Supporting Information

Synthesis of *CH_2*-linked α-galactosylceramide and its glucose analogues through Glycosyl radical-mediated direct *C*-glycosylation

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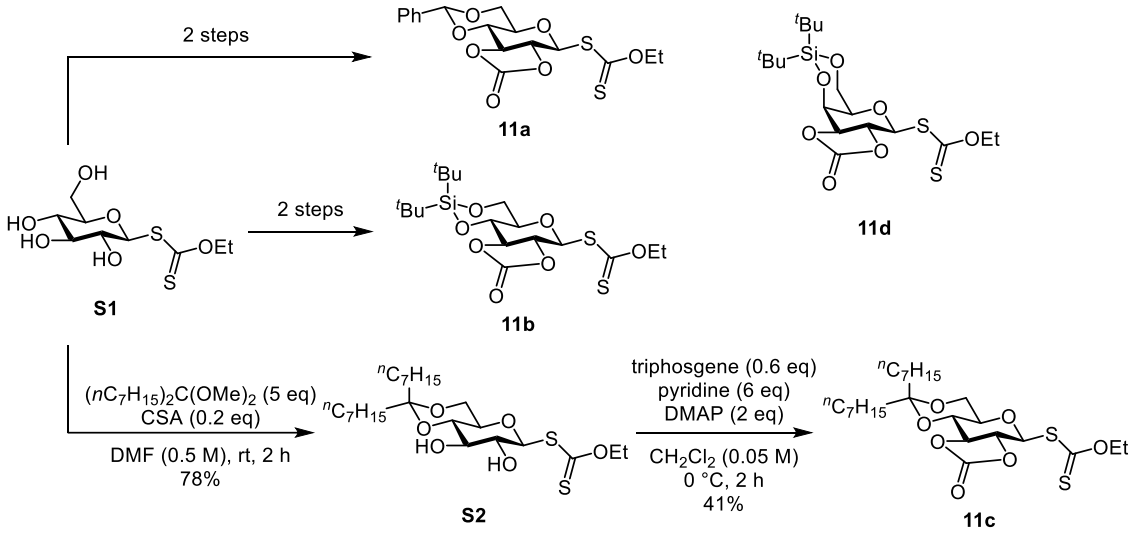
1. Generals

General; In general, reactions were carried out under an argon atmosphere, unless noted otherwise. Reagent grade solvents (1,2-dichloethane, pyridine, triethylamine) were distilled prior to use. Reactions were monitored by thin layer chromatography using Merck Silica Gel 60 F254 plates. Flash chromatography was performed using flash silica gel 60N (spherical neutral, particle size 40–50 μm) purchased from Kanto Chemical Co. Inc. Flash gel permeation chromatography was performed using Sephadex LH-20 purchased from Global Sciences Technologies Japan Co. Ltd.

Instrumentation; NMR spectra were recorded 500 MHz Bruker Avance III, operating at 500 MHz for ^{1}H NMR, and 125 MHz for ^{13}C NMR. Chemical shifts were reported in the scale relative to $CHCl_3$ (δ 7.26 ppm for ^{1}H NMR, δ 77.16 ppm for ^{13}C NMR), CH_3OH (δ 3.31 ppm for ^{1}H NMR, δ 49.00 ppm for ^{13}C NMR), acetone (δ 2.05 ppm for ^{1}H NMR, δ 29.84 ppm for ^{13}C NMR) as an internal reference. Splitting patterns are designated as s: singlet, d: doublet, t: triplet, q: quartet, br: broadening, m: multiplet. High-resolution mass spectrometry (HRMS) was obtained with Bruker MicroTOF II. Middle pressure liquid chromatography (MPLC) was performed on Yamazen, EPCLC-W-Prep 2XY A-Type equipped with RI and UV detectors. Recycling preparative gel permeation chromatography (GPC) was performed using LaboACE LC-5060 (Japan Analytical Industry Co. Inc.) with JAIGEL-2HR column.

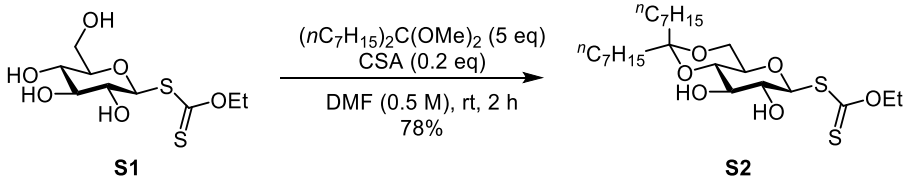
2. Synthesis of Donor 11

Scheme S1. Summary of synthetic route of donor 11



Xanthate **S1** was prepared using reported procedure.[1,2] Donors **11a**, **11b**, and **11d** were synthesized using a protocol developed in our group.[3] Synthetic procedure of donor **11c** is reported below;

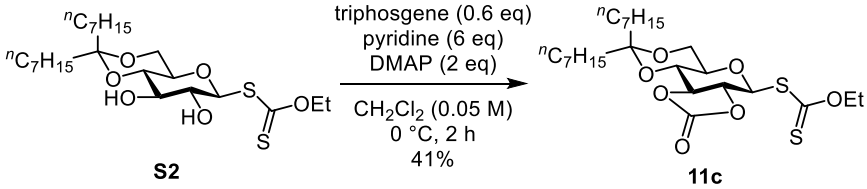
Compound S2



To a solution of **S1** (212 mg, 0.746 mmol, 1.0 equiv) in DMF (1.5 mL, 0.5 M) was subsequently added 8,8-dimethoxypentadecane (1.02 g, 3.73 mmol, 5.0 equiv) and (±)-10-camphorsulfonic acid (34.6 mg, 0.149 mmol, 0.2 equiv) at 0 °C. After stirring for 2 h at room temperature, the solution was cooled to 0 °C and diluted with hexane/EtOAc (4/1, 20 mL) and quenched with saturated aqueous $NaHCO_3$ (20 mL). After separating layers, the aqueous layer was extracted with hexane/EtOAc (4/1, 2 x 20 mL). The combined organic extracts were washed with water (50 mL), dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 10/1 to 3/1) to give 4,6-protected xanthate **S2** as a white amorphous solid (124 mg, 41%). $[\alpha]_D^{26}$ –36.11 (c 1.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.39 (d, *J* = 10.2 Hz, 1H, *H*1), 4.67 (m, 2H, SCSO*CH*$_2$CH$_3$), 3.93 (dd, *J* = 10.7, 5.3 Hz, 1H, *H*6eq), 3.74 (dd, *J* = 8.7, 8.6 Hz, 1H, *H*3), 3.72 (dd, *J* = 10.7, 10.4 Hz, 1H, *H*6ax), 3.64 (dd, *J* = 10.2, 8.6 Hz, 1H, *H*2), 3.53 (dd, *J* = 9.4, 8.7 Hz, 1H, *H*4), 3.40 (ddd, *J* = 10.4, 9.4, 5.3 Hz, 1H, *H*5), 2.88 (br s, 1H, -*OH*), 2.80 (br s, 1H, -*OH*), 1.89 (m, 1H, *H*Alkyl), 1.73

(m, 1H, *H*Alkyl), 1.59 (m, 2H, *H*Alkyl), 1.43 (t, *J* = 7.1 Hz, 3H, SCSOCH$_2$*CH$_3$*), 1.38 (m, 2H, *H*Alkyl), 1.22–1.33 (m, 18H, *H*Alkyl), 0.88 (dd, *J* = 6.8, 6.3 Hz, 6H, *H*Alkyl); ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.1 (S*C*SOCH$_2$CH$_3$), 102.9 (acetal(4º)), 88.3 (*C*1), 75.9 (*C*3), 72.4 (*C*4), 72.2 (*C*2), 71.9 (*C*5), 70.8 (SCSO*CH$_2$*CH$_3$), 61.5 (*C*6), 38.5 (*C*Alkyl), 32.0 (*C*Alkyl), 31.9 (*C*Alkyl), 30.0 (2C, *C*Alkyl), 29.49 (*C*Alkyl), 29.46 (*C*Alkyl), 29.3 (*C*Alkyl), 23.9 (*C*Alkyl), 22.81 (*C*Alkyl), 22.78 (2C, *C*Alkyl), 14.2 (2C, *C*Alkyl), 13.9 (SCSOCH$_2$*CH$_3$*); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{24}H_{44}NaO_6S_2$, 515.2472; found, 515.2472.

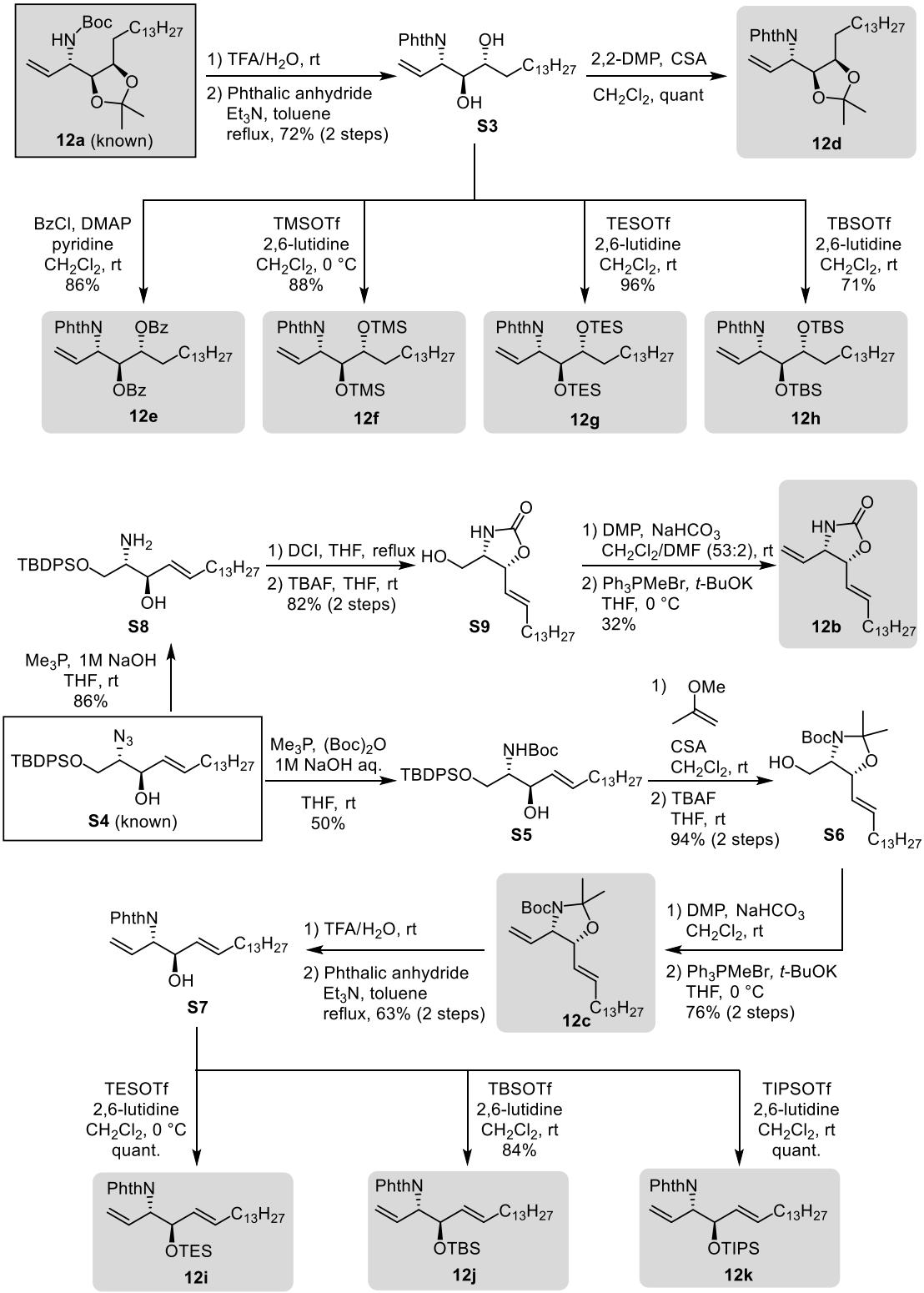
Donor 11c



To a solution of **S2** (288 mg, 0.584 mmol, 1.0 equiv) in CH_2Cl_2 (5.6 mL) was sequentially added pyridine (280 μL, 3.5 mmol, 6.0 equiv), 4-dimethylaminopyridine (DMAP, 143 mg, 1.17 mmol, 2.0 equiv) and triphosgene (0.06 M in CH_2Cl_2, 5.9 mL, 350 μmol, 0.6 equiv) at 0 °C. After stirring for 2 h at 0 °C, the solution was quenched with 10% aqueous H_2SO_4 (20 mL) at 0 °C. After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (50 mL), dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRA PACK Silica-40B, eluent: hexane/EtOAc = 1/0 to 9/1) to give **9c** as a colorless oil (124 mg, 41%). $[\alpha]_D^{25}$ –17.05 (c 0.63, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.84 (d, *J* = 10.3 Hz, 1H, *H*1), 4.68 (q, *J* = 7.1 Hz, 2H, SCSO*CH$_2$*CH$_3$), 4.44 (dd, *J* = 10.6, 9.9 Hz, 1H, *H*3), 4.20 (dd, *J* = 10.6, 10.3 Hz, 1H, *H*2), 4.09 (dd, *J* = 9.9, 9.0 Hz, 1H, *H*4), 3.95 (dd, *J* = 10.8, 5.2 Hz, 1H, *H*6eq), 3.85 (dd, *J* = 10.8, 10.0 Hz, 1H, *H*6ax), 3.51 (ddd, *J* = 10.0, 9.0, 5.2 Hz, 1H, *H*5), 1.87 (m, 1H, *H*Alkyl), 1.76 (m, 1H, *H*Alkyl), 1.59 (m, 2H, *H*Alkyl), 1.43 (t, *J* = 7.1 Hz, 3H, SCSOCH$_2$*CH$_3$*), 1.37 (m, 2H, *H*Alkyl), 1.22–1.32 (m, 18H, *H*Alkyl), 0.88 (m, 6H, *H*Alkyl); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.9 (S*C*SOCH$_2$CH$_3$), 152.5 (-*C*=O), 103.3 (acetal(4º)), 84.5 (*C*1), 82.0 (*C*3), 76.8 (*C*2), 74.5 (*C*5), 71.3 (SCSO*CH$_2$*CH$_3$), 71.0 (*C*4), 61.3 (*C*6), 38.1 (*C*Alkyl), 31.92 (*C*Alkyl), 31.88 (*C*Alkyl), 29.9 (*C*Alkyl), 29.8 (*C*Alkyl), 29.6 (*C*Alkyl), 29.4 (*C*Alkyl), 29.3 (*C*Alkyl), 23.7 (*C*Alkyl), 22.76 (*C*Alkyl), 22.73 (*C*Alkyl), 22.66 (*C*Alkyl), 14.2 (2C, *C*Alkyl), 13.8 (SCSOCH$_2$*CH$_3$*); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{25}H_{42}NaO_7S_2$, 541.2264; found, 515.2248.

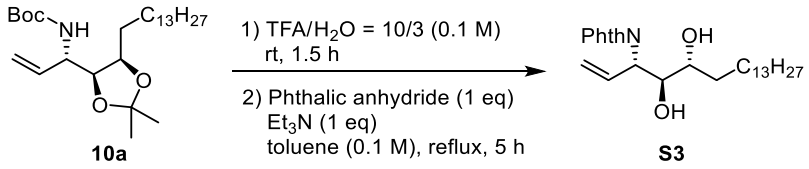
3. Synthesis of Acceptor 12

Scheme S2. Summary of synthetic routes to ceramide acceptor 12



Compounds **12a** and **S4** were synthesized using reported procedure.[4,5] Synthetic procedures of acceptors **12b-k** are shown below;

Compound S3

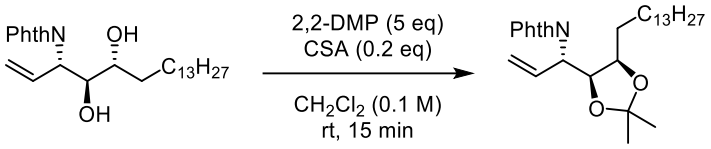


10a **S3**

Compound 12a (541 mg, 1.19 mmol, 1.0 equiv) was dissolved in trifluoroacetic acid and water (TFA/H_2O = 10:3, 11.9 mL, 0.1 M). After stirring for 1.5 h at room temperature, the resulting solution was concentrated under reduced pressure and co-evaporated with toluene three times to remove residual water to give primary amine.

The crude mixture was dissolved in toluene (11.7 mL, 0.1 M) under Ar atmosphere. To the solution was added phthalic anhydride (176 mg, 1.19 mmol, 1.0 equiv) and triethylamine (165 μL, 1.19 mmol, 1.0 equiv) at 0 °C. After stirring for 5 h under reflux condition with Dean-Stark trap, the solution was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (20 mL). After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40B, eluent: hexane/acetone = 7/1 to 2/1) to give compound **S3** as a white amorphous solid (379 mg, 72%). $[\alpha]_D^{31}$ –50.06 (c 0.91, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H, *H*Phth), 7.74 (dd, *J* = 5.4, 3.0 Hz, 2H, *H*Phth), 6.26 (ddd, *J* = 17.1, 10.4, 7.3 Hz, 1H, sph*H*1), 5.29 (ddd, *J* = 10.4, 1.3, 1.1 Hz, 1H, *H*$_2$*C*=C-), 5.24 (ddd, *J* = 17.1, 1.3, 1.1 Hz, 1H, *H*$_2$*C*=C-), 5.22 (ddd, *J* = 7.3, 2.6, 1.3 Hz, 1H, sph*H*2), 4.14 (d, *J* = 2.0 Hz, 1H, 3-*OH*), 3.89 (ddd, *J* = 6.5, 2.6, 2.0 Hz, 1H, sph*H*3), 3.64 (dddd, *J* = 8.8. 6.5, 6.1, 3.2 Hz, 1H, sph*H*4), 1.88 (brd, *J* = 3.2 Hz, 1H, 4-*OH*), 1.80–1.71 (m, 1H, sph*H*5), 1.55–1.44 (m, 2H, sph*H*5 and sph*H*Alkyl), 1.33–1.22 (m, 23H, sph*H*Alkyl), 0.88 (t, *J* = 6.9 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0 (2C, -NC(O)Phth), 134.5 (2C, *C*Phth), 131.8 (2C, *C*Phth), 131.4 (sph*C*2), 123.8 (2C, *C*Phth), 119.4 (*H*$_2$*C*=C-), 76.9 (sph*C*3), 72.5 (sph*C*4), 55.8 (sph*C*1), 33.0 (sph*C*5), 32.1 (sph*C*Alkyl), 29.83 (3C, sph*C*Alkyl), 29.80 (sph*C*Alkyl), 29.79 (sph*C*Alkyl), 29.76 (sph*C*Alkyl), 29.74 (sph*C*Alkyl), 29.72 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 25.6 (sph*C*Alkyl), 22.8 (sph*C*Alkyl), 14.3 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{27}H_{41}NaNO_4$, 466.2928; found, 466.2926.

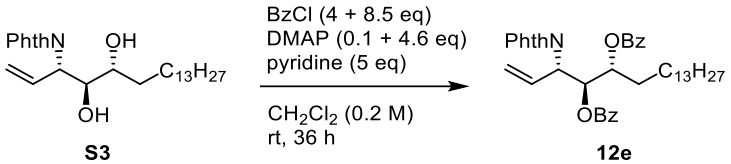
Accepor 12d



S3 **12d**

To a solution of **S3** (70 mg, 0.158 mmol, 1.0 equiv) in CH_2Cl_2 (1.48 mL, 0.1 M) was subsequently added 2,2-dimethoxypropane (96.6 µL, 0.79 mmol, 5.0 equiv) and (±)-10-camphorsulfonic acid (7.34 mg, 0.032 mmol, 0.2 equiv) at 0 °C. After stirring for 2 h at room temperature, the solution was cooled to 0 °C and quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40A, eluent: hexane/EtOAc = 49/1 to 3/1) to give compound **12d** as a colorless oil (75.3 mg, quant). $[\alpha]_D^{29}$ – 45.29 (c 0.74, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.26 (ddd, *J* = 17.2, 10.3, 7.1 Hz, 1H, sph*H*1), 5.22 (d, *J* = 10.3 Hz, 1H, H_2C=C-), 5.19 (d, *J* = 17.2 Hz, 1H, H_2C=C-), 5.04 (dd, *J* = 10.2, 5.2 Hz, 1H, sph*H*3), 4.83 (dd, *J* = 10.2, 7.1 Hz, 1H sph*H*2), 4.06 (ddd, *J* = 10.1, 5.2, 4.0 Hz, 1H, sph*H*4), 1.62–1.53 (m, 1H, sph*H*5), 1.48 (s, 3H, acetonide(-CH_3)), 1.46–1.39 (m, 1H, sph*H*5), 1.37 (s, 3H, acetonide(-CH_3)), 1.32–0.98 (m, 24H, sph*H*Alkyl), 0.87 (t, *J* = 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9 (2C, -NHC(O)Phth), 134.3 (2C, *C*Phth), 133.9 (sph*C*1), 131.8 (2C, *C*Phth), 123.6 (2C, *C*Phth), 118.3 (H_2C=C-), 108.4 (acetonide(4°)), 78.0 (sph*C*4), 75.0 (sph*C*3), 53.1 (sph*C*2), 32.1 (sph*C*Alkyl), 29.81 (sph*C*Alkyl), 29.79 (2C, sph*C*Alkyl), 29.74 (sph*C*Alkyl), 29.72 (sph*C*Alkyl), 29.58 (sph*C*Alkyl), 29.56 (sph*C*Alkyl), 29.49 (2C, sph*C*Alkyl), 28.8 (sph*C*5), 28.5 (acetonide(-CH_3)), 26.4 (sph*C*6), 26.1 (acetonide(-CH_3)), 22.8 (sph*C*Alkyl), 14.2 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{30}H_{45}NaNO_4$, 506.3241; found, 506.3249.

Acceptor 12e

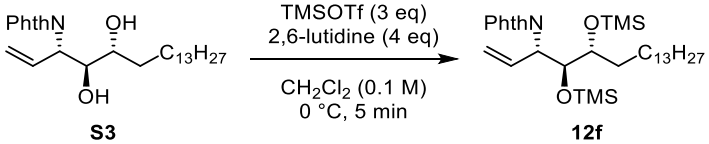


S3 **12e**

To a solution of diol **S3** (60 mg, 0.135 mmol, 1.0 equiv) in CH_2Cl_2 (558 µL, 0.2 M) was subsequently added 4-dimethylaminopyridine (DMAP, 1.65 mg, 0.0135 mmol, 0.1 equiv), pyridine (54.3 µL, 0.675 mmol, 5.0 equiv) and benzoyl chloride (62.7 µL, 0.54 mmol, 4.0 equiv) at 0 °C. After stirring for 14 h at room temperature, the reaction solution was added DMAP (24.8

mg, 0.203 mmol, 1.5 equiv) and benzoyl chloride (30 μL, 0.203 mmol, 1.5 equiv) at 0 °C every 6 h until consuming diol **S3** that was monitored by TLC (Totally DMAP (4.6 equiv) and benzoyl chloride (8.5 equiv) were added in this case). The resulting solution was diluted with Et_2O (5 mL), and quenched with saturated aqueous $NaHCO_3$ (5 mL) at 0 °C. After separating layers, the aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-30A. eluent: hexane/EtOAc = 12/1 to 3/1) to give bis-benzoate **12e** as a colorless oil (75.5 mg, 86%). $[\alpha]_D^{29}$ +26.39 (c 0.51, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 8.4, 1.3 Hz, 2H, *H*Bz), 7.97 (dd, *J* = 8.4, 1.3 Hz, 2H, *H*Bz), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.69 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.59 (dddd, *J* = 7.9, 7.0, 1.3, 1.3 Hz, 1H, *H*Bz), 7.52 (dddd, *J* = 7.1, 1.3 Hz, 1H, *H*Bz), 7.47 (dd, *J* = 7.6, 7.4 Hz, 2H, *H*Bz), 7.38 (dd, *J* = 7.6, 7.4 Hz, 2H, *H*Bz), 6.43 (ddd, *J* = 17.1, 10.1, 8.7 Hz, 1H, sph*H*1), 6.14 (dd, *J* = 8.2, 4.5 Hz, 1H, sph*H*3), 5.37 (ddd, *J* = 7.9, 6.0, 4.5 Hz, 1H, sph*H*4), 5.31 (ddd, *J* = 17.1, 1.0, 0.9 Hz, 1H, H_2C=C-), 5.21 (d, *J* = 10.1 Hz, 1H, H_2C=C-), 5.14 (dd, *J* = 8.7, 8.2 Hz, 1H, sph*H*2), 1.82 (dd, *J* = 7.9, 7.5 Hz, 1H, sph*H*5), 1.80 (dd, *J* = 8.1, 6.0 Hz, 1H, sph*H*5), 1.40–1.10 (m, 24H, sph*H*Alkyl), 0.87 (t, *J* = 6.9 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.6 (2C, -N*C*(O)Phth), 165.8 (-O*C*(O)Ph), 165.5 (-O*C*(O)Ph), 134.3 (2C, *C*Phth), 133.3 (*C*Bz), 133.1 (*C*Bz), 131.9 (2C, *C*Phth), 131.7 (sph*C*1), 130.00 (*C*Bz), 129.96 (3C, *C*Bz), 129.90 (2C, *C*Bz), 128.6 (2C, *C*Bz), 128.4 (2C, *C*Bz), 123.6 (2C, *C*Phth), 121.1 (H_2C=C-), 73.4 (sph*C*4), 72.5 (sph*C*3), 54.5 (sph*C*2), 32.1 (sph*C*Alkyl), 29.81 (sph*C*Alkyl), 29.78 (2C, sph*C*Alkyl), 29.76 (sph*C*Alkyl), 29.68 (2C, sph*C*Alkyl), 29.59 (sph*C*Alkyl), 29.49 (sph*C*Alkyl), 29.43 (2C, sph*C*Alkyl), 25.3 (sph*C*Alkyl), 22.8 (sph*C*Alkyl), 14.3 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{41}H_{49}NaNO_6$, 674.3452; found, 674.3458.

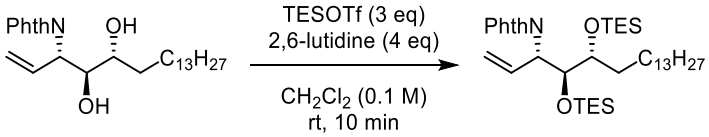
Acceptor 12f



To a solution of diol **S3** (120 mg, 0.264 mmol, 1.0 equiv) in CH_2Cl_2 (2.37 mL, 0.1 M) was subsequently added 2,6-lutidine (123 μL, 1.06 mmol, 4.0 equiv) and trimethylsilyl trifluoromethanesulfonate (143 μL, 0.792 mmol, 3.0 equiv) at 0 °C. After stirring for 5 min at 0 °C, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (10 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The

residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40B, eluent: hexane/EtOAc = 1/0 to 9/1) to give silyl ether **12f** as a colorless oil (137 mg, 88%). $[\alpha]_D^{31}$ +2.75 (c 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.22 (ddd, *J* = 16.8, 10.7, 7.7 Hz, 1H, sph*H*1), 5.174 (ddd, *J* = 10.7, 1.1, 1.0 Hz, 1H, H_2C=C-), 5.166 (ddd, *J* = 16.8, 1.1, 1.0 Hz, 1H, H_2C=C-), 4.66 (dddd, *J* = 9.5, 7.7, 1.0, 1.0 Hz, 1H, sph*H*2), 4.41 (dd, *J* = 9.5, 1.6 Hz, 1H, sph*H*3), 3.42 (dt, *J* = 9.6, 1.8, 1.6 Hz, 1H, sph*H*4), 1.51–1.41 (m, 1H, sph*H*5), 1.38–0.99 (m, 25 H, sph*H*Alkyl), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.15 (s, 9H, Si-CH_3), 0.02 (s, 9H, Si-CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8 (2C, -NH*C*(O)Phth), 134.2 (2C, *C*Phth), 134.1 (sph*C*1), 132.0 (2C, *C*Phth), 123.4 (2C, *C*Phth), 118.6 (H_2C=C-), 75.7 (sph*C*3), 73.6 (sph*C*4), 55.8 (sph*C*2), 32.1 (sph*C*Alkyl), 30.6 (sph*C*5), 29.86 (sph*C*Alkyl), 29.84 (3C, sph*C*Alkyl), 29.77 (3C, sph*C*Alkyl), 29.70 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 26.3 (sph*C*Alkyl), 22.8 (sph*C*Alkyl), 14.3 (sph*C*18), 0.8 (3C, Si-CH_3), 0.5 (3C, Si-CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{33}H_{57}NaNO_4Si_2$, 610.3718; found, 610.3727.

Acceptor 12g

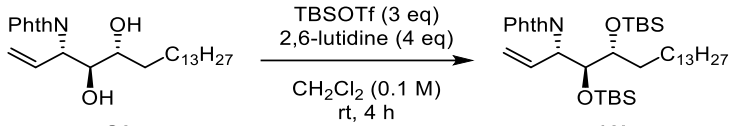


S3 **12g**

To a solution of diol **S3** (100 mg, 0.225 mmol, 1.0 equiv) in CH_2Cl_2 (2.00 mL, 0.1 M) was subsequently added 2,6-lutidine (104 µL, 0.900 mmol, 4.0 equiv) and triethylsilyl trifluoromethanesulfonate (151 µL, 0.675 mmol, 3.0 equiv) at 0 °C. After stirring for 45 min at room temperature, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (10 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40B, eluent: hexane/EtOAc = 1/0 to 9/1) to give silyl ether **12g** as a colorless oil (146 mg, 96%). $[\alpha]_D^{31}$ –13.59 (c 0.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.28 (ddd, *J* = 17.4, 10.0, 7.9 Hz, 1H, sph*H*1), 5.166 (ddd, *J* = 17.4, 1.2, 1.0 Hz, 1H, H_2C=C-), 5.165 (ddd, *J* = 10.0, 1.2, 1.0 Hz, 1H, H_2C=C-), 4.69 (dddd, *J* = 9.8, 7.9, 1.0, 1.0 Hz, 1H, sph*H*2), 4.45 (dd, *J* = 9.8, 1.1 Hz, 1H, sph*H*3), 3.50–3.46 (m, 1H, sph*H*4), 1.46–1.08 (m, 26H, sph*H*Alkyl), 0.99 (dd, *J* = 8.0, 7.9 Hz, 9H, Si-CH_2CH_3), 0.88 (dd, *J* = 7.1, 6.9 Hz, 3H, sph*H*18), 0.86 (dd, *J* = 8.0, 7.9 Hz, 9H, Si-CH_2CH_3), 0.71–0.64 (m, 6H, Si-CH_2CH_3), 0.54–0.48 (m, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ167.8 (2C, -NH*C*(O)Phth), 134.2 (4C, *C*Phth), 132.1 (sph*C*1), 123.3 (2C, *C*Phth), 118.7 (H_2C=C-), 75.4

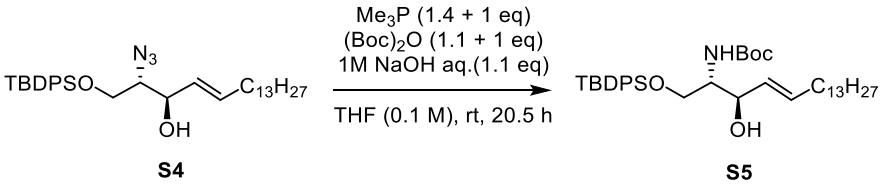
(sph*C*3), 74.5 (sph*C*4), 55.7 (sph*C*2), 32.1 (sph*C*Alkyl), 31.7 (sph*C*Alkyl), 30.0 (sph*C*Alkyl), 29.86 (3C, sph*C*Alkyl), 29.84 (sph*C*Alkyl), 29.79 (sph*C*Alkyl), 29.76 (sph*C*Alkyl), 29.6 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 26.5 (sph*C*Alkyl), 22.9 (sph*C*Alkyl), 14.3 (sph*C*18), 7.12 (3C, Si-CH_2*CH_3*), 7.07 (3C, Si-CH_2*CH_3*), 5.4 (3C, Si-*CH_2*CH_3), 5.2 (3C, Si-*CH_2*CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{39}H_{69}NaNO_4Si_2$, 694.4657; found, 694.4661.

Acceptor 12h



To a solution of diol **S3** (142 mg, 0.32 mmol, 1.0 equiv) in CH_2Cl_2 (2.83 mL, 0.1 M) was subsequently added 2,6-lutidine (148 µL, 1.28 mmol, 4.0 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (221 µL, 0.96 mmol, 3.0 equiv) at 0 °C. After stirring for 4 h at room temperature, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (10 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40A, eluent: hexane/EtOAc = 1/0 to 5/1) to give silyl ether **12h** as a colorless oil (152 mg, 71%). $[\alpha]_D^{31}$ –2.32 (c 0.98, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.26 (dddd, *J* = 17.2, 10.2, 8.1 Hz, 1H, sph*H*1), 5.18 (ddd, *J* = 17.2, 1.1, 1.0 Hz, 1H, *H_2C*=C-), 5.16 (ddd, *J* = 10.2, 1.1, 1.0 Hz, 1H, *H_2C*=C-), 4.72 (dddd, *J* = 9.7, 8.1, 1.0, 1.0 Hz, 1H, sph*H*2), 4.47 (d, *J* = 9.7 Hz, 1H, sph*H*3), 3.53–3.49 (m, 1H, sph*H*4), 1.46–1.08 (m, 26H, sph*H*5 and sph*H*Alkyl), 0.91 (s, 9H, Si-C(*CH_3*)), 0.89–0.84 (m, 12H, sph*H*18 and Si-C(*CH_3*)), 0.15 (s, 3H, Si-*CH_3*), 0.14 (s, 3H, Si-*CH_3*), 0.02 (s, 3H, Si-*CH_3*), –0.16 (s, 3H, Si-*CH_3*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8 (2C, -NH*C*(O)Phth), 134.5 (sph*C*1), 134.2 (2C, *C*Phth), 132.0 (2C, *C*Phth), 123.4 (2C, *C*Phth), 119.0 (*H_2C*=C-), 75.5 (sph*C*3), 74.8 (sph*C*4), 55.7 (sph*C*2), 32.1 (sph*C*Alkyl), 32.0 (sph*C*Alkyl), 29.87 (2C, sph*C*Alkyl), 29.83 (3C, sph*C*Alkyl), 29.76 (sph*C*Alkyl), 29.73 (sph*C*Alkyl), 29.6 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 26.4 (sph*C*Alkyl), 26.3 (3C, Si-C(*CH_3*)), 26.2 (3C, Si-C(*CH_3*)), 22.8 (sph*C*Alkyl), 18.5(Si-*C*(CH_3)), 18.4 (Si-*C*(CH_3)), 14.3 (sph*C*18), –3.3 (Si-*CH_3*), –3.6 (Si-*CH_3*), –4.4 (Si-*CH_3*), –5.0 (Si-*CH_3*); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{39}C_{69}NaNO_4Si_2$, 694.4657; found, 694.4655.

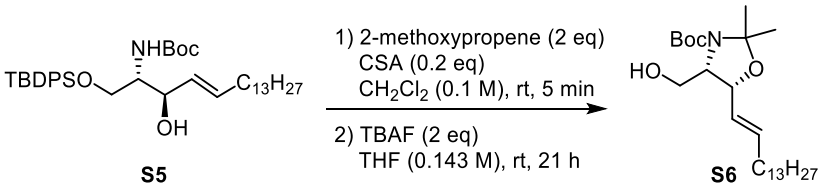
Acceptor S5



S4 **S5**

To a solution of azide **S4** (3.07 g, 5.44 mmol, 1.0 equiv) in THF (44.9 mL, 0.1 M) was subsequently added 1 M aqueous NaOH (5.99 mL, 5.99 mmol, 1.1 equiv), trimethylphosphane (3 M in THF, 2.54 mL, 7.62 mmol, 1.4 equiv) and di-*tert*-butyl dicarbonate (1.7 mL, 5.99 mmol, 1.1 equiv). After stirring for 4.5 h at room temperature, the reaction solution was added trimethylphosphane (1.81 mL, 2.72 mmol, 0.5 equiv) and di-*tert*-butyl dicarbonate (1.76 mL, 2.72 mmol, 0.5 equiv) every 3.5 h until consuming azide **S4** that was monitored by TLC (Totally trimethylphosphine (1.0 equiv) and di-*tert*-butyl dicarbonate (1.0 equiv) were added in this case). The resulting solution was diluted with EtOAc (80 mL) and quenched with saturated aqueous NH_4Cl (50 mL) at 0 °C. After separating layers, the aqueous layer was extracted with EtOAc (2 x 80 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 50/1 to 8/1) to give compound **S5** as a colorless oil (1.75 g, 50%). $[\alpha]_D^{21}$ +9.93 (c 1.89, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63–7.73 (m, 5H, *H*Ph), 7.36–7.46 (m, 7H, *H*Ph), 5.78 (ddd, *J* = 15.4, 7.0, 6.6 Hz, 1H, sph*H*5), 5.48 (dd, *J* = 15.4, 6.0 Hz, 1H, sph*H*4), 5.19 (brd, *J* = 7.5 Hz, 1H, -*NH*CO-), 4.25 (ddd, *J* = 6.0, 5.5, 4.9 Hz, 1H, sph*H*3), 3.91 (dd, *J* = 10.5, 3.7 Hz, 1H, sph*H*1), 3.76 (dd, *J* = 10.5, 1.9 Hz, 1H, sph*H*1), 3.70–3.62 (m, 1H, sph*H*2), 3.16 (d, *J* = 4.9 Hz, 1H, 3-*OH*), 2.03 (ddd, *J* = 7.0, 7.0, 6.6 Hz, 2H, sph*H*6), 1.45 (s, 9H, Boc(–*CH*$_3$)), 1.37–1.26 (m, 22H, sph*H*Alkyl), 1.07 (s, 9H, -C(*CH*$_3$)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0 (-NH*C*(O)-), 135.7 (3C, *C*Ph), 134.9 (*C*Ph), 133.5 (*C*Ph), 132.8 (sph*C*5), 132.7 (*C*Ph), 130.1 (*C*Ph), 129.8 (*C*Ph), 129.3 (sph*C*4), 128.0 (3C, *C*Ph), 127.8 (*C*Ph), 79.6 (Boc(4°)), 74.5 (sph*C*3), 64.3 (sph*C*1), 55.2 (sph*C*2), 32.5 (sph*C*6), 32.1 (sph*C*Alkyl), 29.85 (2C, sph*C*Alkyl), 29.81 (sph*C*Alkyl), 29.78 (sph*C*Alkyl), 29.68 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 29.4 (sph*C*Alkyl), 29.3 (sph*C*Alkyl), 28.6 (3C, Boc(–*CH*$_3$)), 27.0 (3C, -C(*CH*$_3$)$_3$), 26.7 (-*C*(CH$_3$)$_3$), 22.8 (sph*C*Alkyl), 19.3 (sph*C*Alkyl), 14.3 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{39}H_{63}NaNO_4Si$, 660.4424; found, 660.4422.

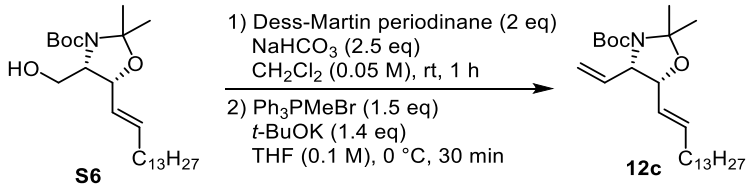
Acceptor S6



To a solution of compound **S5** (1.73 g, 2.71 mmol, 1.0 equiv) in CH_2Cl_2 (27.1 mL, 0.1 M) was subsequently added 2-methoxypropene (509 μL, 5.42 mmol, 2.0 equiv) and (±)-10-camphorsulfonic acid (126 mg, 0.542 mmol, 0.2 equiv) at 0 °C. After stirring for 5 min at room temperature, the mixture was diluted with CH_2Cl_2 (20 mL) and quenched with saturated aqueous $NaHCO_3$ (40 mL) at 0 °C. After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 40 mL). The combined organic extracts were dried over Na_2SO_4, concentrated under reduced pressure and co-evaporated with toluene two times to remove residual water to give crude.

The crude mixture was dissolved in THF (13.6 mL, 0.1 M) under Ar atmosphere. To the solution was added tetrabutylammonium fluoride (1 M in THF, 5.42 mL, 5.42 mmol, 2.0 equiv) at room temperature. After stirring for 21 h at room temperature, the solution was diluted with EtOAc (20 mL) and quenched with saturated aqueous NH_4Cl (20 mL). After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40B, eluent: hexane/EtOAc = 1/0 to 5/1) to give primary alcohol **S6** as a colorless oil (1.12 g, 94%). $[\alpha]_D^{21}$ –1.01 (c 1.74, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 7:3 mixture of rotamers): δ 6.00–5.93 (m, 3/10H, sph*H*1), 5.88 (ddd, *J* = 15.2, 6.5, 6.2 Hz, 7/10H, sph*H*5), 5.61–5.57 (m, 3/10H, sph*H*4), 5.45 (dd, *J* = 15.2, 7.4 Hz, 7/10H, sph*H*4), 4.62–4.54 (m, 1H, sph*H*3), 4.11–4.05 (m, 7/10H, sph*H*2), 3.90–3.83 (m, 3/10H, sph*H*2), 3.83–3.74 (m, 1H, sph*H*1), 3.69–3.57 (m, 1H, sph*H*1), 3.48–3.40 (m, 1H, 1-*OH*), 2.14–2.00 (m, 2H, sph*H*6), 1.65–1.57 (m, 3H, acetonide(-*CH*$_3$)), 1.57–1.52 (m, 3H, acetonide(-*CH*$_3$)), 1.45 (s, 9H, Boc(–*CH*$_3$)), 1.42–1.19 (m, 22H, sph*H*Alkyl), 0.88 (t, *J* = 6.9 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6 (-N*C*(O)-), 137.5 (sph*C*5), 123.4 (sph*C*4), 93.1 (acetonide(4°)), 81.3 (Boc(4°)), 76.7 (sph*C*3), 63.9 (sph*C*1), 62.2 (sph*C*2), 32.5 (sph*C*Alkyl), 32.1 (sph*C*6), 29.8 (4C, sph*C*Alkyl), 29.7 (sph*C*Alkyl), 29.6 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 29.4 (sph*C*Alkyl), 29.0 (sph*C*Alkyl), 28.6 (3C, Boc(–*CH*$_3$)), 28.0 (acetonide(–*CH*$_3$)), 24.9 (acetonide(–*CH*$_3$)), 22.8 (sph*C*Alkyl), 14.3 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{26}H_{49}NaNO_4$, 462.3559; found, 462.3556.

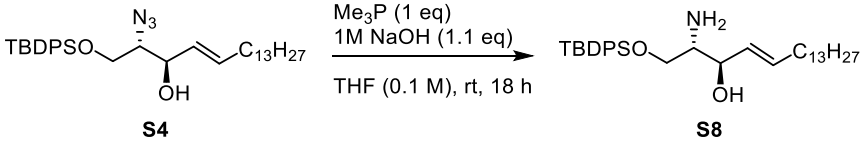
Acceptor 12c



To a solution of **S5** (510 mg, 1.16 mmol, 1.0 equiv) in CH_2Cl_2 (23.2 mL, 0.05 M) was subsequently added $NaHCO_3$ (244 mg, 2.9 mmol, 2.5 equiv) and Dess-Martin periodinane (DMP, 984 mg, 2.32 mmol, 2.0 equiv) at 0 °C. After stirring for 1 h at room temperature, the mixture was diluted with CH_2Cl_2 (20 mL) and quenched with 1 M aqueous $Na_2S_2O_3$ (20 mL) and saturated aqueous $NaHCO_3$ (20 mL). After stirring for 30 min, the aqueous layer was separated and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give the crude aldehyde.

To a white suspension of methyltriphenylphosphonium bromide (Ph_3PMeBr, 622 mg, 1.74 mmol, 1.5 equiv) in THF (6.0 mL) was added potassium *tert*-butoxide (1 M in THF, 1.62 mL, 1.62 mmol, 1.4 equiv) at 0 °C. After stirring for 30 min at 0 °C, a solution of the crude aldehyde in dry THF (2.0 mL) was added dropwise to the mixture. After stirring for 30 min at 0 °C, the reaction solution was diluted with EtOAc (20 mL) and quenched with saturated aqueous NH_4Cl (20 mL). After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40B, eluent: hexane/EtOAc = 1/0 to 4/1) to give terminal olefin **12c** as a colorless oil (386 mg, 76%). $[\alpha]_D^{29}$ – 31.14 (c 0.91, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 3:2 mixture of rotamers): δ 5.81 (ddd, *J* = 15.3, 7.2, 6.7 Hz, 1H, sph*H*5), 5.70 (ddd, *J* = 17.0, 10.2, 7.8 Hz, 1H, sph*H*1), 5.37 (dd, *J* = 15.3, 8.0 Hz, 1H, sph*H*4), 5.24–5.05 (m, 2H, *H*$_2$*C*=C-), 4.51 (dd, *J* = 8.0, 5.7 Hz, 1H, sph*H*3), 4.38–4.29 (m, 2/5H, sph*H*2), 4.23–4.16 (m, 3/5H, sph*H*2), 2.10–1.99 (m, 2H, sph*H*6), 1.67–1.39 (m, 15H, Boc (-*CH*$_3$) and acetonide (-*CH*$_3$)), 1.39–1.21 (m, 22H, sph*H*Alkyl), 0.87 (t, *J* = 6.9 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$, 3:2 mixture of rotamers): δ 152.0 (-O(*CO*)N-), 137.4 (sph*C*5), 134.5 (2/5C, sph*C*1), 133.9 (3/5C, sph*C*1), 124.5 (3/5C, sph*C*4), 124.4 (2/5C, sph*C*4), 117.6 (2/5C, *H*$_2$*C*=C-), 117.2 (3/5C, *H*$_2$*C*=C-), 93.3 (3/5C, acetonide(4°)), 92.9 (2/5C, acetonide(4°)), 80.3 (2/5C, Boc(4°)), 79.6 (3/5C, Boc(4°)), 78.2 (3/5C, sph*C*3), 78.0 (2/5C, sph*C*3), 63.7 (3/5C, sph*C*2), 63.5 (2/5C, sph*C*2), 32.5 (sph*C*6), 32.1 (sph*C*16), 29.82 (2C, sph*C*Alkyl), 29.80 (2C, sph*C*Alkyl), 29.7 (sph*C*Alkyl), 29.6 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 29.3 (sph*C*Alkyl), 29.0 (sph*C*Alkyl), 28.6 (3C, Boc(-*CH*$_3$)), 28.1 (2/5C, acetonide(-*CH*$_3$)), 27.3 (3/5C, acetonide(-*CH*$_3$)), 25.2 (2/5C, acetonide(-*CH*$_3$)), 24.1 (3/5C, acetonide(-*CH*$_3$)), 22.8 (sph*C*17), 14.3 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{27}H_{49}NaNO_3$, 458.3605; found, 458.3602.

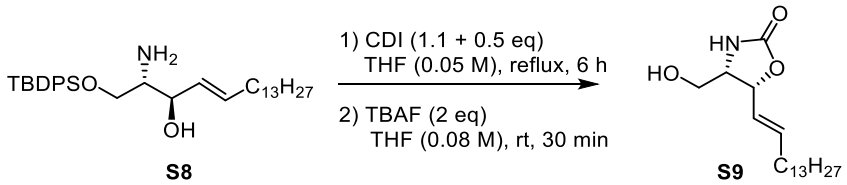
Compound S8



S4 **S8**

To a solution of azide **S4** (224 mg, 0.397 mmol, 1.0 equiv) in THF (3.4 mL, 0.1 M) was subsequently added 1 M aqueous NaOH (437 µL, 0.437 mmol, 1.1 equiv), trimethylphosphine (3 M in THF, 132 µL, 0.397 mmol, 1.0 equiv) at room temperature. After stirring for 18 h at room temperature, the solution was diluted with EtOAc (10 mL) and quenched with 1 M aqueous HCl (20 mL) at 0 °C. After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (50 mL), dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: $CHCl_3$/MeOH = 1/0 to 20/1) to give aminoalcohol **S8** as a colorless oil (184 mg, 86%). ^{1}H NMR spectrum of synthesized compound **S8** was consistent with a previous report.[6]

Compound S9



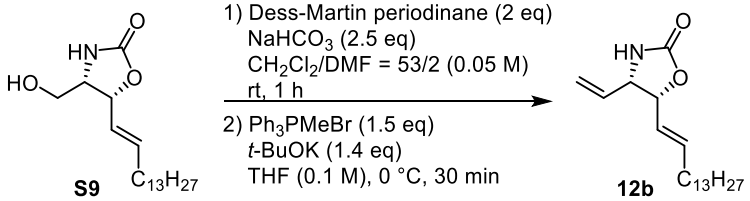
S8 **S9**

To a solution of **S8** (181 mg, 0.336 mmol, 1.0 equiv) in THF (6.72 mL, 0.05 M) was added 1,1'-carbonyldiimidazole (CDI, 60 mg, 0.370 mmo, 1.1 equiv) at 0 °C. After stirring for 4 h under reflux condition, additional CDI (27.2 mg, 0.168 mmol, 0.5 equiv) was added at 0 °C. After stirring for further 2 h under reflux condition, the solution was diluted with EtOAc (10 mL) and quenched with 1 M aqueous $NaHCO_3$ (20 mL) at 0 °C. After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (50 mL), dried over Na_2SO_4, concentrated under reduced pressure and co-evaporated with toluene two times to remove residual water to give cyclic carbamate.

The crude mixture was dissolved in THF (2.69 mL, 0.1 M) under Ar atmosphere. To the solution was added tetrabutylammonium fluoride (1 M in THF, 672 µL, 0.672 mmol, 2.0 equiv) at room temperature. After stirring for 30 min at room temperature, the solution was diluted with EtOAc (5 mL) and quenched with saturated aqueous NH_4Cl (10 mL). After separating layers, the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel

column chromatography (eluent: hexane/acetone = 5/1 to 1/1) to give primary alcohol **S9** as a white amorphous solid (89.8 mg, 82%). ^{1}H NMR spectrum of synthesized compound **S9** was consistent with a previous report.[7]

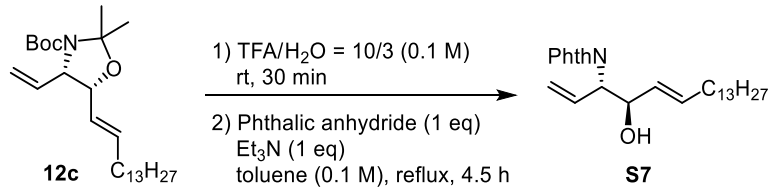
Compound 12b



To a solution of **S9** (89.4 mg, 0.275 mmol) in CH_2Cl_2/DMF (53/2, 5.5 mL, 0.05 M) was subsequently added $NaHCO_3$ (57.8 mg, 0.688 mmol, 2.5 equiv) and Dess-Martin periodinane (DMP, 233 mg, 0.55 mmol, 2.0 equiv) at 0 °C. After stirring for 1 h at room temperature, the solution was diluted with CH_2Cl_2 (10 mL) and quenched with 1 M aqueous $Na_2S_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (10 mL). After stirring for 30 min, the aqueous layer was separated and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give the crude aldehyde.

To a white suspension of methyltriphenylphosphonium bromide (Ph_3PMeBr, 148 mg, 0.413 mmol, 1.5 equiv) in THF (860 μL) was added potassium *tert*-butoxide (1 M in THF, 390 μL, 0.390 mmol, 1.4 equiv) at 0 °C. After stirring for 30 min at 0 °C, a solution of the crude aldehyde in dry THF (1 mL) was added dropwise to the mixture. After stirring for 30 min at 0 °C, the reaction solution was diluted with EtOAc (10 mL) and quenched with saturated aqueous NH_4Cl (20 mL). After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40A, eluent: hexane/EtOAc = 3/1 to 1/1) to give terminal olefin **12b** as a white amorphous (28.2 mg, 32%). $[\alpha]_D^{28}$ –2.70 (c 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 15.3, 8.0, 6.6 Hz, 1H, sph*H*5), 5.74 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H, sph*H*1), 5.42 (dddd, *J* = 15.3, 8.2, 1.4, 1.3 Hz, 1H, sph*H*4), 5.27 (d, *J* = 17.2 Hz, 1H, *H*$_2$*C*=C-), 5.26 (d, *J* = 10.2 H, 1H, *H*$_2$*C*=C-), 5.05 (dd, *J* = 8.2, 8.1 Hz, 1H, sph*H*3), 4.33 (dd, *J* = 8.1, 7.2 Hz, 1H, sph*H*2), 2.12–2.01 (m, 2H, sph*H*6), 1.76 (br s, 1H, *NH*), 1.40–1.32 (m, 2H, sph*H*7), 1.32–1.21 (m, 20H, sph*H*Alkyl), 0.87 (t, *J* = 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3 (-O(*CO*)N-), 138.2 (sph*C*5) 133.8 (sph*C*1), 123.2 (sph*C*4), 118.8 (*H*$_2$*C*=C-), 81.1 (sph*C*3), 58.8 (sph*C*2), 32.3 (sph*C*6), 32.1 (sph*C*Alkyl), 29.8 (4C, sph*C*Alkyl), 29.7 (sph*C*Alkyl), 29.6 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 29.2 (sph*C*Alkyl), 28.8 (sph*C*Alkyl), 22.8 (sph*C*Alkyl), 14.2 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{35}NaNO_2$, 344.2560; found, 344.2562.

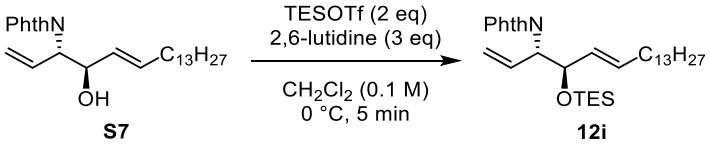
Compound S7



Acetondie **12c** (578 mg, 1.33 mmol, 1.0 equiv) was dissolved in trifluoroacetic acid and water (TFA/H_2O = 10:3, 13.3 mL, 0.1 M). After stirring for 30 min at room temperature, the resulting solution was concentrated under reduced pressure and co-evaporated with toluene for three times to remove residual water to give primary amine.

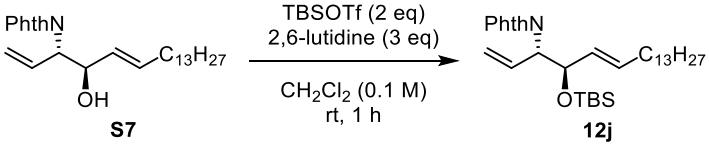
The crude mixture was dissolved in toluene (13.3 mL, 0.1 M) under Ar atmosphere, To the solution was subsequently added phthalic anhydride (197 mg, 1.33 mmol, 1.0 equiv) and triethylamine (180 μL, 1.33 mmol, 1.0 equiv) at 0 °C. After stirring for 4.5 h under reflux condition with Dean-Stark trap, the solution was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (30 mL). After separating layers, the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRA PACK Silica-40B, eluent: hexane/acetone = 7/1 to 2/1) to give secondary alcohol **S7** as a white amorphous solid (357 mg, 63%). $[\alpha]_D^{29}$ –23.34 (c 1.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H, *H*Phth), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, *H*Phth), 6.34 (ddd, *J* = 17.2, 10.4, 7.5 Hz, 1H, sph*H*1), 5.71 (ddd, *J* = 15.3, 7.7, 7.1 Hz, 1H, sph*H*5), 5.42 (dddd, *J* = 15.3, 7.5, 1.3, 1.3 Hz, 1H, sph*H*4), 5.33 (ddd, *J* = 10.4, 1.1, 1.0 Hz, 1H, H_2C=C-), 5.31 (ddd, *J* = 17.2, 1.1, 1.0 Hz, 1H, H_2C=C-), 4.69 (dddd, *J* = 7.5, 7.1, 1.0, 1.0 Hz, 1H, sph*H*2), 4.64 (dd, *J* = 7.5, 7.1 Hz, 1H, sph*H*3), 2.81 (s, 1H, 3-*OH*), 1.97–1.83 (m, 2H, sph*H*6), 1.33–1.04 (m, 22H, sph*H*Alkyl), 0.88 (t, *J* = 6.9 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3 (2C, -NH*C*(O)Phth), 135.8 (sph*C*5), 134.3 (2C, *C*Phth), 131.92 (sph*C*1), 131.87 (2C, *C*Phth), 128.6 (sph*C*4), 123.5 (2C, *C*Phth), 120.2 (H_2C=C-), 72.9 (sph*C*3), 59.2 (sph*C*2), 32.3 (sph*C*6), 32.1 (sph*C*Alkyl), 29.84 (sph*C*Alkyl), 29.81 (3C, sph*C*Alkyl), 29.6 (sph*C*Alkyl), 29.53 (sph*C*Alkyl), 29.51 (sph*C*Alkyl), 29.14 (sph*C*Alkyl), 29.09 (sph*C*Alkyl), 22.8 (sph*C*Alkyl), 14.3 (sph*C*Alkyl); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{27}H_{39}NaNO_3$, 448.2822; found, 448.2819.

