Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplemental Information

1,2-*cis*-Selective Glucosylation Enabled by Halogenated Benzyl Protecting Groups

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GENERAL INFORMATION

All reactions were performed under N_2 atmosphere which was achieved by vacuum purge backfill three times. Dried solvents (CH_2Cl_2, CH_3CN, Et_2O, THF and DMF) were used directly from a PureSolv 400-5 solvent purification system. Dry 1,4-dioxane solvent was obtained through distillation from sodium-benzophenone ketyl. Reagents were purchased from commercial sources (Alfa Aesar, Acros Organics, Chem Impex, Matrix scientific (most *p*-substituted benzyl bromides), Sigma Aldrich, TCI). Column chromatography was performed using silica gel (60 Å) purchased from SiliCyle. Preparative TLC was performed on 60 Å silica gel with fluorescent indicator on a glass plate (Agela Technologies). Analytical TLC was performed using 60 Å silica gel with F254 indicator on aluminum sheets (Merck). Compound visualization on TLC was performed using a hand-held UV hand lamp and/or staining with anisaldehyde. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR experiments were performed using a Bruker AV-400 or a Bruker AV-500 NMR spectrometer. ^{19}F NMR spectra were calibrated with $CFCl_3$ (δ = 0.00 ppm) as internal standard. HRMS was performed using an Agilent 6210 electrospray time-of-flight mass spectrometer. Optical rotation values were obtained using a JASCO P-2000 instrument. Deuterated solvents were obtained from Cambridge Isotope Labs.

Determining Anomeric ratios.

For ^{1}H NMR of anomeric mixtures in both the crude and purified samples, the number of scans used was 16 while relaxation delays were set to 20 seconds. *Alpha:beta* ratios of glycosylation product mixtures were determined using ^{1}H NMR integration of distinct signals from both the *alpha* and *beta* products. In the case of glycosylation reactions using acceptor **12** bearing a free hydroxyl at C6 and a methyl aglycone at the reducing end, anomeric ratios were determined according to the following set of commands using the GSD algorithm (deconvolution) in MestReNova:

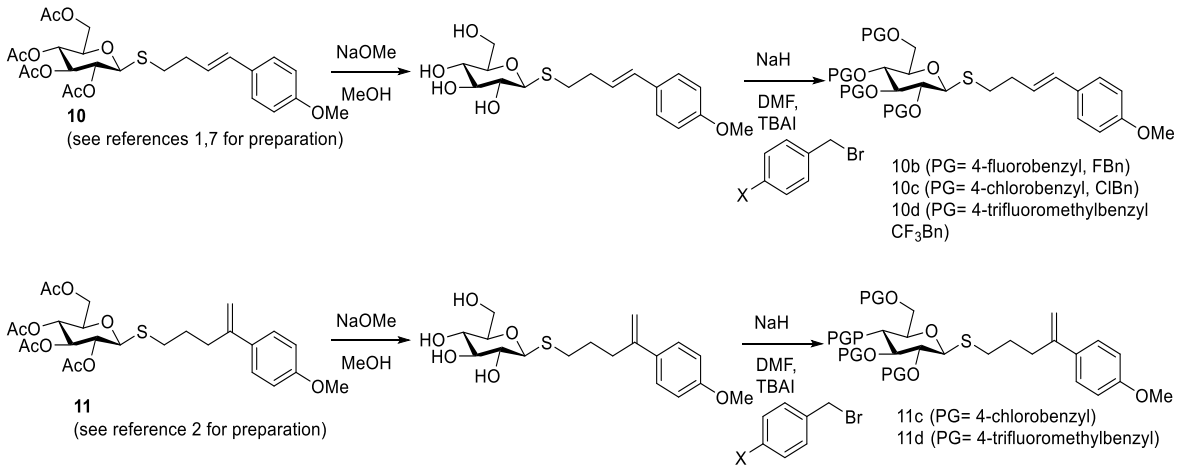
1) Phase correction- Processing> Phase correction> Automatic
2) Baseline correction- Processing> Baseline> Full auto (Bernstein polynomials)

3) Analysis > Peak picking > options = Method - GSD, Refinement level – 5 fitting, Optimized for peaks – average. Then Ok.
4) Analysis > Integration > Options = Calculation method – Sum, Source – autodetect, Algorithm- peak picking, Minimum area – 3%. Then Ok.
5) Analysis > Peak picking > Automatic
6) View > Tables > Peaks.

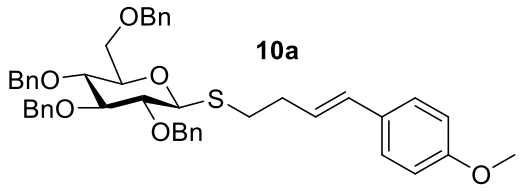
A GSD table containing all the peaks with their respective height, width and area is then generated. We analyzed reducing-end aglycone methyl signals from both the *alpha* and *beta* products which were located at 3.35-3.36 ppm for *alpha* and 3.32-3.33 ppm for *beta*. Areas of these signals were used to determine anomeric ratios in Tables 1 and 2. Anomeric ratios in Scheme 2 were determined through synthesis and chromatographic purification of *alpha* and *beta* anomers of all products and integration of key signals in the ^{1}H NMR spectrum of purified material as detailed below.

Preparation of MBTG and MPTG Donors

Synthetic scheme detailing synthesis of various MBTG/MPTG donors:



((*E*)-4-(4-methoxyphenyl)-3-butenyl β-D-1-thio-2,3,4,6-tetra-*O*-benzyl glucopyranoside) 10a[7]



10a

Compound **10a** was prepared according to a previously published procedure (see reference 7 below).

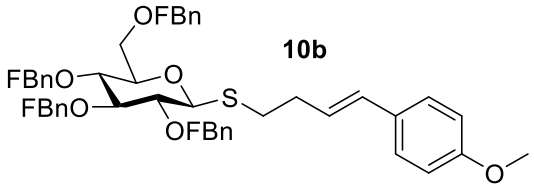
General Procedure A for preparing *p*-substituted benzyl-protected glycosyl donors.

Part 1: To 0.7 g of tetraacetate thioglycoside donor **10**[1,7] (4-(4-methoxyphenyl)-3-butenyl-1-thio-2,3,4,6-tetraacetyl-β-glucoside) or **11**[2] (4-(4-methoxyphenyl)-4-pentenyl-1-thio-2,3,4,6-tetraacetyl-β-glucoside, see synthetic scheme above) in a R.B.F was added 10.0 ml of methanol. A stir bar was added, then a catalytic amount of 5 M sodium methoxide solution was added

dropwise. The reaction was stirred for 10 min after which it was concentrated using a rotary evaporator to give a white powder that was co-evaporated with 2 ml of toluene twice.

Part 2: 50ml of DMF was then added to the aforementioned white powder (tetraol), followed by 0.5 g of tetrabutylammonium iodide (TBAI). The contents of the R.B.F were allowed to stir at 0 °C after which 8-24 equivalents of NaH was added in three portions. Ten minutes later, 8 equivalents of *p*-substituted benzyl bromide was added. The reaction was allowed to stir for 12 hrs while warming to room temperature under a nitrogen atmosphere. The reaction was then placed back into an ice bath quenched at 0°C with the dropwise addition of 10.0 ml of water. Further workup did not commence until gas evolution ceased. 100.0 ml of EtOAc was added. The reaction contents were then transferred to a 500 ml separatory funnel. 200.0 ml of water was then added, and the contents of the separatory funnel were shaken vigorously and then allowed to stand to ensure separation of the aqueous and organic layers. The organic layer was dried using Na_2SO_4 then concentrated to give a crude product which was purified using flash chromatography to give the intended tetrabenzylthioglucoside donor (**10a-d or 11c-d**).

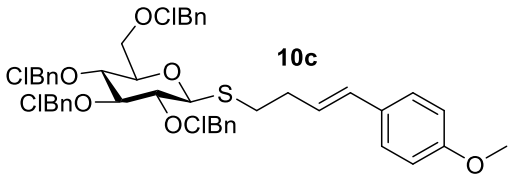
((*E*)-4-(4-methoxyphenyl)-3-butenyl *β*-D-1-thio-2,3,4,6-tetra-*O*-(4-fluoro)benzyl glucopyranoside) 10b



Prepared following the general procedure A. **Part 1**; used 0.70 g of tetraacetate thioglucoside **10**, 10 ml of methanol, and 0.4 ml of 5 M NaOMe. **Part 2**; 30 ml of DMF, 0.40 g of TBAI, 0.42 g of NaH and 1.33 ml of 4-fluorobenzyl bromide. The reaction crude product was purified by flash column chromatography (15% EOAc/hexanes) to give 0.683

g of a white solid **10b** (65% yield). **1H NMR (400 MHz, $CDCl_3$) δ** 7.35-7.16 (m, 8H), 7.13-7.05 (m, 2H), 7.03-6.91 (m, 8H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.08 (dt, *J* = 15.6 Hz, 6.9 Hz, 1H), 4.90-4.74 (m, 3H), 4.71 (d, *J* = 7.4 Hz, 1H), 4.65 (d, *J* = 10.2 Hz 1H), 4.59-4.44 (m, 4H), 3.80 (s, 3H), 3.73-3.52 (m, 4H), 3.46-3.37 (m, 2H), 4.94-4.78 (m, 2H), 2.55 (q, *J* = 7.2 Hz, 2H) **^{13}C NMR (100 MHz, $CDCl_3$) δ** 163.69, 163.61, 163.54, 161.11, 158.97, 134.24, 133.78, 133.70, 130.88, 130.11, 130.08, 130.00, 129.58, 129.53, 129.50, 129.45, 129.30, 129.22, 127.20, 125.98, 115.44-115.10 (m), 113.98, 86.41, 85.29, 81.69, 79.02, 77.82, 74.90, 74.73, 74.21, 72.80, 68.95, 55.31, 33.54, 30.93; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -114.74 – -114.88 (m, 2F), -115.07 (m, 1F), -115.22 (m, 1F). **HRMS (m/z):** Calcd for $C_{45}H_{44}F_4O_6SK$ 827.2432 found 827.2397. **$[\alpha]_D^{25}$ =** +2.3° (c = 1, DCM). **IR (cm^{-1})** 3038, 2916, 2859, 1604, 1509, 1246, 1221, 1067, 823 (*p*-disubstituted benzene), 767, 501

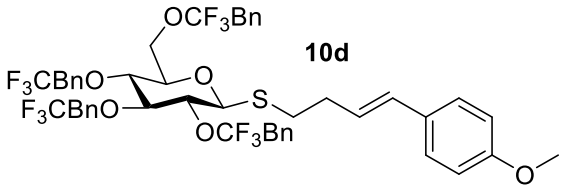
((*E*)-4-(4-methoxyphenyl)-3-butenyl β-D-1-thio-2,3,4,6-tetra-*O*-(4-chloro)benzyl glucopyranoside) 10c



Prepared following the general procedure A. **Part 1**; used 0.69 g of tetraacetate thioglucoside **10** (1.3 mmol), 10 ml of methanol, and 0.4 ml of 5 M NaOMe. **Part 2**; 20 ml of DMF, 0.20 g of TBAI, 0.42 g of NaH and 2.16 g of 4-chlorobenzyl bromide. The reaction crude product was purified by flash column chromatography (15% EOAc/hexanes) to give 0.8180 g of a white product **10c** (74% yield). **1H NMR (400 MHz, $CDCl_3$) δ** 7.31-7.18 (m, 14H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.8 Hz, 6.9 Hz, 1H), 4.86 (d, *J* = 10.6 Hz, 1H), 4.82-4.41 (m, 8H), 3.79 (s, 3H), 3.73-3.51 (m, 4H), 3.46-3.36 (m, 2H),

2.91-2.76 (m, 2H), 2.54 (q, *J* = 7.2 Hz, 2H)); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.99, 136.84, 136.55, 135.41, 136.33, 133.67, 133.63, 133.45, 130.93, 130.08, 129.48, 129.24, 129.04, 128.98, 128.77, 128.61, 128.57, 127.22, 125.91, 114.01, 86.42, 85.23, 81.75, 78.96, 77.85, 74.75, 74.60, 74.09, 72.71, 68.99, 55.31, 33.48, 30.92; **HRMS (m/z):** Calcd for $C_{45}H_{44,}Cl_4O_6SK$ 891.1250 found 891.1225. **$[\alpha]_D^{23}$ =** +13.3° (c = 1, DCM). **IR (cm^{-1})** 3029, 2913, 2859, 1602, 1510, 1491, 1246, 1086, 1015, 841, 806 (*p*-disubstituted benzene), 483.

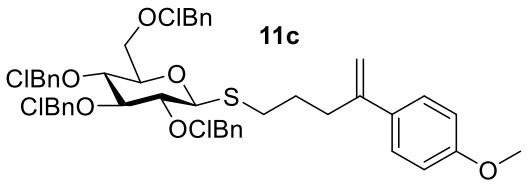
((*E*)-4-(4-methoxyphenyl)-3-butenyl β-D-1-thio-2,3,4,6-tetra-*O*-(4-trifluoromethyl)benzyl glucopyranoside) 10d



Prepared following the general procedure A. **Part 1**; used 0.71 g of tetraacetate thioglucoside **10,** 10.0 ml methanol, and 0.4ml of 5 M NaOMe. **Part 2**; used 20ml of DMF, 0.40g of TBAI, 0.42 g of NaH and 2.59 g of 4-trifluoromethylbenzyl bromide. The reaction crude product was purified by flash column chromatography (20% EOAc/hexanes) to give 1.01g of a white compound **10d** (76% yield). **1H NMR (400 MHz, $CDCl_3$) δ** 7.59-7.19 (m, 18H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8 Hz, 6.9 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 4.89 (d, *J* = 12.1 Hz, 1H), 4.85-4.77 (m, 2H), 4.73-4.56 (m, 4H), 4.52 (d, *J* = 9.6 Hz, 1H), 3.79 (s, 3H), 3.77-3.73 (m, 2H), 3.70-3.63 (m, 2H), 3.54-3.43 (m, 2H), 2.89 (m, 2H), 2.57 (dq, *J* = 7.2 Hz, 1.3 Hz, 2H) **^{13}C NMR** (**100 MHz, $CDCl_3$) δ** 159.06, 142.28, 142.16, 141.94, 141.79, 131.06, 130.22, 130.14, 130.02, 129.82, 129.71, 127.96, 127.58, 127.39, 127.22, 127.19, 125.76, 125.60-125.16 (m), 122.78, 122.71, 114.00, 86.61, 85.24, 82.00, 78.93, 78.05, 74.67, 74.55, 74.02, 72.73, 69.23,

55.25, 55.21, 33.41, 30.98; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.06 (s, 3F), -63.13 (s, 3F), -63.15 (s, 3F), -63.18 (s, 3F). **HRMS (m/z):** Calcd for $C_{49}H_{44,}F_{12}O_6SH$ 989.2745 found 989.2710. **$[\alpha]_D^{25}$ =** +4.5° (c = 1, DCM). **IR (cm^{-1})** 2914, 1511, 1324, 1248, 1161, 1120, 1065, 1018, 967, 822 (*p*-disubstituted benzene), 592.

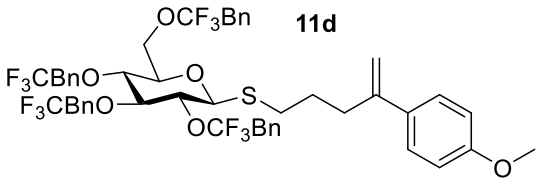
4-(4-methoxyphenyl)pent-4-enyl-2,3,4,6-tetra-*O*-(4-chlorobenzyl)-1-thio-β-D-glucopyranoside 11c



11c

Prepared following the general procedure A. **Part 1**; used 0.81 g of tetraacetate thioglucoside **11** 15.0 ml of MeOH, and 0.5 ml of 5 M NaOMe. **Part 2**; used 50 ml of DMF, 0.60 g of TBAI, 0.48 g of NaH, and 2.47 g of 4-chlorobenzyl bromide. The reaction crude product was purified by flash column chromatography (20% EOAc/hexanes) to give 0.80 g of a white compound **11c** (61% yield). **1H NMR (400 MHz, $CDCl_3$) δ** 7.34-7.19 (m, 14H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H) 6.83 (d, *J* = 8.8 Hz, 2H), 5.21 (d, *J* = 1.4 Hz, 1H), 4.98 (d, *J* = 1.4 Hz, 1H), 4.85 (d, *J* = 10.6 Hz, 1H), 4.81-4.58 (m, 4H), 4.56-4.41 (m, 3H), 4.35 (d, *J* = 9.8 Hz, 1H), 3.78 (s, 3H), 3.62(d, *J* = 3.2 Hz, 2H), 3.58-3.52 (m, 2H), 3.39-3.31 (m, 2H), 2.81-2.63 (m, 2H), 2.62-2.55 (m, 2H), 1.82 (m, 2H) **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.12, 146.59, 136.85, 136.59, 136.44, 136.36, 133.67, 133.62, 133.46, 133.44, 133.16, 129.47, 129.05, 128.97, 128.76,128.61, 128.60, 128.57, 128.55, 127.20, 113.72, 111.41, 86.43, 85.33, 81.70, 78.91, 77.79, 74.74, 74.59, 74.07, 72.67, 68.85, 55.29, 34.25, 30.48, 28.33; **HRMS (m/z):** Calcd for $C_{46}H_{46}Cl_4O_6SH$ 867.1847 found 867.1778. **$[\alpha]_D^{25}$ =** +14.6° (c = 1, DCM). **IR (cm^{-1})** 3053, 2912, 1602, 1264, 1086, 1015, 809 (*p*-disubstituted benzene), 734, 704.

4-(4-methoxyphenyl)pent-4-enyl-2,3,4,6-tetra-*O*-(4-trifluoromethyl)benzyl-1-thio-β-D-glucopyranoside 11d



Prepared following the general procedure A. **Part 1**; used 1.97 g of tetraacetate thioglucoside **11**, 20.0 ml of methanol, and 0.5 ml of 5 M NaOMe. **Part 2**; 70 ml of DMF, 1.17 g of TBAI, 7.00 g of NaH, and 7.19 g of 4-trifluormethylbenzyl bromide. The reaction crude product was purified by flash column chromatography (15% EOAc/hexanes) to give 2.82 g of a white compound **11d** (77% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59-7.19 (m, 18H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.22 (d, *J* = 1.5 Hz, 1H), 5.00-4.95 (m, 2H), 4.90-4.76 (m, 3H), 4.73-4.60 (m, 3H), 4.54 (d, *J* = 12.7 Hz, 1H), 4.40 (d, *J* = 9.8 Hz, 1H), 3.77 (s, 3H), 3.72-3.59 (m, 4H), 3.42 (m, 2H), 2.84-2.67 (m, 2H), 2.60 (m, 2H), 1.89-1.78 (m, 2H) **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.17, 146.57, 142.29, 142.19, 141.96, 141.83, 133.15, 130.15, 130.03, 129.83, 129.71, 127.96, 127.92, 127.58, 127.37, 127.20, 126.63, 125.60-125.19 (m), 122.84-122.64 (m), 113.71, 111.41, 86.60, 85.42, 81.96, 78.87, 77.98, 74.65, 74.51, 73.98, 72.69, 69.10, 55.23, 34.22, 30.56, 28.38; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.06 (s, 3F), -63.14 (s, 3F), -63.15 (s, 3F), -63.19 (s, 3F). **HRMS (m/z):** Calcd for $C_{50}H_{46}F_{12}O_6SH$ 1003.2902 found 1003.2870. **$[\alpha]_D^{25}$ =** +7.9° (c = 1, DCM). **IR (cm^{-1})** 3054, 1325, 1264, 1164, 1165, 822 (*p*-disubstituted benzene), 734, 705.

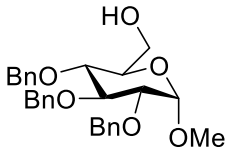
General glycosylation procedure B

To an oven dried 4 ml Wheaton vial with a stir bar, 1 equivalent of a hydroxyl bearing acceptor was added (0.075 mmol), followed by 2 equivalents of tetra-(4-X-benzyl) thioglucoside donor

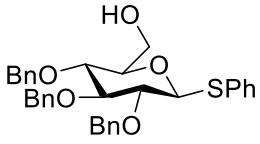
(0.15 mmol X = H,F,Cl or CF_3). Y ml (Y = 1 ml,2.5 ml or 5 ml) of solvent (DCM or 1,4-dioxane) was added. The vial was capped with a septum then flushed with nitrogen gas. TfOH (10 mol% when using DCM and 40 mol% when using 1,4-dioxane) was added dropwise and magnetic stirring commenced. The reaction was monitored by TLC. Once all of the donor was consumed the reaction was quenched with 0.05 ml of Et_3N. The contents were then transferred to a R.B.F, and 2-3 g of silica gel were added, adsorption onto silica occurred by evaporating solvents under low vacuum. Products were purified by flash chromatography (12%-32% EtOAc/Hexanes). In some cases, a premix of (3:1 DCM/EtOAc) was made (referred to herein as DE). Thus, 12%-48% DE/hexanes solvent system was especially important in separating anomers.

Various acceptors used in the substrate scope study:

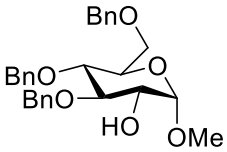
Acceptors utilized herein as well as references for their preparation are provided in the scheme below:



12
(synthesized according to reference 8)



16cc
(synthesized according to reference 11)



17cc
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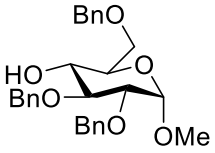

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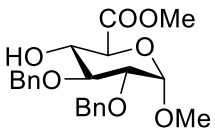

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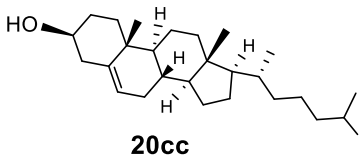
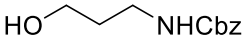


20cc
(purchased from Sigma-Aldrich)

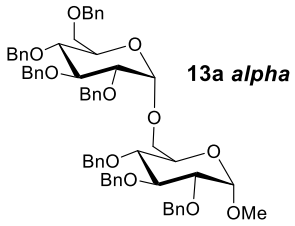


21cc
(synthesized according to reference 12)

Glycosylation using glycosyl acceptor 12

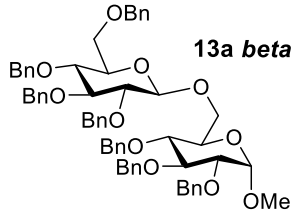
Several glycosylation reactions were performed using glycosyl acceptor **12**. The general procedure B or slight modification thereof (apparent through study of Table 1 in the manuscript) was used. Reaction conditions, yields, and selectivity achieved can be found in Table 1. Below are characterization details of new compounds. ^{1}H NMR data for both anomers of compound **13a** (Table 1, entry 1) matched literature values.[5,6] Tabulated ^{1}H NMR data for both anomers of **13a** from reference 5 is provided below.

Methyl (2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranoside



13a *alpha*

^{1}H NMR data for *alpha* anomer 13a *alpha*:[5] (300 MHz, CDCl3) δ 7.37 – 7.09 (m, 35H), 4.98 – 4.92 (m, 4H), 4.84 – 4.55 (m, 10H), 4.43 (t, *J* = 11.9 Hz, 1H), 4.00 (d, *J* = 8.7 Hz, 1H), 3.94 (d, *J* = 9.2 Hz, 1H), 3.85 – 3.62 (m, 7H), 3.59 – 3.52 (m, 2H), 3.44 (dd, *J* = 9.6, 3.8 Hz, 1H), 3.35 (s, 3H).

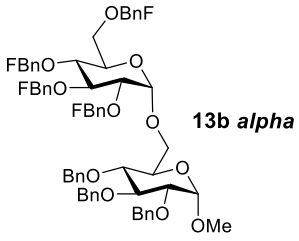


13a *beta*

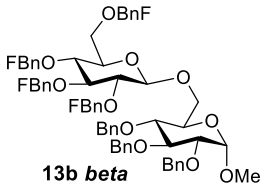
^{1}H NMR data for *beta* anomer 13a *beta*:[5] (300 MHz, CDCl3) δ 7.37 – 7.14 (m, 35H), 4.97 (dd, *J* = 11.3, 2.9 Hz, 1H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 2H), 4.73 (d, *J* = 3.2 Hz, 1H), 4.68 (d, *J* = 9.2 Hz, 1H), 4.62 – 4.49 (m,

3H), 4.56 (d, *J* = 7.5 Hz, 2H), 4.35 (d, *J* = 7.7 Hz, 1H), 4.18 (dd, *J* = 10.7, 1.9 Hz, 1H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.74 – 3.38 (m, 9H), 3.32 (s, 3H).

Methyl (2,3,4,6-tetra-*O*-(4-fluorobenzyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranoside



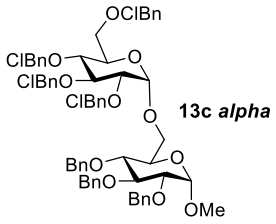
Data for *alpha* anomer 13b *alpha*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-6.88 (m, 31H), 4.99-4.91 (m, 3H), 4.82 (t, *J* = 10.8 Hz, 2H), 4.75-4.51 (m, 9H), 4.37 (t, *J* = 11.3 Hz, 2H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.91-3.82 (m, 2H), 3.78-3.63 (m, 4H), 3.60-3.46 (m, 4H), 3.42 (dd, *J* = 9.6 Hz, 3.6Hz, 1H), 3.35 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.33, 163.29, 163.23, 161.38, 161.33, 161.28, 138.69, 138.40, 138.10, 134.51, 134.49, 134.13, 134.11, 134.04, 134.01, 133.64, 133.62, 129.62, 129.56, 129.50, 129.36, 129.30, 129.20, 129.13, 129.04, 128.45, 128.43, 128.39, 128.23, 128.07, 127.98, 127.93, 127.69, 127.66, 115.34, 115.30, 115.24, 115.17, 115.13, 115.07, 98.05, 97.05, 82.12, 81.45, 80.09, 79.93, 77.68, 77.48, 75.83, 74.95, 74.67, 74.06, 73.39, 72.70, 71.55, 70.36, 70.17,68.33, 68.99, 65.99, 55.19; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -115.21 (m, 2F), -115.31 (m, 1F), -115.47 (m, 1F). **HRMS (m/z):** Calcd for $C_{62}H_{62,}F_4O_{11}K$ 1097.3865 found 1097.3890. **$[\alpha]_D^{25}$ = +**15.1° (c = 1, DCM). **IR (cm^{-1})** 3034, 2920, 1603, 1509, 1262, 1222, 1136, 1072, 1049, 1026, 1015**,** 822 (*p*-disubstituted benzene), 735, 698.



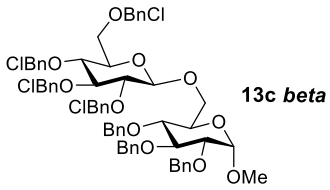
13b *beta*

Data for *beta* anomer 13b *beta*: 1H NMR (400 MHz, $CDCl_3$) δ 7.36-6.93 (m, 29H), 6.87-6.84 (t, *J* =8.6 Hz, 2H), 4.97 (d, *J* =10.8 Hz, 1H), 4.91 (d, *J* =11.2 Hz, 1H), 4.81-4.61 (m, 8H), 4.59 (d, *J* =3.5 Hz, 1H,) 4.56-4.45 (m, 4H), 4.31 (d, *J* =7.7 Hz, 1H), 4.16 (d, *J* =10.9 Hz, 1H), 4.00 (t, *J* =9.2 Hz, 1H), 3.84-3.81 (m, 1H), 3.67-3.62 (m, 3H), 3.57-3.48 (m, 4H), 3.46-3.35 (m, 2H), 3.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.35, 163.29, 163.27, 163.23, 161.39, 161.33, 161.31, 161.28, 138.71, 138.27, 138.09, 134.25, 134.23, 134.06, 134.04, 133.87, 133.85, 133.82, 129.61, 129.55, 129.52, 129.45, 129.44, 129.37, 129.30, 128.49, 128.42, 128.40, 128.16, 128.03, 129.99, 127.68, 127.63, 115.36, 115.32, 115.30, 115.29,119.19, 115.15, 115.13, 115.12, 103.79, 98.10, 84.53, 81.94, 81.85,79.82, 78.02, 77.76, 75.79, 74.94, 74.89, 74.84, 74.16, 74.05, 73.38, 72.73, 69.83, 68.76, 68.70, 55.24; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -114.98 (m, 1F), -115.27 (m, 2F), -115.39 (m, 1F). **HRMS (m/z):** Calcd for $C_{62}H_{62,}F_4O_{11}K$ 1097.3865 found 1097.3882. **$[\alpha]_D^{25}$ = +**25.1° (c = 1, DCM). **IR (cm^{-1})** 3055, 2918, 2850, 1510, 1260, 1223, 1067, 1013, 793 (*p*-disubstituted benzene), 736, 700, 459.

Methyl (2,3,4,6-tetra-*O*-(4-chlorobenzyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranoside



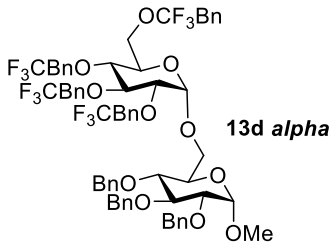
Data for *alpha* anomer 13c *alpha*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.13 (m, 29H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.99-4.91 (m, 3H), 4.80 (dd, *J* = 11.1 Hz, 6.5 Hz, 2H), 4.73-4.5 (m, 9H), 4.36 (t, *J* =11.1 Hz, 2H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.89-3.82 (m, 3H), 3.77-3.63 (m, 4H), 3.59-3.44 (m, 4H), 3.38 (dd, *J* = 9.6 Hz, 3.6Hz, 1H), 3.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.68, 138.40, 138.10, 137.12, 136.75, 136.71, 136.32, 133.55, 133.44, 133.37, 133.32, 129.16, 129.04, 128.87, 128.66, 128.58, 128.54, 128.47, 128.45, 128.41, 128.10, 127.97, 127.92, 127.71, 127.69, 127.71, 127.69, 127.65, 98.06, 97.01, 82.10, 81.46, 80.10, 79.99, 77.62, 77.51, 75.84, 74.94, 74.52, 73.94, 73.40, 72.63, 71.45, 70.45, 70.36, 70.13, 68.37, 65.96, 55.19; **HRMS (m/z):** Calcd for $C_{62}H_{62,}Cl_4O_{11}K$ 1161.2683, found 1161.2683. **$[\alpha]_D^{25}$** = +22.4° (c = 1, DCM). **IR (cm^{-1})** 2921, 1491, 1359, 1264, 1058, 1014, 806 (*p*-disubstituted benzene), 734, 699.



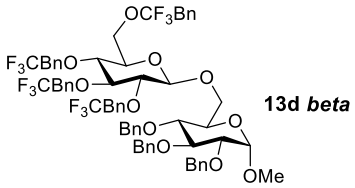
Data for 13c *beta*: 1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.02 (m, 31H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.90 (d, *J* = 11.4 Hz 1H), 4.80-4.73 (m, 4H), 4.69-4.44 (m, 9H), 4.30 (d, *J* = 7.7 Hz, 1H), 4.13-4.09 (m, 1H), 3.99 (t, *J* = 9.2 Hz, 1H) 3.84-3.80 (m, 1H), 3.67-3.64 (m, 3H), 3.55-3.45 (m, 4H), 3.43-3.35 (m, 2H), 3.32 (s, 3H); **^{13}C NMR** (125 M Hz, $CDCl_3$) δ 138.69, 138.25, 138.08, 136.84, 136.66, 136.57, 136.47, 133.59, 133.42, 133.40, 133.38, 129.11, 128.95, 128.93, 128.84, 128.57, 128.53, 128.52, 128.49, 128.44, 128.40, 128.15, 128.04, 127.99, 127.69, 127.63, 103.75, 98.11, 84.52, 81.93, 81.84, 79.82, 78.00, 77.78, 75.80, 74.87, 74.70, 74.05, 73.91, 73.39, 72.63, 69.82, 68.77,

68.70, 55.27; **HRMS (m/z):** Calcd for $C_{62}H_{62,}Cl_4O_{11}K$ 1161.2683 found 1161.2689. **$[\alpha]_D^{25}$ =** +50.2° (c = 1, DCM). **IR (cm^{-1})** 3030, 2911, 1491, 1357, 1066, 1014, 804 (*p*-disubstituted benzene), 736, 696.

Methyl (2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranoside



Data for *alpha* anomer 13d *alpha*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.25 (m, 29H), 7.17 (d, *J* =8.0 Hz, 2H), 5.05 (d, *J* =3.5 Hz, 1H) 4.98-4.89 (m, 3H), 4.81-4.65 (m, 6H), 4.62-4.43 (m, 6H), 4.00 (t, *J* =9.1 Hz, 1H), 3.95-3.86 (m, 2H), 3.80-3.76 (m, 2H), 3.72-3.67 (m, 2H), 3.66-3.50 (m, 4H), 3.39 (dd, *J* = 9.6 Hz, 3.6 Hz, 1H), 3.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.77, 142.39, 142.33, 142.08, 138.78, 138.59, 138.23, 132.20, 130.29, 130.17, 130.07, 130.01, 129.91, 129.81, 128.66, 128.64, 128.60, 128.32, 128.12, 127.97, 127.91, 127.86, 127.77, 127.72, 127.62, 127.51, 127.29, 125.61, 125.58, 125.54, 125.51, 125.48, 125.46, 125.45, 125.43, 125.42, 125.34, 125.31, 123.18, 114.53, 98.31, 97.13, 82.29, 81.94, 80.47, 80.33, 77.90, 77.77, 76.10, 75.13, 74.68, 74.11, 73.59, 72.85, 71.65, 70.52, 70.31, 68.91, 66.25, 55.40; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.08 (s, 3F), -63.21(s, 3F), -63.22 (s, 3F), -63.26 (s, 3F). **HRMS (m/z):** Calcd for $C_{66}H_{62,}F_{12}O_{11}K$ 1297.3738 found 1297.3758. **$[\alpha]_D^{25}$ =** +11.5° (c = 1, DCM). **IR (cm^{-1})** 3055, 2926, 1325, 1264, 1163, 1123, 1065, 1017, 822 (*p*-disubstituted benzene), 734, 702.

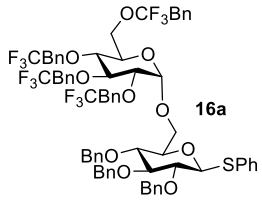


Data for *beta* anomer 13d *beta*: 1H NMR (400 MHz, CDCl3) δ 7.60-7.14 (m, 31H), 5.02 (d, *J* =12.0 Hz, 1H), 4.96 (d, *J* =10.8 Hz, 1H), 4.91-4.56 (m, 12H), 4.51 (dd, 12.3 Hz, 6.4 Hz, 2H), 4.36 (d, *J* =7.7 Hz, 1H), 4.16 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 4.00 (t, *J* =9.2 Hz, 1H), 3.86-3.81 (m, 1H), 3.73-3.66 (m, 3H), 3.62-3.55 (m, 2H), 3.51-3.38 (m, 4H), 3.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.46, 142.34, 142.25, 142.14, 138.79, 138.38, 138.24, 130.42-129.83 (m), 128.68, 128.62, 128.59, 128.33, 128.24, 128.19, 127.93, 127.90, 127.84, 127.72, 127.67, 127.56, 127.52, 127.47, 127.45, 125.65-125.4 (m), 123.17, 103.92, 98.34, 84.90, 82.19, 82.10, 80.02, 78.22, 78.16, 76.03, 75.06, 74.99, 74.83, 74.18, 74.02, 73.58, 72.83, 69.99, 69.19, 68.99, 55.43; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.11 (s, 3F), -63.15 (s, 3F), -63.26 (s, 3F), -63.28 (s, 3F). **HRMS (m/z):** Calcd for $C_{66}H_{62,}F_{12}O_{11}K$ 1297.3738 found 1297.3772. **$[\alpha]_D^{25}$ =** -0.6° (c = 1, DCM). **IR (cm^{-1})** 3063, 2917, 1620, 1324, 1264, 1162, 1121, 1065, 1017, 912, 821 (*p*-disubstituted benzene), 736, 670.

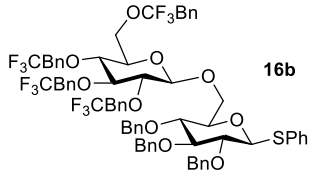
Glycosylation using 16cc as the acceptor

Following the general procedure B, 5.0 ml of 1,4-dioxane used, 154.9 mg (0.1544 mmol) of donor **11d**, 42.2 mg (0.0778 mmol) of alcohol **16cc** and 5.0 µL (0.057 mmol) of TfOH were used. Purified by flash column chromatography (12-28% DE/hexanes) to give 103.2 mg of a colorless oil **16**, yield 99%, *alpha*:*beta* ratio 7.2:1

Phenylthio-(2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (16)



Data for *alpha* anomer 16a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.16 (m, 36H), 5.16 (d, *J*= 3.5 Hz, 1H), 4.98(d, J = 4.2Hz, 1H), 4.94-4.89(m, 2H), 4.86(d, J = 10.9 Hz, 1H), 4.84-4.76(m, 3H), 4.72-4.61(m, 5H), 4.58-4.51(m, 2H), 4.48(d, J = 12.7 Hz, 1H), 3.97(t, J = 9.2 Hz, 1H), 3.93-3.79(m, 3H), 3.74-3.55(m, 6H), 3.47(m, 1H). 3.09(t, J= 8.6Hz, 1H), **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.63, 142.22, 141.92, 138.31, 138.15, 137.87, 136.87, 134.20, 131.55, 130.31-129.44(m), 129.02, 128.47, 128.44, 128.38, 128.04, 127.85, 127.74, 127.73, 127.65, 127.44, 127.34, 127.22, 127.08, 125.52-125.10(m), 97.09, 88.21, 86.55, 81.80, 81.15, 80.39, 78.77, 77.77, 75.79, 75.41, 74.94, 74.58, 73.90, 72.64, 71.29, 70.10, 68.84, 66.09, **^{19}F NMR (471 MHz, $CDCl_3$) δ** -62.94 (s, 3F), -63.09 (s, 3F), -63.11 (s, 3F), -63.15 (s, 3F). **HRMS (m/z):** Calcd for $C_{71}H_{64,}F_{12}O_{10}SNa$ 1359.3921 found 1359.3868. **$[\alpha]_D^{25}$ =** -49.5 (c = 0.5, DCM). **IR (cm^{-1})** 3032, 2922, 2185, 1741, 1620, 1326, 1261, 1162, 1122, 1066, 1018, 821 (*p*-disubstituted benzene), 745, 698, 643.



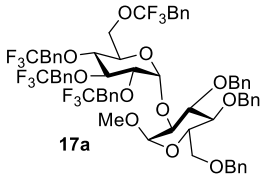
Data for *beta* anomer 16b: ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.64-7.19 (m, 36H), 5.02 (d, *J* = 12.3 Hz, 1H), 4.96-4.90 (m, 3H), 4.87-4.54 (m, 11H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.21 (d, *J* = 11.0 Hz, 1H), 3.83-3.42(m, 11H) **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.36, 142.20, 142.09, 142.02, 138.22, 137.91, 134.13, 131.05, 130.26-129.45(m), 128.91, 128.49, 128.46, 128.44, 128.42, 128.15,

128.01, 127.97, 127.90, 127.87, 127.82, 127.80, 127.75, 127.72, 127.58, 127.57, 127.32, 127.30, 127.17, 125.40-125.08(m), 123.02, 122.95, 103.66, 87.33, 86.67, 84.61, 82.14, 80.88, 78.73, 78.05, 77.96, 75.83, 75.45, 74.92, 74.72, 74.60, 73.96, 73.69, 72.82, 69.05, 68.87; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.03 (s, 6F), -63.14 (s, 3F), -63.16 (s, 3F). **HRMS (m/z):** Calcd for $C_{71}H_{64}F_{12}O_{10}SNa$ 1359.3926 found 1359.3930. **$[\alpha]_D^{25}$ =** -61.6 (c = 1, DCM). **IR (cm^{-1})** 3033, 2869, 1621, 1326, 1210, 1162, 1122, 1066, 1019, 823 (*p*-disubstituted benzene), 739, 698.

Glycosylation using acceptor 17cc

Following the general procedure B, 5.0 ml of 1,4-dioxane, 158.6 mg (0.1581 mmol) of donor **11d**, 36.6 mg (0.0788 mmol) of acceptor **17cc**, and 5.0 µL (0.057 mmol) of TfOH were used. Purified by flash column chromatography (12-24% EtOAc/hexanes) to give 86.3 mg of a colorless oil **17** (87%) yield, *alpha*:*beta* ratio 5.6:1.

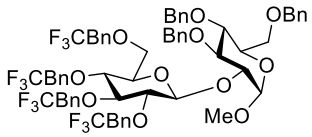
Methyl (2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-D-glucopyranoside) (17)



17a

Data for *alpha* anomer 17a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.07 (m, 31H), 5.09 (d, *J* = 3.6 Hz, 1H), 4.98-4.95 (m, 2H), 4.91 (d, *J* = 10.7 Hz, 1H), 4.84-4.69 (m, 6H), 4.61 (m, 2H), 4.50 (m, 3H), 4.39 (d, *J* = 12.7 Hz, 1H), 4.08-4.01 (m, 3H), 3.89 (dd, *J* = 9.8 Hz, 3.4 Hz, 1H), 3.80-3.74 (m, 2H), 3.70-3.64 (m, 3H), 3.59 (dd, *J* = 9.5 Hz, 3.6 Hz, 1H), 3.50 (d, *J* = 2.4 Hz, 2H), 3.41 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.51, 142.30, 142.11, 141.86, 138.25, 138.12, 137.83, 130.30-129.62(m), 128.43, 128.40, 128.31, 128.26, 127.97, 127.89, 127.83, 127.80, 127.76, 127.73, 127.69, 127.57, 127.48, 127.05, 125.43-125.12 (m), 123.01, 122.98, 122.96, 96.27, 93.41, 81.98,

80.69, 79.53, 77.93, 77.64, 75.94, 75.05, 74.71, 74.55, 73.88, 73.60, 72.61, 71.53, 70.26, 69.98, 68.37, 54.87; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.12 (s, 3F), -63.15 (s, 3F), -63.17 (s, 3F), -63.18 (s, 3F). **HRMS (m/z):** Calcd for $C_{66}H_{62,}F_{12}O_{11}K$ 1297.3738 found 1297.3714. **$[\alpha]_D^{25}$ =** +45.2° (c = 1, DCM). **IR (cm^{-1})** 3032, 2914, 1324,1162, 1120,1064, 1018, 851, 822 (*p*-disubstituted benzene), 736, 699.



17b

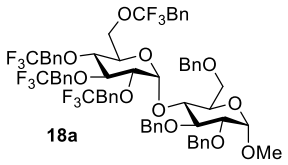
Data for *beta* anomer 17b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d*, J* = 8.0 Hz, 2H), 7.51-7.13 (m, 27H), 7.06 (m, 2H), 5.03 (d, *J* = 12.3 Hz, 1H), 4.95 (d, *J* = 3.5 Hz, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.78-4.44 (m, 13H), 4.02 (t, *J* = 9.8 Hz, 1H), 3.85 (dd, *J* = 9.8 Hz, 3.5 Hz, 1H), 3.82-3.65 (m, 6H), 3.64-3.57 (m, 2H), 3.51 (t, *J* = 8.1 Hz, 1H), 3.44 (m, 1H), 3.40 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.25, 142.11, 141.92, 141.88, 138.39, 138.00, 137.83, 130.12-129.36(m), 128.42, 128.37, 128.26, 127.99, 127.79, 127.77 127.74, 127.66, 127.56, 127.46, 127.36, 127.30, 127.22, 125.44-125.00(m), 122.99, 104.05, 99.66, 84.78, 81.96, 81.57, 78.93, 78.31, 77.91, 75.08, 75.02, 74.55, 74.53, 73.96, 73.66, 73.60, 72.79, 70.03, 69.11, 68.42, 55.12; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.13 (s, 3F), -63.17 (s, 3F), -63.22 (s, 3F), -63.24 (s, 3F). **HRMS (m/z):** Calcd for $C_{66}H_{62,}F_{12}O_{11}K$ 1297.3738 found 1297.3718. **$[\alpha]_D^{25}$ =** +27.2° (c = 1, DCM). **IR (cm^{-1})** 3054, 2927, 1325, 1264, 1165, 1018, 895, 823 (*p*-disubstituted benzene), 734, 703.

Glycosylation using acceptor **18cc**

Following the general procedure B, 5.0 ml of 1,4-dioxane, 182.7 mg of thioglucoside donor **11d** (0.1822 mmol), 35.8 mg (0.0771 mmol) of acceptor **18cc** and 5.0 µL of TfOH (0.057 mmol) were

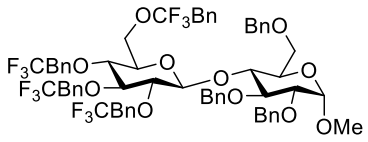
used. Purified by flash column chromatography (12-36% DE/hexanes) to give 70.7 mg (73%) of a colorless thick oil **18**, *alpha*:*beta* ratio = 5.0:1.

Methyl (2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl--D-glucopyranoside (18)



18a

Data for *alpha* anomer 18a : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.13 (m, 31H), 5.78 (d, *J* = 3.6 Hz, 1H), 5.10 (d, *J* = 11.8 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.76-4.70 (m, 4H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.60-4.46 (m, 7H), 4.30 (d*, J* =12.8 Hz, 1H), 4.10-4.08 (m, 2H), 3.92-3.86 (m, 3H), 3.74-3.77 (m, 1H), 3.70-3.61 (m, 3H), 3.46-3.42 (m, 2H), 3.40 (s, 3H), 3.39-3.36 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.52, 142.16, 141.89, 141.77, 138.85, 138.16, 137.81, 130.31-129.30 (m), 128.49, 128.33, 128.27, 128.18, 128.02, 127.82, 127.50, 127.39, 127.26, 127.24, 127.16, 127.14, 126.39, 125.34-125.12 (m), 122.97, 122.95, 97.73, 96.32, 82.08, 81.95, 80.23, 79.73, 77.78, 74.43, 74.31, 73.97, 73.36, 73.27, 72.68, 72.36, 72.11, 70.77, 69.62, 69.14, 68.48, 55.31; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.08 (s, 3F), -63.09 (s, 3F), -63.12 (s, 3F), -63.15 (s, 3F). **HRMS (m/z):** Calcd for $C_{66}H_{62,}F_{12}O_{11}Na$ 1281.3998 found 1281.3996. **$[\alpha]_D^{25}$ =** +39.8° (c = 1, DCM). **IR (cm^{-1})** 3059, 2914, 2867, 1620, 1324, 1266, 1161, 1121, 1065, 1017, 850, 822 (*p*-disubstituted benzene),735, 699, 593.



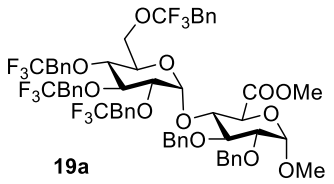
18b

Data for *beta* anomer 18b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.17 (m, 31H), 5.05 (d, *J* = 11.4 Hz, 1H), 4.87-4.58 (m, 12H), 4.45-4.35 (m, 4H), 3.98 (t, *J* = 9.5 Hz, 1H), 3.85 (t, *J* = 9.3 Hz, 1H), 3.79 (dd, *J* = 10.8 Hz, 2.9 Hz, 1H), 3.70 (dd, *J* = 11.2 Hz, 1.9 Hz, 1H), 3.60-3.38 (m, 6H), 3.36 (s, 3H), 3.31-3.27 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.43, 142.35, 142.30, 142.10, 139.42, 138.22, 137.78, 130.05-129.40 (m), 128.53, 128.40, 128.10, 128.04, 128.01, 127.91, 127.88, 127.86, 127.36, 127.32, 127.24, 127.22, 127.15, 127.13, 125.33-125.13 (m), 122.95, 102.19, 98.40, 84.75, 82.79, 80.29, 79.03, 78.25, 76.27, 75.42, 75.00, 74.52, 73.84, 73.82, 73.59, 73.57, 72.54, 69.96, 69.01, 67.85, 55.46; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -62.98 (s, 3F), -63.06 (s, 3F), -63.14 (s, 3F), -63.15 (s, 3F). **HRMS (m/z):** Calcd for $C_{66}H_{62,}F_{12}O_{11}Na$ 1281.3998 found 1281.3990. **$[\alpha]_D^{25}$ =** +25.6° (c = 1, DCM). **IR (cm^{-1})** 3056, 2916, 1324, 1265, 1163, 1122, 1065, 1018, 822 (*p*-disubstituted benzene), 736, 701.

Glucoronate **19cc** as the acceptor

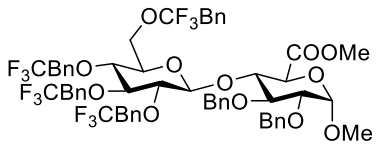
Following the general procedure **B**. 5.0 ml of 1,4-dioxane, 167.7 mg (0.1672 mmol) of thioglucoside donor **11d**, 31.0 mg (0.0770 mmol) of acceptor **19cc**, and 5.0 µL (0.057 mmol) of TfOH were used. Purified by flash column chromatography (12-36% DE/hexanes) to give 65.7 mg of a colorless oil **19** (71%), *alpha*:*beta* ratio 4.2:1.

Methyl (2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranosyl)-1→4-(2,3-di-*O*-benzyl)-D-glucopyranuronic acid methyl ester (19)



19a

Data for *alpha* anomer 19a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.47 (m, 4H), 7.41 (d, *J* = 8.1 Hz, 4H), 7.27-7.23 (m, 10H), 7.19-7.14 (m, 6H), 5.58 (d, *J* = 3.6 Hz, 1H), 5.02 (d, *J* = 11.7 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.82-4.45 (m, 11H), 4.25 (d, *J* = 9.5 Hz, 1H), 4.12 (t, *J* = 9.1 Hz, 1H), 4.05 (t, *J* = 9.0 Hz, 1H), 3.89 (t, *J* = 9.4 Hz, 1H), 3.75-3.70 (m, 1H), 3.69 (s, 3H), 3.66-3.60 (m, 3H), 3.51 (d, *J* = 9.9 Hz, 1H), 3.46-3.43 (m, 1H), 3.42 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.05, 142.39, 142.17, 141.86, 141.74, 138.65, 137.61, 130.40-129.38 (m), 128.54, 128.31, 128.23, 128.14, 127.85, 127.32, 127.30, 127.00, 126.45, 125.39-125.09 (m), 122.95, 98.50, 97.09, 81.49, 80.98, 79.56, 79.20, 77.50, 75.62, 74.82, 74.47, 73.90, 73.53, 72.79, 72.00, 70.75, 70.29, 68.22, 55.81, 52.54; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.15 (s, 6F), -63.20 (s, 3F), -63.22 (s, 3F). **HRMS (m/z):** Calcd for $C_{60}H_{56}F_{12}O_{12}K$ 1235.3217 found 1235.3207. **$[\alpha]_D^{25}$ =** +37.5° (c = 1, DCM). **IR (cm^{-1})** 3057, 2927, 1749, 1324, 1265, 1163, 1122, 1064, 1018, 823 (*p*-disubstituted benzene), 735, 702.



19b

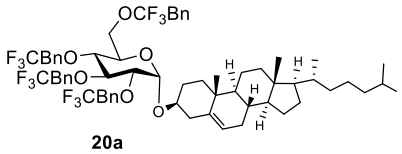
Data for *beta* anomer 19b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.21 (m, 26H), 5.03 (d, *J* = 11.4 Hz, 1H), 4.93 (d, *J* = 12.1 Hz, 1H), 4.87 (d, *J* = 12.1 Hz, 1H), 4.83-4.71 (m, 4H), 4.66-4.57 (m, 4H), 4.47-4.38 (m, 3H), 4.17-4.09 (m, 2H), 3.90 (t, *J* = 8.9 Hz, 1H), 3.74-3.64 (m, 2H), 3.62 (s, 3H), 3.60-3.53 (m, 2H), 3.50 (dd, *J* = 9.5 Hz, 3.7 Hz, 1H), 3.48-3.43 (m, 1H), 3.41 (s, 3H), 3.39-3.35 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.05,142.34, 141.97, 139.09, 137.95, 130.39-129.17 (m), 128.47, 128.36, 128.08, 128.00, 127.89, 127.82, 127.75, 127.35, 127.30, 127.26, 127.11, 127.04, 125.42-125.07 (m), 122.98, 102.19, 98.83, 84.73, 82.59, 79.57, 78.63, 78.14, 77.61, 75.51, 75.01, 74.60, 74.01, 73.83, 73.80, 72.50, 69.90, 68.94, 55.92, 52.63; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.06 (s, 3F), -63.15 (s, 3F), -63.22 (s, 6F). **HRMS (m/z):** Calcd for

$C_{60}H_{56,}F_{12}O_{12}K$ 1235.3217 found 1235.3200. **$[\alpha]_D^{25}$ =** +24.8° (c = 1, DCM). **IR (cm^{-1})** 3061, 2922, 1747, 1620, 1324, 1265, 1162, 1120, 1065,1018, 850, 822 (*p*-disubstituted benzene), 736, 700.

Glycosylation using Cholesterol (20cc) as the acceptor

Following the general procedure B. 5.0 mL of 1,4-dioxane, 154.9 mg (0.1544 mmol) of donor **11d**, 29.7 mg (0.0768 mmol) of cholesterol **20cc** and 5.0 µL (0.057 mmol) of TfOH were used. Purified by flash column chromatography twice since the first purification still had substantial impurity (12-36% DE/hexanes) to give 60.4 mg of a white compound **20** (some product deliberately not collected due to impurity contamination), 67%, *alpha*:*beta* ratio (after first column) 9.6:1.

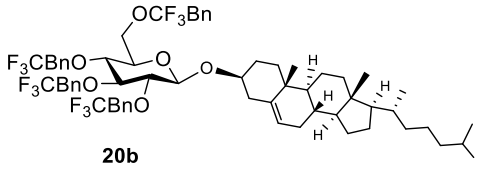
cholesteryl 2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranoside (20)



20a

Data for *alpha* anomer 20a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.50 (m, 8H), 7.43-7.40 (m, 4H), 7.35 (d*, J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.29-5.27 (m, 1H), 5.05 (d, *J* = 3.7 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 4.81 (t, *J* = 11.9 Hz, 2H), 4.71 (s, 2H), 4.65 (d, *J* = 12.7 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 12.7 Hz, 1H), 4.00 (t, *J* = 9.2 Hz, 1H), 3.92 (m, 1H), 3.75 (dd, *J* = 10.7 Hz, 3.8 Hz 1H), 3.69-3.61 (m, 2H), 3.55 (dd, *J* = 9.6 Hz, 3.7 Hz, 1H), 3.46 (m, 1H), 2.44 (t, *J* = 13.3 Hz, 1H), 2.31 (ddd, *J* = 13.2 Hz, 5.0 Hz, 2.0 Hz, 1H), 2.02 (dt, *J* = 16.2 Hz, 3.5 Hz, 1H), 1.99-1.92 (m, 1H), 1.91-1.79 (m, 3H), 1.62-0.96 (m, 20H), 1.01 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 4H), 0.87 (d*, J* = 6.6 Hz, 3H), 0.87 (d*, J* = 6.6 Hz, 3H), 0.68 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.72, 142.04, 141.91, 140.56, 130.07, 129.82, 127.87, 127.68, 127.32, 125.42-125.04 (m), 122.03, 94.51, 82.10, 80.29, 78.06, 74.57, 74.09, 72.67, 71.92, 70.04, 68.97, 56.75, 56.16, 50.14, 42.33,

40.00, 39.76, 39.53, 37.06, 36.78, 36.20, 35.80, 31.90, 31.88, 28.24, 28.03, 27.72, 24.27, 23.84, 22.83, 22.57, 21.07, 19.38, 18.73, 11.86; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.07 (s, 3F), -63.09 (s, 3F), -63.10 (s, 3F), -63.17 (s, 3F). **HRMS (m/z):** Calcd for $C_{65}H_{76,}F_{12}O_6Cl$ 1215.5144 found 1215.5188. **$[\alpha]_D^{25}$ =** +26.6° (c = 1, DCM). **IR (cm^{-1})** 2935, 2868, 1620, 1324, 1210, 1109, 1063, 1016, 822 (*p*-disubstituted benzene), 738, 592



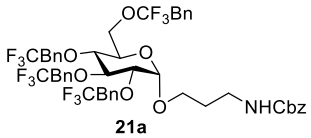
20b

Data for *beta* anomer 20b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.53-7.48 (m, 6H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.33 (d, *J* = 5.4 Hz, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.89 (d, *J* = 12.2 Hz, 1H), 4.80 (d, *J* = 12.0 Hz 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.67-4.57 (m, 3H), 4.52 (d, *J* = 7.8 Hz, 1H), 3.71 (m, 2H), 3.64-3.55 (m, 3H), 3.47-3.41 (m, 2H), 2.36-2.25 (m, 2H), 2.04-1.95 (m, 3H), 1.88-1.79 (m, 2H), 1.68-0.95 (m, 20H), 1.01 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 4H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.68 (s, 3H) ; **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.39, 142.23, 142.01, 130.08-129.68 (m), 127.88, 127.53, 127.37, 127.30, 125.33, 125.31, 125.28, 125.25, 125.22, 123.01, 122.94, 122.22, 102.08, 84.75, 82.28, 79.77, 78.07, 74.57, 73.97, 73.77, 72.60, 69.15, 56.75, 56.16, 53.42, 50.21, 42.34, 39.75, 39.53, 39.07, 37.29, 36.76, 36.20, 35.80, 31.93, 31.88, 30.01, 29.72, 28.24, 28.03, 24.29, 23.84, 22.83, 22.71, 22.67, 22.57, 21.06, 19.38, 18.73, 14.13, 11.87; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.04 (s, 3F), -63.08 (s, 3F) -63.13 (s, 3F), -63.16 (s, 3F). **HRMS (m/z):** Calcd for $C_{65}H_{76,}F_{12}O_6Cl$ 1215.5144 found 1215.5186. **$[\alpha]_D^{25}$ =** +34.5° (c = 1, DCM). **IR (cm^{-1})** 2936, 1325**,** 1264, 1165, 1123, 1065, 1018, 823 (*p*-disubstituted benzene), 735, 704.

Glycosylation using 21cc as the acceptor

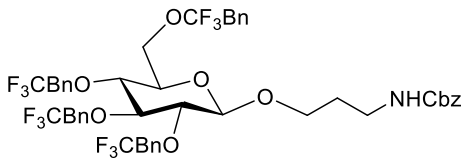
Following the general procedure B, 5.0 ml of 1,4-dioxane used, 155.8 mg (0.1553 mmol) of donor **16b**, 16.6 mg (0.0793 mmol) of alcohol **21cc** and 5.0 µL (0.057 mmol) of TfOH were used. Purified by flash column chromatography (12-40% EtOAc/hexanes) to give 76.6 mg of a colorless oil **21** yield 96%, *alpha*:*beta* ratio 5.5:1

(3′-(*N*-carbobenzyloxy) propyl) 2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranoside (21)



21a

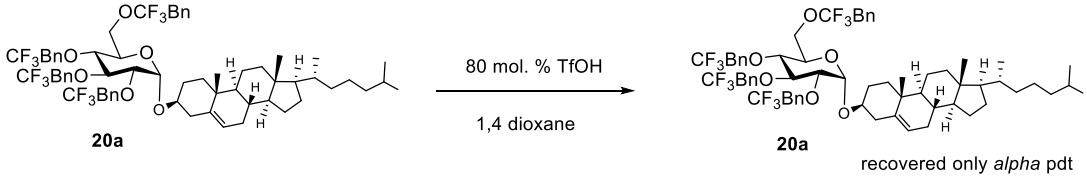
Data for *alpha* anomer 21a: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.17 (m, 21H), 5.76 (t, *J* = 5.7 Hz, 1H), 5.04 (s, 2H), 4.86-4.76 (m, 3H), 4.71-4.58 (m, 4H), 4.51 (m, 2H), 3.99-3.86 (m, 2H), 3.80-3.74 (d, *J* =9.6 Hz, 1H), 3.70-3.51 (m, 5H), 3.51-3.42 (m, 1H), 3.31-3.21 (m, 1H), 1.85 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.50, 142.42, 141.94, 141.79, 136.58, 130.38-128.68 (m), 128.43, 128.05, 128.01, 127.82, 127.74, 127.68, 127.41, 127.25, 125.46-125.08 (m), 122.92, 97.04, 82.15, 80.08, 77.72, 74.63, 74.05, 72.68, 72.26, 70.41, 68.74, 67.69, 66.59, 39.71, 29.19; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.16 (s, 9F), -63.23 (s, 3F). **HRMS** (**m/z):** Calcd for $C_{49}H_{46,}F_{12}NO_8$ 1004.3032 found 1004.3061. **$[\alpha]_D^{25}$ =** +26.6° (c = 1, DCM). **IR (cm^{-1})** 3054,2917, 1716, 1516, 1324,1264, 1163, 1123, 1065, 1018, 823 (*p*-disubstituted benzene),735, 703.



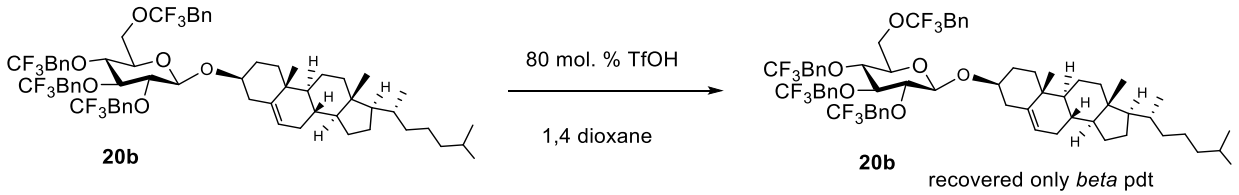
21b

Data for *beta* anomer 21b: 1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.26 (m, 19H), 7.18 (d, *J* =8.0 Hz, 2H), 5.29 (t, *J* =5.9 Hz, 1H), 5.06 (d, *J* =4.7 Hz, 2H), 4.95 (d, *J* =12.0 Hz, 1H), 4.88 (d, *J* =12.1 Hz, 1H), 4.76 (m, 2H), 4.69 (d, *J* =12.0 Hz, 1H), 4.59-4.54 (m, 2H), 4.48 (d, *J* =12.8 Hz, 1H), 4.40 (d, *J* =7.7 Hz, 1H), 3.97-3.91 (m, 1H), 3.73-3.64 (m, 3H), 3.63-3.56 (m, 2H), 3.50-3.27 (m, 4H), 1.83 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.43, 142.30, 142.23, 141.92, 141.83, 136.57, 130.39-129.62 (m), 128.50, 128.19, 128.14, 127.75, 127.65, 127.35, 127.23, 125.37-125.08 (m), 122.99, 122.96, 122.91, 120.83, 103.45, 84.63, 82.20, 77.96, 74.57, 74.43, 73.98, 73.79, 72.61, 68.89, 67.50, 66.65, 38.12, 29.74; **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.12 (s, 3F), -63.14 (s, 3F), -63.19 (s, 3F), -63.24 (s, 3F). **HRMS (m/z):** Calcd for $C_{49}H_{46,}F_{12}NO_8$ 1004.3032 found 1004.3061. **$[\alpha]_D^{25}$ =** +52.4° (c = 1, DCM). **IR (cm^{-1})** 3054, 2917, 1716, 1516, 1324,1264, 1163, 1123, 1065, 1018, 823 (*p*-disubstituted benzene),735, 703.

Probing for anomerization.



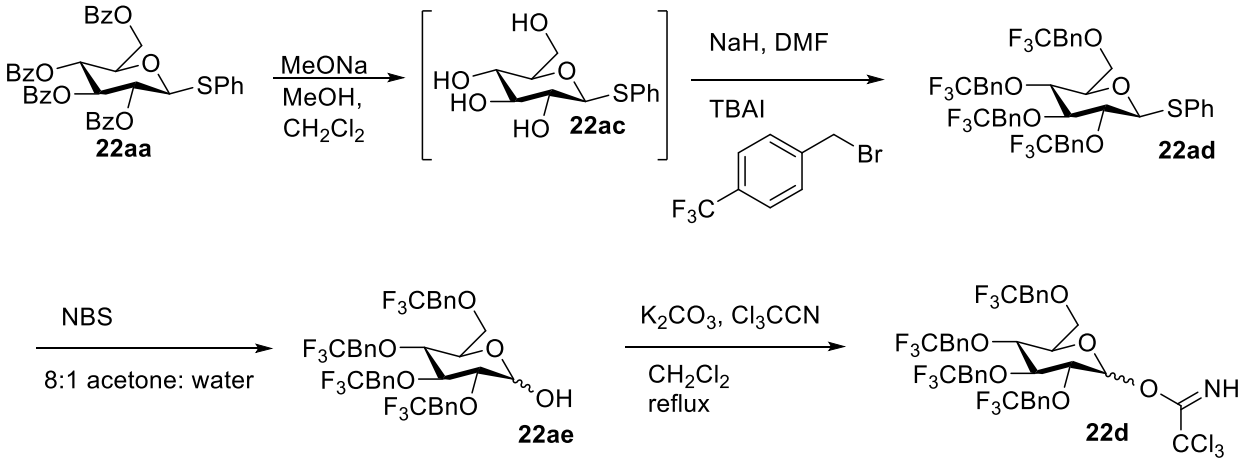
To an oven dried 4ml Wheaton vial with a stir bar, 24.2 mg of **20a** (0.0205 mmol) was added. The vial was capped with a septum then Nitrogen gas was flushed through it. 1.4 mL of 1,4-dioxane was then added under nitrogen atmosphere. Finally, 1.4 µL of TfOH was added and the reaction was allowed to stir at 20 °C for 12 hrs. The reaction mixture was quenched by addition of 0.05 mL of Et_3N then concentrated. ^{1}H NMR of the concentrated material showed no formation of the *beta* product.



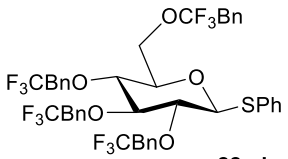
To an oven dried 4ml Wheaton vial with a stir bar, 35.6 mg of **20b** (0.0301 mmol) was added. The vial was capped with a septum then Nitrogen gas was flushed through it. 2.2 mL of 1,4-dioxane was then added under nitrogen atmosphere. Finally, 2.0 µL of TfOH was added and the reaction was allowed to stir at 20 °C for 12 hrs. The reaction mixture was quenched by addition of 0.05 mL of Et_3N then concentrated. NMR of the concentrated material showed no formation of the *alpha* product.

Synthesis of trichloroacetimidate glucosyl donor with *p*-trifluoromethylbenzyl protecting groups (22d)

Synthesis plan:



Synthesis of **22ad.**



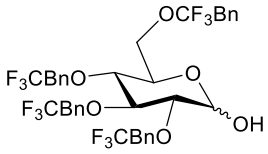
22ad

To 2.21g of **22aa** (3.21 mmol) in a R.B.F with a magnetic stir bar, 30.0 ml of methanol was added followed by 25.0 ml of dichloromethane. The R.B.F was capped with a septum. Three cycles of nitrogen purge backfill were performed followed by dropwise addition of 1.0 ml of 5 M NaOMe. After 30 min, TLC showed reaction was complete. 5.45 g of Dowex ® 50WX8 50-100 (H) resin (Alfa Aesar) was added to neutralize the NaOMe. The mixture was filtered through celite and rinsed with 20.0 ml of methanol. Collected solution was concentrated then co-evaporated with 2.0 ml of toluene twice to give an off white powder (**22ac**). To the powder (**22ac**) in R.B.F with a stir bar, 8.06g of *p*-trifluoromethylbenzyl bromide (33.7 mmol) was added followed by 50.0 ml of DMF. 1.02g of TBAI was then added. After all the solids had dissolved, the R.B.F was placed in an ice bath and cooled to 0 °C. Excess NaH (5.0 g) was then added carefully. After 10 min the reaction was allowed to warm to room temperature under N_2 atmosphere and stir for 16hrs. The reaction was quenched at 0 °C by dropwise addition of water until gas evolution ceased. 200.0ml of EtOAc was added and the contents transferred to a separatory funnel. 1000.0 ml of water was then added, the contents were shaken vigorously to get rid of DMF and then allowed to stand to ensure separation of aqueous and organic layer. The organic layer was dried using Na_2SO_4 then concentrated to give a crude product which was purified using flash chromatography (5-15% EtOAc/hexanes) to give 2.19g (2.42 mmol) of **22ad** white solid (70% two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.51 (m, 10H), 7.49-7.40 (m, 4H), 7.34-7.25 (m, 7H), 5.00(d, *J* = 11.2 Hz, 1H), 4.89 (d, *J* = 12.1 Hz, 1H), 4.86-4.79(m, 2H), 4.77-4.65 (m, 4H), 4.61(d, *J* = 12.6Hz, 1H), 3.86-3.76 (m, 2H), 3.75-3.68 (m, 2H), 3.60-3.51(m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 142.15, 142.11, 141.84, 141.80, 133.43, 131.81, 130.16-129.76(m), 129.03, 127.83, 127.75, 127.54, 127.36, 127.20, 125.40, 125.37, 125.34, 125.31, 87.49, 86.70, 81.10, 78.91, 77.88, 74.72,

74.48, 74.01, 72.67, 69.08. **^{19}F NMR (471 MHz, $CDCl_3$) δ** -63.04 (s, 3F), -63.12 (s, 3F), -63.15 (s, 3F), -63.17 (s, 3F). **HRMS** (**m/z):** Calcd for $C_{44}H_{36,}F_{12}O_5SNa$ 927.1990 found 927.1997 **$[\alpha]_D^{25}$ =** +66.3° (c = 1, DCM). **IR (cm^{-1})** 2874, 1326, 1264, 1165, 1111, 1066, 1019, 823 (*p*-disubstituted benzene), 733, 703.

Synthesis of **22ae**.



22ae

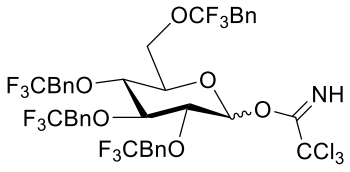
To 2.19g (2.42 mmol) of **22ad** in a R.B.F with a stir bar, 24.0 ml of 8:1 acetone:water was added, followed by addition of 1.72g of NBS (9.66 mmol). The R.B.F was then capped with a septum then three cycles of nitrogen purge backfill were perfomed. T.L.C showed the reaction was complete after 1hr. The contents were then concentrated followed by addition of 30.0 ml of dichloromethane. The resulting solution was then transferred to a separatory funnel and washed with 100.0 ml of water once. The organic layer was then concentrated and purified by flash chromatography (10-40% EtOAc/hexanes) to give 1.15g (1.42mmol) of **22ae** as a colorless gum (59% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.29 (m, 21H), 7.26-7.20 (m, 3H), 5.35 (t, *J* = 3.0 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H), 4.99-4.90 (m, 2H), 4.86-4.72 (m, 6H), 4.69-4.64(m, 2H), 4.63-4.58(m, 2H), 4.54(d, *J* = 12.8Hz, 1H), 4.09(ddd, *J* = 10.2, 3.9, 2.0 Hz, 1H), 4.01(t, *J* = 9.2 Hz, 1H), 3.79-3.54(m, 7H), 3.42(t, *J* = 7.7 Hz, 1H), 3.05-2.96(m, 1H). **^{13}C NMR** (**125 MHz, $CDCl_3$) δ** 142.39-141.57(m), 130.42-129.38(m), 127.83, 127.73, 127.72, 127.36, 127.32, 127.26, 127.22, 125.57-125.21(m), 125.13, 122.90, 97.56, 91.03, 84.50, 83.13, 81.67, 80.35, 77.85, 74.64, 74.61, 73.99, 73.69, 72.78, 72.73, 72.32, 70.24, 69.06, 68.84. **HRMS** (**m/z):** Calcd for $C_{38}H_{32}F_{12}O_6Na$

835.1905 found 835.1947 **$[\alpha]_D^{25}$ =** +32.6° (c = 1, DCM). **IR (cm^{-1})** 3421, 2926, 1326, 1161, 1121, 1110, 1066, 1018, 822 (*p*-disubstituted benzene), 637.

Synthesis of 22d

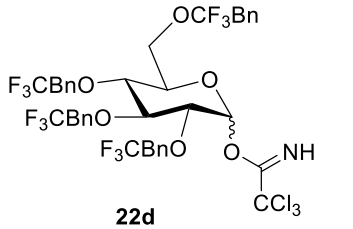
To 1.11 g (1.37 mmol) of **22ae** in R.B.F with stir bar, 25.0 ml of dichloromethane was added followed by of 4.5 g of K_2CO_3 (excess). Lastly, trichloroacetonitrile 5.0 ml (excess) was added. The reaction was allowed to stir at room temperature, however, after 5 hrs, little product formation was observed as shown by T.L.C. A reflux condenser was then attached and the reaction was refluxed for two hours. Product was cleanly formed as judged by T.L.C and NMR. The contents were filtered through celite then the filtrate was concentrated and then put under high vacuum to give 1.20g of a white powder **22d** (91%).



