Supplementary Information

A Short Covalent Synthesis of an All-Carbon Ring [2]Rotaxane

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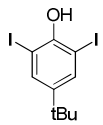
General methods and materials

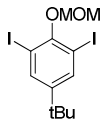
Unless stated otherwise, reactions were performed without special precautions like drying or N_2/Argon atmosphere. Dried CH_2Cl_2 and CH_3CN were obtained by distilling these solvents with CaH_2 as drying agent. Dried THF was obtained by distillation with sodium. All dried solvents were stored under N_2 atmosphere. Dry DMF and DMSO on 4Å molecular sieves were obtained from Sigma-Aldrich and stored under N_2 atmosphere. Reagents were purchased with the highest purity (usually >98%) from Sigma Aldrich and Fluorochem and used as received. Grubbs 2nd generation catalyst was purchased from AK Scientific. Reactions were monitored with thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254). SilaFlash® P60 (particle size 40-63 µm) was used for silica column chromatography. NMR spectra were recorded on Bruker DRX-300, 400 and 500 MHz instruments and calibrated on residual undeuterated solvent signals as internal standard. The ^{1}H-NMR multiplicities were abbreviated as followed: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). FD/FI probe equipped with FD Emitter, Carbotec or Linden (Germany), FD 10 µm. Current rate 51.2 mA/min over 1.2 min machine using field desorption (FD) as ionization method. Melting points were recorded on a Wagner & Munz Polytherm A melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FTIR machine.

Compound **24**



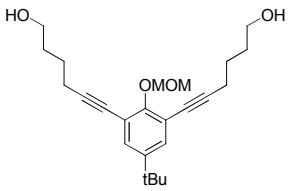
4.50 g 4-*tert*-butylphenol **7** (30 mmol) was dissolved in 150 mL absolute CH_3OH and 7.61 g I_2 (30 mmol, 1.0 equiv) and 6.13 mL 30% H_2O_2 (60 mmol, 2.0 equiv) were added. The reaction was stirred at room temperature for 3 days and was concentrated in *vacuo*. The residue was partitioned between 50 mL CH_2Cl_2 and 50 mL H_2O. The water layer was extracted with 10 mL CH_2Cl_2 and the combined organic layers were washed with 40 mL saturated $Na_2S_2O_3$, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was purified by column chromatography (PE/EtOAc 50:1) to give **24** (10.94 g, 27.22 mmol, 91%) as a red crystalline solid. Melting point: 79-80 ^oC; Spectral data matched those reported in literature.[1]

Compound **8**



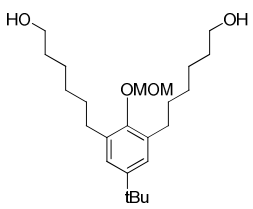
9.93 g **24** (24.70 mmol) and 4.12 mL NEt_3 (29.64 mmol, 1.2 equiv) were dissolved in 50 mL dry CH_2Cl_2 and cooled to 0 °C. After cooling, 2.25 mL MOM-Cl (29.64 mmol, 1.2 equiv) was added dropwise and the reaction was stirred at 0 °C for 1h and overnight at room temperature. The reaction was quenched by addition of 10 mL H_2O and stirred for 10 minutes. The organic layer was washed with 30 mL 1M HCl and the water layer was extracted with 10 mL CH_2Cl_2. The combined organic layers were washed with 30 mL 1M NaOH and dried over $MgSO_4$ and concentrated in *vacuo* to give **8** (10.52 g, 23.58 mmol, 95%) as a faint yellow oil. Spectral data matched those reported in literature.[2]

Compound **25**



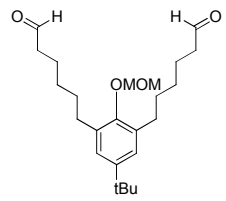
4.92 g **8** (11.03 mmol) and 2.92 mL 5-hexyn-1-ol (26.47 mmol, 2.4 equiv) were dissolved in 55 mL THF/NEt_3 1:1 and the mixture was degassed with five vacuum/N_2cycles. After degassing, 310 mg $Pd(PPh_3)_2Cl_2$ (0.441 mmol, 0.04 equiv) and 168 mg CuI (0.882 mmol, 0.08 equiv) were added and the reaction was stirred overnight at 40 °C. The mixture was concentrated in *vacuo* and the residue was partitioned between 50 mL EtOAc and 50 mL 1M HCl. The water layer was extracted with 3 x 25 mL EtOAc and the combined organic layers were washed with 50 mL brine, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was purified by column chromatography (PE/EtOAc 1:1 → 1:2 → 1:3) to give **25** (4.07 g, 10.54 mmol, 95%) as a thick yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 2H), 5.31 (s, 2H), 3.70 (t, 4H), 3.67 (s, 3H), 2.49 (t, 4H), 1.92 (bs, 2H), 1.74 (m, 8H), 1.28 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.2, 146.6, 130.4, 117.6, 98.8, 93.9, 77.6, 62.4, 57.7, 34.4, 32.0, 31.3, 25.0, 19.5; IR (cm^{-1}): 3346, 2938, 2232, 1454, 1231, 1201

Compound **9**



4.07 g **25** (10.50 mmol) was dissolved in 30 mL dry THF/EtOH 1:1 and 400 mg Pd/C (10% w/w) was added. The mixture was bubbled with H_2 gas for 5 minutes and then the reaction was stirred overnight at 60 °C under H_2 atmosphere. After completion of the reaction, N_2 gas was bubbled through the reaction for 10 minutes and the mixture was filtered through a plug of Celite, which was flushed with EtOAc. The filtrate was concentrated in *vacuo* to give **9** (3.83 g, 9.70 mmol, 92%) as a faint yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 2H), 4.94 (s, 2H), 3.65 (t, 4H), 3.63 (s, 3H), 2.64 (t, 4H), 1.82 (bs, 2H), 1.61 (m, 8H), 1.42 (m, 8H), 1.31 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.8, 146.9, 135.0, 124.8, 99.9, 63.0, 57.4, 34.4, 32.8, 31.6, 30.9, 30.8, 29.5, 25.7; IR (cm^{-1}): 3353, 2930, 2858, 1709, 1479, 1158

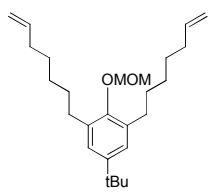
Compound **26**



1.34 g **9** (3.39 mmol) and 4.71 mL NEt_3 (33.90 mmol, 10.0 equiv) were dissolved in 25 mL dry CH_2Cl_2/DMSO 4:1 and cooled to 0 °C. After cooling, 2.16 g pyridine · SO_3 (13.56 mmol, 4.0 equiv) was added and the reaction was stirred at 0 °C for 3 hours, after which the reaction was completed (TLC). The reaction was quenched by addition of 10 mL H_2O and stirred for 10 minutes.

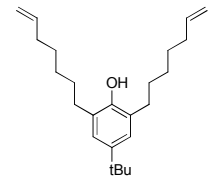
The reaction was diluted with 25 mL CH_2Cl_2 and was washed with 50 mL 1M HCl. The water layer was extracted with 2 x 10 mL CH_2Cl_2. The combined organic layers were washed with 25 mL 1M HCl and 2 x 15 mL H_2O, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was purified by column chromatography (PE/EtOAc 9:1 → 8:1→ 7:1) to give **26** (838 mg, 2.15 mmol, 63%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.79 (t, 2H), 7.03 (s, 2H), 4.93 (s, 2H), 3.62 (s, 3H), 2.64 (t, 4H), 2.46 (dt, 4H), 1.66 (m, 8H), 1.46 (sext, 4H), 1.32 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 203.0, 151.9, 147.0, 134.7, 124.8, 100.0, 57.3, 44.0, 34.4, 31.6, 30.74, 30.68, 29.4, 22.1; IR (cm^{-1}): 2929, 2859, 1723, 1479, 1182

Compound **27**



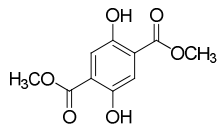
1.80 g methyltriphenylphosphonium bromide (5.03 mmol, 2.5 equiv) was put in a flame-dried flask and dried under vacuum at 70 °C for 1 hour. The flask was cooled and backfilled with N_2 gas. Next, 15 mL dry THF was added and the mixture was cooled to 0 °C. After cooling, 564 mg KOtBu (5.03 mmol, 2.5 equiv) was added and the mixture was stirred for 15 minutes at 0 °C. Next, 785 mg **26** (2.01 mmol) was dissolved in 5 mL dry THF and added dropwise to the aforementioned solution. The reaction was stirred for 1h at 0 °C and 1h at room temperature, and was subsequently quenched with 1 mL acetone. The mixture was concentrated in *vacuo,* dry-loaded on silica and purified by column chromatography (PE/EtOAc 100:0 → 99:1 → 98:2) to give **27** (676 mg, 1.87 mmol, 87%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 2H), 5.82 (m, 2H), 5.02 (d, 2H), 4.98 (d, 2H), 4.94 (s, 2H), 3.63 (s, 3H), 2.63 (t, 4H), 2.08 (q, 4H), 1.67 (m, 4H), 1.44 (m, 8H), 1.32 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.8, 146.8, 139.3, 135.1, 124.8, 114.3, 99.9, 57.3, 34.4, 33.9, 31.6, 30.9, 30.9, 29.5, 29.0; IR (cm^{-1}): 2926, 2857, 1640, 1479, 1182

Compound **10**



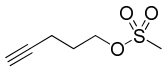
950 mg **27** (2.46 mmol) was dissolved in 13 mL THF/12M HCl/CH_3OH 8:4:1 and was stirred overnight at room temperature. The mixture was diluted with 20 mL H_2O and 20 mL EtOAc. The water layer was extracted with 2 x 20 mL EtOAc and the combine organic layers were washed with 20 mL brine, dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EtOAc 99:1 → 98:2) to give **10** (844 mg, 2.46 mmol, quant) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 2H), 5.85 (m, 2H), 5.03 (d, 2H), 4.97 (d, 2H), 4.53 (s, 1H), 2.62 (t, 4H), 2.10 (q, 4H), 1.65 (quint, 4H), 1.46 (m, 8H), 1.32 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 149.2, 142.9, 139.2, 127.4, 124.7, 114.4, 34.1, 33.9, 31.8, 30.7, 29.9, 29.3, 28.9; IR (cm^{-1}): 3618, 2926, 2856, 1640, 1482, 1188

Compound **12**



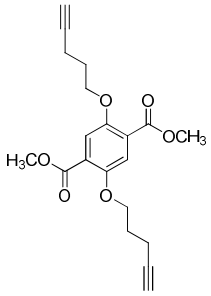
5.70 g dimethyl-2,5-dioxocyclohexane-1,4-dicarboxylate **11** (25 mmol) was suspended in 25 mL AcOH and heated to 80 °C and 3.41 g *N*-chlorosuccinimide (25.5 mmol, 1.02 equiv) was added portionwise over 30 minutes. The reaction was stirred at 80 °C for 90 minutes and was then cooled to room temperature and diluted with 25 mL H_2O. The solid was filtered and washed with 2 x 25 mL H_2O, 2 x 5 mL CH_3OH and dried on air and vacuum to give **12** (5.43 g, 24.02 mmol, 96%) as a yellow powder. Melting point: 173-175 °C; Spectral data matched those reported in literature[3]

Compound **14**



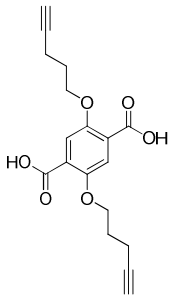
1.86 mL 4-pentynol **13** (20.0 mmol) and 3.33 mL Et_3N (24.0 mmol, 1.2 equiv) were dissolved in 40 mL dry THF and cooled to 0 °C and 1.70 mL methanesulfonyl chloride (22.0 mmol, 1.1 equiv) was added dropwise. The ice bath was removed and the reaction was stirred overnight at room temperature and was then quenched with 20 mL H_2O and stirred for 15 min. The mixture was diluted with 40 mL Et_2O and 20 mL 1M HCl and the water layer was extracted with 2 x 20 mL Et_2O. The combined organic layers were washed with 40 mL brine, dried over $MgSO_4$ and concentrated *in vacuo* to give **14** (3.11 g, 19.18 mmol, 96%) as a slightly yellow oil, which was used without further purification. Spectral data matched those reported in literature[4]

Compound **15**



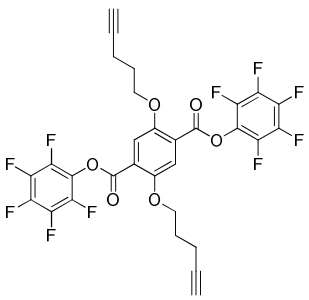
2.93 g **14** (18.04 mmol, 2.4 equiv), 1.70 g **12** (7.52 mmol, 1.0 equiv), 2.49 g K_2CO_3 (18.04 mmol, 2.4 equiv) and 124 mg KI (0.75 mmol, 0.1 equiv) were dissolved in 50 mL dry DMF and stirred overnight at 80 °C. The mixture was cooled to room temperature, concentrated *in vacuo* and to the residue was added EtOAc and the suspension was filtered. The filter cake was washed with EtOAc and the combined organic layers were washed with 2 x 20 mL H_2O and 20 mL brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (PE/EtOAc 4:1) to give **15** (2.11 g, 5.89 mmol, 78%) as a slightly yellow solid. Note: the product is slightly contaminated with the methyl-pentynol-ester. This has no consequence for the next step (saponification). Melting point: 89-93 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 2H), 4.14 (t, 4H), 3.92 (s, 6H), 2.47 (dt, 4H), 2.06 (quint, 4H), 1.98 (t, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 166.2, 151.9, 124.6, 117.0, 83.6, 69.0, 68.2, 52.5, 28.3, 15.2; IR (cm^{-1}): 3299, 2884, 2116, 1725, 1504, 1408, 1201

Compound **16**



1.44 g **15** (4.02 mmol) was dissolved in 30 mL THF/CH_3OH/H_2O 2:1:1 and 901 mg KOH (15.08 mmol, 4.0 equiv) was added. The mixture was stirred overnight at room temperature and was acidified with 3 mL 37% HCl and stirred for 15 minutes. The mixture was diluted with 20 mL H_2O and 20 mL EtOAc. The water layer was extracted with 3 x 20 mL EtOAc and the combined organic layers were washed with 20 mL brine, dried over $MgSO_4$ and concentrated *in vacuo* to give **16** (1.30 g, 3.94 mmol, 98%) as a faint yellow solid. Melting point: 175-178 °C; Yield: ^{1}H-NMR (300 MHz, CD_3OD) δ 7.48 (s, 2H), 4.17 (t, 4H), 2.45 (dt, 4H), 2.25 (t, 2H), 2.02 (quint, 4H); ^{13}C-NMR (75 MHz, CD_3OD) δ 168.8, 152.9, 126.3, 117.6, 84.1, 70.0, 69.3, 29.4, 15.7; IR (cm^{-1}): 3267, 2938, 2875, 1673, 1505, 1217

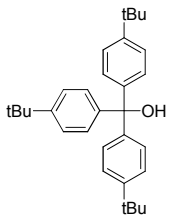
Compound **17**



1.30 g **16** (3.94 mmol), 2.17 g pentafluorophenol (11.82 mmol, 3.0 equiv), 4.11 mL DIPEA (23.64 mmol, 6.0 equiv) and 4.48 g HBTU (11.82 mmol, 3.0 equiv) were dissolved in 80 mL dry THF and stirred overnight at room temperature. The mixture was concentrated *in vacuo* and dry-loaded on silica and purified by column

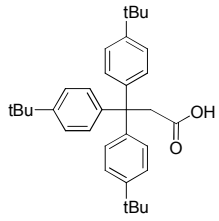
chromatography (PE/EtOAc 10:1 → 8:1 → 6:1) to give **17** (2.07 g, 3.13 mmol, 79%) as an off-white solid. Melting point: 113-115 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 2H), 4.26 (t, 4H), 2.46 (dt, 4H), 2.08 (quint, 4H), 1.98 (t, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 160.9, 152.9, 143.2, 139.8, 138.3, 136.5, 122.3, 117.3, 83.2, 69.2, 68.2, 28.1, 15.1; IR (cm^{-1}): 3316, 2943, 1755, 1519, 1416, 1390, 1230, 1201

Compound **19**



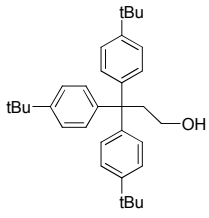
5.20 mL 4-bromo-*tert*-butylbenzene **18** (30 mmol, 3.0 equiv) was dissolved in 60 mL dry THF under N_2 atmosphere and cooled to -78 °C. After cooling, 18.75 mL n-BuLi (1.6 M in hexane, 30 mmol, 3.0 equiv) was added slowly over 15 minutes and the solution was stirred for 45 minutes, after which 0.84 mL dimethyl carbonate (10 mmol) was added dropwise. The dry-ice bath was removed and the reaction was stirred overnight at room temperature. The mixture was concentrated in *vacuo* and the residue was partitioned between 120 mL Et_2O and 60 mL 1M HCl. The water layer was extracted with 30 mL Et_2O and the combined organic layers were washed with 60 mL saturated $NaHCO_3$, 60 mL H_2O, 60 mL brine, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was triturated with 2 x 20 mL cold PE to give **19** (3.62 g, 8.44 mmol, 84%) as a white powder. Melting point: 220-221 °C; Spectral data matched those reported in literature[5]

Compound **20**



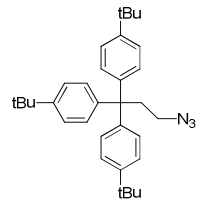
6.24 g **19** (14.57 mmol) and 15.15 g malonic acid (145.60 mmol, 10 equiv) were heated to 180 °C in a 250 mL flask. Around 120 °C the mixture became a viscous yellow liquid and around 170 °C the mixture started to evolve CO_2 gas with bubbling. The mixture was stirred at 180 °C until it dried up, after which it was cooled to room temperature. The slightly yellow residue was dissolved in 150 mL Et_2O and washed with 2 x 50 mL H_2O, 50 mL brine, dried over $MgSO_4$ and concentrated in *vacuo*. The slightly yellow powder was triturated with 2 x 15 mL cold CH_3OH, which removed most of the yellow color. The product was dried in *vacuo* to give **20** (6.22 g, 13.20 mmol, 91%) as a faintly yellow fine powder. Melting point: 249 – 252 °C; Spectral data matched those reported in literature[6]

Compound **21**



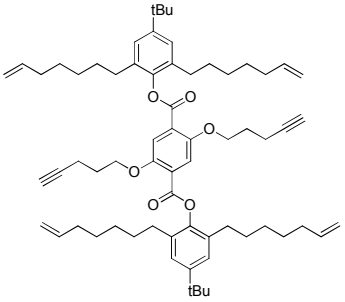
6.20 g **20** (13.17 mmol) was dissolved in 100 mL dry THF under N_2 atmosphere and cooled to 0 °C. After cooling, 3.12 mL $BH_3 \cdot SMe_2$ (32.93 mmol, 2.5 equiv) was added dropwise and the ice bath was removed. The reaction was stirred overnight at room temperature and was quenched carefully with 10 mL H_2O and stirred for 15 minutes. The mixture was concentrated in *vacuo* and the residue was partitioned between 150 mL Et_2O and 75 mL H_2O. The water layer was extracted with 30 mL Et_2O and the combined organic layers were washed with 75 mL brine and dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography (CH_2Cl_2) to give **21** (5.07 g, 11.11 mmol, 84%) as a colorless foam. Melting trajectory: 98 – 110 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (d, 6H), 7.24 (d, 6H), 3.54 (t, 2H), 2.93 (t, 2H), 1.35 (s, 27H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.6, 144.3, 128.7, 124.8, 60.8, 54.1, 43.1, 34.4, 31.5; IR (cm^{-1}): 3340, 2957, 2901, 2866, 1508, 1362, 1269

Compound **22**



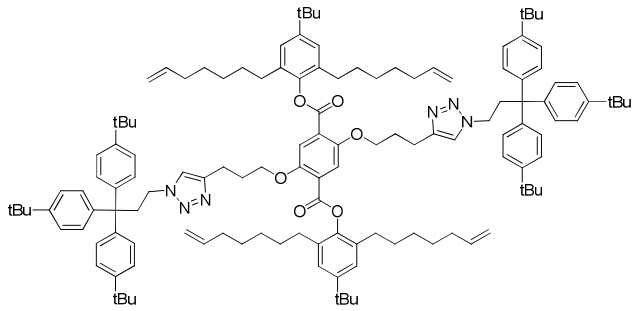
2.32 g **21** (5.08 mmol) was dissolved in 50 mL dry THF under N_2 atmosphere. The solution was cooled to 0 °C and 1.46 g PPh_3 (5.58 mmol, 1.1 equiv) and 1.10 mL DIAD (5.58 mmol, 1.1 equiv) were added and the mixture was stirred for 5 minutes. Next, 1.20 mL DPPA (5.58 mmol, 1.1 equiv) was added dropwise, the ice bath was removed and the reaction was stirred overnight at room temperature. The mixture was concentrated in *vacuo* and the residue was dry-loaded on silica and purified by column chromatography (PE/CH_2Cl_2 7:1) to give **22** (1.94 g, 4.03 mmol, 79%) as a colorless foam. Melting point: 166-169 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (d, 6H), 7.18 (d, 6H), 3.08 (t, 2H), 2.88 (t, 2H), 1.34 (s, 27H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.8, 143.6, 128.6, 125.0, 54.0, 49.1, 39.2, 34.5, 31.5; IR (cm^{-1}): 2960, 2902, 2867, 2092, 1508, 1363, 1268