Acceptor 12i



To a solution of secondary alcohol **S7** (85.9 mg, 0.202 mmol, 1.0 equiv) in CH_2Cl_2 (1.86 mL, 0.1 M) was subsequently added 2,6-lutidine (70.2 µL, 0.606 mmol, 3.0 equiv) and triethylsilyl trifluoromethanesulfonate (TESOTf, 90.7 µL, 0.404 mmol, 2.0 equiv) at 0 °C. After stirring for 5 min at 0 °C, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (10 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 9/1) to give silyl ether **12c** as a colorless oil (111 mg, quant). $[\alpha]_D^{29}$ –18.94 (c 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.68 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.32 (ddd, *J* = 17.6, 10.0, 7.2 Hz, 1H, sph*H*1), 5.48 (ddd, *J* = 15.3 , 7.3, 6.5 Hz, 1H, sph*H*5), 5.29 (dddd, *J* = 15.3, 8.4, 1.3, 1.2 Hz, 1H, sph*H*4), 5.220 (ddd, *J* = 17.6, 1.3, 1.1 Hz, 1H, H_2C=C-), 5.215 (ddd, *J* = 10.0, 1.3, 1.1 Hz, 1H, H_2C=C-), 4.68 (dd, *J* = 9.4, 8.4 Hz, 1H, sph*H*3), 4.61 (dddd, *J* = 9.4, 7.2, 1.1, 1.1 Hz, 1H, sph*H*2), 1.84–1.76 (m, 1H, sph*H*6), 1.76–1.68 (m, 1H, sph*H*6), 1.34–1.10 (m, 14H, sph*H*Alkyl), 1.08–0.90 (m, 17H, sph*H*Alkyl and Si-CH_2CH_3), 0.88 (t, *J* = 6.9 Hz, 3H, sph*H*18), 0.62–0.56 (m, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1 (2C, -NH*C*(O)Phth), 134.7 (sph*C*5), 134.0 (2C, *C*Phth), 133.4 (sph*C*1), 132.1(2C, *C*Phth), 130.5 (sph*C*4), 123.3 (2C, *C*Phth), 118.8 (H_2C=C-), 73.4 (sph*C*3), 58.9 (sph*C*2), 32.11 (sph*C*6), 32.07 (sph*C*Alkyl), 29.84 (sph*C*Alkyl), 29.81 (3C, sph*C*Alkyl), 29.55 (sph*C*Alkyl), 29.50 (2C, sph*C*Alkyl), 29.2 (sph*C*Alkyl), 29.0 (sph*C*Alkyl), 22.8 (sph*C*Alkyl), 14.3 (sph*C*Alkyl), 6.9 (3C, Si-CH_2CH_3), 5.2 (3C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{33}H_{53}NaNO_3Si$, 562.3687; found, 562.3685.

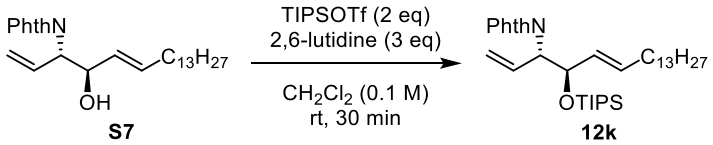
Acceptor 12j



To a solution of secondary alcohol **S7** (21.2 mg, 49.8 µmol, 1.0 equiv) in CH_2Cl_2 (0.458 mL, 0.1 M) was subsequently added 2,6-lutidine (17.0 µL, 0.149 mmol, 3.0 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 22.9 µL, 99.6 µmol, 2.0 equiv) at 0 °C.

After stirring for 1 hour at 0 °C, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (10 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 9/1) to give silyl ether **12j** as a colorless oil (22.7 mg, 84%). $[\alpha]_D^{28}$ –11.08 (c 0.64, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.68 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.31 (ddd, *J* = 17.5, 10.0, 7.4 Hz, 1H, sph*H*1), 5.48 (ddd, *J* = 15.4, 7.2, 7.0 Hz, 1H, sph*H*5), 5.27 (dddd, *J* = 15.4, 8.4, 1.2, 1.2 Hz, 1H, sph*H*4), 5.221 (ddd, *J* = 17.5, 1.3, 1.2 Hz, 1H, *H*$_2$*C*=C-), 5.220 (ddd, *J* = 10.0, 1.3, 1.1 Hz, 1H, *H*$_2$*C*=C-), 4.67 (dd, *J* = 9.4, 8.4 Hz, 1H, sph*H*3), 4.60 (dddd, *J* = 9.4, 7.4, 1.2, 1.1 Hz, 1H, sph*H*2), 1.85–1.76 (m, 1H, sph*H*6), 1.76–1.67 (m, 1H, sph*H*6), 1.34–0.91 (m, 22H, sph*H*Alkyl), 0.91–0.84 (m, 12H, sph*H*18 and Si-C(*CH*$_3$)$_3$), 0.06 (s, 3H, Si-*CH*$_3$), 0.02 (s, 3H, Si-*CH*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1 (2C, -NH*C*(O)Phth), 134.7 (sph*C*5), 134.0 (2C, *C*Phth), 133.5 (sph*C*1), 132.1 (2C, *C*Phth), 130.5 (sph*C*4), 123.3 (2C, *C*Phth), 118.9 (*H*$_2$*C*=C-), 73.7 (sph*C*3), 59.1 (sph*C*2), 32.11 (sph*C*6), 32.08 (sph*C*Alkyl), 29.84 (sph*C*Alkyl), 29.81 (3C, sph*C*Alkyl), 29.55 (sph*C*Alkyl), 29.52 (sph*C*Alkyl), 29.50 (sph*C*Alkyl), 29.2 (sph*C*Alkyl), 29.0 (sph*C*Alkyl), 26.0 (3C, Si-C(*CH*$_3$)$_3$), 22.8 (sph*C*Alkyl), 18.3 (Si-*C*(CH$_3$)$_3$), 14.3 (sph*C*18), –3.8 (Si-*CH*$_3$), –4.5 (Si-*CH*$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{33}H_{53}NaNO_3Si$, 562.3687; found, 562.3686.

Acceptor 12k



To a solution of secondary alcohol **S7** (83.1 mg, 0.195 mmol, 1.0 equiv) in CH_2Cl_2 (1.78 mL, 0.1 M) was subsequently added 2,6-lutidine (68.0 µL, 0.586 mmol, 3.0 equiv) and triisopropylsilyl trifluoromethanesulfonate (TIPSOTf, 106 µL, 0.390 mmol, 2.0 equiv) at 0 °C. After stirring for 30 min at 0 °C, the solution was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 9/1) to give silyl ether **12k** as a colorless oil (113 mg, quant). $[\alpha]_D^{28}$ –29.97 (c 0.60, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 7.68 (dd, *J* = 5.5, 3.1 Hz, 2H, *H*Phth), 6.39 (ddd, *J* = 17.1, 10.5, 7.4 Hz, 1H, sph*H*1), 5.45 (ddd, *J* = 15.4, 7.5, 6.3 Hz, 1H, sph*H*5), 5.31 (dddd, *J* = 15.4, 8.7, 1.2, 1.1 Hz, 1H, sph*H*4), 5.23

(ddd, *J* = 17.1, 1.3, 1.1 Hz, 1H, H_2C=C-), 5.22 (ddd, *J* = 10.5, 1.3, 1.1 Hz, 1H, H_2C=C-), 4.82 (dd, *J* = 9.4, 8.7 Hz, 1H, sph*H*3), 4.61 (dddd, *J* = 9.4, 7.4, 1.1, 1.1 Hz, 1H, sph*H*2), 1.84–1.75 (m, 1H, sph*H*6), 1.75–1.66 (m, 1H, sph*H*6), 1.34–1.10 (m, 14H, sph*H*Alkyl), 1.10–0.90 (m, 29H, sph*H*Alkyl and *H*TIPS), 0.88 (t, *J* = 6.9 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, $CDCl_3$): δ168.3 (2C, -NH*C*(O)Phth), 134.8 (sph*C*5), 134.1 (2C, *C*Phth), 133.7 (sph*C*1), 132.2 (2C, *C*Phth), 131.0 (sph*C*4), 123.4 (2C, *C*Phth), 119.0 (H_2C=C-), 74.0 (sph*C*3), 59.4 (sph*C*2), 32.25 (sph*C*6), 32.22 (sph*C*Alkyl), 29.99 (sph*C*Alkyl), 29.96 (3C, sph*C*Alkyl), 29.69 (sph*C*Alkyl), 29.66 (2C, sph*C*Alkyl), 29.3 (sph*C*Alkyl), 29.2 (sph*C*Alkyl), 23.0 (sph*C*Alkyl), 18.5 (3C, Si-CH(CH_3)$_2$), 18.4 (3C, Si-CH(CH_3)$_2$), 14.4 (sph*C*18), 12.8 (3C, Si-*CH*(CH_3)$_2$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{36}H_{59}NaNO_3Si$, 604.4156; found, 604.4153.

4. Radical Coupling Reaction of Donor 11 with Acceptor 12

General Procedure A for Radical Coupling Reaction

A degassed solution of xanthate donor **10** (1 equiv) and olefin acceptor **11** (2 equiv) in 1,2-dichloromethane (1 M) was refluxed for 15 min. Lauroyl peroxide (15 mol%) in 1,2-dichloroethane was then added to the refluxing solution in three portions every 90 min. After stirring for further 90 min under reflux condition, the reaction mixture was cooled to room temperature and directly purified by silica gel column chromatography or gel permeation chromatography to give the desired coupling product **15** along with recovered donor **11** and acceptor **12**.

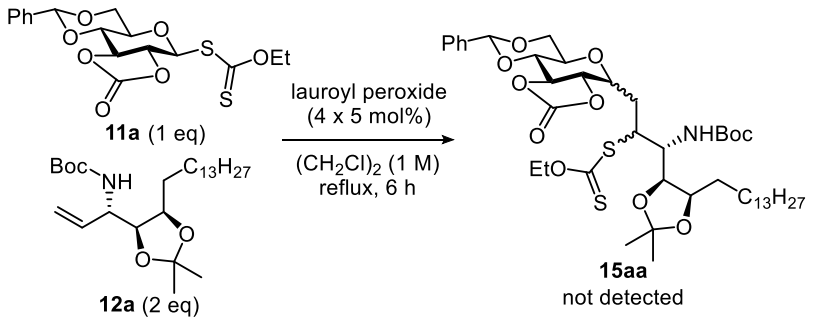
General Procedure B for Reduction of Xanthate

A degassed solution of glycolipid **15** (1 equiv) and tributhyltin hydride (1.5 equiv) in toluene (0.1 M) was stirred for 15 min at 45 °C. To the reaction mixture was added a solution of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70, 10 mol%) in toluene (0.1 M) at 45 °C. After stirring for 3 h at 45 °C, the reaction solution was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give *C*-glycoside **16**.

General Method to Determine the Stereochemistry of Anomeric Position

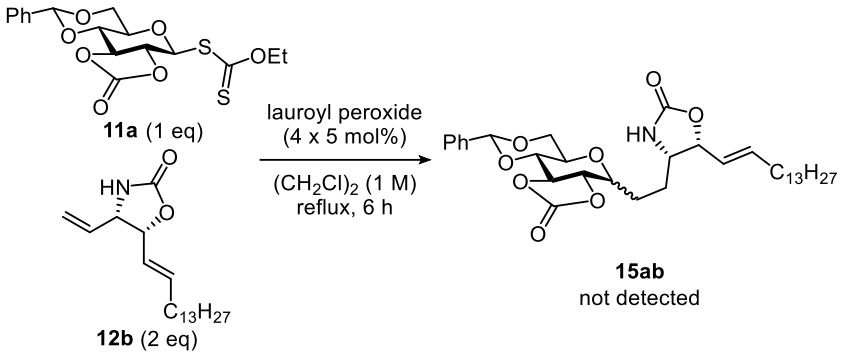
The stereochemistry of anomeric position (*C1*) was determined by the coupling constant between *H*1 and the adjacent *H*2. While β-isomers have large coupling constant (9-11 Hz), α-isomers have small coupling constant (3-6 Hz), due to the rigid chair conformations immobilized by cyclic protecting groups.

Coupling reaction of 11a and 12a (Desired products were not observed)



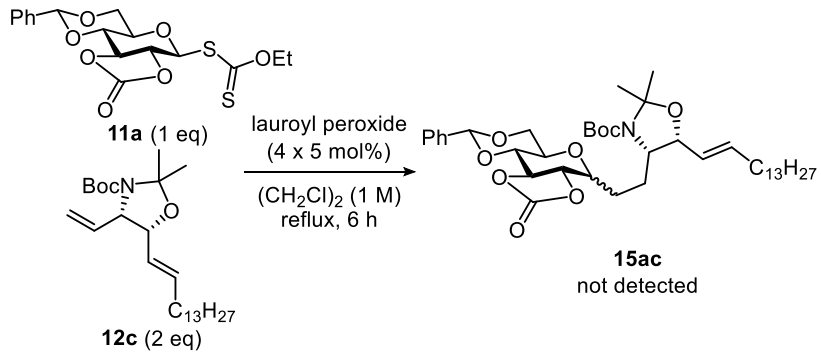
General procedure **A** was followed for the reaction of **11a** (43.4 mg, 109 μmol, 1.0 equiv) and acceptor **12a** (99.1 mg, 217 μmol, 2.0 equiv) with the exception adding lauroyl peroxide (8.8 mg, 22 μmol, 20 mol%) in four portions. The reaction mixture was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40A, eluent: hexane/EtOAc = 50/1 to 3/2) resulting in starting material recovery (donor **11a**: 43.4 mg, quant, α:β = 1:3; acceptor **12a**: 90.2 mg, 91%).

Coupling reaction of 11a and 12b (Desired products were not observed)



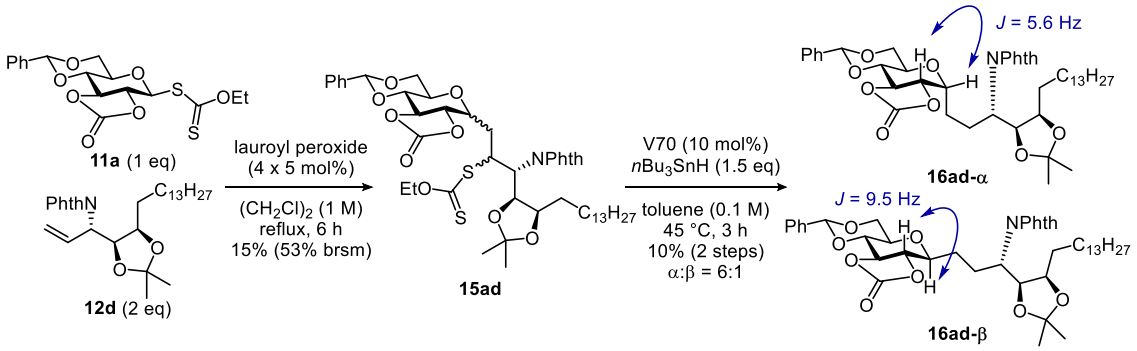
General procedure **A** was followed for the reaction of donor **11a** (17.2 mg, 43.1 μmol, 1.0 equiv) and acceptor **12b** (27.7 mg, 86.2 μmol, 2.0 equiv). The reaction mixture was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40A, eluent: hexane/EtOAc = 9/1 to 3/2) resulting in starting material recovery (donor **11a**: 43.4 mg, 93%, α:β = 1:4; acceptor **12b**: 20.6 mg, 74%).

Coupling reaction of 11a and 12c (Desired products were not observed)



General procedure **A** was followed for the reaction of donor **11a** (21.3 mg, 53.5 μmol, 1.0 equiv) and acceptor **12c** (46.5 mg, 107 μmol, 2.0 equiv). The reaction mixture was purified by MPLC (column: Yamazen, ULTRAPACK Silica-40A, eluent: hexane/EtOAc = 1/0 to 3/2) resulting in starting material recovery (donor **11a**: 14.5 mg, 68%., α:β = 1:6, acceptor **12c** (35.9 mg, 77%).

Coupling products 16ad-α and 16ad-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11a** (35.5 mg, 89.1 μmol, 1.0 equiv) and acceptor **12d** (86.2 mg, 178 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15ad** as a colorless oil (14.0 mg, 18%) along with recovered donor **11a** (23.3 mg, 66%, α:β = 1:3) and acceptor **12d** (63.8 mg, 74%). **15ad**: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{47}H_{63}NaNO_{11}S_2$, 904.3735; found, 904.3749.

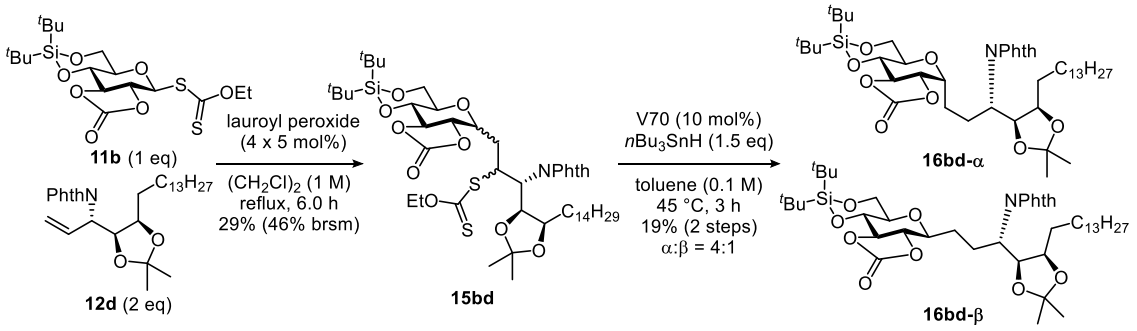
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15ad** (14.0 mg, 15.9 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16ad-α**:**16ad-β** = 6:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 2/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 11/2 to 1/1) to give **16ad-α** as a colorless oil (5.3 mg, 44%) and **16ad-β** as a colorless oil (1.5 mg, 12%).

16ad-α: $[\alpha]_D^{26}$ –27.56 (c 0.53, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.88–7.86 (m, 4H, *H*Phth), 7.49–7.44 (m, 2H, *H*Ph), 7.39–7.35 (m, 3H, *H*Ph), 5.73 (s, 1H, -*CH*Ph), 4.92 (dd, *J* = 10.2, 5.2 Hz, 1H, sph*H*3), 4.87 (dd, *J* = 11.4, 10.0 Hz, 1H, glc*H*3), 4.59 (dd, *J* = 11.4, 5.6 Hz, 1H, glc*H*2), 4.41 (ddd, *J* = 10.6, 5.6, 4.2 Hz, 1H, glc*H*1), 4.37 (ddd, *J* = 10.4, 10.2, 3.7 Hz, 1H, sph*H*2), 4.22 (dd, *J* = 10.2, 4.7 Hz, 1H, glc*H*6eq), 4.21 (dd, *J* = 10.2, 10.0 Hz, 1H, glc*H*4), 4.08 (ddd, *J* = 9.9, 5.2, 4.1 Hz, 1H, sph*H*4), 3.89 (dd, *J* = 10.2, 9.8 Hz, 1H, glc*H*6ax), 3.77 (ddd, *J* = 10.2, 9.8, 4.7 Hz, 1H, glc*H*5), 2.38–2.30 (m, 1H, sph*H*1), 2.22–2.12 (m, 1H, sph*H*1), 2.12–2.02 (m, 1H, glc-*CH*$_2$-sph), 1.72–1.62 (m, 1H, glc-*CH*$_2$-sph), 1.58–1.48 (m, 1H, sph*H*5), 1.48 (s, 3H, acetonide(-*CH*$_3$)), 1.46–1.38 (m, 1H, sph*H*5), 1.35 (s, 3H, acetonide(-*CH*$_3$)), 1.33–1.01 (m, 24H, sph*H*6–*H*17), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, acetone-d6): δ 169.1 (2C, -NH*C*(O)Phth), 154.1 (-*C*=O), 138.4 (*C*Ph), 135.4 (2C, *C*Phth), 132.6 (2C, *C*Phth), 129.8 (*C*Ph), 128.9 (2C, *C*Ph), 127.2 (2C, *C*Ph), 124.0 (2C, *C*Phth), 108.4 (acetonide(4°)), 101.8 (-*CH*Ph), 80.7 (glc*C*4), 78.9 (glc*C*2), 78.5 (sph*C*4), 78.0 (glc*C*3), 76.7 (sph*C*3), 75.4 (glc*C*1), 69.3 (glc*C*6), 66.8 (glc*C*5), 51.6 (sph*C*2), 32.6 (sph*C*Alkyl), 30.4–29.4 (11C, sph*C*Alkyl), 28.8 (acetonide(-*CH*$_3$)),

26.9 (sph*C*1), 26.3 (acetonide(-*CH*$_3$)), 23.3 (sph*C*Alkyl), 22.5 (glc-*CH*$_2$-sph), 14.4 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{44}H_{59}NaNO_{11}$, 784.4031; found, 784.4031.

16ad-β: $[\alpha]_D^{26}$ –31.73 (c 0.15, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.91–7.89 (m, 4H, *H*Phth), 7.49–7.45 (m, 2H, *H*Ph), 7.39–7.35 (m, 3H, *H*Ph), 5.72 (s, 1H, -*CH*Ph), 4.93 (dd, *J* = 10.2, 5.2 Hz, 1H, sph*H*3), 4.73 (dd, *J* = 10.4, 9.8 Hz, 1H, glc*H*3), 4.36–4.27 (m, 1H, sph*H*2), 4.23 (dd, *J* = 10.3, 4.8 Hz, 1H, glc*H*6eq), 4.20 (dd, *J* = 9.8, 8.6 Hz, 1H, glc*H*4), 4.11 (dd, *J* = 10.4, 9.5 Hz, 1H, glc*H*2), 4.08 (ddd, *J* = 11.0, 5.2, 4.0 Hz, 1H, sph*H*4), 4.06 (ddd, *J* = 9.5, 8.1, 4.0 Hz, 1H, glc*H*1), 3.85 (dd, *J* = 10.3, 10.3 Hz, 1H, glc*H*6ax), 3.65 (ddd, *J* = 10.3, 8.6, 4.8 Hz, 1H, glc*H*5), 2.26–2.19 (m, 2H, sph*H*1), 1.76–1.68 (m, 1H, glc-*CH*$_2$-sph), 1.58–1.50 (m, 2H, sph*H*5 and glc-*CH*$_2$-sph), 1.46 (s, 3H, acetonide(-*CH*$_3$)), 1.45–1.39 (m, 1H, sph*H*5), 1.35 (s, 3H, acetonide(-*CH*$_3$)), 1.33–1.01 (m, 24H, sph*H*6–*H*17), 0.88 (dd, *J* = 7.1, 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, acetone-d6): δ 169.1 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 138.3 (*C*Ph), 135.5 (2C, *C*Phth), 132.5 (2C, *C*Phth), 129.8 (*C*Ph), 128.9 (2C, *C*Ph), 127.2 (2C, *C*Ph), 124.1 (2C, *C*Phth), 108.5 (acetonide(4°)), 101.8 (-*CH*Ph), 81.9 (glc*C*3), 80.9 (glc*C*2), 79.6 (glc*C*4), 78.5 (sph*C*4), 77.9 (glc*C*1), 76.5 (sph*C*3), 73.0 (glc*C*5), 68.9 (glc*C*6), 51.3 (sph*C*2), 32.6 (sph*C*Alkyl), 30.4–29.4 (11C, sph*C*Alkyl), 28.9 (acetonide(-*CH*$_3$)), 26.9 (acetonide(-*CH*$_3$)), 26.3 (sph*C*1), 25.7 (glc-*CH*$_2$-sph), 23.3 (sph*C*Alkyl), 14.4 (ph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{44}H_{59}NaNO_{10}$, 784.4037; found, 784.4034.

Coupling products 16bd-α and 16bd-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (27.5 mg, 61.0 µmol, 1.0 equiv) and acceptor **12d** (58.9 mg, 122 µmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bd** as a colorless oil (16.4 mg, 29%) along with recovered donor **11b** (10.1 mg, 37%, α:β = 1:1) and acceptor **12d** (40.5 mg, 69%). **15bd**: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{75}NaNO_{11}S_2Si$, 956.4443; found, 956.4444.

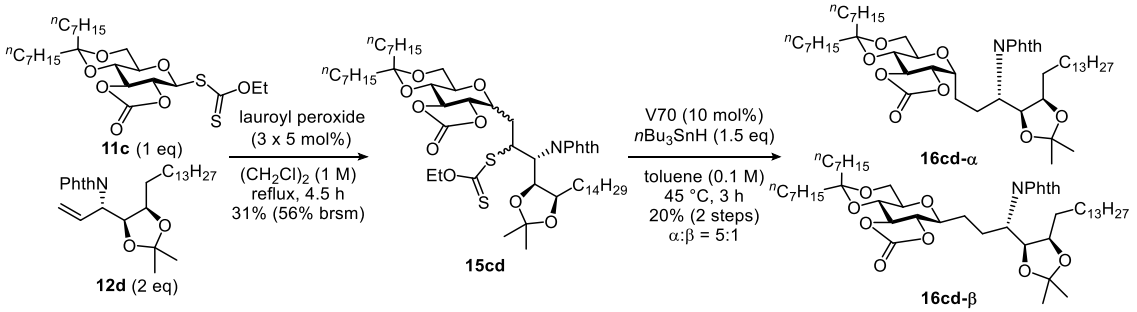
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15bd** (16.4 mg, 17.6 µmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined

by ^{1}H NMR of crude reaction mixture (**16bd-α**:**16bd-β** = 4:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 11/2) to give **16bd-α** as a colorless oil (7.3 mg, 51%) and a mixture of **16bd-β** and unknown byproducts (1.8 mg, <13%).

16bd-α: $[\alpha]_D^{21}$ –15.49 (c 0.73, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.88–7.86 (m, 4H, *H*Phth), 4.88 (dd, *J* = 10.1, 5.1 Hz, 1H, sph*H*3), 4.71 (dd, *J* = 11.6, 9.5 Hz, 1H, glc*H*3), 4.53 (dd, *J* = 11.6, 5.6 Hz, 1H, glc*H*2), 4.37–4.29 (m, 3H, glc*H*1, glc*H*4, and sph*H*2), 4.17 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 4.09 (ddd, *J* = 9.4, 5.1, 4.5 Hz, 1H, sph*H*4), 3.94 (dd, *J* = 10.1, 9.9 Hz, 1H, glc*H*6ax), 3.77 (ddd, *J* = 9.9, 8.9, 5.0 Hz, 1H, glc*H*5), 2.33–2.26 (m, 1H, sph*H*1), 2.21–2.12 (m, 1H, sph*H*1), 2.04–1.94 (m, 1H, glc-*CH*$_2$-sph), 1.65–1.57 (m, 1H, glc-*CH*$_2$-sph), 1.57–1.48 (m, 1H, sph*H*5), 1.46 (s, 3H, acetonide(-*CH*$_3$)), 1.45–1.37 (m, 1H, sph*H*5), 1.34 (s, 3H, acetonide(-*CH*$_3$)), 1.33–1.02 (m, 24H, sph*H*6–*H*17), 1.06 (s, 9H, Si-C(*CH*$_3$)$_3$), 1.01 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.88 (dd, *J* = 7.1, 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, acetone-d6): δ 169.1 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 135.4 (2C, *C*Phth), 132.5 (2C, *C*Phth), 124.0 (2C, *C*Phth), 108.3 (acetonide(4°)), 80.8 (glc*C*3), 78.7 (sph*C*4), 78.1 (glc*C*2), 76.5 (sph*C*3), 76.4 (glc*C*1), 75.1 (glc*C*4), 70.6 (glc*C*5), 67.3 (glc*C*6), 51.7 (sph*C*2), 32.6 (sph*C*Alkyl), 30.4–29.4 (10C, sph*C*Alkyl), 28.9 (acetonide(-*CH*$_3$)), 27.7 (3C, Si-C(*CH*$_3$)$_3$), 27.4 (3C, Si-C(*CH*$_3$)$_3$), 27.1 (sph*C*Alkyl), 26.8 (sph*C*1), 26.2 (acetonide(-*CH*$_3$)), 23.3 (sph*C*Alkyl), 23.1 (Si-*C*(CH$_3$)$_3$), 22.4 (glc-*CH*$_2$-sph), 20.5 (Si-*C*(CH$_3$)$_3$), 14.4 (sph*C*18); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{45}H_{71}NaNO_{10}Si$, 836.4739; found, 836.4736.

16bd-β: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{45}H_{71}NaNO_{10}Si$, 836.4739; found, 836.4743.

Coupling products 16cd-α and 16cd-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11c** (40.5 mg, 78.1 μmol, 1.0 equiv) and acceptor **12d** (75.5 mg, 156 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15ad** as a colorless oil (24.2 mg, 31%) along with recovered donor **11c** (18.1 mg, 45%, α:β = 3:4) and acceptor **12d** (49.7 mg, 73%).

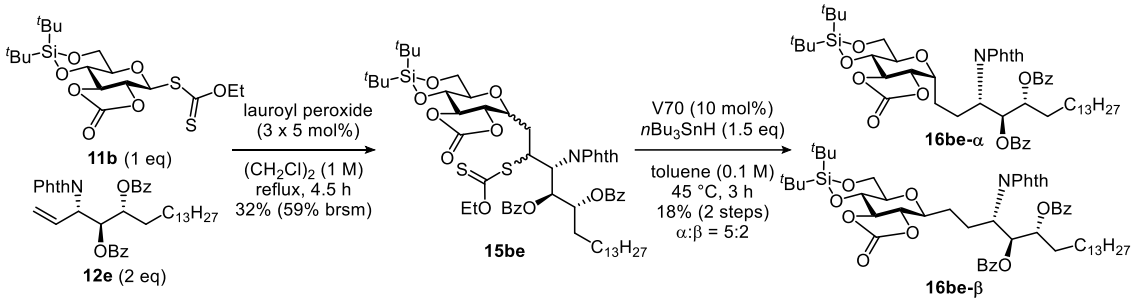
15cd: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{55}H_{87}NaNO_{11}S_2$, 1024.5618; found, 1024.5615.
For analytical sample, a mixture of α-, and β-isomers of compound **11c** were separated by MPLC (column: Yamazen, ULTRA PACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 5/1)
11c-α: $[\alpha]_D^{21}$ +32.41 (c 1.13, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56 (d, *J* = 5.0 Hz, 1H, *H*1), 4.68 (q, *J* = 7.1 Hz, 2H, SCSO*CH*$_2$CH$_3$), 4.56 (dd, *J* = 11.4, 5.0 Hz, 1H, *H*2), 4.30 (dd, *J* = 11.4, 9.6 Hz, 1H, *H*3), 4.09 (dd, *J* = 9.6, 9.4 Hz, 1H, *H*4), 3.90 (dd, *J* = 10.8, 5.7 Hz, 1H, *H*6eq), 3.86 (dd, *J* = 10.8, 9.8 Hz, 1H, *H*6ax), 3.65 (ddd, *J* = 9.8, 9.4, 5.7 Hz, 1H, *H*5), 1.91–1.82 (m, 1H, *H*Alkyl), 1.81–1.72 (m, 1H, *H*Alkyl), 1.65–1.53 (m, 2H, *H*Alkyl), 1.46 (t, *J* = 7.1 Hz, 3H, SCSOCH$_2$*CH*$_3$), 1.41–1.21 (m, 20H, *H*Alkyl), 0.90–0.86 (m, 6H, *H*Alkyl); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.5 (S*C*SOCH$_2$CH$_3$), 152.7 (-*C*=O), 103.4 (acetal(4º)), 84.6 (*C*1), 79.6 (*C*3), 76.5 (*C*2), 71.7 (*C*4), 71.4 (SCSO*CH*$_2$CH$_3$), 69.4 (*C*5), 61.3 (*C*6), 38.2 (*C*Alkyl), 32.0 (*C*Alkyl), 31.9 (*C*Alkyl), 29.94 (*C*Alkyl), 29.86 (*C*Alkyl), 29.7 (*C*Alkyl), 29.4 (*C*Alkyl), 29.3 (*C*Alkyl), 23.8 (*C*Alkyl), 22.81 (*C*Alkyl), 22.79 (*C*Alkyl), 22.69 (*C*Alkyl), 14.2 (2C, *C*Alkyl), 13.8 (SCSOCH$_2$*CH*$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{25}H_{42}NaO_7S_2$, 541.2270; found, 541.2263.

Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15cd** (24.2 mg, 24.1 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16cd-α**:**16cd-β** = 5:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 11/2) to give **16cd-α** as a colorless oil (11.3 mg, 53%) and a mixture of **16cd-β** and unknown byproducts (2.3 mg, <11%).
16cd-α: $[\alpha]_D^{27}$ –6.55 (c 1.13, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.90–7.88 (m, 4H, *H*Phth), 4.90 (dd, *J* = 10.1, 5.2 Hz, 1H, sph*H*3), 4.70 (dd, *J* = 11.4, 9.7 Hz, 1H, glc*H*3), 4.53 (dd, *J* = 11.4, 5.6 Hz, 1H, glc*H*2), 4.38–4.30 (m, 2H, glc*H*1, sph*H*2), 4.21 (dd, *J* = 9.7, 9.4 Hz, 1H, glc*H*4), 4.08 (ddd, *J* = 10.0, 5.2, 4.1 Hz, 1H, sph*H*4), 3.85 (dd, *J* = 10.5, 10.1 Hz, 1H, sph*H*6ax), 3.81 (dd, *J* = 10.5, 5.3 Hz, 1H, glc*H*6eq), 3.55 (ddd, *J* = 10.1, 9.4, 5.3 Hz, 1H, glc*H*5), 2.35–2.27 (m, 1H, sph*H*1), 2.19–2.08 (m, 1H, sph*H*1), 2.05–1.94 (m, 1H, glc-*CH*$_2$-sph), 1.87–1.80 (m, 1H, glc-*CH*$_2$-sph), 1.65–1.49 (m, 3H, sph*H*5 and *H*hep), 1.47 (s, 3H, acetonide(-*CH*$_3$)), 1.46–1.37 (m, 3H, sph*H*5 and *H*hep), 1.35 (s, 3H, acetonide(-*CH*$_3$)), 1.34–0.99 (m, 44H, sph*H*6–*H*17 and *H*hep), 0.92–0.84 (m, 9H, sph*H*18 and *H*hep (-*CH*$_3$)); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 135.4 (2C, *C*Phth), 132.6 (2C, *C*Phth), 124.0 (2C, *C*Phth), 108.4 (acetonide(4°)), 103.3 (acetal(4°)), 78.9 (glc*C*2), 78.6 (sph*C*4), 78.5 (glc*C*3), 76.8 (sph*C*3), 75.4 (glc*C*1), 73.3 (glc*C*4), 67.7 (glc*C*5), 62.5 (glc*C*6), 51.6 (sph*C*2), 39.0 (*C*Alkyl), 32.64 (*C*Alkyl), 32.62 (*C*Alkyl), 32.58 (*C*Alkyl), 30.5 (*C*Alkyl), 30.4–29.4 (15C, *C*Alkyl), 28.8 (acetonide(-*CH*$_3$)),

27.0 (sph*C*1), 26.9 (acetonide(-*CH*$_3$)), 26.3 (*C*Alkyl), 24.5 (*C*Alkyl), 23.34 (2C, *C*Alkyl), 23.30 (*C*Alkyl), 22.6 (glc-*CH*$_2$-sph), 14.4 (3C, sph*C*18 and *C*hep (-*CH*$_3$)); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{52}H_{83}NaNO_{10}$, 904.5909; found, 904.5917.

16cd-β: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{52}H_{83}NaNO_{10}$, 904.5909; found, 904.5912.

Coupling products 16be-α and 16be-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (31.3 mg, 69.5 μmol, 1.0 equiv) and acceptor **12e** (90.6 mg, 139 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15be** as a colorless oil (24.8 mg, 32%) along with recovered donor **11b** (12.6 mg, 40%, α:β = 1:1) and acceptor **12e** (54.7 mg, 60%).

15be: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{59}H_{79}NaNO_{13}S_2Si$, 1124.4654; found, 1124.4651.

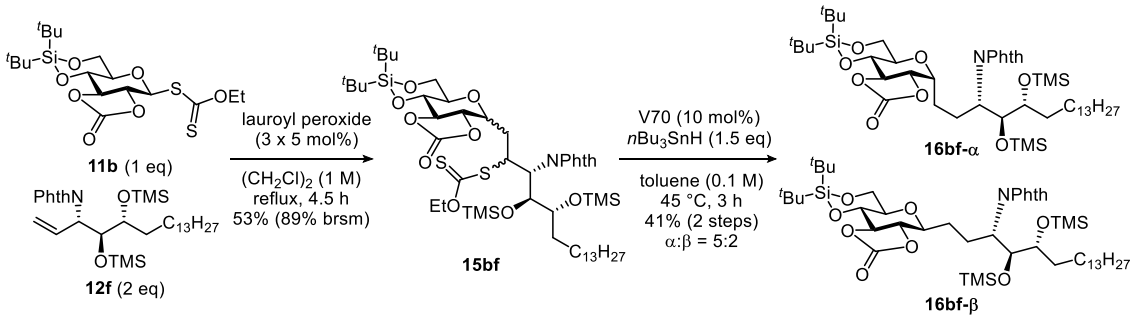
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15be** (24.8 mg, 28.8 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16be-α**:**16be-β** = 5:2). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 9/1 to 3/1) to give **16be-α** as a colorless oil (11.6 mg, 54%) and **16be-β** as a colorless oil (4.1 mg, 20%).

16be-α: $[\alpha]_D^{21}$ +10.12 (c 1.16, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 8.12 (dd, *J* = 8.1, 1.0 Hz, 2H, *H*Bz), 7.96 (dd, *J* = 8.1, 1.0 Hz, 2H, *H*Bz), 7.90–7.85 (m, 4H, *H*Phth), 7.71 (dddd, *J* = 7.7, 7.1, 1.2, 1.2 Hz, 1H, *H*Bz), 7.62 (dddd, *J* = 7.5, 7.3, 1.3, 1.2 Hz, 1H, *H*Bz), 7.57 (dd, *J* = 7.9, 7.6 Hz, 2H, *H*Bz), 7.47 (dd, *J* = 7.9, 7.6 Hz, 2H, *H*Bz), 6.02 (dd, *J* = 7.9, 4.3 Hz, 1H, sph*H*3), 5.40 (ddd, *J* = 10.8, 6.2, 4.3 Hz, 1H, sph*H*2), 4.76 (ddd, *J* = 11.6, 7.9, 3.2 Hz, 1H, sph*H*4), 4.65 (dd, *J* = 11.6, 9.5 Hz, 1H, glc*H*3), 4.49 (dd, *J* = 11.6, 5.7 Hz, 1H, glc*H*2), 4.36 (ddd, *J* = 10.8, 5.7, 3.4 Hz, 1H, glc*H*1), 4.28 (dd, *J* = 9.5, 9.1 Hz, 1H, glc*H*4), 3.98 (dd, *J* = 10.0, 5.1 Hz, 1H, glc*H*6eq), 3.79 (dd, *J* = 10.0, 9.8 Hz, 1H, glc*H*6ax), 3.60 (ddd, *J* = 9.8, 9.1, 5.1 Hz, 1H, glc*H*5), 2.66–2.57 (m, 1H, sph*H*5), 2.19–2.11 (m, 1H, sph*H*5), 2.04–1.97 (m, 1H, glc-*CH*$_2$-sph), 1.91–1.86 (m, 2H,

sph*H*1), 1.70–1.63 (m, 1H, glc-*CH*$_2$-sph), 1.43–1.15 (m, 24H, sph*H*6–*H*17), 1.03 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.95 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.87 (t, *J* = 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 166.3 (-O*C*(O)Ph), 166.2 (-O*C*(O)Ph), 154.3 (-*C*=O), 135.5 (2C, *C*Phth), 134.4 (*C*Bz), 134.1 (*C*Bz), 132.6 (2C, *C*Phth), 130.9 (*C*Bz), 130.8 (*C*Bz), 130.5 (2C, *C*Bz), 130.4 (2C, *C*Bz), 129.6 (2C, *C*Bz), 129.4 (2C, *C*Bz), 124.2 (2C, *C*Phth), 80.7 (glc*C*3), 80.0 (glc*C*2), 76.4 (glc*C*4), 75.3 (glc*C*1), 74.4 (sph*C*3), 73.8 (sph*C*2), 70.6 (glc*C*5), 67.1 (glc*C*6), 52.3 (sph*C*4), 32.6 (sph*C*Alkyl), 30.4–29.4 (10C, sph*C*Alkyl), 27.7 (3C, Si-C(*CH*$_3$)$_3$), 27.4 (3C, Si-C(*CH*$_3$)$_3$), 25.9 (sph*C*1), 24.7 (sph*C*5), 23.3 (sph*C*Alkyl), 23.1 (Si-*C*(CH$_3$)$_3$), 22.1 (glc-*CH*$_2$-sph), 20.5 (Si-*C*(CH$_3$)$_3$), 14.4 (sph*C*18); HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{56}H_{75}NaNO_{12}Si$, 1004.4951; found, 1004.4970.

16be-β: $[\alpha]_D^{21}$ +3.24 (c 0.41, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 8.14 (dd, *J* = 8.4, 1.3 Hz, 2H, *H*Bz), 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H, *H*Bz), 7.91–7.89 (m, 4H, *H*Phth), 7.71 (dddd, *J* = 7.8, 7.0, 1.3, 1.3 Hz, 1H, *H*Bz), 7.60 (dddd, *J* = 7.7, 6.5, 1.3, 1.3 Hz, 1H, *H*Bz), 7.58 (dd, *J* = 7.9, 7.4 Hz, 2H, *H*Bz), 7.44 (dd, *J* = 8.2, 7.6 Hz, 2H, *H*Bz), 6.13 (dd, *J* = 9.0, 3.5 Hz, 1H, sph*H*3), 5.40 (ddd, *J* = 8.1, 4.4, 3.6 Hz, 1H, sph*H*2), 4.76 (ddd, *J* = 11.4, 9.0, 3.7 Hz, 1H, sph*H*4), 4.50 (dd, *J* = 10.6, 9.5 Hz, 1H, glc*H*2), 4.26 (dd, *J* = 9.5, 8.6 Hz, 1H, glc*H*3), 4.03–3.95 (m, 3H, glc*H*6eq, glc*H*4, glc*H*1), 3.78 (dd, *J* = 10.3, 10.2 Hz, 1H, glc*H*6ax), 3.61 (ddd, *J* = 10.3, 8.6, 5.1 Hz, 1H, glc*H*5), 2.52–2.42 (m, 1H, sph*H*5), 2.10–2.04 (m, 1H, sph*H*5), 1.94–1.86 (m, 2H, sph*H*1), 1.76–1.67 (m, 1H, glc-*CH*$_2$-sph), 1.58–1.48 (m, 1H, glc-*CH*$_2$-sph), 1.43–1.14 (m, 24H, sph*H*6–*H*17), 1.02 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.98 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.87 (t, *J* = 6.8 Hz, 3H, sph*H*18); ^{13}C NMR (125 MHz, acetone-d6): δ 168.8 (2C, -NH*C*(O)Phth), 166.2 (C, -O*C*(O)Ph), 166.1 (C, -O*C*(O)Ph), 154.4 (C, -*C*=O), 135.5 (2C, CH, *C*Phth), 134.4 (CH, *C*Bz), 134.0 (*C*Bz), 132.5 (2C, *C*Phth), 130.9 (*C*Bz), 130.8 (*C*Bz), 130.6 (2C, *C*Bz), 130.3 (2C, *C*Bz), 129.6 (2C, *C*Bz), 129.3 (2C, *C*Bz), 124.2 (2C, *C*Phth), 84.8 (glc*C*2), 80.1 (glc*C*1), 77.0 (glc*C*4), 76.5 (glc*C*5), 75.5 (glc*C*3), 74.2 (sph*C*3), 74.0 (sph*C*2), 66.8 (glc*C*6), 51.6 (sph*C*4), 32.6 (sph*C*Alkyl), 30.4–29.4 (11C, sph*C*Alkyl), 27.7 (3C, Si-C(*CH*$_3$)$_3$), 27.3 (3C, Si-C(*CH*$_3$)$_3$), 25.9 (sph*C*1), 23.9 (sph*C*5), 23.3 (glc-*CH*$_2$-sph), 23.0 (Si-*C*(CH$_3$)$_3$), 20.5 (Si-*C*(CH$_3$)$_3$), 14.4 (sph*C*18); HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{56}H_{75}NaNO_{12}Si$, 1004.4951; found, 1004.4968.

Coupling products 16bf-α and 16bf-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (52.7 mg, 117 μmol, 1.0 equiv) and acceptor **12f** (137 mg, 233 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bf** as a colorless oil (64.6 mg, 53%) along with recovered donor **11b** (21.3 mg, 40%, α:β = 1:1) and acceptor **12f** (84.5 mg, 62%).

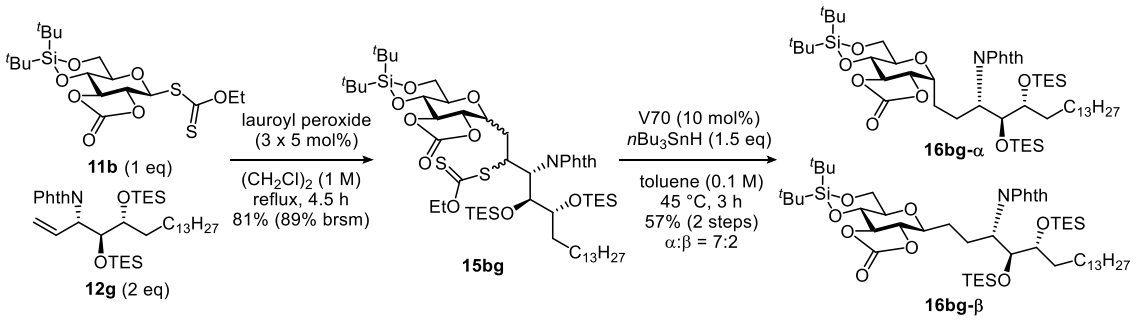
15bf: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{87}NaNO_{11}S_2Si_3$, 1060.4926; found, 1060.4928.

Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15ad** (64.6 mg, 62.2 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16bf-α**:**16bf-β** = 5:2). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 9/1 to 1/1) to give **16bf-α** as a colorless oil (31.7 mg, 55%) and **16bf-β** as a colorless oil (12.4 mg, 22%).

16bf-α: $[\alpha]_D^{21}$ +2.09 (c 1.25, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.89–7.87 (m, 4H, *H*Phth), 4.72 (dd, *J* = 11.6, 9.6 Hz, 1H, glc*H*3), 4.52 (dd, *J* = 11.6, 5.6 Hz, 1H, glc*H*2), 4.36 (dd, *J* = 9.6, 1.3 Hz, 1H, sph*H*3), 4.34 (m, 1H, glc*H*1), 4.33 (dd, *J* = 9.6, 9.1 Hz, 1H, glc*H*4), 4.18 (dd, *J* = 10.0, 5.0 Hz, 1H, glc*H*6eq), 4.12 (ddd, *J* = 9.8, 9.6, 4.4 Hz, 1H, sph*H*2), 3.95 (dd, *J* = 10.1, 10.0 Hz, 1H, glc*H*6ax), 3.67 (ddd, *J* = 10.1, 9.1, 5.0 Hz, 1H, glc*H*5), 3.49 (ddd, *J* = 9.6, 1.5, 1.3 Hz, 1H, sph*H*4), 2.27–2.13 (m, 2H, sph*H*1), 2.00–1.90 (m, 1H, glc-CH_2-sph), 1.60–1.52 (m, 1H, glc-CH_2-sph), 1.52–1.44 (m, 1H, sph*H*5), 1.41–1.18 (m, 25H, sph*H*5 and sph*H*Alkyl), 1.06 (s, 9H, Si-C(CH_3)$_3$), 1.01 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.22 (s, 9H, Si-(CH_3)$_3$), 0.02 (s, 9H, Si-(CH_3)$_3$); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 135.4 (2C, *C*Phth), 132.6 (2C, *C*Phth), 124.0 (2C, *C*Phth), 80.8 (glc*C*3), 78.1 (glc*C*2), 77.8 (sph*C*3), 76.5 (glc*C*4), 75.3 (glc*C*1), 74.1 (sph*C*4), 70.7 (glc*C*5), 67.4 (glc*C*6), 54.1 (sph*C*2), 32.7 (sph*C*Alkyl), 30.9–29.4 (10C, sph*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 26.8 (sph*C*5), 26.2 (sph*C*Alkyl), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (glc-CH_2-sph), 22.5 (sph*C*1), 20.5 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 0.9 (3C, Si-(CH_3)$_3$), 0.5 (3C, Si-(CH_3)$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{83}NaNO_{10}Si_3$, 940.5217; found, 940.5226.

16bf-β: $[\alpha]_D^{21}$ –4.42 (c, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.91–7.89 (m, 4H, *H*Phth), 4.57 (dd, *J* = 10.7, 9.6 Hz, 1H, glc*H*3), 4.39 (dd, *J* = 9.7, 1.2 Hz, 1H, sph*H*3), 4.32 (dd, *J* = 9.6, 8.6 Hz, 1H, glc*H*4), 4.14 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 4.10 (ddd, *J* = 9.7, 8.1, 6.8 Hz, 1H, sph*H*2), 4.06 (dd, *J* = 10.7, 9.5 Hz, 1H, glc*H*2), 3.99 (ddd, *J* = 9.5, 7.2, 4.7 Hz, 1H, glc*H*1), 3.88 (dd, *J* = 10.3, 10.1 Hz, 1H, glc*H*6ax), 3.67 (ddd, *J* = 10.3, 8.6, 5.1 Hz, 1H, glc*H*5), 3.49 (d, *J* = 9.7 Hz, 1H, sph*H*4), 2.19–2.13 (m, 2H, sph*H*1), 1.71–1.59 (m, 1H, glc-CH_2-sph), 1.55–1.45 (m, 2H, glc-CH_2-sph and sph*H*5), 1.41–1.18 (m, 25H, sph*H*Alkyl), 1.04 (s, 9H, Si-C(CH_3)$_3$), 1.00 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 7.1 Hz, 3H, sph*H*18), 0.21 (s, 7H, Si-(CH_3)$_3$), 0.18 (s, 1H, Si-(CH_3)$_3$), 0.15 (s, 1H, Si-(CH_3)$_3$), 0.02 (s, 7H, Si-(CH_3)$_3$), 0.00 (s, 1H, Si-(CH_3)$_3$), –0.01 (s, 1H, Si-(CH_3)$_3$); ^{13}C NMR (125 MHz, acetone-d6): δ 168.9 (2C, -NH*C*(O)Phth), 154.5 (-*C*=O), 135.5 (2C, *C*Phth), 132.5 (2C, *C*Phth), 124.0 (2C, *C*Phth), 84.8 (glc*C*3), 80.2 (glc*C*2), 77.6 (glc*C*1), 77.3 (sph*C*3), 76.6 (glc*C*5), 75.6 (glc*C*4), 74.1 (sph*C*4), 66.9 (glc*C*6), 53.7 (sph*C*2), 32.6 (sph*C*Alkyl), 30.4–29.4 (11C, sph*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.3 (3C, Si-C(CH_3)$_3$), 26.8 (sph*C*Alkyl), 24.9 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (glc-CH_2-sph), 20.5 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 0.9 (3C, Si-(CH_3)$_3$), 0.5 (3C, Si-(CH_3)$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{83}NaNO_{10}Si_3$, 940.5217; found, 940.5224.

Coupling products 16bg-α and 16bg-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (44.8 mg, 99.5 μmol, 1.0 equiv) and acceptor **12g** (134 mg, 199 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bg** as a colorless oil (90.0 mg, 81%) along with recovered donor **11b** (4.2 mg, 9%, α:β = 1:1) and acceptor **12g** (87.6 mg, 65%).

15bg: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{57}H_{99}NaNO_{11}S_2Si_3$, 1144.5860; found, 1144.5858.

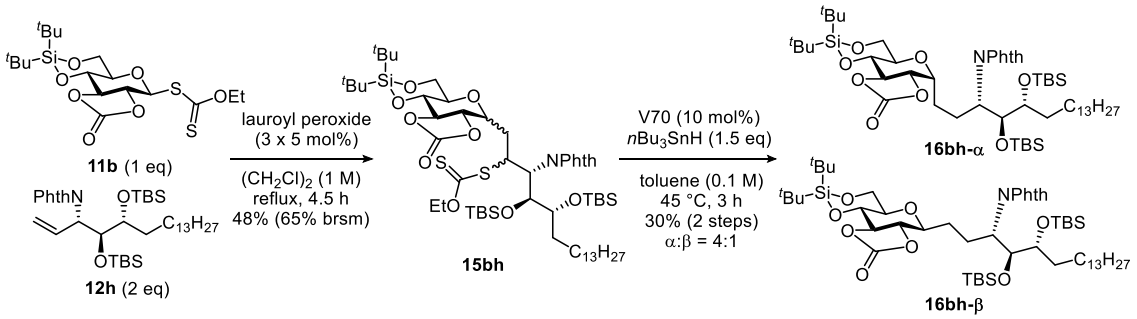
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15bd** (90.0 mg, 80.2 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16bg-α**:**16bg-β** = 7:2). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC

(column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 7/2) to give **16bg-α** as a colorless oil (44.2 mg, 55%) and **16bg-β** as a colorless oil (12.1 mg, 15%).

16bg-α: $[\alpha]_D^{28}$ –5.59 (c 1.76, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.89–7.87 (m, 4H, *H*Phth), 4.73 (dd, *J* = 11.6, 9.6 Hz, 1H, glc*H*3), 4.51 (dd, *J* = 11.6, 5.6 Hz, 1H, glc*H*2), 4.40 (dd, *J* = 9.8, 0.8 Hz, 1H, sph*H*3), 4.34 (dd, *J* = 9.6, 8.9 Hz, 1H, glc*H*4), 4.35–4.31 (m, 1H, glc*H*1), 4.18 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 4.18–4.12 (m, 1H, sph*H*2), 3.96 (dd, *J* = 10.1, 9.7 Hz, 1H, glc*H*6ax), 3.67 (ddd, *J* = 9.7, 8.9, 5.0 Hz, 1H, glc*H*5), 3.55–3.51 (m, 1H, sph*H*4), 2.29–2.23 (m, 2H, sph*H*1), 1.99–1.89 (m, 1H, glc-CH_2-sph), 1.57–1.47 (m, 2H, glc-CH_2-sph and sph*H*5), 1.47–1.39 (m, 2H, sph*H*5 and sph*H*Alkyl), 1.34–1.21 (m, 23H, sph*H*Alkyl), 1.07 (s, 9H, Si-C(CH_3)$_3$), 1.06 (t, *J* = 7.9 Hz, 9H, Si-CH_2CH_3), 1.01 (s, 9H, Si-C(CH_3)$_3$), 0.89 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.86 (t, *J* = 7.9 Hz, 9H, Si-CH_2CH_3), 0.80–0.75 (m, 6H, Si-CH_2CH_3), 0.56–0.50 (m, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 135.4 (2C, *C*Phth), 132.6 (2C, *C*Phth), 123.9 (2C, *C*Phth), 80.7 (glc*C*3), 78.0 (glc*C*2), 77.7 (sph*C*3), 76.6 (glc*C*4), 75.4 (glc*C*1), 74.9 (sph*C*4), 70.7 (glc*C*5), 67.4 (glc*C*6), 54.2 (sph*C*2), 32.7 (sph*C*Alkyl), 31.8 (sph*C*Alkyl), 30.5–29.4 (9C, sph*C*Alkyl), 27.8 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 26.9 (sph*C*Alkyl), 25.9 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (glc-CH_2-sph), 22.5 (sph*C*Alkyl), 20.5 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 7.4 (3C, Si-CH_2CH_3), 7.3 (3C, Si-CH_2CH_3), 6.0 (3C, Si-CH_2CH_3), 5.7 (3C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{54}H_{95}NaNO_{10}Si_3$, 1024.6156; found, 1024.6152.

