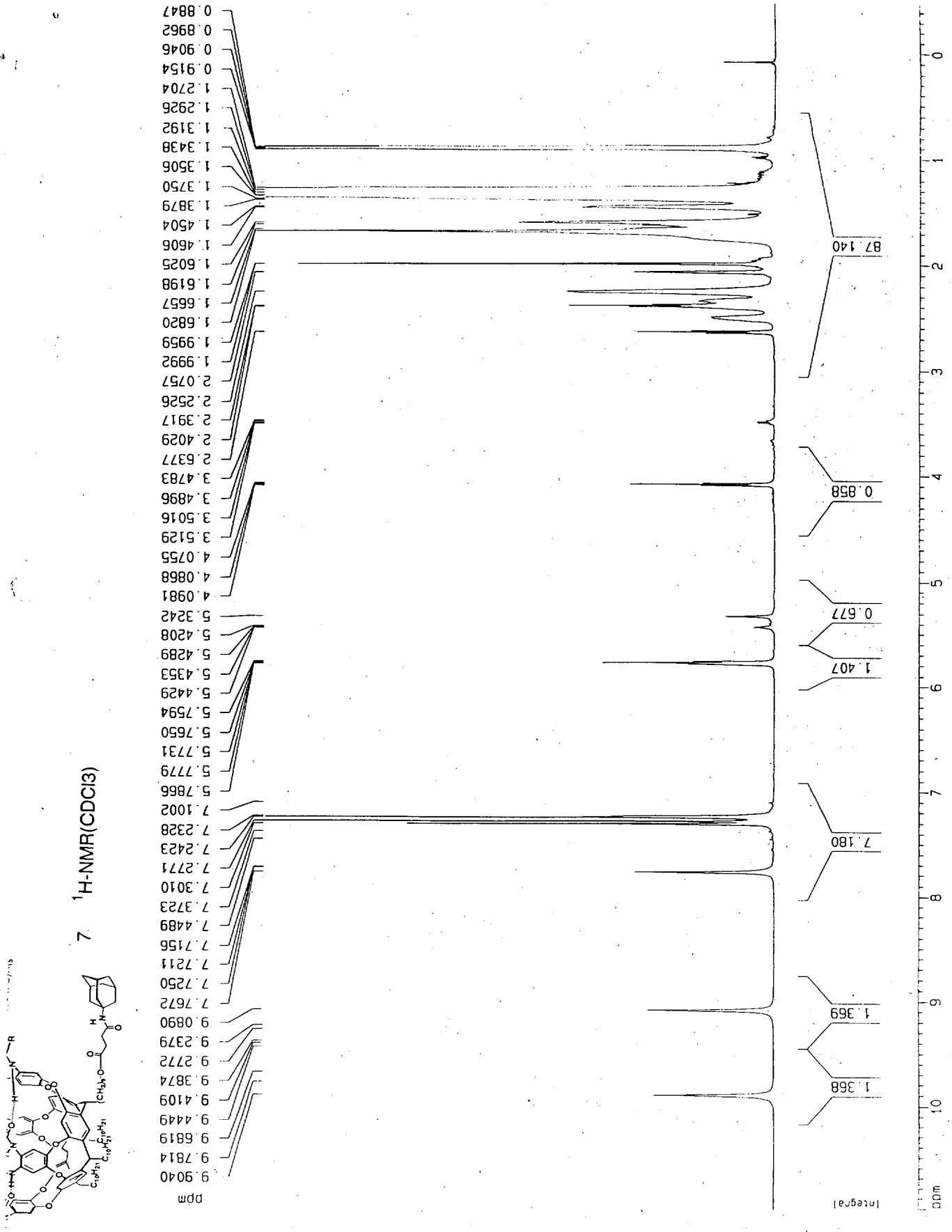
4a ^{1}H-NMR(CDCl3)



4b ^{1}H-NMR(CDCl3)




7
^{1}H-NMR(d-p-xylene)
R = n-C_7H_{15}
-2.6749
-2.6712
-2.6676
-2.6639
-1.7852
-1.7705
-0.9667
-0.7598
-0.7492
0.2055
0.2615
0.4208
0.9291
0.9409
0.9521
0.9677
0.9757
0.9797
0.9915
1.2932
1.3228
1.3859
1.3978
1.9336
2.1119
2.1155
2.1191
2.1227
2.1262
2.1346
2.1382
2.4794
2.5322
4.0081
4.0194
4.0308
4.9932
6.2195
6.2327
6.2454
6.2580
6.7770
6.9079
6.9246
6.9401
6.9613
7.0350
7.1414
7.1578
7.2201
7.2414
7.6757
7.8603
7.8701
7.8721
9.7231
9.7841
9.8563
10.1718
10.1957
ppm
73.629
0.666
23.108
1.310
1.286
Integral
ppm



9
^{1}H-NMR(CDCl3)
R = n-C7H15
C10H21
C10H21
C10H21
(CH2)8