Supplementary Information (SI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Total synthesis of Deinococcucins A-D and their isomeric derivatives *via* stereo- and regio-selective glycosylation: the discovery of a novel anti-angiogenic agent

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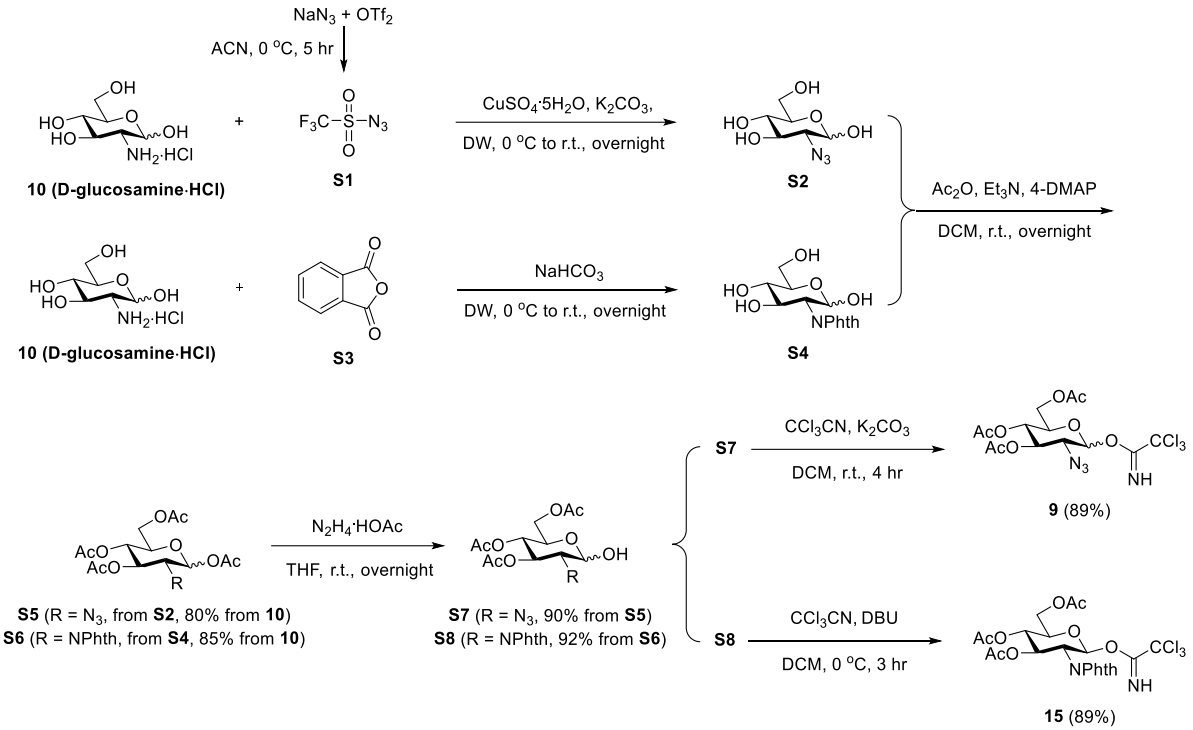
1. General information

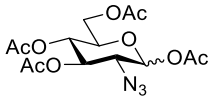
All reactions were carried out under an argon atmosphere using an oven-dried round bottom flask and a sealed tube unless otherwise noted. All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa-Aesar, Acros) were used without further purification. Reactions were monitored by thin layer chromatography on silica gel 60 F254 plate (Merck, Darmstadt, Germany) using UV illumination at 254 nm (VL-4.LC, Vilber Lourmat, Eberhardzell, Germany) or by staining with Hanessian's stain [5% (w/v) ammonium molybdate, 1% (w/v) cerium(II) sulfate and 10% (v/v) sulfuric acid in water]. Column chromatography was performed on silica gel (230~400 mesh; Zeochem, Lake Zurich, Switzerland), using mixture of n-hexane and ethyl acetate as eluents. Melting points were measured on a Büchi B-540 melting point apparatus and were not corrected. Nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C)] spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-*d6* = 2.50 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm, DMSO-*d6* = 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). IR spectra were recorded on a JASCO, FT/IR-4200 Infrared spectrophotometer and are reported as cm^{-1}. All high-resolution mass spectra (HR-MS) were acquired using fast atom bombardments (FAB) ionization method on a double-focusing magnetic sector mass spectrometer, JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan). Optical rotations were acquired on a Jasco P-2000 digital polarimeter and reported as c = g/100 mL at 589 nm (sodium D line) at 25 ℃ and 10 cm path length.

2. Experimental Procedure

2.1. Synthetic procedure of glycosyl donors 9 and 15



(*3R,4R,5S,6R*)-6-(acetoxymethyl)-3-azidotetrahydro-2H-pyran-2,4,5-triyl triacetate (S5)

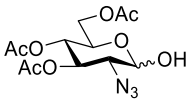


S5

Trifluoromethanesulfonic anhydride (1.95 mL, 11.59 mmol) was added dropwise to a 0 ℃ solution of sodium azide (1.51 g, 23.19 mmol) in dry ACN (16.00 mL). Then, the resulting solution was stirred at 0 ℃ for 5 hr. The resulting solution of trifluoromethanesulfonyl azide **S1** in ACN was added dropwise to a solution of **10** (D-glucosamine·HCl, 1000.0 mg, 4.64 mmol), copper(II) sulfate pentahydrate (11.6 mg, 0.05 mmol), and potassium carbonate (1.28 g, 9.28 mmol) in distilled water (5.00 mL) at 0 ℃ for 30 min. The solution was stirred at 0 ℃ for 1 hr and room temperature for overnight, then lyophilized directly. A mixture of compound **S2** and 4-dimethylaminopyridine (56.7 mg, 0.46 mmol) in dry DCM (18.55 mL) was added triethylamine (6.46 mL, 46.38 mmol) with acetic anhydride (4.38 mL, 46.38 mmol) and stirred at room temperature for overnight. The mixture was diluted with DCM and the organic layer was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 3:1) to afford compound **S5** (1.38 g, 2 steps 80%) as a colorless oil. ^{1}H-

NMR (400 MHz, $CDCl_3$) δ 6.30 (d, J = 3.7 Hz, 1H$_\alpha$), 5.55 (d, J = 8.7 Hz, 1H$_\beta$), 5.46 (dd, J = 10.3, 9.4 Hz, 1H$_\alpha$), 5.14-5.02 (m, 1H$_\alpha$ and 2H$_\beta$), 4.33-4.28 (m, 1H$_\alpha$ and 1H$_\beta$), 4.10-4.04 (m, 2H$_\alpha$ and 1H$_\beta$), 3.82-3.78 (m, 1H$_\beta$), 3.67 (dt, J = 10.2, 4.4 Hz, 1H$_\alpha$ and 1H$_\beta$), 2.19 (s, 3H$_\alpha$ and 3H$_\beta$), 2.11 (s, 3H$_\alpha$), 2.10 (s, 3H$_\beta$), 2.08 (s, 3H$_\alpha$ and 3H$_\beta$), 2.05 (s, 3H$_\alpha$), 2.03 (s, 3H$_\beta$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.7, 169.6, 169.5, 168.5, 168.5, 92.5, 89.9, 72.6, 72.6, 70.7, 69.7, 67.9, 67.8, 62.6, 61.4, 60.2, 20.9, 20.8, 20.7, 20.6, 20.6, 20.5; IR (neat) υ (cm^{-1}) 3931, 3757, 3724, 3364, 2922, 2865, 2349, 2115, 1749, 1370, 1215, 1053, 1033, 1013, 651; HRMS (ESI) m/z calcd for $C_{14}H_{19}N_3O_9$ $[M+NH_4]^+$ 391.1460, found: 391.1469.

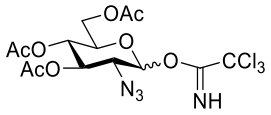
(*2R,3S,4R,5R*)-2-(acetoxymethyl)-5-azido-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (S7)



S7

A solution of **S5** (1.37 g, 3.67 mmol), hydrazine acetate (405.8 mg, 4.41 mmol) in dry THF (18.36 mL) was stirred overnight at room temperature. The mixture was diluted with DCM and washed with distilled water, then the organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 2:1) to afford compound **S7** (1.10 g, 90%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.53 (dd, J = 10.5, 9.2 Hz, 1H$_\beta$), 5.40 (t, J = 3.7 Hz, 1H$_\beta$), 5.08-4.99 (m, 2H$_\alpha$ and 1H$_\beta$), 4.74 (dd, J = 8.0, 5.3 Hz, 1H$_\alpha$), 4.30-4.20 (m, 1H$_\alpha$ and 2H$_\beta$), 4.16-4.09 (m, 1H$_\alpha$ and 1H$_\beta$), 3.90 (d, J = 5.5 Hz, 1H$_\alpha$), 3.74-3.70 (m, 1H$_\alpha$), 3.49 (dt, J = 10.1, 3.9 Hz, 1H$_\alpha$), 3.45-3.42 (m, 2H$_\beta$), 2.09 (s, 6H$_\alpha$), 2.09 (s, 6H$_\beta$), 2.04 (s, 3H$_\alpha$), 2.02 (s, 3H$_\beta$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 171.1, 170.3, 170.3, 170.0, 169.9, 96.3, 92.2, 72.7, 72.0, 70.6, 68.7, 68.4, 67.6, 64.9, 62.1, 61.6, 20.9, 20.8, 20.8, 20.7, 20.7; IR (neat) υ (cm^{-1}) 3931, 3706, 3420, 2972, 2865, 2844, 2349, 2113, 1748, 1371, 1239, 1054, 1033, 1013, 656; HRMS (FAB) m/z calcd for $C_{12}H_{18}N_3O_8$ $[M+H]^+$ 332.1094, found: 332.1094.

(*2R,3S,4R,5R*)-2-(acetoxymethyl)-5-azido-6-(2,2,2-trichloro-1-iminoethoxy)tetrahydro-2H-pyran-3,4-diyl diacetate (9)[1]

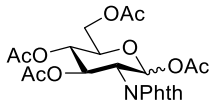


9

A solution of **S7** (94.6 mg, 0.29 mmol), potassium carbonate (78.9 mg, 0.57 mmol), and trichloroacetonitrile (0.17 mL, 1.71 mmol) in dry DCM (1.5 mL) was stirred at room temperature for 4

hr. The reaction mixture was filtered with DCM and the filtrate was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 3:1), to afford compound **9** (120.4 mg, 89%) as a white solid. m.p. (purified from DCM) 113-115 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H$_\alpha$), 8.80 (s, 1H$_\beta$), 6.49 (d, *J* = 3.7 Hz, 1H$_\alpha$), 5.72 (d, *J* = 8.7 Hz, 1H$_\beta$), 5.52 (dd, *J* = 10.5, 9.2 Hz, 1H$_\alpha$), 5.18-5.08 (m, 1H$_\alpha$ and 2H$_\beta$), 4.34-4.26 (m, 1H$_\alpha$ and 1H$_\beta$), 4.21 (dq, *J* = 10.1, 2.0 Hz, 1H$_\alpha$), 4.15-4.08 (m, 1H), 3.86-3.76 (m, 1H$_\alpha$ and 2H$_\beta$), 2.11 (d, *J* = 1.4 Hz, 3H$_\alpha$ and 3H$_\beta$), 2.08 (s, 3H$_\beta$), 2.06 (s, 3H$_\alpha$), 2.06 (s, 3H$_\alpha$), 2.03 (s, 3H$_\beta$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 169.8, 169.7, 169.6, 160.6, 160.5, 96.4, 94.0, 90.5, 90.2, 72.7, 72.6, 70.7, 70.1, 67.9, 63.3, 61.5, 61.4, 60.6, 20.7, 20.7, 20.6; IR (neat) υ (cm^{-1}) 3931, 3724, 3336, 2966, 2865, 2349, 2114, 1749, 1680, 1368, 1226, 1054, 1033, 1016, 649; HRMS (ESI) m/z calcd for $C_{14}H_{17}Cl_3N_4NaO_8$ $[M+Na]^+$ 497.0004, found: 496.9996.

(*3R,4R,5S,6R*)-6-(acetoxymethyl)-3-(1,3-dioxoisoindolin-2-yl)tetrahydro-2H-pyran-2,4,5-triyl triacetate (S6)

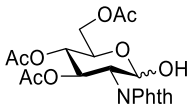


S6

A solution of phthalic anhydride **S3** (1.03 g, 6.96 mmol) in acetone (8.00 mL) was added dropwise to a 0 ℃ solution of **10** (D-glucosamine·HCl, 1000.0 mg, 4.64 mmol), sodium hydroxide (241.1 mg, 6.03 mmol) in methanol (2.00 mL) and water (4.00 mL). Then, sodium bicarbonate (1.01 g, 12.06 mmol) and the additive phthalic anhydride (343.5 mg, 2.32 mmol) were added to the mixture directly at the same temperature. After the warm-up to the room temperature, the solution was stirred for overnight. Then, the mixture was quenched to pH 3 with 2 M aq. HCl solution. Remained solvent was evaporated, then the mixture was lyophilized. A mixture of compound **S4** and 4-dimethylaminopyridine (56.7 mg, 0.46 mmol) in dry DCM (18.55 mL) was added triethylamine (6.46 mL, 46.38 mmol) with acetic anhydride (4.38 mL, 46.38 mmol) and stirred at room temperature for overnight. The mixture was diluted with ethyl acetate and the organic layer was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 2:1) to afford compound **S6** (1.88 g, 2 steps 85%) as a white solid. m.p. (purified from DCM) 66-68 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 2H$_\alpha$ and 2H$_\beta$), 7.76-7.71 (m, 2H$_\alpha$ and 2H$_\beta$), 6.54 (dd, *J* = 11.4, 9.1 Hz, 1H$_\alpha$), 6.49 (d, *J* = 8.7 Hz, 1H$_\beta$), 6.26 (d, *J* = 3.7 Hz, 1H$_\alpha$), 5.86 (dd, *J* = 10.5, 9.1 Hz, 1H$_\beta$), 5.22-5.12 (m, 1H$_\alpha$ and 1H$_\beta$), 4.70 (dd, *J* = 11.4, 3.2 Hz, 1H$_\alpha$), 4.45 (dd, *J* = 10.5, 8.7 Hz, 1H$_\beta$), 4.35 (dd, *J* = 12.3, 4.1 Hz, 1H$_\alpha$ and 1H$_\beta$), 4.30 (dq, *J* = 10.3, 1.9 Hz, 1H$_\alpha$), 4.12 (dq, *J* = 12.3, 2.3 Hz, 1H$_\alpha$ and 1H$_\beta$), 4.01 (dq, *J* = 10.2, 2.2 Hz, 1H$_\beta$), 2.10 (d, *J* = 2.3 Hz, 3H$_\alpha$ and 3H$_\beta$), 2.07 (s, 3H$_\alpha$), 2.04 (s, 3H$_\alpha$), 2.02 (s, 3H$_\beta$), 1.98 (s, 3H$_\beta$), 1.85 (d, *J* = 2.7 Hz, 3H$_\alpha$ and 3H$_\beta$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.1, 169.9, 169.6, 169.6,

169.4, 168.7, 167.5, 134.6, 131.3, 131.2, 123.9, 123.8, 90.6, 89.8, 72.7, 70.6, 70.3, 69.4, 68.4, 67.1, 61.6, 53.6, 52.9, 21.1, 20.9, 20.8, 20.7, 20.7, 20.5; IR (neat) υ (cm^{-1}) 3902, 3840, 3566, 2942, 2372, 2318, 1749, 1720, 1385, 1338, 1221, 1152, 1035, 1013, 968; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_2O_{11}$ $[M+NH_4]^+$ 495.1609, found: 495.1602.

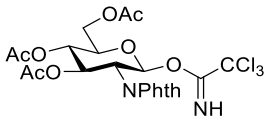
(*2R,3S,4R,5R*)-2-(acetoxymethyl)-5-(1,3-dioxoisoindolin-2-yl)-6-hydroxytetrahydro-2H-pyran-3,4-diyl diacetate (S8)



S8

A solution of **S6** (1.02 g, 2.14 mmol), hydrazine acetate (236.5 mg, 2.57 mmol) in dry THF (10.70 mL) was stirred overnight at room temperature. The mixture was diluted with DCM and washed with water, then the organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 1:1) to afford compound **S8** (857.2 mg, 92%) as a white solid. m.p. (purified from DCM) 187-189 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, $2H_\alpha$ and $2H_\beta$), 7.77-7.69 (m, $2H_\alpha$ and $2H_\beta$), 6.23-6.18 (m, $1H_\alpha$), 5.92-5.86 (m, $1H_\alpha$), 5.83-5.77 (m, $1H_\beta$), 5.62 (d, J = 8.7 Hz, $1H_\beta$), 5.38 (d, J = 5.5 Hz, $2H_\alpha$), 5.18-5.13 (m, J = 9.6 Hz, $1H_\alpha$ and $1H_\beta$), 4.61 (dd, J = 11.4, 3.2 Hz, $1H_\alpha$), 4.47-4.30 (m, $1H_\alpha$ and $1H_\beta$), 4.29-4.23 (m, $2H_\beta$), 4.17 (dd, J = 12.1, 2.1 Hz, $1H_\beta$), 4.12-4.07 (m, $1H_\alpha$), 3.92 (qd, J = 4.9, 2.3 Hz, $1H_\beta$), 2.07 (s, $3H_\alpha$ and $3H_\beta$), 2.01 (s, $3H_\alpha$ and $3H_\beta$), 1.83 (s, $3H_\alpha$ and $3H_\beta$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 170.3, 169.7, 168.0, 134.5, 131.4, 123.8, 92.7, 72.0, 70.7, 69.0, 62.2, 56.1, 20.9, 20.7, 20.6; IR (neat) υ (cm^{-1}) 3841, 3649, 3503, 2925, 2371, 1747, 1715, 1647, 1508, 1388, 1338, 1230, 1160, 1034, 903; HRMS (ESI) m/z calcd for $C_{20}H_{25}N_2O_{10}$ $[M+NH_4]^+$ 453.1504, found: 453.1500.

(*2R,3S,4R,5R,6S*)-2-(acetoxymethyl)-5-(1,3-dioxoisoindolin-2-yl)-6-(2,2,2-trichloro-1-iminoethoxy)tetrahydro-2H-pyran-3,4-diyl diacetate (15)[2]



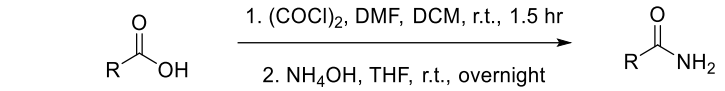
15

Trichloroacetonitrile (0.69 mL, 6.89 mmol) was added dropwise to a 0 °C solution of **S8** (300.0 mg, 0.69 mmol) and 1,8-diazabicyclo(5.4.0)undec-7-ene (2.58 μL, 17.2 μmol) in dry DCM (4.15 mL), and the resulted solution was stirred at the same temperature for 3 hr. The reaction mixture was concentrated *in vacuo*, and purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 2:1) to afford compound **15** (353.6 mg, 89%) as a white solid. m.p. (purified from DCM) 74-76 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.85-7.81 (m, 2H), 7.72 (td, J = 6.2, 3.7 Hz, 2H), 6.61 (d, J = 9.2 Hz,

1H), 5.91 (dd, *J* = 10.8, 9.0 Hz, 1H), 5.27 (t, *J* = 9.7 Hz, 1H), 4.62 (dd, *J* = 10.8, 9.0 Hz, 1H), 4.38 (dd, *J* = 12.6, 4.4 Hz, 1H), 4.19 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.07 (dq, *J* = 10.3, 2.1 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.2, 169.6, 167.5, 160.6, 134.6, 131.3, 123.8, 93.7, 90.2, 72.9, 70.5, 68.5, 61.7, 53.7, 20.9, 20.7, 20.6; IR (neat) υ (cm^{-1}) 3316, 2955, 1749, 1720, 1682, 1469, 1387, 1338, 1229, 1146, 1107, 1042, 974, 899, 840; HRMS (ESI) m/z calcd for $C_{22}H_{21}Cl_3N_2NaO_{10}$ $[M+Na]^+$ 601.0154, found: 601.0161; $[\alpha]_D^{25}$= +20.3 (c=1.0 in $CHCl_3$).

2.2. Synthetic procedure of fatty amines 13b-13d

2.2.1. General Procedure I (GP-I): Synthesis of carboxamides from carboxylic acids

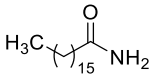


S9 (**heptadecanoic acid,**
R= -$(CH_2)_{15}$-(CH_3))
S10 (**palmitoleic acid,**
R= -$(CH_2)_7$-CH=CH-$(CH_2)_5$-CH_3,
with cis-double bond)

S11 (2 steps 96% from **S9**)
S12 (2 steps 96% from **S10**)

Oxalyl chloride (2.0 eq) was added to a 0 ℃ solution of carboxylic acid **S9-S10** (1.00 eq) and dimethylformamide (1.63 eq) in DCM (0.26 M). The solution was warmed up to room temperature, and stirred for 1.5 hr. Then, the reaction mixture was concentrated *in vacuo* and THF (0.26 M) was added as a new solvent. 25% ammonium hydroxide solution in water (ammonium hydroxide 40.0 eq) was added to the mixture at 0 ℃. The solution was warmed up to room temperature, and stirred for overnight. The mixture was extracted with DCM and the organic layers was dried over $MgSO_4$ and concentrated. The crude products **S11-S12** were used for next steps without further purification.

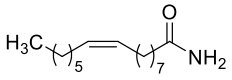
Heptadecanamide (S11)



S11

Following **GP-I**, from **S9** (heptadecanoic acid, 500.0 mg, 1.85 mmol), title compound **S11** (476.1 mg, 96%) was afforded as a white solid. m.p. (purified from DCM) 90-92 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.44 (s, 2H), 2.22 (t, J = 7.5 Hz, 2H), 1.67-1.59 (m, 2H), 1.34-1.23 (m, 26H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.0, 36.0, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 25.7, 22.8, 14.3; IR (neat) υ (cm^{-1}) 3902, 3736, 3649, 3567, 2915, 2850, 2372, 2321, 1748, 1715, 1648, 1543, 1508, 1473, 1339; HRMS (FAB) m/z calcd for $C_{17}H_{36}NO$ $[M+H]^+$ 270.2797, found: 270.2801.

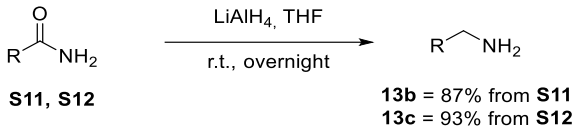
(*Z*)-hexadec-9-enamide (S12)



S12

Following **GP-I**, from **S11** (palmitoleic acid, 170.8 mg, 0.67 mmol), title compound **S12** (163.5 mg, 96%) was afforded as a white solid. m.p. (purified from DCM) 54-56 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.94 (s, 1H), 5.52 (s, 1H), 5.37-5.29 (m, 2H), 2.20 (t, *J* = 7.8 Hz, 2H), 2.03-1.96 (m, 4H), 1.67-1.57 (m, 2H), 1.37-1.22 (m, 16H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.2, 130.1, 129.9, 77.5, 77.2, 76.8, 36.1, 31.9, 29.9, 29.8, 29.4, 29.3, 29.2, 29.1, 27.3, 27.3, 25.6, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3357, 3194, 3004, 2924, 2853, 2372, 2321, 1659, 1631, 1508, 1469, 1411, 1339, 1265, 1135; HRMS (FAB) m/z calcd for $C_{16}H_{32}NO$ $[M+H]^+$ 254.2484, found: 254.2477.

2.2.2. General Procedure II (GP-II): Reduction of carboxamides to primary amines[3]

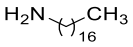


S11, S12

13b = 87% from **S11**
13c = 93% from **S12**

$LiAlH_4$ (2.00 eq) was added portionwise to a 0 °C solution of carboxamide **S11-S12** (1.00 eq) in THF (0.25 M). The solution was warmed up to room temperature, and stirred for overnight. Then, 2M aq. NaOH solution (NaOH 4.00 eq) was added to quench the reaction mixture. The mixture was filtered and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated. The crude products were used for next steps without further purification.

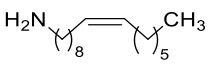
Heptadecan-1-amine (13b)



13b

Following **GP-II**, from **S11** (1.85 g, 6.86 mmol), title compound **13b** (1.53 g, 87%) was afforded as a white solid. m.p. (purified from DCM) 60-62 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.67 (t, *J* = 7.1 Hz, 2H), 1.42 (q, *J* = 6.9 Hz, 2H), 1.31-1.20 (m, 28H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 42.3, 33.8, 32.1, 29.8, 29.6, 29.5, 27.0, 22.8, 14.3; IR (neat) υ (cm^{-1}) 3902, 3840, 3649, 3567, 2918, 2850, 2372, 2321, 1748, 1680, 1565, 1543, 1508, 1489, 1339; HRMS (FAB) m/z calcd for $C_{17}H_{38}N$ $[M+H]^+$ 256.3004, found: 256.3007.

(*Z*)-hexadec-9-en-1-amine (13c)



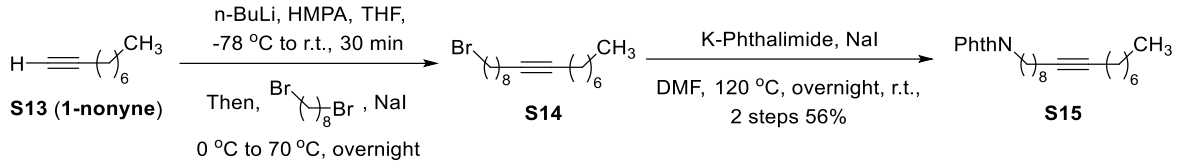
13c

Following **GP-II**, from **S12** (595.2 mg, 2.35 mmol), title compound **13c** (522.4 mg, 93%) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.38-5.30 (m, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 2.01

(q, J = 6.3 Hz, 4H), 1.42 (q, J = 6.9 Hz, 2H), 1.34-1.29 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 130.1, 42.3, 33.8, 31.9, 29.9, 29.6, 29.6, 29.4, 29.1, 27.3, 27.3, 27.0, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3902, 3736, 3649, 3567, 2925, 2854, 2372, 2321, 1748, 1680, 1565, 1543, 1508, 1457, 1339; HRMS (FAB) m/z calcd for $C_{16}H_{34}N$ $[M+H]^+$ 240.2691, found: 240.2705.

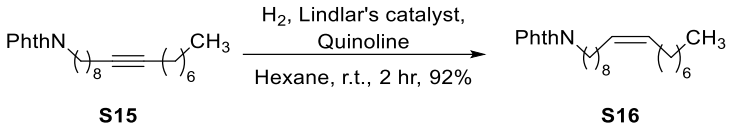
2.2.3. Synthetic procedure of fatty amine 13d

2-(heptadec-9-yn-1-yl)isoindoline-1,3-dione (S15)[4]



2.5 M solution of n-BuLi in hexane (3.22 mL, n-BuLi 8.05 mmol) was added dropwise to a -78 ℃ solution of **S13** (1-nonyne, 500.0 mg, 4.03 mmol) in HMPA (1.50 mL) and THF (4.00 mL). The solution was warmed up to room temperature and stirred for 30 min. Then, the mixture was cooled down to 0 ℃ and other solution of 1,8-dibromooctane (2.22 mL, 12.08 mmol), sodium iodide (60.3 mg, 0.40 mmol) in THF (2.0 mL) was added directly. The resulted solution was warmed up to 70 ℃ and stirred overnight under reflux condition. To quench the reaction mixture, saturated aq. NH_4Cl was added at 0 ℃ until the pH arrives below 6. The mixture was diluted with DCM and the organic layer was washed with distilled water. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (n-hexane 100%). Then, resulted mixture of **S14** was used directly for the next step. To the mixture, potassium phthalimide (5.96 g, 32.20 mmol), sodium iodide (60.3 mg, 0.40 mmol), and DMF (20.12 mL) was added and stirred overnight at 120 ℃. The resulted solution was diluted with ethyl acetate and the organic layer was washed with distilled water. Then the organic layer was filtered with DCM to get rid of unreacted potassium phthalimide. The residue was concentrated *in vacuo* and purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 30:1) to afford compound **S15** (866.9 mg, 2 steps 56%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 7.71-7.67 (m, 2H), 3.65 (t, J = 7.3 Hz, 2H), 2.11 (t, J = 6.5 Hz, 4H), 1.65 (t, J = 6.9 Hz, 2H), 1.46-1.41 (m, 4H), 1.37-1.25 (m, 16H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.6, 133.9, 132.3, 123.2, 80.4, 80.2, 38.1, 31.9, 29.3, 29.2, 29.1, 28.9, 28.9, 28.7, 26.9, 22.7, 18.8, 14.2; IR (neat) υ (cm^{-1}) 3902, 3736, 3649, 3567, 2929, 2856, 2372, 2321, 2137, 1748, 1715, 1648, 1508, 1396, 1362; HRMS (FAB) m/z calcd for $C_{25}H_{36}NO_2$ $[M+H]^+$ 382.2746, found: 382.2750.

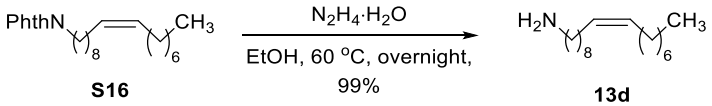
(*Z*)-2-(heptadec-9-en-1-yl)isoindoline-1,3-dione (S16)



S15 **S16**

A solution of compound **S15** (353.5 mg, 0.93 mmol), Lindlar's catalyst (70.7 mg), and quinoline (54.9 μL, 0.46 mmol) was stirred at room temperature for 2 hr under H_2 atmosphere (1 atm). The catalyst was removed by celite filtration with ethyl acetate. The filtrate was concentrated *in vacuo* and purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 60:1) to afford compound **S16** (325.4 mg, 92%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 2H), 7.72-7.67 (m, 2H), 5.37-5.28 (m, 2H), 3.66 (t, J = 7.3 Hz, 2H), 2.02-1.96 (m, 4H), 1.69-1.62 (m, 2H), 1.32-1.26 (m, 20H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.6, 133.9, 132.3, 130.1, 129.9, 123.3, 38.2, 32.0, 29.9, 29.8, 29.5, 29.4, 29.3, 29.3, 28.7, 27.3, 27.3, 27.0, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3902, 3841, 3736, 3649, 3567, 2925, 2371, 2321, 1748, 1715, 1648, 1508, 1489, 1396, 1362; HRMS (FAB) m/z calcd for $C_{25}H_{38}NO_2$ $[M+H]^+$ 384.2903, found: 384.2905.

(*Z*)-heptadec-9-en-1-amine (13d)

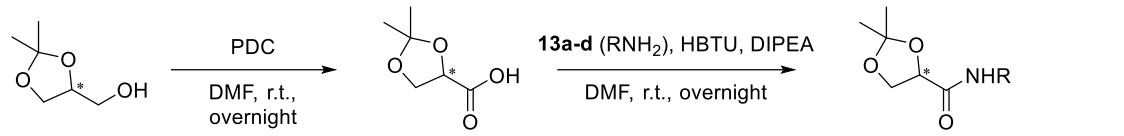


S16 **13d**

A solution of compound **S16** (296.4 mg, 0.77 mmol) and hydrazine monohydrate (193.5 mg, 3.86 mmol) in ethanol (7.72 mL) was stirred at 60 °C for overnight. The mixture was diluted with DCM and the organic layer was washed with distilled water. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford compound **13d** (193.9 mg, 99%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.38-5.30 (m, 2H), 2.69 (t, J = 7.1 Hz, 2H), 2.13 (s, 2H), 2.00 (q, J = 6.4 Hz, 4H), 1.44 (q, J = 6.9 Hz, 2H), 1.26 (d, J = 12.8 Hz, 20H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 130.1, 129.9, 77.5, 77.2, 76.8, 42.1, 33.4, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.4, 27.3, 27.0, 22.8, 14.3; IR (neat) υ (cm^{-1}) 3902, 3736, 3649, 3005, 2925, 2854, 2372, 2321, 1748, 1680, 1648, 1543, 1508, 1463, 1376; HRMS (ESI) m/z calcd for $C_{17}H_{36}N$ $[M+H]^+$ 254.2842, found: 254.2842.

2.3. Synthetic procedure of glyceric amides 11a-11e

2.3.1. General Procedure III (GP-III): Synthesis of ketal-protected glyceric amides



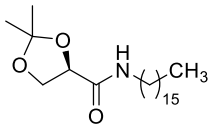
(*S*)-12a for 17a-d,
(*R*)-12b for 17e

16a (from 12a)
16b (from 12b)

17a (from 16a & 13a, 71% from 12a)
17b (from 16a & 13b, 58% from 13b)
17c (from 16a & 13c, 74% from 13c)
17d (from 16a & 13d, 58% from 13d)
17e (from 16b & 13c, 64% from 13c)

A solution of solketal **12a** or **12b** and pyridinium dichromate (5.0 eq of **12a-b**) in DMF (0.13 M relative to **12a-b**) was stirred for overnight at room temperature. The resulted reaction mixture of **16a** or **16b** was filtered through celite with ethyl acetate and concentrated *in vacuo*. Then, primary amine **13a-d**, HBTU (1.5 eq of **13a-d**), and DIPEA (1.5 eq of **13a-d**) were added to mentioned mixture of compound **16a-b** in DMF, and stirred for overnight at room temperature. The mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (chloroform/ethyl acetate, 20:1) to afford desired products.

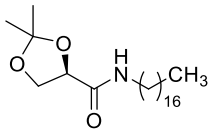
(*R*)-*N*-hexadecyl-2,2-dimethyl-1,3-dioxolane-4-carboxamide (17a)



17a

Following **GP-III**, from **12a** (1.00 mL, 8.05 mmol) and **13a** (hexadecylamine, 2.91 g, 12.08 mmol), title compound **17a** (2.11 g, 2 steps 71% from **12a**) was afforded as a white solid. m.p. (purified from DCM) 58-60 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 4.47 (dd, *J* = 7.5, 5.3 Hz, 1H), 4.29 (dd, *J* = 8.7, 7.8 Hz, 1H), 4.09 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.33-3.20 (m, 2H), 1.55-1.49 (m, 5H), 1.39 (s, 3H), 1.32-1.23 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 110.9, 75.2, 67.9, 39.1, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 27.0, 26.3, 25.2, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3734, 3338, 2917, 2850, 1681, 1645, 1527, 1471, 1373, 1223, 1157, 1057, 866, 718, 671; HRMS (FAB) m/z calcd for $C_{22}H_{44}NO_3$ $[M+H]^+$ 370.3321, found: 370.3324; $[\alpha]_D^{25}$= +5.6 (c=1.0 in MeOH).

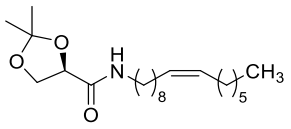
(*R*)-*N*-heptadecyl-2,2-dimethyl-1,3-dioxolane-4-carboxamide (17b)



17b

Following **GP-III**, from **12a** (0.73 mL, 5.87 mmol) and **13b** (1.00 g, 3.91 mmol), title compound **17b** (864.4 mg, 58% from **13b**) was afforded as a white solid. m.p. (purified from DCM) 46-48 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 4.45 (dd, *J* = 7.5, 5.3 Hz, 1H), 4.27 (dd, *J* = 8.7, 7.8 Hz, 1H), 4.07 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.25 (tt, *J* = 19.5, 6.5 Hz, 2H), 1.54-1.49 (m, 2H), 1.47 (s, 3H), 1.38 (s, 3H), 1.32-1.21 (m, 28H), 0.86 (t, *J* = 6.9 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 110.9, 75.2, 67.9, 39.1, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 27.0, 26.3, 25.2, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3735, 3336, 2917, 2849, 1682, 1644, 1525, 1470, 1373, 1249, 1223, 1157, 1074, 1057, 865; HRMS (FAB) m/z calcd for $C_{23}H_{46}NO_3$ $[M+H]^+$ 384.3478, found: 384.3479; $[\alpha]_D^{25}$= +7.3 (c=1.0 in MeOH).

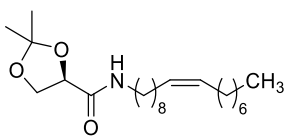
(*R*,*Z*)-*N*-(hexadec-9-en-1-yl)-2,2-dimethyl-1,3-dioxolane-4-carboxamide (17c)



17c

Following **GP-III**, from **12a** (0.47 mL, 3.77 mmol) and **13c** (602.0 mg, 2.51 mmol), title compound **17c** (684.8 mg, 74% from **13c**) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 1H), 5.36-5.28 (m, 2H), 4.44 (dd, *J* = 7.5, 5.3 Hz, 1H), 4.26 (dd, *J* = 8.7, 7.8 Hz, 1H), 4.07 (q, *J* = 4.6 Hz, 1H), 3.31-3.18 (m, 2H), 1.99 (q, *J* = 6.4 Hz, 4H), 1.53-1.46 (m, 5H), 1.37 (s, 3H), 1.35-1.21 (m, 18H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 130.1, 129.9, 110.9, 75.2, 67.9, 39.0, 31.9, 29.8, 29.6, 29.5, 29.3, 29.3, 29.1, 27.3, 27.3, 26.9, 26.3, 25.1, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3902, 3341, 2926, 2855, 2371, 2321, 1680, 1529, 1457, 1373, 1259, 1218, 1153, 1071, 846; HRMS (FAB) m/z calcd for $C_{22}H_{42}NO_3$ $[M+H]^+$ 368.3165, found: 368.3155; $[\alpha]_D^{25}$= +6.4 (c=1.0 in $CHCl_3$).

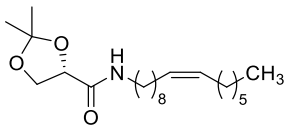
(*R*,*Z*)-*N*-(heptadec-9-en-1-yl)-2,2-dimethyl-1,3-dioxolane-4-carboxamide (17d)



17d

Following **GP-III**, from **12a** (0.14 mL, 1.11 mmol) and **13d** (188.1 mg, 0.74 mmol), title compound **17d** (165.3 mg, 58% from **13d**) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 5.39-5.30 (m, 2H), 4.47 (dd, *J* = 7.5, 5.3 Hz, 1H), 4.29 (dd, *J* = 9.0, 7.4 Hz, 1H), 4.09 (dd, *J* = 8.7, 5.5 Hz, 1H), 3.33-3.20 (m, 2H), 2.01 (q, *J* = 6.4 Hz, 4H), 1.53-1.49 (m, 5H), 1.40 (s, 3H), 1.35-1.24 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 130.1, 129.9, 110.9, 75.2, 67.9, 39.0, 32.0, 29.9, 29.8, 29.7, 29.5, 29.4, 29.4, 27.3, 27.3, 27.0, 26.3, 25.2, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3902, 3339, 2925, 2854, 2371, 2321, 1748, 1680, 1527, 1457, 1374, 1218, 1153, 1071, 845; HRMS (FAB) m/z calcd for $C_{23}H_{44}NO_3$ $[M+H]^+$ 382.3321, found: 382.3323; $[\alpha]_D^{25}$= +7.9 (c=1.0 in MeOH).

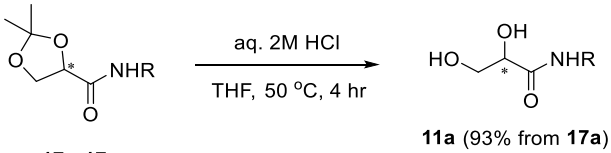
(*S,Z*)-*N*-(hexadec-9-en-1-yl)-2,2-dimethyl-1,3-dioxolane-4-carboxamide (17e)



17e

Following **GP-III**, from **12b** (0.45 mL, 3.59 mmol) and **13c** (573.2 mg, 2.39 mmol), title compound **17e** (562.0, 64% from **13c**) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 5.39-5.30 (m, 2H), 4.47 (dd, *J* = 7.3, 5.5 Hz, 1H), 4.29 (dd, *J* = 8.5, 7.5 Hz, 1H), 4.09 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.33-3.20 (m, 2H), 2.01 (q, *J* = 6.3 Hz, 4H), 1.53-1.46 (m, 5H), 1.40 (s, 3H), 1.36-1.29 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 130.0, 129.8, 110.9, 75.1, 67.9, 39.0, 31.9, 29.8, 29.6, 29.5, 29.3, 29.3, 29.1, 27.3, 27.2, 26.9, 26.2, 25.1, 22.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3337, 2926, 2855, 2371, 2321, 1680, 1526, 1457, 1374, 1259, 1218, 1153, 1069, 845; HRMS (FAB) m/z calcd for $C_{22}H_{42}NO_3$ $[M+H]^+$ 368.3165, found: 368.3162; $[\alpha]_D^{25}$= -6.2 (c=1.0 in $CHCl_3$).

2.3.2. General Procedure IV (GP-IV): Hydrolysis of ketal-protected glyceric amides

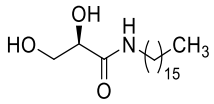


17a-17e

11a (93% from **17a**)
11b (96% from **17b**)
11c (99% from **17c**)
11d (86% from **17d**)
11e (99% from **17e**)

2 M aq. HCl (16.0 eq as HCl) was added to a solution of **17a-17e** (1.00 eq) in THF (0.25 M related to **17a-e**) and stirred for 4 hr at 50 °C. For **11a-11b**, the reaction mixture was filtered with n-hexane to afford the desired products. For **11c-11e**, the mixture was diluted with DCM and the organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the desired products.

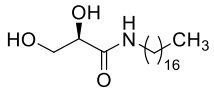
(*R*)-*N*-hexadecyl-2,3-dihydroxypropanamide (11a)



11a

Following **GP-IV**, from **17a** (50.0 mg, 0.14 mmol), title compound **11a** (41.3 mg, 93%) was afforded as a white solid. m.p. (purified from DCM) 107-109 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 4.18-4.12 (m, 1H), 3.94-3.86 (m, 1H), 3.86-3.79 (m, 1H), 3.33-3.24 (m, 2H), 3.14 (d, *J* = 4.3 Hz, 1H), 2.30 (s, 1H), 1.57-1.47 (m, 2H), 1.36-1.20 (m, 26H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 72.0, 64.4, 39.4, 32.1, 29.8, 29.7, 29.7, 29.5, 29.4, 27.0, 22.8, 14.3; IR (neat) υ (cm^{-1}) 3325, 2953, 2918, 2849, 2349, 1748, 1618, 1543, 1468, 1318, 1157, 1114, 1055, 1033, 1007; HRMS (FAB) m/z calcd for $C_{19}H_{40}NO_3$ $[M+H]^+$ 330.3008, found: 330.3005; $[\alpha]_D^{25}$= +7.2 (c=0.5 in $CHCl_3$).

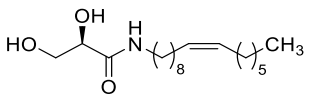
(*R*)-*N*-heptadecyl-2,3-dihydroxypropanamide (11b)



11b

Following **GP-IV**, from **17b** (400.0 mg, 1.04 mmol), title compound **11b** (342.3 mg, 96%) was afforded as a white solid. m.p. (purified from DCM) 82-84 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 4.16 (q, *J* = 5.2 Hz, 1H), 3.94-3.89 (m, 1H), 3.86-3.82 (m, 1H), 3.29 (qd, *J* = 6.9, 2.7 Hz, 2H), 3.01 (q, *J* = 2.4 Hz, 1H), 2.12 (s, 1H), 1.57-1.47 (m, 2H), 1.36-1.20 (m, 28H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 171.6, 72.7, 38.0, 31.0, 28.9, 28.7, 28.5, 28.4, 28.3, 26.1, 21.8, 13.6; IR (neat) υ (cm^{-1}) 3396, 2953, 2918, 2848, 2371, 2321, 1707, 1622, 1543, 1472, 1462, 1312, 1155, 1104, 1075; HRMS (FAB) m/z calcd for $C_{20}H_{42}NO_3$ $[M+H]^+$ 344.3165, found: 344.3169; $[\alpha]_D^{25}$= +19.3 (c=0.5 in $CHCl_3$).

(*R*,*Z*)-*N*-(hexadec-9-en-1-yl)-2,3-dihydroxypropanamide (11c)

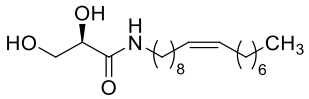


11c

Following **GP-IV**, from **17c** (55.9 mg, 0.15 mmol), title compound **11c** (49.3 mg, 99%) was afforded as a white solid. m.p. (purified from DCM) 47-49 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.39-

5.30 (m, 2H), 4.15 (t, *J* = 5.3 Hz, 1H), 3.91 (q, *J* = 5.4 Hz, 1H), 3.84 (q, *J* = 5.5 Hz, 1H), 3.33-3.25 (m, 2H), 2.01 (q, *J* = 6.4 Hz, 4H), 1.56-1.49 (m, 2H), 1.30 (d, *J* = 16.1 Hz, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.7, 130.1, 129.8, 72.7, 64.6, 39.4, 31.9, 29.9, 29.8, 29.6, 29.5, 29.4, 29.4, 29.1, 27.3, 27.0, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3404, 3299, 3003, 2955, 2919, 2850, 2321, 1623, 1541, 1467, 1441, 1373, 1303, 1102, 1075; HRMS (FAB) m/z calcd for $C_{19}H_{38}NO_3$ $[M+H]^+$ 328.2852, found: 328.2846; $[\alpha]_D^{25}$= +3.3 (c=1.0 in $CHCl_3$).

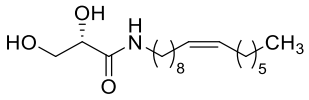
(*R,Z*)-*N*-(heptadec-9-en-1-yl)-2,3-dihydroxypropanamide (11d)



11d

Following **GP-IV**, from **17d** (101.2 mg, 0.27 mmol), title compound **11d** (78.0 mg, 86%) was afforded as a white solid. m.p. (purified from DCM) 53-55 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 5.39-5.30 (m, 2H), 4.15 (q, *J* = 5.2 Hz, 1H), 3.94-3.88 (m, 1H), 3.86-3.81 (m, 1H), 3.35-3.23 (m, 2H), 3.05 (d, *J* = 5.5 Hz, 1H), 2.17 (t, *J* = 5.7 Hz, 1H), 2.01 (q, *J* = 6.4 Hz, 4H), 1.51 (q, *J* = 7.4 Hz, 2H), 1.27 (t, *J* = 8.0 Hz, 20H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3, 130.1, 129.9, 72.4, 64.4, 39.4, 32.0, 29.9, 29.9, 29.8, 29.6, 29.4, 29.4, 27.4, 27.0, 22.8, 14.3; IR (neat) υ (cm^{-1}) 3649, 3298, 3003, 2919, 2850, 2321, 1748, 1658, 1624, 1543, 1467, 1374, 1306, 1102, 1075; HRMS (FAB) m/z calcd for $C_{20}H_{40}NO_3$ $[M+H]^+$ 342.3008, found: 342.3002; $[\alpha]_D^{25}$= +4.8 (c=1.0 in MeOH).

(*S,Z*)-*N*-(hexadec-9-en-1-yl)-2,3-dihydroxypropanamide (11e)

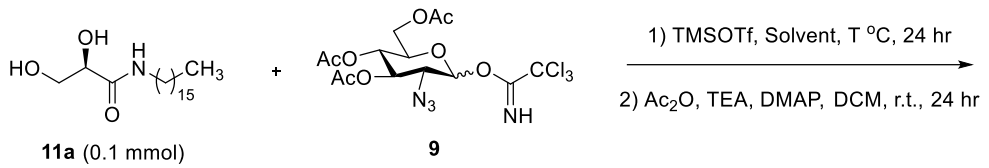


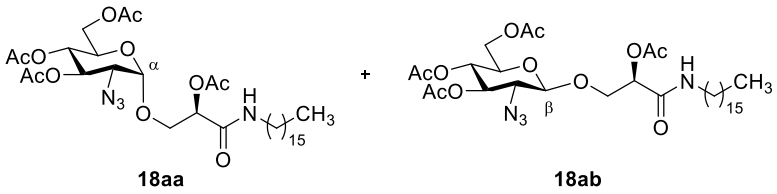
11e

Following **GP-IV**, from **17e** (510.5 mg, 1.39 mmol), title compound **11e** (449.4 mg, 99%) was afforded as a white solid. m.p. (purified from DCM) 47-49 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.39-5.30 (m, 2H), 4.16 (q, *J* = 5.2 Hz, 1H), 3.94-3.89 (m, 1H), 3.86-3.81 (m, 1H), 3.33-3.25 (m, 2H), 3.03 (d, *J* = 5.0 Hz, 1H), 2.15 (s, 1H), 2.01 (q, *J* = 6.4 Hz, 4H), 1.55-1.49 (m, 2H), 1.32-1.25 (m, 18H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 130.1, 129.9, 72.5, 64.5, 39.4, 31.9, 29.9, 29.6, 29.4, 29.1, 27.3, 27.0, 22.8, 14.2; IR (neat) υ (cm^{-1}) 3400, 3300, 3004, 2955, 2920, 2851, 2321, 1623, 1542, 1467, 1442, 1374, 1305, 1103, 1075; HRMS (FAB) m/z calcd for $C_{19}H_{38}NO_3$ $[M+H]^+$ 328.2852, found: 328.2860; $[\alpha]_D^{25}$= -2.9 (c=1.0 in $CHCl_3$).

2.4. Procedure of glycosylation reactions

2.4.1. Optimization for the α-stereoselective Schmidt glycosylation between 9 and 11a

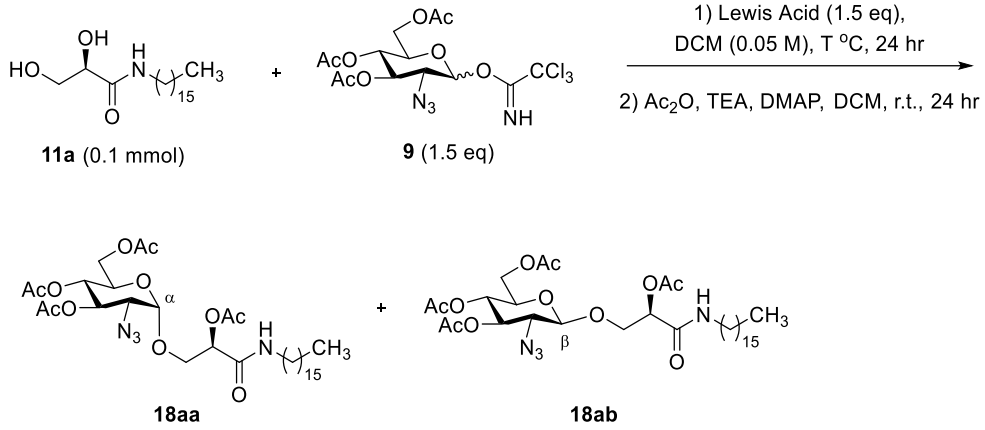




Entry	**11a** (eq.)	TMSOTf (eq.)	**9** (eq.)	T (℃)	Solvent (mL)	Total yields* (18aa+18ab)	**18aa**	**18ab**	**18aa : 18ab** (α : β)
1	1.0	1.0	1.5	-40	DCM (2)	31%	25%	6%	4.1 : 1
2	**1.0**	**1.5**	**1.5**	**-40**	**DCM (2)**	**57%**	**45%**	**12%**	**3.7 : 1**
3	1.0	2.0	1.5	-40	DCM (2)	55%	43%	12%	3.5 : 1
4	1.0	1.5	1.2	-40	DCM (2)	26%	20%	6%	3.3 : 1
5	1.0	1.5	2.0	-40	DCM (2)	43%	35%	7%	4.9 : 1
6	1.0	1.5	1.5	-30	DCM (2)	53%	42%	11%	3.9 : 1
7	1.0	1.5	1.5	-50	DCM (2)	16%	12%	4%	3.5 : 1
8	1.0	1.5	1.5	-40	DCM (1)	52%	40%	12%	3.3 : 1
9	1.0	1.5	1.5	-40	DCM (3)	46%	36%	10%	3.7 : 1
10	1.0	1.5	1.5	-40	Chloroform (2)	55%	43%	12%	3.6 : 1
11	1.0	1.5	1.5	-40	Toluene (2)	30%	21%	9%	2.5 : 1
12	1.0	1.5	1.5	-40	THF (2)	8%	5%	3%	1.7 : 1
13	1.0	1.5	1.5	-40	Acetonitrile (2)	Not detected			
14	1.0	1.5	1.5	-40	DMF (2)	Not detected			

* Yields were evaluated by NMR analysis using dimethyl sulfone as the internal standard.

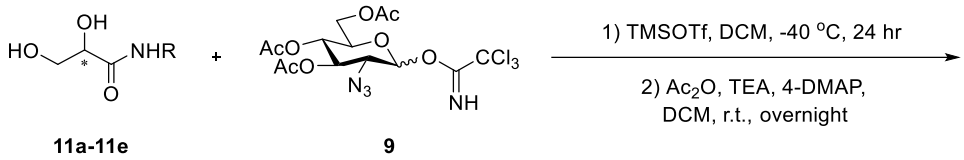
The reaction conditions for glycosylation reaction between **9** and **11a** were optimized to afford **18aa** as major product, various conditions for the equivalence of TMSOTf or **9**, temperature and solvent were tested as shown. **Entry 5** showed the highest stereoselectivity with α : β = 4.9:1. However, **Entry 2** was applied for our further syntheses to get more amounts of **18aa** with higher yields.

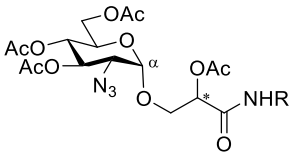


Entry	**11a** (eq.)	**9** (eq.)	T (℃)	Lewis Acid (1.5 eq)	Total yields* (18aa+18ab)	**18aa**	**18ab**	**18aa : 18ab** (α : β)
2	1.0	1.5	-40	TMSOTf	57%	45%	12%	3.7 : 1
15	1.0	1.5	-40	$Sc(OTf)_3$	Not detected			
16	1.0	1.5	-40	$Cu(OTf)_2$	Not detected			
17	1.0	1.5	-40	$Yb(OTf)_3$	Not detected			
18	1.0	1.5	-40	$Fe(OTf)_3$	Not detected			
19	1.0	1.5	-40	$FeCl_3$	3%	2%	1%	2.0 : 1
20	1.0	1.5	-40	$ZnCl_2$	Not detected			
21	1.0	1.5	-40	$BF_3{\cdot}OEt_2$	Not detected			
22	1.0	1.5	-40	Ag_2O	Not detected			
23	1.0	1.5	r.t.	$BF_3{\cdot}OEt_2$	Trace (< 7%)	Cannot be determined (Overlap in NMR)		

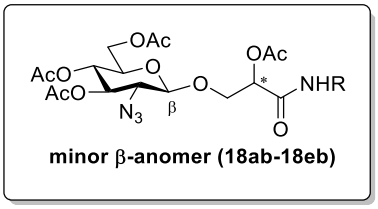
In cases of tested reactions using other Lewis acids ($Sc(OTf)_3$, $Cu(OTf)_2$, $Yb(OTf)_3$, $Fe(OTf)_3$, $FeCl_3$, $ZnCl_2$, $BF_3{\cdot}OEt_2$, Ag_2O) instead of TMSOTf, **18aa** was not detected or obtained with only trace amounts.

