Supporting Material for *Angewandte Chemie*

Towards Six-Fold Functionalization of Buckminsterfullerene (C_{60}) at Fully Addressable Octahedral Sites

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Experimental Section

General Remarks. All reactions were performed under argon and, for $^1O_2$ sensitive compounds (all C_{60} derivatives containing the cyclohexene moiety), in absence of light. All NMR studies were carried out on Bruker AMX-500 or AMX-400 spectrometers. Me_4Si was used as the internal standard for ^1H NMR and the deuterated solvent was used as a standard for ^{13}C NMR. ^{13}C NMR spectra were resolution enhanced with Gaussian broadening (LB = -1, GB = 0.3) to resolve most overlapping lines. The matrix used for FAB mass spectra was *m*-nitrobenzyl alcohol; FT-IR spectra were recorded on a Perkin-Elmer Paragon-1000 instrument. Column chromatography was performed on silica gel 230-400 mesh (flash) from E. Merck or from Scientific Absorbents; thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} from E. Merck.

Materials. Pure C_{60} (99.8%) was obtained from MER Corporation, Tucson, Arizona 85706 or from the Southern Chemical Group, Stone Mountain, Georgia 30087. Details on separations and solvent purification can be found in ref. 12.

Synthesis. 3-Phenyl-2-cyclobuten-1-ol (C). To a solution of 570 mg (3.95 mmol) of 3-phenylcyclobutenone (**A**)[1] in 25 mL of MeOH was added 1.5 g of $CeCl_3 \cdot 7H_2O$. After cooling in an ice bath, 170 mg (4.5 mmol) of sodium borohydride was added in portions and the reaction mixture was stirred at 0 ˚C for 30 min. The solvent was evaporated carefully at 25 ˚C under reduced pressure. The residue was treated with water, extracted with ether, dried over anh. $MgSO_4$ and evaporated to dryness. The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2) to give 530 mg (92%) of product **C** as a white unstable solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.75 (br s, 1H), 2.59 (dt, *J* = 12.9, 1.2 Hz, 1H), 3.17 (ddd, *J* = 12.9, 3.9, 0.9 Hz, 1H), 4.77 (d, *J* = 3.9 Hz, 1H), 6.36 (dd, *J* = 1.2, 0.9 Hz, 1H), 7.29-7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 40.47, 67.32, 125.37, 128.38,

[1] Danheiser, R. L.; Savariar, S.; Cha, D. D. *Org. Synth. Coll. Vol. VIII* **1993**, 82-86.

128.65, 129.29, 133.71, 147.18; FT-IR (KBr) ν (cm^{-1}) 3340 vs, 2922.9 m, 1684.0 m, 1448.9 s, 1244.3 m, 1113.6 s, 691.0 s. HRMS (EI^+) calcd for $C_{10}H_{10}O$: 146.0732, found: 146.0729.

3-(4-*t*-Butylphenyl)-cyclobuten-1-ol (D). To a solution of 600 mg (3 mmol) of 3-(4-*t*-butylphenyl)cyclobutenone (**B**) in 40 mL of MeOH, 0.85 g of $CeCl_3 \cdot 7H_2O$ was added. After cooling in an ice bath, 120 mg (3.16 mmol) of sodium borohydride was added in portions. After stirring at 0 ˚C for 20 min, the solvent was carefully evaporated at room temperature under reduced pressure. The crude product was then purified by flash chromatography (SiO_2, CH_2Cl_2) to give 580 mg (96%) of **D** as white unstable crystals. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.31 (s, 9H), 1.86 (br s, 1H), 2.58 (d, *J* = 12.9, Hz, 1H), 3.17 (dd, *J* = 12.9, 4.0 Hz, 1H), 4.78 (d, *J* = 4.0 Hz, 1H), 6.32 (s, 1H), 7.33 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.37 (dd, *J* = 8.2, 1.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 31.23, 34.73, 40.52, 67.40, 125.19, 125.30, 128.41, 131.08, 147.06, 151.90; FT-IR (KBr) υ (cm^{-1}) 3329 br s, 2959 s, 1618 w, 1502 m, 1460 m, 1408 s, 1361 m, 1238 s, 1102 s, 828 s. HRMS (EI^+) calcd for $C_{14}H_{18}O$: 202.1358, found: 202.1354.

Methyl 4-(trimethylsilylethynyl)phenylacetate (F). A total of 4.58 g (20 mmol) of methyl 4-bromophenylacetate (**E**), 500 mg (0.712 mmol) of bis(triphenylphos-phine)palladium(II) chloride, 500 mg (1.9 mmol) of triphenylphosphine, and 100 mg (0.53 mmol) of cuprous iodide were mixed in 60 mL of redistilled triethylamine. The solution was degassed for 15 min, then 10 g (0.1 mol) of trimethylsilylacetylene was added via syringe. The reaction solution was heated to 85 ˚C for 12 h. After cooling to room temperature, the solution was filtered. The filtrate was evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) gave 4.9 g (99.5%) of **5** as a white solid (m.p. 48.5-49.5 ˚C). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.22 (s, 9H), 3.59 (s, 2H), 3.66 (s, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4, Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) –0.09, 40.98, 52.05, 94.22, 104.73, 121.94, 129.11, 132.07, 134.30, 171.48; FT-IR (KBr) ν (cm^{-1}) 2951 m, 2158 s, 1741 s, 1503 m, 1438 m, 1246 s, 1162 m, 1020 s, 850 m. HRMS (EI^+) calcd for $C_{14}H_{18}O_2Si$: 246.1076, found: 246.1075.

Methyl 4-(ethynyl)phenylacetate (G). A mixture of 9.8 g (40 mmol) of **F,** 10 g of potassium carbonate in 40 mLof MeOH were stirred at room temperature for 1 h. The solvent was evaporated, the residue mixed with chloroform and passed through a pad of silical gel. The filtrate was evaporated to obtain 6.8 g (98%) of the product as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.05 (s, 1H), 3.61 (s, 2H), 3.68 (s, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.04, 52.19, 83.36, 77.32, 121.00, 129.31, 132.34, 134.73, 171.55; FT-IR (KBr) ν (cm^{-1}) 3286 s, 3033 m, 3001 m, 2952 s, 2108 m, 1736 s, 1610 m, 1509 s,1436 s, 1341 m, 1257 s, 1162 s, 1013 s, 821 s. HRMS (EI^+) calcd for $C_{11}H_{10}O_2$: 174.0681, found: 174.0681.

Compound H. A solution of 706 mg (4.06 mmol) of compound **G**, 918 mg (4 mmol) of 4-bromophenylacetate (**E**), 100 mg (0.142 mmol) of bis(triphenylphos-phine)palladium(II) chloride, 100

mg (0.381 mmol) of triphenylphosphine, and 20 mg (0.11 mmol) of cuprous iodide in 40 mL of degassed, redistilled triethylamine was heated up to 90 ˚C for 4.5 h. After cooling to 20 ˚C, the mixture was filtered and the filtrate evaporated to dryness. Flash chromatography (SiO_2, $CHCl_3$) gave the product as a yellow solid. Recrystalization from cyclohexane yielded 881 mg (66%) of **H**, as white crystals (m.p. 100-101.5 ˚C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.64 (s, 4H), 3.70 (s, 6H), 7.27 (d, *J* = 8.2 Hz, 4H), 7.49 (d, *J* = 8.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.04, 52.13, 89.20, 122.09, 129.30, 131.75, 134.10, 171.59; FT-IR (KBr) ν (cm^{-1}) 1737 s, 1521 m, 1436 m, 1305 m, 1245 s, 1136 s, 1002 s. HRMS (EI^+) calcd for $C_{20}H_{18}O_4$: 322.1205, found: 332.1206.

Compound I. A total of 2 g (6.02 mmol) of compound **H** was suspended in 40 mL of aqueous KOH (4 g). The mixture was heated at reflux for 2 h until the solution became clear. The solution was cooled to room temperature and filtered. The filtrate was treated carefully with 3 M sulfuric acid until *p*H = 3. The precipitate that developed was collected by vacuum filtration, wased with water and then dried at 50 ˚C *in vacuo* for 3 h to give 1.74 g (95%) of **I** as a white solid. ^{1}H NMR (400 MHz, MeOD) δ (ppm) 3.61 (s, 4H), 7.28 (d, *J* = 8.4 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 4H); FT-IR (KBr) ν (cm-1) 3300-2700 br s, 1695 s, 1513 m, 1411 s, 1251 s. HRMS (EI^+) Calcd for $C_{18}H_{14}O_4$: 294.0892, found: 294.0891.

Compound 1a (mixture of diastereomers). To a stirred solution of 441 mg (1.5 mmol) of compound **I** in 30 mL of dry THF at 0 ˚C was added 5 mL (26 mmol) of oxalyl chloride. The flask was fitted with a drying tube and the mixture was stirred at room temperature for 12 h. The solvent and the excess of oxalyl chloride were evaporated under reduced pressure to dryness. The residue was cooled to 0 ˚C in an ice bath. A total of 420 mg (2.8 mmol) of alcohol **C** in 35 mL of dry methylene chloride was added, followed by 1 mL of dry pyridine. After stirring at 0 ˚C for 1 h, the solvent was evaporated. The residue was purified by flash chromatography (SiO_2, $CHCl_3$), to give 323 mg (42%) of compound **1a** as a white solid (m.p. 145-146.5 ˚C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.74 (d, *J* = 13.1 Hz, 2H), 3.21 (dd, *J* = 13.1, 3.9 Hz, 2H), 3.64 (s, 4H), 5.45 (d, *J* = 3.8 Hz, 2H), 6.31 (s, 2H), 7.26-7.48 (m, 18H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 37.16, 41.35, 69.14, 89.27, 122.10, 125.38, 125.54, 128.48, 129.08, 129.35, 131.80, 133.14, 134.20, 148.58, 171.25; FT-IR (KBr) ν (cm^{-1}) 1721 s, 1330 s, 1232 s, 1145 s. HRMS (EI^+) calcd for $C_{38}H_{30}O_4$: 550.2144, found: 550.2137.

Compound 1b (mixture of diastereomers). To a stirred solution of 441 mg (1.5 mmol) of compound **I** in 30 mL of dry THF at 0 ˚C was added 4 mL (20.8 mmol) of oxalyl chloride. The flask was fitted with a drying tube and the mixture was stirred at room temperature for 14 h during which the milky solution turned clear. The solvent was evaporated and the residue maintained under high vacuum for 30 min. After cooling to 0 ˚C, 460 mg (2.27 mmol) of compound **D** in 30 mL of dry CH_2Cl_2 was added. Then, 0.5 mL of dry pyridine was added via syringe. After stirring at 0 ˚C for 30 min, the solvent was evaporated. The residue was separated by flash chromatography (SiO_2, CH_2Cl_2) to give 401 mg (53%) of compound **1b** as a white solid (m.p. 154-155.5˚C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.32 (s, 18H), 2.74 (d, *J* = 13.0 Hz, 2H), 3.20 (dd, *J* = 13.0, 3.8 Hz, 2H), 3.65 (s, 4H), 5.46 (d, *J* = 3.8 Hz,

2H) 6.26 (s, 2H), 7.25-7.49 (m, 16H); ^{13}C NMR (100.6 MHz. $CDCl_3$) δ (ppm) 31.20, 34.77, 37.16, 41.34, 69.28, 89.24, 122.06, 124.43, 125.34, 125.37, 129.30, 130.44, 131.76, 134.21, 148.43, 152.34, 171.23; FT-IR (KBr) υ (cm^{-1}) 2961 m, 1730 s, 1157 s. HRMS (FAB^+) calcd for $C_{46}H_{46}O_4$: 662.3396, found: 662.3403.

Compound 3a (mixture of *rac/meso* diastereomers). A solution of 720 mg (1 mmol) of C_{60} and 550 mg (1 mmol) of compound **1a** in 1.2 L of toluene was degassed with a stream of argon for 20 min. The solution was then stirred at 105 ˚C for 24 h. The solvent was evaporated and the residual mixture purified by flash chromatography (SiO_2, toluene/hexanes 4:1 to 10:1) to give 310 mg (25%) of **3a** as a brown solid. ^{1}H NMR (500 MHz, $CDCl_2$-$CDCl_2$) δ (ppm) 3.85 (s, 2H), 3.86 (s, 2H), 4.54 (br d, *J* = 14.5 Hz, 2H), 4.73 (d, *J* = 14.5 Hz, 2H), 6.95-7.05 (m, 8H), 7.08-7.11 (m, 2H), 7.21-7.24 (m, 2H), 7.44-7.47 (m, 4H), 7.75-7.78 (m, 4H); FT-IR (KBr) υ (cm^{-1}) 2962 w, 2927 w, 1735 s, 1511 w, 1447 w, 1425 w, 1235, s, 1132 m, 1101 w, 1032 w, 815 w, 798 w. HRMS (FAB^+) Calcd for $C_{98}H_{30}O_4$: 1270.2144, found: 1270.2134.

The remaining brown fraction eluted with the same solvent afforded after evaporation 500 mg (39%) of a diastereomeric mixture of *trans*-2 bisadducts, as deduced from the UV-vis spectrum (see also HPLC trace). This fraction was not investigated further for this work.

Compound 3b (mixture of *rac/meso* diastereomers). A solution of 200 mg (0.28 mmol) of C_{60} and 166 mg (0.25 mmol) of **1b** in 600 mL of dry toluene was degassed for 20 min and then heated at reflux for 7 h. After evaporation of the solvent, flash chromatography (SiO_2, toluene/hexanes 4:1) gave 62 mg (18%) of **3b** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.397 (s, 9H), 1.403 (s, 9H), 3.84-3.90 (m, 4H), 4.56 (br d, *J* = 14.2 Hz, 2H), 4.77 (dd, *J* = 14.2, 1.5 Hz, 2H), 6.90-7.15 (m, 14 H), 7.266 (d, *J* = 8.4 Hz, 1H), 7.274 (d, *J* = 8.4 Hz, 1H), 7.470 (d, *J* = 8.4 Hz, 2H), 7.477 (d, *J* = 8.4 Hz, 2H), 7.683 (d, *J* = 8.4 Hz, 2H), 7.691 (d, *J* = 8.4 Hz, 2H); FT-IR (KBr) υ (cm^{-1}) 2958 m, 2923 m, 2854 w, 1736 s, 1517 w, 1509 w, 1457 w, 1236 vs, 1127 m, 1049 w, 816 m. HRMS (FAB^+) Calcd for $C_{106}H_{46}O_4$: 1382.3396, found: 1382.3456.

The remaining brown fraction eluted with the same solvent afforded after evaporation 103 mg (30%) of a diastereomeric mixture of *trans*-2 bisadducts, as deduced from the UV-vis spectrum. This fraction was not investigated further.

Compound 4a (mixture of *rac/meso* diastereomers). To a solution of 102 mg (0.08 mmol) of **3a**, 106 mg (0.8 mmol) of dimethyl malonate and 265 mg (0.8 mmol) of CBr_4 in 10 mL of degassed dry toluene was added 244 mg (1.6 mmol) of DBU. The reaction mixture was stirred at room temperature for 2.5 h and evaporated to dryness. Flash chromatography (SiO_2, first CH_2Cl_2 and then CH_2Cl_2/ethyl acetate 99:1) gave 102 mg (77%) of **4a** as a bright orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 3.686 (s, 2H), 3.692 (s, 2H), 3.75-3.90 (m, 13H), 3.9-4.0 (m, 9H), 6.55-6.58 (m, 2H), 6.58-6.6 (m, 2H), 7.07 (t, *J* = 9.4 Hz, 2H), 7.10-7.20 (m, 6H), 7.30-7.35 (m, 2H), 7.37-7.42 (m, 4H), 7.50-7.54 (m, 4H); FT-IR (KBr) υ (cm^{-1}) 2952, 1744 s, 1434 m, 1384 w, 1251 vs, 1044 w, 758 w, 528 w. HRMS (FAB^+)

Calcd for $C_{113}H_{48}O_{16}$: 1660.2942, found: 1660.2976.

Compound 4b (mixture of *rac/meso* diastereomers). To a solution of 42.3 mg (0.033 mmol) of compound **3a** and 83 mg (0.35 mmol) of diethyl bromomalonate in 7 mL of degassed dry toluene was added 50 mg (0.33 mmol) of DBU. The reaction mixture was stirred at RT for 24 h and evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2, then CH_2Cl_2/ethyl acetate 99:1) gave 48 mg (83%) of **4b** as a bright orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.18-1.31 (m, 12H), 1.35-1.44 (m, 6H), 3.77-4.08 (m, 8H), 4.12-4.31 (m, 8H), 4.36-4.49 (m, 4H), 6.56-6.73 (m, 4H), 7.04-7.62 (m,18H); FT-IR (KBr) υ (cm^{-1}) 2979 w, 2929 w, 2851 w, 1745 s, 1517 w, 1463 w, 1445 w, 1368 w, 1296 m, 1249 vs, 1126 w, 1097 w, 1077 w, 1029 m, 758 m. HRMS (FAB^+) calcd for $C_{119}H_{60}O_{16}$: 1744.3881, found: 1744.3925.

Compound 5a. A degassed solution containing 56 mg (0.034 mmol) of compound **4a**, 85 mg (0.6 mmol) of dimethyl acetylenedicarboxylate (DMAD) and 23 mg (0.12 mmol) of $TsOH{\cdot}H_2O$ in 15 mL of toluene was refluxed for 6 h during which time the color of the solution turned from orange to reddish brown. After evaporation of the solvent, flash chromatography (SiO_2, CH_2Cl_2) gave 29.1 mg (78%) of **5a** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.96 (s, 6H), 4.09 (s, 6H), 4.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 46.24, 50.95, 53.85, 54.08, 54.11, 70.40, 71.23, 138.95, 139.85, 142.29, 142.53, 142.72, 143.01, 143.73, 143.74, 143.76, 145.01, 145.36, 145.46, 145.63, 147.24, 147.53, 163.76, 164.50, 164.56 (C_{2v} symmetry, 25 of the required 25 lines are observed); FT-IR (KBr) υ (cm^{-1}) 2951 w, 1747 s, 1434 m, 1384 w, 1251 vs, 1217 m, 1108 w, 1078 w, 1025 w, 528 w; UV/Vis (CH_2Cl_2) λ_{max} (nm) 232 (ε 106 000), 246 sh (91 900), 264 sh (77 300), 294 (48 200), 353 sh (15 900), 391 sh (5 800), 406 (5 200), 431 sh (2 800) nm; HRMS (FAB^+) calcd for $C_{75}H_{18}O_{12}$: 1110.0798, found: 1110.0750.