16bg-β: $[\alpha]_D^{27}$ –14.80 (c 1.21, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.91–7.89 (m, 4H, *H*Phth), 4.57 (dd, *J* = 10.5, 9.1 Hz, 1H, glc*H*3), 4.41 (d, *J* = 9.8 Hz, 1H, sph*H*3), 4.32 (dd, *J* = 9.1, 8.7 Hz, 1H, glc*H*4), 4.14 (dd, *J* = 10.2, 5.1 Hz, 1H, glc*H*6eq), 4.17–4.11 (m, 1H, sph*H*2), 4.06 (dd, *J* = 10.5, 9.6 Hz, 1H, glc*H*2), 4.00 (ddd, *J* = 9.6, 7.4, 4.7 Hz, 1H, glc*H*1), 3.90 (dd, *J* = 10.2, 10.2 Hz, 1H, glc*H*6ax), 3.66 (ddd, *J* = 10.2, 8.7, 5.1 Hz, 1H, glc*H*5), 3.53 (dd, *J* = 8.9, 1.2 Hz, 1H, sph*H*4), 2.28–2.16 (m, 2H, sph*H*1), 1.65–1.57 (m, 1H, glc-CH_2-sph), 1.56–1.46 (m, 2H, glc-CH_2-sph and sph*H*5), 1.46–1.37 (m, 2H, sph*H*5 and sph*H*Alkyl), 1.33–1.19 (m, 23H, sph*H*Alkyl), 1.053 (s, 9H, Si-C(CH_3)$_3$), 1.050 (t, *J* = 8.1 Hz, 9H, Si-CH_2CH_3), 1.00 (s, 9H, Si-C(CH_3)$_3$), 0.90–0.86 (m, 3H, sph*H*18), 0.86 (t, *J* = 8.1 Hz, 9H, Si-CH_2CH_3), 0.80–0.74 (m, 6H, Si-CH_2CH_3), 0.56–0.50 (m, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 168.9 (2C, -NH*C*(O)Phth), 154.4 (-*C*=O), 135.5 (2C, *C*Phth), 132.5 (2C, *C*Phth), 124.0 (2C, *C*Phth), 84.8 (glc*C*3), 80.1 (glc*C*2), 77.6 (sph*C*3), 77.2 (glc*C*1), 76.6 (glc*C*5), 75.6 (glc*C*4), 75.0 (sph*C*4), 66.9 (glc*C*6), 53.7 (sph*C*2), 32.7 (sph*C*Alkyl), 31.9 (sph*C*5), 30.5–29.4 (10C, sph*C*Alkyl and glc-CH_2-sph), 27.7 (3C, Si-C(CH_3)$_3$), 27.3 (3C, Si-C(CH_3)$_3$), 26.9 (sph*C*Alkyl), 24.3 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (sph*C*Alkyl), 20.5 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 7.4 (3C, Si-CH_2CH_3), 7.3 (3C, Si-CH_2CH_3), 5.9 (3C, Si-CH_2CH_3), 5.7 (3C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{54}H_{95}NaNO_{10}Si_3$, 1024.6156; found, 1024.6151.

Coupling products 16bh-α and 16bh-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (24.6 mg, 54.5 μmol, 1.0 equiv) and acceptor **12h** (73.1 mg, 109 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bh** as a colorless oil (29.1 mg, 48%) along with recovered donor **11b** (6.6 mg, 27%, α:β = 1:1) and acceptor **12h** (48.0 mg, 66%).

15bh: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{57}H_{99}NaNO_{11}S_2Si_3$, 1144.5865; found, 1144.5869.

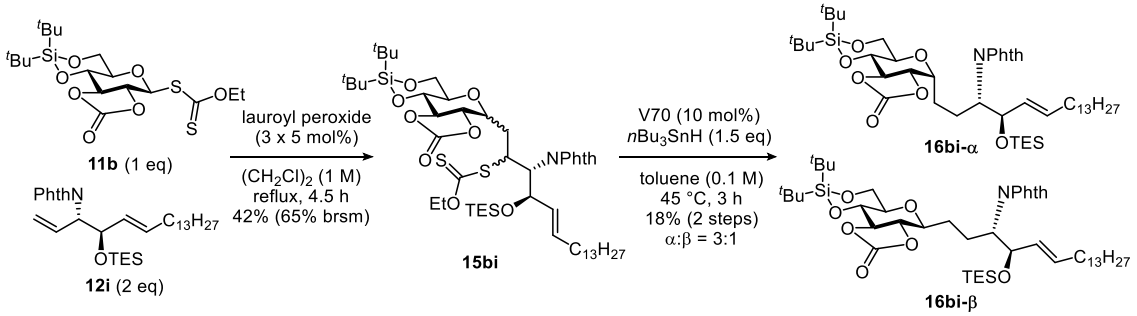
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15bh** (29.1 mg, 25.9 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16bh-α**:**16bh-β** = 4:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 3/1) to give **16bh-α** as a colorless oil (13.0 mg, 50%) and **16bh-β** as a colorless oil (3.0 mg, 12%).

16bh-α: $[\alpha]_D^{20}$ –0.36 (c 1.35, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.90–7.88 (m, 4H, *H*Phth), 4.73 (dd, *J* = 11.6, 9.5 Hz, 1H, glc*H*3), 4.50 (dd, *J* = 11.6, 5.7 Hz, 1H, glc*H*2), 4.40 (dd, *J* = 9.7, 0.5 Hz, 1H, sph*H*3), 4.33 (dd, *J* = 9.5, 8.9 Hz, 1H, glc*H*4), 4.32 (ddd, *J* = 11.2, 5.7, 3.3 Hz, 1H, glc*H*1), 4.18 (ddd, *J* = 11.5, 9.7, 3.4 Hz, 1H, sph*H*2), 4.17 (dd, *J* = 10.1, 4.9 Hz, 1H, glc*H*6eq), 3.94 (dd, *J* = 10.1, 9.9 Hz, 1H, glc*H*6ax), 3.67 (ddd, *J* = 9.9, 8.9, 4.9 Hz, 1H, glc*H*5), 3.55 (dd, *J* = 9.7, 1.9 Hz, 1H, sph*H*4), 2.33–2.16 (m, 2H, sph*H*1), 1.99–1.90 (m, 1H, glc-CH_2-sph), 1.55–1.46 (m, 2H, glc-CH_2-sph and sph*H*5), 1.46–1.37 (m, 2H, sph*H*5 and sph*H*Alkyl), 1.34–1.15 (m, 23H, sph*H*Alkyl), 1.06 (s, 9H, Si-C(CH_3)$_3$), 1.01 (s, 9H, Si-C(CH_3)$_3$), 1.00 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.87 (s, 9H, Si-C(CH_3)$_3$), 0.24 (s, 3H, Si-CH_3), 0.23 (s, 3H, Si-CH_3), 0.03 (s, 3H, Si-CH_3), –0.17 (s, 3H, Si-CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 135.5 (2C, *C*Phth), 132.6 (2C, *C*Phth), 124.0 (2C, *C*Phth), 80.7 (glc*C*3), 78.0 (glc*C*2), 77.8 (sph*C*3), 76.6 (glc*C*4), 75.5 (glc*C*1), 75.3 (sph*C*4), 70.7 (glc*C*5), 67.4 (glc*C*6), 54.4 (sph*C*2), 32.7 (sph*C*Alkyl), 32.2 (sph*C*5), 30.4–29.4 (9C, sph*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 26.9 (sph*C*Alkyl), 26.7 (3C, Si-C(CH_3)$_3$), 26.6 (3C, Si-C(CH_3)$_3$), 26.2 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (sph*C*Alkyl), 22.5 (glc-CH_2-sph), 20.5 (Si-

C(CH_3)$_3$), 19.1 (Si-*C*(CH_3)$_3$), 18.8 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), –2.7 (Si-*CH*$_3$), –3.4 (Si-*CH*$_3$), –4.6 (Si-*CH*$_3$), –4.9 (Si-*CH*$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{54}H_{95}NaNO_{10}Si_3$, 1024.6162; found, 1024.6165.

16bh-β: $[\alpha]_D^{21}$ –13.57 (c 0.30, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.92–7.90 (m, 4H, *H*Phth), 4.56 (dd, *J* = 10.5, 9.5 Hz, 1H, glc*H*3), 4.42 (d, *J* = 9.7 Hz, 1H, sph*H*3), 4.32 (dd, *J* = 9.5, 8.5 Hz, 1H, glc*H*4), 4.21–4.13 (m, 1H, sph*H*2), 4.15 (dd, *J* = 10.2, 5.1 Hz, 1H, glc*H*6eq), 4.05 (dd, *J* = 10.5, 9.6 Hz, 1H, glc*H*2), 4.00 (ddd, *J* = 9.6, 7.3, 4.5 Hz, 1H, glc*H*1), 3.90 (dd, *J* = 10.3, 10.2 Hz, 1H, glc*H*6ax), 3.66 (ddd, *J* = 10.3, 8.5, 5.1 Hz, 1H, glc*H*5), 3.57 (dd, *J* = 9.0, 2.3 Hz, 1H, sph*H*4), 2.24–2.18 (m, 2H, sph*H*1), 1.64–1.56 (m, 1H, glc-*CH*$_2$-sph), 1.55–1.47 (m, 2H, glc-*CH*$_2$-sph and sph*H*5), 1.46–1.36 (m, 2H, sph*H*5 and sph*H*Alkyl), 1.33–1.18 (m, 23H, sph*H*Alkyl), 1.05 (s, 9H, Si-C(*CH*$_3$)$_3$), 1.01 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.99 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.87 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.229 (s, 3H, Si-*CH*$_3$), 0.226 (s, 3H, Si-*CH*$_3$), 0.04 (s, 3H, Si-*CH*$_3$), –0.15 (s, 3H, Si-*CH*$_3$); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.4 (-*C*=O), 135.6 (2C, *C*Phth), 132.5 (2C, *C*Phth), 124.1 (2C, *C*Phth), 84.8 (glc*C*3), 80.0 (glc*C*2), 77.5 (sph*C*3), 77.0 (glc*C*1), 76.6 (glc*C*5), 75.6 (glc*C*4), 75.5 (sph*C*4), 66.9 (glc*C*6), 53.7 (sph*C*2), 32.7 (sph*C*5), 30.4–29.4 (10C, glc-*CH*$_2$-sph and sph*C*Alkyl), 27.7 (3C, Si-C(*CH*$_3$)$_3$), 27.44 (sph*C*Alkyl), 27.36 (3C, Si-C(*CH*$_3$)$_3$), 26.9 (sph*C*Alkyl), 26.7 (3C, Si-C(*CH*$_3$)$_3$), 26.6 (3C, Si-C(*CH*$_3$)$_3$), 24.3 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (sph*C*Alkyl), 20.5 (Si-*C*(CH_3)$_3$), 19.1 (Si-*C*(CH_3)$_3$), 18.8 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), –2.8 (Si-*CH*$_3$), –3.4 (Si-*CH*$_3$), –4.6 (Si-*CH*$_3$), –4.8 (Si-*CH*$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{54}H_{95}NaNO_{10}Si_3$, 1024.6162; found, 1024.6163.

Coupling products 16bi-α and 16bi-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (46.0 mg, 102 μmol, 1.0 equiv) and acceptor **12i** (110 mg, 204 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bi** as a colorless oil (42.8 mg, 42%) along with recovered donor **11b** (16.4 mg, 36%, α:β = 1:1) and acceptor **12i** (70.2 mg, 64%).

15bi: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{83}NaNO_{10}S_2Si_2$, 1012.4895; found, 1012.4892.

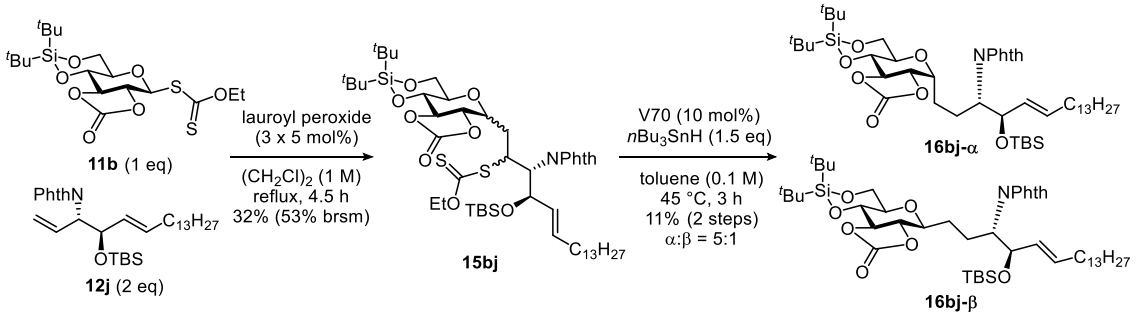
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15bi** (42.8 mg, 43.2 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16bi-α**:**16bi-β** = 3:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 11/2) to give **16bi-α** as a colorless oil (12.3 mg, 21%) and **16bi-β** as a colorless oil (4.1 mg, 7%).

16bi-α: $[\alpha]_D^{21}$ –7.92 (c 0.44, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.86–7.81 (m, 4H, *H*Phth), 5.49 (ddd, *J* = 15.3, 7.6, 6.2 Hz, 1H, sph*H*5), 5.28 (dddd, *J* = 15.3, 8.9, 1.3, 1.1 Hz, 1H, sph*H*4), 4.76 (dd, *J* = 11.6, 9.6 Hz, 1H, glc*H*3), 4.61 (dd, *J* = 9.0, 8.9 Hz, 1H, sph*H*3), 4.53 (dd, *J* = 11.6, 5.6 Hz, 1H, glc*H*2), 4.36 (ddd, *J* = 11.1, 5.6, 3.5 Hz, 1H, glc*H*1), 4.34 (dd, *J* = 9.6, 8.9 Hz, 1H, glc*H*4), 4.17 (dd, *J* = 10.0, 5.0 Hz, 1H, glc*H*6eq), 4.07 (ddd, *J* = 9.2, 9.0, 6.8 Hz, 1H, sph*H*2), 3.95 (dd, *J* = 10.0, 10.0 Hz, 1H, glc*H*6ax), 3.67 (ddd, *J* = 10.0, 8.9, 5.0 Hz, 1H, glc*H*5), 2.36–2.25 (m, 2H, sph*H*1), 2.03–1.96 (m, 1H, glc-CH_2-sph), 1.86–1.77 (m, 1H, sph*H*6), 1.76–1.68 (m, 1H, sph*H*6), 1.68–1.60 (m, 1H, glc-CH_2-sph), 1.34–0.95 (m, 22H, sph*H*Alkyl), 1.06 (s, 9H, Si-C(CH_3)$_3$), 1.000 (t, *J* = 7.8 Hz, 9H, Si-CH_2CH_3), 0.996 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.68–0.61 (m, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.1 (2C, -NH*C*(O)Phth), 154.3 (-*C*=O), 135.14 (2C, *C*Phth), 135.05 (sph*C*5), 132.8 (2C, *C*Phth), 131.6 (sph*C*4), 123.8 (2C, *C*Phth), 80.8 (glc*C*3), 78.1 (glc*C*2), 76.5 (glc*C*4), 75.4 (glc*C*1), 75.3 (sph*C*3), 70.7 (glc*C*5), 67.4 (glc*C*6), 57.6 (sph*C*2), 32.65 (sph*C*6), 32.61 (sph*C*Alkyl), 30.4–29.4 (9C, sph*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 25.4 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (glc-CH_2-sph), 22.9 (sph*C*Alkyl), 20.5 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 7.2 (3C, Si-CH_2CH_3), 5.8 (3C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{79}NaNO_9Si_2$, 892.5191; found, 892.5192.

16bi-β: $[\alpha]_D^{21}$ –21.77 (c 0.44, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.90–7.83 (m, 4H, *H*Phth), 5.49 (ddd, *J* = 15.3, 7.7, 6.2 Hz, 1H, sph*H*5), 5.27 (dddd, *J* = 15.3, 8.6, 1.2, 1.1 Hz, 1H, sph*H*4), 4.64 (dd, *J* = 9.0, 8.6 Hz, 1H, sph*H*3), 4.59 (dd, *J* = 10.7, 9.6 Hz, 1H, glc*H*3), 4.33 (dd, *J* = 9.6, 8.6 Hz, 1H, glc*H*4), 4.14 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 4.07 (dd, *J* = 10.7, 9.5 Hz, 1H, glc*H*2), 4.06–3.98 (m, 2H, sph*H*2, glc*H*1), 3.90 (dd, *J* = 10.3, 10.1 Hz, 1H, glc*H*6ax), 3.68 (ddd, *J* = 10.3, 8.6, 5.0 Hz, 1H, glc*H*5), 2.30–2.23 (m, 2H, sph*H*1), 1.85–1.78 (m, 1H, sph*H*6), 1.77–1.71 (m, 1H, sph*H*6), 1.71–1.63 (m, 1H, glc-CH_2-sph), 1.61–1.54 (m, 1H, glc-CH_2-sph), 1.54–1.45 (m, 1H, sph*H*Alkyl), 1.38–0.93 (m, 21H, sph*H*Alkyl), 1.05 (s, 9H, Si-C(CH_3)$_3$), 1.01 (s, 9H, Si-C(CH_3)$_3$), 0.99 (t, *J* = 7.8 Hz, 9H, Si-CH_2CH_3), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.65 (q, *J* = 7.8 Hz, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.5 (-*C*=O), 135.2 (2C, *C*Phth), 135.0 (sph*C*5), 132.7 (2C, *C*Phth), 131.7 (sph*C*4), 123.8 (2C, *C*Phth), 84.8 (glc*C*3), 80.2 (glc*C*2), 77.1 (glc*C*1), 76.5 (glc*C*5), 75.6 (glc*C*4), 75.2 (sph*C*3), 66.9 (glc*C*6), 57.2 (sph*C*2), 32.65 (sph*C*6), 32.59 (sph*C*Alkyl), 30.4–29.4 (10C, sph*C*Alkyl), 27.7 (3C,

Si-C(CH_3)$_3$), 27.3 (3C, Si-C(CH_3)$_3$), 24.0 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (glc-CH_2-sph), 20.5 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 7.2 (3C, Si-CH_2CH_3), 5.7 (3C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{79}NaNO_9Si_2$, 892.5191; found, 892.5194.

Coupling products 16bj-α and 16bj-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (16.3 mg, 36.2 μmol, 1.0 equiv) and acceptor **12j** (39.1 mg, 72.4 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bj** as a colorless oil (8.2 mg, 23%) along with recovered donor **11b** (9.9 mg, 61%, α:β = 1:1) and acceptor **12j** (25.1 mg, 64%).

15bj: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{83}NaNO_{10}S_2Si_2$, 1012.4889; found, 1012.4863.

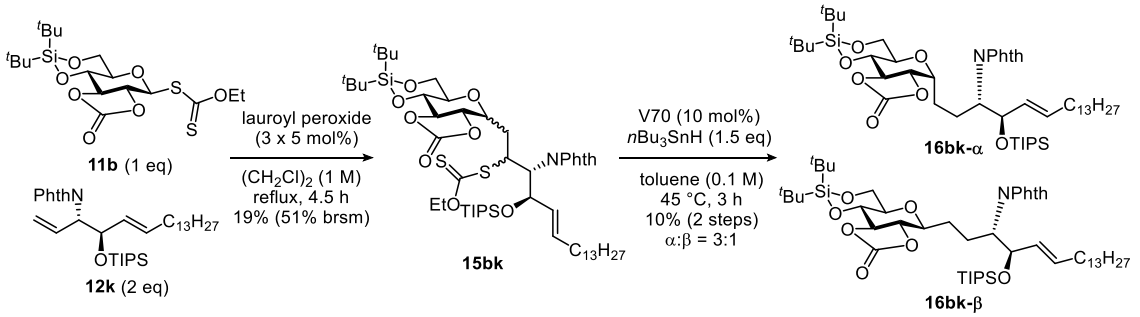
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15bj** (8.2 mg, 8.3 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16bj-α**:**16bj-β** = 5:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 11/2) to give **16bj-α** as a colorless oil (2.7 mg, 28%) and **16bj-β** as a colorless oil (0.6 mg, 6%).

16bj-α: $[\alpha]_D^{21}$ –5.28 (c 0.24, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.89–7.81 (m, 4H, *H*Phth), 5.49 (ddd, *J* = 15.2, 7.6, 6.3 Hz, 1H, sph*H*5), 5.27 (dddd, *J* = 15.2, 8.8, 1.3, 1.2 Hz, 1H, sph*H*4), 4.77 (dd, *J* = 11.6, 9.5 Hz, 1H, glc*H*3), 4.60 (dd, *J* = 8.9, 8.8 Hz, 1H, sph*H*3), 4.53 (dd, *J* = 11.6, 5.7 Hz, 1H, glc*H*2), 4.35 (ddd, *J* = 9.0, 5.7, 3.4, 1H, glc*H*1), 4.34 (dd, *J* = 9.5, 8.8 Hz, 1H, glc*H*4), 4.17 (dd, *J* = 10.0, 5.0 Hz, 1H, glc*H*6eq), 4.08 (ddd, *J* = 9.2, 8.9, 6.4 Hz, 1H, sph*H*2), 3.94 (dd, *J* = 10.0, 9.9 Hz, 1H, glc*H*6ax), 3.67 (ddd, *J* = 9.9, 8.8, 5.0 Hz, 1H, glc*H*5), 2.33–2.25 (m, 2H, sph*H*1), 2.03–1.96 (m, 1H, glc-CH_2-sph), 1.86–1.78 (m, 1H, sph*H*6), 1.78–1.70 (m, 1H, sph*H*6), 1.64–1.56 (m, 1H, glc-CH_2-sph), 1.39–0.96 (m, 22H, sph*H*Alkyl), 1.06 (s, 9H, Si-C(CH_3)$_3$), 1.00 (s, 9H, Si-C(CH_3)$_3$), 0.95 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.15 (s, 3H, Si-CH_3), 0.07 (s, 3H, Si-CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.1 (2C, -

NH*C*(O)Phth), 154.4 (-*C*=O), 135.2 (3C, *C*Phth and sph*C*5), 132.8 (2C, *C*Phth), 131.7 (sph*C*4), 123.8 (2C, *C*Phth), 80.8 (glc*C*3), 78.1 (glc*C*2), 76.6 (glc*C*4), 75.5 (glc*C*1), 75.3 (sph*C*3), 70.6 (glc*C*5), 67.4 (glc*C*6), 57.6 (sph*C*2), 32.66 (sph*C*6), 32.61 (sph*C*Alkyl), 30.4–29.4 (9C, sph*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 26.3 (3C, Si-C(CH_3)$_3$), 25.4 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (glc-CH_2-sph), 22.9 (sph*C*Alkyl), 20.5 (Si-*C*(CH_3)$_3$), 18.7 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), –3.4 (Si-CH_3), –4.5 (Si-CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{79}NaNO_9Si_2$, 892.5186; found, 892.5183.

16bj-β: $[\alpha]_D^{21}$ –22.13 (c 0.09, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.88–7.82 (m, 4H, *H*Phth), 5.48 (ddd, *J* = 15.0, 7.5, 6.5 Hz, 1H, sph*H*5), 5.26 (dddd, *J* = 15.0, 8.7, 1.3, 1.2 Hz, 1H, sph*H*4), 4.62 (dd, *J* = 8.9, 8.7 Hz, 1H, sph*H*3), 4.60 (dd, *J* = 10.7, 9.6 Hz, 1H, glc*H*3), 4.33 (dd, *J* = 9.6, 8.6 Hz, 1H, glc*H*4), 4.15 (dd, *J* = 10.2, 5.1 Hz, 1H, glc*H*6eq), 4.07 (dd, *J* = 10.7, 9.5 Hz, 1H, glc*H*2), 4.08–3.98 (m, 2H, sph*H*2, glc*H*1), 3.90 (dd, *J* = 10.3, 10.2 Hz, 1H, glc*H*6ax), 3.69 (ddd, *J* = 10.3, 8.6, 5.1 Hz, 1H, glc*H*5), 2.28–2.23 (m, 2H, sph*H*1), 1.84–1.80 (m, 1H, glc-CH_2-sph), 1.78–1.70 (m, 1H, sph*H*6), 1.70–1.62 (m, 1H, sph*H*6), 1.61–1.53 (m, 1H, glc-CH_2-sph), 1.50–0.94 (m, 22H, sph*H*Alkyl), 1.05 (s, 9H, Si-C(CH_3)$_3$), 1.01 (s, 9H, Si-C(CH_3)$_3$), 0.93 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.15 (s, 3H, Si-CH_3), 0.07 (s, 3H, Si-CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.5 (-*C*=O), 135.2 (2C, *C*Phth), 135.1 (sph*C*5), 132.7 (2C, *C*Phth), 131.7 (sph*C*4), 123.9 (2C, *C*Phth), 84.8 (glc*C*3), 80.2 (glc*C*2), 77.1 (glc*C*1), 76.5 (glc*C*5), 75.6 (glc*C*4), 75.3 (sph*C*3), 67.0 (glc*C*6), 57.2 (sph*C*2), 32.7 (sph*C*6), 32.6 (sph*C*Alkyl), 30.4–29.0 (10C, glc-CH_2-sph and sph*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 26.3 (3C, Si-C(CH_3)$_3$), 23.9 (sph*C*1), 23.3 (Si-*C*(CH_3)$_3$), 23.1 (sph*C*Alkyl), 20.5 (Si-*C*(CH_3)$_3$), 18.7 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), –3.5 (Si-CH_3), –4.5 (Si-CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{48}H_{79}NaNO_9Si_2$, 892.5186; found, 892.5182.

Coupling products 16bk-α and 16bk-β



Radical Coupling: General procedure **A** was followed for the reaction of donor **11b** (43.7 mg, 97.0 μmol, 1.0 equiv) and acceptor **12k** (113 mg, 194 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15bk** as a

colorless oil (19.2 mg, 19%) along with recovered donor **11b** (27.4 mg, 63%, α:β = 5:7) and acceptor **12k** (81.2 mg, 72%).

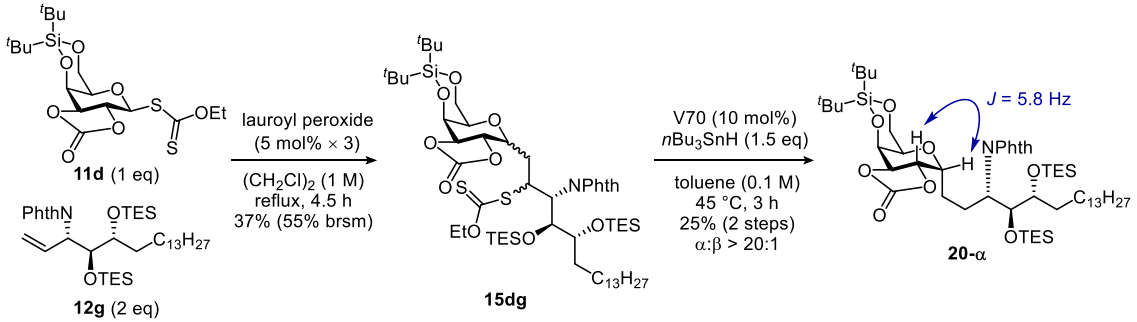
15bk: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{54}H_{89}NaNO_{10}S_2Si_2$, 1054.5359; found, 1054.5348.

Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15bk** (19.2 mg, 18.6 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**16bk-α**:**16bk-β** = 3:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 3/1) to give a mixture of **16bk-α** and unknown byproducts (6.8 mg, <40%) and a mixture of **16bk-β** and unknown byproducts (2.1 mg, <12%).

16bk-α: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{85}NaNO_9Si_2$, 934.5655; found, 934.5658.

16bk-β: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{85}NaNO_9Si_2$, 934.5655; found, 934.5648.

Coupling product 20-α



Radical Coupling: General procedure **A** was followed for the reaction of donor **11d** (45.1 mg, 100 μmol, 1.0 equiv) and acceptor **12g** (134 mg, 200 μmol, 2.0 equiv). The reaction mixture was purified by recycling preparative GPC (column: JAIGEL-2HR, eluent: $CHCl_3$) to give **15dg** as a colorless oil (41.9 mg, 37%) along with recovered donor **11d** (14.8 mg, 33%, α:β = 1:2) and acceptor **12g** (98.6 mg, 74%).

15dg: HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{57}H_{99}NaNO_{11}S_2Si_3$, 1144.5865; found, 1144.5867.

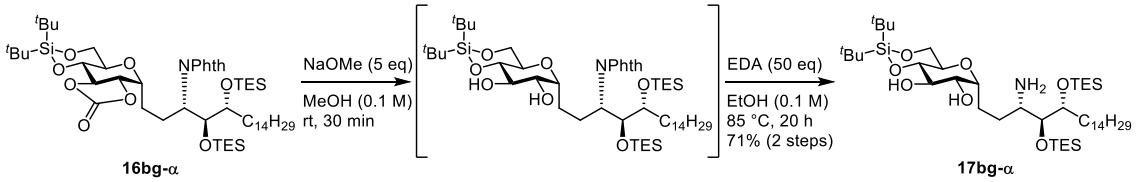
Reduction of Xanthate: General procedure **B** was followed for the reaction of xanthate **15dg** (41.9 mg, 37.3 μmol, 1.0 equiv). The diastereomeric ratio at anomeric position was determined by ^{1}H NMR of crude reaction mixture (**20-α**:**20-β** > 20:1). The reaction mixture was purified by silica gel column chromatography (eluent; hexane/EtOAc = 1/0 to 5/1) followed by MPLC (column: Yamazen, ULTRAPACK Silica-30A, eluent: hexane/EtOAc = 1/0 to 3/1) to give **20** as a colorless oil (25.1 mg, 25% (2 steps)).

Compound **20-α**

$[\alpha]_D^{21}$ +18.05 (c 0.71, $CHCl_3$); ^{1}H NMR (500 MHz, acetone-d6): δ 7.89–7.87 (m, 4H, *H*Phth), 5.00 (dd, *J* = 12.0, 5.8 Hz, 1H, gal*H*2), 4.94 (d, *J* = 2.4 Hz, 1H, gal*H*4), 4.75 (dd, *J* = 12.0, 2.4 Hz, 1H, gal*H*3), 4.44–4.40 (m, 1H, gal*H*1), 4.404 (dd, *J* = 12.5, 2.3 Hz, 1H, gal*H*6), 4.396 (dd, *J* = 9.9, 0.9 Hz, 1H, sph*H*3), 4.16 (dd, *J* = 12.5, 1.3 Hz, 1H, gal*H*6), 4.11 (ddd, *J* = 9.9, 9.9, 4.5 Hz, 1H, sph*H*2), 3.82 (s, 1H, gal*H*5), 3.50 (ddd, *J* = 9.2, 2.1, 0.9 Hz, 1H, sph*H*4), 2.34–2.22 (m, 2H, sph*H*1), 1.93–1.82 (m, 1H, glc-CH_2-sph), 1.56–1.45 (m, 2H, glc-CH_2-sph and sph*H*5), 1.45–1.34 (m, 2H, sph*H*5 and sph*H*Alkyl), 1.33–1.17 (m, 23H, sph*H*Alkyl), 1.06 (s, 9H, Si-C(CH_3)$_3$), 1.05 (t, *J* = 7.9 Hz, 9H, Si-CH_2CH_3), 1.02 (s, 9H, Si-C(CH_3)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.85 (t, *J* = 7.9 Hz, 9H, Si-CH_2CH_3), 0.77 (m, 6H, Si-CH_2CH_3), 0.52 (q, *J* = 7.9 Hz, 6H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, acetone-d6): δ 169.0 (2C, -NH*C*(O)Phth), 154.2 (-*C*=O), 135.4 (2C, *C*Phth), 132.6 (2C, *C*Phth), 123.9 (2C, *C*Phth), 79.0 (gal*C*3), 77.8 (sph*C*3), 75.2 (gal*C*1), 74.7 (sph*C*4), 74.5 (gal*C*2), 71.4 (gal*C*4), 69.4 (gal*C*5), 68.2 (gal*C*6), 54.5 (sph*C*2), 32.6 (sph*C*Alkyl), 31.5 (sph*C*5), 30.5–29.4 (9C, sph*C*Alkyl), 27.9 (3C, Si-C(CH_3)$_3$), 27.7 (3C, Si-C(CH_3)$_3$), 26.9 (sph*C*6), 25.9 (sph*C*1), 23.7 (Si-*C*(CH_3)$_3$), 23.3 (sph*C*Alkyl), 22.3 (gal-CH_2-sph), 21.3 (Si-*C*(CH_3)$_3$), 14.4 (sph*C*18), 7.4 (3C, Si-CH_2CH_3), 7.3 (3C, Si-CH_2CH_3), 6.0 (3C, Si-CH_2CH_3), 5.7 (3C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{54}H_{95}NaNO_{10}Si_3$, 1024.6162; found, 1024.6164.

5. Synthesis of *CH₂*-linked GlcCer and GalCer Analogues

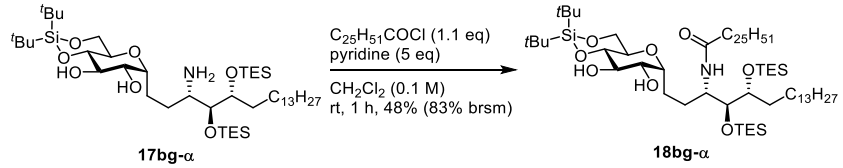
4,6-Di-*tert*-butylsilylene-2'-NH_2-3',4'-OTES- α -GlcCer (17bg-α)



To a solution of **16bg-α** (25.6 mg, 25.5 μmol, 1.0 equiv) in MeOH (260 μL, 0.1 M) was added NaOMe (6.9 mg, 128 μmol, 5.0 equiv) at room temperature. After stirring for 30 min at room temperature, the solution was filtrated through cation exchange resin (IR-120, prior to use the resin was washed with 1 M HCl and deionized water) and concentrated under reduced pressure to give the crude diol.

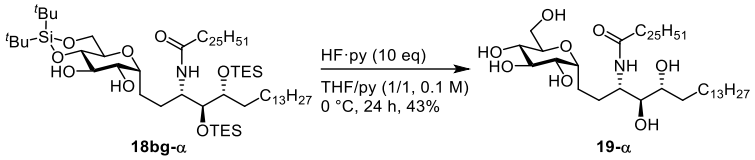
The crude mixture was dissolved in EtOH (170 μL, 0.1 M) under Ar atmosphere. To the solution was added ethylenediamine (EDA, 86 μL, 1.28 mmol, 50 equiv) at room temperature. After stirring for 20 h at 85 °C, the solution was cooled to room temperature, diluted with $CHCl_3$ (5 mL), and quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with $CHCl_3$ (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 1/1 to 0/1) to give aminoalcohol **17bg-α** as a colorless oil (15.4 mg, 71%). $[\alpha]_D^{27}$ +15.80 (c 1.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.06 (dd, *J* = 10.0, 5.0 Hz, 1H, glc*H*6eq), 3.99 (ddd, *J* = 9.9, 6.1, 3.4 Hz, 1H, sph*H*4), 3.82 (dd, *J* = 9.0, 6.2 Hz, 1H, glc*H*2), 3.81 (dd, *J* = 10.0, 9.6 Hz, 1H, glc*H*6ax), 3.77 (m, 1H, glc*H*1), 3.64 (dd, *J* = 9.0, 8.7 Hz, 1H, glc*H*3), 3.60 (dd, *J* = 9.4, 8.7 Hz, 1H, glc*H*4), 3.51 (ddd, *J* = 9.6, 9.4, 5.0 Hz, 1H, glc*H*5), 3.39 (dd, *J* = 5.7, 3.4 Hz, 1H, sph*H*3), 2.75 (ddd, *J* = 10.5, 5.7, 2.4 Hz, 1H, sph*H*2), 2.05–1.96 (m, 1H, sph*H*5), 1.91 (dddd, *J* = 13.6, 11.2, 4.5, 2.4 Hz, 1H, sph*H*1), 1.59 (dddd, *J* = 14.3, 10.2, 9.9, 5.3 Hz, 1H, sph*H*5), 1.54–1.43 (m, 2H, glc-*CH₂*-sph), 1.43–1.34 (m, 1H, sph*H*Alkyl), 1.31–1.20 (m, 23H, sph*H*Alkyl), 1.20–1.11 (m, 1H, sph*H*1), 1.05 (s, 9H, Si-C(*CH₃*)₃), 0.99 (s, 9H, Si-C(*CH₃*)₃), 0.960 (t, *J* = 7.9 Hz, 9H, Si-CH_2*CH₃*), 0.958 (t, *J* = 7.8 Hz, 9H, Si-CH_2*CH₃*), 0.88 (t, *J* = 6.8 Hz, 3H, sph*H*18), 0.65–0.58 (m, 12H, Si-*CH₂*CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 80.6 (sph*C*3), 78.2 (glc*C*4), 77.8 (sph*C*4), 75.5 (glc*C*1), 74.7 (glc*C*3), 71.8 (glc*C*2), 67.5 (glc*C*6), 67.3 (glc*C*5), 55.4 (sph*C*2), 34.2 (glc-*CH₂*-sph), 32.1 (sph*C*Alkyl), 30.1 (sph*C*Alkyl), 30.0 (sph*C*Alkyl), 29.85 (3C, sph*C*Alkyl), 29.81 (3C, sph*C*Alkyl), 29.78 (2C, sph*C*Alkyl), 29.5 (sph*C*1), 27.6 (3C, Si-C(*CH₃*)₃), 27.2 (3C, Si-C(*CH₃*)₃), 26.0 (sph*C*Alkyl), 23.0 (sph*C*5), 22.8 (Si-*C*$(CH_3)_3$), 20.1 (Si-*C*$(CH_3)_3$), 14.3 (sph*C*18), 7.21 (3C, Si-CH_2*CH₃*), 7.18 (3C, Si-CH_2*CH₃*), 5.5 (3C, Si-*CH₂*CH_3), 5.4 (3C, Si-*CH₂*CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{45}H_{96}NO_7Si_3$, 846.6489; found, 846.6487.

4,6-Di-*tert*-butylsilylene-3',4'-OTES-α-GlcCer (18bg-α)



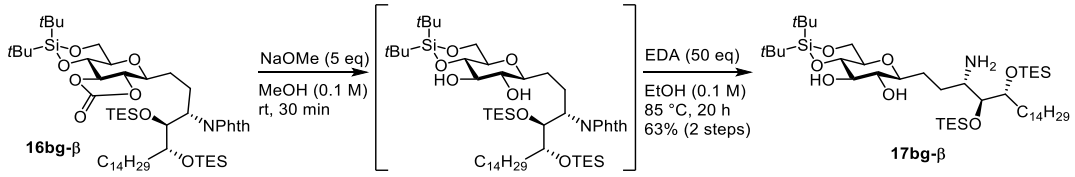
To a solution of **17bg-α** (15.4 mg, 18.2 μmol, 1.0 equiv) in CH_2Cl_2 (180 μL, 0.1 M) was sequentially added pyridine (7.3 μL, 91.0 μmol, 5.0 equiv) and hexacosanoyl chloride (8.3 mg, 91.0 μmol, 1.1 equiv) at 0 °C. After stirring for 1 h at room temperature, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/acetone = 50/1 to 5/1) to give amide **18bg-α** as a colorless oil (10.7 mg, 48%). $[\alpha]_D^{26}$ +2.17 (c 0.82, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.42 (d, *J* = 9.3 Hz, 1H, cer*NH*), 4.07 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 4.09–4.03 (m, 1H, cer*H*2), 3.92 (ddd, *J* = 10.9, 6.2, 3.2 Hz, 1H, glc*H*1), 3.79 (dd, *J* = 10.1, 9.5 Hz, 1H, glc*H*6ax), 3.82–3.77 (m, 1H, glc*H*2), 3.65 (ddd, *J* = 6.7, 4.2, 4.0, 1H, cer*H*4), 3.63–3.55 (m, glc*H*3, glc*H*4, and cer*H*3), 3.49 (ddd, *J* = 9.5, 9.5, 5.0 Hz, 1H, glc*H*5), 2.71 (s, 1H, *OH*), 2.46 (s, 1H, *OH*), 2.14 (dd, *J* = 8.3, 6.8 Hz, 2H, cer*H*2'), 2.01 (dddd, 1H, cer*H*1), 1.76 (dddd, 1H, glc-CH_2-cer), 1.66–1.41 (m, 5H, glc-CH_2-cer, cer*H*3', and cer*H*5), 1.41–1.21 (m, 69H, cer*H*Alkyl and cer*H*1), 1.05 (s, 9H, Si-C(CH_3)$_3$), 0.99 (s, 9H, Si-C(CH_3)$_3$), 0.97 (t, *J* = 7.8 Hz, 9H, Si-CH_2CH_3), 0.96 (t, *J* = 7.9 Hz, 9H, Si-CH_2CH_3), 0.88 (t, *J* = 6.8 Hz, 6H, cer*H*18 and cer*H*26'), 0.66–0.57 (m, 12H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.6 (-NH*CO*-), 78.7 (sph*C*3), 78.0 (glc*C*4), 77.2 (glc*C*1), 75.3 (cer*C*4), 74.6 (glc*C*3), 71.8 (glc*C*2), 67.4 (glc*C*5), 67.2 (glc*C*6), 51.7 (cer*C*2), 37.3 (cer*C*2'), 33.6 (cer*C*Alkyl), 32.1 (2C, cer*C*Alkyl), 30.2 (cer*C*Alkyl), 29.9 (19C, cer*C*Alkyl), 29.8 (6C, cer*C*Alkyl), 29.7 (cer*C*Alkyl), 29.62 (cer*C*Alkyl), 29.60 (cer*C*Alkyl), 29.5 (2C, cer*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.2 (4C, Si-C(CH_3)$_3$ and glc-CH_2-cer), 25.9 (cer*C*Alkyl), 22.8 (2C, cer*C*Alkyl and Si-*C*(CH_3)$_3$), 21.8 (cer*C*1), 20.1 (Si-*C*(CH_3)$_3$), 14.3 (2C, cer*C*18 and cer*C*26'), 7.2 (6C, Si-CH_2CH_3), 5.4 (6C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for, $C_{71}H_{145}NaNO_8Si_3$, 1247.0170; found, 1247.0088.

α-GlcCer (19-α)



To a solution of **18bg-α** (5.7 mg, 4.7 μmol, 1.0 equiv) in THF (47 μL) was sequentially added pyridine (41 μL) and HF·py (4.2 μl, 47 μmol, 10 equiv) at 0 °C. After stirring for 24 h at 0 °C, the solution was quenched with solid $NaHCO_3$ (20 mg). Excess solids were filtered off over a plug of cotton wool, rinsed with $CHCl_3$/MeOH (1/1), and the filtrate was concentrated. The residue was purified by gel permeation chromatography (Sephadex LH-20, eluent; $CHCl_3$/MeOH = 1/1). Further purification was carried out by adsorption chromatography on Iatrobeads 6RS-8060 (LSI Medience Co., eluent: $CHCl_3$/MeOH = 50/1 to 8/1) to give **19-α** as a white amorphous solid (1.7 mg, 43%). $[\alpha]_D^{23}$ +4.43 (c 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ = 1/1): δ 4.26 (brs, 1H, *OH*), 4.02 (ddd, *J* = 10.7, 4.4, 3.3 Hz, 1H, cer*H*2), 3.85 (ddd, *J* = 10.9, 5.6, 3.6 Hz, 1H, glc*H*1), 3.82 (dd, *J* = 11.8, 2.5 Hz, 1H, glc*H*6), 3.65–3.55 (m, 2H, glc*H*6 and glc*H*2), 3.52 (dd, *J* = 9.3, 8.4 Hz, 1H, glc*H*3), 3.46–3.40 (m, 2H, glc*H*5 and cer*H*4), 3.38 (dd, *J* = 6.9, 4.4 Hz, 1H, cer*H*3), 3.19 (dd, *J* = 9.2, 8.4 Hz, 1H, glc*H*4), 2.20–2.15 (m, 2H, cer*H*2'), 1.91–1.82 (m, 1H, cer*H*1), 1.71–1.65 (m, 1H, glc-*CH*$_2$-cer), 1.63–1.55 (m, 3H, glc-*CH*$_2$-cer and cer*H*3'), 1.43–1.19 (m, 71H, cer*H*1 and cer*H*Alkyl), 0.88 (t, *J* = 6.8 Hz, 6H, cer*H*18 and cer*H*26'); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ = 1/1): δ 175.6 (-NH*CO*-), 77.7 (cer*C*3), 76.8 (glc*C*1), 74.6 (glc*C*3), 73.7 (glc*C*5 or glc*C*2 or cer*C*4), 72.6 (glc*C*2 or glc*C*5 or cer*C*4), 72.5 (cer*C*4 or glc*C*2 or glc*C*5), 72.1 (glc*C*4), 63.0 (glc*C*6), 52.2 (cer*C*2), 37.1 (cer*C*2'), 33.6 (cer*C*Alkyl), 32.5 (2C, cer*C*Alkyl), 30.39 (cer*C*Alkyl), 30.37 (cer*C*Alkyl), 30.31 (11C, cer*C*Alkyl), 30.25 (10C, cer*C*Alkyl), 30.15 (cer*C*Alkyl), 30.04 (cer*C*Alkyl), 30.02 (cer*C*Alkyl), 29.97 (cer*C*Alkyl), 29.95 (cer*C*Alkyl), 26.6 (glc-*CH*$_2$-cer), 26.4 (cer*C*1), 25.7 (cer*C*Alkyl), 23.2 (2C, cer*C*5 and cer*C*Alkyl), 22.1 (cer*C*Alkyl), 18.2 (cer*C*Alkyl), 14.3 (2C, cer*C*18 and cer*C*26'); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{101}NaNO_8$, 878.7419; found, 878.7449.

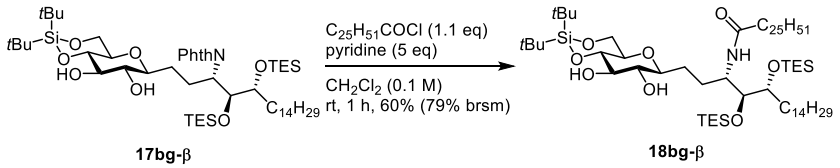
4,6-Di-*tert*-butylsilylene-2'-NH_2-3',4'-OTES-β-GlcCer (17bg-β)



To a solution of **16bg-β** (32.0 mg, 31.9 μmol, 1.0 equiv) in MeOH (320 μL, 0.1 M) was added NaOMe (8.6 mg, 160 μmol, 5.0 equiv) at room temperature. After stirring for 30 min at room temperature, the solution was filtrated through cation exchange resin (IR-120, prior to use the resin was washed with 1 M HCl and deionized water) and concentrated under reduced pressure to give the crude diol.

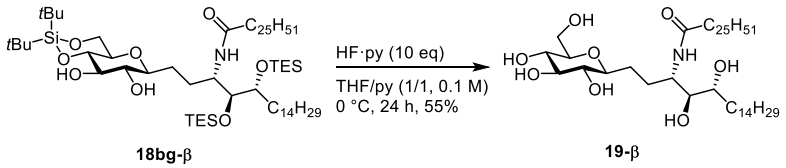
The crude mixture was dissolved in EtOH (210 μL, 0.1 M) under Ar atmosphere. To the solution was added ethylenediamine (EDA, 110 μL, 159 μmol, 50 equiv) at room temperature. After stirring for 20 h at 85 °C, the solution was cooled to room temperature, diluted with $CHCl_3$ (5 mL), and quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with $CHCl_3$ (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 1/1 to 0/1) to give aminoalcohol **17bg-β** as a colorless oil (16.9 mg, 63%). $[\alpha]_D^{29}$ –15.41 (c 0.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.12 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 3.80 (dd, *J* = 10.2, 10.1 Hz, 1H, glc*H*6ax), 3.74 (ddd, *J* = 6.3, 4.3, 4.3 Hz, 1H, sph*H*4), 3.62 (dd, *J* = 9.1, 9.0 Hz, 1H, glc*H*4), 3.51 (dd, *J* = 9.0, 8.0 Hz, 1H, glc*H*3), 3.39 (dd, *J* = 5.2, 4.3 Hz, 1H, sph*H*3), 3.36 (ddd, *J* = 10.2, 9.1, 5.0 Hz, 1H, glc*H*5), 3.35–3.28 (m, 2H, glc*H*1 and glc*H*2), 2.73 (ddd, *J* = 10.7, 5.2. 2.3 Hz, 1H, sph*H*2), 1.93–1.85 (m, 1H, glc-*CH*$_2$-sph), 1.76–1.61 (m, 2H, sph*H*1 and glc-*CH*$_2$-sph), 1.56–1.42 (m, 2H, sph*H*5), 1.43–1.32 (m, 2H, sph*H*1 and sph*H*Alkyl), 1.32–1.18 (m, 23H, sph*H*Alkyl), 1.05 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.99 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.96 (t, *J* = 7.9 Hz, 18H, Si-CH$_2$*CH*$_3$), 0.88 (t, *J* = 6.7 Hz, 3H, sph*H*18), 0.62 (q, *J* = 7.9 Hz, 6H, Si-*CH*$_2$CH$_3$), 0.60 (q, *J* = 7.9 Hz, 6H, Si-*CH*$_2$CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 80.5 (sph*C*3), 79.4 (glc*C*1), 78.4 (glc*C*3), 77.6 (glc*C*4), 75.3 (sph*C*4), 74.5 (glc*C*5), 72.8 (glc*C*2), 66.7 (glc*C*6), 54.7 (sph*C*2), 34.3 (sph*C*5), 32.1 (sph*C*Alkyl), 30.2 (sph*C*Alkyl), 29.85 (3C, sph*C*Alkyl), 29.81 (3C, sph*C*Alkyl), 29.78 (2C, sph*C*Alkyl), 29.5 (glc-*CH*$_2$-sph), 28.5 (sph*C*Alkyl), 27.6 (3C, Si-C(*CH*$_3$)$_3$), 27.2 (3C, Si-C(*CH*$_3$)$_3$), 27.0 (sph*C*1), 25.7 (sph*C*Alkyl), 22.8 (Si-*C*(CH$_3$)$_3$), 20.1 (Si-*C*(CH$_3$)$_3$), 14.3 (sph*C*18), 7.2 (6C, Si-CH$_2$*CH*$_3$), 5.5 (3C, Si-*CH*$_2$CH$_3$), 5.4 (3C, Si-*CH*$_2$CH$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{45}H_{96}NO_7Si_3$, 846.6489; found, 846.6493.

4,6-Di-*tert*-butylsilylene-3',4'-OTES-β-GlcCer (18bg-β)



To a solution of **17bg-β** (16.9 mg, 20.0 μmol, 1.0 equiv) in CH_2Cl_2 (190 μL, 0.1 M) was sequentially added pyridine (8.1 μL, 100 μmol, 5.0 equiv) and hexacosanoyl chloride (9.1 mg, 22.0 μmol, 1.1 equiv) at 0 °C. After stirring for 1 h at room temperature, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/acetone = 50/1 to 5/1) to give amide **18bg-β** as a colorless oil (14.7 mg, 60%). $[\alpha]_D^{20}$ –15.61 (c 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.65 (d, *J* = 9.2 Hz, 1H, cer*NH*), 4.12 (dd, *J* = 10.1, 5.0 Hz, 1H, glc*H*6eq), 4.11–4.05 (m, 1H, cer*H*2), 3.80 (dd, *J* = 10.2, 10.1 Hz, 1H, glc*H*6ax), 3.66 (ddd, *J* = 6.6, 4.8, 4.0 Hz, 1H, cer*H*4), 3.61 (dd, *J* = 9.2, 8.7 Hz, 1H, glc*H*4), 3.58 (dd, *J* = 4.0, 3.9 Hz, 1H, cer*H*3), 3.50 (dd, *J* = 8.8, 8.7 Hz, 1H, glc*H*3), 3.40–3.33 (m, 2H, glc*H*1 and glc*H*5), 3.22 (dd, *J* = 9.1, 8.8 Hz, 1H, glc*H*2), 2.14 (dt, *J* = 14.5, 7.5 Hz, 1H, cer*H*2'), 2.11 (dt, *J* = 14.5, 7.3 Hz, 1H, cer*H*2'), 1.89–1.78 (m, 2H, cer*H*1 and glc-*CH*$_2$-cer), 1.65–1.57 (m, 2H, cer*H*3'), 1.55–1.44 (m, 3H, cer*H*1 and cer*H*5), 1.44–1.34 (m, 2H, glc-*CH*$_2$-cer and cer*H*Alkyl), 1.34–1.18 (m, 67H, cer*H*Alkyl), 1.05 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.99 (s, 9H, Si-C(*CH*$_3$)$_3$), 0.97 (t, *J* = 7.9 Hz, 9H, Si-CH$_2$*CH*$_3$), 0.96 (t, *J* = 7.9 Hz, 9H, Si-CH$_2$*CH*$_3$), 0.88 (t, *J* = 6.8 Hz, 6H, cer*H*18 and cer*H*26'), 0.68–0.56 (m, 12H, Si-*CH*$_2$CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2 (-NH*CO*-), 78.93 (glc*C*5), 78.86 (glc*C*3), 77.9 (cer*C*3), 77.3 (glc*C*4), 75.9 (cer*C*4), 74.4 (glc*C*1), 73.9 (glc*C*2), 66.6 (glc*C*6), 51.2 (cer*C*2), 37.3 (cer*C*2'), 33.9 (cer*C*Alkyl), 32.1 (2C, cer*C*Alkyl), 30.1 (glc-*CH*$_2$-cer), 29.9 (17C, cer*C*Alkyl), 29.8 (7C, cer*C*Alkyl), 29.7 (cer*C*Alkyl), 29.60 (cer*C*Alkyl), 29.57 (cer*C*Alkyl), 29.52 (2C, cer*C*Alkyl), 27.9 (cer*C*Alkyl), 27.6 (3C, Si-C(*CH*$_3$)$_3$), 27.2 (3C, Si-C(*CH*$_3$)$_3$), 25.91 (cer*C*Alkyl), 25.88 (cer*C*5), 25.7 (cer*C*1), 22.9 (2C, cer*C*Alkyl and Si-*C*(CH$_3$)$_3$), 20.1 (Si-*C*(CH$_3$)$_3$), 14.3 (2C, cer*C*18 and cer*C*26'), 7.18 (3C, Si-CH$_2$*CH*$_3$), 7.17 (3C, Si-CH$_2$*CH*$_3$), 5.4 (6C, Si-*CH*$_2$CH$_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for, $C_{71}H_{145}NaNO_8Si_3$, 1247.0170; found, 1247.0169.

