SUPPORTING INFORMATION

Organocatalyzed Stetter reaction as a bio-inspired tool for the synthesis of nucleic acids-based bioconjugates.

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Experimental section

General information:

All reactions were carried out under an argon atmosphere (except for Jonhson-Lemieux oxidation). THF was dried over activated molecular sieves (3Å). EtOH was distilled from magnesium. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials, unless otherwise stated. All reagent-grade chemicals were obtained from commercial suppliers and were used as received, unless otherwise stated.

^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75.46 MHz) spectrometer using $CDCl_3$ as internal reference and at 293K unless otherwise indicated. The chemical shifts (ŭ) and coupling constants (*J*) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. FT-IR spectra were recorded on a Perkin-Elmer FT spectrometer Spectrum two (UATR two). HRMS were recorded with a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) mode, a Bruker Maxis 4G or Thermo Fisher Q-Exactive. Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light, potassium permanganate or sulfuric acid. Flash chromatography was performed on silica gel (0.043-0.063 mm).

Thymidine Protection

Compounds **2a** and **3** were synthesized following a procedure described in the literature [4c]

Compound 2b

Thymidine (1 g, 4.13 mmol) was dissolved in pyridine (20 mL) under an argon atmosphere and TIPSCl (1.060 mL, 4.95 mmol) was added, followed by a spatula tip of 4-dimethylaminopyridine. The reaction mixture was agitated overnight at room temperature. It was then concentrated under reduced pressure and dichloromethane and water were added. The aqueous layer was extracted three times with dichloromethane and the combined organic extracts were dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a white foam (839 mg, 51%).

Rf = 0.36 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}); 3475, 3167, 3032, 2942, 2895, 2866, 1683, 1664, 1467, 1434, 1404, 1384, 1367, 1316, 1272, 1203, 1122, 1091, 1055, 1002, 960, 940, 919, 882, 800, 778, 733, 717, 680, 664, 634, 612, 557, 493, 464; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 10.18 (s, 1H), 7.48 (d, *J* = 1.2 Hz, 1H), 6.35 (dd, *J* = 5.7, 8.1 Hz, 1H), 4.50 (brs, 1H), 4.08-4.02 (m, 2H), 3.96-3.84 (m, 2H), 2.40 (ddd, *J* = 1.2, 5.1, 12.9 Hz, 1H), 2.12-2.00 (m, 1H), 1.85 (d, *J* = 0.6 Hz, 3H), 1.16-0.98 (m, 21H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 164.4, 150.9, 135.6, 110.9, 87.5, 85.0, 72.0, 63.7, 41.1, 18.0, 12.4, 12.4, 11.9; HRMS (ESI) : Calcd. for $C_{19}H_{34}N_2O_5SiNa$ $[M+Na]^+$ 421.21292, found 421.2132.

Synthesis of allylated nucleosides

General procedure A for microwaves assisted allylation step adapted from the literature[12].

NaH (60% dispersion in oil) was added by portions to a solution of the alcohol in the corresponding solvent (0.1 g/mL) in a suitable vial and the reaction mixture was activated under microwaves at 40°C during 2 minutes. Allyl bromide was then added at a time followed by a second activation under microwaves (6 to 60 minutes) at 40°C depending on the substrate.

After being cooled at room temperature, the reaction was quenched with NH_4Cl and dichloromethane was added. The aqueous layer was extracted three times with dichloromethane. The combined organic extracts were then dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (Pentane/EtOAc).

Compound 4a

Synthesized according to the general procedure **A** from **2a** (500 mg, 1.40 mmol), sodium hydride (60% dispersion in oil, 140 mg, 3.51 mmol) and allyl bromide (303 µL, 3.51 mmol) in THF (5 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 70/30) to afford the title compound as a colorless gum (417 mg, 75%).

Rf = 0.6 (Pentane/EtOAC 50/50); Analytical data were consistent with the litterature.[12]

Compound 4b

Synthesized according to the general procedure **A** from **2b** (500 mg, 1.25 mmol), sodium hydride (60% dispersion in oil, 125 mg, 3.14 mmol) and allyl bromide (271 µL, 3.14 mmol) in THF (5 mL) with 60 minutes second microwave activation time. The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a colorless gum (484 mg, 88%).

Rf = 0.4 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3180, 3049, 2944, 2867, 1689, 1466, 1383, 1367, 1323, 1274, 1200, 1127, 1097, 1065, 995, 960, 920, 883, 803, 720, 685, 608, 557, 492; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.98 (s, 1H), 7.41 (s, 1H), 6.25 (dd, *J* = 5.7, 8.1 Hz, 1H), 5.92 - 5.75 (m, 1H), 5.28 - 5.10 (m, 2H), 4.21-4.14 (m, 1H), 4.07 - 3.77 (m, 5H), 2.40 (ddd, *J* = 2.1, 5.7, 13.5 Hz, 1H), 2.00-1.85 (m, 1H), 1.87 (s, 3H), 1.23-0.91 (m, 21H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 164.3, 150.6, 135.2, 134.1, 117.4, 110.8, 85.1, 84.8, 78.3, 70.2, 63.5, 38.0, 18.0, 12.4, 11.8; HRMS (ESI) : Calcd. for $C_{28}H_{38}N_2O_5SiNa$ $[M+Na]^+$ 461.2442, found 461.2440.

Compound 5

Synthesized according to the general procedure **A** from **3** (500 mg, 1.04 mmol), sodium hydride (60% dispersion in oil, 104 mg, 2.60 mmol) and allyl bromide (225 µL, 2.60 mmol) in THF (5 mL) with with 60 minutes second microwave activation time. The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 70/30) to afford the title compound as a colorless gum (330 mg, 61%).

Rf = 0.45 (PE/EtOAC 70/30); IR (ATR) ν_{max} (cm^{-1}) 3183, 3071, 2933, 2894, 1690, 1471, 1428, 1365, 1329, 1276, 1199, 1109, 1069, 1033, 1007, 966, 931, 900, 859, 823, 778, 742, 704, 611, 559, 508; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.90 (s, 1H), 7.71-7.59 (m, 4H), 7.56 (s, 1H), 7.51-7.34 (m, 6H), 6.52 (dd, *J* = 6.3, 7.8 Hz, 1H), 5.83 - 5.66 (m, 1H), 5.20 - 5.07 (m, 2H), 4.51-4.39 (m, 1H), 4.07-3.97 (m, 1H), 3.90-3.72 (m, 2H), 3.46 (dd, *J* = 2.1, 10.5, 1H), 2.97 (dd, *J* = 2.4, 10.8, 1H), 2.35 (ddd, *J* = 2.4, 5.7, 13.2 Hz, 1H), 2.08-1.88 (m, 1H), 1.84 (s, 3H), 1.09 (s, 9H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 164.3, 150.7, 136.0, 135.8, 135.7, 133.9, 133.3, 133.1, 130.0, 127.9, 117.3, 110.8, 86.7, 85.0, 73.7, 72.1, 69.6, 41.2, 26.9, 19.0, 12.5; HRMS (ESI) : Calcd. for $C_{29}H_{36}N_2O_5SiNa$ $[M+Na]^+$ 543.22857, found 543.2288.

Compound 6

Synthesized according to the general procedure **A** from **3** (500 mg, 1.04 mmol), sodium hydride (60% dispersion in oil, 50 mg, 1.25 mmol) and allyl bromide (108 µL, 1.25 mmol) in DMF (5 mL) with a 6 minutes second microwave activation. The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 70/30) to afford the title compound as a colorless gum (457 mg, 84%).

Rf = 0.39 (Pentane/EtOAC 70/30); IR (ATR) ν_{max} (cm^{-1}) 3460, 3073, 2932, 2859, 1702, 1666, 1633, 1590, 1466, 1428, 1398, 1363, 1334, 1274, 1242, 1193, 1158, 1103, 1064, 1024, 998, 932, 823, 772, 740, 701, 651, 622, 609, 577, 544, 506, 486; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.72-7.57 (m, 4H), 7.49-7.29 (m, 7H), 6.39-6.28 (m, 1H), 5.93 - 5.71 (m, 1H), 5.29 - 5.07 (m, 2H), 4.56-4.38 (m, 1H), 4.02-3.92 (m, 1H), 3.67-3.52 (m, 1H), 3.30-3.14 (m, 1H), 2.74-2.59 (m, 1H), 2.37-2.20 (m, 1H), 2.15-1.95 (m, 1H), 1.84 (brs, 3H), 1.08 (brs, 9H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 163.2, 150.7, 135.7, 135.7, 134.0, 133.3, 133.1, 131.6, 130.1, 130.1, 127.9, 118.0, 110.1, 87.8, 87.1, 73.3, 62.1, 43.3, 40.6, 26.9, 19.0, 13.2; HRMS (ESI) : Calcd. for $C_{29}H_{36}N_2O_5SiNa$ $[M+Na]^+$ 543.22857, found 543.2285.

Synthesis of nucleoside-based aldehydes partners

General procedure B for the Johnson-Lemieux oxidation step

OsO_4 (2.5 w% in t-BuOH, 0.03 eq.) was added to a stirred solution of the allylated compound (1 eq.) in a dioxane/water mixture (2/1, 0,1 M) followed by $NaIO_4$ (3 eq.) and 2,6-lutidine (2 eq.) under air conditions. The resulting white precipitate was stirred at r.t. during 4-5 hours. After addition of water, the mixture was extracted 3 times with CH_2Cl_2. The combined extracts were treated with $Na_2S_2O_5$, dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (Pentane/EtOAc).

Compound 7a

Synthesized according to the general procedure **B** from **4a** (810 mg, 2.04 mmol), osmium tetroxide (2.5% in t-BuOH, 700 µL, 0.068 mmol), sodium periodate (131 mg, 6.13 mmol) and 2,6-lutidine (473 µL, 4.08 mmol) in a dioxane/water mixture (2/1, 20 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 30/70) to afford the title compound as white foam (619 mg, 76%).

Rf = 0.3 (Pentane/EtOAC 30/70); IR (ATR) ν_{max} (cm^{-1}) 3418, 3196, 3066, 2954, 2931, 2859, 1689, 1469, 1364, 1323, 1258, 1201, 1223, 1073, 1004, 960, 937, 834, 779, 733, 672, 606, 559, 492; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.70 (s, 1H), 8.84 (s, 1H), 7.45 (brs, 1H),), 6.30 (dd, *J* = 5.4, 8.7 Hz, 1H),4.24-4.07 (m, 3H), 3.85 (ddd, *J* = 2.7, 11.1, 24.9 Hz,2H), 2.51-2.39 (m, 1H), 2.05-1.85 (m, 1H), 1.90 (brs, 3H), 0.91 (brs, 9H), 0.11 (s, 3H), 0.10 (s, 3H) ; ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 199.4, 163.8, 150.4, 135.3, 111.1, 85.1, 81.1, 77.4, 74.6, 63.7, 37.8, 26.0, 18.5, 12.7, -5.2, -5.4.

Compound 7b

Synthesized according to the general procedure **B** from **4b** (180 mg, 0.41 mmol), osmium tetroxide (2.5% in t-BuOH, 125 µL, 0.012 mmol) sodium periodate (263 mg, 1.23 mmol) and 2,6-lutidine (95 µL, 0.82 mmol) in a dioxane/water mixture (2/1, 4 mL). The crude product was then purified by flash

chromatography over silica gel (Pentane/EtOAc 30/70) to afford the title compound as white foam (149 mg, 82%).

Rf = 0.2 (Pentane/EtOAC 50/50); IR (ATR) ν_{max} (cm^{-1}) 3386, 3192, 3064, 2944, 2895, 2867, 2252, 1685, 1464, 1404, 1383, 1368, 1323, 1274, 1200, 1120, 1100, 1066, 1012, 997, 961, 916, 882, 803, 779, 731, 683, 649, 610, 559, 492, 462; ^{1}H-NMR (300 MHz, C_6D_6, 353K) δ (ppm) 10.77 (s, 1H), 9.29 (s, 1H), 7.26 (brs, 1H),), 6.41 (dd, *J* = 5.7, 8.1 Hz, 1H),4.09-4.01 (m, 2H), 3.80-3.49 (m, 4H), 2.38-2.26 (m, 1H), 1.97-1.80 (m, 1H), 1.89 (s, 3H), 1.21-0.90 (m, 3H), 1.02 (s, 18H); ^{13}C-NMR (75.5 MHz, C_6D_6, 353K) δ (ppm) 198.5, 163.8, 150.8, 135.3, 110.9, 85.8, 85.3, 80.7, 74.9, 64.0, 37.8, 18.2, 12.4, 12.4; HRMS (ESI) : Calcd. for $C_{21}H_{36}N_2O_6SiNa$ $[M+Na]^+$ 463.22349, found 463.2241.

Compound 8

Synthesized according to the general procedure **B** from **5** (1 g, 2.92 mmol), osmium tetroxide (2.5% in t-BuOH, 658 µL, 0.065 mmol), sodium periodate (1.232 g, 5.76 mmol) and 2,6-lutidine (444 µL, 3.83 mmol) in a dioxane/water mixture (2/1, 19 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as white foam (772 mg, 77%).

Rf = 0.5 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3192, 3062, 2934, 2895, 2860, 1691, 1469, 1429, 1370, 1324, 1276, 1249, 1198, 1109, 1081, 1032, 1008, 962, 901, 823, 777, 740, 704, 611, 560, 509, 490; ^{1}H-NMR (300 MHz, C_6D_6, 353K) δ (ppm) 9.07 (brs, 2H), 7.73-7.63 (m, 4H), 7.29-7.19 (m, 6H), 7.14-7.09 (m, 1H),), 6.53-6.4 (m, 1H), 4.52-4.44 (m, 1H), 4.00-3.93 (m, 1H), 3.32-3.26 (m, 1H), 3.21 (dd, *J* = 3.0, 10.6 Hz, 1H), 2.97 (dd, *J* = 3.0, 10.5 Hz, 1H), 2.21 (ddd, *J* = 3.1, 6.0, 10.6, 13.4 Hz, 1H), 1.91-1.71 (m, 4H), 1.13 (s, 9H); ^{13}C-NMR (75.5 MHz, C_6D_6, 353K) δ (ppm) 197.9, 163.6, 150.4, 136.0, 136.0, 135.9, 133.4, 133.1, 130.3, 128.1, 111.2, 86.3, 85.1, 76.6, 73.7, 71.1, 41.0, 27.0, 19.2, 12.6; HRMS (ESI) : Calcd. for $C_{28}H_{34}N_2O_6SiNa$ $[M+Na]^+$ 545.20784, found 545.2078.

Compound 9

Synthesized according to the general procedure **B** from **6** (580 mg, 1.11 mmol), osmium tetroxide (2.5% in t-BuOH, 340 µL, 0.033 mmol) sodium periodate (715 mg, 3.34 mmol) and 2,6-lutidine (258 µL, 2.23 mmol) in a dioxane/water mixture (2/1, 11 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 50/50) to afford the title compound as white foam (448 mg, 77%).

Rf =0.13 (pentane/AcOEt 50/50) IR (ATR) ν_{max} (cm^{-1}) 3186, 3060, 2953, 2929, 2857, 1683, 1470, 1257, 1068, 831; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.51 (brs, 1H), 7.72-7.54 (m, 4H), 7.52-7.30 (m, 7H), 6-57-6.21 (m, 1H), 4.78-4.66 (m, 1H), 4.52-4.30 (m, 1H), 4.11-3.87 (m, 2H), 3.86-3.12 (m, 2H), 2.89-2.46 (m, 1H), 2.41-2.13 (m, 1H), 2.05-1.73 (m, 4H), 1.09 (brs, 9H), ^{13}C-NMR (75.5 MHz, CDCl3) ***ŭ*** (ppm) : 194.6 (m), 162.9 (m), 162.9 (m), 150.5 (m), 135.7, 135.7 (m), 133.1 (m), 130.1,

127.9, 109.9 (m), 95.0 (m), 87.7, 87.1 (m), 77.4, 73.1 (m), 67.1 (m), 62.0 (m), 53.5, 50.1, 45.2, 40.6 (m), 26.9, 18.9, 13.1. HRMS (ESI) : Calcd. for $C_{28}H_{34}N_2O_6SiNa$ $[M+Na]^+$ 545.20784, found 545.2080.

Synthesis of lipid-based enones partners

Enones **10A-D** were synthesized from the corresponding aldehydes by a vinylation-oxidation two-step sequence. Commercially available aldehydes were used for the synthesis of **10A-C** and the oleic aldehyde was obtained by oxidation of oleic alcohol.

General procedure C for the Vinylation step:

Vinylmagnesium bromide (1 M in THF, 2 eq.) was added dropwise to a stirred solution of the aldehyde (1 eq.) in THF (0.3 M) at -78°C and the reaction mixture was stirred at this temperature during 4h. After quenching by aq. sat. NH_4Cl, it was allowed to warm up at room temperature and CH_2Cl_2 was added. The organic layer was recovered and the aqueous layer was extracted two times with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure.

General procedure D for the Swern oxidation step:

At -60°C, anhydrous DMSO (2.4 eq.) was added dropwise to a stirred solution of oxalyl chloride (1.2 eq.) in anhydrous CH_2Cl_2 (1 M) and the reaction mixture was stirred at -60°C during 30 minutes. Then, a solution of the crude allylic alcohol (1 eq.) in CH_2Cl_2 (6 M) was added dropwise and stirring was continued for 2h at -60°C before addition of Et_3N (3.8 eq.). The reaction mixture was stirred 2h at -60°C and then allowed to warm up at 0°C. Water was added and the reaction mixture was allowed to warm up at room temperature. CH_2Cl_2 was added and the organic layer was recovered before being washed successively with aq. HCl (1 M), water and aq. sat. $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography over silica gel (Pentane/EtOAc 99/1).

Compound 10A

The allylic alcohol was synthesized according to the general procedure **C** from octanal (0.821 g, 6.40 mmol) and vinylmagnesium bromide (1M in THF, 12.81 mL, 12.81 mmol) in THF (19 mL).

It was oxidized without further purification following procedure **D**, using oxalyl chloride (659 µL, 7.68 mmol), dimethylsulfoxide (1.092 mL, 15.37 mmol) and triethylamine (3.4 mL, 24.33 mmol) in dichloromethane (9.3 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 99/1) to afford the title compound as a yellow oil (389 mg, 39%).

Rf = 0.5 (Pentane/EtOAC 99/1); IR (ATR) ν_{max} (cm^{-1}) 2956, 2927, 2857, 1701, 1682, 1616, 1463, 1402, 1377, 1299, 1264, 1206, 1186, 1131, 1082, 986, 961, 775, 724, 655, 558, 489; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.34 (dd, *J* = 10.3, 17.7 Hz, 1H), 6.19 (dd, *J* = 1.5, 17.7 Hz, 1H), 5.80 (dd, *J* =

1.4, 10.2 Hz, 1H), 2.56 (appearing t, *J* = 7.3, 7.6 Hz), 1.67-1.54 (m, 2H), 1.35-1.19 (m, 8H), 0.90-0.82 (m, 3H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 201.0, 136.6, 127.7, 39.6, 31.7, 29.2, 29.1, 24.0, 22.6, 14.1; HRMS (ESI) : Calcd. for $C_{10}H_{18}ONa$ $[M+Na]^+$ 177.12499, found 177.1250.

Compound 10B

The allylic alcohol was synthesized according to the general procedure **C** from decanal (0.83 g, 5.31 mmol) and vinylmagnesium bromide (1M in THF, 10.62 mL, 10.62 mmol) in THF (15.5 mL).

It was oxidized without further purification following procedure **D**, using oxalyl chloride (547 µL, 6.37 mmol), dimethylsulfoxide (905 µL, 12.75 mmol) and triethylamine (2.8 mL, 20.18 mmol) in dichloromethane (7.7 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 99/1) to afford the title compound as a yellow oil (422 mg, 44%).

Rf = 0.5 (Pentane/EtOAC 99/1); IR (ATR) $з_{max}$ (cm^{-1}) 2926, 2856, 1701, 1684, 1617, 1464, 1402, 1377, 1200, 1130, 1086, 987, 961, 723; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.35 (dd, *J* = 10.3, 17.7 Hz, 1H), 6.20 (dd, *J* = 1.4, 17.7 Hz, 1H), 5.81 (dd, *J* = 1.5, 10.3 Hz, 1H), 2.57 (appearing t, *J* = 7.2, 7.6 Hz), 1.66-1.55 (m, 2H), 1.35-1.21 (m, 12H), 0.91-0.83 (m, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 201.3, 136.7, 128.0, 39.8, 32.0, 29.6, 29.4, 24.2, 22.8, 14.2; HRMS (ESI) : Calcd. for $C_{12}H_{22}ONa$ $[M+Na]^+$ 205.15629, found 205.1562.

Compound 10C

The allylic alcohol was synthesized according to the general procedure **C** from dodecyl aldehyde (1 g, 5.42 mmol) and vinylmagnesium bromide (1M in THF, 10.85 mL, 10.85 mmol) in THF (16 mL).

It was oxidized without further purification following procedure **D**, using oxalyl chloride (558 µL, 6.50 mmol), dimethylsulfoxide (924 µL, 13.01 mmol) and triethylamine (2.9 mL, 20.60 mmol) in dichloromethane (7.9 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 99/1) to afford the title compound as a yellow oil (936 mg, 82%).

Rf = 0.5 (Pentane/EtOAC 99/1); IR (ATR) $з_{max}$ (cm^{-1}) = 2924, 2854, 1702, 1684, 1616, 1464, 1401, 1376, 1301, 1195, 1131, 986, 961, 722, 655, 558, 488; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.33 (dd, *J* = 10.5, 17.7 Hz, 1H), 6.19 (dd, *J* = 1.5, 17.7 Hz, 1H), 5.79 (dd, *J* = 1.5, 10.2 Hz, 1H), 2.56 (t, *J* = 7.5 Hz), 1.66-1.53 (m, 2H), 1.33-1.19 (m, 16H), 0.88-0.82 (m, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 201.3, 136.7, 128.0, 39.8, 32.0, 29.7, 29.6, 29.6, 29.5, 29.4, 24.2, 22.8, 14.3; HRMS (ESI) : Calcd. for $C_{14}H_{26}ONa$ $[M+Na]^+$ 233.18759, found 233.1873.

Compound 10D

Oleyl alcohol (285 mg, 1.06 mmol) was oxidized following procedure **D**, using oxalyl chloride (109 µL, 1.27 mmol), dimethylsulfoxide (181 µL, 2.55 mmol) and triethylamine (0.56 mL, 4.03 mmol) in dichloromethane (1.5 mL).

The crude aldehyde was then allylated without further purification to afford the allylic alcohol according to the general procedure **C** using vinylmagnesium bromide (1M in THF, 2.12 mL, 2.12 mmol) in THF (3 mL).

It was then submitted to oxidation step without further purification following procedure **D**, using oxalyl chloride (109 µL, 1.27 mmol), dimethylsulfoxide (181 µL, 2.55 mmol) and triethylamine (0.56 mL, 4.03 mmol) in dichloromethane (1.5 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 99/1) to afford the title compound as a yellow oil (87 mg, 28%).

Rf = 0.5 (Pentane/EtOAC 99/1); IR (ATR) $з_{max}$ (cm^{-1}) = 3005, 2924, 2855, 1728, 1702, 1685, 1617, 1461, 1403, 1374, 1276, 1195, 1104, 1074, 986, 960, 808, 722; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.33 (ddd, *J* = 10.2, 17.4 Hz, 1H), 6.19 (ddd, *J* = 1.5, 17.7 Hz, 1H), 7.79 (ddd, *J* = 1.5, 10.2 Hz, 1H), 5.39-5.27 (m, 2H), 2.56 (appearing t, *J* = 7.3, 7.5 Hz, 2H), 2.05-1.93 (m, 4H), 1.67 ï 1.54 (m, 2H), 1.37-1.19 (m, 20H), 0.89-0.83 (m, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 201.2, 136.7, 130.1, 129.9, 127.9, 39.8, 32.0, 29.9, 29.8, 29.7, 29.4, 29.4, 29.2, 27.3, 27.3, 24.1, 22.8, 22.2, 14.23; HRMS (ESI) : Calcd. for $C_{20}H_{36}ONa$ $[M+Na]^+$ 315.26584, found 315.2661.

Compound 10E

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoic acid (250 mg, 0.51 mmol) was dissolved in THF (5 mL) before addition of carbonyldiimidazole (132 mg, 0.81 mmol). After 10 minutes of stirring, N,O-dimethylhydroxylamine hydrochloride (124 mg, 1.27 mmol) was introduced and the reaction mixture was stirred at room temperature during 23h. After this period, the reaction was quenched with 1M aq. HCl. Water was added and the aqueous layer was extracted three times using dichloromethane. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure, affording a yellow oil.

The crude product was engaged in the vinylation reaction without further purification and following general procedure **C**.

The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 99/1) to afford the title compound as a white foam (80 mg, 31%).

Rf = 0.5 (Pentane/EtOAC 99/1); IR (ATR) $з_{max}$ (cm^{-1}) = 2959, 2926, 2856, 1704, 1680, 1625, 1465, 1440, 1406, 1372, 1336, 1198, 1146, 1103, 1057, 1033, 985, 969, 868, 833, 800, 735, 704, 652, 617, 606, 577, 558, 524; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 6.40 (ddd, *J* = 1.5, 9.9, 17.7 Hz, 1H), 6.33-6.25 (m, 1H), 5.96-5.90 (m, 1H), 2.96-2.88 (m, 2H), 2.57-2.37 (m, 2H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 196.9, 136.0, 129.4, 121.8 (appearing t, *J* = 32.1, 32.7 Hz), 119.7-118.0 (m), 115.8-114.5 (m), 30.4, 25.3 (t, *J* = 22 Hz); ^{19}F-NMR (282.4 MHz, $CDCl_3$) δ (ppm) -80.73 (t, *J* = 9.9 Hz, 3F), -114.02 - -114.44 (m, 2F), -121.45 - -122.08 (m, 6F), -122.54 - -122.88 (m, 2F), -123.27 - -123.64 (m, 2F), -125.93 - -126.24 (m, 2F); HRMS (ESI) : Calcd. for $C_{13}H_7OF_{17}Na$ $[M+Na]^+$ 525.0118, found 525.0119.

Synthesis of diketones

General procedure E for Stetter reaction

The ***N***-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide precatalyst (0.3 eq.) previously dried during 1 day at 45°C under high vacuum was loaded in a Schlenk tube and placed under argon atmosphere. A solution of the aldehyde (1.5 eq.) in THF (0,5 M) was added followed by DBU (0.3 eq.). The reaction mixture became orange, indicating the formation of the Breslow intermediate. The enone (1 eq.) was then added and the reaction mixture was stirred overnight at 75°C. After complete consumption of the enone (TLC control), concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (Pentane/EtOAc).

Diketone 12A

Synthesized according to the general procedure **E** from **8** (200 mg, 0.38 mmol), **10A** (39 mg, 0.26 mmol), catalyst T (19 mg, 0.08 mmol) and DBU (11 µL, 0.08 mmol) in THF (0.7 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 60/40) to afford the title compound as a yellow gum (80 mg, 46%).

Rf = 0.4 (Pentane/EtOAC 60/40); IR (ATR) ν_{max} (cm^{-1}) 3184, 3071, 2930, 2858, 1691, 1469, 1428, 1402, 1368, 1325, 1276, 1247, 1198, 1107, 1033, 962, 893, 823, 778, 742, 704, 611, 559, 508, 490; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.27 (s, 1H), 7.67 - 7.58 (m, 5H), 7.48 - 7.33 (m, 6H), 6.52 (dd, *J* = 5.7, 8.7 Hz, 1H), 4.48 - 4.43 (m, 1H), 4.05 - 3.95 (m, 3H), 3.46 (dd, *J* = 2.1, 10.2 Hz, 1H), 2.93 (dd, *J* = 2.4, 10.2 Hz, 1H), 2.69 (dd, *J* = 5.1, 7.5 Hz, 2H),2.49 - 2.36 (m, 4H), 2.29 (ddd, *J* = 1.8, 5.7, 13.2 Hz, 1H), 2.08 - 1.96 (m, 1H) 1.79 (s, 3H), 1.59 - 1.46 (m, 2H), 1.24 (brs, 8H), 1.07 (s, 9H), 0.90 - 0.80 (m, 3H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 209.3, 205.4, 164.2, 150.7, 136.3, 135.9, 135.8, 135.7, 133.4, 133.1, 130.1, 128.0, 128.0, 127.9, 111.1, 86.4, 85.1, 75.8, 74.0, 70.9, 42.7, 40.9, 35.8, 32.1, 31.7, 29.2, 29.1, 26.9, 26.9, 23.8, 22.6, 19.1, 14.1, 12.3; HRMS (ESI) : Calcd. for $C_{38}H_{52}N_2O_7SiNa$ $[M+Na]^+$ 699.3436, found 699.3433.

Diketone 12B

Synthesized according to the general procedure **E** from **8** (200 mg, 0.38 mmol), **10B** (46 mg, 0.26 mmol), catalyst **T** (19 mg, 0.08 mmol) and DBU (11 µL, 0.08 mmol) in THF (0.7 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 65/35) to afford the title compound as a yellow gum (115 mg, 64%).

Rf = 0.7 (Pentane/EtOAC 60/40); IR (ATR) ν_{max} (cm^{-1}) 3188, 3071, 2928, 2857, 1687, 1466, 1428, 1402, 1368, 1324, 1275, 1198, 1104, 1032, 961, 899, 822, 741, 702, 611, 558, 507, 489; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.37 (s, 1H), 7.70 - 7.57 (m, 5H), 7.48 - 7.31 (m, 6H), 6.52 (dd, *J* = 5.7, 8.4 Hz, 1H), 4.49 - 4.42 (m, 1H), 4.04 - 3.95 (m, 3H), 3.46 (dd, *J* = 2.1, 10.2 Hz, 1H), 2.93 (dd, *J* = 2.4, 10.2 Hz, 1H), 2.74-2.65 (m, 2H), 2.49-2.36 (m, 4H), 2.31 (ddd, *J* = 1.8, 6.0, 13.5 Hz, 1H), 2.08-1.97 (m, 1H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.60-1.45 (m, 2H), 1.24 (brs, 12H), 1.07 (s, 9H), 0.89-0.80 (m,

3H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 209.3, 205.4, 164.2, 150.7, 136.3, 135.8, 135.8, 135.7, 133.4, 133.1, 130.1, 127.9, 111.1, 86.4, 85.1, 75.8, 74.1, 70.9, 42.6, 40.9, 35.8, 32.0, 31.9, 29.4, 29.4, 29.3, 29.2, 26.9, 23.8, 22.7, 19.0, 14.2, 12.3, 12.3; HRMS (ESI) : Calcd. for $C_{40}H_{56}N_2O_7SiNa$ $[M+Na]^+$ 727.3749, found 727.3746.

Diketone 12C

Synthesized according to the general procedure **E** from **8** (177 mg, 0.34 mmol), **10C** (47 mg, 0.23 mmol), catalyst **T** (17 mg, 0.07 mmol) and DBU (9 µL, 0.07 mmol) in THF (0.6 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 60/40) to afford the title compound as a yellow gum (113 mg, 68%).

Rf = 0.4 (Pentane/EtOAC 60/40); IR (ATR) ν_{max} (cm^{-1}) 3183, 3071, 2928, 2857, 1691, 1468, 1428, 1402, 1368, 1324, 1276, 1247, 1198, 1107, 1033, 961, 893, 823, 778, 742, 704, 611, 559, 508, 490; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.49 (s, 1H), 7.65 - 7.60 (m, 5H), 7.46 - 7.34 (m, 6H), 6.52 (dd, *J* = 5.4, 8.4 Hz, 1H), 4.48 - 4.43 (m, 1H), 4.03 - 3.93 (m, 3H), 3.46 (dd, *J* = 2.4, 10.2 Hz, 1H), 2.93 (dd, *J* = 2.7, 10.2 Hz, 1H), 2.72 - 2.64 (m, 2H), 2.49 - 2.35 (m, 4H), 2.30 (ddd, *J* = 1.8, 5.7, 13.2 Hz, 1H), 2.08 - 1.95 (m, 1H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.59 - 1.44 (m, 2H), 1.24 (brs, 16H), 1.07 (s, 9H), 0.90 - 0.78 (m, 3H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 209.3, 205.4, 164.3, 150.7, 136.3, 135.8, 135.7, 135.7, 133.4, 133.1, 130.0, 127.9, 111.1, 86.4, 85.1, 75.7, 74.0, 70.8, 42.6, 40.8, 35.8, 32.0, 31.6, 29.7, 29.1, 29.0, 26.9, 23.8, 22.6, 19.0, 14.1, 12.3; HRMS (ESI) : Calcd. for $C_{42}H_{60}N_2O_7SiNa$ $[M+Na]^+$ 755.4062, found 755.4063.

Diketone 12D

Synthesized according to the general procedure **E** from **8** (174 mg, 0.33 mmol), **10D** (65 mg, 0.22 mmol), catalyst **T** (17 mg, 0.07 mmol) and DBU (9 µL, 0.07 mmol) in THF (0.6 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 65/35) to afford the title compound as a yellow gum (79 mg, 44%).

Rf = 0.5 (Pentane/EtOAC 65/35); IR (ATR) ν_{max} (cm^{-1}) 3186, 3060, 3006, 2927, 2856, 1693, 1466, 1428, 1402, 1368, 1324, 1276, 1247, 1198, 1107, 1033, 962, 939, 892, 856, 823, 778, 741, 704, 611, 559, 508, 490; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.17 (s, 1H), 7.67-7.58 (m, 5H), 7.48-7.33 (m, 6H), 6.52 (dd, *J* = 5.7, 8.7 Hz, 1H), 5.38 - 5.28 (m, 2H) 4.49 - 4.42 (m, 1H), 4.04-3.95 (m, 3H), 3.47 (dd, *J* = 2.4, 10.2 Hz, 1H), 2.94 (dd, *J* = 2.7, 10.5 Hz, 1H), 2.73-2.67 (m, 2H), 2.49-2.37 (m, 4H), 2.30 (ddd, *J* = 1.8, 5.7, 13.2 Hz, 1H), 2.10-1.92 (m, 5H 1H), 1.80 (d, *J* = 0.9 Hz, 3H), 1.60-1.47 (m, 2H), 1.39-1.17 (m, 20H), 1.08 (s, 9H), 0.91-0.81 (m, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 209.3, 205.4, 164.1, 150.7, 136.3, 135.9, 135.8, 135.7, 133.4, 133.2, 130.1, 130.0, 129.8, 128.0, 127.9, 111.1, 86.4, 85.1, 75.8, 74.1, 70.9, 42.7, 40.9, 35.8, 32.1, 32.0, 29.8, 29.8, 29.7, 29.6, 29.4, 29.4, 29.2, 29.2,

27.3, 27.2, 27.0, 23.8, 22.8, 19.1, 14.2, 12.3; HRMS (ESI) : Calcd. for $C_{48}H_{70}N_2O_7SiNa$ $[M+Na]^+$ 837.48445, found 837.4847.

Diketone 12E

Synthesized according to the general procedure **E** from **8** (87 mg, 0.17 mmol), **10E** (56 mg, 0.11 mmol), catalyst **T** (8 mg, 0.03 mmol) and DBU (5 µL, 0.03 mmol) in THF (0.3 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 55/45) to afford the title compound as a yellow gum (52 mg, 46%).

Rf = 0.3 (Pentane/EtOAC 60/40);); IR (ATR) ν_{max} (cm^{-1}) 3178, 3065, 2928, 2858, 1694, 1470, 1429, 1366, 1242, 1208, 1150, 1112, 1033, 963, 893, 824, 778, 742, 705, 657, 612, 563, 510, 491, 465; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.87 (s, 1H), 7.69 - 7.59 (m, 4H), 7.56 (d, *J* = 1.2 Hz, 1H), 7.49 - 7.32 (m, 6H), 6.50 (dd, *J* = 5.7, 8.4 Hz, 1H), 4.51 - 4.41 (m, 1H), 4.04 - 3.95 (m, 3H), 3.47 (dd, *J* = 2.1, 10.2 Hz, 1H), 2.95 (dd, *J* = 2.7, 10.2 Hz, 1H), 2.85 - 2.68 (m, 4H), 2.59 - 2.50 (m, 2H), 2.48 - 2.26 (m, 3H), 2.09-1.93 (m, 1H), 1.80 (d, *J* = 0.9 Hz, 3H), 1.08 (s, 9H); ^{13}C-NMR (75.5 MHz, CDCl3) δ (ppm) 205.4, 205.3, 164.0, 150.6, 136.2, 135.9, 135.9, 133.5, 133.2, 130.2, 128.0, 111.2, 86.4, 85.2, 77.4, 75.8, 74.0, 71.0, 40.9, 35.8, 33.3, 32.3, 27.0, 25.1 (t, *J* = 90 Hz), 19.1, 12.3; ^{19}F-NMR (282.4 MHz, CDCl3) δ (ppm) -80.73 (t, *J* = 9.9 Hz, 3F), -114.04 - -114.48 (m, 2F), -121.50 - -122.13 (m, 6F), -122.57 - -122.88 (m, 2F), -123.26 - -123.64 (m, 2F), -125.92 - -126.23 (m, 2F);HRMS (ESI) : Calcd. for $C_{41}H_{41}N_2O_7F_{17}SiNa$ $[M+Na]^+$ 1047.23038, found 1047.2300.

Diketone 11aA

Synthesized according to the general procedure **E** from **7a** (216 mg, 0.54 mmol), **10A** (56 mg, 0.36 mmol), catalyst **T** (27 mg, 0.11 mmol) and DBU (15 µL, 0.11 mmol) in THF (1 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a yellow gum (88 mg, 47%).

Rf = 0.4 (Pentane/EtOAC 50/50); IR (ATR) ν_{max} (cm^{-1}) 3186, 3062, 2953, 2929, 2857, 1686, 1465, 1402, 1365, 1323, 1274, 1256, 1200, 1125, 1105, 1077, 1003, 960, 936, 834, 779, 723, 671, 605, 558, 491; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.56 (s, 1H), 7.46 (d, *J* = 1.2 Hz, 1H), 6.27 (dd, *J* = 5.4, 8.7 Hz, 1H), 4.23 - 4.02 (m, 4H), 3.82 (ddd, *J* = 2.4, 11.4, 24.9 Hz, 2H), 2.77 - 2.56 (m, 4H), 2.48 - 2.34 (m, 3H), 1.99 - 1.89 (m, 1H), 1.87 (d, *J* = 0.9 Hz, 3H), 1.57 - 1.45 (m, 2H), 1.32-1.14 (m, 8H), 0.87 (s, 9H), 0.87 - 0.75 (m, 3H), 0.06 (d, *J* = 2.1 Hz, 6H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 209.5, 207.0, 164.1, 150.5, 135.3, 111.0, 85.1, 85.0, 80.8, 74.2, 63.7, 42.7, 37.9, 36.0, 32.3, 31.7, 29.2, 29.1, 26.0, 23.9, 22.6, 14.1, 12.6, 12.5, -5.4, -5.5; HRMS (ESI) : Calcd. for $C_{28}H_{48}N_2O_7SiNa$ $[M+Na]^+$ 575.3123, found 575.3128.

Diketone 11aB

Synthesized according to the general procedure **E** from **7a** (165 mg, 0.41 mmol), **10B** (58 mg, 0.28 mmol), catalyst **T** (21 mg, 0.08 mmol) and DBU (12 µL, 0.08 mmol) in THF (0.8 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a yellow gum (98 mg, 61%).

Rf = 0.5 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3188, 3052, 2958, 2927, 2857, 1701, 1687, 1467, 1408, 1359, 1324, 1272, 1255, 1196, 1122, 1081, 1004, 955, 938, 837, 777, 715, 669, 603, 561, 488; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.57 (s, 1H), 7.46 (d, *J* = 1.2 Hz, 1H), 6.28 (dd, *J* = 5.4, 8.7 Hz, 1H), 4.23 - 4.02 (m, 4H), 3.82 (ddd, *J* = 2.4, 11.4, 25.2 Hz, 2H), 2.77 - 2.56 (m, 4H), 2.49 - 2.33 (m, 3H), 1.99 - 1.89 (m, 1H), 1.87 (d, *J* = 0.9 Hz, 3H), 1.57 - 1.45 (m, 2H), 1.34-1.07 (m, 12H), 0.87 (s, 9H), 0.86 - 0.76 (m, 3H), 0.06 (d, *J* = 2.1 Hz, 6H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 209.5, 207.0, 164.1, 150.6, 135.4, 111.0, 85.1, 85.0, 80.8, 74.2, 63.7, 42.7, 37.8, 36.0, 32.3, 31.9, 29.4, 29.3, 29.2, 26.0, 23.9, 22.7, 18.4, 14.2, 12.6, -5.4, -5.5; HRMS (ESI) : Calcd. for $C_{30}H_{52}N_2O_7SiNa$ $[M+Na]^+$ 603.3436, found 603.3443.

Diketone 11aC

Synthesized according to the general procedure **E** from **7a** (295 mg, 0.74 mmol), **10C** (104 mg, 0.49 mmol), catalyst **T** (37 mg, 0.15 mmol) and DBU (21 µL, 0.15 mmol) in THF (1.4 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 50/50) to afford the title compound as a yellow gum (189 mg, 63%).

Rf = 0.5 (Pentane/EtOAC 50/50); IR (ATR) ν_{max} (cm^{-1}) 3186, 3055, 2926, 2856, 1689, 1465, 1403, 1367, 1323, 1277, 1256, 1200, 1125, 1079, 1002, 960, 935, 883, 834, 779, 722, 672, 606, 558, 490; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.70 (s, 1H), 7.45 (d, *J* = 0.9 Hz, 1H), 6.27 (dd, *J* = 5.4, 8.4 Hz, 1H), 4.23 - 4.03 (m, 4H), 3.81 (ddd, *J* = 2.7, 11.4, 24.6 Hz, 2H), 2.76 - 2.56 (m, 4H), 2.48 - 2.33 (m, 3H), 1.98 - 1.86 (m, 1H), 1.86 (d, *J* = 0.6 Hz, 3H), 1.57 - 1.44 (m, 2H), 1.27-1.11 (m, 16H), 0.86 (s, 9H), 0.85 - 0.74 (m, 3H), 0.05 (d, *J* = 1.8 Hz, 6H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 209.4, 206.9, 164.1, 150.6, 135.3, 110.9, 85.1, 85.0, 80.8, 74.2, 63.7, 42.6, 37.8, 35.9, 32.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.9, 23.8, 22.7, 18.3, 14.1, 12.5, -5.4, -5.5; HRMS (ESI) : Calcd. for $C_{32}H_{56}N_2O_7SiNa$ $[M+Na]^+$ 631.3749, found 631.3754.

Diketone 11bB

Synthesized according to the general procedure **E** from **7b** (196 mg, 0.44 mmol), **10B** (54 mg, 0.30 mmol), catalyst **T** (22 mg, 0.09 mmol) and DBU (13 µL, 0.09 mmol) in THF (0.8 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 60/40) to afford the title compound as a yellow gum (92 mg, 50%).