Compound 5b. A degassed solution of 8.0 mg (0.0046 mmol) of **4b**, 100 mg (0.7 mmol) of DMAD and 5 mg (0.026 mmol) of $TsOH{\cdot}H_2O$ in 10 mL of toluene was refluxed for 6 h during which time the color of the solution turned from orange to reddish brown. After evaporating the solvent, flash chromatography (SiO_2, CH_2Cl_2) gave 4.5 mg (81%) of **5b** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.39 (t, J = 7.1 Hz, 6H), 1.48 (t, J = 7.1 Hz, 6H), 1.54 (t, J = 7.1 Hz, 6H), 4.43 (q, J = 7.1 Hz, 4H), 4.55 (q, J = 7.1 Hz, 4H), 4.61 (q, J = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 14.13, 14.19, 14.26, 46.48, 51.10, 63.10, 63.32*, 70.49, 71.42, 138.91, 139.82, 142.33, 142.70*, 143.16, 143.69, 143.75, 143.80, 145.17, 145.43*, 145.66, 147.23, 147.56, 163.38, 164.07, 164.12 (C_{2v} symmetry, 25 of the required 28 lines are observed. Asterisks indicate lines with double intensity due to accidental overlap); FT-IR (KBr) υ (cm^{-1}) 2980 w, 2929 w, 1744 s, 1463 w, 1444 w, 1385 w, 1367 w, 1298 w, 1249 vs, 1214 m, 1174 w, 1108 w, 1095 w, 1076 w, 1027 w, 733 w, 528 w. HRMS (FAB^+) Calcd for $C_{81}H_{30}O_{12}$: 1194.1737, found: 1194.1707.

Compound 7a. To a stirred solution of 16.7 mg (0.015 mmol) of trisadduct **5a**, 8.4 mg (0.05 mmol)

of 4,5-diazafluorene (**6a**) and 16.6 mg (0.05 mmol) of CBr_4 in 10 mL of dry toluene, was added dropwise via a syringe pump a solution of 15.2 mg (0.1 mmol) of DBU in 5 mL of dry toluene. The redish brown solution quickly turned into a yellow suspension. After stirring at room temperature for 1 h, the solution was directly submitted to column chromatography (SiO_2, CH_2Cl_2/MeOH 98:2) to afford 12 mg (50%) of the hexaadduct **7a** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 3.81 (s, 6H), 3.90 (s, 6H), 4.02 (s, 6H), 7.21 (dd, *J* = 8.0 Hz, 4.5 Hz, 2H), 7.46 (dd, *J* = 8.0 Hz, 4.5 Hz, 4H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.73 (d, *J* = 4.5 Hz, 2H), 8.74 (d, *J* = 8.0 Hz, 4H), 8.87 (d, *J* = 4.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 36.79, 37.40, 45.37, 45.90, 53.86, 54.12, 54.23, 69.42, 69.53, 74.62, 74.70, 74.96, 122.84, 123.19, 132.35, 132.68, 137.76, 138.06, 140.88, 141.57, 141.94, 142.30, 142.98, 143.18, 145.82, 145.91, 145.93, 145.98, 146.03*, 150.26, 150.38, 157.87, 158.02, 163.96, 164.36, 164.43 (C_{2v} symmetry, 36 of the required 37 lines are observed. The asterisk indicates a line with double intensity due to accidental overlap); FT-IR (KBr) υ (cm^{-1}) 2957 m, 2922 s, 2851 m, 1745 s, 1588 w, 1407 m, 1258 s, 1229 m, 1167 w, 751 w. HRMS (FAB$^+$) calcd for $C_{108}H_{37}N_6O_{12}$ (MH^+): 1609.2469, found: 1609.2523.

Compound 7b. To a stirred solution of 4.8 mg (0.002 mmol) of trisadduct **5b**, 3.4 mg (0.013 mmol) of 2,7-dinitrofluorene (**6b**) and 4.4 mg (0.013 mmol) of CBr_4 in 10 mL of CH_2Cl_2, was added dropwise a solution of 4.0 mg (0.026 mmol) of DBU in 1 mL of CH_2Cl_2. The redish brown solution quickly turned into yellow. After stirring at room temperature for 1 h, the solution was directly submitted to flash column chromatography (SiO_2, CH_2Cl_2/ethyl acetate 99:1) to afford 7.0 mg (89%) of the hexaadduct **7b** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.27 (t, *J* = 7.1 Hz, 6H), 1.37 (t, *J* = 7.1 Hz, 6H), 1.42 (t, *J* = 7.1 Hz, 6H), 4.24 (q, *J* = 7.1 Hz, 4H), 4.34 (q, *J* = 7.1 Hz, 4H), 4.45 (q, *J* = 7.1 Hz, 4H), 8.06 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 4H), 8.33 (dd, *J* = 8.4, 1.8Hz, 2H), 8.48 (dd, *J* = 8.4, 1.8 Hz, 4H), 9.17 (d, *J* = 1.8 Hz, 2H), 9.42 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 14.02, 14.04, 39.16, 39.45, 45.34, 46.14, 63.13, 63.25, 63.31, 69.68, 69.84, 74.71, 74.98, 75.06, 120.71, 121.22, 121.44, 121.58, 124.07, 124.26, 141.13, 141.72, 141.83, 142.14, 142.34, 142.37, 144.34, 144.51, 144.97, 144.98, 145.73, 145.94, 145.98, 146.16, 146.34, 146.58, 147.95, 148.29, 163.28*, 163.40 (C_{2v} symmetry, 40 of the required 42 lines are observed. The asterisk indicates a line with double intensity due to accidental overlap; the line at 14.04 ppm has also two overlapping signals); FT-IR (KBr) υ (cm^{-1}) 2983 w, 2924 w, 2856 w, 1746 s, 1588 w, 1529 s, 1480 m, 1412 m, 1341 vs, 1258 s, 1226 s, 1092 m, 836 m, 737 m. HRMS (FAB$^+$) Calcd for $C_{120}H_{49}O_{24}N_6$ (MH^+): 1957.2798, found: 1957.2713.

Compound 8a. A suspension of 66.0 mg (0.05 mmol) of compound **3a** in 35 mL of dry toluene was cooled to 0 ˚C and 0.8 mL of DIBAL (1.0 M solution in hexanes) was added. The mixture was stirred under argon at room temperature for 5 min during which the brown suspension became a clear brown solution. The solution was quenched with ice-water, washed with saturated NH_4Cl solution, dried over sodium sulfate, and evaporated to dryness. Flash chromatography (SiO_2, $CHCl_2$) gave 44.5 mg (88%) of the corresponding inseparable diastereomeric diols as a brown solid. ^{1}H NMR (400 MHz,

$CS_2/CDCl_3$ 3:1) δ (ppm) 3.11 (br d, *J* = 4.9 Hz, 2H), 4.56 (d, *J* = 14.3 Hz, 2H), 4.90 (br s, 2H), 6.28 (m, 2H), 7.15 (br s, 2H), 7.37 (m, 2H), 7.47 (m, 4H), 7.79 (m, 4H); FT-IR (KBr) υ (cm^{-1}) 3450 br s, 1656 w, 1384 w, 1110 br s, 758 w, 695 w.

To a solution of 8.0 mg (0.0079 mmol) of the above diols in 15 mL of CH_2Cl_2 was added 10 mg (0.024 mmol) of Dess-Martin reagent. After stirring under argon for 30 min, the solvent was evaporated. Flash chromatography (SiO_2, CH_2Cl_2) gave 2.4 mg (30%) of compound **8a** as a very poorly soluble brown solid. ^{1}H NMR (500 MHz, $CDCl_2$-$CDCl_2$) δ (ppm) 4.92 (s, 4H), 7.44 (s, 2H), 7.57-7.61 (m, 6H), 7.98 (d, *J* = 7.8 Hz, 4H). ^{13}C NMR and MS could not be carried out due to the low solubility, see **8b** for an analogous system.

Compound 8b. A solution of 20 mg (0.014 mmol) of compound **3b** in 10 mL of dry toluene was cooled to 0 ˚C and 1.4 mL of DIBAL (1.0 M solution in hexanes) was added. The mixture was stirred under argon at room temperature for 30 min. The solution was then washed with brine, dried over sodium sulfate, and evaporated to dryness. Flash chromatography (SiO_2, $CHCl_3$) gave 14.5 mg (89%) of the corresponding inseparable diastereomeric diols as a brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$ 1:1) δ (ppm) 1.388 (s, 9H), 1.391 (s, 9H), 3.21 (brs, 2H), 4.55 (d, *J* =14.2 Hz, 2H), 4.90 (brs, 2H), 6.30 (t, *J* = 4.5, 2H), 7.15 (brs, 2H), 7.49 (dd, *J* = 8.3 Hz, 1.7 Hz, 4H), 7.75 (dd, *J* = 8.3 Hz, 1.7 Hz, 4H); FT-IR (KBr) υ (cm^{-1}) 3450 br s, 2958 s, 2927 s, 2855 m, 1459 m, 1384 m, 1285 m, 1122 br m, 1078 s.

To a solution of 13.0 mg (0.012 mmol) of the above diols in 20 mL of CH_2Cl_2 was added 20 mg (0.047 mmol) of Dess-Martin reagent. After stirring under argon for 30 min, the solvent was evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2) gave 11.8 mg (91%) of **8b** as a black solid. ^{1}H NMR (400 MHz, $CDCl_2$-$CDCl_2$) δ (ppm) 1.36 (s, 18H), 4.90 (s, 4H), 7.42 (s, 2H), 7.59 (d, *J* = 7.2 Hz, 4H), 7.91 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_2$-$CDCl_2$) δ (ppm) 31.54, 35.29, 41.44, 60.38, 74.36, 125.04, 126.73, 127.01, 134.78, 135.82, 136.19, 141.45, 141.59, 142.24, 142.64, 144.23, 144.49, 145.45, 145.76, 145.88, 148.10, 148.38, 151.38, 154.16, 155.11, 155.35, 192.08 (C_{2v} symmetry, 27 of the required 27 lines are observed); FT-IR (KBr) ν (cm^{-1}) 2959 m, 1673 s, 1654 m, 1606 m, 1192 s, 1110 m, 1028 w, 830 w, 744 w; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 238 (90400), 262 (93100), 320 (58600), 364 (sh, 15400), 442 (sh, 2500), 464 (sh, 1500), 497 (3200) nm; HRMS (FAB^+) calcd for $C_{88}H_{33}O_2$ (MH^+): 1221.2481, found: 1121.2438.

Compounds 10a-c. To a degassed solution of 190 mg (0.15 mmol) of **3a** in 50 mL of PhCl was added 36 mg (0.15 mmol) of diethyl bromomalonate (90% purity) and 33 mg (0.22 mmol) of DBU. The reaction mixture was stirred at 25 ˚C for 12 h and then directly submitted to flash chromatography (SiO_2, hexanes, then CH_2Cl_2) to give 40 mg of recovered **3a**, 36 mg (17%) of **10a** (*anti*/*anti*), 68 mg (32%) of **10b** (*syn*/*anti*), 40 mg (18%) of **10c** (*syn*/*syn*), and less than 10% of the three distinct diastereomeric bis-Bingel adducts (3 red spots on TLC).[2] Overall yield of double e-face mono-Bingel adduct is 67% (85%

[2] These adducts and related ones having different proportions of dimethyl- or diethylmalonates at each stage of addition (as shown by tether removal) were independently characterized and will be the subject of a full paper following publication of this work.

based on recovered **3a**). No isomeric double e-edge mono-Bingel adduct was found.

Isomer 10a (single diastereomer, redish-brown solid). ^{1}H NMR (500 MHz, $CDCl_3$, enhanced with Gaussian broadening) δ (ppm) 1.25 (t, *J* = 7.1 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 3.83 (d part of AB-q, *J* = 13.8 Hz, 2H), 3.88 (d part of AB-q, *J* = 13.8 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.43 (ddd, *J* = 14.5, 2.7, 1.1 Hz, 2H), 4.58 (dd, *J* = 14.5, 2.0 Hz, 2H), 6.84 (dt, *J* = 3.4, 2.4 Hz, 2H), 6.88 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.03 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.06 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.11 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.14 (dd, *J* = 3.4, 1.1 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 4H), 7.69 (d, *J* = 7.4 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 13.97, 14.06, 42.23, 42.78, 50.09, 62.85, 62.90, 64.08, 67.95, 72.63, 75.64, 95.32, 123.20, 125.96, 127.78, 128.28, 128.30, 128.92, 130.71, 130.82, 132.95, 133.08, 135.37, 135.64, 137.65, 138.72, 138.82, 139.54, 140.40, 140.58, 141.17, 141.28, 141.41, 141.55, 142.21, 142.24, 143.79, 144.18, 144.46, 144.95, 145.13, 145.54, 145.59, 146.02, 146.21, 147.60, 148.00, 148.67, 149.30, 150.22, 150.31, 153.82, 153.87, 163.42*, 170.54 (C_s symmetry, 55 of the required 56 lines are observed. The asterisk indicates a line with double intensity due to accidental overlap); FT-IR (KBr) υ (cm $^{-1}$) 3027 w, 2979 ,w, 2924 w, 2852 w, 1743 s, 1516 w, 1494 w, 1446 w, 1367 w, 1238 vs, 1126 m, 1103 m, 1058 m, 1028 m, 818 w, 750 s. HRMS (FAB$^+$) calcd for $C_{105}H_{40}O_8$: 1428.2723, found: 1428.2681.

Isomer 10b (single diastereomer, redish-brown solid). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.29 (t, *J* = 7.1 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 3.81- 3.90 (m, 4H), 4.29-4.33 (m, 3H), 4.38-4.43 (m, 3H), 4.57 (ddd, *J* = 7.5, 4.1, 1.6 Hz, 2H), 6.84 (q, *J* = 2.6 Hz, 1H), 6.88 (q, *J* = 2.6 Hz, 1H), 6.89-7.15 (m, 10H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 14.03, 14.11, 42.15, 42.18, 42.69, 42.74, 50.52, 62.85, 62.94, 63.85, 63.99, 67.70, 67.86, 72.52, 72.87, 75.60, 75.66, 95.39, 95.46, 123.01, 123.12, 125.95, 126.00, 127.74, 127.94, 128.31, 128.24, 128.50, 128.71, 128.91*, 130.35, 130.59, 131.25, 131.89, 131.96, 132.58, 133.02*, 135.26, 135.44, 136.19, 136.22, 137.69, 138.11, 138.64, 138.70, 138.93, 138.94, 139.58, 139.70, 140.30, 140.53*, 140.96, 141.19, 141.25, 141.36*, 141.46, 141.62, 142.02, 142.38, 143.57, 143.62, 144.24, 144.61, 144.63, 144.64, 144.69, 144.76, 145.13, 145.22, 145.41, 145.48, 145.68, 145.76, 145.89, 146.29, 146.42, 147.33, 147.59, 147.63, 147.68, 147.72, 147.94, 148.39, 149.31, 149.80, 149.97, 150.18, 150.26, 150.37, 153.46, 153.75, 153.83, 153.91, 163.28, 163.42, 170.41, 170.48 (C_1 symmetry, 97 of the required 101 lines are observed. Asterisks indicate lines with double intensity due to accidental overlap); FT-IR (KBr) δ (cm^{-1}) 2969 w, 1741 vs, 1638 w, 1517 w, 1444 w, 1366 w, 1236 s, 1109 w, 1060 w, 818 w, 751 m, 695 w. HRMS (FAB$^+$) Calcd for $C_{105}H_{40}O_8$: 1428.2723, found: 1428.2651.

Isomer 10c (single diastereomer, redish-brown solid). ^{1}H NMR (500 MHz, $CDCl_3$, enhanced with Gaussian broadening) δ (ppm) 1.33 (t, *J* = 7.1 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 3.85 (d part of AB-q, *J* = 14.3 Hz, 2H), 3.86 (d part of AB-q, *J* = 14.3 Hz, 2H), 4.32 (ddd, *J* = 14.5, 2.7, 1.0 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 4.58 (dd, *J* = 14.5, 1.9 Hz, 2H), 6.91 (q, *J* = 2.6 Hz, 2H), 6.96 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.99 (dd, *J* = 7.8, 1.8 Hz, 4H), 7.02 (dd, *J* = 3.1, 1.0 Hz, 2H), 7.14 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 4H), 7.76 (d, *J* = 7.4 Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 14.04, 14.11, 42.24, 42.76, 50.91, 62.86, 62.97, 63.96, 67.84, 72.80, 75.58,

95.38, 123.08, 126.01, 127.94, 128.30, 128.37, 128.93, 130.60, 131.29, 132.58, 133.08, 136.06, 136.37, 138.14, 138.87, 138.98, 139.66, 139.89, 140.35, 140.94, 141.35, 141.46, 141.51, 141.66, 142.30, 143.54, 144.54, 144.75, 144.90, 145.29, 145.32, 145.75, 146.41, 146.99, 147.72, 147.86, 149.01, 149.80, 149.92, 150.26, 153.52, 153.86, 163.19, 163.47, 170.44 (C_s symmetry, 56 of the required 56 lines are observed) FT-IR (KBr) υ (cm^{-1}) 2977 w, 2928 w, 2851 w, 1744 s, 1516 w, 1446 w, 1238 vs, 1127 w, 1103 w, 1061 w, 760 m, 528 m. HRMS (FAB^+) Calcd for $C_{105}H_{40}O_8$: 1428.2723, found: 1428.2694.

