Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

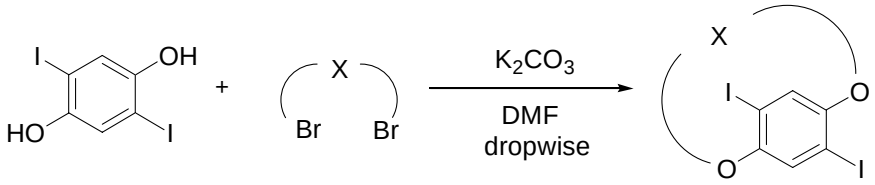
The first asymmetric Sonogashira coupling for the enantioselective generation of planar chirality of paracyclophanes

Kazumasa Kanda, Tamami Koike, Kohei Endo and Takanori Shibata*

General

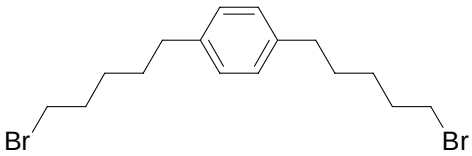
All reactions were examined under an argon atmosphere. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 using TMS as an internal standard and $CDCl_3$ was used as a solvent. Mass spectra were measured with JEOL JMS-SX102A and elemental analyses with Perkin Elmer PE2400II. Optical rotations were measured with Jasco DIP-1000 polarimeter.

Synthetic pathway of diiododioxa[n, n]paracyclophane (1)



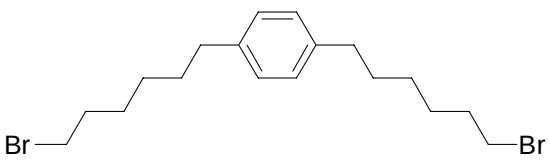
Syntheses of dibromides

Representative procedure. To a solution of 1,4-bis(6-hydroxy-1-hexyl)benzene[1] (0.765 g, 2.75 mmol) in CH_2Cl_2 (27 mL) at 0 °C was added CBr_4 (2.79 g, 8.24 mmol) and PPh_3 (1.92 g, 6.87 mmol). The solution was stirred at room temperature for 5 min, then washed with saturated $NaHCO_3$ solution and brine, and dried Na_2SO_4. The solvent was removed under reduced pressure, and the crude products were purified by flash column chromatography (Hexane/AcOEt = 50/1) to give **3b** (1.05 g, 95 %).



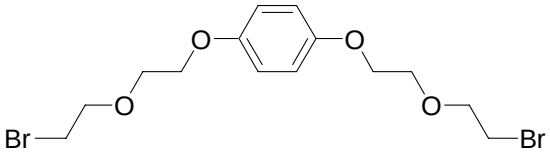
1,4-bis(5-bromo-1-pentyl)benzene (3a):

3a was obtained by using the same protocol used for the preparation of **3b** by substituting 1,4-bis(5-hydroxy-1-pentyl)benzene[1] for 1,4-bis(6-hydroxy-1-hexyl)benzene. Colorless oil; IR (CH_2Cl_2) 2933, 2856, 1514, 1460, 1263, 1246, 821, 644, 561 cm^{-1}; ^1H NMR δ= 1.48 (quint, *J*= 7.4 Hz, 4H), 1.63 (quint, *J*= 7.4 Hz, 4H), 1.89 (quint, *J*= 7.4 Hz, 4H), 2.59 (t, *J*= 7.4 Hz, 4H), 3.40 (t, *J*= 7.4 Hz, 4H), 7.09 (s, 4H); ^{13}C NMR δ=27.8, 30.7, 32.7, 33.8, 35.3, 128.3, 140.0; HRMS (FAB^+) for M found m/z 376.0195, calcd for $C_{16}H_{24}{}^{79}Br^{81}Br$: 376.0224.



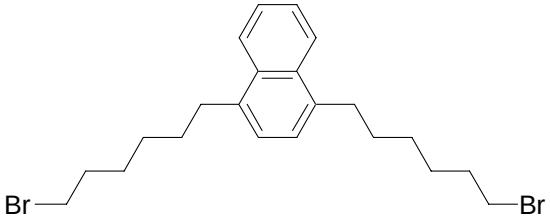
1,4-Bis(6-bromo-1-hexyl)benzene (3b):

White solid. mp 34 °C; IR (CH_2Cl_2) 2931, 2854, 1513, 1461, 1252, 725, 644, 584 cm^{-1}; ^1H NMR δ= 1.35 (quint, *J*= 7.4 Hz, 4H), 1.46 (quint, *J*= 7.4 Hz, 4H), 1.62 (quint, *J*= 7.4 Hz, 4H), 1.85 (quint, *J*= 7.4 Hz, 4H), 2.57 (t, *J*= 7.4 Hz, 4H), 3.40 (t, *J*= 7.4 Hz, 4H), 7.08 (s, 4H); ^{13}C NMR δ=28.0, 28.4, 31.3, 32.7, 34.0, 35.4, 128.3, 139.8; HRMS (FAB^+) for M^+ found m/z 402.0542, calcd for $C_{18}H_{28}Br_2$: 402.0558.



1,4-Bis[2-(2-bromoethoxy)ethoxy]benzene (3c):

3c was obtained by using the same protocol as **3b** except that 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene[2] was used in place of 1,4-bis(6-hydroxy-1-hexyl)benzene and purified by flash column chromatography (Hexane/AcOEt = 5/1). White solid. 42 °C IR (CH_2Cl_2) 2924, 2871, 1508, 1454, 1279, 1230, 1128, 827 cm^{-1}; ^1H NMR δ= 3.50 (t, *J*= 6.3 Hz, 4H), 3.86 (t, *J*= 4.6 Hz, 4H), 3.88 (t, *J*= 6.3 Hz, 4H), 4.09 (t, *J*= 4.6 Hz, 4H), 6.85 (s, 4H); ^{13}C NMR δ= 30.2, 68.1, 69.8, 71.4, 115.6, 153.1; HRMS (FAB^+) for M found m/z 409.9739, calcd for $C_{14}H_{20}Br_2O_4$: 409.9728.

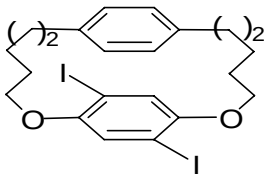


1,4-Bis(6-bromo-1-hexyl)naphthalene (3d):

3d was obtained by using the same protocol as **3b** except that 1,4-bis(6-hydroxy-1-hexyl)naphthalene was used in place of 1,4-bis(6-hydroxy-1-hexyl)benzene. Colorless oil; IR (CH_2Cl_2) 2931, 2856, 1463, 1255, 759 cm^{-1}; ^1H NMR δ= 1.37-1.58 (m, 8H), 1.76 (quint, *J*= 7,2 Hz, 4H), 1.87 (quint, *J*= 6.9 Hz, 4H), 3.04 (t, *J*= 7.8 Hz, 4H), 3.40 (t, *J*= 6.8 Hz, 4H), 7.22 (s, 2H), 7.50 (dd, J= 3.2 Hz, 6.4 Hz, 2H), 8.05 (dd, J= 3.2 Hz, 6.4 Hz, 2H); ^{13}C NMR δ=28.1, 28.9, 30.6, 32.8, 33.0, 33.9, 124.5, 125.2, 125.6, 132.2, 136.8; HRMS (FAB^+) for M^+ found m/z 454.0684, calcd for $C_{22}H_{30}{}^{79}Br^{81}Br$: 454.0694.

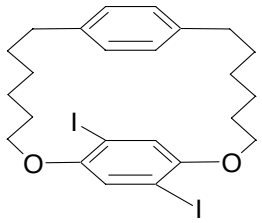
Syntheses of diiododioxaparacyclophanes.

Representative procedure: 2,5-diiodohydroquinone[3] (362.3 mg, 1.0 mmol) and 1,4-bis(6-bromo-1-hexyl)benzene **3b** (404.7 mg, 1.0 mmol) in DMF (30 mL) were added within 6 h to a suspension of K_2CO_3 (346.3 mg, 2.5 mmol) in DMF (50 mL) at 120°C. The solvent was removed under reduced pressure to about one ten of its original volume. The solution was filtered and washed with EtOAc. The filtrate was washed with 1N HCl, saturated $NaHCO_3$ solution, water and brine, and dried Na_2SO_4. The solvent was removed under reduced pressure, and the crude products were purified by thin-layer chromatography (Hexane/CH_2Cl_2 = 4/1) to give **1b** (284.1 mg, 47 %).



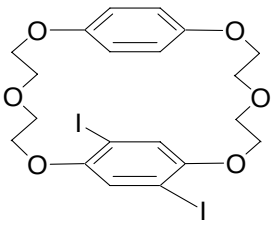
20,23-Diiodo-1,18-dioxa[6.6]paracyclophane (1a).

1a was obtained by using the same protocol as **1b** except that **3a** was used in place of **3b**. White solid. mp 84 °C; IR (CH_2Cl_2) 2925, 2854, 1475, 1466, 1342, 1203, 1051, 1020, 728 cm^{-1}; ^1H NMR δ= 1.10-1.24 (m, 4H), 1.36-1.50 (m, 2H), 1.57-1.74 (m, 6H), 2.48-2.61 (m, 4H), 4.13-4.19 (m, 4H), 6.97(s, 4H), 7.04 (s, 2H); ^{13}C NMR δ= 24.5, 29.2, 30.1, 34.5, 68.7, 86.2, 122.8, 128.5, 138.6, 151.4; HRMS (FAB^+) for M^+ found m/z 576.0025, calcd for $C_{22}H_{26}I_2O_2$: 576.0022. Two enantiomers were observed by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min and 8 min).



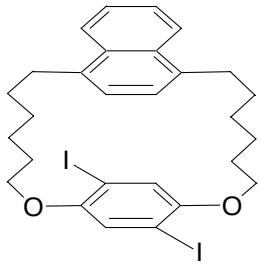
22,25-Diiodo-1,20-dioxa[7.7]paracyclophane (1b).

White solid. mp 146 °C; IR (CH_2Cl_2) 2931, 2858, 1483, 1460, 1342, 1203, 1053, 989, 854 cm^{-1}; ^1H NMR δ= 1.05-1.24 (br, 4H), 1.28-1.43 (br, 2H), 1.43-1.58 (br, 4H), 1.58-1.74 (br, 2H), 1.74-1.98 (br, 4H), 2.37-2.60 (br, 4H), 3.83-4.18 (br, 4H), 6.72 (s, 4H), 7.15 (s, 2H); ^{13}C NMR δ= 23.1, 25.2, 27.2, 29.8, 33.2, 68.1, 86.5, 122.8, 128.4, 139.0, 151.8; HRMS (FAB^+) for M^+ found m/z 604.0333, calcd for $C_{24}H_{30}I_2O_2$: 604.0335. Anal. Calcd for $C_{24}H_{30}I_2O_2$: C, 47.70; H, 5.00. Found: C, 47.76; H, 5.00.



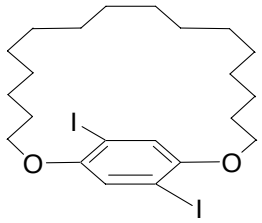
22,25-Diiodo-1,4,7,14,17,20-hexaoxa[7.7]paracyclophane (1c).

1c was obtained by using the same protocol as **1b** except that **3c** was used in place of **3b**, and purified by thin-layer chromatography (benzene/EtOAc =20/1) to give **1c**. White solid. mp 147 °C; IR (CH_2Cl_2) 2921, 2864, 1504, 1479, 1209, 1138, 1065, 906, 825 cm^{-1}; ^1H NMR δ= 3.70-4.22 (m, 16H), 6,59 (s, 4H), 7.04 (s, 2H); ^{13}C NMR δ= 69.0, 69.7, 69.8, 70.3, 86.1, 116.0, 122.8, 152.2, 152.3; HRMS (FAB^+) for M found m/z 611.9497, calcd for $C_{20}H_{22}O_6$: 611.9506.



24,27-Diiodo-1,22-dioxa[7](1,4)naphthaleno[7]paracyclophane (1d).

1d was obtained by using the same protocol as **1b** except that **3d** was used in place of **3b**. White solid. mp 200 °C; IR (CH_2Cl_2) 2927, 2856, 1483, 1460, 1344,1203, 1055, 993, 985, 756, 735 cm^{-1}; ^1H NMR δ= 1.00-1.29 (br, 4H), 1.30-1.47 (br, 2H), 1.56-1.77 (br, 6H), 1.77-1.91 (br, 2H), 1.91-2.15 (br, 2H), 2.69-2.98 (br, 2H), 2.98-3.31 (br, 2H), 3.82-4.21 (br, 4H), 6,46 (s, 2H), 7.18 (s, 2H), 7.44 (dd, *J*= 3.2, 6.6 Hz, 2H), 8.00 (dd, *J*= 3.2, 6.6 Hz, 2H); ^{13}C NMR δ= 22.9, 25.2, 27.4, 28.3, 30.2, 68.2, 86.6, 123.0, 124.5, 124.9, 126.3, 132.2, 135.5, 152.0; Anal. Calcd for $C_{24}H_{30}I_2O_2$: C, 51.39; H, 4.93. Found: C, 51.40; H, 4.88.

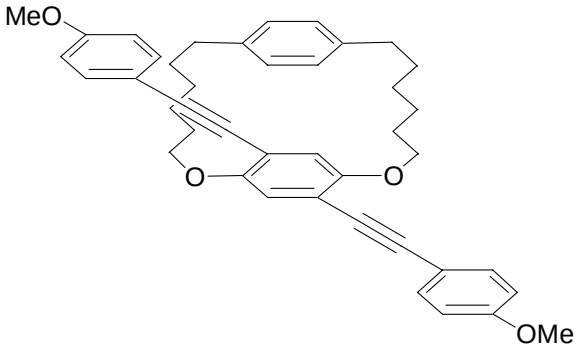


20,23-Diiodo-1,18-dioxa[18]paracyclophane (1e).

1e was obtained by using the same protocol as **1b** except that 1,16-dibromohexadecane[4] was used in place of **3b**. White solid. mp 84 °C; IR (CH_2Cl_2) 2924, 2852, 1483 1460, 1342, 1207, 1053, 997, 854 cm^{-1}; ^1H NMR δ= 1.05-1.14 (br, 8H), 1.17-1.34 (m, 12H), 1.41-1.61 (br, 4H), 1.67-1.82 (br, 4H), 4.08 (t, *J*= 5.9 Hz, 4H), 7.19 (s, 2H); ^{13}C NMR δ= 23.9, 26.7, 27.5, 27.9, 28.1, 28.8, 29.4, 68.8, 86.2, 122.9, 152.2; HRMS (FAB^+) for M^+ found m/z 584.0627, calcd for $C_{22}H_{34}I_2O_2$: 584.0648.

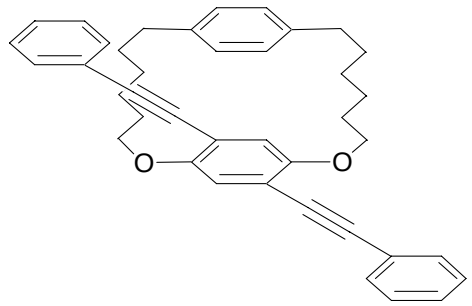
Typical Experimental Procedure for Enantionselective Sonogashira Coupling.

A solution of $PdCl_2(CH_3CN)_2$ (1.3 mg, 0.005 mmol) and TANIAPHOS1 (3.4 mg, 0.005 mmol) in THF (0.2 ml) was stirred for 10 min. To the solution were added diiodoparacyclophane (0.05 mmol) in THF (0.8 ml), alkyne (0.2 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol) and CuI (1.0 mg, 0.005 mmol) in order. The resulting mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After the reaction was complete, to the mixture was added water, and extracted with ethyl acetate. The organic layer was washed with brine, dried Na_2SO_4. The solvent was removed under reduced pressure, and the crude products were purified by thin-layer chromatography to give pure product.



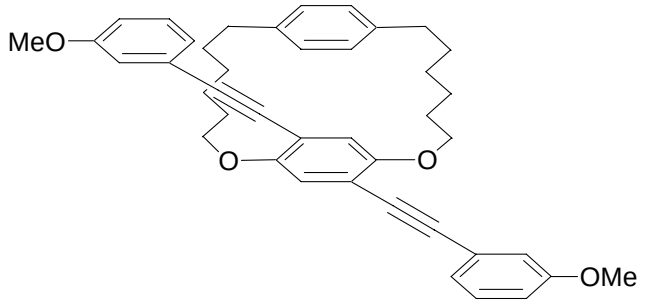
22,25-Bis{2-(4-methoxyphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2ba).

28.3 mg (91 %). Yellow solid. mp 136 °C; IR (CH_2Cl_2) 2933, 2856, 1604, 1515, 1247, 1203, 1031, 831 cm^{-1}; ^1H NMR δ= 1.13-1.29 (m, 4H), 1.32-1.45 (m, 2H), 1.45-1.58 (m, 4H), 1.63-1.77 (m, 2H), 1.78-1.96 (m, 4H), 2.40-2.56 (m, 4H), 3.83 (s, 6H), 3.98-4.09 (m, 2H), 4.09-4.19 (m, 2H), 6.82 (s, 4H), 6.89 (d, *J*= 8.8 Hz, 4H), 6.96 (s, 2H), 7.49 (d, *J*= 8.8 Hz, 4H); ^{13}C NMR δ= 23.3, 25.6, 27.5, 29.9, 33.6, 55.3, 67.8, 84.8, 94.7, 114.0, 114.4, 115.7, 117.5, 128.3, 133.0, 139.0, 152.8, 159.6; HRMS (FAB^+) for M^+ found m/z 612.3216, calcd for $C_{42}H_{44}O_4$: 612.3240. $[\alpha]^{26}_D$= +19.0 (*c* 1.34, $CHCl_3$, 52% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 8 min for minor isomer).



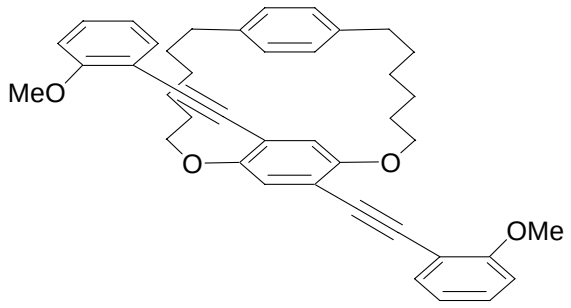
22,25-Bis{2-phenyl-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bb).

24.2 mg (87 %). Yellow solid. mp 131 °C; IR (CH_2Cl_2) 2931, 2858, 1596, 1506, 1485, 1414, 1279,1207, 999, 756, 690 cm^{-1}; ^1H NMR δ= 1.14-1.29 (m, 4H), 1.32-1.45 (m, 2H), 1.45-1.60 (m, 4H), 1.63-1.79 (m, 2H), 1.80-1.98 (m, 4H), 2.40-2.56 (m, 4H), 3.99-4.10 (m, 2H), 4.10-4.20 (m, 2H), 6.82 (s, 4H), 6.99 (s, 2H), 7.30-7.42 (m, 6H), 7.50-7.62 (m, 4H); ^{13}C NMR δ= 23.2, 25.4, 27.5, 29.9, 33.5, 67.7, 86.0, 94.8, 114.3, 117.5, 123.5, 128.2, 128.3, 128.3, 131.6, 139.0, 152.9; HRMS (FAB^+) for M^+ found m/z 552.3025, calcd for $C_{40}H_{40}O_2$: 552.3028. $[\alpha]^{24}_D$= +14.9 (*c* 1.09, $CHCl_3$, 56% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 10 min for minor isomer).



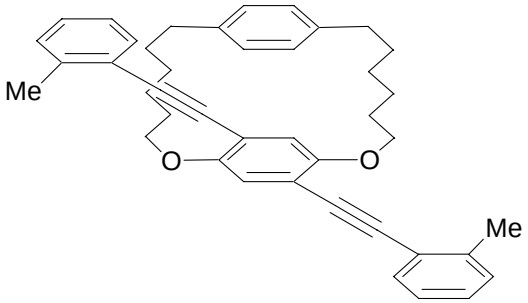
22,25-Bis{2-(3-methoxyphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bc).

28.0 mg (92 %). Yellow solid. mp 100 °C; IR (CH_2Cl_2) 2933, 2856, 1598, 1573, 1504, 1280, 1225, 1209, 1045, 993, 785, 687 cm^{-1};^{1}H NMR δ= 1.15-1.32 (m, 4H), 1.32-1.45 (m, 2H), 1.45-1.61 (m, 4H), 1.64-1.80 (m, 2H), 1.80-2.01 (m, 4H), 2.40-2.60 (m, 4H), 3.83 (s, 6H), 4.00-4.11 (m, 2H), 4.11-4.22 (m, 2H), 6.81 (s, 4H), 6.91 (d, *J*= 7.5 Hz, 2H), 6.99 (s, 2H), 7.10 (s, 2H), 7.16 (d, *J*= 7.5 Hz, 2H) 7.27 (dd, *J*= 7.5 Hz, 7.5 Hz, 2H); ^{13}C NMR δ= 23.3, 25.5, 27.5, 29.9, 33.5, 55.3, 67.7, 85.9, 94.8, 114.3, 114.9, 116.3, 117.5, 124.1, 124.5, 128.3, 129.4, 139.0, 152.9, 159.3; HRMS (FAB^+) for M^+ found m/z 612.3234, calcd for $C_{42}H_{44}O_4$: 612.3240. $[\alpha]^{26}_D$= +9.6 (*c* 1.565, $CHCl_3$, 72% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 15 min for minor isomer).



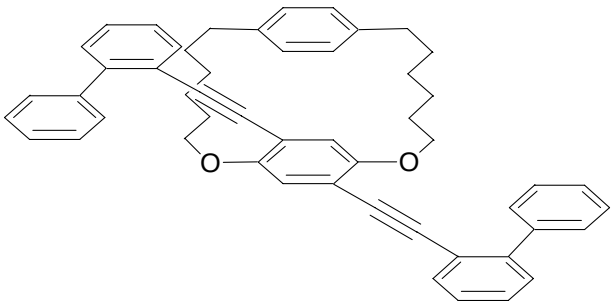
22,25-Bis{2-(2-methoxyphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bd).

28.1 mg (92 %). Yellow solid. mp 170 °C; IR (CH_2Cl_2) 2933, 2858, 1593, 1574, 1506, 1462, 1433, 1412, 1274, 1246, 1207, 1024, 752 cm^{-1}; ^{1}H NMR δ= 1.14-1.31 (m, 4H), 1.32-1.45 (m, 2H), 1.45-1.59 (m, 4H), 1.64-1.79 (m, 2H), 1.80-2.02 (m, 4H), 2.40-2.57 (m, 4H), 3.92 (s, 6H), 4.02-4.11 (m, 2H), 4.11-4.19 (m, 2H), 6.84 (s, 4H), 6.91 (d, *J*= 8.0 Hz, 2H), 6.95 (t, *J*= 7.6 Hz, 2H), 7.00 (s, 2H), 7.30 (dt, J_d= 1.6 Hz, J_t= 7.6 Hz, 2H) 7.52 (dd, *J*= 1.6 Hz, 8.0 Hz, 2H); ^{13}C NMR δ= 23.3, 25.6, 27.5, 29.9, 33.6, 55.8, 67.7, 90.2, 91.2, 110.7, 112.9, 114.6, 117.7, 120.4, 128.3, 129.6, 133.6, 139.0, 152.8, 159.9; HRMS (FAB^+) for M^+ found m/z 612.3211, calcd for $C_{42}H_{44}O_4$: 612.3240. $[\alpha]^{24}_D$= +7.8 (*c* 1.41, $CHCl_3$, 69% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 8 min for minor isomer).



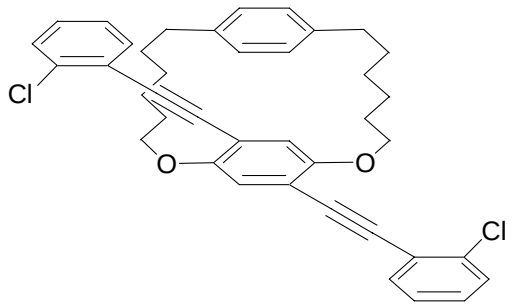
22,25-Bis{2-(2-methylphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2be).

26.1 mg (90 %). Yellow solid. mp 148 °C; IR (CH_2Cl_2) 2931, 2858, 1504, 1412, 1275, 1209, 756 cm^{-1}; ^1H NMR δ= 1.13-1.28 (m, 4H), 1.28-1.43 (m, 2H), 1.43-1.59 (m, 4H), 1.66-1.80 (m, 2H), 1.80-2.01 (m, 4H), 2.38-2.54 (m, 4H), 2.59 (s, 6H), 4.04-4.19 (m, 4H), 6.78 (s, 4H), 7.00 (s, 2H), 7.14-7.22 (m, 2H), 7.22-7.28 (m, 4H), 7.50-7.56 (m, 2H); ^{13}C NMR δ= 20.8, 23.1, 25.3, 27.5, 29.9, 33.3, 67.4, 90.0, 93.8, 114.4, 117.1, 123.3, 125.5, 128.2, 128.4, 129.4, 131.8, 139.0, 140.3, 152.7; HRMS (FAB^+) for M^+ found m/z 580.3374, calcd for $C_{42}H_{44}O_2$:580.3341. $[\alpha]^{24}_D$= +17.7 (*c* 1.28, $CHCl_3$, 62% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 7 min for minor isomer).



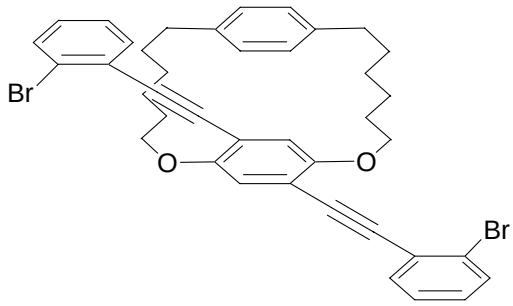
22,25-Bis{2-(2-biphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bf).

31.7 mg (90 %). Yellow solid. mp 46 °C; IR (CH_2Cl_2) 2930, 2854, 1506, 1207, 756, 698 cm^{-1}; ^1H NMR δ= 1.06-1.22 (m, 4H), 1.22-1.37 (m, 2H), 1.37-1.51 (m, 4H), 1.52-1.65 (m, 2H), 1.65-1.81 (m, 4H), 2.33-2.50 (m, 4H), 3.81-4.93 (m, 2H), 3.93-4.05 (m, 2H), 6.59 (s, 2H), 6.73 (s, 4H), 7.29-7.50 (m, 12H) 7.61-7.76 (m, 6H); ^{13}C NMR δ= 23.5, 25.7, 27.3, 29.8, 33.6, 67.7, 89.2, 94.6, 114.5, 117.9, 121.8, 127.0, 127.3, 127.8, 128.2, 128.4, 129.5, 129.5, 132.9, 139.0, 140.6, 143.8, 152.4; HRMS (FAB^+) for M found m/z 704.3636, calcd for $C_{52}H_{48}O_2$: 704.3654. $[\alpha]^{25}_D$= +5.8 (*c* 1.54, $CHCl_3$, 61% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 13 min for minor isomer).



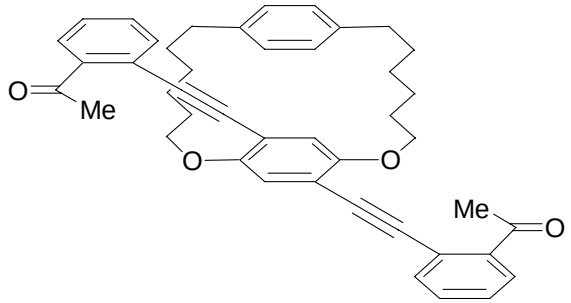
22,25-Bis{2-(2-chlorophenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bg).

25.3 mg (81 %). Yellow solid. mp 174 °C; IR (CH_2Cl_2) 2929, 2859, 2208, 1728, 1504, 1288, 1275, 1209, 1126, 1054, 754 cm^{-1}; ^1H NMR δ= 1.10-1.31 (m, 4H), 1.31-1.44 (m, 2H), 1.45-1.64 (m, 4H), 1.64-1.81 (m, 2H), 1.81-2.08 (m, 4H), 2.38-2.63 (m, 4H), 4.01-4.27 (m, 4H), 6.80 (s, 4H), 7.03 (s, 2H), 7.19-7.37 m, 4H) 7.39-7.54 (m, 2H), 7.54-7.69 (m, 2H); ^{13}C NMR δ= 23.2, 25.4, 27.4, 29.9, 33.4, 67.7, 91.1, 91.6, 114.4, 117.6, 123.4, 126.4, 128.3, 129.2, 129.3, 133.3, 135.8, 139.1, 152.9; HRMS (FAB^+) for M^+ found m/z 620.2252, calcd for $C_{40}H_{38}Cl_2O_2$: 620.2249. $[\alpha]^{24}_D$= +7.6 (*c* 0.78, $CHCl_3$, 56% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 6 min for major isomer and 10 min for minor isomer).



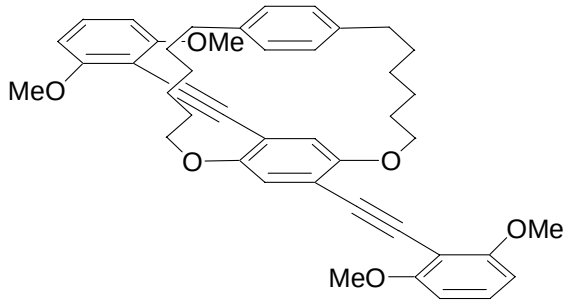
22,25-Bis{2-(2-bromophenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bh).

30.1 mg (85 %). Yellow solid. mp 157 °C; IR (CH_2Cl_2) 2975, 2931, 2858, 2206, 1593, 1572, 1506, 1485, 1446, 1412, 1382, 1373, 1275, 1246, 1209, 1115, 953, 750 cm^{-1}; ^1H NMR δ= 1.13-1.30 (m, 4H), 1.33-1.43 (m, 2H), 1.43-1.59 (m, 4H), 1.66-1.80 (m, 2H), 1.80-2.02 (m, 4H), 2.39-2.58 (m, 4H), 4.00-4.23 (m, 4H), 6.81 (s, 4H), 7.03 (s, 2H), 7.18 (dt, J_d= 1.6 Hz, J_t=7.7 Hz, 2H),7.30 (dt, J_d= 0.9 Hz, J_t=7.7 Hz, 2H),7.59 (dd, *J*= 1.6 Hz, 7.7 Hz, 2H) 7.63 (dd, *J*= 0.9 Hz, 7.7 Hz, 2H); ^{13}C NMR δ= 23.3, 25.5, 27.4, 29.9, 33.5, 67.7, 90.6, 93.4, 114.4, 117.7, 125.4, 125.7, 127.0, 128.3, 129.4, 132.5, 133.4, 139.1, 152.9; HRMS (FAB^+) for M found m/z708.1235, calcd for $C_{40}H_{38}Br_2O_2$: 708.1239. $[\alpha]^{25}_D$= +10.3 (*c* 1.37, $CHCl_3$, 72% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 8 min for minor isomer).