Compound **23**



651 mg **10** (1.90 mmol, 2.0 equiv), 629 mg **17** (0.95 mmol), 1.23 g Cs_2CO_3 (3.80 mmol, 4.0 equiv) and 300 mg 4Å MS were dissolved in 20 mL dry CH_3CN and the reaction was stirred overnight at 50 °C under N_2 atmosphere. The mixture was concentrated in *vacuo*, dry-loaded on silica and purified by column chromatography (PE/EtOAc 25:1 → 20:1) to give **23** (851 mg, 0.867 mmol, 91%) as a thick colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.18 (s, 4H), 5.80 (m, 4H), 4.98 (d, 2H), 4.94 (d, 4H), 4.26 (t,4H), 2.60 (t, 8H), 2.47 (dt, 4H), 2.09 (m, 12H), 1.96 (t, 2H), 1.67 (quint, 8H), 1.49-1.36 (m, 34H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 163.8, 152.5, 148.7, 145.1, 139.0, 133.9, 125.0, 124.2, 117.0, 114.4, 83.3, 69.2, 68.0, 34.5, 33.8, 31.6, 30.9, 30.1, 29.2, 28.8, 28.3, 15.2; IR (cm^{-1}): 3310, 2927, 2858, 1747, 1718, 1411, 1163

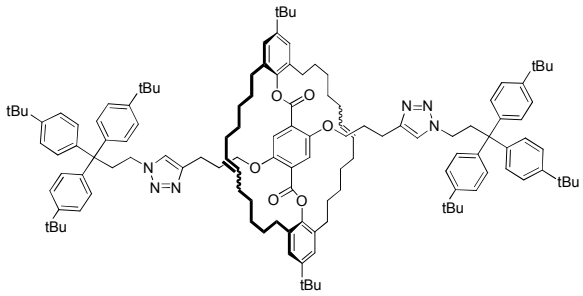
Compound **2**



158 mg **23** (0.162 mmol) and 156 mg **22** (0.324 mmol, 2.0 equiv), 0.014 mL DIPEA (0.081 mmol, 0.5 equiv) and 0.009 mL 2,6-lutidine (0.081 mmol, 0.5 equiv) were dissolved in 5 mL dry CH_3CN/THF 4:1 and was degassed with five vacuum/N_2 cycles. After degassing, 6 mg CuI (0.032 mmol, 0.20 equiv) was added and the mixture was stirred overnight at room temperature. The mixture was concentrated in *vacuo* and the residue was partitioned between 10 mL CH_2Cl_2 and 8 mL 1M HCl. The water layer was extracted with 5 mL CH_2Cl_2 and the combined organic layers were concentrated in *vacuo* and the residue was purified by column chromatography (PE/EtOAc 10:1 → 8:1) to give **2** (274 mg, 0.141 mmol, 87%) as a colorless foam. Melting point: 98-102 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.34 (d, 12H), 7.26 (d, 12H), 7.18 (s, 4H), 7.14 (s, 2H), 5.77 (m, 4H), 4.98-4.88 (m, 8H), 4.22 (t, 4H), 4.07 (t, 4H), 3.18 (t, 4H), 2.97 (t, 4H), 2.61 (t, 8H), 2.28 (quint, 4H), 2.04 (q, 8H), 1.67 (quint, 8H), 1.46-1.27 (m, 88H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 163.7, 152.4, 148.9, 148.7, 146.9, 145.1, 143.3, 138.8, 133.8, 128.5, 125.4, 125.03, 124.95, 124.2, 121.0, 116.7, 114.3, 77.4, 68.8, 54.2, 47.9, 40.9, 34.5, 34.4, 33.7, 31.6, 31.4, 30.9, 30.1, 29.2, 28.7, 22.2 IR

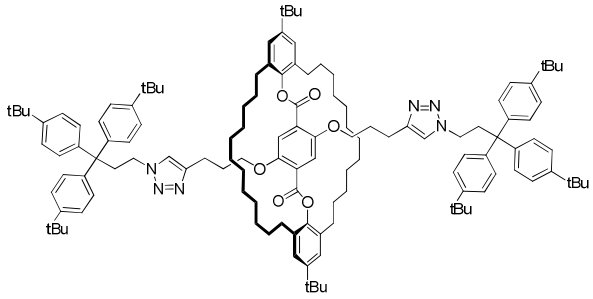
(cm^{-1}): 2957, 2930, 2863, 1745, 1505, 1462, 1164; Due to decomposition during the analysis, satisfactory HRMS (FD) data could not be obtained.

Compound **4**



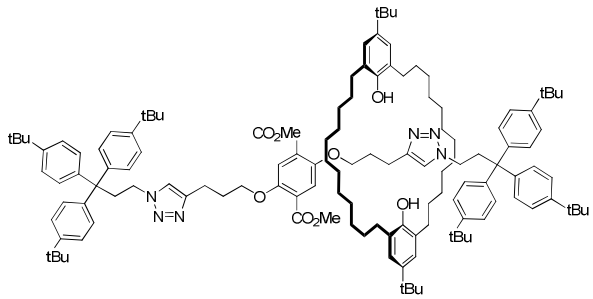
270 mg **2** (0.139 mmol) was dissolved in 140 mL dry CH_2Cl_2 and the solution was degassed with five vacuum/N_2 cycles. After degassing, 23 mg Grubbs II (0.028 mmol, 0.20 equiv) was added and the reaction was stirred overnight at 40 °C under N_2 atmosphere. The reaction was concentrated in *vacuo*, dry-loaded on silica and purified by column chromatography (PE/EtOAc 10:1 → 8:1 → 6:1) to give **4** (212 mg, 0.112 mmol, 80%) as an off-white film. ^{1}H-NMR: broad signals and E/Z mixture, see page 49 for the spectrum; IR (cm^{-1}): 2957, 2929, 2865, 1743, 1717, 1506, 1461, 1164; HRMS (FD) calcd for $C_{128}H_{168}N_6O_6$ [M^+]: 1885.3025, found: 1885.3045

Compound **4-H_4**



210 mg **4** (0.111 mmol) was dissolved in 5 mL THF/EtOH 1:1 and 60 mg Pd/C (10% w/w) was added. Through the mixture was bubbled H_2 gas for 5 minutes and the reaction was stirred overnight at 60 °C under H_2 atmosphere (balloon). The mixture was filtered over a plug of Celite, which was flushed with EtOAc. The filtrate was concentrated in *vacuo* to give **4-H_4** (199 mg, 0.105 mmol, 95%) as a colorless film. ^{1}H-NMR: broad signals, see page 50 for the spectrum; HRMS (FD) calcd for $C_{128}H_{172}N_6O_6$ [M^+]: 1889.3338, found: 1889.3275

Compound **1**



18 mg **4-H_4** (0.0095 mmol) was dissolved in 2 mL dioxane in a pressure tube and 0.5 mL 20% KOH was added. The reaction was stirred at 130 °C for 2h and was cooled to room temperature. The mixture was diluted with H_2O and was acidified with HCl to pH 1. To the water layer was added 10 mL EtOAc and the mixture was stirred vigorously for 15 min. The water layer was extracted with an additional 10 mL EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in *vacuo* to give the di-acid (17 mg, 0.0089 mmol, 94%) as a colorless film.

This was dissolved in 2 mL dry CH_2Cl_2/CH_3OH 1:1, cooled to 0 °C and 0.1 mL TMS-diazomethane (1M in hexane, 0.100 mmol, 12 equiv) was added. The ice bath was removed and the reaction was stirred

at room temperature for 2h. The reaction was quenched with 1 droplet of AcOH and the organic layer was concentrated in *vacuo*. The residue was purified by column chromatography (PE/EtOAc 9:1 → 3:2) to give **1** (16.5 mg, 0.0084 mmol, 95%) as a colorless film. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.30 (d, 12H), 7.24 (s, 2H), 7.21 (d, 12H), 7.14 (s, 2H), 6.97 (s, 4H), 4.05 (m, 8H), 3.75 (s, 6H), 3.13 (m, 4H), 2.94 (t, 4H), 2.63 (t, 8H), 2.21 (quint, 4H), 1.57 (quint, 8H), 1.32 (s, 54H), 1.28 (s, 18H), 1.19-1.10 (m, 32H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 165.7, 151.9, 150.0, 148.8, 147.0, 143.1, 142.3, 129.2, 128.4, 124.9, 124.4, 124.1, 121.2, 116.6, 68.8, 54.0, 52.2, 48.0, 40.8, 34.3, 33.9, 31.7, 31.32, 31.27, 30.6, 29.5, 29.2, 29.13, 29.05, 22.0; IR (cm^{-1}): 2959, 2926, 2854, 1731, 1464, 1205; HRMS (FD) calcd for $C_{130}H_{180}N_6O_8$ [M^+]: 1953.3863, found: 1953.3888

References

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DFT calculations

DFT calculations were performed at the PM6//wB97XD/6-31G(d) level of theory using the Gaussian 09 program suite.[7]

XYZ-coordinates structures **4**, **5** and **6**:

Compound 4

E(PM6// wB97XD/6-31G(d): -4499.27520815 a.u.

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C	1.93458620	3.50596025	2.69220222
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H	4.34043331	-4.03923335	1.00648209
H	7.70548153	-5.72878553	-1.20823208
H	9.52979369	-6.18388855	-2.81710320
H	10.16961476	-4.46759245	-4.50422033
H	8.97382970	-2.28245527	-4.55361533
H	7.16886257	-1.80955121	-2.95746421

H	-2.31790318	-1.68729610	-1.37873009
H	-2.17460618	-2.60906517	-2.86955921
H	-0.14254503	-3.35667825	-2.15307515
H	0.50929504	-1.74233913	-2.40739817
H	-0.20985601	-1.11314608	-0.02440899
H	-0.81461508	-2.75270120	0.20571203
H	1.53331709	-3.65891029	-0.30637501
H	2.11407416	-1.99415317	-0.44985902
H	0.85806305	-3.28477726	2.08274817
H	2.47453018	-1.93971017	3.30683126
H	4.07667832	-1.36355614	0.96364909
H	2.75809123	-0.16916404	0.93038908
H	3.30691328	0.52129901	3.30488027
H	4.63726536	-0.64819610	3.33591827
H	5.63740747	0.55288199	1.27497011
H	4.37004637	1.77916909	1.43366112
H	6.71901158	2.22418210	2.53791221
H	6.23458452	1.07448702	3.78586830
H	4.01992535	2.57828216	3.97725832
H	5.50656146	3.06088018	4.78206838
C	0.00374810	7.46434757	-2.72049519
H	0.41505313	7.83956859	-3.67893027
H	-0.31288794	6.42054148	-2.92472221

Compound 5

E(PM6// wB97XD/6-31G(d): -4499.22513469 a.u.

C	0.24104402	0.92489704	0.81841206
C	1.46609111	0.29803498	1.11000608
C	2.68493920	0.92308002	0.78417305
C	2.67255721	2.10051311	0.03128000
C	1.45090912	2.67893016	-0.33820803
C	0.23143702	2.12668213	0.11727400
C	-1.06141107	2.83689319	-0.09985501
C	4.00825831	0.33091897	1.12468408
O	-1.55601011	3.70731626	0.56757304
O	4.65161735	-0.40659709	0.41527703
O	-1.67451512	2.28636815	-1.21272610
C	-2.89235421	2.85358220	-1.65563413
C	-2.82794720	3.74726627	-2.73930822
C	-4.04362030	4.22371530	-3.25267725
C	-5.25694439	3.82924128	-2.68386321
C	-5.28608640	2.94545822	-1.60165413
C	-4.09662930	2.43216717	-1.06623809
C	-1.51492710	4.15327629	-3.34177326
C	-1.21660707	5.65257041	-3.18246725

C	-0.90264304	6.02518644	-1.72895814
C	-0.34597400	7.44513754	-1.57648413
C	1.04198611	7.61558056	-2.21878718
C	1.75555917	8.80862263	-1.65975113
C	2.95444926	8.80826961	-1.06815009
O	1.32256312	3.80060025	-1.11964609
C	2.46463521	4.23004428	-1.92179416
C	2.75328622	3.23659220	-3.03938924
C	4.25878334	3.02397818	-3.26955926
C	4.58214035	1.60030706	-3.53338327
O	4.65686236	0.70246700	2.29259917
C	4.01335331	1.39231505	3.34000025
C	4.01722231	2.79857916	3.35608325
C	3.49203328	3.43328821	4.49405633
C	2.99500224	2.68999516	5.56473042
C	3.03811024	1.29543205	5.53494944
C	3.55899627	0.61516300	4.42583833
C	4.60950536	3.62151122	2.24709716
C	3.69529930	4.78934431	1.84709914
C	4.27786735	5.63135839	0.70629905
C	3.37353228	6.83538946	0.40814402
C	3.68575828	-0.88150412	4.43285033
O	1.57066411	-0.92140111	1.73281813
C	0.48607902	-1.88457518	1.52494511
C	-0.54740806	-1.70987016	2.62725119
C	-1.54205014	-2.87284925	2.66958420
C	-2.50873321	-2.80883323	1.54716411
C	-3.62179729	-1.97382117	1.36846010
N	-4.15989533	-2.35880820	0.13440700
N	-3.41091228	-3.37491028	-0.39252704
N	-2.43059121	-3.64845930	0.41855303
C	4.47702234	0.48334498	-2.68905421
N	4.92818337	-0.59025110	-3.46185727
N	5.29496142	-0.13923107	-4.70031436
N	5.09261439	1.14573503	-4.76415437
C	-5.39738240	-1.85070915	-0.49424304
C	5.03786137	-2.00160721	-3.03507224
C	-6.57217950	-2.77549222	-0.14439102
C	-7.94631660	-2.28190417	-0.68161106
C	-9.04526270	-3.30563824	-0.35625203
C	-8.19140065	-0.94956207	0.03342700
C	-7.98632362	-2.17679016	-2.20843717
C	-10.38388683	-2.88753921	-0.26281603
C	-11.39914487	-3.81012227	-0.00329401
C	-11.09487985	-5.16576938	0.15886801

C	-9.76893476	-5.59140043	0.05031400
C	-8.75110667	-4.66861335	-0.21072102
C	-8.68631468	-0.94758507	1.34932610
C	-8.85491669	0.25202703	2.04345315
C	-8.51569365	1.46822812	1.44106110
C	-8.00599859	1.47094611	0.14133500
C	-7.84264062	0.27214002	-0.55950405
C	-7.11679856	-2.92728023	-3.01288324
C	-7.19336056	-2.84884322	-4.40720035
C	-8.14937663	-2.03285015	-5.01640839
C	-9.03917870	-1.30294309	-4.22150433
C	-8.96314471	-1.37900710	-2.82953522
C	6.12835145	-2.14889423	-1.96419715
C	6.34253848	-3.62005134	-1.50552512
C	7.25601652	-3.61751634	-0.26899203
C	4.95109835	-4.17395438	-1.18464710
C	7.08631150	-4.47546041	-2.53629220
C	7.01471053	-4.46834341	0.81989106
C	7.87555656	-4.47136041	1.92145514
C	8.99303968	-3.63284435	1.94617814
C	9.25011071	-2.79535129	0.85637906
C	8.39190761	-2.79150229	-0.24562003
C	4.34494830	-5.16896045	-1.96169316
C	3.05361020	-5.61722248	-1.65932613
C	2.34956015	-5.06907843	-0.58596305
C	2.94267720	-4.06182436	0.18390001
C	4.22825530	-3.61250033	-0.11427802
C	7.35237452	-5.82352350	-2.22573918
C	8.04723658	-6.63740356	-3.11966925
C	8.49515861	-6.11923955	-4.34064734
C	8.24612658	-4.78189644	-4.65141036
C	7.54978255	-3.96308237	-3.75381730
C	-3.99498630	1.38927109	2.65631620
C	-2.49250219	1.36627408	2.96849922
C	-2.16908717	1.17878906	4.45791033
C	-2.58314220	-0.15419603	5.00288237
C	-1.81826715	-0.96126010	5.74718746
C	-0.39594704	-0.69106508	6.13621248
C	0.42886702	-1.98176919	6.27927947
C	1.93565414	-1.73221417	6.12055243
C	2.35224817	-1.60975217	4.64805835
H	-0.70212305	0.47203201	1.15054108
H	3.61363828	2.56579515	-0.27143503
H	-4.03694129	4.91076836	-4.09756332
H	-6.19168444	4.21593731	-3.08884624

H	-6.24443749	2.65970920	-1.16257810
H	-1.51200410	3.88544527	-4.41936334
H	-0.68431104	3.56145224	-2.89174723
H	-0.36111900	5.91442541	-3.83510830
H	-2.06920714	6.25571245	-3.54845928
H	-1.81921011	5.91787040	-1.11221709
H	-0.18878899	5.29425539	-1.29175710
H	-1.05089605	8.18124659	-2.00620116
H	-0.28404599	7.68497956	-0.49509404
H	1.63565815	6.68198145	-2.07919117
H	0.93849811	7.73524055	-3.31727826
H	1.20121214	9.74452069	-1.76974914
H	3.37657130	9.74219369	-0.69136406
H	2.06783918	5.21180036	-2.28233618
H	3.33008527	4.41449329	-1.24924510
H	2.25639818	2.26703713	-2.81283822
H	2.27468919	3.56223723	-3.98472931
H	4.60026236	3.64989222	-4.12569732
H	4.85377838	3.37255120	-2.39849519
H	3.48032928	4.52257730	4.54190534
H	2.58456721	3.20140820	6.43487748
H	2.66684820	0.71559201	6.38732947
H	5.59628743	4.00928225	2.58543119
H	4.84295138	2.98767517	1.36815010
H	2.69656722	4.40027529	1.56079311
H	3.51408929	5.43957535	2.72780120
H	5.29775944	5.97584542	0.96197406
H	4.38802635	5.00596133	-0.20750802
H	2.32324320	6.50352843	0.27283501
H	3.35462029	7.51750052	1.28065109
H	1.05837906	-2.83819725	1.60159011
H	0.07135499	-1.79214217	0.50758103
H	-0.02455901	-1.61381816	3.60870927
H	-1.09712309	-0.74349009	2.50671218
H	-1.00526010	-3.84786532	2.65695320
H	-2.09248918	-2.84768424	3.63725827
H	-4.01648232	-1.18092010	1.98701214
H	4.14615431	0.38537798	-1.66909313
H	-5.56799942	-0.79796407	-0.14337702
H	-5.24864341	-1.79767514	-1.60125913
H	4.04500029	-2.33093923	-2.64110421
H	5.25672938	-2.63795026	-3.92658731
H	-6.35861949	-3.79594829	-0.53631705
H	-6.64550653	-2.89497022	0.95695207
H	-10.63882580	-1.83585913	-0.39570704

H	-12.43191497	-3.47226824	0.06898800
H	-11.88655892	-5.88392141	0.36188002
H	-9.52400079	-6.64656452	0.16399501
H	-7.72575061	-5.02744838	-0.31095003
H	-8.94717070	-1.88848914	1.83636513
H	-9.24999169	0.23929703	3.05850322
H	-8.64655865	2.40318319	1.98213615
H	-7.71747761	2.41266218	-0.33506203
H	-7.44110156	0.29944802	-1.57413713
H	-6.37686351	-3.59194828	-2.56500620
H	-6.50494049	-3.43212527	-5.01799639
H	-8.20665662	-1.97097515	-6.10121746
H	-9.79783874	-0.67693104	-4.68887436
H	-9.67601976	-0.81814005	-2.22469017
H	7.08362354	-1.72161420	-2.33129619
H	5.85781545	-1.53602318	-1.07050009
H	6.15332745	-5.13681445	0.81951206
H	7.67272355	-5.13236246	2.76213820
H	9.66006173	-3.63346936	2.80494521
H	10.12293677	-2.14473524	0.86395306
H	8.61632464	-2.14444324	-1.09340309
H	4.86571434	-5.60381948	-2.81572522
H	2.59692816	-6.39456052	-2.27018318
H	1.34343607	-5.41546847	-0.35534003
H	2.39078816	-3.61697832	1.01712307
H	4.67358134	-2.80816527	0.48023203
H	7.01499650	-6.23522456	-1.27390010
H	8.24503557	-7.67731464	-2.86532922
H	9.03635464	-6.75401660	-5.03848839
H	8.59514464	-4.36656041	-5.59598141
H	7.38491056	-2.91985429	-4.02527531
H	-4.54885534	1.80403512	3.52264126
H	-4.37210534	0.35156401	2.53283919
H	-1.99240215	0.56063302	2.37886118
H	-2.02950715	2.31935615	2.62771419
H	-1.07926708	1.34526007	4.60720235
H	-2.66547620	1.97534113	5.05391938
H	-3.61152628	-0.43448305	4.76773836
H	-2.22441918	-1.89806517	6.13431745
H	0.08585600	-0.01019903	5.39931538
H	-0.38205203	-0.12956704	7.09420354
H	0.23121300	-2.43750522	7.26878054
H	0.09567099	-2.73536124	5.53870739
H	2.22357316	-0.81432611	6.67948648
H	2.50144518	-2.55457824	6.59867752

H	1.55713311	-1.09017612	4.06411230
H	2.42268717	-2.62179724	4.20247632
H	4.42039433	-1.17694315	5.21218239
H	4.13672831	-1.22822215	3.47514826
C	3.82905733	7.60940951	-0.83895207
H	4.88402041	7.92965355	-0.72041506
H	3.82317032	6.94855248	-1.72808314
C	-4.32370332	2.23192215	1.41660510
H	-5.37311539	2.58114219	1.47175010
H	-3.70342027	3.15771322	1.41699710
C	-4.10839531	1.47838910	0.09498700
H	-4.90741337	0.71312805	-0.04268001
H	-3.15549524	0.90906805	0.12800500

Compound 6

E(PM6// wB97XD/6-31G(d): -4499.24639768 a.u.