Compound 11. To a solution of 38 mg (0.027 mmol) of **10b** and 7 mg (0.021 mmol) of CBr_4 in 10 mL of degassed chlorobenzene were added 2.8 mg (0.021 mmol) of dimethyl malonate in 1 mL of PhCl and 6.4 mg (0.042 mmol) of DBU in 0.5 mL of PhCl. The reaction mixture was stirred at 25 ˚C for 18 h and then directly submitted to flash chromatography (SiO_2, hexanes, then CH_2Cl_2) to give 11 mg of recovered **10b**, 24 mg (58%, 81% based on recovered **10b**) of **11** as a red solid, and less than 10% of the three distinct diastereomeric bis-Bingel adducts (3 orange spots on TLC).[2] ^1H NMR (500 MHz, $CDCl_3$, enhanced with Gaussian broadening) δ (ppm) 1.21 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 3.74 (s, 6H), 3.79-3.94 (m, 6H), 4.02-4.08 (m, 2H), 4.15-4.24 (m, 2H), 4.33-4.40 (m, 2H), 6.63 (d, *J* = 3.1 Hz, 1H), 6.65 (d, *J* = 3.1 Hz, 1H), 6.69 (dt, *J* = 3.5 Hz, 2.2 Hz, 1H), 6.82 (d, *J* = 3.1 Hz, 1H), 7.05 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.13 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.17-7.20 (m, 3H), 7.23-7.29 (m, 3H), 7.33-7.38 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 13.96, 14.11, 42.78*, 42.81, 42.83, 52.43, 52.56, 53.39, 53.41, 62.46, 62.60, 62.72, 62.81, 66.47, 66.64, 66.95, 67.20, 71.45, 71.73, 75.09, 75.12, 96.34, 96.40, 123.53, 123.66, 125.95, 126.03, 127.58, 127.76, 128.15, 128.19, 128.74, 128.86*, 128.93, 130.59, 130.84, 131.59, 132.24, 132.29, 132.92, 133.22*, 138.85, 139.12, 139.15, 139.70, 139.76, 139.91, 139.99, 140.21, 140.26, 140.37, 140.99, 141.03, 141.23, 141.51, 141.77, 142.01, 142.22, 142.37, 142.79, 142.91, 143.25*, 143.33, 143.47, 143.77, 143.90, 143.99, 144.16, 144.28, 144.67, 144.77, 144.85, 144.98, 145.03, 145.55, 145.69, 145.72, 145.83, 146.30, 146.42, 147.50, 147.86, 147.96, 148.22, 148.54, 149.19, 150.01*, 150.77, 150.94, 151.51, 151.82, 152.04, 152.41*, 153.33, 163.20, 163.39, 163.96, 163.99, 170.35, 170.43 (C_1 symmetry, 100 of the required 106 lines are observed. The asterisks indicate lines with double intensity due to accidental overlap; the line at 42.78 ppm has four overlapping signals); FT-IR (KBr) υ (cm^{-1}) 2958 w, 2928 w, 2860 w, 1741 s, 1701 w, 1652 m, 1618 m, 1492 w, 1458 w, 1395 w, 1365 w, 1248 s, 1181 w, 1103 w, 826 w. HRMS (FAB^+) Calcd for $C_{110}H_{46}O_{12}$: 1558.2989, found: 1558.2907.

Compound 12. To a degassed solution containing 30 mg (0.019 mmol) of **11**, 11 mg (0.029 mmol) of bis-4-nitrobenzyl malonate and 10 mg (0.030 mmol) of CBr_4 in 15 mL of chlorobenzene was added 16 mg (0.11 mmol) of DBU. After stirring at room temperature for 1 h, two other portions of the same amount of bis-4-nitrobenzyl malonate and CBr_4 were added after each hour. The mixture was directly submitted to flash chromatography (SiO_2, CH_2Cl_2, then CH_2Cl_2/ethyl acetate 98:2) to give 24 mg (65%) of **12** as an orange solid. The product was contaminated with a small amount (~10%) of a bis-4-

nitrobenzyl malonate self-condensation product co-eluting with **12**.[3] This impurity does not affect the next deprotection step and compound **13** is isolated as a single isomer upon chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.27 (t, *J* = 7.1 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 3.69 (s, 3H), 3.70 (s, 3H), 3.78-3.86 (m, 6H), 3.92-3.97 (m, 2H), 4.23-4.27 (m, 2H), 4.43-4.46 (m, 2H), 5.23 (d part of AB-q, *J* = 13.0 Hz, 1H), 5.25 (d part of AB-q, *J* = 13.0 Hz, 1H), 5.46 (d part of AB-q, *J* = 13.5 Hz, 1H), 5.49 (d part of AB-q, *J* = 13.5 Hz, 1H), 6.58-6.63 (m, 4H), 7.02-7.06 (m, 2H), 7.10-7.17 (m, 6H), 7.30-7.44 (m, 8H), 7.52-7.56 (m, 6H), 8.16 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 13.96, 14.11, 42.23, 42.30, 42.68, 42.74, 44.18, 45.03, 52.71, 53.37, 62.31, 62.35, 62.82, 62.90, 66.27, 66.29, 66.43, 66.50, 66.70, 66.83, 66.86, 70.09, 70.33, 70.68, 70.96, 74.72, 74.79, 96.06, 96.15, 123.24, 123.33, 123.60, 123.71, 123.83, 123.87, 125.81, 125.83, 126.96, 127.34, 127.50, 128.13, 128.20, 128.42, 128.52, 128.58, 128.69, 128.79, 128.81, 128.97, 130.52, 130.61, 131.67, 131.86, 132.42, 132.62, 133.12, 137.56, 137.70, 138.45, 138.63, 138.65, 138.67, 139,92, 140.14, 140.71, 140.77, 140.83, 140.86, 140.94, 141.01, 141.16, 141.26, 141.34, 141.77, 141.84, 141.89, 141.92, 141.97, 142.02, 142.17, 142.24, 142.46, 142.61, 142.87, 143.04, 143.99, 144.44, 144.64, 145.01, 145.18, 145.20, 145.24, 145.44, 145.56, 145.65, 147.92, 147.94, 148.02, 148.26, 148.35, 149.31, 149.51, 151.85, 152.15, 152.25, 152.29, 152.76, 152.87, 152.92, 153.44, 163.20, 163.26, 163.52, 163.60, 163.74, 170.25, 170.37 (10 lines overlapping due to complexity of molecule); FT-IR (KBr) υ (cm^{-1}) 2970 w, 2931 w, 1742 s, 1653 w, 1616 m, 1523 m, 1348 m, 1249 s, 1196 w, 1104 w, 1080 w, 754 w. HRMS (FAB^+) Calcd for $C_{127}H_{58}O_{20}N_2$: 1930.3583, found: 1930.3483.

Compound 13. A degassed solution containing 28 mg (0.0145 mmol) of **12** (see note above for purity), 100 mg (0.70 mmol) of DMAD and 14 mg (0.074 mmol) of $TsOH{\cdot}H_2O$ in 10 mL of toluene was refluxed for 2 h during which the color of the solution turned from orange to reddish brown. After evaporation of the solvent, flash chromatography (SiO_2, CH_2Cl_2) gave 16 mg (80%) of **13** as a brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.49 (t, *J* = 7.1 Hz, 3H), 1.53 (t, *J* = 7.1 Hz, 3H), 3.98 (s, 6H), 4.56 (q, *J* = 7.1 Hz, 2H), 4.61 (q, *J* = 7.1 Hz, 2H), 5.55 (s, 2H), 5.63 (s, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 8.26 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 14.18, 14.25, 45.46, 45.56, 51.03, 53.95, 63.39, 63.40, 67.29, 67.46, 70.09, 70.61, 71.07, 71.41, 123.92, 123.94, 129.21, 129.35, 138.91, 139.00, 139.83, 139.93, 141.12, 141.48, 141.67, 141.91, 142.56, 142.68, 142.82, 142.84, 143.01, 143.11, 143.60, 143.78*, 143.98, 144.83, 145.06, 145.11, 145.23, 145.45, 145.48*, 145.72, 147.21, 147.33, 147.35, 147.65, 148.16, 148.20, 163.60, 163.61, 163.80, 163.96, 164.00 (C_s symmetry, 53 of the required 55 lines are observed. The asterisks indicate lines with double intensity due to accidental overlap); FT-IR (KBr) υ (cm^{-1}) 2964 w, 1746 s, 1608 w, 1523 m, 1454 w, 1437 w, 1347 m, 1248 vs, 1210 m, 1109 w, 1074 m, 1017 w, 737 m. HRMS (FAB^+) Calcd for $C_{89}H_{28}O_{16}N_2$: 1380.1439, found: 1380.1393.

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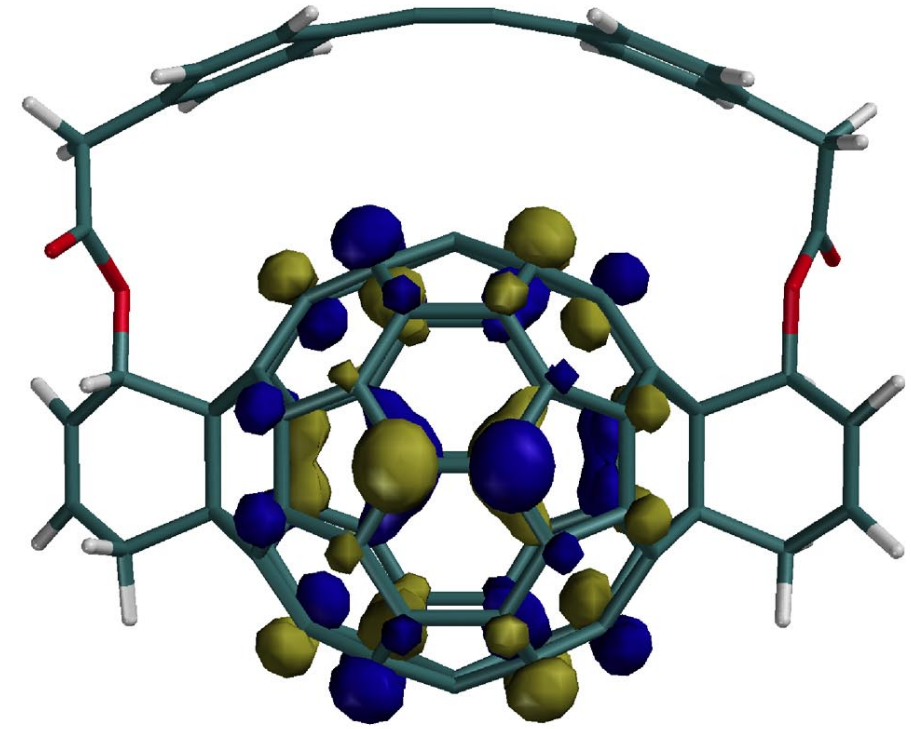
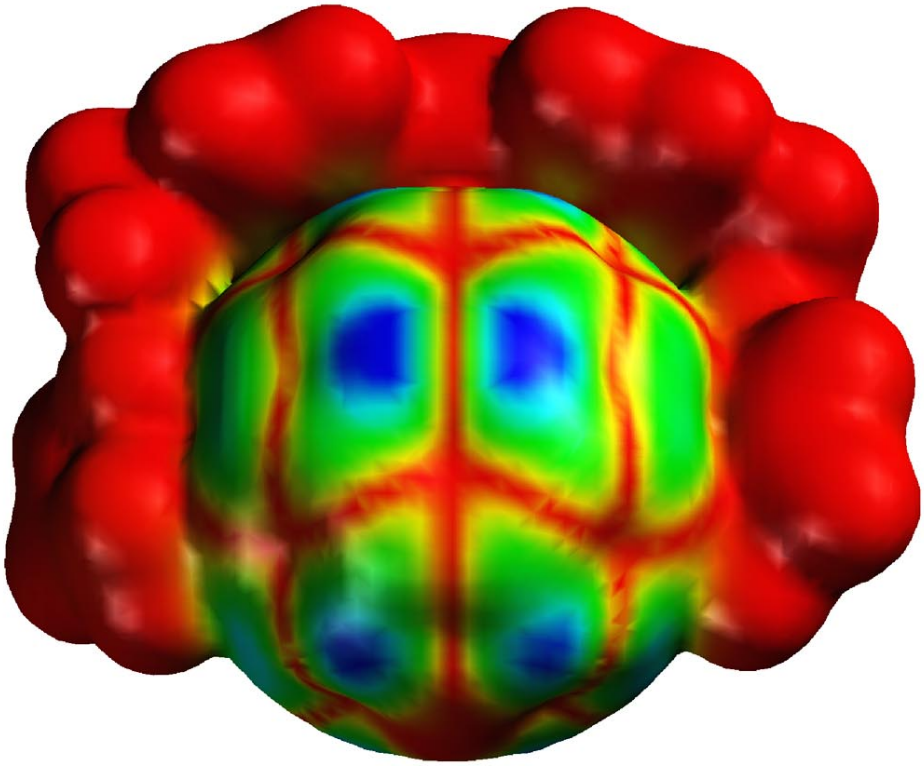
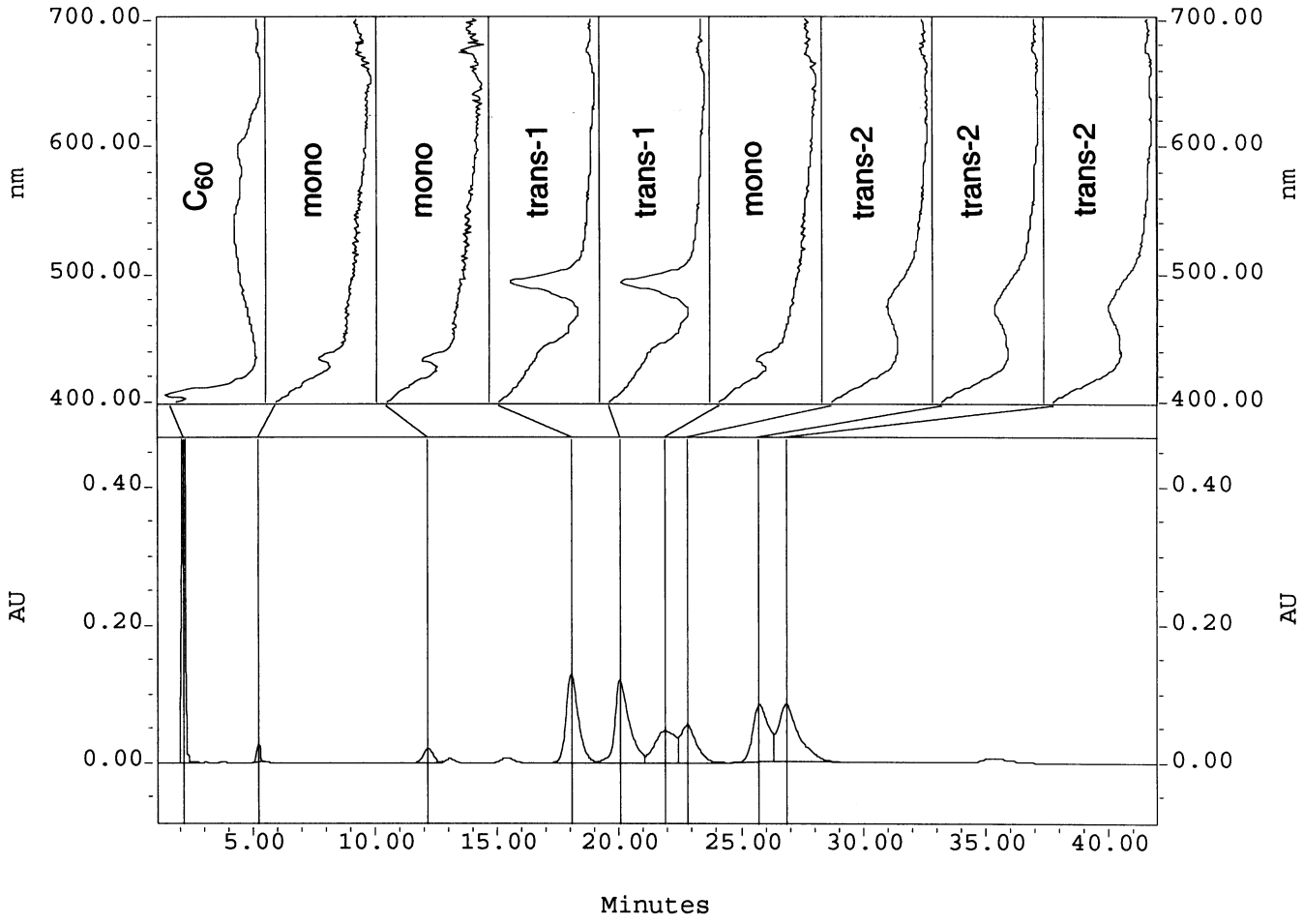
[3] This byproduct was also found in an independent reaction carried out under similar conditions, with no fullerene derivative (**11**) present. A number of other products are also formed, presumably the alkene and alkane dimerization compounds together with Dieckman condensation products.