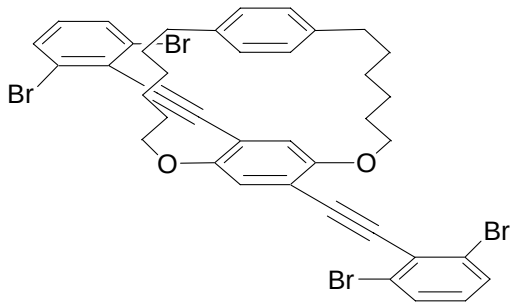
22,25-Bis{2-(2-acetylphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bi).

22.8 mg (71 %). Yellow solid. mp 96 °C; IR (CH_2Cl_2) 2931, 2856, 1684, 1504, 1412, 1279, 1207, 762 cm^{-1}; ^1H NMR δ= 1.11-1.24 (m, 4H), 1.31-1.42 (m, 2H), 1.43-1.59 (m, 4H), 1.60-1.95 (m, 6H), 2.31-2.65 (m, 4H), 2.89 (s, 6H), 3.91- 4.36 (m, 4H), 6.77 (s, 4H), 7.00 (s, 2H), 7.41 (dd, *J*=7.0 Hz, 7.0 Hz, 2H), 7.49 (dd, 7.2 Hz, 7.2 Hz, 2H), 7.67 (d, *J*= 7.3 Hz, 2H), 7.77 (d, *J*=7.6 Hz, 2H); ^{13}C NMR δ= 23.1, 25.4, 27.3, 29.9, 30.5, 33.4, 67.5, 92.1, 93.9, 114.3, 117.2, 121.8, 128.3, 128.4, 128.6, 131.3, 134.0, 139.1, 140.7, 152.9, 200.8; HRMS (FAB^+) for $[M+H]^+$ found m/z 637.3292, calcd for $C_{44}H_{45}O_4$: 637.3318. $[\alpha]^{25}_D$= +24.1 (*c* 1.07, $CHCl_3$, 77% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 50% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 4 min for major isomer and 6 min for minor isomer).



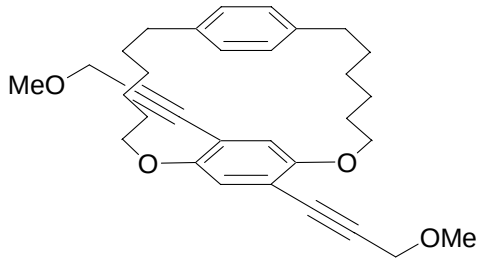
22,25-Bis{2-(2,6-dimethoxyphenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bj).

34.6 mg (99 %). Yellow solid. mp 168 °C; IR (CH_2Cl_2) 2933, 2856, 2212, 1591, 1581, 1506, 1473, 1431, 1412, 1255, 1207, 1113, 777, 729 cm^{-1}; ^1H NMR δ= 1.14-1.30 (m, 4H), 1.30-1.44 (m, 2H), 1.45-1.57 (m, 4H), 1.64-1.78 (m, 2H), 1.80-1.92 (m, 2H), 1.92-2.04 (m, 2H), 2.40-2.59 (m, 4H), 3.91 (s, 12H), 4.03-4.20 (m, 4H), 6.55 (d, *J*= 8.5 Hz, 4H), 6.85 (s, 4H), 7.02 (s, 2H), 7.22 (t, *J*= 8.5 Hz, 2H); ^{13}C NMR δ= 23.3, 25.7, 27.6, 29.9, 33.7, 56.0, 67.7, 87.1, 94.6, 102.2, 103.4, 114.8, 117.9, 128.4, 129.5, 139.0, 152.7, 161.4; HRMS (FAB^+) for M found m/z 672.3423, calcd for $C_{44}H_{48}O_6$: 672.3451. $[\alpha]^{24}_D$= -3.6 (*c* 1.58, $CHCl_3$, 66% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 7 min for major isomer and 8 min for minor isomer).



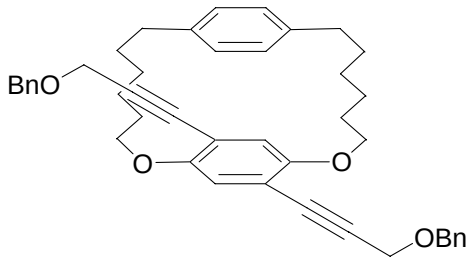
22,25-Bis{2-(2,6-dibromophenyl)-1-ethynyl}-1,20-dioxa[7.7]paracyclophane (2bk).

32.3 mg (71 %). Yellow solid. mp 140 °C; IR (CH_2Cl_2) 2931, 2858, 2216, 1541, 1502, 1440, 1421, 1402, 1433, 1281, 1209, 1190 1051, 997, 769, 737, 727, 715 cm^{-1}; ^1H NMR δ= 1.13-1.28 (m, 4H), 1.28-1.41 (m, 2H), 1.44-1.59 (m, 4H), 1.67-1.80 (m, 2H), 1.80-2.08 (m, 4H), 2.38-2.62 (m, 4H), 4.04-4.24 (m, 4H), 6.83 (s, 4H), 7.02 (t, *J*= 8.0 Hz, 2H), 7.06 (s, 2H), 7.58 (d, *J*= 8.0 Hz, 4H); ^{13}C NMR δ= 23.4, 25.5, 27.4, 30.0, 33.5, 67.7, 92.8, 95.3, 114.5, 117.9, 126.3, 127.4, 128.3, 129.6, 131.3, 139.1, 153.0; Anal. Calcd for $C_{40}H_{36}Br_4O_2$: C, 55.33; H, 4.18. Found: C, 55.28; H, 4.04. $[\alpha]^{24}_D$= +5.7 (*c* 1.81, $CHCl_3$, 72% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 6 min for major isomer and 9 min for minor isomer).



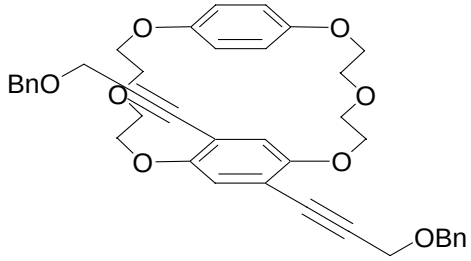
22,25-Bis(3-methoxy-1-propynyl)-1,20-dioxa[7.7]paracyclophane (2bl).

16.7 mg (73 %). Yellow oil; IR (neat) 2931, 2858, 2225, 1498, 1471, 1412, 1352, 1273, 1227, 1201, 1099, 1053, 1003, 903, 870 cm^{-1}; ^1H NMR δ= 1.07-1.24 (m, 4H), 1.26-1.40 (m, 2H), 1.41-1.59 (m, 4H), 1.59-1.72 (m, 2H), 1.72-1.87 (m, 4H), 2.39-2.56 (m, 4H), 3.48 (s, 6H), 3.91-4.13 (m, 4H), 4.39 (s, 4H), 6.78 (s, 4H), 6.88 (s, 2H) ; ^{13}C NMR δ= 23.1, 25.4, 27.3, 29.9, 33.4, 57.6, 60.5, 67.5, 82.7, 90.2, 113.8, 117.7, 128.3, 139.0, 152.7; HRMS (FAB^+) for M^+ found m/z 488.2930, calcd for $C_{32}H_{40}O_4$: 488.2927. $[\alpha]^{24}_D$= +8.3 (*c* 0.87, $CHCl_3$, 79% ee).Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 11 min for minor isomer).



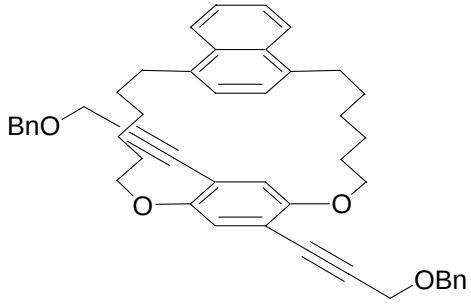
22,25-Bis(3-benzyloxy-1-propynyl)-1, 20-dioxa[7.7]paracyclophane (2bm).

27.9 mg (87 %). Yellow oil; IR (CH_2Cl_2) 2933, 2856, 1498, 1412, 1352, 1201, 1090, 1072, 1028, 1003, 737, 698 cm^{-1}; ^1H NMR δ= 1.11-1.24 (m, 4H), 1.24-1.38 (m, 2H), 1.40-1.54 (m, 4H), 1.62-1.73 (m, 2H), 1.74-1.94 (m 4H), 2.36-2.55 (m, 4H), 3.87-4.16 (m, 4H), 4.47 (s, 4H), 4.73 (s, 4H), 6.77 (s, 4H), 6.90 (s, 2H), 7.26-7.58 (m, 10H); ^{13}C NMR δ= 23.1, 25.3, 27.3, 29.8, 33.4, 58.0, 67.5, 71.4, 82.9, 90.4, 113.8, 117.7, 127.8, 128.1, 128.3, 128.4, 137.5, 139.0, 152.7; HRMS (FAB^+) for M^+ found m/z 640.3541, calcd for $C_{44}H_{48}O_4$: 640.3553. $[\alpha]^{25}_D$= +17.2 (*c* 1.26, $CHCl_3$, 78% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 6 min for major isomer and 16 min for minor isomer).



22,25-Bis(3-benzyloxy-1-propynyl)-1,4,7,14,17,20-hexaoxa[7.7]paracyclophane (2cm).

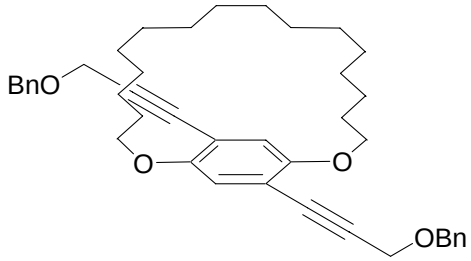
26.1 mg (81 %). 26.1 mg, 81 %; Yellow oil; IR (CH_2Cl_2) 2927, 2862, 2227, 1454, 1409, 1351, 1240, 1207, 1135, 1091, 1068, 741, 698 cm^{-1}; ^1H NMR δ= 3.66-3.74 (m, 2H), 3.77-3.86 (m, 2H), 3.88-3.97 (m, 4H), 3.98-4.08 (m, 4H), 4.10-4.23 (m, 4H), 4.42 (s, 4H), 4.70 (s, 4H), 6.60 (s, 4H), 6.82 (s, 2H), 7.28-7.50 (m, 10H); ^{13}C NMR δ= 58.1, 69.1, 69.6, 69.6, 69.9, 71.5, 82.9, 90.1, 113.2, 116.3, 117.5, 127.9, 128.1, 128.4, 137.5, 152.3, 153.0; HRMS (FAB^+) for M found m/z 648.2723, calcd for $C_{40}H_{40}O_8$: 648.2714 .$[\alpha]^{24}_D$= +5.31 (*c* 1.50, $CHCl_3$, 78% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 50% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 9 min for minor isomer).



24,27-Bis(3-benzyloxy-1-propynyl)-1,22-dioxa[7](1,4)naphthaleno[7]paracyclophane (2dm).

31.6 mg (91 %). Yellow oil; IR (CH_2Cl_2) 2935, 2858, 2225, 1498, 1412, 1352, 1227, 1201, 1090, 1072, 737, 698 cm^{-1}; ^1H NMR δ= 1.09-1.28 (m, 4H) 1.28-1.43 (m, 2H), 1.58-1.76 (m, 6H), 1.78-1.90 (m, 2H), 1.90-2.08 (m, 2H), 2.72-2.90 (m, 2H), 3.02-3.19 (m, 2H), 3.95-4.06 (m, 2H), 4.07-4.17 (m,2H), 4.48 (s, 4H), 4.74 (s, 4H), 6.61 (s, 2H), 6.93 (s, 2H), 7.27-7.52 (m, 12H), 7.99 (dd, *J*= 3.3 Hz, 6.5 Hz, 2H); ^{13}C NMR δ= 22.8, 25.4, 27.4, 28.3,

30.3, 58.0, 67.4, 71.4, 82.9, 90.6, 113.9, 117.7, 124.5, 124.8, 126.3, 127.8, 128.1, 128.4, 132.1, 135.5, 137.6, 152.9; HRMS (FAB$^+$) for M^+ found m/z 390.3710, calcd for $C_{48}H_{50}O_4$: 690.3709. $[\alpha]^{24}_D$= +40.1 (*c* 1.68, $CHCl_3$, 73% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 6 min for major isomer and 15 min for minor isomer).

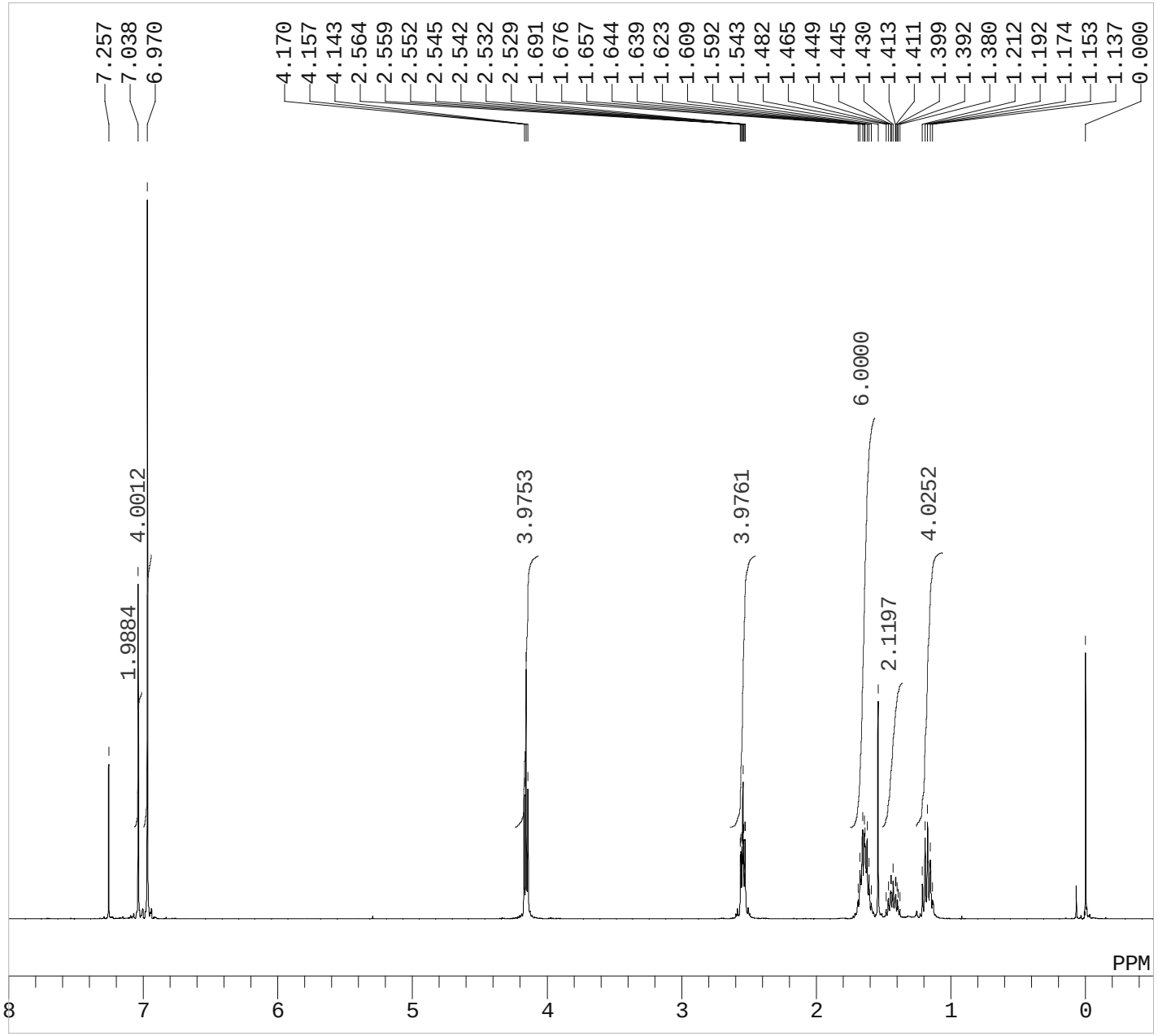


20,23-Bis(3-benzyloxy-1-propynyl)-1,18-dioxa[18]paracyclophane (2em).

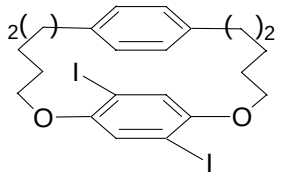
27.4 mg (89 %). Yellow oil; IR (CH_2Cl_2) 2925, 2852, 2227, 1498, 1412, 1349, 1203, 1090, 1072, 737, 698 cm^{-1}; ^{1}H NMR δ= 0.99-1.44 (m, 22H), 1.53-1.74 (m, 4H), 1.74-1.92 (m, 2H), 4.00-4.24 (m, 4H), 4.45 (s, 4H), 4.71(s, 4H), 6.93 (s, 2H), 7.28-7.51 (m, 10H); ^{13}C NMR δ= 23.9, 26.8, 27.5, 27.8, 28.1, 28.7, 29.3, 58.0, 68.3, 71.4, 82.9, 90.2, 113.6, 117.6, 127.8, 128.2, 128.4, 137.5, 153.0; HRMS (FAB$^+$) for M^+ found m/z 620.3844, calcd for $C_{42}H_{52}O_4$: 620.3866. $[\alpha]^{24}_D$= +10.8 (*c* 1.32, $CHCl_3$, 77% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel IA: 4 x 250mm, 254nm UV detector, rt, eluent: 30% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 13 min for minor isomer).

References

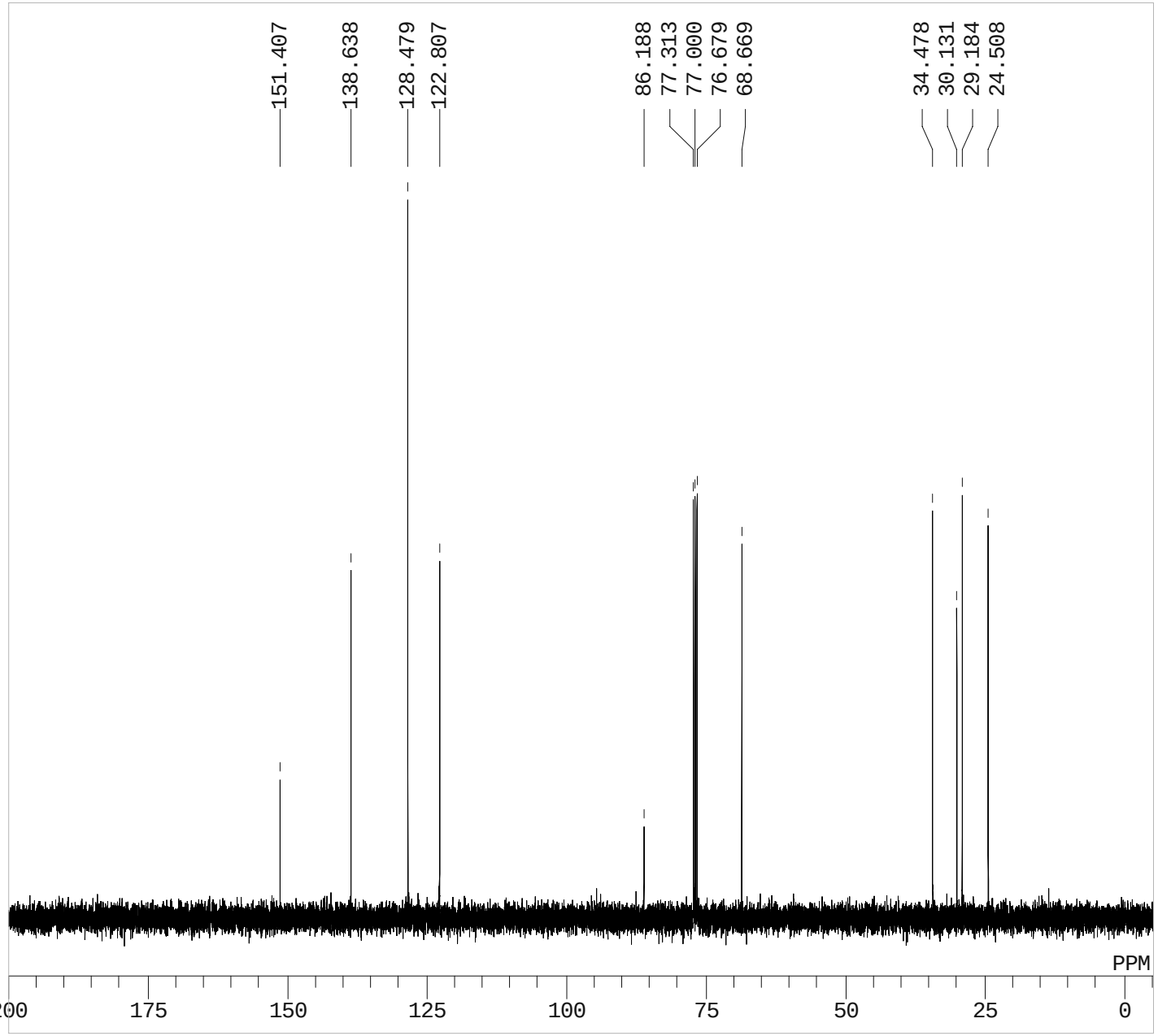
1. T. Ueda, N. Kanomata and H. Machida, *Org. Lett.* 2005, **7**, 2365.
2. P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolf, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, M. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *J.Am. Chem. Soc.* 1992, **114**, 193.
3. Q. Zhou, T. M. Swager, *J. Am. Chem. Soc.* 1995, **117**, 12593.
4. P. Y. Vuillaume, C. G. Bazuin, and J-C. Galin, *Macromolecules* 2000**, 33**, 781.



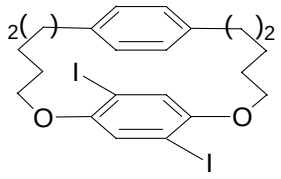
DFILE	F:\NMR\1a_1H.als
COMNT	
DATIM	Tue Oct 07 18:20:25 2008
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	7992.0 Hz
SCANS	16
ACQTM	4.100 sec
PD	2.900 sec
PW1	6.6 us
IRNUC	1H
CTEMP	28.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	18



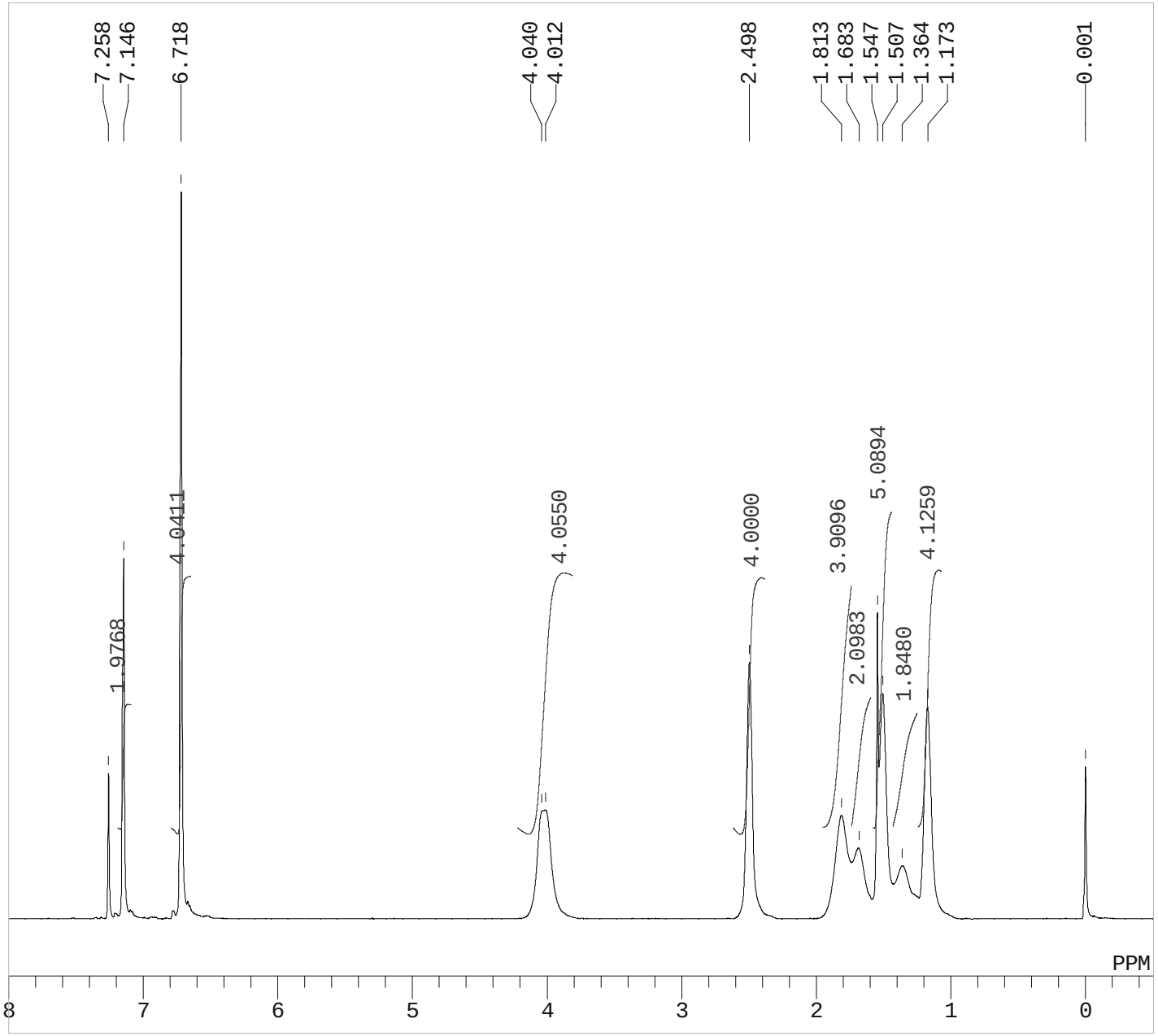
1a



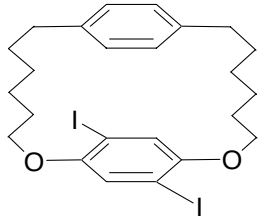
DFILE	F:\NMR\1a_13C.als
COMNT	1127
DATIM	Thu Feb 01 15:49:09 2007
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	257
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.6 us
IRNUC	1H
CTEMP	25.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



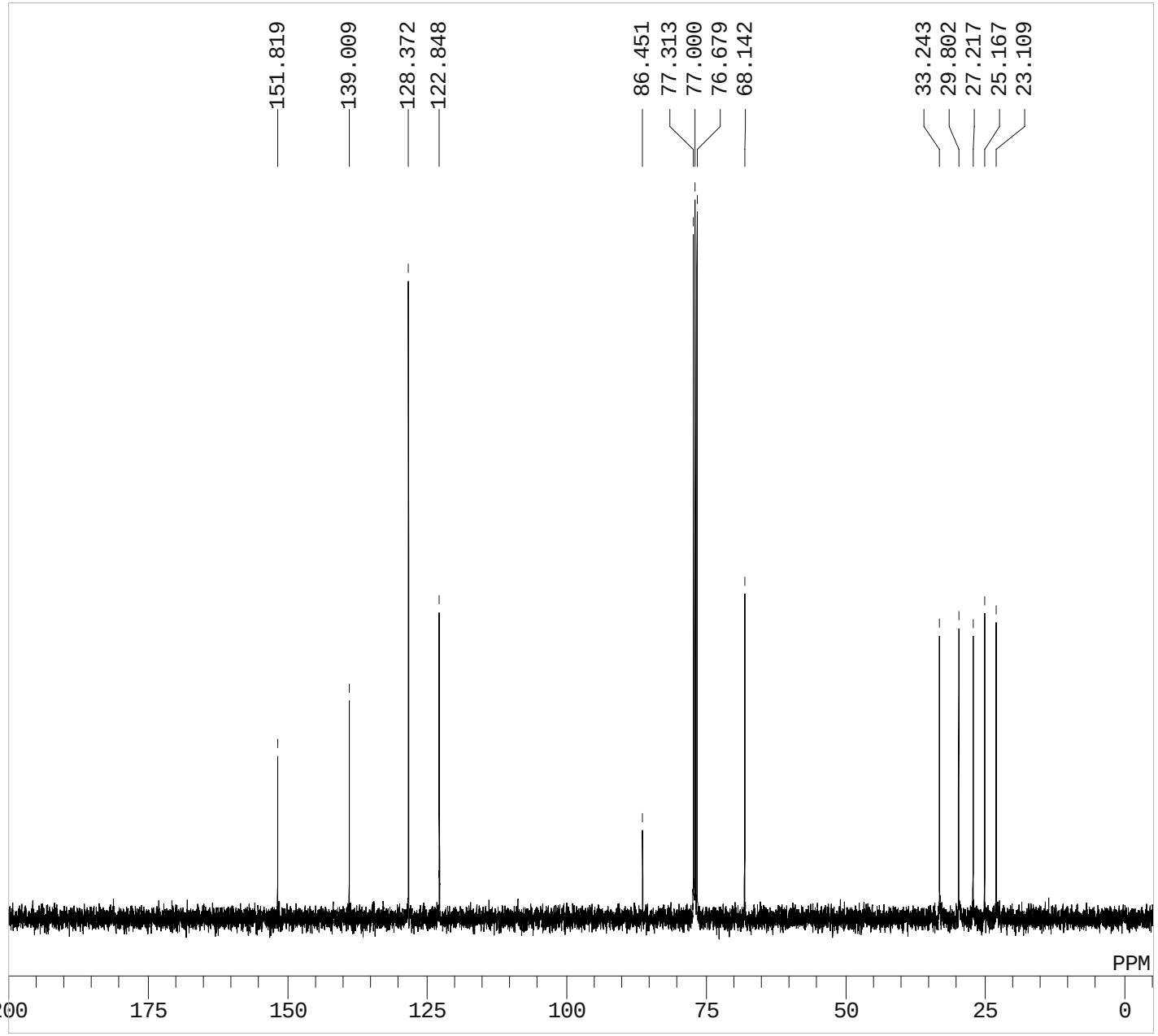
1a



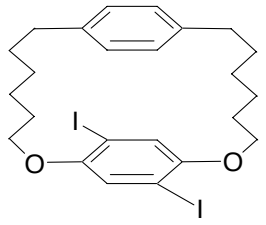

```
DFILE   F:\NMR\1b_1H.als
COMNT
DATIM   Wed Oct 11 18:31:47 2006
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS               8
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.6 us
IRNUC   1H
CTEMP           26.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.00 Hz
RGAIN             18
```