C	1.33392012	1.99442517	-0.33466204
C	0.24827402	2.87382922	-0.43304404
C	-0.55180604	3.15755924	0.69745504
C	-0.25796101	2.54898919	1.91471013
C	0.79847108	1.62192013	2.00046914
C	1.60906015	1.35486013	0.88087006
C	2.78414525	0.43940907	0.88475006
C	-1.73424614	4.06400429	0.60248104
O	3.90041633	0.69630510	0.49397103
O	-2.80560222	3.84904326	0.09738100
O	2.42777524	-0.80764103	1.35176509
C	3.29683831	-1.90156610	1.10616407
C	2.81417929	-2.83517518	0.16514700
C	3.60137236	-3.96413226	-0.09345702
C	4.80798746	-4.15709625	0.58678704
C	5.23770448	-3.23978418	1.54556811
C	4.48679441	-2.08422910	1.82586813
C	4.95986443	-1.12882902	2.88027821
C	4.43711140	-1.51933506	4.27268331
C	2.94355128	-1.21524805	4.42072933
C	2.42270324	-1.45279308	5.84243841
C	2.13457124	-2.93487219	6.14373347
C	0.67064213	-3.25144424	6.05163848
C	-6.27449851	7.31074351	-1.80269215
C	1.47710919	-2.64834118	-0.48994805
O	1.13246111	0.99821409	3.17923623
C	0.03007404	0.53027904	4.02376429
C	-0.75050901	-0.58230405	3.33972424
C	-2.10958112	-0.12143103	2.79613320

C	-2.88984016	-1.26252413	2.25788316
O	-1.42294313	5.22704539	1.27988909
C	-2.37615922	6.26322344	1.40923210
C	-2.27704923	7.36305352	0.53758303
C	-3.08527030	8.47733264	0.81448105
C	-3.94165036	8.48369361	1.91776414
C	-4.03260636	7.36890051	2.75313620
C	-3.27251728	6.21809245	2.49310418
C	-1.32168215	7.40799157	-0.61950206
C	-1.58763316	6.38675145	-1.73868714
C	-3.05648527	6.04530840	-1.99862016
C	-3.87324235	7.19904350	-2.58804321
C	-3.42009828	4.99885334	3.35715425
O	-0.10678501	3.54983827	-1.57576013
C	0.24512002	2.96293423	-2.86633323
C	1.59007212	3.51932329	-3.32768827
C	2.22406418	2.63801423	-4.41390635
C	2.87176924	1.42726815	-3.85065830
C	4.23666335	1.12791614	-3.71424829
N	4.26926337	-0.14083296	-3.12418325
N	2.99391627	-0.57491500	-2.91200823
N	2.15477620	0.32908705	-3.33881627
C	-3.11974718	-1.64260916	0.92648806
N	-3.91654623	-2.79041526	1.01605307
N	-4.16071624	-3.07307528	2.33251717
N	-3.56309821	-2.18981721	3.07835222
C	5.47466345	-0.90924600	-2.73933922
C	-4.48609926	-3.58003233	-0.09514402
C	5.97627649	-0.51109196	-1.34440711
C	7.52724463	-0.46311294	-1.24208310
C	7.97101362	-0.06126690	0.17215800
C	7.99329670	-1.87806704	-1.59945613
C	8.13322963	0.63153215	-2.12658317
C	9.26281477	-0.39600591	0.61531903
C	9.70703478	0.00678712	1.87572313
C	8.87198869	0.75880117	2.70922019
C	7.59173461	1.10387918	2.27077416
C	7.14273656	0.69726414	1.00992107
C	7.97462267	-2.87952112	-0.61376106
C	8.34080173	-4.19060521	-0.92400408
C	8.72136474	-4.52575424	-2.22744218
C	8.72458176	-3.54055816	-3.21787226
C	8.35752368	-2.22721907	-2.90852823
C	7.39593559	1.78288423	-2.44182020
C	7.95964160	2.79989231	-3.21740226

C	9.27461770	2.68834432	-3.67629829
C	10.02864781	1.56029824	-3.33756727
C	9.46638074	0.54423516	-2.56169121
C	-5.87387037	-3.04229630	-0.47759505
C	-6.68055844	-4.03141539	-1.36873012
C	-7.95278950	-3.33225035	-1.87023315
C	-5.73937035	-4.41411141	-2.51476920
C	-7.18991144	-5.25415449	-0.59884706
C	-8.45549857	-3.57888537	-3.15713625
C	-9.63072668	-2.95879034	-3.59028028
C	-10.32559271	-2.09277928	-2.74136222
C	-9.84272070	-1.85915426	-1.45049712
C	-8.66846860	-2.47880329	-1.01534809
C	-5.10128528	-5.66119848	-2.55985821
C	-4.20235521	-5.96061348	-3.58910928
C	-3.92119520	-5.01514043	-4.57776536
C	-4.54250426	-3.76231234	-4.53114836
C	-5.44062534	-3.46187333	-3.50606428
C	-7.84864747	-6.27428059	-1.31125311
C	-8.35362952	-7.39308968	-0.64886006
C	-8.21450750	-7.51109668	0.73888704
C	-7.57344948	-6.49818157	1.45386610
C	-7.06756746	-5.37363050	0.79103805
C	0.33665010	-2.79057121	0.53233303
C	0.24182711	-4.20541731	1.12143508
C	-0.37137494	-4.21645633	2.52792319
C	0.66026014	-3.88487829	3.61635127
C	0.02695609	-3.67062728	4.95682337
C	-6.55773656	6.73262546	-0.63004306
C	-5.96453447	5.45467934	-0.12262002
C	-6.25361749	5.22898132	1.36896010
C	-5.39659340	4.10009025	1.96495214
C	-4.85075538	4.42789728	3.36346125
H	1.96729617	1.79709617	-1.20532310
H	-0.84027506	2.78897621	2.80626621
H	3.26789435	-4.69826332	-0.82474907
H	5.41292349	-5.03710131	0.37059702
H	6.16122055	-3.41992018	2.09359415
H	4.65213740	-0.09033695	2.63332319
H	6.07045454	-1.09676001	2.89530921
H	5.01286443	-0.96731901	5.04082237
H	4.62880643	-2.59269714	4.46338333
H	2.35316824	-1.82408611	3.69381327
H	2.75304025	-0.16202298	4.12157231
H	3.14421129	-1.05804404	6.58210649

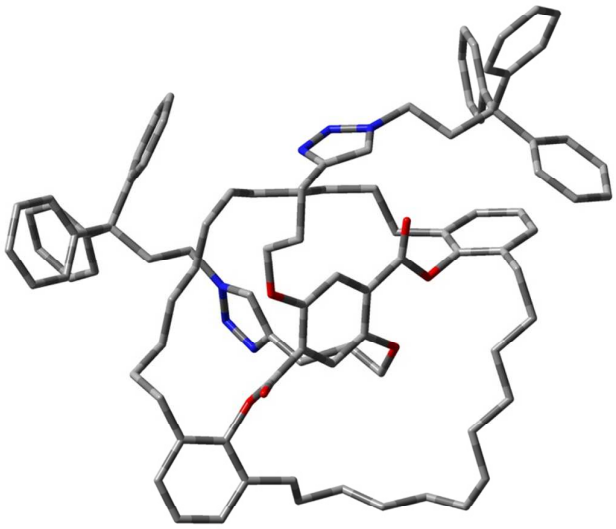
H	1.49591916	-0.85292904	5.98401745
H	2.71992929	-3.58456824	5.46151541
H	2.50035827	-3.18434721	7.16000652
H	0.12574409	-3.11143623	6.98656952
H	-6.74641259	8.25713653	-2.07066217
H	1.43182017	-1.64212911	-0.96495308
H	1.33804819	-3.36470724	-1.32321811
H	0.61437209	0.15474402	4.89735837
H	-0.58123302	1.39296310	4.32919032
H	-0.13070996	-1.02755208	2.51807518
H	-0.90448401	-1.42324712	4.05435530
H	-2.69513217	0.37105000	3.60501427
H	-1.97250912	0.64351503	2.00239614
H	-3.04403631	9.34752869	0.16127400
H	-4.54821843	9.36462869	2.12425215
H	-4.70669441	7.38449452	3.60785727
H	-1.31713616	8.42688564	-1.05972309
H	-0.29113607	7.24669057	-0.23076103
H	-1.12110513	6.76042848	-2.67088021
H	-1.04903610	5.44245243	-1.49852512
H	-3.10148726	5.16898236	-2.67520922
H	-3.54116330	5.69810442	-1.04918109
H	-3.84179235	8.06649556	-1.90034616
H	-3.41261131	7.54503552	-3.53118728
H	-0.60037205	3.31937325	-3.48575528
H	0.22075703	1.85952615	-2.80491223
H	1.46097610	4.55216437	-3.70778329
H	2.27588117	3.62082631	-2.46082320
H	1.45568812	2.33747220	-5.16168940
H	2.97166123	3.23252729	-4.98169739
H	5.10957641	1.69078619	-3.98575331
H	-2.79172416	-1.20053412	0.00612699
H	5.22870546	-1.99933508	-2.76173922
H	6.25552952	-0.73604998	-3.51770828
H	-3.78929821	-3.54266831	-0.96505408
H	-4.54879725	-4.65202641	0.21911501
H	5.54114944	0.46713511	-1.02863009
H	5.57972350	-1.22311202	-0.58564806
H	9.92794480	-0.97219195	-0.02763301
H	10.70853188	-0.26071989	2.20795716
H	9.22047572	1.07677520	3.68925427
H	6.93730857	1.69697222	2.90844921
H	6.13320649	0.98154615	0.69049004
H	7.66805065	-2.63415310	0.40493102
H	8.32863272	-4.95394927	-0.14762102

H	9.00964981	-5.54660033	-2.46844320
H	9.01263977	-3.79432517	-4.23689633
H	8.36090068	-1.47851000	-3.70090729
H	6.38156250	1.90418623	-2.05803517
H	7.37494255	3.68740938	-3.45317427
H	9.71345672	3.47854639	-4.28148634
H	11.06140786	1.47602225	-3.67268329
H	10.07737879	-0.31573990	-2.28516619
H	-6.45605541	-2.80834429	0.44069102
H	-5.76827538	-2.07605323	-1.01148309
H	-7.93568453	-4.25952842	-3.83211130
H	-10.00649666	-3.15510736	-4.59327136
H	-11.23881781	-1.60850626	-3.08038224
H	-10.38461974	-1.19551821	-0.77811907
H	-8.32075856	-2.30137328	0.00257399
H	-5.29755428	-6.41327053	-1.79417615
H	-3.71980316	-6.93674955	-3.61568529
H	-3.22210614	-5.24920144	-5.37801843
H	-4.32396725	-3.01818028	-5.29588944
H	-5.91787538	-2.48149726	-3.48004128
H	-7.97011249	-6.18888959	-2.39130319
H	-8.86093751	-8.17415673	-1.21272310
H	-8.60763952	-8.38381776	1.25573709
H	-7.46503043	-6.57655659	2.53528318
H	-6.58355538	-4.59564143	1.38523310
H	0.48159710	-2.04087615	1.34934909
H	-0.62147197	-2.51881720	0.05205499
H	-0.35954993	-4.84586737	0.44928602
H	1.24454420	-4.67680734	1.15314608
H	-1.22017701	-3.50615828	2.57811019
H	-0.81240896	-5.21181241	2.73167720
H	1.41007420	-4.70088934	3.68344327
H	1.25237417	-2.97905021	3.32920924
H	-1.04523199	-3.88326931	5.00270537
H	-7.27210161	7.20791045	0.04597299
H	-6.33669652	4.59900828	-0.72040306
H	-4.85278340	5.46434836	-0.28801503
H	-6.06969750	6.17461239	1.91631613
H	-7.32600757	5.00407529	1.51567011
H	-5.99376448	3.17060917	2.01008614
H	-4.55167135	3.86491624	1.28117409
H	-4.85439938	3.50796221	3.98099930
H	-5.53085445	5.13139233	3.88126929
H	-3.12264326	5.25319836	4.39698332
H	-2.71081522	4.20988629	3.03584522

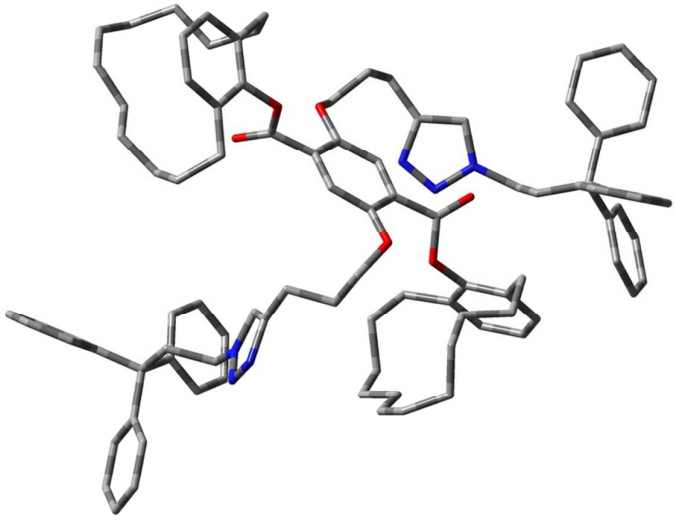
C	-5.33515947	6.78324248	-2.84696423
H	-5.64975047	7.15180247	-3.84363430
H	-5.41668245	5.67876135	-2.91179923

Tube representations of structures **4**, **5** and **6**:

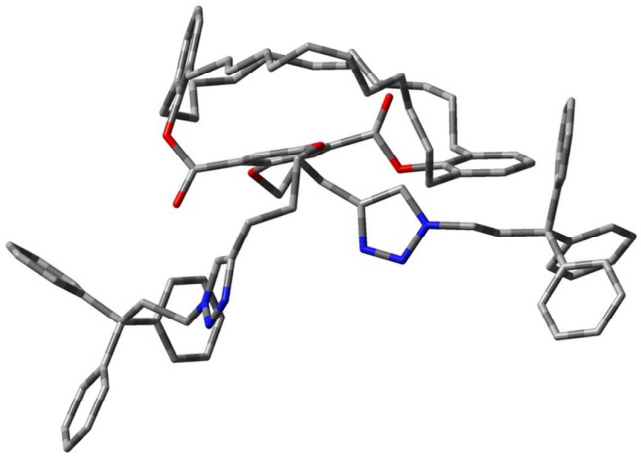
Structure 4

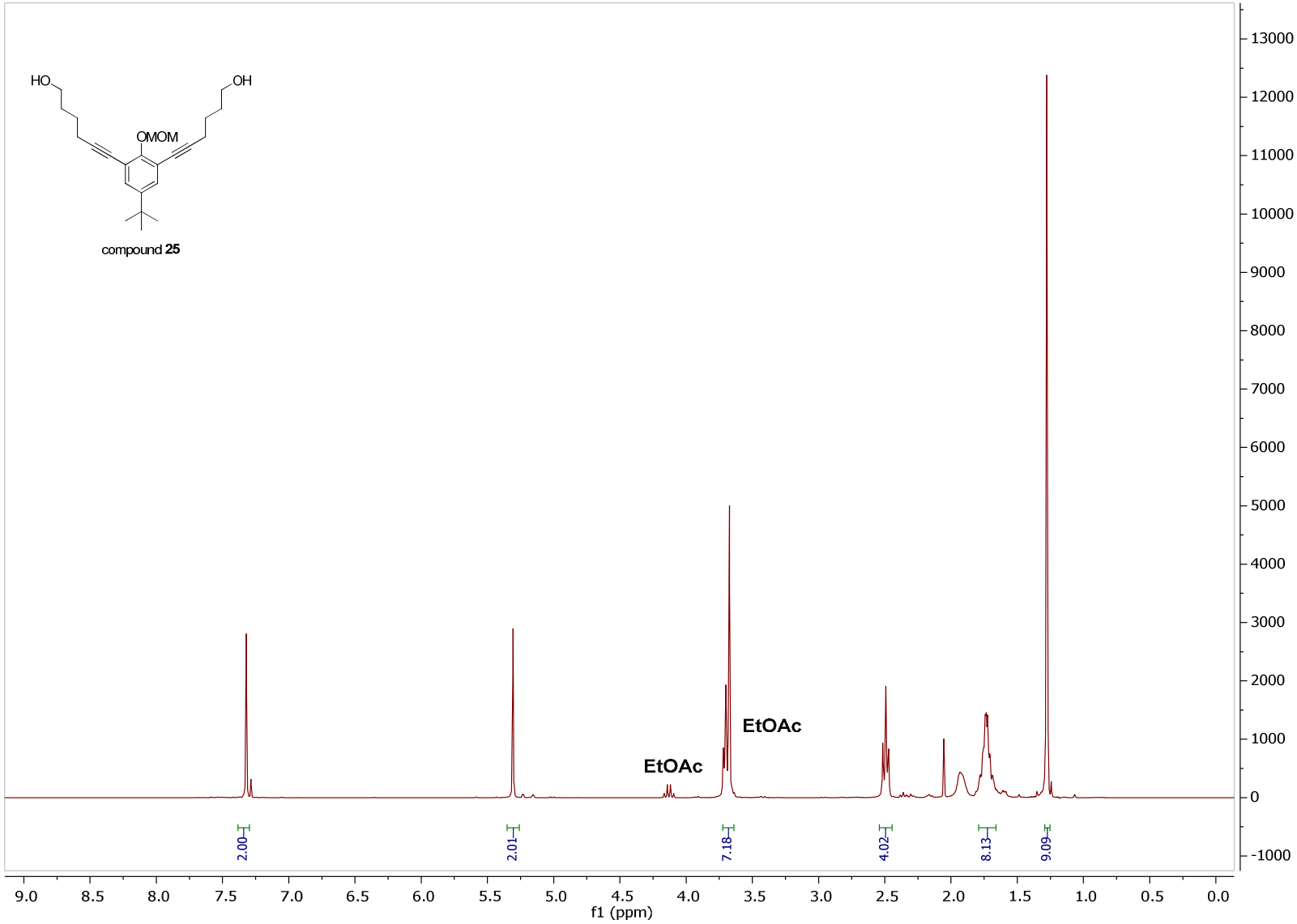


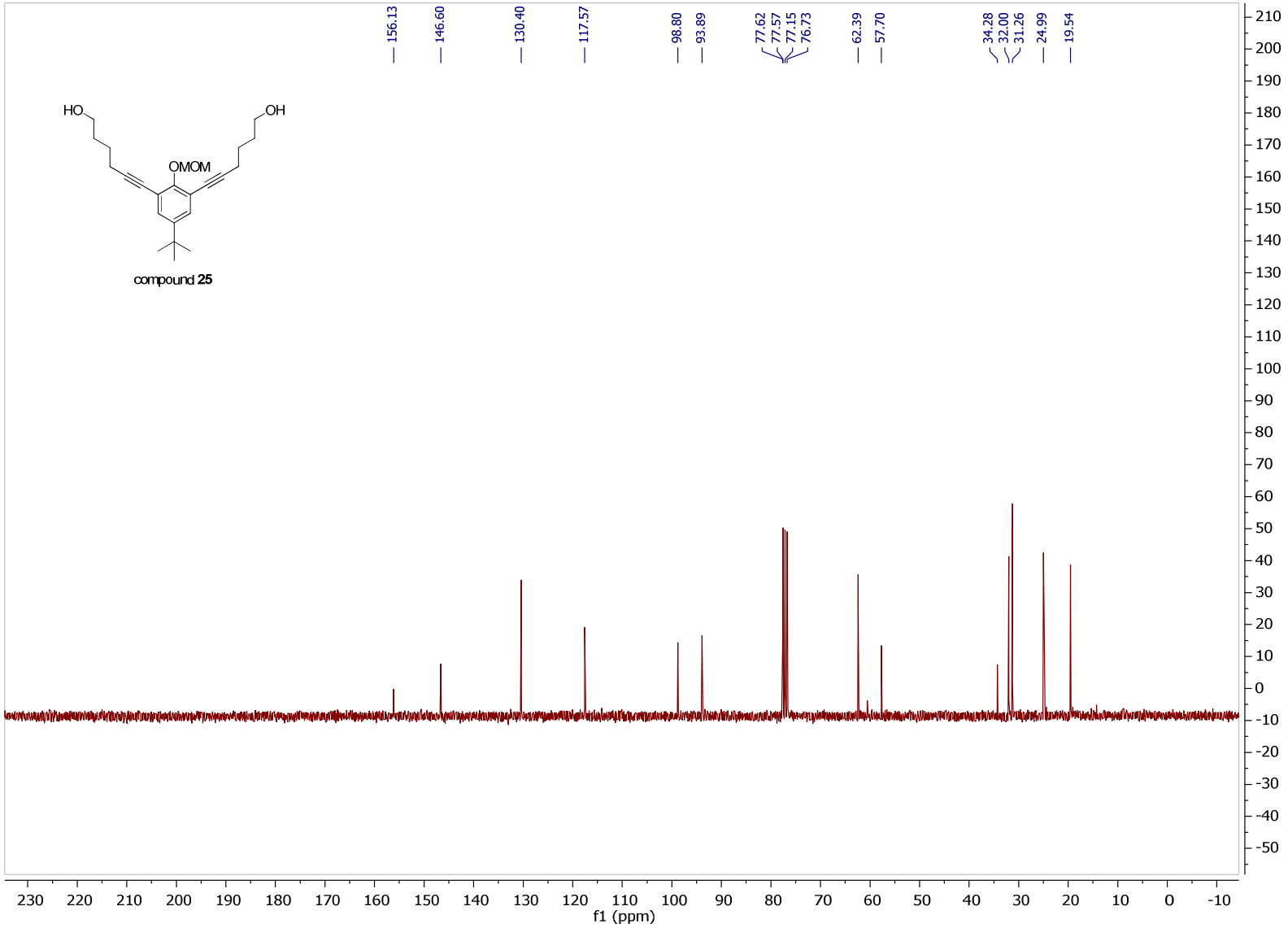
Structure 5

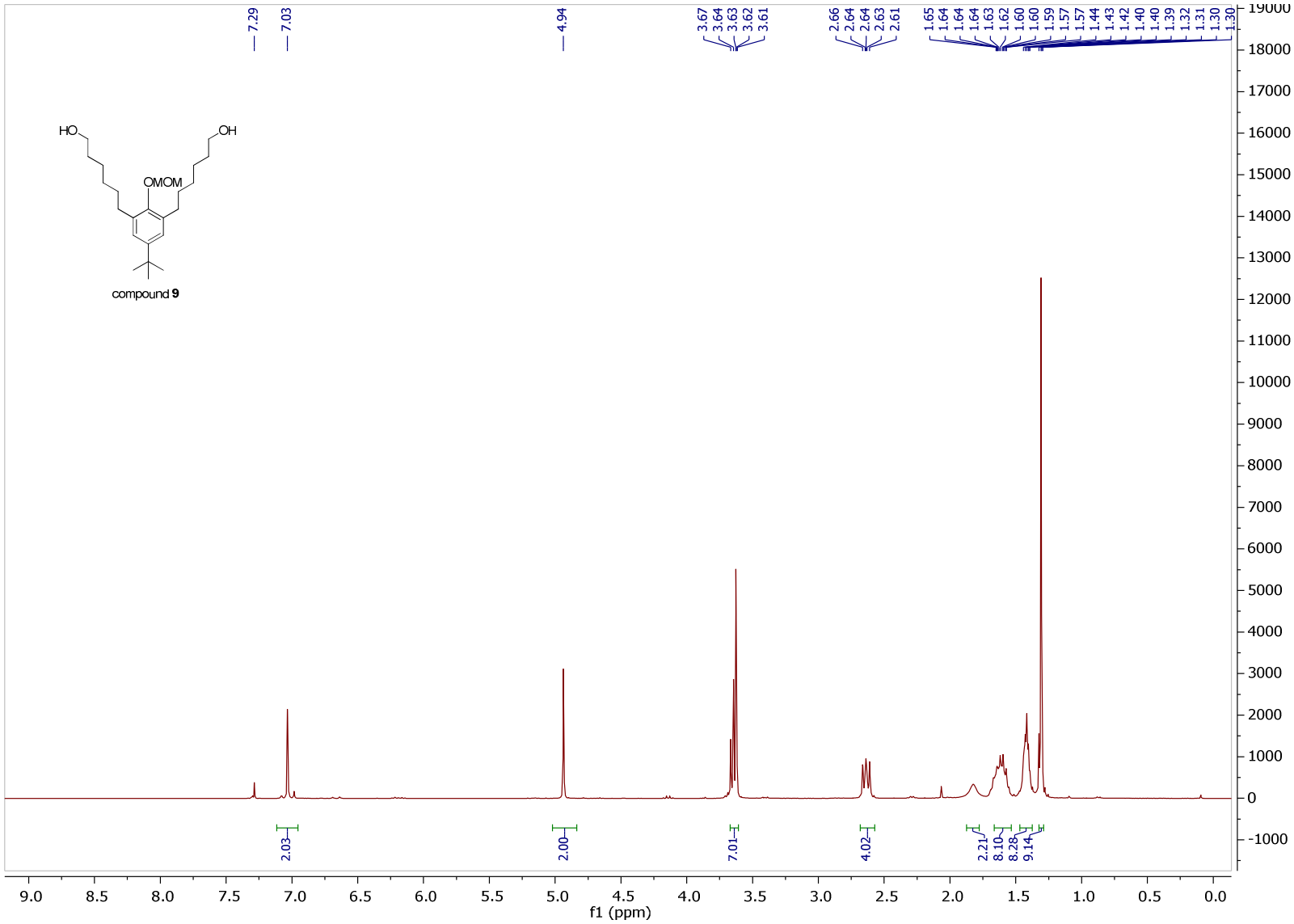


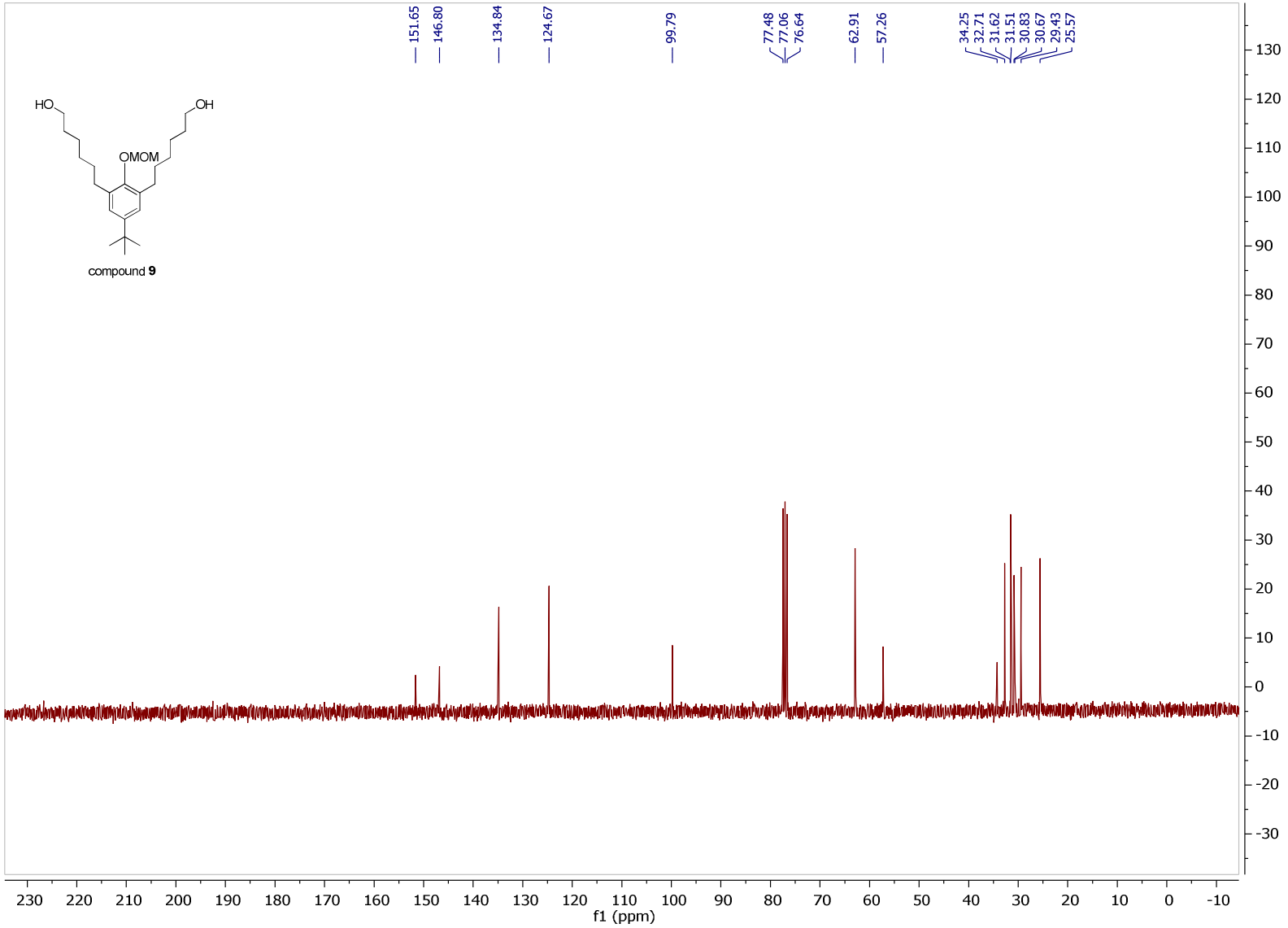
Structure 6

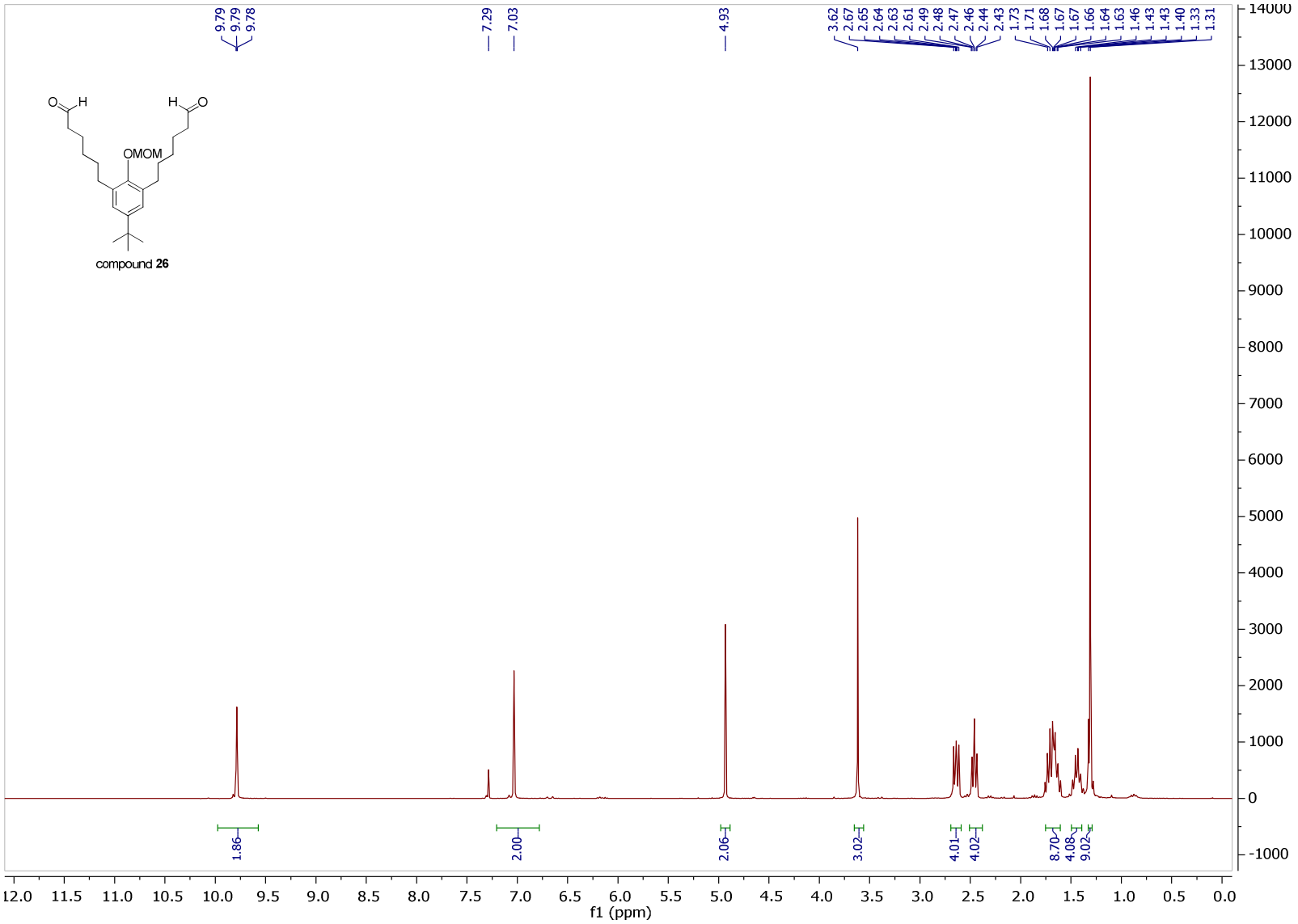


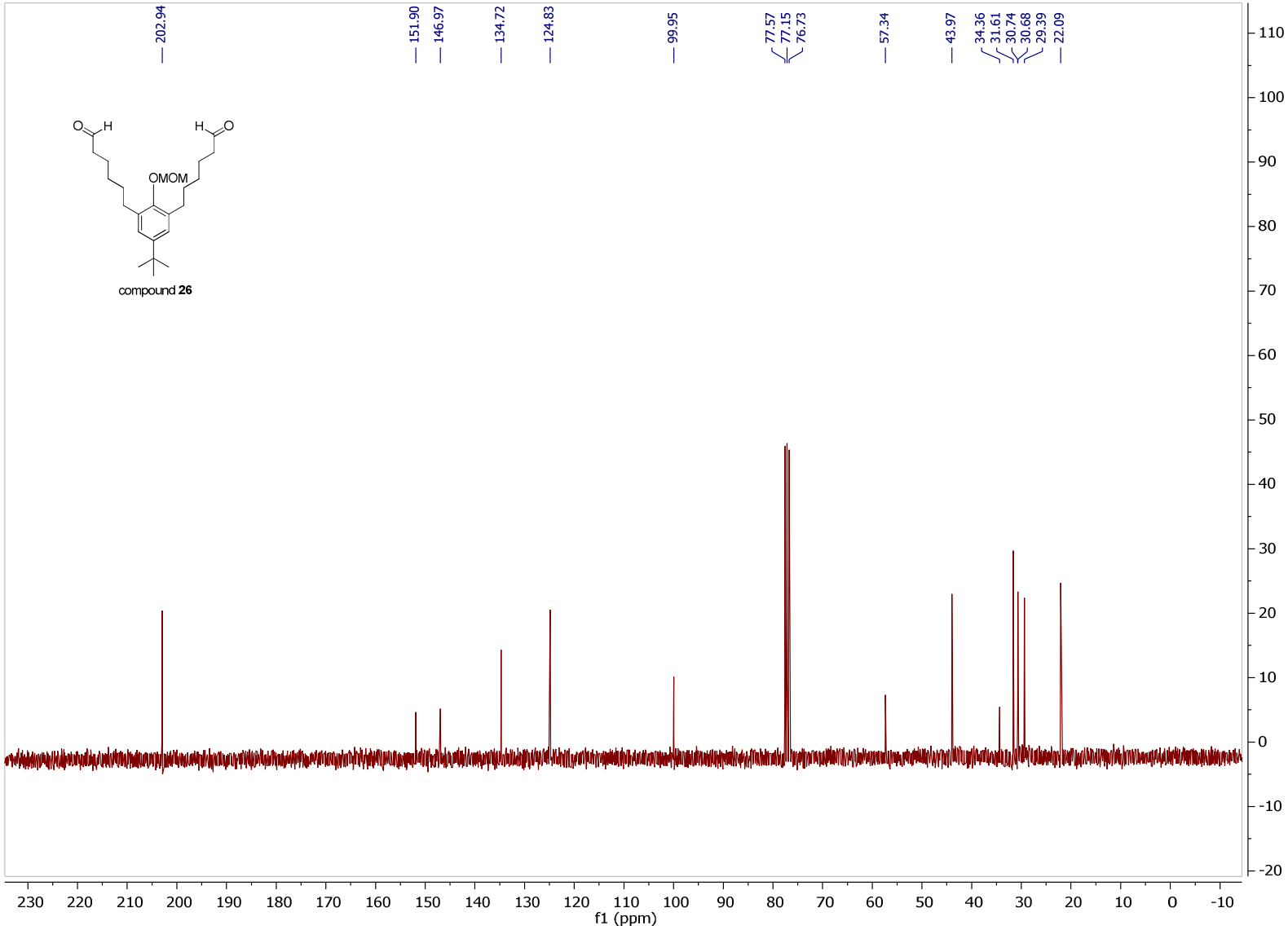

HO
OH
OMOM
compound 25
EtOAc
EtOAc
2.00
2.01
7.18
4.02
8.13
9.09
f1 (ppm)

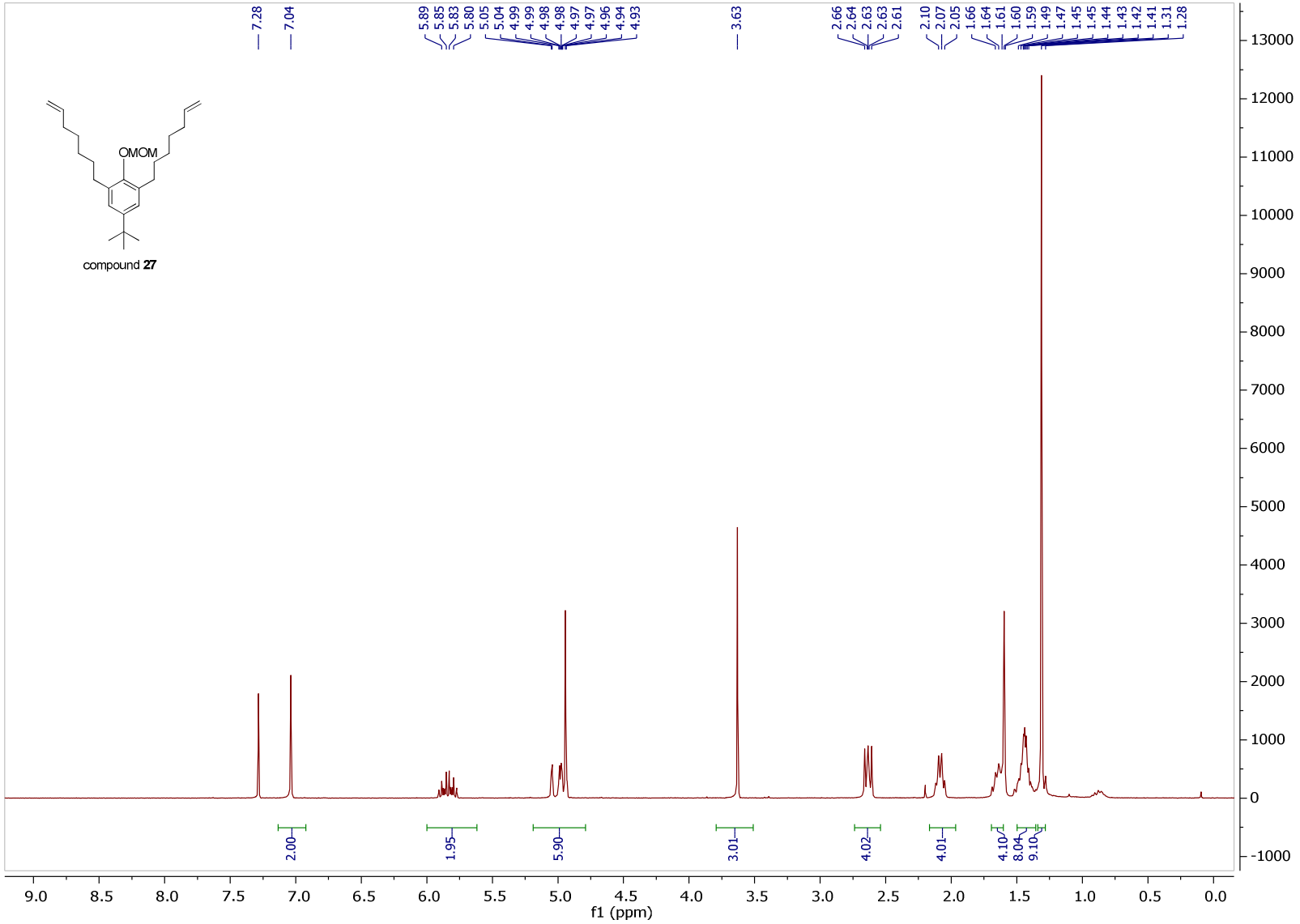

156.13
146.60
130.40
117.57
98.80
93.89
77.62
77.57
77.15
76.73
62.39
57.70
34.28
32.00
31.26
24.99
19.54
HO
OH
OMOM
compound 25
f1 (ppm)

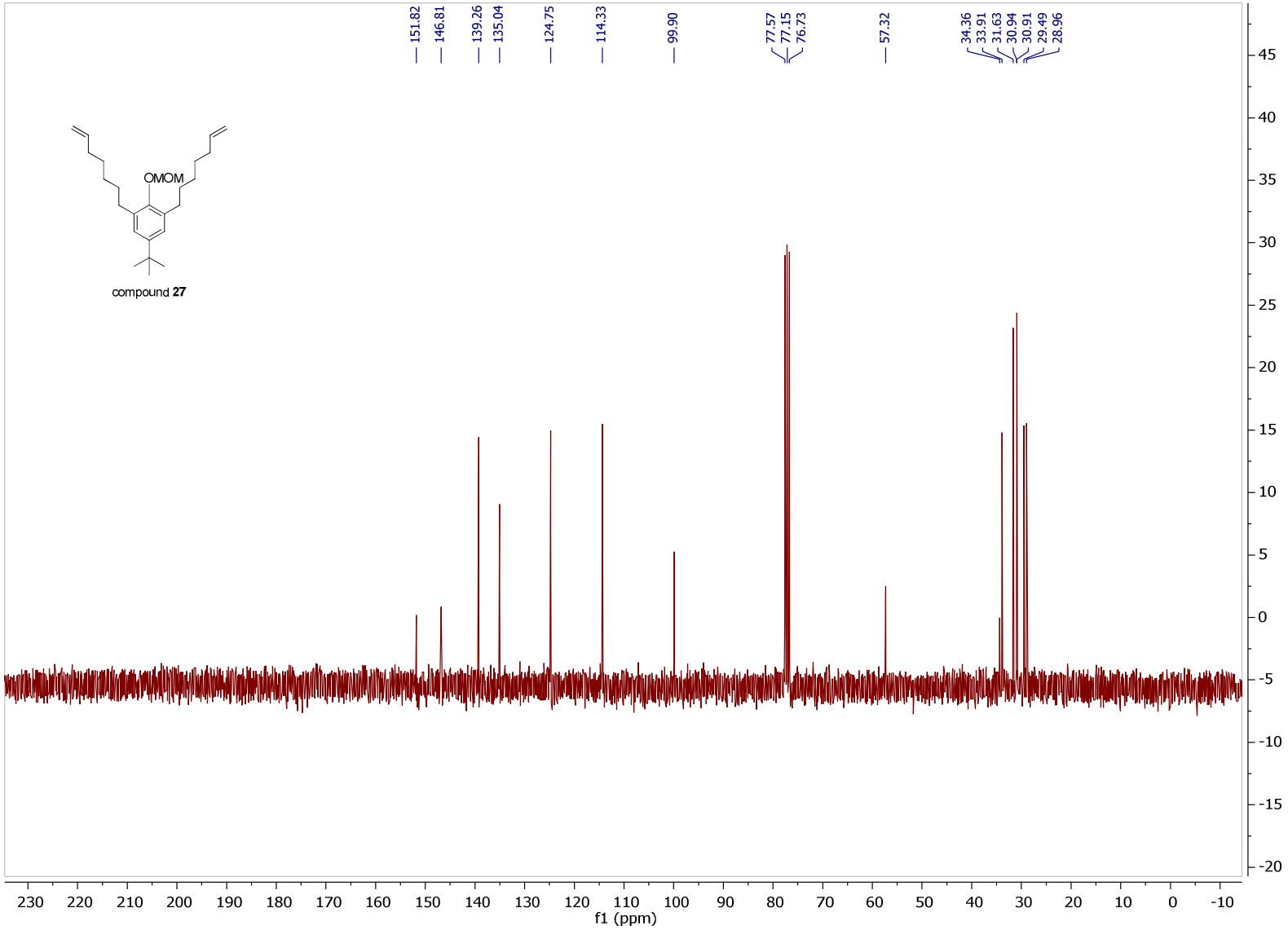

7.29
7.03
4.94
3.67
3.64
3.63
3.62
3.61
2.66
2.64
2.64
2.63
2.61
1.65
1.64
1.64
1.64
1.63
1.62
1.60
1.60
1.59
1.57
1.57
1.44
1.43
1.42
1.40
1.40
1.39
1.32
1.31
1.30
1.30
HO
OH
OMOM
compound 9
2.03
2.00
7.01
4.02
2.21
8.10
8.28
9.14
f1 (ppm)