22d
mostly *beta* anomer

Data for *beta* anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.56-7.24 (m, 16H), 5.82 (dd, *J* = 5.4, 2.2Hz, 1H), 4.99 (d, *J* = 11.8 Hz, 1H), 4.88 (d, *J* = 12.2 Hz, 1H), 4.84-4.71 (m, 3H), 4.69-4.61 (m, 2H), 4.58(d, *J* = 12.8 Hz, 1H), 3.83-3.63(m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 161.07, 142.10, 141.79, 141.69, 130.31-129.64(m), 127.84, 127.65, 127.37, 127.19, 125.36, 125.33, 125.30, 98.08, 90.78, 84.51, 80.96, 77.38, 77.21, 75.64, 74.55, 73.97, 73.88, 72.63, 68.37. **HRMS (m/z):** Calcd for $C_{40}H_{32}Cl_3F_{12}NO_6Na$ 978.1001 found 978.1024 **$[\alpha]_D^{25}$ =** -15.5° (c

= 1, DCM). **IR (cm^{-1})** 2923, 1325, 1263, 1121, 1066, 1018, 822(*p*-disubstituted benzene), 797, 736, 703.



22d
mostly *alpha* anomer

Data for *alpha* anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.64-7.22 (m, 16H), 6.60 (d, *J* = 3.4 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.92-4.74 (m, 3H), 4.74-4.59 (m, 3H), 4.54 (d, *J* = 12.7 Hz, 1H), 4.12-4.00 (m, 2H), 3.87-3.66 (m, 4H).). **^{13}C NMR** (**125 MHz, $CDCl_3$) δ** 161.18, 142.31, 141.81, 141.66, 130.51-129.36(m), 127.69, 127.48, 127.46, 127.42, 125.36-125.27(m), 125.12, 122.96, 93.84, 81.45, 79.71, 77.22, 76.97, 74.65, 74.30, 73.04, 72.73, 72.09, 68.36. **HRMS** (**m/z):** Calcd for $C_{40}H_{32}Cl_3F_{12}NO_6Na$ 978.1001 found 978.1003 **$[\alpha]_D^{25}$ =** +43.5° (c = 1, DCM). **IR (cm^{-1})** 2921, 1738, 1672, 1325, 1163, 1121, 1066, 1018, 822 (*p*-disubstituted benzene), 795, 737, 643.

General procedure C

Glycosylation using trichloroacetimidate glucosyl donors

0.15 mmol of 2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranose trichloroacetimidate donor (**22d**) or 2,3,4,6-tetra-O-benzyl-D-glucopyranose trichloroacetimidate (**22a**) (1 equiv) was put in an oven dried test tube with a stir bar followed by addition of 0.105 mmol of acceptor **12** (0.7 eq). The test tube was capped with a septum and flushed with nitrogen gas for 1 min. 1,4

dioxane (volume is specified below) was then added with nitrogen line still attached. Finally, 13.2 µL (0.15 mmol) of TfOH (1equiv) was added using a micro-syringe and the reaction allowed to stir at 20 °C for 12hrs. The reaction was quenched by addition of 0.05 ml of Et_3N. Concentration using rotary evaporator was followed by purification using flash column chromatography (12-28% EtOAc/hexanes).

Entry 1 Table 2

Following the general procedure **C**. 2.5 ml of 1,4-dioxane, 102.9 mg (0.150 mmol) of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose trichloroacetimidate donor (**22a**), 50.1 mg (0.108 mmol) of acceptor **12**, and 13.2 µL (0.15 mmol) of TfOH were used. Purified by flash column chromatography (12-28% EtOAc/hexanes) to give 80.7 mg of a colorless oil (76%) which was a mixture of **13a-*alpha*** and **13a-*beta***, *alpha*:*beta* ratio 5.2:1.

Entry 2 Table 2

Following the general procedure **C**. 2.5 ml of 1,4-dioxane, 144.2 mg (0.1507 mmol) of 2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranose trichloroacetimidate donor (**22d**), 49.9 mg (0.1074 mmol) of acceptor **12**, and 13.2 µL (0.15 mmol) of TfOH were used. Purified by flash column chromatography (12-28% EtOAc/hexanes) to give 111.6 mg of colorless oil (83%) which was a mixture of **13d-*alpha*** and **13d-*beta***, *alpha*:*beta* ratio 10.0:1.

Entry 3 Table 2

Following the general procedure **C**. 5.0 ml of 1,4-dioxane, 104.8 mg (0.1530 mmol) of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose trichloroacetimidate donor (**22a**), 49.7 mg (0.107 mmol) of acceptor **12**, and 13.2 µL (0.15 mmol) of TfOH were used. Purified by flash column

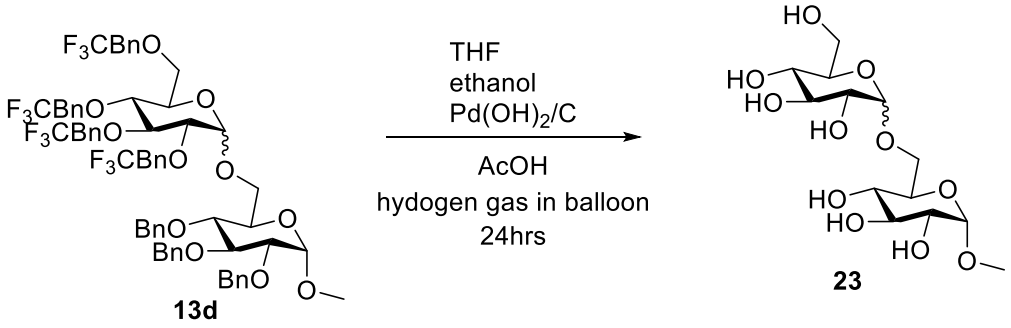
chromatography (12-28% EtOAc/hexanes) to give 99.2 mg of a colorless oil (94%) which was a mixture of **13a-*alpha*** and **13a-*beta***, *alpha*:*beta* ratio 5.0:1.

Entry 4 Table 2

Following the general procedure **C**. 5.0 ml of 1,4-dioxane, 144.6 mg (0.1511 mmol) of 2,3,4,6-tetra-*O*-(4-trifluoromethylbenzyl)-D-glucopyranose trichloroacetimidate donor (**22d**), 49.9 mg (0.1074 mmol) of acceptor **12**, and 13.2 µL (0.15 mmol) of TfOH were used. Purified by flash column chromatography (12-28% EtOAc/hexanes) to give 105.7 mg of colorless oil (78%) which was a mixture of **13d-*alpha*** and **13d-*beta***, *alpha*:*beta* ratio 14.0:1

Debenzylation Procedure

Methyl 6-*O*-(D-Glucopyranosyl)-α-D-glucopyranoside (23)



To 74.8 mg of **13d** (α:β 8.7:1) (0.0594 mmols) in a vial, 1.5 ml of THF was added followed by 2.2 ml of ethanol then 0.5 ml of water. 156 mg of 20% $Pd(OH)_2$ on carbon was then added in one portion. Lastly, 0.5 ml of acetic acid was added. The vial was capped with a septum and hydrogen gas in a balloon was connected via a needle. Three cycles of vacuuming and back-filling with hydrogen gas were perfomed. The reaction was allowed to stir under hydrogen gas atmosphere at 20 °C for 24 hrs. The solid particles were filtered out by passing the reaction mixture through a cotton plug and rinsing with MeOH. The crude Product was purified by flash

chromatography (10-50% MeOH/CH_2Cl_2) to give 20.0 mg of a white solid (94%). ^{1}H NMR and ^{13}C NMR spectra match those reported in the literature.[4]

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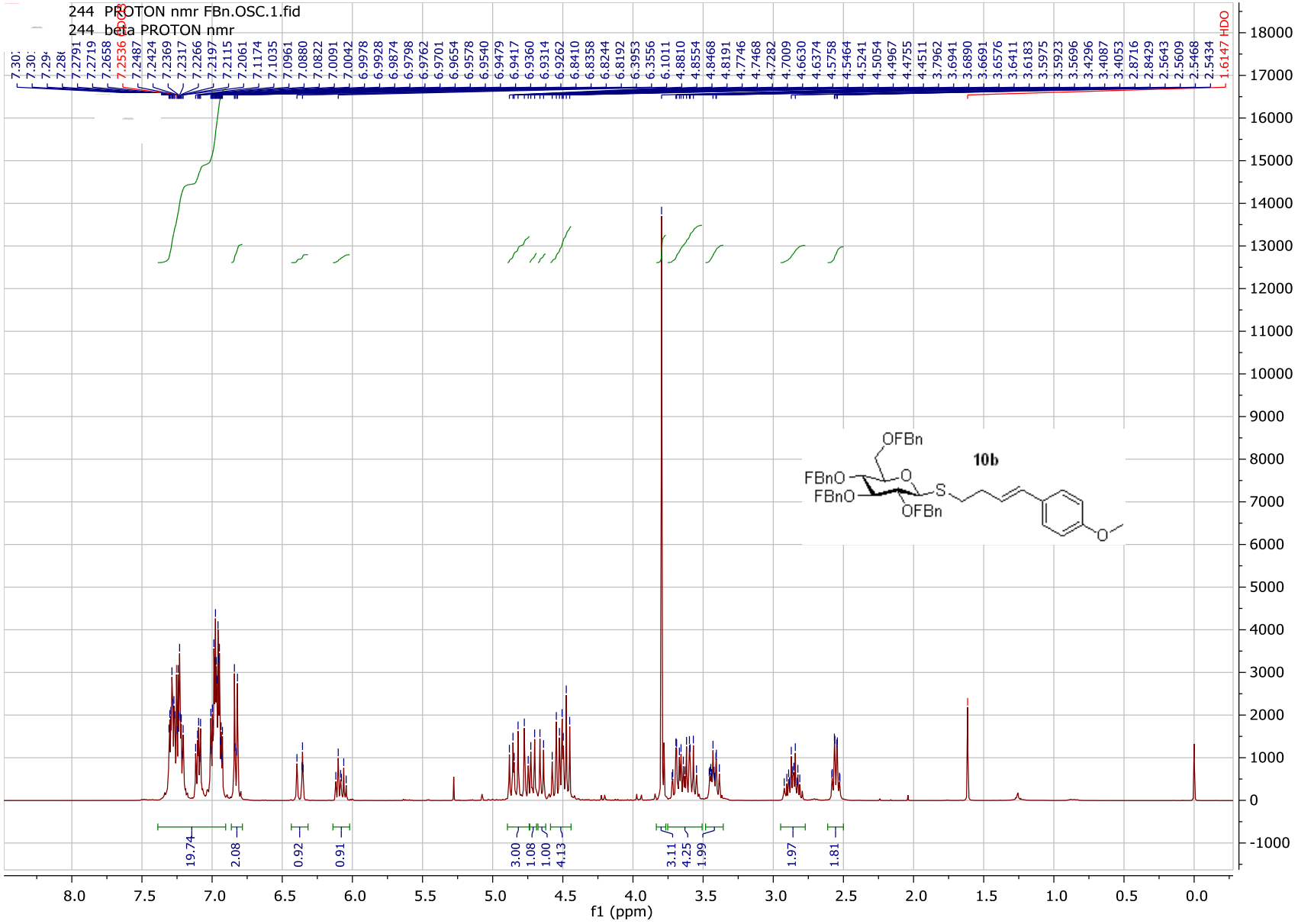
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10b
O
19.74
2.08
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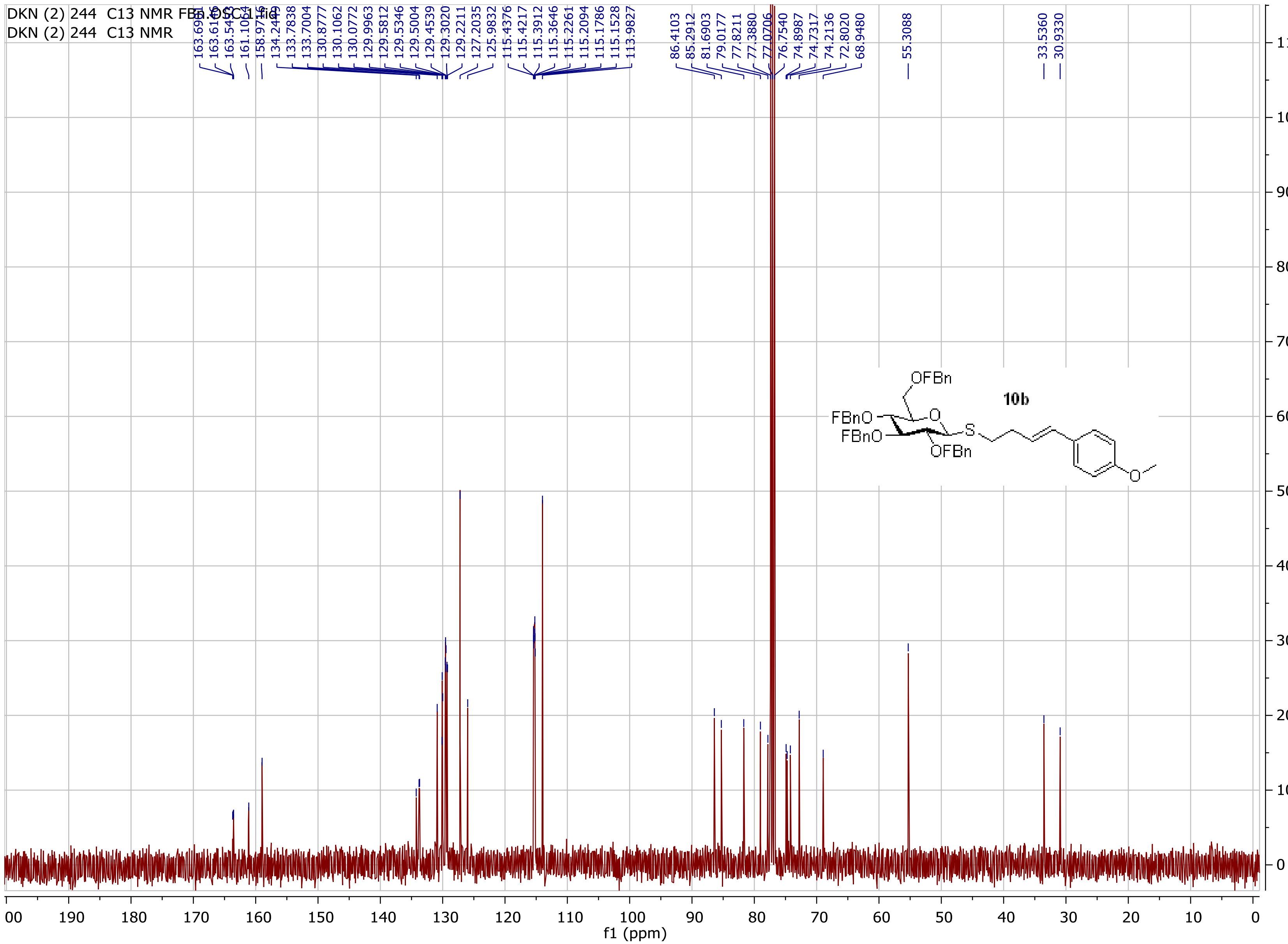
f1 (ppm)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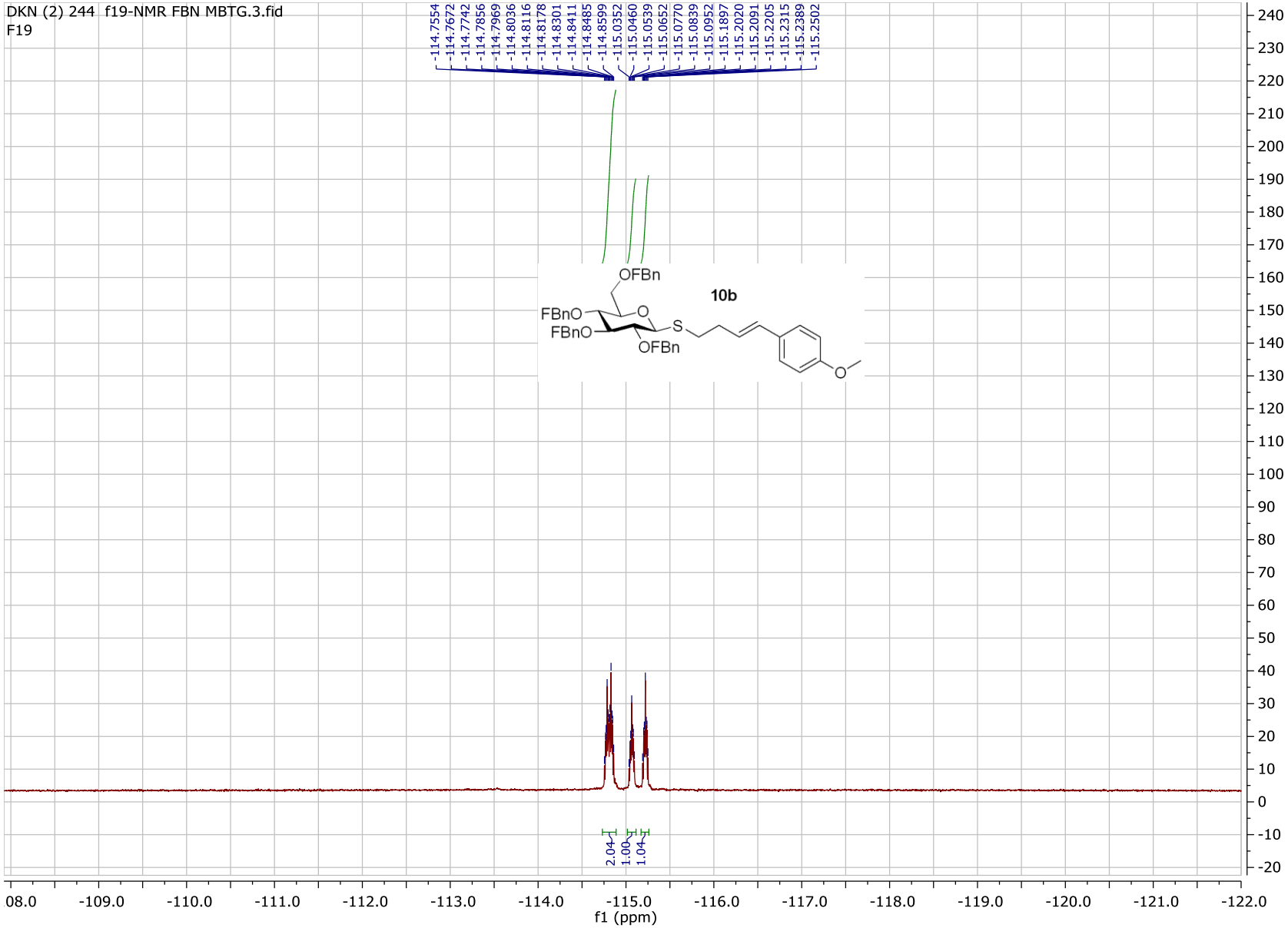
f1 (ppm)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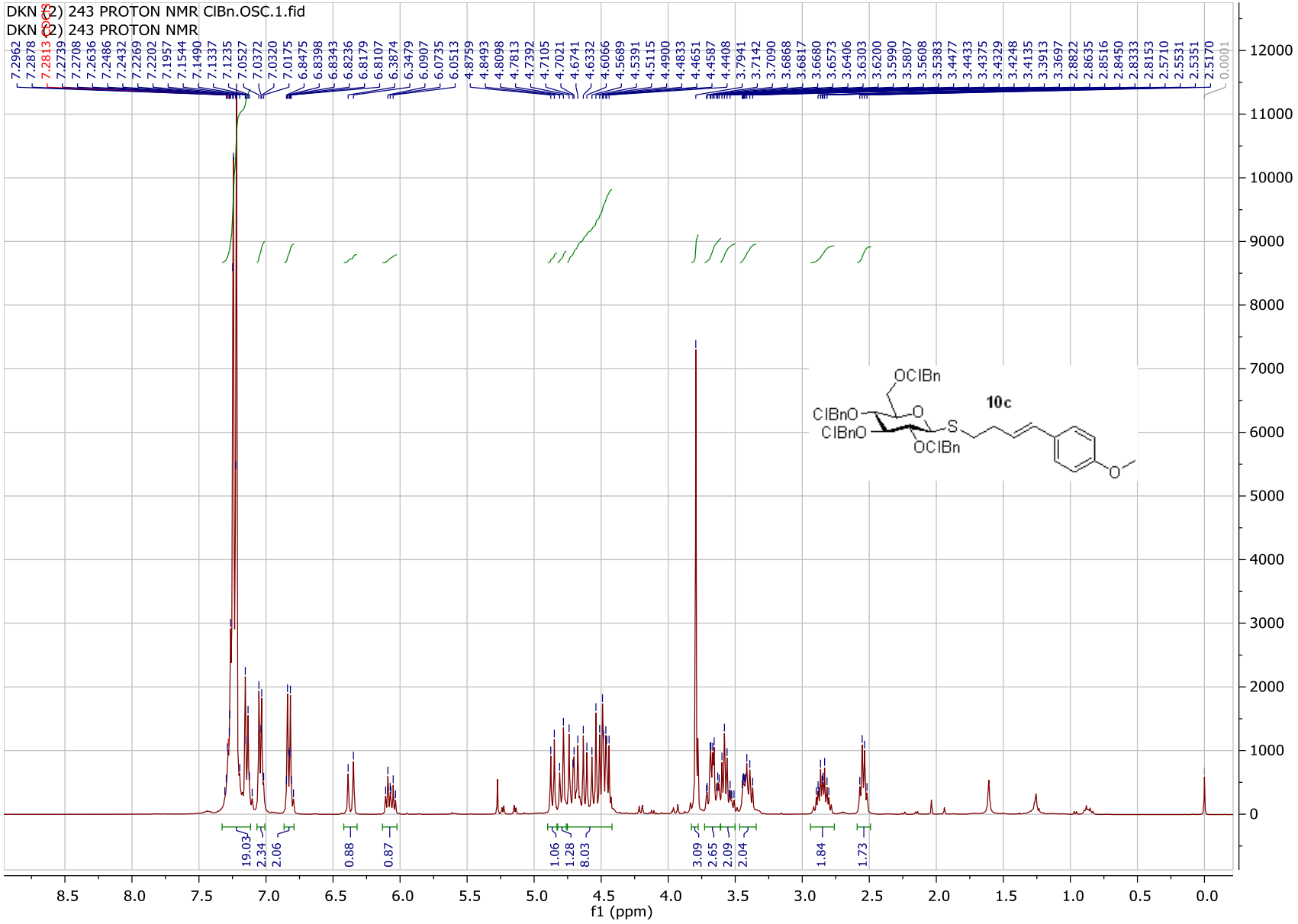
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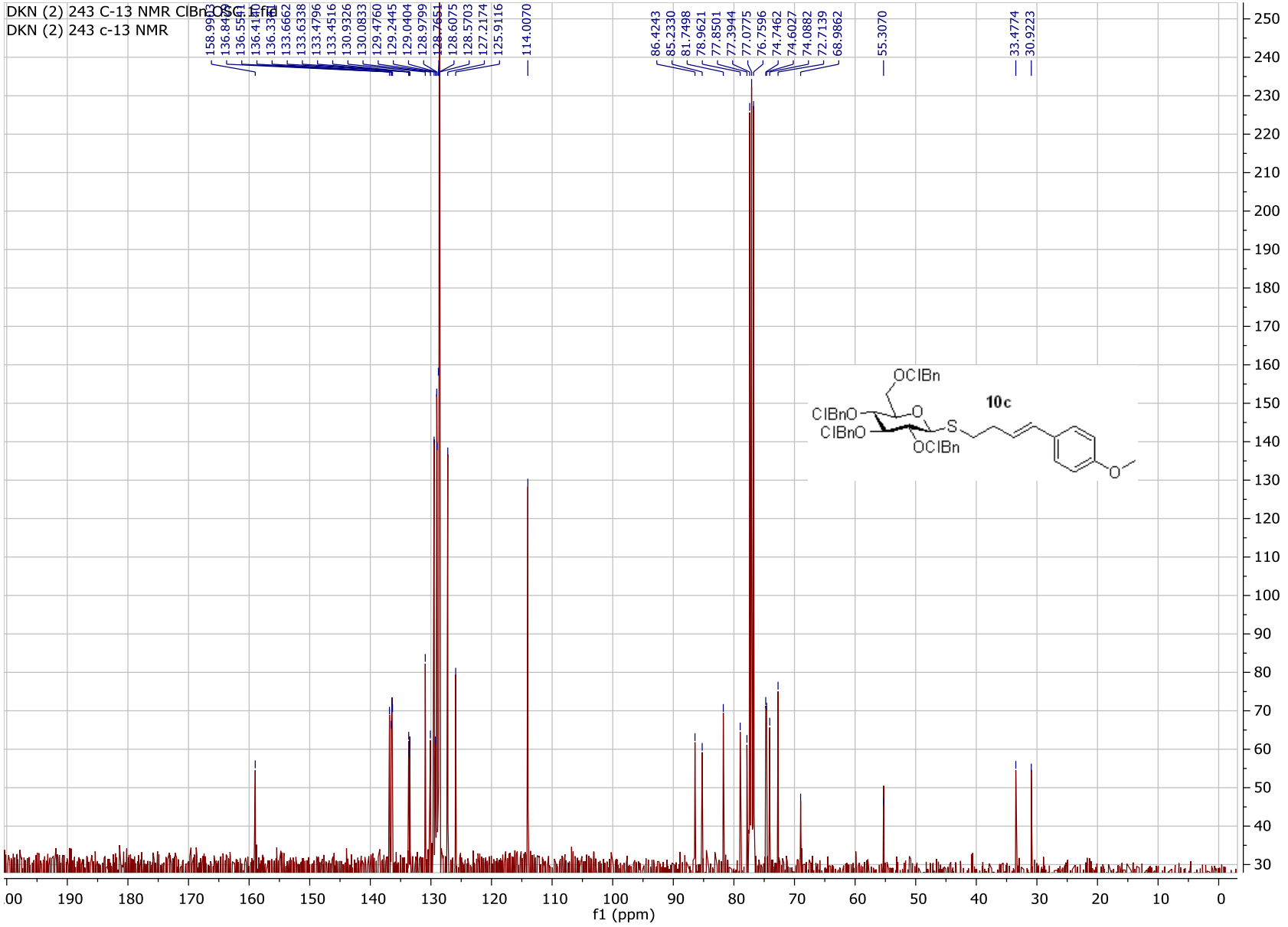
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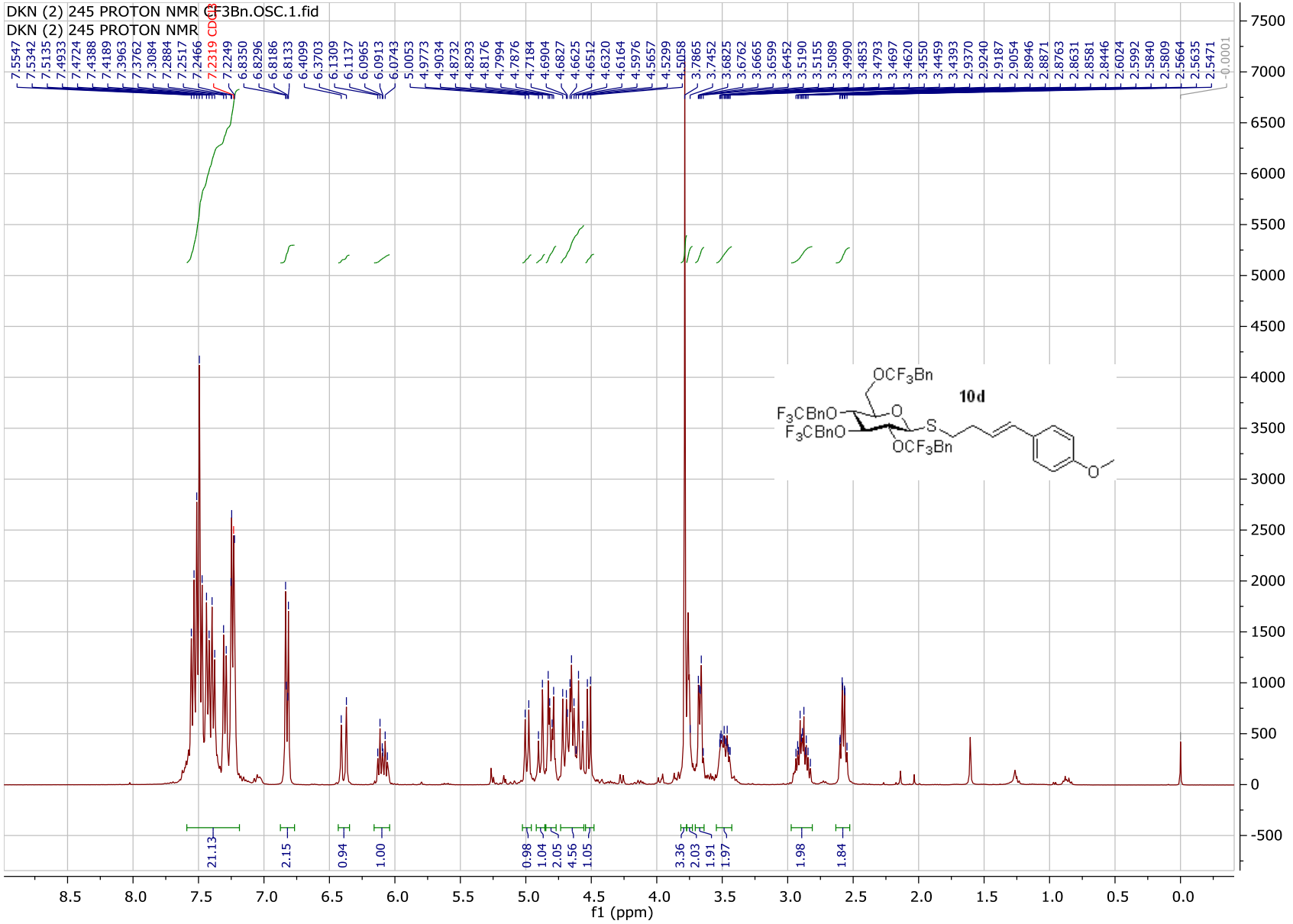
f1 (ppm)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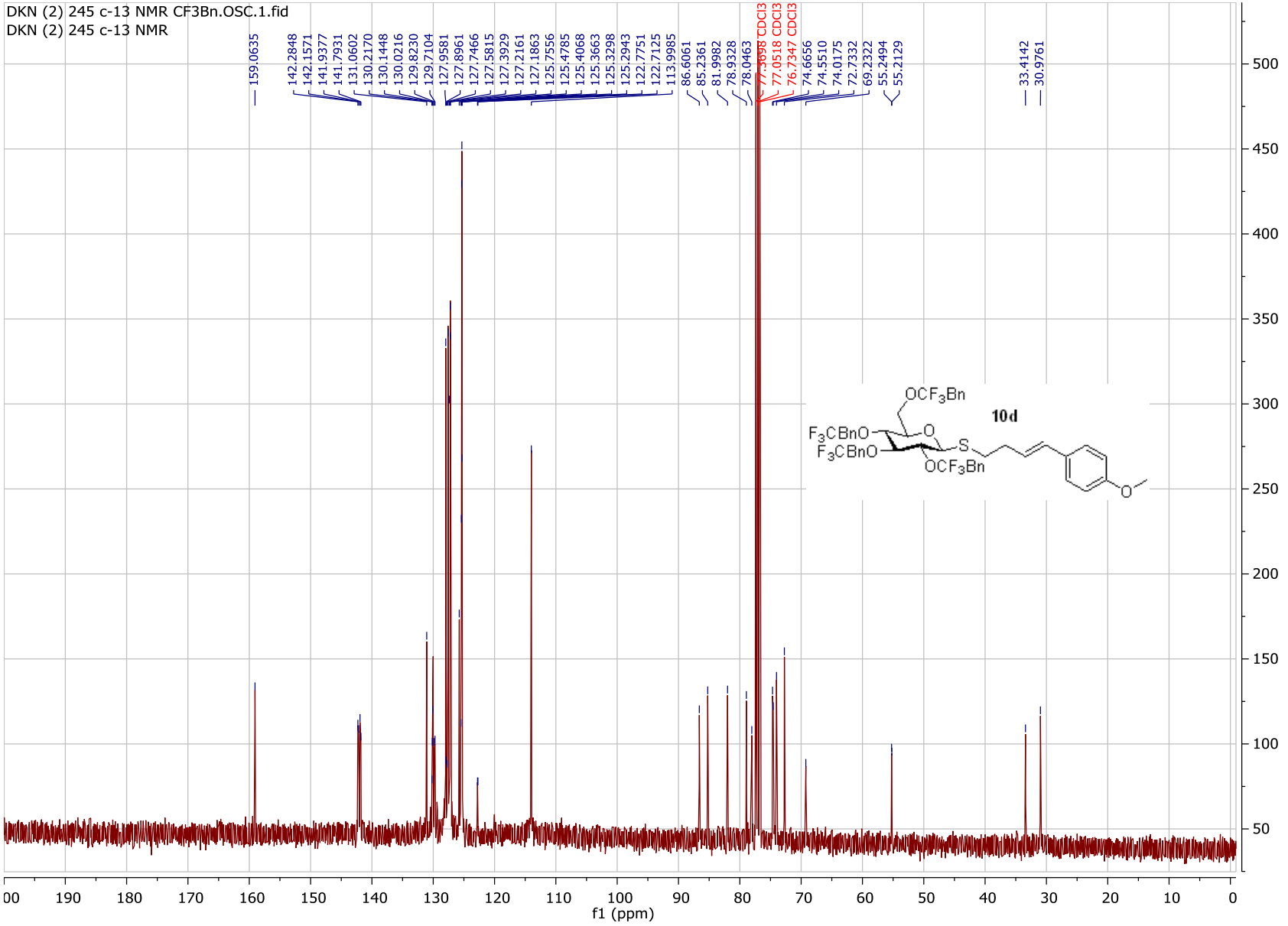
10d
f1 (ppm)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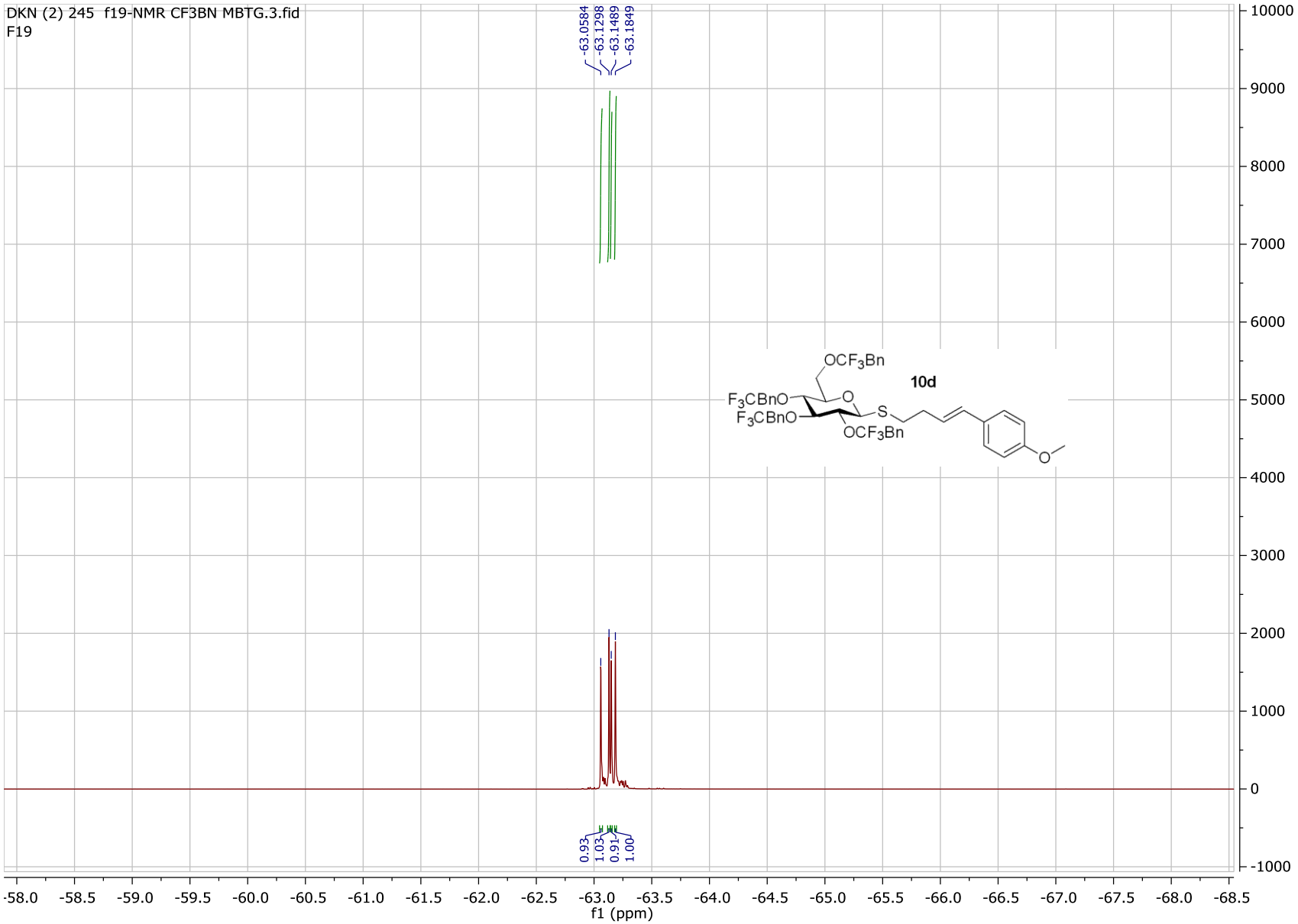
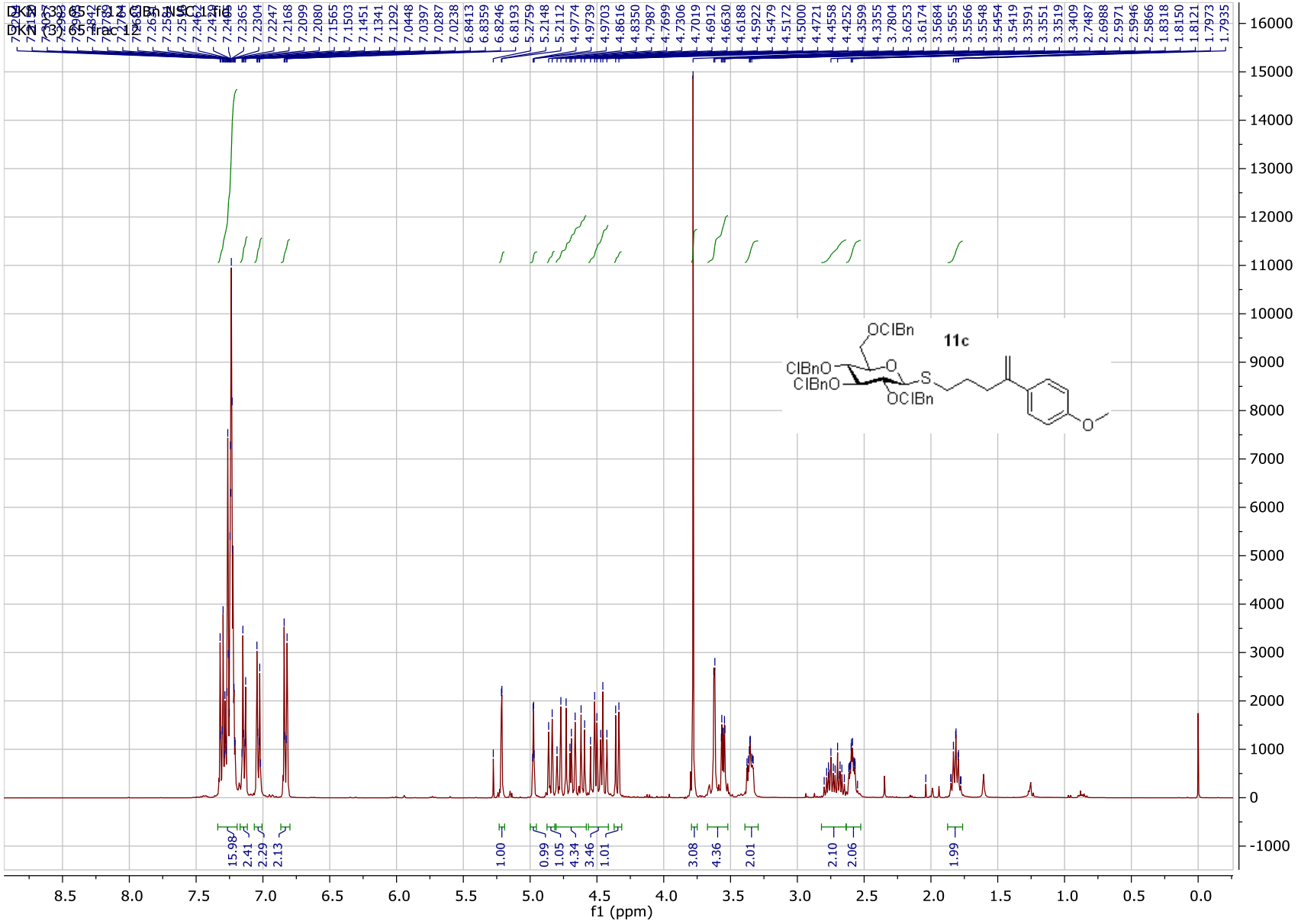
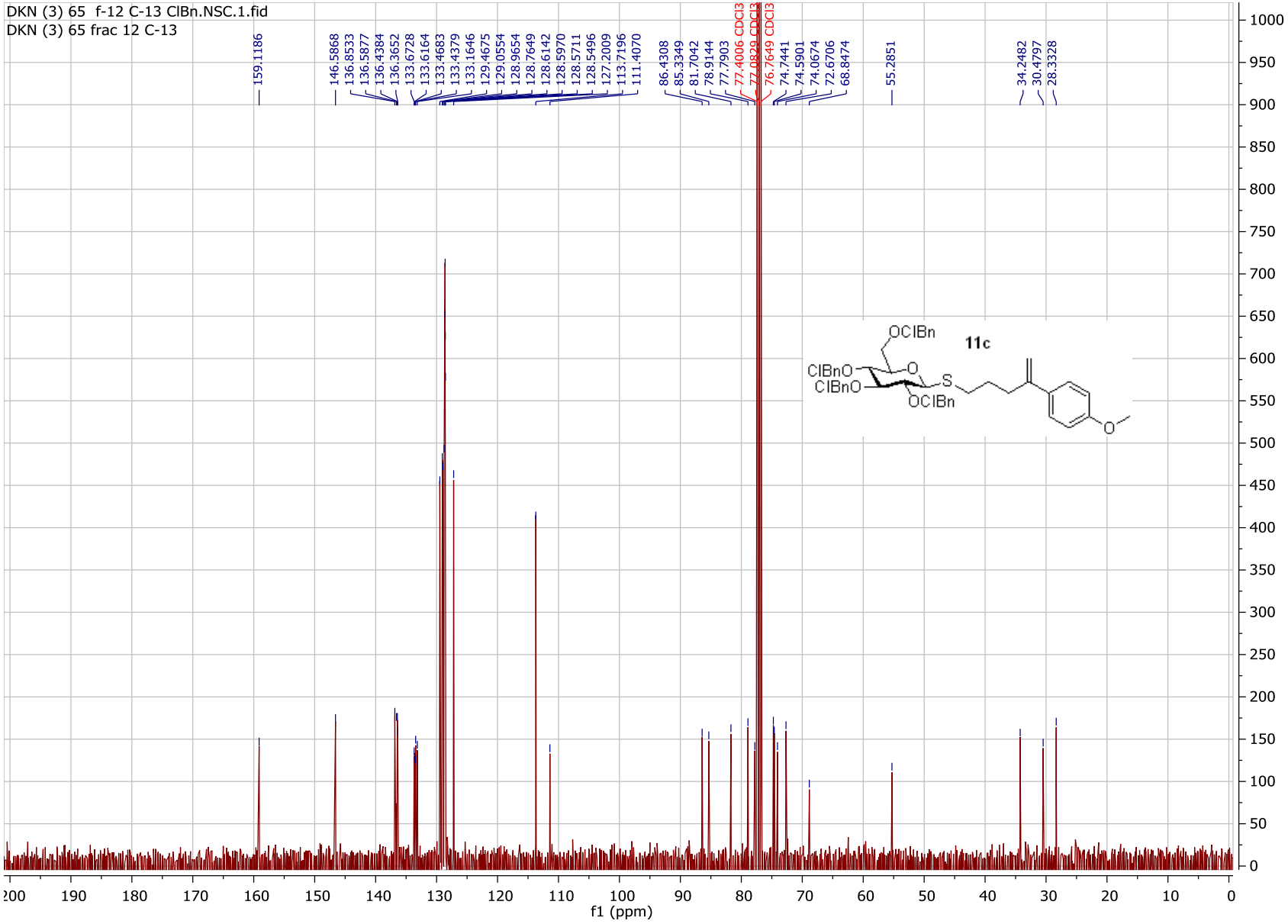
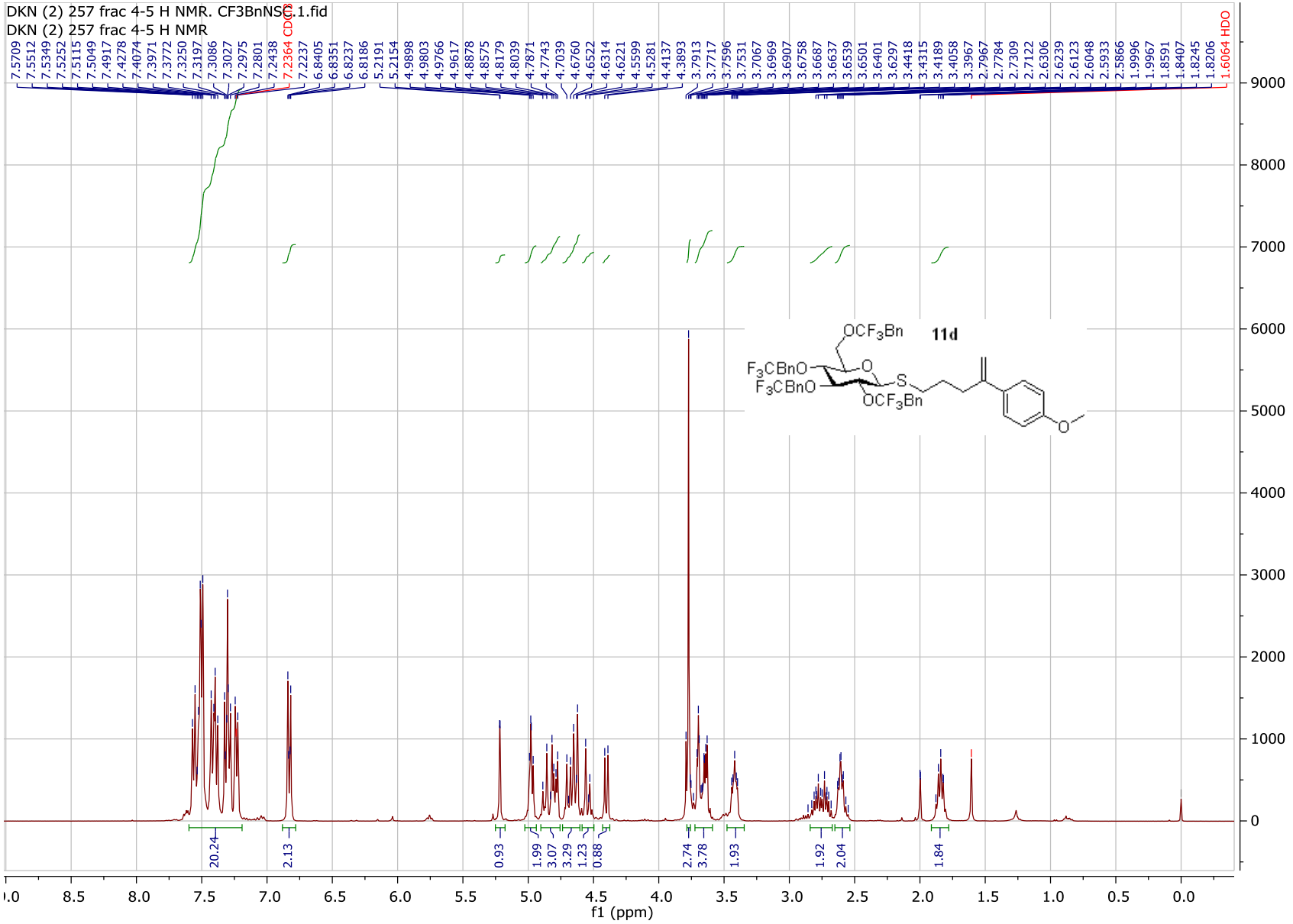
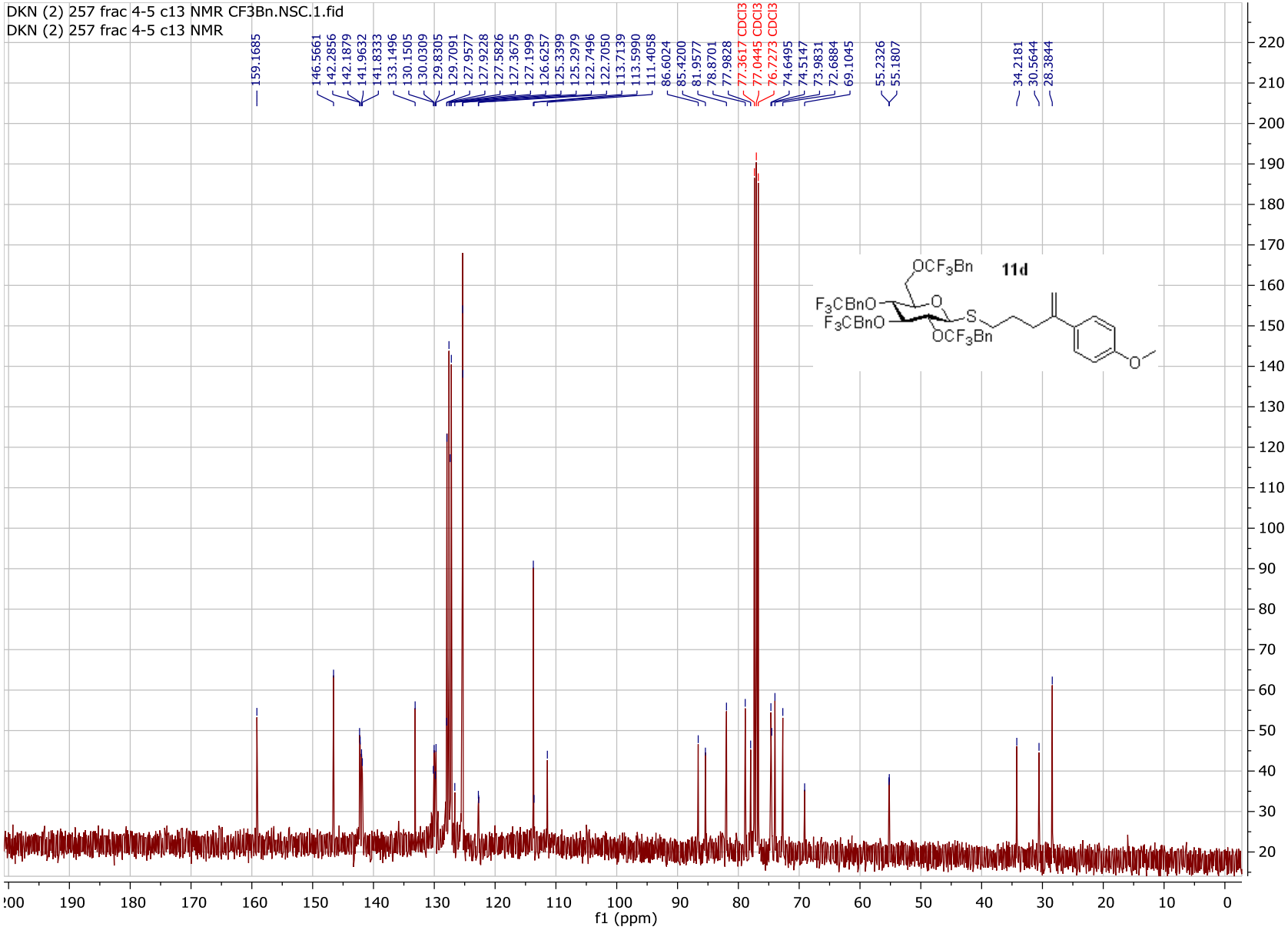
127.1863
125.7556
125.4785
125.4068
125.3663
125.3298
125.2943
122.7751
122.7125
113.9985
86.6061
85.2361
81.9982
78.9328
78.0463
77.3698 CDCl3
77.0518 CDCl3
76.7347 CDCl3
74.6656
74.5510
74.0175
72.7332
69.2322
55.2494
55.2129
33.4142
30.9761
OCF3Bn
F3CBnO
F3CBnO
O
S
OCF3Bn
10d
O
f1 (ppm)

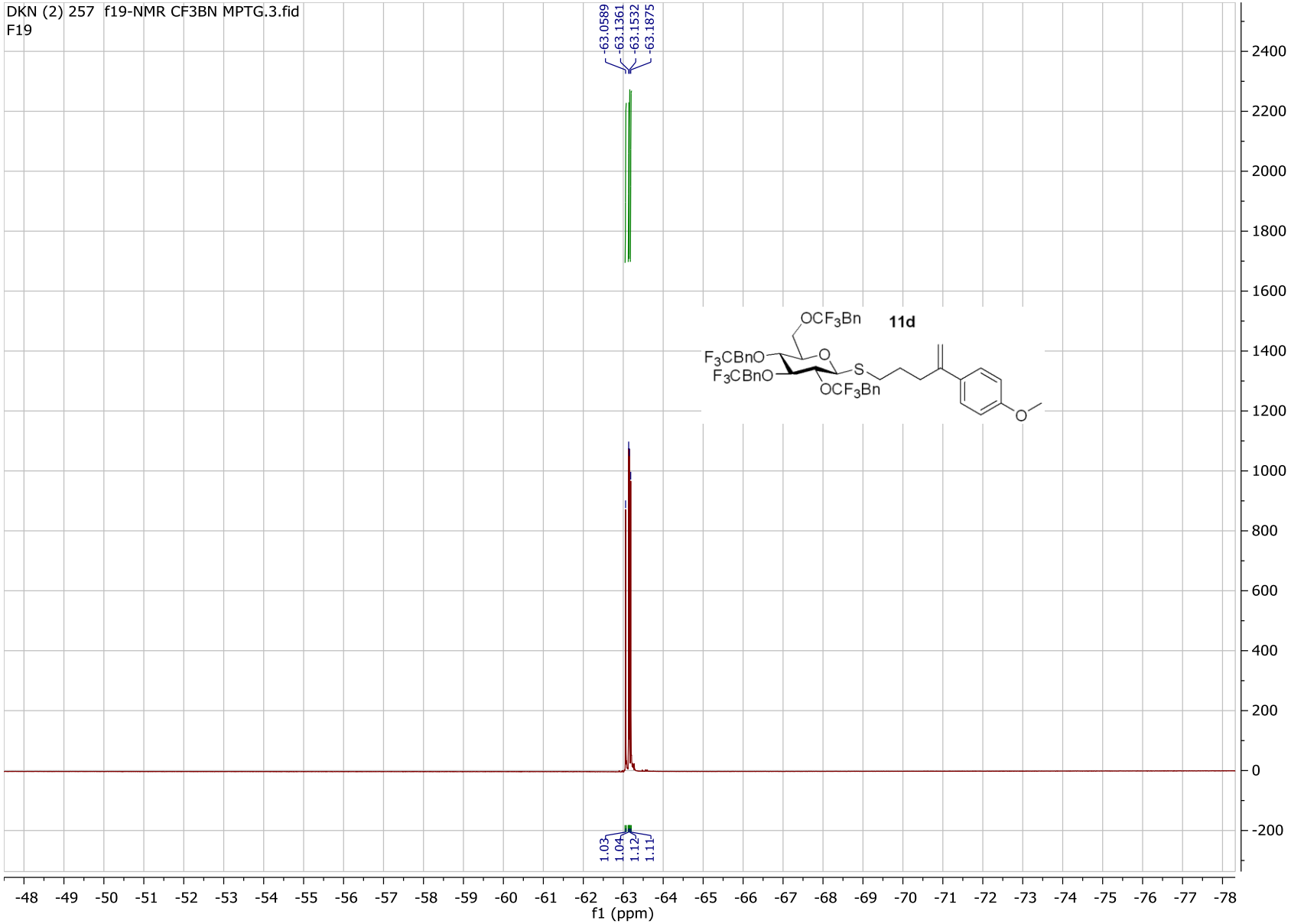

DKN (2) 245 f19-NMR CF3BN MBTG.3.fid
F19
-63.0584
-63.1298
-63.1489
-63.1849
10d
OCF3Bn
F3CBnO
F3CBnO
O
S
OCF3Bn
O
0.93
1.03
0.91
1.00
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-58.0
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
f1 (ppm)

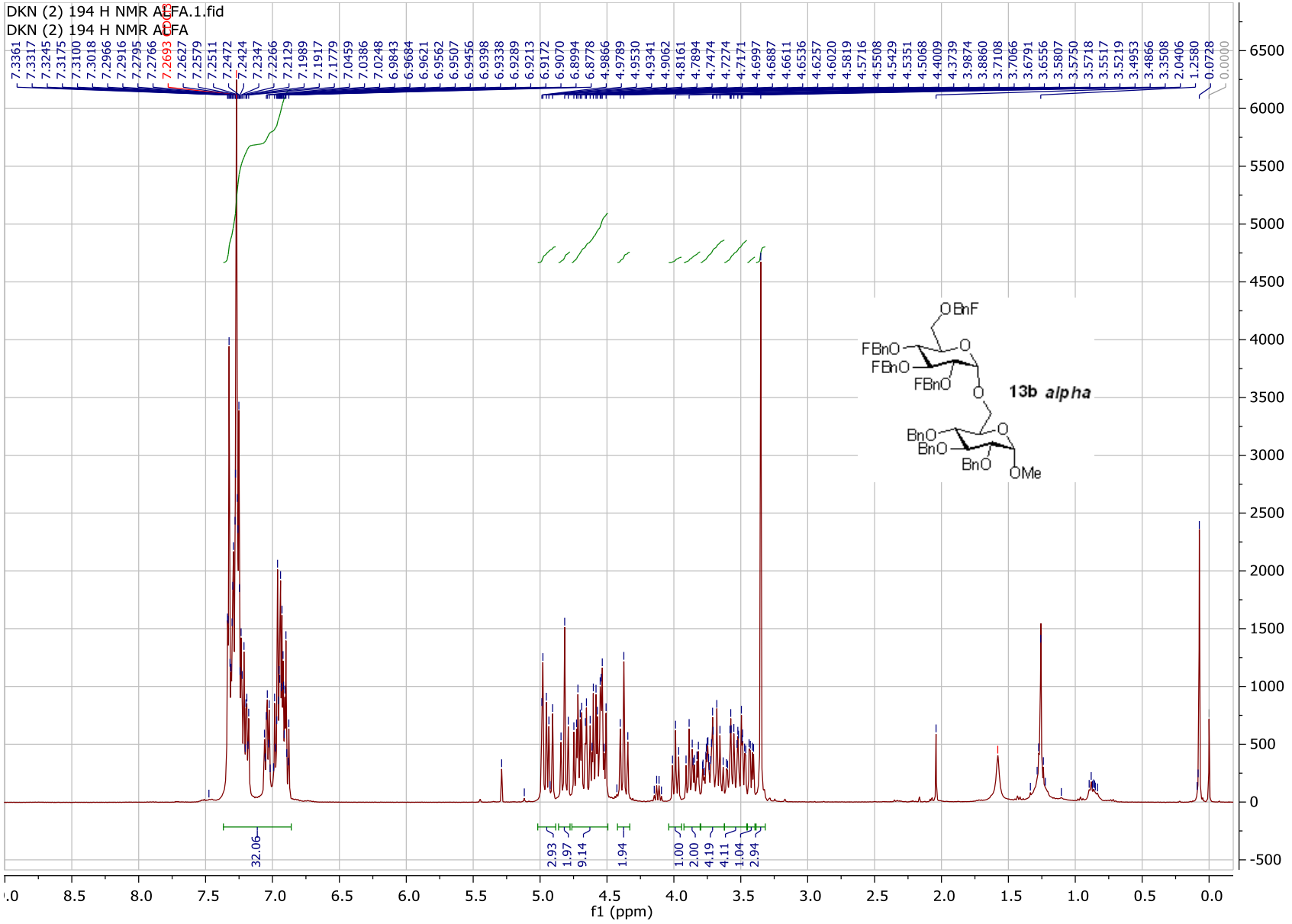

DKN (3) 65 frac 12 CDCl3 NSC 12[6]
DKN (3) 65 frac 12
OClBn
ClBnO
ClBnO
O
S
OClBn
11c
O
f1 (ppm)

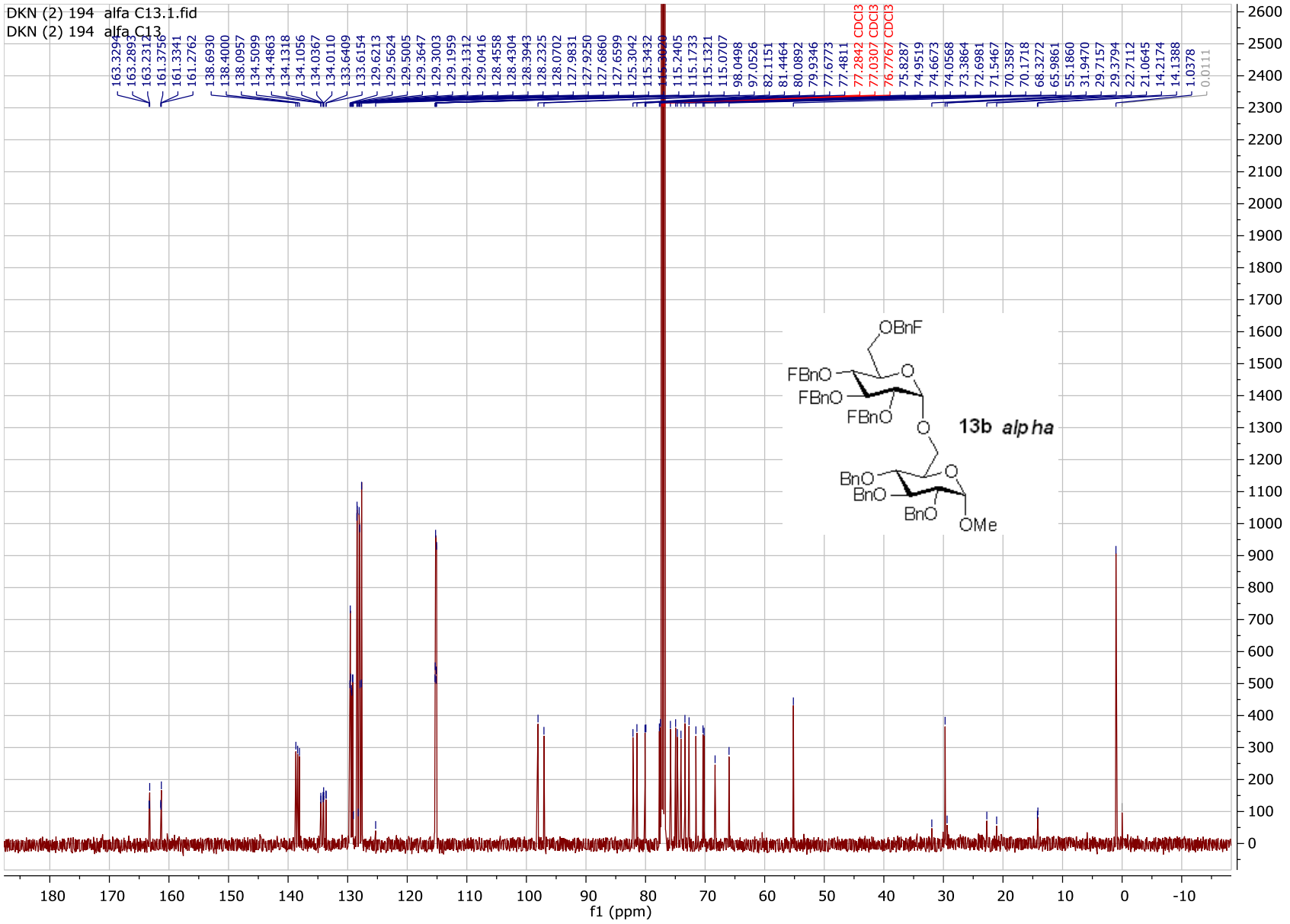

DKN (3) 65 f-12 C-13 ClBn.NSC.1.fid
DKN (3) 65 frac 12 C-13
159.1186
146.5868
136.8533
136.5877
136.4384
136.3652
133.6728
133.6164
133.4683
133.4379
133.1646
129.4675
129.0554
128.9654
128.7649
128.6142
128.5970
128.5711
128.5496
127.2009
113.7196
111.4070
86.4308
85.3349
81.7042
78.9144
77.7903
77.4006 CDCl3
77.0829 CDCl3
76.7649 CDCl3
74.7441
74.5901
74.0674
72.6706
68.8474
55.2851
34.2482
30.4797
28.3328
11c
OClBn
ClBnO
ClBnO
OClBn
S
O
f1 (ppm)

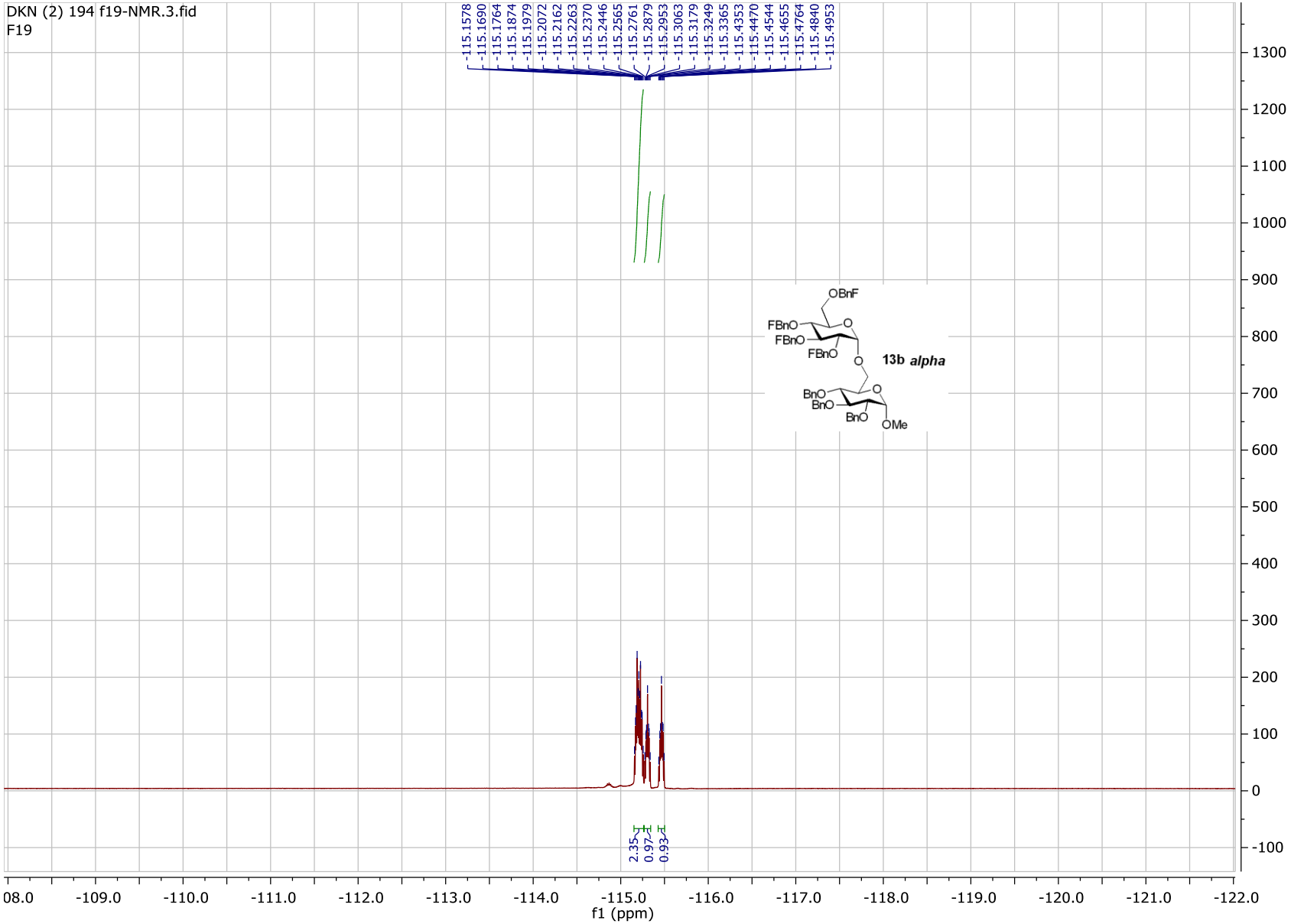

DKN (2) 257 frac 4-5 H NMR. CF3BnNSC.1.fid
DKN (2) 257 frac 4-5 H NMR
7.5709 7.5512 7.5349 7.5252 7.5115 7.5049 7.4917 7.4278 7.4074 7.3971 7.3772 7.3250 7.3197 7.3086 7.3027 7.2975 7.2801 7.2438 7.2364 CDCl3 7.2237 6.8405 6.8351 6.8237 6.8186 5.2191 5.2154 4.9898 4.9803 4.9766 4.9617 4.8878 4.8575 4.8179 4.8039 4.7871 4.7743 4.7039 4.6760 4.6522 4.6314 4.6221 4.5599 4.5281 4.4137 4.3893 3.7913 3.7717 3.7596 3.7531 3.7067 3.6969 3.6907 3.6758 3.6687 3.6637 3.6539 3.6501 3.6401 3.6297 3.4418 3.4315 3.4189 3.4058 3.3967 2.7967 2.7784 2.7309 2.7122 2.6306 2.6239 2.6123 2.6048 2.5933 2.5866 1.9996 1.9967 1.8591 1.8407 1.8245 1.8206 1.6064 HDO
OCF3Bn
11d
F3CBnO
F3CBnO
O
S
OCF3Bn
O
20.24
2.13
0.93
1.99
3.07
3.29
1.23
0.88
2.74
3.78
1.93
1.92
2.04
1.84
f1 (ppm)

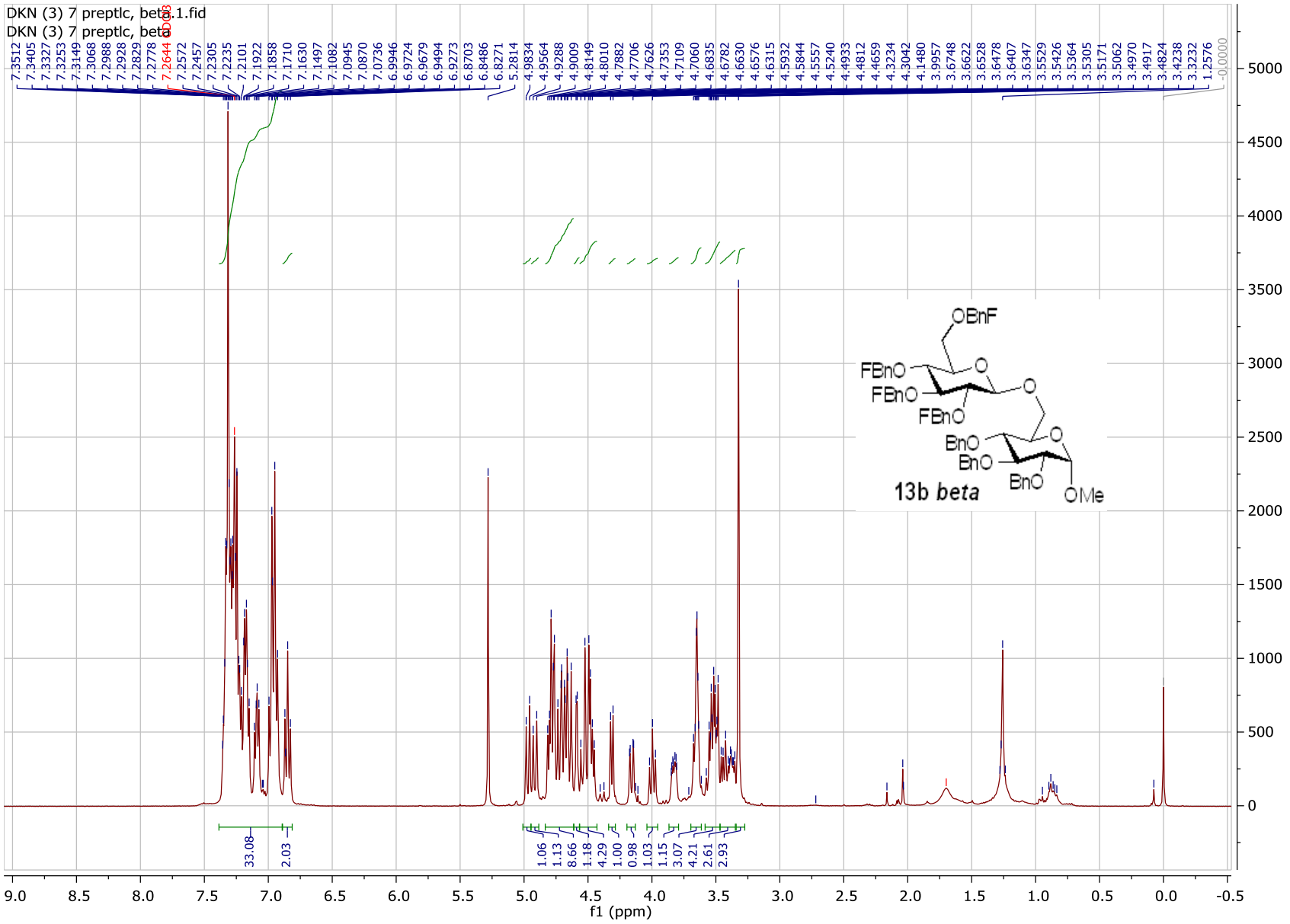

DKN (2) 257 frac 4-5 c13 NMR CF3Bn.NSC.1.fid
DKN (2) 257 frac 4-5 c13 NMR
159.1685
146.5661
142.2856
142.1879
141.9632
141.8333
133.1496
130.1505
130.0309
129.8305
129.7091
127.9577
127.9228
127.5826
127.3675
127.1999
126.6257
125.3399
125.2979
122.7496
122.7050
113.7139
113.5990
111.4058
86.6024
85.4200
81.9577
78.8701
77.9828
77.3617 CDCl3
77.0445 CDCl3
76.7273 CDCl3
74.6495
74.5147
73.9831
72.6884
69.1045
55.2326
55.1807
34.2181
30.5644
28.3844
OCF3Bn
11d
F3CBnO
F3CBnO
O
S
OCF3Bn
O
f1 (ppm)

