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Supporting Information

Total Synthesis of Belizentrin Methyl Ester: Report on a Likely Conquest

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General. All reactions were carried out under Ar in glassware dried with a heat gun under vacuum (Schlenk line). The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), acetone (B_2O_3), CH_2Cl_2, toluene (Na/K), MeOH (Mg, stored over 3Å MS), DMPU (CaH_2); DMF, CH_3CN, NEt_3 and pyridine were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254); Flash chromatography: Silica VWR (40-63 μm) with pre-distilled or HPLC grade solvents. Melting points: BÜCHI B-540 apparatus; IR: ALPHA spectrometer (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

NMR: Spectra were recorded on a Bruker AV 400, AV 500 or AV 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$ at 7.26 and 77.16 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; C_6D_6 at 7.16 ppm and 128.06 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; [D_5]-pyridine at 8.70, 7.55 and 7.15 ppm for ^1H NMR and 149.64, 135.26 and 123.25 ppm for ^{13}C NMR spectroscopy, respectively).

Where indicated, the signal assignments in the NMR spectra are unambiguous; the numbering scheme is arbitrary and shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygpqf, cosydqtp, cosygpmfphpp*); HSQC (*hsqcedetgpsisp2.2*) optimized for $^1J_{C,H}$ = 145 Hz; HMBC (*hmbcetgpl3nd*) for correlations via $^nJ_{C,H}$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms; NOESY (noesygpph).

Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Strem, TCI) were used as received.

Preparation of the Tetrahydrofuran Segment

(*S*)-5-(Hydroxymethyl)dihydrofuran-2(3*H*)-one (S-2). conc. aq. HCl (25 mL) was slowly added to a stirred solution of L-glutamic acid **3** (25.0g, 170 mmol) in water (60 mL) at ambient temperature. The resulting solution was cooled to 0 °C before a solution of $NaNO_2$ (15.2 g, 221 mmol) in water (80.0 mL) was added dropwise over the course of 45 min, causing a gentle evolution of N_2 gas. Once the addition of $NaNO_2$ was complete the colorless mixture was warmed to ambient temperature and stirring was continued for 23 h. The solvents were evaporated and the resulting white solid was triturated with EtOAc (100 mL) and filtered off. The filter cake was washed with EtOAc (2 x 100 mL) and the combined filtrates were dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated to give acid **S-1** as a white solid (17.5 g, 79%) which was used in the next step without further purification.

$BH_3 \cdot SMe_2$ (15.2 mL, 170 mmol) was slowly added to a stirred solution of the crude carboxylic acid **S-1** (17.5 g, 170 mmol) in THF (280 mL) at 0 °C over the course of 15 min. Once the addition of $BH_3 \cdot SMe_2$ was complete, the resulting mixture was allowed to reach ambient temperature and stirring was continued for 18 h. The mixture was cooled to 0 °C and the reaction was quenched with MeOH (70 mL). The solvents were evaporated and the resulting oil was passed through a short plug of Celite®, eluting with EtOAc. Evaporation of the combined filtrates afforded compound **S-2** as a white solid (10.8 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (ddd, *J* = 7.5, 6.9, 4.6 Hz, 1H), 3.91 (dd, *J* = 12.4, 2.9 Hz, 1H), 3.66 (dd, *J* = 12.5, 4.7 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.27 (dddd, *J* = 13.2, 9.6, 7.6, 5.8 Hz, 1H), 2.15 (dddd, *J* = 12.9, 10.0, 8.4, 7.0 Hz, 1H), 2.03 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.4, 80.7, 64.4, 28.8, 23.3 ppm; HRMS (ESI): *m/z* calcd. for $C_5H_8O_3Na^+$: 139.0366, found: 139.0365. The analytical and spectroscopic data are in agreement with those previously reported in the literature.[1]

(*S*)-5-((Trityloxy)methyl)dihydrofuran-2(3*H*)-one (S-3). Trityl chloride (8.48 g, 30.4 mmol) was added to a stirred solution of alcohol **S-2** (2.94 g, 25.4 mmol) in pyridine (13.5 mL, 167 mmol) at ambient temperature and the resulting mixture was stirred for 16 h. The reaction was quenched with water (110 mL), the aqueous phase was extracted with

[1] S. Höck, H.-J. Borschberg, *Helv. Chim. Acta* **2003**, *86*, 1397-1409.

EtOAc (3 x 45 mL). The combined extracts were subsequently washed with water (45 mL) and brine (45 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 9:1 to 2:1) followed by recrystallization from boiling hexane/EtOAc (5:1) to give the title compound as a colorless crystalline solid (6.62 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.40 (m, 6H), 7.34 – 7.28 (m, 6H), 7.27 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 4.65 (dddd, *J* = 7.9, 5.8, 4.3, 3.5 Hz, 1H), 3.42 (dd, *J* = 10.4, 3.5 Hz, 1H), 3.16 (dd, *J* = 10.4, 4.3 Hz, 1H), 2.69 (ddd, *J* = 17.9, 10.1, 6.6 Hz, 1H), 2.51 (ddd, *J* = 17.8, 10.1, 6.9 Hz, 1H), 2.25 (dddd, *J* = 12.8, 10.1, 7.9, 6.6 Hz, 1H), 2.04 (dddd, *J* = 12.8, 10.1, 6.9, 5.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.6, 143.6 (3C), 128.8 (6C), 128.1 (6H), 127.3 (3C), 87.1, 79.2, 65.4, 28.6, 24.4 ppm; HRMS (ESI): *m/z* calcd. for $C_{24}H_{22}O_3Na^+$: 381.1461, found: 381.1459. The analytical and spectroscopic data are in agreement with those previously reported in the literature.[1]

(3*R*,5*S*)-3-Methyl-5-((trityloxy)methyl)dihydrofuran-2(3*H*)-one (S-4). *n*-BuLi (1.6 M in hexane, 20.9 mL, 33.5 mmol) was slowly added to a stirred solution of diisopropylamine (5.47 mL, 39.1 mmol) in THF (130 mL) at –78 °C. Once the addition was complete, the resulting reaction mixture was warmed to 0 °C and stirring was continued for 15 min. The mixture was cooled to –78 °C and a solution of lactone **S-3** in THF (65 mL) was slowly added. Stirring was continued for 15 min before a solution of MeI (2.08 mL, 33.5 mmol) in THF (30 mL) was slowly added to the mixture, which was then allowed to reach –30 °C over the course of 4 h. The reaction was quenched with sat. aq. Na_2SO_4 (100 mL) and the aq. phase was extracted with *tert*-butyl methyl ether (4 x 100 mL). The combined extracts were washed with water (75 mL) and brine (75 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated to give the title compound as a colorless crystalline solid (10.2 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.38 (m, 6H), 7.34 – 7.28 (m, 6H), 7.27 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 4.60 (dq, *J* = 8.6, 3.7 Hz, 1H), 3.42 (dd, *J* = 10.4, 3.7 Hz, 1H), 3.13 (dd, *J* = 10.4, 4.1 Hz, 1H), 2.87 (tq, *J* = 9.2, 7.3 Hz, 1H), 2.26 (ddd, *J* = 12.8, 9.4, 3.5 Hz, 1H), 1.93 (dt, *J* = 12.9, 8.8 Hz, 1H), 1.28 (d, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.5, 143.6 (3C), 128.8 (6C), 128.1 (6C), 127.3 (3C), 87.2, 76.8, 65.4, 34.3, 32.7, 16.5 ppm; HRMS (ESI): *m/z* calcd. for $C_{25}H_{24}O_3Na^+$: 395.1618;

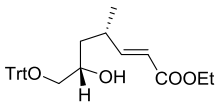
found: 395.1616. The analytical and spectroscopic data are in agreement with those previously reported in the literature.[2]

(3*S*,5*S*)-3-Methyl-5-((trityloxy)methyl)dihydrofuran-2(3*H*)-one (4). *n*-BuLi (1.6 M in hexane, 42.3 mL, 67.6 mmol) was slowly added to a stirred solution of diisopropylamine (11.1 mL, 78.9 mmol) in THF (260 mL) at −78 °C. Once the addition was complete, the resulting mixture was warmed to 0 °C and stirring was continued for 15 min. The mixture was cooled to −78 °C and a solution of lactone **S-4** in THF (155 mL) was slowly added, and stirring was continued for 30 min. The reaction was quenched with sat. aq. Na_2SO_4 (200 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (4 x 125 mL). The combined extracts were washed with water (150 mL) and brine (150 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 9:1 to 2:1) to give the title compound as a colorless crystalline solid (20.1 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 – 7.43 (m, 6H), 7.34 – 7.29 (m, 6H), 7.27 – 7.22 (m, 3H), 4.52 (dddd, *J* = 10.1, 6.0, 5.3, 3.9 Hz, 1H), 3.30 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.26 (dd, *J* = 10.4, 5.4 Hz, 1H), 2.68 (ddq, *J* = 11.7, 8.9, 7.0 Hz, 1H), 2.37 (ddd, *J* = 12.6, 9.0, 6.1 Hz, 1H), 1.69 (ddd, *J* = 12.6, 11.8, 10.2 Hz, 1H), 1.28 (d, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.5, 143.7 (3C), 128.8 (6C), 128.0 (6C), 127.3 (3C), 86.9, 77.3, 65.2, 35.5, 33.2, 15.5 ppm; HRMS (ESI): *m/z* calcd. for $C_{25}H_{24}O_3Na^+$: 395.1618, found: 395.1617. The analytical and spectroscopic data are in agreement with those previously reported in the literature.[2]

Ethyl (4*S*,6*S*,*E*)-6-hydroxy-4-methyl-7-(trityloxy)hept-2-enoate (S-6). Dibal-H (1.2 M in toluene, 48.0 mL, 57.6 mmol) was slowly added to a stirred solution of lactone **4** (18.7 g, 50.1 mmol) in CH_2Cl_2 (200 mL) at −78 °C over the course of 15 min and the resulting mixture was stirred for 3 h. The reaction was quenched with MeOH (40 mL) at −78 °C. The resulting mixture was transferred into an Erlenmeyer flask containing sat. aq. Rochelle salt solution (200 mL) and was vigorously stirred for 16 h at ambient temperature. The resulting biphasic mixture was diluted with water (400 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 200 mL). The combined extracts were washed with water (200 mL) and brine (200 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered

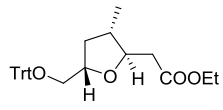
[2] M. Kögl, L. Brecker, R. Warrass, J. Mulzer, *Eur. J. Org. Chem*. **2008**, 2714-2730.

off and the solvent was evaporated to afford lactol **S-5** as a colorless oil (18.4 g, 98%, mixture of diastereomers), which was used in the next step without further purification**.**



Ph_3P=CHCOOEt (18.1 g, 50.8 mmol) was added to a stirred solution of the crude lactol **S-5** (18.2 g, 48.7 mmol) in toluene (250 mL) at ambient temperature. The resulting mixture was stirred for 17 h at 80 °C before it was cooled to ambient temperature and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 20:1 to 9:1) to give the title compound **S-6** as a colorless oil (15.0 g, 69%). $[\alpha]_D^{20}$ = +24.8 (c = 1.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.40 (m, 6H), 7.37 – 7.31 (m, 6H), 7.28 – 7.27 (m, 1H), 7.26 – 7.24 (m, 2H), 6.86 (dd, *J* = 15.7, 7.7 Hz, 1H), 5.70 (dd, *J* = 15.7, 1.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.82 (tq, *J* = 8.0, 3.8 Hz, 1H), 3.20 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.02 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.44 (dtd, *J* = 8.0, 6.6, 5.3 Hz, 1H), 2.28 (d, *J* = 3.8 Hz, 1H), 1.58 (ddd, *J* = 13.6, 8.5, 6.3 Hz, 1H), 1.35 – 1.30 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 154.2, 143.9 (3C), 128.8 (6C), 128.1 (6C), 127.3 (3C), 119,7, 86.9, 68.7, 67.8, 60.4, 39.3, 32.9, 19.0, 14.4 ppm; IR (film): $\tilde{\nu}$ = 3486, 3058, 3022, 2962, 2930, 2871, 1714, 1651, 1597, 1490, 1448, 1368, 1302, 1277, 1211, 1180, 1153, 1072, 1033, 985, 948, 900, 869, 775, 763, 747, 706, 703, 667, 649, 633, 618, 528, 407 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{32}O_4Na^+$: 467.2193, found: 467.2189.

Ethyl 2-((2*R*,3*S*,5*S*)-3-methyl-5-((trityloxy)methyl)tetrahydrofuran-2-yl)acetate (5). A



solution of TBAF·3H_2O (14.5 g, 45.8 mmol) in THF (45 mL) was slowly added to a stirred solution of **S-6** (13.6 g, 30.5 mmol) in THF (155 mL) at 0 °C and the resulting mixture was stirred for 3 h. The solvent was evaporated and the crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 10:1) to give the title compound as a colorless crystalline solid (11.2 g, 82%). m. p. = 113-114°C; $[\alpha]_D^{20}$ = +5.0 (c = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 – 7.44 (m, 6H), 7.32 – 7.26 (m, 6H), 7.25 – 7.19 (m, 3H), 4.27 – 4.19 (m, 1H), 4.18 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.90 (ddd, *J* = 9.0, 8.1, 4.1 Hz, 1H), 3.16 (dd, *J* = 9.4, 5.3 Hz, 1H), 3.02 (dd, *J* = 9.4, 4.8 Hz, 1H), 2.57 (dd, *J* = 14.8, 4.2 Hz, 1H), 2.49 (dd, *J* = 14.8, 8.1 z, 1H), 2.19 (dt, *J* = 12.3, 7.0 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.43 (ddd, *J* = 12.3, 10.8, 8.9 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 144.3 (3C), 128.9 (6C), 127.9, (6C), 127.0 (3C), 86.5,

81.6, 77.4, 66.8, 60.6, 40.0, 39.6, 37.9, 16.3, 14.4 ppm; IR (film): $\tilde{\nu}$ = 3059, 3022, 2961, 2928, 2871, 1733, 1597, 1490, 1448, 1382, 1318, 1276, 1250, 1196, 1152, 1091, 1074, 1031, 1002, 991, 946, 914, 899, 850, 816, 746, 697, 667, 646, 632, 561, 537, 493 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{32}O_4Na^+$: 467.2193, found: 467.2193.

2-((2*R*,3*S*,5*S*)-3-Methyl-5-((trityloxy)methyl)tetrahydrofuran-2-yl)ethan-1-ol (6). A solution of $LiAlH_4$ (1.0 M in THF, 23.4 mL, 23.4 mmol) was slowly added to a stirred solution of ester **5** (9.91 g, 22.3 mmol) in THF (27 mL) at –20 °C over the course of 15 min and the resulting mixture was stirred for 1 h. The mixture was warmed to ambient temperature and stirring was continued for 1 h before the mixture was diluted with Et_2O (100 mL) and the reaction was quenched with sat. aq. NH_4Cl (20 mL). The resulting mixture was filtered through a plug of Celite® which was rinsed with EtOAc (3 x 100 mL). The combined filtrates were dried over anhydrous Na_2SO_4, the drying agent was filtered off and the solvent was evaporated to give the title compound as a colorless oil (8.96 g, quant.). $[\alpha]_D^{20}$ = +0.8 (c = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.44 (m, 6H), 7.33 – 7.27 (m, 6H), 7.25 – 7.20 (m, 3H), 4.25 (dddd, *J* = 9.3, 6.7, 5.4, 4.2 Hz, 1H), 3.88 – 3.82 (m, 2H), 3.62 (td, *J* = 9.3, 2.7 Hz, 1H), 3.11 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.06 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.05 (t, *J* = 5.8 Hz, 1H), 2.13 (dt, *J* = 12.2, 6.9 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.74 – 1.63 (m, 1H), 1.41 (ddd, *J* = 12.3, 11.0, 9.1 Hz, 1H), 1.02 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.3 (3C), 128.9 (6C), 127.9 (6C), 127.1 (3C), 86.5, 86.0, 77.6, 66.9, 62.3, 40.3, 37.2, 35.4, 16.0 ppm; IR (film): $\tilde{\nu}$ = 3416, 3086, 3059, 3031, 2959, 2927, 2870, 1596, 1491, 1449, 1380, 1321, 1221, 1182, 1154, 1092, 1067, 1034, 1002, 990, 947, 899, 872, 776, 765, 747, 702, 646, 633, 619, 557, 536, 513, 493, 478, 462, 454, 443, 425, 420, 413, 404 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{30}O_3Na^+$: 425.2087, found: 425.2087.

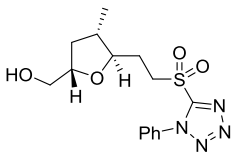
5-((2-((2*R*,3*S*,5*S*)-3-Methyl-5-((trityloxy)methyl)tetrahydrofuran-2-yl)ethyl)thio)-1-phenyl-1*H*-tetrazole (7). 1-Phenyl-1*H*-tetrazole-5-thiol (0.76 g, 4.29 mmol) and PPh_3 (1.24 g, 4.71 mmol) were added to a stirred solution of alcohol **6** (1.15 g, 2.86 mmol) in THF (23 mL) at ambient temperature. The resulting mixture was cooled to 0 °C before a solution of DIAD (0.84 mL, 4.29 mmol) in THF (7 mL) was slowly introduced over the course of 15 min. Stirring was continued for 1 h at 0°C and for another 16 h at ambient temperature. The solvent was evaporated and the crude product was

purified by flash chromatography (SiO_2, hexane:EtOAc, 10:1) to give the title compound as a colorless oil (1.39 g, 87%). $[\alpha]_D^{20}$ = +5.0 (c = 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.44 (m, 11H), 7.31 – 7.18 (m, 9H), 4.21 (dddd, *J* = 9.0, 6.6, 5.3, 4.1 Hz, 1H), 3.69 – 3.50 (m, 3H), 3.11 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.04 (dd, *J* = 9.6, 4.1 Hz, 1H), 2.24 (dddd, *J* = 14.0, 8.5, 7.4, 2.7 Hz, 1H), 2.16 (dt, *J* = 12.2, 7.0 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.42 (ddd, *J* = 12.4, 10.9, 9.0 Hz, 1H), 1.02 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.7, 144.3 (3C), 133.9, 130.1, 129.9 (2C), 128.9 (6C), 127.9 (6C), 127.1 (3C), 124.0 (2C), 86.5, 83.5, 77.3, 67.0, 39.9, 37.8, 33.5, 30.8, 16.2 ppm; IR (film): $\tilde{\nu}$ = 3058, 3023, 2957, 2927, 2871, 1739, 1596, 1499, 1448, 1412, 1386, 1318, 1277, 1243, 1221, 1183, 1156, 1089, 1074, 1044, 1016, 988, 942, 900, 841, 760, 689, 667, 645, 632, 551, 495 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{34}H_{34}N_4O_2SNa^+$: 585.2295, found: 585.2289.

5-((2-((2*R*,3*S*,5*S*)-3-methyl-5-((trityloxy)methyl)tetrahydrofuran-2-yl)ethyl)sulfonyl)-1-phenyl-1*H*-tetrazole (S-7). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (175 mg, 141 μmol) and H_2O_2 (35% in water, 481 μL, 14.1 mmol) was added to a stirred solution of thiol **7** (795 mg, 1.41 mmol) in EtOH (10.3 mL) at ambient temperature and the reaction mixture was stirred for 5 d. The reaction was quenched with water (50 mL) and the aqueous phase was extracted with EtOAc (5 x 50 mL). The combined extracts were washed with water (150 mL) and brine (150 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil (593 mg, 71%). $[\alpha]_D^{20}$ = –1.9 (c = 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.43 (m, 11H), 7.34 – 7.27 (m, 6H), 7.25 – 7.20 (m, 3H), 4.19 (ddd, *J* = 11.5, 9.2, 5.2 Hz, 1H), 4.01 (ddd, *J* = 14.6, 11.3, 3.8 Hz, 1H), 3.83 (ddd, *J* = 14.6, 11.1, 4.8 Hz, 1H), 3.55 (td, *J* = 8.9, 2.9 Hz, 1H), 3.12 (dd, *J* = 9.7, 5.3 Hz, 1H), 3.05 (dd, *J* = 9.6, 4.3 Hz, 1H), 2.30 (dddd, *J* = 14.0, 11.3, 4.8, 2.9 Hz, 1H), 2.19 (dt, *J* = 12.4, 7.0 Hz, 1H), 2.01 (dddd, *J* = 13.6, 11.1, 8.8, 4.7 Hz, 1H), 1.96 – 1.83 (m, 1H), 1.46 (ddd, *J* = 12.4, 10.9, 9.0 Hz, 1H), 1.04 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.7, 144.2 (3C), 133.2, 131.6, 129.9 (2C), 128.9 (6C), 127.9 (6C), 127.1 (3C), 125.3 (2C), 86.6, 82.8, 77.6, 66.9, 53.9, 40.0, 37.8, 26.4, 16.2 ppm; IR (film): $\tilde{\nu}$ = 3060, 3023, 2959, 2927, 2871, 1735, 1596, 1495, 1448, 1382, 1342, 1270, 1219, 1151, 1093, 1075, 1039, 1002, 989, 941, 916, 900, 825, 760, 749, 701, 667, 633,

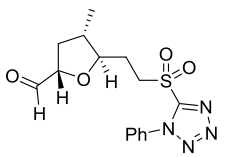
561, 536, 509, 423 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{34}H_{34}N_4O_4SNa^+$: 617.2193, found: 617.2197.

((2*S*,4*S*,5*R*)-4-Methyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)tetrahydrofuran-2-yl)methanol (8). Trifluoroacetic acid (2.41 mL, 31.5 mmol) was added to a stirred solution of



compound **S-7** (750 mg, 1.26 mmol) in CH_2Cl_2 (26.7 mL) at 0 °C and the resulting mixture was stirred for 1 h. The reaction was quenched and neutralized with sat. aq. $NaHCO_3$ (ca. 26 mL) and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined extracts were washed with brine (15 mL) and the solvent was evaporated. The crude product was dissolved in EtOAc (60 mL), sat. aq. K_2CO_3 (25 mL) was added and the resulting mixture was stirred at ambient temperature for 15 min. The aqueous phase was extracted with EtOAc (20 mL), the organic extract was washed with water (20 mL) and brine (20 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 2:1 to 1:3) to give the title compound as a colorless oil (435 mg, 98%). $[\alpha]_D^{20}$ = +22.3 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.56 (m, 5H), 4.10 (dtd, *J* = 9.3, 6.0, 3.1 Hz, 1H), 3.97 (ddd, *J* = 14.6, 10.7, 4.90 Hz, 1H), 3.83 (ddd, *J* = 14.7, 10.5, 5.3 Hz, 1H), 3.70 – 3.63 (m, 1H), 3.56 (td, *J* = 8.7, 3.0 Hz, 1H), 3.48 (dd, *J* = 11.7, 5.9 Hz, 1H), 2.30 (dddd, *J* = 13.8, 10.7, 5.3, 3.0 Hz, 1H), 2.12 (ddd, *J* = 12.2, 7.1, 6.2 Hz, 1H), 2.06 – 1.90 (m, 2H), 1.85 (s, 1H), 1.43 (ddd, *J* = 12.2, 10.7, 9.5 Hz, 1H), 1.06 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.7, 133.2, 131.6, 129.9 (2C), 125.3 (2C), 82.9, 79.1, 65.1, 53.7, 40.1, 36.5, 26.6, 16.3 ppm; IR (film): $\tilde{\nu}$ = 3426, 3068, 2960, 2929, 2873, 1595, 1498, 1461, 1399, 1339, 1295, 1236, 1153, 1112, 1078, 1041, 1015, 982, 917, 874, 826, 764, 689, 633, 536, 508, 437, 420 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{20}N_4O_4SNa^+$: 375.1098, found: 375.1098.

(2*S*,4*S*,5*R*)-4-Methyl-5-(2-((1-phenyl-1*H*-tetrazol-5-yl)sulfonyl)ethyl)tetrahydrofuran-2-

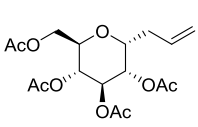


carbaldehyde (9). DMSO (279 µL, 3.93 mmol) was added dropwise to a stirred solution of oxalyl chloride (169 µL, 1.97 mmol) in CH_2Cl_2 (8.2 mL) at –78 °C. The mixture was stirred for 5 min before a solution of alcohol **8** (315 mg, 894 µmol) in CH_2Cl_2 (3.3 mL) was added dropwise and stirring was continued for 20 min. Next, di-isopropylethylamine (1.56 mL, 8.94 mmol) was added over the course of 5 min and stirring was continued for another 5 min at this temperature. The mixture was allowed to

reach ambient temperature and stirring was continued for 1 h. The reaction was quenched with water (50 mL) and the organic phase was washed with aq. phosphate buffer (200 mM, pH 7, 2 x 50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 2:1 to 1:1) to give the title compound as a colorless oil (295 mg, 94%). $[\alpha]_D^{20}$ = –12.4 (c = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63 (d, *J* = 1.9 Hz, 1H), 7.72 – 7.57 (m, 5H), 4.33 (ddd, *J* = 8.6, 7.8, 2.0 Hz, 1H), 4.02 (ddd, *J* = 14.7, 10.8, 4.9 Hz, 1H), 3.85 (ddd, *J* = 14.7, 10.6, 5.2 Hz, 1H), 3.66 (td, *J* = 8.7, 2.9 Hz, 1H), 2.45 – 2.30 (m, 2H), 2.13 – 2.05 (m, 1H), 2.04 – 1.93 (m, 1H), 1.64 (ddd, *J* = 12.8, 9.7, 8.6 Hz, 1H), 1.07 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 202.0, 153.6, 133.1, 131.7, 129.9 (2C), 125.2 (2C), 84.5, 82.0, 53.6, 39.4, 35.9, 26.7, 16.2 ppm; IR (film): $\tilde{\nu}$ = 3701, 2962, 2928, 2875, 2814, 1730, 1659, 1595, 1497, 1461, 1440, 1385, 1340, 1295, 1236, 1150, 1105, 1087, 1077, 1040, 1015, 982, 918, 903, 762, 688, 666, 633, 532, 508, 473, 408 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{17}N_4O_4S^-$: 349.0976, found: 349.0980.

Preparation of the Tetrahydropyran Segment

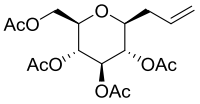
(2*R*,3*R*,4*R*,5*S*,6*R*)-2-(Acetoxymethyl)-6-allyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate (S-8).



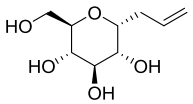
Allyltrimethylsilane (30.5 mL, 192 mmol) and $BF_3{\cdot}OEt_2$ (23.7 mL, 192 mmol) were successively added to a stirred solution of compound **10** (15.0 g, 38.4 mmol) in MeCN (250 mL). The resulting mixture was stirred for 23 h at 80 °C before it was cooled to ambient temperature and the solvent was evaporated. The crude product was dissolved in $CHCl_3$ (150 mL), the organic phase was washed with water (2 x 100 mL), sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography twice (first column: SiO_2, hexane:EtOAc, 4:1 to 2:1; second column: SiO_2, PhMe:EtOAc, 20:1 to 5:1) to give compound **S-8** as an anomeric mixture (11.3 g, 79%, α:β = 7:1). The anomers were separated by recrystallization from boiling $CHCl_3$ (7.8 mL) and forced precipitation with hexane (130 mL), affording the major α-anomer as precipitate whereas the minor β-anomer remained in solution. The precipitate was washed with ice-cold hexane and dried in vacuum.

Analytical and spectral data of the major α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75 (dddd, *J* = 17.5, 10.2, 7.5, 6.1 Hz, 1H), 5.37 – 5.31 (m, 1H), 5.19 – 5.05 (m, 3H), 4.98 (dd, *J* = 9.5, 8.8 Hz, 1H), 4.28 (ddd, *J* = 10.7, 5.6, 4.5 Hz, 1H), 4.21 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.08 (dd, *J* = 12.2, 2.6 Hz, 1H), 3.86 (ddd, *J* = 9.5, 5.4, 2.6 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.38 – 2.29 (m, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 170.3, 169.8, 169.7, 133.1, 118.0, 72.0, 70.5, 70.4, 68.92, 68.90, 62.4, 30.7, 20.9, 20.89, 20.87, 20.8 ppm; HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}O_9Na^+$: 395.1313, found: 395.1313.

Analytical and spectral data of the minor β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 – 5.74 (m, 1H), 5.16 (t, *J* = 9.4 Hz, 1H), 5.09 – 5.01 (m, 3H), 4.91 (t, *J* = 9.6 Hz, 1H), 4.23 (dd, *J* = 12.3, 5.0 Hz, 1H), 4.08 (dd, *J* = 12.2, 2.3 Hz, 1H), 3.62 (ddd, *J* = 10.0, 5.0, 2.3 Hz, 1H), 3.49 (ddd, *J* = 9.7, 7.0, 4.2 Hz, 1H), 2.35 – 2.21 (m, 2H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 170.6, 169.73, 169.66, 133.1, 117.9, 77.3, 75.7, 74.5, 71.7, 68.6, 62.4, 36.0, 20.93, 20.89, 20.82, 20.79 ppm; HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}O_9Na^+$: 395.1313, found: 395.1316. For both anomers, the analytical and spectroscopic data are in agreement with those previously reported in the literature.[3]



(2*R*,3*R*,4*R*,5*S*,6*R*)-2-Allyl-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (S-9). NaOEt (165 mg, 2.42 mmol) was added to a stirred solution of compound **S-8** (9.00 g, 24.2 mmol) in MeOH (110 mL) and the resulting mixture was stirred for 4 h at ambient temperature. The reaction was neutralized with the weakly acidic ion exchange resin Amberlite®. The resin was filtered off and washed with MeOH, the combined filtrates were dried over anhydrous Na_2SO_4 and the solvent was evaporated to give the title compound as a colorless crystalline solid, which was used without further purification (4.84 g, 98%). ^{1}H NMR (400 MHz, CD_3OD): δ = 5.88 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.12 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.04 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1H), 3.95 (ddd, *J* = 10.5, 5.6, 4.3 Hz, 1H), 3.74 (dd, *J* = 11.8, 2.5 Hz, 1H), 3.64 (dd, *J* = 11.7, 5.2 Hz, 1H), 3.60 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.53 (dd, *J* = 9.5, 8.4 Hz, 1H), 3.45 (ddd, *J* = 9.6, 5.3, 2.6 Hz, 1H), 3.28 (dd, *J* = 9.6, 8.4 Hz, 1H), 2-53 – 2.36 (m, 2H) ppm; ^{13}C NMR (101 MHz, CD_3OD): δ = 136.6, 116.9, 77.1, 75.1, 74.4, 72.9, 72.2, 62.9, 30.5 ppm; ^{1}H NMR (400 MHz, D_2O): δ = 5.78 – 5.65 (m, 1H), 5.09 (dq, *J* =

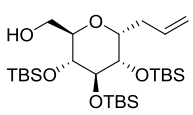


[3] G. J. McGarvey, C. A. LeClair, B. A. Schmidtmann, *Org. Lett*. **2008**, *10*, 4727-4730.

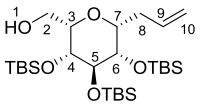
17.3, 1.5 Hz, 1H), 5.05 – 5.00 (m, 1H), 3.97 (ddd, *J* = 11.5, 5.8, 4.0 Hz, 1H), 3.69 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.62 (dd, *J* = 9.7, 5.7 Hz, 1H), 3.58 (dd, *J* = 11.9, 5.2 Hz, 1H), 3.55 (dd, *J* = 9.8, 8.7 Hz, 1H), 3.47 (ddd, *J* = 10.1, 5.3, 2.3 Hz, 1H), 3.25 (dd, *J* = 10.0, 8.7 Hz, 1H), 2.45 – 2.26 (m, 2H) ppm; ^{13}C NMR (101 MHz, D_2O): δ = 134.3, 117.4, 75.2, 73.0, 72.2, 70.9, 70.0, 60.6, 28.7 ppm; HRMS (ESI): *m/z* calcd. for $C_9H_{16}O_5Na^+$: 227.0890, found: 227.0891. The analytical and spectroscopic data are in agreement with those previously reported in the literature.[4]

(((2*R*,3*S*,4*R*,5*R*,6*R*)-2-Allyl-6-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl)tris(oxy))tris(*tert*-butyldimethylsilane) (11). TBSOTf (36.7 mL, 160 mmol) was slowly added to a stirred suspension of compound **S-9** (5.44 g, 26.6 mmol) and 2,6-lutidine (24.8 mL, 213 mmol) in CH_2Cl_2 (135 mL) at 0 °C over the course of 30 min. The mixture was allowed to reach ambient temperature and stirring was continued for 2.25 h. Next, 2,6-lutidine (6.20 mL, 53.2 mmol) and TBSOTf (6.11 mL, 26.6 mmol) were successively added at 0 °C, the mixture was allowed to reach ambient temperature and stirring was continued for 17 h. The mixture was diluted with *tert*-butyl methyl ether (200 mL) and cautiously poured into aq. HCl (1.0 M, 100 mL). The organic phase was washed with water (100 mL) and brine (100 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 100:1 to 20:1) to give the title compound as a colorless oil (16.9 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (dddd, *J* = 17.5, 10.2, 7.5, 6.0 Hz, 1H), 5.10 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.05 – 5.01 (m, 1H), 3.91 – 3.70 (m, 5H), 3.69 – 3.66 (m, 1H), 3.46 – 3.43 (m, 1H), 2.44 (dddt, *J* = 11.9, 7.8, 5.9, 1.7 Hz, 1H), 2.10 (dddt, *J* = 14.1, 7.6, 5.2, 1.3 Hz, 1H), 0.92 (s, 9H), 0.89 (s, 9H), 0.88 (s, 18H), 0.10 (s, 6H), 0.08 (s, 3H), 0.07 (s, 3H), 0.065 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H), 0.025 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.1, 116.3, 78.2, 74.3, 71.5, 70.6, 69.4, 62.5, 36.0, 26.34 (3C), 26.2 (3C), 26.1 (3C), 25.9 (3C), 18.5, 18.5, 18.3, 18.0, -3.3, -4.0, -4.2, -4.48, -4.50, -4.9, -5.0, -5.2 ppm; HRMS (ESI): *m/z* calcd. for $C_{33}H_{72}O_5Si_4Na^+$: 683.4349, found: 683.4352. The analytical and spectroscopic data are in agreement with those previously reported in the literature.[3]

[4] R. Y. Tam, S. S. Ferreira, P. Czechura, J. L. Chaytor, R. N. Ben, *J. Am. Chem. Soc*. **2008**, *130*, 17494-17501.

((2*R*,3*R*,4*R*,5*S*,6*R*)-6-Allyl-3,4,5-tris((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)methanol (12). 

HF·pyridine (12.5% in THF/pyridine 2.5:1, 13.8 mL, 19.2 mmol) was added to a stirred solution of compound **11** (911 mg, 1.38 mmol) in THF (29 mL) at 0 °C. The mixture was allowed to reach ambient temperature over 30 min and stirring was continued for 16 h. The reaction was quenched with sat. aq. $NaHCO_3$ (100 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 75 mL). The combined extracts were washed with brine (75 mL) and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 40:1 to 20:1) to give by-product *epi*-**12** (81 mg, 11%) and compound **12** (647 mg, 86%) as a colorless oil each. $[\alpha]_D^{20}$ = +18.5 (c = 1.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.14 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.09 (ddt, *J* = 10.3, 2.2, 1.1 Hz, 1H), 3.95 (ddd, *J* = 8.6, 5.1, 3.5 Hz, 1H), 3.88 (ddd, *J* = 9.1, 4.5, 2.4 Hz, 1H), 3.80 – 3.78 (m, 1H), 3.78 (ddd, *J* = 11.5, 8.5, 3.5 Hz, 1H), 3.60 – 3.55 (m, 1H), 3.55 (ddd, *J* = 11.4, 8.6, 3.5 Hz, 1H), 3.49 (dt, *J* = 5.1, 1.2 Hz, 1H), 2.49 (dddt, *J* = 14.3, 8.7, 7.1, 1.3 Hz, 1H), 2.11 (dddt, *J* = 14.2, 7.0, 4.5, 1.3 Hz, 1H), 2.04 (dd, *J* = 8.6, 3.5 Hz, 1H), 0.93 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.115 (s, 3H), 0.105 (s, 3H), 0.085 (s, 6H), 0.075 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.8, 117.2, 76.6, 74.8, 72.3, 72.0, 69.7, 61.9, 35.8, 26.2 (3C), 26.2 (3C), 25.9 (3C), 18.4, 18.3, 18.0, -3.5, -3.9, -4.0, -4.5, -4.7, -4.9 ppm; IR (film): $\tilde{\nu}$ = 3485, 2953, 2929, 2886, 2858, 1642, 1472, 1463, 1433, 1406, 1389, 1361, 1322, 1253, 1187, 1130, 1088, 1005, 963, 939, 911, 881, 858, 833, 813, 774, 670, 666, 568, 494, 479, 466, 448, 434, 426, 413 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{58}O_5Si_3Na^+$: 569.3484, found: 569.3487.

Analytical and spectral data of the minor isomer epi-**12**: $[\alpha]_D^{20}$ = –1.5 (c = 1.05, $CHCl_3$); 

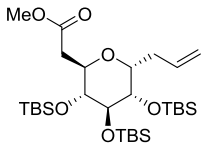
^{1}H NMR (600 MHz, C_6D_6): δ = 5.99 (ddt, *J* = 17.2, 10.3, 6.9 Hz, 1H, H-9), 5.18 (ddt, *J* = 17.2, 2.2, 1.5 Hz, 1H, H-10a), 5.08 (ddt, *J* = 10.3, 2.3, 1.2 Hz, 1H, H-10b), 3.99 (ddd, *J* = 5.0, 2.1, 1.2 Hz, 1H, H-4), 3.94 (t, *J* = 2.2 Hz, 1H, H-5), 3.88 – 3.82 (m, 3H, H-7 & H-3 & H-1a), 3.80 (ddd, *J* = 4.7, 2.1, 1.3 Hz, 1H, H-6), 3.76 – 3.70 (m, 1H, H-1b), 2.62 – 2.56 (m, 1H, H-8a), 2.53 – 2.47 (m, 1H, H-8b), 1.86 (t, *J* = 6.0 Hz, 1H, H-1), 0.98 (s, 9H, *t*-Bu), 0.97 (s, 9H, *t*-Bu), 0.96 (s, 9H, *t*-Bu), 0.17 (s, 3H, Me), 0.155 (s, 3H, Me), 0.15 (s, 3H, Me), 0.14 (s, 3H, Me), 0.10 (s, 3H, Me), 0.09 (s, 3H, Me) ppm; ^{13}C NMR (151 MHz, C_6D_6): δ = 135.6 (C-9), 117.1 (C-10), 80.8 (C-3), 80.0 (C-7), 78.2 (C-5), 75.1 (C-6), 72.3 (C-4),

64.0 (C-2), 39.2 (C-8), 26.1 (6C *t*-Bu), 26.0 (3C *t*-Bu), 18.2 (2C *t*-Bu), 18.1 (*t*-Bu), -3.6 (Me), -3.8 (Me), -4.0 (Me), -4.1 (Me), -4.4 (Me), -4.6 (Me) ppm; IR (film): $\tilde{\nu}$ = 3484, 2953, 2929, 2894, 2857, 1642, 1472, 1463, 1389, 1361, 1342, 1251, 1085, 1005, 938, 914, 880, 853, 831, 813, 772, 670, 576, 520, 472, 418 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{58}O_5Si_3Na^+$: 569.3484, found: 569.3488.

(2*S*,3*R*,4*R*,5*S*,6*R*)-6-Allyl-3,4,5-tris((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-carbaldehyde (S-10). DMSO (377 µL, 5.31 mmol) was added dropwise to a stirred solution of oxalyl chloride (228 µL, 2.65 mmol) in CH_2Cl_2 (8.0 mL) at –78 °C and the reaction mixture was stirred for 5 min. A solution of alcohol **12** (660 mg, 1.21 mmol) in CH_2Cl_2 (2.5 mL, rinsed with 2 x 2.5 mL) was added dropwise and stirring was continued for 20 min. Next, di-isopropylethylamine (2.10 mL, 12.1 mmol) was added over the course of 5 min and stirring was continued for 5 min at –78°C and for another 30 min at ambient temperature. The reaction was quenched with water (20 mL), the organic phase was washed with aq. phosphate buffer (200 mM, pH 7, 2 x 15 mL) and with brine (15 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 50:1) to give the title compound as a colorless oil (589 mg, 90%). $[\alpha]_D^{20}$ = +67.9 (c = 1.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 5.95 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.18 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.11 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.17 – 4.14 (m, 1H), 4.05 – 3.99 (m, 2H), 3.81 (t, *J* = 2.9 Hz, 1H), 3.37 – 3.33 (m, 1H), 2.57 (dddt, *J* = 14.8, 8.2, 6.4, 1.5 Hz, 1H), 2.19 (dddt, *J* = 14.7, 7.3, 4.9, 1.4 Hz, 1H), 0.94 (s, 9H), 0.93 (s, 9H), 0.84 (s, 9H), 0.12 (s, 3H), 0.115 (s, 3H), 0.11 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.3, 135.4, 116.9, 84.0, 71.4, 71.1, 70.2, 70.1, 36.0, 26.5 (3C), 26.3 (3C), 25.7 (3C), 18.8, 18.4, 17.9, -3.2, -4.2, -4.5, -4.6, -4.7, -4.9 ppm; IR (film): $\tilde{\nu}$ = 2952, 2929, 2886, 2858, 1734, 1643, 1472, 1463, 1390, 1362, 1305, 1252, 1131, 1086, 1041, 1005, 968, 939, 914, 882, 831, 812, 773, 673, 666, 600, 573, 538, 466 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{56}O_5Si_3Na^+$: 567.3328, found: 567.3331.

(((2*R*,3*S*,4*R*,5*R*,6*R*)-2-Allyl-6-(2-methoxyvinyl)tetrahydro-2*H*-pyran-3,4,5-triyl)tris(oxy))-tris(*tert*-butyldimethylsilane) (14). A solution of KO*t*-Bu (824 mg, 7.34 mmol) in THF (4.0 mL, rinsed with 4.0 mL) was dried over 5 Å MS

before it was slowly added at −50 °C over the course of 25 min to a stirred suspension containing [$MeOCH_2PPh_3$]Cl (2.52 g, 7.34 mmol) and 5 Å MS in THF (17 mL), causing a fast color change from colorless to deep orange. Stirring was continued for 10 min before the mixture was cooled to −78 °C. After stirring for 10 min, a solution of aldehyde **S-10** (2.00 g, 3.67 mmol) in THF (4.0 mL, pre-dried over 5 Å MS, rinsing with 4.0 mL THF) was added over the course of 15 min. The resulting mixture was allowed to reach ambient temperature and stirring was continued for 17.5 h. The reaction was quenched with water (25 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL). The combined extracts were washed with brine (50 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 50:1 to 20:1) to give compound **13** as an inseparable mixture of *E/Z* isomers, which was immediately use in the next step (1.85 g, 88%).

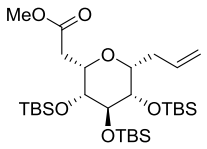


PCC (1.39 g, 6.44 mmol) was added to a stirred solution of **13** (1.85 g, 3.22 mmol) in CH_2Cl_2 (185 mL) and the resulting mixture was stirred for 6 h at ambient temperature. A second patch of PCC (347 mg, 1.61 mmol) was added to the reaction mixture and stirring was continued for 17 h before a third patch of PCC (347 mg, 1.61 mmol) was introduced. Once TLC indicated complete conversion, Celite® was added and the solvent was evaporated. The loaded Celite® was added on top of a silica gel column and the product was purified by flash chromatography (fine SiO_2, hexane:EtOAc, 100:1 to 40:1) to give an epimeric by-product (*epi*-**14**, 340 mg, 18%) and compound **14** (1.16 g, 61%) as a colorless oil each.

Analytical and spectroscopic data of the major product **14**: $[\alpha]_D^{20}$ = +22.9 (c = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.08 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.03 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 4.33 (ddd, *J* = 9.2, 5.8, 3.7 Hz, 1H), 3.85 (ddd, *J* = 9.0, 4.5, 2.2 Hz, 1H), 3.80 (t, *J* = 2.5 Hz, 1H), 3.67 (s, 3H), 3.52 – 3.47 (m, 2H), 2.73 (dd, *J* = 14.6, 8.9 Hz, 1H), 2.68 (dd, *J* = 14.5, 5.8 Hz, 1H), 2.45 (dddt, *J* = 14.5, 9.3, 6.4, 1.5 Hz, 1H), 2.07 (dddt, *J* = 14.3, 7.2, 4.5, 1.3 Hz, 1H), 0.93 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.10 (s, 6H), 0.09 (s, 6H), 0.075 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 135.9, 116.4, 74.5, 74.1, 73.9, 71.7, 69.5, 51.7, 37.5, 35.8, 26.3 (3C), 26.2 (3C), 25.9 (3C), 18.5, 18.4, 18.0, -3.3, -4.0, -4.1, -4.5 (2C), -4.9 ppm; IR (film): $\tilde{\nu}$ = 2952, 2929, 2886, 2858, 1743, 1472,

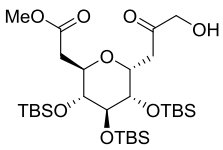
1463, 1436, 1409, 1390, 1361, 1339, 1253, 1124, 1082, 1005, 939, 911, 833, 813, 774, 673, 666, 559, 486, 427 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{60}O_6Si_3Na^+$: 611.3590, found: 611.3593.

*Analytical and spectroscopic data of epi-***14**: $[\alpha]_D^{20}$ = +10.5 (c = 1.03, $CHCl_3$);



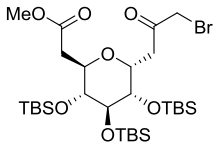
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (dddd, *J* = 17.5, 10.3, 7.3, 5.6 Hz, 1H), 5.07 (dq, *J* = 17.3, 1.8 Hz, 1H), 5.01 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.08 (ddd, *J* = 8.5, 5.1, 1.8 Hz, 1H), 3.78 (t, *J* = 2.5 Hz, 1H), 3.67 (s, 3H), 3.65 (ddd, *J* = 9.7, 3.9, 1.8 Hz, 1H), 3.43 – 3.41 (m, 1H), 3.34 – 3.31 (m, 1H), 2.72 (dd, *J* = 15.9, 8.5 Hz, 1H), 2.48 (dddt, *J* = 15.0, 9.2, 5.6, 1.7 Hz, 1H), 2.43 (dd, *J* = 15.9, 5.1 Hz, 1H), 2.02 (dddt, *J* = 15.0, 7.3, 4.0, 1.2 Hz, 1H), 0.925 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.095 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 136.2, 115.8, 76.7, 73.5, 73.3, 72.0, 71.5, 51.6, 36.9, 35.8, 26.51 (3C), 26.48 (3C), 25.9 (3C), 18.6, 18.5, 18.0, -2.9, -3.1, -4.32, -4.34, -4.8, -5.1 ppm; IR (film): $\tilde{\nu}$ = 2952, 2929, 2887, 2858, 1742, 1473, 1463, 1436, 1406, 1390, 1379, 1361, 1349, 1288, 1252, 1195, 1162, 1137, 1121, 1085, 1071, 1005, 982, 939, 914, 869, 830, 813, 770, 674, 593, 564, 509, 463 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{60}O_6Si_3Na^+$: 611.3590, found: 611.3593.

Methyl 2-((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4,5-tris((*tert*-butyldimethylsilyl)oxy)-6-(3-hydroxy-2-oxopropyl)tetrahydro-2*H*-pyran-2-yl)acetate (15).



A solution of $KMnO_4$ (159 mg, 1.01 mmol) in acetone (2.45 mL) and water (0.8 mL) was added to a stirred solution of alkene **14** (370 mg, 628 μmol) in acetone (6.25 mL), water (1.4 mL) and AcOH (302 μL). The mixture was stirred for 3.25 h at ambient temperature before the reaction was quenched with EtOH (1.0 mL). The resulting mixture was filtered through a plug of silica gel, rinsing with *tert*-butyl methyl ether. The combined filtrates were washed with sat. aq. $NaHCO_3$ (2 x 30 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL). The combined extracts were dried over anhydrous Na_2SO_4, the drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 10:1 to 5:1) to give the title compound as a colorless oil (301 mg, 77%). $[\alpha]_D^{20}$ = +34.5 (c = 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.36 – 4.25 (m, 3H), 4.21 (dd, *J* = 19.3, 5.0 Hz, 1H), 3.80 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.67 (s, 3H), 3.62 – 3.60 (m, 1H), 3.48 (dt, *J* = 4.4, 1.3 Hz, 1H), 3.09 (t, *J* = 4.9 Hz, 1H), 2.94 (dd, *J* = 15.2, 9.1 Hz, 1H), 2.71 (dd, *J* = 15.3, 5.2 Hz, 1H), 2.63 (dd, *J* = 15.3, 9.1 Hz, 1H), 2.29 (dd, *J* = 15.3, 3.9 Hz,

1H), 0.93 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.115 (s, 3H), 0.11 (s, 3H), 0.105 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.5, 172.0, 74.4, 73.9, 73.5, 71.8, 69.4, 67.1, 51.8, 40.7, 37.2, 26.3 (3C), 26.2 (3C), 25.9 (3C), 18.4, 18.3, 18.0, -3.5, -3.9, -4.1, -4.5, -4.6, -5.1 ppm; IR (film): $\tilde{\nu}$ = 3505, 2953, 2929, 2896, 2858, 1739, 1472, 1463, 1437, 1390, 1361, 1341, 1253, 1171, 1122, 1083, 1005, 938, 893, 867, 831, 812, 773, 672, 547, 475 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{60}O_8Si_3Na^+$: 643.3488, found: 643.3489.

Methyl 2-((2*R*,3*R*,4*R*,5*S*,6*R*)-6-(3-bromo-2-oxopropyl)-3,4,5-tris((*tert*-butyldimethyl-silyl)-oxy)tetrahydro-2*H*-pyran-2-yl)acetate (16). 

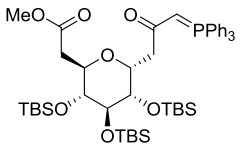
PPh_3 (129 mg, 490 μmol) was added to a stirred solution of α-hydroxy ketone **15** (290 mg, 467 μmol) and CBr_4 (163 mg, 490 μmol) in CH_2Cl_2 (6.0 mL). The mixture was stirred for 40 min at ambient temperature before CBr_4 (77 mg, 234 μmol) and PPh_3 (61 mg, 234 μmol) were successively added and stirring was continued for 40 min. The mixture was filtered through a plug of silica gel which was rinsed with *tert*-butyl methyl ether. The filtrate was evaporated and the crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 40:1 to 30:1) to give the title compound as a colorless oil (257 mg, 81%). $[\alpha]_D^{20}$ = +43.7 (c = 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.35 – 4.26 (m, 2H), 4.01 (s, 2H), 3.80 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.67 (s, 3H), 3.62 – 3.59 (m, 1H), 3.49 (dt, *J* = 4.5, 1.3 Hz, 1H), 3.13 (dd, *J* = 15.8, 8.9 Hz, 1H), 2.72 (dd, *J* = 15.3, 5.3 Hz, 1H), 2.65 (dd, *J* = 15.3, 9.1 Hz, 1H), 2.50 (dd, *J* = 15.8, 4.0 Hz, 1H), 0.94 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.11 (s, 3H), 0.105 (s, 6H), 0.09 (s, 3H), 0.08 (s, 3H), 0.04 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.0, 172.0, 74.4, 73.9, 73.5, 71.6, 67.3, 51.8, 42.1, 37.1, 36.2, 26.3 (3C), 26.2 (3C), 25.9 (3C), 18.4, 18.3, 18.0, -3.5, -3.9, -4.1, -4.5, -4.6, -5.0 ppm; ^{1}H NMR (400 MHz, C_6D_6): δ = 4.63 – 4.55 (m, 2H) 3.98 – 3.95 (m, 1H), 3.77 – 3.74 (m, 1H), 3.72 (ddd, *J* = 4.0, 1.8, 1.0 Hz, 1H), 3.51 (d, *J* = 13.3 Hz, 1H), 3.44 (d, *J* = 13.3 Hz, 1H), 3.39 (s, 3H), 3.05 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.92 (dd, *J* = 15.5, 6.0 Hz, 1H), 2.81 (dd, *J* = 15.5, 8.3 Hz, 1H), 2.47 (dd, *J* = 16.3, 4.8 Hz, 1H), 1.04 (s, 9H), 0.97 (s, 9H), 0.95 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, C_6D_6): δ = 199.4, 171.6, 74.8, 74.0, 73.9, 71.9, 67.2, 51.3, 41.8, 37.1, 35.9, 26.4 (3C), 26.3 (3C), 25.9 (3C), 18.53, 18.45, 18.1, -3.4, -3.8, -4.3, -4.5 (2C), -5.0 ppm; IR (film): $\tilde{\nu}$ = 2952, 2929, 2895, 2857, 1739, 1472, 1463, 1437, 1390, 1361, 1253, 1172, 1124, 1084, 1042, 1005, 970, 938, 893, 870, 832, 813, 774, 673, 575, 551, 475 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{59}O_7BrSi_3Na^+$: 705.2644, found: 705.2650.

Compound 17. A solution of PPh_3 (101 mg, 384 μmol) in benzene (2.0 mL, rinsing with 2.0 mL), which had been dried for 1 h over 4 Å MS, was combined with a solution of α-bromo ketone **16** (250 mg, 66 μmol) in benzene (4.0 mL, pre-dried for 1 h over 4 Å MS) at ambient temperature. The mixture was stirred for 5 min before it was stored at –20 °C for 49 h. The mixture was then allowed to reach ambient temperature and the resulting solution of **17** was used in the next step without purification or removal of the solvent (contains some unreacted PPh_3). ^{1}H NMR (4:1 tautomer ratio, asterisk denotes minor tautomer peaks, 600 MHz, C_6D_6): δ = 14.16* (d, *J* = 2.5 Hz, 1H, H-11), 7.88 (dd, *J* = 18.1, 10.5 Hz, 1H, H-10a), 7.85 – 7.80 (m, 6H, o-Ph), 7.33 – 7.26* (m, 6H, o-Ph), 7.04 – 6.98 (m, 6H, m-Ph), 6.97 – 6.93 (m, 3H, p-Ph), 6.97 – 6.93* (m, 3H, p-Ph), 6.91 – 6.87* (m, 6H, m-Ph), 6.21 (dd, *J* = 18.0, 12.8 Hz, 1H, H-10b), 5.40 (dt, *J* = 11.1, 2.1 Hz, 1H, H-7), 5.33* (d, *J* = 10.6 Hz, 1H, H-7), 4.82* (dt, *J* = 8.4, 5.7 Hz, 1H, H-3), 4.72* (dd, *J* = 21.1, 2.4 Hz, 1H, H-10), 4.72* (t, *J* = 2.6 Hz, 1H, H-6), 4.66 (dt, *J* = 8.4, 5.6 Hz, 1H, H-3), 4.34 – 4.31 (m, 1H, H-6), 4.17* (d, *J* = 12.9 Hz, 1H, H-8a), 4.16* (d, *J* = 3.8 Hz, 1H, H-5), 4.07 (dd, *J* = 3.3, 1.3 Hz, 1H, H-5), 3.92 – 3.90* (m, 1H, H-4), 3.92 (dd, *J* = 15.3, 2.3 Hz, 1H, H-8a), 3.74 (dt, *J* = 5.5, 1.0 Hz, 1H, H-4), 3.46 (ddd, *J* = 14.8, 11.1, 3.4 Hz, 1H, H-8b), 3.30* (dd, *J* = 15.7, 5.2 Hz, 1H, H-2a), 3.25 (s, 3H, Me), 3.25* (d, *J* = 23.2 Hz, 1H, H-8b), 3.00* (s, 3H, Me), 2.92 – 2.86 (m, 2H, H-2), 2.67* (dd, *J* = 15.7, 8.2 Hz, 1H, H-2b), 1.13* (s, 9H, *t*-Bu), 1.11* (s, 9H, *t*-Bu), 1.09 (s, 9H, *t*-Bu), 1.05 (s, 9H, *t*-Bu), 0.97* (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu), 0.67* (s, 3H, Me), 0.54 (s, 3H, Me), 0.52* (s, 3H, Me), 0.35* (s, 3H, Me), 0.34 (s, 3H, Me), 0.31* (s, 3H, Me), 0.24 (s, 3H, Me), 0.23 (s, 3H, Me), 0.22* (s, 3H, Me), 0.16 (s, 3H, Me), 0.13* (s, 3H, Me), 0.07 (s, 3H, Me) ppm; ^{13}C NMR (4:1 tautomer ratio, asterisk denotes minor tautomer peaks, 151 MHz, C_6D_6): δ = 203.5 (d, $J_{31P,13C}$ = 7.2 Hz, C-9), 185.0* (C-9), 172.4* (C-1), 172.3 (C-1), 134.5 (d, $J_{31P,13C}$ = 10.9 Hz, 6C, o-Ph), 133.9 (d, $J_{31P,13C}$ = 2.9 Hz, 3C, p-Ph), 133.5* (d, $J_{31P,13C}$ = 10.7 Hz, 6C, o-Ph), 133.4* (d, $J_{31P,13C}$ = 2.2 Hz, 3C, p-Ph), 129.7 (d, $J_{31P,13C}$ = 13.0 Hz, 6C, m-Ph), 129.5* (d, $J_{31P,13C}$ = 12.9 Hz, 6C, m-Ph), 122.6* (d, $J_{31P,13C}$ = 91.4 Hz, 3C, i-Ph), 119.8 (d, $J_{31P,13C}$ = 88.7 Hz, 3C, i-Ph), 76.4* (C-4), 76.2 (C-4), 76.0* (C-5), 75.6 (C-5), 73.5 (C-3), 72.6* (C-3), 71.9* (C-6), 71.6* (C-7), 71.5 (C-6), 71.1* (d, $J_{31P,13C}$ = 97.1 Hz, C-10), 68.9 (C-7), 51.3 (C-12), 50.6* (C-12), 48.0 (d, $J_{31P,13C}$ = 5.7 Hz, C-8), 40.2 (d, $J_{31P,13C}$ = 58.0 Hz, C-10), 39.6* (d, $J_{31P,13C}$ = 11.8 Hz, C-8), 39.0 (C-2), 38.6* (C-2), 26.6* (3C, *t*-Bu), 26.53* (3C, *t*-Bu), 26.50 (3C, *t*-Bu), 26.45 (3C, *t*-Bu), 26.4* (3C, *t*-Bu), 26.3 (3C, *t*-Bu),

18.6* (*t*-Bu), 18.47* (2C, *t*-Bu), 18.47 (*t*-Bu), 18.45 (*t*-Bu), 18.4 (*t*-Bu), -2.6* (Me), -2.8 (Me), -3.4* (Me), -3.5* (Me), -3.6 (Me), -3.7 (Me), -4.1* (Me), -4.36* (Me), -4.39 (Me), -4.56* (Me), -4.57 (Me), -4.59 (Me) ppm; ^{31}P NMR (4:1 tautomer ratio, asterisk denotes minor tautomer peak, 162 MHz, C_6D_6): δ = 20.9, 13.4* ppm; HRMS (ESI): *m/z* calcd. for $C_{47}H_{74}O_7PSi_3^+$: 865.4475, found: 865.4472.

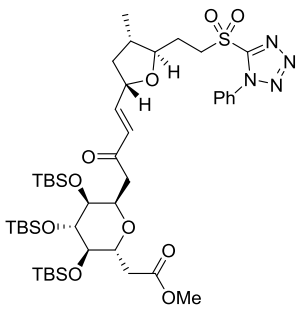
Preparation of the Sidechain

Enone S-11. *Formation of Ylid* **18**. Di-isopropylethylamine (140 µL, 804 µmol) was added to a solution of the crude phosphonium salt **17** (346 mg, 366 µmol) in benzene (8.0 mL) and the resulting mixture was stirred for 1 h at ambient temperature, leading to the formation of a white precipitate. This suspension of ylid **18** was used in the next step without purification or removal of the solvent.



A solution of aldehyde **9** (141 mg, 402 µmol) in benzene (2.0 mL, rinsed with 1.0 mL, pre-dried for 1 h over 4 Å MS) was added to the suspension of ylid **18** (316 mg, 366 µmol) described above. The mixture was stirred for 18 h at ambient temperature before it was diluted with *tert*-butyl methyl ether (50 mL) and washed with aq. phosphate buffer (200 mM, pH 7, 2x 25 mL). The combined aqueous phases were extracted with *tert*-butyl methyl ether (2 x 25 mL) and the extracts were dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 7:1 to 3:1) to give (***Z***)-**S-11** (14 mg, 4%) and the desired *E*-isomer **S-11** (256 mg, 75%) as a colorless oil each.

Analytical and spectral data of compound **S-11**: $[\alpha]_D^{20}$ = +3.3 (c = 0.95, $CHCl_3$);

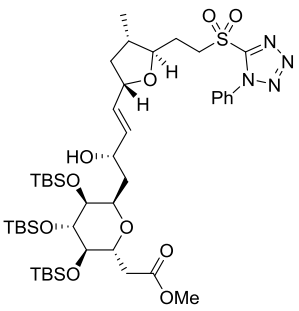


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.57 (m, 5H), 6.71 (dd, *J* = 15.9, 5.3 Hz, 1H), 6.23 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.57 (dddd, *J* = 9.5, 6.7, 5.2, 1.5 Hz, 1H), 4.39 (td, *J* = 6.5, 2.4 Hz, 1H), 4.28 (ddd, *J* = 9.3, 5.7, 3.8 Hz, 1H), 3.97 (ddd, *J* = 14.7, 11.1, 4.8 Hz, 1H), 3.82 – 3.79 (m, 1H), 3.81 (ddd, *J* = 14.8, 11.0, 5.1 Hz, 1H), 3.70 – 3.67 (m, 1H), 3.66 (s, 3H), 3.61 (td, *J* = 8.8, 2.5 Hz, 1H), 3.51 (ddd, *J* = 4.0, 1.8, 1.0 Hz, 1H), 2.94 (dd, *J* = 17.0, 6.6 Hz, 1H), 2.79 (dd, *J* = 15.2, 5.8 Hz, 1H), 2.73 (dd, *J* = 17.0, 6.3 Hz, 1H), 2.69 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.41 – 2.25 (m, 2H), 2.10 – 1.93 (m, 2H), 1.42 (ddd, *J* = 12.4, 10.5, 9.4 Hz, 1H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H), 0.91 (s, 9H), 0.89 (s, 9H), 0.14 (s,

3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), -0.01 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.6, 172.1, 153.6, 146.2, 133.2, 131.6, 129.9 (2C), 128.6, 125.3 (2C), 83.3, 77.3, 74.3, 73.9, 73.73, 71.2, 66.2, 53.7, 51.7, 42.0, 41.3, 40.3, 37.2, 26.8, 26.3 (3C), 26.3 (3C), 25.9 (3C), 18.5, 18.3, 18.0, 16.3, -3.4, -3.9, -4.2, -4.58, -4.60, -5.0 ppm; IR (film): $\tilde{\nu}$ = 2955, 2929, 2894, 2857, 1737, 1673, 1632, 1596, 1498, 1472, 1463, 1437, 1407, 1389, 1344, 1258, 1216, 1153, 1124, 1083, 1043, 1005, 973, 938, 894, 866, 832, 812, 773, 752, 688, 667, 633, 536, 506, 467, 448, 436, 418 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{76}N_4O_{10}Si_3SNa^+$: 959.4482, found: 959.4487.

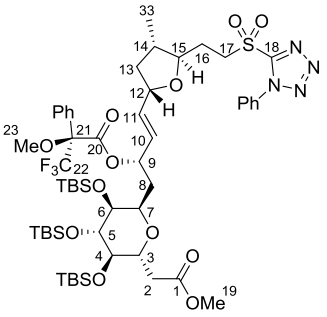
Analytical and spectroscopic data of the minor Z-isomer ((**Z**)-**S-11**): $[\alpha]_D^{20}$ = +5.3 (c = 1.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.56 (m, 5H), 6.17 (dd, *J* = 11.5, 1.4 Hz, 1H), 6.06 (dd, *J* = 11.6, 7.0 Hz, 1H), 5.27 – 5.18 (m, 1H), 4.34 (ddd, *J* = 7.6, 4.6, 2.4 Hz, 1H), 4.28 (ddd, *J* = 9.4, 5.7, 3.9 Hz, 1H), 3.94 (ddd, *J* = 14.7, 10.8, 5.0 Hz, 1H), 3.81 – 3.78 (m, 1H), 3.80 (ddd, *J* = 14.6, 10.4, 5.2 Hz, 1H), 3.65 (s, 3H), 3.64 – 3.60 (m, 1H), 3.60 – 3.57 (m, 1H), 3.50 (ddd, *J* = 4.1, 1.7, 1.0 Hz, 1H), 2.90 (dd, *J* = 16.5, 8.0 Hz, 1H), 2.81 (dd, *J* = 15.2, 5.8 Hz, 1H), 2.66 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.59 (dt, *J* = 12.9, 6.6 Hz, 1H), 2.48 (dd, *J* = 16.6, 4.7 Hz, 1H), 2.27 (tdd, *J* = 10.7, 5.2, 3.0 Hz, 1H), 2.06 – 1.92 (m, 2H), 1.29 (ddd, *J* = 12.5, 10.6, 9.5 Hz, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.92 (s, 9H), 0.91 (s, 9H), 0.89 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.095 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.01 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.1, 172.1, 153.7, 148.8, 133.2, 131.6, 129.9 (2C), 126.8, 125.3 (2C), 83.3, 76.1, 74.4, 73.74, 73.66, 71.6, 66.7, 53.7, 51.7, 45.4, 41.1, 40.0, 37.2, 26.7, 26.3 (3C), 26.2 (3C), 25.9 (3C), 18.5, 18.3, 18.0, 16.4, -3.4, -3.9, -4.1, -4.57, -4.58, -5.1 ppm; IR (film): $\tilde{\nu}$ = 2953, 2929, 2894, 2857, 1739, 1690, 1618, 1498, 1472, 1463, 1437, 1409, 1389, 1346, 1257, 1154, 1125, 1084, 1038, 1005, 971, 938, 889, 868, 833, 813, 774, 762, 688, 673, 630, 536, 508, 473, 466, 438, 429, 420 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{76}N_4O_{10}Si_3SNa^+$: 959.4482, found: 959.4487.

Compound 19. (*R*)-(+)-2-Methyl-CBS-oxazaborolidine 22 (68 mg, 0.25 mmol) was added to a stirred solution of enone **S-11** (220 mg, 235 μmol) in THF (3.8 mL) at –20 °C and the resulting mixture was stirred for 20 min. $BH_3{\cdot}SMe_2$ (31.5 μL, 352 μmol) was introduced and stirring was continued for 1.5 h at –20 °C. The reaction was quenched with aq. NaH_2PO_4 (1 M, 20 mL) at



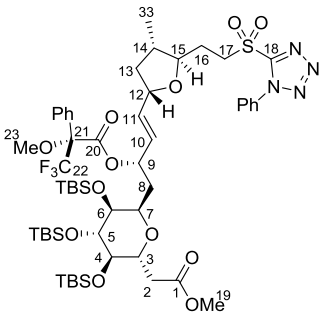
0 °C and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined extracts were washed with aq. phosphate buffer (200 mM, pH 7, 2 x 10 mL), the aqueous phase was extracted with EtOAc (10 mL), and the combined extracts were dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 4:1 to 2:1) to give the title compound as a colorless oil (200 mg, 91%). $[\alpha]_D^{20}$ = +6.2 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 – 7.56 (m, 5H), 5.73 – 5.62 (m, 2H), 4.42 – 4.27 (m, 3H), 4.04 (dt, *J* = 10.7, 2.2 Hz, 1H), 3.94 (ddd, *J* = 14.8, 10.9, 4.9 Hz, 1H), 3.78 – 3.76 (m, 1H), 3.77 (ddd, *J* = 14.7, 10.7, 5.0 Hz, 1H), 3.70 (s, 3H), 3.57 (td, *J* = 8.7, 3.0 Hz, 1H), 3.49 (ddd, *J* = 3.9, 1.9, 1.0 Hz, 1H), 3.46 – 3.42 (m, 1H), 3.24 (d, *J* = 1.7 Hz, 1H), 2.78 (dd, *J* = 15.0, 9.6 Hz, 1H), 2.67 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.31 – 2.18 (m, 2H), 2.08 – 1.88 (m, 3H), 1.44 – 1.32 (m, 2H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.92 (s, 9H), 0.90 (s, 18H), 0.11 (s, 3H), 0.09 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 153.7, 134.0, 133.2, 131.6, 131.0, 129.9 (2C), 125.4 (2C), 82.9, 78.8, 74.1, 74.0, 73.6, 72.4, 71.6, 69.8, 53.9, 52.0, 42.0, 40.3, 38.6, 37.3, 26.9, 26.3 (3C), 26.2 (3C), 25.9 (3C), 18.5, 18.4, 18.0, 16.5, -3.5, -3.9, -4.2, -4.5, -4.6, -4.8 ppm; IR (film): $\tilde{\nu}$ = 3502, 2953, 2929, 2887, 2857, 1738, 1596, 1498, 1472, 1463, 1437, 1389, 1345, 1253, 1150, 1127, 1083, 1006, 972, 939, 916, 833, 813, 774, 761, 688, 668, 633, 506, 466, 424 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{78}N_4O_{10}Si_3SNa^+$: 961.4639, found: 961.4645.

Mosher-Ester Analysis. (*R*)-Mosher acid chloride (3.6 µL, 19 µmol) was added to a stirred solution of alcohol **19** (6 mg, 6 µmol) and pyridine (2.6 µL, 32 µmol) in CH_2Cl_2 (200 µL) and the resulting mixture was stirred for 4 h at ambient temperature. After that time, additional pyridine (2.6 µL, 32 µmol) and (*R*)-Mosher acid chloride (3.6 µL, 19 µmol) were added and stirring was continued for 3 d. The reaction was quenched with water (2 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 3 mL). The combined extracts were dried over Na_2SO_4, the drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 7:1) to give the title compound as a colorless oil (7 mg, 95%). $[\alpha]_D^{20}$ = +0.9 (c = 0.71, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72



– 7.34 (m, 10H, Ph), 5.88 (dd, *J* = 14.5, 6.0 Hz, 1H, H-11), 5.66 (ddd, *J* = 12.2, 8.1, 1.2 Hz, 1H, H-10), 5.62 (ddd, *J* = 14.5, 8.0, 4.0 Hz, 1H, H-9), 4.39 (dt, *J* = 9.4, 6.1 Hz, 1H, H-12), 4.32 (ddd, *J* = 9.1, 5.7, 3.7 Hz, 1H, H-3), 3.93 (ddd, *J* = 14.6, 11.1, 4.7 Hz, 1H, H-17a), 3.83 – 3.72 (m, 3H, H-17b & H-7 & H-5), 3.70 (s, 3H, H-19), 3.55 (td, *J* = 8.7, 3.0 Hz, 1H, H-15), 3.53 (s, 3H, H-23), 3.51 – 3.49 (m, 1H, H-4), 3.43 – 3.39 (m, 1H, H-6), 2.78 (dd, *J* = 15.1, 5.7 Hz, 1H, H-2a), 2.57 (dd, *J* = 15.1, 8.6 Hz, 1H, H-2b), 2.29 (ddd, *J* = 13.7, 8.1, 3.1 Hz, 1H, H-16a), 2.28 – 2.22 (m, 1H, H-8a), 2.23 (dd, *J* = 12.5, 6.2 Hz, 1H, H-13a), 2.01 (dddd, *J* = 12.2, 9.7, 7.8, 4.1 Hz, 1H, H-16b), 1.94 (ddt, *J* = 10.5, 8.5, 6.9 Hz, 1H, H-14), 1.47 (ddd, *J* = 13.5, 9.9, 2.5 Hz, 1H, H-8b), 1.36 (ddd, *J* = 12.4, 10.6, 9.4 Hz, 1H, H-13b), 1.03 (d, *J* = 6.6 Hz, 3H, H-33), 0.89 (s, 9H, *t*-Bu), 0.88 (s, 9H, *t*-Bu), 0.86 (s, 9H, *t*-Bu), 0.09 (s, 6H, Si-Me), 0.08 (s, 3H, Si-Me), 0.07 (s, 3H, Si-Me), 0.06 (s, 3H, Si-Me), 0.01 (3H, Si-Me) ppm; ^{13}C NMR (101 MHz, $CDCl_3$):[5] δ = 171.9, 165.3, 153.6, 137.4, 133.2, 132.6, 131.6, 129.9 (2C), 129.6, 128.5 (2C), 127.7 (2C), 126.8, 125.3 (2C), 83.0, 78.1, 75.0, 74.2, 73.74, 73.65, 72.2, 65.9, 55.4, 53.8, 51.9, 42.0, 40.2, 37.4, 36.3, 26.8, 26.3 (3C), 26.1 (3C), 25.9 (3C), 18.5, 18.3, 18.0, 16.4, -3.5, -4.0, -4.3, -4.52, -4.53, -5.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.6 ppm (3F) ; IR (film): $\tilde{\nu}$ = 2954, 2929, 2896, 2857, 1743, 1596, 1498, 1463, 1439, 1390, 1346, 1254, 1167, 1121, 1082, 1015, 938, 917, 897, 833, 813, 774, 761, 720, 696, 668, 636, 524, 506, 466 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{54}H_{85}N_4O_{12}F_3Si_3SNa^+$: 1177.5037, found: 1177.5047.

Diastereomeric Mosher Ester. Prepared analogously from **19** and (*S*)-Mosher acid chloride as a colorless oil (7 mg, 95%). $[\alpha]_D^{20}$ = +33.9 (c = 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.35 (m, 10H, Ph), 5.77 (dd, *J* = 15.1, 6.1 Hz, 1H, H-11), 5.61 (ddd, *J* = 9.8, 7.7, 4.2 Hz, 1H, H-9), 5.54 (ddd, *J* = 15.1, 7.7, 1.2 Hz, 1H, H-10), 4.39 – 4.30 (m, 2H, H-12 & H-3), 3.91 (ddd, *J* = 14.7, 11.3, 4.7 Hz, 1H, H-17a), 3.81 (dt, *J* = 11.4, 2.8 Hz, 1H, H-7), 3.79 – 3.76 (m, 1H, H-5), 3.74 (ddd, *J* = 14.8, 9.8, 4.9 Hz, 1H, H-17b), 3.69 (s, 3H, H-19), 3.57 (s, 3H, H-23), 3.53 – 3.50 (m, 1H, H-4), 3.50 (dd, *J* = 9.2, 3.0 Hz, 1H, H-15), 3.45 – 3.41 (m, 1H, H-6), 2.75 (dd, *J* = 15.1, 5.6 Hz, 1H, H-2a), 2.60 (dd, *J* = 15.1, 8.8 Hz, 1H, H-2b), 2.31 (ddd, *J* = 13.6, 10.6, 4.3 Hz, 1H, H-8a), 2.26 (ddd, *J* = 11.4, 8.7, 5.6 Hz, 1H, H-16a), 2.21 (dt, *J* = 12.5, 6.2 Hz, 1H, H-13a), 2.00 (dddd, *J* = 14.1, 11.7, 9.0, 5.0 Hz, 1H, H-16b), 1.92 (ddt, *J* = 10.5, 8.6, 6.0 Hz, 1H,

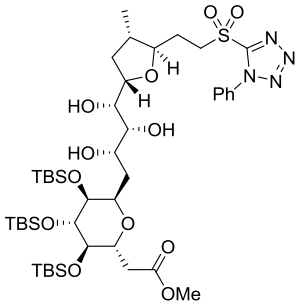


[5] The signals of the quarternary C-atoms C-21 and C-22 were not detected.

H-14), 1.52 (ddd, *J* = 13.6, 9.9, 2.4 Hz, 1H, H-8b), 1.32 (ddd, *J* = 12.3, 10.7, 9.5 Hz, 1H, H-13b), 1.04 (d, *J* = 6.6 Hz, 3H, H-33), 0.91 (s, 9H, *t*-Bu), 0.89 (s, 9H, *t*-Bu), 0.86 (s, 9H, *t*-Bu), 0.09 (s, 9H, Si-Me), 0.08 (s, 3H, Si-Me), 0.07 (s, 3H, Si-Me), 0.05 (s, 3H, Si-Me) ppm; ^{13}C NMR (101 MHz, $CDCl_3$):[5] δ = 171.9, 165.2, 153.6, 136.8, 133.2, 132.7, 131.6, 129.9 (2C), 129.6, 128.4 (2C), 127.6 (2C), 126.7, 125.3 (2C), 82.9, 78.1, 74.6, 74.2, 73.8, 73.6, 72.2, 66.1, 55.7, 53.8, 51.9, 42.0, 40.2, 37.3, 36.5, 26.7, 26.3 (3C), 26.1 (3C), 25.9 (3C), 18.5, 18.3, 18.0, 16.4, -3.4, -4.0, -4.3, -4.51, -4.54, -5.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -71.5 (3F) ppm; IR (film): $\tilde{\nu}$ = 2954, 2929, 2896, 2857, 1745, 1597, 1498, 1463, 1452, 1390, 1346, 1257, 1167, 1122, 1081, 1015, 992, 939, 917, 897, 833, 813, 775, 762, 720, 703, 635, 526, 506, 466, 445, 432 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{54}H_{85}N_4O_{12}F_3Si_3SNa^+$: 1177.5037, found: 1177.5046.

Compound 20. $(DHQD)_2AQN$ **23** (50 mM in *t*-BuOH, 160 µL, 8 µmol), an aqueous stock solution of $MeSO_2NH_2$ (0.1 M, 639 µL, 64 µmol), $K_3[Fe(CN)_6]$ (0.3 M, 192 µmol) and K_2CO_3 (0.3 M, 192 µmol) and aq. $K_2OsO_2(OH)_4$ (50 mM, 6.4 µmol, 128 µL) were subsequently added to a stirred solution of alcohol **19** (30 mg, 32 µmol) in *t*-BuOH (1.85 mL) and water (1.27 mL) at ambient temperature. After stirring for 21 h, the mixture was diluted with EtOAc (2.5 mL) and water (2.5 mL) and the reaction was quenched with aq. $NaHSO_3$ (2.5 M, 153 µL). The aqueous phase was extracted with EtOAc (8 x 2.5 mL) and the combined extracts were dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 3:1 to 1:1) to give triol **20** (15 mg, 48%) and an isomeric triol **S-12** (4 mg, 11%) as a colorless oil each.

Analytical and spectral data of triol **20**: $[\alpha]_D^{20}$ = +16.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.57 (m, 5H), 4.32 (dt, *J* = 10.1, 4.1 Hz, 1H), 4.16 (dt, *J* = 9.6, 5.9 Hz, 1H), 4.12 (dt, *J* = 10.9, 2.1 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.91 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.86 – 3.84 (m, 1H), 3.83 (ddd, *J* = 14.8, 10.6, 5.4 Hz, 1H), 3.79 – 3.76 (m, 1H), 3.69 (s, 3H), 3.66 – 3.62 (m, 1H), 3.60 (td, *J* = 8.7, 3.0 Hz, 1H), 3.50 – 3.42 (m, 3H), 3.29 (d, *J* = 3.4 Hz, 1H), 3.05 (d, *J* = 6.5 Hz, 1H), 2.85 (dd, *J* = 15.0, 10.2 Hz, 1H), 2.63 (dd, *J* = 15.0, 4.4 Hz, 1H), 2.30 (tdd, *J* = 10.8, 5.2, 3.1 Hz, 1H), 2.24 – 2.12 (m, 2H), 2.02 (dddd, *J* = 13.2, 10.4, 8.1, 4.9 Hz, 1H), 1.94 (dtd, *J* = 10.4, 8.8, 6.6 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.42 (dt, *J* = 14.4, 2.3 Hz, 1H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H), 0.90 (s, 18H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 6H), 0.08 (s, 6H) ppm;



^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 153.6, 133.2, 131.6, 129.9 (2C), 125.3 (2C), 83.1, 80.2, 74.9, 74.1, 74.0, 73.7, 73.6, 73.4, 72.3, 69.6, 53.6, 52.0, 39.8, 37.14, 37.11, 34.5, 26.5, 26.3 (3C), 26.2 (3C), 25.9 (3C), 18.5, 18.4, 18.0, 16.1, -3.6, -3.9, -4.2, -4.5, -4.6, -4.8 ppm; IR (film): $\tilde{\nu}$ = 3480, 2954, 2930, 2893, 2858, 1737, 1597, 1499, 1463, 1438, 1389, 1339, 1256, 1150, 1130, 1087, 1044, 1006, 916, 834, 813, 775, 689, 667, 632, 529, 507, 452, 420 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{80}N_4O_{12}Si_3SNa^+$: 995.4694, found: 995.4700.

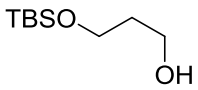
Analytical and spectral data of the isomeric triol **S-12** (the sample contained traces of $(DHQD)_2AQN$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.54 (m, 5H), 4.34 (dt, *J* = 9.7, 4.1 Hz, 1H), 4.21 – 4.09 (m, 2H), 4.08 – 3.97 (m, 2H), 3.96 – 3.85 (m, 1H), 3.83 – 3.74 (m, 2H), 3.72 – 3.68 (m, 1H), 3.69 (s, 3H), 3.62 (s, 1H), 3.59 – 3.51 (m, 2H), 3.50 – 3.44 (m, 3H), 2.88 (dd, *J* = 15.0, 10.2, 4.8 Hz, 1H), 3.63 (dd, *J* = 15.0, 4.3 Hz, 1H), 2.40 – 2.13 (m, 3H), 2.07 – 1.84 (m, 2H), 1.63 – 1.49 (m, 1H), 1.47 – 1.36 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.93 (s, 9H), 0.89 (s, 18H), 0.11 (s, 3H), 0.105 (s, 3H), 0.095 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.075 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 153.7, 133.2, 131.6, 129.9 (2C), 125.3 (2C), 83.2, 78.9, 75.3, 74.2 (2C), 73.9, 73.5, 73.2, 72.2, 70.4, 53.9, 52.0, 39.9, 38.4, 37.1, 34.8, 26.3 (3C), 26.2 (3C), 25.93, 25.90 (3C), 18.5, 18.4, 18.0, 16.5, -3.6, -3.9, -4.1, -4.5, -4.56, -4.59 ppm; IR (film): $\tilde{\nu}$ = 3433, 2953, 2929, 2894, 2857, 1736, 1598, 1501, 1462, 1438, 1388, 1345, 1256, 1149, 1128, 1083, 1043, 1006, 964, 938, 917, 833, 813, 775, 737, 689, 673, 634, 567, 536, 506, 466 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{80}N_4O_{12}Si_3SNa^+$: 995.4694, found: 995.4700.

Compound 21. TESOTf (293 µL, 1.29 mmol) was added to a stirred solution of triol **20** (280 mg, 288 µmol) and 2,6-lutidine (201 µL, 1.73 mmol) in CH_2Cl_2 (11 mL) at 0 °C and stirring was continued for 1 h. The mixture was diluted with *tert*-butyl methyl ether (25 mL) and the reaction was quenched with aq. phosphate buffer (200 mM, pH 7, 25 mL). The organic extract was washed with water (10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 30:1), affording the title compound as a colorless oil (310 mg, 82%). $[\alpha]_D^{20}$ = +24.3 (c = 0.98,

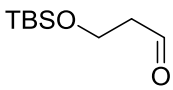
$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 – 7.67 (m, 2H), 7.65 – 7.57 (m, 3H), 4.22 – 4.13 (m, 2H), 4.06 (ddd, *J* = 9.8, 7.8, 5.5 Hz, 1H), 3.95 (ddd, *J* = 14.5, 11.6, 4.8 Hz, 1H), 3.85 – 3.74 (m, 3H), 3.68 – 3.63 (m, 1H), 3.65 (s, 3H), 3.63 – 3.60 (m, 1H), 3.60 – 3.57 (m, 1H), 3.45 (td, *J* = 8.5, 3.1 Hz, 1H), 3.38 – 3.34 (m, 1H), 3.23 (dd, *J* = 15.4, 9.5 Hz, 1H), 2.41 (dd, *J* = 15.4, 4.1 Hz, 1H), 2.31 – 2.16 (m, 2H), 2.05 – 1.96 (m, 1H), 1.92 (ddd, *J* = 14.8, 10.7, 1.8 Hz, 1H), 1.83 (ddt, *J* = 11.1, 8.7, 6.5 Hz, 1H), 1.51 (dd, *J* = 14.5, 8.4 Hz, 1H), 1.45 – 1.33 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.99 (s, 3H), 0.97 (s, 6H), 0.955 (s, 3H), 0.95 (s, 6H), 0.935 (s, 6H), 0.93 (s, 9H), 0.91 (s, 3H), 0.895 (s, 9H), 0.89 (s, 9H), 0.67 – 0.54 (m, 18H), 0.10 (s, 6H), 0.09 (s, 3H), 0.07 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 153.7, 133.3, 131.6, 129.8 (2C), 125.3 (2C), 81.9, 81.1, 77.0, 75.4, 74.5, 73.6, 73.1, 71.8, 69.8, 65.5, 53.9, 51.5, 40.0, 38.0, 36.9, 36.2, 26.5, 26.30 (3C), 26.27 (3C), 25.8 (3C), 18.36, 18.35, 18.0, 16.3, 7.3 (3C), 7.2 (6C), 5.7 (6C), 5.5 (3C), -3.3, -3.6, -4.3, -4.6, -4.8 (2C) ppm; IR (film): $\tilde{\nu}$ = 2953, 2931, 2910, 2877, 2858, 1740, 1597, 1499, 1462, 1437, 1414, 1389, 1345, 1252, 1149, 1126, 1078, 1044, 1005, 972, 919, 899, 872, 833, 813, 774, 760, 738, 726, 687, 673, 636, 536, 507, 465, 434 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{62}H_{122}N_4O_{12}Si_6SNa^+$: 1337.7288, found: 1337.7290.

Macrocycle: Preparation of the Building Blocks

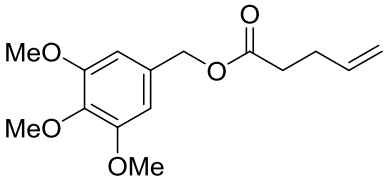
3-((*tert*-Butyldimethylsilyl)oxy)propan-1-ol (28). A solution of *tert*-butyldimethylsilyl chloride



(48.9 g, 324 mmol) in CH_2Cl_2 (150 mL) was added to a stirred solution of 1,3-propanediol (49.0 mL, 678 mmol) and triethylamine (50.0 mL, 359 mmol) in CH_2Cl_2 (500 mL) at 0 °C. The mixture was stirred at room temperature for 23 h before the reaction was quenched with saturated aqueous $NaHCO_3$ solution (150 mL). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 80 mL). The combined organic layers were washed with water (150 mL) and saturated aqueous NaCl solution (150 mL), dried over sodium sulfate, and concentrated under reduced pressure. The red crude material was distilled *in vacuo*. The pure product was collected (after a small forerun) at 93 - 95 °C / 10 - 12 mbar as colorless oil (53.5g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (t, *J* = 5.6 Hz, 2H), 3.82 – 3.76 (m, 2H), 2.57 (brs, 1H), 1.78 (tt, *J* = 6.1, 5.2 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.1, 62.7, 34.3, 26.0, 18.3, −5.3. IR (film): $\tilde{\nu}$ = 2953, 2929, 2857, 1472, 1389, 1361, 1254, 1081, 1006, 960, 939, 832, 773, 721, 662, 512 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_9H_{22}O_2SiNa$ [M+Na^+]: 213.12813, found 213.12814.

3-((*tert*-Butyldimethylsilyl)oxy)propanal (29). 2,2′-Bipyridyl (715 mg, 4.58 mmol, 4.5 mol%), 

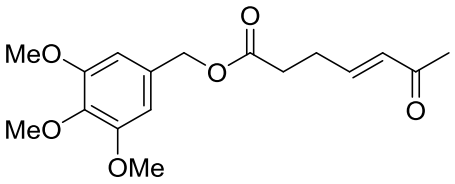
$[Cu(MeCN)_4]BF_4$ (1.44 g, 4.58 mmol, 4.5 mol%), TEMPO (716 mg, 4.58 mmol, 4.5 mol%) and N-methylimidazole (0.73 mL, 9.1 mmol, 9 mol%) were added to a stirred solution of compound **28** (19.2 g, 101 mmol) in MeCN (500 mL). The resulting reddish-brown solution was stirred vigorously under O_2 atmosphere for 3 h; at this point, the mixture had turned blue. The mixture was diluted with water (500 mL) and extracted with pentane (7 x 100 mL). The combined organic layers were dried over sodium sulfate and carefully concentrated under reduced pressure. The crude aldehyde was obtained as a reddish liquid (20 g, 99 %), which was ≈94% pure [^{1}H NMR] and used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 2.1 Hz, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 2.60 (td, *J* = 6.0, 2.1 Hz, 2H), 0.88 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 57.5, 46.6, 25.9, 18.3, -5.3. IR (film): $\tilde{\nu}$ = 2955, 2930, 2886, 2857, 2728, 1727, 1472, 1389, 1362, 1254, 1212, 1094, 1006, 970, 939, 832, 775, 680, 568, 529 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_9H_{21}O_2Si$ [M+H$^+$]: 189.13053, found 189.13024.

3,4,5-Trimethoxybenzyl pent-4-enoate (25). Oxalyl chloride (2.8 mL, 33 mmol) was added 

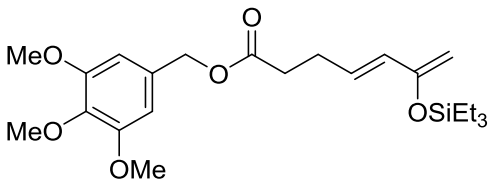
slowly to 4-pentenoic acid (3.2 mL, 31 mmol) at 0 °C. The orange-brown mixture was vigorously stirred and was allowed to reach room temperature. After 4 h the evolution of gas had ceased, the turbid crude acid chloride was dissolved in CH_2Cl_2 (30 mL) and the resulting solution was cooled to 0 °C. 4-(Dimethylamino)pyridine (37 mg, 0.3 mmol), potassium carbonate (6.22 g, 45 mmol) and 3,4,5-trimethoxybenzyl alcohol (4.8 mL, 30 mmol) were added and stirring continued at room temperature for 18 h. Triethylamine (1.0 mL, 7.2 mmol) was added and the mixture was stirred for another 1 h. The reaction was quenched with water (30 mL), the layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 30 mL), the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 4:1) yielded the product as a colorless oil (7.58 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 5.83 (ddt, *J* = 17.1, 10.2, 6.2 Hz, 1H), 5.18 – 4.90 (m, 4H), 3.87 (s, 6H), 3.84 (s, 3H), 2.50 – 2.45 (m, 2H), 2.44 – 2.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 153.5, 138.1, 136.7, 131.7, 115.7, 105.6, 66.6, 61.0, 56.3, 33.7, 29.0, 14.4. IR (film): $\tilde{\nu}$ = 3078, 2940, 2839, 1732, 1641, 1591, 1507, 1459, 1421, 1378, 1331,1235, 1154, 1123,1044, 1004, 960, 915, 824, 781,

696, 639, 583, 527 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{15}H_{20}O_5Na$ [M+Na^+]: 303.12029, found: 303.12025.