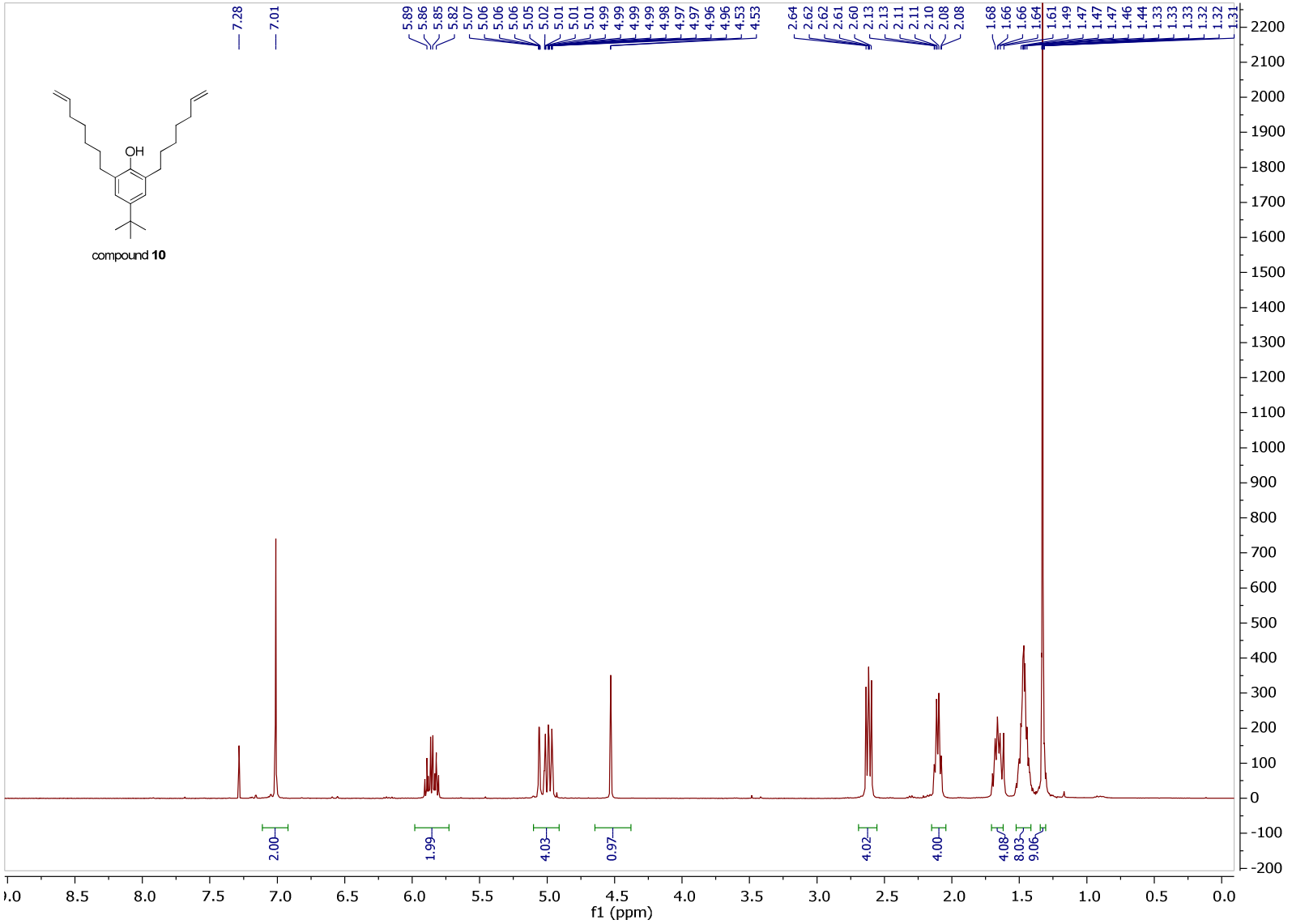

151.65
146.80
134.84
124.67
99.79
77.48
77.06
76.64
62.91
57.26
34.25
32.71
31.62
31.51
30.83
30.67
29.43
25.57
HO
OH
OMOM
compound 9
f1 (ppm)

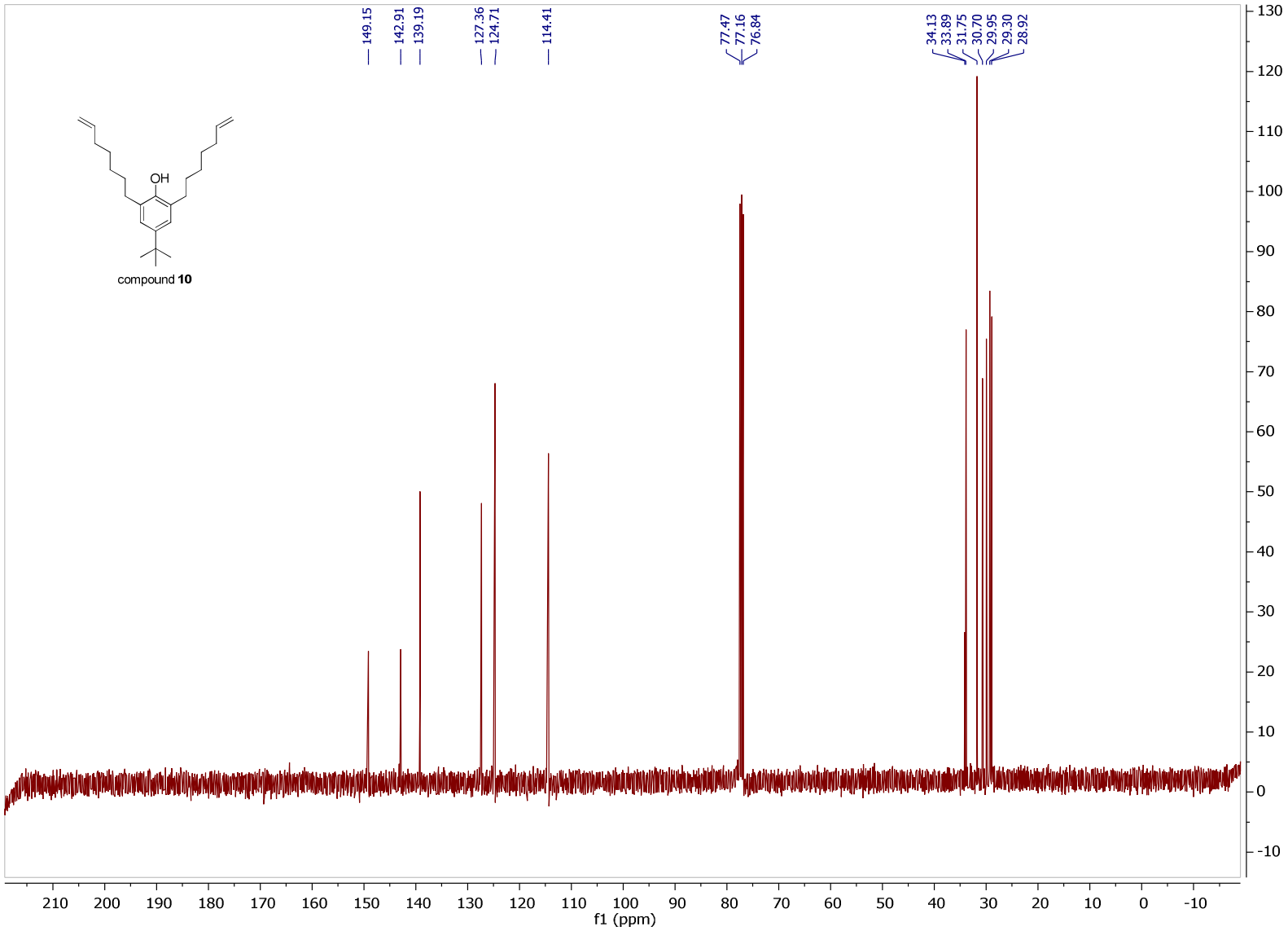

9.79
9.79
9.78
7.29
7.03
4.93
3.62
2.67
2.65
2.64
2.63
2.61
2.49
2.48
2.47
2.46
2.44
2.43
1.73
1.71
1.68
1.67
1.67
1.66
1.64
1.63
1.46
1.43
1.43
1.40
1.33
1.31
O
H
H
O
OMOM
compound 26
1.86
2.00
2.06
3.02
4.01
4.02
8.70
4.08
9.02
f1 (ppm)

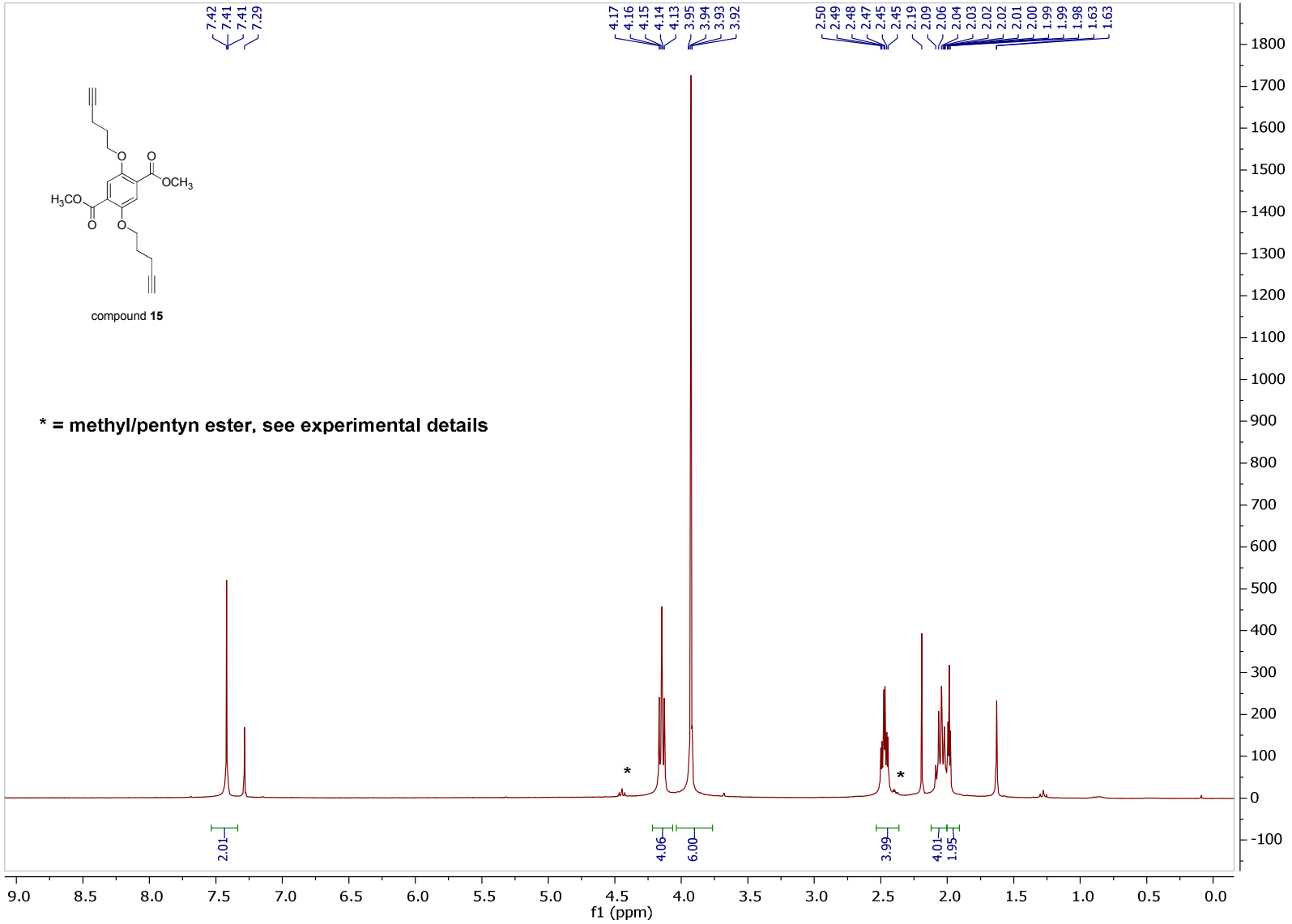

202.94
151.90
146.97
134.72
124.83
99.95
77.57
77.15
76.73
57.34
43.97
34.36
31.61
30.74
30.68
29.39
22.09
OMOM
compound 26
f1 (ppm)

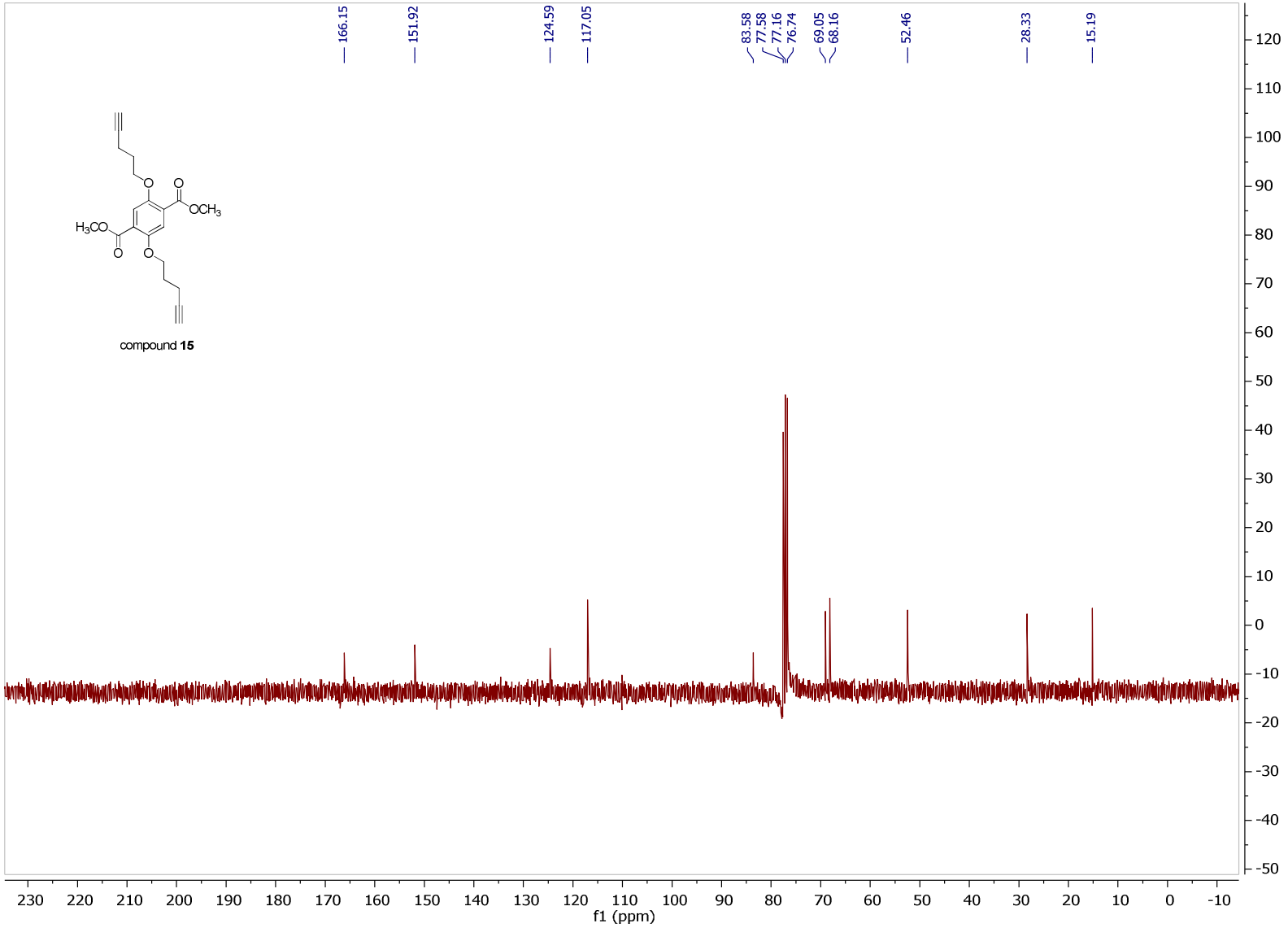

7.28
7.04
5.89
5.85
5.83
5.80
5.05
5.04
4.99
4.99
4.98
4.98
4.97
4.97
4.96
4.94
4.93
3.63
2.66
2.64
2.63
2.63
2.61
2.10
2.07
2.05
1.66
1.64
1.61
1.60
1.59
1.49
1.47
1.45
1.45
1.44
1.43
1.42
1.41
1.31
1.28
OMOM
compound 27
2.00
1.95
5.90
3.01
4.02
4.01
4.10
8.04
9.10
f1 (ppm)

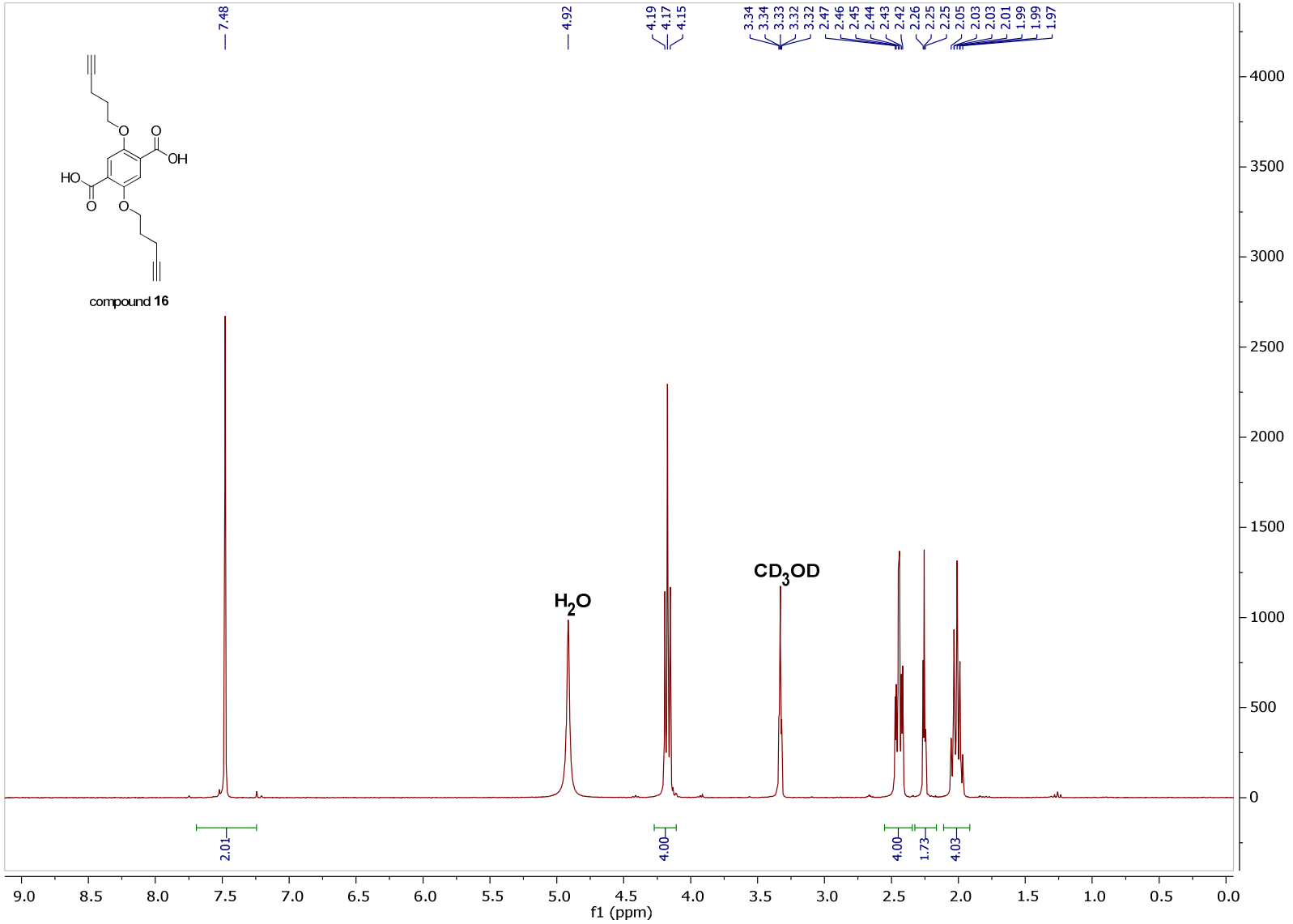

151.82
146.81
139.26
135.04
124.75
114.33
99.90
77.57
77.15
76.73
57.32
34.36
33.91
31.63
30.94
30.91
29.49
28.96
OMOM
compound 27
f1 (ppm)