LUMO orbitals (density below) of compound **3a** showing good agreement with the fact that only the double *e*-face position gets attacked by the *Bingel* nucleophile





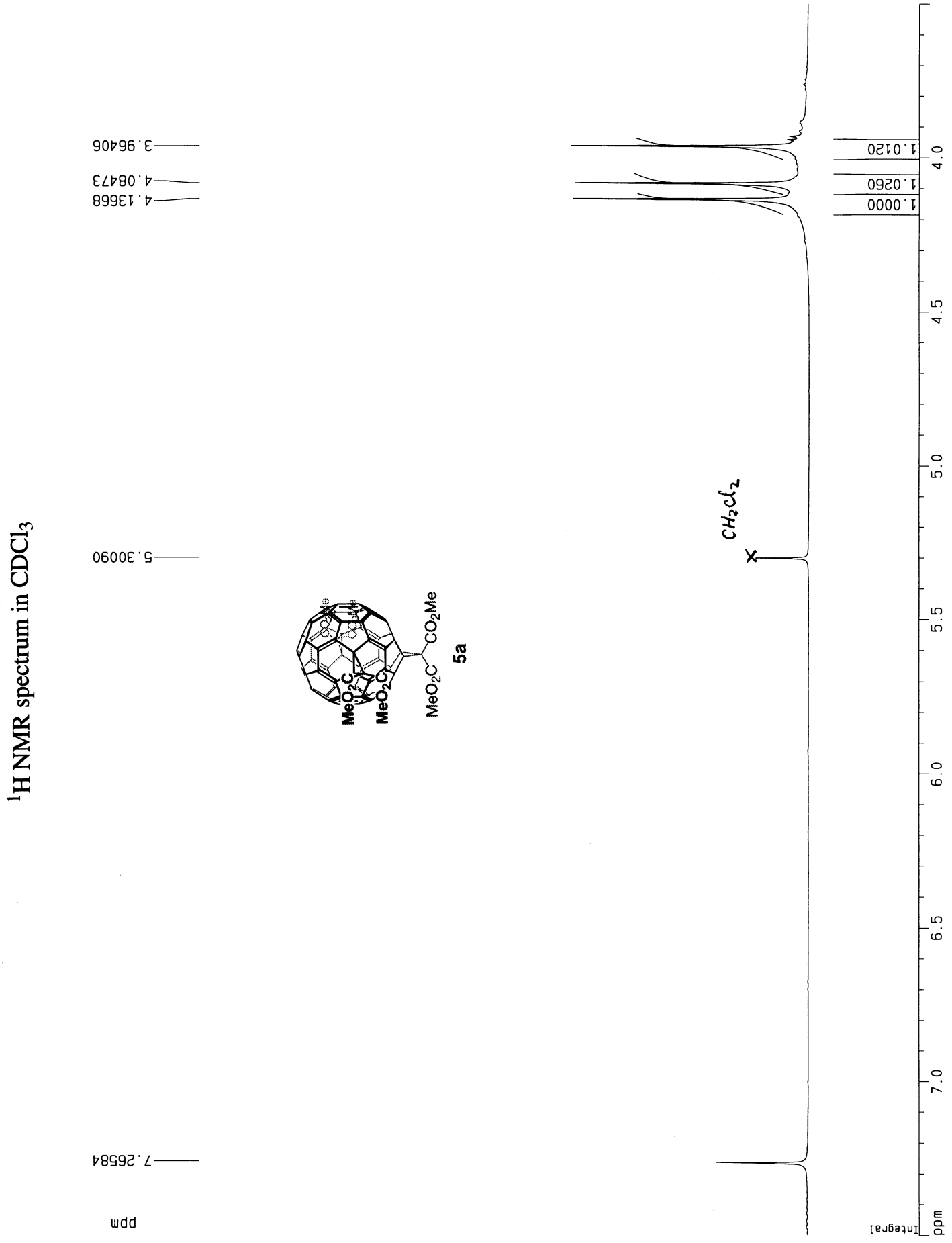


HPLC chromatogram and UV-vis spectra for the crude cyclization mixture of 3a

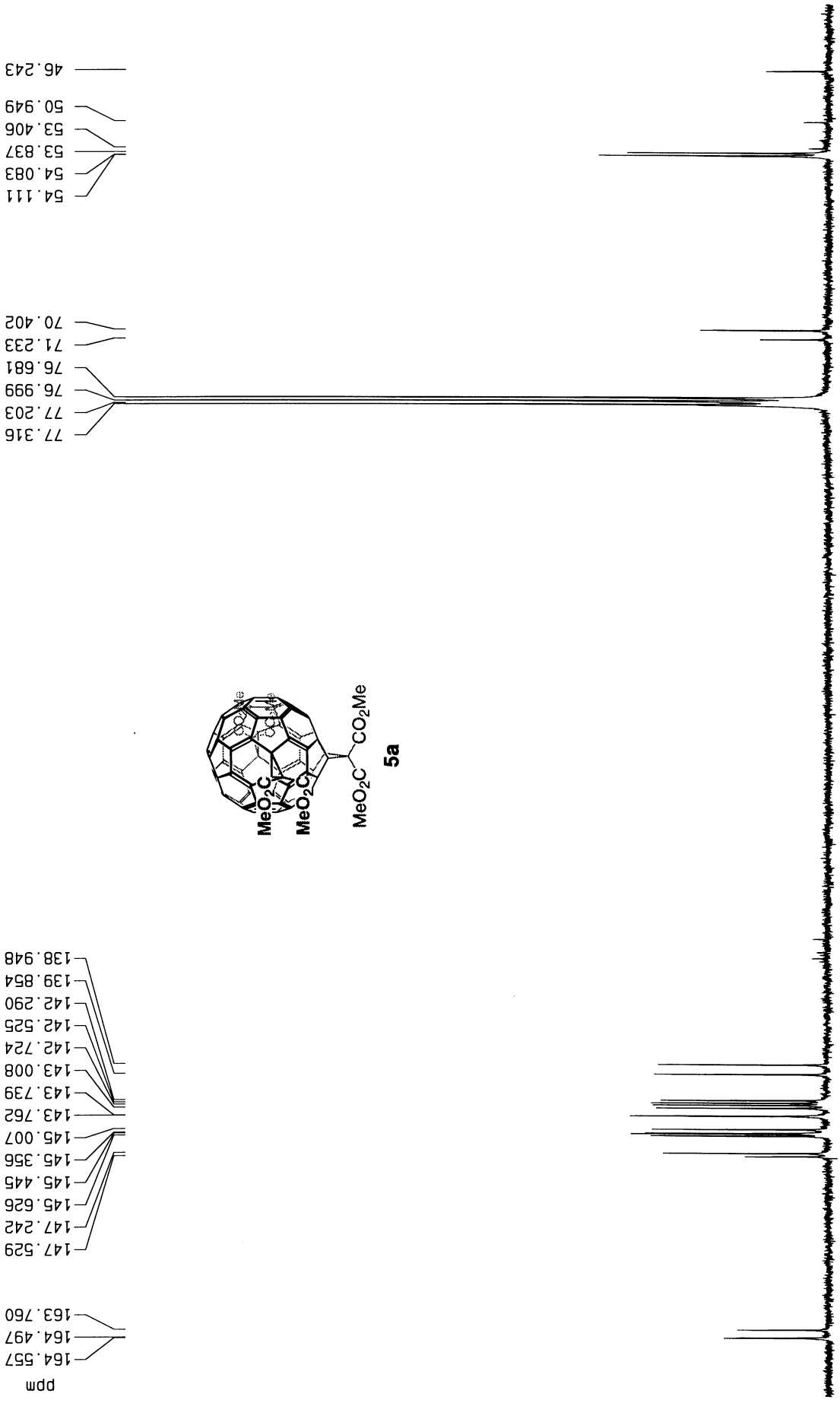
The silica gel-filtered reaction mixture was injected into an analytical column (HPLC conditions: toluene/hexane 7:3, SiO_2 Econosil 5 μ, 1.5 mL/min flowrate, uncalibrated ratios at 340 nm). Bisadduct regioisomers were identified by comparison of their UV-vis spectra (Waters PDA 996 detector) with the spectra of the diethyl malonate bisadducts.

Under this separation condition, two diastereomers of *trans*-1 (**3a**) and three diastereomers of *trans*-2 bisadducts were detected. Possible structures of the detected three monoadducts are: C_{60} oxidation product, the C_{60}/**1a** 2:1 adduct (dumbbell structure), C_{60}/**1a** 1:1 monoadduct (**2a**), and/or other possible $^1O_2$ oxidation product of the mono adducts.

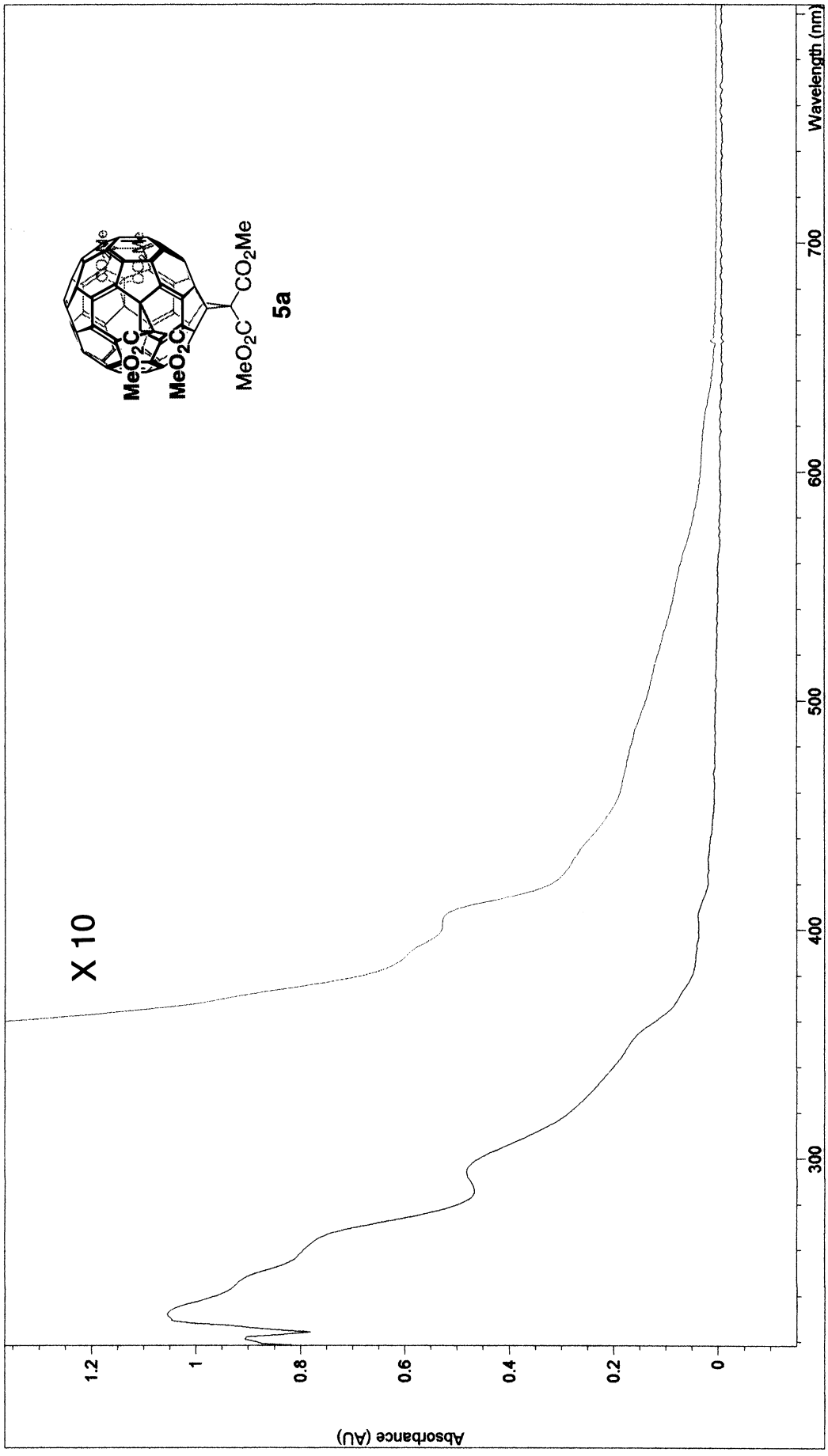
^{1}H NMR spectrum in $CDCl_3$



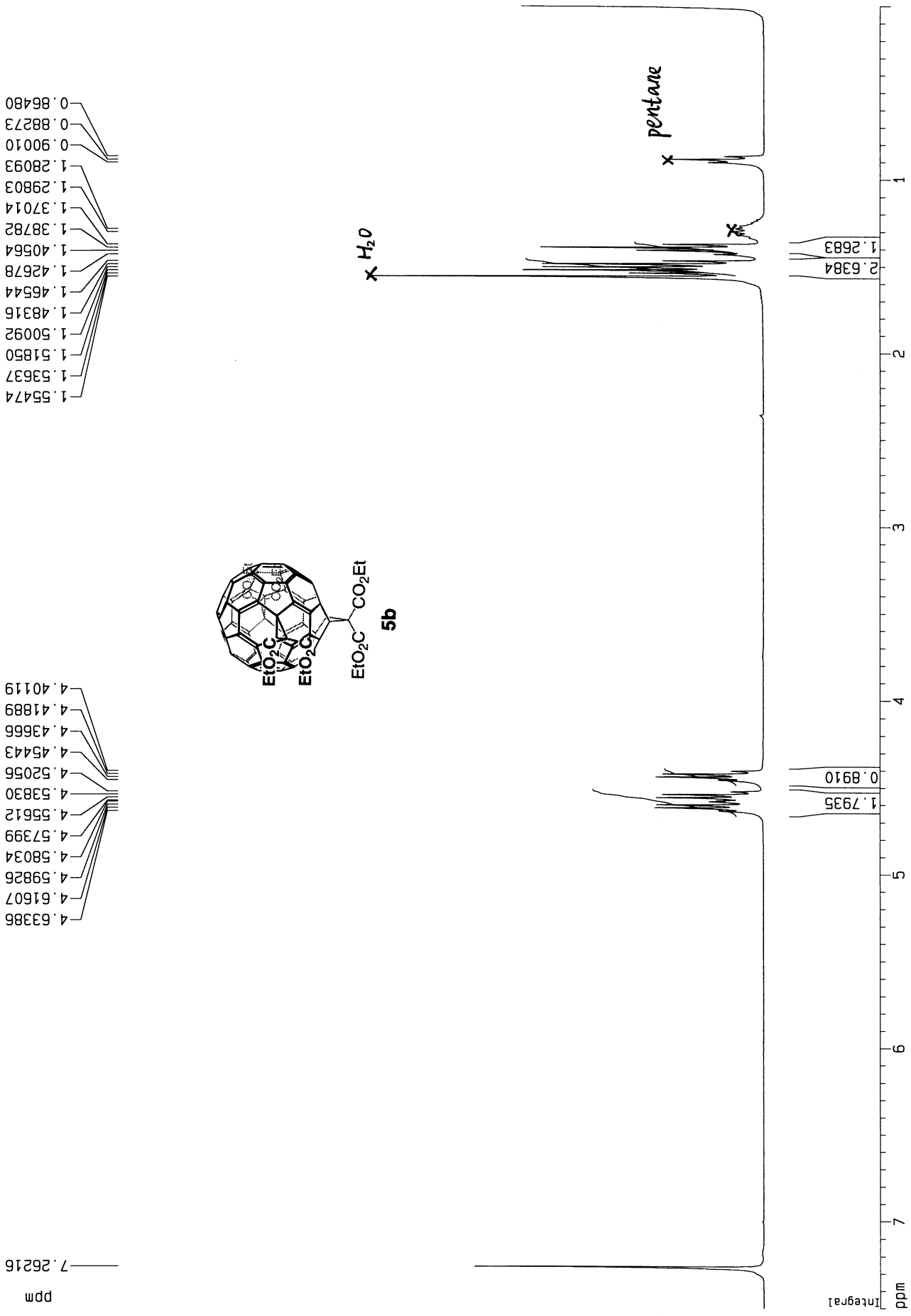
^{13}C NMR spectrum in $CDCl_3$



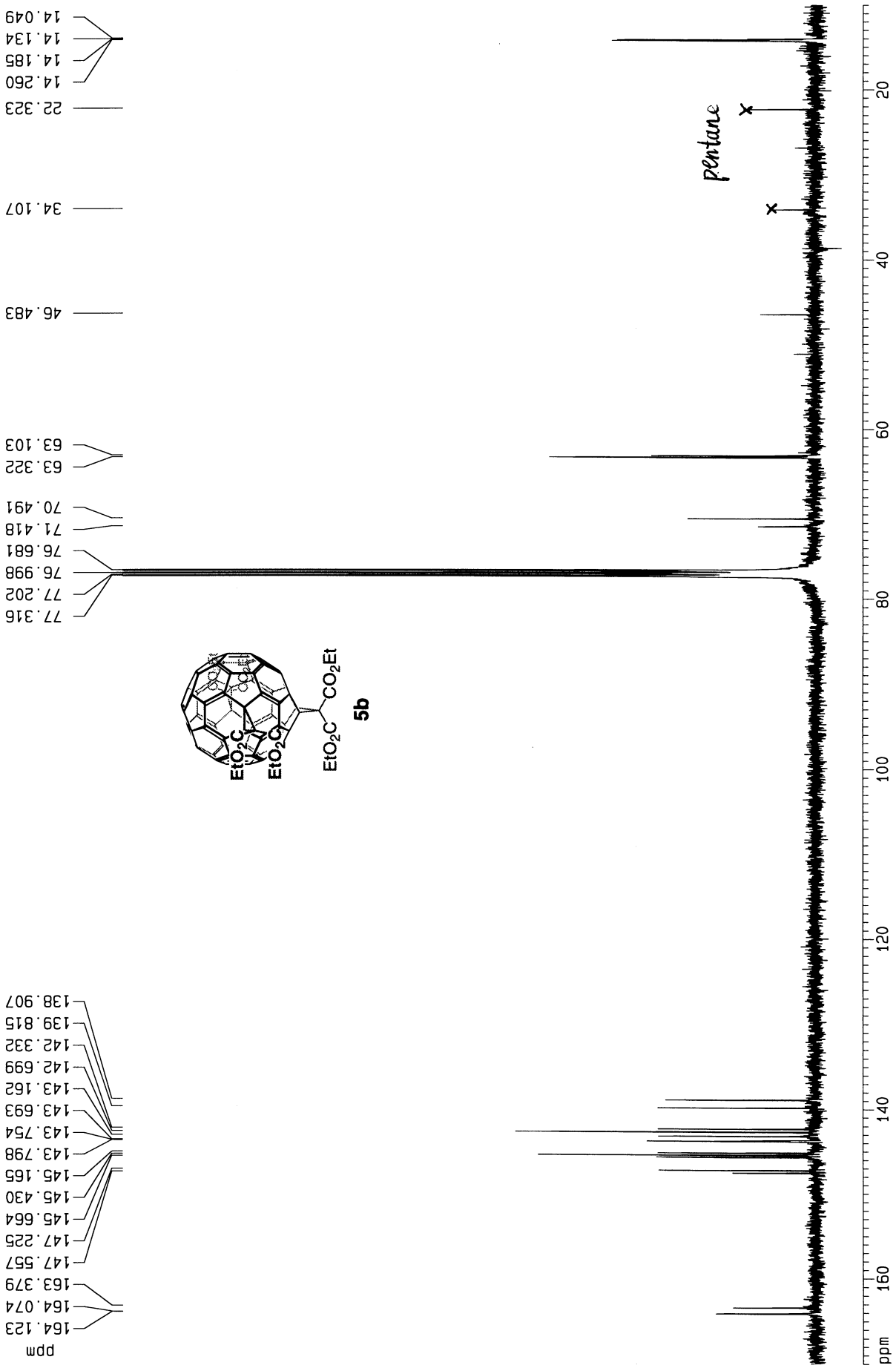
Electronic absorption spectrum in CH_2Cl_2