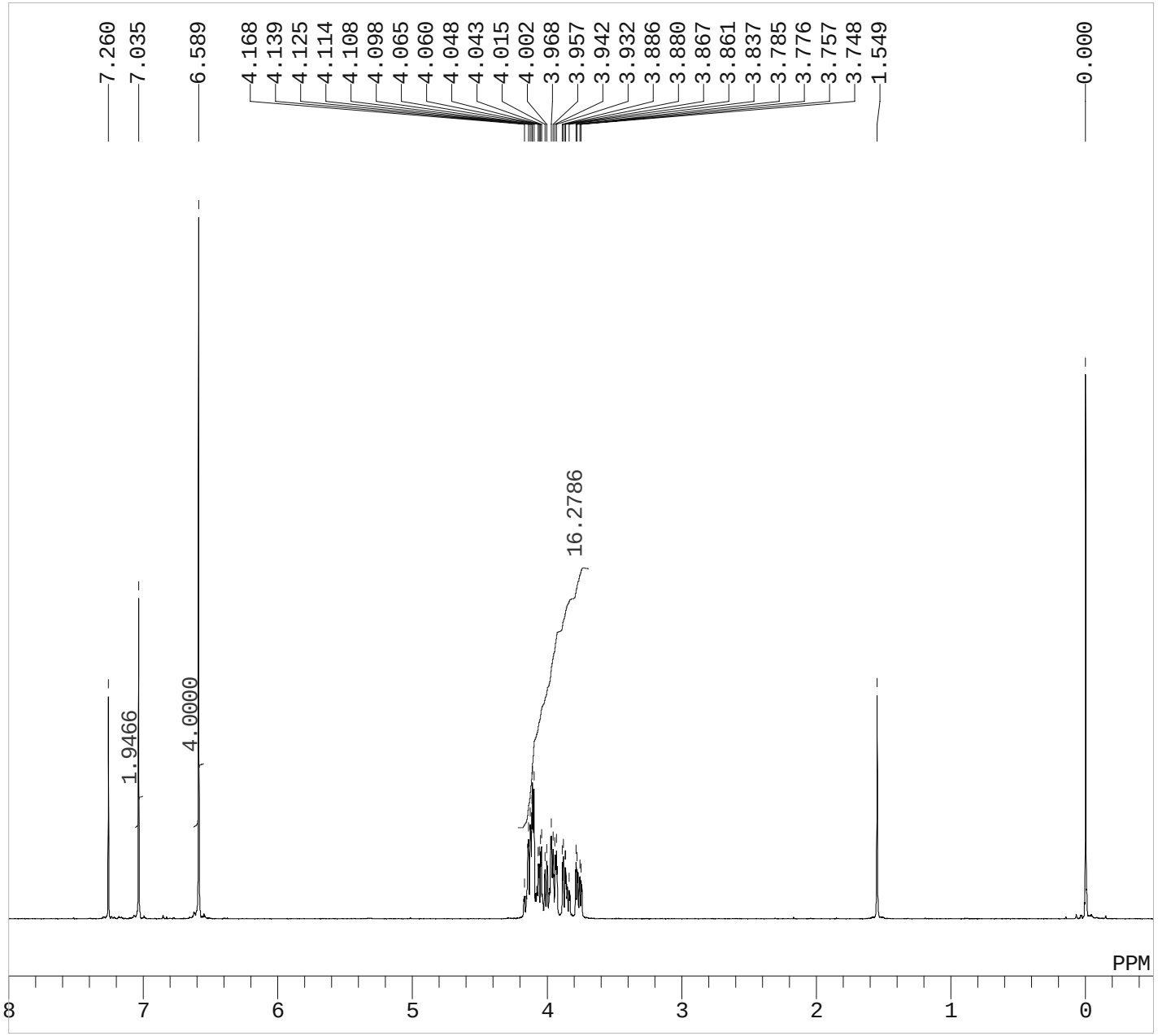
1b



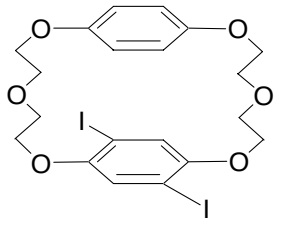

```
DFILE  F:\NMR\1b_13C.als
COMNT
DATIM  Wed Oct 11 18:47:01 2006
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN     10500.0 Hz
POINT         32768
FREQU     27118.6 Hz
SCANS           257
ACQTM         1.208 sec
PD            1.792 sec
PW1             4.6 us
IRNUC  1H
CTEMP          26.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.00 Hz
RGAIN            25
```



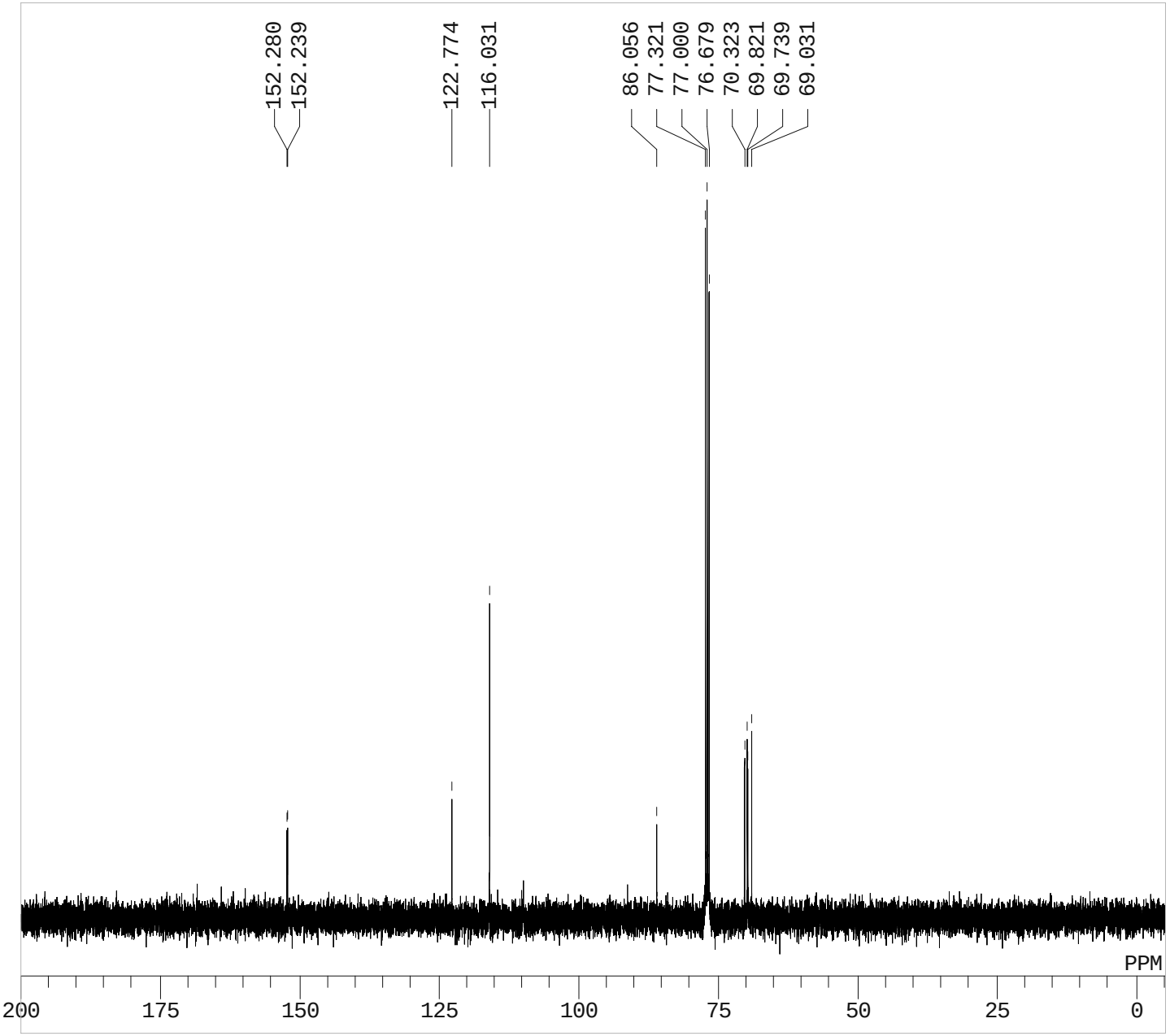
1b



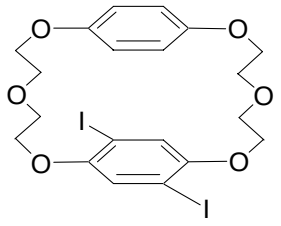

```
DFILE   F:\NMR\1c_1H.als
COMNT
DATIM   Tue Jul 29 20:06:13 2008
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS             16
ACQTM          4.100 sec
PD             1.500 sec
PW1              6.6 us
IRNUC   1H
CTEMP           28.7 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN             22
```



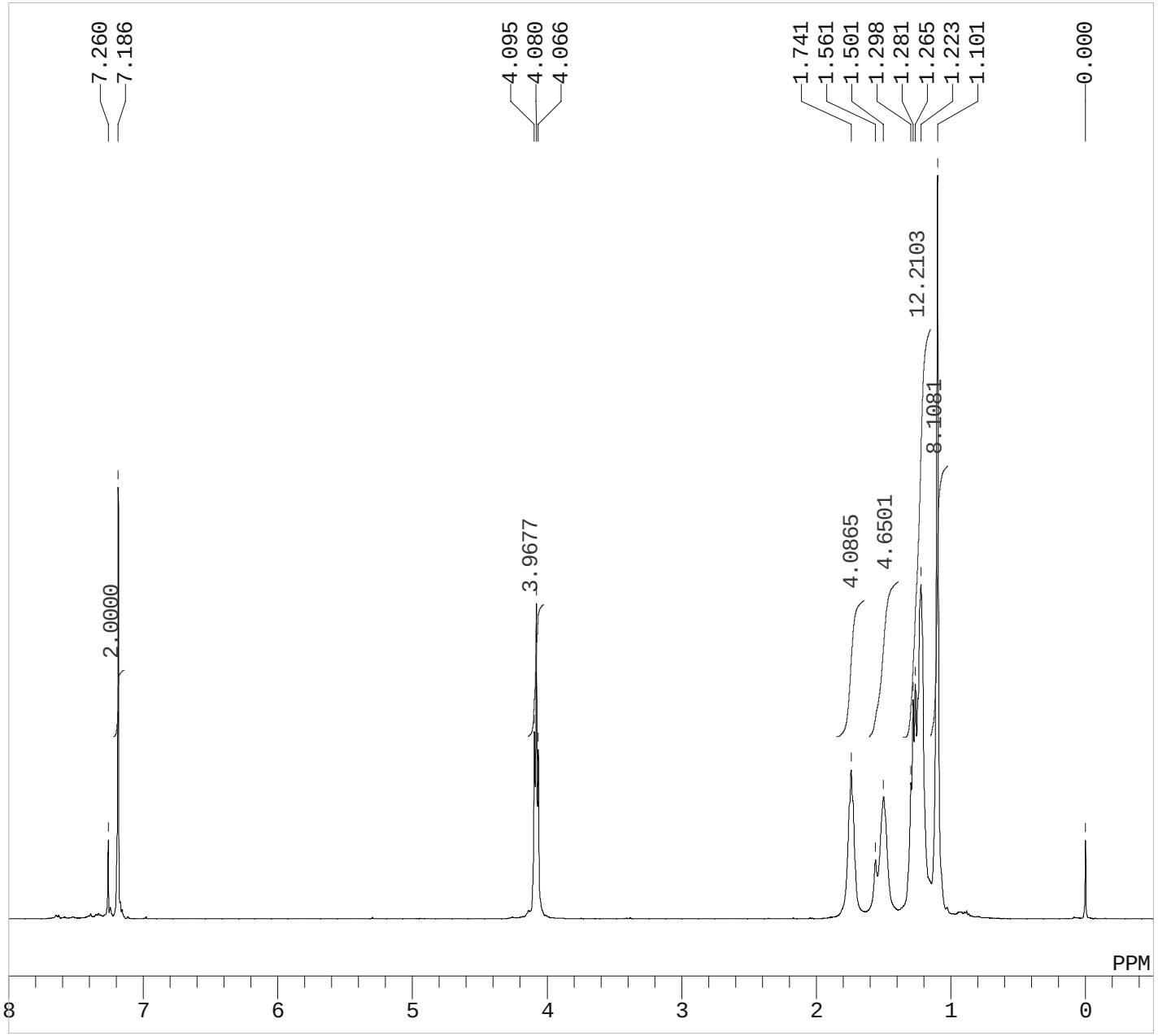
1c



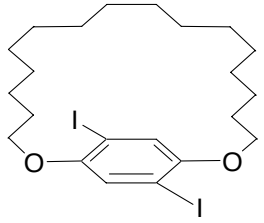
DFILE	F:\NMR\1c_13C.als	
COMNT		
DATIM	Thu Jul 31 20:47:26 2008	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	100.40	MHz
OBSET	125.00	KHz
OBFIN	10500.0	Hz
POINT	32768	
FREQU	27118.6	Hz
SCANS	257	
ACQTM	1.208	sec
PD	1.792	sec
PW1	4.7	us
IRNUC	1H	
CTEMP	27.8	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	0.12	Hz
RGAIN	26	



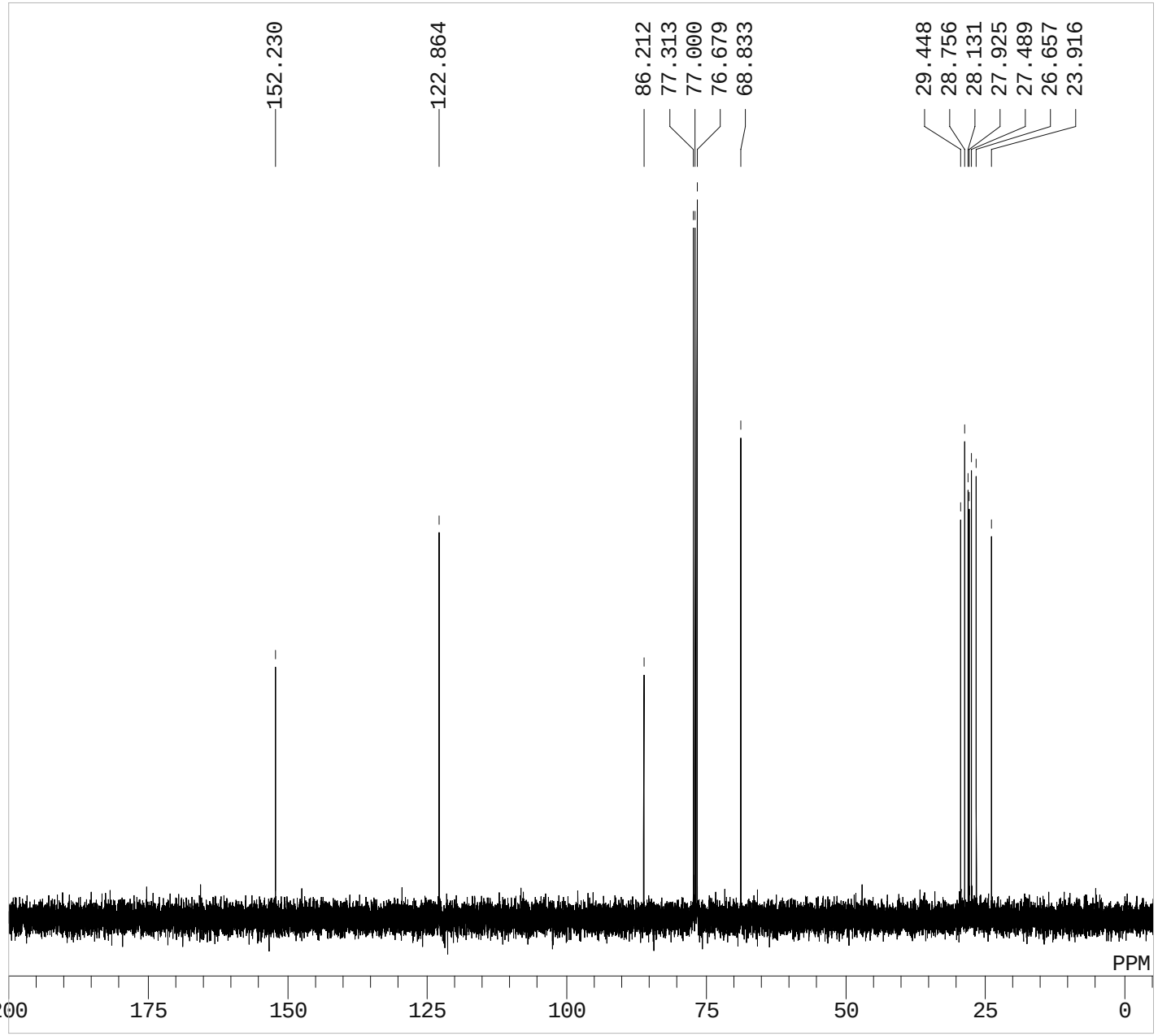
1c



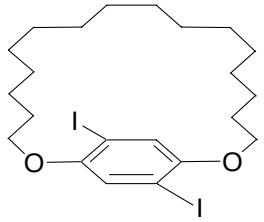

```
DFILE   F:\NMR\1e_1H.als
COMNT
DATIM   Sat Jul 19 17:59:18 2008
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS             16
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.6 us
IRNUC   1H
CTEMP           27.5 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             15
```



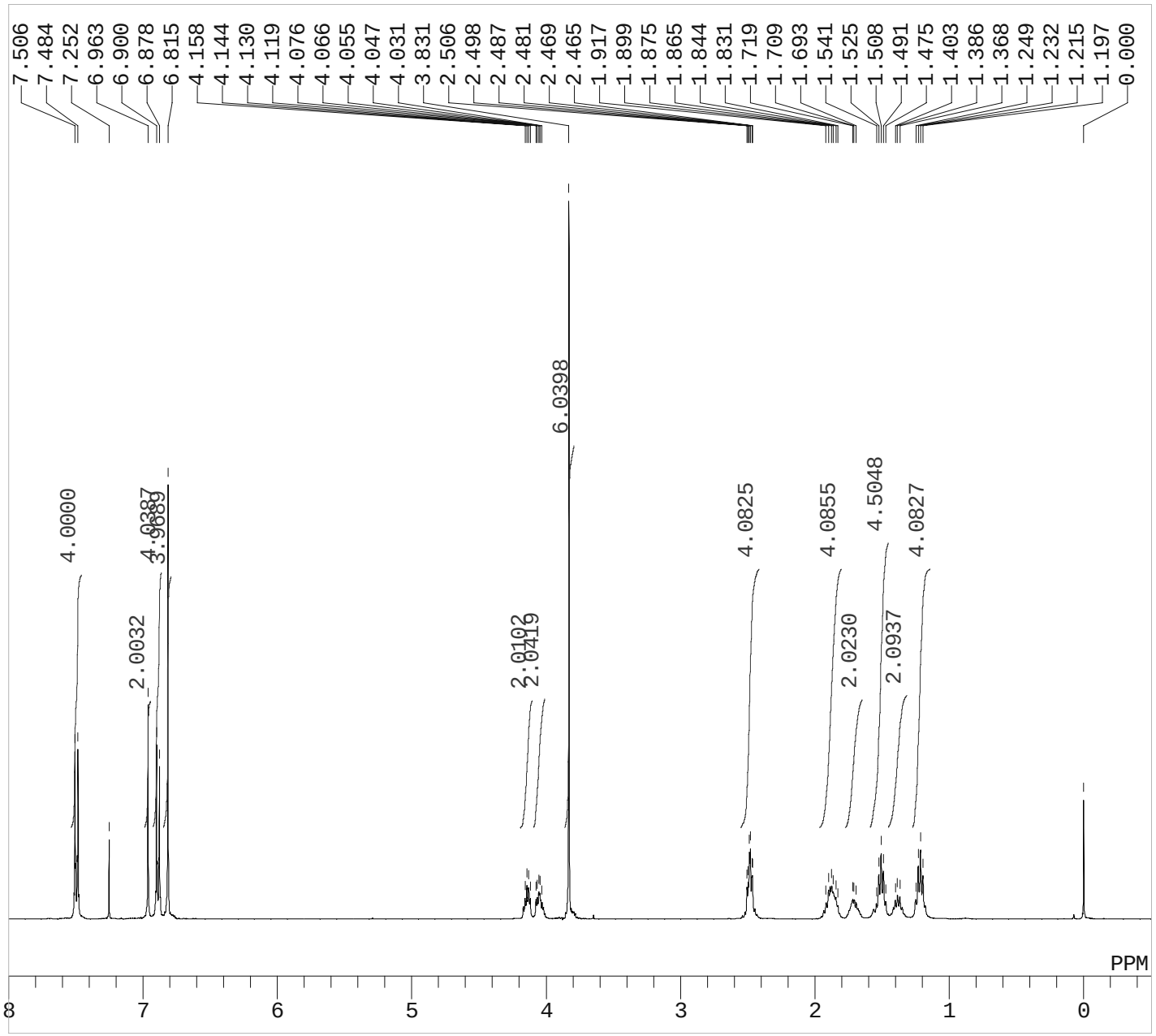
1e



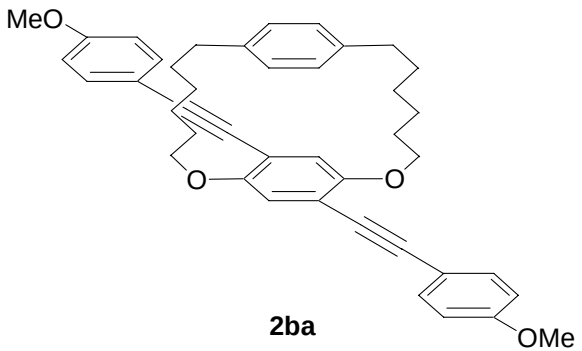
DFILE	F:\NMR\1e_13C.als
COMNT	
DATIM	Sat Jul 19 18:10:41 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	197
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	28.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



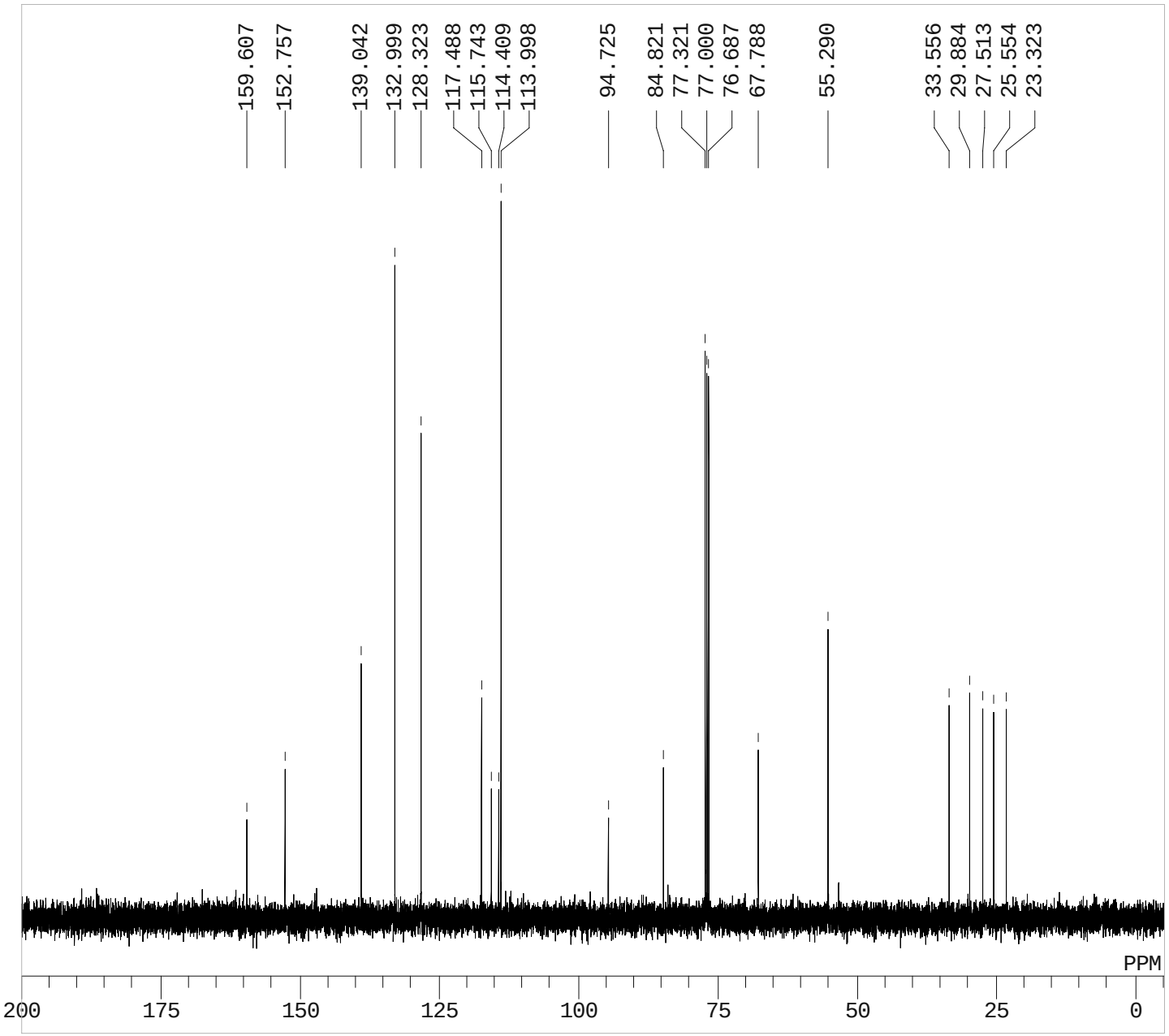
1e



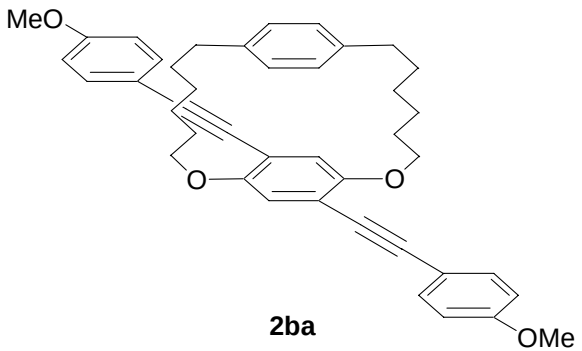
DFILE F:\NMR\2ba_1H.als
COMNT
DATIM Tue Dec 09 12:28:26 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15



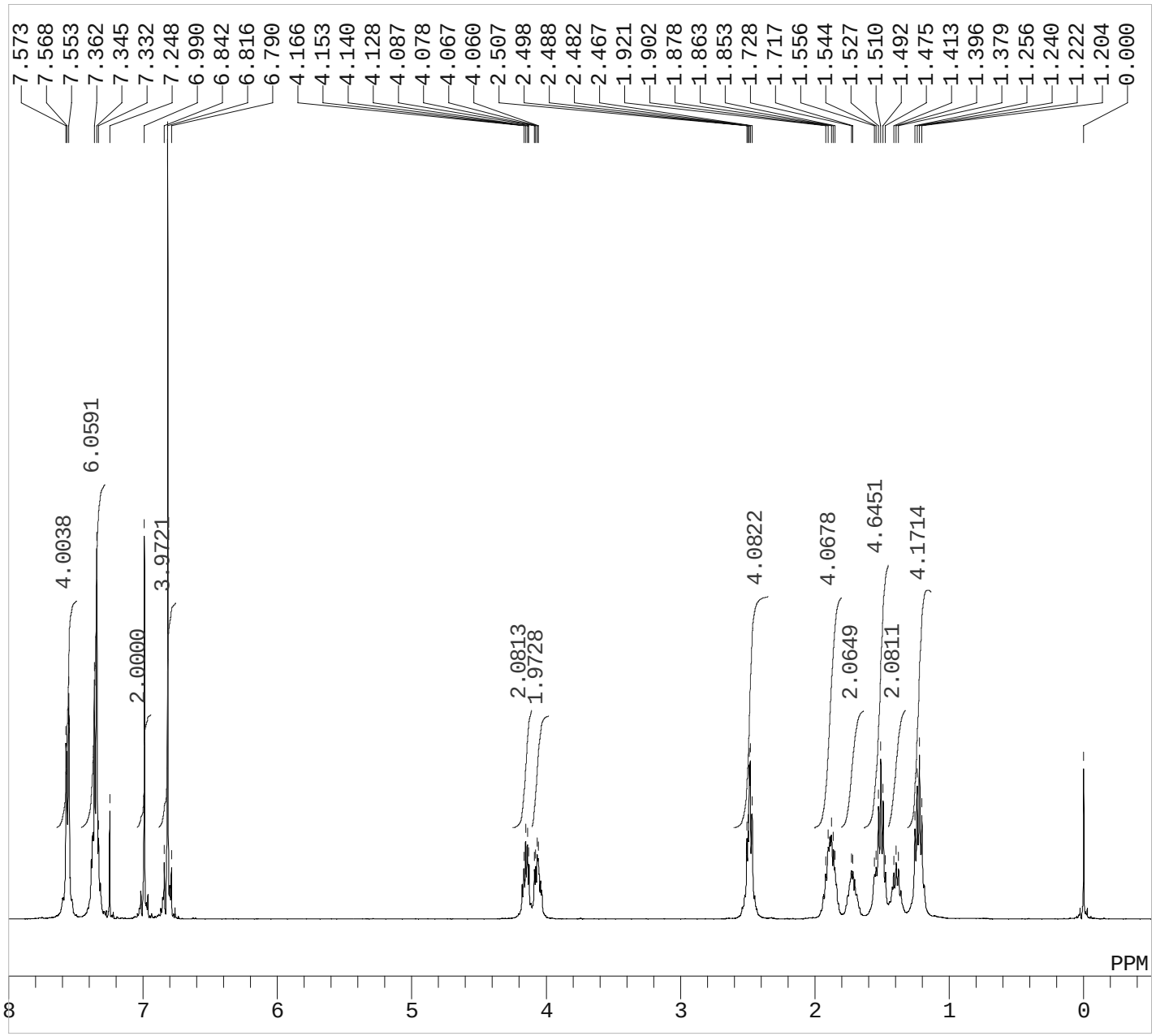
2ba



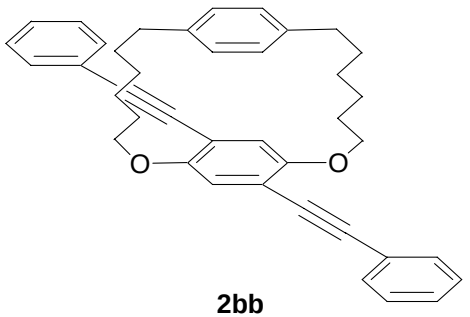
DFILE	F:\NMR\2ba_13C.als
COMNT	
DATIM	Sat Oct 07 17:45:49 2006
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	129
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.6 us
IRNUC	1H
CTEMP	27.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