Rf = 0.3 (Pentane/EtOAC 60/40); IR (ATR) ν_{max} (cm^{-1}) 3421, 3188, 3065, 2927, 2866, 1692, 1466, 1404, 1370, 1325, 1275, 1200, 1126, 1105, 1068, 998, 961, 920, 883, 804, 780, 721, 685, 558, 492; ^{1}H-NMR (300 MHz, C_6D_6, 353 K) δ (ppm) 8.88-8.63 (m, 1H), 7.13-7.08 (m, 1H), 6.30-6.22 (m, 1H), 4.15-4.09 (m, 1H), 4.08-4.03 (m, 1H), 3.88-3.83 (m, 2H), 3.83-3.73 (m, 2H), 2.48 -2.38 (m, 4H), 2.30 (ddd, *J* = 2.4, 5.9, 13.7 Hz, 1H), 2.15 (t, *J* = 7.3 Hz, 2H), 1.94-1.80 (m, 4H), 1.60-1.47 (m, 2H), 1.37-1.17 (m, 12H), 1.09-1.01 (m, 21H), 0.93-0.86 (m, 3H); ^{13}C-NMR (75.5 MHz, C_6D_6, 353 K) δ (ppm) 207.7, 206.0, 163.3, 150.5, 135.2, 110.8, 85.9, 85.5, 80.7, 74.7, 64.3, 42.8, 38.0, 36.1, 32.7, 32.3, 29.8, 29.8, 29.6, 24.3, 23.0, 18.2, 14.1, 12.5, 12.3; HRMS (ESI) : Calcd. for $C_{33}H_{58}N_2O_7SiNa$ $[M+Na]^+$ 645.39055, found 645.3903.

Diketone 13C

Synthesized according to the general procedure **E** from **9** (396 mg, 0.76 mmol), **10C** (106 mg, 0.51 mmol), catalyst **T** (38 mg, 0.15 mmol) and DBU (21 µL, 0.15 mmol) in THF (1.4 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 60/40) to afford the title compound as a yellow gum as a non separable mixture with an impurity. Yield was based on ^{1}H NMR spectra. Compound **13C** was submitted to subsequent Paal-Knorr reaction without further purification.

Synthesis of pyrrole-based nucleolipids

General procedure F for Paal-Knorr pyrrole synthesis

A solution of the 1,4-diketone (1 eq.) in THF (0.6 M) was poured into a Schlenk tube containing activated molecular sieves (3Å) under argon atmosphere. Propylamine (3 eq.) was added to the reaction mixture followed by a solution of PTSA monohydrate (2 eq.) in ethanol (1.1 M) and the reaction mixture was stirred at 70°C during 5-8h. After complete consumption of the diketone (TLC control), water was added and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (Pentane/EtOAc).

Compound 15A

Synthesized according to the general procedure **F** from **12A** (81 mg, 0.12 mmol), propylamine (30 µL, 0.36 mmol) and monohydrated PTSA (46 mg, 0.24 mmol) in THF/EtOH (1/1, 0.4 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (37 mg, 44%).

Rf = 0.3 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3183, 3059, 2956, 2929, 2857, 1685, 1503, 1466, 1429, 1401, 1363, 1275, 1248, 1197, 1105, 1065, 1023, 966, 894, 855, 823, 796, 771, 740, 703, 645, 611, 559, 539, 508, 489 ; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.83 (s, 1H), 7.64 ï 7.59 (m, 4H), 7.48 ï 7.34 (m, 7H), 6.46 (dd, *J* = 5.8, 7.9 Hz, 1H), 5.95 (d, *J* = 3.5 Hz, 1H), 5.79 (d, *J* = 3.5 Hz, 1H),

4.36 ï 4.17 (m, 3H), 4.04 ï 4.00 (m, 1H) 3.63 ï 3.54 (m, 2H), 3.40 (dd, *J* = 2.5, 10.7, 1H), 3.00 (dd, *J* = 2.9, 10.7 Hz, 1H), 2.44 (appearing t, *J* = 7.4, 8.2, 2H), 2.33 (ddd, *J* = 2.4, 5.8, 13.3 Hz, 1H), 1.92 ï 1.82 (m, 1H) 1.72 (d, *J* = 1 Hz, 3H) 1.68 ï 1.45 (m, 4H), 1.45 ï 1.20 (m, 8H), 1.08 (s, 9H), 1.95 ï 0.85 (m, 3H), 0.78 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.9, 150.5, 136.0, 135.9, 135.8, 135.3, 133.4, 133.2, 130.2, 128.0, 126.5, 111.0, 109.9, 104.3, 86.7, 85.0, 74.0, 68.9, 65.4, 45.3, 41.2, 31.9, 29.8, 29.7, 29.3, 27.0, 26.6, 24.7, 22.8, 19.1, 14.2, 12.5, 11.4; HRMS (ESI) : Calcd. for $C_{41}H_{57}N_3O_5NaSi$ $[M+Na]^+$ 722.39597, found 729.3962.

Compound 15B

Synthesized according to the general procedure **F** from **12B** (55 mg, 0.078 mmol), propylamine (19 µL, 0.23 mmol) and monohydrated PTSA (27 mg, 0.16 mmol) in THF/EtOH (1/1, 0.3 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (38 mg, 67%).

Rf = 0.4 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3180, 3052, 2956, 2928, 2856, 1686, 1590, 1503, 1466, 1429, 1401, 1364, 1275, 1247, 1199, 1106, 1065, 1026, 965, 911, 895, 854, 823, 737, 702, 647, 611, 558, 539, 507, 489 ; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.76 (s, 1H), 7.67 ï 7.56 (m, 4H), 7.49 ï 7.30 (m, 7H), 6.46 (dd, *J* = 5.9, 7.9 Hz, 1H), 5.94 (d, *J* = 3.5 Hz, 1H), 5.79 (d, *J* = 3.4 Hz, 1H), 4.36 ï 4.16 (m, 3H), 4.04 ï 3.99 (m, 1H) 3.66 ï 3.53 (m, 2H), 3.40 (dd, *J* = 2.5, 10.8, 1H), 2.99 (dd, *J* = 2.8, 10.7 Hz, 1H), 2.43 (appearing t, *J* = 7.5, 8.1, 2H), 2.28 (ddd, *J* = 2.3, 5.9, 13.4 Hz, 1H), 1.93 ï 1.76 (m, 2H) 1.72 (d, *J* = 0.7 Hz, 3H) 1.67 ï 1.47 (m, 4H), 1.43 ï 1.18 (m, 12H), 1.07 (s, 9H), 1.92 ï 0.85 (m, 3H), 0.78 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.9, 150.5, 136.1, 135.9, 135.8, 135.3, 133.3, 133.2, 130.2, 128.0, 126.4, 111.0, 109.9, 104.3, 86.7, 85.0, 74.0, 68.9, 65.3, 45.3, 41.2, 32.0, 29.8, 29.7, 29.6, 29.5, 28.7, 27.0, 26.6, 24.7, 22.8, 19.1, 14.3, 12.5, 11.4; HRMS (ESI) : Calcd. for $C_{43}H_{61}N_3O_5NaSi$ $[M+Na]^+$ 750.42727, found 750.4271.

Compound 15C

Synthesized according to the general procedure **F** from **12C** (36 mg, 0.05 mmol), propylamine (12 µL, 0.15 mmol) and monohydrated PTSA (17 mg, 0.1 mmol) in THF/EtOH (1/1, 0.2 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (28 mg, 74%).

Rf = 0.5 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3181, 3052, 2927, 2856, 1686, 1590, 1504, 1467, 1428, 1364, 1275, 1247, 1199, 1106, 1065, 1026, 966, 910, 855, 823, 767, 733, 702, 647, 611, 558, 539, 507, 488 ; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.60 ï 8.52 (m, 1H), 7.64 ï 7.57 (m, 4H), 7.49 ï 7.34 (m, 7H), 6.46 (dd, *J* = 5.9, 7.9 Hz, 1H), 5.94 (d, *J* = 3.4 Hz, 1H), 5.78 (d, *J* = 3.4 Hz, 1H), 4.35 ï 4.17 (m, 3H), 4.04 ï 3.99 (m, 1H), 3.63 ï 3.53 (m, 2H), 3.39 (dd, *J* = 2.4, 10.7, 1H), 2.99 (dd, *J* = 2.8, 10.7 Hz, 1H), 2.44 (appearing t, *J* = 7.5, 8.0, 2H), 2.28 (ddd, *J* = 2.3, 5.9, 13.4 Hz, 1H), 1.92 ï 1.82 (m, 1H), 1.72 (s, 3H), 1.67 ï 1.46 (m, 4H), 1.42 ï 1.16 (m, 16H), 1.07 (s, 9H), 0.91 ï 0.84 (m,

3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.8, 150.4, 136.1, 135.9, 135.8, 135.3, 133.4, 133.2, 130.2, 128.0, 128.0, 126.4, 111.0, 109.9, 104.3, 86.7, 85.0, 74.0, 68.9, 65.4, 45.3, 41.2, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 28.7, 27.0, 26.6, 24.8, 22.8, 19.1, 14.3, 14.3, 14.2, 12.5, 11.4; HRMS (ESI) : Calcd. for $C_{45}H_{65}N_3O_5NaSi$ $[M+Na]^+$ 778.45857, found 778.4595.

Compound 15D

Synthesized according to the general procedure **F** from **12C** (79 mg, 0.10 mmol), propylamine (24 µL, 0.29 mmol) and monohydrated PTSA (37 mg, 0.19 mmol) in THF/EtOH (1/1, 0.3 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (44 mg, 54%).

Rf = 0.4 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3184, 3052, 3004, 2928, 2856, 1691, 1466, 1429, 1365, 1275, 1200, 1111, 1066, 1030, 894, 855, 824, 741, 704, 612, 558, 508, 490 ; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.64 (s, 1H), 7.64 ï 7.58 (m, 4H), 7.48 ï 7.34 (m, 7H), 6.45 (dd, *J* = 5.9, 7.7 Hz, 1H), 5.94 (d, *J* = 3.5 Hz, 1H), 5.78 (d, *J* = 3.4 Hz, 1H), 5.41 ï 5.29 (m, 2H), 4.36 ï 4.17 (m, 3H), 4.04 ï 3.99 (m, 1H), 3.72 (q, *J* = 7.0 Hz, 1H), 3.63 ï 3.53 (m, 2H), 3.39 (dd, *J* = 2.3, 10.7, 1H), 3.00 (dd, *J* = 2.8, 10.7 Hz, 1H), 2.44 (appearing t, *J* = 7.5, 8.0, 2H), 2.28 (ddd, *J* = 2.3, 5.8, 13.4 Hz, 1H), 2.07 ï 1.97 (m, 4H), 1.93 ï 1.82 (m, 1H), 1.78 ï 1.68 (m, 4H), 1.67 ï 1.47 (m, 4H), 1.43 ï 1.21 (m, 18H), 1.07 (s, 9H), 0.92 ï 0.85 (m, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.8, 150.4, 136.1, 135.9, 135.8, 135.2, 133.4, 133.2, 130.2, 130.1, 129.9, 128.0, 126.5, 111.0, 109.9, 104.3, 86.7, 85.0, 74.0, 68.9, 65.4, 58.6, 45.3, 41.2, 32.0, 29.9, 29.8, 29.8, 29.7, 29.6, 29.4, 29.4, 28.7, 27.3, 27.0, 26.6, 24.7, 22.8, 19.1, 18.6, 14.2, 12.5, 11.4; HRMS (ESI) : Calcd. for $C_{51}H_{75}N_3O_5NaSi$ $[M+Na]^+$ 860.53682, found 860.5366.

Compound 14A

Synthesized according to the general procedure **F** from **11aA** (82 mg, 0.16 mmol), propylamine (39 µL, 0.47 mmol) and monohydrated PTSA (54 mg, 0.31 mmol) in THF/EtOH (1/1, 0.6 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (46 mg, 51%).

Rf = 0.4 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3184, 3055, 2956, 2929, 2858, 1691, 1503, 1466, 1432, 1404, 1362, 1322, 1274, 1257, 1199, 1129, 1088, 1033, 960, 931, 886, 835, 779, 672, 605, 558, 491; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.22 (s, 1H), 7.50 ï 7.48 (m, 1H), 6.30 (dd, *J* = 5.6, 7.6 Hz, 1H), 6.02 (d, *J* = 3.5 Hz, 1H), 5.80 (d, *J* = 3.5 Hz, 1H), 4.45 (dd, *J* = 12.8, 26.8 Hz, 2H), 4.12 ï 4.07 (m, 1H), 4.00 ï 3.96 (m, 1H), 3.86 ï 3.61 (m, 4H), 2.50 (appearing t, *J* = 7.5, 8.0, 2H), 2.33 (ddd, *J* = 1.5, 5.6, 13.4 Hz, 1H), 1.96 ï 1.85 (m, 4H), 1.74 ï 1.58 (m, 4H), 1.43 ï 1.20 (m, 8H), 1.00 ï 0.84 (m, 15H), 0.08 ï 0.07 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 164.1, 150.5, 135.6, 135.5, 126.4, 110.9, 109.9, 104.4, 82.2, 85.2, 63.7, 63.4, 58.5, 45.5, 38.2, 31.9, 29.8, 29.7, 29.3, 28.8,

26.6, 26.0, 24.8, 22.8, 18.5, 18.5, 14.2, 12.6, 11.5, -5.29, -5.39; HRMS (ESI) : Calcd. for $C_{31}H_{53}N_3O_5NaSi$ $[M+Na]^+$ 598.36467, found 598.3652.

Compound 14B

Synthesized according to the general procedure **F** from **11aB** (80 mg, 0.17 mmol), propylamine (42 µL, 0.51 mmol) and monohydrated PTSA (58 mg, 0.34 mmol) in THF/EtOH (1/1, 0.6 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 70/30) to afford the title compound as a slightly orange gum (54 mg, 53%).

Rf = 0.5 (Pentane/EtOAC 70/30); IR (ATR) ν_{max} (cm^{-1}) 3183, 3053, 2954, 2927, 2857, 2857, 1686, 1504, 1465, 1432, 1403, 1361, 1322, 1273, 1257, 1199, 1128, 1087, 1070, 1032, 960, 930, 886, 835, 779, 671, 629, 604, 558, 489; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.47 ï 9.16 (brs, 1H), 7.50 ï 7.48 (m, 1H), 6.30 (dd, *J* = 5.6, 8.5 Hz, 1H), 6.01 (d, *J* = 3.4 Hz, 1H), 5.80 (d, *J* = 3.4 Hz, 1H), 4.45 (dd, *J* = 12.7, 27.3 Hz, 2H), 4.12 ï 4.07 (m, 1H), 4.00 ï 3.96 (m, 1H), 3.86 ï 3.60 (m, 4H), 2.50 (appearing t, *J* = 7.6, 7.9, 2H), 2.33 (ddd, *J* = 1.4, 5.6, 13.4 Hz, 1H), 1.96 ï 1.85 (m, 4H), 1.74 ï 1.57 (m, 4H), 1.44 ï 1.19 (m, 12H), 0.99 ï 0.83 (m, 15H), 0.08 ï 0.07 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 164.1, 150.5, 135.6, 135.6, 135.5, 126.4, 110.9, 109.9, 104.4, 85.2, 85.2, 63.7, 63.4, 58.5, 45.5, 38.2, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 28.9, 26.6, 26.0, 24.8, 22.8, 18.5, 18.4, 14.2, 12.6, 11.5, -5.3, -5.4; HRMS (ESI) : Calcd. for $C_{33}H_{57}N_3O_5NaSi$ $[M+Na]^+$ 626.39597, found 626.3962.

Compound 14C

Synthesized according to the general procedure **F** from **11aC** (116 mg, 0.19 mmol), propylamine (47 µL, 0.57 mmol) and monohydrated PTSA (72 mg, 0.38 mmol) in THF/EtOH (1/1, 0.7 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (72 mg, 60%).

Rf = 0.4 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3183, 3057, 2955, 2929, 2858, 1690, 1466, 1362, 1274, 1257, 1200, 1129, 1086, 1033, 930, 836, 779,557, 491; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.42 (s, 1H), 7.51 ï 7.47 (m, 1H), 6.30 (dd, *J* = 5.5, 8.5 Hz, 1H), 6.02 (d, *J* = 3.4 Hz, 1H), 5.80 (d, *J* = 3.5 Hz, 1H), 4.45 (dd, *J* = 12.7, 27.6 Hz, 2H), 4.13 ï 4.08 (m, 1H), 4.01 ï 3.97 (m, 1H), 3.87 ï 3.61 (m, 4H), 2.50 (appearing t, *J* = 7.5, 8.0, 2H), 2.34 (ddd, *J* = 1.5, 5.6, 13.4 Hz, 1H), 1.96 ï 1.84 (m, 4H), 1.75 ï 1.56 (m, 4H), 1.44 ï 1.18 (m, 16H), 1.00 ï 0.82 (m, 15H), 0.08 ï 0.07 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.6, 150.2, 135.7, 135.6, 126.4, 110.9, 109.9, 104.4, 85.3, 85.2, 63.8, 63.5, 45.6, 38.2, 32.0, 29.7, 29.3, 28.9, 26.6, 26.1, 24.9, 22.8, 18.5, 14.3, 12.7, 11.6, -5.2, -5.3; HRMS (ESI) : Calcd. for $C_{35}H_{61}N_3O_5NaSi$ $[M+Na]^+$ 654.42627, found 654.4271.

Compound 16C

Synthesized according to the general procedure **F**, **13C** was used as a non pure mixture (0.05 mmol), propylamine (13 µL, 0.16 mmol) and monohydrated PTSA (20 mg, 0.11 mmol) in THF/EtOH (1/1, 0.5 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 80/20) to afford the title compound as a slightly orange gum (23 mg, 57% (12% over two steps from aldehyde **9)**).

Rf = 0.3 (Pentane/EtOAC 80/20); IR (ATR) ν_{max} (cm^{-1}) 3463, 3073, 2927, 2856, 1700, 1667, 1639, 1464, 1429, 1367, 1346, 1296, 1274, 1240, 1293, 1104, 1065, 1024, 1002, 958, 941, 916, 896, 878, 823, 770, 740, 703, 652, 610, 546, 508, 489; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.68 ï 7.60 (m, 4H), 7.50 ï 7.36 (m, 6H), 7.23 ï 7.20 (m, 1H), 6.26 ï 6.18 (m, 2H), 5.81 (d, *J* = 3.6 Hz, 1H), 5.09 ï 5.05 (m, 2H), 4.47 ï 4.41 (m, 1H), 4.06 ï 3.98 (m, 2H), 3.98 ï 3.93 (m, 1H), 3.65 ï 3.56 (m, 1H), 3.26 ï 3.16 (m, 1H), 2.48 (appearing t, *J* = 7.5, 8.2, 2H), 2.32 ï 2.09 (m, 3H), 1.8- (d, *J* = 1.0 Hz, 3H), 1.70 ï 1.53 (m, 4H), 1.44 ï 1.19 (m, 16H), 1.09 (s, 9H), 0.98 ï 0.85 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.3, 151.0, 135.9, 135.8, 134.9, 133.5, 133.5, 133.3, 130.3, 130.2, 128.0, 126.5, 110.4, 109.4, 104.7, 87.8, 87.7, 73.1, 62.3, 45.1, 40.4, 36.6, 32.0, 29.8, 29.8, 29.7, 29.7, 29.5, 28.8, 27.0, 26.8, 25.3, 22.8, 19.2, 14.2, 13.4, 11.4; HRMS (ESI) : Calcd. for $C_{45}H_{65}N_3O_5NaSi$ $[M+Na]^+$ 778.45857, found 778.4586.

General procedure G for silyl ethers deprotection

TBAF (1 eq, 1 M in THF solution) was added to a stirred solution of the silylated compound (1 eq) in THF (0.09 mol/L) at 0°C and stirred at this temperature to completion (TLC control). The reaction was then quenched with water and DCM was added. The aqueous layer was extracted three times with DCM and the combined organic extracts were dried over Na_2SO_4. Concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (Pentane/EtOAc).

Compound 18A

Synthesized according to the general procedure **G** from **15A** (31 mg, 0.04 mmol) and TBAF (1M in THF, 44 µL, 0.04 mmol) in THF (0.5 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a slightly orange gum (15 mg, 73%).

Rf = 0.2 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3429, 3182, 3064, 2961, 2928, 2857, 1688, 1469, 1366, 1274, 1201, 1096, 1058, 1018, 959, 752, 558, 475; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.91 (s, 1H), 7.57 ï 7.51 (m, 1H), 6.34 (t, *J* = 6.6 Hz, 1H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.82 (d, *J* = 3.3 Hz, 1H), 4.49 (dd, *J* = 12.5, 26.9 Hz, 2H), 4.40 ï 4.31 (m, 1H) 4.08 ï 3.99 (m, 1H), 3.82 ï 3.57 (m, 4H), 2.68 ï 2.55 (brs, 1H), 2.50 (appearing t, *J* = 7.6, 8.0 Hz, 2H), 2.39 ï 2.27 (m, 1H), 2.21 ï 2.08 (m,

1H), 1.85 ï 1.56 (m, 7H), 1.45 ï 1.17 (m, 8H), 0.99 ï 0.76 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.9, 150.5, 136.0, 135.6, 126.5, 111.1, 110.1, 104.5, 85.9, 85.0, 72.3, 69.0, 65.6, 45.5, 40.8, 31.9, 29.8, 29.7, 29.3, 28.8, 26.7, 24.9, 22.8, 14.2, 12.6, 11.6; HRMS (ESI) : Calcd. for $C_{25}H_{39}N_3O_5Na$ $[M+Na]^+$ 484.27819, found 484.2785.

Compound 18B

Synthesized according to the general procedure **G** from **15B** (30 mg, 0.04 mmol) and TBAF (1M in THF, 40 µL, 0.04 mmol) in THF (0.5 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as an orange gum (14 mg, 69%).

Rf = 0.2 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3420, 3188, 3062, 2926, 2855, 1688, 1468, 1431, 1365, 1274, 1201, 1095, 1059, 1018, 963, 888, 752, 618, 560, 493; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.91 (s, 1H), 7.54 ï 7.52 (m, 1H), 6.35 (t, *J* = 6.6 Hz, 1H), 6.07 (d, *J* = 3.5 Hz, 1H), 5.82 (d, *J* = 3.4 Hz, 1H), 4.49 (dd, *J* = 12.5, 27.0 Hz, 2H), 4.41 ï 4.33 (m, 1H) 4.07 ï 4.01 (m, 1H), 3.80 ï 3.73 (m, 2H), 3.72 ï 3.60 (m, 2H), 2.60 ï 2.54 (m, 1H), 2.50 (appearing t, *J* = 7.6, 8.0 Hz, 2H), 2.32 (ddd, *J* = 3.6, 6.1, 13.6 Hz, 1H), 2.19 ï 2.08 (m, 1H), 1.81 ï 1.76 (m, 3H) 1.73 ï 1.57 (m, 4H) 1.44 ï 1.20 (m, 12H), 0.97 ï 0.82 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.9, 150.5, 136.0, 135.6, 126.5, 111.1, 110.1, 104.4, 85.9, 85.0, 72.3, 69.0, 65.6, 45.5, 40.8, 32.0, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 28.8, 26.7, 24.9, 22.8, 14.3, 12.6, 11.6; HRMS (ESI) : Calcd. for $C_{27}H_{43}N_3O_5Na$ $[M+Na]^+$ 512.30949, found 512.3096.

Compound 18C

Synthesized according to the general procedure **G** from **15C** (28 mg, 0.04 mmol) and TBAF (1M in THF, 37 µL, 0.04 mmol) in THF (0.4 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a slightly orange gum (14 mg, 73%).

Rf = 0.3 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3420, 3188, 3062, 2926, 2855, 1688, 1468, 1431, 1365, 1274, 1201, 1095, 1059, 1018, 963, 888, 752, 618, 560, 493; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.36 (s, 1H), 7.54 ï 7.51 (m, 1H), 6.33 (t, *J* = 6.6 Hz, 1H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.82 (d, *J* = 3.4 Hz, 1H), 4.50 (dd, *J* = 12.6, 29.1 Hz, 2H), 4.39 ï 4.34 (m, 1H), 4.05 ï 4.00 (m, 1H), 3.81 ï 3.73 (m, 2H), 3.72 ï 3.59 (m, 2H), 2.50 (appearing t, *J* = 7.6, 8.0, 2H), 2.36 - 2.27 (m, 1H), 2.20 ï 2.05 (m, 2H), 1.82 ï 1.76 (m, 3H), 1.74 ï 1.56 (m, 4H), 1.34 ï 1.19 (m, 16H), 0.97 ï 0.84 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 164.1, 150.7, 136.1, 135.5, 126.6, 111.1, 110.0, 104.4, 86.0, 85.0, 72.2, 69.1, 65.6, 58.5, 45.4, 40.8, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 28.8, 26.7, 24.9, 22.8, 18.5, 14.2, 12.5, 11.5; HRMS (ESI) : Calcd. for $C_{29}H_{47}N_3O_5Na$ $[M+Na]^+$ 540.34079, found 540.3409.

Compound 18D

Synthesized according to the general procedure **G** from **15B** (33 mg, 0.04 mmol) and TBAF (1M in THF, 36 µL, 0.04 mmol) in THF (0.4 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a slightly orange gum (15 mg, 63%).

Rf = 0.3 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3407, 3191, 3121, 3050, 2924, 2854, 1725, 1656, 1469, 1432, 1363, 1275, 1203, 1114, 1085, 1052, 1019, 963, 890, 748, 659, 608, 555; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.89 (s, 1H), 7.55 ï 7.51 (m, 1H), 6.34 (t, *J* = 6.6 Hz, 1H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.82 (d, *J* = 3.4 Hz, 1H), 5.40 ï 5.29 (m, 2H), 4.49 (dd, *J* = 12.6, 27.6 Hz, 2H), 4.40 ï 4.33 (m, 1H), 4.08 - 4.00 (m,1H), 3.83 ï 3.58 (m, 5H), 2.70 ï 2.57 (m, 1H), 2.49 (appearing t, *J* = 7.6, 7.9, 2H), 2.37 ï 2.27 (m, 1H), 2.21 - 2.08 (m, 1H), 2.06 ï 1.96 (m, 5H), 1.83 ï 1.75 (m, 3H), 1.73 ï 1.57 (m, 4H), 1.39 ï 1.21 (m, 24H), 0.97 ï 0.84 (m, 6H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.8, 150.5, 136.0, 135.5, 130.2, 129.9, 126.6, 111.1, 110.1, 104.4, 85.8, 85.0, 72.2, 69.0, 65.6, 58.6, 45.5, 40.8, 32.0, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 27.3, 26.7, 24.9, 22.8, 18.5, 14.2, 12.6, 11.6; HRMS (ESI) : Calcd. for $C_{35}H_{57}N_3O_5Na$ $[M+Na]^+$ 622.41904, found 622.4193.

Compound 17A

Synthesized according to the general procedure **G** from **14A** (46 mg, 0.08 mmol) and TBAF (1M in THF, 80 µL, 0.08 mmol) in THF (0.9 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as an orange gum (22 mg, 60%).

Rf = 0.3 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3423, 3185, 3059, 2953, 2927, 2856, 1683, 1507, 1468, 1431, 1366, 1324, 1274, 1201, 1101, 1060, 1033, 958, 908, 753, 735, 645, 609, 559, 491; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.29 (s, 1H), 7.39 ï 7.37 (m, 1H), 6.13 (t, *J* = 6.9 Hz, 1H), 6.04 (d, *J* = 3.3 Hz, 1H), 5.81 (d, *J* = 3.3 Hz, 1H), 4.46 (dd, *J* = 12.6, 18.3 Hz, 2H), 4.26 ï 4.19 (m, 1H), 4.02 ï 3.96 (m, 1H), 3.91 ï 3.57 (m, 4H), 2.86 (brs, 1H), 2.50 (t, *J* = 7.8 Hz, 2H), 2.34 ï 2.18 (m, 2H), 1.89 (s, 3H), 1.76 ï 1.57 (m, 4H), 1.45 ï 1.20 (m, 8H), 0.95 (appearing t, *J* = 7.2, 7.5 Hz, 3H), 0.88 (appearing t, *J* = 6.0, 7.2 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 164.1, 150.5, 137.0, 135.7, 126.6, 111.1, 109.8, 104.4, 86.9, 85.1, 77.4, 77.0, 63.8, 62.6, 45.5, 37.4, 31.9, 29.7, 29.3, 28.8, 26.6, 24.8, 22.8, 14.2, 12.6, 11.5; HRMS (ESI) : Calcd. for $C_{25}H_{39}N_3O_5Na$ $[M+Na]^+$ 484.27819, found 484.2784.

Compound 17B

Synthesized according to the general procedure **G** from **14B** (54 mg, 0.09 mmol) and TBAF (1M in THF, 89 µL, 0.09 mmol) in THF (1 mL). The crude product was then purified by flash

chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as an orange gum (26 mg, 59%).

Rf = 0.3 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3422, 3188, 3060, 2926, 2855, 1690, 1468, 1432, 1366, 1275, 1201, 1103, 1061, 1037, 959, 895, 755, 609, 560, 492; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.00 (s, 1H), 7.37 (d, *J* = 1.2 Hz, 1H), 6.12 (t, *J* = 6.9 Hz, 1H), 6.05 (d, *J* = 3.6 Hz, 1H), 5.81 (d, *J* = 3.6 Hz, 1H), 4.46 (q, *J* = 12.6 Hz, 2H), 4.25 ï 4.19 (m, 1H), 4.02 ï 3.96 (m, 1H), 3.89 ï 3.59 (m, 4H), 2.75 ï 2.59 (brs, 1H), 2.51 (appearing t, *J* = 7.5, 8.1 Hz, 2H), 2.31 ï 2.23 (m, 2H), 1.89 (d, *J* = 0.9 Hz, 3H), 1.76 ï 1.56 (m, 4H), 1.45 ï 1.20 (m, 12H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.91-0.84 (m, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.9, 150.5, 137.0, 135.8, 126.6, 111.2, 109.9, 104.4, 87.0, 85.1, 77.4, 77.0, 63.8, 62.7, 58.6, 45.6, 37.4, 32.0, 29.8, 29.7, 29.7, 29.6, 29.4, 28.9, 26.6, 24.9, 22.8, 18.5, 14.2, 12.6, 11.6; HRMS (ESI) : Calcd. for $C_{27}H_{43}N_3O_5Na$ $[M+Na]^+$ 512.30949, found 512.3093.

Compound 17C

Synthesized according to the general procedure **G** from **14C** (72 mg, 0.11 mmol) and TBAF (1M in THF, 114 µL, 0.11 mmol) in THF (1.3 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a slightly orange gum (37 mg, 63%).

Rf = 0.4 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3423, 3187, 3059, 2926, 2855, 1695, 1469, 1432, 1366, 1276, 1202, 1104, 1060, 1039, 959, 896, 754, 609, 561, 491; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.31 (s, 1H), 7.39 (s, 1H), 6.13 (t, *J* = 7.0 Hz, 1H), 6.04 (d, *J* = 3.5 Hz, 1H), 5.81 (d, *J* = 3.4 Hz, 1H), 4.46 (q, *J* = 12.6 Hz, 2H), 4.26 ï 4.19 (m, 1H), 4.02 ï 3.97 (m, 1H), 3.89 ï 3.60 (m, 4H), 2.96 ï 2.80 (brs, 1H), 2.50 (appearing t, *J* = 7.6, 7.9, 2H), 2.34 ï 2.16 (m, 2H), 1.89 (s, 3H), 1.78 ï 1.55 (m, 4H), 1.45 ï 1.18 (m, 16H), 0.9 ((t, *J* = 7.5 Hz, 3H), 0.87 ((t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 164.1, 150.5, 137.0, 135.7, 126.6, 111.1, 109.8, 104.4, 86.9, 85.1, 77.4, 77.0, 63.8, 62.6, 45.5, 37.4, 32.0, 29.8, 29.7, 29.6, 29.4, 28.8, 26.6, 24.8, 22.8, 14.2, 12.6, 11.5; HRMS (ESI) : Calcd. for $C_{29}H_{47}N_3O_5Na$ $[M+Na]^+$ 540.34079, found 540.3412.

Compound 19C

Synthesized according to the general procedure **G** from **16C** (20 mg, 0.03 mmol) and TBAF (1M in THF, 26 µL, 0.03 mmol) in THF (0.3 mL). The crude product was then purified by flash chromatography over silica gel (Pentane/EtOAc 40/60) to afford the title compound as a slightly orange gum (10 mg, 73%).

Rf = 0.2 (Pentane/EtOAC 40/60); IR (ATR) ν_{max} (cm^{-1}) 3422, 3080, 2956, 2924, 1699, 1666, 1634, 1465, 1345, 1272, 1097, 918, 767, 546,; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.31 (d, *J* = 0.9 Hz, 1H), 6.22 ï 6.13 (m, 2H), 5.80 (d, *J* = 3.6 Hz, 1H), 5.08 (s, 2H), 4.61 ï 4.51 (m, 1H), 4.09 ï 3.94 (m, 3H), 3.85 (ddd, *J* = 3, 12, 29.1, 2H), 3.72 (q, *J* = 7.1, 1H), 2.54-2.22 (m, 5H), 1.91 (d, *J* = 0.9 Hz, 3H),

1.75 (brs, 2H), 1.70 ï 1.53 (m, 4H),), 1.45 ï 1.16 (m, 16H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (75,5 MHz, $CDCl_3$) δ (ppm) 163.3, 151.1, 134.9, 133.6, 126.4, 110.6, 109.3, 104.7, 87.6, 86.9, 77.4, 71.6, 62.5, 45.1, 40.2, 36.6, 32.0, 29.8, 29.8, 29.7, 29.7, 29.5, 28.8, 26.8, 25.3, 22.8, 14.3, 13.5, 11.4; HRMS (ESI) : Calcd. for $C_{29}H_{47}N_3O_5NaSi$ $[M+Na]^+$ 540.34079, found 540.3410.

Synthesis of pyrrole-based GlycosideNucleoLipid

3'-Protected GNL 22

K_2CO_3 (50 mg, 0.36 mmol) was added to a stirred solution of **12C** (176 mg, 0.24 mmol) in DMF (2 mL) under an argon atmosphere. Then TBAI (9 mg, 0.024 mmol) was added followed by propargyl bromide (80% in toluene sol., 40µL, 0.36 mmol) and the reaction mixture was stirred at room temperature during 22h. After complete consumption of **12C** (TLC control), the reaction mixture was diluted in EtOAc and washed with water and brine. The organic layer was then dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded **20** as a crude product which was engaged in the CuAAC click reaction without further purification.

It was dissolved in t-BuOH (1.2 mL) and water was added (1.2 mL), followed by 1-azido-1-deoxy-ß-D-glucopyranoside (49 mg, 0.24 mmol). After degassing for 10 minutes at room temperature with argon, the reaction mixture was warmed up at 75°C and pentahydrated $CuSO_4$ (6 mg, 0.024 mmol) was added, followed by sodium ascorbate (10 mg, 0.048 mmol). The reaction medium was stirred overnight at 75°C. After complete conversion of **20** (TLC control), it was allowed to cool down at room temperature and concentration under reduced pressure afforded the crude product which was then purified by flash chromatography over silica gel (DCM/MeOH 95/5) to obtain **22** as a yellow gum. (176 mg, 75% over the two steps).

Rf = 0.3 (DCM/MeOH 95/5); IR (ATR) ν_{max} (cm^{-1}) 3387, 3074, 2926, 2856, 1702, 1665, 1641, 1467, 1428, 1404, 1368, 1273, 1244, 1195, 1093, 1102, 1031, 925, 898, 823, 781, 742, 703, 660, 611, 553, 507, 488, 456; ^{1}H-NMR (300 MHz, $(CD_3)_2CO$) δ (ppm) 8.00 (s, 1H), 7.79 (d, *J* = 1.0 Hz, 1H), 7.74 - 7.67 (m, 4H), 7.53 - 7.41 (m, 6H), 6.56 (dd, *J* = 5.6, 8.6 Hz, 1H), 5.60 (d, *J* = 9.2, 1H), 5.18 (q, *J* = 14.5 Hz, 2H), 4.66 (dd, *J* = 4.7, 21.1 Hz, 1H), 4.45 (brs, 2H) 4.15 (s, 2H) 4.12 - 4.07 (m, 1H), 3.99 (td, *J* = 6.3, 8.9 Hz, 2H) 3.92 - 3.80 (m, 2H), 3.74 - 3.50 (m, 5H), 3.23 (dd, *J* = 2.6, 10.4 Hz, 1H), 2.92 (s, 1H), 2.76 - 2.65 (m, 2H), 2.58 ï 2.50 (m, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 2.29 (ddd, *J* = 1.6, 5.6, 13.2 Hz, 1H), 2.23 - 2.11 (m, 1H), 1.79 (d, *J* = 0.8 Hz, 3H), 1.58 - 1.45 (m, 2H), 1.37-1.21 (m, 16H), 1.11 (s, 9H), 0.94 - 0.81 (m, 3H); ^{13}C-NMR (75.5 MHz, $(CD_3)_2CO$) δ (ppm) 209.3, 206.7, 163.5, 151.6, 144.3, 136.6, 136.6, 135.7, 134.2, 134.1, 131.0, 128.9, 123.2, 110.4, 88.9, 87.3, 86.5, 80.7, 78.5, 76.3, 75.5, 73.5, 71.6, 70.9, 62.4, 42.8, 41.3, 37.0, 36.3, 32.8, 32.6, 30.3, 30.2, 30.1, 27.3, 24.5, 23.3, 19.6, 14.4, 13.2; HRMS (ESI) : Calcd. for $C_{50}H_{72}N_5O_{12}Si$ $[M+H]^+$ 976.50978, found 976.5104.

Deprotected GNL 23

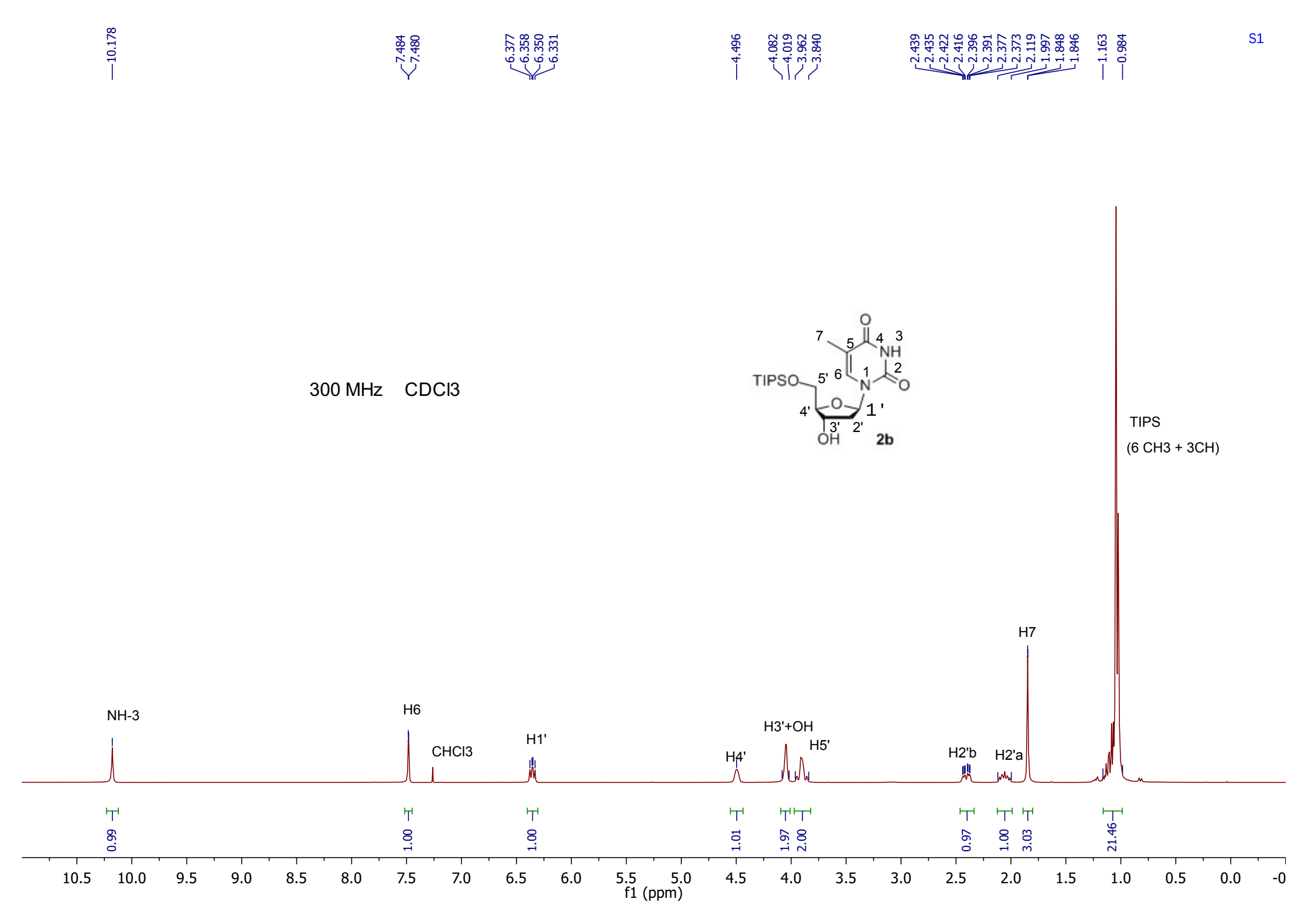
A 1M solution of TBAF in THF (180 µL, 0.18 mmol) was added to a stirred solution of **22** (176 mg, 0.18 mmol) in THF (2 mL) at 0°C and the reaction mixture was stirred at this temperature. After 1h, the medium had become a gel so it was allowed to warm up at room temperature, DCM was added to break the gel and concentration under reduced pressure afforded the crude product. It was purified by flash chromatography over silica gel (DCM/MeOH 95/5 to 90/10) to afford the title compound **23** as a white foam (87 mg, 65%). noter quantité SM récupéré

Rf = 0.4 (DCM/MeOH 90/10); IR (ATR) ν_{max} (cm^{-1}) 3385, 2925, 2855, 1700, 1664, 1638, 1467, 1407, 1371, 1345, 1319, 1271, 1197, 1093, 1076, 1047, 924, 900, 831, 784, 750, 722, 604, 552, 500, 455; ^{1}H-NMR (300 MHz, CD_3OD) δ (ppm) 8.12 (s, 1H), 7.94 (s, 1H), 6.38 (appearing t, *J* = 6.6, 6.9 Hz, 1H), 5.57 (d, *J* = 9.3, 1H), 5.22 (s, 2H), 4.50 - 4.44 (m, 1H), 4.33 (d, *J* = 2.7 Hz, 2H) 4.07 - 4.00 (m, 1H) 3.92 - 3.63 (m, 5H) 3.60 - 3.43 (m, 3H), 3.29 - 3.18 (m, 1H), 2.81 - 2.74 (m, 2H), 2.65 - 2.57 (m, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.30 - 2.20 (m, 2H), 1.87 (s, 3H), 1.74 - 1.34 (m, 4H), 1.37-1.22 (m, 16H), 0.96 - 0.84 (m, 3H); ^{13}C-NMR (75.5 MHz, CD_3OD) δ (ppm) 211.9, 208.3, 164.9, 152.2, 136.8, 110.9, 89.6, 87.6, 87.4, 81.0, 78.4, 76.7, 73.9, 73.0, 72.3, 70.8, 62.4, 59.5, 43.2, 41.2, 37.1, 36.8, 33.1, 33.0, 30.7, 30.6, 30.5, 30.4, 30.2, 24.9, 24.8, 23.7, 20.7, 20.7, 14.4, 13.9, 13.2; HRMS (ESI) : Calcd. for $C_{35}H_{55}N_5O_{12}Na$ $[M+Na]^+$ 760.37394, found 760.3741.