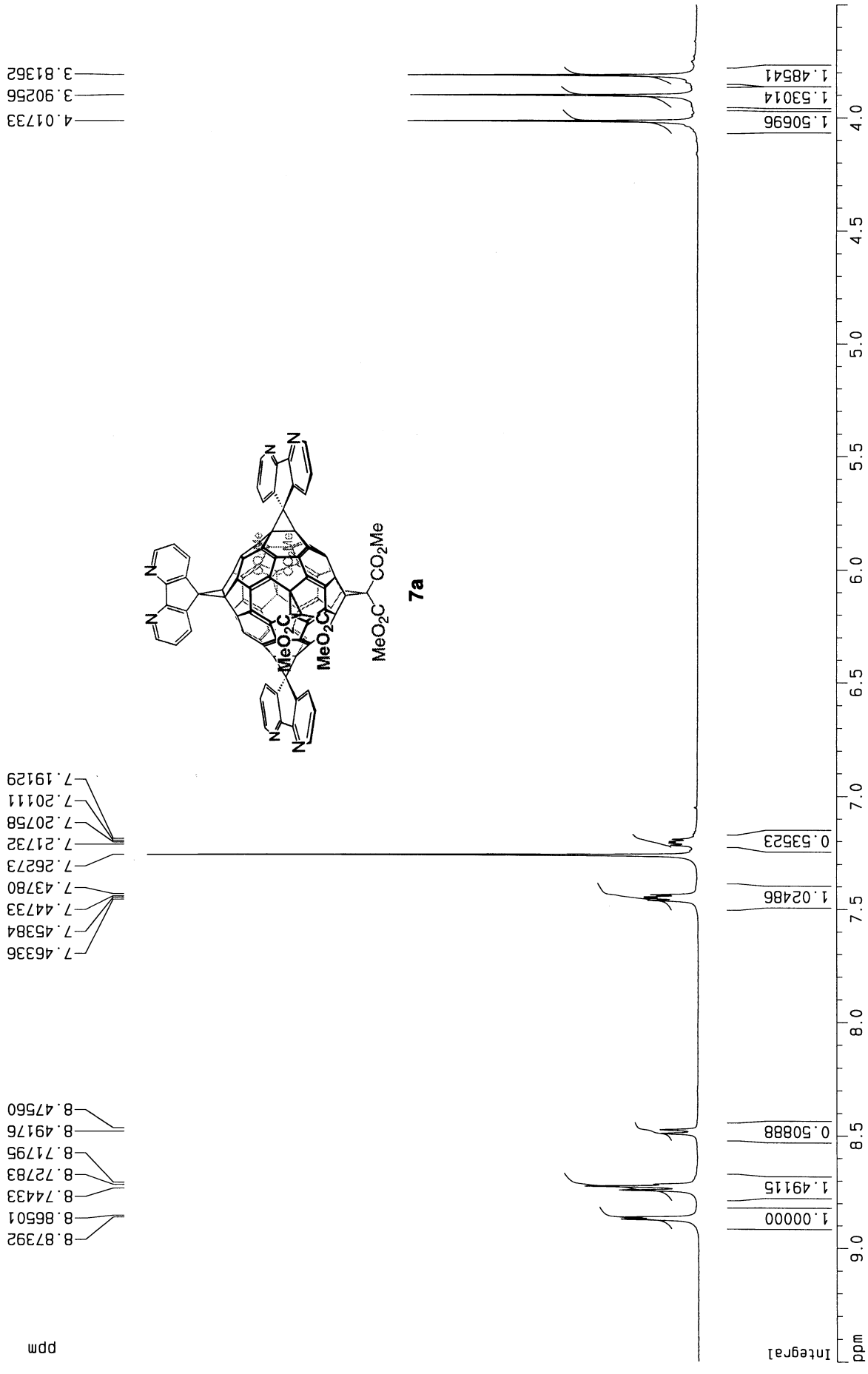
^{1}H NMR spectrum in $CDCl_3$



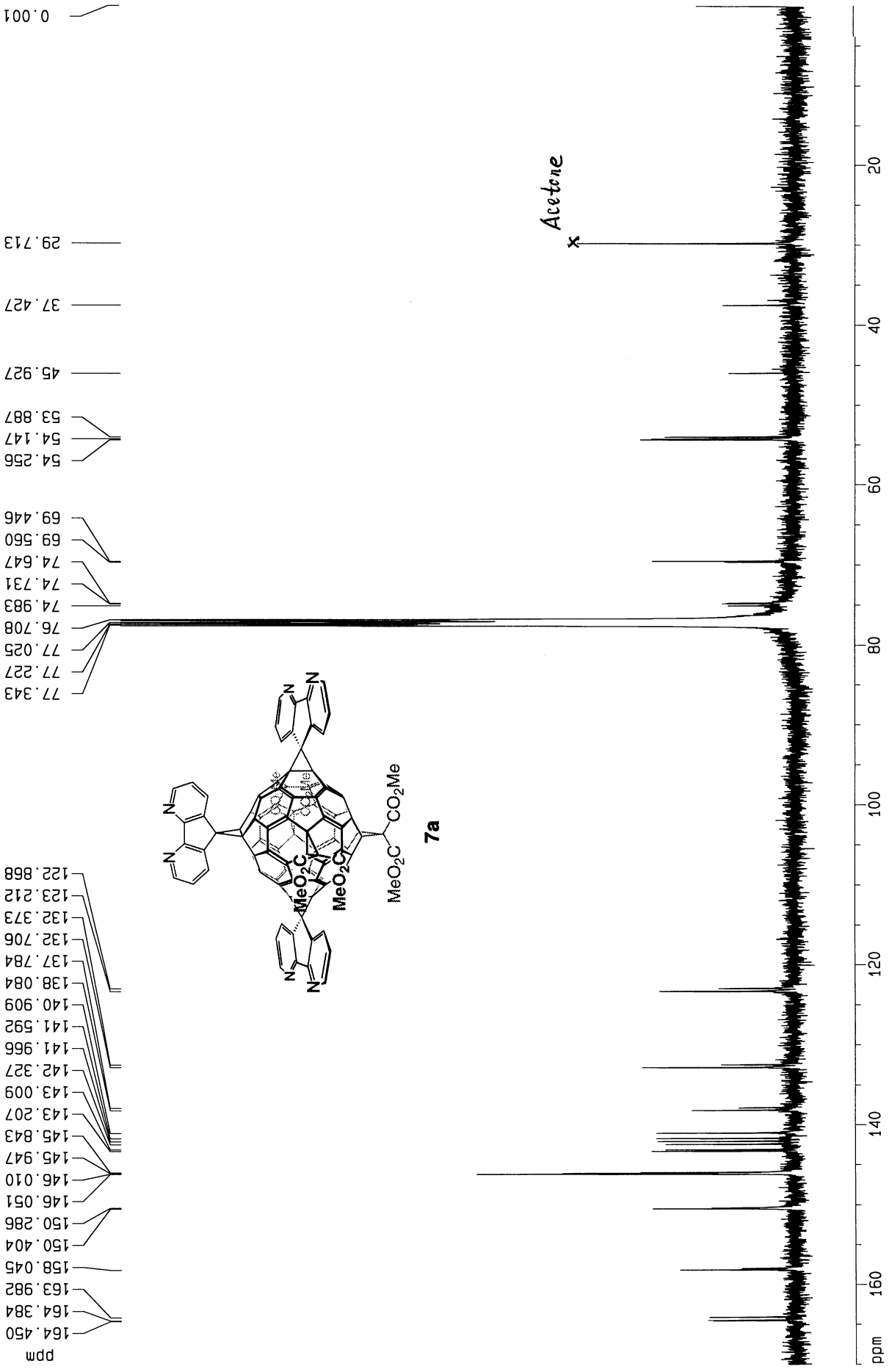
^{13}C NMR spectrum in $CDCl_3$



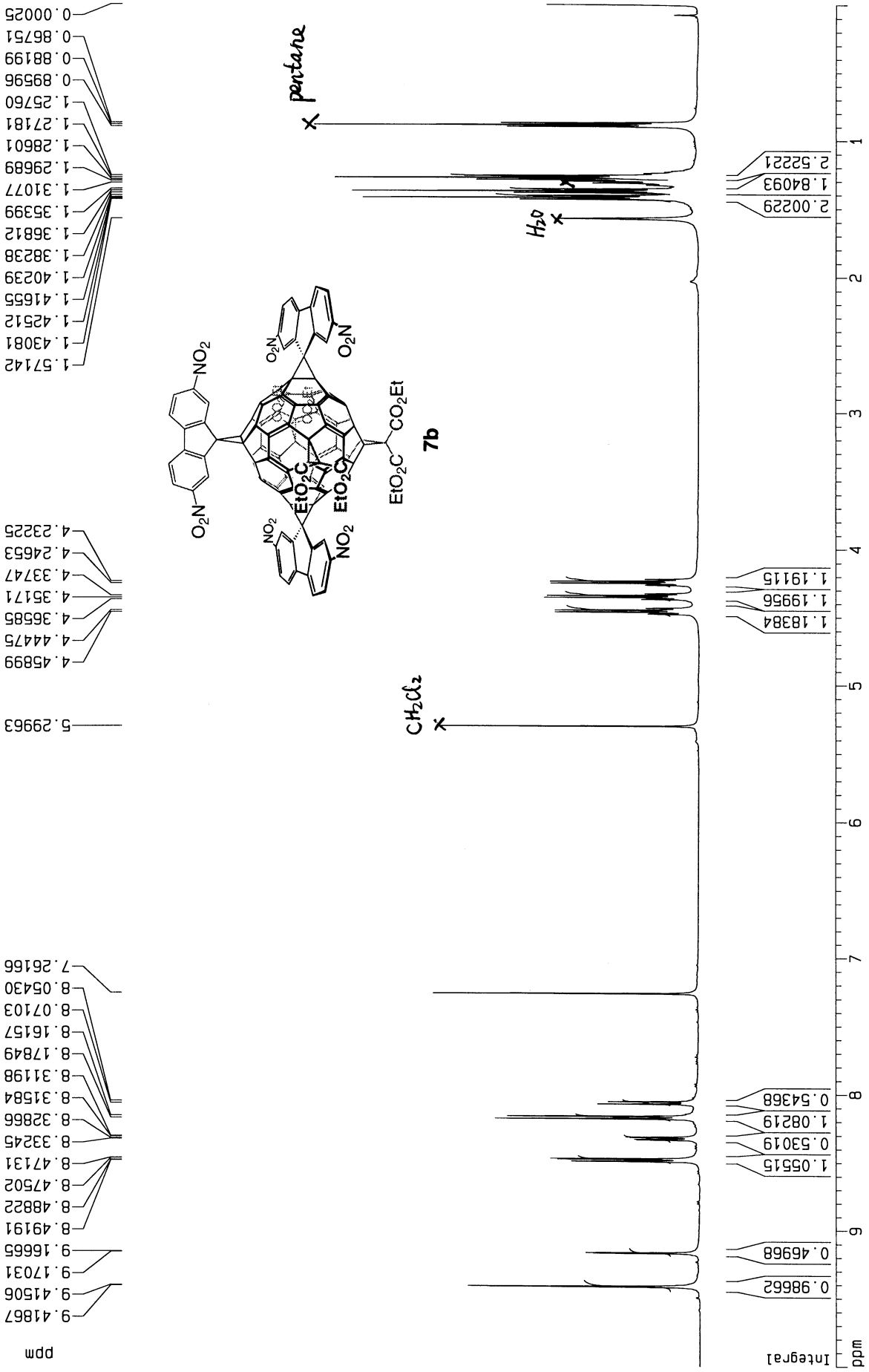
^{1}H NMR spectrum in $CDCl_3$



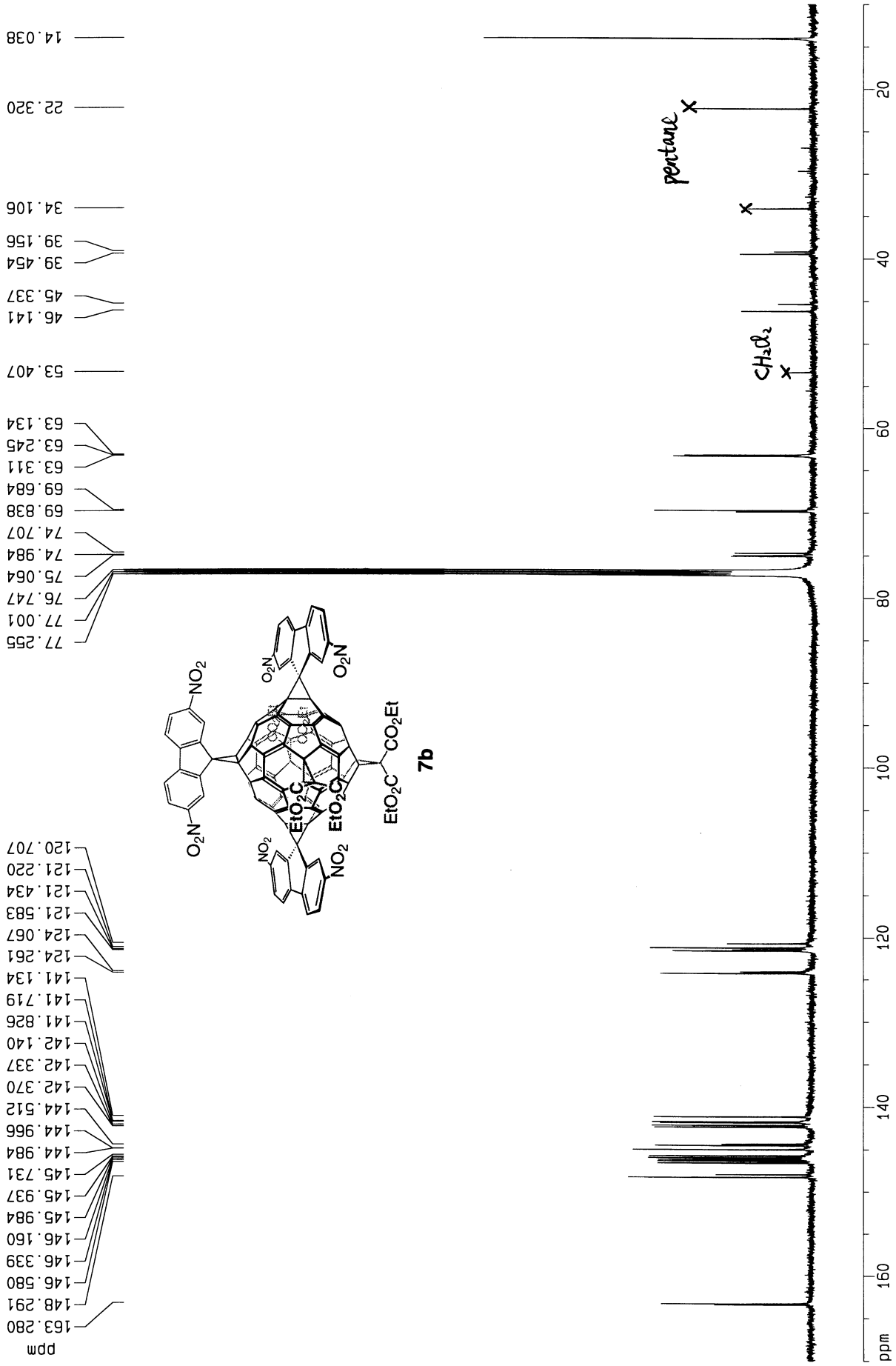
^{13}C NMR spectrum in $CDCl_3$



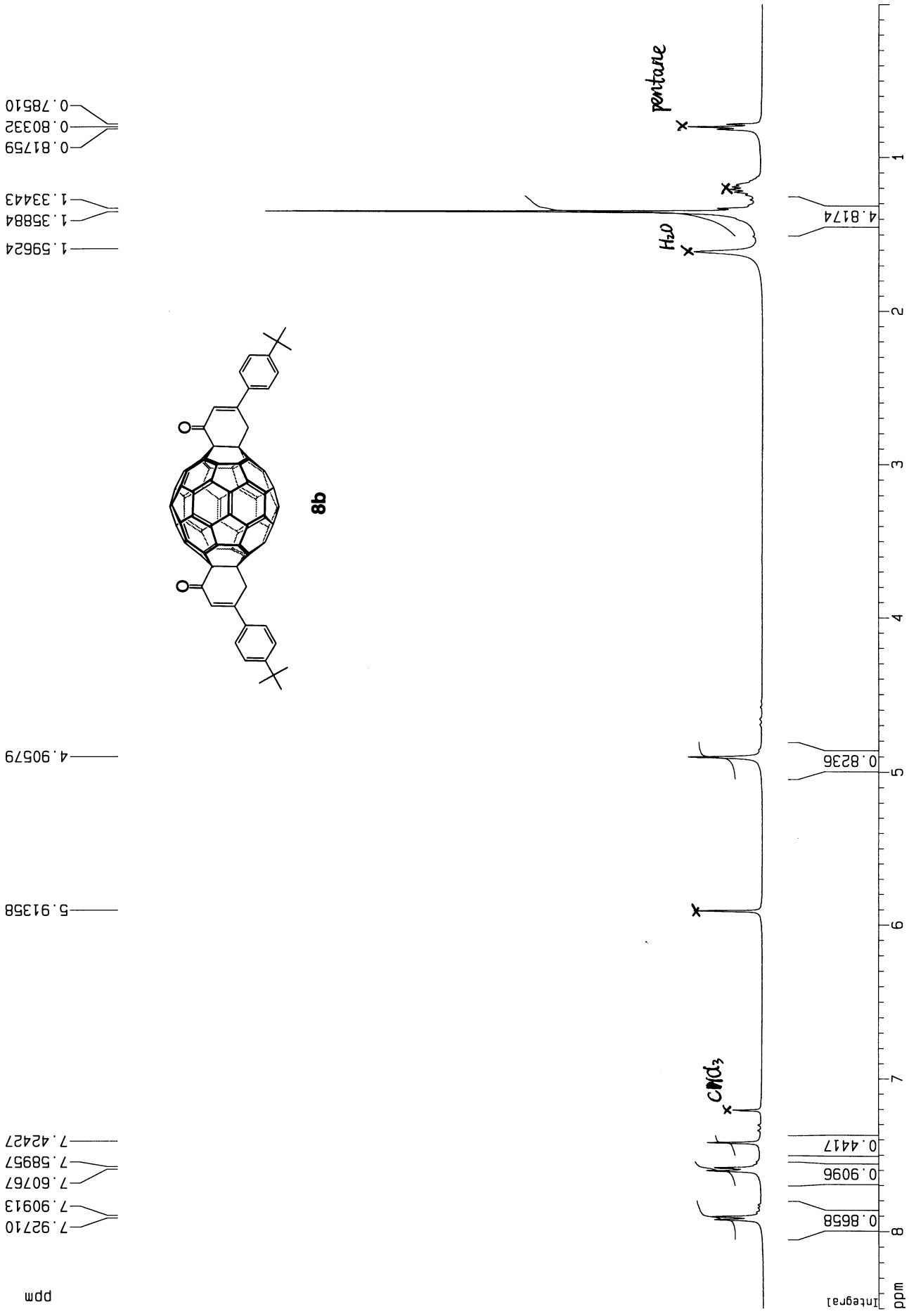