2.4.2. General Procedure V (GP-V): α-Stereoselective Schmidt glycosylation of 11a-11e





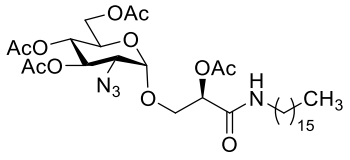
18aa (44% from **11a**)[a], [total 57%, α : β = 3.7 : 1][c]
18ba[b] (26% from **11b**)[a], [total 40%, α : β = 4.0 : 1][c]
18ca (51% from **11c**)[a], [total 88%, α : β = 2.5 : 1][c]
18da (47% from **11d**)[a], [total 66%, α : β = 3.1 : 1][c]
18ea (47% from **11e**)[a], [total 70%, α : β = 3.7 : 1][c]



[a] Isolated yields, [b] Chloroform was used as solvent at the glycosylation step, [c] NMR analysis using dimethyl sulfone as t he internal standard.

A solution of **9** (71.4 mg, 0.15 mmol) in DCM (for **11a**, **11c-11e**, 1.0 mL) or chloroform (for **11b**, 1.0 mL) was added to a solution of **11a-11e** (0.10 mmol) and TMSOTf (27.1 μL, 0.15 mmol) in DCM (1.0 mL), dropwise at -40 ℃ for 10 min. Then, the resulting solution was stirred for 24 hr at the same temperature. The mixture was diluted with DCM and the organic layer was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then, the residue was diluted with DCM (2.0 mL) again. To the solution, 4-dimethylaminopyridine (1.2 mg, 0.01 mmol), acetic anhydride (94.5 μL, 1.00 mmol), and triethylamine (139.4 μL, 1.00 mmol) were added and stirred for overnight at the room temperature. The mixture was diluted with DCM and the organic layer was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Dimethylsulfone (4.7 mg, 0.05 mmol) was added to the residue as an internal standard, and the yields of α- or β- glycosylated products were estimated by ^{1}H NMR. Then, to isolate α-glycosylated products **18aa-18ea** for the next reaction, the residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 3:1). In case of β-glycosylated products, only **18cb** was characterized.

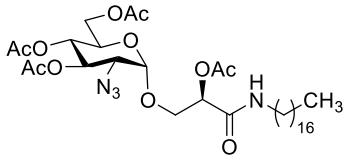
(*2R,3S,4R,5R,6S*)-6-((*R*)-2-acetoxy-3-(hexadecylamino)-3-oxopropoxy)-2-(acetoxymethyl)-5-azidotetrahydro-2*H*-pyran-3,4-diyl diacetate (18aa)



18aa

Following **GP-V**, from **11a** (33.0 mg, 0.10 mmol), the mixture of **18aa** and its β-anomer **18ab** were obtained (2 steps 45%, 12% in ^{1}H NMR, respectively). After the isolation, the title compound **18aa** (30.1 mg, 44%) was afforded as a white solid. m.p. (purified from DCM) 69-71 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.38 (t, *J* = 5.7 Hz, 1H), 5.37-5.31 (m, 2H), 5.01 (t, *J* = 9.6 Hz, 1H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.28-4.22 (m, 2H), 4.05 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.93 (dq, *J* = 10.3, 2.1 Hz, 1H), 3.73 (dd, *J* = 10.5, 2.8 Hz, 1H), 3.28 (tt, *J* = 20.2, 6.9 Hz, 2H), 3.15 (dd, *J* = 10.5, 3.7 Hz, 1H), 2.17 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.59-1.53 (m, 2H), 1.33-1.19 (m, 26H), 0.85 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 169.6, 169.3, 167.0, 97.8, 72.6, 69.8, 68.1, 68.1, 67.0, 61.6, 60.9, 39.7, 32.0, 29.8, 29.7, 29.7, 29.6, 29.4, 29.3, 27.1, 22.8, 21.0, 20.8, 20.7, 20.6, 14.2; IR (neat) υ (cm^{-1}) 3902, 3757, 3384, 2923, 2855, 2381, 2110, 1749, 1680, 1534, 1456, 1372, 1226, 1149, 1052; HRMS (FAB) m/z calcd for $C_{33}H_{57}N_4O_{11}$ $[M+H]^+$ 685.4024, found: 685.4012; $[\alpha]_D^{25}$= +10.7 (c=1.0 in MeOH).

(*2R,3S,4R,5R,6S*)-6-((*R*)-2-acetoxy-3-(heptadecylamino)-3-oxopropoxy)-2-(acetoxymethyl)-5-azidotetrahydro-2*H*-pyran-3,4-diyl diacetate (18ba)

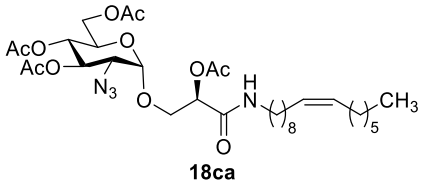


18ba

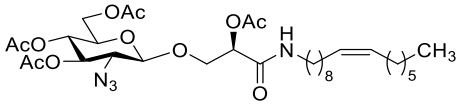
Following **GP-V**, from **11b** (34.4 mg, 0.10 mmol), the mixture of **18ba** and its β-anomer **18bb** were obtained (2 steps 32%, 8% in ^{1}H NMR, respectively). After the isolation, the title compound **18ba** (18.0 mg, 2 steps 26%) was afforded as a white solid. m.p. (purified from DCM) 47-49 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.39 (t, *J* = 5.7 Hz, 1H), 5.39-5.33 (m, 2H), 5.03 (dd, *J* = 10.1, 9.2 Hz, 1H), 4.97 (d, *J* = 3.2 Hz, 1H), 4.29-4.24 (m, 2H), 4.07 (dd, *J* = 12.4, 1.8 Hz, 1H), 3.95 (dq, *J* = 10.3, 2.1 Hz, 1H), 3.75 (dd, *J* = 10.6, 2.3 Hz, 1H), 3.36-3.24 (m, 2H), 3.17 (dd, *J* = 10.6, 3.2 Hz, 1H), 2.18 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.63-1.56 (m, 2H), 1.30-1.24 (m, 28H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.0, 169.6, 169.4, 167.0, 97.8, 72.7, 69.9, 68.1, 67.0, 61.6, 60.9, 39.7, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 27.1, 22.8, 21.1, 20.8, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902,

3757, 3383, 2925, 2854, 2370, 2111, 1751, 1680, 1534, 1457, 1373, 1226, 1149, 1046; HRMS (FAB) m/z calcd for $C_{34}H_{59}N_4O_{11}$ $[M+H]^+$ 699.4180, found: 699.4190; $[\alpha]_D^{25}$= +17.4 (c=1.0 in MeOH).

(*2R,3S,4R,5R,6S*)-6-((*R*)-2-acetoxy-3-(((*Z*)-hexadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)-5-azidotetrahydro-2*H*-pyran-3,4-diyl diacetate (18ca), (*2R,3S,4R,5R,6R*)-6-((*R*)-2-acetoxy-3-(((*Z*)-hexadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)-5-azidotetrahydro-2*H*-pyran-3,4-diyl diacetate (18cb)



18ca



18cb

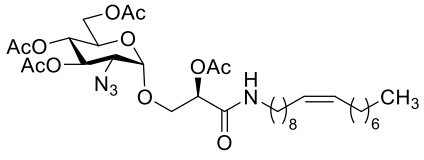
Following **GP-V**, from **11c** (32.8 mg, 0.10 mmol), the mixture of **18ca** and its β-anomer **18cb** were obtained (2 steps 63%, 25% in ^{1}H NMR, respectively). After the isolation, the title compound **18ca** (34.6 mg, 2 steps 51%) and **18cb** (9.2 mg, 2 steps 13%) were afforded.

18ca: colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.38 (t, *J* = 5.7 Hz, 1H), 5.38-5.28 (m, 4H), 5.02 (t, *J* = 9.8 Hz, 1H), 4.97 (d, *J* = 3.2 Hz, 1H), 4.29-4.23 (m, 2H), 4.06 (dd, *J* = 12.3, 1.8 Hz, 1H), 3.94 (dt, *J* = 10.4, 1.9 Hz, 1H), 3.74 (dd, *J* = 10.5, 2.7 Hz, 1H), 3.36-3.23 (m, 2H), 3.16 (dd, *J* = 10.7, 3.4 Hz, 1H), 2.18 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.01-1.97 (m, 7H), 1.62-1.52 (m, 2H), 1.30-1.27 (m, 18H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.0, 169.6, 169.4, 167.0, 130.1, 129.9, 97.8, 72.7, 69.9, 68.1, 68.1, 67.0, 61.6, 60.9, 39.7, 31.9, 29.9, 29.8, 29.6, 29.6, 29.4, 29.3, 29.1, 27.3, 27.1, 22.8, 21.1, 20.8, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 2925, 2371, 2321, 2110, 1749, 1680, 1565, 1543, 1489, 1374, 1338, 1225, 1050; HRMS (FAB) m/z calcd for $C_{33}H_{55}N_4O_{11}$ $[M+H]^+$ 683.3867, found: 683.3860; $[\alpha]_D^{25}$= +16.5 (c=1.0 in MeOH).

18cb: colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.25 (t, *J* = 5.3 Hz, 1H), 5.34 (t, *J* = 16.9 Hz, 3H), 5.01-4.91 (m, 2H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.27-4.20 (m, 2H), 4.10-4.06 (m, 2H), 3.65-3.62 (m, 1H), 3.46 (t, *J* = 8.7 Hz, 1H), 3.36-3.16 (m, 2H), 2.18 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.04-1.96 (m, 7H), 1.50 (t, *J* = 6.4 Hz, 2H), 1.26 (d, *J* = 14.6 Hz, 18H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.0, 169.8, 169.6, 167.0, 130.1, 129.9, 102.4, 73.1, 72.4, 72.0, 68.9, 68.4, 63.9, 61.9, 39.7, 31.9, 29.9, 29.6, 29.5, 29.4, 29.1, 27.3, 27.3, 27.0, 22.8, 21.1, 20.9, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 2926, 2371, 2321, 2114, 1754, 1680, 1564, 1543, 1457, 1373, 1338, 1228, 1053;

HRMS (FAB) m/z calcd for $C_{33}H_{55}N_4O_{11}$ $[M+H]^+$ 683.3867, found: 683.3858; $[\alpha]_D^{25}$= +9.7 (c=1.0 in MeOH).

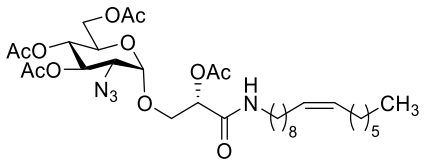
(*2R,3S,4R,5R,6S*)-6-((*R*)-2-acetoxy-3-(((*Z*)-heptadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)-5-azidotetrahydro-2*H*-pyran-3,4-diyl diacetate (18da)



18da

Following **GP-V**, from **11d** (34.2 mg, 0.10 mmol), the mixture of **18da** and its β-anomer **18db** were obtained (2 steps 50%, 16% in ^{1}H NMR, respectively). After the isolation, the title compound **18da** (32.5 mg, 2 steps 47%) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.37 (t, *J* = 5.7 Hz, 1H), 5.39-5.29 (m, 4H), 5.03 (t, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 3.7 Hz, 1H), 4.30-4.24 (m, 2H), 4.07 (dd, *J* = 12.4, 1.8 Hz, 1H), 3.95 (dq, *J* = 10.2, 2.1 Hz, 1H), 3.75 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.37-3.24 (m, 2H), 3.17 (dd, *J* = 10.8, 3.4 Hz, 1H), 2.19 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.02-1.97 (m, 7H), 1.61-1.54 (m, 2H), 1.32-1.24 (m, 20H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.0, 169.6, 169.4, 167.0, 130.1, 129.9, 97.9, 72.7, 69.9, 68.1, 68.1, 67.0, 61.6, 60.9, 39.7, 32.0, 29.9, 29.8, 29.8, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 27.3, 27.1, 22.8, 21.1, 20.8, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 2926, 2371, 2321, 2110, 1751, 1680, 1565, 1534, 1457, 1373, 1339, 1226, 1047; HRMS (FAB) m/z calcd for $C_{34}H_{57}N_4O_{11}$ $[M+H]^+$ 697.4024, found: 697.4025; $[\alpha]_D^{25}$= +17.1 (c=1.0 in MeOH).

(*2R,3S,4R,5R,6S*)-6-((*S*)-2-acetoxy-3-(((*Z*)-hexadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)-5-azidotetrahydro-2*H*-pyran-3,4-diyl diacetate (18ea)



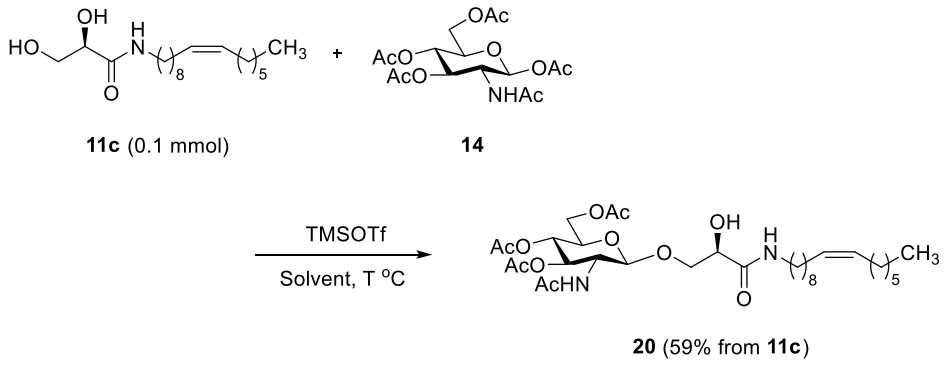
18ea

Following **GP-V**, from **11e** (32.8 mg, 0.10 mmol), the mixture of **18ea** and its β-anomer **18eb** were obtained (2 steps 55%, 15% in ^{1}H NMR, respectively). After the isolation, the title compound **18ea**

(31.8 mg, 2 steps 47%) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.28 (t, *J* = 5.7 Hz, 1H), 5.43 (t, *J* = 9.8 Hz, 1H), 5.37-5.29 (m, 3H), 5.02-4.97 (m, 2H), 4.25 (dd, *J* = 12.3, 5.0 Hz, 1H), 4.08-3.96 (m, 4H), 3.35-3.17 (m, 3H), 2.20 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.99 (q, *J* = 6.4 Hz, 4H), 1.56-1.48 (m, 2H), 1.36-1.23 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.1, 169.7, 169.5, 166.9, 130.1, 129.9, 98.5, 72.7, 70.1, 68.7, 68.0, 67.2, 61.9, 60.9, 39.7, 31.9, 29.8, 29.5, 29.5, 29.3, 29.1, 27.3, 27.3, 27.0, 22.8, 21.1, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3736, 2926, 2371, 2321, 2110, 1749, 1680, 1565, 1542, 1457, 1373, 1339, 1227, 1047; HRMS (FAB) m/z calcd for $C_{33}H_{55}N_4O_{11}$ $[M+H]^+$ 683.3867, found: 683.3862; $[\alpha]_D^{25}$= +11.5 (c=1.0 in MeOH).

2.4.3. β-Stereoselective glycosylation of 11c and its optimization

(*2R,3S,4R,5R,6R*)-5-acetamido-2-(acetoxymethyl)-6-((*R*)-3-(((*Z*)-hexadec-9-en-1-yl)amino)-2-hydroxy-3-oxopropoxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (20)[5]



11c (0.1 mmol) **14**

20 (59% from **11c**)

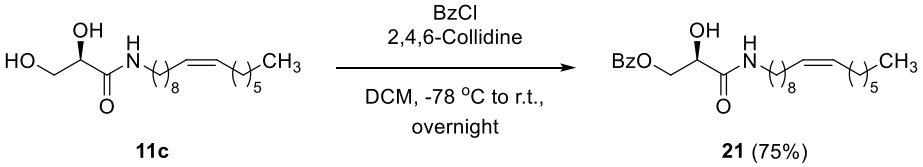
Entry	**11c** (eq.)	**14** (eq.)	TMSOTf (eq.)	T (℃)	Solvent (0.1 M)	Time (hr)	Yields of **20**
1	1.0	2.5	2.0	50	DCE	24	47%
2	1.0	3.0	2.0	50	DCE	24	52%
3	1.0	3.5	2.0	50	DCE	24	48%
4	1.0	3.0	1.0	50	DCE	24	47%
5	1.0	3.0	1.5	50	DCE	24	52%
6	1.0	3.0	2.5	50	DCE	24	48%
7	**1.0**	**3.0**	**2.0**	**40**	**DCE**	**24**	**59%**
8	1.0	3.0	1.5	40	DCE	24	56%
9	1.0	3.0	2.0	30	DCE	24	41%

10	1.0	3.0	2.0	40 (reflux)	DCM	24	47%
11	1.0	3.0	2.0	40	ACN	24	32%
12	1.0	3.0	2.0	40	DMF	24	17%
13	1.0	3.0	2.0	40	DCE	48	56%
14	1.0	3.0	2.0	40	DCE	72	48%

Reaction conditions tested at **Entry 7** was used for the synthesis of **20**, shown in optimization table above. TMSOTf (36.0 μL, 0.20 mmol) was added to a mixture of **11c** (32.6 mg, 0.10 mmol) and **7** (2-acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-b-D-glucopyranose, 116.3 mg, 0.30 mmol) in DCE (1.0 mL), and the solution was stirred at 40 ℃ for 24 hr. The resulted mixture was diluted with ethyl acetate and the organic layer was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then, the residue was purified by flash column chromatography on C18 (distilled water : acetonitrile = 40:60 to 20:80) to afford the title compound **24** (38.3 mg, 59%) as a white solid. m.p. (purified from DCM) 104-106 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.89 (t, *J* = 4.6 Hz, 1H), 5.94 (s, 1H), 5.38-5.29 (m, 2H), 5.16 (t, *J* = 10.1 Hz, 1H), 5.05 (t, *J* = 9.6 Hz, 1H), 4.61 (d, *J* = 8.2 Hz, 1H), 4.24 (q, *J* = 5.9 Hz, 1H), 4.14 (t, *J* = 5.0 Hz, 2H), 4.03 (q, *J* = 5.0 Hz, 1H), 3.97-3.85 (m, 2H), 3.71 (qd, *J* = 5.0, 2.4 Hz, 1H), 3.36-3.14 (m, 2H), 2.09 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02-1.97 (m, 4H), 1.94 (s, 3H), 1.52 (t, *J* = 6.6 Hz, 2H), 1.35-1.23 (m, 18H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.3, 171.1, 171.1, 170.9, 169.5, 130.1, 129.9, 102.0, 72.3, 72.2, 71.7, 70.7, 68.4, 62.1, 54.7, 39.5, 31.9, 29.9, 29.6, 29.6, 29.4, 29.1, 27.3, 27.0, 23.5, 22.8, 20.9, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 3649, 3297, 2925, 2854, 2371, 2321, 1748, 1659, 1648, 1543, 1374, 1228, 1046; HRMS (FAB) m/z calcd for $C_{33}H_{57}N_2O_{11}$ $[M+H]^+$ 657.3962, found: 657.3966; $[\alpha]_D^{25}$= -23.8 (c=1.0 in MeOH).

2.4.4. α- or β-Stereoselective Schmidt glycosylation reactions of 21

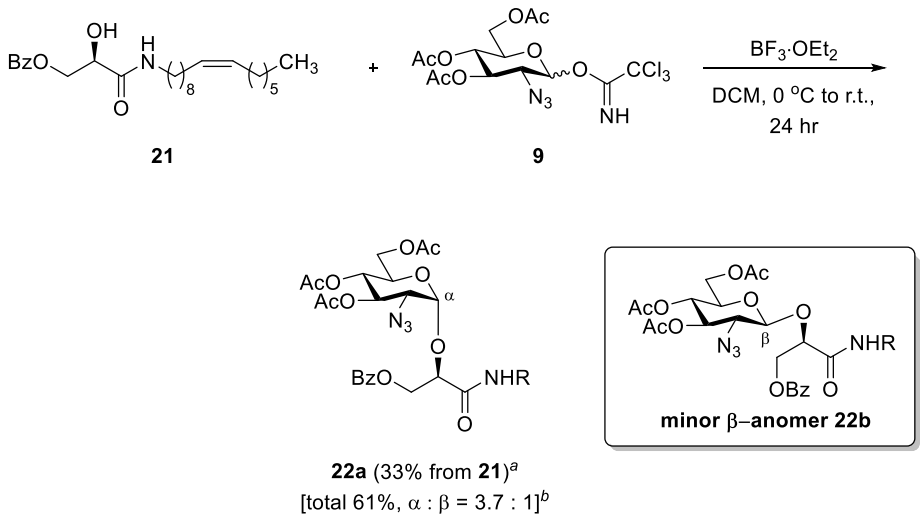
(*R*,*Z*)-3-(hexadec-9-en-1-ylamino)-2-hydroxy-3-oxopropyl benzoate (21)[6]



Benzoyl chloride (16.2 μL, 0.14 mmol) was added dropwise to a -78 ℃ solution of **11c** (32.6 mg, 0.10

mmol) and 2,4,6-collidine (32.9 μL, 0.25 mmol) in DCM (1.0 mL), and stirred for 3 hr at the same temperature. The solution was warmed up to room temperature, and stirred for 24 hr. The mixture was diluted with ethyl acetate and the organic layer was washed with aqueous 1 M HCl. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then, the residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 2:1) to afford the title compound **21** (32.0 mg, 75%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.82 (s, 1H), 5.39-5.30 (m, 2H), 4.77 (dd, *J* = 11.9, 2.8 Hz, 1H), 4.62 (q, *J* = 5.8 Hz, 1H), 4.44 (q, *J* = 2.6 Hz, 1H), 3.94 (s, 1H), 3.36-3.21 (m, 2H), 2.01-1.97 (m, 4H), 1.47 (q, *J* = 7.0 Hz, 2H), 1.30-1.24 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 167.8, 133.6, 130.1, 129.9, 129.9, 129.4, 128.5, 71.7, 67.6, 39.4, 31.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.1, 27.3, 27.3, 27.0, 22.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 2925, 2854, 2371, 2321, 1747, 1723, 1648, 1543, 1452, 1375, 1274, 1118, 1032; HRMS (FAB) m/z calcd for $C_{26}H_{42}NO_4$ $[M+H]^+$ 432.3114, found: 432.3120; $[\alpha]_D^{25}$= +10.6 (c=1.0 in MeOH).

(*2R,3S,4R,5R,6R*)-2-(acetoxymethyl)-5-azido-6-(((*R*)-3-(benzoyloxy)-1-(((*Z*)-hexadec-9-en-1-yl)amino)-1-oxopropan-2-yl)oxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (22a)

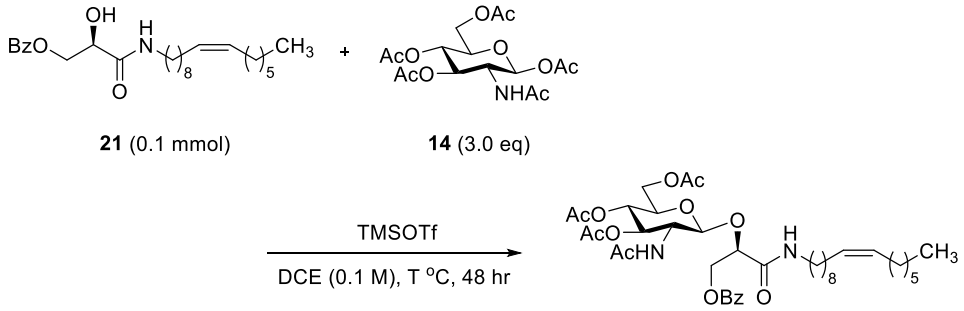


[a] Isolated yields, [b]NMR analysis using dimethyl sulfone as the internal standard

BF_3·OEt_2 (0.25 mL, 2.02 mmol) was added to a solution of **21** (43.6 mg, 0.10 mmol) and **9** (72.1 mg, 0.15 mmol) in DCM (2.02 mL), dropwise for 1 hr at 0 ℃, and stirred for 30 min at the same temperature. The solution was warmed up to room temperature, and stirred for 24 hr. The mixture was diluted with DCM and the organic layer was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Dimethylsulfone (4.7 mg, 0.05 mmol) was added to

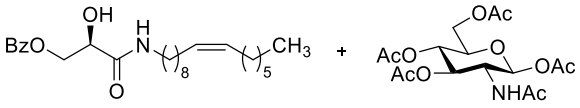
the residue as an internal standard, and the yields of **22a** and its β-anomer **22b** were obtained (48%, 13%, in ^{1}H NMR, respectively). Then, the residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 3:1) to afford **22a** (24.8 mg, 33%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 5.5 Hz, 1H), 5.48-5.43 (m, 1H), 5.37-5.29 (m, 2H), 4.99 (t, *J* = 9.9 Hz, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 4.74 (dd, *J* = 11.7, 2.5 Hz, 1H), 4.57 (q, *J* = 6.1 Hz, 1H), 4.47 (q, *J* = 2.9 Hz, 1H), 4.15 (dq, *J* = 10.2, 2.1 Hz, 1H), 4.03 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.83-3.79 (m, 2H), 3.37-3.23 (m, 2H), 2.08 (s, 3H), 2.02-1.97 (m, 7H), 1.96 (s, 3H), 1.56-1.47 (m, 2H), 1.36-1.23 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.7, 167.6, 166.0, 133.5, 130.1, 129.9, 129.8, 129.7, 128.6, 97.2, 77.9, 71.8, 68.6, 68.1, 65.2, 61.8, 61.4, 39.5, 31.9, 29.8, 29.5, 29.4, 29.4, 29.1, 27.3, 27.3, 27.0, 22.8, 20.8, 20.7, 20.6, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 2926, 2371, 2321, 2113, 1755, 1681, 1534, 1453, 1368, 1316, 1227, 1121, 1047; HRMS (FAB) m/z calcd for $C_{38}H_{57}N_4O_{11}$ $[M+H]^+$ 745.4024, found: 745.4033; $[\alpha]_D^{25}$= -28.3 (c=1.0 in MeOH).

First trials for β-Stereoselective glycosylation reactions of 21 using 14 as a glycosyl donor:

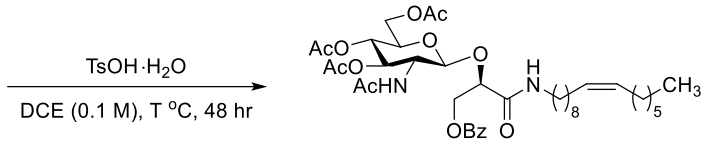


21 (0.1 mmol) **14** (3.0 eq) **25**

Entry	**21** (eq.)	**14** (eq.)	TMSOTf (eq.)	T (℃)	Yields of **25**	Remained **21**
1	1.0	3.0	1.00	50	19%	43%
2	1.0	3.0	0.50	50	21%	63%
3	1.0	3.0	0.50	70	32%	12%
4	1.0	3.0	0.25	70	**38%**	40%
5	1.0	3.0	0.25	80	36%	12%
6	1.0	3.0	0.15	70	25%	53%
7	1.0	3.0	0.15	80	35%	33%

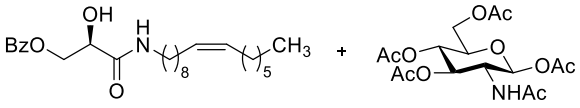


21 (0.1 mmol) **14**

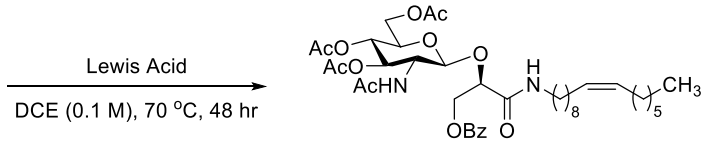


25

Entry	**21** (eq.)	**14** (eq.)	$TsOH \cdot H_2O$ (eq.)	T (°C)	Yields of **25**	Remained **21**
8	1.0	2.0	0.1	70	19%	62%
9	1.0	2.0	0.3	70	29%	53%
10	1.0	2.0	0.5	70	28%	53%
11	1.0	2.0	0.7	70	23%	59%
12	1.0	3.0	0.3	70	35%	45%
13	1.0	4.0	0.3	70	31%	46%
14	1.0	3.0	0.3	50	Not Detected	83%
15	1.0	3.0	0.3	90 (reflux)	21%	44%



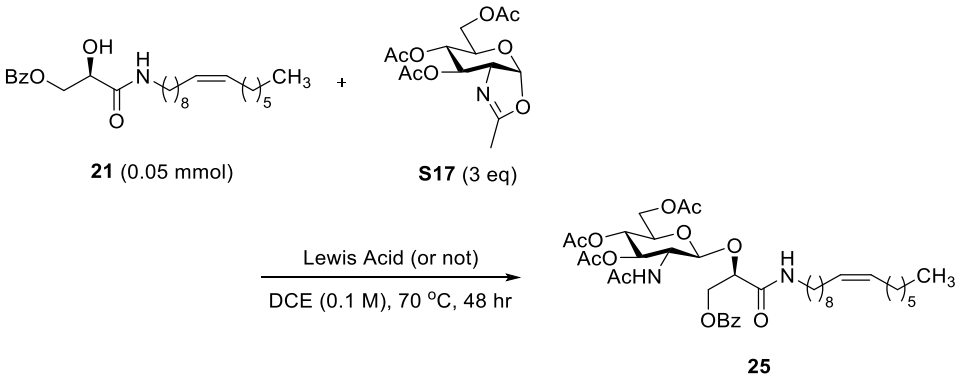
21 (0.1 mmol) **14** (3.0 eq)



25

Entry	**21** (eq.)	**14** (eq.)	Lewis Acid (eq.)	T (°C)	Yields of **25**	Remained **21**
16	1.0	3.0	$Cu(OTf)_2$ (0.25)	70	24%	62%
17	1.0	3.0	$Cu(OTf)_2$ (0.5)	70	25%	43%
18	1.0	3.0	$Cu(OTf)_2$ (1.0)	70	16%	50%
19	1.0	3.0	$FeCl_3$ (0.5)	70	22%	50%

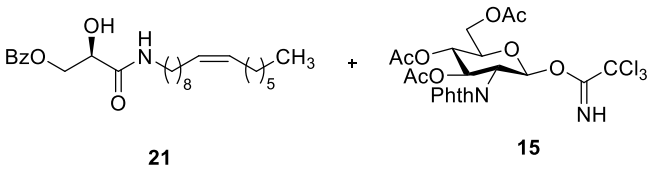
Additional trials for β-Stereoselective glycosylation reactions of 21 using oxazoline S17[7]

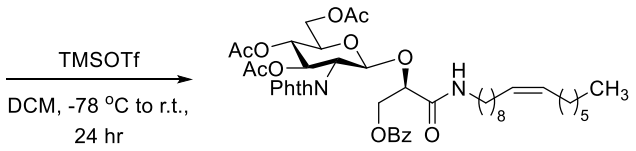


Entry	**21** (eq.)	**S17** (eq.)	Lewis Acid (eq.)	T (°C)	Yields of **25**	Remained **21**
1	1.0	3.0	Nothing	70	Not Detected	87%
2	1.0	3.0	TMSOTf (0.15)	70	11%	55%
3	1.0	3.0	TMSOTf (0.50)	70	14%	7%
4	1.0	3.0	$TsOH{\cdot}H_2O$ (0.10)	70	18%	60%

Finally successed β-Stereoselective Schmidt glycosylation reactions of 21 using 15 as a glycosyl donor:

(*2R,3S,4R,5R,6S*)-2-(acetoxymethyl)-6-(((*R*)-3-(benzoyloxy)-1-(((*Z*)-hexadec-9-en-1-yl)amino)-1-oxopropan-2-yl)oxy)-5-(1,3-dioxoisoindolin-2-yl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (24)



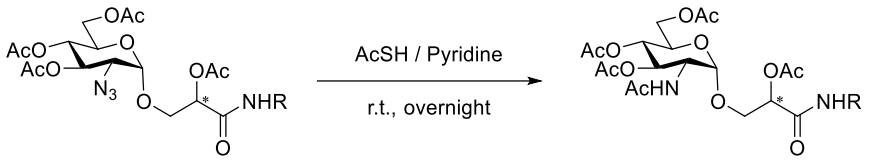


24 (79% from **21**)

A solution of TMSOTf (9.3 μL, 0.051 mmol) in DCM (1.0 mL) was stirred at -78 ℃ for 3 min. Then, this diluted solution (0.1 mL, with 5.1 μmol of TMSOTf) was added to a solution of **21** (22.2 mg, 0.051 mmol) and **15** (44.7 mg, 0.077 mmol) in DCM (0.4 mL), dropwise at -78℃ for 3 min and stirred at the same temperature for 30 min. The mixture was warmed up to the room temperature slowly and stirred for 24 hr. Then, the reaction was quenched with triethylamine (0.1 mL) and concentrated *in vacuo* directly. The residue was purified by flash column chromatography on C18 (distilled water : acetonitrile = 20:80 to 10:90) to afford the title compound **24** (34.6 mg, 79%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56-7.45 (m, 7H), 7.28 (s, 1H), 7.24 (s, 1H), 6.73 (t, *J* = 5.7 Hz, 1H), 5.85 (dd, *J* = 10.5, 9.1 Hz, 1H), 5.56 (d, *J* = 8.2 Hz, 1H), 5.39-5.31 (m, 2H), 5.16 (dd, *J* = 10.1, 9.1 Hz, 1H), 4.58 (dd, *J* = 11.9, 2.3 Hz, 1H), 4.47 (q, *J* = 2.1 Hz, 1H), 4.43-4.32 (m, 3H), 4.12 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.92 (qd, *J* = 5.0, 2.3 Hz, 1H), 3.37-3.19 (m, 2H), 2.11 (s, 3H), 2.04-1.99 (m, 7H), 1.84 (s, 3H), 1.54-1.43 (m, 2H), 1.35-1.23 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 170.0, 169.6, 167.8, 167.7, 165.6, 134.2, 133.0, 131.1, 130.1, 129.9, 129.6, 129.2, 128.2, 123.5, 97.8, 78.2, 72.3, 70.3, 68.9, 63.8, 62.0, 54.7, 39.5, 31.9, 29.9, 29.9, 29.7, 29.6, 29.4, 29.1, 27.4, 27.0, 22.8, 20.8, 20.7, 20.5, 14.2; IR (neat) υ (cm^{-1}) 3902, 3735, 2926, 2854, 2371, 2321, 1749, 1720, 1681, 1533, 1489, 1456, 1338, 1227, 1040; HRMS (FAB) m/z calcd for $C_{46}H_{61}N_2O_{13}$ $[M+H]^+$ 849.4174, found: 849.4186; $[\alpha]_D^{25}$= -19.9 (c=1.0 in MeOH).

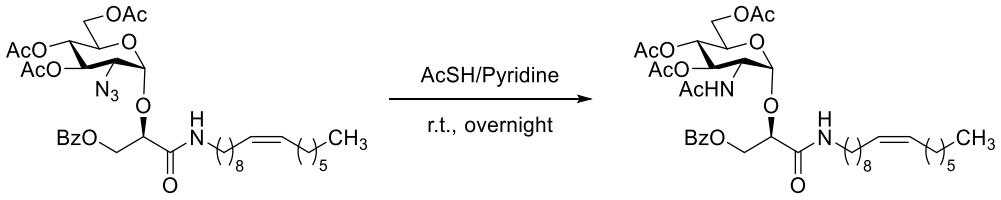
2.5. Completion of synthesis of Deinococcucins (1-8) after the glycosylations

2.5.1. General Procedure VI (GP-VI): Conversion of azide to *N*-acetylamide[8]



18aa - 18ea

19a (87% from **18aa**)
19b (95% from **18ba**)
19c (93% from **18ca**)
19d (94% from **18da**)
19e (95% from **18ea**)

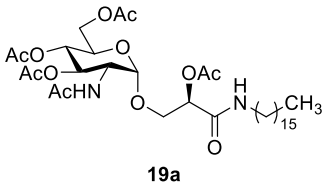


22a

23 (83%)

A solution of **18aa-18ea** or **22a** (0.03-0.12 mmol) in thioacetic acid (1.0 mL) and pyridine (0.5 mL) was stirred for overnight at the room temperature. The mixture was diluted with ethyl acetate and the organic layer was washed with aqueous 1 M HCl twice, and saturated aqueous $NaHCO_3$ twice. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Then, the residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 1:5) to afford desired products **19a-19e**, and **23**.

(*2R,3S,4R,5R,6S*)-5-acetamido-6-((*R*)-2-acetoxy-3-(hexadecylamino)-3-oxopropoxy)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (19a)

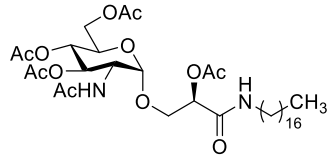


19a

Following **GP-VI**, from **18aa** (51.8 mg, 0.076 mmol), title compound **19a** (46.2 mg, 87%) was afforded as a white solid. m.p. (purified from DCM) 138-140 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.19 (t, *J* = 5.7 Hz, 1H), 6.10 (d, *J* = 9.6 Hz, 1H), 5.39 (q, *J* = 2.9 Hz, 1H), 5.16-5.09 (m, 2H), 4.87 (d, *J* = 3.7 Hz, 1H), 4.38-4.32 (m, 1H), 4.24 (dd, *J* = 12.6, 4.4 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.04 (q, *J* = 5.7 Hz, 1H), 3.95-3.91 (m, 1H), 3.85 (dd, *J* = 11.2, 3.4 Hz, 1H), 3.29 (q, *J* = 6.9 Hz, 2H), 2.23 (s, 3H), 2.10 (s,

3H), 2.01 (s, 6H), 1.98 (s, 3H), 1.58-1.50 (m, 2H), 1.31-1.25 (m, 26H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.3, 170.8, 170.4, 169.6, 169.3, 166.8, 97.9, 72.7, 71.3, 68.3, 68.0, 67.7, 61.8, 51.6, 39.6, 32.0, 29.8, 29.7, 29.7, 29.6, 29.4, 29.3, 27.0, 23.1, 22.8, 21.1, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3840, 3648, 3614, 3308, 2850, 2371, 2321, 1745, 1659, 1565, 1542, 1375, 1338, 1229, 1038; HRMS (FAB) m/z calcd for $C_{35}H_{61}N_2O_{12}$ $[M+H]^+$ 701.4225, found: 701.4218; $[\alpha]_D^{25}$= +14.6 (c=1.0 in MeOH).

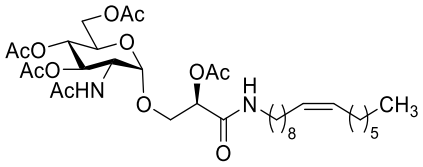
(*2R,3S,4R,5R,6S*)-5-acetamido-6-((*R*)-2-acetoxy-3-(heptadecylamino)-3-oxopropoxy)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (19b)



19b

Following **GP-VI**, from **18ba** (20.9 mg, 0.030 mmol), title compound **19b** (20.2 mg, 95%) was afforded as a white solid. m.p. (purified from DCM) 113-115 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.19 (t, J = 5.9 Hz, 1H), 6.08 (d, J = 9.6 Hz, 1H), 5.39 (q, J = 3.0 Hz, 1H), 5.16-5.09 (m, 2H), 4.87 (d, J = 3.2 Hz, 1H), 4.35 (td, J = 9.5, 4.3 Hz, 1H), 4.24 (dd, J = 12.3, 4.1 Hz, 1H), 4.11-4.02 (m, 2H), 3.95-3.92 (m, 1H), 3.85 (dd, J = 11.4, 3.2 Hz, 1H), 3.29 (q, J = 6.7 Hz, 2H), 2.23 (s, 3H), 2.10 (s, 3H), 2.01 (s, 6H), 1.98 (s, 3H), 1.54 (q, J = 7.2 Hz, 2H), 1.30-1.25 (m, 28H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.4, 170.9, 170.3, 169.6, 169.3, 166.8, 98.0, 72.8, 71.3, 68.3, 68.1, 67.8, 61.9, 51.7, 39.7, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 27.0, 23.2, 22.8, 21.1, 20.9, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3841, 3649, 3614, 3308, 2851, 2371, 2321, 1745, 1660, 1564, 1543, 1375, 1339, 1230, 1042; HRMS (FAB) m/z calcd for $C_{36}H_{63}N_2O_{12}$ $[M+H]^+$ 715.4381, found: 715.4369; $[\alpha]_D^{25}$= +11.3 (c=1.0 in MeOH).

(*2R,3S,4R,5R,6S*)-5-acetamido-6-((*R*)-2-acetoxy-3-(((*Z*)-hexadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (19c)

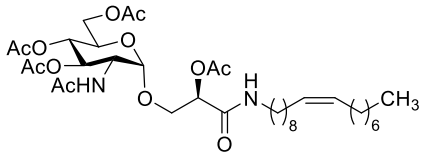


19c

Following **GP-VI**, from **18ca** (79.6 mg, 0.12 mmol), title compound **19c** (75.7 mg, 93%) was afforded as a white solid. m.p. (purified from DCM) 81-83 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.18 (t, J = 5.5 Hz, 1H), 6.05 (d, J = 9.6 Hz, 1H), 5.40-5.29 (m, 3H), 5.16-5.08 (m, 2H), 4.87 (d, J = 3.7 Hz, 1H), 4.34

(td, J = 9.8, 3.8 Hz, 1H), 4.23 (dd, J = 12.3, 4.1 Hz, 1H), 4.09 (dd, J = 12.6, 2.1 Hz, 1H), 4.03 (q, J = 5.6 Hz, 1H), 3.93-3.92 (m, 1H), 3.85 (dd, J = 11.4, 3.2 Hz, 1H), 3.28 (q, J = 6.9 Hz, 2H), 2.22 (s, 3H), 2.09 (s, 3H), 2.04-1.95 (m, 13H), 1.58-1.50 (m, 2H), 1.36-1.21 (m, 18H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.4, 170.8, 170.3, 169.6, 169.3, 166.8, 130.1, 129.8, 98.0, 72.8, 71.3, 68.3, 68.1, 67.8, 61.9, 51.7, 39.7, 31.9, 29.8, 29.7, 29.5, 29.3, 29.3, 29.1, 27.3, 27.3, 27.0, 23.2, 22.8, 21.1, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3841, 3649, 3567, 3310, 2855, 2371, 2321, 1747, 1658, 1543, 1374, 1339, 1229, 1044; HRMS (FAB) m/z calcd for $C_{35}H_{59}N_2O_{12}$ $[M+H]^+$ 699.4068, found: 699.4061; $[\alpha]_D^{25}$= +6.0 (c=1.0 in MeOH).

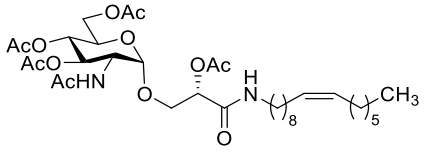
(*2R,3S,4R,5R,6S*)-5-acetamido-6-((*R*)-2-acetoxy-3-(((*Z*)-heptadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (19d)



19d

Following **GP-VI**, from **18da** (54.1 mg, 0.078 mmol), title compound **19d** (52.2 mg, 94%) was afforded as a white solid. m.p. (purified from DCM) 83-85 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.19 (t, J = 5.7 Hz, 1H), 6.06 (d, J = 9.6 Hz, 1H), 5.39 (q, J = 2.9 Hz, 1H), 5.37-5.29 (m, 2H), 5.12 (ddd, J = 14.9, 9.6, 3.9 Hz, 2H), 4.87 (d, J = 3.7 Hz, 1H), 4.39-4.31 (m, 1H), 4.23 (dd, J = 12.3, 4.1 Hz, 1H), 4.11-4.01 (m, 2H), 3.94-3.91 (m, 1H), 3.85 (dd, J = 11.4, 3.7 Hz, 1H), 3.28 (q, J = 7.0 Hz, 2H), 2.22 (s, 3H), 2.09 (s, 3H), 2.01-1.98 (m, 13H), 1.54 (t, J = 6.4 Hz, 2H), 1.29-1.25 (m, 20H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.4, 170.8, 170.3, 169.6, 169.3, 166.8, 130.1, 129.8, 98.0, 72.8, 71.3, 68.3, 68.0, 67.8, 61.9, 51.7, 39.6, 32.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 27.3, 27.0, 23.2, 22.8, 21.1, 20.9, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3841, 3649, 3567, 3309, 2854, 2371, 2321, 1746, 1658, 1542, 1374, 1339, 1230, 1043; HRMS (FAB) m/z calcd for $C_{36}H_{61}N_2O_{12}$ $[M+H]^+$ 713.4225, found: 713.4241; $[\alpha]_D^{25}$= +6.9 (c=1.0 in MeOH).

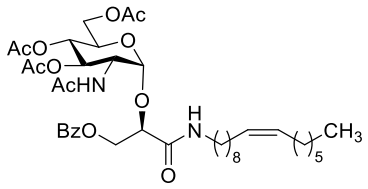
(*2R,3S,4R,5R,6S*)-5-acetamido-6-((*S*)-2-acetoxy-3-(((*Z*)-hexadec-9-en-1-yl)amino)-3-oxopropoxy)-2-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (19e)



19e

Following **GP-VI**, from **18ea** (32.9 mg, 0.048 mmol), title compound **19e** (32.0 mg, 95%) was afforded as a white solid. m.p. (purified from DCM) 89-91 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.29 (t, *J* = 5.5 Hz, 1H), 5.97 (d, *J* = 9.2 Hz, 1H), 5.37 (dd, *J* = 7.4, 4.6 Hz, 1H), 5.34-5.28 (m, 2H), 5.16 (t, *J* = 10.1 Hz, 1H), 5.07 (t, *J* = 9.9 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 4.31 (td, *J* = 10.0, 3.4 Hz, 1H), 4.20 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.07 (dd, *J* = 11.9, 2.3 Hz, 1H), 4.02 (dd, *J* = 11.3, 3.0 Hz, 1H), 3.95 (qd, *J* = 4.8, 2.4 Hz, 1H), 3.89 (q, *J* = 5.4 Hz, 1H), 3.28 (tt, *J* = 20.4, 6.7 Hz, 2H), 2.19 (s, 3H), 2.07 (s, 3H), 2.00 (t, *J* = 3.4 Hz, 10H), 1.94 (s, 3H), 1.53 (t, *J* = 6.9 Hz, 2H), 1.34-1.22 (m, 18H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.3, 170.8, 170.3, 169.4, 169.3, 167.0, 130.1, 129.8, 98.3, 72.8, 71.3, 68.3, 68.3, 62.0, 51.8, 39.6, 31.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.3, 29.1, 27.3, 27.3, 27.0, 23.1, 22.7, 21.1, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3841, 3649, 3567, 3284, 2855, 2371, 2321, 1749, 1649, 1544, 1372, 1339, 1231, 1046; HRMS (FAB) m/z calcd for $C_{35}H_{59}N_2O_{12}$ $[M+H]^+$ 699.4068, found: 699.4056; $[\alpha]_D^{25}$= +6.9 (c=1.0 in MeOH).

(*2R,3S,4R,5R,6R*)-5-acetamido-2-(acetoxymethyl)-6-(((*R*)-3-(benzoyloxy)-1-(((*Z*)-hexadec-9-en-1-yl)amino)-1-oxopropan-2-yl)oxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (23)

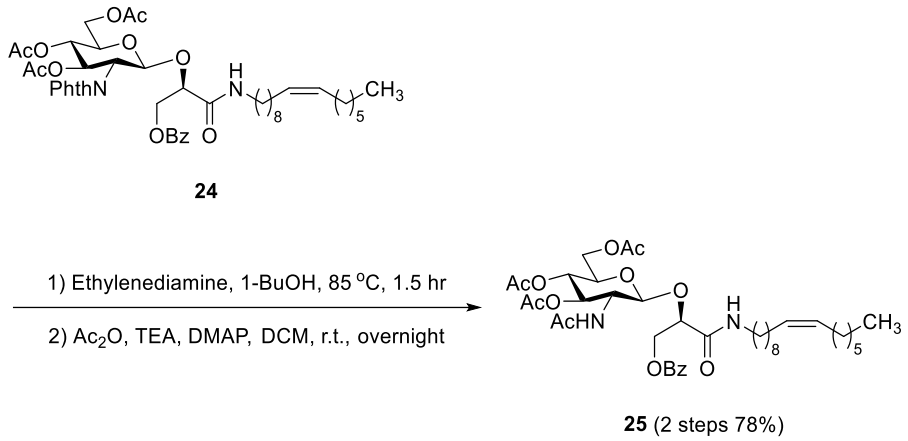


23

Following **GP-VI**, from **22a** (56.8 mg, 0.076 mmol), title compound **23** (48.0 mg, 83%) was afforded as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 8.3 Hz, 1H), 6.34 (t, *J* = 5.5 Hz, 1H), 5.38-5.29 (m, 2H), 5.22 (t, *J* = 10.1 Hz, 1H), 5.07 (t, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 4.69 (dd, *J* = 11.9, 2.8 Hz, 1H), 4.57 (dd, *J* = 11.7, 7.1 Hz, 1H), 4.48 (q, *J* = 3.2 Hz, 1H), 4.29 (ddd, *J* = 11.3, 7.8, 3.0 Hz, 1H), 4.05-3.97 (m, 2H), 3.83 (d, *J* = 10.6 Hz, 1H), 3.32-3.25 (m, 2H), 2.00 (dd, *J* = 11.9, 7.4 Hz, 13H), 1.94 (s, 3H), 1.49 (t, *J* = 6.7 Hz, 2H), 1.34-1.22 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 170.7, 170.6, 169.2, 167.8, 166.3, 133.8, 130.1, 129.9, 129.8, 129.4, 128.7, 97.1 76.3, 71.2, 68.6, 67.8, 65.3, 61.7, 52.3, 39.8, 31.9, 29.9, 29.8, 29.6, 29.5, 29.5, 29.4, 29.4, 29.1, 27.4, 27.3, 27.0, 23.2, 22.8, 20.9, 20.7, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3841, 3735, 3567, 2855, 2371, 2321, 1749, 1688, 1648, 1543, 1374, 1230, 1121, 1043; HRMS (FAB) m/z calcd for $C_{40}H_{61}N_2O_{12}$ $[M+H]^+$ 761.4225, found: 761.4226; $[\alpha]_D^{25}$= -27.1 (c=1.0 in MeOH).

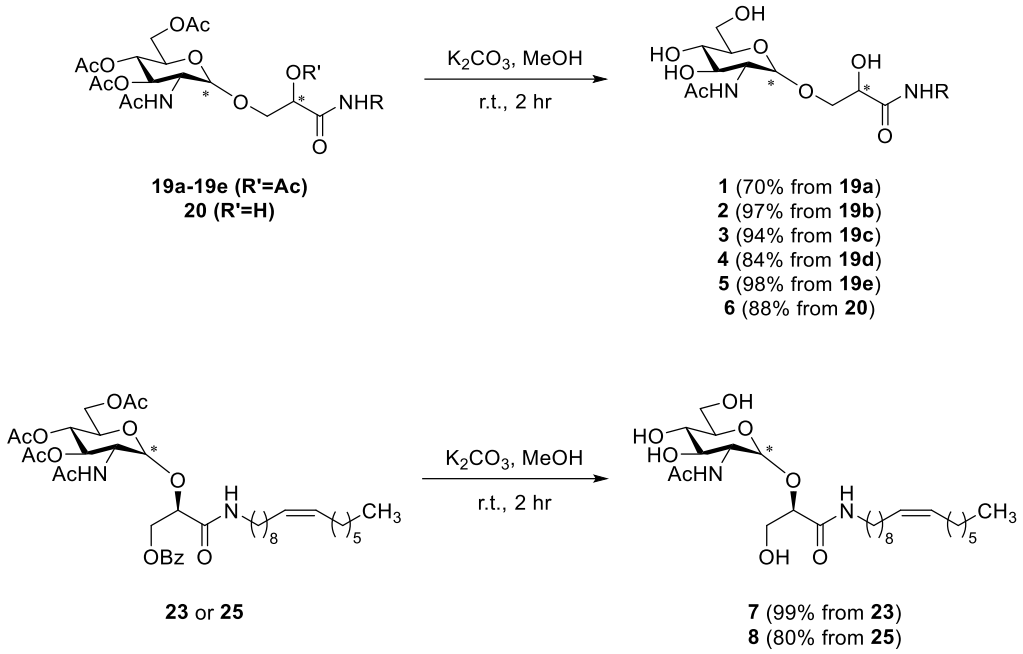
2.5.2. Conversion of *N*-phthalimide to *N*-acetylamide[9]

(*2R,3S,4R,5R,6S*)-5-acetamido-2-(acetoxymethyl)-6-(((*R*)-3-(benzoyloxy)-1-(((*Z*)-hexadec-9-en-1-yl)amino)-1-oxopropan-2-yl)oxy)tetrahydro-2*H*-pyran-3,4-diyl diacetate (25)



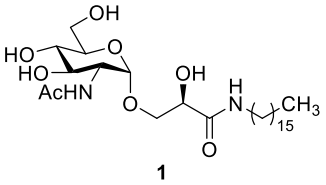
A solution of **24** (31.2 mg, 0.037 mmol) and ethylenediamine (0.12 mL, 1.84 mmol) in 1-butanol (2.0 mL) was stirred at 85 ℃ for 1.5 hr. Then, the mixture was distilled with methanol (2.0 mL) twice, toluene (2.0 mL) twice, and concentrated *in vacuo*. The residue, acetic anhydride (69.5 μL, 0.74 mmol), triethylamine (102.4 μL, 0.74 mmol) and 4-dimethylaminopyridine (0.5 mg, 3.7 μmol) were diluted with DCM (2.0 mL) and stirred at the room temperature for overnight. The mixture was diluted with DCM and the organic layer was washed with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (n-hexane/ethyl acetate, 1:5) to afford the title compound **25** (21.8 mg, 2 steps 78%) as a white solid**.** m.p. (purified from DCM) 148-150 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d*, J* = 7.3 Hz, 2H), 7.58 (t*, J* = 7.3 Hz, 1H), 7.44 (t*, J* = 7.8 Hz, 2H), 6.99 (t*, J* = 5.7 Hz, 1H), 5.56 (d*, J* = 9.1 Hz, 1H), 5.38-5.30 (m, 2H), 5.13-5.06 (m, 3H), 4.76 (d*, J* = 8.2 Hz, 1H), 4.56 (t*, J* = 2.7 Hz, 1H), 4.50 (dd*, J* = 12.1, 3.0 Hz, 1H), 4.26 (dd*, J* = 12.3, 5.0 Hz, 1H), 4.15-4.07 (m, 2H), 3.71 (td*, J* = 4.8, 2.6 Hz, 1H), 3.30 (dtd*, J* = 73.4, 13.4, 7.2 Hz, 2H), 2.08 (d*, J* = 8.7 Hz, 3H), 2.03-1.98 (m, 10H), 1.54 (t*, J* = 6.9 Hz, 2H), 1.46 (s, 3H), 1.29-1.25 (m, 18H), 0.87 (t*, J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.4, 170.8, 170.7, 169.4, 168.1, 166.6, 133.7, 130.1, 130.0, 129.8, 129.5, 128.7, 98.5, 75.5, 72.5, 72.4, 68.3, 62.0, 61.6, 54.3, 39.6, 31.9, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.1, 27.4, 27.1, 22.9, 22.8, 22.8, 20.9, 20.8, 20.7, 14.2; IR (neat) υ (cm^{-1}) 3902, 3841, 3736, 3649, 3567, 3298, 2855, 2371, 2321, 1744, 1551, 1457, 1375, 1371, 1124; HRMS (FAB) m/z calcd for $C_{40}H_{61}N_2O_{12}$ $[M+H]^+$ 761.4225, found: 761.4226; $[\alpha]_D^{25}$= +5.6 (c=1.0 in MeOH).