GNL 24

Synthesized according to the general procedure for Paal-Knorr reaction from **23** (74 mg, 0.10 mmol), propylamine (18 mg, 0.30 mmol) and monohydrated PTSA (39 mg, 0.20 mmol) in a 1/1 THF/EtOH mixture (0.4 mL). The crude product was then purified by flash chromatography over silica gel (DCM/MeOH 90/10) to afford the title compound **24** as a white foam (74 mg, 97%).

Rf = 0.3 (DCM/MeOH 90/10); IR (ATR) ν_{max} (cm^{-1}) 3382, 2925, 2855, 1697, 1665, 1635, 1467, 1431, 1352, 1306, 1270, 1196, 1095, 1063, 1022, 923, 899, 827, 783, 749, 671, 640, 602, 549, 490, 515, 456; ^{1}H-NMR (300 MHz, CD_3OD) δ (ppm) 8.10 (s, 1H), 7.76 (d, *J* = 1.2 Hz, 1H), 6.31 (t, *J* = 6.5 Hz, 1H), 6.02 (d, *J* = 3.6 Hz, 1H), 5.75 (d, *J* = 3.6 Hz, 1H), 5.56 (d, *J* = 9.0, 1H), 5.24-5.14 (m, 2H), 4.51 (s, 2H), 4.38 - 4.32 (m, 1H), 4.01 - 3.97 (m, 1H), 3.92 - 3.79 (m, 4H) 3.69 (ddd, *J* = 3.0, 10.8, 23.1 Hz, 3H), 3.43 - 3.59 (m, 4H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.31 - 2.12 (m, 2H), 1.74 - 1.55 (m, 4H), 1.69 (d, *J* = 0.9 Hz, 3H), 1.46-1.23 (m, 20H), 0.96 - 0.85 (m, 6H); ^{13}C-NMR (75.5 MHz, CD_3OD) δ (ppm) 164.9, 152.1, 136.5, 136.1, 128.2, 124.2, 110.8, 105.4, 89.6, 87.4, 87.1, 81.1, 78.4, 73.9, 72.2, 70.9, 70.00, 66.4, 62.4, 46.2, 41.4, 37.1, 33.0, 30.7, 30.6, 30.6, 30.4, 30.1, 27.4, 25.9, 23.7, 14.4, 13.2, 11.6; HRMS (ESI) : Calcd. for $C_{38}H_{60}N_6O_{10}Na$ $[M+Na]^+$ 783.42631, found 783.4267.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2.396
2.391
2.377
2.373
2.119
1.997
1.848
1.846
1.163
0.984
S1
300 MHz CDCl3
TIPSO
OH
2b
TIPS
(6 CH3 + 3CH)
NH-3
H6
CHCl3
H1'
H4'
H3'+OH
H5'
H2'b
H2'a
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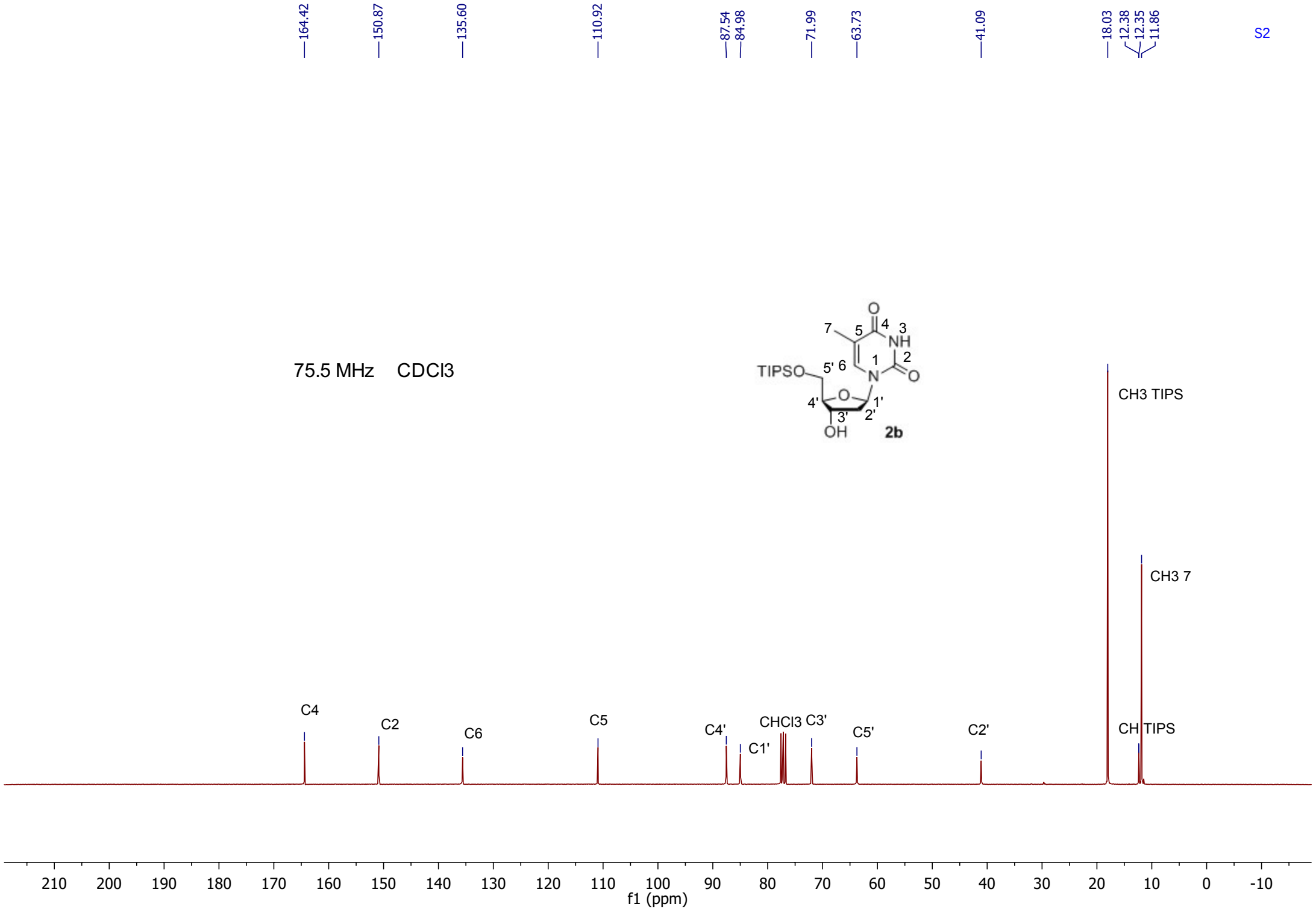
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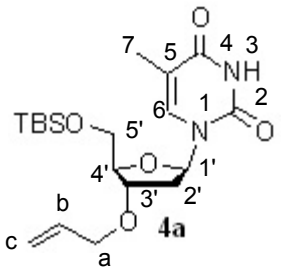
75.5 MHz CDCl3
TIPSO
OH
2b
CH3 TIPS
CH3 7
CH TIPS
C4
C2
C6
C5
C4'
C1'
CHCl3
C3'
C5'
C2'
f1 (ppm)

10.288 7.428 6.252 6.233 6.225 6.206 5.899 5.708 5.295 5.022 4.096 4.030 3.653 2.396 2.377 2.352 2.333 2.011 1.822 1.755 0.830 0.022



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CH3
TBS=TBDMS

H7

a+H3'+H4'+H5'

H6

NH-3

H1'

Hb

Hc

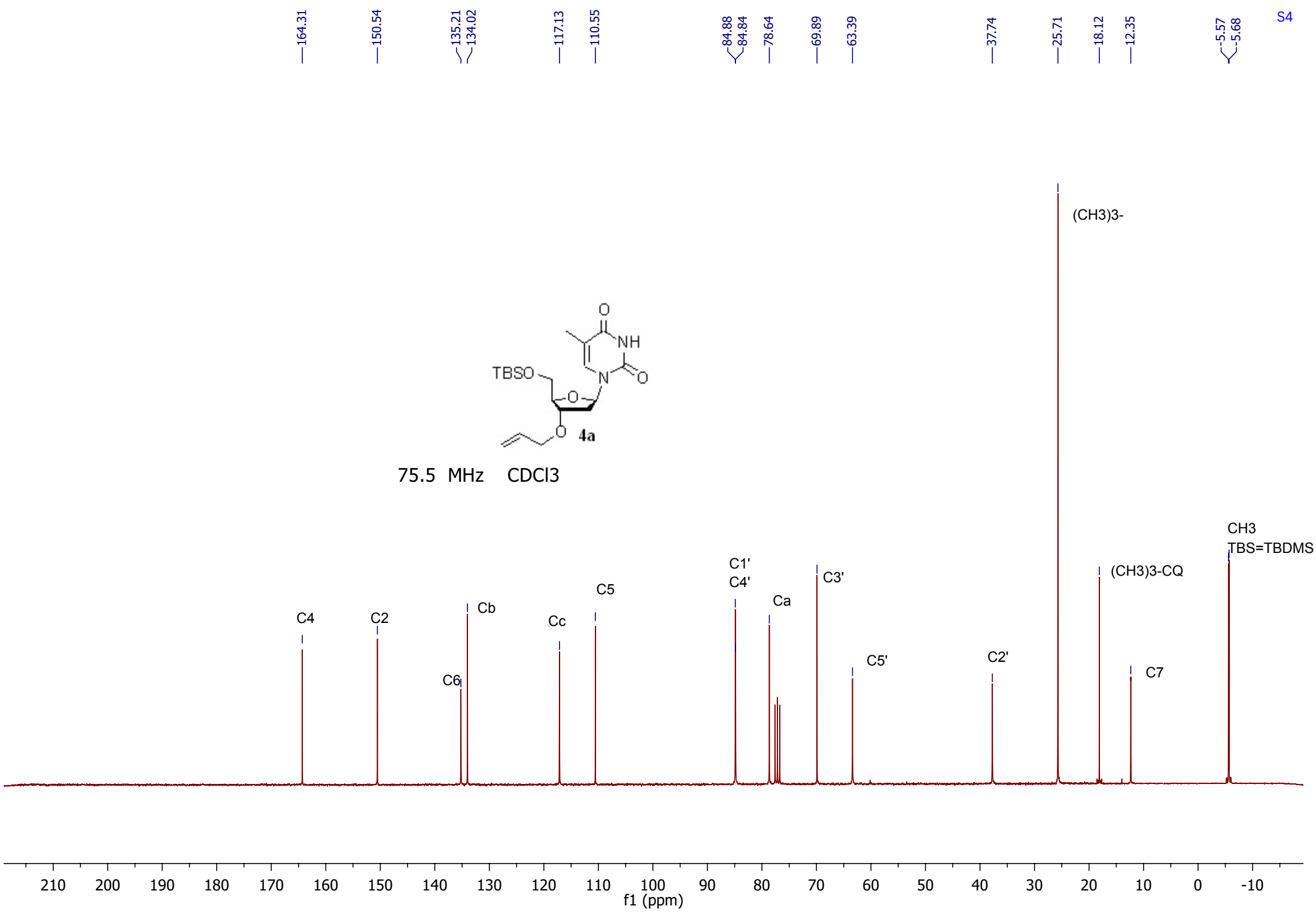
H2'b

H2'a

1.00 1.01 1.02 1.00 2.15 6.26 1.01 4.19 8.68 5.94

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

f1 (ppm)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O
O
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4a
75.5 MHz CDCl3
(CH3)3-
CH3
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C1'
C4'
C3'
C5
Cb
Ca
Cc
C4
C2
C6
C5'
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140
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120
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100
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80
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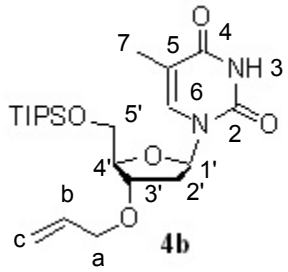
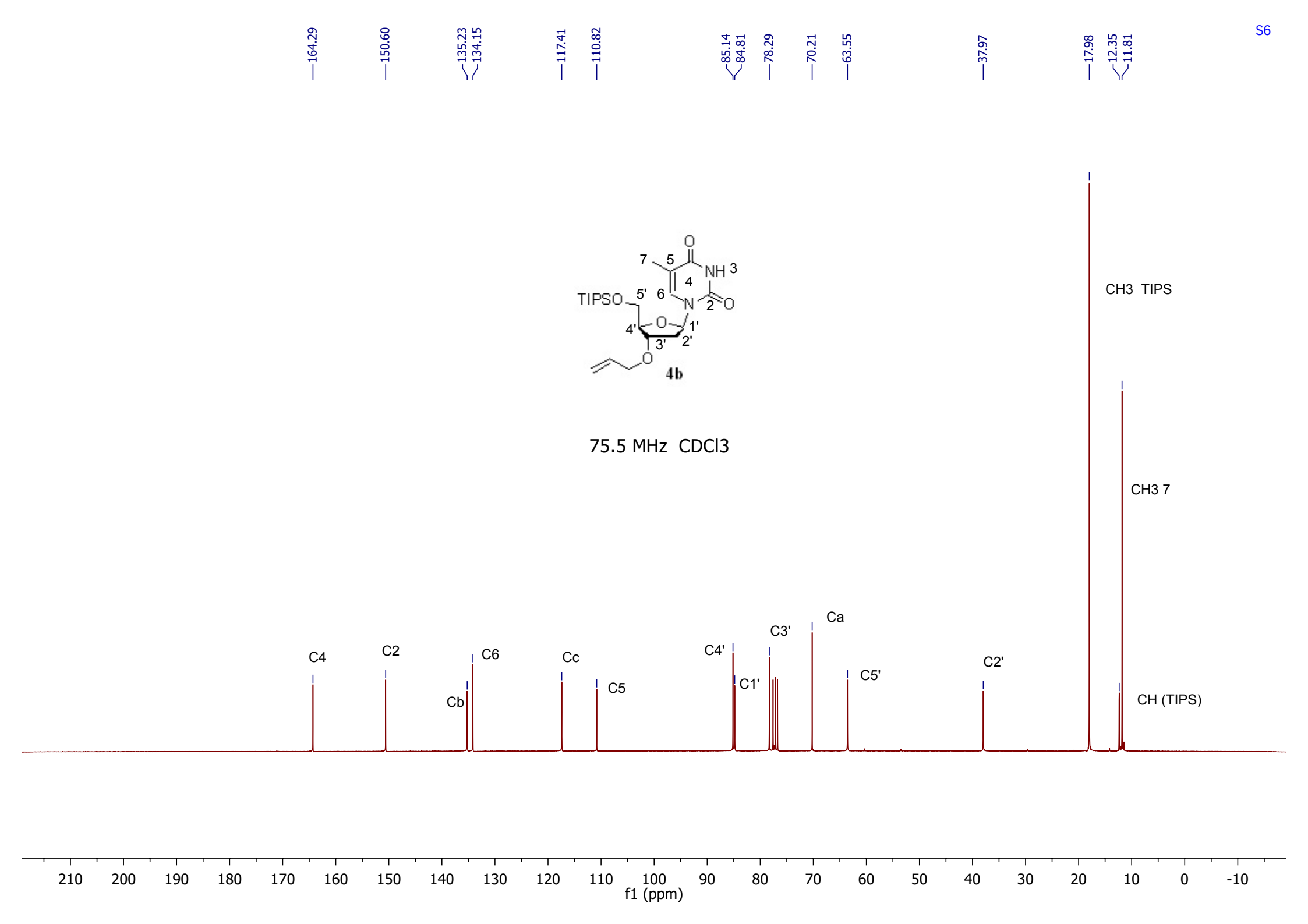
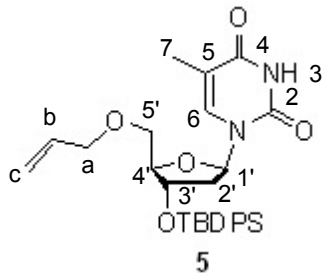
40
30
20
10
0
-10
f1 (ppm)



4b

300 MHz CDCl3

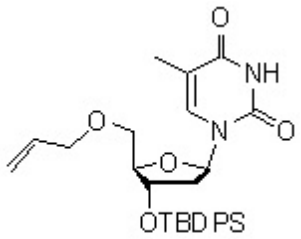

164.29
150.60
135.23
134.15
117.41
110.82
85.14
84.81
78.29
70.21
63.55
37.97
17.98
12.35
11.81
TIPSO
NH
O
N
4b
75.5 MHz CDCl3
CH3 TIPS
CH3 7
CH (TIPS)
C4
C2
Cb
C6
Cc
C5
C4'
C1'
C3'
Ca
C5'
C2'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



5

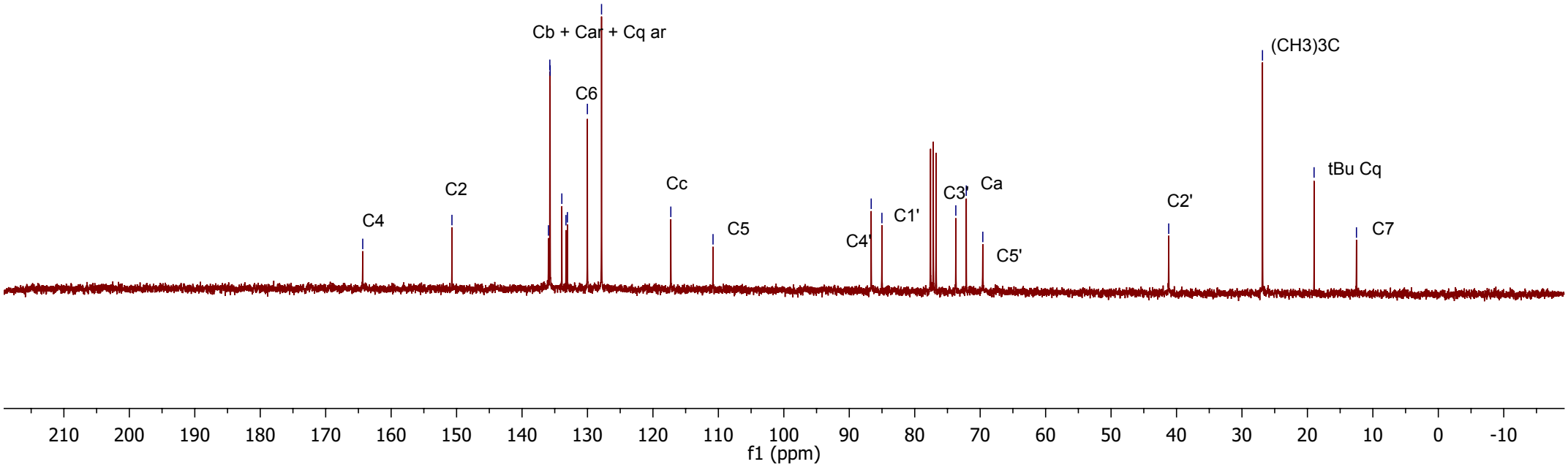
300 MHz CDCl3

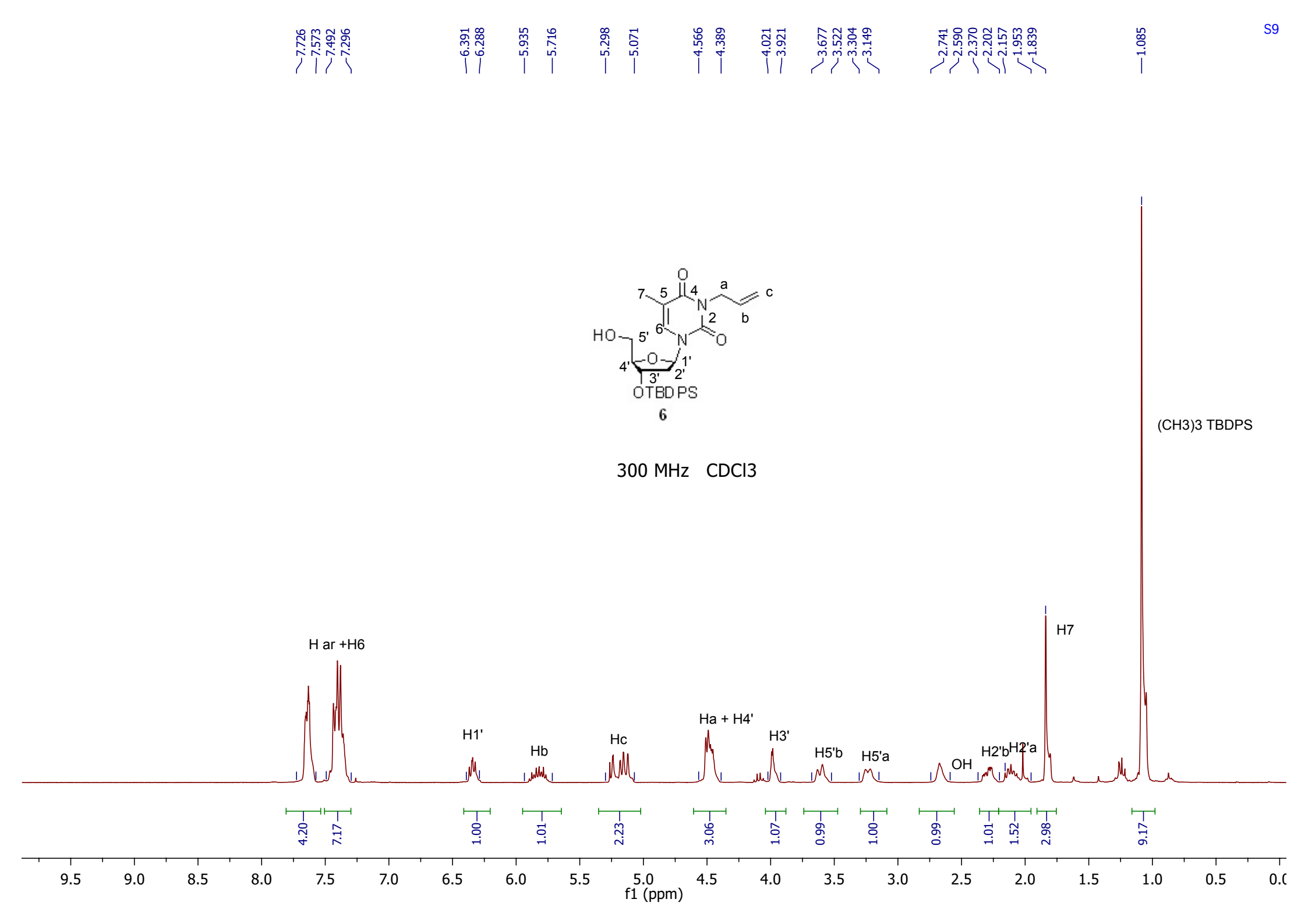
164.34 150.71 135.96 135.75 135.71 133.92 133.29 133.07 130.02 127.85 117.27 110.82 86.65 85.01 73.72 72.12 69.60 41.19 26.87 18.98 12.51

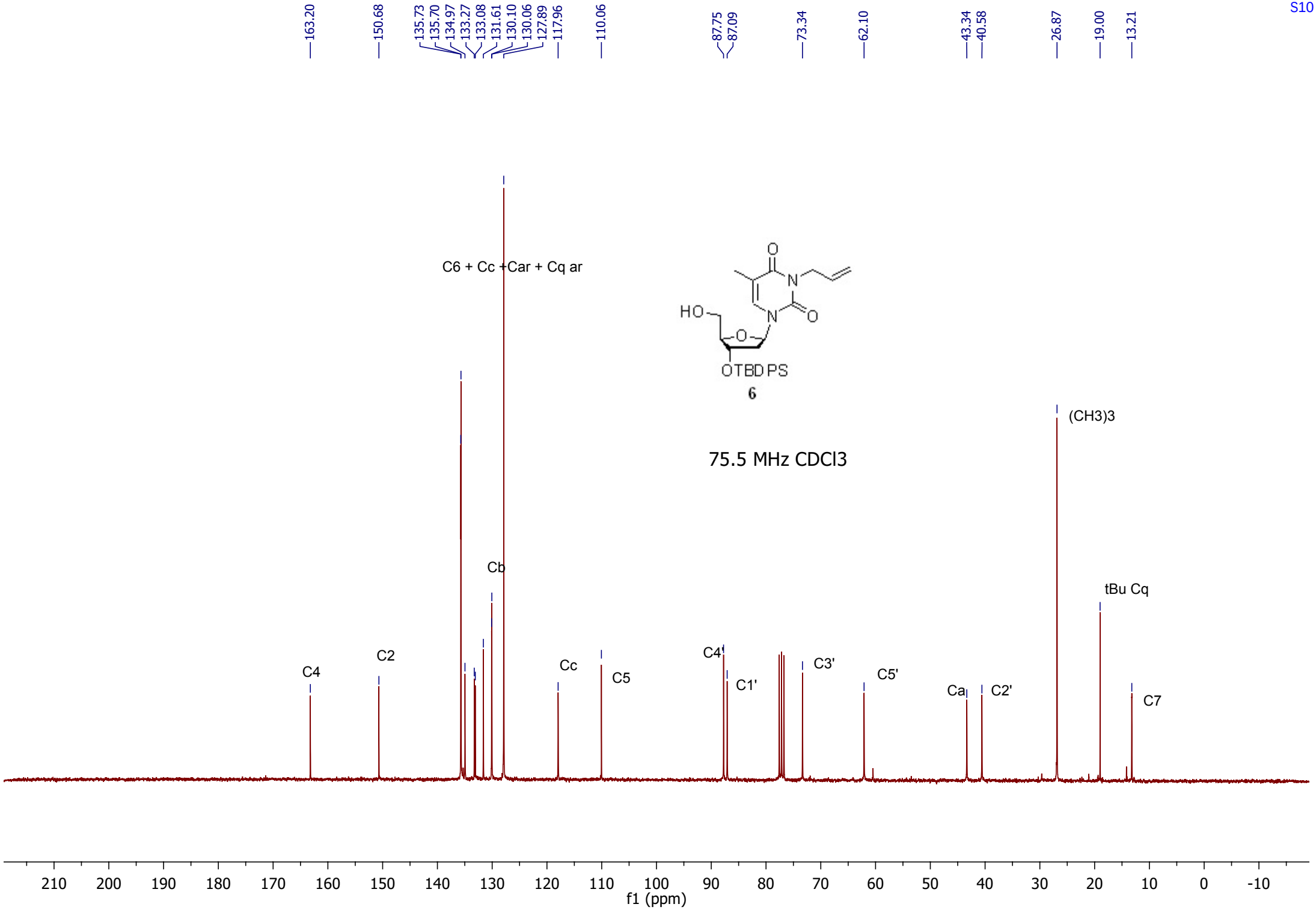


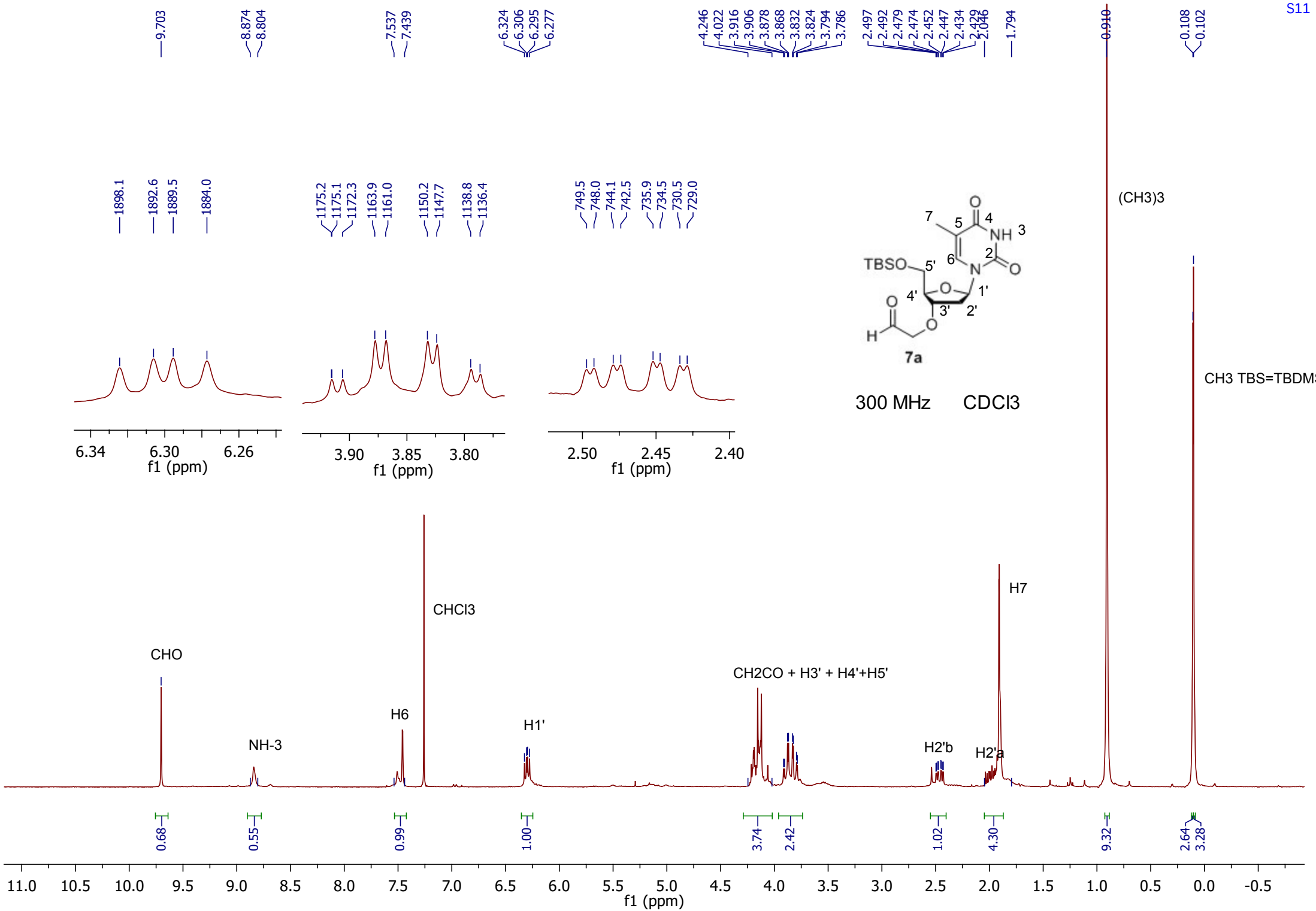
5

75.5 MHz CDCl3



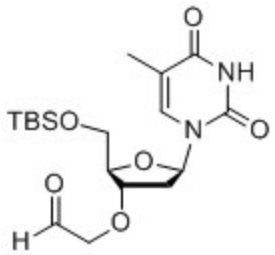

7.726
7.573
7.492
7.296
6.391
6.288
5.935
5.716
5.298
5.071
4.566
4.389
4.021
3.921
3.677
3.522
3.304
3.149
2.741
2.590
2.370
2.202
2.157
1.953
1.839
1.085
HO
OTBDPS
6
300 MHz CDCl3
(CH3)3 TBDPS
H ar +H6
H1'
Hb
Hc
Ha + H4'
H3'
H5'b
H5'a
OH
H2'b
H2'a
H7
4.20
7.17
1.00
1.01
2.23
3.06
1.07
0.99
1.00
0.99
1.01
1.52
2.98
9.17
f1 (ppm)


163.20
150.68
135.73
135.70
134.97
133.27
133.08
131.61
130.10
130.06
127.89
117.96
110.06
87.75
87.09
73.34
62.10
43.34
40.58
26.87
19.00
13.21
C6 + Cc +Car + Cq ar
HO
O
N
N
O
O
OTBDPS
6
75.5 MHz CDCl3
(CH3)3
tBu Cq
Cb
C4
C2
Cc
C5
C4'
C1'
C3'
C5'
Ca
C2'
C7
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)

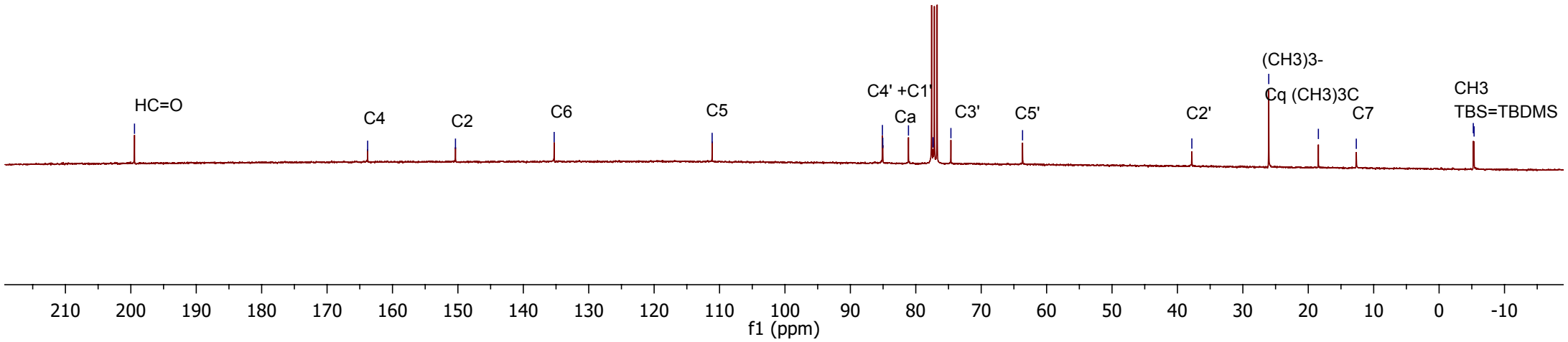

9.703
8.874
8.804
7.537
7.439
6.324
6.306
6.295
6.277
4.246
4.022
3.916
3.906
3.878
3.868
3.832
3.824
3.794
3.786
2.497
2.492
2.479
2.474
2.452
2.447
2.434
2.429
2.046
1.794
0.910
0.108
0.102
1898.1
1892.6
1889.5
1884.0
1175.2
1175.1
1172.3
1163.9
1161.0
1150.2
1147.7
1138.8
1136.4
749.5
748.0
744.1
742.5
735.9
734.5
730.5
729.0
(CH3)3
CH3 TBS=TBDMS
300 MHz CDCl3
7a
CHO
NH-3
H6
CHCl3
H1'
CH2CO + H3' + H4'+H5'
H2'b
H2'a
H7
0.68
0.55
0.99
1.00
3.74
2.42
1.02
4.30
9.32
2.64
3.28
f1 (ppm)

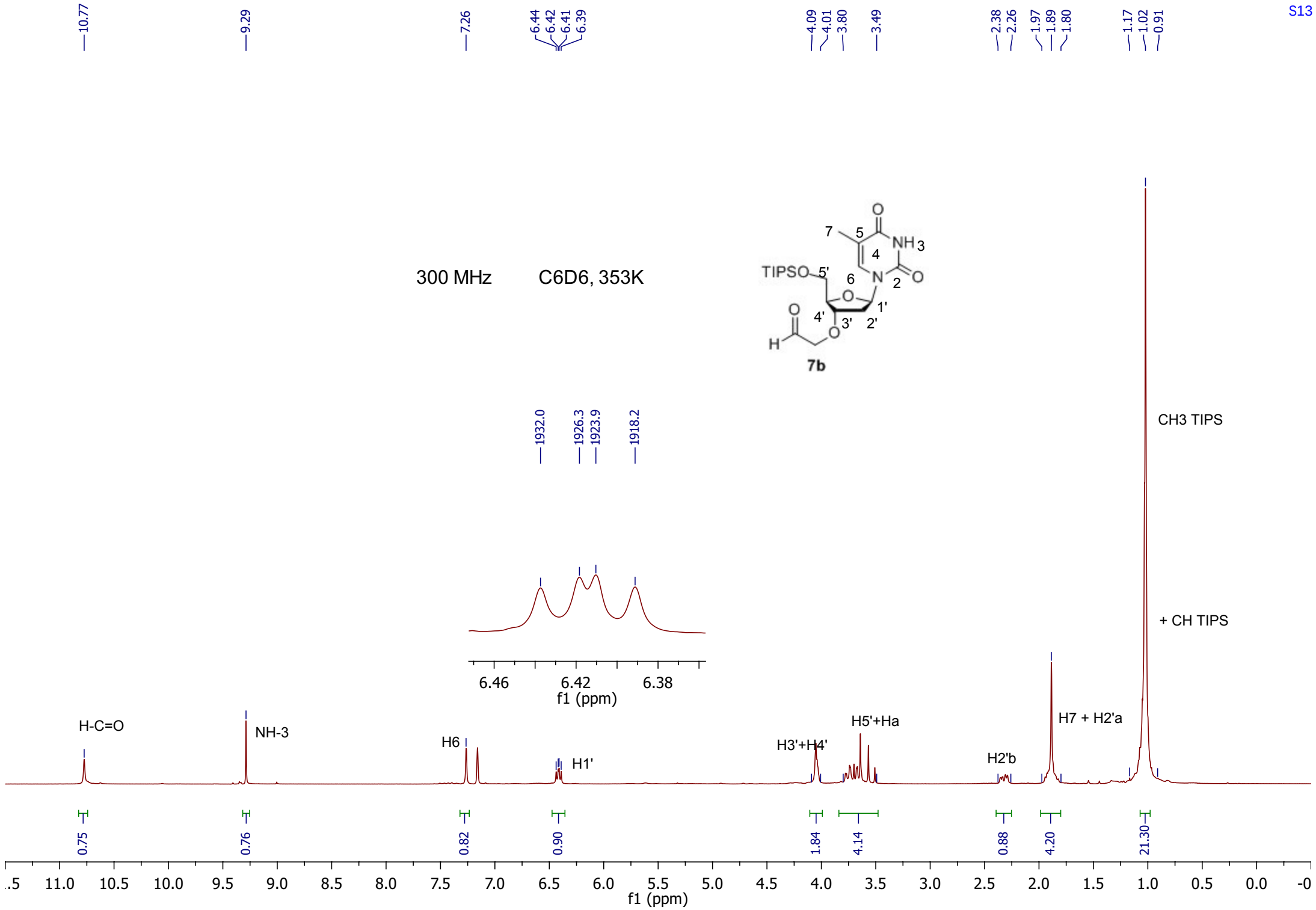
199.4 163.8 150.4 135.3 111.1 85.1 85.0 81.1 77.4 74.6 63.7 37.8 26.0 18.5 12.7 -5.2 -5.3

75.5 MHz CDCl3



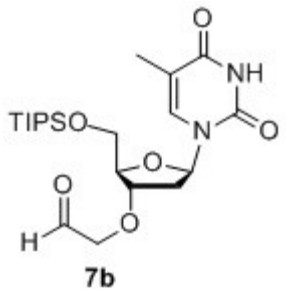
7a



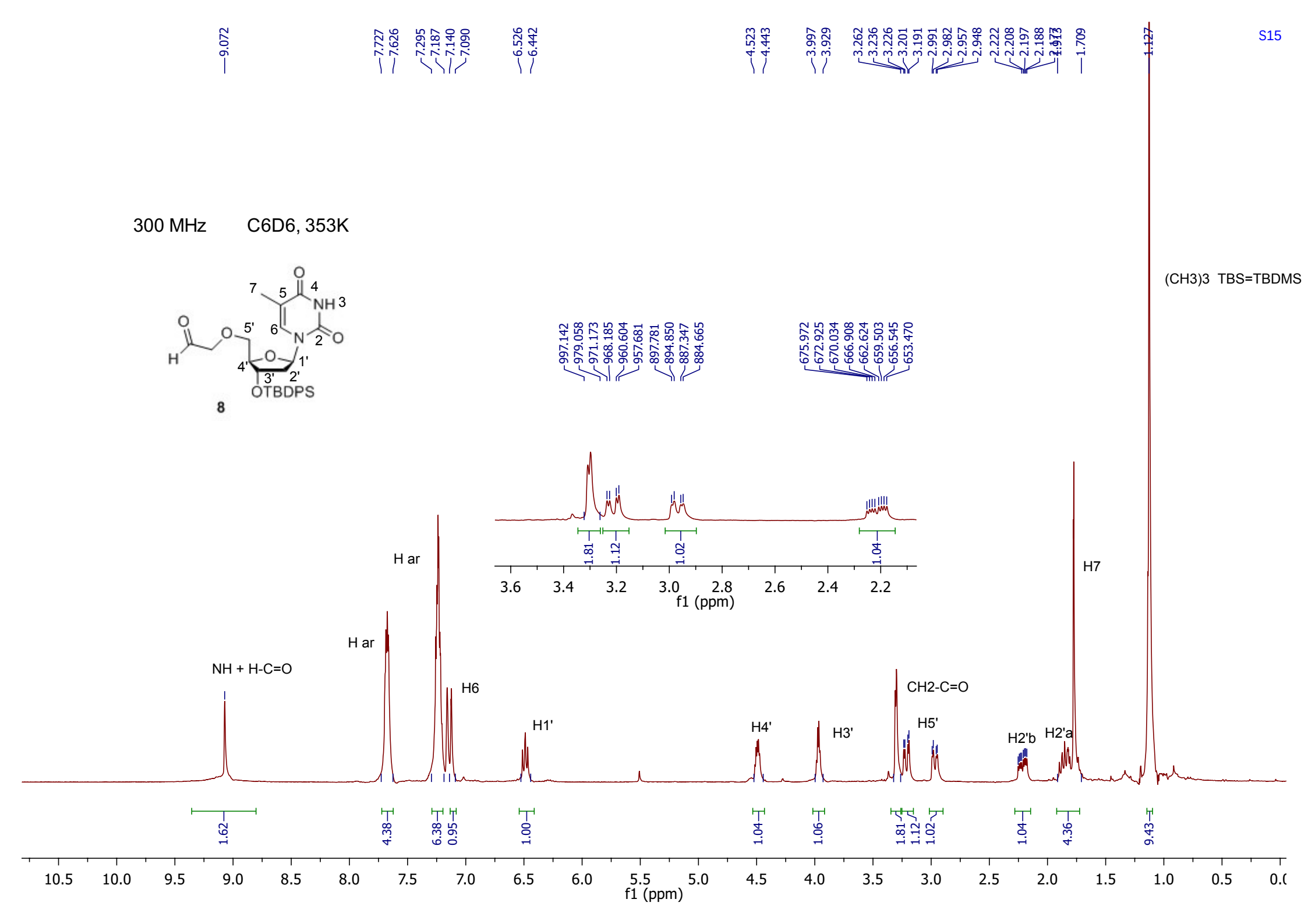

10.77
9.29
7.26
6.44
6.42
6.41
6.39
4.09
4.01
3.80
3.49
2.38
2.26
1.97
1.89
1.80
1.17
1.02
0.91
300 MHz
C6D6, 353K
TIPSO
7b
1932.0
1926.3
1923.9
1918.2
6.46
6.42
6.38
f1 (ppm)
CH3 TIPS
+ CH TIPS
H-C=O
NH-3
H6
H1'
H3'+H4'
H5'+Ha
H2'b
H7 + H2'a
0.75
0.76
0.82
0.90
1.84
4.14
0.88
4.20
21.30
f1 (ppm)

