Supplementary material

Synthesis and study of the pancreatic α-amylase inhibitory activity of methyl acarviosin and its derivatives

Eisuke Kato,* Fumiaki Chikahisa, and Jun Kawabata

Laboratory of Food Biochemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060-8589, Japan

*Corresponding author:

e-mail: eikato@chem.agr.hokudai.ac.jp, Tel/Fax: +81-11-706-2496.

Contents

Experimental procedures

General methods.

All commercially available chemicals were purchased from Wako Pure Chem. Ind. Ltd., unless otherwise noted, and used without further purification. Structures of the synthetic compounds were determined by NMR and Mass spectrometry. Bruker AMX500 or Jeol JNM-EX 270 was used to obtain NMR spectrum and either tetramethylsilane (TMS) or residual solvent peak was used as an internal standard (^{1}H NMR: TMS 0.00 ppm (for $CDCl_{3)}$, CD_3OD 3.30 ppm, D_2O 4.75 ppm; ^{13}C NMR: $CDCl_3$ 77.0 ppm, CD_3OD 49.0 ppm). Jeol JMS SX-102A (FAB-MS) or Jeol JMS-T100GCV (FD-MS) or Thermo Scientific Exactive (ESI-MS) was used to obtain mass spectrum. Combination of Aquity UPLC system (Waters Co.) and LCT-premier (Waters Co.) were used for UPLC-Tof-MS analysis. Absorbance was measured by Synergy^{TM} MX (Bio-tech Instruments Inc.,) microplate reader.

Determination of pancreatic amylase inhibitory activity

The α-amylase inhibitory activity was determined by using the method described by Ali *et al.* with a modification.[S1] Porcine pancreatic amylase (PPA, Sigma-Aldrich Co.) was dissolved in sodium phosphate buffer (20 mM, pH 6.9) containing 6.7 mM of NaCl to give a concentration of 1 unit/mL solution. Soluble starch (10 mg/mL) in the same buffer was used as a substrate solution. A coloring reagent (DNS) was prepared by mixing 4.8 M aq. 3,5-dinitrosalicylic acid (20 mL) and a solution of (+)-sodium potassium tartrate tetrahydrate (12 g) in 2 M NaOH (8 mL). A sample solution (100 μL) in 50% dimethyl sulfoxide (DMSO) and the PPA solution (150 μL) were mixed in a micro tube (1.5 mL). The tube was pre-incubated at 37 ºC for 15 min. The starch solution (250 μL) was then added and the mixture was incubated at 37 °C for 15 min. To terminate the reaction, the tube was dipped in boiling water for 1 min. After cooling, the reaction mixture was directly passed through a small ODS (Cosmosil 75C18-OPN, Nacalai Tesque Co., Kyoto, Japan) column (3 mL) to remove any sample constituents that may interfere with the following color reaction. The reaction mixture (100 μL) was then mixed with coloring reagent (50 μL) and heated in boiling water for 15 min. The mixture was cooled on ice and then diluted with water (450 μL). The obtained solution (200 μL) was transferred into 96-well micro plate, and the optical density was determined at a wavelength of 540 nm. The control experiment was performed using 50% aq. DMSO in place of the sample solution. Blank experiments for sample and control were performed using the sodium phosphate buffer in place of the enzyme solution and each blank value was subtracted from the sample and the control values, respectively. The inhibitory activity (%) was calculated as [{1-A_{540} (sample) / A_{540} (control)} × 100]. Each experiment is tested in duplicate and repeated at least twice.

UPLC-Tof-MS analysis of the enzyme reaction mixture

The enzyme reaction was performed according to the above method and the mixture before passing through the small ODS column was used for the analysis. UPLC-Tof-MS analysis was achieved using Waters Acquity UPLC / LCT Premier (Waters Co.) system with ESI as an ion source. Inertsustain C18 column (2 μm, φ2.1 mm×100 mm, GL Science Co.) was employed for the separation with the following elution condition.

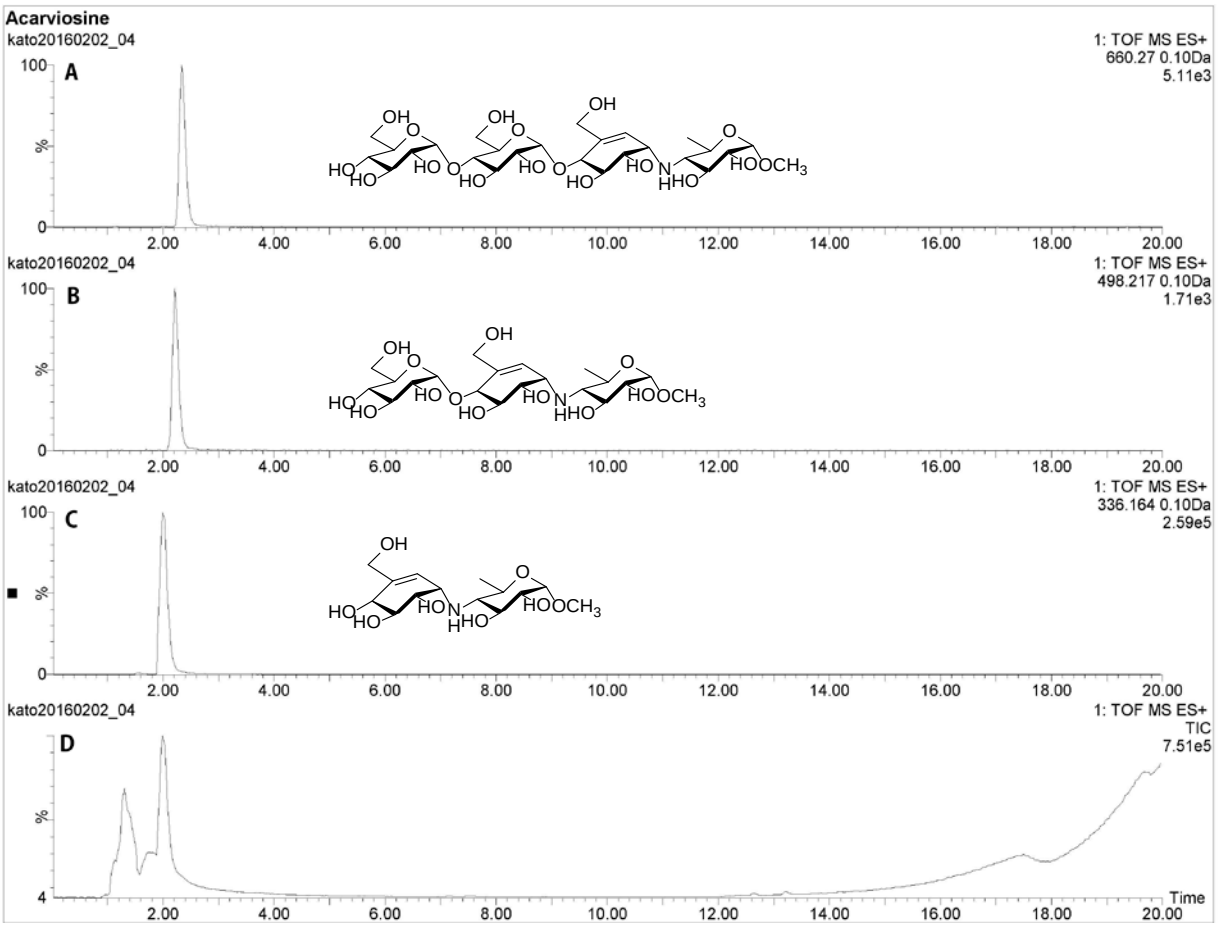
Moble phase:

0 to 10 min: 5% aq. methanol with 0.1% formic acid

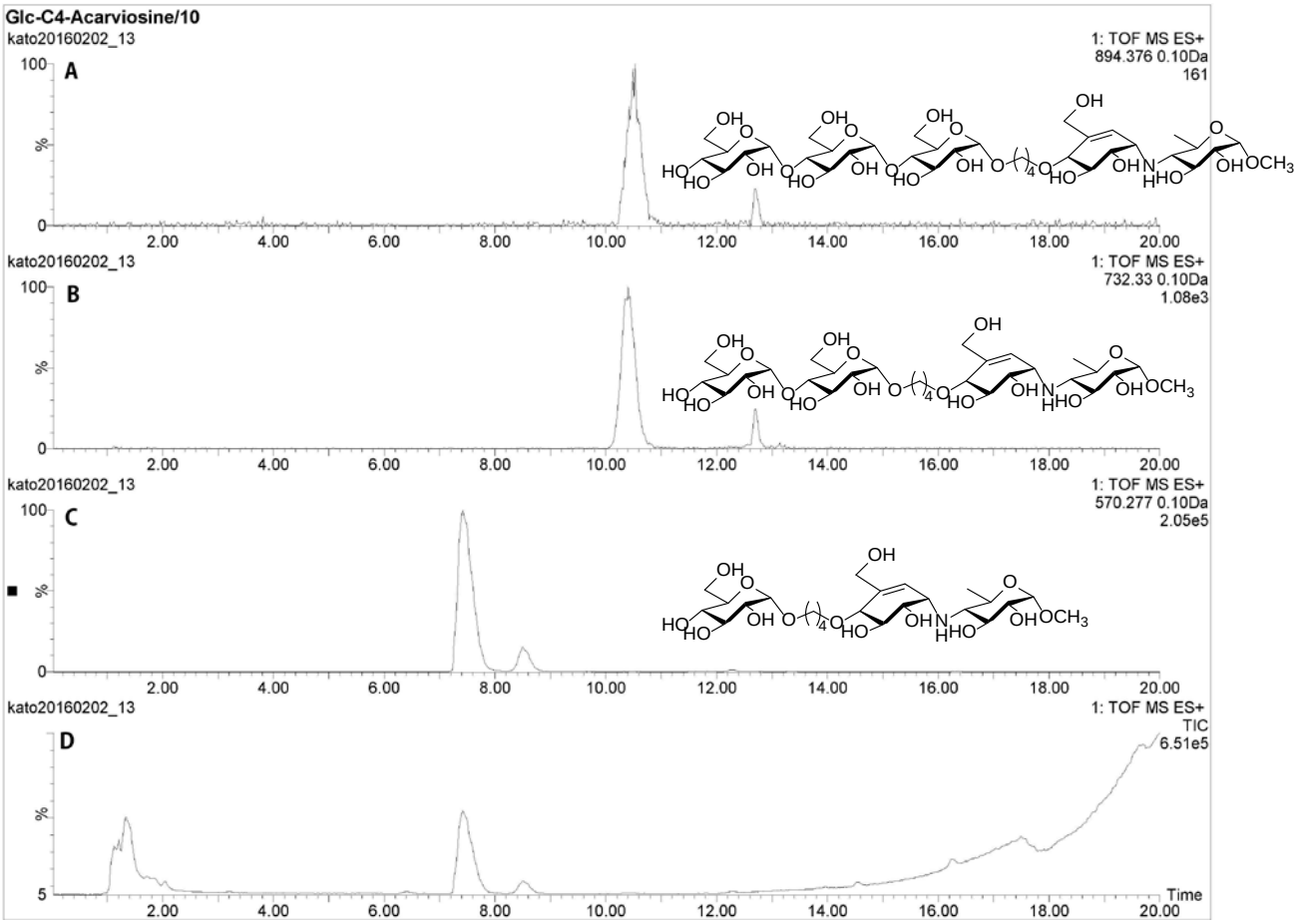
10 to 20 min: gradient elution from 5% aq. methanol up to 95% aq. methanol, with 0.1% formic acid

Flow rate: 0.20 mL/min.

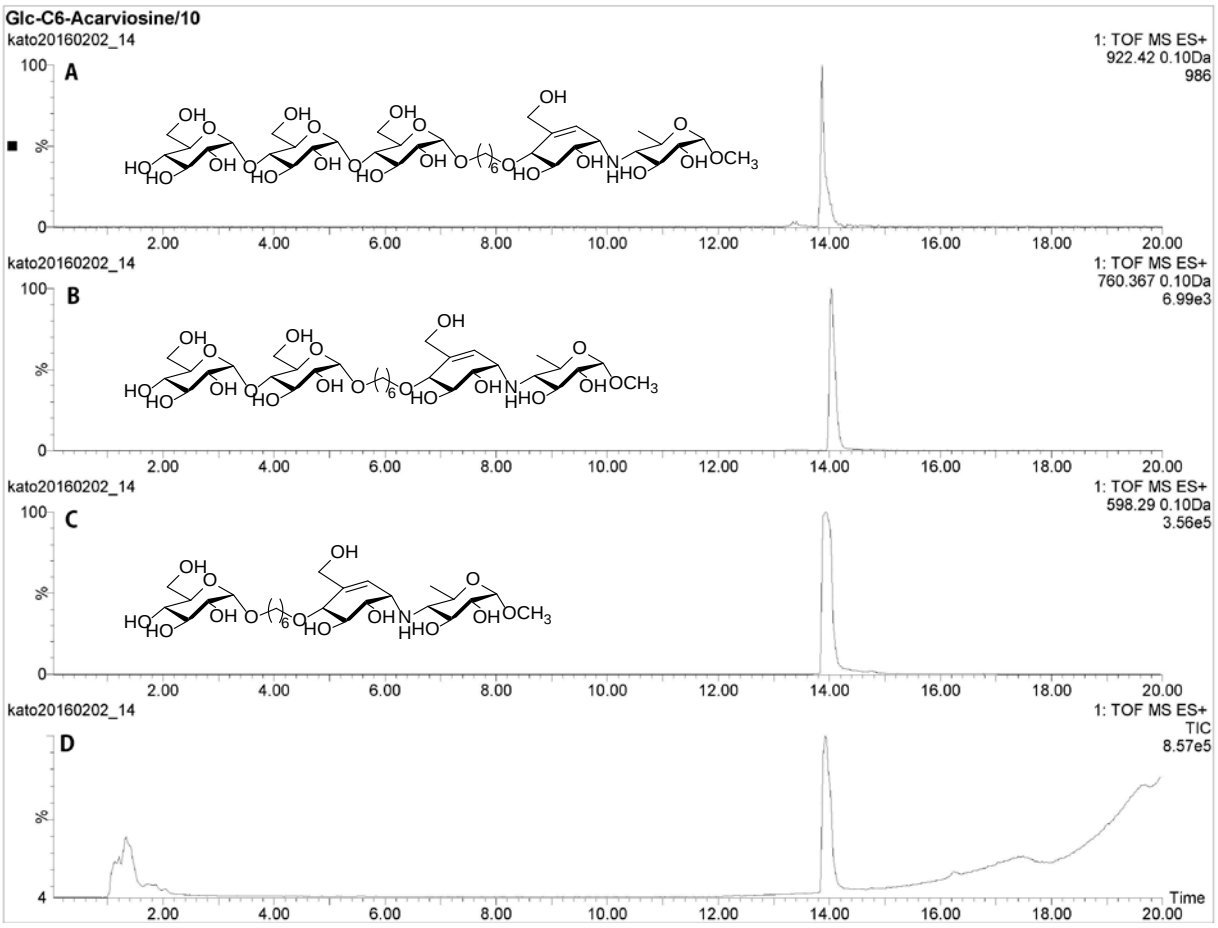
Mass spectrum was measured by positive mode between *m/z* 100-1500.



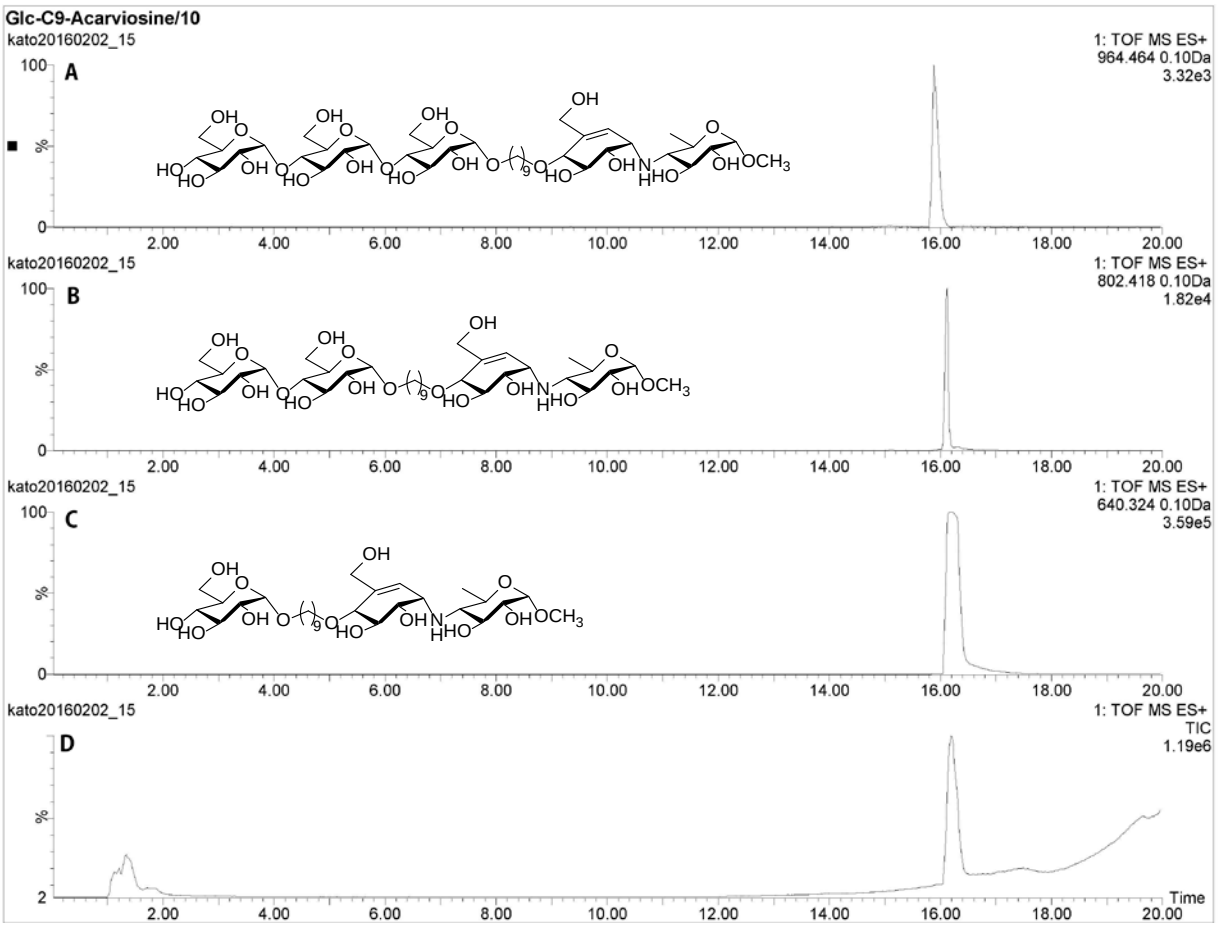
Supplementary Figure 1. Total ion chromatogram (TIC) and selected ion chromatogram (SIC) of the UPLC-Tof-MS analysis of enzyme reaction mixture with methyl α-acarviosin (**1**) as the inhibitor. A: SIC, *m/z* 680.27 corresponding to [methyl α-acarviosin + maltose+H]$^+$; B: SIC, *m/z* 498.22 corresponding to [methyl α-acarviosin + glucose+H]$^+$; C: SIC, *m/z* 336.16 corresponding to [methyl α-acarviosin+H]$^+$; D: TIC.



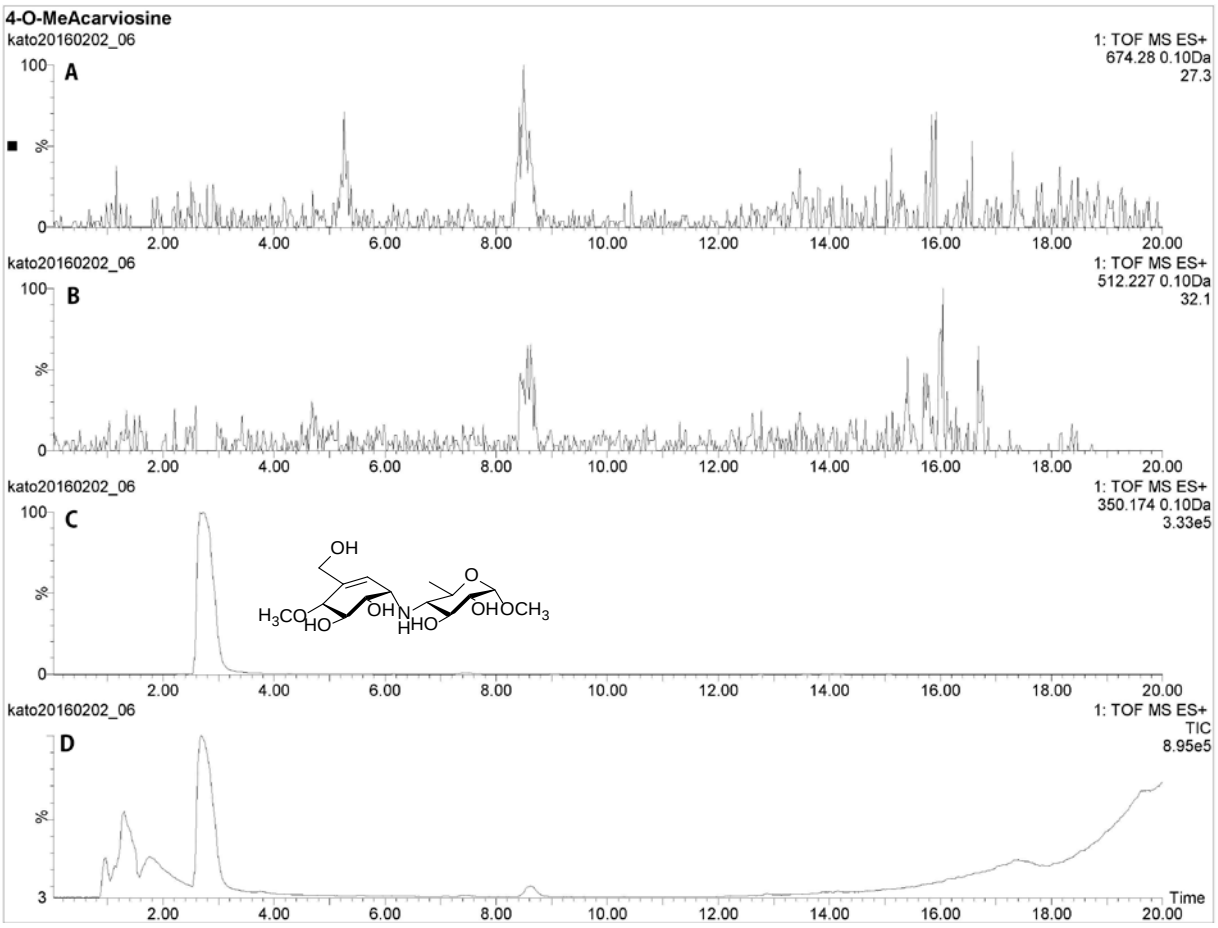
Supplementary Figure 2. TIC and SIC of the UPLC-Tof-MS analysis of enzyme reaction mixture with compound **6** as the inhibitor. A: SIC, *m/z* 894.37 corresponding to [**6** + maltose + H]$^+$; B: SIC, *m/z* 731.33 corresponding to [**6** + glucose + H]$^+$; C: SIC, *m/z* 570.27 corresponding to [**6** + H]$^+$; D: TIC.



Supplementary Figure 3. TIC and SIC of the UPLC-Tof-MS analysis of enzyme reaction mixture with compound **7** as the inhibitor. A: SIC, *m/z* 922.42 corresponding to [**7** + maltose + H]$^+$; B: SIC, *m/z* 760.36 corresponding to [**7** + glucose + H]$^+$; C: SIC, *m/z* 597.29 corresponding to [**7** + H]$^+$; D: TIC.



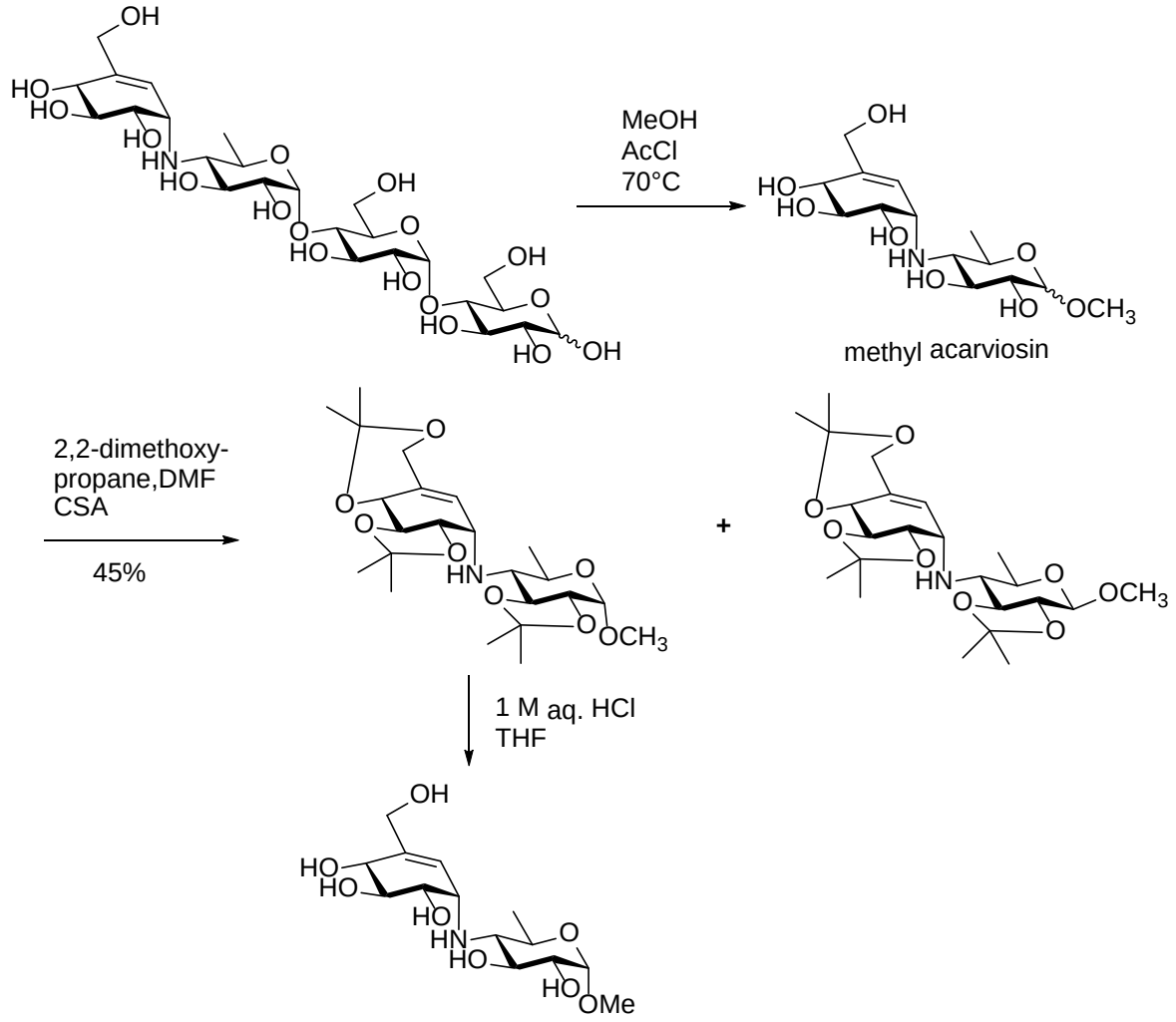
Supplementary Figure 4. TIC and SIC of the UPLC-Tof-MS analysis of enzyme reaction mixture with compound **8** as the inhibitor. A: SIC, *m/z* 964.46 corresponding to [**8** + maltose + H]$^+$; B: SIC, *m/z* 802.42 corresponding to [**8** + glucose + H]$^+$; C: SIC, *m/z* 640.32 corresponding to [**8** + H]$^+$; D: TIC.



Supplementary Figure 5. TIC and SIC of the UPLC-Tof-MS analysis of enzyme reaction mixture with compound **9** as the inhibitor. A: SIC, *m/z* 674.28 corresponding to [**9** + maltose + H]$^+$; B: SIC, *m/z* 512.23 corresponding to [**9** + glucose + H]$^+$; C: SIC, *m/z* 350.17 corresponding to [**9** + H]$^+$; D: TIC.