3,4,5-Trimethoxybenzyl (*E*)-6-oxohept-4-enoate (26). Hoveyda-Grubbs II catalyst (44 mg, 70 µmol, 0.1 mol%) was added to a stirred solution of 3-buten-2-one (14.0 mL, 173 mmol) and compound **25** (19.3 g, 68.8 mmol) in CH_2Cl_2, (500 mL). The green mixture was stirred at reflux temperature for 4 h, cooled to room temperature and concentrated under reduced pressure. Purification of the dark residue by flash chromatography (hexane/EtOAc = 3:2 → 1:1) yielded the product as a pale yellow oil (22.2 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.74 (m, 1H), 6.58 (s, 2H), 6.10 (dt, *J* = 15.9, 1.4 Hz, 1H), 5.05 (s, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 2.62 – 2.53 (m, 4H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 172.2, 153.5, 145.5, 138.3, 132.0, 131.3, 105.8, 67.0, 61.0, 56.3, 32.6, 27.5, 27.2. IR (film): $\tilde{\nu}$ = 2998, 2942, 2840, 1732, 1697, 1673, 1628, 1592, 1507, 1460, 1422, 1360, 1332, 1237, 1154, 1125,1044, 1006, 976, 828, 781, 693, 610, 585, 528 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{17}H_{22}O_6Na$ [M+Na^+]: 345.13086, found: 345.13094.

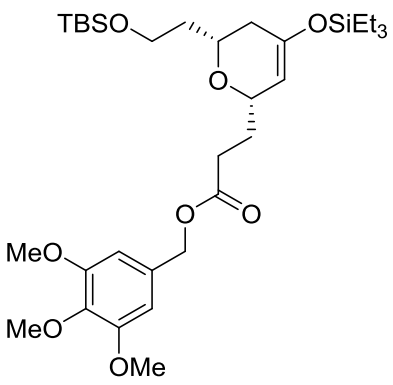


3,4,5-Trimethoxybenzyl (*E*)-6-((triethylsilyl)oxy)hepta-4,6-dienoate (27). Triethylsilyl trifluoromethanesulfonate (11.5 mL, 51.1 mmol) was added dropwise to a stirred solution of compound **26** (14.0 g, 43.4 mmol) and triethylamine (12.0 mL, 86.1 mmol) in Et_2O (150 mL) at 0 °C. The slightly turbid mixture was stirred at 0 °C for 1.5 h before it was poured into saturated aqueous $NaHCO_3$ solution (150 mL). The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 100 mL), the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 5:1 + 0.5% triethylamine) yielded the product as a pale yellow oil (16.9 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 6.10 – 5.83 (m, 2H), 5.04 (s, 2H), 4.24 (d, *J* = 0.7 Hz, 1H), 4.20 (d, *J* = 0.8 Hz, 1H), 3.86 (s, 6H), 3.84 (s, 3H), 2.52 – 2.40 (m, 4H), 1.02 – 0.94 (m, 9H), 0.71 (td, *J* = 8.0, 0.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 154.8, 153.5, 138.1, 131.7, 129.1, 129.0, 105.6, 94.5, 66.7, 61.0, 56.3, 34.0, 27.4, 6.9, 5.1. IR (film): $\tilde{\nu}$ = 2955, 2913, 2877, 2839, 1734, 1655, 1591, 15081459, 1421, 1378, 1330, 1236, 1151, 1126, 1005, 962,



921, 822, 781, 730, 585, 527, 463 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{23}H_{36}O_6SiNa$ [M+Na^+]: 459.21734, found 459.21754.

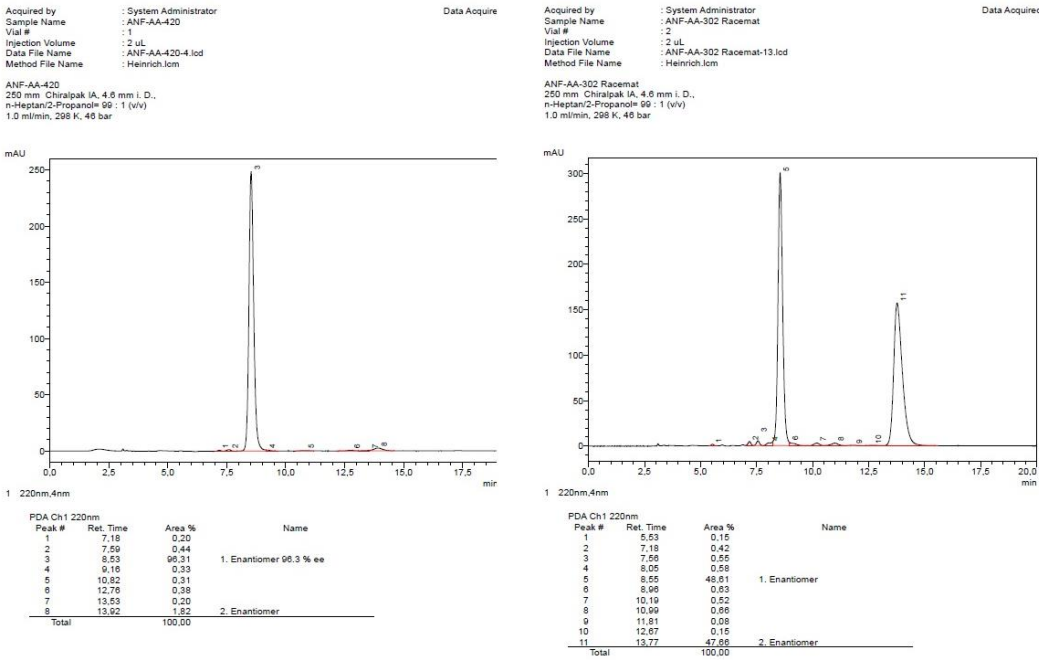
3,4,5-Trimethoxybenzyl 3-((2*S*,6*R*)-6-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-((triethylsilyl)-oxy)-5,6-dihydro-2*H*-pyran-2-yl)propanoate (30). Aldehyde **29** (1.96 g, 10.1 mmol) and diene



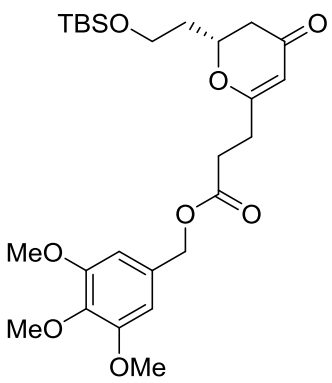
27 (2.32 g, 5.32 mmol) were added to a mixture of the chromium complex **35** (262 mg, 0.5 mmol, 9 mol%)[6] and powdered molecular sieves (4 Å, 1.08 g). The resulting thick brown suspension was stirred at room temperature for 72 h. A second portion of aldehyde **29** (1.86 g, 9.58 mmol) was introduced and stirring continued for a total of 144 h. The mixture was diluted with hexane:EtOAc (4:1, 10 mL) and filtered through a pad of silica, which was carefully rinsed with hexane:EtOAc 4:1 (90 mL in total); the combined filtrates were concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 6:1 + 1% triethylamine) yielded the product as a yellow oil (2.51 g, 76% yield). $[\alpha]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = −32.6 (c = 0.98, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 6.52 (s, 2H), 5.06 (s, 2H), 4.76 (t, *J* = 1.6 Hz, 1H), 4.31 – 4.10 (m, 1H), 3.82 (s, 3H), 3.77 (ddt, *J* = 10.0, 8.3, 4.4 Hz, 2H), 3.64 (dt, *J* = 10.3, 5.4 Hz, 1H), 3.39 (s, 6H), 2.71 – 2.52 (m, 2H), 2.19 – 1.99 (m, 2H), 1.98 – 1.87 (m, 2H), 1.79 – 1.59 (m, 2H), 0.99 (t, *J* = 8.1 Hz, 9H), 0.97 (s, 9H), 0.68 – 0.61 (t, *J* = 8.1 Hz 6H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 173.2, 154.2, 150.1, 139.5, 132.1, 106.6, 105.5, 73.3, 71.1, 66.6, 60.5, 59.5, 55.8, 39.4, 36.9, 32.1, 30.3, 26.2, 18.5, 7.0, 5.5, −5.17, −5.23. IR (film): $\tilde{\nu}$ = 2954, 2934, 2878, 2856, 1736, 1668, 1592, 1508, 1461, 1421, 1382, 1360, 1332, 1238, 1198, 1156, 1127, 1094, 1006, 960, 903, 834, 775, 744, 729, 665, 581, 527 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{32}H_{56}O_8Si_2Na$ [M+Na^+]: 647.34060, found 647.34120.

[6] D. E. Chavez, E. N. Jacobsen, *Org. Synth*. **2005**, *82*, 34-42.

HPLC chromatogram on chiral column: [250 mm Chiralpak IA, 4.6 mm i. d., *n*-heptane/2-propanol = 99 : 1 (v/v),1.0 ml/min, 298 K, 46 bar, 95% ee, (t_R(major) = 8.5 min, t_R(minor) = 13.9 min)]



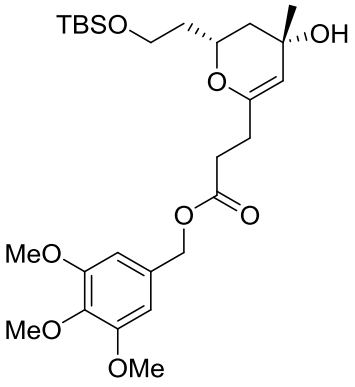
3,4,5-Trimethoxybenzyl (*R*)-3-(2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-oxo-3,4-dihydro-2*H*-pyran-6-yl)propanoate (31).



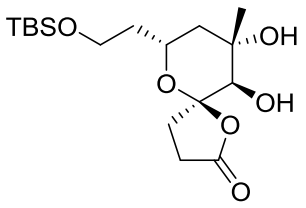
Palladium(II) acetate (174 mg, 0.775 mmol, 10 mol%) was added to a stirred solution of compound **30** (4.75 g, 7.6 mmol) in DMSO (8 mL) and the resulting orange mixture was stirred vigorously under O_2 atmosphere for 48 h. The mixture was diluted with Et_2O (50 mL) and poured onto water (100 mL). The layers were separated and the aqueous phase was extracted with Et_2O (7 x 50 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 3:1 → 1:1 + 1% triethylamine) yielded the product as a pale yellow oil (3.02 g, 78%). $[\alpha]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +58.1 (c = 1.08, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 6.51 (s, 2H), 5.32 (d, *J* = 0.8 Hz, 1H), 4.98 (s, 2H), 4.29 – 4.20 (m, 1H), 3.82 (s, 3H), 3.55 – 3.40 (m, 2H), 3.43 (s, 6H), 2.25 (s, 4H), 2.21 – 2.03 (m, 2H), 1.63 (ddt, *J* = 14.1, 8.0, 5.2 Hz, 1H), 1.43 (dddd, *J* = 14.0, 8.0, 5.9, 4.8 Hz, 1H), 0.92 (s, 9H), 0.004 (s, 3H), −0.002 (s,

3H). ^{13}C NMR (101 MHz, C_6D_6) δ 190.7, 173.4, 171.4, 154.3, 139.8, 131.5, 106.9, 104.8, 76.6, 67.1, 60.5, 58.8, 56.0, 41.5, 37.5, 30.9, 29.8, 26.1, 18.4, −5.29, −5.34. IR (film): $\tilde{\nu}$ = 2953, 2930, 2886, 2856, 1735, 1666, 1607, 1593, 1508, 1462, 1422, 1398, 1386, 1332, 1292, 1237, 1154, 1126, 1089, 1045, 1005, 963, 887, 864, 834, 809, 776, 733, 693, 684, 665, 606, 583, 548, 527, 504, 470, 455, 439, 432 527 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{26}H_{40}O_8SiNa$ [M+Na$^+$]: 531.23847, found: 531.23863.

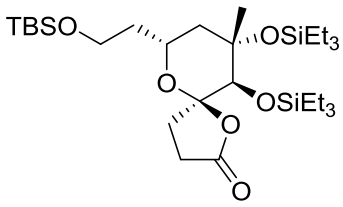
3,4,5-Trimethoxybenzyl 3-((2*R*,4*S*)-2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-hydroxy-4-methyl-3,4-dihydro-2*H*-pyran-6-yl)propanoate (32). Methylmagnesium chloride (6.4 mL, 3 M in THF, 19.2 mmol) was added to a solution of compound **31** (1.64 g, 3.22 mmol) in THF (32 mL) at – 65 °C. After stirring at this temperature for 6 h, the reaction was carefully quenched with aqueous phosphate buffer (10 mL, pH 7, 0.1 M) and the mixture was diluted with *tert*-butyl methyl ether (50 mL). The resulting slurry was warmed to room temperature, the precipitate was allowed to settle and the supernatant solution was decanted. The grey residue was extracted with *tert*-butyl methyl ether (3 x 50 mL), and the combined organic layers were washed with brine (50 mL). The brine layer was back extracted with *tert*-butyl methyl ether (50 mL). The combined organic phases were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 3:2 + 1% triethylamine) yielded the product as a colorless oil (1.30 g, 77%). $[\alpha]_D^{20}$ = +3.5 (c = 1.07, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6) δ 6.53 (s, 2H), 5.04 (d, *J* = 0.7 Hz, 2H), 4.49 – 4.47 (m, 1H), 4.03 (dddd, *J* = 11.2, 8.0, 4.7, 2.3 Hz, 1H), 3.82 (s, 3H), 3.70 (ddd, *J* = 10.1, 8.0, 5.2 Hz, 1H), 3.63 (dt, *J* = 10.1, 5.7 Hz, 1H), 3.41 (s, 6H), 2.53 – 2.43 (m, 2H), 2.40 (ddt, *J* = 7.4, 6.7, 0.7 Hz, 2H), 1.82 (ddt, *J* = 13.5, 8.1, 5.3 Hz, 1H), 1.70 (ddd, *J* = 13.2, 2.3, 1.7 Hz, 1H), 1.65 (dddd, *J* = 12.6, 8.0, 5.9, 4.7 Hz, 1H), 1.59 – 1.54 (m, 1H), 1.25 (s, Hz, 3H), 0.96 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (151 MHz, C_6D_6) δ 172.3, 154.3, 152.8, 139.6, 131.9, 106.8, 105.8, 72.4, 66.8, 66.7, 60.5, 59.5, 55.9, 44.1, 38.5, 32.2, 30.7, 29.7, 26.1, 18.5, −5.2, −5.3. IR (film): $\tilde{\nu}$ = 3501, 3478, 3444, 2953, 2929, 2884, 2856, 1735, 1671, 1592, 1508, 1461, 1422, 1379, 1360, 1332, 1289, 1237, 1152, 1126, 1098, 1005, 947, 891, 834, 775, 734, 664, 581, 527, 432 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{27}H_{44}O_8SiNa$ [M+Na$^+$]: 547.26977, found: 547.27013.



(5*R*,7*R*,9*S*,10*R*)-7-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-9,10-dihydroxy-9-methyl-1,6-dioxaspiro[4.5]decan-2-one (S-13). A solution of potassium hexacyanoferrate(III) (2.9 g, 8.8 mmol), potassium carbonate (1.22 g, 8.83 mmol), methanesulfonamide (0.56 g, 5.9 mmol), potassium osmate (VI) dihydrate (33 mg, 0.088 mmol, 3mol%) and $(DHQD)_2PHAL$ (172 mg, 0.221 mmol, 7.5 mol%) in water (15 mL) and *tert*-butanol (2 mL) was added to a solution of compound **32** (1.75 g, 2.93 mmol) in *tert*-butanol (15 mL) at room temperature. After stirring for 3 h, the mixture was diluted with EtOAc (10 mL) and the reaction was carefully quenched with $NaHSO_3$ (3.7 g, 36 mmol) in small portions. When the frothing had subsided, the layers were separated and the deep blue aqueous layer was extracted with EtOAc (10 x 20 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/*tert*-butyl methyl ether = 1:9 → pure *tert*-butyl methyl ether) yielded the product as a colorless oil (0.86 g, 81%). $[\alpha]_D^{20}$ = +50.5 (c = 0.98, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 4.06 (dddd, *J* = 12.1, 7.9, 4.6, 2.2 Hz, 1H), 3.64 – 3.52 (m, 2H), 3.32 (s, 1H), 2.26 – 2.01 (m, 4H), 1.80 (brs, 1H), 1.70 – 1.47 (m, 5H), 1.28 (d, *J* = 0.8 Hz, 3H), 0.99 (s, 9H), 0.66 (brs, ½ H_2O, 1H),[7] 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 175.7, 108.2, 78.4, 71.4, 68.1, 59.2, 45.2, 38.8, 31.7, 27.9, 26.1, 21.6, 18.5, −5.2, −5.3. IR (film): $\tilde{\nu}$ = 3428, 2952, 2929, 2857, 1765, 1472, 1388, 1360, 1335, 1252, 1204, 1126, 1088, 1021, 994, 964, 906, 874, 834, 809, 774, 733, 649, 604, 563, 526,497, 439 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{17}H_{32}O_6SiNa$ [M+Na$^+$]: 383.18604, found: 383.18573.



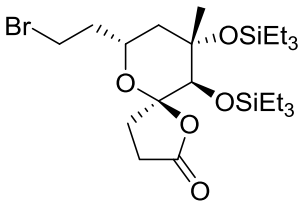
(5*R*,7*R*,9*S*,10*R*)-7-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-9-methyl-9,10-bis((triethylsilyl)-oxy)-1,6-dioxaspiro[4.5]decan-2-one (33). Chlorotriethylsilane (0.8 mL, 4.8 mmol) was added to a solution of compound **S-13** (362 mg, 1.0 mmol), 4-(dimethylamino)pyridine (248 mg, 2.0 mmol) and silver nitrate (692 mg, 4.1 mmol) in DMF (5 mL) and pyridine (5 mL) at room temperature, causing the precipitation of a colorless solid. After stirring for 3.5 h, the mixture was diluted with *tert*-butyl methyl ether (10 mL) and filtered through a pad of silica, which was carefully rinsed with *tert*-butyl methyl ether (5 x10 mL). The



[7] The water signal shows cross peaks in the 2D NMR spectra to signals of the sample; it could not be removed by aceotropic distillation and drying of the sample in high vacuum. Therefore it is believed that the water molecule is tightly bound to the compound via H-bonds.

slightly turbid combined filtrates were washed with brine (60 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 40 mL) and the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 25:1) yielded the product as a colorless solid (450 mg, 76%). Mp = 50 – 52 °C. $[\alpha]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +50.3 (c = 0.37, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 4.17 (dddd, *J* = 12.0, 7.7, 4.5, 1.9 Hz, 1H), 3.73 – 3.64 (m, 2H), 3.63 (s, 1H), 2.35 – 2.10 (m, 3H), 1.90 – 1.64 (m, 5H), 1.53 (s, Hz, 3H), 1.01 (s, 9H), 1.01 – 0.96 (m, 18H), 0.73 – 0.65 (m, 6H), 0.61 (q, *J* = 7.7 Hz, 6H), 0.13 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 174.5, 108.3, 80.7, 75.9, 67.7, 59.5, 46.9, 39.0, 32.4, 27.9, 26.1, 22.7, 18.6, 7.4, 7.3, 7.2, 5.6, −5.2, −5.3. IR (film): $\tilde{\nu}$ = 2954, 2936, 2877, 1791, 1461, 1417, 1384, 1361, 1337, 1240, 1203, 1142, 1127, 1099, 1005, 970, 915, 884, 839, 777, 741, 672 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{29}H_{60}O_6Si_3Na$ [M+Na$^+$]: 611.35810, found: 611.35935.

(5*R*,7*S*,9*S*,10*R*)-7-(2-Bromoethyl)-9-methyl-9,10-bis((triethylsilyl)oxy)-1,6-dioxaspiro[4.5]-decan-2-one (34). Bromine (100 µL, 1.95 mmol) was added to a solution of triphenylphosphine



(568 mg, 2.16 mmol) in CH_2Cl_2 (22 mL) at 0 °C. The mixture was stirred for 10 min at 0 °C and for another 15 min at ambient temperature. The resulting solution was added to a solution of compound **33** (1.02 g, 1.73 mmol) in CH_2Cl_2 (11 mL) at 0 °C over the course of 5 min. After stirring at 0 °C for 6 h, the mixture was slowly added to a well stirred mixture of CH_2Cl_2 (20 mL) and saturated aqueous $NaHCO_3$ solution (20 mL) at 0 °C. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (4 x 20 mL) and the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 100:5 → 100:6) yielded the product as a colorless oil (828 mg, 89%). $[\alpha]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = + 54.0 (c = 0.45, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 3.76 (dddd, *J* = 11.0, 8.9, 3.6, 2.1 Hz, 1H), 3.53 (s, 1H), 3.12 (ddd, *J* = 9.9, 8.7, 5.1 Hz, 1H), 3.00 (ddd, *J* = 9.9, 8.2, 7.4 Hz, 1H), 2.26 – 2.04 (m, 3H), 1.77 – 1.49 (m, 5H), 1.46 (s, 3H), 0.98 (m, Hz, 18H), 0.67 (qd, *J* = 7.9, 3.8 Hz, 6H), 0.62 – 0.55 (m, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 174.0, 107.5, 79.9, 75.3, 68.6, 45.8, 38.4, 31.7, 28.2, 27.3, 22.3, 7.0, 6.9, 6.8, 5.2. IR (film): $\tilde{\nu}$ = 2954, 2912, 2877, 1789, 1459, 1417, 1384, 1340, 1266, 1236, 1203, 1139, 1114, 1019, 1005, 977, 918, 880, 841, 741, 727, 674 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{23}H_{45}O_5BrSi_2Na$ [M+Na$^+$]: 559.18813, found: 559.18807.

(*S*)-2-(((4-Methoxybenzyl)oxy)methyl)oxirane (39). 4-Methoxybenzyl chloride (5.0 mL, 37 mmol) was slowly added to a suspension of sodium hydride (1.15 g, 47.9 mmol) in DMF (60 mL) at 0 °C. After 10 min (*R*)-glycidol (2.3 mL, 35 mmol) was added dropwise and the mixture was allowed to reach room temperature. After stirring for 18 h the mixture was carefully poured into saturated aqueous NH_4Cl solution (60 mL) and the resulting mixture was extracted with *tert*-butyl methyl ether (4 x 60 mL). The organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/*tert*-butyl methyl ether = 7:3) yielded the product as a colorless oil (5.84 g, 87%). $[\alpha]_D^{20}$ = −5.2 (c = 1.10, $CHCl_3$). ^{1}H NMR (400 MHz, CDCl3): δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 3.81 (s, 3H), 3.73 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.42 (dd, *J* = 11.4, 5.8 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.79 (dd, *J* = 5.0, 4.1 Hz, 1H), 2.61 (dd, *J* = 5.0, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 130.1, 129.6, 114.0, 73.1, 70.7, 55.4, 51.0, 44.5. IR (film): $\tilde{\nu}$ = 3051, 2998, 2934, 2912, 2860, 2837, 1613, 1586, 1513, 1464, 1302, 1248, 1175, 1091, 1034, 901, 822, 766, 583, 522 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{11}H_{14}O_3Na$ $[M+Na^+]$: 217.08351, found: 217.08334.

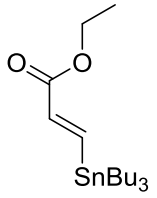
Dimethyl(phenyl)silyllithium. Chloro(dimethyl)phenylsilane (5.1 mL, 30 mmol) was added dropwise to a well stirred suspension of lithium sand (0.47 g, 68 mmol, containing 2% sodium) in THF (30 mL) at 0 °C. The mixture slowly turned red and finally brown. After stirring at 0 °C for 14 h, the brown mixture was filtered into a flame dried Schlenk flask and the filtrate was used directly in the next step.

Propyne Stock Solution. Propyne (1.0 mL, 0.66 g, 17 mmol) was condensed into a graduated Schlenk flask at −78 °C from a steel cylinder (ABCR, Karlsruhe). Pre-cooled THF was added to give a total volume of 17 mL. The resulting stock solution (1 M) was thoroughly mixed by moving a stir bar up and down with a magnet, taking care to keep it cold. The solution was stored at dry ice temperature.

(*S*,*Z*)-5-(Dimethyl(phenyl)silyl)-1-((4-methoxybenzyl)oxy)-4-methylpent-4-en-2-ol (37). Dimethyl(phenyl)silyllithium (28 mL, 1 M in THF, 28 mmol) was added to a well stirred suspension of copper(I) cyanide (1.25 g, 14 mmol) in THF (15 mL) at 0 °C. The intense reddish-brown mixture

was stirred at 0 °C for 30 min before being cooled to −78 °C. A cold (−78 °C) solution of propyne (14 mL, 1 M in THF, 14 mmol) was added quickly via cannula, and the resulting mixture was stirred at −78 °C for 4 h. A solution of epoxide **39** (1.75 g, 9.0 mmol) in THF (10 mL + 2 x10 mL to rinse) was added to the mixture, immediately followed by addition of boron trifluoride diethyl etherate (2.2 mL, 18 mmol). After 1 h triethylamine (4.0 mL, 30 mmol) and EtOH (5 mL) were added and the resulting dark mixture was allowed to reach room temperature. The mixture was concentrated under reduced pressure to give a tar-like residue, which was re-dissolved in *tert*-butyl methyl ether (50 mL). Silica (10 g) was added and the solvent was evaported. The loaded silica was added on top of a silica gel column and the product purified by flash chromatography (CH_2Cl_2:*tert*-butyl methyl ether = 99:1 → 98.5:1.5) to yield the title compound as a pale yellow oil (1.76 g, 51%). $[\alpha]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = −3.9 (c = 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, CDCl3): δ 7.58 – 7.50 (m, 2H), 7.34 – 7.31 (m, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.52 (t, *J* = 1.4 Hz, 1H), 4.39 (s, 2H), 3.89 (dddt, *J* = 8.6, 7.2, 4.9, 3.5 Hz, 1H), 3.81 (s, 3H), 3.25 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.09 (dd, *J* = 9.6, 7.3 Hz, 1H), 2.28 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.13 (dd, *J* = 13.6, 4.9 Hz, 1H), 1.98 (d, *J* = 3.7 Hz, 1H), 1.92 (d, *J* = 1.4 Hz, 3H), 0.38 (s, 3H), 0.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 153.5, 140.2, 134.0, 130.2, 129.5, 129.0, 128.0, 126.3, 114.0, 74.2, 73.1, 69.0, 55.4, 41.1, 27.1, −0.5, −0.7. IR (film): $\tilde{\nu}$ = 3568, 3453, 3067, 3046, 2998, 2952, 2907, 2860, 1613, 1513, 1427, 1370, 1302, 1247, 1174, 1110, 1036, 828, 731, 701, 646, 571, 474 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{30}O_3SiNa$ [M+Na$^+$]: 393.18564, found: 393.18585.

Ethyl (*E*)-3-(tributylstannyl)acrylate (S-14): Tributyltin hydride (7.3 mL, 27 mmol) was added to a stirred solution of ethyl propiolate (2.6 mL, 26 mmol) and 2,2′-azobis(2-methylpropionitrile) (255 mg, 1.55 mmol) in toluene (100 mL). The mixture was stirred at 70 °C for 16 h before it was cooled to room temperature and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 99:1 → 96:4) yielded the product as a colorless oil (4.4 g, 44%).). ^{1}H NMR (400 MHz, CDCl3): δ 7.74 (d, *J* = 19.4 Hz, 1H), 6.30 (d, *J* = 19.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.59 – 1.39 (m, 6H), 1.36 – 1.24 (m, 9H), 1.06 – 0.93 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 152.6, 136.5, 60.5, 29.1, 27.4, 14.4, 13.8, 9.8. IR (film): $\tilde{\nu}$ = 2956, 2922, 2872, 2853, 1724, 1590, 1464, 1366, 1307, 1261, 1204, 1152,



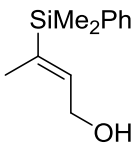
1073, 1035, 997, 961, 865, 841, 825, 747, 691, 666, 600, 507, 461 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{17}H_{34}O_2SnNa$ $[M+Na^+]$: 413.14723, found: 413.14686.

(*E*)-3-(Tributylstannyl)acrylic acid (40). A solution of ester **S-14** (4.4 g, 11 mmol) in THF (40 mL) was added to a stirred solution of lithium hydroxide (1.35 g, 56.5 mmol) in water (50 mL) and methanol (40 mL) at room temperature. After stirring for 48 h the mixture was transferred to a separatory funnel and was washed with hexane (2 x100 mL). The aqueous layer was adjusted to pH 1 with aqueous HCl (2 M, 40 mL) and extracted with EtOAc (4 x 100 mL). The organic layers were dried over sodium sulfate and concentrated under reduced pressure. The product was obtained as colorless oil (3.2 g, 78%) which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 19.4, 0.7 Hz, 1H), 6.32 (d, *J* = 19.4 Hz, 1H), 1.61 – 1.39 (m, 6H), 1.36 – 1.26 (m, 6H), 1.07 – 0.93 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 156.7, 135.6, 29.1, 27.4, 13.8, 9.9. IR (film): $\tilde{\nu}$ = 2955, 2922, 2871, 2854, 1702, 1638, 1592, 1530, 1463, 1405, 1377, 1359, 1293, 1246, 1181, 1076, 1044, 996, 961, 866, 842, 827, 754, 670, 601, 553, 512, 457 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{15}H_{31}O_2Sn$ $[M+H^+]$: 363.13399, found: 363.13363.

(*S,Z*)-5-(Dimethyl(phenyl)silyl)-1-((4-methoxybenzyl)oxy)-4-methylpent-4-en-2-yl (*E*)-3-(tributylstannyl)acrylate (38). 2,4,6-Trichlorobenzoyl chloride (1.35 mL, 8.6 mmol) was added to a solution of compound **40** (3.23 g, 8.9 mmol) and triethylamine (4.9 mL, 35 mmol) in toluene (23 mL) at 0 °C. After 5 min, the mixture was allowed to reach room temperature and stirring continued for 2 h before the mixture was cooled again to 0 °C. A solution of compound **37** (2.6 g, 7.0 mmol) in toluene (5 mL + 2 x 5 mL to rinse) and 4-(dimethylamino)pyridine (20 mg, 0.16 mmol) were added and the resulting mixture was stirred for 2 h at room temperature. The mixture was diluted with *tert*-butyl methyl ether (200 mL) and was washed with aqueous HCl (100 mL, 1 M), water (100 mL) and aqueous saturated $NaHCO_3$ solution (100 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 19:1 → 14:1) yielded the product as a colorless oil (3.24 g, 63%).). $[\alpha]_D^{20}$ = +23.8 (c = 1.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 19.4 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.32 (dd, *J* = 4.4, 2.0 Hz, 3H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.29

(d, *J* = 19.4 Hz, 1H), 5.46 (d, *J* = 1.5 Hz, 1H), 5.31 – 5.24 (m, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 3.80 (s, 3H), 3.35 (dd, *J* = 5.0, 1.4 Hz, 2H), 2.50 (dd, *J* = 14.0, 9.1 Hz, 1H), 2.29 (dd, *J* = 14.0, 4.6 Hz, 1H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.56 – 1.42 (m, 6H), 1.31 (h, *J* = 7.3 Hz, 6H), 1.06 – 0.92 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H), 0.39 (s, 3H), 0.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 159.3, 153.0, 152.6, 140.1, 136.5, 134.0, 130.3, 129.3, 128.9, 127.9, 126.3, 113.9, 72.8, 71.2 (two signals overlap), 55.4, 39.1, 29.1, 27.4, 27.0, 13.8, 9.8, −0.3, −0.6. IR (film): $\tilde{\nu}$ = 3068, 2955, 2926, 2852, 1718, 1614, 1587, 1513, 1463, 1442, 1427, 1375, 1302, 1246, 1153, 1111, 1038, 996, 961, 821, 729, 699, 647, 598, 512, 473 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{37}H_{58}O_4SnNa$ [M+Na$^+$]: 737.30179, found: 737.30241.

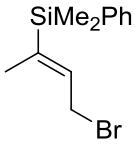
(*E*)-3-(Dimethyl(phenyl)silyl)but-2-en-1-ol (42). Chloro(dimethyl)phenylsilane (11 mL, 64 mmol) was added dropwise to a well stirred suspension of lithium sand (0.99 g, 143 mmol, contains 2% sodium) in THF (65 mL) at 0 °C. The mixture slowly turned red and finally brown. After being stirred at 0 °C for 14 h, the brown mixture was filtered into a flame dried Schlenk flask and the filtrate was directly used in the next step.



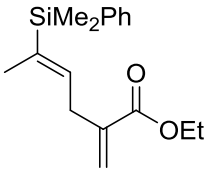
Dimethyl(phenyl)silyllithium (60 mL, 1 M in THF, 60 mmol) was slowly added via cannula to a well stirred solution of triethylaluminum (35 mL, 25% in toluene, 64 mmol) at 0 °C. The resulting brown mixture was stirred at 0 °C for 30 min. Copper(I) cyanide (107 mg, 1.2 mmol, 4 mol%) and a solution of but-2-yn-1-ol (2.2 mL, 30 mmol) in THF (20 mL + 2 x 5 mL to rinse) were sequentially added and the resulting mixture was stirred at 0 °C for 1 h. The mixture was carefully poured into aqueous saturated NH_4Cl solution (150 mL) at 0 °C. The thick reddish-brown suspension was filtered through a pad of silica; the residue and silica were carefully rinsed with *tert*-butyl methyl ether (4x100 mL). The combined layers of the biphasic filtrate were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/ *tert*-butyl methyl ether = 8:2 → 7:3) yielded the product as pale yellow oil (5.42 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 5.96 (tq, *J* = 5.9, 1.7 Hz, 1H), 4.29 (t, *J* = 4.9 Hz, 2H), 1.70 (dt, *J* = 1.8, 0.9 Hz, 3H), 0.36 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.0, 137.6, 134.1, 129.2, 127,9, 59.9, 15.2, −3.5. IR (film): $\tilde{\nu}$ = 3321, 3068, 3009, 2956, 2905, 1427, 1360,

1247, 1109, 1065, 1008, 944, 815, 773, 730, 699, 641, 473, 425 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{12}H_{18}OSiNa$ [M+Na^+]: 229.10191, found: 229.10195.

(*E*)-(4-Bromobut-2-en-2-yl)dimethyl(phenyl)silane (43). A solution of triphenylphosphine (6.0 g, 23 mmol) in CH_2Cl_2 (40 mL) was added over the course of 1 h to a well stirred solution of compound **42** (4.3 g, 21 mmol) and carbon tetrabromide (7.3 g, 22 mmol) in CH_2Cl_2 (40 mL) at room temperature. The resulting mixture was stirred for 30 min before silica (35 g) was added and the solvent was evaporated under reduced pressure. The loaded silica was added on top of a silica column; purification via flash chromatography (hexane/ *tert*-butyl methyl ether = 199:1) yielded the product as colorless oil (5.63 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.39 – 7.34 (m, 3H), 6.09 (tq, *J* = 7.9, 1.8 Hz, 1H), 4.03 (d, *J* = 7.6 Hz, 2H), 1.77 (d, *J* = 1.8 Hz, 3H), 0.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 137.5, 135.1, 134.1, 129.3, 128.0, 27.4, 14.6, −3.6. IR (film): $\tilde{\nu}$ = 3068, 3049, 3020, 2957, 1427, 1248, 1202, 1110, 1058, 941, 830, 809, 773, 729, 698, 579, 481, 466 cm^{-1}. HRMS (EI): *m/z* calcd. for $C_{12}H_{17}SiBr$ [M^+]: 268.02830, found: 268.02838.



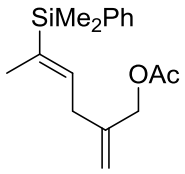
Ethyl (*E*)-5-(dimethyl(phenyl)silyl)-2-methylenehex-4-enoate (44). Ethyl benzoylacetate (4.1 mL, 22 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (3.5 mL, 23 mmol) were added to a stirred solution of compound **42** (5.6 g, 21 mmol) in toluene (40 mL) at room temperature, causing the formation of a colorless precipitate and gentle warming of the orange mixture. After stirring for 1 h, the mixture was diluted with *tert*-butyl methyl ether (100 mL) before it was washed with water (2 x 50 mL) and brine (50 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure.



The remaining orange oil was dissolved in THF (40 mL). Paraformaldehyde (1.26 g, 42 mmol) and potassium carbonate (5.77 g, 42 mmol) were added and the orange mixture was stirred at reflux temperature for 19 h. The mixture was cooled to room temperature and filtered through a pad of Celite, which was carefully rinsed with *tert*-butyl methyl ether (2 x 50 mL). The combined filtrates were concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/ *tert*-butyl methyl ether = 29:1 → 24:1) yielded the product as colorless oil (4.62 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.37 – 7.31 (m, 3H), 6.17 (d, *J* = 1.3 Hz, 1H), 5.83 (tq, *J* = 6.9, 1.8 Hz, 1H), 5.51 (q, *J* = 1.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz,

2H), 3.14 (dt, *J* = 6.9, 0.9 Hz, 2H), 1.69 (dt, *J* = 1.7, 0.8 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 139.4, 138.6, 137.2, 137.1, 134.1, 129.1, 127.8, 124.8, 60.8, 30.9, 14.9, 14.4, −3.3. IR (film): $\tilde{\nu}$ = 3069, 3050, 2957, 2907, 1717, 1632, 1616, 1427, 1368, 1323, 1301, 1247, 1206, 1135, 1111, 1027, 943, 831, 812, 773, 731, 700, 644, 473, 455 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}O_2SiNa$ [M+Na$^+$]: 311.14378, found: 311.14350.

(*E*)-5-(Dimethyl(phenyl)silyl)-2-methylenehex-4-en-1-yl acetate (45). A solution of compound



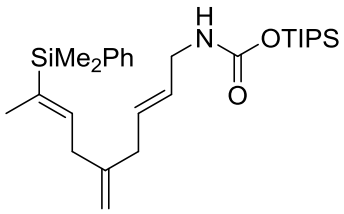
44 (4.6 g, 16 mmol) in Et_2O (40 mL) was slowly added to a solution of di-isobutylaluminum hydride (35 mL, 1 M in CH_2Cl_2, 35 mmol) at 0 °C. The mixture was allowed to reach room temperature over the course of 4 h. After stirring for another 10 h, aqueous HCl (65 mL, 2 M) was carefully added. After frothing had subsided, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over potassium carbonate and sodium sulfate and concentrated under reduced pressure to a volume of ~ 50 mL.

Triethylamine (4.5 mL, 32 mmol), acetic anhydride (1.8 mL, 19 mmol) and 4-(dimethylamino)pyridine (10 mg, 0.08 mmol) were added to the solution at 0 °C. The mixture was allowed to reach room temperature and stirring was continued for 4 h. The mixture was poured into water (50 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/*tert*-butyl methyl ether = 24:1 → 19:1) yielded the product as colorless oil (4.31 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ **7**.54 – 7.45 (m, 2H), 7.39 – 7.31 (m, 3H), 5.83 (tq, *J* = 7.1, 1.8 Hz, 1H), 5.05 (d, *J* = 1.3 Hz, 1H), 4.96 (dt, *J* = 1.5, 0.8 Hz, 1H), 4.52 (dd, *J* = 1.4, 0.8 Hz, 2H), 2.91 (d, *J* = 7.0 Hz, 2H), 2.08 (s, 3H), 1.68 (d, *J* = 1.7 Hz, 3H), 0.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 142.6, 138.5, 137.2, 137.1, 134.1, 129.0, 127.9, 113.1, 67.1, 32.6, 21.1, 14.9, −3.3. IR (film): $\tilde{\nu}$ = 3086, 3008, 2956, 1741, 1655, 1615, 1428, 1372, 1224, 1110, 1027, 957, 907, 813, 772, 730, 696, 635, 605, 475, 459 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}O_2SiNa$ [M+Na$^+$]: 311.14378, found: 311.14365.

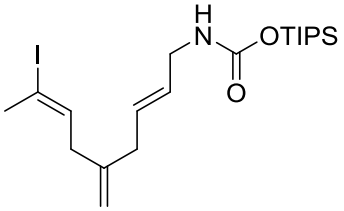
***tert*-Butyl (*E*)-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate (49).** Pinacol borane (4.5 mL, 31 mmol) and a suspension of dicyclohexylborane (0.36 g, 2 mmol) in THF (2 mL) were added to a solution of *N*-Boc-propargylamine (3.53 g, 20.7 mmol) in THF (20 mL) and the resulting mixture was stirred at 40 – 50 °C for 3 h. The mixture was cooled to room temperature and air was bubbled through for 2 h. The solvent was evaporated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 85:15 → 80:20) yielded the product as a colorless solid (5.82 g, 99%). Mp = 69 – 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (dt, *J* = 18.1, 4.7 Hz, 1H), 5.58 (dt, *J* = 18.0, 1.9 Hz, 1H), 4.62 (s, 1H), 3.90 – 3.76 (m, 2H), 1.44 (s, 9H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 149.5, 119.3 (weak), 83.5, 79.6, 44.1, 28.6, 24.9. IR (film): $\tilde{\nu}$ = 3361, 2977, 2930, 1698, 1643, 1520, 1455, 1365, 1322, 1271, 1248, 1167, 1144, 1051, 996, 971, 890, 850, 780, 623, 579 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{14}H_{26}NO_4BNa$ [M+Na^+]: 306.18471, found: 306.18441.

***tert*-Butyl ((2*E*,7*E*)-8-(dimethyl(phenyl)silyl)-5-methylenenona-2,7-dien-1-yl)carbamate (46).** Dichlorobis(tri(2-furyl)phosphine)palladium(II) (255 mg, 0.40 mmol, 2.7 mol%)[8] was added to a stirred solution of compound **45** (4.23 g, 14.6 mmol), compound **49** (5.73 g, 20.2 mmol) and potassium fluoride (2.4 g, 41 mmol) in MeOH (75 mL) at room temperature. After stirring for 4 h, the mixture was diluted with brine (150 mL) and extracted with EtOAc (4 x 150 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 11:1 → 10:1) yielded the product as colorless oil (5.1 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.37 – 7.32 (m, 3H), 5.83 (ddt, *J* = 7.0, 5.3, 1.8 Hz, 1H), 5.61 (dtt, *J* = 14.8, 6.6, 1.3 Hz, 1H), 5.52 – 5.43 (m, 1H), 4.76 (dd, *J* = 6.6, 0.9 Hz, 2H), 4.51 (s, 1H), 3.70 (d, *J* = 6.1 Hz, 2H), 2.83 (d, *J* = 6.4 Hz, 2H), 2.73 (d, *J* = 6.4 Hz, 2H), 1.66 (d, *J* = 1.8 Hz, 3H), 1.45 (s, 9H), 0.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.8, 138.7, 138.3, 136.3, 134.1, 130.3, 129.0, 128.5, 127.9, 110.8, 79.4, 42.6, 39.4, 35.3, 28.6, 14.9, −3.3. IR (film): $\tilde{\nu}$ = 3350, 3069, 2976, 2928, 1704, 1645, 1614, 1503, 1428, 1391, 1366, 1247, 1170, 1111, 971, 894, 831, 814, 773, 732, 701, 636, 474 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{23}H_{35}NO_2SiNa$ [M+Na^+]: 408.23293, found: 408.23276.

[8] X. Zheng, Q. Hu, M. Qian, E. Negishi, *J. Am. Chem. Soc*. **2003**, *125*, 13636-13637.

Triisopropylsilyl ((2*E*,7*E*)-8-(dimethyl(phenyl)silyl)-5-methylenenona-2,7-dien-1-yl)-carbamate (S-15). 

Triisopropylsilyl triflate (2.2 mL, 7.9 mmol) was added dropwise to a stirred solution of compound **46** (2.7 g, 7.0 mmol) and 2,6-lutidine (2.1 mL, 18 mmol) in CH_2Cl_2 (60 mL) at 0 °C. The mixture was stirred for 6 h at ambient temperature before it was poured into saturated aqueous $NaHCO_3$ solution (50 mL). The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL), and the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 100:0 → 14:1) furnished the product as colorless oil (3.0 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.36 – 7.32 (m, 3H), 5.83 (td, *J* = 7.0, 1.7 Hz, 1H), 5.67 – 5.58 (m, 1H), 5.53 – 5.45 (m, 1H), 4.79 – 4.69 (m, 3H), 3.77 – 3.71 (m, 2H), 2.83 (d, *J* = 7.0 Hz, 2H), 2.73 (d, *J* = 6.8 Hz, 2H), 1.66 (d, *J* = 1.8 Hz, 3H), 1.36 – 1.23 (m, 3H), 1.08 (d, *J* = 7.4 Hz, 18H), 0.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 146.8, 138.7, 138.3, 136.3, 134.1, 130.5, 129.0, 128.3, 127.9, 110.8, 43.1, 39.4, 35.3, 18.0, 14.9, 12.3, −3.3. IR (film): $\tilde{\nu}$ = 3462, 3342, 3069, 2945, 2867, 1695, 1614, 1504, 1464, 1428, 1389, 1247, 1139, 1111, 1017, 999, 971, 920, 884, 831, 813, 773, 731, 700, 672, 459 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{28}H_{47}NO_2Si_2Na$ [M+Na$^+$]: 508.30376, found: 508.30359.

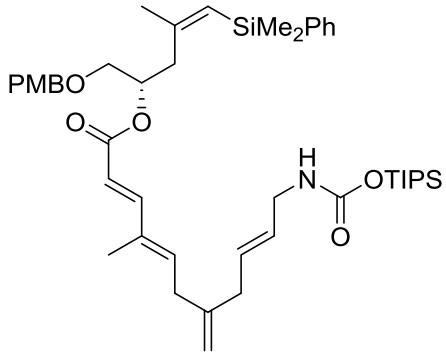
Triisopropylsilyl ((2*E*,7*E*)-8-iodo-5-methylenenona-2,7-dien-1-yl)carbamate (7). 

N-Iodosuccinimide (2.6 g, 11 mmol) was added to a stirred solution of compound **S-15** (3.4 g, 7.0 mmol) and 2,6-lutidine (1.4 mL, 12 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (22 mL) at 0 °C. After stirring at 0 °C for 1 h, the dark red mixture was poured into saturated aqueous $Na_2S_2O_3$ solution (50 mL). The resulting almost colorless mixture was extracted with CH_2Cl_2 (5 x 50 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 14:1) yielded the product as an orange oil (2.1 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (td, *J* = 7.7, 1.5 Hz, 1H), 5.64 – 5.47 (m, 2H), 4.79 4.82 – 4.68 (m, 3H), 3.75 (dt, *J* = 6.0, 3.1 Hz, 2H), 2.72 (d, *J* = 6.3 Hz, 2H), 2.69 (d, *J* = 8.0 Hz, 2H), 2.36 (d, *J* = 1.4 Hz, 3H), 1.35 – 1.24 (m, 3H), 1.08 (d, *J* = 7.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 145.1, 138.4, 130.0, 128.6, 111.8, 95.2, 43.1, 39.1, 37.1, 27.6, 18.00, 12.2.

IR (film): $\tilde{\nu}$ = 3342, 2944, 2893, 2866, 1690, 1504, 1463, 1428, 1388, 1344, 1256, 1140, 1079, 1050, 1016, 999, 971, 883, 784, 669, 514, 459, 416 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{20}H_{36}NO_2ISiNa$ [M+Na^+]: 500.14522, found: 500.14509.

Assembly of the Macrocycle and Completion of the Total Synthesis

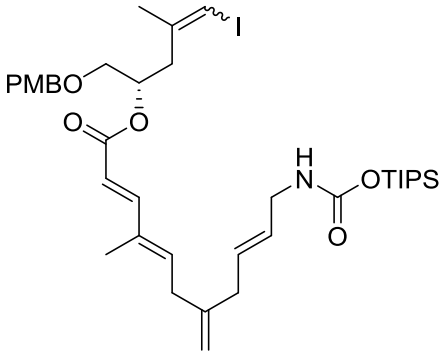
(*S*,*Z*)-5-(Dimethyl(phenyl)silyl)-1-((4-methoxybenzyl)oxy)-4-methylpent-4-en-2-yl



(2*E*,4*E*,9*E*)-4-methyl-7-methylene-11-((((triisopropylsilyl)oxy)carbonyl)amino)undeca-2,4,9-trienoate (50). Tetrakis(triphenylarsine)palladium(0) (0.36 g, 0.27mmol, 6 mol%)[9] was added to a solution of stannane **38** (3.18 g, 4.45 mmol) and alkenyl iodide **47** (2.15 g, 4.5 mmol) in DMF (20 mL). The mixture was vigorously stirred at room temperature for 16 h before it was diluted with brine (100 mL) and extracted with *tert*-butyl methyl ether (5 x 100 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane:EtOAc = 9:1 → 5:1) yielded the product as pale yellow oil (2.82 g, 82%). $[\alpha]_D^{20}$ = +25.3 (c = 1.35, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.35 – 7.30 (m, 4H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.90 (t, *J* = 7.7 Hz, 1H), 5.78 (d, *J* = 15.7 Hz, 1H), 5.66 – 5.58 (m, 1H), 5.56 – 5.48 (m, 1H), 5.46 (d, *J* = 1.5 Hz, 1H), 5.30 (ddt, *J* = 9.1, 5.7, 4.5 Hz, 1H), 4.84 – 4.71 (m, 3H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 3.80 (s, 3H), 3.75 (dt, *J* = 5.8, 2.9 Hz, 2H), 3.38 – 3.30 (m, 2H), 2.89 (d, *J* = 7.6 Hz, 2H), 2.74 (d, *J* = 6.5 Hz, 2H), 2.51 (dd, *J* = 14.0, 9.1 Hz, 1H), 2.29 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.91 (d, *J* = 1.3 Hz, 3H), 1.76 (d, *J* = 1.2 Hz, 3H), 1.35 – 1.24 (m, 3H), 1.08 (d, *J* = 7.4 Hz, 18H), 0.39 (s, 3H), 0.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 159.3, 154.9, 152.6, 149.6, 145.7, 140.1, 138.7, 134.4, 133.9, 130.3, 129.9, 129.3, 128.9, 128.7, 127.9, 126.2, 116.3, 113.9, 111.7, 72.8, 71.8, 70.9, 55.4, 43.1, 39.5, 39.1, 35.3, 27.0, 18.0, 12.3, 12.2, −0.3, −0.7. IR (film): $\tilde{\nu}$ = 3361, 3067, 2945, 2866, 1701, 1619, 1512, 1464, 1427, 1390, 1365, 1301, 1245, 1167, 1111, 1036, 1018, 981, 883, 856, 821, 805, 782, 729, 699, 670, 647, 573, 513, 474 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{45}H_{67}NO_6Si_2Na$ [M+Na^+]: 796.43992, found 796.44058.

[9] R. D. W. Kemmitt, P. McKenna, D. R. Russel, L. J. S. Sherry, *J. Chem. Soc. Dalton Trans*. **1985**, 259-268.

(*S*,*Z*)-5-Iodo-1-((4-methoxybenzyl)oxy)-4-methylpent-4-en-2-yl (2*E*,4*E*,9*E*)-4-methyl-7-methylene-11-((((triisopropylsilyl)oxy)carbonyl)amino)undeca-2,4,9-trienoate (51). A

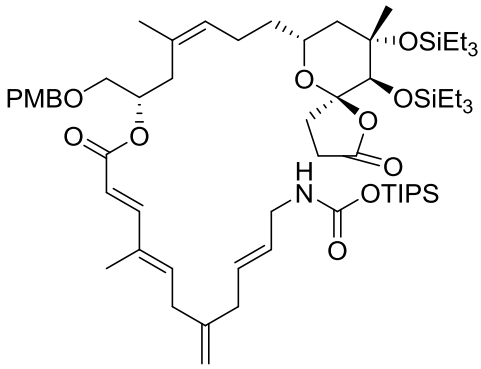


solution of bis(pyridine)iodonium tetrafluoroborate (400 mg, 1.08 mmol) in MeCN (10 mL + 2 x 5 mL to rinse) was added to a stirred solution of compound **50** (743 mg, 0.96 mmol) in MeCN (20 mL) at −20 °C. After stirring for 2 h, aqueous saturated $Na_2S_2O_3$ solution (20 mL) was added and the resulting mixture was warmed to ambient temperature and extracted with CH_2Cl_2 (1 x 100 and 3 x 20 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane:EtOAc = 88:12 → 85:15) yielded the product as colorless oil (453 mg, 62%). The product consists of an inseparable *Z*/*E*-isomer mixture (*Z*:*E* = 3:1). $[\alpha]_D^{20}$ = +11.3 (c = 0.62, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6, major (*Z*)-isomer) δ 7.66 (d, *J* = 15.6 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.01 (d, *J* = 15.6 Hz, 1H), 5.72 – 5.59 (m, 3H), 5.39 – 5.31 (m, 1H), 5.22 (dt, *J* = 15.3, 5.8 Hz, 1H), 4.75 (s, 1H), 4.68 (s, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.20 (s, 1H), 3.57 (dd, *J* = 10.3, 5.7 Hz, 1H), 3.54 – 3.48 (m, 2H), 3.40 (d, *J* = 4.8 Hz, 1H) 3.30 (s, 3H), 2.81 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.57 (d, *J* = 7.6 Hz, 2H), 2.50 – 2.40 (m, 3H), 1.65 (d, *J* = 1.4 Hz, 3H), 1.48 (s, 3H), 1.42 – 1.32 (m, 3H), 1.18 (d, *J* = 7.4 Hz, 18H). ^{13}C NMR (101 MHz, C_6D_6, major (*Z*)-isomer) δ 166.6, 159.8, 154.7, 149.8, 145.72, 144.0, 138.6, 134.5, 130.7, 130.6, 129.6, 129.5, 129.2, 116.9, 114.1, 111.6, 77.7, 73.1, 71.4, 70.6 54.8, 43.1, 40.9, 39.5, 35.30, 23.5, 18.2, 12.6, 12.0. IR (film): $\tilde{\nu}$ = 3375, 2944, 2866, 1700, 1620, 1512, 1463, 1390, 1364, 1301, 1246, 1166, 1092, 1036, 1018, 980, 884, 807, 674, 572, 517, 480 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{37}H_{57}NO_6ISi$ [M+H$^+$]: 766.29944, found 766.30002.

(*S*,*Z*)-1-((4-Methoxybenzyl)oxy)-4-methyl-7-((5*R*,7*R*,9*S*,10*R*)-9-methyl-2-oxo-9,10-bis-((triethylsilyl)oxy)-1,6-dioxaspiro[4.5]decan-7-yl)hept-4-en-2-yl (2*E*,4*E*,9*E*)-4-methyl-7-methylene-11-((((triisopropylsilyl)oxy)carbonyl)amino)undeca-2,4,9-trienoate (53). Rieke zinc (111 mg, 1.7 mmol)[10] and DMF (4.2 mL) were added to compound **34** (460 mg, 0.855 mmol) and the resulting suspension was vigorously stirred at room temperature for 6 h to yield an

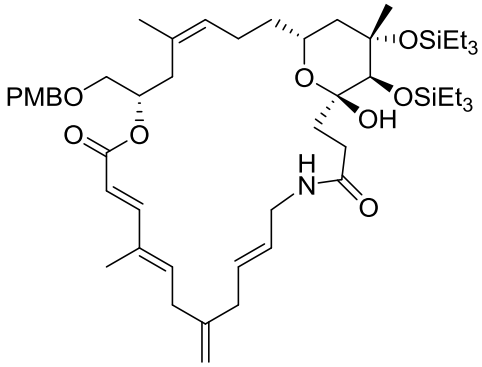
[10] R. D. Rieke, P. T.-J. Li, T. P. Burns, S. T. Uhm, *J. Org. Chem*. **1981**, *46*, 4323-4324.

approximately 0.2 M solution of the required organozinc reagent **52**. Excess zinc was allowed to settle and the supernatant solution (4.1 mL) was used in the cross coupling step.



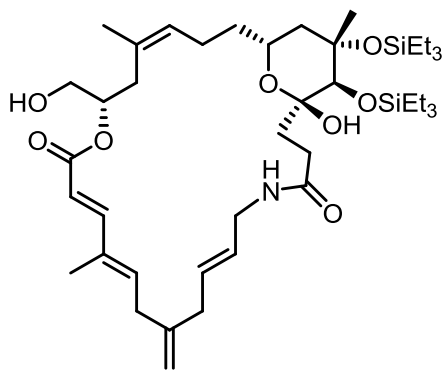
In a separate Schlenk flask manganese dust (55 mg, 1.0 mmol) was added to a stirred solution of $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (84 mg, 0.10 mmol) and triphenylarsine (71 mg, 0.23 mmol) in DMF (5 mL). The mixture was stirred for 15 min, excess manganese was allowed to settle and 3.5 mL of the intense purple supernatant solution was transferred into a stirred solution of alkenyl iodide **51** (493 mg, 0.64 mmol, *Z*:*E* = 3:1) in THF (4 mL). After 5 min the solution of the organozinc compound **52** (vide supra) was slowly introduced. The color of the mixture first turned reddish brown and then greenish-yellow. After stirring for 2.5 h the mixture was diluted with water (50 mL) and extracted with *tert*-butyl methyl ether (6 x 50 mL). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane:*tert*-butyl methyl ether = 4:1) provided the product as pale yellow oil (370 mg, 52%, 70% with respect to the *Z*-isomer). $[\alpha]_D^{20}$ = +17.9 (c = 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 7.67 (d, *J* = 15.7 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.05 (d, *J* = 15.6 Hz, 1H), 5.69 (t, *J* = 7.6 Hz, 1H), 5.67 – 5.61 (m, 1H), 5.40 – 5.19 (m, 3H), 4.76 (s, 1H), 4.70 (s, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.27 – 4.18 (m, 1H), 3.89 (dddd, *J* = 11.9, 10.0, 5.2, 1.8 Hz, 1H), 3.64 (s, 1H), 3.60 (d, *J* = 4.6 Hz, 2H), 3.52 (t, *J* = 6.0 Hz, 2H), 3.33 (s, 3H), 2.68 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.63 – 2.52 (m, 3H), 2.47 (d, *J* = 6.9 Hz, 2H), 2.44 – 2.11 (m, 5H), 1.90 – 1.78 (m, 5H), 1.68 (t, *J* = 12.2 Hz, 1H), 1.62 – 1.56 (m, 1H), 1.54 (s, 3H), 1.52 (s, 3H), 1.45 - 129 (m, 4H), 1.18 (d, *J* = 7.4 Hz, 18H), 1.05 – 0.97 (m, 18H), 0.76 – 0.57 (m, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 174.9, 166.7, 159.8, 154.7, 149.6, 145.8, 138.6, 134.5, 132.2, 130.8, 129.6, 129.5, 129.2, 117.1, 114.2, 111.6, 108.4, 80.7, 75. 9, 73.2, 71.6, 71.3, 70.1, 54.8, 46.8, 43.1, 39.5, 36.1, 35.3, 34.0, 32.4, 28.0, 24.44, 24.39, 22.8, 18.2, 12.6, 12.1, 7.5, 7.4, 7.3, 5.6. IR (film): $\tilde{\nu}$ = 3369, 2952, 2874, 1786, 1704, 1622, 1514, 1462, 1384, 1301, 1247, 1163, 1139, 1115, 1018, 917, 884, 847, 742, 675, 547, 488 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{60}H_{101}NO_{11}Si_3Na$ $[M+Na^+]$: 1118.65747, found: 1118.65688.

(1*S*,7*E*,12*E*,14*E*,18*S*,20*Z*,24*R*,26*S*,27*R*)-1-Hydroxy-18-(((4-methoxybenzyl)oxy)methyl)-13,20,26-trimethyl-10-methylene-26,27-bis((triethylsilyl)oxy)-17,28-dioxa-5-azabicyclo-[22.3.1]octacosa-7,12,14,20-tetraene-4,16-dione (55).



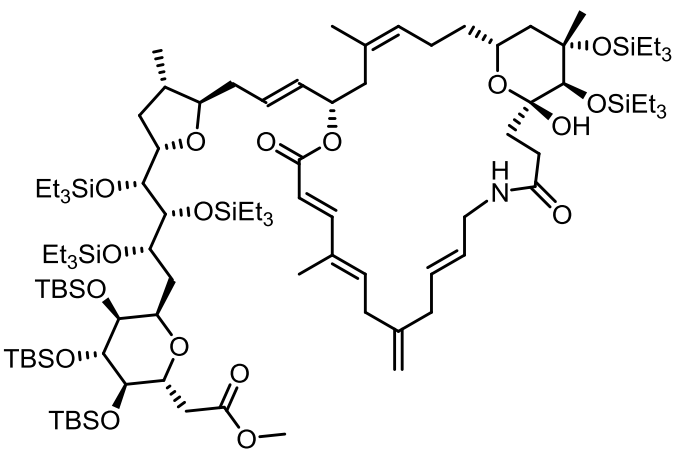
HF·pyridine (70% HF, 0.72 mL, 5.6 mmol) was added to a stirred solution of compound **53** (205 mg, 187 µmol) in THF (15 mL) at 0 °C. After 10 min at 0 °C, the mixture was quenched with aqueous sodium hydroxide solution (2 M, 25 mL) and the resulting mixture was extracted with CH_2Cl_2 (7 x 30 mL). The combined organic layers were dried over $MgSO_4$, diluted with toluene (100 mL) and concentrated under reduced pressure to a volume of ~100 mL. This procedure was repeated twice, taking care to keep the total volume ≥ 100 mL. The remaining solution was diluted with toluene to a total volume of 190 mL. 2-Hydroxypyridine (355 mg, 3.74 mmol) was added and the resulting mixture was stirred at 90 °C for 64 h. The mixture was cooled to room temperature and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane:EtOAc = 3:1 → 2:1) yielded the product as colorless oil (75 mg, 45%). $[\alpha]_D^{20}$ = +27.6 (c = 0.70, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 7.54 (dd, *J* = 15.7, 0.8 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.03 (d, *J* = 15.6 Hz, 1H), 5.72 – 5.56 (m, 2H), 5.42 – 5.37 (m, 1H), 5.19 – 5.06 (m, 2H), 5.05 – 5.01 (m, 1H), 4.71 – 4.69 (m, 2H), 4.64 (s, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.35 (d, *J* = 11.7 Hz, 1H), 4.07 (ddt, *J* = 10.7, 8.0, 2.7 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.59 (d, *J* = 4.6 Hz, 2H), 3.40 – 3.27 (m, 4H), 2.95 – 2.80 (m, 2H), 2.72 – 2.56 (m, 3H), 2.46 (d, *J* = 5.5 Hz, 2H), 2.38 (dd, *J* = 14.4, 7.4 Hz, 2H), 2.31 – 2.22 (m, 2H), 1.91 – 1.73 (m, 6H), 1.68 – 1.62 (m, 1H), 1.59 (s, 3H), 1.54 – 1.45 (m, 1H), 1.50 (d, *J* = 1.2 Hz, 3H), 1.16 – 1.10 (m, 9H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.91 – 0.83 (m, 6H), 0.69 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 173.5, 166.8, 159.9, 149.7, 146.0, 140.1, 133.3, 131.3, 130.8, 130.7, 129.6, 128.7, 128.5, 116.9, 114.2, 113.1, 97.9, 82.0, 76.5, 73.1, 71.4, 71.2, 66.7, 54.8, 47.3, 41.4, 40.1, 36.6, 35.6, 34.0, 29.5, 24.4, 24.1, 23.3, 12.2, 7.53, 7.50, 7.48, 5.8. IR (film): $\tilde{\nu}$ = 3309, 3074, 2952, 2912, 2876, 1710, 1625, 1514, 1458, 1380, 1361, 1302, 1247, 1168, 1107, 1020, 982, 849, 740 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{50}H_{81}NO_9Si_2Na$ [M+Na^+]: 918.53421, found: 918.53471.

(1*S*, 7*E*, 12*E*, 14*E*, 18*S*, 20*Z*, 24*R*, 26*S*, 27*R*)-1-Hydroxy-18-(hydroxymethyl)-13,20,26-trimethyl-10-methylene-26,27-bis((triethylsilyl)oxy)-17,28-dioxa-5-azabicyclo[22.3.1]-



octacosa-7,12,14,20-tetraene-4,16-dione (S-16). A cold (0 °C) solution of trityl tetrafluoroborate (0.95 mL, 0.05 M, 47.5 µmol) in CH_2Cl_2 was added to a stirred solution of compound **55** (42 mg, 47 µmol) in CH_2Cl_2 (10 mL) at 0 °C. The progress of the reaction was monitored by TLC (hexane:EtOAc = 2:1, UV and anisaldehyde). After 1 h, a second portion of trityl tetrafluoroborate (0.6 mL, 0.05 M, 30 µmol) in cold CH_2Cl_2 was added. The mixture was stirred for 2 h at this temperature before 2,6-di-*tert*-butylpyridine (30.0 µL, 25.6 mg, 134 µmol) was added. The mixture was concentrated *in vacuo* and the residue was purified by flash chromatography (hexane:EtOAC = 2:1 → 3:2) to give the product as colorless oil (16 mg, 44%). $[\alpha]_D^{20}$ = +15.5 (c = 0.20, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6) δ 7.55 (dd, *J* = 15.7, 0.7 Hz, 1H), 5.98 (dd, *J* = 15.7, 0.6 Hz, 1H), 5.71 (t, *J* = 8.0 Hz, 1H), 5.36 – 5.30 (m, 2H), 5.20 – 5.07 (m, 3H), 4.72 – 4.70 (m, 2H), 4.47 (s, 1H), 4.04 – 3.97 (m, 1H), 3.73 (d, *J* = 11.9 Hz, 1H), 3.63 (s, 1H), 3.63 – 3.57 (m, 1H), 3.52 – 3.46 (m, 2H), 2.87 – 2.79 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.55 (ddd, *J* = 13.7, 7.9, 6.9 Hz, 1H), 2.48 (d, *J* = 6.6 Hz, 2H), 2.44 – 2.38 (m, 2H), 2.38 – 2.33 (m, 1H), 2.17 (dd, *J* = 13.4, 6.8 Hz, 1H), 1.89 (dt, *J* = 13.4, 6.5 Hz, 1H), 1.80 (dd, *J* = 12.4, 2.0 Hz, 1H), 1.75 – 1.70 (m, 4H), 1.60 (dt, *J* = 15.9, 6.9 Hz, 1H), 1.55 (s, 3H), 1.52 (d, *J* = 1.5 Hz, 3H), 1.50 – 1.44 (m, 1H), 1.10 (t, *J* = 7.9 Hz, 9H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.87 – 0.82 (m, 6H), 0.68 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (151 MHz, C_6D_6) δ 173.7, 167.1, 149.9, 146.0, 140.2, 133.2, 131.3, 130.8, 128.7, 128.4, 116.8, 113.3, 98.1, 81.8, 76.4, 73.8, 66.8, 64.5, 47.4, 41.4, 40.3, 36.9, 36.6, 36.0, 33.6, 29.8, 24.5, 24.3, 23.3, 12.2, 7.51, 7.48, 7.4, 5.8. IR (film): $\tilde{\nu}$ = 3364, 3075, 2952, 2916, 2876, 1708, 1646, 1625, 1541, 1458, 1379, 1261, 1241, 1167, 1134, 1106, 1068, 1019, 982, 856, 807, 739, 681 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{42}H_{73}NO_8Si_2Na$ [M+Na$^+$]: 798.47670, found: 798.47684.

Compound 57. Sulfur trioxide pyridine complex (23.0 mg, 145 µmol) was added to a stirred solution of compound **S-16** (9.0 mg, 12 µmol), *N*,*N*-diisopropylethylamine (37 µL, 27 mg, 0.21 mmol) and dimethyl sulfoxide (90 µL, 99 mg, 1.3 mmol) in CH_2Cl_2 (1 mL) at –20 °C. After 1 h, aqueous saturated NH_4Cl solution (2 mL) was added and the mixture was allowed to reach



ambient temperature. The resulting mixture was extracted with *tert*-butyl methyl ether (80 mL). The organic layer was washed with aqueous saturated NH_4Cl solution (4 x 10 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The resulting crude aldehyde **56** was used in the next step without further purification.

A solution of lithium hexamethyl-disilazide (78 µL, 0.46 M, 36 µmol) in THF was added to a solution of compound **21** (47.6 mg, 36 µmol) in DMF/DMPU (3:1 *v/v*, 0.6 mL) at –40 °C. After stirring at this temperature for 2 min a solution of $ZnCl_2$ (72 µL, 0.5 M, 36 µmol) in THF was added. The mixture was stirred for 3 min before the resulting solution was added via canula to a solution of the crude aldehyde **56** in DMF/DMPU (3:1 *v/v*, 0.3 mL) at –40 °C; the flask and the canula were rinsed with DMF/DMPU (3:1 *v/v*, 2 x 0.3 mL). The resulting mixture was stirred at the same temperature for 5 min and was then warmed to ambient temperature. After stirring for a total of 72 h, the mixture was diluted with aqueous saturated NaCl solution (20 mL) and extracted with *tert*-butyl methyl ether (4 x 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (hexane:EtOAC = 19:1 → 5:1) yielded the product as colorless oil (6.1 mg, 28%). $[\alpha]_D^{20}$ = +24.5 (c = 0.22, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6) δ 7.55 (d, *J* = 15.6 Hz, 1H), 6.13 (dt, *J* = 14.7, 7.1 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 5.91 (dd, *J* = 8.8, 7.2, Hz, 1H), 5.76 (dd, *J* = 15.5, 6.9 Hz, 1H), 5.62 (t, *J* = 7.7 Hz, 1H), 5.46 (t, *J* = 7.5 Hz, 1H), 5.17 – 5.02 (m, 2H), 4.95 (s, 1H), 4.89 (s, 1H), 4.69 (d, *J* = 2.3 Hz, 2H), 4.60 – 4.53 (m, 2H), 4.38 (td, *J* = 9.1, 5.7 Hz, 1H), 4.19 (d, *J* = 10.5 Hz, 1H), 4.17 – 4.11 (m, 1H), 4.07 – 3.96 (m, 3H), 3.93 (m, 1H), 3.68 (s, 1H), 3.67 – 3.43 (m, 5H), 3.39 (s, 3H), 3.03 (dd, *J* = 13.3, 8.8 Hz, 1H), 2.91 (ddd, *J* = 15.1, 8.5, 5.8 Hz, 1H), 2.81 (dd, *J* = 15.6, 3.7 Hz, 1H), 2.74 – 2.64 (m, 2H), 2.62 – 2.54 (m, 2H), 2.52 – 2.22 (m, 9H), 1.99 – 1.81 (m, 7H), 1.78 (t, *J* = 12.1 Hz, 1H), 1.73 – 1.47 (m, 9H), 1.41 – 0.77 (m, 99H), 0.71 (q, *J* = 7.9 Hz, 6H). 0.272 (s, 3H), 0.269 (s, 3H), 0.26 (s, 3H), 0.25 (s, 3H), 0.20 (s, 3H), 0.19 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 173.5, 171.9, 166.4, 149.4, 146.0, 139.9, 133.28, 131.19, 131.16, 131.1, 130.7, 128.6, 128.5, 117.1, 113.1, 97.9, 84.2, 82.0, 80.7, 77.7, 76.5, 76.0, 74.8, 74.5, 73.5, 73.0, 71.6, 70.8, 66.9, 65.5, 51.2, 47.3, 41.3, 40.14,

40.10, 38.7, 37. 9, 37.8, 36.9, 36.8, 36.7, 36.3, 35.6, 29.6, 26.6, 26.5, 26.0, 24.5, 24.3, 23.3, 18.7, 18.6, 18.1, 16.9, 12.3, 7.8, 7.6, 7.54, 7.51, 7.47, 6.3, 6.1, 6.0, 5.8, -3.1, -3.4, -4.3, -4.52, -4.53, -4.54. IR (film): $\tilde{\nu}$ = 3363, 2953, 2929, 2877, 2858, 1716, 1741, 1627, 1649, 1549, 1512, 1461, 1415, 1379, 1361, 1334, 1252, 1164, 1092, 1006, 972, 938, 920, 900, 875, 835, 814, 776, 741, 678, 560, 437, 459, 424, 408 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{97}H_{187}NO_{17}Si_8Na$ [M+Na^+]: 1885.18455, found: 1885.18397.

Belizentrin Methylester (2). Aqueous hydrogen fluoride (0.28 mL, 51%, 8.2 mmol) was added to a stirred solution of compound **57** (12 mg, 6.4 µmol) in MeCN (2.7 mL). After 6 h, trimethylsilanol (1.6 mL, 17 mmol) was added and stirring was continued for another 30 min. The resulting mixture was concentrated *in vacuo* and the residue was purified by preparative HPLC [YMC Triart C18 5 µm 10150 00550, gradient MeOH/water: 70:30 → 100:0, 4.0 mL/min, 7.5 MPa] to give the product as colorless oil that solidified in the freezer (2.2 mg, 36%). $[\alpha]_D^{25}$ = +8.3 (c = 0.02, MeOH); $[\alpha]_D^{25}$ = +57.3 (c = 2.6, MeOH). ^{1}H NMR (500 MHz, [D_4]-Methanol) δ 7.27 (d, *J* = 15.6 Hz, 1H), 5.93 (dd, *J* = 6.7, 8.5 Hz, 1H), 5.86 – 5.74 (m, 1H), 5.79 (d, *J* = 15.9 Hz, 1H), 5.59 (ddt, *J* = 15.1, 6.8, 1.1 Hz, 1H), 5.57 – 5.49 (m, 1H), 5.48 – 5.46 (m, 1H), 5.45 (ddd, *J* = 9.5, 6.9, 5.1 Hz, 1H), 5.28 (t, *J* = 7.4 Hz, 1H), 4.85 (m, 2H, overlapped by H_2O signal), 4.12 (ddd, *J* = 10.2, 5.9, 4.5 Hz, 1H), 4.05 (dt, *J* = 9.8, 4.6 Hz, 1H), 3.99 (td, *J* = 6.6, 2.8 Hz, 1H), 3.92 (ddd, *J* = 9.6, 8.4, 2.9 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.75 (dd, *J* = 15.4, 5.1 Hz, 1H), 3.67 (s, 3H), 3.69 – 3.61 (m, 1H), 3.61 – 3.47 (m, 5H), 3.28 (s, 1H), 3.10 (t, *J* = 8.4 Hz, 1H), 3.04 (dd, *J* = 15.7, 8.5 Hz, 1H), 2.92 (dd, *J* = 16.1, 6.7 Hz, 1H), 2.87 (dd, *J* = 15.9, 2.9 Hz, 1H), 2.80 – 2.,73 (m, *J* = 2H), 2.69 (dd, *J* = 13.5, 9.5 Hz, 1H), 2.52 (ddd, *J* = 15.5, 9.1, 6.7 Hz, 1H), 2.42 (dd, *J* = 16.0, 9.6 Hz, 1H), 2.39 – 2.31 (m, 2H), 2.25 – 2.00 (m, 7H), 1.97 – 1.86 (m, 3H), 1.79 (s, 3H), 1.76 – 1.72 (m, 1H) 1.72 (s, 3H), 1.63 – 1.42 (m, 4H), 1.39 (s, 3H), 1.03 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, [D_4]-Methanol) δ 176.2, 173.9, 168.3, 150.7, 147.3, 140.9, 135.1, 132.1, 131.9, 131.3, 131.1, 129.4, 129.2, 117.2, 113.1, 98.5, 86.2, 80.2, 79.4, 75.8, 75.3, 74.8, 74.7, 73.7, 73.6, 73.0, 72.8, 71.5, 71.4, 68.0, 52.3, 46.5, 41.9, 40.6, 40.5, 38.4 (two signals overlap), 38.3, 37.9, 37.0, 36.6, 36.2, 31.0, 30.4, 24.8, 23.9, 21.8, 16.7, 12.8. IR (film): $\tilde{\nu}$ = 3358, 2924, 2856, 1707, 1624, 1555, 1437, 1360, 1380, 1305, 1268, 1170, 1065, 1080, 1016, 979, 894, 844, 735, 702, 613, 628, 581, 566, 543, 525, 489, 415, 432 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{49}H_{75}NO_{17}Na$ [M+Na^+]: 972.49272, found: 972.49351.

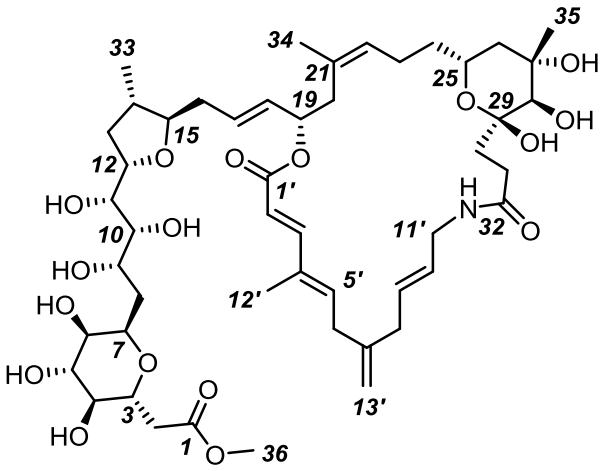


Table S-1. Comparison of the ^{13}C NMR spectra ([D_4]-MeOH) of synthetic methyl ester 2 and isolated acid 1; numbering scheme as shown in the insert;

color code: $\Delta\delta \leq 0.5$ ppm; $0.5 < \Delta\delta < 1$ ppm; $\Delta\delta \geq 1$ ppm

position	δ (ppm)[11] Synthetic 2	δ (ppm)[11,12] Natural 1	Δδ	Δδ – 0.4 ppm[13]
1	173.9	179.4	[-5.5]	[-5.9]
2	38.4	41.7	[-3.3]	[-3.7]
3	71.4	71.4	0.0	-0.4
4	75.3	75.6	-0.3	-0.7
5	74.7	74.5	0.2	-0.2
6	73.0	72.8	0.2	-0.2
7	74,8	76.2	-1.4	-1.8
8	30.4	29.8	0.6	0.2
9	71.5	73.3	-1.8	-2.2
10	73.5	72.8	0.7	0.3
11	75.8	76.0	-0.2	-0.6
12	80.2	78.9	1.3	0.9
13	38.3	38.2	0.1	-0.3
14	40.5	40.0	0.5	0.1
15	86.2	85,5	0.7	0.3
16	37.9	37.3	0.6	0.2
17	131.1	130.6	0.5	0.1
18	132.1	131.2	0.9	0.5
19	73.7	73.0	0.7	0.3

[11] In making the comparison, one should also keep in mind that the ^{13}C shifts of belizentrin (**1**) were indirectly determined via HSQC and HMBC experiments (private communication, Dr. Antonio Hernández Daranas); the listed data of **2**, in contrast, were directly determined by 1D $^{13}C\{^1H\}$.

[12] H. J. Domínguez, J. G. Napolitano, M. T. Fernández-Sánchez, D. Cabrera-García, A. Novelli, M. Norte, J. J. Fernández, A. H. Daranas, *Org. Lett*. **2014**, *16*, 4546-4549.

[13] Corrected for what seems to be a systematic drift of ca. –0.4 ppm.