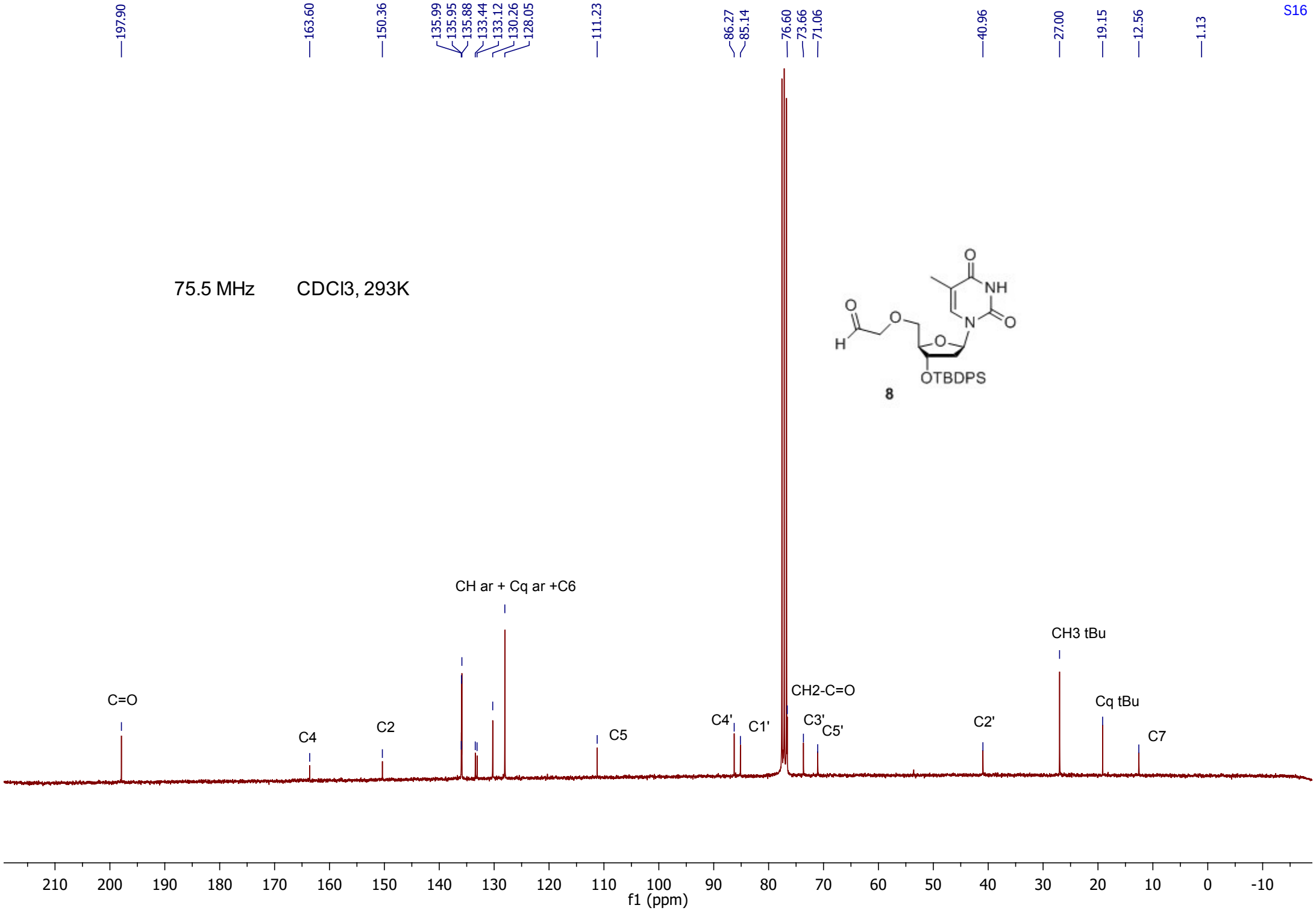
198.51 163.77 150.83 135.27 110.94 85.84 85.33 80.71 74.90 64.05 37.85 18.18 12.44 12.35

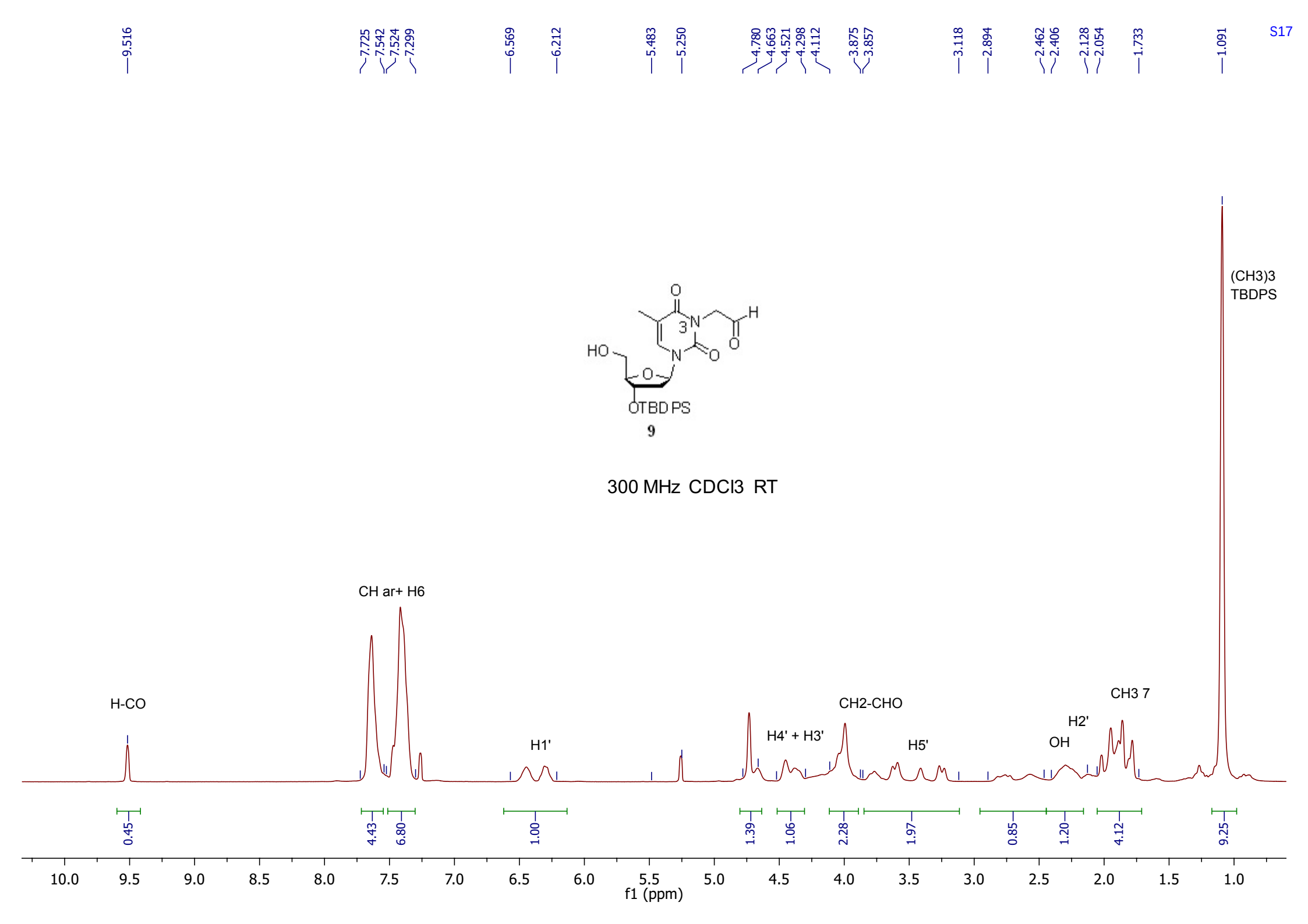
75.5 MHz C6D6, 353K



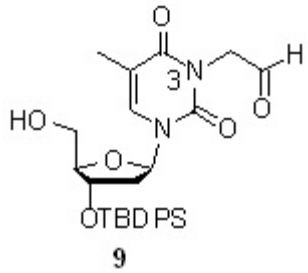
7b


9.072
7.727
7.626
7.295
7.187
7.140
7.090
6.526
6.442
4.523
4.443
3.997
3.929
3.262
3.236
3.226
3.201
3.191
2.991
2.982
2.957
2.948
2.222
2.208
2.197
2.188
1.709
1.127
300 MHz C6D6, 353K
(CH3)3 TBS=TBDMS
997.142
979.058
971.173
968.185
960.604
957.681
897.781
894.850
887.347
884.665
675.972
672.925
670.034
666.908
662.624
659.503
656.545
653.470
OTBDPS
8
H ar
H ar
NH + H-C=O
H6
H1'
H4'
H3'
CH2-C=O
H5'
H2'b
H2'a
H7
1.81
1.12
1.02
1.04
f1 (ppm)
1.62
4.38
6.38
0.95
1.00
1.04
1.06
1.81
1.12
1.02
1.04
4.36
9.43
f1 (ppm)


197.90
163.60
150.36
135.99
135.95
135.88
133.44
133.12
130.26
128.05
111.23
86.27
85.14
76.60
73.66
71.06
40.96
27.00
19.15
12.56
1.13
75.5 MHz
CDCl3, 293K
NH
O
N
O
H
O
O
OTBDPS
8
CH ar + Cq ar +C6
C=O
C4
C2
C5
C4'
C1'
CH2-C=O
C3'
C5'
C2'
CH3 tBu
Cq tBu
C7
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)


9.516
7.725
7.542
7.524
7.299
6.569
6.212
5.483
5.250
4.780
4.663
4.521
4.298
4.112
3.875
3.857
3.118
2.894
2.462
2.406
2.128
2.054
1.733
1.091
(CH3)3
TBDPS
HO
O
N
3
H
OTBDPS
9
300 MHz CDCl3 RT
CH ar+ H6
H-CO
H1'
H4' + H3'
CH2-CHO
H5'
OH
H2'
CH3 7
0.45
4.43
6.80
1.00
1.39
1.06
2.28
1.97
0.85
1.20
4.12
9.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

194.890
194.558
162.870
150.534
135.701
135.668
135.425
134.859
133.228
133.063
130.107
127.893
110.066
109.921
95.038
87.753
87.081
77.361
73.129
67.089
61.972
53.467
50.122
45.225
40.960
40.584
26.865
18.983
13.064



9

75.5 MHz CDCl3 RT

CH + Cq ar

(CH3)3 tBu

tBu Cq

C7

H-C=O

C4

C2

C5

C4'

C1'

C3'

C5'

CH2-CO

C2'

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

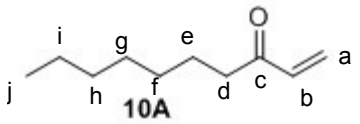
f1 (ppm)

6.39 6.35 6.33 6.29 6.23 6.22 6.17 6.16 5.82 5.81 5.78 5.78

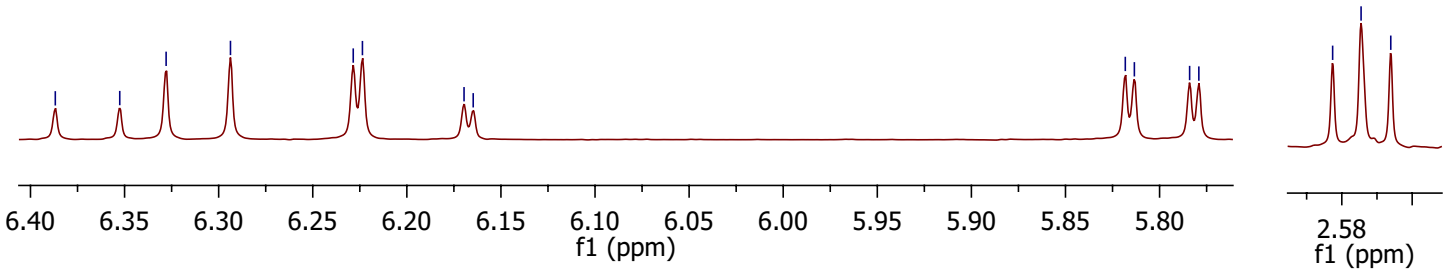
2.59 2.56 2.54

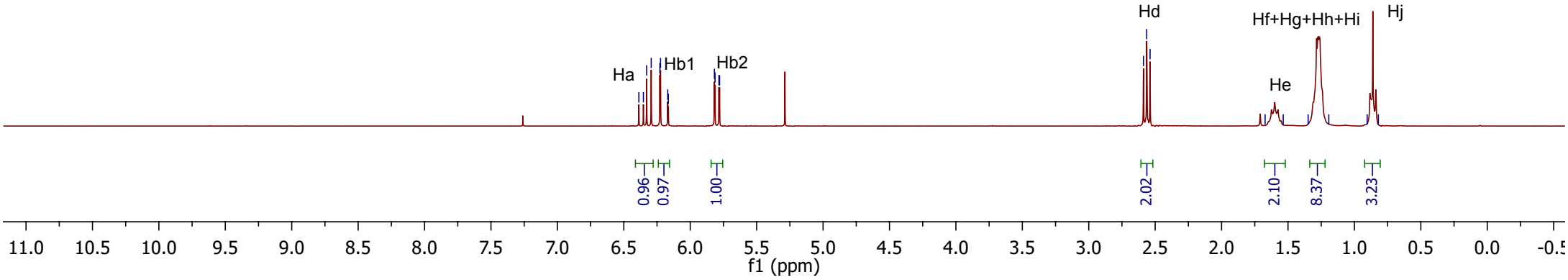
1.67 1.54 1.35 1.19 0.90 0.82

300 MHz CDCl3



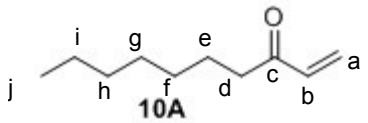
1916.9 1906.6 1899.2 1888.9 1869.4 1867.9 1851.7 1850.2 1746.2 1744.8 1736.0 1734.5 776.7 769.4 761.8



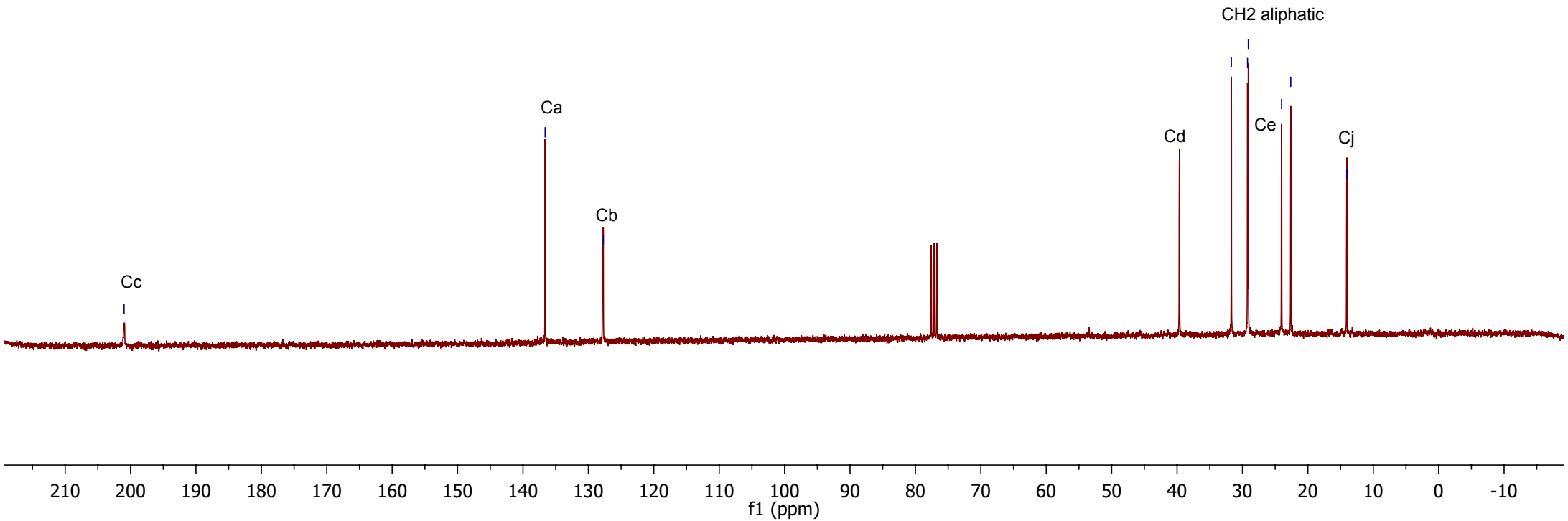


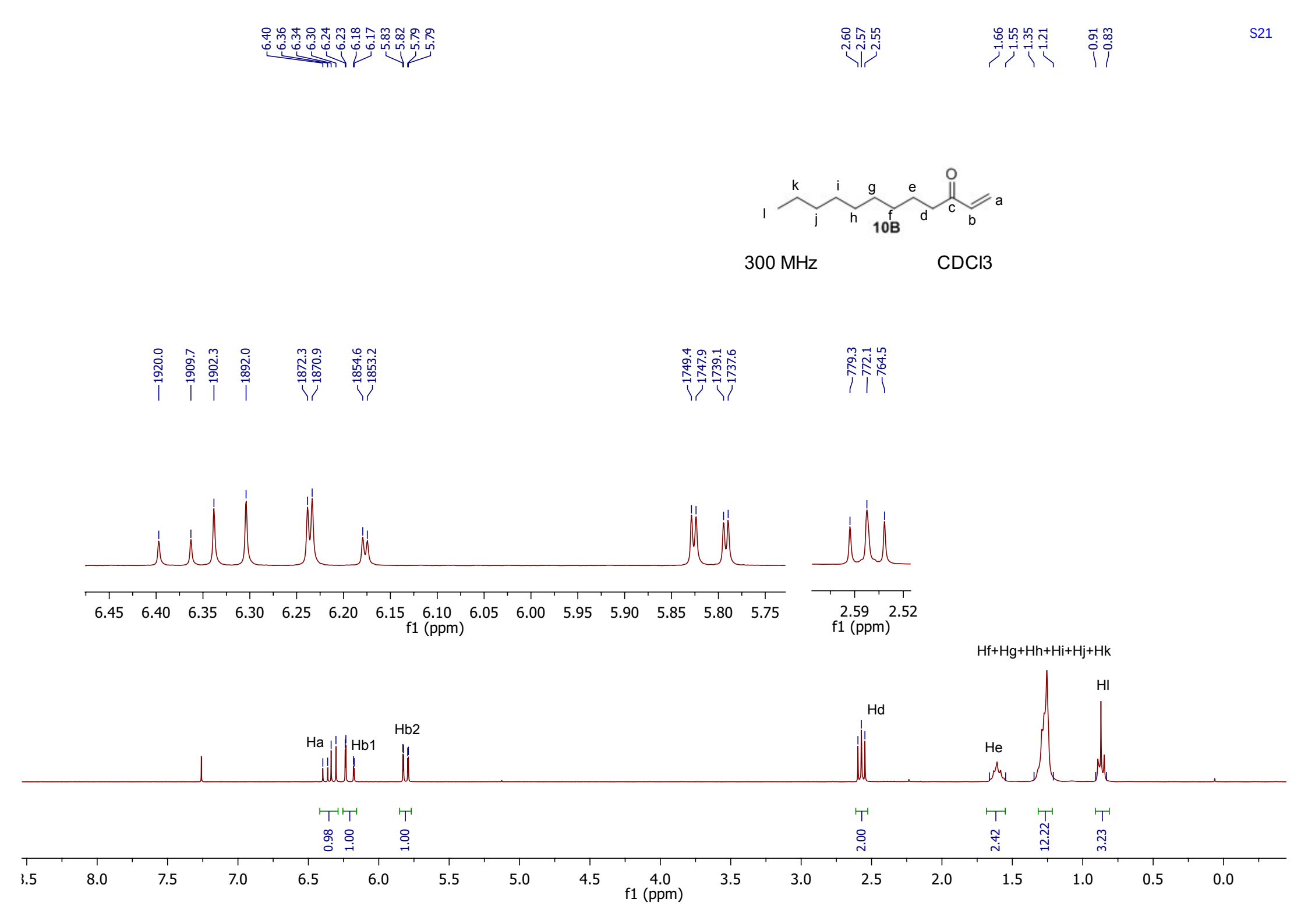
201.0 136.6 127.7 39.6 31.7 29.2 29.1 24.0 22.6 14.1

75.5 MHz CDCl3



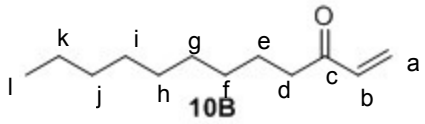
10A

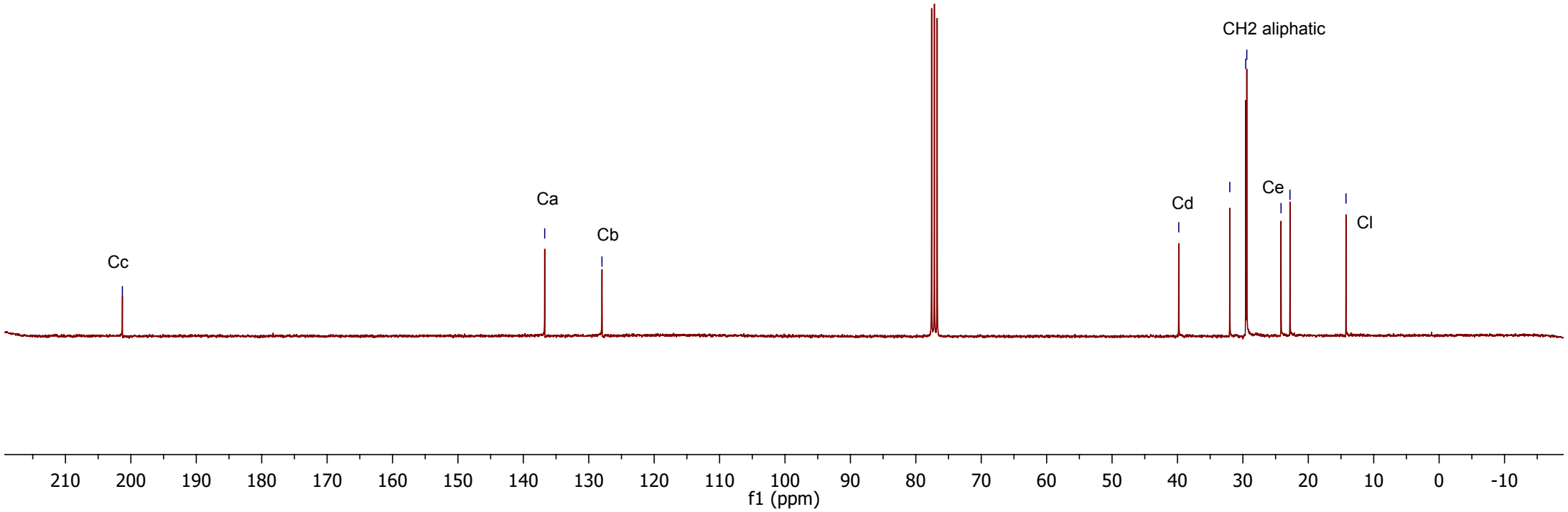


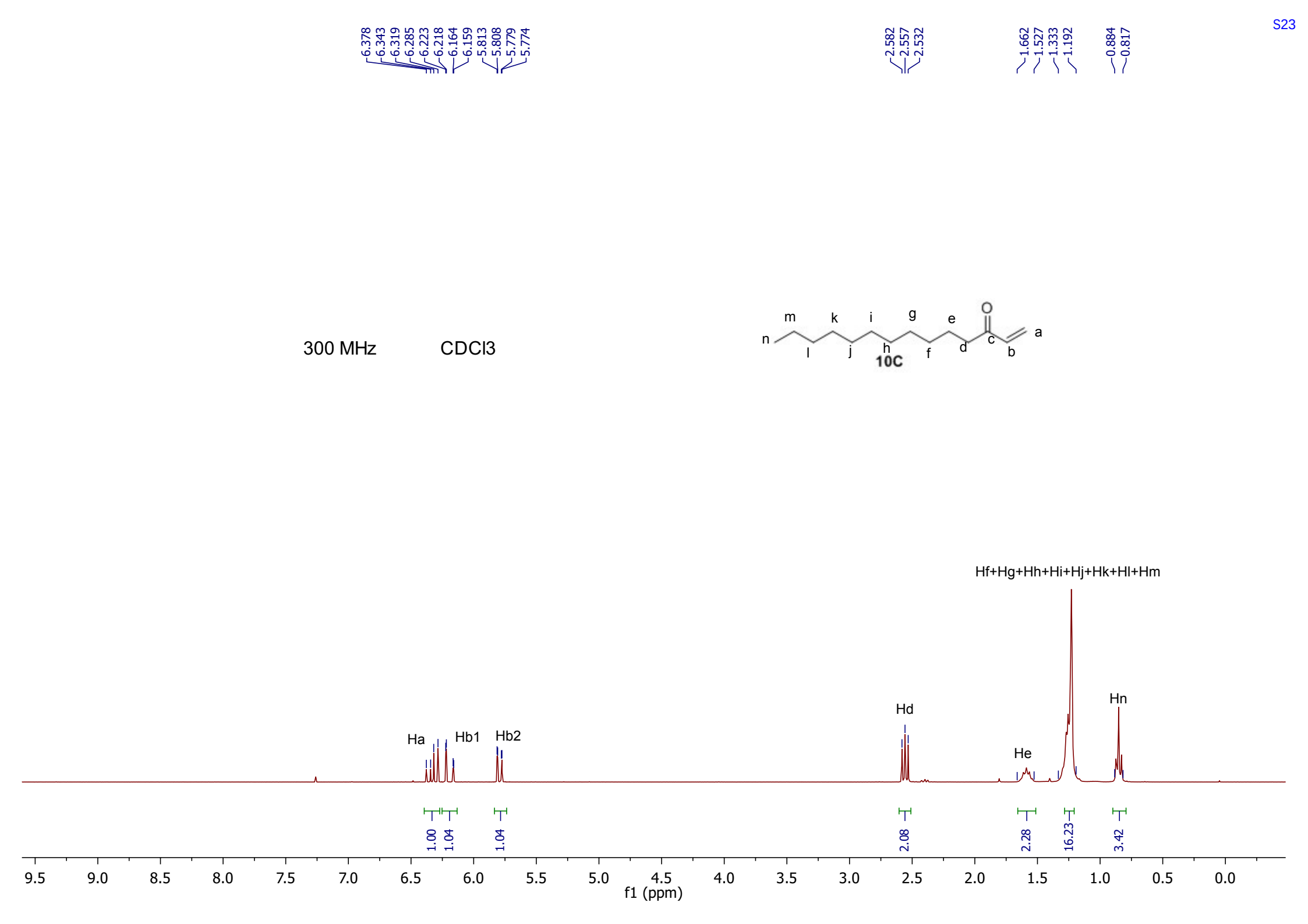

6.40
6.36
6.34
6.30
6.24
6.23
6.18
6.17
5.83
5.82
5.79
5.79
2.60
2.57
2.55
1.66
1.55
1.35
1.21
0.91
0.83
k
i
g
e
O
a
l
j
h
f
d
c
b
10B
300 MHz
CDCl3
1920.0
1909.7
1902.3
1892.0
1872.3
1870.9
1854.6
1853.2
1749.4
1747.9
1739.1
1737.6
779.3
772.1
764.5
6.45 6.40 6.35 6.30 6.25 6.20 6.15 6.10 6.05 6.00 5.95 5.90 5.85 5.80 5.75
f1 (ppm)
2.59 2.52
f1 (ppm)
Hf+Hg+Hh+Hi+Hj+Hk
Hl
Hd
Hb2
Ha
Hb1
He
0.98
1.00
1.00
2.00
2.42
12.22
3.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

201.3 136.7 128.0 39.8 32.0 29.6 29.4 24.2 22.8 14.2

75.5 MHz CDCl3

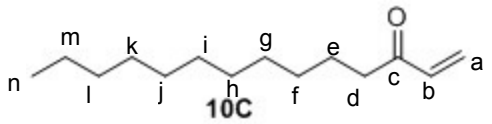


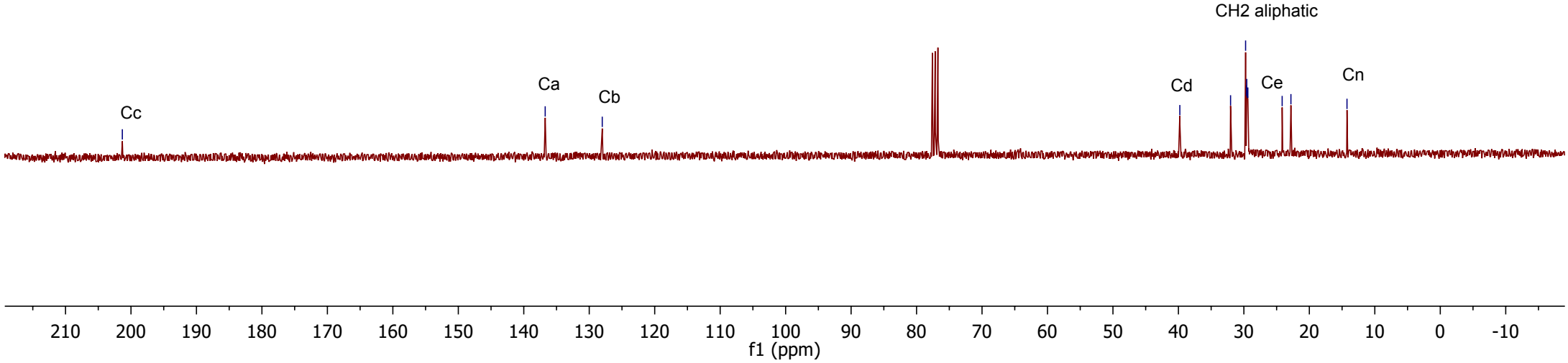


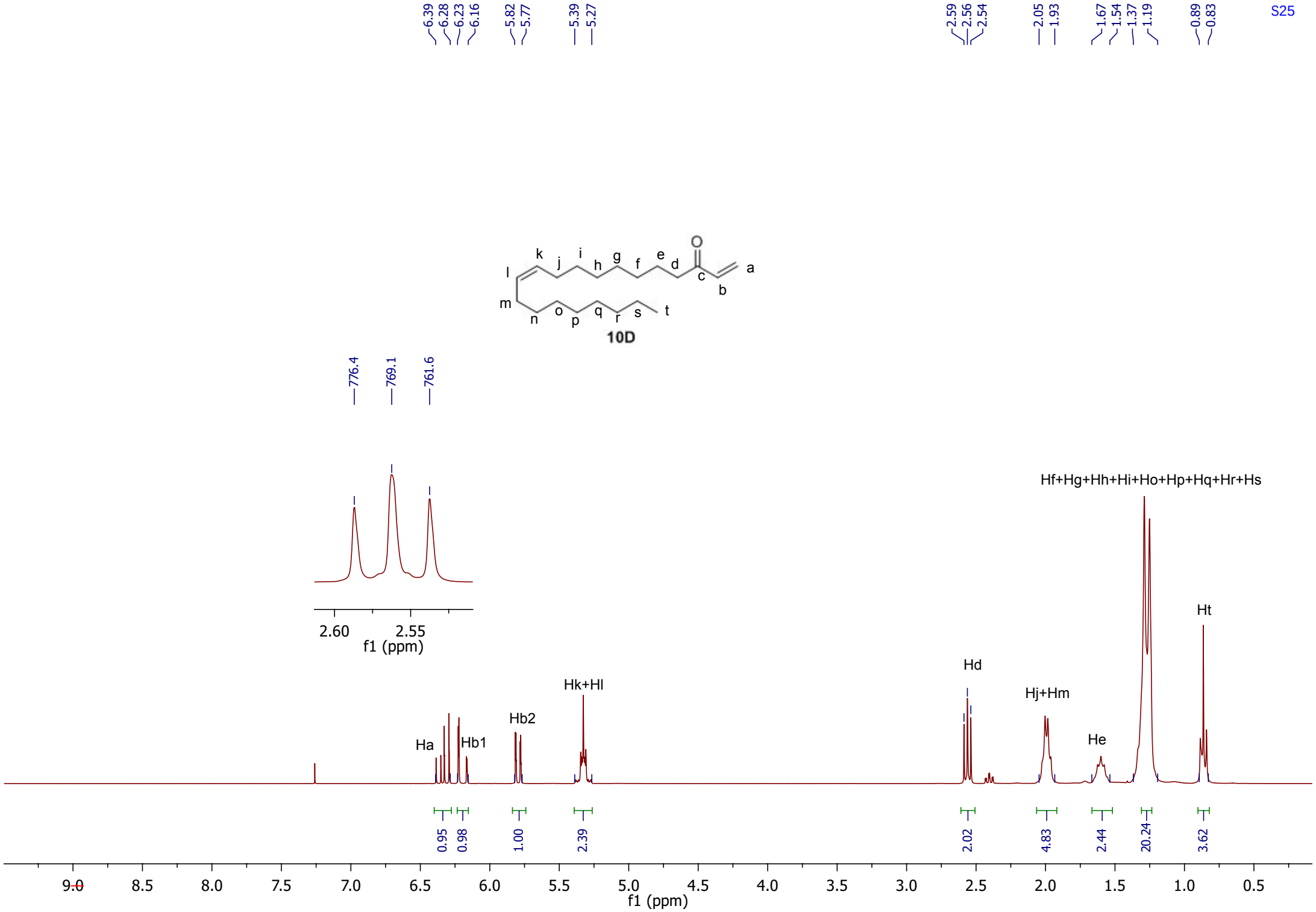

6.378
6.343
6.319
6.285
6.223
6.218
6.164
6.159
5.813
5.808
5.779
5.774
2.582
2.557
2.532
1.662
1.527
1.333
1.192
0.884
0.817
300 MHz
CDCl3
m
k
i
g
e
O
n
a
l
j
h
f
d
c
b
10C
Hf+Hg+Hh+Hi+Hj+Hk+Hl+Hm
Hn
Hd
He
Ha
Hb1
Hb2
1.00
1.04
1.04
2.08
2.28
16.23
3.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

201.32
136.73
128.01
39.78
32.03
29.74
29.61
29.56
29.47
29.39
24.15
22.81
14.25

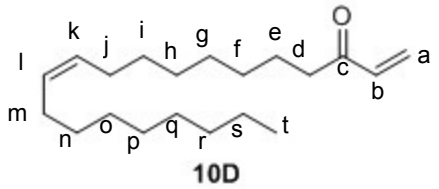
75 MHz CDCl3





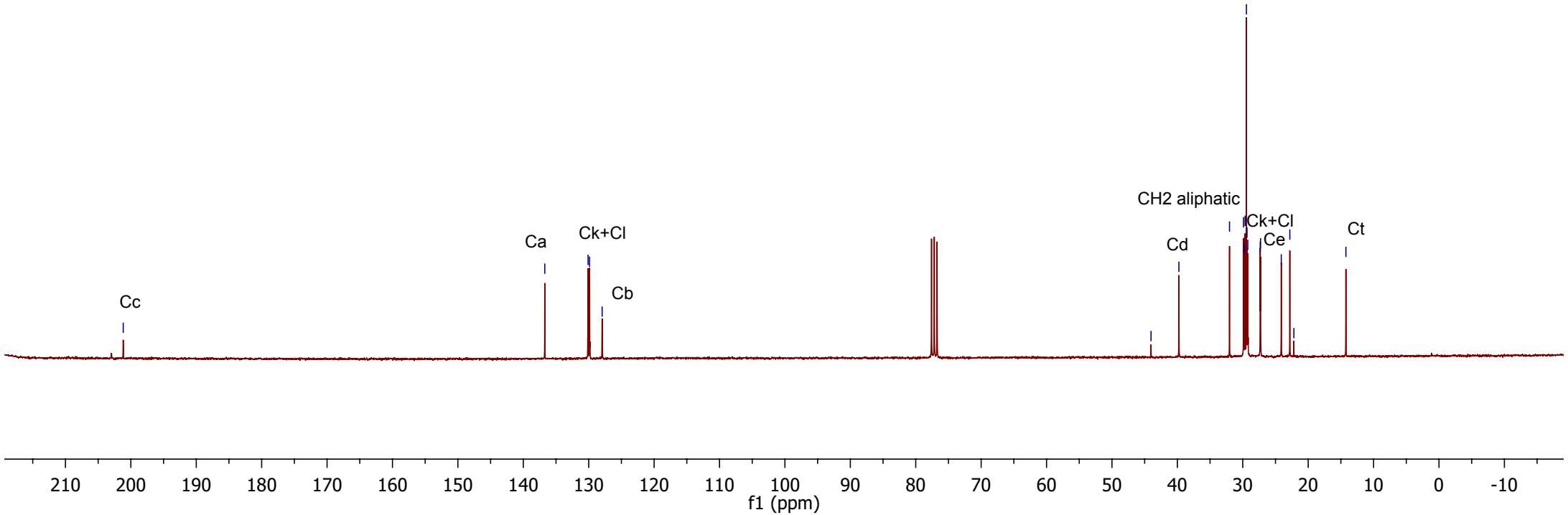

6.39
6.28
6.23
6.16
5.82
5.77
5.39
5.27
2.59
2.56
2.54
2.05
1.93
1.67
1.54
1.37
1.19
0.89
0.83
10D
776.4
769.1
761.6
2.60
2.55
f1 (ppm)
Ha
Hb1
Hb2
Hk+Hl
Hd
Hj+Hm
He
Hf+Hg+Hh+Hi+Ho+Hp+Hq+Hr+Hs
Ht
0.95
0.98
1.00
2.39
2.02
4.83
2.44
20.24
3.62
f1 (ppm)

201.17
136.71
130.09
129.86
127.94
44.03
39.76
32.03
29.89
29.65
29.44
29.35
29.23
27.28
22.80
14.23



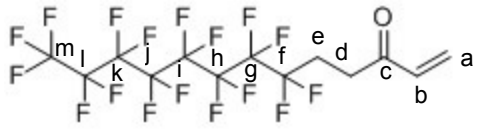
10D

75.5 MHz CDCl3

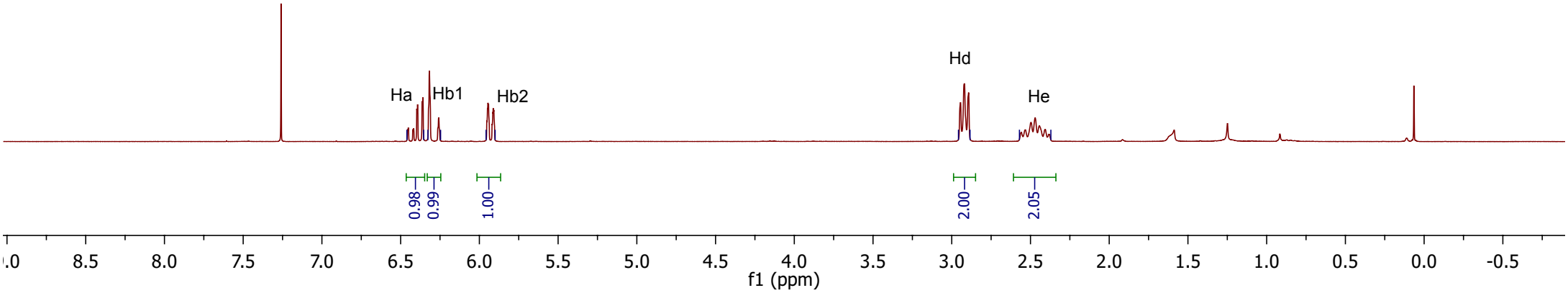


6.460 6.354 6.327 6.246 5.958 5.900 2.957 2.884 2.570 2.370

300 MHz CDCl3



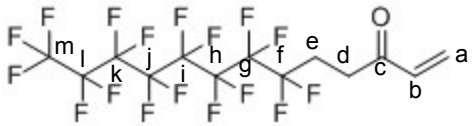
10E



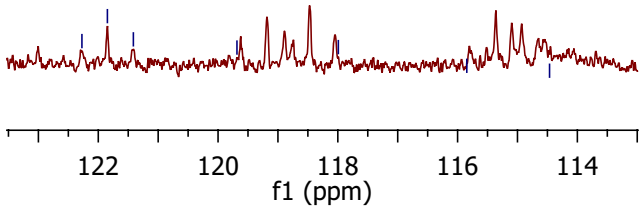
196.9 136.0 129.4 122.3 121.8 121.4 119.7 118.0 115.8 114.5 30.4 25.6 25.3 25.0

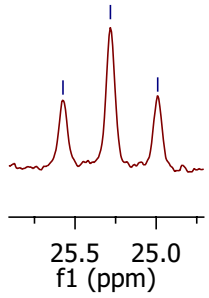
9227.7 9195.6 9162.9 9032.3 8904.6 8742.7 8638.4 1930.0 1908.0 1886.0

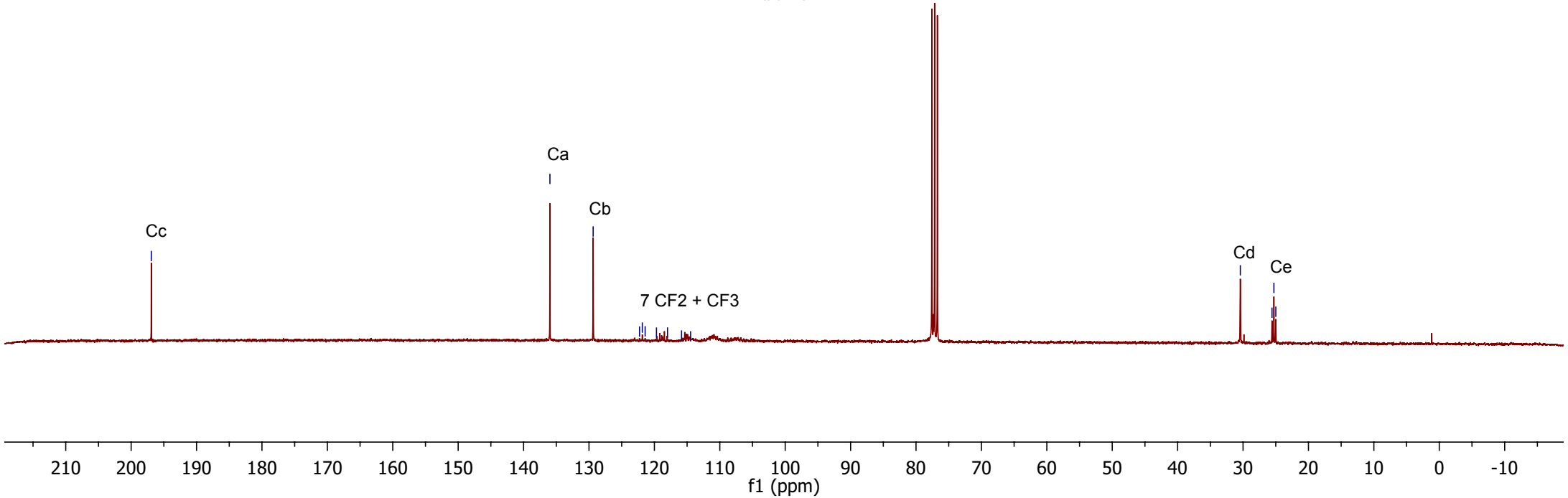
75.5 MHz CDCl3



10E

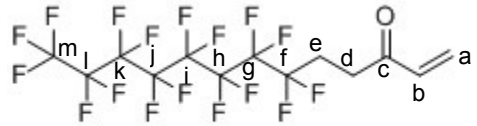






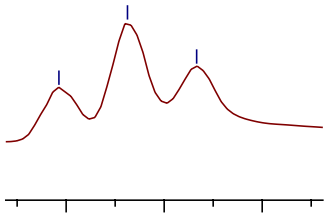
-80.70
-80.73
-80.77
-114.02
-114.44
-121.45
-122.08
-122.54
-122.88
-123.27
-123.64
-125.93
-126.24