Synthesis

Preparation of methyl α-acarviosin from acarbose



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Acarbose hydrate (7.03 g)(TCI Co., A2485) was dissolved in 10% acetyl chloride/methanol (100 mL) and stirred for 14 hrs at 70°C. The reaction mixture was cooled and evaporated to dryness. The residue was purified by silica-gel column chromatography (stepwise elution: ethyl acetate/methanol/water = 60/8/1 → 40/8/1 → 5/4/1) to obtain methyl acarviosin as α and β mixture (2.59 g, 7.72 mmol). Anomer mixture of acarviosin was then dissolved in 1:5 mixture of DMF and 2,2-dimethoxypropane, and catalytic amount of camphorsulfonic acid (CSA) was added. The mixture was stirred for 2hrs at 60°C. The reaction mixture was cooled, diluted with sat. aq. sodium hydrogen carbonate and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was separated by silica-gel column chromatography (stepwise elution: hexane/ethyl acetate = 5/1 → 4/1 → 2/1) to obtain isopropylidene protected α-anomer (640 mg, 1.40 mmol) and β-anomer (570 mg, 1.25 mmol) separately.[S2] Part of the α-anomer (7.1 mg, 0.0156 mmol) was then dissolved in 1:1 mixture of 1 M hydrogen chloride solution and THF (2.0 mL) and stirred for an hour. The reaction mixture was evaporated and the residue was purified by silica-gel column chromatography (ethyl acetate/methanol/water = 40/8/1) to obtain methyl α-acarviosin (**1**, 4.7 mg, 0.0140 mmol, 89%).[S3]

Isopropylidene protected methyl acarviosin

α- anomer[S2]: ^{1}H-NMR (270 MHz, $CDCl_3$, rt): δ 1.33 (3H, d, *J* = 6.2 Hz), 1.41 (s, 3H), 1.44 (s, 6H), 1.46 (s, 3H), 1.47 (s, 3H), 1.57 (s, 3H), 2.78 (1H, t, *J* = 9.7 Hz), 3.37-3.46 (4H, m), 3.50 (1H, dd, *J* = 3.2, 9.7 Hz), 3.59 (1H, dd, *J* = 4.8, 9.9 Hz), 3.84 (1H, t, *J* = 9.7 Hz), 4.04 (1H, t, *J* = 4.8 Hz), 4.14 (1H, dd, *J* = 8.5, 9.9 Hz), 4.19 (1H, d, *J* = 13.5 Hz), 4.48 (1H, d, *J* = 13.5 Hz), 4.53 (1H, d, *J* = 8.5 Hz), 4.98 (1H, d, *J* = 3.2 Hz), 5.68 (1H, d, *J* = 4.8 Hz) ppm ; ESI-MS (positive): *m/z* = 456 ($[M+Na]^+$)

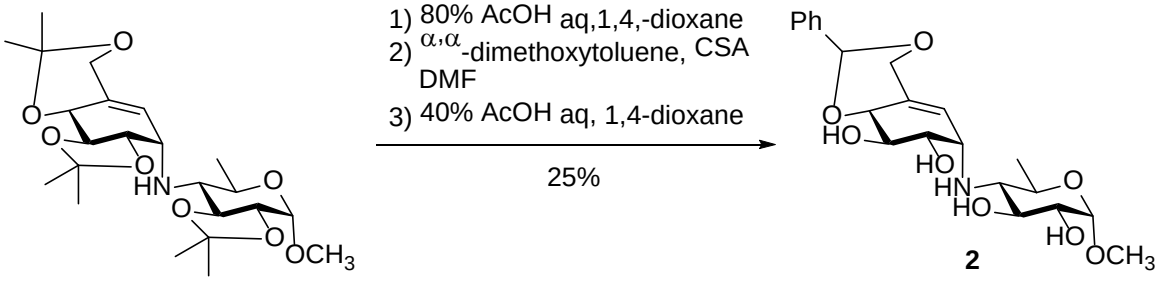
β-anomer: ^{1}H-NMR (270 MHz, $CDCl_3$, rt): δ 1.38 (1H, d, *J* = 6.3 Hz), 1.42 (6H, s),1.44 (3H, s), 1.47 (6H, s), 1.57 (3H, s), 2.82 (1H, t, *J* =9.0 Hz), 3.17-3.45 (3H, m), 3.55 (3H, s), 3.60 (1H, dd, *J* = 4.6, 9.8 Hz), 4.03 (1H, t, *J* = 4.6 Hz), 4.09 (1H, dd, *J* = 8.2, 9.8 Hz), 4.20 (1H, d, *J* = 13.8 Hz), 4.44-4.55 (3H, m), 5.66 (1H, d, *J* = 4.7 Hz) ppm ; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): δ 18.11, 20.03, 26.44, 26.68, 26.72, 27.06, 27.91, 50.93, 56.44, 60.07, 62.96, 71.70, 74.40, 75.20, 77.09, 77.63, 82.17, 99.03, 102.24, 111.05, 111.41, 121.73, 133.78 ppm; HR ESI MS (positive): $[M+H]^+$ found *m/z* 456.2592, $C_{23}H_{38}NO_8^+$ requires *m/z* 456.2597; IR (neat) ν: 755, 843, 1107, 1236, 1373, 2934, 2986 cm^{-1}; $[\alpha]_D^{21}$ +101.8° (*c* 1.00, $CHCl_3$)

Methyl α-acarviosin (**1**)[S3]

^{1}H-NMR (270 MHz, D_2O, rt): 1.31 (3H, d, *J* = 6.3 Hz), 2.43 (1H, t, *J* = 9.7 Hz), 3.36 (3H, s), 3.48-3.58 (3H, m), 3.59-3.76 (3H, m), 4.00 (1H, d, *J* = 6.6 Hz), 4.07 (1H, d, *J* = 13.8 Hz), 4.19 (1H, d, *J* = 13.8 Hz), 4.71 (1H, d, *J* = 3.0 Hz), 5.86 (1H, d, *J* = 5.0 Hz) ppm; ESI-MS (positive): *m/z* = 336 ($[M+H]^+$)

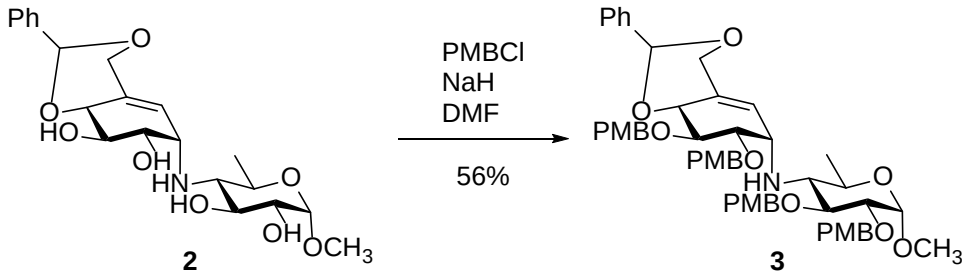
*Synthesis of selectively protected methyl α-acarviosin (**4**)*

Methyl 4,6-*O*-benzylidene α-acarviosin (**2**)



Isopropylidene protected methyl α-acarviosin (640 mg, 1.41 mmol) was dissolved in 1,4-dioxane (5.0 mL) and 80% aq. acetic acid (30.0 mL). After stirring for 6 hrs at 50°C, the reaction mixture was evaporated. The residue was dissolved in DMF (4.0 mL) and α,α-dimethoxytoluene (20 mL), CSA (32.8 mg, 0.14 mmol) was added. After stirring for 2 hrs at 80°C, the reaction mixture was cooled, triethylamine (TEA) was added and evaporated. The residue was dissolved in 1,4-dioxane (15.0 mL) and 40% aq. acetic acid (15.0 mL). After stirring for 14 hrs, the reaction mixture was evaporated and the residue was purified by silica-gel column chromatography (ethyl acetate/ methanol = 20/1 then ethyl acetate/methanol/water = 20/8/1) to obtain **2** (248 mg, 0.586 mmol, 42%) as a white solid. ^{1}H-NMR (270 MHz, CD_3OD, rt): 1.30 (3H, d, *J* = 6.3 Hz), 2.34 (1H, t, *J* =9.6 Hz), 3.35 (3H, s), 3.38-3.57 (5H, m), 3.88 (1H, dd, *J* = 7.5, 9.7 Hz), 4.26 (1H, d, *J* =7.5 Hz), 4.42 (1H, d, *J* = 12.9 Hz), 4.50 (1H, d, *J* = 12.9 Hz), 4.58 (1H, d, *J* = 3.6 Hz), 5.69 (1H, s), 5.76 (1H, brd, *J* = 3.7 Hz), 7.29-7.36 (3H, m), 7.44-7.51 (2H, m) ppm; ^{13}C-NMR (67.5 MHz, CD_3OD, rt): 18.68, 55.49, 58.61, 68.09, 69.86, 70.89, 72.13, 73.71, 74.77, 75.36, 81.18, 101.4, 102.31, 123.76, 127.60, 129.19, 129.98, 132.76, 139.83 ppm; HR FD MS (positive): $[M+H]^+$ found *m/z* 424.19809, $C_{21}H_{30}NO_8^+$ requires *m/z* 424.19714; IR (neat) υ: 700. 750, 1061, 1110, 1367, 1455, 2904, 3367 cm^{-1}; $[\alpha]_D^{23}$ +155.4° (*c* 1.00, CH_3OH)

Methyl 2,3,2',3'-tetra-*O*-*p*-methoxybenzyl-4,6-*O*-benzylidene α-acarviosin (**3**)

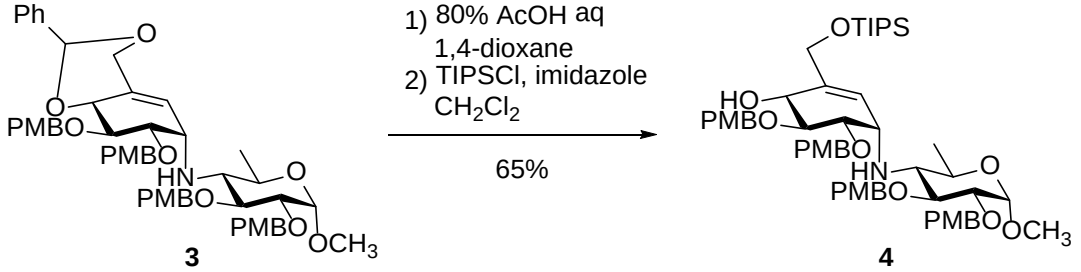


Compound **2** (248 mg, 0.586 mmol) was dissolved in anhydrous DMF (6.00 mL) and sodium hydride (144 mg, 6.00 mmol) was added at 0°C under argon atmosphere. After stirring for 30 min at 0°C, 4-methoxybenzyl chloride (0.80 0 mL, 0.587 mmol) was added and further stirred for 20 hrs at rt. The reaction mixture was further stirred at 70°C for 3 hrs and then cooled to rt. Water was added to quench the reaction and then the mixture was extracted by ethyl acetate. Organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column

chromatography (hexane/ethyl acetate = 4/1→2/1) to obtain **3** (295 mg, 0.327 mmol, 56%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.24 (3H, d, *J* =6.3 Hz), 2.44 (1H, t, *J* = 9.6 Hz), 3.35 (3H, s), 3.47-3.52 (3H, m), 3.65 (1H, t, *J* = 9.2 Hz), 3.74 (3H, s), 3.77 (3H, s), 3.78 (3H,s), 3.79 (3H, s), 3.98 (1H, t, *J* = 4.3 Hz), 4.30 (1H, dd, *J* =6.9, 10.0 Hz), 4.35-4.44 (2H, m), 4.50 (1H, d, *J* = 3.4 Hz), 4.54 (1H, d, *J* = 11.7 Hz), 4.56 (1H, d, *J* = 11.5 Hz), 4.58 (1H, d, *J* = 10.6 Hz), 4.65 (1H, d, *J* = 11.7 Hz), 4.69 (1H, d, *J* =11.5 Hz), 4.73 (1H, d, *J* = 10.9 Hz), 4.77 (1H, d, *J* = 10.9 Hz), 4.95 (1H, d, *J* = 10.6 Hz), 5.63 (1H, s), 5.67 (1H, d, *J* = 4.3 Hz), 6.74-6.87 (8H, m), 7.10-7.47 (13H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 18.82, 52.97, 54.96, 55.15, 55.20, 60.25, 68.46, 70.26, 72.55, 72.67, 74.51, 74.87, 78.22, 78.60, 80.90, 81.05, 83.43, 97.79, 100.79, 113.59, 113.68, 113.77, 122.97, 126.12, 126.65, 128.09, 128.68, 128.92, 129.16, 129.45, 129.50, 129.69, 130.26, 130.53, 131.12, 131.25, 132.15, 138.21, 158.92, 159.00, 159.06, 159.32 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 903.42043, $C_{53}H_{61}NO_{12}^+$ requires *m/z* 903.41937; IR (neat) υ: 821, 1075, 1250, 1514, 1613, 2835 cm^{-1}; $[\alpha]_D^{21}$ + 13.3° (*c* 1.00, $CHCl_3$)

Methyl 2,3,2',3'-tetra-*O*-*p*-methoxybenzyl-6-*O*-isopropylsilyl α-acarviosin (**4**)

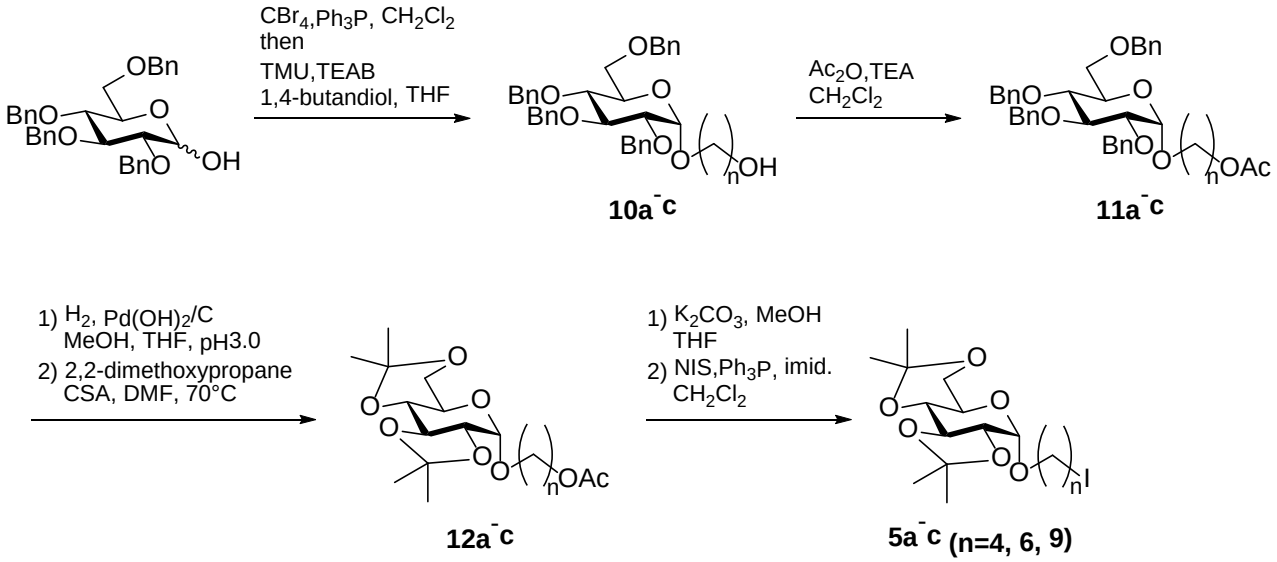


Compound **3** (262 mg, 0.290 mmol) was suspended in 80% aq. acetic acid (5.00 mL) and 1,4-dioxane was added until the compound dissolved. The reaction mixture was stirred for overnight and then further stirred for 24 hrs at 50°C. Sat. aq. sodium hydrogen carbonate was added to the reaction mixture and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. To the residue was dissolved in dichloromethane (3.00 mL) and triisopropylsilyl chloride (0.100 mL, 0.472 mmol), imidazole (38.4 mg, 0.564 mmol) was added at 0°C. The reaction mixture was stirred for overnight under argon atmosphere. Water was added to the reaction mixture and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→2/1) to obtain **4** (183 mg, 0.188 mmol, 65%) as a colorless oil.

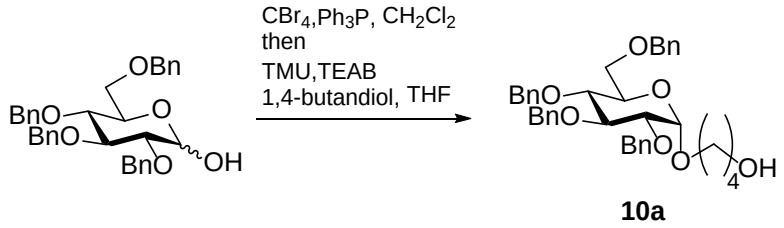
^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.03-1.15 (21H, m), 1.22 (3H, d, *J* =6.2 Hz), 2.44 (1H, t, *J* = 9.7 Hz), 3.36 (3H, s), 3.49 (1H, dd, *J* =3.5, 9.5 Hz), 3.52 (1H, dd, *J* = 6.3, 9.7 Hz), 3.62-3.68 (2H, m), 3.74 (3H, s), 3.76 (3H, s), 3.78 (3H,s), 3.79 (3H, s), 3.93 (1H, br t, *J* = 3.8 Hz), 4.00 (1H, dd, *J* =4.3, 6.9 Hz), 4.06 (1H, d, *J* = 4.3 Hz), 4.27 (1H, d, *J* = 13.9 Hz), 4.31 (1H, d, *J* = 13.9 Hz), 4.47-4.62 (7H, m), 4.65 (1H, d, *J* = 11.7 Hz), 4.91 (1H, d, *J* = 10.6 Hz), 5.81 (1H, d, *J* = 3.8 Hz), 6.73-6.89 (8H, m), 7.12-7.26 (8H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 11.89, 17.99, 18.91, 52.79, 54.98, 55.13, 55.15, 55.17, 61.30, 64.58, 68.04, 69.82, 72.38, 72.57, 72.63, 74.79, 78.46, 78.61, 80.72, 82.75, 97.92, 113.60, 113.72, 123.25, 128.94, 129.21, 129.32, 129.65, 130.09, 130.29, 130.78, 131.09,

138.99, 158.84, 159.08, 159.17, 159.28 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 971.52132, $C_{55}H_{77}NO_{12}Si^+$ requires *m/z* 971.52150; IR (neat) υ: 821, 1173, 1302, 1464, 1613, 2865, 2865, 2939, 3514 cm^{-1}; $[\alpha]_D^{21}$ +26.3° (*c* 1.00, $CHCl_3$)

*Synthesis of iodoalkyl glucose (**5a-c**)*



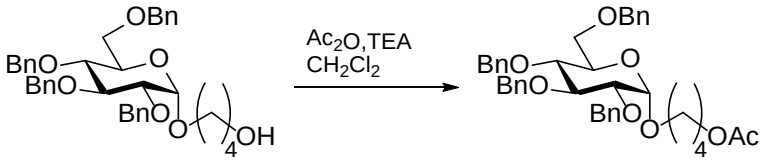
2,3,4,6-tetra-*O*-benzyl-1-*O*-(4-hydroxybutyl)-α-D-glucopyranose (**10a**)



2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1.23 g, 2.28 mmol) was dissolved in dichloromethane (20.0 mL) and triphenylphosphine (2.09 g, 7.97 mmol), carbon tetrabromide (2.35 g, 7.08 mmol) was added and stirred for 14 hrs at rt. To this reaction mixture, 1,4-butandiol (448 mg, 4.98 mmol), 1,1,3,3-tetramethylurea (TMU, 1.64 mL, 13.7 mmol), tetraethylammonium bromide (TEAB, 575 mg, 2.74 mmol) dissolved in THF (20.0 mL) was added dropwise and stirred for 2 days at rt. The reaction mixture was diluted by 1 M hydrogen chloride and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→3/1→1/1) to obtain **10a** (773 mg, 1.26 mmol, 55%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$, rt): 1.55-1.78 (4H, m), 3.38-3.49 (1H, m), 3.55 (1H, dd, *J* = 3.5, 9.6 Hz), 3.59-3.80 (7H, m), 3.97 (1H, t, *J* = 9.3 Hz), 4.47 (2H, d, *J* = 11.9 Hz), 4.59 (1H, d, *J* =12.2 Hz), 4.64 (1H, d, *J* =12.9 Hz), 4.74 (1H, d, *J* = 3.6 Hz), 4.76-4.86 (3H, m), 4.98 (1H, d, *J* =10.9 Hz), 7.11-7.17 (2H, m), 7.24-7.37 (18H, m) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 25.94, 29.84, 62.35, 67.96, 68.50, 70.21, 73.17, 73.41, 75.02, 75.60, 76.53, 77.00, 77.48, 77.68, 79.89, 82.03, 97.02, 127.58, 127.73, 127.91, 127.96, 128.11, 128.39, 128.47, 137.97, 138.27, 138.89 ppm; HR FD MS (positive): $[M+Na]^+$ found *m/z* 635.2995, $C_{38}H_{44}O_7Na^+$ requires *m/z* 635.2985; IR (neat) υ: 680, 737, 1071, 1361, 1454, 2868, 2919, 3482 cm^{-1}; $[\alpha]_D^{25}$ +26.7° (*c* 1.00, $CHCl_3$)

2,3,4,6-tetra-*O*-benzyl-1-*O*-(4-(acetyloxy)butyl)-α-D-glucopyranose (**11a**)

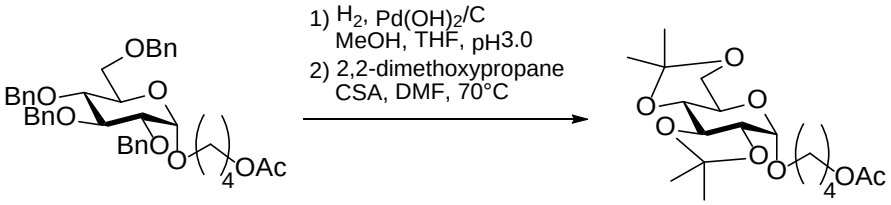


10a **11a**

Compound **10a** (773 mg, 1.26 mmol) was dissolved in anhydrous dichloromethane (12.0 mL) and TEA (0.260 mL, 1.87 mmol), acetic anhydride (0.140 mL, 1.48 mmol) was added. After stirring for overnight, TEA (0.260 mL, 1.87 mmol), acetic anhydride (0.140 mL, 1.48 mmol), and catalytic amount of 4-dimethylaminopyridine (DMAP) was added. The reaction mixture was stirred for an hour and then diluted by chloroform. The solution was washed by sat. aq. sodium hydrogen carbonate and then by brine. The organic layer was dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1→5/1) to obtain **11a** (717 mg, 1.10 mmol, 87%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.65-1.74 (4H, m), 2.03 (3H, s), 3.39-3.46 (1H, m), 3.56 (1H, dd, *J* = 3.7, 9.7 Hz), 3.61-3.96 (3H,m), 3.72 (1H, dd, *J* = 3.7, 10.4 Hz), 3.74-3.78 (1H, m), 4.00 (1H, t, *J* = 9.7 Hz), 4.07 (2H, t, *J* = 6.3 Hz), 4.47 (2H, d, *J* = 12.0 Hz), 4.60 (1H, d, *J* = 12.3 Hz), 4.64 (1H, d, *J* = 12.0 Hz), 4.74 (1H, d, *J* = 3.5 Hz), 4.78 (1H, d, *J* = 12.0 Hz), 4.82 (1H, d, *J* = 10.7 Hz), 4.83 (1H, d, *J* = 10.7 Hz), 4.99 (1H, d, *J* = 11.0 Hz), 7.12-7.16 (2H, m), 7.24-7.37 (18H, m) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 20.83, 25.37, 25.86, 64.13, 67.54, 68.47, 70.19, 73.17, 73.44, 75.08, 75.62, 77.72, 80.11, 82.04, 97.04, 127.60, 127.74, 127.77, 127.91, 127.96, 128.02, 128.07, 128.44, 128.49, 138.02, 138.31, 138.41, 138.98, 171.27 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 654.31932, $C_{40}H_{46}O_8^+$ requires *m/z* 654.31927; IR (neat) υ: 698, 738, 1071, 1244, 1363, 1455, 1736, 2869, 2918 cm^{-1}; $[\alpha]_D^{25}$ +28.7° (*c* 1.00, $CHCl_3$)

2,3;4,6-di-*O*-isopropylidene-1-*O*-(4-(acetyloxy)butyl)-α-D-glucopyranose (**12a**)

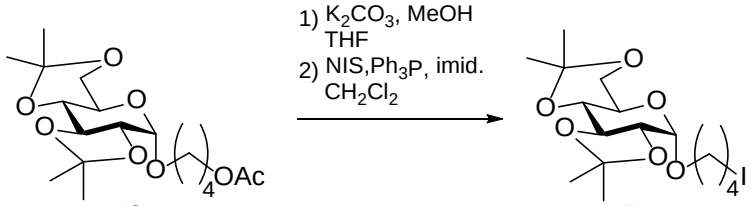


11a **12a**

Compound **11a** (717 mg, 1.10 mmol) was dissolved in methanol (8.00 mL) and THF (2.00 mL). The solution was adjusted to pH3 by addition of 1 M aq. hydrogen chloride. Palladium hydroxide on carbon (53.6 mg) was added to the solution and stirred for 90 min. under hydrogen atmosphere. The reaction mixture was passed through Celite® pad and evaporated. The residue was dissolved in 2,2-dimethoxypropane (10.0 mL) and DMF (1.00 mL), CSA (14.1 mg, 0.0607 mmol) was added and stirred for overnight at 70ºC. TEA was added to the reaction mixture and the evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 8/1→2/1) to obtain **12a** (287 mg, 0.767 mmol, 70%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$, rt): 1.43-1.48 (9H, m), 1.55 (3H, s), 1.69-1.77 (4H, m), 2.06 (3H, s), 3.49-3.60 (3H, m), 3.72-3.81 (1H, m), 3.83-3.94 (3H, m), 4.04 (1H, t, *J* = 9.3 Hz), 4.11 (2H, t, *J* = 6.3 Hz), 5.13 (1H, d, *J* = 3.1 Hz) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 18.99, 20.78, 25.31, 25.91, 26.16, 26.67, 28.88, 62.29, 64.03, 65.06, 68.04, 73.71, 73.93, 76.82, 97.87, 99.65, 111.39, 171.18 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 374.19538, $C_{18}H_{30}O_8^+$ requires *m/z* 374.19407; IR (neat) υ: 854, 966, 1092, 1239, 1372, 1740, 2938, 2989 cm^{-1}; $[\alpha]_D^{23}$ + 69.6° (*c* 1.00, $CHCl_3$)

2,3;4,6-di-*O*-isopropylidene-1-*O*-(4-iodobutyl)-α-D-glucopyranose (**5a**)

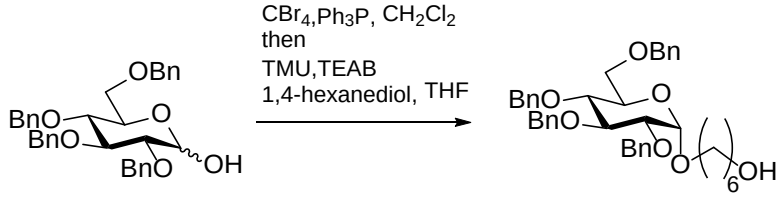


12a **5a**

Compound **12a** (287 mg, 0.767 mmol) was dissolved in methanol (4.00 mL) and THF (1.00 mL). Potassium carbonate (89.7 mg, 0.650 mmol) was added to the solution and stirred for 6.5 hrs at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was dissolved in dichloromethane (8.00 mL) and triphenylphosphine (239 mg, 0.911 mmol), imidazole (79.6 mg, 1.17 mmol), *N*-iodosuccinimide (NIS, 215 mg, 0.956 mmol) was added. After stirring for overnight, the reaction mixture was diluted with chloroform, washed with sat. aq. sodium hydrogen carbonate and brine. The organic layer was dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 8/1→4/1) to obtain **5a** (293 mg, 0.663 mmol, 86%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$, rt): 1.45 (6H, s), 1.47 (3H, s), 1.55 (3H, s), 1.68-1.83 (2H, m), 1.88-2.01 (2H, m), 3.25 (2H, t, *J* = 6.8 Hz), 3.48-3.59 (3H, m), 3.73-3.94 (4H, m), 4.03 (1H, t, *J* = 9.4 Hz), 5.12 (1H, d, *J* = 3.1 Hz) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 6.41, 18.99, 26.22, 26.68, 28.88, 30.10, 30.18, 62.28, 65.09, 67.54, 73.70, 73.88, 76.76, 97.90, 99.66, 111.43 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 442.08667, $C_{16}H_{27}IO_6^+$ requires *m/z* 442.08523; IR (neat) υ: 839, 956, 1092, 1203, 1373, 1456, 2933, 2988 cm^{-1}; $[\alpha]_D^{23}$ +60.3° (*c* 1.00, $CHCl_3$)

2,3,4,6-tetra-*O*-benzyl-1-*O*-(6-hydroxyhexyl)-α-D-glucopyranose (**10b**)



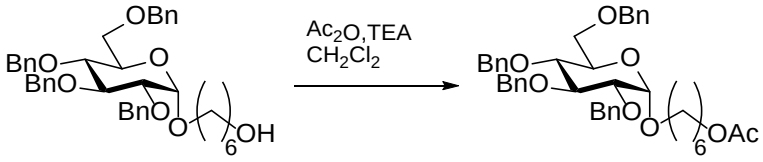
10b

2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (912.3 mg, 1.69 mmol) was dissolved in dichloromethane (15.0 mL) and triphenylphosphine (1.43 g, 5.45 mmol), carbon tetrabromide (1.63 g, 4.91 mmol) was

added and stirred for 3 hrs at rt. To this reaction mixture, 1,4-hexanediol (438 mg, 3.72 mmol), TMU (1.20 mL, 10.0 mmol), TEAB (437 mg, 2.08 mmol) dissolved in THF (15.0 mL) was added dropwise and stirred over night at rt. The reaction mixture was diluted by 1 M hydrogen chloride and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 5/1→2/1) to obtain **10b** (507 mg, 0.792 mmol, 47%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.34-1.44 (4H, m), 1.51-1.58 (2H, m), 1.60-1.67 (2H, m), 3.38-3.46 (1H, m), 3.55 (1H, dd, *J* = 3.4, 9.3 Hz), 3.57-3.67 (5H, m), 3.71 (1H, dd, *J* = 3.7 10.5 Hz), 3.75-3.80 (1H, m), 3.98 (1H, t, *J* = 9.3 Hz), 4.47 (2H, d, *J* = 11.7 Hz), 4.60 (1H, d, *J* = 12.1 Hz), 4.64 (1H, d, *J* =12.2 Hz), 4.75 (1H, d, *J* = 3.7 Hz), 4.77 (1H, d, *J* = 12.1 Hz), 4.81 (1H, d, *J* = 10.9 Hz), 4.83 (1H, d, 10.7 Hz), 4.99 (1H, d, *J* = 10.9 Hz), 7.12-7.15 (2H, m), 7.25-7.38 (18H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 25.46, 25.97, 29.30, 32.61, 62.78, 68.07, 68.67, 70.17, 73.07, 73.45, 75.03, 75.59, 77.86, 80.18, 82.09, 96.91, 127.47, 127.60, 127.63, 127.76, 127.83, 127.87, 127.90, 127.94, 128.31, 128.36, 138.01, 138.29, 138.37, 138.94 ppm; HR ESI MS (positive): $[M+Na]^+$ found *m/z* 663.3286, $C_{40}H_{48}O_7Na^+$ requires *m/z* 663.3298; IR (neat) υ: 687, 736, 1069, 2862, 2930, 3446 cm^{-1}; $[\alpha]_D^{24}$ + 22.6° (*c* 1.00, $CHCl_3$)

2,3,4,6-tetra-*O*-benzyl-1-*O*-(6-(acetyloxy)hexyl)-α-D-glucopyranose (**11b**)

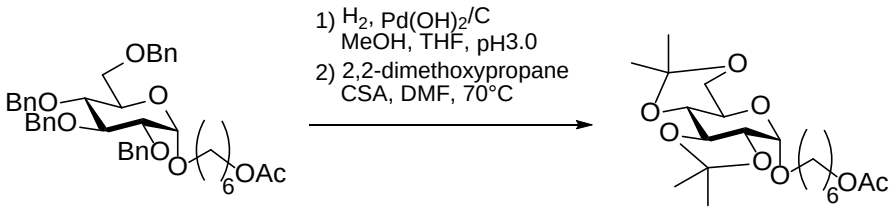


10b **11b**

Compound **10b** (267mg, 0.392 mmol) was dissolved in anhydrous dichloromethane (4.0 mL) and TEA (0.10 mL, 0.719 mmol), acetic anhydride (0.050 mL, 0.529 mmol) was added. After stirring for overnight, the reaction mixture was diluted by chloroform, washed by sat. aq. sodium hydrogen carbonate and then by brine. The organic layer was dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1→5/1) to obtain **11b** (202 mg, 0.296 mmol, 76%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.33-1.43 (4H, m), 1.57-1.67 (4H, m), 2.03 (3H, s), 3.38-3.45 (1H, m), 3.55 (1H, dd, J = 3.7, 9.7 Hz), 3.59-3.67 (3H, m), 3.72 (1H, dd, J = 3.7,10.5 Hz), 3.75-3.79 (1H, m), 3.98 (1H, t, J = 9.3 Hz), 4.04 (2H, t, J = 6.7 Hz), 4.47 (2H, d, J = 12.0 Hz), 4.60 (1H, d, J = 12.1 Hz), 4.64 (1H, d, J = 12.0 Hz), 4.75 (1H, d, J = 3.7 Hz), 4.78 (1H, d, J = 12.0 Hz), 4.82 (1H, d, J =11.0 Hz), 4.83 (1H, d, J = 10.7 Hz), 4.99 (1H, d, J =10.7 Hz), 7.12-7.15 (2H, m), 7.25-7.38 (18H, m) ppm**;** ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 20.95, 25.72, 25.81, 28.47, 29.25, 64.44, 67.99, 68.50, 70.09, 73.08, 73.41, 75.04, 75.60, 77.72, 80.06, 82.06, 96.89, 127.48, 127.61, 127.63, 127.76, 127.83, 127.84, 127.89, 127.94, 128.29, 128.31, 128.34, 137.90, 138.18, 138.29, 138.86, 171.11 ppm; HR ESI MS (positive): $[M+Na]^+$ found *m/z* 705.3412, $C_{42}H_{50}O_8Na^+$ requires *m/z* 705.3403; IR (neat) υ: 698, 738, 1071, 1239, 1363, 1455, 1736, 2863, 2931 cm^{-1}; $[\alpha]_D^{25}$ +33.3° (*c* 1.00, $CHCl_3$)

5-3-22. 2,3;4,6-di-*O*-isopropylidene-1-*O*-(6-(acetyloxy)hexyl)-α-D-glucopyranose (**12b**) の合成

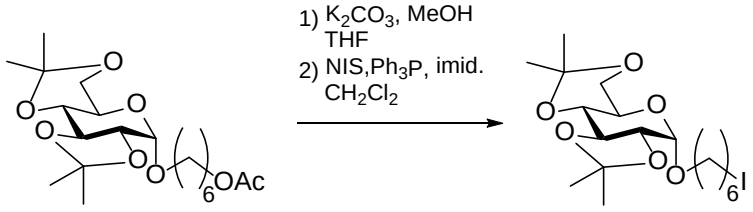


11b **12b**

Compound **11b** (186 mg, 0.253 mmol) was dissolved in methanol (4.00 mL) and THF (1.00 mL). The solution was adjusted to pH3 by addition of 1 M aq. hydrogen chloride. Palladium hydroxide on carbon (53.6 mg) was added to the solution and stirred for 90 min under hydrogen atmosphere. The reaction mixture was passed through Celite® pad and evaporated. The residue was dissolved in 2,2-dimethoxypropane (4.0 mL), DMF (1.00 mL), and CSA (6.0 mg, 0.026 mmol) was added and stirred for overnight at 60ºC. After cooling to rt, sat. aq. sodium hydrogen carbonate was added and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 6/1→4/1) to obtain **12b** (61.5 mg, 0.174 mmol, 69%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$, rt): 1.34-1.48 (13H, m), 1.55 (3H, s), 1.58-1.70 (4H, m), 2.05 (3H, s), 3.46-3.60 (3H, m), 3.66-3.77 (1H, m), 3.82-3.93 (3H, m), 4.00-4.08 (1H, m), 4.06 (2H, t, J = 6.6 Hz), 5.12 (1H, d, J = 3.1 Hz) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 19.04, 20.86, 25.61, 25.65, 26.22, 26.72, 28.43, 28.93, 29.22, 62.38, 64.42, 65.01, 68.51, 73.79, 74.01, 76.92, 97.90, 99.70, 111.41, 171.34 ppm; HR ESI MS (positive): $[M+Na]^+$ found *m/z* 425.2140, $C_{20}H_{34}O_8Na^+$ requires *m/z* 425.2151; IR (neat) υ: 840, 1091, 1235, 1372, 1739, 2937 cm^{-1}; $[\alpha]_D^{23}$ + 95.9° (*c* 0.720, $CHCl_3$)