20	38.4	38.0	0.4	0.0
21	131.9	131.5	0.4	0.0
22	129.2	129.2	0.0	-0.4
23	24.8	25.5	-0.7	-1.1
24	37.0	37.0	0.0	-0.4
25	68.0	68.4	-0.4	-0.8
26	46.5	46.5	0.0	-0.4
27	72.8	72.2	0.6	0.2
28	79.4	78.8	0.6	0.2
29	98.5	97.9	0.6	0.2
30	36.6	35.8	0.8	0.4
31	31.0	30.5	0.5	0.1
32	176.3	175.7	0.6	0.2
33	16.7	16.4	0.3	-0.1
34	23.9	23.2	0.7	0.3
35	21.8	21.4	0.4	0.0
36	52.3	n.d.		
1'	168.3	167.8	0.5	0.1
2'	117.2	116.8	0.4	0.0
3'	150.7	150.1	0.6	0.2
4'	135.1	134.9	0.2	-0.2
5'	140.9	139.8	1.1	0.7
6'	36.2	35.2	1.0	0.6
7'	147.3	146.7	0.6	0.2
8'	40.6	40.1	0.5	0.1
9'	131,3	130.8	0.5	0.1
10'	129.4	129.1	0.3	-0.1
11'	41.9	41.3	0.6	0.2
12'	12.8	12.4	0.4	0.0
13'	113.1	112.4	0.7	0.3

Table S-2. Comparison of the ^{1}H NMR spectra ([D_4]-MeOH) of synthetic methyl ester 2 and isolated acid 1; for the numbering scheme, see insert in the previous Table

position	Synthetic 2 δ (ppm)	1 δ (ppm)[12]	Δδ	Synthetic 2 *J* (Hz)	1 *J* (Hz)
2a	2.87	2,67	0,20	2.9 / 15.9	4.3 / 16.7
2b	2.42	2,16	0,26	9.4 /16.7	9.4 /16.7
3	3.92	3,85	0,07	9.6 / 8.4 / 2.9	9.4 / 8.9 / 4.3
4	3.10	2,97	0,13	8.4 / 8.4	8.9 / 8.9
5	3.54	3,43	0,11	8.4 / ?	8.9 / 10.5
6	3.57	3,48	0,09		10.5 / 4.2
7	4,05	3,94	0,11	9.8 / 4.6 / 4.6	4.2 / 10.6 / 3.1
8a	2,04	1,89	0,15		
8b	1,92	1,89	0,03		
9	3,99	3,83	0,16	6.6 / 6.6 / 2.8	8.9 / 5.7 / 3.9
10	3,52	3,48	0,04	2.8 / 4.0	2.8 / 3.9
11	3,57	3,56	0,01	4.0 / 4.5	2.8 / 5.8
12	4.12	3,97	0,15	4.5 / 5.9 /10.2	5.8 / 9.0 / 6.1
13a	2,10	2,09	0,01		
13b	1,56	1,45	0,11		
14	1,91	1,83	0,08		
15	3.50	3,38	0,12		
16a	2,35	2,23	0,12		
16b	2,20	2,14	0,06		
17	5,81	5,71	0,10		
18	5,59	5,51	0,08	15.4 / 6.9	15.3 / 9.2
19	5,45	5,36	0,09	9.5 / 6.9 / 5.1	9.2 / 8.9 /4.8
20a	2,69	2,64	0,05	9.5 / 13.7	8.9 / 14.2
20b	2,09	1,92	0,17	5.1 / 13.7	4.8 / 14.2
22	5,28	5,12	0,16	7.4 / 7.4	6.4 / 8.5
23a	2,13	2,10	0,03		
23b	2,10	1,96	0,14		
24a	1,52	1,42	0,10		
24b	1,45	1,26	0,19		
25	3.90	3,78	0,12		
26a	1.73	1,64	0,09		3.5 / 14.5
26b	1.45	1,30	0,15		10.5 / 14.5
28	3.28	3,18	0,10		
30a	2.09	1,93	0,16		
30b	1.88	1,82	0,06		
31a	2.52	2,42	0,10	15.5 / 9.1 / 6.7	
31b	2.35	2,26	0,09		

33	1.02	0,92	0,10	6,4	6,5
34	1.71	1,61	0,10		
35	1.38	1,29	0,09		
36	3.67				
2'	5.79	5,72	0,07	15,6	15,7
3'	7.27	7,17	0,10	15,6	15,7
5'	5.93	5,83	0,10	6.7 / 8.5	7.6 / 8.2
6'a	3.04	2,86	0,18	8.5 / 15.7	7.6 / 15.4
6'b	2.92	2,86	0,06	6.7 / 15.7	8.2 / 15.4
8'	2,77	2,66	0,11		
9'	5,53	5,45	0,08		6.7 / 8.0 / 15.5
10'	5,46	5,39	0,07		15.5 / 6.9 / 5.9
11'a	3,75	3,84	-0,09	15.4 / 5.1	14.9 / 6.9
11'b	3,65	3,41	0,24		14.9 / 5.9
12'	1,78	1,67	0,11		
13'a	4,84	4,75	0,09		1.3 / 1.3
13'b		4,72			

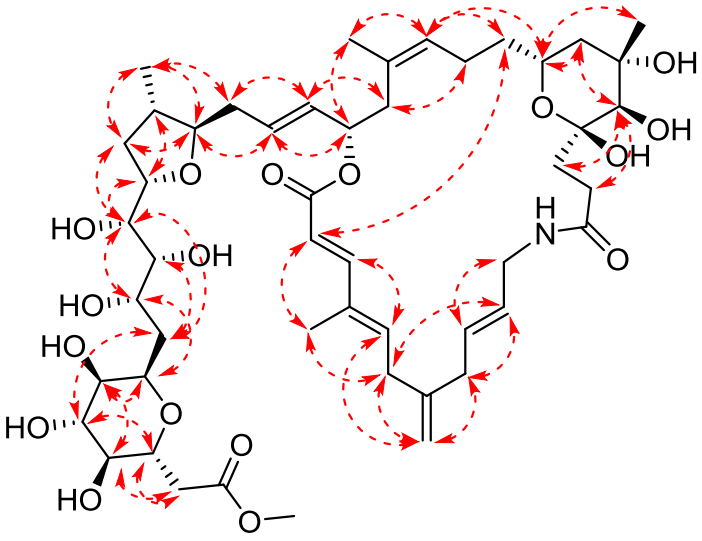
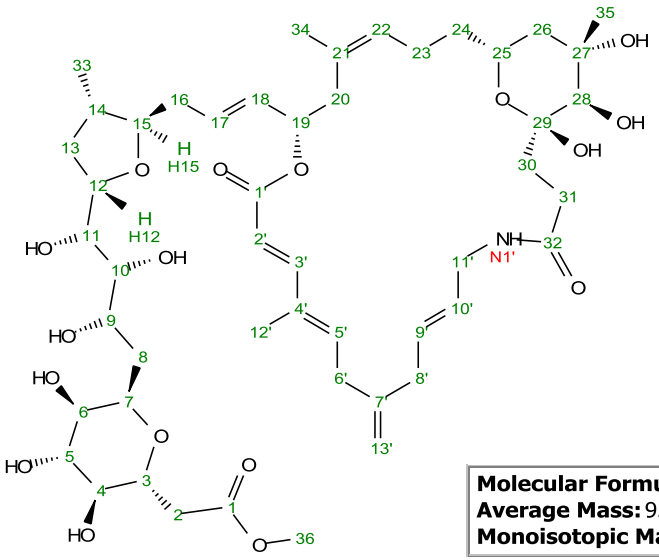


Figure S-1. Graphical representation of relevant NOE and/or ROESY correlations observed for belizentrin methyl ester (2), which very closely match those reported by the isolation team for the free carboxylic acid belzientrin (1).[12]

ANF-AB-323-01 2 mg MeOD 298 K



Molecular Formula: $C_{49}H_{75}NO_{17}$
Average Mass: 950.12
Monoisotopic Mass: 949.50

P-ID:	CW00379	
Measured on:	08.03.2018	
CHIFFRE:	ANF-AB-323-01	
Client:	Anderl	
Group:	Fürstner	
Analyst:	Wirtz	
Assignment Date:	13.04.2018	
Amount:	2 mg	
Solvent:	MeOD	
Reference:	solvent	
Temperature:	298K	
Spectrometer:	AV-500as BBFO	
Experiments:	1H, 13C{1H}, COSYPH, HSQCed, HMBC, ROESY,	
	NOESY, 1D-NOESY, 1D-TOCSY, 1D-COSY, 1D-ROESY	

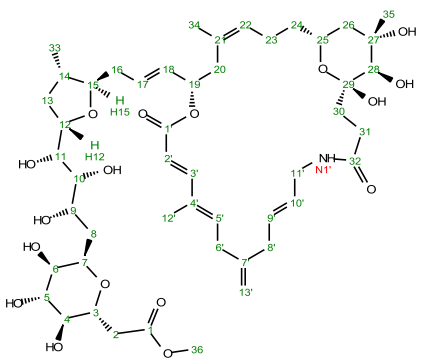
Atom	Chemical Shift	J	COSY	HSQC	HMBC	NOESY
1C	173.93				36, 2a, 2b, 3	
2C	38.40			2a, 2b	3, 4	
Ha	2.87	15.90(2b), 2.90(3)	3, 2b	2	1, 3	3, 2b, 4
Hb	2.42	9.60(3), 15.90(2a)	2a, 3	2	1, 4, 3	3, 2a, 7, 4
3C	71.42			3	2a, 2b, 4	
H	3.92	9.60(2b), 2.90(2a), 8.40(4)	2a, 2b, 4	3	1, 4, 2	8b, 2b, 2a, 5
4C	75.27			4	2b, 3, 5	
H	3.10	8.40(3), 8.40(5)	3, 5	4	5, 3, 2	2b, 2a, 6
5C	74.71			5	4, 6	
H	3.54	8.40(4)	4, 6	5	4, 6	3, 8a, 8b
6C	72.96			6	5	
H	3.57		7, 5	6	5, 7, 8	7, 4
7C	74.82			7	8b, 6, 9	
H	4.05	9.80(?), 4.60(?), 4.60(?)	8a, 8b, 6	7		10, 8a, 6, 9, 8b, 2b
8C	30.38			8a, 8b	6, 9	
Ha	2.04	6.60(9)	9, 8b, 7	8		9, 10, 11, 8b, 5, 7
Hb	1.92	6.60(9)	8a, 9, 7	8	10, 7, 9	3, 9, 10, 11, 8a, 5, 7
9C	71.47			9	8b	
H	3.99	6.60(8a), 6.60(8b), 2.80(10)	10, 8a, 8b	9	7, 8	8b, 10, 11, 8a, H12, 7
10C	73.55			10	8b	
H	3.52	2.80(9), 4.00(11)	11, 9	10		9, 13b, 8b, 8a, 13a, H12, 7
11C	75.77			11	13b	
H	3.57	4.00(10), 4.50(H12), 4.30(?), 5.00(?)	H12, 10	11		9, 13b, 8b, 8a, 13a, H12
12C	80.17			H12	13b	
H	4.12	4.50(11), 5.90(13a), 10.20(13b)	13a, 13b, 11	12		9, 10, 11, 14, 13a
13C	38.27			13a, 13b	19	
Ha	2.1	5.90(H12)	14, 13b, H12	13	15, 14	10, 11, 14, 13b, H12
Hb	1.56	10.20(H12)	13a, 14, H12	13	12, 11, 33, 14	H15, 10, 11, 13a, 19
14C	40.45			14	33, 13a, 13b, 16b	
H	1.91	6.40(19)	19, H15, 13a, 13b	14		H15, 13a, 16a, 33, H12
15C	86.23			H15	33, 17, 16a, 16b, 13a	
H	3.50	9.00(?), 6.70(?), 4.60(?)	16b, 16a, 14	15	19	13b, 16b, 17, 14, 16a, 33
16C	37.86			16a, 16b	17, 18	
Ha	2.35		17, 16b, H15	16	18, 17, 15	H15, 16b, 14, 17, 18, 33
Hb	2.2		17, 16a, H15	16	18, 17, 15, 14	H15, 16a, 33
17C	131.11			17	16a, 16b	
H	5.81	15.40(18)	18, 16b, 16a	17	15, 19, 16	19, H15, 16a, 33
18C	132.09			18	16a, 16b, 20a, 20b	
H	5.59	15.40(17), 6.90(19)	19, 17	18	19, 16, 20	20b, 34, 16a, 20a

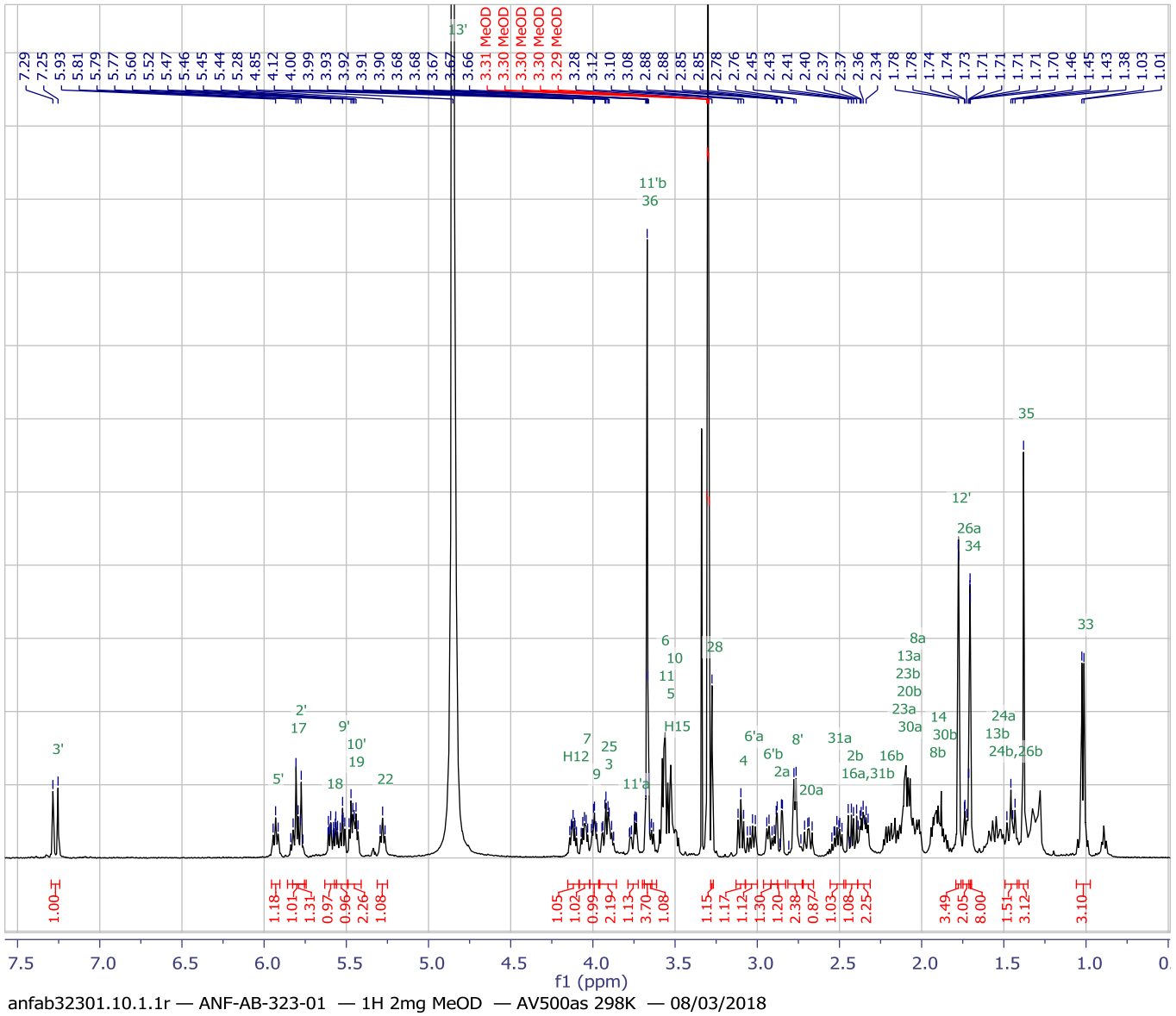
ANF-AB-323-01 2 mg MeOD 298 K

Atom	ChemicalShift	J	COSY	HSQC	HMBC	NOESY
19C	78.72			19	17, 18, 20a, 20b	
H	5.45	6.50(18), 5.10(20b), 9.50(20a)	20a, 20b, 18	19		34, 17, 20b, 20a
20C	38.4			20a, 20b	34, 18, 22	
Ha	2.69	9.50(19), 13.70(20b)	20b, 19	20	34, 18, 22, 19	34, 19, 18, 20b, 23b
Hb	2.09	5.10(19), 13.70(20a)	20a, 19	20	34, 18, 22, 19	34, 19, 18, 20a
21C	151.88				23a, 23b, 34	
22C	109.2			22	34,20a, 20b, 24a, 24b	
H	5.28	7.40(23a), 7.40(23b)	23b, 23a, 34	22	34, 23, 20, 24	23a, 23b, 34, 24a, 24b, 25
23C	34.77			23a, 23b	34a, 34b, 22	
Ha	2.13	7.40(22)	34a, 34b, 23b, 22	23	21, 25, 24	22, 25
Hb	2.1	7.40(22)	34a, 34b, 23a, 22	23	21,24	22,25, 20a
24C	37.04			34a, 34b	22,23a, 23b, 26a, 26b	
Ha	1.52		25, 24b, 23b, 23a	24	26, 23, 22, 25	22, 25
Hb	1.45		25, 24a, 23b, 23a	24	26, 23, 22, 25	28, 2, 22, 25
25C	67.68			25	34a, 24b, 28b, 23a	
H	3.90		28b, 26a, 24b, 24a	25		35,26a, 22, 23a, 23b, 24a, 24b
26C	46.46			26a, 26b	34a, 34b, 35	
Ha	1.73		26b, 25	26	27, 28, 35, 34	35, 25
Hb	1.45		26a, 25	26	27, 25, 35, 34	28
27C	72.79				28, 26a, 28b, 35	
28C	79.43			28	35, 28a, 30a	
H	3.28		35	28	29, 27, 35, 30	30b, 30a, 26b, 35, 24b, 31a, 31b
29C	98.52				30a, 30b, 31a, 31b, 28	
30C	36.59			30a, 30b	28, 31a, 31b	
Ha	2.09		31b, 30b, 31a	30	31, 29, 28, 31	30b, 28
Hb	1.88		30a, 31b, 31a	30	31, 29, 31	30a, 28, 31b
31C	31.01			31a, 31b	30a, 30b	
Ha	2.52	15.50(?), 9.10(?), 6.70(?)	30a, 30b, 31b	31	32, 29, 30	28, 31b
Hb	2.35		30a, 30b, 31a	31	32, 29, 30	28, 31a, 30b
32C	176.35				11'a, 11'b, 30a, 30b, 31a, 31b	
33C	16.68			33	H15, 13b	
H3	1.02	6.40(14)	34	33	13, 15, 14	13b, H15, 14, 16a, 16b, 17
34C	13.91			34	20a, 20b, 22	
H3	1.71		22	34	21, 22, 20	20b, 19, 22, 18, 20a
35C	11.82			35	28, 26a, 26b	
H3	1.38		28	35	26, 27, 28	26a, 28, 25
36C	52.30					
H3	3.67				1	

Atom	Chemical Shift	J	COSY	HSQC	HMBC	NOESY
N 1' H						
1' C	168.32				3', 2'	
2' C	117.21			2'	3'	
H	5.79	15.60(?)	3'	2'	4', 1'	12', 24b
3' C	150.72			3'	12', 5	
H	7.27	15.60(?)	2'	3'	4', 5', 12', 1', 2'	5'
4' C	135.10				3', 2', 6a, 6' b, 12'	
5' C	140.86			5'	12', 3', 6a, 6' b	
H	5.93	8.50(6a), 6.70(6' b)	6' a, 6' b, 12'	5'	3', 7, 12', 6'	3', 13', 6' b, 6' a, 8'
6' C	96.19			6' a, 6' b	13', 5', 8'	
Ha	3.04	15.70(6' b), 8.50(5')	6' b, 5', 13'	6'	4', 5', 7', 13', 8'	12', 13', 5', 10', 6' b, 8'
Hb	2.92	15.70(6' a), 6.70(5')	6' a, 5', 13'	6'	4', 5', 7', 13', 8'	12', 13', 5', 10', 6' a, 8'
7' C	147.34				5', 13', 6' a, 6' b, 8', 9'	
8' C	40.57			8'	13', 9', 10', 6' a, 6' b	
H2	2.77		9', 13'	8'	7', 10', 9', 13', 6'	9', 13', 5', 10', 6' a, 6' b
9' C	131.34			9'	11' a, 11' b, 8'	
H	5.53		8', 10'	9'	7', 11', 8'	12', 11' a, 11' b, 8'
10' C	129.38			10'	11' a, 11' b, 8'	
H	5.46		9', 11' a, 11' b	10'	11', 8'	12', 11' a, 11' b, 6' b, 6' a, 8'
11' C	41.86			11' a, 11' b	9', 10'	
Ha	3.75	15.40(?), 5.10(?)	10', 11' b	11'	10', 9', 32	9', 10'
Hb	3.65		11' a, 10'	11'	10', 9', 32	9', 10'
12' C	12.79			12'	3', 5'	
H3	1.78		5'	12'	3', 4', 5'	2', 6' b, 9', 10', 6' a
13' C	113.05			13'	6' a, 6' b, 8'	
H2	4.84		6' a, 6' b, 8'	13'	7', 6', 8'	6' b, 5', 6' a, 8'

ANF-AB-323-01 2 mg MeOD 298 K

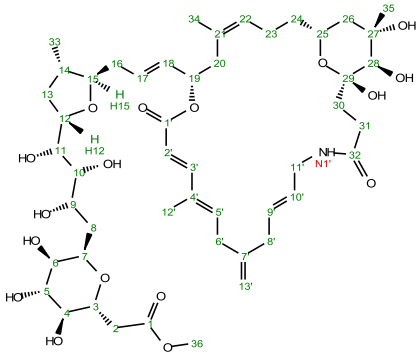


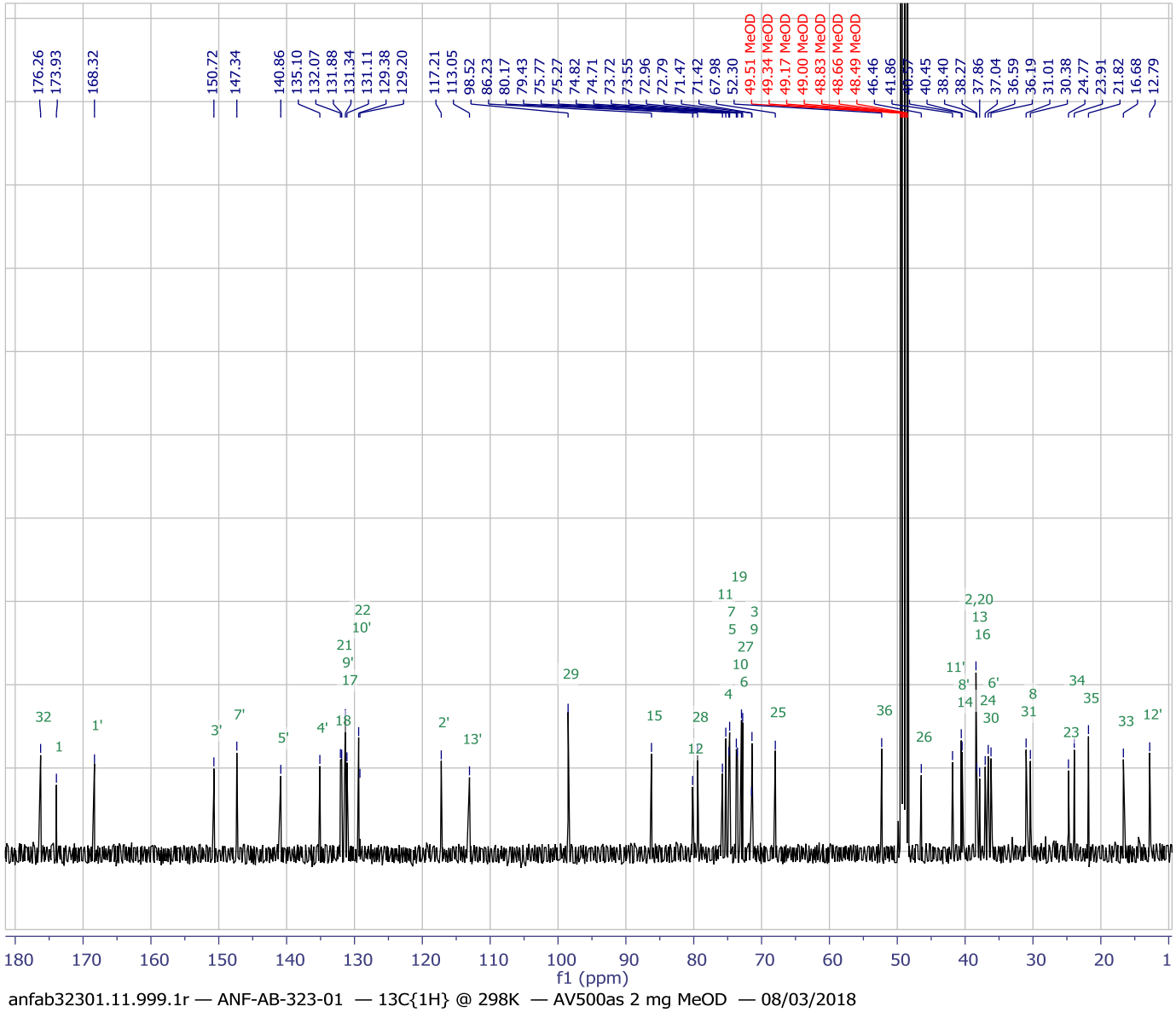


anfab32301.10.1.1r — ANF-AB-323-01 — 1H 2mg MeOD — AV500as 298K — 08/03/2018

ANF-AB-323-01

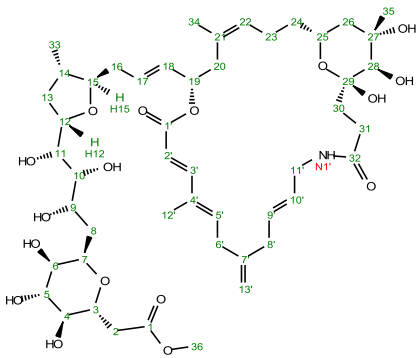
2 mg MeOD 298 K

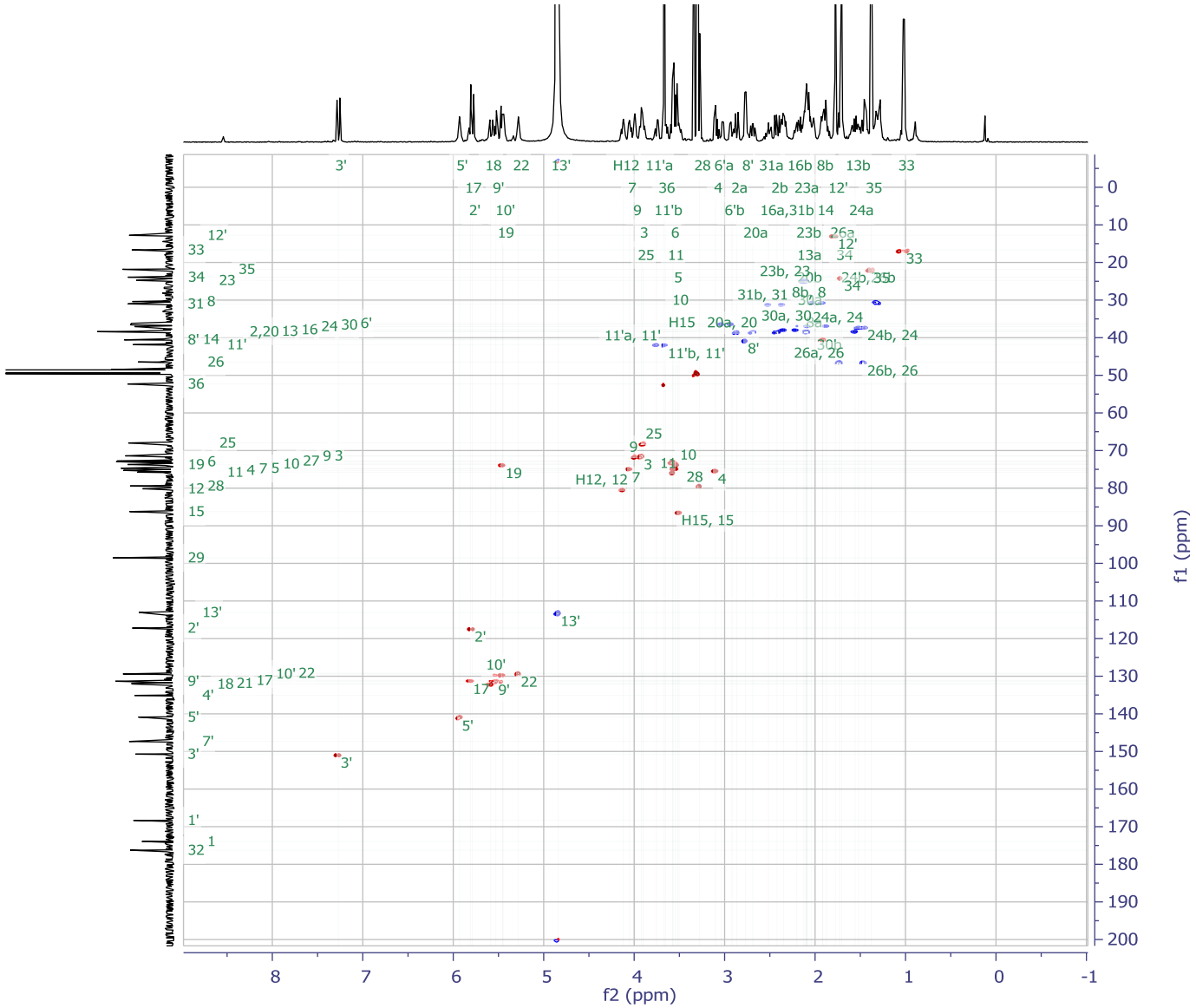




anfab32301.11.999.1r — ANF-AB-323-01 — 13C{1H} @ 298K — AV500as 2 mg MeOD — 08/03/2018

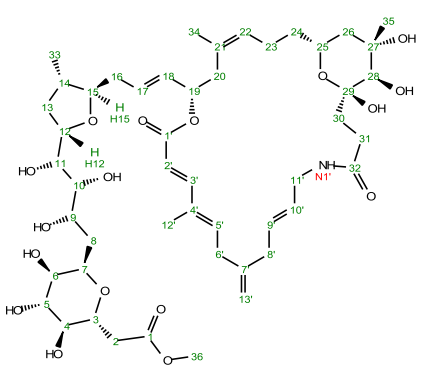
ANF-AB-323-01 2 mg MeOD 298 K

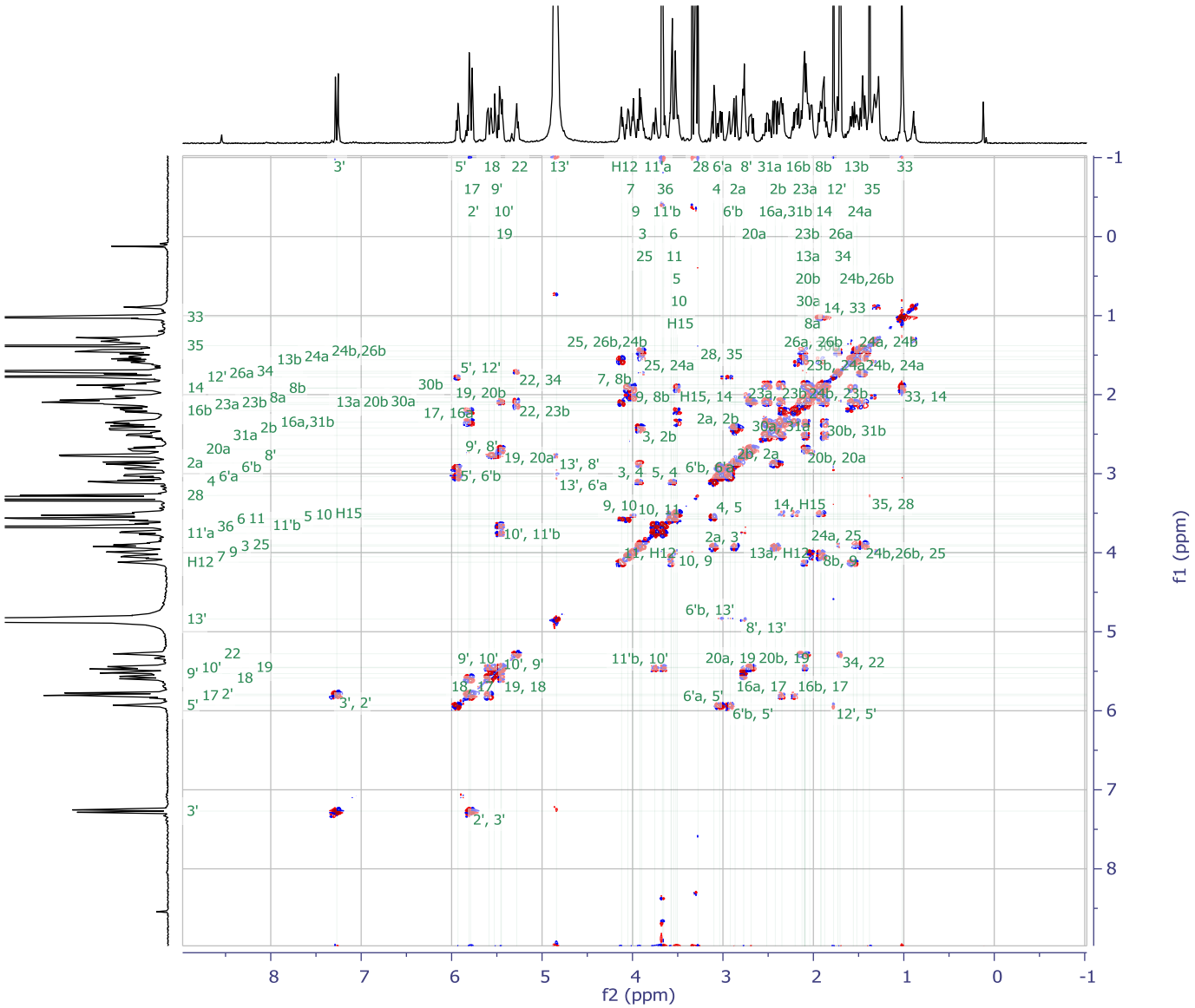




anfab32301.16.1.2rr — ANF-AB-323-01 — HSQCEDETGPSI @ 298K — AV500as 2 mg MeOD — 09/03/2018

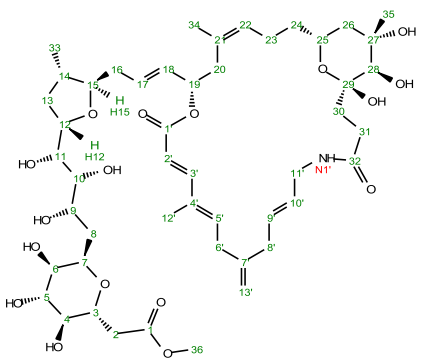
ANF-AB-323-01 2 mg MeOD 298 K

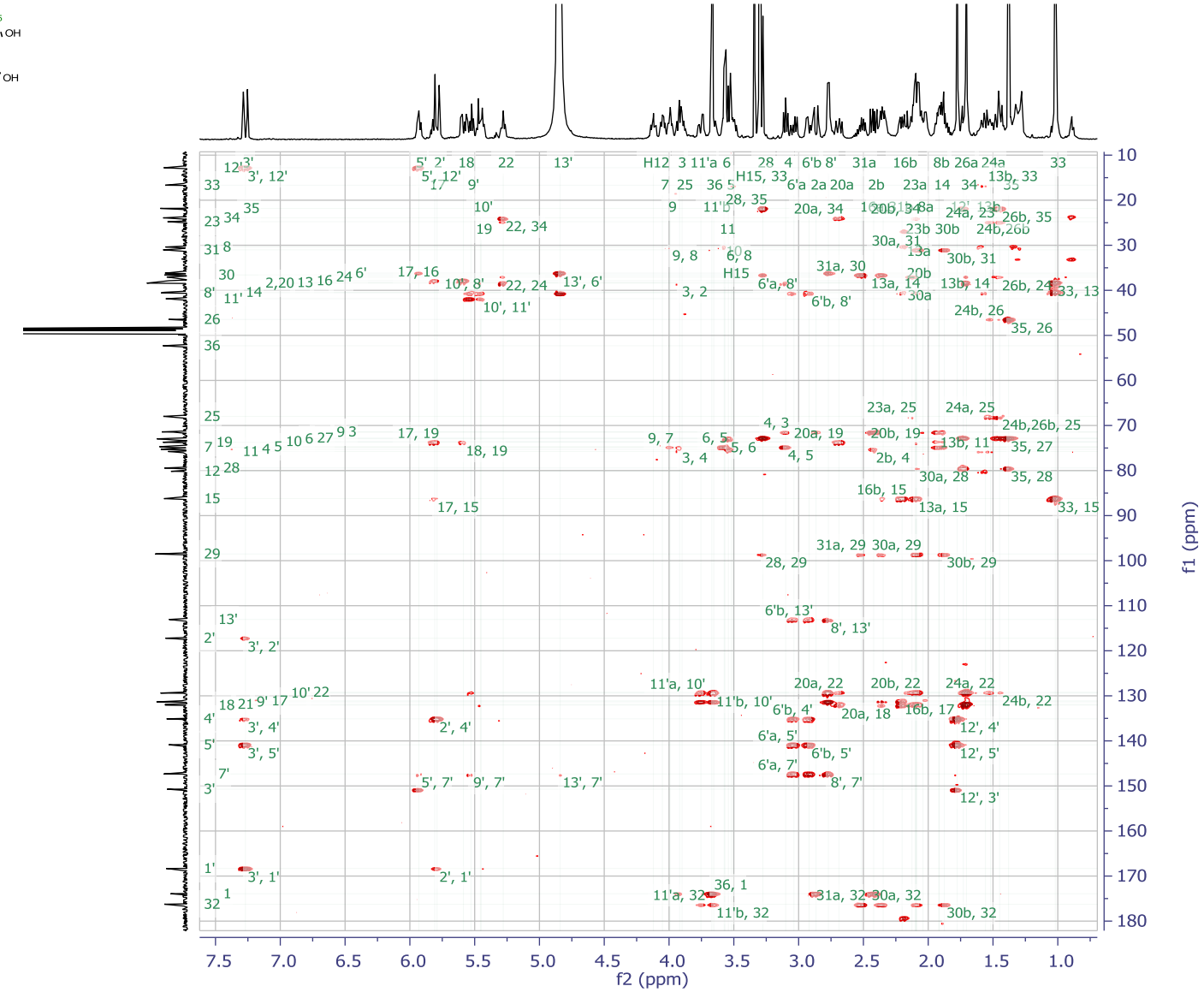




anfab32301.15.1.2rr — ANF-AB-323-01 — 2 mg 298 K C6D6 — cosygpmfphpp AV500as — 09/03/2018

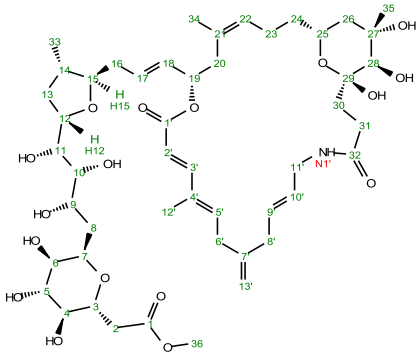
ANF-AB-323-01 2 mg MeOD 298 K

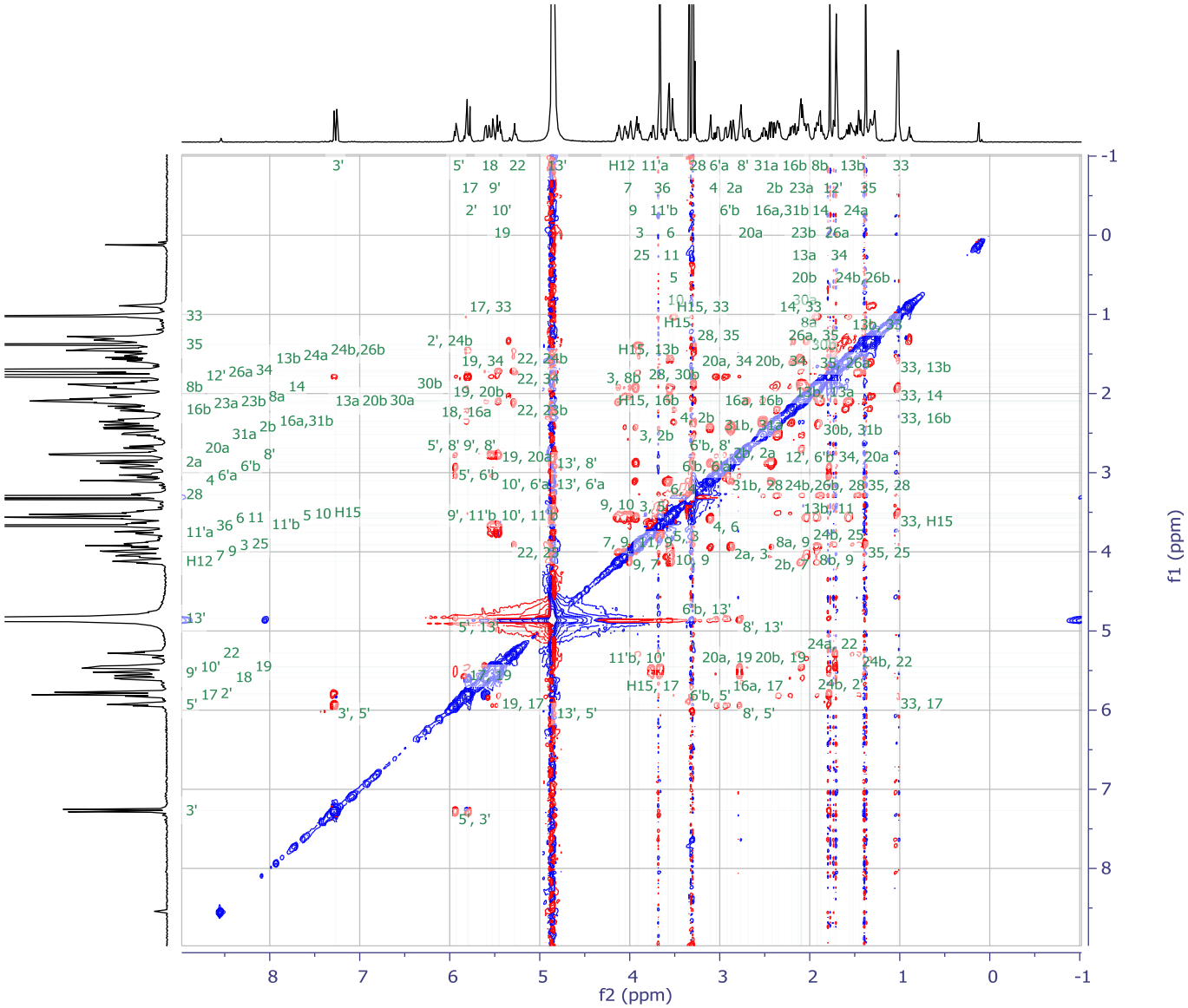




anfab32301.17.1.2rr — ANF-AB-323-01 — HMBC @298K — AV500as 2 mg MeOD — 10/03/2018

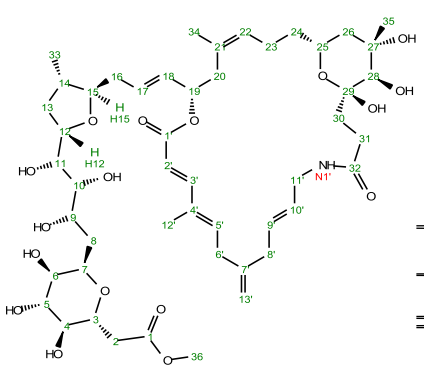
ANF-AB-323-01 2 mg MeOD 298 K

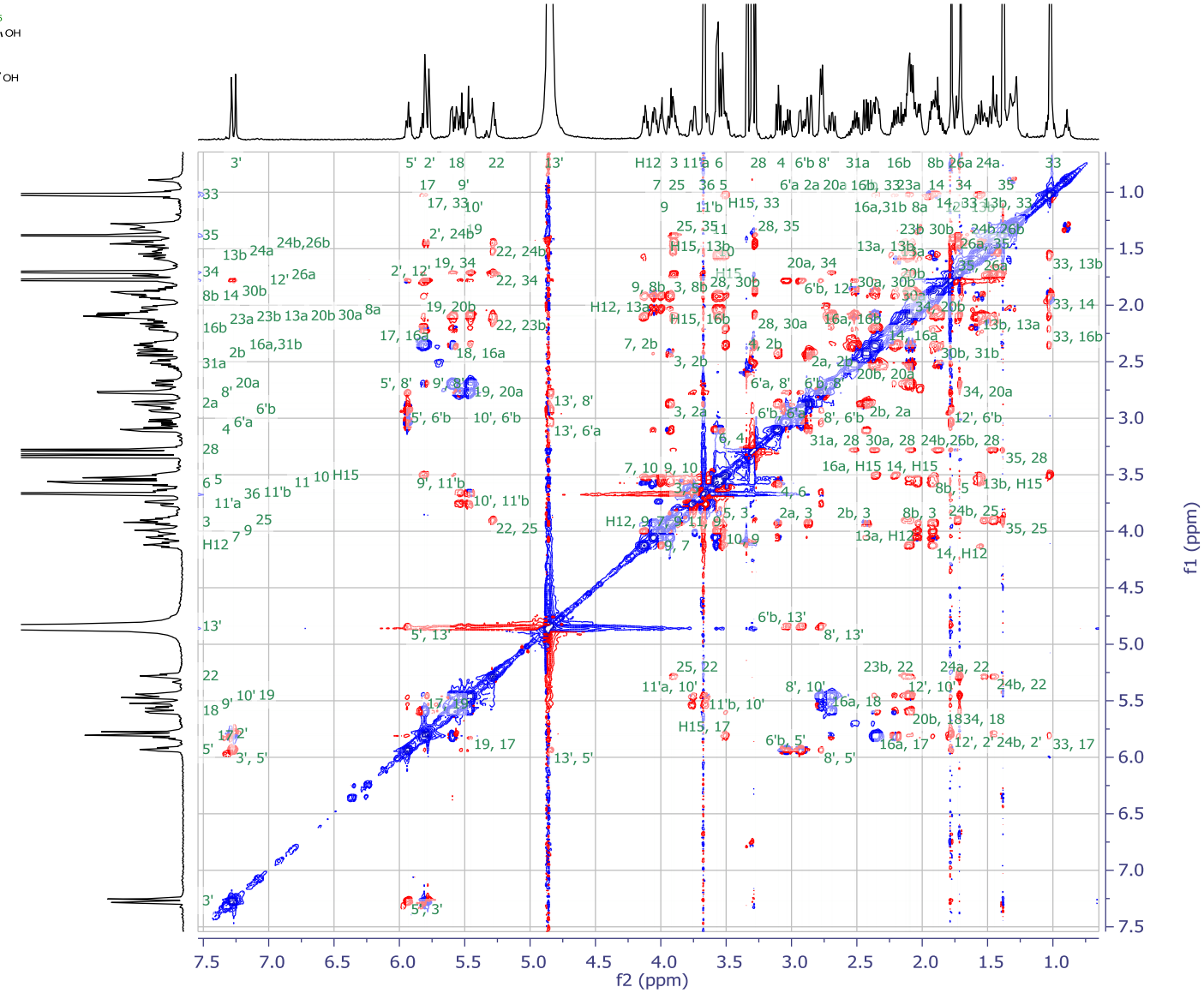




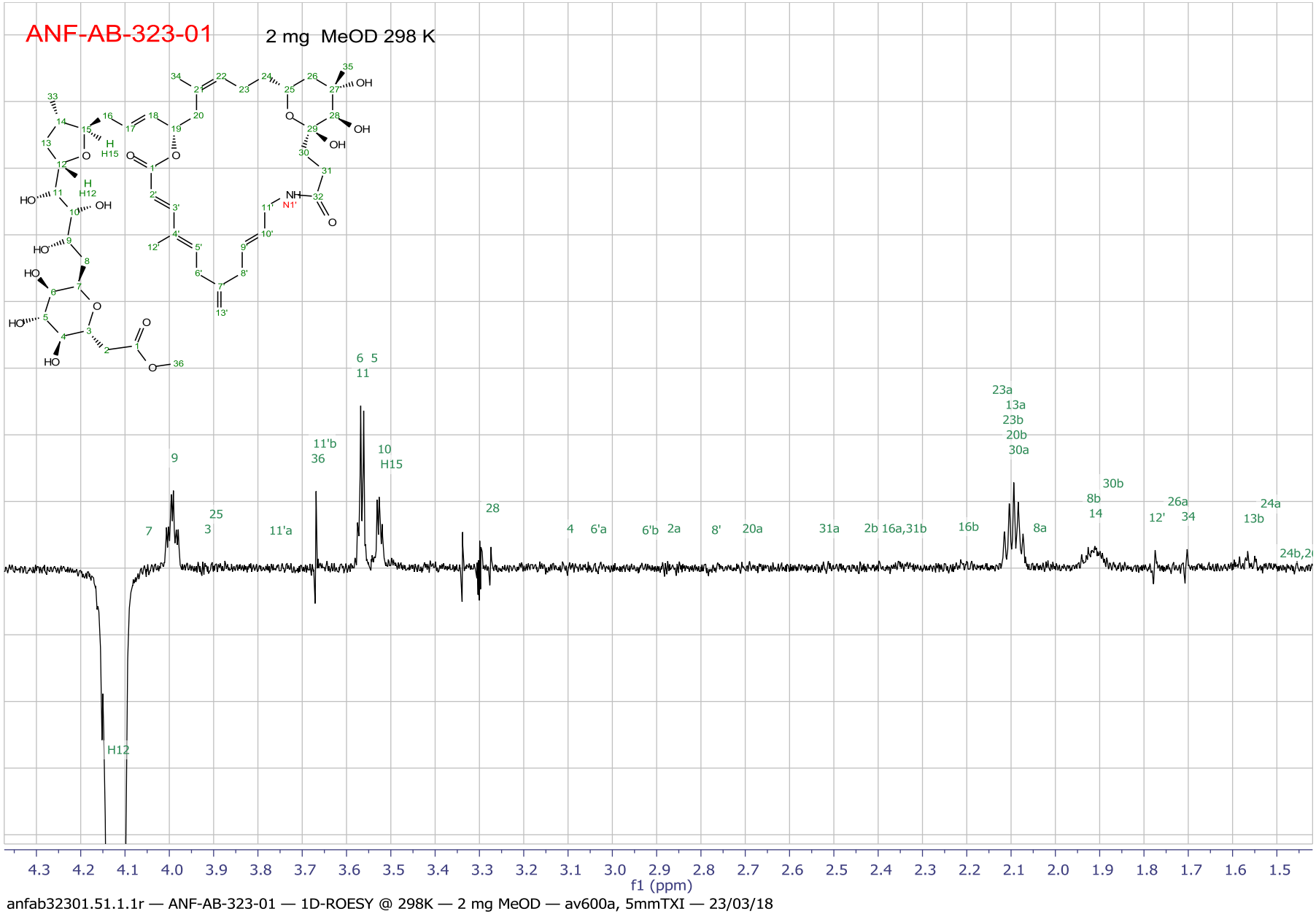
anfab32301.18.1.2rr — ANF-AB-323-01 — noesygpph @ 298K — AV500as 2 mg MeOD — 11/03/2018

ANF-AB-323-01 2 mg MeOD 298 K

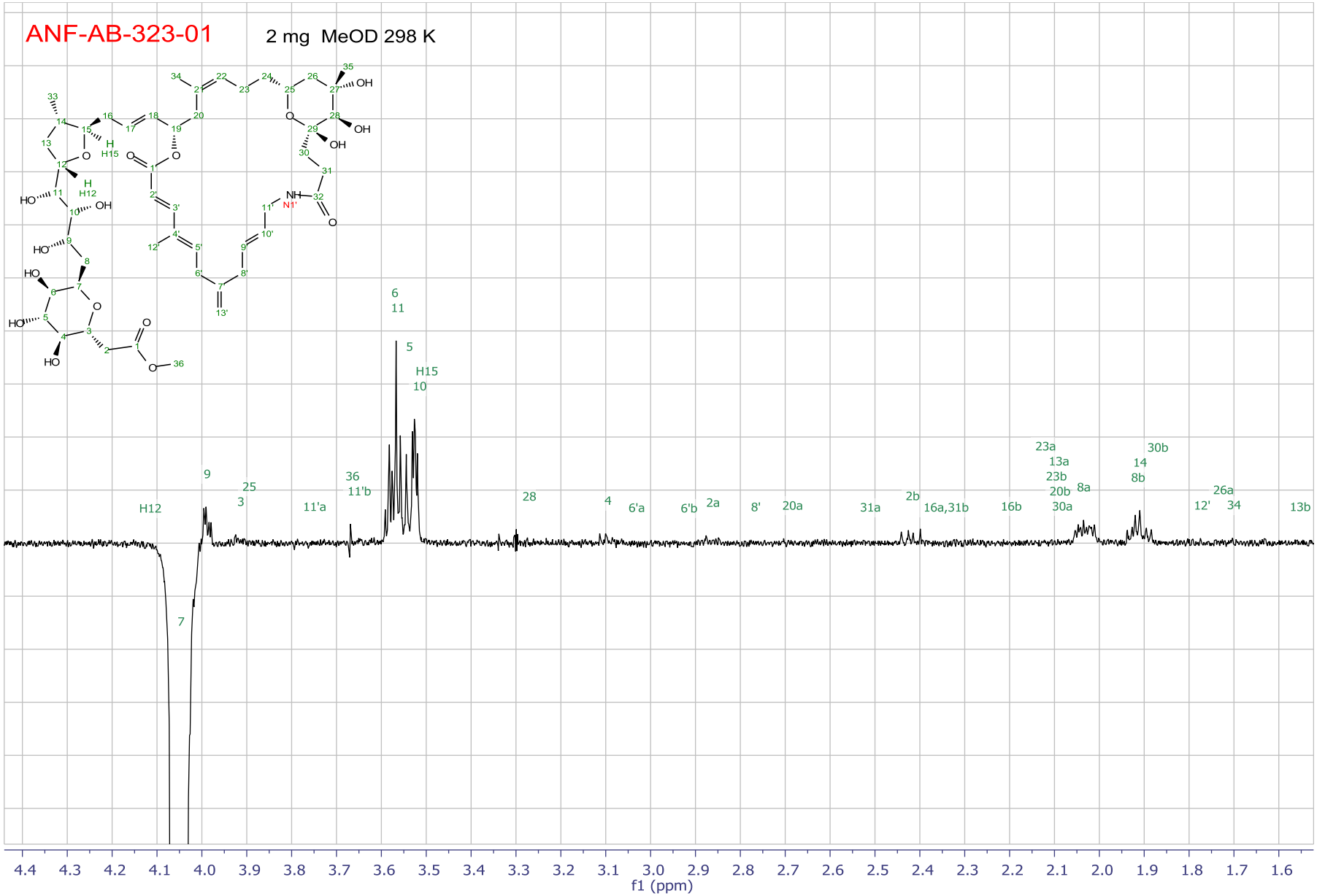




anfab32301_TXI.17.1.2rr — ANF-AB-323-01 — roesygpph @ 298K — 2 mg MeOD — av600a, 5mmTXI — 23/03/18

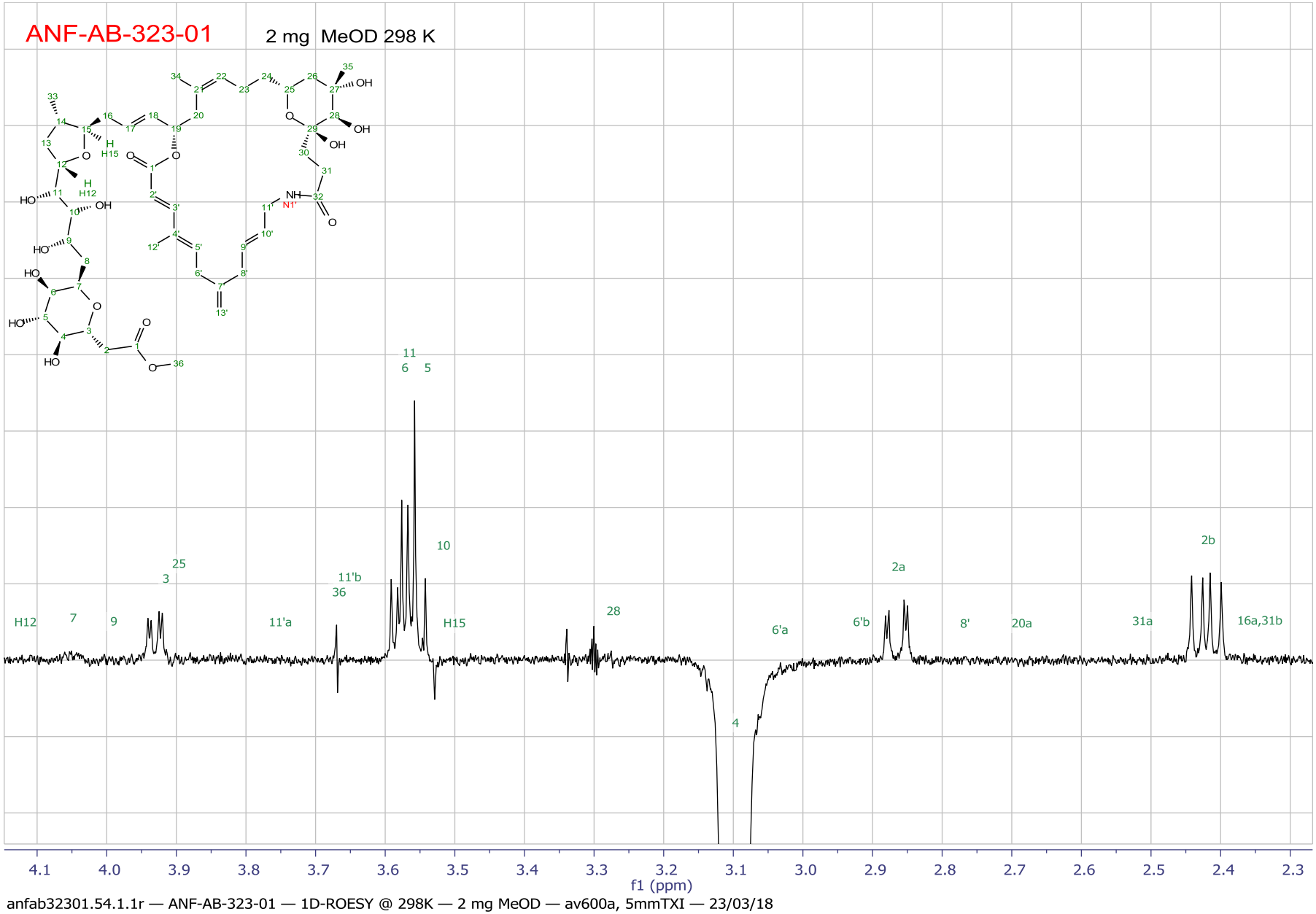


anfab32301.51.1.1r — ANF-AB-323-01 — 1D-ROESY @ 298K — 2 mg MeOD — av600a, 5mmTXI — 23/03/18



anfab32301.52.1.1r — ANF-AB-323-01 — 1D-ROESY @ 298K — 2 mg MeOD — av600a, 5mmTXI — 23/03/18

anfab32301.53.1.1r — ANF-AB-323-01 — 1D-ROESY @ 298K — 2 mg MeOD — av600a, 5mmTXI — 23/03/18



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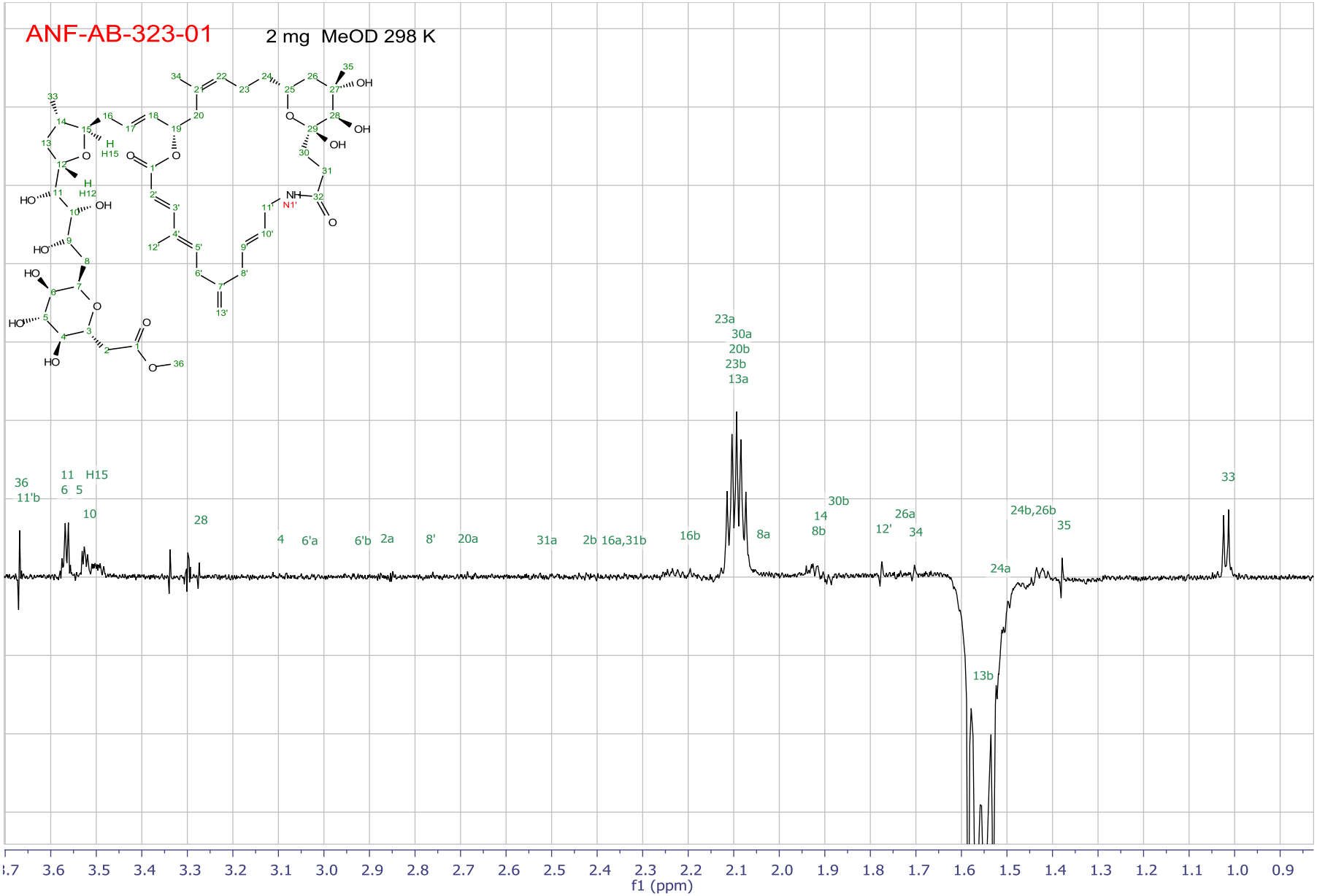

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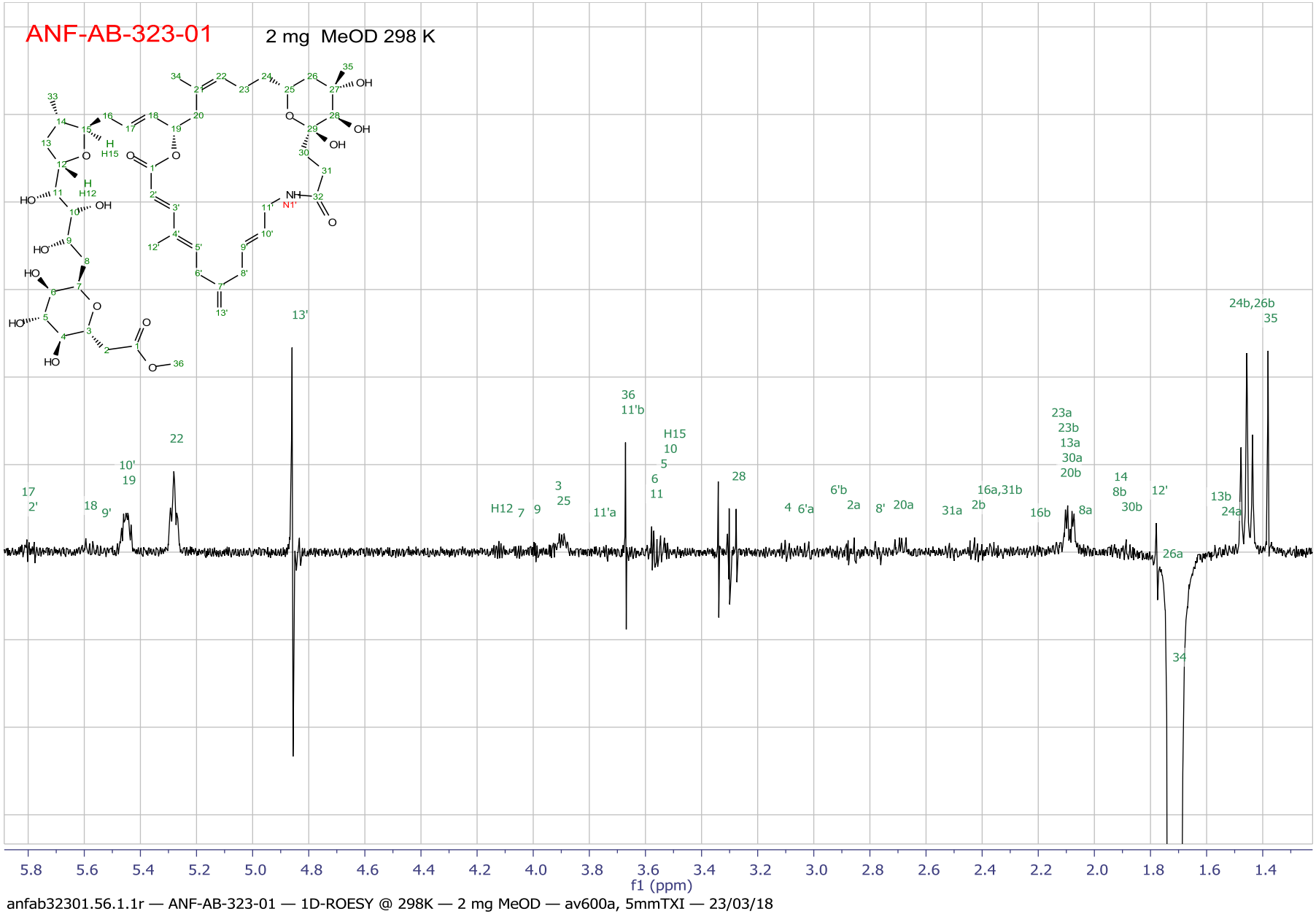
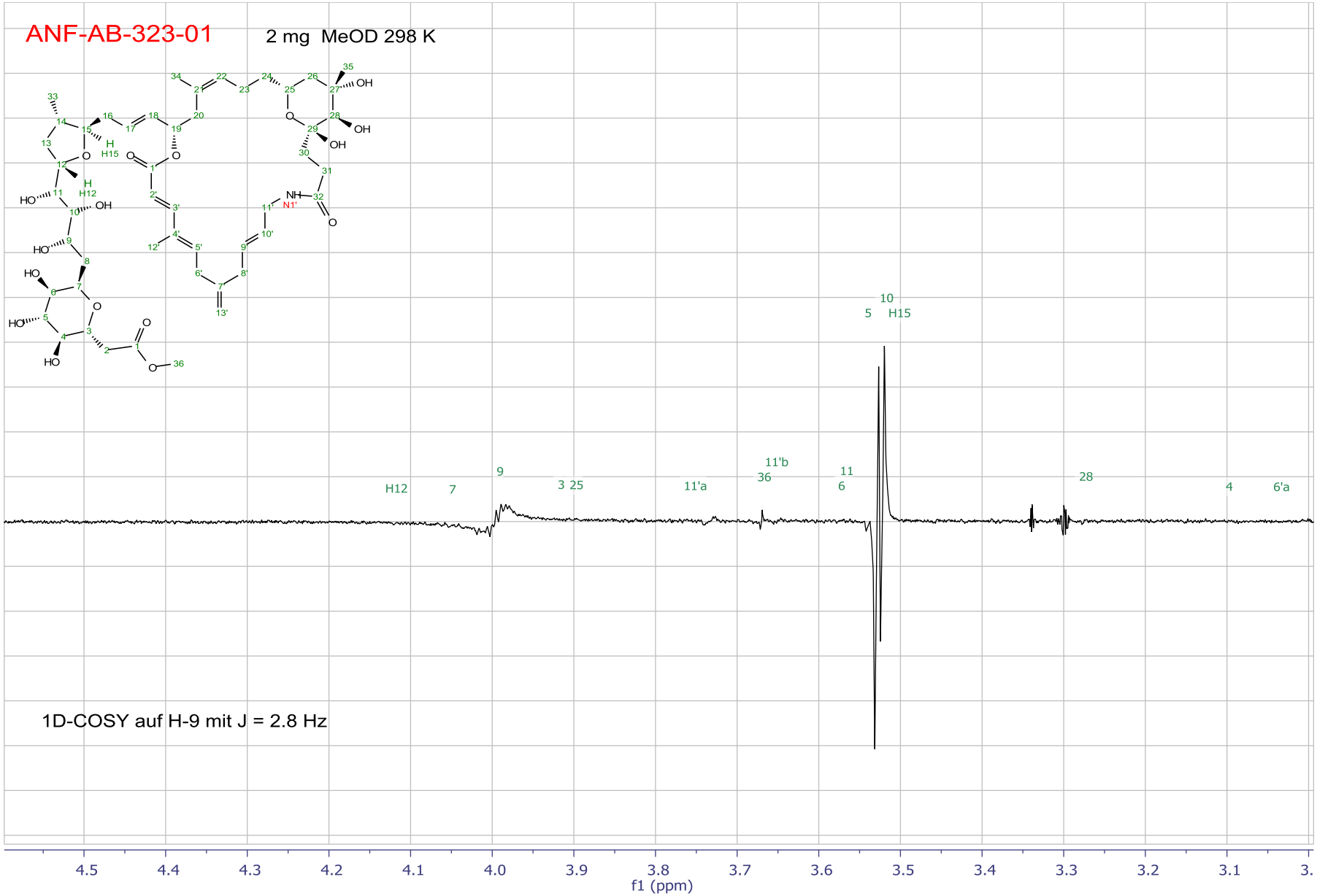
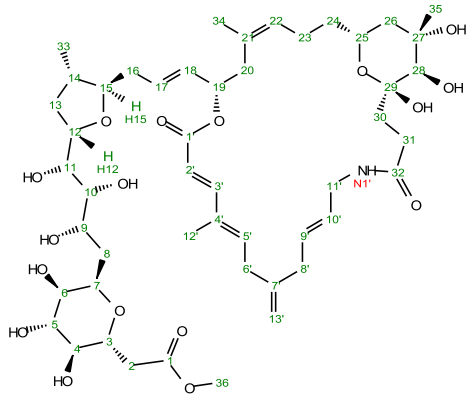


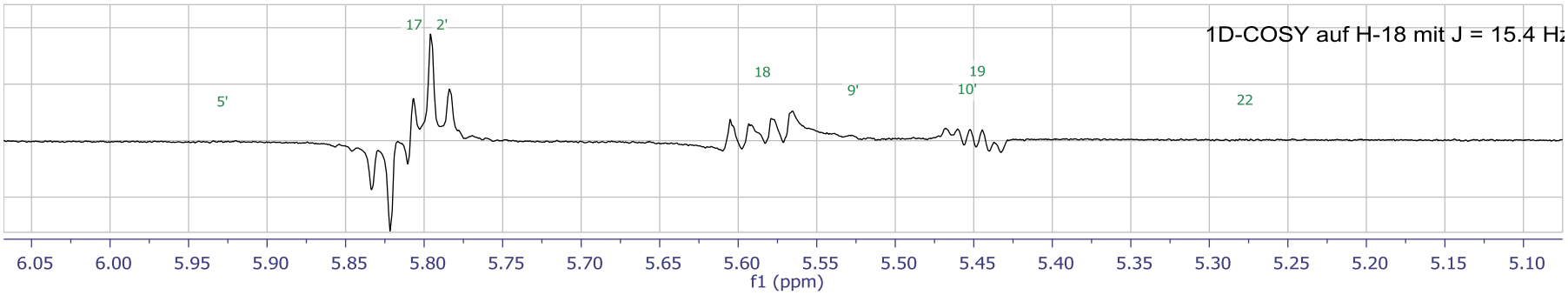
anfab32301.56.1.1r — ANF-AB-323-01 — 1D-ROESY @ 298K — 2 mg MeOD — av600a, 5mmTXI — 23/03/18

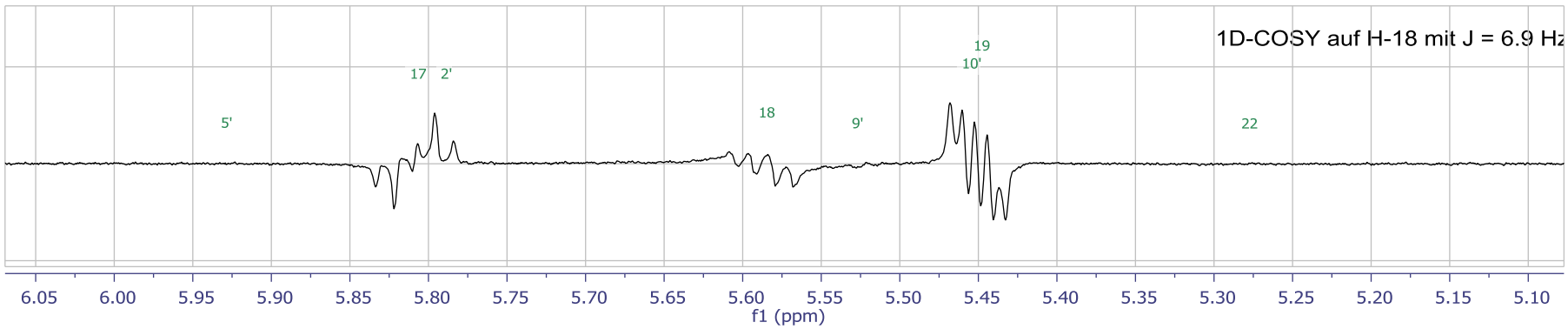


anfab32301.33.1.1r — ANF-AB-323-01 — 1D-COSY @ 298K — H9, J = 2.8 Hz — 2 mg MeOD — av600a, 5mmTXI — 16/03/18

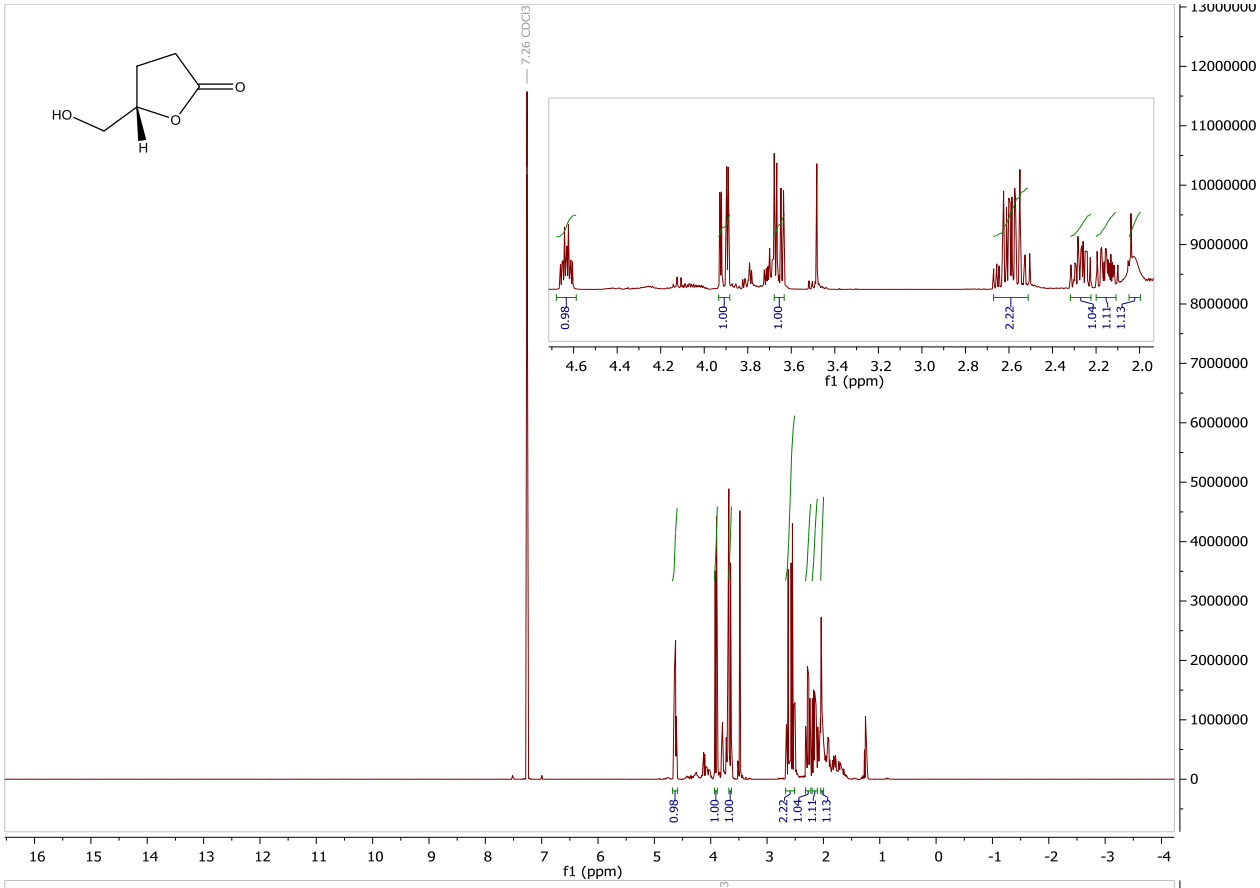
ANF-AB-323-01 2 mg MeOD 298 K

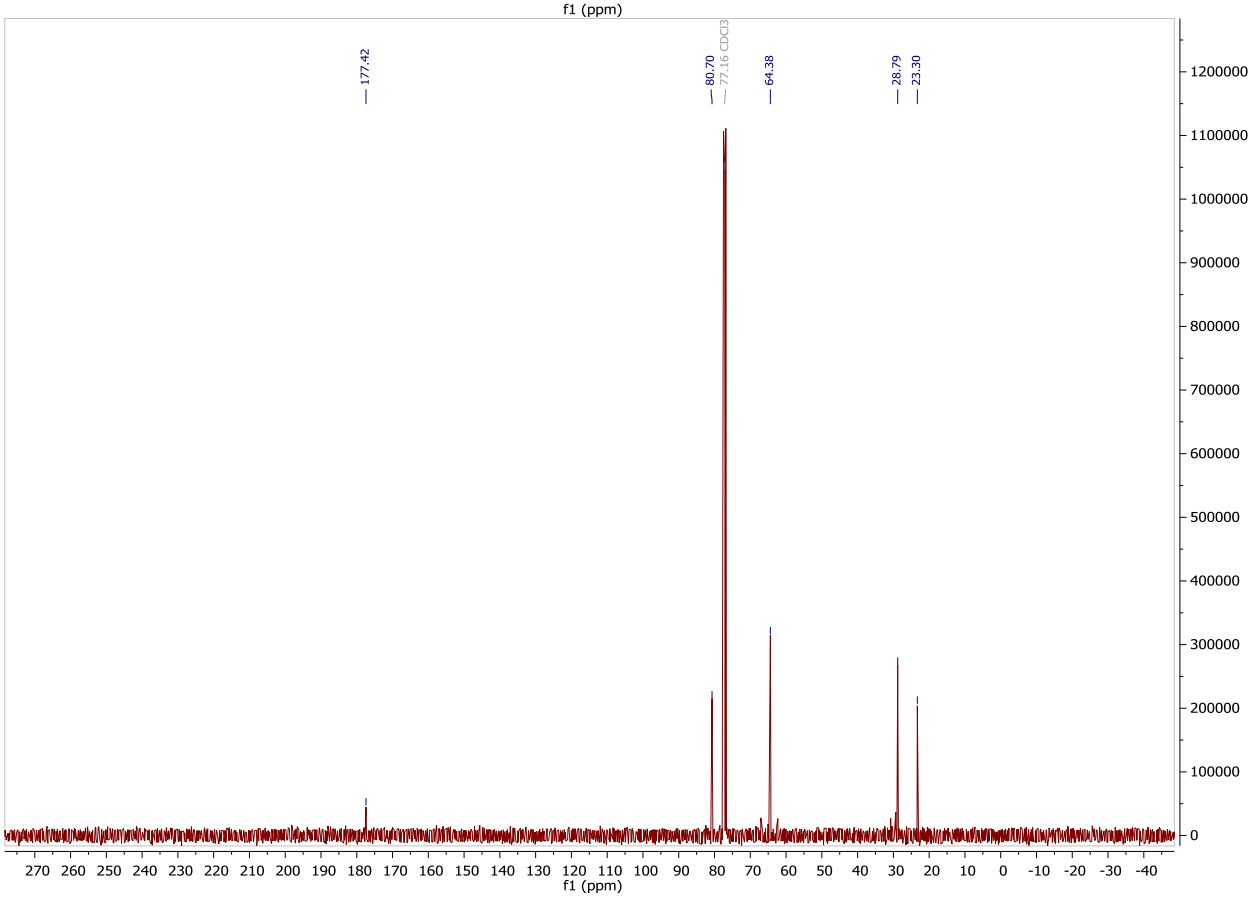


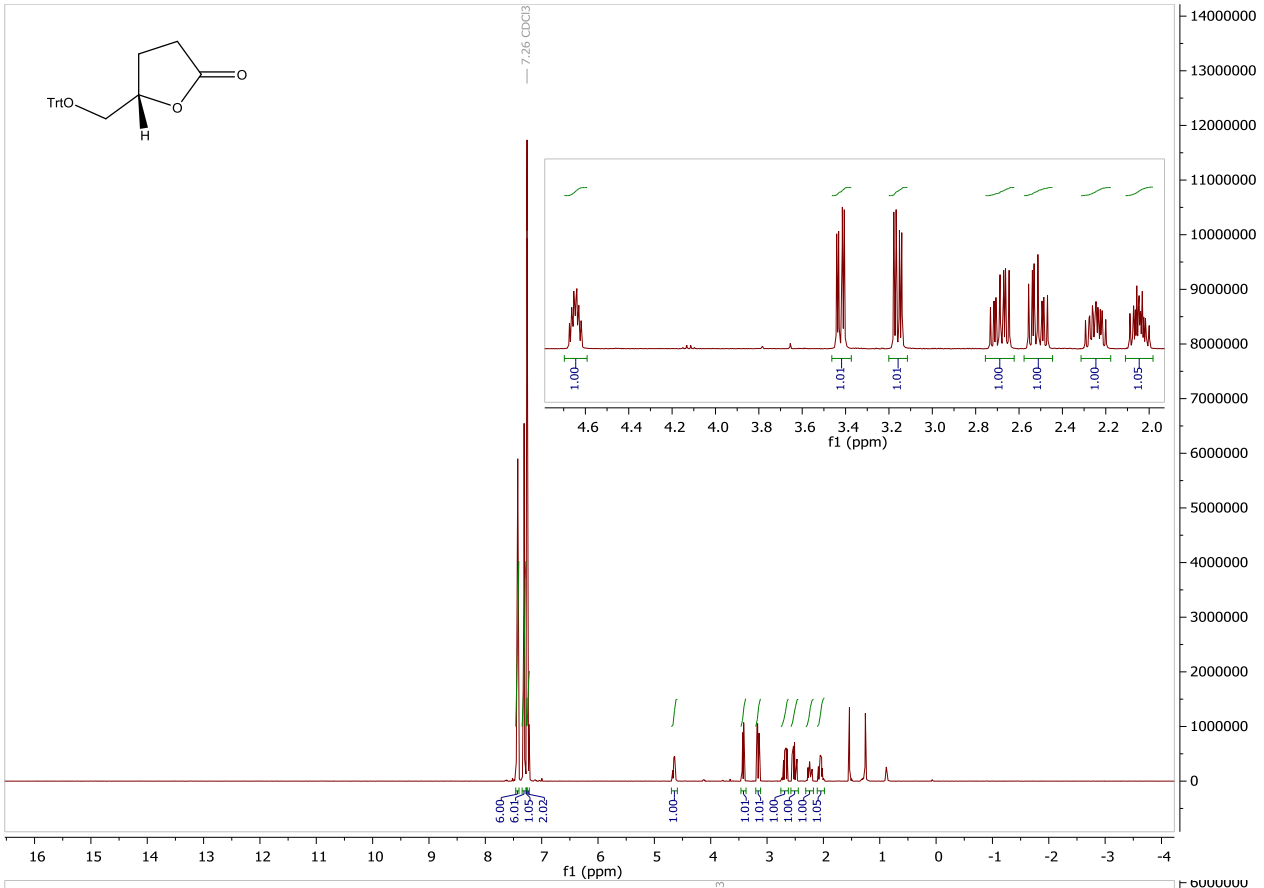


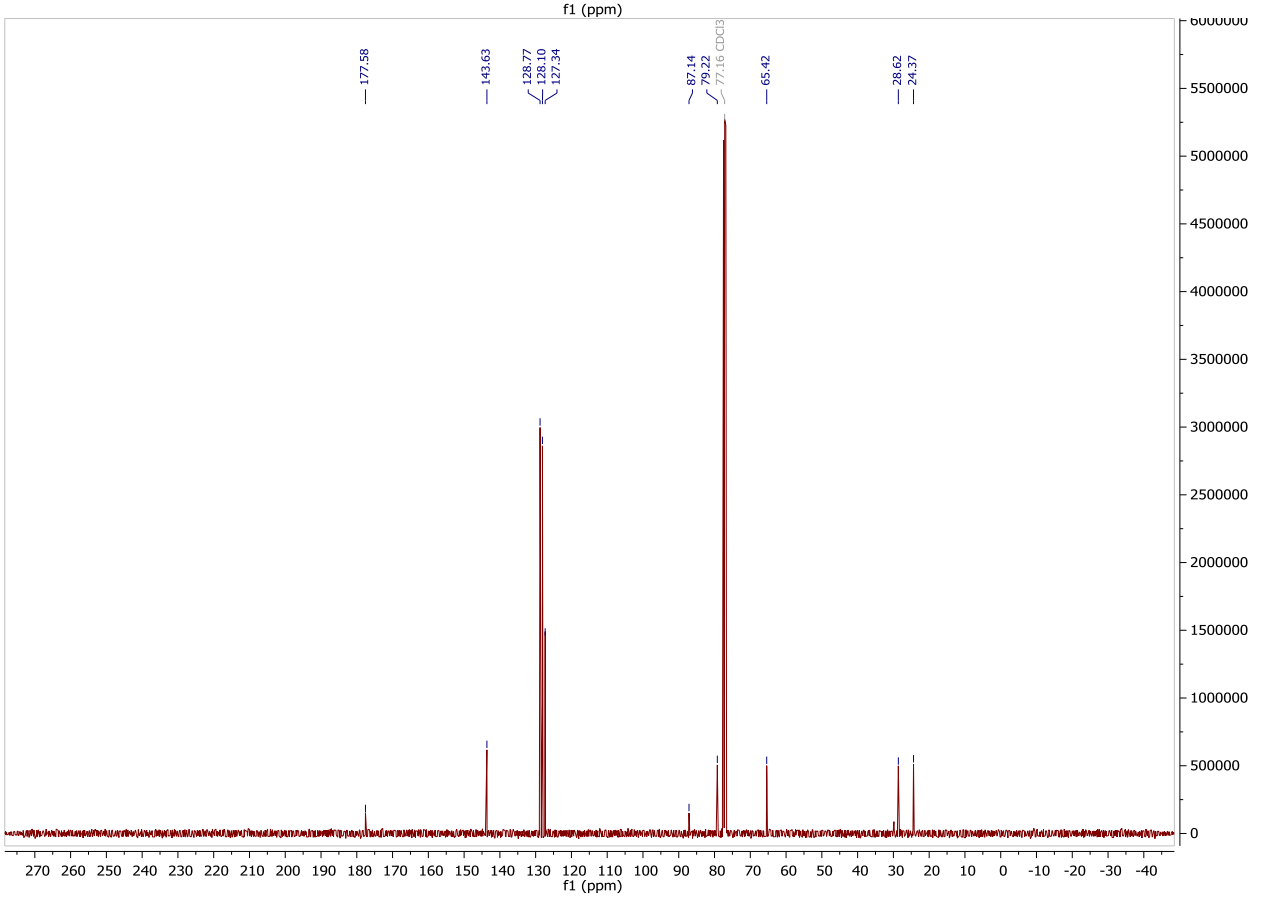


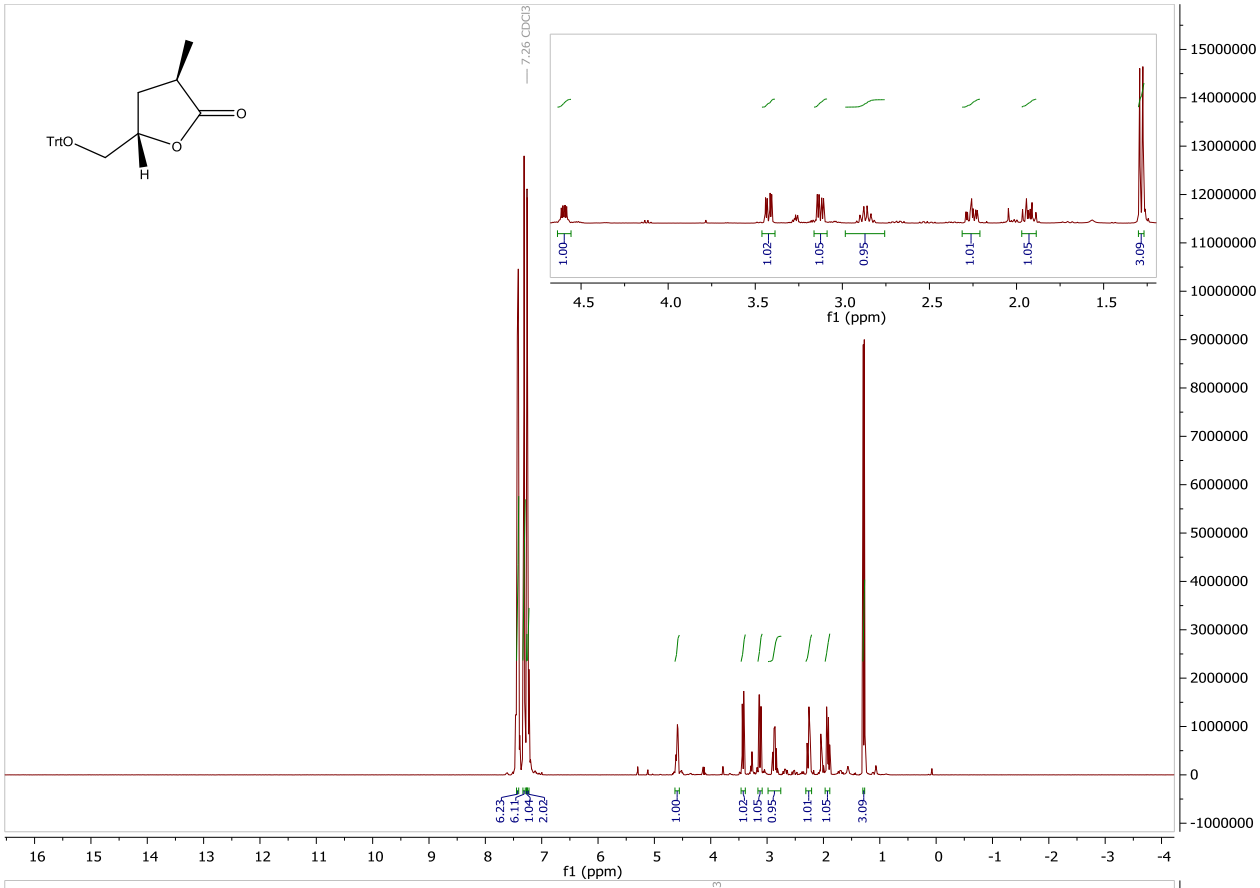
anfab32301.38.1.1r — ANF-AB-323-01 — 1D-COSY @ 298K — H18, J = 6.9 Hz — 2 mg MeOD — av600a, 5mmTXI — 05/04/18

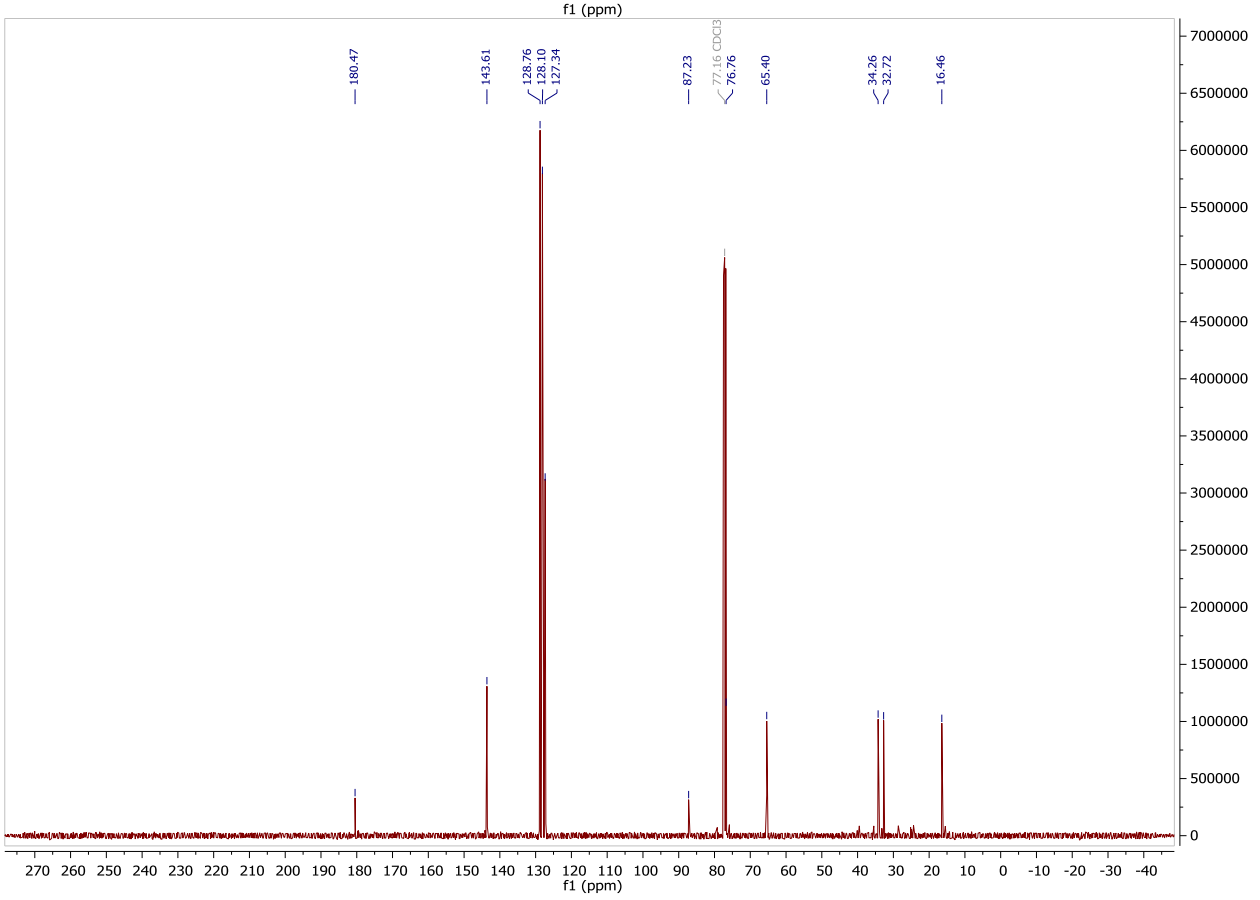

HO
O
O
H
7.26 CDCl3
0.98
1.00
1.00
2.22
1.04
1.11
1.13
f1 (ppm)

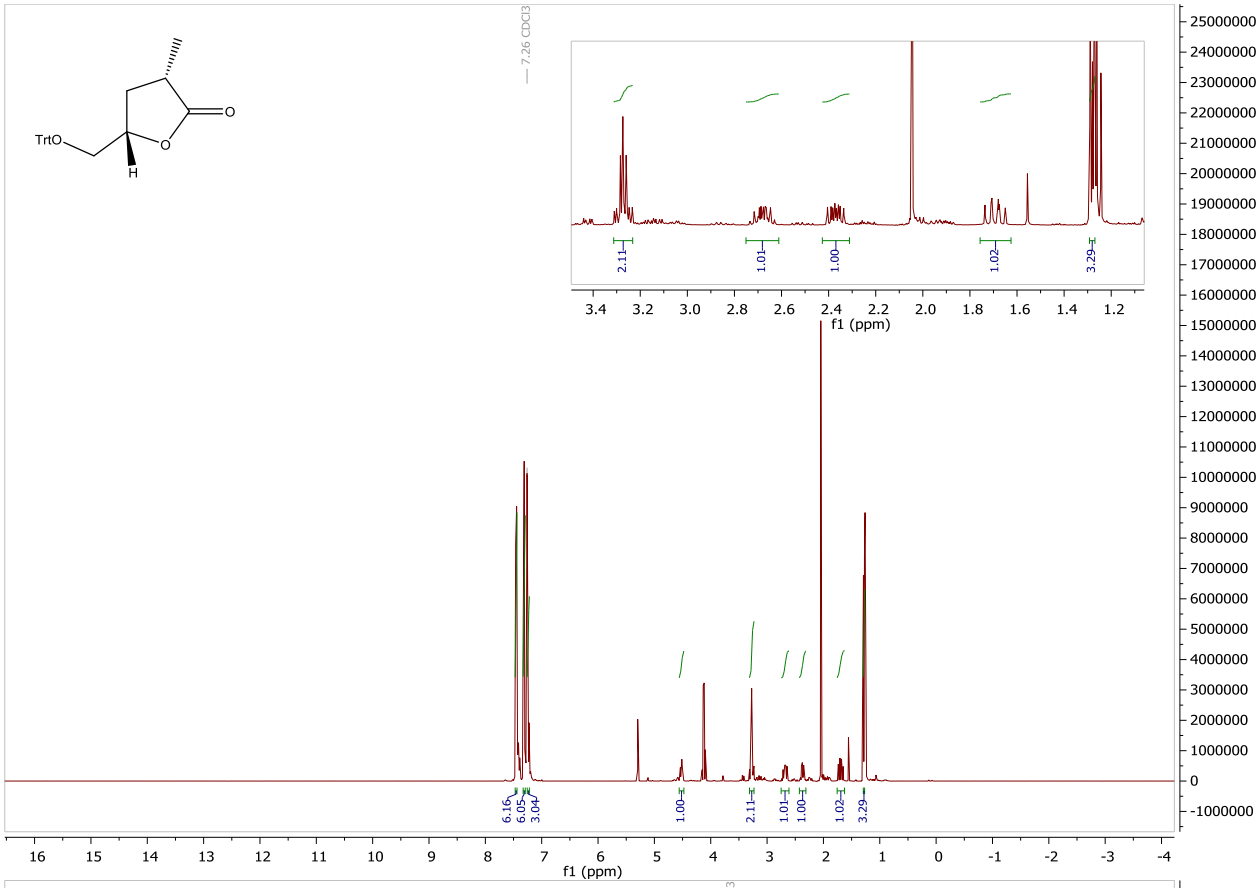

177.42
80.70
77.16 CDCl3
64.38
28.79
23.30
f1 (ppm)

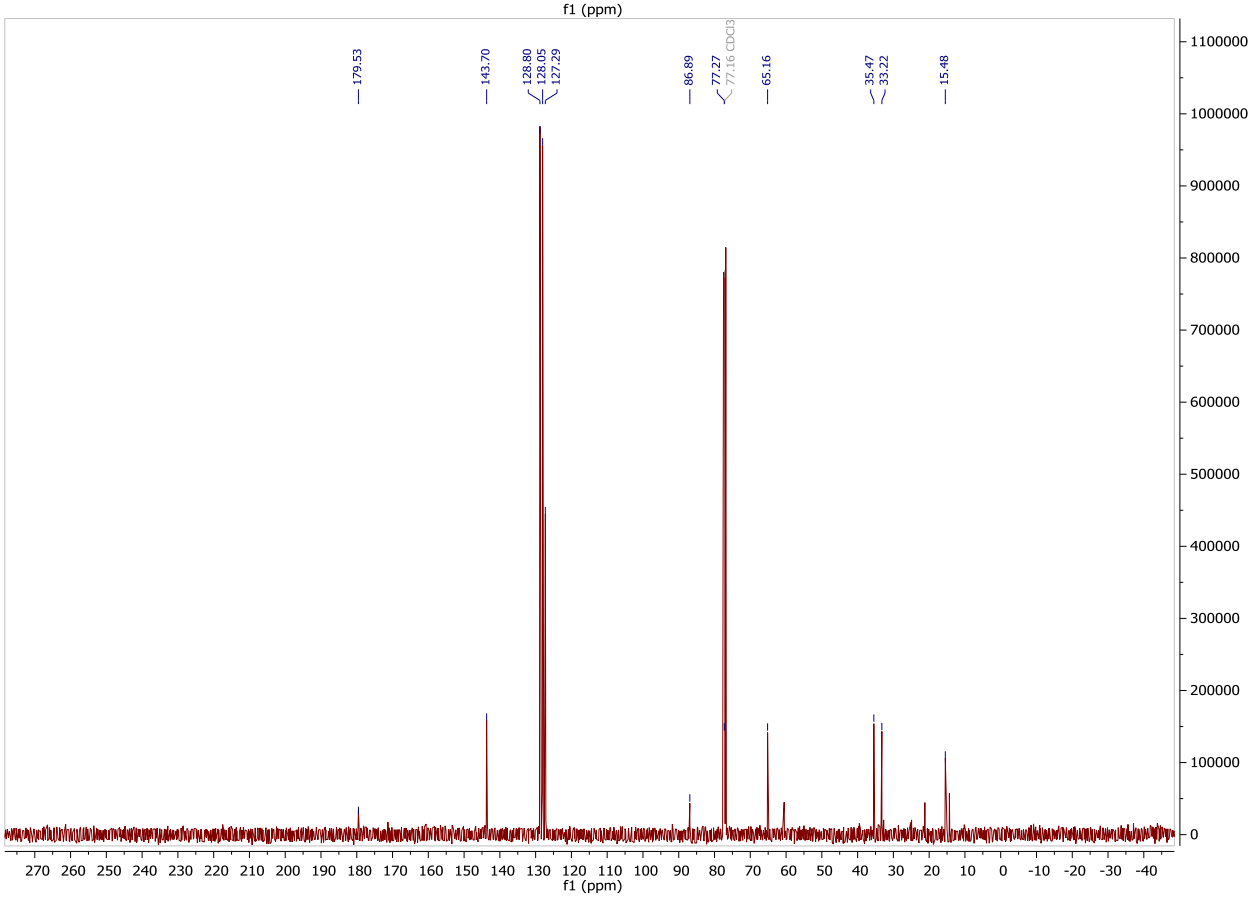

TrtO
O
O
H
7.26 CDCl3
f1 (ppm)