2.5.3. General Procedure VII (GP-VII): Global deprotections of *O*-acyl groups



A solution of **19a-e, 20, 23 or 25** (0.03-0.06 mmol, 1.0 eq) and potassium carbonate (10.0 eq) in methanol (1.0 mL) was stirred at the room temperature for 2 hr. Then, the reaction mixture was purified by flash column chromatography on C18 (distilled water : acetonitrile = 30:70 to 20:80) directly to afford the desired products.

(*R*)-3-(((*2S,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-hexadecyl-2-hydroxypropanamide (Deinococcucin A, 1)

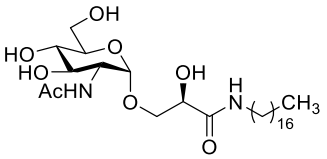


1

Following **GP-VII**, from **19a** (31.0 mg, 0.044 mmol), title compound **1** (20.7 mg, 88%) was afforded as a white solid. m.p. (purified from methanol) 169-171 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.72 (t, *J* = 5.7 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 5.43 (d, *J* = 6.0 Hz, 1H), 4.96 (d, *J* = 5.1 Hz, 1H), 4.71 (d, *J* = 5.5 Hz, 1H), 4.62 (d, *J* = 3.2 Hz, 1H), 4.44 (t, *J* = 5.7 Hz, 1H), 4.01-3.99 (m, 1H), 3.70-3.57 (m, 4H), 3.50-3.40 (m, 3H), 3.16 (td, *J* = 9.1, 4.9 Hz, 1H), 3.05 (td, *J* = 12.6, 6.4 Hz, 2H), 1.85 (s, 3H), 1.40 (t, *J* = 6.0 Hz, 2H), 1.26-1.21 (m, 26H), 0.85 (t, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 171.2, 169.4, 97.2, 72.7, 70.9, 70.8, 70.5, 69.7, 60.7, 53.6, 38.3, 31.3, 29.2, 29.1, 28.8, 28.7, 26.5, 22.8, 22.1,

14.0; IR (neat) υ (cm^{-1}) 3902, 3840, 3735, 3308, 2850, 2371, 2321, 1746, 1705, 1649, 1544, 1468, 1378, 1317, 1121; HRMS (FAB) m/z calcd for $C_{27}H_{53}N_2O_8$ $[M+H]^+$ 533.3802, found: 533.3800; $[\alpha]_D^{25}$= +26.5 (c=0.5 in MeOH).

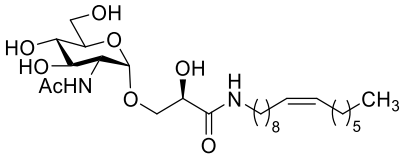
(*R*)-3-(((*2S,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-heptadecyl-2-hydroxypropanamide (Deinococcucin B, 2)



2

Following **GP-VII**, from **19b** (23.0 mg, 0.032 mmol), title compound **2** (17.1 mg, 97%) was afforded as a white solid. m.p. (purified from methanol) 158-160 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.77 (t, *J* = 5.5 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 5.49 (s, 1H), 5.01 (s, 1H), 4.78 (s, 1H), 4.61 (d, *J* = 2.7 Hz, 1H), 4.47 (s, 1H), 4.00 (m, 1H), 3.69-3.57 (m, 3H), 3.49-3.40 (m, 4H), 3.15 (t, *J* = 9.1 Hz, 1H), 3.04 (qd, *J* = 12.7, 6.5 Hz, 2H), 1.84 (s, 3H), 1.42-1.37 (m, 2H), 1.26-1.21 (m, 28H), 0.85 (t, *J* = 6.2 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 171.2, 169.4, 97.2, 72.7, 70.9, 70.8, 70.5, 69.6, 60.7, 53.6, 38.3, 31.3, 29.2, 29.0, 29.0, 28.8, 28.7, 26.4, 22.8, 22.1, 14.0; IR (neat) υ (cm^{-1}) 3902, 3841, 3735, 3298, 2580, 2371, 2321, 1747, 1705, 1648, 1544, 1468, 1375, 1316, 1126; HRMS (FAB) m/z calcd for $C_{28}H_{55}N_2O_8$ $[M+H]^+$ 547.3958, found: 547.3946; $[\alpha]_D^{25}$= +26.9 (c=0.5 in MeOH).

(*R*)-3-(((*2S,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-((*Z*)-hexadec-9-en-1-yl)-2-hydroxypropanamide (Deinococcucin C, 3)

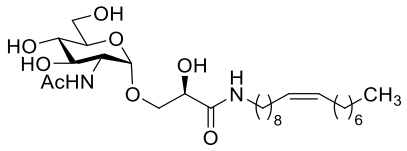


3

Following **GP-VII**, from **19c** (40.0 mg, 0.057 mmol), title compound **3** (28.4 mg, 94%) was afforded as a white solid. m.p. (purified from methanol) 151-153 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.71 (t, *J* = 6.0 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 5.41 (d, *J* = 6.0 Hz, 1H), 5.36-5.28 (m, 2H), 4.95 (d, *J* = 4.6 Hz, 1H), 4.70 (d, *J* = 5.1 Hz, 1H), 4.62 (d, *J* = 3.7 Hz, 1H), 4.43 (t, *J* = 5.7 Hz, 1H), 4.01 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.70-3.57 (m, 3H), 3.51-3.37 (m, 4H), 3.16 (td, *J* = 9.2, 4.6 Hz, 1H), 3.05 (qd, *J* = 12.7, 6.4 Hz, 2H), 1.98 (q, *J* = 6.0 Hz, 4H), 1.85 (s, 3H), 1.40 (t, *J* = 6.7 Hz, 2H), 1.31-1.24 (m, 18H), 0.85 (t, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 171.2, 169.4, 129.6, 97.2, 72.7, 70.9, 70.8, 70.5,

69.6, 60.7, 53.6, 38.3, 31.1, 29.2, 29.1, 29.1, 28.9, 28.7, 28.6, 28.3, 26.6, 26.6, 26.4, 22.8, 22.1, 13.9; IR (neat) υ (cm^{-1}) 3902, 3841, 3735, 3309, 2925, 2371, 2321, 1747, 1648, 1543, 1457, 1376, 1338, 1126; HRMS (FAB) m/z calcd for $C_{27}H_{51}N_2O_8$ $[M+H]^+$ 531.3645, found: 531.3644; $[\alpha]_D^{25}$= +32.1 (c=0.5 in MeOH).

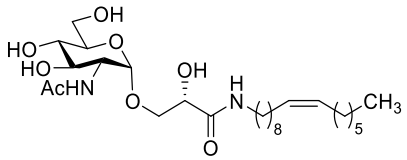
(*R*)-3-(((*2S,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-((*Z*)-heptadec-9-en-1-yl)-2-hydroxypropanamide (Deinococcucin D, 4)



4

Following **GP-VII**, from **19d** (21.9 mg, 0.031 mmol), title compound **4** (14.1 mg, 84%) was afforded as a white solid. m.p. (purified from methanol)124-126 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.73 (t, *J* = 5.5 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 5.43 (d, *J* = 5.9 Hz, 1H), 5.36-5.28 (m, 2H), 4.97 (d, *J* = 5.0 Hz, 1H), 4.72 (d, *J* = 5.0 Hz, 1H), 4.62 (d, *J* = 3.2 Hz, 1H), 4.45 (t, *J* = 5.9 Hz, 1H), 4.01 (d, *J* = 3.2 Hz, 1H), 3.70-3.57 (m, 3H), 3.50-3.36 (m, 4H), 3.19-3.13 (m, 1H), 3.05 (td, *J* = 12.6, 6.4 Hz, 2H), 1.98 (d, *J* = 5.5 Hz, 4H), 1.85 (s, 3H), 1.40 (t, *J* = 5.9 Hz, 2H), 1.31-1.20 (m, 20H), 0.85 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 171.2, 169.4, 129.7, 97.2, 72.7, 70.9, 70.8, 70.5, 69.6, 60.7, 53.6, 38.3, 31.3, 29.2, 29.1, 28.9, 28.8, 28.7, 28.6, 26.6, 26.6, 26.4, 22.8, 22.1, 14.0; IR (neat) υ (cm^{-1}) 3902, 3841, 3736, 3309, 2925, 2371, 2321, 1748, 1648, 1542, 1457, 1396, 1375, 1339, 1033; HRMS (FAB) m/z calcd for $C_{28}H_{53}N_2O_8$ $[M+H]^+$ 545.3802, found: 545.3794; $[\alpha]_D^{25}$= +33.2 (c=0.5 in MeOH).

(*S*)-3-(((*2S,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-((*Z*)-hexadec-9-en-1-yl)-2-hydroxypropanamide (5)

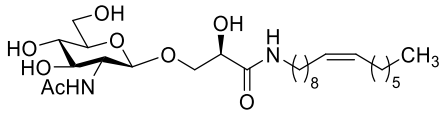


5

Following **GP-VII**, from **19e** (22.9 mg, 0.033 mmol), title compound **5** (17.1 mg, 98%) was afforded as a white solid. m.p. (purified from methanol) 132-134 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.75 (t, *J* = 5.7 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 5.54 (d, *J* = 4.6 Hz, 1H), 5.32 (t, *J* = 4.6 Hz, 2H), 4.99 (d, *J* = 5.0 Hz, 1H), 4.76 (d, *J* = 5.5 Hz, 1H), 4.60 (d, *J* = 3.2 Hz, 1H), 4.53 (t, *J* = 5.5 Hz, 1H), 4.07 (d, *J* = 6.4

Hz, 1H), 3.76 (dd, *J* = 10.5, 2.7 Hz, 1H), 3.71-3.57 (m, 2H), 3.45 (dq, *J* = 23.2, 5.4 Hz, 3H), 3.29 (s, 1H), 3.16-3.10 (m, 1H), 3.08-2.99 (m, 2H), 1.98 (d, *J* = 5.5 Hz, 4H), 1.83 (s, 3H), 1.40 (d, *J* = 5.9 Hz, 2H), 1.27-1.21 (m, 18H), 0.85 (t, *J* = 6.2 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 170.8, 169.3, 129.7, 98.1, 73.0, 71.1, 70.6, 70.3, 60.8, 53.5, 38.2, 31.2, 29.1, 29.1, 28.9, 28.8, 28.6, 28.3, 26.6, 26.4, 22.8, 22.1, 14.0; IR (neat) υ (cm^{-1}) 3903, 3841, 3736, 3649, 3309, 2854, 2371, 2321, 1748, 1648, 1543, 1457, 1376, 1338, 1033; HRMS (FAB) m/z calcd for $C_{27}H_{51}N_2O_8$ $[M+H]^+$ 531.3645, found: 531.3649; $[\alpha]_D^{25}$= +8.9 (c=1.0 in MeOH).

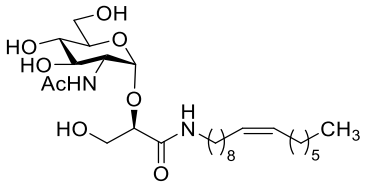
(*R*)-3-(((*2R,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-((*Z*)-hexadec-9-en-1-yl)-2-hydroxypropanamide (6)



6

Following **GP-VII**, from **20** (33.4 mg, 0.051 mmol), title compound **6** (23.8 mg, 88%) was afforded as a white solid. m.p. (purified from methanol)138-140 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.68-7.64 (m, 2H), 5.44 (s, 1H), 5.32 (t, *J* = 4.8 Hz, 2H), 4.99 (d, *J* = 18.4 Hz, 2H), 4.54 (t, *J* = 5.3 Hz, 1H), 4.32 (d, *J* = 8.7 Hz, 1H), 3.98 (s, 1H), 3.84 (dd, *J* = 10.6, 3.2 Hz, 1H), 3.68 (dd, *J* = 11.0, 4.1 Hz, 1H), 3.52-3.38 (m, 3H), 3.26 (t, *J* = 7.6 Hz, 1H), 3.10-2.99 (m, 4H), 1.97 (t, *J* = 5.7 Hz, 4H), 1.80 (s, 3H), 1.39 (t, *J* = 6.4 Hz, 2H), 1.29-1.22 (m, 18H), 0.85 (t, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 171.2, 169.4, 129.7, 101.6, 77.0, 74.5, 71.5, 71.3, 70.6, 61.1, 55.5, 38.3, 31.2, 29.2, 29.1, 28.9, 28.8, 28.6, 28.3, 26.6, 26.4, 23.1, 22.1, 14.0; IR (neat) υ (cm^{-1}) 3902, 3841, 3735, 3649, 3309, 2925, 2854, 2371, 2321, 1748, 1648, 1565, 1543, 1375, 1033; HRMS (FAB) m/z calcd for $C_{27}H_{51}N_2O_8$ $[M+H]^+$ 531.3645, found: 531.3649; $[\alpha]_D^{25}$= +6.3 (c=1.0 in MeOH).

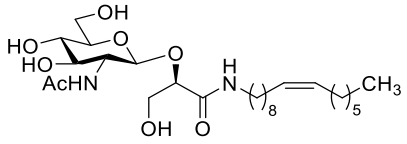
(*R*)-2-(((*2R,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-((*Z*)-hexadec-9-en-1-yl)-3-hydroxypropanamide (7)



7

Following **GP-VII**, from **23** (22.0 mg, 0.029 mmol), title compound **7** (15.2 mg, 99%) was afforded as a white solid. m.p. (purified from methanol) 177-179 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.99 (d, *J* = 9.1 Hz, 1H), 7.58 (t, *J* = 5.7 Hz, 1H), 5.36-5.28 (m, 2H), 5.06 (d, *J* = 5.0 Hz, 1H), 4.89 (d, *J* = 5.5 Hz, 1H), 4.74 (t, *J* = 5.3 Hz, 1H), 4.54 (d, *J* = 3.7 Hz, 1H), 4.51 (t, *J* = 5.7 Hz, 1H), 3.91 (t, *J* = 3.7 Hz, 1H), 3.75-3.53 (m, 6H), 3.51-3.46 (m, 1H), 3.20-3.10 (m, 2H), 2.99 (td, *J* = 13.0, 6.6 Hz, 1H), 1.98 (d, *J* = 5.0 Hz, 4H), 1.84 (s, 3H), 1.43-1.37 (m, 2H), 1.34-1.18 (m, 18H), 0.85 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 169.4, 169.3, 129.7, 98.0, 80.1, 73.2, 70.6, 70.5, 62.4, 60.6, 53.4, 38.3, 31.2, 29.3, 29.2, 29.1, 28.9, 28.8, 28.6, 28.3, 26.6, 26.3, 22.6, 22.1, 14.0; IR (neat) υ (cm^{-1}) 3902, 3841, 3735, 3649, 3306, 2854, 2371, 2321, 1748, 1648, 1527, 1457, 1375, 1338, 1033; HRMS (FAB) m/z calcd for $C_{27}H_{51}N_2O_8$ $[M+H]^+$ 531.3645, found: 531.3635; $[\alpha]_D^{25}$= +13.7 (c=1.0 in MeOH).

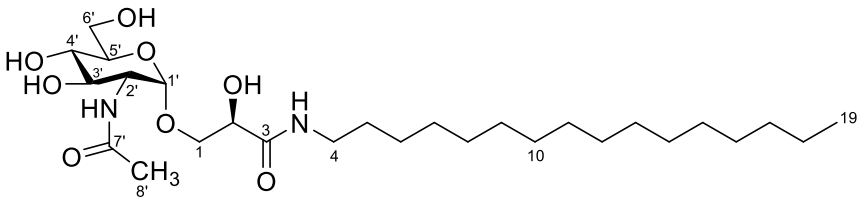
(*R*)-2-(((*2S,3R,4R,5S,6R*)-3-acetamido-4,5-dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-((*Z*)-hexadec-9-en-1-yl)-3-hydroxypropanamide (8)



8

Following **GP-VII**, from **25** (21.2 mg, 0.028 mmol), title compound **8** (11.8 mg, 80%) was afforded as a white solid. m.p. (purified from methanol) 184-186 ℃; ^{1}H-NMR (400 MHz, DMSO-*d6*) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.41 (t, *J* = 5.7 Hz, 1H), 5.36-5.28 (m, 2H), 5.08 (s, 1H), 5.04 (d, *J* = 4.1 Hz, 1H), 4.51-4.47 (m, 3H), 4.03 (dd, *J* = 4.8, 3.4 Hz, 1H), 3.68-3.64 (m, 2H), 3.57-3.42 (m, 3H), 3.10 (s, 2H), 3.05 (q, *J* = 6.7 Hz, 2H), 1.97 (t, *J* = 5.9 Hz, 4H), 1.81 (s, 3H), 1.40 (t, *J* = 6.2 Hz, 2H), 1.31-1.24 (m, 18H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-*d6*) δ 170.1, 169.5, 129.7, 100.4, 79.6, 77.1, 73.7, 70.5, 61.4, 61.0, 56.1, 38.4, 31.2, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.3, 26.6, 26.4, 23.2, 22.1, 14.0; IR (neat) υ (cm^{-1}) 3902, 3841, 3735, 3649, 3308, 2854, 2371, 2321, 1748, 1648, 1565, 1457, 1375, 1338, 1076; HRMS (FAB) m/z calcd for $C_{27}H_{51}N_2O_8$ $[M+H]^+$ 531.3645, found: 531.3651; $[\alpha]_D^{25}$= +7.0 (c=1.0 in MeOH).

2.5.4. Comparison of synthetic Deinococcucins with natural Deinococcucins[10]

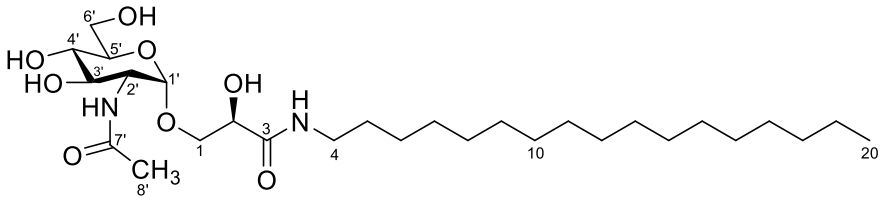


Deinococcucin A (1)

	Natural Deinococcucin A (**1**)[a]		Synthetic Deinococcucin A (**1**)[b]	
Position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
1	69.6, CH_2	3.63, m	69.7, CH_2	3.70-3.57 (overlap)
		3.45, m		3.50-3.40 (overlap)
2	70.8, CH	3.97, dd	70.9, CH	4.01-3.99, m
		(5.5, 3.0)		
3	171.1, C		171.2, C	
4	38.2, CH_2	3.02, m	38.3, CH_2	3.05, td (12.6, 6.4)
5	29.1, CH_2	1.35, m	29.2, CH_2	1.40, t (6.0)
6	26.1, CH_2	1.22, m	26.5, CH_2	1.26-1.21 (overlap)
7-16	28.9-28.4, 10CH_2	1.26-1.15, m	29.1-28.7, 10CH_2	1.26-1.21 (overlap)
17	31.0, CH_2	1.37, m	31.3, CH_2	1.26-1.21 (overlap)
18	22.4, CH_2	1.24, m	22.1, CH_2	1.26-1.21 (overlap)
19	13.9, CH_3	0.85, t (6.5)	14.0, CH_3	0.85, t (6.4)
2-OH		5.52, br s		5.43, d (6.0)
3-NH		7.76, t (5.5)		7.72, t (5.7)
1’	97.1, CH	4.62, d (3.5)	97.2, CH	4.62, d (3.2)
2’	53.4, CH	3.67, dd	53.6, CH	3.70-3.57 (overlap)
		(8.5, 3.5)		
3’	70.8, CH	3.44, dd	70.8, CH	3.50-3.40 (overlap)
		(10.0, 8.5)		
4’	70.4, CH	3.12, ddd	70.5, CH	3.16, td (9.1, 4.9)
		(10.0, 9.0, 2.5)		
5’	72.6, CH	3.35, ddd	72.7, CH	3.50-3.40 (overlap)
		(9.0, 5.0, 2.5)		
6’	60.6, CH_2	3.55, m	60.7, CH_2	3.70-3.57 (overlap)
		3.47, m		3.50-3.40 (overlap)
7’	169.3, C		169.4, C	
8’	22.8, CH_3	1.85, s	22.8, CH_3	1.85, s

2’-NH		7.56, d (8.5)		7.51, d (8.7)
3’-OH		4.78, br s		4.71, d (5.5)
4’-OH		5.00, br s		4.96, d (5.1)
6’-OH		4.45, dd (12.0, 3.5)		4.44, t (5.7)

[a]Data obtained from ref x recorded in DMSO-d_6 at 600 MHz ^{1}H-NMR and 125 MHz ^{13}C-NMR. [b]Data recorded in in DMSO-d_6 at 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR.

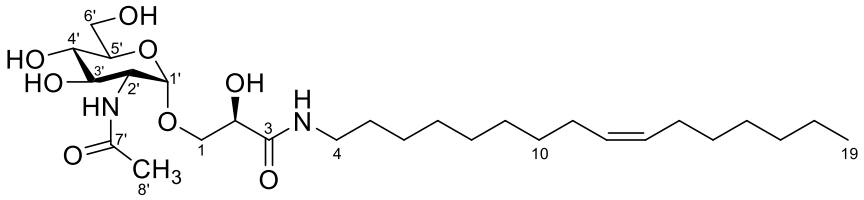


Deinococcucin B (2)

	Natural Deinococcucin B (**2**)[a]		Synthetic Deinococcucin B (**2**)[b]	
Position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
1	69.6, CH_2	3.63, m	69.6, CH_2	3.69-3.57 (overlap)
		3.49, m		3.49-3.40 (overlap)
2	70.8, CH	4.00, dd (5.5, 3.0)	70.9, CH	4.00, m
3	171.1, C		171.2, C	
4	38.5, CH_2	3.05, m	38.3, CH_2	3.04, qd (12.7, 6.5)
5	29.4, CH_2	1.40, m	29.2, CH_2	1.42-1.37 (overlap)
6	26.4, CH_2	1.23, m	26.4, CH_2	1.26-1.21 (overlap)
7-16	28.9-28.3, 10CH_2	1.31-1.19, m	29.0-28.7 (10CH_2, overlap)	1.26-1.21 (overlap)
17	28.3, CH_2	1.13, m	29.0-28.7 (CH_2, overlap)	1.26-1.21 (overlap)
18	31.2, CH_2	1.41, m	31.3, CH_2	1.26-1.21 (overlap)
19	22.0, CH_2	1.20, m	22.1, CH_2	1.26-1.21 (overlap)
20	14.0, CH_3	0.85, t (5.5)	14.0, CH_3	0.85, t (6.2)
2-OH		5.50, br s		5.49, br s
3-NH		7.76, t (5.5)		7.77, t (5.5)
1’	97.0, CH	4.61, d (3.5)	97.2, CH	4.61, d (2.7)
2’	53.4, CH	3.67, dd (8.5, 3.5)	53.6, CH	3.69-3.57 (overlap)

3’	70.7, CH	3.41, dd (10.0, 8.5)	70.8, CH	3.49-3.40 (overlap)
4’	70.4, CH	3.16, ddd (10.0, 9.0, 2.5)	70.5, CH	3.15, t (9.1)
5’	72.7, CH	3.37, ddd (9.0, 5.0, 2.5)	72.7, CH	3.49-3.40 (overlap)
6’	60.5, CH_2	3.57, m	60.7, CH_2	3.69-3.57 (overlap)
		3.46, m		3.49-3.40 (overlap)
7’	169.2, C		169.4, C	
8’	22.6, CH_3	1.85, s	22.8, CH_3	1.84, s
2’-NH		7.60, d (8.5)		7.57, d (8.2)
3’-OH		4.78, br s		4.78, br s
4’-OH		5.00, br s		5.01, br s
6’-OH		4.45, dd (12.0, 3.5)		4.47, br s

[a]Data obtained from ref x recorded in DMSO-d_6 at 600 MHz ^{1}H-NMR and 125 MHz ^{13}C-NMR. [b]Data recorded in in DMSO-d_6 at 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR.

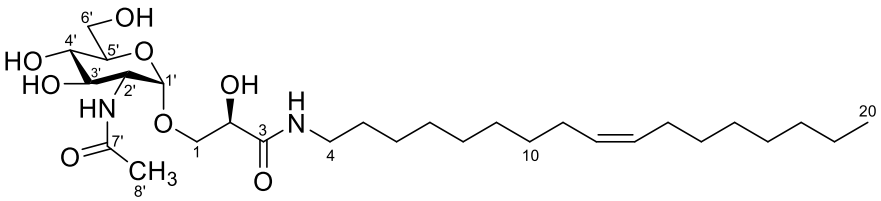


Deinococcucin C (3)

	Natural Deinococcucin C (**3**)[a]		Synthetic Deinococcucin C (**3**)[b]	
Position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
1	69.6, CH_2	3.63, m	69.6, CH_2	3.70-3.57 (overlap)
		3.49, m		3.51-3.37 (overlap)
2	70.8, CH	4.00, dd (5.5, 3.0)	70.9, CH	4.01, dd (9.2, 5.5)
3	171.1, C		171.2, C	
4	38.2, CH_2	3.06, m	38.3, CH_2	3.05, qd (12.7. 6.4)
5	29.1, CH_2	1.39, m	29.1, CH_2	1.40, t (6.7)
6	26.1, CH_2	1.22, m	26.6, CH_2	1.31-1.24 (overlap)
7-10	28.9-28.4, 4CH_2	1.33-1.26, m	28.9-28.3, (4CH_2, overlap)	1.31-1.24 (overlap)
11	28.5, CH_2	1.97, m	28.9-28.3,	1.98, q (6.0)

			(CH_2, overlap)	
12-13	129.0, 2CH	5.33, m	129.6, 2CH	5.36-5.28, m
14	28.5, CH_2	1.97, m	28.9-28.3,	1.98, q (6.0)
			(CH_2, overlap)	
15-17	31.0-29.9, $3CH_2$	1.33-1.26, m	31.1-29.1, $3CH_2$	1.31-1.24 (overlap)
18	22.4, CH_2	1.26, m	22.1, CH_2	1.31-1.24 (overlap)
19	13.9, CH_3	0.85, t (6.5)	13.9, CH_3	0.85, t (6.7)
2-OH		5.45, br s		5.41, d (6.0)
3-NH		7.73, t (5.5)		7.71, t (6.0)
1’	97.1, CH	4.62, d (3.5)	97.2, CH	4.62, d (3.7)
2’	53.4, CH	3.67, dd (8.5, 3.5)	53.6, CH	3.70-3.57 (overlap)
3’	70.8, CH	3.44, dd (10.0, 8.5)	70.8, CH	3.51-3.37 (overlap)
4’	70.4, CH	3.16, ddd	70.5, CH	3.16, td
		(10.0, 9.0, 2.5)		(9.2, 4.6)
5’	72.6, CH	3.39, ddd	72.7, CH	3.51-3.37 (overlap)
		(9.0, 5.0, 2.5)		
6’	60.6, CH_2	3.58, m	60.7, CH_2	3.70-3.57 (overlap)
		3.47, m		3.51-3.37 (overlap)
7’	169.3, C		169.4, C	
8’	22.8, CH_3	1.85, s	22.8, CH_3	1.85, s
2’-NH		7.52, d (8.5)		7.50, d (8.3)
3’-OH		4.78, br s		4.70, d (5.1)
4’-OH		5.00, br s		4.95, d (4.6)
6’-OH		4.45, dd (12.0, 3.5)		4.43, t (5.7)

[a]Data obtained from ref x recorded in DMSO-d_6 at 600 MHz ^{1}H-NMR and 125 MHz ^{13}C-NMR. [b]Data recorded in in DMSO-d_6 at 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR.



Deinococcucin D (4)

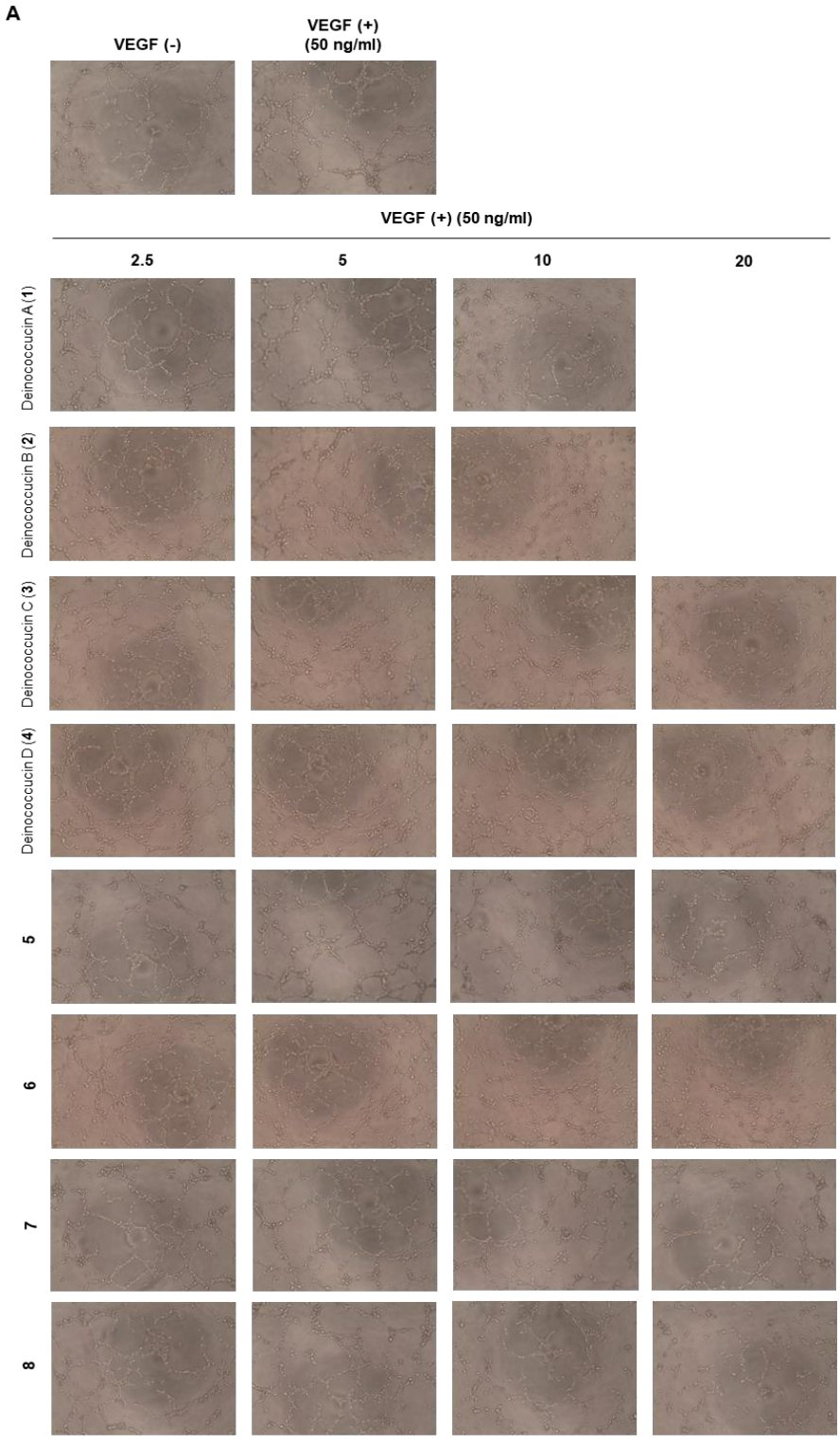
	Natural Deinococcucin D (**4**)[a]		Synthetic Deinococcucin D (**4**)[b]	
Position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	69.6, CH_2	3.62, m	69.6, CH_2	3.70-3.57 (overlap)

		3.47, m		3.50-3.36 (overlap)
2	70.6, CH	4.00, dd (5.5, 3.0)	70.8, CH	4.01, d (3.2)
3	171.0, C		171.2, C	
4	38.2, CH_2	3.05, m	38.3, CH_2	3.05, td (12.6, 6.4)
5	29.1, CH_2	1.40, m	29.2, CH_2	1.40, t (5.9)
6	26.1, CH_2	1.22, m	26.4, CH_2	1.31-1.20 (overlap)
7-10	28.9-28.4, 4CH_2	1.33-1.25, m	28.9-26.6, ($4CH_2$, overlap)	1.31-1.20 (overlap)
11	28.3, CH_2	1.95, m	28.9-26.6, (CH_2, overlap)	1.98, d (5.5)
12-13	129.6, 2CH	5.32, m	129.7, 2CH	5.36-5.28, m
14	28.3, CH_2	1.95, m	28.9-26.6, (CH_2, overlap)	1.98, d (5.5)
15-17	29.9-29.4, 3CH_2	1.35-1.25, m	31.3-29.1, ($3CH_2$, overlap)	1.31-1.20 (overlap)
18	31.2, CH_2	1.28, m	31.3, CH_2	1.31-1.20 (overlap)
19	22.0, CH_2	1.26, m	22.1, CH_2	1.31-1.20 (overlap)
20	14.0, CH_3	0.84, t (6.5)	14.0, CH_3	0.85, t (6.6)
2-OH		5.50, br s		5.43, d (5.9)
3-NH		7.78, t (5.5)		7.73, t (5.5)
1’	97.0, CH	4.61, d (3.5)	97.2, CH	4.62, d (3.2)
2’	53.4, CH	3.67, dd (8.5, 3.5)	53.6, CH	3.70-3.57 (overlap)
3’	70.7, CH	3.41, dd (10.0, 8.5)	70.9, CH	3.50-3.36 (overlap)
4’	70.4, CH	3.16, ddd (10.0, 9.0, 2.5)	70.5, CH	3.19-3.13, m
5’	72.7, CH	3.37, ddd (9.0, 5.0, 2.5)	72.7, CH	3.50-3.36 (overlap)
6’	60.5, CH_2	3.57, m	60.7, CH_2	3.70-3.57 (overlap)
		3.46, m		3.50-3.36 (overlap)
7’	169.2, C		169.4, C	
8’	22.6, CH_3	1.85, s	22.8, CH_3	1.85, s
2’-NH		7.60, d (8.5)		7.52, d (8.2)
3’-OH		4.78, br s		4.72, d (5.0)
4’-OH		5.00, br s		4.97, d (5.0)
6’-OH		4.45, dd (12.0, 3.5)		4.45, t (5.9)

[a]Data obtained from ref x recorded in DMSO-d_6 at 600 MHz ^{1}H-NMR and 125 MHz ^{13}C-NMR. [b]Data recorded in in DMSO-d_6 at 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR.

3. Bioactivity assay for synthetic Deinococcucins

Tube Formation and Cell Viability Assay



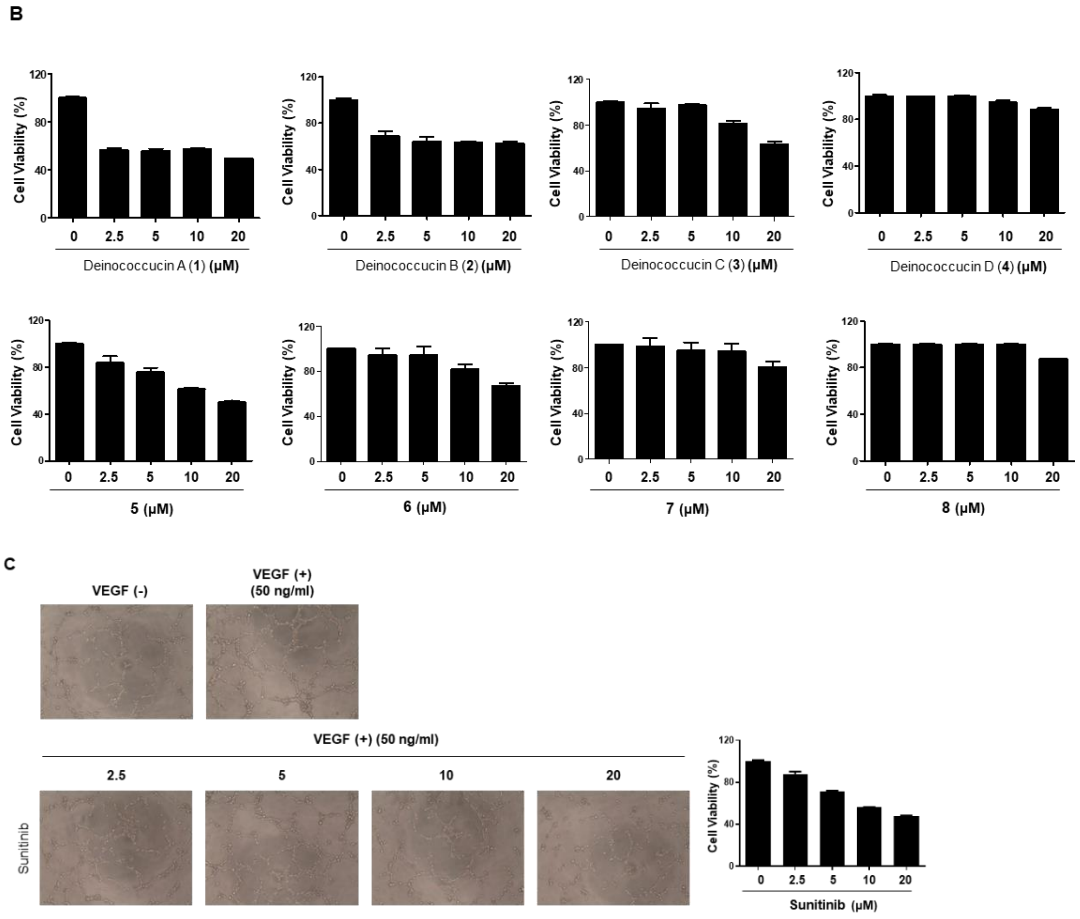


Figure S1. (**A**) Effects of Deinococcucins A-D (**1-4**) and its derivatives (**5-8**) on VEGF-induced tube formation on Matrigel in HUVEC cells. (**B**) Effects on cell viability. (**C**) Effects of Sunitinib on the VEGF-induced tube formation and cell growth of HUVECs.

HUVEC cells (1.5 x 10^4 cells/well) were mixed with various concentration of compounds (0-20 μM) and seeded into each well of a Matrigel-coated 96-well plate. The cells were incubated for 6 h at 37 °C in a 5% CO_2 atmosphere, and the formation of tubular structures was photographed under an inverted microscope. We used the angiogenesis analyzer in ImageJ software to calculate the total segment lengths of tubular structures per image. For normalized tube data, the following formula was used for quantification: 100 x (total segment lengths of compound$_{avg}$ – total segment length of VEGF(-)$_{avg}$)/(total segment length of VEGF(+)$_{avg}$ – total segment length of VEGF(-)$_{avg}$).

For cell viability, HUVEC cells were seeded in 96-well plates (1.6 x 10^4 cells/well). After incubation for 24 h, the cells were incubated in serum-starved condition for overnight. On the next day, the cells were treated with various concentrations of compounds (0-20 μM) in EBM-2 media with 2% FBS for 24 h in the presence of VEGF (50 ng/mL). Cell viability was evaluated using the MTT method. The IC_{50} values were determined by nonlinear regression analysis (percent survival versus concentration).[11]

4. References

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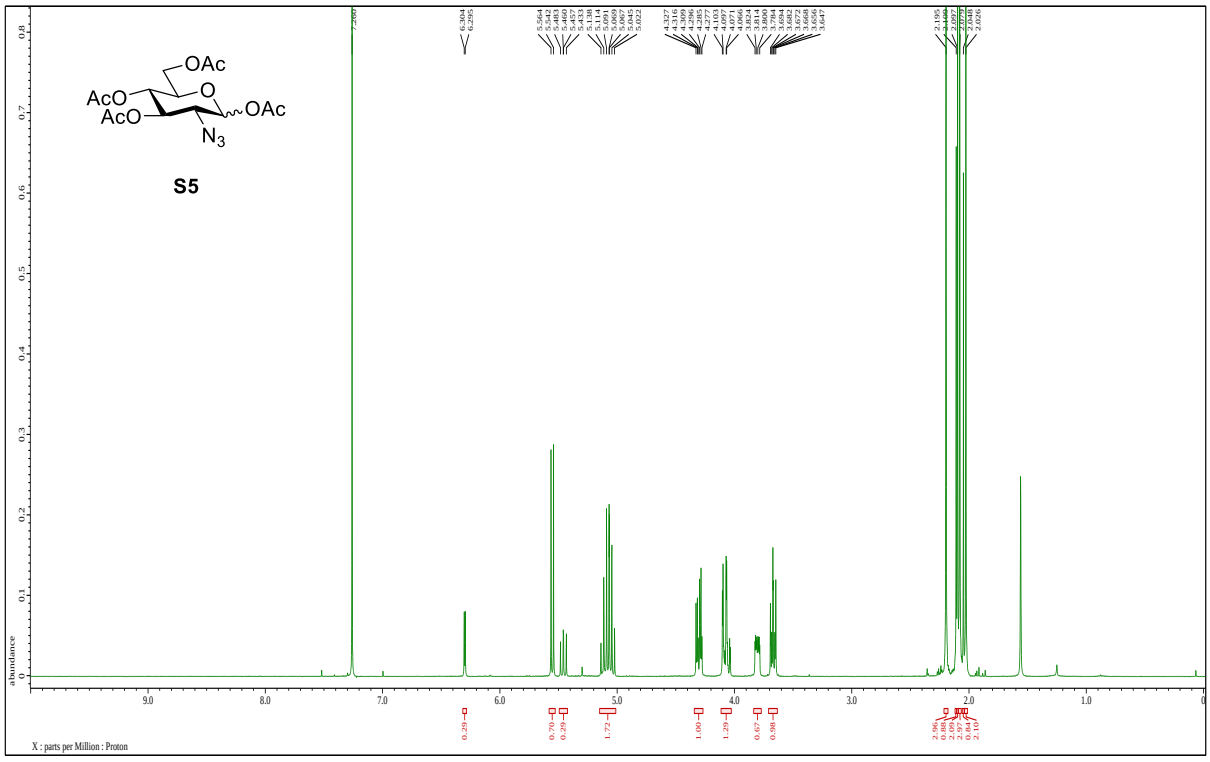
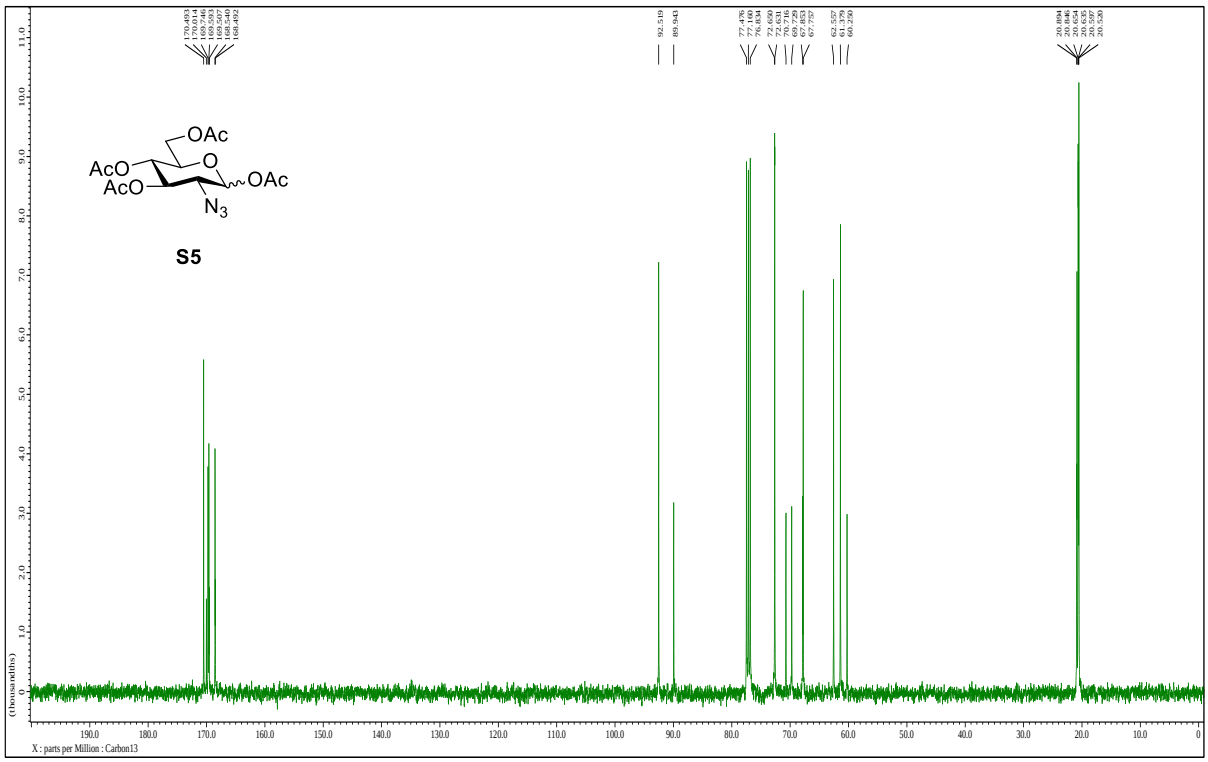
5. NMR spectra

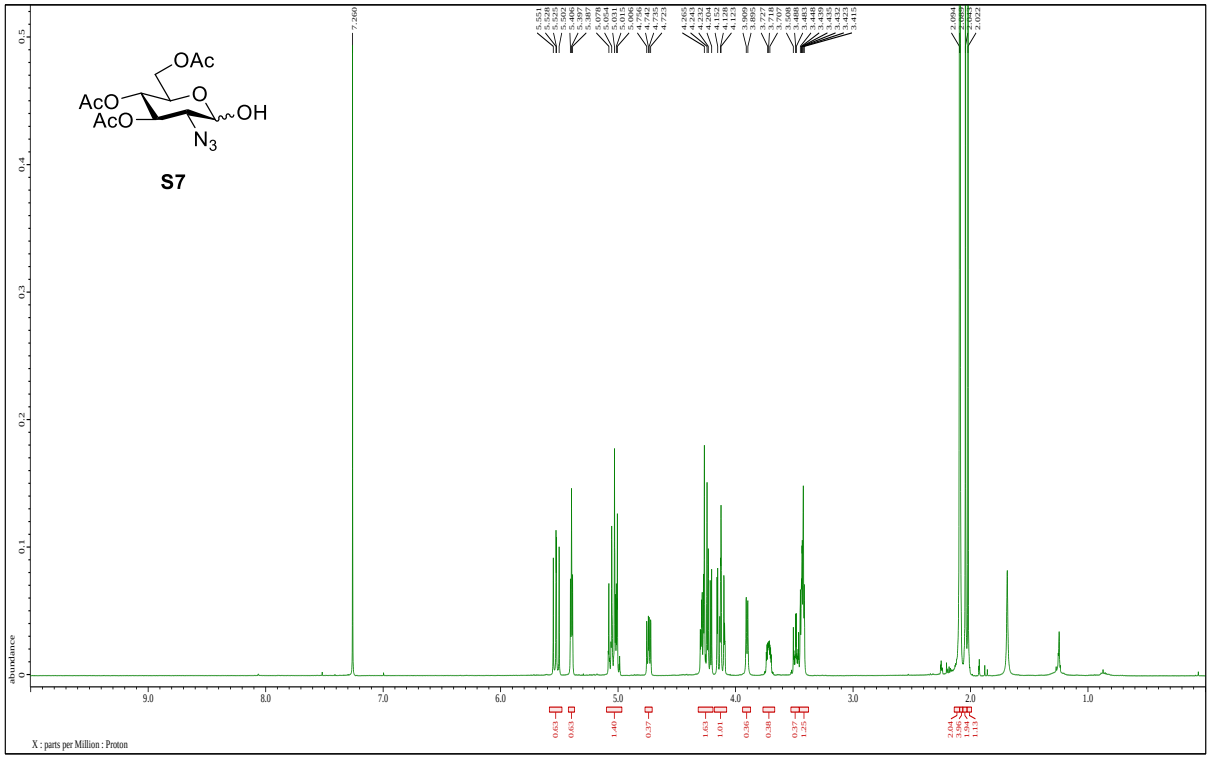
^{1}H-NMR of compound **S5** ($CDCl_3$, 400MHz)



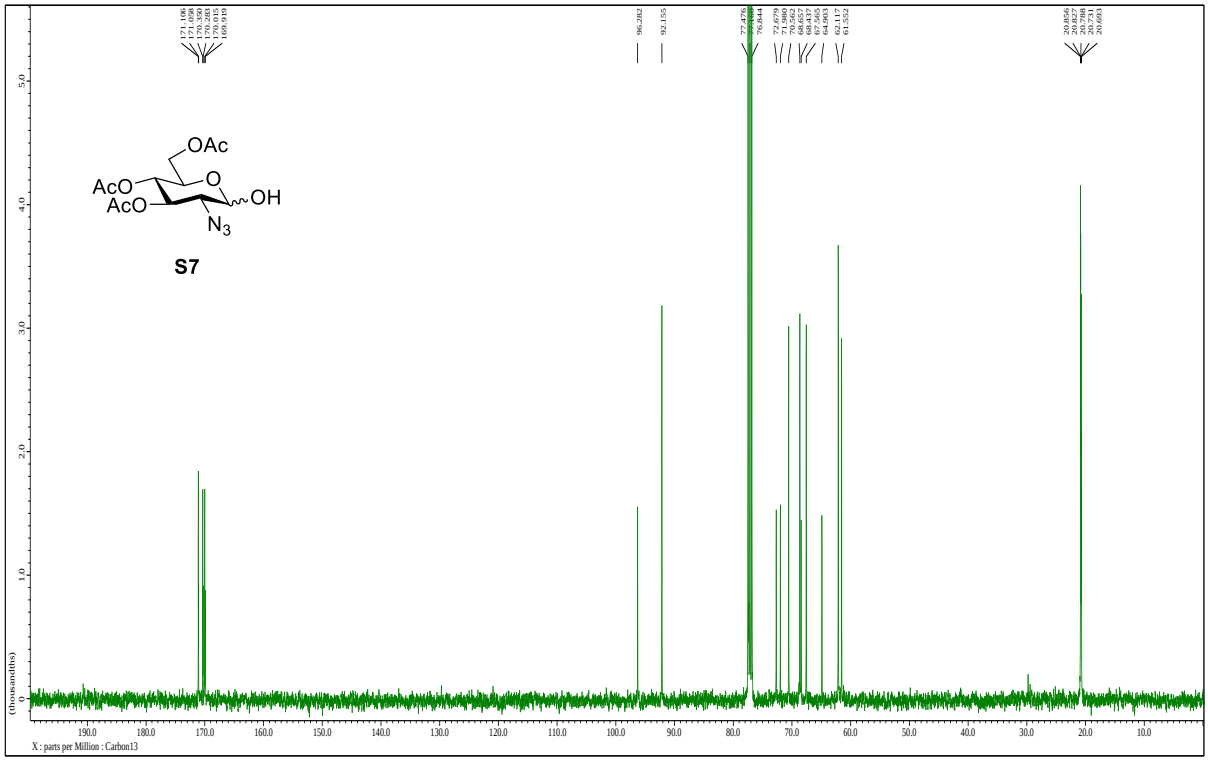
^{13}C-NMR of compound **S5** ($CDCl_3$, 100MHz)



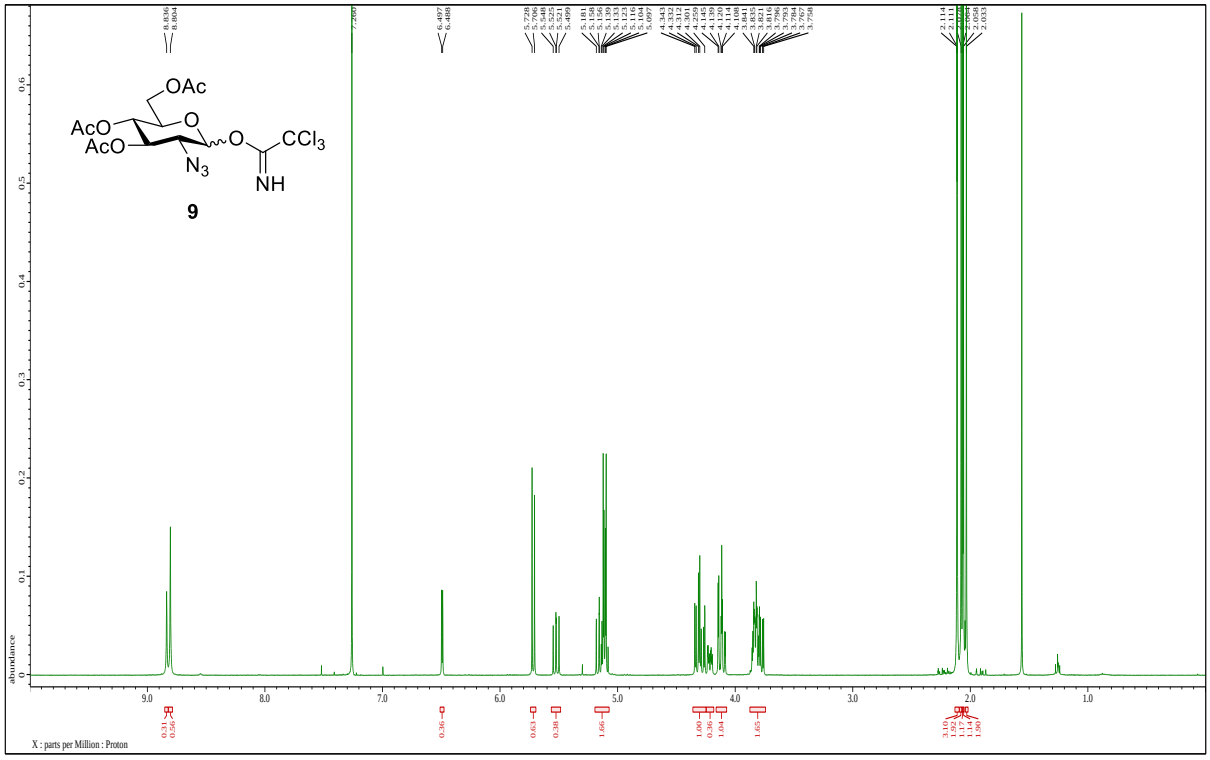
^{1}H-NMR of compound **S7** ($CDCl_3$, 400MHz)