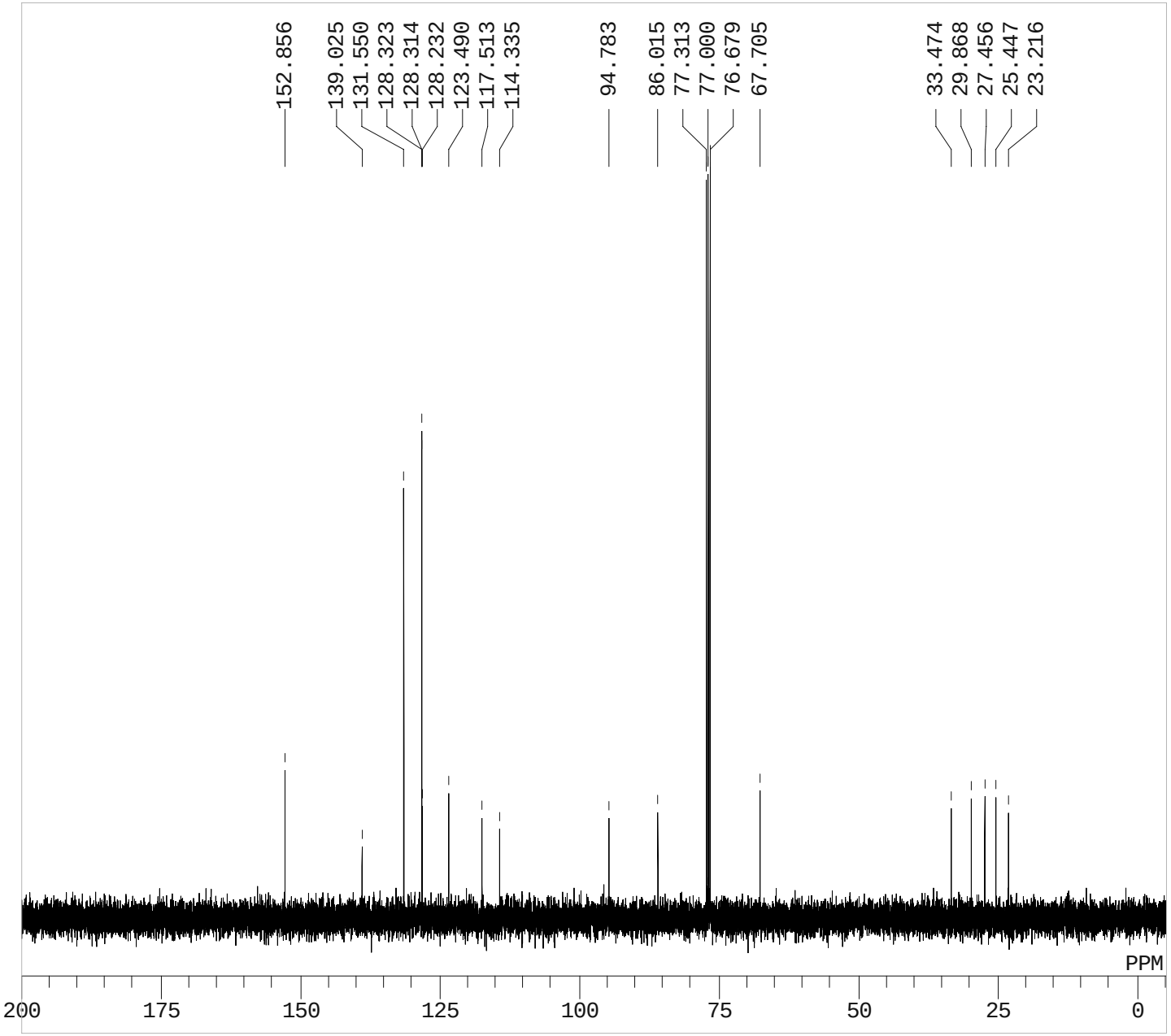
2ba



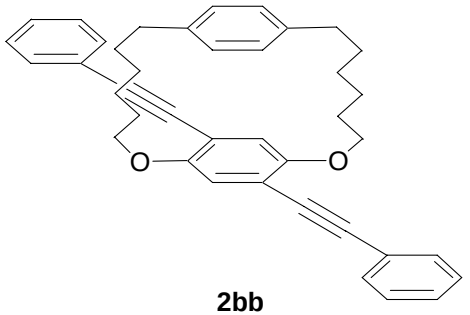
DFILE	F:\NMR\2bb_1H.als
COMNT	
DATIM	Thu Oct 23 14:58:25 2008
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	7992.0 Hz
SCANS	8
ACQTM	4.100 sec
PD	2.900 sec
PW1	6.6 us
IRNUC	1H
CTEMP	24.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	15



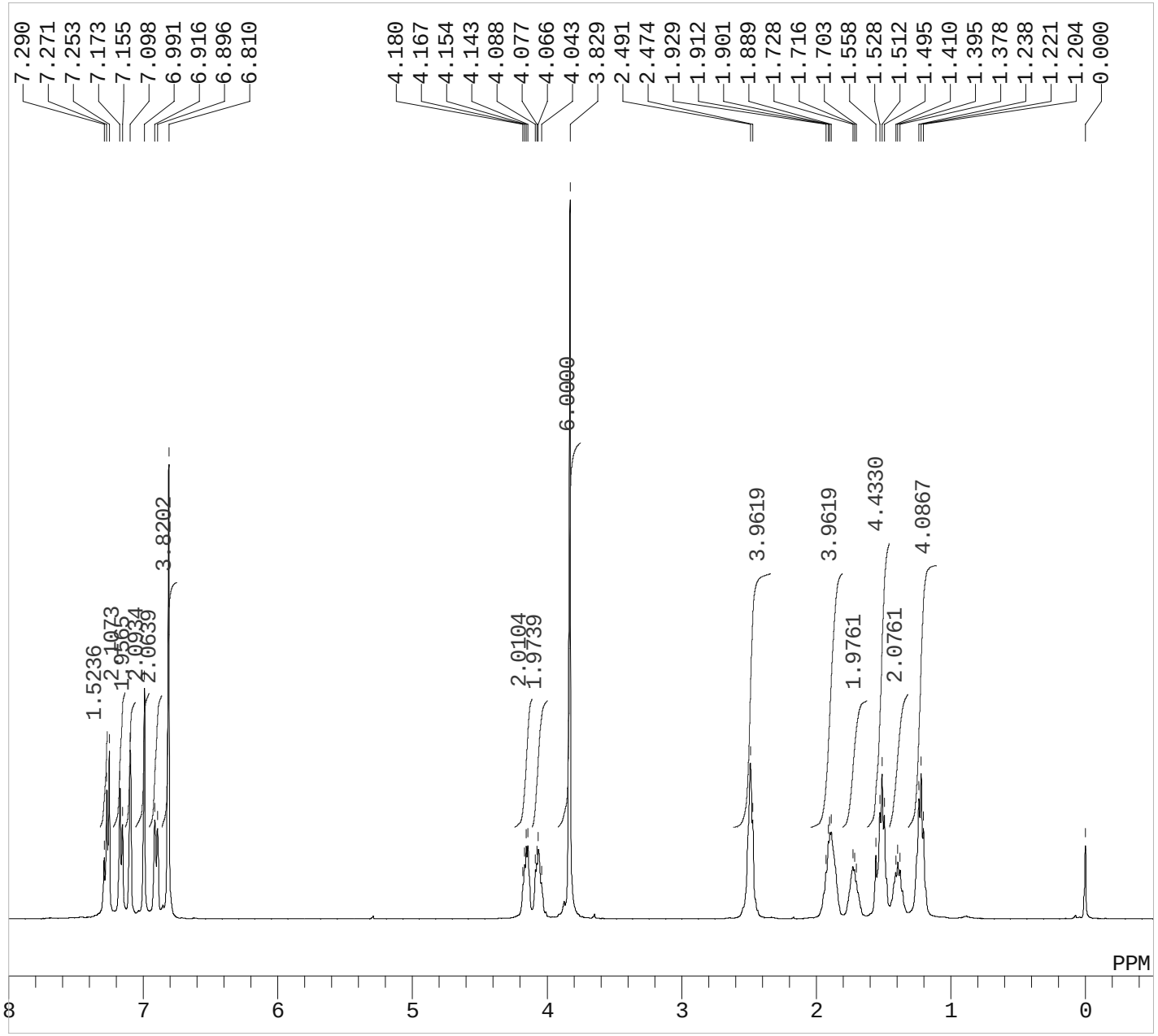
2bb



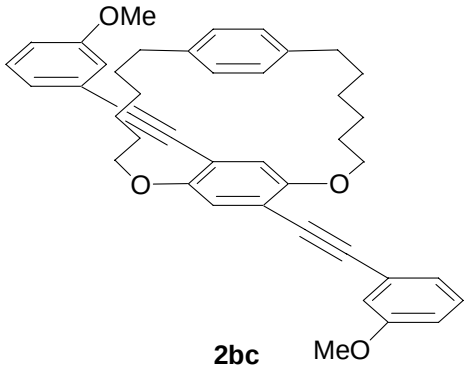
DFILE	F:\NMR\2bb_13C.als
COMNT	
DATIM	Wed Dec 26 11:57:19 2007
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	200
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.6 us
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



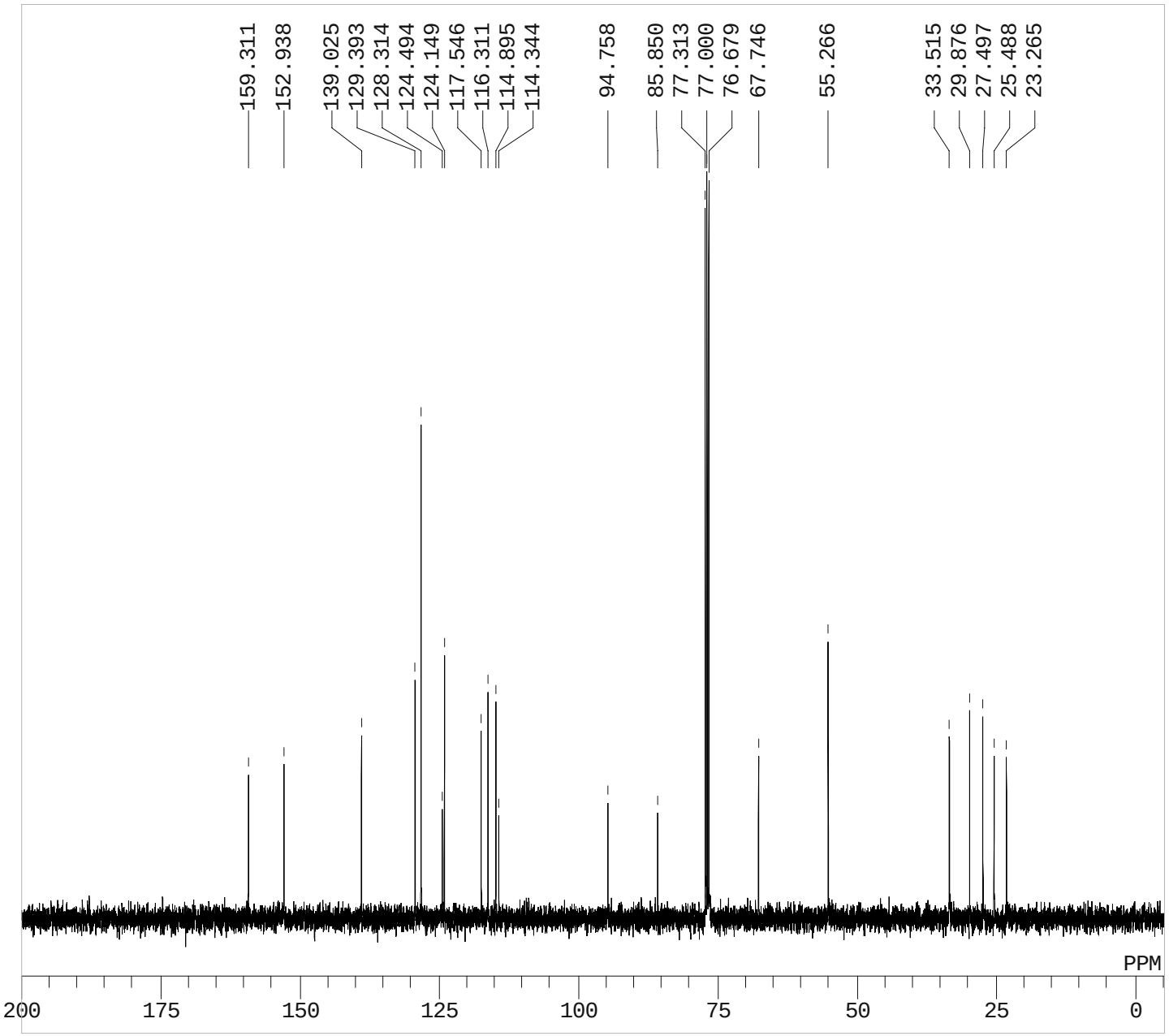
2bb



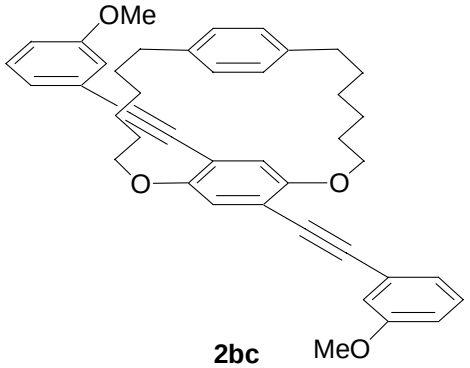
DFILE F:\NMR\2bc_1H.als
COMNT
DATIM Wed Jan 30 11:08:45 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 17



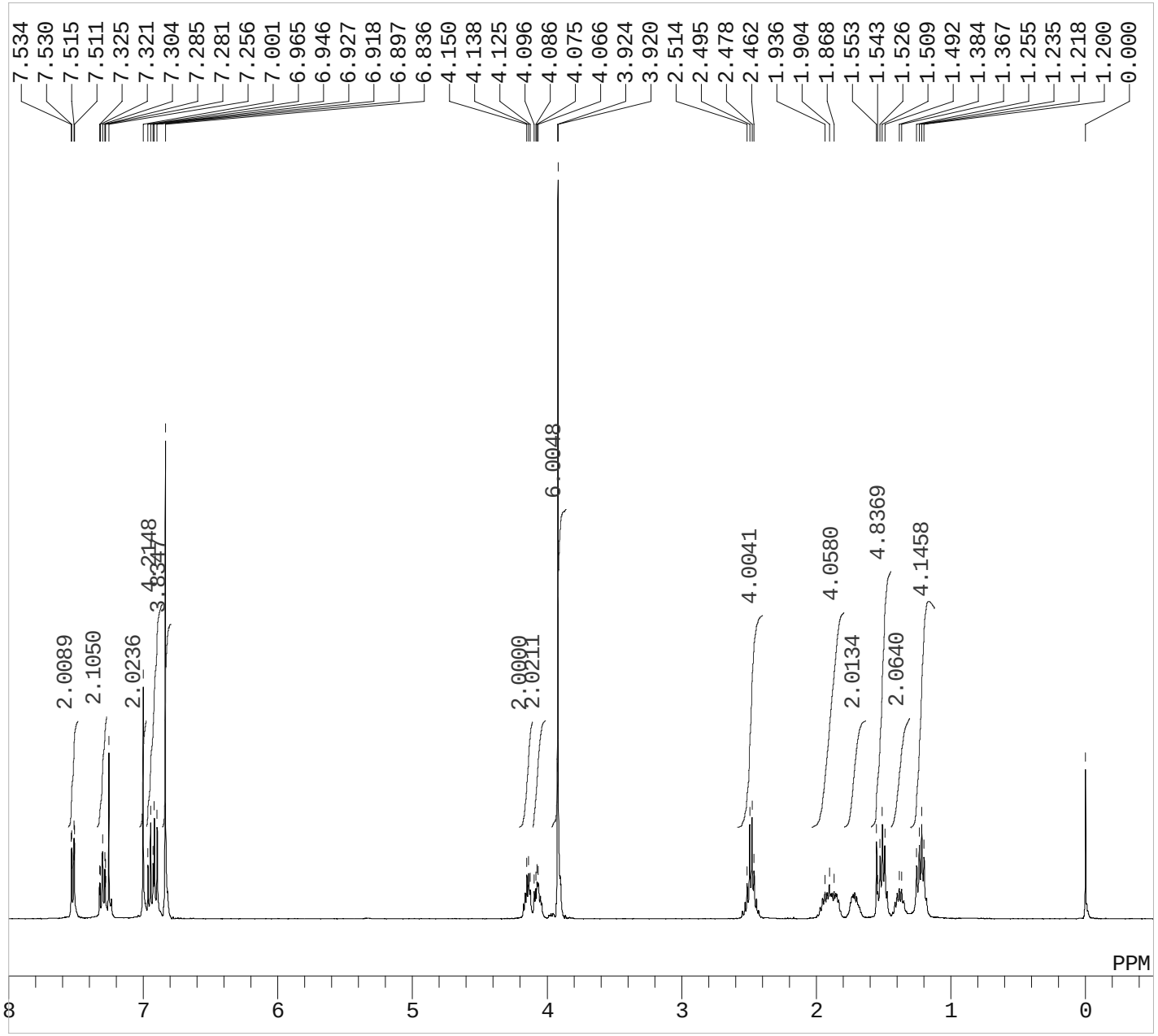
2bc



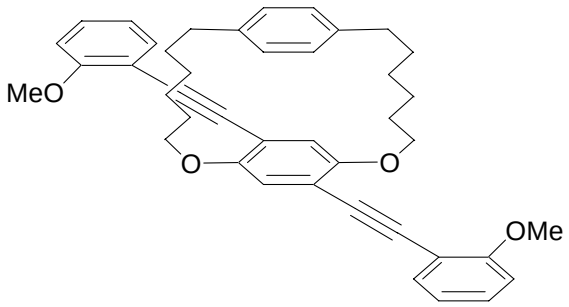
DFILE F:\NMR\2bc_13C.als
COMNT
DATIM Wed Jan 30 11:16:38 2008
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27118.6 Hz
SCANS 129
ACQTM 1.208 sec
PD 1.792 sec
PW1 4.6 us
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 24



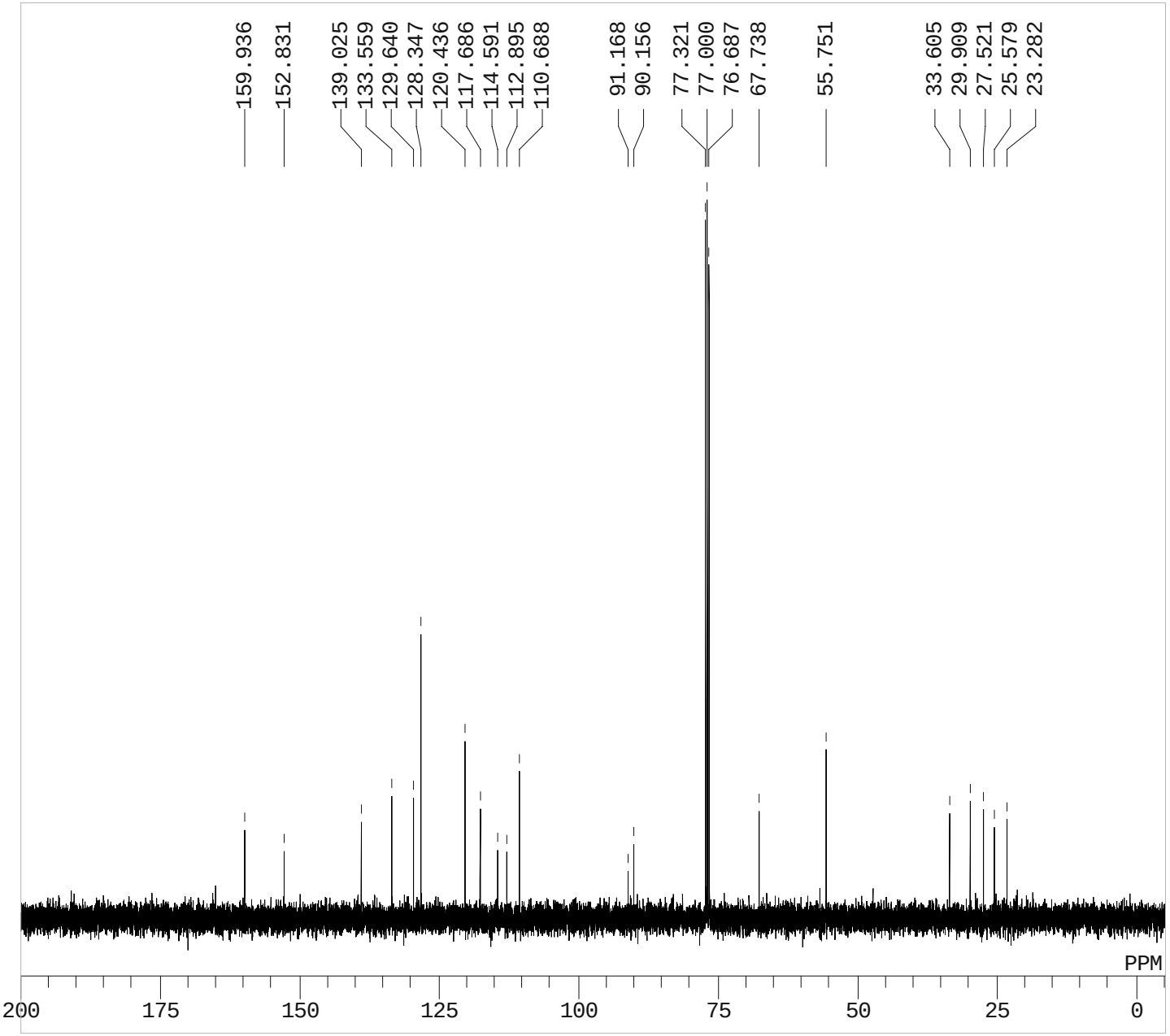
2bc



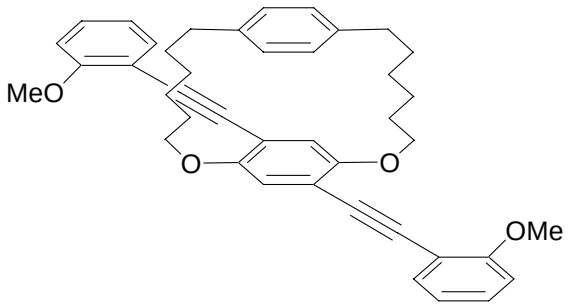
DFILE	F:\NMR\2bd_1H.als
COMNT	
DATIM	Mon Mar 31 19:44:41 2008
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	7992.0 Hz
SCANS	16
ACQTM	4.100 sec
PD	2.900 sec
PW1	6.6 us
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	20



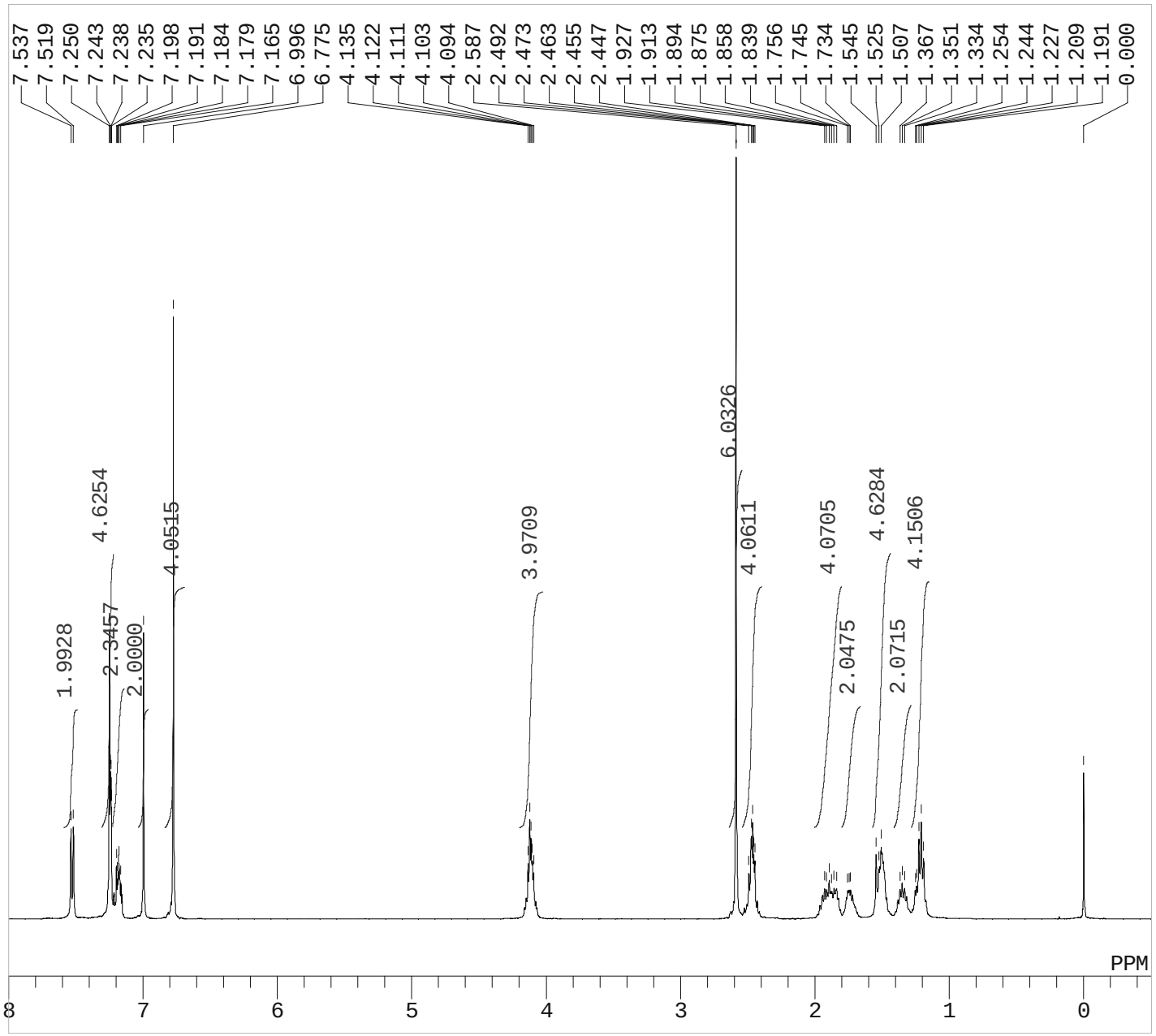
2bd



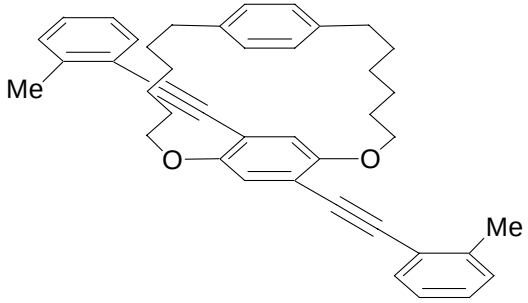

```
DFILE   F:\NMR\2bd_13C.als
COMNT
DATIM   Mon Mar 31 19:57:21 2008
OBNUC   13C
EXMOD   BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27118.6 Hz
SCANS           229
ACQTM         1.208 sec
PD            1.792 sec
PW1             4.6 us
IRNUC   1H
CTEMP          25.8 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            25
```



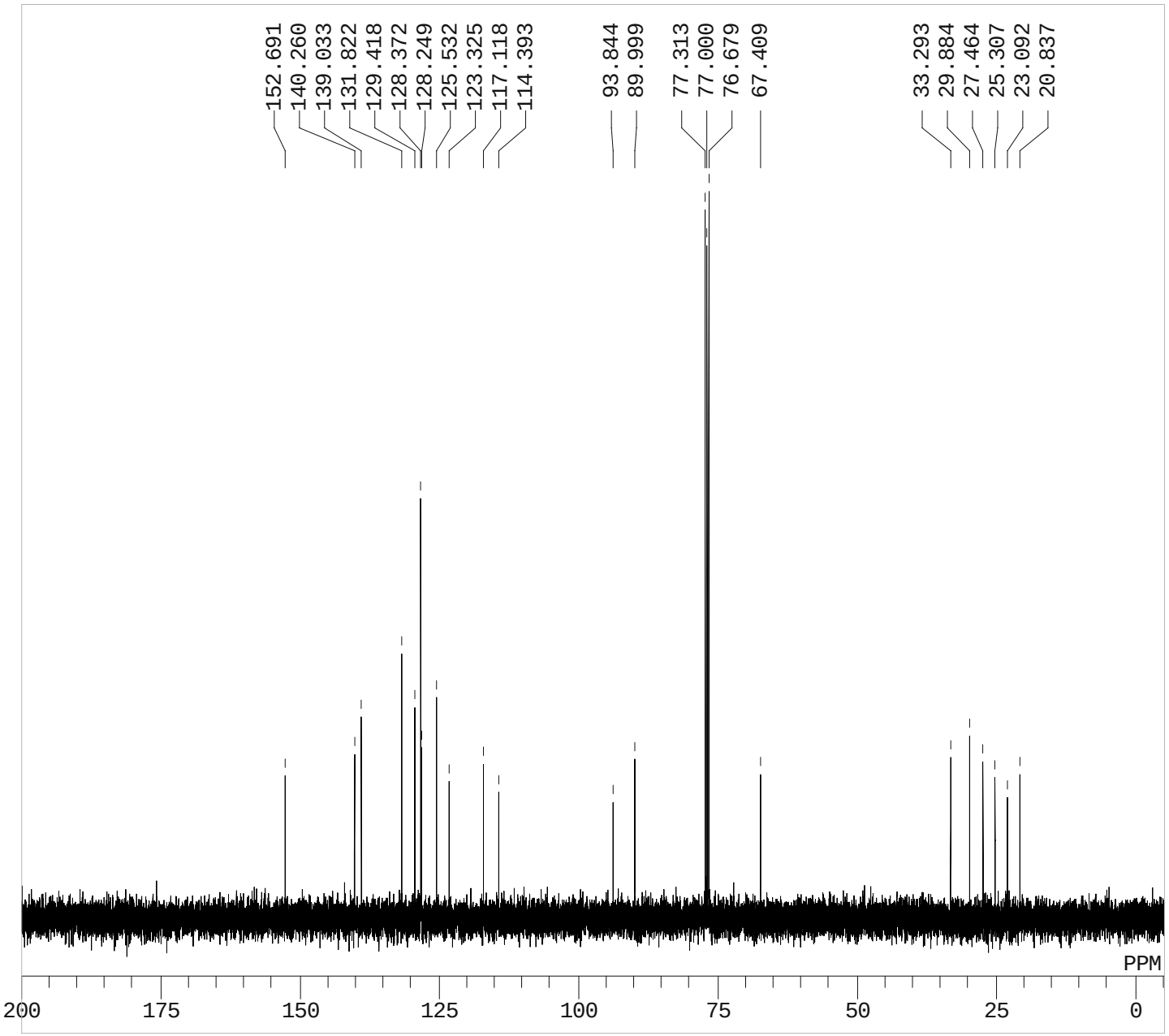
2bd



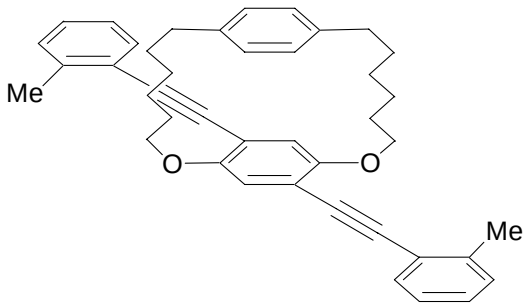
DFILE F:\NMR\2be_1H.als
COMNT
DATIM Tue Mar 11 11:04:31 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19