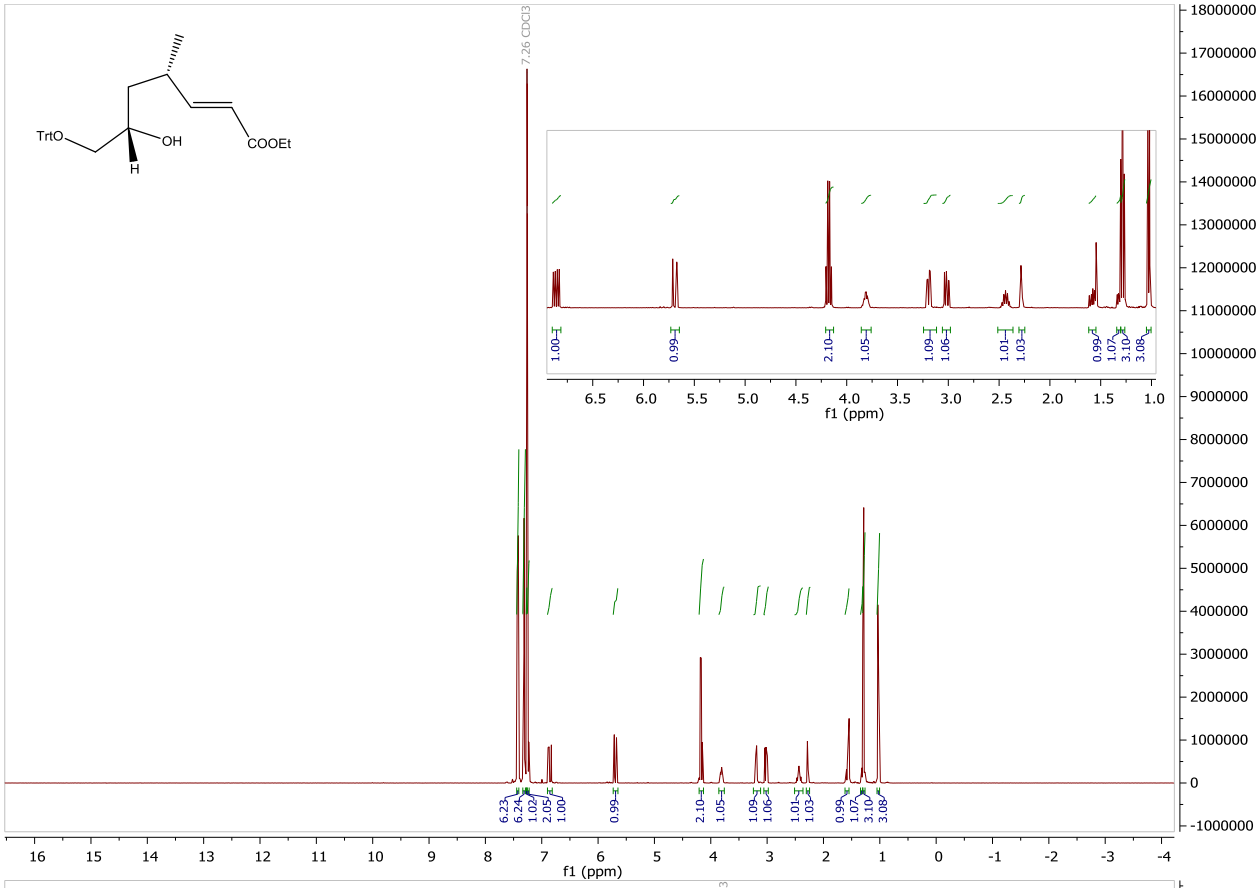

177.58
143.63
128.77
128.10
127.34
87.14
79.22
77.16 CDCl3
65.42
28.62
24.37
f1 (ppm)

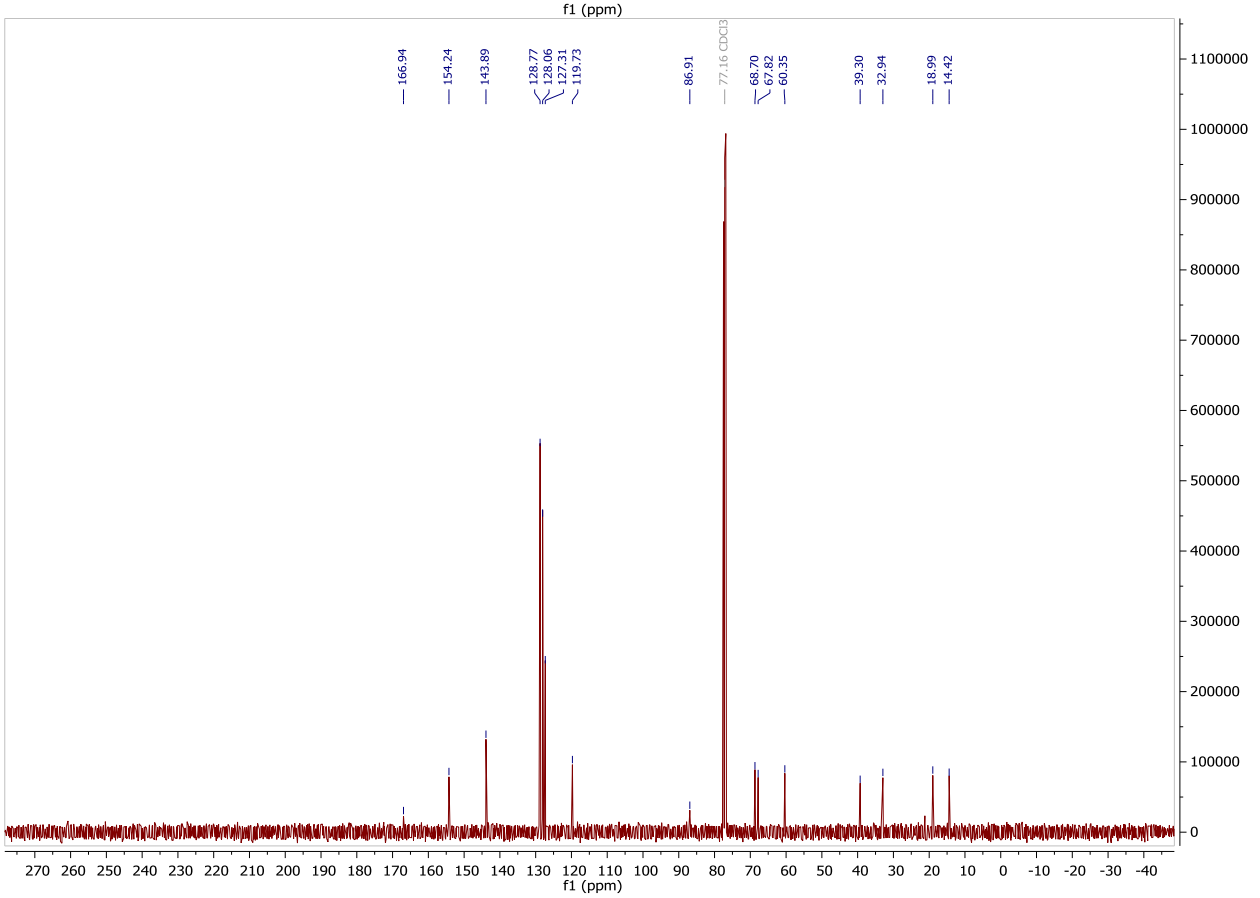

TrtO
O
O
H
7.26 CDCl3
f1 (ppm)
6.23
6.11
1.04
2.02
1.00
1.02
1.05
0.95
1.01
1.05
3.09

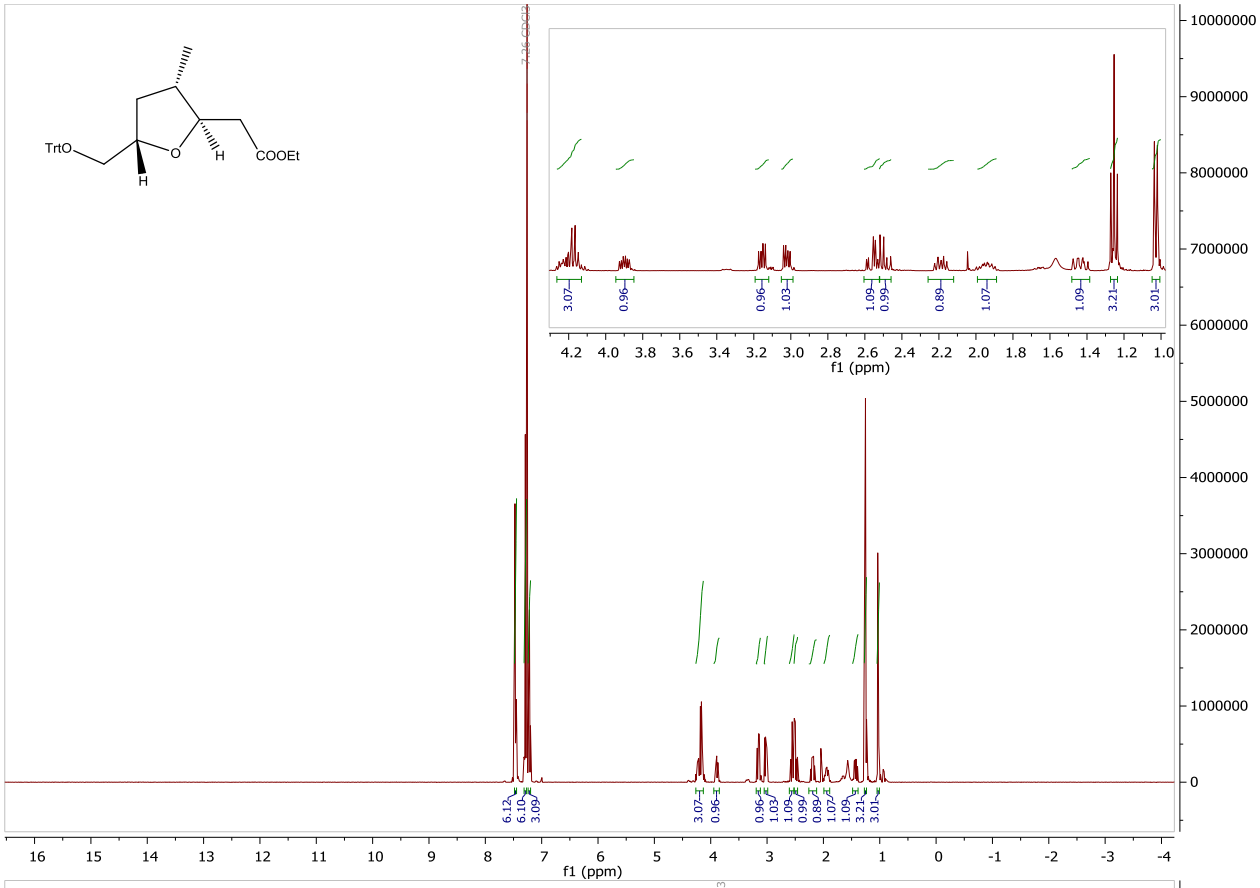

180.47
143.61
128.76
128.10
127.34
87.23
77.16 CDCl3
76.76
65.40
34.26
32.72
16.46
f1 (ppm)

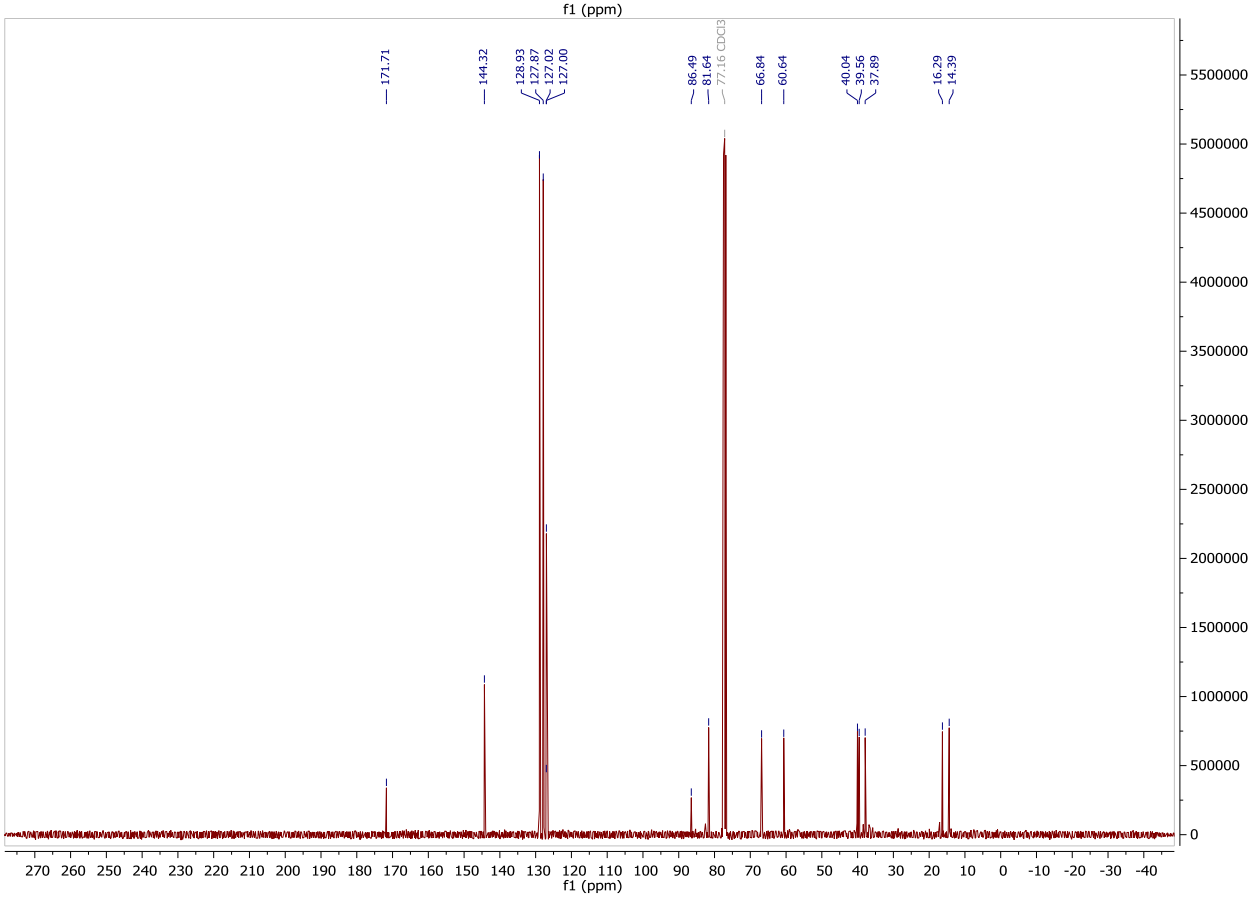

TrtO
O
O
H
7.26 CDCl3
2.11
1.01
1.00
1.02
3.29
f1 (ppm)
6.16
6.05
3.04
1.00
2.11
1.01
1.00
1.02
3.29
f1 (ppm)

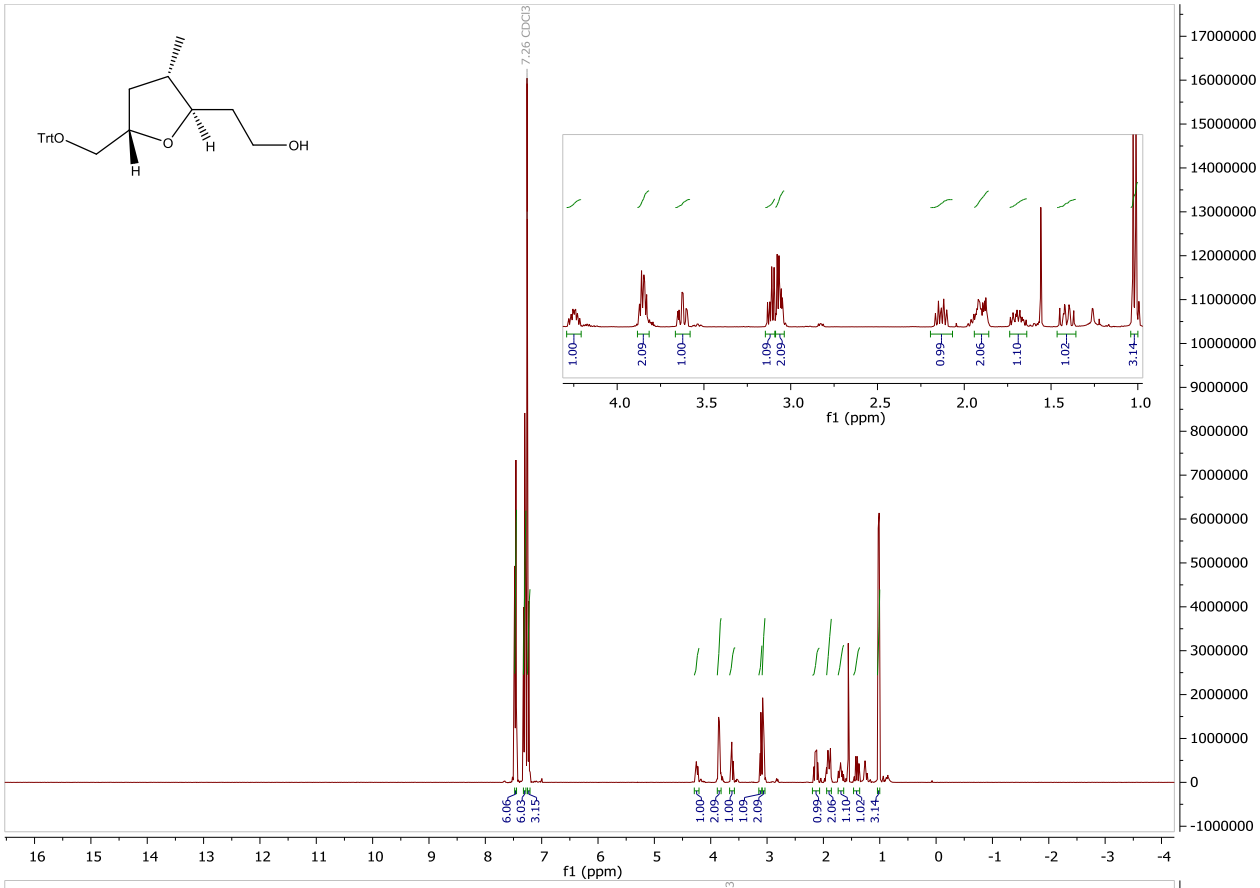

179.53
143.70
128.80
128.05
127.29
86.89
77.27
77.16 CDCl3
65.16
35.47
33.22
15.48
f1 (ppm)

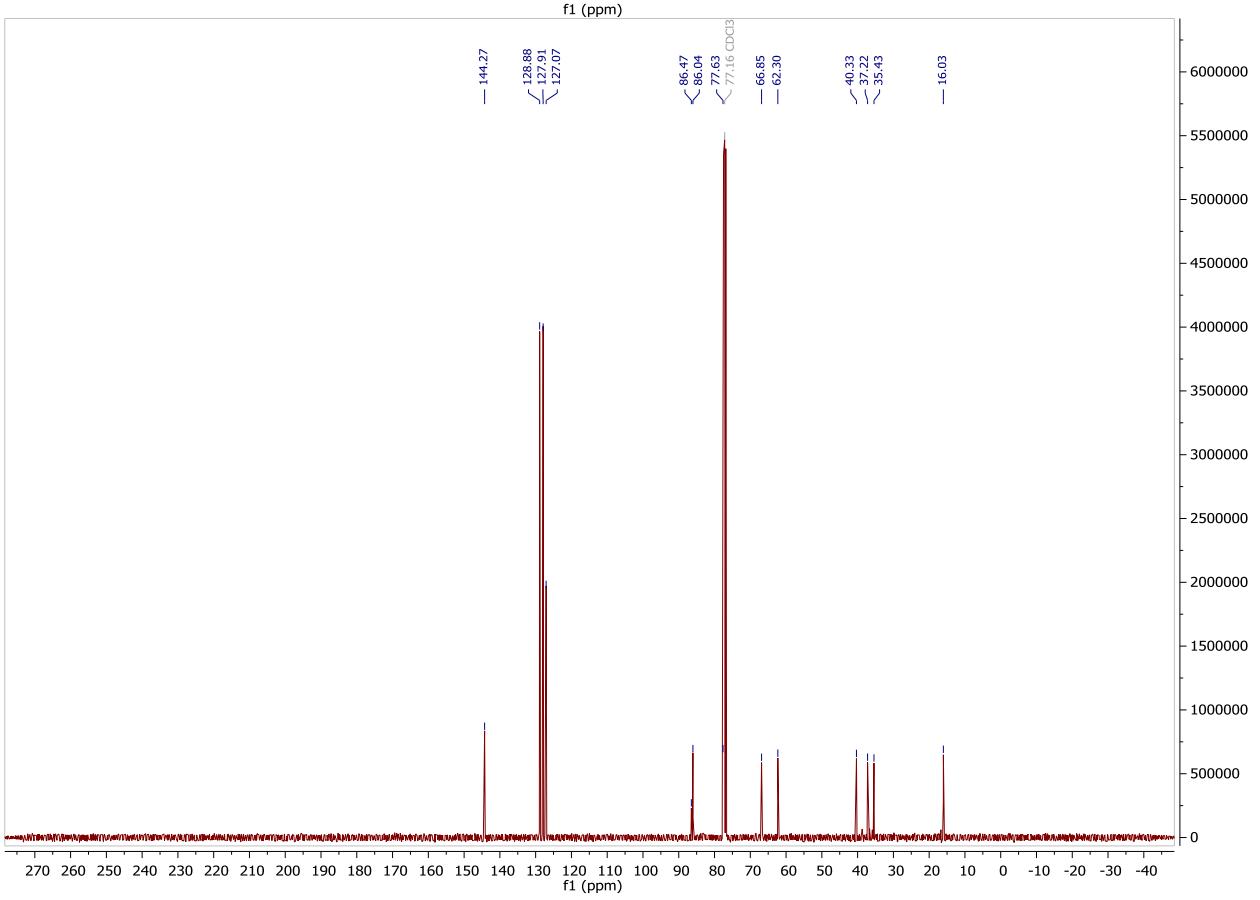

TrtO
OH
COOEt
H
7.26 CDCl3
f1 (ppm)

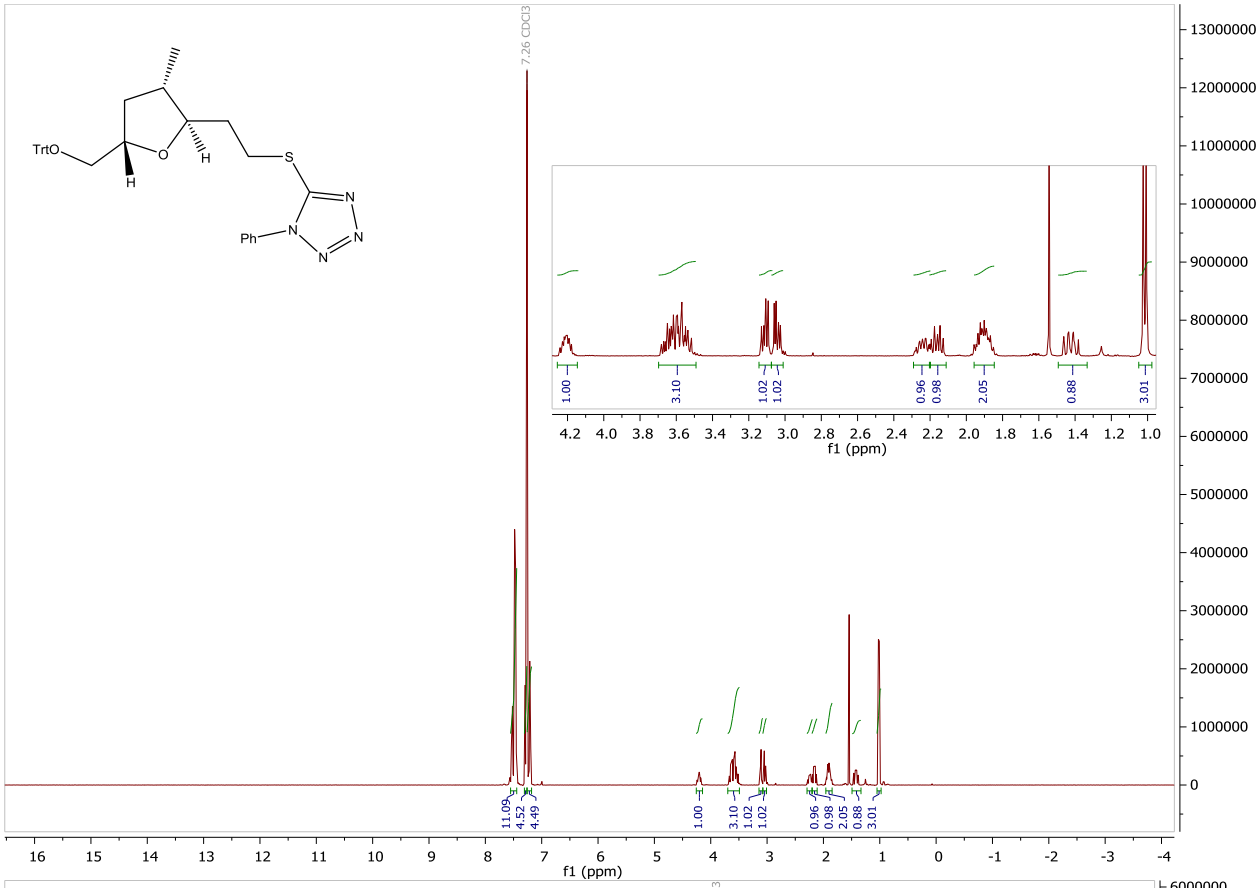

166.94
154.24
143.89
128.77
128.06
127.31
119.73
86.91
77.16 CDCl3
68.70
67.82
60.35
39.30
32.94
18.99
14.42
f1 (ppm)

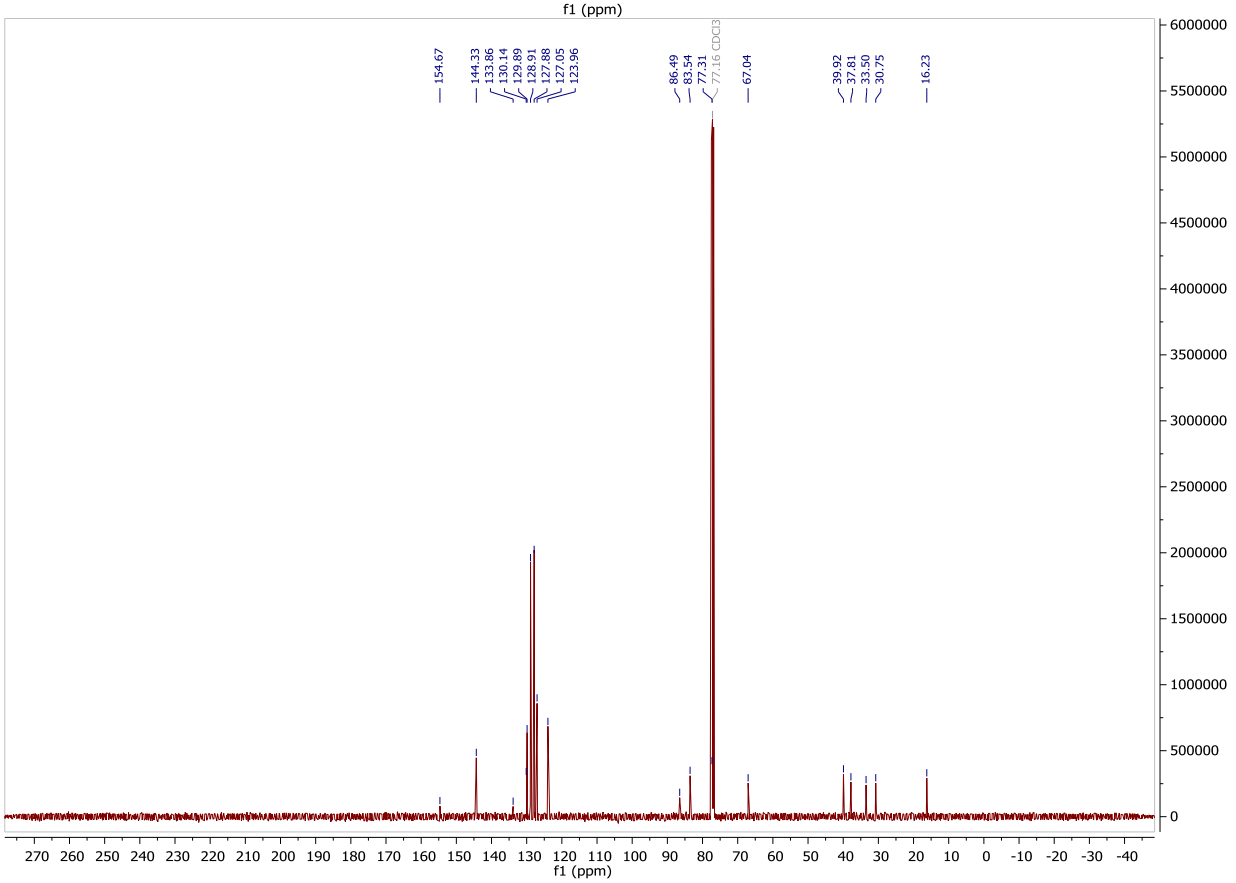

TrtO
O
H
COOEt
H
7.26 CDCl3
3.07
0.96
0.96
1.03
1.09
0.99
0.89
1.07
1.09
3.21
3.01
f1 (ppm)
6.12
6.10
3.09
3.07
0.96
0.96
1.03
1.09
0.99
0.89
1.07
1.09
3.21
3.01
f1 (ppm)

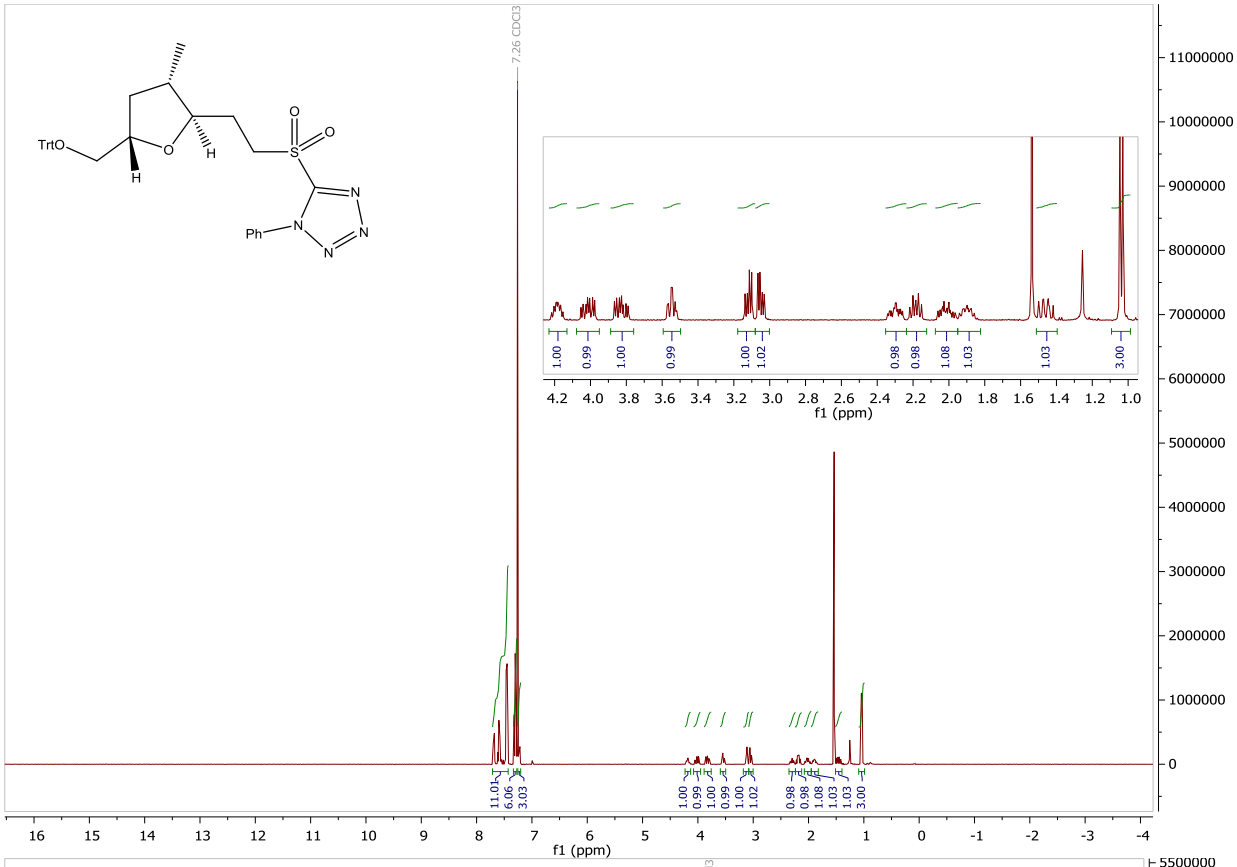

171.71
144.32
128.93
127.87
127.02
127.00
86.49
81.64
77.16 CDCl3
66.84
60.64
40.04
39.56
37.89
16.29
14.39
f1 (ppm)

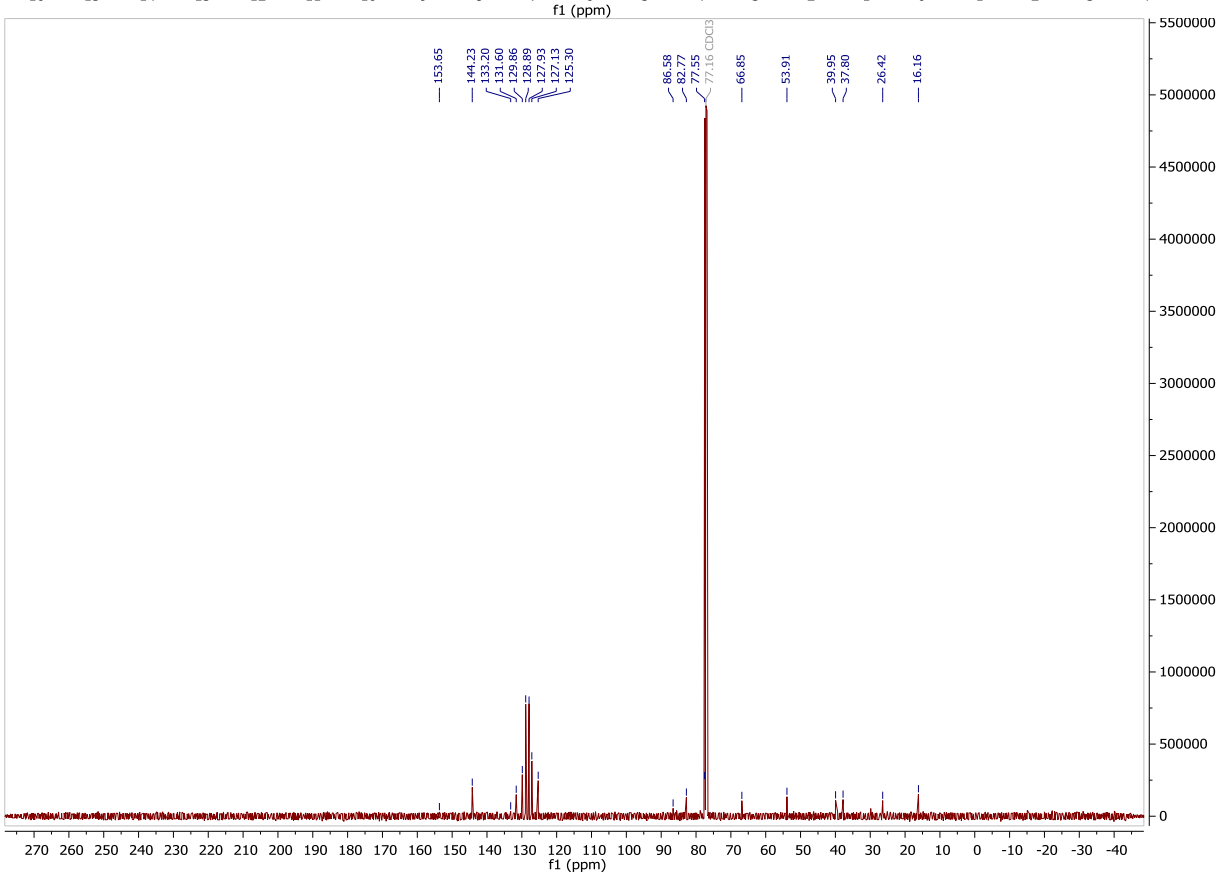

TrtO
O
H
H
OH
7.26 CDCl3
f1 (ppm)

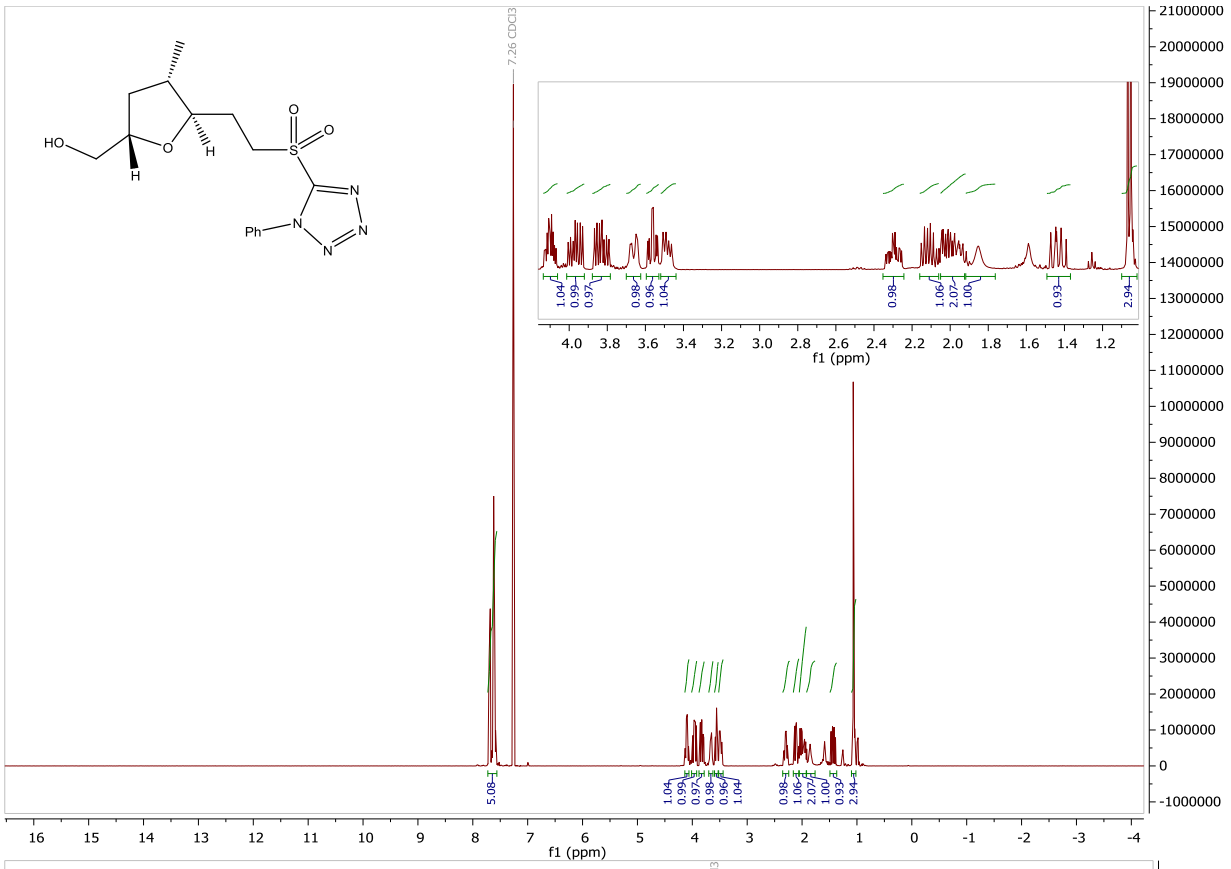

144.27
128.88
127.91
127.07
86.47
86.04
77.63
77.16 CDCl3
66.85
62.30
40.33
37.22
35.43
16.03
f1 (ppm)

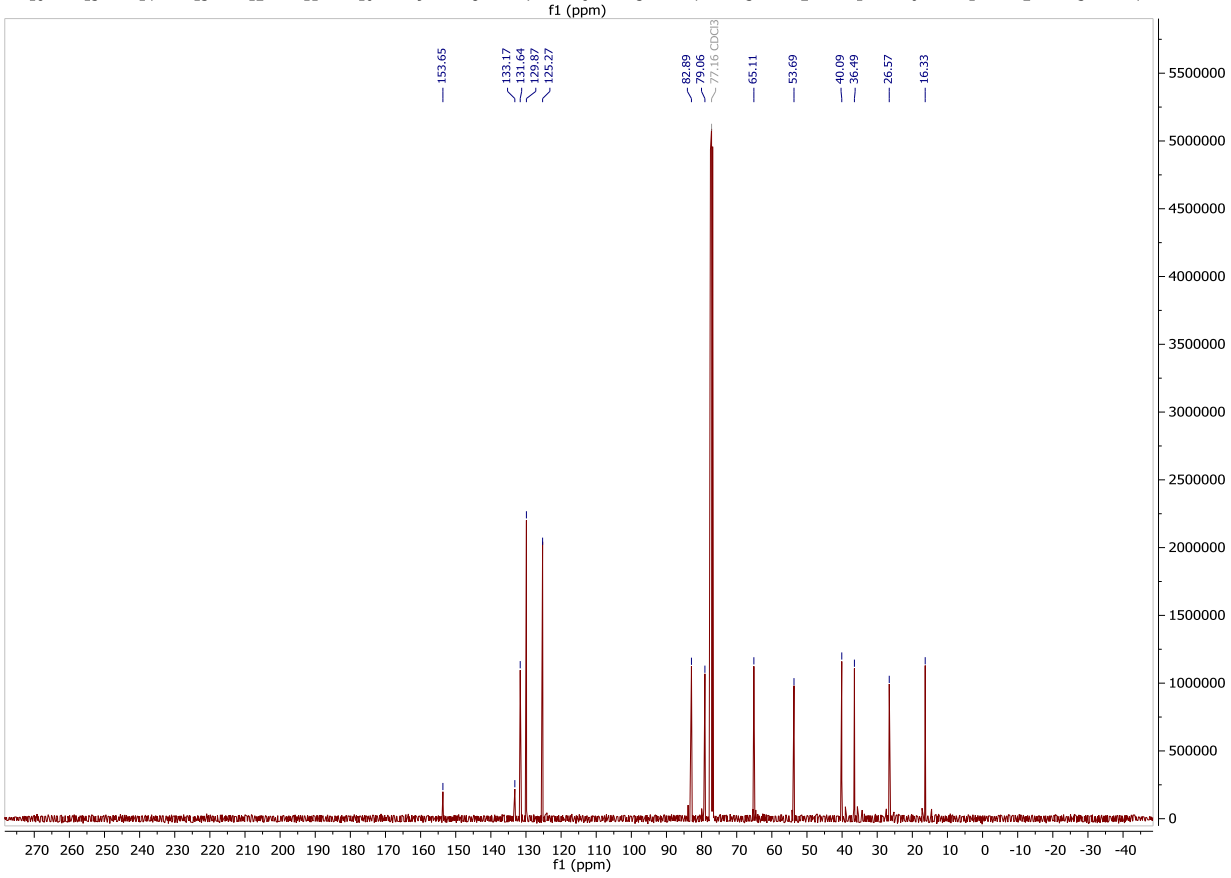

TrtO
O
H
H
S
N
N
N
N
Ph
7.26 CDCl3
f1 (ppm)
11.09
4.52
4.49
1.00
3.10
1.02
1.02
0.96
0.98
2.05
0.88
3.01

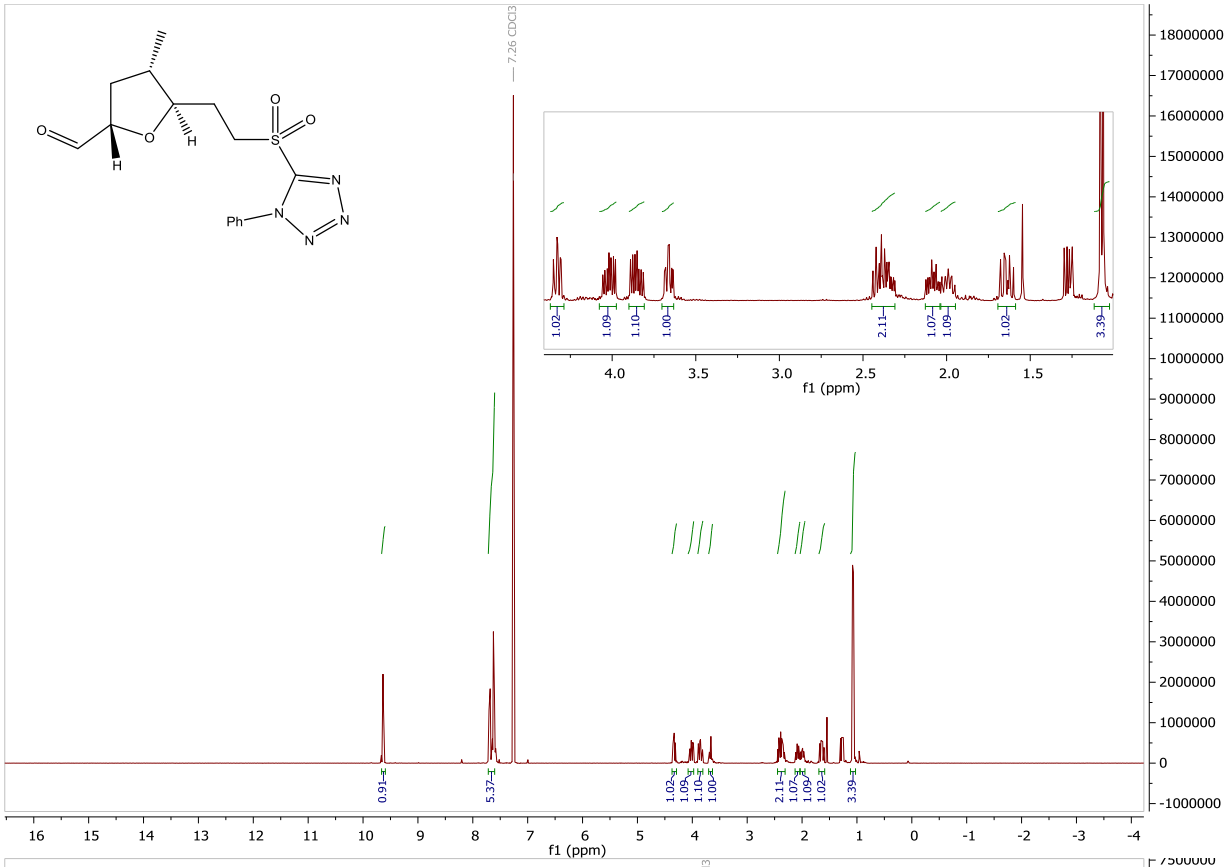

154.67
144.33
133.86
130.14
129.89
128.91
127.88
127.05
123.96
86.49
83.54
77.31
77.16 CDCl3
67.04
39.92
37.81
33.50
30.75
16.23
f1 (ppm)

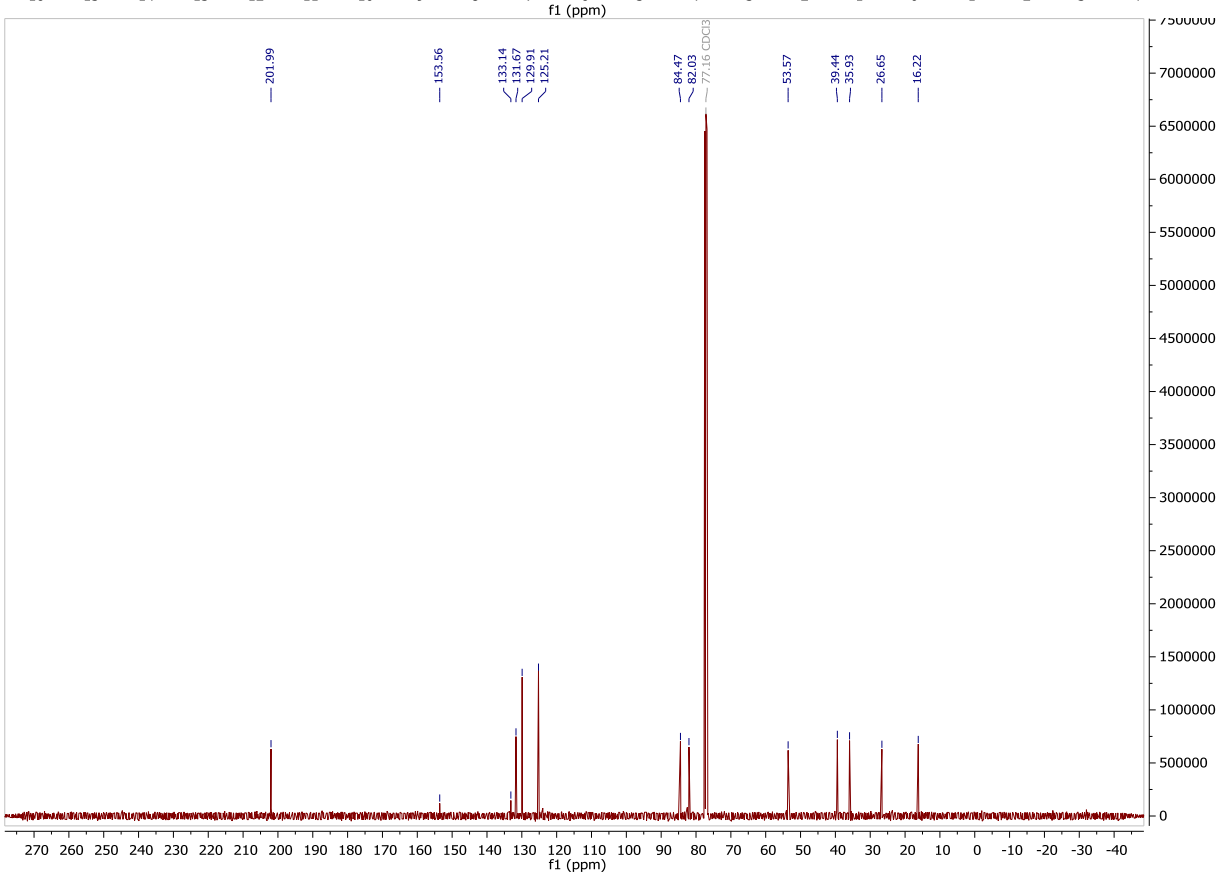

TrtO
O
H
H
O
S
O
N
N
N
N
Ph
7.26 CDCl3
f1 (ppm)

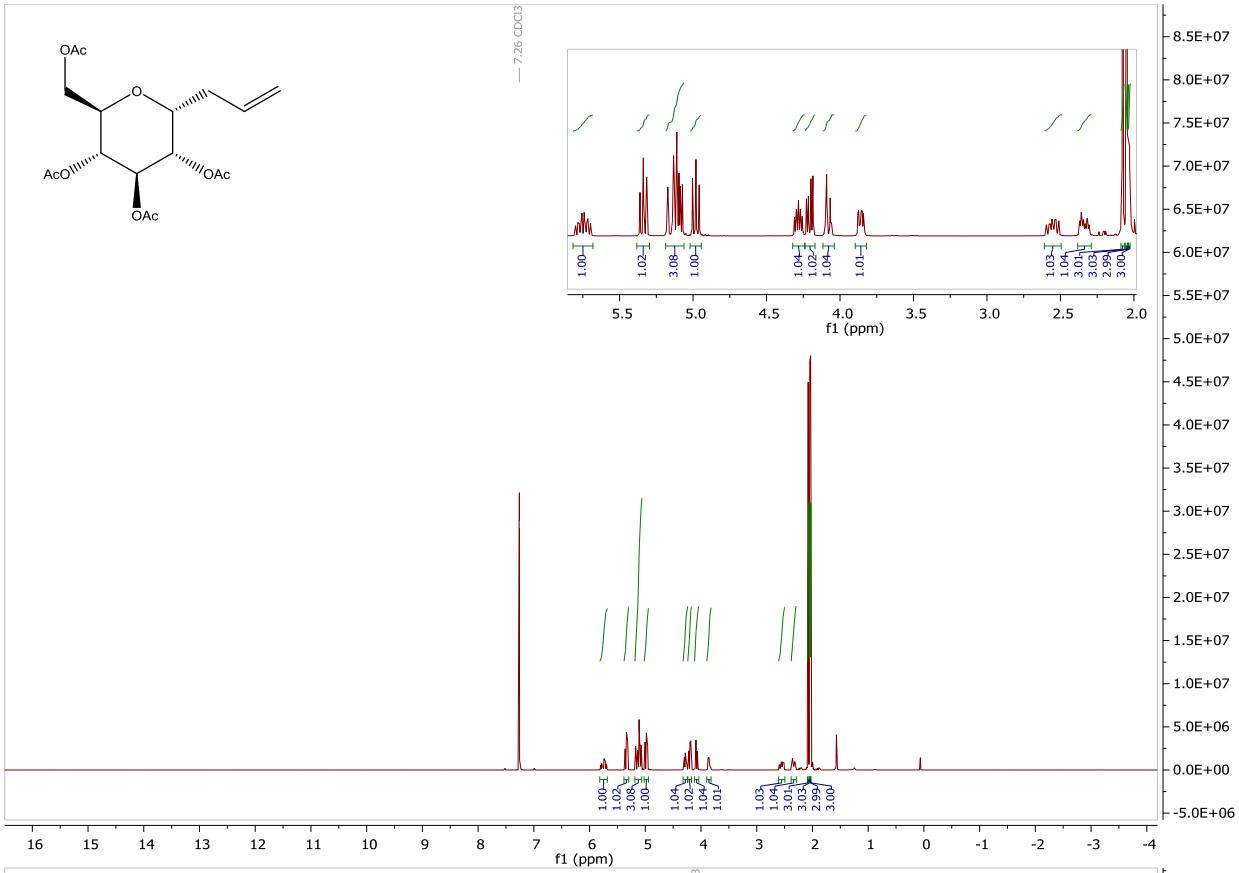

153.65
144.23
133.20
131.60
129.86
128.89
127.93
127.13
125.30
86.58
82.77
77.55
77.16 CDCl3
66.85
53.91
39.95
37.80
26.42
16.16
f1 (ppm)

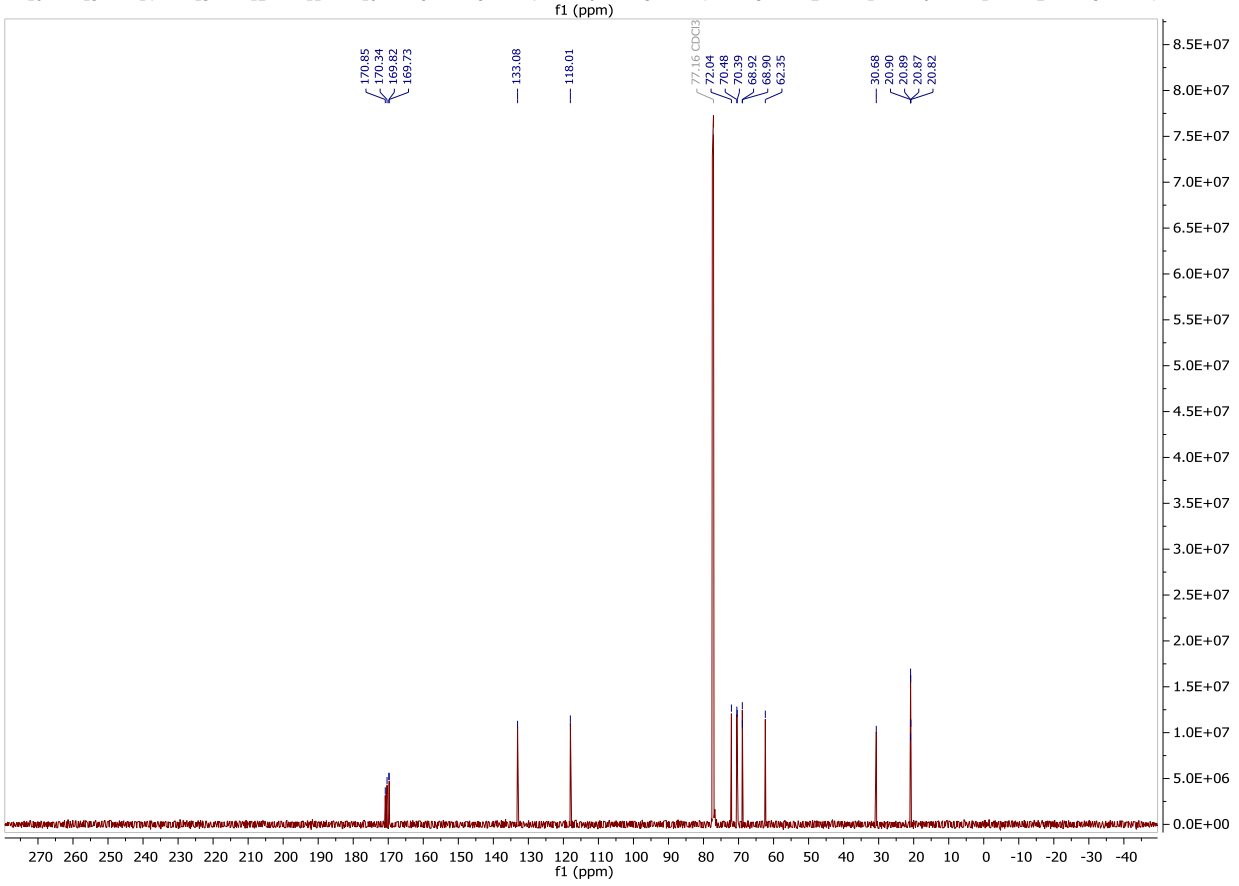

HO
O
H
H
O
O
S
N
N
N
N
Ph
7.26 CDCl3
f1 (ppm)

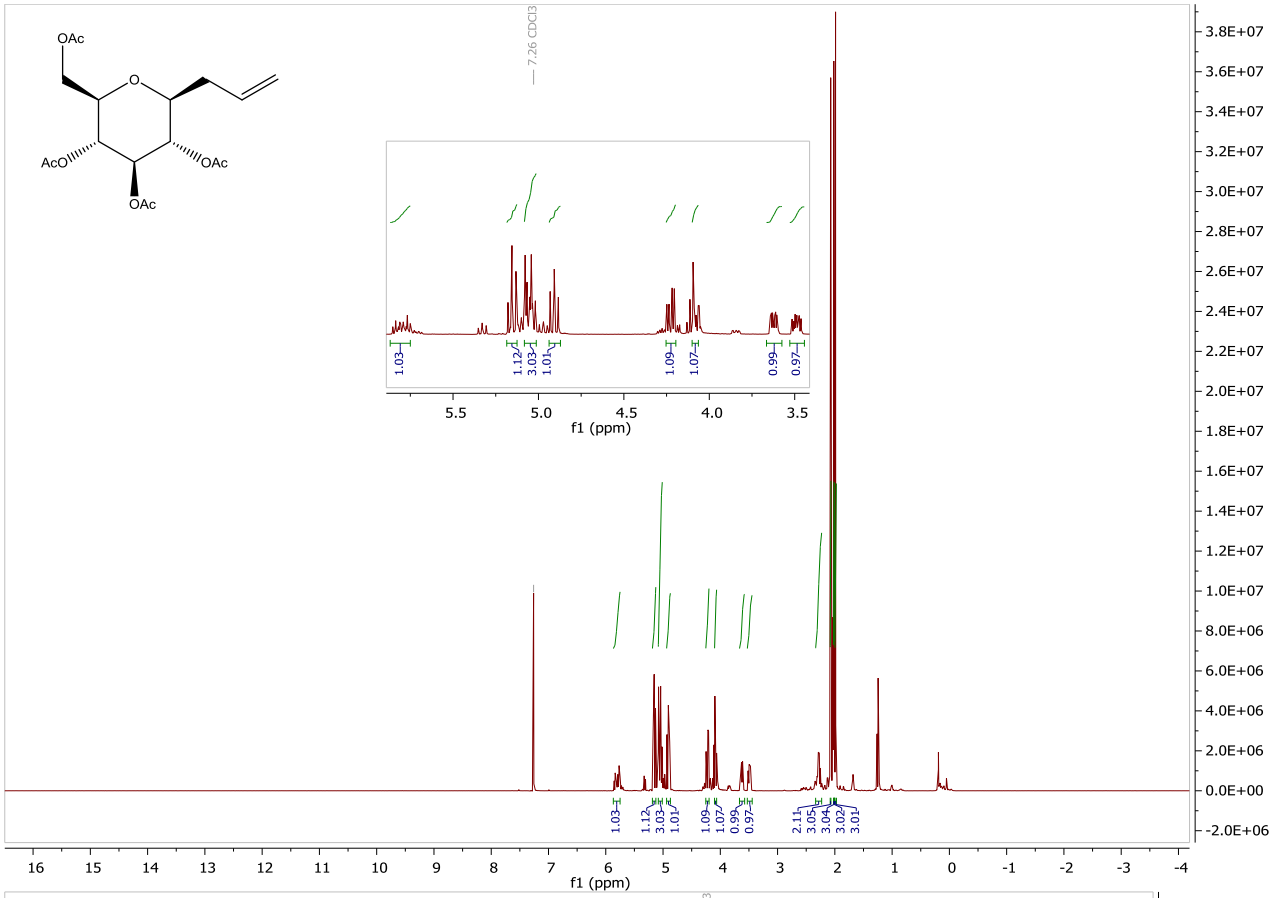

153.65
133.17
131.64
129.87
125.27
82.89
79.06
77.16 CDCl3
65.11
53.69
40.09
36.49
26.57
16.33
f1 (ppm)

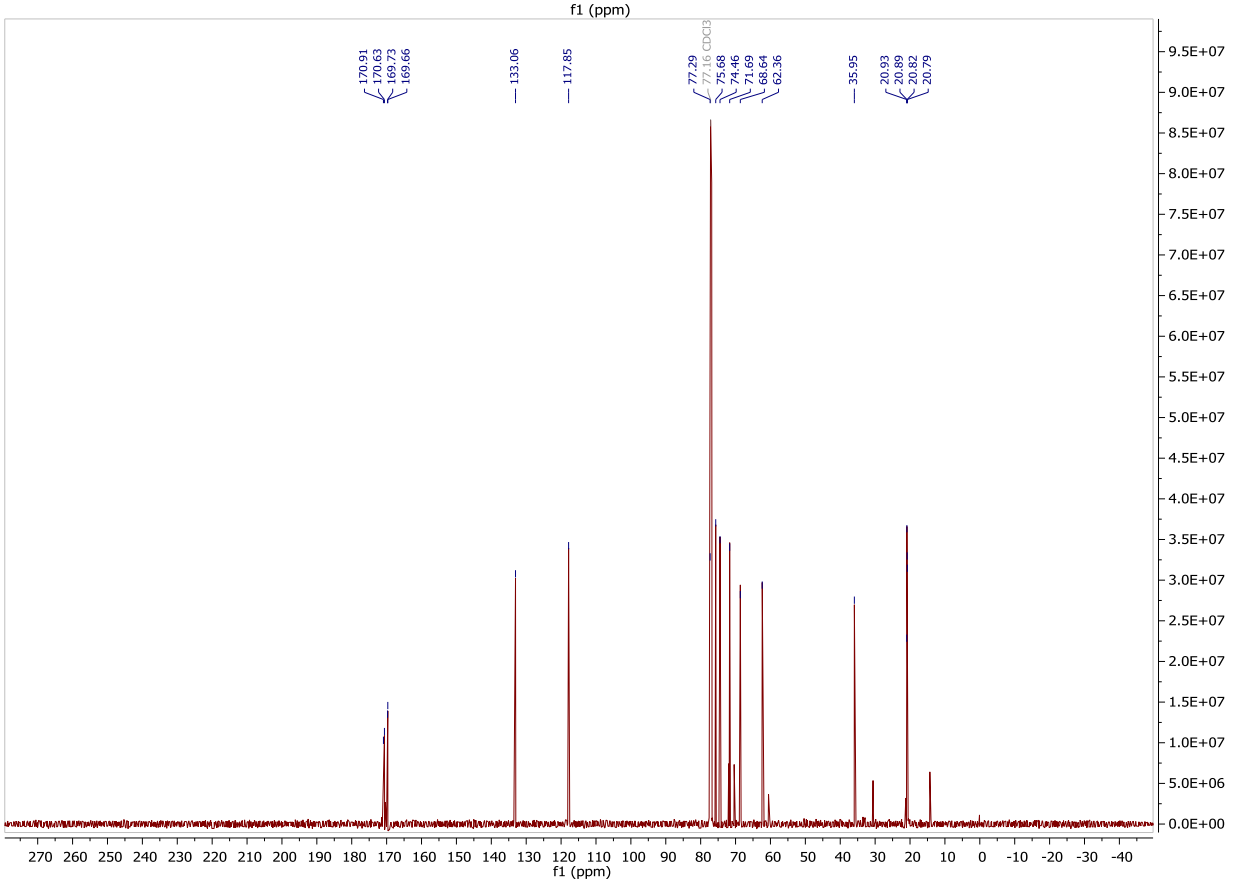

7.26 CDCl3
f1 (ppm)
0.91
5.37
1.02
1.09
1.10
1.00
2.11
1.07
1.09
1.02
3.39

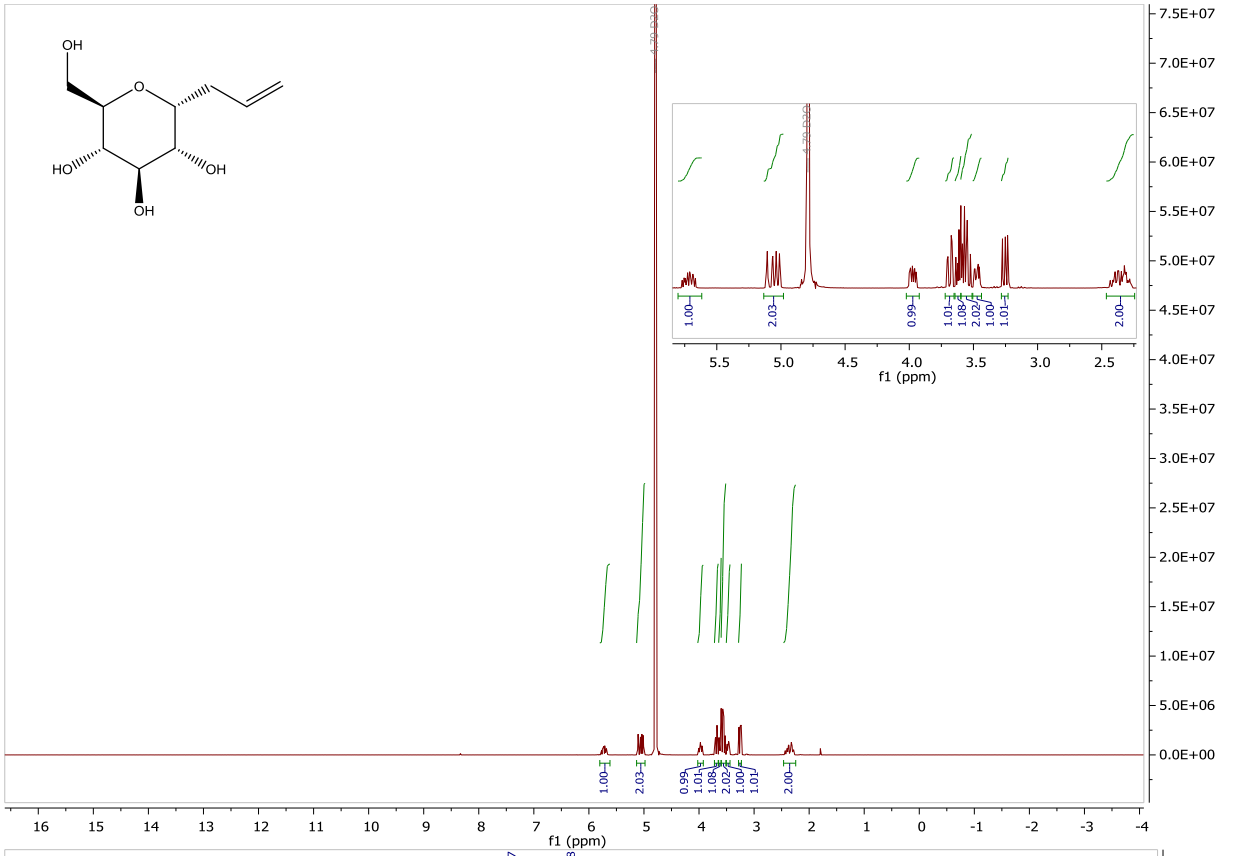

201.99
153.56
133.14
131.67
129.91
125.21
84.47
82.03
77.16 CDCl3
53.57
39.44
35.93
26.65
16.22
f1 (ppm)

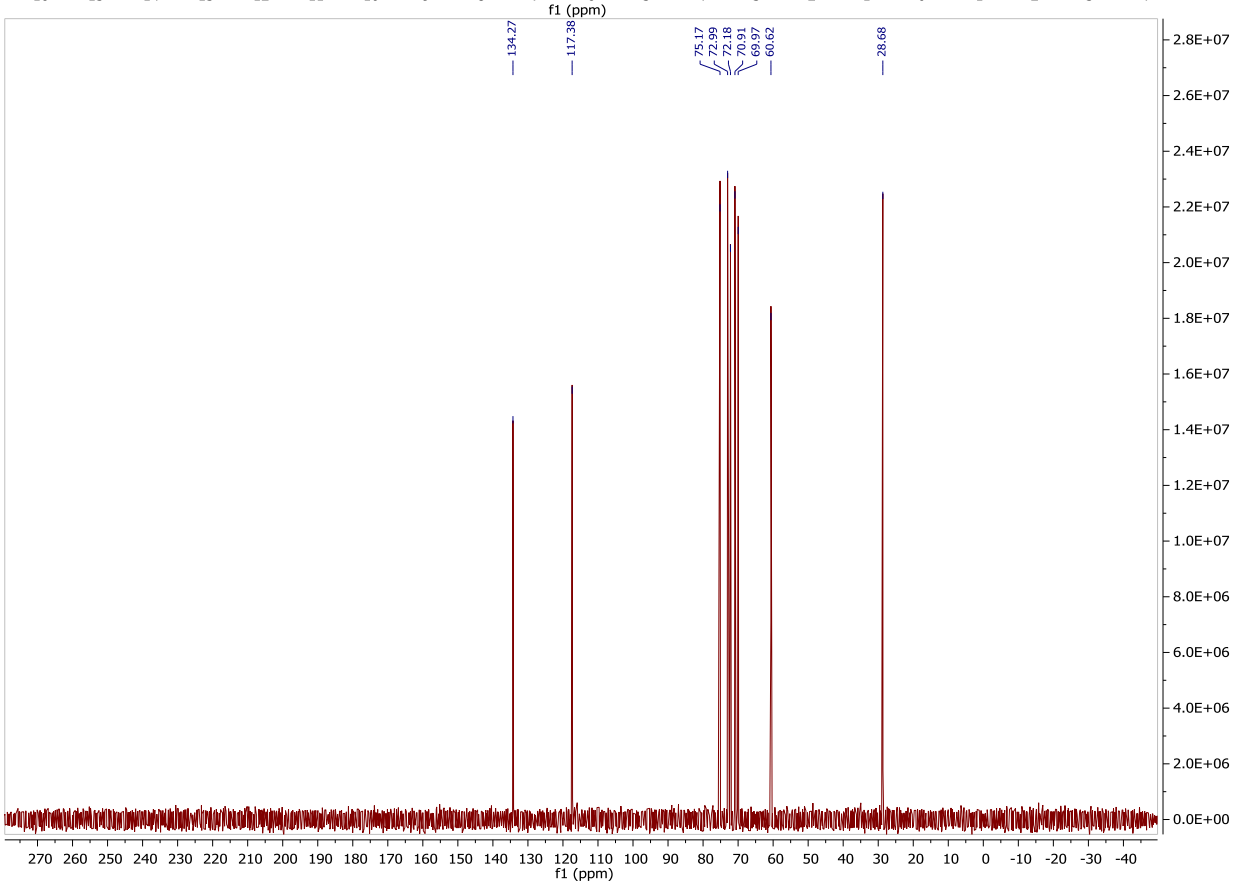

OAc
O
AcO
OAc
OAc
7.26 CDCl3
f1 (ppm)
f1 (ppm)

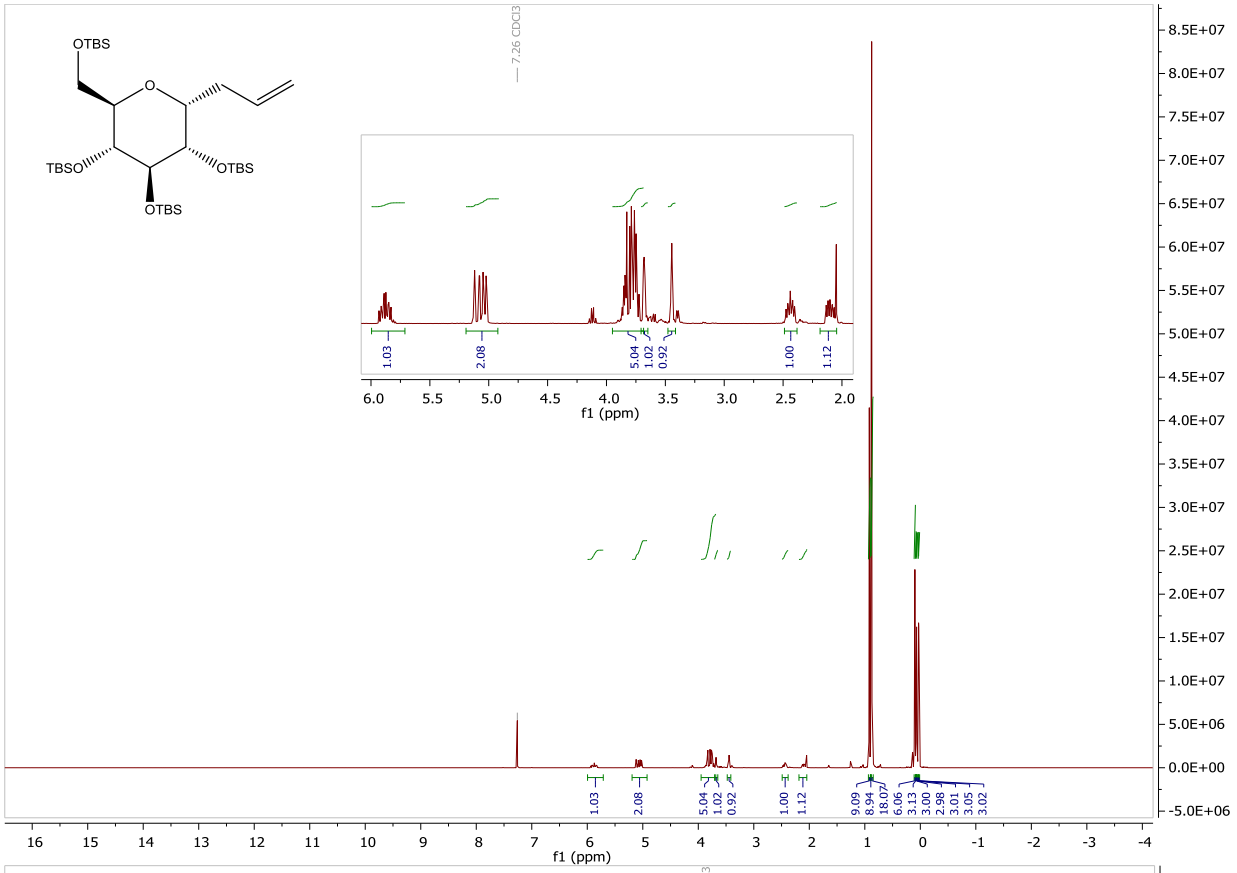

170.85
170.34
169.82
169.73
133.08
118.01
77.16 CDCl3
72.04
70.48
70.39
68.92
68.90
62.35
30.68
20.90
20.89
20.87
20.82
f1 (ppm)

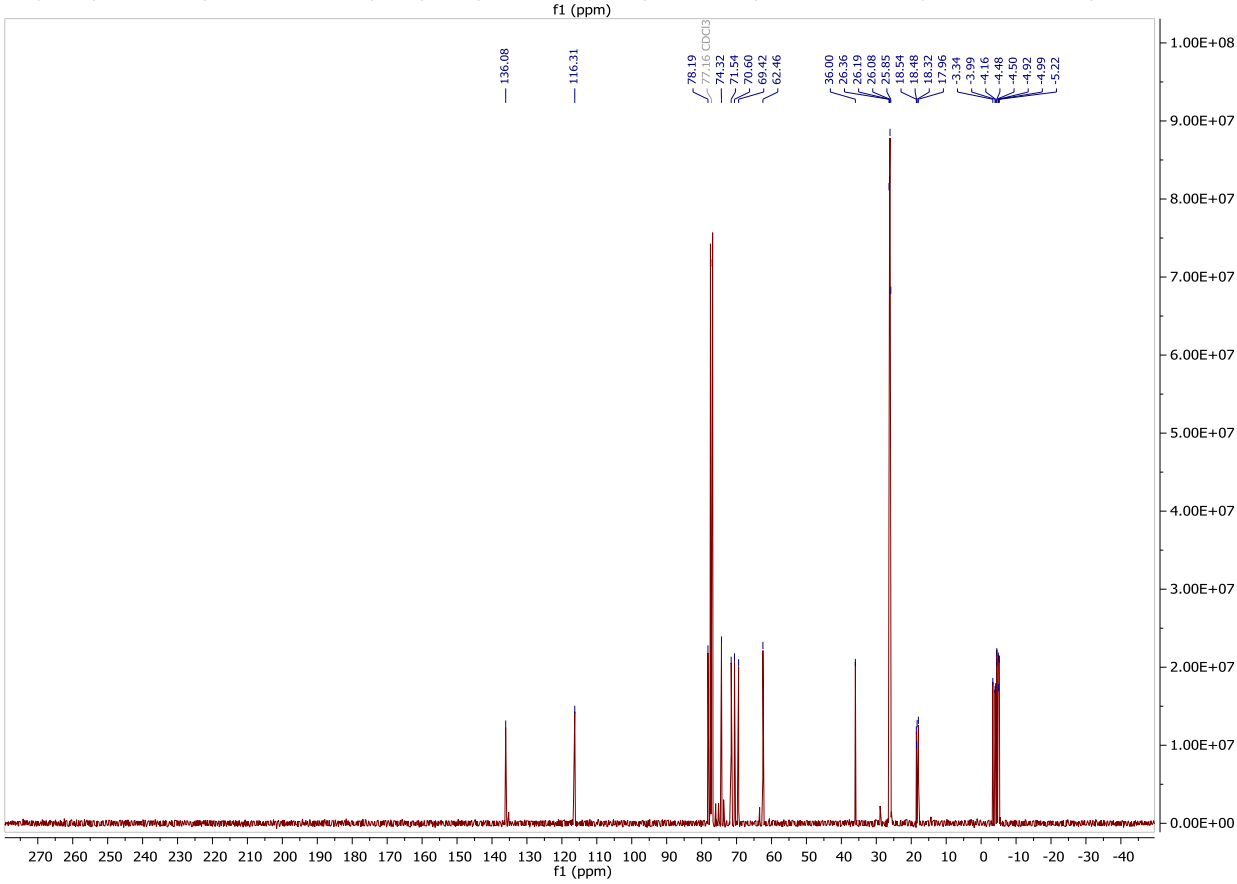

OAc
AcO
OAc
OAc
O
7.26 CDCl3
1.03
1.12
3.03
1.01
1.09
1.07
0.99
0.97
f1 (ppm)
1.03
1.12
3.03
1.01
1.09
1.07
0.99
0.97
2.11
3.05
3.04
3.02
3.01
f1 (ppm)

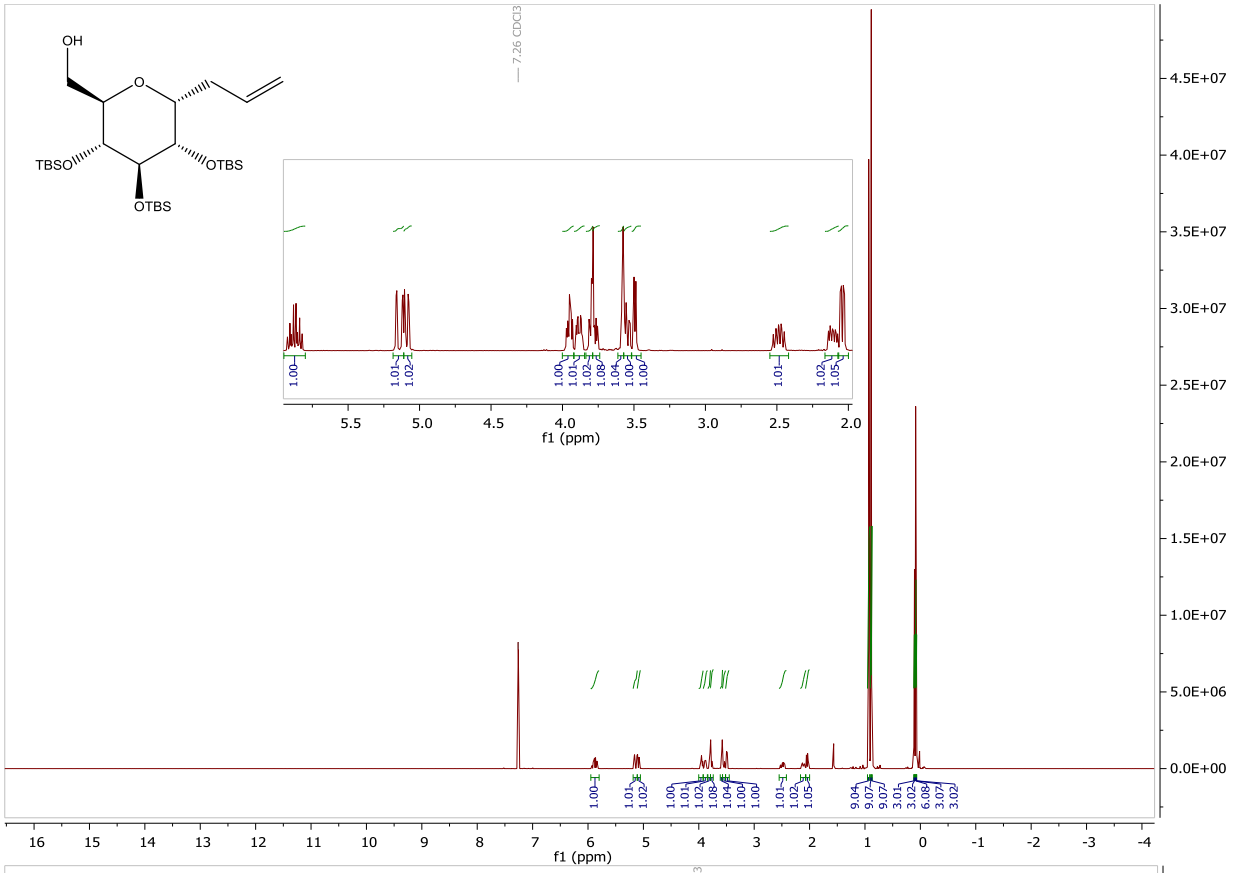

170.91
170.63
169.73
169.66
133.06
117.85
77.29
77.16 CDCl3
75.68
74.46
71.69
68.64
62.36
35.95
20.93
20.89
20.82
20.79
f1 (ppm)

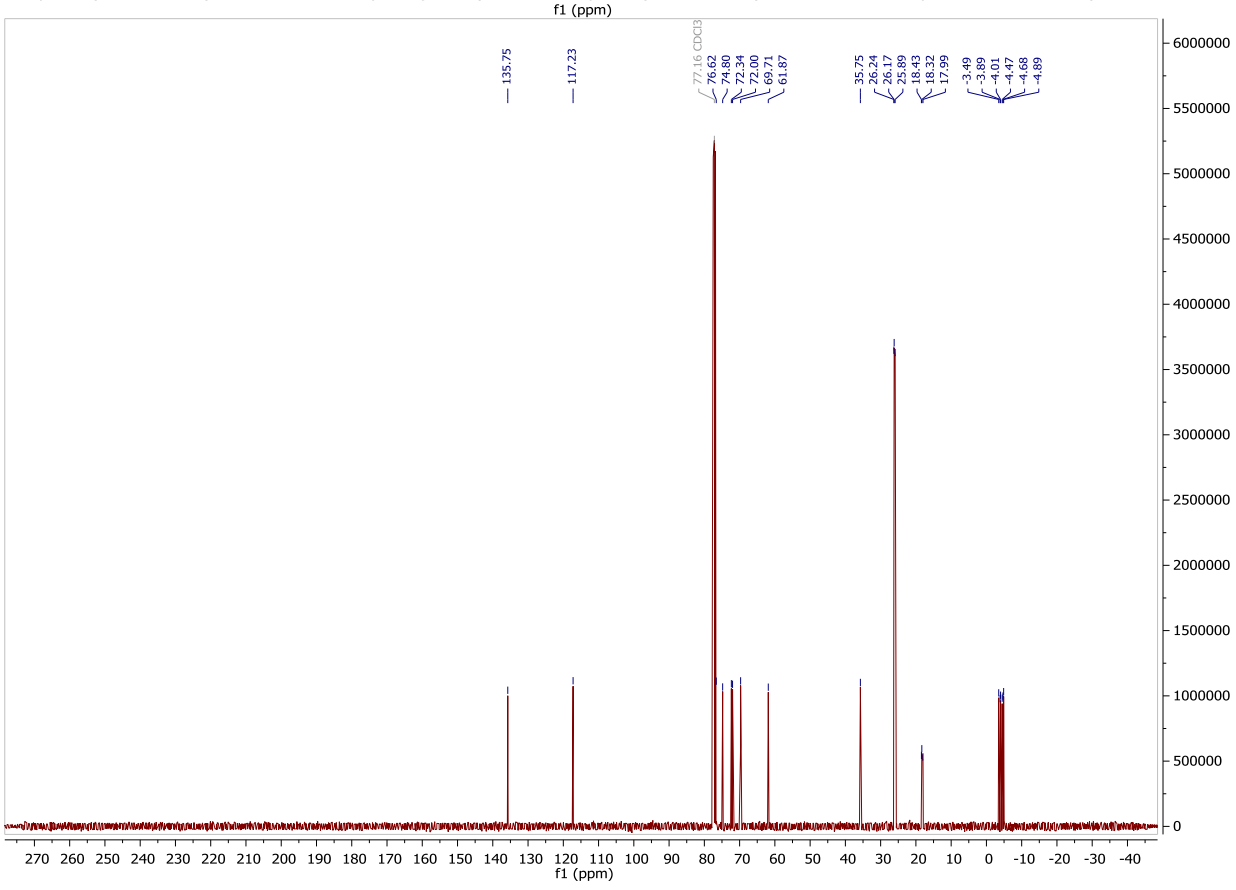

OH
O
HO
OH
OH
4.99
1.00
2.03
0.99
1.01
1.08
2.02
1.00
1.01
2.00
f1 (ppm)
f1 (ppm)

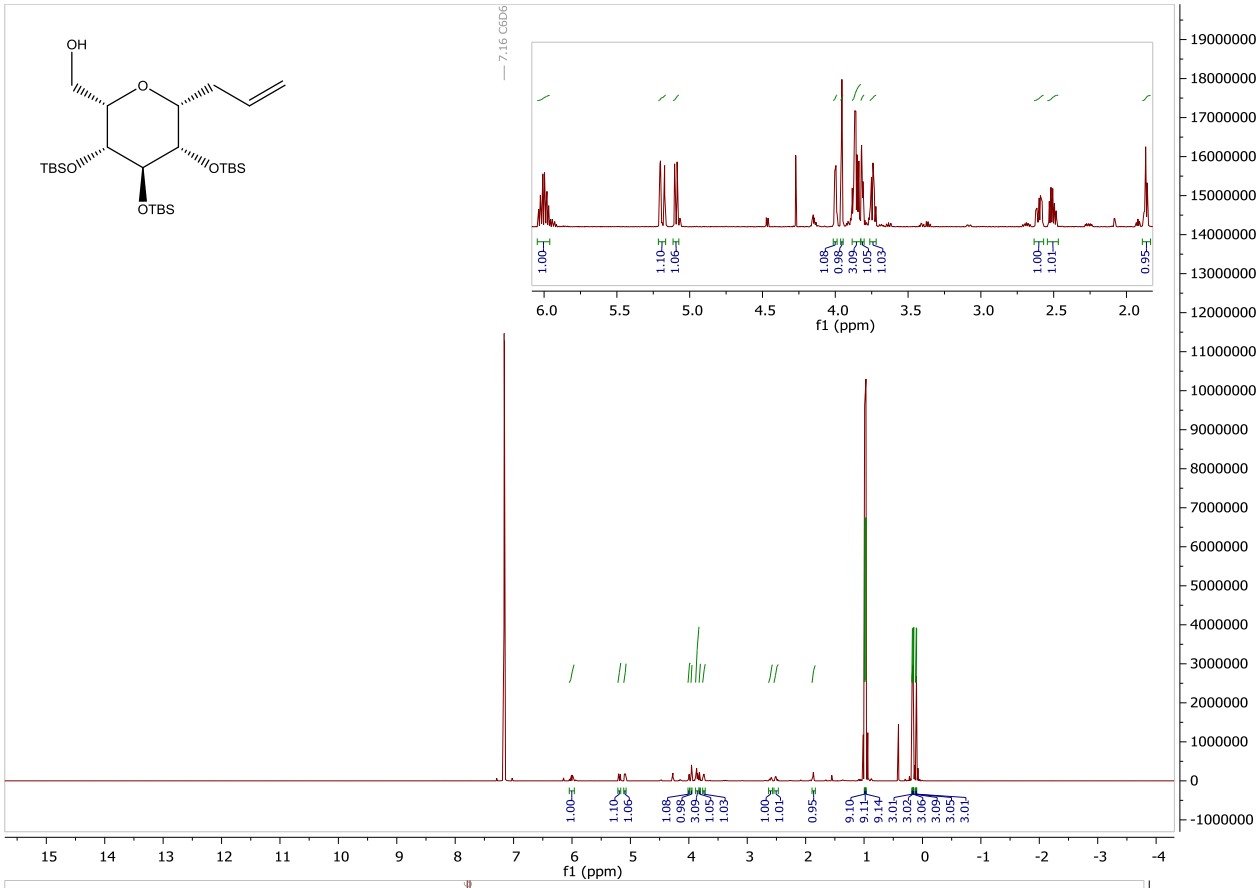

134.27
117.38
75.17
72.99
72.18
70.91
69.97
60.62
28.68
f1 (ppm)