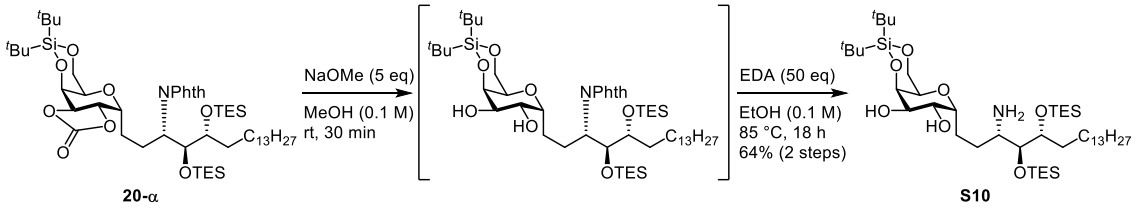
β-GlcCer (19-β)



18bg-β **19-β**

To a solution of **18bg-β** (5.2 mg, 4.2 μmol, 1.0 equiv) in THF (47 μL) was sequentially added pyridine (24 μL) and HF·py (1.9 μL, 21 μmol, 10 equiv) at 0 °C. After stirring for 24 h at 0 °C, the solution was quenched with solid $NaHCO_3$ (20 mg). Excess solids were filtered off over a plug of cotton wool, rinsed with $CHCl_3$/MeOH (1/1), and the filtrate was concentrated. The residue was purified by gel permeation chromatography (Sephadex LH-20, eluent; $CHCl_3$/MeOH = 1/1). Further purification was carried out by adsorption chromatography on Iatrobeads 6RS-8060 (LSI Medience Co., eluent: $CHCl_3$/MeOH = 50/1 to 8/1) to give **19-β** as a white amorphous solid (2.0 mg, 55%). $[\alpha]_D^{23}$ –10.38 (c 0.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.07 (ddd, *J* = 11.2, 4.0, 2.9 Hz, 1H, cer*H*2), 3.82 (dd, *J* = 11.9, 2.3 Hz, 1H, glc*H*6), 3.60 (dd, *J* = 11.9, 5.8 Hz, 1H, glc*H*6), 3.43–3.38 (m, 1H, cer*H*4), 3.37 (dd, *J* = 7.2, 4.0 Hz, 1H, cer*H*3), 3.34–3.29 (m, 1H, glc*H*3), 3.23 (dd, *J* = 9.6, 8.3 Hz, 1H, glc*H*4), 3.22–3.15 (m, 2H, glc*H*5 and glc*H*1), 3.07 (dd, *J* = 9.2, 9.0 Hz, 1H, glc*H*2), 2.22–2.12 (m, 2H, cer*H*2'), 1.84–1.74 (m, 2H, cer*H*1 and glc-*CH*$_2$-cer), 1.72–1.64 (m, 1H, cer*H*5), 1.64–1.55 (m, 3H, cer*H*1 and cer*H*3'), 1.55–1.48 (m, 1H, cer*H*6), 1.48–1.40 (m, 1H, glc-*CH*$_2$-cer), 1.23–1.30 (m, 68H, cer*H*5 and cer*H*Alkyl), 0.86 (t, *J* = 6.8 Hz, 6H, cer*H*18 and cer*H*26'); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.5 (-NH*CO*-), 80.6 (glc*C*5), 79.2 (glc*C*3 or glc*C*1), 79.1 (glc*C*1 or glc*C*3), 77.5 (cer*C*3), 74.5 (glc*C*2), 72.6 (cer*C*4), 71.4 (glc*C*4), 62.7 (glc*C*6), 51.3 (cer*C*2), 37.1 (cer*C*2'), 33.8 (cer*C*Alkyl), 32.5 (2C, cer*C*Alkyl), 30.33 (cer*C*Alkyl), 30.28 (cer*C*Alkyl), 30.23 (11C, cer*C*Alkyl), 30.19 (11C, cer*C*Alkyl), 30.09 (cer*C*Alkyl), 29.97 (cer*C*Alkyl), 29.92 (cer*C*Alkyl), 29.89 (2C, cer*C*Alkyl), 28.2 (cer*C*Alkyl), 26.6 (cer*C*5), 26.3 (cer*C*1), 24.2 (glc-*CH*$_2$-cer), 23.2 (2C, cer*C*Alkyl), 14.3 (2C, cer*C*18 and cer*C*26'); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for, $C_{51}H_{101}NaNO_8$, 878.7419; found, 878.7414.

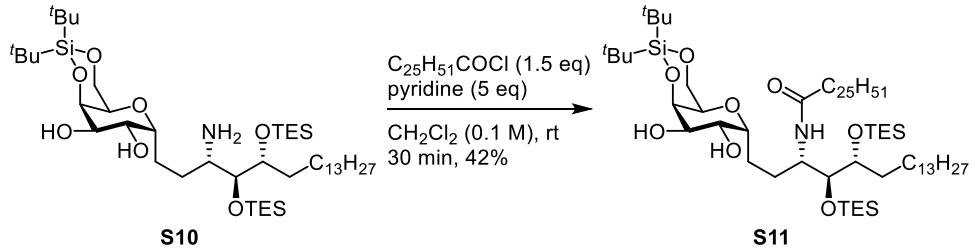
4,6-Di-*tert*-butylsilylene-2'-NH_2-3',4'-OTES-α-GalCer (S10)



To a solution of **20-α** (28.4 mg, 28.3 μmol, 1.0 equiv) in MeOH (280 μL, 0.1 M) was added NaOMe (7.7 mg, 140 μmol, 5.0 equiv) at room temperature. After stirring for 30 min at room temperature, the solution was filtrated through cation exchange resin (IR-120, prior to use the resin was washed with 1 M HCl and deionized water) and concentrated under reduced pressure to give the crude diol.

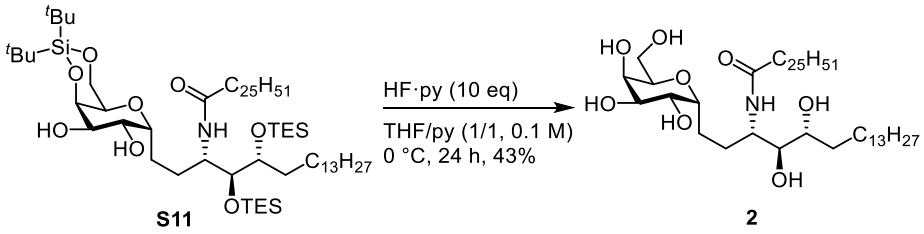
The crude mixture was dissolved in EtOH (190 μL, 0.1 M) under Ar atmosphere. To the solution was added ethylenediamine (EDA, 96 μL, 1.40 mmol, 50 equiv) at room temperature. After stirring for 18 h at 85 °C, the solution was cooled to room temperature, diluted with $CHCl_3$ (5 mL), quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with $CHCl_3$ (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 1/1 to 0/1) to give aminoalcohol **S10** as a colorless oil (15.4 mg, 64%). $[\alpha]_D^{20}$ +29.70 (c 0.49, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.40 (dd, *J* = 3.6, 1.2 Hz, 1H, gal*H*4), 4.24 (dd, *J* = 12.3, 2.2 Hz, 1H, gal*H*6), 4.14 (dd, *J* = 12.3, 1.6 Hz, 1H, gal*H*6), 4.07 (m, 1H, gal*H*1), 4.06 (dd, *J* = 6.3, 6.0 Hz, 1H, gal*H*2), 3.77 (ddd, *J* = 6.5, 4.3, 3.6 Hz, 1H, sph*H*4), 3.58 (ddd, *J* = 9.4, 6.0, 3.6 Hz, 1H, gal*H*3), 3.54 (dd, *J* = 2.2, 1.2 Hz, 1H, gal*H*5), 3.38 (dd, *J* = 5.7, 3.6 Hz, 1H, sph*H*3), 2.71 (ddd, *J* = 9.9, 5.7, 2.5 Hz, 1H, sph*H*2), 2.52 (d, *J* = 10.9 Hz, 1H, *OH*), 1.95–1.83 (m, 2H, sph*H*1 and gal-*CH*$_2$-sph), 1.55–1.33 (m, 3H, sph*H*5 and gal-*CH*$_2$-sph), 1.32–1.12 (m, 24H, sph*H*Alkyl), 1.21–1.12 (m, 1H, sph*H*1), 1.05 (s, 18H, Si-C(*CH*$_3$)$_3$), 0.96 (t, *J* = 7.9 Hz, 18H, Si-CH_2*CH*$_3$), 0.88 (t, *J* = 6.9 Hz, 3H, sph*H*18), 0.65–0.57 (m, 12H, Si-*CH*$_2$$CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 80.7 (sph*C*3), 77.4 (gal*C*1), 75.2 (sph*C*4), 73.3 (gal*C*4), 71.5 (gal*C*3), 69.7 (gal*C*2), 67.9 (gal*C*5), 67.6 (gal*C*6), 55.1 (sph*C*2), 33.9 (sph*C*5), 32.1 (sph*C*Alkyl), 30.2 (sph*C*1), 30.1 (sph*C*Alkyl), 29.9 (3C, sph*C*Alkyl), 29.82 (3C, sph*C*Alkyl), 29.79 (sph*C*Alkyl), 29.5 (sph*C*Alkyl), 27.7 (3C, Si-C(*CH*$_3$)$_3$), 27.5 (3C, Si-C(*CH*$_3$)$_3$), 25.9 (sph*C*Alkyl), 23.5 (sph*C*Alkyl), 22.9 (Si-*C*$(CH_3)_3$), 21.7 (gal-*CH*$_2$-sph), 20.9 (Si-*C*$(CH_3)_3$), 14.3 (sph*C*18), 7.23 (3C, Si-CH_2*CH*$_3$), 7.20 (3C, Si-CH_2*CH*$_3$), 5.5 (3C, Si-*CH*$_2$$CH_3$), 5.4 (3C, Si-*CH*$_2$$CH_3$); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{45}H_{96}NO_7Si_3$, 846.6489; found, 846.6510.

4,6-Di-*tert*-butylsilylene-3',4'-OTES-α-GalCer (S11)



To a solution of **S10** (11.0 mg, 13.0 μmol, 1.0 equiv) in CH_2Cl_2 (125 μL, 0.1 M) was sequentially added pyridine (5.2 μL, 65.0 μmol, 5.0 equiv) and hexacosanoyl chloride (8.1 mg, 19.5 μmol, 1.5 equiv) at 0 °C. After stirring for 1 h at room temperature, the solution was diluted with CH_2Cl_2 (5 mL) and quenched with saturated aqueous $NaHCO_3$ (5 mL). After separating layers, the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/acetone = 50/1 to 5/1) to give amide **S11** as a colorless oil (6.7 mg, 42%). $[\alpha]_D^{20}$ +11.53 (c 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.45 (d, *J* = 9.3 Hz, 1H, cer*NH*), 4.38 (dd, *J* = 3.6, 0.8 Hz, 1H, gal*H*4), 4.25 (dd, *J* = 12.4, 2.2 Hz, 1H, gal*H*6), 4.14 (dd, *J* = 12.4, 1.5 Hz, 1H, gal*H*6), 4.07–3.98 (m, 3H, gal*H*1, gal*H*2, and cer*H*2), 3.63 (ddd, *J* = 6.9, 4.3, 4.1 Hz, 1H, cer*H*4), 3.57–3.50 (m, 3H, gal*H*3, cer*H*3, and gal*H*5), 2.48 (d, *J* = 10.9 Hz, 1H, *OH*), 2.33 (s, 1H, *OH*), 2.13 (dd, *J* = 8.2, 7.1 Hz, 2H, cer*H*2'), 1.97 (dddd, *J* = 13.9, 11.1, 4.7, 2.7 Hz, 1H, cer*H*1), 1.75–1.66 (m, 1H, gal-CH_2-cer), 1.65–1.58 (m, 2H, cer*H*3'), 1.55–1.41 (m, 3H, cer*H*5 and gal-CH_2-cer), 1.25–1.38 (m, 69H, cer*H*Alkyl), 1.05 (s, 9H, Si-C(CH_3)$_3$), 1.04 (s, 9H, Si-C(CH_3)$_3$), 0.96 (t, *J* = 7.9 Hz, 18H, Si-CH_2CH_3), 0.88 (t, *J* = 6.9 Hz, 6H, cer*H*18 and cer*H*26'), 0.68–0.55 (m, 12H, Si-CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.6 (-NH*CO*-), 78.7 (cer*C*3), 76.4 (gal*C*1), 75.2 (cer*C*4), 73.3 (gal*C*4), 71.3 (gal*C*3), 69.7 (gal*C*2), 67.8 (gal*C*5), 67.6 (gal*C*6), 51.8 (cer*C*2), 37.3 (cer*C*2'), 33.5 (cer*C*5), 32.1 (2C, cer*C*Alkyl), 30.2 (cer*C*1), 29.9 (17C, cer*C*Alkyl), 29.8 (6C, cer*C*Alkyl), 29.7 (cer*C*Alkyl), 29.63 (cer*C*Alkyl), 29.60 (cer*C*Alkyl), 29.5 (2C, cer*C*Alkyl), 27.7 (3C, Si-C(CH_3)$_3$), 27.4 (3C, Si-C(CH_3)$_3$), 27.0 (cer*C*Alkyl), 25.9 (cer*C*Alkyl), 25.8 (cer*C*Alkyl), 23.5 (cer*C*Alkyl), 22.8 (2C, gal-CH_2-cer and Si-*C*(CH_3)$_3$), 20.9 (Si-*C*(CH_3)$_3$), 20.6 (cer*C*Alkyl), 14.3 (2C, cer*C*18 and cer*C*26'), 7.2 (6C, Si-CH_2CH_3), 5.4 (6C, Si-CH_2CH_3); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for, $C_{71}H_{145}NaNO_8Si_3$, 1247.0170; found, 1247.0088.

α-GalCer (2)



To a solution of **S11** (6.0 mg, 4.9 μmol, 1.0 equiv) in THF (49 μL) was sequentially added pyridine (43 μL) and HF·py (4.4 μL, 49 μmol, 10 equiv) at 0 °C. After stirring for 24 h at 0 °C, the solution was quenched with solid $NaHCO_3$ (20 mg). Excess solids were filtered off over a plug of cotton wool, rinsed with $CHCl_3$/MeOH (1/1), and the filtrate was concentrated. The residue was purified by gel permeation chromatography (Sephadex LH-20, eluent; $CHCl_3$/MeOH = 1/1). Further purification was carried out by adsorption chromatography on Iatrobeads 6RS-8060 (LSI Medience Co., eluent: $CHCl_3$/MeOH = 50/1 to 8/1) to give **2** as a white amorphous solid (1.8 mg, 43%). $[\alpha]_D^{22}$ +29.34 (c 0.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (ddd, *J* = 10.7, 4.3, 3.2 Hz, 1H, cer*H*2), 3.93–3.86 (m, 3H, gal*H*1, gal*H*2, and gal*H*3), 3.77 (dd, *J* = 11.6, 7.1 Hz, 1H, gal*H*6), 3.67 (dd, *J* = 11.6, 4.3 Hz, 1H, gal*H*6), 3.65–3.59 (m, 3H, gal*H*5, gal*H*4, and cer*H*4), 3.37 (dd, *J* = 7.2, 4.3 Hz, 1H, cer*H*3), 2.22–2.12 (m, 2H, cer*H*2'), 1.87–1.79 (m, 1H, cer*H*1), 1.72–1.61 (m, 2H, cer*H*5 and glc-CH_2-cer), 1.61–1.48 (m, 4H, glc-CH_2-cer, cer*H*3', and cer*H*6), 1.44–1.33 (m, 2H, cer*H*1 and cer*H*5), 1.33–1.19 (m, 67H, cer*H*Alkyl), 0.85 (t, *J* = 6.9 Hz, 6H, cer*H*18 and cer*H*26'); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.5 (-NH*CO*-), 77.6 (cer*C*3), 76.2 (gal*C*1), 72.7 (cer*C*4 or gal*C*5), 72.5 (gal*C*5 or cer*C*4), 71.2 (gal*C*4), 69.9 (gal*C*2 or gal*C*3), 69.6 (gal*C*3 or gal*C*2), 62.4 (gal*C*6), 52.1 (cer*C*2), 37.0 (cer*C*2'), 33.6 (cer*C*Alkyl), 32.5 (2C, cer*C*Alkyl), 30.32 (cer*C*Alkyl), 30.29 (cer*C*Alkyl), 30.23 (11C, cer*C*Alkyl), 30.18 (11C, cer*C*Alkyl), 30.08 (cer*C*Alkyl), 29.96 (cer*C*Alkyl), 29.94 (cer*C*Alkyl), 29.87 (cer*C*Alkyl), 26.6 (cer*C*Alkyl), 26.3 (cer*C*Alkyl), 25.7 (cer*C*1), 23.2 (2C, cer*C*Alkyl), 21.9 (gal-CH_2-cer), 14.3 (2C, cer*C*18 and cer*C*26'); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{51}H_{101}NaNO_8$, 878.7419; found, 878.7416.

6. Computational Methods and Figure S1

The modeling studies were performed using Spartan 08 (Wavefunction). The conformational analysis of olefin **12d** was conducted using the conformer distribution method (MMFF force field). The stable conformations were subsequently optimized at the DFT (M06-2X/6-31G**) level in 1,2-dichloroethane using the 16 A.03 revision of Gaussian 16. Frequencies were analytically computed at the same level of theory to give Gibbs free energies (298 K, 1 atm) and to confirm whether the structures are minima (no imaginary frequencies) or transition states (one imaginary frequency). Bulk solvent effects (1,2-dichloroethane) were evaluated by using the solvation model of density (SMD).

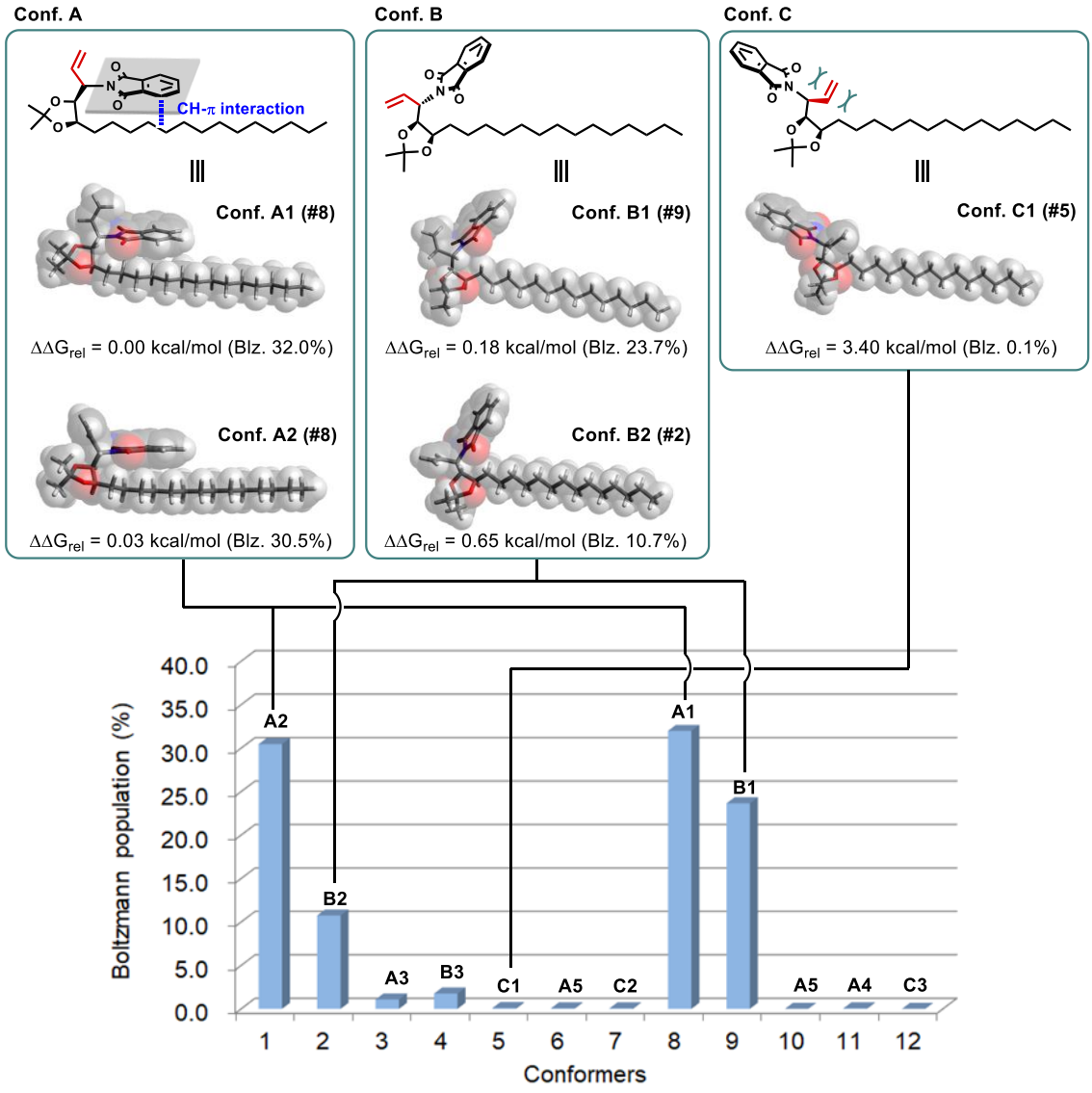


Figure. S1. The Boltzmann conformational population for optimized structure **12d** (M06-2X/6-31G**/SMD=1,2-dichloroethane).

6. References

1) Sakata, M.; Haga, M.; Tejima, S. *Carbohydr. Res.* **1970**, *13*, 379.

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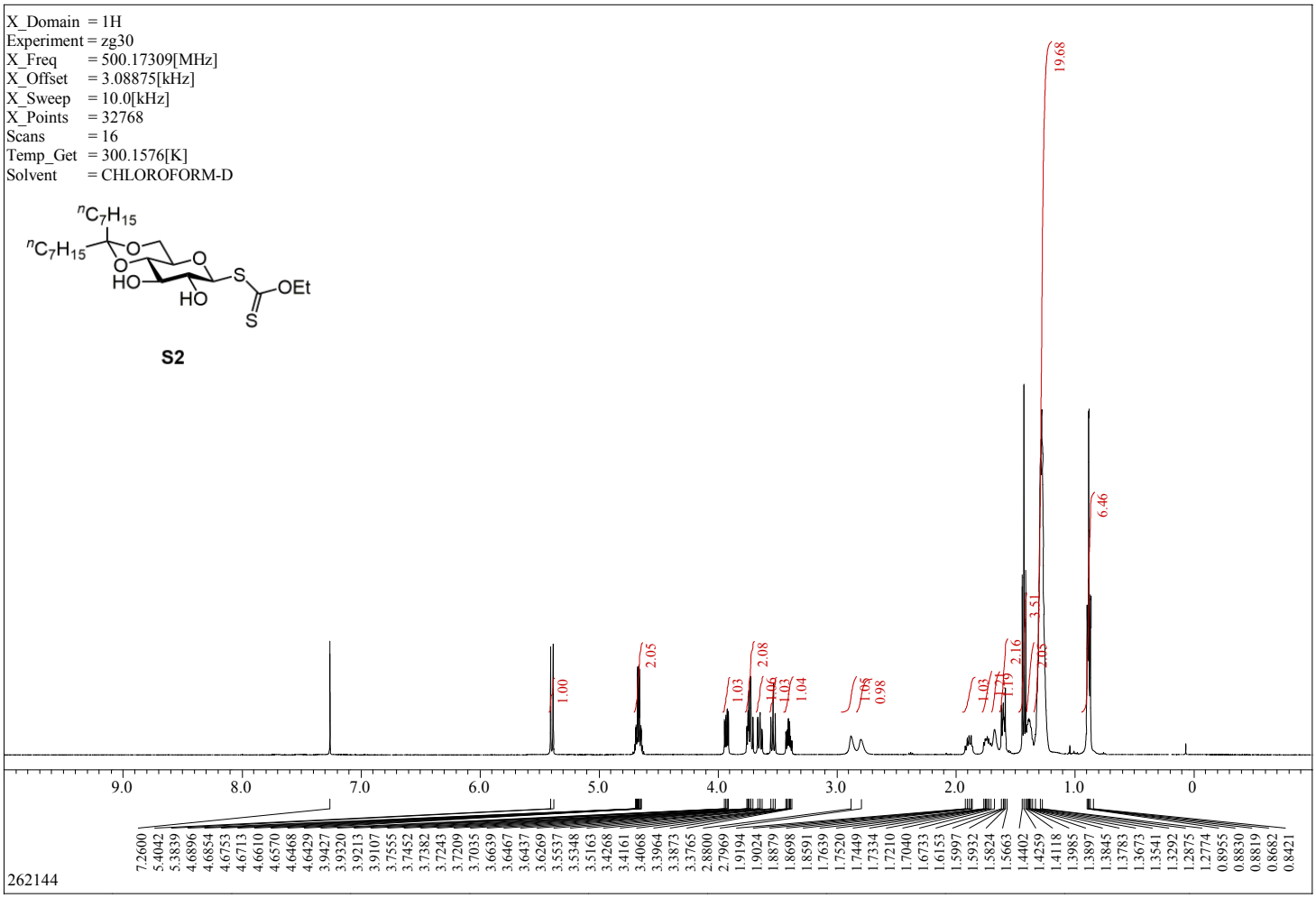
7) Disadee, W.; Ishikawa, T. *J. Org. Chem.* **2005**, *70*, 9399.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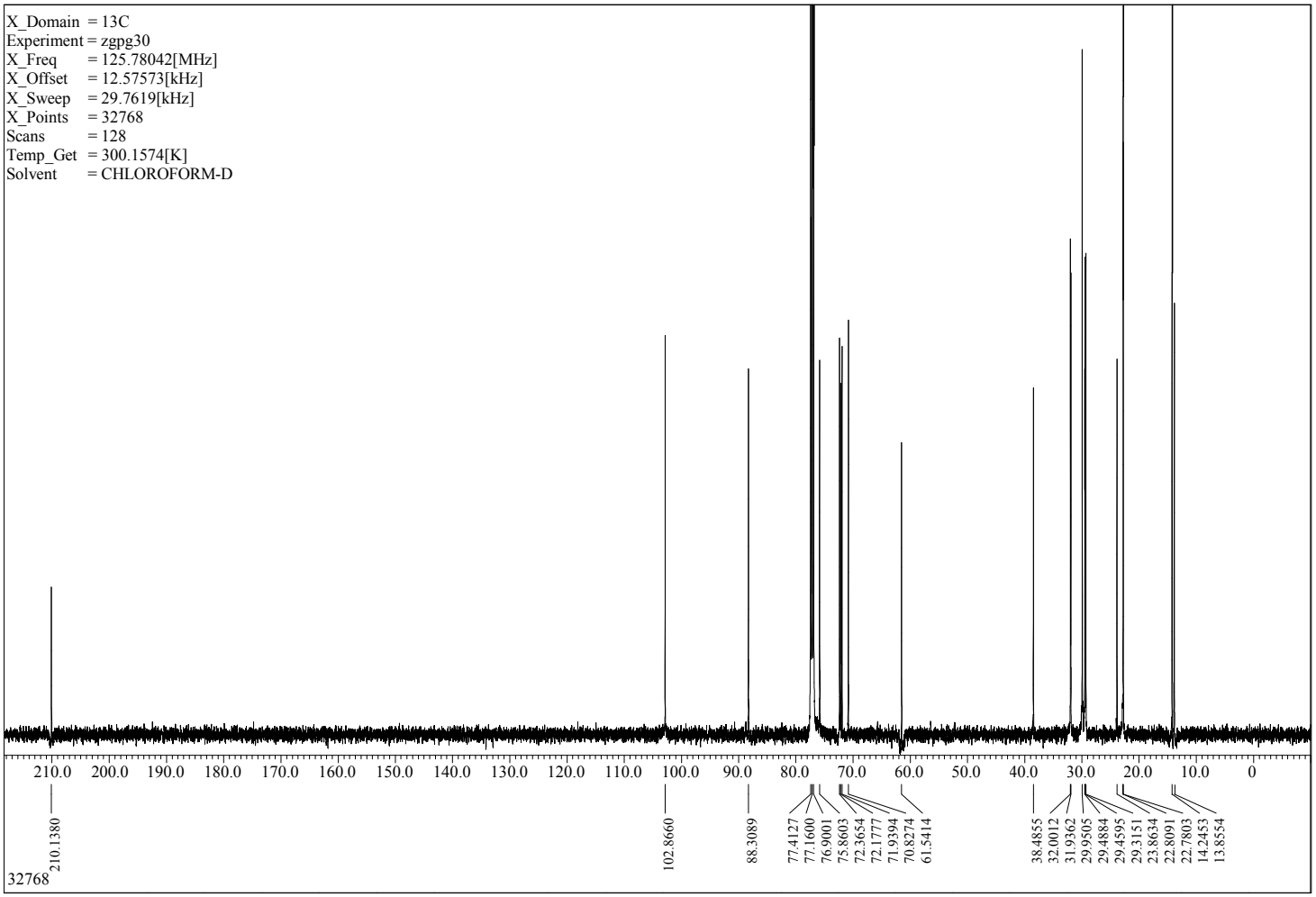
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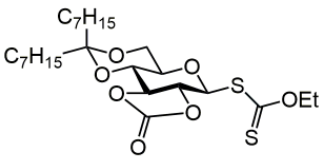

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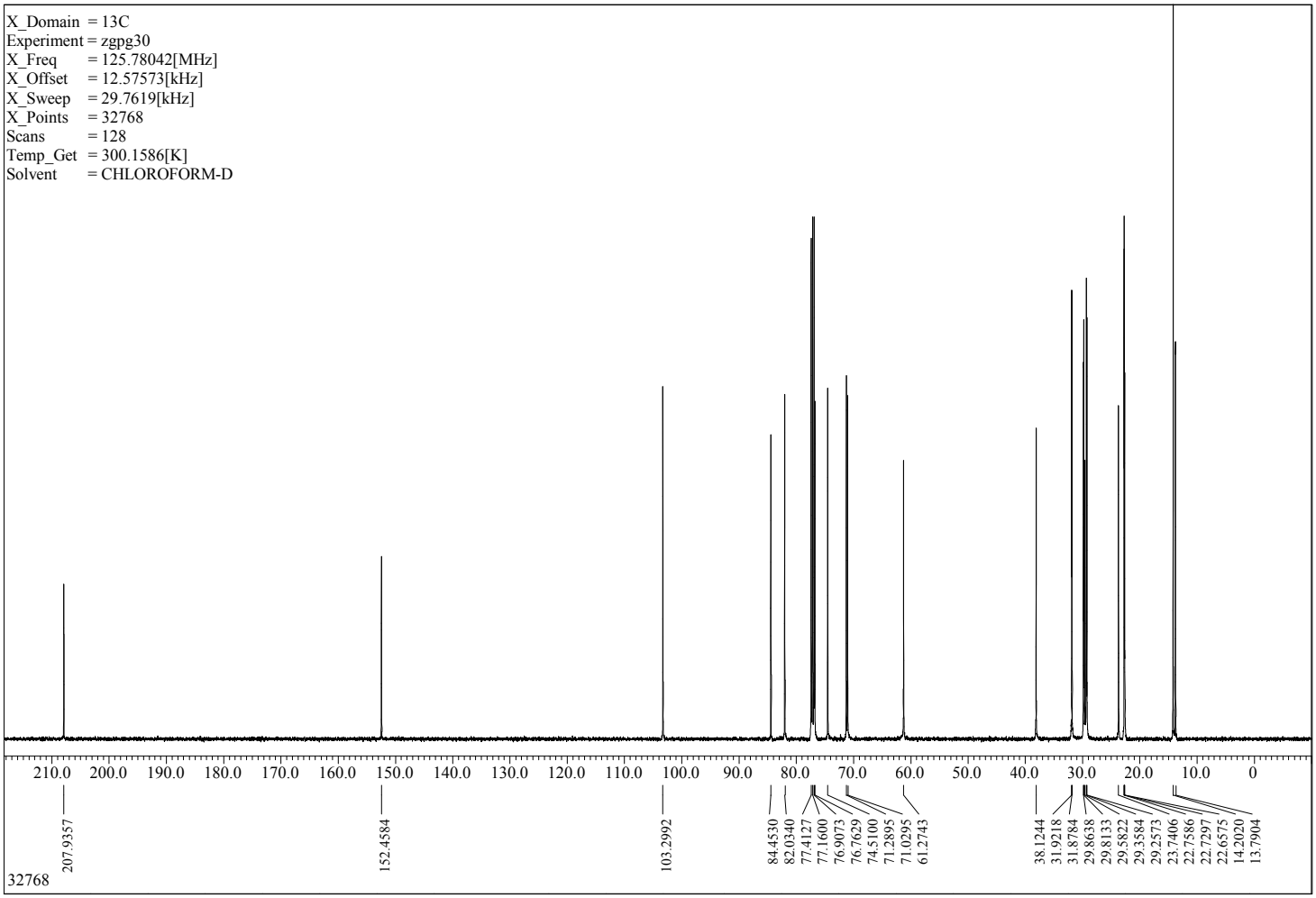

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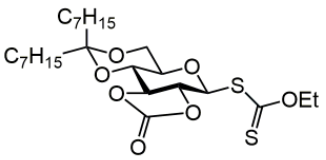

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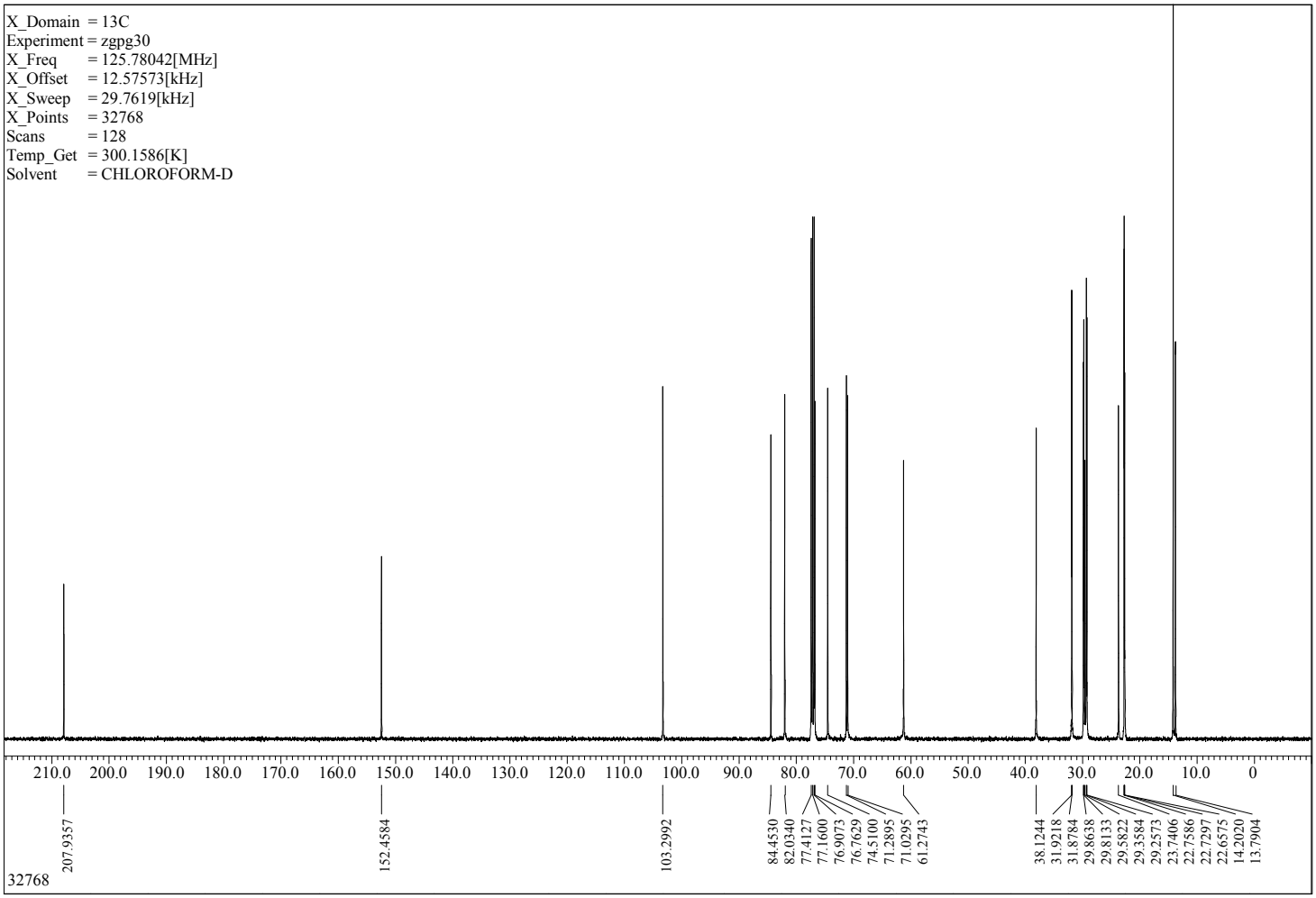

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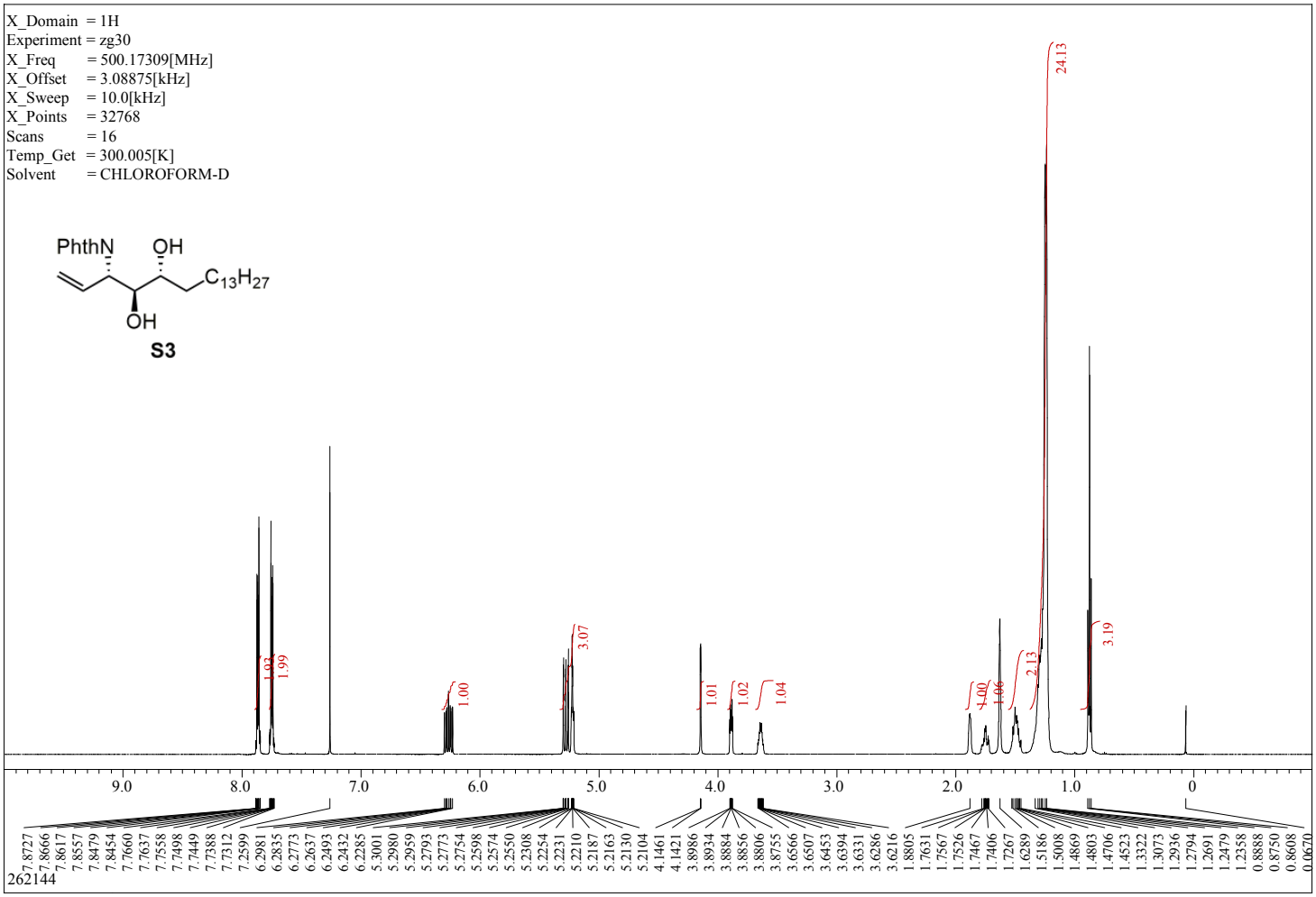
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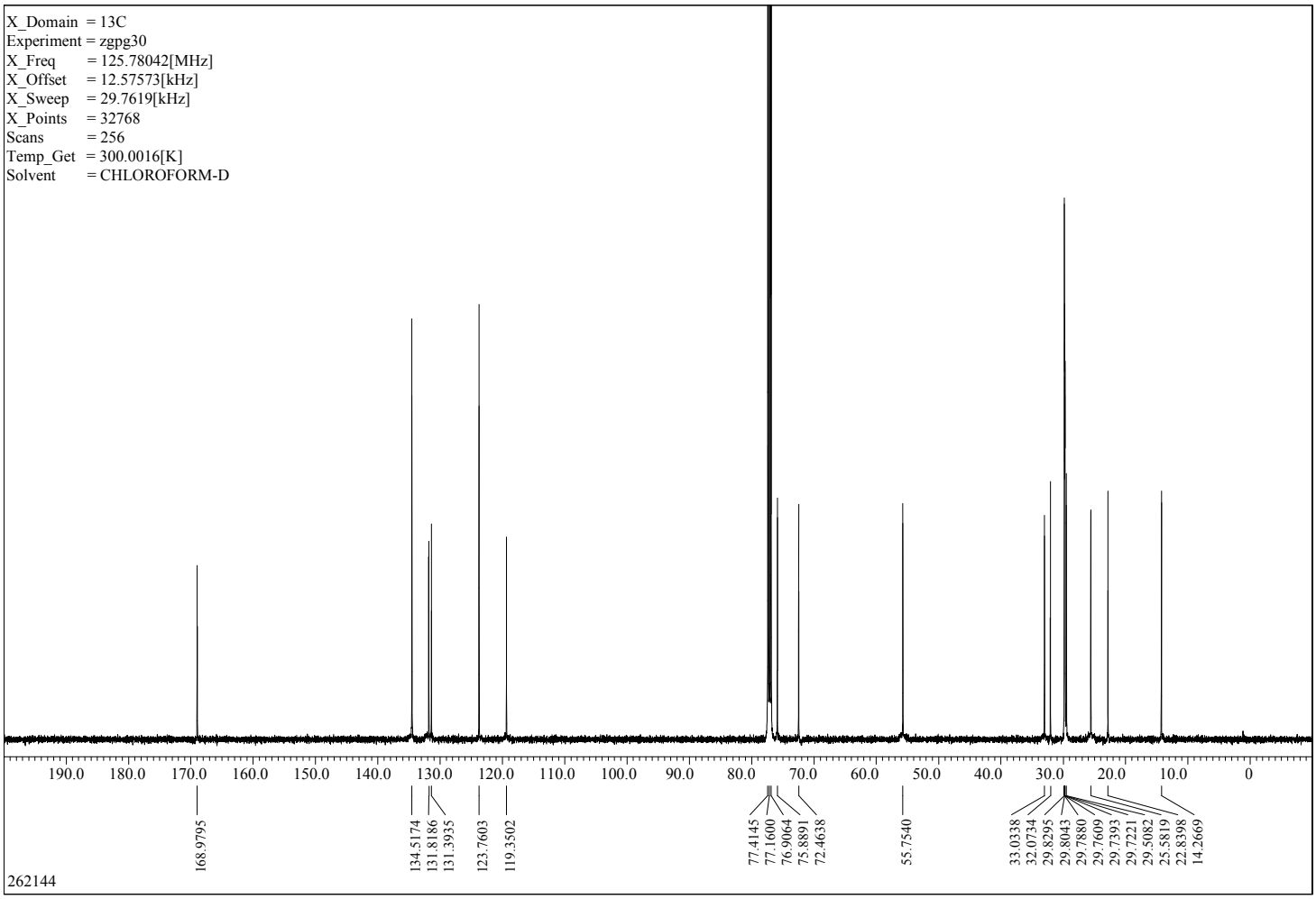
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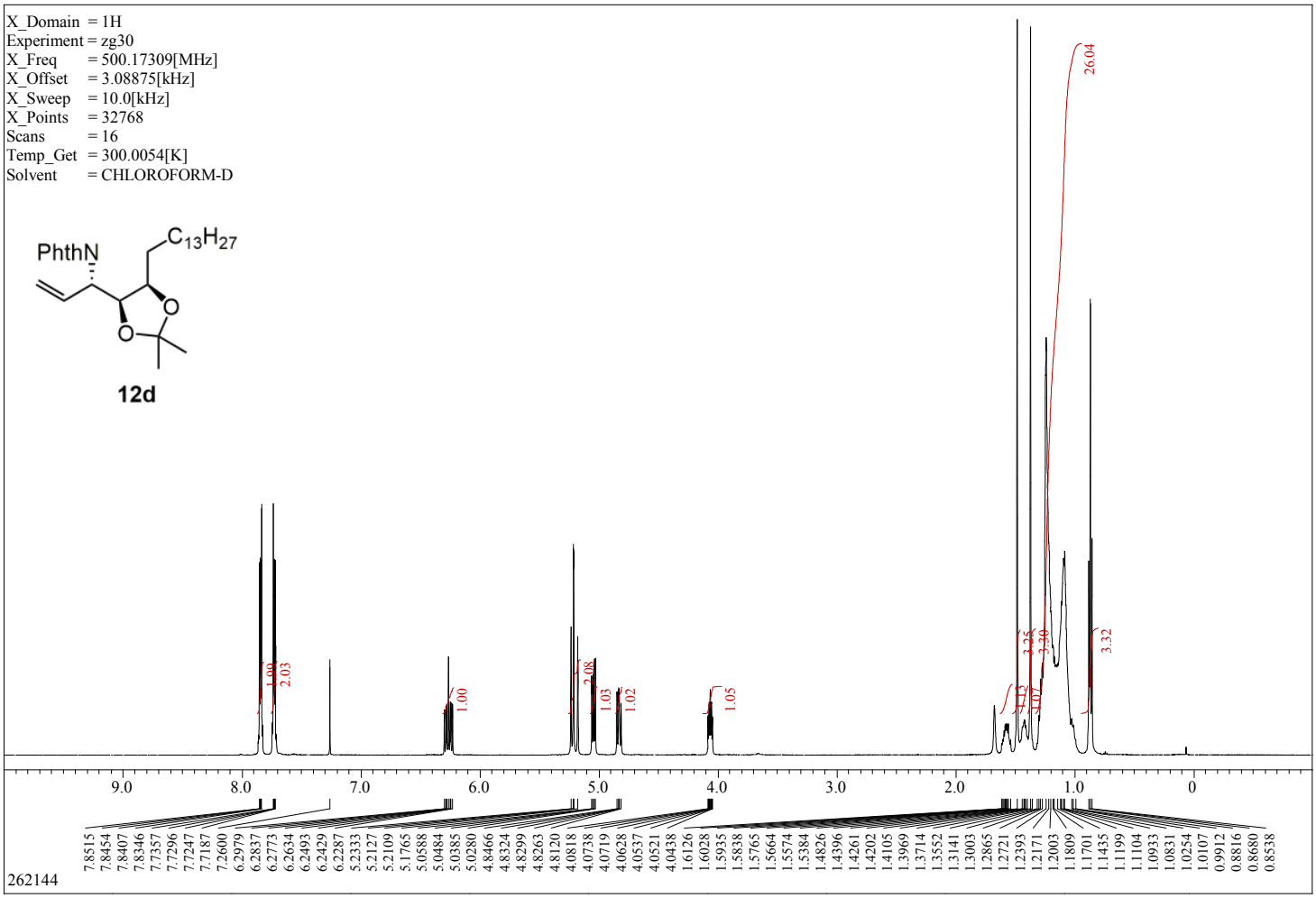
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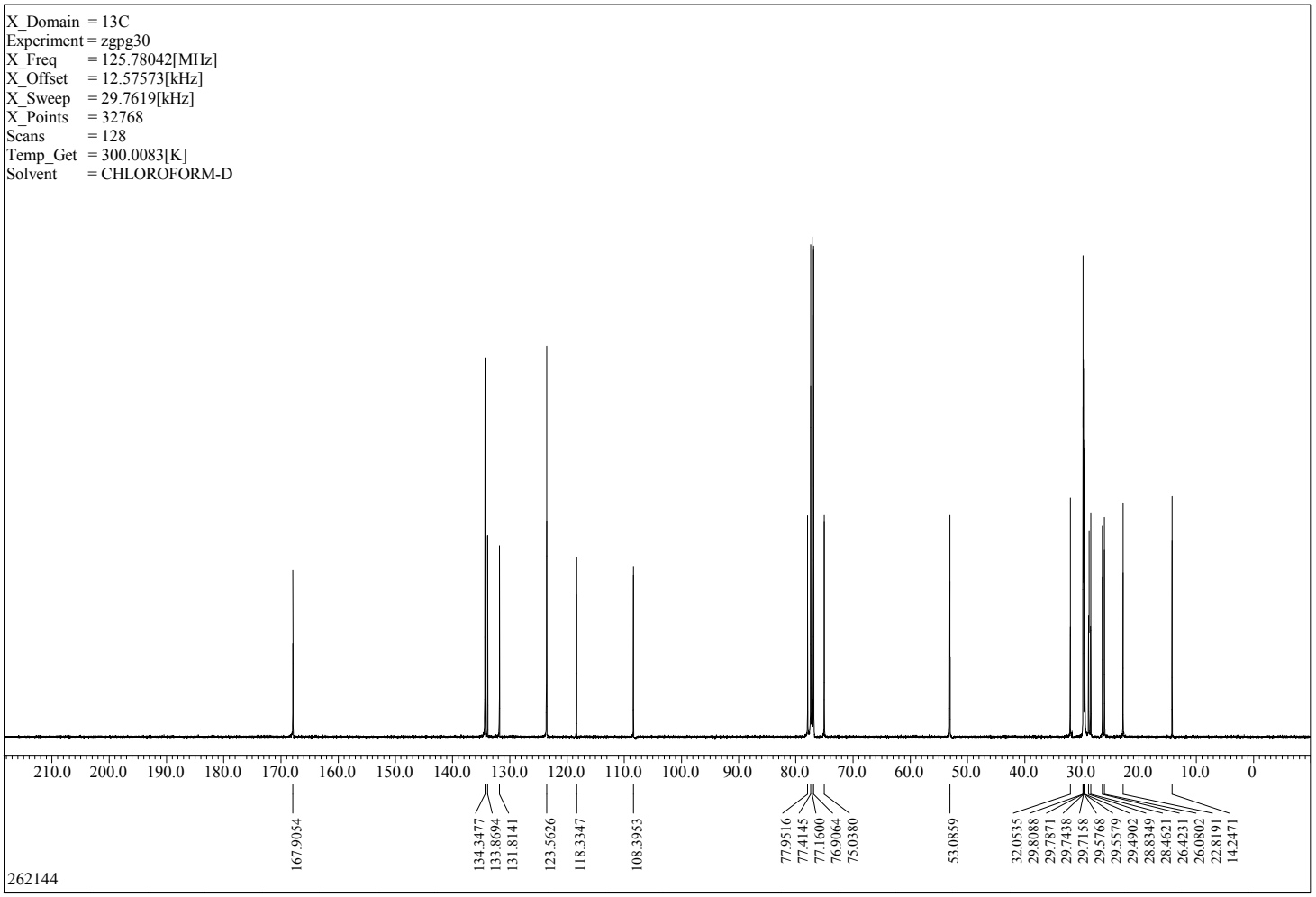
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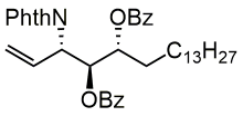

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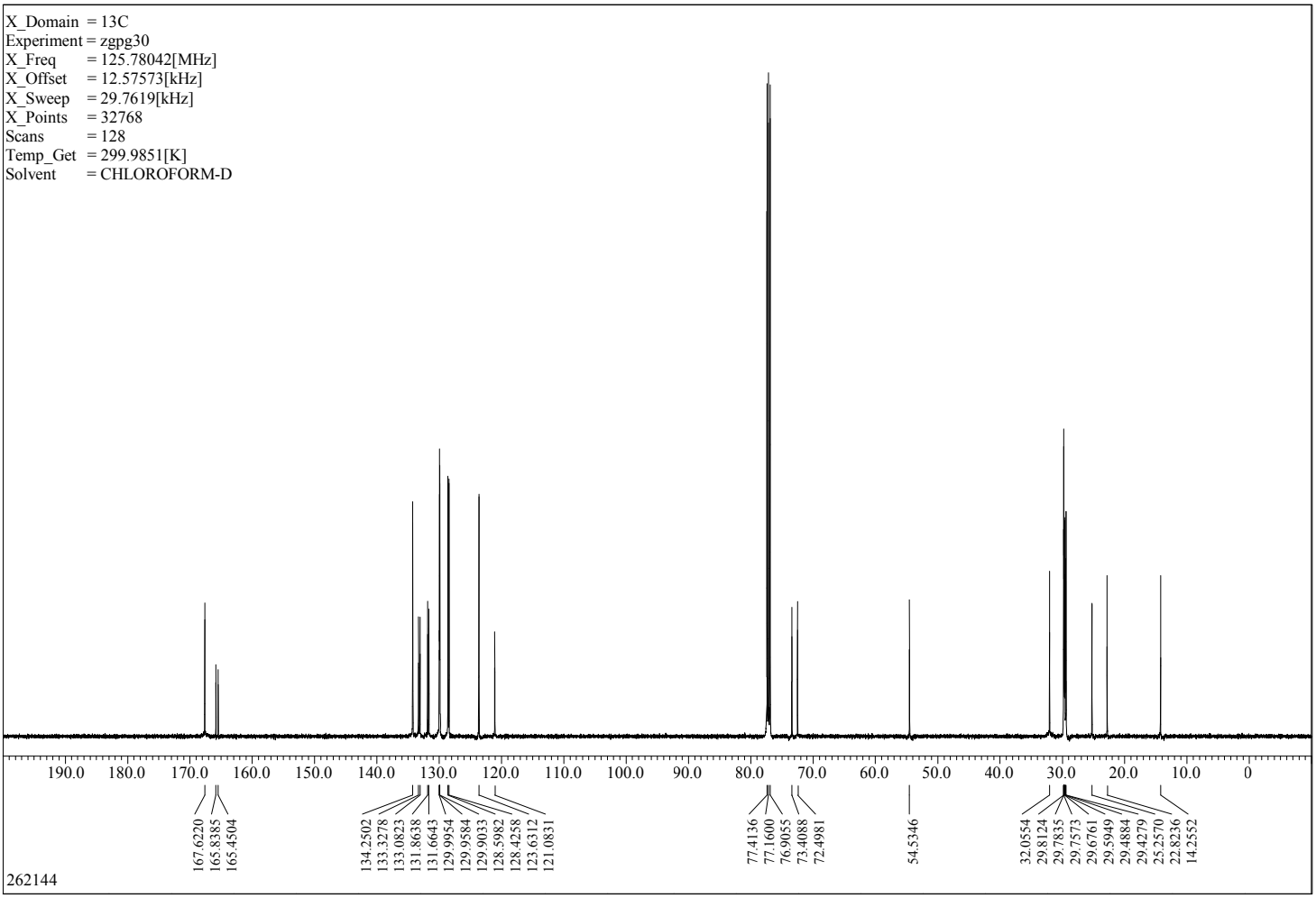

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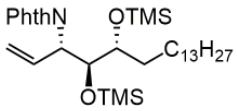

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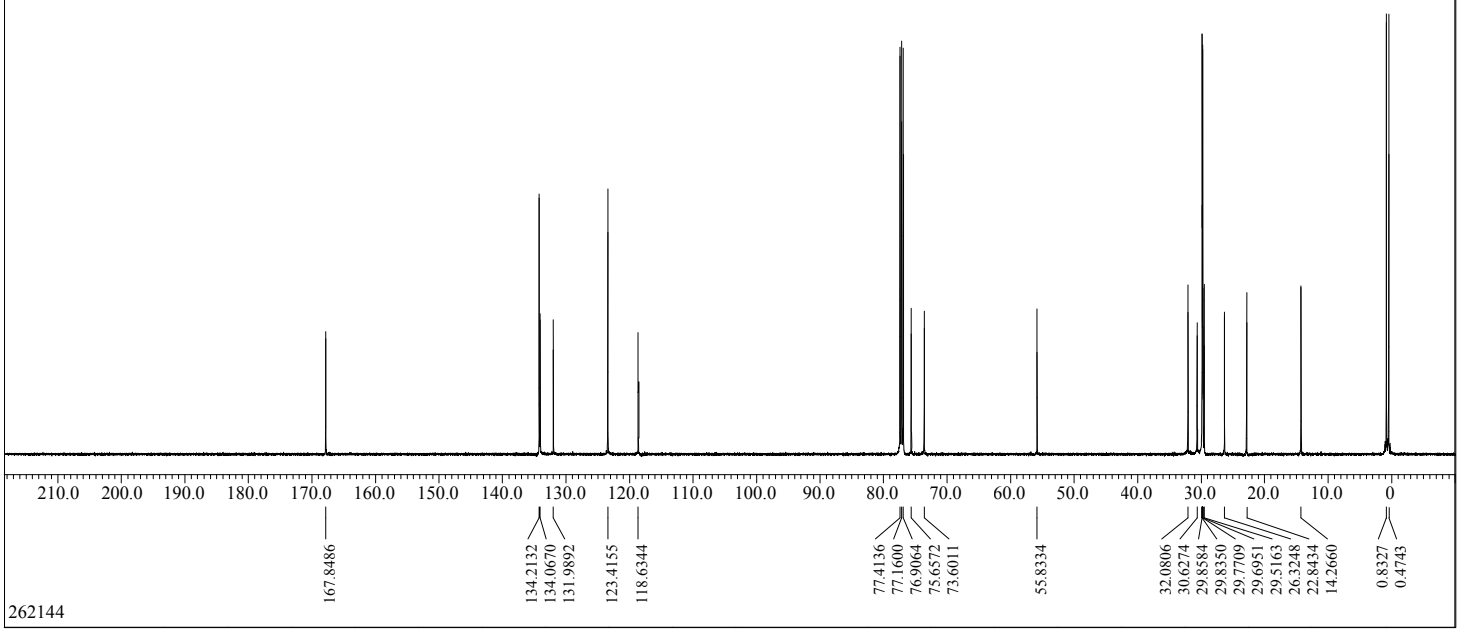