2,3;4,6-di-*O*-isopropylidene-1-*O*-(6-iodohexyl)-α-D-glucopyranose (**5b**) の合成

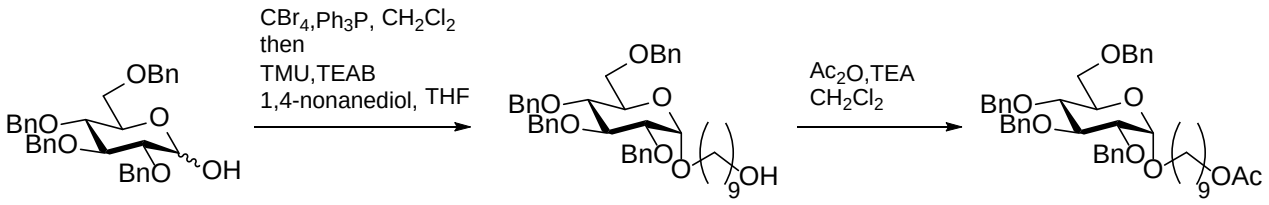


12b **5b**

Compound **12b** (61.5 mg, 0.174 mmol) was dissolved in methanol (2.00 mL) and THF (1.00 mL). Potassium carbonate (20.5 mg, 0.149 mmol) was added to the solution and stirred for overnight at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was dissolved in dichloromethane (2.00 mL) and triphenylphosphine (54.7 mg, 0.209 mmol), imidazole (18.7 mg, 0.275 mmol), NIS (63.2 mg, 0.281 mmol) was added. After stirring for overnight, the reaction mixture was diluted with chloroform, washed with sat. aq. sodium hydrogen carbonate and brine. The organic layer was dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1→5/1) to obtain **5b** (56.3 mg, 0.119

mmol, 69%) as a colorless oil.
^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.37-1.49 (13H, m), 1.55 (3H, s), 1.61-1.69 (2H, m), 1.81-1.88 (2H, m), 3.20 (2H, t, *J* = 6.9 Hz), 3.49-3.59 (3H, m), 3.70-3.76 (1H, m), 3.83 (1H, t, *J* = 10.6 Hz), 3.89-3.91 (2H, m), 4.03 (1H, t, *J* = 9.3 Hz), 5.12 (1H, d, *J* =3.1 Hz) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 6.87, 19.14, 24.99, 26.35, 26.80, 29.03, 29.19, 30.16, 33.31, 62.39, 65.00, 68.42, 73.76, 73.97, 76.87, 97.82, 99.64, 111.33 ppm; HR ESI MS (positive): $[M+Na]^+$ found *m/z* 493.1057, $C_{18}H_{31}O_6INa^+$ requires *m/z* 493.1063; IR (neat) υ: 852, 1092, 1204, 1372, 2873, 2933, 2988 cm^{-1}; $[\alpha]_D^{23}$ +56.3° (*c* 1.00, $CHCl_3$)

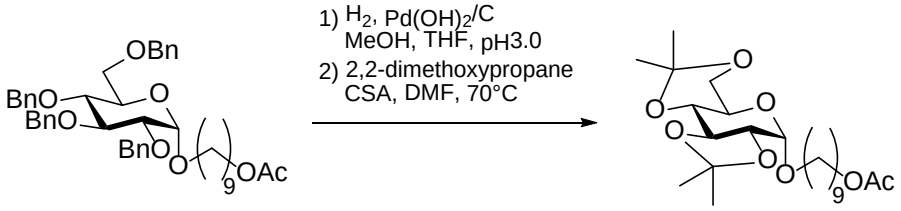
2,3,4,6-tetra-*O*-benzyl-1-*O*-(9-(acetyloxy)nonyl)-α-D-glucopyranose (**11c**)



10c **11c**

2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1.98 g, 3.67 mmol) was dissolved in dichloromethane (30.0 mL) and triphenylphosphine (3.34 g, 12.7 mmol), carbon tetrabromide (3.58 g, 10.8 mmol) was added and stirred for 3 hrs at rt. To this reaction mixture, 1,4-nonanediol (1.42 g, 8.86 mmol), TMU (2.90 mL, 24.2 mmol), TEAB (1.04 g, 4.95 mmol) dissolved in THF (30.0 mL) was added dropwise and stirred for 24 hrs at rt. The reaction mixture was diluted by 1 M aq. hydrogen chloride and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was partly purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→2/1) to obtain crude **10c**. The crude **10c** was dissolved in anhydrous dichloromethane (15.0 mL) and TEA (2.20 mL, 15.8 mmol), acetic anhydride (1.20 mL, 12.7 mmol), catalytic amount of DMAP was added. After stirring for 4.5 hrs, the reaction mixture was diluted by chloroform, washed by sat. aq. sodium hydrogen carbonate and then by brine. The organic layer was dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1→5/1) to obtain **11c** (573 mg, 0.791 mmol, 22%) as a colorless oil.
^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.27-1.37 (10H, m), 1.57-1.65 (4H, m), 2.03 (3H, s), 3.38-3.45 (1H, m), 3.56 (1H, dd, *J* = 3.6, 9.6 Hz), 3.59-3.66 (3H,m), 3.73 (1H, dd, *J* = 3.7, 10.6 Hz), 3.76-3.80 (1H, m), 3.99 (1H, t, *J* = 9.6 Hz), 4.04 (2H, t, *J* = 6.8 Hz), 4.46 (2H, d, *J* = 11.4 Hz), 4.61 (1H, d, *J* = 12.0 Hz), 4.65 (1H, d, *J* = 12.3 Hz), 4.76 (1H, d, *J* = 3.8 Hz), 4.77 (1H, d, *J* = 12.6 Hz), 4.82 (1H, d, *J* = 11.0 Hz), 4.83 (1H, d, *J* = 10.7 Hz), 4.99 (1H, d, *J* = 10.8 Hz), 7.12-7.15 (2H, m), 7.25-7.38 (18H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 20.93, 20.95, 25.82, 26.05, 28.50, 29.13, 29.26, 29.30, 29.33, 64.52, 68.10, 68.44, 70.00, 73.02, 73.37, 75.01, 75.59, 77.69, 80.02, 82.04, 96.80, 127.45, 127.57, 127.60, 127.71, 127.80, 127.83, 127.86, 127.92, 128.25, 128.28, 128.30, 137.88, 138.17, 138.28, 138.84, 171.11 ppm; HR ESI MS (positive): $[M+Na]^+$ found *m/z* 747.3845, $C_{45}H_{56}O_8Na^+$ requires *m/z* 747.3873; IR (neat) υ: 698, 737, 1072, 1242, 1363, 1455, 1737, 2856, 2927 cm^{-1}; $[\alpha]_D^{25}$ +29.2° (*c* 1.00, $CHCl_3$)

2,3;4,6-di-*O*-isopropylidene-1-*O*-(9-(acetyloxy)nonyl)-α-D-glucopyranose (**12c**)

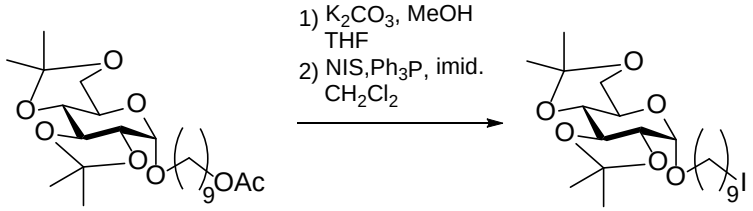


11c **12c**

Compound **11c** (573 mg, 0.791 mmol) was dissolved in methanol (10.0 mL) and THF (2.00 mL). The solution was adjusted to pH3 by addition of 1 M aq. hydrogen chloride. Palladium hydroxide on carbon (85.0 mg) was added to the solution and stirred for an hour under hydrogen atmosphere. The reaction mixture was passed through Celite® pad and evaporated. The residue was dissolved in 2,2-dimethoxypropane (10.0 mL), DMF (2.00 mL), and CSA (14.5 mg, 0.0625 mmol) was added and stirred for overnight at 70ºC. After cooling to rt, TEA was added to the mixture and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 8/1→5/1) to obtain **12c** (222 mg, 0.500 mmol, 63%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$, rt): 1.28-1.41 (10H, m), 1.45 (6H, s), 1.47 (3H, s), 1.55 (3H, s), 1.57-1.71 (4H, m), 2.04 (3H, s), 3.46-3.61 (3H, m), 3.66-3.77 (1H, m), 3.82-3.93 (3H, m), 4.05 (1H, t, *J* = 9.4 Hz), 4.05 (2H, t, *J* = 6.8 Hz), 5.12 (1H, d, *J* = 3.1 Hz) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 19.02, 20.84, 25.75, 25.86, 26.21, 26.70, 28.46, 28.93, 29.03, 29.12, 29.26, 29.30, 62.37, 64.54, 64.94, 68.64, 73.77, 74.00, 76.92, 97.86, 99.65, 111.35, 171.32 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 444.27274, $C_{23}H_{40}O_8^+$ requires *m/z* 444.27232; IR (neat) υ: 840, 965, 1048, 1233, 1372, 1740, 2857, 2931, 2988 cm^{-1}; $[\alpha]_D^{23}$ + 55.7° (*c* 1.00, $CHCl_3$)

2,3;4,6-di-*O*-isopropylidene-1-*O*-(9-iodononyl)-α-D-glucopyranose (**5c**)



12c **5c**

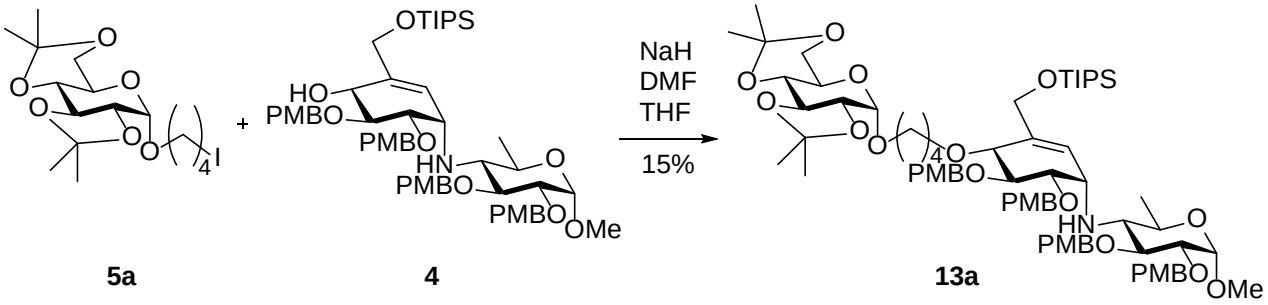
Compound **12c** (131 mg, 0.295 mmol) was dissolved in methanol (2.00 mL) and THF (1.00 mL). Potassium carbonate (25.4 mg, 0.184 mmol) was added to the solution and stirred for 2.5 hrs at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was dissolved in dichloromethane (3.0 mL) and triphenylphosphine (93.5 mg, 0.356 mmol), imidazole (32.4 mg, 0.476 mmol), NIS (99.0 mg, 0.440 mmol) was added. After stirring for overnight, the reaction mixture was diluted with chloroform, washed with sat. aq. sodium hydrogen carbonate and brine. The organic layer was dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 8/1→4/1) to obtain **5c** (95.4 mg, 0.186 mmol, 63%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$, rt): 1.26-1.41 (10H, m), 1.45 (6H, s), 1.46 (3H, s), 1.55 (3H,s), 1.57-1.71 (2H, m), 1.76-1.88 (2H, m), 3.19 (2H, t, *J* = 6.9 Hz), 3.47-3.62 (3H, m), 3.63-3.95 (4H, m), 4.04 (1H, t, *J* = 9.6 Hz), 5.12 (1H, d, *J* = 3.1 Hz) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 7.00, 19.00, 25.81, 26.20, 26.68, 28.28, 28.92, 29.07, 29.13, 29.26, 30.31, 33.38, 62.33, 64.90, 68.59, 73.73, 73.96, 76.88, 97.81, 99.61, 111.32 ppm; HR FD MS (positive): $[M+H]^+$ found *m/z* 513.17235, $C_{21}H_{38}IO_6^+$ requires *m/z* 513.17131; IR (neat) υ: 840, 1049, 1076, 1116, 1203, 1372, 2855, 2929, 2988 cm^{-1}; $[\alpha]_D^{21}$ +49.1° (*c* 1.00, $CHCl_3$)

*Coupling of **4** and **5***

Methyl

4-[4-(2,3;4,6-di-*O*-isopropylidene-α-D-glucopyranosyloxy)butyloxy]-2,3,2',3'-tetra-*O*-(*p*-methoxybenzyl)-6-*O*-isopropylsilyl-α-acarviosin (**13a**)

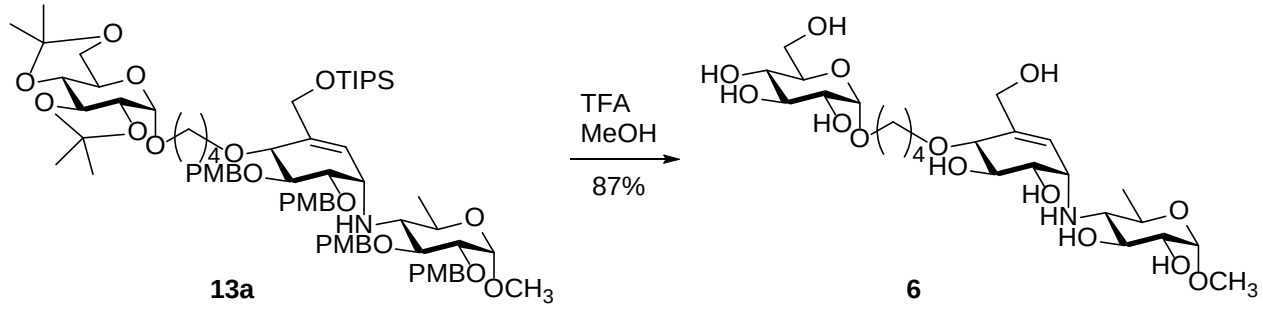


5a **4** **13a**

Compound **5a** (92.6 mg, 0.218 mmol) and **4** (62.6 mg, 0.0645 mmol) was dissolved in THF (0.50 mL), DMF (0.50 mL). The solution was cooled to 0°C, sodium hydride (30.5 mg, 1.27 mmol) was added and stirred for overnight under argon atmosphere at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→2/1) to obtain **13a** (12.2 mg, 0.00948 mmol, 15%).

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.01-1.13 (21H, m), 1.18 (3H, d, J = 6.0 Hz), 1.42-1.48 (9H, m), 1.54 (3H, s), 1.57-1.70 (4H, m), 2.41 (1H, t, J = 9.8 Hz), 3.35 (3H, s), 3.44-3.57 (7H, m), 3.60-3.66 (2H, m), 3.67-3.73 (1H, m), 3.75 (3H, s), 3.77 (3H, s), 3.789 (3H, s), 3.793 (3H, s), 3.81-3.90 (3H, m), 3.94 (1H, d, J = 6.5 Hz), 3.99 (1H, t, J = 4.5 Hz), 4.03 (1H, t, J =9.4 Hz), 4.17 (1H, dd, J = 6.5, 9.5 Hz), 4.19 (1H, d, J = 13.8 Hz), 4.25 (1H, d, J =13.8 Hz), 4.49 (1H, d, J = 3.6 Hz), 4.51 (1H, d, J = 11.7 Hz), 4.52 (1H, d, J = 11.7 Hz), 4.58 (1H, d, J = 10.9 Hz), 4.59-4.66 (3H, m), 4.79 (1H, d, J = 10.9 Hz), 4.93 (1H, d, J =10.6 Hz), 5.10 (1H, d, J = 3.0 Hz), 5.92 (1H, d, J =4.5 Hz), 6.76-6.86 (8H, m), 7.13-7.17 (4H, m), 7.21-7.23 (4H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 11.86, 17.97, 18.78, 19.05, 26.24, 26.40, 26.73, 26.96, 28.94, 52.30, 54.93, 55.17, 55.17, 55.17, 55.17, 60.32, 62.36, 63.47, 64.99, 68.44, 68.52, 70.17, 72.26, 72.61, 73.77, 74.02, 74.02, 74.73, 76.92, 78.82, 79.97, 80.24, 81.05, 83.80, 97.87, 97.92, 99.67, 111.38, 113.70, 113.78, 113.79, 113.85, 123.11, 128.81, 129.24, 129.60, 129.80, 130.46, 130.81, 131.34, 131.40, 140.37, 159.00, 159.23, 159.23, 159.49 ppm; HR FD MS (positive): $[M+H]^+$ found *m/z* 1286.70214, $C_{71}H_{104}NO_{18}Si^+$ requires *m/z* 1286.70226; IR (neat) ν: 821, 1070, 1247, 1514, 2886, 2935 cm^{-1}; $[\alpha]_D^{21}$ +30.8° (*c* 0.813, $CHCl_3$)

Methyl 4-[4-(α-D-glucopyranosyloxy)butyloxy]-α-acarviosin (**6**)

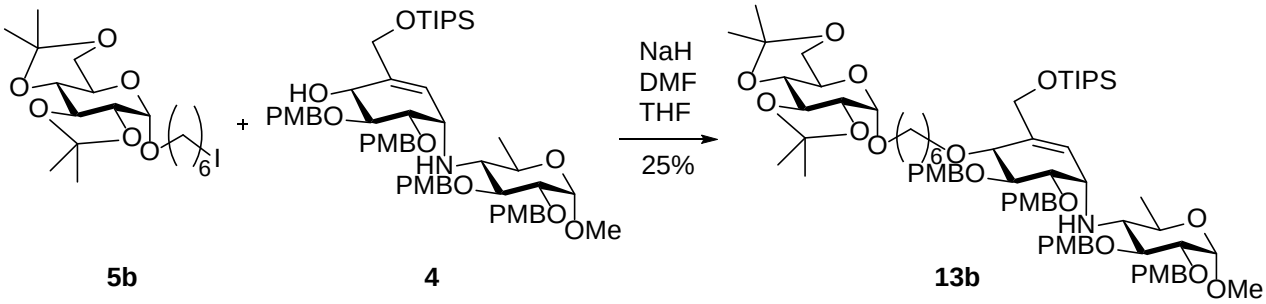


13a **6**

Compound **13a** (12.2 mg, 9.48 μmol) was dissolved in methanol (0.200 mL). The solution was cooled to 0°C and trifluoroacetic acid (TFA, 0.50 mL) was added. The reaction mixture was stirred for 9 hrs at rt. After concentration of the mixture, the solution was charged on BondElut C18 column (Varian, Inc.) and eluted by 30% aq. methanol to obtain **6** (4.70 mg, 8.26 μmol, 87%) as a colorless oil.

^{1}H-NMR (500 MHz, CD_3OD, rt): 1.42 (3H, d, *J* = 6.2 Hz)**,** 1.69-1.79 (4H, m), 3.05 (1H, t, *J* = 10.2 Hz), 3.27-3.32 (1H, m), 3.42 (1H, dd, *J* = 3.8, 9.6 Hz), 3.44 (3H, s), 3.47-3.50 (1H, m), 3.52 (1H, dd, *J* = 3.6, 9.1 Hz), 3.57-3.72 (4H, m), 3.77-3.85 (3H, m), 3.91-4.11 (5H, m), 4.17 (1H, br s), 4.21 (1H, d, *J* = 15.0 Hz), 4.26 (1H, d, *J* =15.0 Hz), 4.70 (1H, d, *J* = 3.6 Hz), 4.80 (1H, d, *J* = 3.8 Hz), 5.90 (1H, d, *J* = 2.7 Hz) ppm; ^{13}C-NMR (67.5 MHz, CD_3OD, rt): 18.60, 27.23, 28.00, 56.03, 57.26, 62.88, 63.00, 64.37, 64.99, 68.36, 68.91, 69.69, 71.30, 72.01, 73.19, 73.61, 73.79, 74.11, 75.16, 79.43, 100.22, 101.22, 116.21, 147.49 ppm**;** HR ESI MS (positive): $[M+H]^+$ found *m/z* 570.2787, $C_{24}H_{44}NO_{14}^+$ requires *m/z* 570.2762; IR (neat) υ: 1049, 1138, 1202, 1672, 2937, 3359 cm^{-1}; $[\alpha]_D^{21}$ +79.7° (*c* 0.310, CH_3OH)

Methyl 4-[4-(2,3;4,6-di-*O*-isopropylidene-α-D-glucopyranosyloxy)hexyloxy]-2,3,2’,3’-tetra-*O*-(*p*-methoxybenzyl)-6-*O*-isopropylsilyl-α-acarviosin (**13b**)



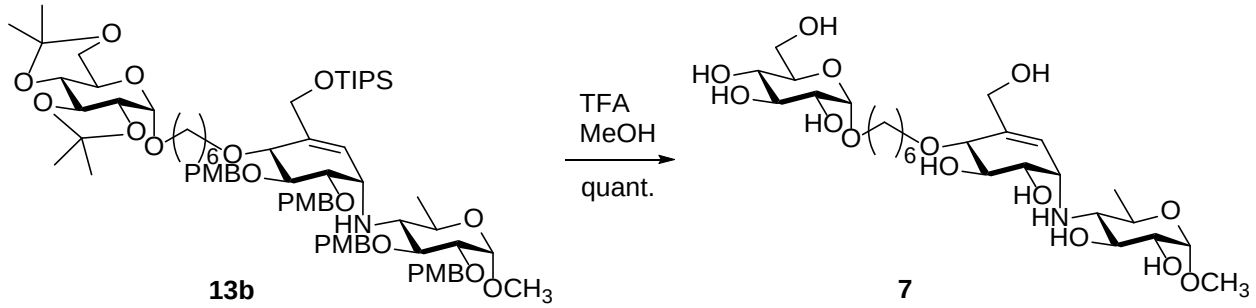
5b **4** **13b**

Compound **5b** (134 mg, 0.284 mmol) and **4** (71.5 mg, 0.0736 mmol) was dissolved in THF (0.50 mL), DMF (0.50 mL). The solution was cooled to 0°C, sodium hydride (34.7 mg, 1.45 mmol) was added and stirred for overnight under argon atmosphere at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→2/1) to obtain **13b** (23.8 mg, 0.0181mmol, 25%).

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.02-1.13 (21H, m), 1.19 (3H, d, *J* = 5.9 Hz), 1.28-1.39

(4H, m), 1.42-1.49 (12H, m), 1.55 (3H, s), 1.57-1.67 (4H, m), 2.42 (1H, t, *J* = 9.5 Hz), 3.35 (3H, s), 3.40-3.72 (10H, m), 3.75 (3H, s), 3.76 (3H, s), 3.78 (3H, s), 3.79 (3H, s), 3.81-3.91 (3H, m), 3.94 (1H, d, *J* = 6.3 Hz), 3.99 (1H, brs), 4.04 (1H, t, *J* =9.3 Hz), 4.15-4.20 (1H, m), 4.21 (1H, d, *J* = 14.5 Hz), 4.25 (1H, d, *J* =14.5 Hz), 4.48-4.65 (7H, m), 4.78 (1H, d, *J* = 10.8 Hz), 4.93 (1H, d, *J* =10.5 Hz), 5.11 (1H, d, *J* = 3.0 Hz), 5.93 (1H, brs), 6.75-6.86 (8H, m), 7.12-7.18 (4H, m), 7.21-7.27 (4H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 11.90, 18.02, 18.83, 19.07, 25.97, 26.11, 26.26, 26.75, 28.97, 29.19, 29.41, 52.29, 53.72, 54.90, 55.09, 55.11, 55.12, 55.15, 60.28, 62.32, 63.36, 64.91, 68.36, 68.53, 70.07, 72.21, 72.53, 73.71, 73.94, 74.65, 76.85, 78.44, 79.85, 80.10, 80.93, 83.68, 97.73, 97.80, 99.55, 111.23, 113.54, 113.60, 113.68, 122.84, 128.64, 129.07, 129.43, 129.62, 130.26, 130.64, 131.17, 131.20, 140.13, 158.74, 158.97, 158.98, 159.24 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 1313.72327, $C_{73}H_{107}NO_{18}Si^+$ requires *m/z* 1313.72574; IR (neat) ν: 1075, 1247, 1457, 1514, 2865, 2935 cm^{-1}; $[\alpha]_D^{22}$ +36.0° (*c* 0.992, $CHCl_3$)

Methyl 4-[6-(α-D-glucopyranosyloxy)hexyloxy]-α-acarviosin (**7**)

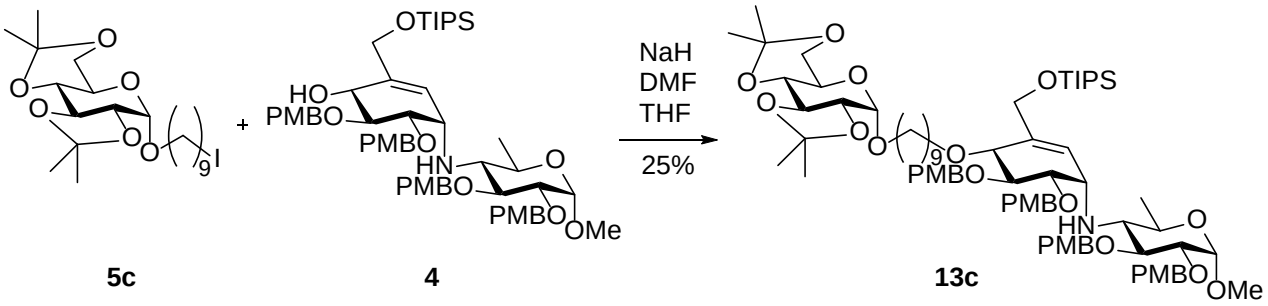


13b **7**

Compound **13b** (23.8 mg, 0.0181mmol) was dissolved in methanol (0.66 mL). The solution was cooled to 0°C and trifluoroacetic acid (TFA, 1.70 mL) was added. The reaction mixture was stirred for 23 hrs at rt. After concentration of the mixture, the solution was charged on to BondElut C18 column (Varian, Inc.) and eluted by 30% aq. methanol to obtain **7** (10.9 mg, 0.0181 mmol, quant.) as a colorless oil.

^{1}H-NMR (500 MHz, CD_3OD, rt): 1.39 (3H, d, *J* = 6.3 Hz), 1.41-1.47 (4H, m), 1.58-1.68 (4H, m), 3.03 (1H, t, *J* = 10.3 Hz), 3.25-3.31 (1H, m), 3.38 (1H, dd, *J* = 3.8, 9.8 Hz), 3.42 (3H, s), 3.42-3.47 (1H, m), 3.49 (1H, dd, *J* = 3.7, 9.1 Hz), 3.53-3.58 (1H, m), 3.60-3.68 (3H, m), 3.71-3.76 (1H, m), 3.77-3.81 (2H, m), 3.84-3.90 (1H, m), 3.92-3.99 (3H, m), 4.01-4.08 (1H, m), 4.13-4.25 (3H, m), 4.68 (1H, d, *J* = 3.7 Hz), 4.76 (1H, d, *J* = 3.8 Hz), 5.86 (1H, d, *J* = 2.5 Hz) ppm; ^{13}C-NMR (67.5 MHz, CD_3OD, rt): 18.60, 27.01, 27.08, 30.45, 31.01, 56.03, 57.28, 62.80, 62.98, 64.36, 65.00, 68.36, 69.03, 69.68, 71.27, 71.96, 73.41, 73.63, 73.73, 74.10, 75.17, 79.46, 100.16, 101.22, 116.08, 147.49 ppm; HR ESI MS (positive): $[M+H]^+$ found *m/z* 598.3065, $C_{26}H_{48}NO_{14}^+$ requires *m/z* 598.3075; IR (neat) υ: 1049, 1144, 1202, 1671, 2871, 2937, 3365 cm^{-1}; $[\alpha]_D^{24}$ +95.4° (*c* 0.500, CH_3OH)

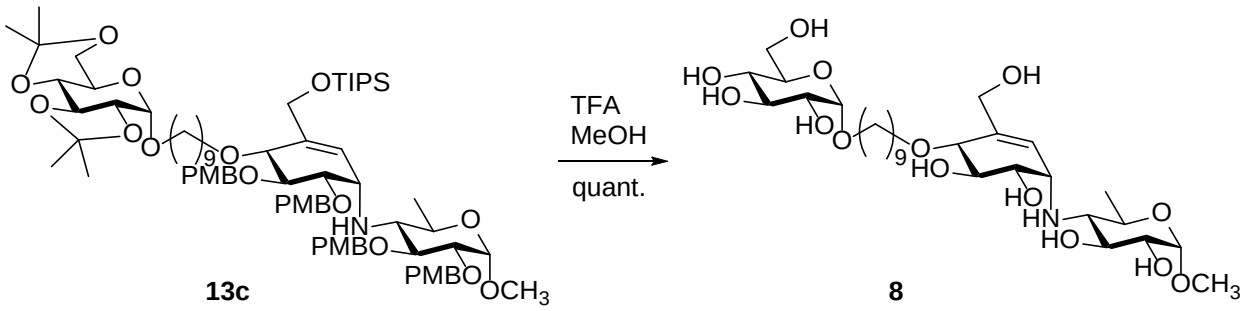
Methyl
4-[4-(2,3;4,6-di-*O*-isopropylidene-α-D-glucopyranosyloxy)nonyloxy]-2,3,2',3'-tetra-*O*-(*p*-methoxybenzyl)-6-*O*-isopropylsilyl-α-acarviosin (**13c**)



5c **4** **13c**

Compound **5c** (117 mg, 0.228 mmol) and **4** (72.8 mg, 0.0750 mmol) was dissolved in THF (0.50 mL), DMF (0.50 mL). The solution was cooled to 0°C, sodium hydride (35.9 mg, 1.50 mmol) was added and stirred for overnight under argon atmosphere at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→2/1) to obtain product containing **4**. This was dissolved in dichloromethane (1.0 mL) and acetic anhydride (0.01 mL), TEA(0.02 mL) was added and stirred for 3.5 hrs at rt. The reaction mixture was diluted with chloroform, washed with sat. aq. sodium hydrogen carbonate and brine, and dried over sodium sulfate. After evaporation, the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 4/1→5/2) to obtain **13c** (25.6 mg, 0.0199 mmol, 25%). ^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.02-1.13 (21H, m), 1.19 (3H, d, J = 6.3 Hz), 1.23-1.37 (10H, m), 1.44 (3H, s), 1.45 (3H, s), 1.46 (3H, s), 1.46-1.54 (2H, m), 1.55 (3H, s), 1.58-1.68 (2H, m), 2.42 (1H, t, J = 9.6 Hz), 3.35 (3H, s), 3.40-3.59 (8H, m), 3.64 (1H, t, J = 9.6 Hz), 3.68-3.73 (1H, m), 3.74 (3H, s), 3.76 (3H, s), 3.78 (3H, s), 3.79 (3H, s), 3.80-3.91 (3H, m), 3.94 (1H, d, J = 6.7 Hz), 3.99 (1H, t, J = 4.7 Hz), 4.05 (1H, t, J =9.3 Hz), 4.19 (1H, dd, J = 6.7, 9.3 Hz), 4.24 (2H, br s), 4.49 -4.66 (7H, m), 4.77 (1H, d, J = 10.7 Hz), 4.93 (1H, d, J =10.8 Hz), 5.12 (1H, d, J = 3.1 Hz), 5.94 (1H, d, J =4.7 Hz), 6.75-6.86 (8H, m), 7.14-7.18 (4H, m), 7.21-7.28 (4H, m) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$, rt): 11.87, 17.98, 18.80, 19.04, 25.94, 26.22, 26.24, 26.72, 28.93, 29.27, 29.35, 29.49, 30.31, 52.26, 54.85, 55.04, 55.06, 55.07, 55.09, 60.22, 62.30, 63.31, 64.86, 68.32, 68.60, 70.00, 72.19, 72.49, 73.68, 73.88, 73.92, 74.60, 76.83, 78.30, 79.81, 80.06, 80.90, 83.64, 97.71, 97.76, 99.50, 111.18, 113.50, 113.56, 113.64, 122.76, 128.60, 129.04, 129.41, 129.58, 130.22, 130.62, 131.15, 131.17, 140.11, 158.71, 158.93, 158.95, 159.21 ppm; HR FD MS (positive): $[M]^+$ found *m/z* 1355.77361, $C_{76}H_{113}NO_{18}Si^+$ requires *m/z* 1355.77269; IR (neat) ν: 1075, 1247, 1514, 2864, 2932 cm^{-1}; $[\alpha]_D^{21}$ +39.7° (*c* 0.985, $CHCl_3$)

Methyl 4-[9-(α-D-glucopyranosyloxy)nonyloxy]-α-acarviosin (**8**)

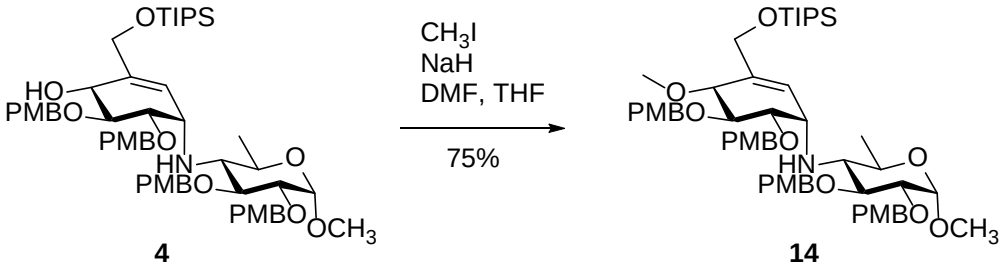


13c **8**

Compound **13c** (25.4 mg, 0.0187 mmol) was dissolved in methanol (0.66 mL). The solution was cooled to 0°C and trifluoroacetic acid (TFA, 1.70 mL) was added. The reaction mixture was stirred for 23 hrs at rt. After concentration of the mixture, the solution was charged on BondElut C18 column (Varian, Inc.) and eluted by 30% aq. methanol to obtain **8** (12.0 mg, 0.0188 mmol, quant.) as a colorless oil.