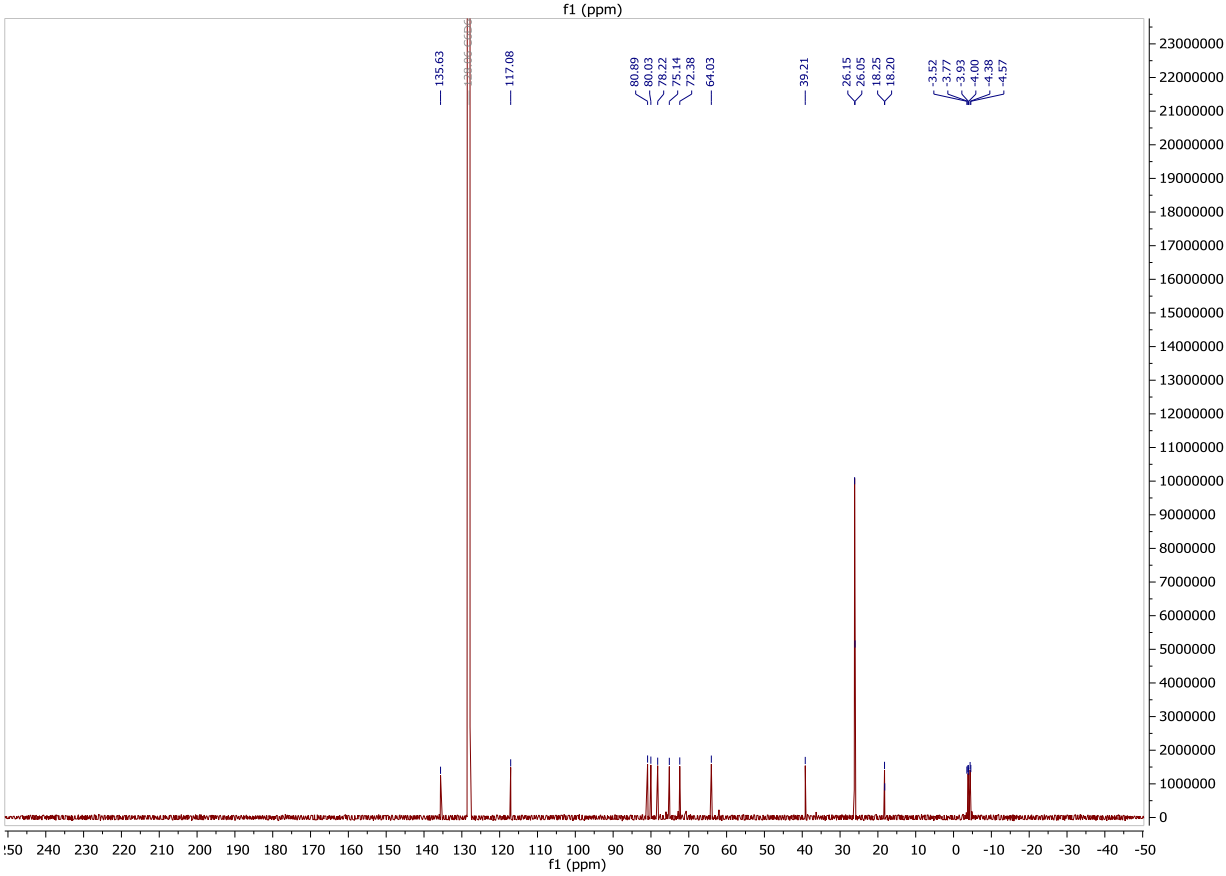

OTBS
TBSO
OTBS
OTBS
7.26 CDCl3
1.03
2.08
5.04
1.02
0.92
1.00
1.12
f1 (ppm)
9.09
8.94
18.07
6.06
3.13
3.00
2.98
3.01
3.05
3.02

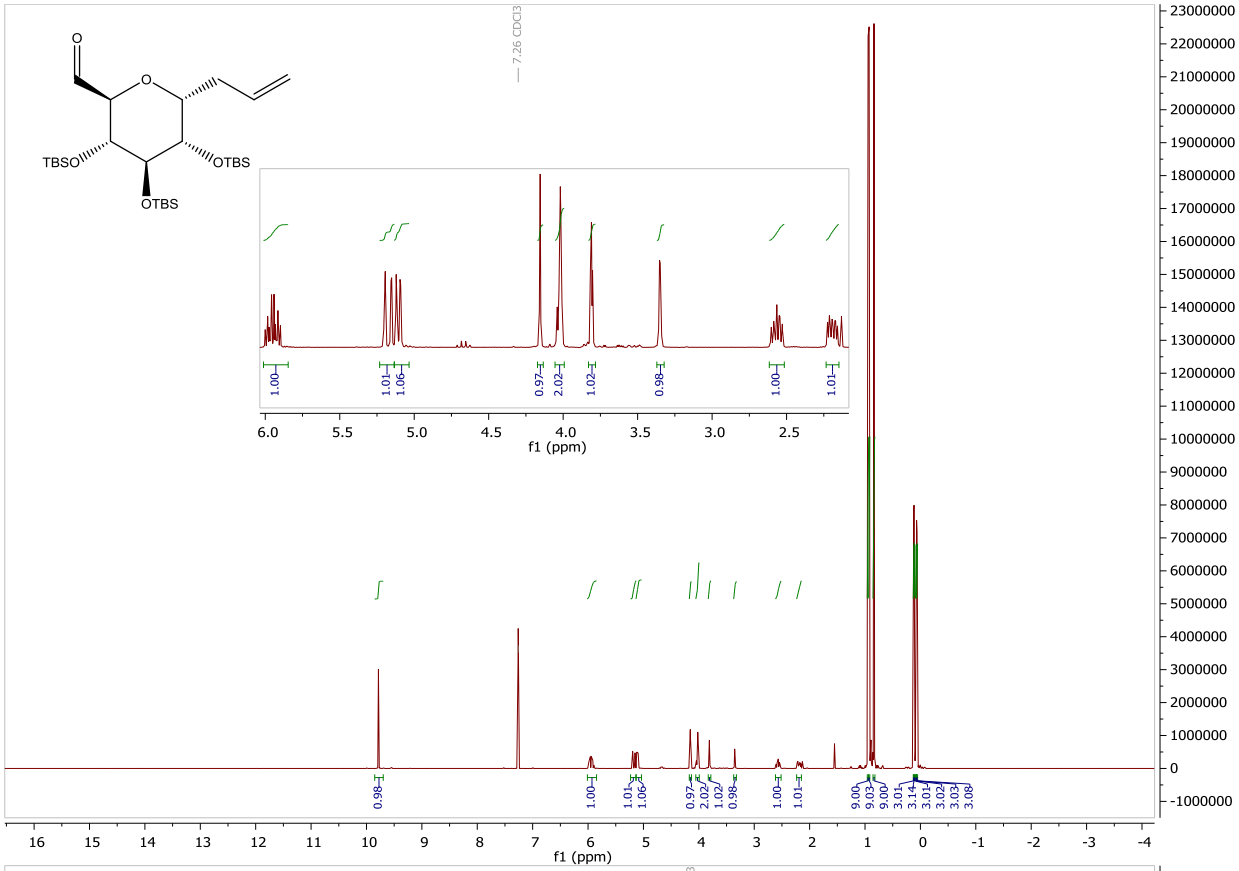

136.08
116.31
78.19
77.16 CDCl3
74.32
71.54
70.60
69.42
62.46
36.00
26.36
26.19
26.08
25.85
18.54
18.48
18.32
17.96
-3.34
-3.99
-4.16
-4.48
-4.50
-4.92
-4.99
-5.22
f1 (ppm)

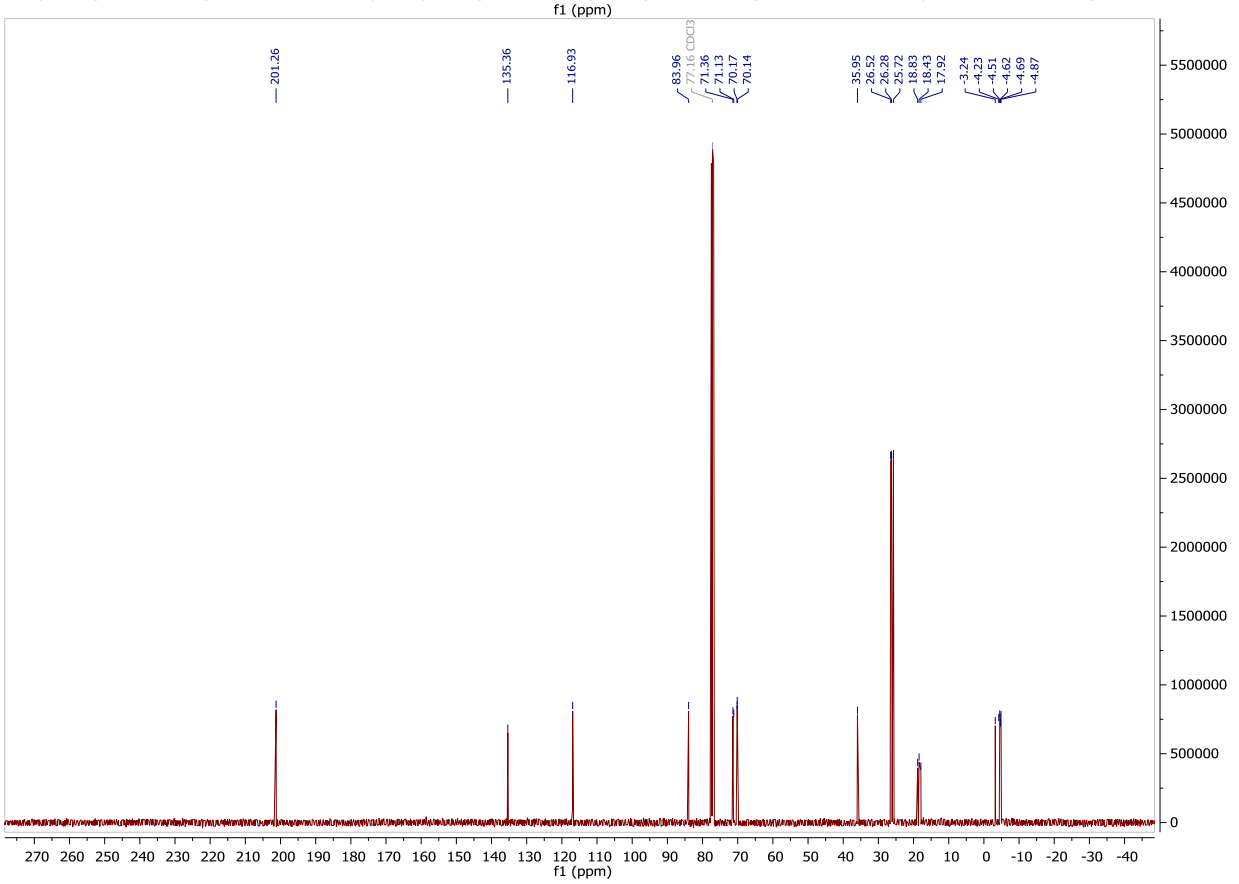

OH
O
TBSO
OTBS
OTBS
7.26 CDCl3
f1 (ppm)

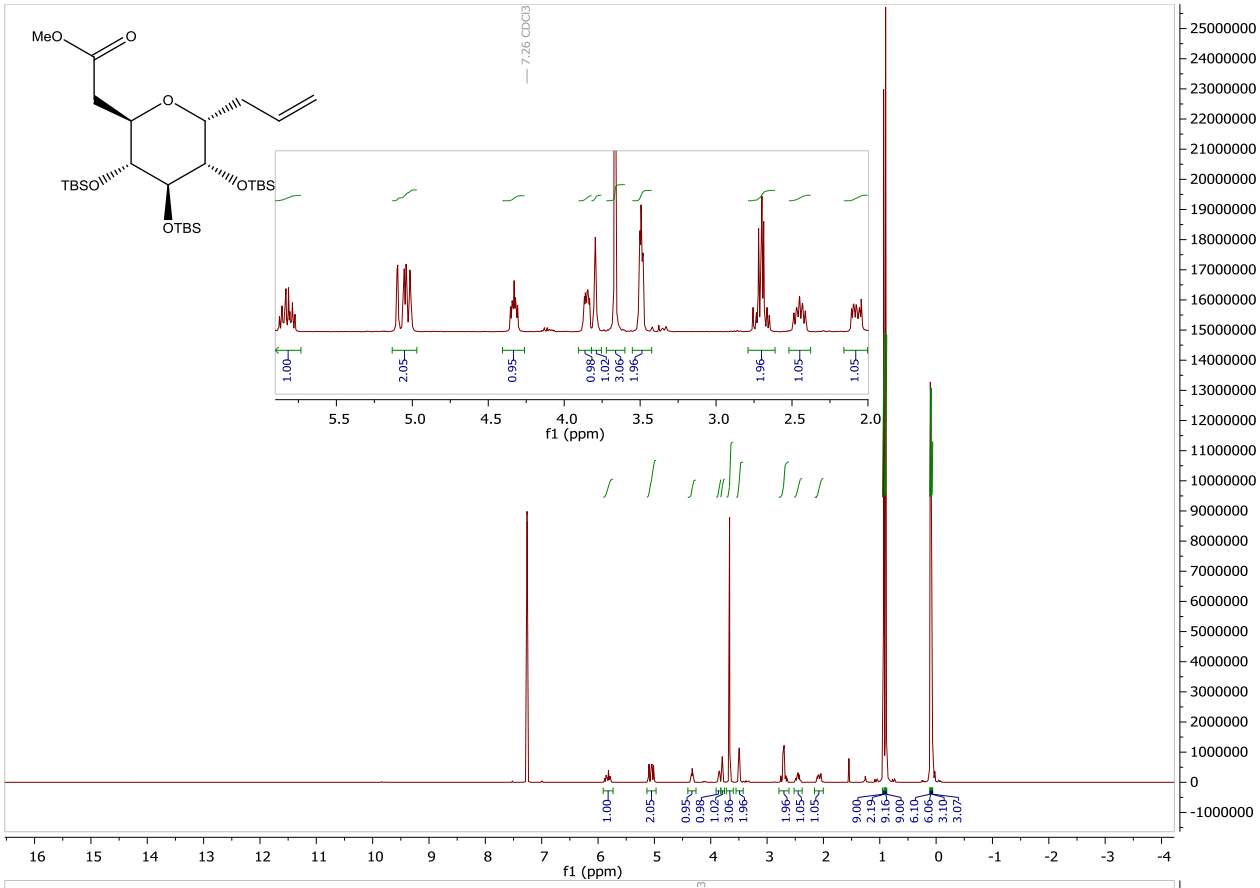

135.75
117.23
77.16 CDCl3
76.62
74.80
72.34
72.00
69.71
61.87
35.75
26.24
26.17
25.89
18.43
18.32
17.99
-3.49
-3.89
-4.01
-4.47
-4.68
-4.89
f1 (ppm)

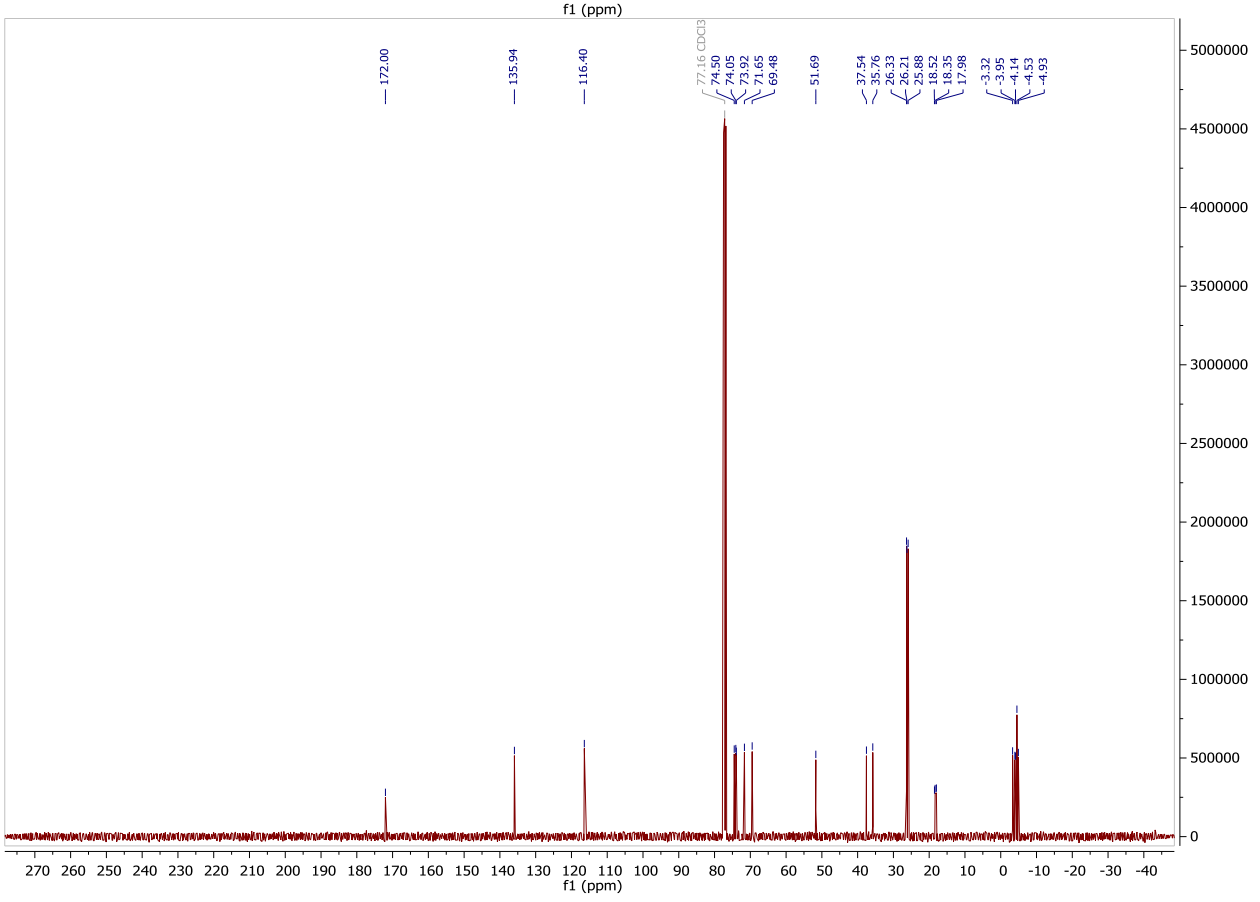

OH
O
TBSO
OTBS
OTBS
7.16 C6D6
f1 (ppm)

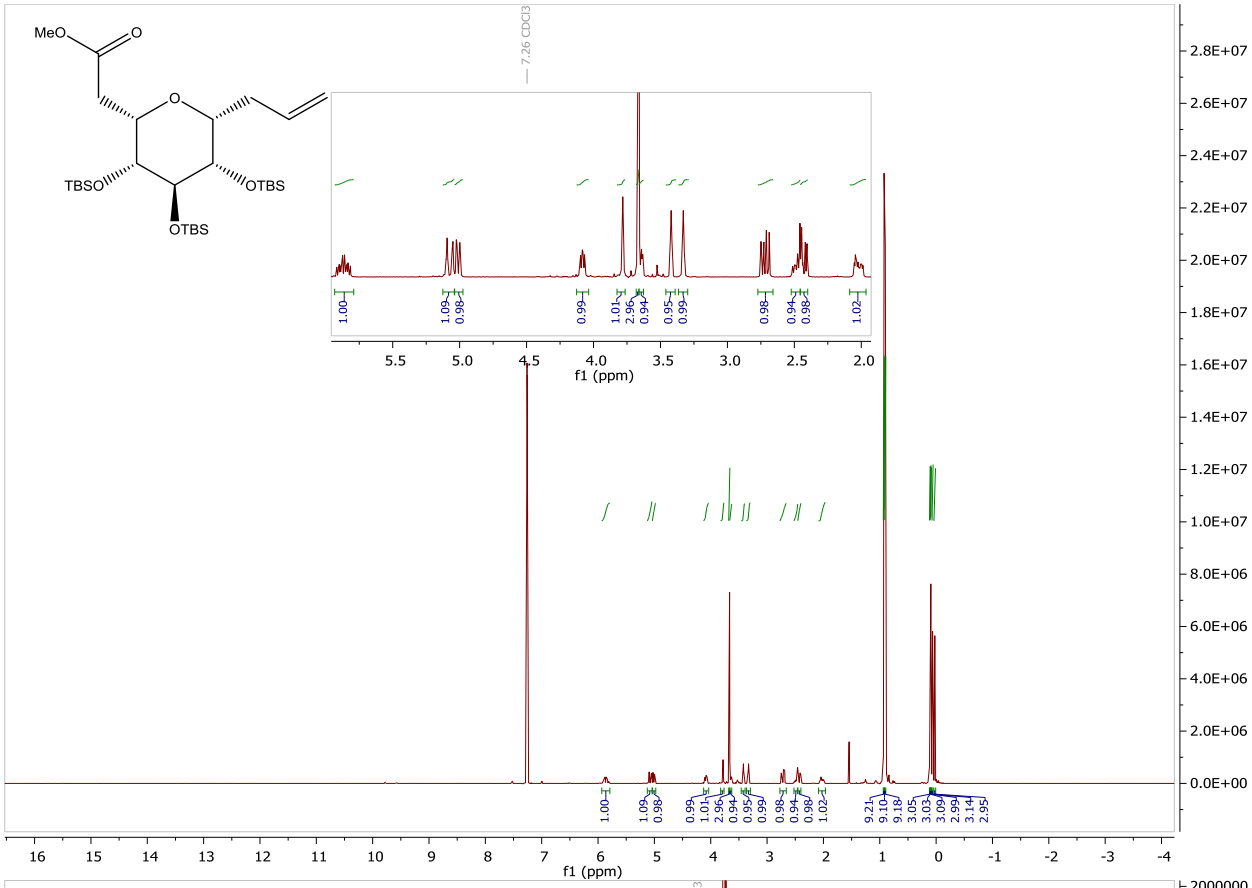

135.63
117.08
80.89
80.03
78.22
75.14
72.38
64.03
39.21
26.15
26.05
18.25
18.20
-3.52
-3.77
-3.93
-4.00
-4.38
-4.57
f1 (ppm)

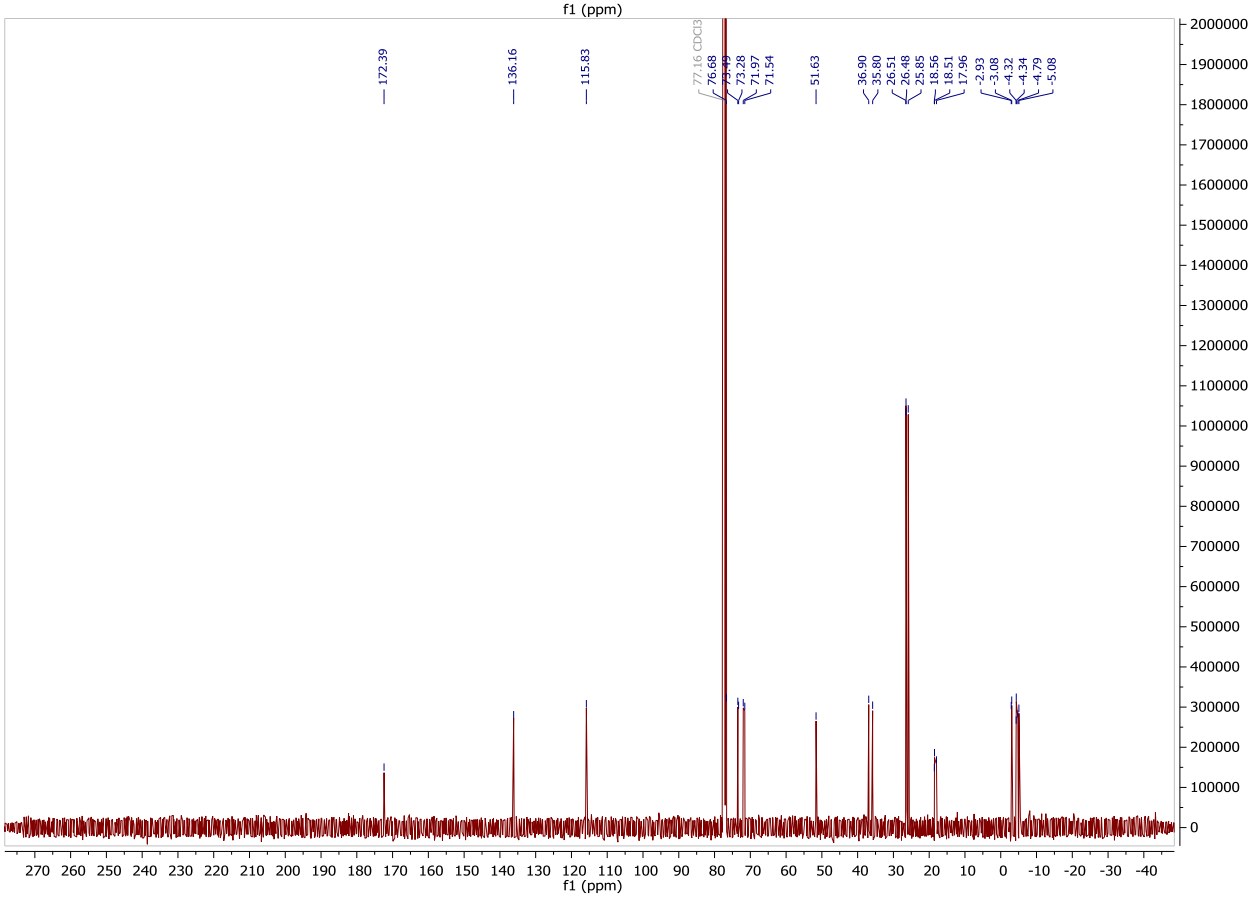

TBSO
OTBS
OTBS
O
O
7.26 CDCl3
1.00
1.01
1.06
0.97
2.02
1.02
0.98
1.00
1.01
f1 (ppm)
0.98
1.00
1.01
1.06
0.97
2.02
1.02
0.98
1.00
1.01
9.00
9.03
9.00
3.01
3.14
3.01
3.02
3.03
3.08
f1 (ppm)

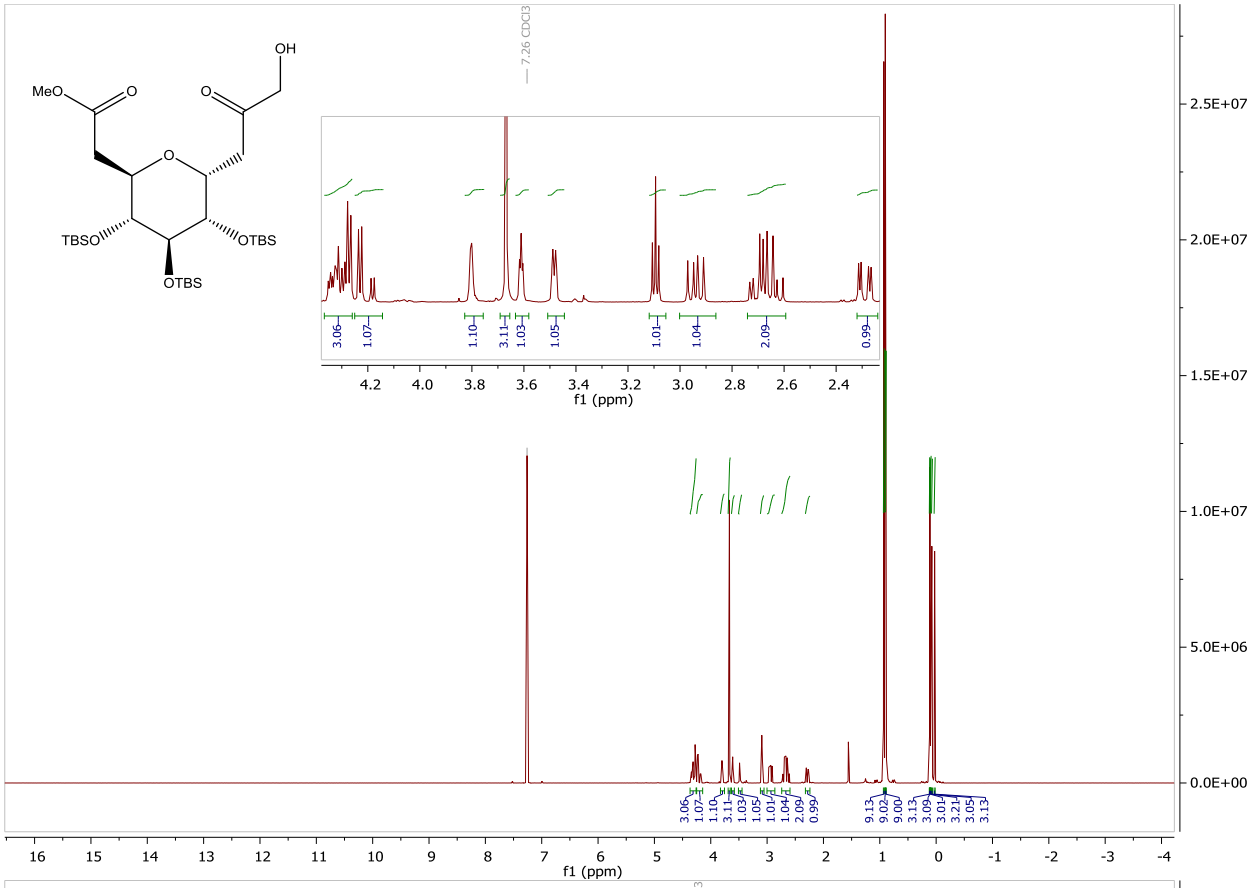

201.26
135.36
116.93
83.96
77.16 CDCl3
71.36
71.13
70.17
70.14
35.95
26.52
26.28
25.72
18.43
18.43
17.92
-3.24
-4.23
-4.51
-4.62
-4.69
-4.87
f1 (ppm)

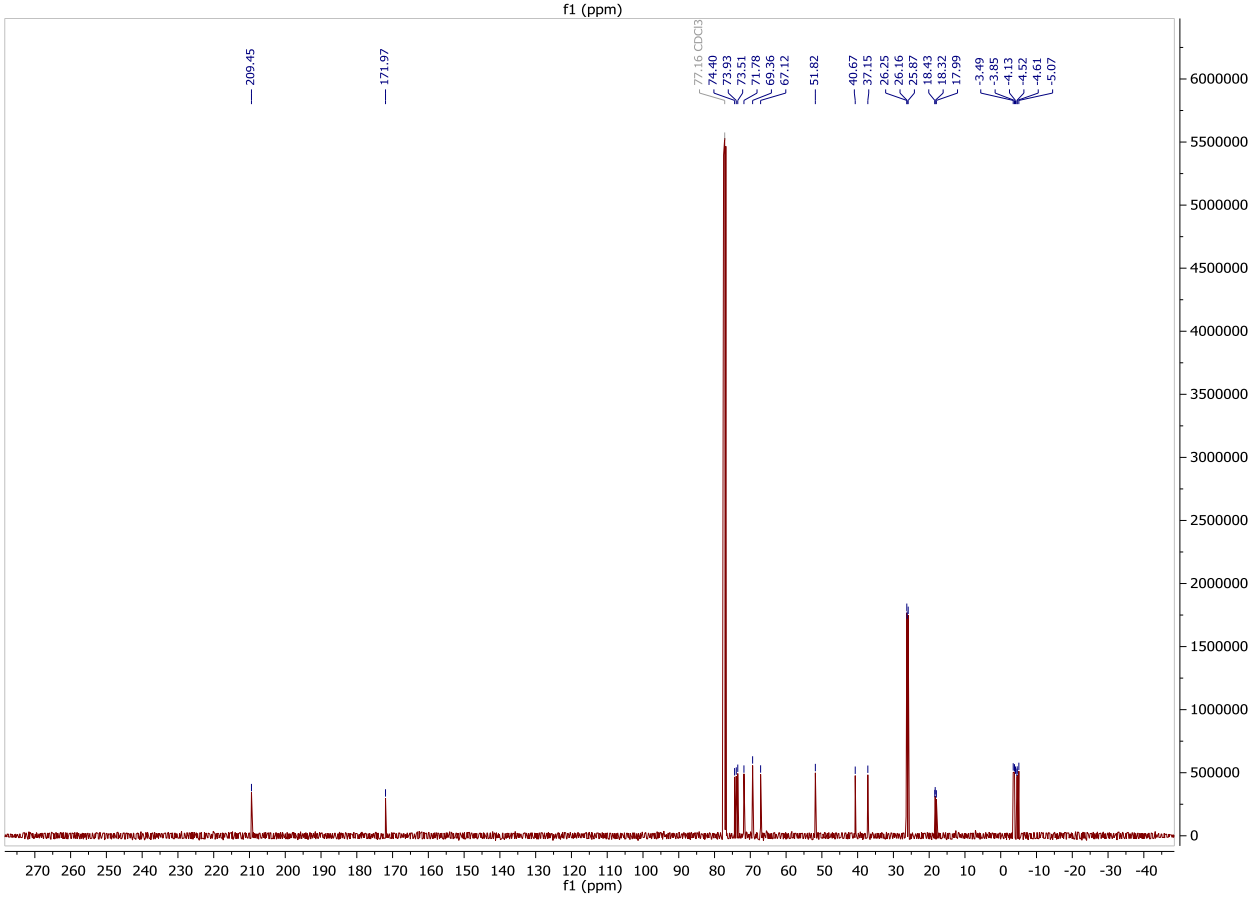

MeO
O
O
TBSO
OTBS
OTBS
7.26 CDCl3
f1 (ppm)

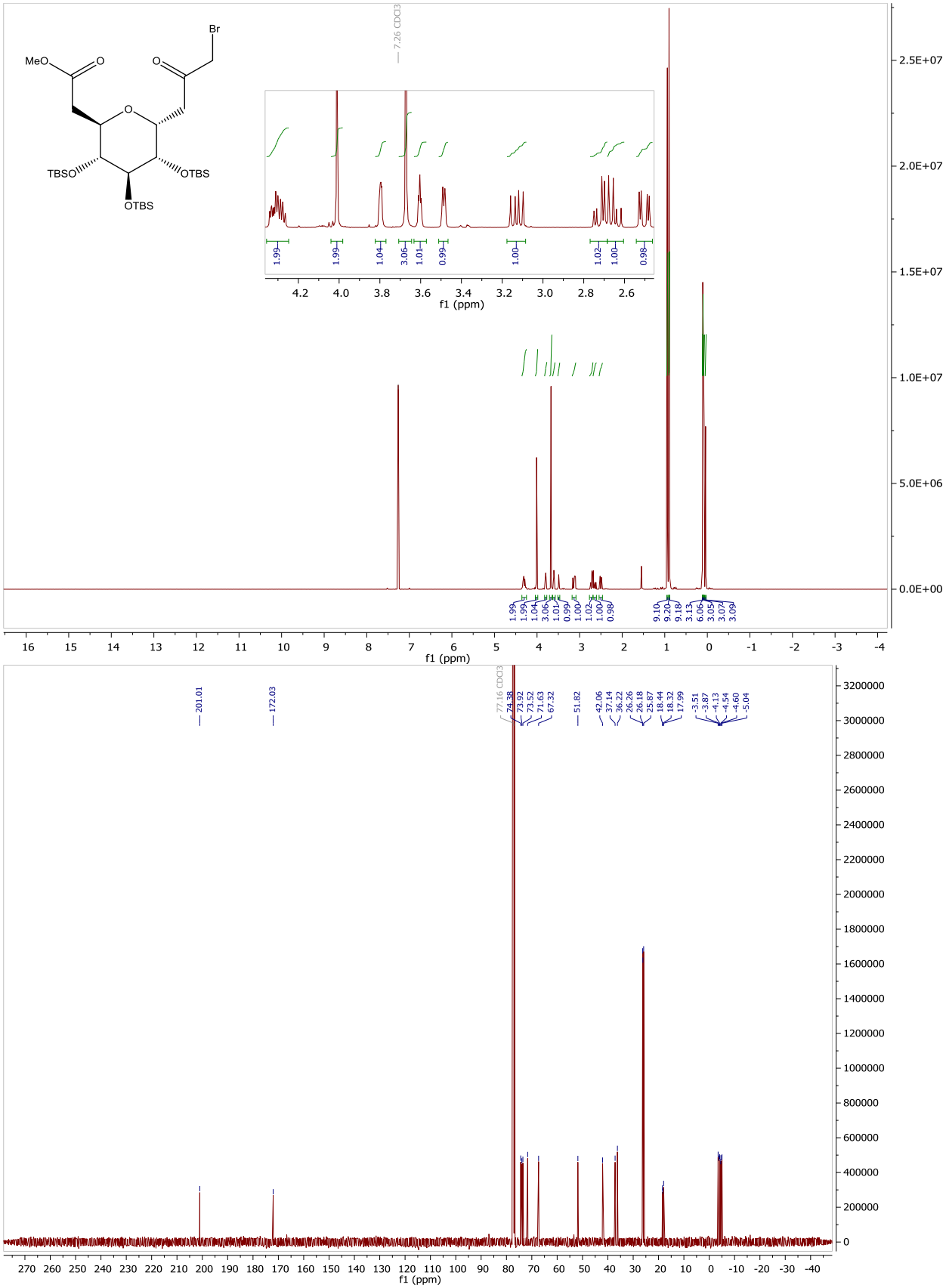

172.00
135.94
116.40
77.16 CDCl3
74.50
74.05
73.92
71.65
69.48
51.69
37.54
35.76
26.33
26.21
25.88
18.52
18.35
17.98
-3.32
-3.95
-4.14
-4.53
-4.93
f1 (ppm)

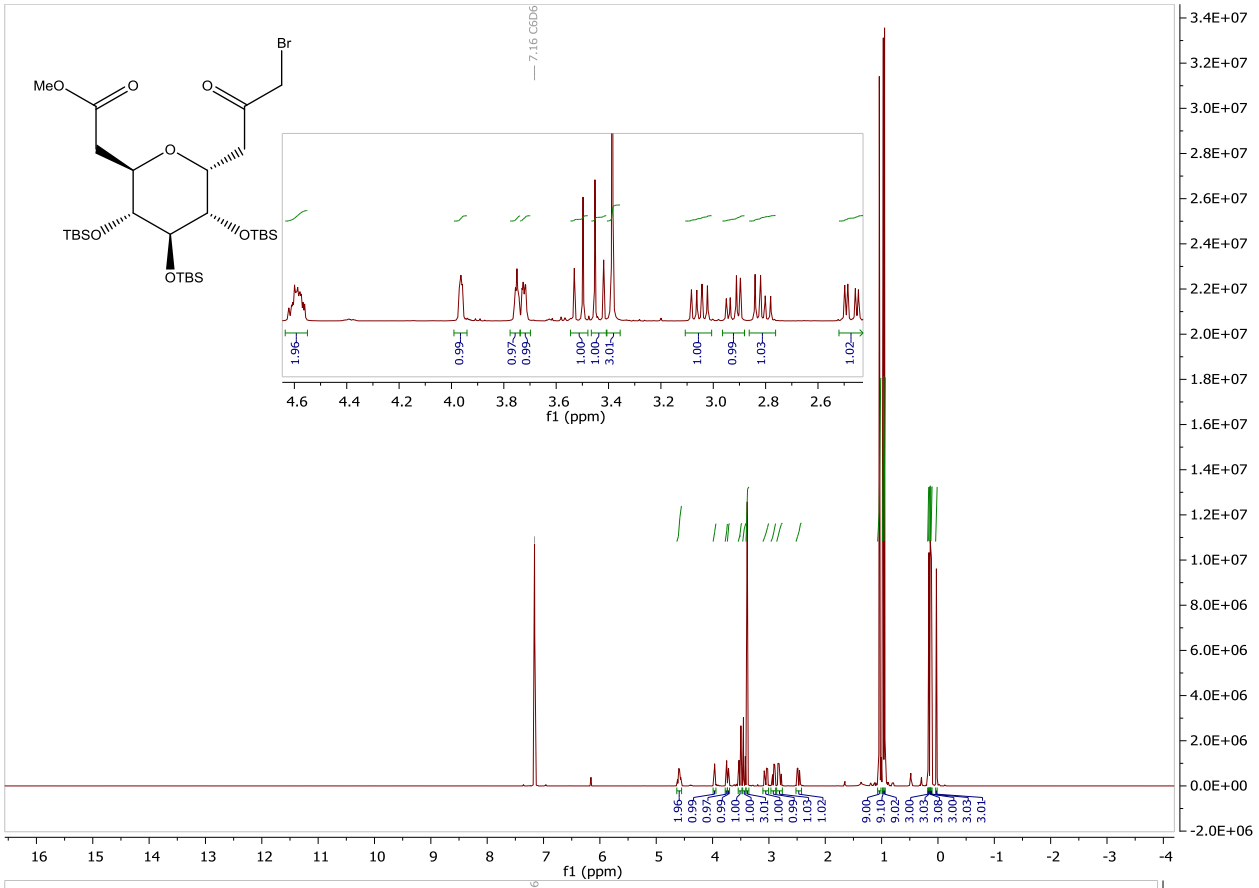

MeO
O
O
TBSO
OTBS
OTBS
7.26 CDCl3
f1 (ppm)
f1 (ppm)

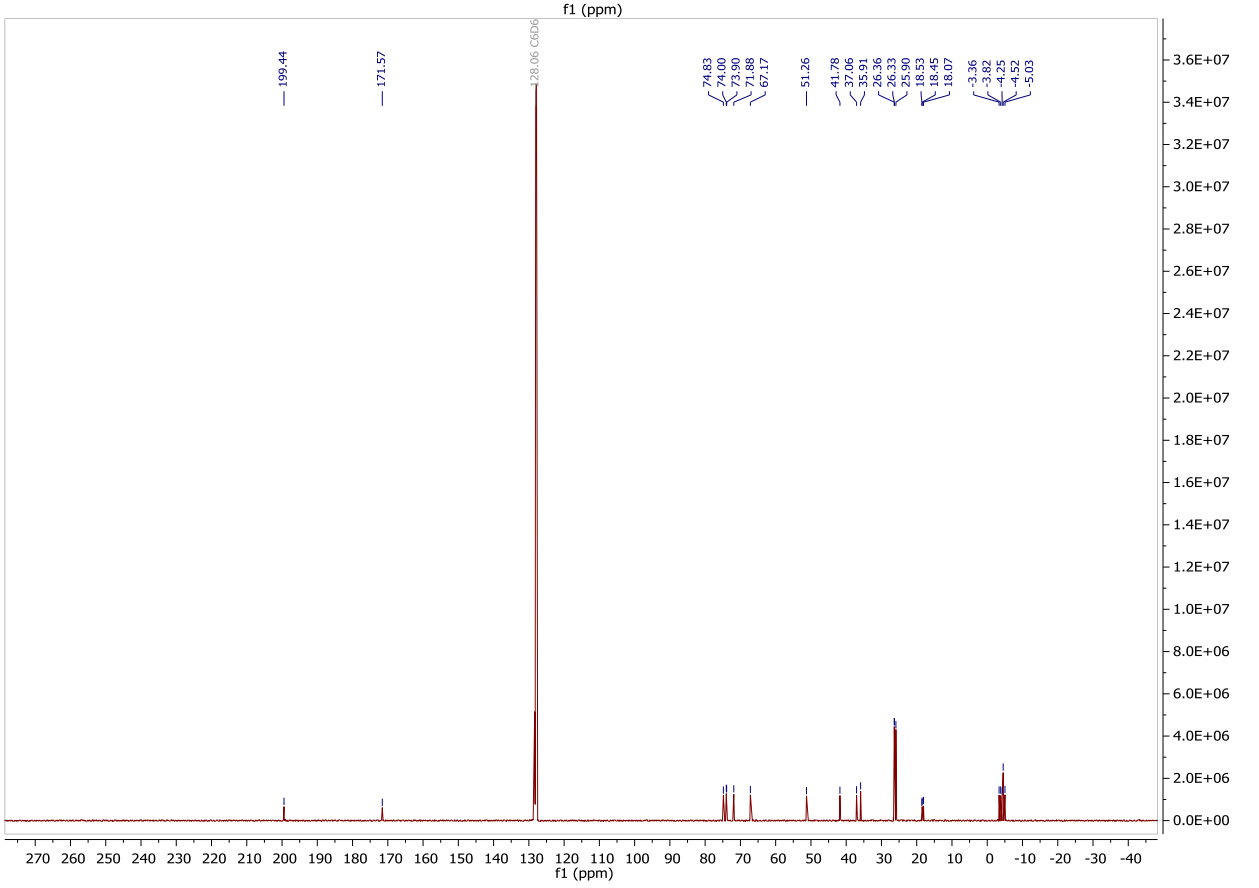

172.39
136.16
115.83
77.16 CDCl3
76.68
73.49
73.28
71.97
71.54
51.63
36.90
35.80
26.51
26.48
25.85
18.56
18.51
17.96
-2.93
-3.08
-4.32
-4.34
-4.79
-5.08
f1 (ppm)

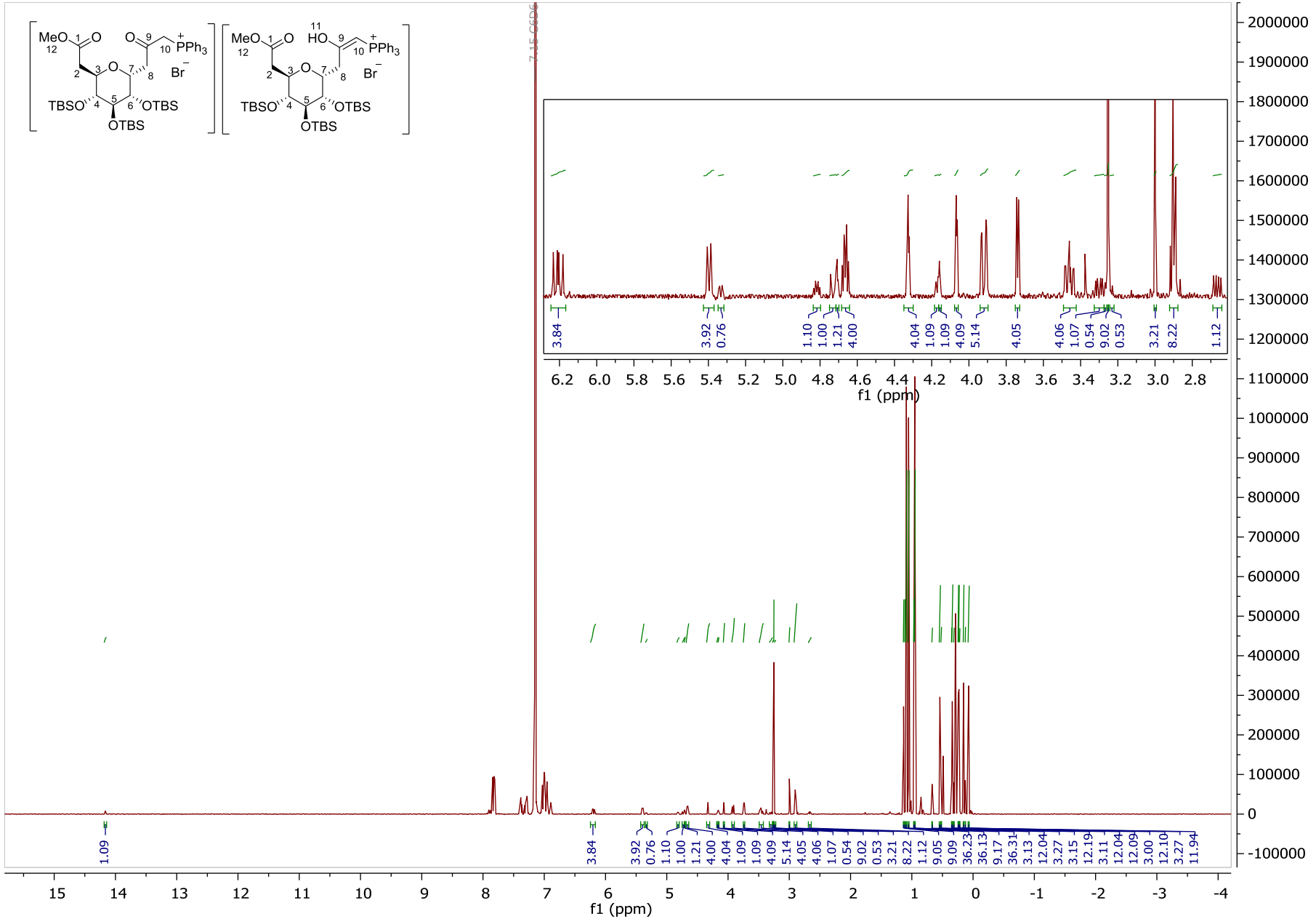

OH
MeO
O
O
O
TBSO
OTBS
OTBS
7.26 CDCl3
3.06
1.07
1.10
3.11
1.03
1.05
1.01
1.04
2.09
0.99
f1 (ppm)
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
f1 (ppm)

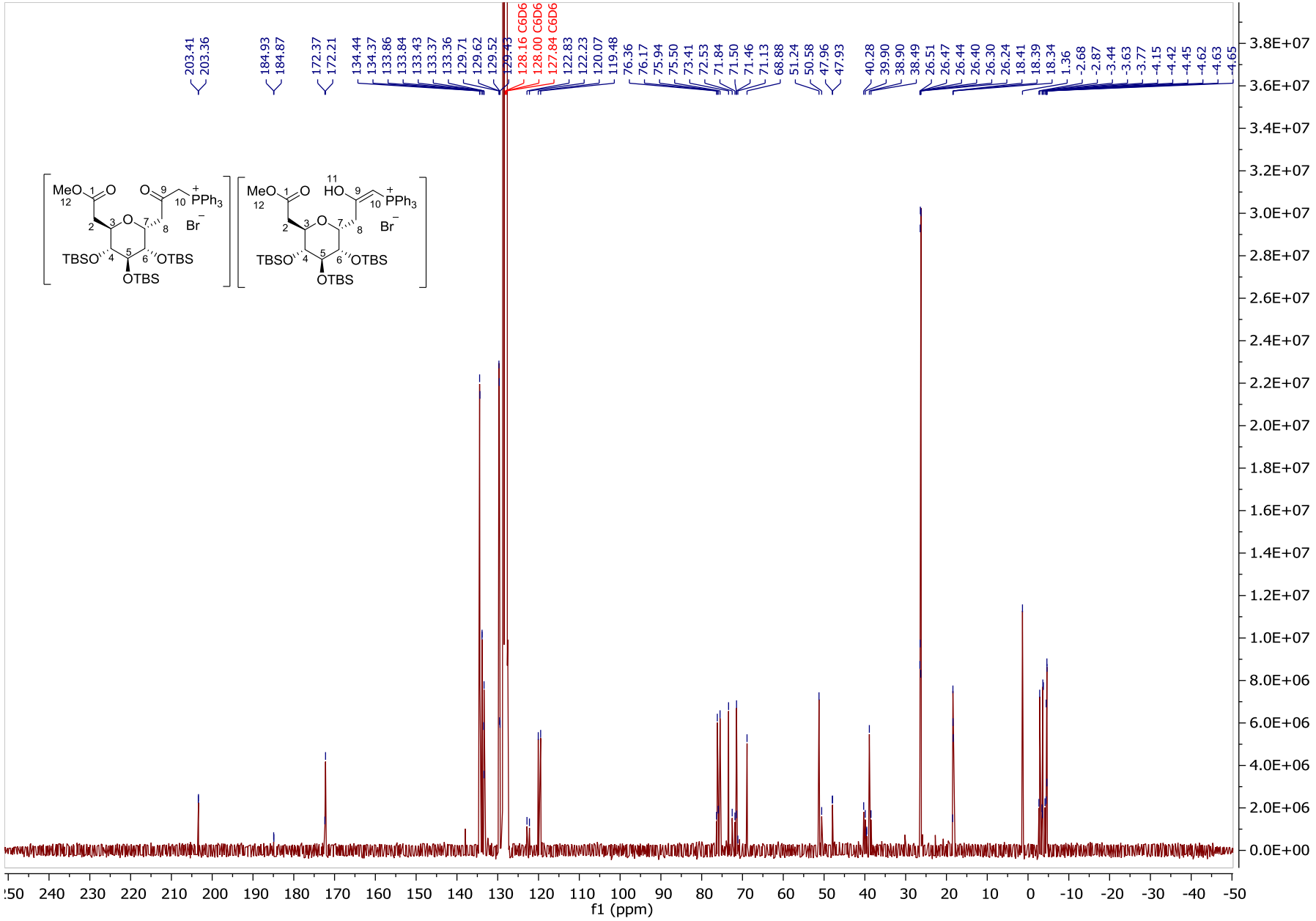

209.45
171.97
77.16 CDCl3
74.40
73.93
73.51
71.78
69.36
67.12
51.82
40.67
37.15
26.25
26.16
25.87
18.43
18.32
17.99
-3.49
-3.85
-4.13
-4.52
-4.61
-5.07
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
f1 (ppm)

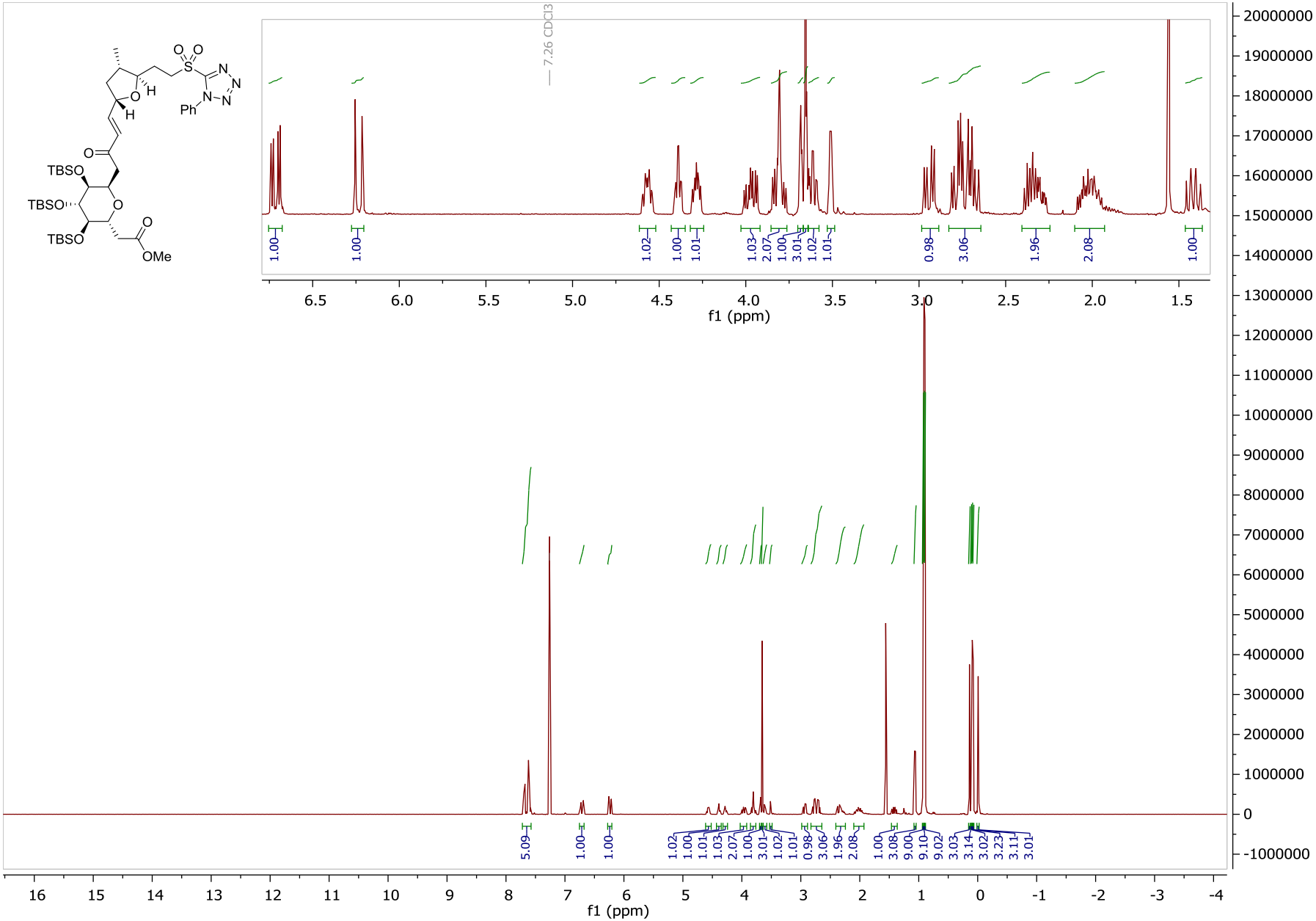

MeO
O
O
Br
O
TBSO
OTBS
OTBS
7.26 CDCl3
f1 (ppm)
77.16 CDCl3
201.01
172.03
51.82
42.06
37.14
36.22
26.26
26.18
25.87
18.44
18.32
17.99
-3.51
-3.87
-4.13
-4.54
-4.60
-5.04
f1 (ppm)

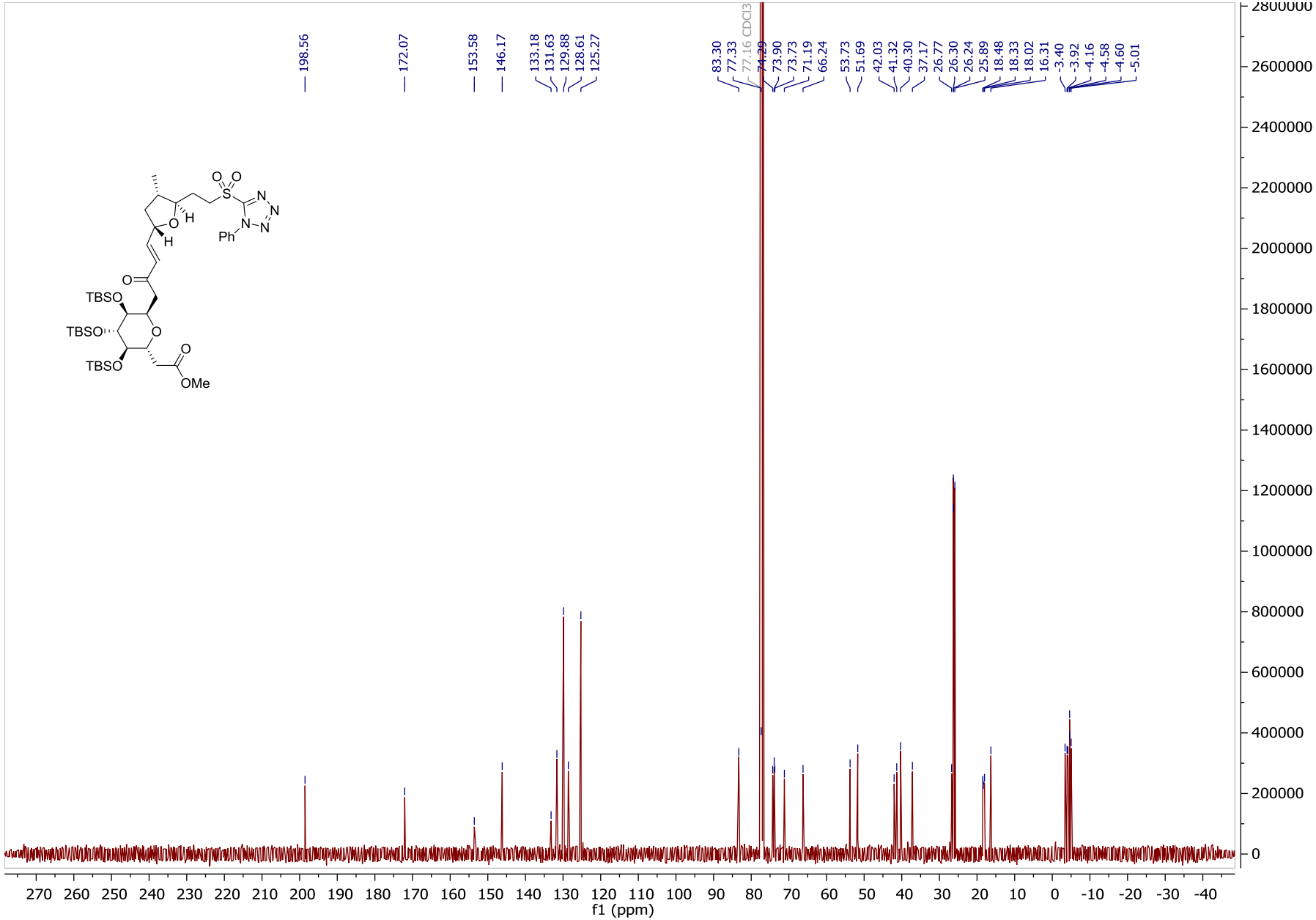

Br
MeO
O
O
O
TBSO
OTBS
OTBS
7.16 C6D6
f1 (ppm)
f1 (ppm)

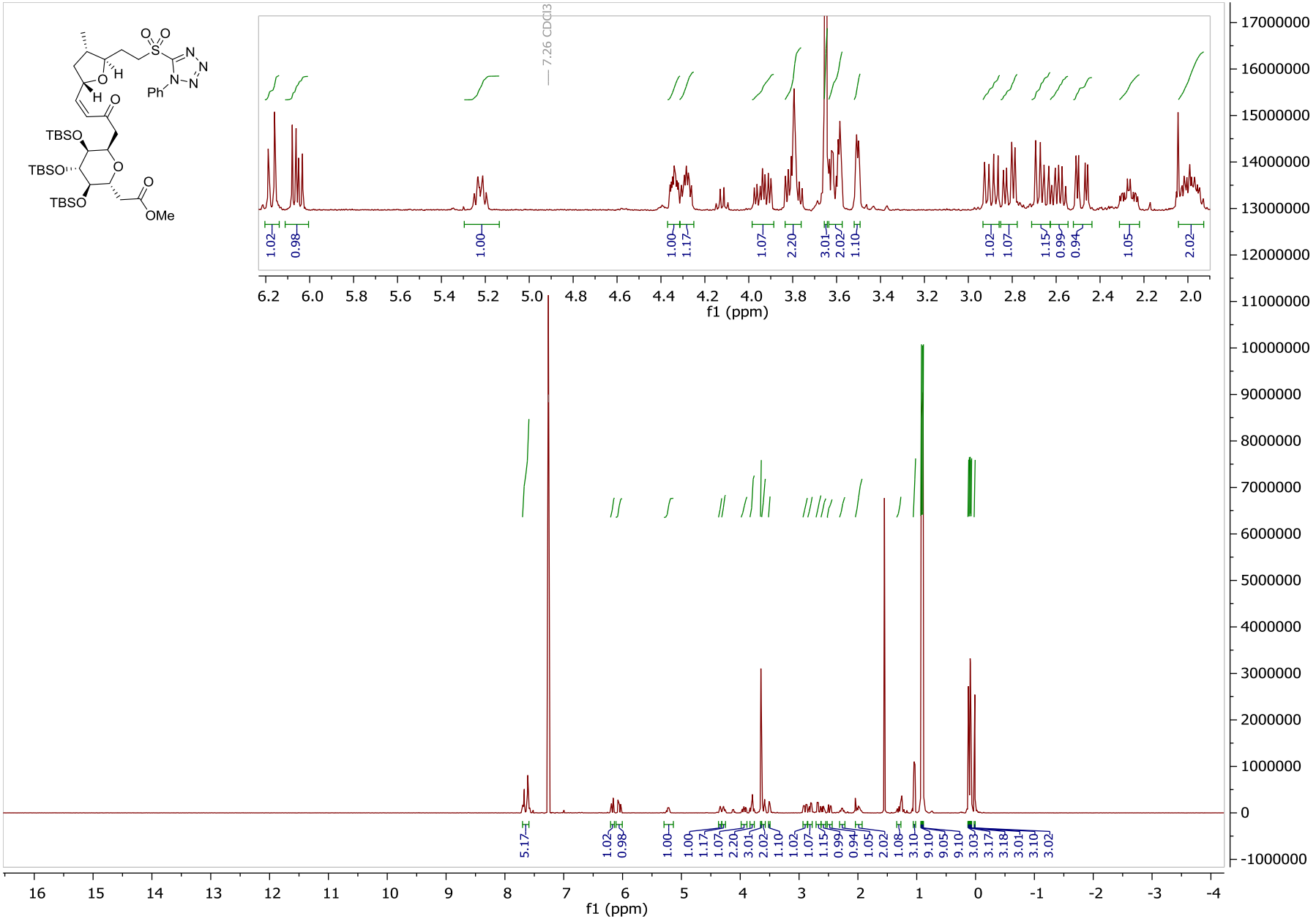

199.44
171.57
128.06 C6D6
74.83
74.00
73.90
71.88
67.17
51.26
41.78
37.06
35.91
26.36
26.33
25.90
18.53
18.45
18.07
-3.36
-3.82
-4.25
-4.52
-5.03
f1 (ppm)

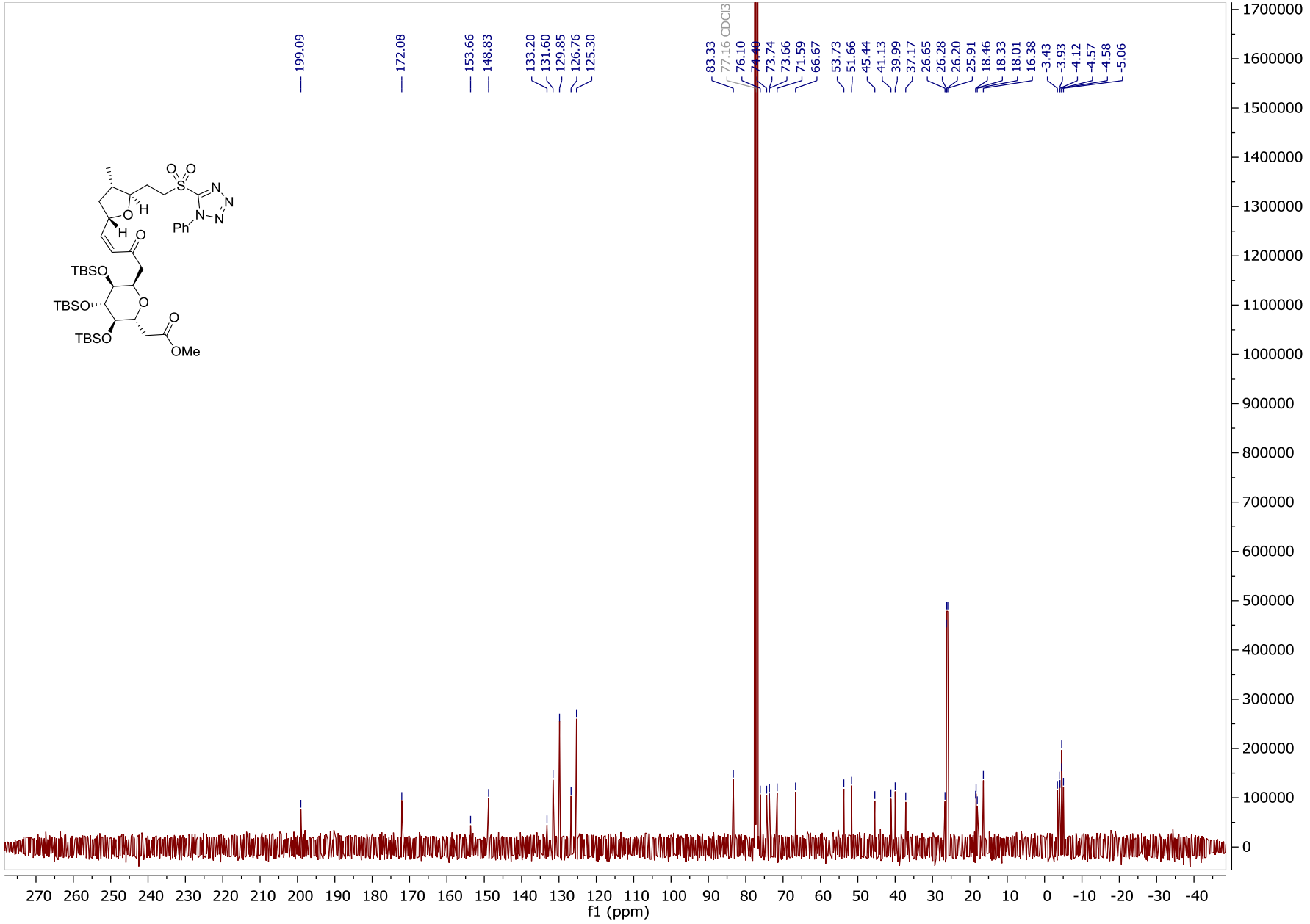

MeO
12
1
O
O
9
10
PPh3
Br
2
3
O
7
8
TBSO
4
5
6
OTBS
OTBS
11
HO
f1 (ppm)

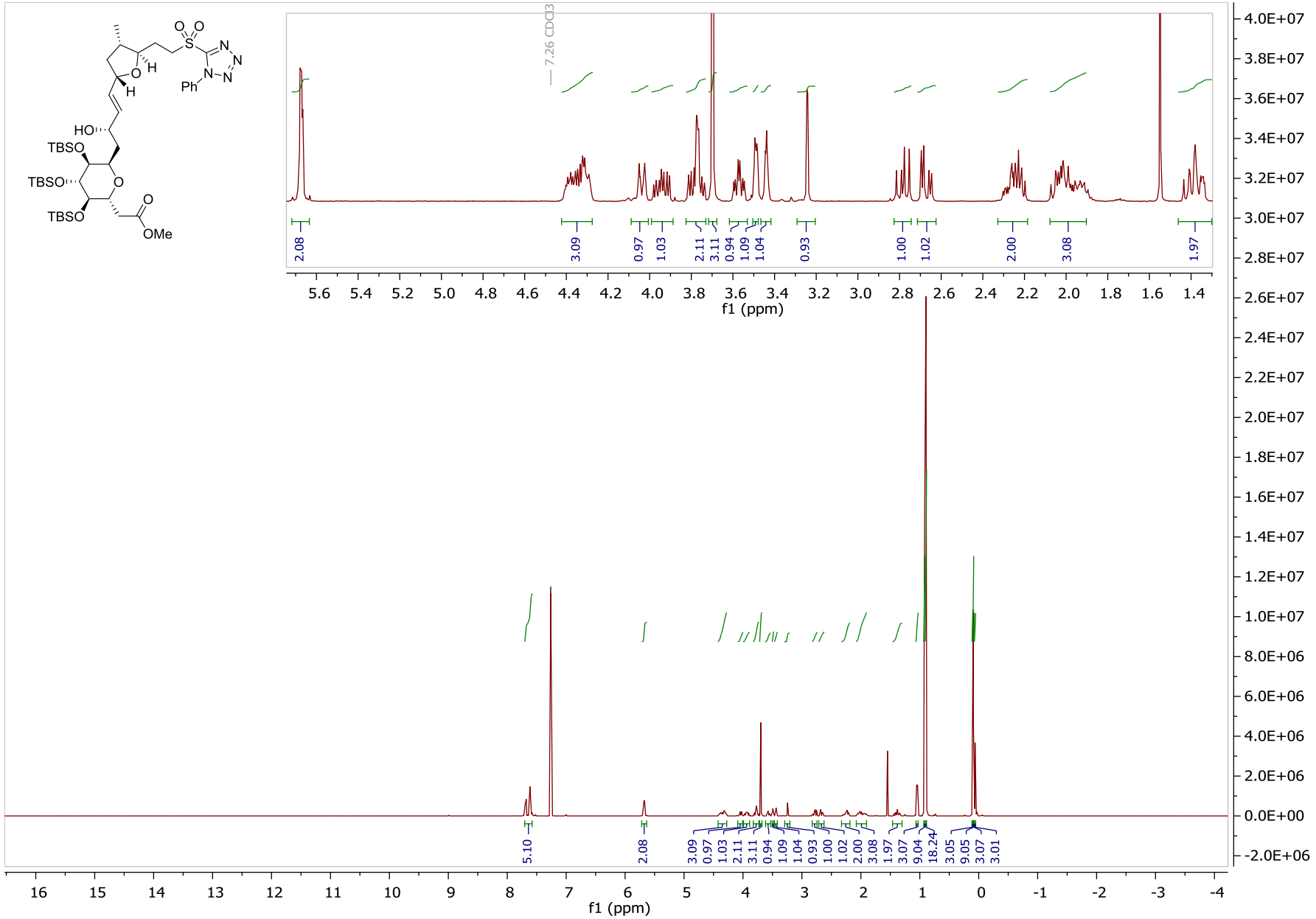

203.41
203.36
184.93
184.87
172.37
172.21
134.44
134.37
133.86
133.84
133.43
133.37
133.36
129.71
129.62
129.52
129.43
128.16 C6D6
128.00 C6D6
127.84 C6D6
122.83
122.23
120.07
119.48
76.36
76.17
75.94
75.50
73.41
72.53
71.84
71.50
71.46
71.13
68.88
51.24
50.58
47.96
47.93
40.28
39.90
38.90
38.49
26.51
26.47
26.44
26.40
26.30
26.24
18.41
18.39
18.34
1.36
-2.68
-2.87
-3.44
-3.63
-3.77
-4.15
-4.42
-4.45
-4.62
-4.63
-4.65
MeO
O
PPh3
Br
TBSO
OTBS
OTBS
HO
f1 (ppm)

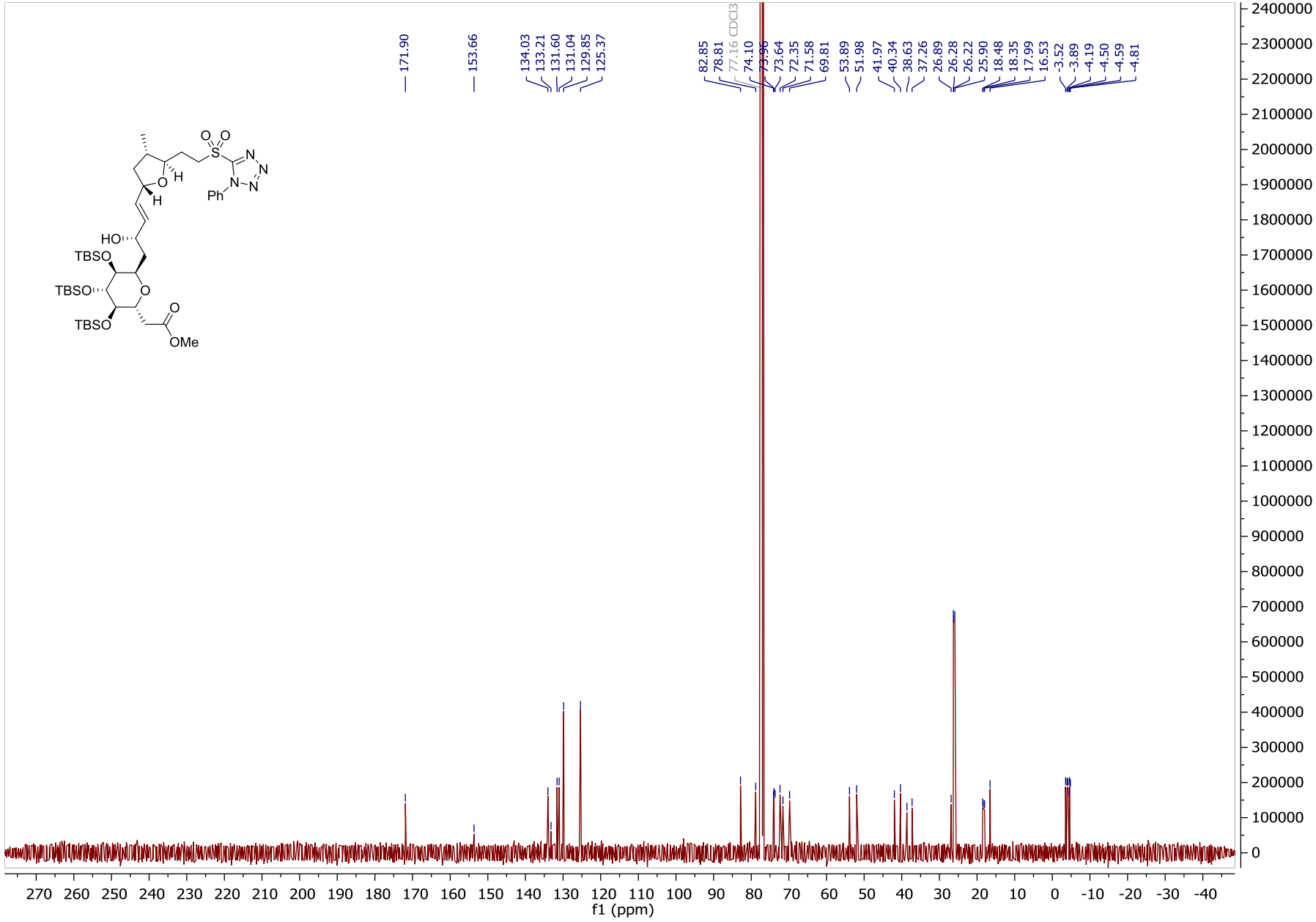

TBSO
TBSO
TBSO
OMe
Ph
— 7.26 CDCl3
f1 (ppm)
f1 (ppm)

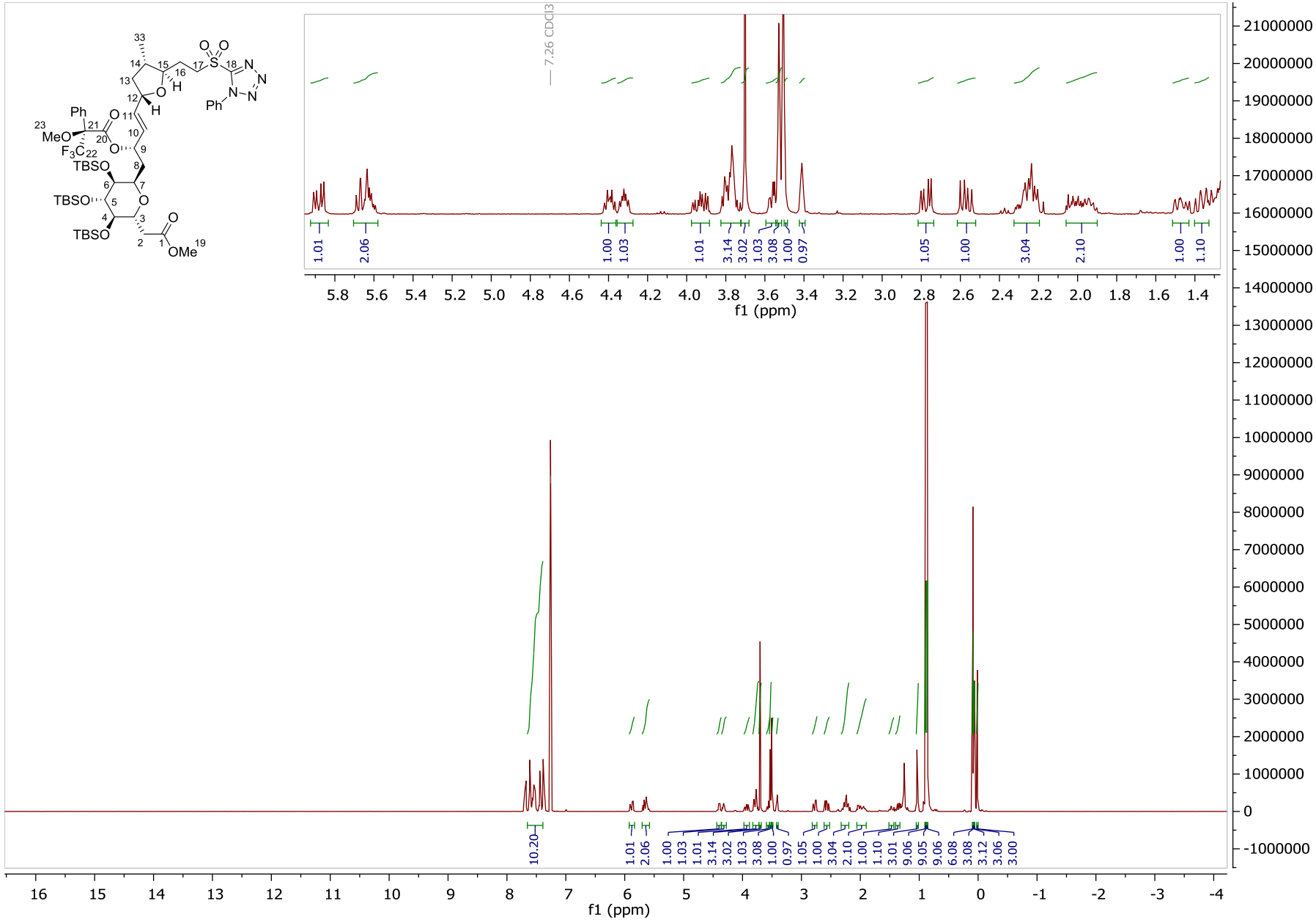

198.56
172.07
153.58
146.17
133.18
131.63
129.88
128.61
125.27
83.30
77.33
77.16 CDCl3
74.29
73.90
73.73
71.19
66.24
53.73
51.69
42.03
41.32
40.30
37.17
26.77
26.30
26.24
25.89
18.48
18.33
18.02
16.31
-3.40
-3.92
-4.16
-4.58
-4.60
-5.01
TBSO
TBSO
TBSO
OMe
Ph
f1 (ppm)

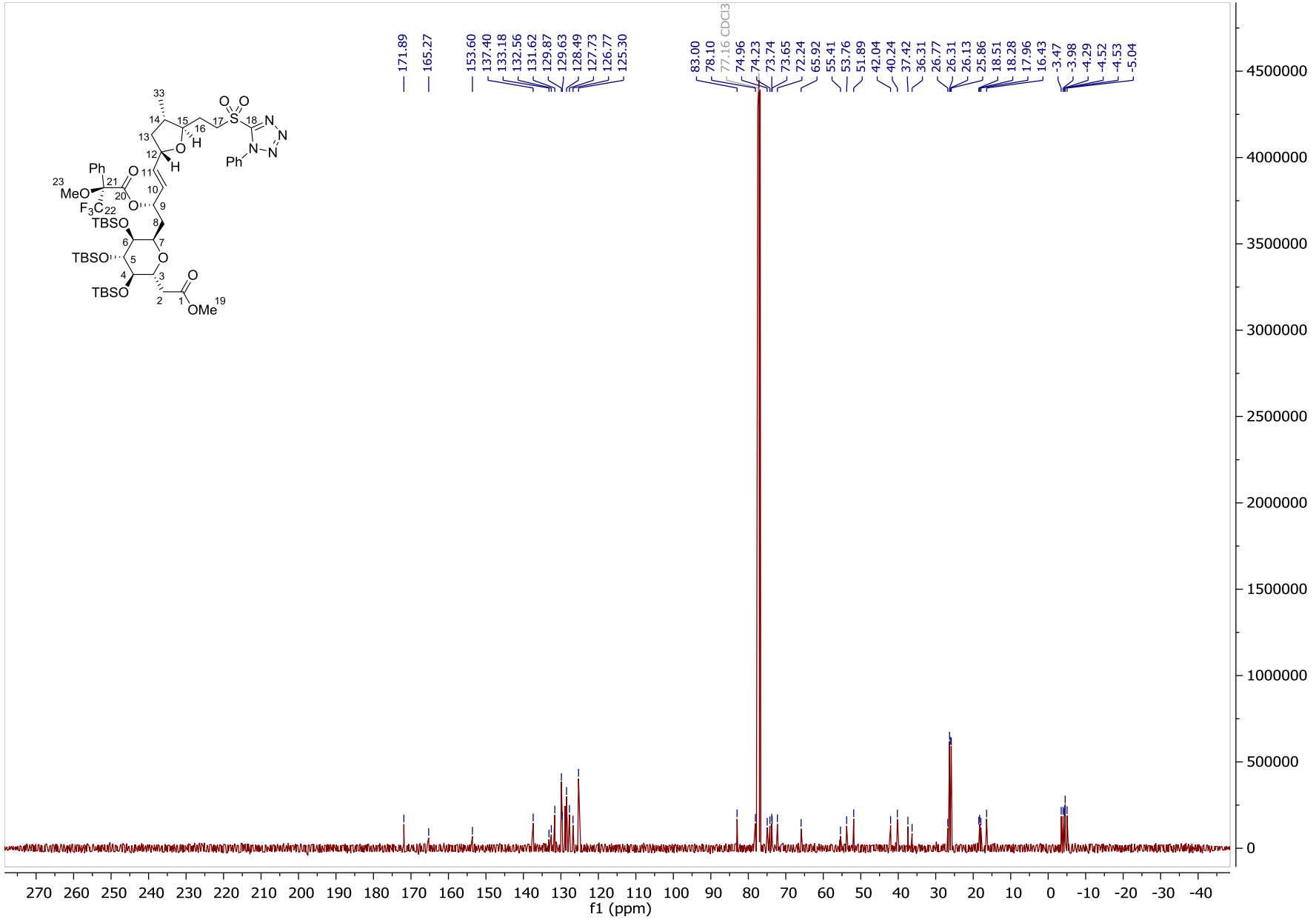

TBSO
TBSO
TBSO
OMe
Ph
— 7.26 CDCl3
f1 (ppm)
f1 (ppm)

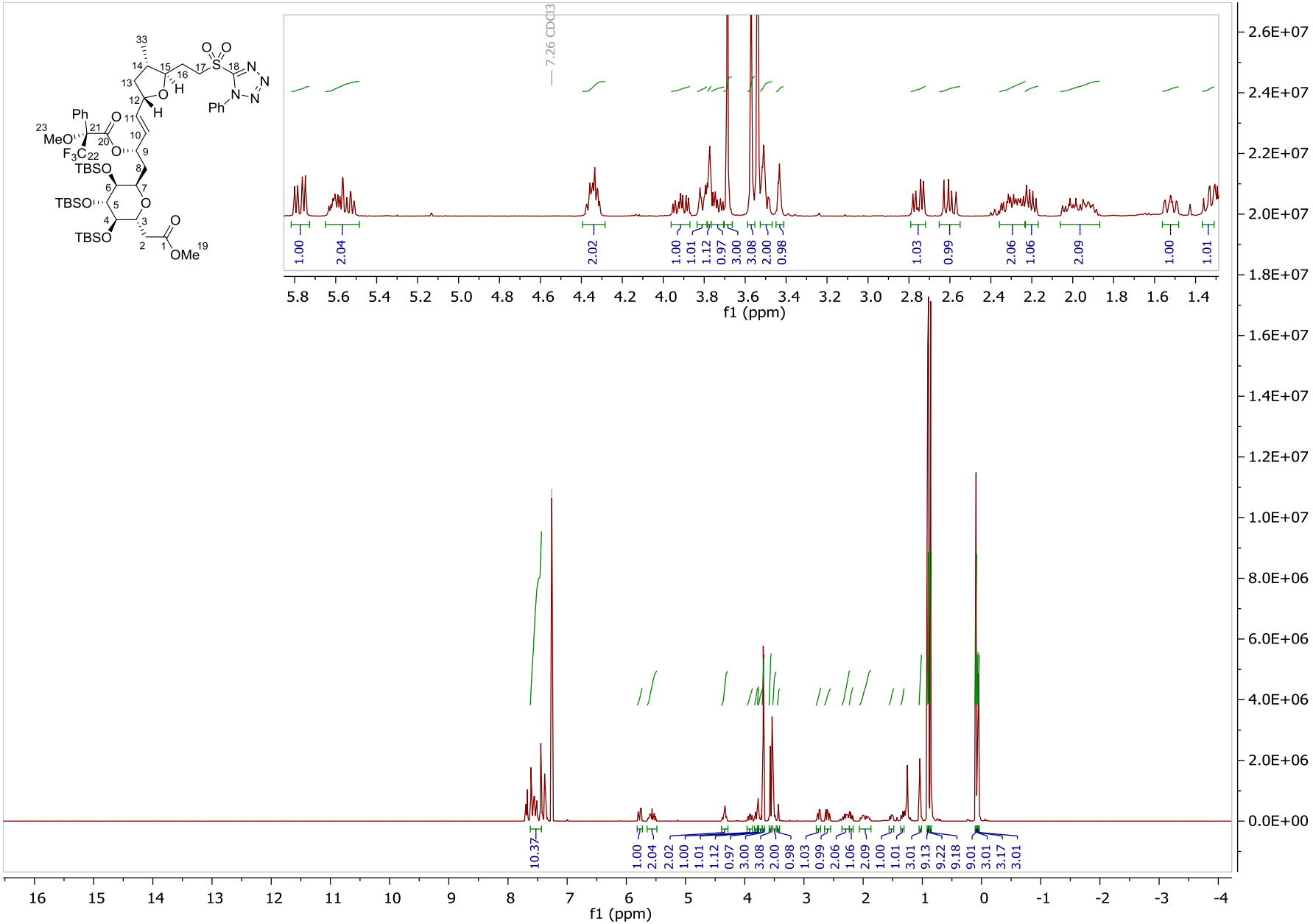

199.09
172.08
153.66
148.83
133.20
131.60
129.85
126.76
125.30
83.33
77.16 CDCl3
76.10
74.40
73.74
73.66
71.59
66.67
53.73
51.66
45.44
41.13
39.99
37.17
26.65
26.28
26.20
25.91
18.46
18.33
18.01
16.38
-3.43
-3.93
-4.12
-4.57
-4.58
-5.06
TBSO
TBSO
TBSO
OMe
Ph
f1 (ppm)