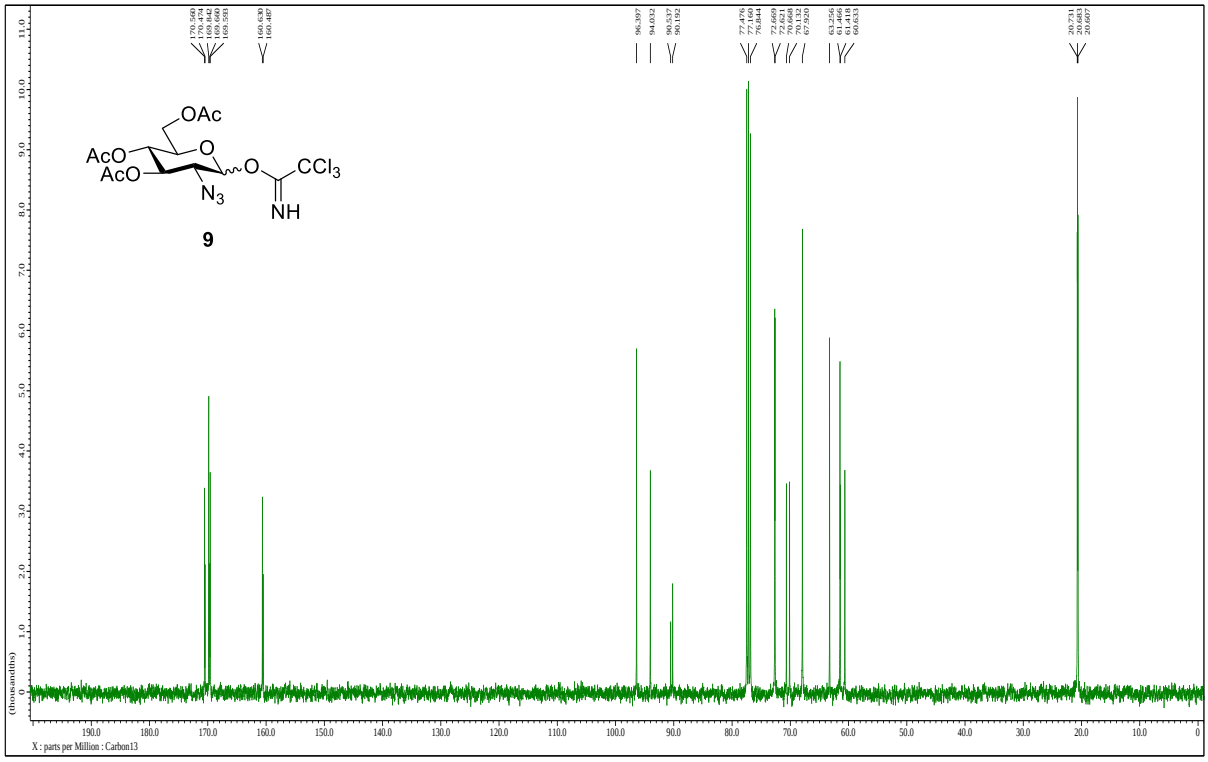
^{13}C-NMR of compound **S7** ($CDCl_3$, 100MHz)



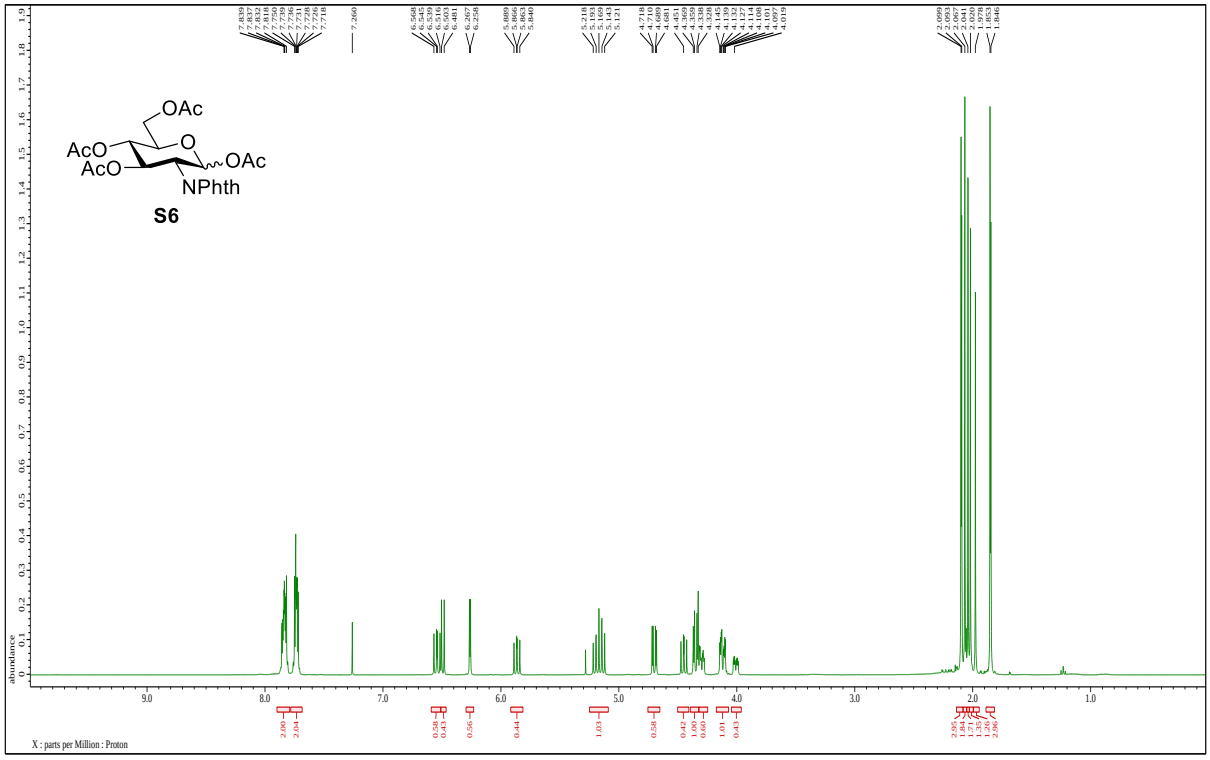
^{1}H-NMR of compound **9** ($CDCl_3$, 400MHz)



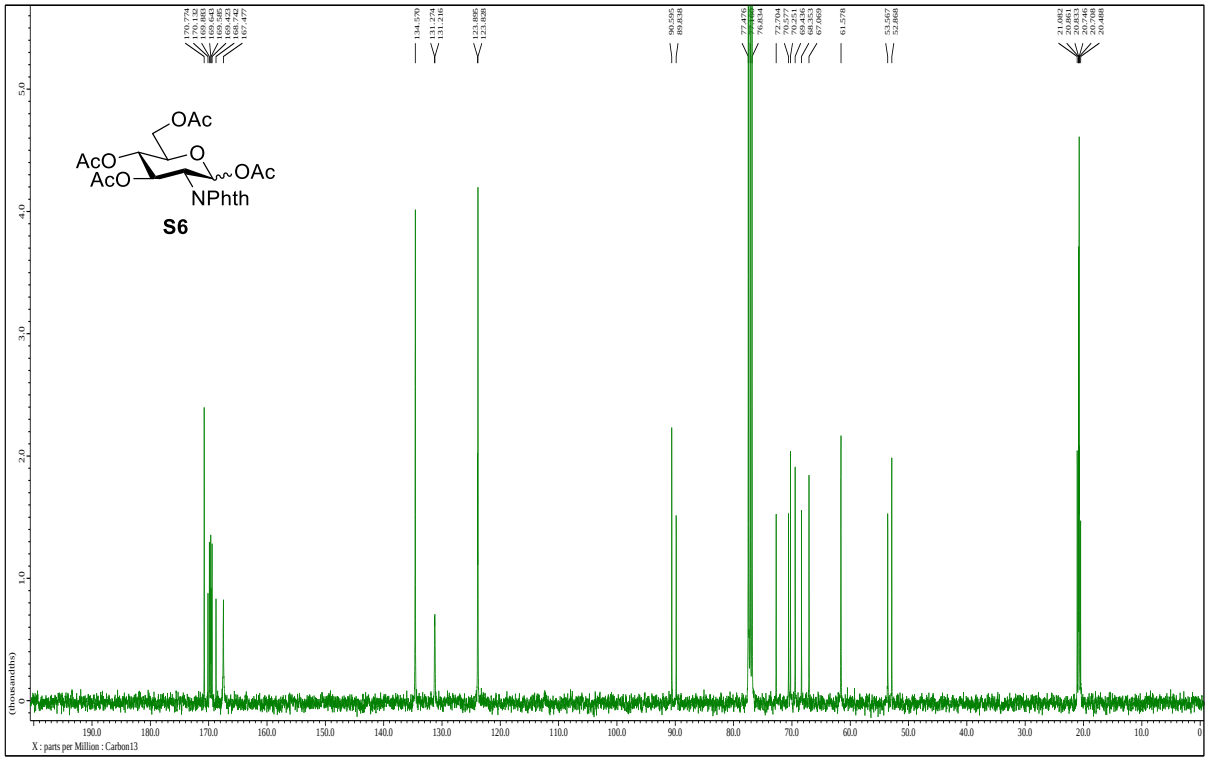
^{13}C-NMR of compound **9** ($CDCl_3$, 100MHz)



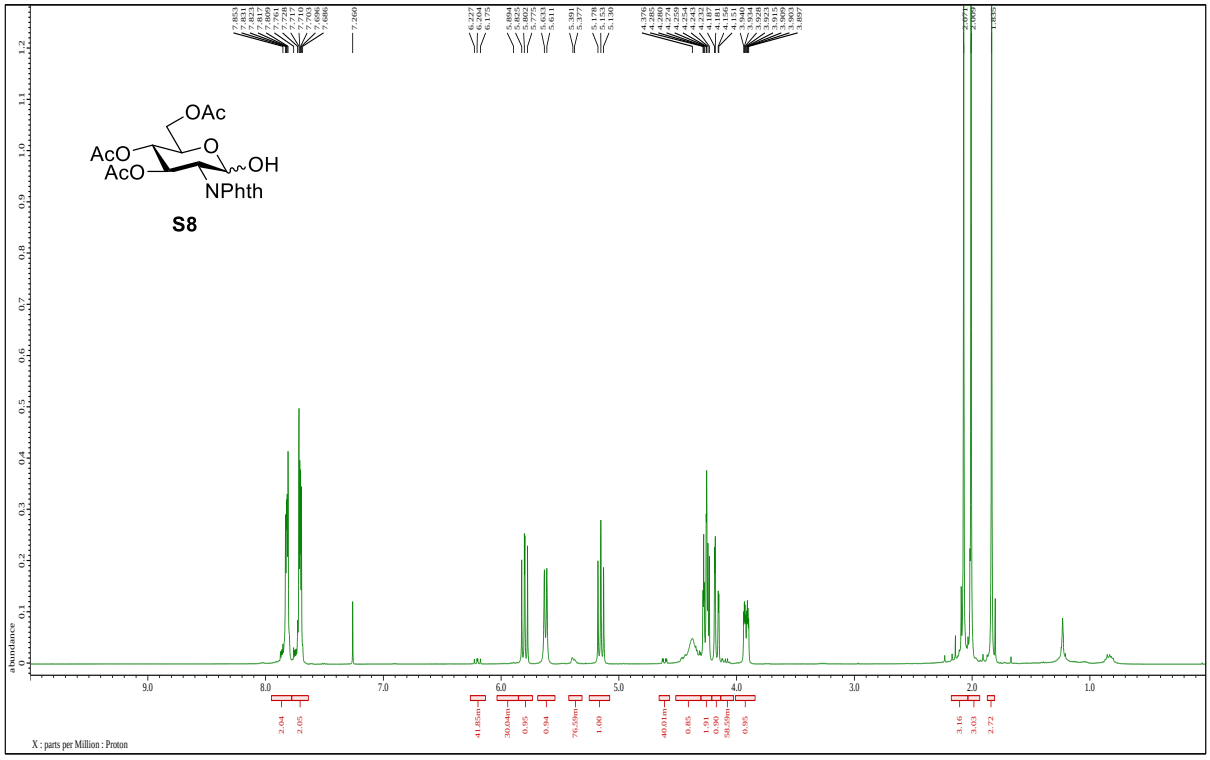
^{1}H-NMR of compound **S6** ($CDCl_3$, 400MHz)



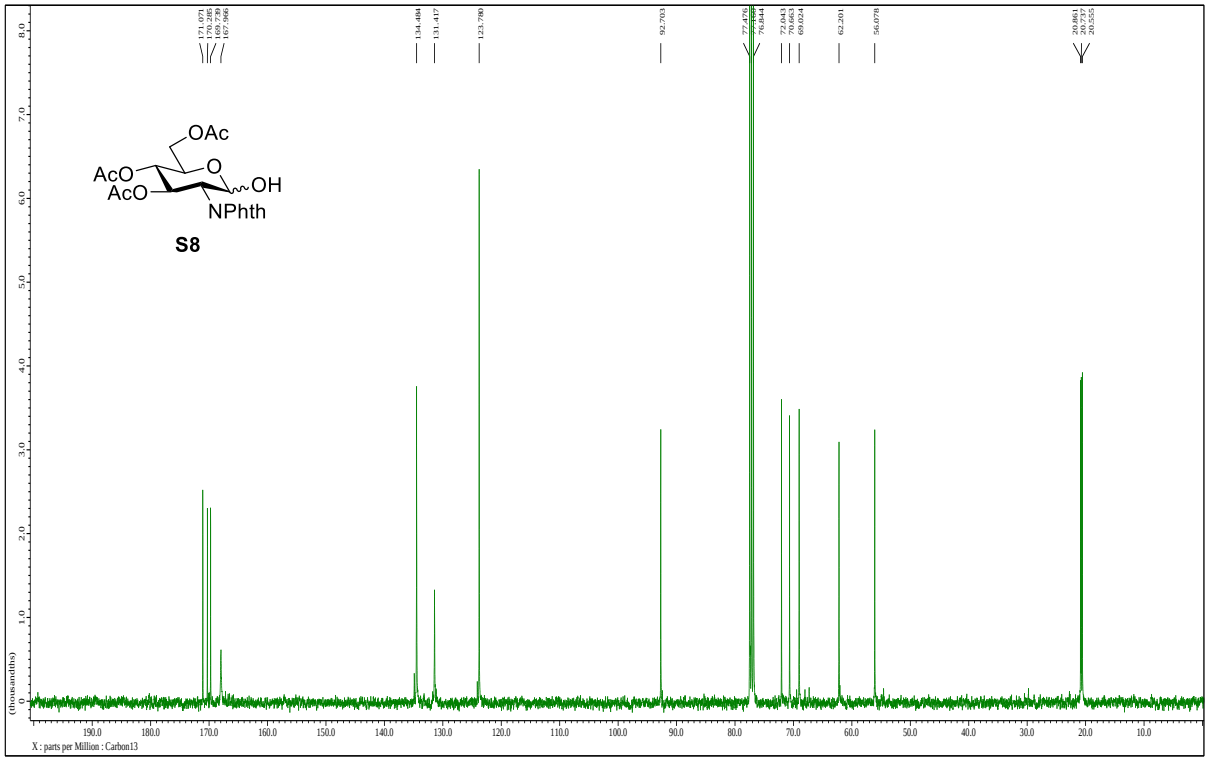
^{13}C-NMR of compound **S6** ($CDCl_3$, 100MHz)



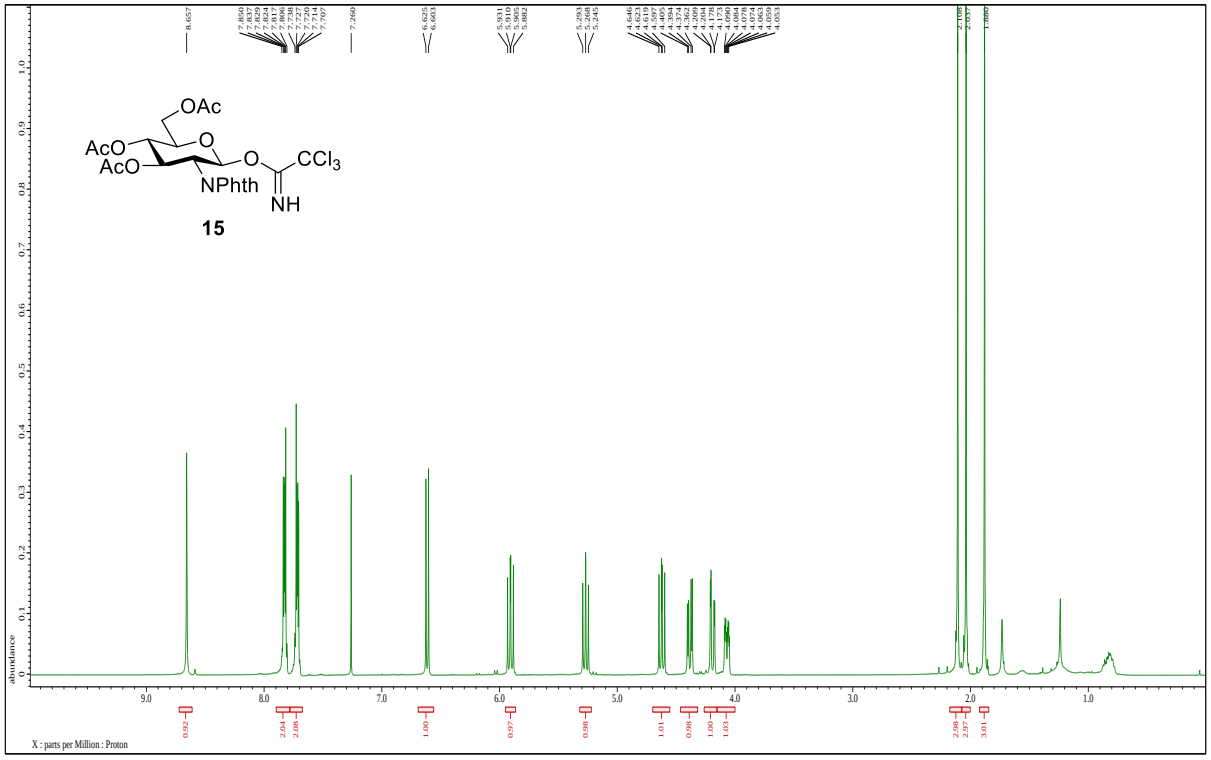
^{1}H-NMR of compound **S8** ($CDCl_3$, 400MHz)



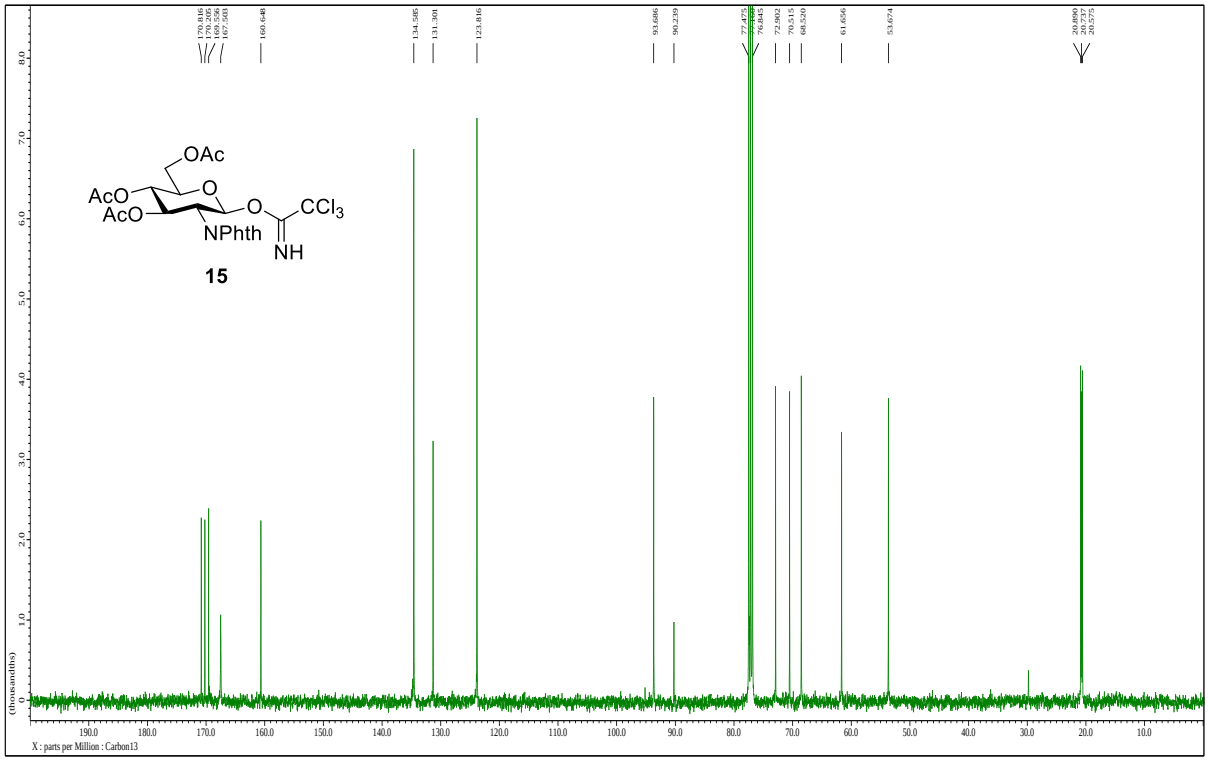
^{13}C-NMR of compound **S8** ($CDCl_3$, 100MHz)



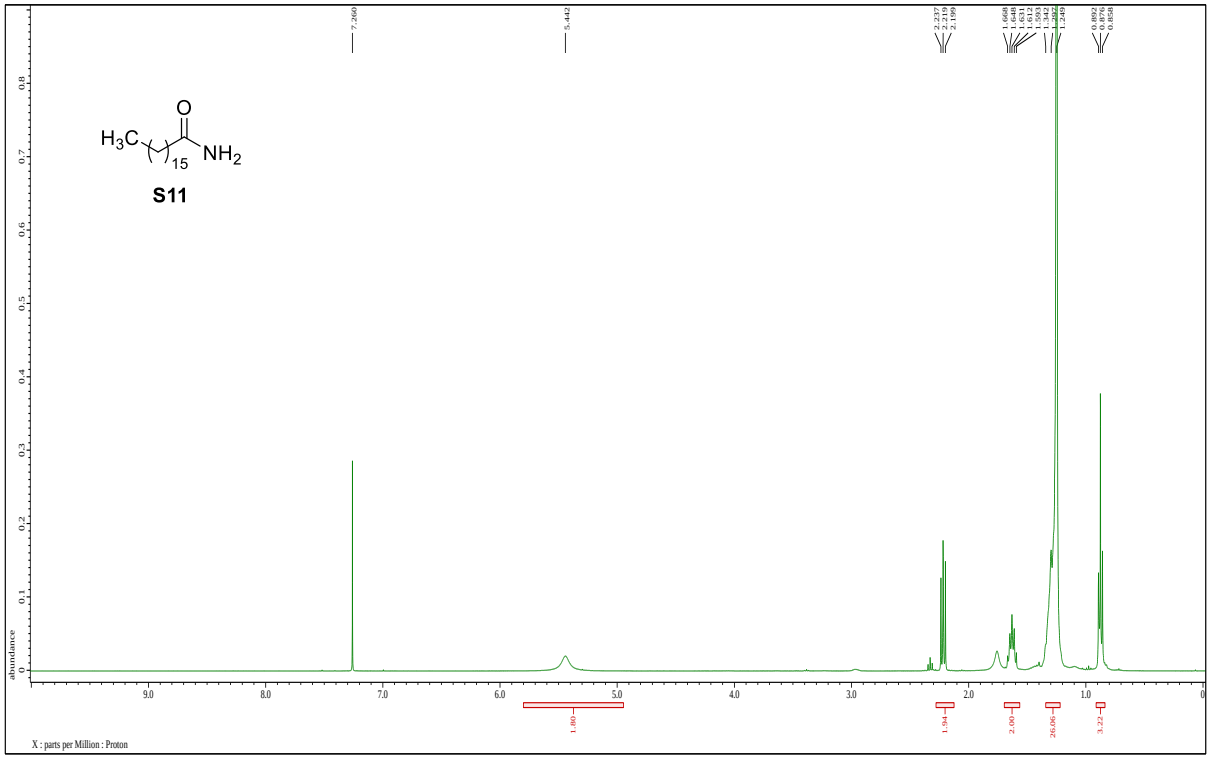
^{1}H-NMR of compound **15** ($CDCl_3$, 400MHz)



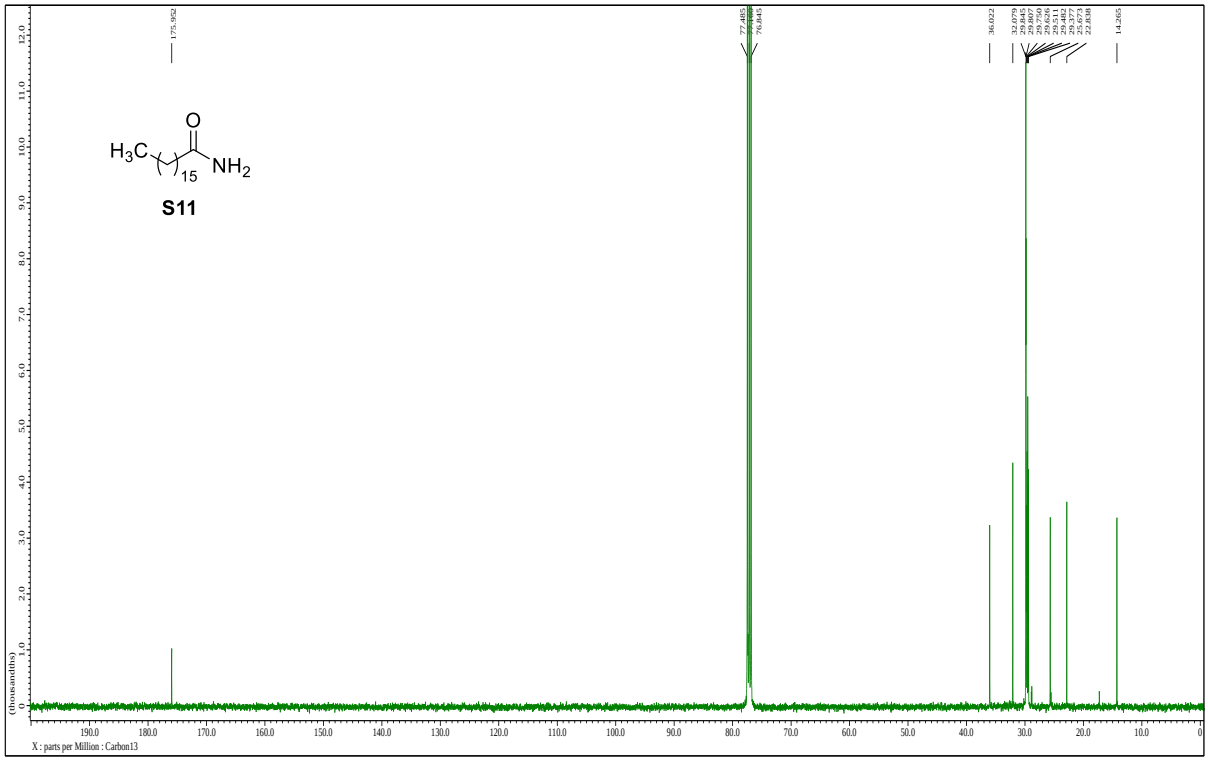
^{13}C-NMR of compound **15** ($CDCl_3$, 100MHz)



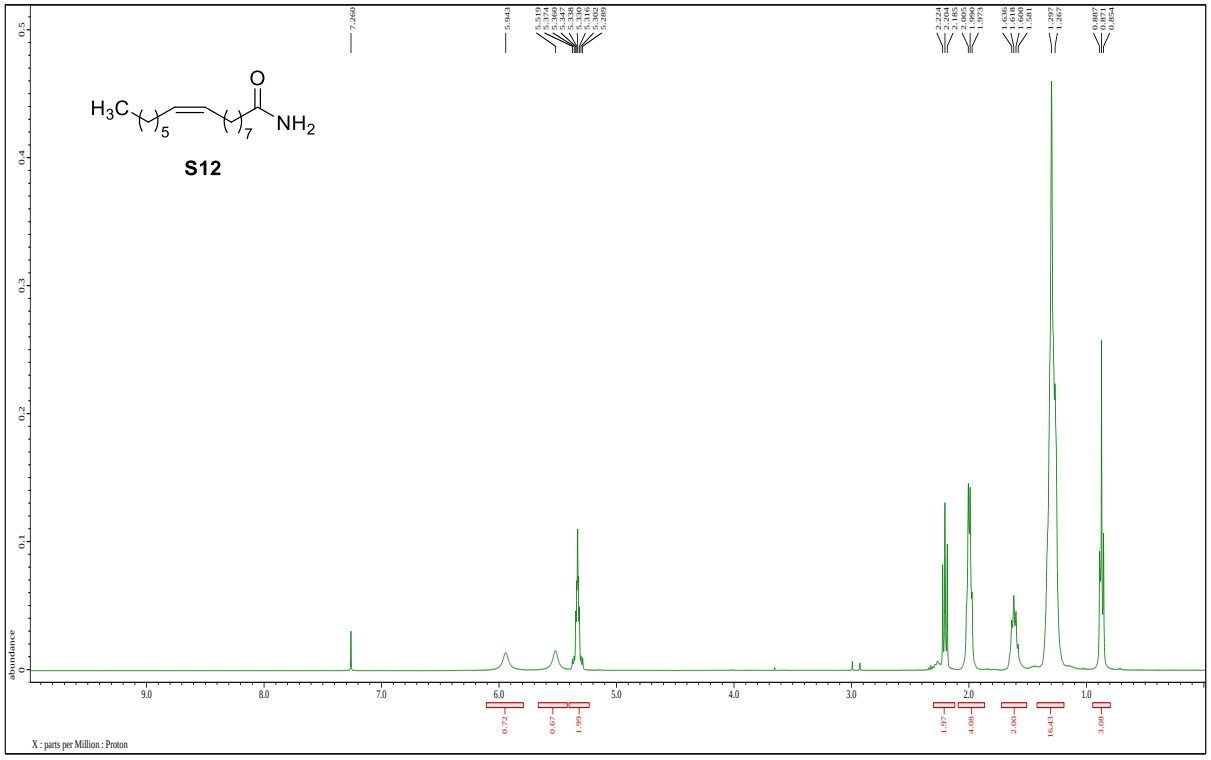
^{1}H-NMR of compound **S11** ($CDCl_3$, 400MHz)



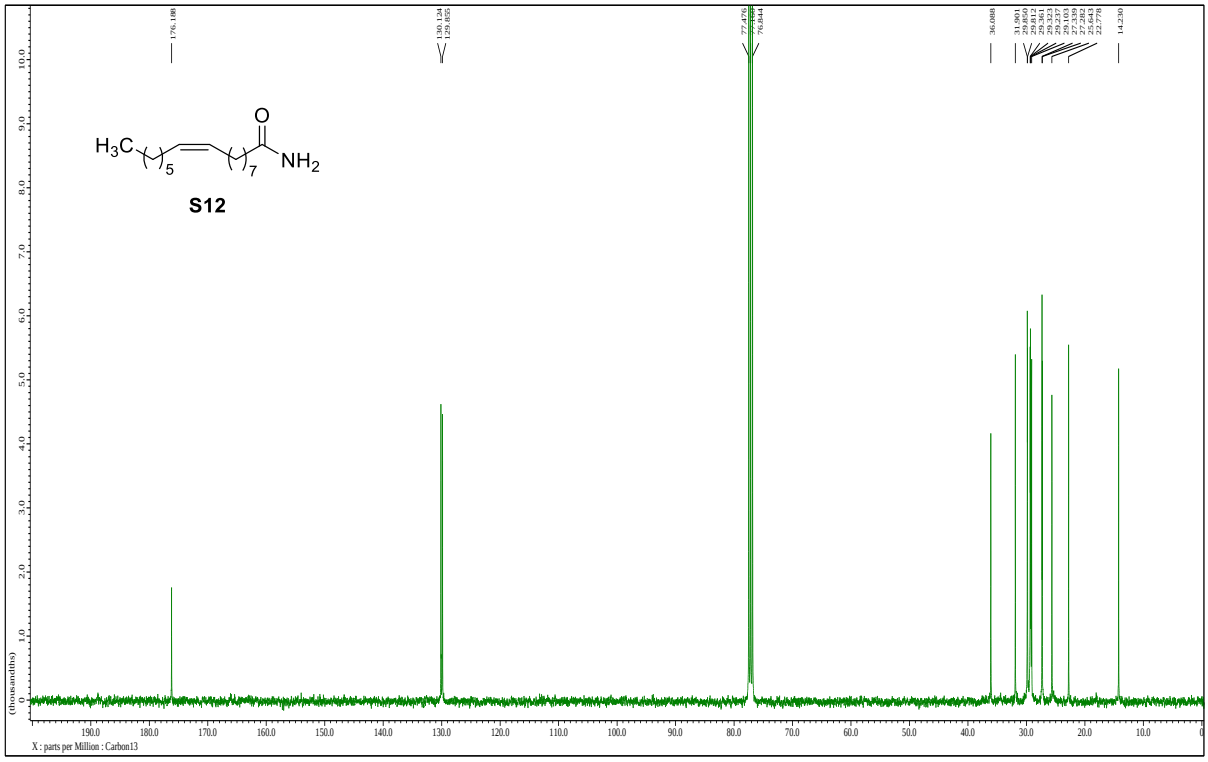
^{13}C-NMR of compound **S11** ($CDCl_3$, 100MHz)



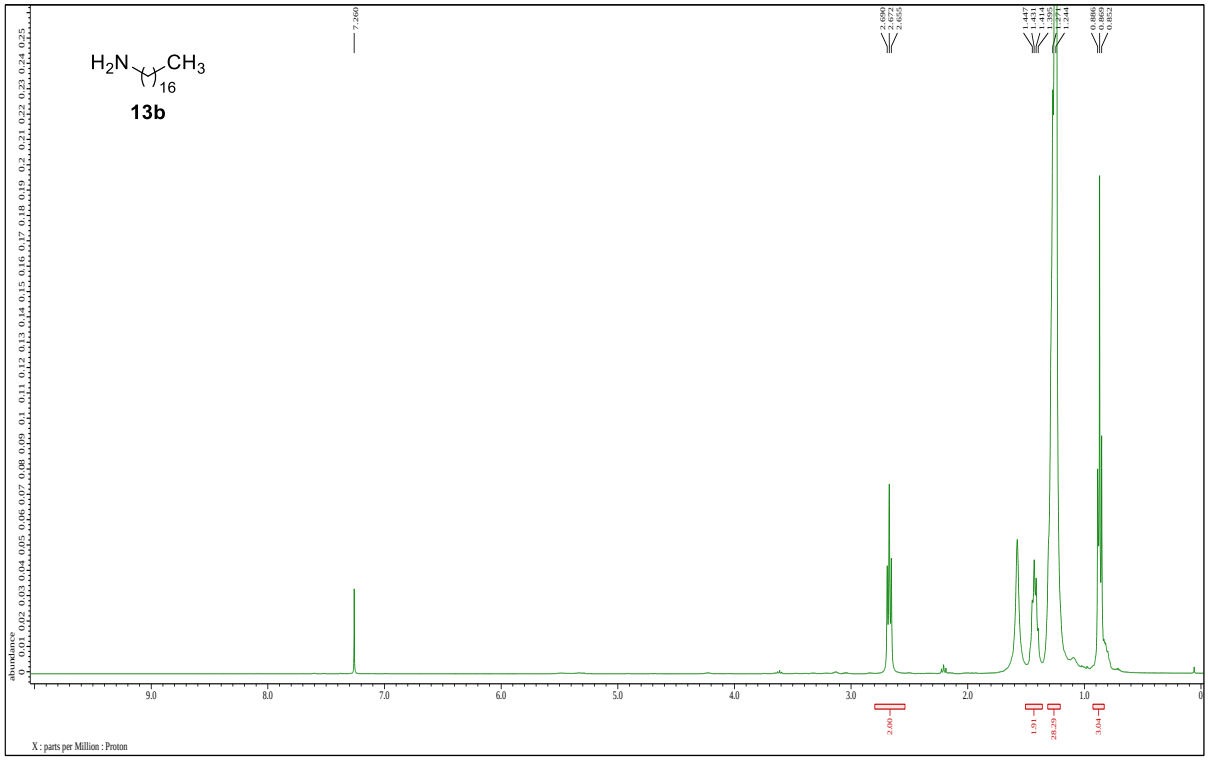
^{1}H-NMR of compound **S12** ($CDCl_3$, 400MHz)



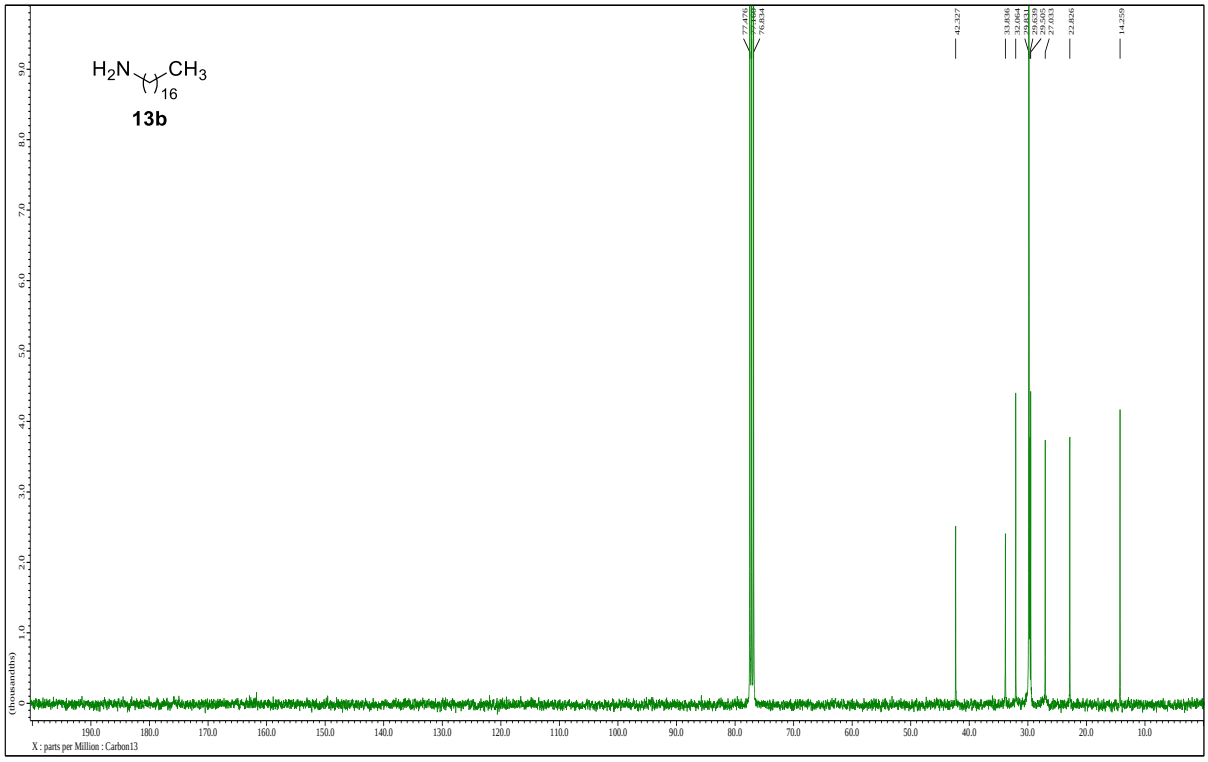
^{13}C-NMR of compound **S12** ($CDCl_3$, 100MHz)



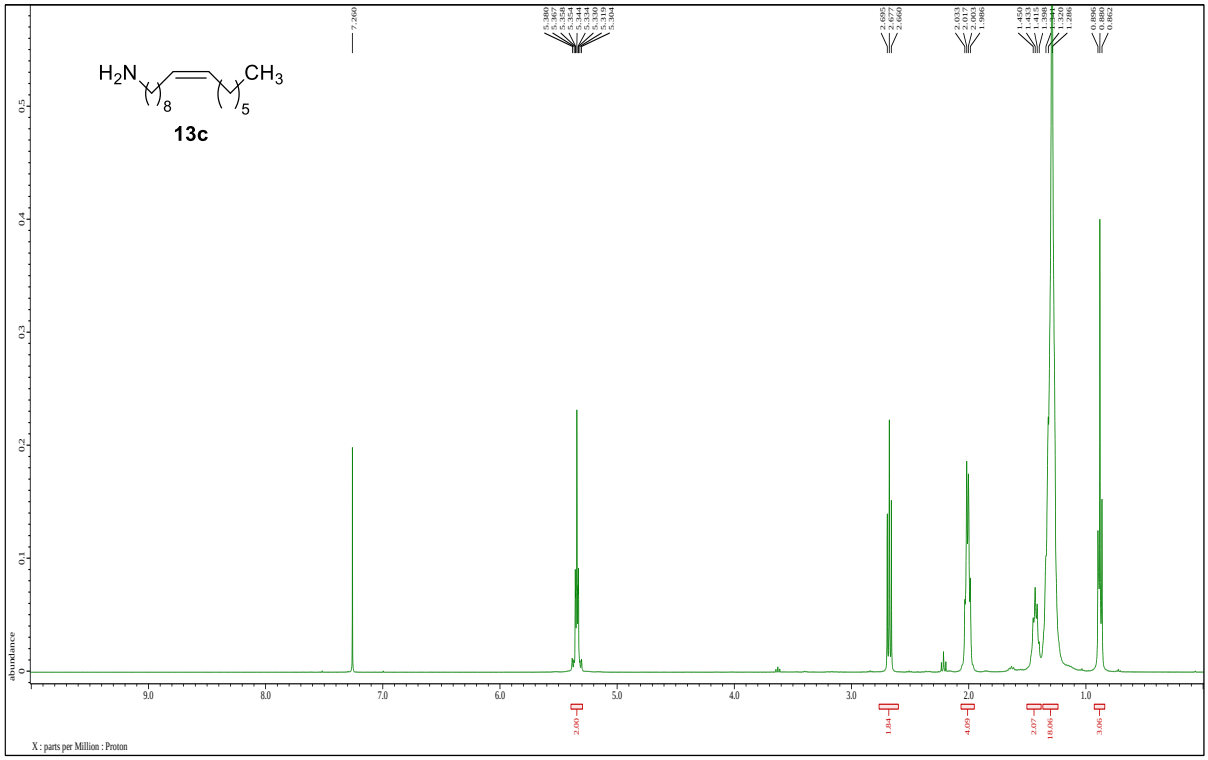
[1]H-NMR of compound **13b** ($CDCl_3$, 400MHz)



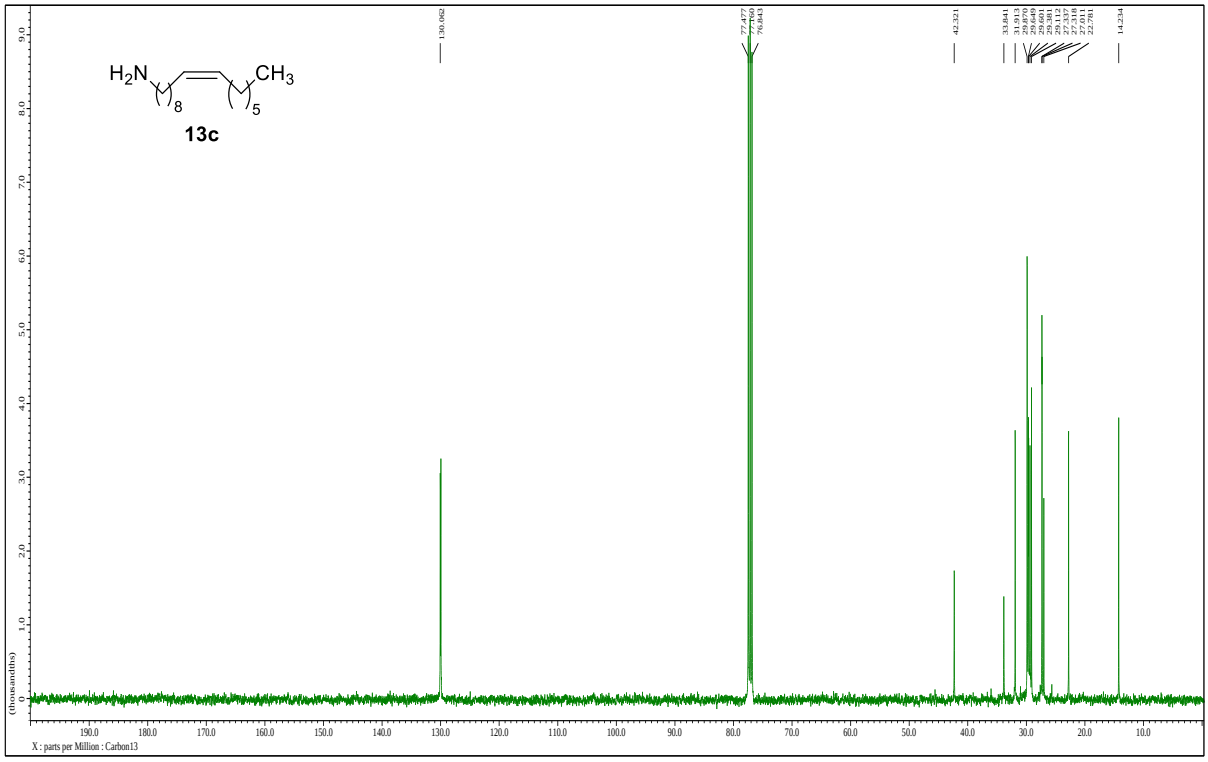
[13]C-NMR of compound **13b** ($CDCl_3$, 100MHz)



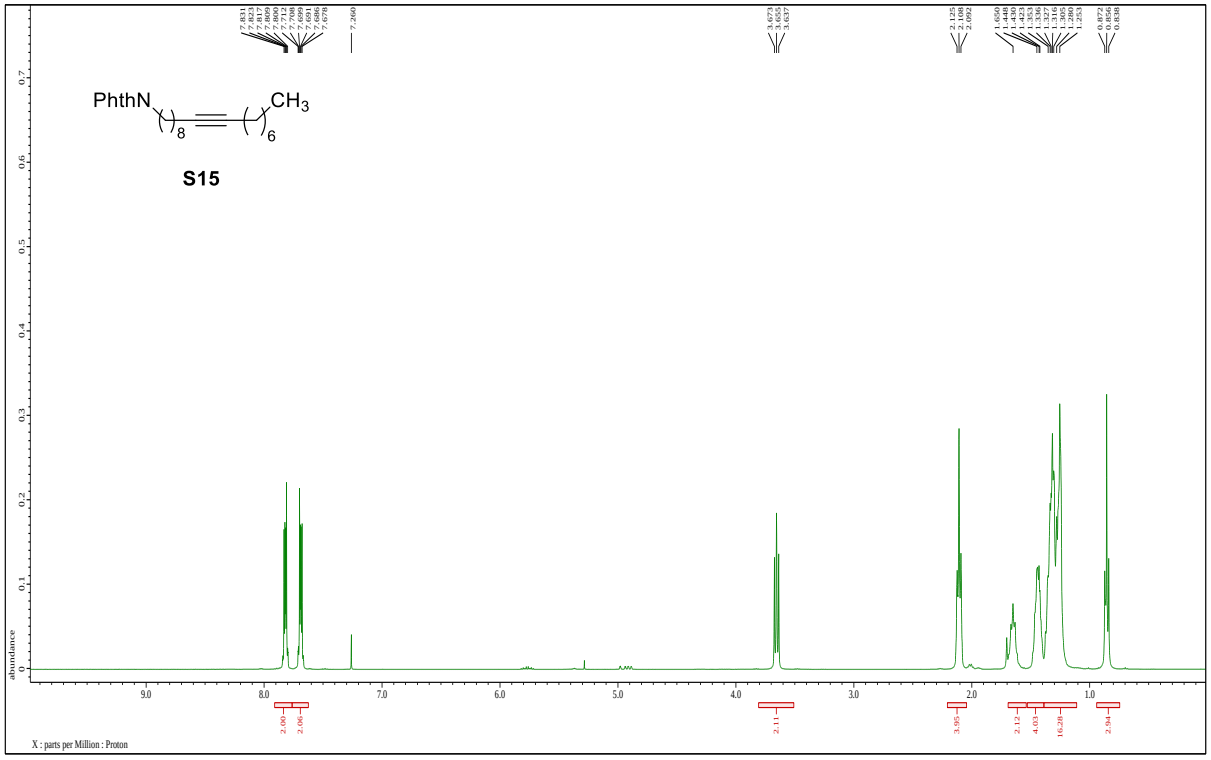
[1]H-NMR of compound **13c** ($CDCl_3$, 400MHz)



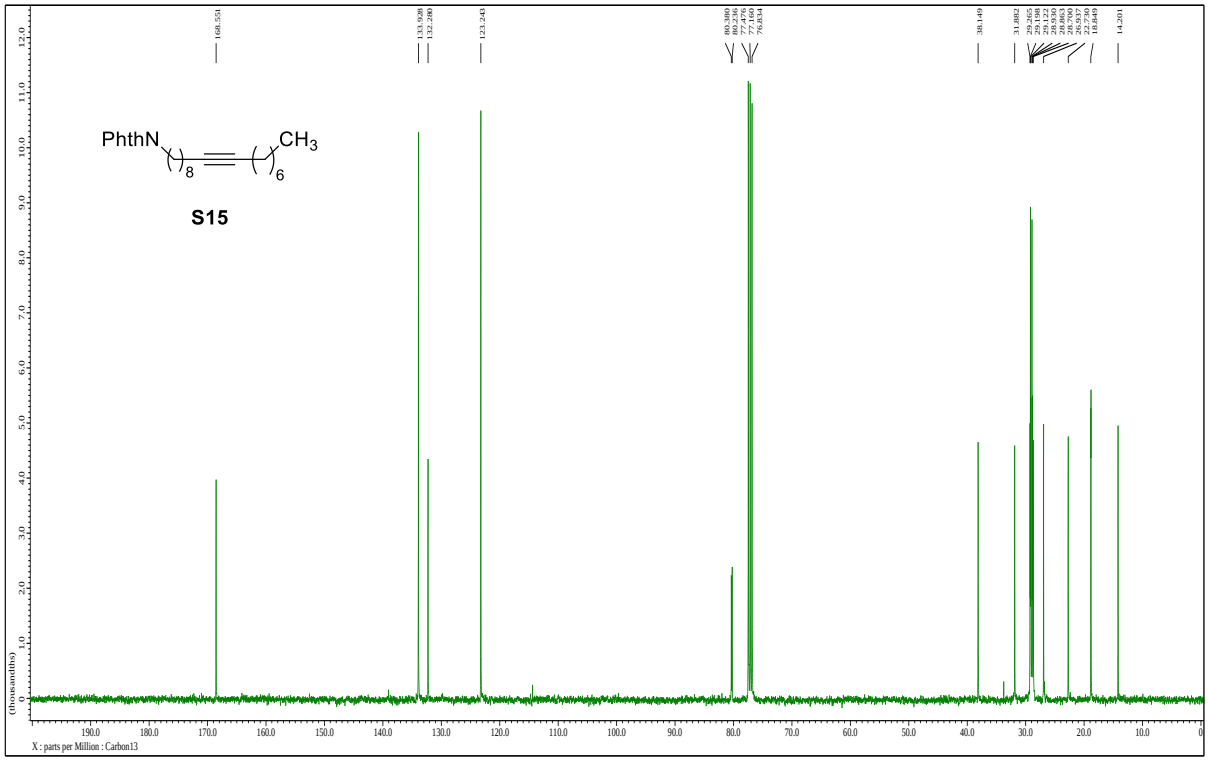
[13]C-NMR of compound **13c** ($CDCl_3$, 100MHz)



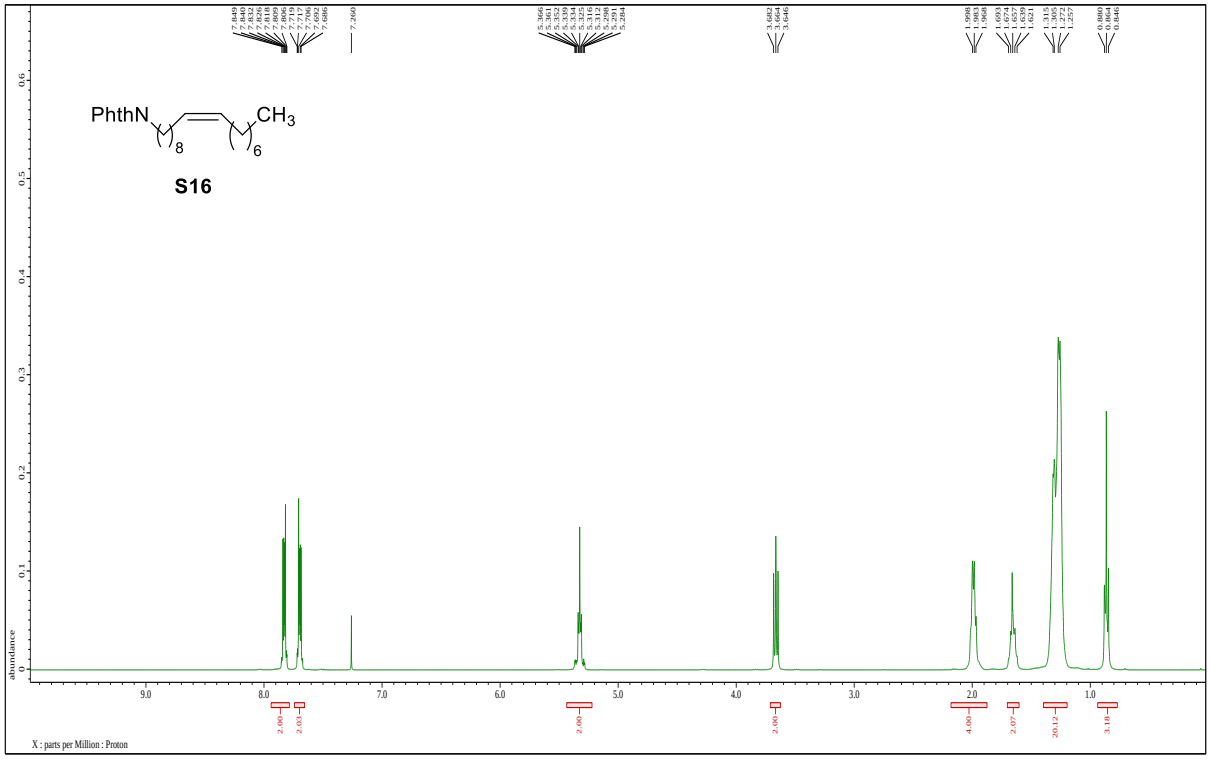
^{1}H-NMR of compound **S15** ($CDCl_3$, 400MHz)