^{1}H-NMR (500 MHz, CD_3OD, rt): 1.30-1.41 (13H, m), 1.55-1.67 (4H, m), 3.03 (1H, t, *J* = 10.3 Hz), 3.25-3.30 (1H, m), 3.38 (1H, dd, *J* = 3.7, 9.8 Hz), 3.41 (3H, s), 3.42-3.46 (1H, m), 3.49 (1H, dd, *J* = 3.7, 9.2 Hz), 3.54-3.58 (1H, m), 3.69-3.75 (4H, m), 3.76-3.81 (2H, m), 3.83-3.90 (1H, m), 3.92-4.00 (3H, m), 4.02-4.08 (1H, m), 4.13-4.25 (3H, m), 4.68 (1H, d, *J* = 3.7 Hz), 4.76 (1H, d, *J* =3.7 Hz), 5.87 (1H, *J* = 2.5 Hz) ppm; ^{13}C-NMR (125 MHz, CD_3OD, rt): 18.66, 27.17, 27.25, 30.42, 30.44, 30.58, 31.16, 55.99, 57.29, 62.68, 62.93, 64.33, 64.93, 68.25, 69.10, 69.65, 71.15, 71.82, 73.41, 73.56, 73.61, 74.01, 75.13, 79.34, 100.06, 101.07, 115.94, 147.20 ppm; HR ESI MS (positive): $[M+H]^+$ found *m/z* 640.3530, $C_{29}H_{54}NO_{14}^+$ requires *m/z* 640.3544; IR (neat) υ: 1040, 1140, 1200, 1671, 2857, 2930, 3364 cm^{-1}; $[\alpha]_D^{21}$ +80.2° (*c* 0.500, CH_3OH)

Methyl 2,3,2',3'-tetra-*O*-*p*-methoxybenzyl-4-*O*-methyl-6-*O*-triisopropylsilyl-α-acarviosin (**14**)



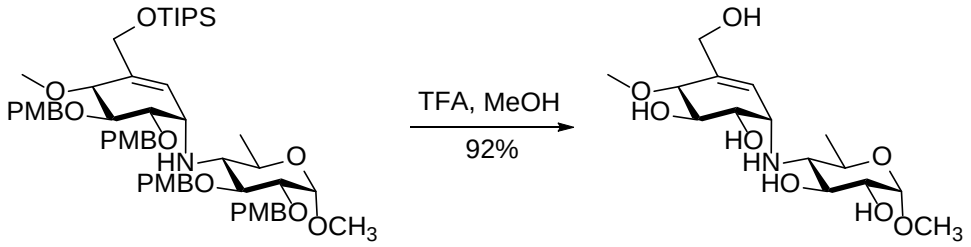
4 **14**

Compound **4** (62.8 mg, 0.0647 mmol) was dissolved in THF (0.50 mL), DMF (0.50 mL). The solution was cooled to 0°C, sodium hydride (34.7 mg, 1.45 mmol), iodomethane (0.05 mL) was added and stirred for four hrs under argon atmosphere at rt. The reaction mixture was diluted with water and extracted by ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and evaporated. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 2/1) to obtain **14** (48.1 mg, 0.0488 mmol, 75%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$, rt): 1.02-1.15 (21H, m), 1.17 (3H, d, *J* = 6.1 Hz), 2.46 (1H, t, *J* = 9.5 Hz), 3.35 (3H, s), 3.40 (3H, s), 3.44-3.50 (3H, m), 3.63 (1H, t, *J* = 9.3 Hz), 3.75 (3H, s), 3.77 (3H, s), 3.787 (3H, s), 3.79 (3H, s), 3.91 (1H, d, *J* = 6.9 Hz), 4.01 (1H, t, *J* = 4.7 Hz), 4.15-4.21 (2H, m), 4.27 (1H, d, *J* = 13.6 Hz), 4.49 (1H, d, *J* = 3.3 Hz), 4.50-4.67 (6H, m), 4.79 (1H, d, *J* = 10.6 Hz), 4.94 (1H,

d, *J* = 10.7 Hz), 5.93 (1H, d, *J* = 5.4 Hz), 6.77-6.87 (8H, m), 7.13-7.28 (8H, m) ppm; ^{13}C-NMR (67.5 MHz, $CDCl_3$, rt): 11.81, 17.93, 18.75, 52.25, 54.89, 55.10, 55.11, 55.13, 55.16, 57.76, 60.12, 63.38, 68.37, 72.32, 72.56, 74.03, 74.69, 78.29, 79.86, 81.01, 81.50, 83.87, 97.87, 113.68, 113.73, 113.75, 113.81, 123.57, 128.78, 129.23, 129.64, 129.76, 130.40, 130.76, 131.30, 131.33, 140.23, 158.97, 159.21, 159.46 ppm; HR ESI MS (positive): $[M+H]^+$ found *m/z* 986.5445, $C_{56}H_{80}NO_{12}Si^+$ requires *m/z* 986.5450; IR (neat) υ: 821, 1078, 1173, 1249, 1302, 1458, 1514, 1614, 2865, 2938 cm^{-1}; $[\alpha]_D^{23}$ +37.9° (*c* 0.500, $CHCl_3$)

Methyl 4-*O*-methyl α-acarviosin (**9**) の合成



14 **9**

Compound **14** (40.6 mg, 0.0412 mmol) was dissolved in methanol (0.67 mL). The solution was cooled to 0°C and TFA (1.70 mL) was added. The reaction mixture was stirred for 38 hrs at rt. After evaporation the residue was purified by silica-gel column chromatography (ethyl acetate/methanol = 16/1) to obtain **9** (13.2 mg, 0.0378 mmol, 92%) as a colorless oil.
^{1}H-NMR (500 MHz, CD_3OD, rt): 1.29 (3H, d, *J* = 6.2 Hz), 2.34 (1H, t, *J* = 9.7 Hz), 3.36 (3H, s), 3.40 (1H, dd, *J* = 3.7, 9.1 Hz), 3.46-3.58 (7H, m), 3.72 (1H, d, *J* = 6.7 Hz), 3.91 (1H, dd, *J* = 6.7, 9.1 Hz), 4.03 (1H, d, *J* = 13.6 Hz), 4.13 (1H, d, *J* = 13.6 Hz), 4.59 (1H, d, *J* = 3.7 Hz), 5.87 (1H, d, *J* = 4.7 Hz) ppm; ^{13}C-NMR (125 MHz, CD_3OD, rt): 18.67, 55.50, 57.69, 58.98, 63.15, 67.31, 69.53, 72.55, 72.93, 74.63, 74.91, 82.30, 101.20, 124.85, 140.93 ppm; HR ESI MS (positive): $[M+H]^+$ found *m/z* 350.1818, $C_{15}H_{28}NO_8^+$ requires *m/z* 350.1815; IR (neat) υ: 1055, 1137, 1204, 1673, 2930, 3336 cm^{-1}; $[\alpha]_D^{23}$ + 129.3° (*c* 0.500, CH_3OH)

Reference

S1. Ali, H.; Houghton, P. J.; Soumyanath, A. *J. Ethnopharmacol.* **2006**, *107*, 449–455.

S2. Shibata, Y.; Kosuge, Y.; Mizukoshi, T.; Ogawa, S. *Carbohydr. Res.* **1992**, *228*, 377–398.

S3. Junge, B.; Heiker, F.-R.; Kurz, J.; Müller, L.; Schmidt, D. D.; Wünsche, C. *Carbohydr. Res.* **1984**, *128*, 235–268.

Supplementary material2

Synthesis and study of the pancreatic α-amylase inhibitory activity of methyl acarviosin and its derivatives

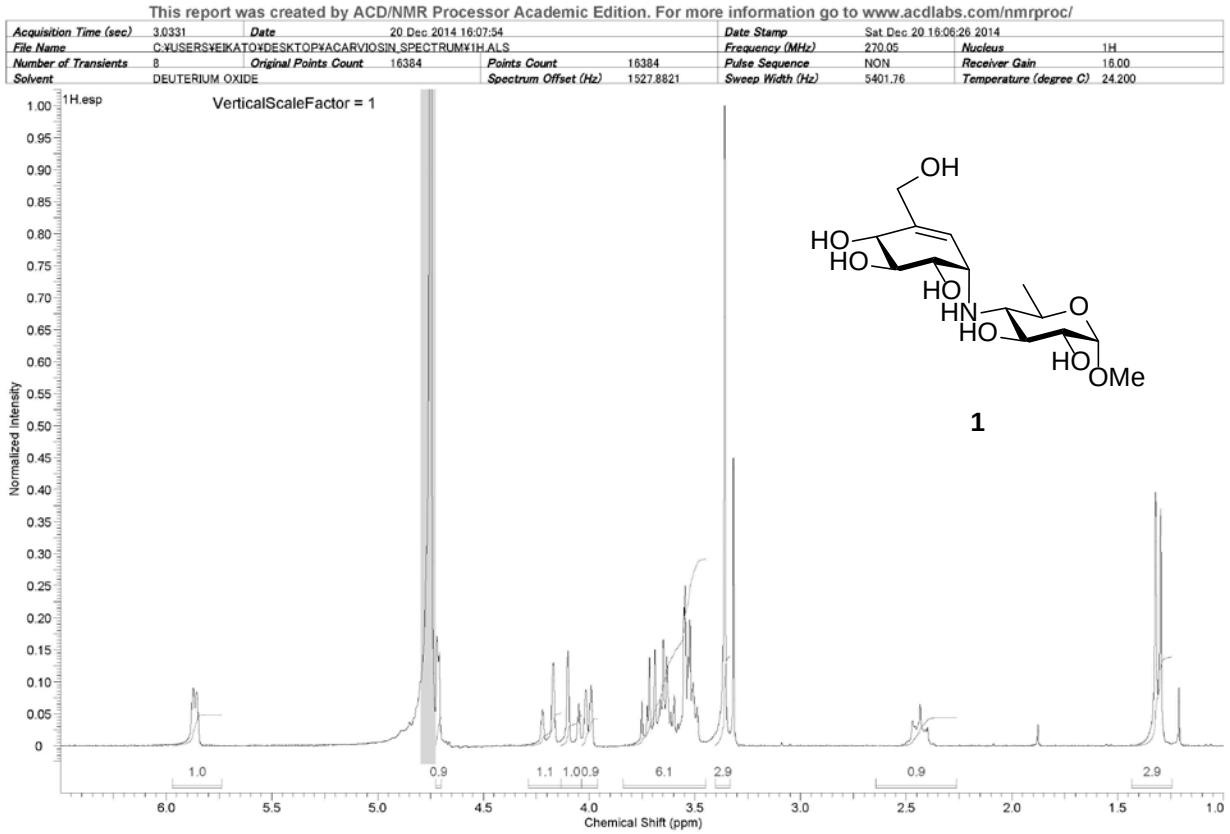
Eisuke Kato,* Fumiaki Chikahisa, and Jun Kawabata

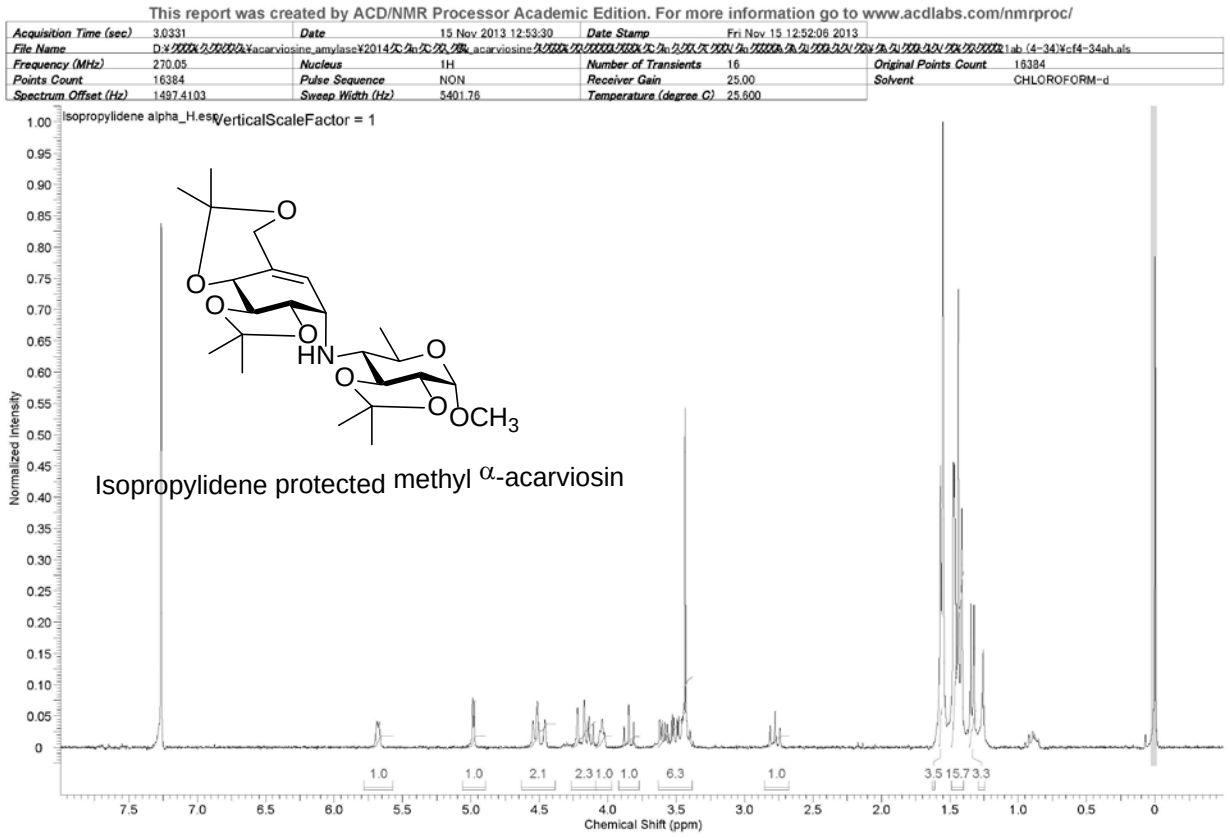
Laboratory of Food Biochemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060-8589, Japan

*Corresponding author:

e-mail: eikato@chem.agr.hokudai.ac.jp, Tel/Fax: +81-11-706-2496.

NMR spectrum of the synthetic compounds





Isopropylidene protected methyl α-acarviosin

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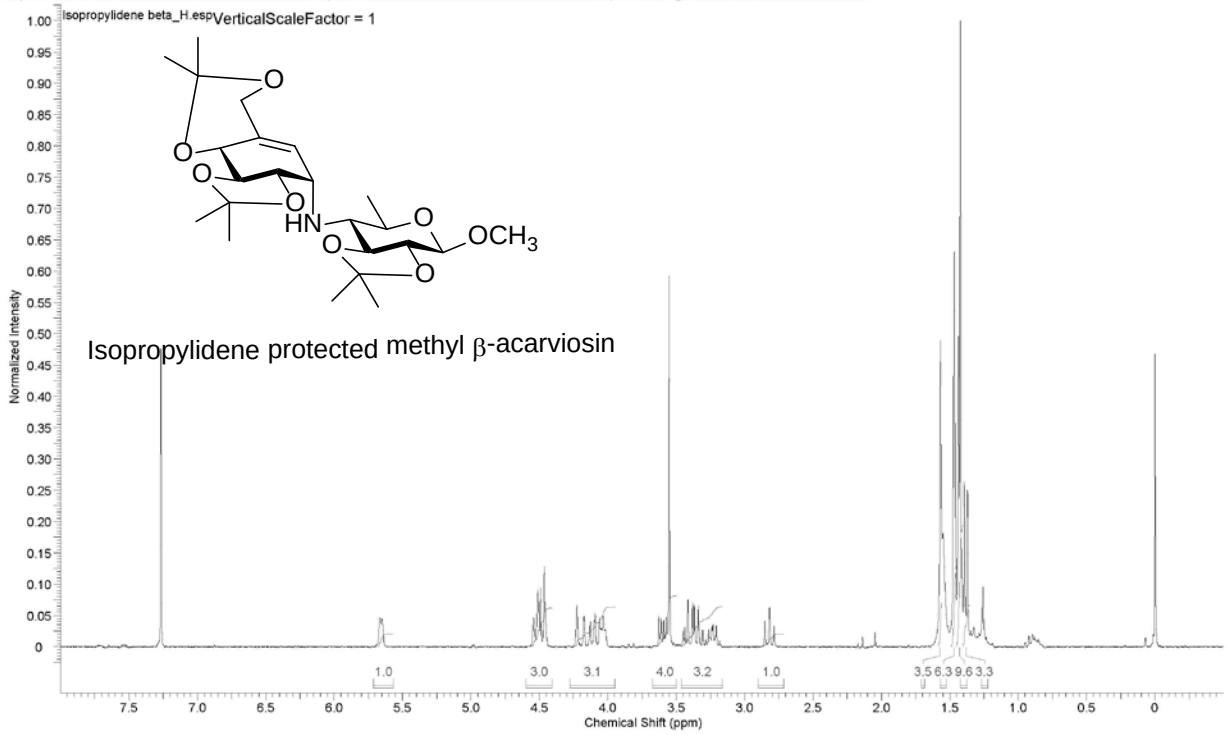

Isopropylidene protected methyl β-acarviosin

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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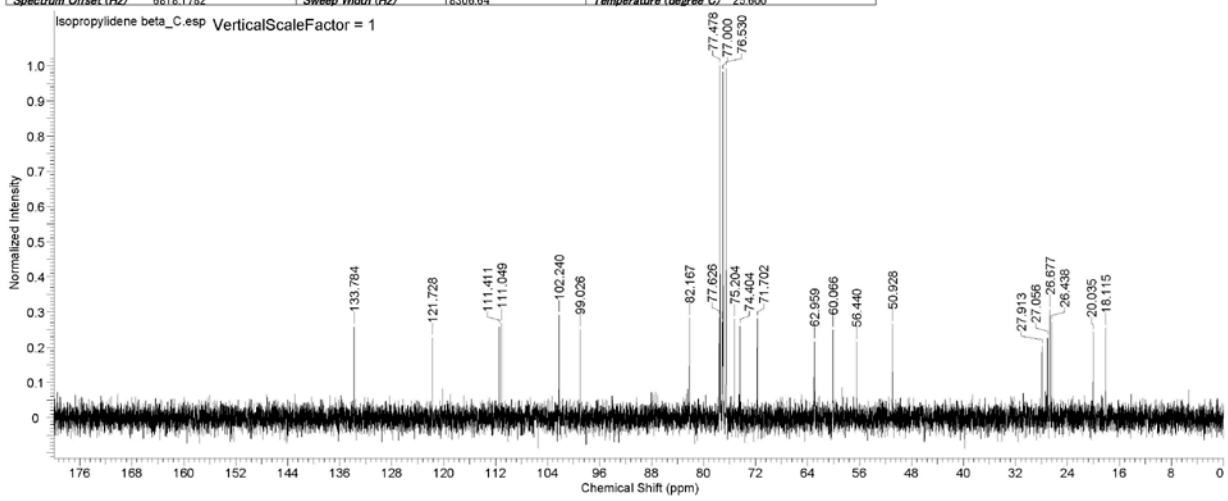

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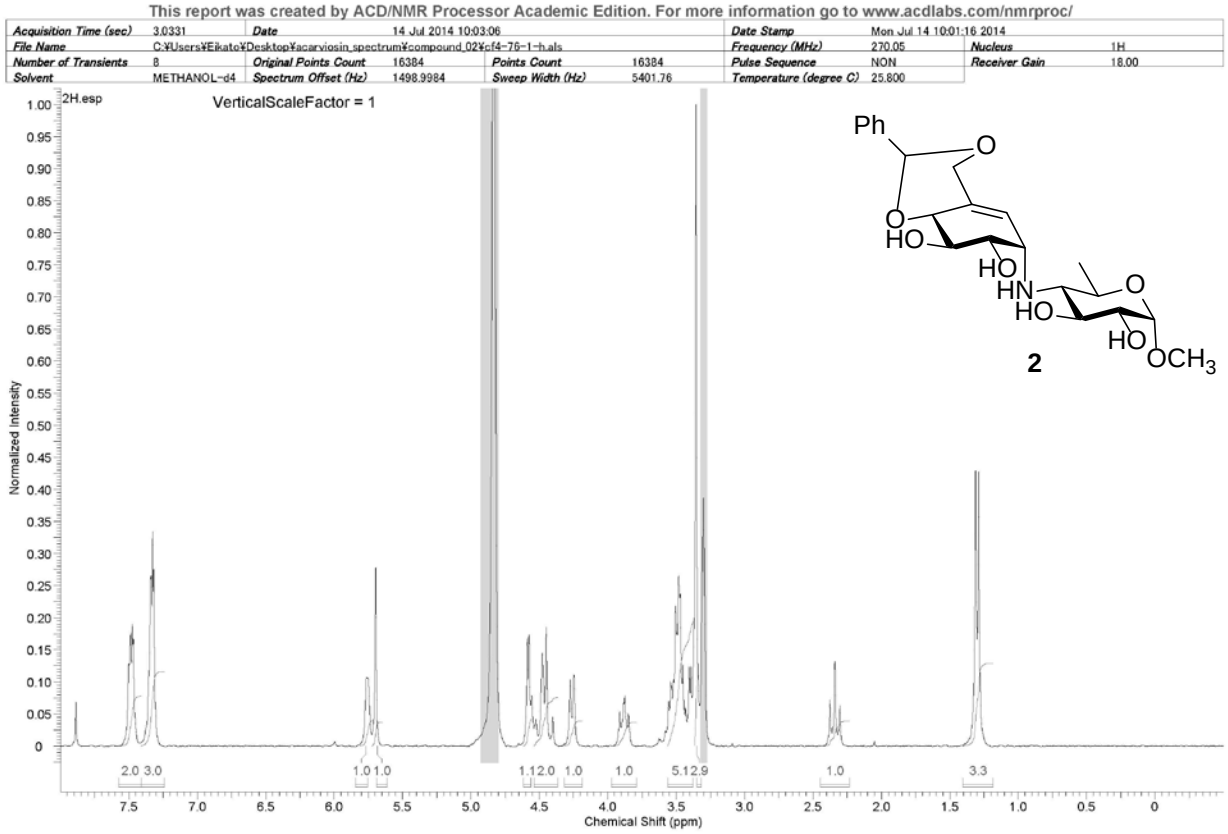
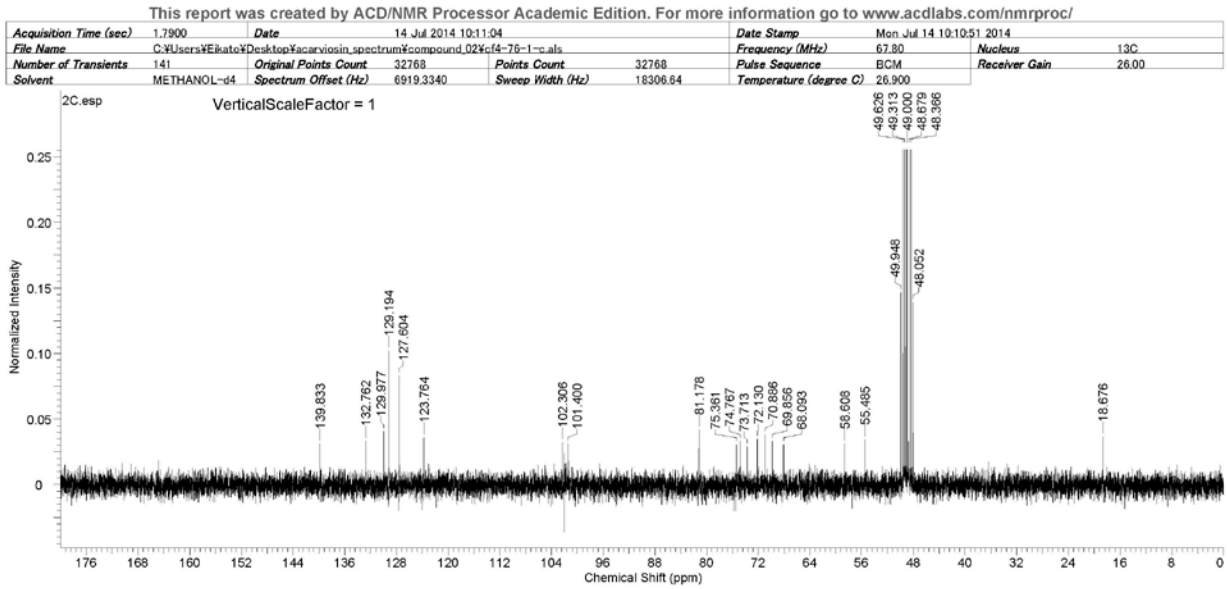
1	18.11	1228.2	6	27.06	1834.4	11	62.96	4268.6	16	77.00	5220.6	21	99.03	6714.0	26	133.78	9070.5
2	20.03	1358.4	7	27.91	1892.5	12	71.70	4861.4	17	77.09	5226.7	22	102.24	6931.9			
3	26.44	1792.5	8	50.93	3452.9	13	74.40	5044.6	18	77.48	5253.0	23	111.05	7529.1			
4	26.68	1808.7	9	56.44	3826.7	14	75.20	5098.8	19	77.63	5263.1	24	111.41	7553.7			
5	26.72	1811.5	10	60.07	4072.5	15	76.53	5188.8	20	82.17	5570.9	25	121.73	8253.2			





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1	18.68	1266.2	6	49.31	3343.4	11	68.09	4616.7	16	74.77	5069.2	21	123.76	8391.2	26	139.83	9480.7
2	48.05	3258.0	7	49.63	3364.7	12	69.86	4736.2	17	75.36	5109.5	22	127.60	8651.6			
3	48.37	3279.2	8	49.95	3386.4	13	70.89	4806.1	18	81.18	5503.9	23	129.19	8759.4			
4	48.68	3300.4	9	55.49	3761.9	14	72.13	4890.4	19	101.40	6874.9	24	129.98	8812.5			
5	49.00	3322.2	10	58.61	3973.6	15	73.71	4997.7	20	102.31	6936.4	25	132.76	9001.3			

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Acquisition Time (sec)	3.1719	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	25 Nov 2014 09:14:56
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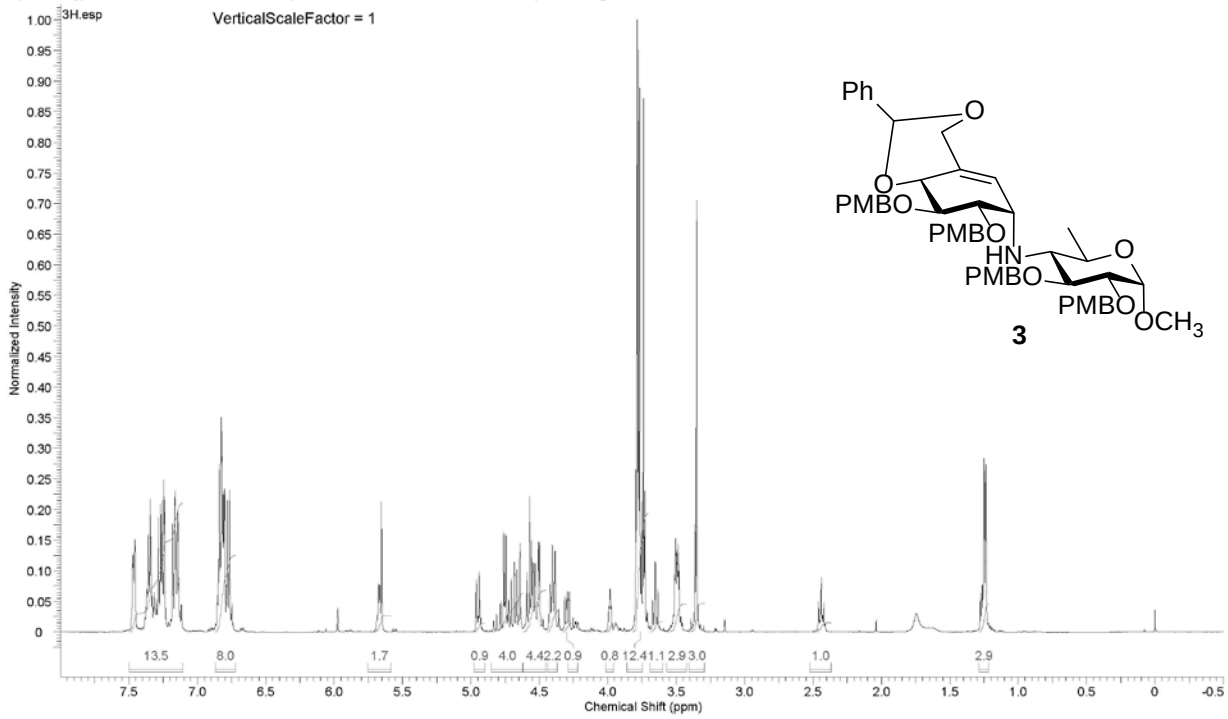

3

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Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	5792.60	*SW(cyclical) (Hz)*	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13824.3008
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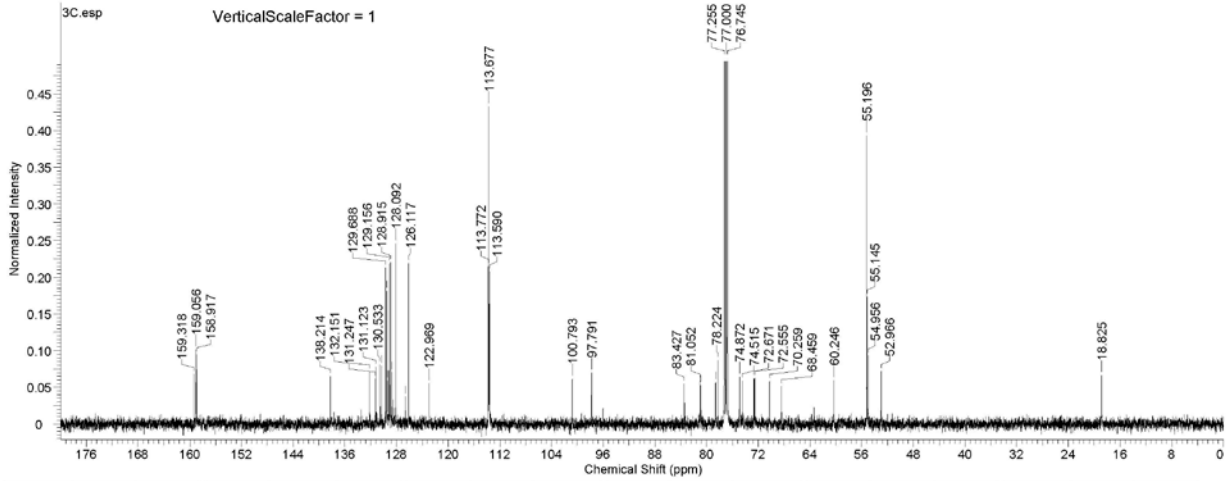