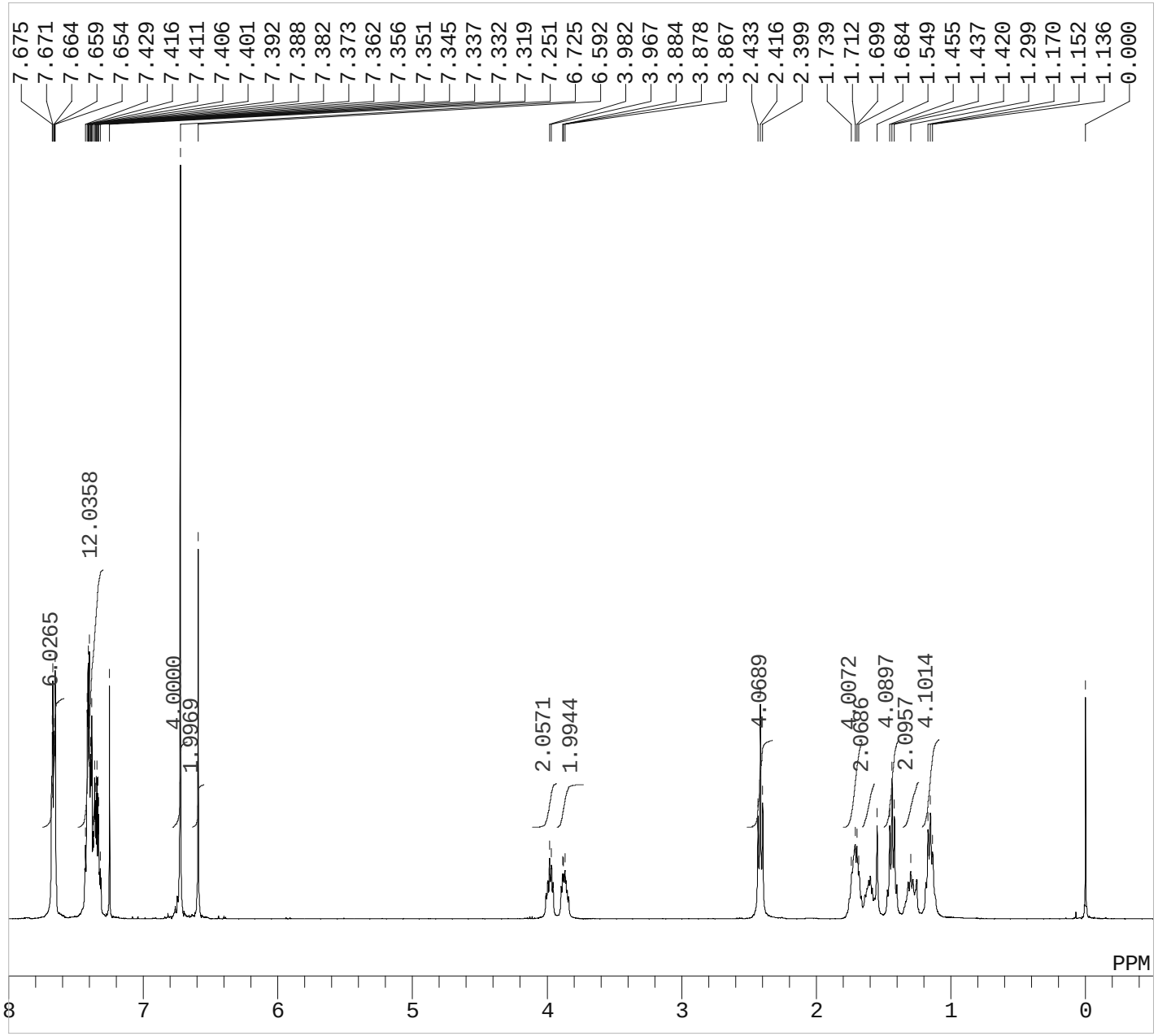
2be



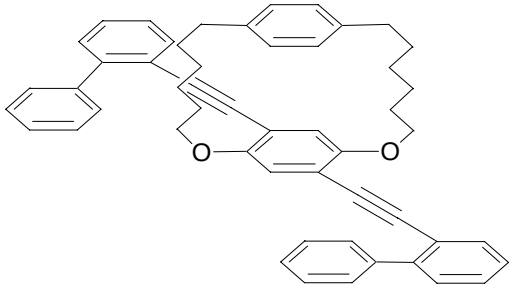
DFILE	F:\NMR\2be_13C.als
COMNT	
DATIM	Tue Mar 11 11:13:14 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	142
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.6 us
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	24



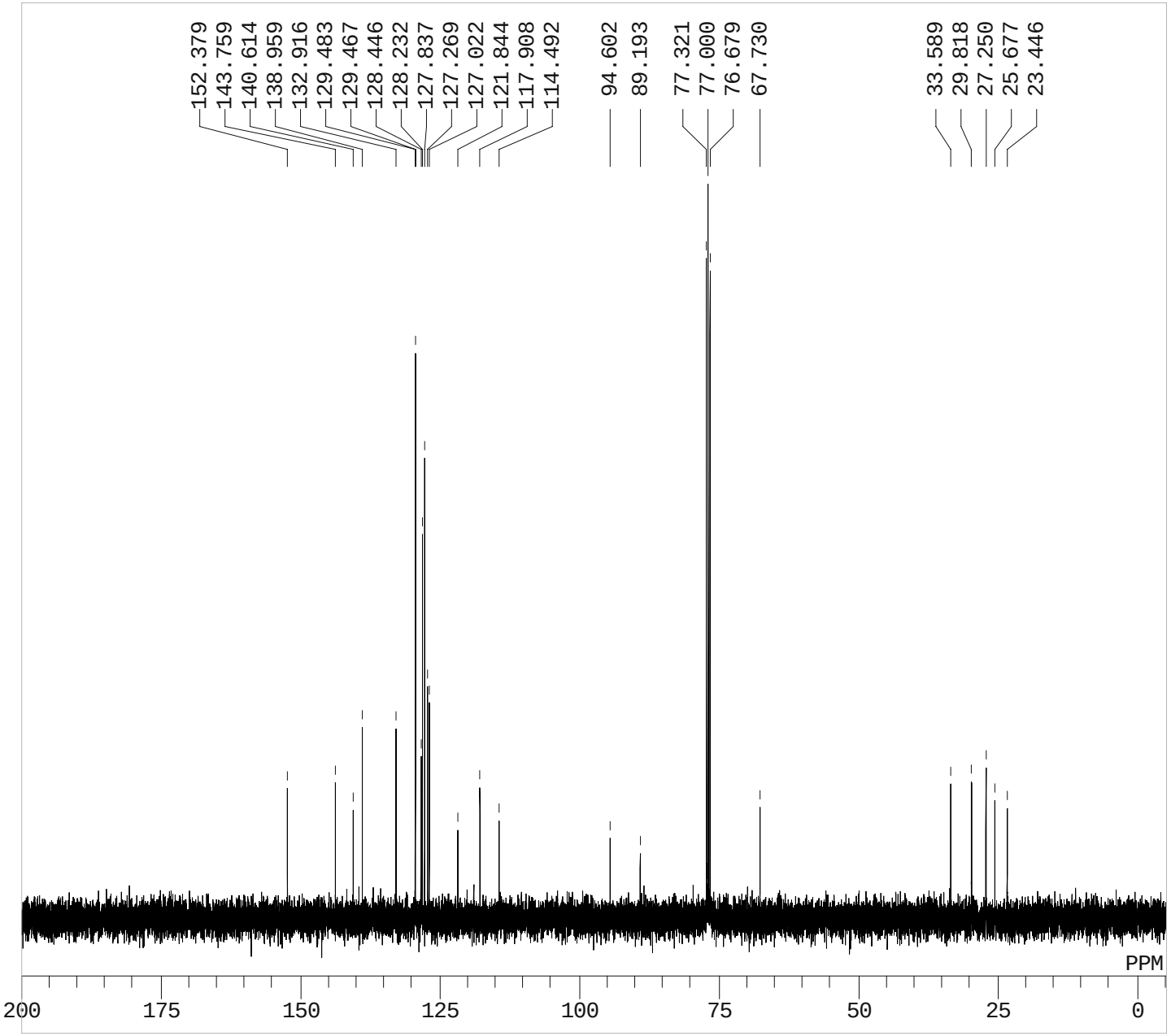
2be



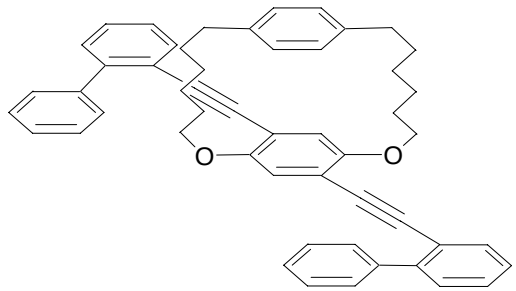
DFILE F:\NMR\2bf_1H.als
COMNT
DATIM Tue Dec 09 10:53:30 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18



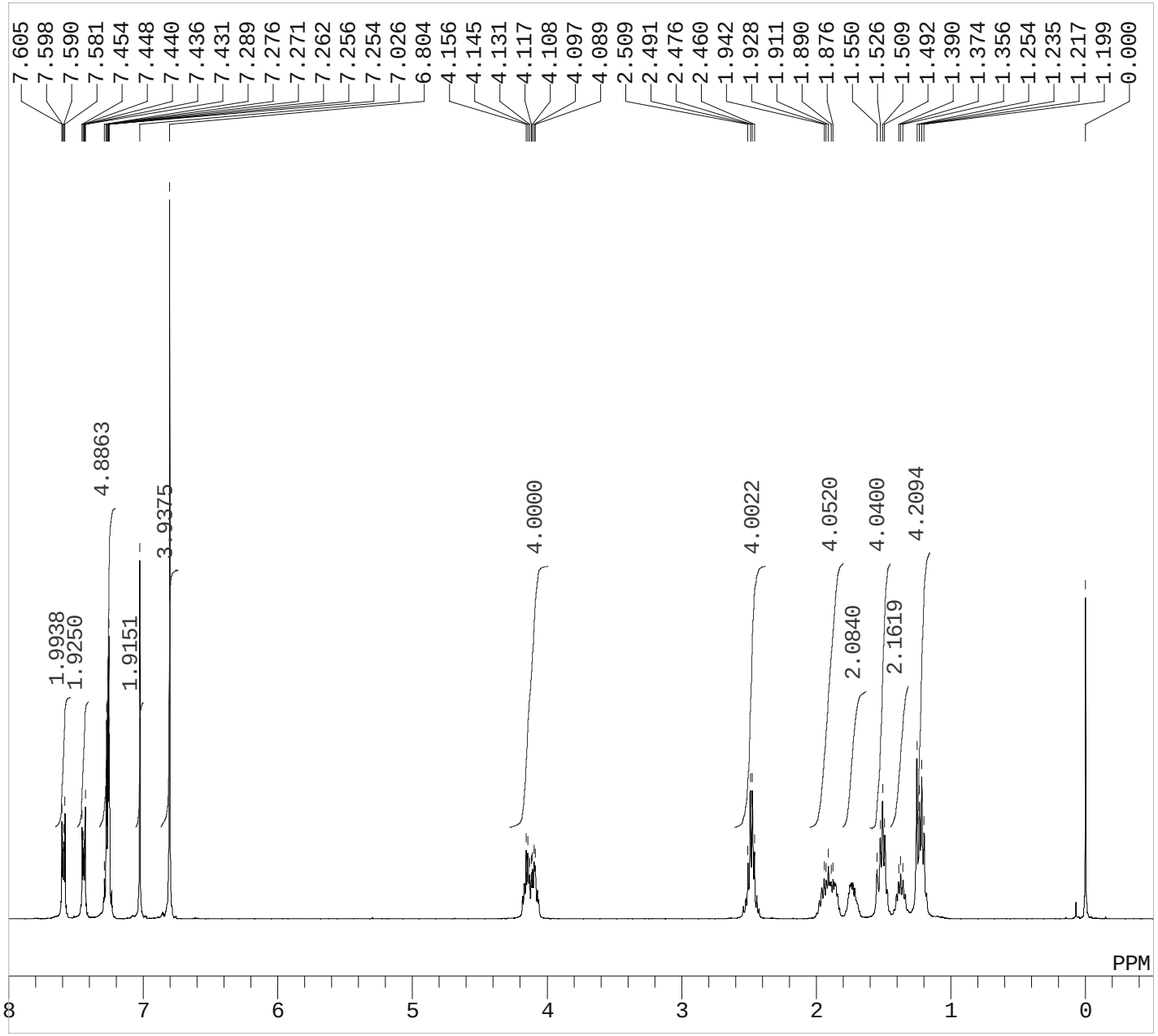
2bf



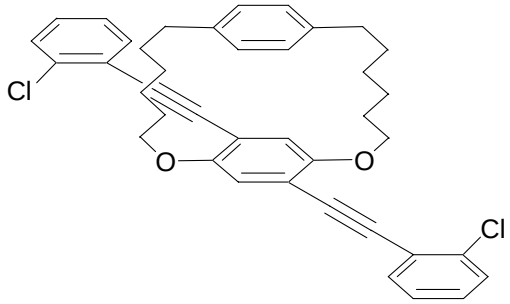

```
DFILE   F:\NMR\2bf_13C.als
COMNT
DATIM   Tue Dec 09 11:01:31 2008
OBNUC   13C
EXMOD   BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27118.6 Hz
SCANS           129
ACQTM         1.208 sec
PD            1.792 sec
PW1             4.7 us
IRNUC   1H
CTEMP          22.4 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            25
```



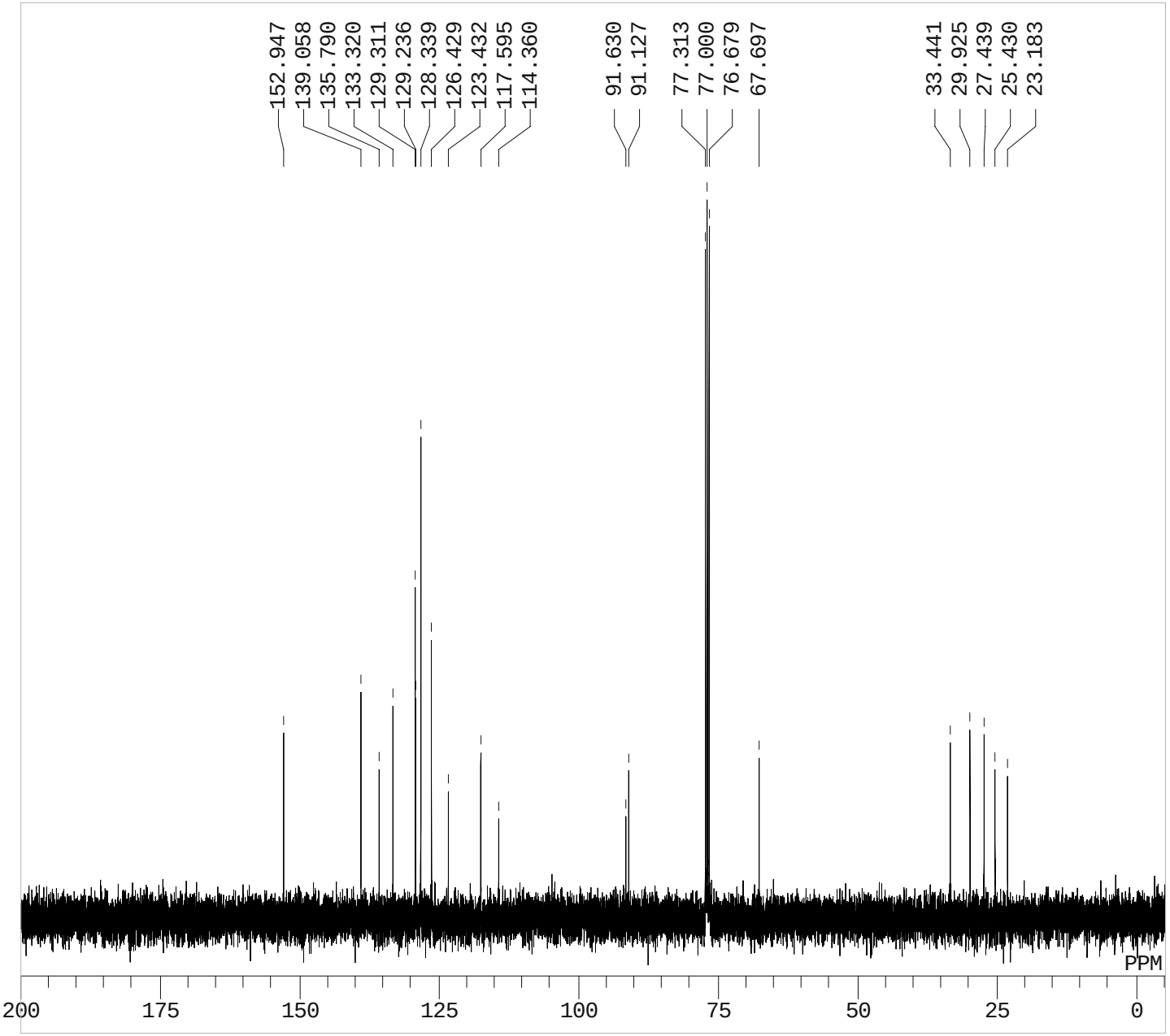
2bf



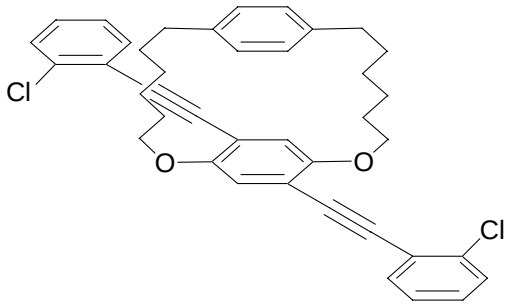
DFILE F:\NMR\2bg_1H.als
COMNT
DATIM Mon Dec 08 20:37:59 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19



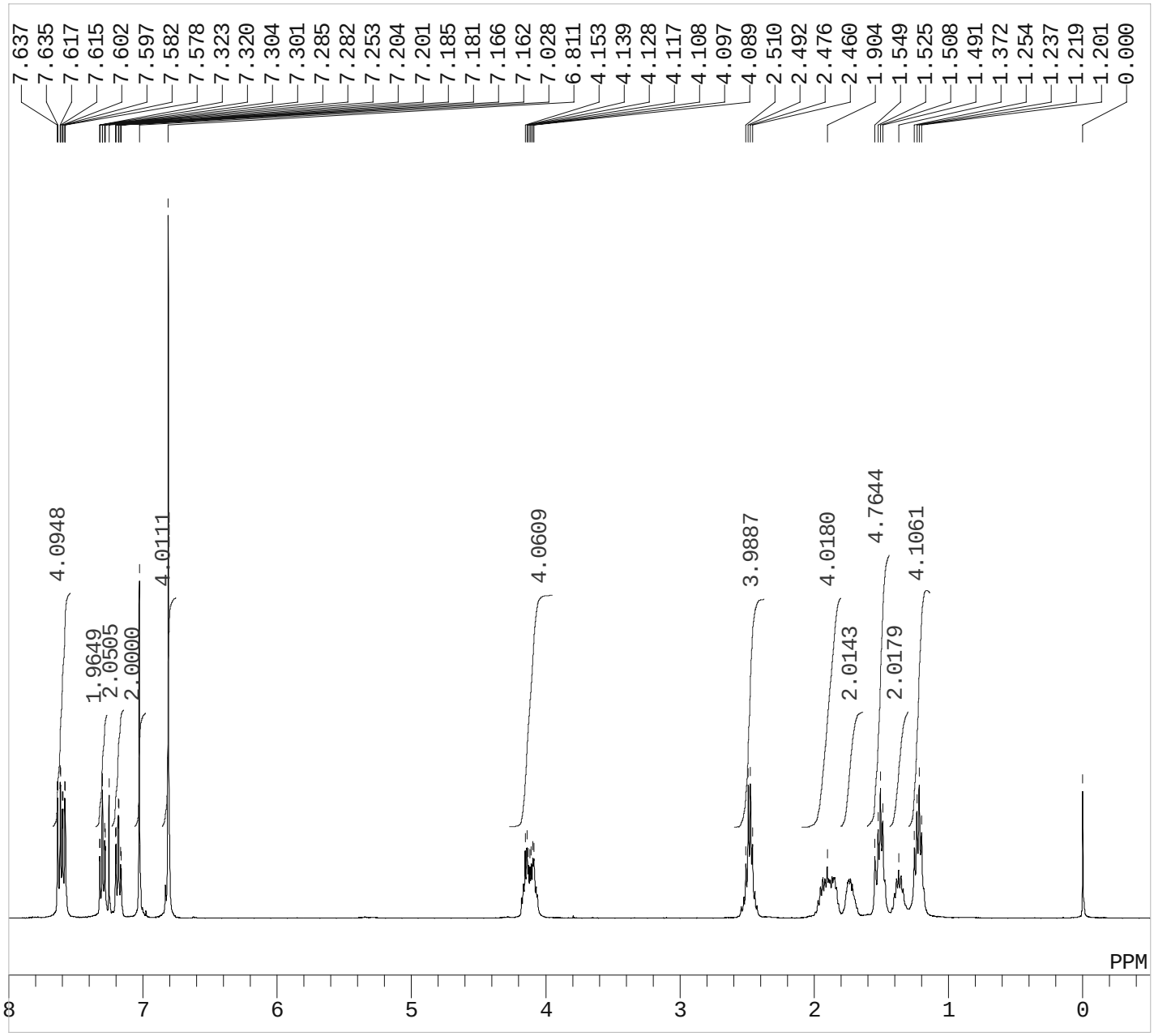
2bg



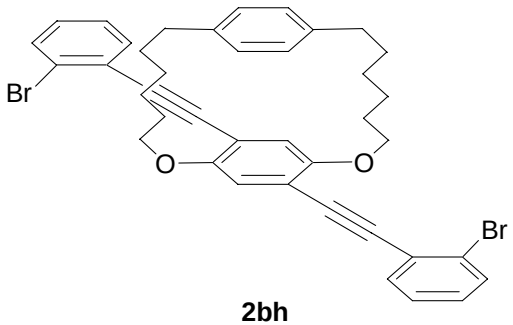
DFILE	F:\NMR\2bg_13C.als
COMNT	
DATIM	Fri Mar 07 18:52:52 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	130
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.6 us
IRNUC	1H
CTEMP	24.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



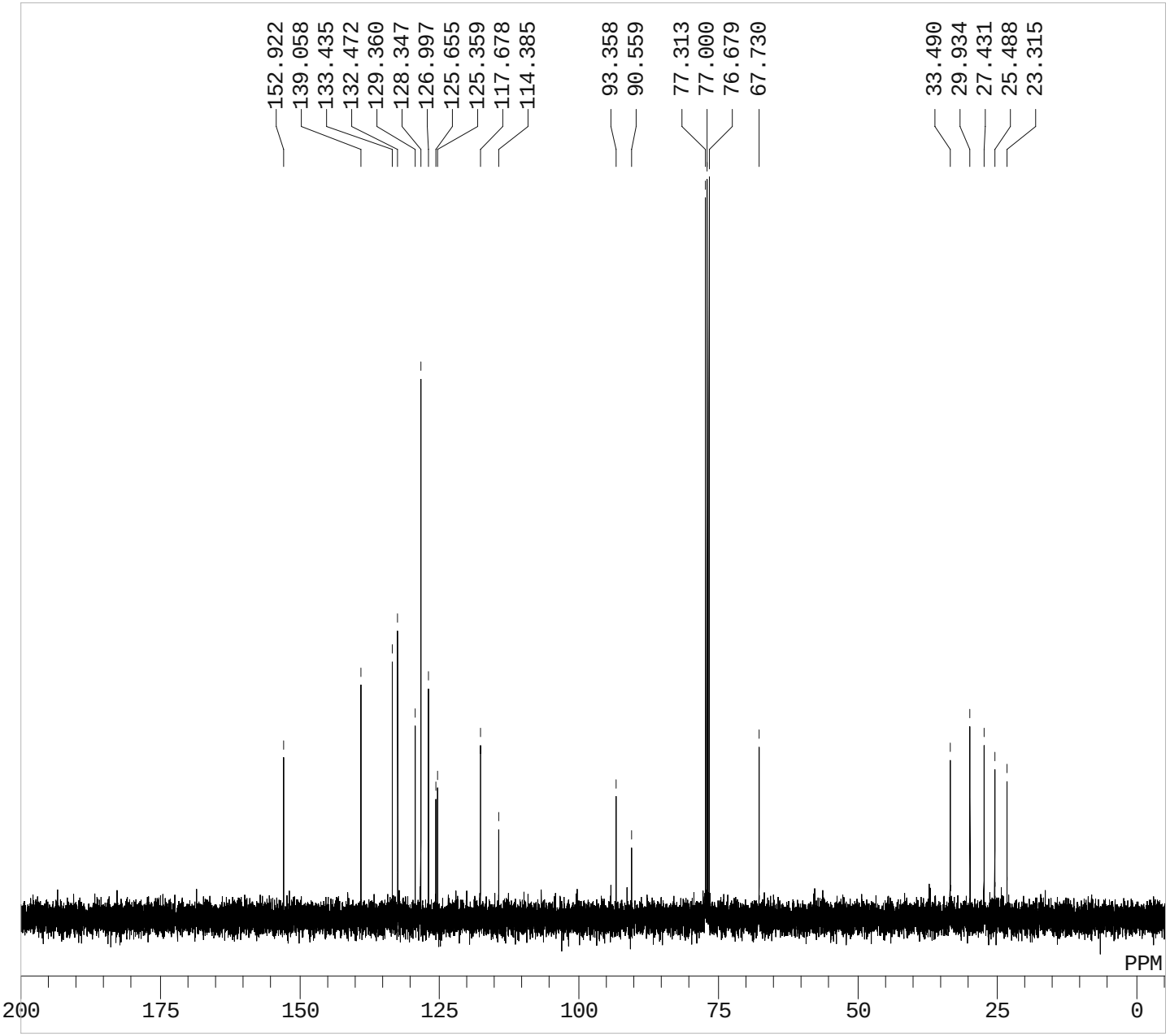
2bg



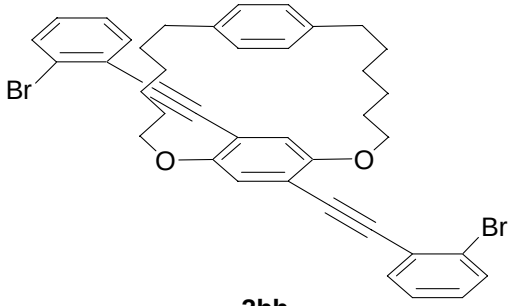
DFILE F:\NMR\2bh_1H.als
COMNT
DATIM Fri Mar 07 17:28:10 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19



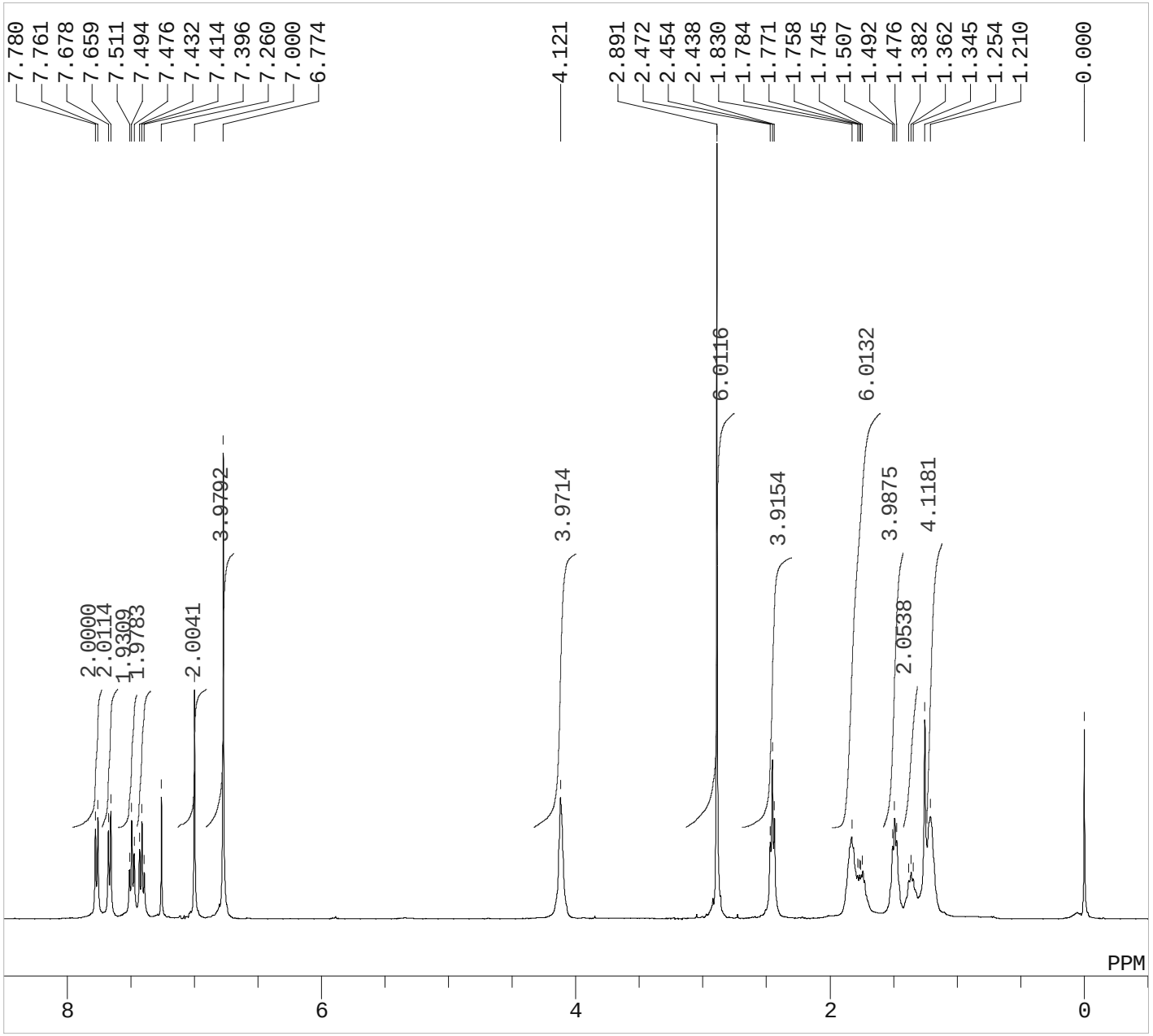
2bh



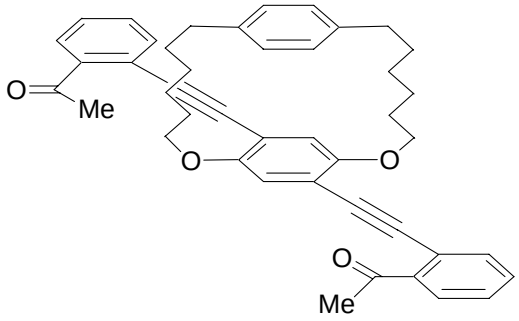
DFILE F:\NMR\2bh_13C.als
COMNT
DATIM Fri Mar 07 17:35:43 2008
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27118.6 Hz
SCANS 129
ACQTM 1.208 sec
PD 1.792 sec
PW1 4.6 us
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25