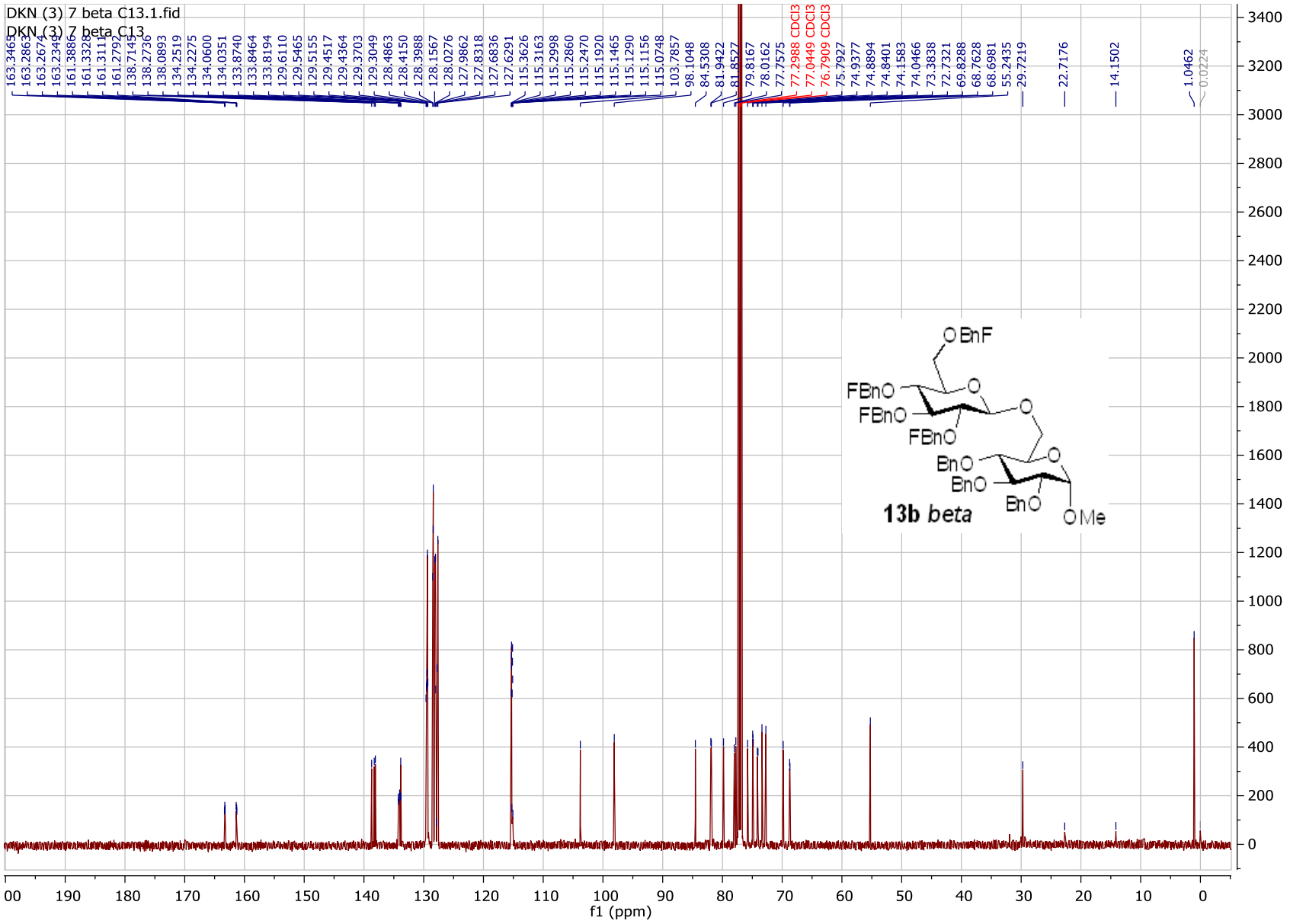

DKN (2) 257 f19-NMR CF3BN MPTG.3.fid
F19
-63.0589
-63.1361
-63.1532
-63.1875
11d
OCF3Bn
F3CBnO
F3CBnO
O
S
OCF3Bn
O
1.03
1.04
1.12
1.11
f1 (ppm)

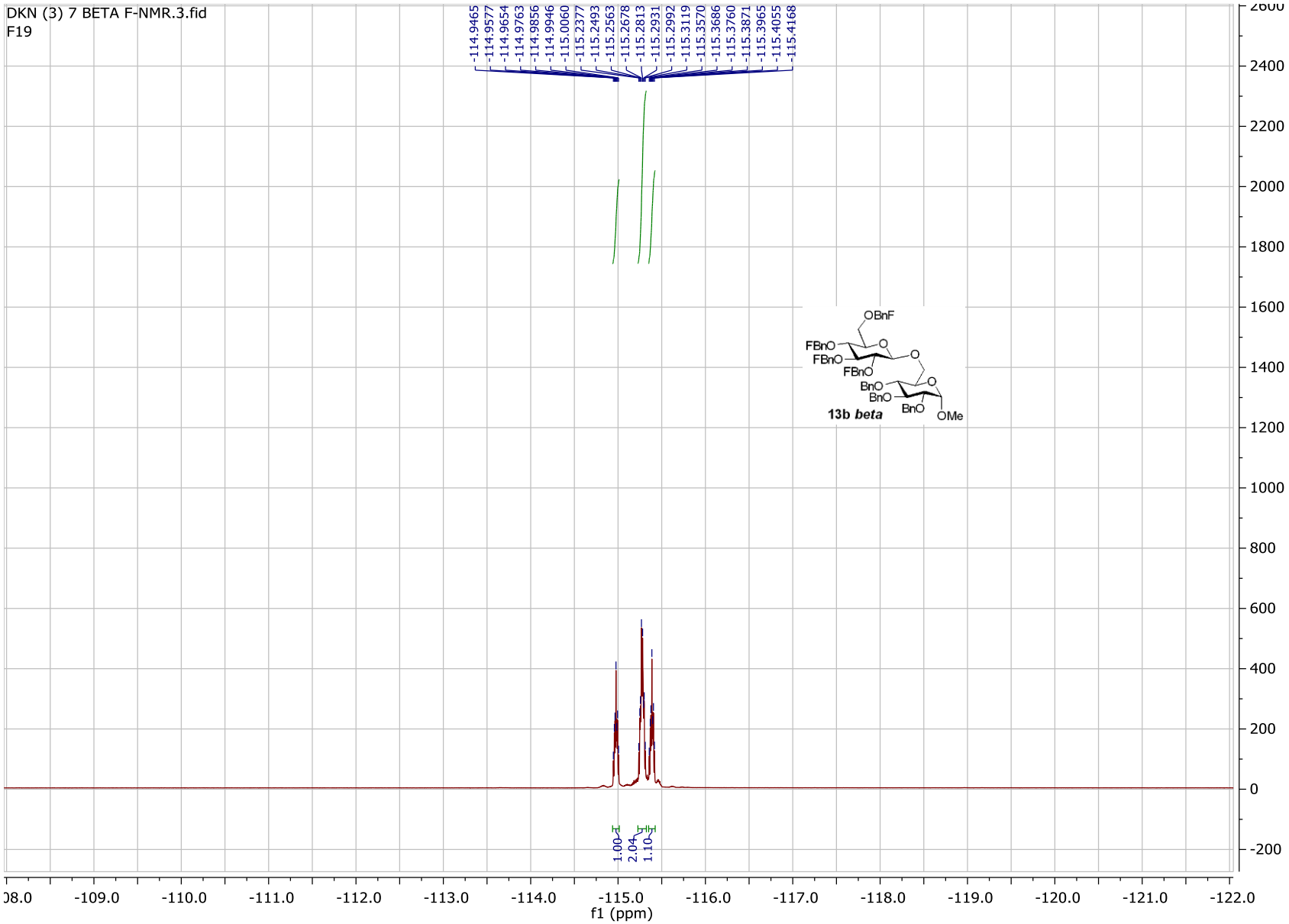

DKN (2) 194 H NMR ALFA.1.fid
DKN (2) 194 H NMR ALFA
OBnF
FBnO
FBnO
FBnO
O
O
13b alpha
BnO
BnO
BnO
O
OMe
32.06
2.93
1.97
9.14
1.94
1.00
2.00
4.19
4.11
1.04
2.94
f1 (ppm)

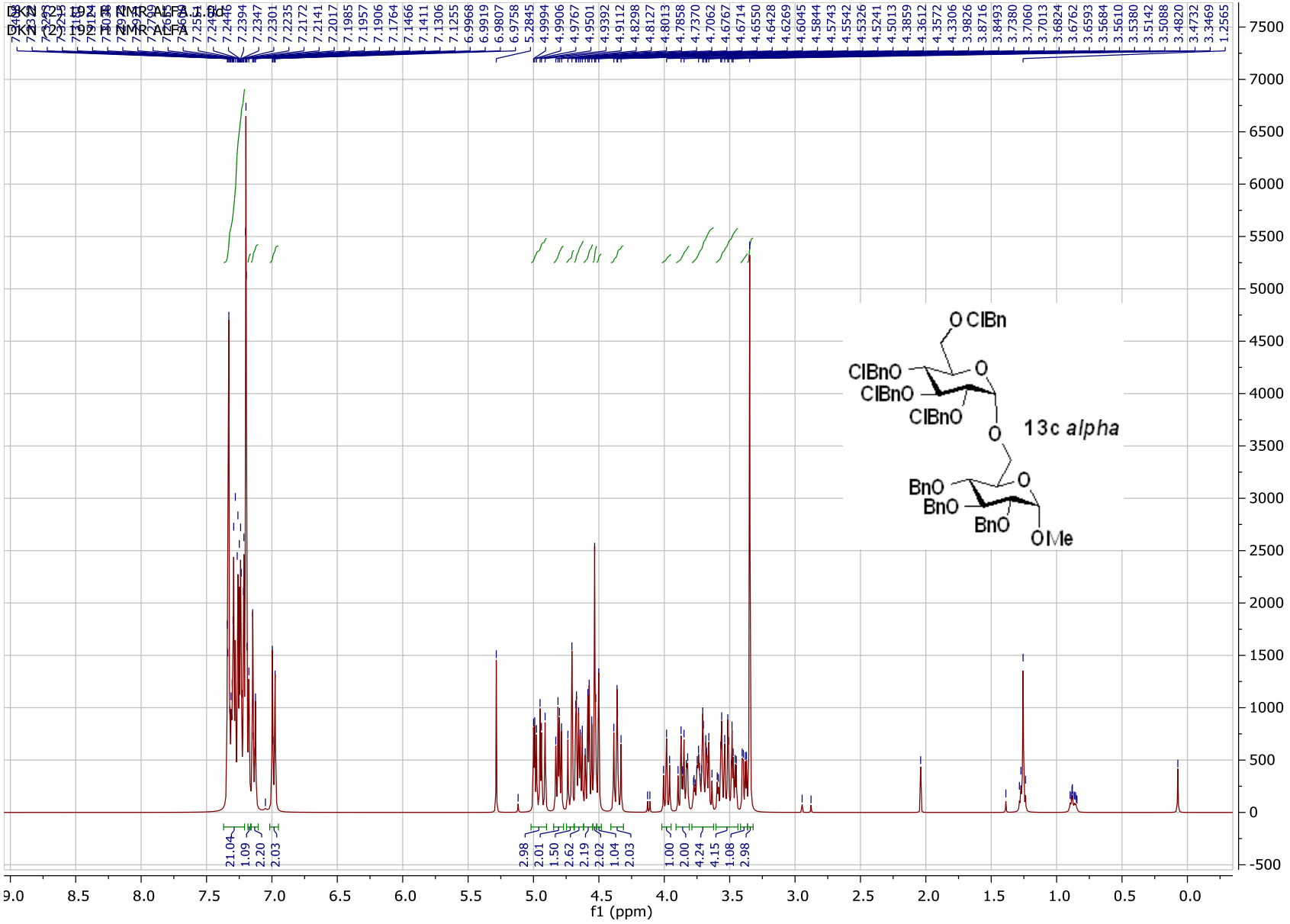

DKN (2) 194 alfa C13.1.fid
DKN (2) 194 alfa C13
163.3294
163.2893
163.2316
161.3756
161.3341
161.2762
138.6930
138.4000
138.0957
134.5099
134.4863
134.1318
134.1056
134.0367
134.0110
133.6409
133.6154
129.6213
129.5624
129.5005
129.3647
129.3003
129.1959
129.1312
129.0416
128.4558
128.4304
128.3943
128.2325
128.0702
127.9831
127.9250
127.6860
127.6599
125.3042
115.3432
115.3030
115.2405
115.1733
115.1321
115.0707
98.0498
97.0526
82.1151
81.4464
80.0892
79.9346
77.6773
77.4811
77.2842 CDCl3
77.0307 CDCl3
76.7767 CDCl3
75.8287
74.9519
74.6673
74.0568
73.3864
72.6981
71.5467
70.3587
70.1718
68.3272
65.9861
55.1860
31.9470
29.7157
29.3794
22.7112
21.0645
14.2174
14.1388
1.0378
0.0111
OBnF
FBnO
FBnO
FBnO
O
O
13b alpha
BnO
BnO
BnO
O
OMe
f1 (ppm)

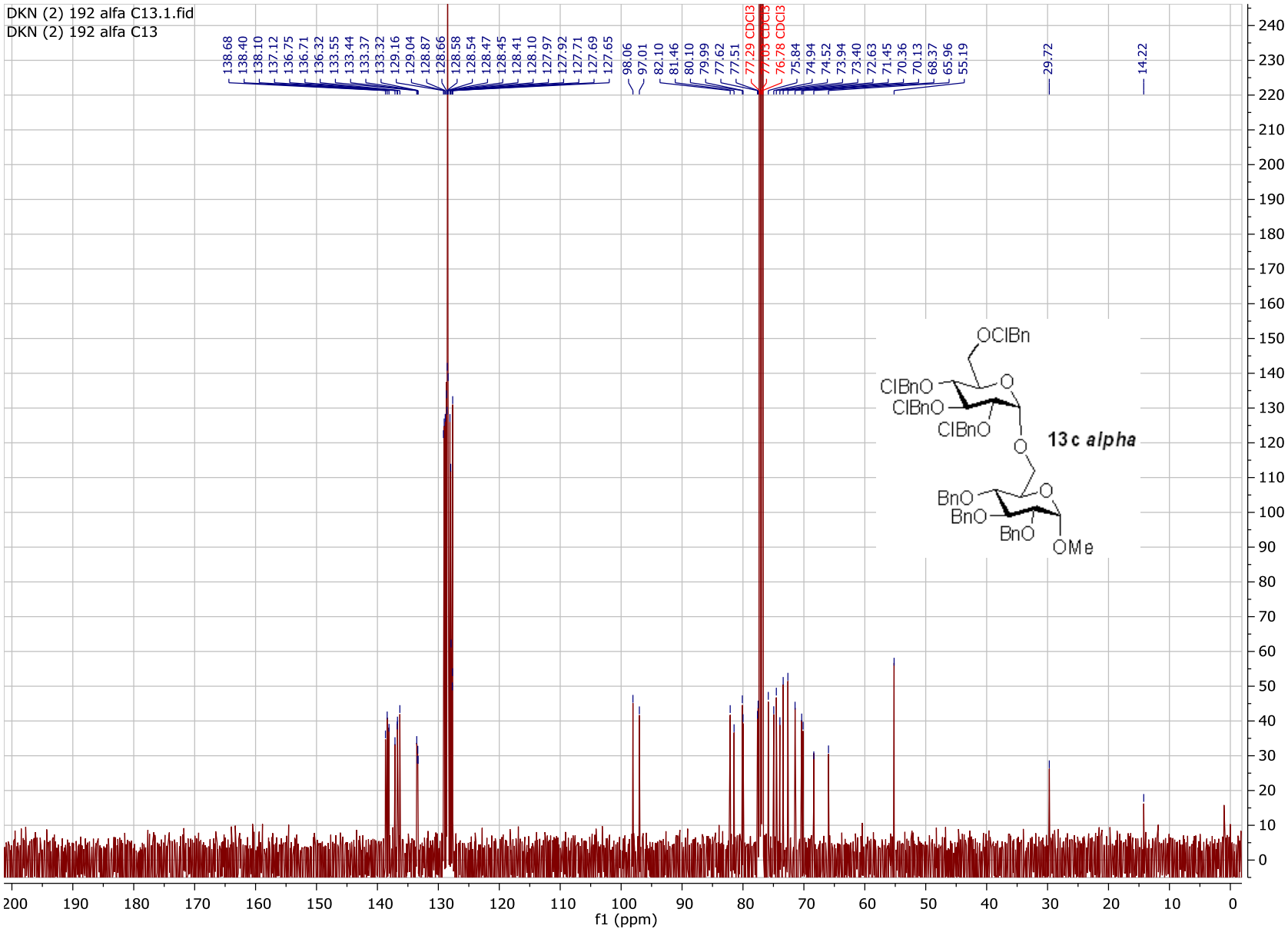

DKN (2) 194 f19-NMR.3.fid
F19
-115.1578
-115.1690
-115.1764
-115.1874
-115.1979
-115.2072
-115.2162
-115.2263
-115.2370
-115.2446
-115.2565
-115.2761
-115.2879
-115.2953
-115.3063
-115.3179
-115.3249
-115.3365
-115.4353
-115.4470
-115.4544
-115.4655
-115.4764
-115.4840
-115.4953
OBnF
FBnO
FBnO
FBnO
O
O
13b alpha
BnO
BnO
BnO
OMe
2.35
0.97
0.93
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
08.0
-109.0
-110.0
-111.0
-112.0
-113.0
-114.0
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
-121.0
-122.0
f1 (ppm)

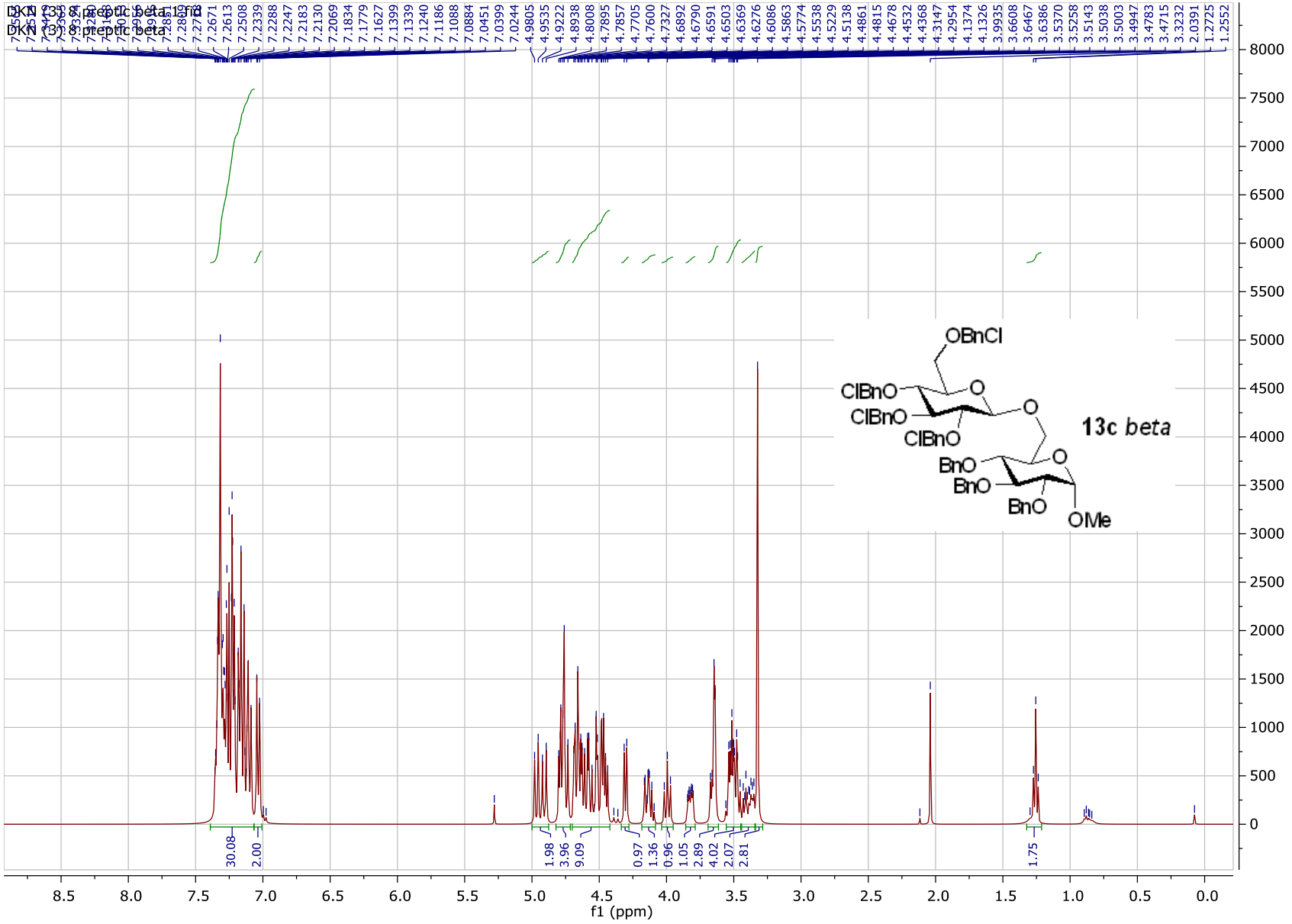

DKN (3) 7 preptlc, beta.1.fid
DKN (3) 7 preptlc, beta
OBnF
FBnO
FBnO
FBnO
O
O
BnO
BnO
BnO
OMe
13b beta
f1 (ppm)

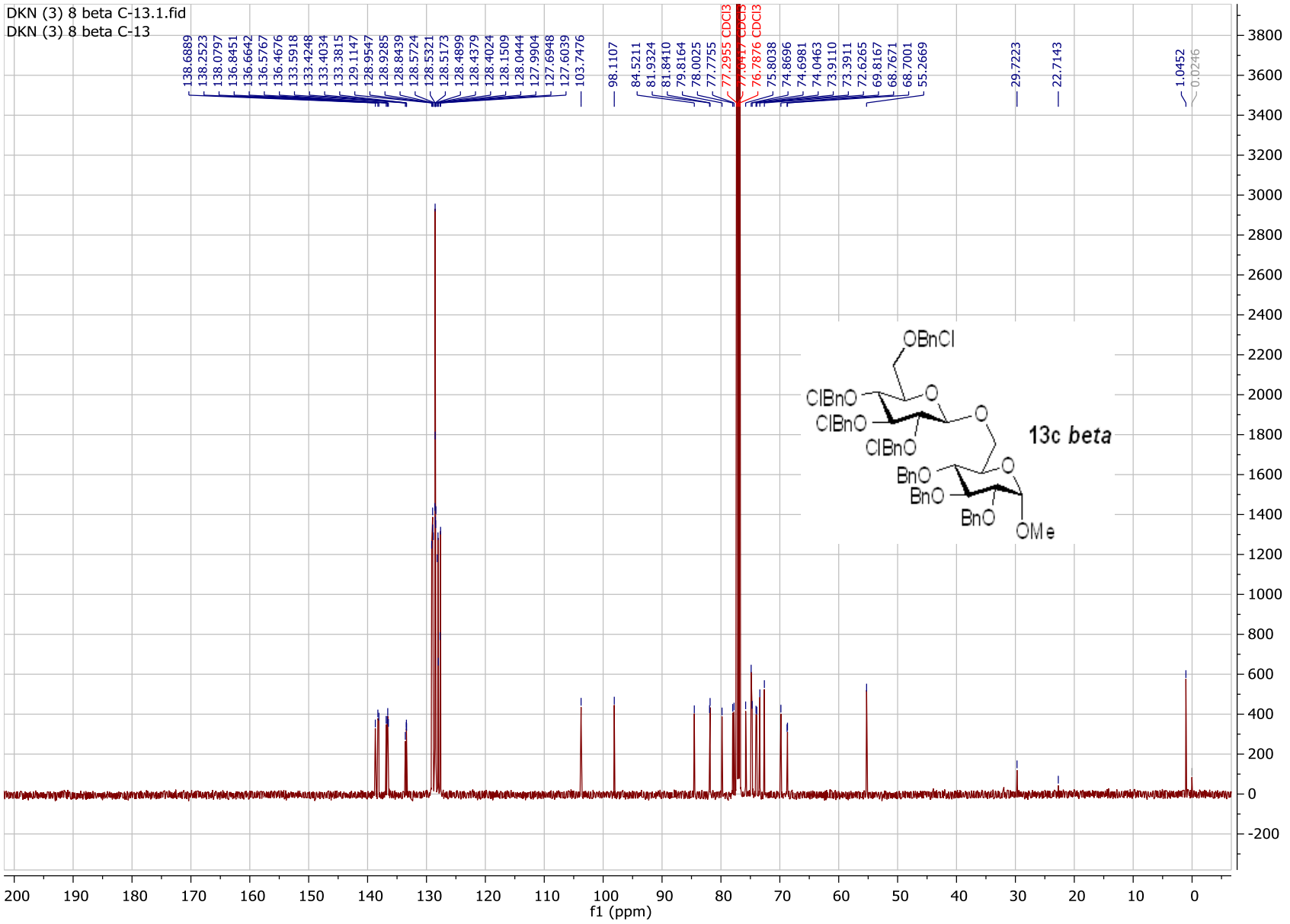

DKN (3) 7 beta C13.1.fid
DKN (3) 7 beta C13
163.3465
163.2863
163.2674
163.2349
161.3886
161.3328
161.3117
161.2797
138.7145
138.2736
138.0893
134.2519
134.2275
134.0600
134.0351
133.8740
133.8464
133.8194
129.6110
129.5465
129.5155
129.4517
129.4364
129.3703
129.3049
128.4863
128.4150
128.3988
128.1567
128.0276
127.9862
127.8318
127.6836
127.6291
115.3626
115.3163
115.2998
115.2860
115.2470
115.1920
115.1465
115.1290
115.1156
115.0748
103.7857
98.1048
84.5308
81.9422
81.8527
79.8167
78.0162
77.7575
77.2988 CDCl3
77.0449 CDCl3
76.7909 CDCl3
75.7927
74.9377
74.8894
74.8401
74.1583
74.0466
73.3838
72.7321
69.8288
68.7628
68.6981
55.2435
29.7219
22.7176
14.1502
1.0462
0.0224
OBnF
FBnO
FBnO
FBnO
O
O
O
BnO
BnO
BnO
OMe
13b beta
f1 (ppm)

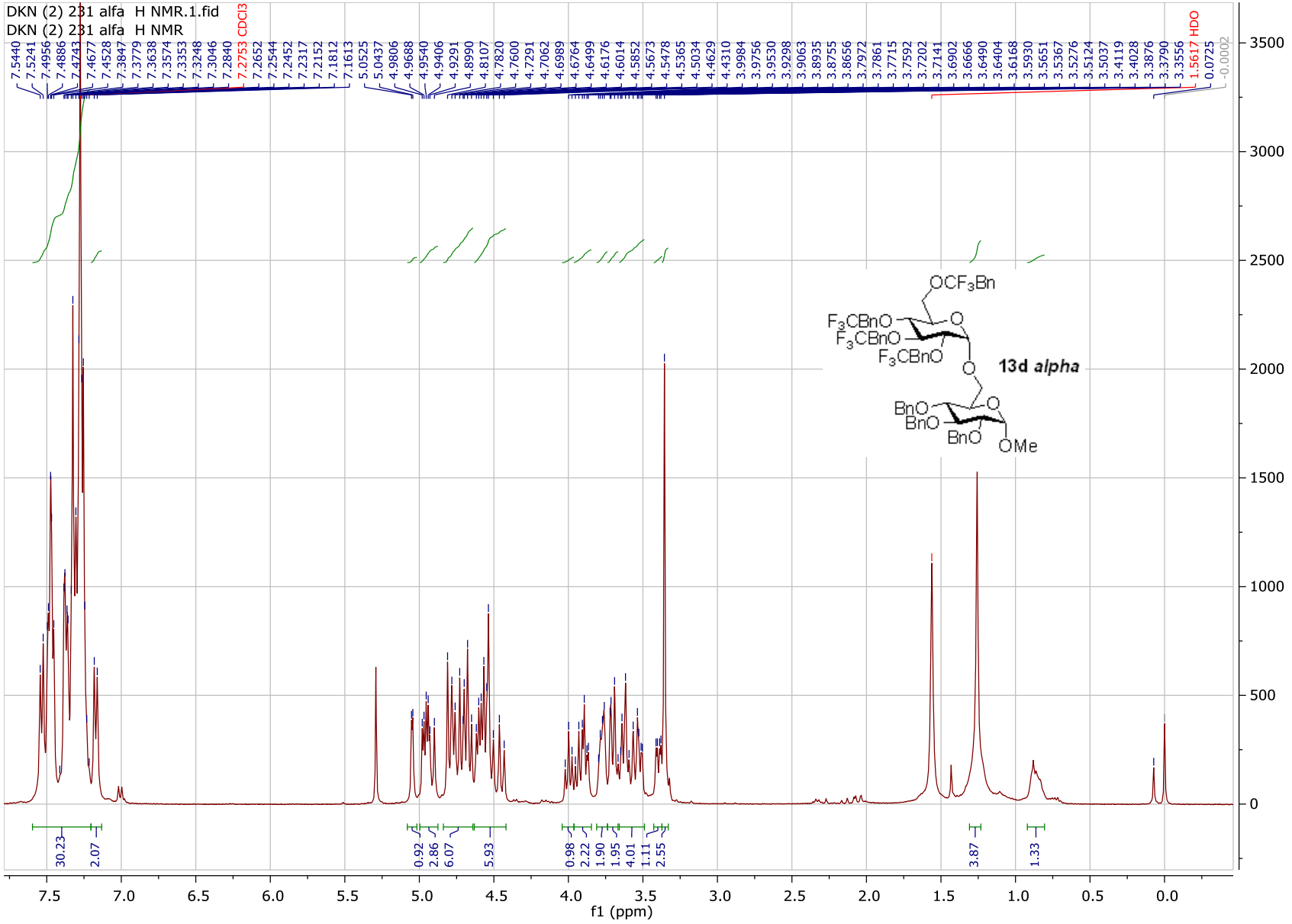

DKN (3) 7 BETA F-NMR.3.fid
F19
-114.9465
-114.9577
-114.9654
-114.9763
-114.9856
-114.9946
-115.0060
-115.2377
-115.2493
-115.2563
-115.2678
-115.2813
-115.2931
-115.2992
-115.3119
-115.3570
-115.3686
-115.3760
-115.3871
-115.3965
-115.4055
-115.4168
OBnF
FBnO
FBnO
FBnO
BnO
BnO
BnO
OMe
13b beta
1.00
2.04
1.10
f1 (ppm)

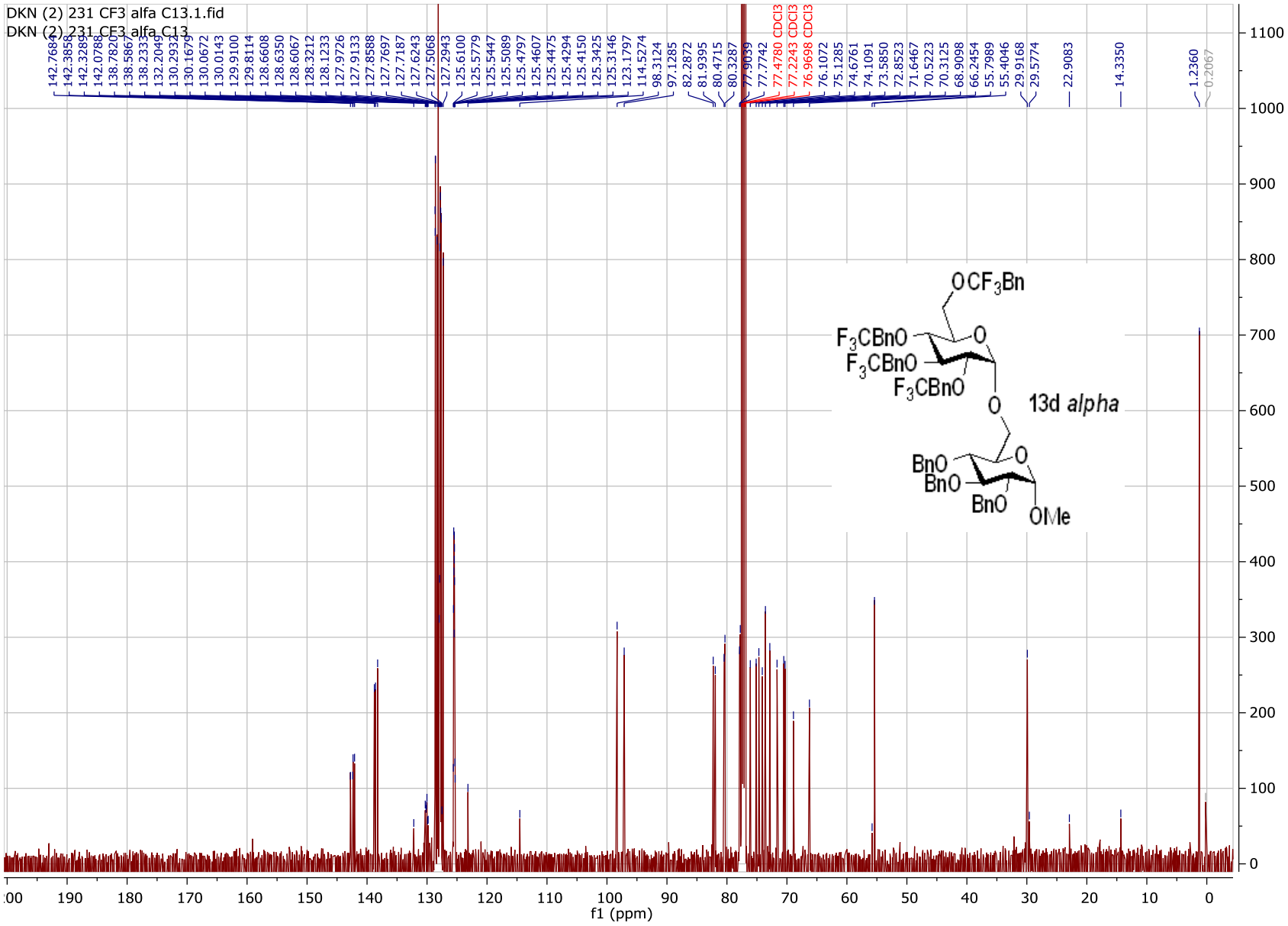

DKN (2).192.1.fid NMR ALFA 1.8d
DKN (2).192.1 H NMR ALFA
O ClBn
ClBnO
ClBnO
ClBnO
O
O
13c alpha
BnO
BnO
BnO
O
OMe
f1 (ppm)

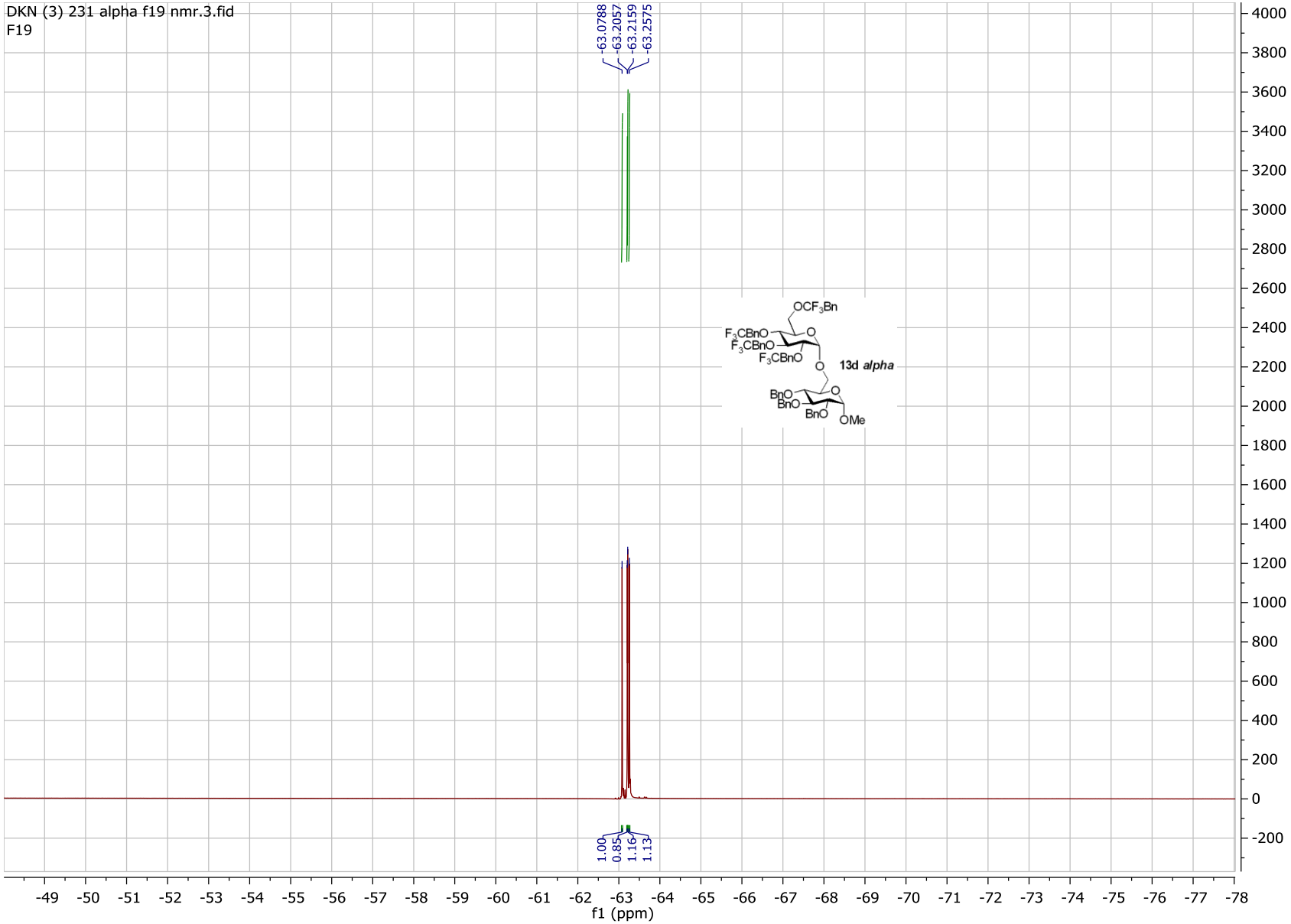

DKN (2) 192 alfa C13.1.fid
DKN (2) 192 alfa C13
138.68
138.40
138.10
137.12
136.75
136.71
136.32
133.55
133.44
133.37
133.32
129.16
129.04
128.87
128.66
128.58
128.54
128.47
128.45
128.41
128.10
127.97
127.92
127.71
127.69
127.65
98.06
97.01
82.10
81.46
80.10
79.99
77.62
77.51
77.29 CDCl3
77.03 CDCl3
76.78 CDCl3
75.84
74.94
74.52
73.94
73.40
72.63
71.45
70.36
70.13
68.37
65.96
55.19
29.72
14.22
OClBn
ClBnO
ClBnO
ClBnO
O
O
13c alpha
BnO
BnO
BnO
O
OMe
f1 (ppm)

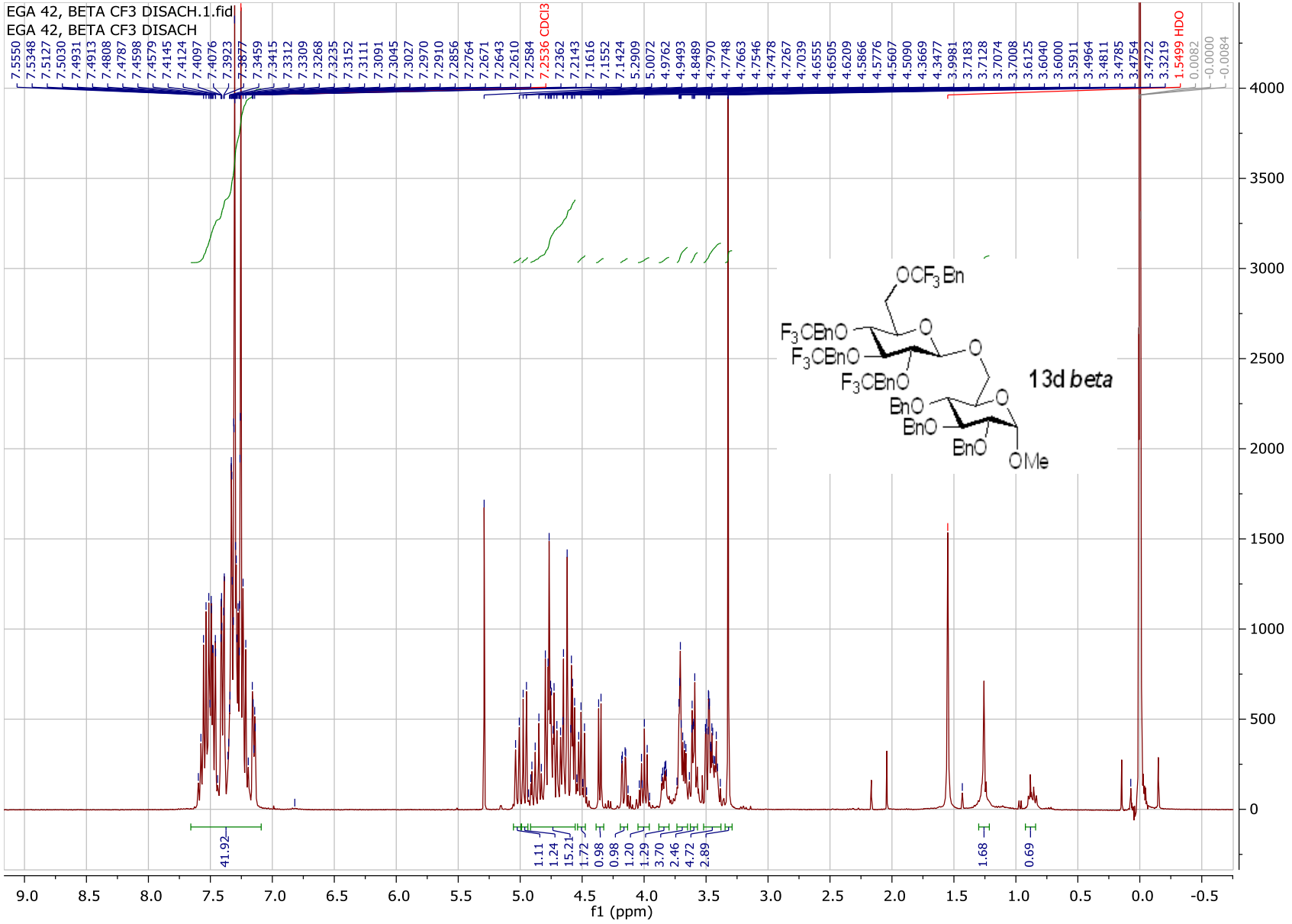

DKN (3) 8 preptlc beta.1r2
DKN (3) 8 preptlc beta
OBnCl
ClBnO
ClBnO
ClBnO
O
O
O
BnO
BnO
BnO
OMe
13c beta
30.08
2.00
1.98
3.96
9.09
0.97
1.36
0.96
1.05
2.89
4.02
2.07
2.81
1.75
f1 (ppm)

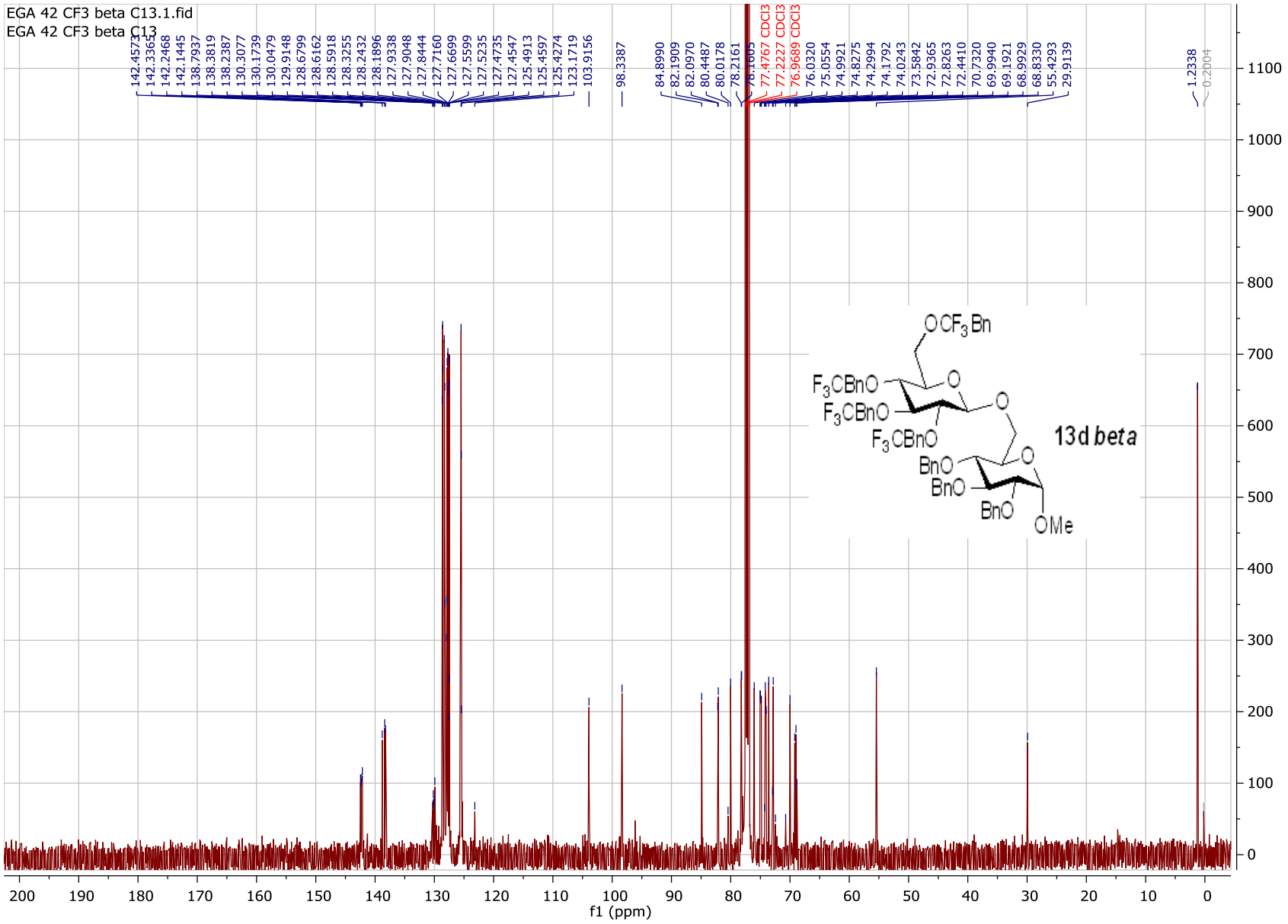

DKN (3) 8 beta C-13.1.fid
DKN (3) 8 beta C-13
138.6889
138.2523
138.0797
136.8451
136.6642
136.5767
136.4676
133.5918
133.4248
133.4034
133.3815
129.1147
128.9547
128.9285
128.8439
128.5724
128.5321
128.5173
128.4899
128.4379
128.4024
128.1509
128.0444
127.9904
127.6948
127.6039
103.7476
98.1107
84.5211
81.9324
81.8410
79.8164
78.0025
77.7755
77.2955 CDCl3
76.7876 CDCl3
75.8038
74.8696
74.6981
74.0463
73.9110
73.3911
72.6265
69.8167
68.7671
68.7001
55.2669
29.7223
22.7143
1.0452
0.0246
OBnCl
ClBnO
ClBnO
ClBnO
BnO
BnO
BnO
OMe
13c beta
f1 (ppm)

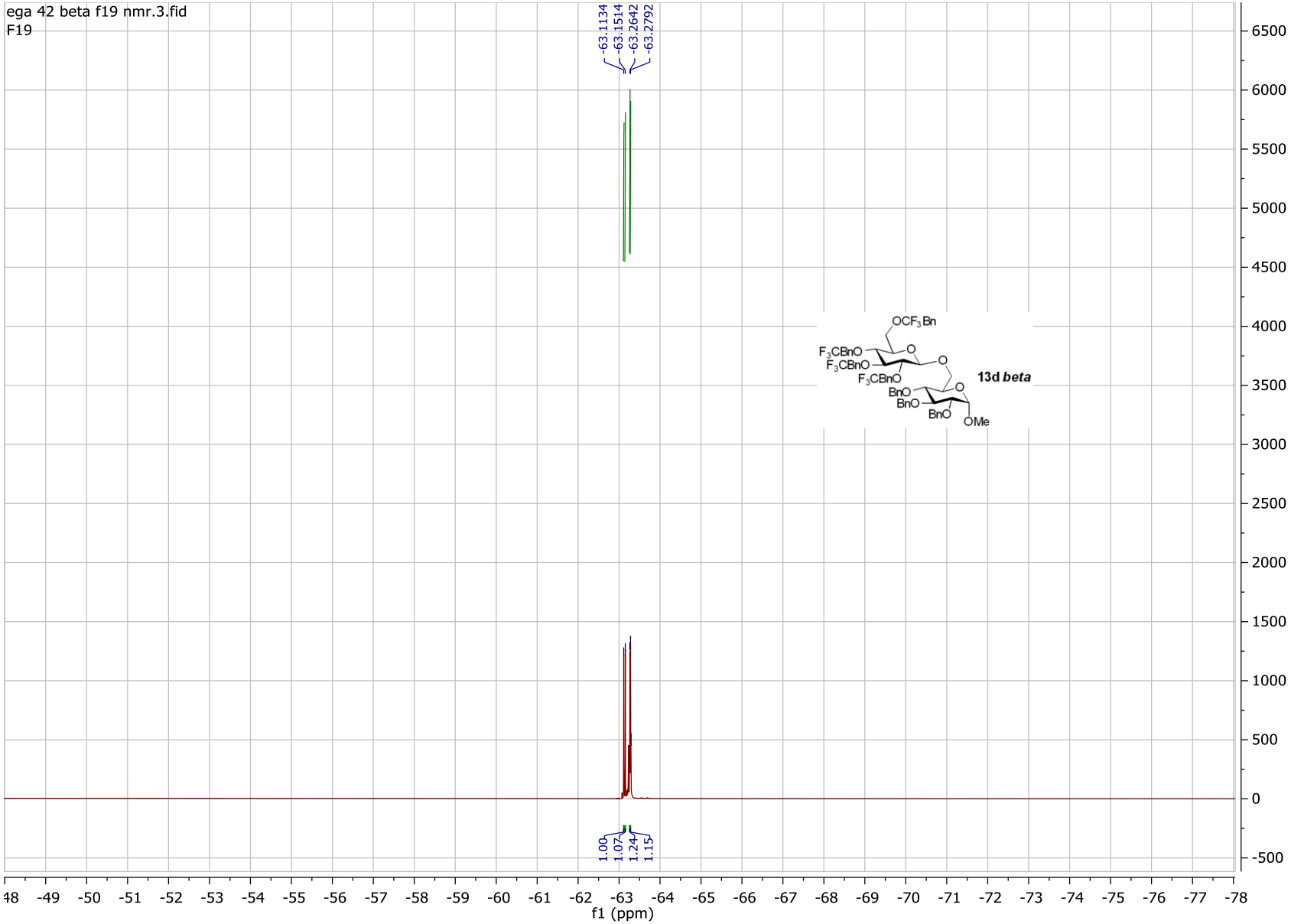

DKN (2) 231 alfa H NMR.1.fid
DKN (2) 231 alfa H NMR
CDCl3
HDO
13d alpha
f1 (ppm)

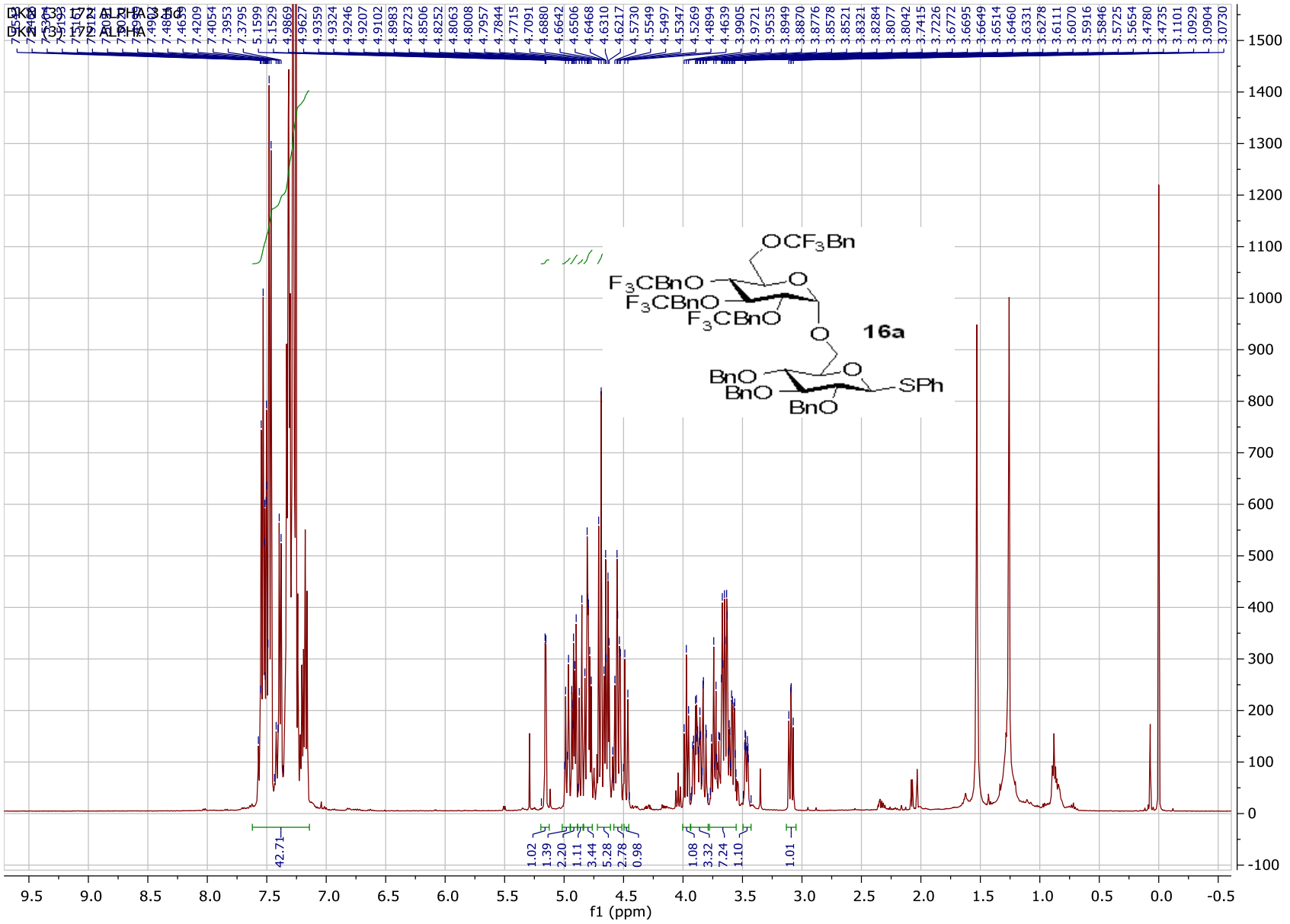

DKN (2) 231 CF3 alfa C13.1.fid
DKN (2) 231 CF3 alfa C13
142.7684
142.3856
142.3289
142.0788
138.7820
138.5867
138.2333
132.2049
130.2932
130.1679
130.0672
130.0143
129.9100
129.8114
128.6608
128.6350
128.6067
128.3212
128.1233
127.9726
127.9133
127.8588
127.7697
127.7187
127.6243
127.5068
127.2943
125.6100
125.5779
125.5447
125.5089
125.4797
125.4607
125.4475
125.4294
125.4150
125.3425
125.3146
123.1797
114.5274
98.3124
97.1285
82.2872
81.9395
80.4715
80.3287
77.9039
77.7742
77.4780 CDCl3
77.2243 CDCl3
76.9698 CDCl3
76.1072
75.1285
74.6761
74.1091
73.5850
72.8523
71.6467
70.5223
70.3125
68.9098
66.2454
55.7989
55.4046
29.9168
29.5774
22.9083
14.3350
1.2360
0.2067
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
13d alpha
BnO
BnO
BnO
OMe
f1 (ppm)

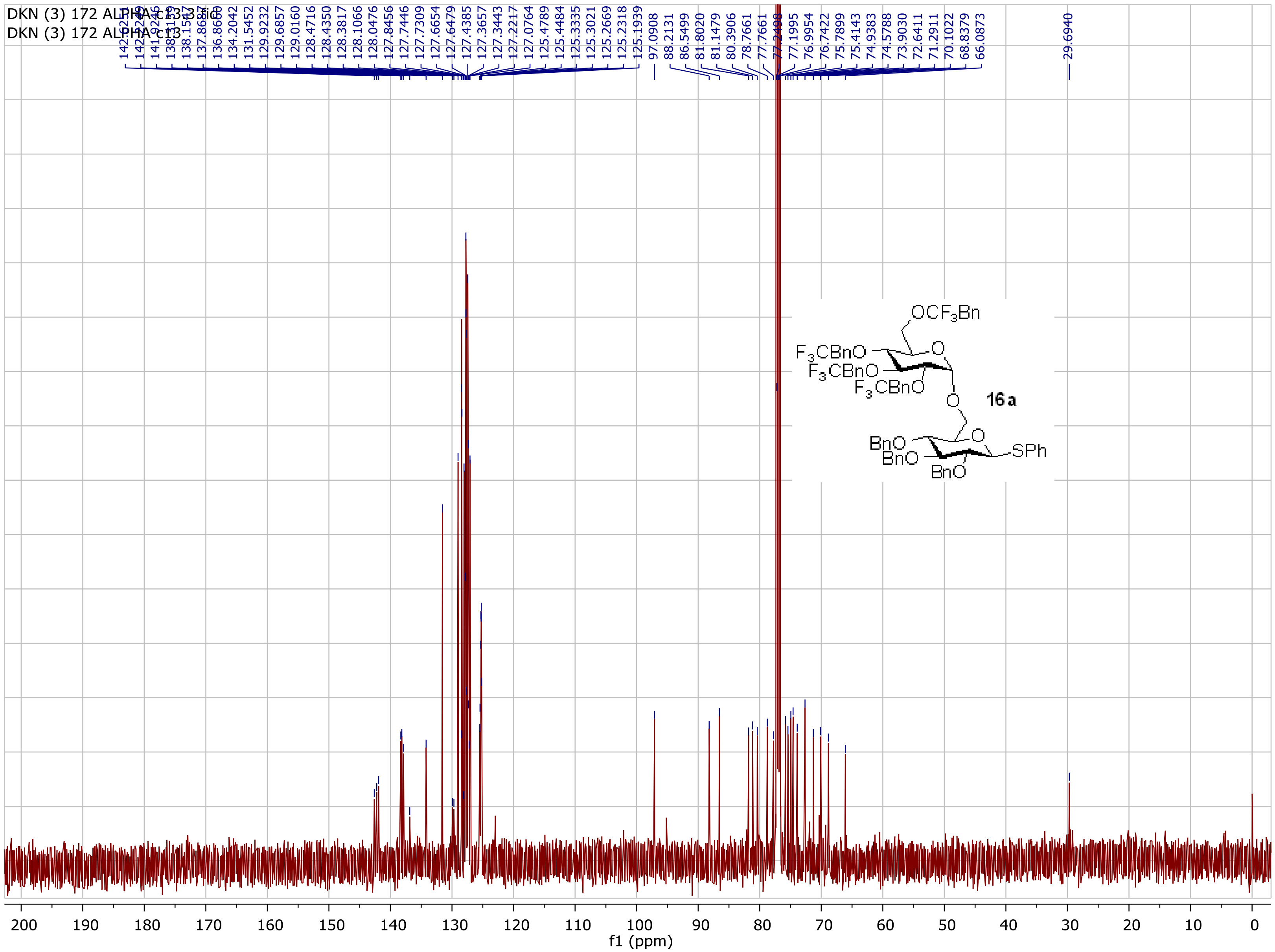

DKN (3) 231 alpha f19 nmr.3.fid
F19
-63.0788
-63.2057
-63.2159
-63.2575
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
13d alpha
BnO
BnO
BnO
OMe
1.00
0.85
1.16
1.13
f1 (ppm)

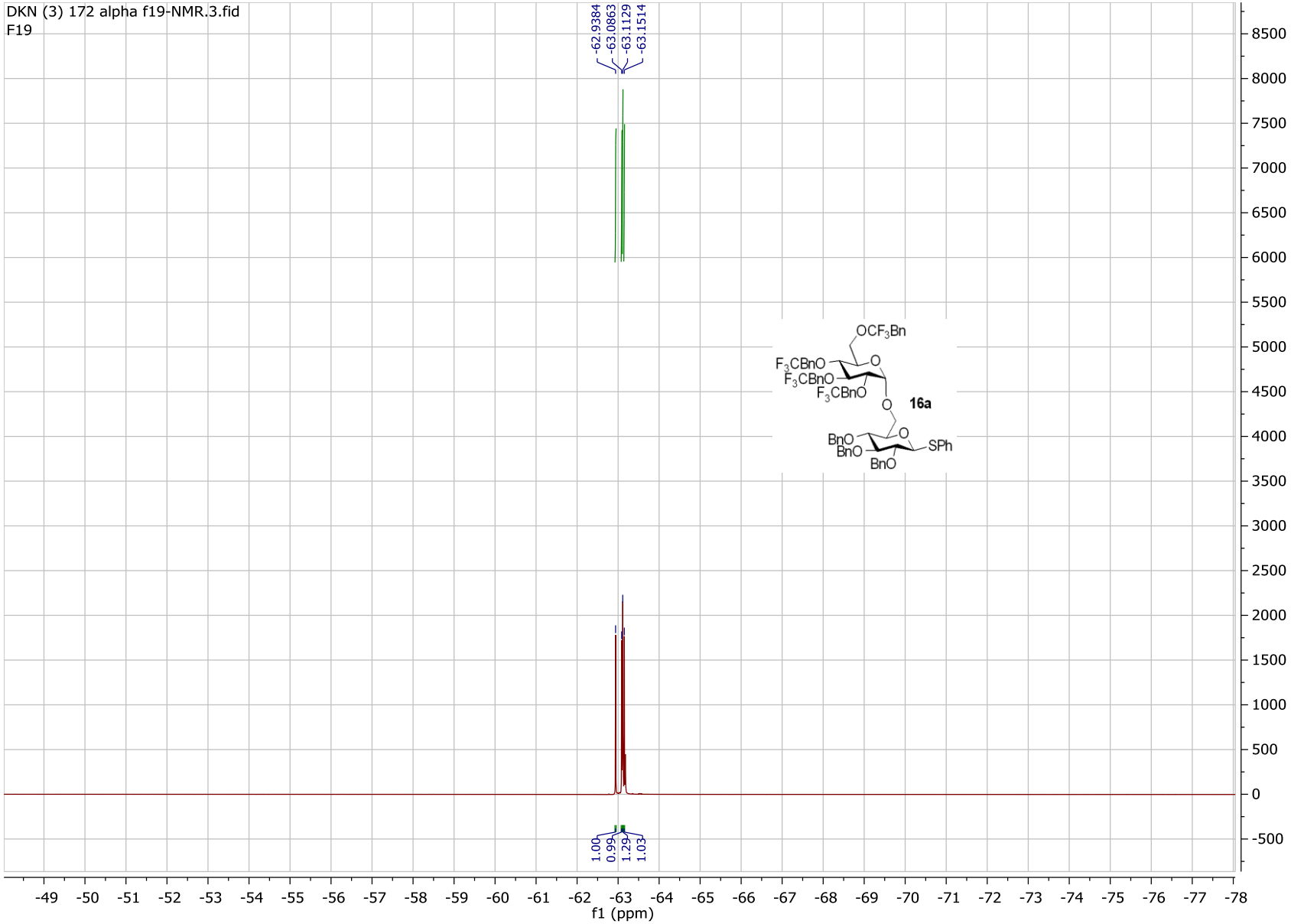

EGA 42, BETA CF3 DISACH.1.fid
EGA 42, BETA CF3 DISACH
7.5550 7.5348 7.5127 7.5030 7.4931 7.4913 7.4808 7.4787 7.4598 7.4579 7.4145 7.4124 7.4097 7.4076 7.3923 7.3877 7.3459 7.3415 7.3312 7.3309 7.3268 7.3235 7.3152 7.3111 7.3091 7.3045 7.3027 7.2970 7.2910 7.2856 7.2764 7.2671 7.2643 7.2610 7.2584 7.2536 CDCl3 7.2362 7.2143 7.1616 7.1552 7.1424 5.2909 5.0072 4.9762 4.9493 4.8489 4.7970 4.7748 4.7663 4.7546 4.7478 4.7267 4.7039 4.6555 4.6505 4.6209 4.5866 4.5776 4.5607 4.5090 4.3669 4.3477 3.9981 3.7183 3.7128 3.7074 3.7008 3.6125 3.6040 3.6000 3.5911 3.4964 3.4811 3.4785 3.4754 3.4722 3.3219 1.5499 HDO 0.0082 -0.0000 -0.0084
OCF3 Bn
F3CBnO
F3CBnO
F3CBnO
BnO
BnO
BnO
OMe
13d beta
41.92
1.11 1.24 15.21 1.72 0.98 0.98 1.20 1.29 3.70 2.46 4.72 2.89
1.68
0.69
f1 (ppm)

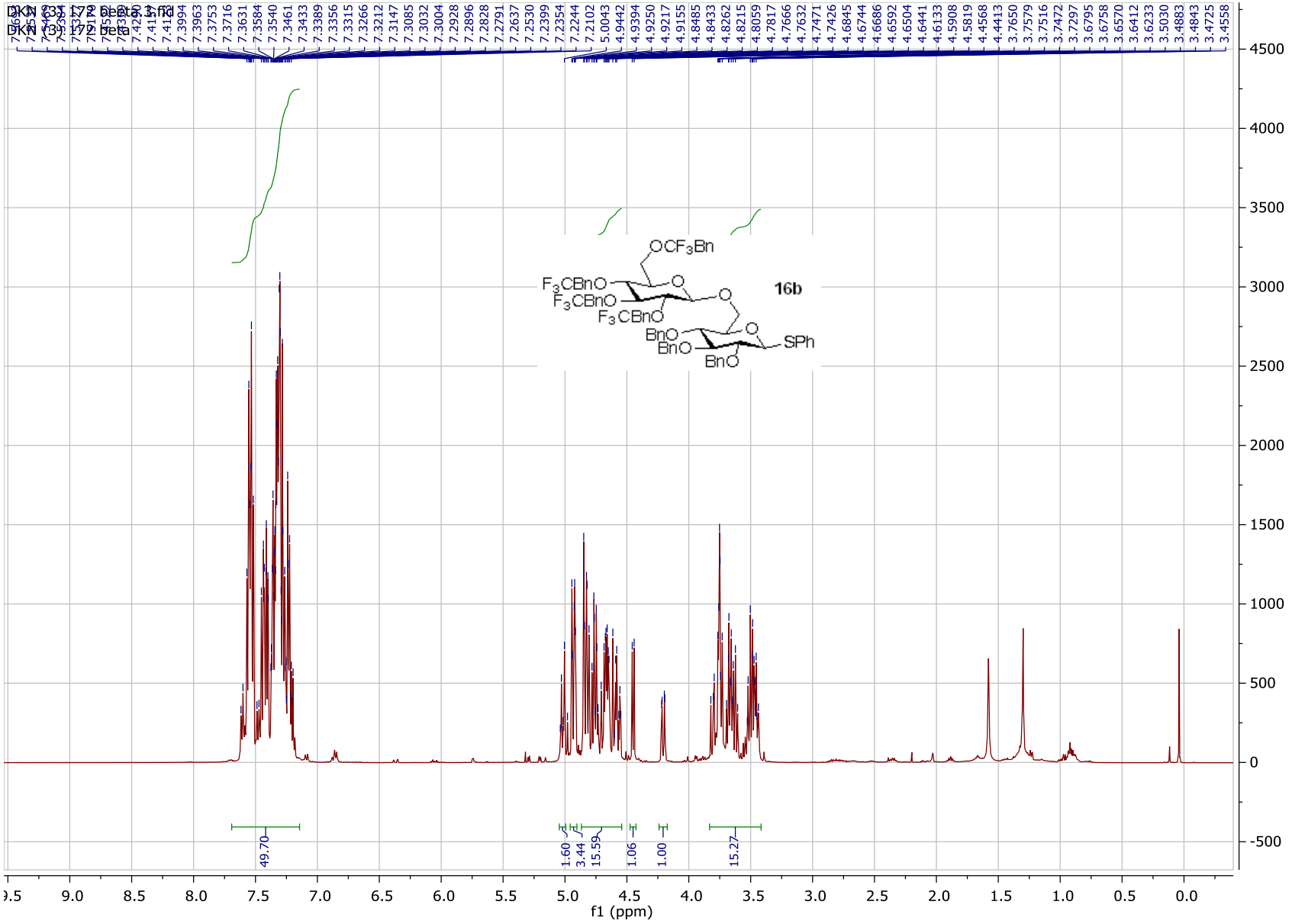

EGA 42 CF3 beta C13.1.fid
EGA 42 CF3 beta C13
142.4573
142.3363
142.2468
142.1445
138.7937
138.3819
138.2387
130.3077
130.1739
130.0479
129.9148
128.6799
128.6162
128.5918
128.3255
128.2432
128.1896
127.9338
127.9048
127.8444
127.7160
127.6699
127.5599
127.5235
127.4735
127.4547
125.4913
125.4597
125.4274
123.1719
103.9156
98.3387
84.8990
82.1909
82.0970
80.4487
80.0178
78.2161
78.1805
77.4767 CDCl3
77.2227 CDCl3
76.9689 CDCl3
76.0320
75.0554
74.9921
74.8275
74.2994
74.1792
74.0243
73.5842
72.9365
72.8263
72.4410
70.7320
69.9940
69.1921
68.9929
68.8330
55.4293
29.9139
1.2338
0.2004
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
BnO
BnO
BnO
OMe
13d beta
f1 (ppm)