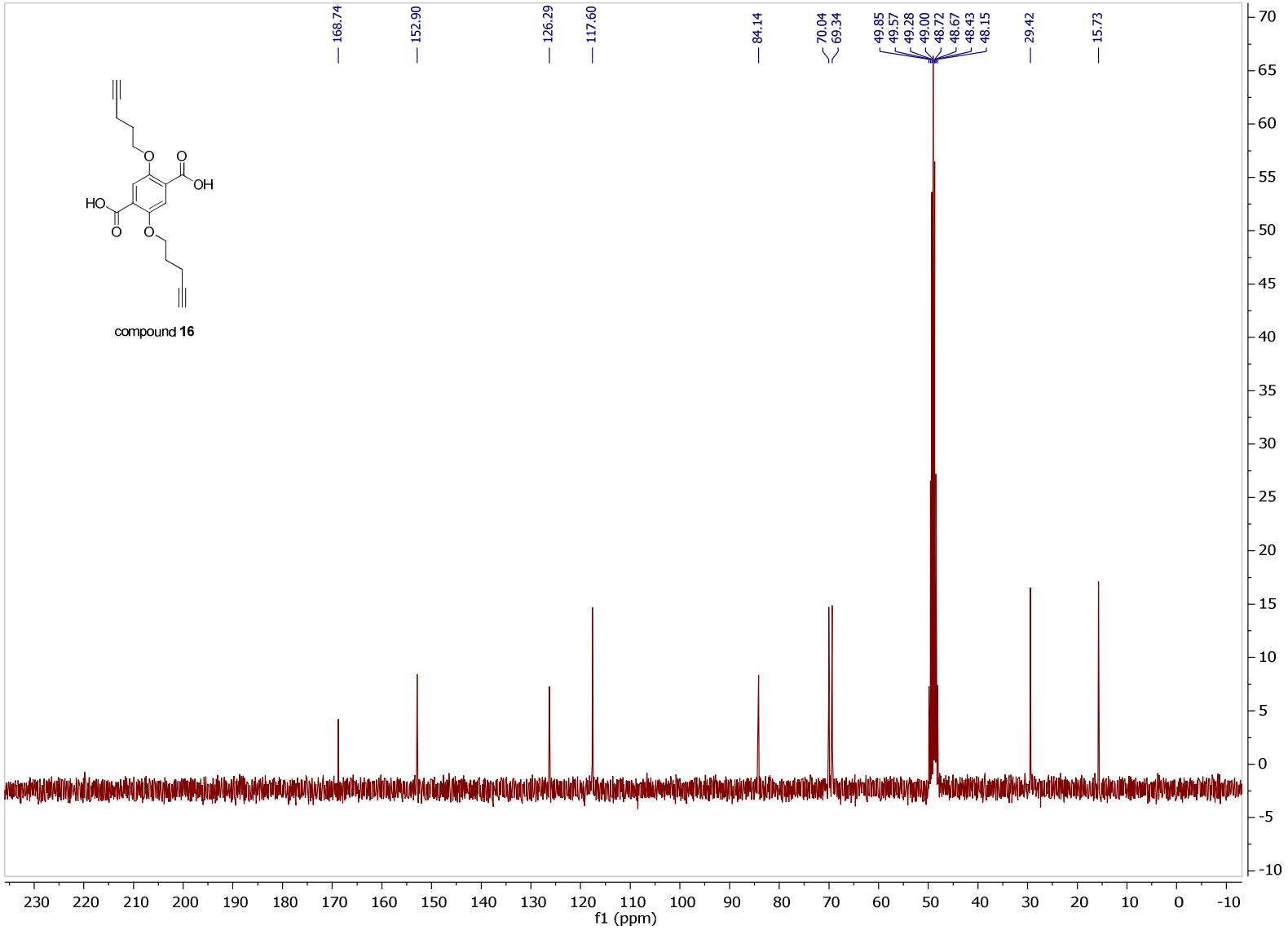

OH
compound 10
7.28
7.01
5.89
5.86
5.85
5.82
5.07
5.06
5.06
5.06
5.05
5.02
5.01
5.01
5.01
4.99
4.99
4.99
4.99
4.98
4.97
4.97
4.96
4.96
4.53
4.53
2.64
2.62
2.62
2.61
2.60
2.13
2.13
2.11
2.11
2.10
2.08
2.08
1.68
1.66
1.66
1.64
1.61
1.49
1.47
1.47
1.47
1.46
1.44
1.33
1.33
1.33
1.32
1.32
1.31
2.00
1.99
4.03
0.97
4.02
4.00
4.08
8.03
9.06
f1 (ppm)

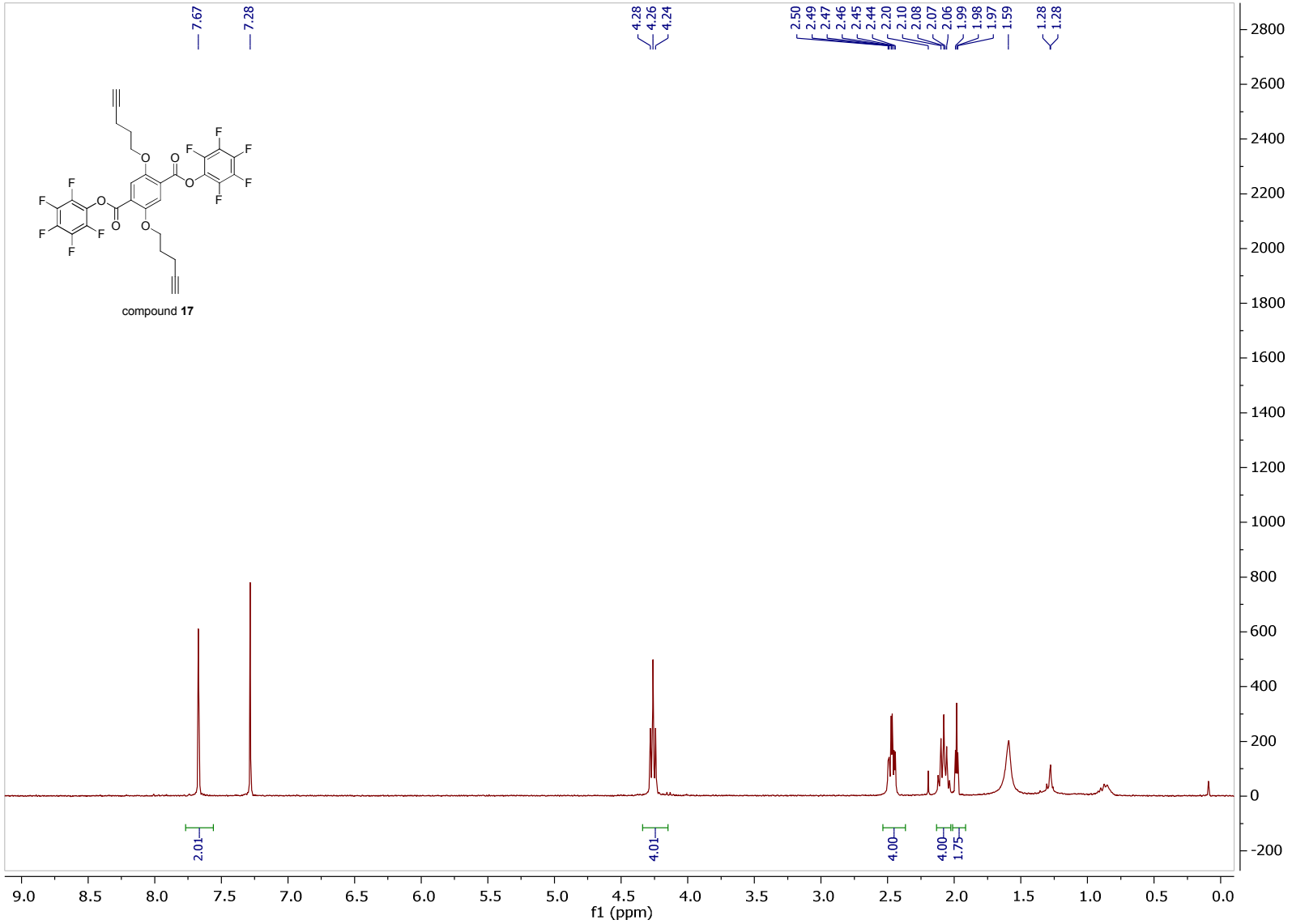

149.15
142.91
139.19
127.36
124.71
114.41
77.47
77.16
76.84
34.13
33.89
31.75
30.70
29.95
29.30
28.92
OH
compound 10
f1 (ppm)

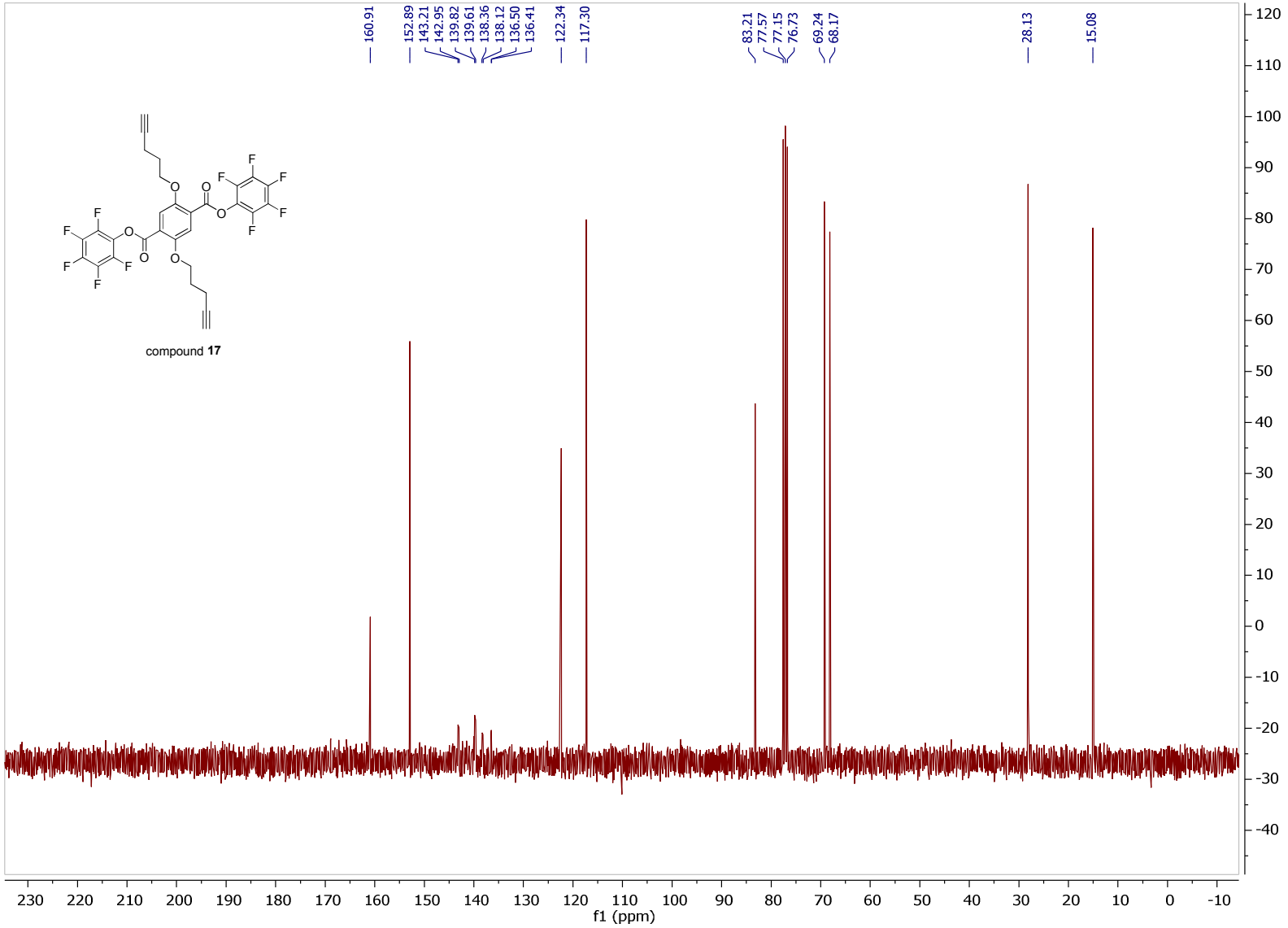

7.42
7.41
7.41
7.29
4.17
4.16
4.15
4.14
4.13
3.95
3.94
3.93
3.92
2.50
2.49
2.48
2.47
2.45
2.45
2.19
2.09
2.06
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.99
1.98
1.63
1.63
H3CO
OCH3
compound 15
* = methyl/pentyn ester, see experimental details
*
*
2.01
4.06
6.00
3.99
4.01
1.95
f1 (ppm)

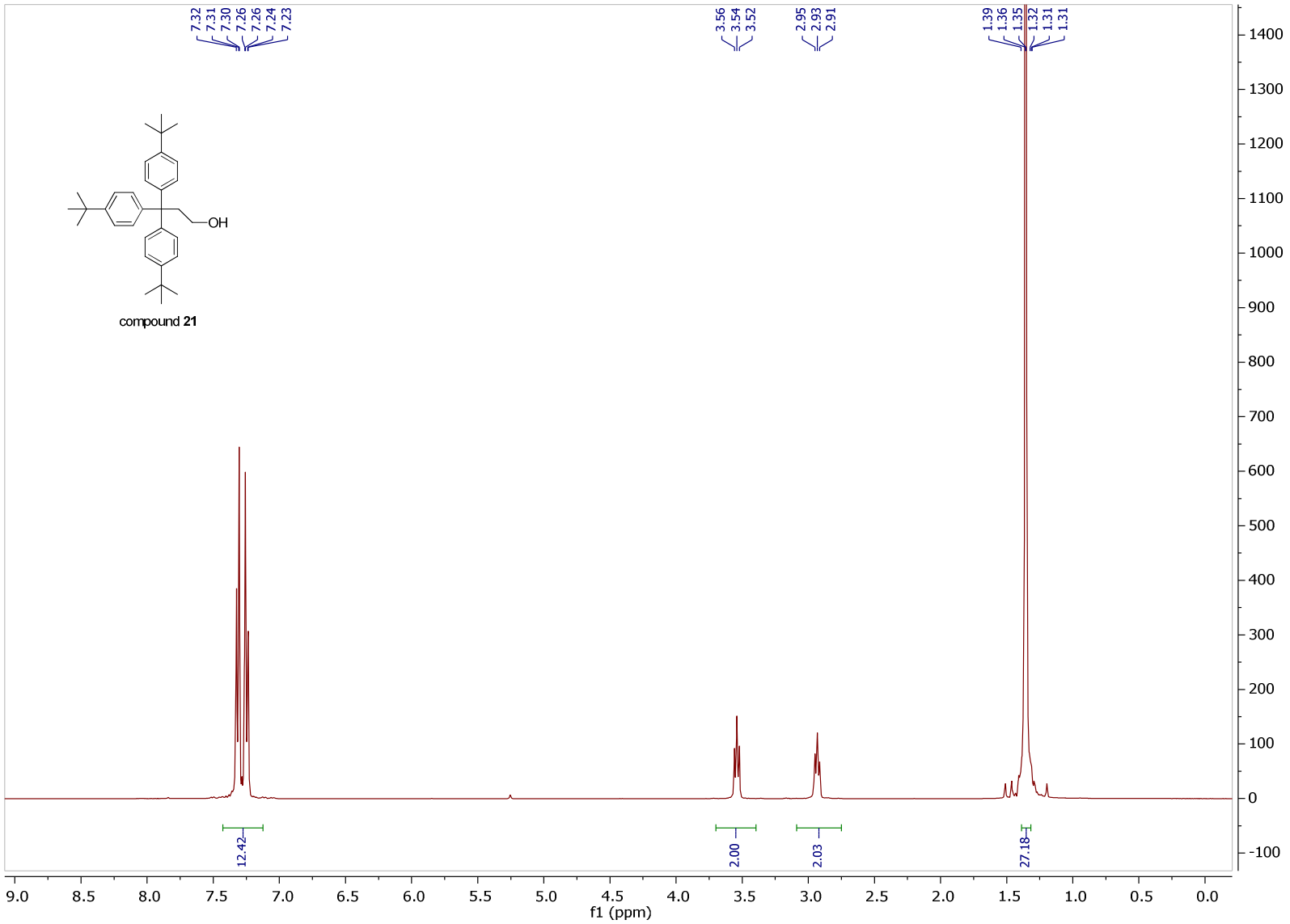

166.15
151.92
124.59
117.05
83.58
77.58
77.16
76.74
69.05
68.16
52.46
28.33
15.19
compound 15
f1 (ppm)

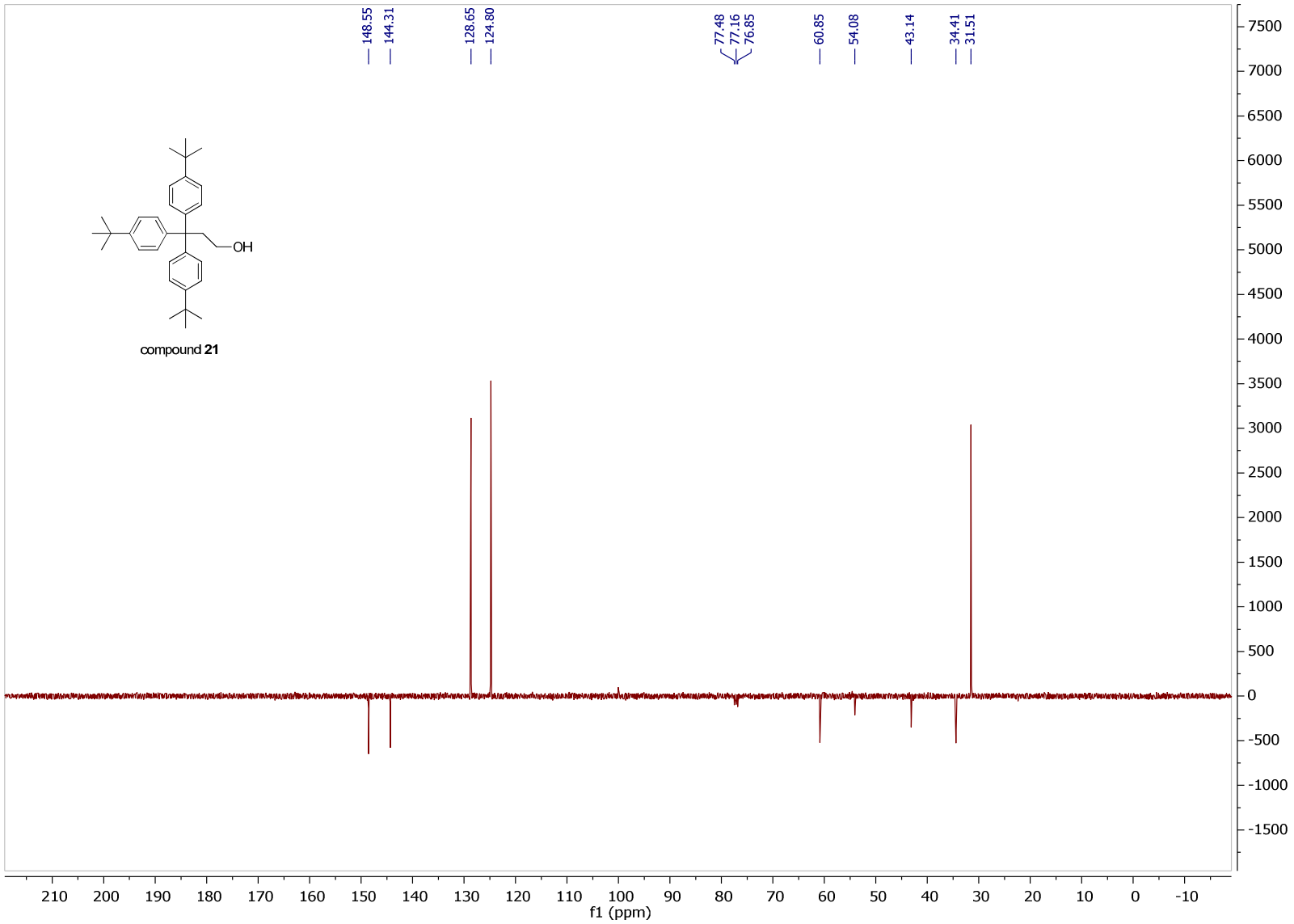

7.48
4.92
4.19
4.17
4.15
3.34
3.34
3.33
3.32
3.32
2.47
2.46
2.45
2.44
2.43
2.42
2.26
2.25
2.25
2.05
2.03
2.03
2.01
1.99
1.99
1.97
HO
O
O
O
OH
O
compound 16
H2O
CD3OD
2.01
4.00
4.00
1.73
4.03
f1 (ppm)