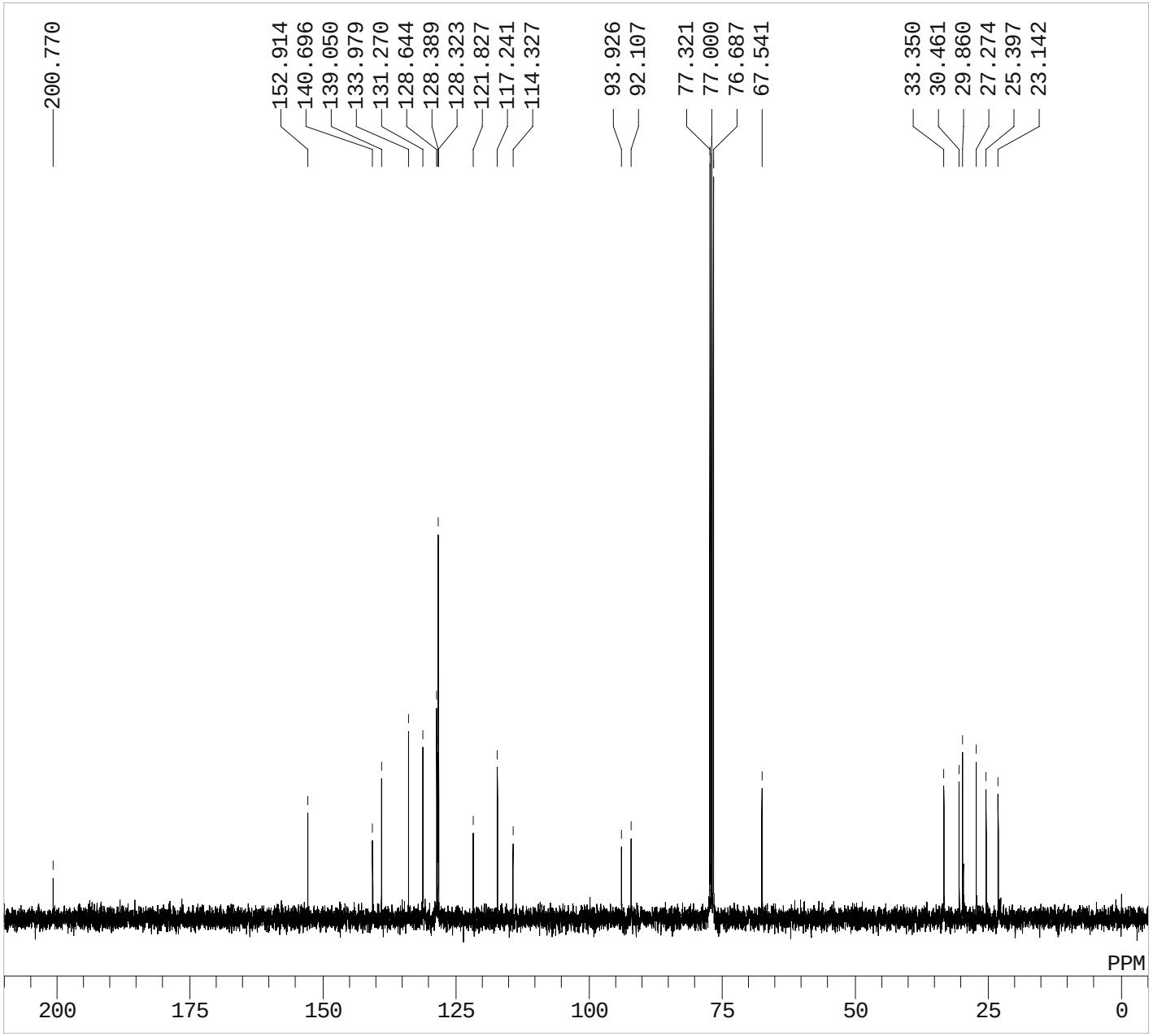
2bh



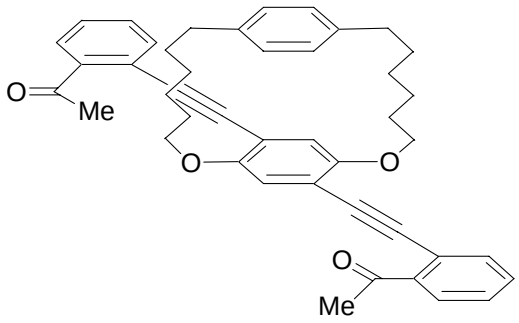
DFILE F:\NMR\2bi_1H.als
COMNT
DATIM Wed Sep 24 13:10:56 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.12 Hz
RGAIN 21



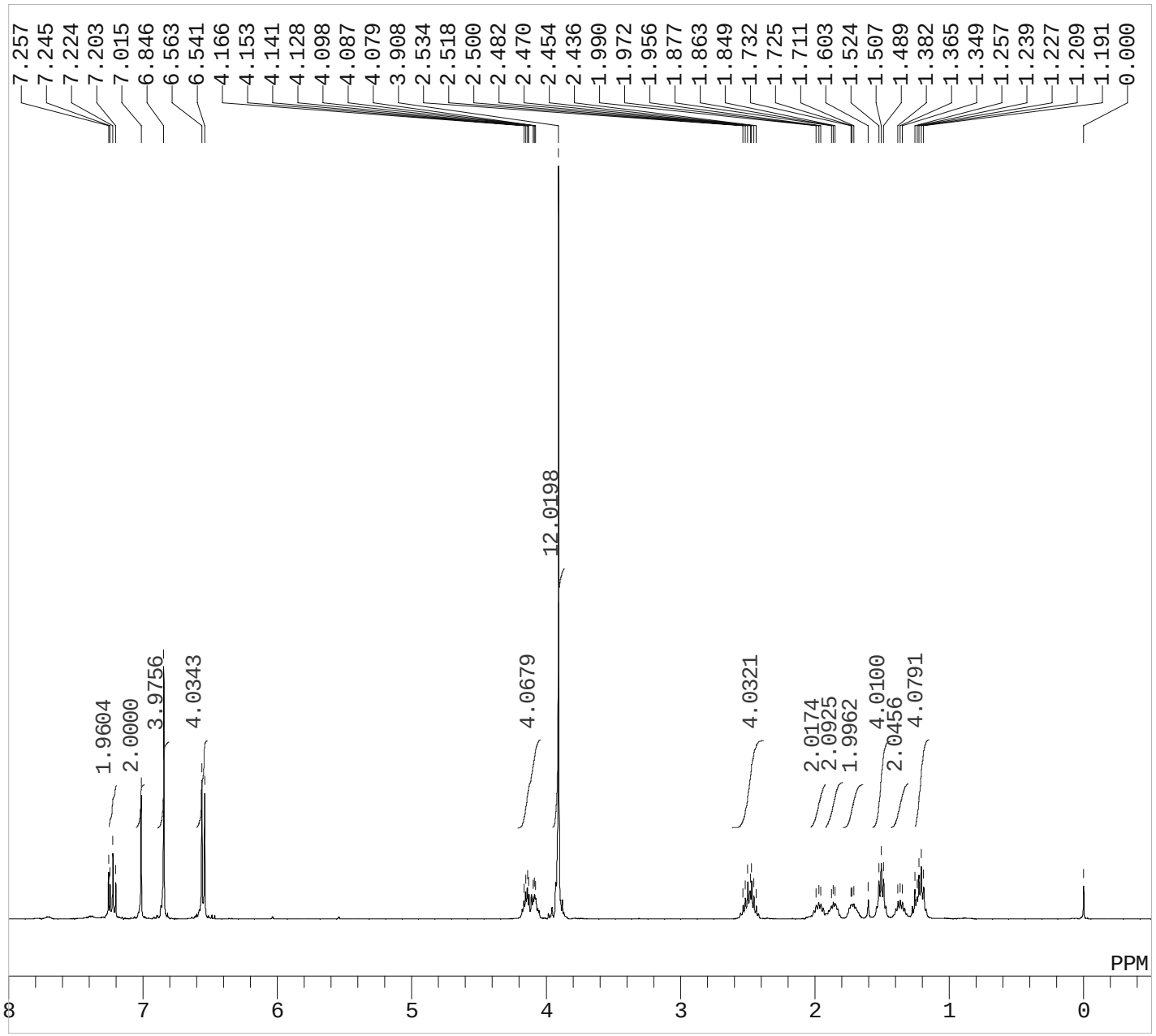
2bi



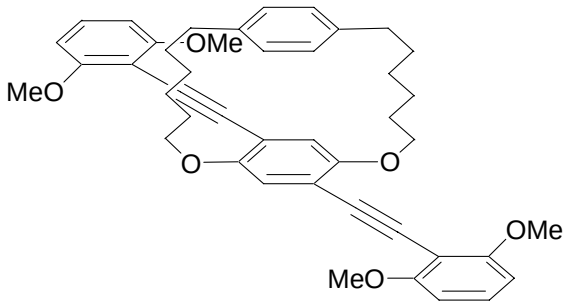
DFILE	F:\NMR\2bi_13C.als
COMNT	
DATIM	Wed Sep 24 13:27:22 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	201
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	24.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.12 Hz
RGAIN	27



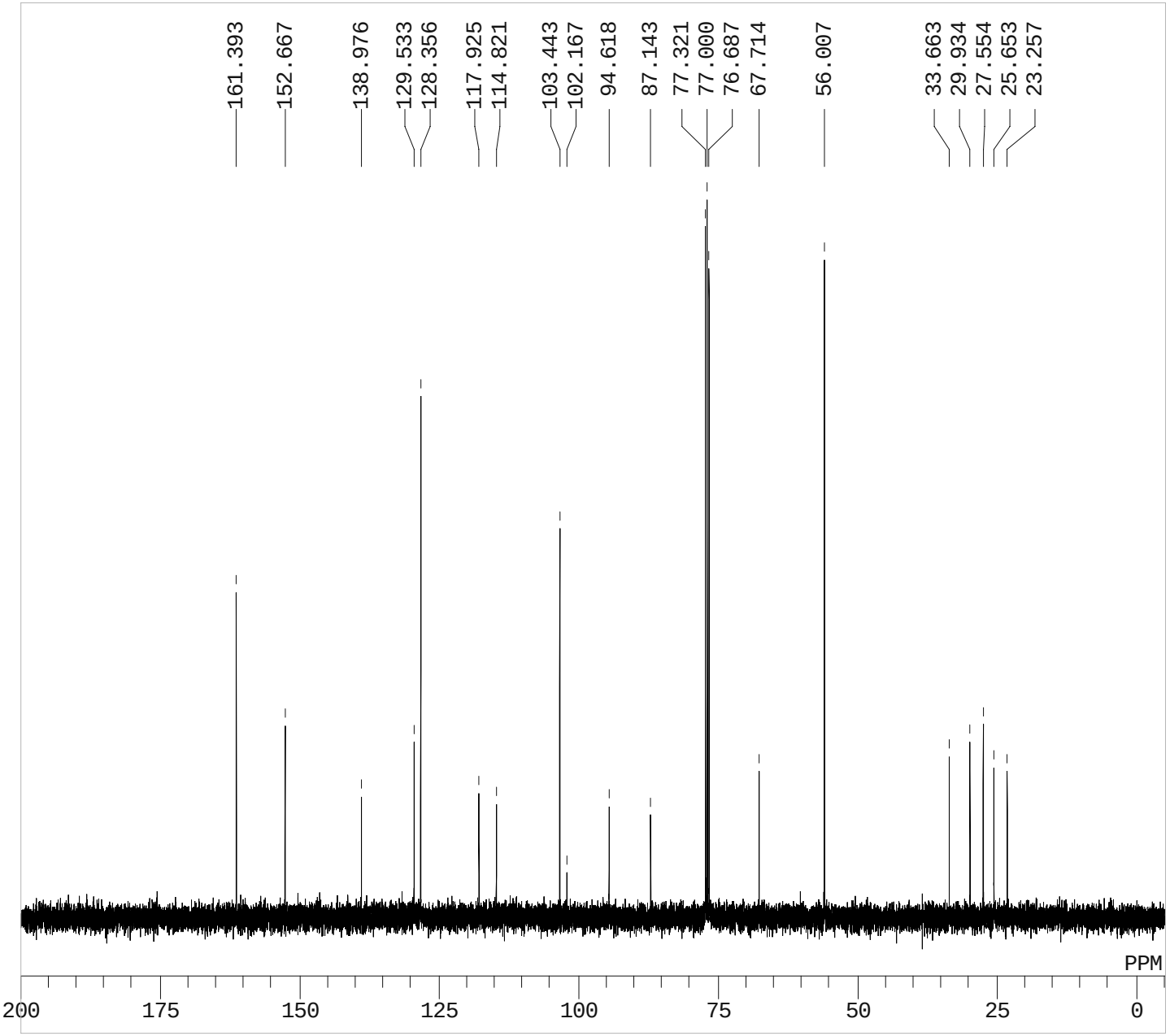
2bi



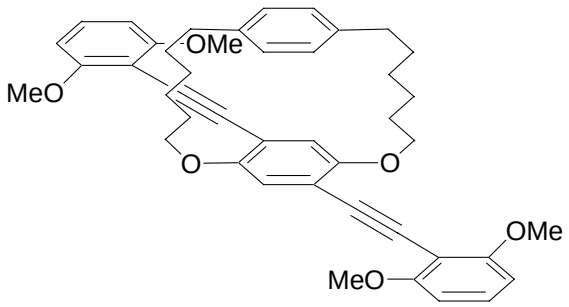
DFILE F:\NMR\2bj_1H.als
COMNT
DATIM Wed Apr 02 10:28:02 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18



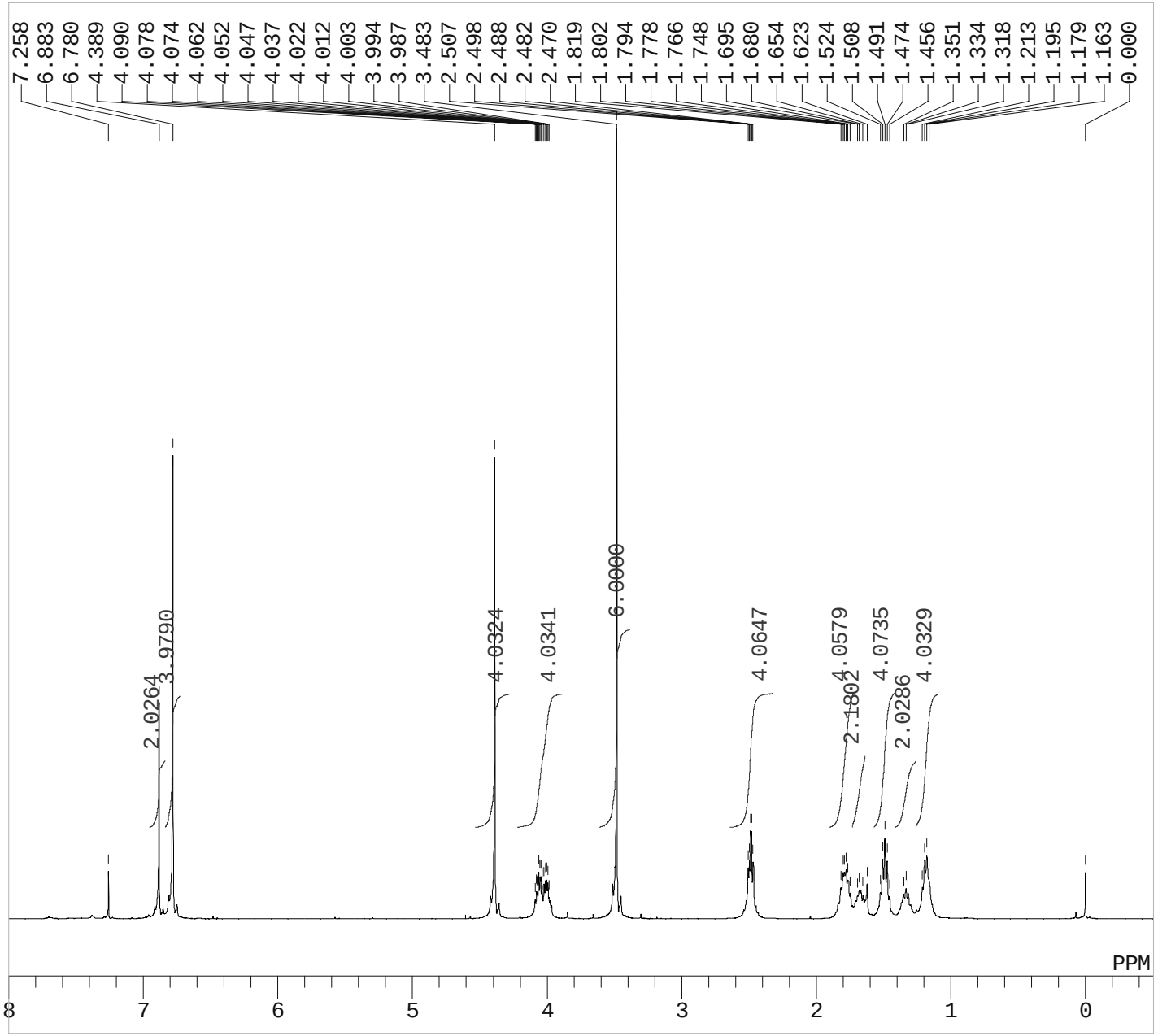
2bj



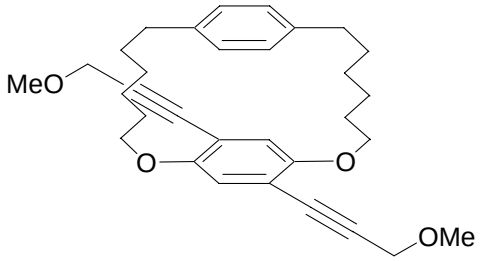

```
DFILE   F:\NMR\2bj_13C.als
COMNT
DATIM   Wed Apr 02 10:42:36 2008
OBNUC   13C
EXMOD   BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27118.6 Hz
SCANS           257
ACQTM         1.208 sec
PD            1.792 sec
PW1             4.6 us
IRNUC   1H
CTEMP          26.5 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            25
```



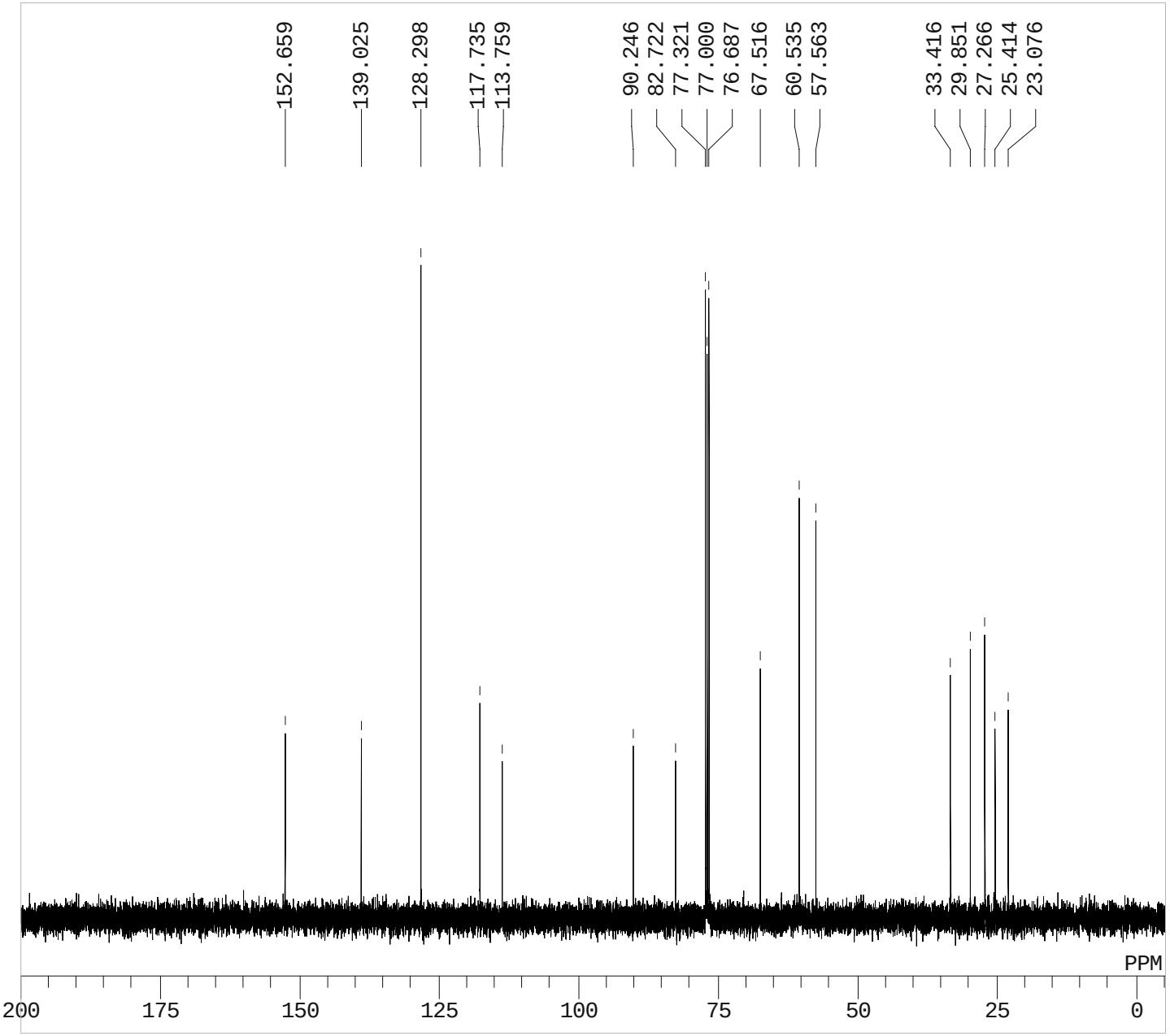
2bj



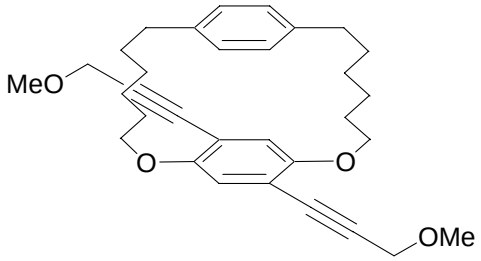
DFILE F:\NMR\2bl_1H.als
COMNT
DATIM Fri Oct 03 17:33:10 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18



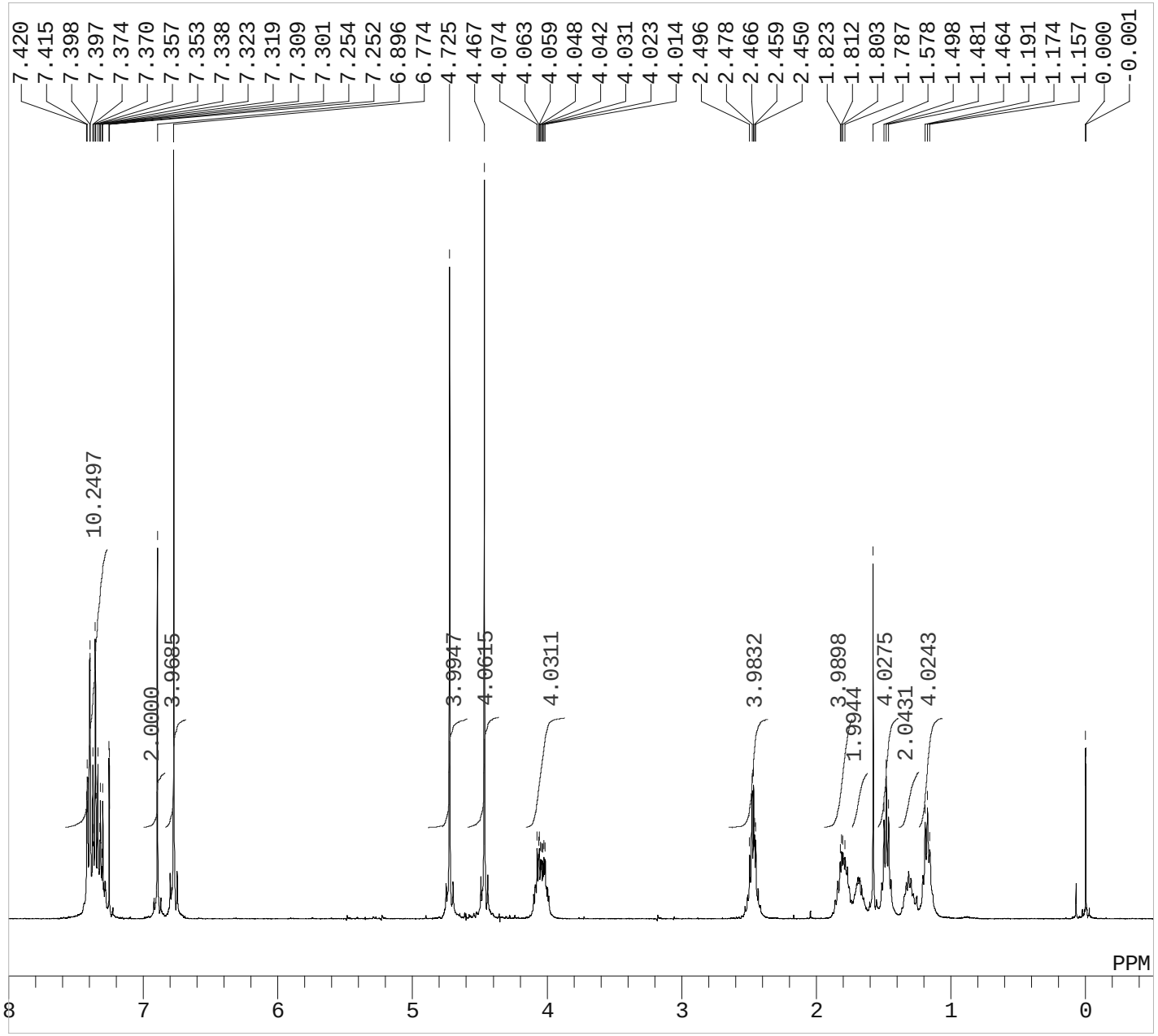
2bl



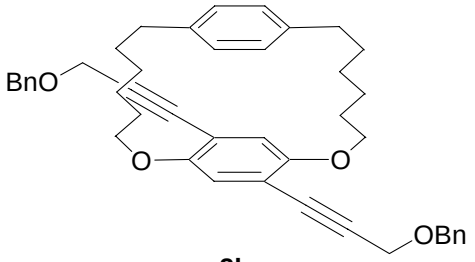
DFILE	F:\NMR\2bl_13c.als
COMNT	
DATIM	Tue Dec 09 14:49:53 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	129
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



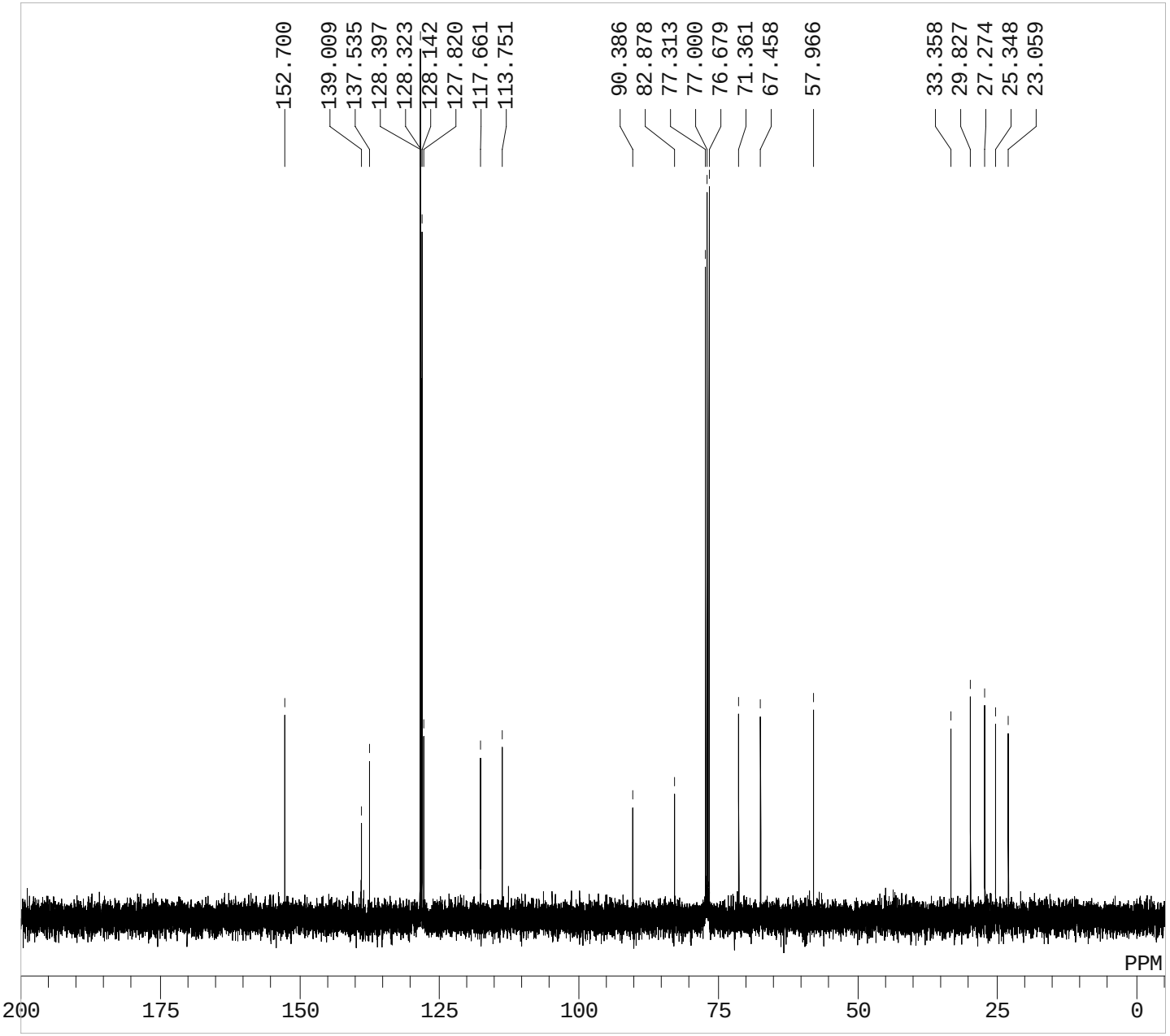
2bl



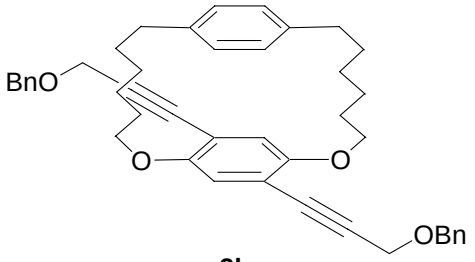
DFILE F:\NMR\2bm_1H.als
COMNT
DATIM Mon Oct 06 13:37:21 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.02 Hz
RGAIN 18