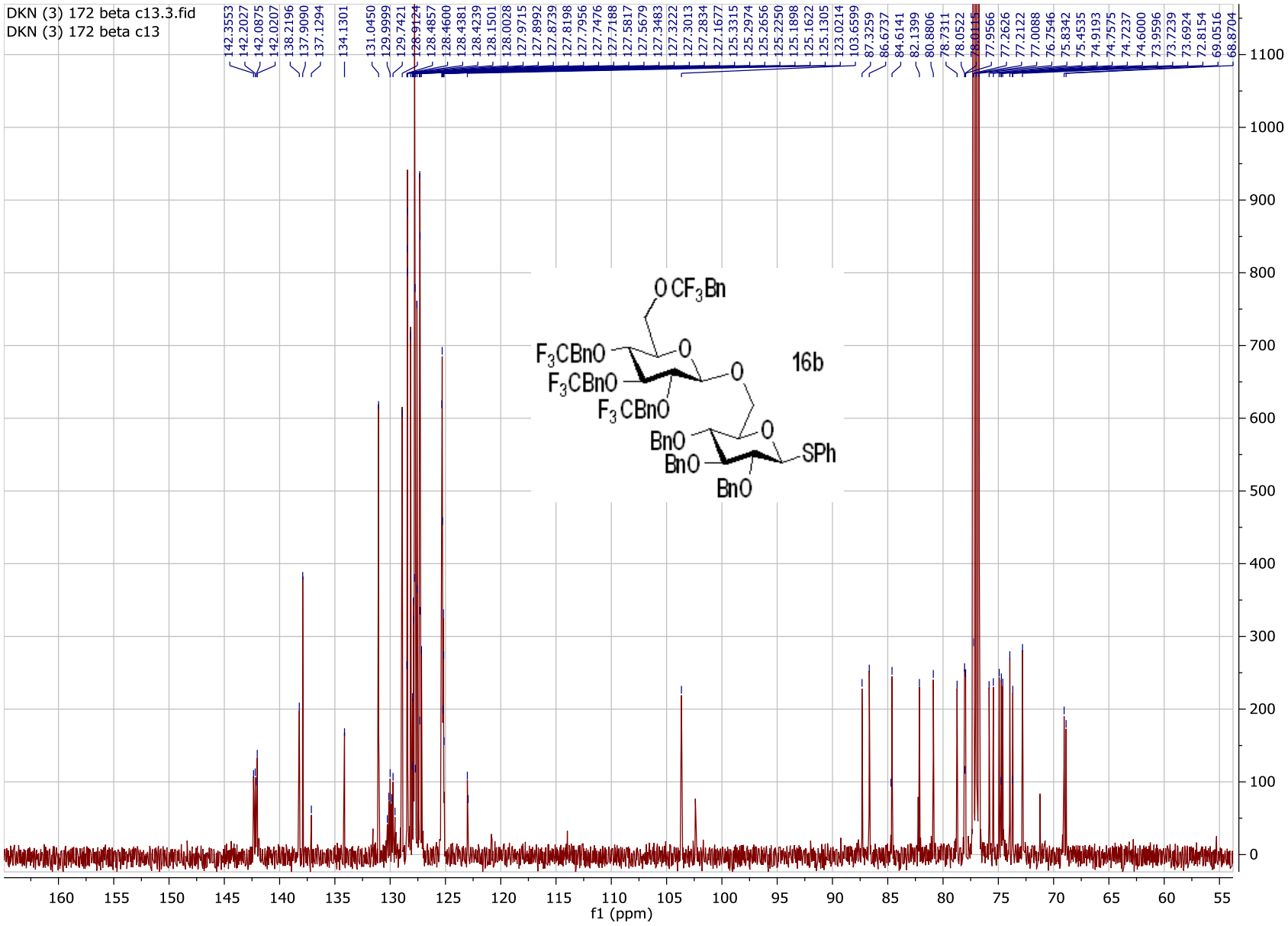

ega 42 beta f19 nmr.3.fid
F19
-63.1134
-63.1514
-63.2642
-63.2792
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
BnO
BnO
BnO
OMe
13d beta
1.00
1.07
1.24
1.15
f1 (ppm)

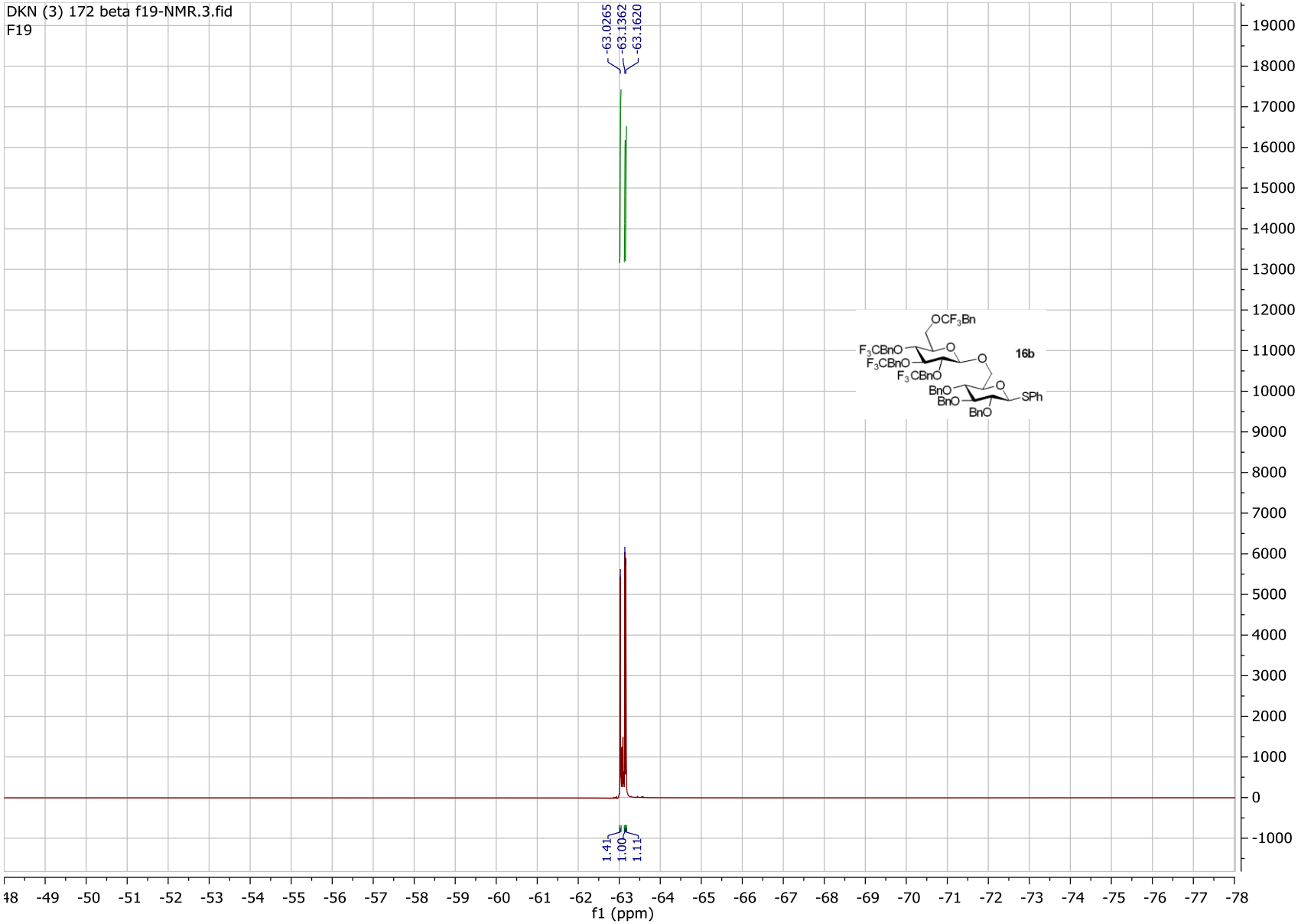

DKN (3) 172 ALPHA
DKN (3) 172 ALPHA
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
16a
BnO
BnO
BnO
O
SPh
42.71
1.02
1.39
2.20
1.11
3.44
5.28
2.78
0.98
1.08
3.32
7.24
1.10
1.01
f1 (ppm)

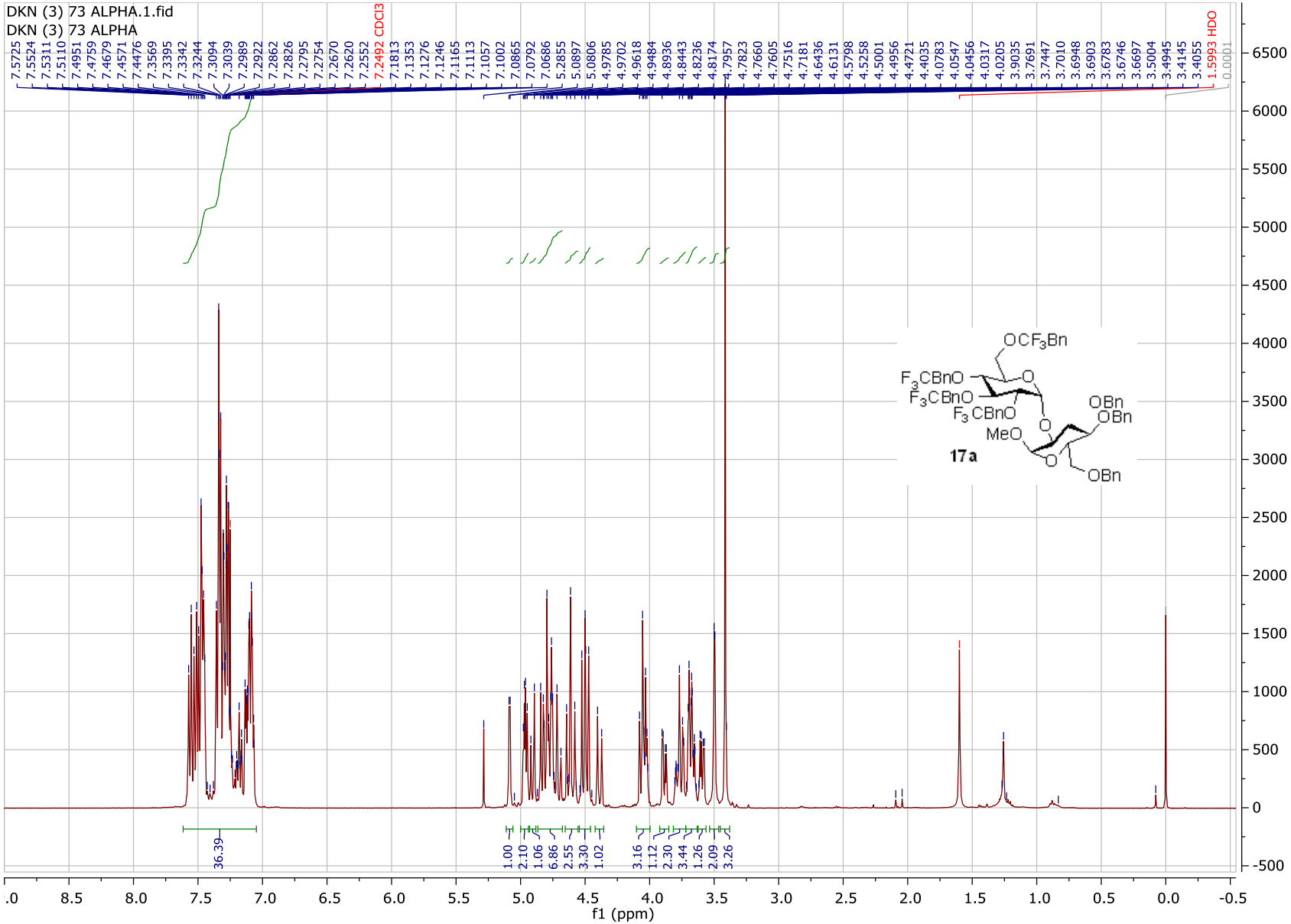

DKN (3) 172 ALPHA c13
DKN (3) 172 ALPHA c13
134.2042
131.5452
129.9232
129.6857
129.0160
128.4716
128.4350
128.3817
128.1066
128.0476
127.8456
127.7446
127.7309
127.6654
127.6479
127.4385
127.3657
127.3443
127.2217
127.0764
125.4789
125.4484
125.3335
125.3021
125.2669
125.2318
125.1939
97.0908
88.2131
86.5499
81.8020
81.1479
80.3906
78.7661
77.7661
77.1995
76.9954
76.7422
75.7899
75.4143
74.9383
74.5788
73.9030
72.6411
71.2911
70.1022
68.8379
66.0873
29.6940
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
16 a
BnO
BnO
BnO
SPh
f1 (ppm)

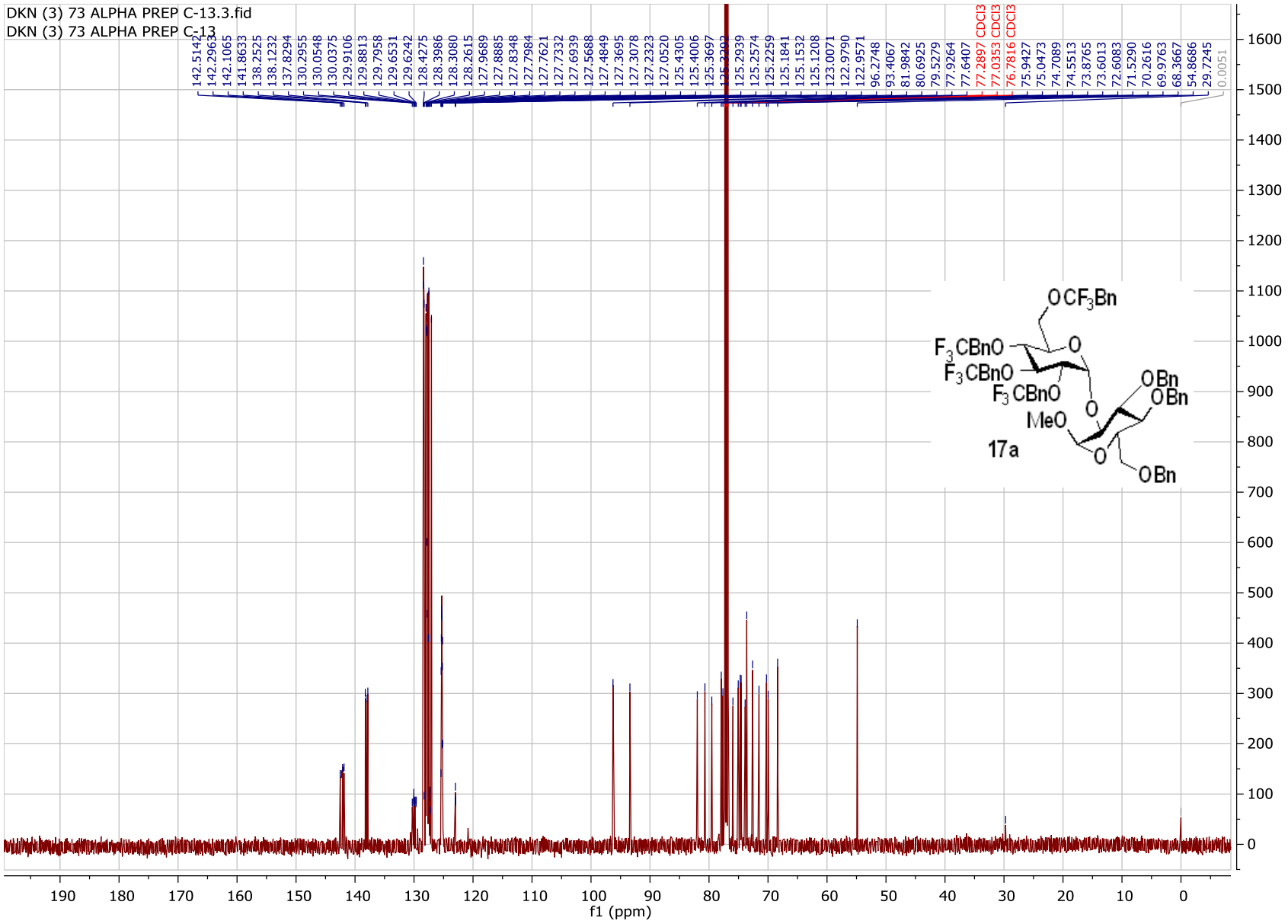

DKN (3) 172 alpha f19-NMR.3.fid
F19
-62.9384
-63.0863
-63.1129
-63.1514
1.00
0.99
1.29
1.03
16a
f1 (ppm)

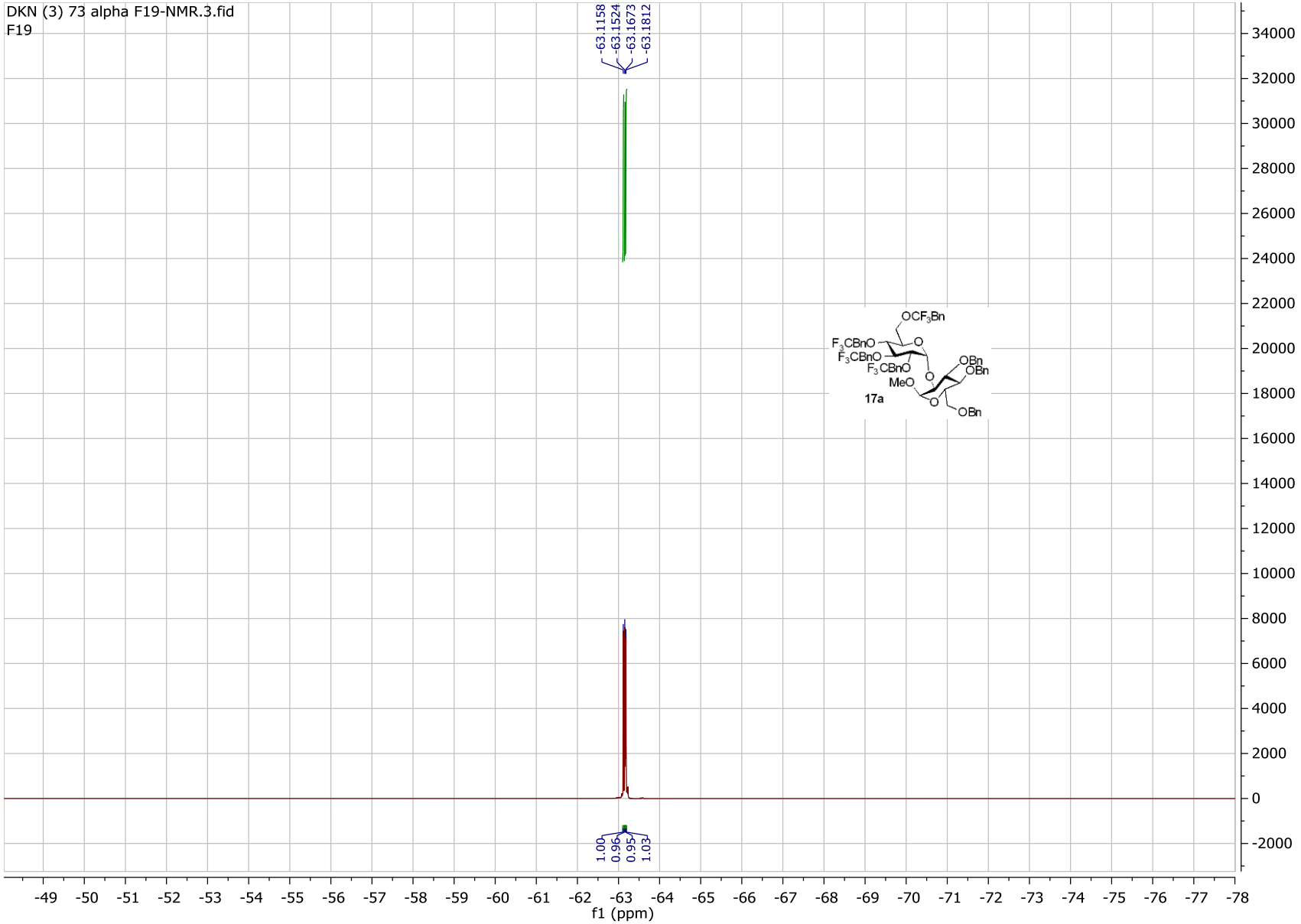

DKN (3) 172 beta 3.fid
DKN (3) 172 beta
16b
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
BnO
BnO
BnO
SPh
49.70
1.60
3.44
15.59
1.06
1.00
15.27
f1 (ppm)

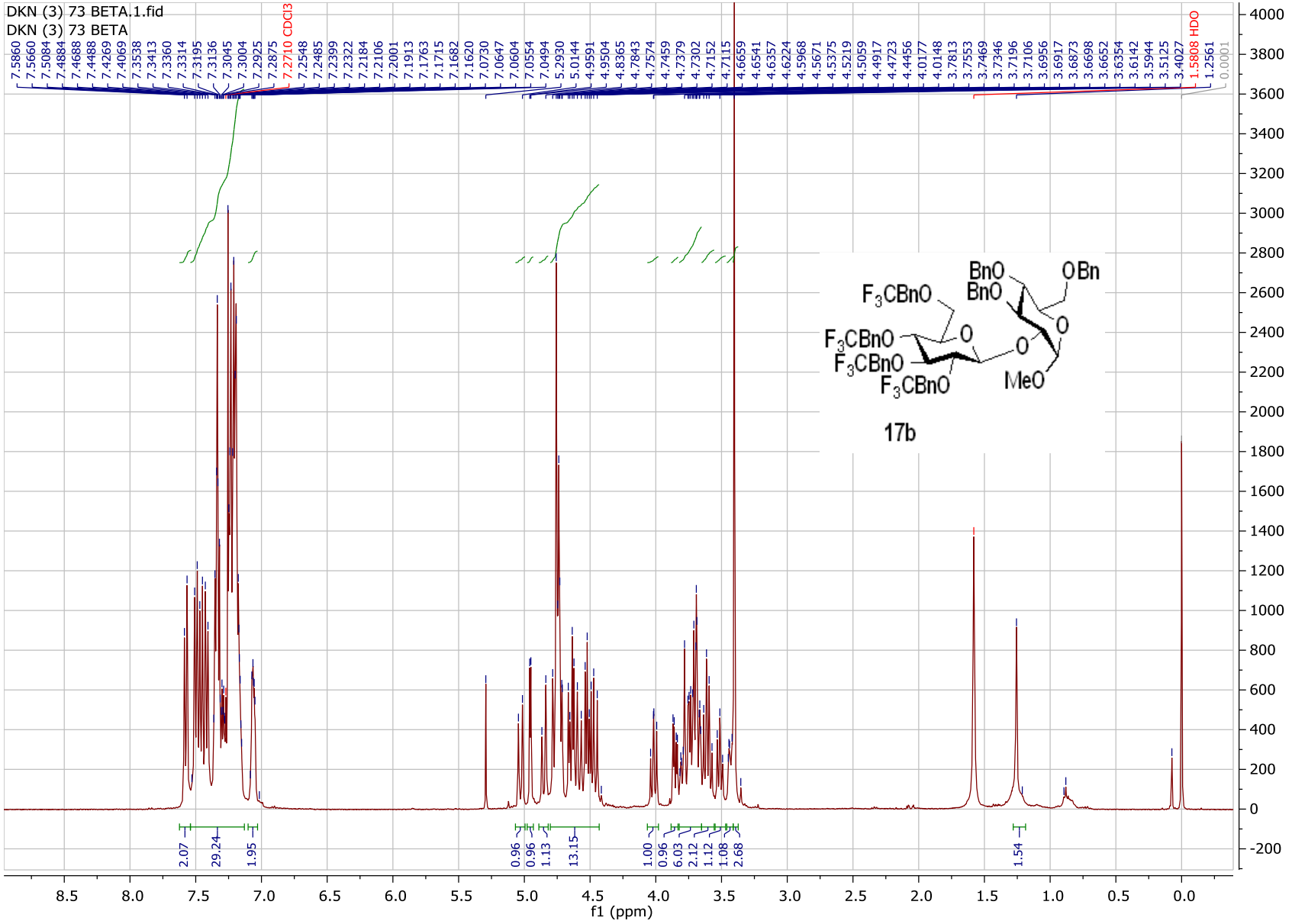

DKN (3) 172 beta c13.3.fid
DKN (3) 172 beta c13
142.3553
142.2027
142.0875
142.0207
138.2196
137.9090
137.1294
134.1301
131.0450
129.9999
129.7421
128.9124
128.4857
128.4600
128.4381
128.4239
128.1501
128.0028
127.9715
127.8992
127.8739
127.8198
127.7956
127.7476
127.7188
127.5817
127.5679
127.3483
127.3222
127.3013
127.2834
127.1677
125.3315
125.2974
125.2656
125.2250
125.1898
125.1622
125.1305
123.0214
103.6599
87.3259
86.6737
84.6141
82.1399
80.8806
78.7311
78.0522
78.0115
77.9566
77.2626
77.2122
77.0088
76.7546
75.8342
75.4535
74.9193
74.7575
74.7237
74.6000
73.9596
73.7239
73.6924
72.8154
69.0516
68.8704
O CF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
O
BnO
BnO
BnO
O
SPh
16b
1100
1000
900
800
700
600
500
400
300
200
100
0
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

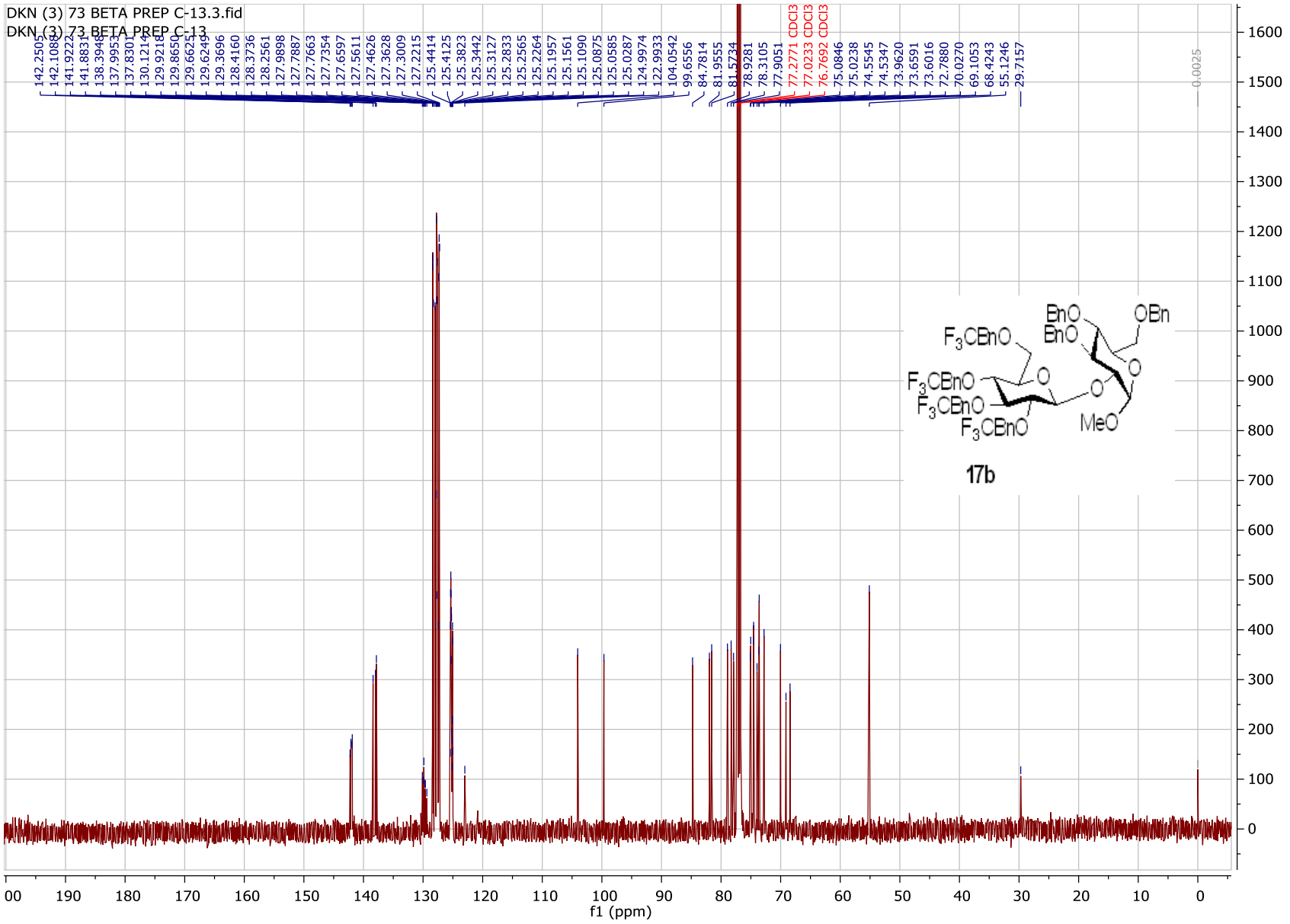

DKN (3) 172 beta f19-NMR.3.fid
F19
-63.0265
-63.1362
-63.1620
1.41
1.00
1.11
16b
f1 (ppm)

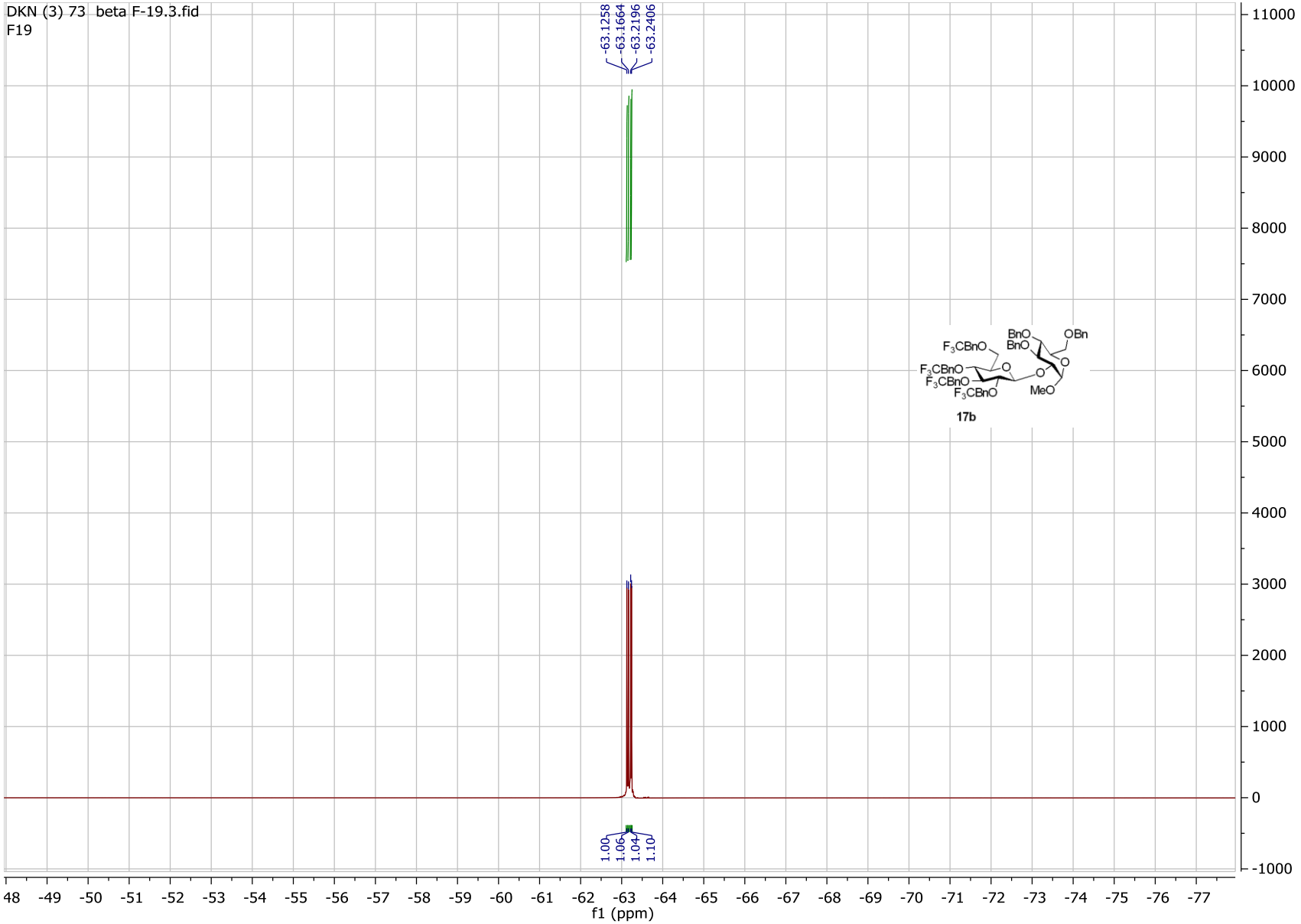

DKN (3) 73 ALPHA.1.fid
DKN (3) 73 ALPHA
7.5725 7.5524 7.5311 7.5110 7.4951 7.4759 7.4679 7.4571 7.4476 7.3569 7.3395 7.3342 7.3244 7.3094 7.3039 7.2989 7.2922 7.2862 7.2826 7.2795 7.2754 7.2670 7.2620 7.2552 7.2492 CDCl3 7.1813 7.1353 7.1276 7.1246 7.1165 7.1113 7.1057 7.1002 7.0865 7.0792 7.0686 5.2855 5.0897 5.0806 4.9785 4.9702 4.9618 4.9484 4.8936 4.8443 4.8236 4.8174 4.7957 4.7823 4.7660 4.7605 4.7516 4.7181 4.6436 4.6131 4.5798 4.5258 4.5001 4.4956 4.4721 4.4035 4.0783 4.0547 4.0456 4.0317 4.0205 3.9035 3.7691 3.7447 3.7010 3.6948 3.6903 3.6783 3.6746 3.6697 3.5004 3.4945 3.4145 3.4055 1.5993 HDO 0.0001
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
OBn
OBn
MeO
OBn
17a
36.39
1.00 2.10 1.06 6.86 2.55 3.30 1.02 3.16 1.12 2.30 3.44 1.26 2.09 3.26
f1 (ppm)

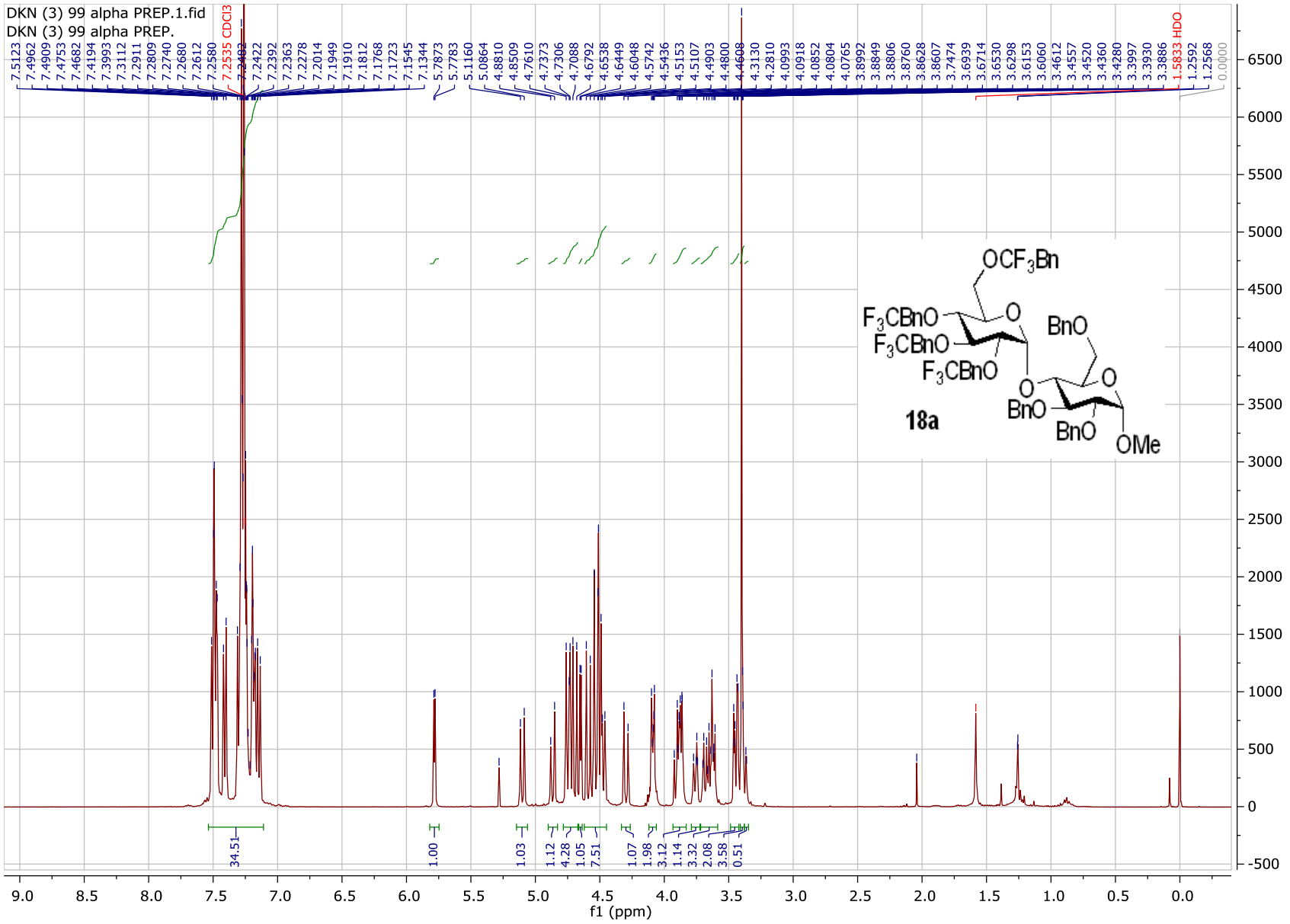

DKN (3) 73 ALPHA PREP C-13.3.fid
DKN (3) 73 ALPHA PREP C-13
142.5142
142.2963
142.1065
141.8633
138.2525
138.1232
137.8294
130.2955
130.0548
130.0375
129.9106
129.8813
129.7958
129.6531
129.6242
128.4275
128.3986
128.3080
128.2615
127.9689
127.8885
127.8348
127.7984
127.7621
127.7332
127.6939
127.5688
127.4849
127.3695
127.3078
127.2323
127.0520
125.4305
125.4006
125.3697
125.2939
125.2574
125.2259
125.1841
125.1532
125.1208
123.0071
122.9790
122.9571
96.2748
93.4067
81.9842
80.6925
79.5279
77.9264
77.6407
77.2897 CDCl3
77.0353 CDCl3
76.7816 CDCl3
75.9427
75.0473
74.7089
74.5513
73.8765
73.6013
72.6083
71.5290
70.2616
69.9763
68.3667
54.8686
29.7245
0.0051
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
OBn
OBn
MeO
O
O
OBn
17a
f1 (ppm)

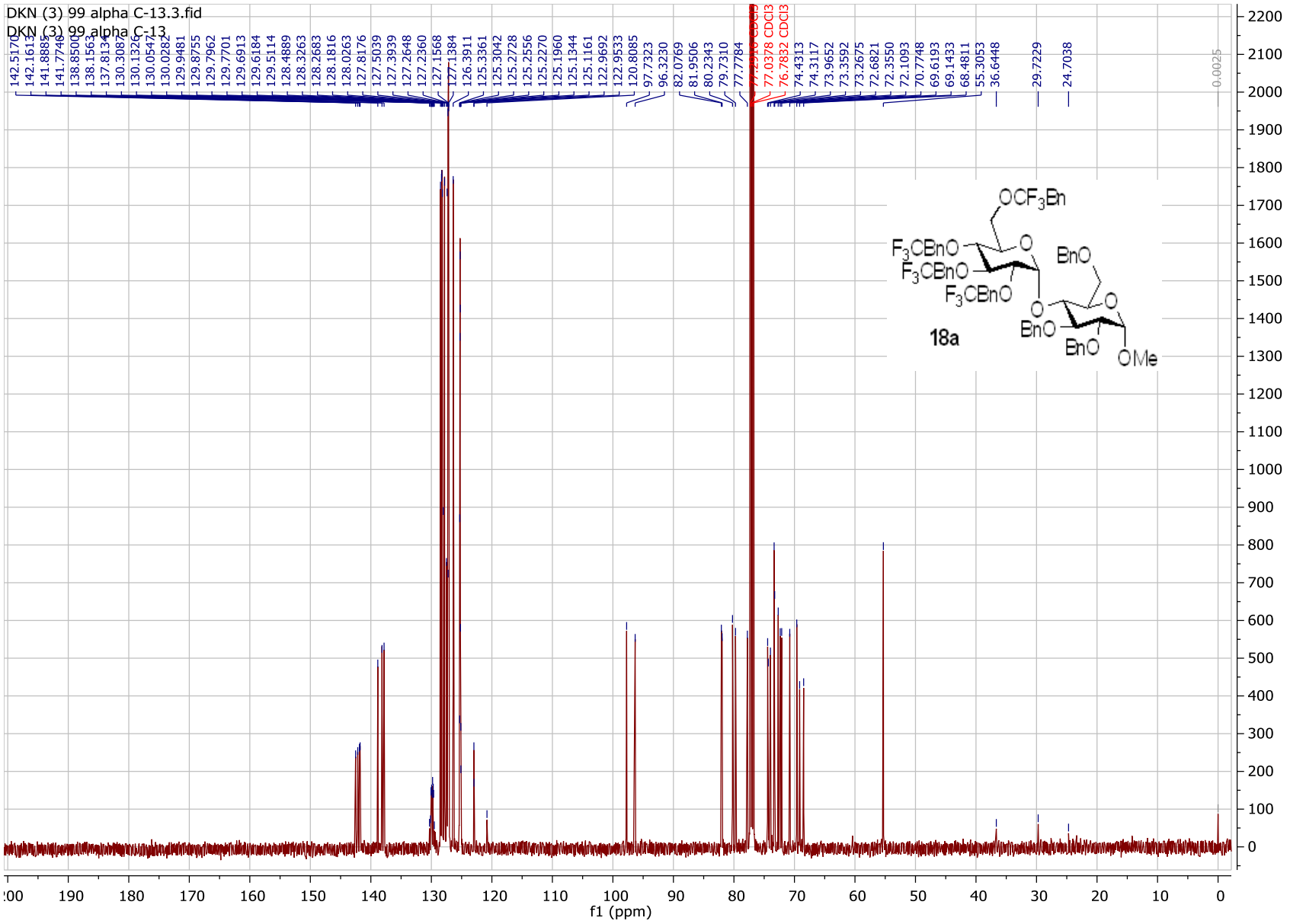

DKN (3) 73 alpha F19-NMR.3.fid
F19
-63.1158
-63.1524
-63.1673
-63.1812
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
MeO
OBn
OBn
OBn
17a
1.00
0.96
0.95
1.03
f1 (ppm)


DKN (3) 73 BETA.1.fid
DKN (3) 73 BETA
7.5860 7.5660 7.5084 7.4884 7.4688 7.4488 7.4269 7.4069 7.3538 7.3413 7.3360 7.3314 7.3195 7.3136 7.3045 7.3004 7.2925 7.2875 7.2710 CDCl3 7.2548 7.2485 7.2399 7.2322 7.2184 7.2106 7.2001 7.1913 7.1763 7.1715 7.1682 7.1620 7.0730 7.0647 7.0604 7.0554 7.0494 5.2930 5.0144 4.9591 4.9504 4.8365 4.7843 4.7574 4.7459 4.7379 4.7302 4.7152 4.7115 4.6659 4.6541 4.6357 4.6224 4.5968 4.5671 4.5375 4.5219 4.5059 4.4917 4.4723 4.4456 4.0177 4.0148 3.7813 3.7553 3.7469 3.7346 3.7196 3.7106 3.6956 3.6917 3.6873 3.6698 3.6652 3.6354 3.6142 3.5944 3.5125 3.4027 1.5808 HDO 1.2561 0.0001
BnO
OBn
BnO
F3CBnO
O
O
O
F3CBnO
F3CBnO
F3CBnO
MeO
17b
2.07 29.24 1.95 0.96 0.96 1.13 13.15 1.00 0.96 6.03 2.12 1.12 1.08 2.68 1.54
f1 (ppm)


DKN (3) 73 BETA PREP C-13.3.fid
DKN (3) 73 BETA PREP C-13
142.2505
142.1088
141.9222
141.8831
138.3948
137.9953
137.8301
130.1214
129.9218
129.8650
129.6623
129.6249
129.3696
128.4160
128.3736
128.2561
127.9898
127.7887
127.7663
127.7354
127.6597
127.5611
127.4626
127.3628
127.3009
127.2215
125.4414
125.4125
125.3823
125.3442
125.3127
125.2833
125.2565
125.2264
125.1957
125.1561
125.1090
125.0875
125.0585
125.0287
124.9974
122.9933
104.0542
99.6556
84.7814
81.9555
81.5734
78.9281
78.3105
77.9051
77.2771 CDCl3
77.0233 CDCl3
76.7692 CDCl3
75.0846
75.0238
74.5545
74.5347
73.9620
73.6591
73.6016
72.7880
70.0270
69.1053
68.4243
55.1246
29.7157
0.0025
BnO
BnO
OBn
F3CBnO
F3CBnO
F3CBnO
F3CBnO
MeO
17b
f1 (ppm)


DKN (3) 73 beta F-19.3.fid
F19
-63.1258
-63.1664
-63.2196
-63.2406
1.00
1.06
1.04
1.10
f1 (ppm)
17b


DKN (3) 99 alpha PREP.1.fid
DKN (3) 99 alpha PREP.
7.5123 7.4962 7.4909 7.4753 7.4682 7.4194 7.3993 7.3112 7.2911 7.2809 7.2740 7.2680 7.2612 7.2580 7.2535 CDCl3 7.2482 7.2422 7.2392 7.2363 7.2278 7.2014 7.1949 7.1910 7.1812 7.1768 7.1723 7.1545 7.1344 5.7873 5.7783 5.1160 5.0864 4.8810 4.8509 4.7610 4.7373 4.7306 4.7088 4.6792 4.6538 4.6449 4.6048 4.5742 4.5436 4.5153 4.5107 4.4903 4.4800 4.4608 4.3130 4.2810 4.0993 4.0918 4.0852 4.0804 4.0765 3.8992 3.8849 3.8806 3.8760 3.8628 3.8607 3.7474 3.6939 3.6714 3.6530 3.6298 3.6153 3.6060 3.4612 3.4557 3.4520 3.4360 3.4280 3.3997 3.3930 3.3886 1.5833 HDO 1.2592 1.2568 0.0000
34.51 1.00 1.03 1.12 4.28 1.05 7.51 1.07 1.98 3.12 1.14 3.32 2.08 3.58 0.51
f1 (ppm)
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
BnO
BnO
BnO
OMe
18a


DKN (3) 99 alpha C-13.3.fid
DKN (3) 99 alpha C-13
142.5170
142.1613
141.8885
141.7746
138.8500
138.1563
137.8134
130.3087
130.1326
130.0547
130.0282
129.9481
129.8755
129.7962
129.7701
129.6913
129.6184
129.5114
128.4889
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128.2683
128.1816
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127.8176
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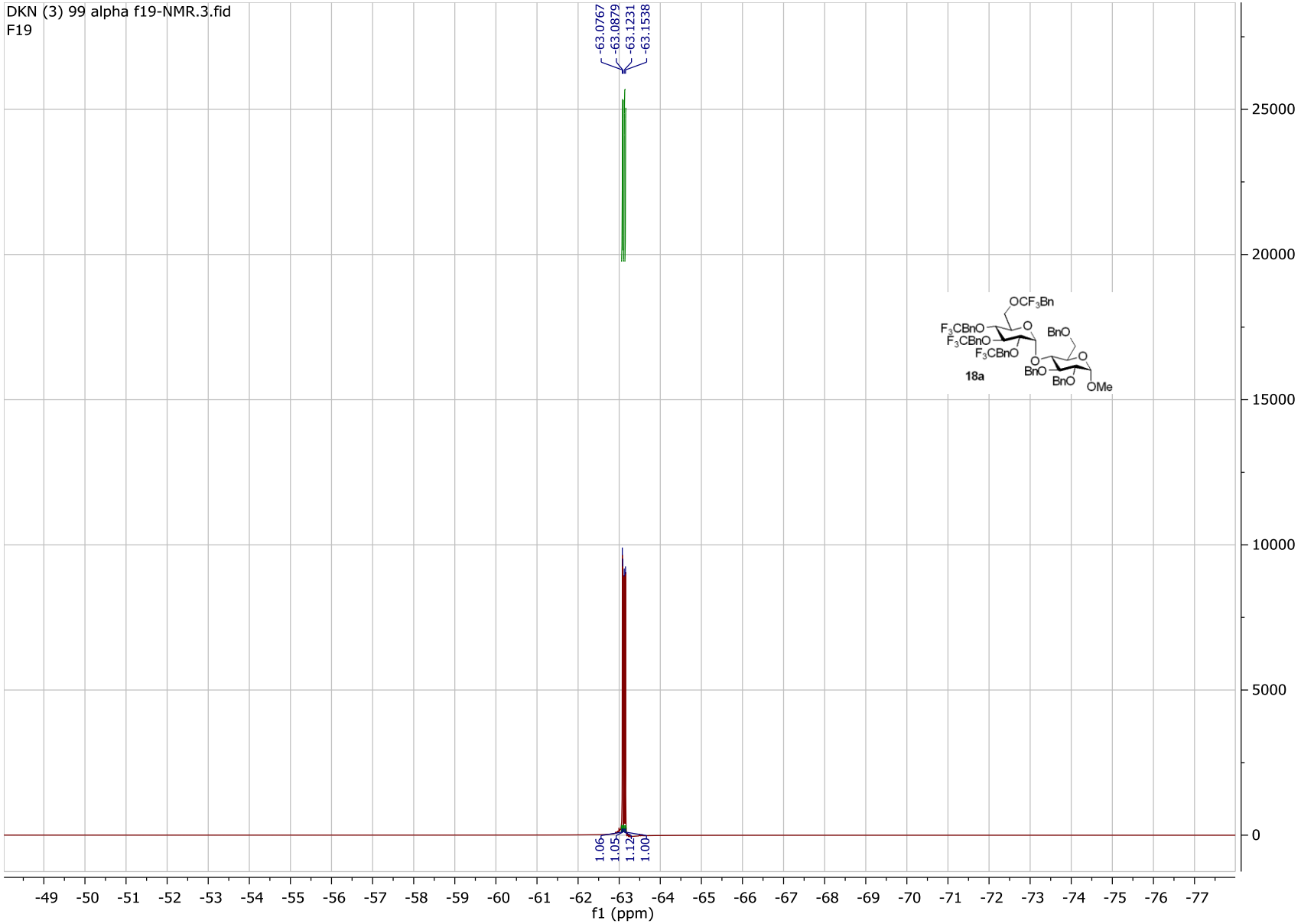
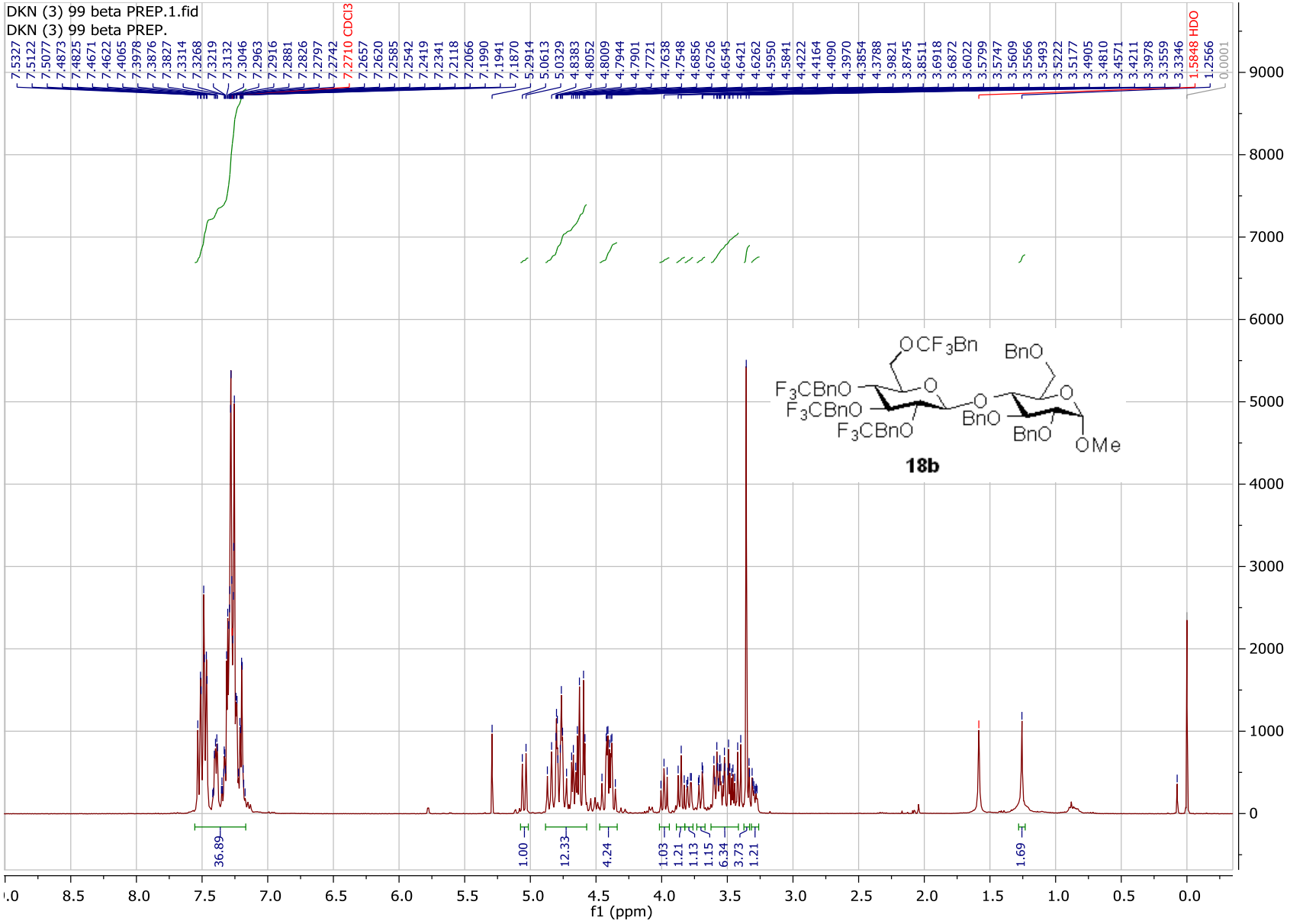
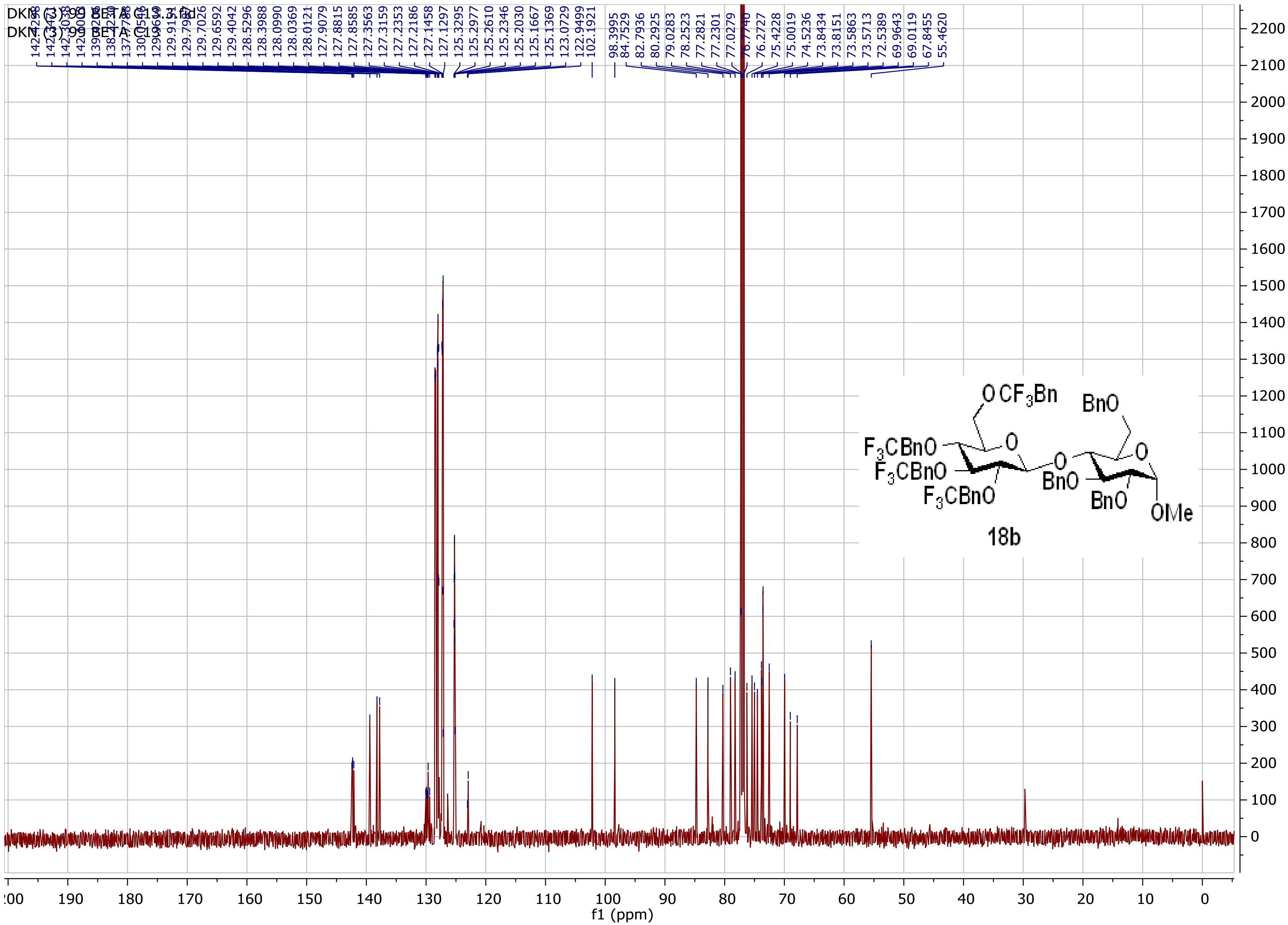
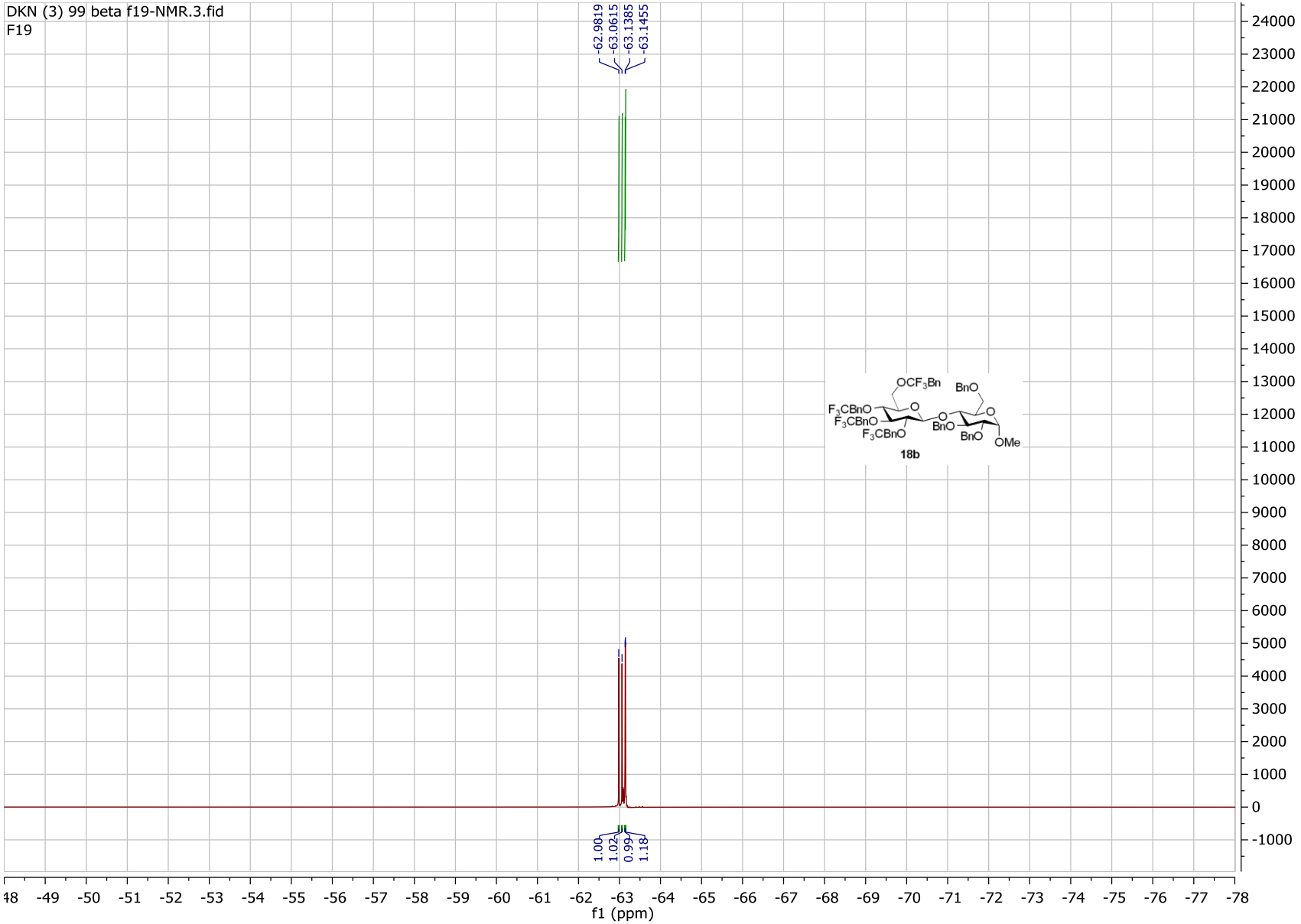
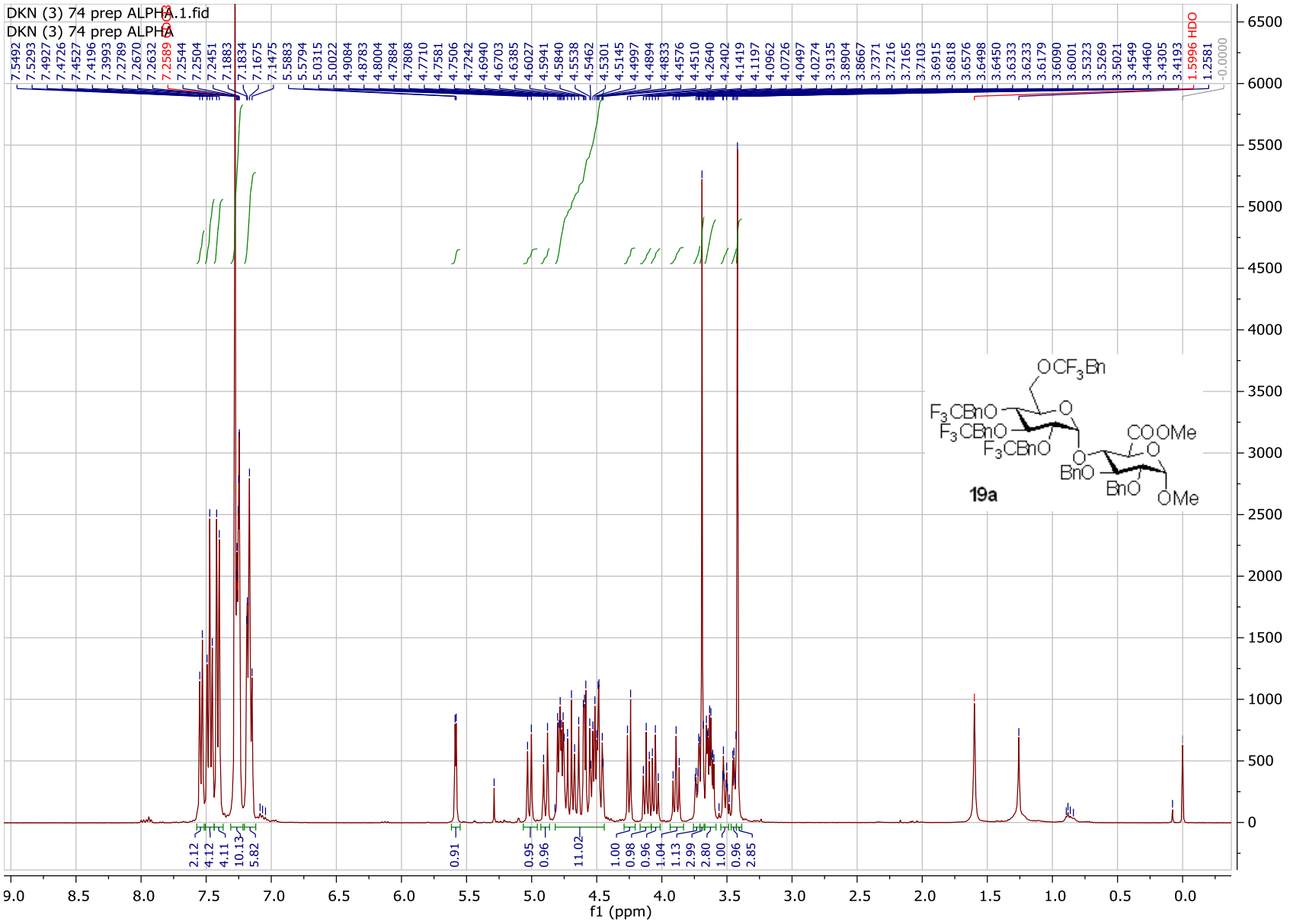
127.3939
127.2648
127.2360
127.1568
127.1384
126.3911
125.3361
125.3042
125.2728
125.2556
125.2270
125.1960
125.1344
125.1161
122.9692
122.9533
120.8085
97.7323
96.3230
82.0769
81.9506
80.2343
79.7310
77.7784
77.0378 CDCl3
76.7832 CDCl3
74.4313
74.3117
73.9652
73.3592
73.2675
72.6821
72.3550
72.1093
70.7748
69.6193
69.1433
68.4811
55.3053
36.6448
29.7229
24.7038
0.0025
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
BnO
O
O
BnO
BnO
OMe
18a
f1 (ppm)

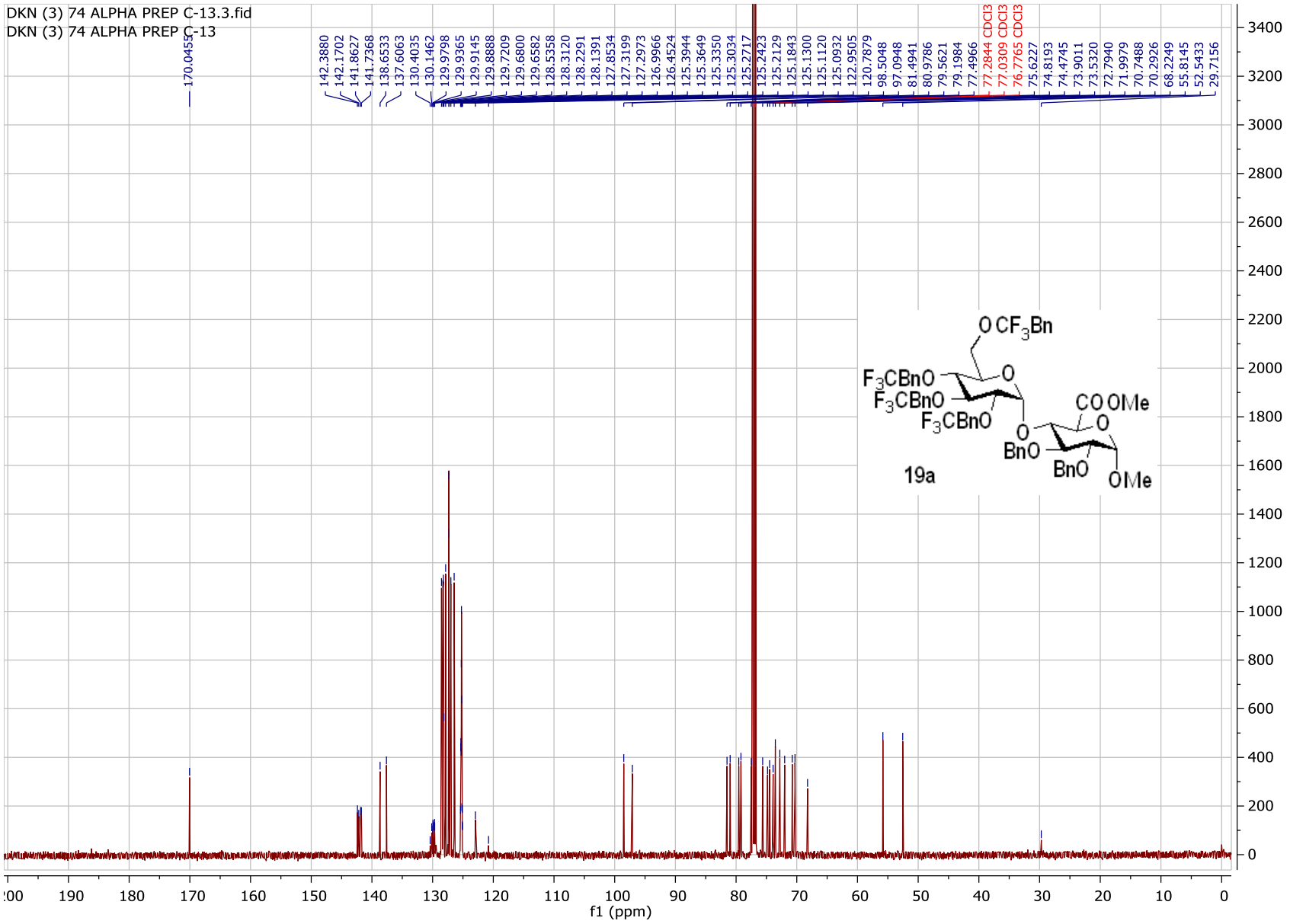

DKN (3) 99 alpha f19-NMR.3.fid
F19
-63.0767
-63.0879
-63.1231
-63.1538
25000
20000
15000
10000
5000
0
1.06
1.05
1.12
1.00
-49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77
f1 (ppm)
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
BnO
O
BnO
BnO
O
OMe
18a

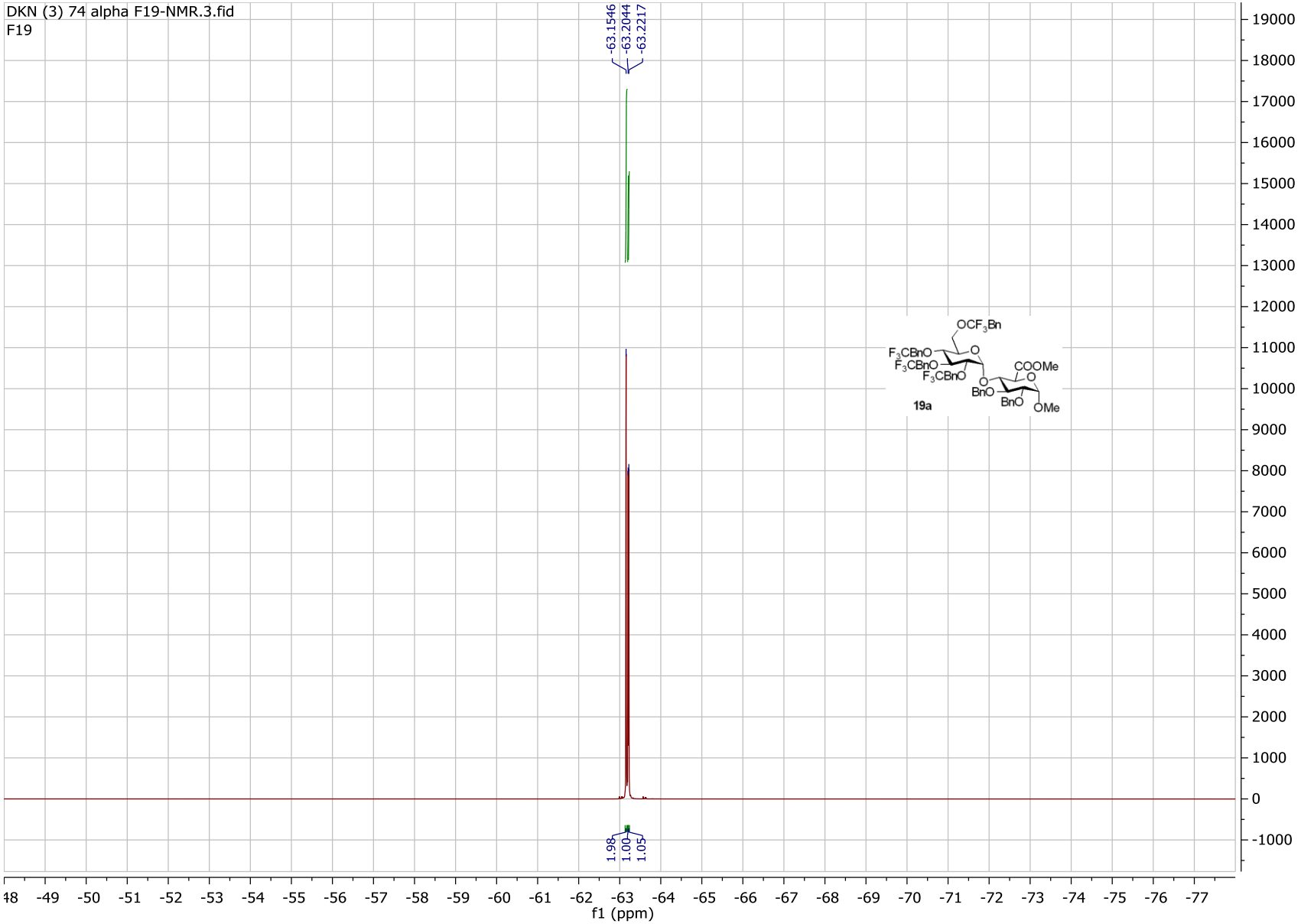

DKN (3) 99 beta PREP.1.fid
DKN (3) 99 beta PREP.
7.2710 CDCl3
1.5848 HDO
18b
f1 (ppm)