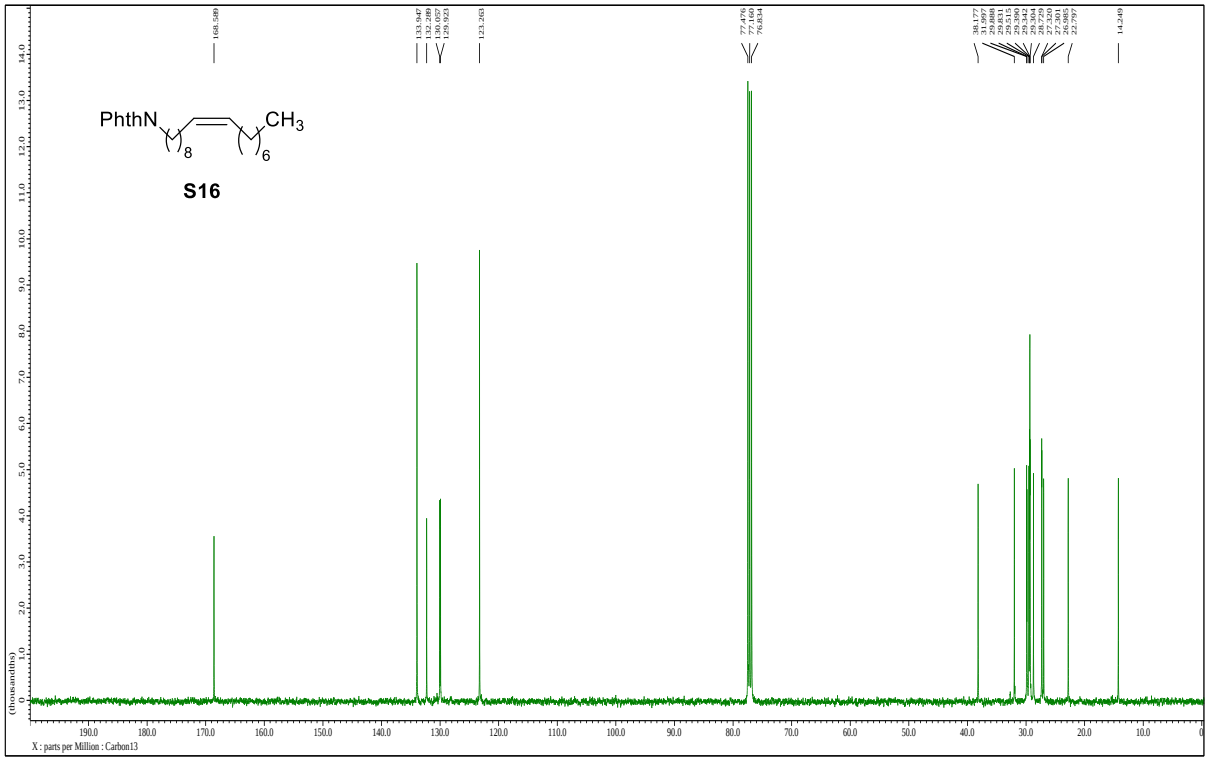
^{13}C-NMR of compound **S15** ($CDCl_3$, 100MHz)



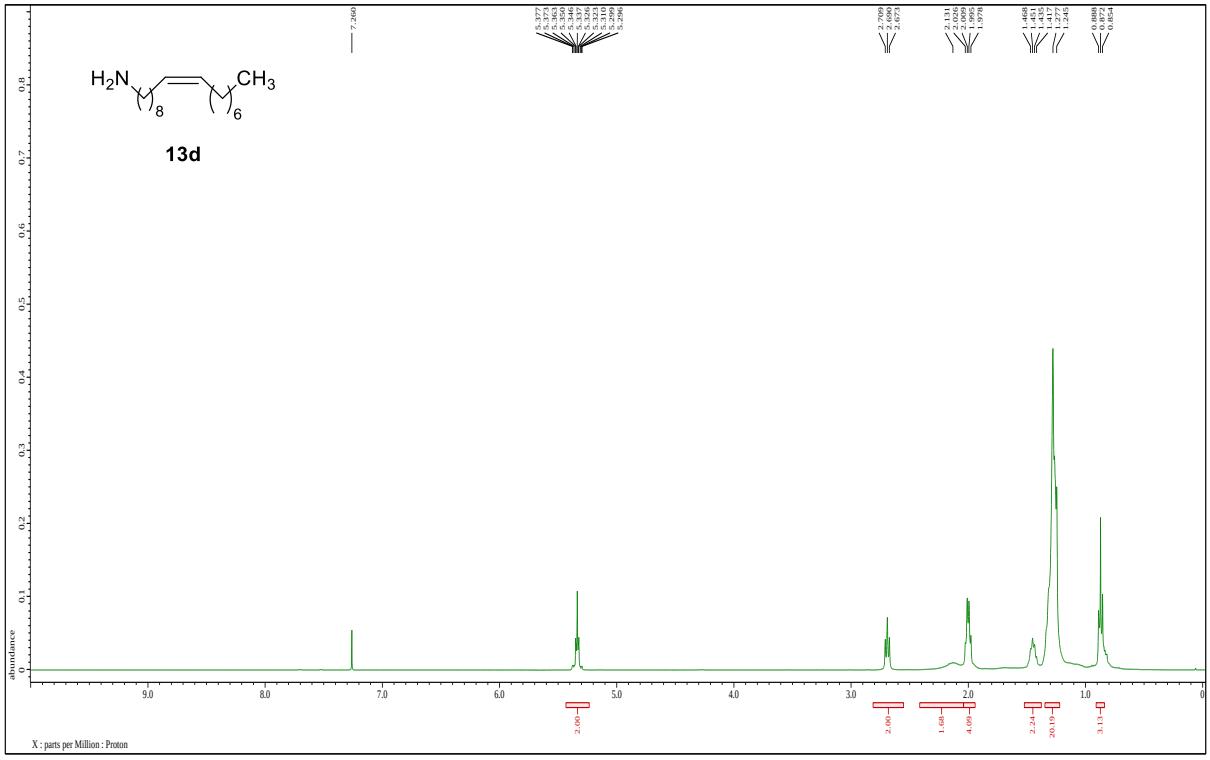
^{1}H-NMR of compound **S16** ($CDCl_3$, 400MHz)



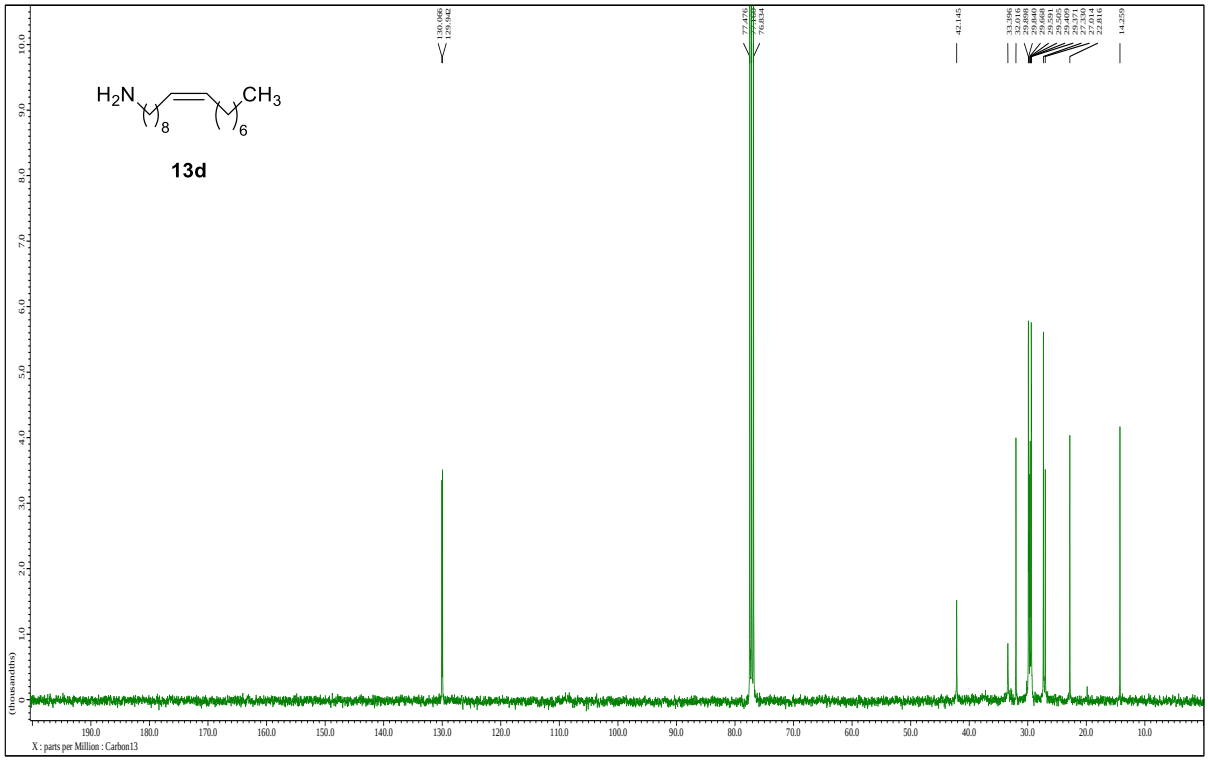
^{13}C-NMR of compound **S16** ($CDCl_3$, 100MHz)



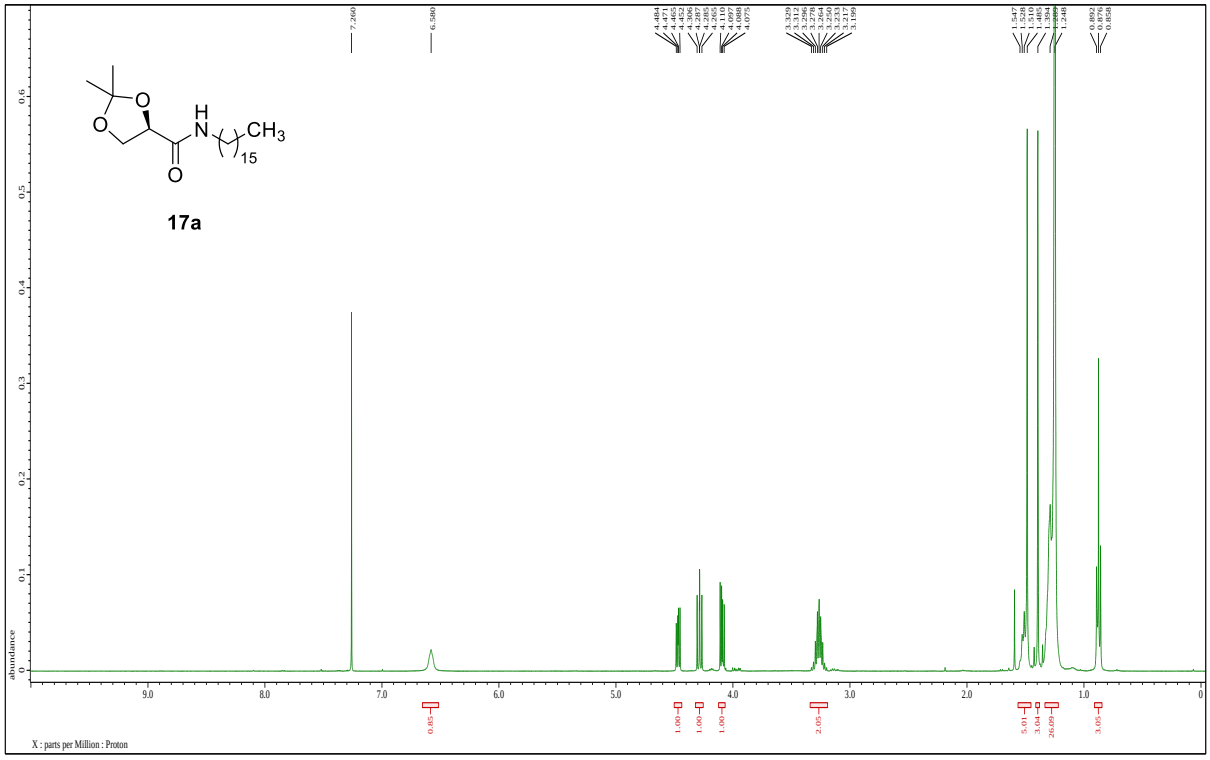
^{1}H-NMR of compound **13d** ($CDCl_3$, 400MHz)



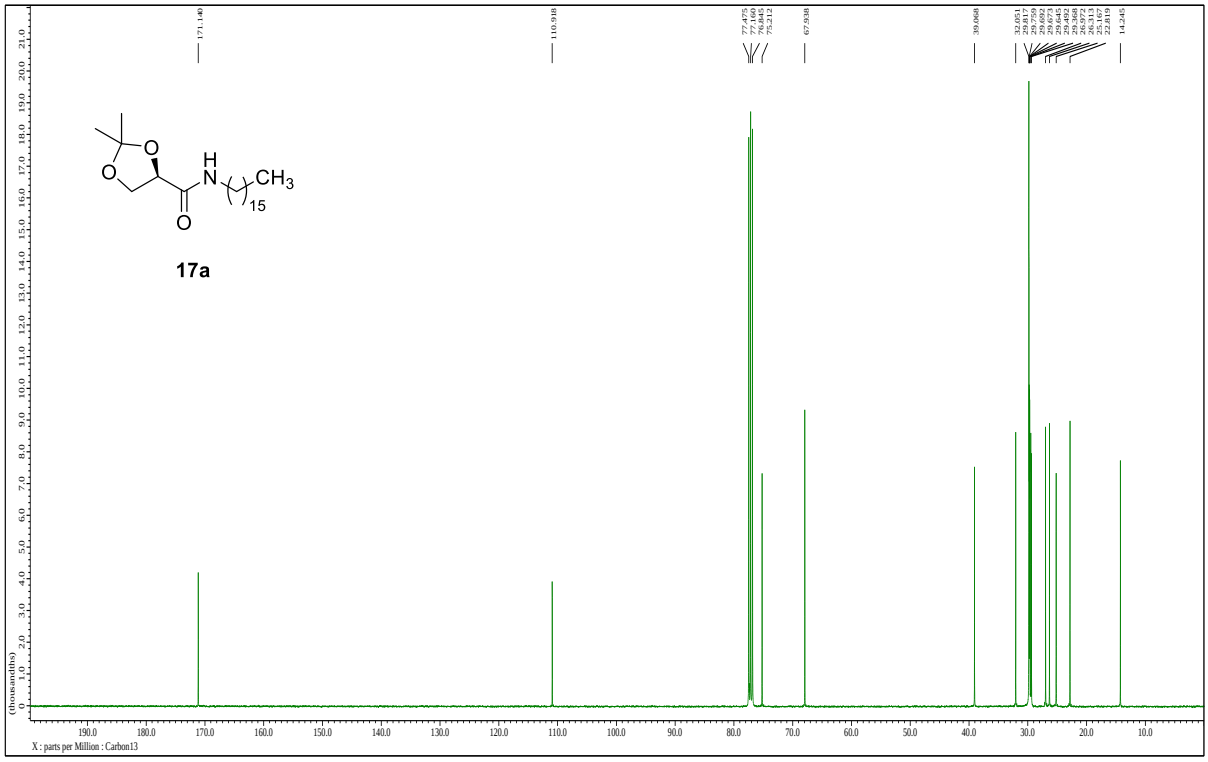
^{13}C-NMR of compound **13d** ($CDCl_3$, 100MHz)



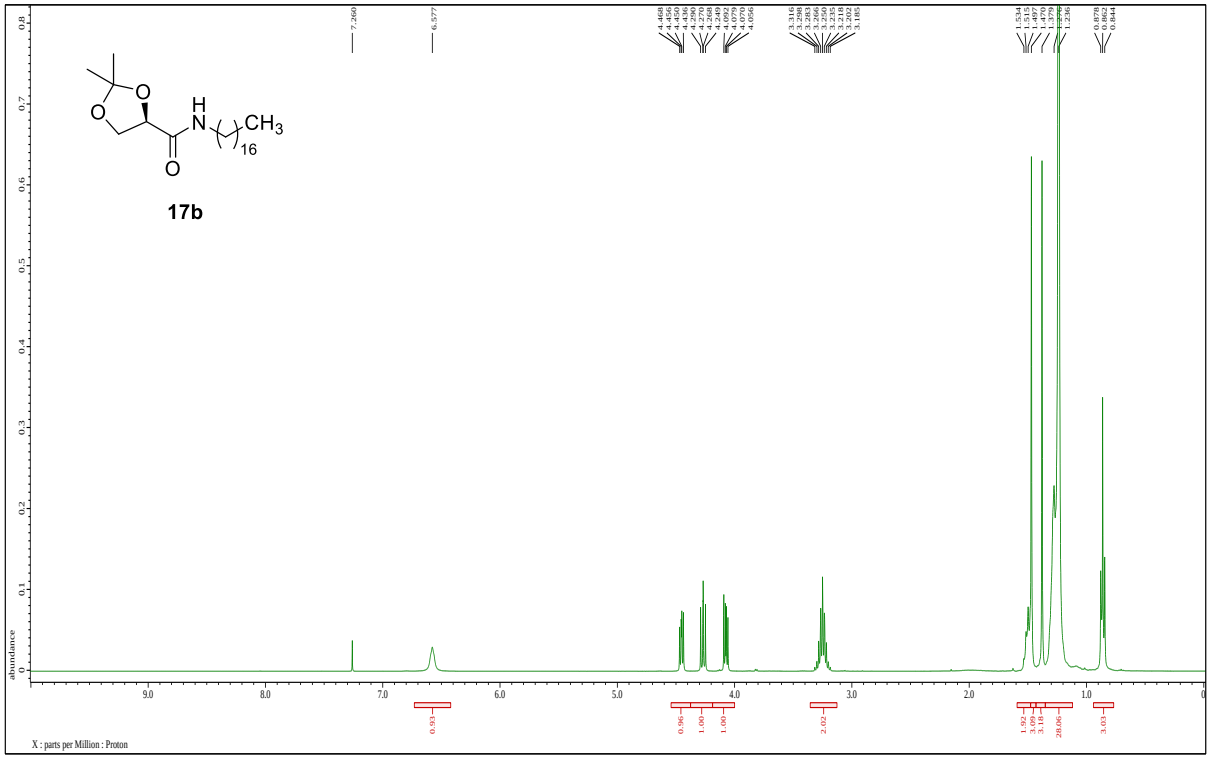
^{1}H-NMR of compound **17a** ($CDCl_3$, 400MHz)



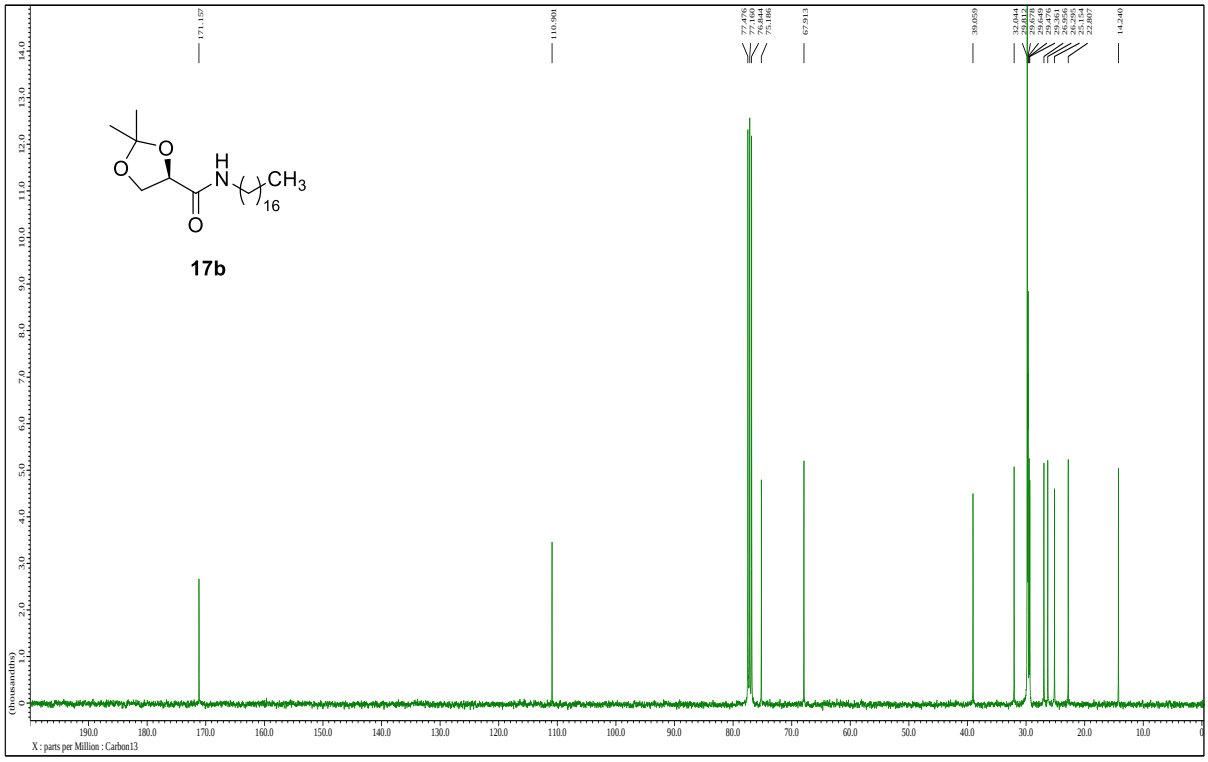
^{13}C-NMR of compound **17a** ($CDCl_3$, 100MHz)



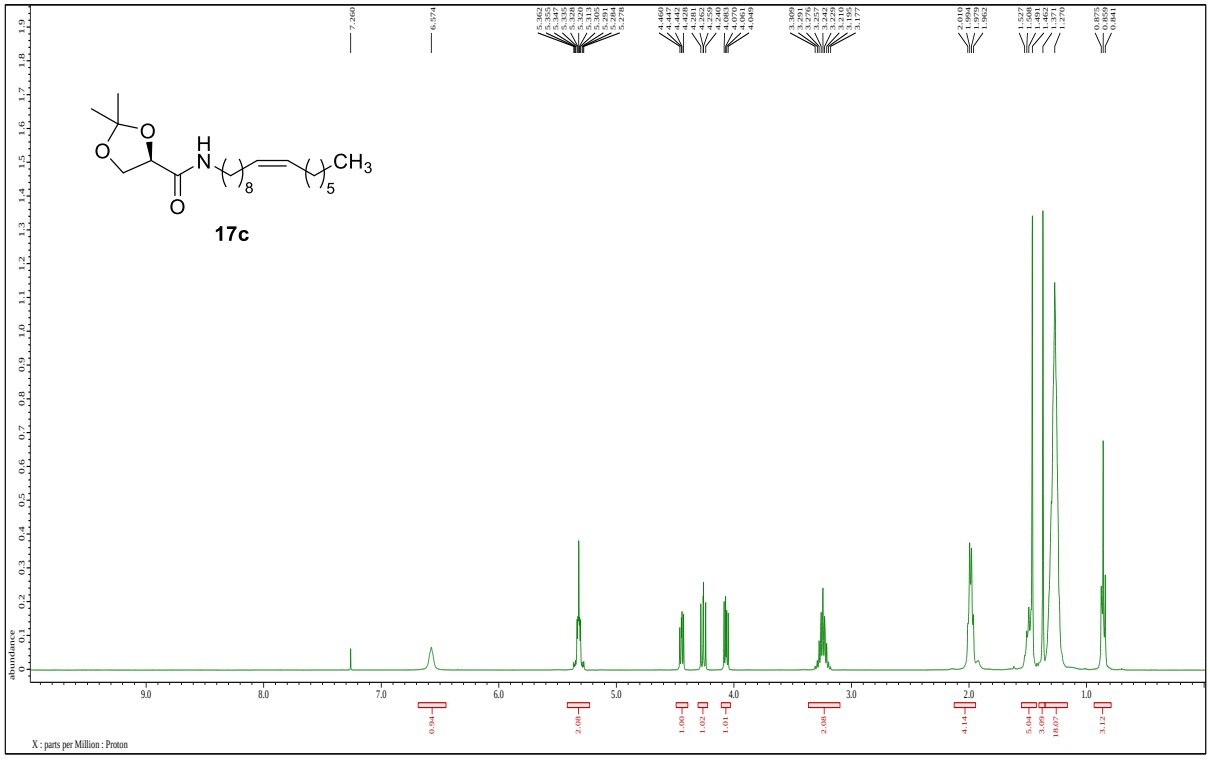
[1]H-NMR of compound **17b** ($CDCl_3$, 400MHz)



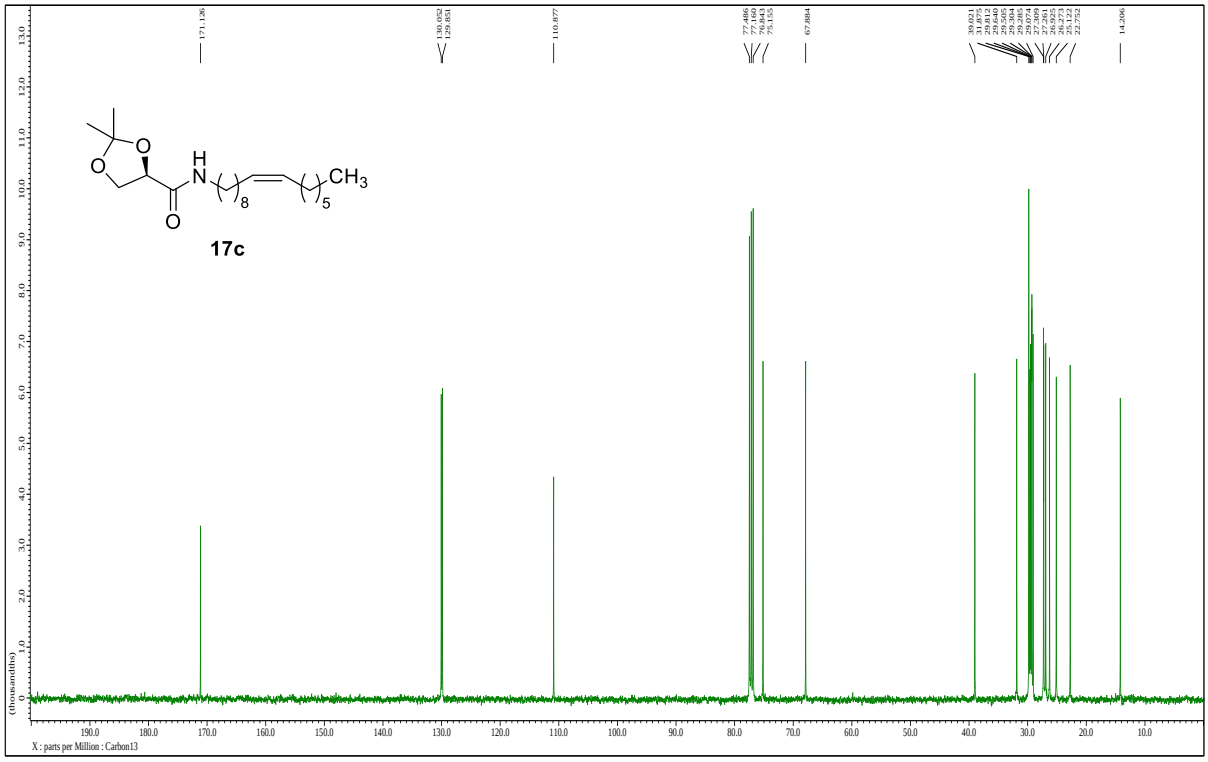
[13]C-NMR of compound **17b** ($CDCl_3$, 100MHz)



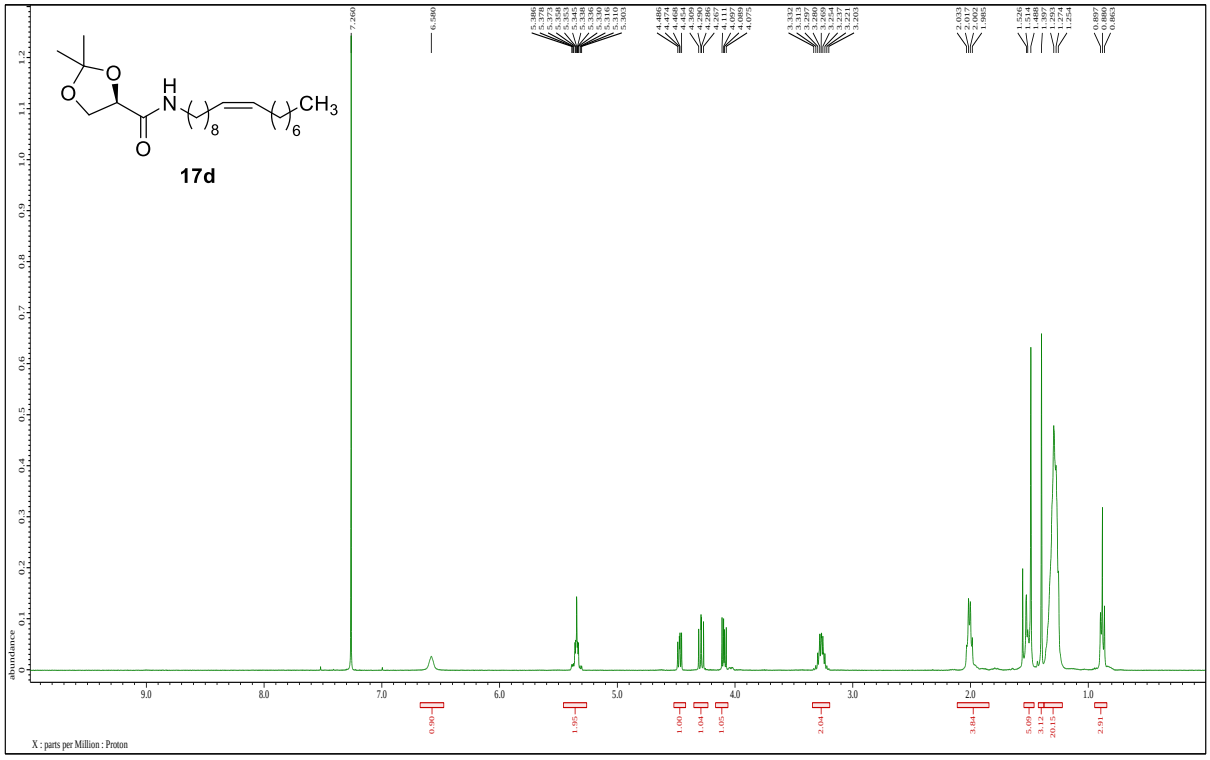
[1]H-NMR of compound **17c** ($CDCl_3$, 400MHz)



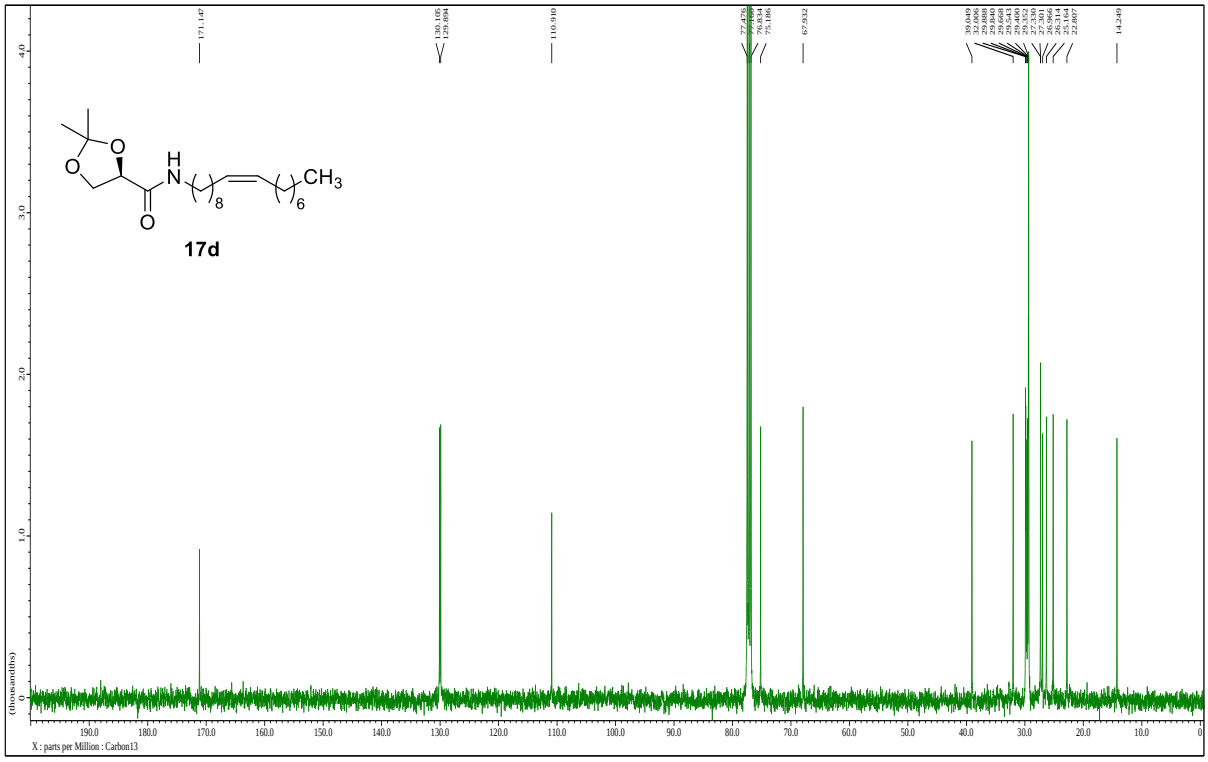
[13]C-NMR of compound **17c** ($CDCl_3$, 100MHz)



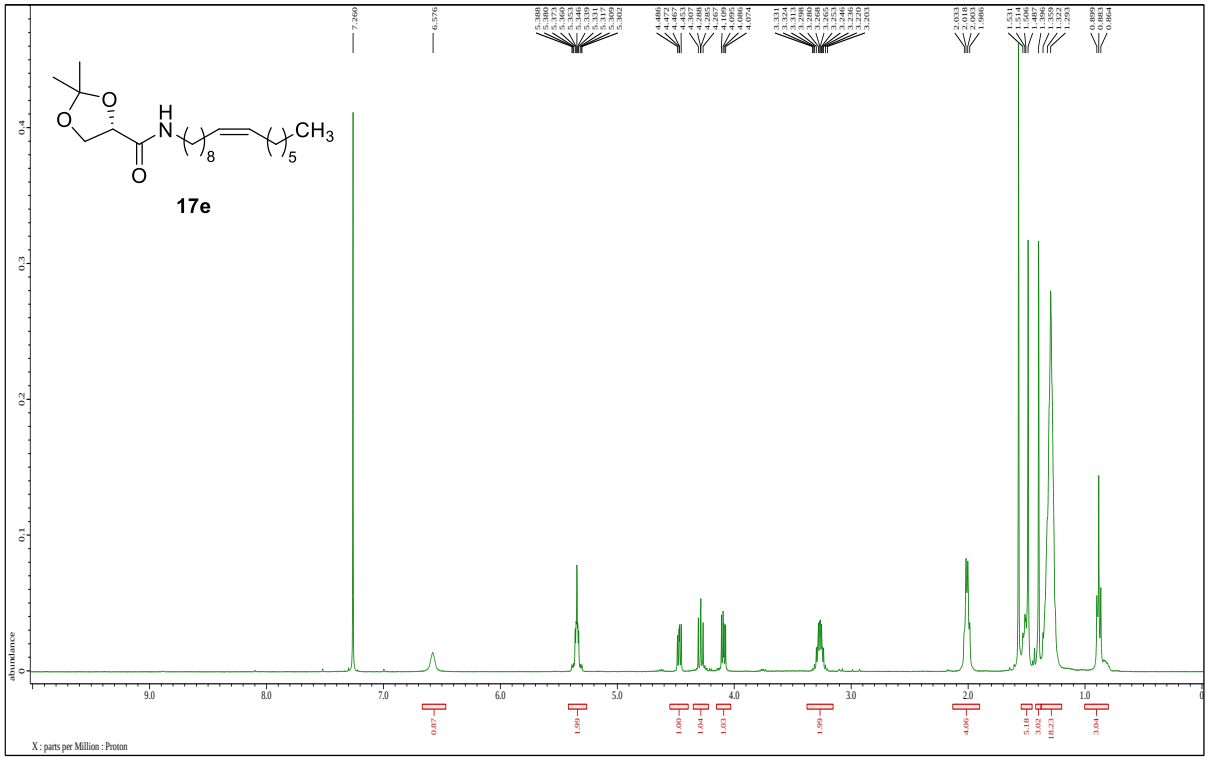
^{1}H-NMR of compound **17d** ($CDCl_3$, 400MHz)



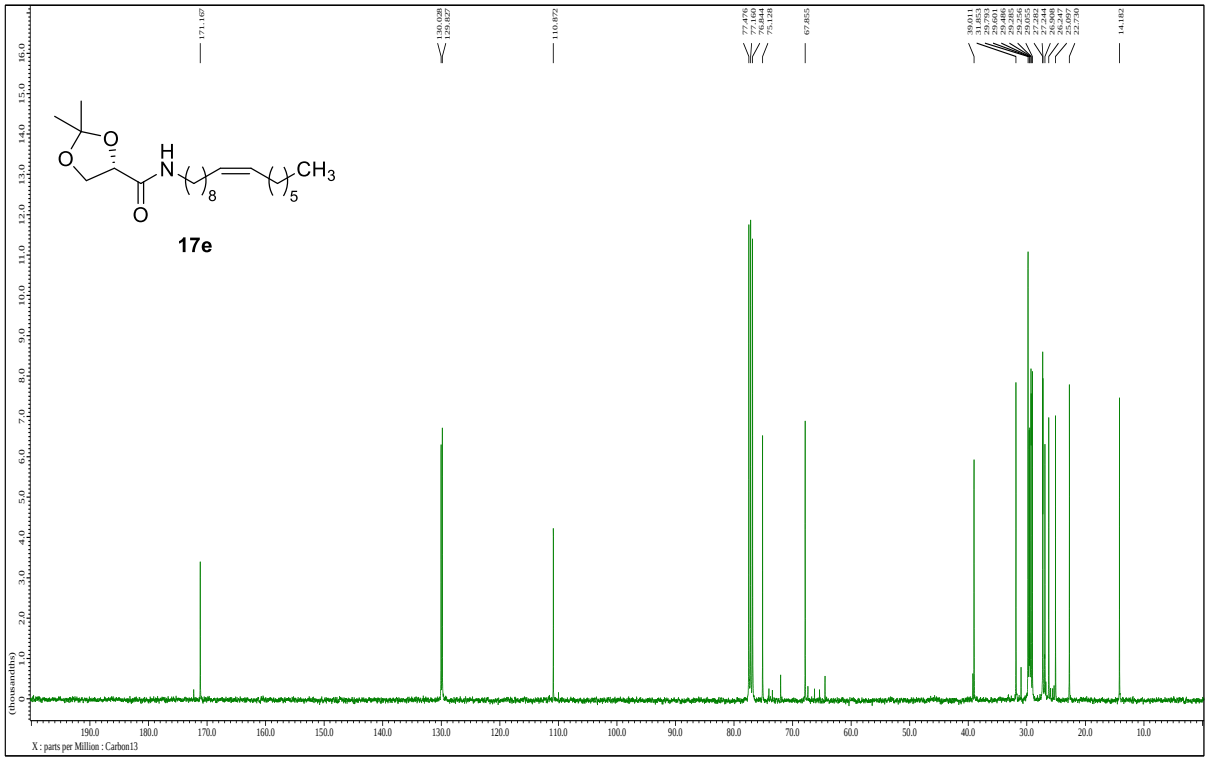
^{13}C-NMR of compound **17d** ($CDCl_3$, 100MHz)



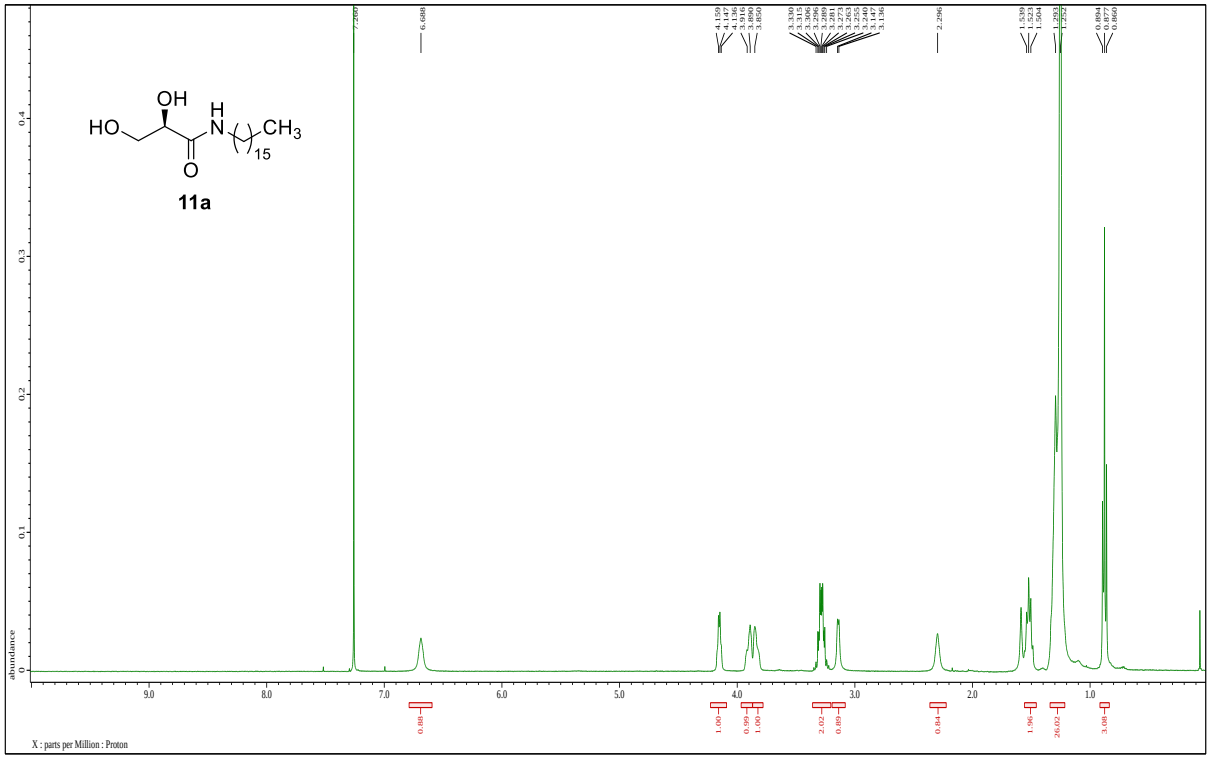
^{1}H-NMR of compound **17e** ($CDCl_3$, 400MHz)



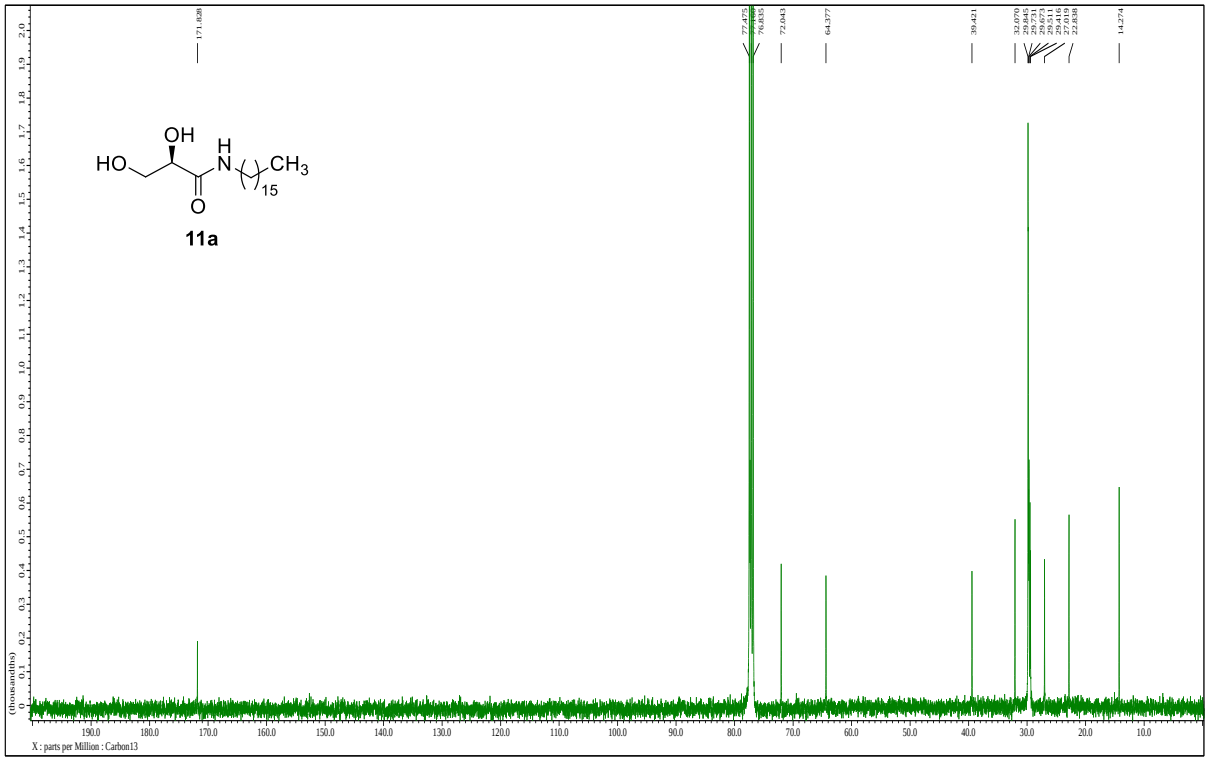
^{13}C-NMR of compound **17e** ($CDCl_3$, 100MHz)



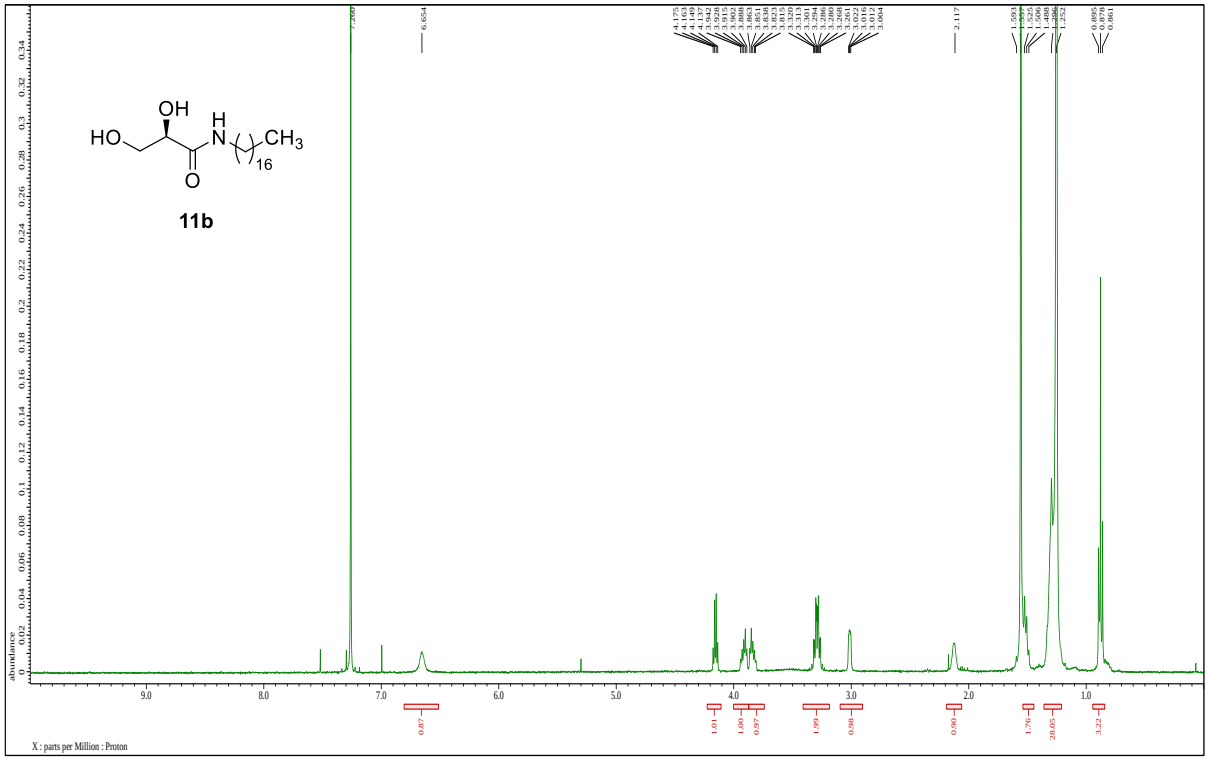
^{1}H-NMR of compound **11a** ($CDCl_3$, 400MHz)



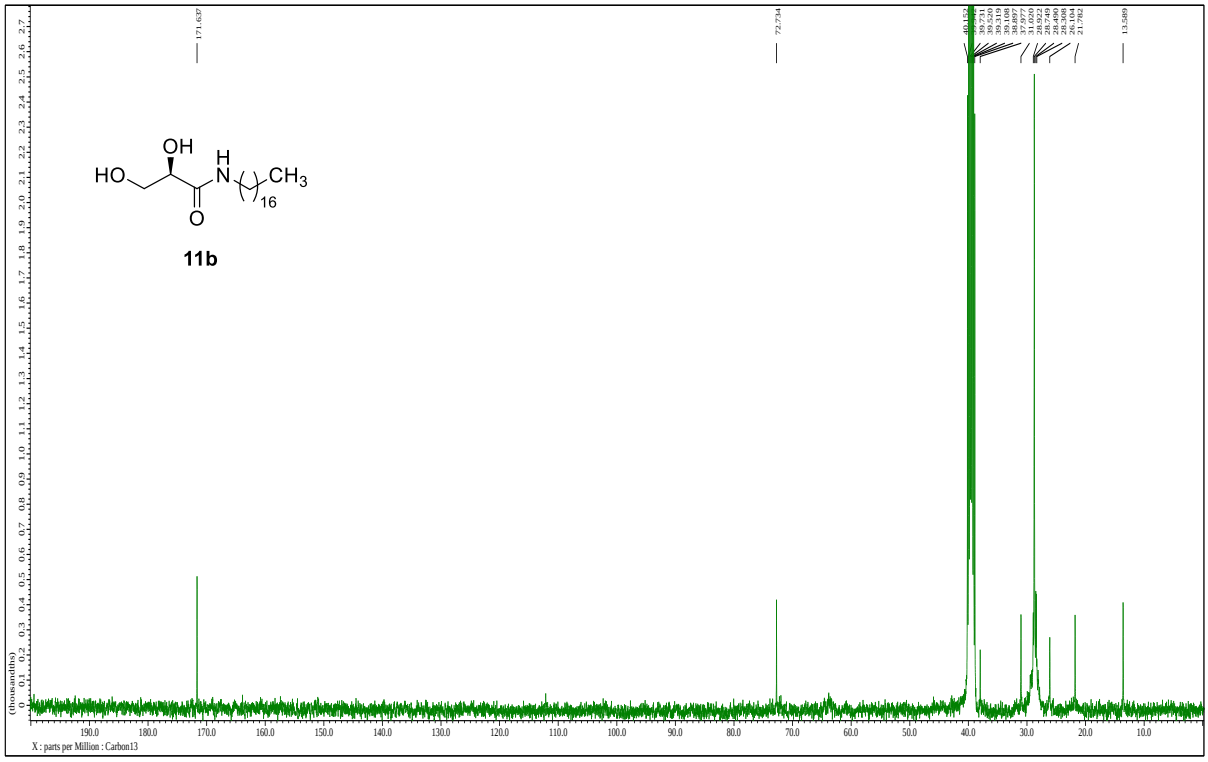
^{13}C-NMR of compound **11a** ($CDCl_3$, 100MHz)



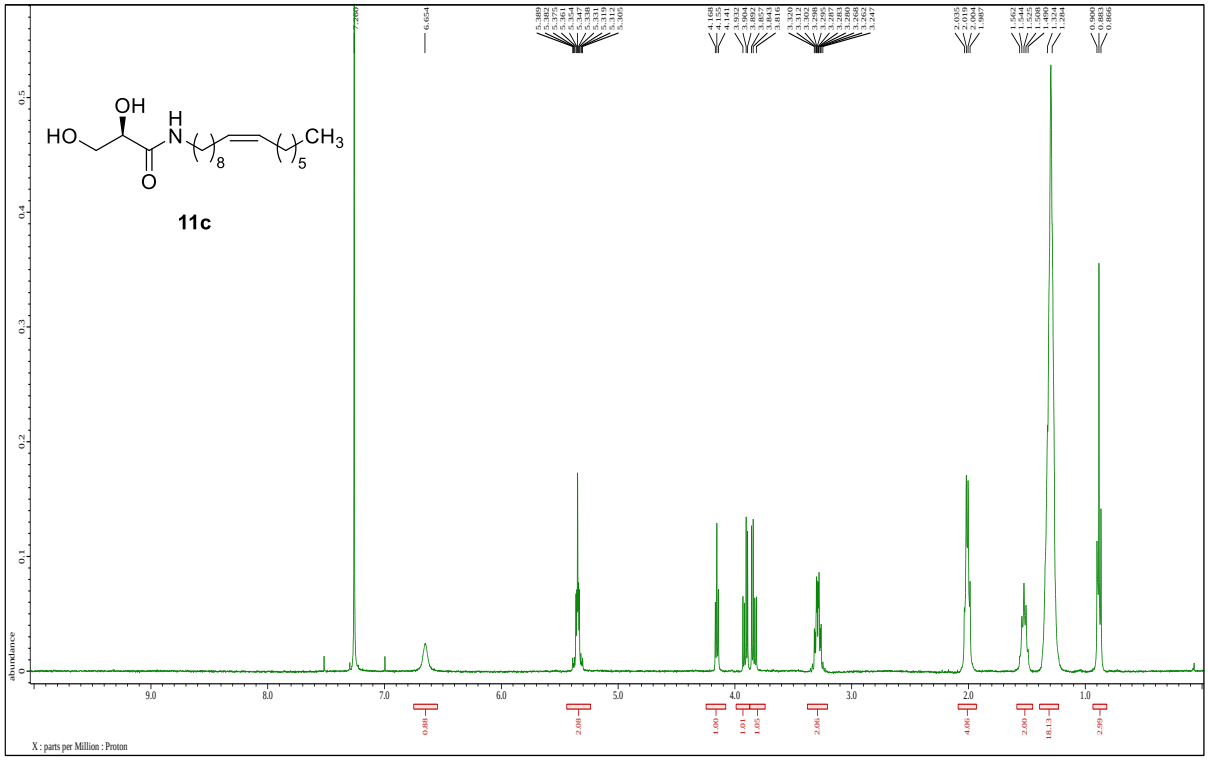
[1]H-NMR of compound **11b** ($CDCl_3$, 400MHz)