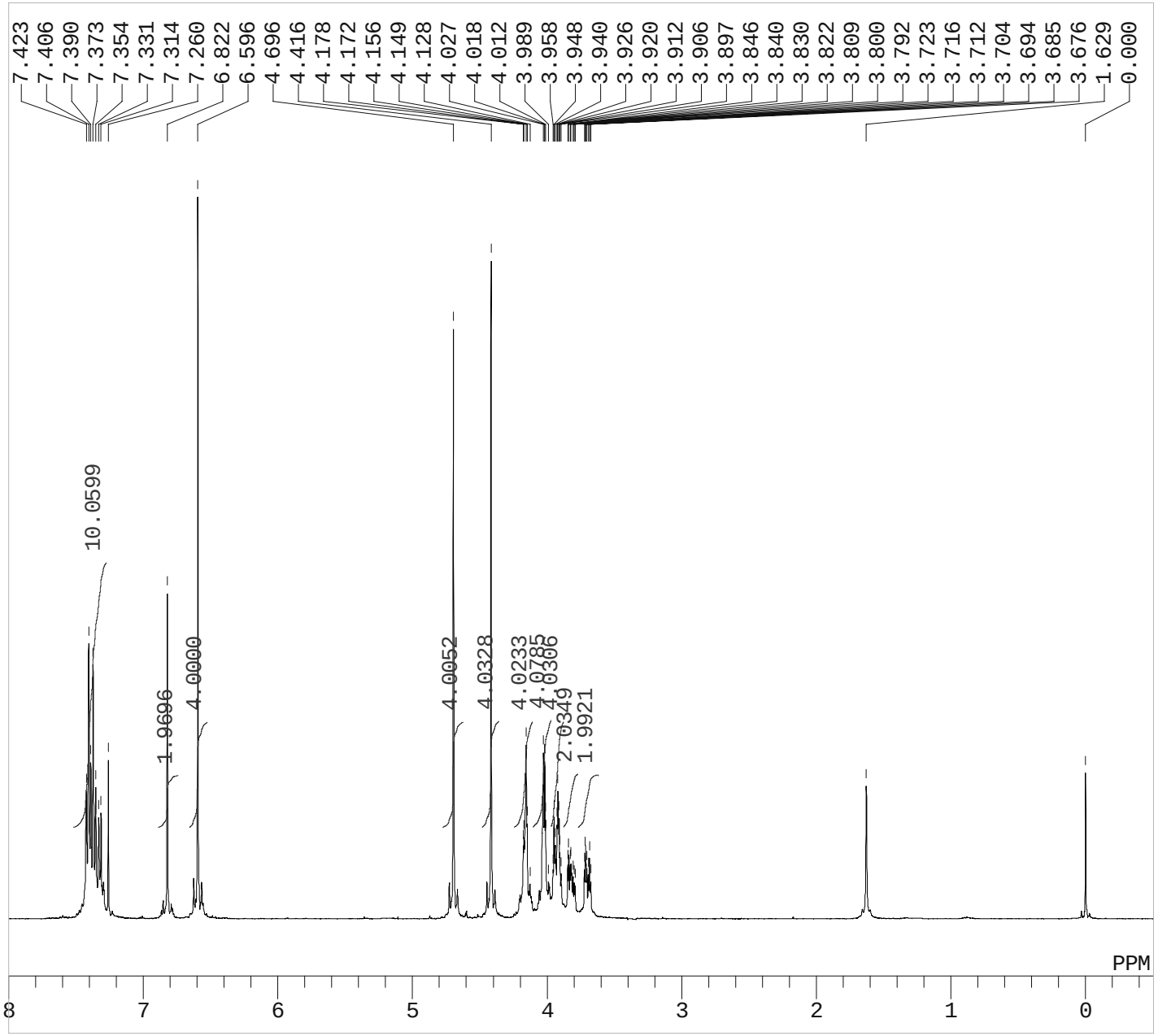
2bm



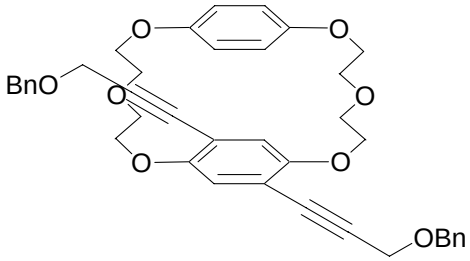

```
DFILE   F:\NMR\2bm_13C.als
COMNT
DATIM   Mon Oct 06 13:57:04 2008
OBNUC   13C
EXMOD   BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU       27118.6 Hz
SCANS           257
ACQTM         1.208 sec
PD            1.792 sec
PW1             4.7 us
IRNUC   1H
CTEMP          23.3 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.02 Hz
RGAIN            26
```



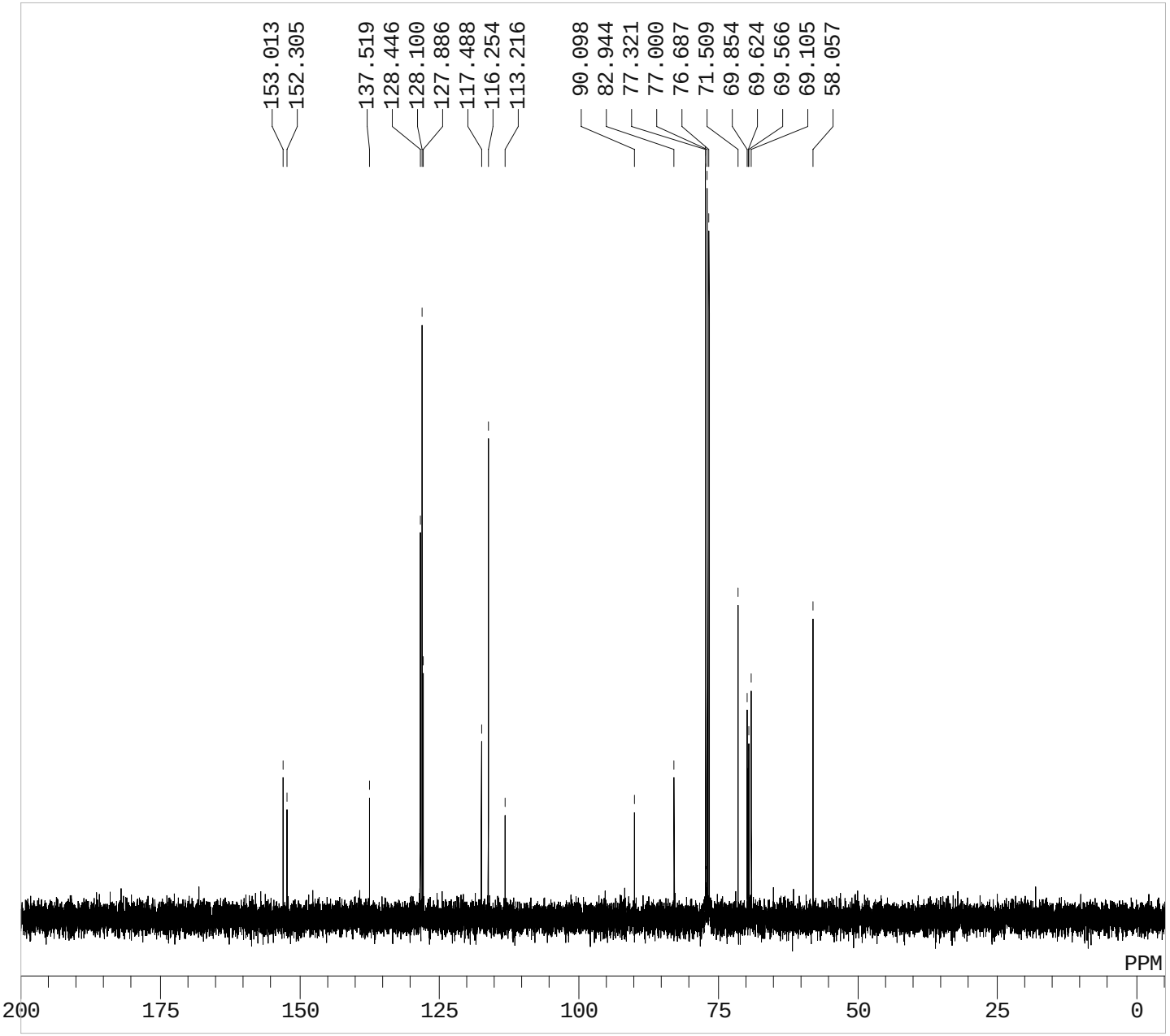
2bm



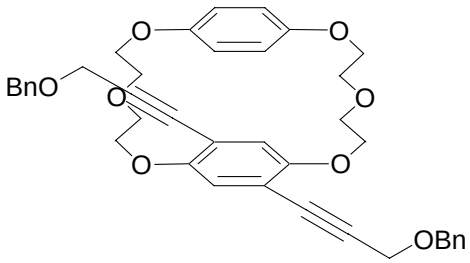
DFILE	F:\NMR\2cm_1H.als
COMNT	
DATIM	Sat Oct 04 17:16:58 2008
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	7992.0 Hz
SCANS	16
ACQTM	4.100 sec
PD	2.900 sec
PW1	6.6 us
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	18



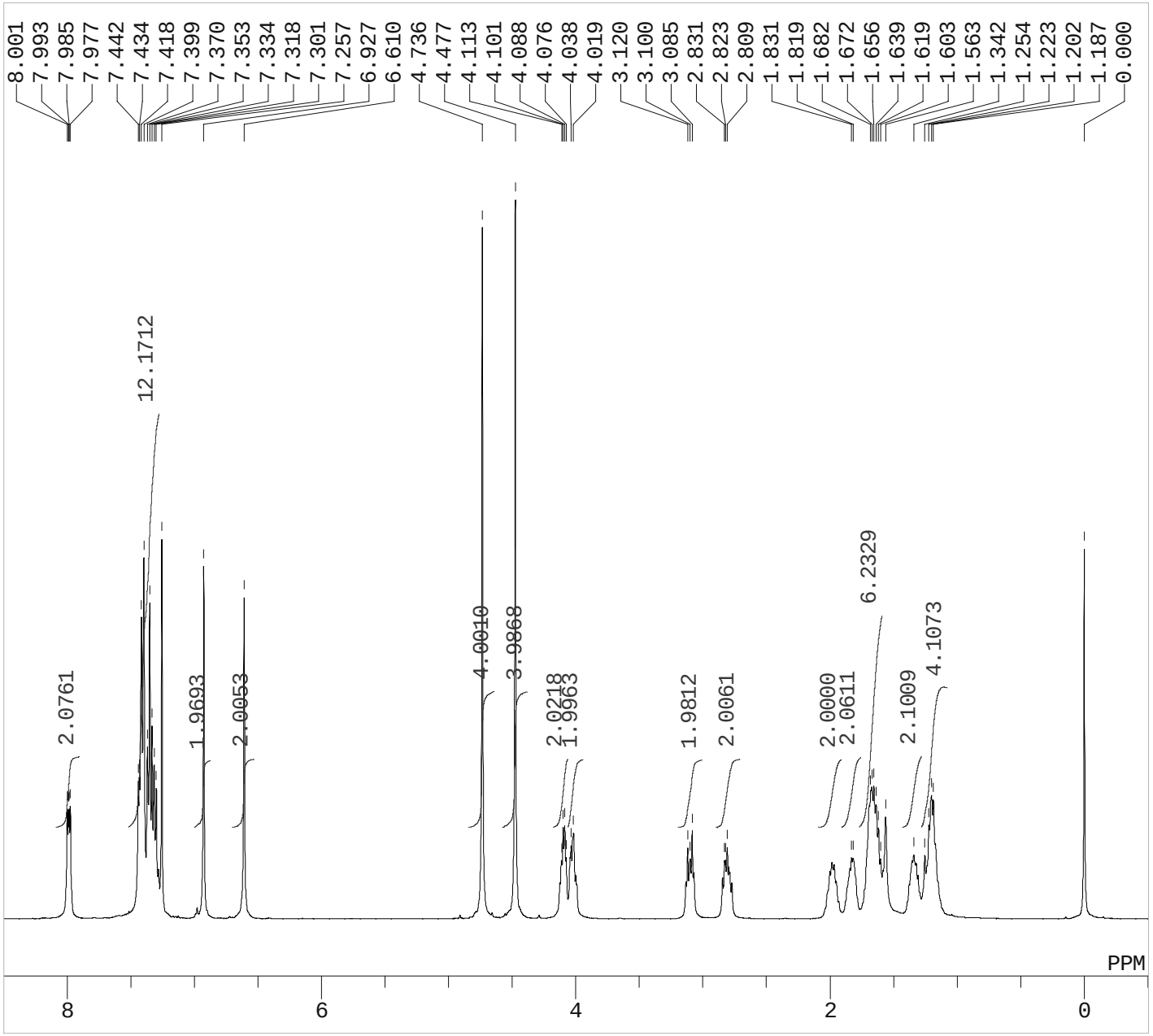
2cm



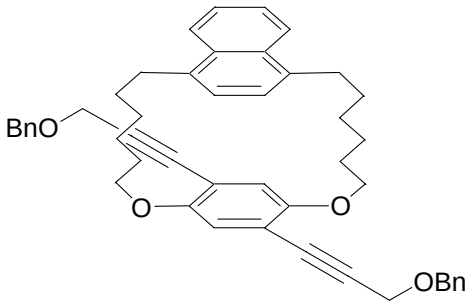
DFILE	F:\NMR\2cm_13C.als
COMNT	
DATIM	Sat Oct 04 17:28:19 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	201
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	24.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	26



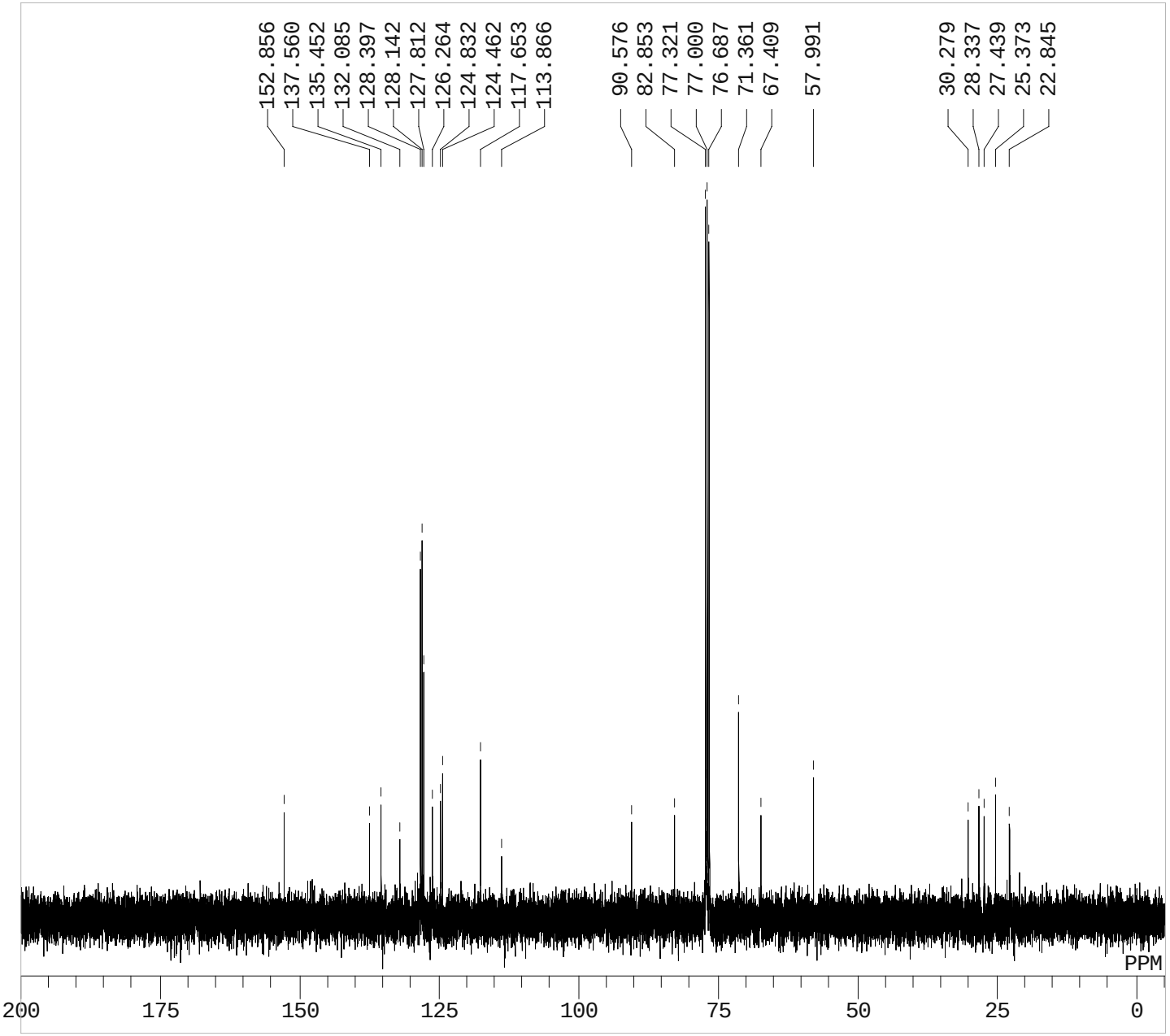
2cm



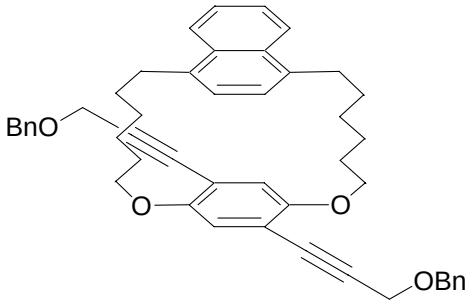
DFILE F:\NMR\2dm_1H.als
COMNT
DATIM Mon Dec 08 18:13:47 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.12 Hz
RGAIN 20



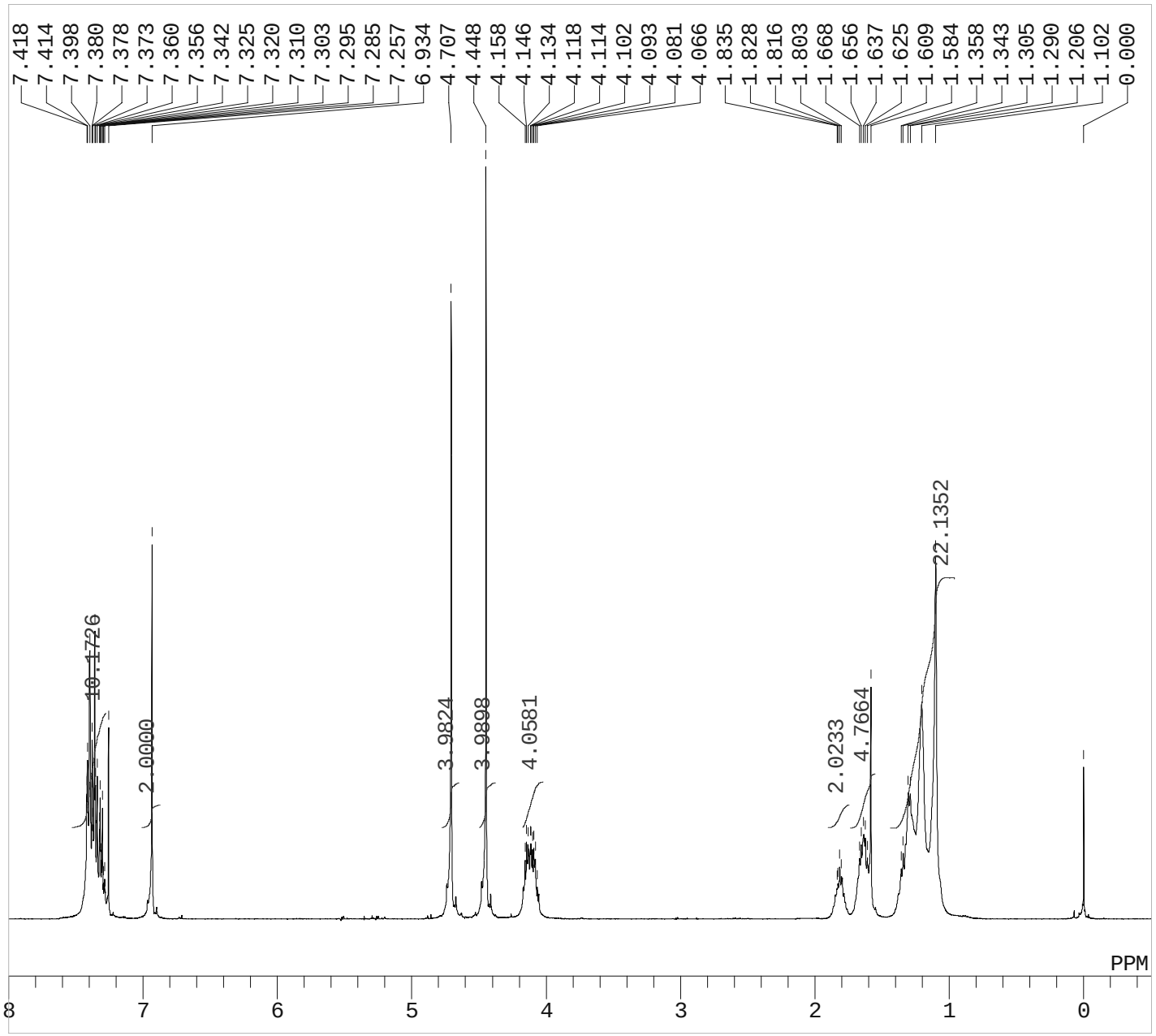
2dm



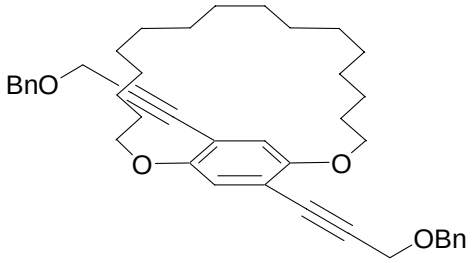
DFILE	F:\NMR\2dm_13C.als
COMNT	
DATIM	Sat Oct 04 16:16:33 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	200
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	26



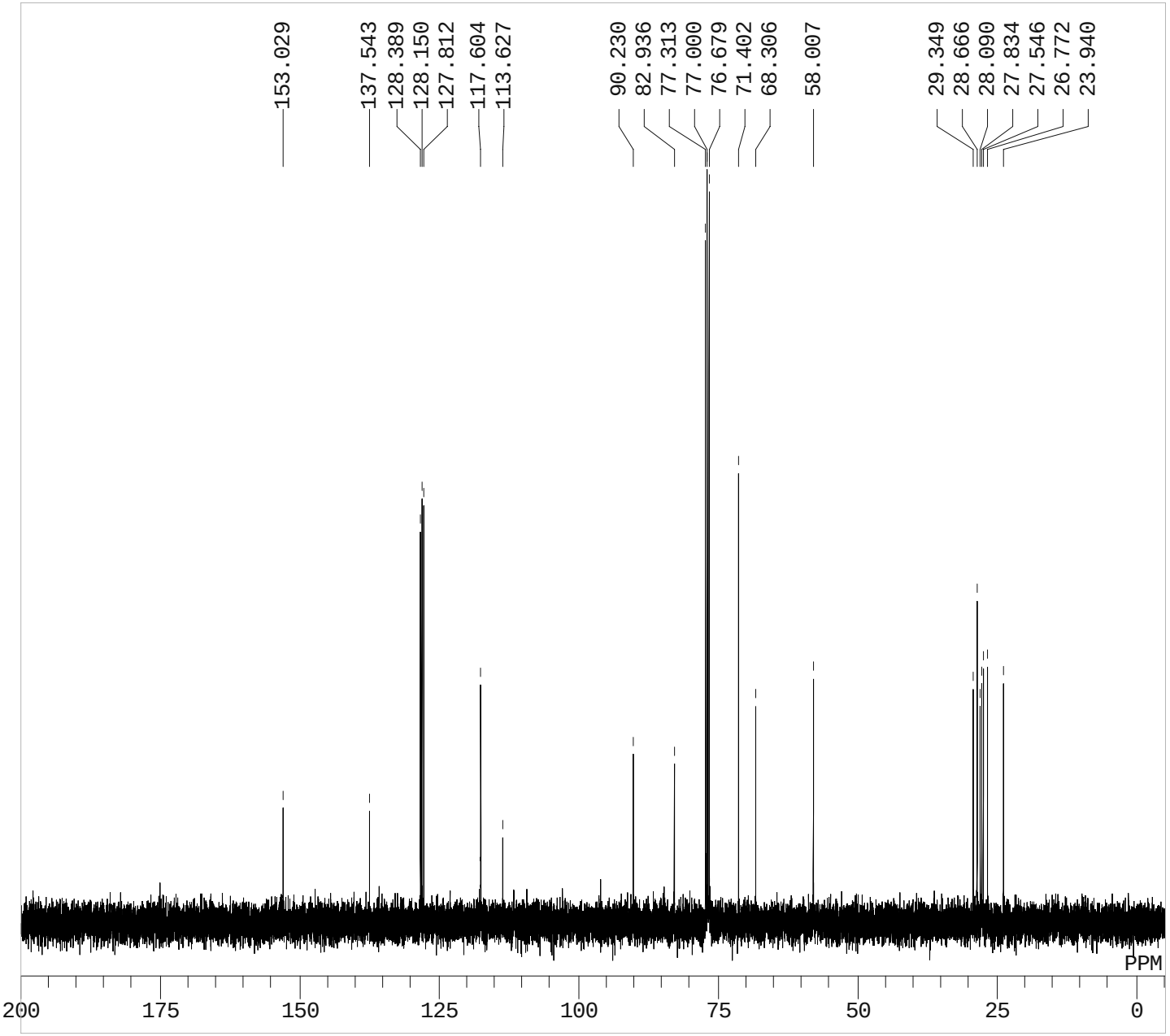
2dm



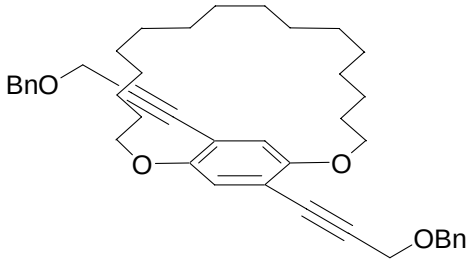
DFILE	F:\NMR\2em_1H.als
COMNT	
DATIM	Fri Oct 03 21:50:42 2008
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	7992.0 Hz
SCANS	16
ACQTM	4.100 sec
PD	2.900 sec
PW1	6.6 us
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	19



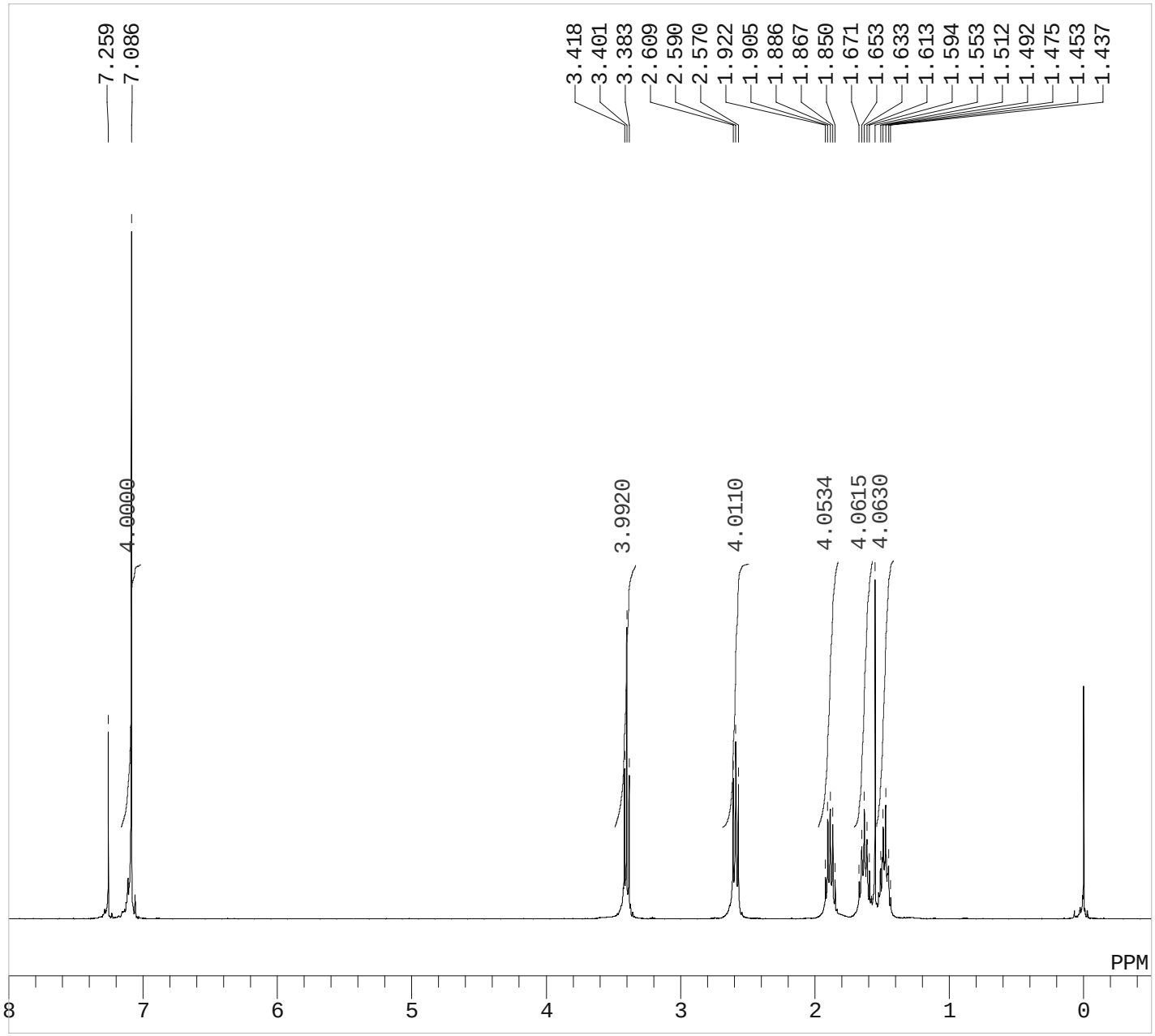
2em



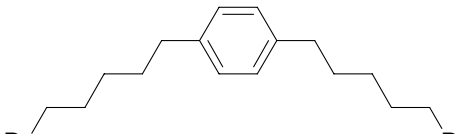
DFILE	F:\NMR\2em_13C.als
COMNT	
DATIM	Fri Oct 03 22:07:18 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	201
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	26