282 MHz CDCl3

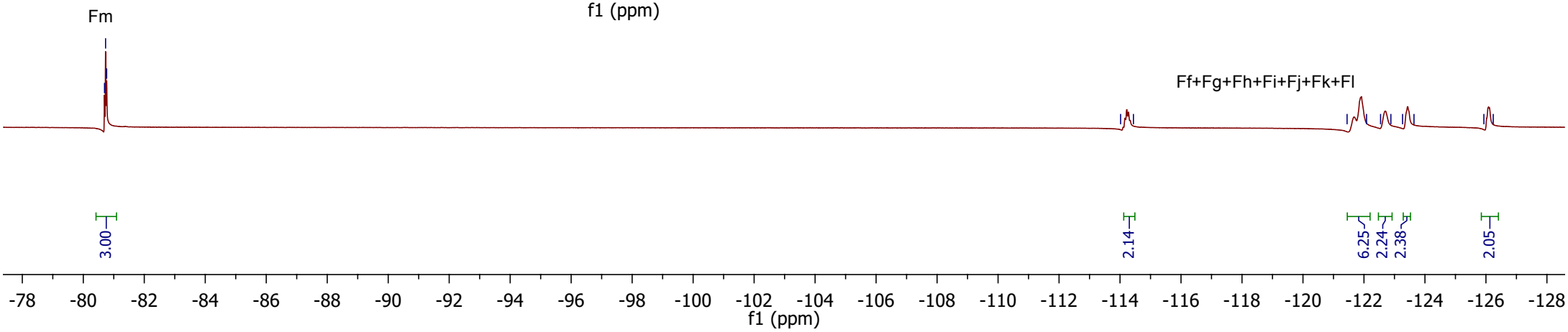


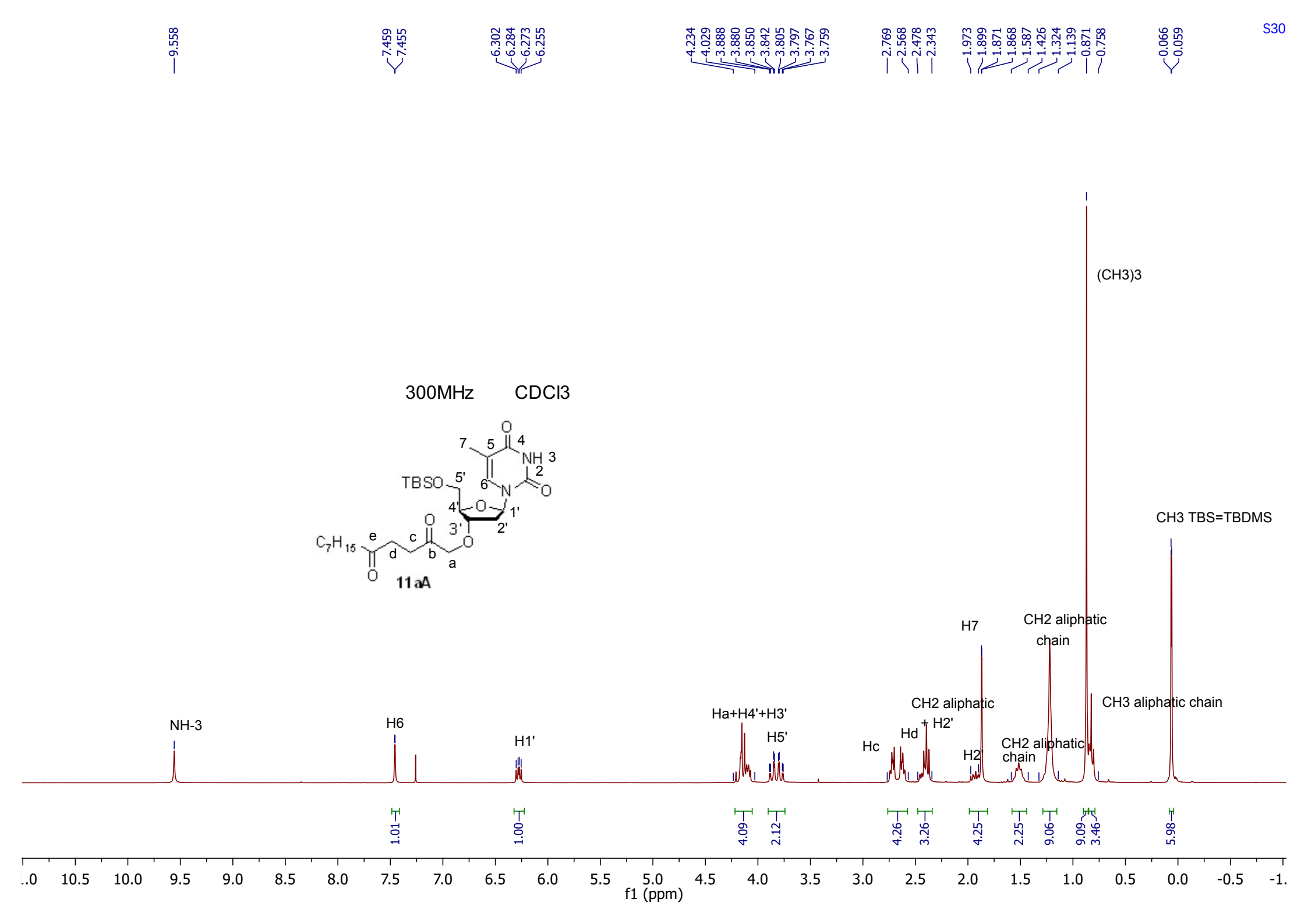
10E

-22796.6
-22806.5
-22816.4



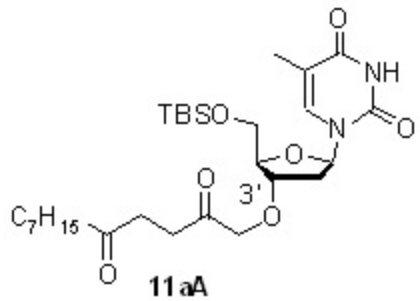
-80.75
f1 (ppm)



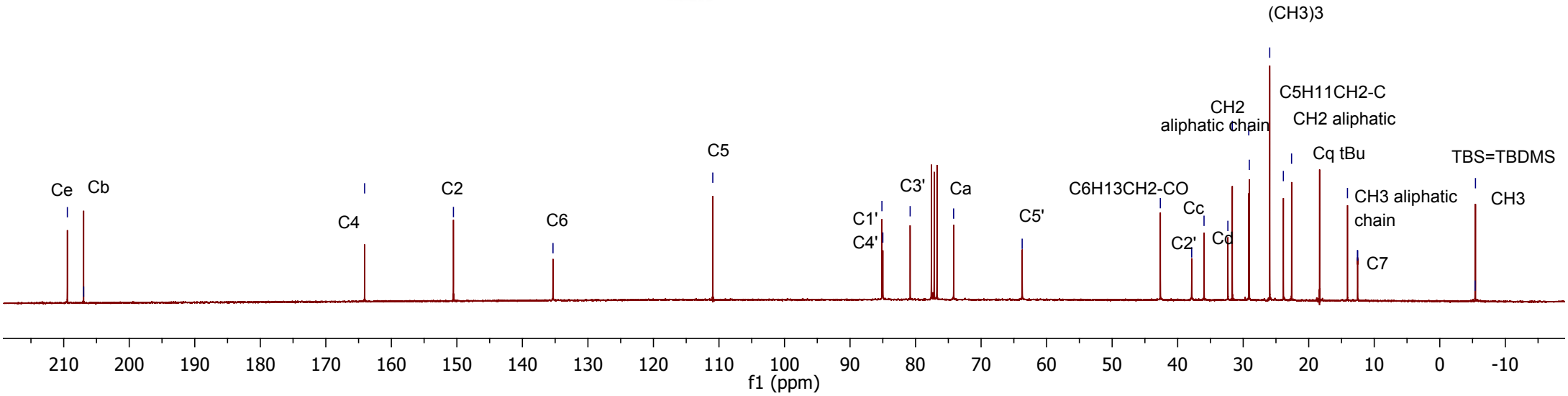

9.558
7.459
7.455
6.302
6.284
6.273
6.255
4.234
4.029
3.888
3.880
3.850
3.842
3.805
3.797
3.767
3.759
2.769
2.568
2.478
2.343
1.973
1.899
1.871
1.868
1.587
1.426
1.324
1.139
0.871
0.758
0.066
0.059
300MHz CDCl3
TBSO
C7H15
11aA
(CH3)3
CH3 TBS=TBDMS
NH-3
H6
H1'
Ha+H4'+H3'
H5'
Hc
Hd
CH2 aliphatic + H2'
H7
H2'
CH2 aliphatic chain
CH2 aliphatic chain
CH3 aliphatic chain
1.01
1.00
4.09
2.12
4.26
3.26
4.25
2.25
9.06
9.09
3.46
5.98
f1 (ppm)

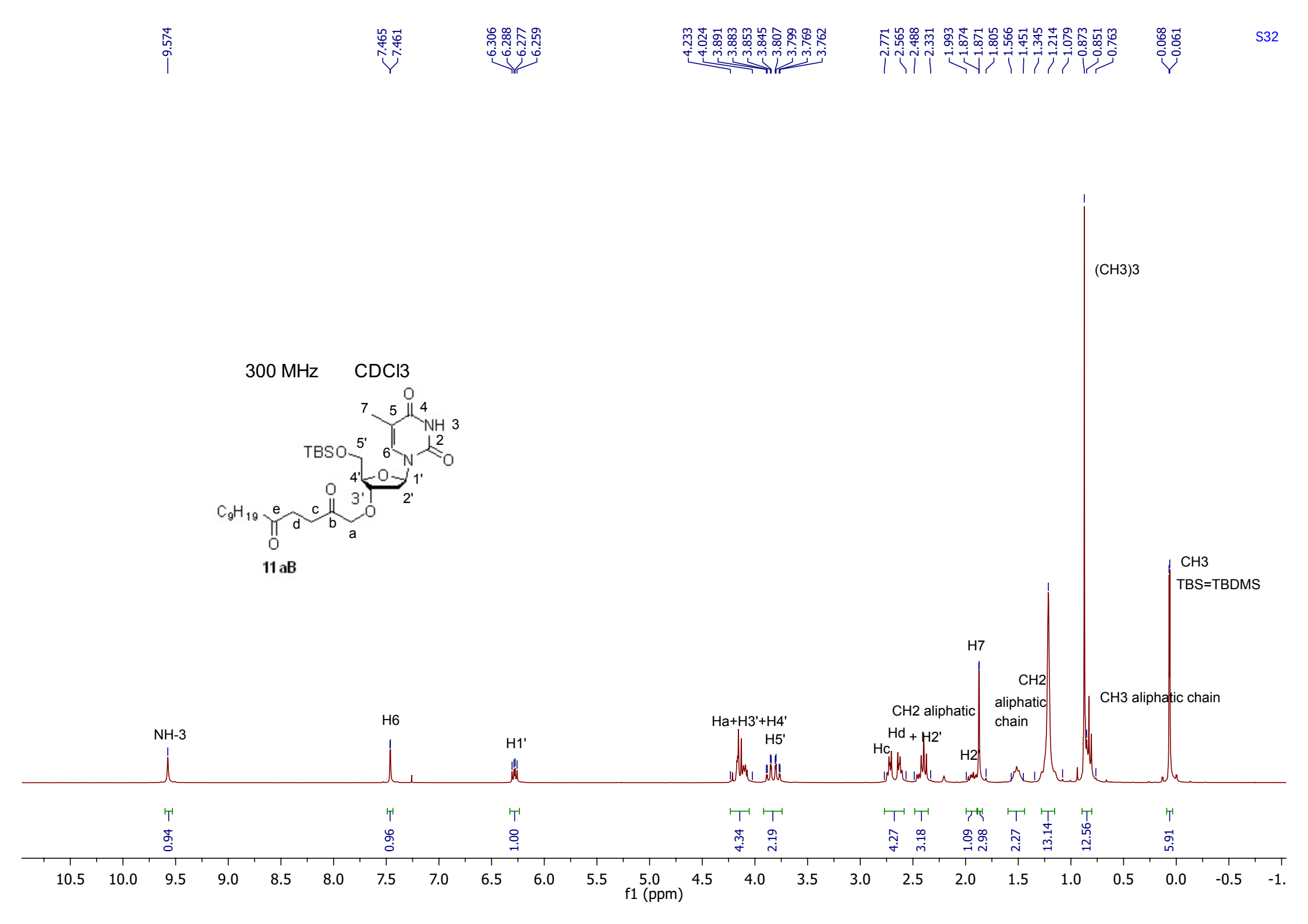
209.45
206.96
164.08
150.52
135.33
110.95
85.13
84.99
80.83
74.19
63.73
42.65
37.86
35.98
32.34
31.66
29.15
29.07
25.95
23.87
22.62
14.08
12.55
12.53
-5.39
-5.45

75.5 MHz CDCl3



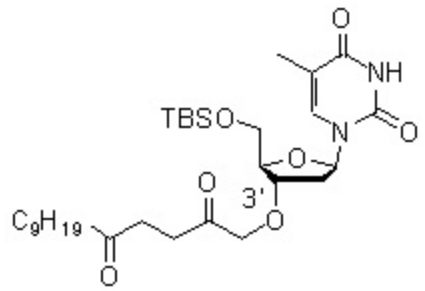
11aA




9.574
7.465
7.461
6.306
6.288
6.277
6.259
4.233
4.024
3.891
3.883
3.853
3.845
3.807
3.799
3.769
3.762
2.771
2.565
2.488
2.331
1.993
1.874
1.871
1.805
1.566
1.451
1.345
1.214
1.079
0.873
0.851
0.763
0.068
0.061
300 MHz CDCl3
11 aB
(CH3)3
CH3
TBS=TBDMS
H7
CH2
aliphatic
chain
CH3 aliphatic chain
CH2 aliphatic
Hd + H2'
Hc
H2
Ha+H3'+H4'
H5'
NH-3
H6
H1'
0.94
0.96
1.00
4.34
2.19
4.27
3.18
1.09
2.98
2.27
13.14
12.56
5.91
f1 (ppm)

209.52
207.00
164.14
150.55
135.35
110.96
85.13
84.98
80.84
74.16
63.74
42.65
37.84
35.98
32.32
31.88
29.43
29.29
29.21
25.95
23.86
22.68
18.35
14.15
12.57
-5.38
-5.45

75.5 MHz CDCl3

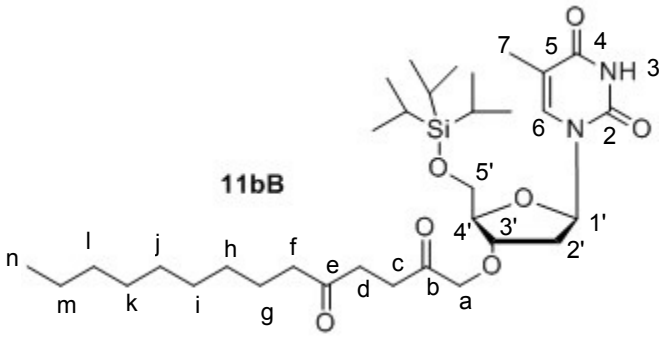


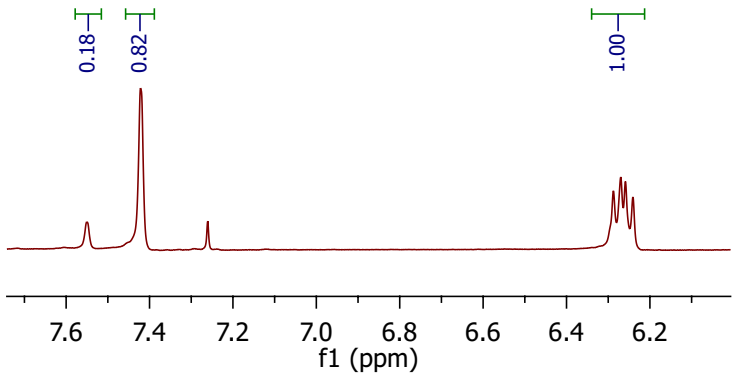
11 aB

4.26 4.12 3.98 3.82 2.78 2.60 2.50 2.43 2.41 2.38 2.35 2.05 1.87 1.62 1.44 1.22 1.15 0.98 0.91 0.77

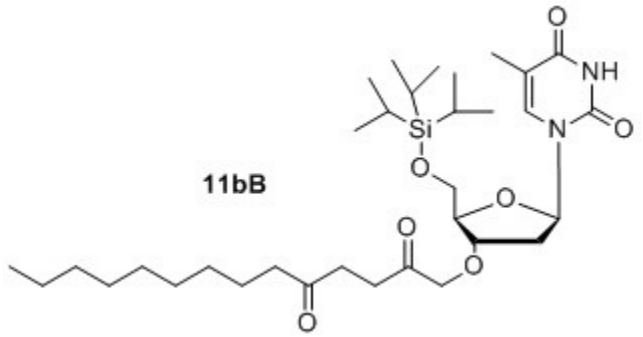
300 MHz CDCl3, 293 K

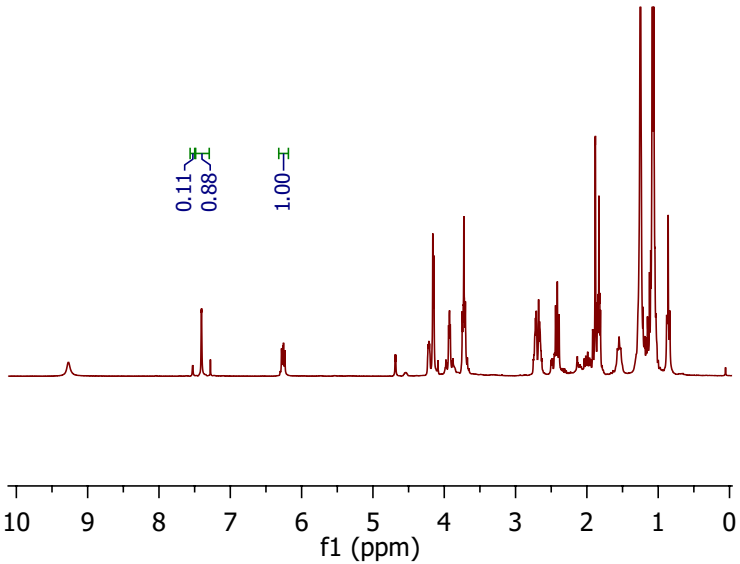
11bB

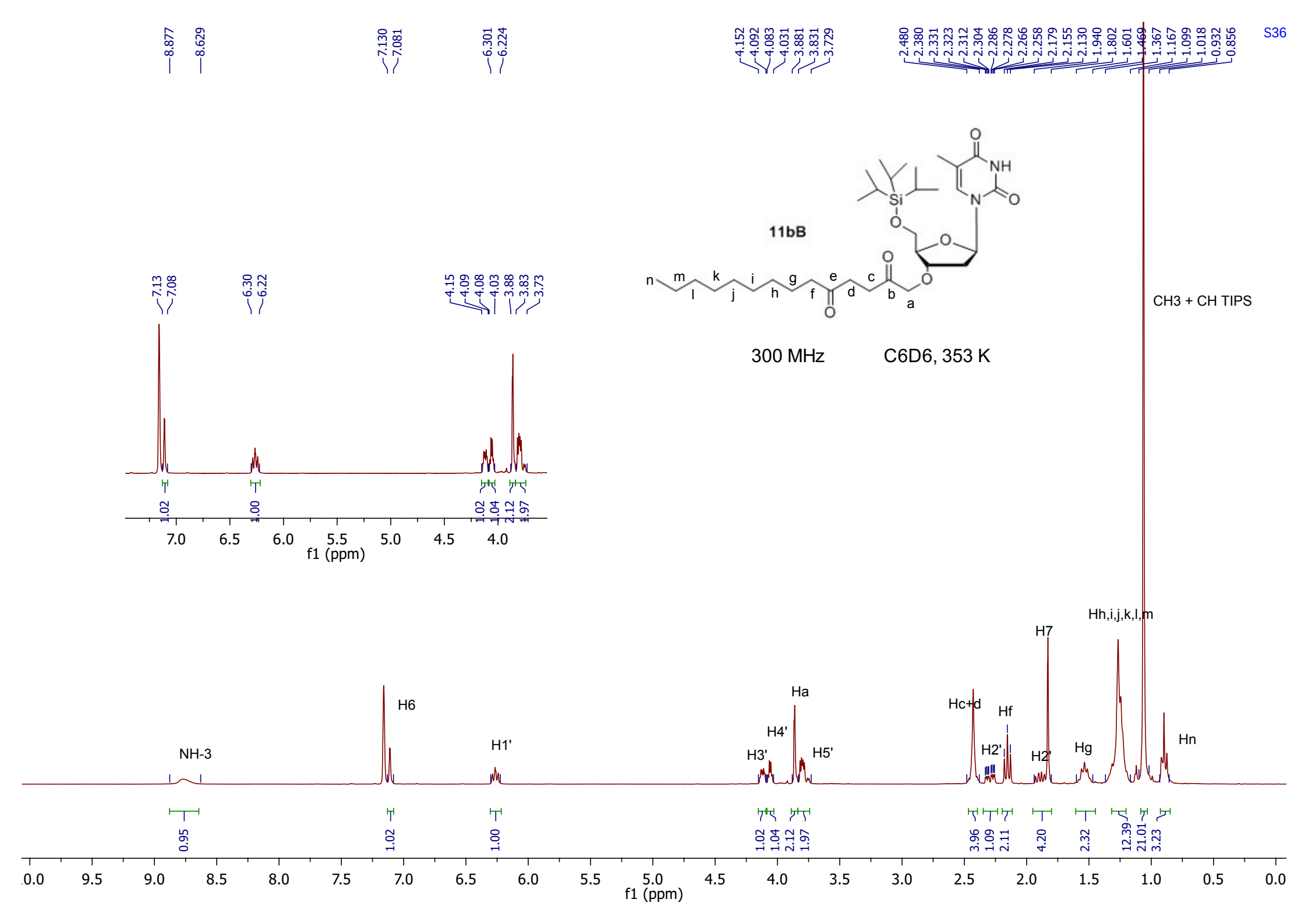


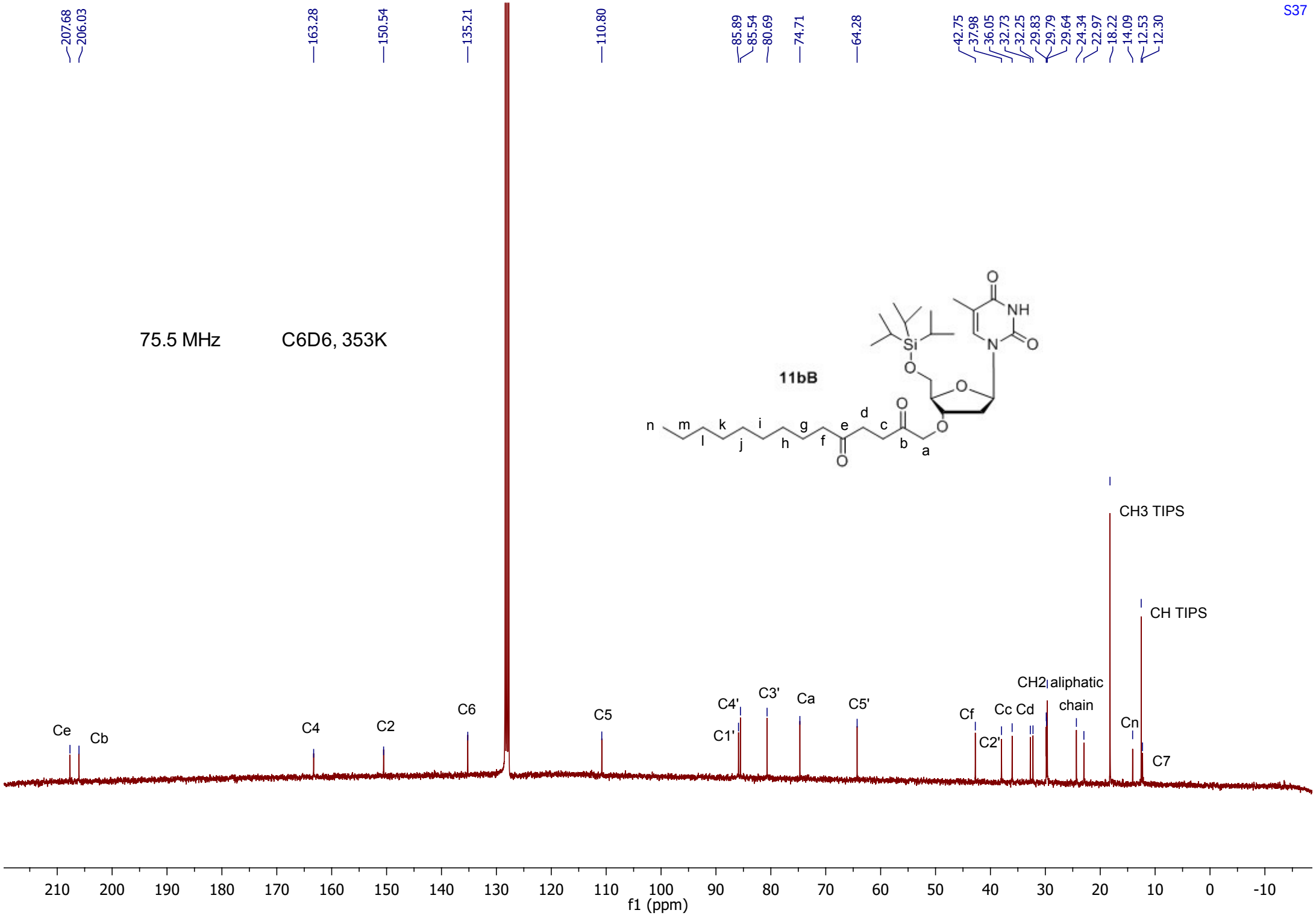


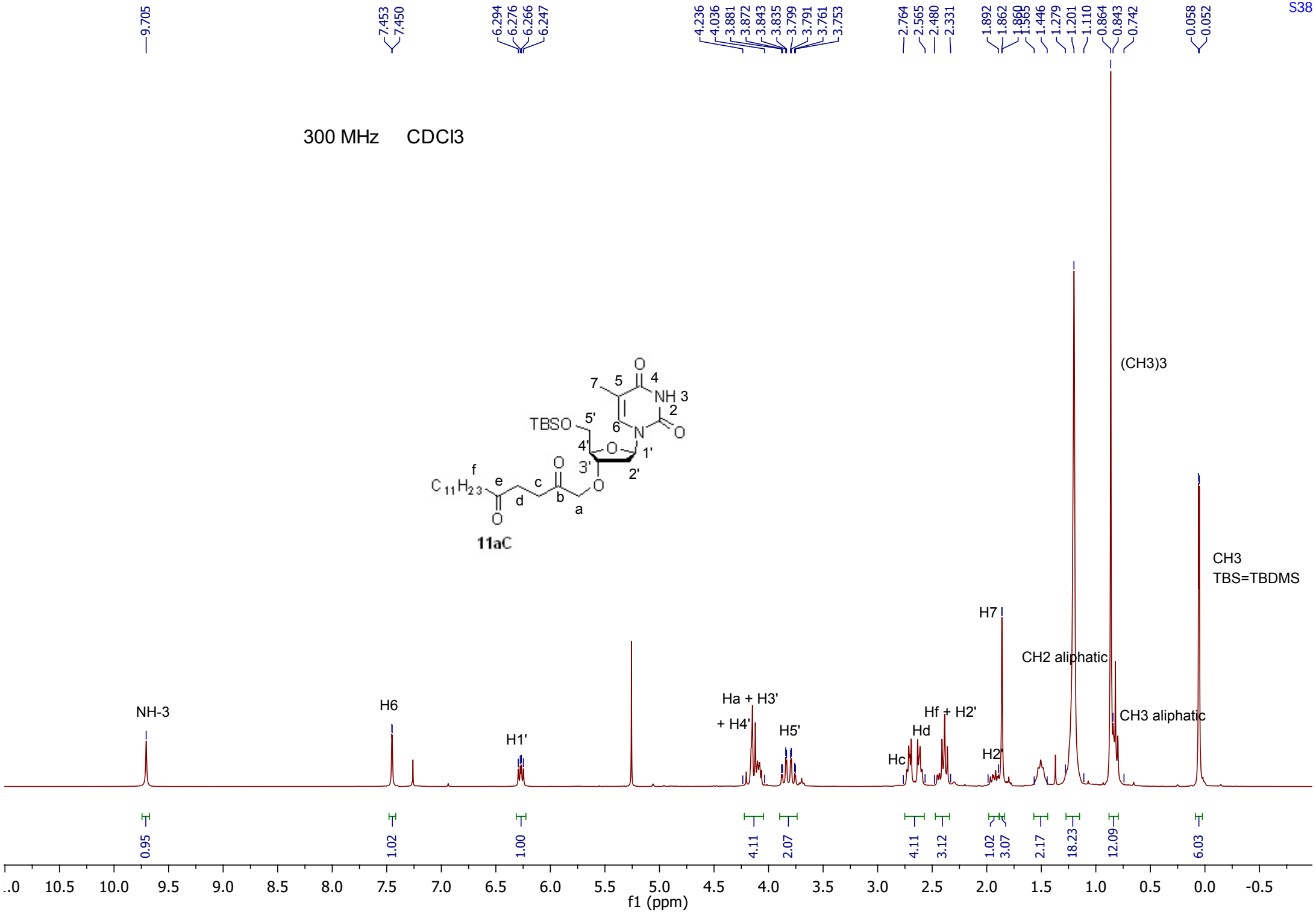
300 MHz CDCl3, 313 K





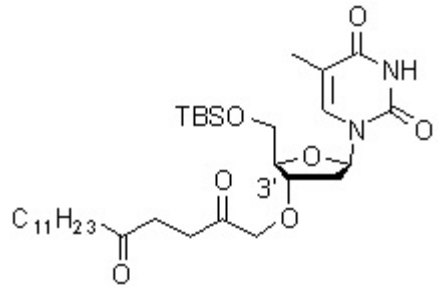

11bB
300 MHz
C6D6, 353 K
CH3 + CH TIPS
NH-3
H6
H1'
H3'
H4'
Ha
H5'
Hc+d
Hf
H2'
H7
H2'
Hg
Hh,i,j,k,l,m
Hn
f1 (ppm)


207.68
206.03
163.28
150.54
135.21
110.80
85.89
85.54
80.69
74.71
64.28
42.75
37.98
36.05
32.73
32.25
29.83
29.79
29.64
24.34
22.97
18.22
14.09
12.53
12.30
75.5 MHz
C6D6, 353K
11bB
CH3 TIPS
CH TIPS
CH2 aliphatic chain
Ce
Cb
C4
C2
C6
C5
C4'
C1'
C3'
Ca
C5'
Cf
C2'
Cc
Cd
Cn
C7
f1 (ppm)

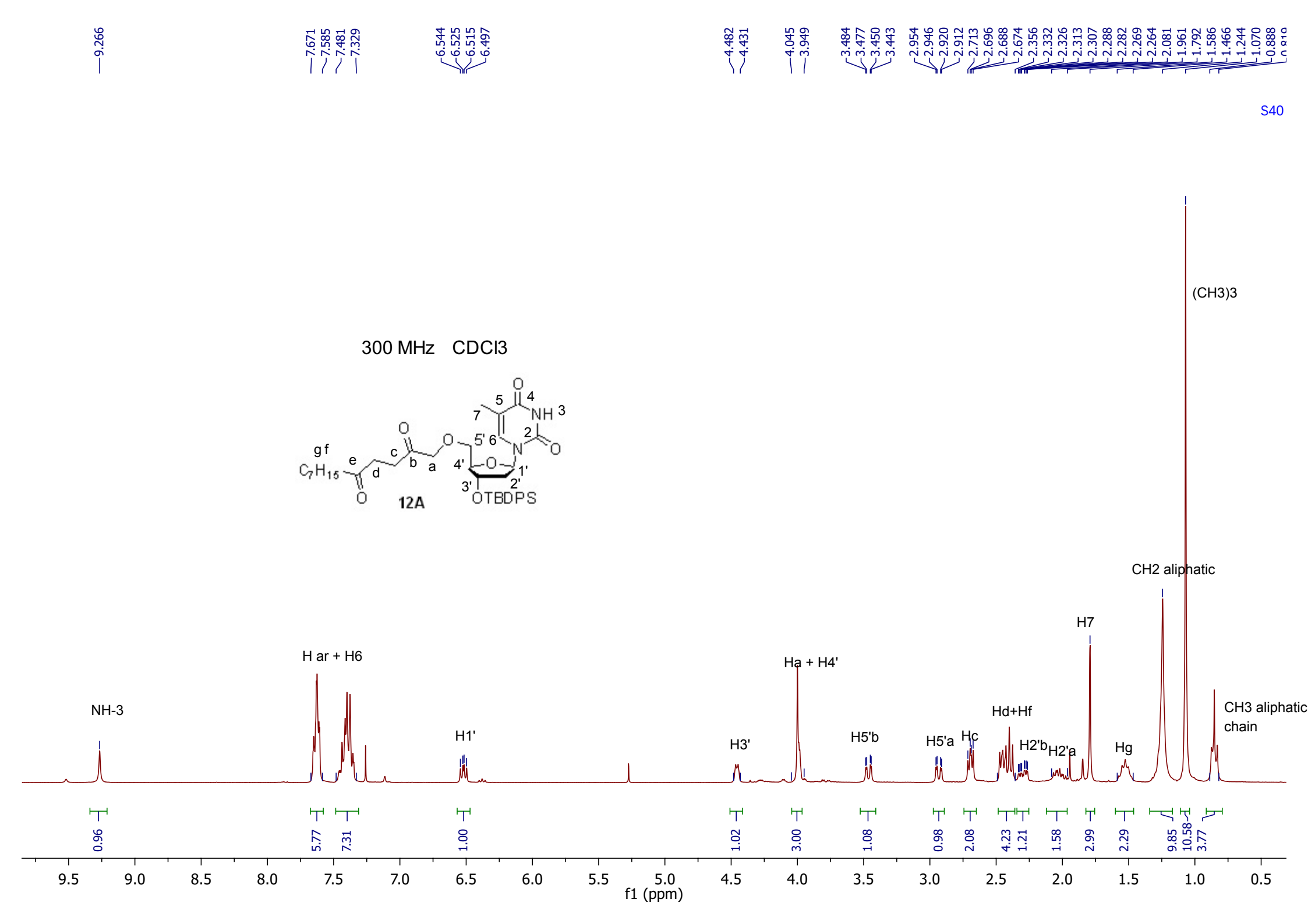

9.705
7.453
7.450
6.294
6.276
6.266
6.247
4.236
4.036
3.881
3.872
3.843
3.835
3.799
3.791
3.761
3.753
2.764
2.565
2.480
2.331
1.892
1.862
1.565
1.446
1.279
1.201
1.110
0.864
0.843
0.742
0.058
0.052
300 MHz CDCl3
TBSO
NH 3
11aC
(CH3)3
CH3
TBS=TBDMS
H7
CH2 aliphatic
CH3 aliphatic
NH-3
H6
H1'
Ha + H3'
+ H4'
H5'
Hc
Hd
Hf + H2'
H2'
0.95
1.02
1.00
4.11
2.07
4.11
3.12
1.02
3.07
2.17
18.23
12.09
6.03
f1 (ppm)

209.41
206.94
164.13
150.55
135.31
110.90
85.11
84.97
80.79
74.15
63.70
42.62
37.83
35.94
32.30
31.89
29.67
29.59
29.45
29.40
29.31
29.19
25.92
23.84
22.66
18.31
14.11
12.51
-5.42
-5.48

75.5 MHz CDCl3

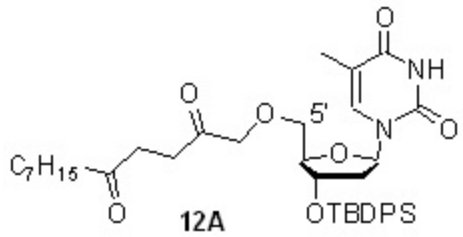


11aC

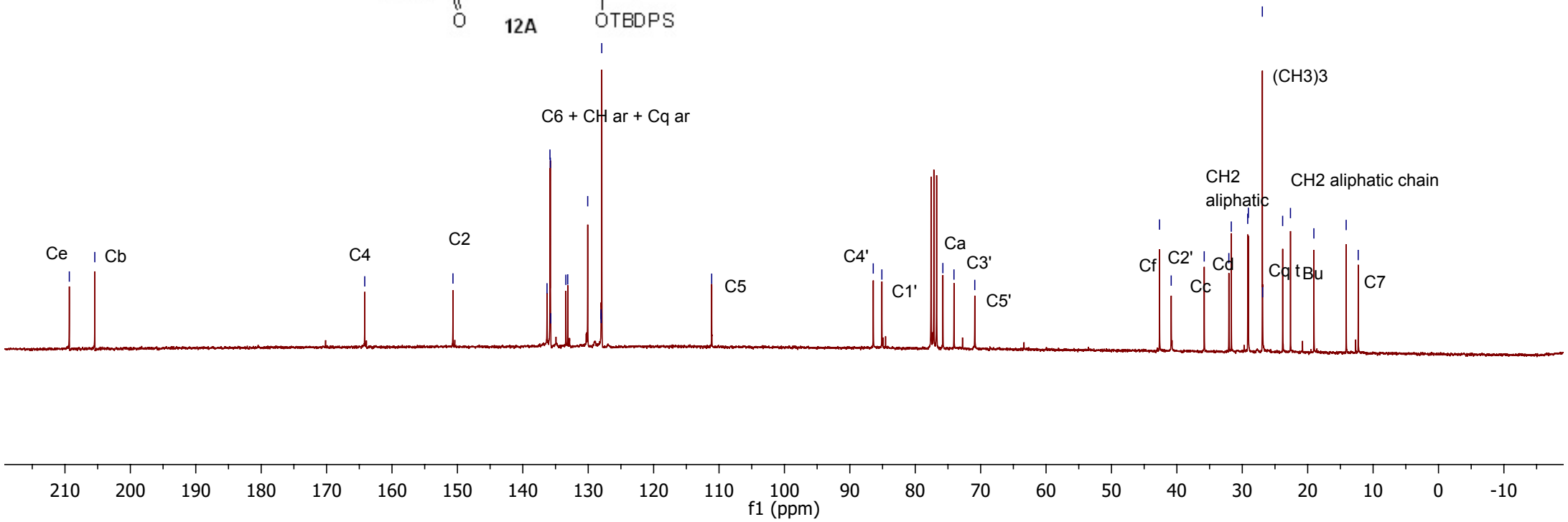

9.266
7.671
7.585
7.481
7.329
6.544
6.525
6.515
6.497
4.482
4.431
4.045
3.949
3.484
3.477
3.450
3.443
2.954
2.946
2.920
2.912
2.713
2.696
2.688
2.674
2.356
2.332
2.326
2.313
2.307
2.288
2.282
2.269
2.264
2.081
1.961
1.792
1.586
1.466
1.244
1.070
0.888
300 MHz CDCl3
12A
(CH3)3
CH2 aliphatic
H7
H ar + H6
Ha + H4'
Hd+Hf
NH-3
H1'
H3'
H5'b
H5'a
Hc
H2'b
H2'a
Hg
CH3 aliphatic chain
0.96
5.77
7.31
1.00
1.02
3.00
1.08
0.98
2.08
4.23
1.21
1.58
2.99
2.29
9.85
10.58
3.77
f1 (ppm)

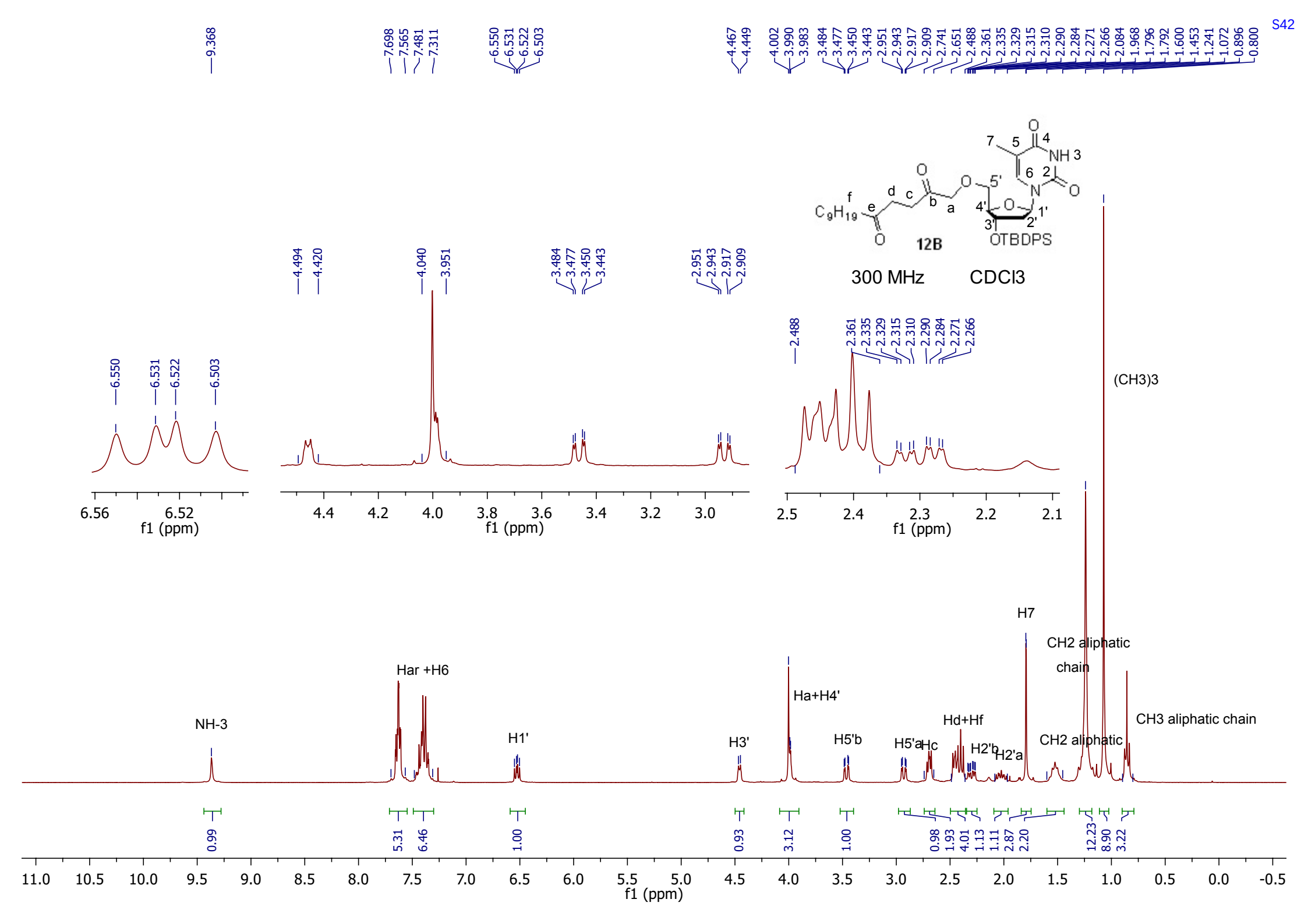
209.33
205.44
164.17
150.68
136.30
135.85
135.79
135.73
133.42
133.13
130.08
128.04
128.01
127.93
111.12
86.42
85.10
75.78
74.08
70.90
42.66
40.87
35.82
32.05
31.68
29.17
29.07
26.93
26.89
23.83
22.63
19.05
14.12
12.28