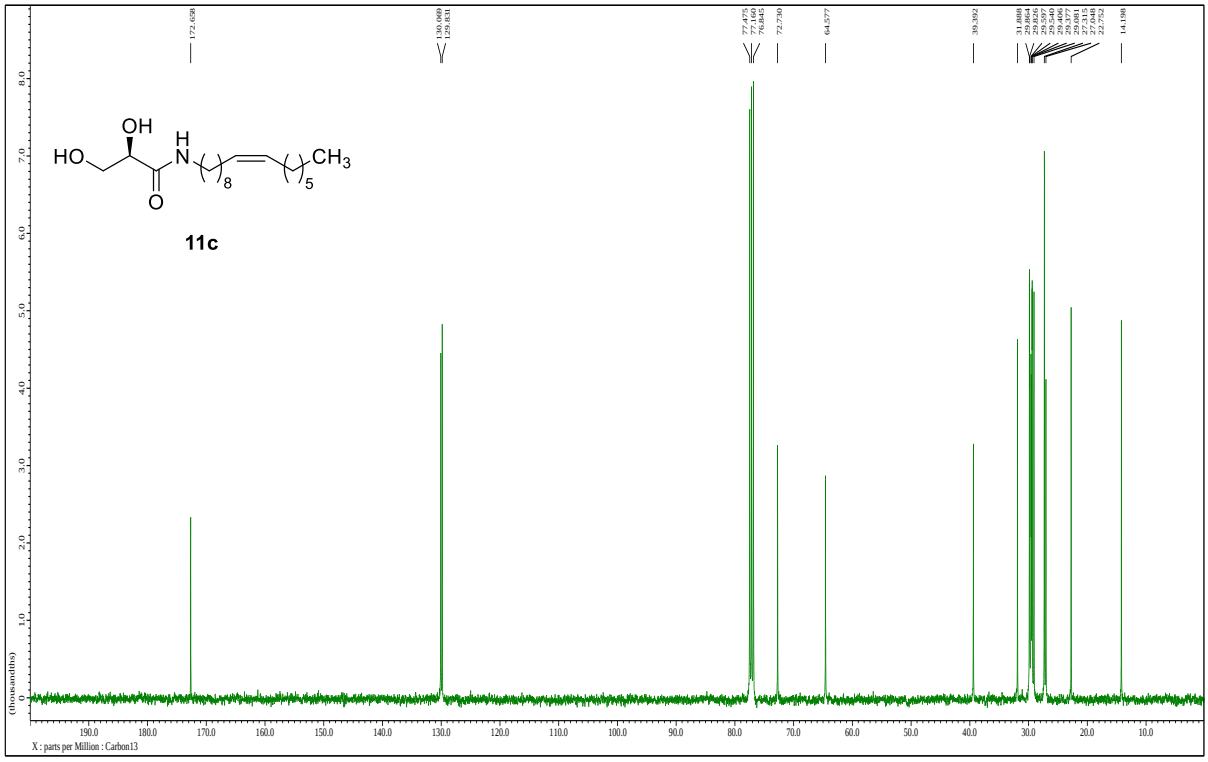
[13]C-NMR of compound **11b** (DMSO-d_6, 100MHz)



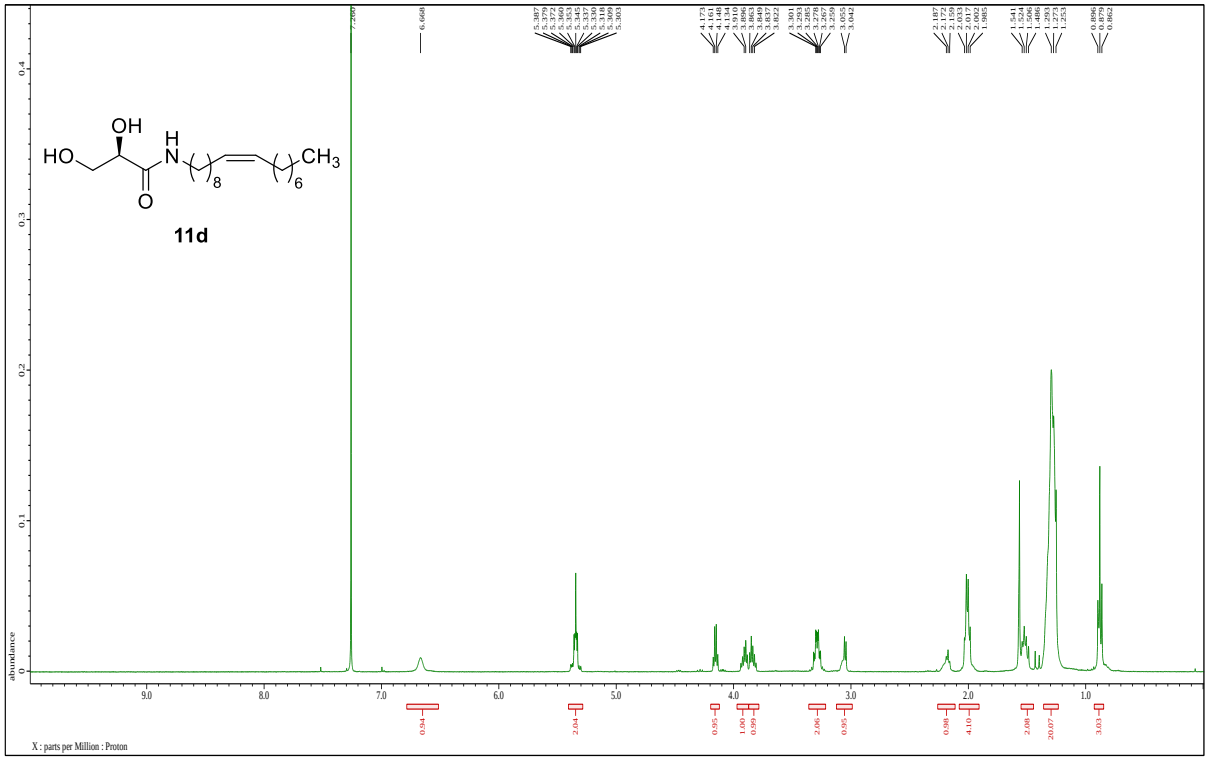
^{1}H-NMR of compound **11c** ($CDCl_3$, 400MHz)



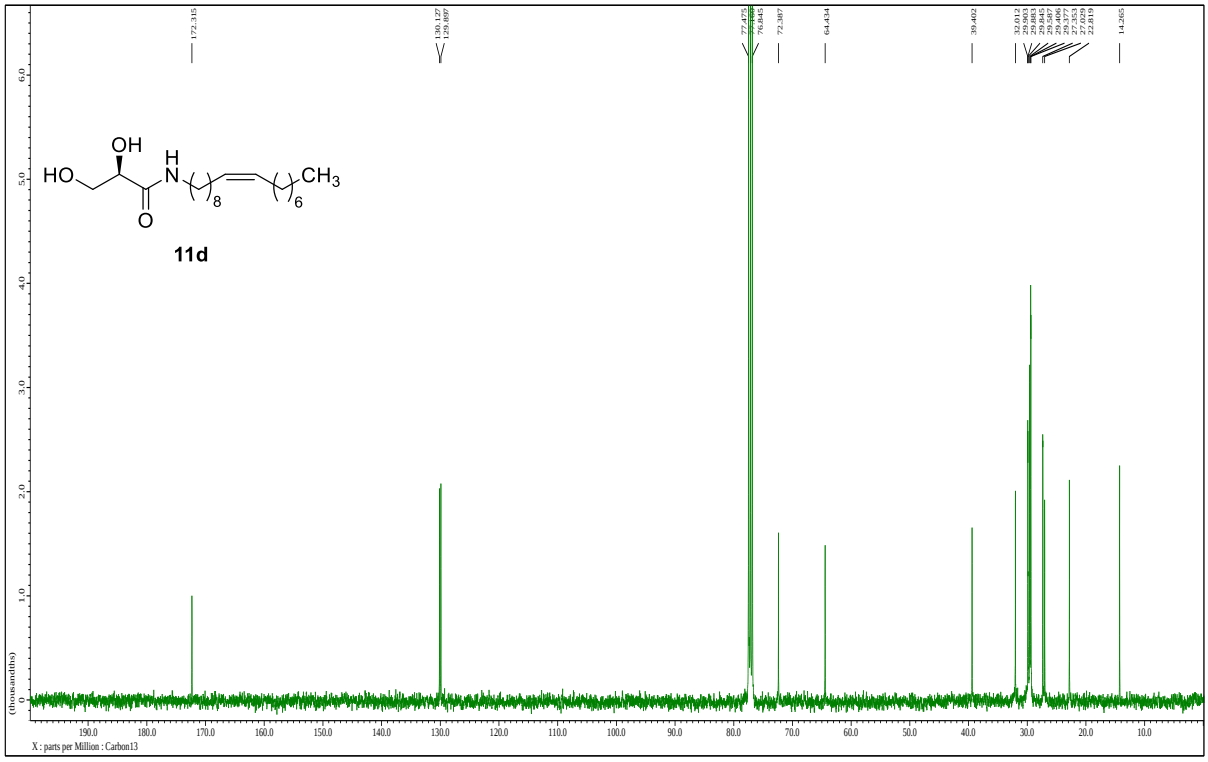
^{13}C-NMR of compound **11c** ($CDCl_3$, 100MHz)



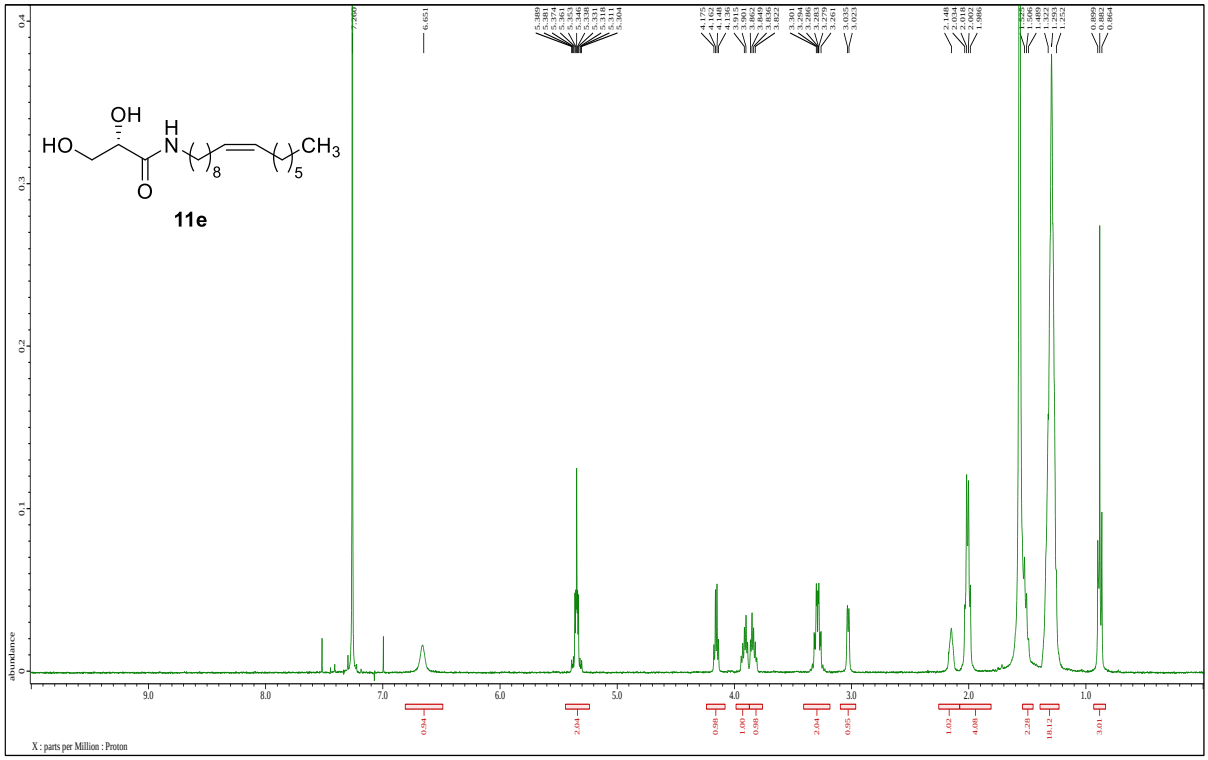
^{1}H-NMR of compound **11d** ($CDCl_3$, 400MHz)



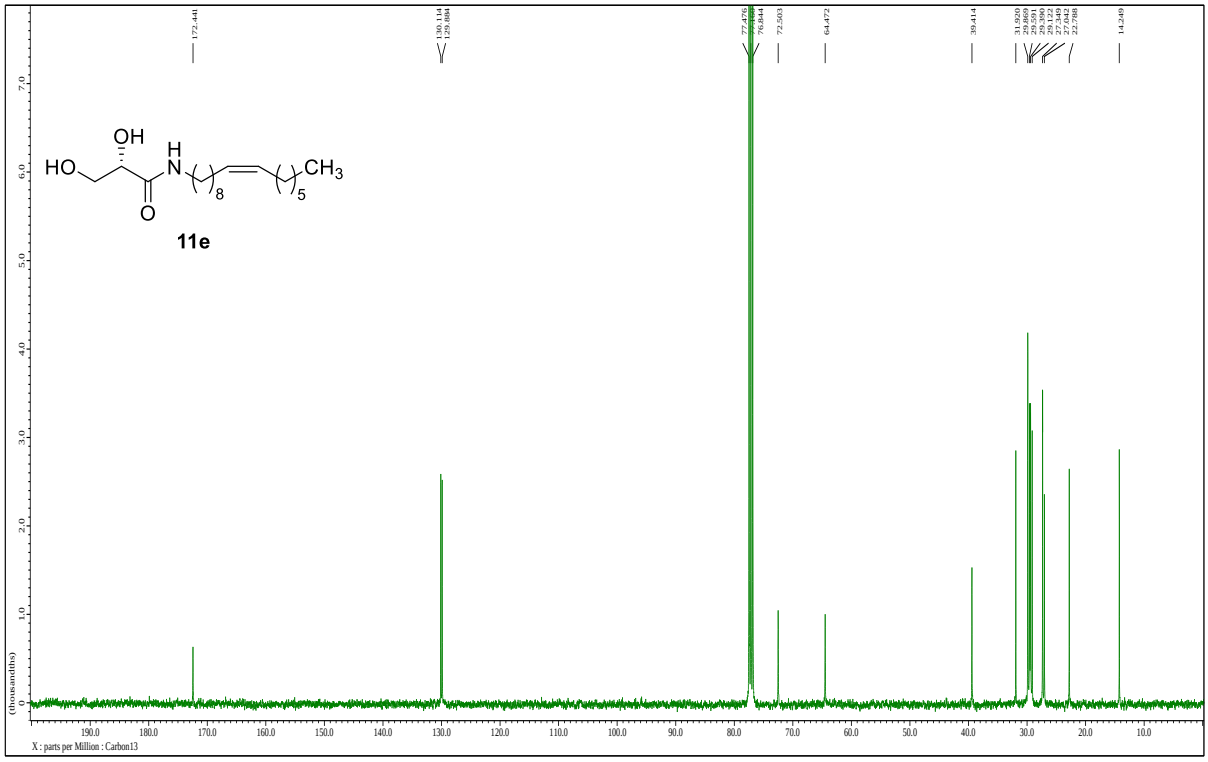
^{13}C-NMR of compound **11d** ($CDCl_3$, 100MHz)



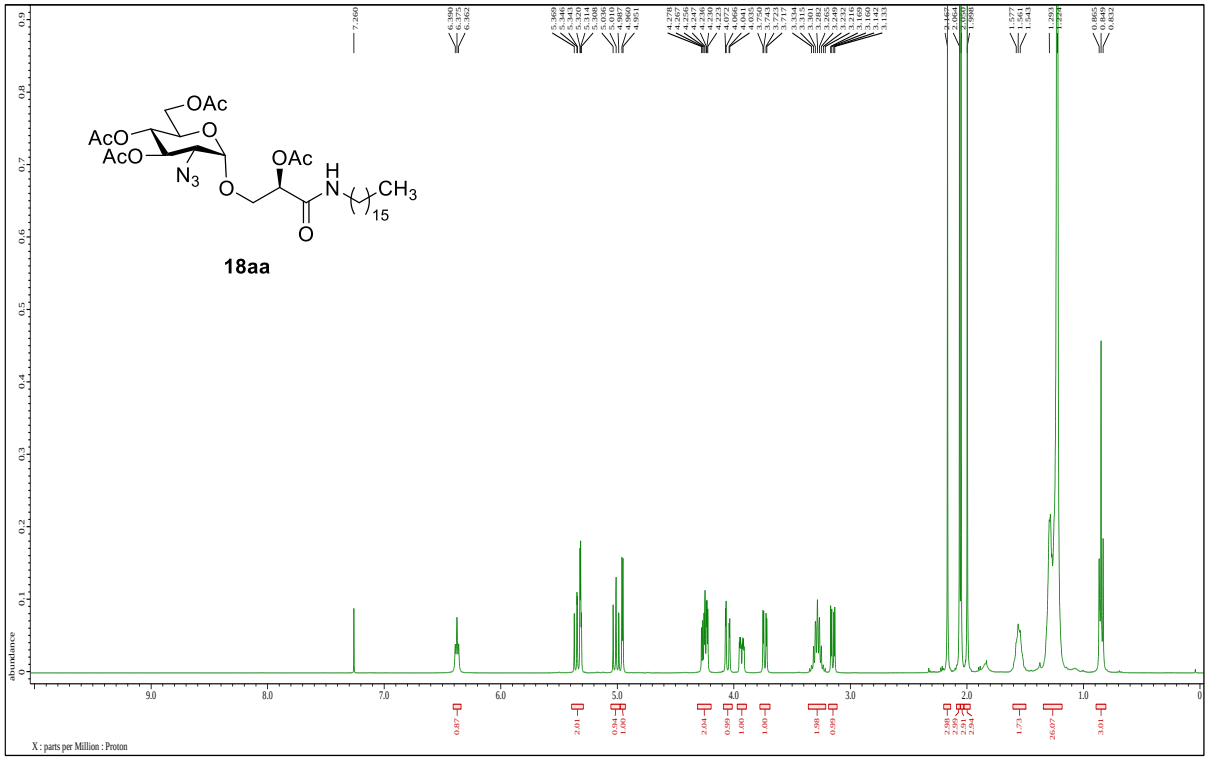
^{1}H-NMR of compound **11e** ($CDCl_3$, 400MHz)



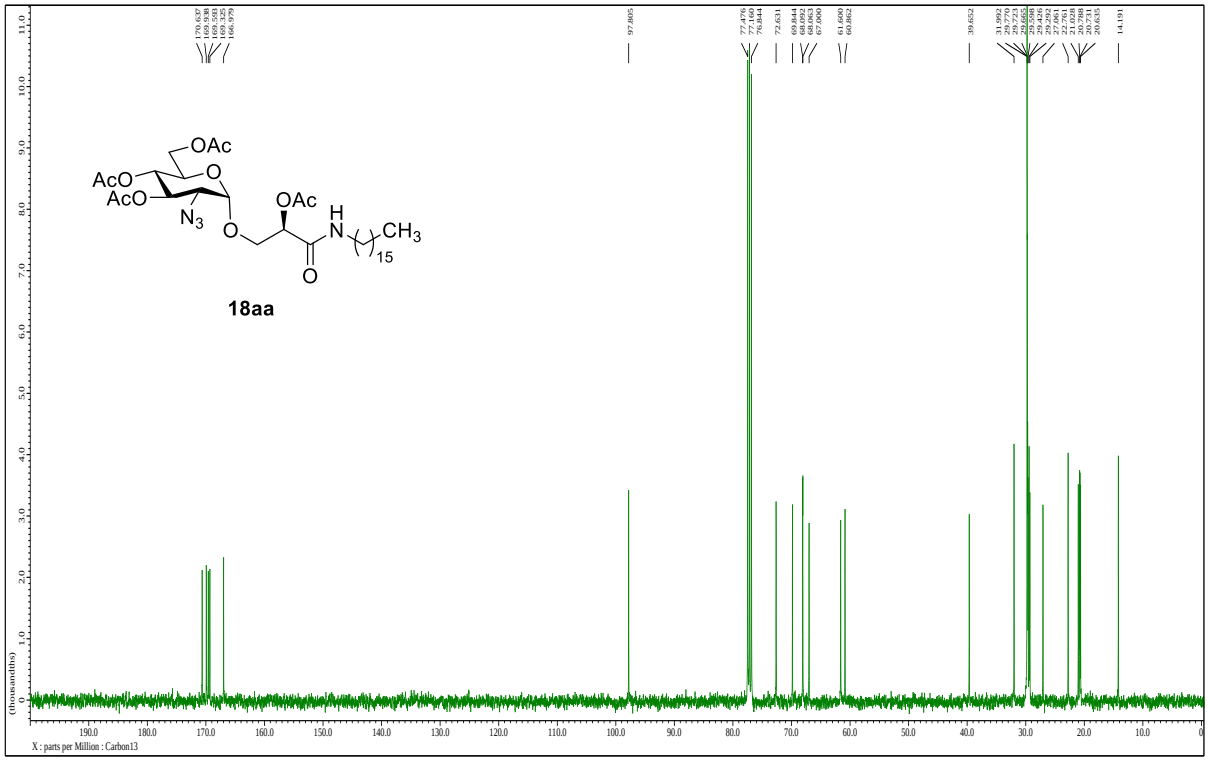
^{13}C-NMR of compound **11e** ($CDCl_3$, 100MHz)



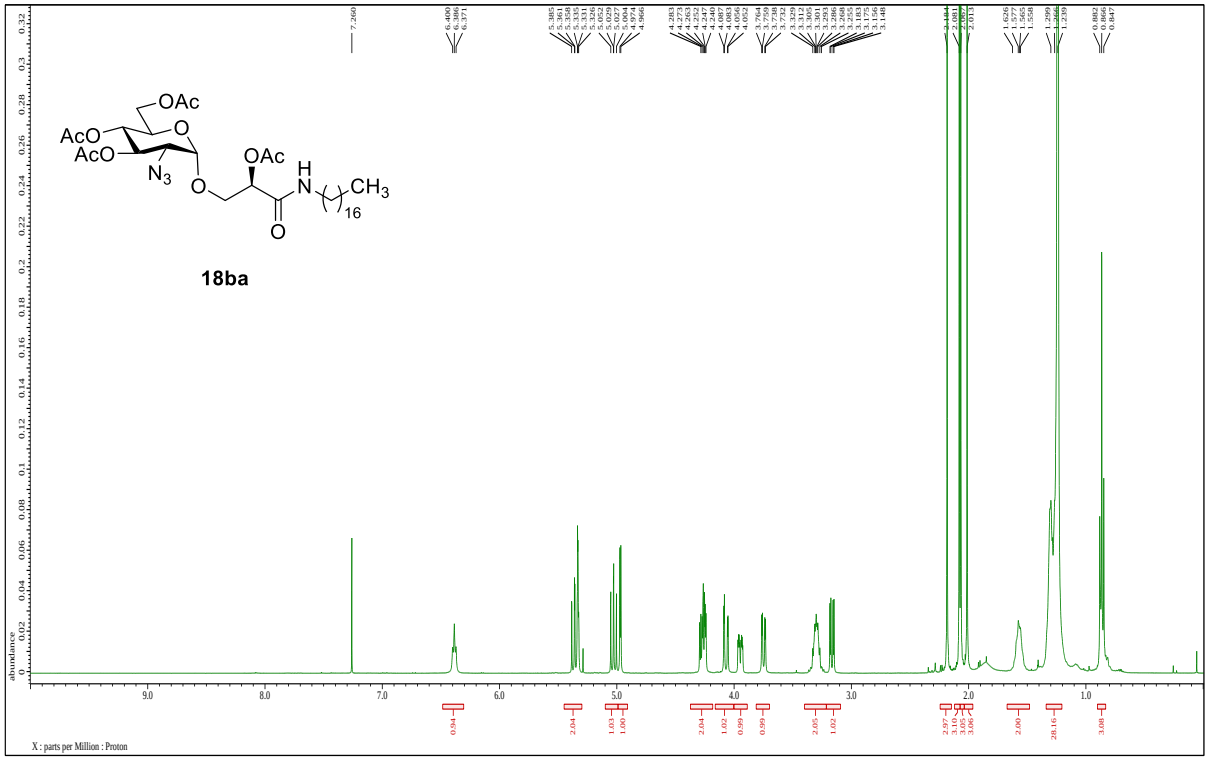
^{1}H-NMR of compound **18aa** ($CDCl_3$, 400MHz)



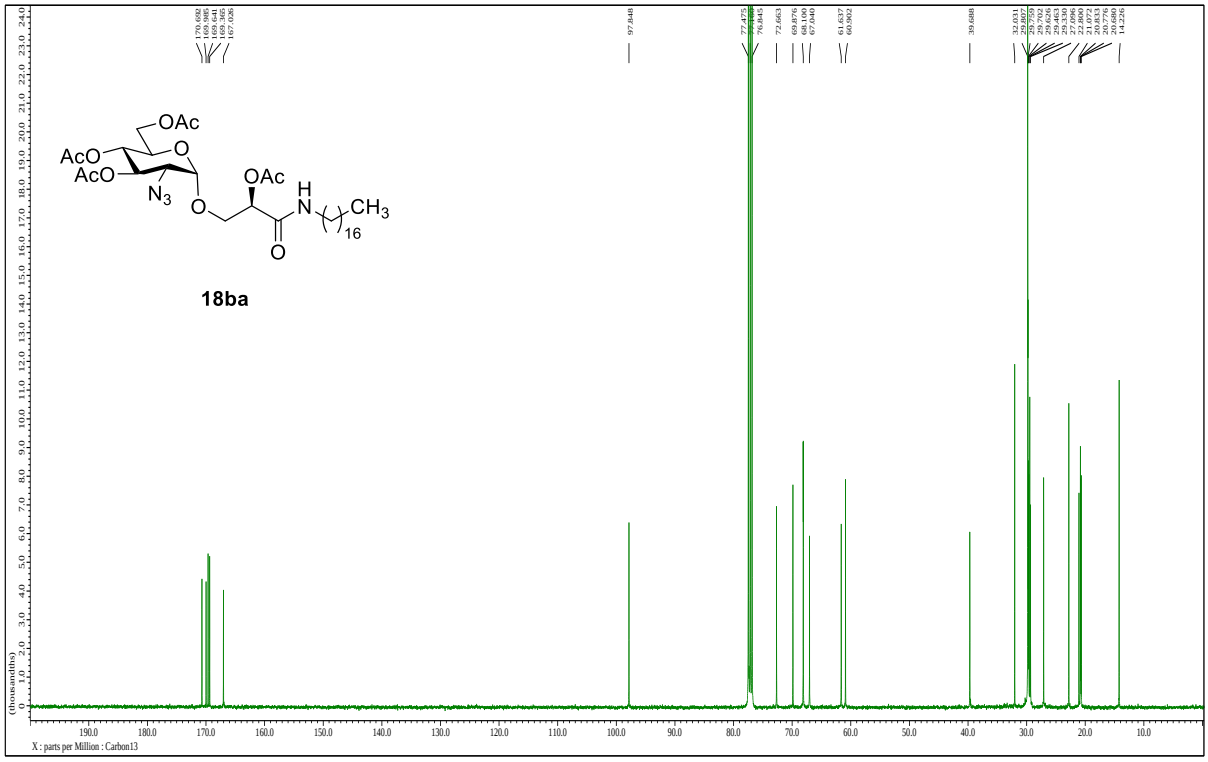
^{13}C-NMR of compound **18aa** ($CDCl_3$, 100MHz)



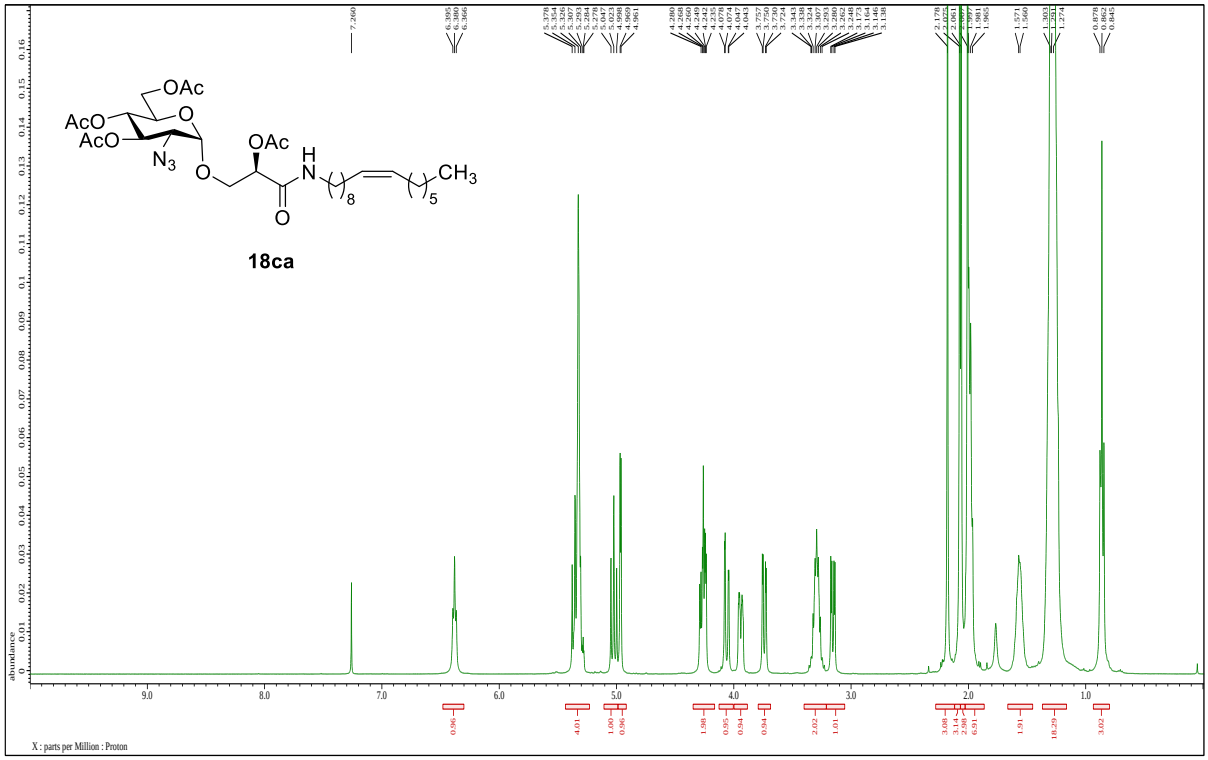
^{1}H-NMR of compound **18ba** ($CDCl_3$, 400MHz)



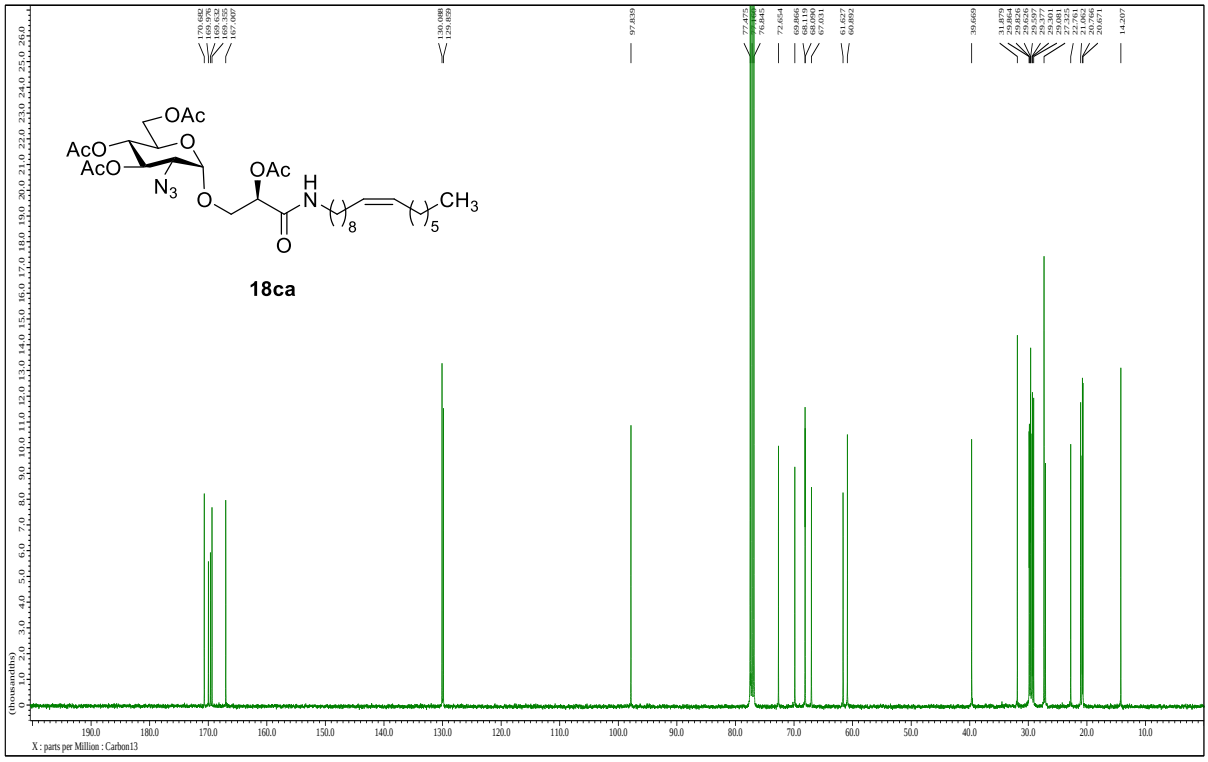
^{13}C-NMR of compound **18ba** ($CDCl_3$, 100MHz)



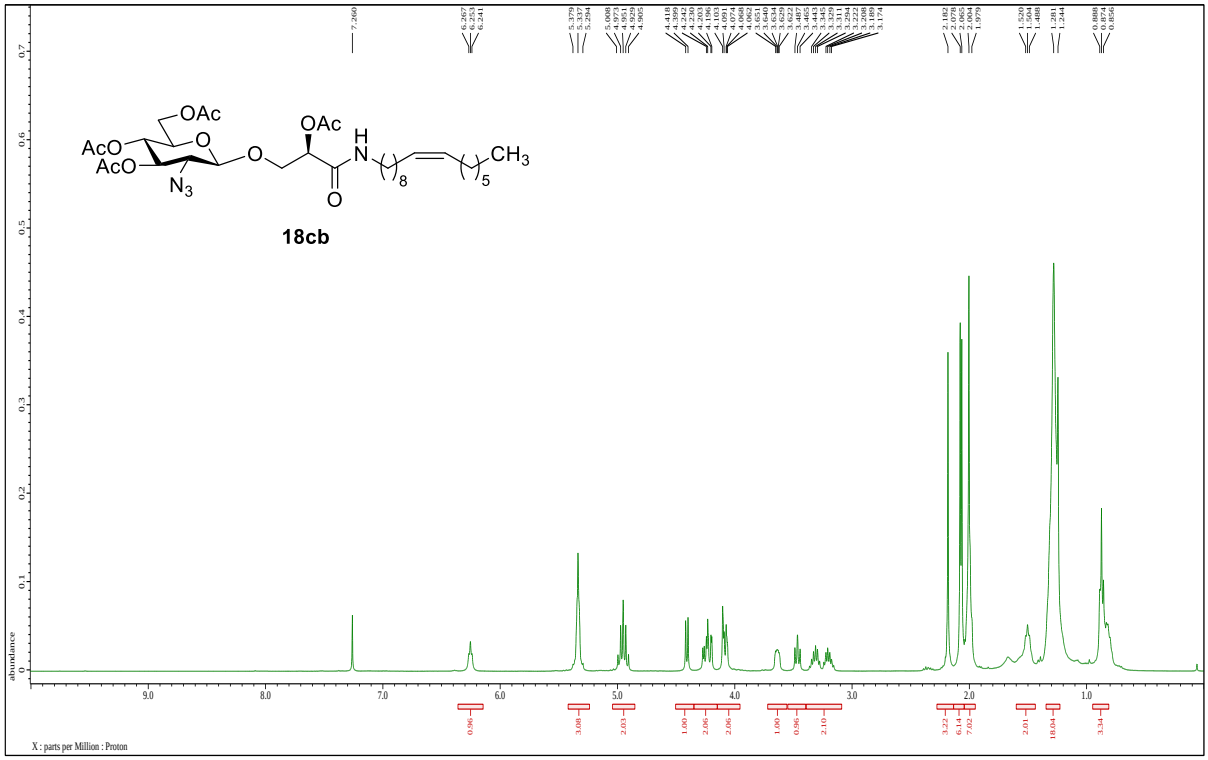
^{1}H-NMR of compound **18ca** ($CDCl_3$, 400MHz)



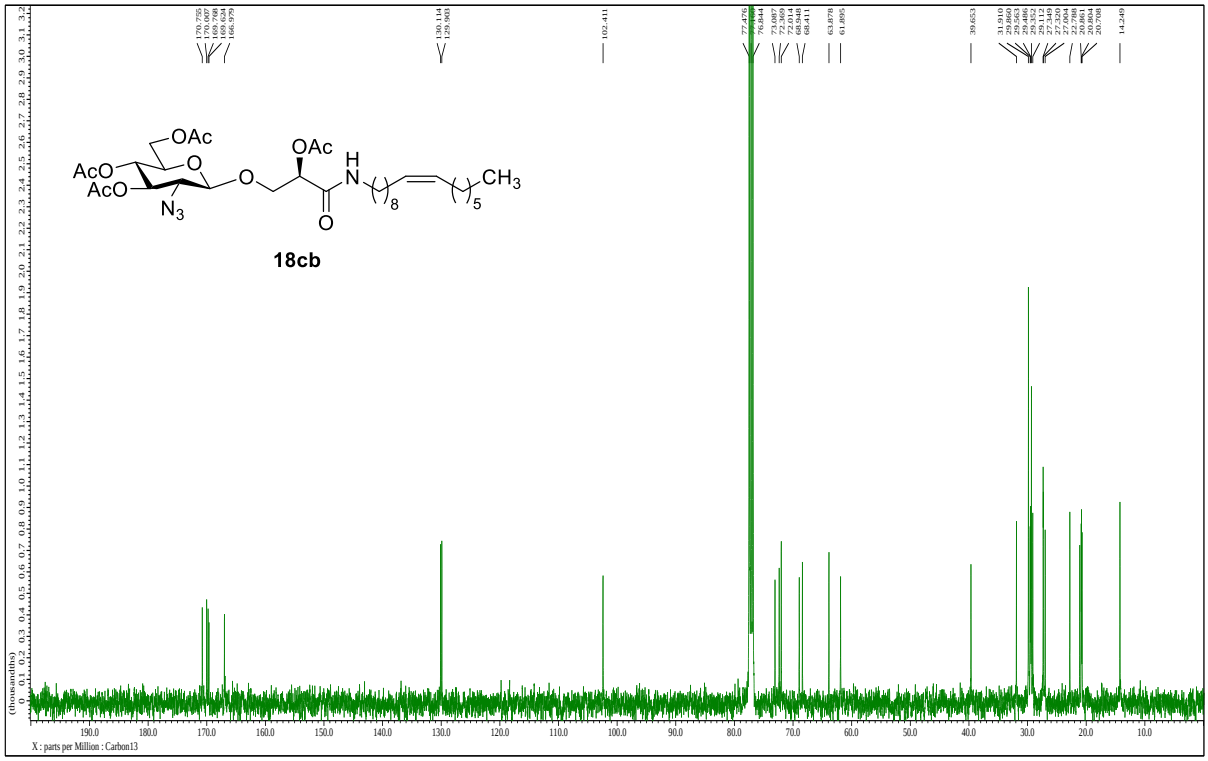
^{13}C-NMR of compound **18ca** ($CDCl_3$, 100MHz)



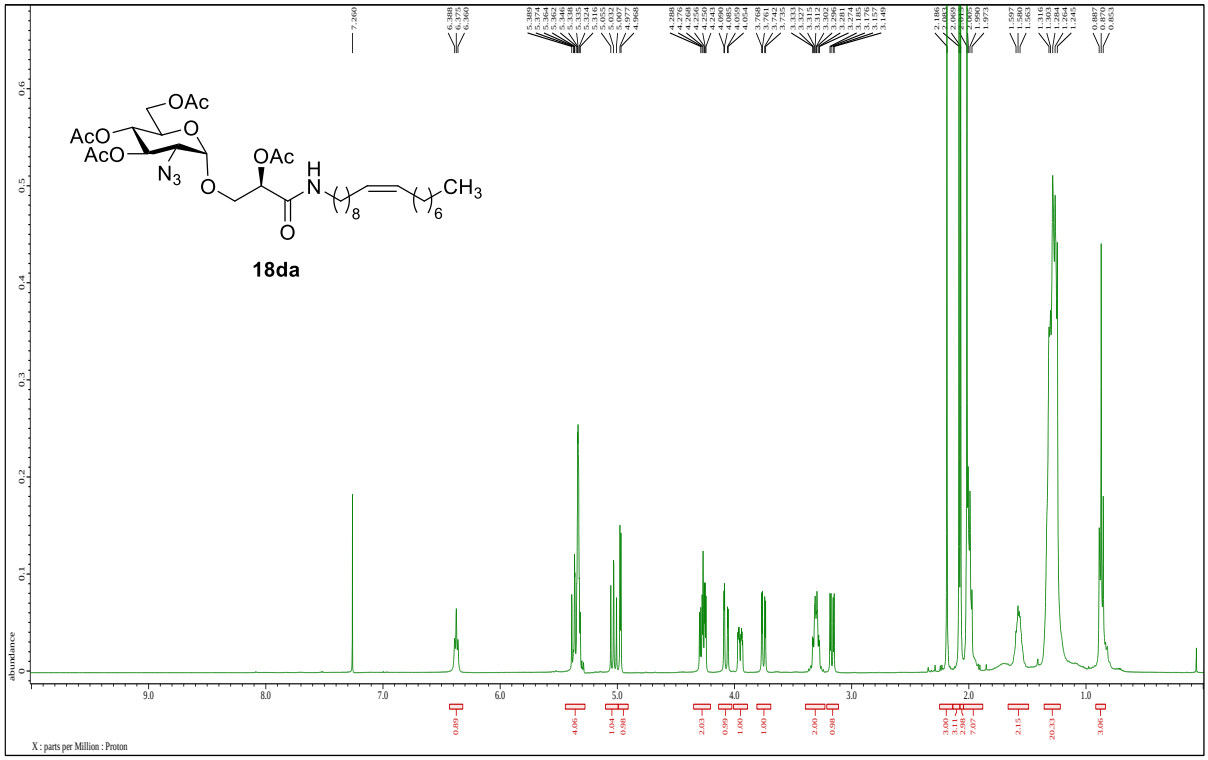
^{1}H-NMR of compound **18cb** ($CDCl_3$, 400MHz)



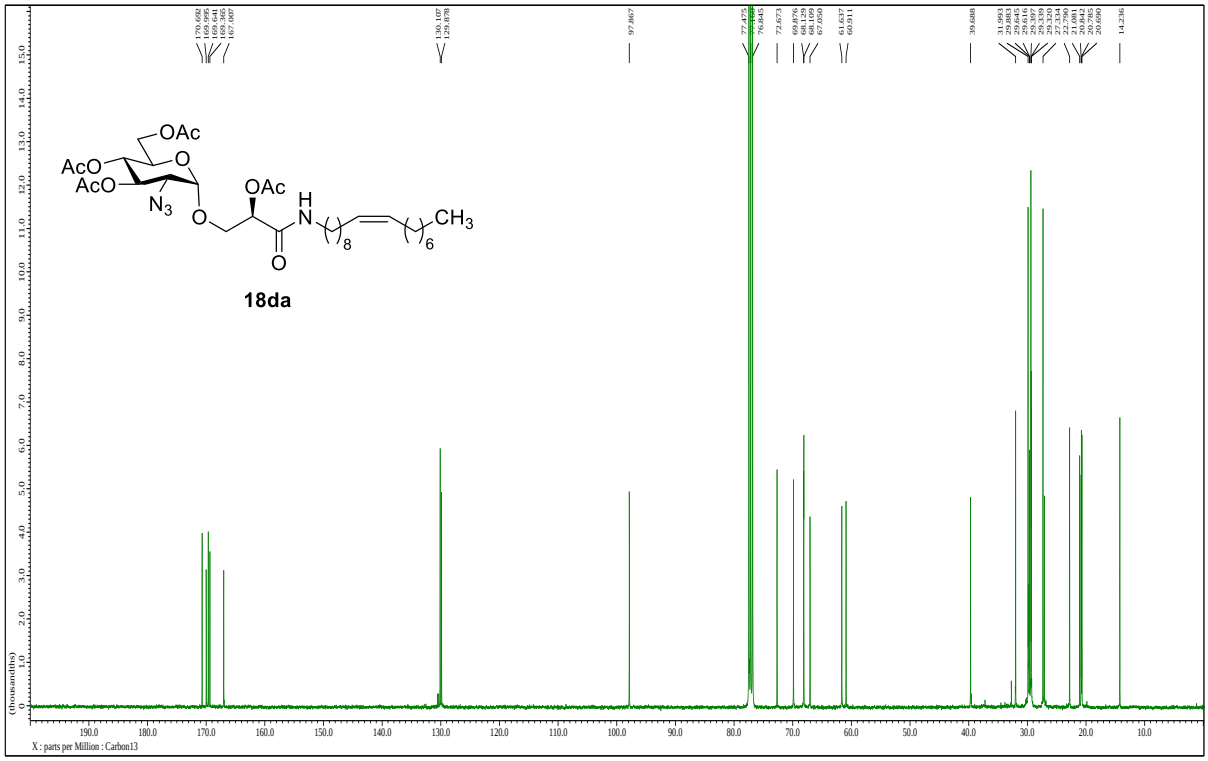
^{13}C-NMR of compound **18cb** ($CDCl_3$, 100MHz)



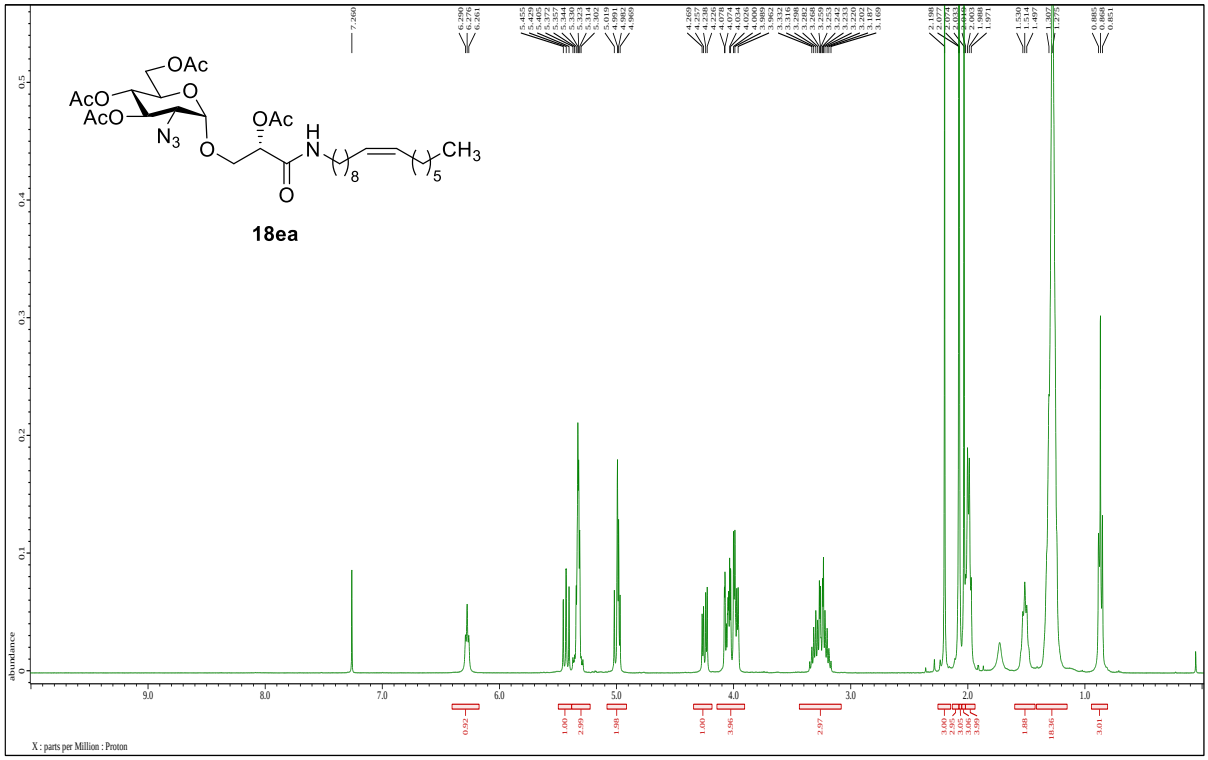
^{1}H-NMR of compound **18da** ($CDCl_3$, 400MHz)



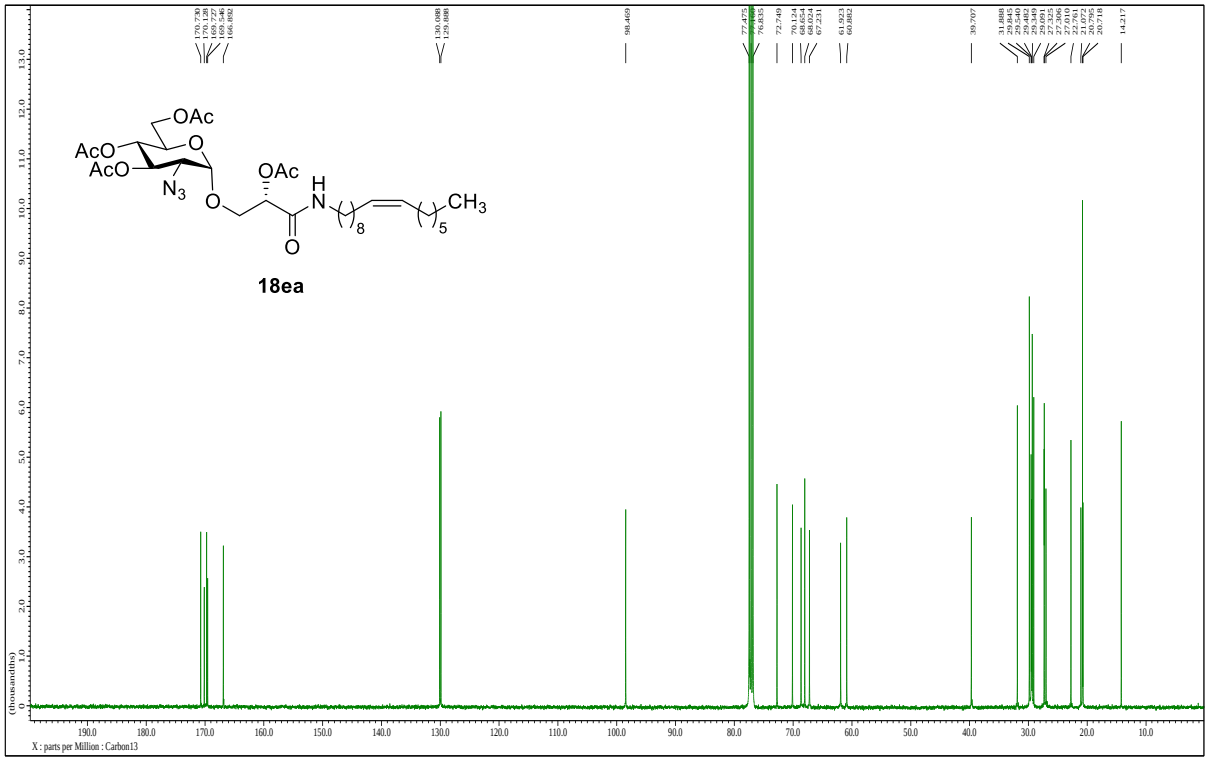
^{13}C-NMR of compound **18da** ($CDCl_3$, 100MHz)



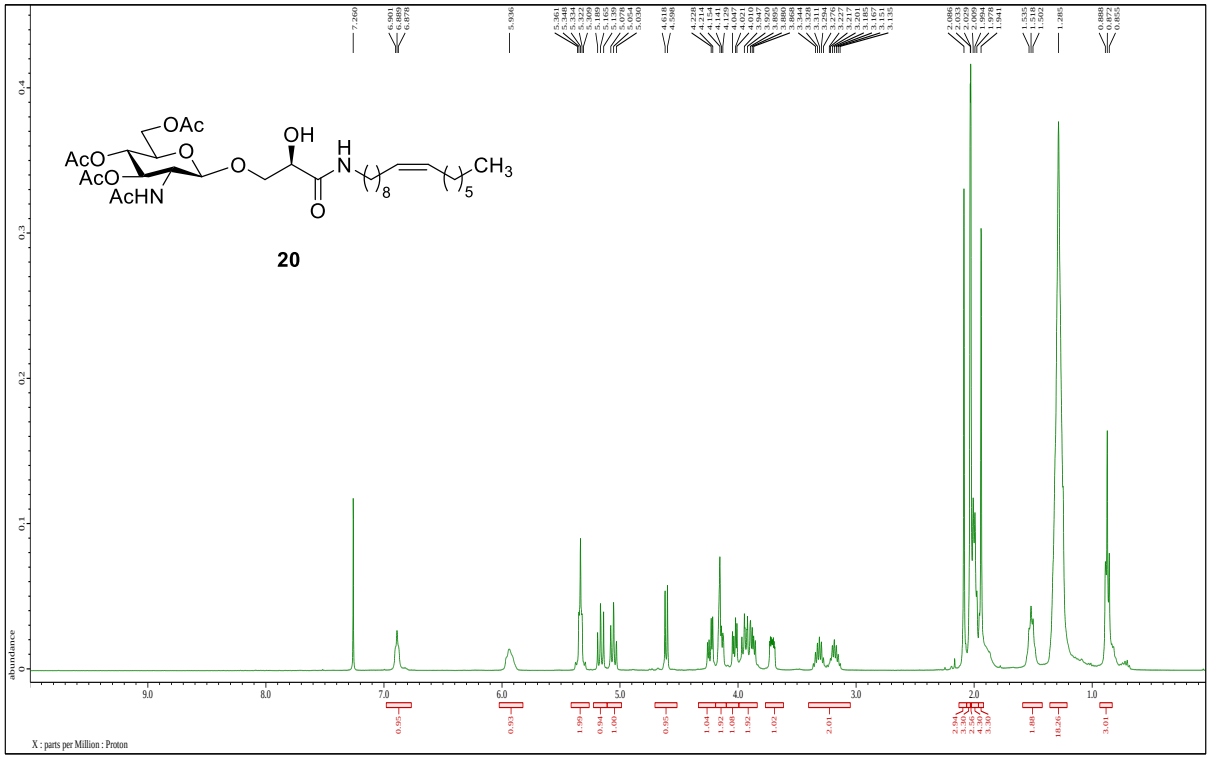
^{1}H-NMR of compound **18ea** ($CDCl_3$, 400MHz)