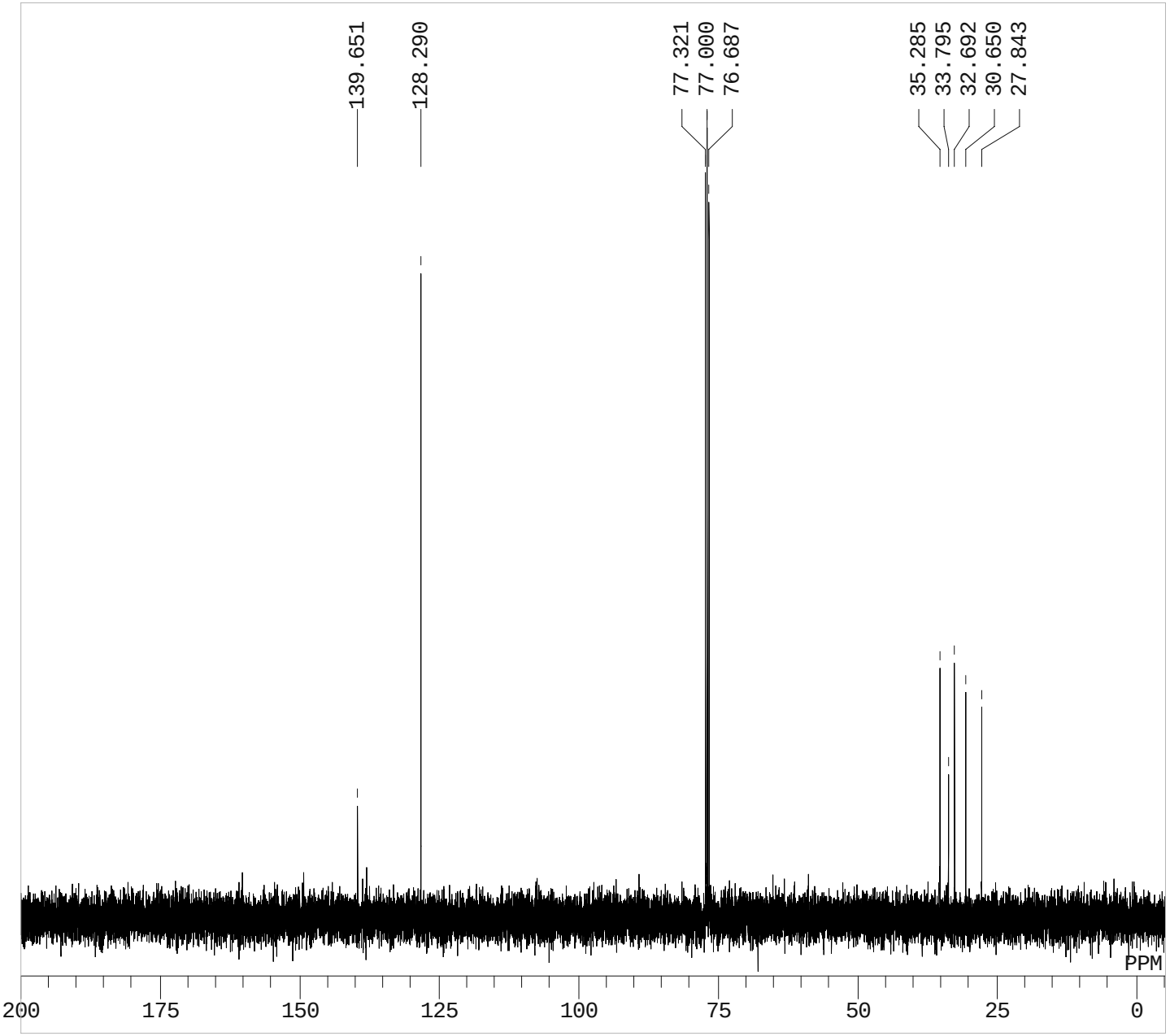
2em



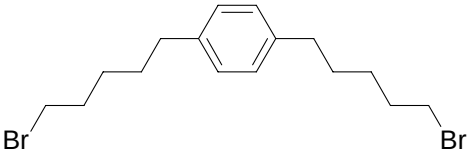

```
DFILE   F:\NMR\3a_1H.als
COMNT
DATIM   Fri Oct 17 21:05:21 2008
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS             16
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.6 us
IRNUC   1H
CTEMP           24.7 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             20
```



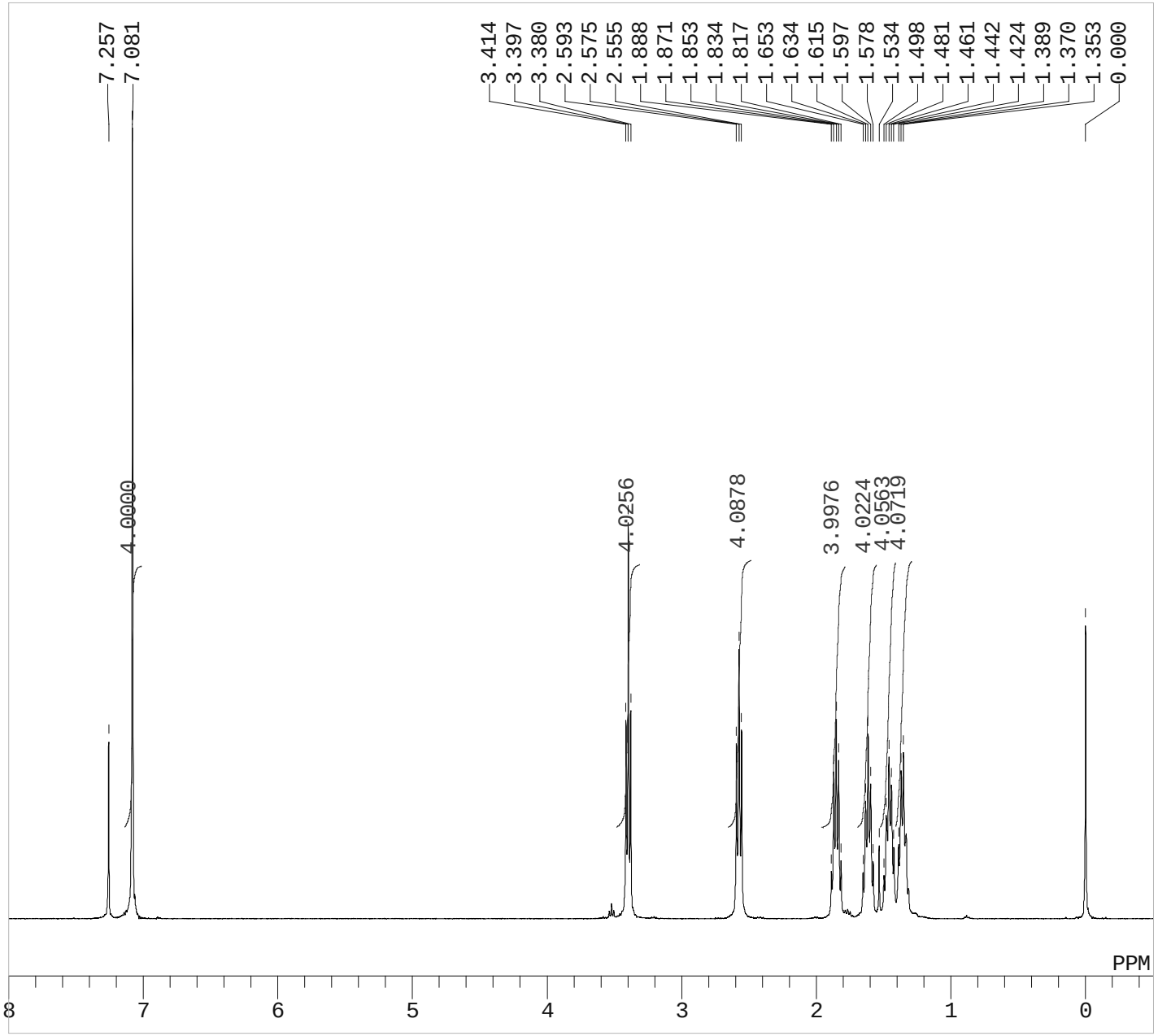
3a



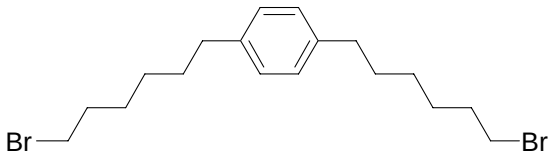
DFILE	F:\NMR\3a_13C.als
COMNT	
DATIM	Fri Oct 17 21:12:56 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	129
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.7 us
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	26



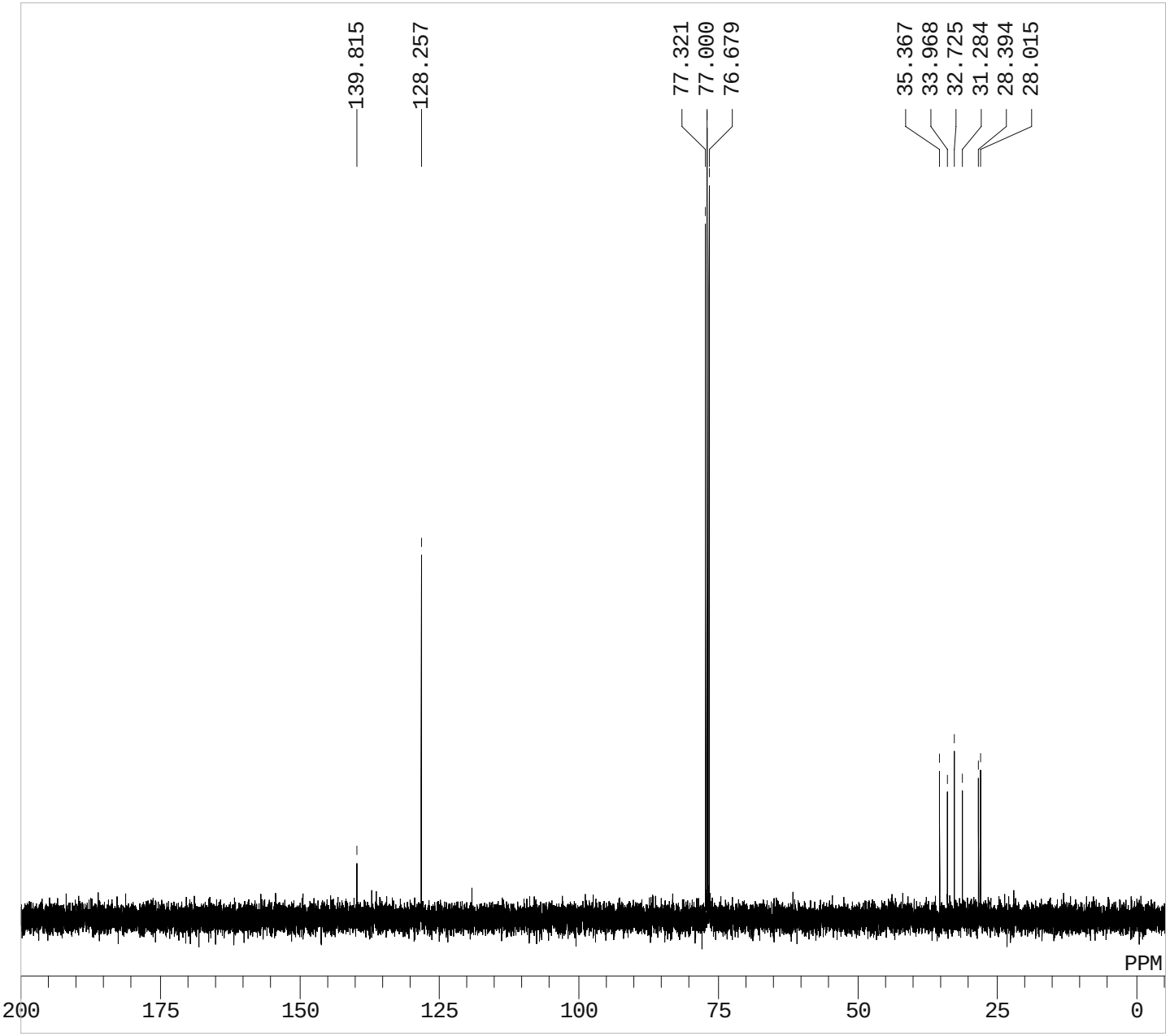
3a



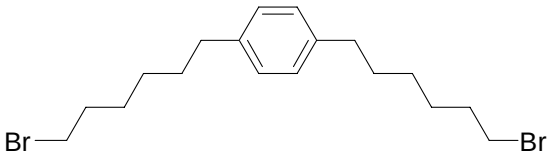

```
DFILE   F:\NMR\3b_1H.als
COMNT
DATIM   Mon Mar 03 16:31:45 2008
OBNUC   1H
EXMOD   NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS            16
ACQTM         4.100 sec
PD            2.900 sec
PW1             6.6 us
IRNUC   1H
CTEMP          24.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            20
```



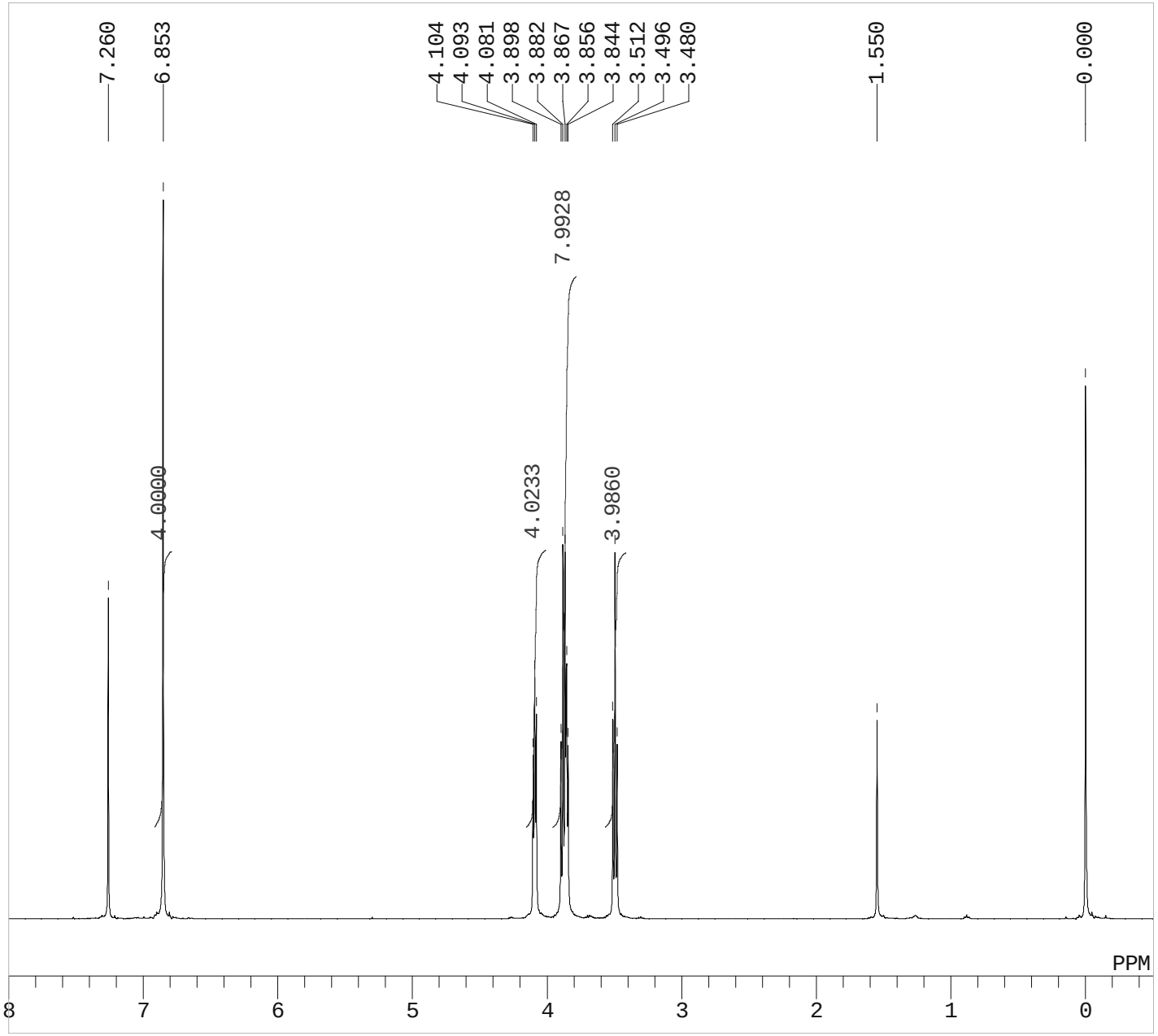
3b



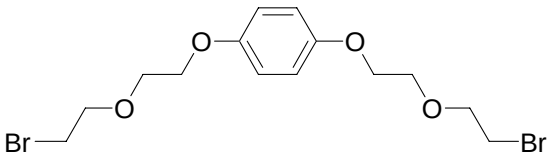
DFILE	F:\NMR\3b_13C.als
COMNT	
DATIM	Mon Mar 03 16:41:08 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
POINT	32768
FREQU	27118.6 Hz
SCANS	129
ACQTM	1.208 sec
PD	1.792 sec
PW1	4.6 us
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



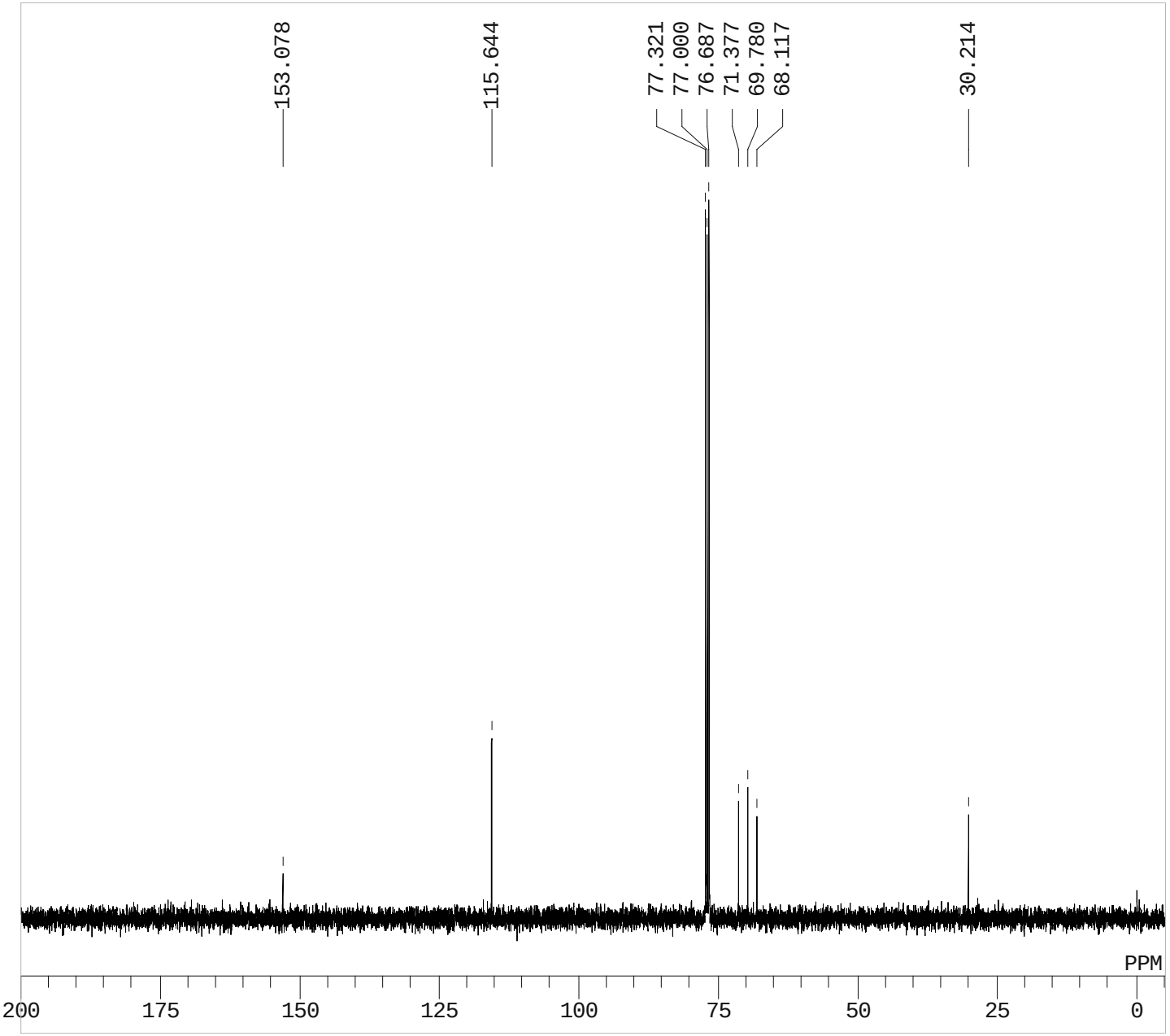
3b



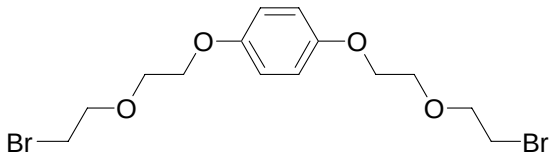

```
DFILE   F:\NMR\3c_1H.als
COMNT
DATIM   Thu Jul 05 16:37:44 2007
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS             16
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.6 us
IRNUC   1H
CTEMP           25.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.00 Hz
RGAIN             22
```



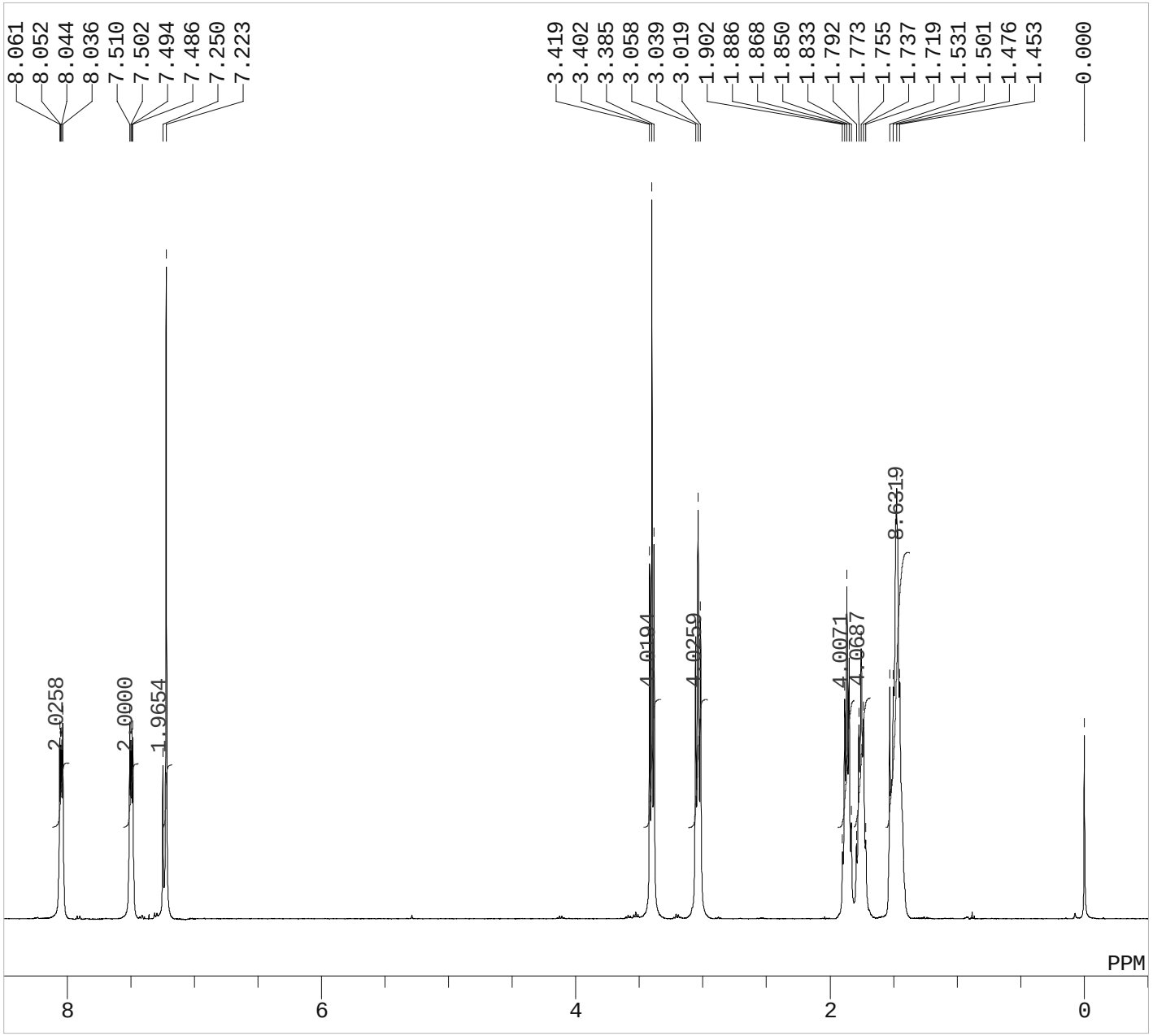
3c



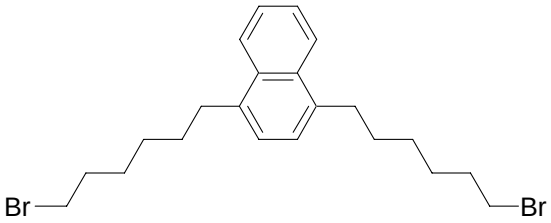

```
DFILE  F:\NMR\3c_13C.als
COMNT
DATIM  Thu Jul 05 16:45:40 2007
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27118.6 Hz
SCANS          129
ACQTM        1.208 sec
PD           1.792 sec
PW1            4.6 us
IRNUC  1H
CTEMP         26.0 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.00 Hz
RGAIN           25
```



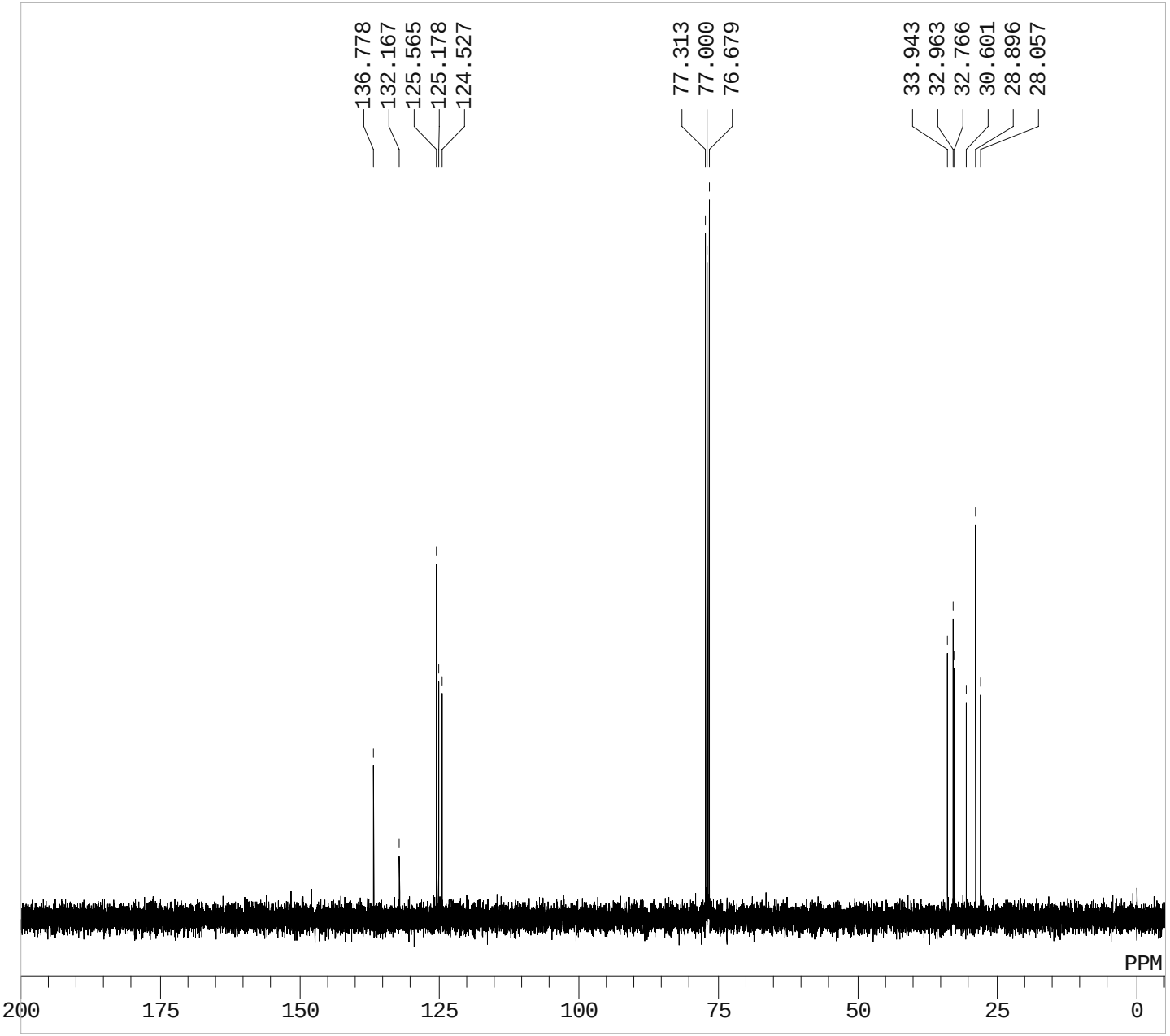
3c



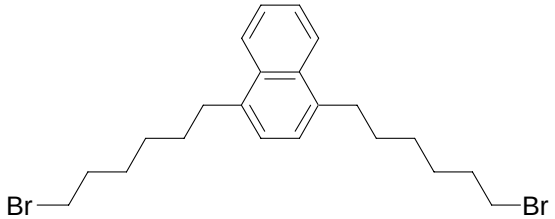
DFILE F:\NMR\3d_1H.als
COMNT
DATIM Wed Jan 31 15:04:35 2007
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 7992.0 Hz
SCANS 16
ACQTM 4.100 sec
PD 2.900 sec
PW1 6.6 us
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17



3d




```
DFILE  F:\NMR\3d_13C.als
COMNT
DATIM  Mon Feb 05 12:55:48 2007
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN      10500.0 Hz
POINT        32768
FREQU      27118.6 Hz
SCANS          129
ACQTM        1.208 sec
PD           1.792 sec
PW1            4.6 us
IRNUC  1H
CTEMP         25.7 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           24
```



3d