75.5 MHz CDCl3

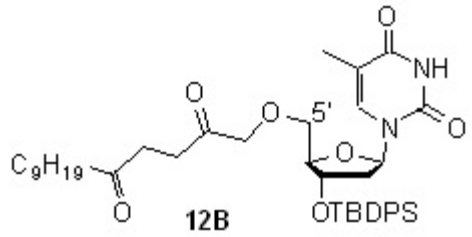


12A



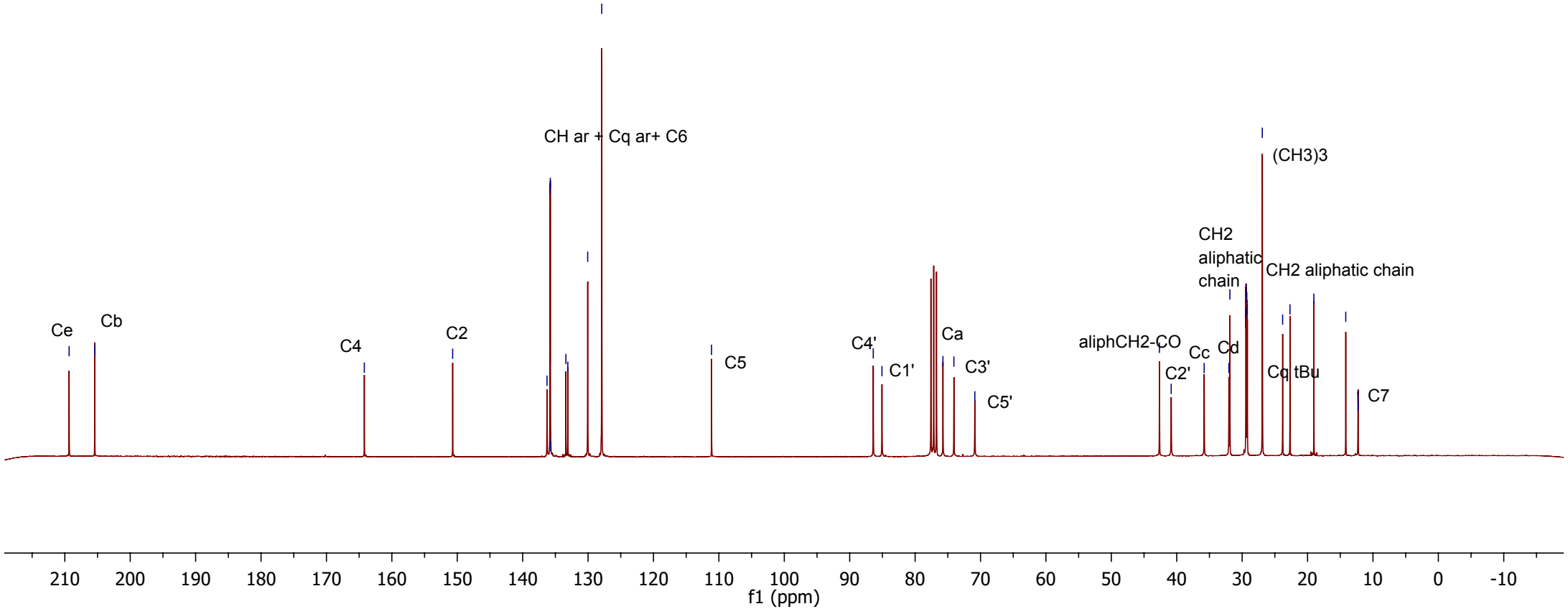

12B
300 MHz
CDCl3
OTBDPS
NH-3
Har +H6
H1'
H3'
Ha+H4'
H5'b
H5'a
Hc
Hd+Hf
H2'b
H2'a
H7
CH2 aliphatic chain
CH2 aliphatic
CH3 aliphatic chain
(CH3)3
f1 (ppm)

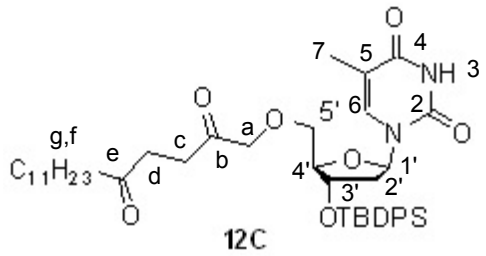
209.34
205.43
164.21
150.70
136.28
135.83
135.77
135.71
133.39
133.10
130.06
127.91
111.12
86.40
85.07
75.75
74.07
70.87
42.64
40.85
35.81
32.03
31.87
29.44
29.41
29.28
29.21
26.91
23.81
22.69
19.03
14.16
12.29
12.26



12B

75.5 MHz CDCl3





12C

(CH3)3

H7

CH2 aliphatic chain

CH3 aliphatic chain

H aro+ H6

Ha
+ H4'

Hd+Hf

NH-3

H1'

H3'

H5'b

H5'a

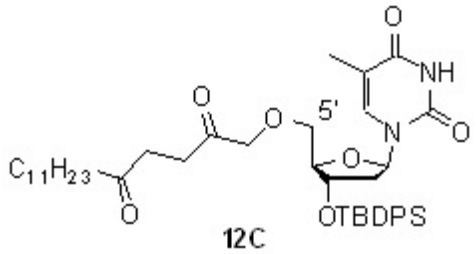
Hc

H2'b

H2'a

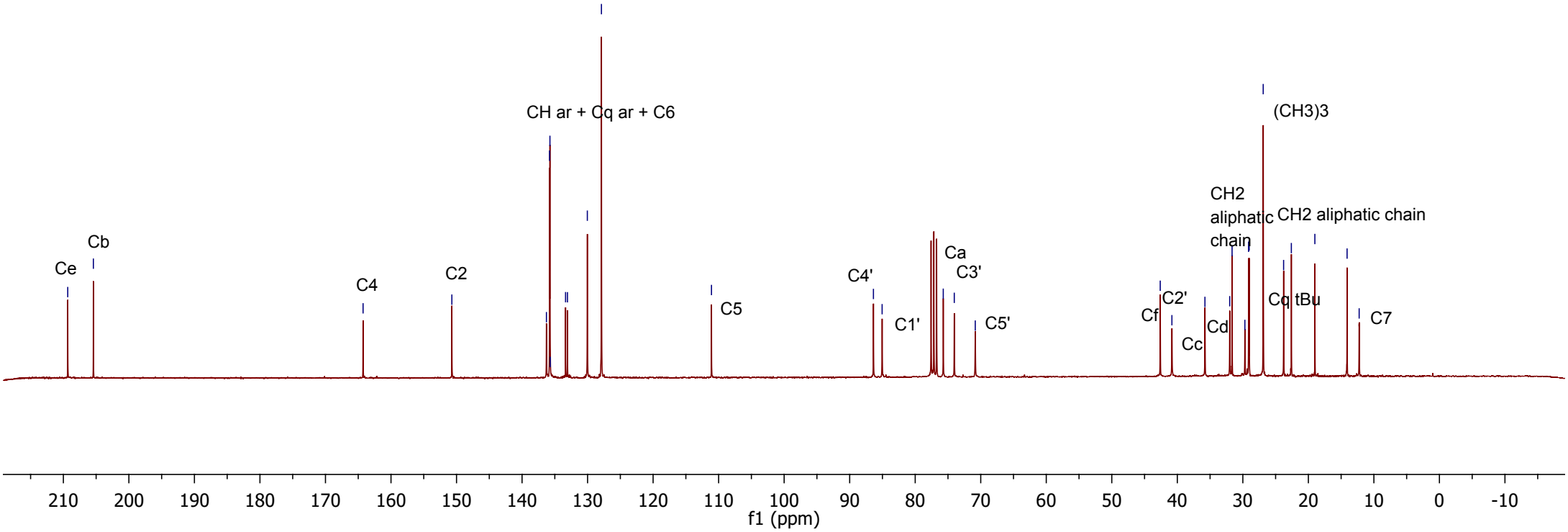
f1 (ppm)

209.33 205.42 164.26 150.71 136.28 135.80 135.74 135.70 133.36 133.07 130.04 127.88 111.09 86.38 85.05 75.72 74.04 70.84 42.61 40.82 35.78 32.00 31.64 29.69 29.13 29.03 26.89 23.78 22.60 19.01 14.09 12.25

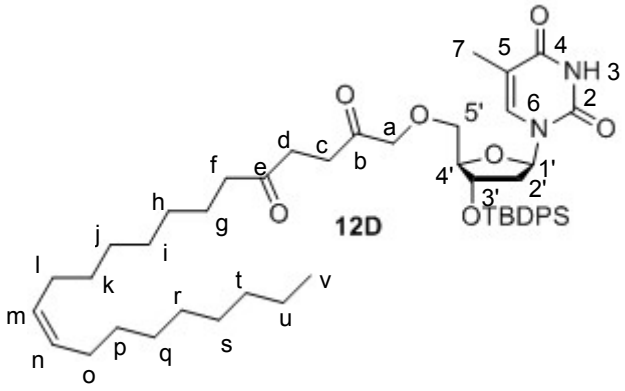


12C

75.5 MHz CDCl3

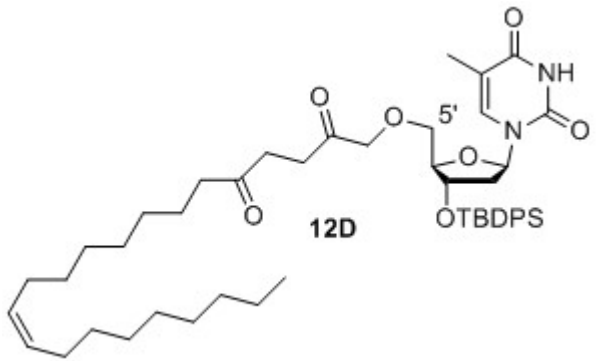


300MHz CDCl3

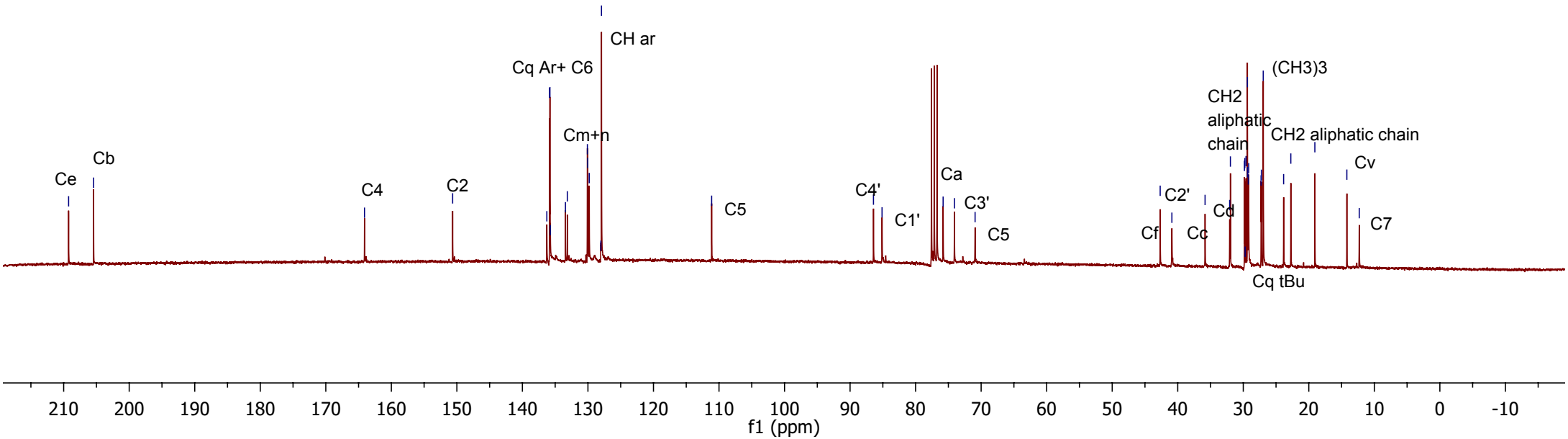


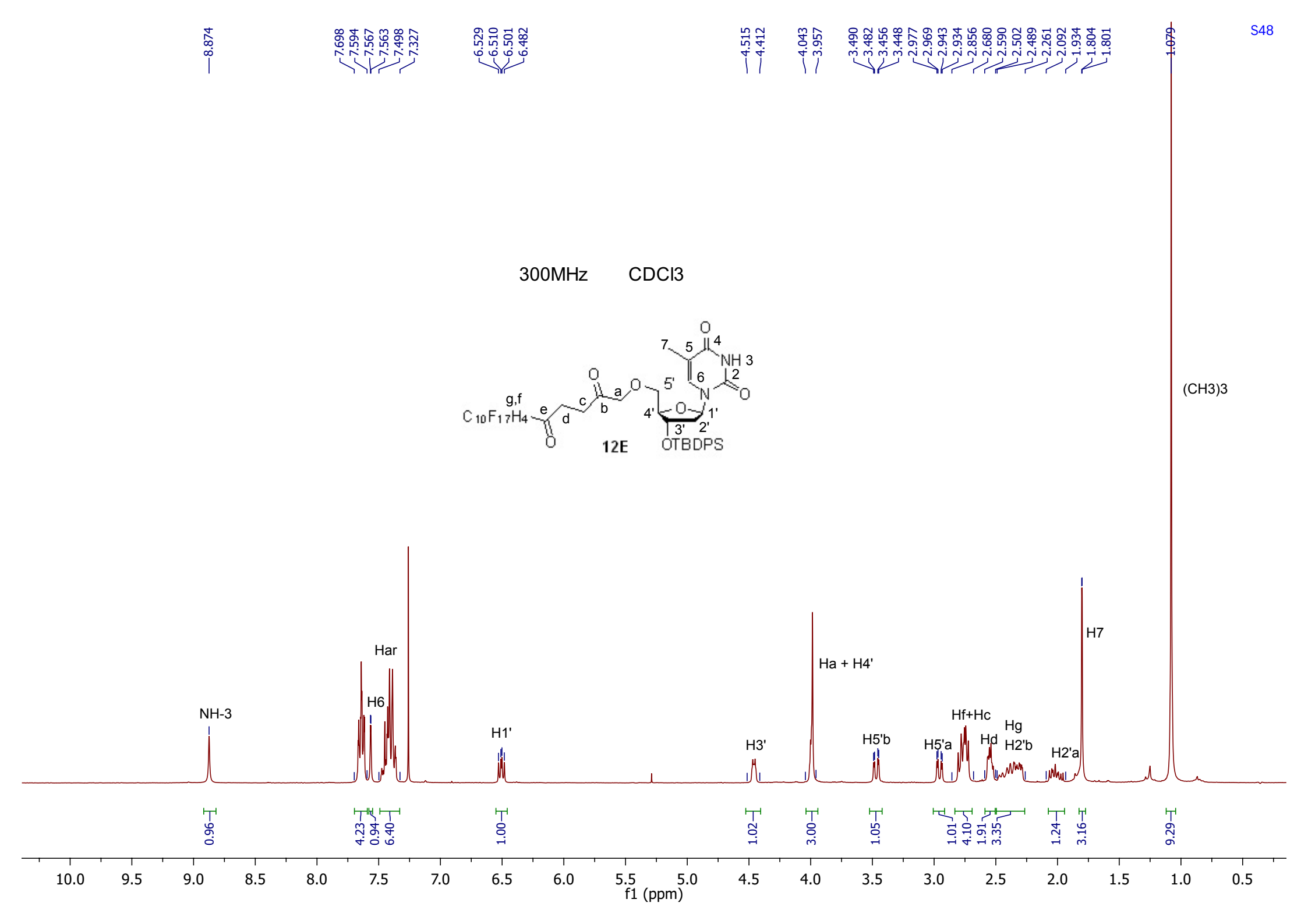
209.25 205.43 164.09 150.65 136.27 135.86 135.80 135.74 133.43 133.15 130.08 130.04 129.80 128.03 127.93 111.12 86.43 85.12 75.80 74.08 70.92 42.68 40.89 35.83 32.07 31.96 29.83 29.76 29.72 29.58 29.38 29.35 29.23 29.17 27.28 27.24 26.95 23.84 22.75 19.08 14.19 12.30

75.5 MHz CDCl3



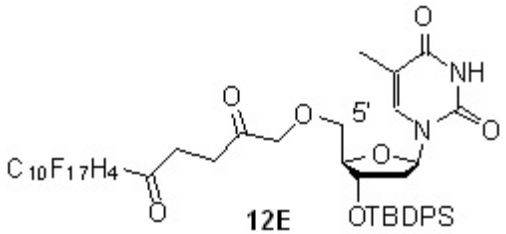
12D

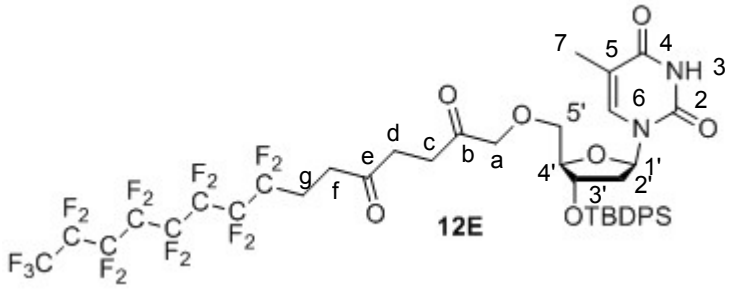



8.874
7.698
7.594
7.567
7.563
7.498
7.327
6.529
6.510
6.501
6.482
4.515
4.412
4.043
3.957
3.490
3.482
3.456
3.448
2.977
2.969
2.943
2.934
2.856
2.680
2.590
2.502
2.489
2.261
2.092
1.934
1.804
1.801
1.079
300MHz CDCl3
12E
OTBDPS
(CH3)3
NH-3
Har
H6
H1'
H3'
Ha + H4'
H5'b
H5'a
Hf+Hc
Hd
Hg
H2'b
H2'a
H7
0.96
4.23
0.94
6.40
1.00
1.02
3.00
1.05
1.01
4.10
1.91
3.35
1.24
3.16
9.29
f1 (ppm)

205.42
205.25
163.97
150.60
136.22
135.93
135.87
133.48
133.17
130.16
128.00
111.15
86.39
85.17
77.36
75.78
73.99
71.01
40.91
35.75
33.29
32.30
26.96
25.38
25.08
24.79
19.12
12.33

75.5 MHz CDCl3



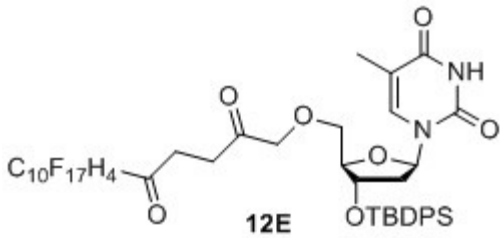


-80.69
-80.73
-80.76

-22795.0
-22804.9
-22814.8

-80.7
f1 (ppm)

19FNMR 282.4 MHz CDCl3



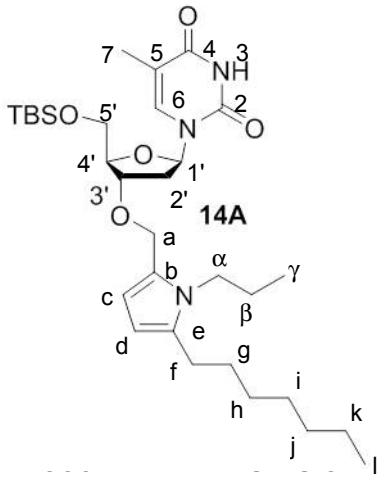
12E

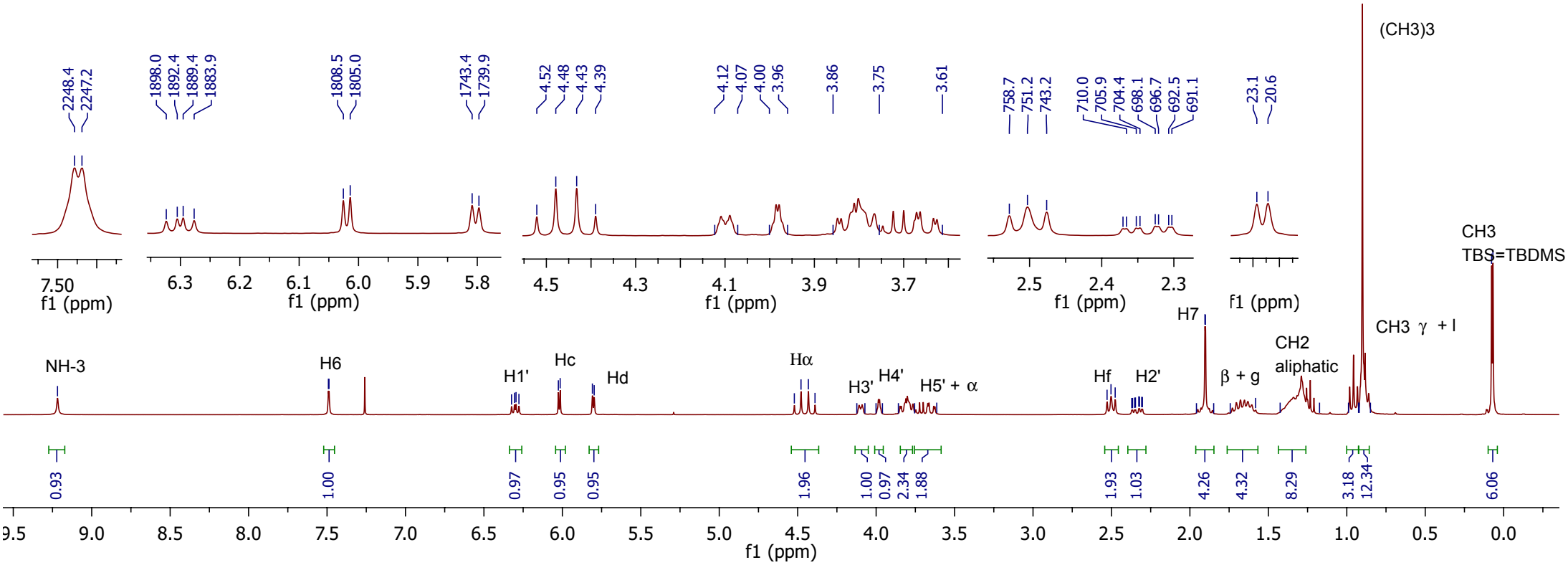
CF3

CF2

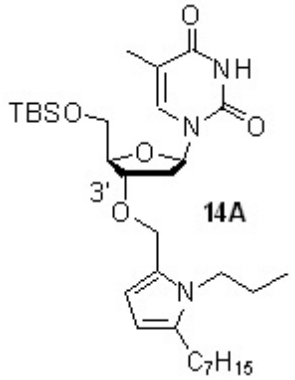
3.00
2.12
6.29
2.41
2.28
2.39

-78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128
f1 (ppm)


TBSO
14A

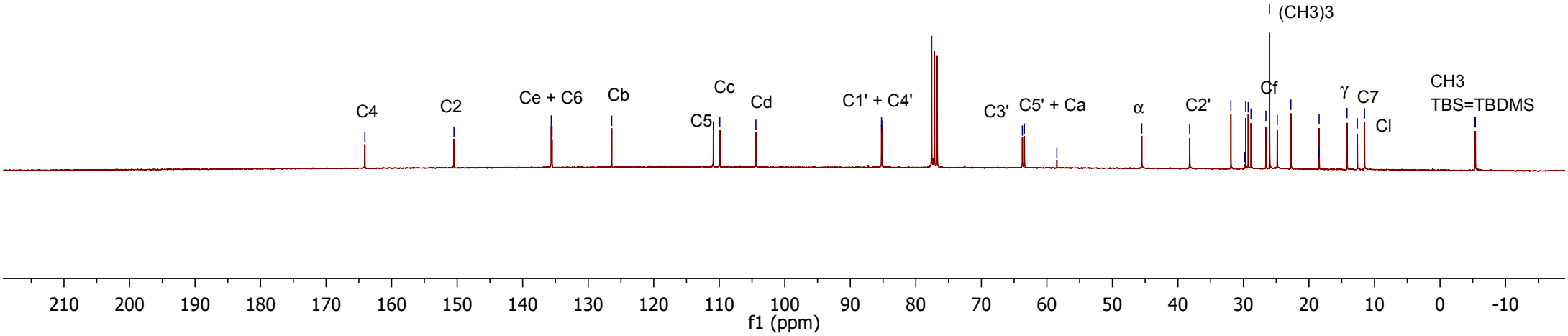

NH-3
H6
H1'
Hc
Hd
Hα
H3'
H4'
H5' + α
Hf
H2'
H7
β + g
CH2
aliphatic
CH3 γ + l
(CH3)3
CH3
TBS=TBDMS
f1 (ppm)

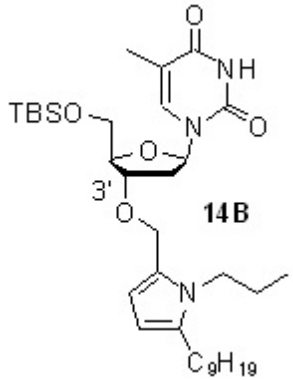
164.08 150.49 135.64 135.52 126.41 110.90 109.92 104.41 85.24 85.20 63.74 63.43 58.47 45.52 38.21 31.92 29.79 29.65 29.27 28.84 26.57 26.02 24.84 22.76 18.50 18.45 14.20 12.62 11.52 -5.29 -5.39



14A

75.5 MHz CDCl3

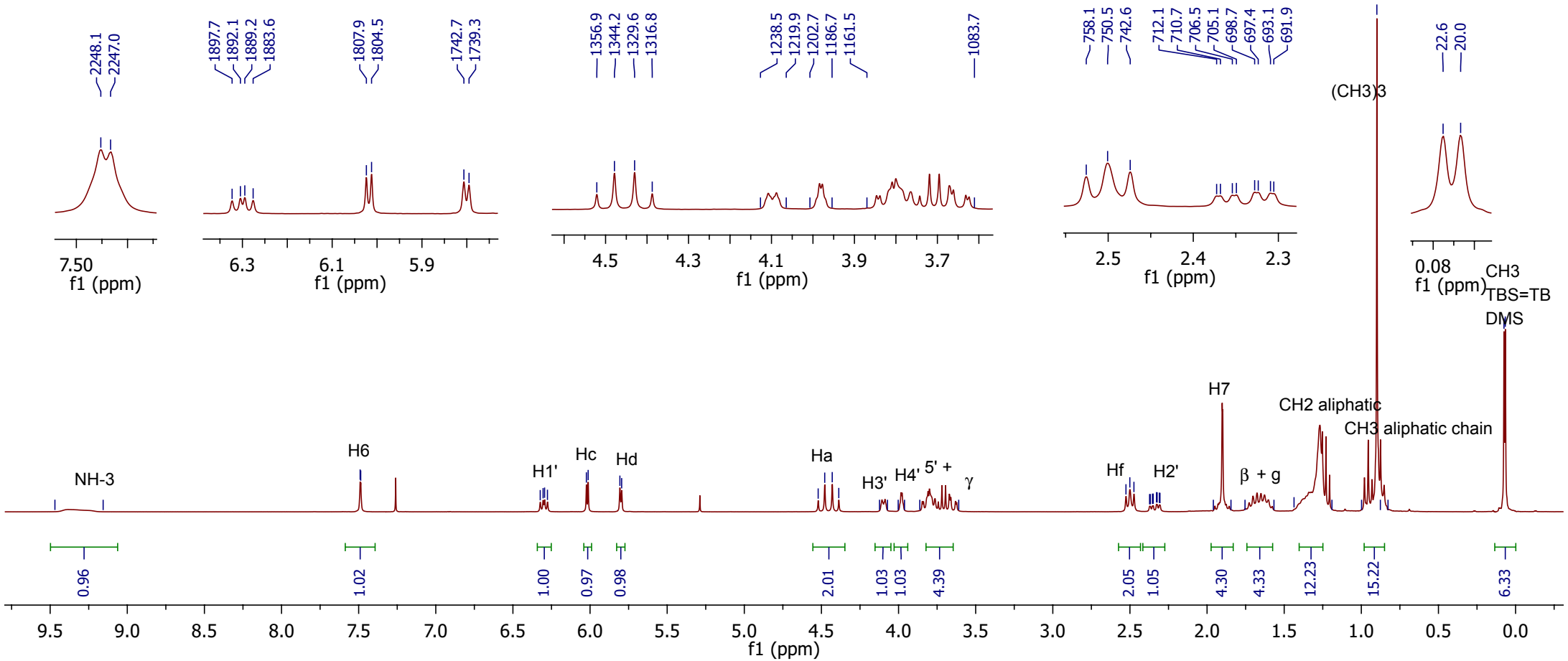




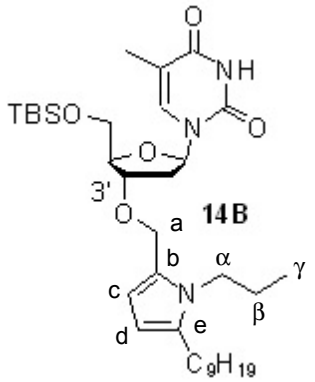
14B

similar numbering as 14A

300 MHz CDCl3

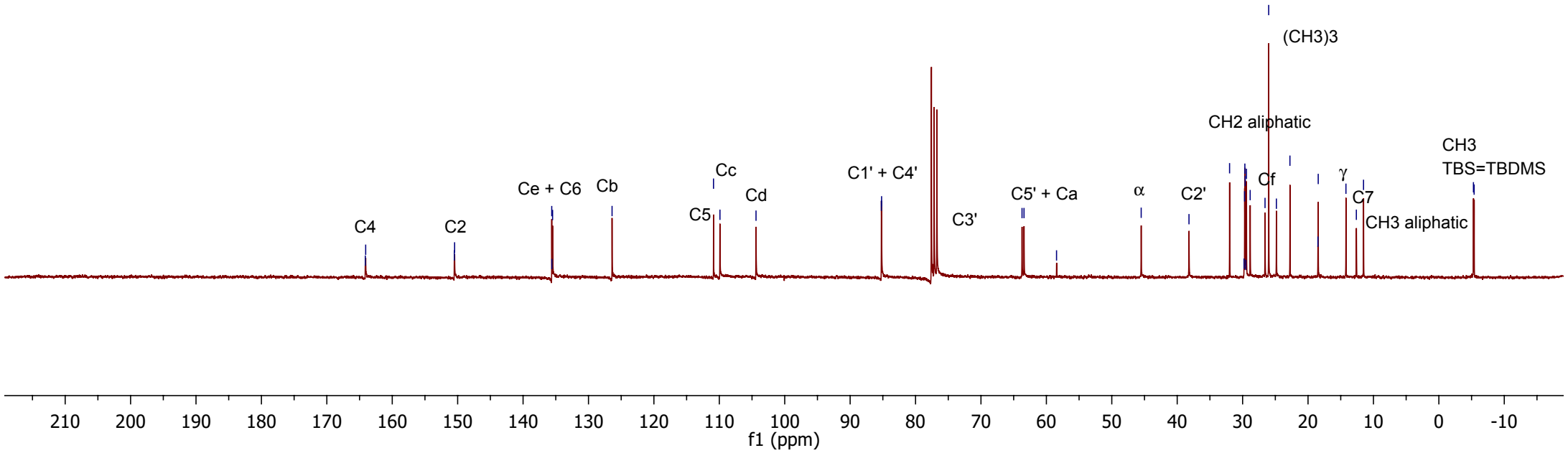


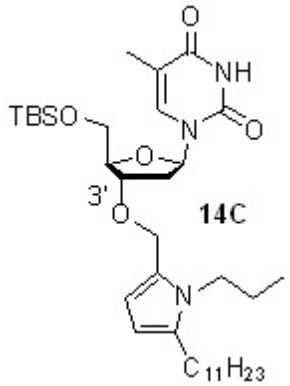
164.12
164.06
150.51
150.47
135.62
135.59
135.49
126.40
110.89
109.90
104.39
85.22
85.19
63.72
63.42
58.45
45.51
38.20
31.99
29.70
29.66
29.61
29.41
28.85
26.57
26.01
24.84
22.77
18.44
14.20
12.61
11.52
-5.29
-5.39



similar numbering as 14A

75.5 MHz CDCl3





similar numbering as 14A

300 MHz CDCl3

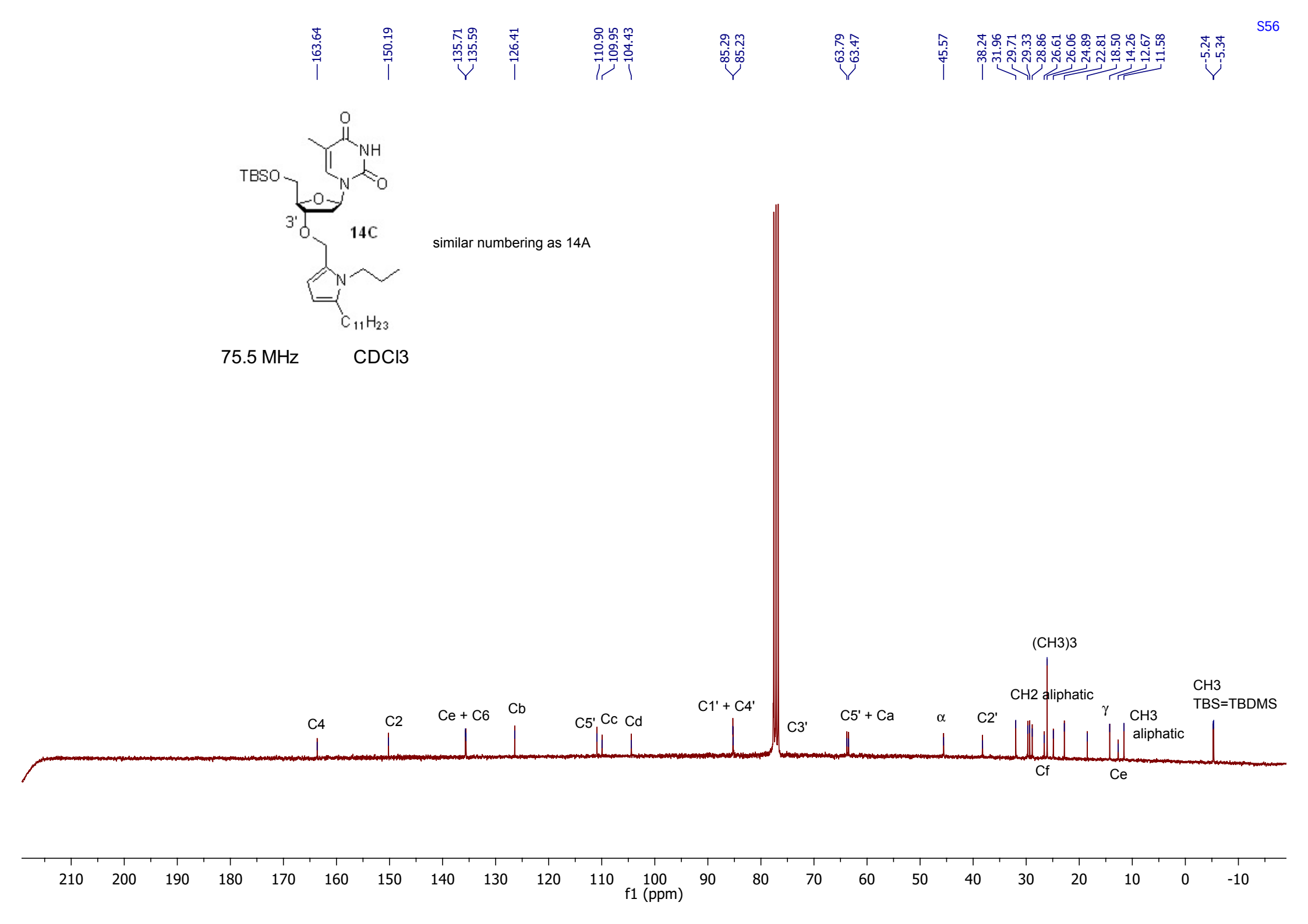
(CH3)3

CH3 TBS =TBDMS

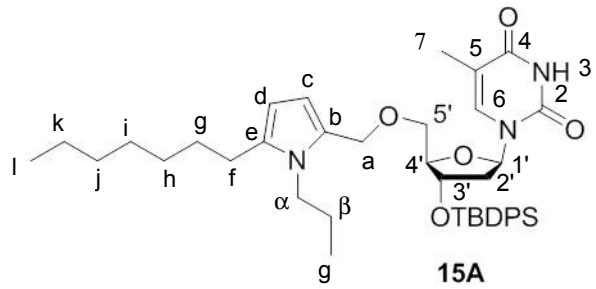
CH3 aliphatic

NH-3 H6 H1' Hc Hd Ha H3' H4' H5' γ Hf H2' H7 g +β CH2 aliphatic

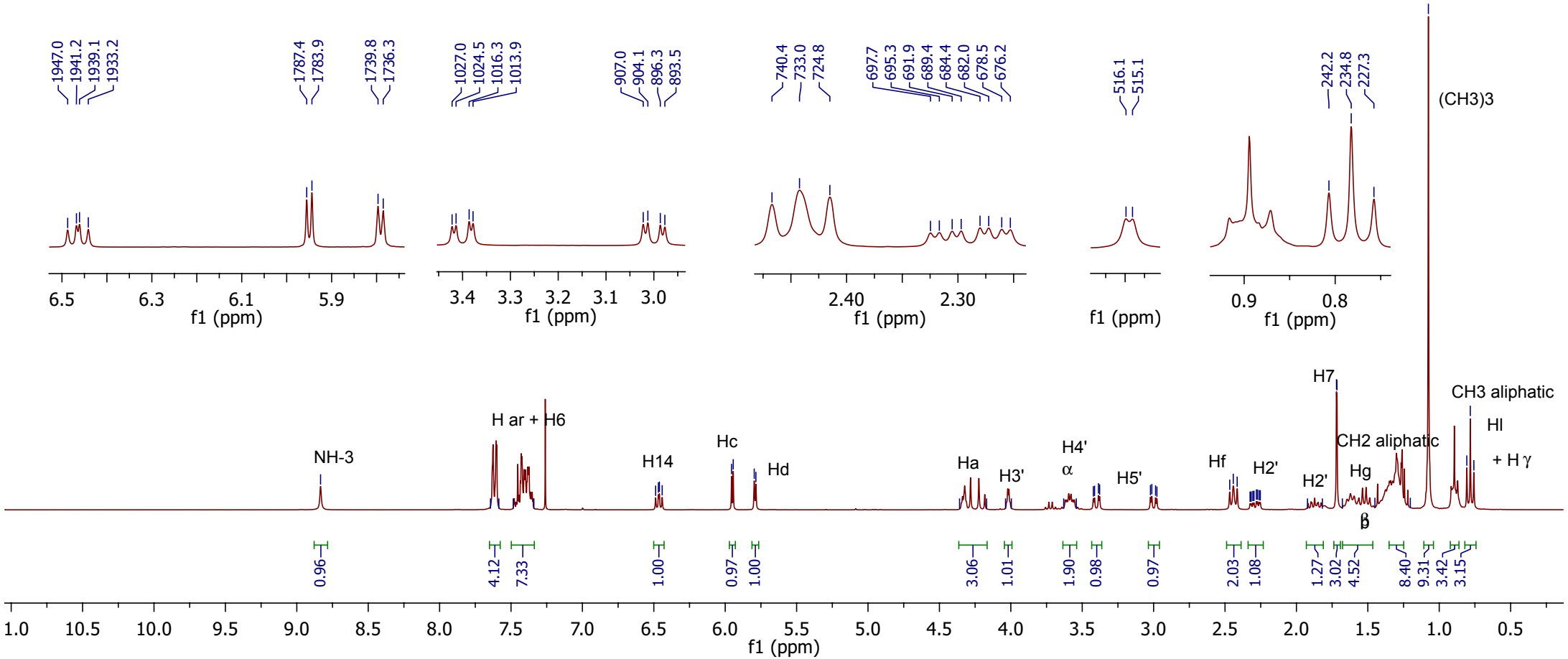
f1 (ppm)


163.64
150.19
135.71
135.59
126.41
110.90
109.95
104.43
85.29
85.23
63.79
63.47
45.57
38.24
31.96
29.71
29.33
28.86
26.61
26.06
24.89
22.81
18.50
14.26
12.67
11.58
-5.24
-5.34
TBSO
O
NH
N
O
3'
O
14C
C11H23
similar numbering as 14A
75.5 MHz
CDCl3
C4
C2
Ce + C6
Cb
C5'
Cc
Cd
C1' + C4'
C3'
C5' + Ca
α
C2'
(CH3)3
CH2 aliphatic
γ
CH3
aliphatic
CH3
TBS=TBDMS
Cf
Ce
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)