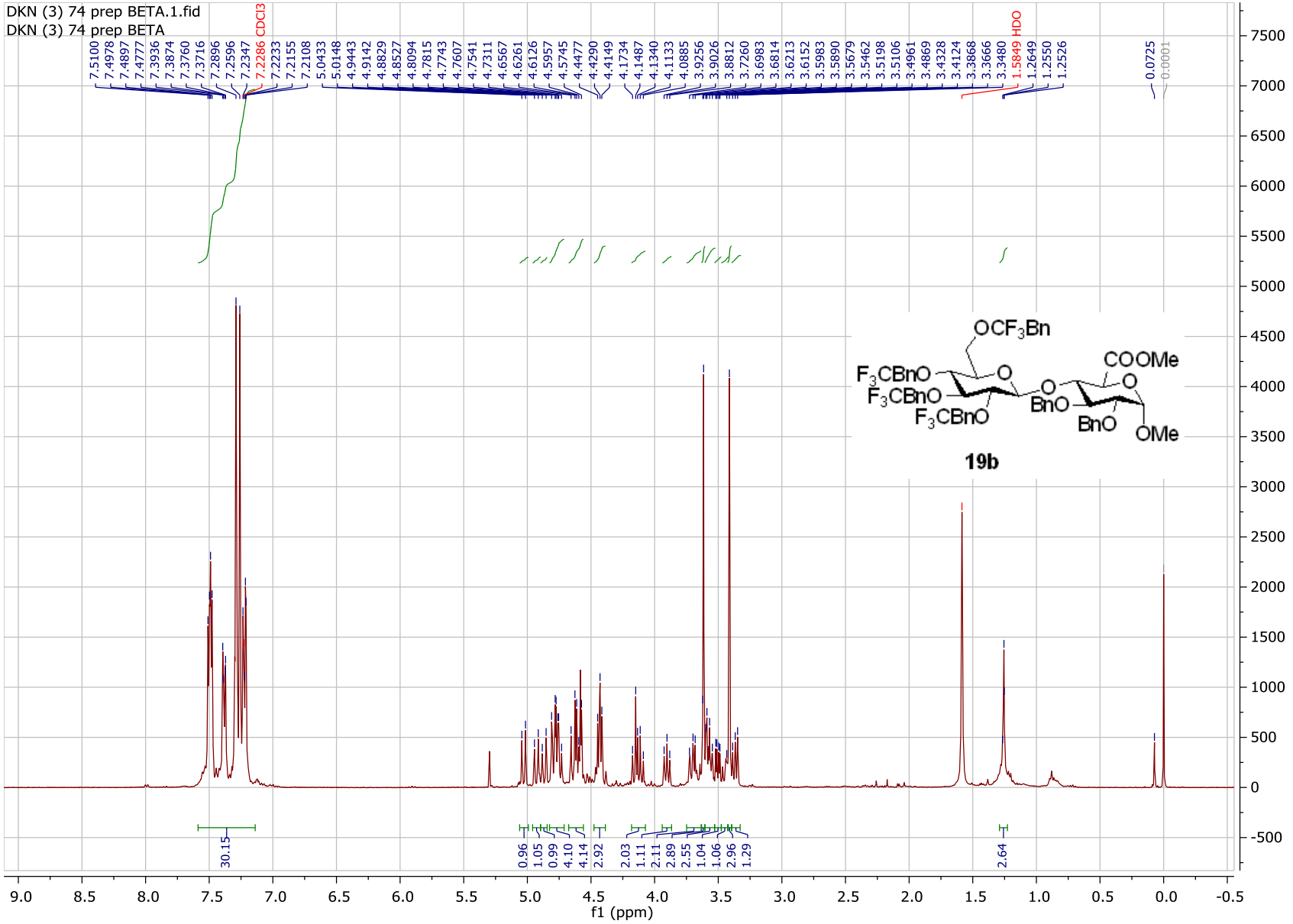

129.7026
129.6592
129.4042
128.5296
128.3988
128.0990
128.0369
128.0121
127.9079
127.8815
127.8585
127.3563
127.3159
127.2353
127.2186
127.1458
127.1297
125.3295
125.2977
125.2610
125.2346
125.2030
125.1667
125.1369
123.0729
122.9499
102.1921
98.3995
84.7529
82.7936
80.2925
79.0283
78.2523
77.2821
77.2301
77.0279
76.7740
76.2727
75.4228
75.0019
74.5236
73.8434
73.8151
73.5863
73.5713
72.5389
69.9643
69.0119
67.8455
55.4620
OCF$_3$Bn
BnO
F$_3$CBnO
F$_3$CBnO
F$_3$CBnO
O
O
O
BnO
BnO
OMe
18b
f1 (ppm)

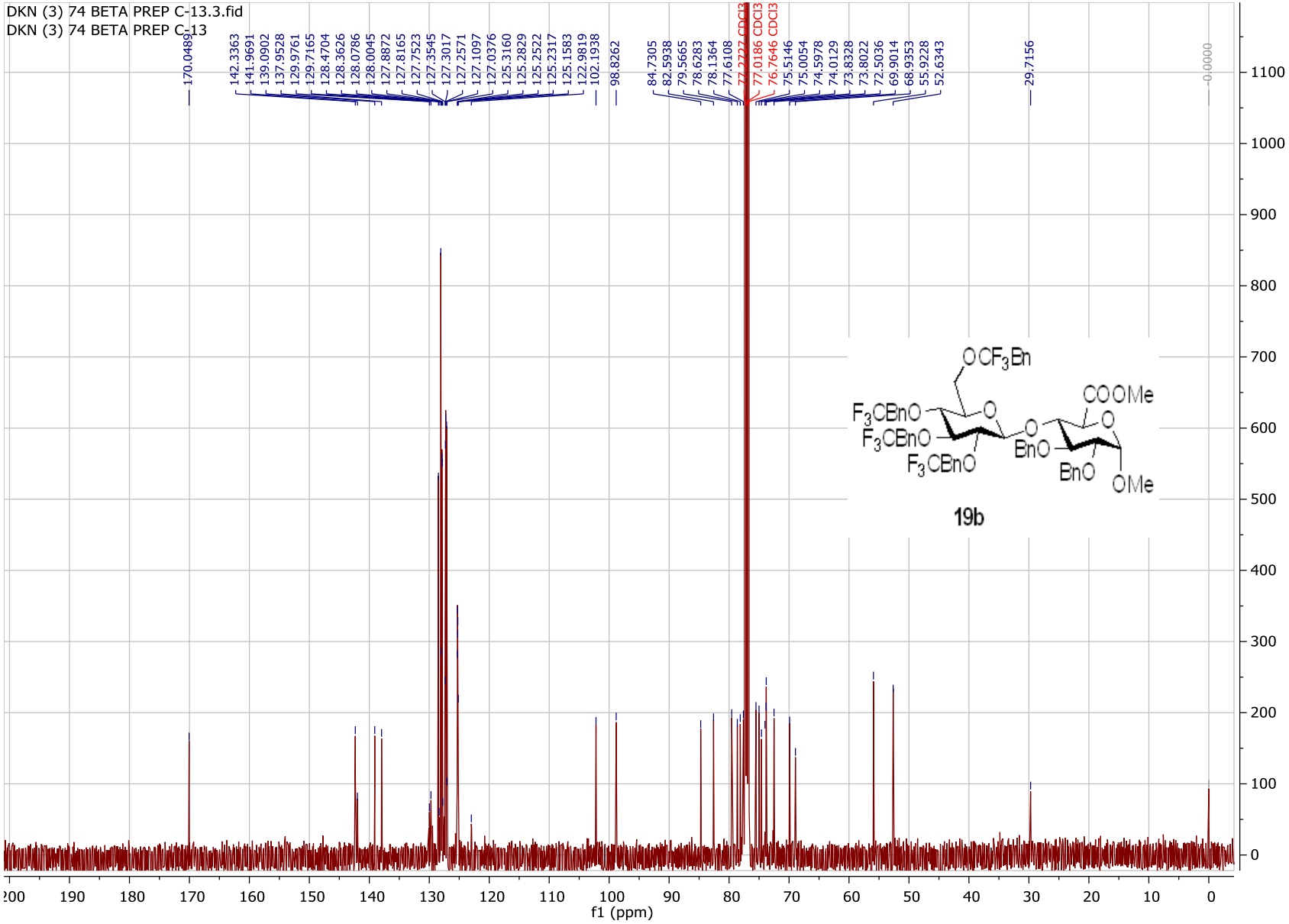

DKN (3) 99 beta f19-NMR.3.fid
F19
-62.9819
-63.0615
-63.1385
-63.1455
1.00
1.02
0.99
1.18
18b
f1 (ppm)

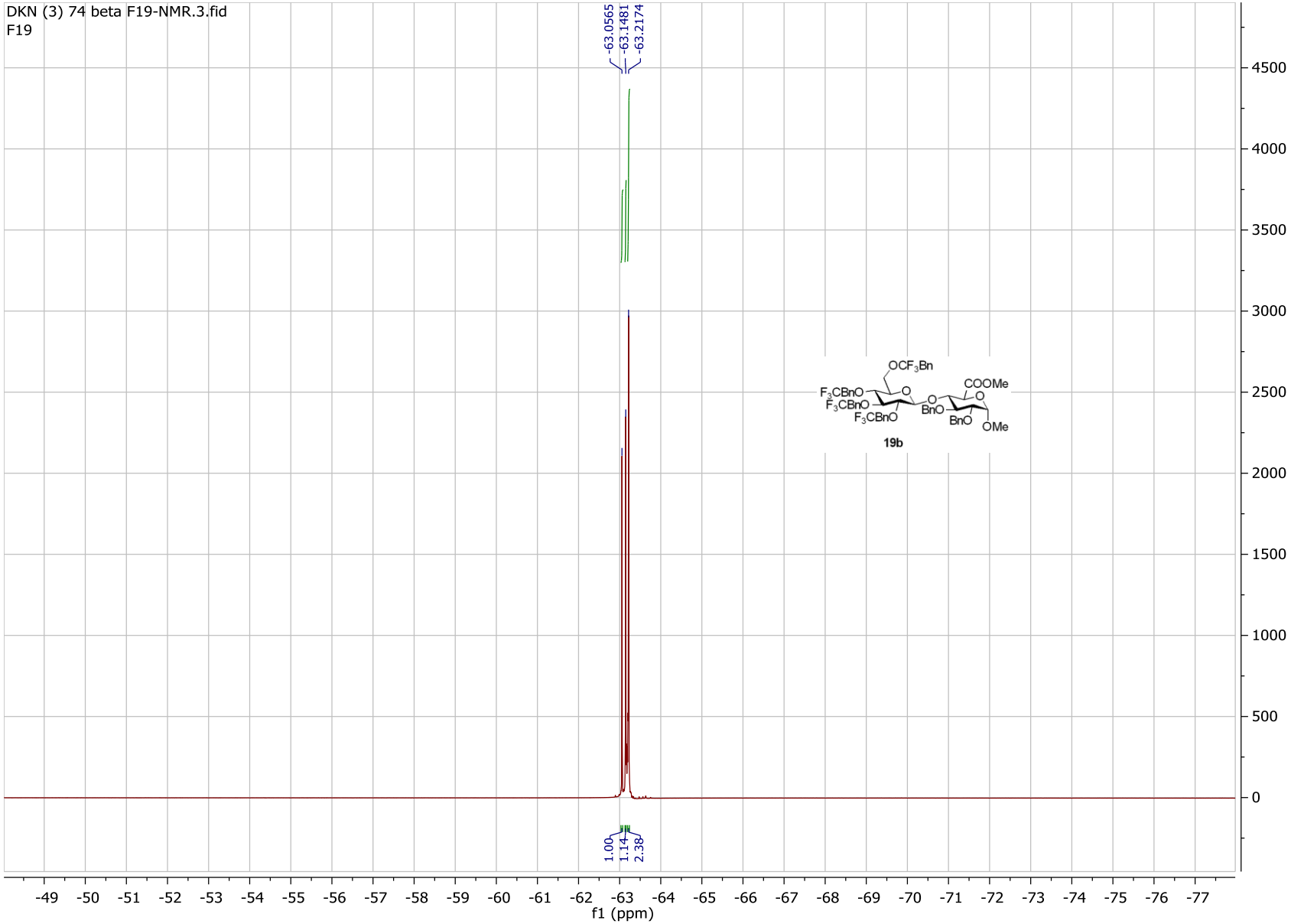

DKN (3) 74 prep ALPHA.1.fid
DKN (3) 74 prep ALPHA
CDCl3
HDO
19a
f1 (ppm)

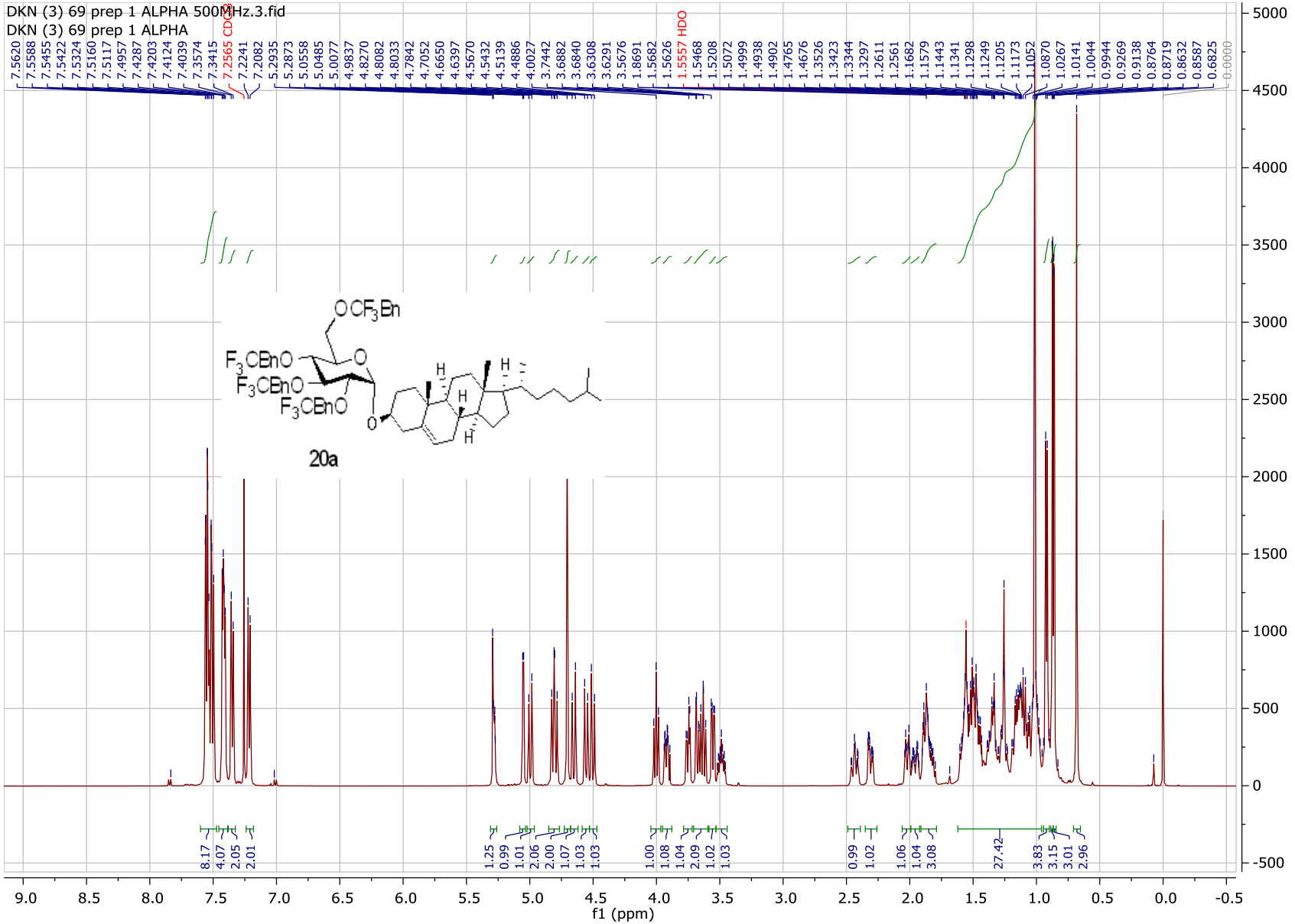

DKN (3) 74 ALPHA PREP C-13.3.fid
DKN (3) 74 ALPHA PREP C-13
170.0455
142.3880
142.1702
141.8627
141.7368
138.6533
137.6063
130.4035
130.1462
129.9798
129.9365
129.9145
129.8888
129.7209
129.6800
129.6582
128.5358
128.3120
128.2291
128.1391
127.8534
127.3199
127.2973
126.9966
126.4524
125.3944
125.3649
125.3350
125.3034
125.2717
125.2423
125.2129
125.1843
125.1300
125.1120
125.0932
122.9505
120.7879
98.5048
97.0948
81.4941
80.9786
79.5621
79.1984
77.4966
77.2844 CDCl3
77.0309 CDCl3
76.7765 CDCl3
75.6227
74.8193
74.4745
73.9011
73.5320
72.7940
71.9979
70.7488
70.2926
68.2249
55.8145
52.5433
29.7156
f1 (ppm)
19a

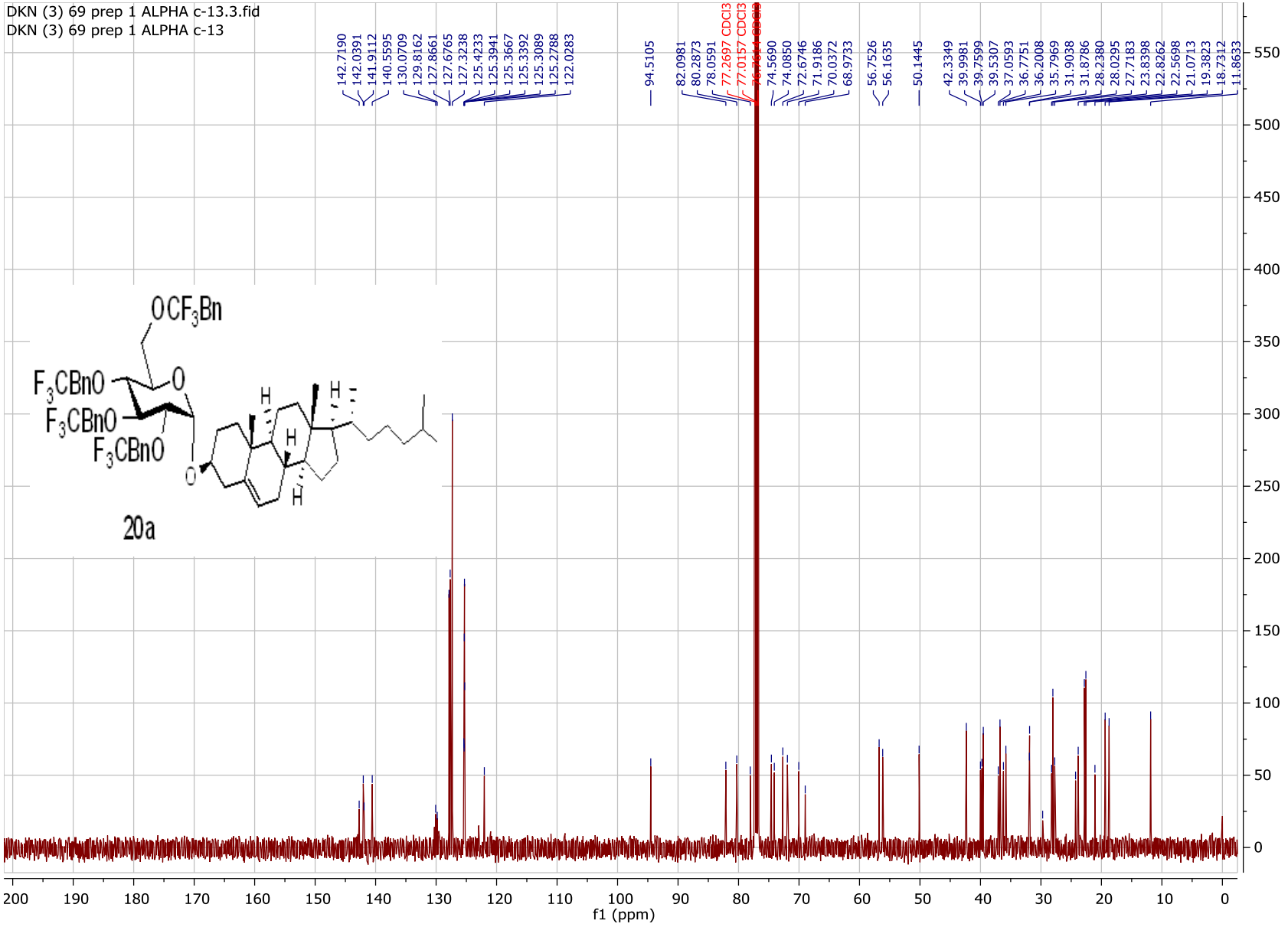

DKN (3) 74 alpha F19-NMR.3.fid
F19
-63.1546
-63.2044
-63.2217
1.98
1.00
1.05
f1 (ppm)
19a

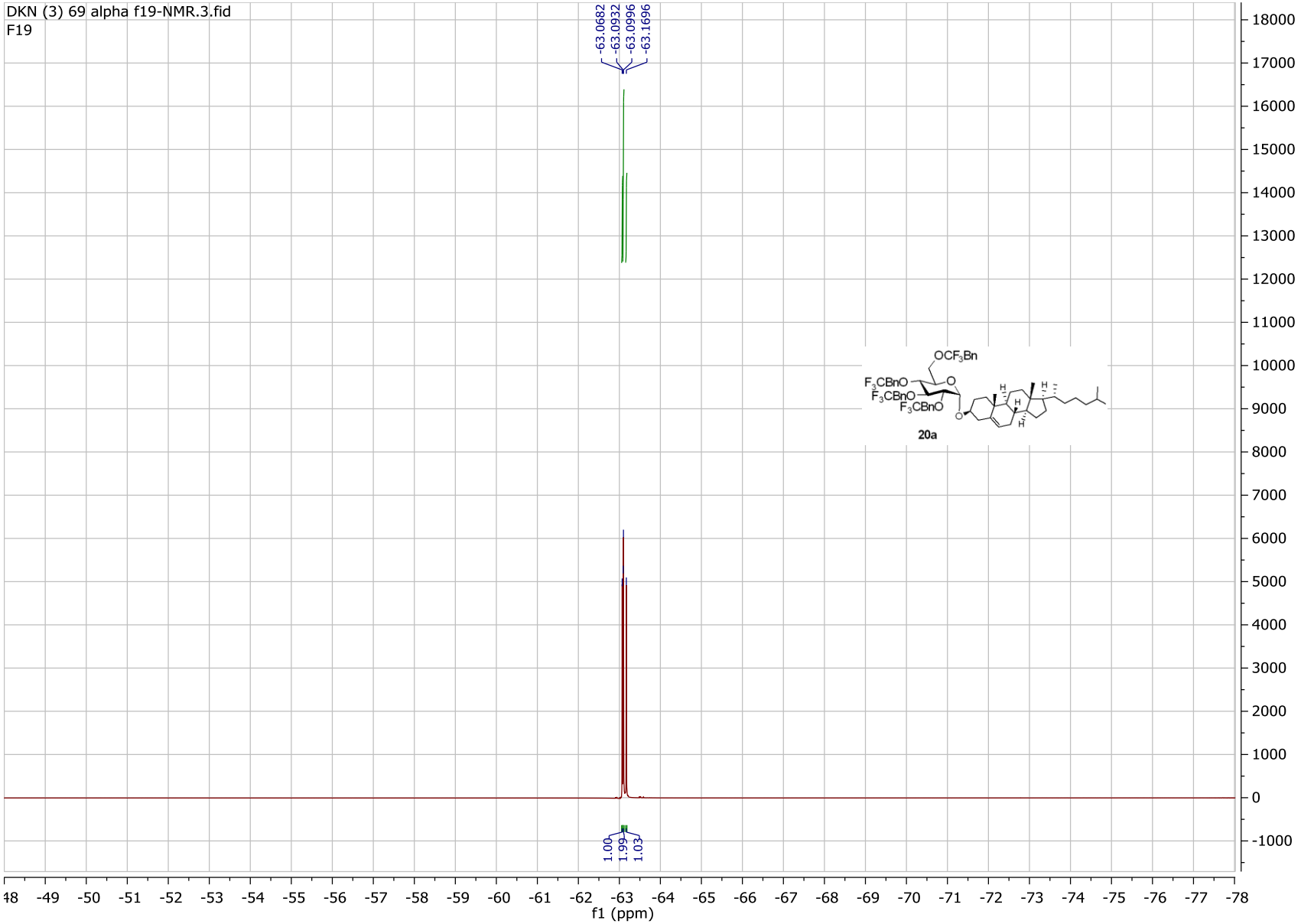

DKN (3) 74 prep BETA.1.fid
DKN (3) 74 prep BETA
CDCl3
HDO
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
BnO
BnO
COOMe
OMe
19b
f1 (ppm)

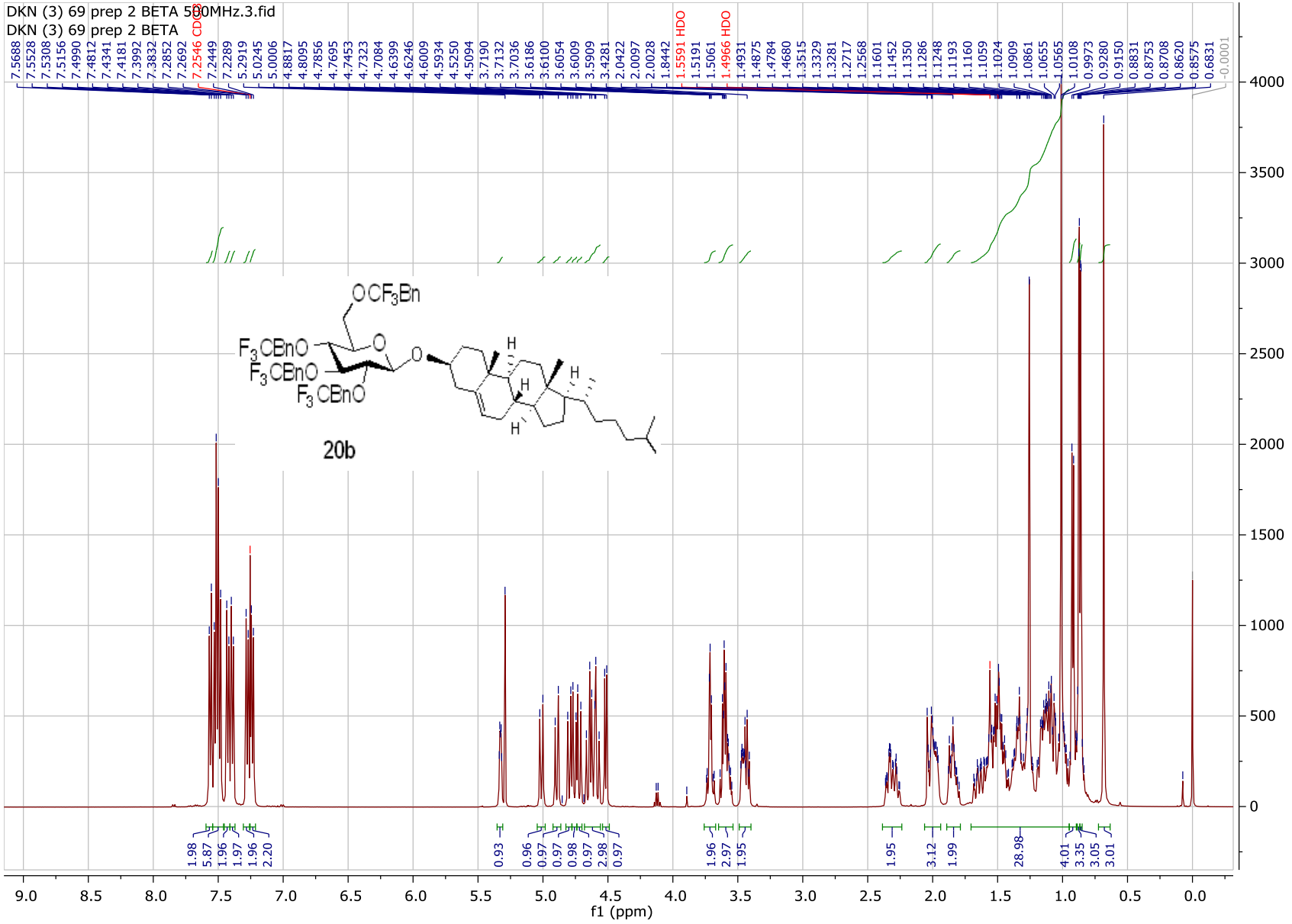

DKN (3) 74 BETA PREP C-13.3.fid
DKN (3) 74 BETA PREP C-13
170.0489
142.3363
141.9691
139.0902
137.9528
129.9761
129.7165
128.4704
128.3626
128.0786
128.0045
127.8872
127.8165
127.7523
127.3545
127.3017
127.2571
127.1097
127.0376
125.3160
125.2829
125.2522
125.2317
125.1583
122.9819
102.1938
98.8262
84.7305
82.5938
79.5665
78.6283
78.1364
77.6108
77.2727 CDCl3
77.0186 CDCl3
76.7646 CDCl3
75.5146
75.0054
74.5978
74.0129
73.8328
73.8022
72.5036
69.9014
68.9353
55.9228
52.6343
29.7156
0.0000
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
BnO
COOMe
O
BnO
OMe
19b
f1 (ppm)

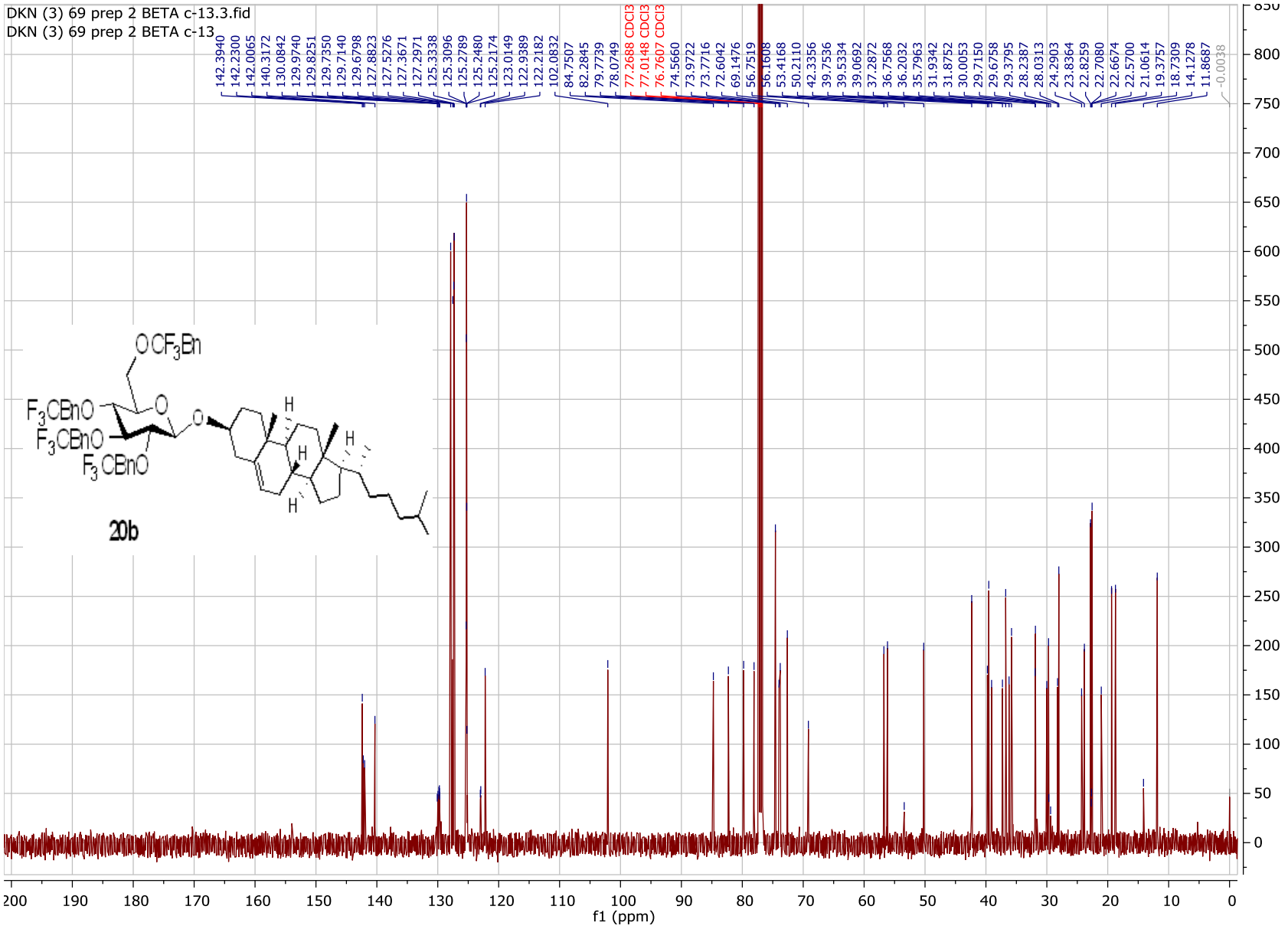

DKN (3) 74 beta F19-NMR.3.fid
F19
-63.0565
-63.1481
-63.2174
1.00
1.14
2.38
f1 (ppm)
19b

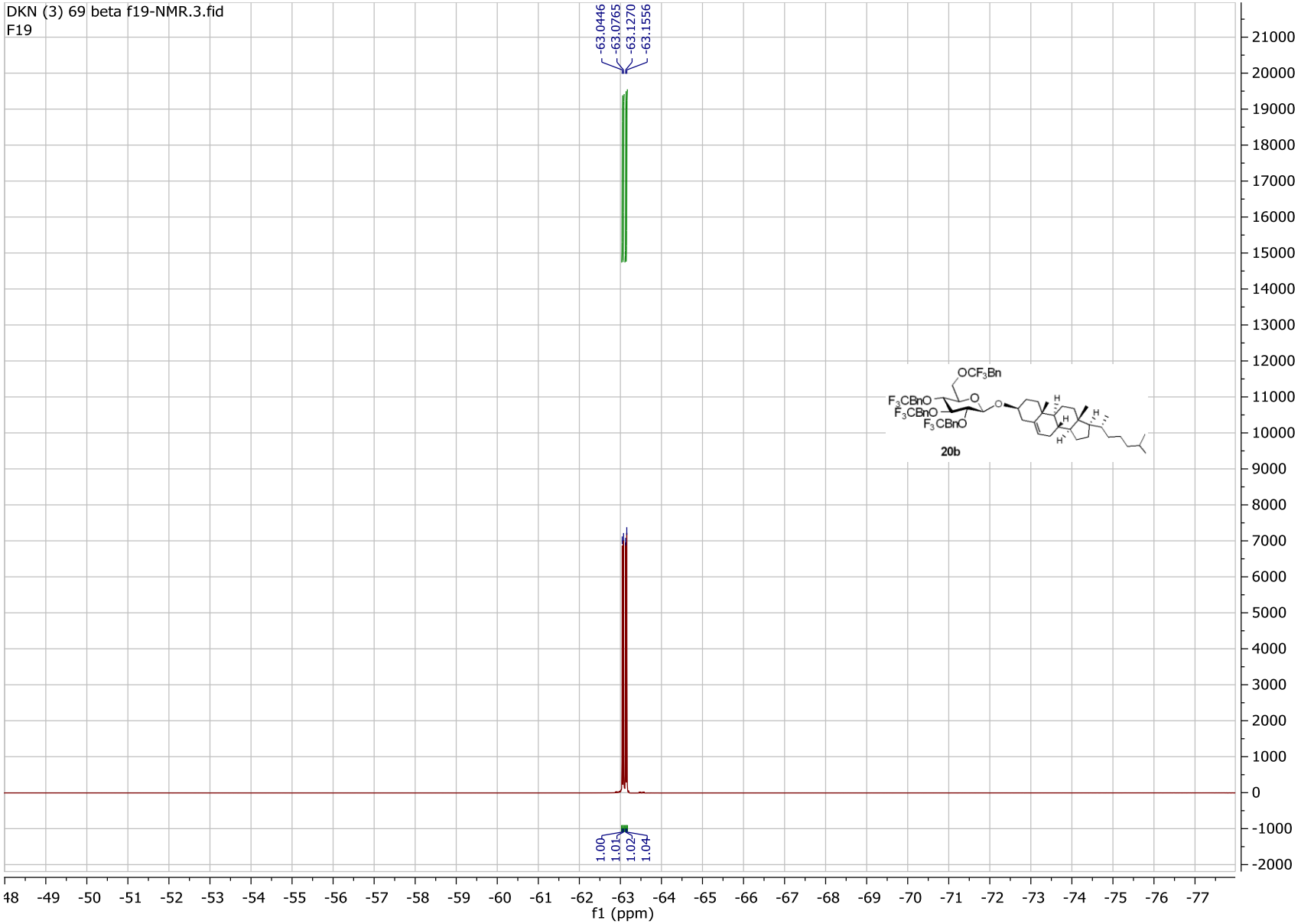

DKN (3) 69 prep 1 ALPHA 500MHz.3.fid
DKN (3) 69 prep 1 ALPHA
7.5620 7.5588 7.5455 7.5422 7.5324 7.5160 7.5117 7.4957 7.4287 7.4203 7.4124 7.4039 7.3574 7.3415 7.2565 CDCl3 7.2241 7.2082 5.2935 5.2873 5.0558 5.0485 5.0077 4.9837 4.8270 4.8082 4.8033 4.7842 4.7052 4.6650 4.6397 4.5670 4.5432 4.5139 4.4886 4.0027 3.7442 3.6882 3.6840 3.6308 3.6291 3.5676 1.8691 1.5682 1.5626 1.5557 HDO 1.5468 1.5208 1.5072 1.4999 1.4938 1.4902 1.4765 1.4676 1.3526 1.3423 1.3344 1.3297 1.2611 1.2561 1.1682 1.1579 1.1443 1.1341 1.1298 1.1249 1.1205 1.1173 1.1052 1.0870 1.0267 1.0141 1.0044 0.9944 0.9269 0.9138 0.8764 0.8719 0.8632 0.8587 0.6825 0.0000
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
H
H
H
H
20a
8.17 4.07 2.05 2.01
1.25 0.99 1.01 2.06 2.00 1.07 1.03 1.03
1.00 1.08 1.04 2.09 1.02 1.03
0.99 1.02
1.06 1.04 3.08
27.42
3.83 3.15 3.01 2.96
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

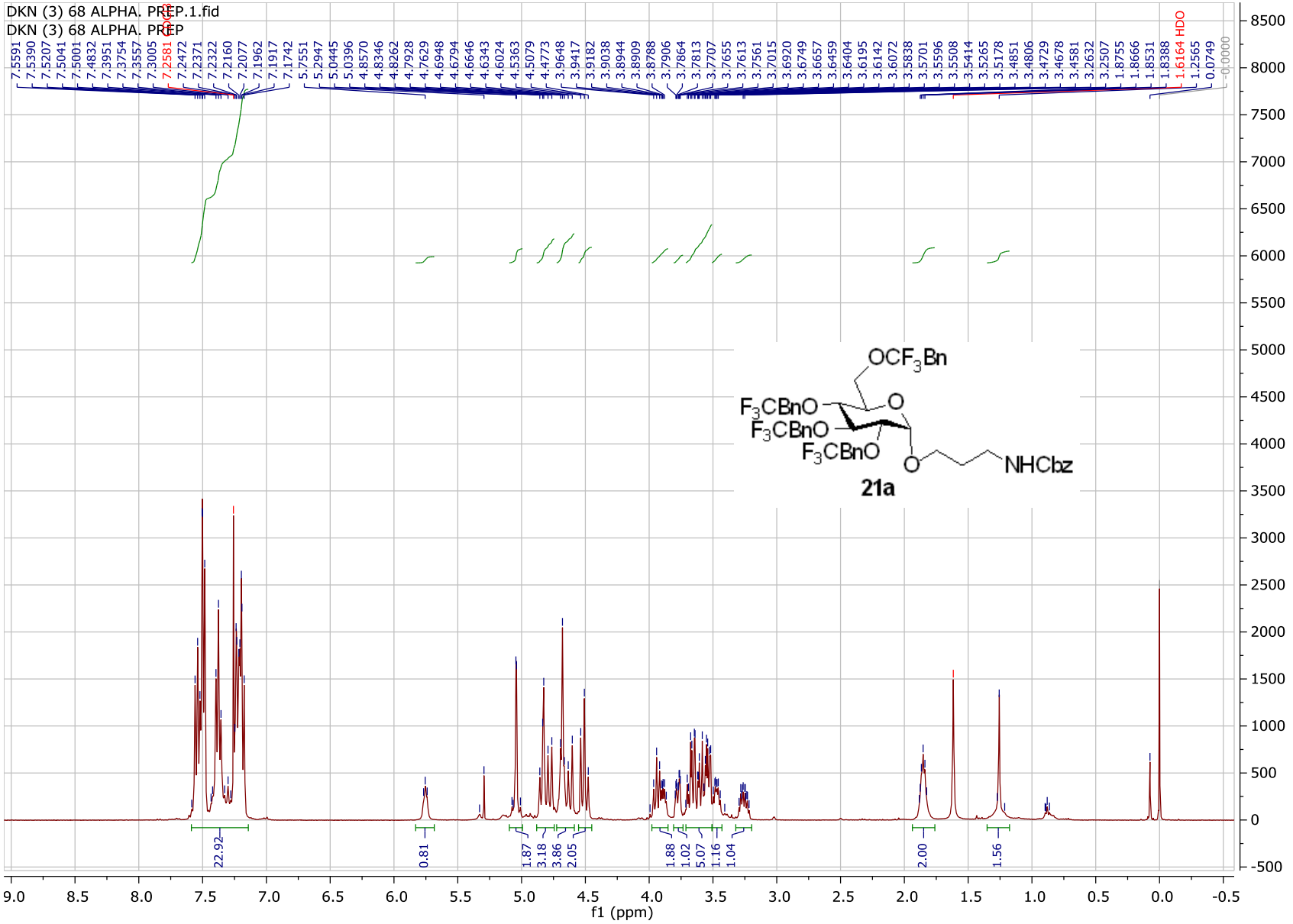

DKN (3) 69 prep 1 ALPHA c-13.3.fid
DKN (3) 69 prep 1 ALPHA c-13
142.7190
142.0391
141.9112
140.5595
130.0709
129.8162
127.8661
127.6765
127.3238
125.4233
125.3941
125.3667
125.3392
125.3089
125.2788
122.0283
94.5105
82.0981
80.2873
78.0591
77.2697 CDCl3
77.0157 CDCl3
74.5690
74.0850
72.6746
71.9186
70.0372
68.9733
56.7526
56.1635
50.1445
42.3349
39.9981
39.7599
39.5307
37.0593
36.7751
36.2008
35.7969
31.9038
31.8786
28.2380
28.0295
27.7183
23.8398
22.8262
22.5698
21.0713
19.3823
18.7312
11.8633
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
H
H
H
H
20a
f1 (ppm)

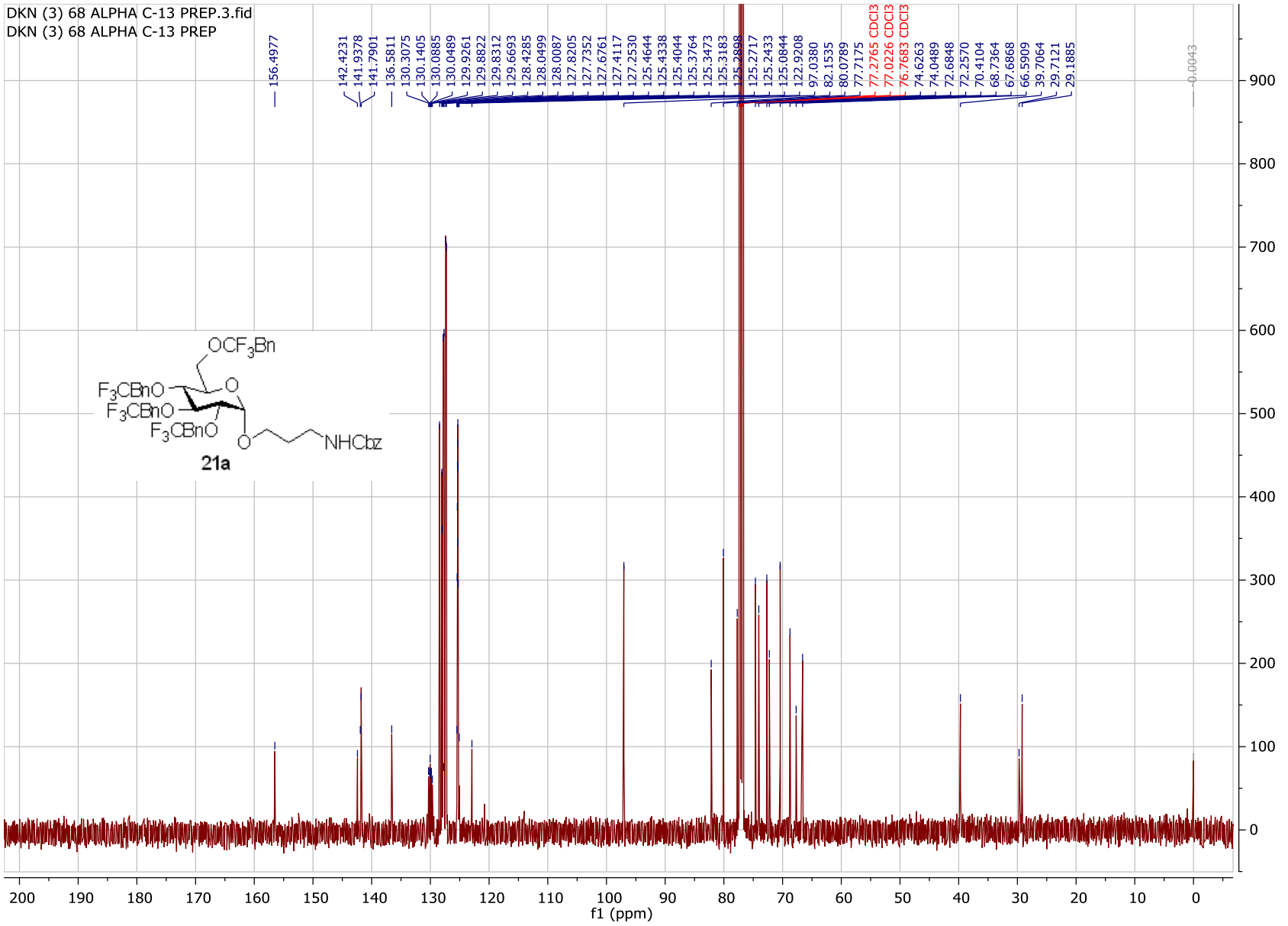

DKN (3) 69 alpha f19-NMR.3.fid
F19
-63.0682
-63.0932
-63.0996
-63.1696
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
20a
1.00
1.99
1.03
f1 (ppm)

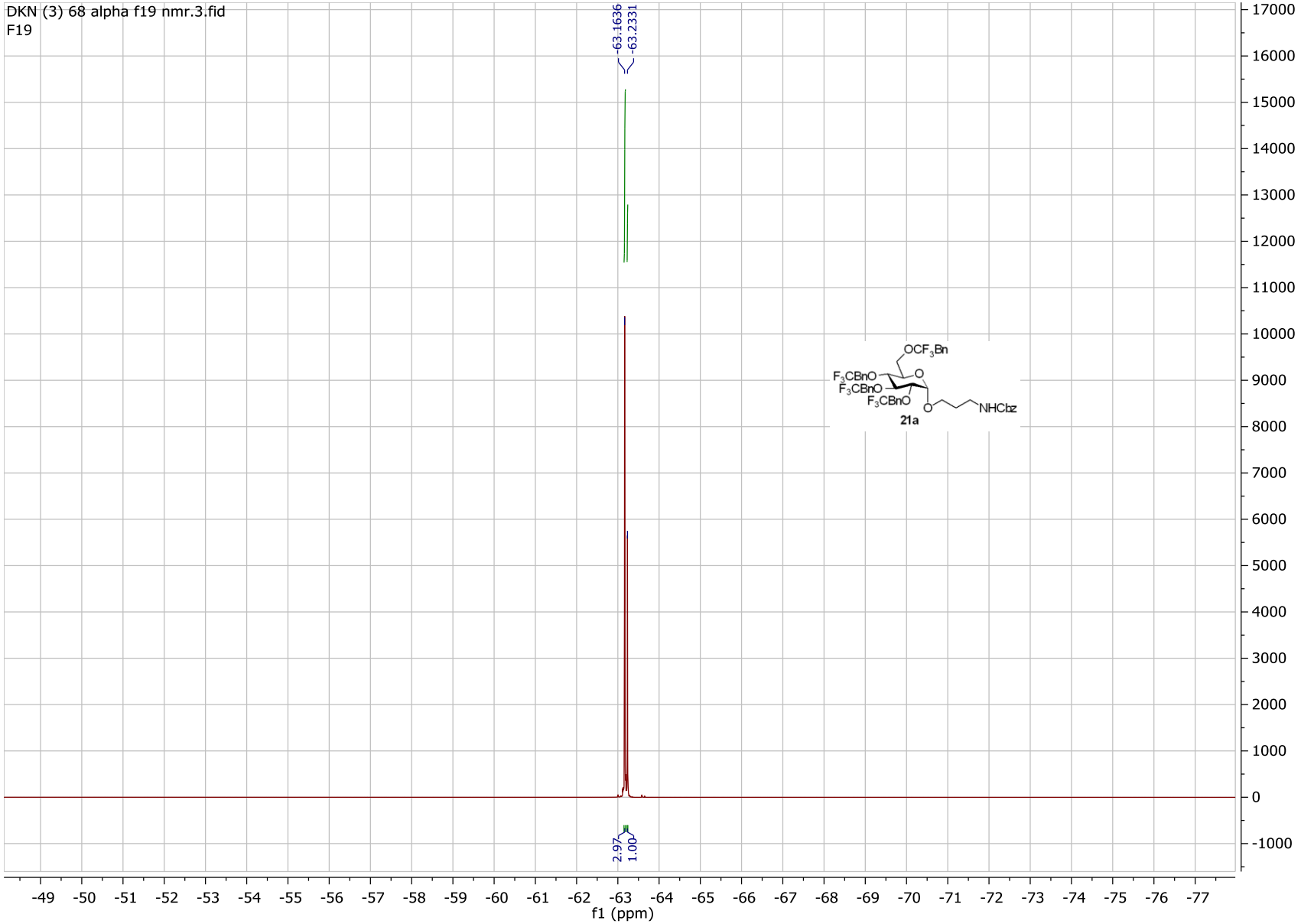

DKN (3) 69 prep 2 BETA 500MHz.3.fid
DKN (3) 69 prep 2 BETA
7.5688 7.5528 7.5308 7.5156 7.4990 7.4812 7.4341 7.4181 7.3992 7.3832 7.2852 7.2692 7.2546 CDCl3 7.2449 7.2289 7.2919 5.0245 5.0006 4.8817 4.8095 4.7856 4.7695 4.7453 4.7323 4.7084 4.6399 4.6246 4.6009 4.5934 4.5250 4.5094 3.7190 3.7132 3.7036 3.6186 3.6100 3.6054 3.6009 3.5909 3.4281 2.0422 2.0097 2.0028 1.8442 1.5591 HDO 1.5191 1.5061 1.4966 HDO 1.4931 1.4875 1.4784 1.4680 1.3515 1.3329 1.3281 1.2717 1.2568 1.1601 1.1452 1.1350 1.1286 1.1248 1.1193 1.1160 1.1059 1.1024 1.0909 1.0861 1.0655 1.0565 1.0108 0.9973 0.9280 0.9150 0.8831 0.8753 0.8708 0.8620 0.8575 0.6831 -0.0001
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
H
H
H
H
20b
1.98 5.87 1.96 1.97 1.96 2.20
0.93 0.96 0.97 0.97 0.98 0.97 2.98 0.97
1.96 2.97 1.95
1.95 3.12 1.99 28.98 4.01 3.35 3.05 3.01
4000 3500 3000 2500 2000 1500 1000 500 0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

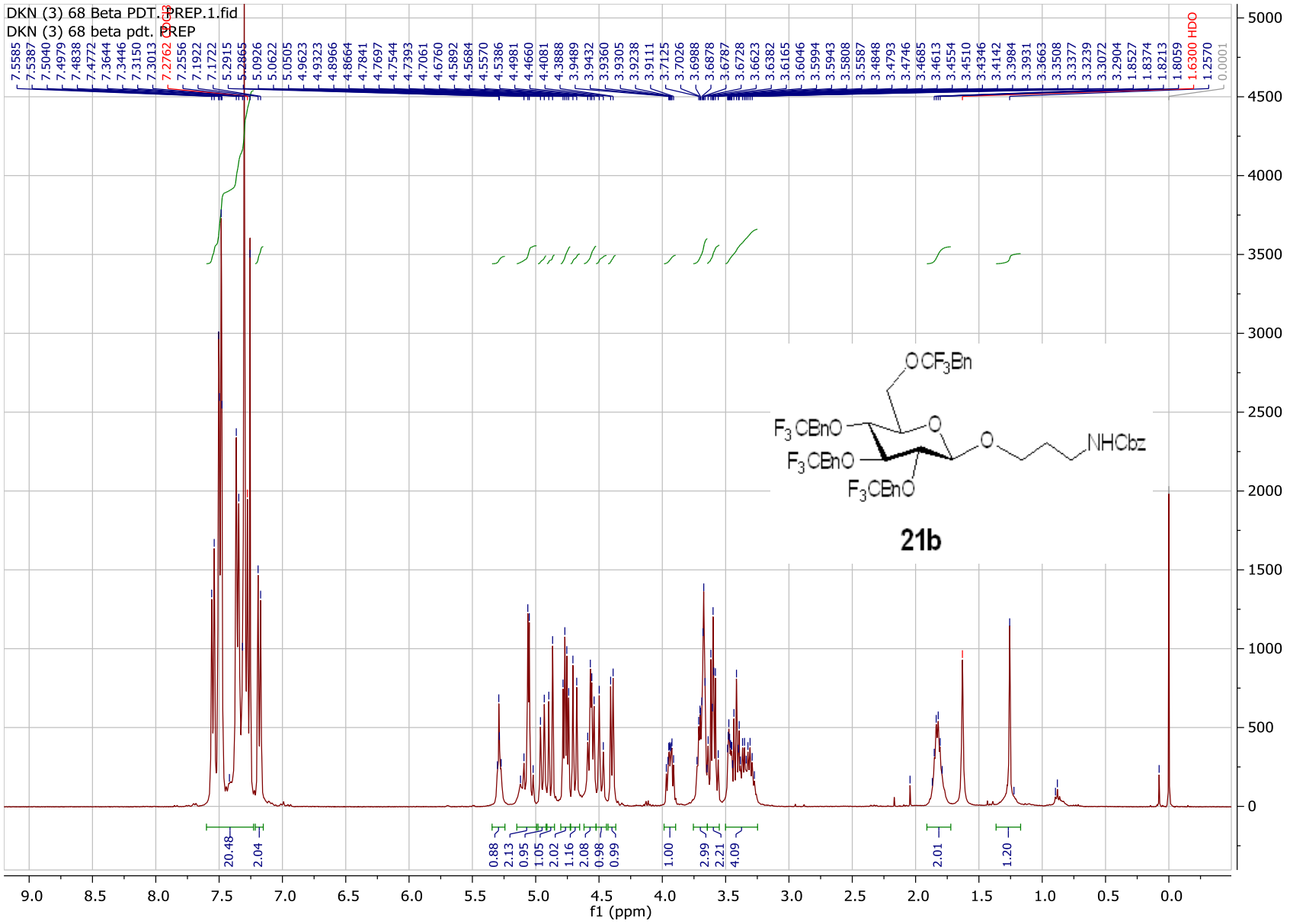

DKN (3) 69 prep 2 BETA c-13.3.fid
DKN (3) 69 prep 2 BETA c-13
142.3940
142.2300
142.0065
140.3172
130.0842
129.9740
129.8251
129.7350
129.7140
129.6798
127.8823
127.5276
127.3671
127.2971
125.3338
125.3096
125.2789
125.2480
125.2174
123.0149
122.9389
122.2182
102.0832
84.7507
82.2845
79.7739
78.0749
77.2688 CDCl3
77.0148 CDCl3
76.7607 CDCl3
74.5660
73.9722
73.7716
72.6042
69.1476
56.7519
56.1608
53.4168
50.2110
42.3356
39.7536
39.5334
39.0692
37.2872
36.7568
36.2032
35.7963
31.9342
31.8752
30.0053
29.7150
29.6758
29.3795
28.2387
28.0313
24.2903
23.8364
22.8259
22.7080
22.6674
22.5700
21.0614
19.3757
18.7309
14.1278
11.8687
-0.0038
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
H
H
H
H
20b
f1 (ppm)

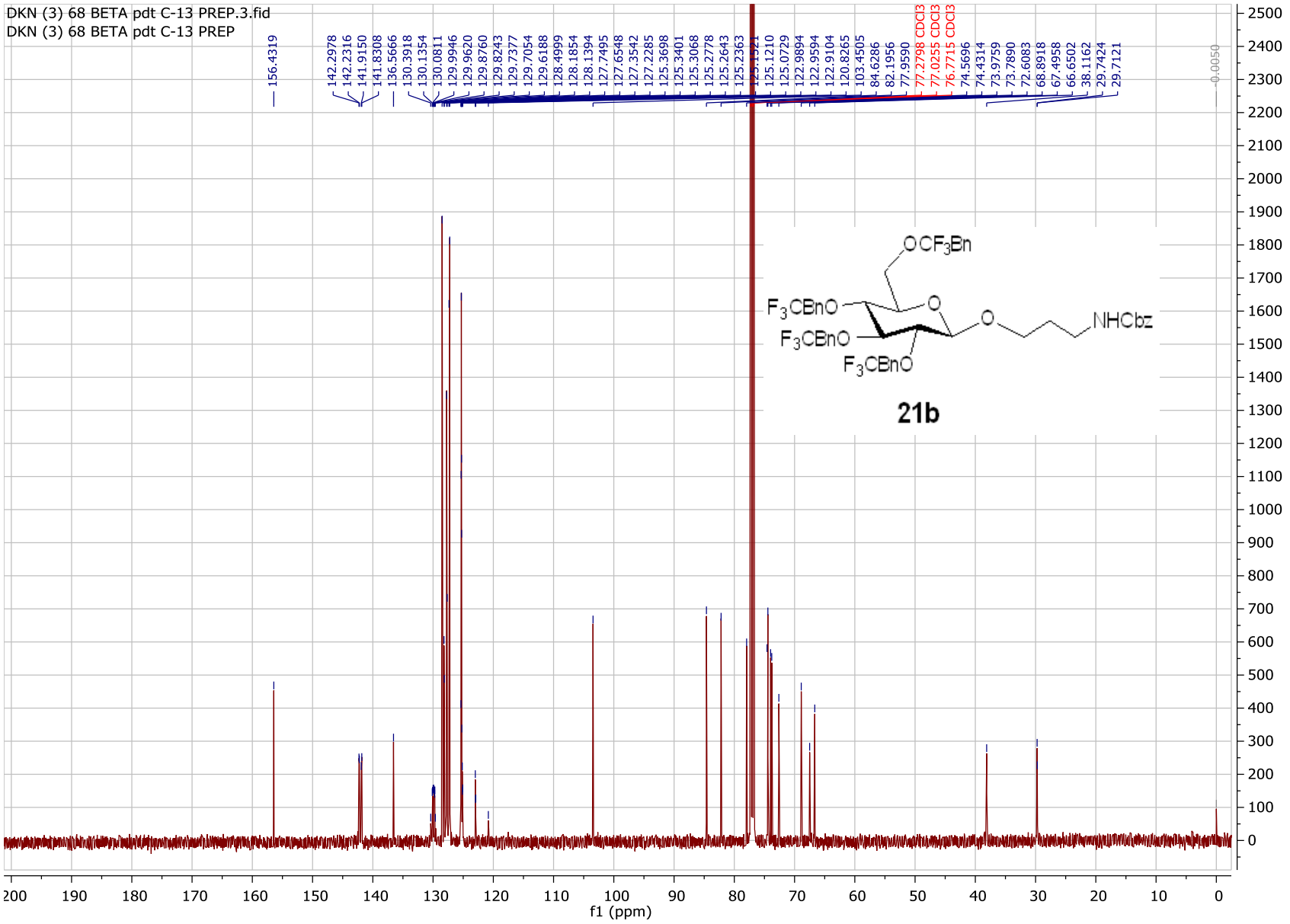

DKN (3) 69 beta f19-NMR.3.fid
F19
-63.0446
-63.0765
-63.1270
-63.1556
1.00
1.01
1.02
1.04
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
20b
f1 (ppm)

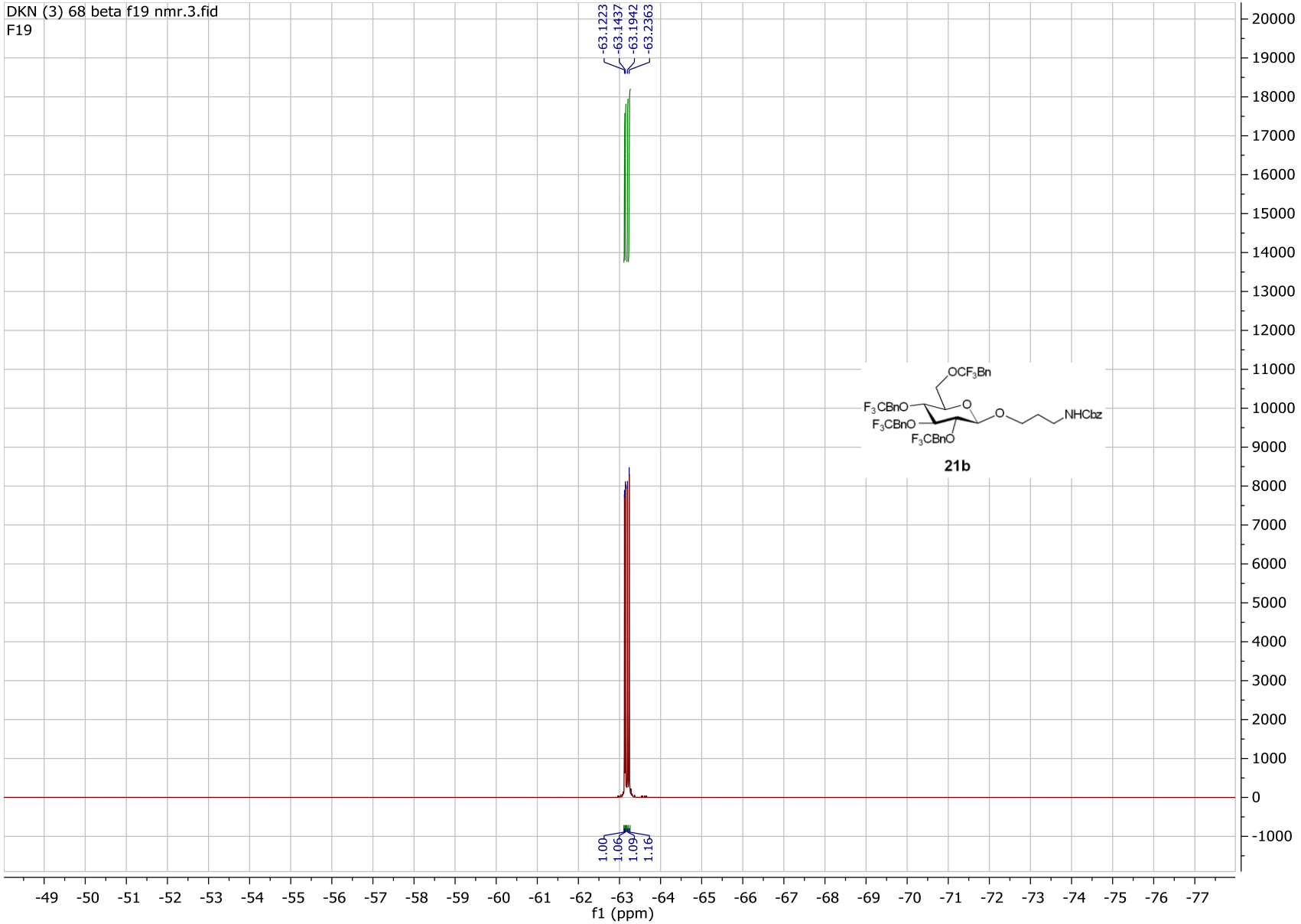

DKN (3) 68 ALPHA. PREP.1.fid
DKN (3) 68 ALPHA. PREP
7.2581 CDCl3
1.6164 HDO
0.0000
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21a
22.92
0.81
1.87
3.18
3.86
2.05
1.88
1.02
5.07
1.16
1.04
2.00
1.56
f1 (ppm)

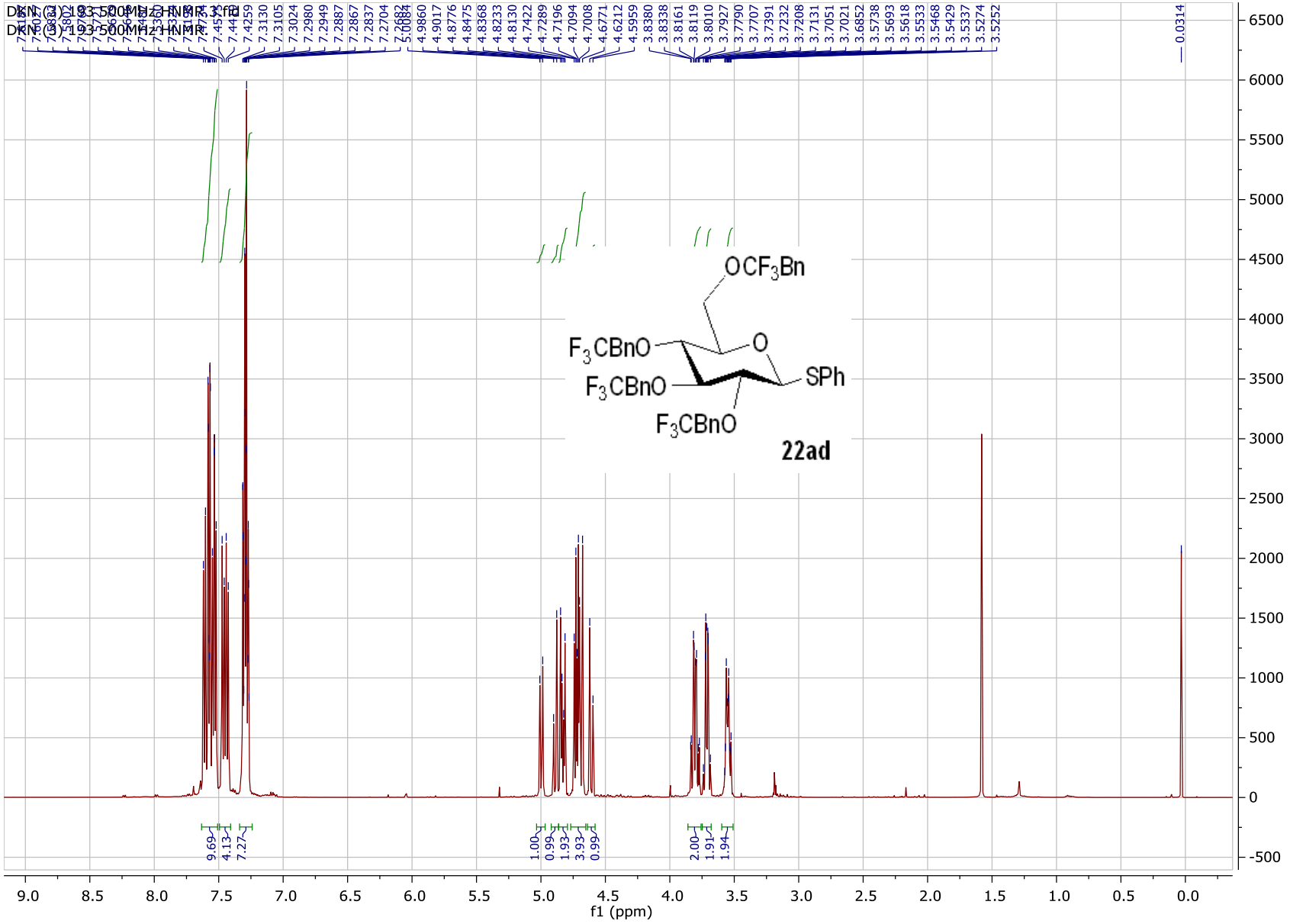

DKN (3) 68 ALPHA C-13 PREP.3.fid
DKN (3) 68 ALPHA C-13 PREP
156.4977
142.4231
141.9378
141.7901
136.5811
130.3075
130.1405
130.0885
130.0489
129.9261
129.8822
129.8312
129.6693
128.4285
128.0499
128.0087
127.8205
127.7352
127.6761
127.4117
127.2530
125.4644
125.4338
125.4044
125.3764
125.3473
125.3183
125.2898
125.2717
125.2433
125.0844
122.9208
97.0380
82.1535
80.0789
77.7175
77.2765 CDCl3
77.0226 CDCl3
76.7683 CDCl3
74.6263
74.0489
72.6848
72.2570
70.4104
68.7364
67.6868
66.5909
39.7064
29.7121
29.1885
-0.0043
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21a
f1 (ppm)

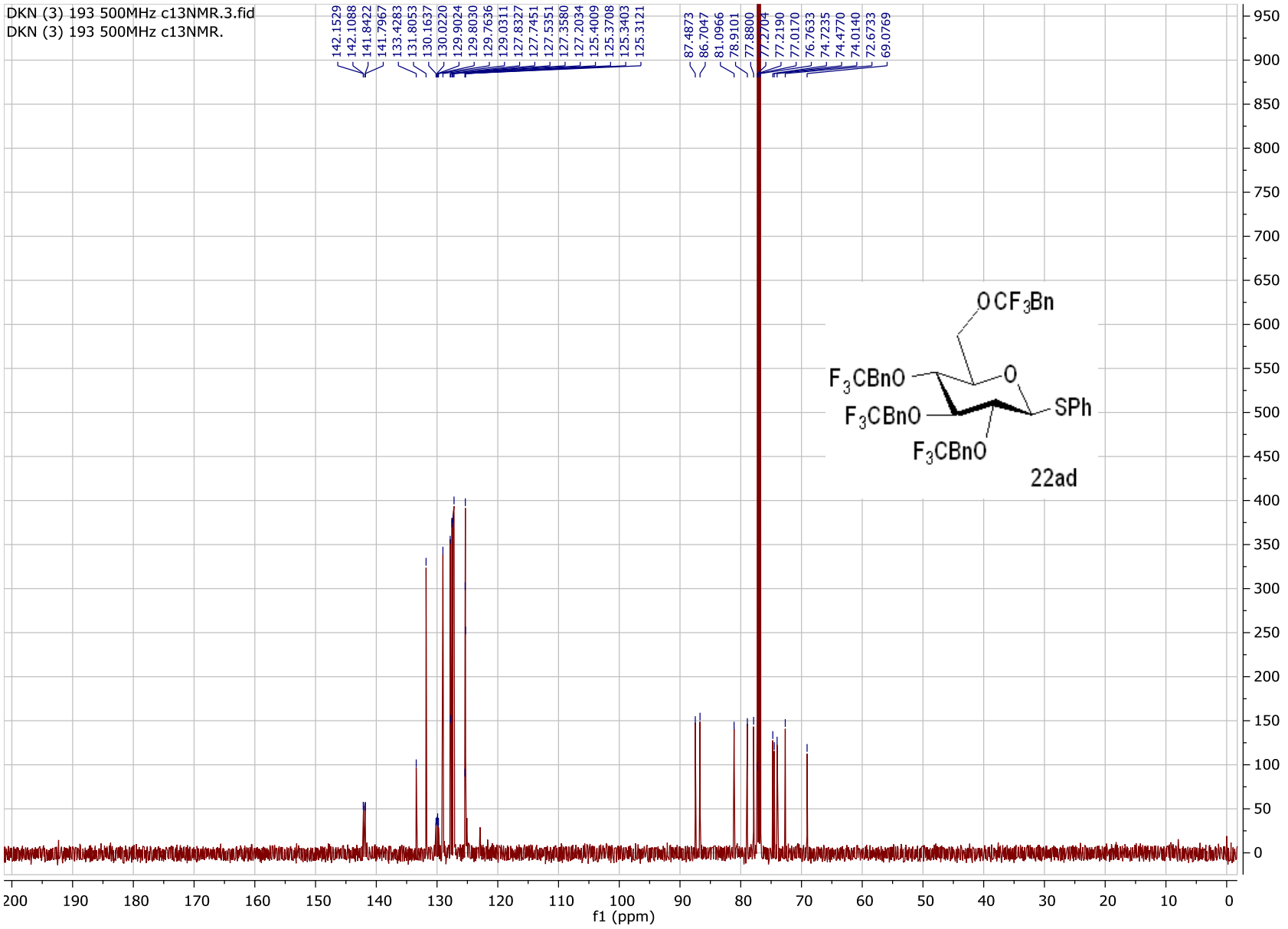

DKN (3) 68 alpha f19 nmr.3.fid
F19
-63.1636
-63.2331
2.97
1.00
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21a
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77
f1 (ppm)