^{1}H NMR spectrum in $CDCl_3$



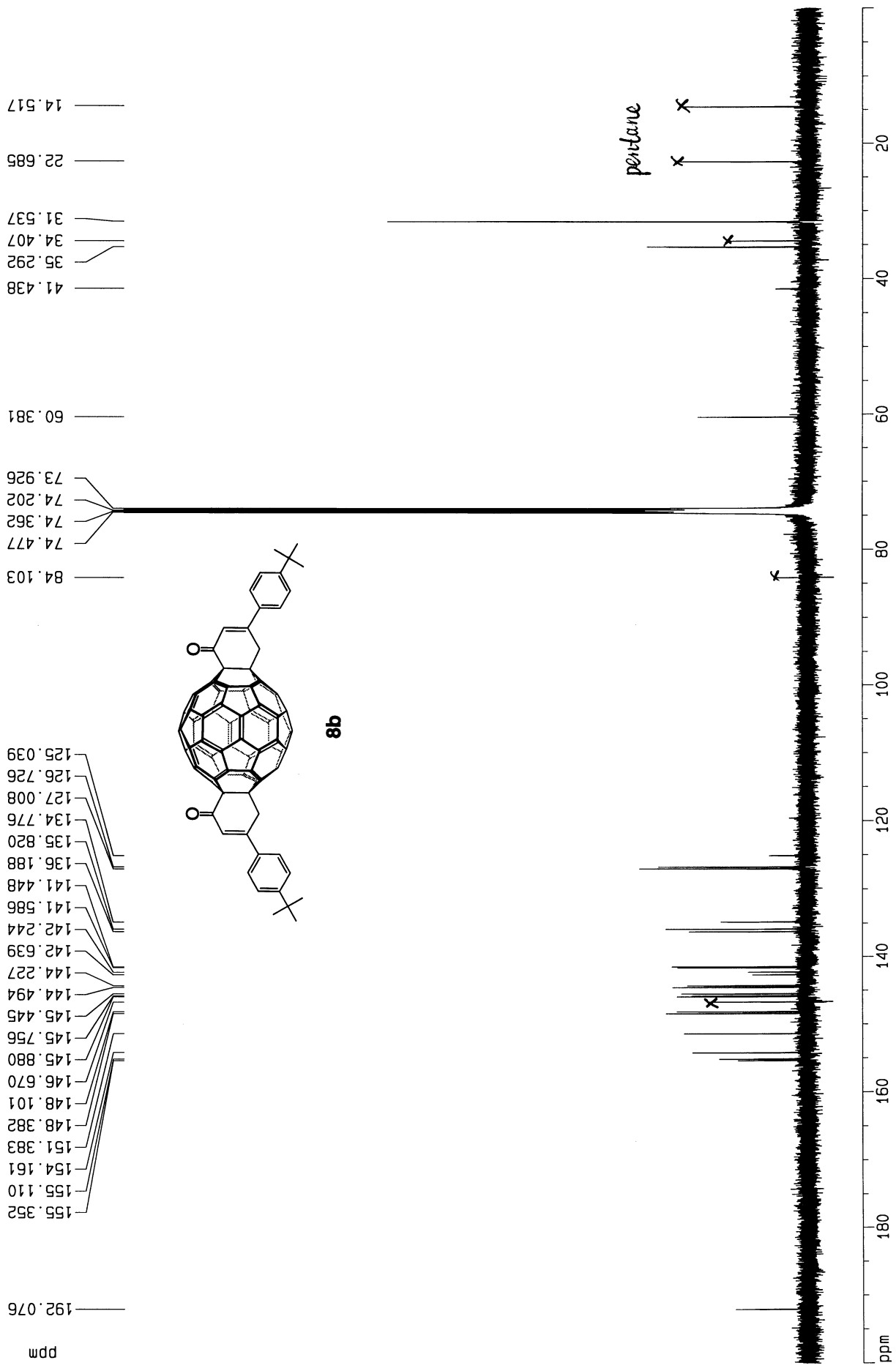
^{13}C NMR spectrum in $CDCl_3$



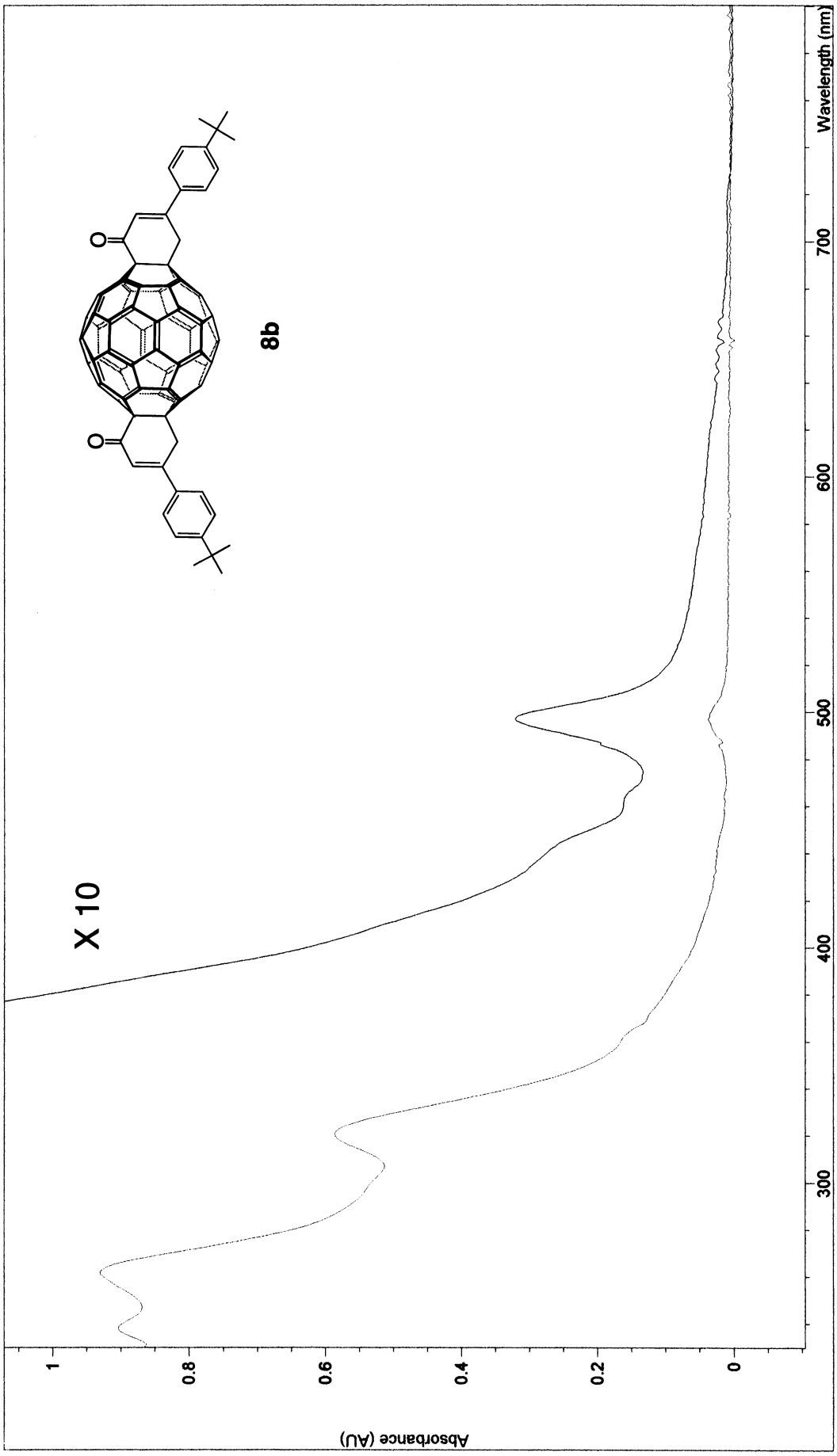
^{1}H NMR spectrum in $C_2D_2Cl_4$



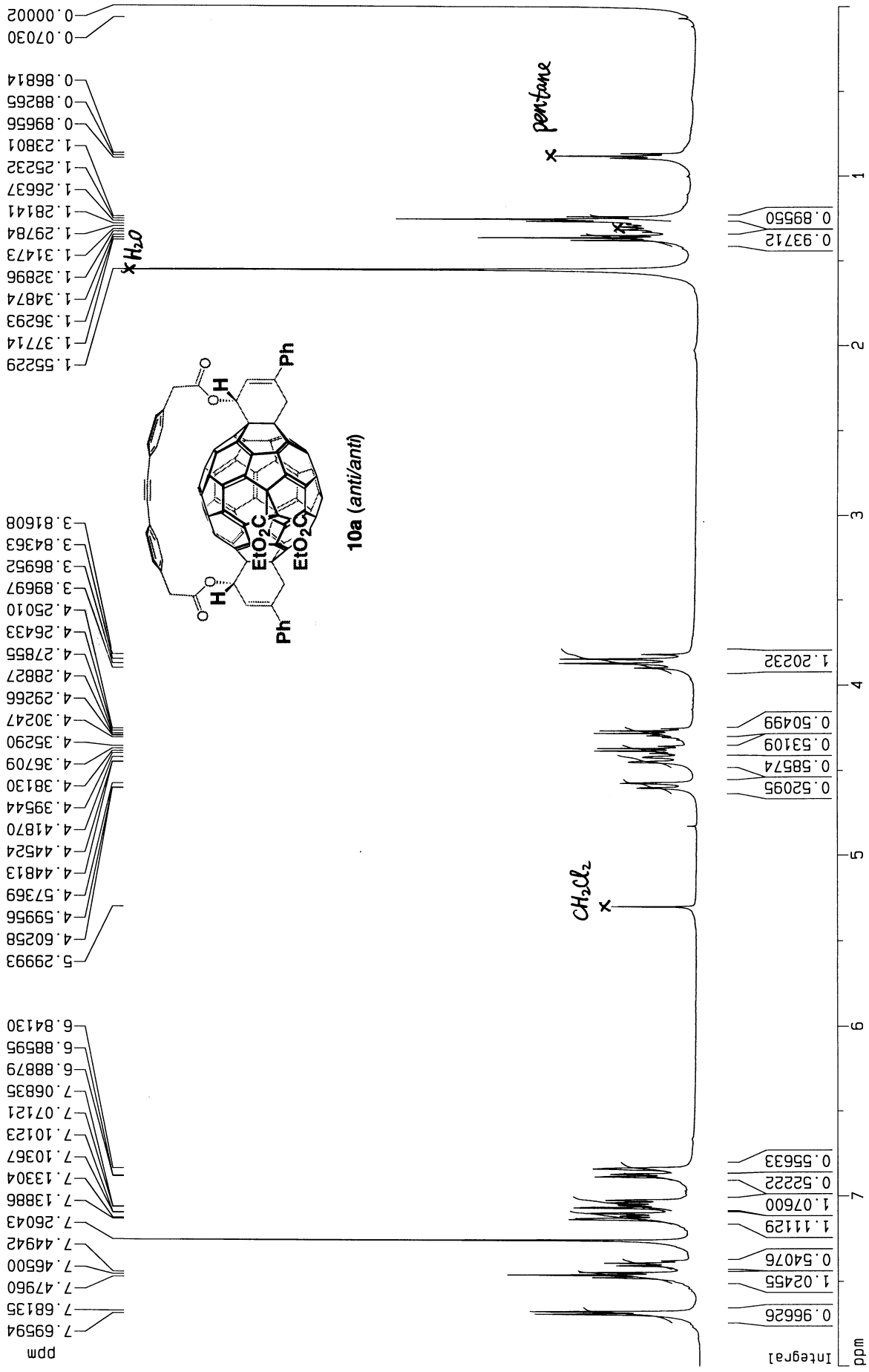
^{13}C NMR spectrum in $C_2D_2Cl_4$



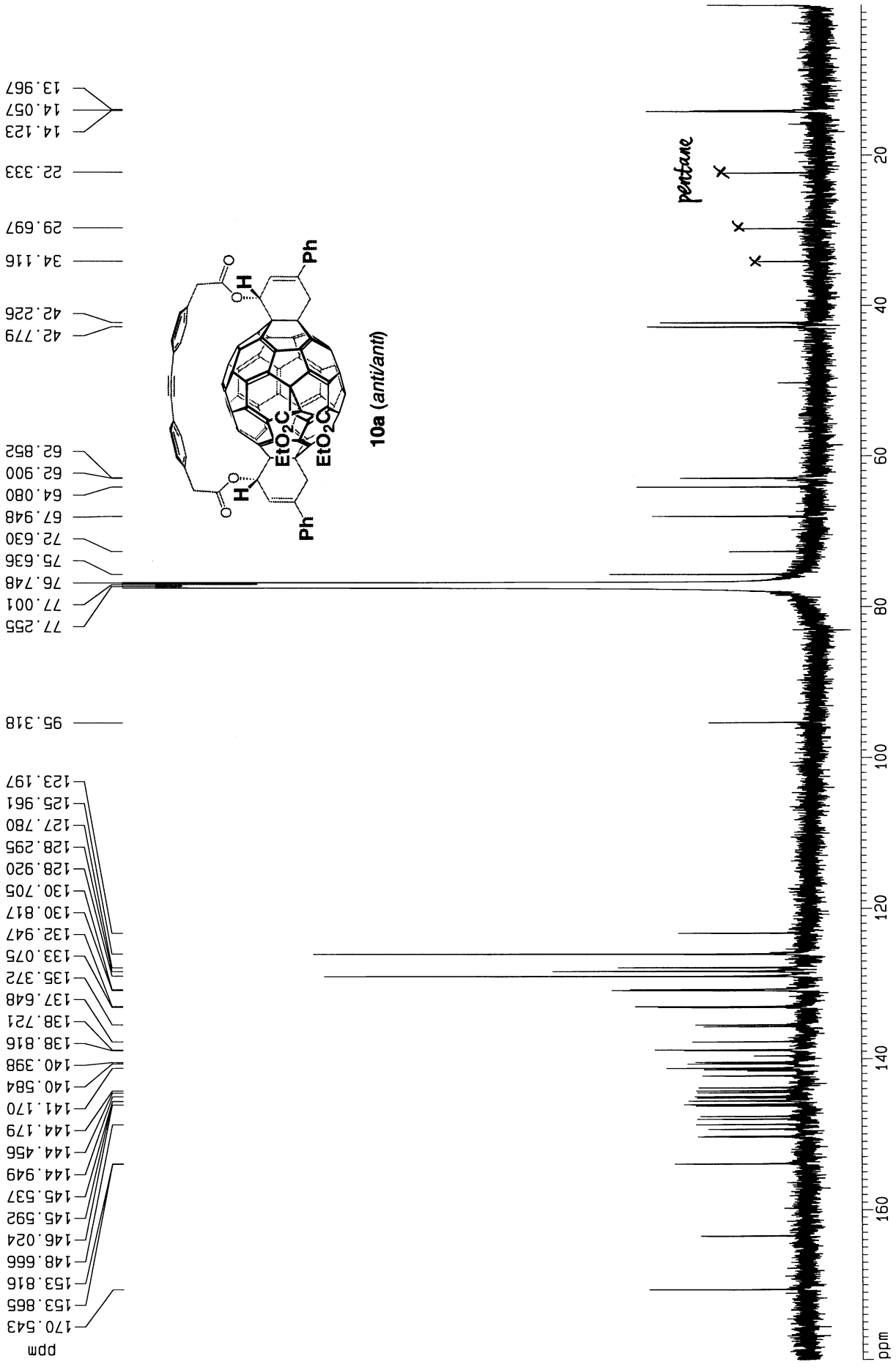
Electronic absorption spectrum in CH_2Cl_2