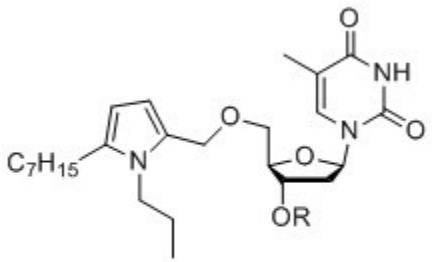
300 MHz CDCl3



15A

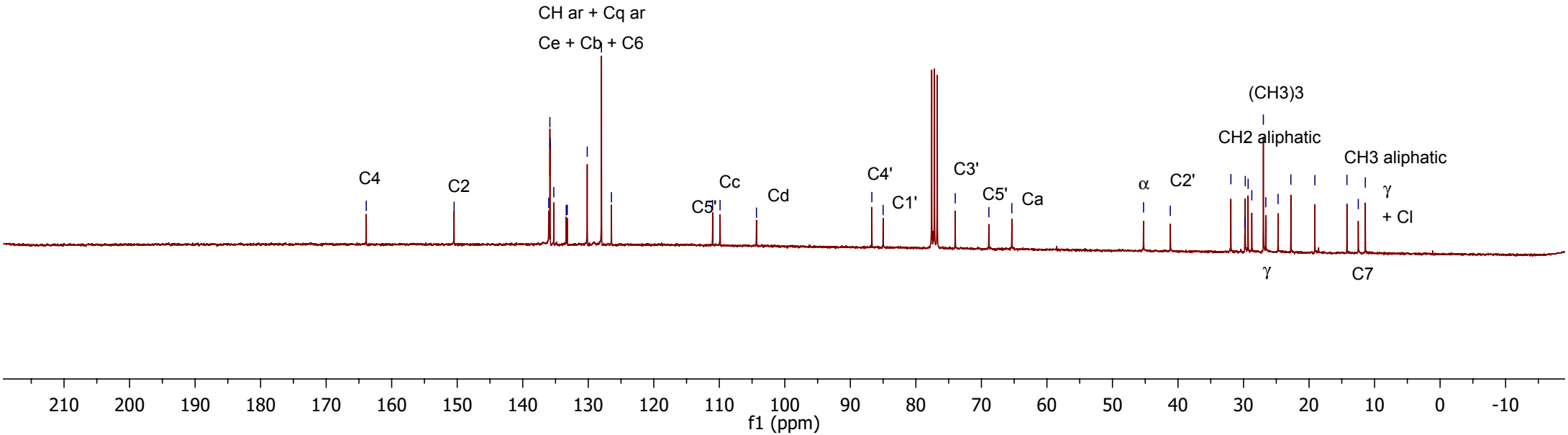


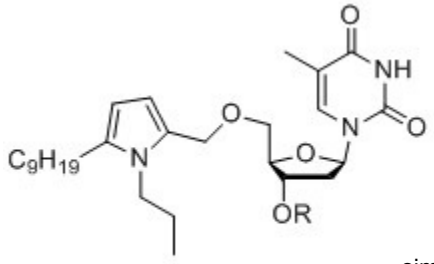
163.88 150.47 136.04 135.86 135.82 135.26 133.36 133.20 130.16 127.98 126.46 111.02 109.88 104.33 86.72 85.00 74.00 68.86 65.36 45.26 41.17 31.93 29.80 29.73 29.30 28.73 26.97 26.60 24.73 22.77 19.11 14.22 12.48 11.41



15A

75.5 MHz CDCl3

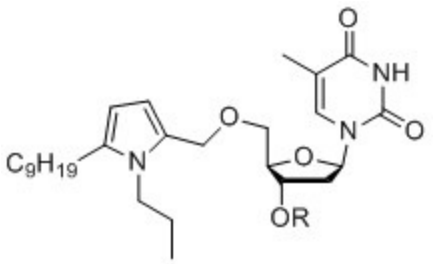




15B

300 MHz CDCl3

similar numbering as 15A

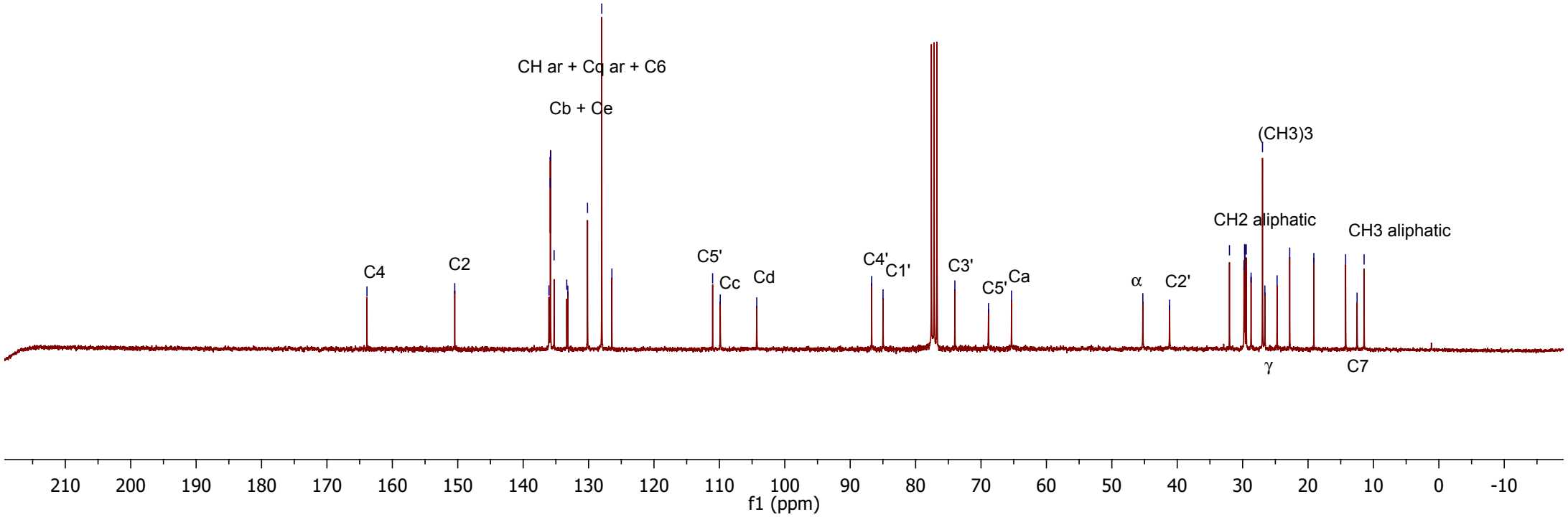


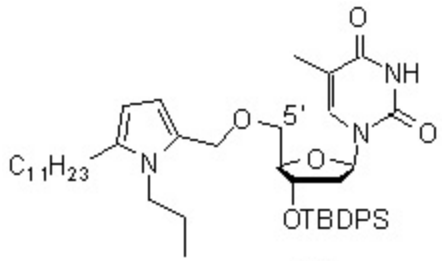
15B

R=TBDPS

similar numbering as 15A

75.5 MHz CDCl3

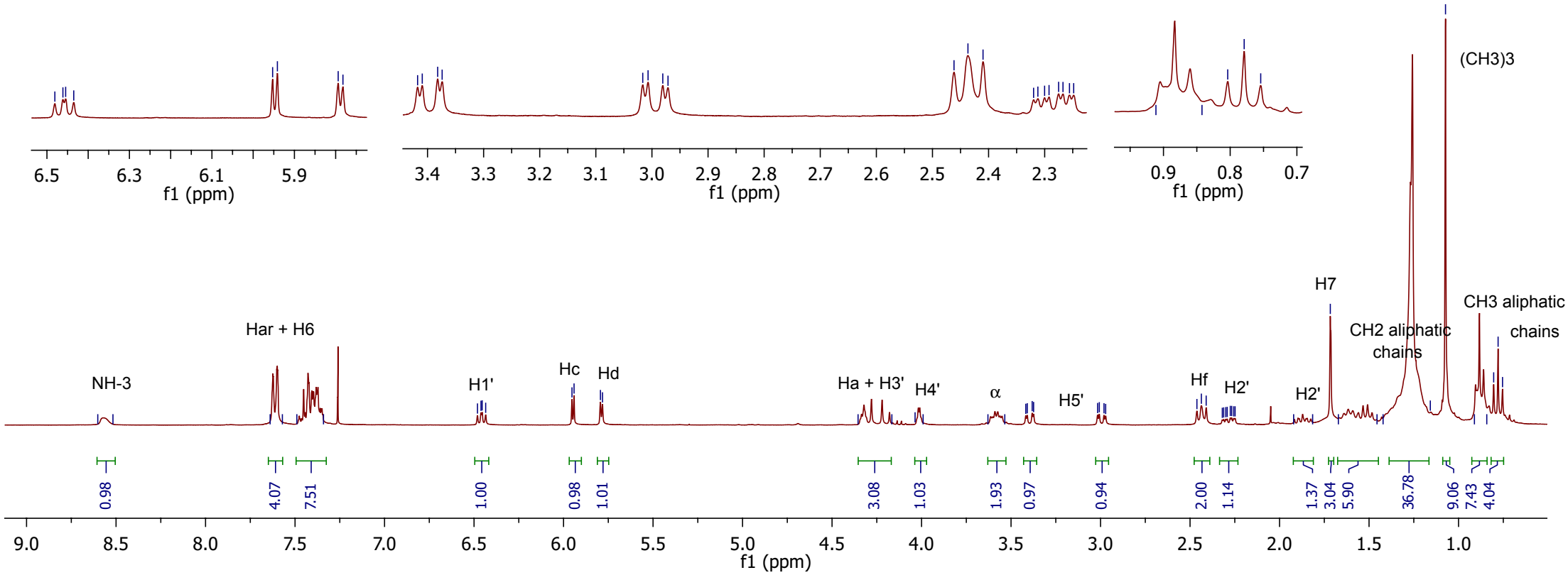




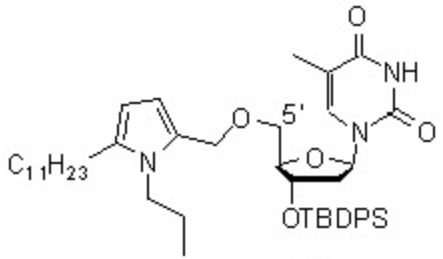
15C

similar numbering as 15A

300 MHz CDCl3



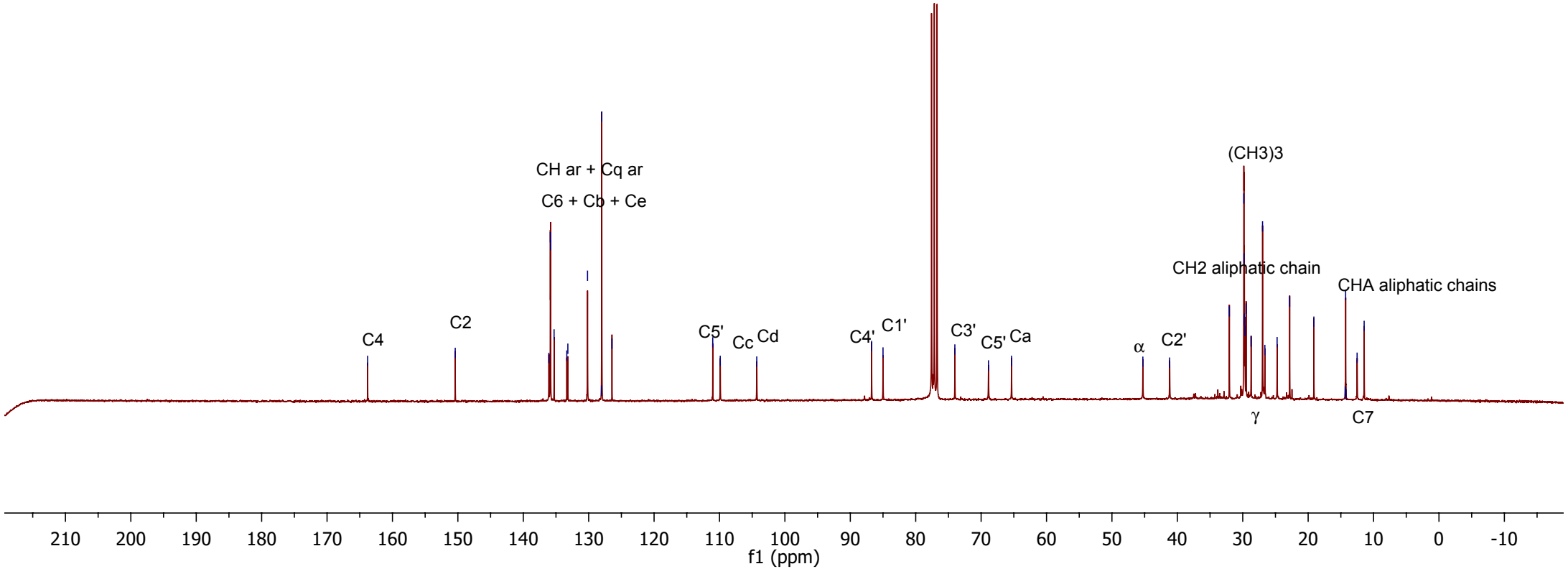
163.80 150.40 136.09 135.87 135.83 135.29 133.35 133.18 130.18 128.04 128.00 126.44 111.03 109.89 104.30 86.74 85.00 74.02 68.87 65.35 45.27 41.18 32.05 29.84 29.81 29.77 29.75 29.67 29.49 28.73 26.97 26.62 24.75 22.83 19.13 14.33 14.27 14.21 12.52 11.44

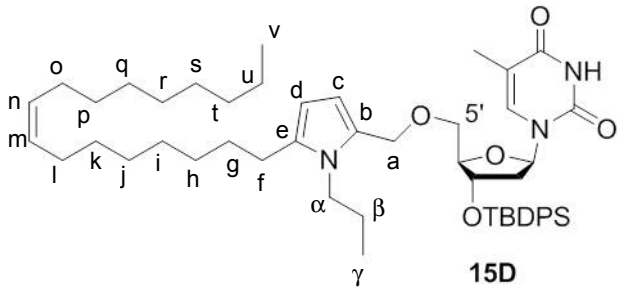


15C

similar numbering as 15A

75.5 MHz CDCl3



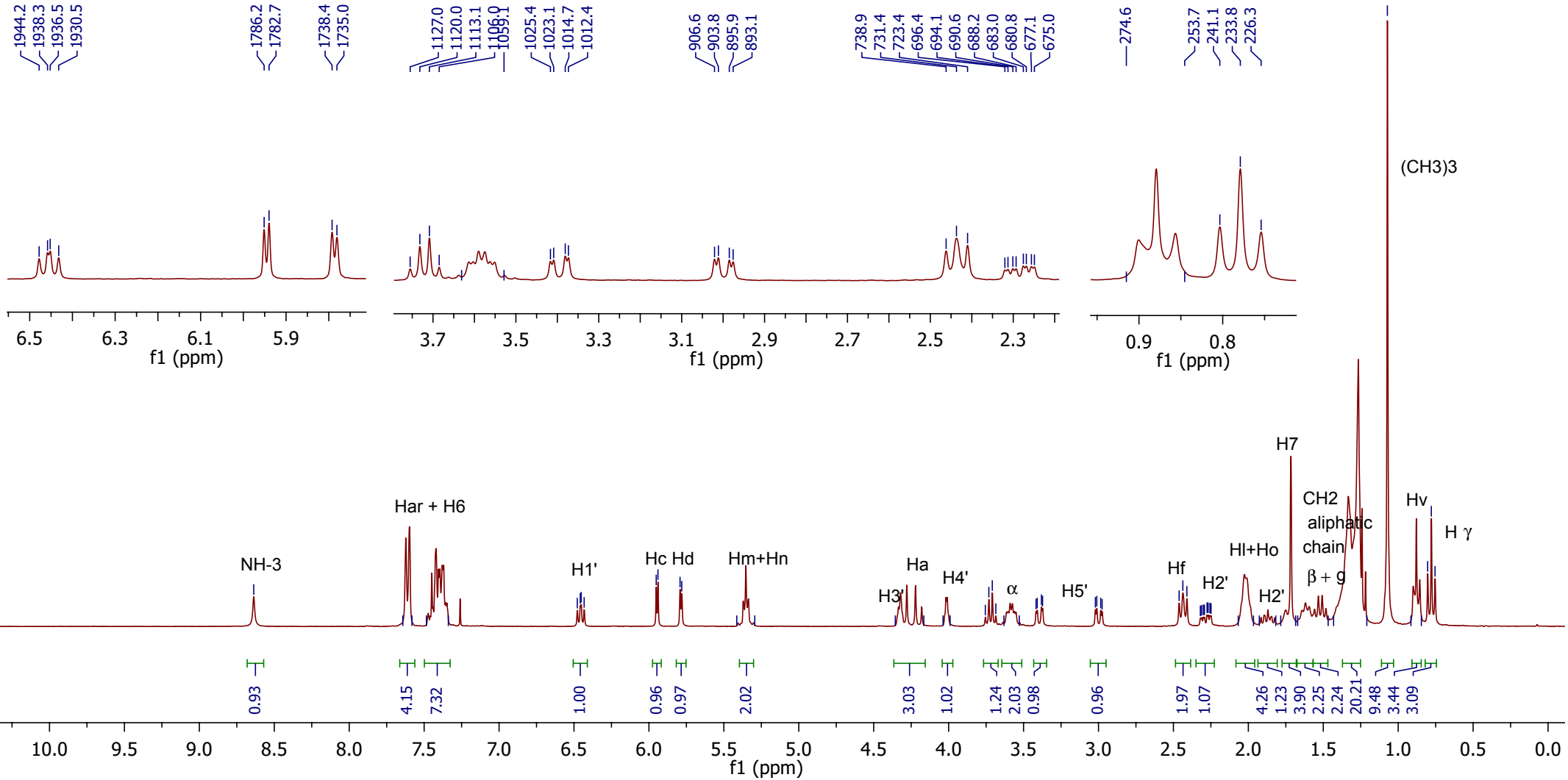


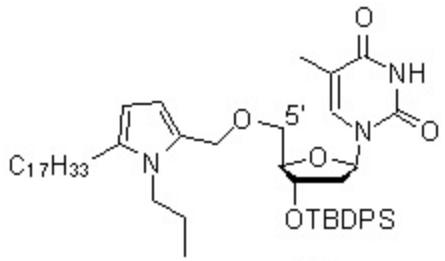
15D

300 MHz CDCl3

8.637 7.642 7.581 7.485 7.339 6.478 6.458 6.452 6.432 5.951 5.940 5.792 5.781 5.414 5.294 4.356 4.166 4.037 3.990 3.755 3.732 3.709 3.685 3.631 3.529 3.417 3.409 3.381 3.373 3.021 3.011 2.985 2.462 2.437 2.410 2.320 2.313 2.301 2.293 2.276 2.268 2.256 2.249 1.685 1.671 1.467 1.431 1.209 1.072 0.915 0.845 0.803 0.779

1944.2 1938.3 1936.5 1930.5 1786.2 1782.7 1738.4 1735.0 1127.0 1120.0 1113.1 1106.0 1059.1 1025.4 1023.1 1014.7 1012.4 906.6 903.8 895.9 893.1 738.9 731.4 723.4 696.4 694.1 690.6 688.2 683.0 680.8 677.1 675.0 274.6 253.7 241.1 233.8 226.3



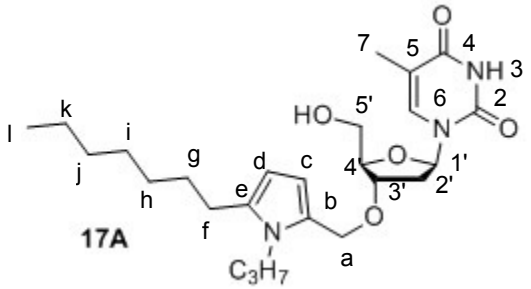


15D

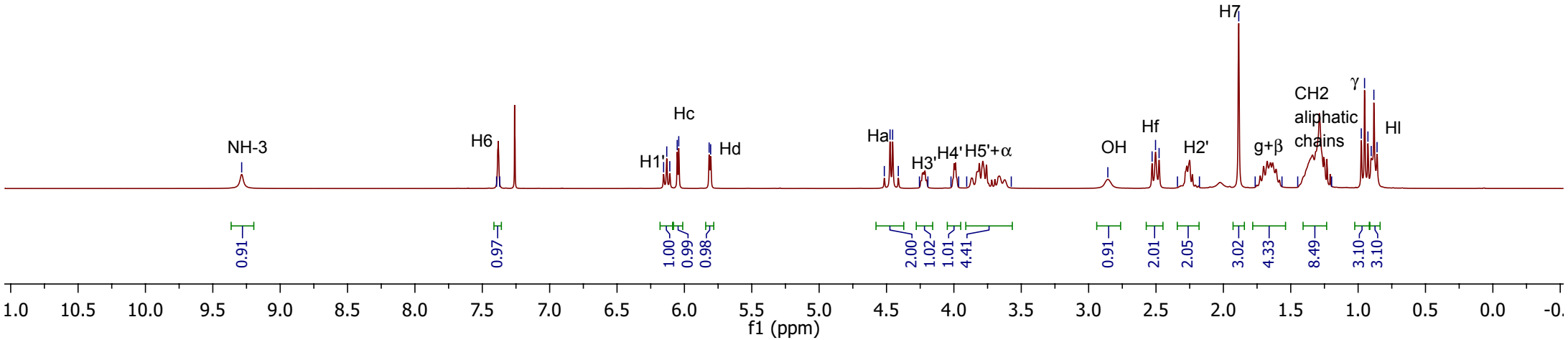
75.5 MHz CDCl3

9.286 | 7.394 7.371 | 6.154 6.131 6.109 6.053 6.042 5.816 5.805 | 4.516 4.474 4.455 4.413 4.256 4.193 4.022 3.964 3.905 3.574 | 2.857 2.529 2.503 2.477 2.341 2.178 1.886 1.764 1.565 1.448 1.197 0.976 0.952 0.927 0.903 0.883 0.859

300 MHz CDCl3

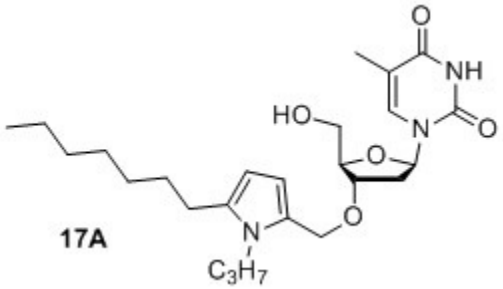


α, β, γ for positions of N-C3H7

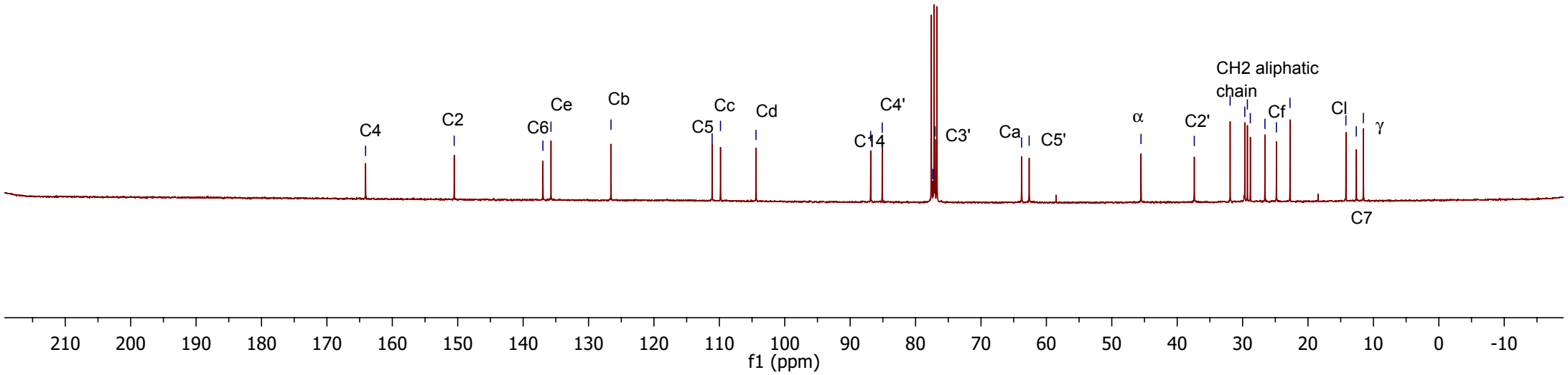


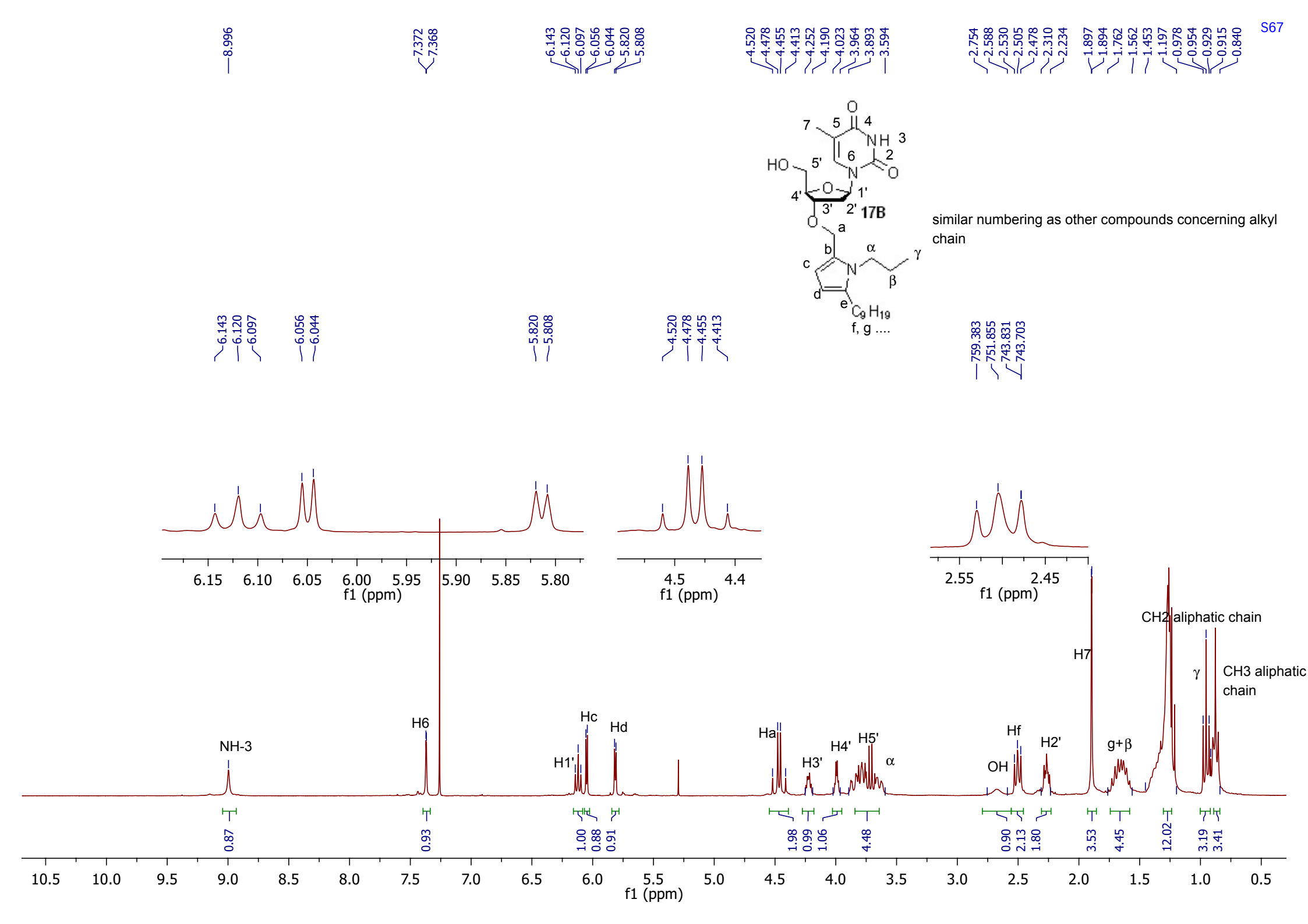
164.09 150.54 136.98 135.74 126.57 111.10 109.82 104.39 86.87 85.10 77.36 77.01 63.79 62.64 45.54 37.39 31.91 29.67 29.27 28.82 26.58 24.83 22.76 14.21 12.62 11.53

75.5 MHz CDCl3



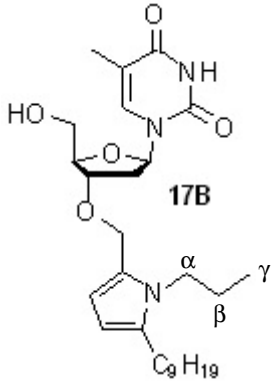
17A



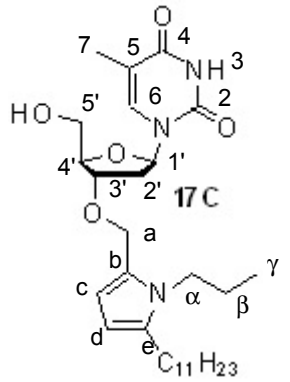

8.996
7.372
7.368
6.143
6.120
6.097
6.056
6.044
5.820
5.808
4.520
4.478
4.455
4.413
4.252
4.190
4.023
3.964
3.893
3.594
2.754
2.588
2.530
2.505
2.478
2.310
2.234
1.897
1.894
1.762
1.562
1.453
1.197
0.978
0.954
0.929
0.915
0.840
17B
f, g ....
similar numbering as other compounds concerning alkyl chain
759.383
751.855
743.831
743.703
NH-3
H6
H1'
Hc
Hd
Ha
H3'
H4'
H5'
α
OH
Hf
H2'
H7
g+β
γ
CH2 aliphatic chain
CH3 aliphatic chain
f1 (ppm)
0.87
0.93
1.00
0.88
0.91
1.98
0.99
1.06
4.48
0.90
2.13
1.80
3.53
4.45
12.02
3.19
3.41

163.90 150.47 136.97 135.80 126.59 111.15 109.87 104.44 87.02 85.11 77.36 77.02 63.83 62.72 58.57 45.56 37.41 32.02 29.82 29.73 29.68 29.64 29.44 28.86 26.62 24.86 22.80 18.53 14.23 12.65 11.55

75.5 mHz CDCl3

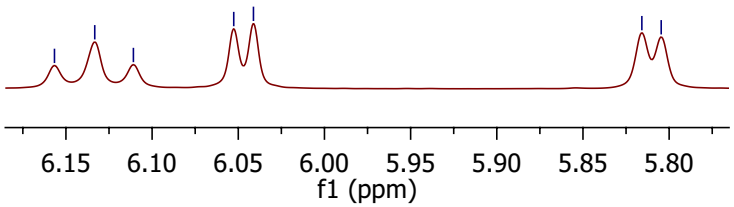


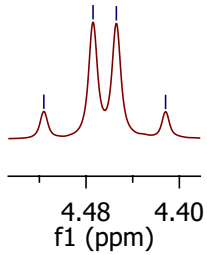
9.314 7.387 6.157 6.133 6.111 6.053 6.041 5.816 5.805 4.516 4.474 4.454 4.412 4.259 4.193 4.023 3.970 3.887 3.596 2.959 2.797 2.528 2.503 2.476 2.341 2.156 1.886 1.779 1.553 1.447 1.177 0.976 0.951 0.927 0.896 0.875 0.852

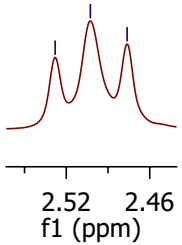


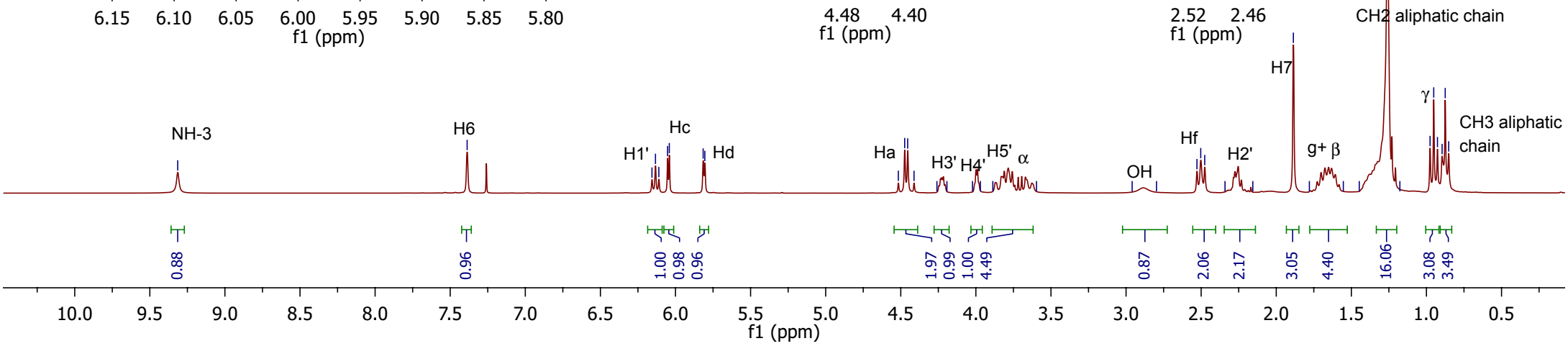
300 MHz CDCl3

1847.8 1840.8 1834.1 1816.6 1813.1 1745.5 1742.1 1355.4 1342.8 1336.8 1324.1 758.7 751.1 743.2

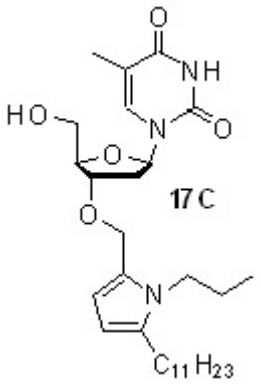






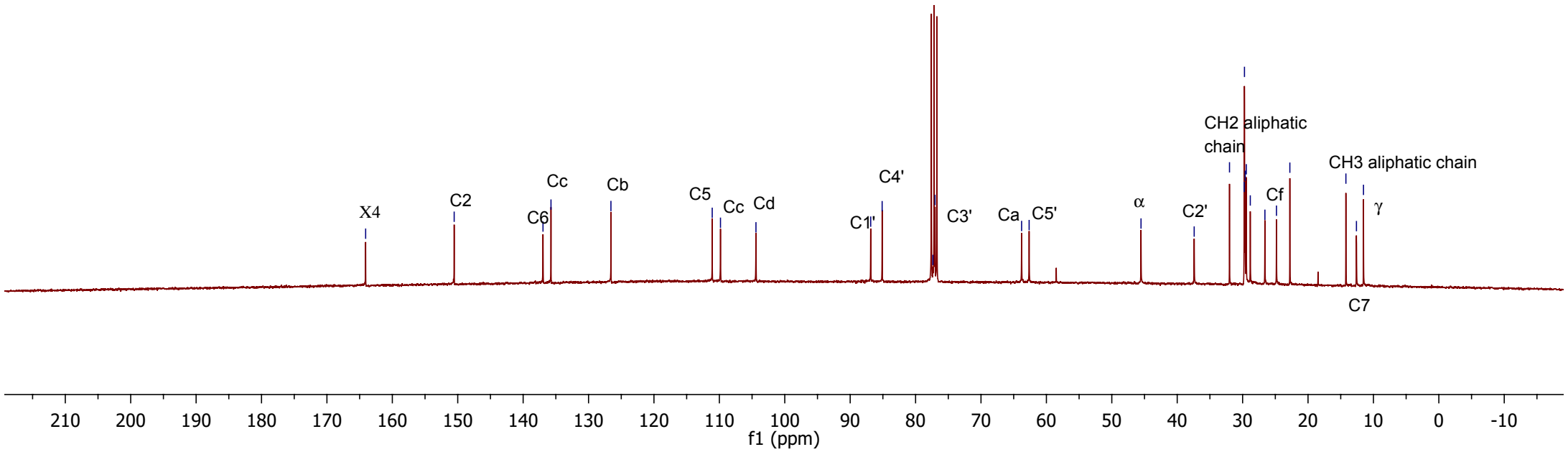


164.08 150.54 136.97 135.74 126.58 111.09 109.83 104.41 86.86 85.11 77.35 77.03 63.79 62.64 45.53 32.00 29.76 29.72 29.61 29.44 28.83 26.59 24.82 22.78 14.21 12.60 11.52