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1	18.82	2367.4	9	72.55	9124.3	17	78.60	9884.1	25	113.77	14307.7	33	129.45	16279.0	41	138.21	17381.5
2	52.97	6660.9	10	72.67	9139.0	18	80.90	10173.6	26	122.97	15464.3	34	129.50	16285.4	42	158.92	19985.1
3	54.96	6911.1	11	74.51	9370.8	19	81.05	10192.9	27	126.12	15860.2	35	129.69	16309.2	43	159.00	19995.2
4	55.15	6934.9	12	74.87	9415.7	20	83.43	10491.7	28	126.65	15927.1	36	130.26	16381.6	44	159.06	20002.5
5	55.20	6941.3	13	76.74	9651.3	21	97.79	12298.0	29	128.09	16108.5	37	130.53	16415.5	45	159.32	20035.5
6	60.25	7576.4	14	77.00	9683.3	22	100.79	12675.5	30	128.68	16182.8	38	131.12	16489.8			
7	68.46	8609.3	15	77.26	9715.4	23	113.59	14284.8	31	128.92	16212.1	39	131.25	16505.4			
8	70.26	8835.6	16	78.22	9837.3	24	113.68	14295.8	32	129.16	16242.3	40	132.15	16619.0			

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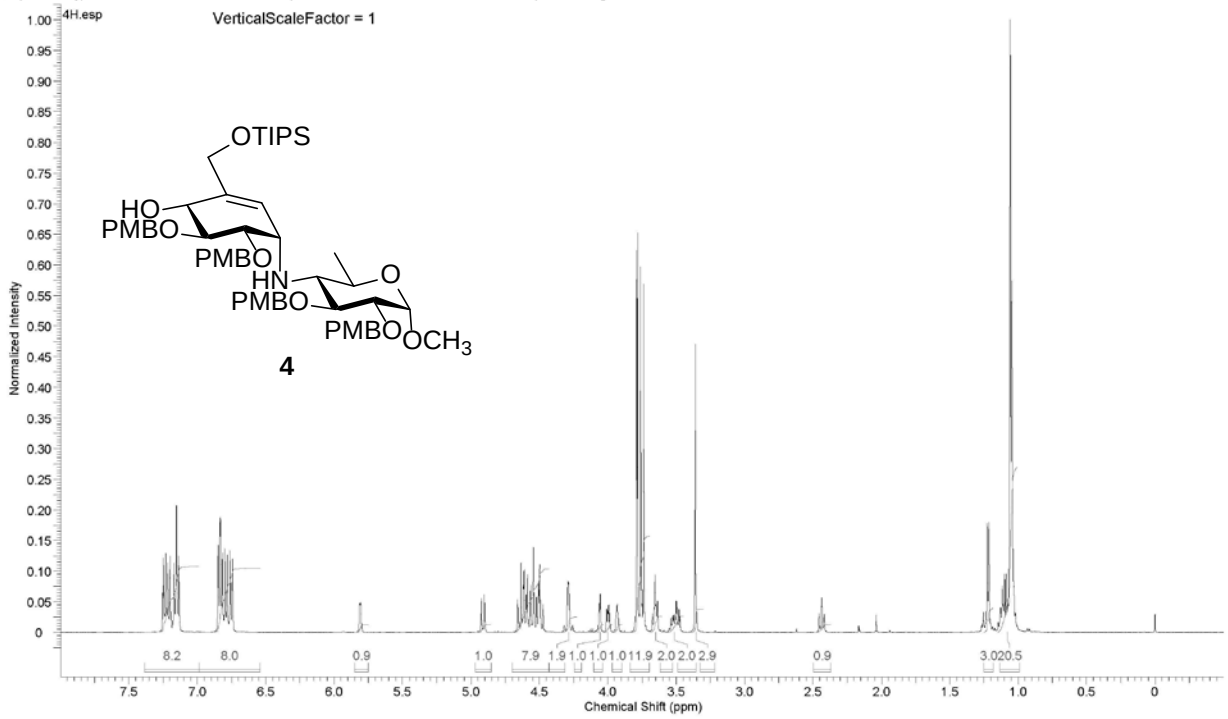

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30
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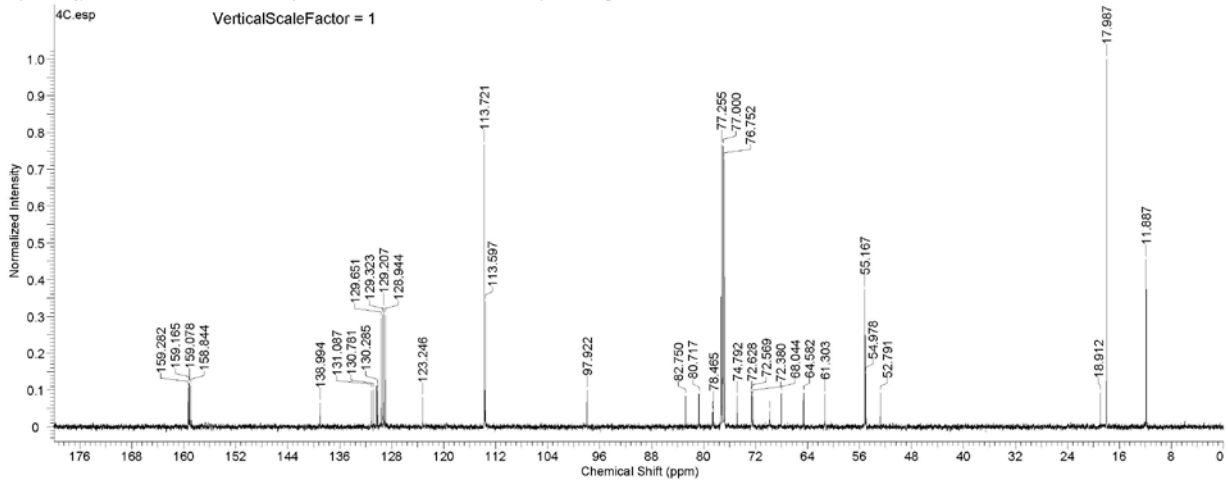

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1	11.89	1494.9	8	55.17	6937.7	15	72.63	9133.5	22	80.72	10150.7	29	129.21	16248.8	36	138.99	17479.5
2	17.99	2262.0	9	61.30	7709.3	16	74.79	9405.7	23	82.75	10406.4	30	129.32	16263.4	37	158.84	19975.9
3	18.91	2378.4	10	64.58	8121.7	17	76.75	9652.2	24	97.92	12314.5	31	129.65	16304.7	38	159.08	20005.3
4	52.79	6638.9	11	68.04	8557.0	18	77.00	9683.3	25	113.60	14285.7	32	130.09	16359.6	39	159.17	20016.3
5	54.98	6913.9	12	69.82	8780.7	19	77.26	9715.4	26	113.72	14301.3	33	130.29	16384.4	40	159.28	20030.9
6	55.13	6933.1	13	72.38	9102.3	20	78.46	9867.6	27	123.25	15499.1	34	130.78	16446.7			
7	55.15	6934.9	14	72.57	9126.2	21	78.61	9885.9	28	128.94	16215.8	35	131.09	16485.2			

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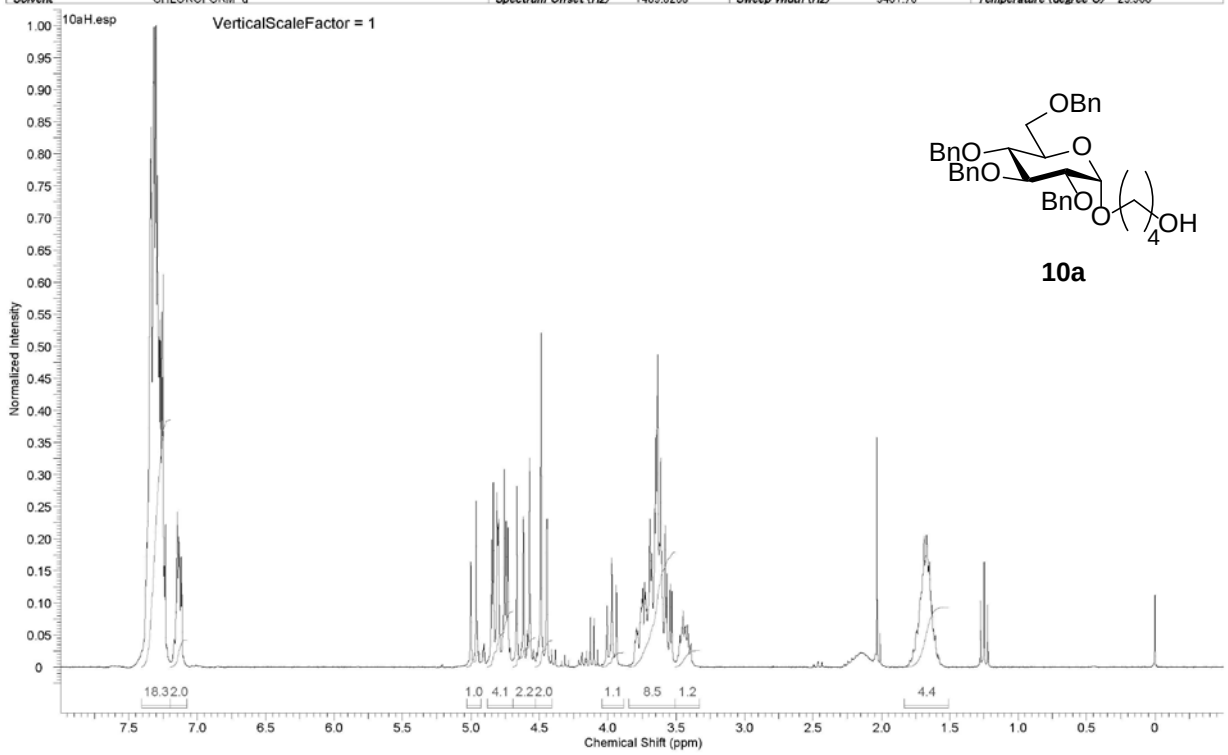

10a

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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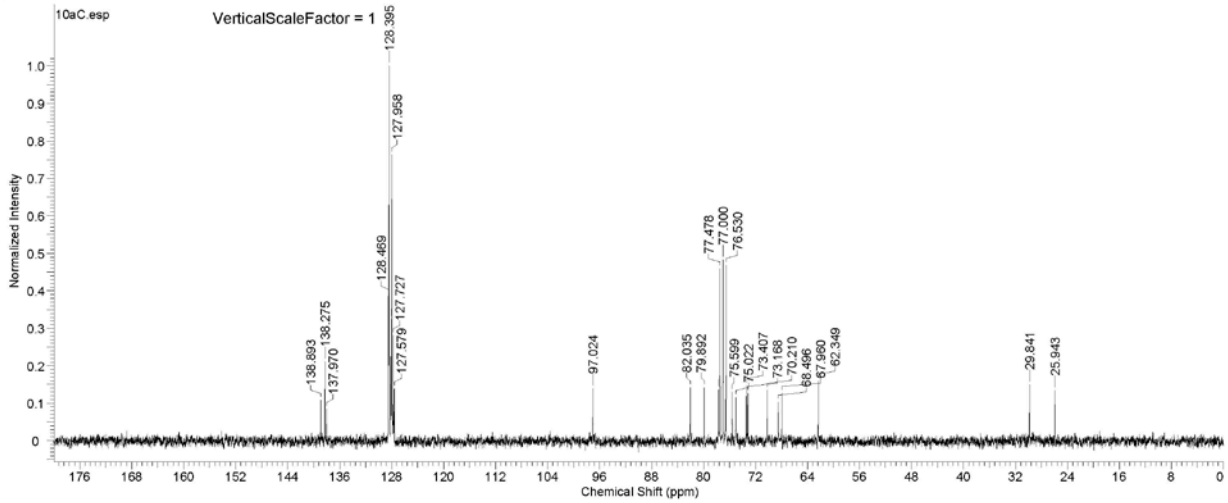

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1	25.94	1758.9	6	70.21	4760.2	11	76.53	5188.8	16	82.03	5562.0	21	127.96	8675.5	26	138.27	9375.0
2	29.84	2023.2	7	73.17	4960.8	12	77.00	5220.6	17	97.02	6578.2	22	128.11	8685.6	27	138.89	9416.9
3	62.35	4227.2	8	73.41	4977.0	13	77.48	5253.0	18	127.58	8649.8	23	128.39	8705.2			
4	67.96	4607.7	9	75.02	5086.5	14	77.68	5266.4	19	127.73	8659.9	24	128.47	8710.2			
5	68.50	4644.0	10	75.60	5125.6	15	79.89	5416.7	20	127.91	8672.2	25	137.97	9354.4			

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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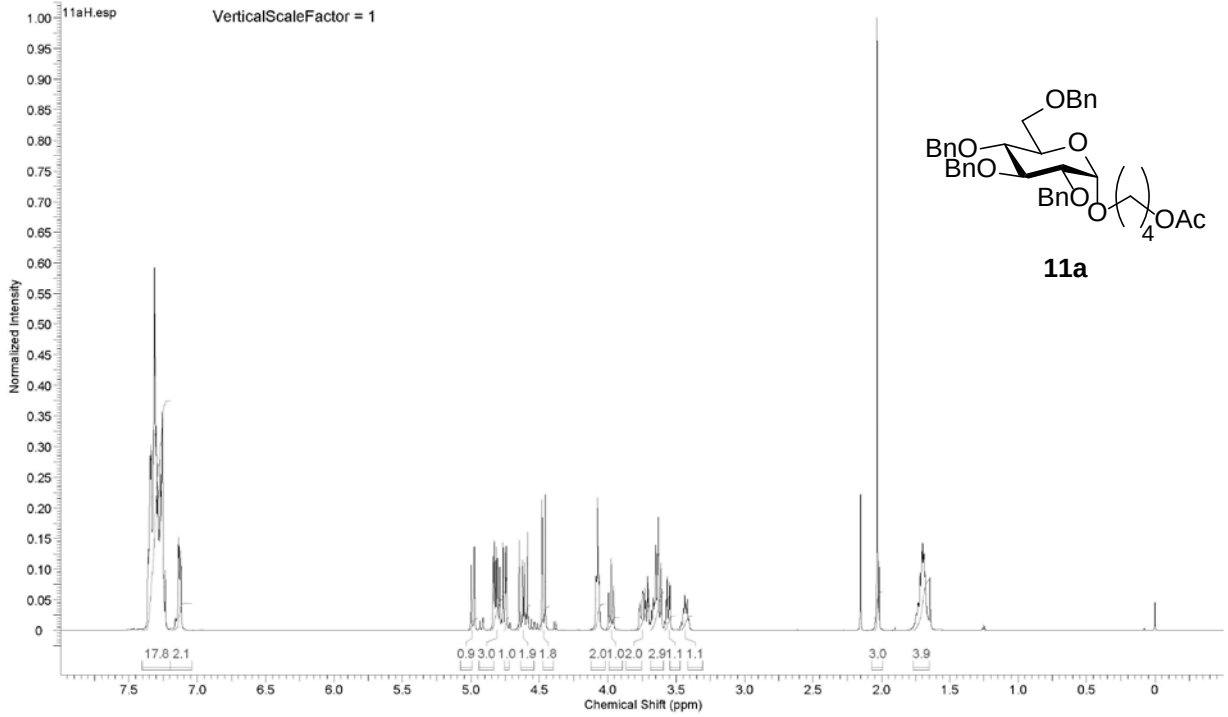

11a

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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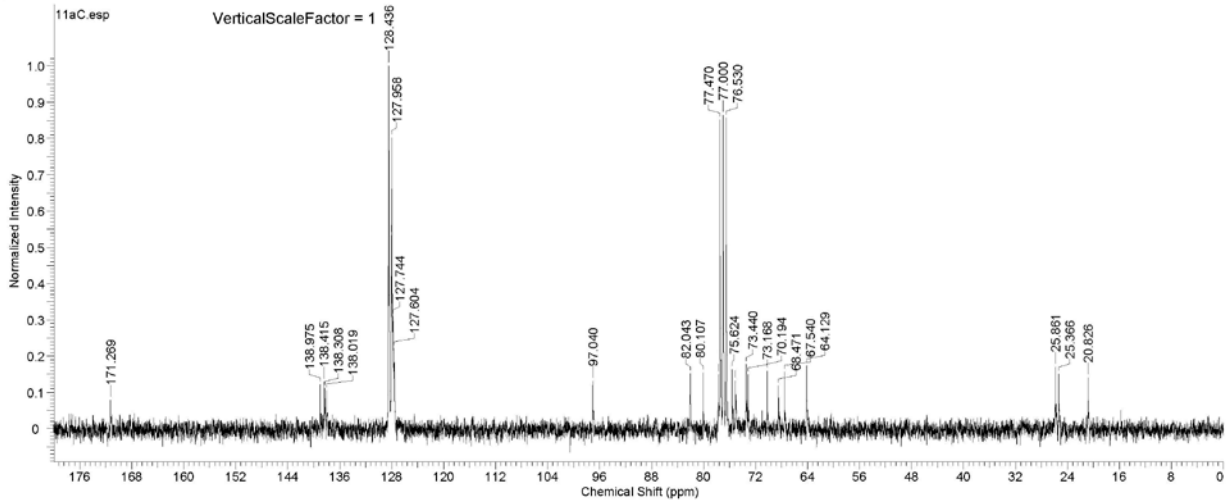

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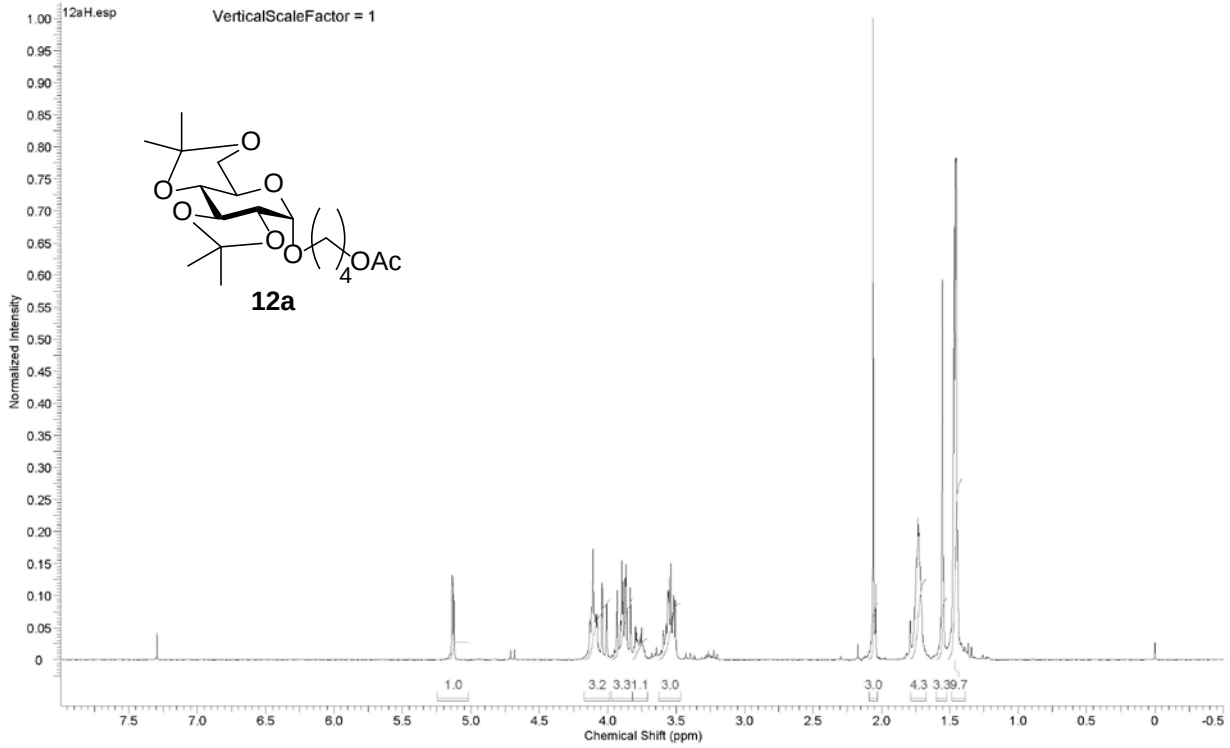
1	20.83	1412.0	7	70.19	4759.1	13	77.00	5220.6	19	127.60	8651.5	25	128.07	8682.8	31	138.98	9422.5
2	25.37	1719.8	8	73.17	4960.8	14	77.47	5252.4	20	127.74	8661.0	26	128.44	8708.0	32	171.27	11612.0
3	25.86	1753.4	9	73.44	4979.2	15	77.72	5269.2	21	127.77	8662.7	27	128.49	8711.3			
4	64.13	4347.9	10	75.08	5090.4	16	80.11	5431.2	22	127.91	8672.2	28	138.02	9357.7			
5	67.54	4579.2	11	75.62	5127.3	17	82.04	5562.5	23	127.96	8675.5	29	138.31	9377.3			
6	68.47	4642.4	12	76.53	5188.8	18	97.04	6579.3	24	128.02	8680.0	30	138.41	9384.5			

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.0331	*Date*	27 Nov 2014 16:15:42	*Date Stamp*	Thu Nov 27 16:14:33 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_12a¥cf4-148-h.als			*Frequency (MHz)*	270.05	*Nucleus*	1H
Number of Transients	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	NON	*Receiver Gain*	13.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	1506.3126	*Sweep Width (Hz)*	5401.76	*Temperature (degree C)*	24.400



12a

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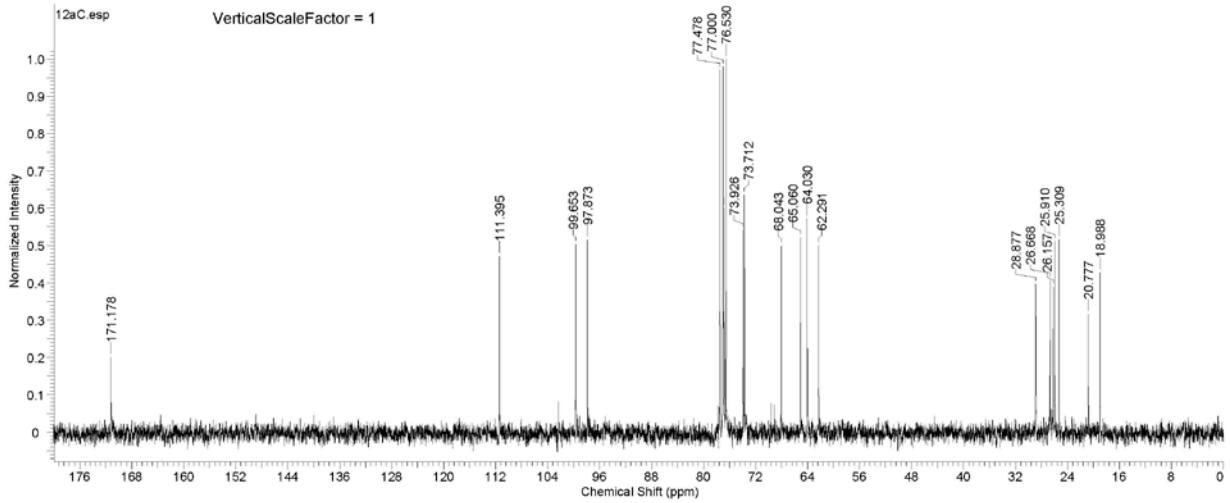
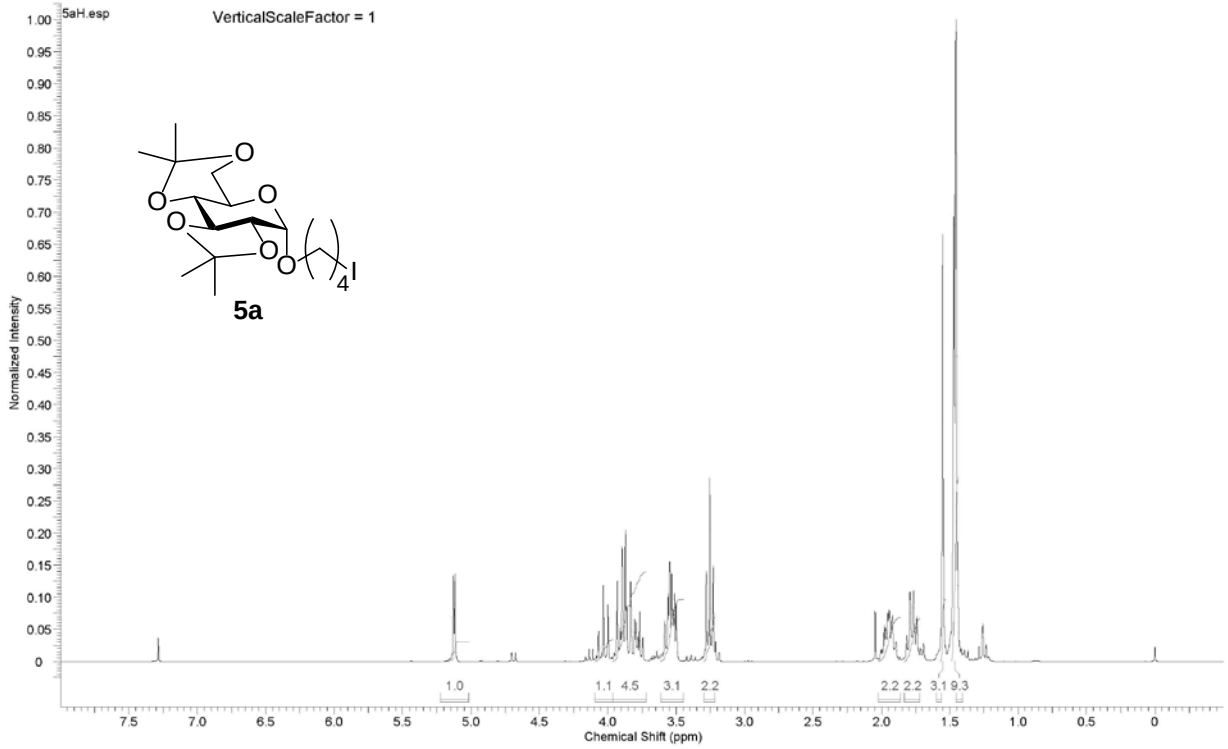
Acquisition Time (sec)	1.7900	*Date*	27 Nov 2014 16:21:44	*Date Stamp*	Thu Nov 27 16:21:29 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_12a¥cf4-148-c.als			*Frequency (MHz)*	67.80	*Nucleus*	13C
Number of Transients	102	*Original Points Count*	32768	*Points Count*	32768	*Pulse Sequence*	BCM	*Receiver Gain*	26.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	6816.5015	*Sweep Width (Hz)*	18306.64	*Temperature (degree C)*	26.000



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	18.99	1287.4	5	26.16	1773.5	9	64.03	4341.2	13	73.93	5012.2	17	77.48	5253.0	21	171.18	11605.9
2	20.78	1408.6	6	26.67	1808.1	10	65.06	4411.1	14	76.53	5188.8	18	97.87	6635.8			
3	25.31	1715.9	7	28.88	1957.8	11	68.04	4613.3	15	76.82	5208.3	19	99.65	6756.4			
4	25.91	1756.7	8	62.29	4223.3	12	73.71	4997.7	16	77.00	5220.6	20	111.39	7552.6			

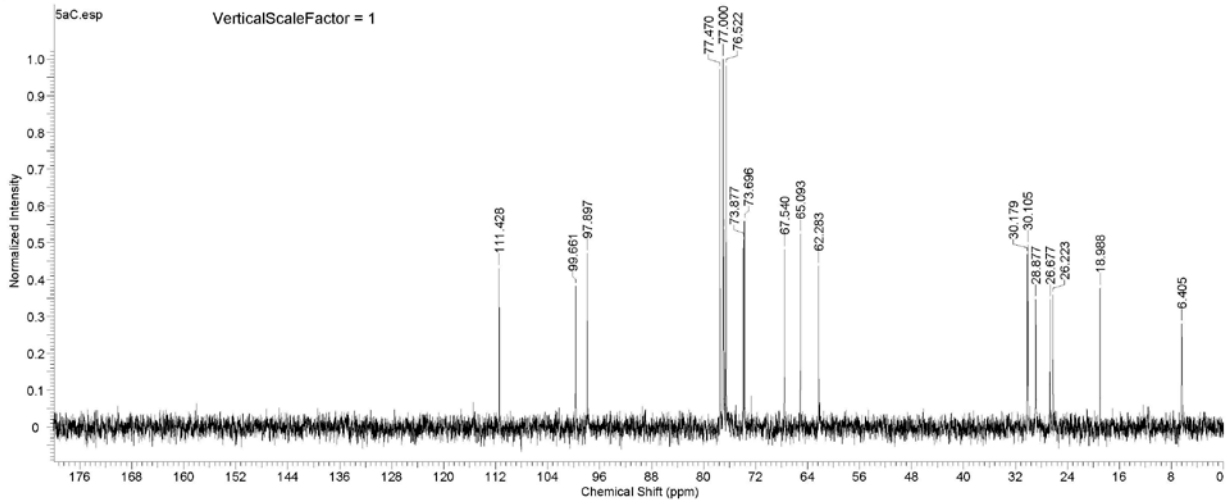
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.0331	*Date*	02 Dec 2014 14:45:38	*Date Stamp*	Tue Dec 02 14:44:44 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_05a¥cf4-150-h.als			*Frequency (MHz)*	270.05	*Nucleus*	1H
Number of Transients	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	NON	*Receiver Gain*	12.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	1503.6749	*Sweep Width (Hz)*	5401.76	*Temperature (degree C)*	22.400



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.7900	*Date*	02 Dec 2014 14:49:10	*Date Stamp*	Tue Dec 02 14:48:56 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_05a¥cf4-150-c.als			*Frequency (MHz)*	67.80	*Nucleus*	13C
Number of Transients	54	*Original Points Count*	32768	*Points Count*	32768	*Pulse Sequence*	BCM	*Receiver Gain*	26.00
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	6815.3843	*Sweep Width (Hz)*	18306.64	*Temperature (degree C)*	24.500



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	6.41	434.3	5	28.88	1957.8	9	65.09	4413.3	13	76.52	5188.2	17	97.90	6637.4
2	18.99	1287.4	6	30.10	2041.1	10	67.54	4579.2	14	76.76	5204.4	18	99.66	6757.0
3	26.22	1777.9	7	30.18	2046.1	11	73.70	4996.6	15	77.00	5220.6	19	111.43	7554.8
4	26.68	1808.7	8	62.28	4222.8	12	73.88	5008.9	16	77.47	5252.4			