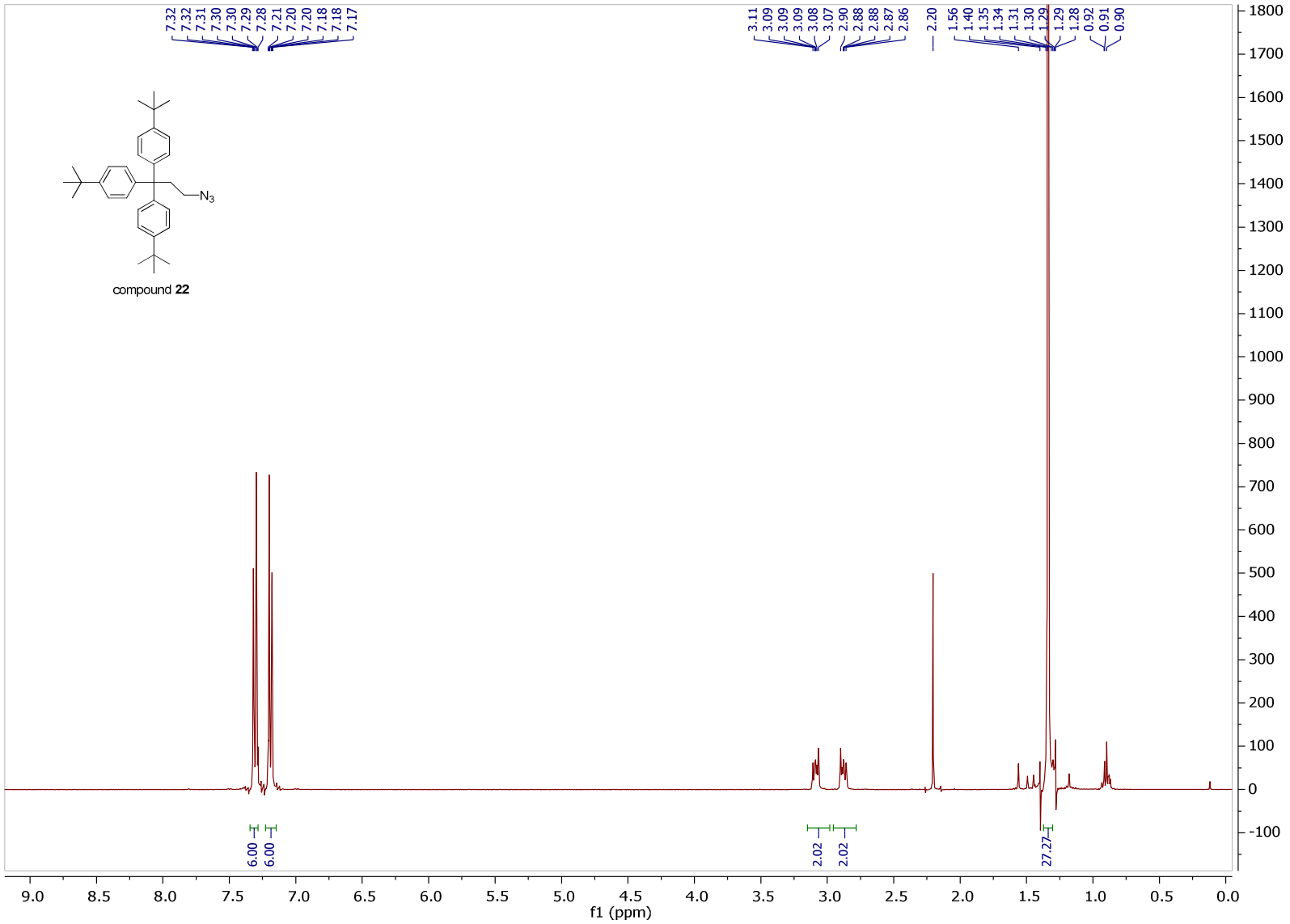

168.74
152.90
126.29
117.60
84.14
70.04
69.34
49.85
49.57
49.28
49.00
48.72
48.67
48.43
48.15
29.42
15.73
HO
O
O
O
OH
O
compound 16
f1 (ppm)

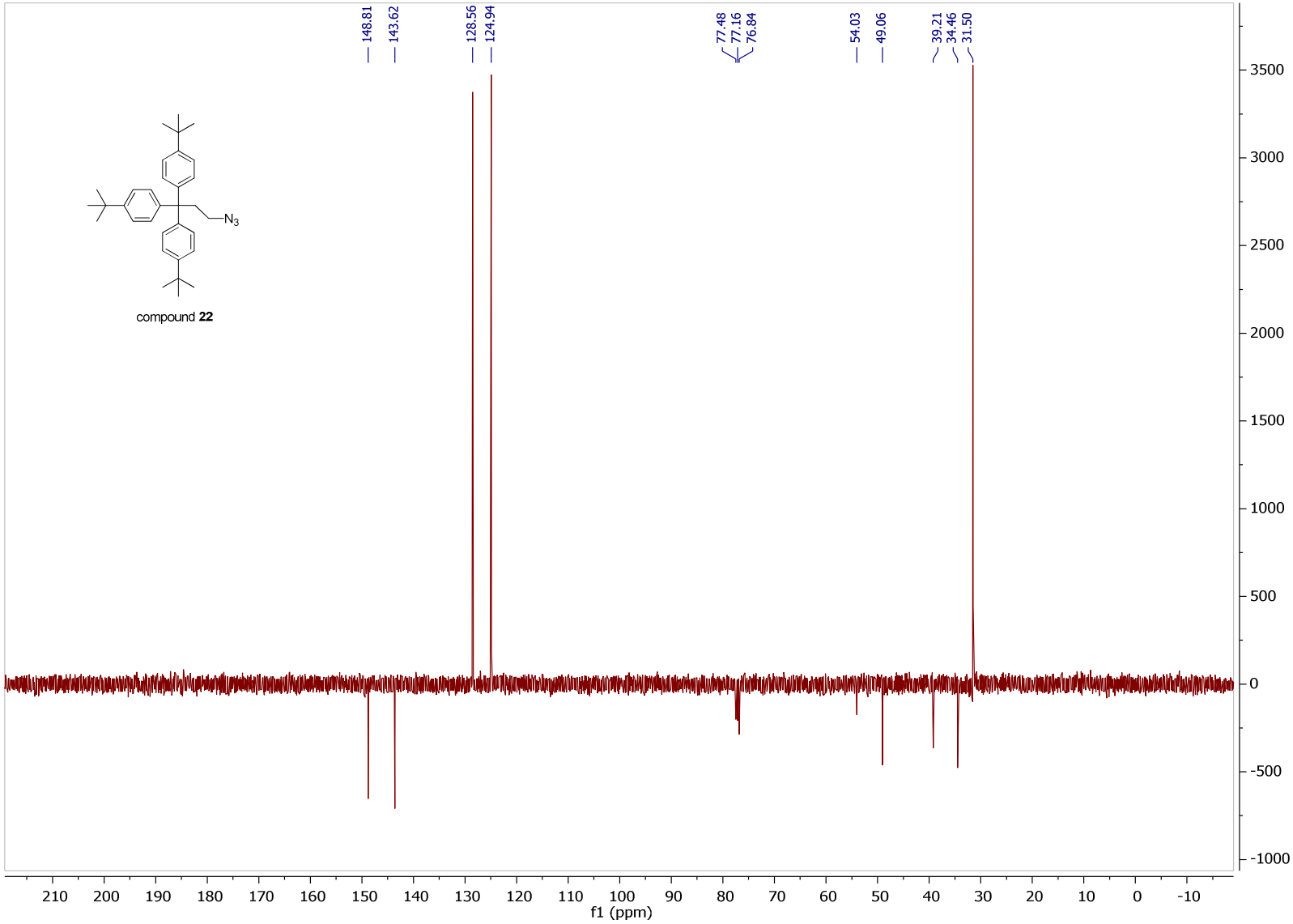

7.67
7.28
4.28
4.26
4.24
2.50
2.49
2.47
2.46
2.45
2.44
2.20
2.10
2.08
2.07
2.06
1.99
1.98
1.97
1.59
1.28
1.28
compound 17
2.01
4.01
4.00
4.00
1.75
f1 (ppm)

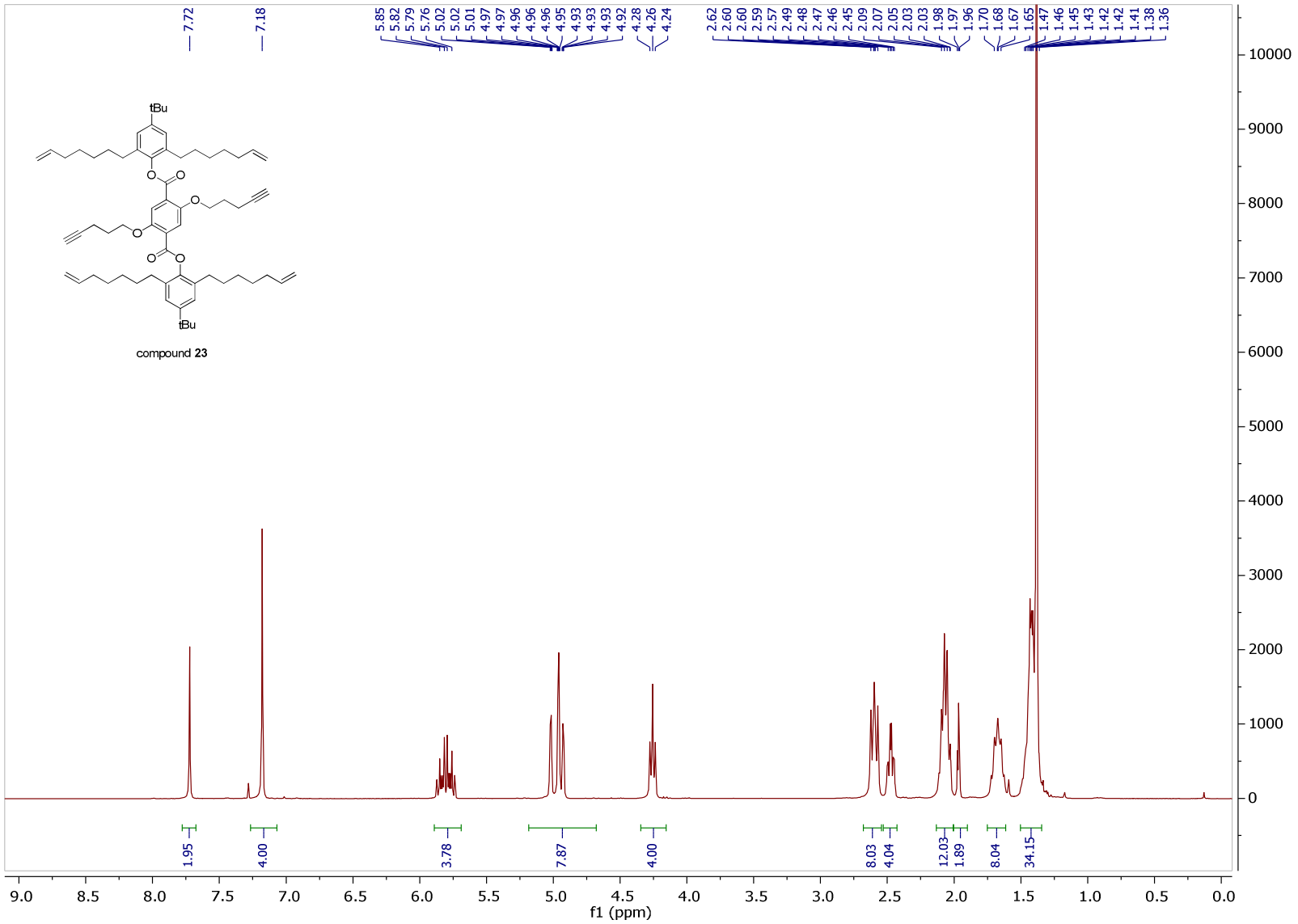

160.91
152.89
143.21
142.95
139.82
139.61
138.36
138.12
136.50
136.41
122.34
117.30
83.21
77.57
77.15
76.73
69.24
68.17
28.13
15.08
compound 17
f1 (ppm)

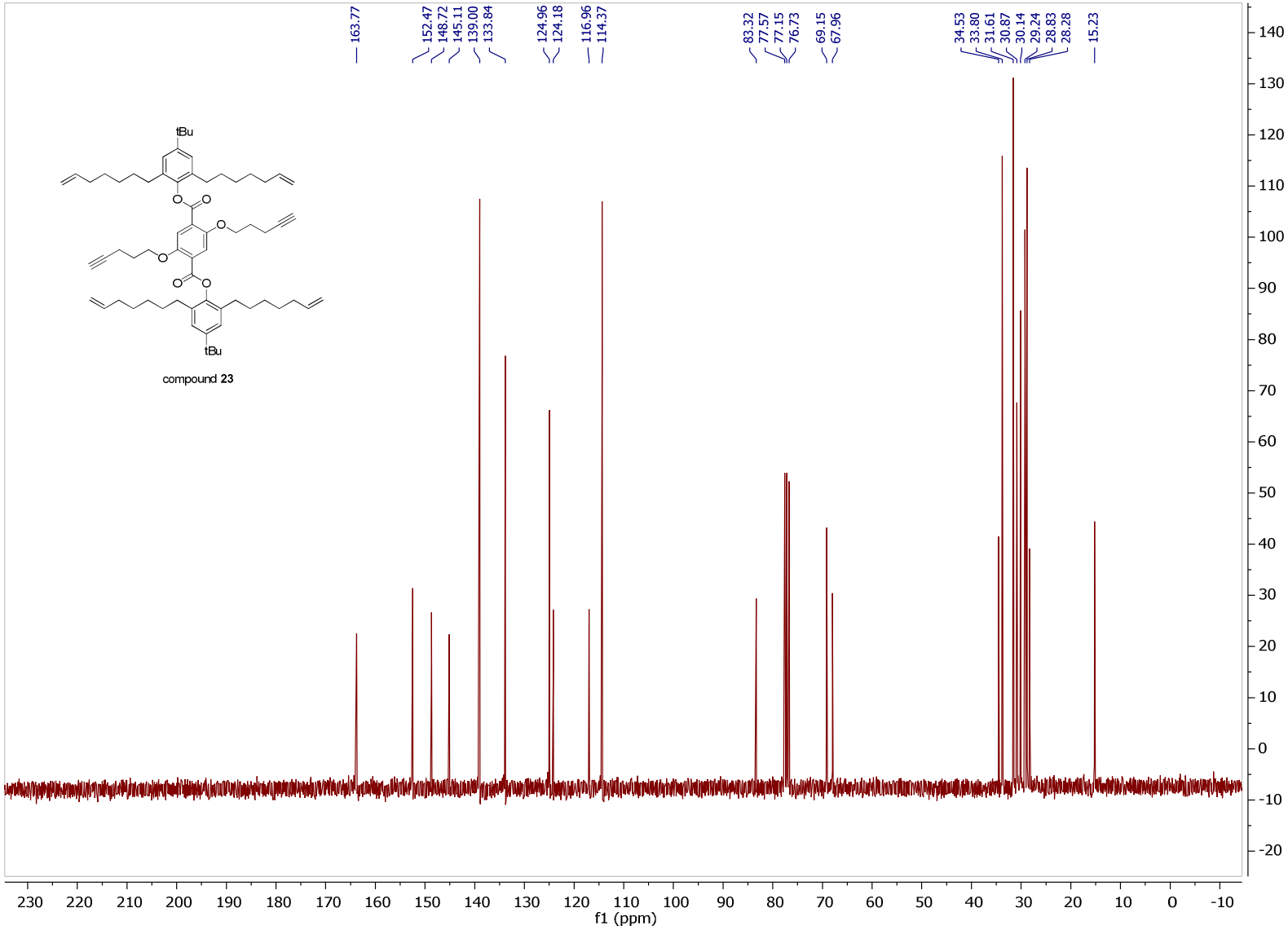

7.32
7.31
7.30
7.26
7.26
7.24
7.23
3.56
3.54
3.52
2.95
2.93
2.91
1.39
1.36
1.35
1.32
1.31
1.31
OH
compound 21
12.42
2.00
2.03
27.18
f1 (ppm)

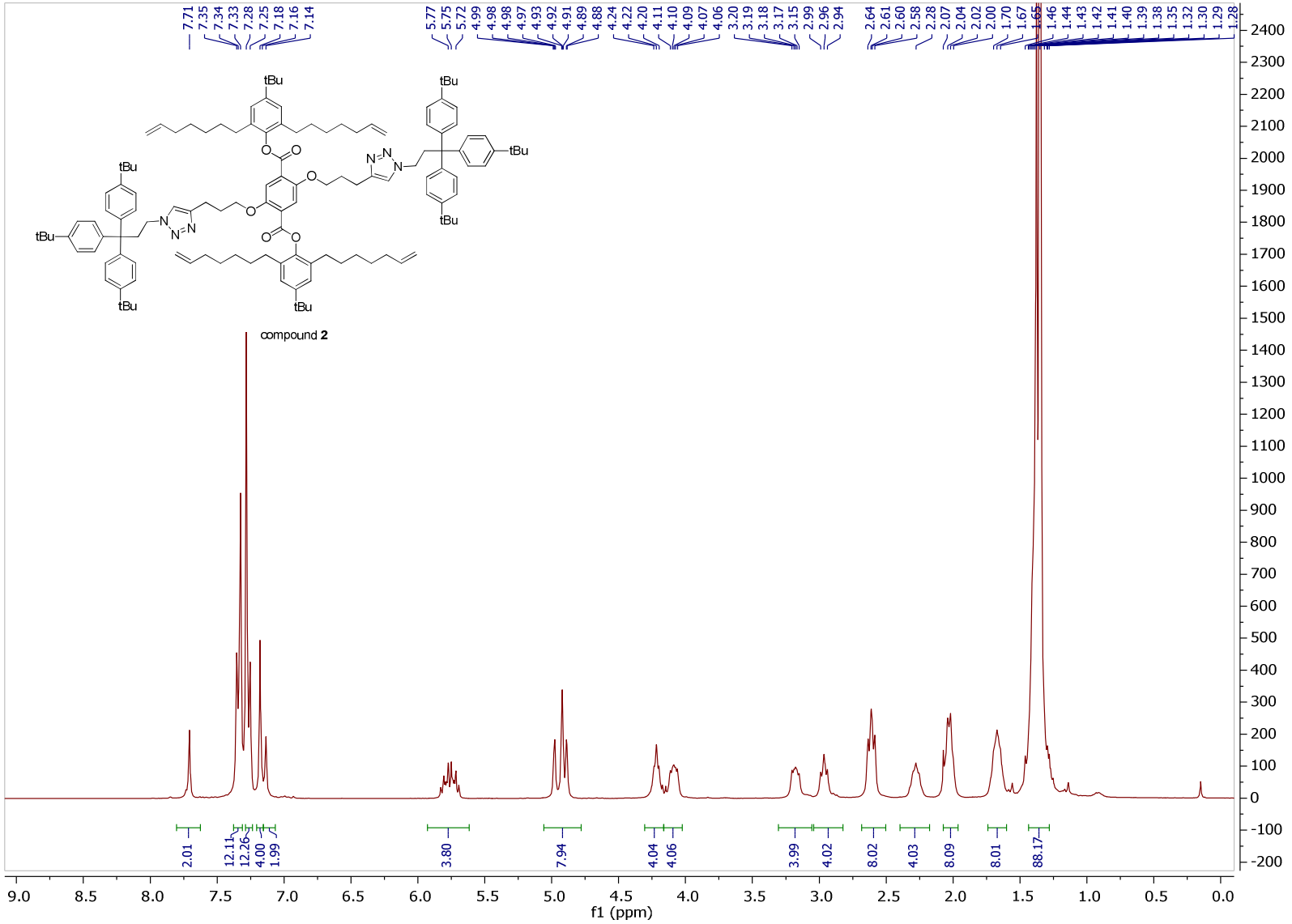

148.55
144.31
128.65
124.80
77.48
77.16
76.85
60.85
54.08
43.14
34.41
31.51
OH
compound 21
f1 (ppm)