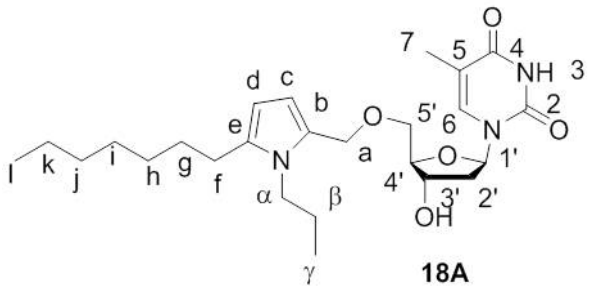


17 C

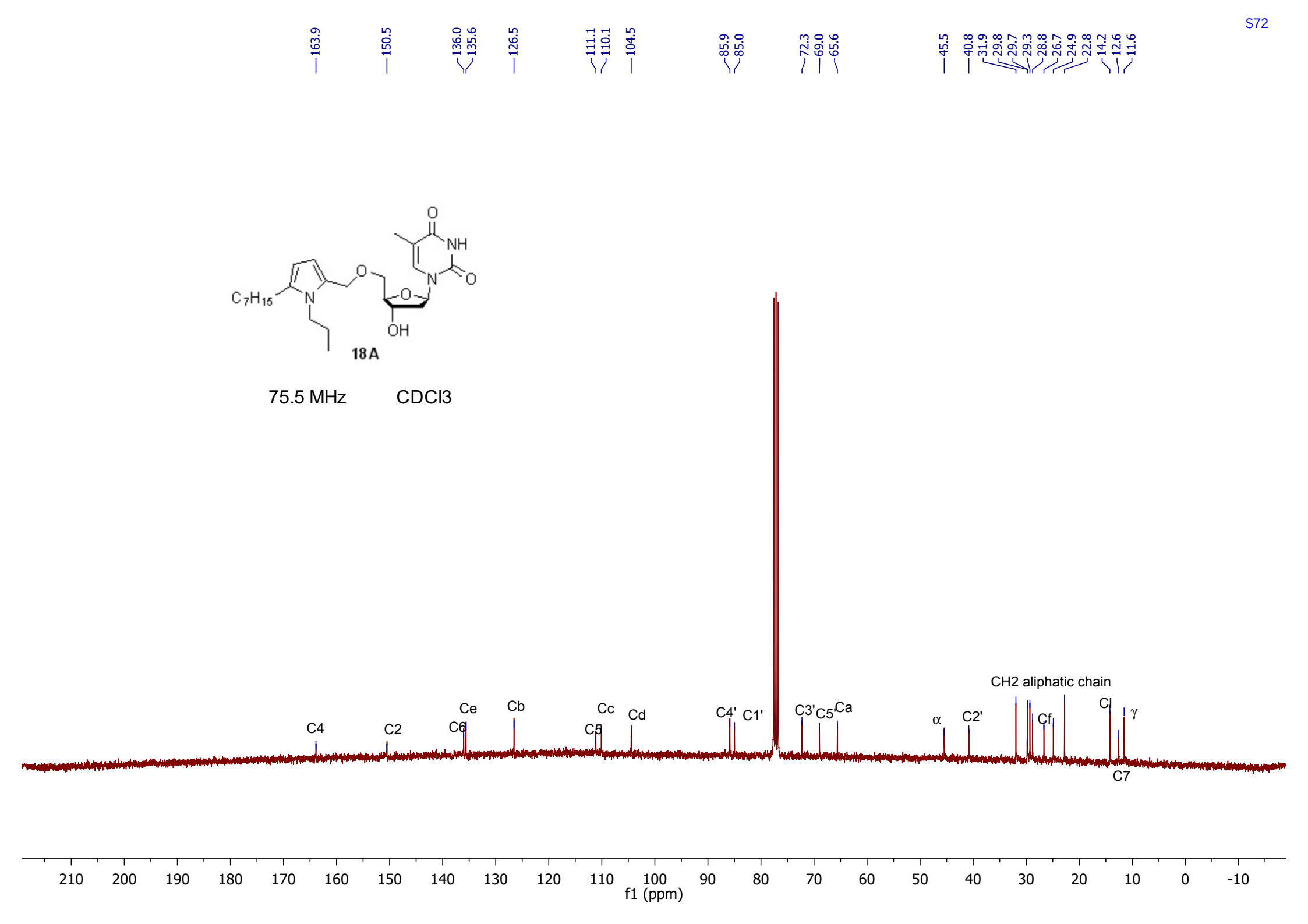
75.5 MHz CDCl3

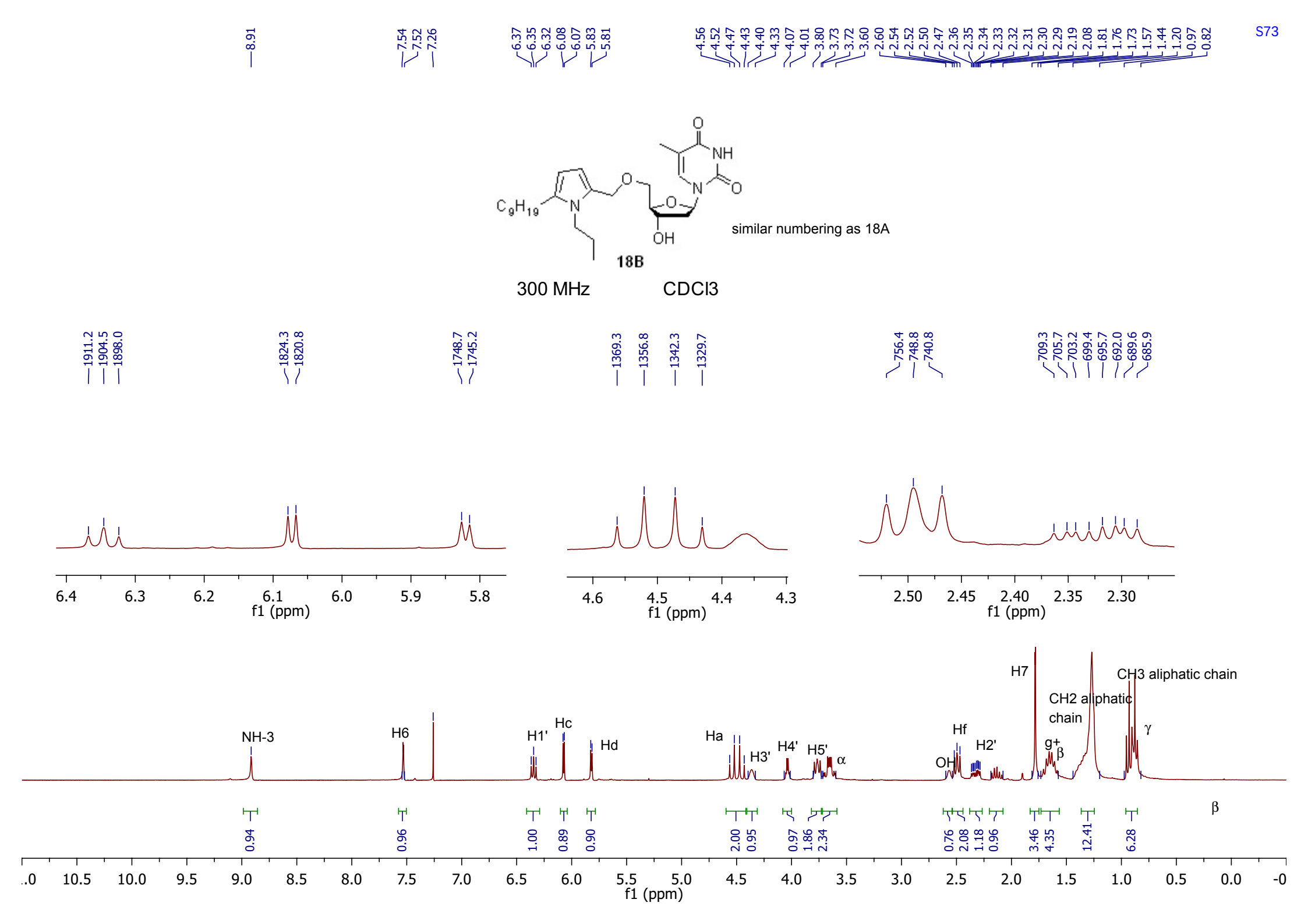


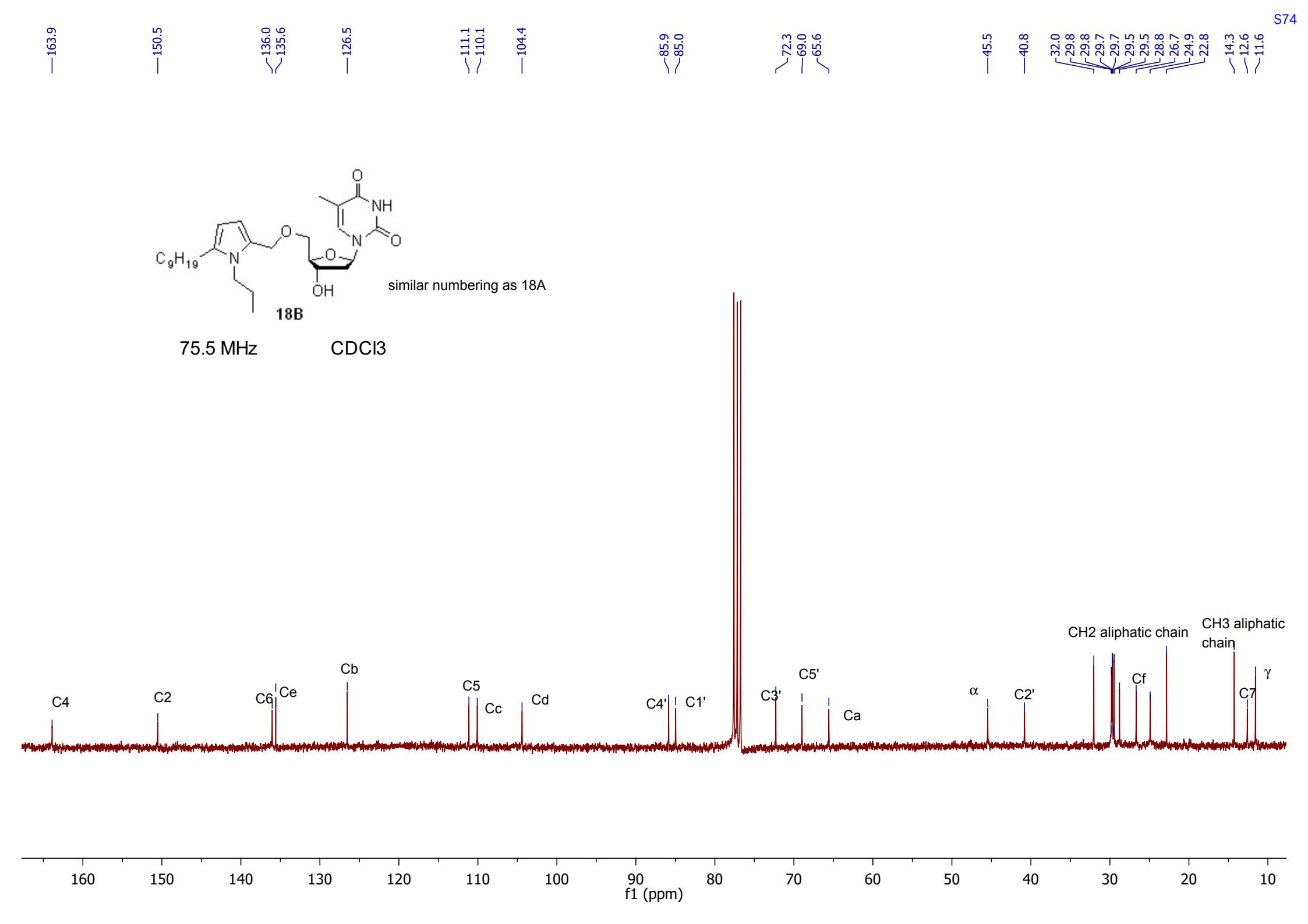
300 MHz CDCl3

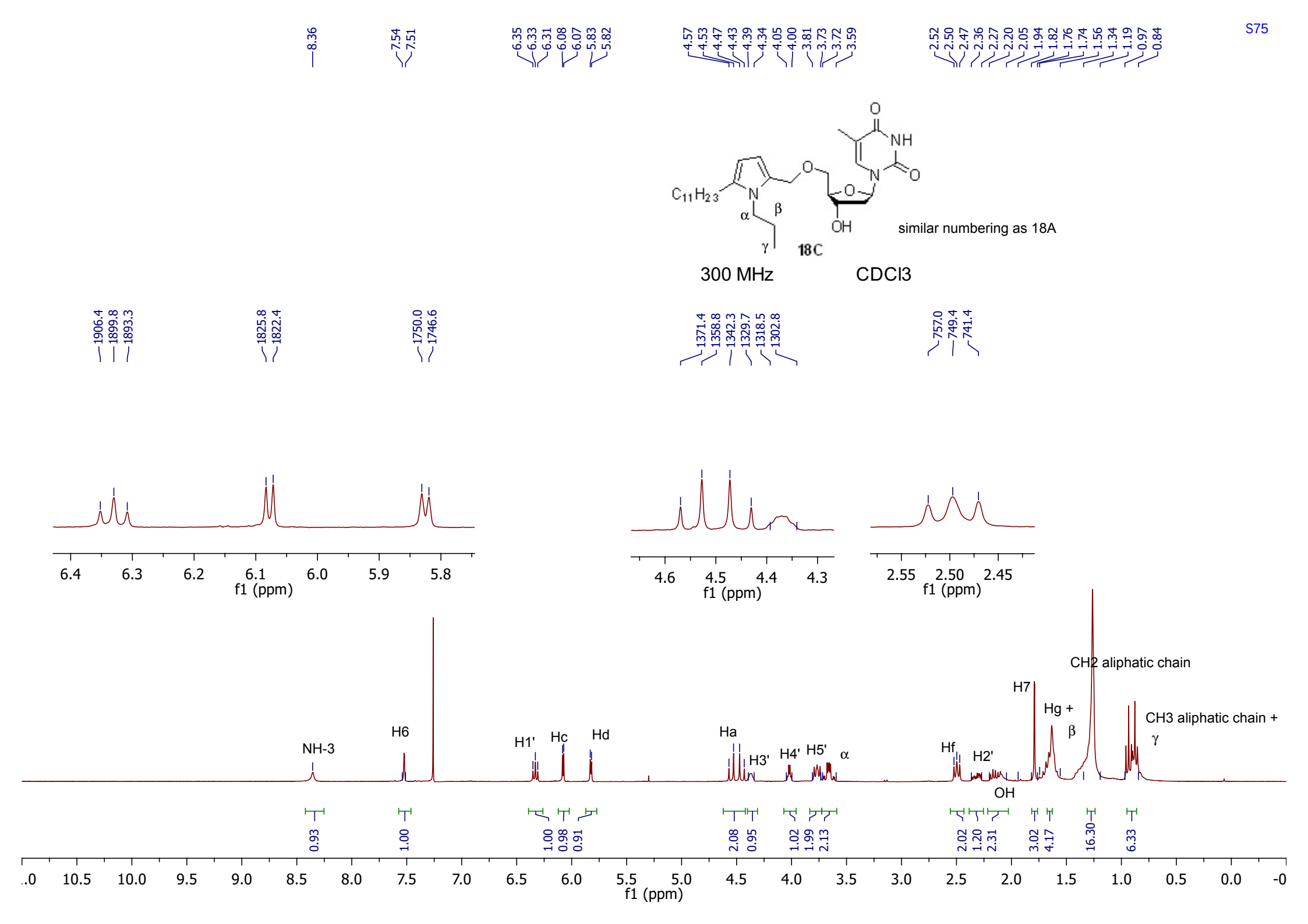


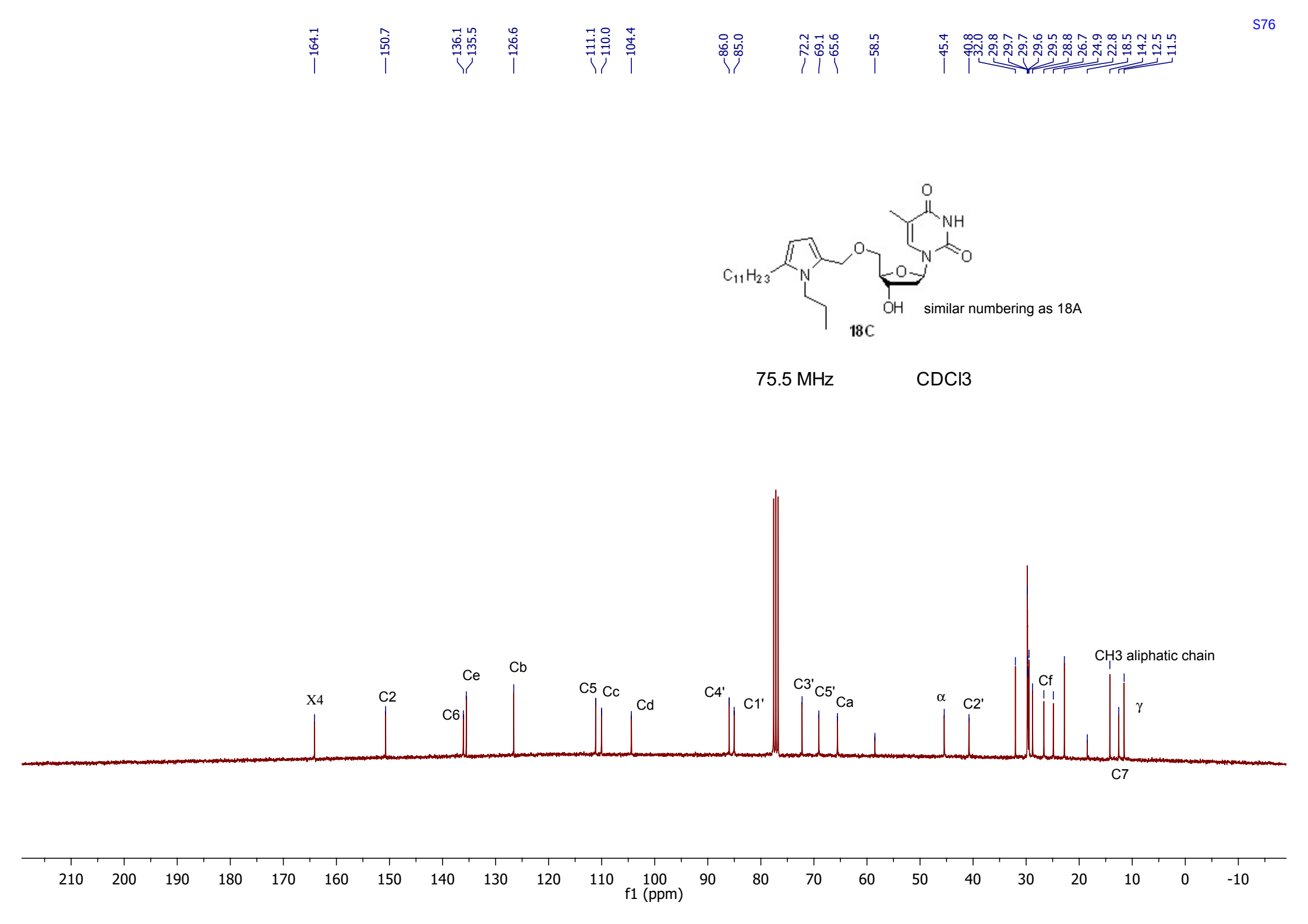
18A


163.9
150.5
136.0
135.6
126.5
111.1
110.1
104.5
85.9
85.0
72.3
69.0
65.6
45.5
40.8
31.9
29.8
29.7
29.3
28.8
26.7
24.9
22.8
14.2
12.6
11.6
O
NH
N
O
O
N
O
OH
C7H15
18A
75.5 MHz
CDCl3
C4
C2
Ce
C6
Cb
Cc
C5
Cd
C4'
C1'
C3'
C5'
Ca
α
C2'
CH2 aliphatic chain
Cf
Cl
γ
C7
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)

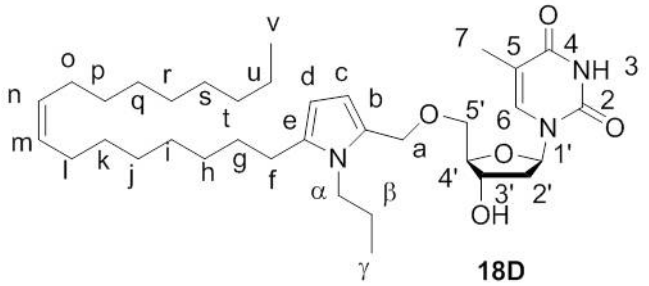

8.91
7.54
7.52
7.26
6.37
6.35
6.32
6.08
6.07
5.83
5.81
4.56
4.52
4.47
4.43
4.40
4.33
4.07
4.01
3.80
3.73
3.72
3.60
2.60
2.54
2.52
2.50
2.47
2.36
2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.19
2.08
1.81
1.76
1.73
1.57
1.44
1.20
0.97
0.82
O
NH
N
O
O
N
O
OH
C_9H_{19}
18B
similar numbering as 18A
300 MHz
CDCl3
1911.2
1904.5
1898.0
1824.3
1820.8
1748.7
1745.2
1369.3
1356.8
1342.3
1329.7
756.4
748.8
740.8
709.3
705.7
703.2
699.4
695.7
692.0
689.6
685.9
6.4
6.3
6.2
6.1
6.0
5.9
5.8
f1 (ppm)
4.6
4.5
4.4
4.3
f1 (ppm)
2.50
2.45
2.40
2.35
2.30
f1 (ppm)
NH-3
H6
H1'
Hc
Hd
Ha
H3'
H4'
H5'
α
OH
Hf
H2'
H7
CH2 aliphatic chain
g+
β
CH3 aliphatic chain
γ
β
0.94
0.96
1.00
0.89
0.90
2.00
0.95
0.97
1.86
2.34
0.76
2.08
1.18
0.96
3.46
4.35
12.41
6.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.9
150.5
136.0
135.6
126.5
111.1
110.1
104.4
85.9
85.0
72.3
69.0
65.6
45.5
40.8
32.0
29.8
29.8
29.7
29.7
29.5
29.5
28.8
26.7
24.9
22.8
14.3
12.6
11.6
O
NH
N
O
O
N
O
OH
C_9H_{19}
18B
similar numbering as 18A
75.5 MHz
CDCl3
C4
C2
C6
Ce
Cb
C5
Cc
Cd
C4'
C1'
C3'
C5'
Ca
α
C2'
CH2 aliphatic chain
CH3 aliphatic chain
Cf
C7
γ
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.36
7.54
7.51
6.35
6.33
6.31
6.08
6.07
5.83
5.82
4.57
4.53
4.47
4.43
4.39
4.34
4.05
4.00
3.81
3.73
3.72
3.59
2.52
2.50
2.47
2.36
2.27
2.20
2.05
1.94
1.82
1.76
1.74
1.56
1.34
1.19
0.97
0.84
C11H23
NH
O
N
O
OH
α
β
γ
18C
similar numbering as 18A
300 MHz
CDCl3
1906.4
1899.8
1893.3
1825.8
1822.4
1750.0
1746.6
1371.4
1358.8
1342.3
1329.7
1318.5
1302.8
757.0
749.4
741.4
f1 (ppm)
NH-3
H6
H1'
Hc
Hd
Ha
H3'
H4'
H5'
α
Hf
H2'
OH
H7
Hg +
β
CH2 aliphatic chain
CH3 aliphatic chain +
γ
0.93
1.00
1.00
0.98
0.91
2.08
0.95
1.02
1.99
2.13
2.02
1.20
2.31
3.02
4.17
16.30
6.33


164.1
150.7
136.1
135.5
126.6
111.1
110.0
104.4
86.0
85.0
72.2
69.1
65.6
58.5
45.4
40.8
32.0
29.8
29.7
29.7
29.6
29.5
28.8
26.7
24.9
22.8
18.5
14.2
12.5
11.5
O
NH
O
N
O
O
N
C11H23
OH
18C
similar numbering as 18A
75.5 MHz
CDCl3
X4
C2
C6
Ce
Cb
C5
Cc
Cd
C4'
C1'
C3'
C5'
Ca
α
C2'
Cf
CH3 aliphatic chain
γ
C7
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)

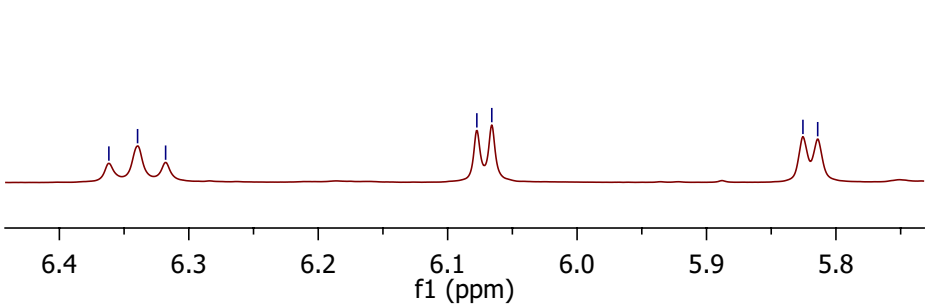
8.89 | 7.55 7.51 | 6.36 6.34 6.32 6.08 6.07 5.83 5.81 | 5.40 5.29 | 4.56 4.52 4.47 4.43 4.40 4.33 4.08 4.00 3.83 3.58 | 2.70 2.57 2.52 2.49 2.47 2.37 2.27 2.21 2.08 2.06 1.96 1.83 1.75 1.73 1.57 1.39 1.21 0.97 0.84

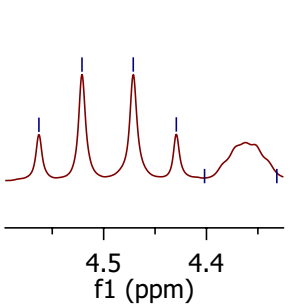


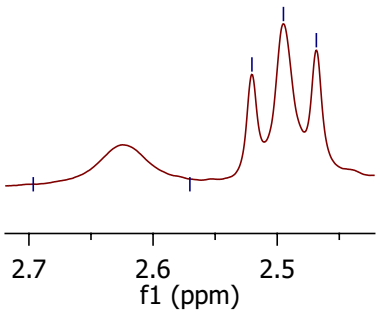
18D

300 MHz CDCl3

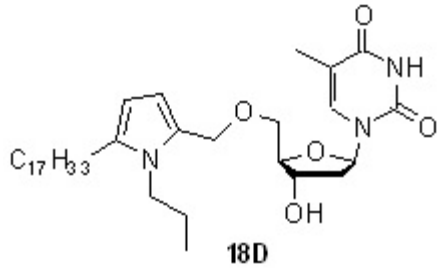
1909.4 1902.7 1896.2 | 1824.0 1820.6 | 1748.4 1745.0 | 1369.5 1356.9 | 1341.9 1329.4 1321.1 | 1300.0 | 809.3 | 771.4 | 756.4 748.8 740.9





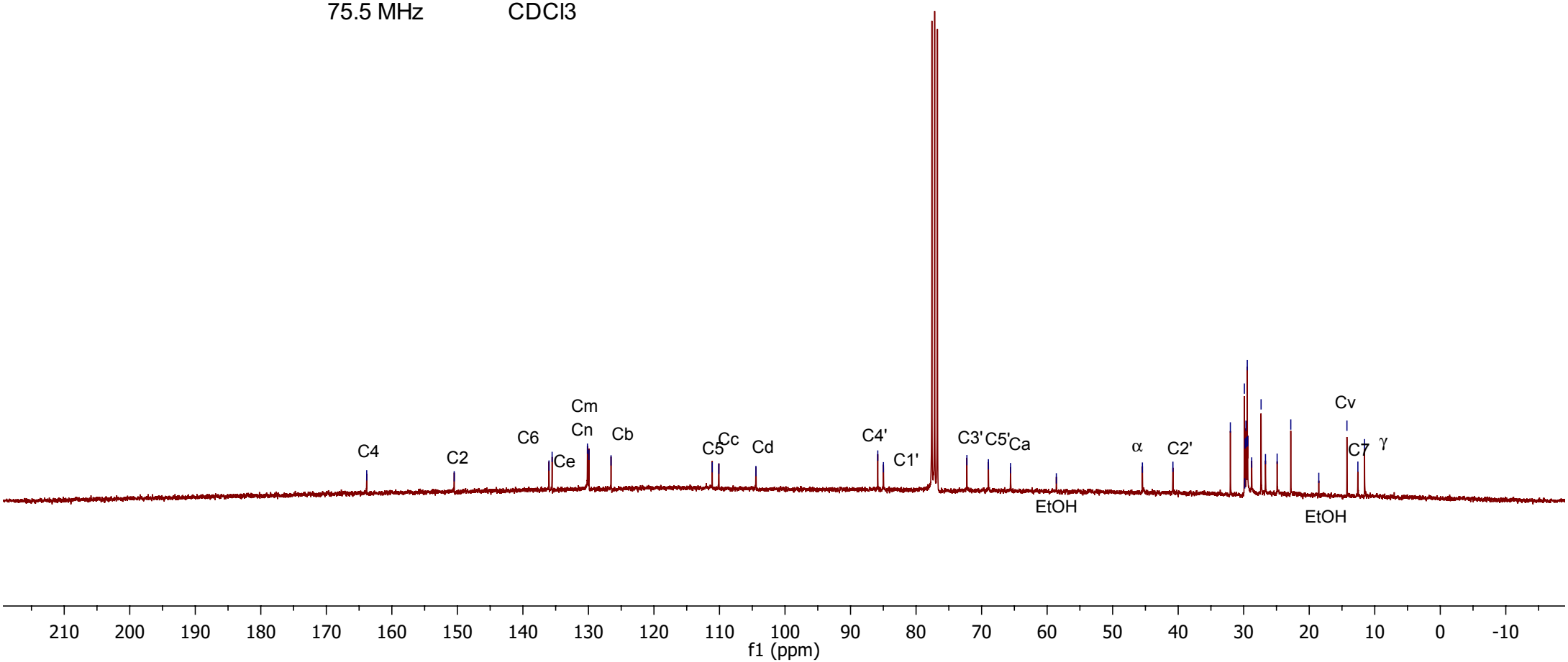


163.8 150.5 136.0 135.5 130.2 129.9 126.6 111.1 110.1 104.4 85.8 85.0 72.2 69.0 65.6 58.6 45.5 40.8 32.0 29.9 29.8 29.8 29.7 29.6 29.5 29.4 28.8 27.3 26.7 24.9 22.8 18.5 14.2 12.6 11.6

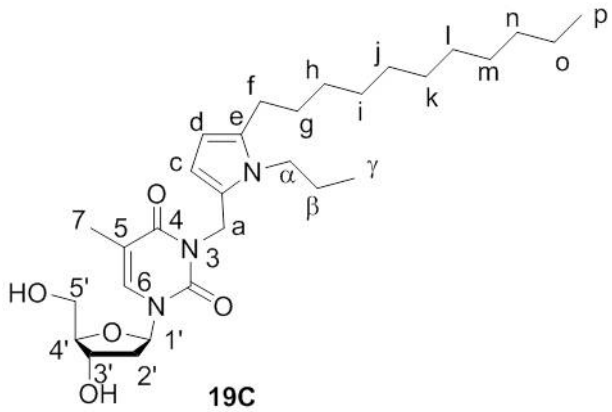


18D

75.5 MHz CDCl3

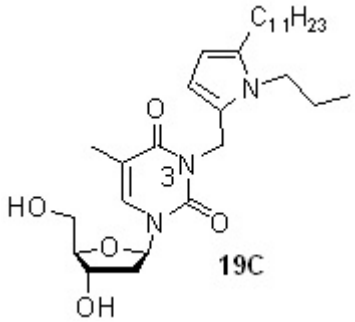


7.315 7.312 6.229 6.128 5.814 5.802 5.079 4.608 4.511 4.085 3.943 3.928 3.918 3.888 3.879 3.831 3.821 3.792 3.782 3.754 3.730 3.707 3.684 2.538 2.216 1.913 1.910 1.697 1.530 1.447 1.163 0.980 0.955 0.930 0.896 0.874 0.851



300 MHz CDCl3

163.331 151.079 134.899 133.633 126.434 110.613 109.353 104.657 87.629 86.901 77.362 71.641 62.530 45.104 40.213 36.557 32.045 29.843 29.773 29.730 29.662 29.480 28.752 26.767 25.296 22.820 14.256 13.516 11.433

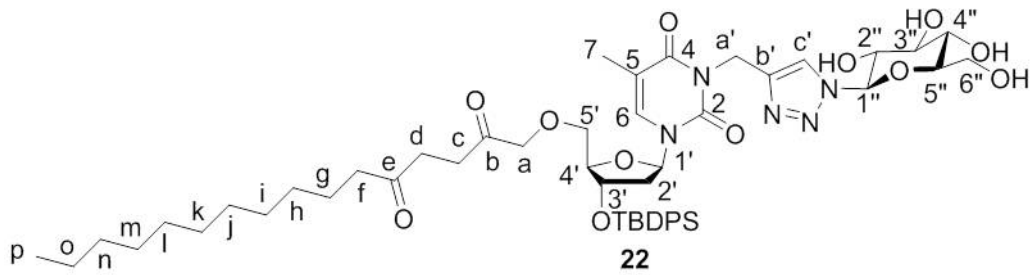


75.5 MHz CDCl3

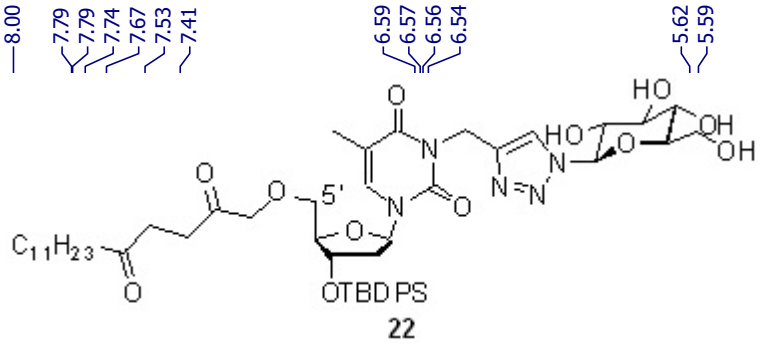
C4 C2 C6 Ce Cb C5 Cc Cd C1' C4' C3' C5' α C2' Ca Cp γ C7

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

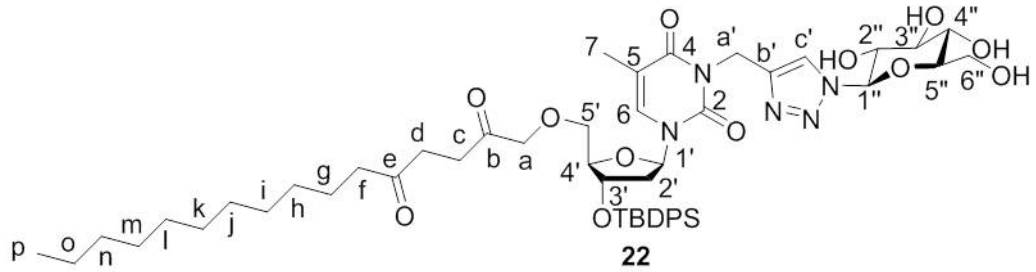


300 MHz (CD3)2CO



22

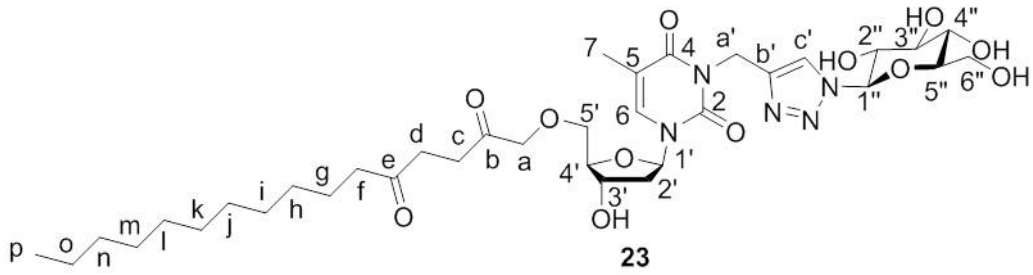
300 MHz (CD3)2CO

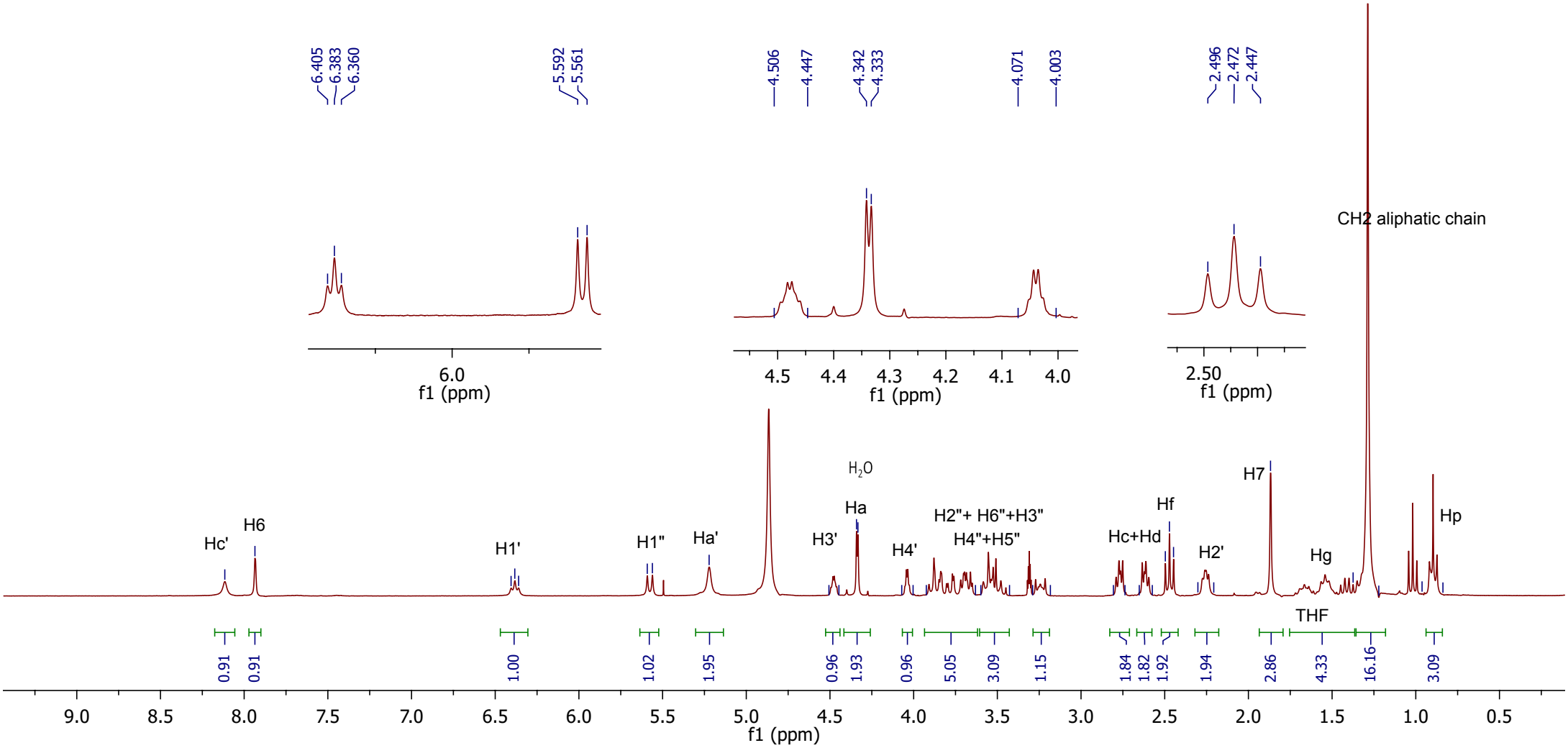


22

75.5 MHz (CD3)2CO

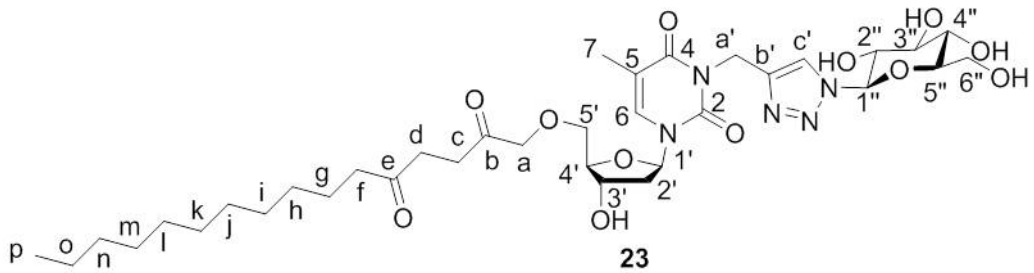
300 MHz CD3OD





211.89 208.33 164.92 152.17 136.84 110.90 89.56 87.57 87.41 81.03 78.36 76.71 73.90 72.99 72.31 70.83 62.36 59.53 43.24 41.20 36.76 33.11 33.01 30.68 30.58 30.50 30.40 30.24 24.92 24.76 23.67 20.68 14.43 13.92 13.17

75.5 MHz CD3OD



23

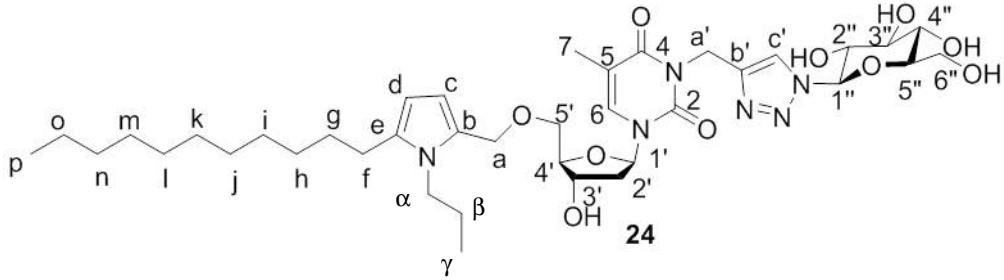
Ce Cb C4 C2 C6 Cc' C5 C1'' C4'+ C1' C2'' C3'' C5'' C5' C4'' C6'' Ca C3' Cf C2' Ca' Cc+ Cd CH2 aliphatic chain Cg CH2 aliph Cp C7

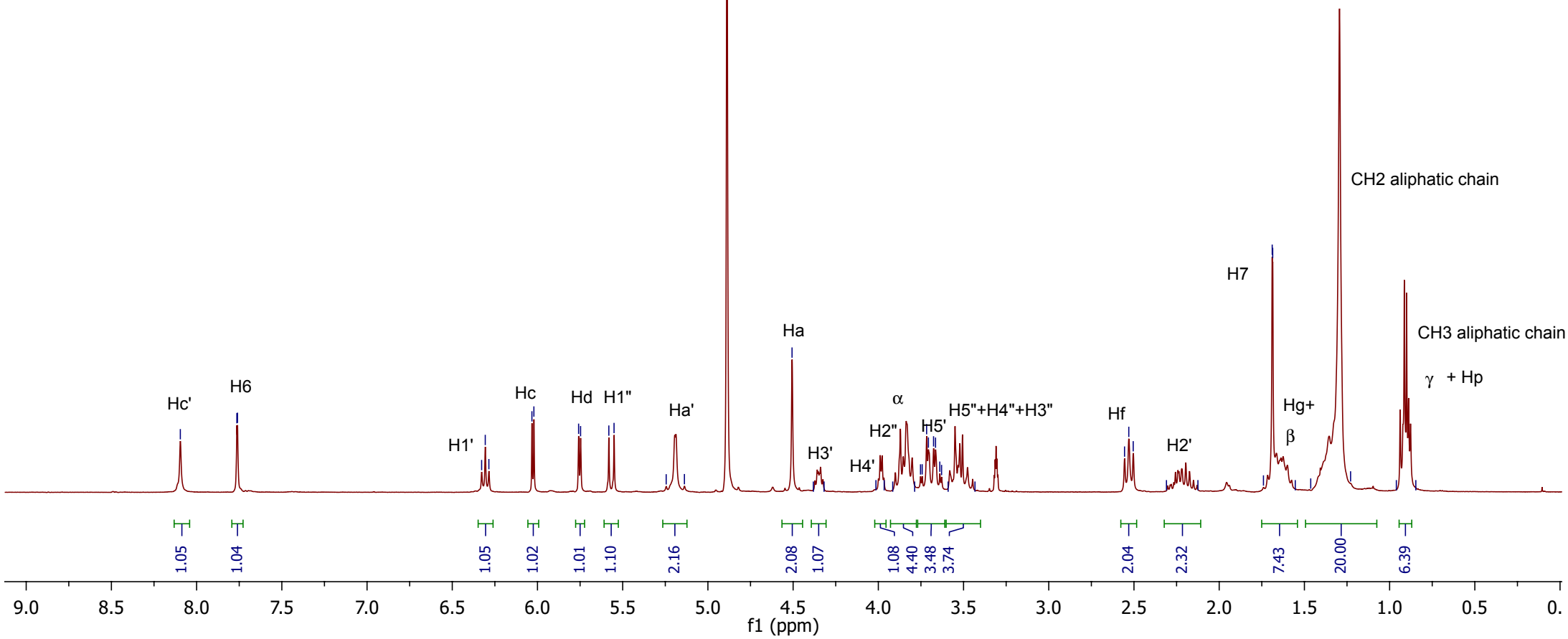
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

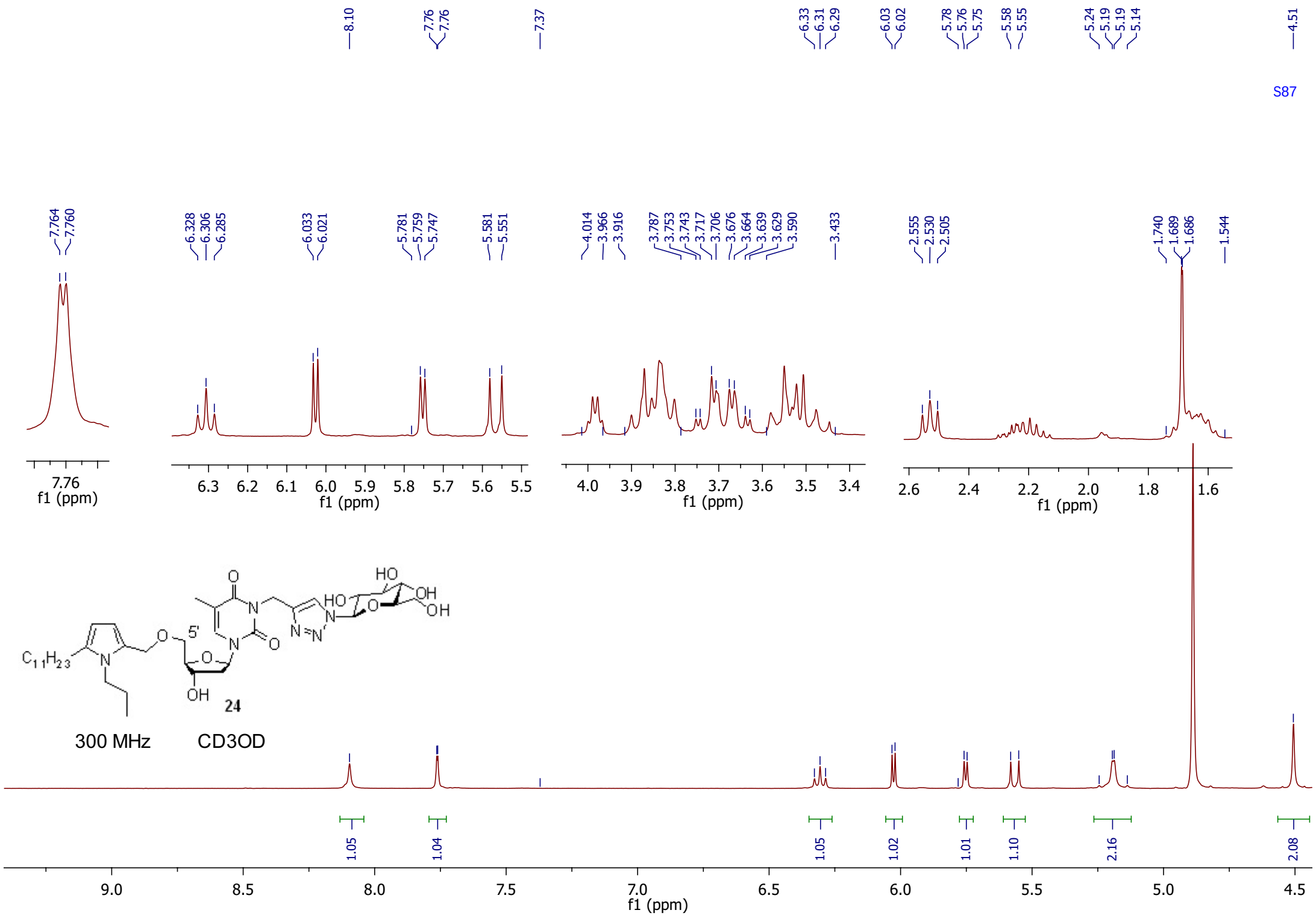
f1 (ppm)

8.10 7.76 7.76 6.33 6.31 6.29 6.03 6.02 5.76 5.75 5.58 5.55 5.24 5.14 4.51 4.38 4.32 4.01 3.97 3.92 3.79 3.75 3.74 3.72 3.71 3.68 3.66 3.64 3.63 3.59 3.43 2.56 2.53 2.50 2.31 2.12 1.74 1.69 1.69 1.55 1.46 1.23 0.96 0.85

300 MHz CD3OD






8.10
7.76
7.76
7.37
6.33
6.31
6.29
6.03
6.02
5.78
5.76
5.75
5.58
5.55
5.24
5.19
5.19
5.14
4.51
7.764
7.760
6.328
6.306
6.285
6.033
6.021
5.781
5.759
5.747
5.581
5.551
4.014
3.966
3.916
3.787
3.753
3.743
3.717
3.706
3.676
3.664
3.639
3.629
3.590
3.433
2.555
2.530
2.505
1.740
1.689
1.686
1.544
f1 (ppm)
HO
OH
OH
HO
O
N
N
N
N
O
O
5'
O
O
OH
$C_{11}H_{23}$
N
24
300 MHz
CD3OD
1.05
1.04
1.05
1.02
1.01
1.10
2.16
2.08
f1 (ppm)

164.85 152.05 136.51 136.05 128.22 124.20 110.76 105.42 89.58 87.43 87.11 81.06 78.39 73.93 72.18 70.85 70.00 66.43 62.37 46.22 41.39 37.06 33.03 30.73 30.70 30.59 30.55 30.43 30.12 27.43 25.89 23.70 14.44 13.17 11.57

75.5 MHz CD3OD