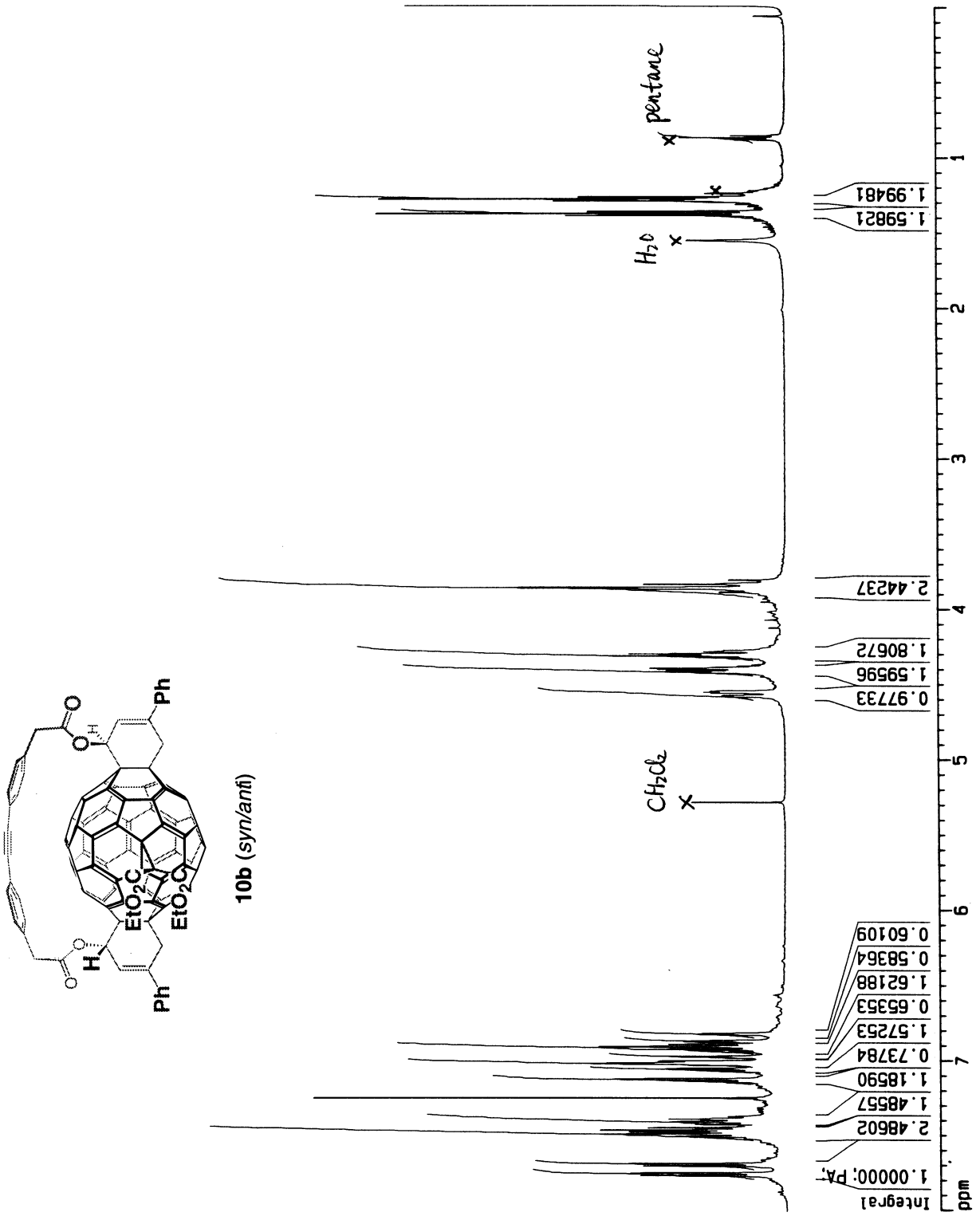
^{1}H NMR spectrum in $CDCl_3$



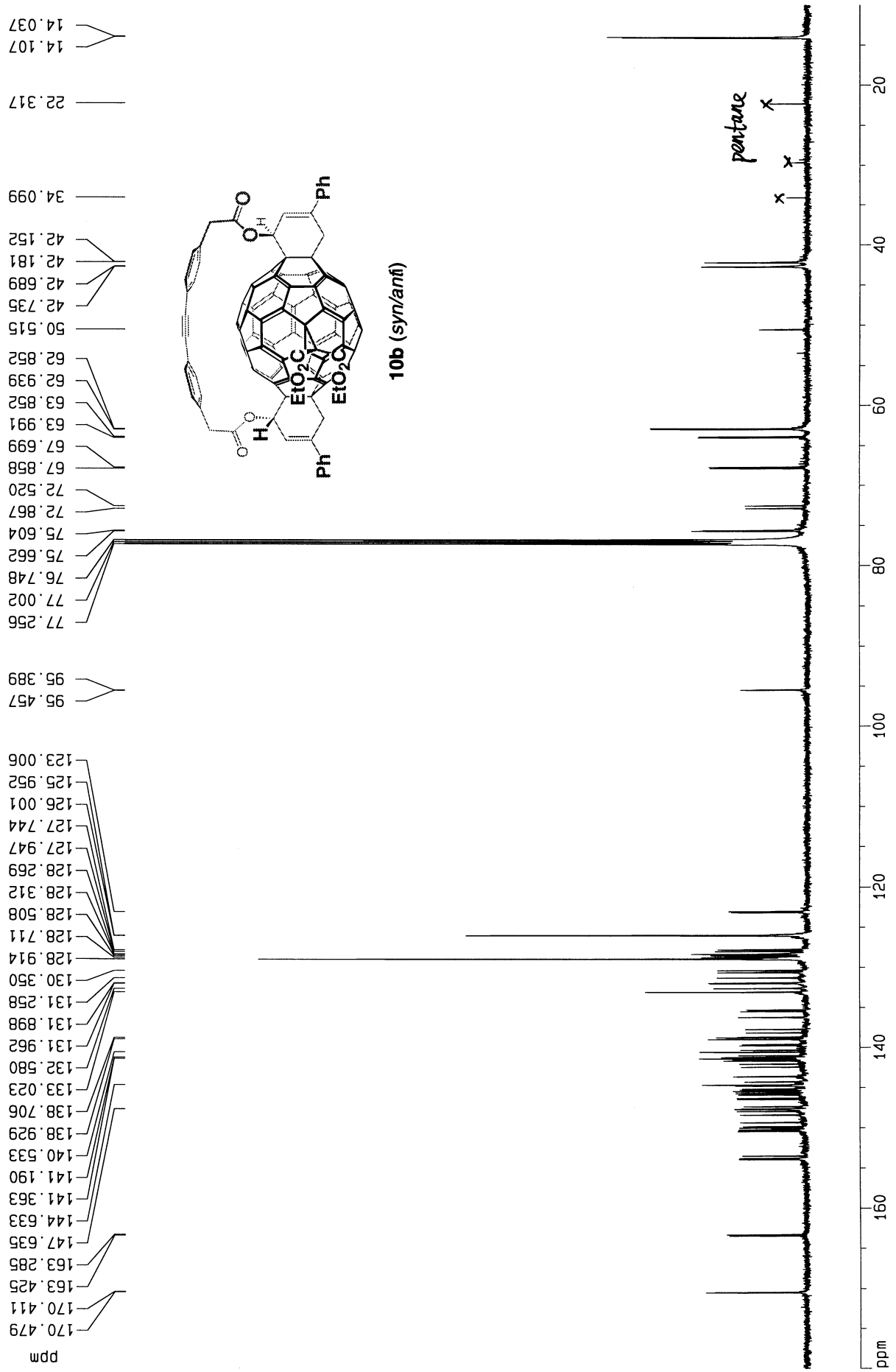
^{13}C NMR spectrum in $CDCl_3$



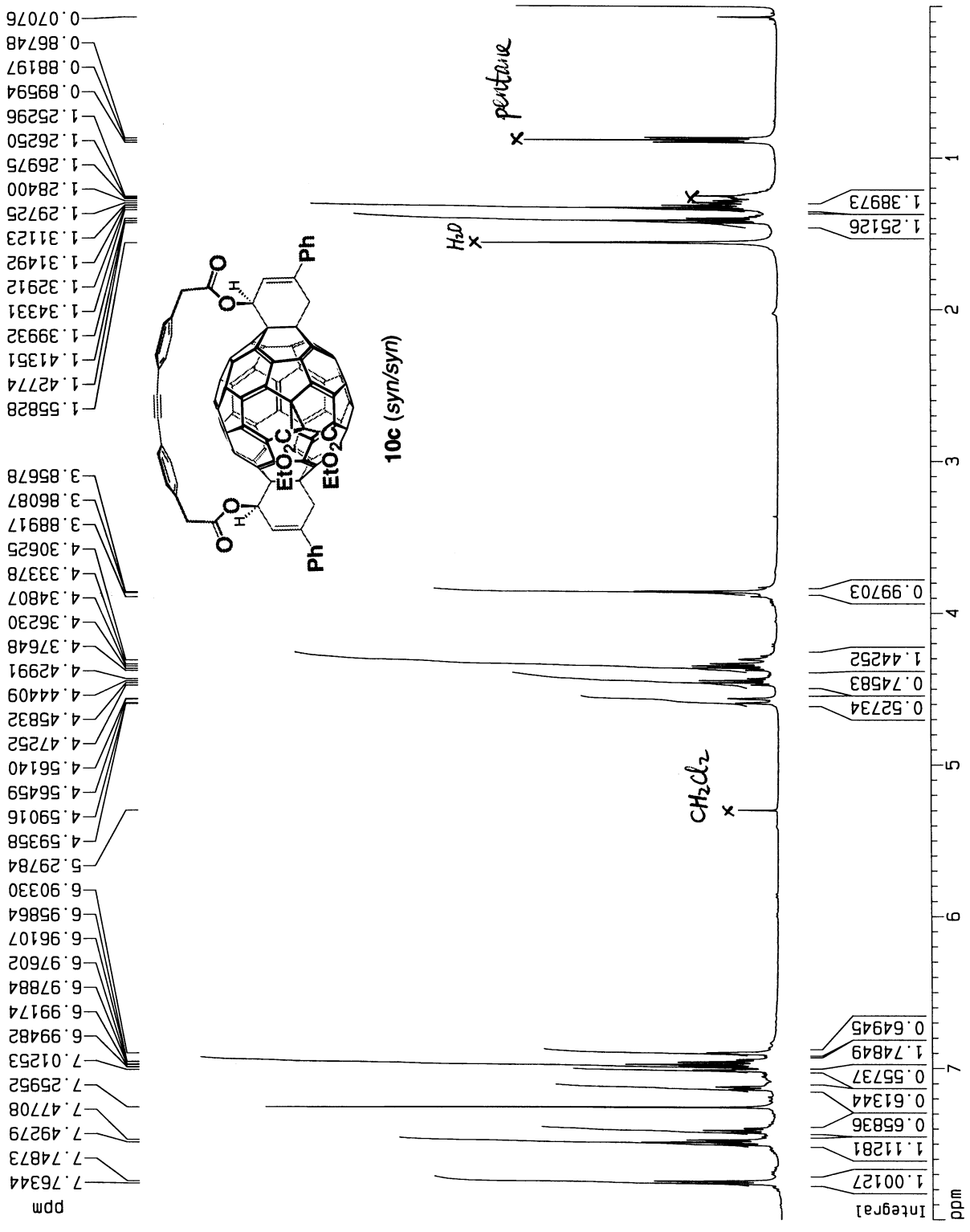
^{1}H NMR spectrum in $CDCl_3$



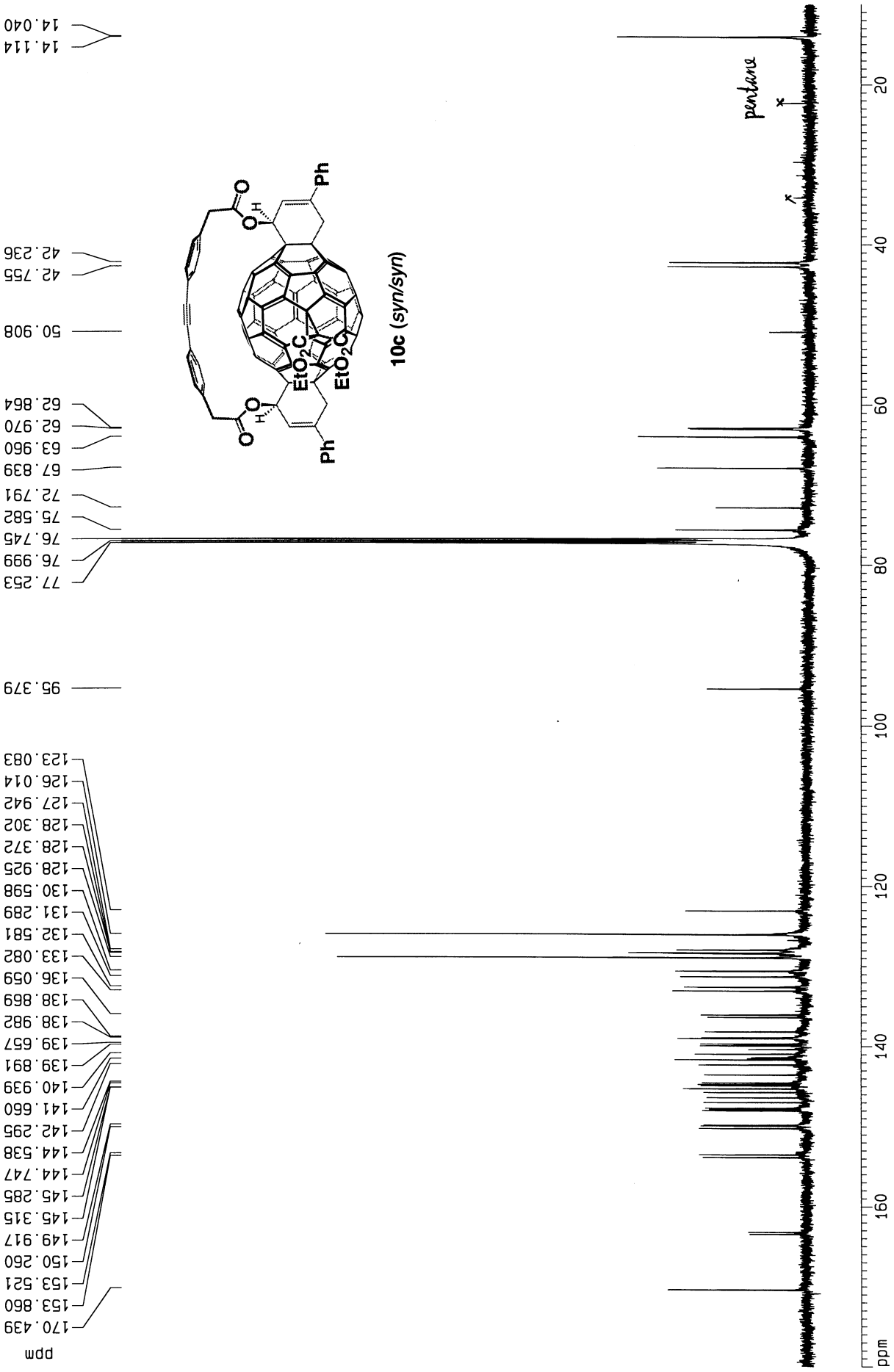
^{13}C NMR spectrum in $CDCl_3$



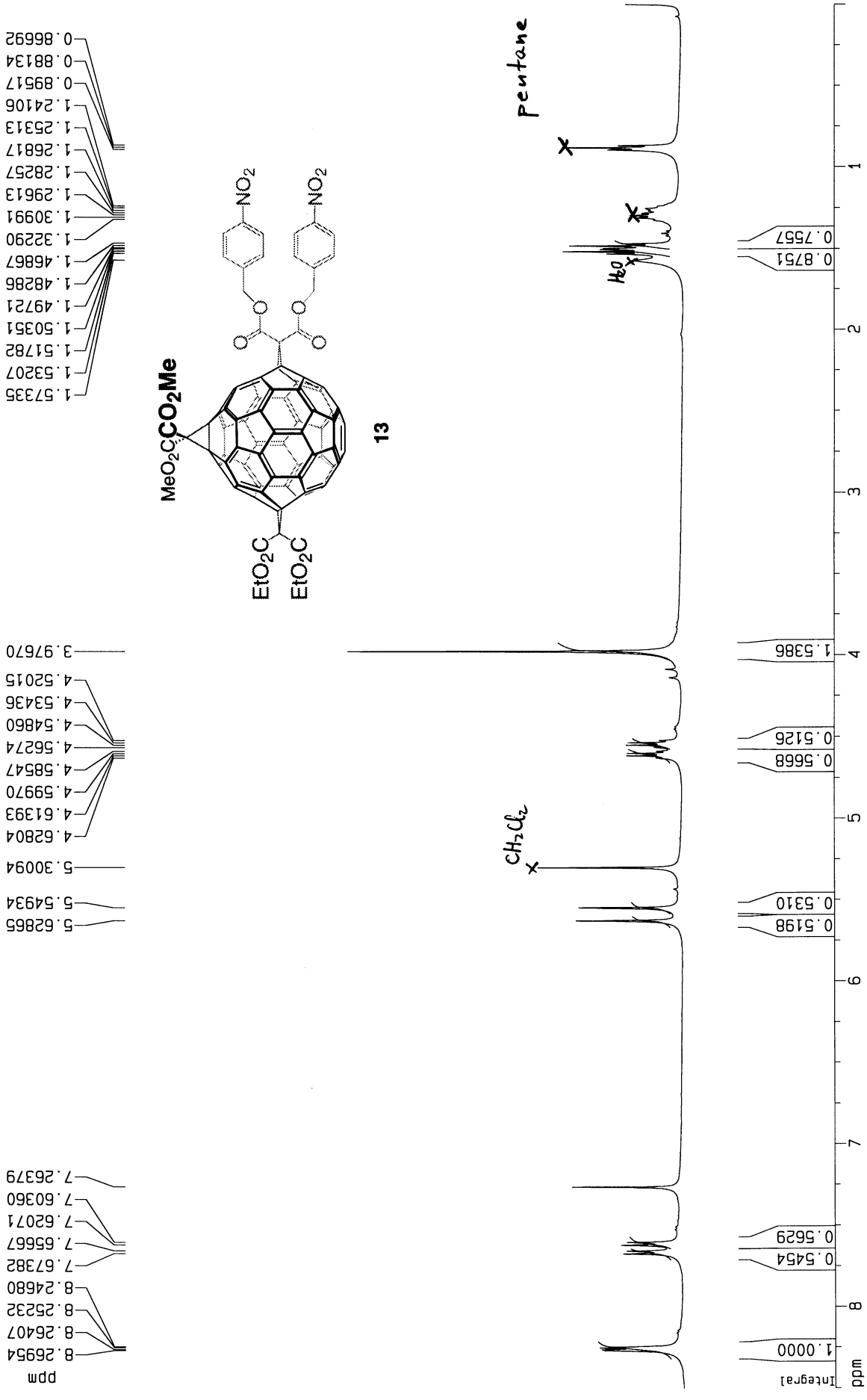
^{1}H NMR spectrum in $CDCl_3$



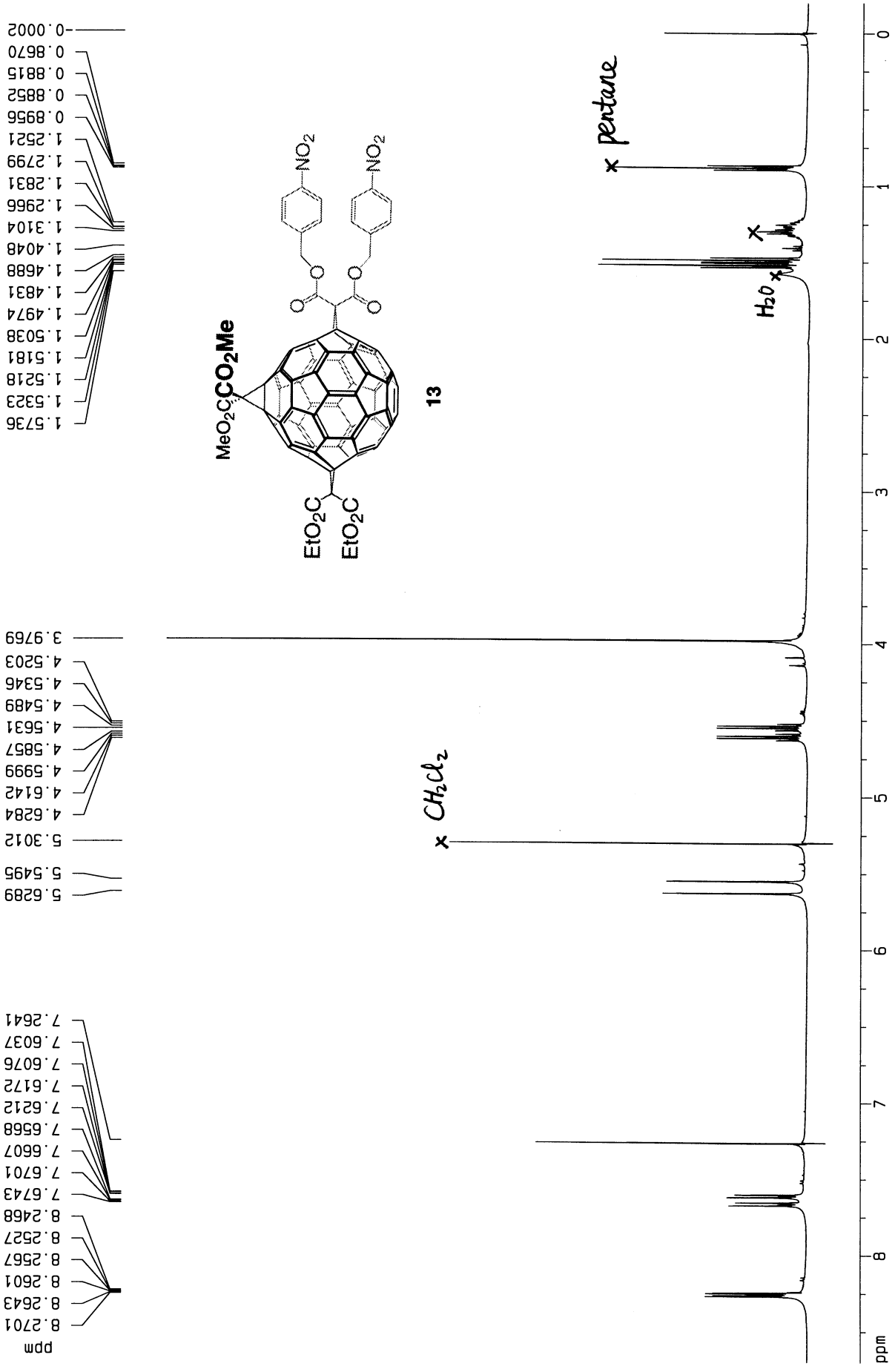
^{13}C NMR spectrum in $CDCl_3$



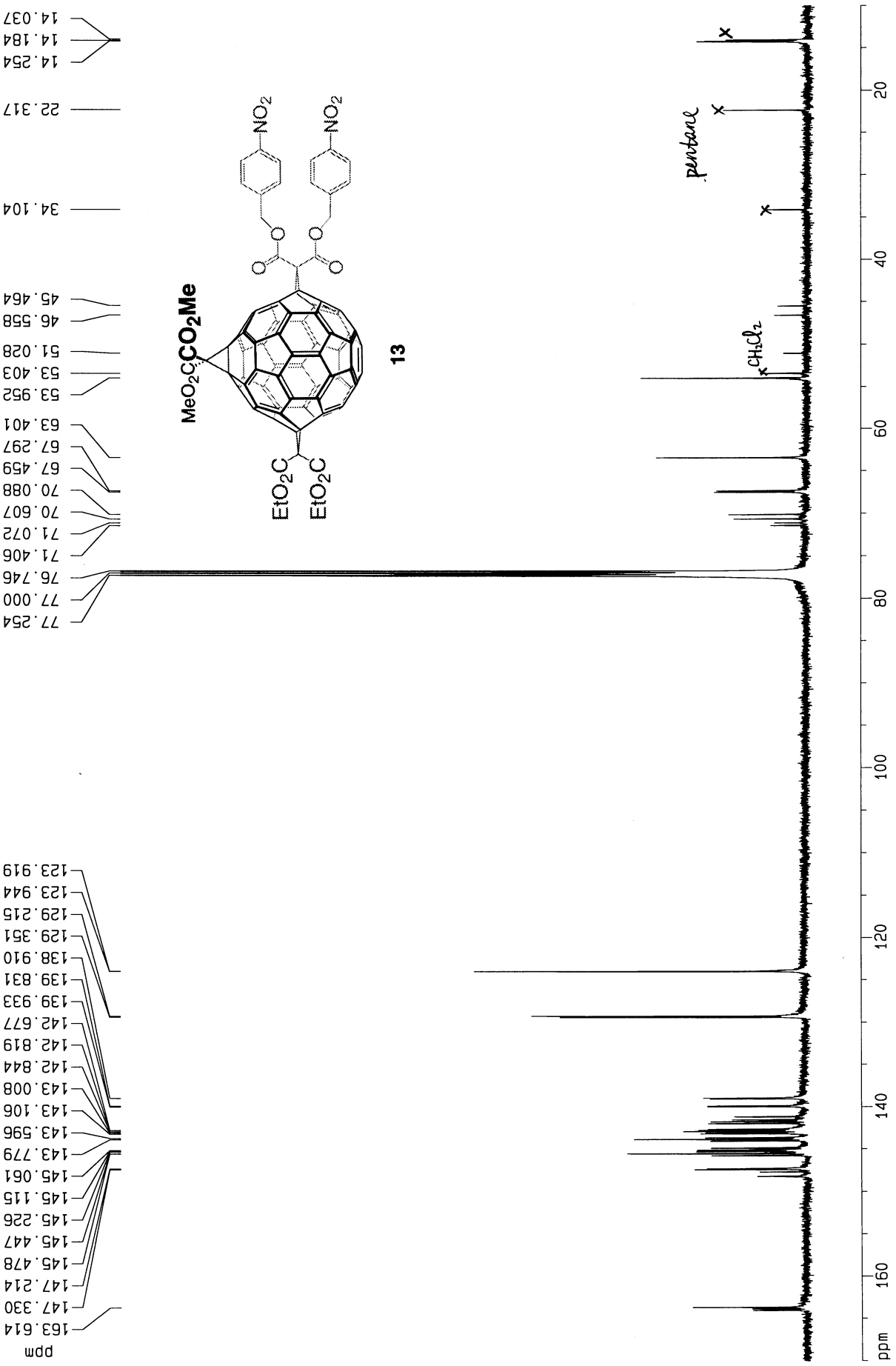
^{1}H NMR spectrum in $CDCl_3$



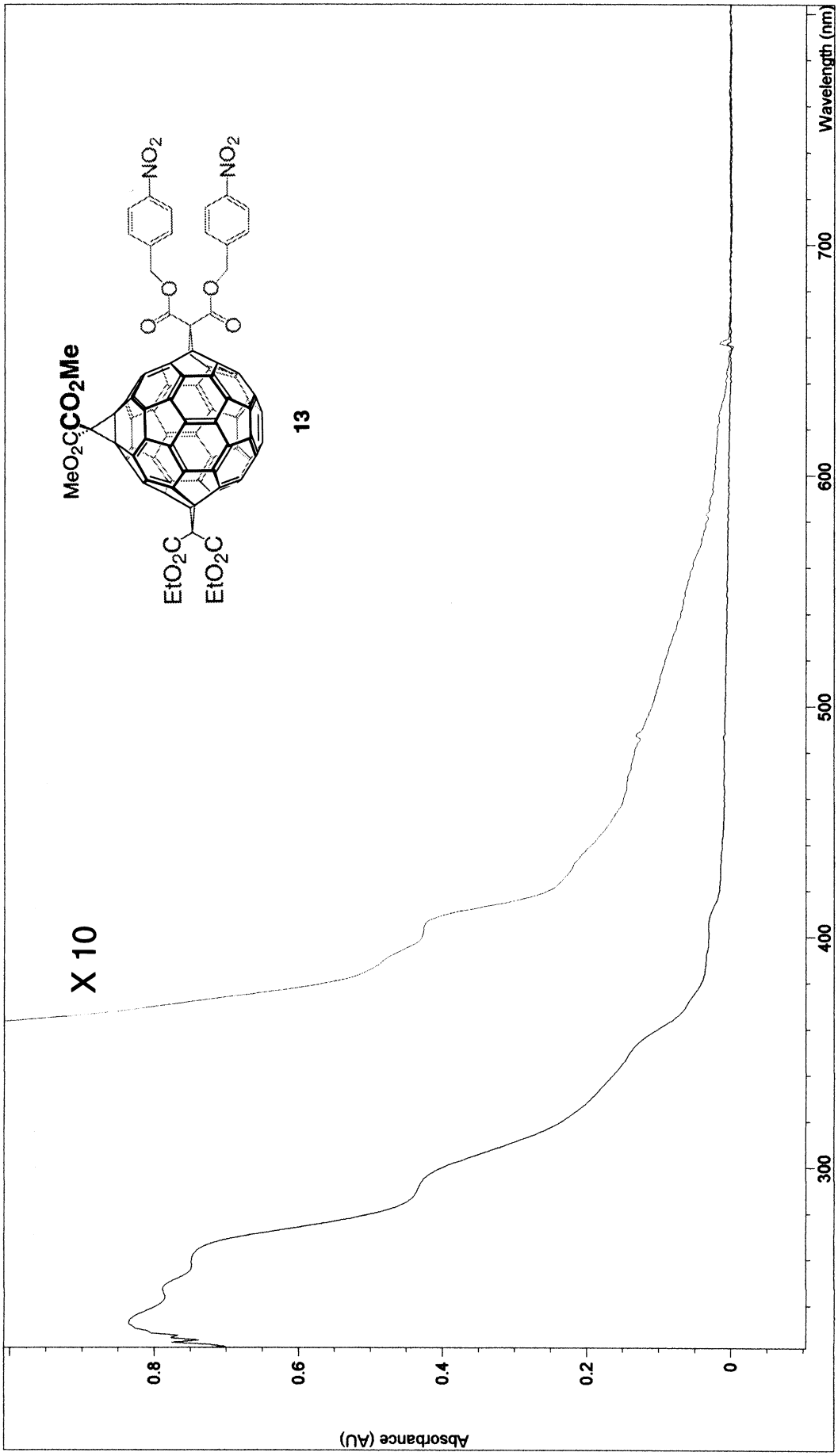