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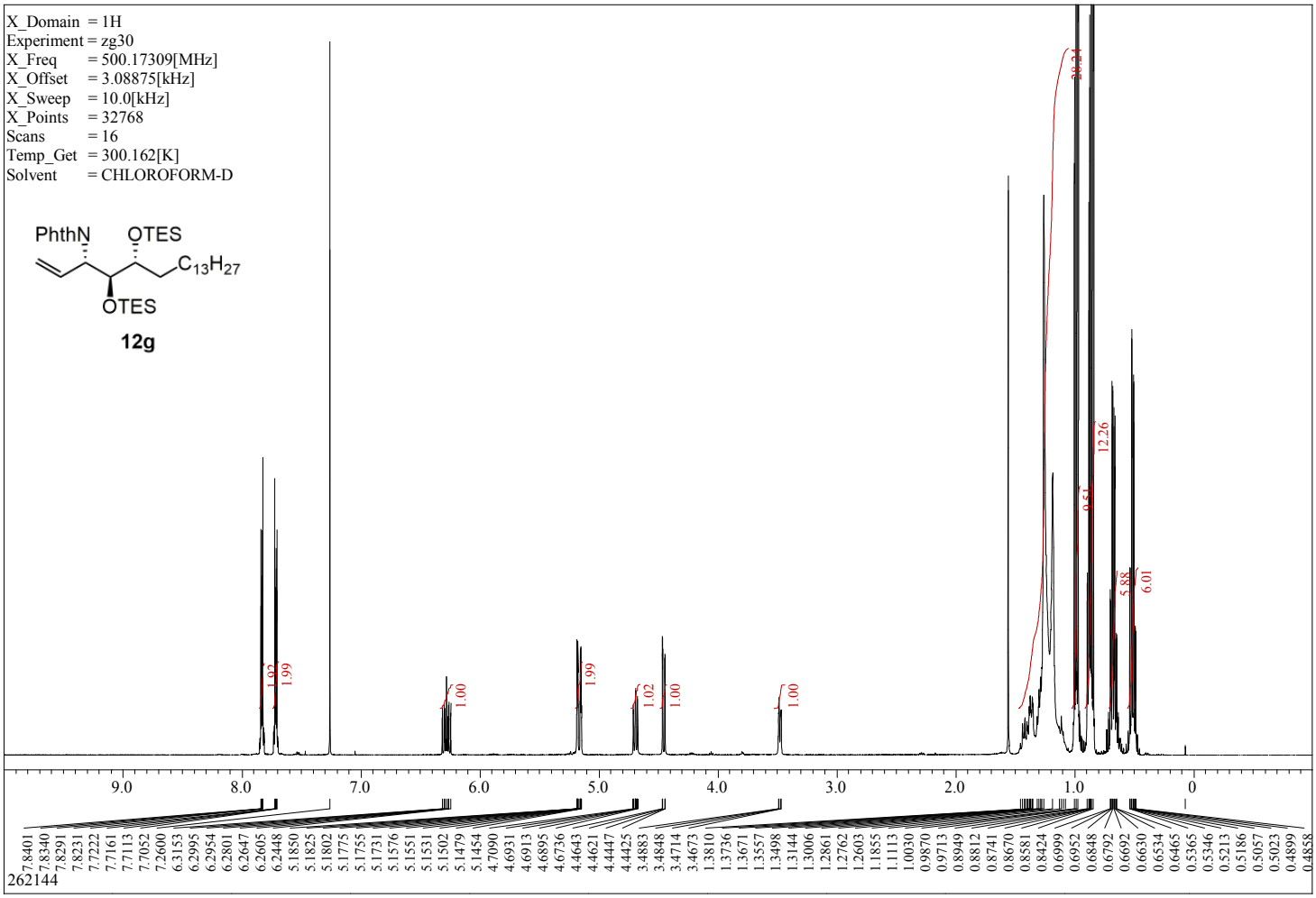
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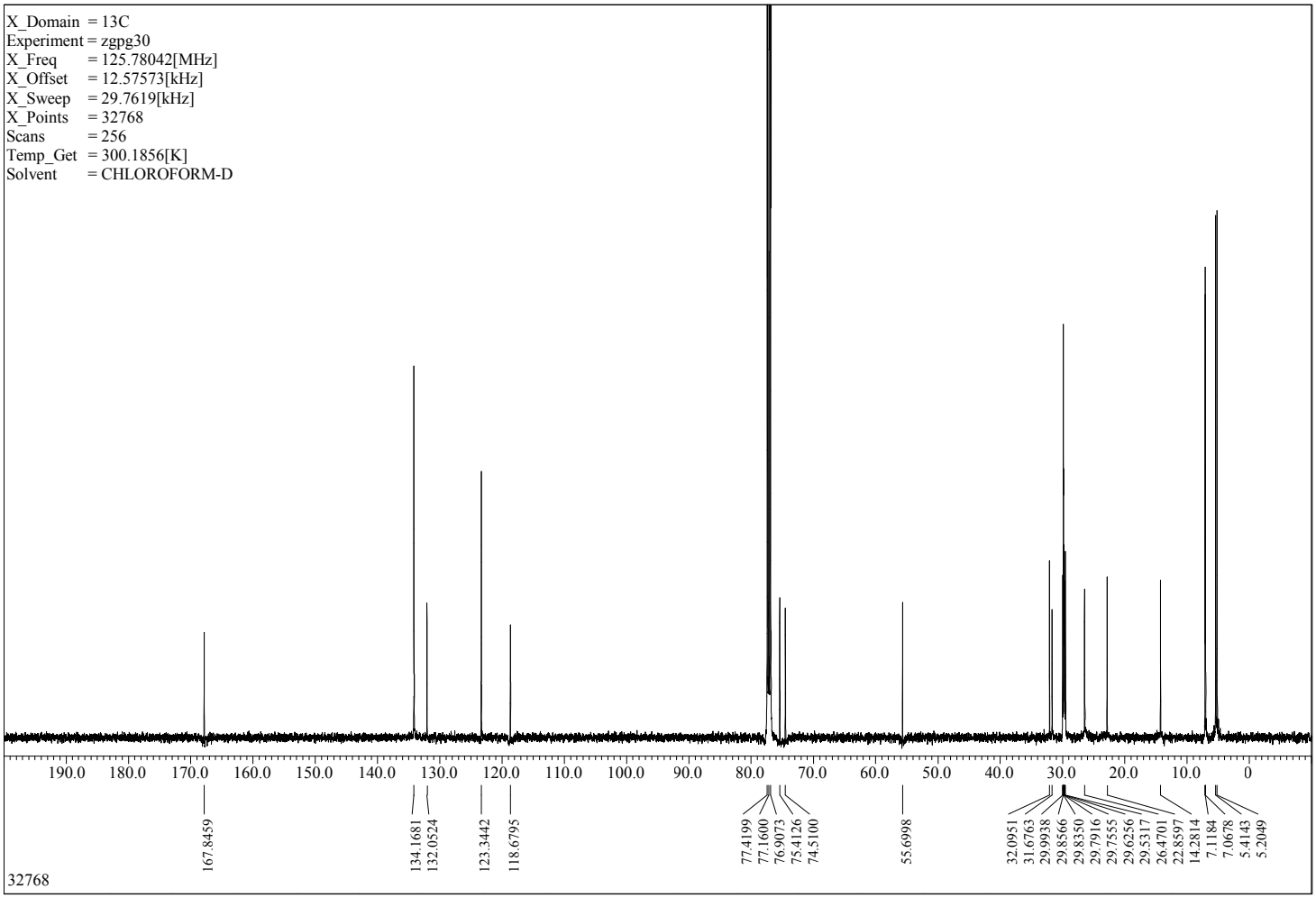
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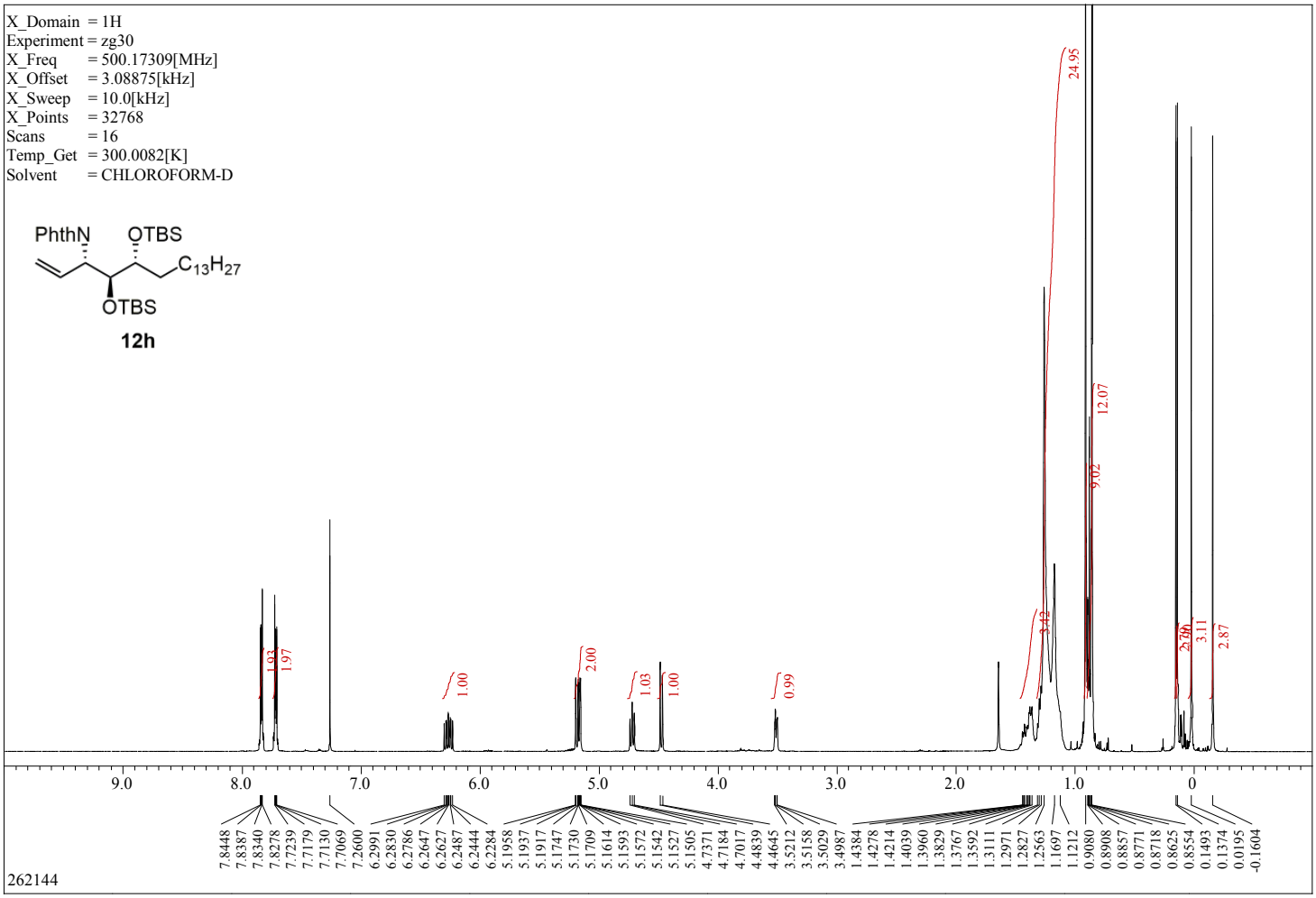
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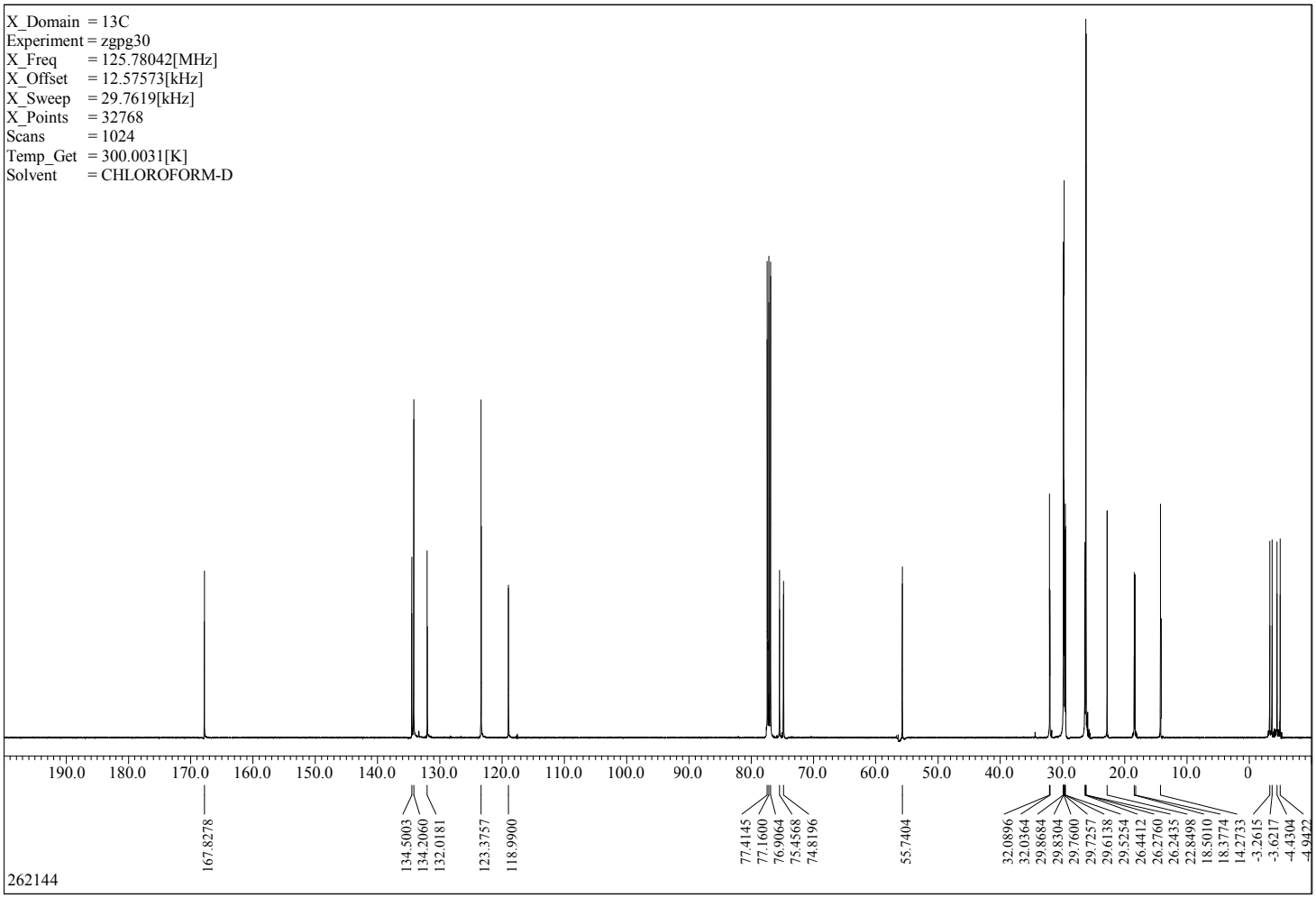
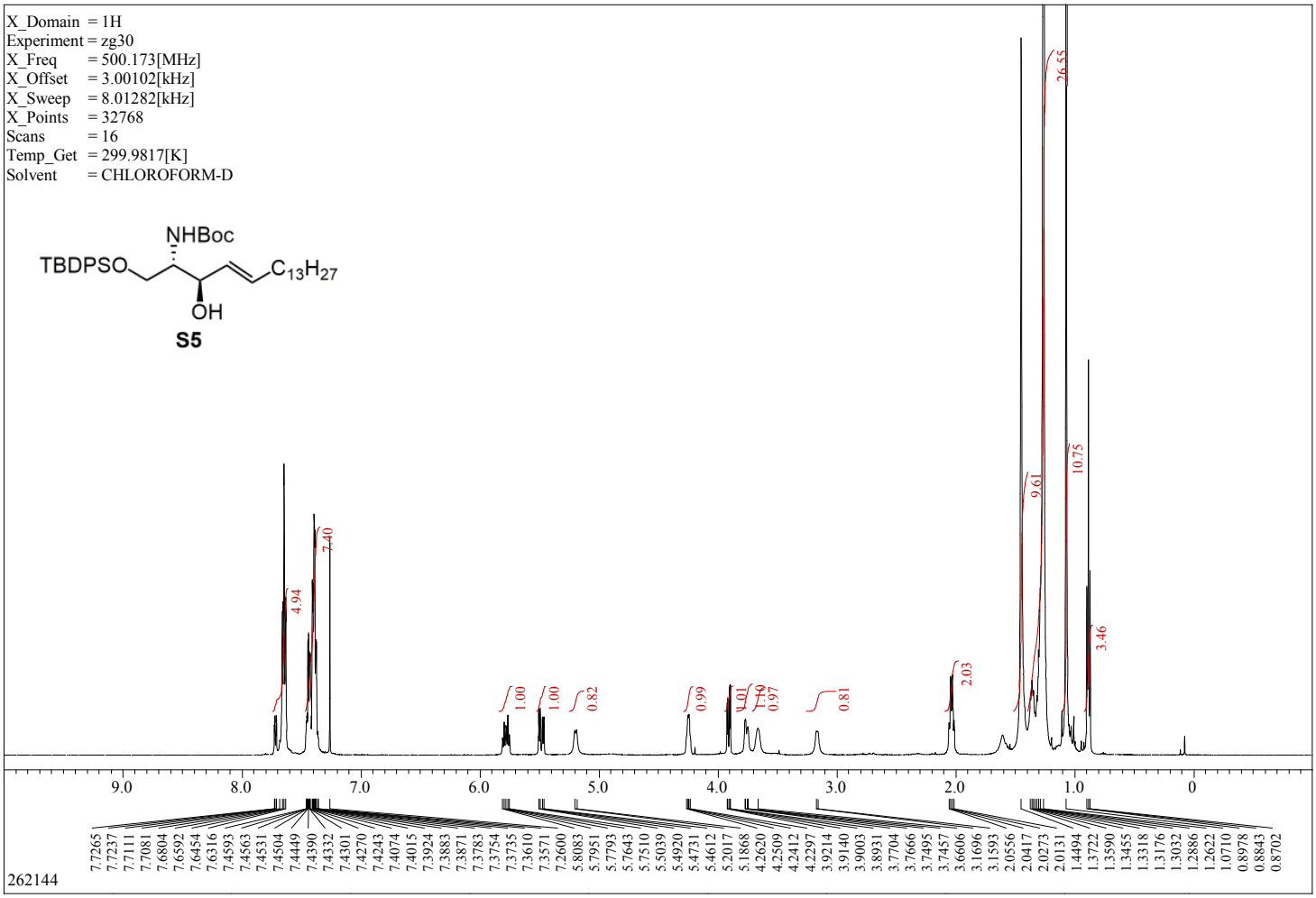
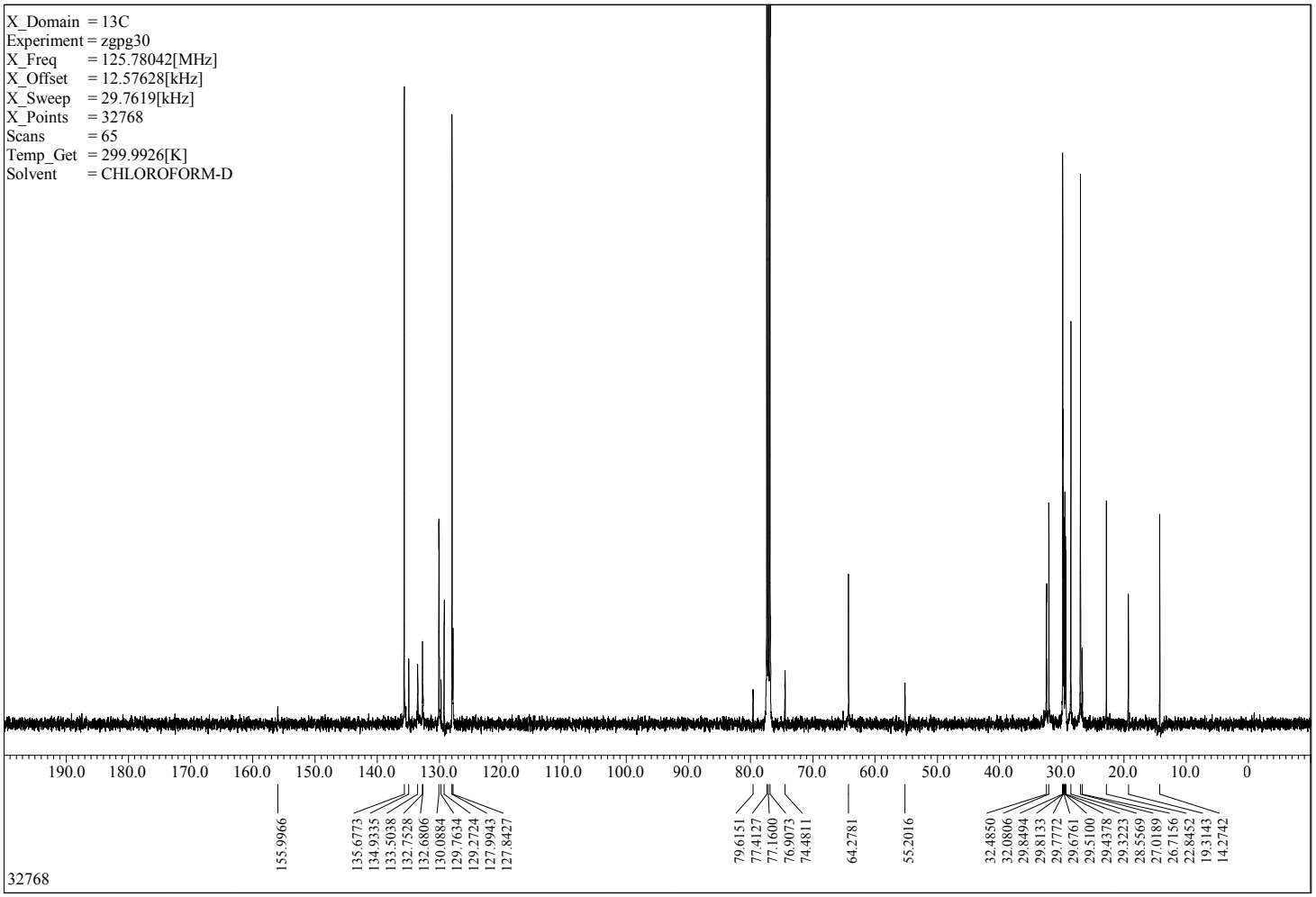
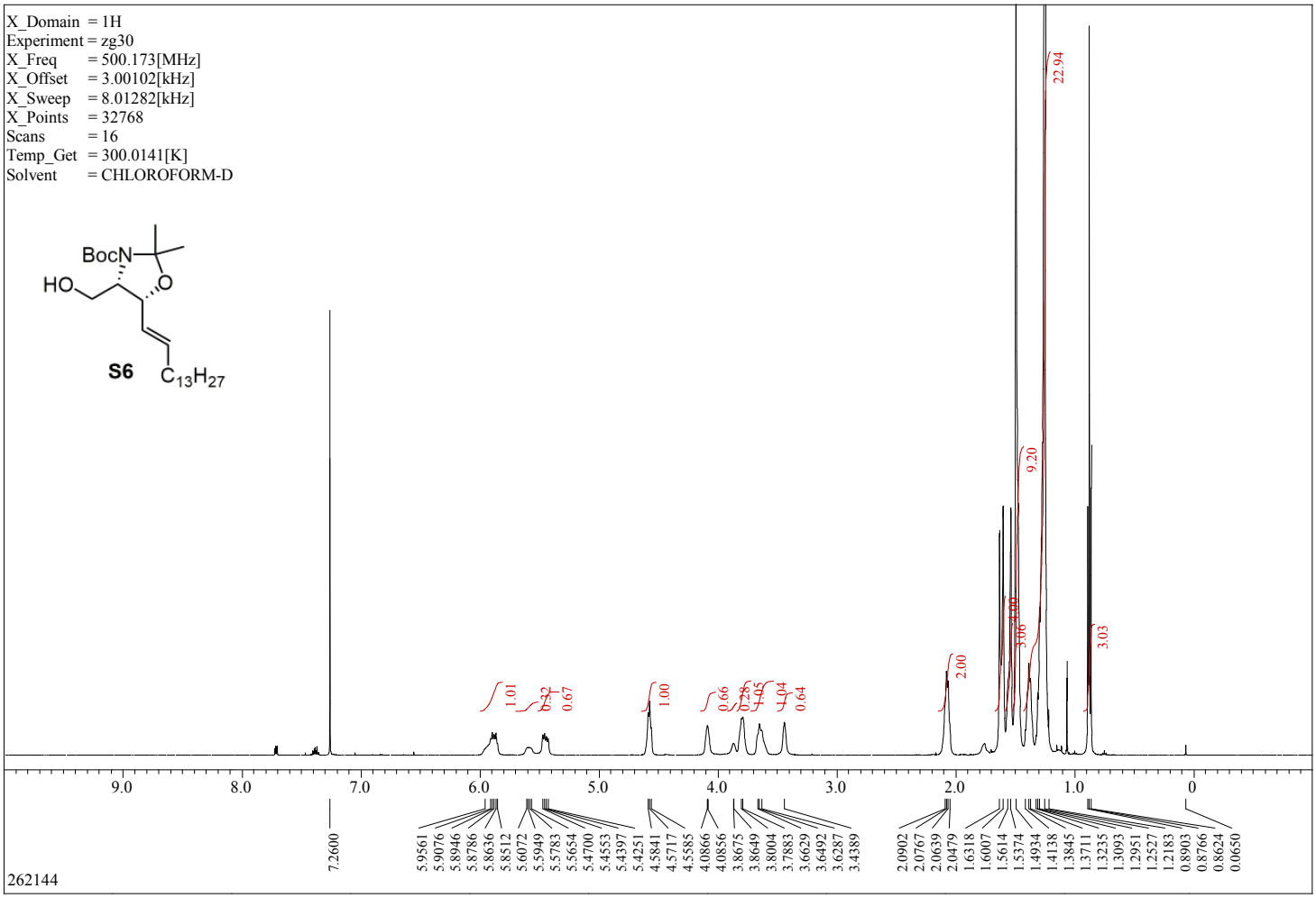
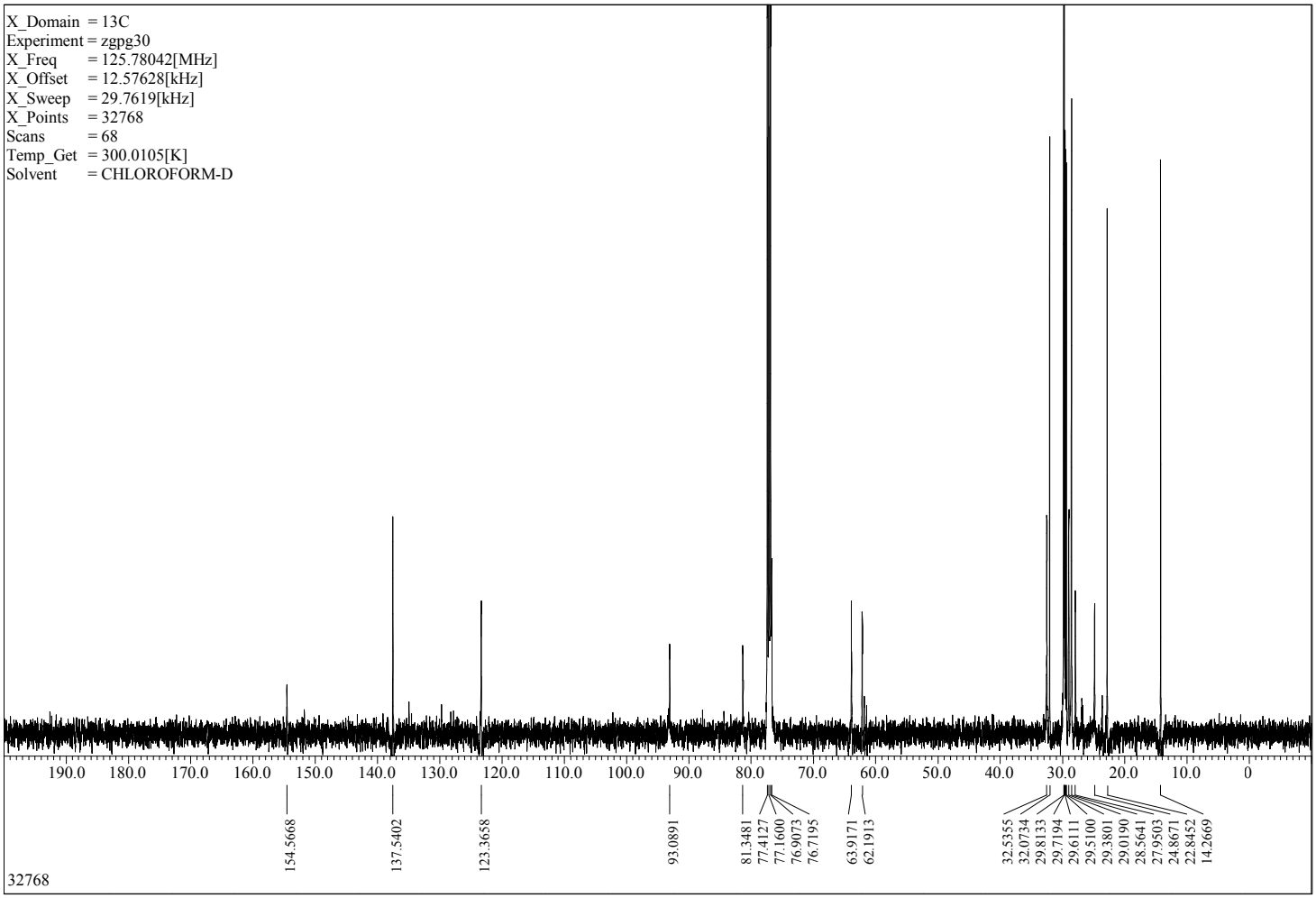
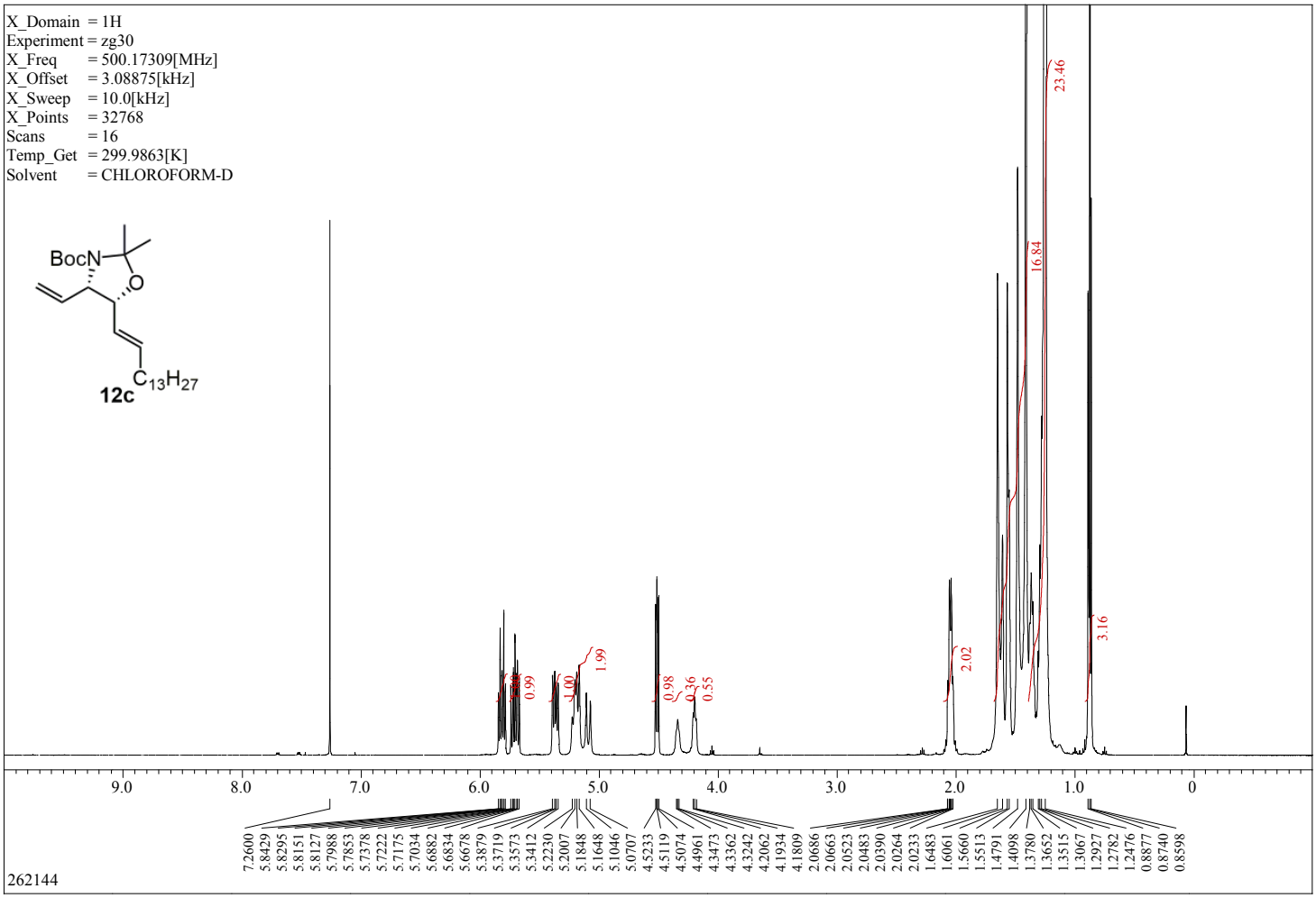

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 300.0031[K]
Solvent = CHLOROFORM-D
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.8278
134.5003
134.2060
132.0181
123.3757
118.9900
77.4145
77.1600
76.9064
75.4568
74.8196
55.7404
32.0896
32.0364
29.8684
29.8304
29.7600
29.7257
29.6138
29.5254
26.4412
26.2760
26.2435
22.8498
18.5010
18.3774
14.2733
-3.2615
-3.6217
-4.4304
-4.9422
262144

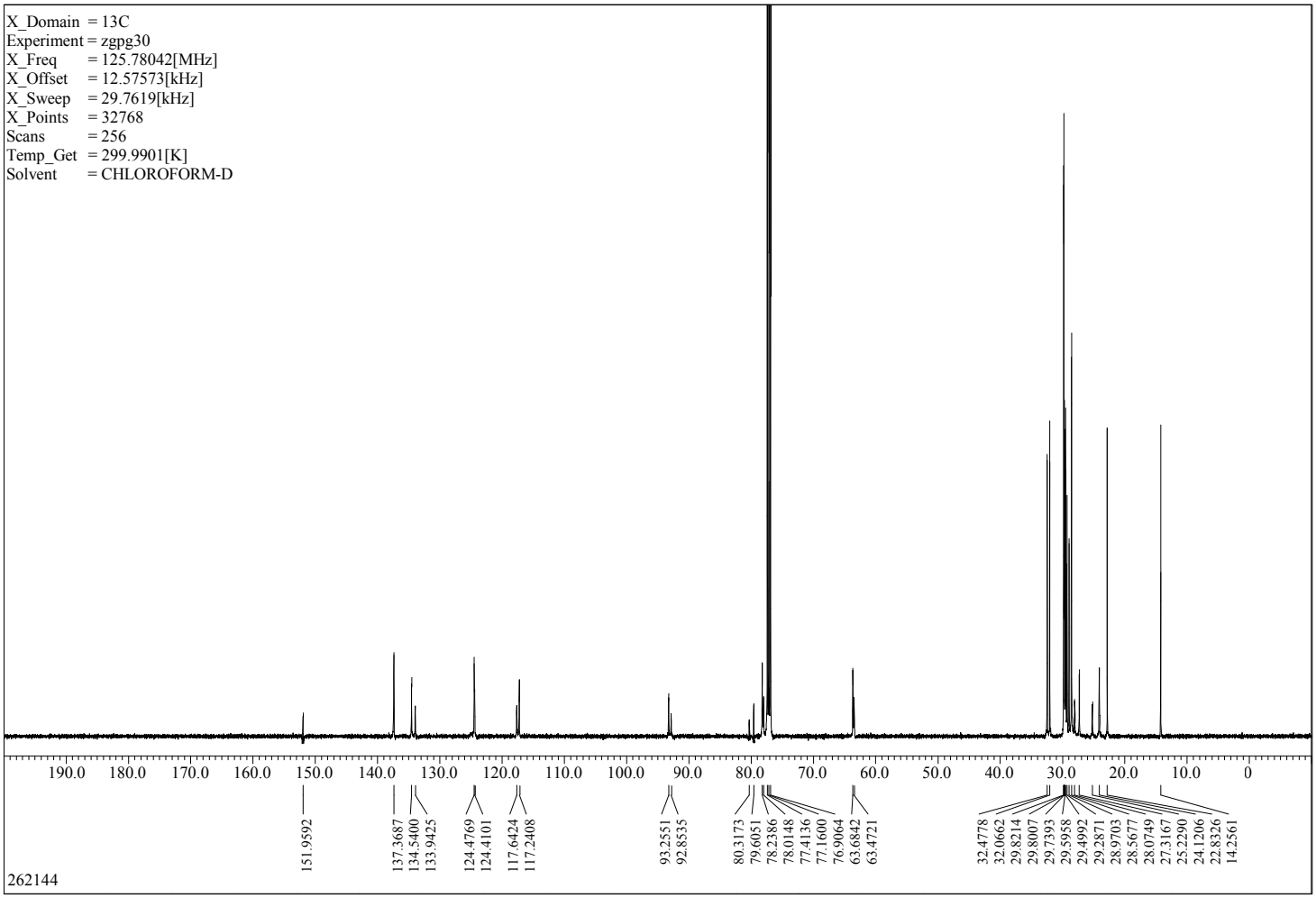

X_Domain = 1H
Experiment = zg30
X_Freq = 500.173[MHz]
X_Offset = 3.00102[kHz]
X_Sweep = 8.01282[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9817[K]
Solvent = CHLOROFORM-D
NHBoc
TBDPSO
C13H27
OH
S5
262144

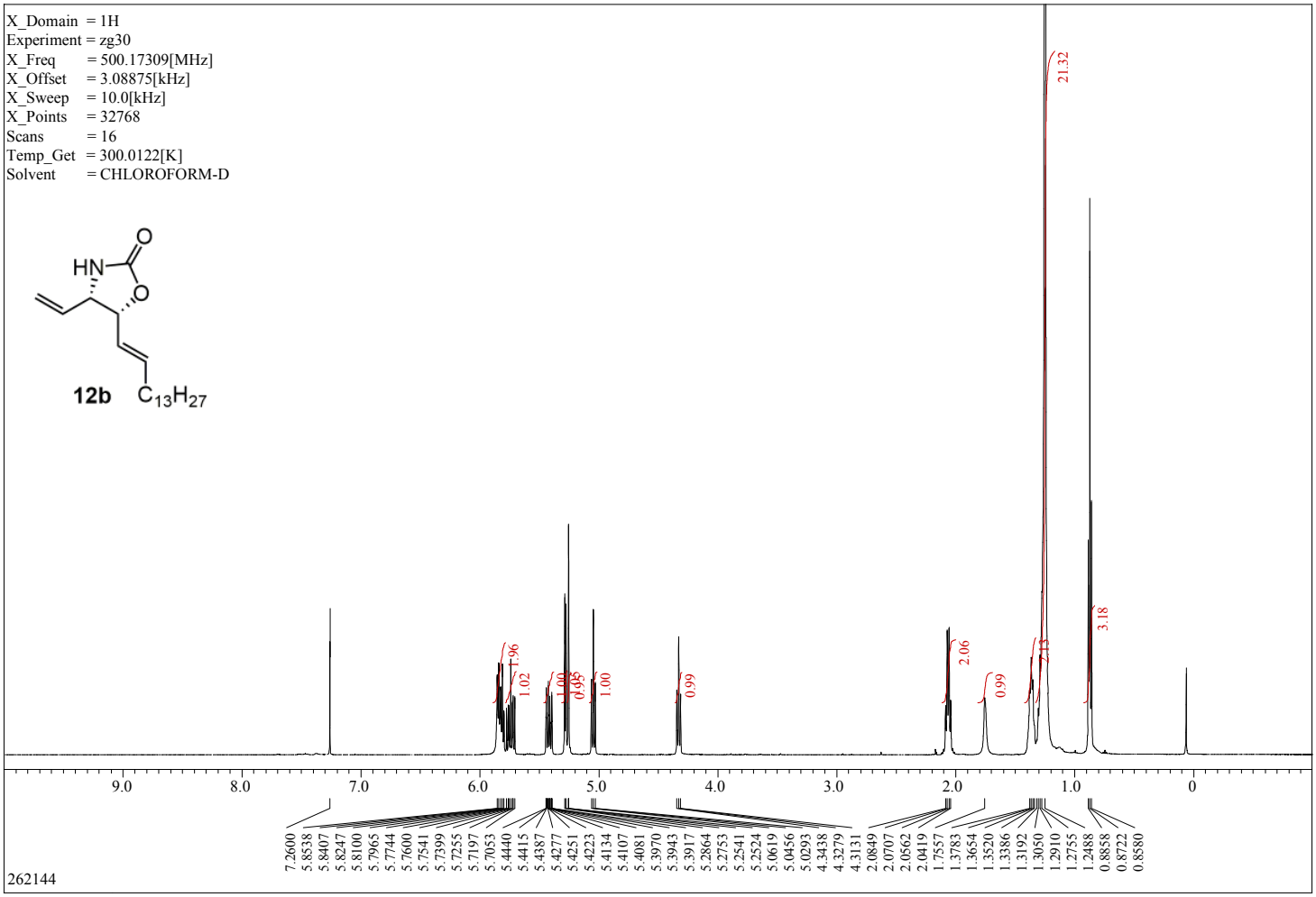

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57628[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 65
Temp_Get = 299.9926[K]
Solvent = CHLOROFORM-D
32768

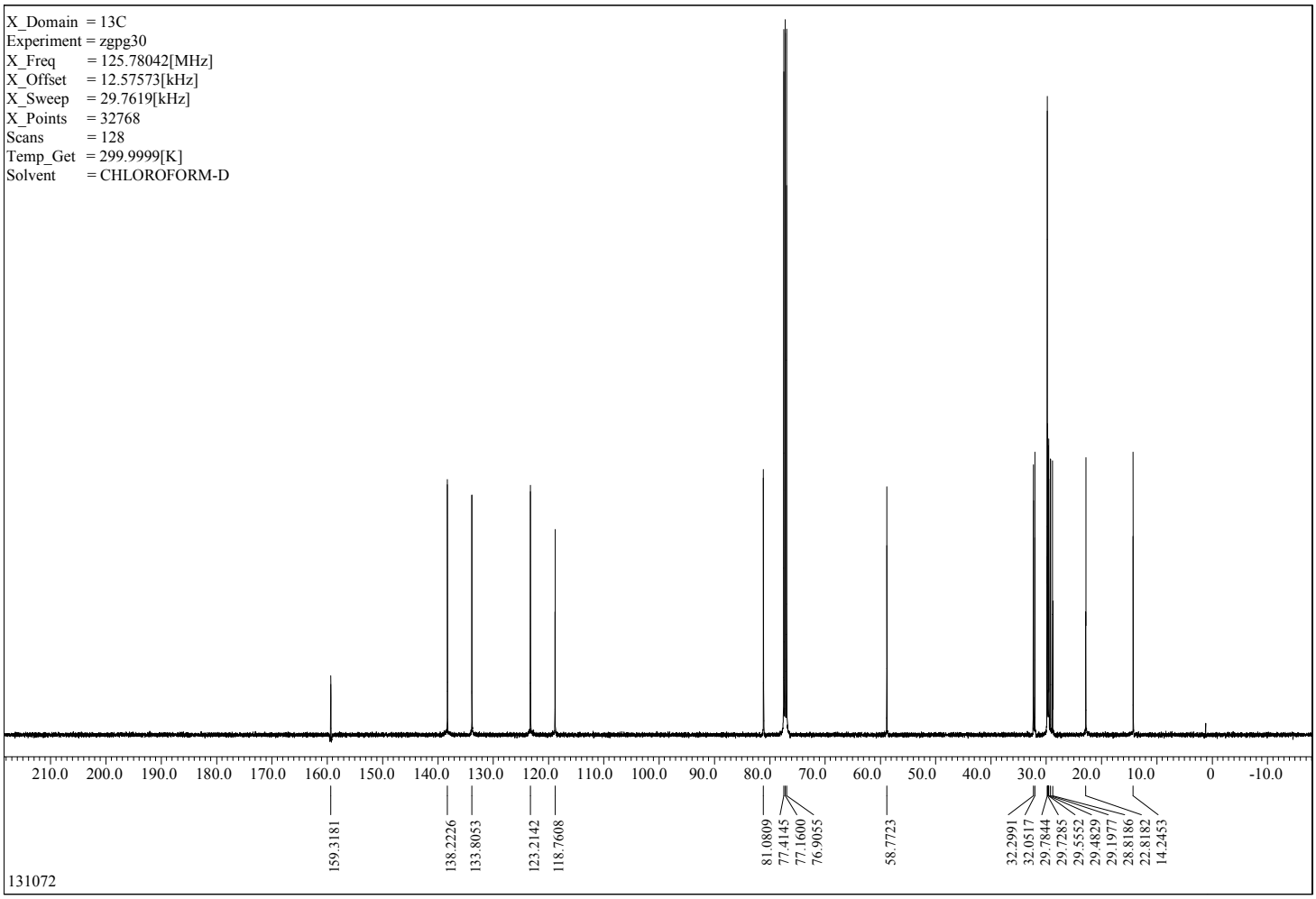

X_Domain = 1H
Experiment = zg30
X_Freq = 500.173[MHz]
X_Offset = 3.00102[kHz]
X_Sweep = 8.01282[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.0141[K]
Solvent = CHLOROFORM-D
BocN
HO
O
S6
C13H27
22.94
9.20
3.06
3.06
3.03
2.00
1.01
0.32
0.67
1.00
0.66
0.28
1.05
1.04
0.64
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2600
5.9561
5.9076
5.8946
5.8786
5.8636
5.8512
5.6072
5.5949
5.5783
5.5654
5.4700
5.4553
5.4397
5.4251
4.5841
4.5717
4.5585
4.0866
4.0856
3.8675
3.8649
3.8004
3.7883
3.6629
3.6492
3.6287
3.4389
2.0902
2.0767
2.0639
2.0479
1.6318
1.6007
1.5614
1.5374
1.4934
1.4138
1.3845
1.3711
1.3235
1.3093
1.2951
1.2527
1.2183
0.8903
0.8766
0.8624
0.0650
262144

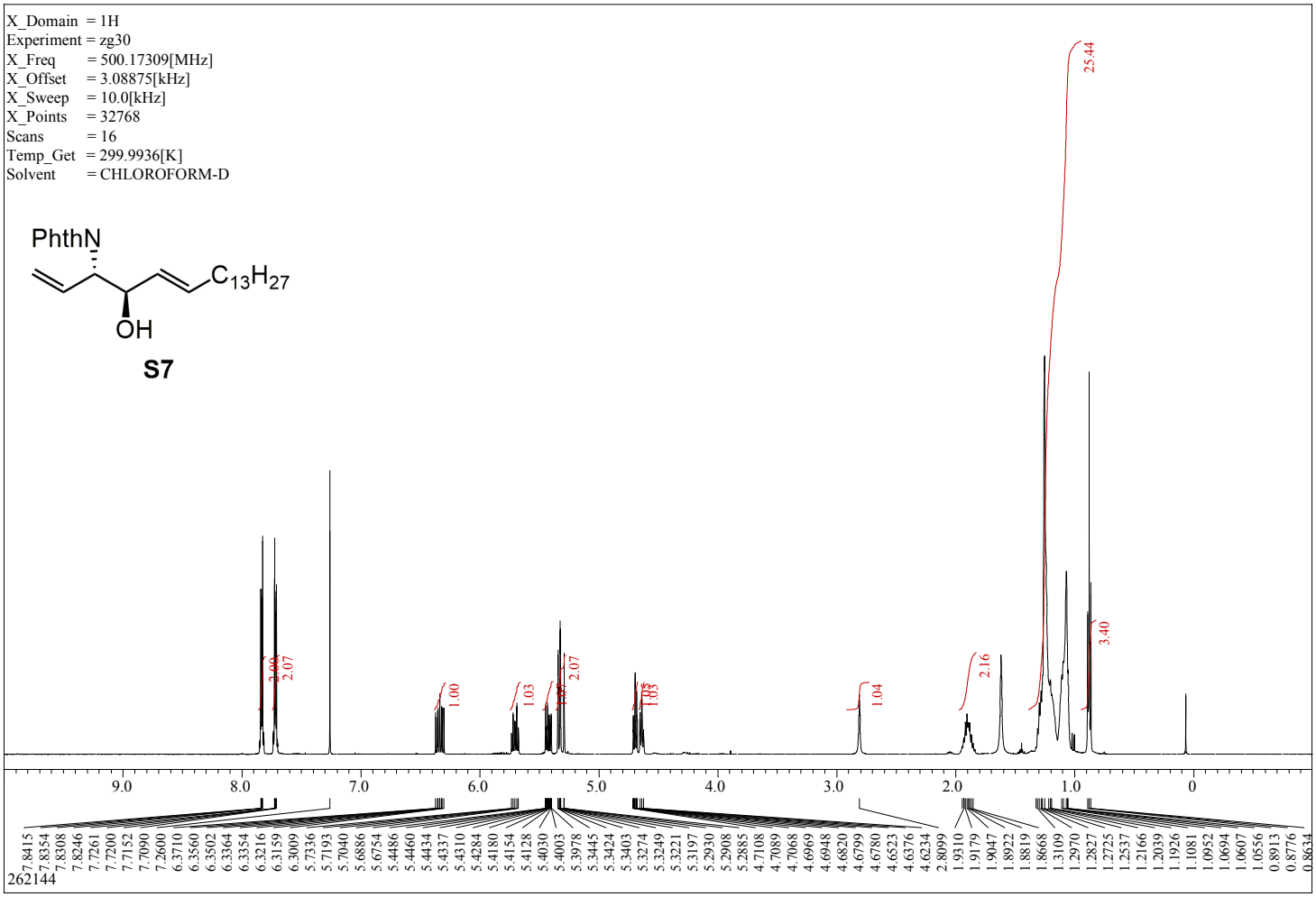

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57628[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 68
Temp_Get = 300.0105[K]
Solvent = CHLOROFORM-D
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.5668
137.5402
123.3658
93.0891
81.3481
77.4127
77.1600
76.9073
76.7195
63.9171
62.1913
32.5355
32.0734
29.8133
29.7194
29.6111
29.5100
29.3801
29.0190
28.5641
27.9503
24.8671
22.8452
14.2669
32768

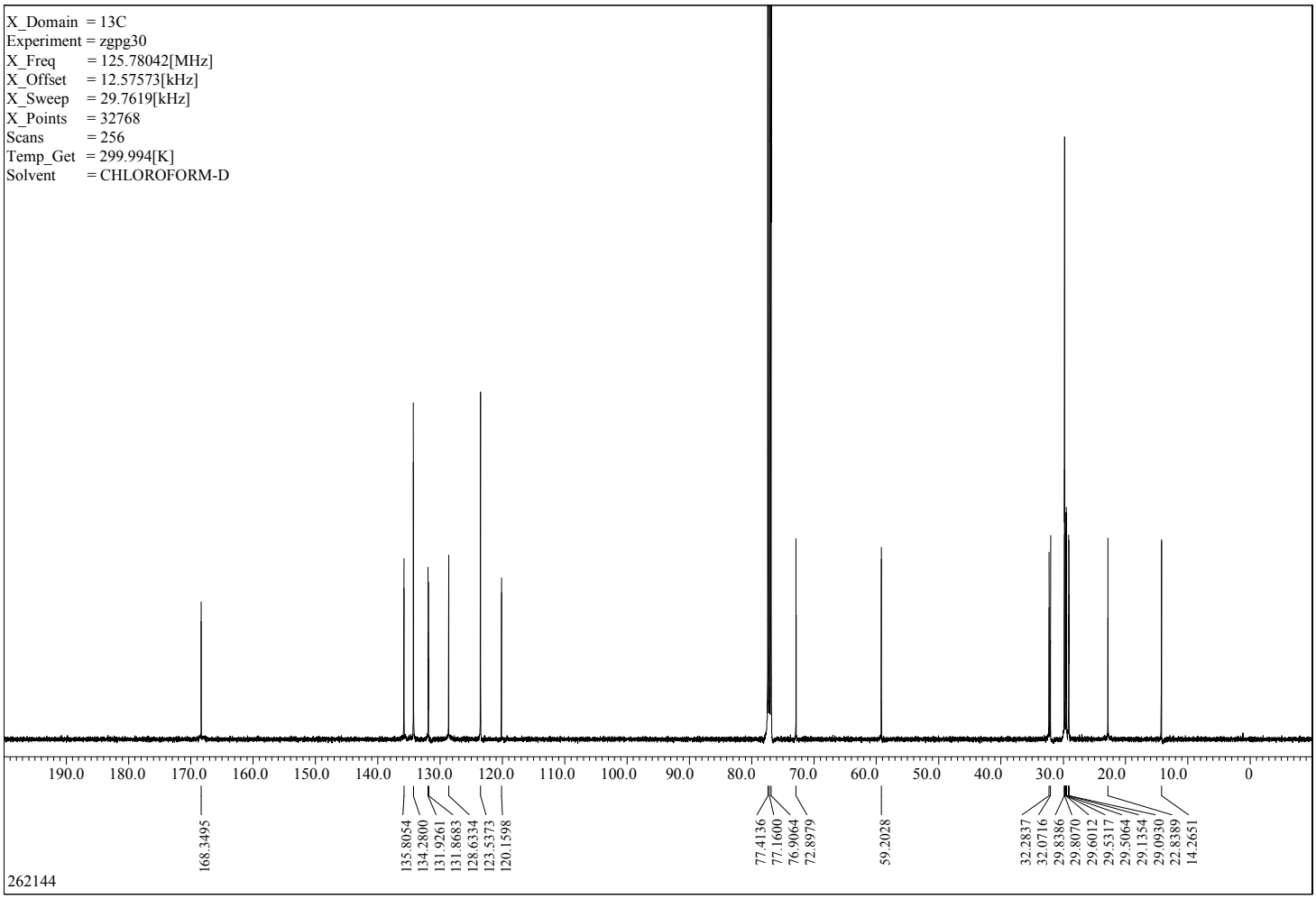

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9863[K]
Solvent = CHLOROFORM-D
BocN
O
C13H27
12c
23.46
16.84
3.16
2.02
1.99
0.99
1.00
0.98
0.36
0.55
262144