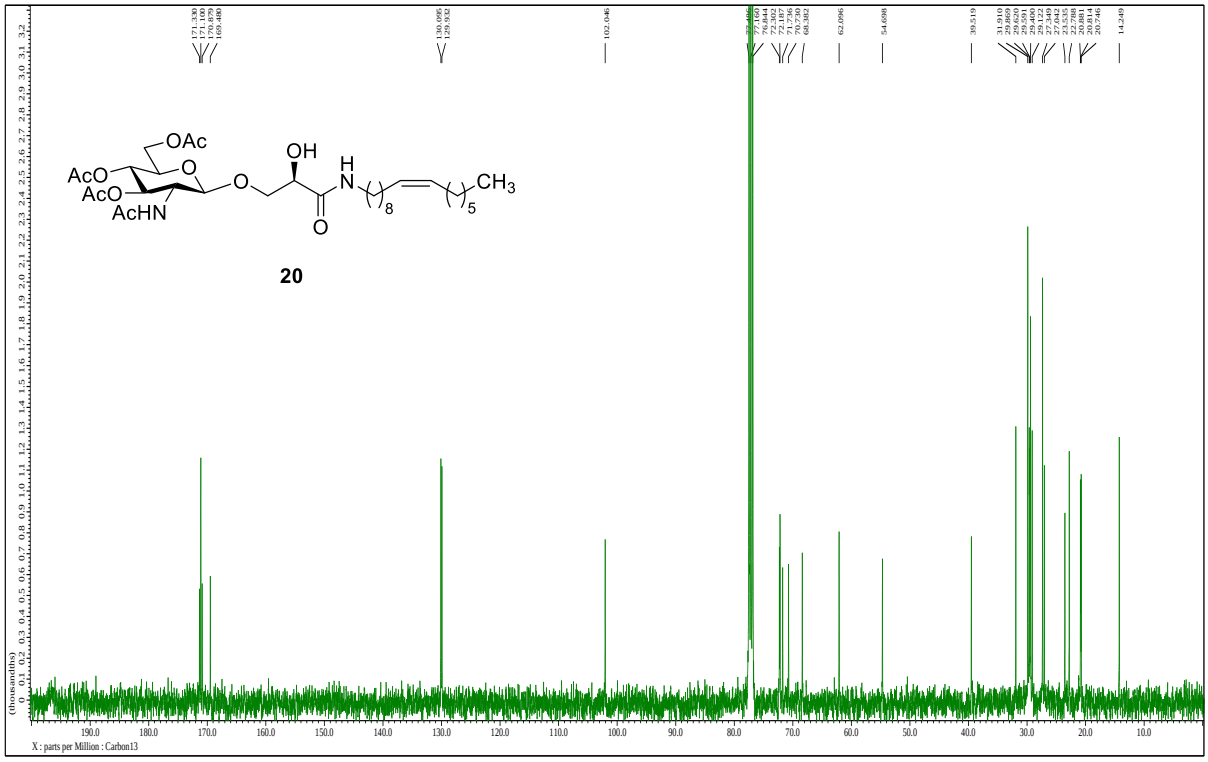
^{13}C-NMR of compound **18ea** ($CDCl_3$, 100MHz)



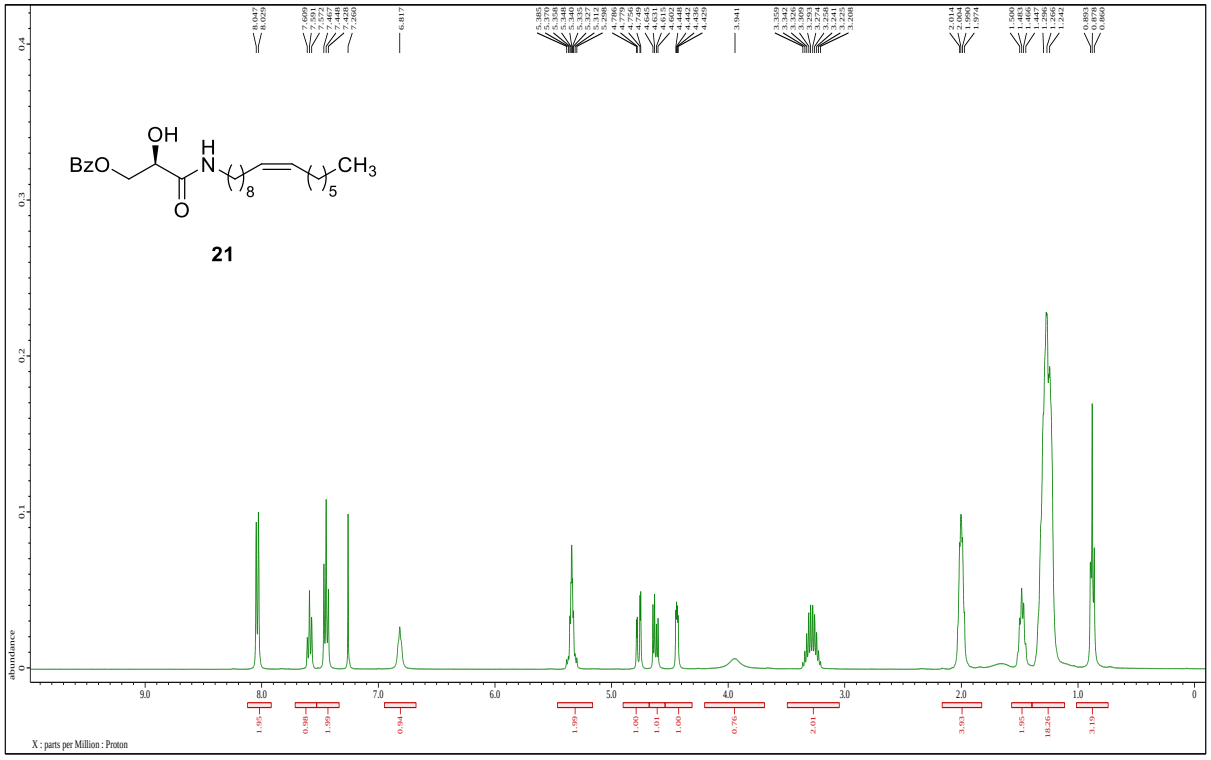
^{1}H-NMR of compound **20** ($CDCl_3$, 400MHz)



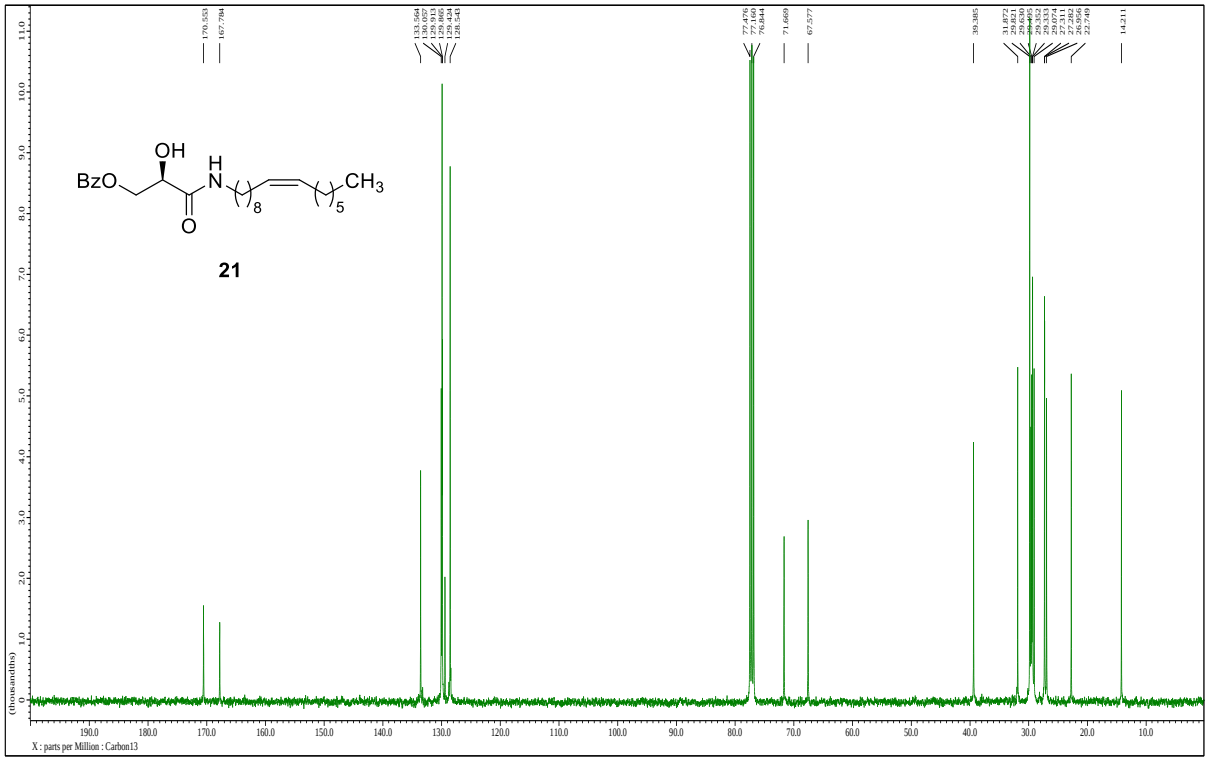
^{13}C-NMR of compound **20** ($CDCl_3$, 100MHz)



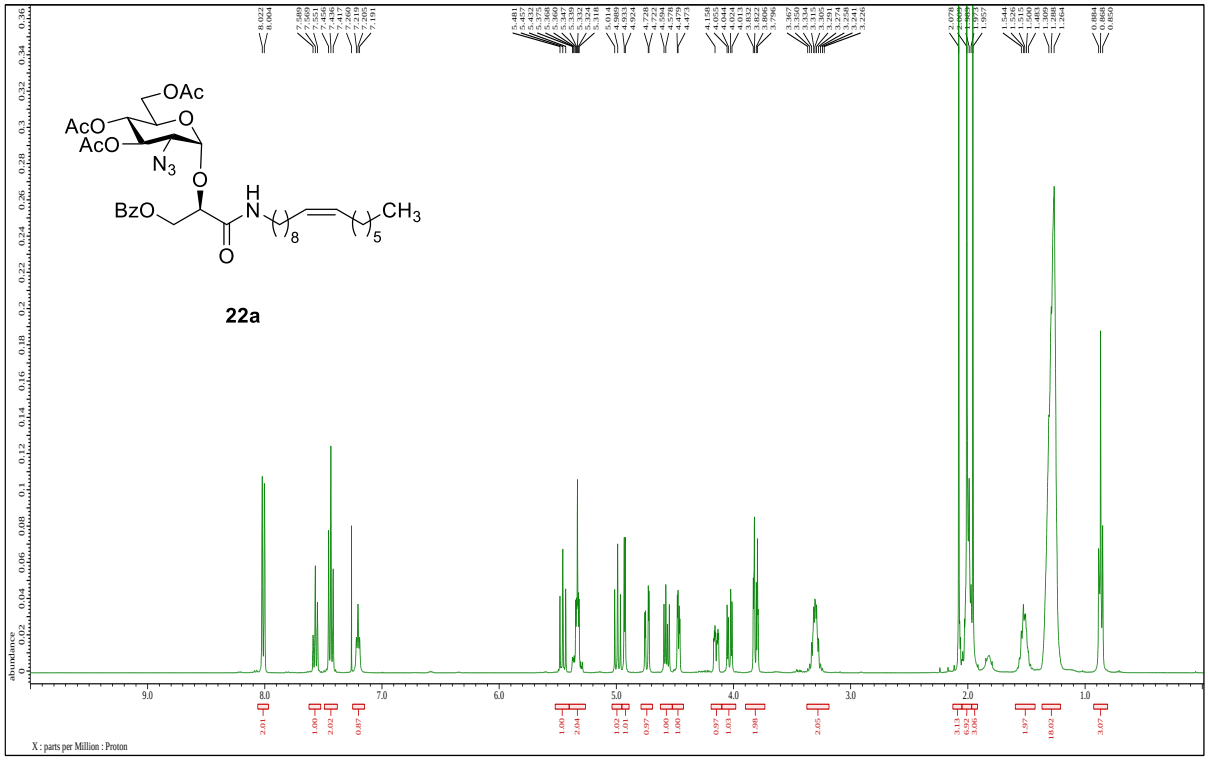
^{1}H-NMR of compound **21** ($CDCl_3$, 400MHz)



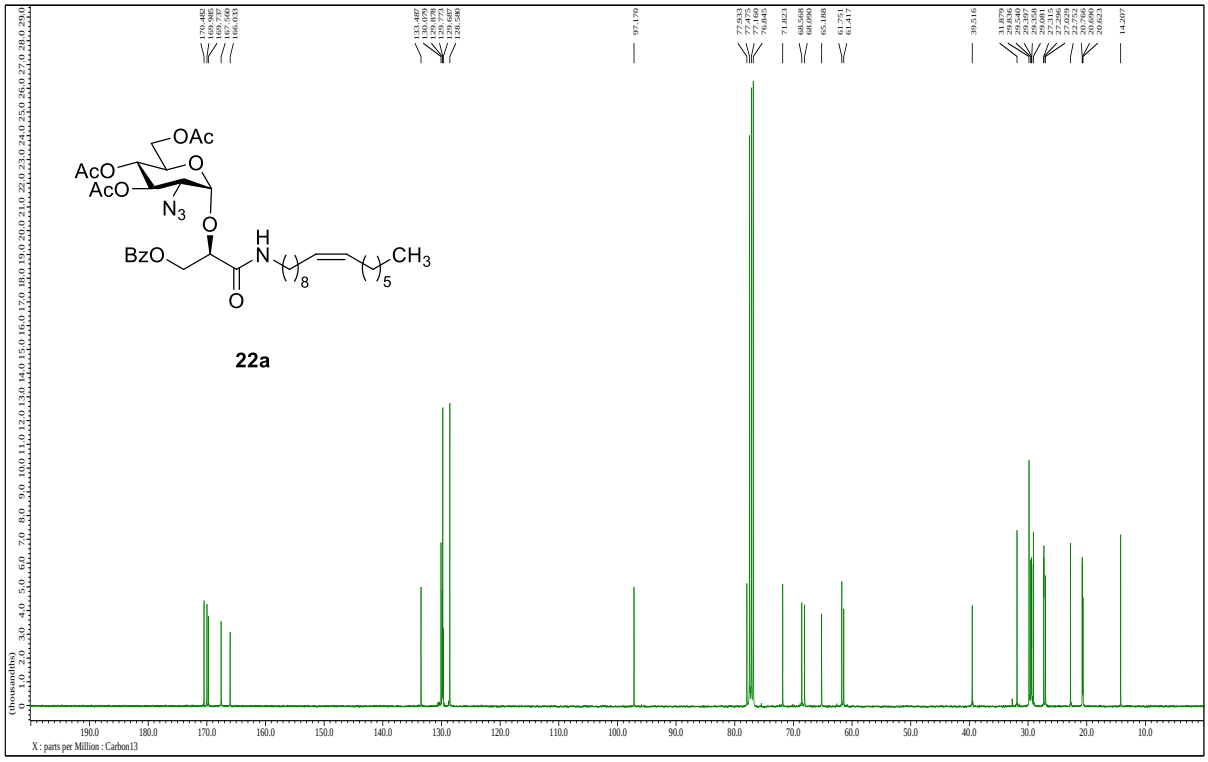
^{13}C-NMR of compound **21** ($CDCl_3$, 100MHz)



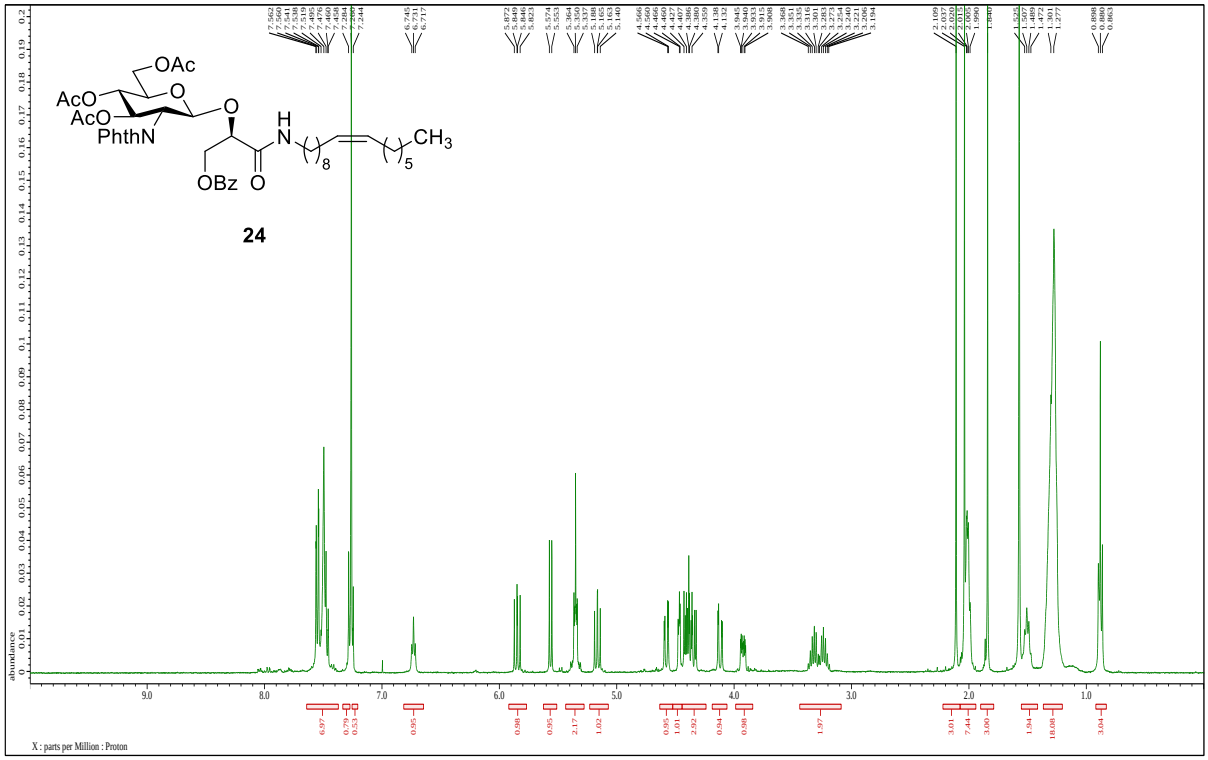
^{1}H-NMR of compound **22a** ($CDCl_3$, 400MHz)



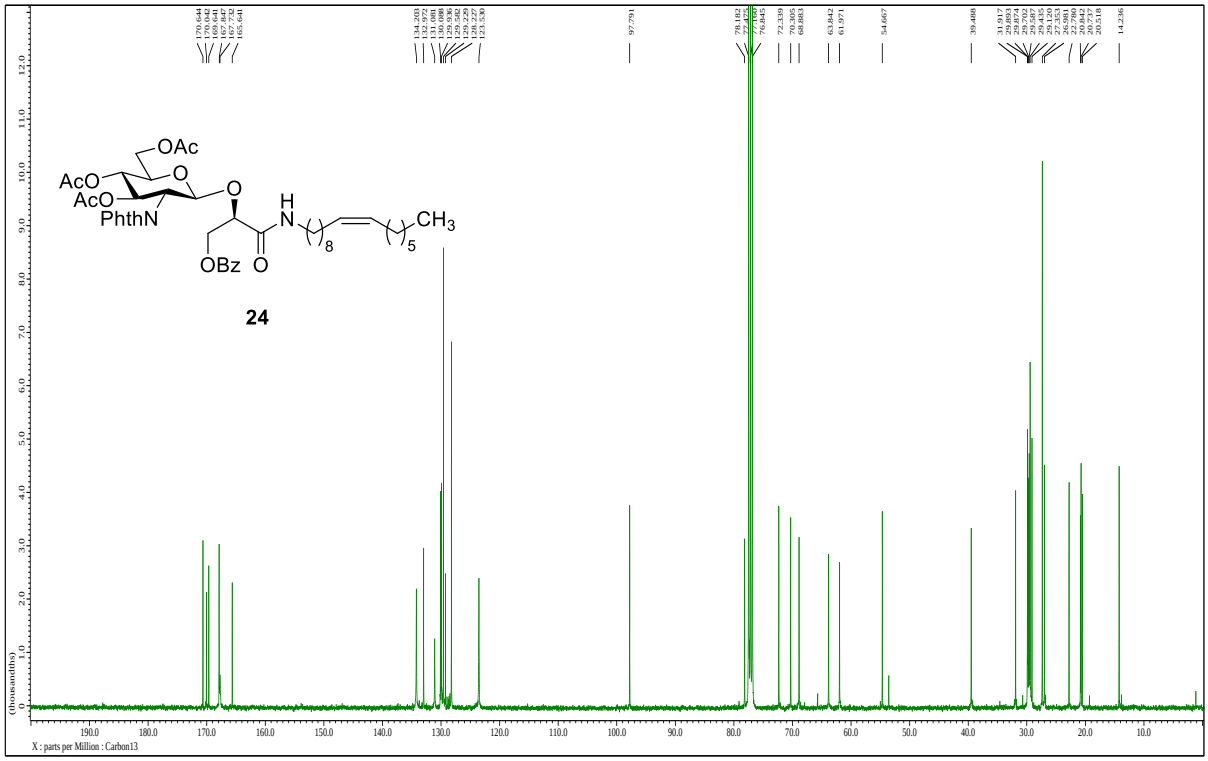
^{13}C-NMR of compound **22a** ($CDCl_3$, 100MHz)



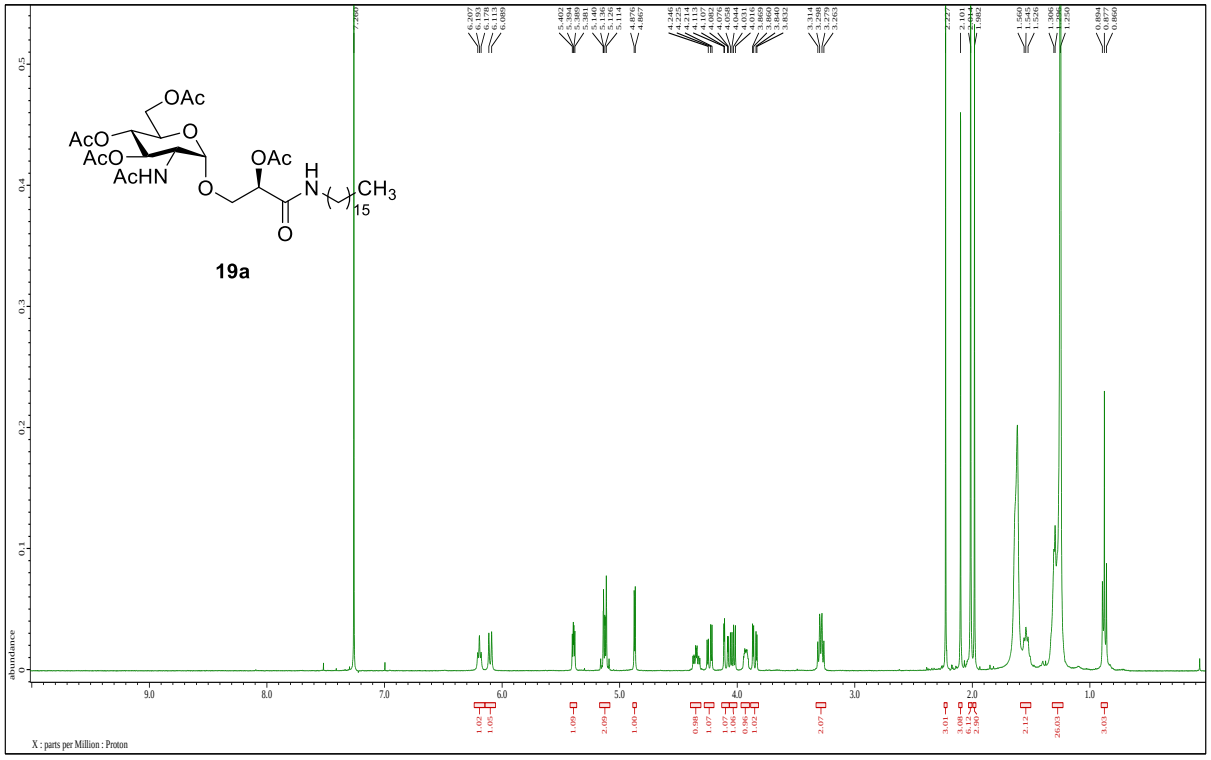
^{1}H-NMR of compound **24** ($CDCl_3$, 400MHz)



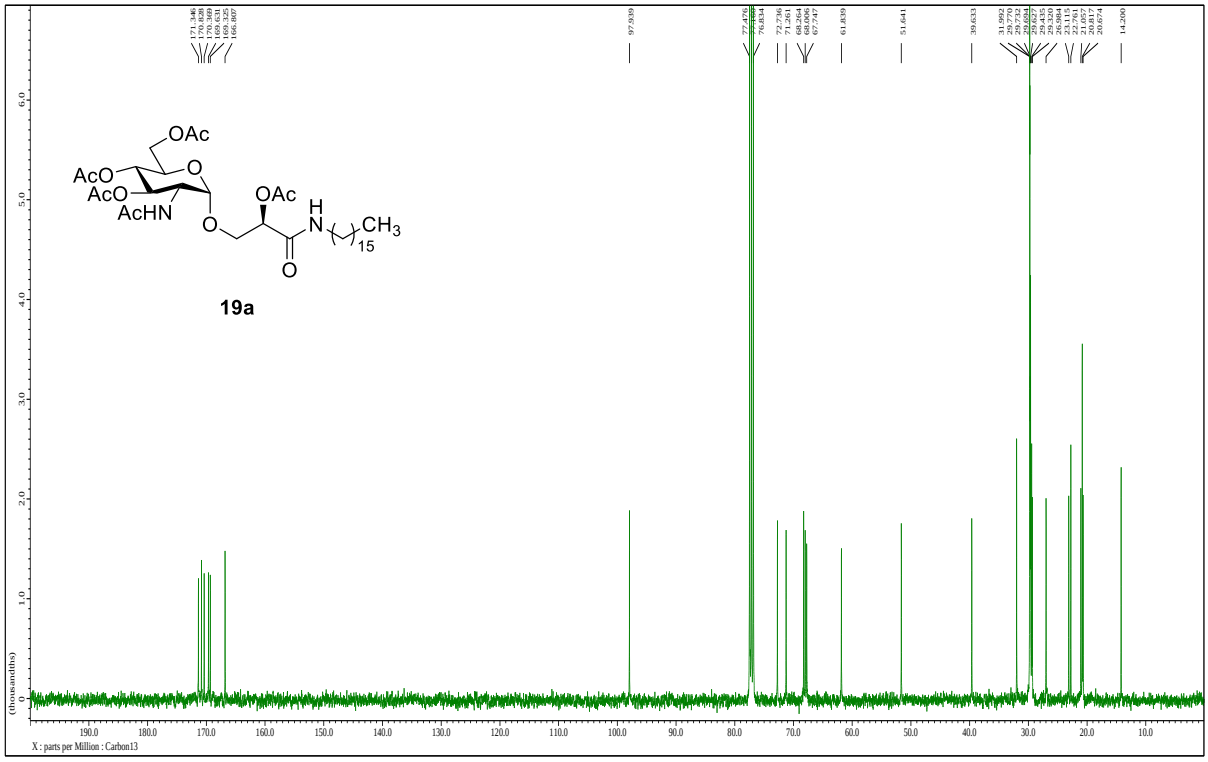
^{13}C-NMR of compound **24** ($CDCl_3$, 100MHz)



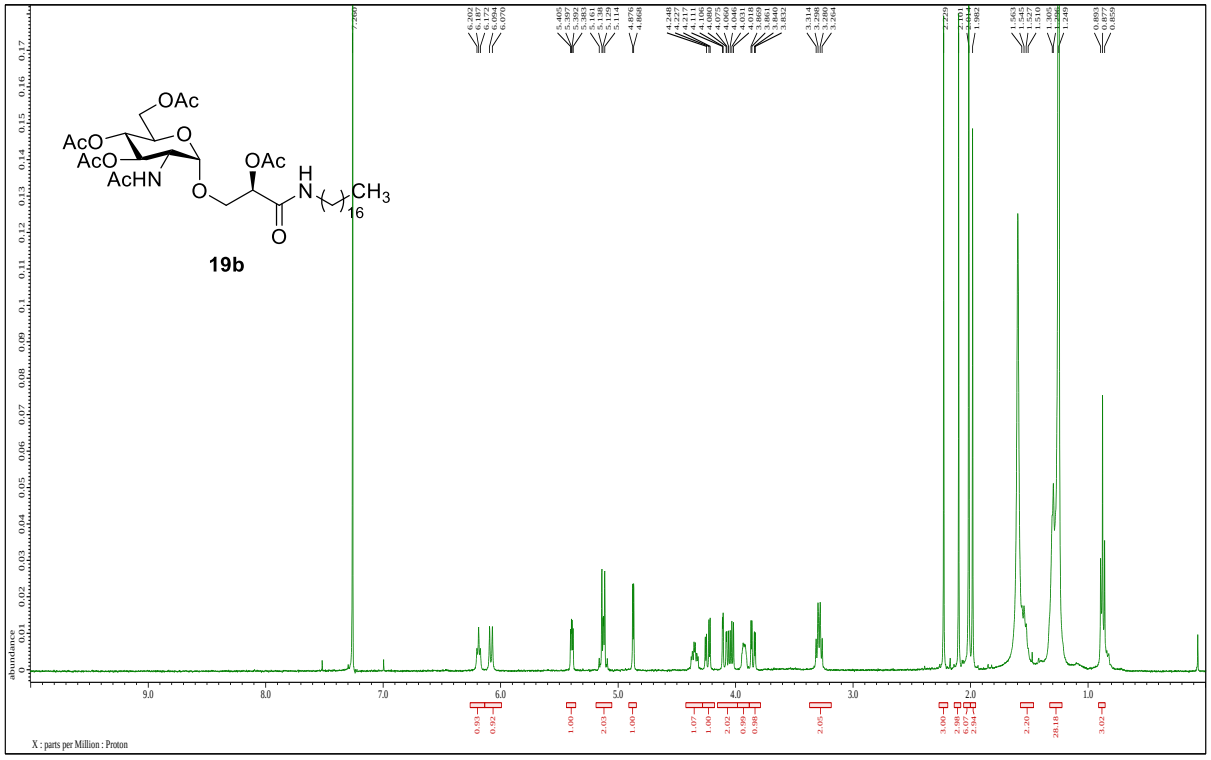
^{1}H-NMR of compound **19a** ($CDCl_3$, 400MHz)



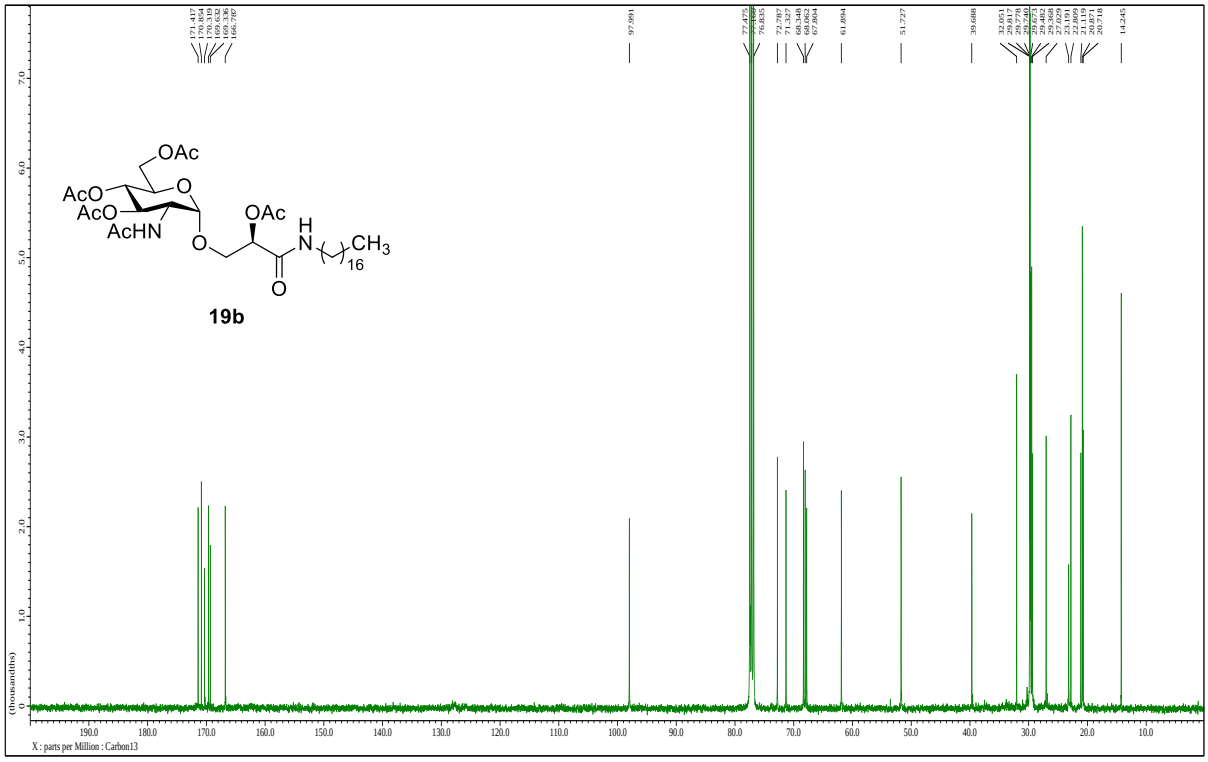
^{13}C-NMR of compound **19a** ($CDCl_3$, 100MHz)



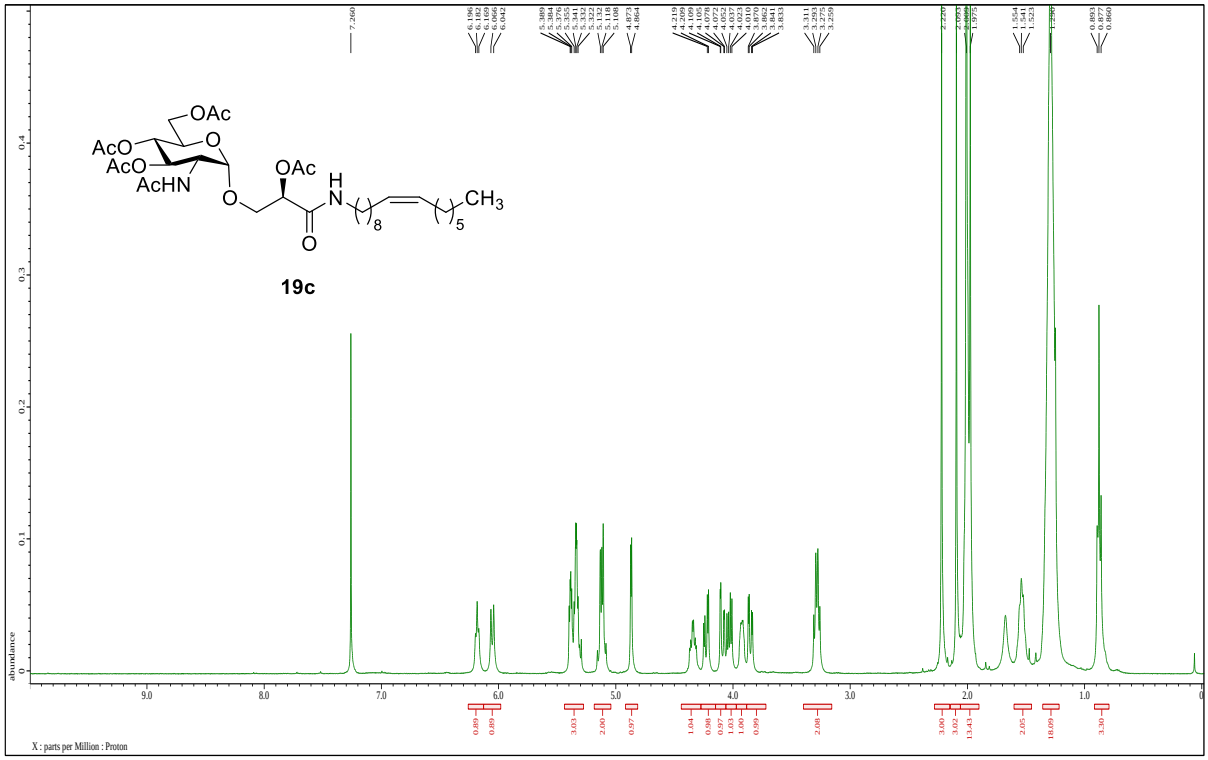
^{1}H-NMR of compound **19b** ($CDCl_3$, 400MHz)



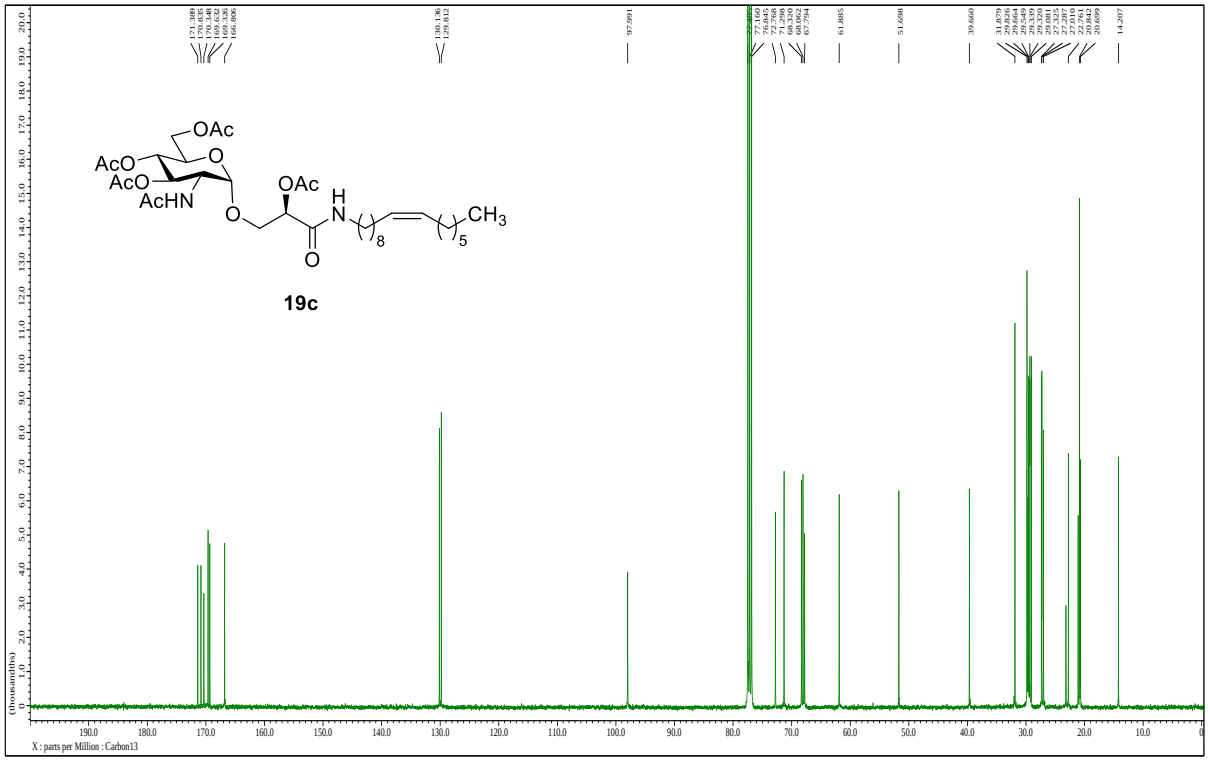
^{13}C-NMR of compound **19b** ($CDCl_3$, 100MHz)



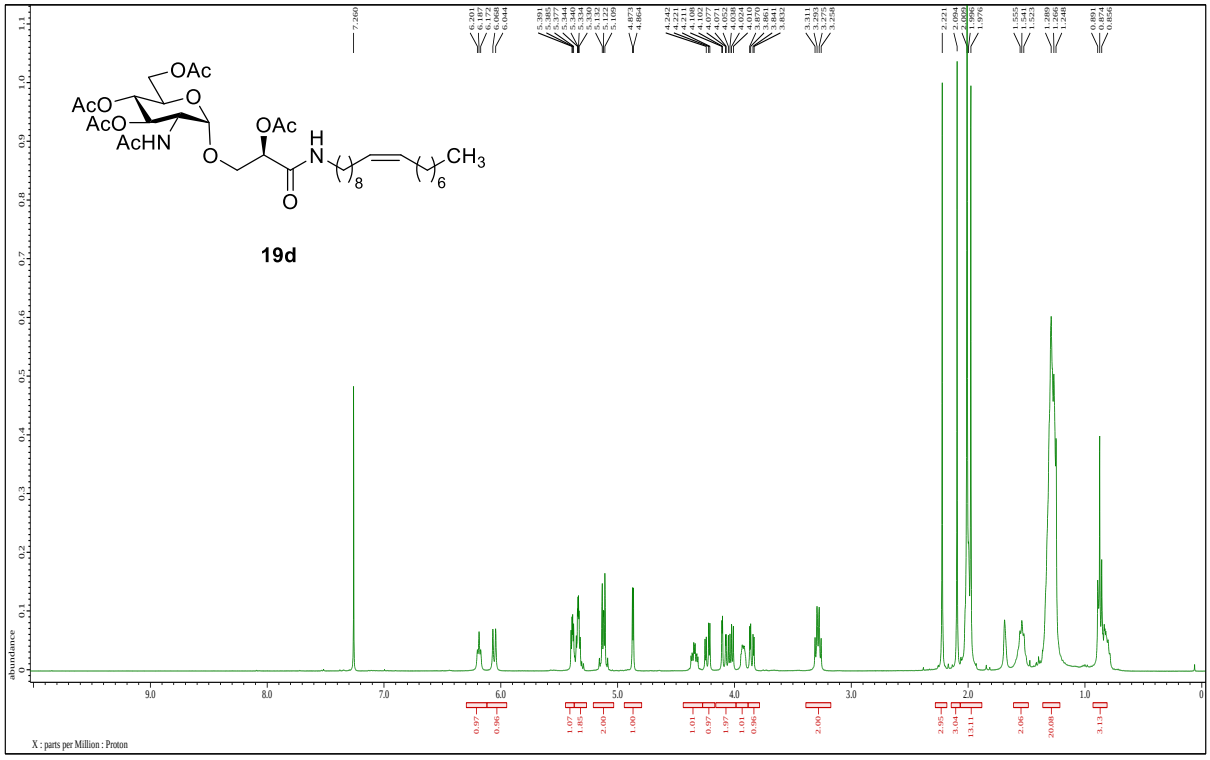
^{1}H-NMR of compound **19c** ($CDCl_3$, 400MHz)



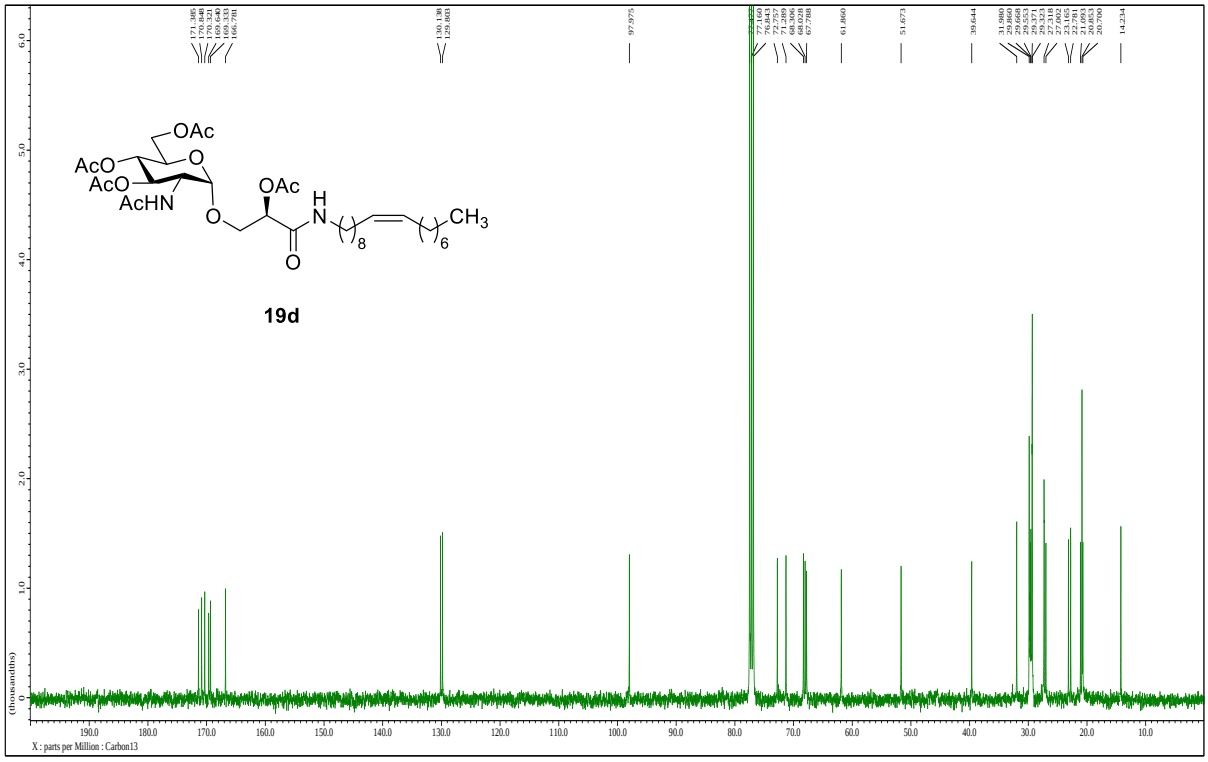
^{13}C-NMR of compound **19c** ($CDCl_3$, 100MHz)



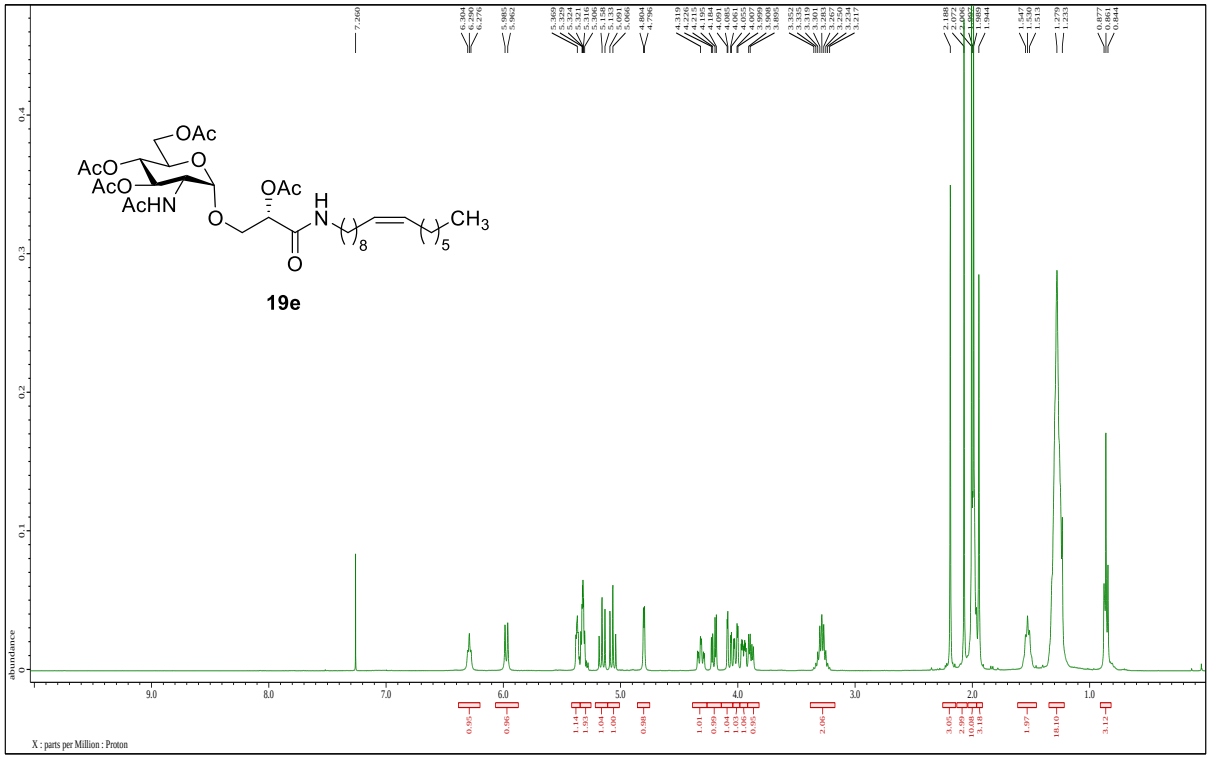
^{1}H-NMR of compound **19d** ($CDCl_3$, 400MHz)



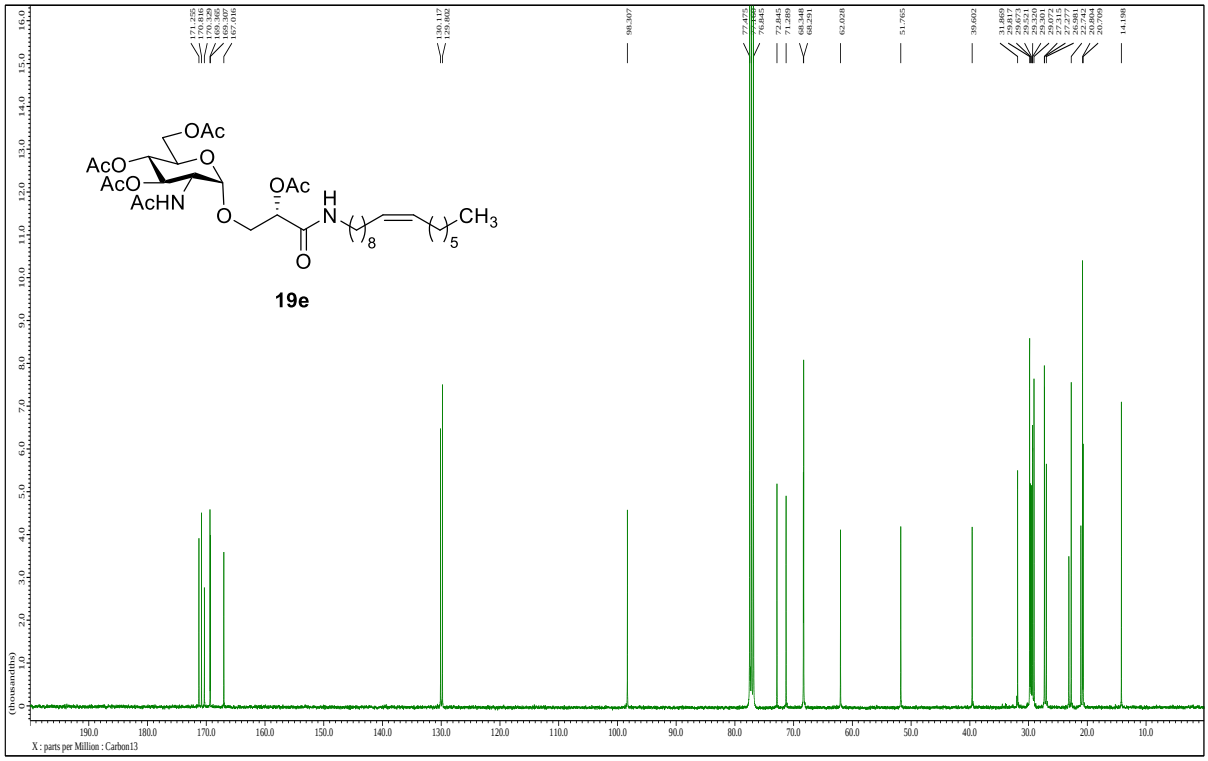
^{13}C-NMR of compound **19d** ($CDCl_3$, 100MHz)



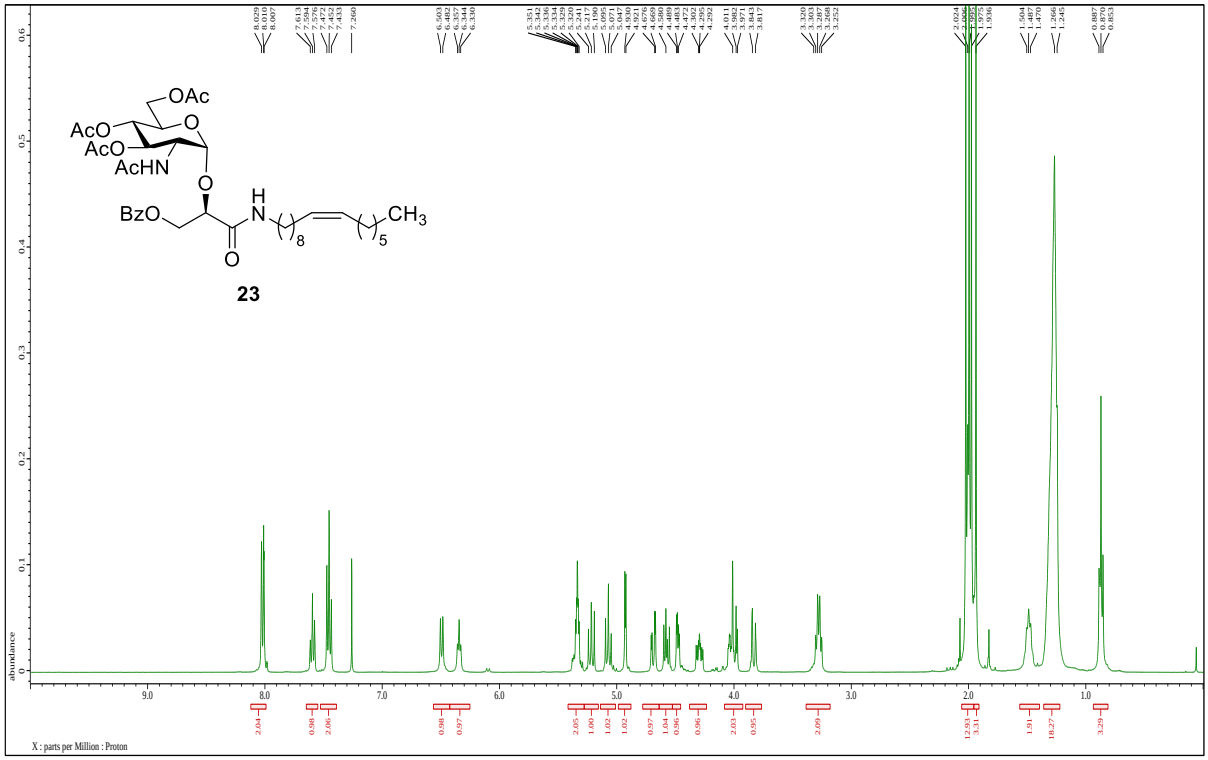
^{1}H-NMR of compound **19e** ($CDCl_3$, 400MHz)