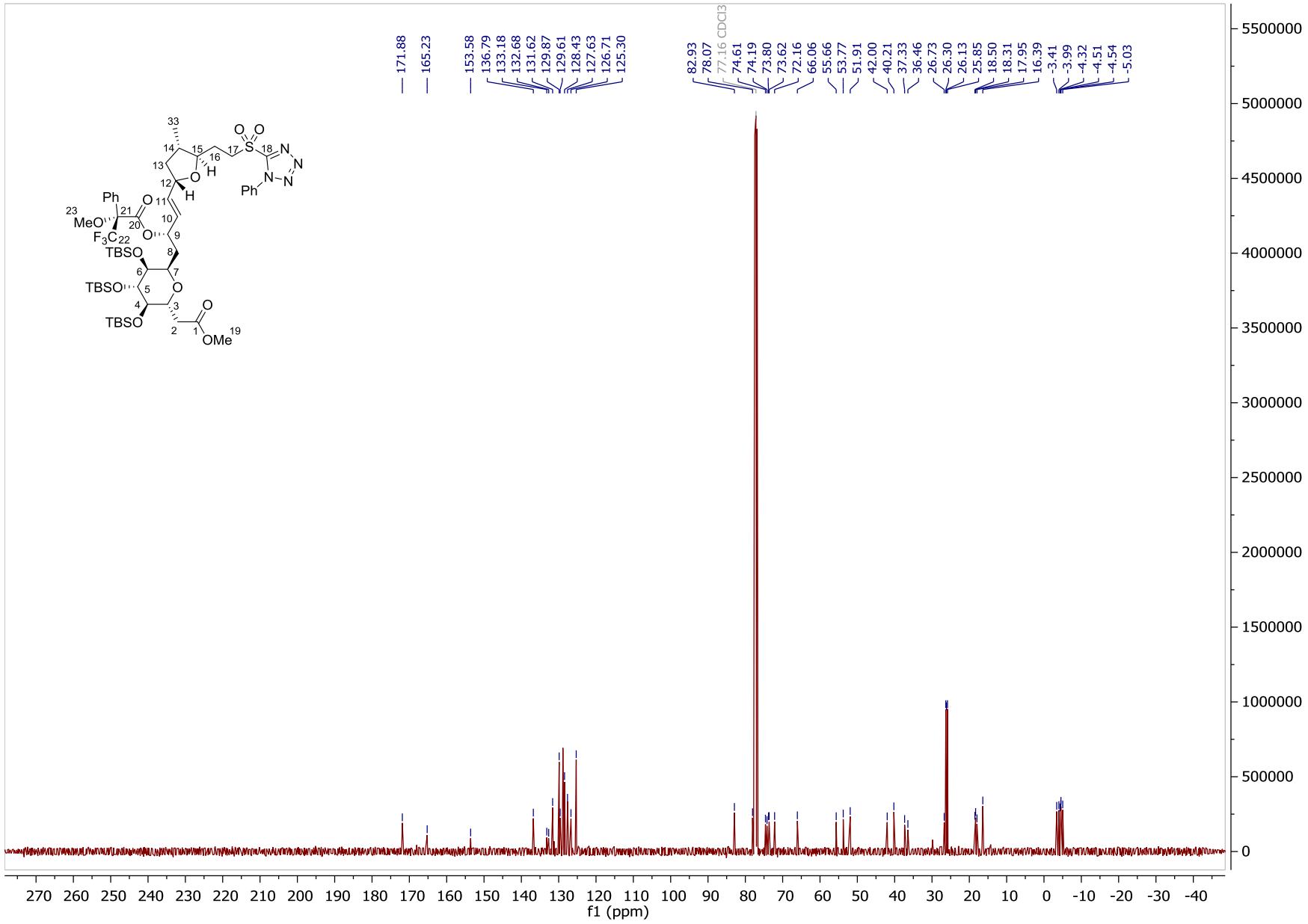

HO
TBSO
TBSO
TBSO
OMe
Ph
— 7.26 CDCl3
2.08
3.09
0.97
1.03
2.11
3.11
0.94
1.09
1.04
0.93
1.00
1.02
2.00
3.08
1.97
f1 (ppm)
5.10
2.08
3.09
0.97
1.03
2.11
3.11
0.94
1.09
1.04
0.93
1.00
1.02
2.00
3.08
1.97
3.07
9.04
18.24
3.05
9.05
3.07
3.01
f1 (ppm)

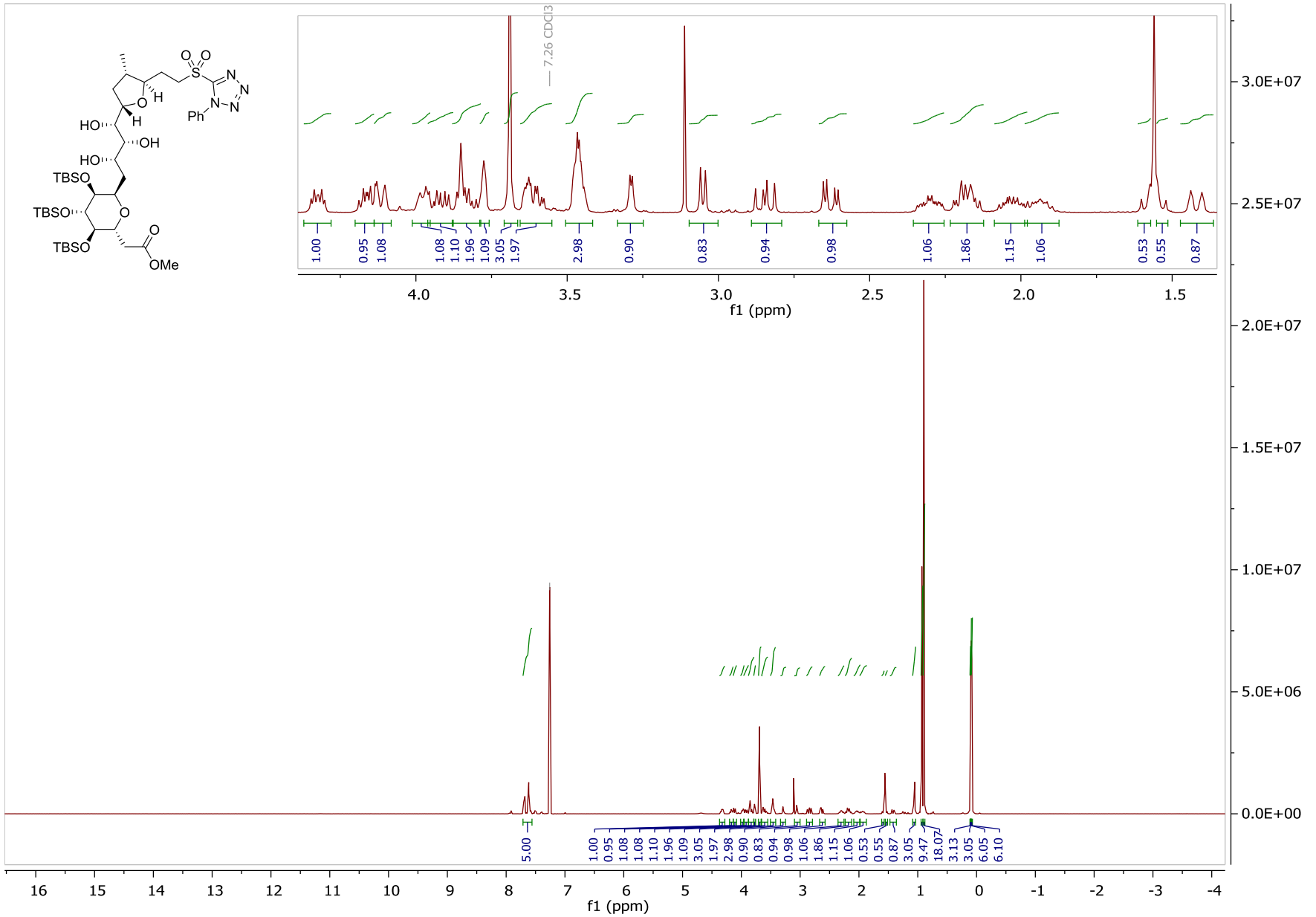

171.90
153.66
134.03
133.21
131.60
131.04
129.85
125.37
82.85
78.81
77.16 CDCl3
74.10
73.96
73.64
72.35
71.58
69.81
53.89
51.98
41.97
40.34
38.63
37.26
26.89
26.28
26.22
25.90
18.48
18.35
17.99
16.53
-3.52
-3.89
-4.19
-4.50
-4.59
-4.81
HO
TBSO
TBSO
TBSO
OMe
Ph
f1 (ppm)

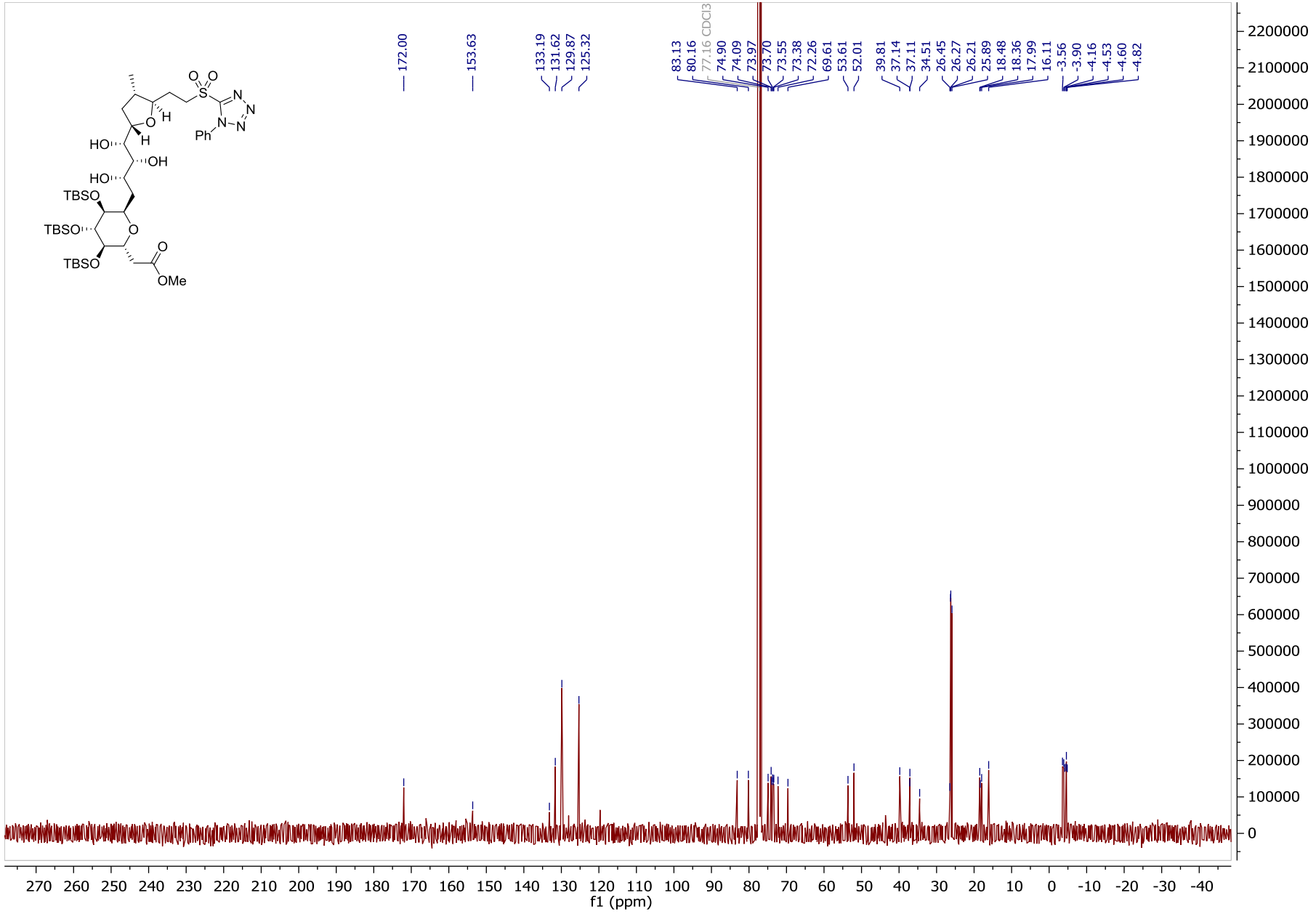

7.26 CDCl3
f1 (ppm)
f1 (ppm)

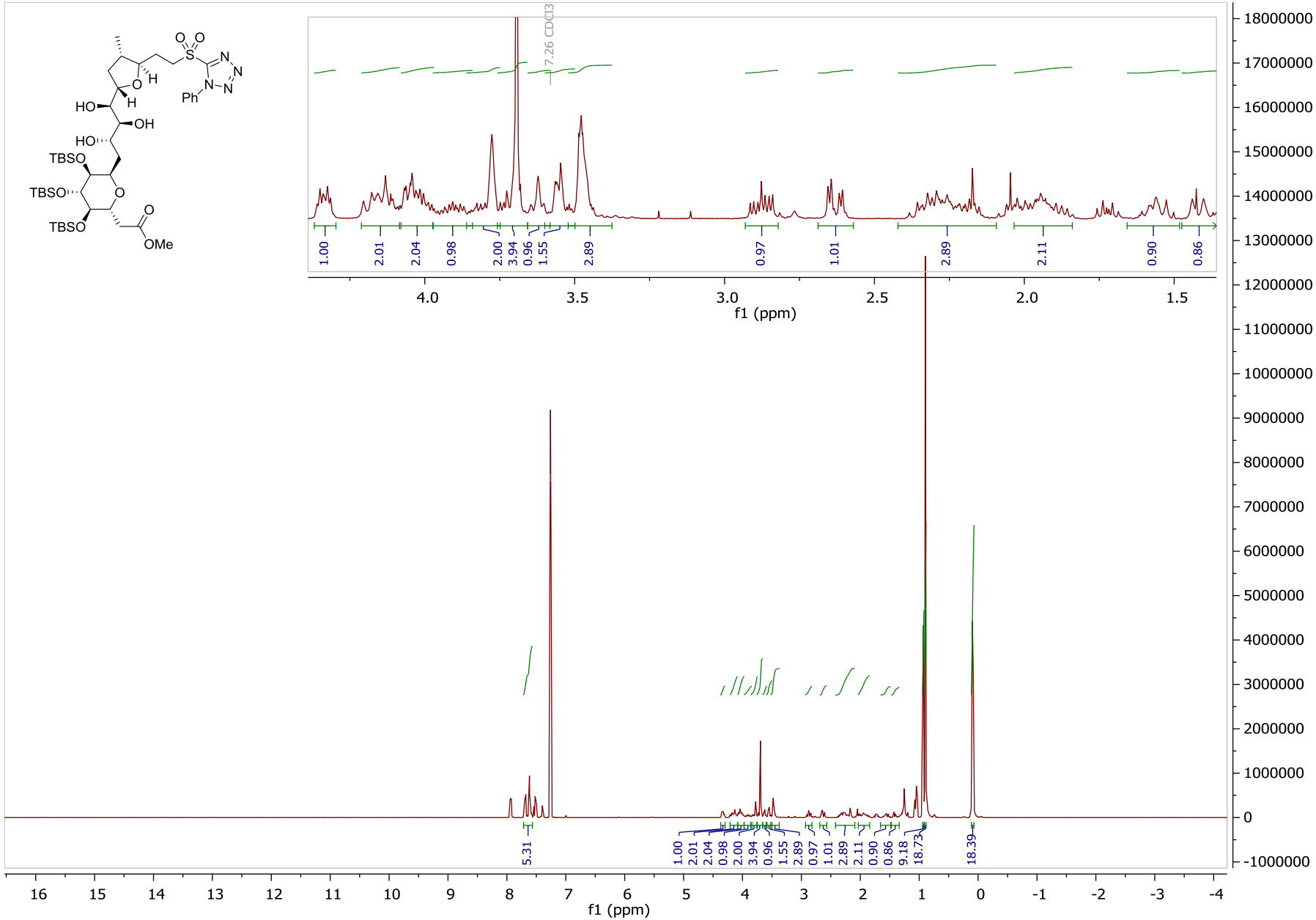

171.89
165.27
153.60
137.40
133.18
132.56
131.62
129.87
129.63
128.49
127.73
126.77
125.30
83.00
78.10
77.16 CDCl3
74.96
74.23
73.74
73.65
72.24
65.92
55.41
53.76
51.89
42.04
40.24
37.42
36.31
26.77
26.31
26.13
25.86
18.51
18.28
17.96
16.43
-3.47
-3.98
-4.29
-4.52
-4.53
-5.04
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

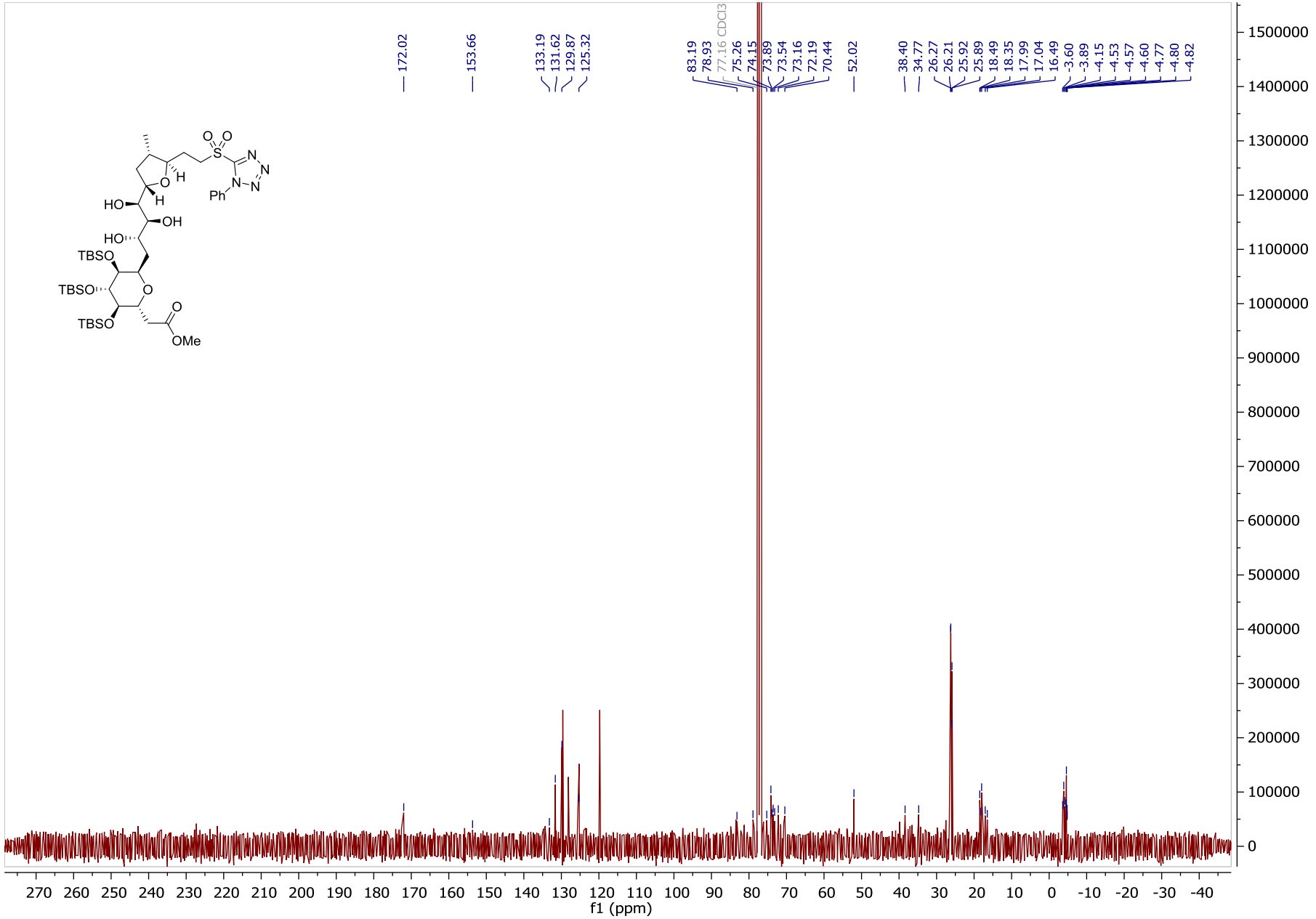

7.26 CDCl3
f1 (ppm)
f1 (ppm)

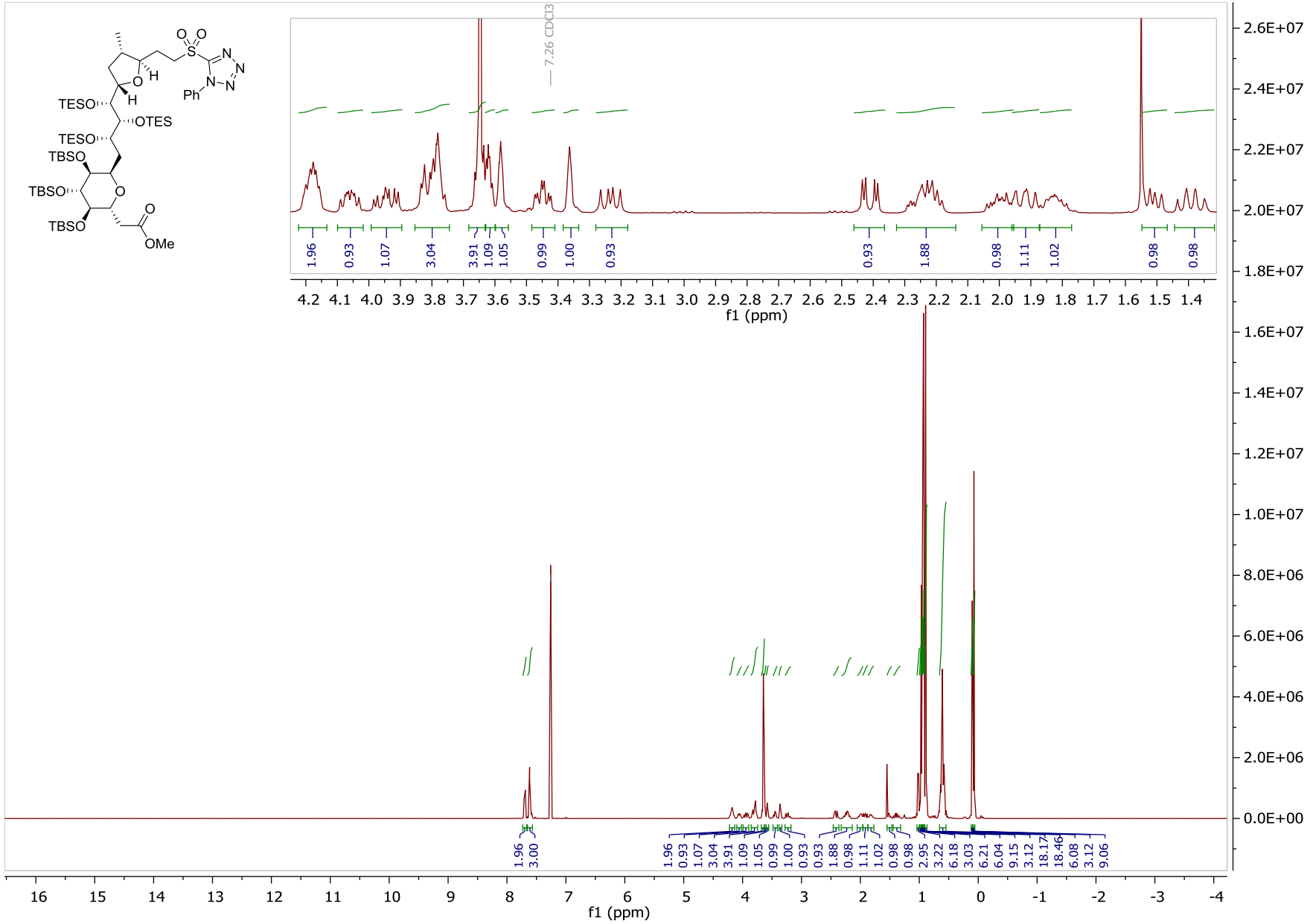

171.88
165.23
153.58
136.79
133.18
132.68
131.62
129.87
129.61
128.43
127.63
126.71
125.30
82.93
78.07
77.16 CDCl3
74.61
74.19
73.80
73.62
72.16
66.06
55.66
53.77
51.91
42.00
40.21
37.33
36.46
26.73
26.30
26.13
25.85
18.50
18.31
17.95
16.39
-3.41
-3.99
-4.32
-4.51
-4.54
-5.03
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

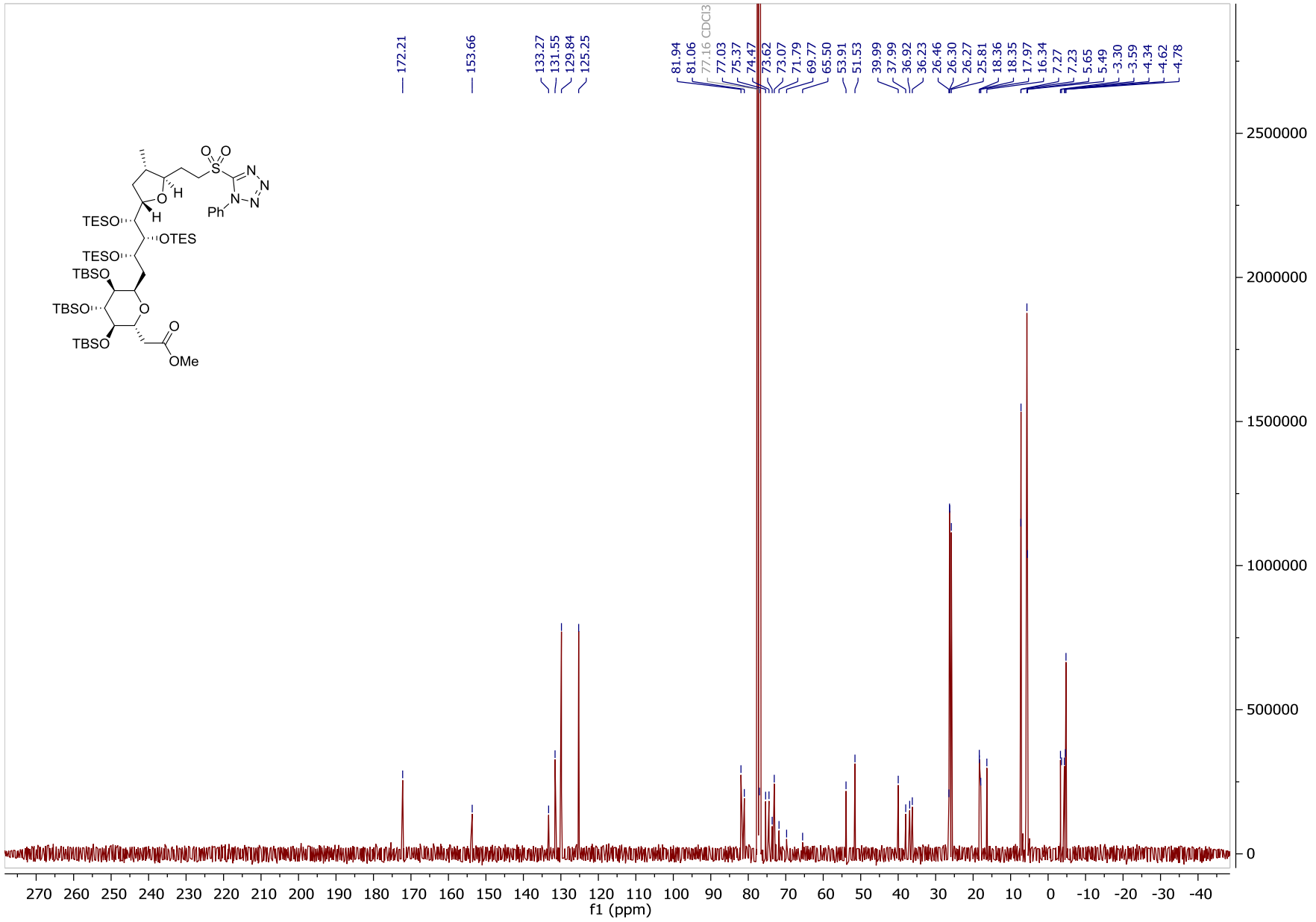

7.26 CDCl3
f1 (ppm)
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
HO
OH
HO
TBSO
TBSO
TBSO
O
O
OMe
Ph
N
N
N
S
O
O
H
H

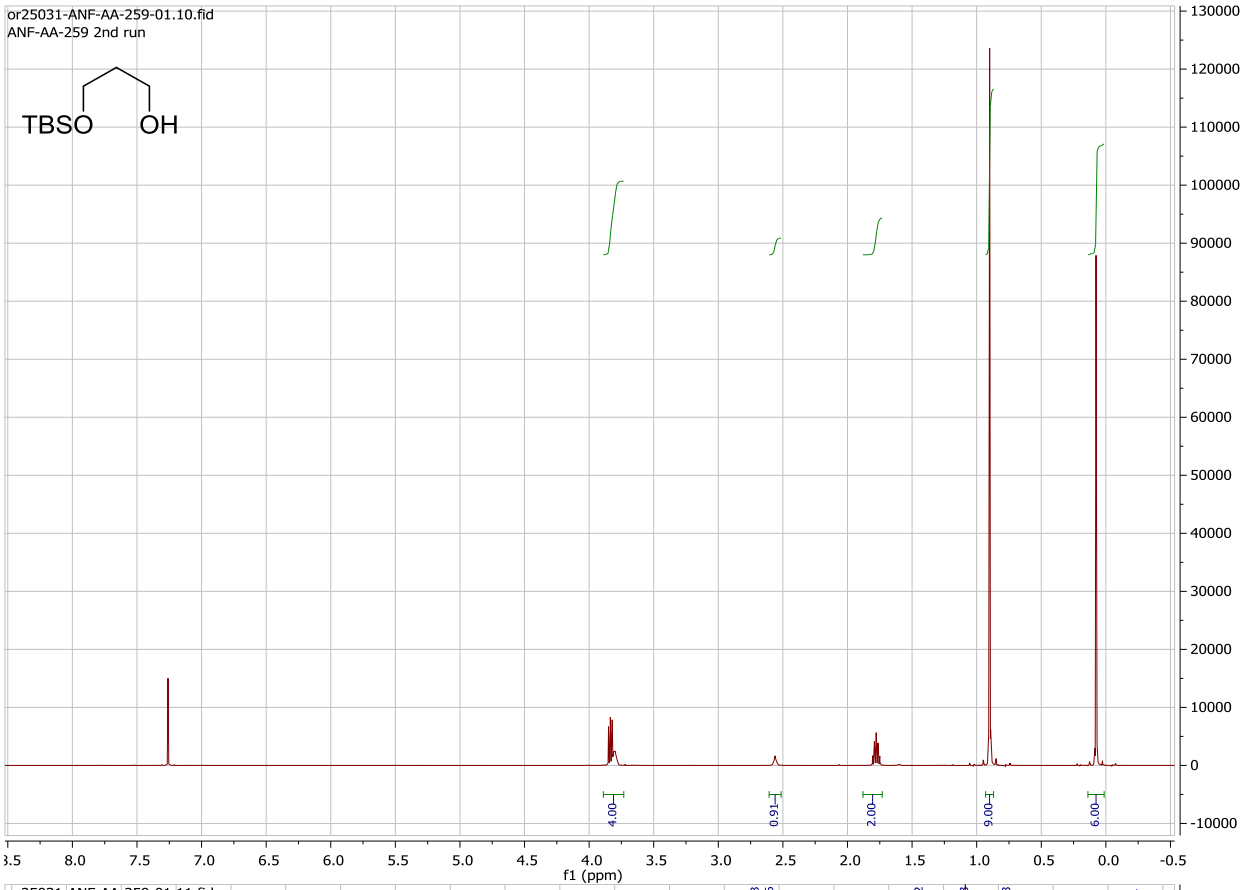

172.00
153.63
133.19
131.62
129.87
125.32
83.13
80.16
77.16 CDCl3
74.90
74.09
73.97
73.70
73.55
73.38
72.26
69.61
53.61
52.01
39.81
37.14
37.11
34.51
26.45
26.27
26.21
25.89
18.48
18.36
17.99
16.11
-3.56
-3.90
-4.16
-4.53
-4.60
-4.82
HO
OH
HO
TBSO
TBSO
TBSO
OMe
Ph
f1 (ppm)

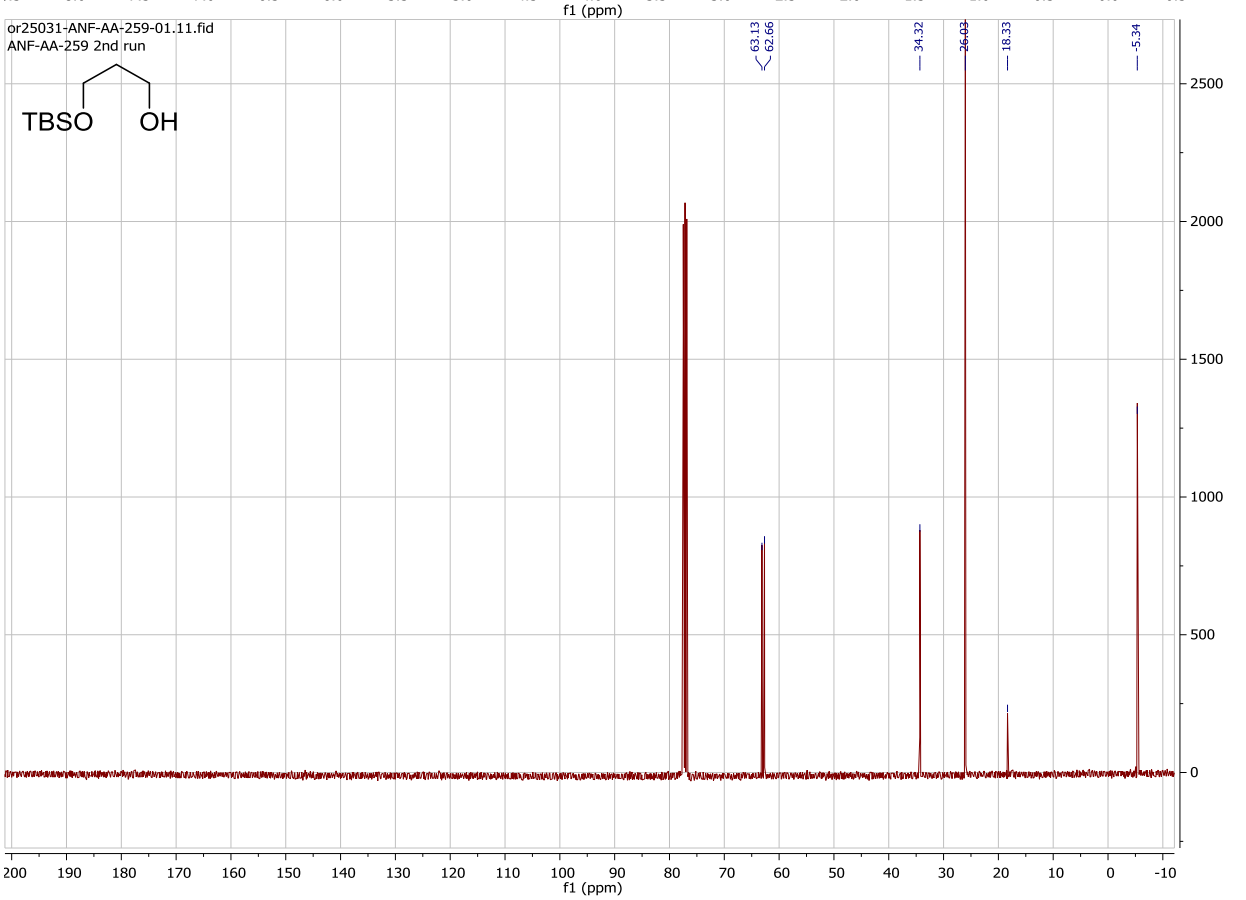

7.26 CDCl3
f1 (ppm)
1.00
2.01
2.04
0.98
2.00
3.94
0.96
1.55
2.89
0.97
1.01
2.89
2.11
0.90
0.86
5.31
18.39
18.73
9.18

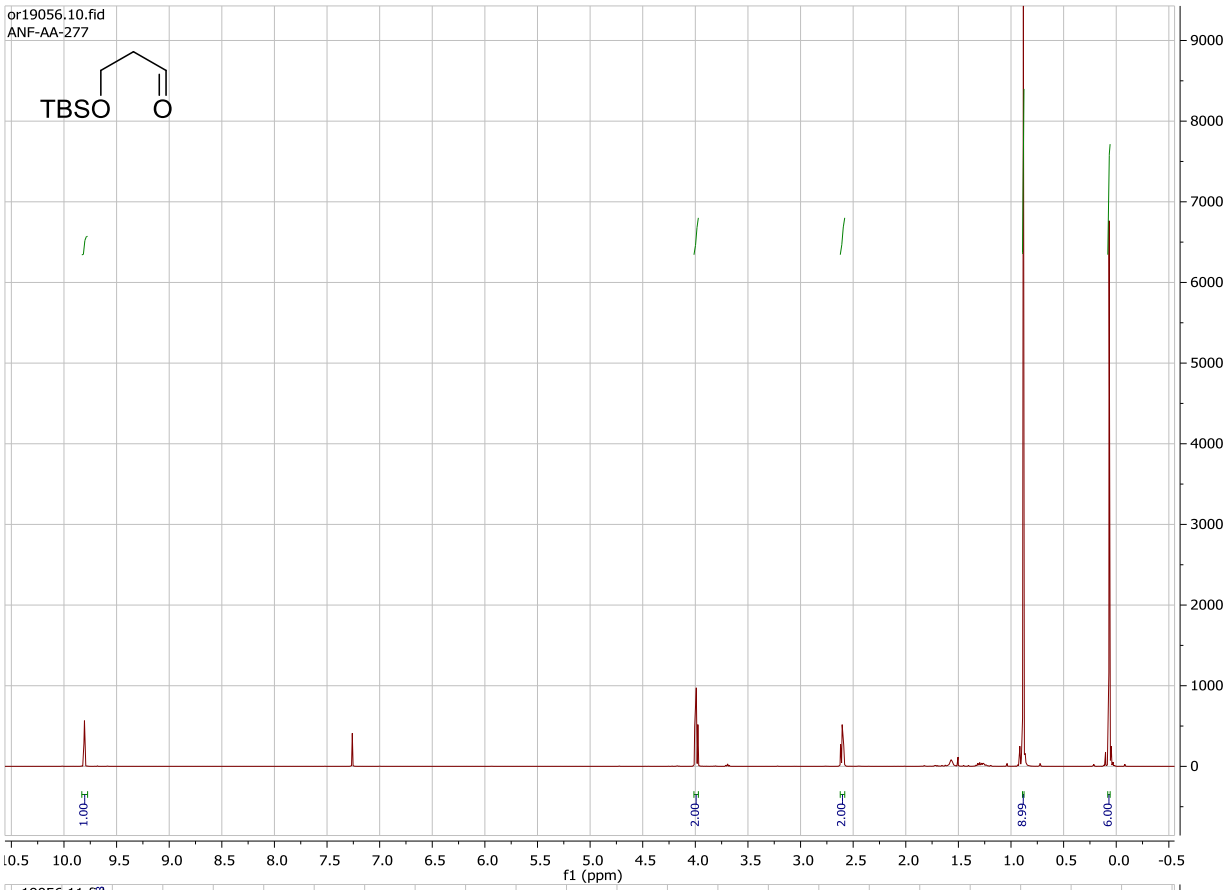

172.02
153.66
133.19
131.62
129.87
125.32
83.19
78.93
77.16 CDCl3
75.26
74.15
73.89
73.54
73.16
72.19
70.44
52.02
38.40
34.77
26.27
26.21
25.92
25.89
18.49
18.35
17.99
17.04
16.49
-3.60
-3.89
-4.15
-4.53
-4.57
-4.60
-4.77
-4.80
-4.82
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)
O
O
S
N
N
N
Ph
O
H
H
HO
OH
HO
TBSO
TBSO
TBSO
O
O
OMe

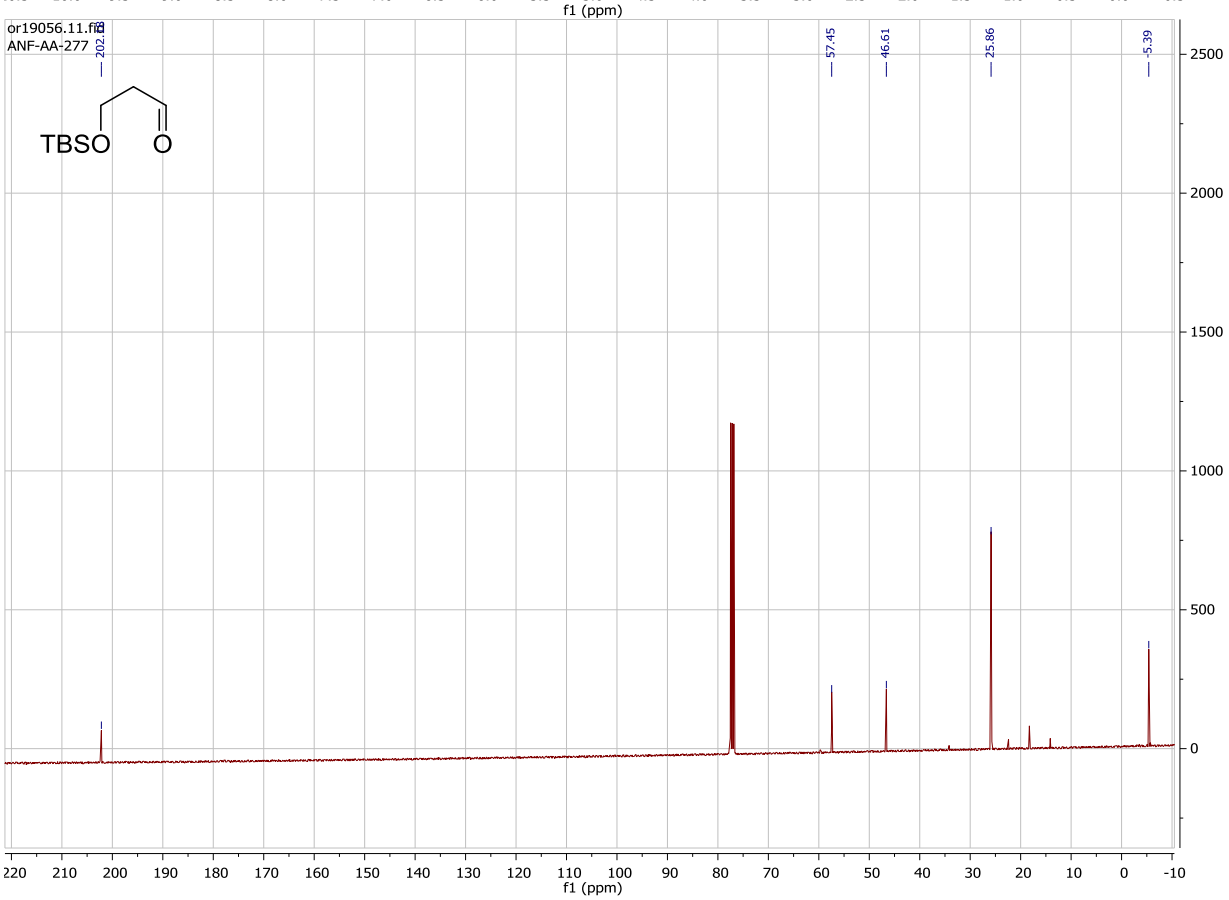

TESO
OTES
TESO
TBSO
TBSO
TBSO
OMe
Ph
7.26 CDCl3
f1 (ppm)
f1 (ppm)

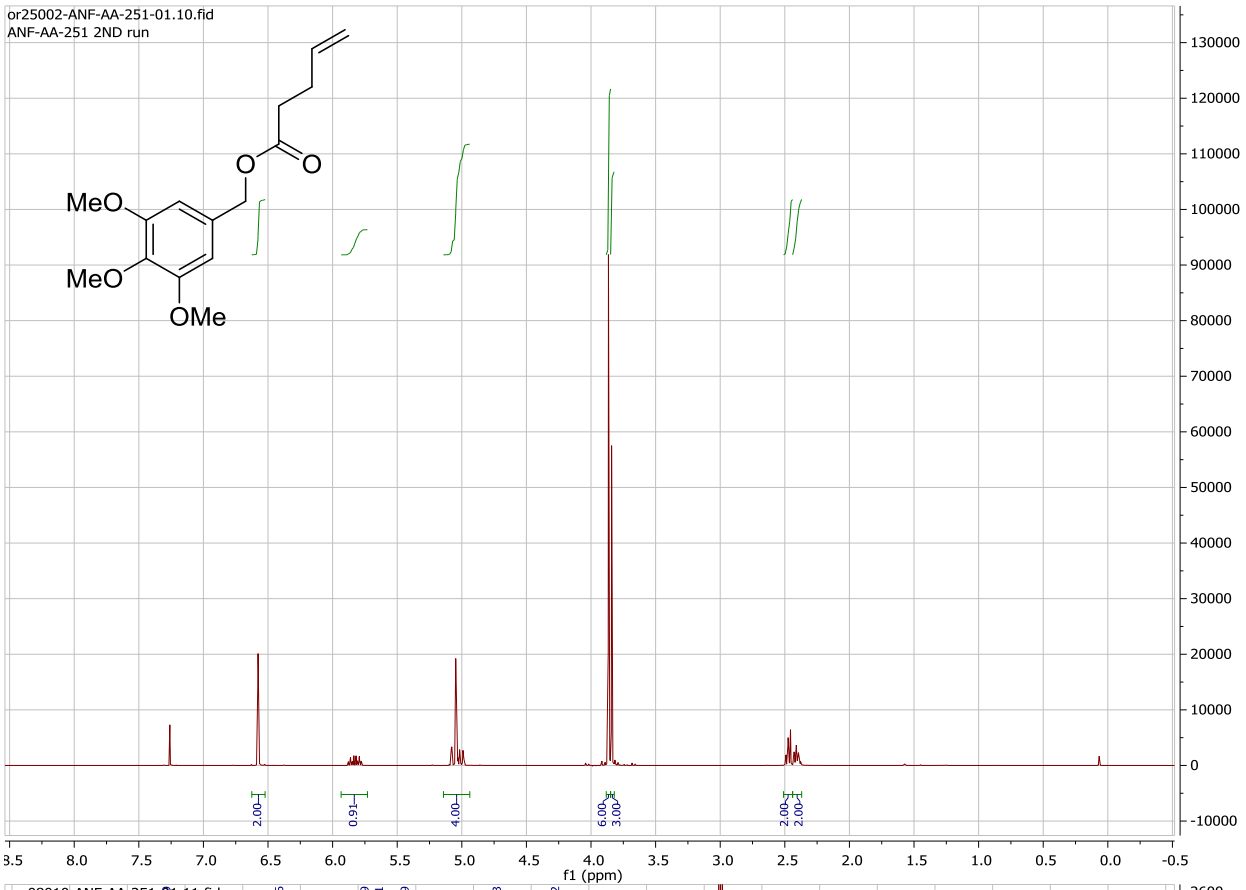

172.21
153.66
133.27
131.55
129.84
125.25
81.94
81.06
77.16 CDCl3
77.03
75.37
74.47
73.62
73.07
71.79
69.77
65.50
53.91
51.53
39.99
37.99
36.92
36.23
26.46
26.30
26.27
25.81
18.36
18.35
17.97
16.34
7.27
7.23
5.65
5.49
-3.30
-3.59
-4.34
-4.62
-4.78
TESO
OTES
TESO
TBSO
TBSO
TBSO
OMe
Ph
2500000
2000000
1500000
1000000
500000
0
f1 (ppm)

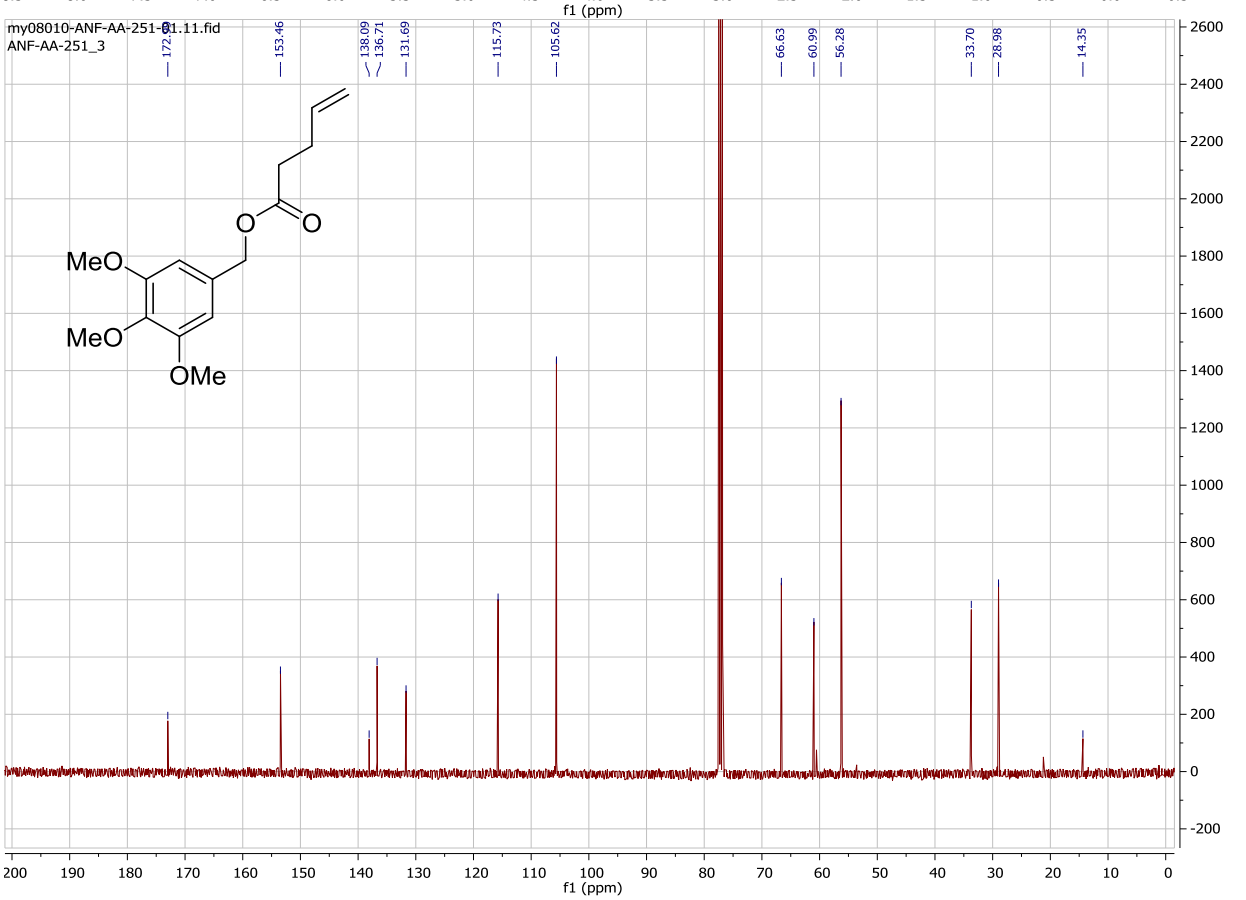

or25031-ANF-AA-259-01.10.fid
ANF-AA-259 2nd run
TBSO
OH
4.00
0.91
2.00
9.00
6.00
f1 (ppm)

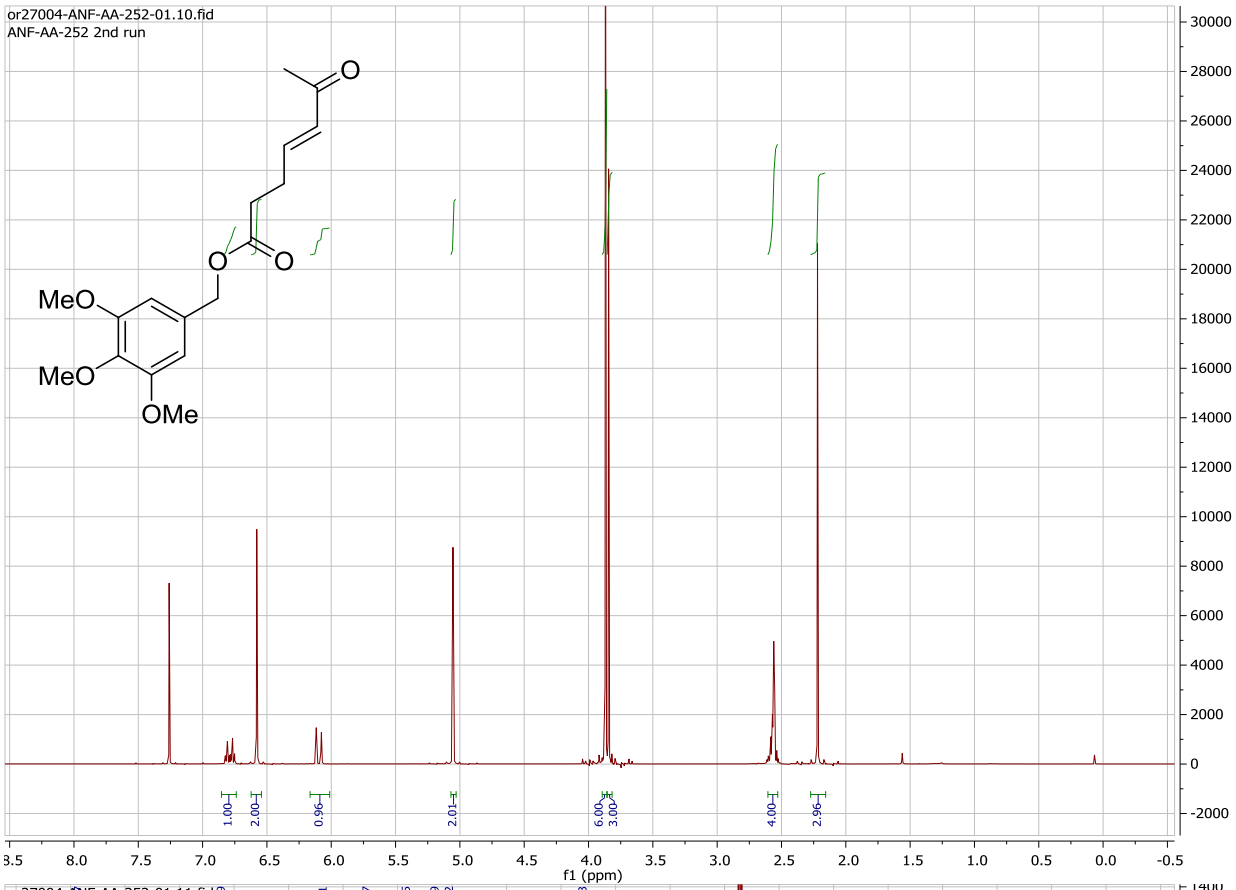

or25031-ANF-AA-259-01.11.fid
ANF-AA-259 2nd run
TBSO
OH
63.13
62.66
34.32
26.03
18.33
-5.34
f1 (ppm)

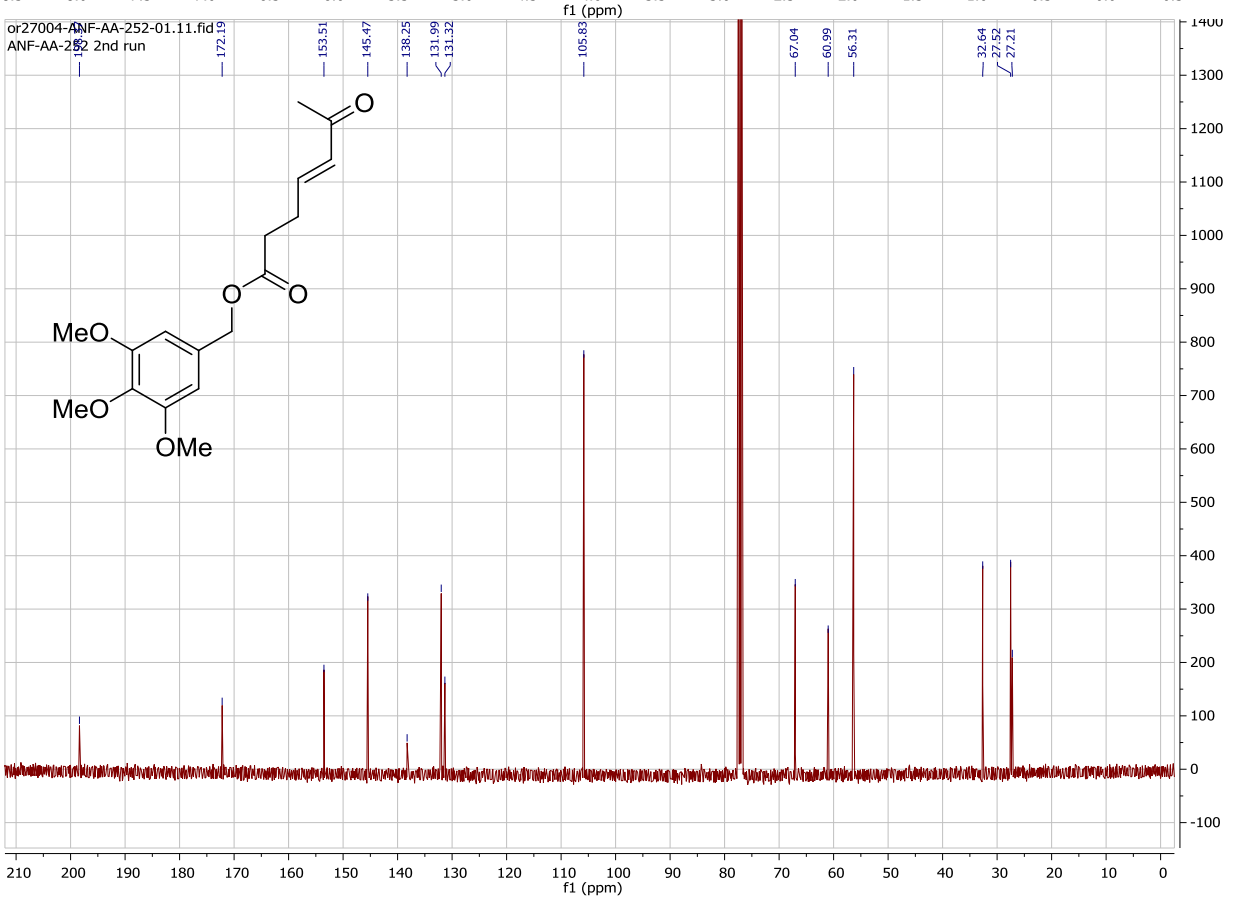

or19056.10.fid
ANF-AA-277
TBSO
O
1.00
2.00
2.00
8.99
6.00
f1 (ppm)

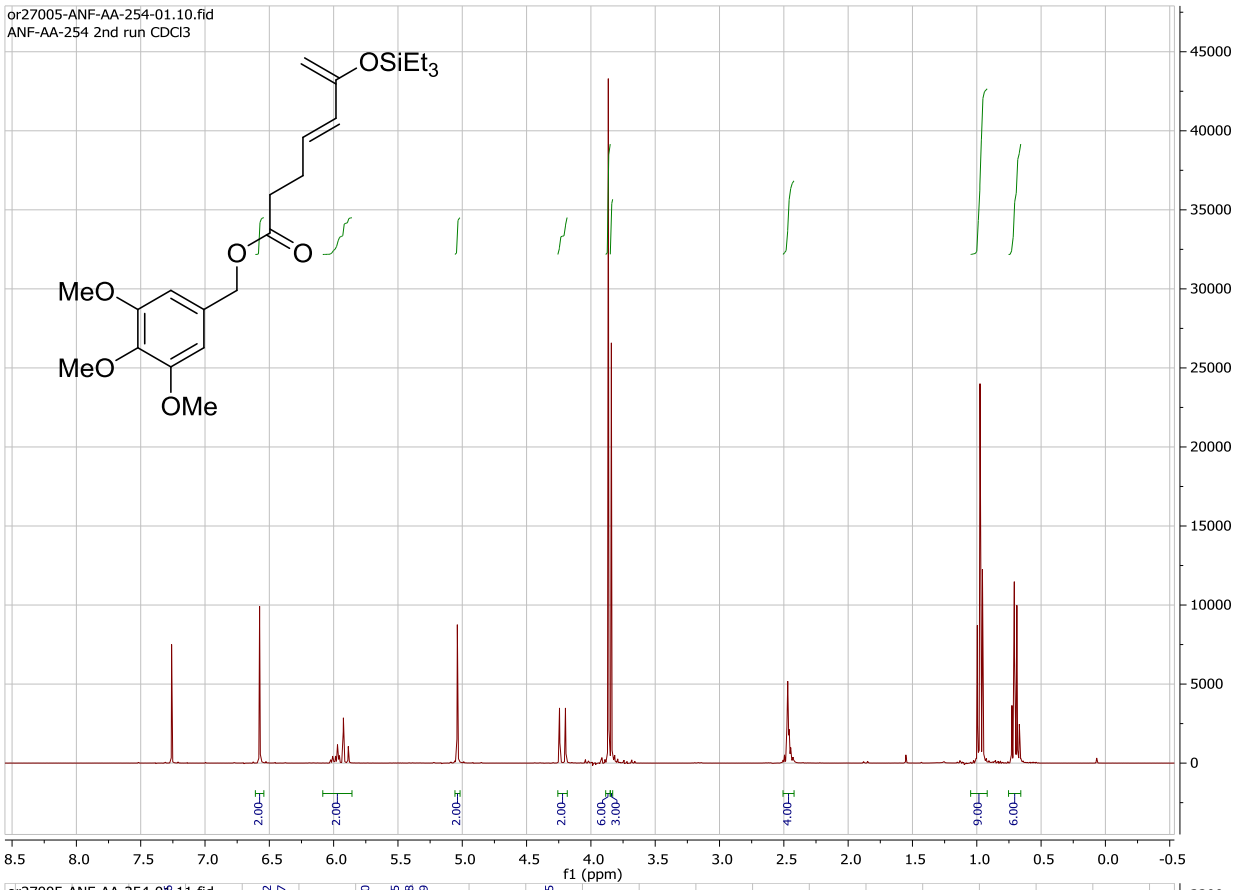

or19056.11.fid
ANF-AA-277
TBSO
O
202.8
57.45
46.61
25.86
-5.39
f1 (ppm)

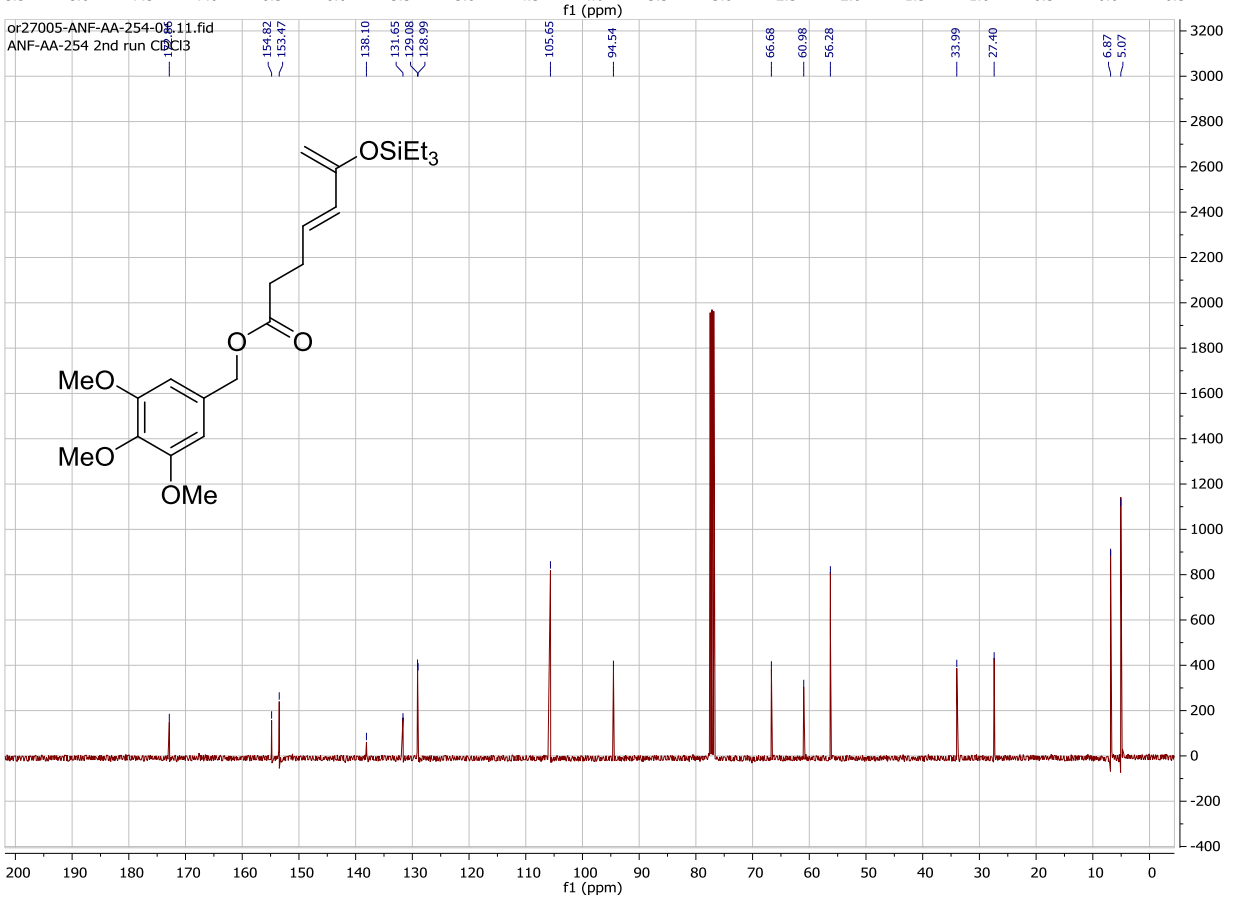

or25002-ANF-AA-251-01.10.fid
ANF-AA-251 2ND run
MeO
MeO
OMe
O
O
2.00
0.91
4.00
6.00
3.00
2.00
2.00
f1 (ppm)

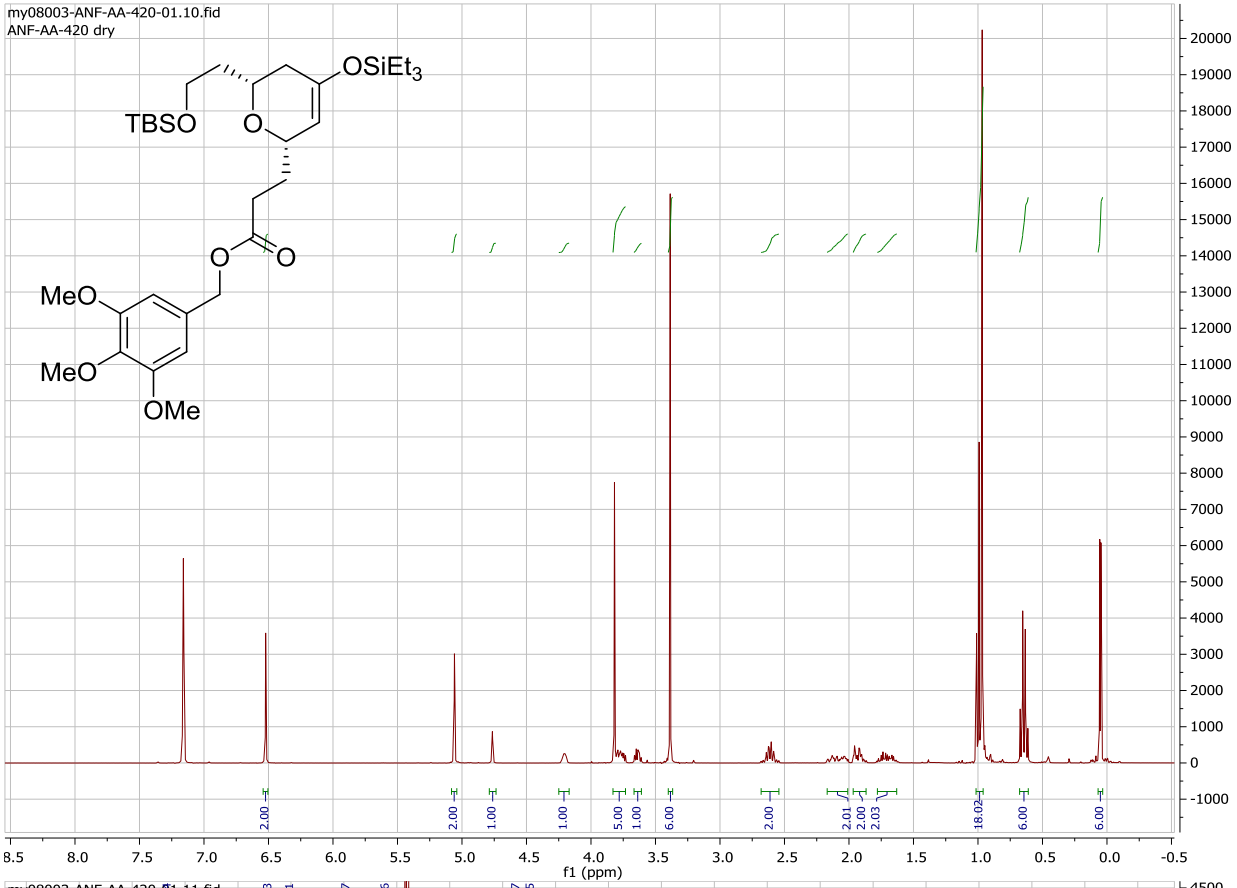

my08010-ANF-AA-251-01.11.fid
ANF-AA-251_3
172.21
153.46
138.09
136.71
131.69
115.73
105.62
66.63
60.99
56.28
33.70
28.98
14.35
MeO
MeO
OMe
O
O
f1 (ppm)

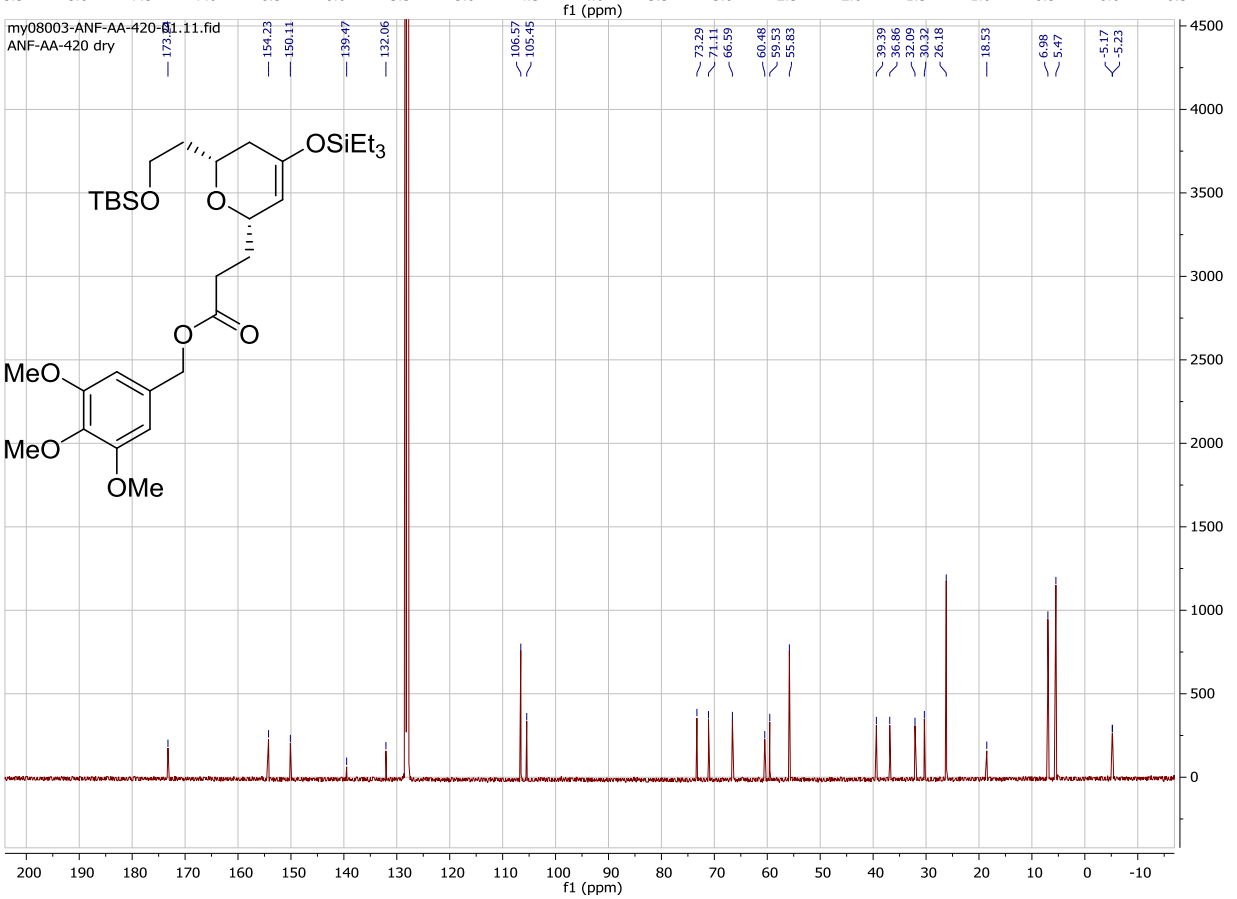

or27004-ANF-AA-252-01.10.fid
ANF-AA-252 2nd run
MeO
MeO
OMe
O
O
O
1.00
2.00
0.96
2.01
6.00
3.00
4.00
2.96
f1 (ppm)

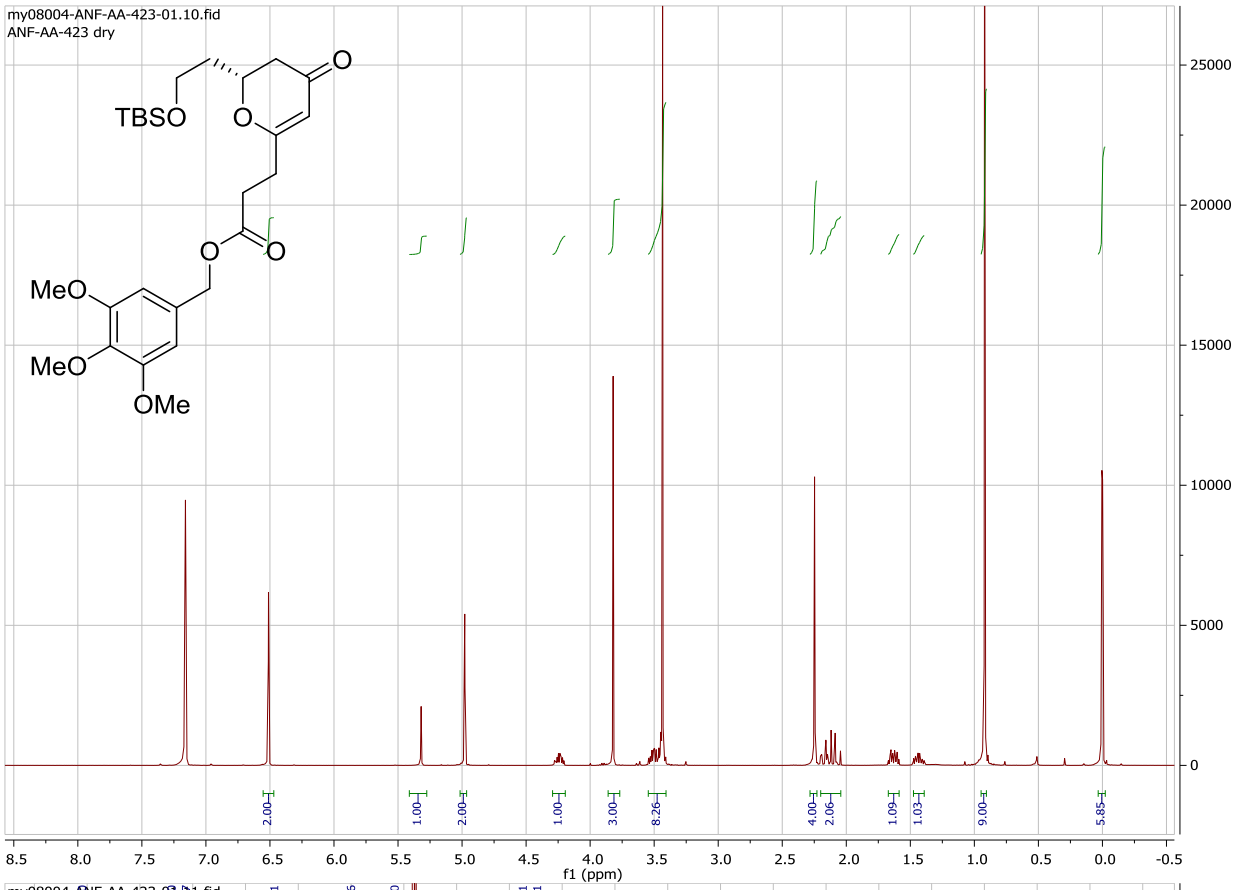

or27004-ANF-AA-252-01.11.fid
ANF-AA-252 2nd run
172.19
153.51
145.47
138.25
131.99
131.32
105.83
67.04
60.99
56.31
32.64
27.52
27.21
MeO
MeO
OMe
O
O
O
f1 (ppm)

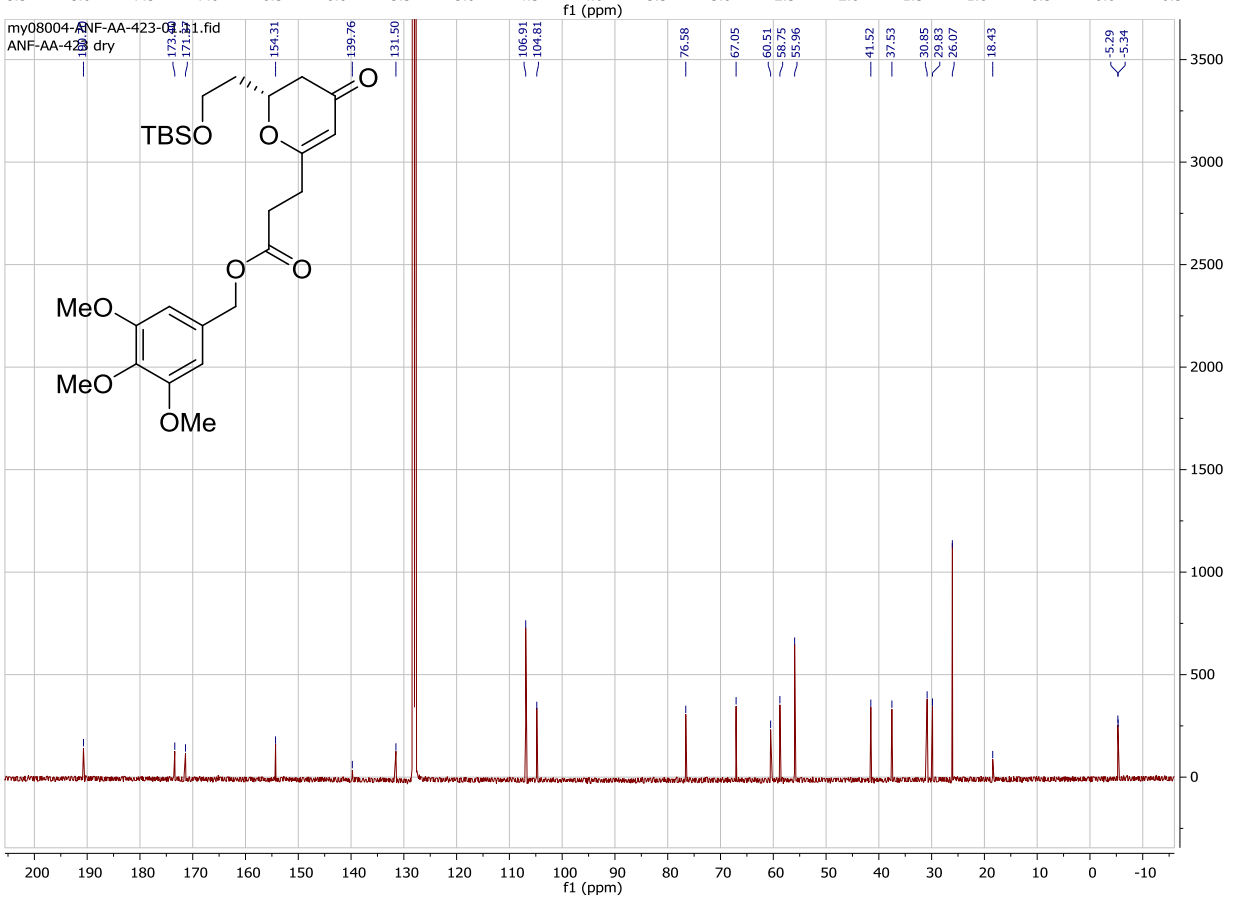

or27005-ANF-AA-254-01.10.fid
ANF-AA-254 2nd run CDCl3
OSiEt3
O
O
MeO
MeO
OMe
2.00
2.00
2.00
2.00
6.00
3.00
4.00
9.00
6.00
f1 (ppm)

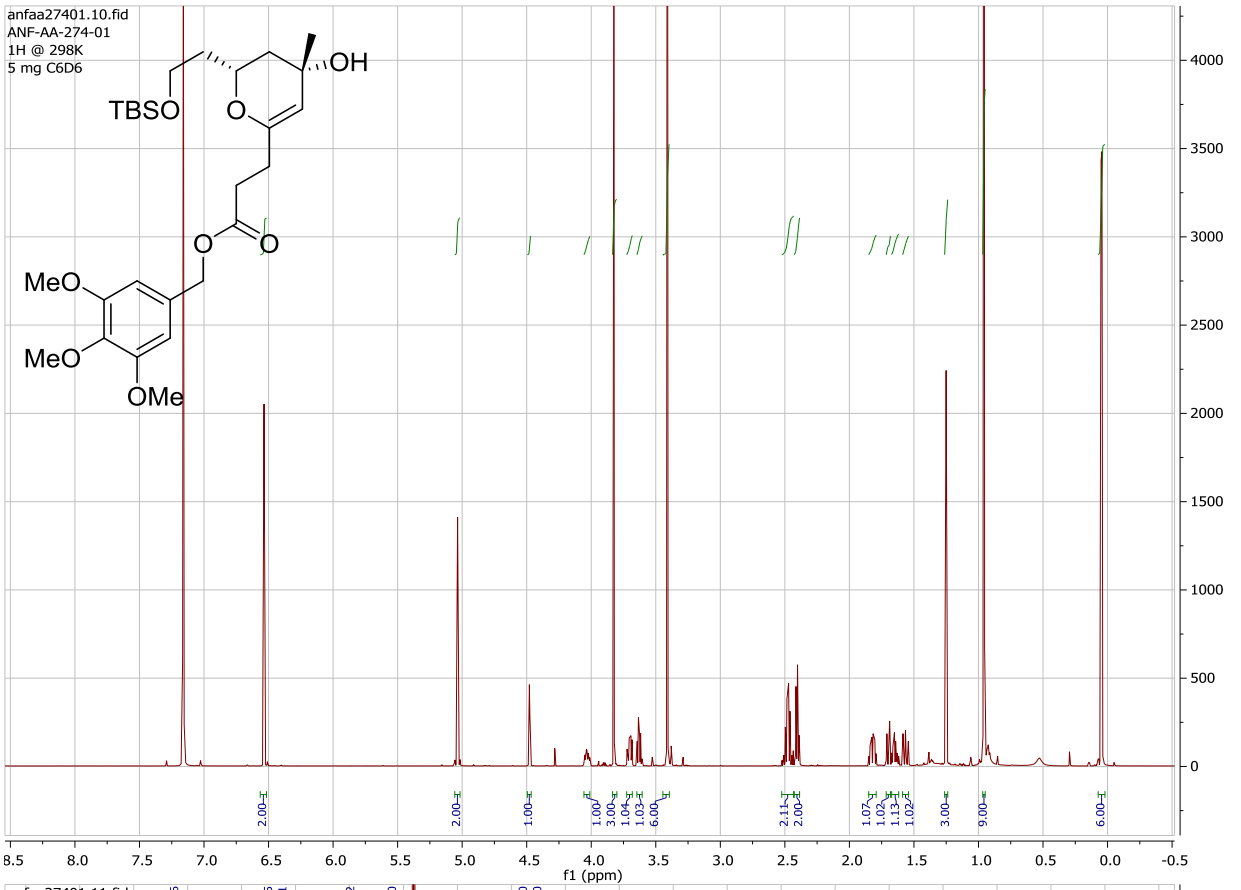

or27005-ANF-AA-254-01.11.fid
ANF-AA-254 2nd run CDCl3
154.82
153.47
138.10
131.65
129.08
128.99
105.65
94.54
66.68
60.98
56.28
33.99
27.40
6.87
5.07
OSiEt3
O
O
MeO
MeO
OMe
f1 (ppm)

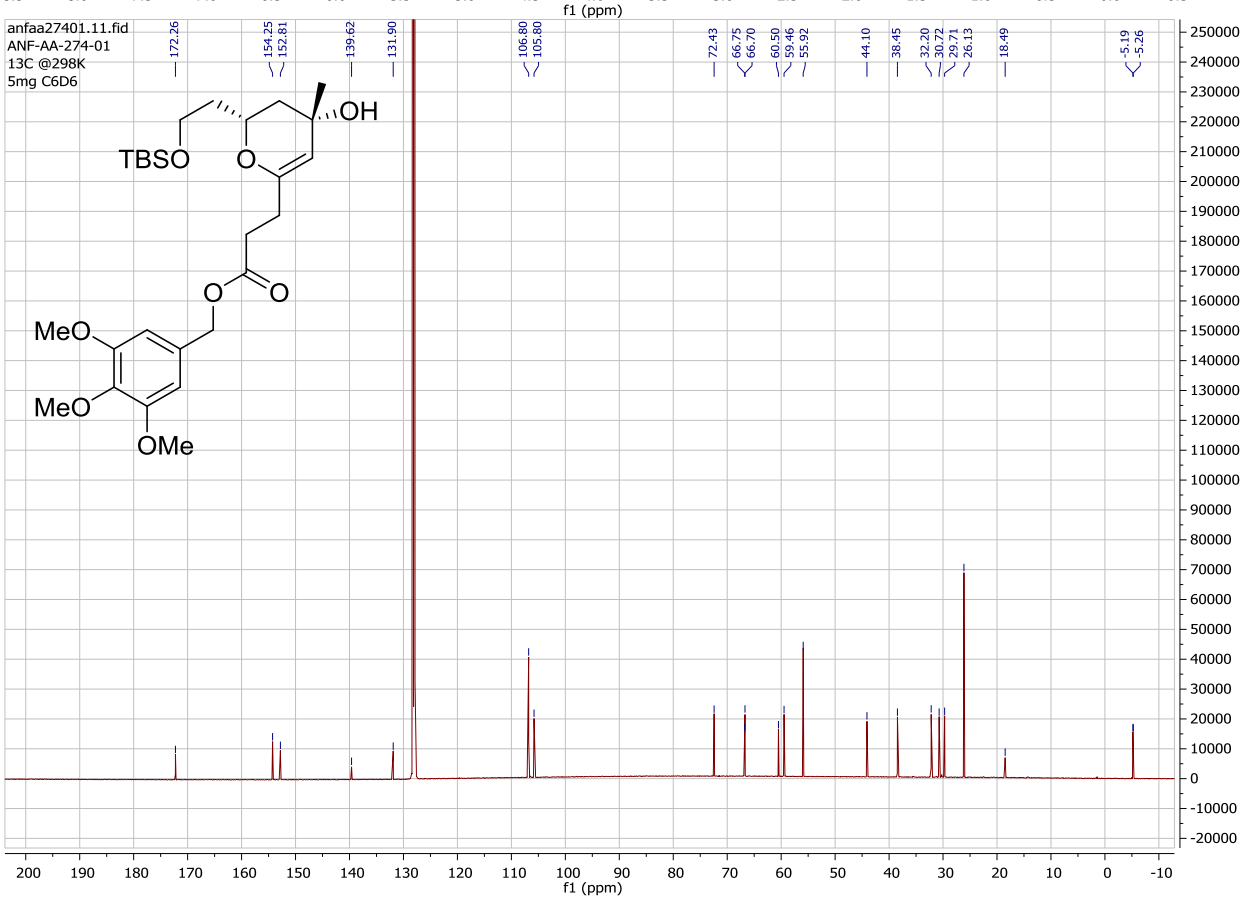

my08003-ANF-AA-420-01.10.fid
ANF-AA-420 dry
OSiEt3
TBSO
O
O
O
MeO
MeO
OMe
f1 (ppm)

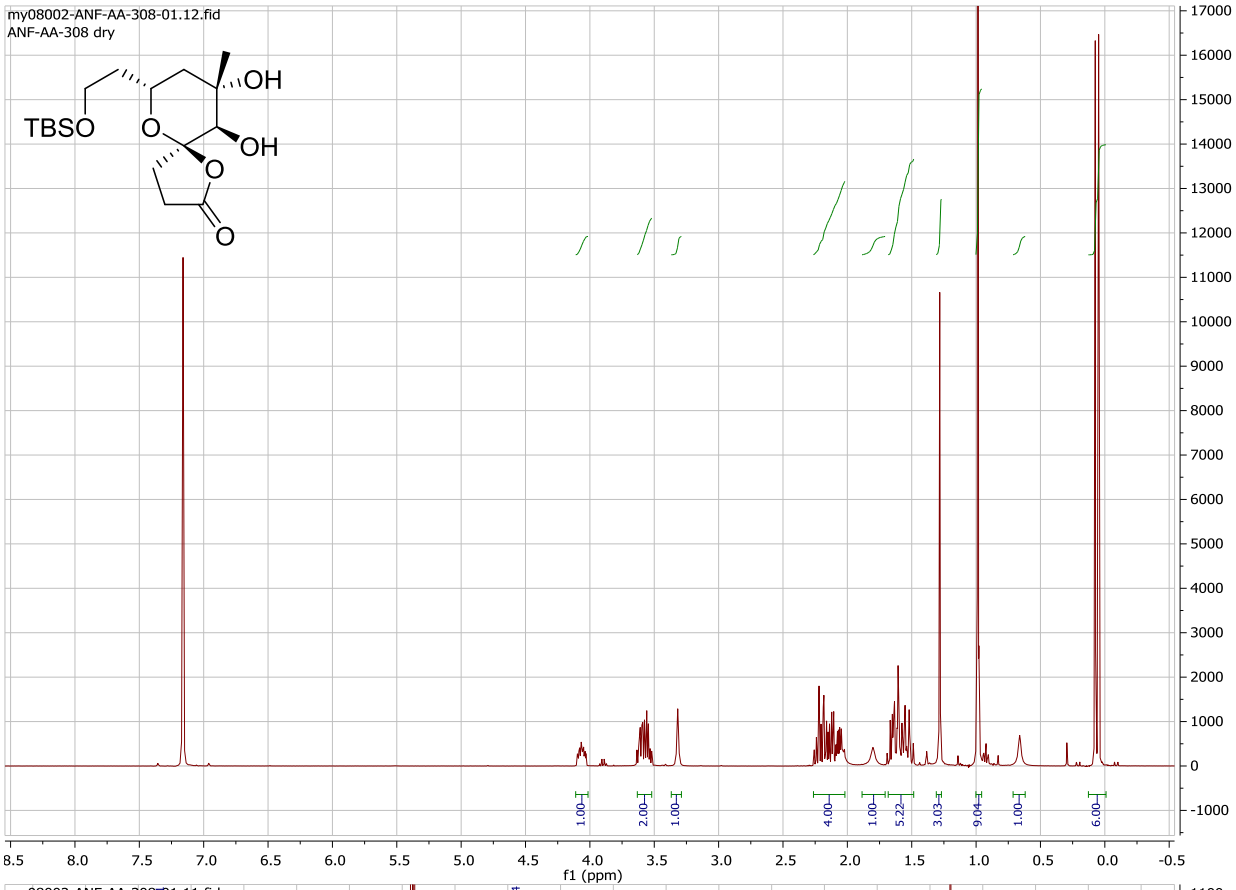

my08003-ANF-AA-420-01.11.fid
ANF-AA-420 dry
154.23
150.11
139.47
132.06
106.57
105.45
73.29
71.11
66.59
60.48
59.53
55.83
39.39
36.86
32.09
30.32
26.18
18.53
6.98
5.47
-5.17
-5.23
OSiEt3
TBSO
O
O
O
MeO
MeO
OMe
f1 (ppm)