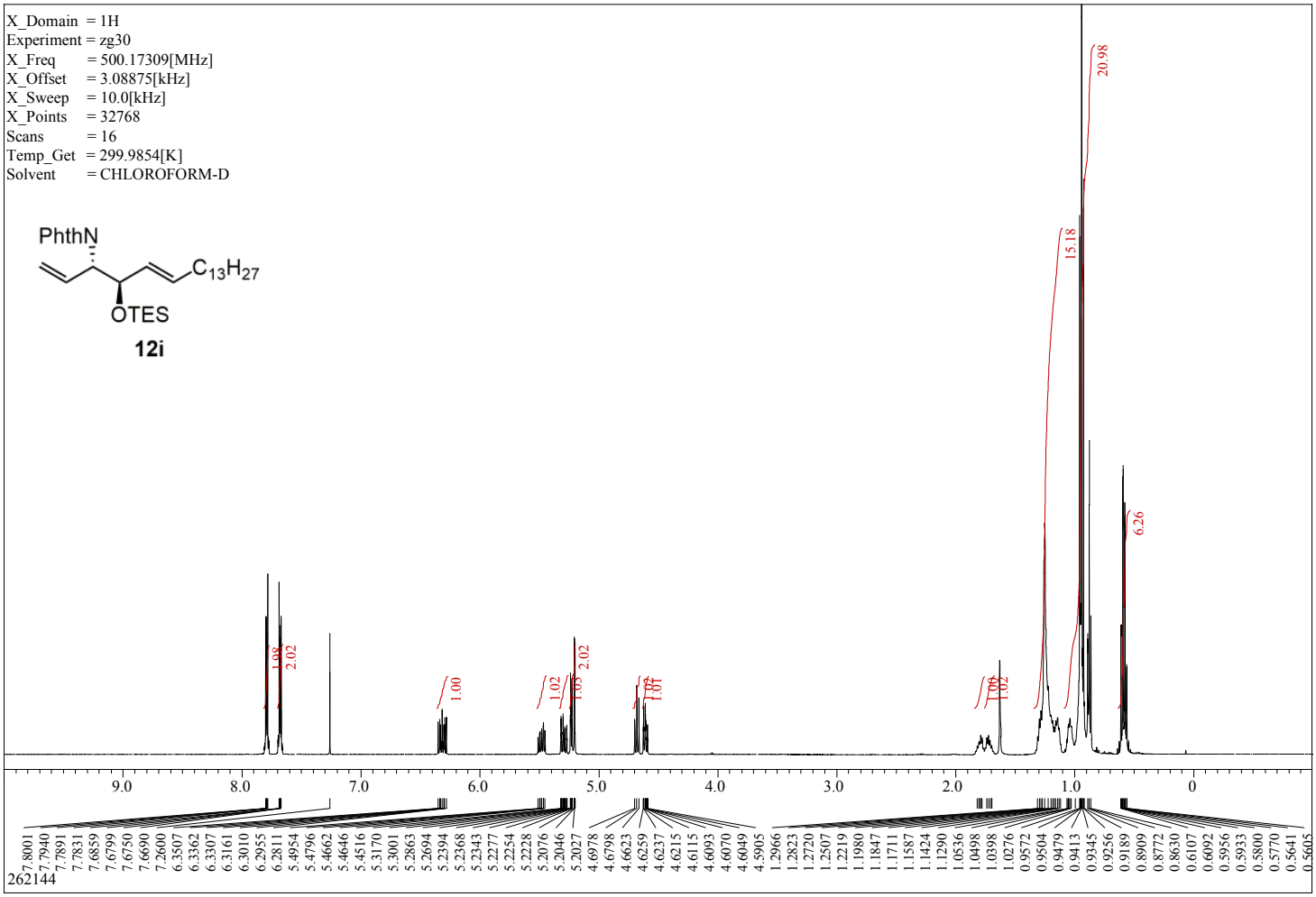

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 299.9901[K]
Solvent = CHLOROFORM-D
262144

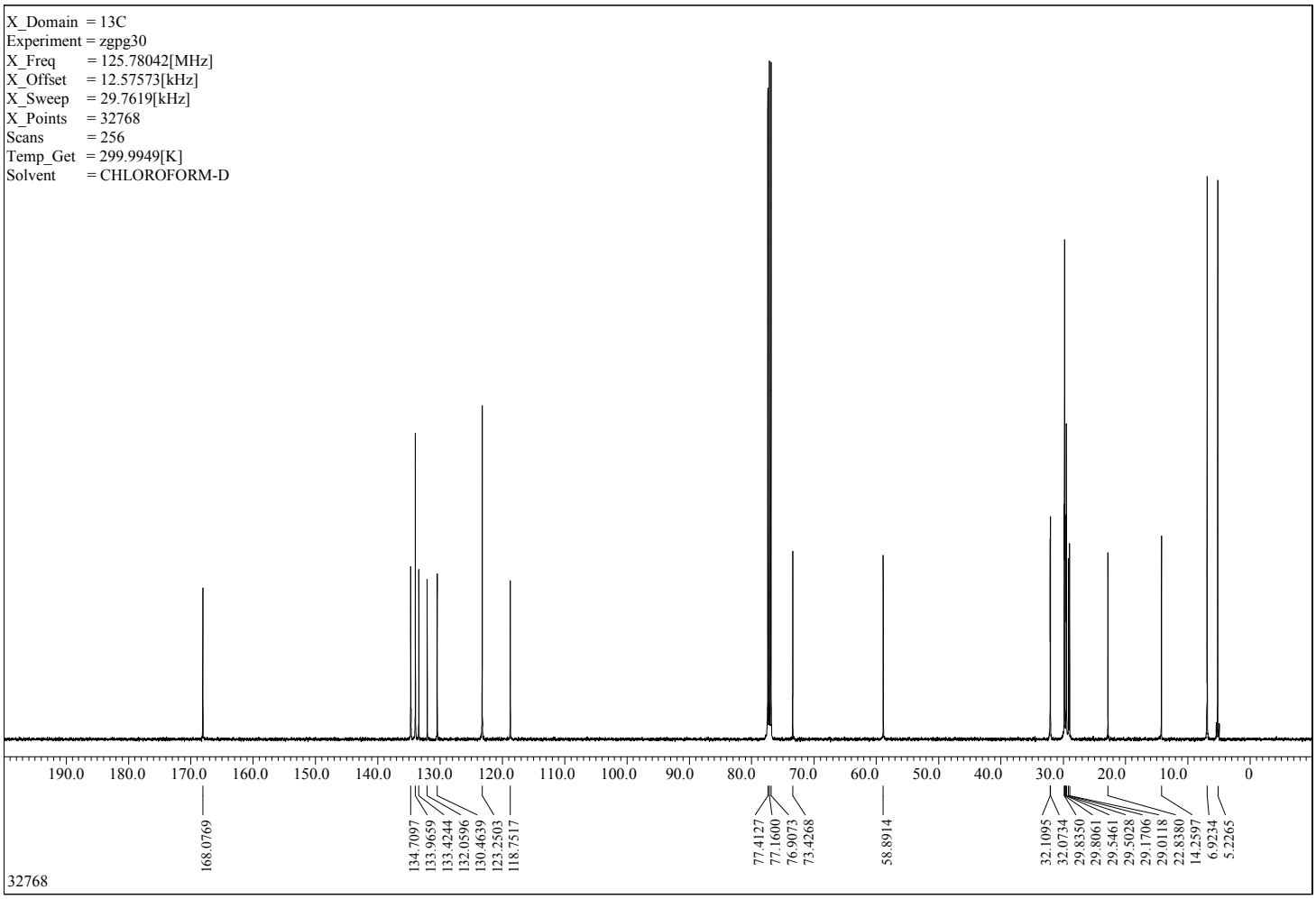

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.0122[K]
Solvent = CHLOROFORM-D
HN
O
O
12b
C13H27
21.32
1.96
1.02
1.00
0.99
1.00
2.06
0.99
2.13
3.18
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2600
5.8538
5.8407
5.8247
5.8100
5.7965
5.7744
5.7600
5.7541
5.7399
5.7255
5.7197
5.7053
5.4440
5.4415
5.4387
5.4277
5.4251
5.4223
5.4134
5.4107
5.4081
5.3970
5.3943
5.3917
5.2864
5.2753
5.2541
5.2524
5.0619
5.0456
5.0293
4.3438
4.3279
4.3131
2.0849
2.0707
2.0562
2.0419
1.7557
1.3783
1.3654
1.3520
1.3386
1.3192
1.3050
1.2910
1.2755
1.2488
0.8858
0.8722
0.8580
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 299.9999[K]
Solvent = CHLOROFORM-D
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
159.3181
138.2226
133.8053
123.2142
118.7608
81.0809
77.4145
77.1600
76.9055
58.7723
32.2991
32.0517
29.7844
29.7285
29.5552
29.4829
29.1977
28.8186
22.8182
14.2453
131072


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9936[K]
Solvent = CHLOROFORM-D
PhthN
C13H27
OH
S7
25.44
3.40
2.16
2.07
1.00
1.03
1.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 299.994[K]
Solvent = CHLOROFORM-D
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.3495
135.8054
134.2800
131.9261
131.8683
128.6334
123.5373
120.1598
77.4136
77.1600
76.9064
72.8979
59.2028
32.2837
32.0716
29.8386
29.8070
29.6012
29.5317
29.5064
29.1354
29.0930
22.8389
14.2651
262144


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9854[K]
Solvent = CHLOROFORM-D
PhthN
C13H27
OTES
12i
20.98
15.18
6.26
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 299.9949[K]
Solvent = CHLOROFORM-D
168.0769
134.7097
133.9659
133.4244
132.0596
130.4639
123.2503
118.7517
77.4127
77.1600
76.9073
73.4268
58.8914
32.1095
32.0734
29.8350
29.8061
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29.5028
29.1706
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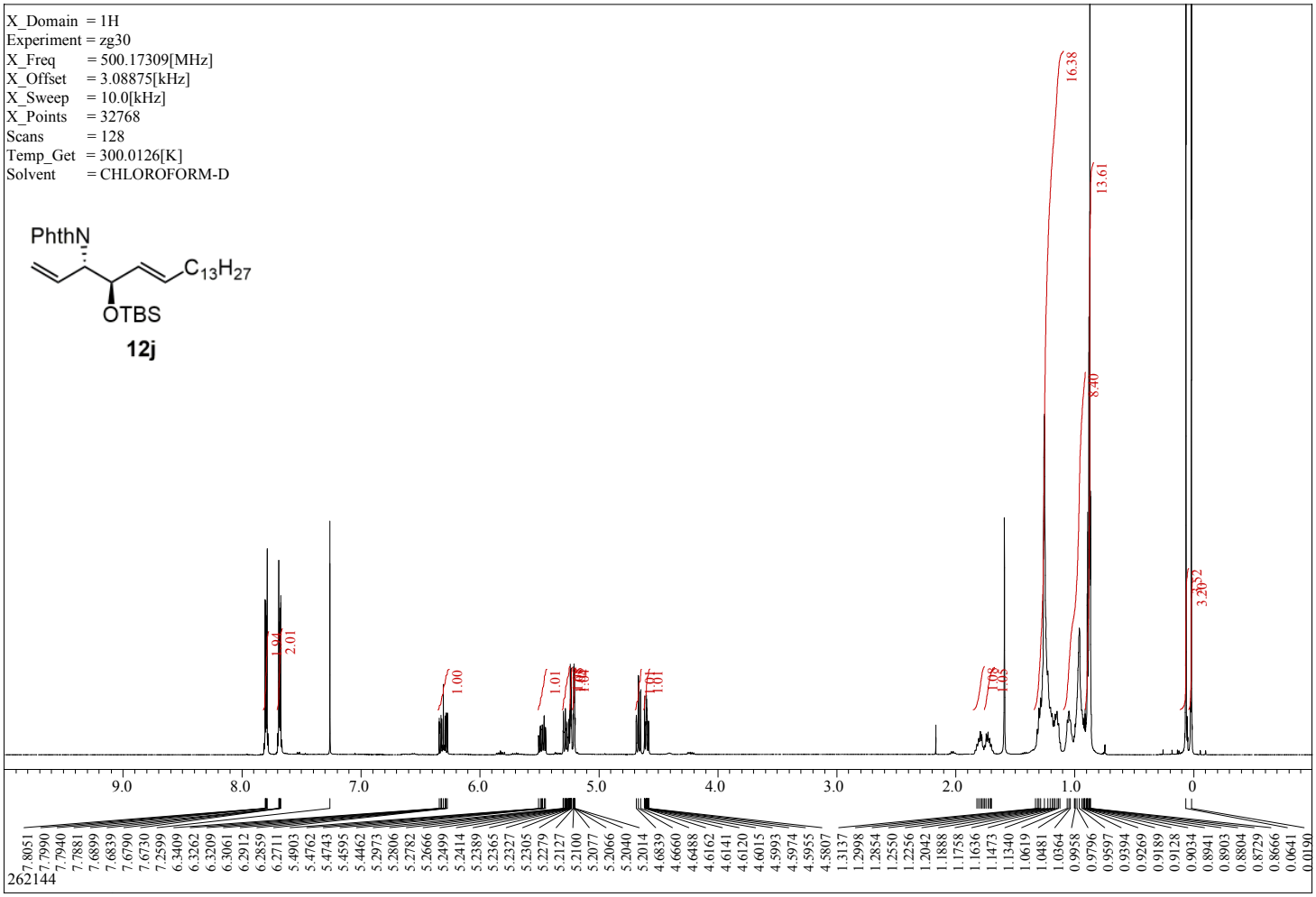
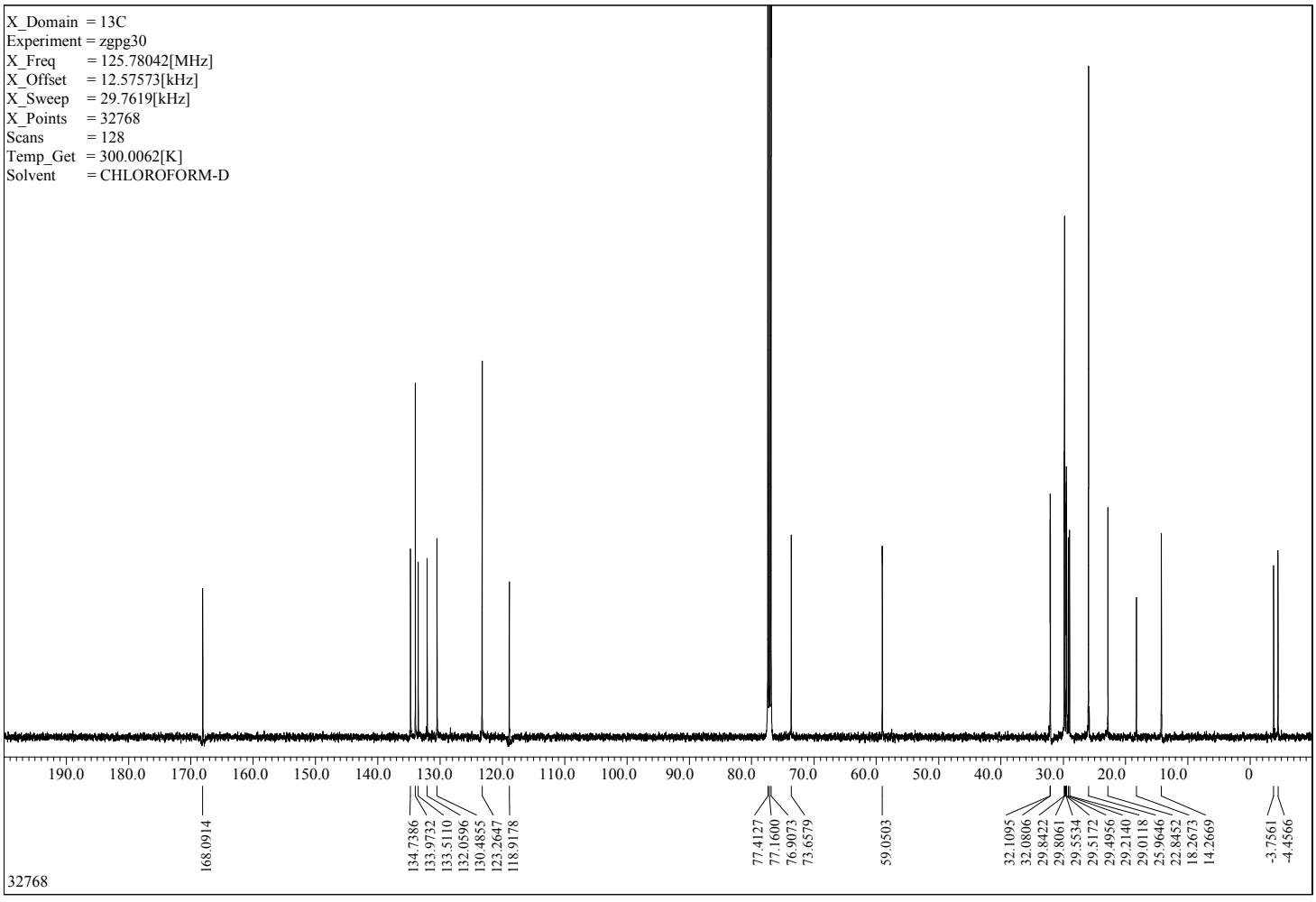
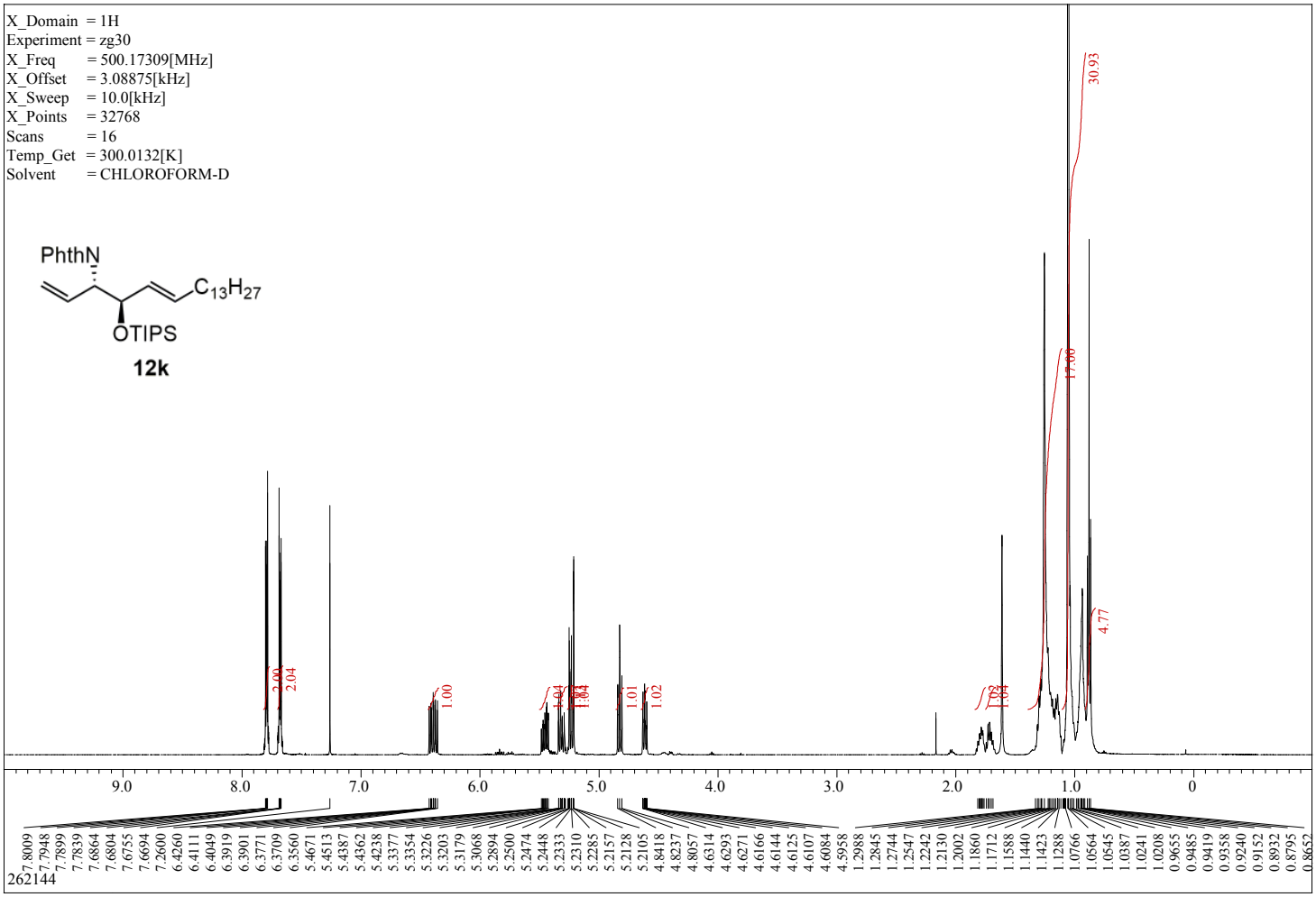
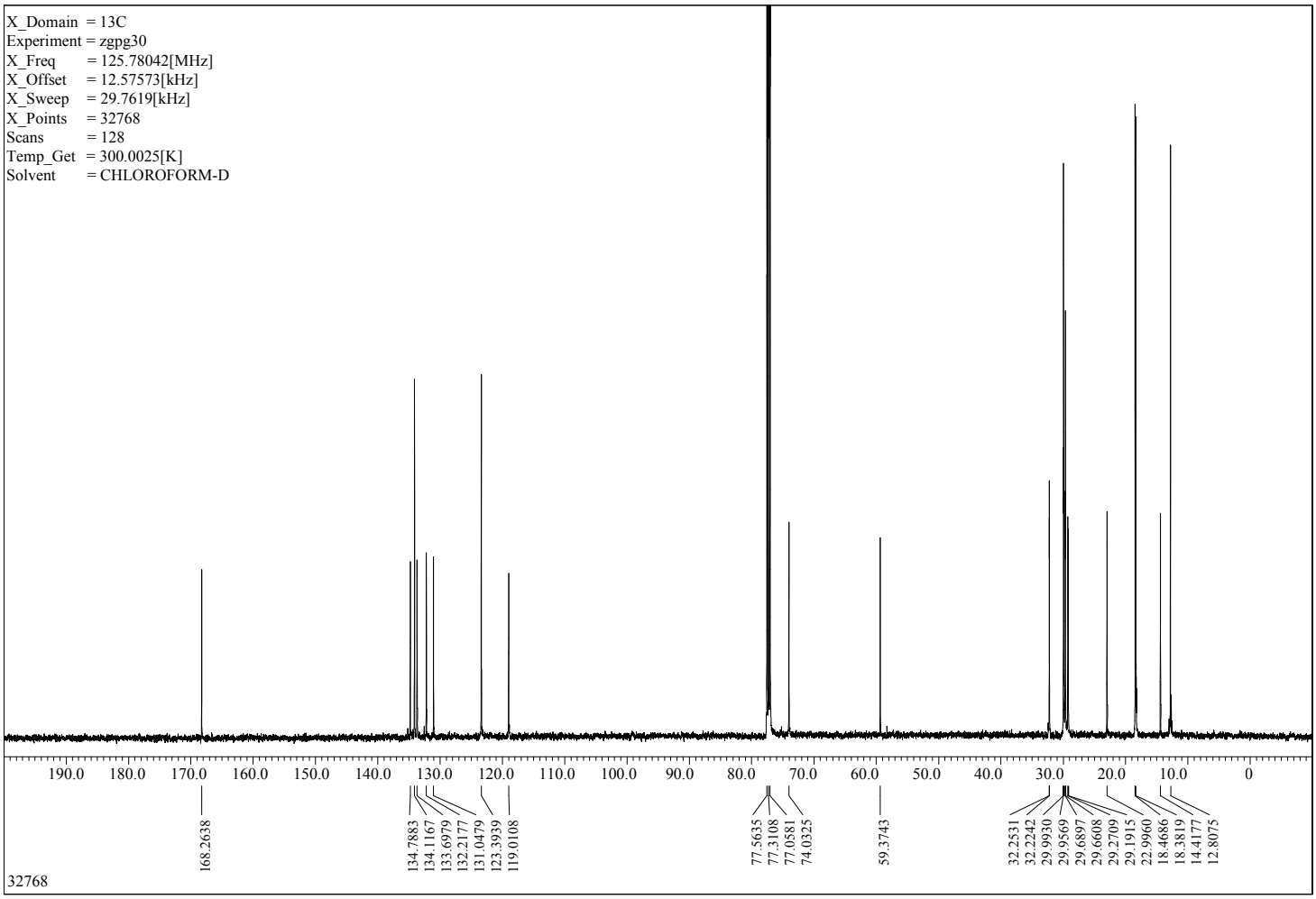
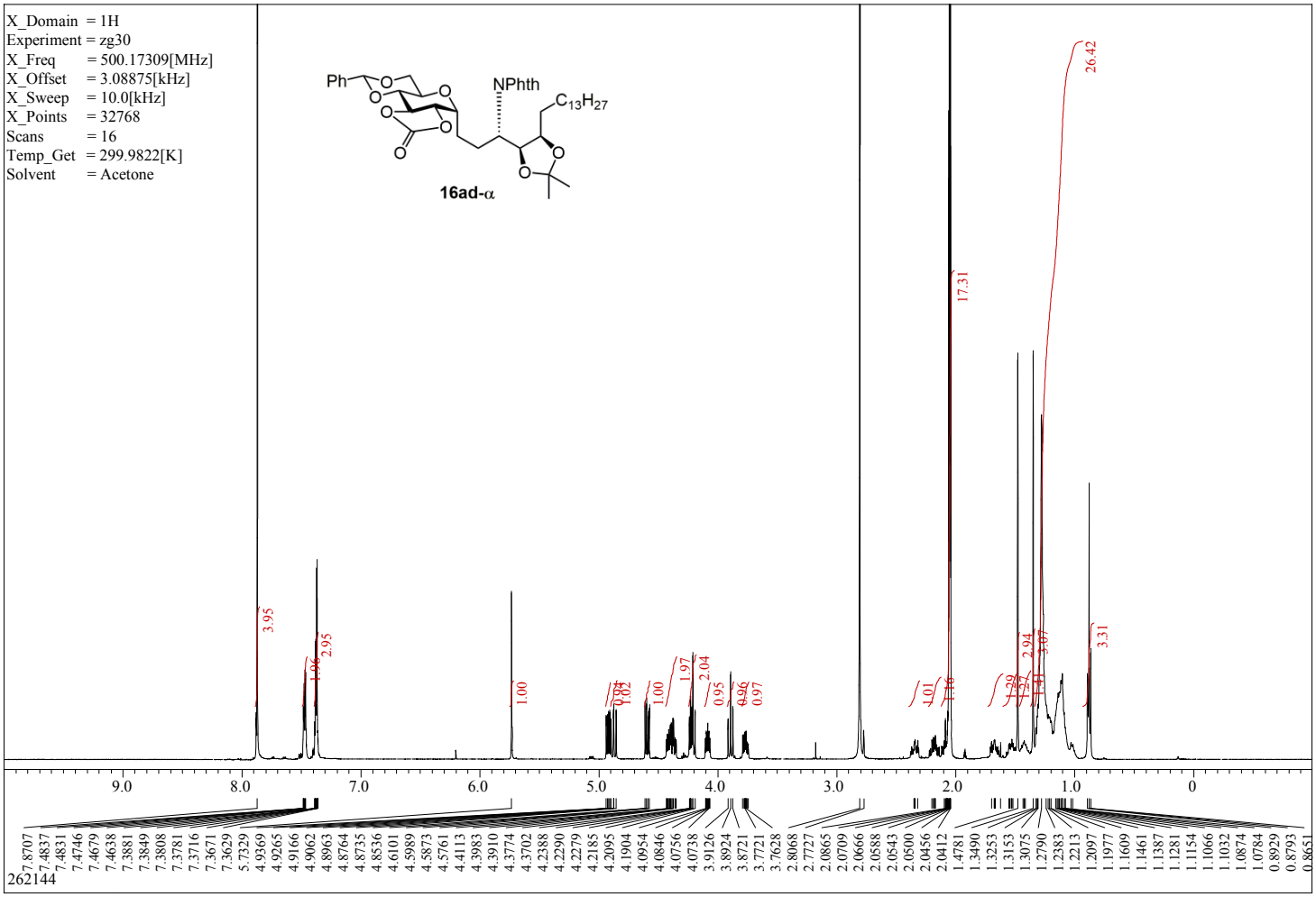
22.8380
14.2597
6.9234
5.2265
32768

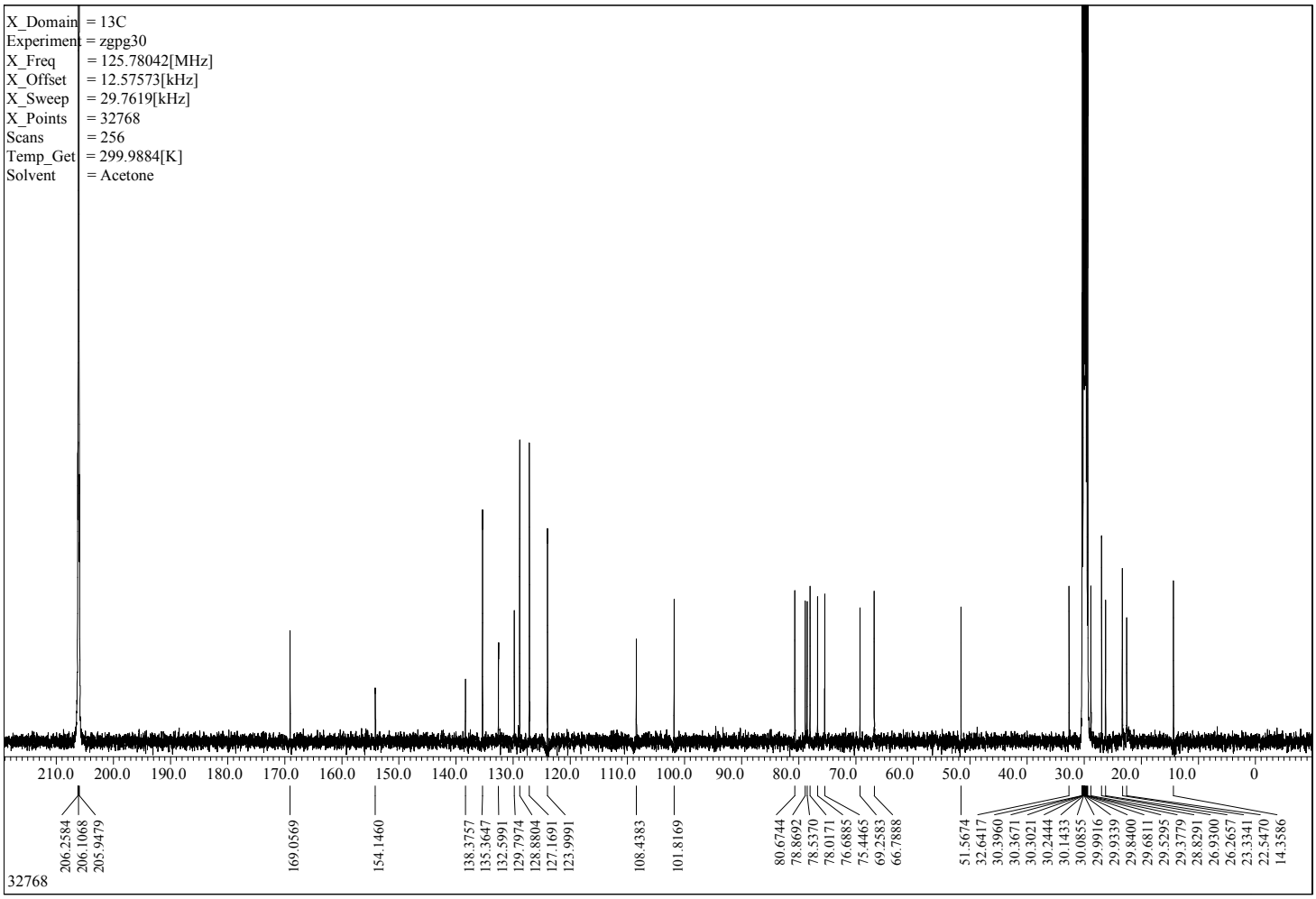

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 300.0126[K]
Solvent = CHLOROFORM-D
PhthN
C13H27
OTBS
12j
262144

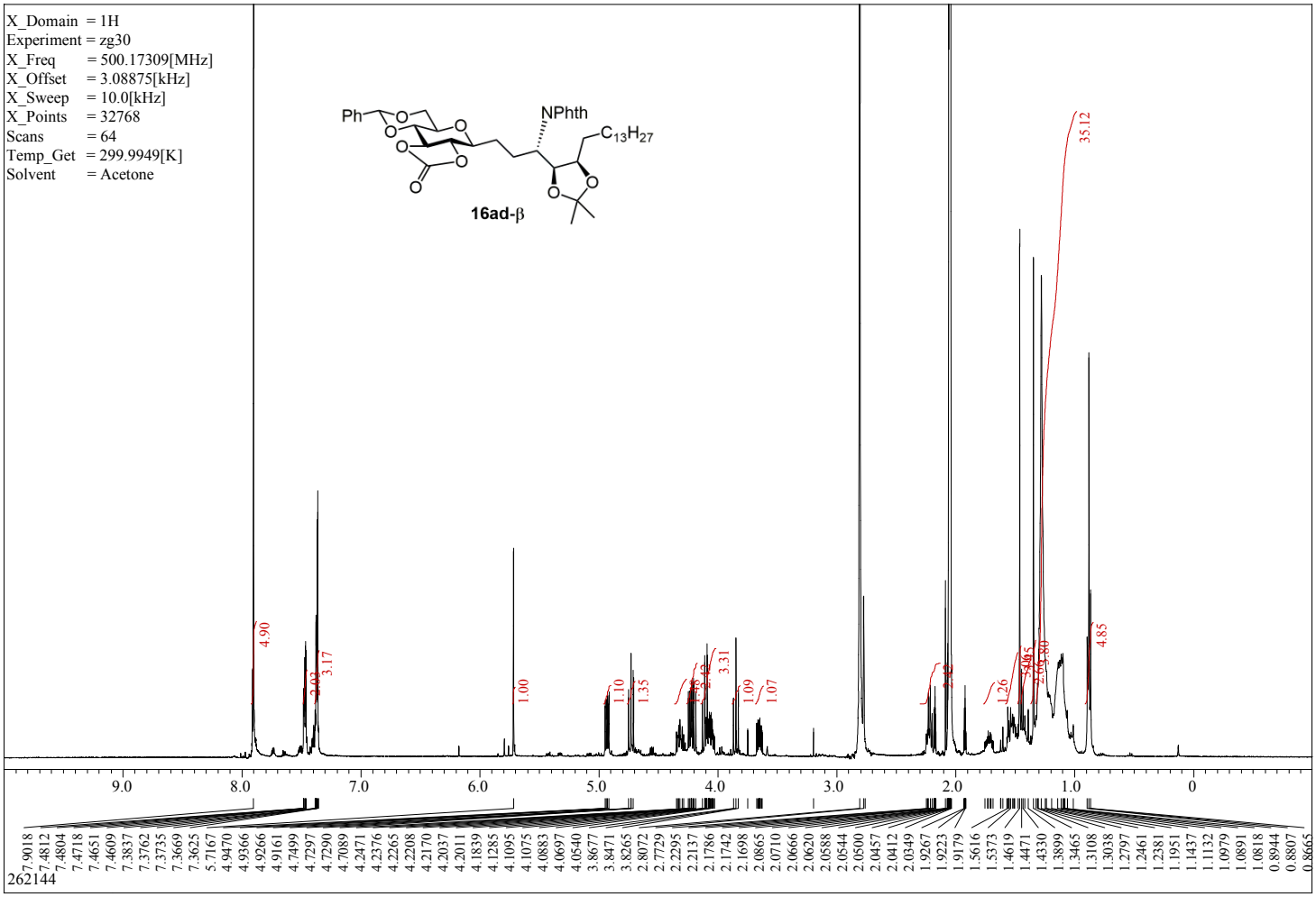

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 300.0062[K]
Solvent = CHLOROFORM-D
32768

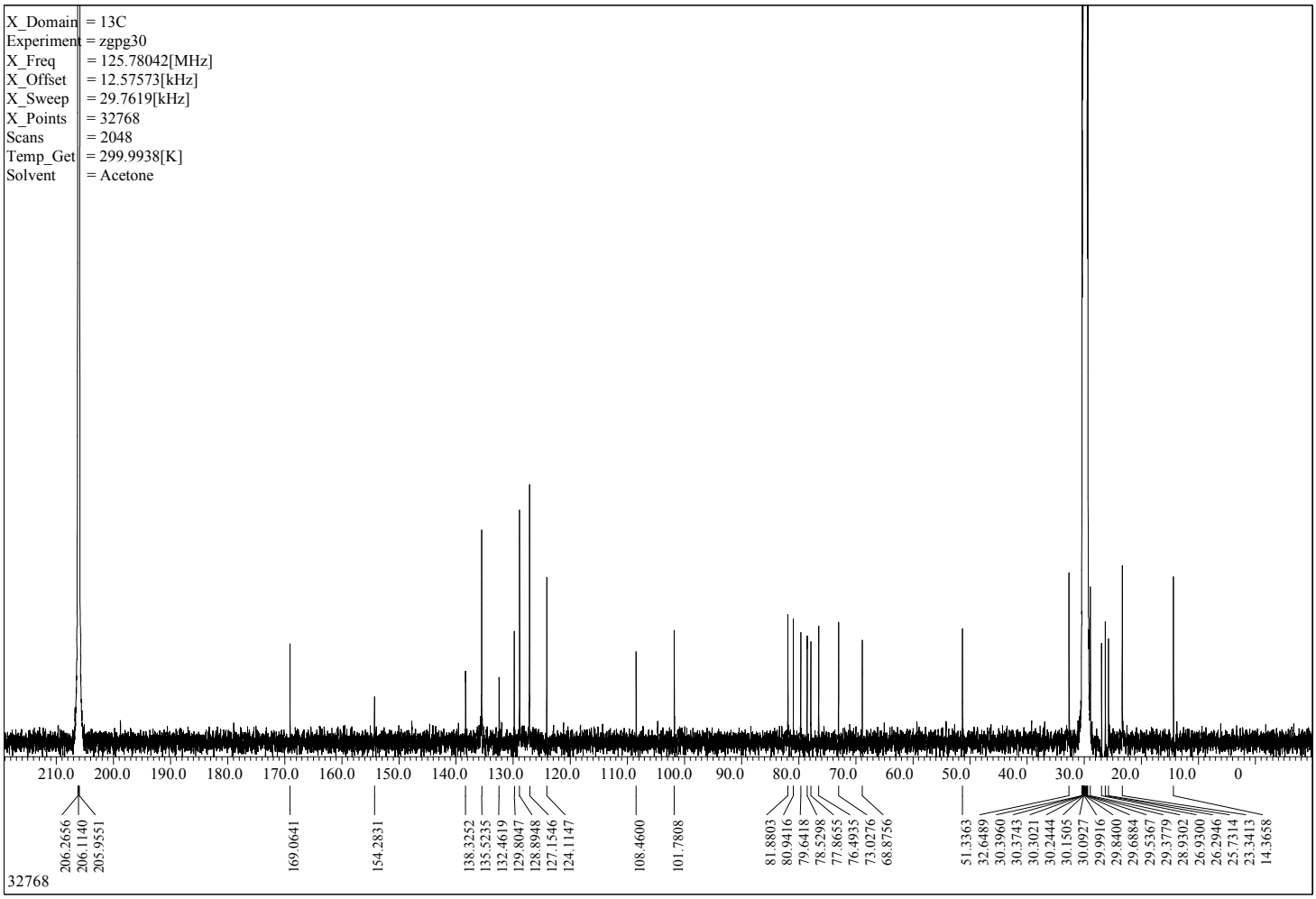

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.0132[K]
Solvent = CHLOROFORM-D
PhthN
C13H27
OTIPS
12k
262144

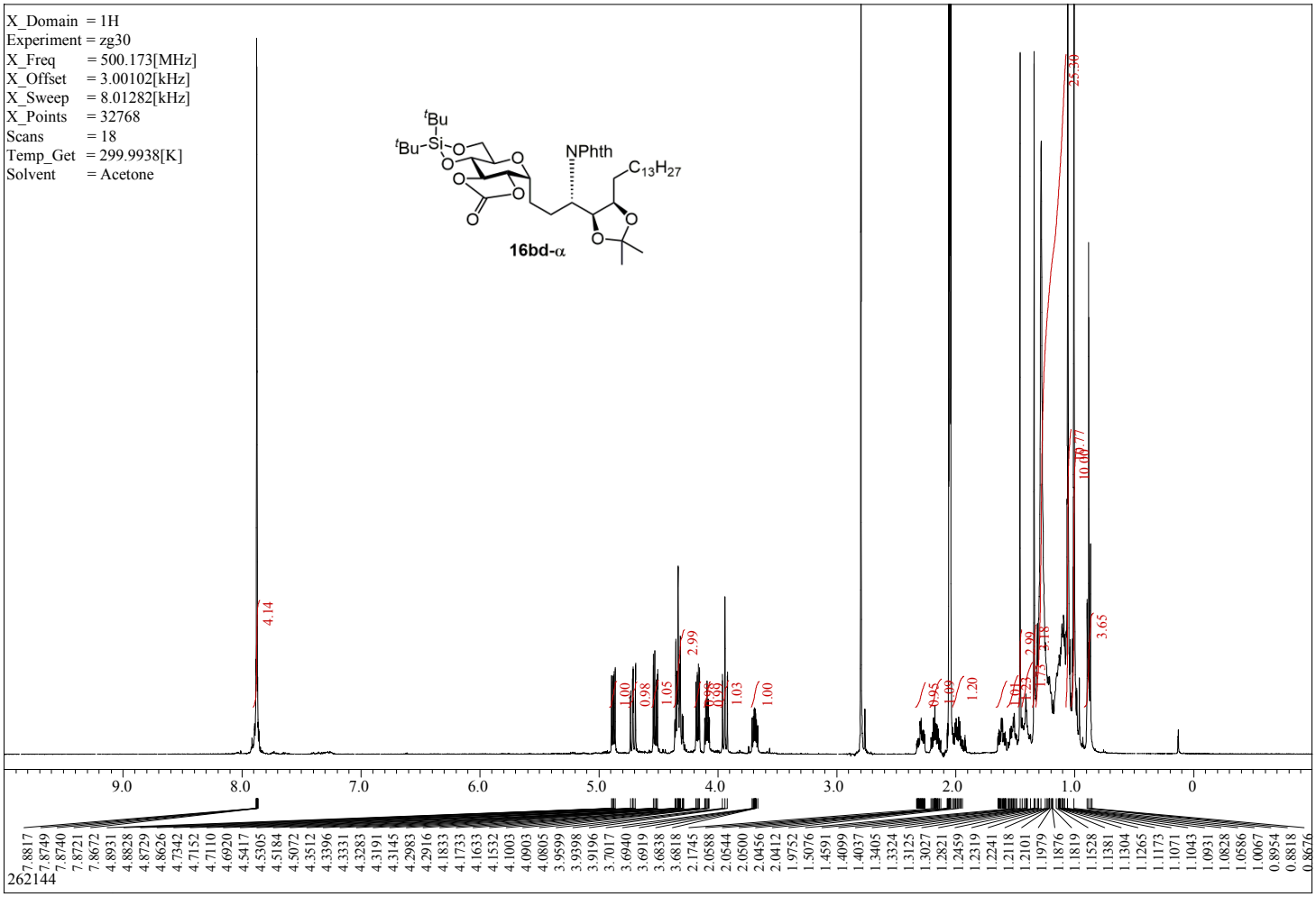

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 300.0025[K]
Solvent = CHLOROFORM-D
32768

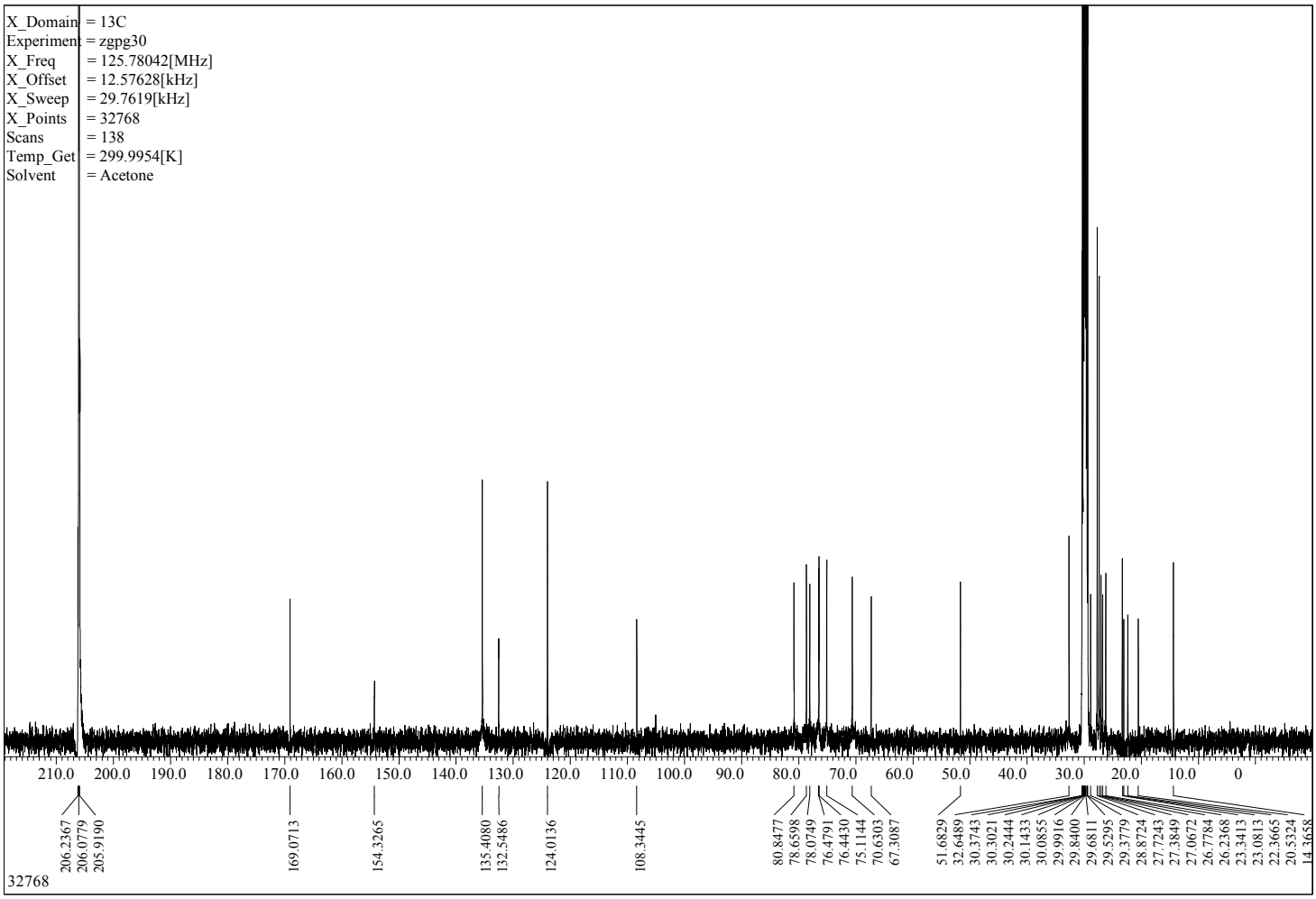

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9822[K]
Solvent = Acetone
Ph
NPhth
C13H27
16ad-α
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 299.9884[K]
Solvent = Acetone
32768

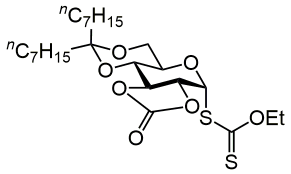

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 299.9949[K]
Solvent = Acetone
Ph
NPhth
C13H27
16ad-β
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 2048
Temp_Get = 299.9938[K]
Solvent = Acetone
32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.173[MHz]
X_Offset = 3.00102[kHz]
X_Sweep = 8.01282[kHz]
X_Points = 32768
Scans = 18
Temp_Get = 299.9938[K]
Solvent = Acetone
16bd-α
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57628[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 138
Temp_Get = 299.9954[K]
Solvent = Acetone
32768

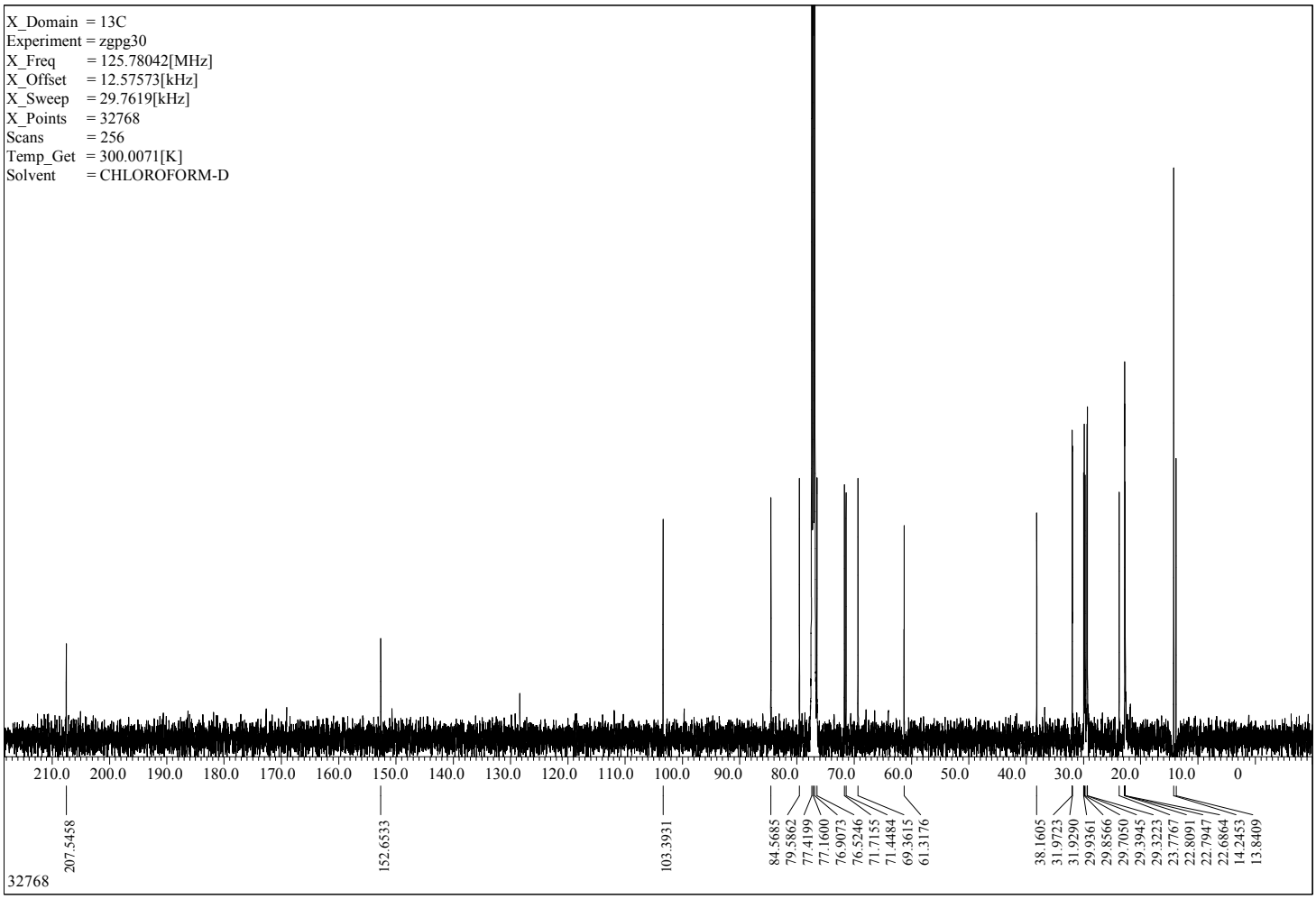
X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.0042[K]
Solvent = CHLOROFORM-D