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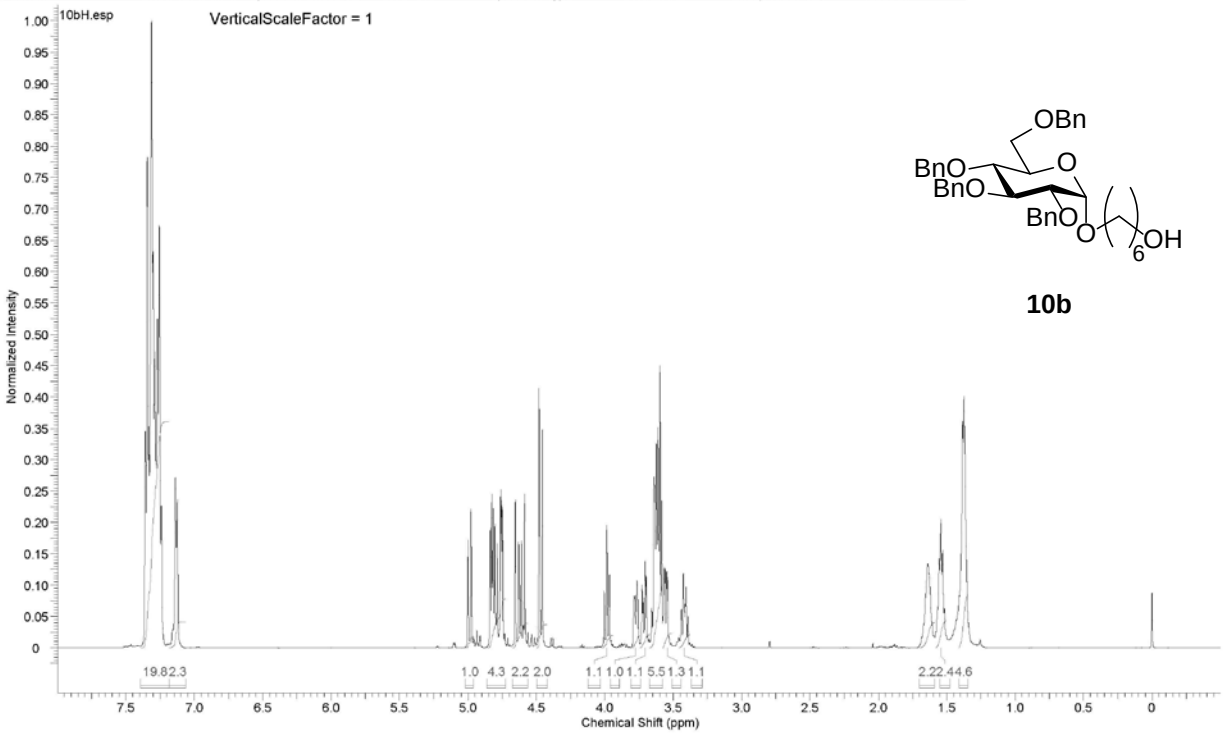
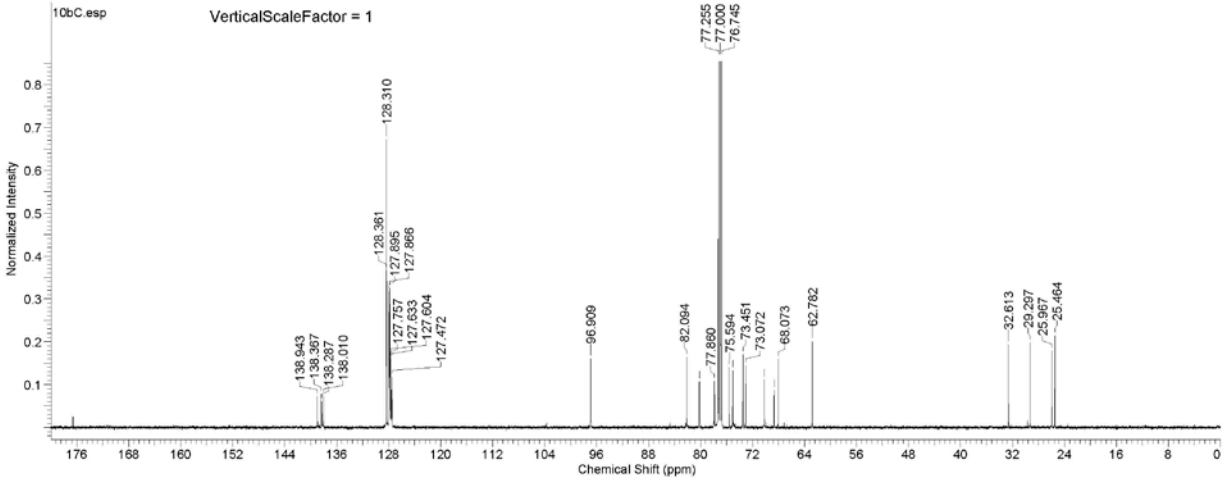
Acquisition Time (sec)	3.1719	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	20 Jan 2015 10:50:56				
Date Stamp	20 Jan 2015 10:50:56			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_10b¥4-88.H.C.COSY¥1H¥pdata¥1¥1r						
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768		
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	71.80	*SW(cyclical) (Hz)*	10330.58		
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	3978.1616	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	10330.26				



10b

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.0912	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	20 Jan 2015 10:55:12				
Date Stamp	20 Jan 2015 10:55:12			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_10b¥4-88.H.C.COSY¥C¥pdata¥1¥1r						
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	512	*Origin*	spect				
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30				
Receiver Gain	8192.00	*SW(cyclical) (Hz)*	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13827.0498				
Spectrum Type	STANDARD	*Sweep Width (Hz)*	30029.11								



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	25.46	3202.3	7	68.67	8635.9	13	76.74	9651.3	19	96.91	12187.1	25	127.87	16080.1	31	138.29	17390.6
2	25.97	3265.5	8	70.17	8824.6	14	77.00	9683.3	20	127.47	16030.6	26	127.90	16083.8	32	138.37	17400.7
3	29.30	3684.3	9	73.07	9189.4	15	77.26	9715.4	21	127.60	16047.1	27	127.94	16089.3	33	138.94	17473.1
4	32.61	4101.3	10	73.45	9237.0	16	77.86	9791.5	22	127.63	16050.8	28	128.31	16136.0			
5	62.78	7895.4	11	75.03	9435.9	17	80.18	10082.9	23	127.76	16066.4	29	128.36	16142.4			
6	68.07	8560.7	12	75.59	9506.5	18	82.09	10323.9	24	127.83	16075.5	30	138.01	17355.8			

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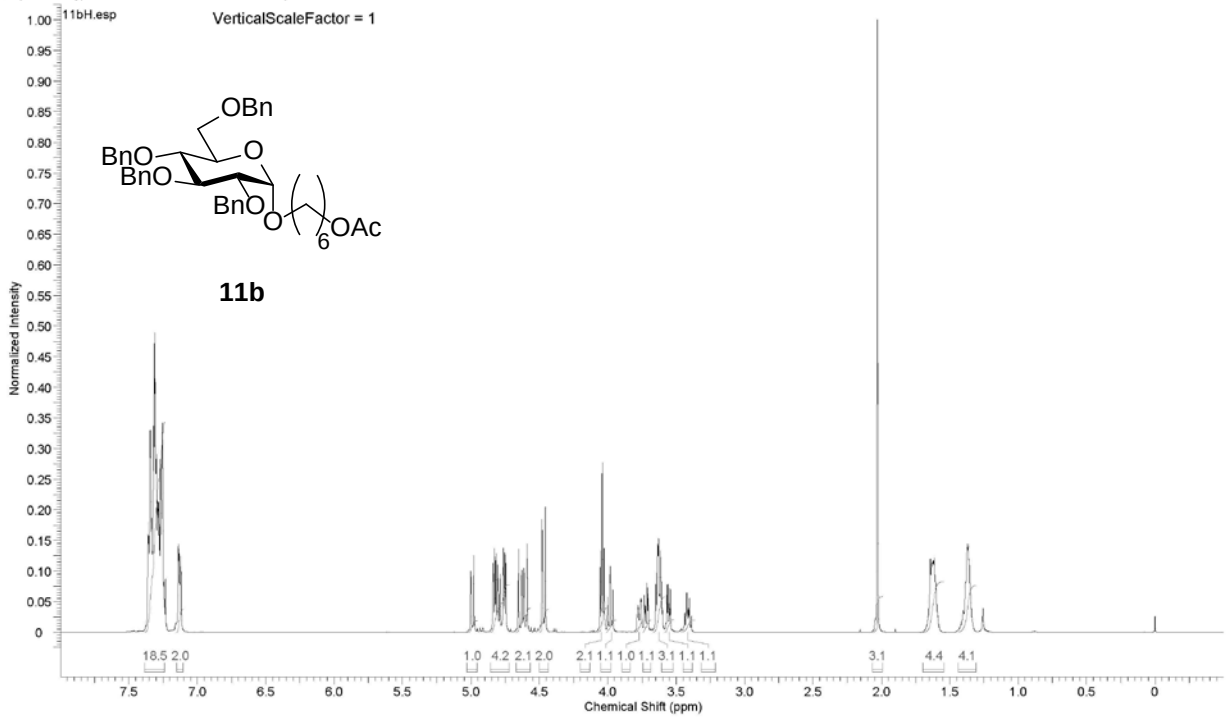
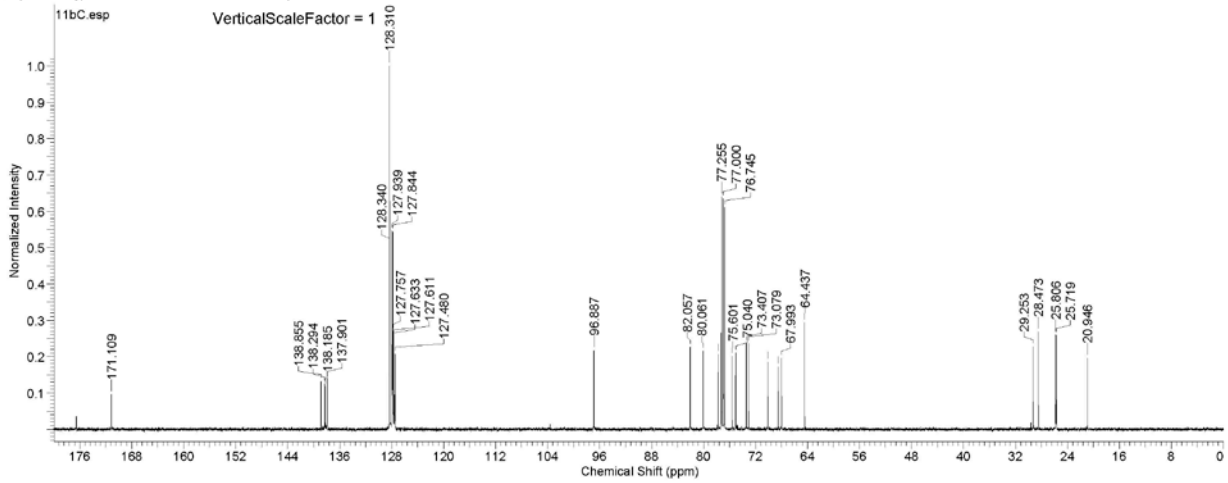
Acquisition Time (sec)	3.1719	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	06 Jan 2015 09:17:04
Date Stamp	06 Jan 2015 09:17:04			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_11b¥ckhs4-120-500MHzNMR¥H¥pdata¥1¥1r		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	40.30	*SW(cyclical) (Hz)*	10330.58	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	3974.3784
Spectrum Type	STANDARD	*Sweep Width (Hz)*	10330.26				



11b

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.0912	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	06 Jan 2015 09:19:12
Date Stamp	06 Jan 2015 09:19:12			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_11b¥ckhs4-120-500MHzNMR¥C¥pdata¥1¥1r		
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	512	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	13004.00	*SW(cyclical) (Hz)*	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13820.6348
Spectrum Type	STANDARD	*Sweep Width (Hz)*	30029.11				



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	20.95	2634.1	7	67.99	8550.6	13	75.60	9507.4	19	82.06	10319.4	25	127.83	16075.5	31	128.34	16139.7
2	25.72	3234.3	8	68.50	8613.9	14	76.74	9651.3	20	96.89	12184.3	26	127.84	16077.4	32	137.90	17342.1
3	25.81	3245.3	9	70.09	8814.6	15	77.00	9683.3	21	127.48	16031.6	27	127.89	16082.9	33	138.18	17377.8
4	28.47	3580.8	10	73.08	9190.3	16	77.26	9715.4	22	127.61	16048.1	28	127.94	16089.3	34	138.29	17391.6
5	29.25	3678.8	11	73.41	9231.5	17	77.72	9774.1	23	127.63	16050.8	29	128.29	16133.3	35	138.86	17462.1
6	64.44	8103.4	12	75.04	9436.8	18	80.06	10068.3	24	127.76	16066.4	30	128.31	16136.0	36	171.11	21518.3

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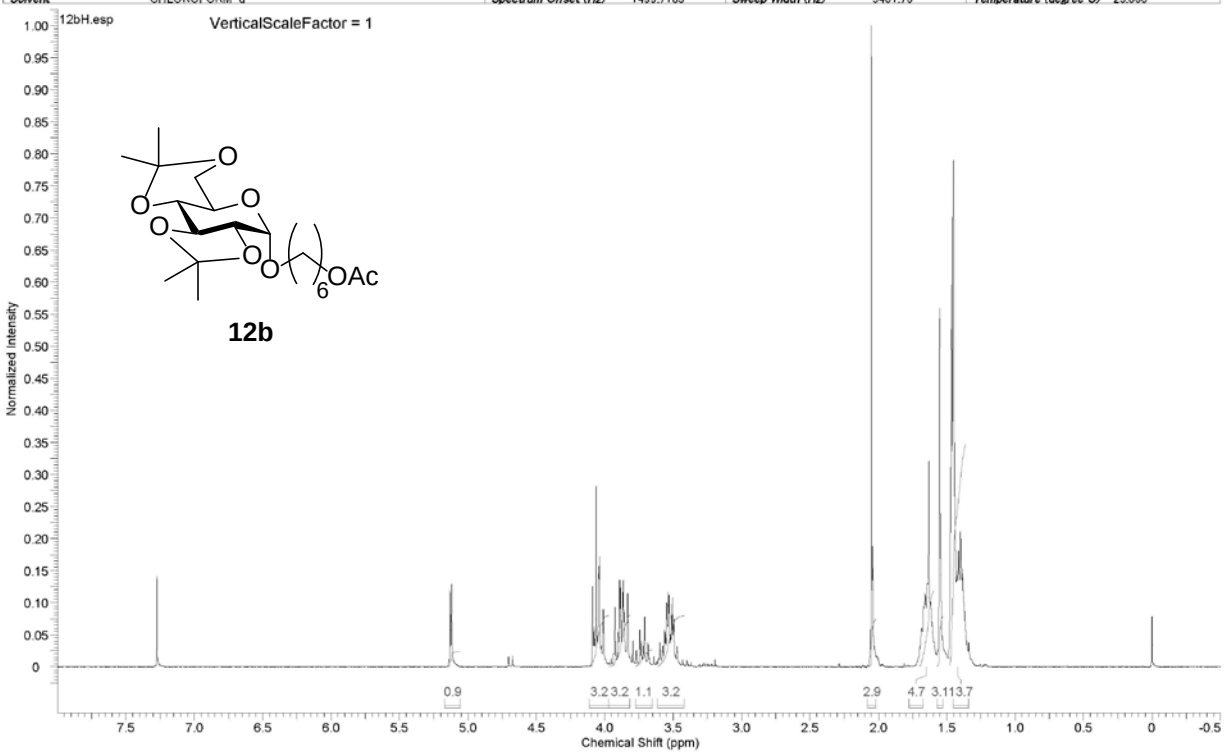
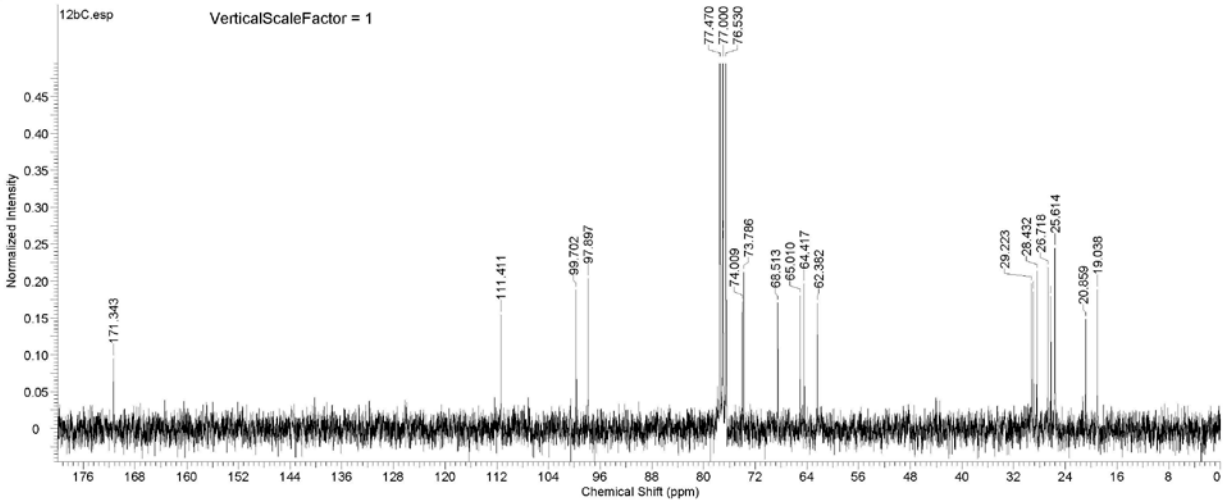
Acquisition Time (sec)	3.0331	Date	09 Oct 2014 20:30:40	Date Stamp	Thu Oct 09 20:29:27 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_12b¥cf4-121-h.als			Frequency (MHz)	270.05	Nucleus	1H
Number of Transients	8	Original Points Count	16384	Points Count	16384	Pulse Sequence	NON	Receiver Gain	17.00
Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	1499.7183	Sweep Width (Hz)	5401.76	Temperature (degree C)	25.000



12b

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.7900	Date	09 Oct 2014 20:38:40	Date Stamp	Thu Oct 09 20:38:27 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_12b¥cf4-121-c.als			Frequency (MHz)	67.80	Nucleus	13C
Number of Transients	142	Original Points Count	32768	Points Count	32768	Pulse Sequence	BCM	Receiver Gain	25.00
Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	6818.7368	Sweep Width (Hz)	18306.64	Temperature (degree C)	26.900



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	19.04	1290.8	5	26.22	1777.9	9	29.22	1981.3	13	68.51	4645.1	17	76.92	5215.0	21	99.70	6759.8
2	20.86	1414.2	6	26.72	1811.5	10	62.38	4229.5	14	73.79	5002.7	18	77.00	5220.6	22	111.41	7553.7
3	25.61	1736.6	7	28.43	1927.7	11	64.42	4367.5	15	74.01	5017.8	19	77.47	5252.4	23	171.34	11617.1
4	25.65	1738.8	8	28.93	1961.8	12	65.01	4407.7	16	76.53	5188.8	20	97.90	6637.4			

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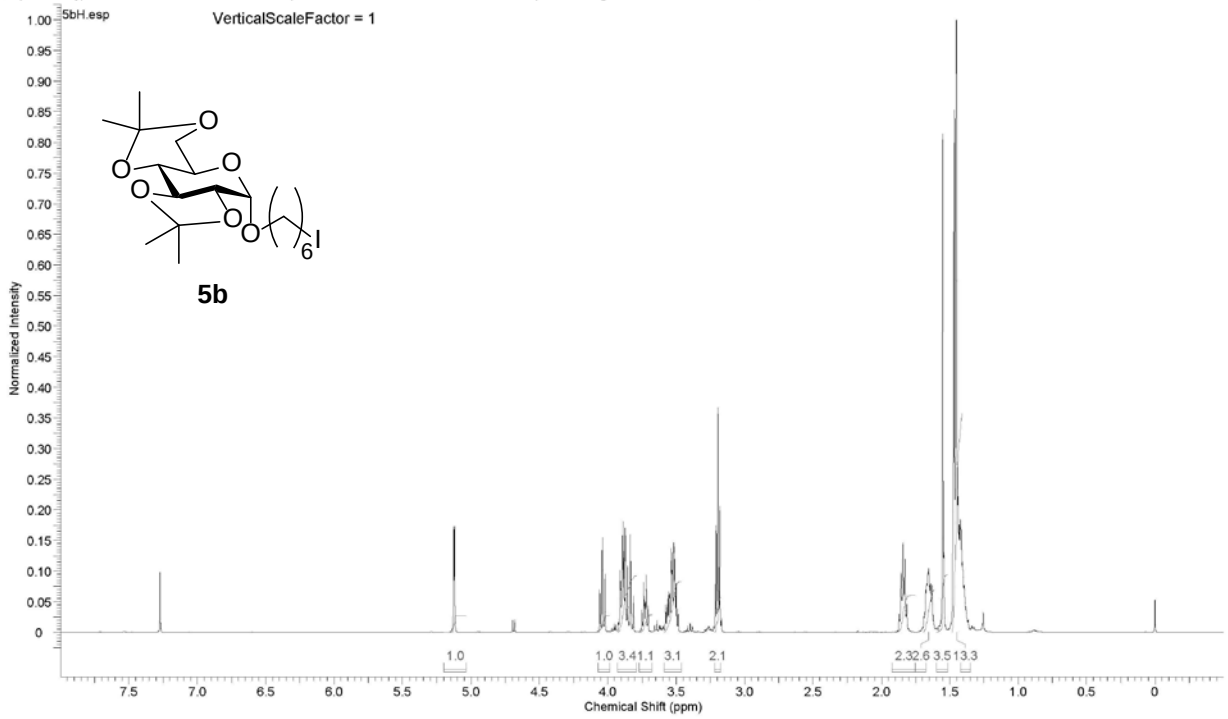
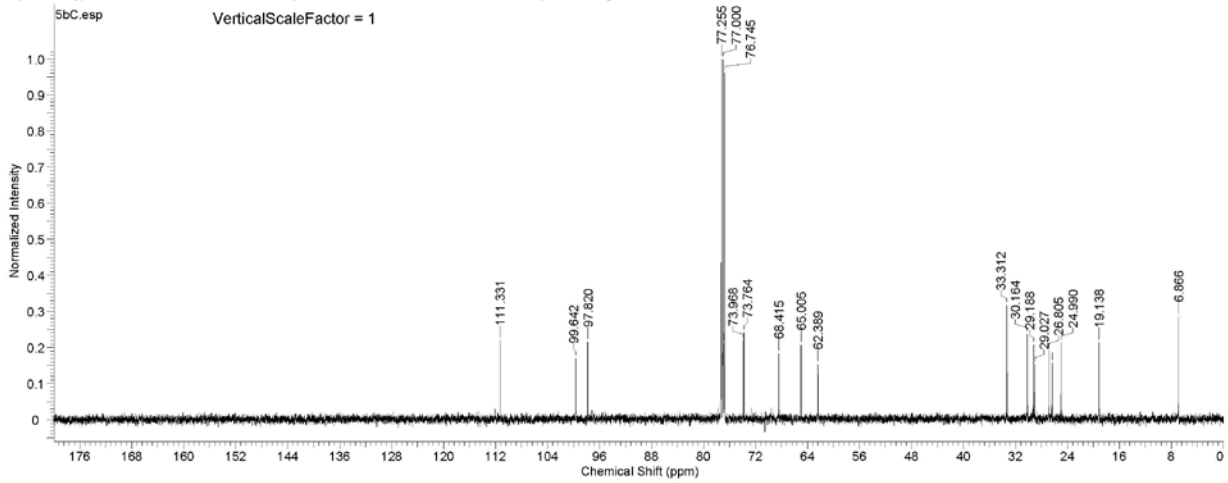
Acquisition Time (sec)	3.1719	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	14 Oct 2014 09:27:44
Date Stamp	14 Oct 2014 09:27:44			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_05b¥ckhs4-122-500MHzNMR¥H¥pdata¥1¥1r		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	40.30	*SW(cyclical) (Hz)*	10330.58	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	3993.9248
Spectrum Type	STANDARD	*Sweep Width (Hz)*	10330.26	*Temperature (degree C)*	26.400		



5b

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

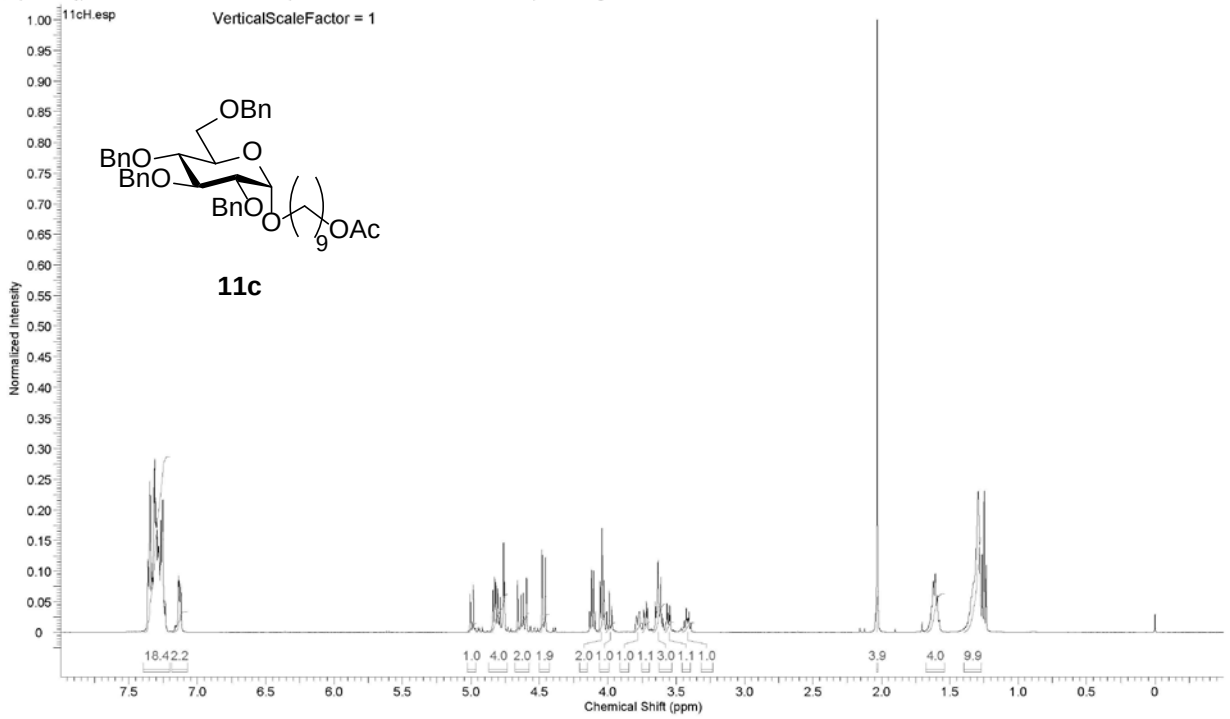
Acquisition Time (sec)	1.0912	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	14 Oct 2014 09:29:52
Date Stamp	14 Oct 2014 09:29:52			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_05b¥ckhs4-122-500MHzNMR¥C¥pdata¥1¥1r		
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	240	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	5792.60	*SW(cyclical) (Hz)*	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13827.9668
Spectrum Type	STANDARD	*Sweep Width (Hz)*	30029.11	*Temperature (degree C)*	26.400		



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	6.87	863.5	5	26.80	3370.9	9	33.31	4189.3	13	73.76	9276.4	17	77.00	9683.3	21	111.33	14000.7
2	19.14	2406.8	6	29.03	3650.4	10	62.39	7845.9	14	73.97	9302.1	18	77.26	9715.4			
3	24.99	3142.7	7	29.19	3670.6	11	65.00	8174.9	15	76.74	9651.3	19	97.82	12301.6			
4	26.35	3313.1	8	30.16	3793.4	12	68.42	8603.8	16	76.87	9666.9	20	99.64	12530.7			

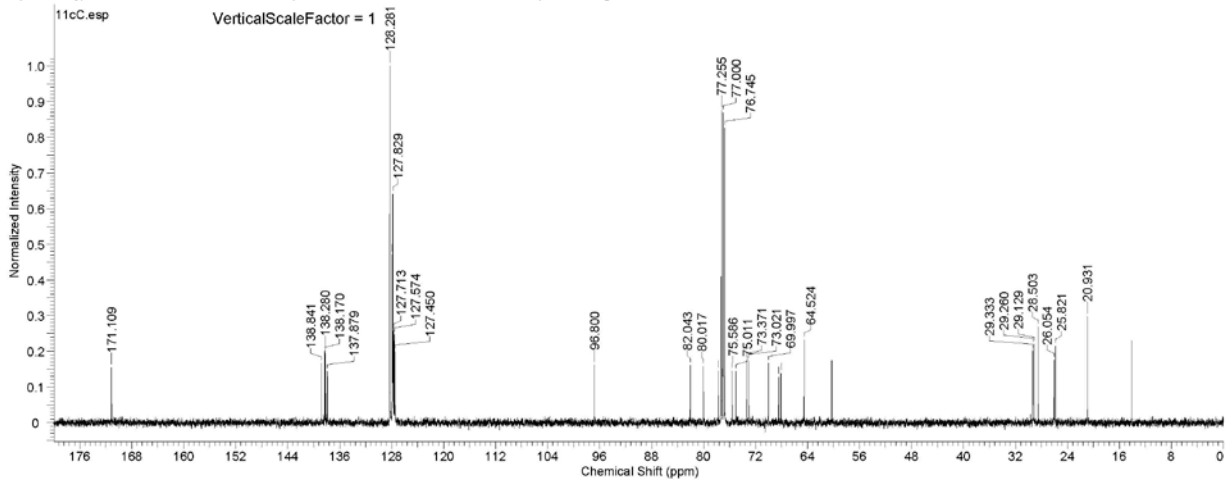
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.1719	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	09 Dec 2014 10:10:24
Date Stamp	09 Dec 2014 10:10:24			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_11c¥ckhs4-133-500MHz¥H¥pdata¥1¥1r		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	22.60	*SW(cyclical) (Hz)*	10330.58	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	3975.0090
Spectrum Type	STANDARD	*Sweep Width (Hz)*	10330.26	*Temperature (degree C)*	23.600		

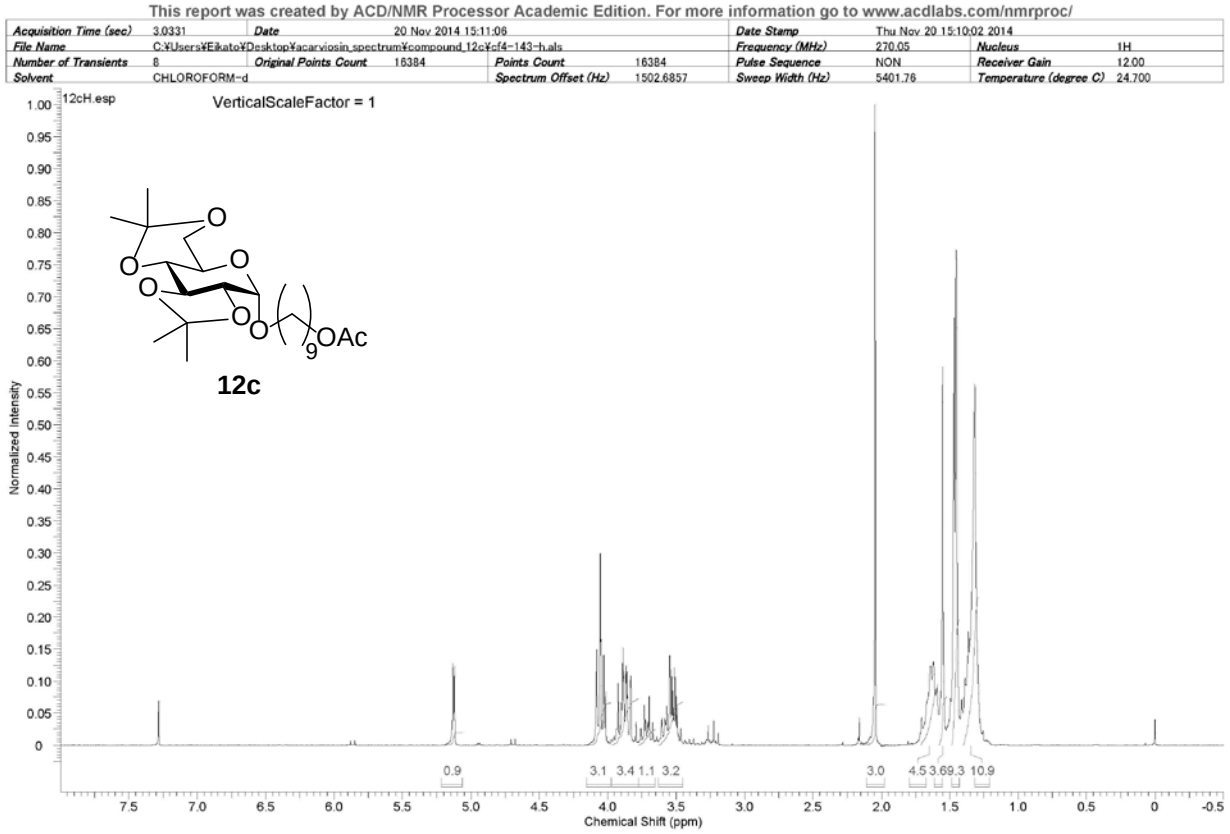


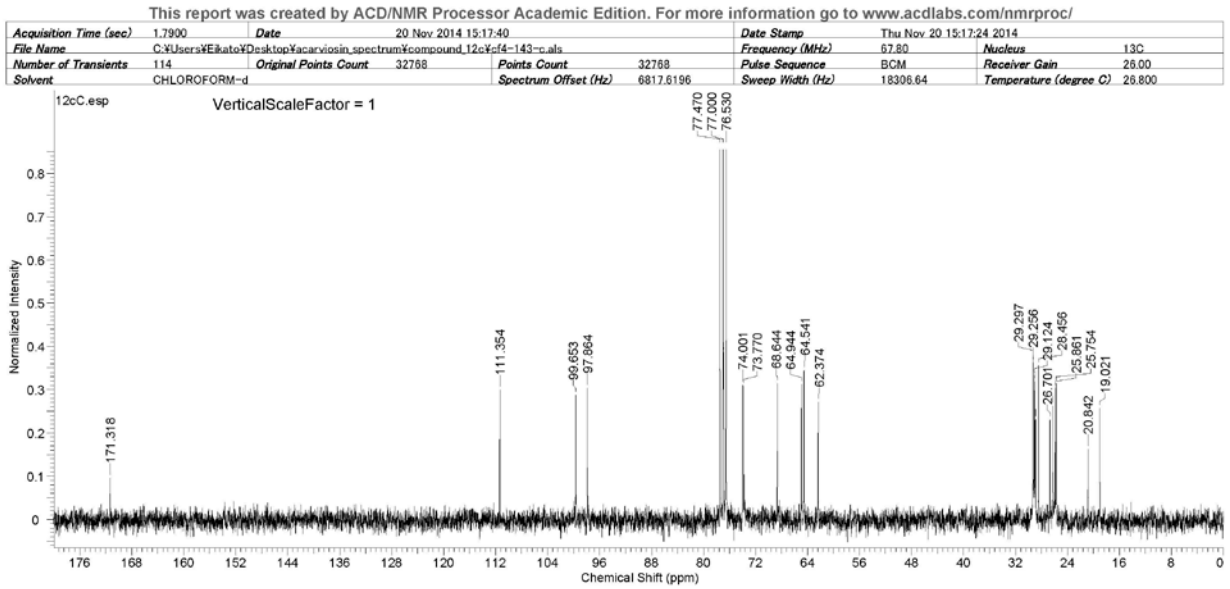
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.0912	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	09 Dec 2014 10:12:32
Date Stamp	09 Dec 2014 10:12:32			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_11c¥ckhs4-133-500MHz¥C¥pdata¥1¥1r		
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	256	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	20642.50	*SW(cyclical) (Hz)*	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13816.9697
Spectrum Type	STANDARD	*Sweep Width (Hz)*	30029.11	*Temperature (degree C)*	23.600		