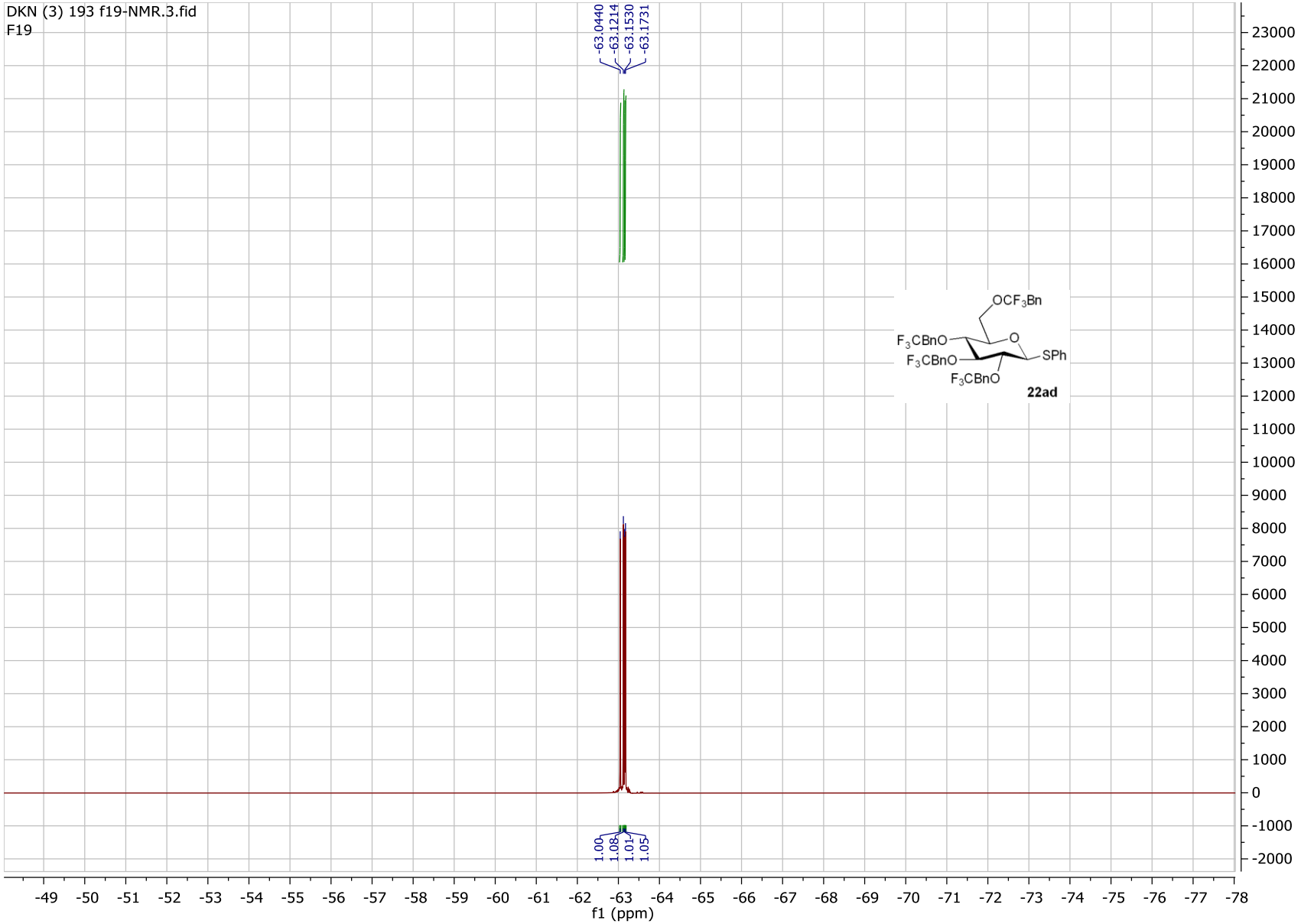

DKN (3) 68 Beta PDT. PREP.1.fid
DKN (3) 68 beta pdt. PREP
7.5585 7.5387 7.5040 7.4979 7.4838 7.4772 7.3644 7.3446 7.3150 7.3013 7.2762 CHCl3 7.2556 7.1922 7.1722 5.2915 5.2865 5.0926 5.0622 5.0505 4.9623 4.9323 4.8966 4.8664 4.7841 4.7697 4.7544 4.7393 4.7061 4.6760 4.5892 4.5684 4.5570 4.5386 4.4981 4.4660 4.4081 4.3888 3.9489 3.9432 3.9360 3.9305 3.9238 3.9111 3.7125 3.7026 3.6988 3.6878 3.6787 3.6728 3.6623 3.6382 3.6165 3.6046 3.5994 3.5943 3.5808 3.5587 3.4848 3.4793 3.4746 3.4685 3.4613 3.4554 3.4510 3.4346 3.4142 3.3984 3.3931 3.3663 3.3508 3.3377 3.3239 3.3072 3.2904 1.8527 1.8374 1.8213 1.8059 1.6300 HDO 1.2570 0.0001
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21b
20.48 2.04 0.88 2.13 0.95 1.05 2.02 1.16 2.08 0.98 0.99 1.00 2.99 2.21 4.09 2.01 1.20
f1 (ppm)

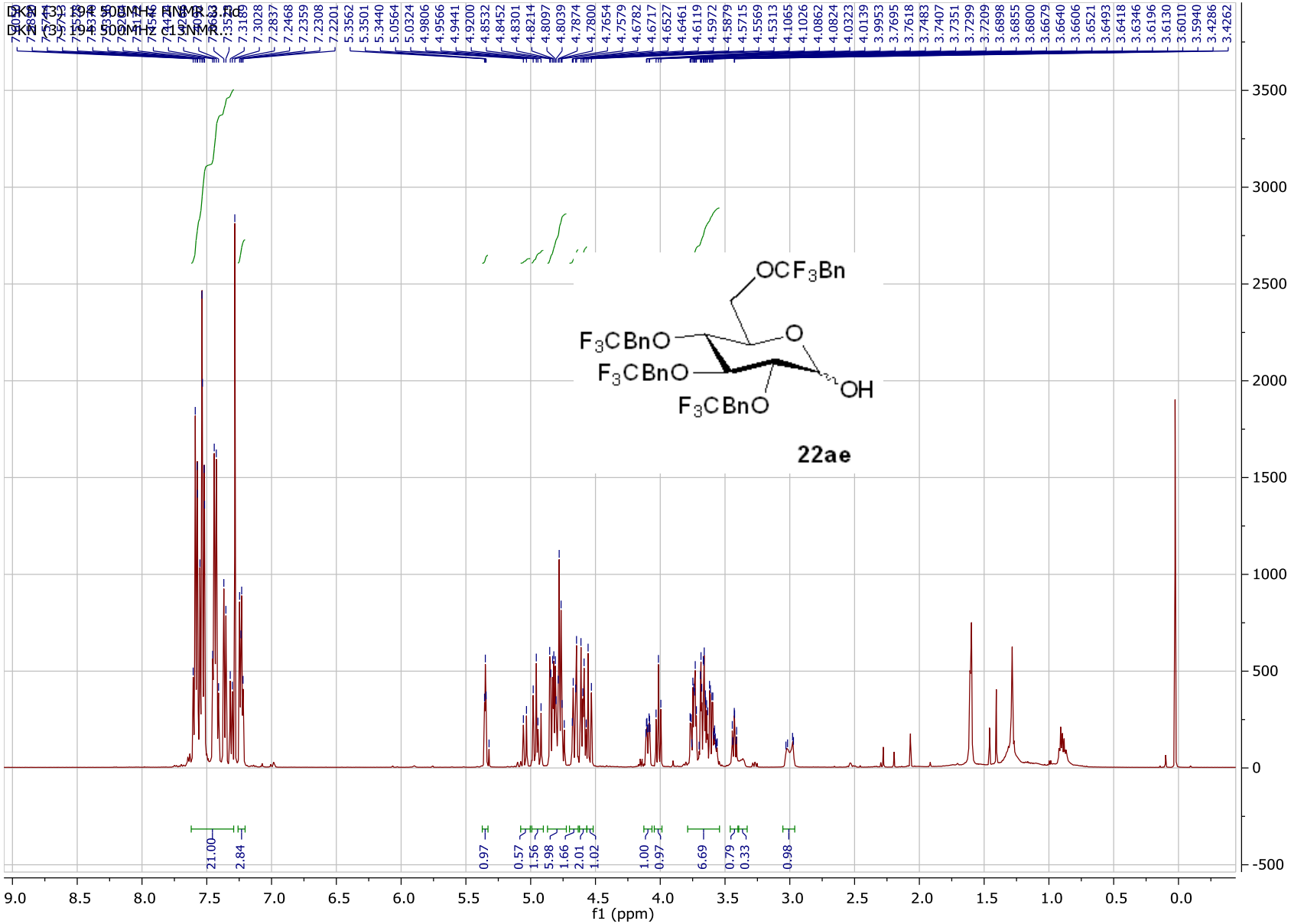

DKN (3) 68 BETA pdt C-13 PREP.3.fid
DKN (3) 68 BETA pdt C-13 PREP
156.4319
142.2978
142.2316
141.9150
141.8308
136.5666
130.3918
130.1354
130.0811
129.9946
129.9620
129.8760
129.8243
129.7377
129.7054
129.6188
128.4999
128.1854
128.1394
127.7495
127.6548
127.3542
127.2285
125.3698
125.3401
125.3068
125.2778
125.2643
125.2363
125.1521
125.1210
125.0729
122.9894
122.9594
122.9104
120.8265
103.4505
84.6286
82.1956
77.9590
77.2798 CDCl3
77.0255 CDCl3
76.7715 CDCl3
74.5696
74.4314
73.9759
73.7890
72.6083
68.8918
67.4958
66.6502
38.1162
29.7424
29.7121
-0.0050
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21b
f1 (ppm)

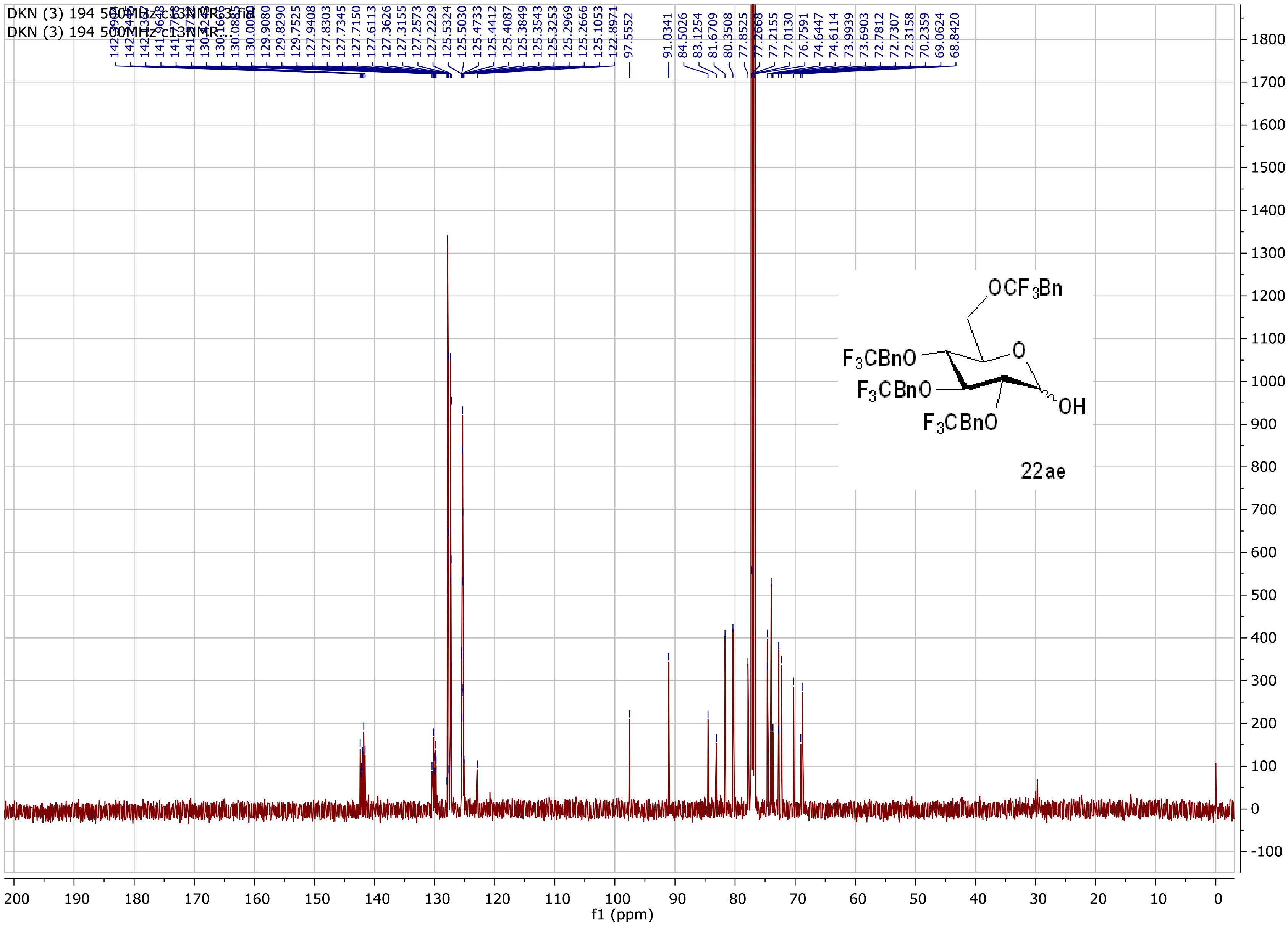

DKN (3) 68 beta f19 nmr.3.fid
F19
-63.1223
-63.1437
-63.1942
-63.2363
1.00
1.06
1.09
1.16
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21b
f1 (ppm)

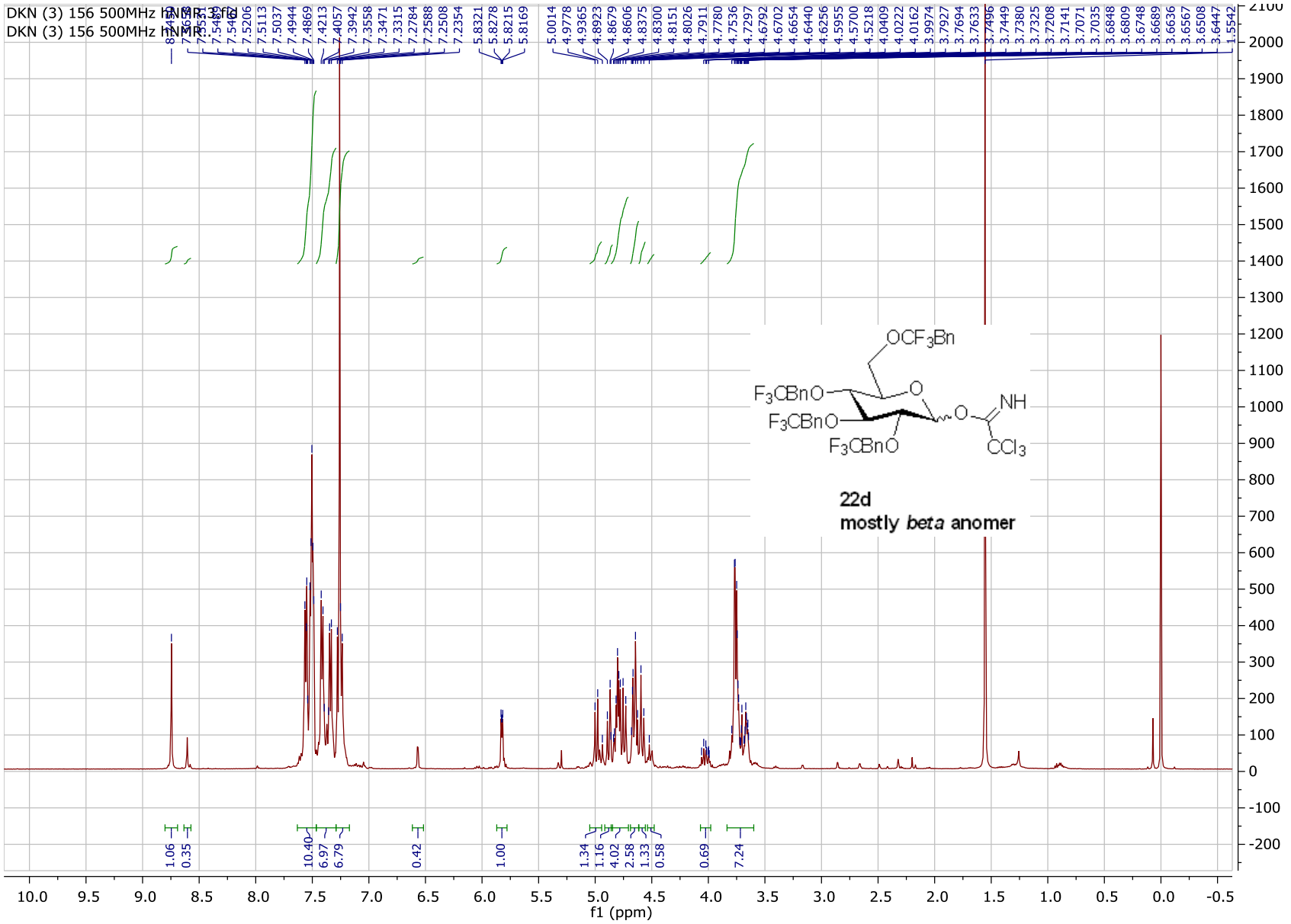

DKN (3) 193-500MHz-HNMR-3.fid
DKN (3) 193-500MHz-HNMR
OCF3Bn
F3CBnO
O
SPh
F3CBnO
F3CBnO
22ad
f1 (ppm)

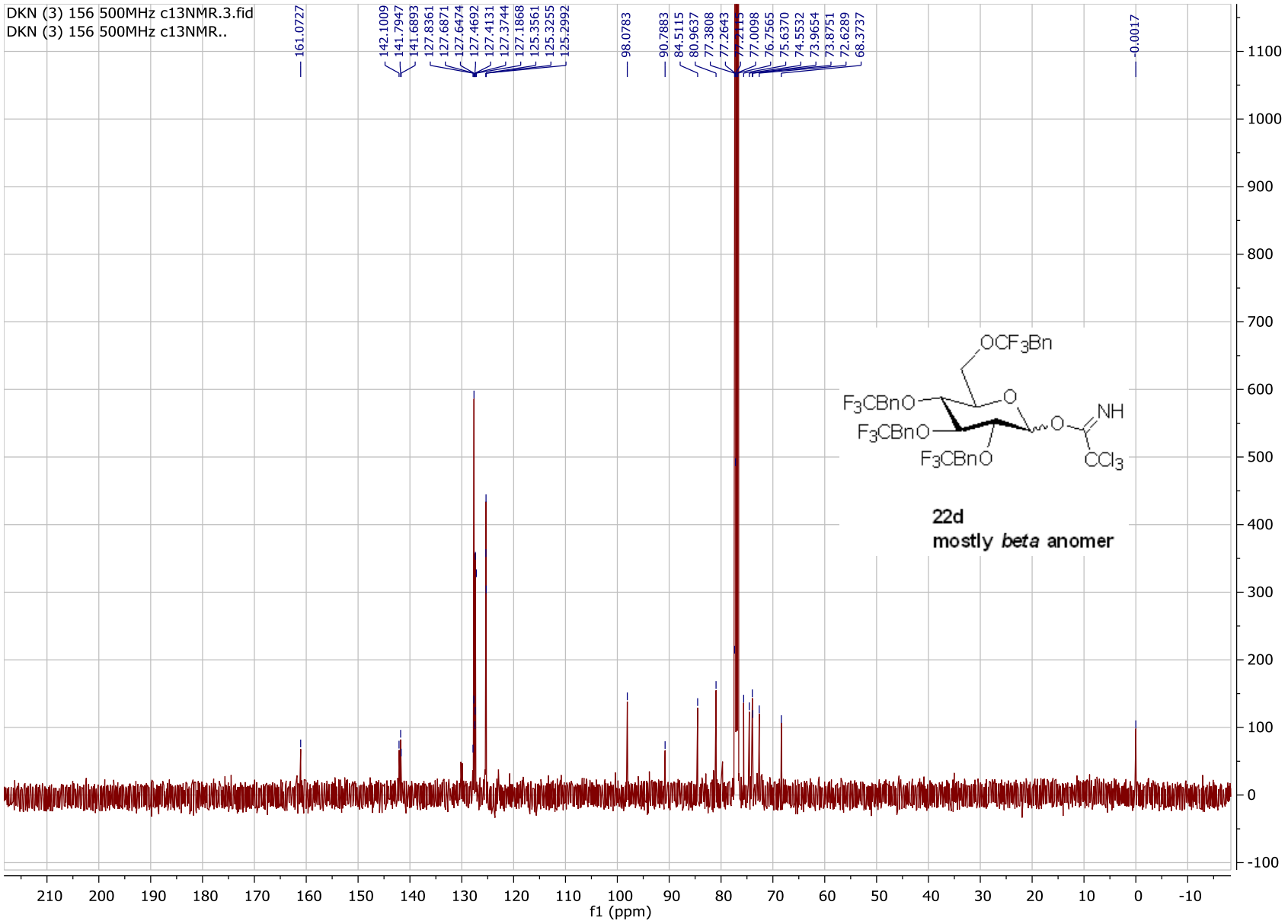

DKN (3) 193 500MHz c13NMR.3.fid
DKN (3) 193 500MHz c13NMR.
142.1529
142.1088
141.8422
141.7967
133.4283
131.8053
130.1637
130.0220
129.9024
129.8030
129.7636
129.0311
127.8327
127.7451
127.5351
127.3580
127.2034
125.4009
125.3708
125.3403
125.3121
87.4873
86.7047
81.0966
78.9101
77.8800
77.2704
77.2190
77.0170
76.7633
74.7235
74.4770
74.0140
72.6733
69.0769
OCF3Bn
F3CBnO
O
SPh
F3CBnO
F3CBnO
22ad
f1 (ppm)

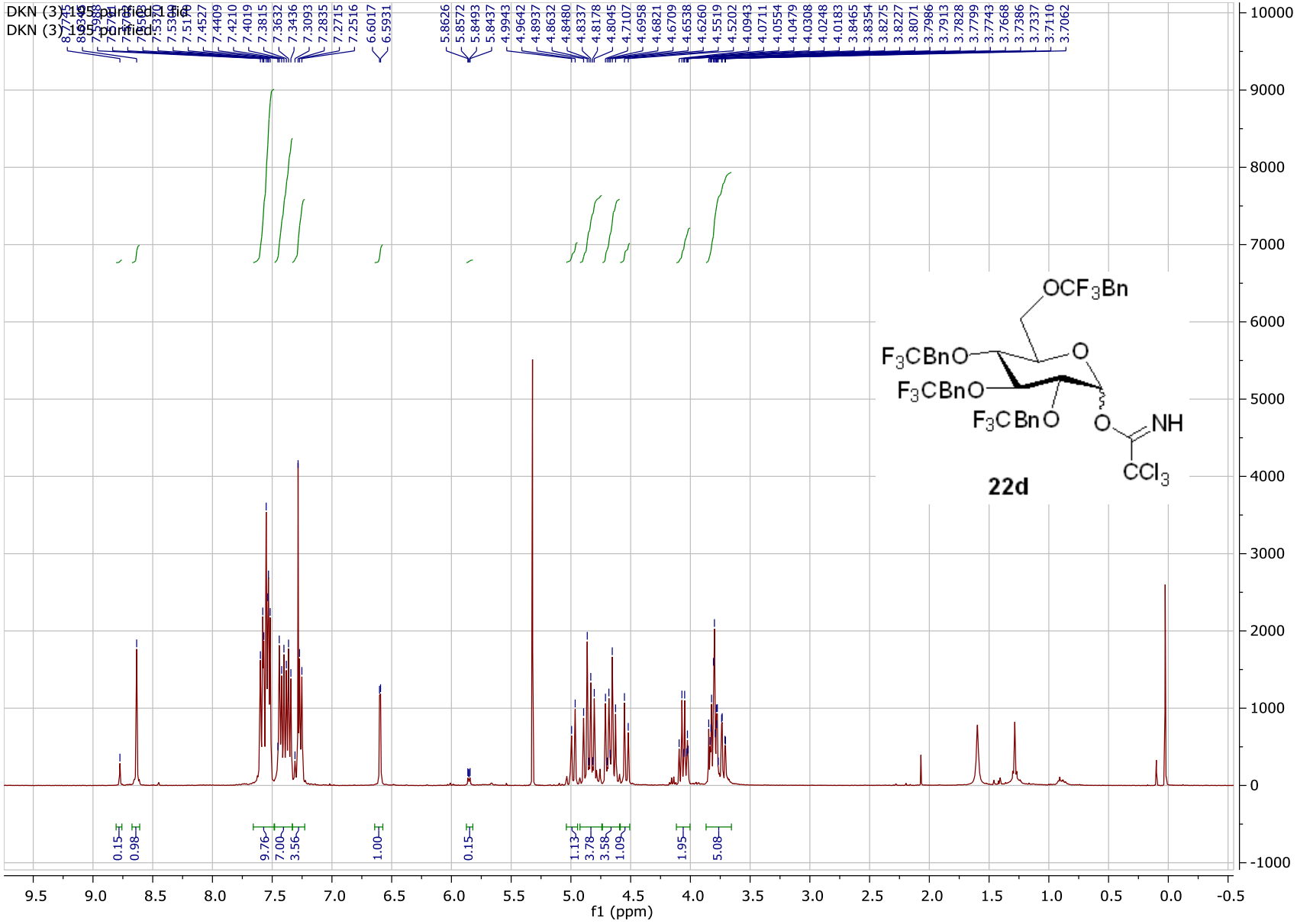

DKN (3) 193 f19-NMR.3.fid
F19
-63.0440
-63.1214
-63.1530
-63.1731
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
SPh
22ad
1.00
1.08
1.01
1.05
f1 (ppm)

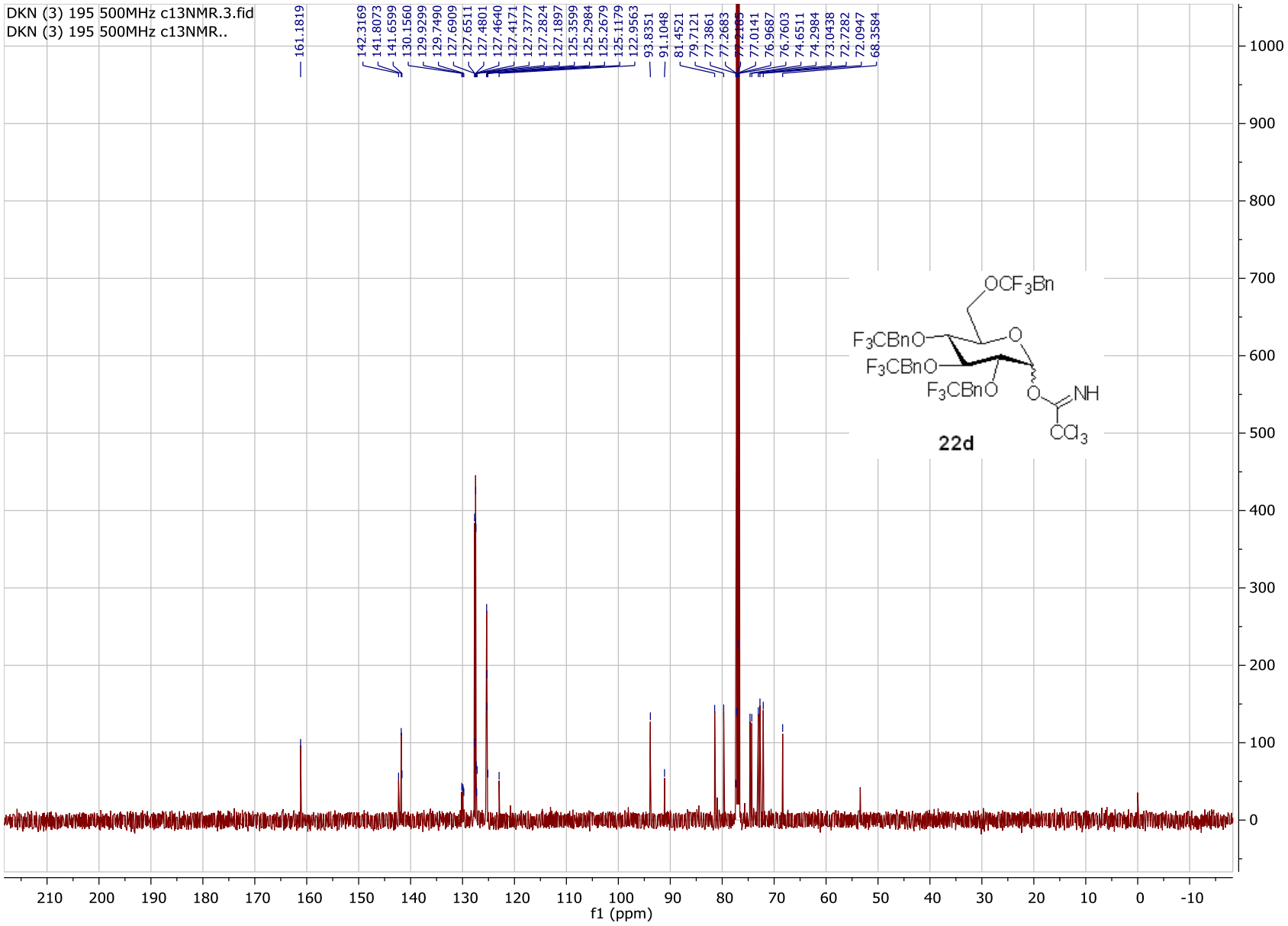

DKN (3) 194 500MHz FNMR.3.fid
DKN (3) 194 500MHz C13NMR.
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
OH
22ae
21.00
2.84
0.97
0.57
1.56
5.98
1.66
2.01
1.02
1.00
0.97
6.69
0.79
0.33
0.98
f1 (ppm)

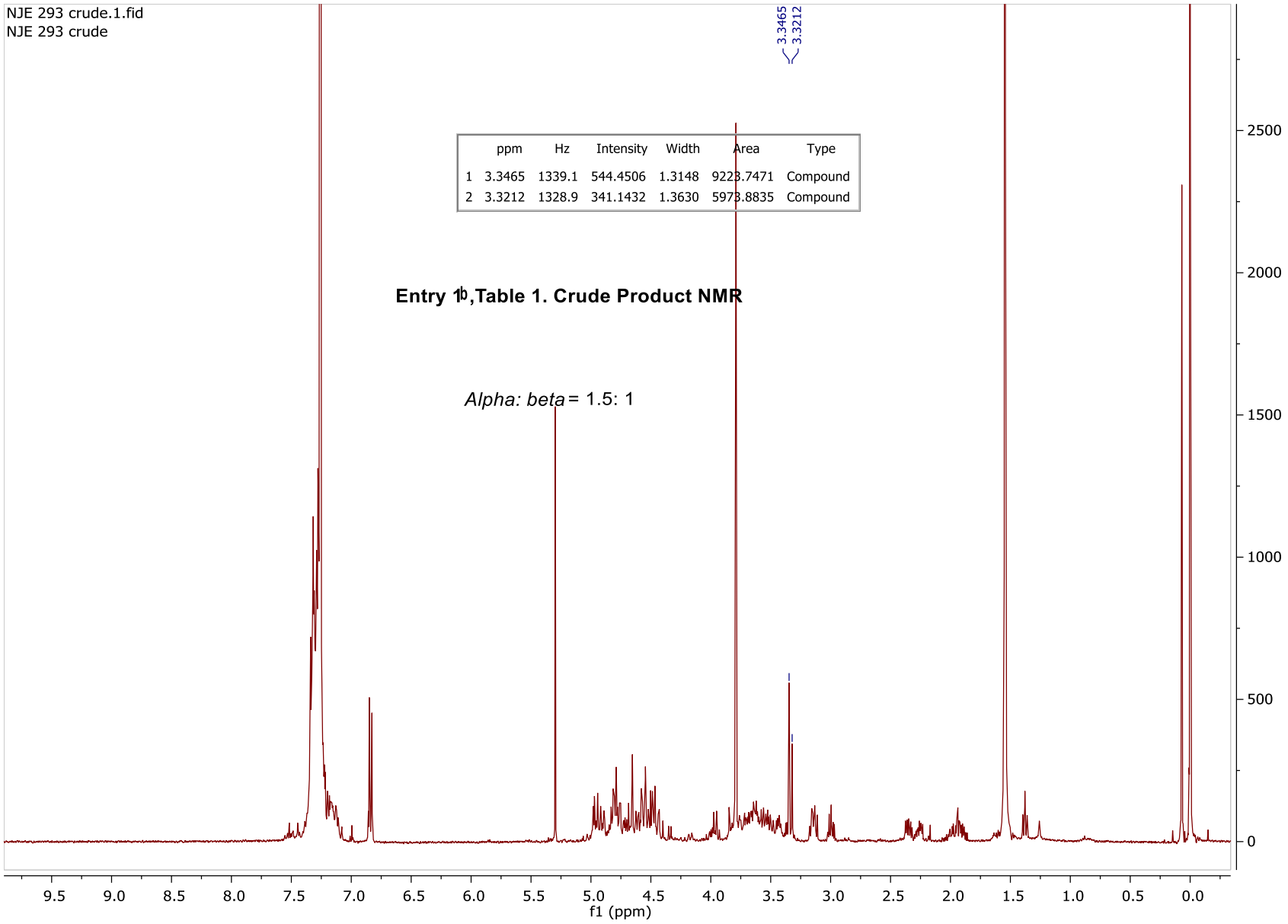

DKN (3) 194 500MHz c13NMR
f1 (ppm)
22ae

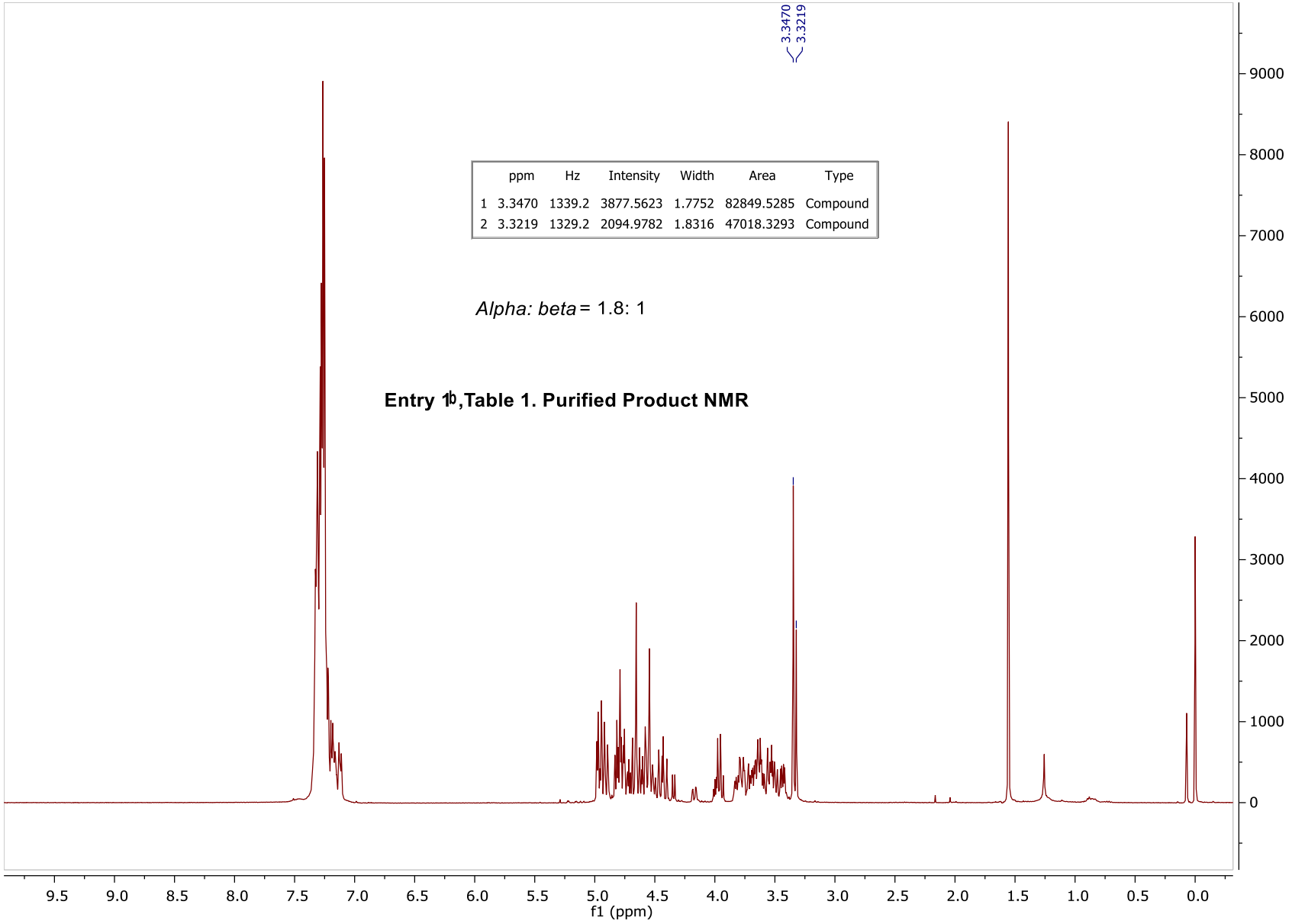

DKN (3) 156 500MHz hNMR.1.fid
DKN (3) 156 500MHz hNMR.3.fid
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NH
CCl3
22d
mostly beta anomer
f1 (ppm)


DKN (3) 156 500MHz c13NMR.3.fid
DKN (3) 156 500MHz c13NMR..
161.0727
142.1009
141.7947
141.6893
127.8361
127.6871
127.6474
127.4692
127.4131
127.3744
127.1868
125.3561
125.3255
125.2992
98.0783
90.7883
84.5115
80.9637
77.3808
77.2643
77.2115
77.0098
76.7565
75.6370
74.5532
73.9654
73.8751
72.6289
68.3737
-0.0017
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NH
CCl3
22d
mostly beta anomer
f1 (ppm)


DKN (3)-195-purified-1H
DKN (3)-195-purified
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NH
CCl3
22d
f1 (ppm)


DKN (3) 195 500MHz c13NMR.3.fid
DKN (3) 195 500MHz c13NMR..
161.1819
142.3169
141.8073
141.6599
130.1560
129.9299
129.7490
127.6909
127.6511
127.4801
127.4640
127.4171
127.3777
127.2824
127.1897
125.3599
125.2984
125.2679
125.1179
122.9563
93.8351
91.1048
81.4521
79.7121
77.3861
77.2683
77.2165
77.0141
76.9687
76.7603
74.6511
74.2984
73.0438
72.7282
72.0947
68.3584
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NH
CCl3
22d
f1 (ppm)

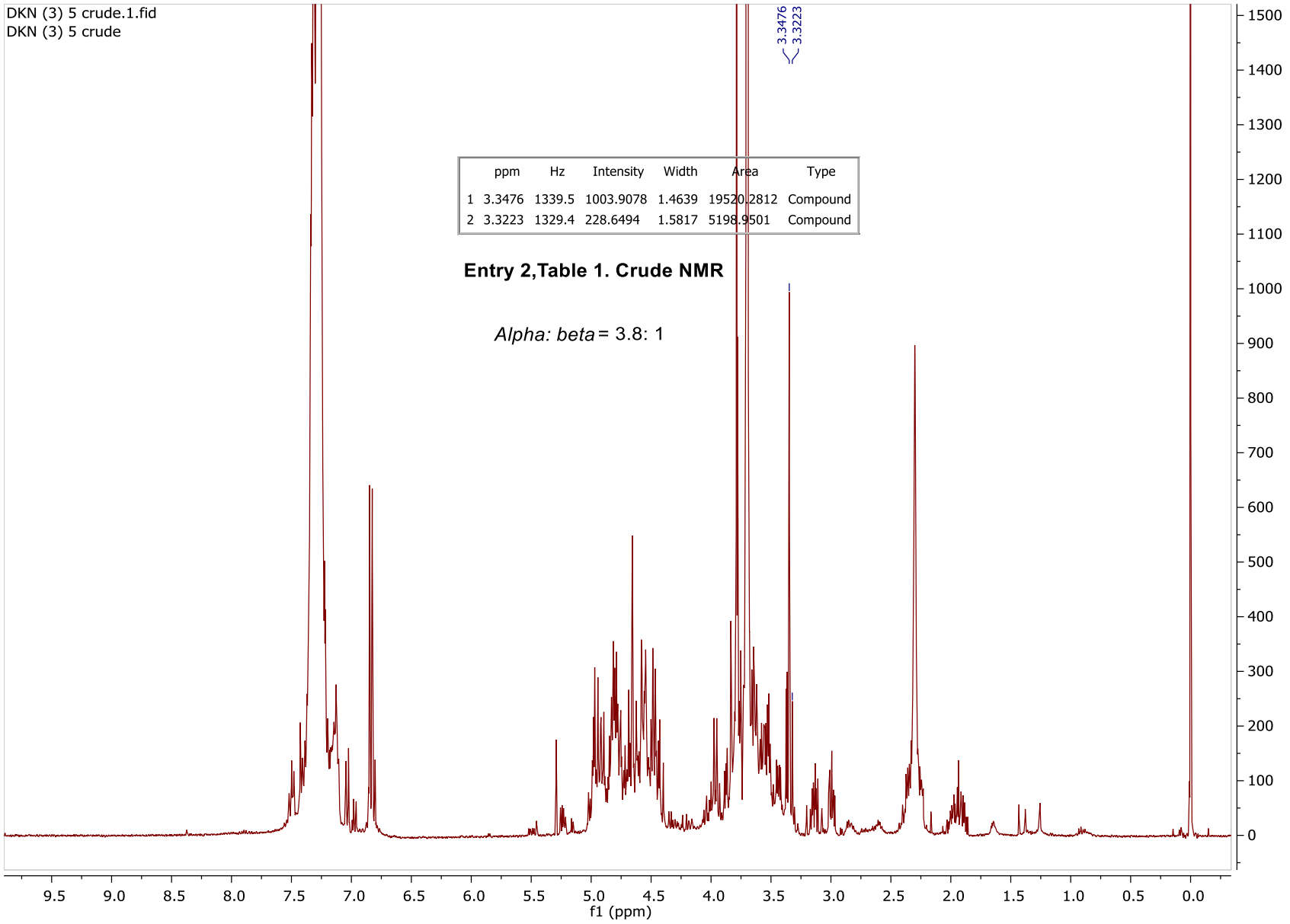

NJE 293 crude.1.fid
NJE 293 crude
3.3465
3.3212
ppm Hz Intensity Width Area Type
1 3.3465 1339.1 544.4506 1.3148 9223.7471 Compound
2 3.3212 1328.9 341.1432 1.3630 5973.8835 Compound
Entry 1b,Table 1. Crude Product NMR
Alpha: beta = 1.5: 1
2500
2000
1500
1000
500
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

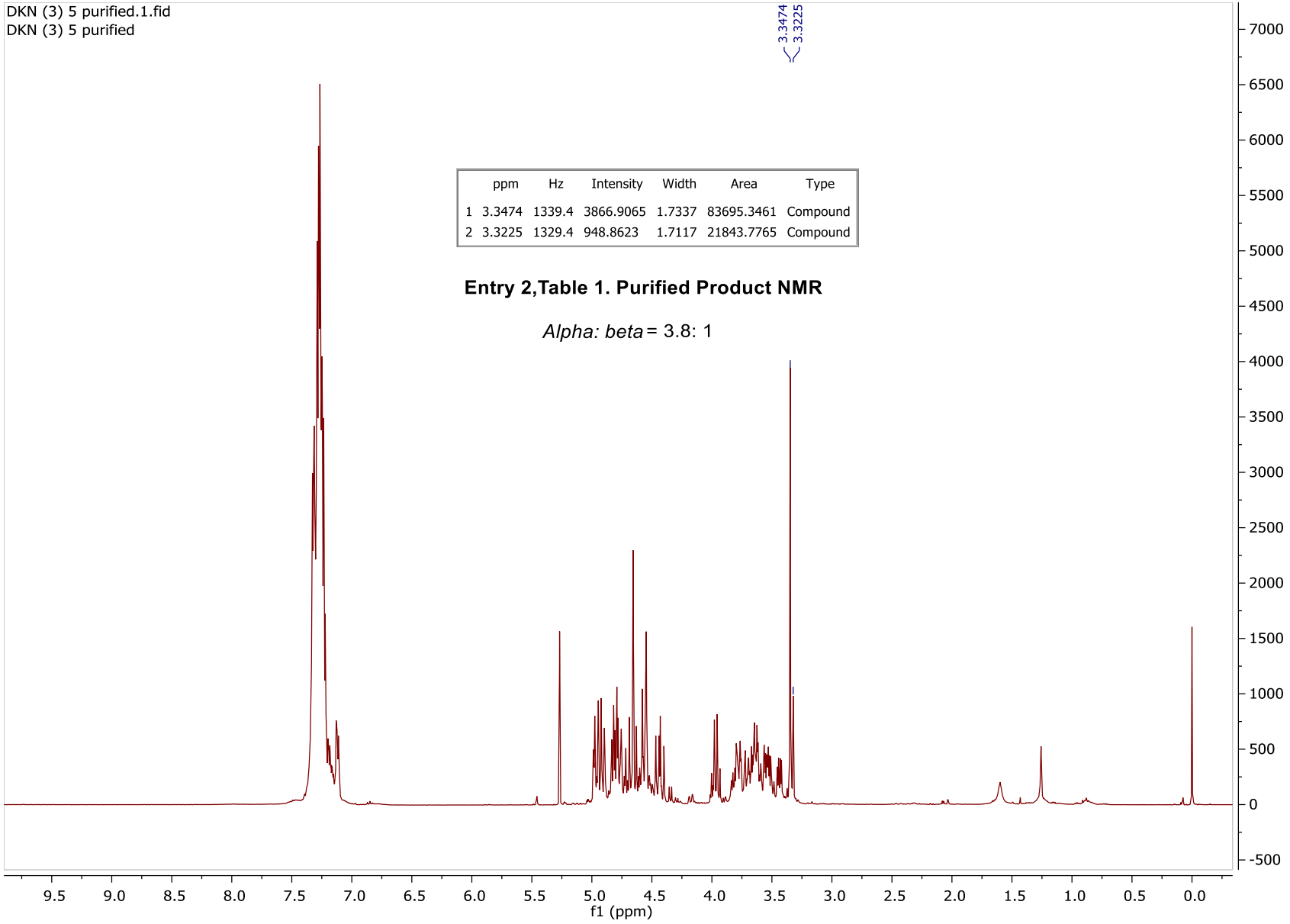


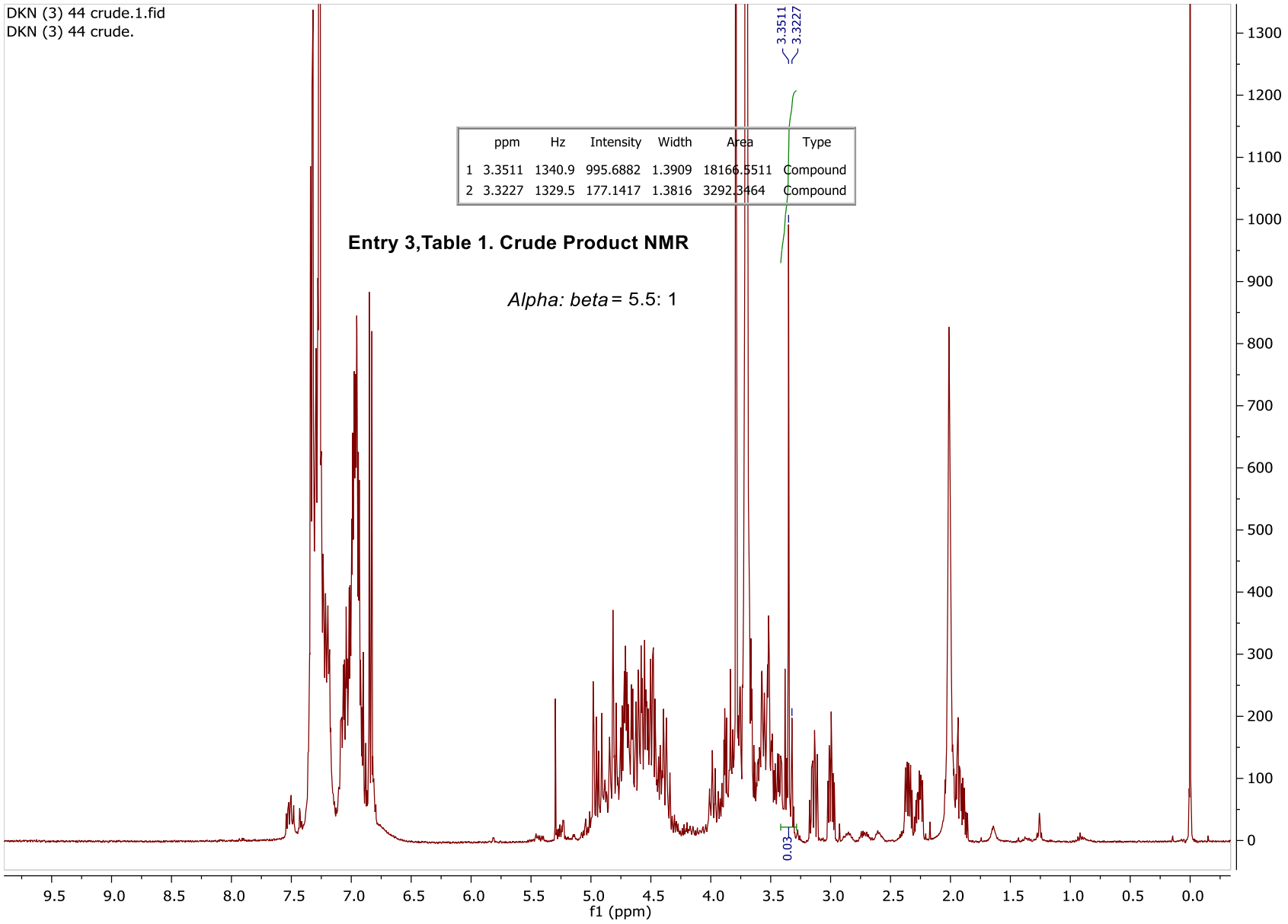
	ppm	Hz	Intensity	Width	Area	Type
1	3.3470	1339.2	3877.5623	1.7752	82849.5285	Compound
2	3.3219	1329.2	2094.9782	1.8316	47018.3293	Compound

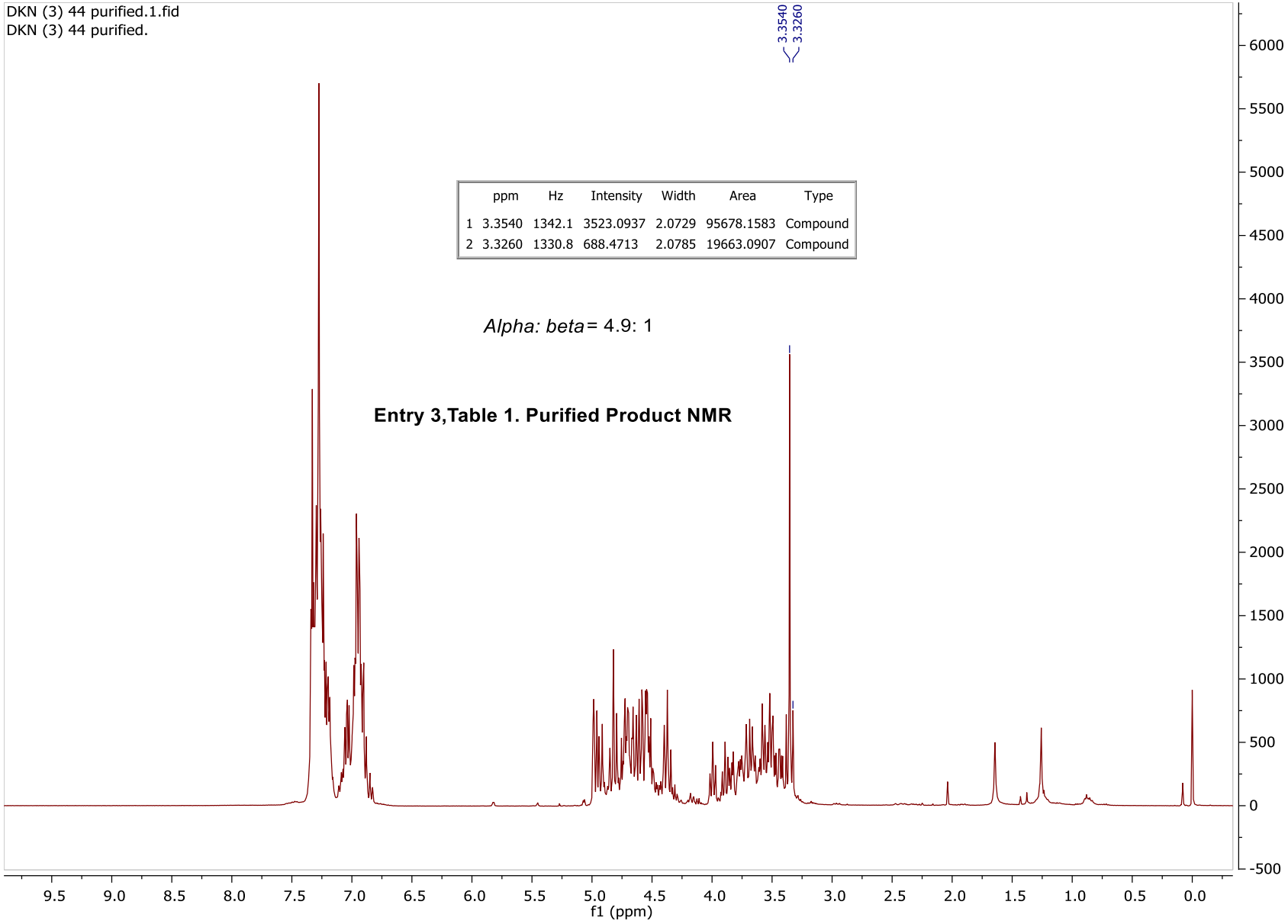
Alpha: beta = 1.8: 1

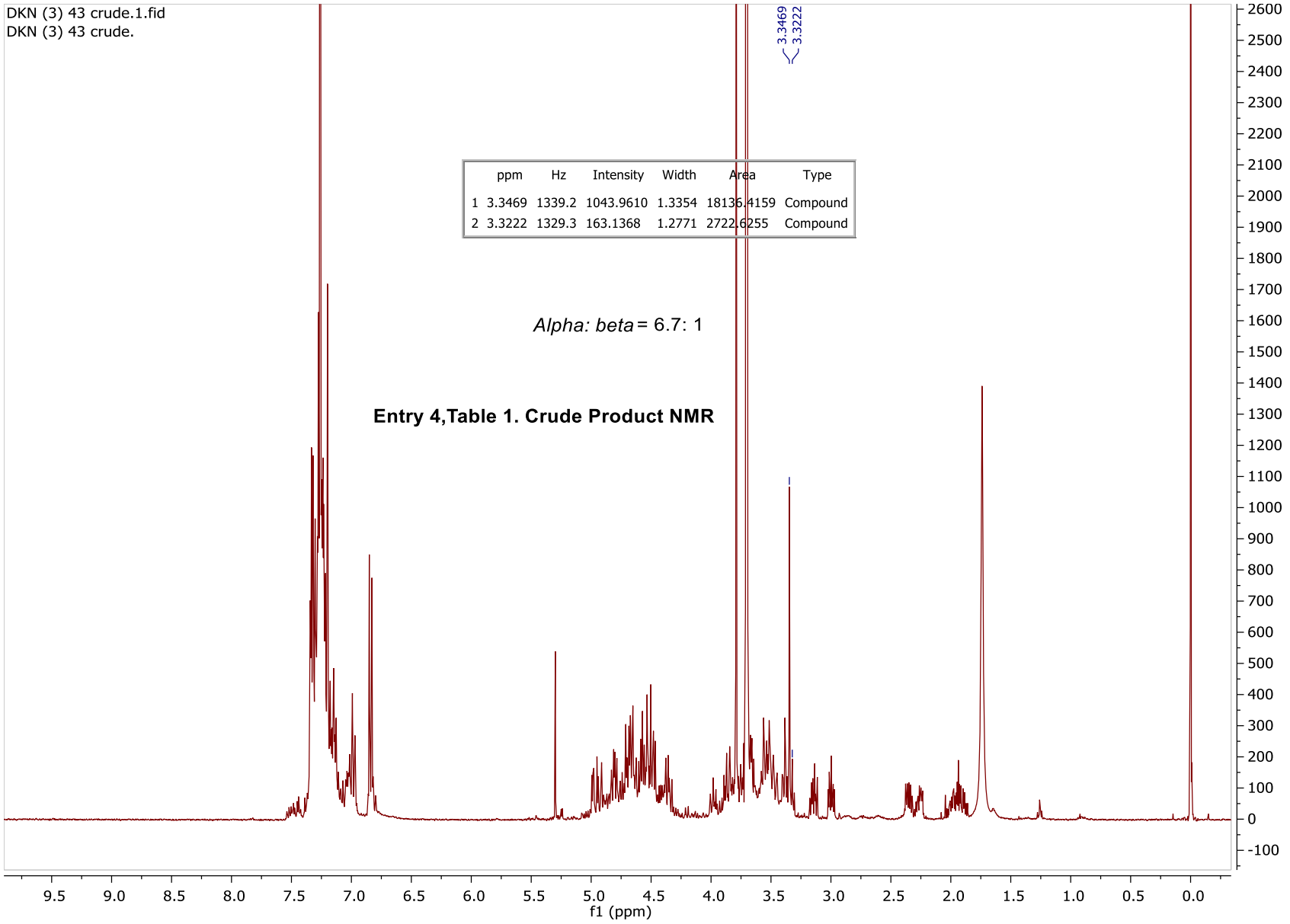
Entry 1[b],Table 1. Purified Product NMR

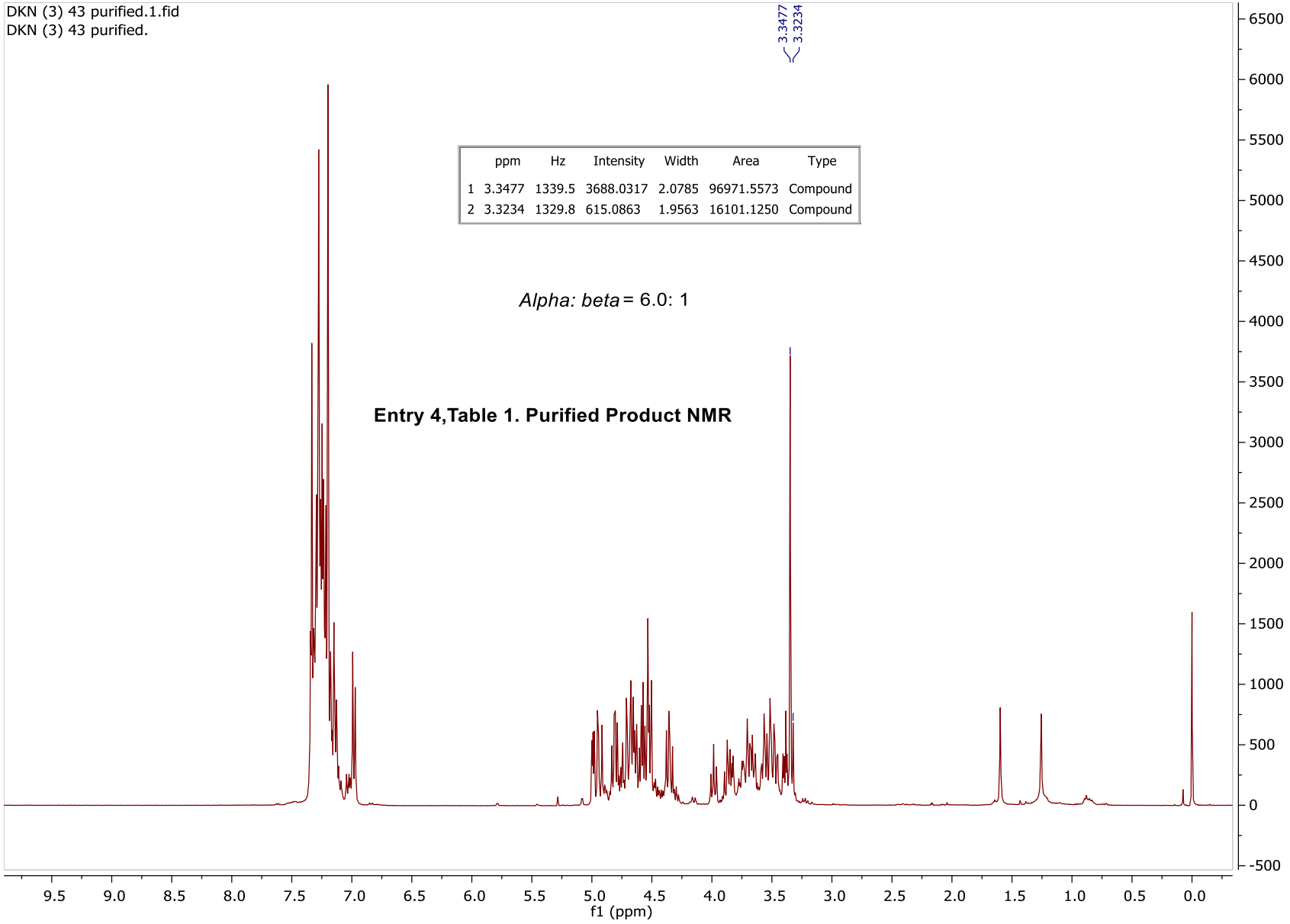

DKN (3) 5 crude.1.fid
DKN (3) 5 crude
3.3476
3.3223
ppm Hz Intensity Width Area Type
1 3.3476 1339.5 1003.9078 1.4639 19520.2812 Compound
2 3.3223 1329.4 228.6494 1.5817 5198.9501 Compound
Entry 2,Table 1. Crude NMR
Alpha: beta = 3.8: 1
f1 (ppm)

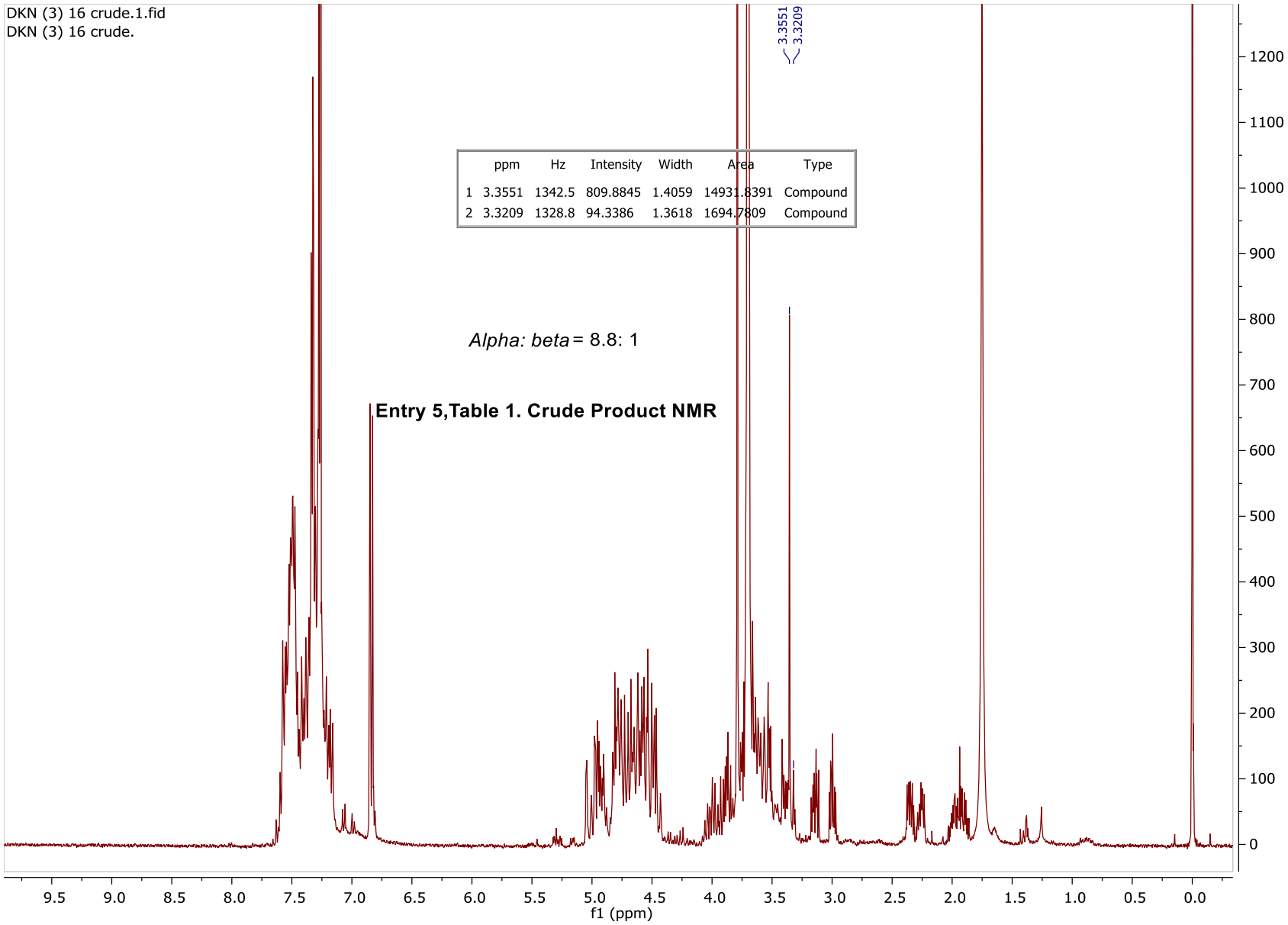

DKN (3) 5 purified.1.fid
DKN (3) 5 purified
3.3474
3.3225
ppm Hz Intensity Width Area Type
1 3.3474 1339.4 3866.9065 1.7337 83695.3461 Compound
2 3.3225 1329.4 948.8623 1.7117 21843.7765 Compound
Entry 2,Table 1. Purified Product NMR
Alpha: beta = 3.8: 1
f1 (ppm)

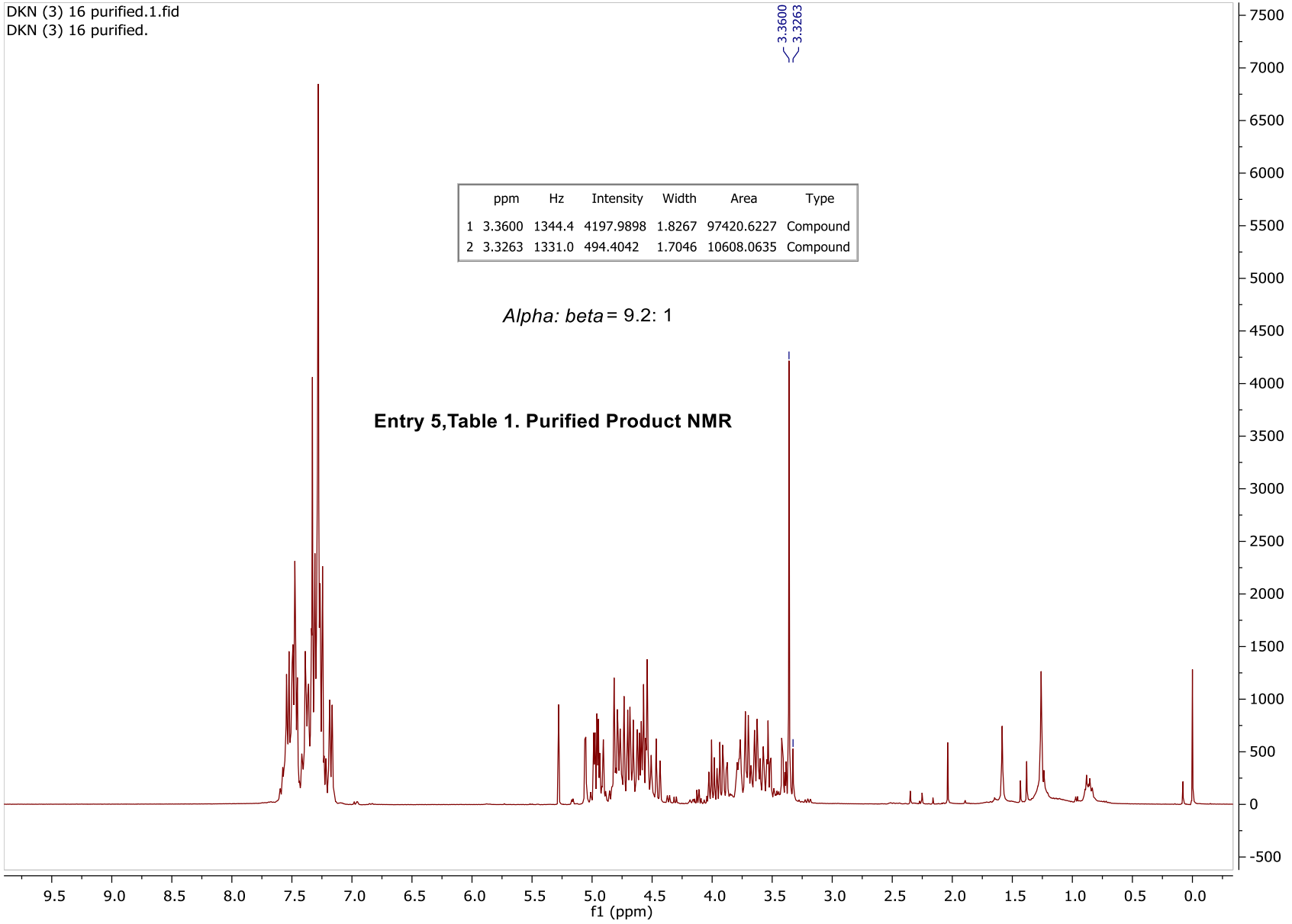

DKN (3) 44 crude.1.fid
DKN (3) 44 crude.
3.3511
3.3227
ppm Hz Intensity Width Area Type
1 3.3511 1340.9 995.6882 1.3909 18166.5511 Compound
2 3.3227 1329.5 177.1417 1.3816 3292.3464 Compound
Entry 3,Table 1. Crude Product NMR
Alpha: beta = 5.5: 1
0.03
f1 (ppm)

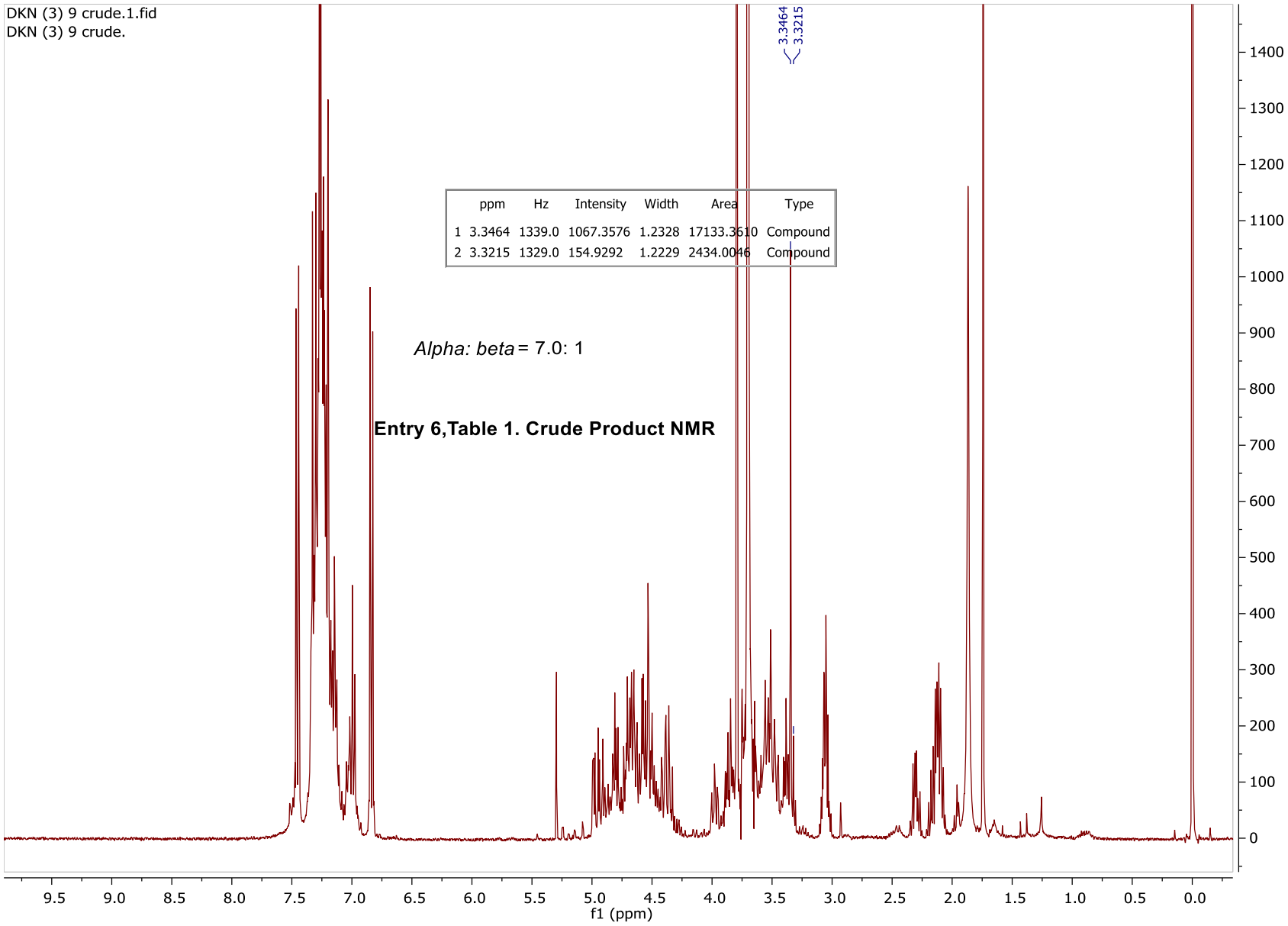

DKN (3) 44 purified.1.fid
DKN (3) 44 purified.
3.3540
3.3260
ppm Hz Intensity Width Area Type
1 3.3540 1342.1 3523.0937 2.0729 95678.1583 Compound
2 3.3260 1330.8 688.4713 2.0785 19663.0907 Compound
Alpha: beta = 4.9: 1
Entry 3,Table 1. Purified Product NMR
f1 (ppm)