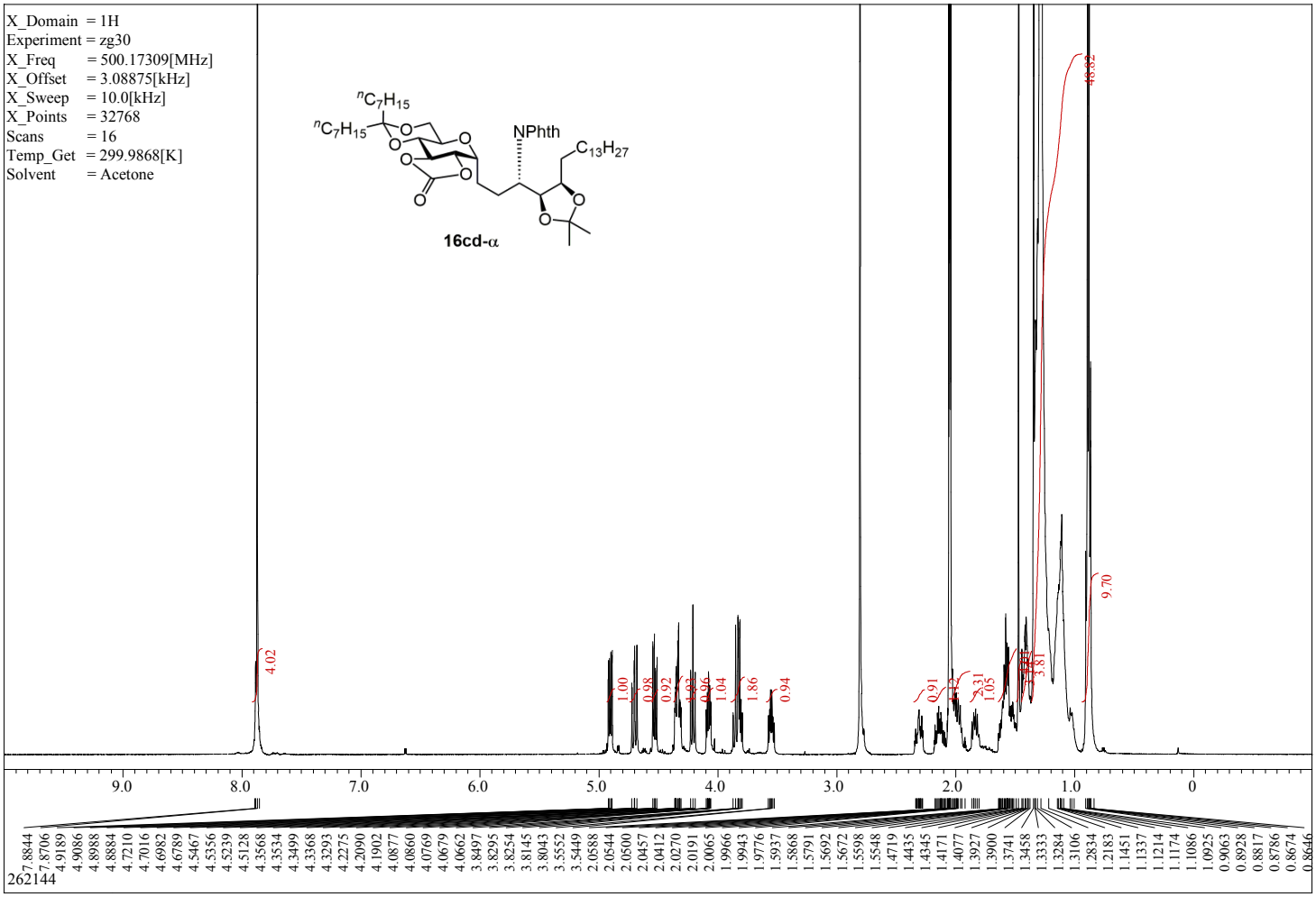
11c-α

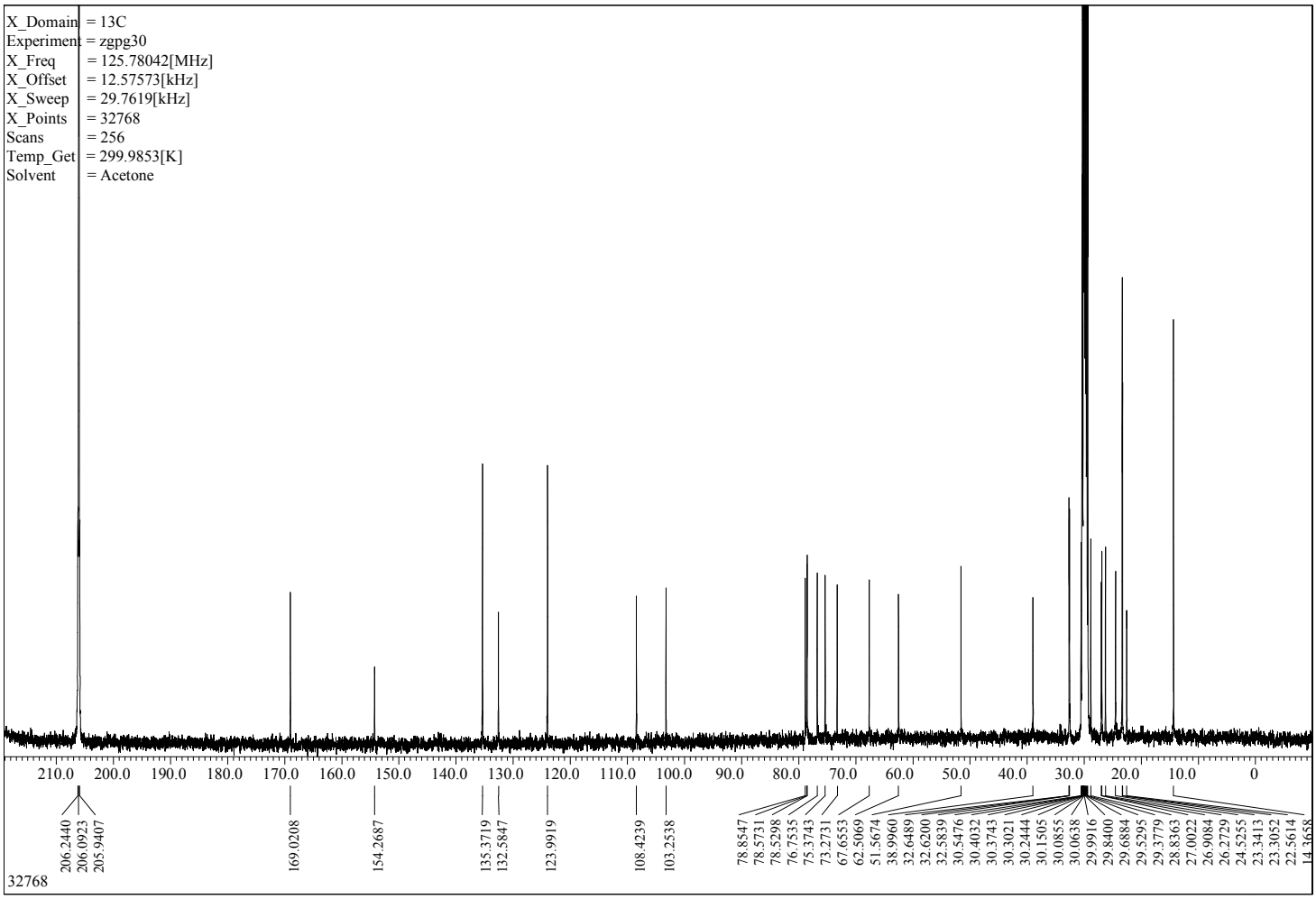
262144

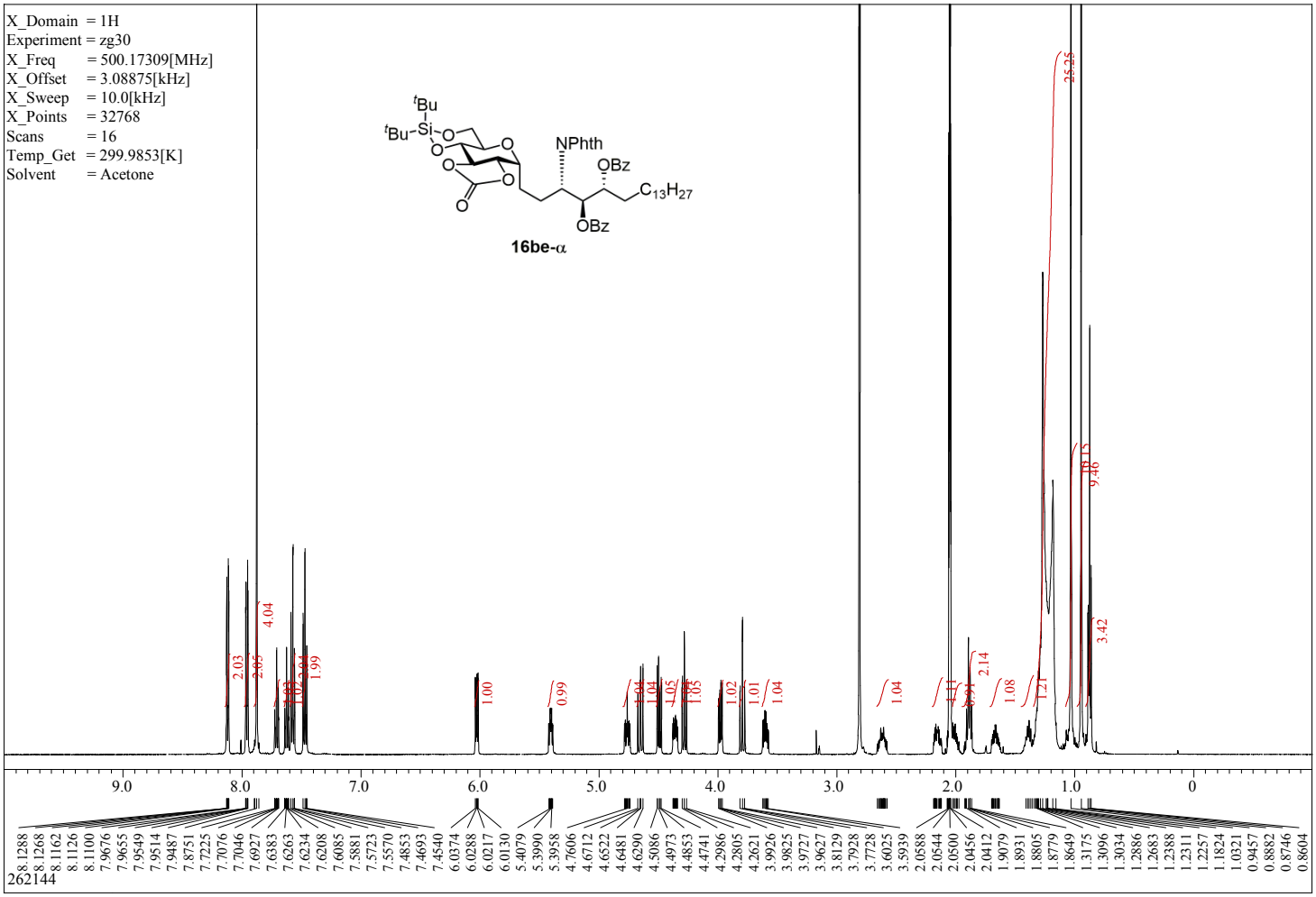
X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 300.0071[K]
Solvent = CHLOROFORM-D

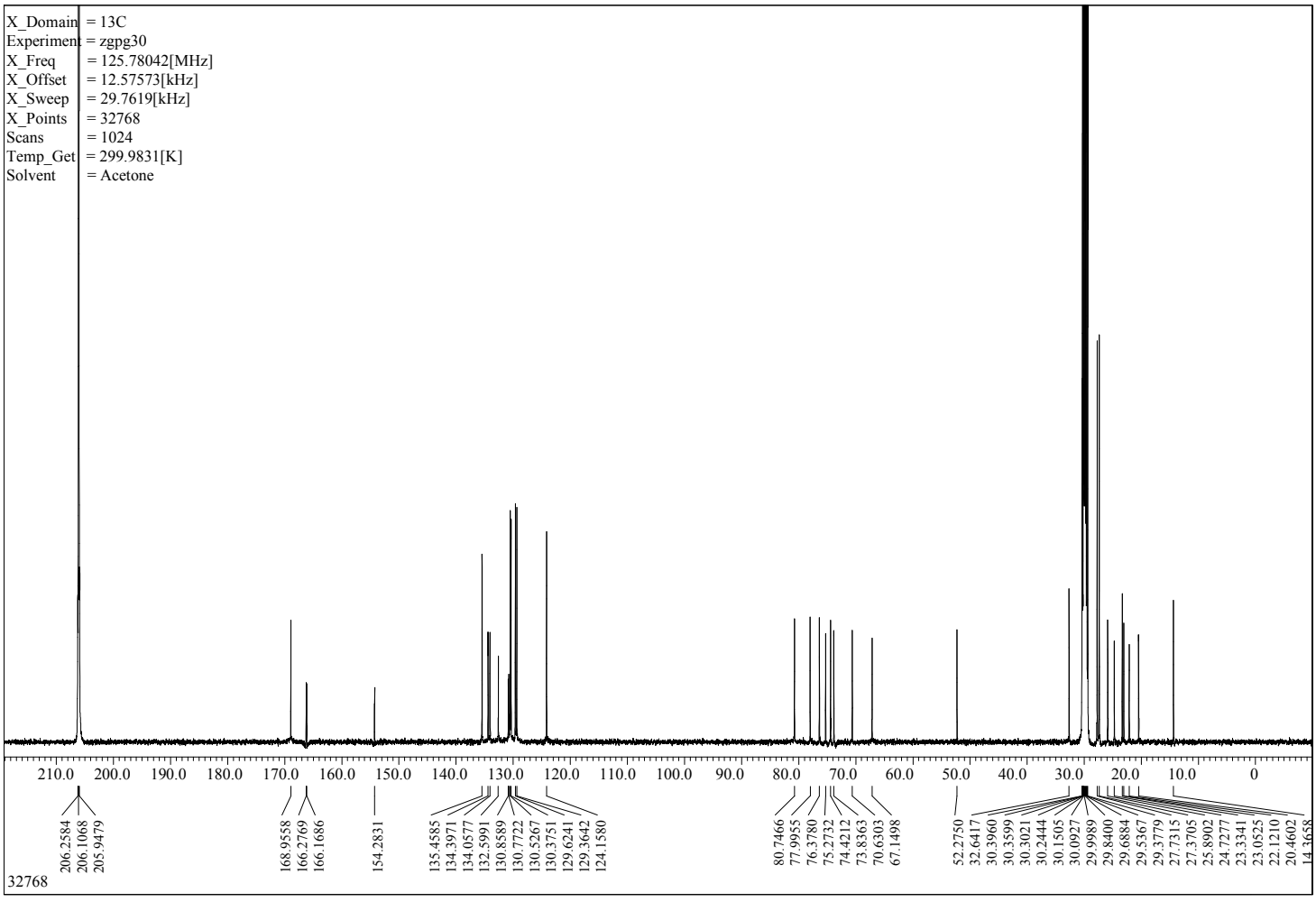


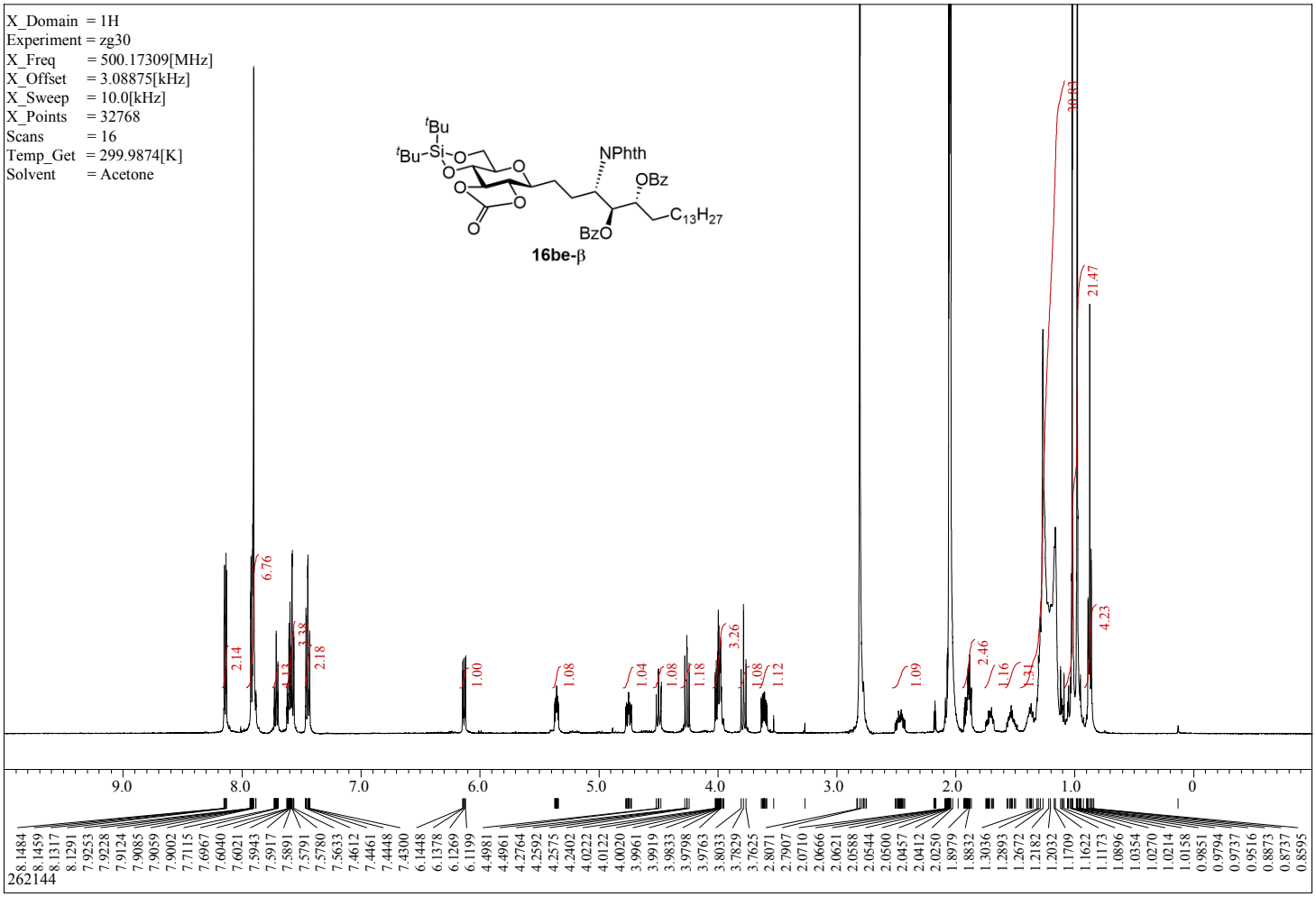
32768

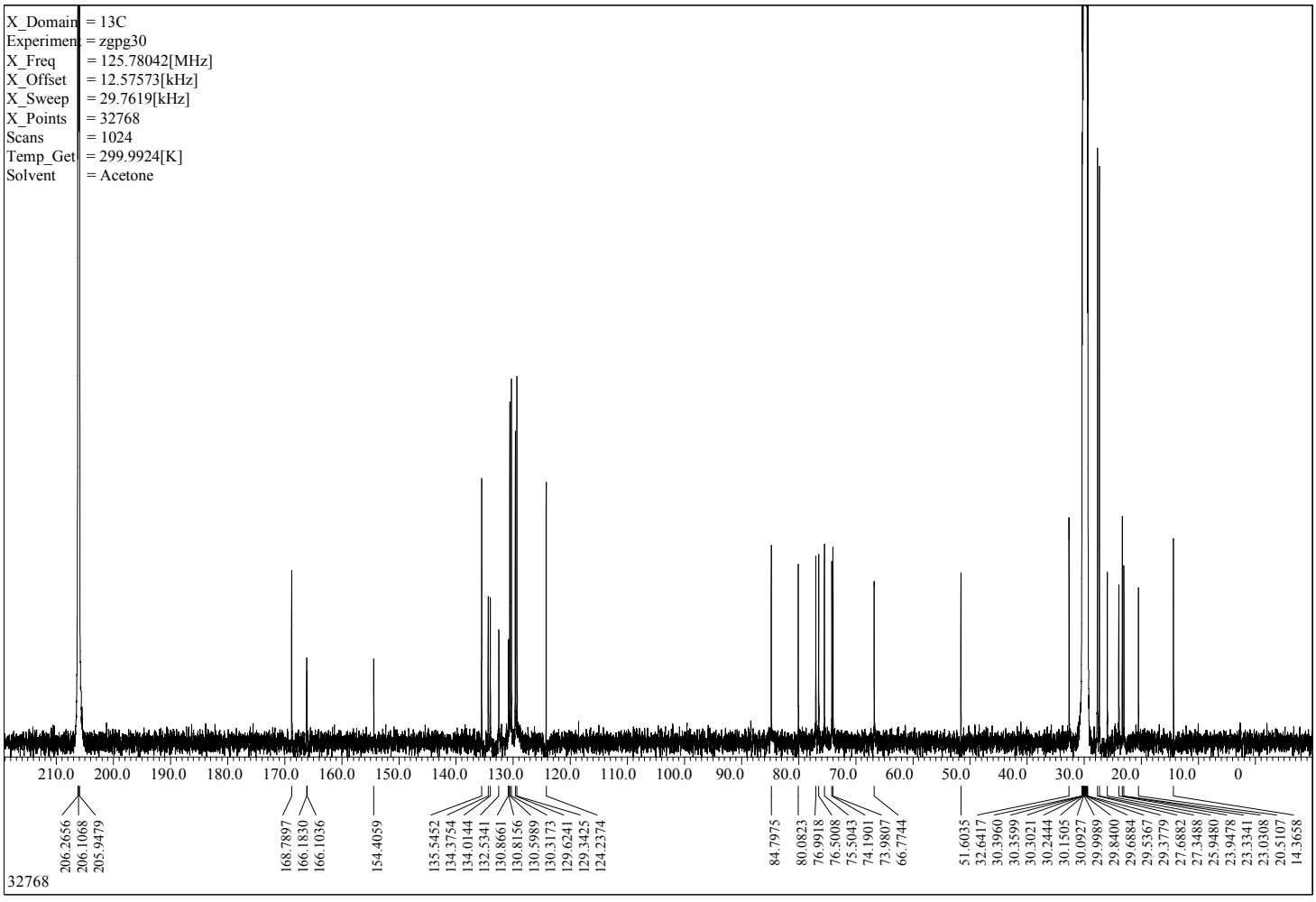

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9868[K]
Solvent = Acetone
16cd-α
262144

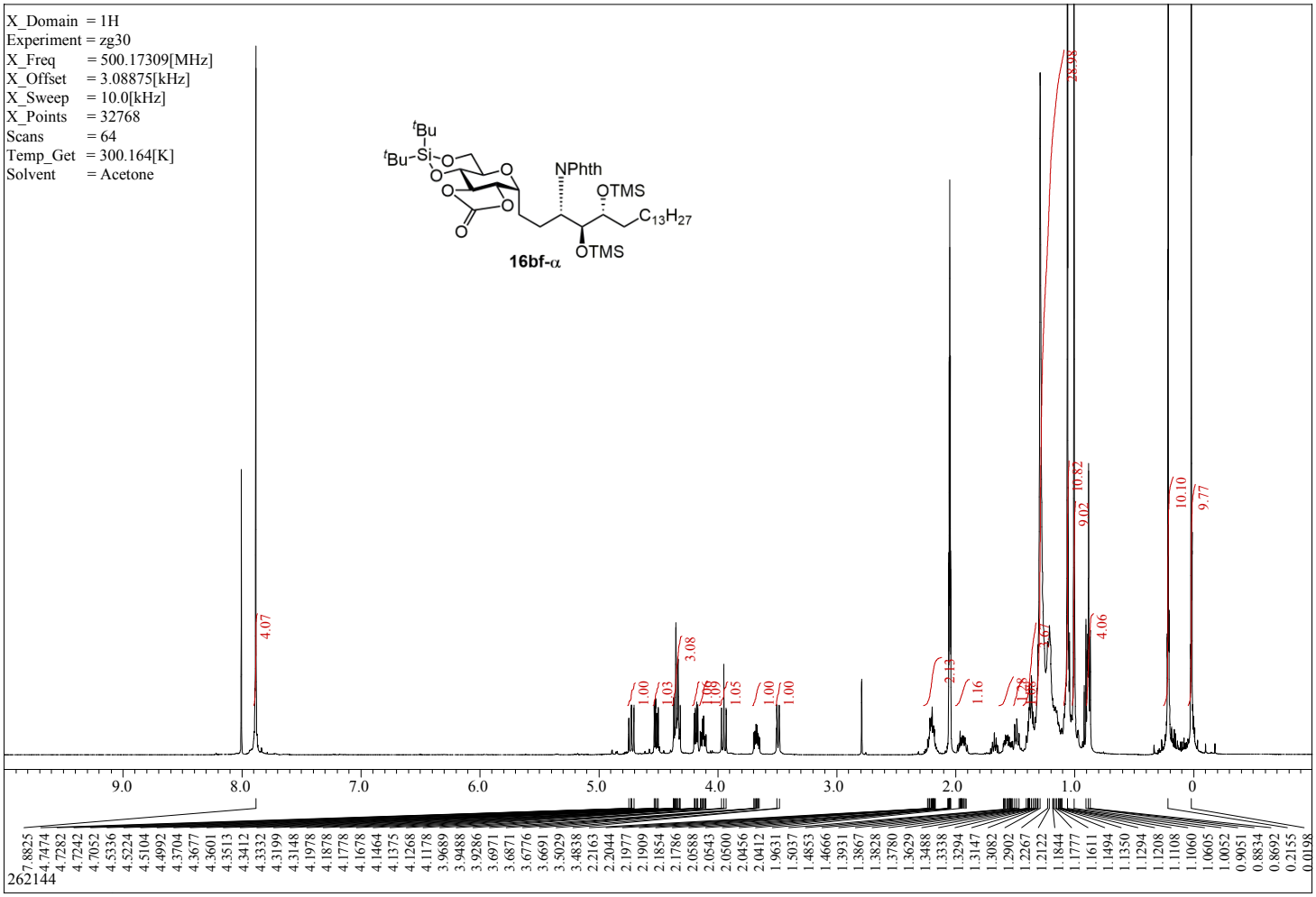

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 299.9853[K]
Solvent = Acetone
32768

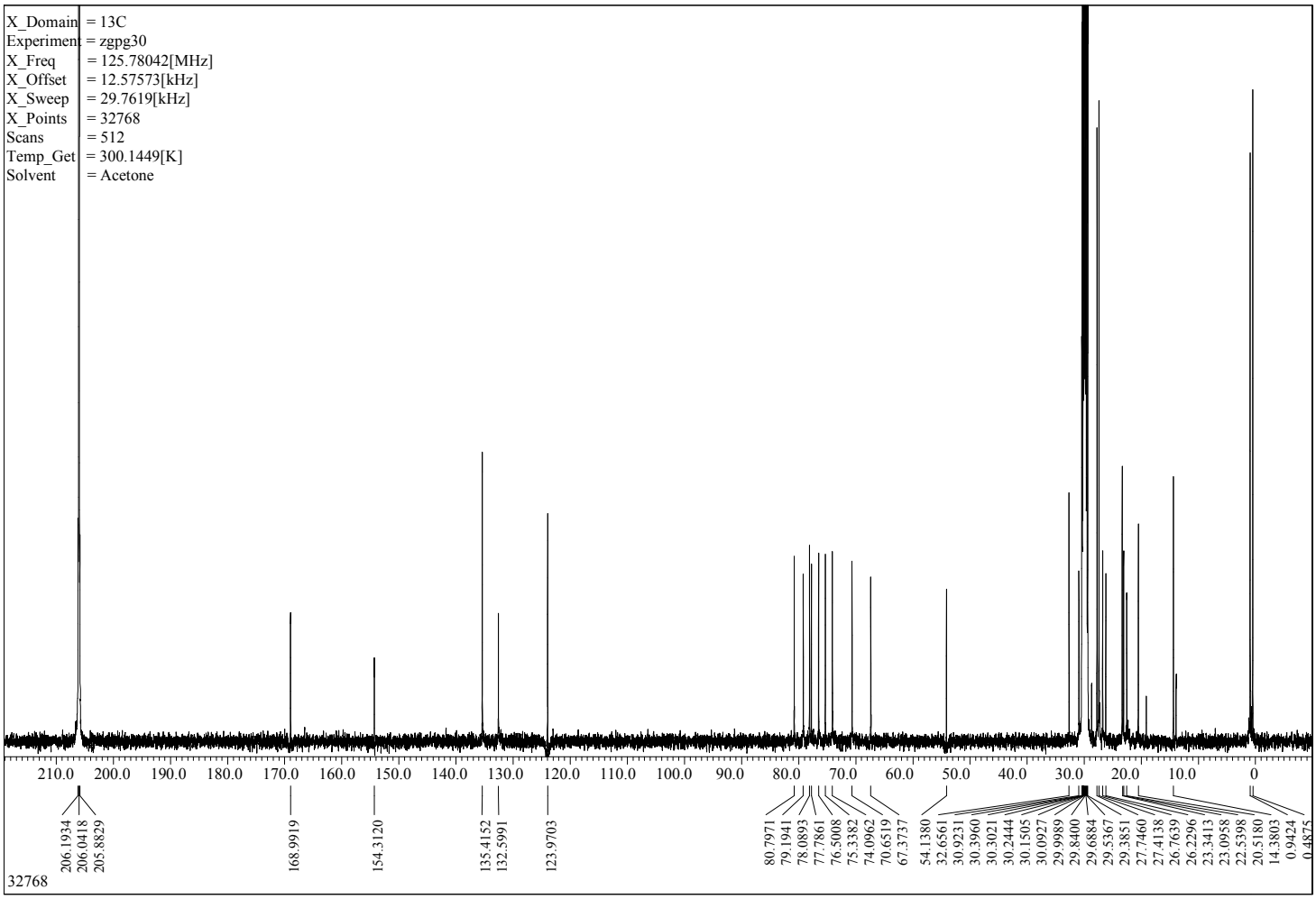

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9853[K]
Solvent = Acetone
NPhth
OBz
OBz
C13H27
16be-α
262144

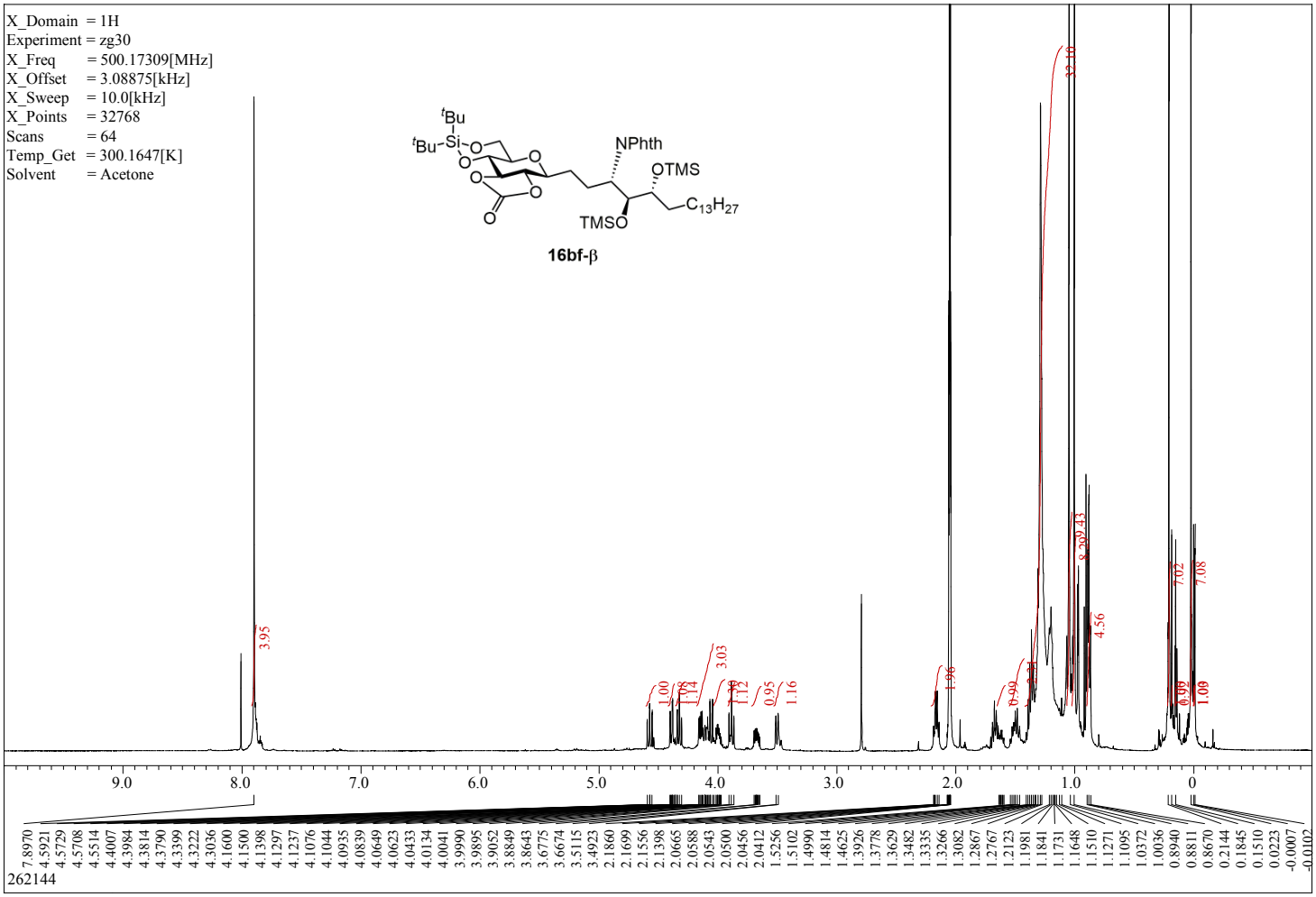

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 299.9831[K]
Solvent = Acetone
32768

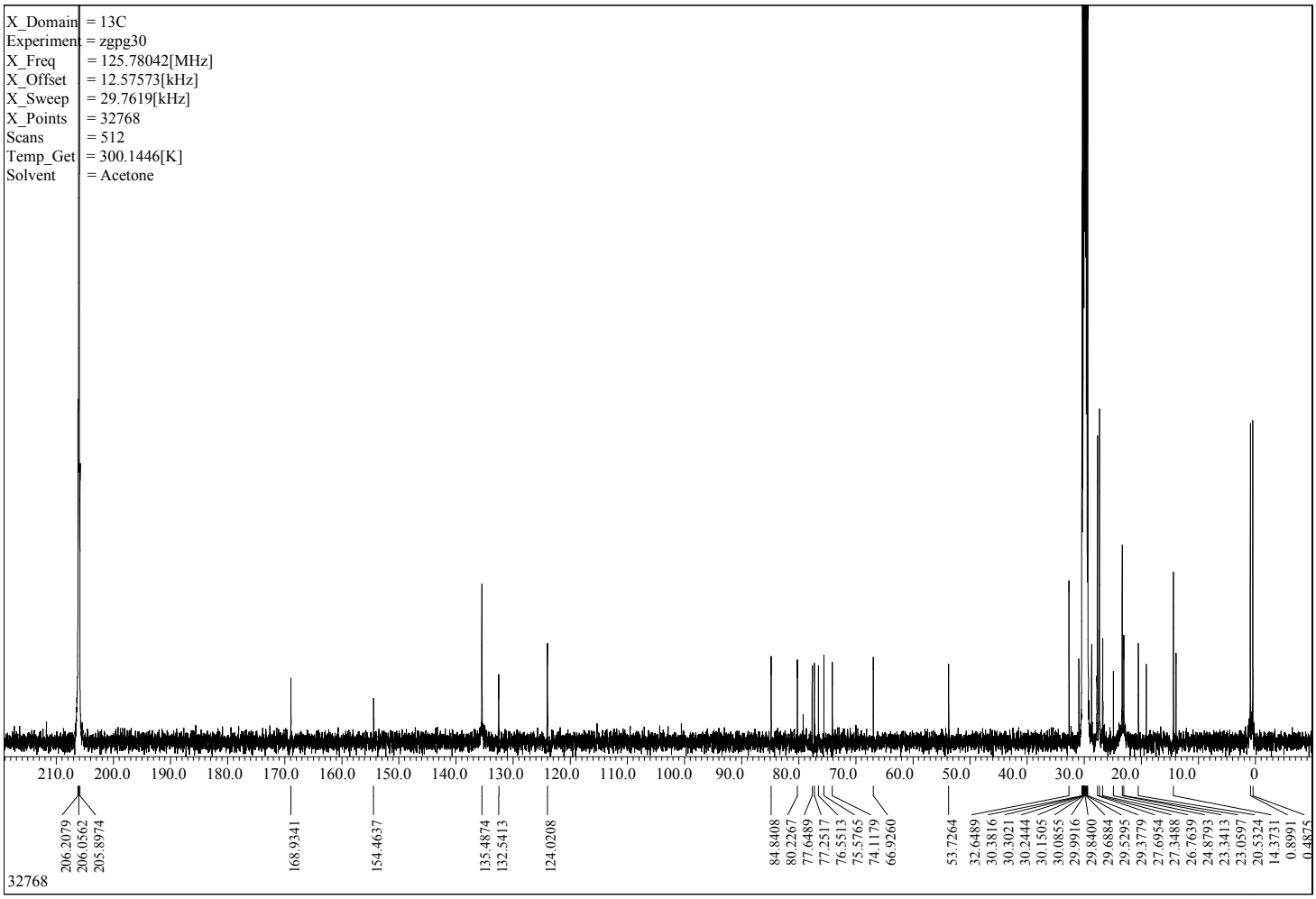

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9874[K]
Solvent = Acetone
16be-β
262144

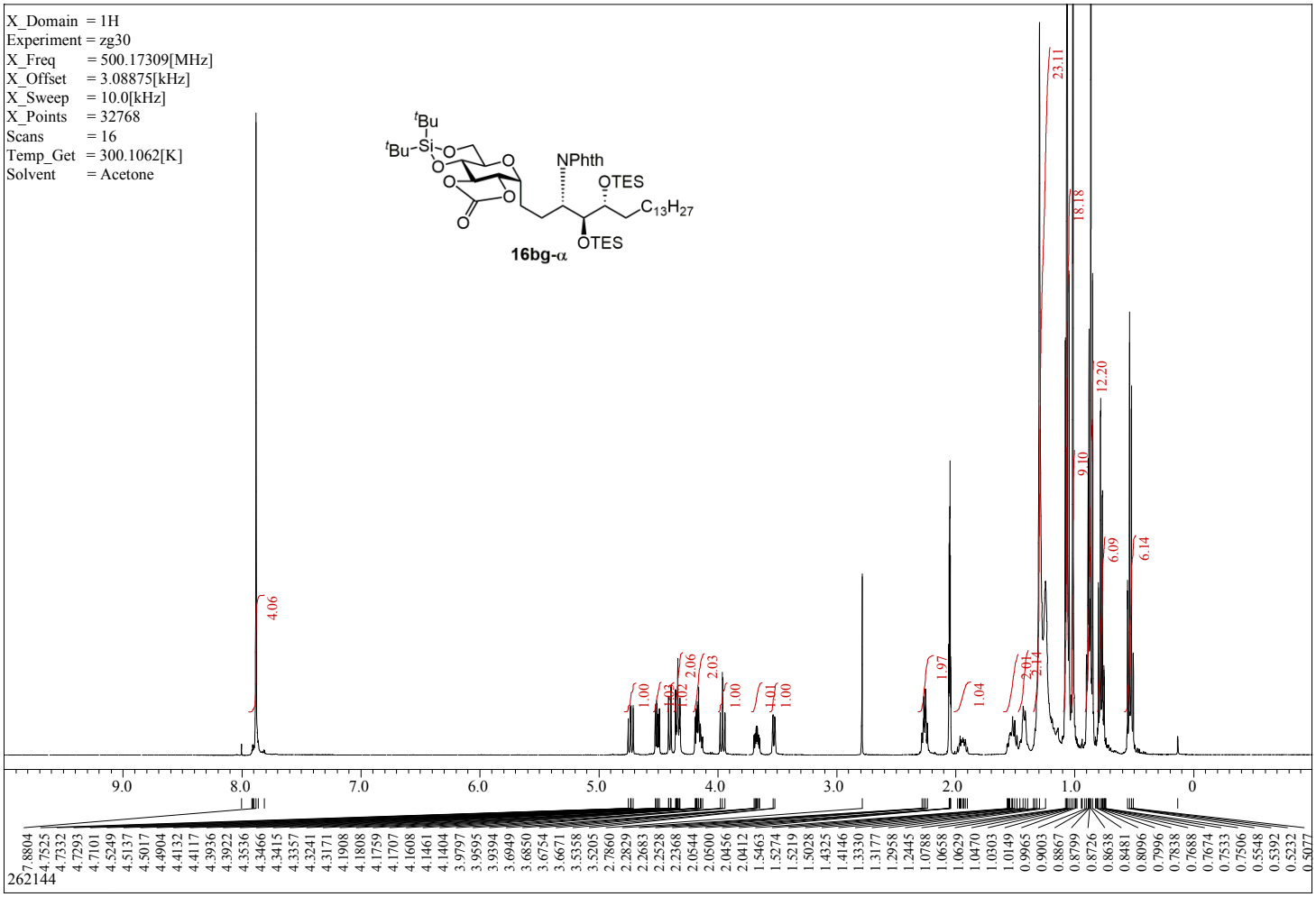

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 299.9924[K]
Solvent = Acetone
32768

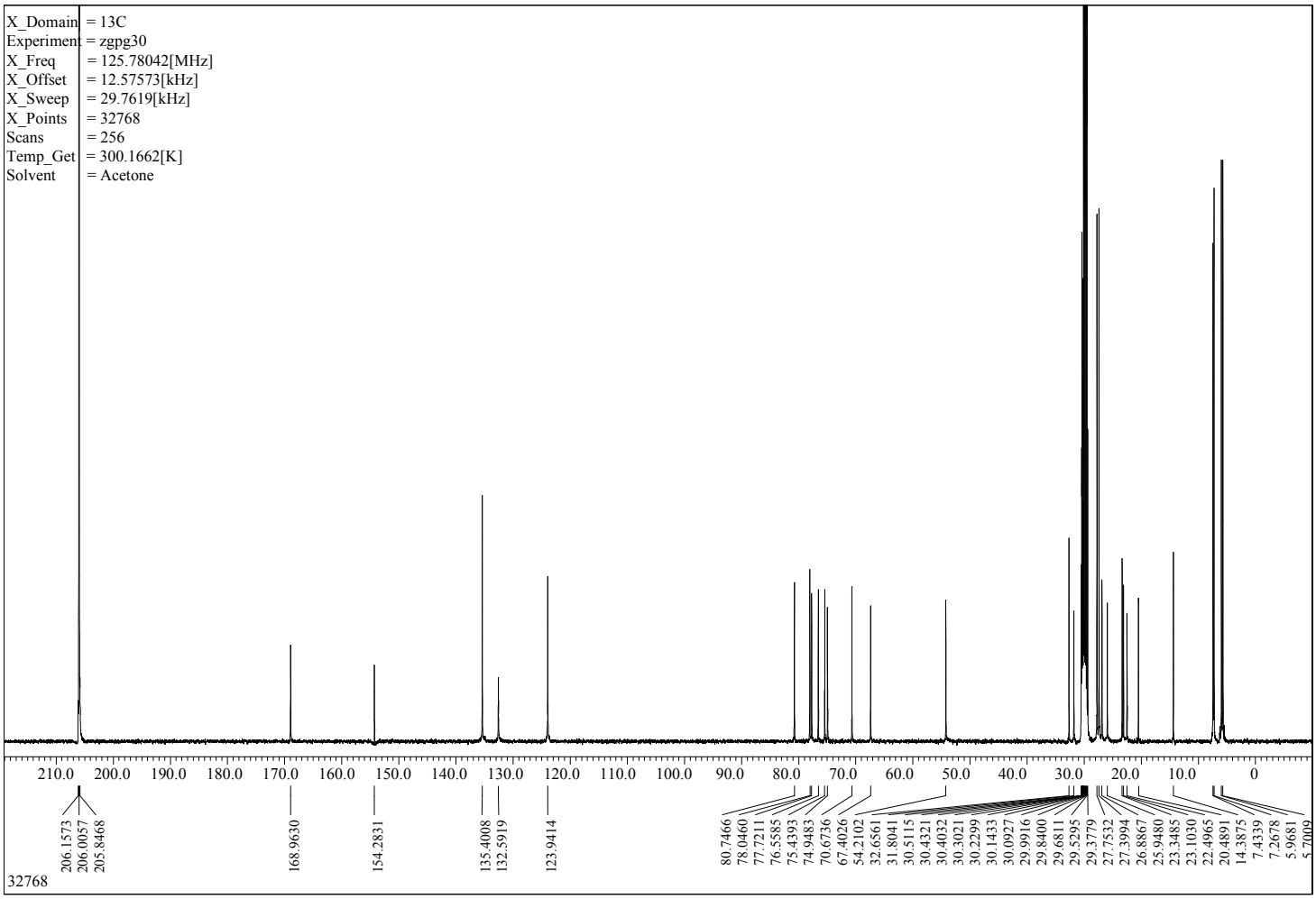

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 300.164[K]
Solvent = Acetone
NPhth
OTMS
OTMS
16bf-α
262144

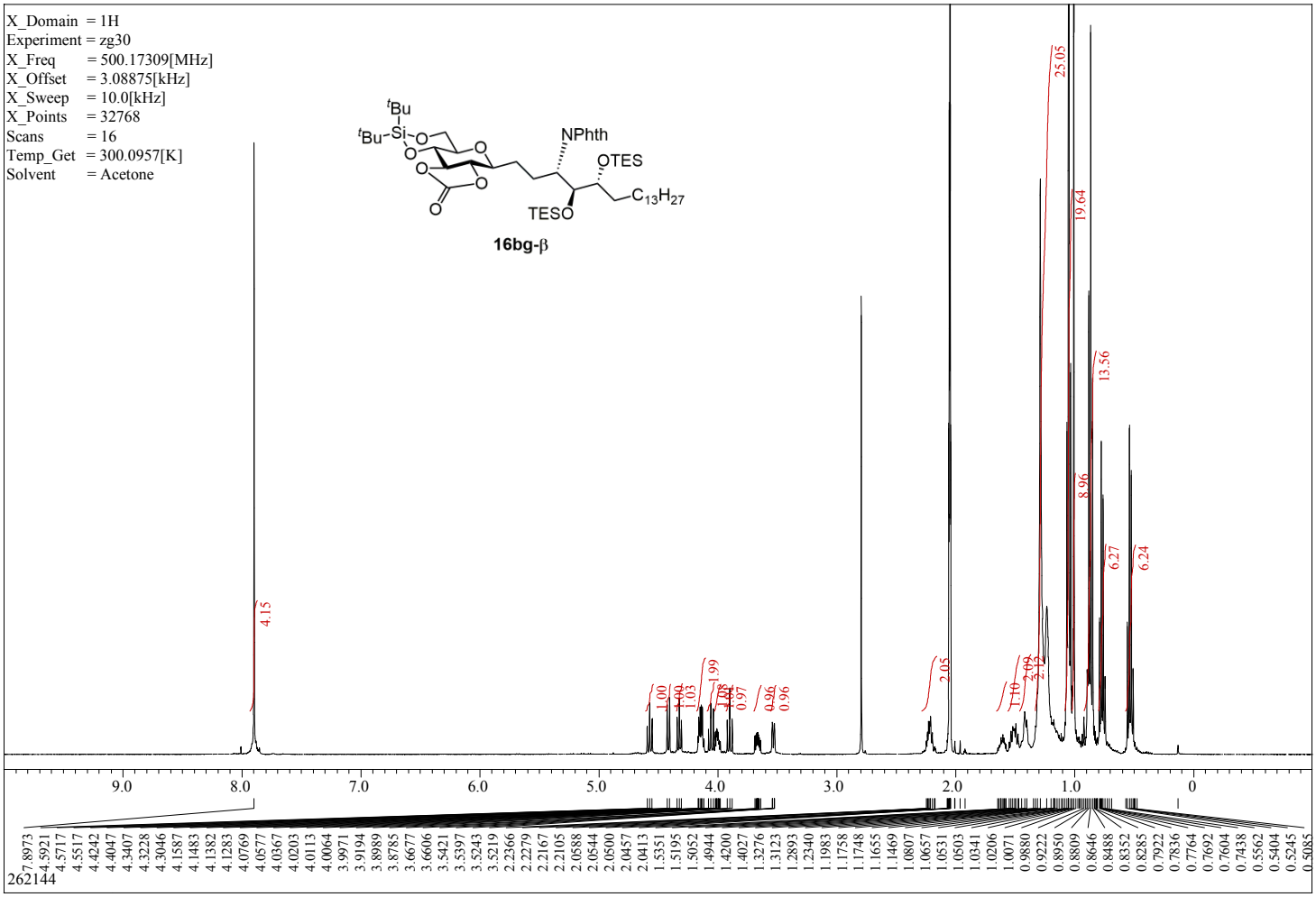

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 512
Temp_Get = 300.1449[K]
Solvent = Acetone
32768

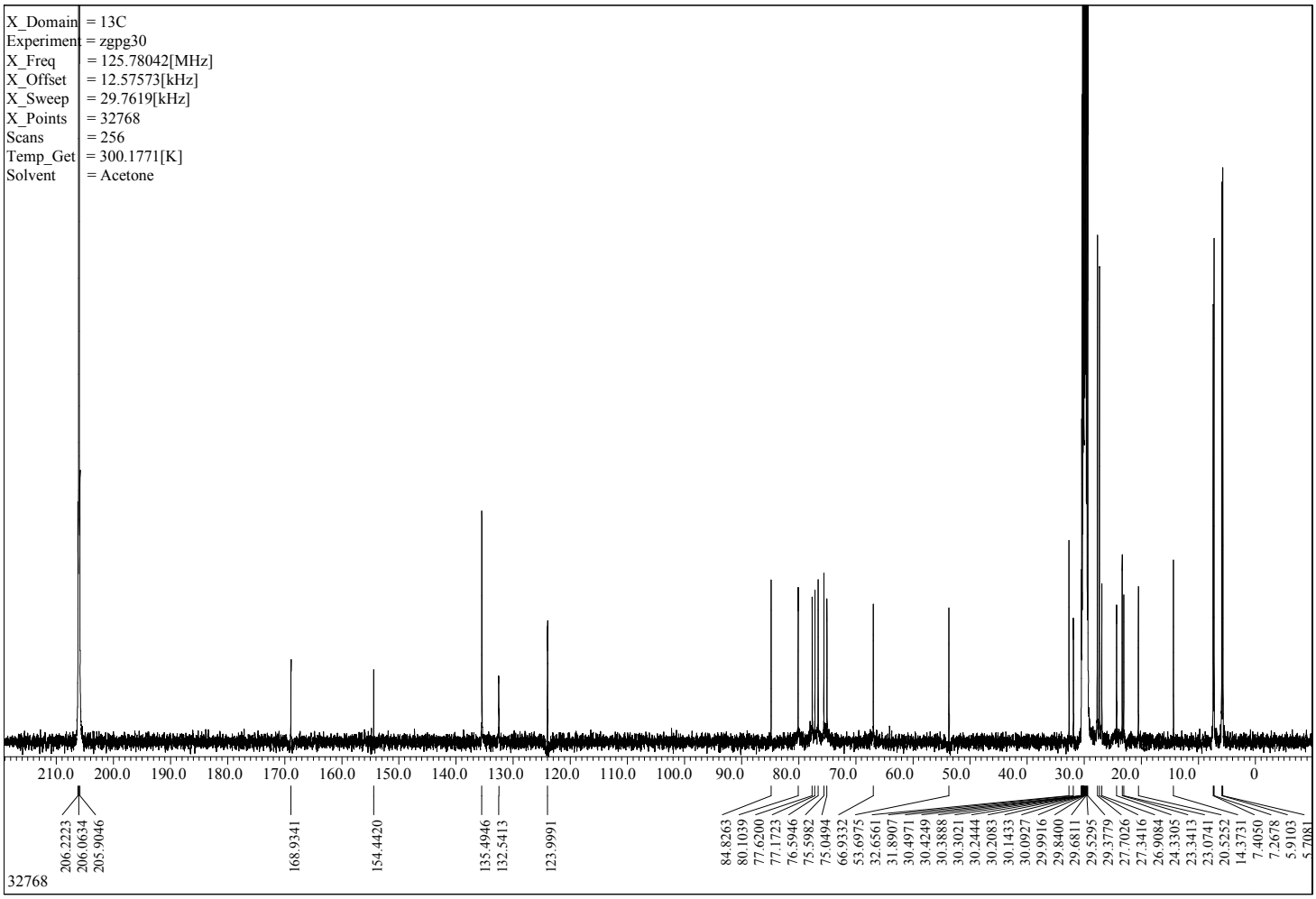

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 300.1647[K]
Solvent = Acetone
tBu
tBu-Si-O
NPhth
OTMS
TMSO
C13H27
16bf-β
262144

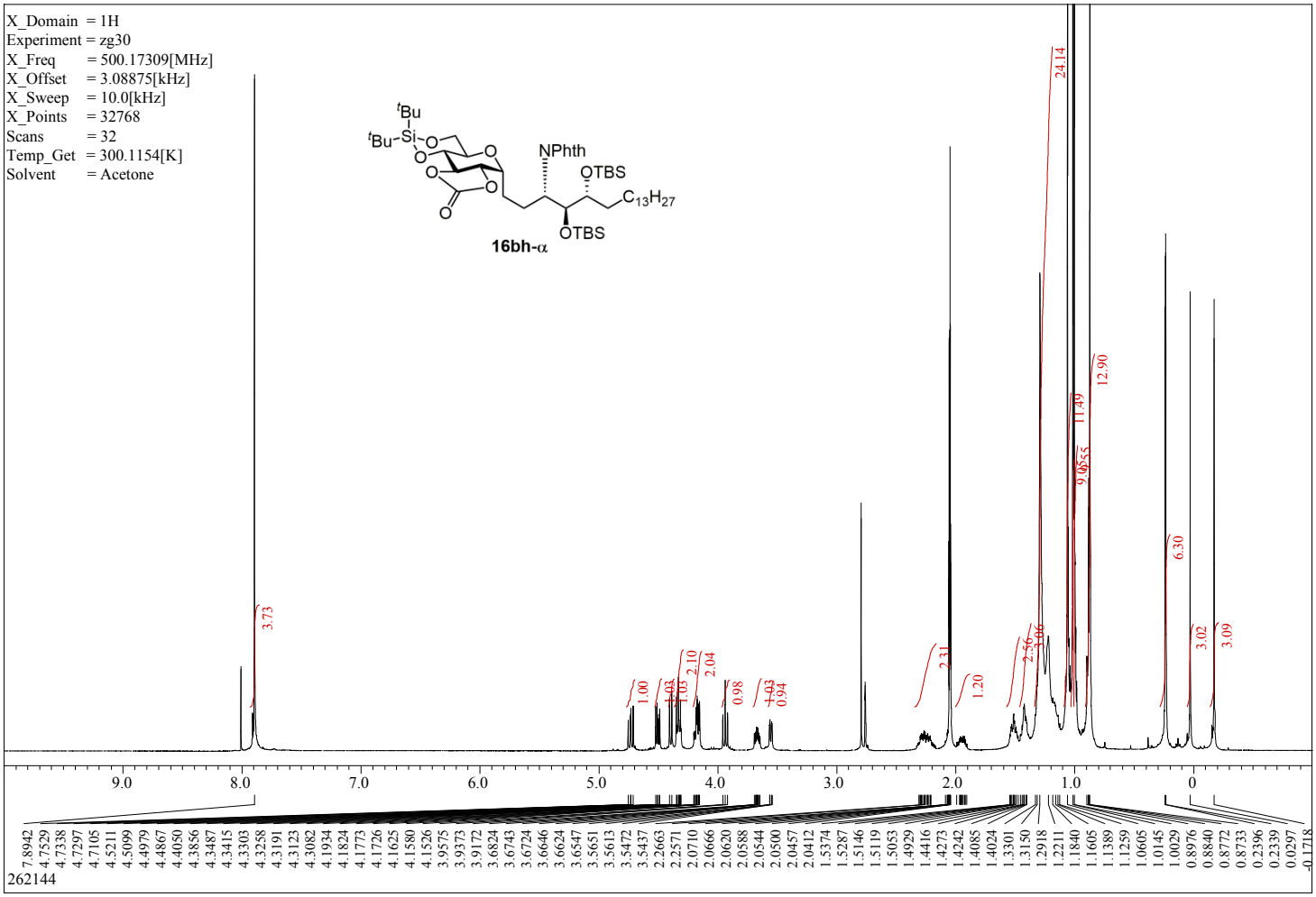

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 512
Temp_Get = 300.1446[K]
Solvent = Acetone
32768

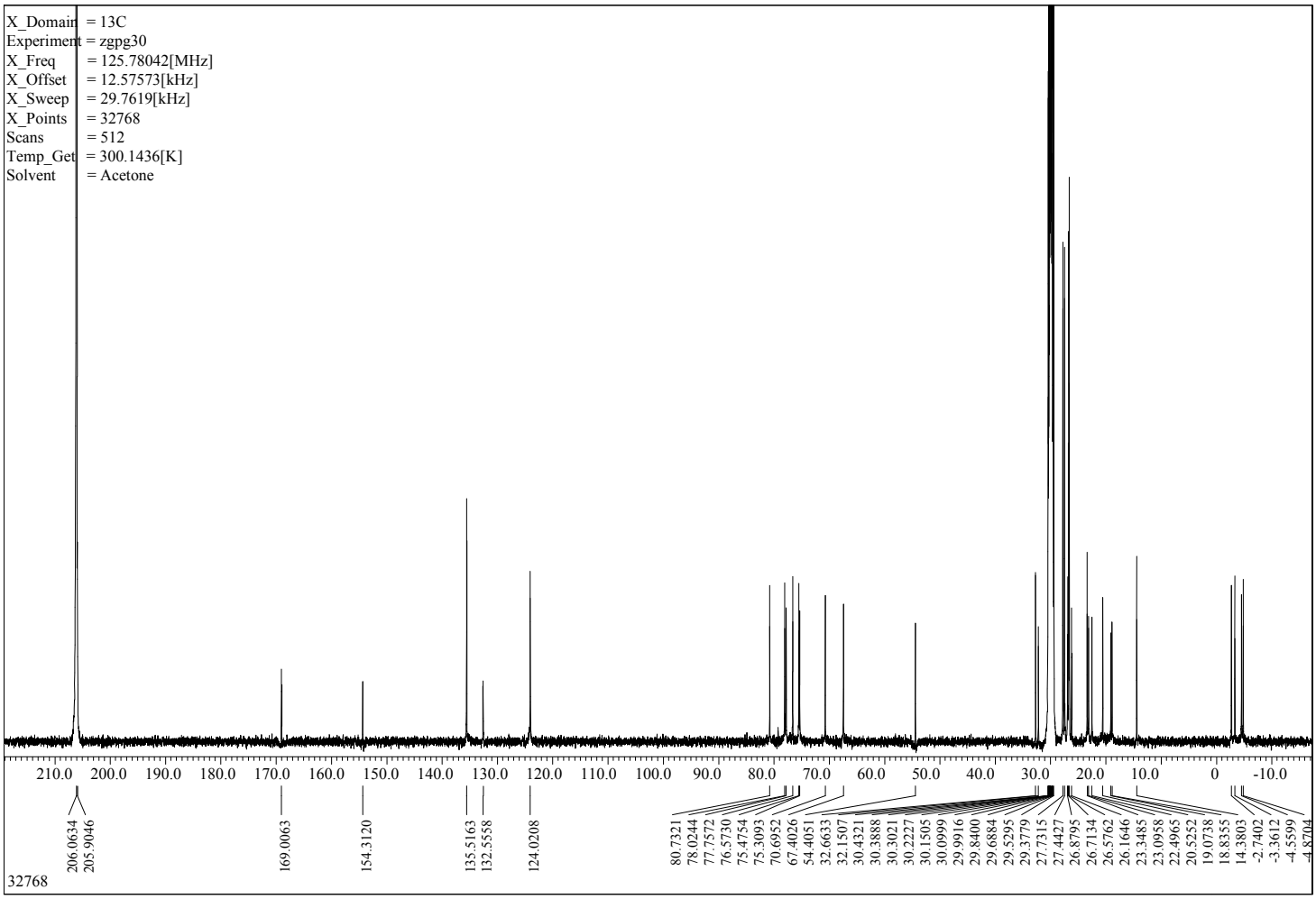

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.1062[K]
Solvent = Acetone
NPhth
OTES
OTES
16bg-α
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 300.1662[K]
Solvent = Acetone
32768