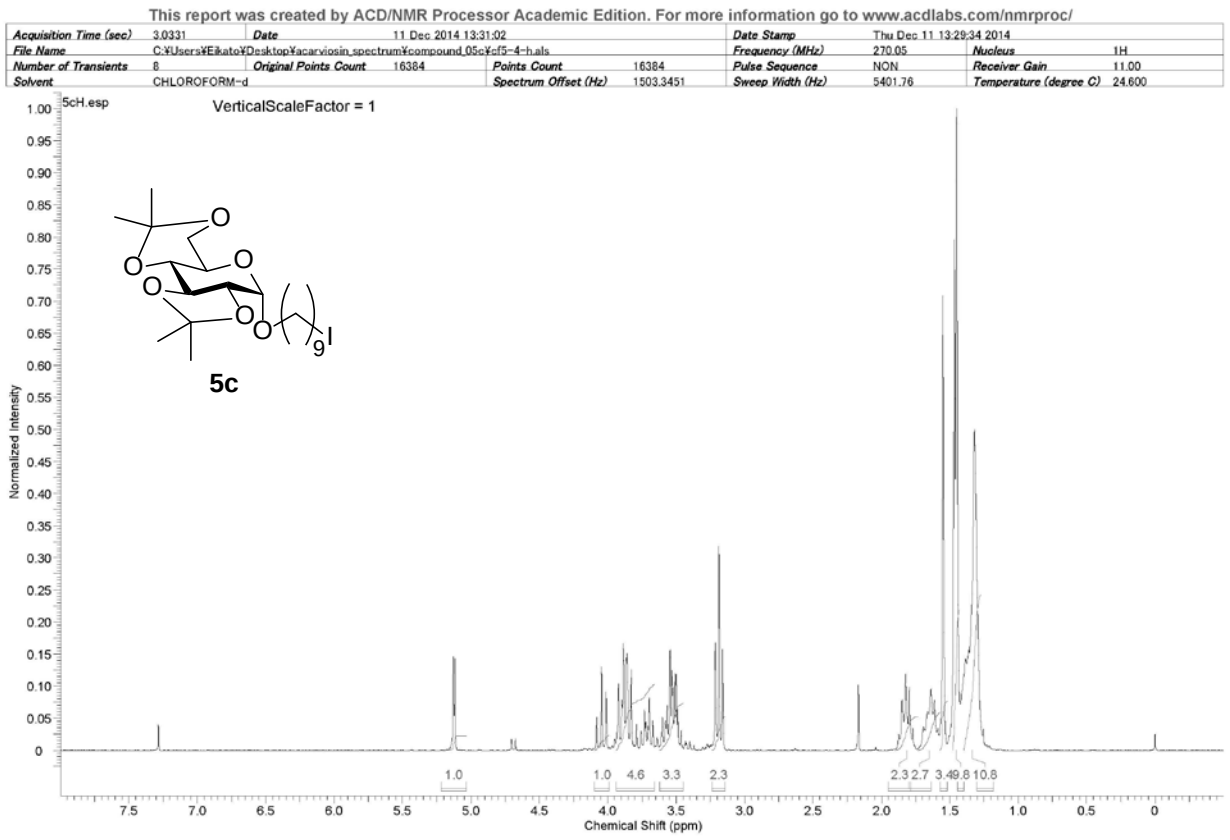


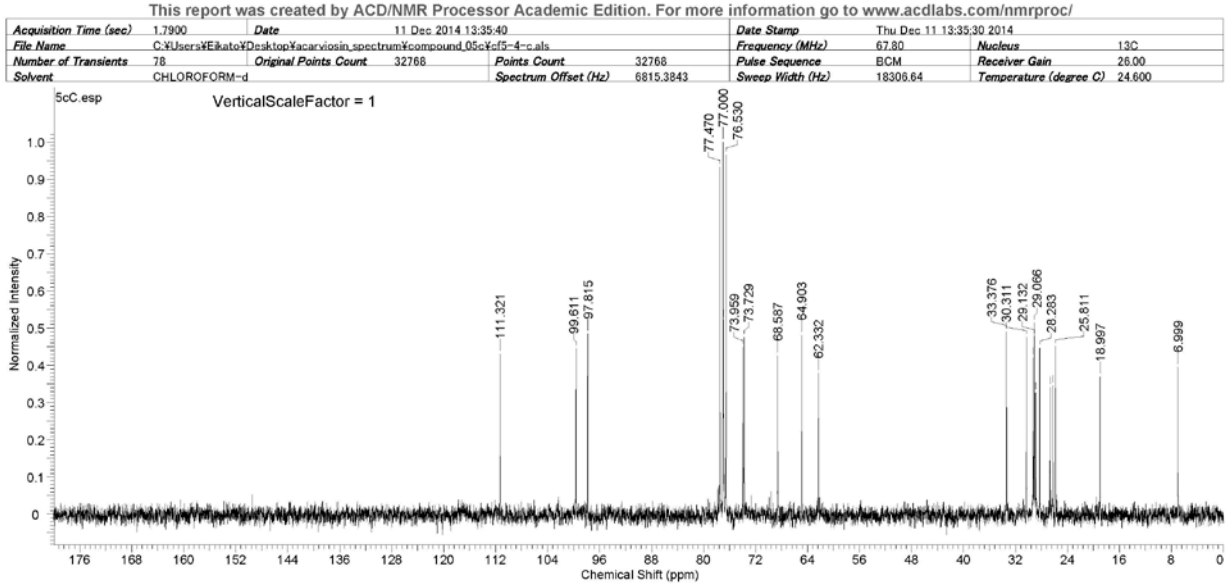
No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	20.93	2632.2	8	29.30	3685.2	15	73.37	9227.0	22	80.02	10062.8	29	127.80	16071.9	36	137.88	17339.3
2	20.95	2635.0	9	29.33	3688.9	16	75.01	9433.2	23	82.04	10317.5	30	127.83	16075.5	37	138.17	17376.0
3	25.82	3247.2	10	64.52	8114.4	17	75.59	9505.6	24	96.80	12173.3	31	127.86	16079.2	38	138.28	17389.7
4	26.05	3276.5	11	68.10	8564.4	18	76.74	9651.3	25	127.45	16027.9	32	127.92	16087.5	39	138.84	17460.3
5	28.50	3584.4	12	68.44	8606.5	19	77.00	9683.3	26	127.57	16043.5	33	128.25	16128.7	40	171.11	21518.3
6	29.13	3663.2	13	70.00	8802.6	20	77.26	9715.4	27	127.60	16047.1	34	128.28	16132.4			
7	29.26	3679.7	14	73.02	9183.0	21	77.69	9769.5	28	127.71	16060.9	35	128.30	16135.1			





No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	19.02	1289.6	6	26.70	1810.3	11	29.26	1983.5	16	68.64	4654.1	21	77.00	5220.6	26	171.32	11615.4
2	20.84	1413.1	7	28.46	1929.4	12	29.30	1986.3	17	73.77	5001.6	22	77.47	5252.4			
3	25.75	1746.1	8	28.93	1961.2	13	62.37	4228.9	18	74.00	5017.2	23	97.86	6635.2			
4	25.86	1753.4	9	29.03	1968.5	14	64.54	4375.9	19	76.53	5188.8	24	99.65	6756.4			
5	26.21	1776.8	10	29.12	1974.6	15	64.94	4403.2	20	76.92	5215.0	25	111.35	7549.8			





No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	7.00	474.5	5	26.68	1809.2	9	29.13	1975.2	13	62.33	4226.1	17	73.96	5014.4	21	77.47	5252.4
2	19.00	1288.0	6	28.28	1917.6	10	29.26	1983.5	14	64.90	4400.4	18	76.53	5188.8	22	97.81	6631.9
3	25.81	1750.0	7	28.92	1960.6	11	30.31	2055.1	15	68.59	4650.2	19	76.88	5212.2	23	99.61	6753.6
4	26.20	1776.3	8	29.07	1970.7	12	33.38	2262.9	16	73.73	4998.8	20	77.00	5220.6	24	111.32	7547.5

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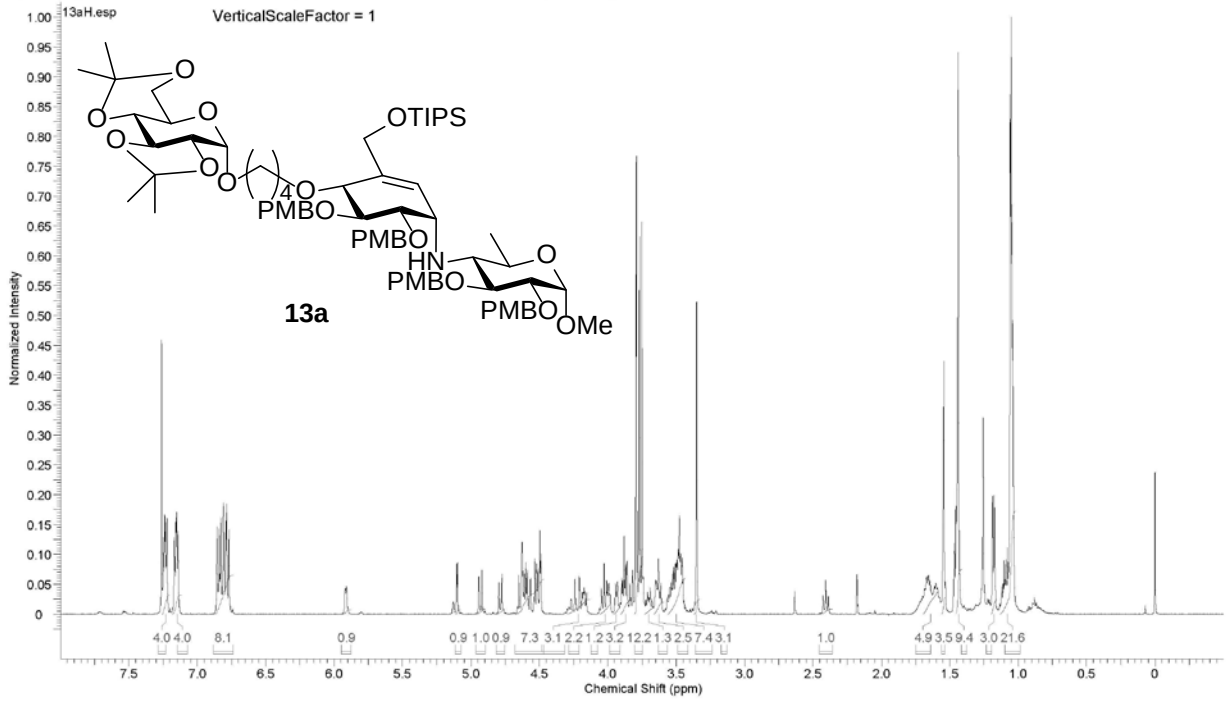
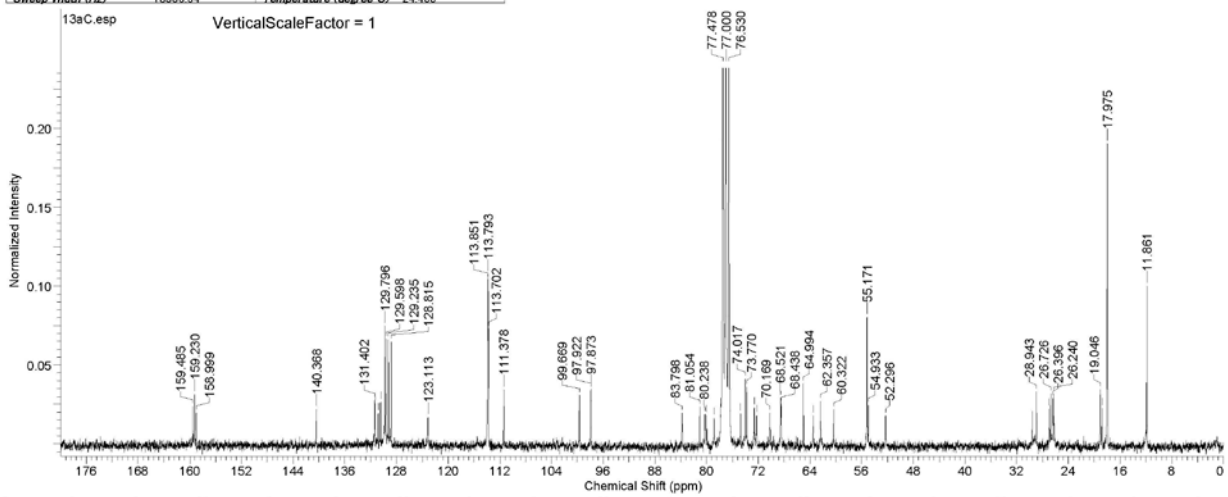
Acquisition Time (sec)	3.1719	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	09 Dec 2014 09:34:08
Date Stamp	09 Dec 2014 09:34:08						
File Name	D:¥[redacted]¥acarviosine_amylase¥acarviosin_spectrum¥compound_13a¥ckhs4-151-500MHzNMR¥H¥pdata¥1¥1r						
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	90.50	*SW(cyclical) (Hz)*	10330.58	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	3988.5652
Spectrum Type	STANDARD	*Sweep Width (Hz)*	10330.26	*Temperature (degree C)*	23.500		



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.7900	*Date*	10 Dec 2014 08:47:08			*Date Stamp*	Wed Dec 10 08:46:31 2014
File Name	D:¥[redacted]¥acarviosine_amylase¥acarviosin_spectrum¥compound_13a¥cf4-151-c.als					*Frequency (MHz)*	67.80
Nucleus	13C	*Number of Transients*	16264	*Original Points Count*	32768	*Points Count*	32768
Pulse Sequence	BCM	*Receiver Gain*	26.00	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	6818.7368
Sweep Width (Hz)	18306.64	*Temperature (degree C)*	24.400				



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	11.86	804.1	11	54.93	3724.4	21	72.61	4922.8	31	81.05	5495.5	41	123.11	8347.0	51	159.00	10780.1
2	17.97	1218.7	12	55.17	3740.6	22	73.77	5001.6	32	83.80	5681.5	42	128.81	8733.7	52	159.23	10795.8
3	18.78	1273.4	13	60.32	4089.8	23	74.02	5018.4	33	97.87	6635.8	43	129.24	8762.1	53	159.49	10813.1
4	19.05	1291.3	14	62.36	4227.8	24	74.73	5067.0	34	97.92	6639.1	44	129.60	8786.7			
5	26.24	1779.1	15	63.47	4303.2	25	76.53	5188.8	35	99.67	6757.6	45	129.80	8800.1			
6	26.40	1789.7	16	64.99	4406.6	26	77.00	5220.6	36	111.38	7551.5	46	130.46	8845.4			
7	26.73	1812.0	17	68.44	4640.1	27	77.48	5253.0	37	113.70	7709.0	47	130.81	8868.9			
8	26.96	1827.7	18	68.52	4645.7	28	78.82	5344.1	38	113.78	7714.0	48	131.34	8904.6			
9	28.94	1962.3	19	70.17	4757.4	29	79.97	5422.3	39	113.79	7715.2	49	131.40	8909.1			
10	52.30	3545.6	20	72.26	4899.4	30	80.24	5440.2	40	113.85	7719.1	50	140.37	9516.9			

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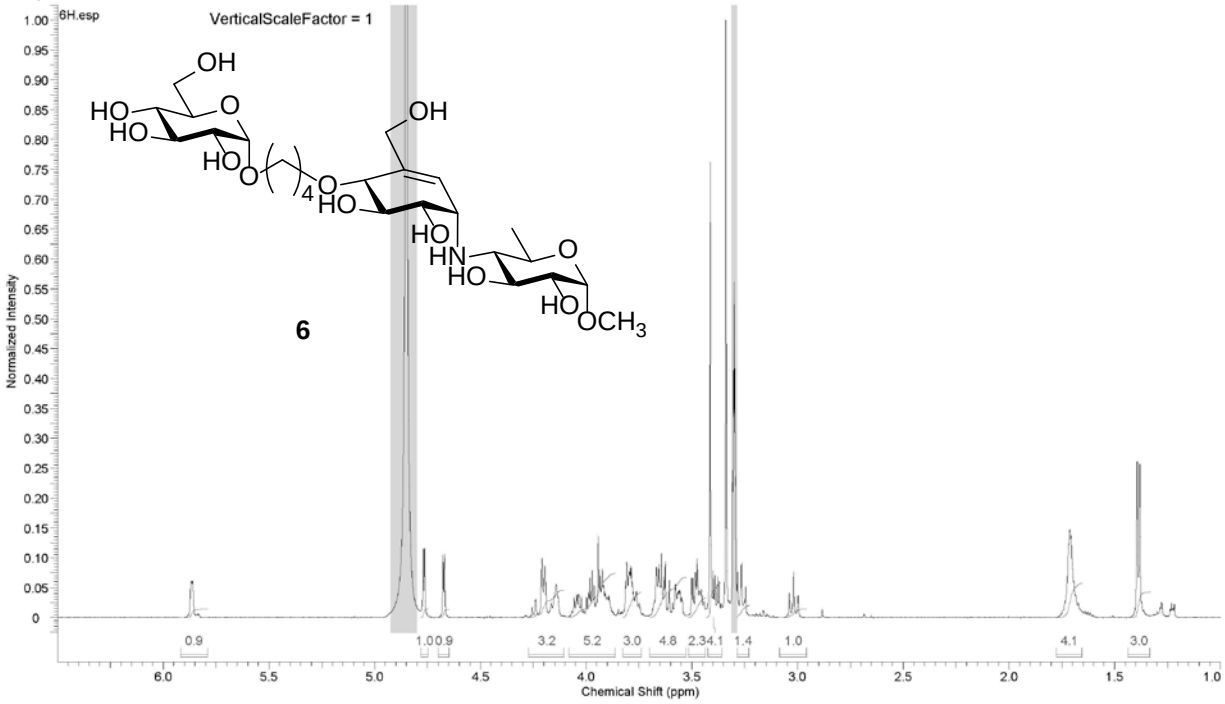
Acquisition Time (sec)	3.1719	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	24 Dec 2014 11:20:48
Date Stamp	24 Dec 2014 11:20:48						
File Name	C:¥USERS¥EIKATO¥DESKTOP¥ACARVIOSIN_SPECTRUM¥COMPOUND_06¥CF5-6 (500MHZ)¥H¥PDATA¥1¥1R					*Frequency (MHz)*	500.13
Nucleus	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	181.00
SW(cyclical) (Hz)	10330.58	*Solvent*	METHANOL-d4	*Spectrum Offset (Hz)*	3985.4333	*Spectrum Type*	STANDARD
Sweep Width (Hz)	10330.26						



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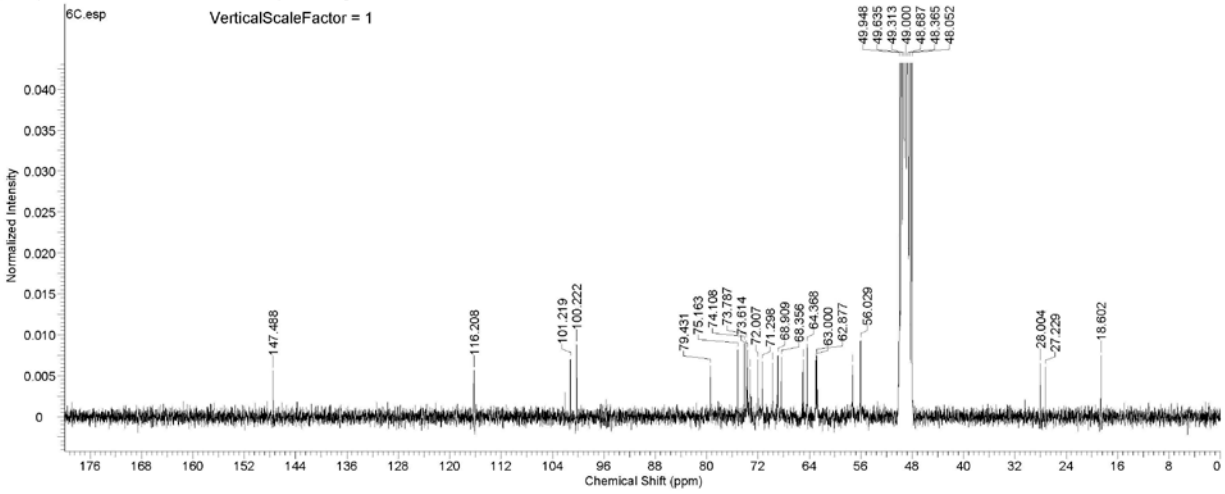
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

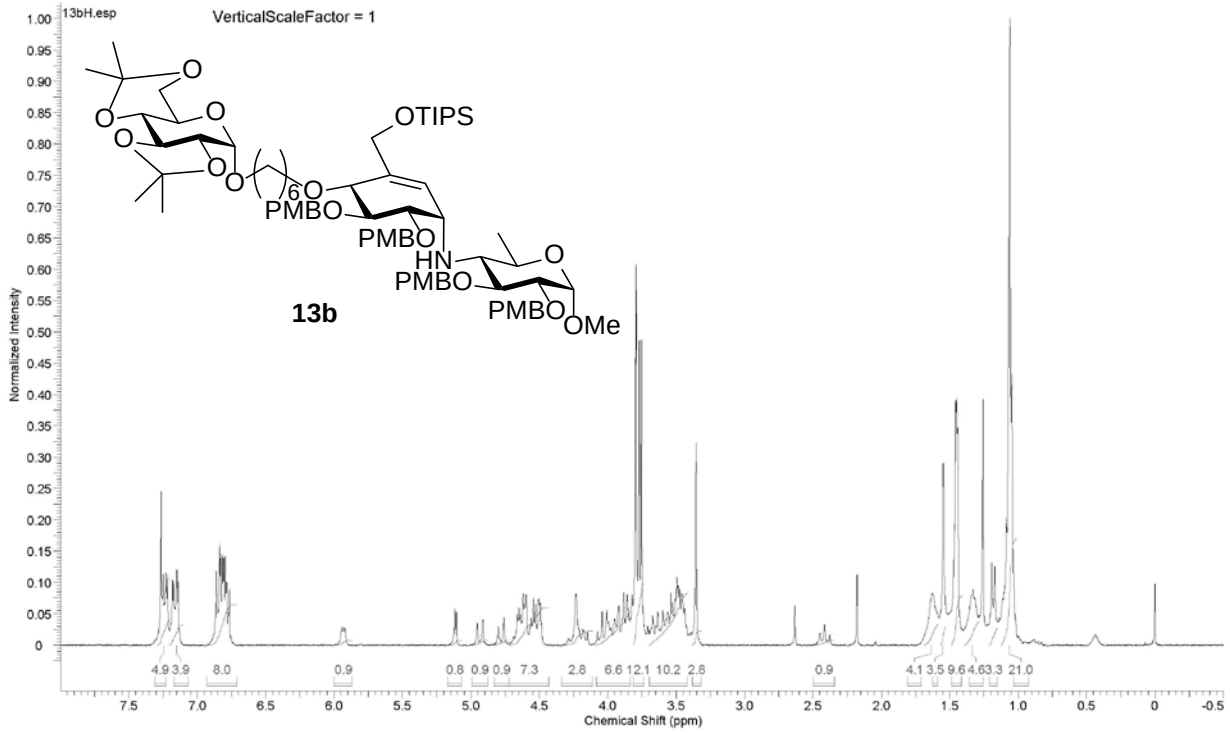
Acquisition Time (sec)	1.7900	*Date*	17 Dec 2014 08:56:06			*Date Stamp*	Wed Dec 17 08:55:33 2014
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_06¥cf5-6-c (270 MHz).als					*Frequency (MHz)*	67.80
Nucleus	13C	*Number of Transients*	15980	*Original Points Count*	32768	*Points Count*	32768
Pulse Sequence	BCM	*Receiver Gain*	26.00	*Solvent*	METHANOL-d4	*Spectrum Offset (Hz)*	6919.8926
Sweep Width (Hz)	18306.64	*Temperature (degree C)*	24.700				



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	18.60	1261.2	7	49.00	3322.2	13	62.88	4263.0	19	69.69	4725.1	25	74.11	5024.5	31	147.49	9999.7
2	27.23	1846.1	8	49.31	3343.4	14	63.00	4271.4	20	71.30	4834.0	26	75.16	5096.0			
3	28.00	1898.7	9	49.63	3365.2	15	64.37	4364.2	21	72.01	4882.1	27	79.43	5385.4			
4	48.05	3258.0	10	49.95	3386.4	16	64.99	4406.6	22	73.19	4962.5	28	100.22	6795.0			
5	48.37	3279.2	11	56.03	3798.8	17	68.36	4634.6	23	73.61	4991.0	29	101.22	6862.6			
6	48.69	3301.0	12	57.26	3882.0	18	68.91	4672.0	24	73.79	5002.7	30	116.21	7878.9			

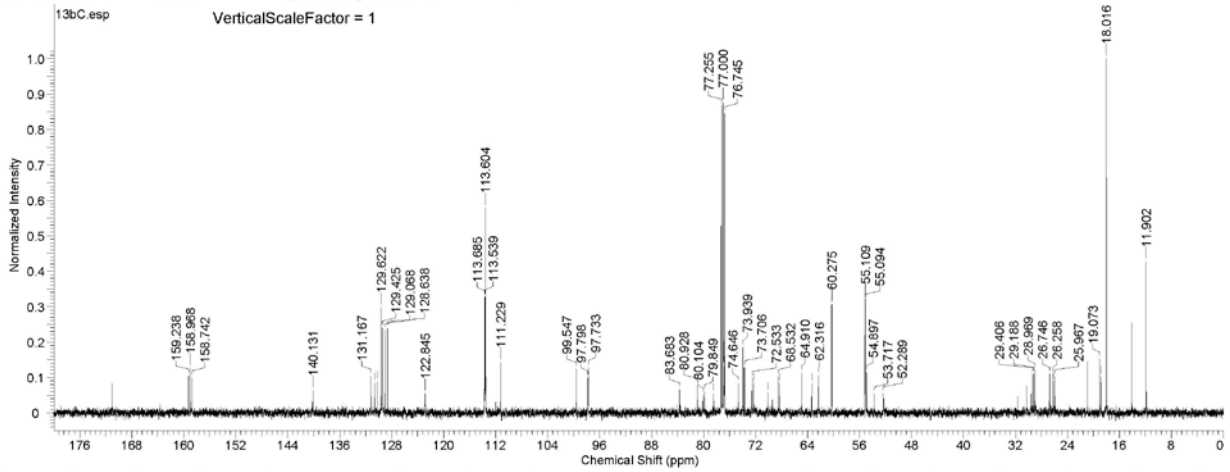
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.0331	*Date*	10 Dec 2014 14:34:16			*Date Stamp*	Wed Dec 10 14:33:30 2014
File Name	D:¥[illegible]¥acarviosine_amylase¥acarviosin_spectrum¥compound_13b¥cf5-2-h.als					*Frequency (MHz)*	270.05
Nucleus	1H	*Number of Transients*	8	*Original Points Count*	16384	*Points Count*	16384
Pulse Sequence	NON	*Receiver Gain*	17.00	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	1498.3994	*Sweep Width (Hz)*	5401.76	*Temperature (degree C)*	24.100		



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

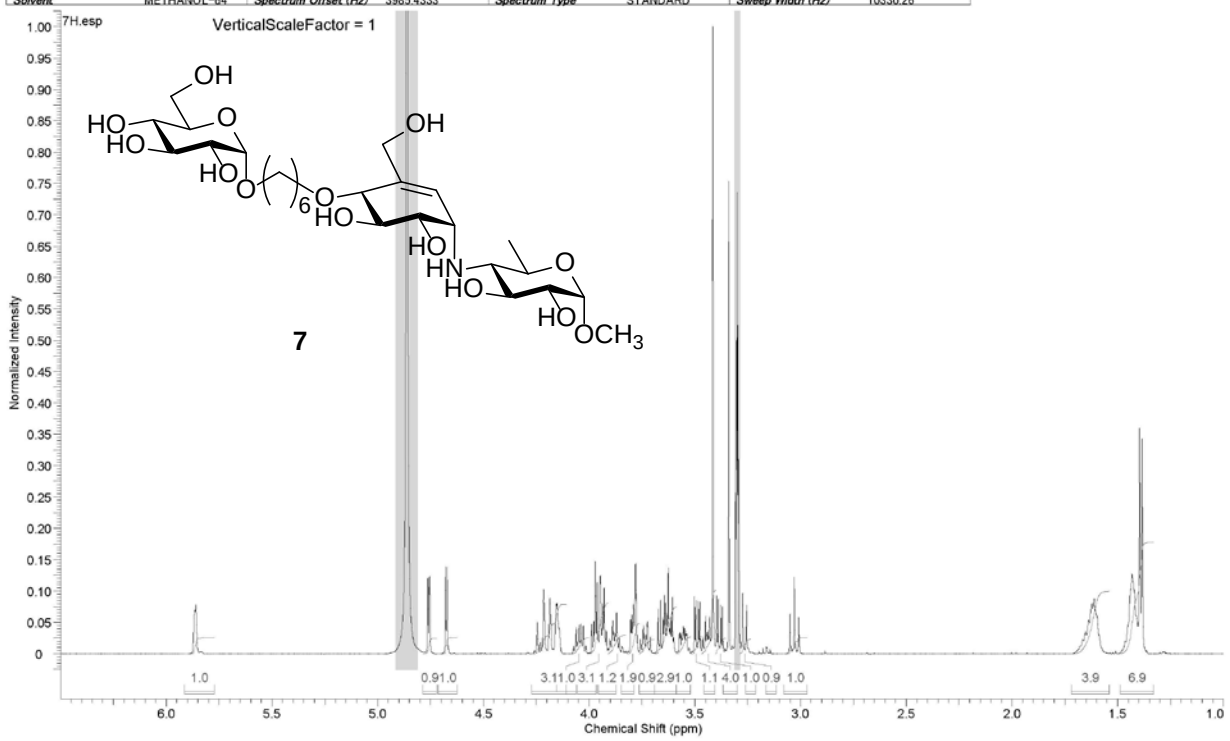
Acquisition Time (sec)	1.0912	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	16 Dec 2014 09:12:48
Date Stamp	16 Dec 2014 09:12:48						
File Name	D:¥[illegible]¥acarviosine_amylase¥acarviosin_spectrum¥compound_13b¥ckhs5-2-500MHzNMR¥C¥pdata¥1¥1r					*Frequency (MHz)*	125.76
Nucleus	13C	*Number of Transients*	512	*Origin*	spect	*Original Points Count*	32768
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	5160.60
SW(cyclical) (Hz)	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13821.5527	*Spectrum Type*	STANDARD
Sweep Width (Hz)	30029.11	*Temperature (degree C)*	24.700				