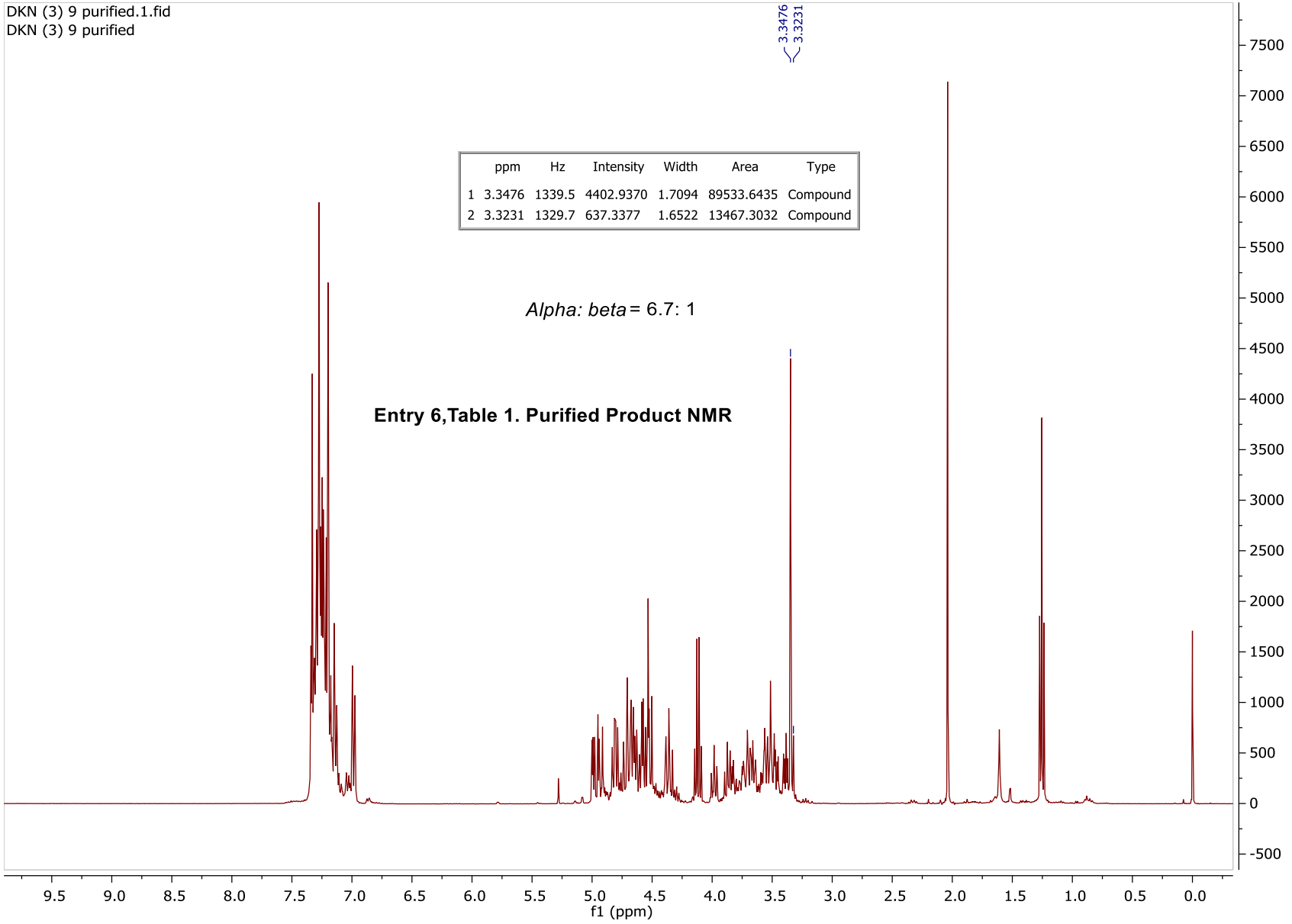

DKN (3) 43 crude.1.fid
DKN (3) 43 crude.
3.3469
3.3222
ppm Hz Intensity Width Area Type
1 3.3469 1339.2 1043.9610 1.3354 18136.4159 Compound
2 3.3222 1329.3 163.1368 1.2771 2722.6255 Compound
Alpha: beta = 6.7: 1
Entry 4,Table 1. Crude Product NMR
f1 (ppm)

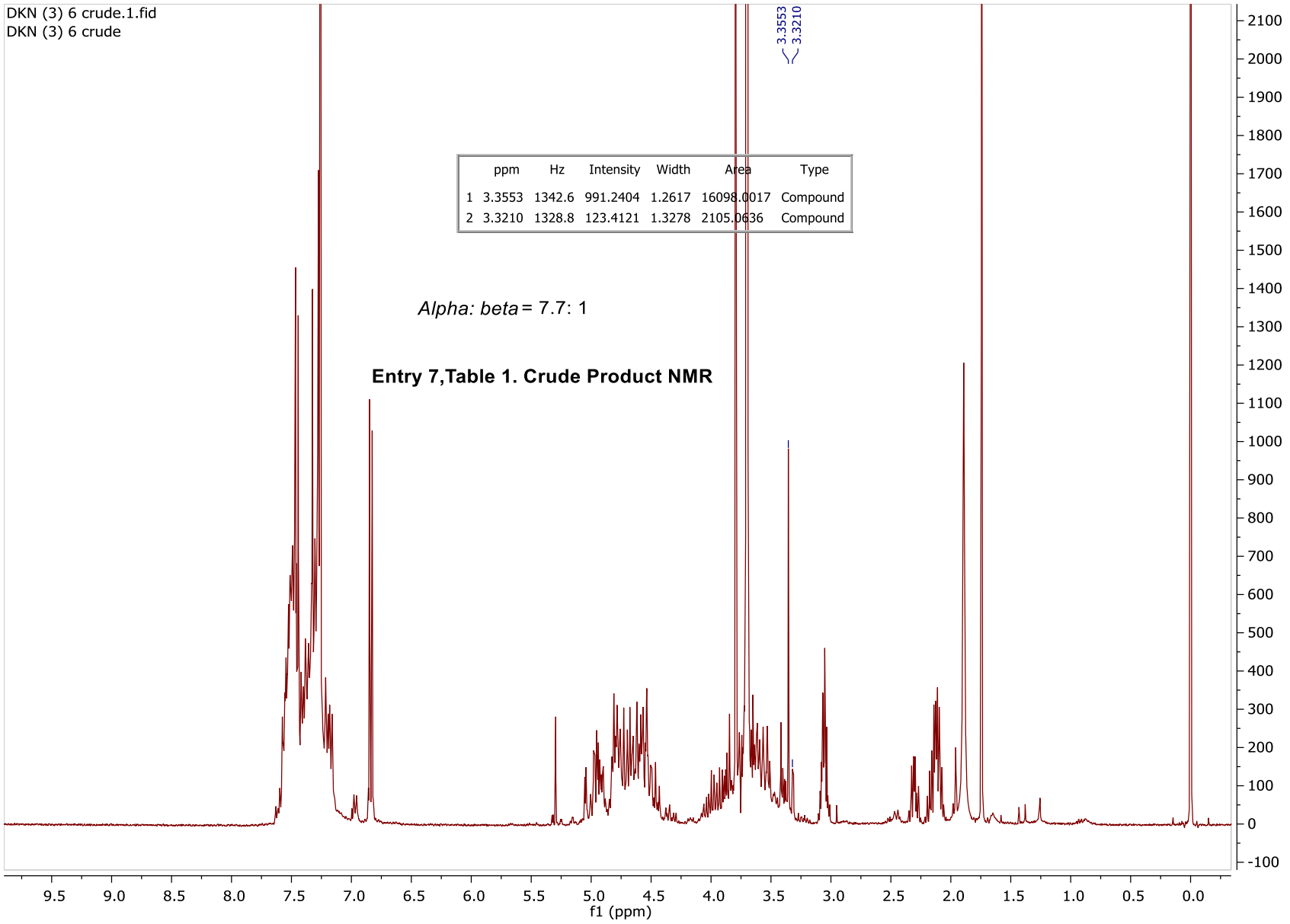

DKN (3) 43 purified.1.fid
DKN (3) 43 purified.
3.3477
3.3234
ppm Hz Intensity Width Area Type
1 3.3477 1339.5 3688.0317 2.0785 96971.5573 Compound
2 3.3234 1329.8 615.0863 1.9563 16101.1250 Compound
Alpha: beta = 6.0: 1
Entry 4,Table 1. Purified Product NMR
f1 (ppm)

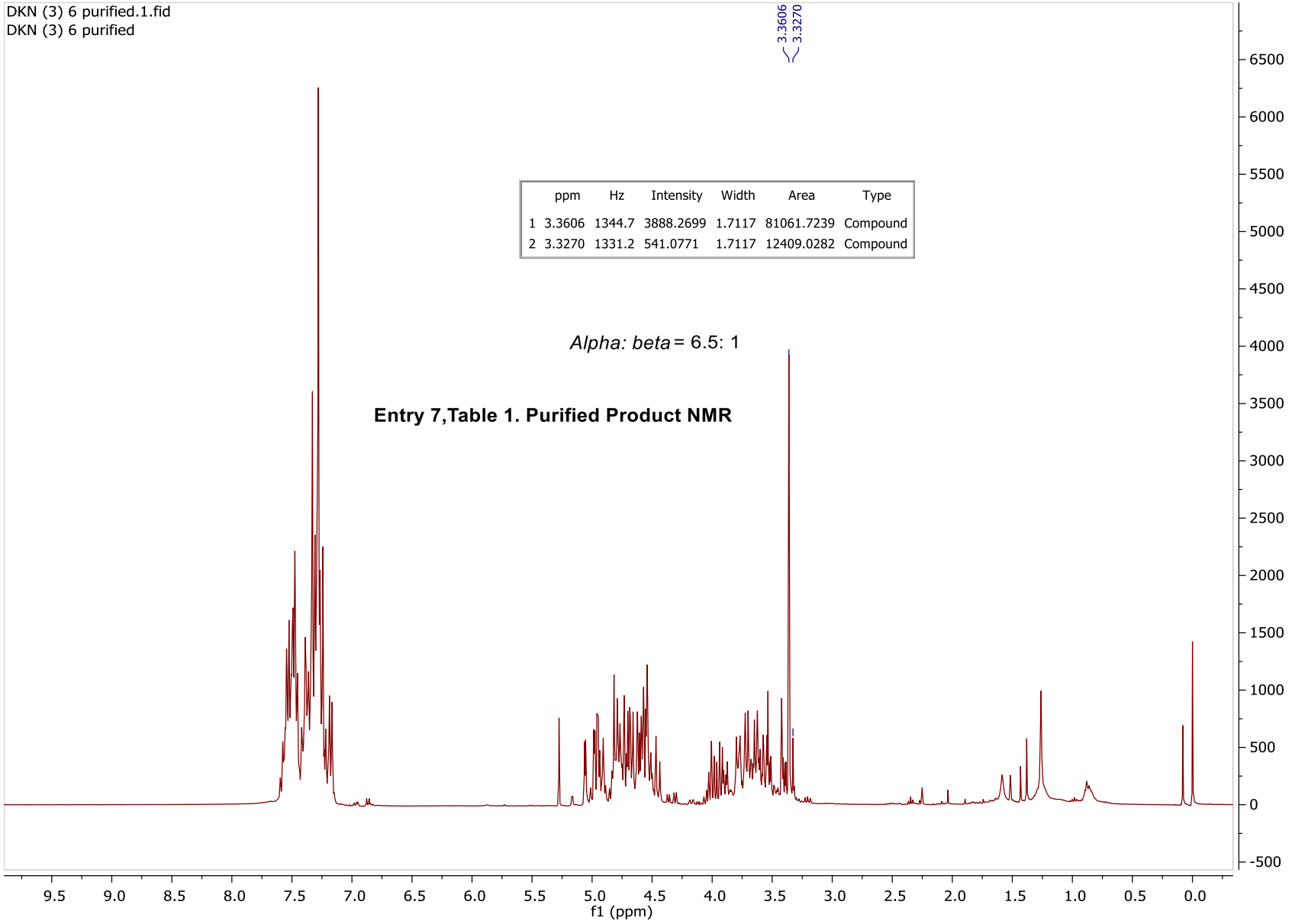

DKN (3) 16 crude.1.fid
DKN (3) 16 crude.
3.3551
3.3209
ppm Hz Intensity Width Area Type
1 3.3551 1342.5 809.8845 1.4059 14931.8391 Compound
2 3.3209 1328.8 94.3386 1.3618 1694.7809 Compound
Alpha: beta = 8.8: 1
Entry 5,Table 1. Crude Product NMR
f1 (ppm)

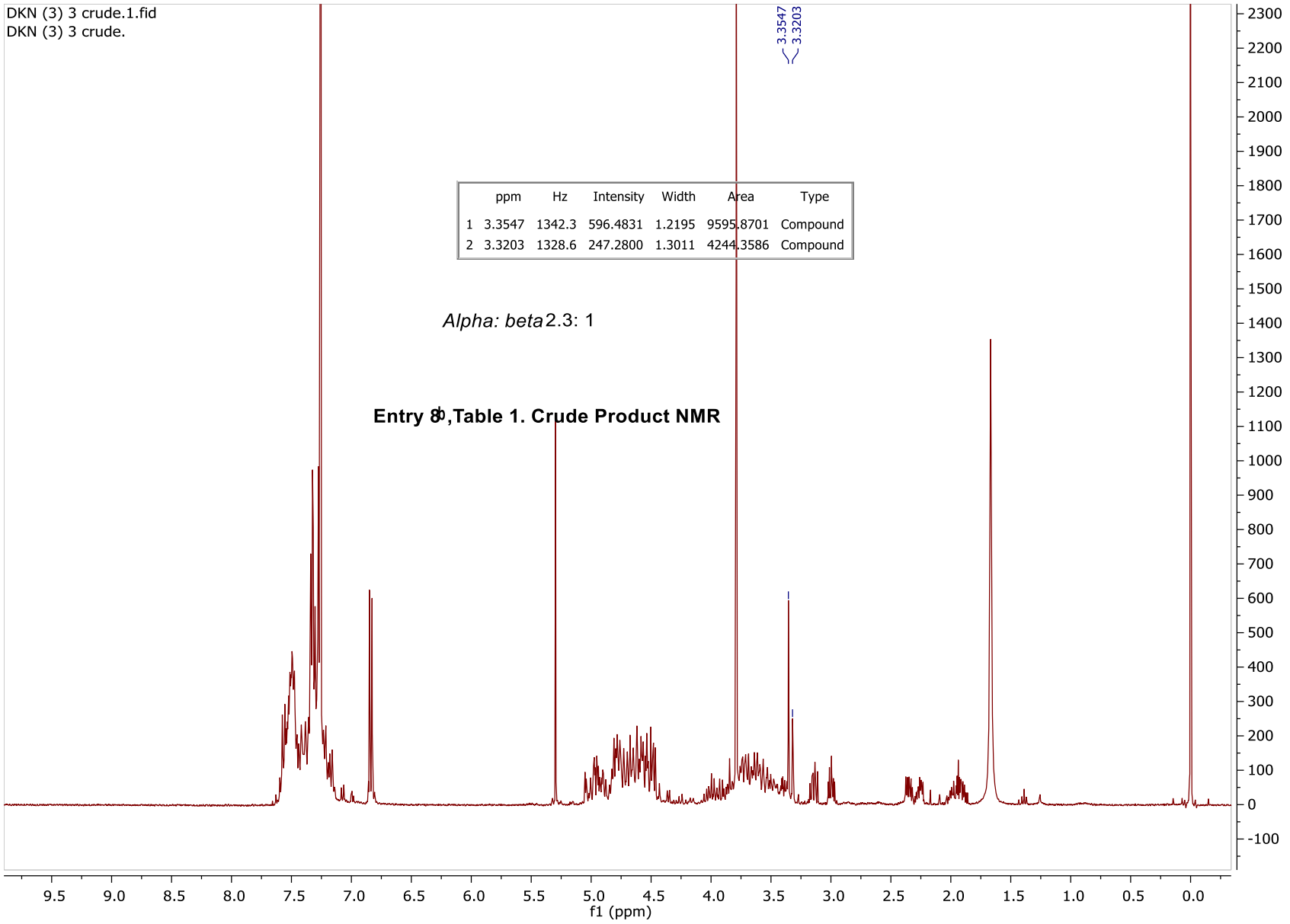

DKN (3) 16 purified.1.fid
DKN (3) 16 purified.
3.3600
3.3263
ppm Hz Intensity Width Area Type
1 3.3600 1344.4 4197.9898 1.8267 97420.6227 Compound
2 3.3263 1331.0 494.4042 1.7046 10608.0635 Compound
Alpha: beta = 9.2: 1
Entry 5,Table 1. Purified Product NMR
f1 (ppm)

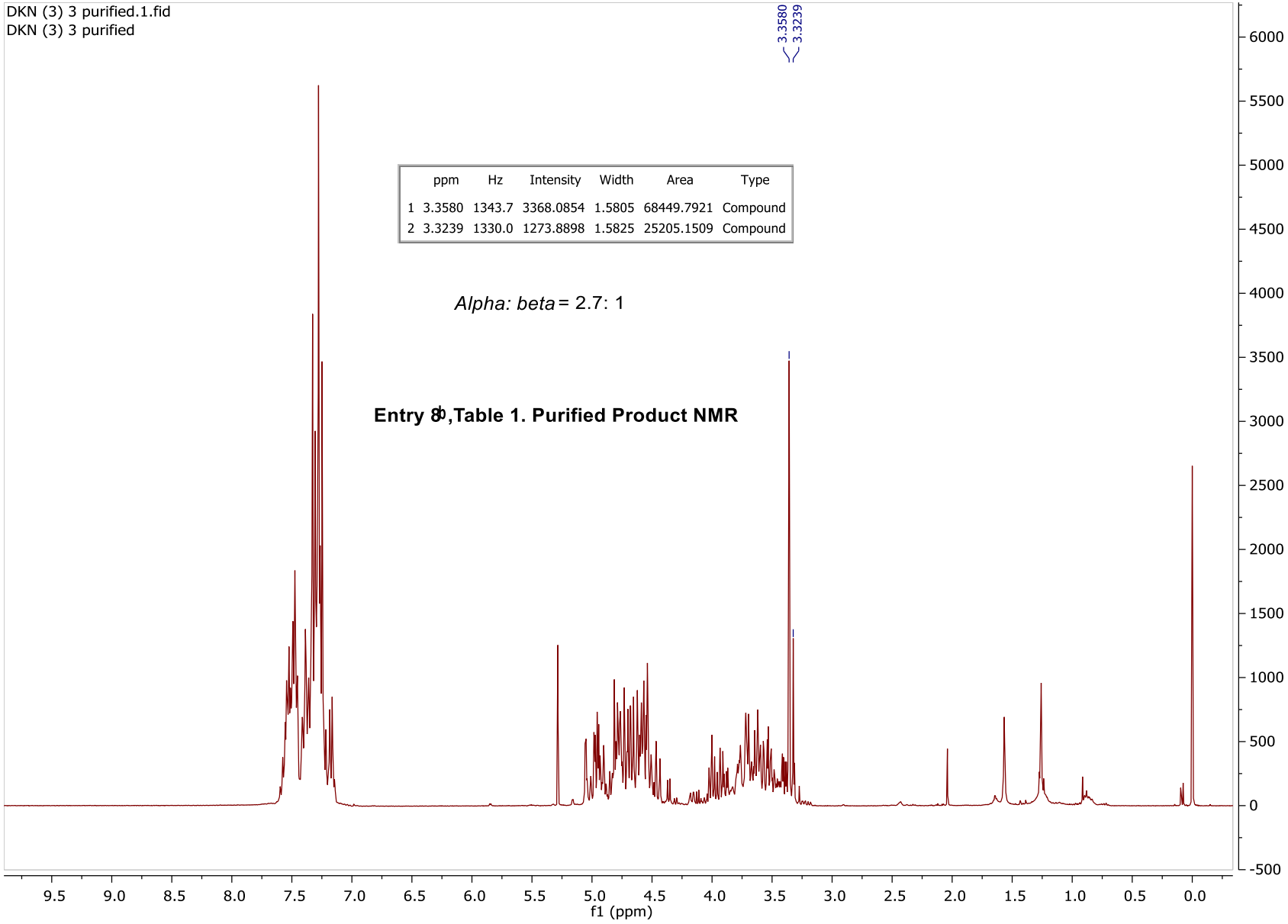

DKN (3) 9 crude.1.fid
DKN (3) 9 crude.
3.3464
3.3215
ppm Hz Intensity Width Area Type
1 3.3464 1339.0 1067.3576 1.2328 17133.3610 Compound
2 3.3215 1329.0 154.9292 1.2229 2434.0046 Compound
Alpha: beta = 7.0: 1
Entry 6,Table 1. Crude Product NMR
f1 (ppm)

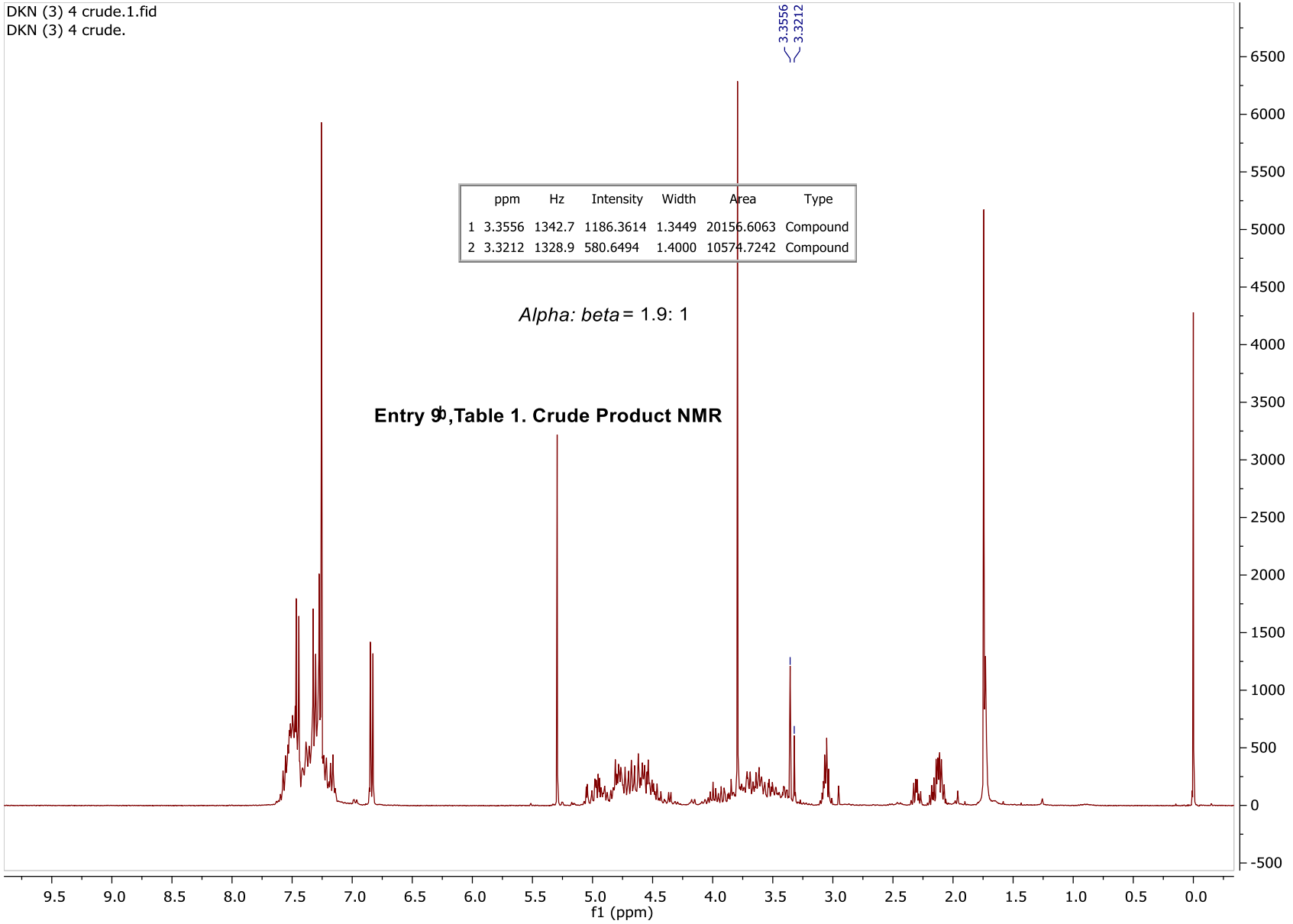

DKN (3) 9 purified.1.fid
DKN (3) 9 purified
3.3476
3.3231
ppm Hz Intensity Width Area Type
1 3.3476 1339.5 4402.9370 1.7094 89533.6435 Compound
2 3.3231 1329.7 637.3377 1.6522 13467.3032 Compound
Alpha: beta = 6.7: 1
Entry 6,Table 1. Purified Product NMR
f1 (ppm)

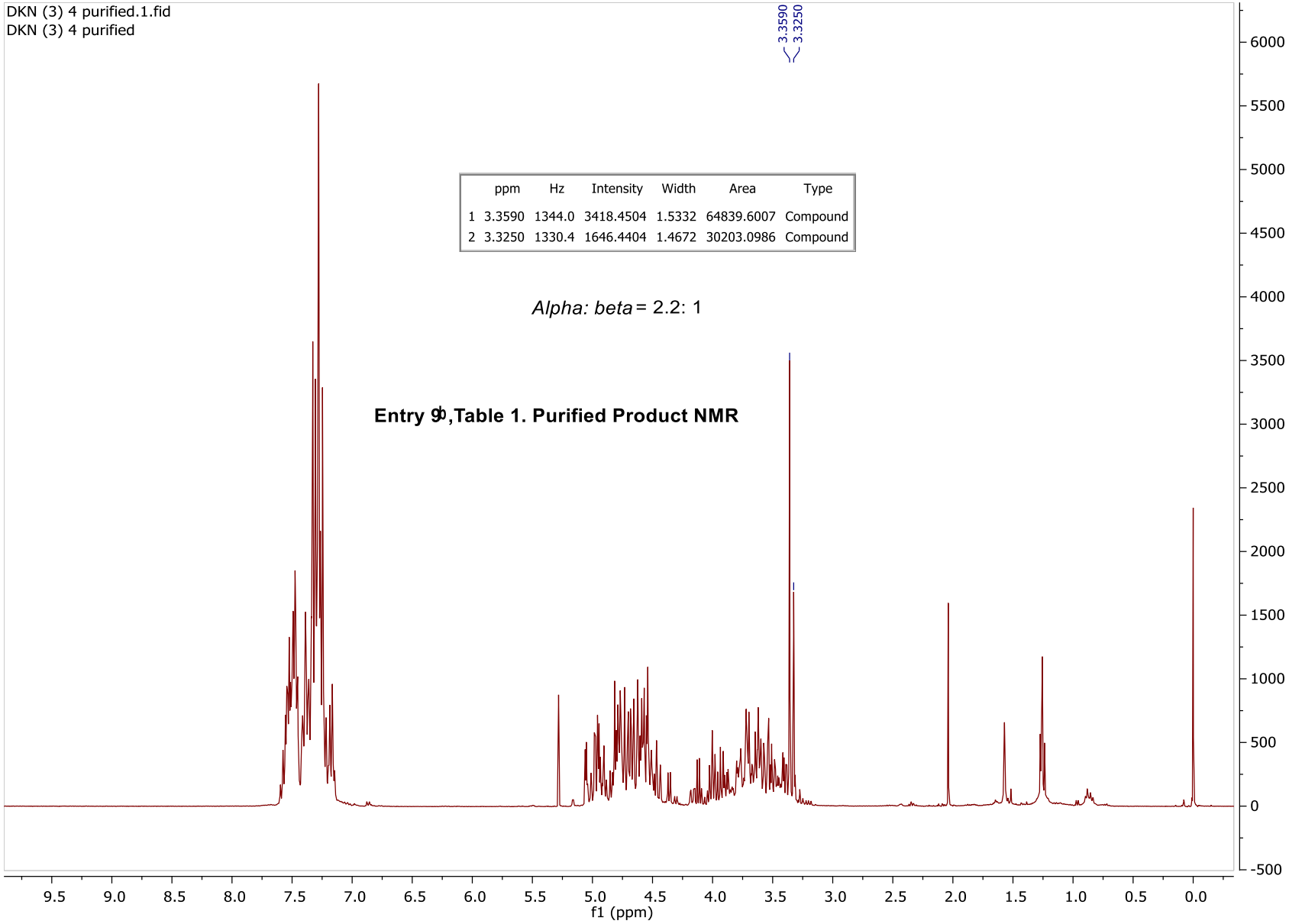

DKN (3) 6 crude.1.fid
DKN (3) 6 crude
3.3553
3.3210
ppm Hz Intensity Width Area Type
1 3.3553 1342.6 991.2404 1.2617 16098.0017 Compound
2 3.3210 1328.8 123.4121 1.3278 2105.0636 Compound
Alpha: beta = 7.7: 1
Entry 7,Table 1. Crude Product NMR
f1 (ppm)

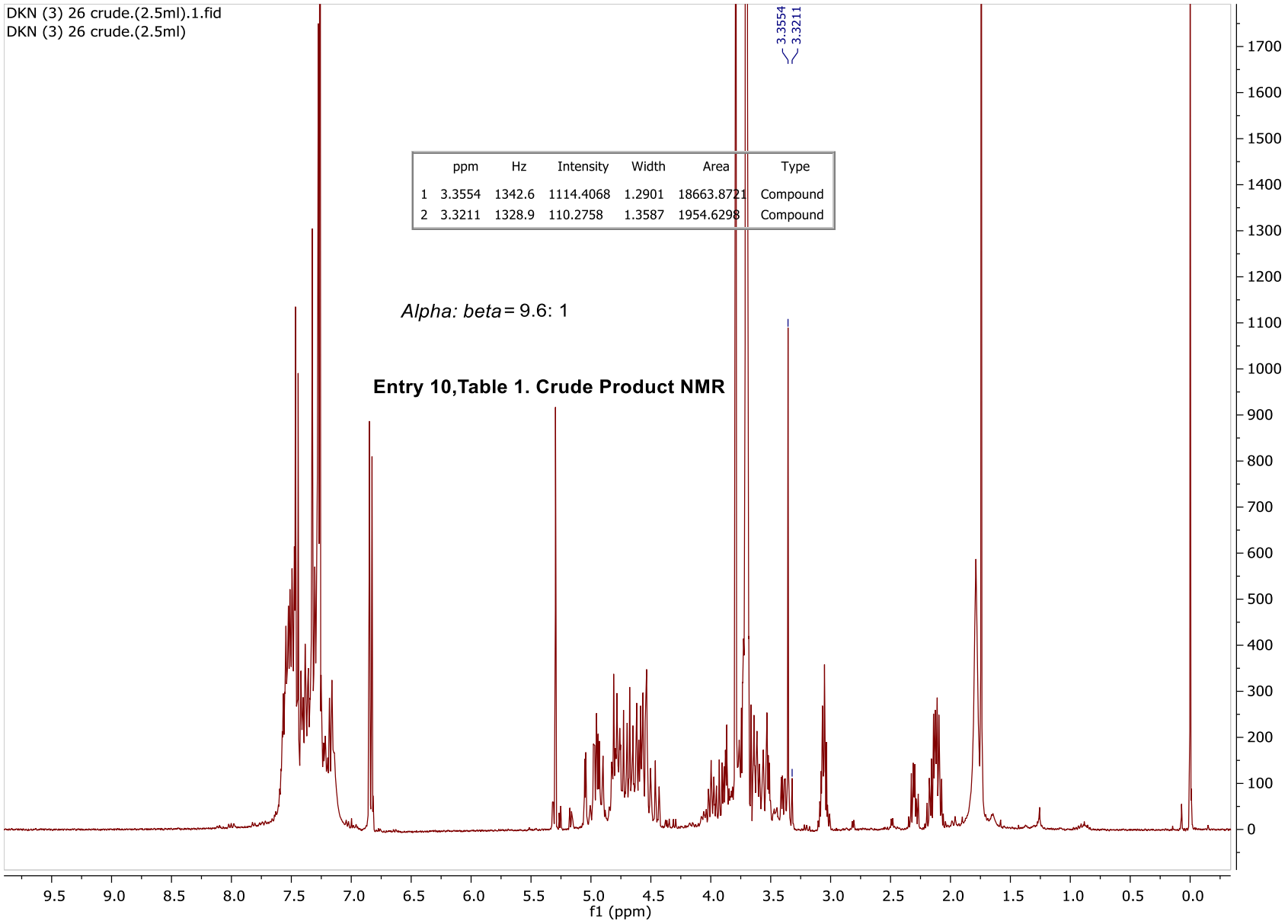

DKN (3) 6 purified.1.fid
DKN (3) 6 purified
3.3606
3.3270
ppm Hz Intensity Width Area Type
1 3.3606 1344.7 3888.2699 1.7117 81061.7239 Compound
2 3.3270 1331.2 541.0771 1.7117 12409.0282 Compound
Alpha: beta = 6.5: 1
Entry 7,Table 1. Purified Product NMR
f1 (ppm)

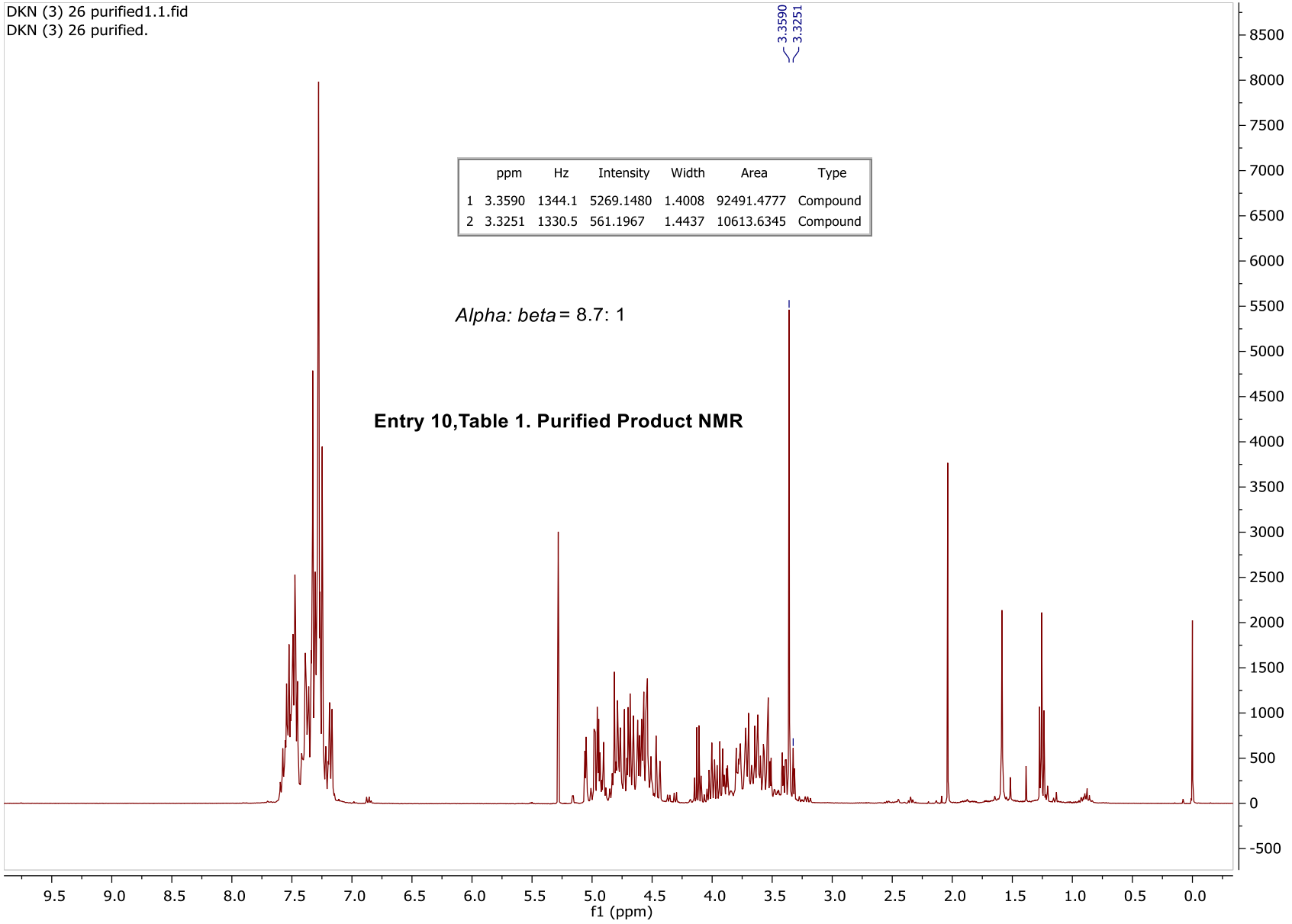

DKN (3) 3 crude.1.fid
DKN (3) 3 crude.
3.3547
3.3203
ppm Hz Intensity Width Area Type
1 3.3547 1342.3 596.4831 1.2195 9595.8701 Compound
2 3.3203 1328.6 247.2800 1.3011 4244.3586 Compound
Alpha: beta 2.3: 1
Entry 8b, Table 1. Crude Product NMR
f1 (ppm)

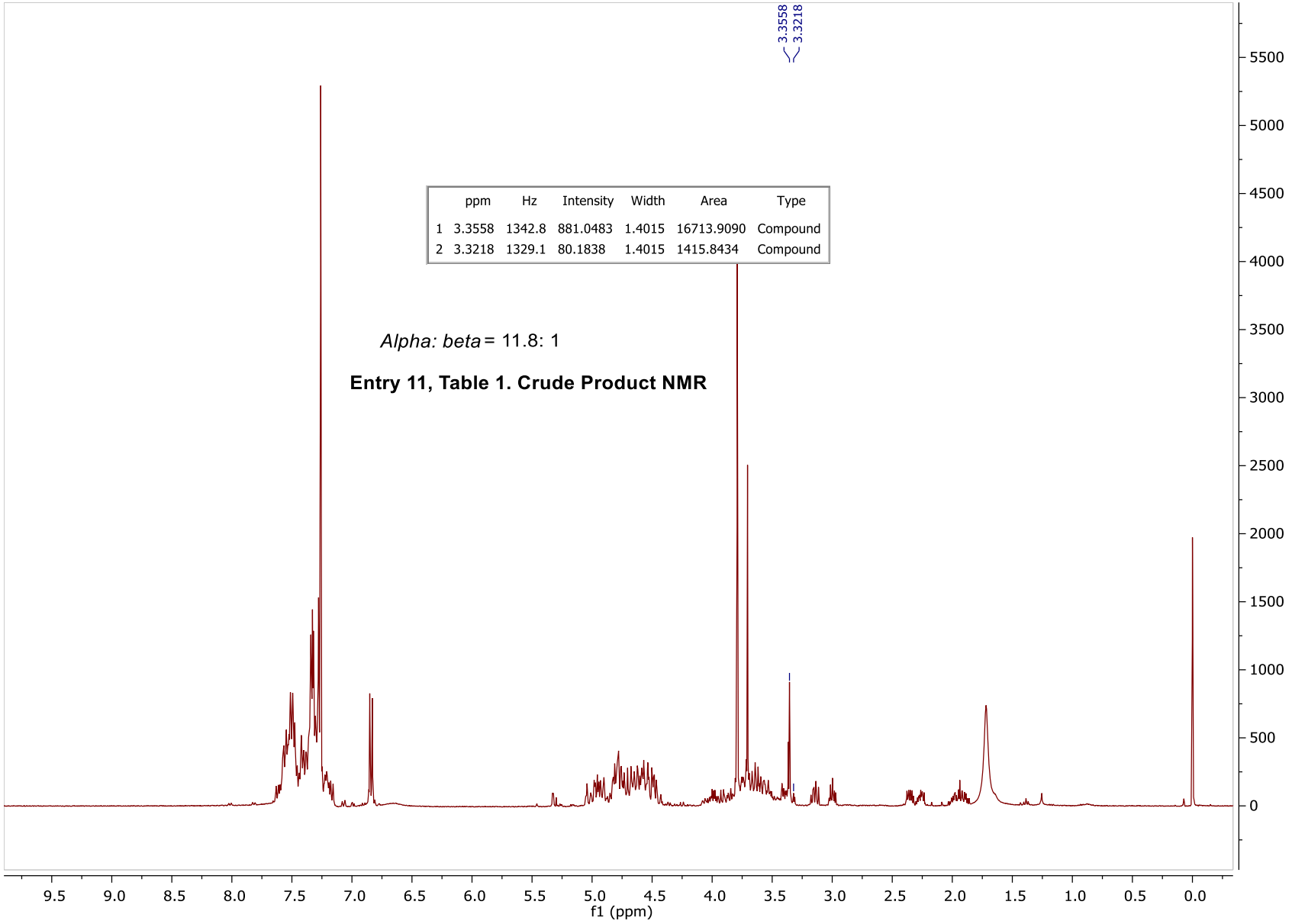

DKN (3) 3 purified.1.fid
DKN (3) 3 purified
3.3580
3.3239
ppm Hz Intensity Width Area Type
1 3.3580 1343.7 3368.0854 1.5805 68449.7921 Compound
2 3.3239 1330.0 1273.8898 1.5825 25205.1509 Compound
Alpha: beta = 2.7: 1
Entry 8b,Table 1. Purified Product NMR
f1 (ppm)

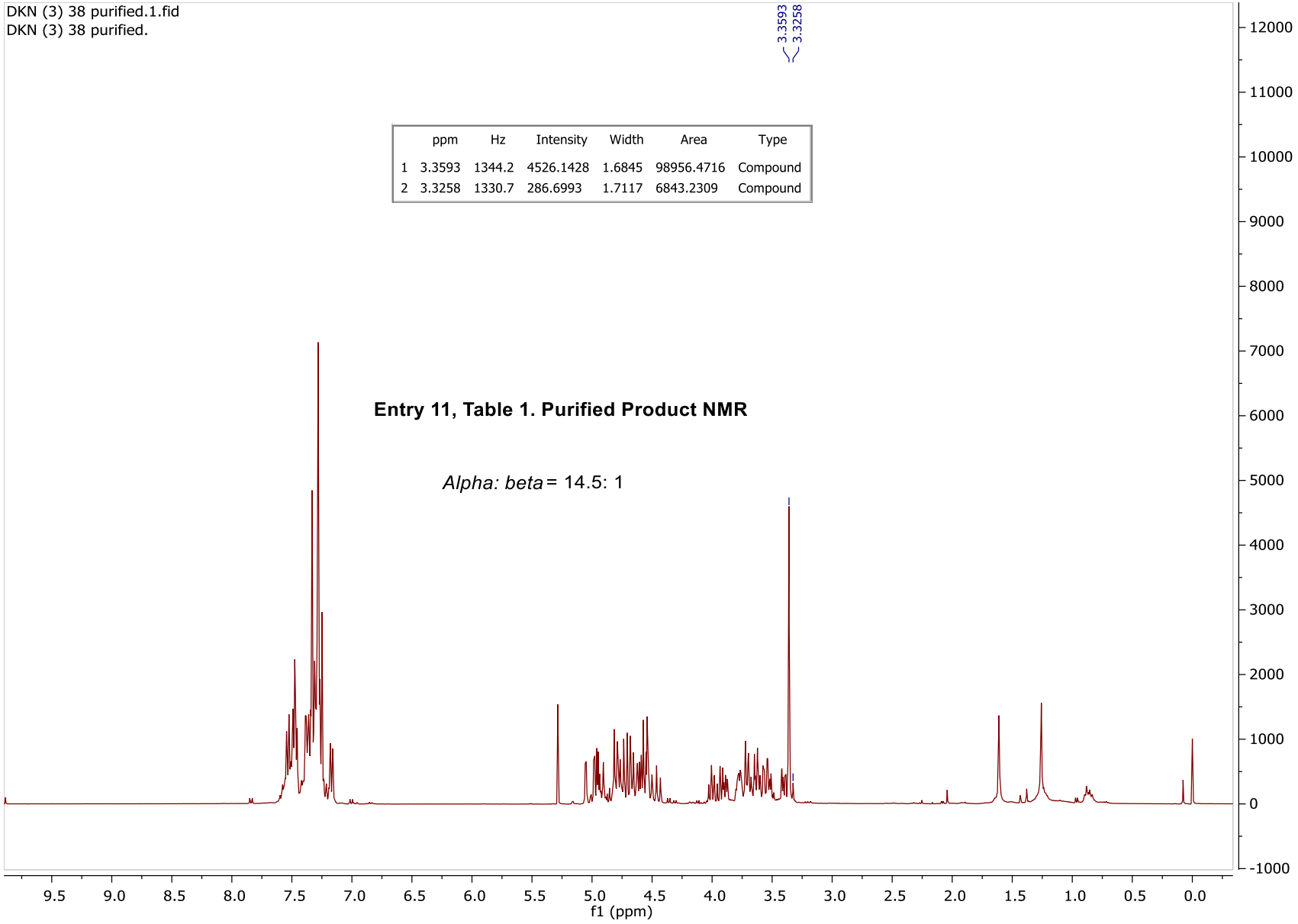

DKN (3) 4 crude.1.fid
DKN (3) 4 crude.
3.3556
3.3212
ppm Hz Intensity Width Area Type
1 3.3556 1342.7 1186.3614 1.3449 20156.6063 Compound
2 3.3212 1328.9 580.6494 1.4000 10574.7242 Compound
Alpha: beta = 1.9: 1
Entry 9b,Table 1. Crude Product NMR
f1 (ppm)

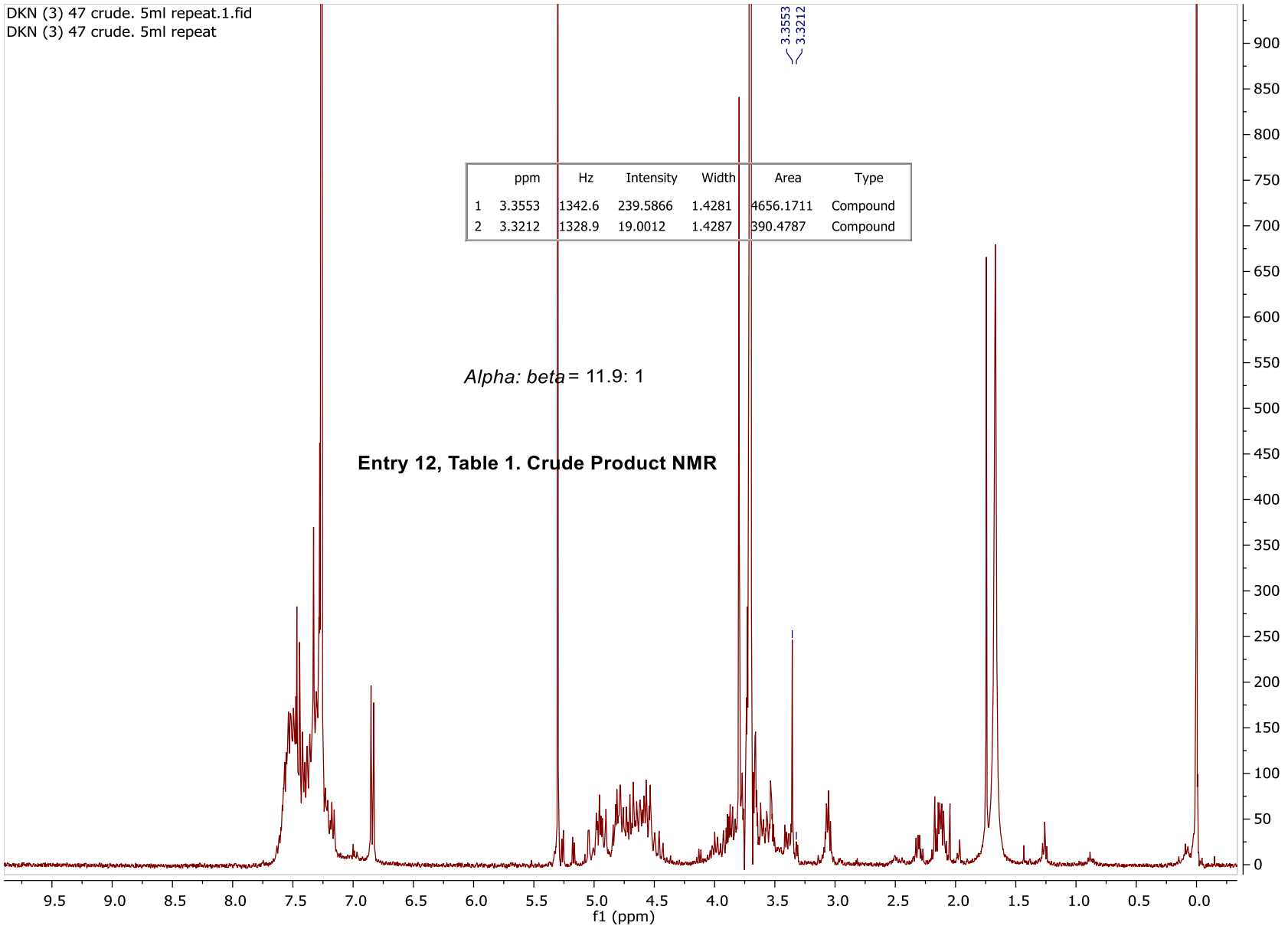

DKN (3) 4 purified.1.fid
DKN (3) 4 purified
3.3590
3.3250
ppm Hz Intensity Width Area Type
1 3.3590 1344.0 3418.4504 1.5332 64839.6007 Compound
2 3.3250 1330.4 1646.4404 1.4672 30203.0986 Compound
Alpha: beta = 2.2: 1
Entry 9b,Table 1. Purified Product NMR
f1 (ppm)

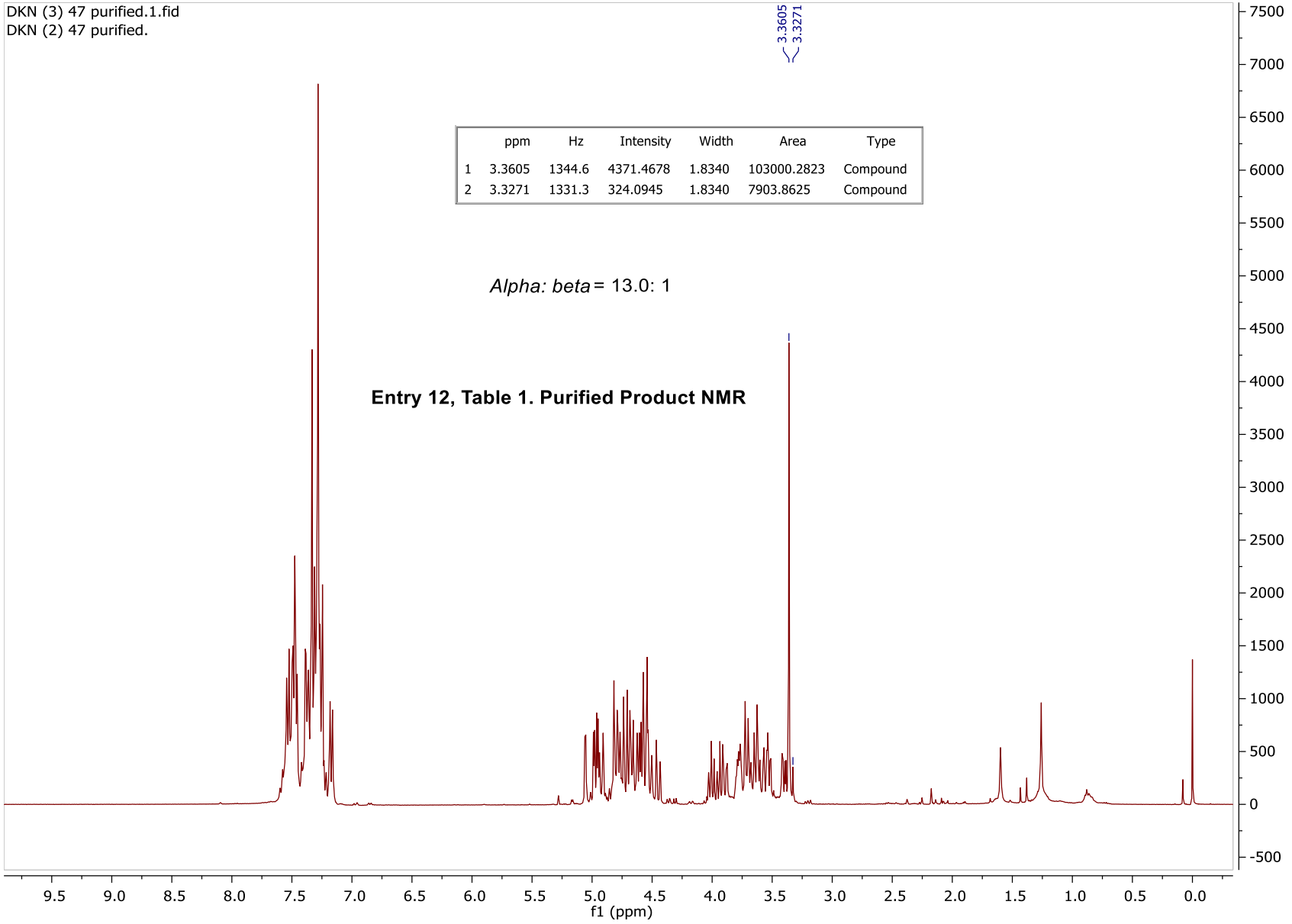

DKN (3) 26 crude.(2.5ml).1.fid
DKN (3) 26 crude.(2.5ml)
3.3554
3.3211
ppm Hz Intensity Width Area Type
1 3.3554 1342.6 1114.4068 1.2901 18663.8721 Compound
2 3.3211 1328.9 110.2758 1.3587 1954.6298 Compound
Alpha: beta = 9.6: 1
Entry 10,Table 1. Crude Product NMR
f1 (ppm)

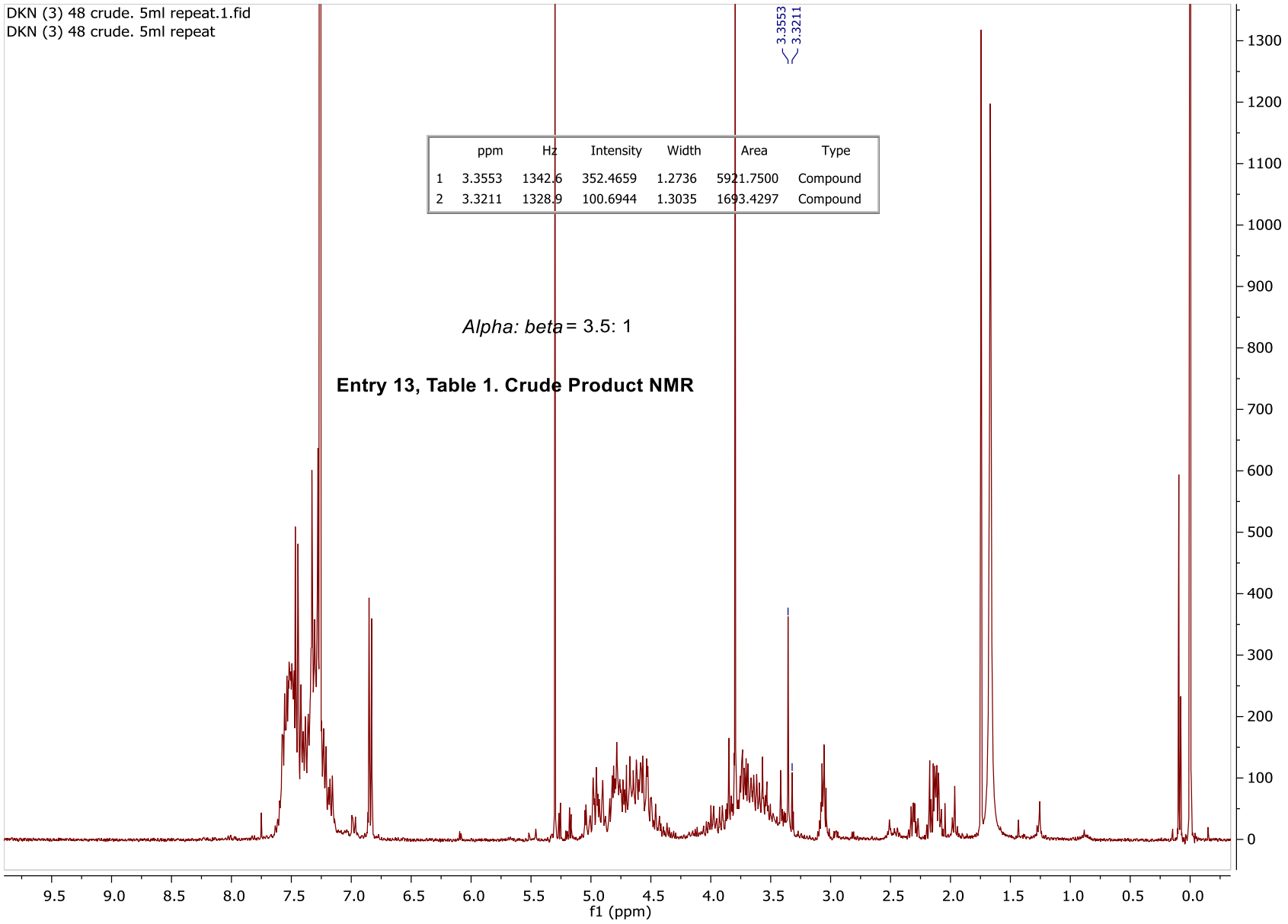

DKN (3) 26 purified1.1.fid
DKN (3) 26 purified.
3.3590
3.3251
ppm Hz Intensity Width Area Type
1 3.3590 1344.1 5269.1480 1.4008 92491.4777 Compound
2 3.3251 1330.5 561.1967 1.4437 10613.6345 Compound
Alpha: beta = 8.7: 1
Entry 10,Table 1. Purified Product NMR
f1 (ppm)

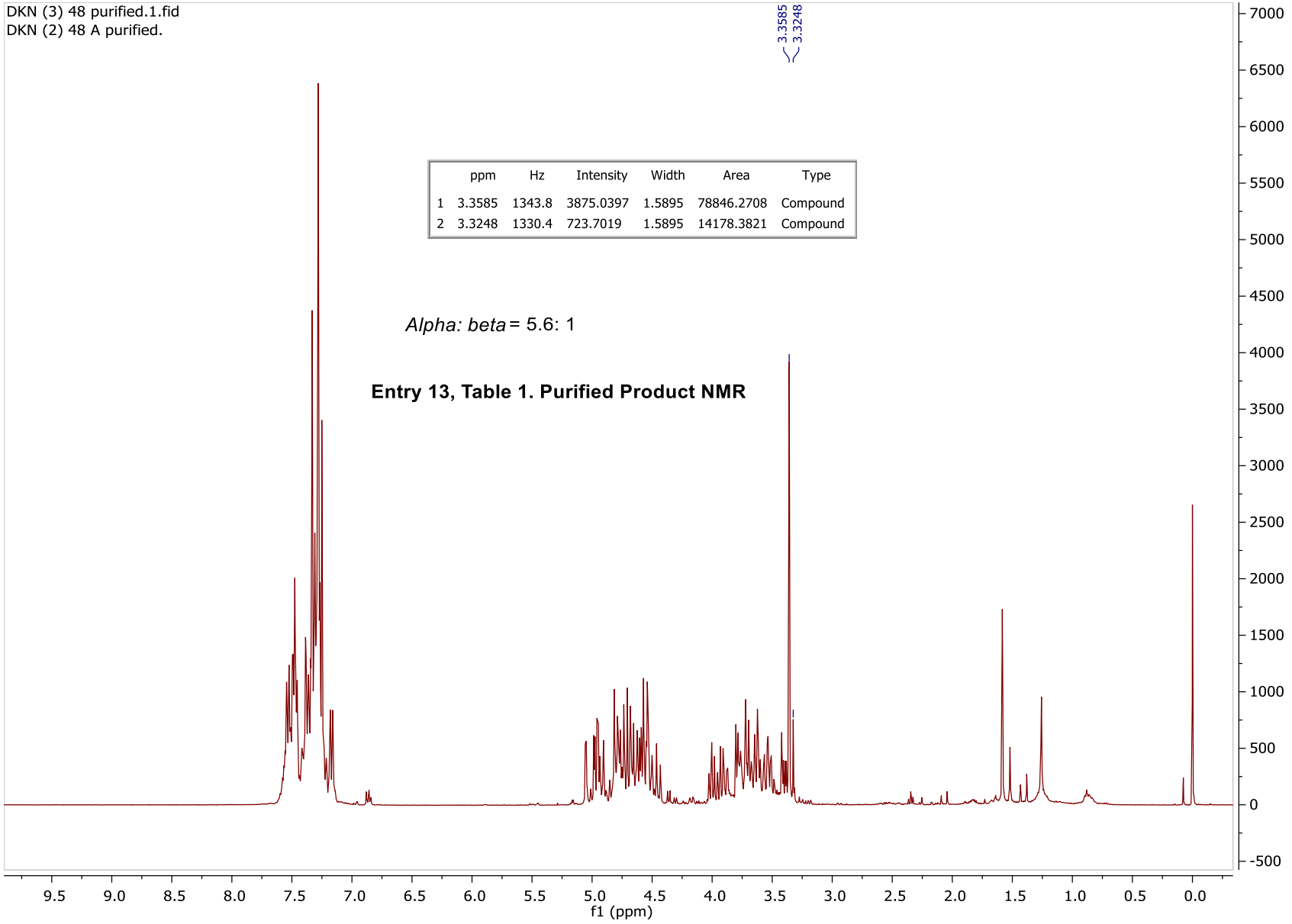

3.3558
3.3218
ppm Hz Intensity Width Area Type
1 3.3558 1342.8 881.0483 1.4015 16713.9090 Compound
2 3.3218 1329.1 80.1838 1.4015 1415.8434 Compound
Alpha: beta = 11.8: 1
Entry 11, Table 1. Crude Product NMR
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

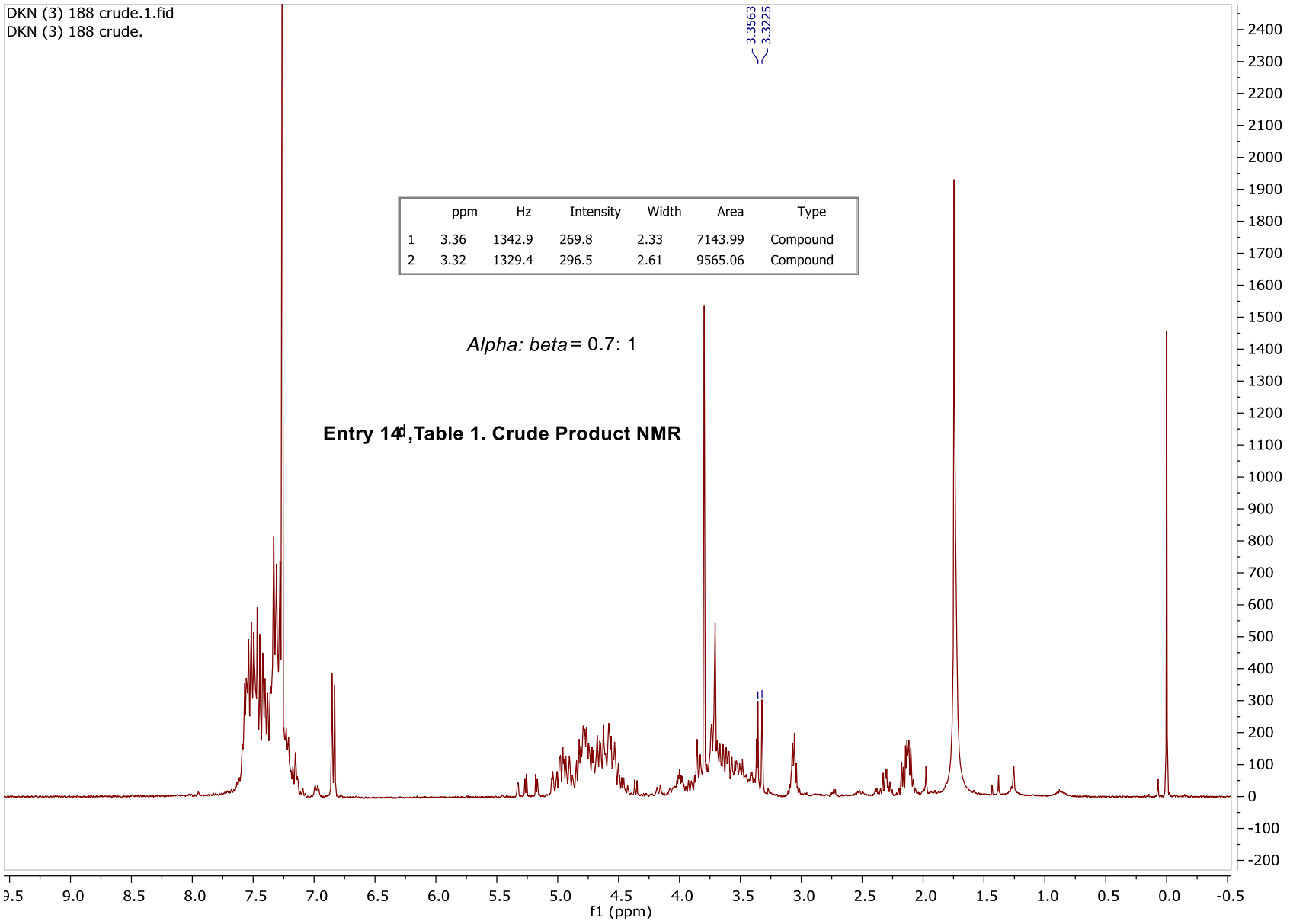

DKN (3) 38 purified.1.fid
DKN (3) 38 purified.
3.3593
3.3258
ppm Hz Intensity Width Area Type
1 3.3593 1344.2 4526.1428 1.6845 98956.4716 Compound
2 3.3258 1330.7 286.6993 1.7117 6843.2309 Compound
Entry 11, Table 1. Purified Product NMR
Alpha: beta = 14.5: 1
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

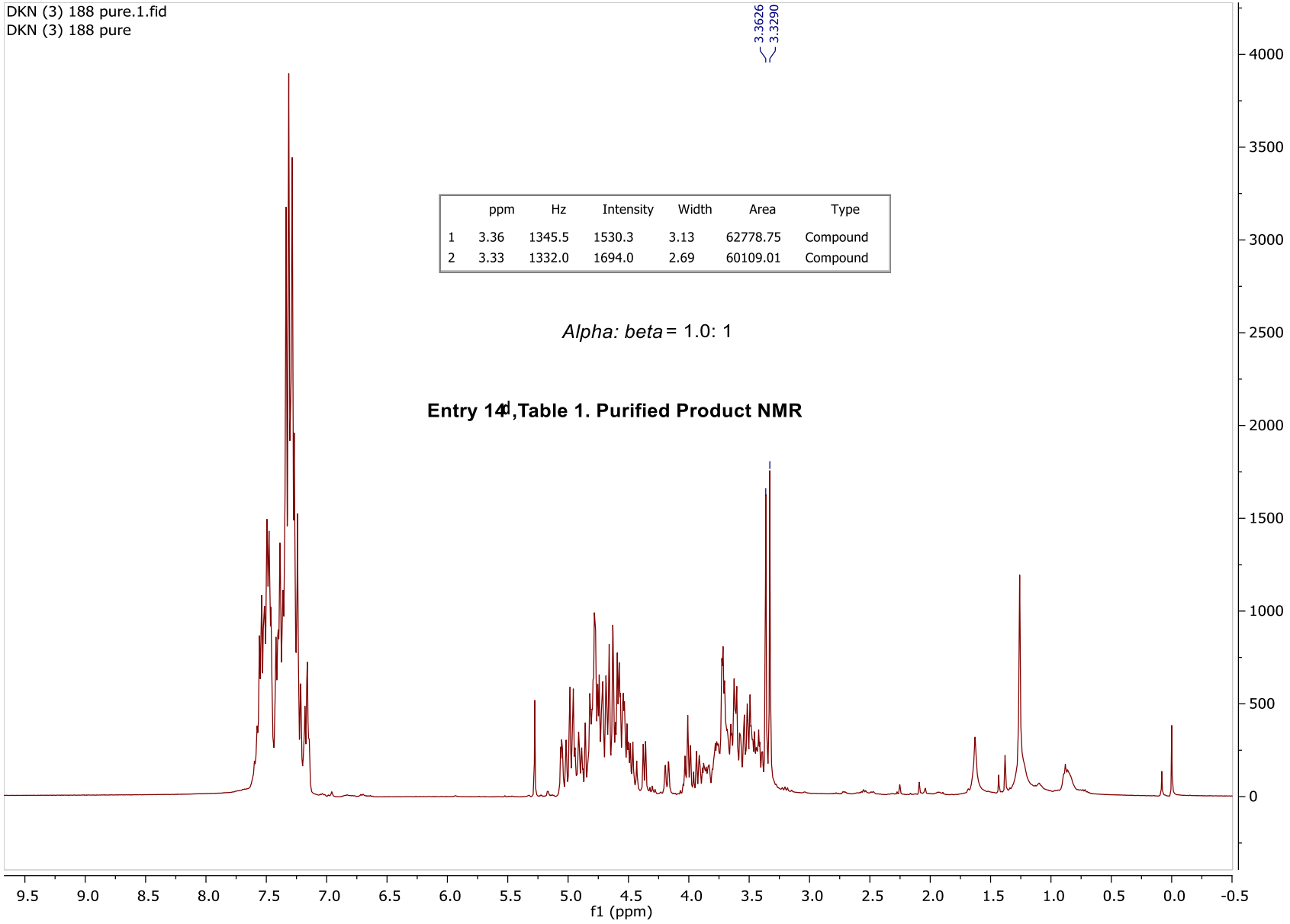

DKN (3) 47 crude. 5ml repeat.1.fid
DKN (3) 47 crude. 5ml repeat
3.3553
3.3212
ppm Hz Intensity Width Area Type
1 3.3553 1342.6 239.5866 1.4281 4656.1711 Compound
2 3.3212 1328.9 19.0012 1.4287 390.4787 Compound
Alpha: beta = 11.9: 1
Entry 12, Table 1. Crude Product NMR
f1 (ppm)

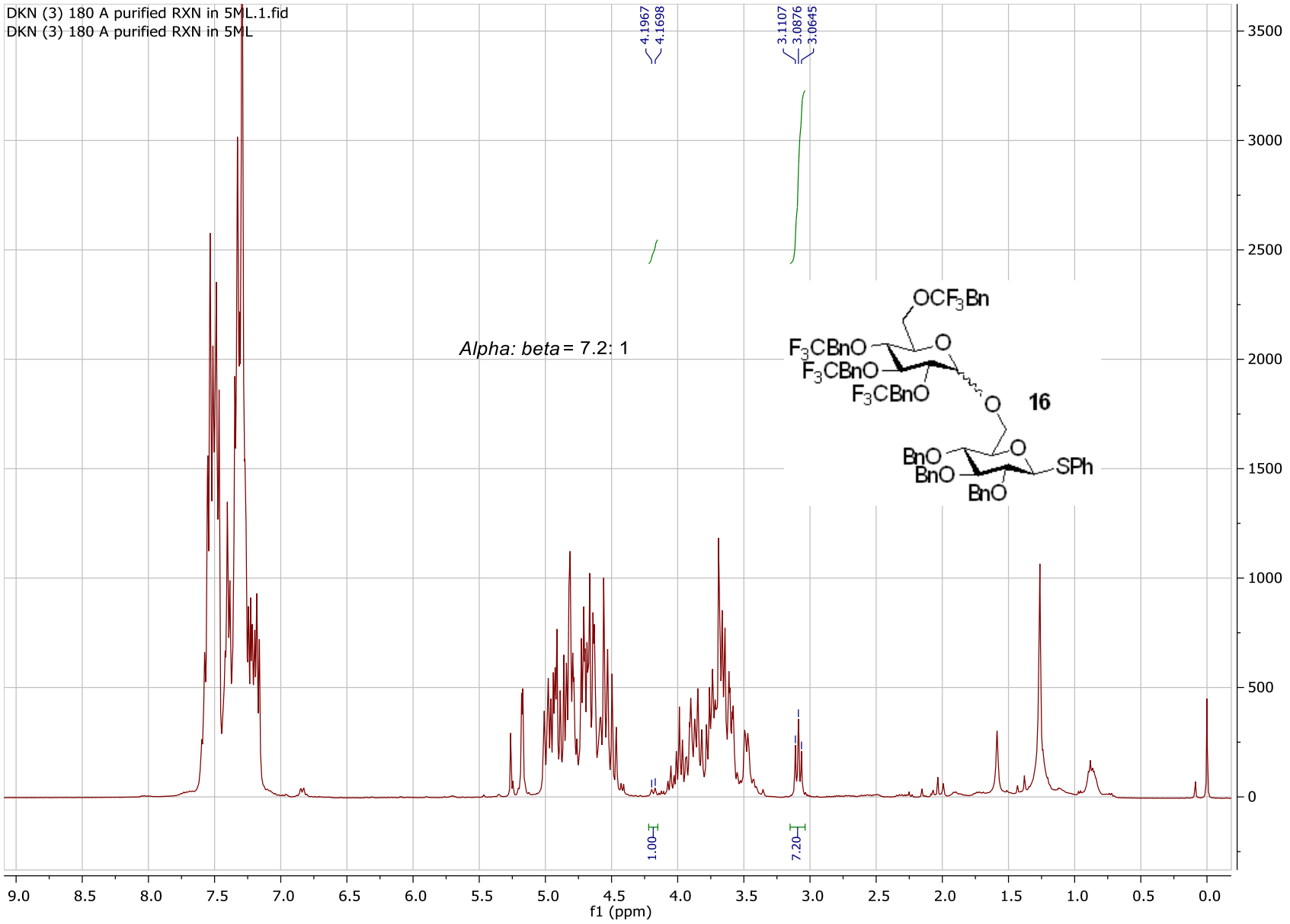

DKN (3) 47 purified.1.fid
DKN (2) 47 purified.
3.3605
3.3271
ppm Hz Intensity Width Area Type
1 3.3605 1344.6 4371.4678 1.8340 103000.2823 Compound
2 3.3271 1331.3 324.0945 1.8340 7903.8625 Compound
Alpha: beta = 13.0: 1
Entry 12, Table 1. Purified Product NMR
f1 (ppm)