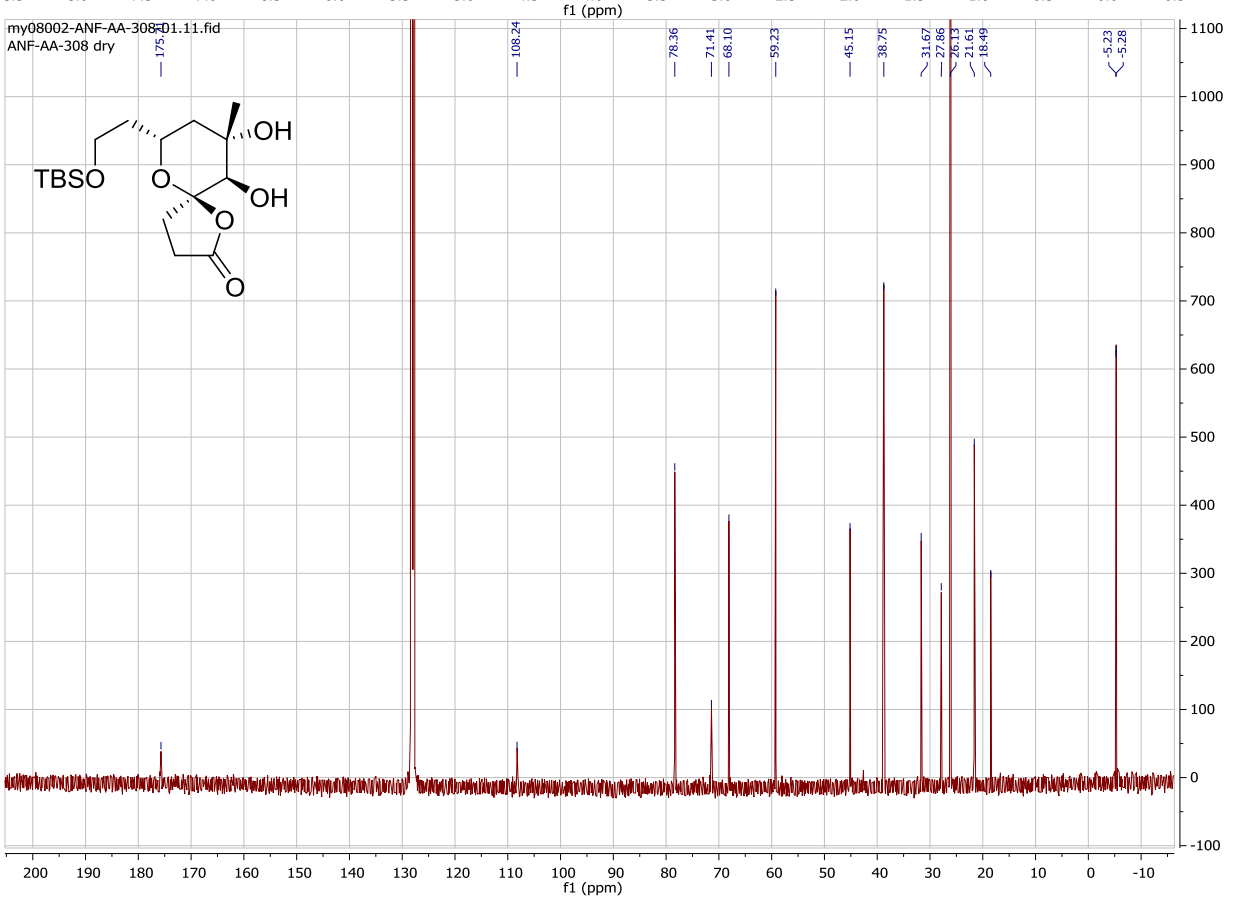

my08004-ANF-AA-423-01.10.fid
ANF-AA-423 dry
TBSO
O
O
O
O
MeO
MeO
OMe
2.00
1.00
2.00
1.00
3.00
8.26
4.00
2.06
1.09
1.03
9.00
5.85
f1 (ppm)

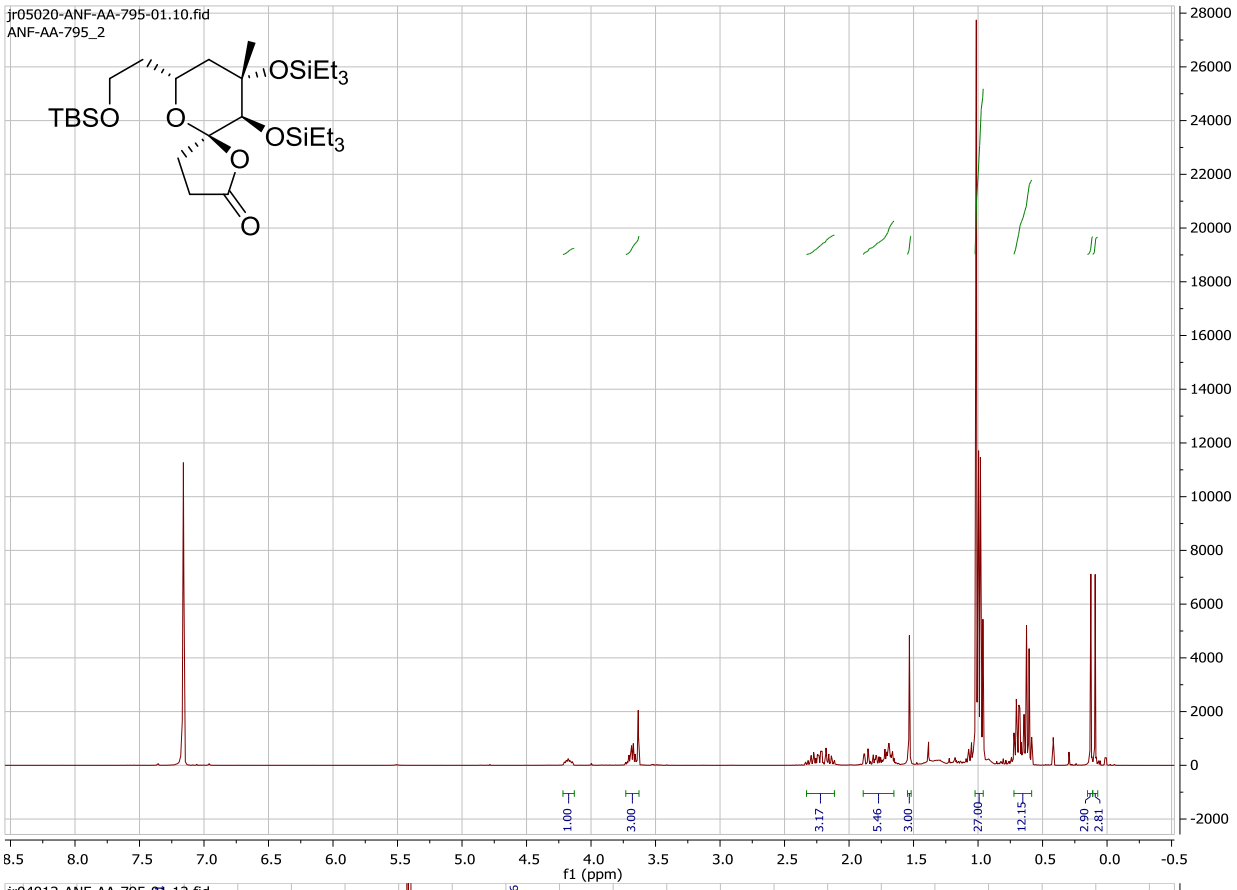

my08004-ANF-AA-423-01.11.fid
ANF-AA-423 dry
154.31
139.76
131.50
106.91
104.81
76.58
67.05
60.51
58.75
55.96
41.52
37.53
30.85
29.83
26.07
18.43
-5.29
-5.34
TBSO
O
O
O
O
MeO
MeO
OMe
f1 (ppm)

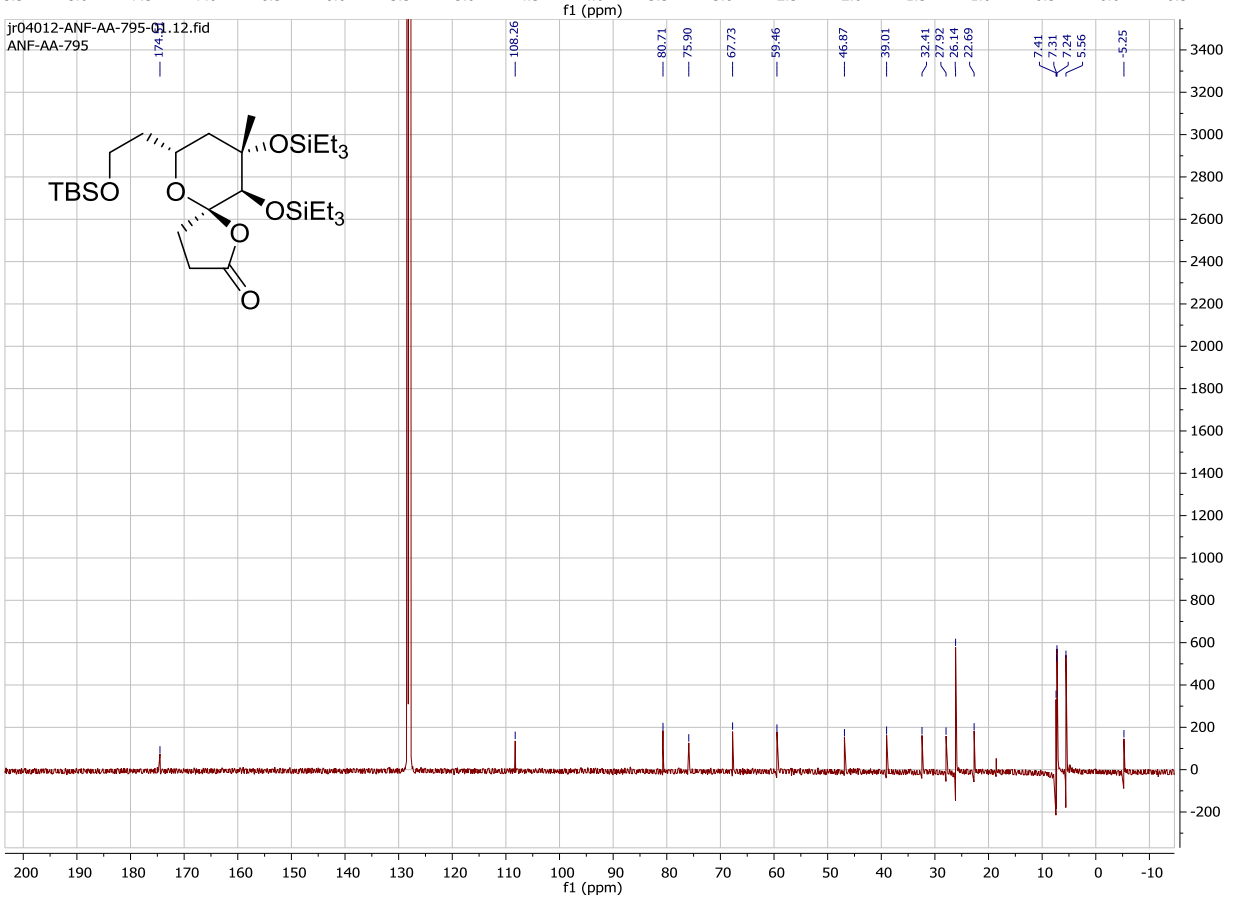

anfaa27401.10.fid
ANF-AA-274-01
1H @ 298K
5 mg C6D6
TBSO
OH
O
O
O
MeO
MeO
OMe
f1 (ppm)

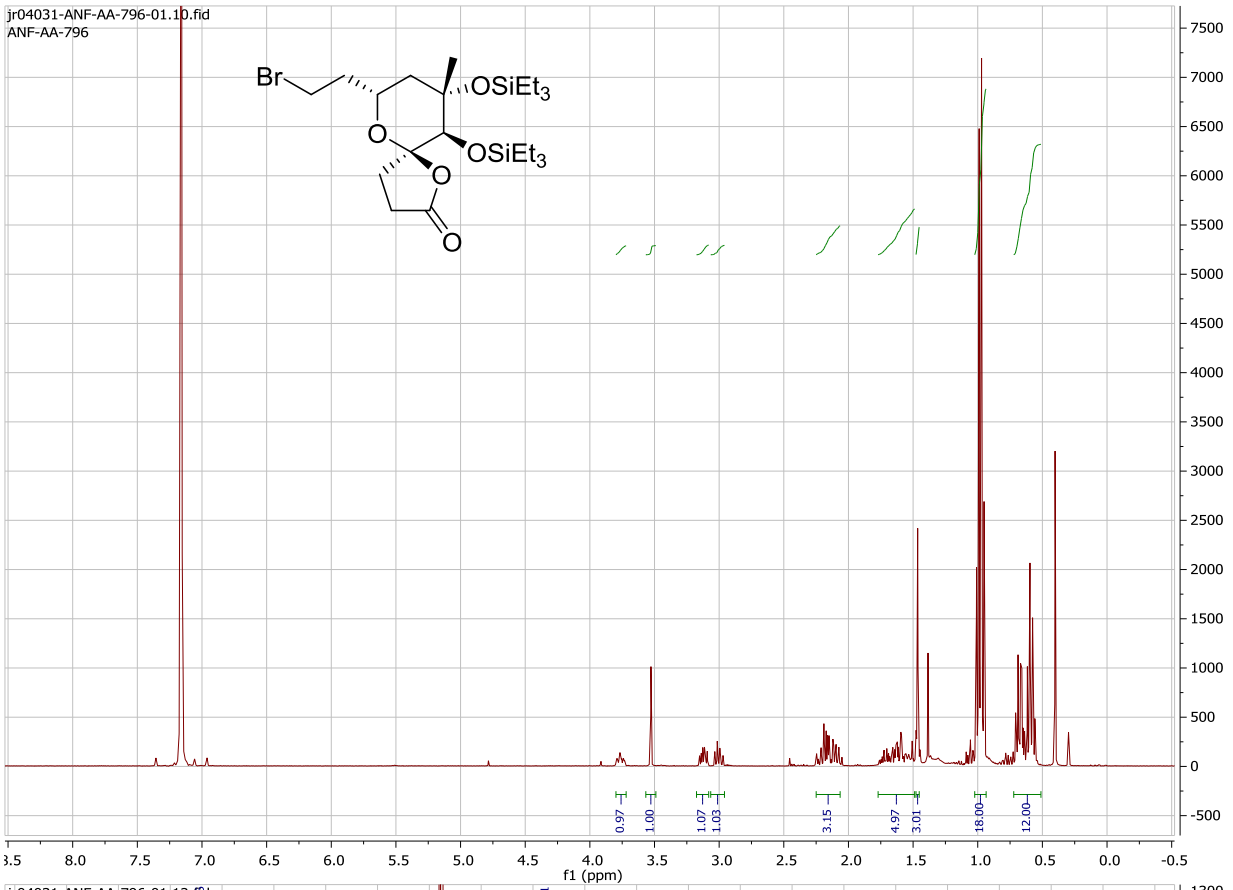

anfaa27401.11.fid
ANF-AA-274-01
13C @298K
5mg C6D6
172.26
154.25
152.81
139.62
131.90
106.80
105.80
72.43
66.75
66.70
60.50
59.46
55.92
44.10
38.45
32.20
30.72
29.71
26.13
18.49
-5.19
-5.26
TBSO
OH
O
O
O
MeO
MeO
OMe
f1 (ppm)

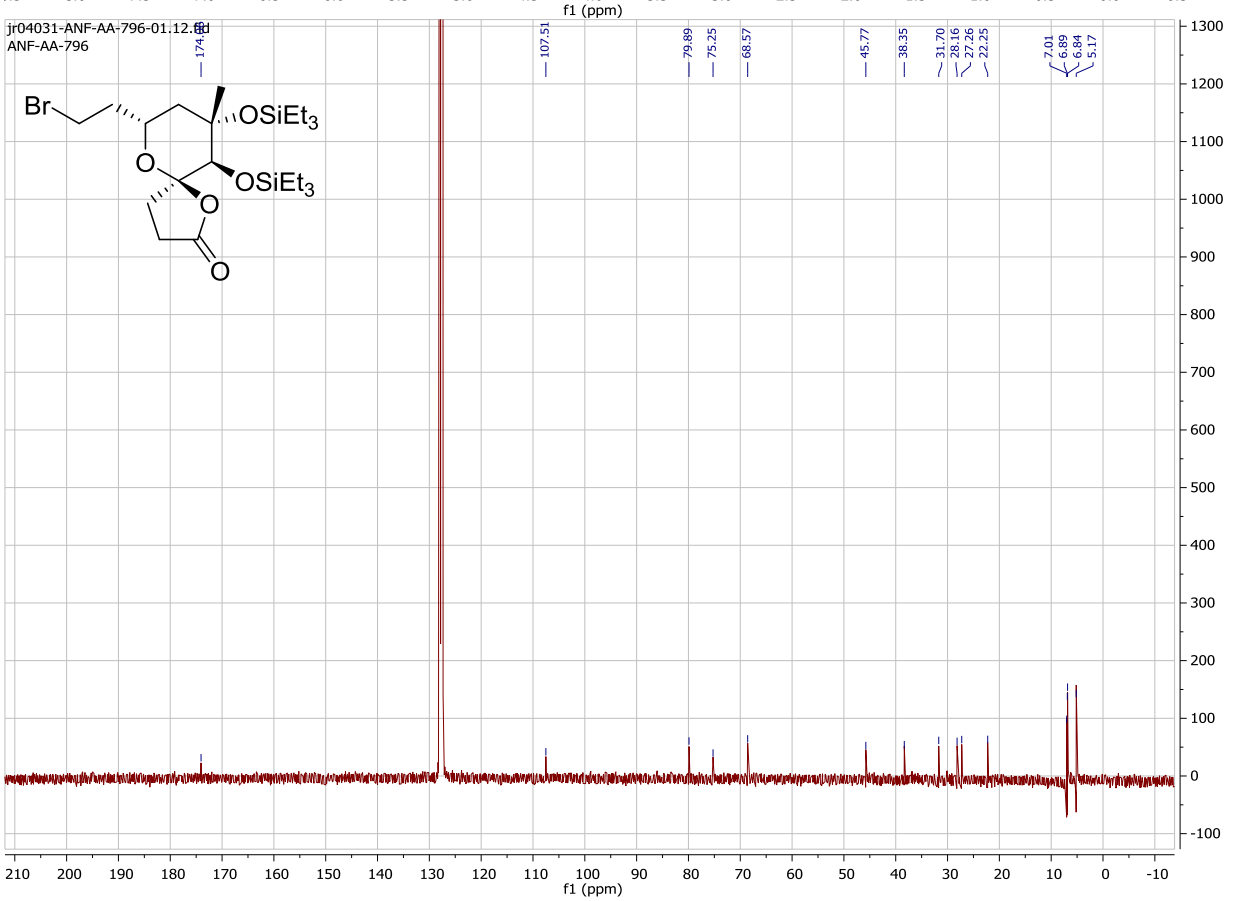

my08002-ANF-AA-308-01.12.fid
ANF-AA-308 dry
TBSO
OH
OH
O
O
O
1.00
2.00
1.00
4.00
1.00
5.22
3.03
9.04
1.00
6.00
f1 (ppm)

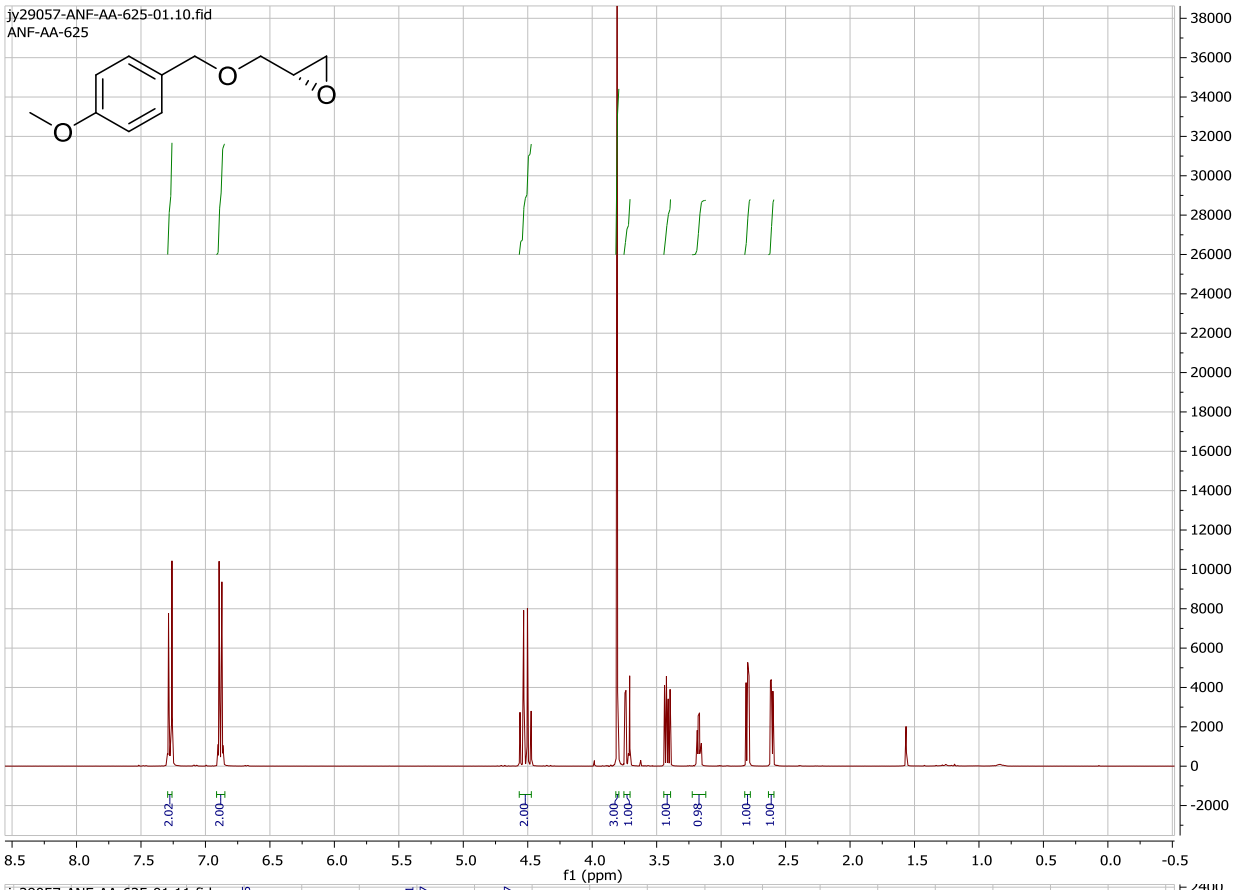

my08002-ANF-AA-308-01.11.fid
ANF-AA-308 dry
TBSO
OH
OH
O
O
O
175.21
108.24
78.36
71.41
68.10
59.23
45.15
38.75
31.67
27.86
26.13
21.61
18.49
-5.23
-5.28
f1 (ppm)

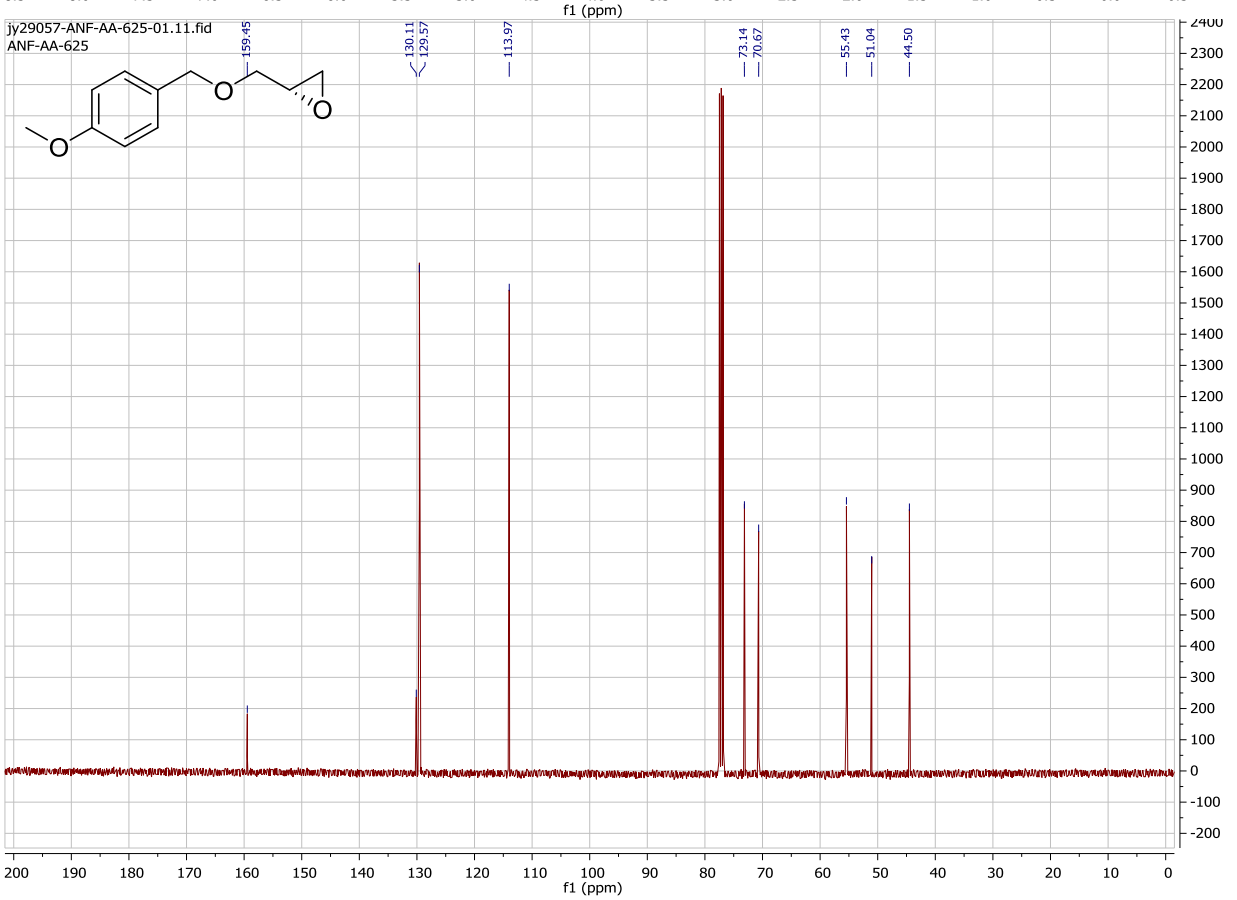

jr05020-ANF-AA-795-01.10.fid
ANF-AA-795_2
TBSO
OSiEt3
OSiEt3
O
O
O
1.00
3.00
3.17
5.46
3.00
27.00
12.15
2.90
2.81
f1 (ppm)

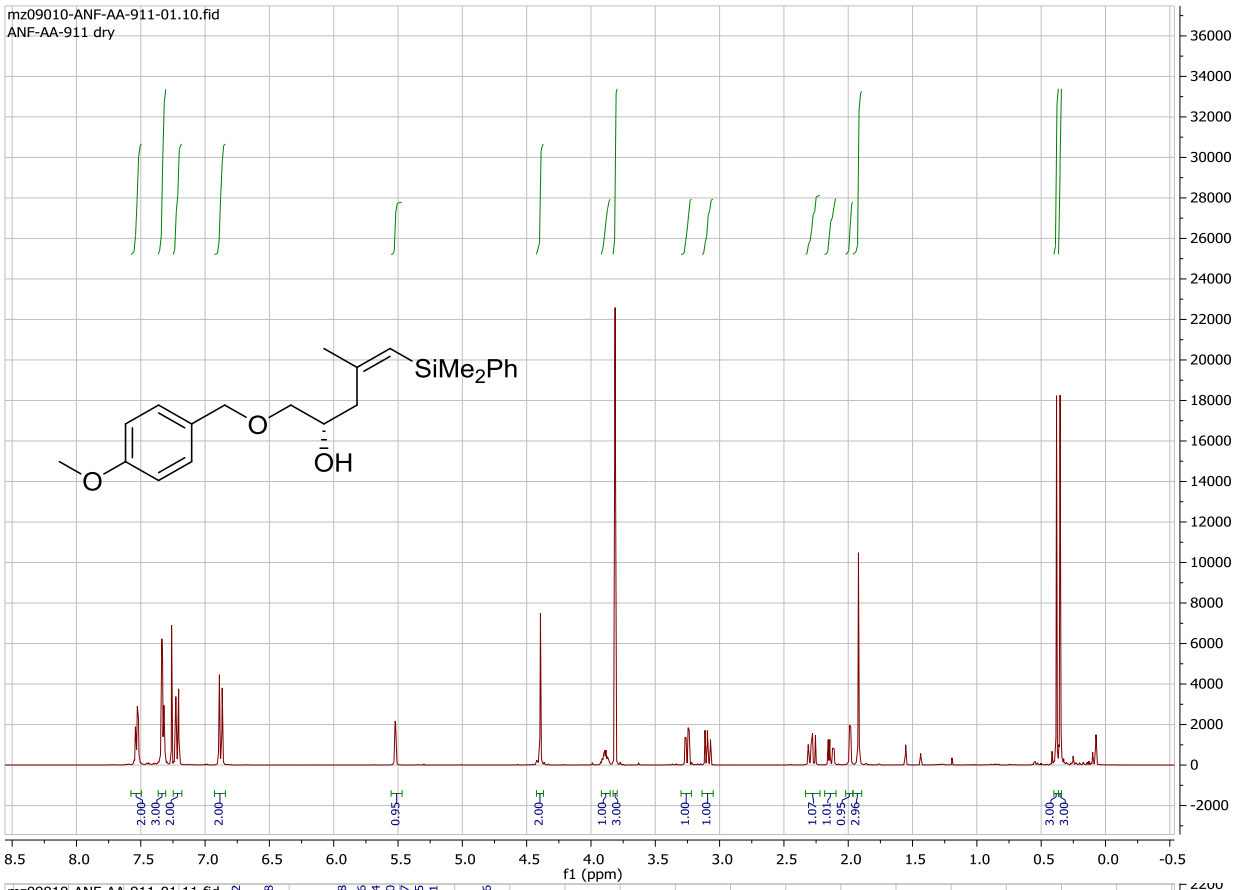

jr04012-ANF-AA-795-01.12.fid
ANF-AA-795
174.21
108.26
80.71
75.90
67.73
59.46
46.87
39.01
32.41
27.92
26.14
22.69
7.41
7.31
7.24
5.56
-5.25
TBSO
OSiEt3
OSiEt3
O
O
O
f1 (ppm)

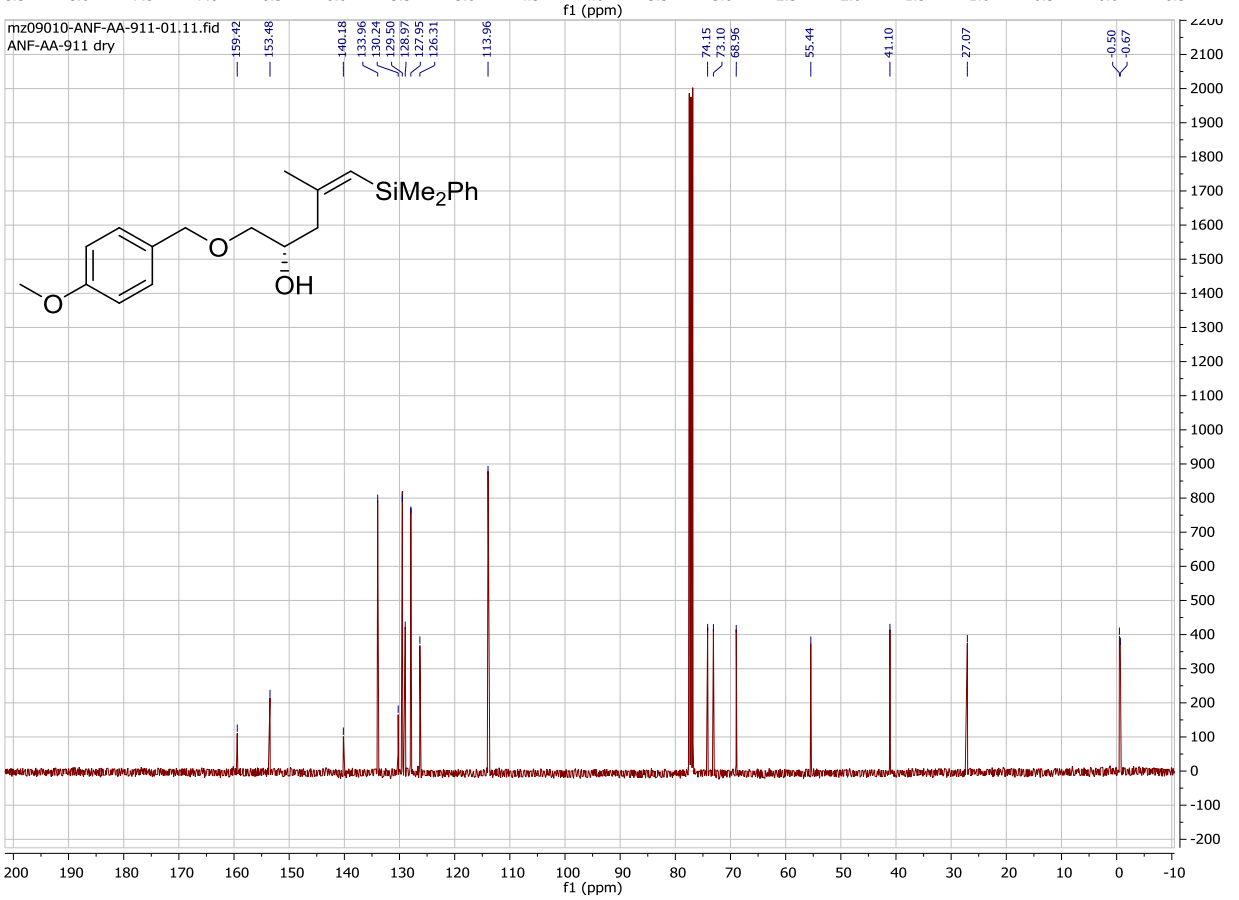

jr04031-ANF-AA-796-01.10.fid
ANF-AA-796
Br
OSiEt3
OSiEt3
O
O
O
0.97
1.00
1.07
1.03
3.15
4.97
3.01
18.00
12.00
f1 (ppm)

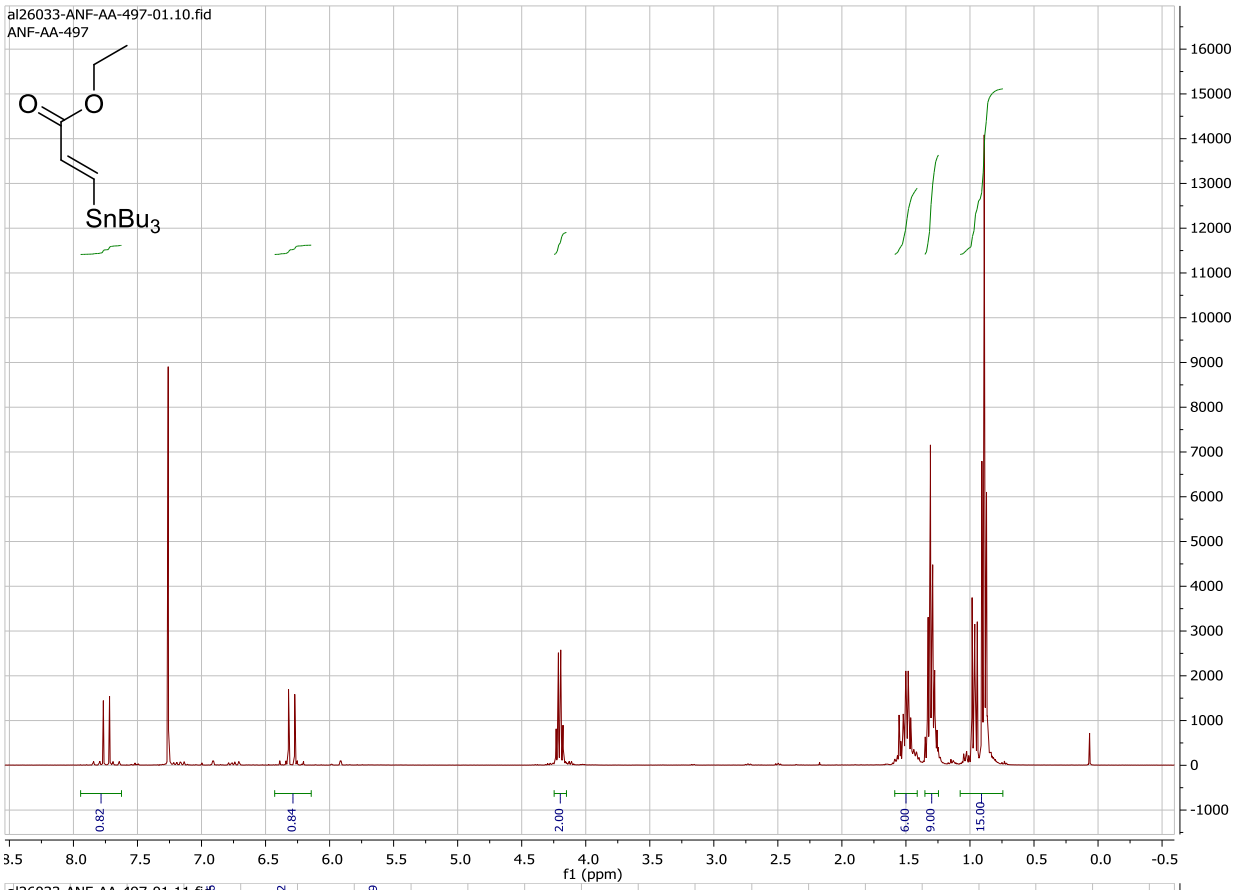

jr04031-ANF-AA-796-01.12.fid
ANF-AA-796
174.66
107.51
79.89
75.25
68.57
45.77
38.35
31.70
28.16
27.26
22.25
7.01
6.89
6.84
5.17
Br
OSiEt3
OSiEt3
O
O
O
f1 (ppm)

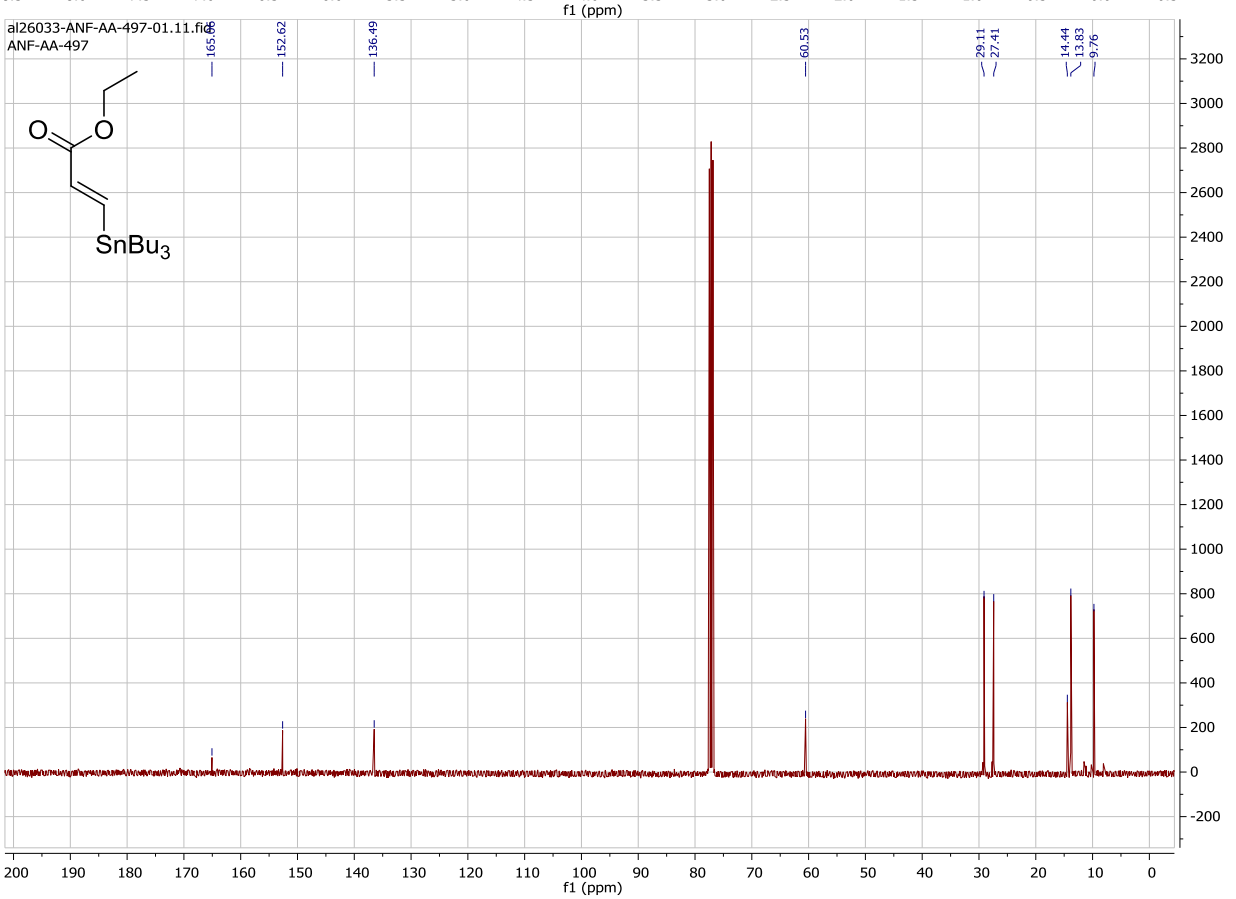

jy29057-ANF-AA-625-01.10.fid
ANF-AA-625
2.02
2.00
2.00
3.00
1.00
1.00
0.98
1.00
1.00
f1 (ppm)

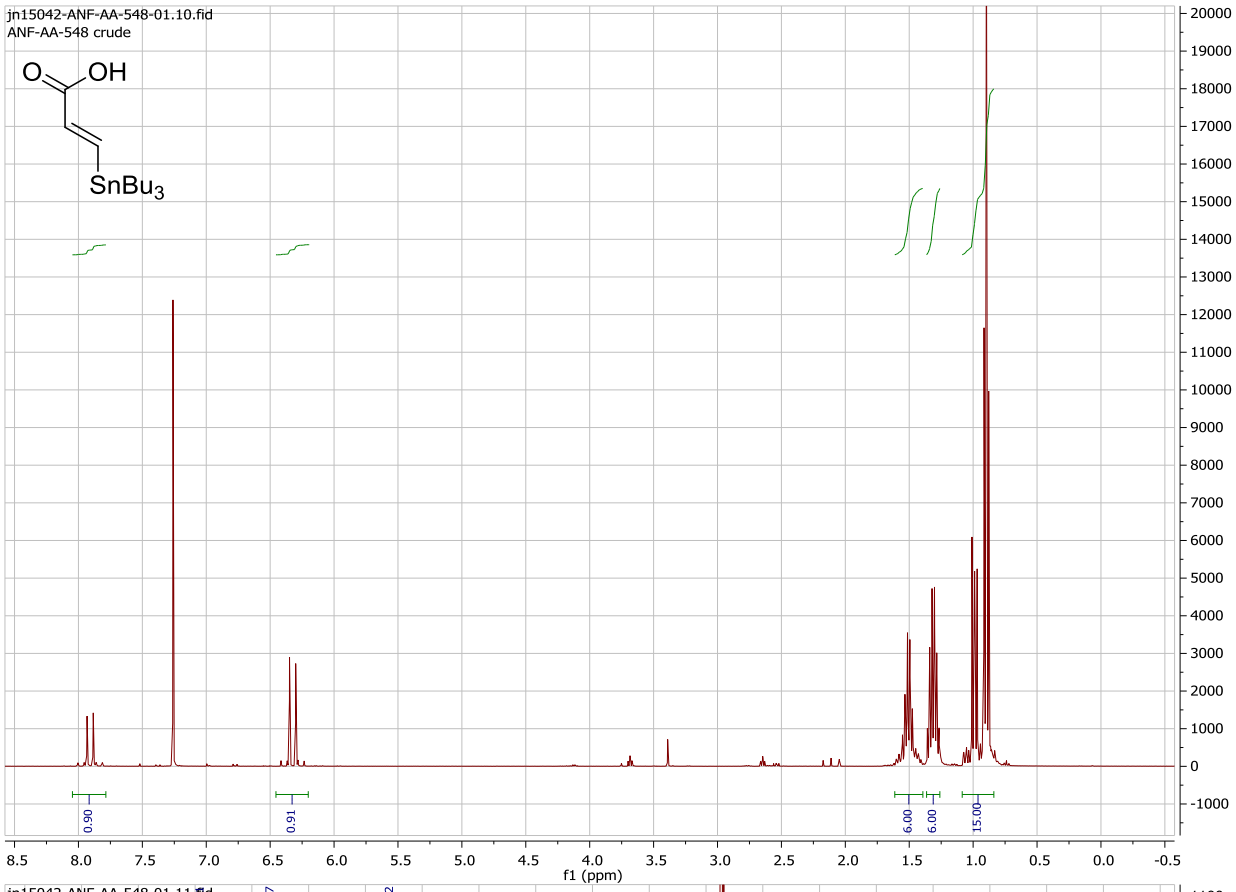

jy29057-ANF-AA-625-01.11.fid
ANF-AA-625
159.45
130.11
129.57
113.97
73.14
70.67
55.43
51.04
44.50
f1 (ppm)

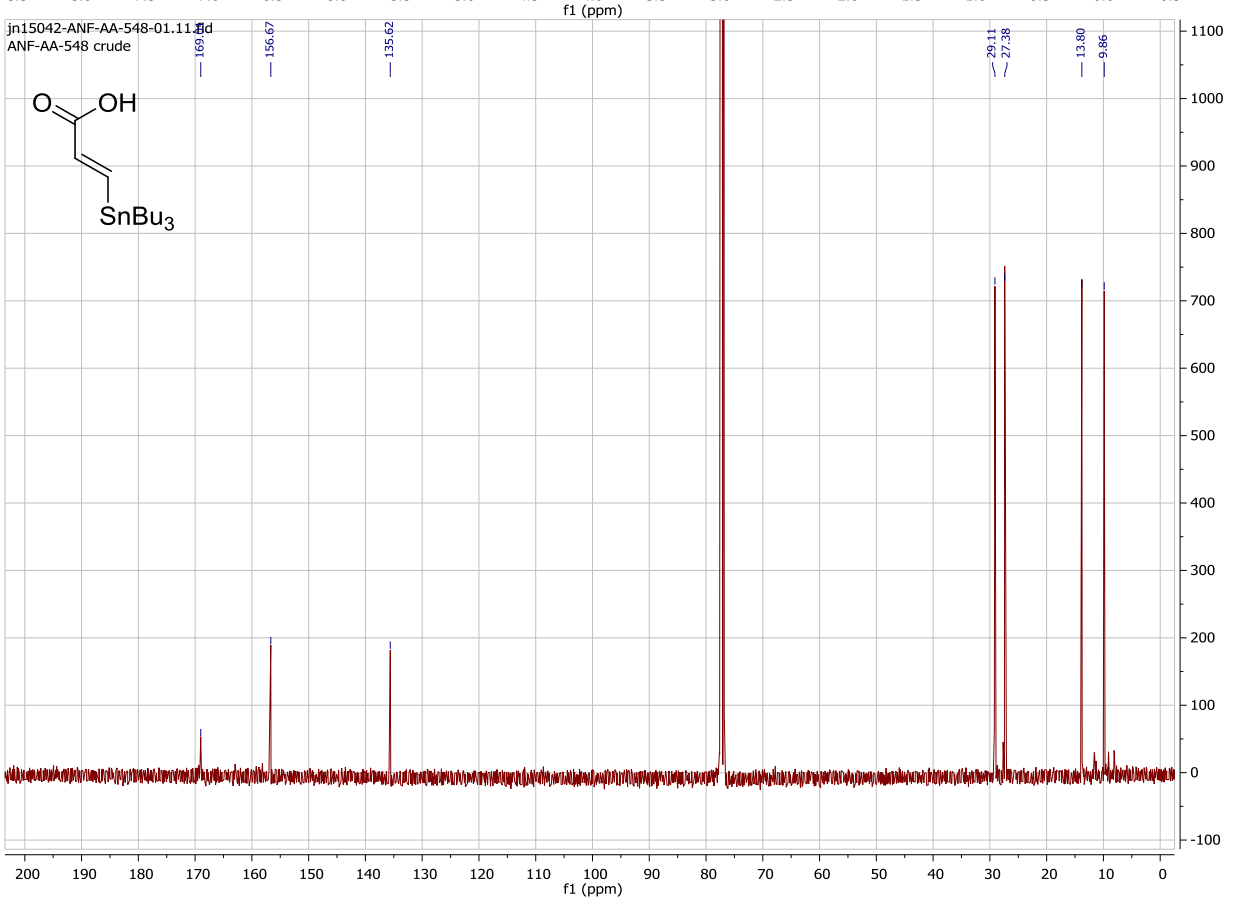

mz09010-ANF-AA-911-01.10.fid
ANF-AA-911 dry
SiMe2Ph
O
OH
O
2.00
3.00
2.00
2.00
0.95
2.00
1.00
3.00
1.00
1.00
1.07
1.01
0.95
2.96
3.00
3.00
f1 (ppm)

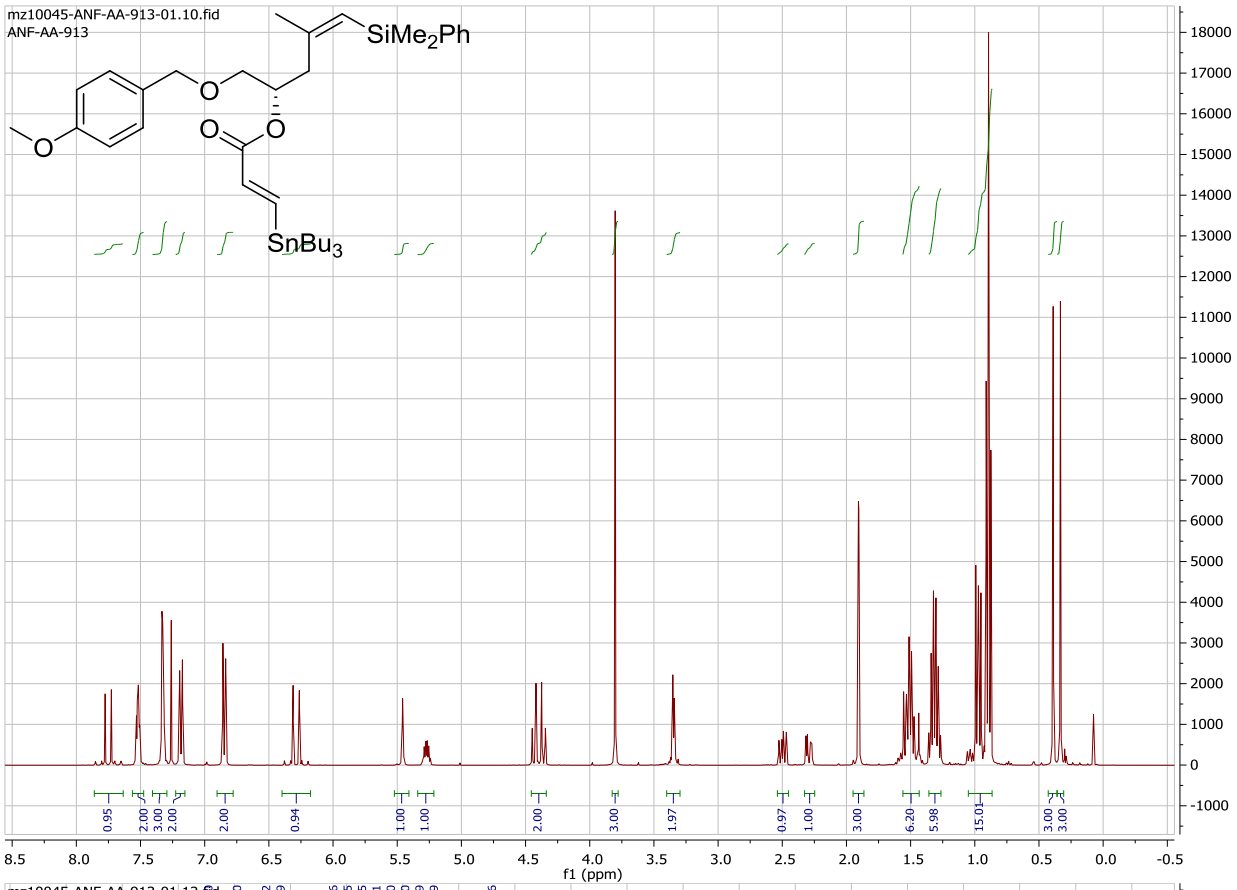

mz09010-ANF-AA-911-01.11.fid
ANF-AA-911 dry
159.42
153.48
140.18
133.96
130.24
129.50
128.97
127.95
126.31
113.96
74.15
73.10
68.96
55.44
41.10
27.07
-0.50
-0.67
SiMe2Ph
O
OH
O
f1 (ppm)

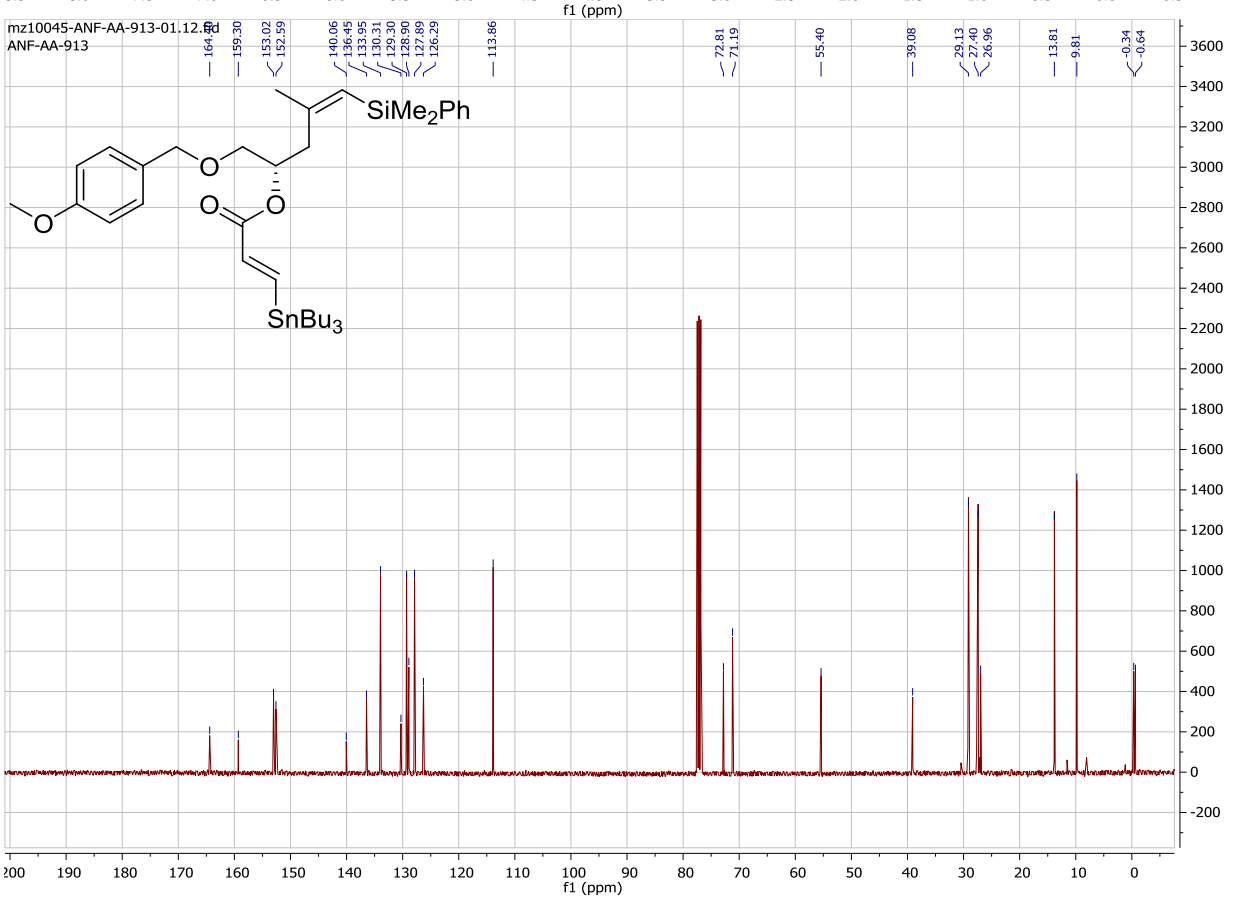

al26033-ANF-AA-497-01.10.fid
ANF-AA-497
O
O
SnBu3
0.82
0.84
2.00
6.00
9.00
15.00
f1 (ppm)

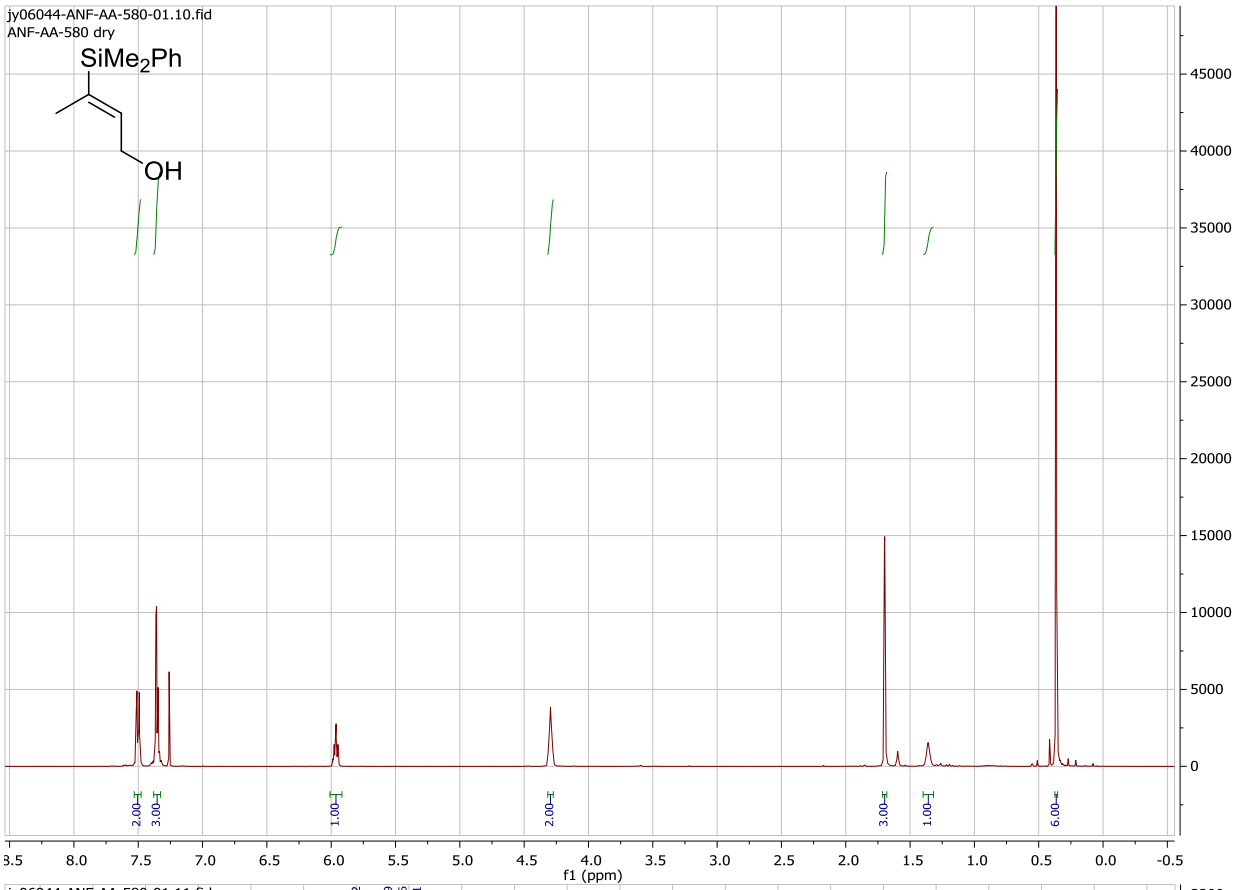

al26033-ANF-AA-497-01.11.fid
ANF-AA-497
O
O
SnBu3
165.88
152.62
136.49
60.53
29.11
27.41
14.44
13.83
9.76
f1 (ppm)

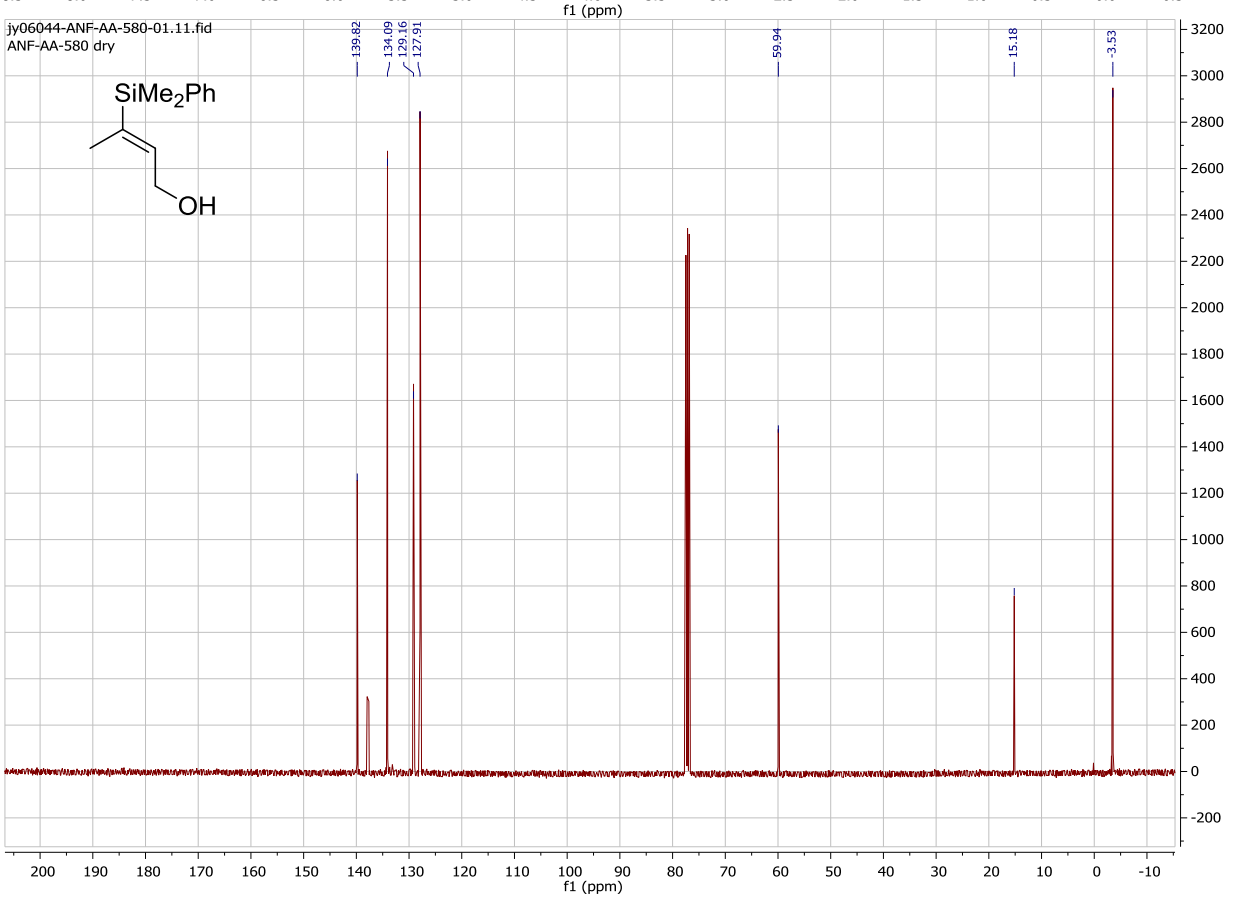

jn15042-ANF-AA-548-01.10.fid
ANF-AA-548 crude
O
OH
SnBu3
0.90
0.91
6.00
6.00
15.00
f1 (ppm)

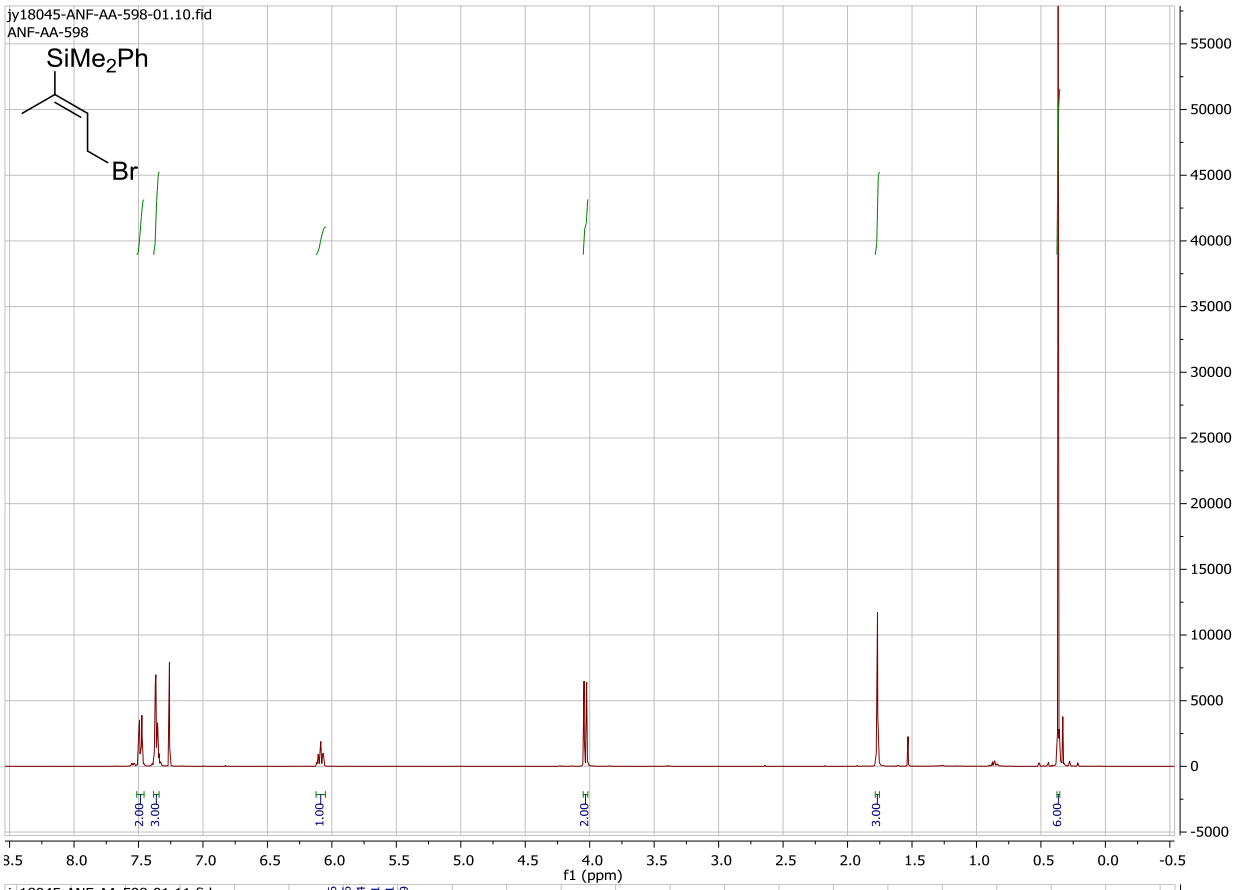

jn15042-ANF-AA-548-01.11.fid
ANF-AA-548 crude
169.61
156.67
135.62
29.11
27.38
13.80
9.86
O
OH
SnBu3
f1 (ppm)

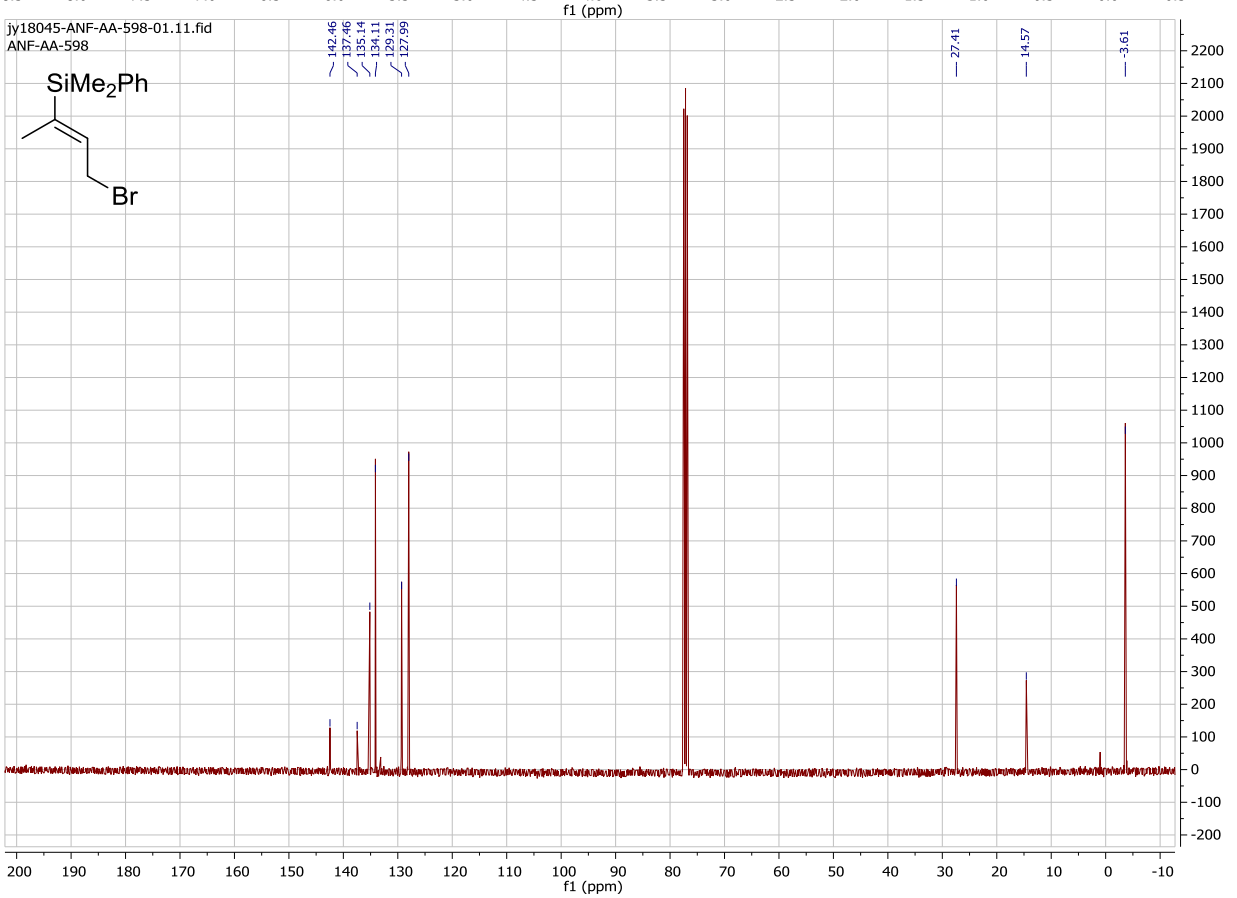

mz10045-ANF-AA-913-01.10.fid
ANF-AA-913
SiMe2Ph
SnBu3
f1 (ppm)

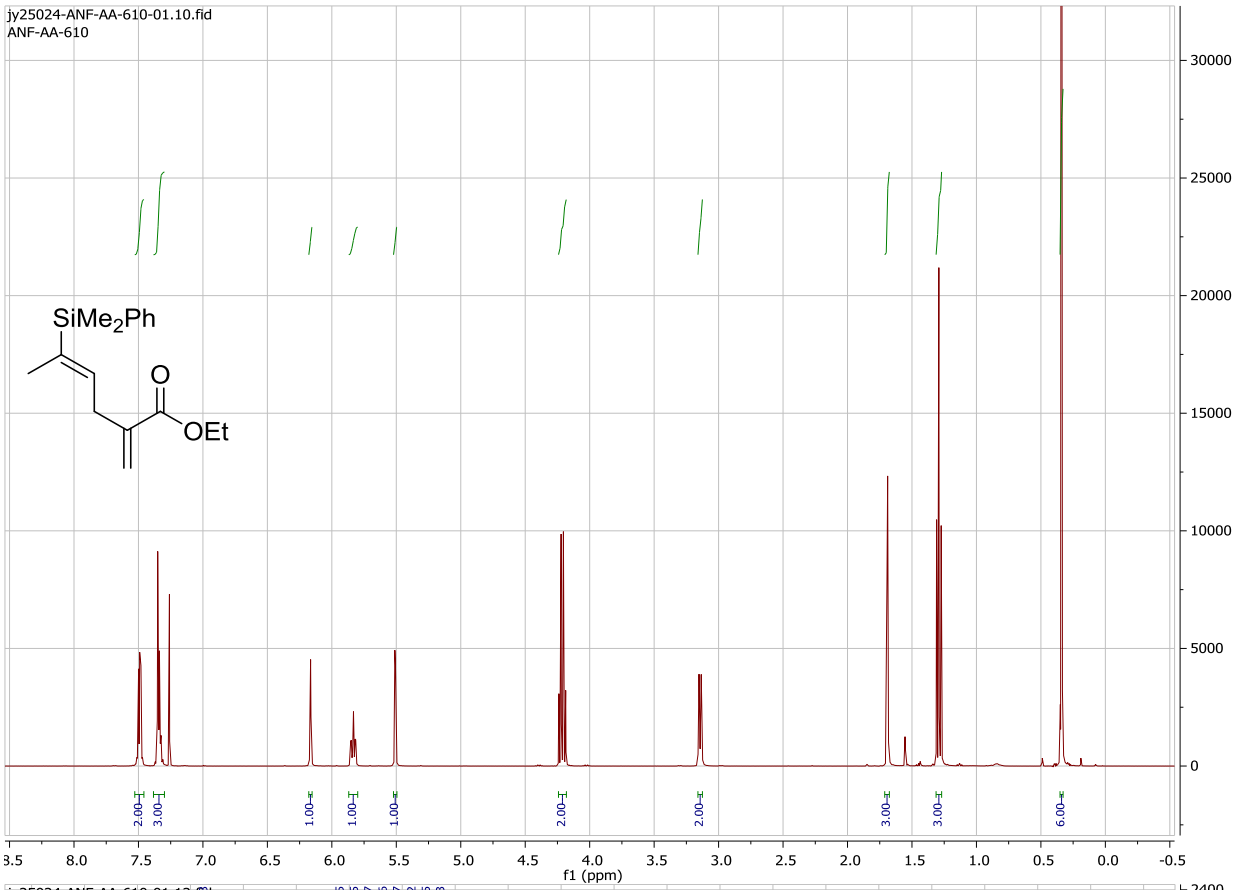

mz10045-ANF-AA-913-01.12.fid
ANF-AA-913
SiMe2Ph
SnBu3
f1 (ppm)

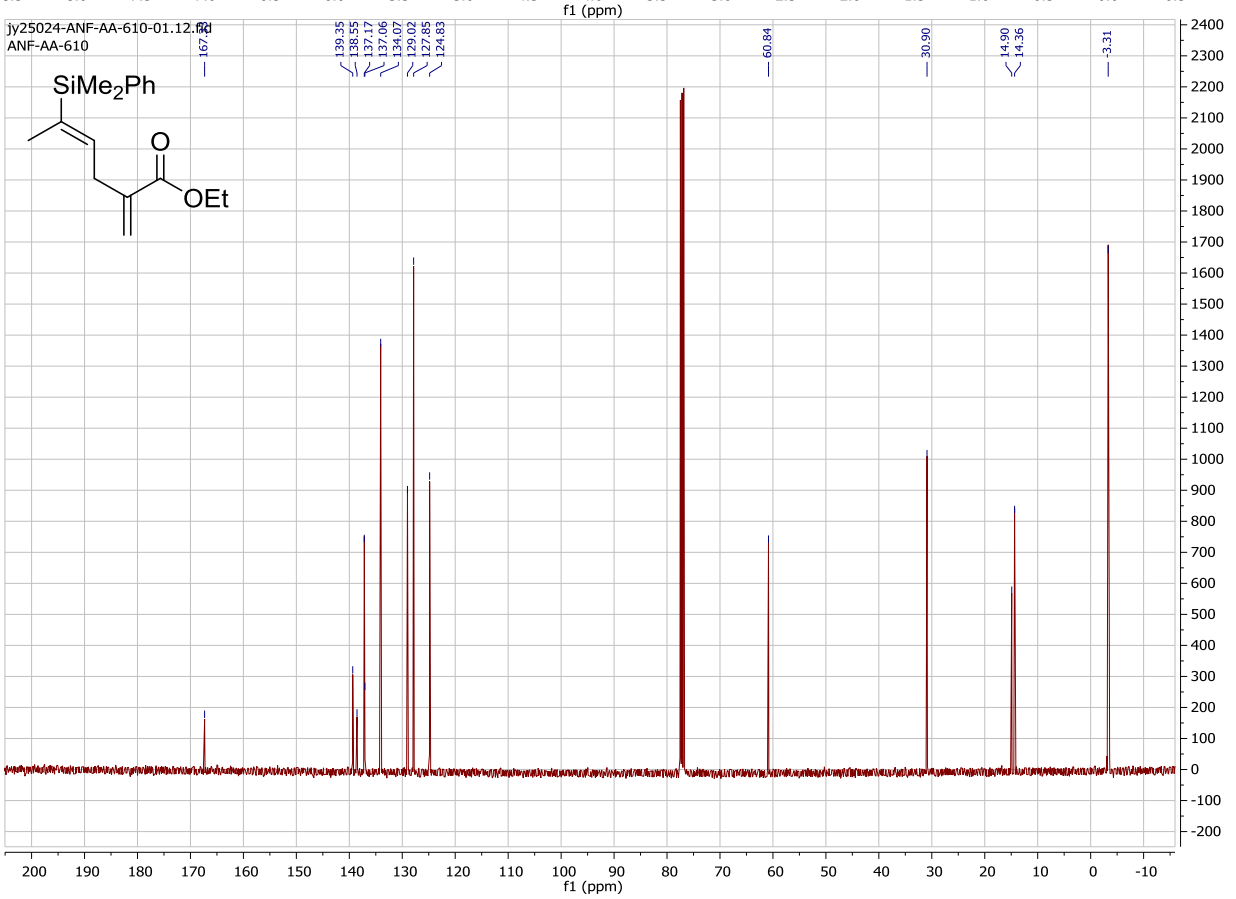

jy06044-ANF-AA-580-01.10.fid
ANF-AA-580 dry
SiMe2Ph
OH
2.00
3.00
1.00
2.00
3.00
1.00
6.00
f1 (ppm)

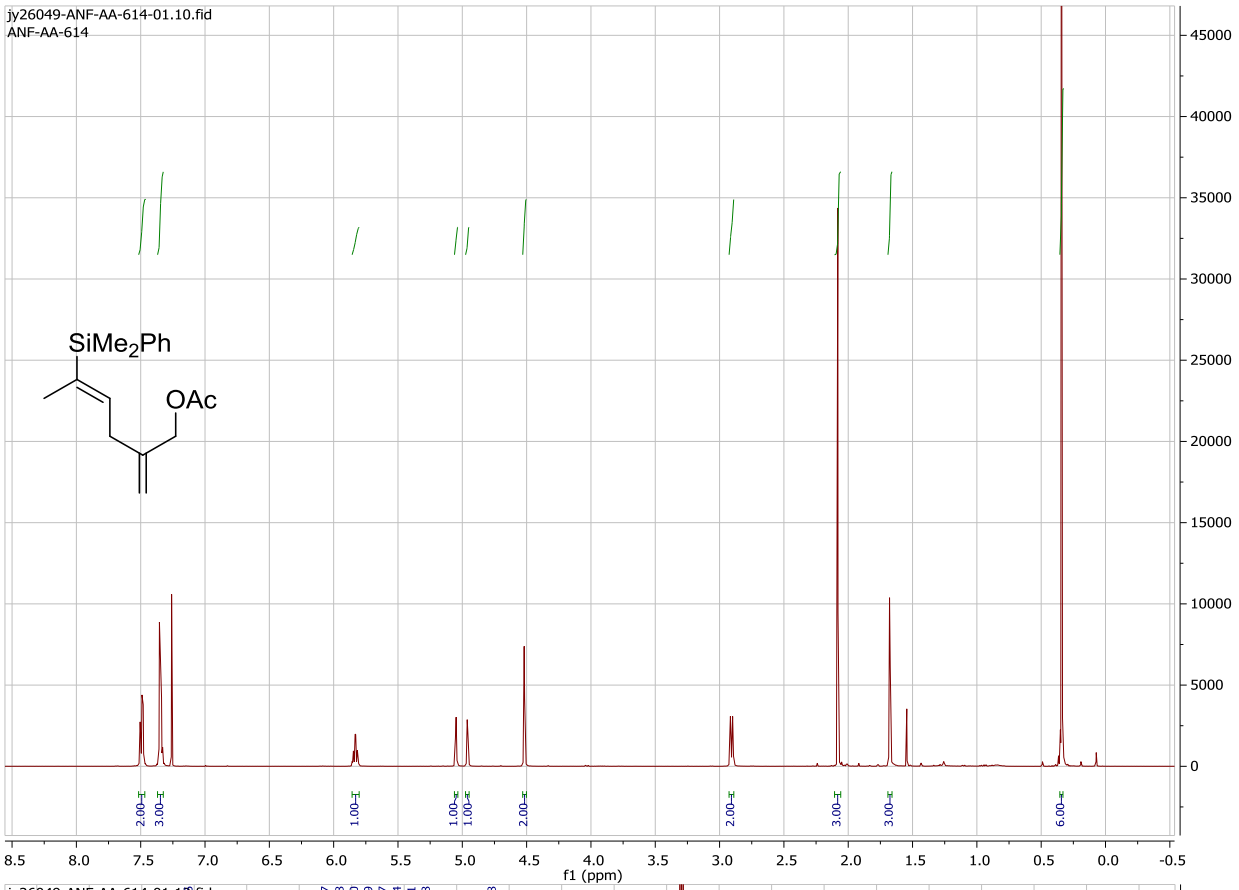

jy06044-ANF-AA-580-01.11.fid
ANF-AA-580 dry
SiMe2Ph
OH
139.82
134.09
129.16
127.91
59.94
15.18
-3.53
f1 (ppm)

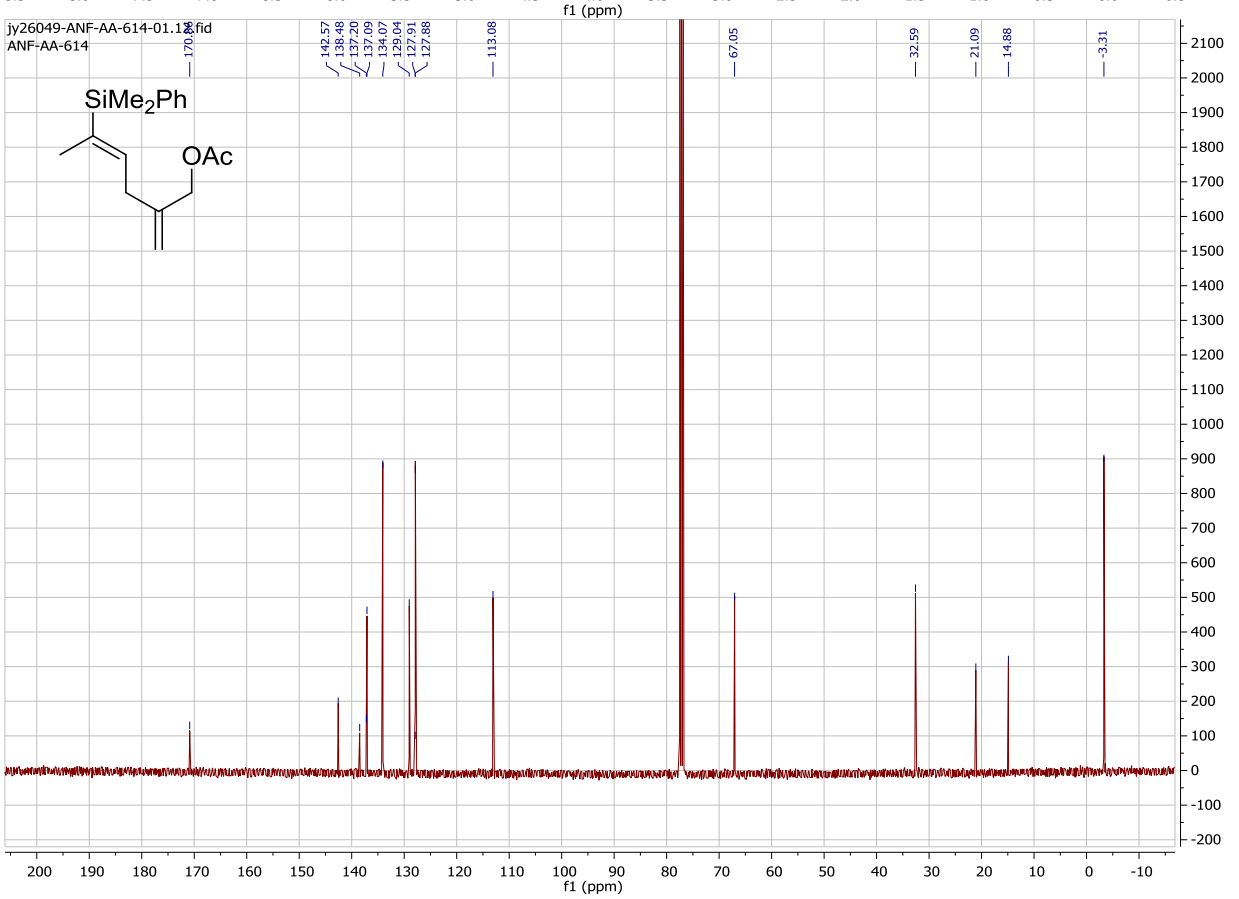

jy18045-ANF-AA-598-01.10.fid
ANF-AA-598
SiMe2Ph
Br
2.00
3.00
1.00
2.00
3.00
6.00
f1 (ppm)

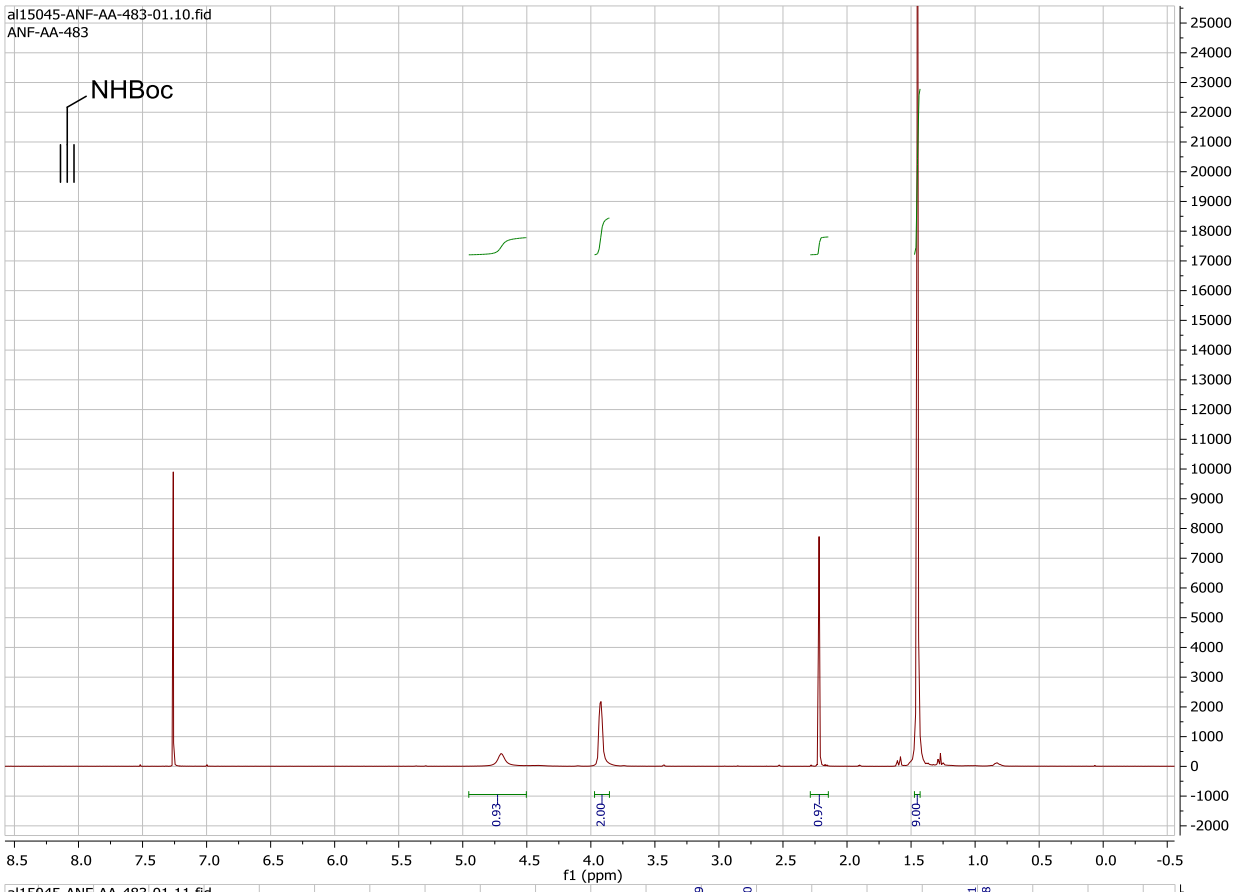

jy18045-ANF-AA-598-01.11.fid
ANF-AA-598
SiMe2Ph
Br
142.46
137.46
135.14
134.11
129.31
127.99
27.41
14.57
-3.61
f1 (ppm)