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	11.90	1496.8	12	52.29	6575.7	23	68.36	8596.4	34	77.26	9715.4	45	113.60	14286.6	56	140.13	17622.5
2	18.02	2265.7	13	53.72	6755.3	24	68.53	8618.4	35	78.44	9864.8	46	113.68	14296.7	57	158.74	19963.1
3	18.83	2368.3	14	54.90	6903.8	25	70.07	8811.8	36	79.85	10041.7	47	122.84	15448.7	58	158.97	19991.5
4	19.07	2398.5	15	55.09	6928.5	26	72.21	9081.2	37	80.10	10073.8	48	128.64	16177.3	59	158.98	19993.3
5	25.97	3265.5	16	55.11	6930.4	27	72.53	9121.6	38	80.93	10177.3	49	129.07	16231.3	60	159.24	20025.4
6	26.11	3283.8	17	55.12	6932.2	28	73.71	9269.1	39	83.68	10523.7	50	129.43	16276.2			
7	26.26	3302.2	18	55.15	6935.9	29	73.94	9298.4	40	97.73	12290.6	51	129.62	16301.0			
8	26.75	3363.6	19	60.28	7580.1	30	74.65	9387.3	41	97.80	12298.9	52	130.26	16380.7			
9	28.97	3643.1	20	62.32	7836.7	31	76.74	9651.3	42	99.55	12518.8	53	130.64	16429.3			
10	29.19	3670.6	21	63.36	7967.8	32	76.85	9664.1	43	111.23	13987.9	54	131.17	16495.3			
11	29.41	3698.1	22	64.91	8163.0	33	77.00	9683.4	44	113.54	14278.4	55	131.20	16498.9			

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.1719	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	24 Dec 2014 10:46:40				
Date Stamp	24 Dec 2014 10:46:40			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_07¥ckhs5-8 (500MHz)¥1H¥pdata¥1¥1r						
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768		
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	181.00	*SW(cyclical) (Hz)*	10330.58		
Solvent	METHANOL-d4	*Spectrum Offset (Hz)*	3985.4333	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	10330.26				



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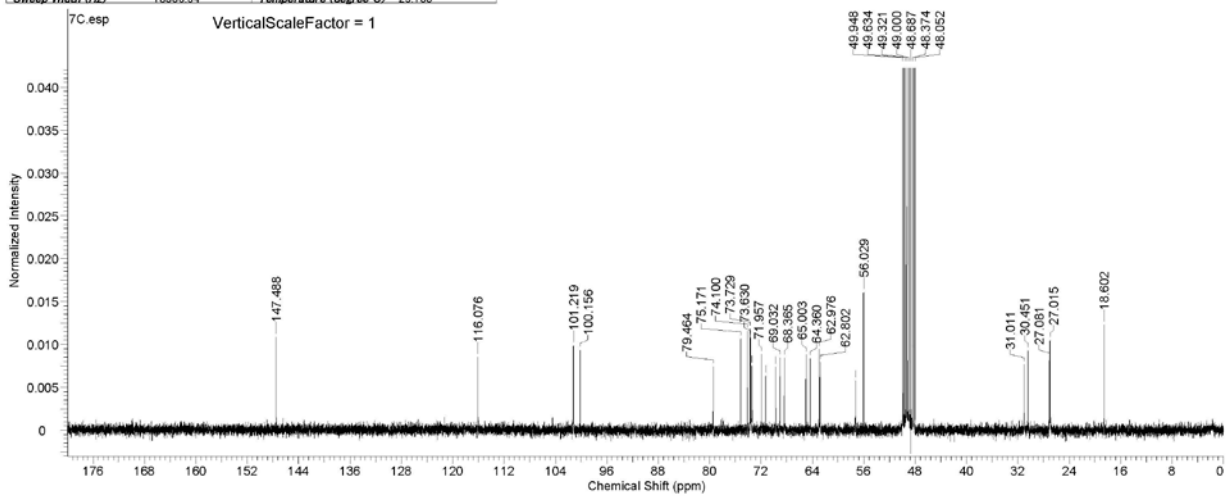
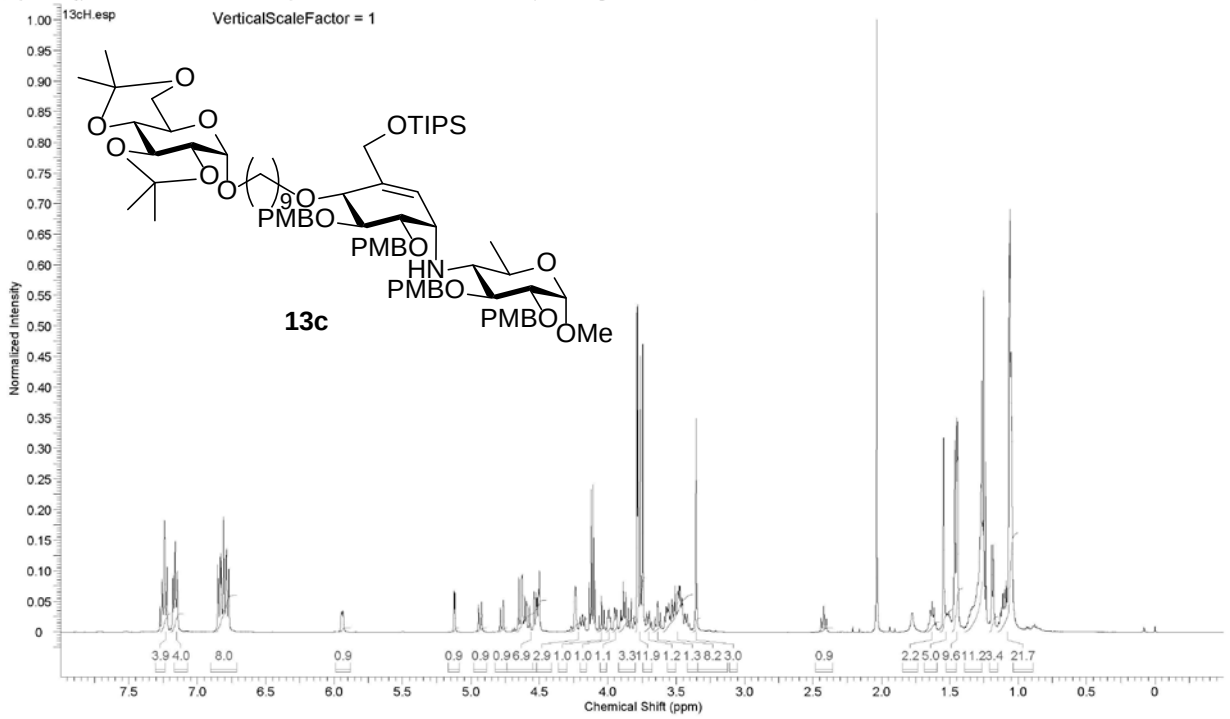
Acquisition Time (sec)	1.7900	*Date*	22 Dec 2014 08:45:54			*Date Stamp*	Mon Dec 22 08:44:17 2014		
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_07¥cf5-8-c-270MHz.als					*Frequency (MHz)*	67.80		
Nucleus	13C	*Number of Transients*	16166	*Original Points Count*	32768	*Points Count*	32768		
Pulse Sequence	BCM	*Receiver Gain*	26.00	*Solvent*	METHANOL-d4	*Spectrum Offset (Hz)*	6920.4512		
Sweep Width (Hz)	18306.64	*Temperature (degree C)*	25.100						



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	18.60	1261.2	7	48.37	3279.7	13	56.03	3798.8	19	68.36	4635.1	25	73.63	4992.1	31	101.22	6862.6
2	27.01	1831.6	8	48.69	3301.0	14	57.28	3883.7	20	69.03	4680.4	26	73.73	4998.8	32	116.08	7869.9
3	27.08	1836.1	9	49.00	3322.2	15	62.80	4258.0	21	69.68	4724.5	27	74.10	5024.0	33	147.49	9999.7
4	30.45	2064.6	10	49.32	3344.0	16	62.98	4269.7	22	71.27	4831.8	28	75.17	5096.6			
5	31.01	2102.6	11	49.63	3365.2	17	64.36	4363.6	23	71.96	4878.7	29	79.46	5387.7			
6	48.05	3258.0	12	49.95	3386.4	18	65.00	4407.2	24	73.41	4977.0	30	100.16	6790.6			

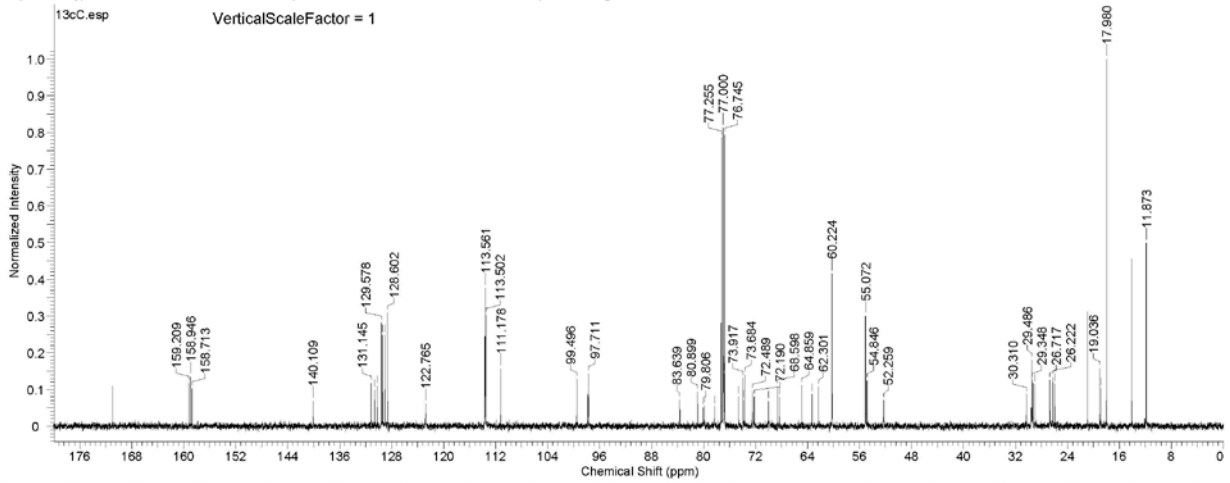
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.1719	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	16 Dec 2014 10:12:32
Date Stamp	16 Dec 2014 10:12:32			*File Name*	D:¥[illegible]¥acarviosine_amylase¥acarviosin_spectrum¥compound_13c¥ckhs5-7¥1H¥pdata¥1¥1r		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	18.00	*SW(cyclical) (Hz)*	10330.58	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	3994.8706
Spectrum Type	STANDARD	*Sweep Width (Hz)*	10330.26	*Temperature (degree C)*	24.600		

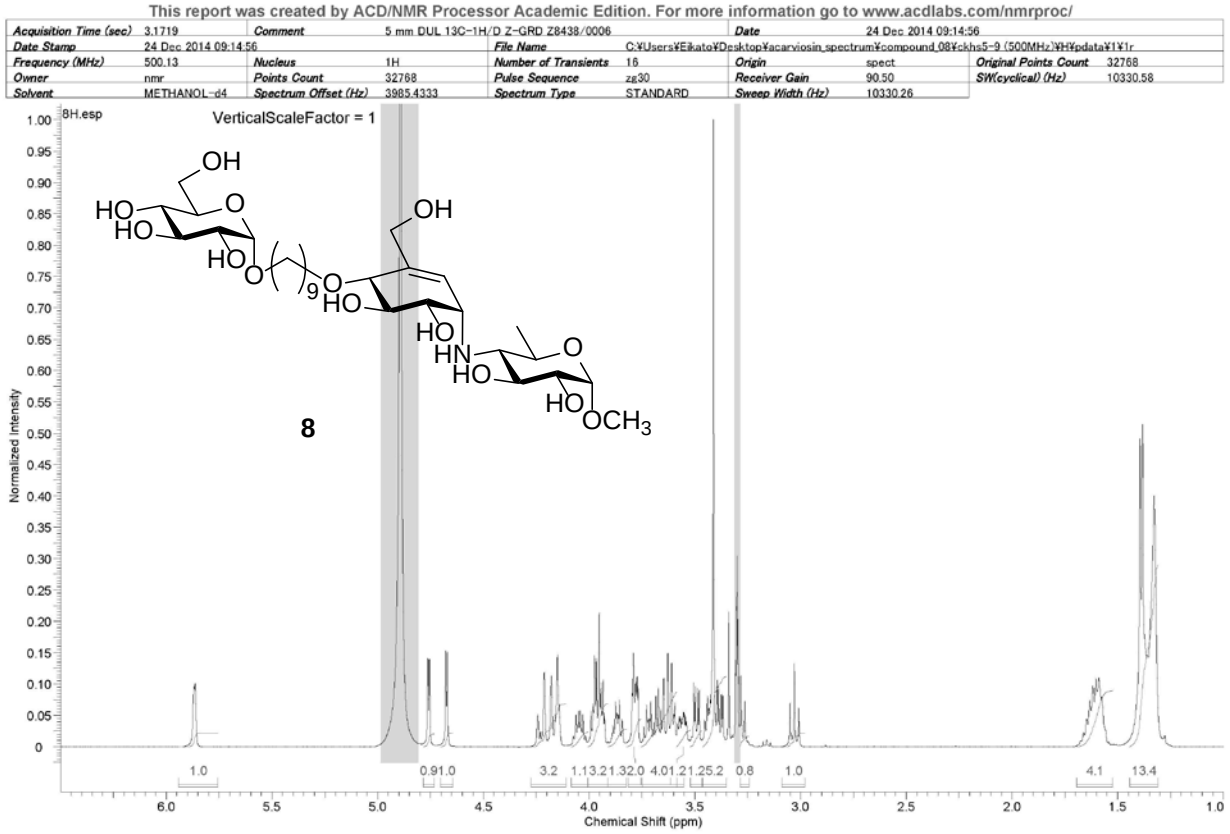


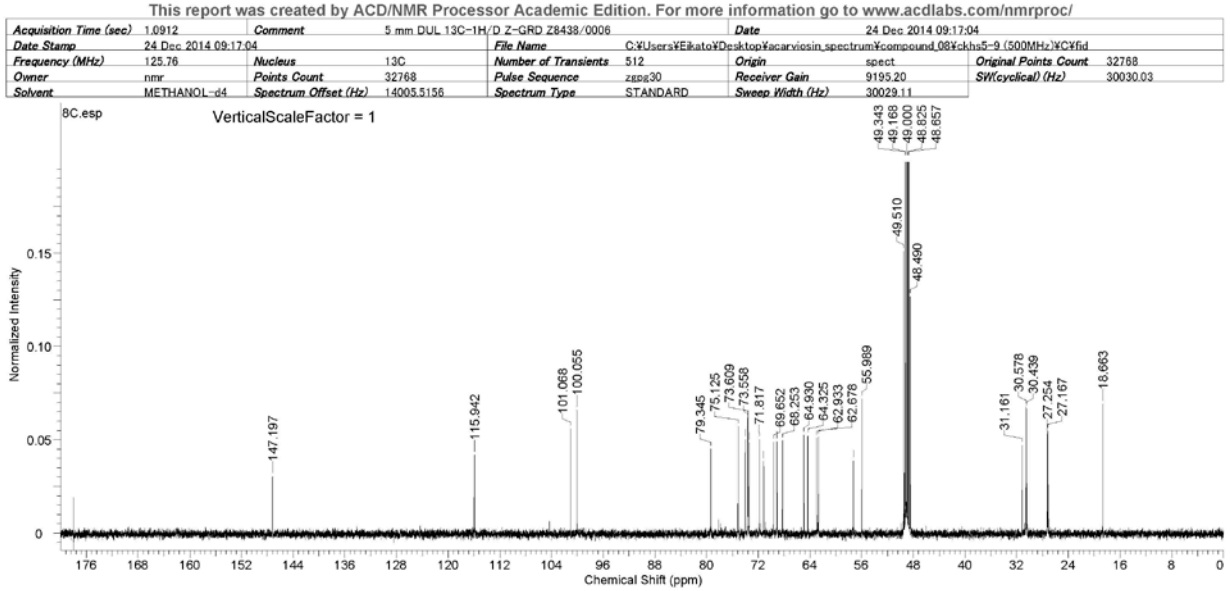
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.0912	*Comment*	5 mm TXI 1H/D-13C/15N Z-GRD Z8161/37			*Date*	16 Dec 2014 10:14:40
Date Stamp	16 Dec 2014 10:14:40			*File Name*	D:¥[illegible]¥acarviosine_amylase¥acarviosin_spectrum¥compound_13c¥ckhs5-7¥1C¥pdata¥1¥1r		
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	512	*Origin*	spect
Original Points Count	32768	*Owner*	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	4096.00	*SW(cyclical) (Hz)*	30030.03	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13817.8857
Spectrum Type	STANDARD	*Sweep Width (Hz)*	30029.11	*Temperature (degree C)*	24.800		



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	11.87	1493.1	12	29.49	3708.1	23	64.86	8156.6	34	76.83	9662.3	45	111.18	13981.5	56	131.15	16492.5
2	17.98	2261.1	13	30.31	3811.7	24	68.32	8591.9	35	77.00	9683.3	46	113.50	14273.8	57	131.17	16495.3
3	18.80	2363.7	14	52.26	6572.0	25	68.60	8626.7	36	77.26	9715.4	47	113.56	14281.1	58	140.11	17619.8
4	19.04	2394.0	15	54.85	6897.4	26	70.00	8802.6	37	78.30	9846.5	48	113.64	14291.2	59	158.71	19959.4
5	25.94	3262.7	16	55.04	6922.1	27	72.19	9078.5	38	79.81	10036.2	49	122.76	15438.6	60	158.93	19986.9
6	26.22	3297.6	17	55.06	6923.9	28	72.49	9116.1	39	80.06	10068.3	50	128.60	16172.7	61	158.95	19988.8
7	26.24	3300.3	18	55.07	6925.8	29	73.68	9266.4	40	80.90	10173.6	51	129.04	16227.7	62	159.21	20021.8
8	26.72	3359.9	19	55.09	6928.5	30	73.88	9291.1	41	83.64	10518.2	52	129.41	16274.4			
9	28.93	3638.5	20	60.22	7573.7	31	73.92	9295.7	42	97.71	12287.9	53	129.58	16295.5			
10	29.27	3681.6	21	62.30	7834.9	32	74.60	9381.8	43	97.76	12294.3	54	130.22	16376.1			
11	29.35	3690.7	22	63.31	7962.3	33	76.74	9651.3	44	99.50	12512.4	55	130.62	16426.5			





No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	18.66	2347.0	7	31.16	3918.7	13	49.34	6205.2	19	64.33	8089.4	25	71.82	9031.5	31	79.34	9978.2
2	27.17	3416.5	8	48.49	6098.0	14	49.51	6226.3	20	64.93	8165.5	26	73.41	9231.3	32	100.06	12582.7
3	27.25	3427.5	9	48.66	6119.1	15	55.99	7041.0	21	68.25	8583.4	27	73.56	9250.5	33	101.07	12710.1
4	30.42	3825.2	10	48.83	6140.1	16	57.29	7204.1	22	69.10	8689.7	28	73.61	9257.0	34	115.94	14580.6
5	30.44	3827.9	11	49.00	6162.1	17	62.68	7882.3	23	69.65	8759.3	29	74.01	9307.4	35	147.20	18511.2
6	30.58	3845.4	12	49.17	6183.2	18	62.93	7914.4	24	71.15	8948.1	30	75.13	9447.6			

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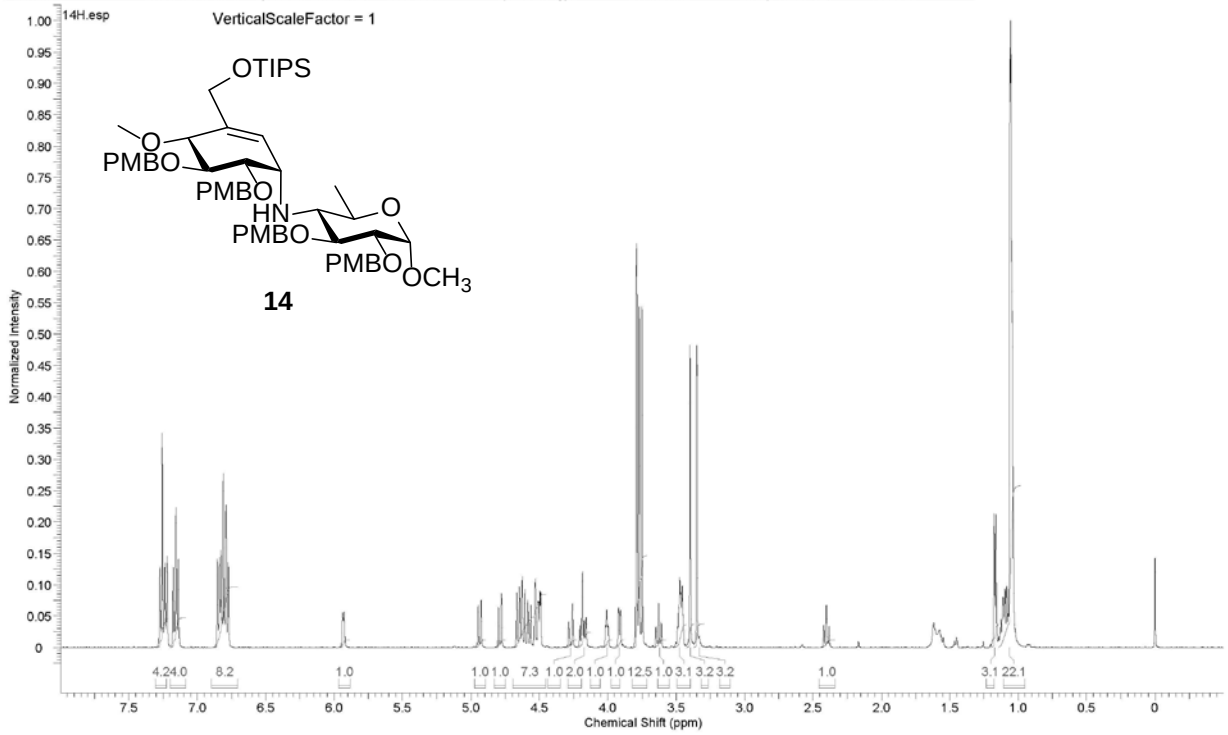
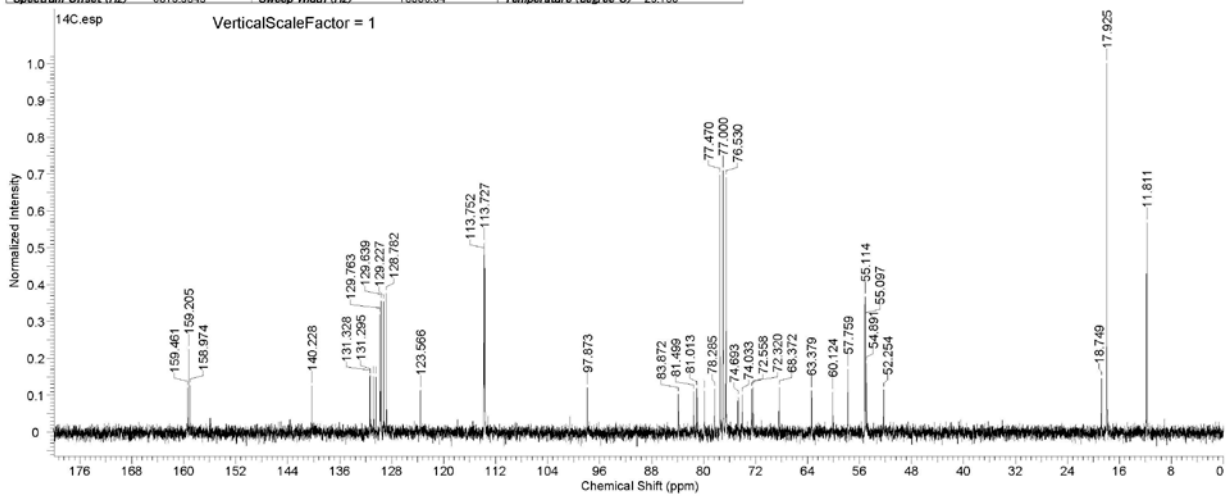
Acquisition Time (sec)	3.1719	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	20 Jan 2015 10:14:40				
Date Stamp	20 Jan 2015 10:14:40			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_14¥ckhs5-16 (500MHz)¥1¥pdata¥1¥1r						
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768		
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	161.30	*SW(cyclical) (Hz)*	10330.58		
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	3986.3584	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	10330.26				



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

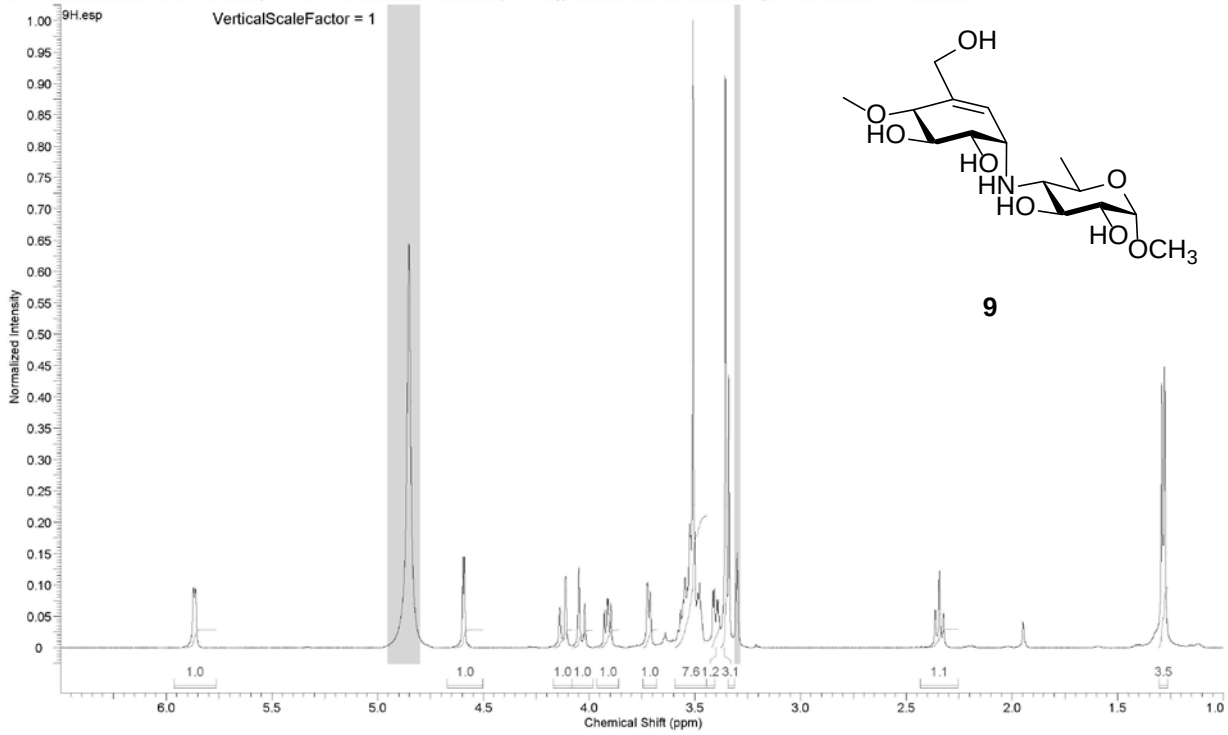
Acquisition Time (sec)	1.7900	*Date*	13 Jan 2015 19:27:20			*Date Stamp*	Tue Jan 13 19:27:08 2015
File Name	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_14¥cf5-16-c (270MHz).als					*Frequency (MHz)*	67.80
Nucleus	13C	*Number of Transients*	158	*Original Points Count*	32768	*Points Count*	32768
Pulse Sequence	BCM	*Receiver Gain*	26.00	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	6815.3843	*Sweep Width (Hz)*	18306.64	*Temperature (degree C)*	25.100		



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	11.81	800.8	9	55.16	3739.5	17	74.69	5064.2	25	83.87	5686.5	33	129.23	8761.6	41	158.97	10778.5
2	17.93	1215.3	10	57.76	3916.1	18	76.53	5188.8	26	97.87	6635.8	34	129.64	8789.5	42	159.21	10794.1
3	18.75	1271.2	11	60.12	4076.4	19	77.00	5220.6	27	113.68	7707.3	35	129.76	8797.9	43	159.46	10811.4
4	52.25	3542.9	12	63.38	4297.1	20	77.47	5252.4	28	113.73	7710.7	36	130.40	8840.9			
5	54.89	3721.6	13	68.37	4635.7	21	78.29	5307.8	29	113.75	7712.4	37	130.76	8865.5			
6	55.10	3735.6	14	72.32	4903.3	22	79.86	5414.5	30	113.81	7716.3	38	131.30	8901.8			
7	55.11	3736.7	15	72.56	4919.5	23	81.01	5492.7	31	123.57	8377.8	39	131.33	8904.1			
8	55.13	3737.8	16	74.03	5019.5	24	81.50	5525.6	32	128.78	8731.4	40	140.23	9507.4			

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	3.1719	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	20 Jan 2015 09:12:48				
Date Stamp	20 Jan 2015 09:12:48			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_09¥ckhs5-17 500MHz¥H¥pdata¥1¥1r						
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect	*Original Points Count*	32768		
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	114.00	*SW(cyclical) (Hz)*	10330.58		
Solvent	METHANOL-d4	*Spectrum Offset (Hz)*	3985.4333	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	10330.26				



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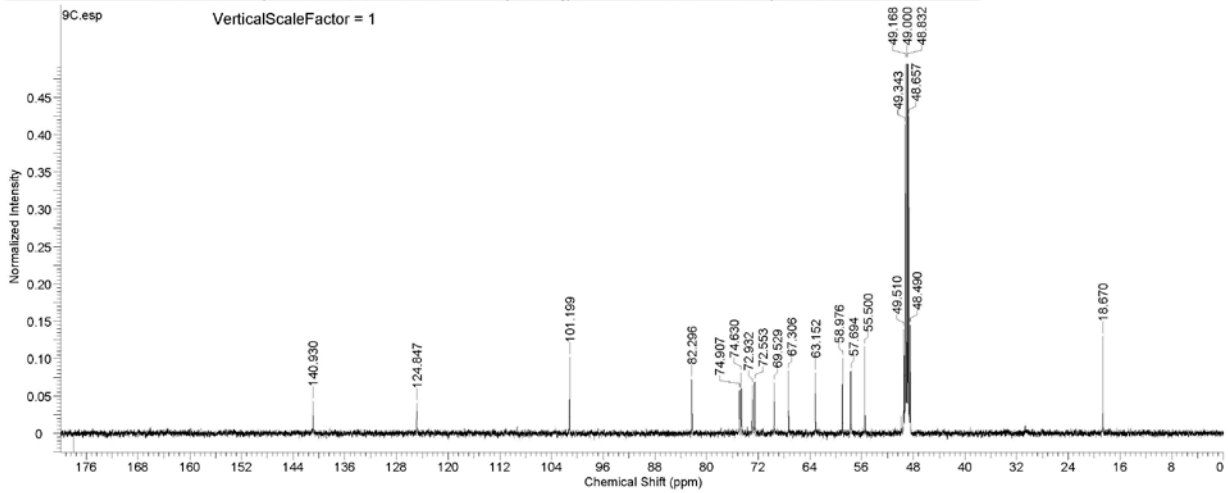
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Acquisition Time (sec)	1.0912	*Comment*	5 mm DUL 13C-1H/D Z-GRD Z8438/0006			*Date*	20 Jan 2015 09:17:04				
Date Stamp	20 Jan 2015 09:17:04			*File Name*	C:¥Users¥Eikato¥Desktop¥acarviosin_spectrum¥compound_09¥ckhs5-17 500MHz¥C¥pdata¥1¥1r						
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	512	*Origin*	spect	*Original Points Count*	32768		
Owner	nmr	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	5160.60	*SW(cyclical) (Hz)*	30030.03		
Solvent	METHANOL-d4	*Spectrum Offset (Hz)*	14006.4326	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	30029.11				



No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)	No.	(ppm)	(Hz)
1	18.67	2347.9	5	49.00	6162.1	9	55.50	6979.6	13	67.31	8464.2	17	74.63	9385.3	21	124.85	15700.5
2	48.49	6098.0	6	49.17	6183.2	10	57.69	7255.4	14	69.53	8743.8	18	74.91	9420.1	22	140.93	17723.1
3	48.66	6119.1	7	49.34	6205.2	11	58.98	7416.7	15	72.55	9124.1	19	82.30	10349.4			
4	48.83	6141.1	8	49.51	6226.3	12	63.15	7941.9	16	72.93	9171.7	20	101.20	12726.6			