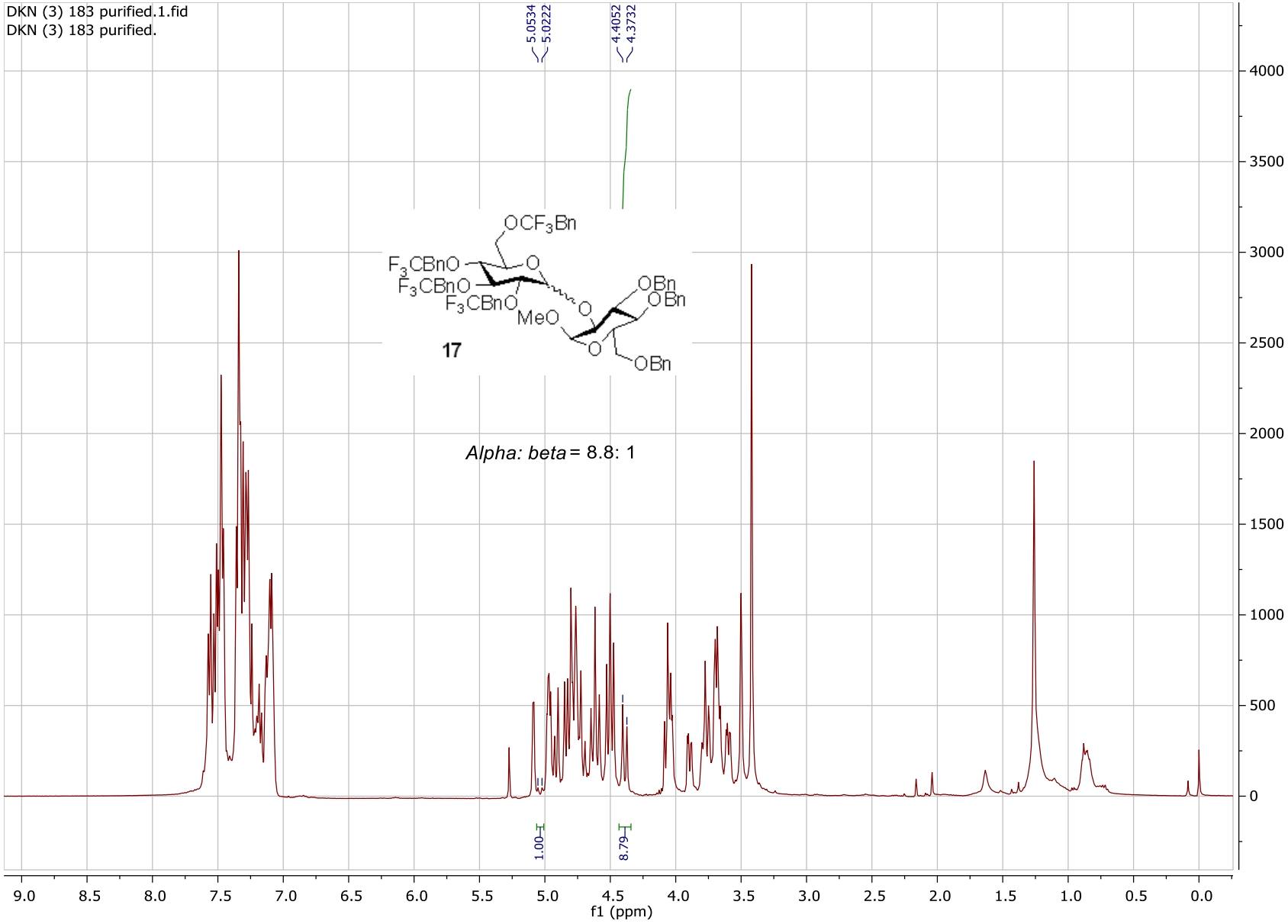

DKN (3) 48 crude. 5ml repeat.1.fid
DKN (3) 48 crude. 5ml repeat
3.3553
3.3211
ppm Hz Intensity Width Area Type
1 3.3553 1342.6 352.4659 1.2736 5921.7500 Compound
2 3.3211 1328.9 100.6944 1.3035 1693.4297 Compound
Alpha: beta = 3.5: 1
Entry 13, Table 1. Crude Product NMR
f1 (ppm)

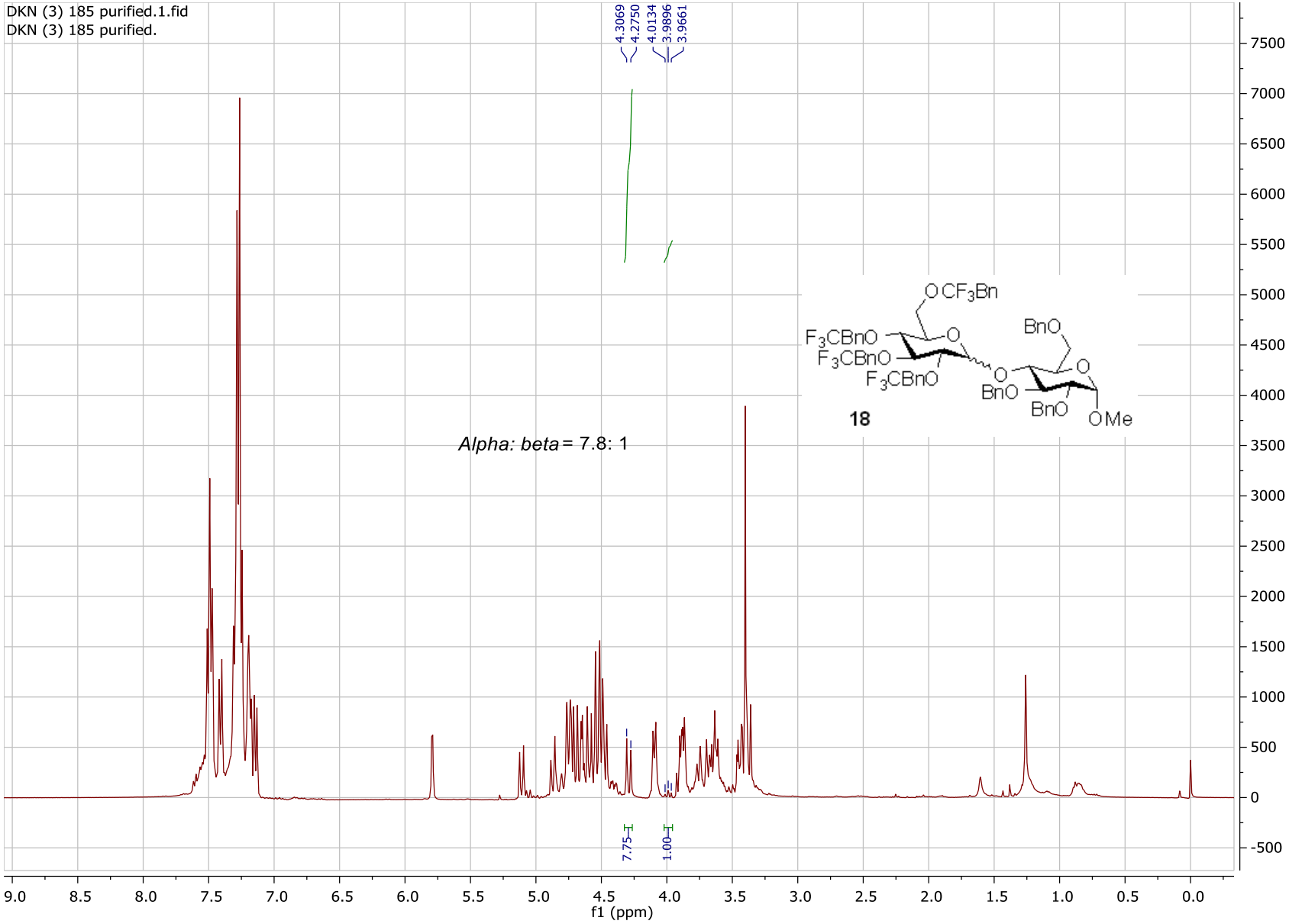

DKN (3) 48 purified.1.fid
DKN (2) 48 A purified.
3.3585
3.3248
ppm Hz Intensity Width Area Type
1 3.3585 1343.8 3875.0397 1.5895 78846.2708 Compound
2 3.3248 1330.4 723.7019 1.5895 14178.3821 Compound
Alpha: beta = 5.6: 1
Entry 13, Table 1. Purified Product NMR
f1 (ppm)

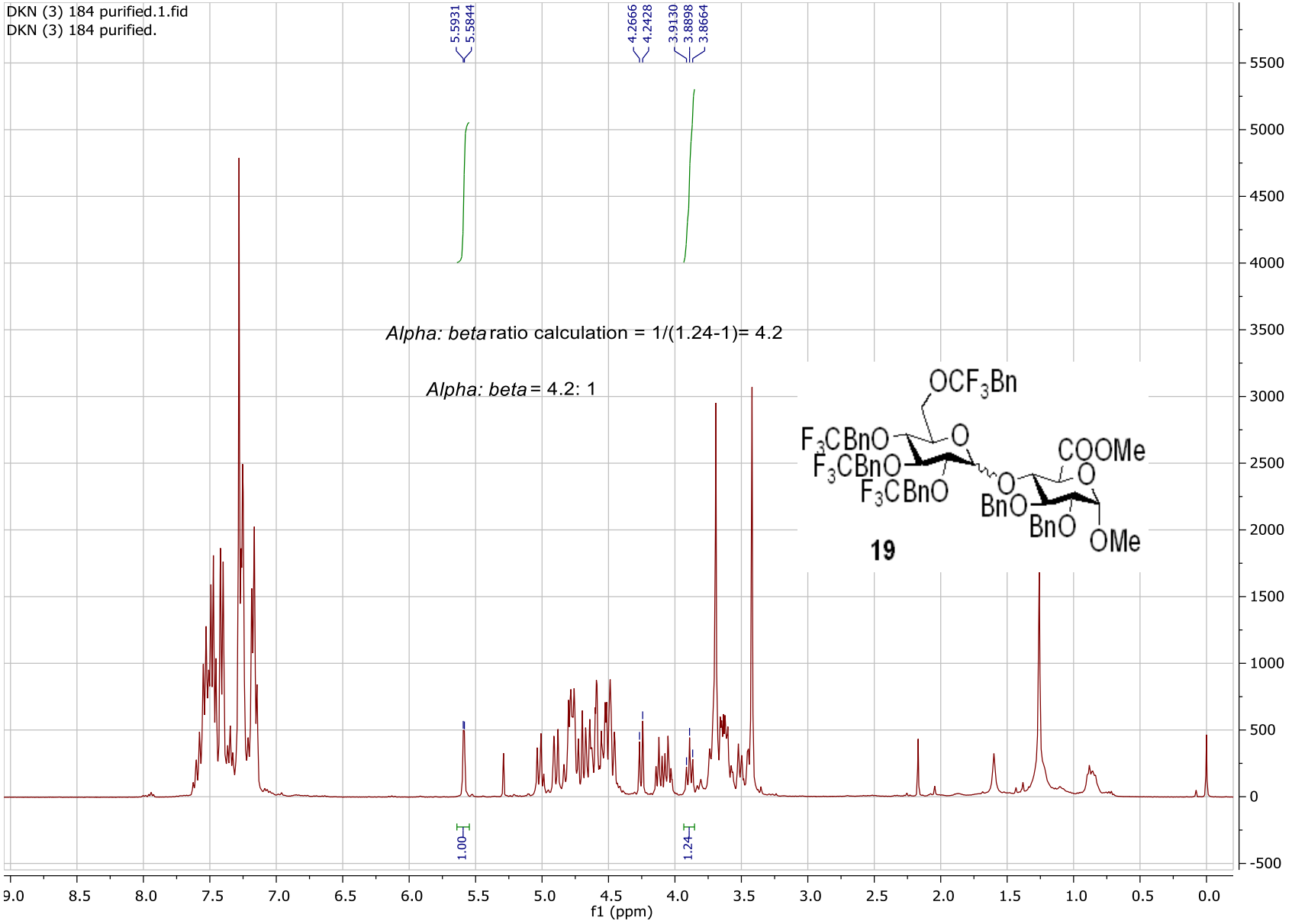

DKN (3) 188 crude.1.fid
DKN (3) 188 crude.
3.3563
3.3225
ppm Hz Intensity Width Area Type
1 3.36 1342.9 269.8 2.33 7143.99 Compound
2 3.32 1329.4 296.5 2.61 9565.06 Compound
Alpha: beta = 0.7: 1
Entry 14d,Table 1. Crude Product NMR
f1 (ppm)

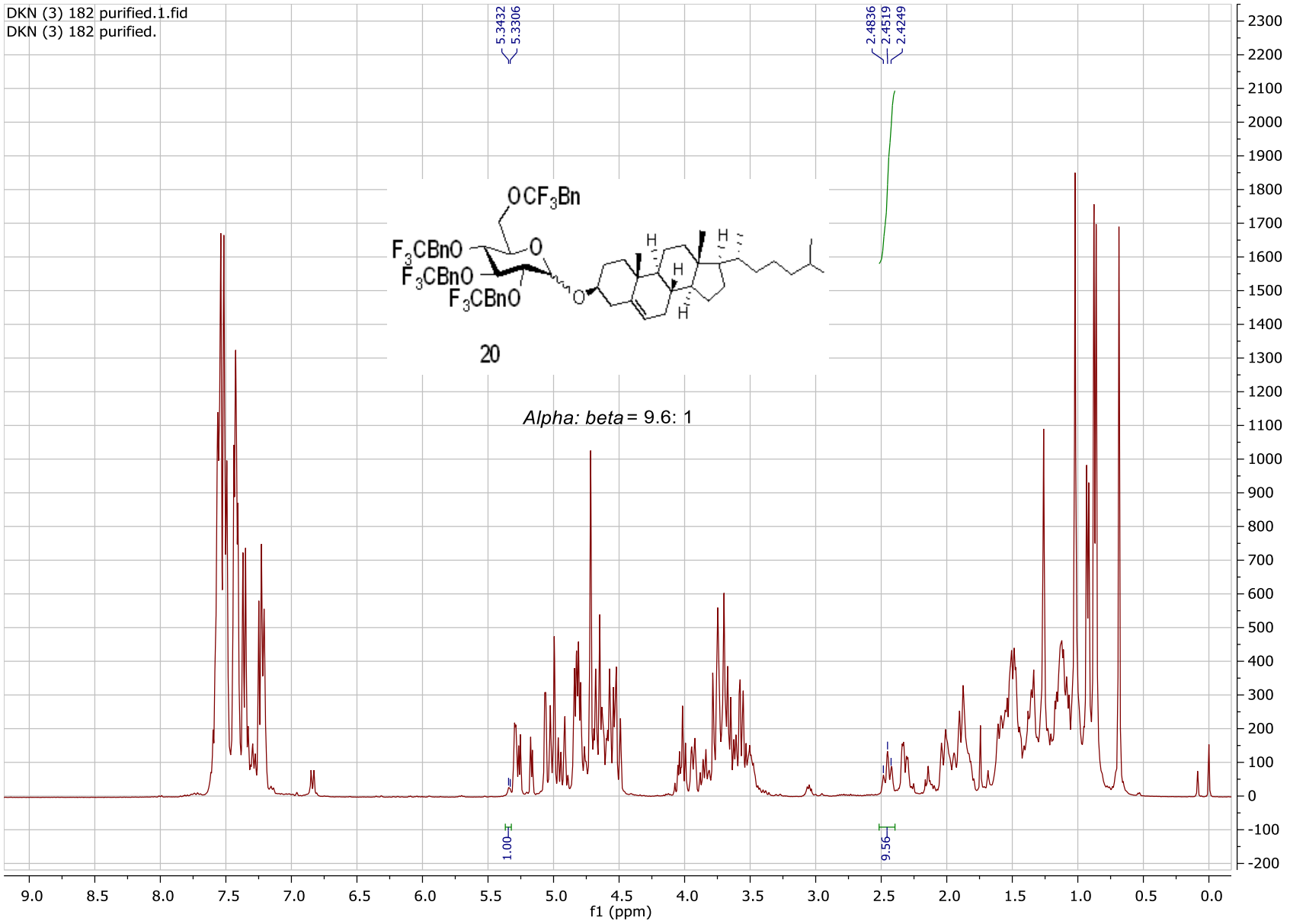

DKN (3) 188 pure.1.fid
DKN (3) 188 pure
3.3626
3.3290
ppm Hz Intensity Width Area Type
1 3.36 1345.5 1530.3 3.13 62778.75 Compound
2 3.33 1332.0 1694.0 2.69 60109.01 Compound
Alpha: beta = 1.0: 1
Entry 14d,Table 1. Purified Product NMR
4000
3500
3000
2500
2000
1500
1000
500
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

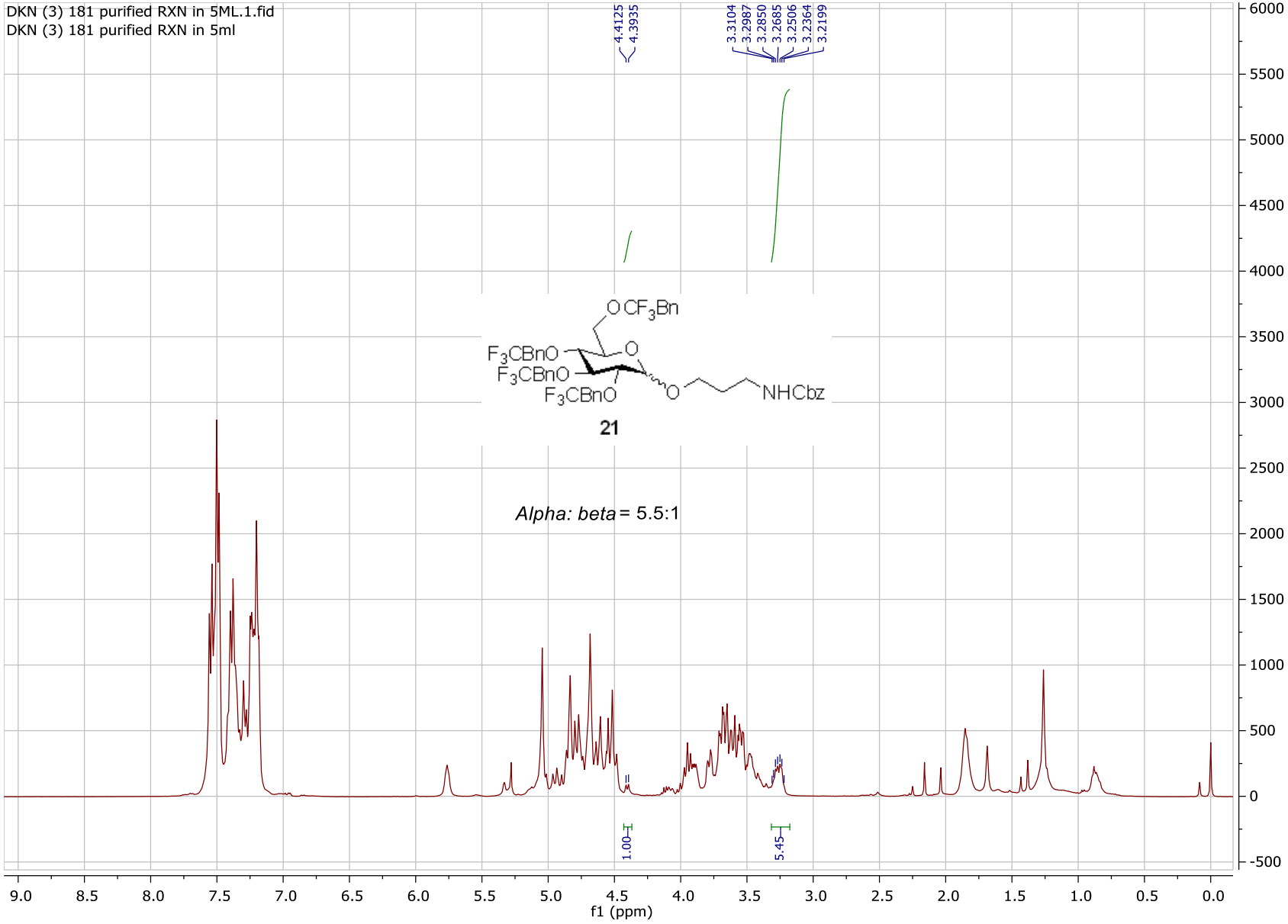

DKN (3) 180 A purified RXN in 5ML.1.fid
DKN (3) 180 A purified RXN in 5ML
4.1967
4.1698
3.1107
3.0876
3.0645
Alpha: beta = 7.2: 1
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
16
O
BnO
BnO
BnO
SPh
1.00
7.20
3500
3000
2500
2000
1500
1000
500
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

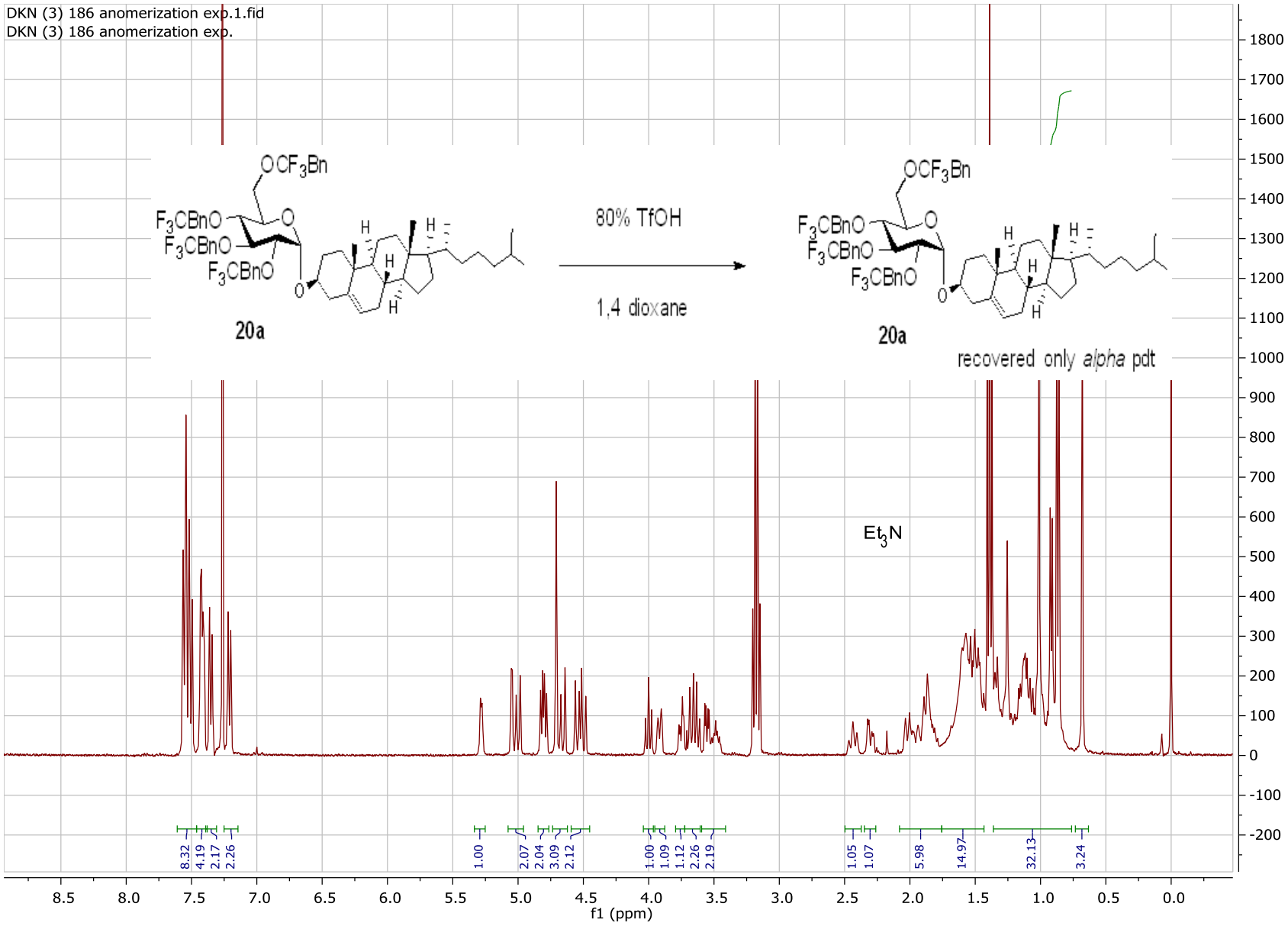

DKN (3) 183 purified.1.fid
DKN (3) 183 purified.
5.0534
5.0222
4.4052
4.3732
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
MeO
O
O
OBn
OBn
OBn
17
Alpha: beta = 8.8: 1
1.00
8.79
4000
3500
3000
2500
2000
1500
1000
500
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

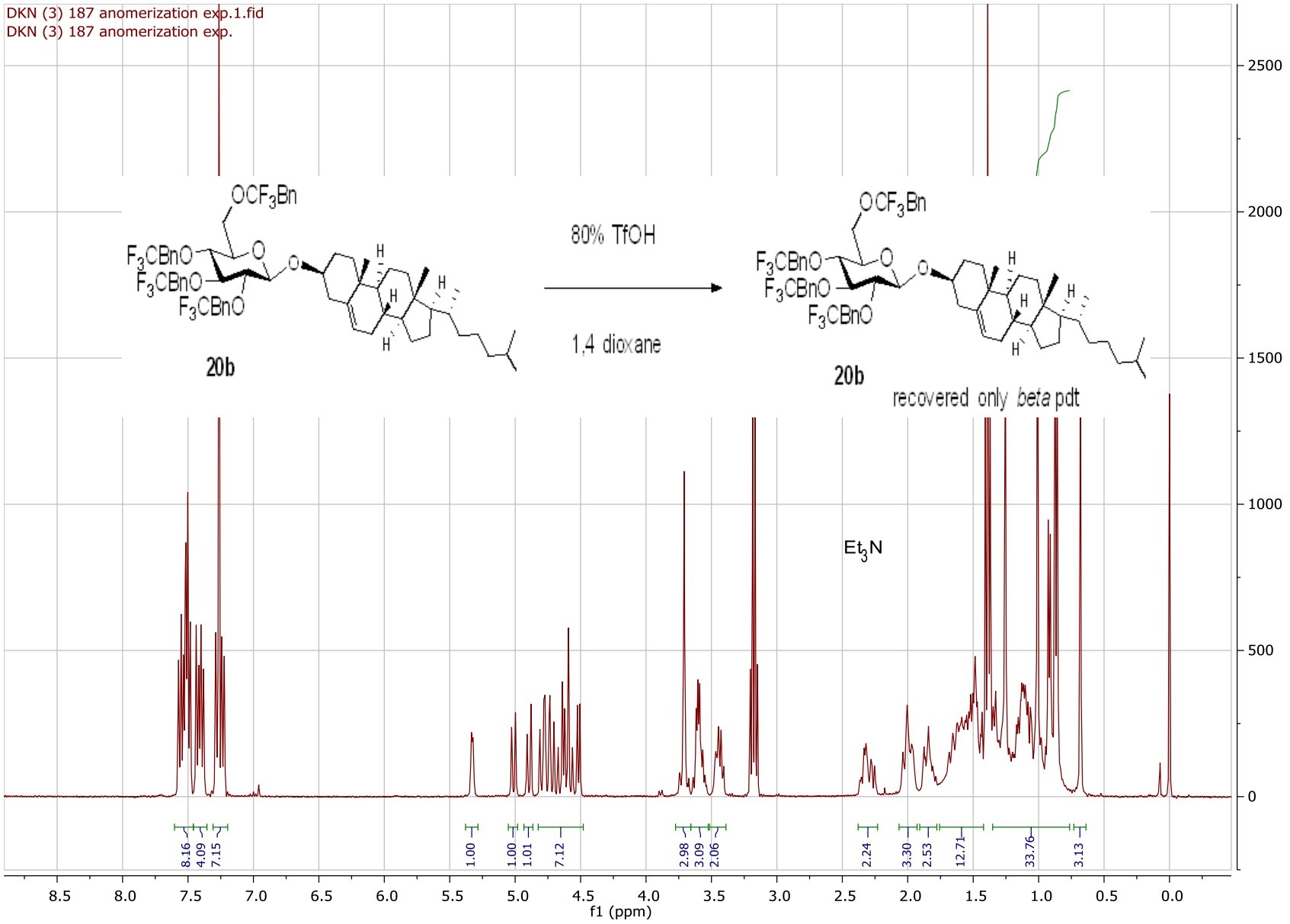

DKN (3) 185 purified.1.fid
DKN (3) 185 purified.
4.3069
4.2750
4.0134
3.9896
3.9661
Alpha: beta = 7.8: 1
18
7.75
1.00
f1 (ppm)

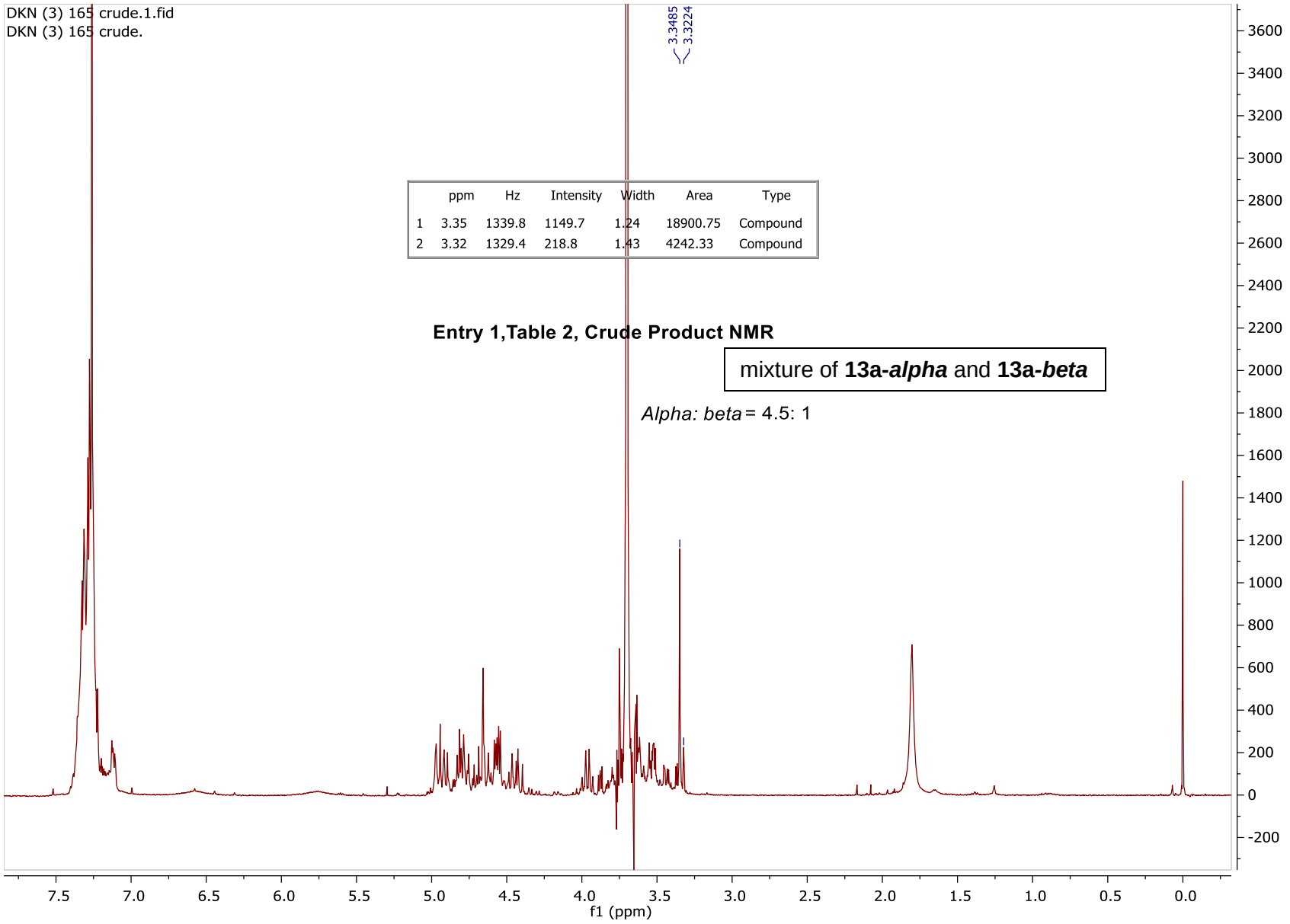

DKN (3) 184 purified.1.fid
DKN (3) 184 purified.
5.5931
5.5844
4.2666
4.2428
3.9130
3.8898
3.8664
Alpha: beta ratio calculation = 1/(1.24-1)= 4.2
Alpha: beta = 4.2: 1
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
COOMe
O
BnO
BnO
OMe
19
1.00
1.24
f1 (ppm)

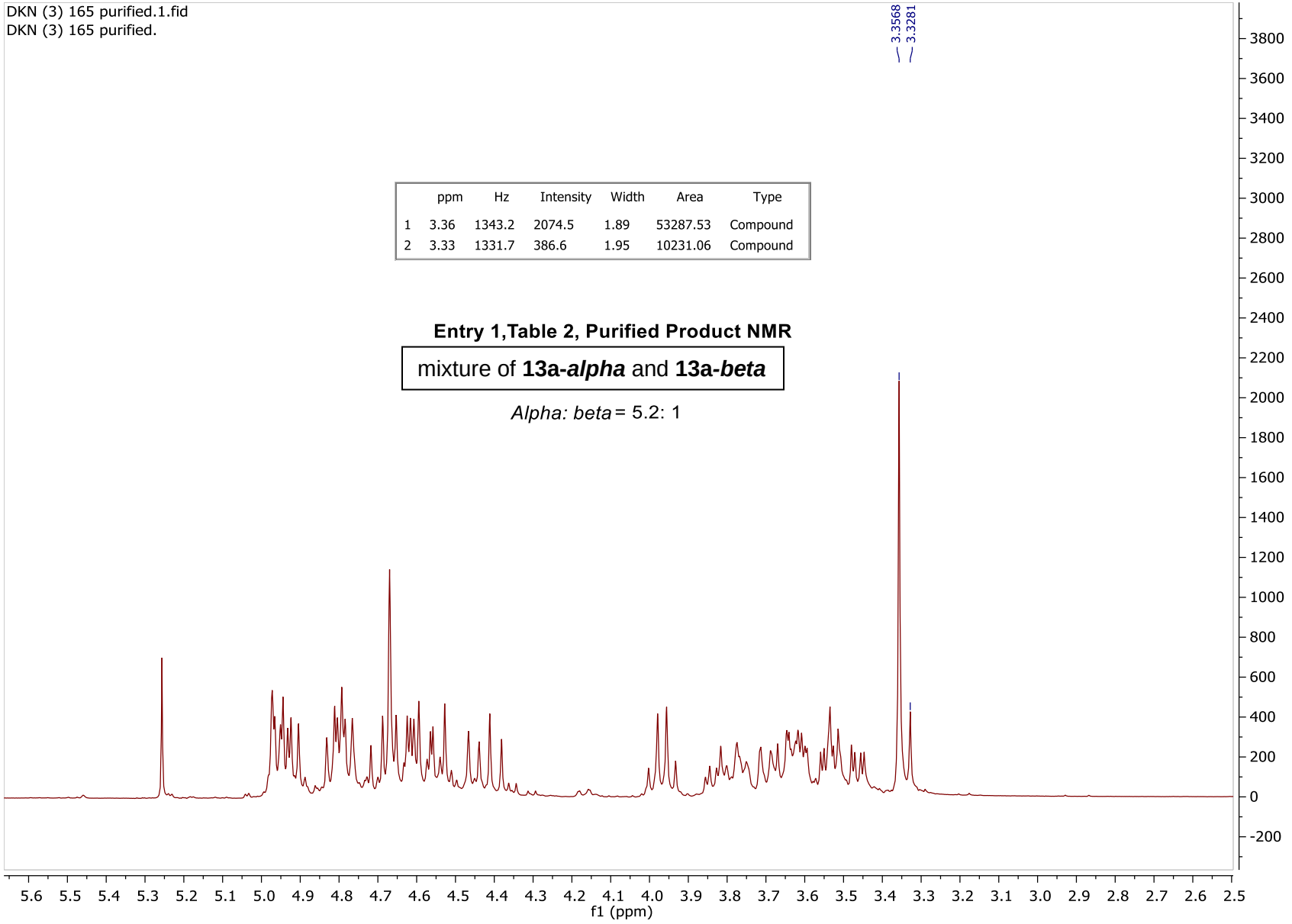

DKN (3) 182 purified.1.fid
DKN (3) 182 purified.
5.3432
5.3306
2.4836
2.4519
2.4249
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
H
H
H
H
O
20
Alpha: beta = 9.6: 1
1.00
9.56
f1 (ppm)

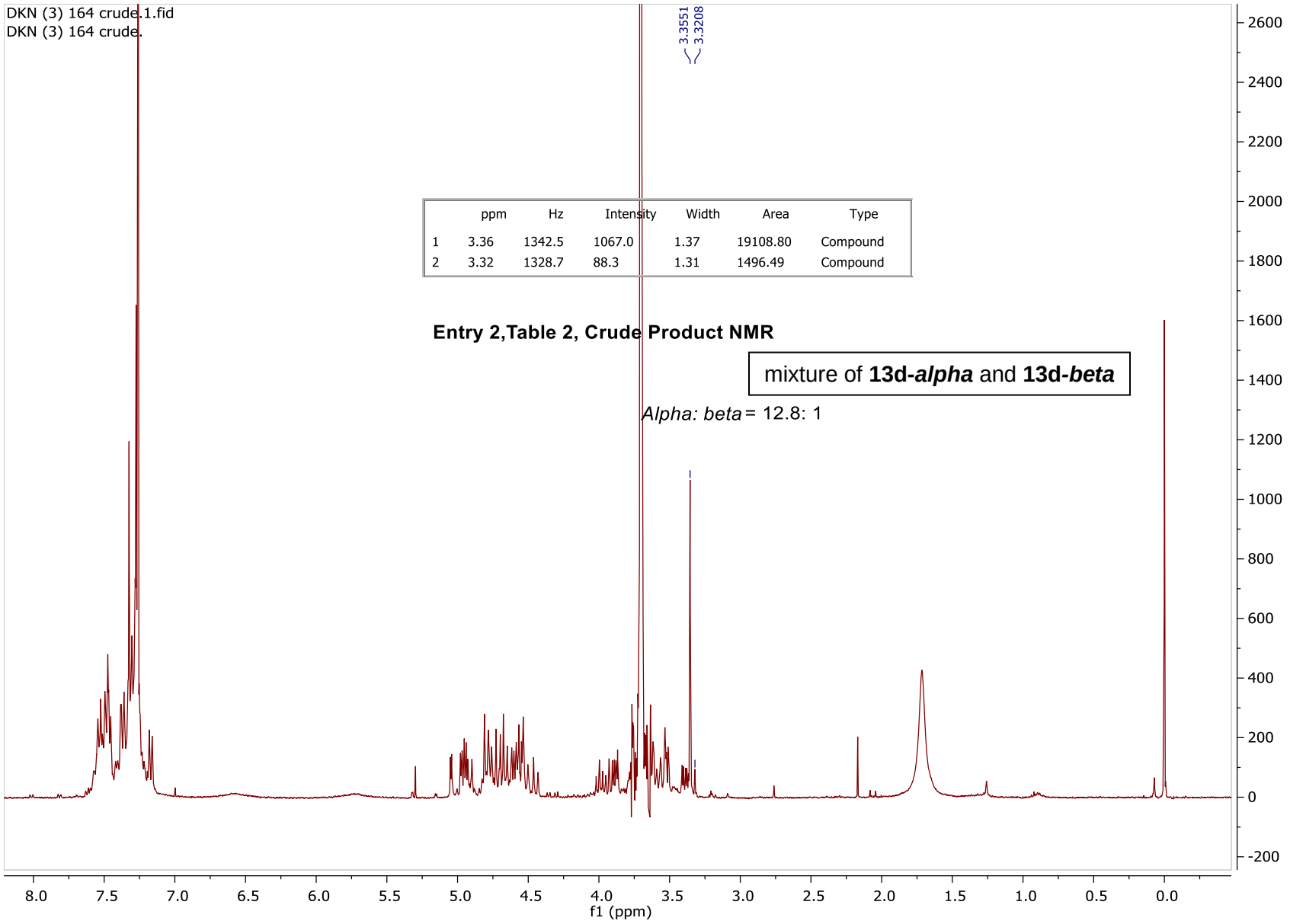

DKN (3) 181 purified RXN in 5ML.1.fid
DKN (3) 181 purified RXN in 5ml
4.4125
4.3935
3.3104
3.2987
3.2850
3.2685
3.2506
3.2364
3.2199
O CF3Bn
F3CBnO
F3CBnO
F3CBnO
O
O
NHCbz
21
Alpha: beta = 5.5:1
1.00
5.45
f1 (ppm)

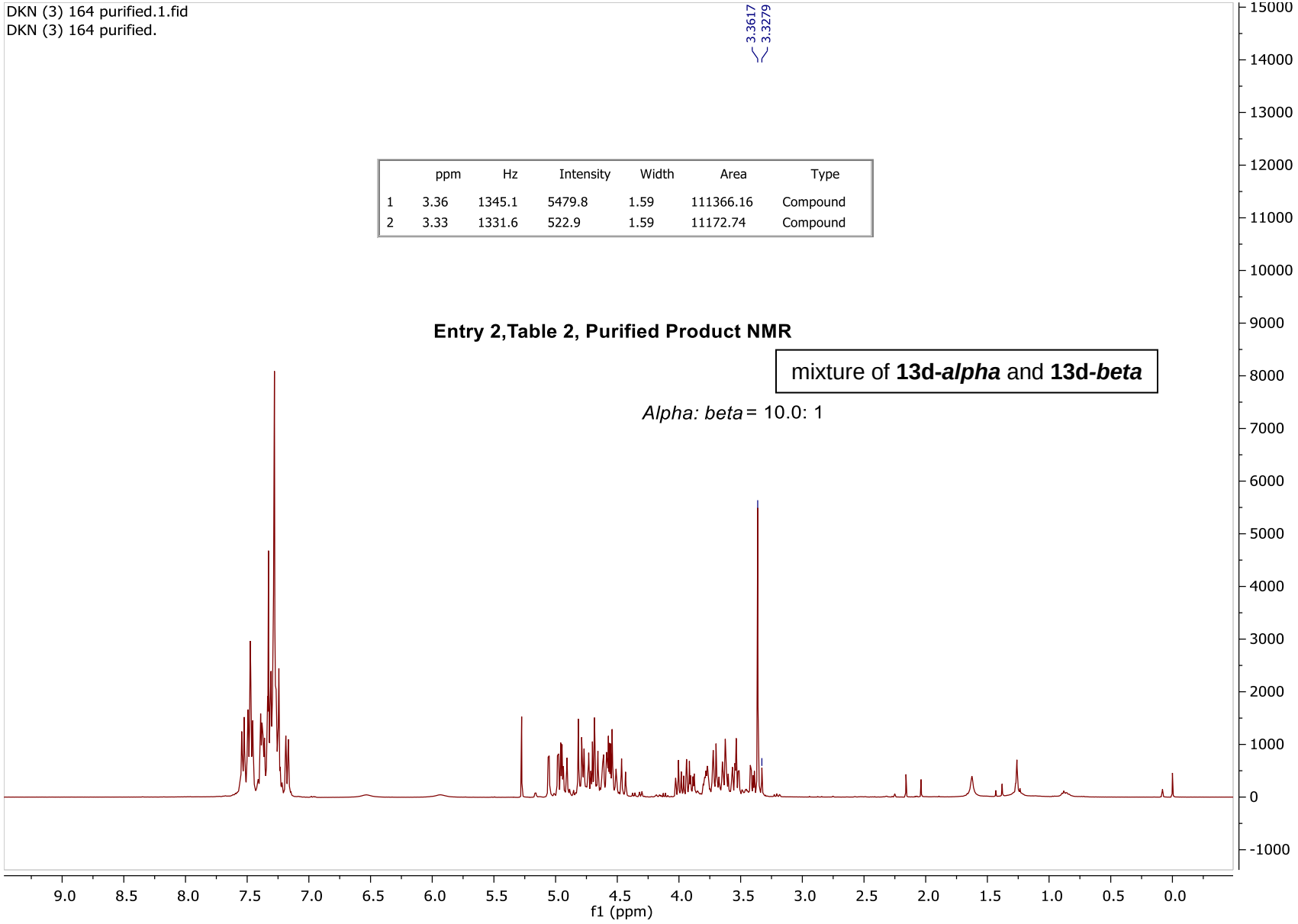

DKN (3) 186 anomerization exp.1.fid
DKN (3) 186 anomerization exp.
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
H
H
H
20a
80% TfOH
1,4 dioxane
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
O
H
H
H
20a
recovered only alpha pdt
Et3N
8.32
4.19
2.17
2.26
1.00
2.07
2.04
3.09
2.12
1.00
1.09
1.12
2.26
2.19
1.05
1.07
5.98
14.97
32.13
3.24
f1 (ppm)

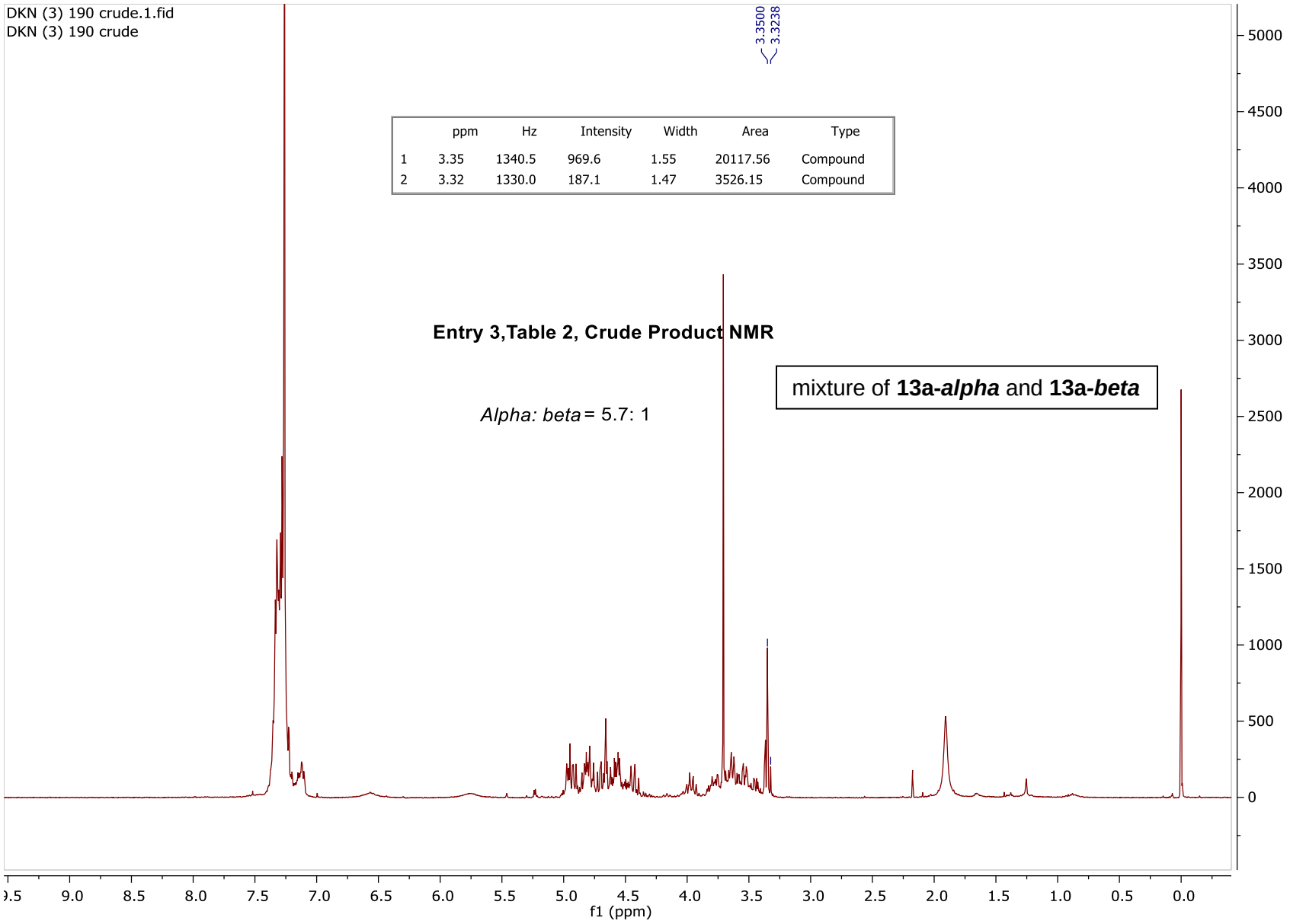

DKN (3) 187 anomerization exp.1.fid
DKN (3) 187 anomerization exp.
OCF3Bn
F3CBnO
F3CBnO
F3CBnO
20b
80% TfOH
1,4 dioxane
recovered only beta pdt
Et3N
f1 (ppm)

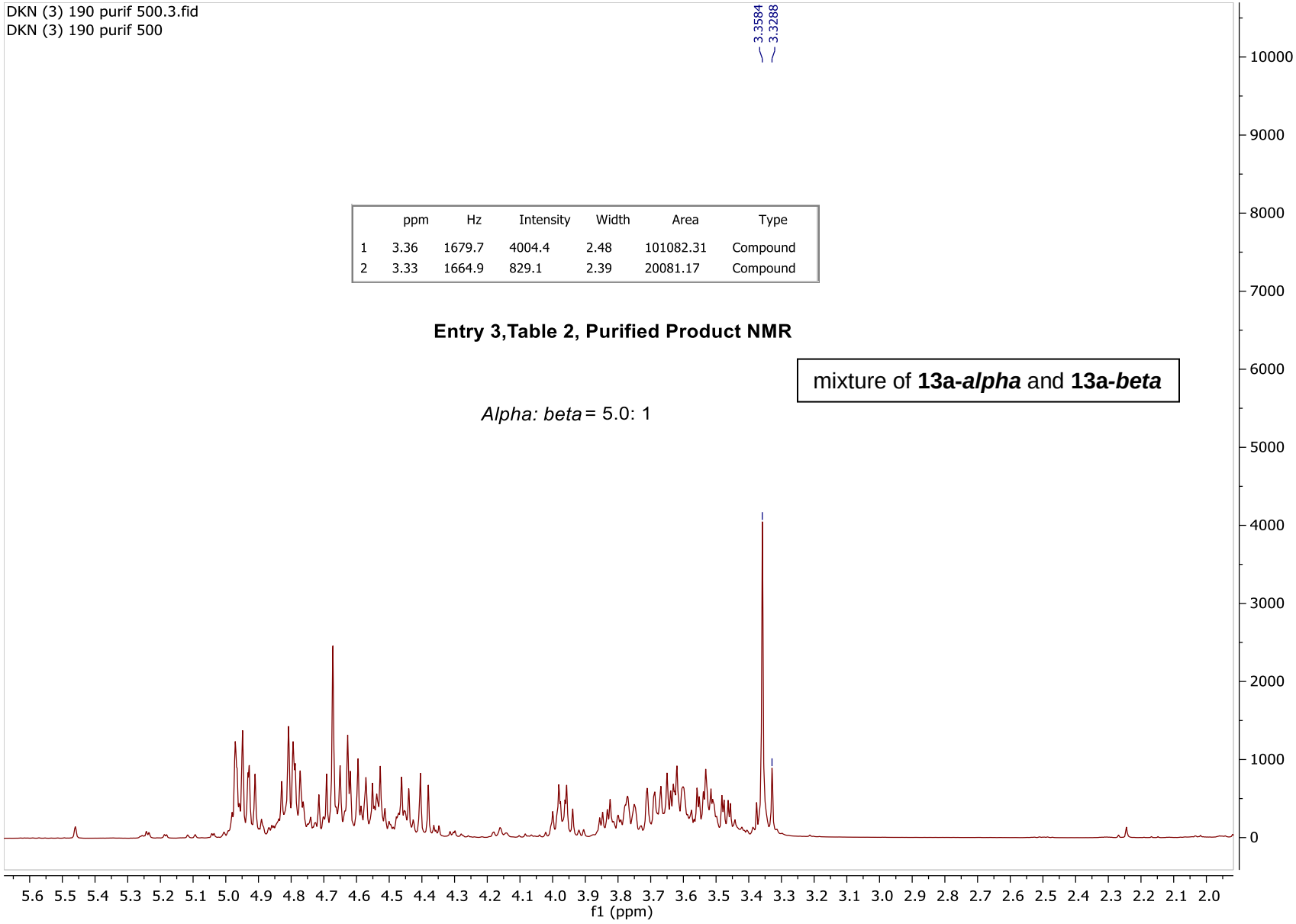

DKN (3) 165 crude.1.fid
DKN (3) 165 crude.
3.3485
3.3224
ppm Hz Intensity Width Area Type
1 3.35 1339.8 1149.7 1.24 18900.75 Compound
2 3.32 1329.4 218.8 1.43 4242.33 Compound
Entry 1,Table 2, Crude Product NMR
mixture of 13a-alpha and 13a-beta
Alpha: beta = 4.5: 1
f1 (ppm)

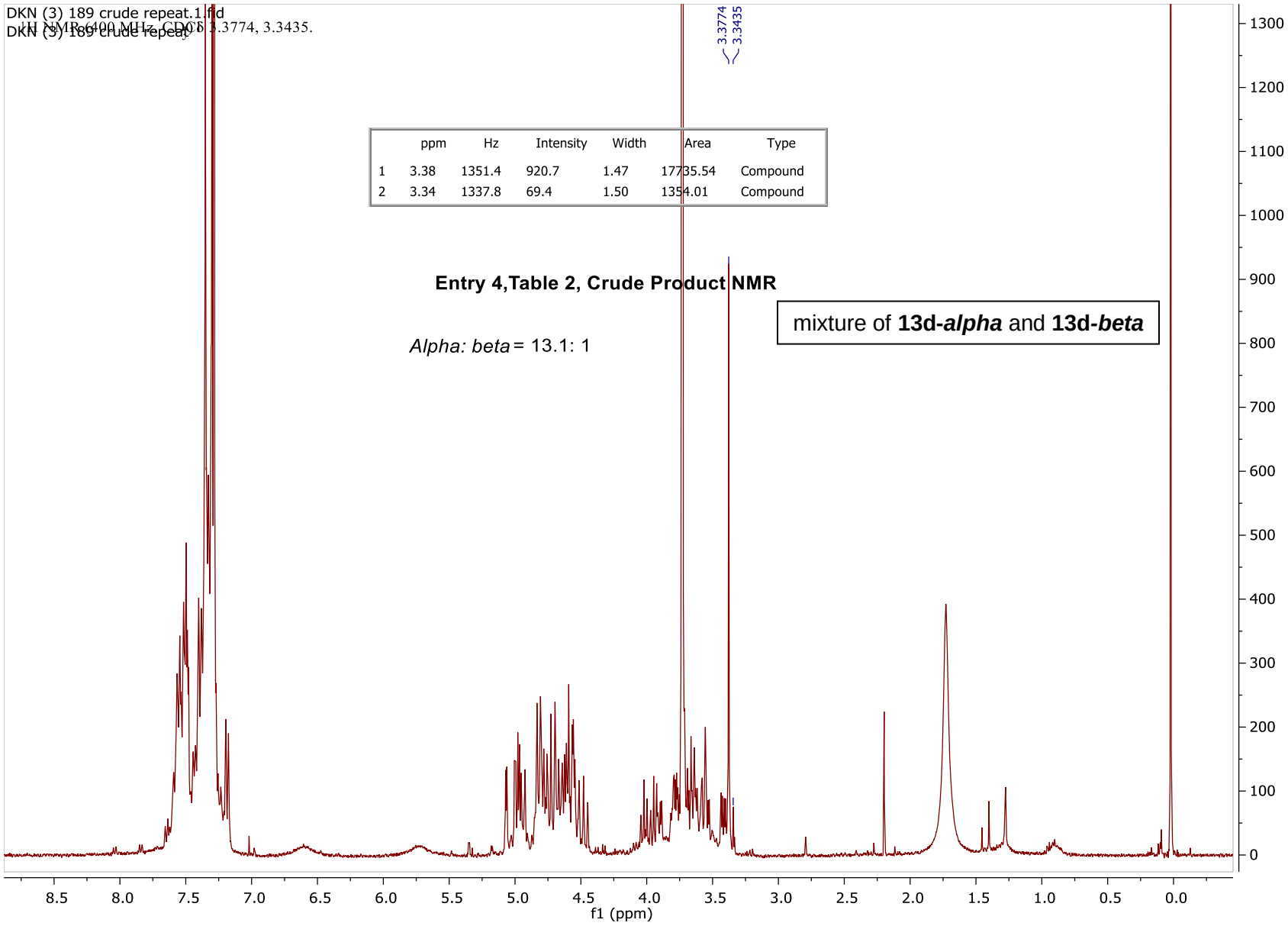

DKN (3) 165 purified.1.fid
DKN (3) 165 purified.
3.3568
3.3281
ppm Hz Intensity Width Area Type
1 3.36 1343.2 2074.5 1.89 53287.53 Compound
2 3.33 1331.7 386.6 1.95 10231.06 Compound
Entry 1,Table 2, Purified Product NMR
mixture of 13a-alpha and 13a-beta
Alpha: beta = 5.2: 1
f1 (ppm)

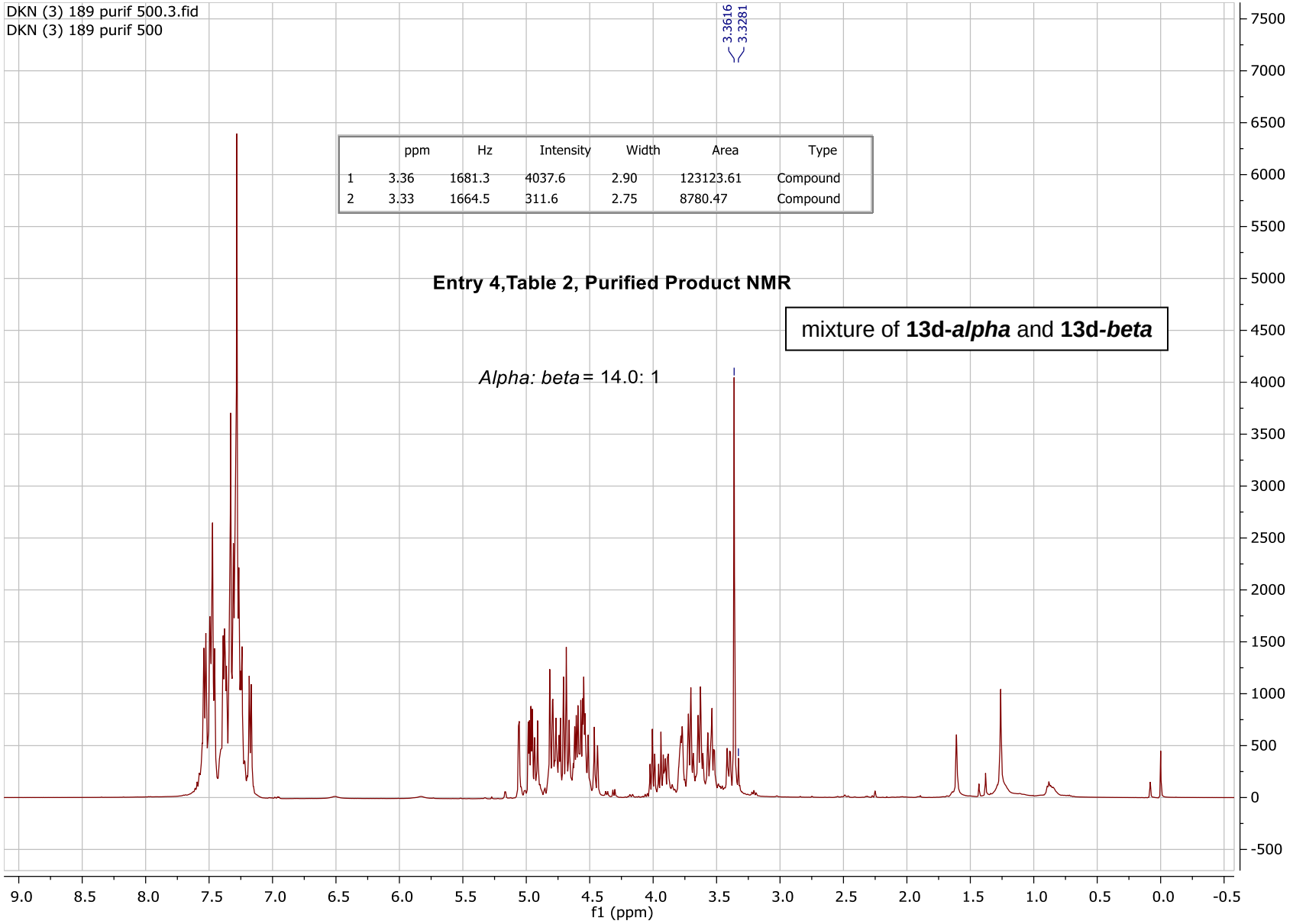

DKN (3) 164 crude.1.fid
DKN (3) 164 crude.
3.3551
3.3208
ppm Hz Intensity Width Area Type
1 3.36 1342.5 1067.0 1.37 19108.80 Compound
2 3.32 1328.7 88.3 1.31 1496.49 Compound
Entry 2,Table 2, Crude Product NMR
mixture of 13d-alpha and 13d-beta
Alpha: beta = 12.8: 1
f1 (ppm)

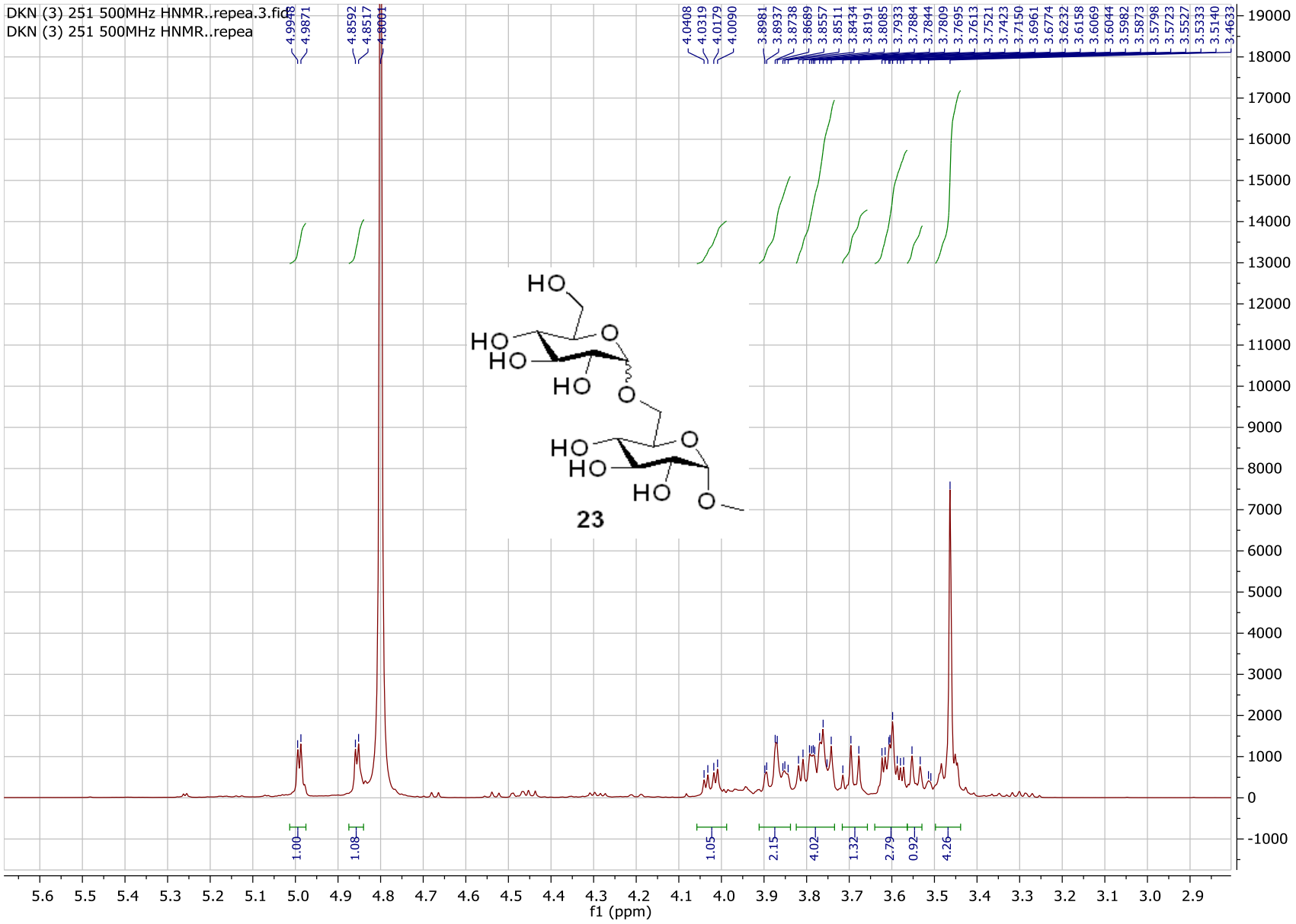

DKN (3) 164 purified.1.fid
DKN (3) 164 purified.
3.3617
3.3279
ppm Hz Intensity Width Area Type
1 3.36 1345.1 5479.8 1.59 111366.16 Compound
2 3.33 1331.6 522.9 1.59 11172.74 Compound
Entry 2,Table 2, Purified Product NMR
mixture of 13d-alpha and 13d-beta
Alpha: beta = 10.0: 1
f1 (ppm)

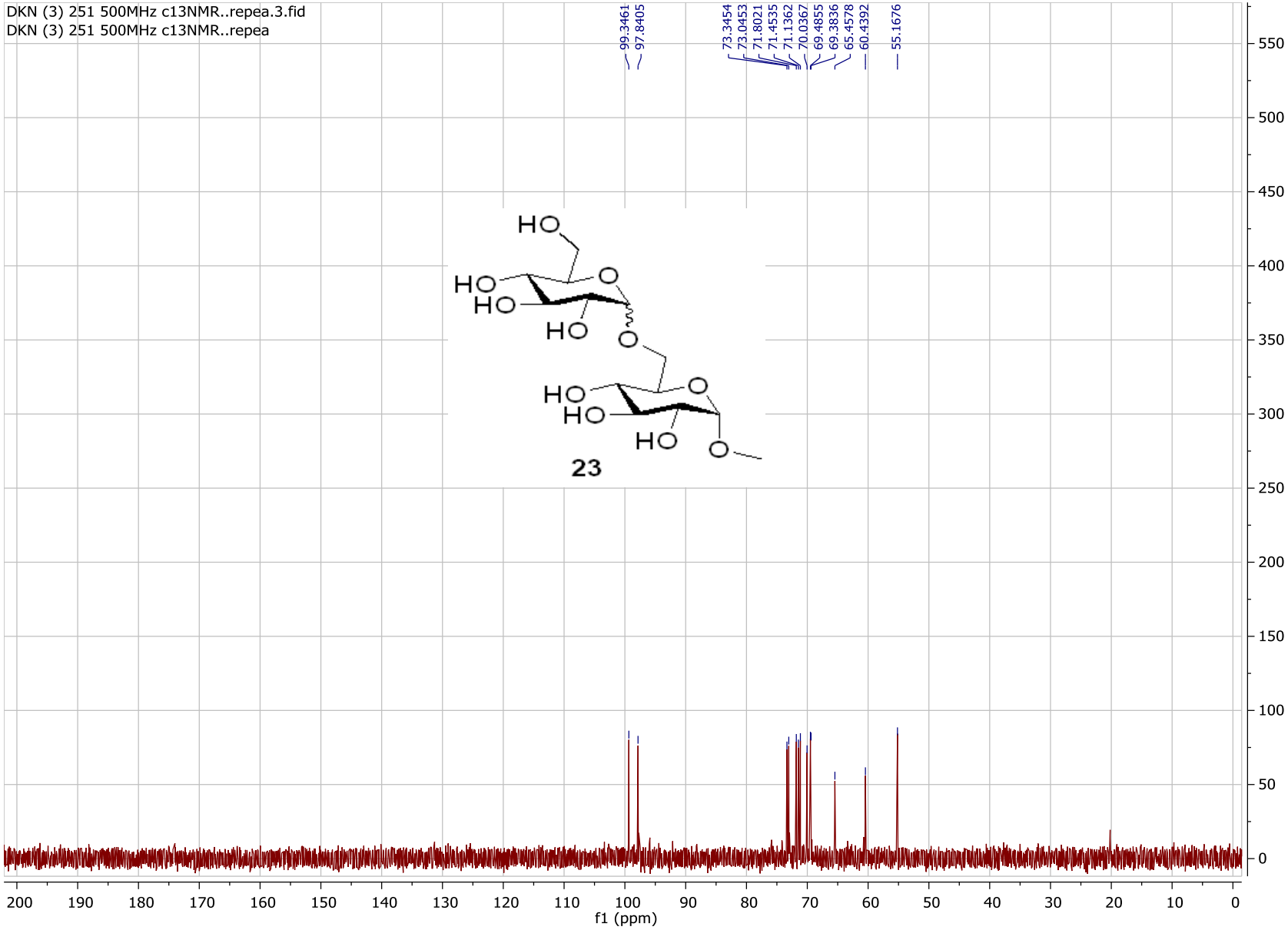

DKN (3) 190 crude.1.fid
DKN (3) 190 crude
3.3500
3.3238
ppm Hz Intensity Width Area Type
1 3.35 1340.5 969.6 1.55 20117.56 Compound
2 3.32 1330.0 187.1 1.47 3526.15 Compound
Entry 3,Table 2, Crude Product NMR
mixture of 13a-alpha and 13a-beta
Alpha: beta = 5.7: 1
f1 (ppm)


DKN (3) 190 purif 500.3.fid
DKN (3) 190 purif 500
3.3584
3.3288
ppm Hz Intensity Width Area Type
1 3.36 1679.7 4004.4 2.48 101082.31 Compound
2 3.33 1664.9 829.1 2.39 20081.17 Compound
Entry 3,Table 2, Purified Product NMR
mixture of 13a-alpha and 13a-beta
Alpha: beta = 5.0: 1
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
f1 (ppm)


DKN (3) 189 crude repeat.1.fid
DKN (3) 189 crude repeat
1H NMR (400 MHz, CDCl3) δ 3.3774, 3.3435.
3.3774
3.3435
ppm Hz Intensity Width Area Type
1 3.38 1351.4 920.7 1.47 17735.54 Compound
2 3.34 1337.8 69.4 1.50 1354.01 Compound
Entry 4,Table 2, Crude Product NMR
mixture of 13d-alpha and 13d-beta
Alpha: beta = 13.1: 1
f1 (ppm)


DKN (3) 189 purif 500.3.fid
DKN (3) 189 purif 500
3.3616
3.3281
ppm Hz Intensity Width Area Type
1 3.36 1681.3 4037.6 2.90 123123.61 Compound
2 3.33 1664.5 311.6 2.75 8780.47 Compound
Entry 4,Table 2, Purified Product NMR
mixture of 13d-alpha and 13d-beta
Alpha: beta = 14.0: 1
f1 (ppm)


DKN (3) 251 500MHz HNMR..repea.3.fid
DKN (3) 251 500MHz HNMR..repea
4.9948
4.9871
4.8592
4.8517
4.8001
4.0408
4.0319
4.0179
4.0090
3.8981
3.8937
3.8738
3.8689
3.8557
3.8511
3.8434
3.8191
3.8085
3.7933
3.7884
3.7844
3.7809
3.7695
3.7613
3.7521
3.7423
3.7150
3.6961
3.6774
3.6232
3.6158
3.6069
3.6044
3.5982
3.5873
3.5798
3.5723
3.5527
3.5333
3.5140
3.4633
HO
HO
HO
HO
O
O
HO
HO
HO
O
23
1.00
1.08
1.05
2.15
4.02
1.32
2.79
0.92
4.26
f1 (ppm)


DKN (3) 251 500MHz c13NMR..repea.3.fid
DKN (3) 251 500MHz c13NMR..repea
99.3461
97.8405
73.3454
73.0453
71.8021
71.4535
71.1362
70.0367
69.4855
69.3836
65.4578
60.4392
55.1676
HO
HO
HO
HO
O
O
HO
HO
HO
O
O
23
f1 (ppm)