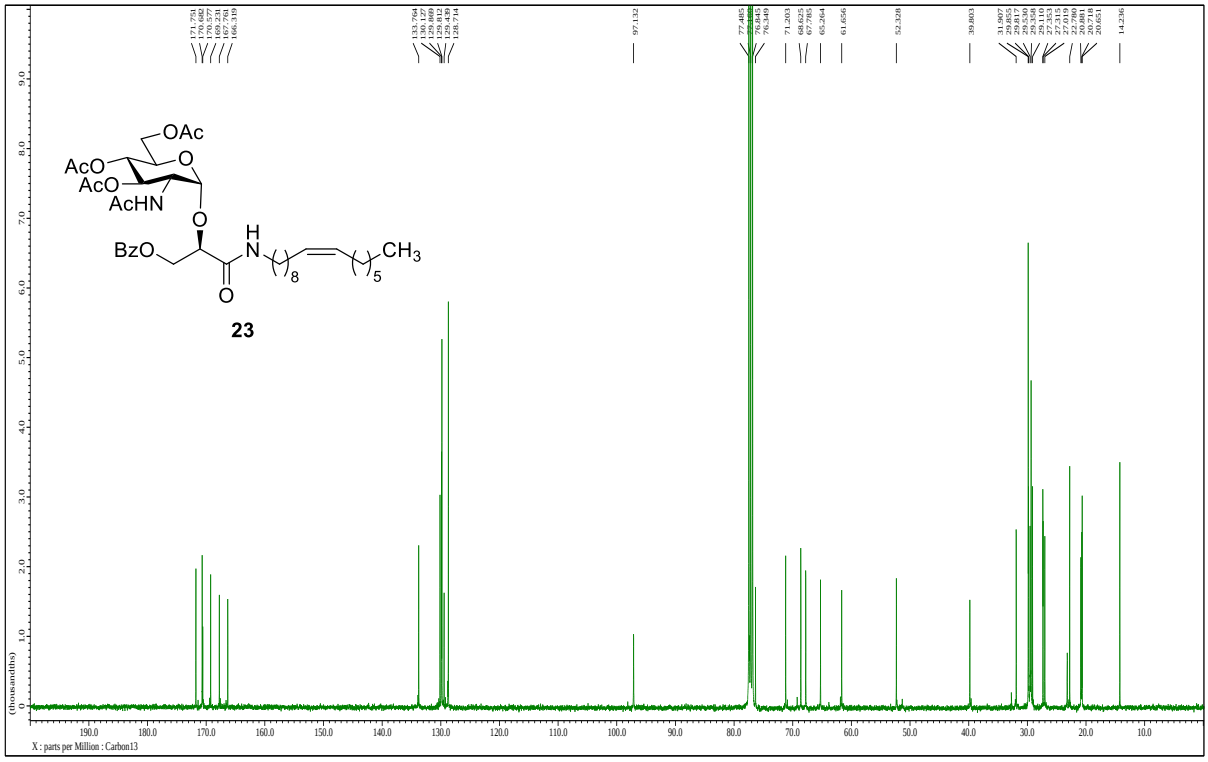
^{13}C-NMR of compound **19e** ($CDCl_3$, 100MHz)



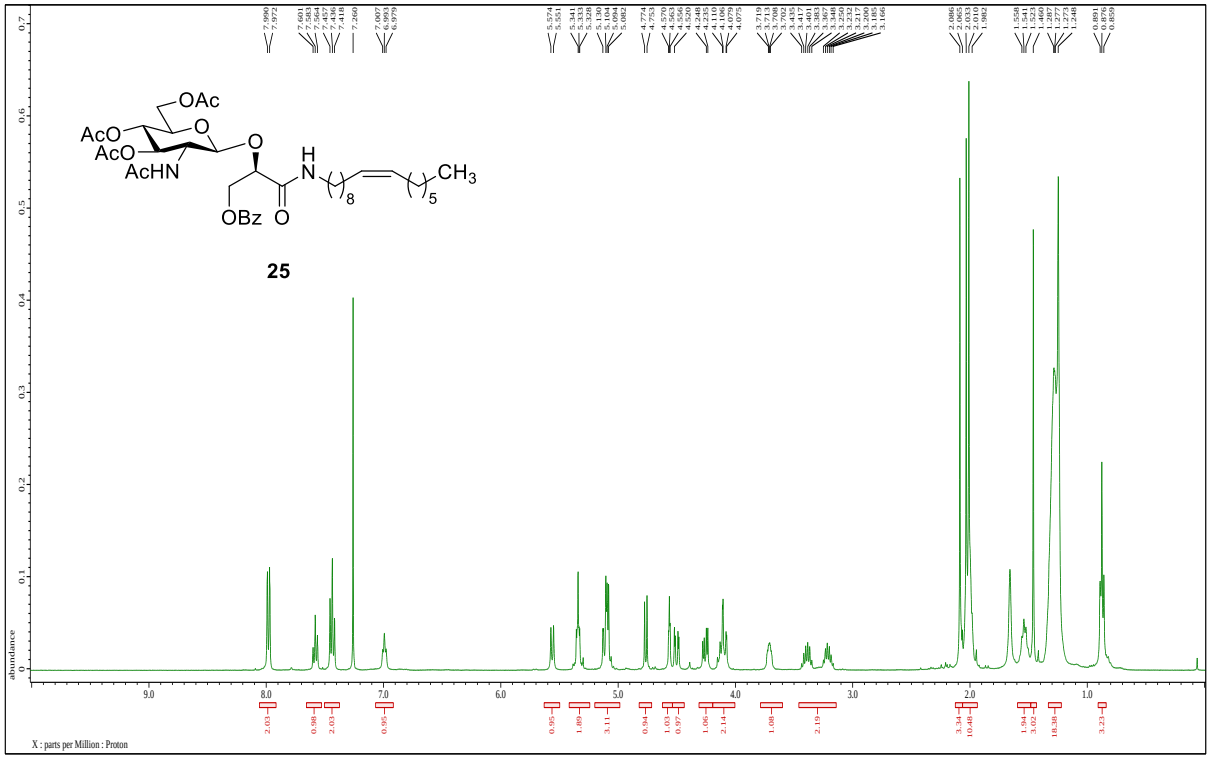
[1]H-NMR of compound **23** ($CDCl_3$, 400MHz)



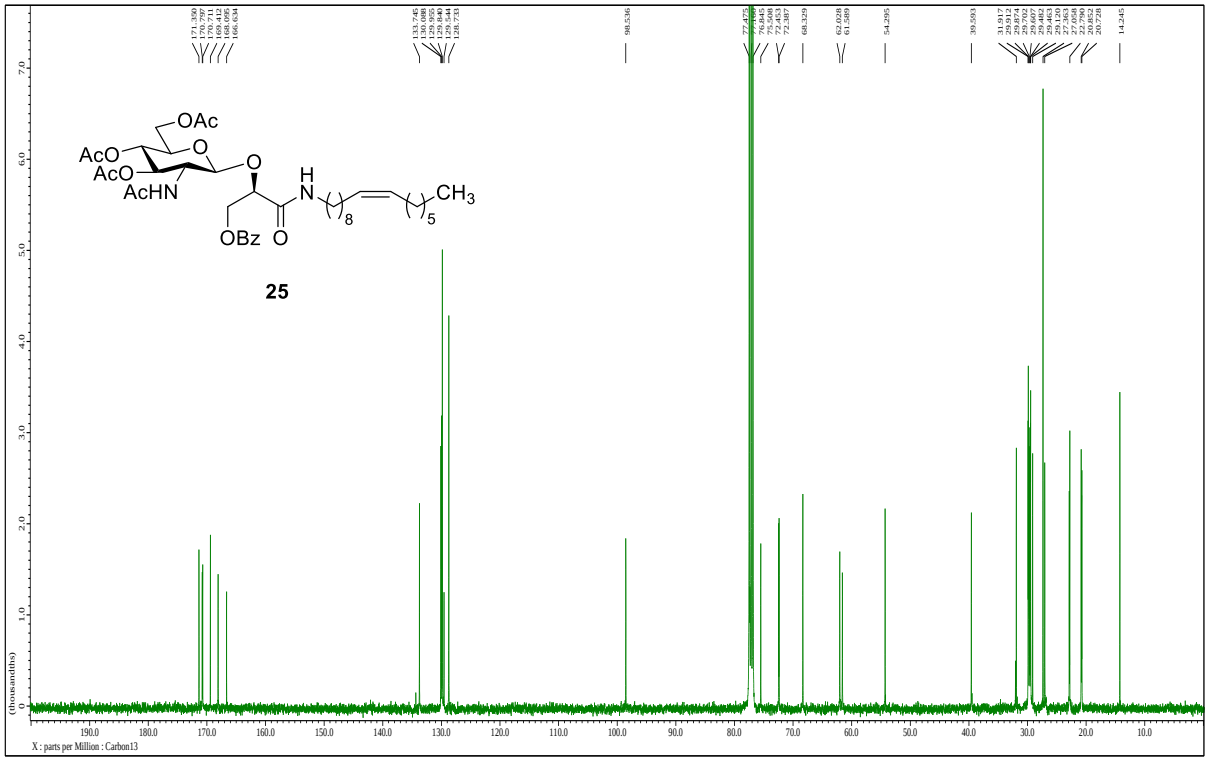
[13]C-NMR of compound **23** ($CDCl_3$, 100MHz)



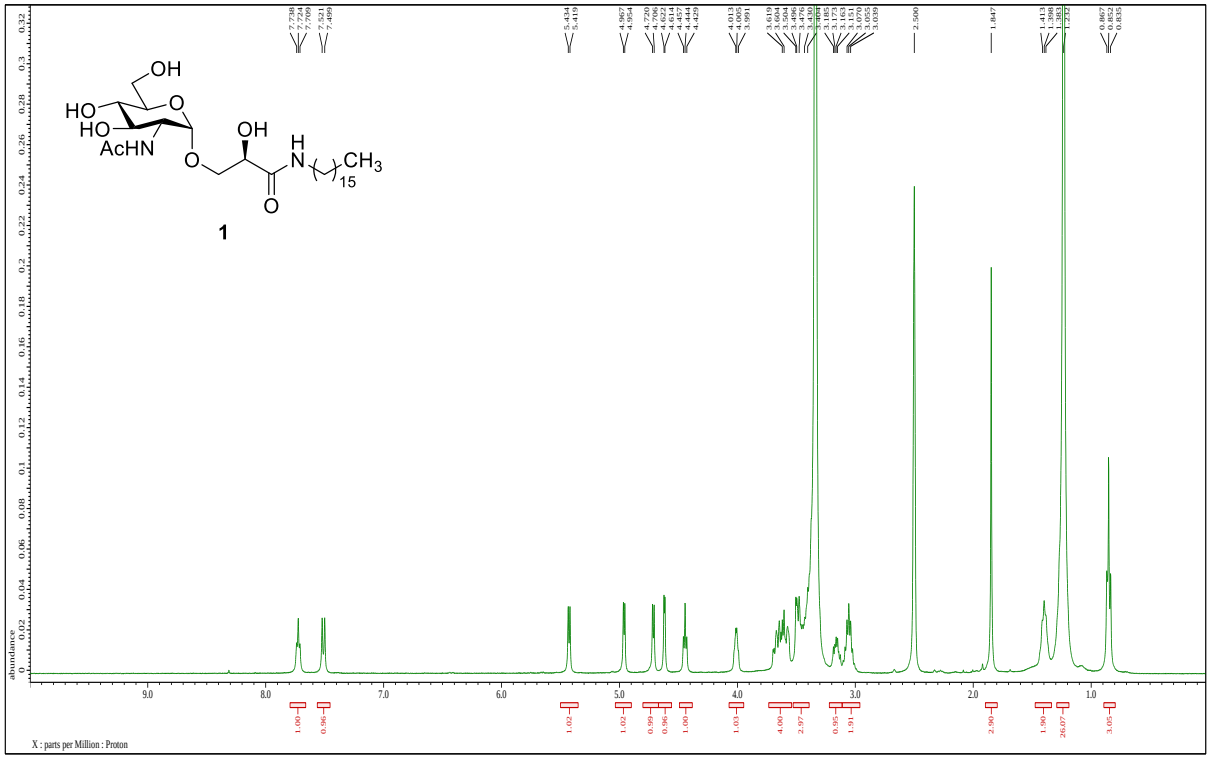
^{1}H-NMR of compound **25** ($CDCl_3$, 400MHz)



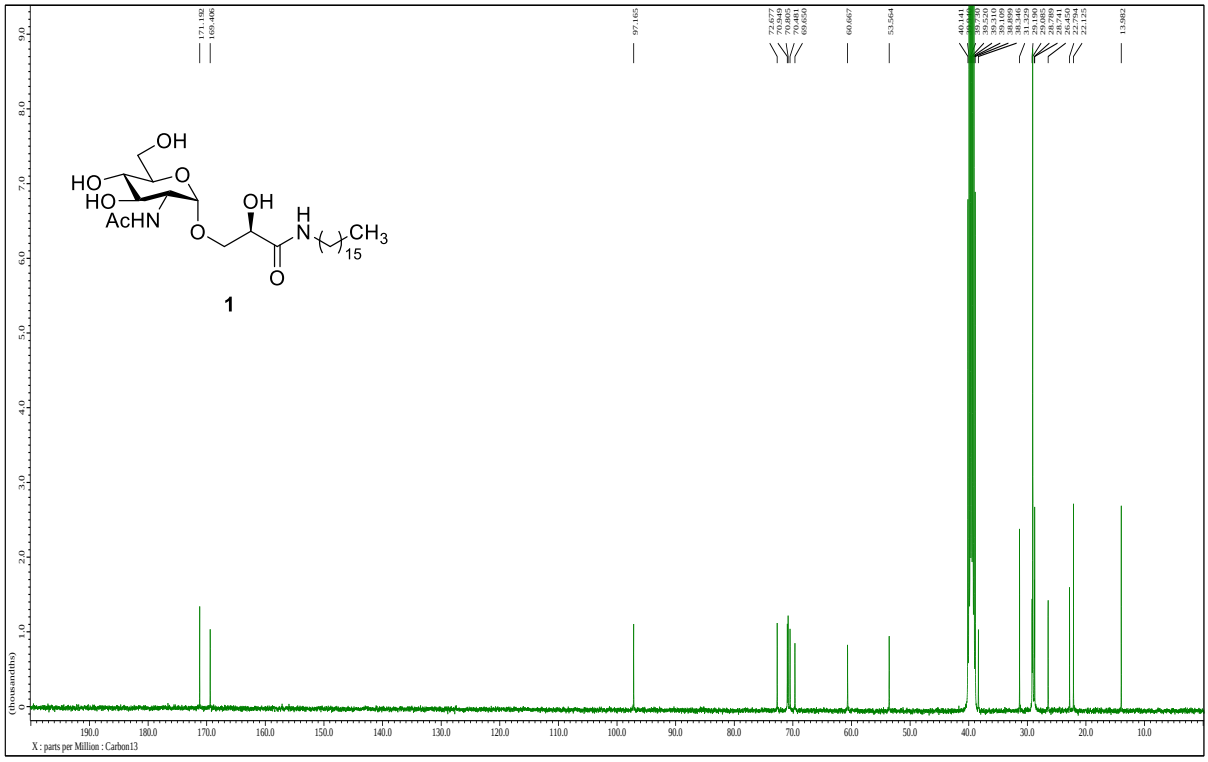
^{13}C-NMR of compound **25** ($CDCl_3$, 100MHz)



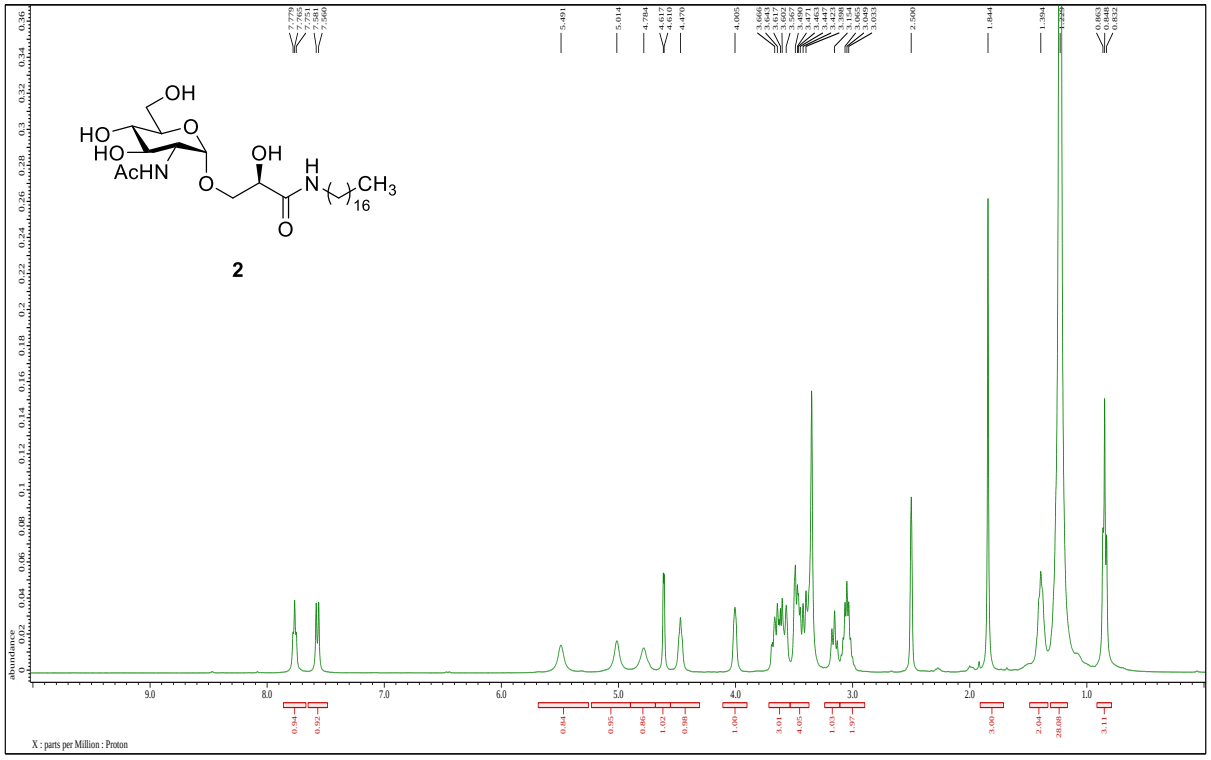
[1]H-NMR of synthesized Deinococcucin A (**1**) (DMSO-*d6*, 400MHz)



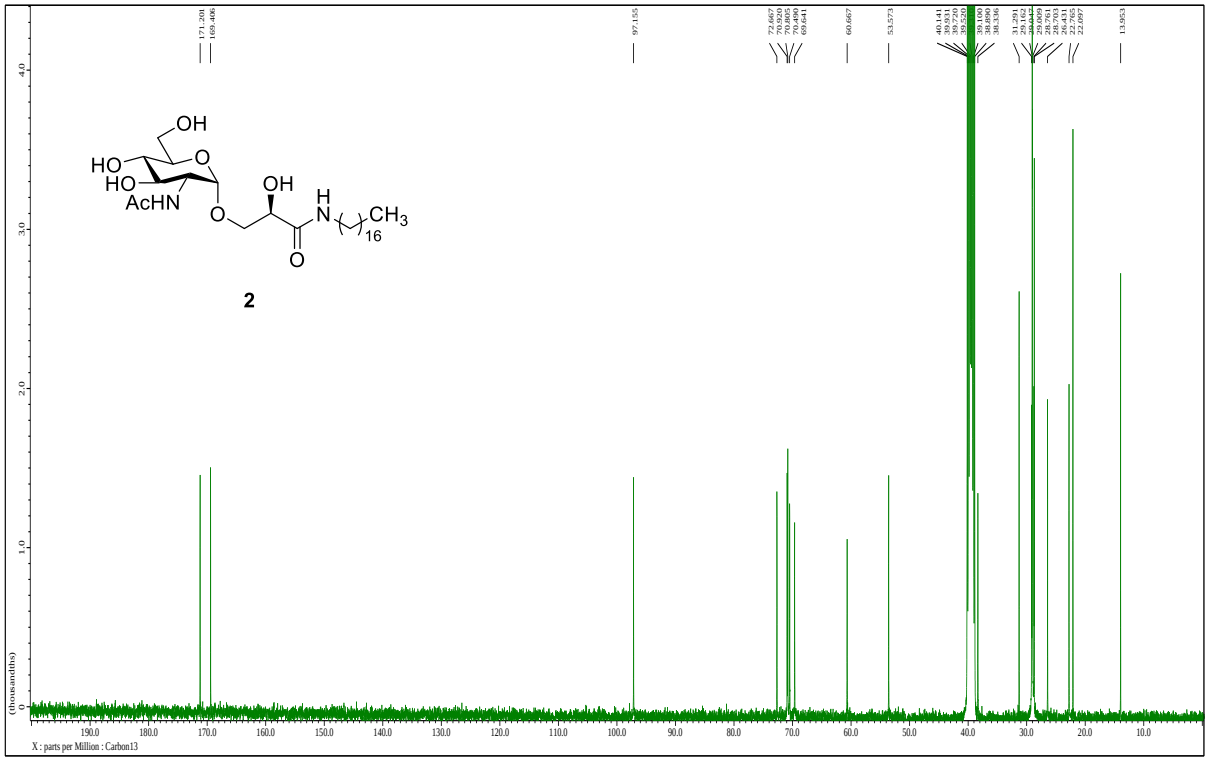
[13]C-NMR of synthesized Deinococcucin A (**1**) (DMSO-*d6*, 100MHz)



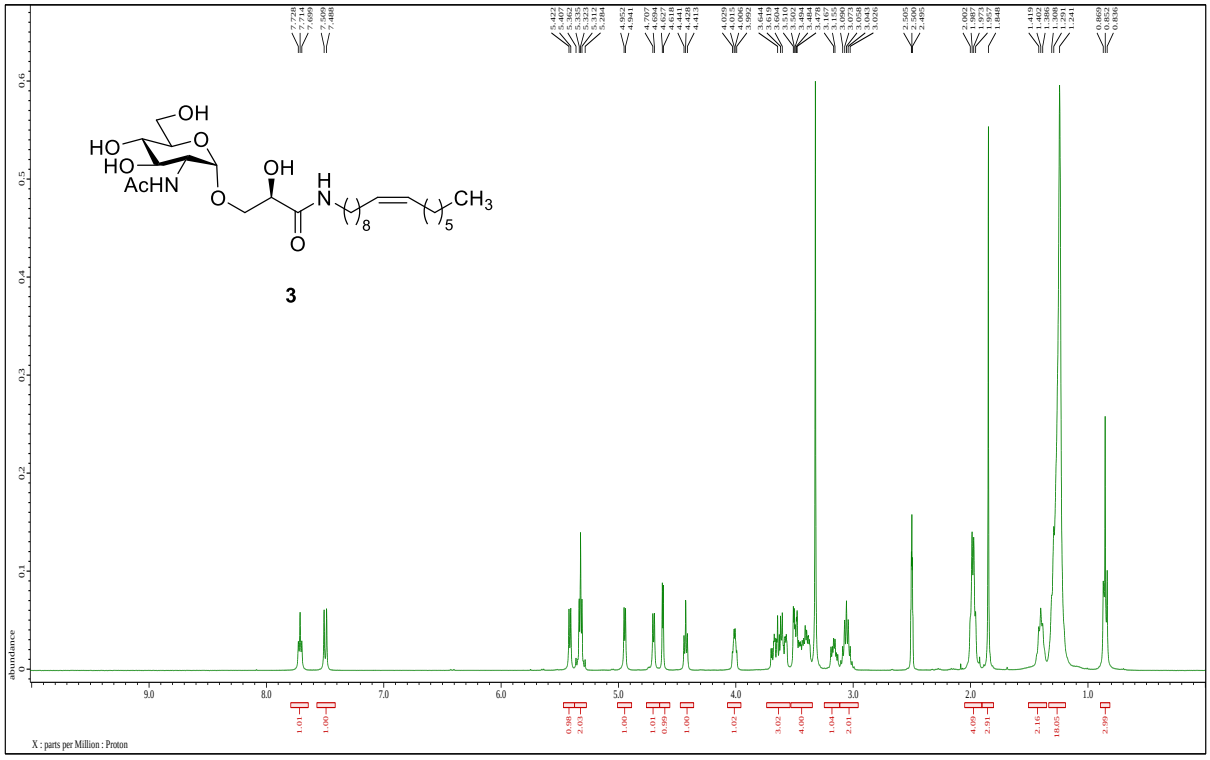
^{1}H-NMR of synthesized Deinococcucin B (**2**) (DMSO-*d6*, 400MHz)



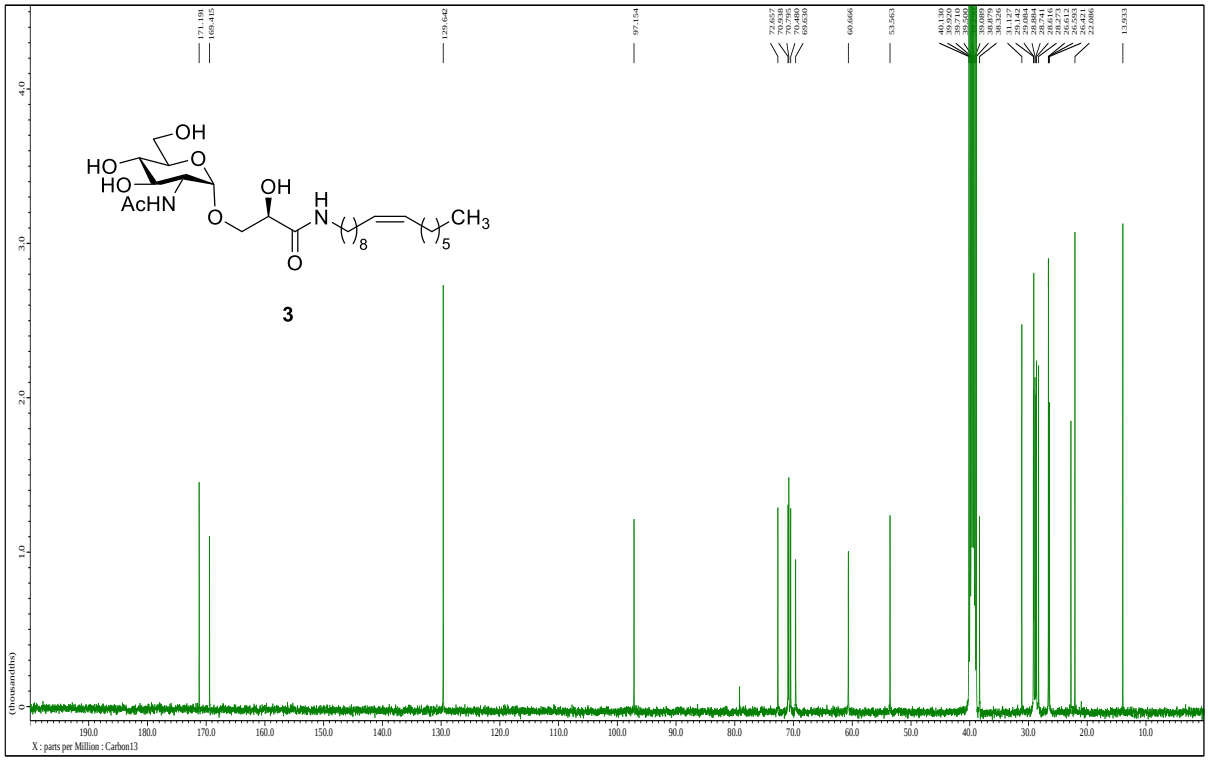
^{13}C-NMR of synthesized Deinococcucin B (**2**) (DMSO-*d6*, 100MHz)



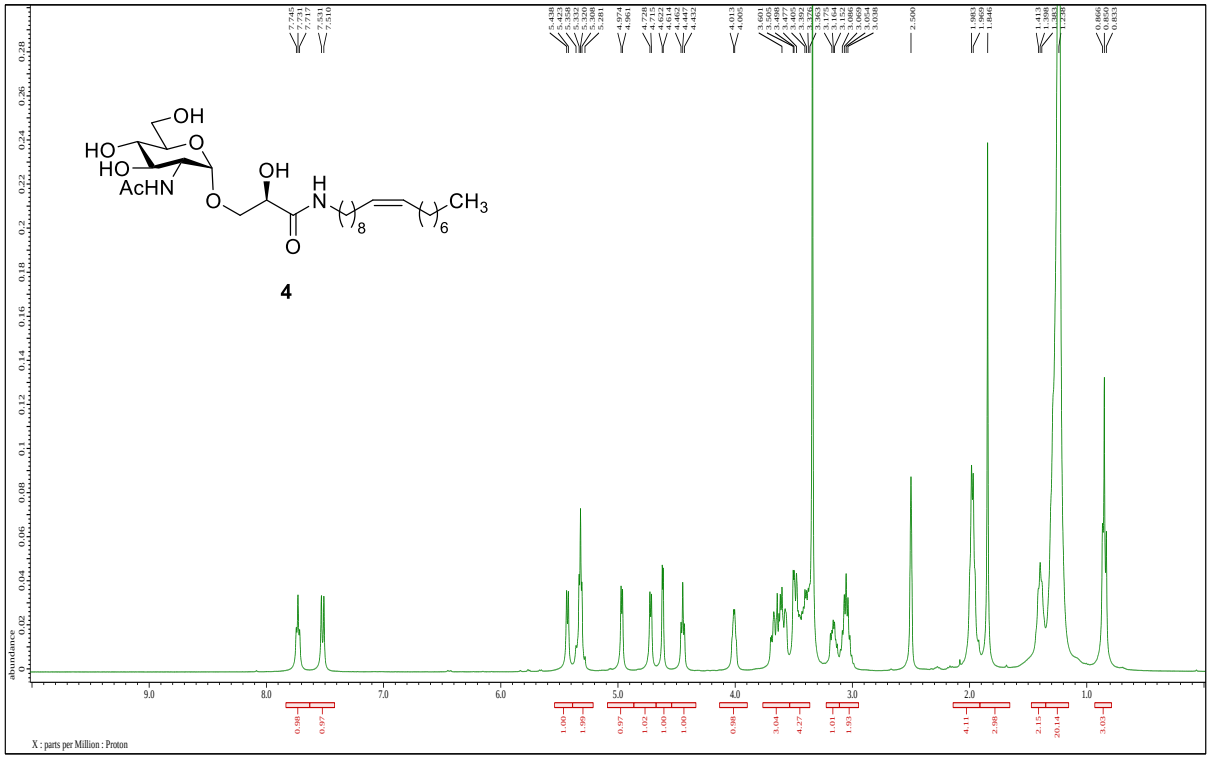
[1]H-NMR of synthesized Deinococcucin C (**3**) (DMSO-*d6*, 400MHz)



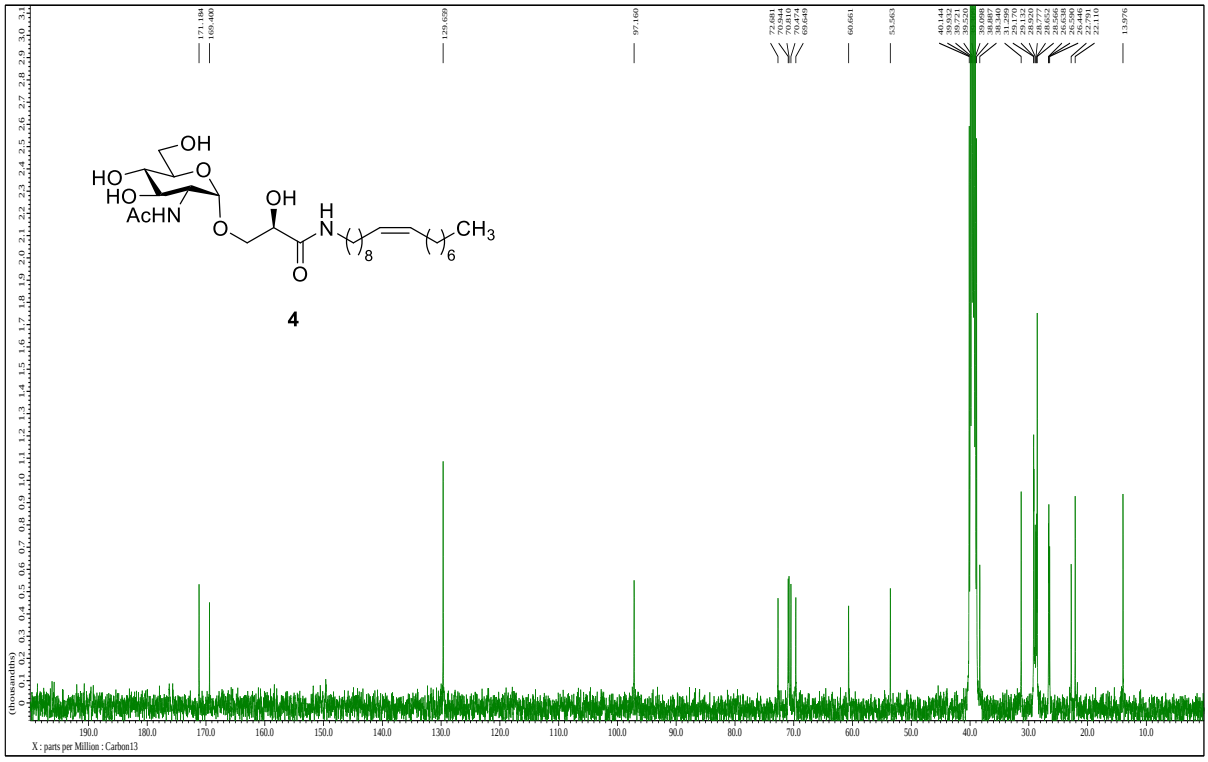
[13]C-NMR of synthesized Deinococcucin C (**3**) (DMSO-*d6*, 100MHz)



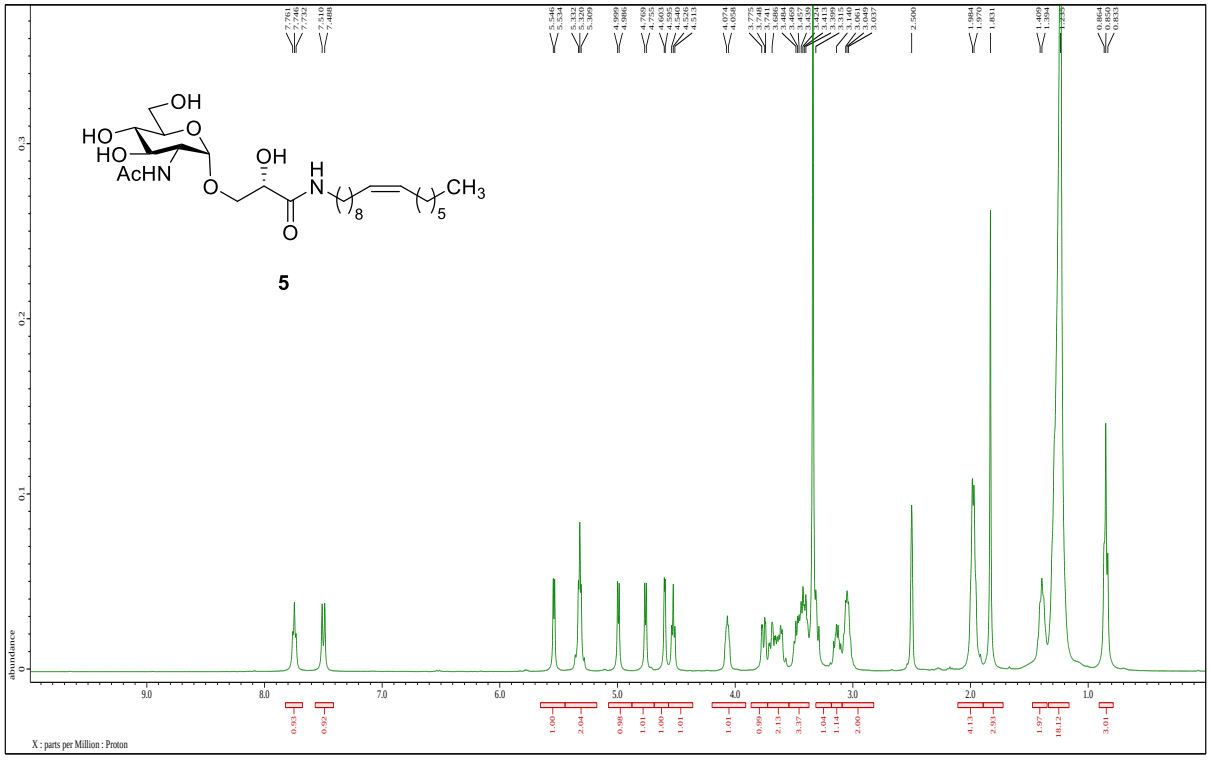
[1]H-NMR of synthesized Deinococcucin D (**4**) (DMSO-*d6*, 400MHz)



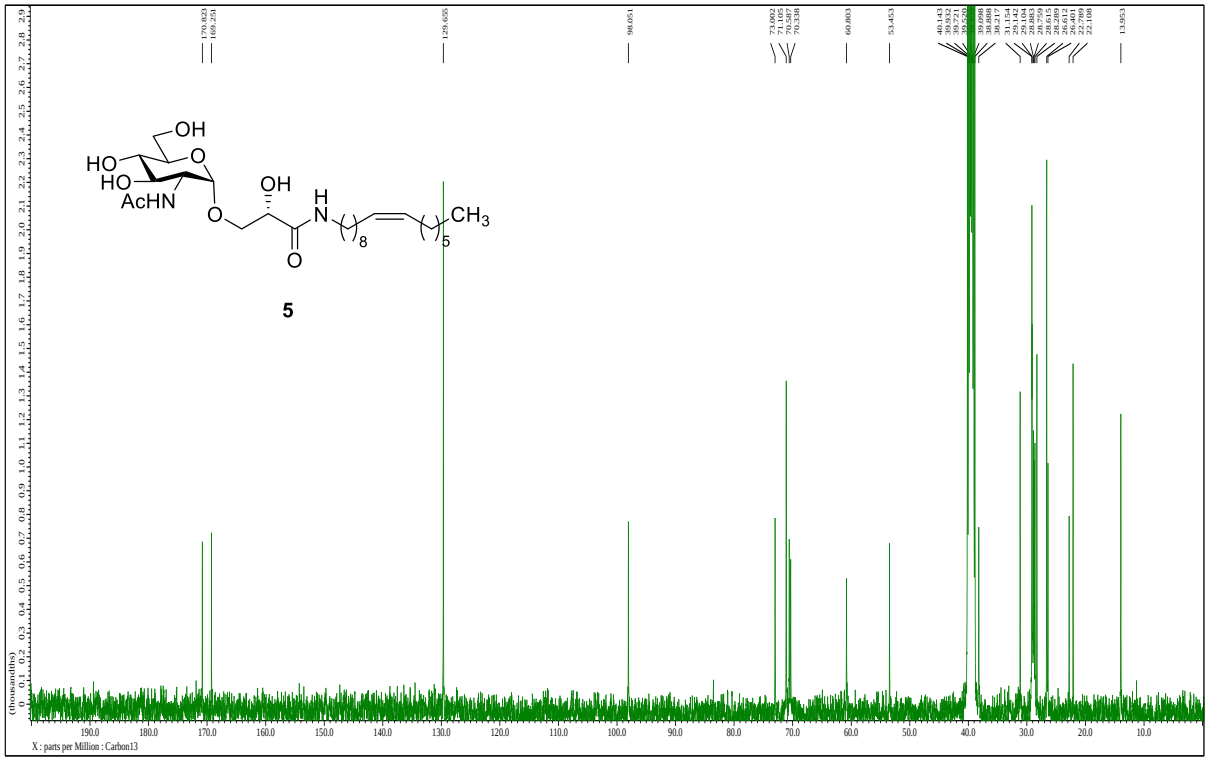
[13]C-NMR of synthesized Deinococcucin D (**4**) (DMSO-*d6*, 100MHz)



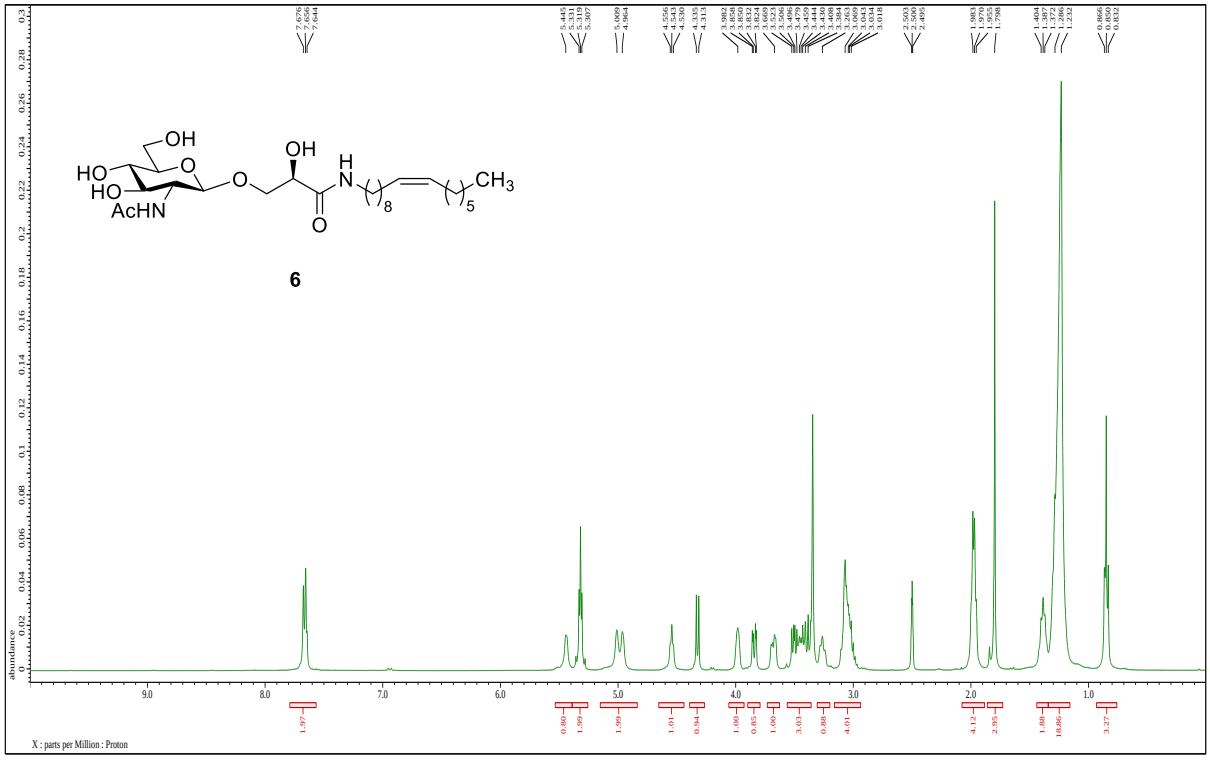
[1]H-NMR of compound **5** (DMSO-*d6*, 400MHz)



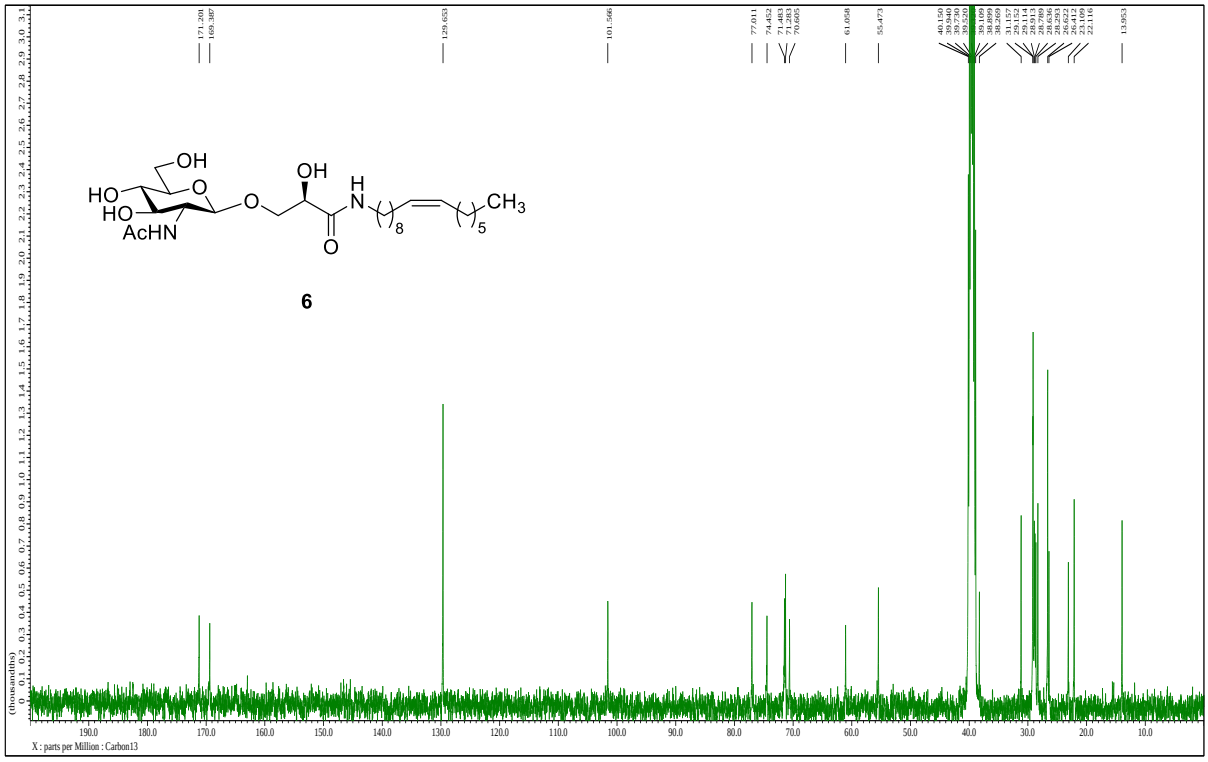
[13]C-NMR of compound **5** (DMSO-*d6*, 100MHz)



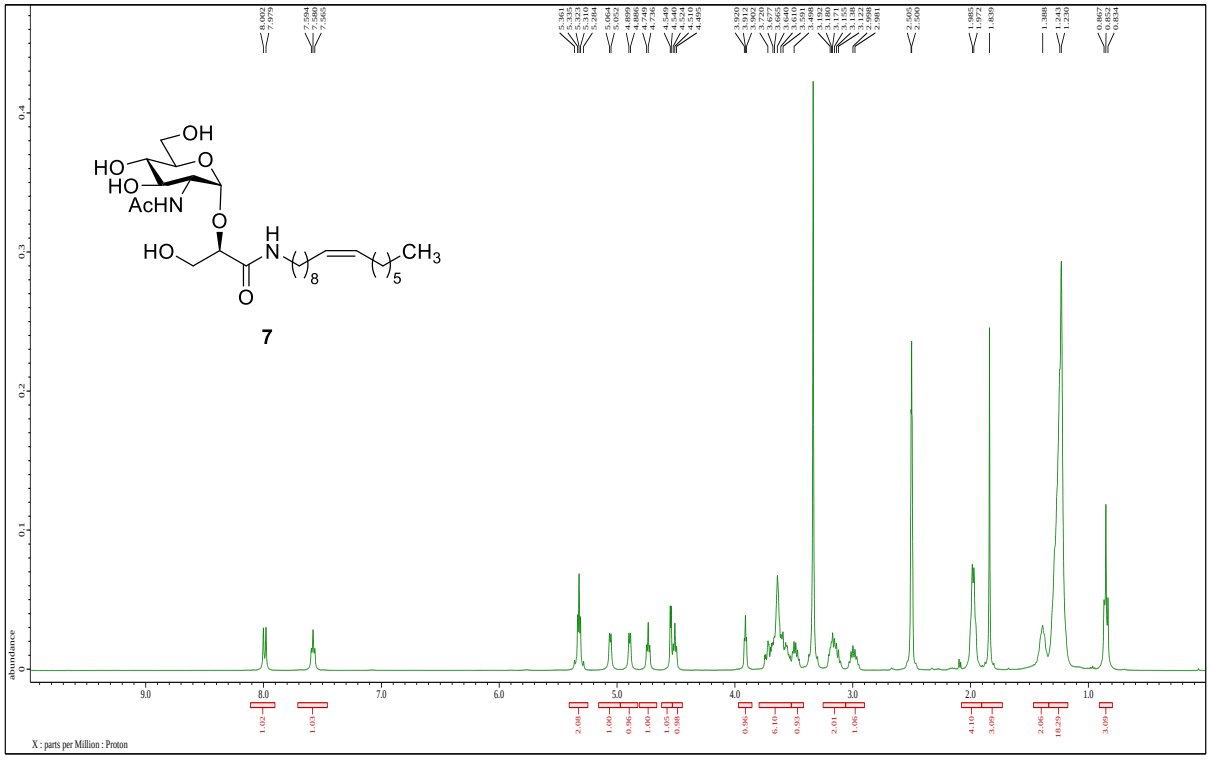
[1]H-NMR of compound **6** (DMSO-*d6*, 400MHz)



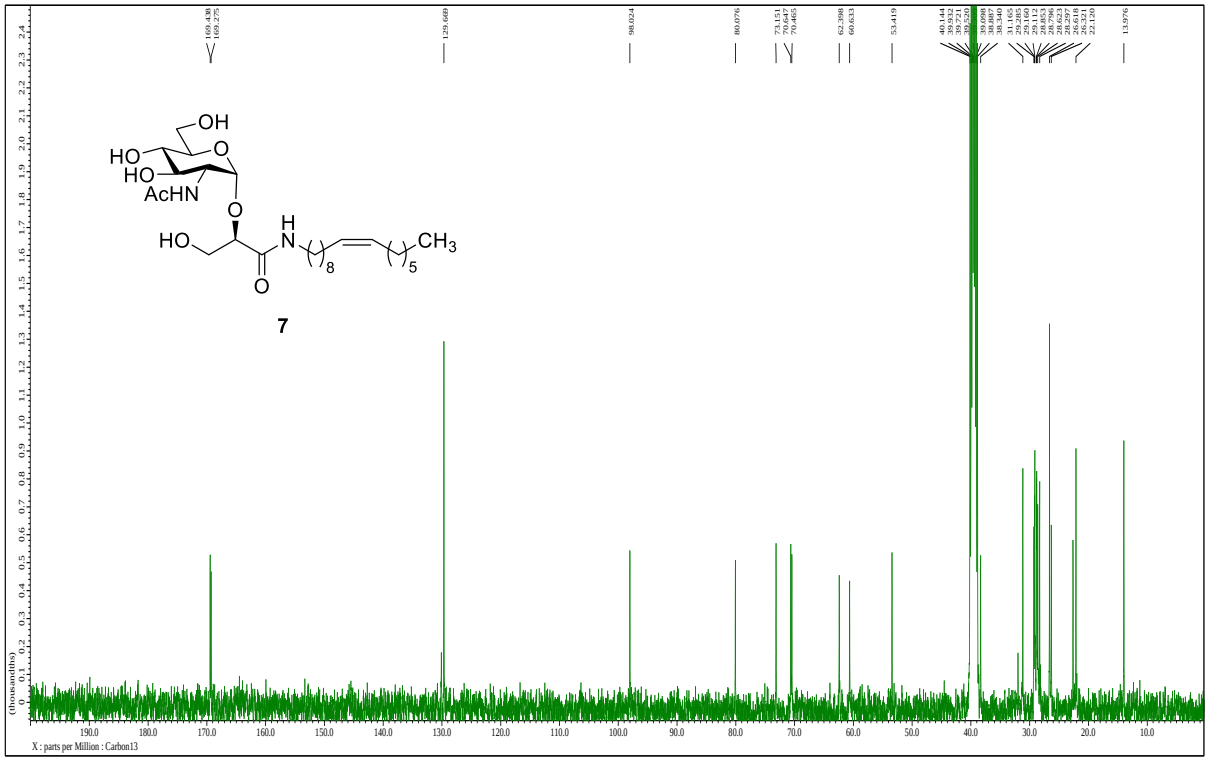
[13]C-NMR of compound **6** (DMSO-*d6*, 100MHz)



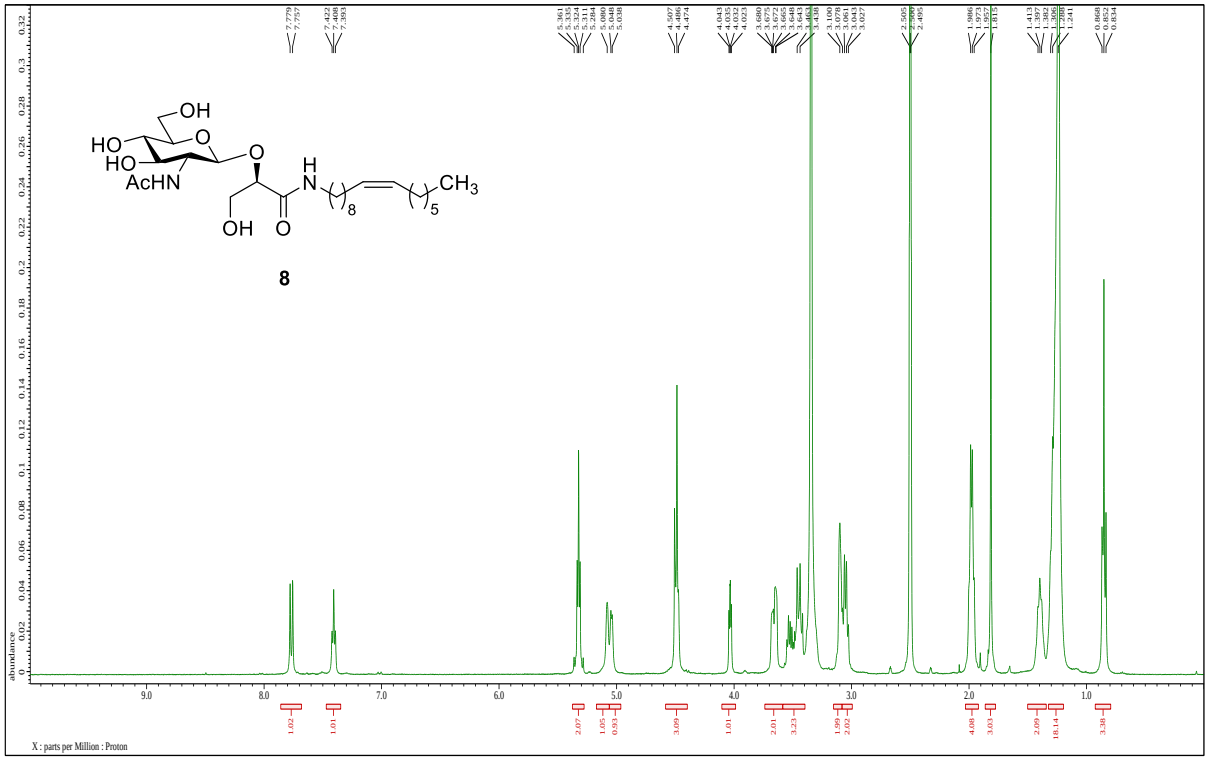
[1]H-NMR of compound **7** (DMSO-*d6*, 400MHz)



[13]C-NMR of compound **7** (DMSO-*d6*, 100MHz)



[1]H-NMR of compound **8** (DMSO-*d6*, 400MHz)



[13]C-NMR of compound **8** (DMSO-*d6*, 100MHz)