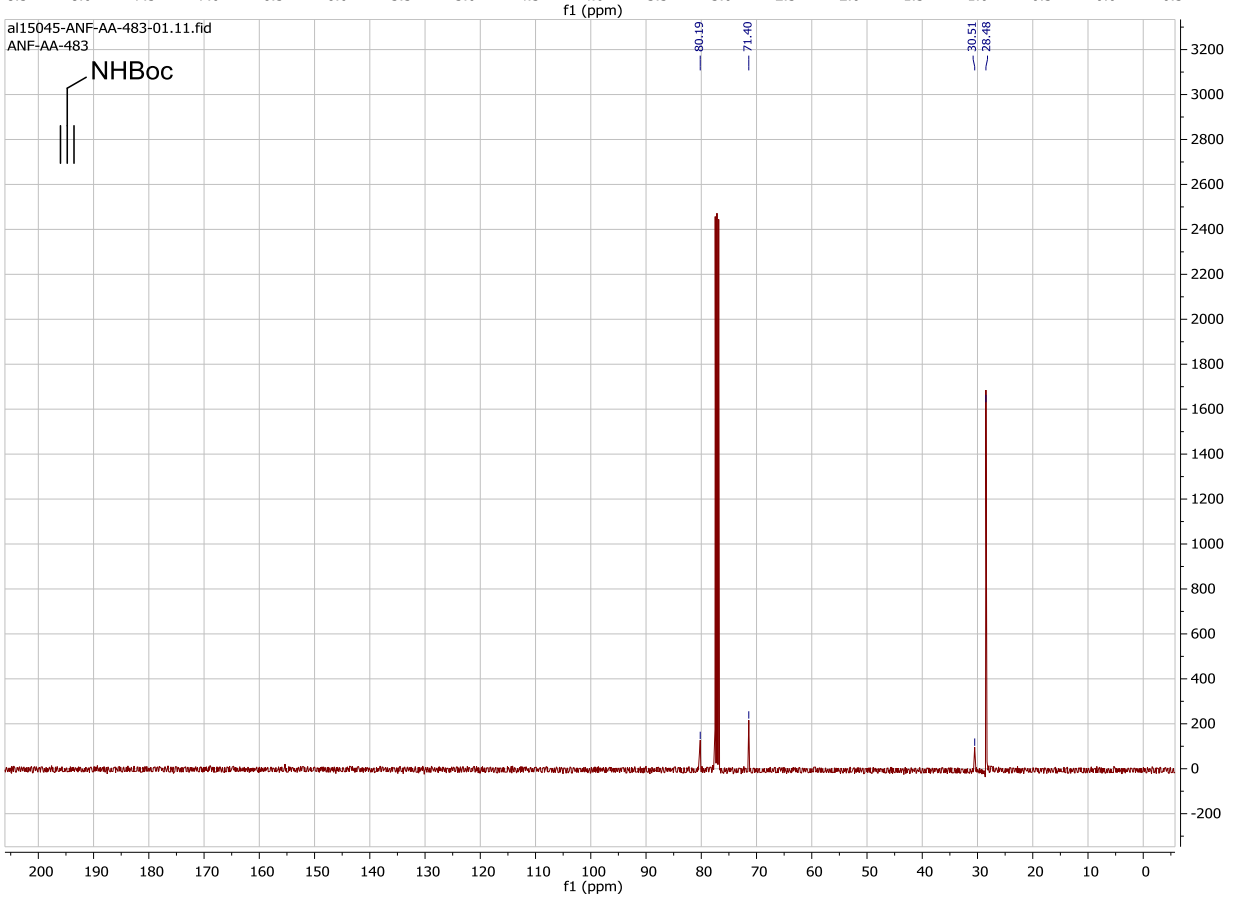

jy25024-ANF-AA-610-01.10.fid
ANF-AA-610
SiMe2Ph
O
OEt
2.00
3.00
1.00
1.00
1.00
2.00
2.00
3.00
3.00
6.00
f1 (ppm)

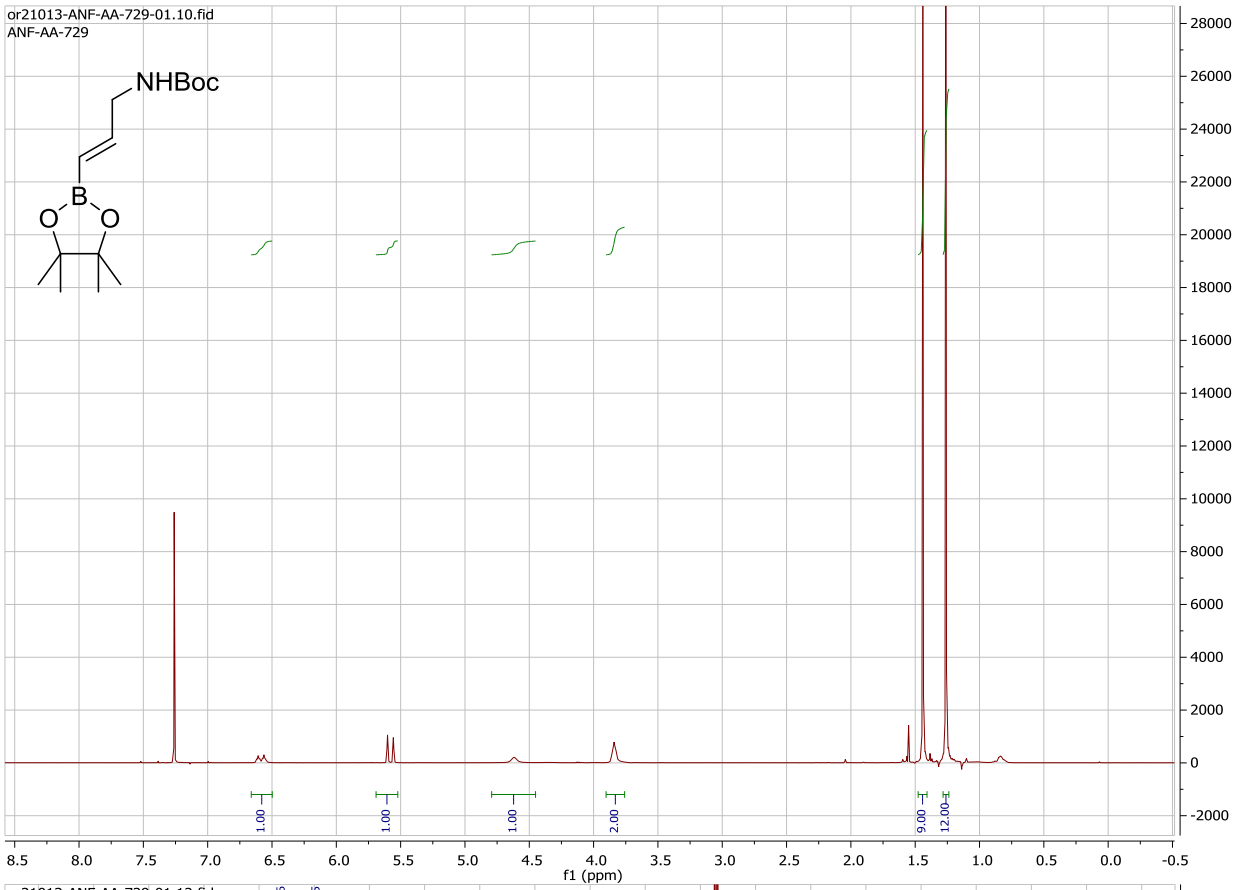

jy25024-ANF-AA-610-01.12.fid
ANF-AA-610
SiMe2Ph
O
OEt
167.22
139.35
138.55
137.17
137.06
134.07
129.02
127.85
124.83
60.84
30.90
14.90
14.36
-3.31
f1 (ppm)

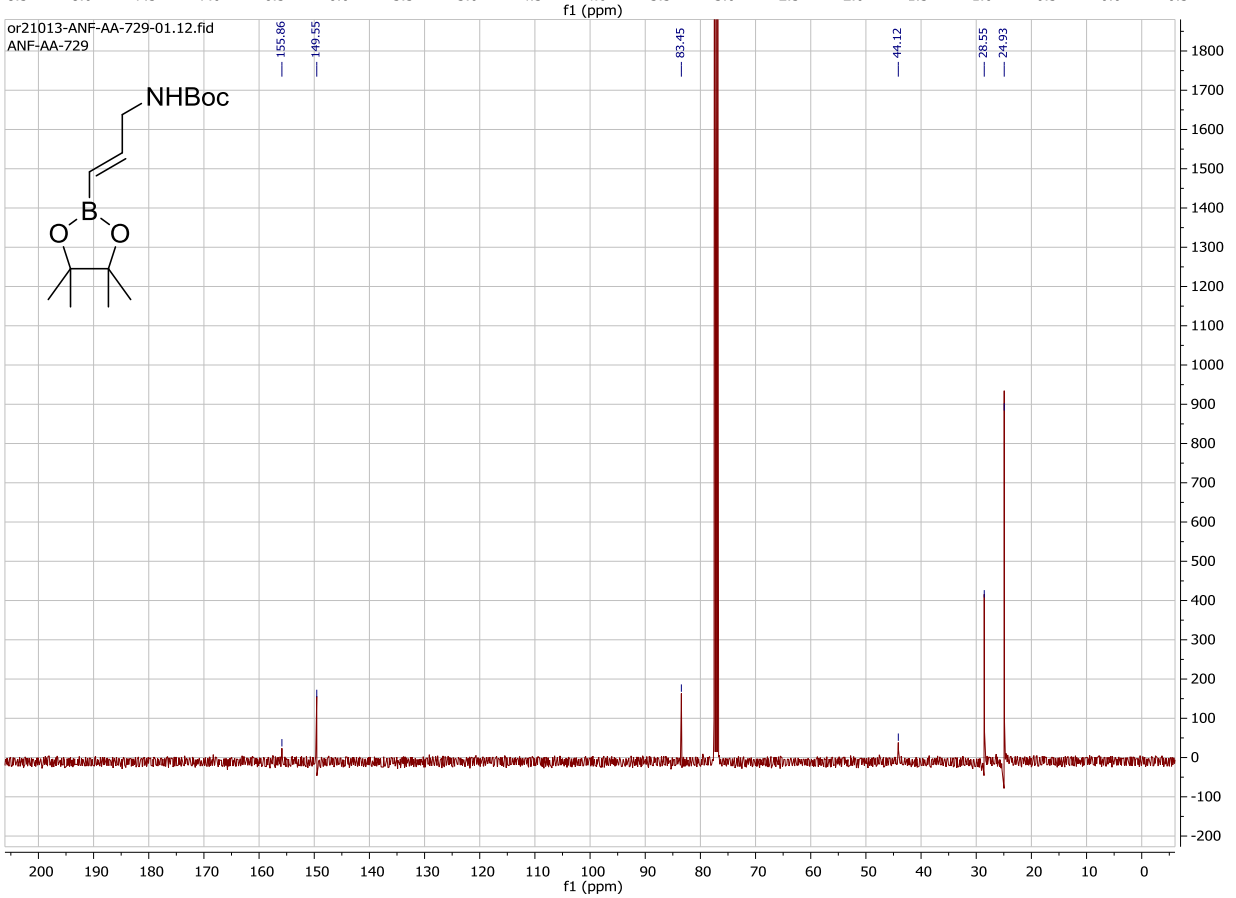

jy26049-ANF-AA-614-01.10.fid
ANF-AA-614
SiMe2Ph
OAc
2.00
3.00
1.00
1.00
1.00
2.00
2.00
3.00
3.00
6.00
f1 (ppm)

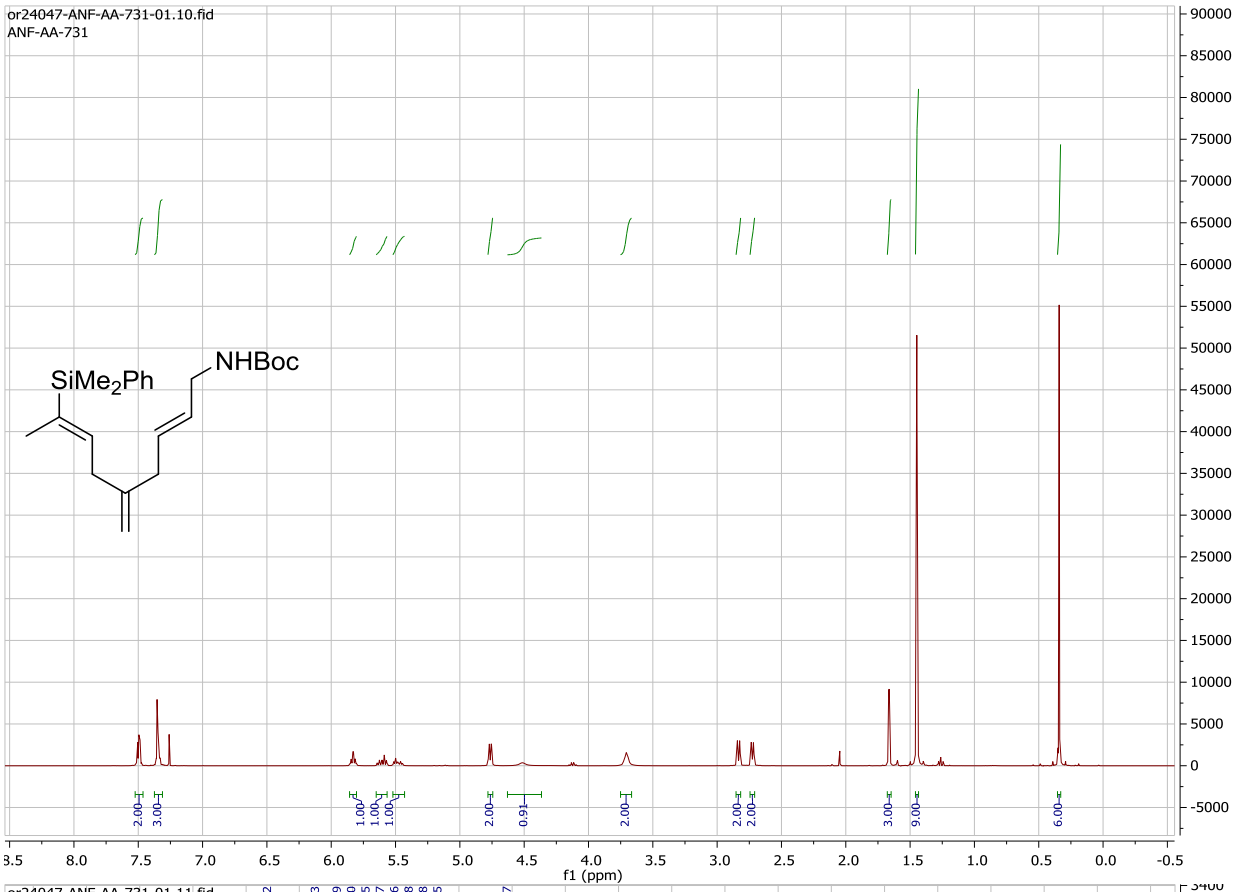

jy26049-ANF-AA-614-01.13.fid
ANF-AA-614
SiMe2Ph
OAc
170.82
142.57
138.48
137.20
137.09
134.07
129.04
127.91
127.88
113.08
67.05
32.59
21.09
14.88
-3.31
f1 (ppm)

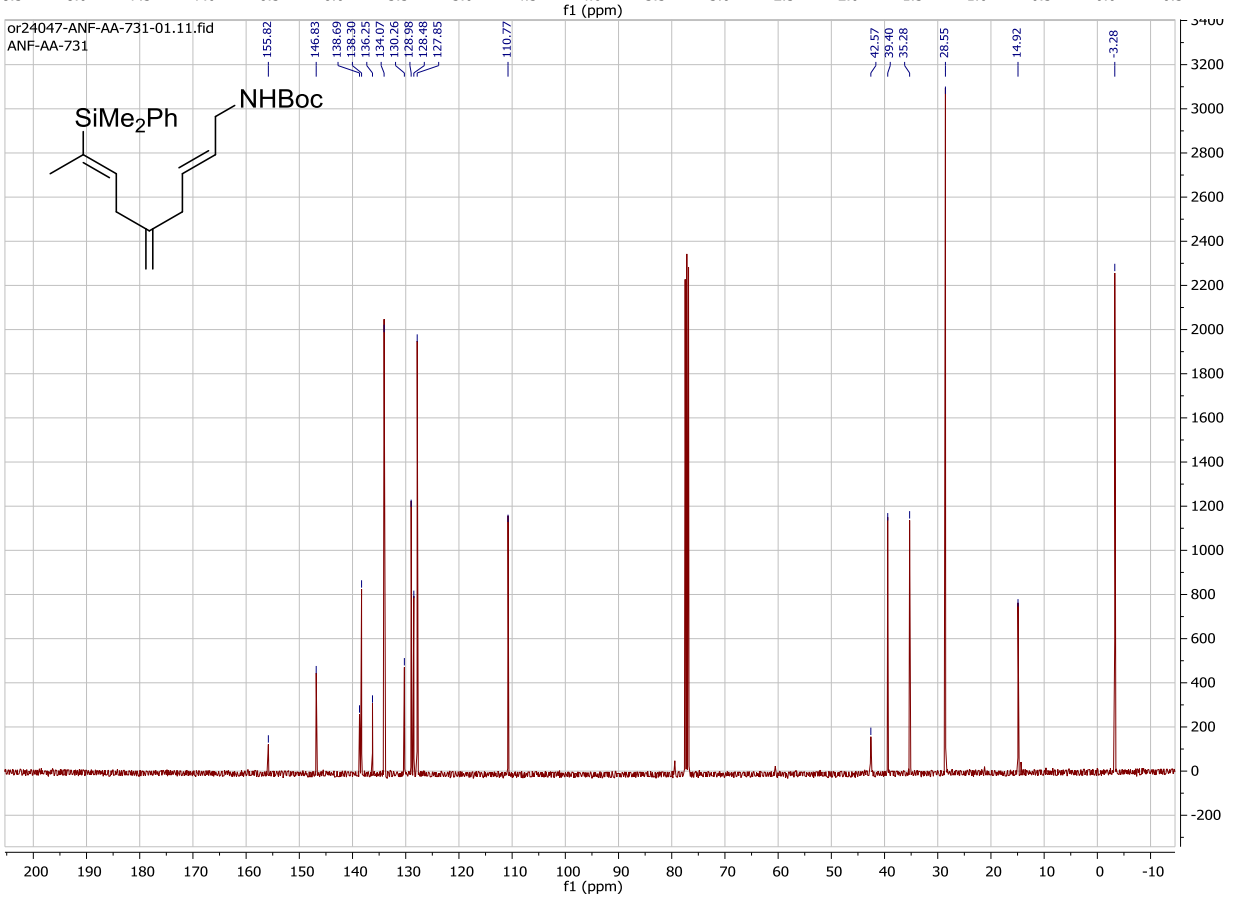

al15045-ANF-AA-483-01.10.fid
ANF-AA-483
NHBoc
0.93
2.00
0.97
9.00
f1 (ppm)

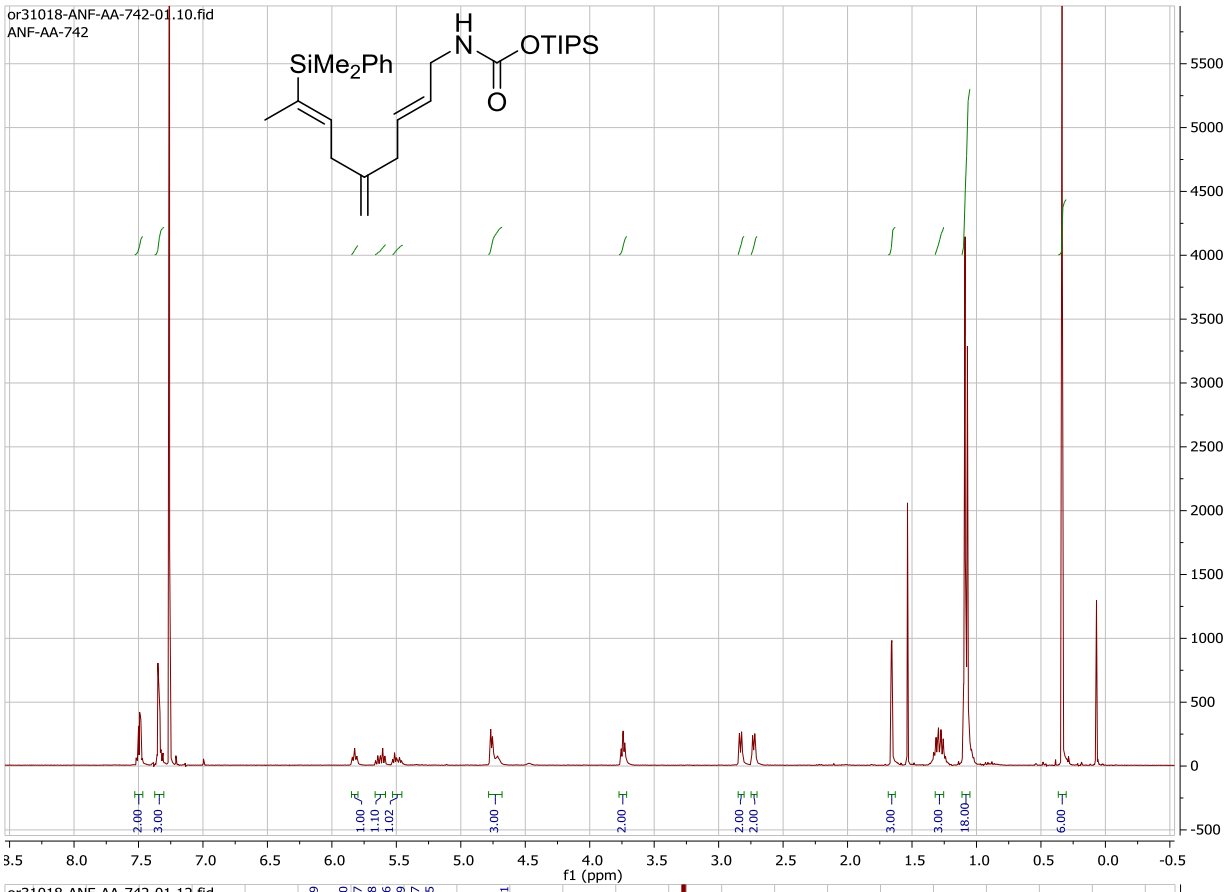

al15045-ANF-AA-483-01.11.fid
ANF-AA-483
NHBoc
80.19
71.40
30.51
28.48
f1 (ppm)

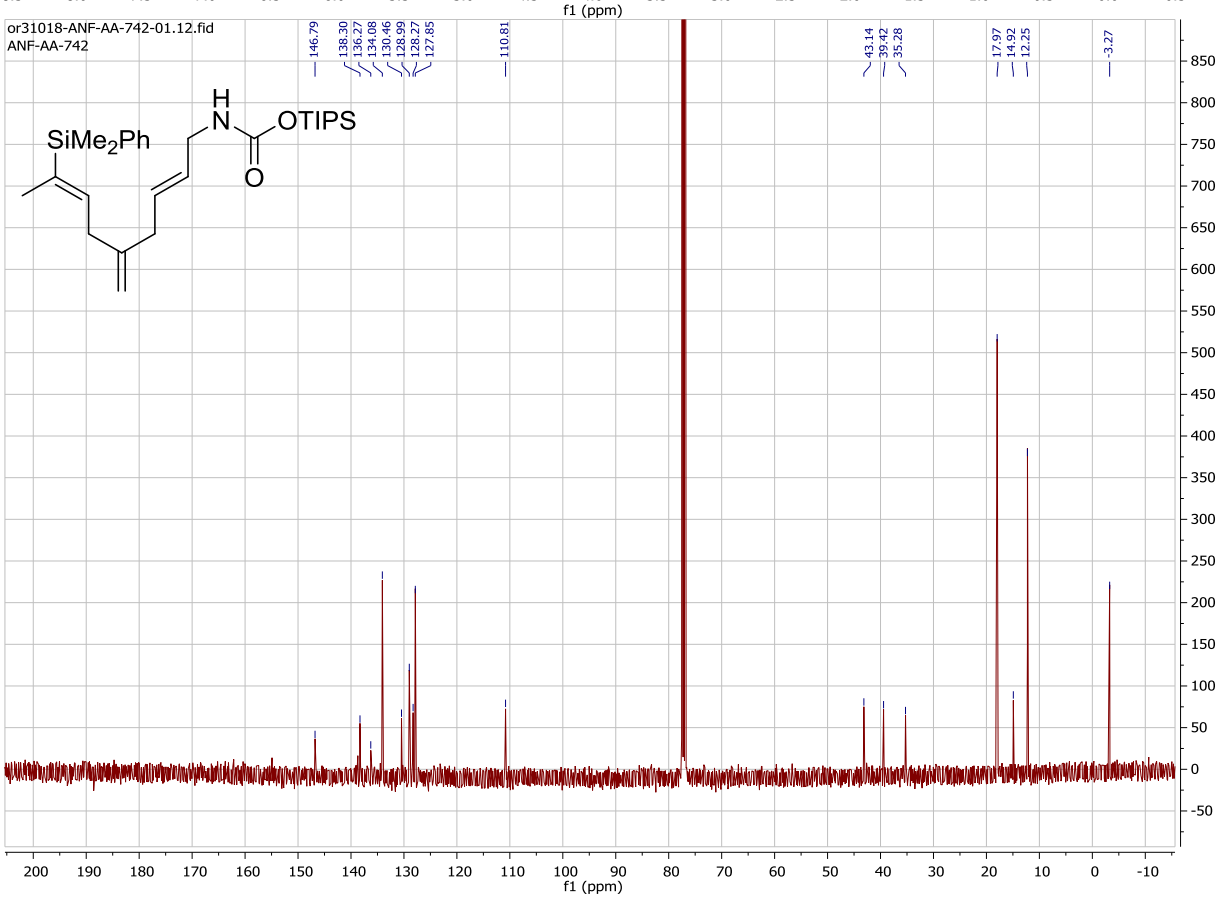

or21013-ANF-AA-729-01.10.fid
ANF-AA-729
NHBoc
B
O
O
1.00
1.00
1.00
2.00
9.00
12.00
f1 (ppm)

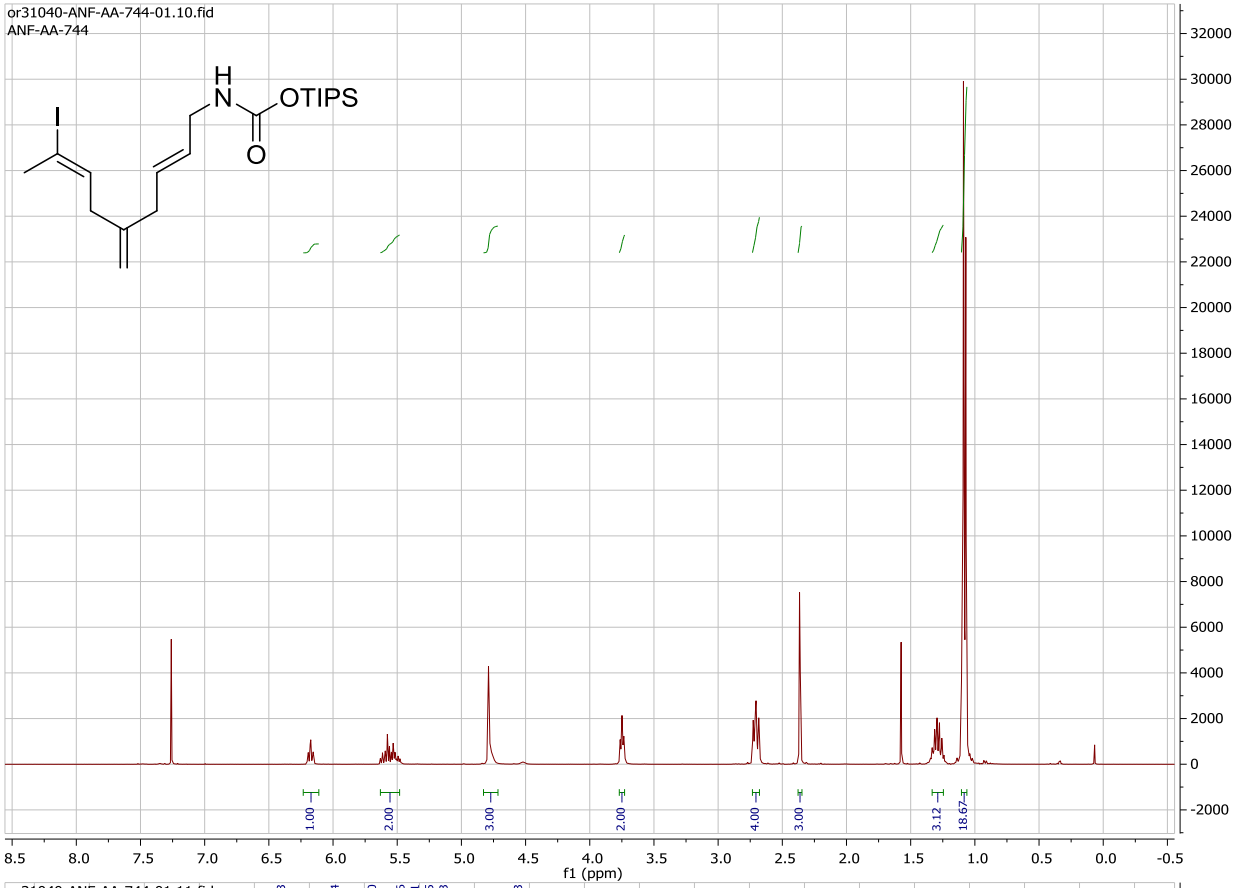

or21013-ANF-AA-729-01.12.fid
ANF-AA-729
NHBoc
B
O
O
155.86
149.55
83.45
44.12
28.55
24.93
f1 (ppm)

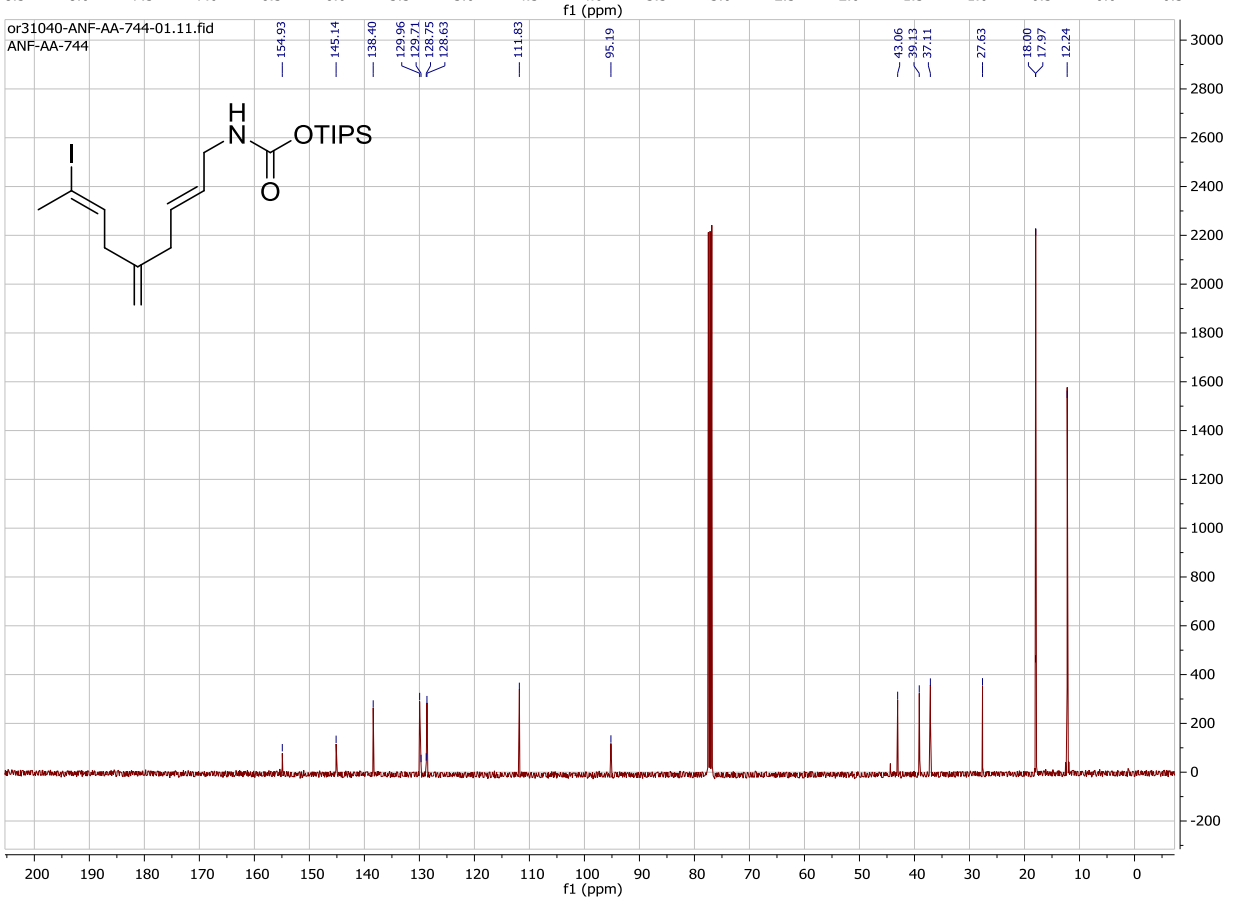

or24047-ANF-AA-731-01.10.fid
ANF-AA-731
SiMe2Ph
NHBoc
f1 (ppm)

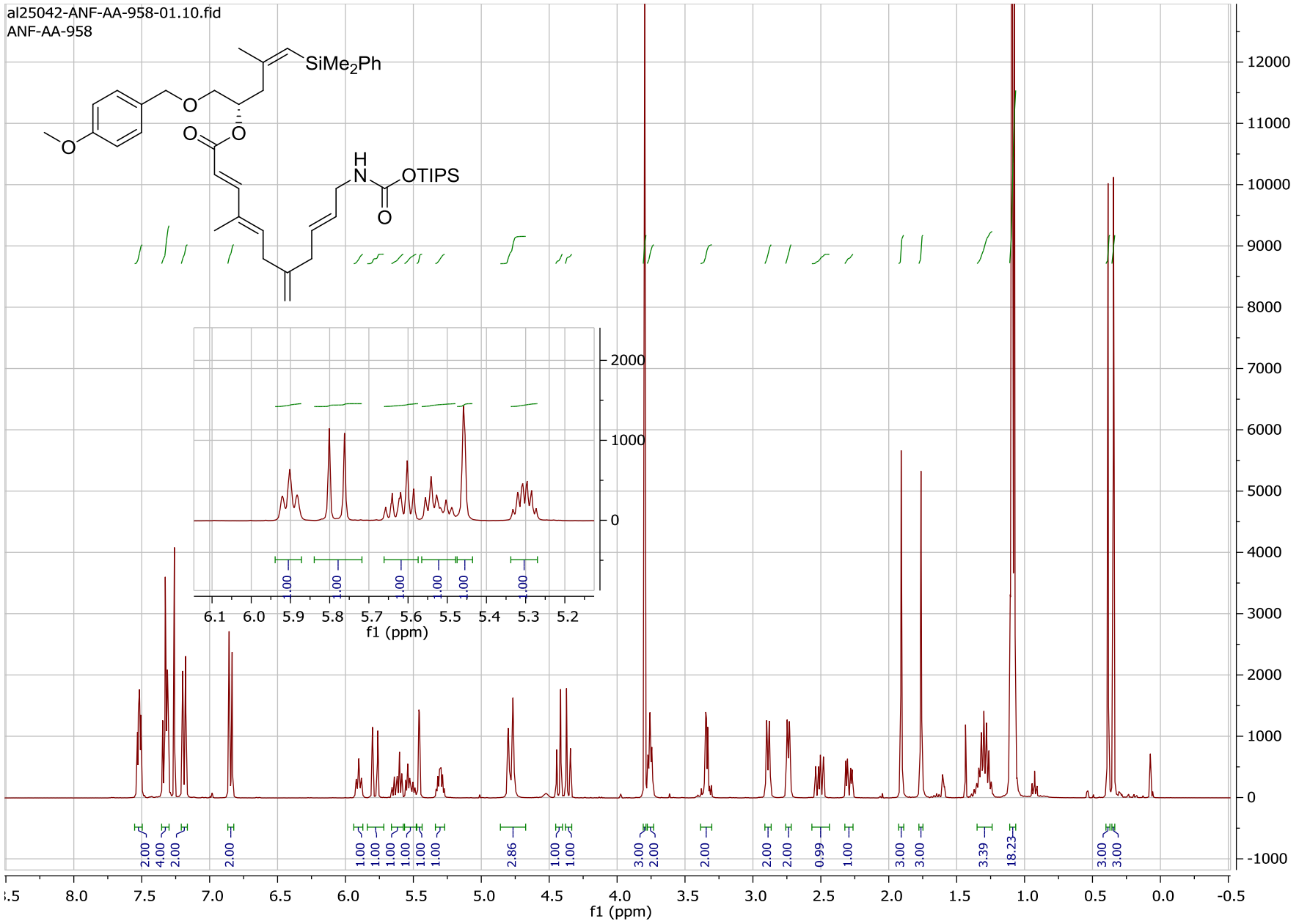

or24047-ANF-AA-731-01.11.fid
ANF-AA-731
SiMe2Ph
NHBoc
155.82
146.83
138.69
138.30
136.25
134.07
130.26
128.98
128.48
127.85
110.77
42.57
39.40
35.28
28.55
14.92
-3.28
f1 (ppm)

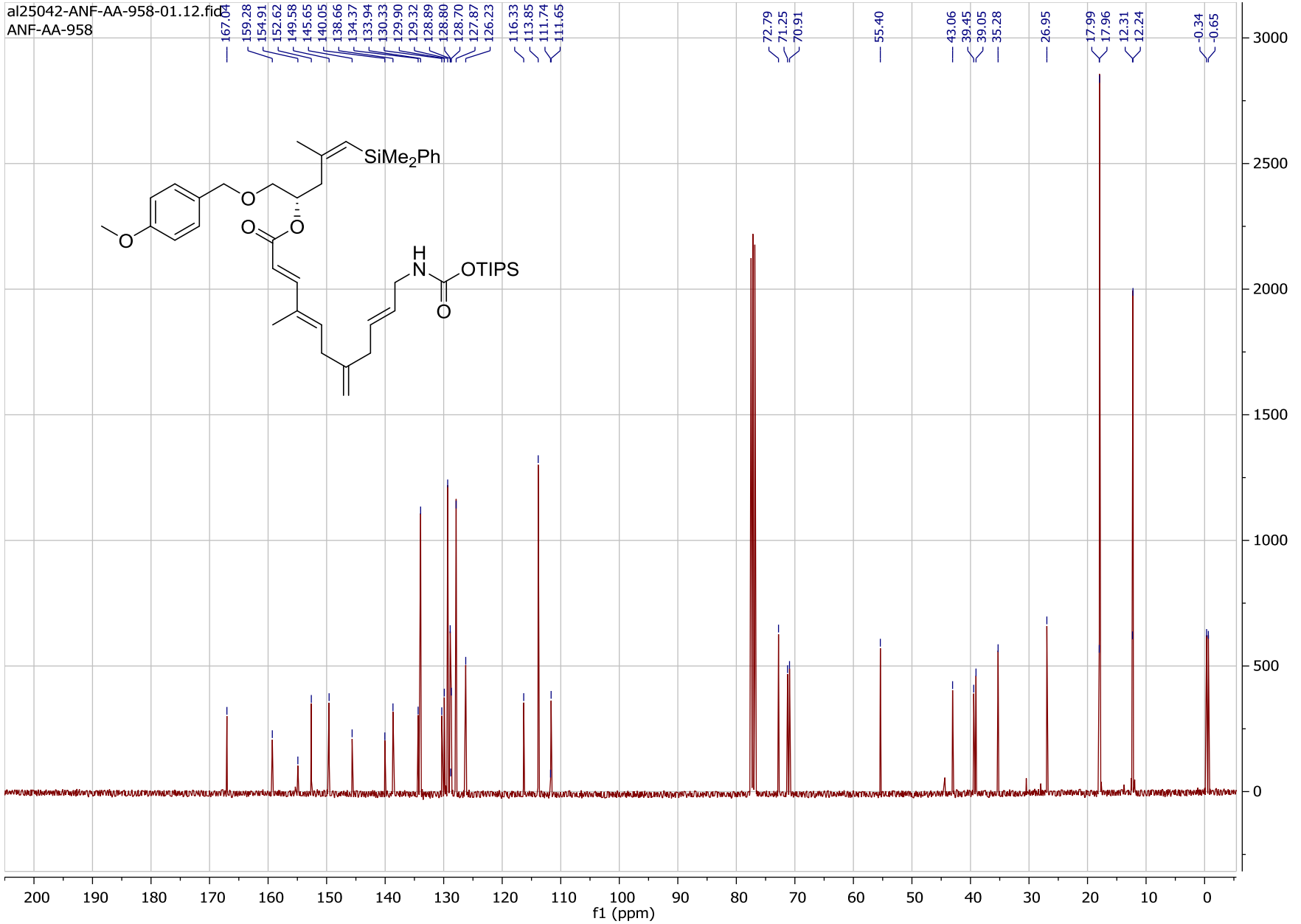

or31018-ANF-AA-742-01.10.fid
ANF-AA-742
SiMe2Ph
H
N
OTIPS
O
2.00
3.00
1.00
1.10
1.02
3.00
2.00
2.00
2.00
3.00
3.00
18.00
6.00
f1 (ppm)

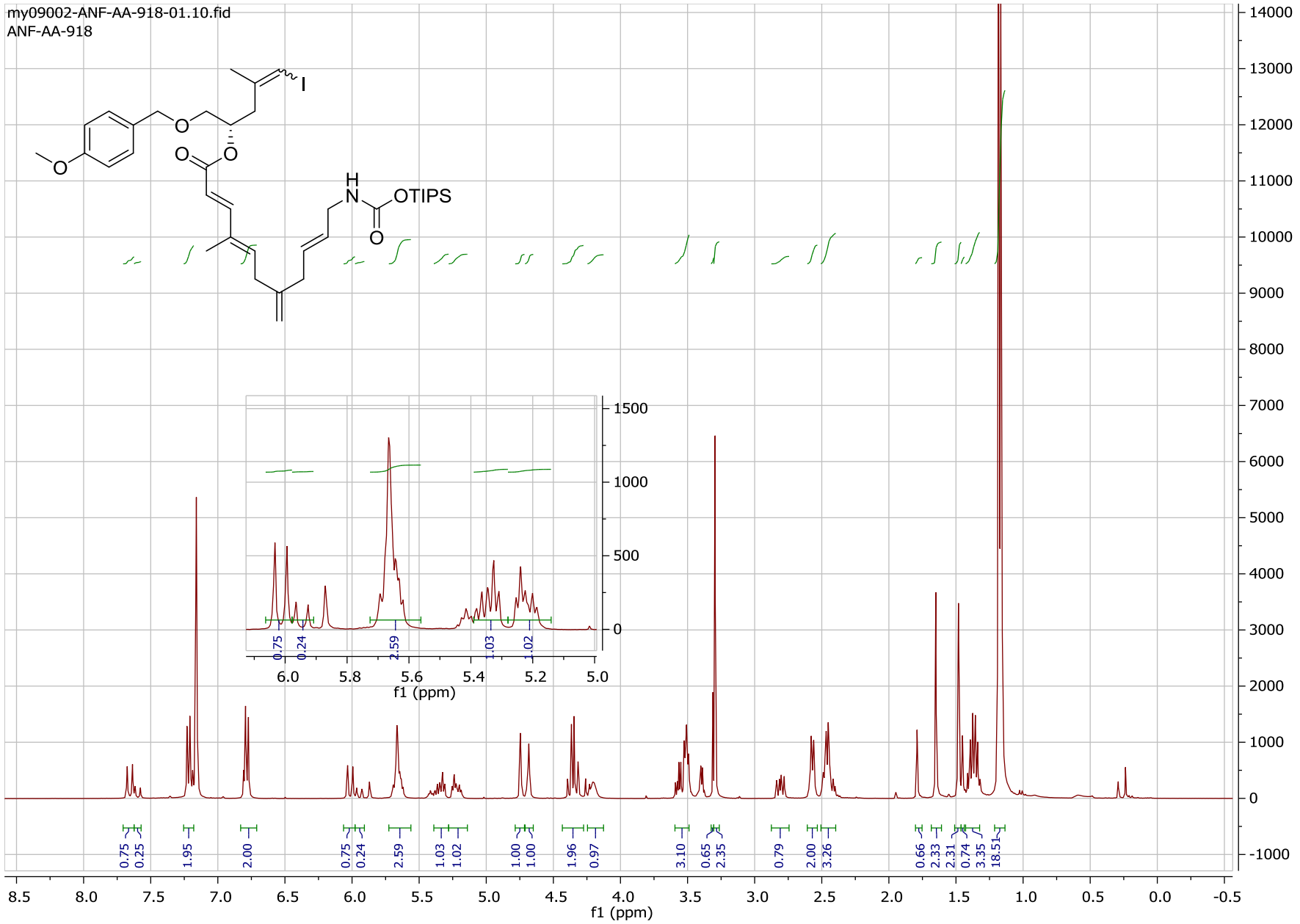

or31018-ANF-AA-742-01.12.fid
ANF-AA-742
SiMe2Ph
H
N
OTIPS
O
146.79
138.30
136.27
134.08
130.46
128.99
128.27
127.85
110.81
43.14
39.42
35.28
17.97
14.92
12.25
-3.27
f1 (ppm)

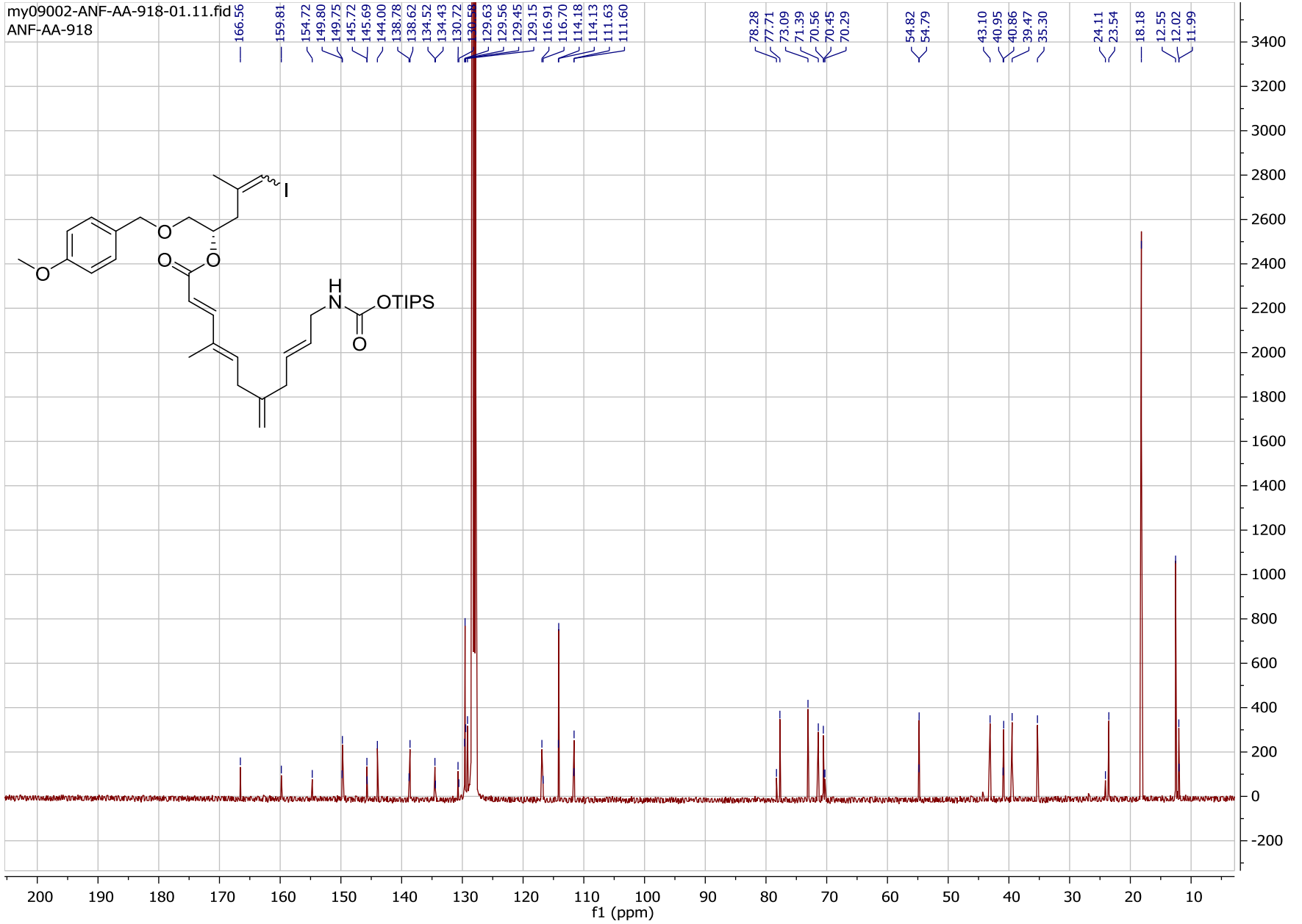

or31040-ANF-AA-744-01.10.fid
ANF-AA-744
H
N
OTIPS
O
I
1.00
2.00
3.00
2.00
4.00
3.00
3.12
18.67
f1 (ppm)

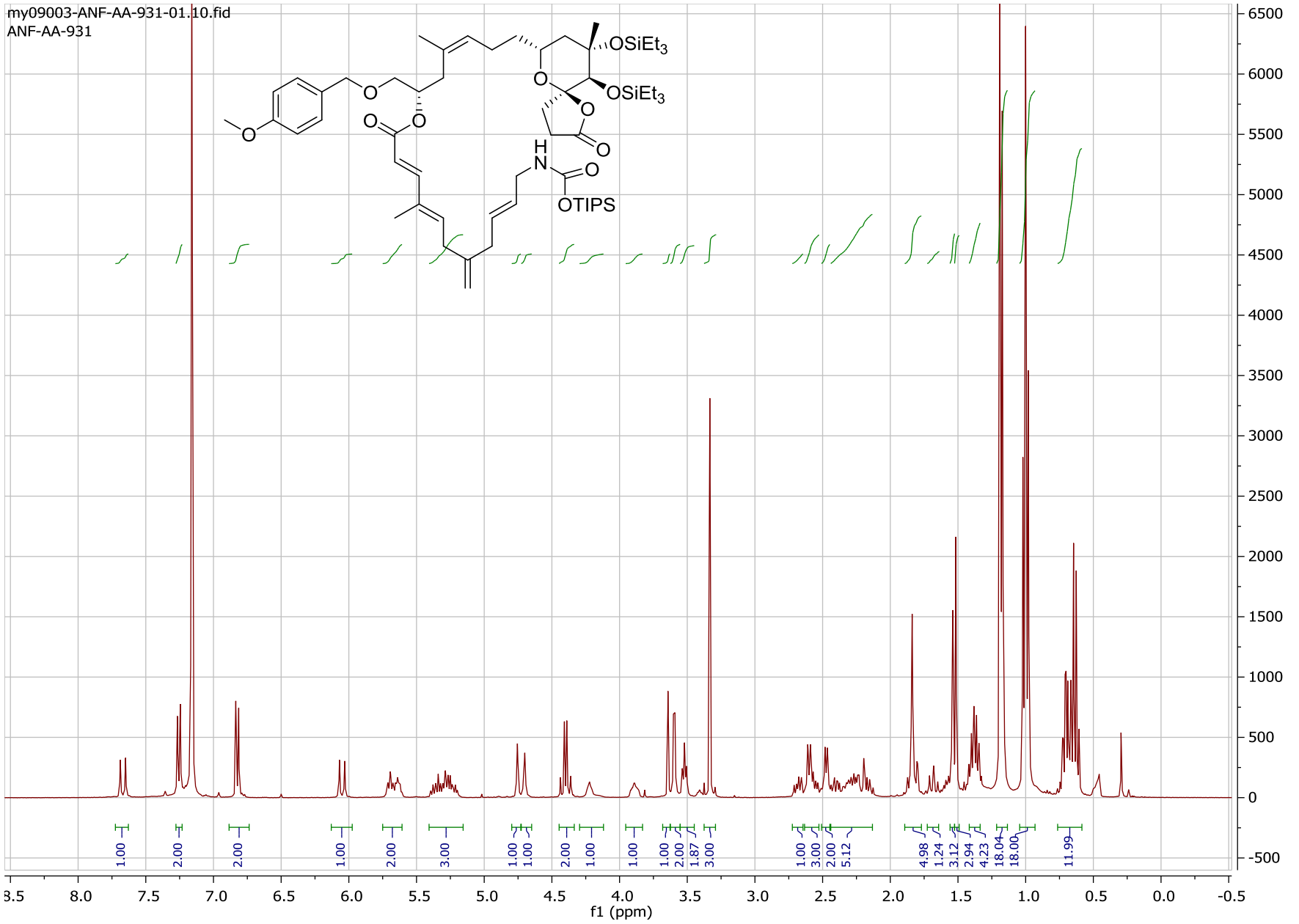

or31040-ANF-AA-744-01.11.fid
ANF-AA-744
154.93
145.14
138.40
129.96
129.71
128.75
128.63
111.83
95.19
43.06
39.13
37.11
27.63
18.00
17.97
12.24
H
N
OTIPS
O
I
f1 (ppm)

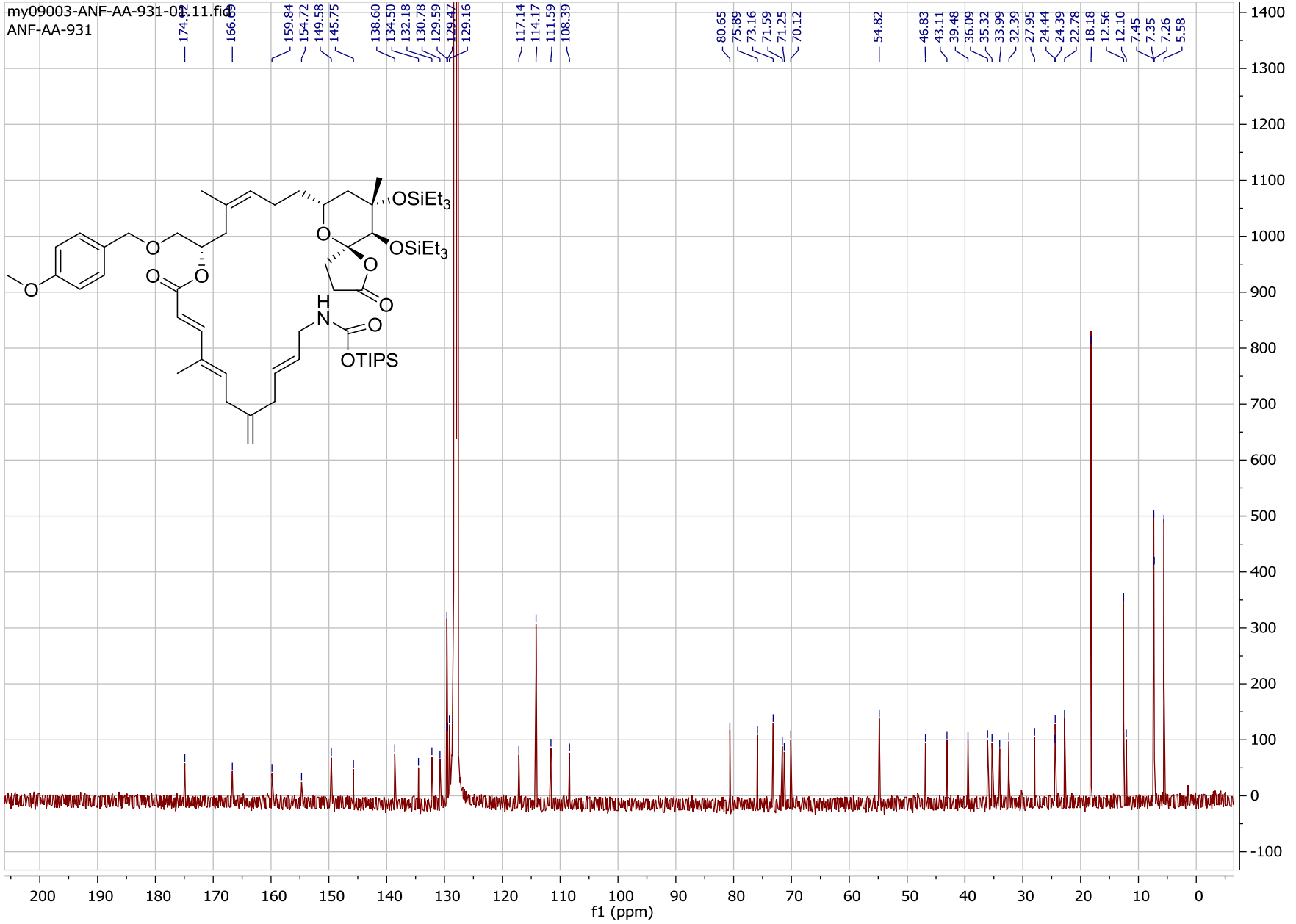

al25042-ANF-AA-958-01.10.fid
ANF-AA-958
SiMe2Ph
O
O
O
O
H
N
OTIPS
O
f1 (ppm)
f1 (ppm)

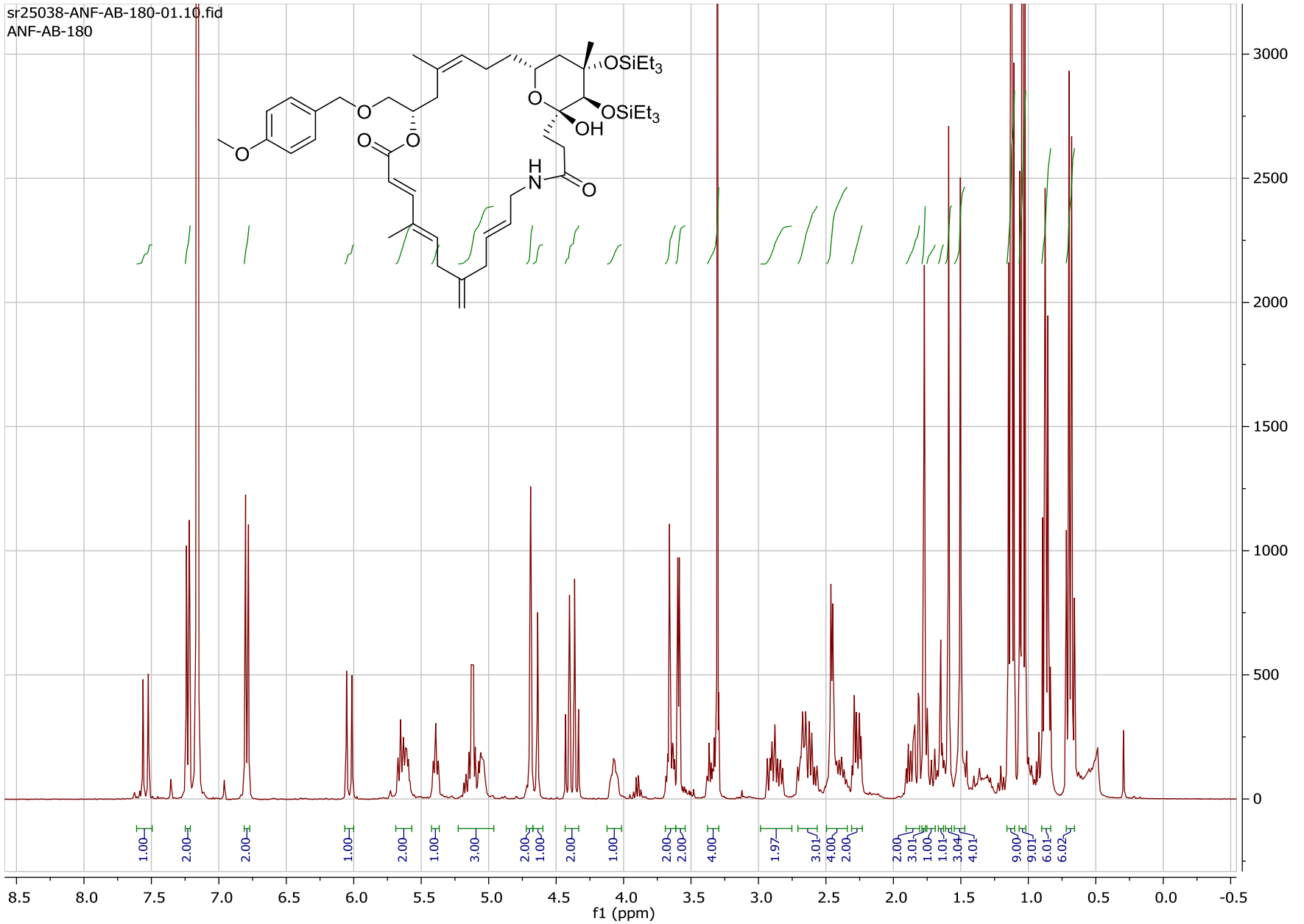

al25042-ANF-AA-958-01.12.fid
ANF-AA-958
167.04
159.28
154.91
152.62
149.58
145.65
140.05
138.66
134.37
133.94
130.33
129.90
129.32
128.89
128.80
128.70
127.87
126.23
116.33
113.85
111.74
111.65
72.79
71.25
70.91
55.40
43.06
39.45
39.05
35.28
26.95
17.99
17.96
12.31
12.24
-0.34
-0.65
SiMe2Ph
O
O
O
O
H
N
OTIPS
O
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

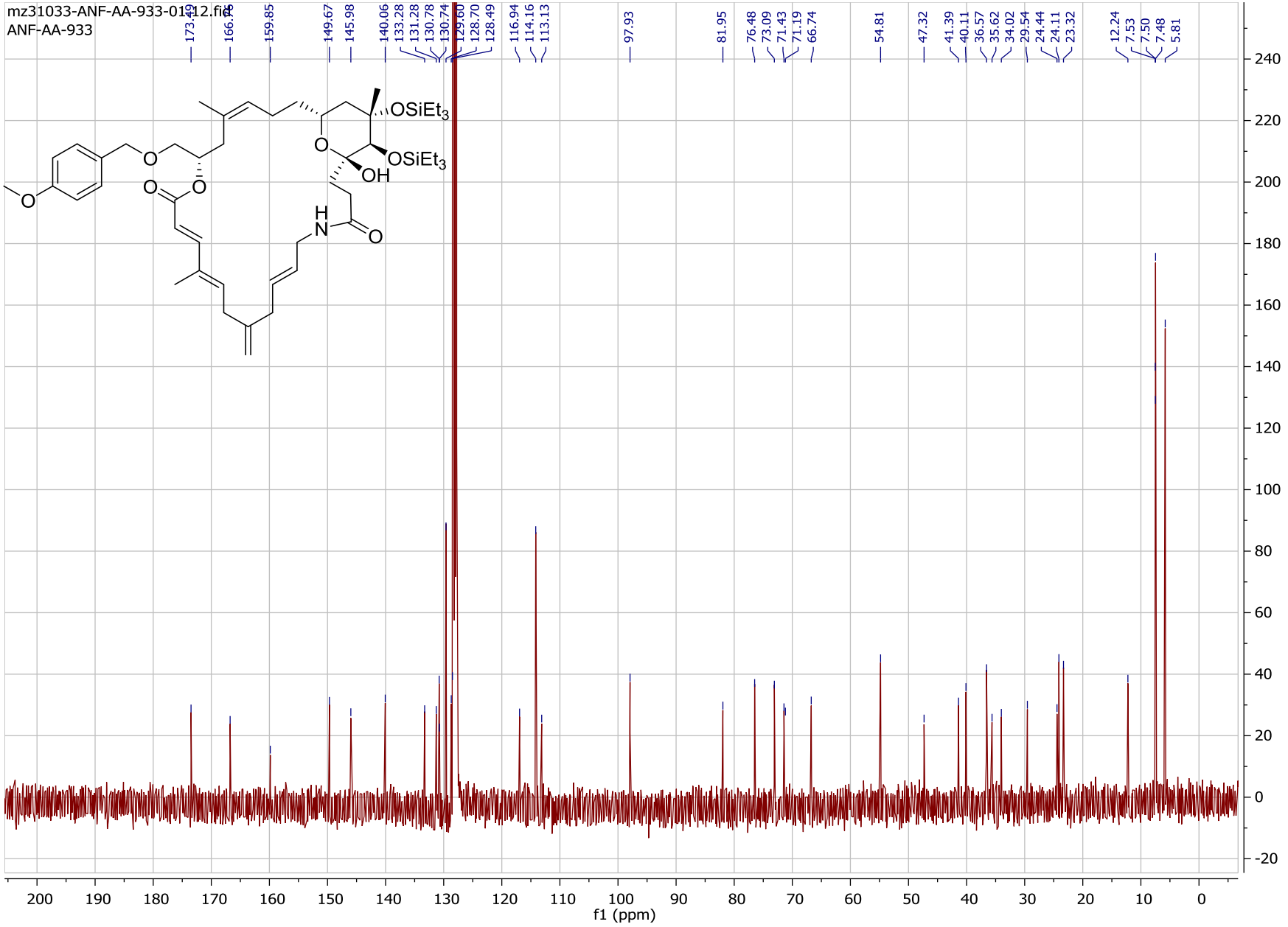

my09002-ANF-AA-918-01.10.fid
ANF-AA-918
I
O
O
O
O
H
N
OTIPS
O
f1 (ppm)
0.75
0.24
2.59
1.03
1.02
f1 (ppm)
0.75
0.25
1.95
2.00
0.75
0.24
2.59
1.03
1.02
1.00
1.00
1.96
0.97
3.10
0.65
2.35
0.79
2.00
3.26
0.66
2.33
2.31
0.74
3.35
18.51

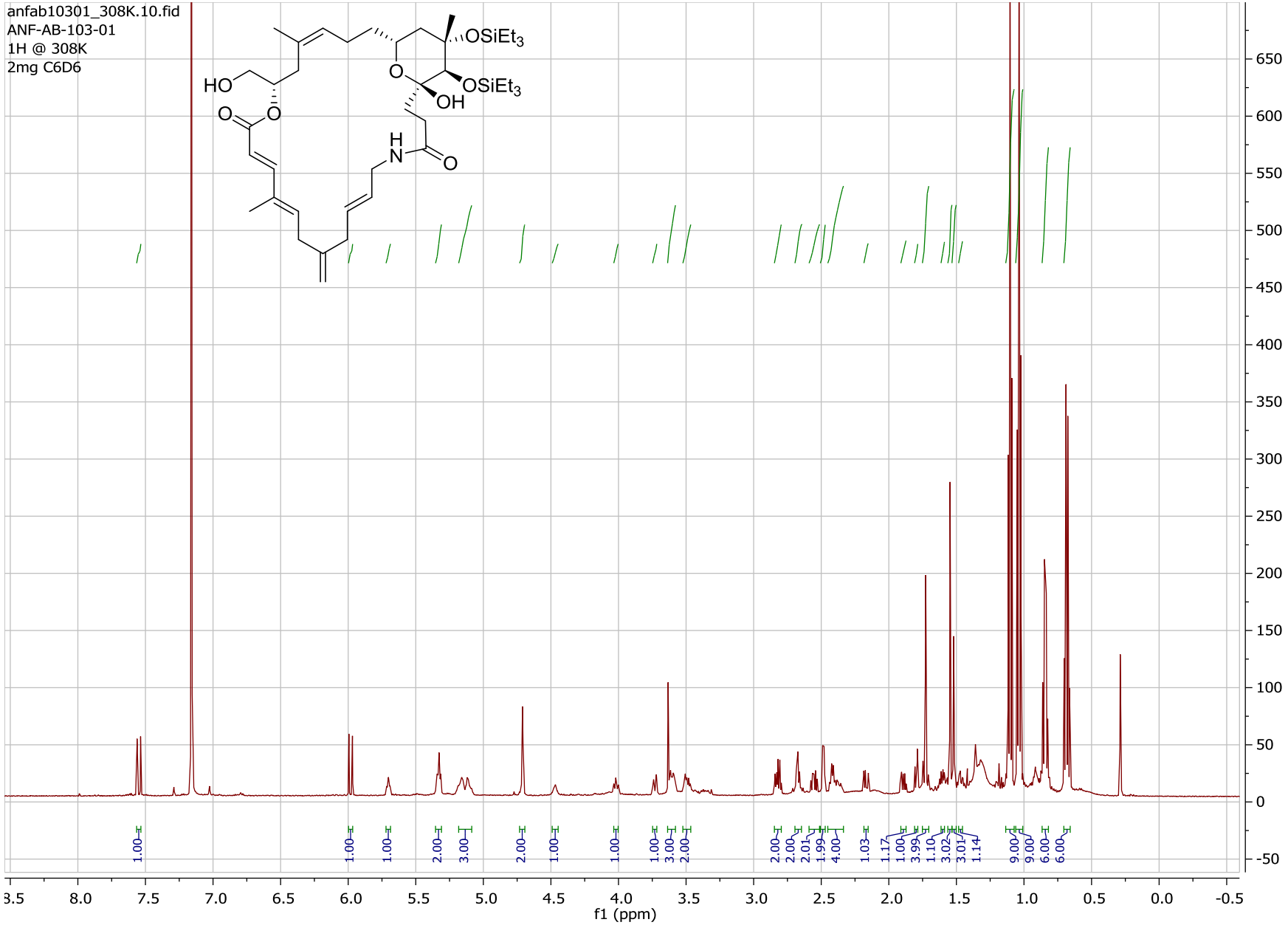

my09002-ANF-AA-918-01.11.fid
ANF-AA-918
166.56
159.81
154.72
149.80
149.75
145.72
145.69
144.00
138.78
138.62
134.52
134.43
130.72
129.63
129.56
129.45
129.15
116.91
116.70
114.18
114.13
111.63
111.60
78.28
77.71
73.09
71.39
70.56
70.45
70.29
54.82
54.79
43.10
40.95
40.86
39.47
35.30
24.11
23.54
18.18
12.55
12.02
11.99
I
O
O
O
O
H
N
OTIPS
O
f1 (ppm)

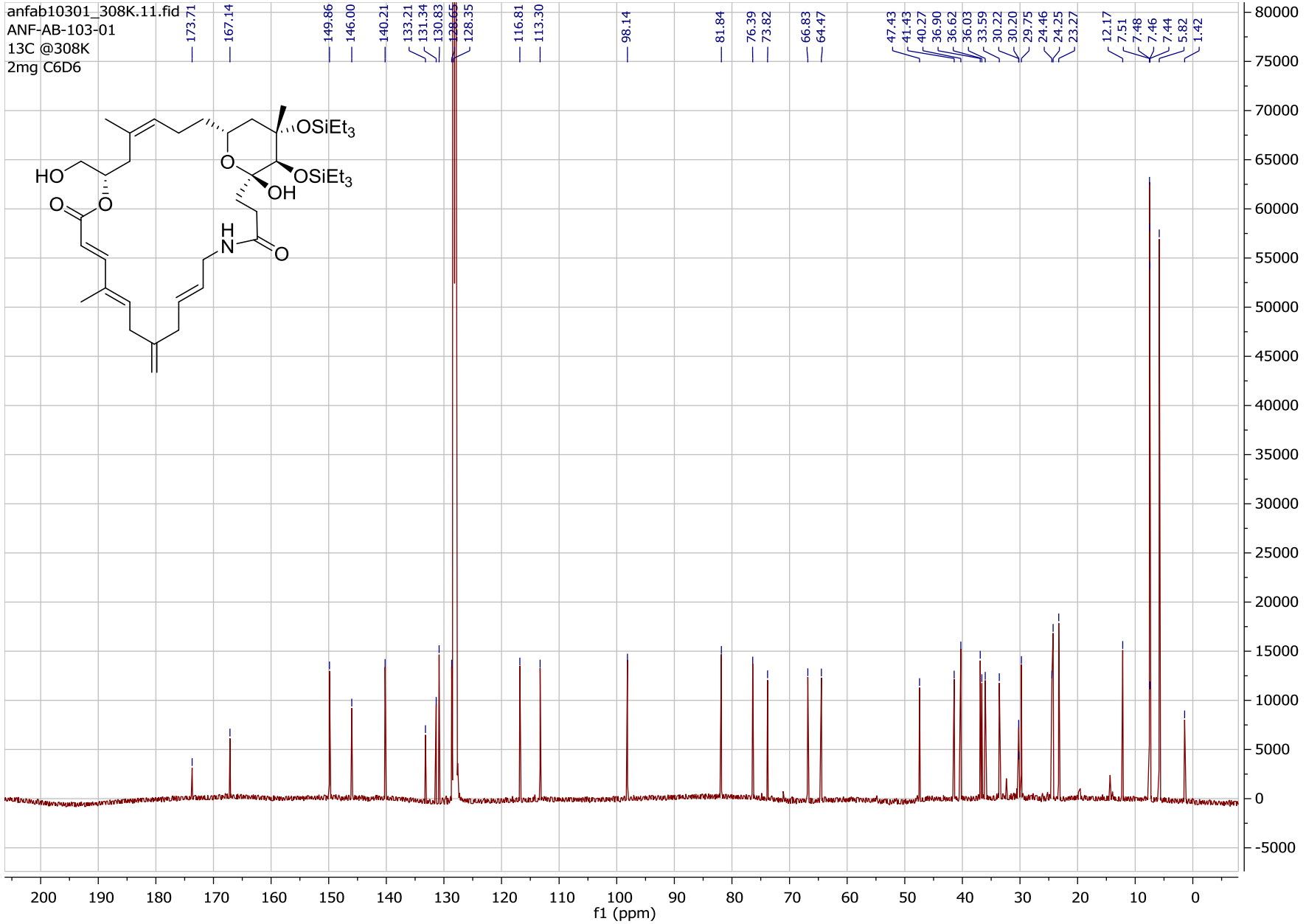

my09003-ANF-AA-931-01.10.fid
ANF-AA-931
OSiEt3
OSiEt3
OTIPS
f1 (ppm)

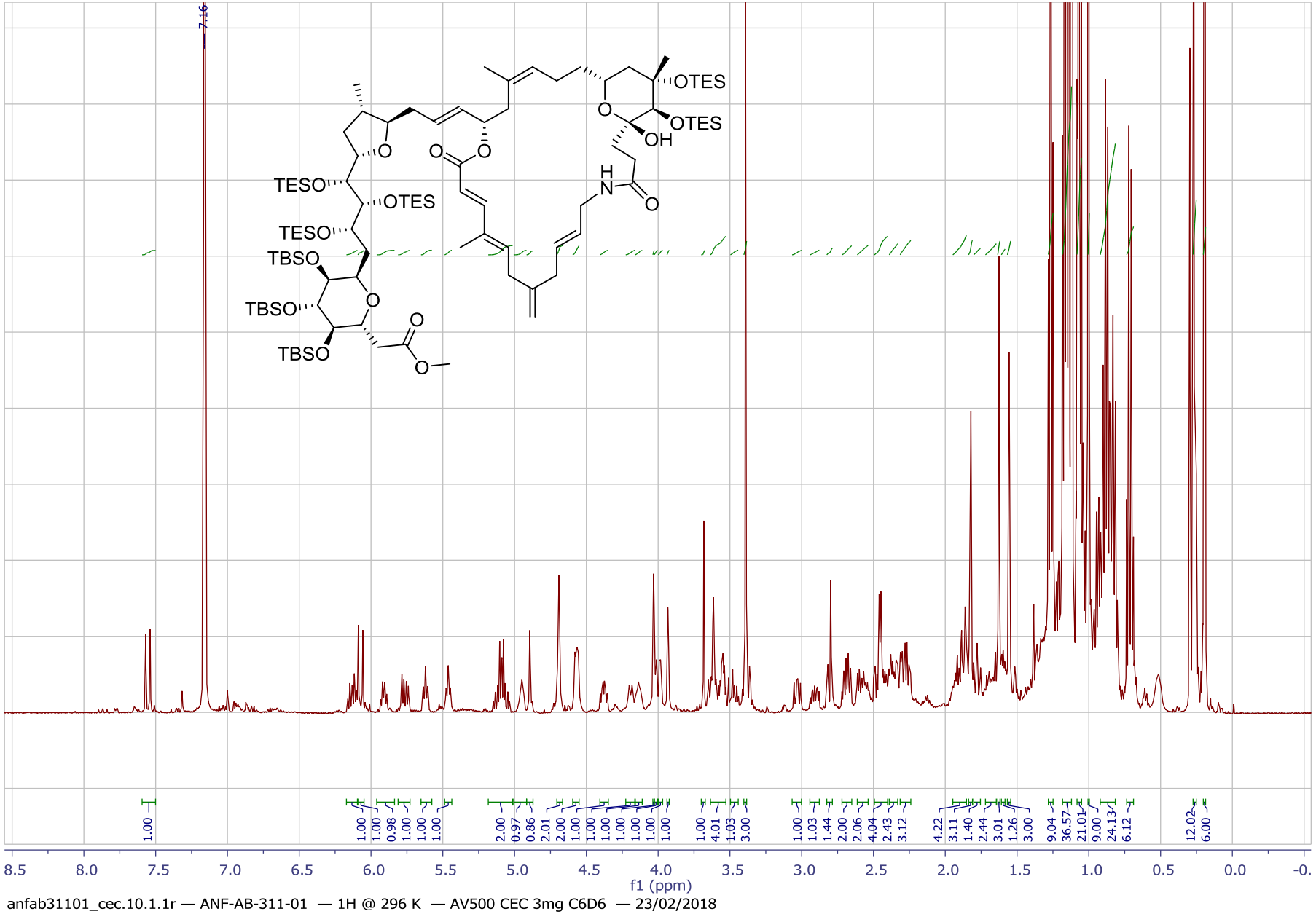

my09003-ANF-AA-931-01.11.fid
ANF-AA-931
174.92
166.89
159.84
154.72
149.58
145.75
138.60
134.50
132.18
130.78
129.59
129.47
129.16
117.14
114.17
111.59
108.39
80.65
75.89
73.16
71.59
71.25
70.12
54.82
46.83
43.11
39.48
36.09
35.32
33.99
32.39
27.95
24.44
24.39
22.78
18.18
12.56
12.10
7.45
7.35
7.26
5.58
OSiEt3
OSiEt3
O
O
O
O
O
O
H
N
O
OTIPS
f1 (ppm)

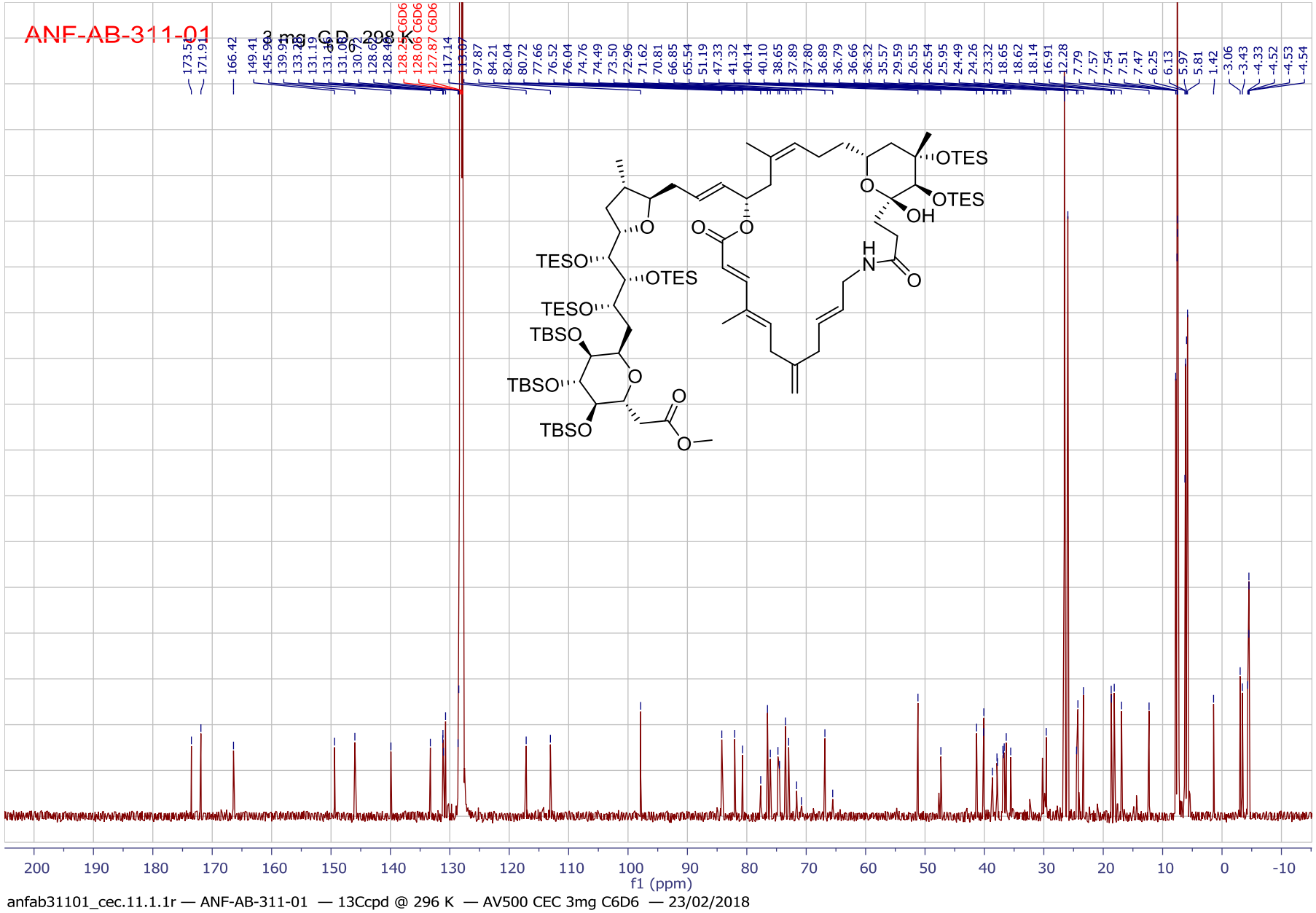

sr25038-ANF-AB-180-01.10.fid
ANF-AB-180
OSiEt3
OSiEt3
OH
O
O
O
O
O
H
N
O
3000
2500
2000
1500
1000
500
0
1.00
2.00
2.00
1.00
2.00
1.00
3.00
2.00
1.00
2.00
1.00
2.00
2.00
4.00
1.97
3.01
4.00
2.00
2.00
3.01
1.00
1.01
3.04
4.01
9.00
9.01
6.01
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

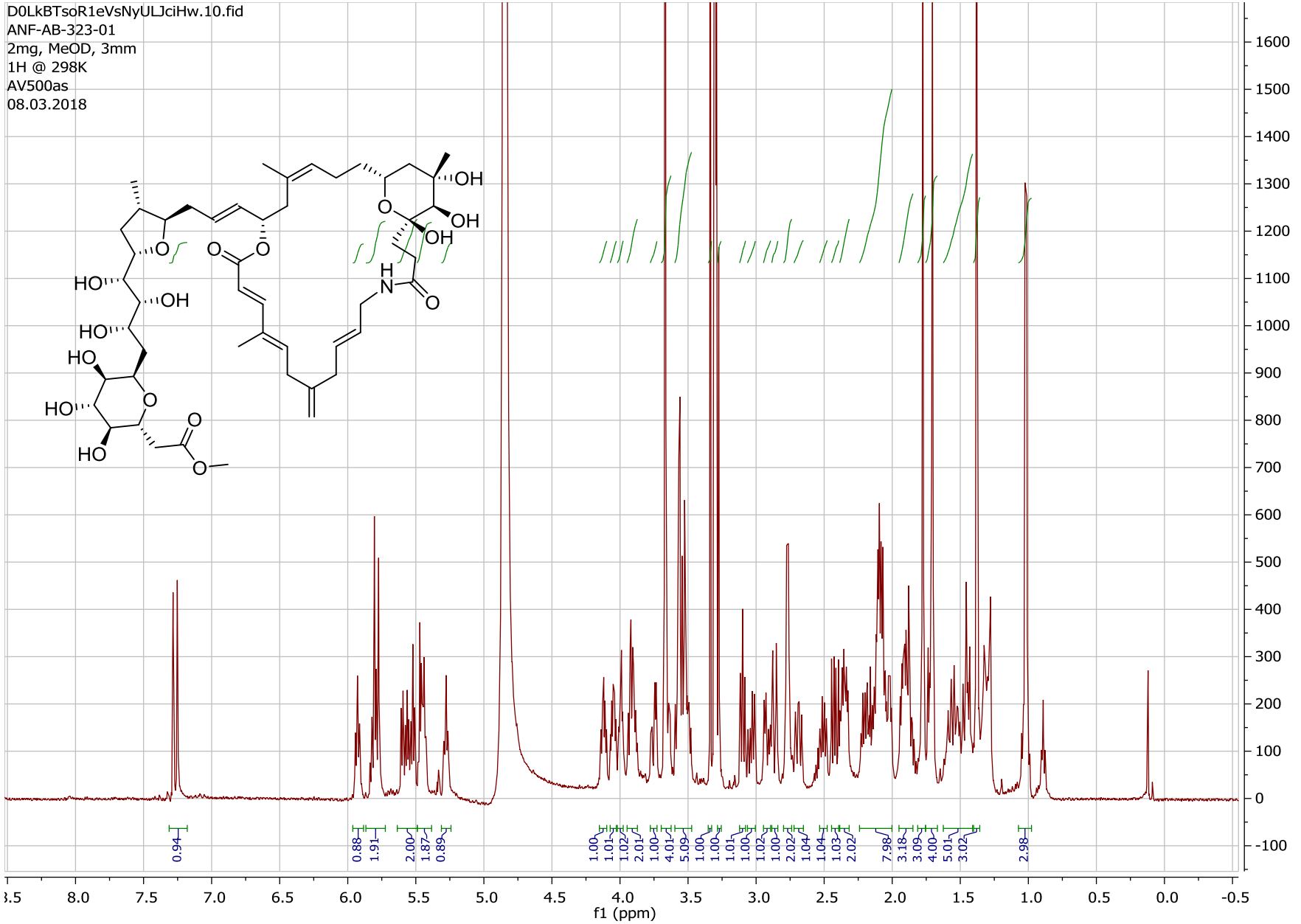

mz31033-ANF-AA-933-01-12.fid
ANF-AA-933
173.42
166.45
159.85
149.67
145.98
140.06
133.28
131.28
130.78
130.74
129.60
128.70
128.49
116.94
114.16
113.13
97.93
81.95
76.48
73.09
71.43
71.19
66.74
54.81
47.32
41.39
40.11
36.57
35.62
34.02
29.54
24.44
24.11
23.32
12.24
7.53
7.50
7.48
5.81
OSiEt3
OSiEt3
OH
O
O
O
O
O
H
N
O
f1 (ppm)

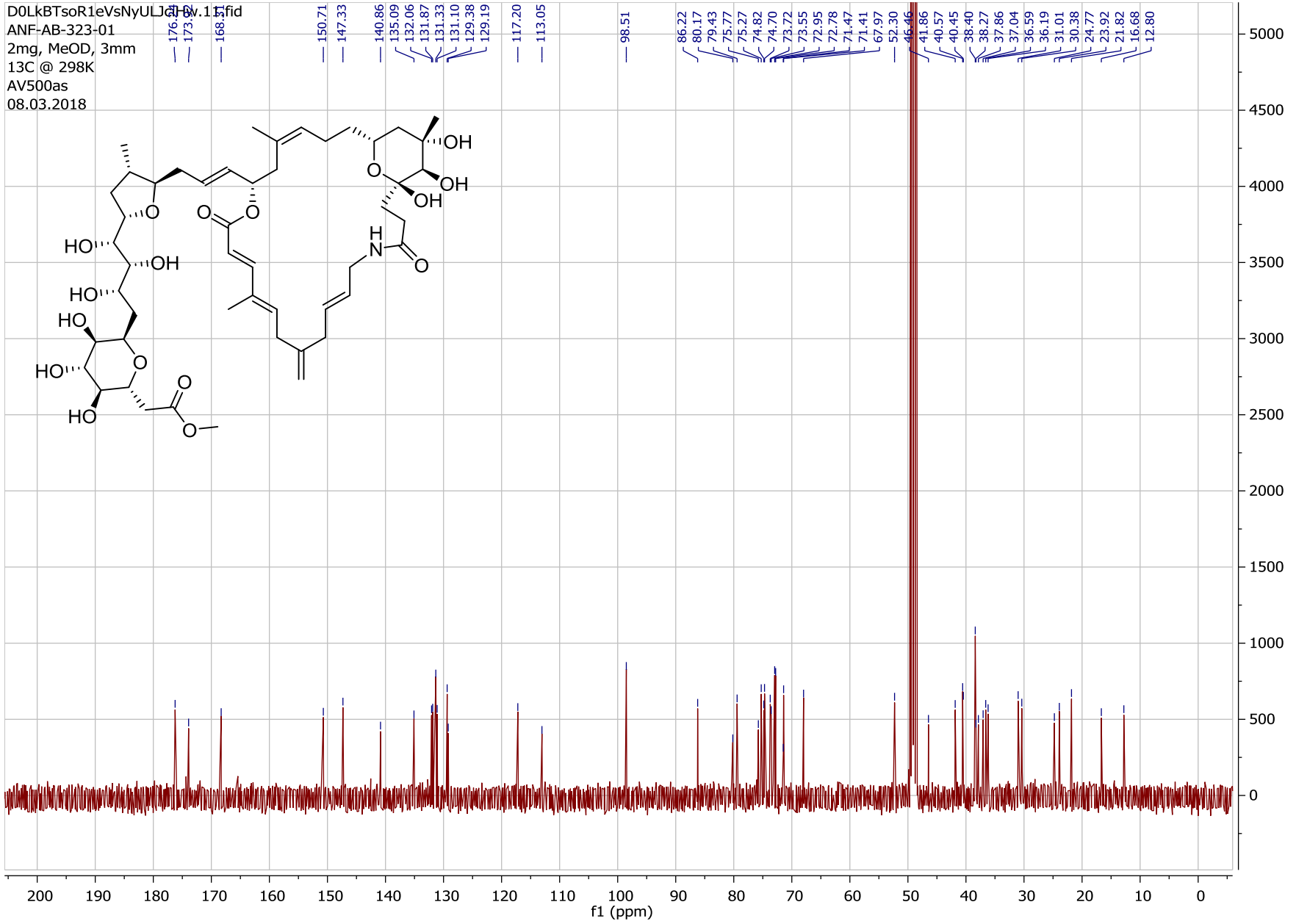

anfab10301_308K.10.fid
ANF-AB-103-01
1H @ 308K
2mg C6D6
HO
O
O
OSiEt3
O
OSiEt3
OH
H
N
O
f1 (ppm)


anfab10301_308K.11.fid
ANF-AB-103-01
13C @308K
2mg C6D6
173.71
167.14
149.86
146.00
140.21
133.21
131.34
130.83
128.65
128.35
116.81
113.30
98.14
81.84
76.39
73.82
66.83
64.47
47.43
41.43
40.27
36.90
36.62
36.03
33.59
30.22
30.20
29.75
24.46
24.25
23.27
12.17
7.51
7.48
7.46
7.44
5.82
1.42
HO
O
O
O
OSiEt3
OSiEt3
OH
H
N
O
f1 (ppm)


OTES
OTES
OH
TESO
OTES
TESO
TBSO
TBSO
TBSO
f1 (ppm)
anfab31101_cec.10.1.1r — ANF-AB-311-01 — 1H @ 296 K — AV500 CEC 3mg C6D6 — 23/02/2018


ANF-AB-311-01
3 mg C6D6 298 K
f1 (ppm)
anfab31101_cec.11.1.1r — ANF-AB-311-01 — 13Ccpd @ 296 K — AV500 CEC 3mg C6D6 — 23/02/2018


D0LkBTsoR1eVsNyULJciHw.10.fid
ANF-AB-323-01
2mg, MeOD, 3mm
1H @ 298K
AV500as
08.03.2018
f1 (ppm)


D0LkBTsoR1eVsNyULJcHw.11.fid
ANF-AB-323-01
2mg, MeOD, 3mm
13C @ 298K
AV500as
08.03.2018
176.21
173.62
168.51
150.71
147.33
140.86
135.09
132.06
131.87
131.33
131.10
129.38
129.19
117.20
113.05
98.51
86.22
80.17
79.43
75.77
75.27
74.82
74.70
73.72
73.55
72.95
72.78
71.47
71.41
67.97
52.30
46.46
41.86
40.57
40.45
38.40
38.27
37.86
37.04
36.59
36.19
31.01
30.38
24.77
23.92
21.82
16.68
12.80
OH
OH
OH
O
O
O
HO
OH
HO
HO
HO
O
HO
O
O
H
N
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)