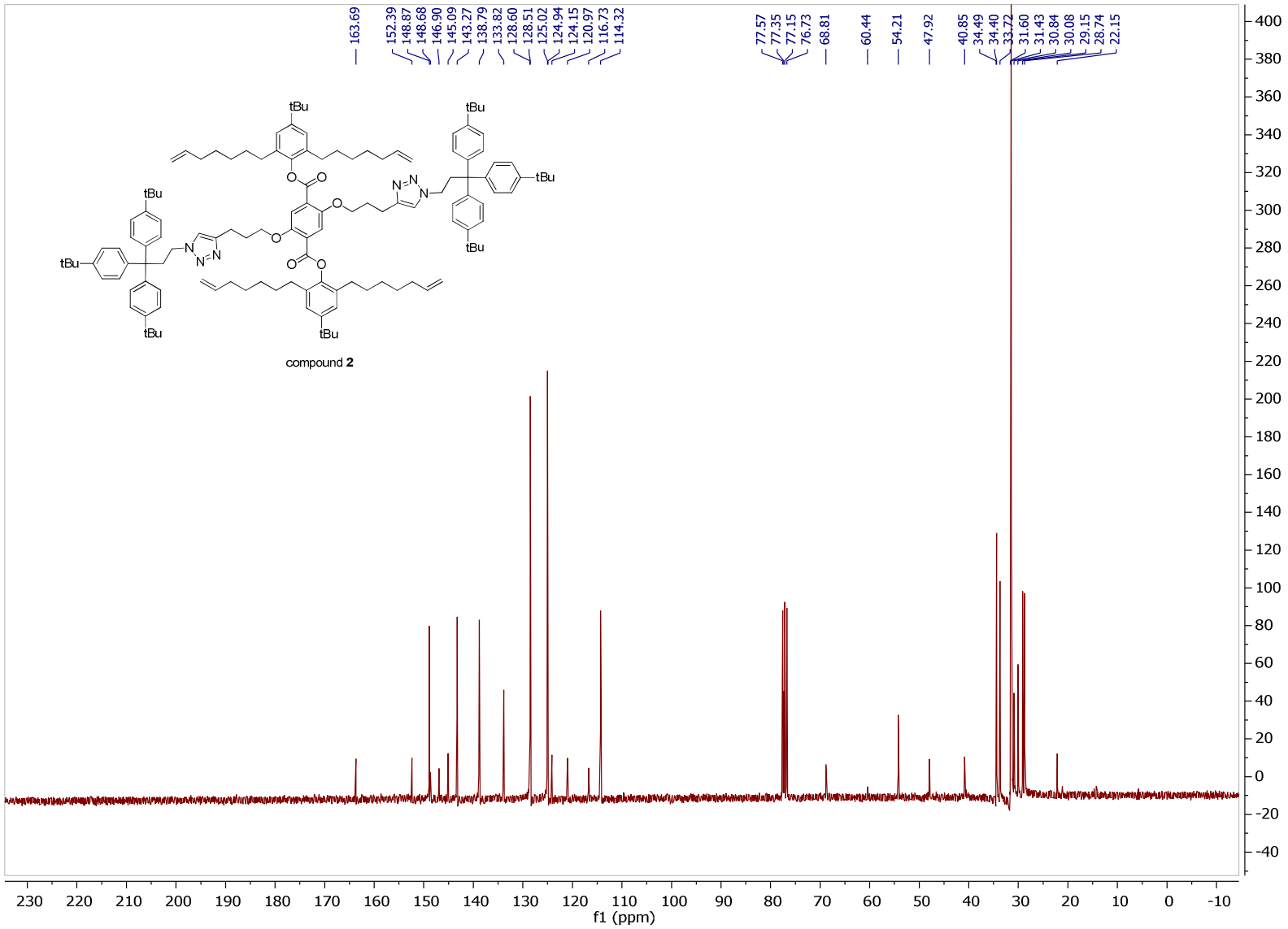

7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.21
7.20
7.20
7.18
7.18
7.17
3.11
3.09
3.09
3.09
3.08
3.07
2.90
2.88
2.88
2.87
2.86
2.20
1.56
1.40
1.35
1.34
1.31
1.30
1.29
1.29
1.28
0.92
0.91
0.90
N3
compound 22
6.00
6.00
2.02
2.02
27.27
f1 (ppm)

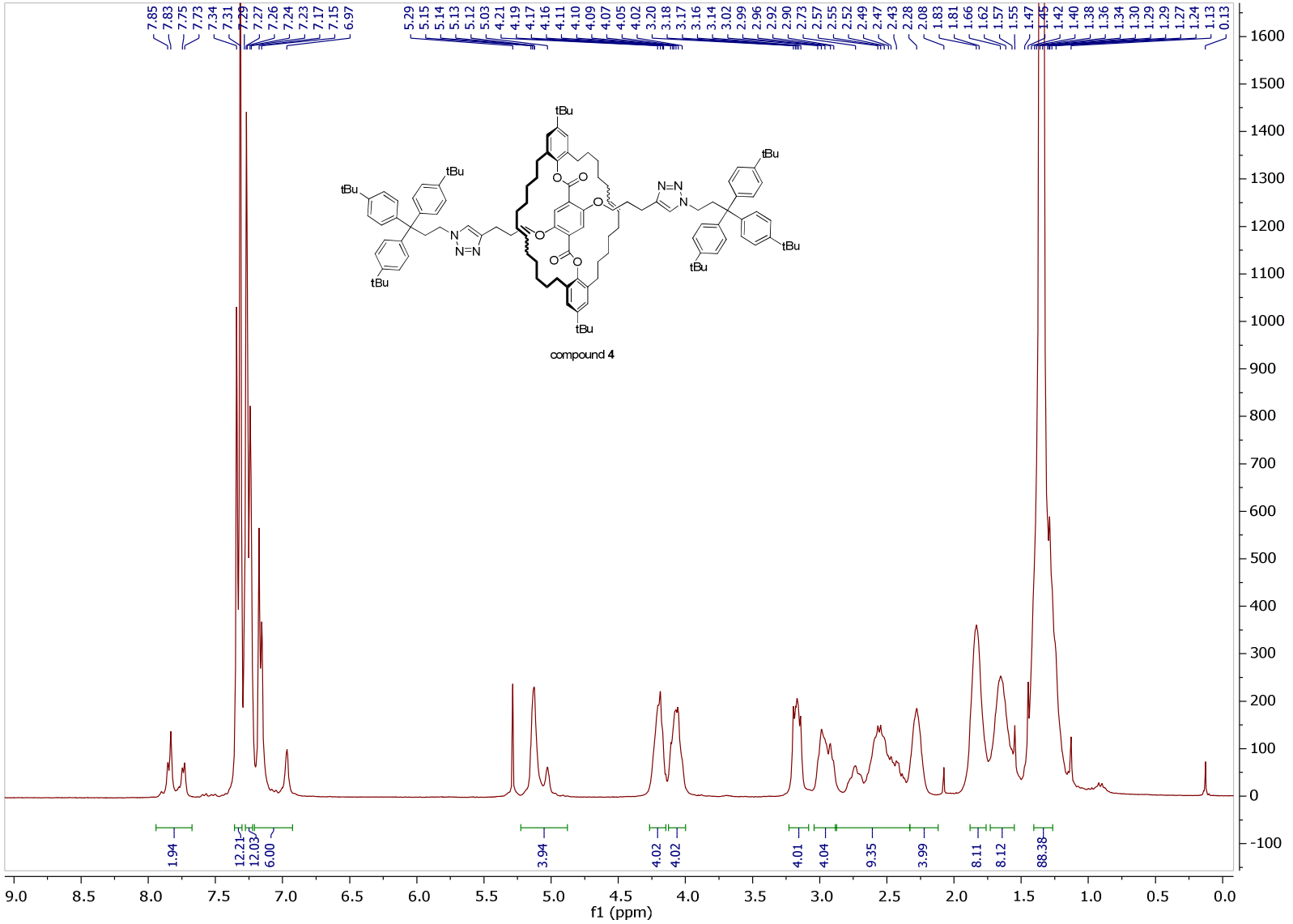

148.81
143.62
128.56
124.94
77.48
77.16
76.84
54.03
49.06
39.21
34.46
31.50
N3
compound 22
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

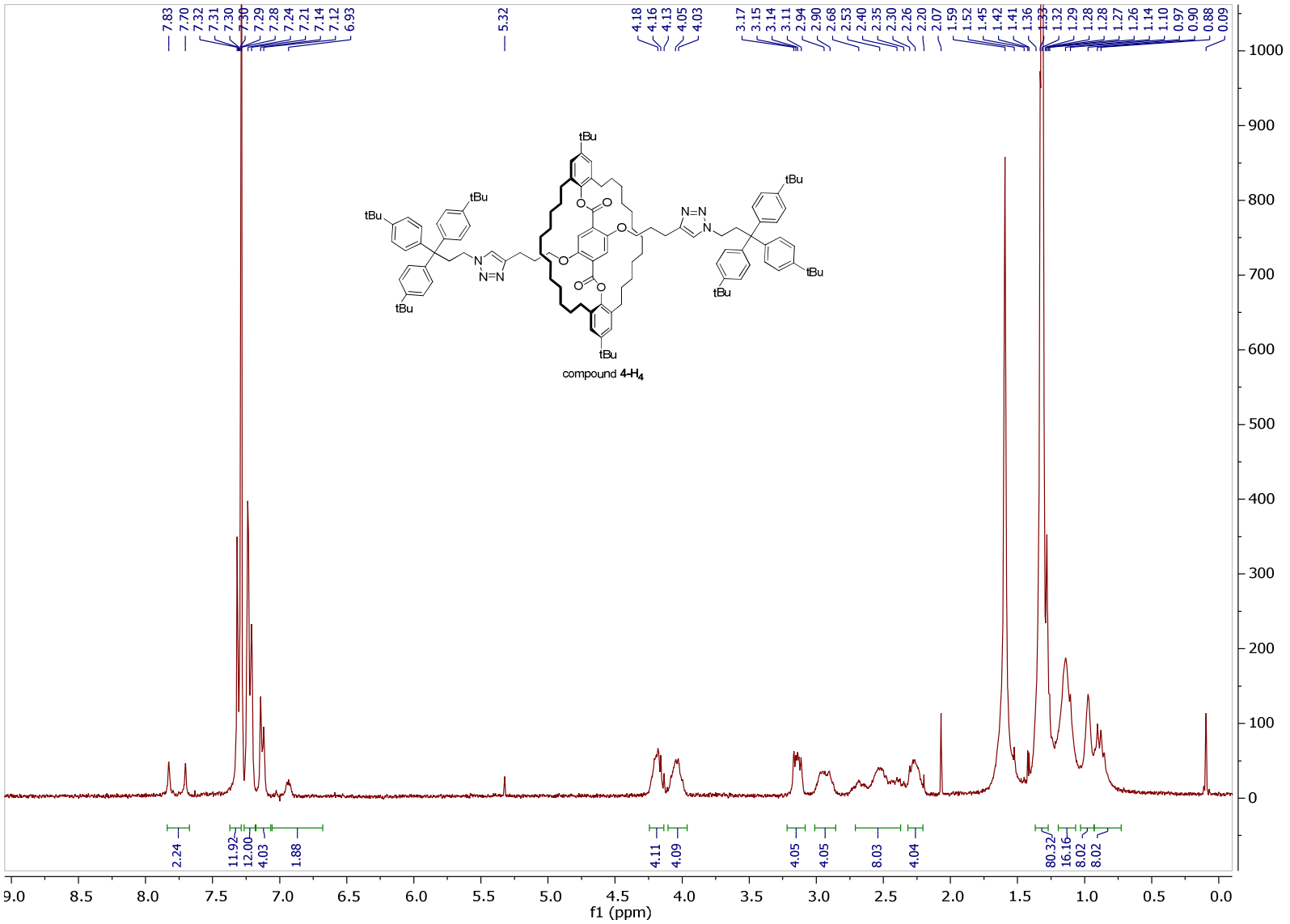

7.72
7.18
5.85
5.82
5.79
5.76
5.02
5.02
5.01
4.97
4.97
4.96
4.96
4.96
4.95
4.93
4.93
4.93
4.92
4.28
4.26
4.24
2.62
2.60
2.60
2.59
2.57
2.49
2.48
2.47
2.46
2.45
2.09
2.07
2.05
2.03
2.03
1.98
1.97
1.96
1.70
1.68
1.67
1.65
1.47
1.46
1.45
1.43
1.42
1.42
1.41
1.38
1.36
tBu
tBu
compound 23
1.95
4.00
3.78
7.87
4.00
8.03
4.04
12.03
1.89
8.04
34.15
f1 (ppm)

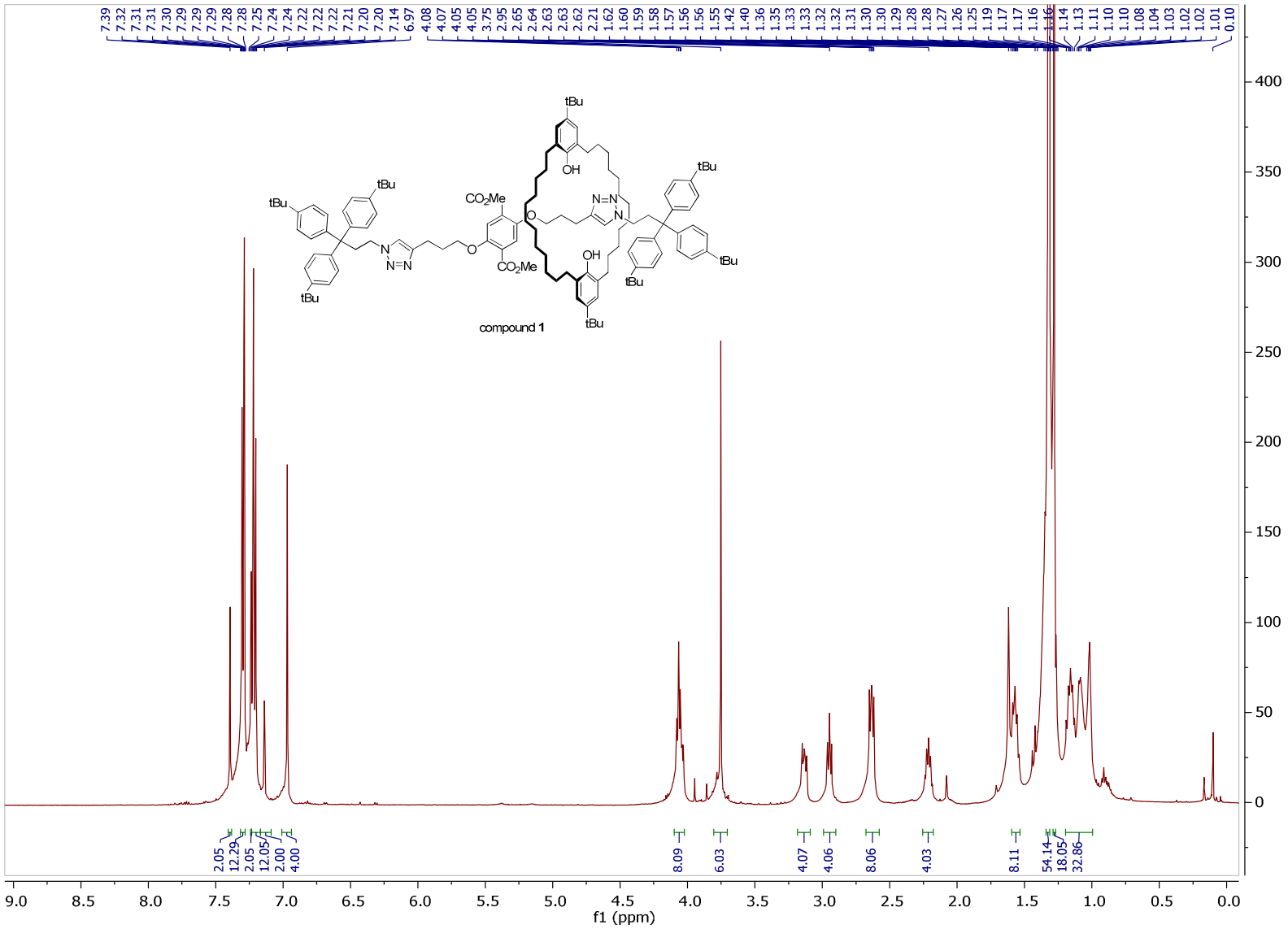

163.77
152.47
148.72
145.11
139.00
133.84
124.96
124.18
116.96
114.37
83.32
77.57
77.15
76.73
69.15
67.96
34.53
33.80
31.61
30.87
30.14
29.24
28.83
28.28
15.23
tBu
tBu
compound 23
f1 (ppm)

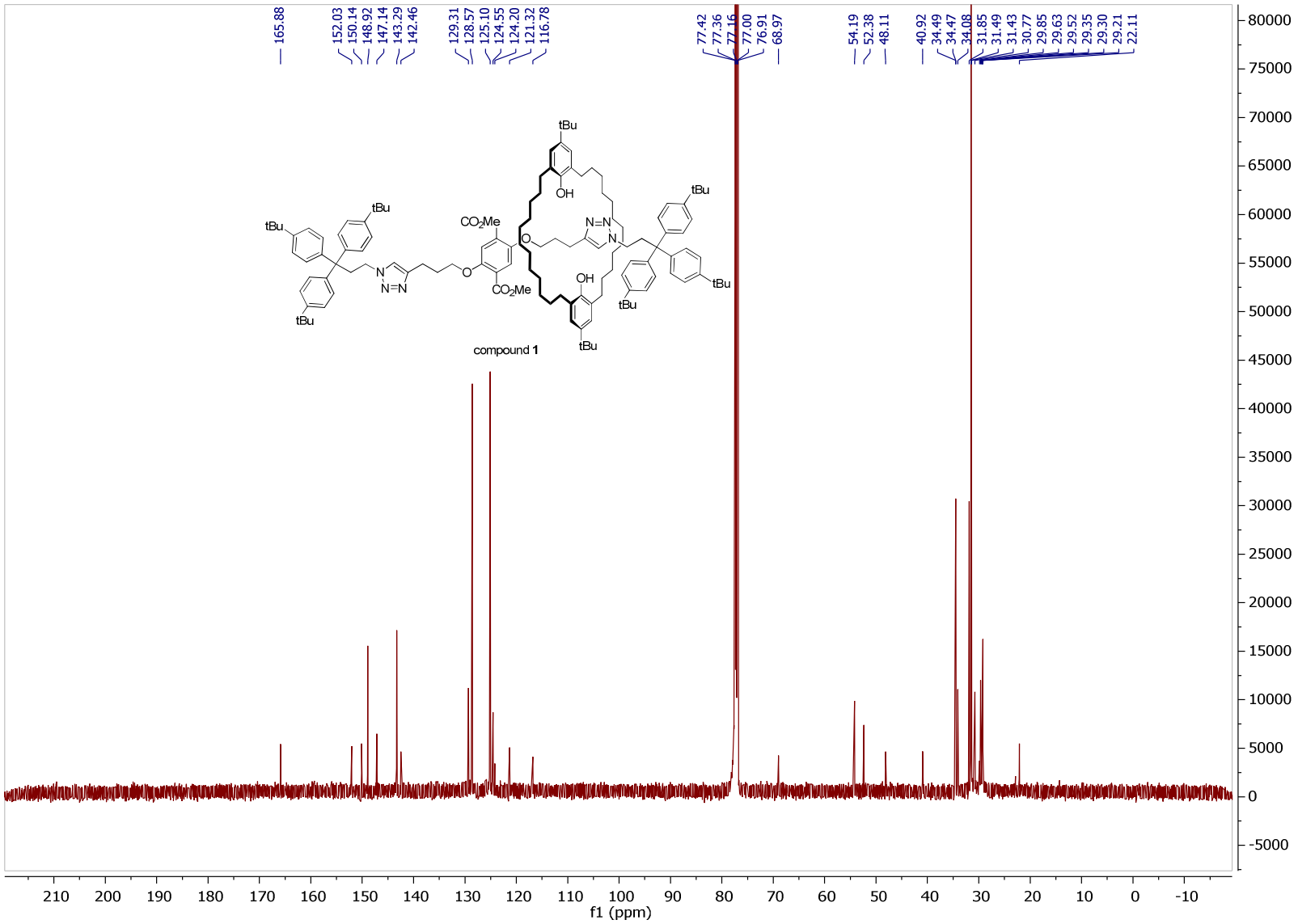

compound 2
f1 (ppm)


163.69
152.39
148.87
148.68
146.90
145.09
143.27
138.79
133.82
128.60
128.51
125.02
124.94
124.15
120.97
116.73
114.32
77.57
77.35
77.15
76.73
68.81
60.44
54.21
47.92
40.85
34.49
34.40
33.72
31.60
31.43
30.84
30.08
29.15
28.74
22.15
tBu
compound 2
f1 (ppm)


compound 4
f1 (ppm)

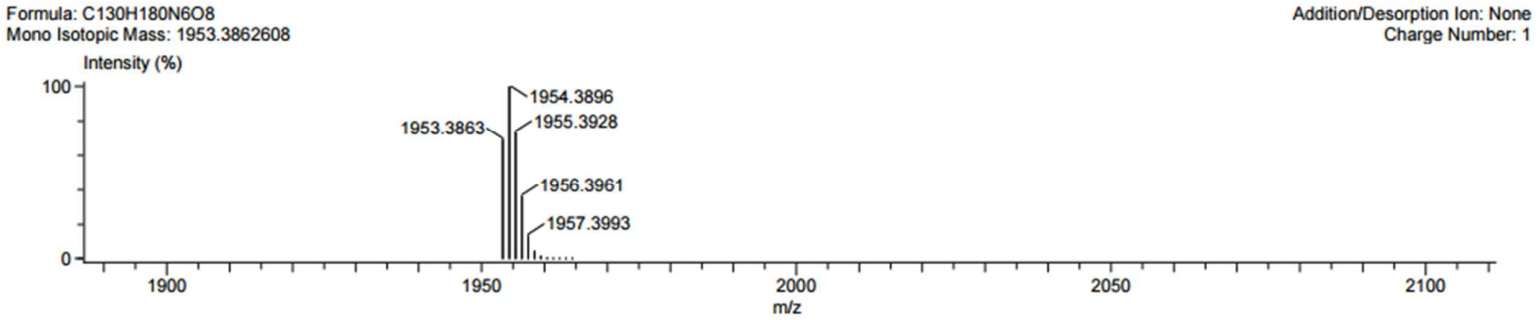

7.83
7.70
7.32
7.31
7.30
7.30
7.29
7.28
7.24
7.21
7.14
7.12
6.93
5.32
4.18
4.16
4.13
4.05
4.03
3.17
3.15
3.14
3.11
2.94
2.90
2.68
2.53
2.40
2.35
2.30
2.26
2.20
2.07
1.59
1.52
1.45
1.42
1.41
1.36
1.33
1.32
1.29
1.28
1.28
1.27
1.26
1.14
1.10
0.97
0.90
0.88
0.09
tBu
tBu
tBu
tBu
tBu
tBu
tBu
tBu
N=N
N=N
O
O
O
O
O
O
compound 4-H4
2.24
11.92
12.00
4.03
1.88
4.11
4.09
4.05
4.05
8.03
4.04
80.32
16.16
8.02
8.02
f1 (ppm)


compound 1
f1 (ppm)


165.88
152.03
150.14
148.92
147.14
143.29
142.46
129.31
128.57
125.10
124.55
124.20
121.32
116.78
77.42
77.36
77.16
77.00
76.91
68.97
54.19
52.38
48.11
40.92
34.49
34.47
34.08
31.85
31.49
31.43
30.77
29.85
29.63
29.52
29.35
29.30
29.21
22.11
compound 1
f1 (ppm)

HRMS-spectrum compound **1**

Calculated spectrum



Observed spectrum