^{1}H NMR spectrum in $CDCl_3$ (enhanced with Gaussian broadening)



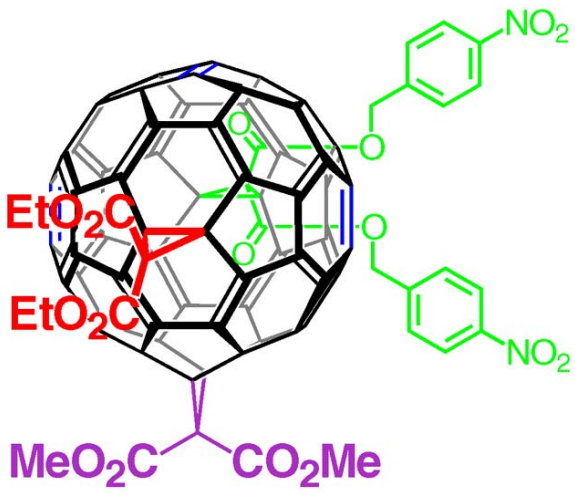
^{13}C NMR spectrum in $CDCl_3$



Electronic absorption spectrum in CH_2Cl_2

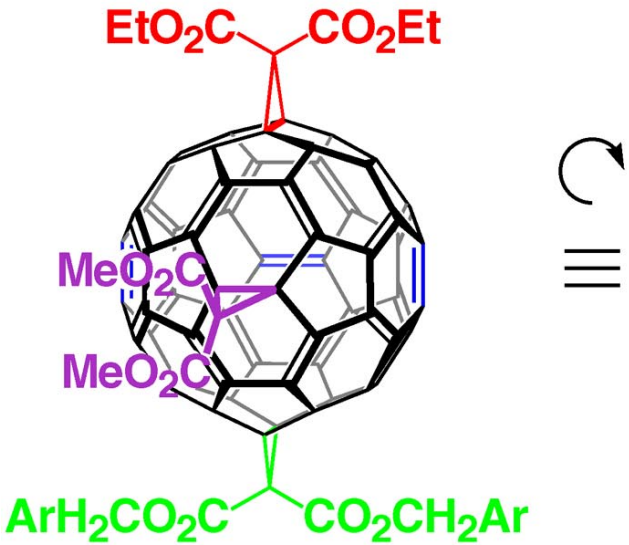


There are only two possible isomers for a
sequentially-differentiated trisadduct lying at equatorial positions of C_{60}



Rubin *et al.* addition pattern
(2 Et, 1 Me, 2 Bn signals in ^{1}H NMR)

OR



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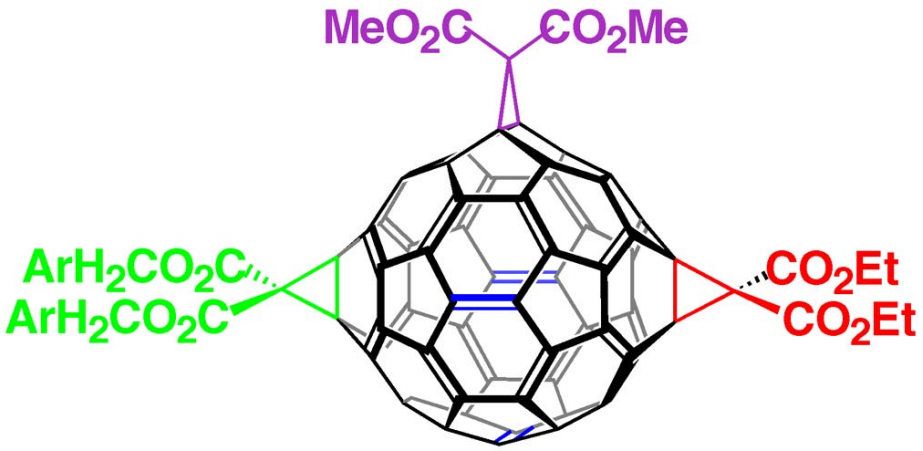

Diederich *et al.* addition pattern
(1Et, 2 Me, 1 Bn signals in ^{1}H NMR)