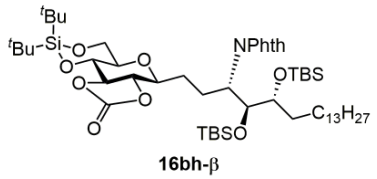

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.0957[K]
Solvent = Acetone
NPhth
OTES
TESO
C13H27
16bg-β
25.05
19.64
13.56
8.96
6.27
6.24
4.15
2.05
1.99
1.00
1.00
1.03
1.08
1.08
0.97
0.96
0.96
1.16
2.09
2.12
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 256
Temp_Get = 300.1771[K]
Solvent = Acetone
206.2223
206.0634
205.9046
168.9341
154.4420
135.4946
132.5413
123.9991
84.8263
80.1039
77.6200
77.1723
76.5946
75.5982
75.0494
66.9332
53.6975
32.6561
31.8907
30.4971
30.4249
30.3888
30.3021
30.2444
30.2083
30.1433
30.0927
29.9916
29.8400
29.6811
29.5295
29.3779
27.7026
27.3416
26.9084
24.3305
23.3413
23.0741
20.5252
14.3731
7.4050
7.2678
5.9103
5.7081
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 32
Temp_Get = 300.1154[K]
Solvent = Acetone
tBu
tBu-Si-O
NPhth
OTBS
C13H27
OTBS
16bh-α
24.14
12.90
11.49
6.30
3.73
3.09
3.02
2.31
2.10
2.04
1.20
1.00
0.98
0.94
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 512
Temp_Get = 300.1436[K]
Solvent = Acetone
206.0634
205.9046
169.0063
154.3120
135.5163
132.5558
124.0208
80.7321
78.0244
77.7572
76.5730
75.4754
75.3093
70.6952
67.4026
54.4051
32.6633
32.1507
30.4321
30.3888
30.3021
30.2227
30.1505
30.0999
29.9916
29.8400
29.6884
29.5295
29.3779
27.7315
27.4427
26.8795
26.7134
26.5762
26.1646
23.3485
23.0958
22.4965
20.5252
19.0738
18.8355
14.3803
-2.7402
-3.3612
-4.5599
-4.8704
32768

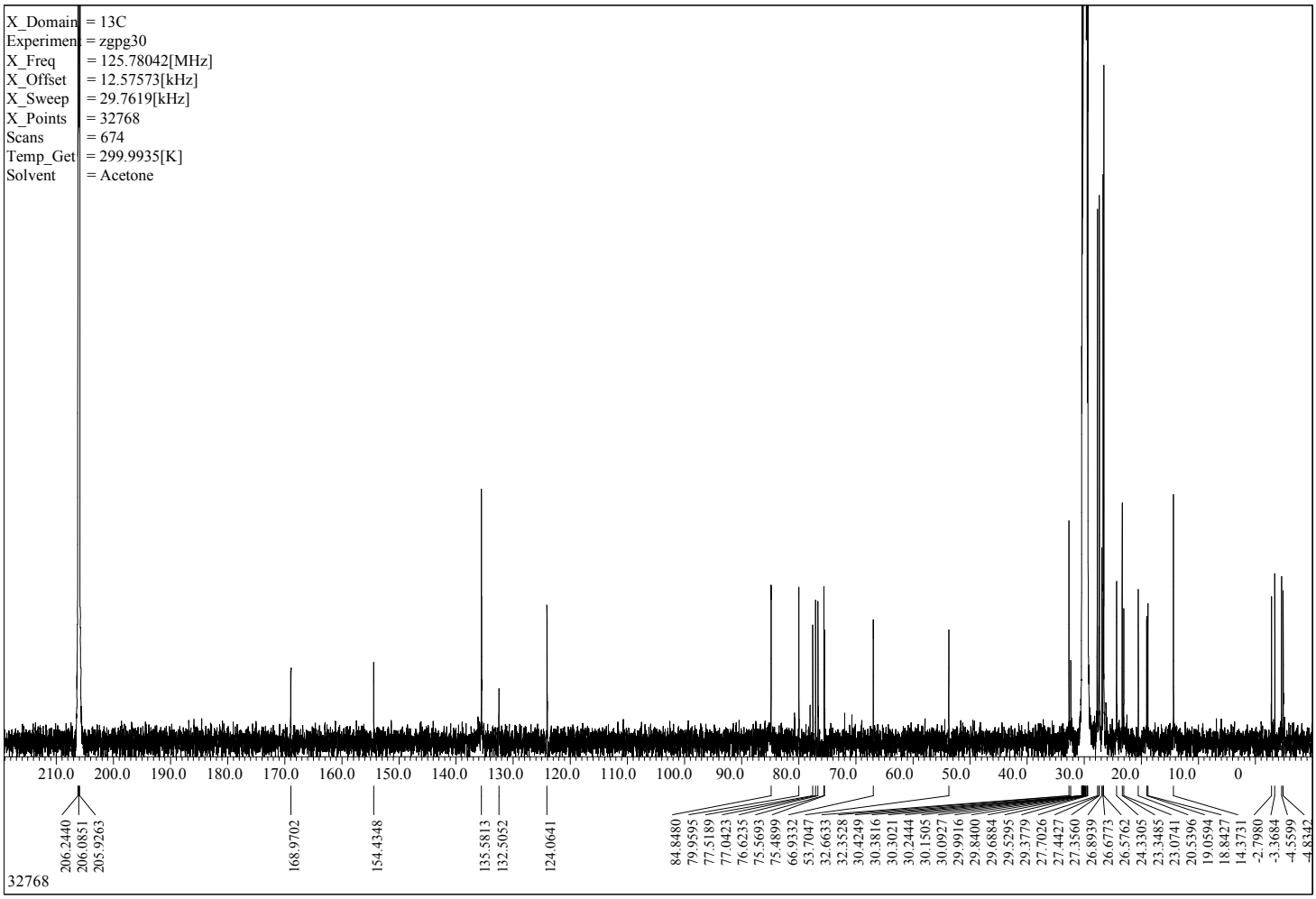
X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 32
Temp_Get = 300.1444[K]
Solvent = Acetone



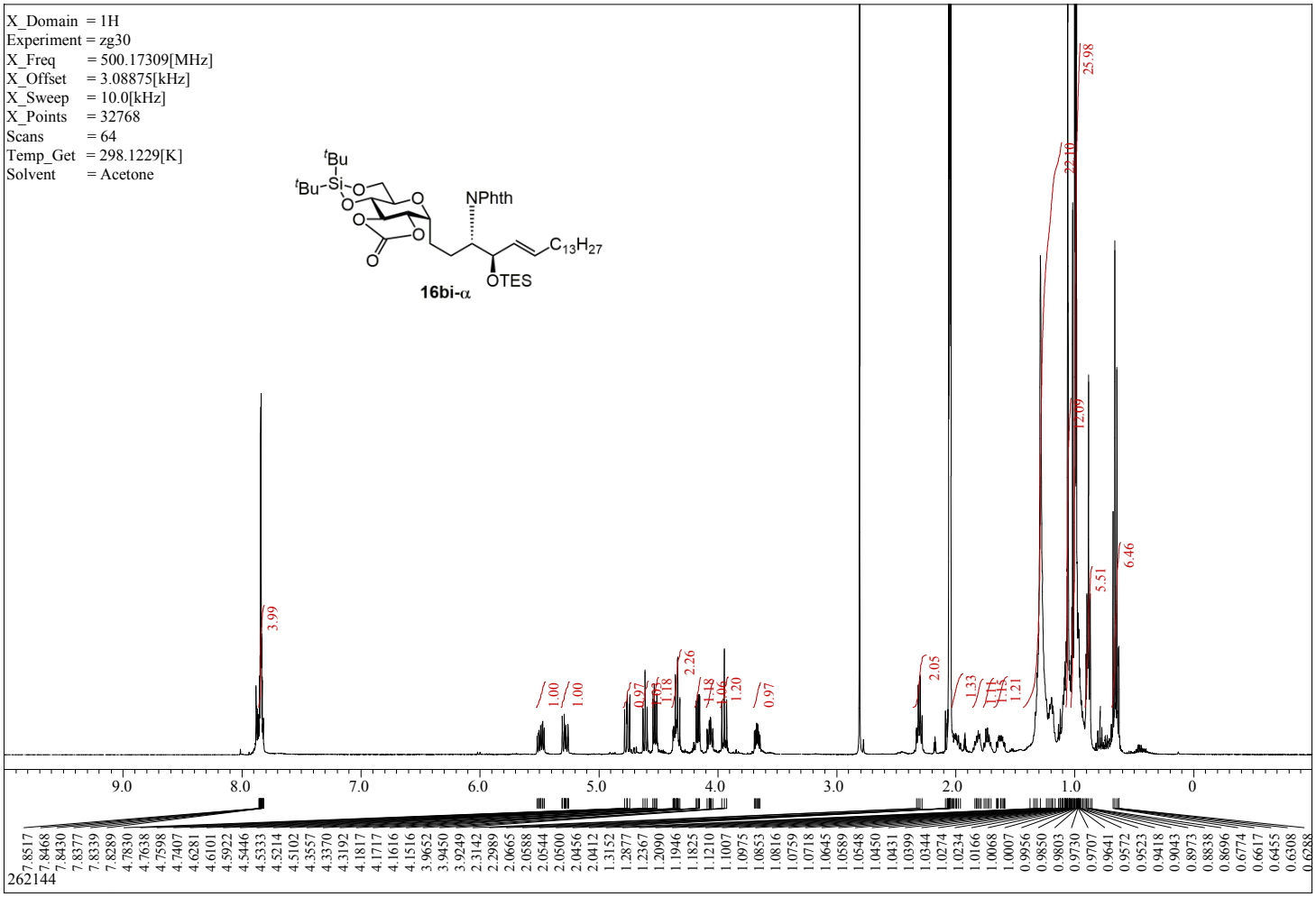
16bh-β

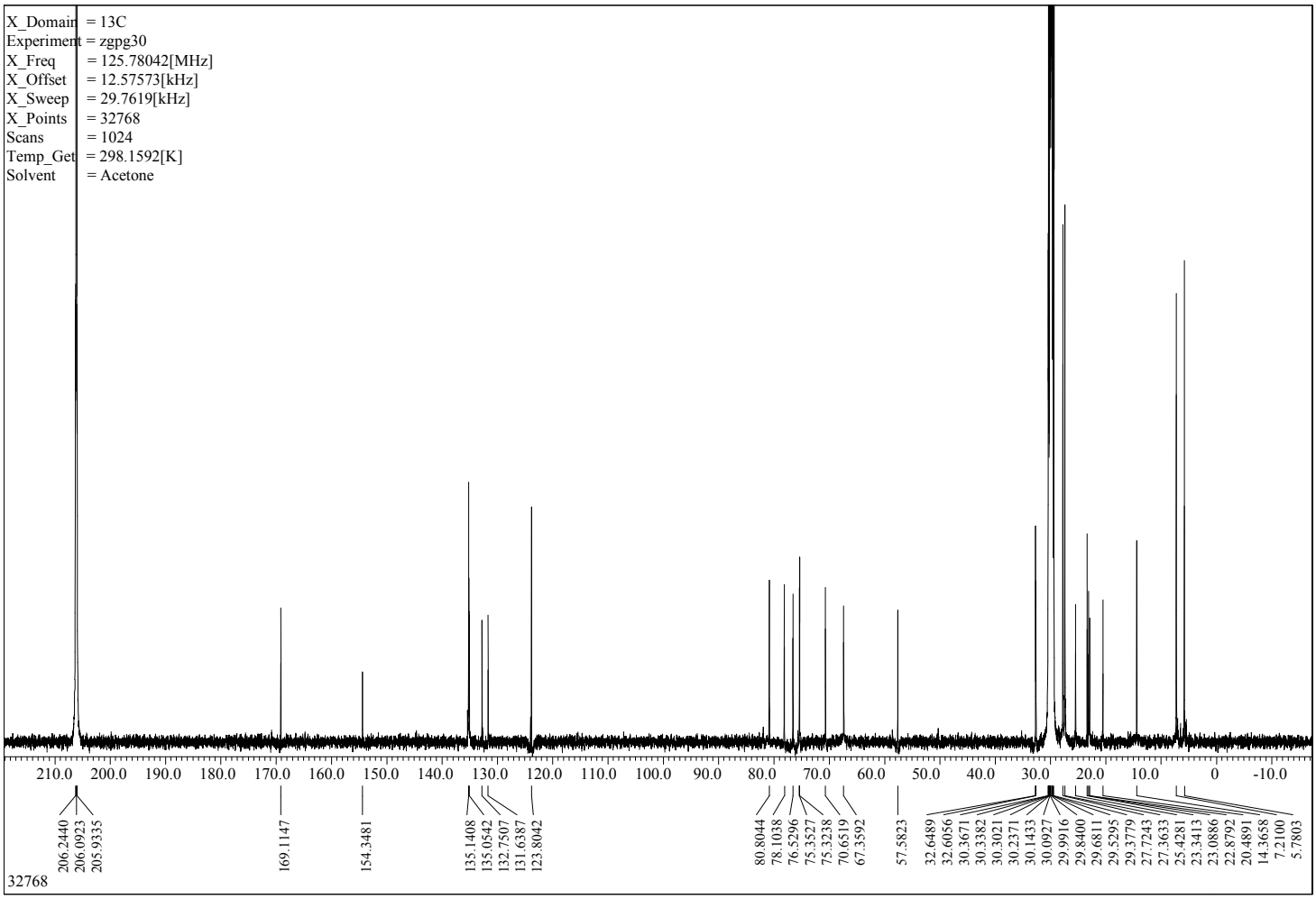
262144

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 674
Temp_Get = 299.9935[K]
Solvent = Acetone

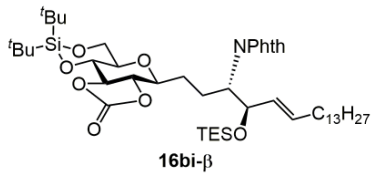


32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 298.1229[K]
Solvent = Acetone
tBu
tBu-Si
NPhth
C13H27
OTES
16bi-α
262144

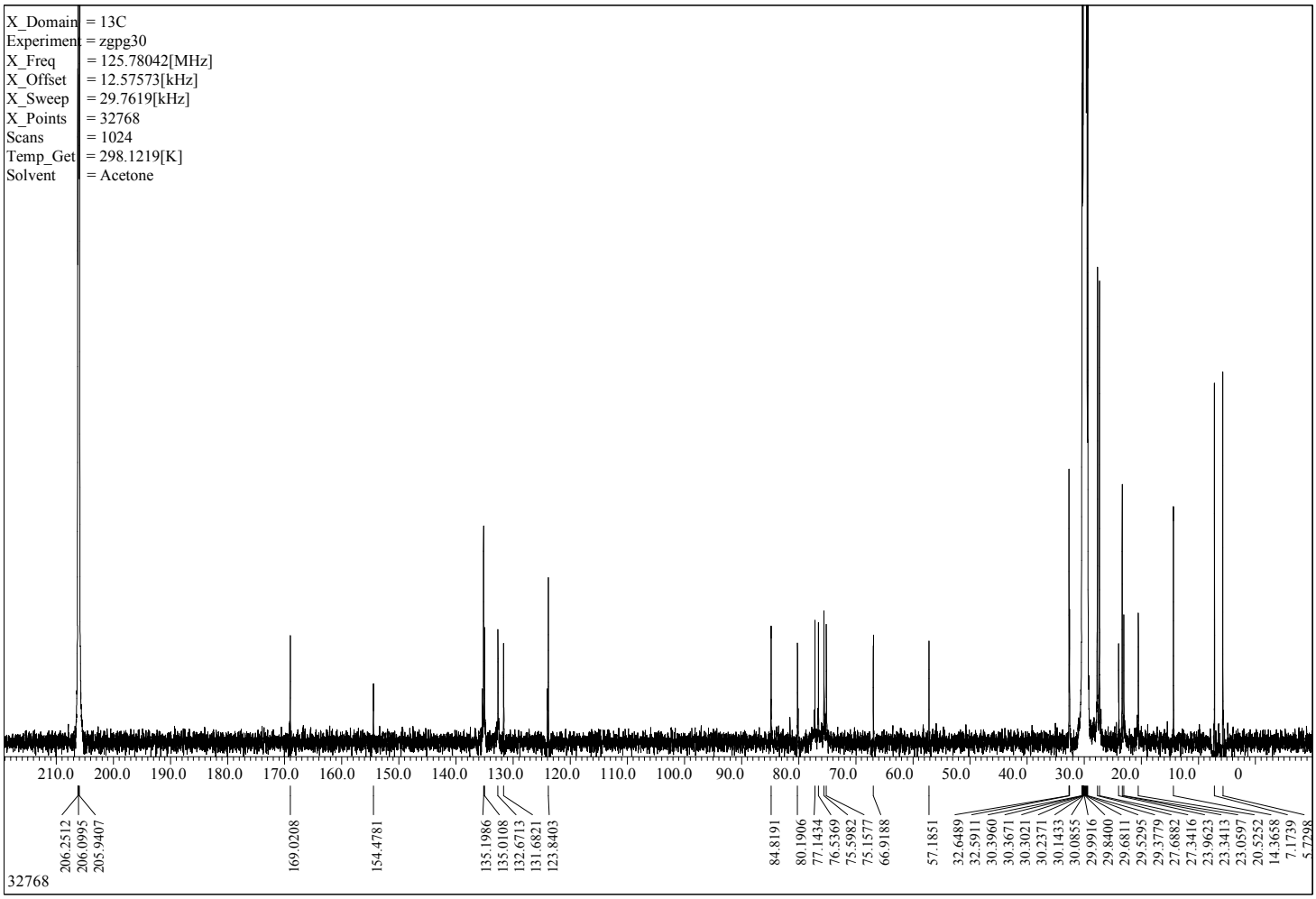

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 298.1592[K]
Solvent = Acetone
32768

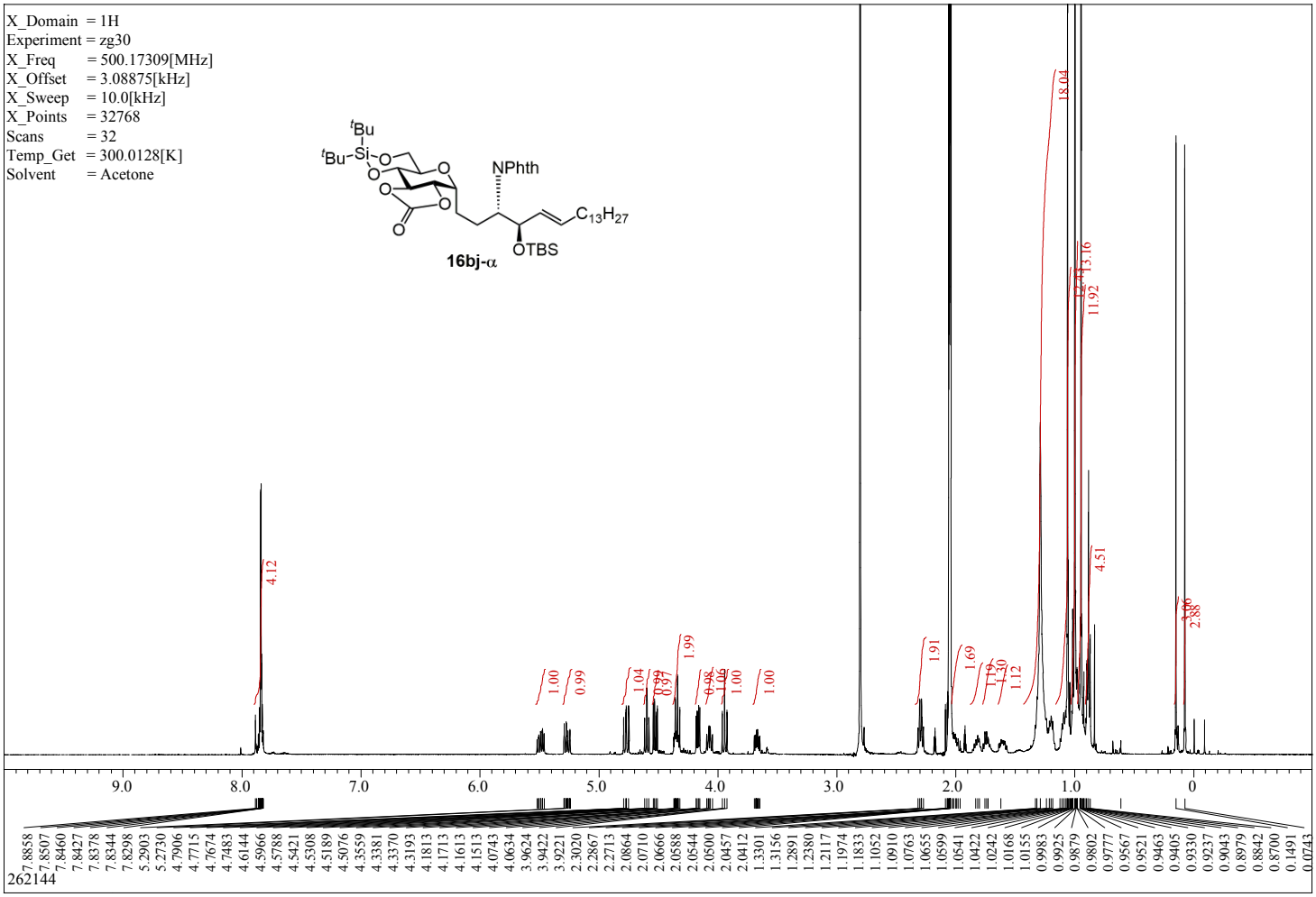
X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 298.1822[K]
Solvent = Acetone

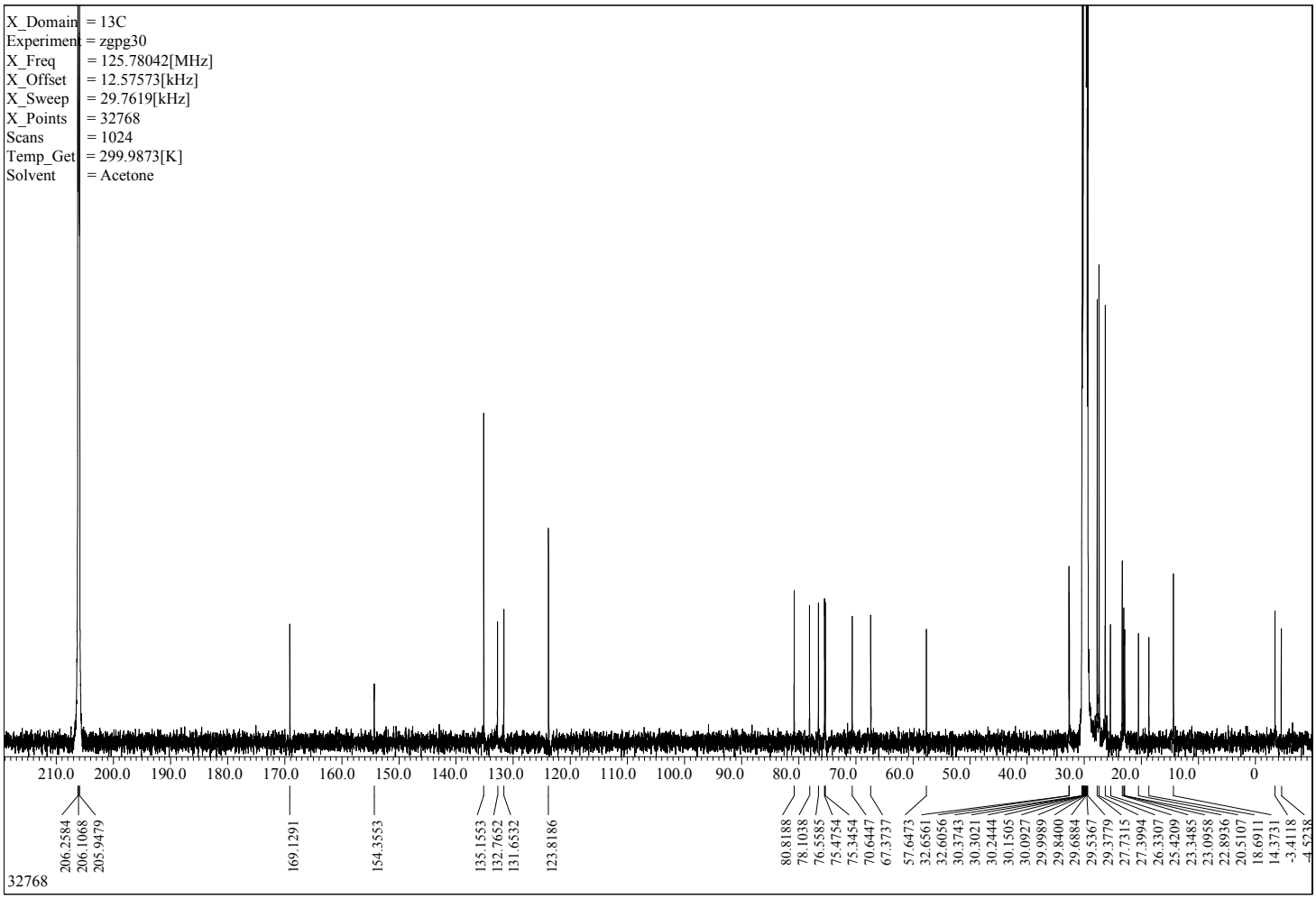


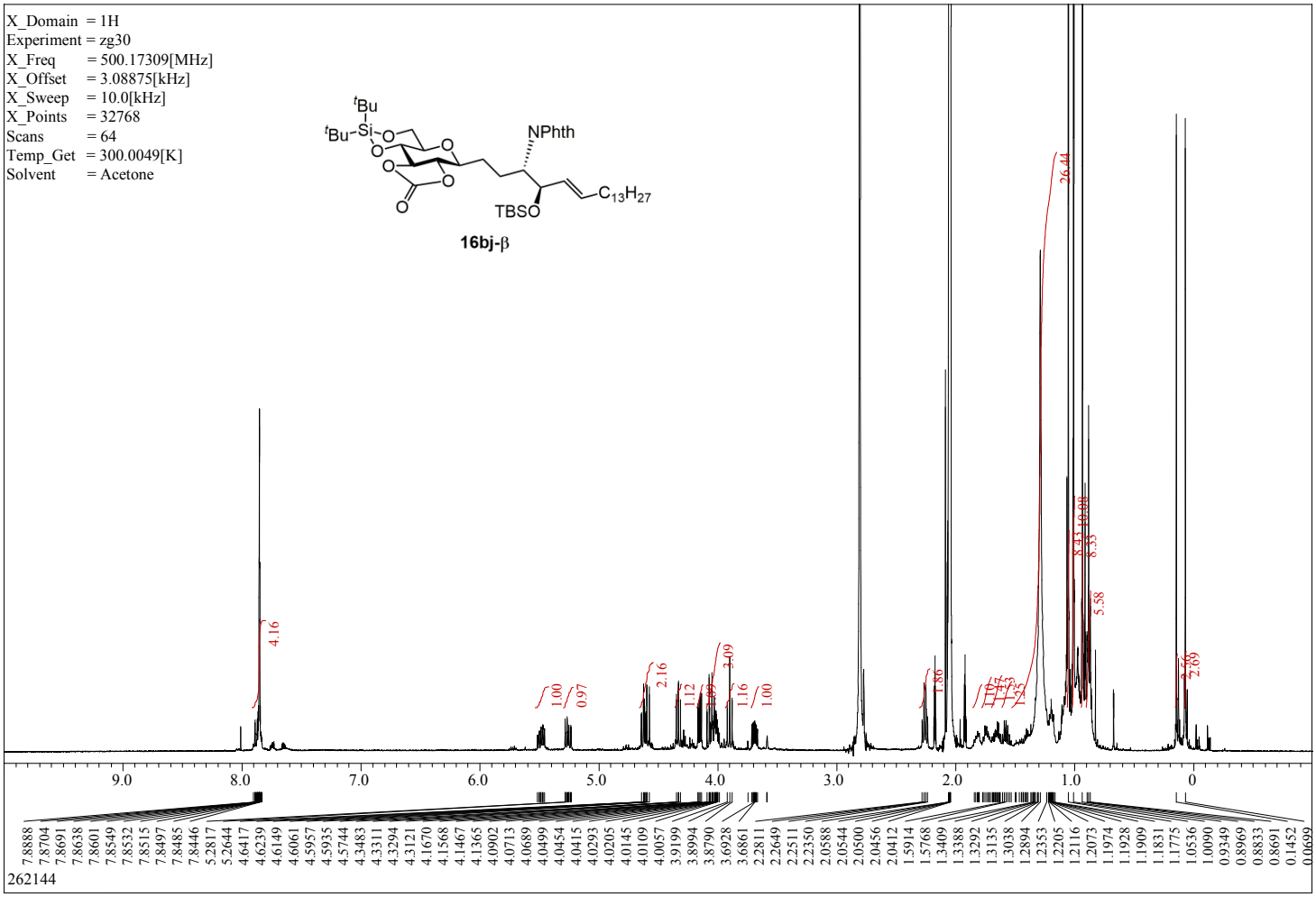
16bi-β

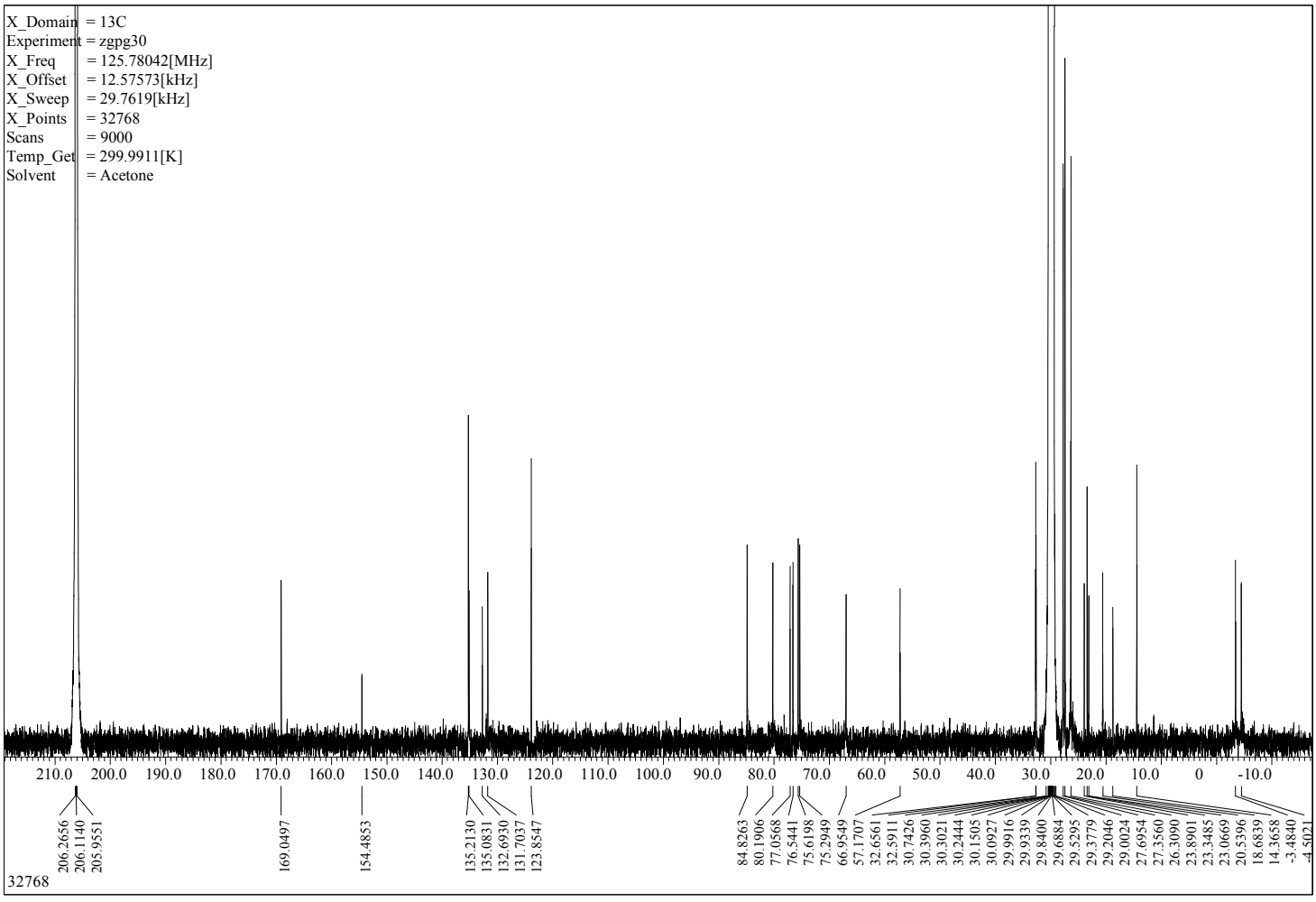
X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 298.1219[K]
Solvent = Acetone

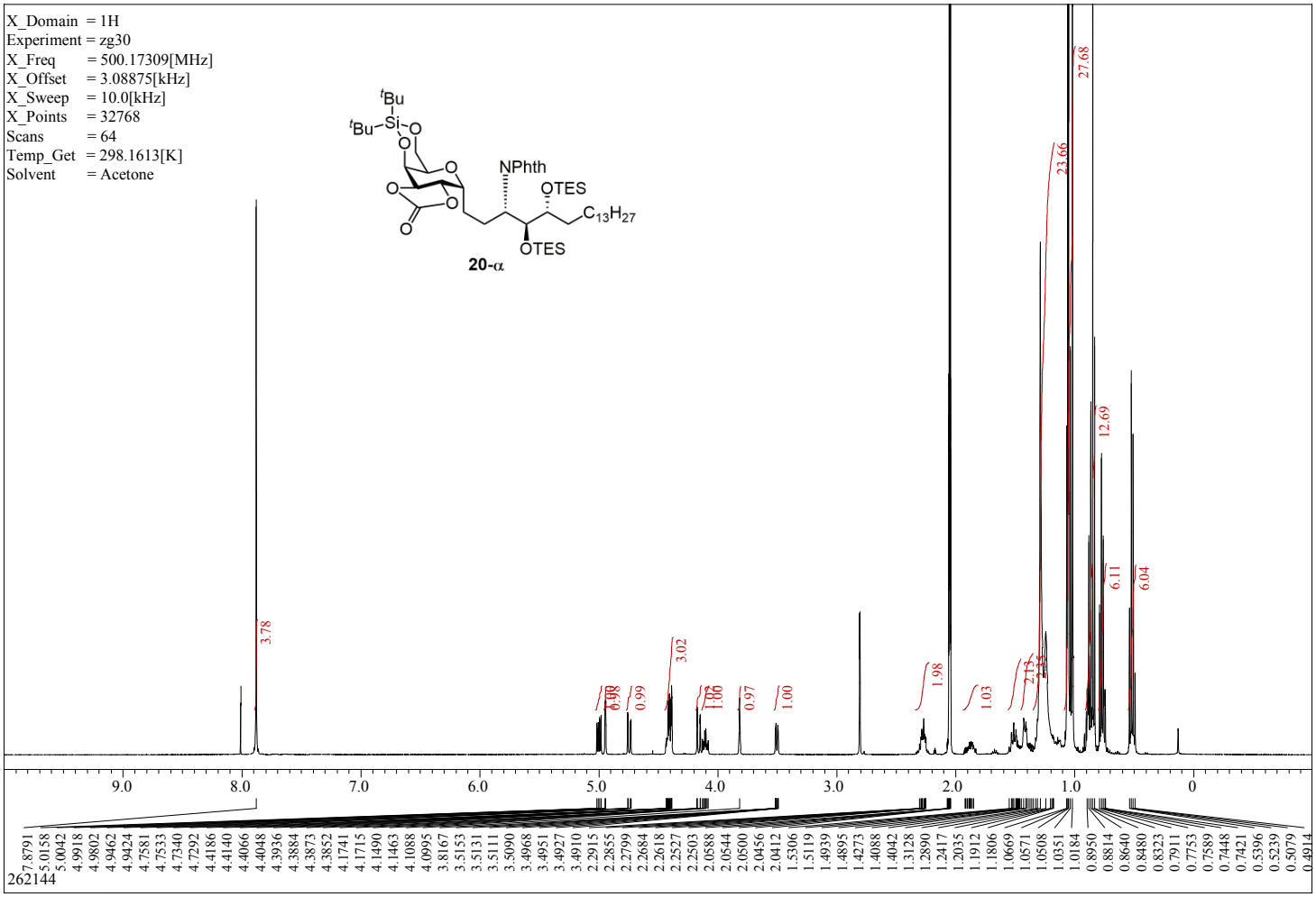


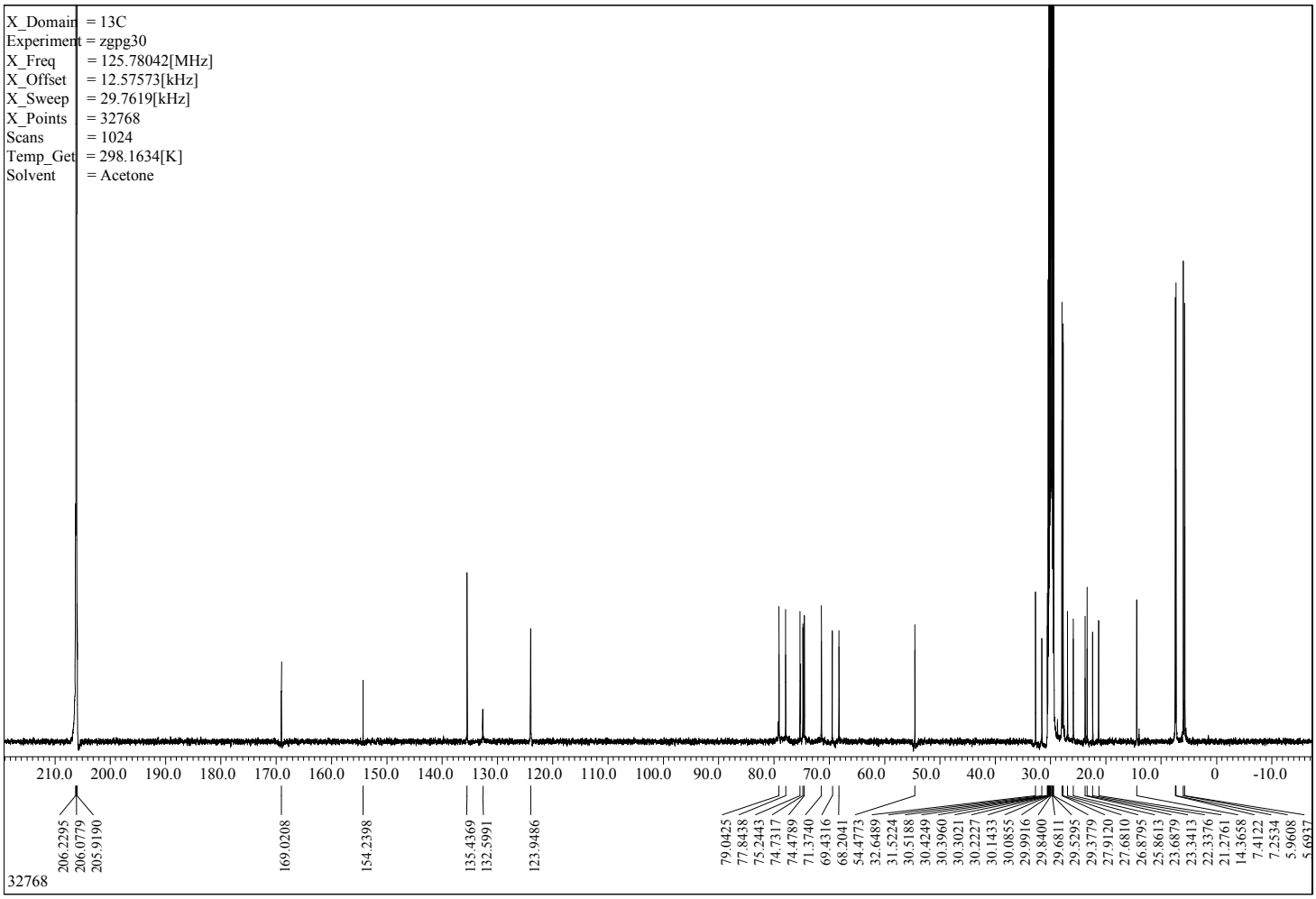

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 32
Temp_Get = 300.0128[K]
Solvent = Acetone
NPhth
C13H27
OTBS
16bj-α
262144

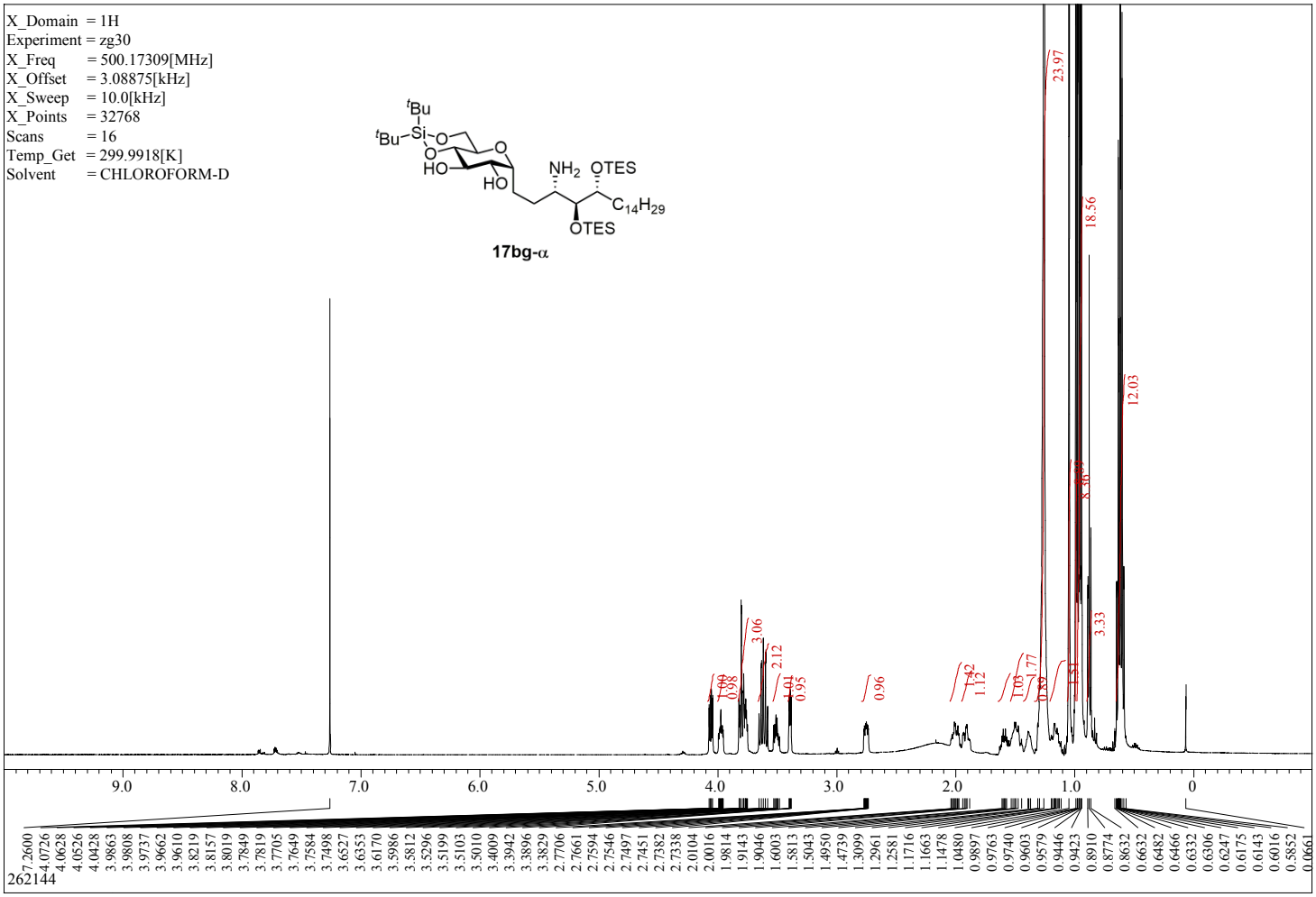

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 299.9873[K]
Solvent = Acetone
32768

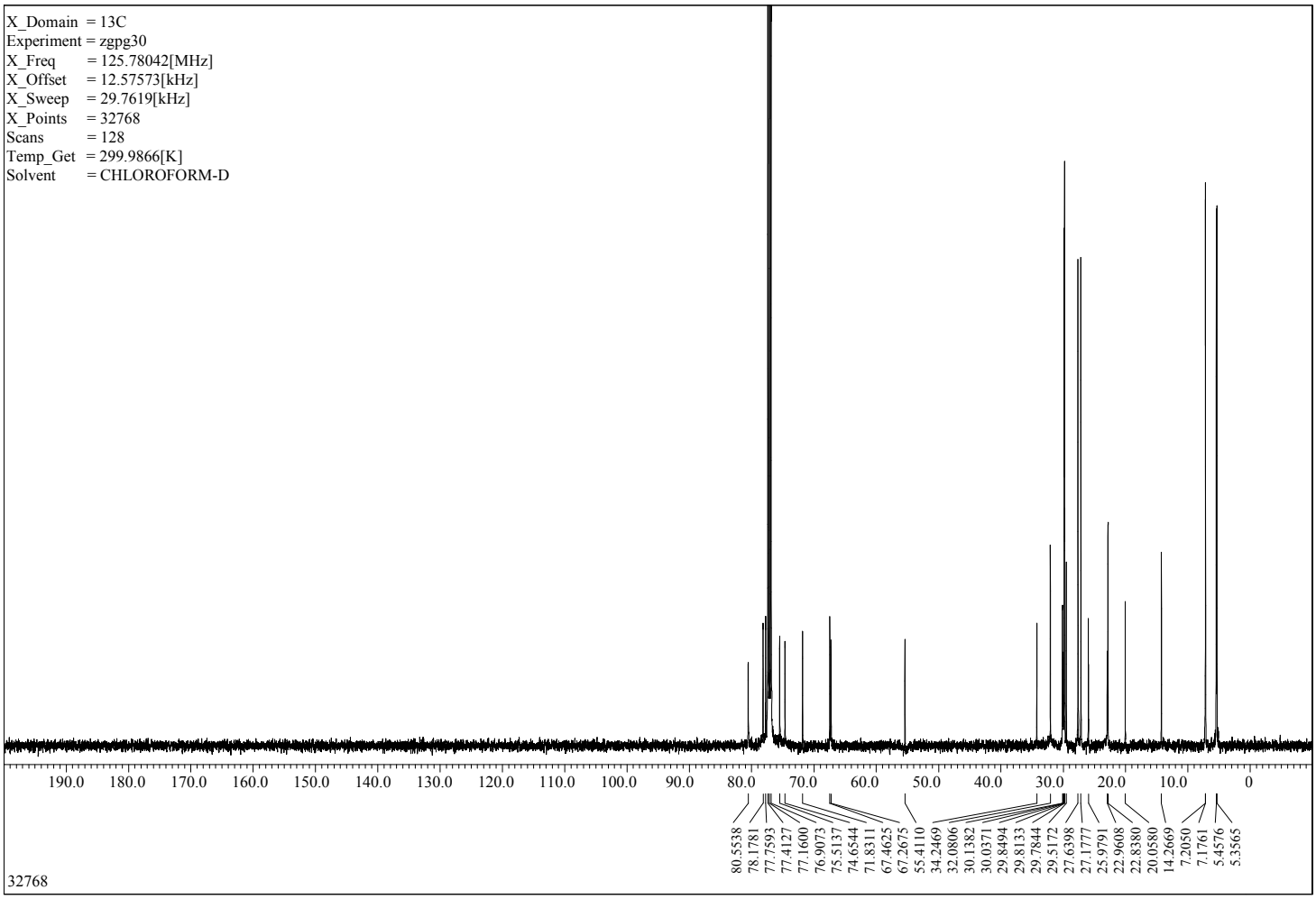

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 300.0049[K]
Solvent = Acetone
NPhth
TBSO
C13H27
16bj-β
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 9000
Temp_Get = 299.9911[K]
Solvent = Acetone
32768

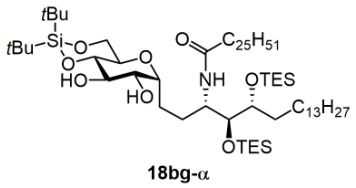

X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 298.1613[K]
Solvent = Acetone
tBu
tBu–Si–O
NPhth
OTES
C13H27
OTES
20-α
27.68
23.66
12.69
6.11
6.04
3.78
3.02
1.98
1.03
0.99
0.97
1.00
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 298.1634[K]
Solvent = Acetone
206.2295
206.0779
205.9190
169.0208
154.2398
135.4369
132.5991
123.9486
79.0425
77.8438
75.2443
74.7317
74.4789
71.3740
69.4316
68.2041
54.4773
32.6489
31.5224
30.5188
30.4249
30.3960
30.3021
30.2227
30.1433
30.0855
29.9916
29.8400
29.6811
29.5295
29.3779
27.9120
27.6810
26.8795
25.8613
23.6879
23.3413
22.3376
21.2761
14.3658
7.4122
7.2534
5.9608
5.6937
32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9918[K]
Solvent = CHLOROFORM-D
17bg-α
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 299.9866[K]
Solvent = CHLOROFORM-D
32768

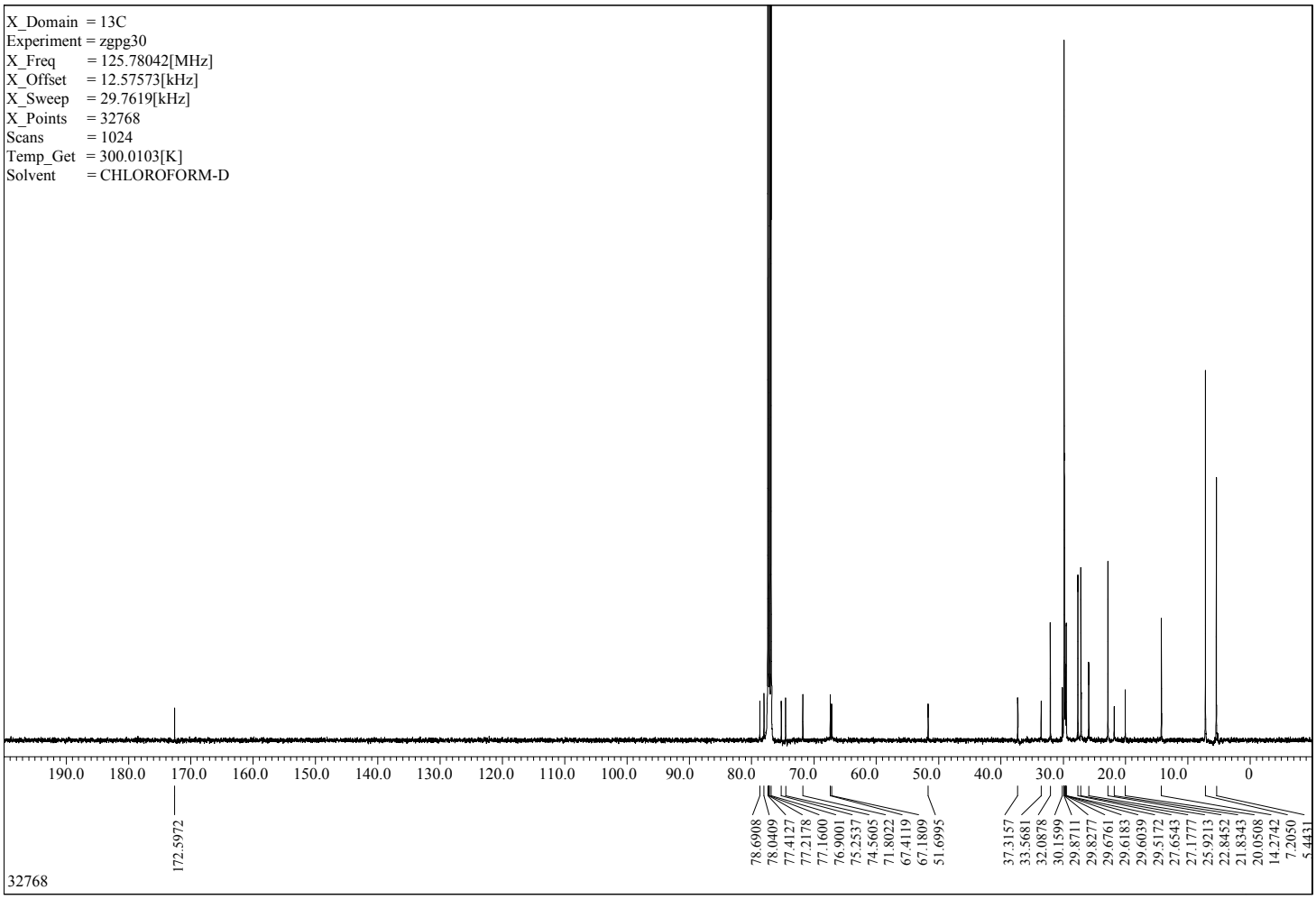
X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 32
Temp_Get = 300.0108[K]
Solvent = CHLOROFORM-D



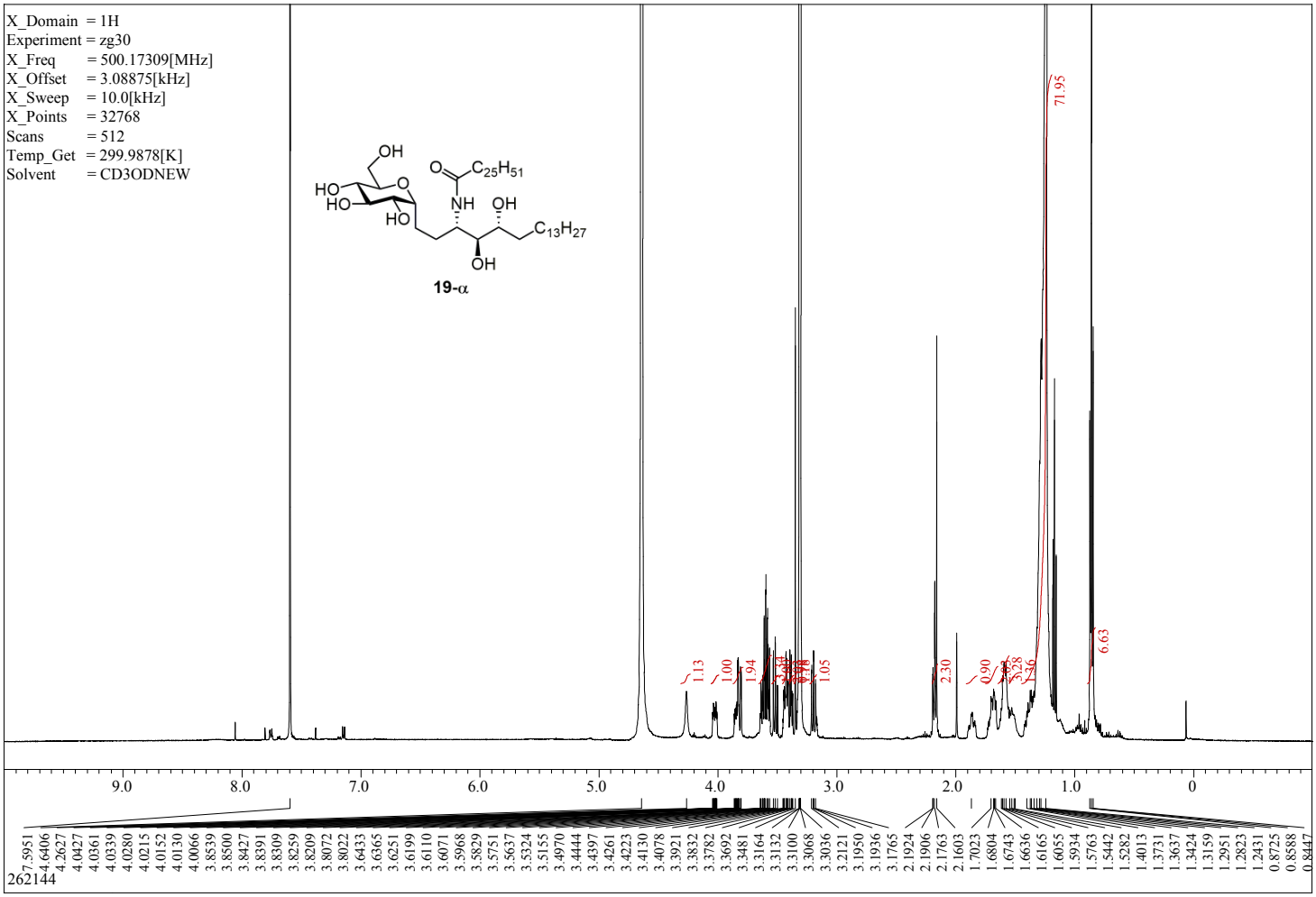
18bg-α

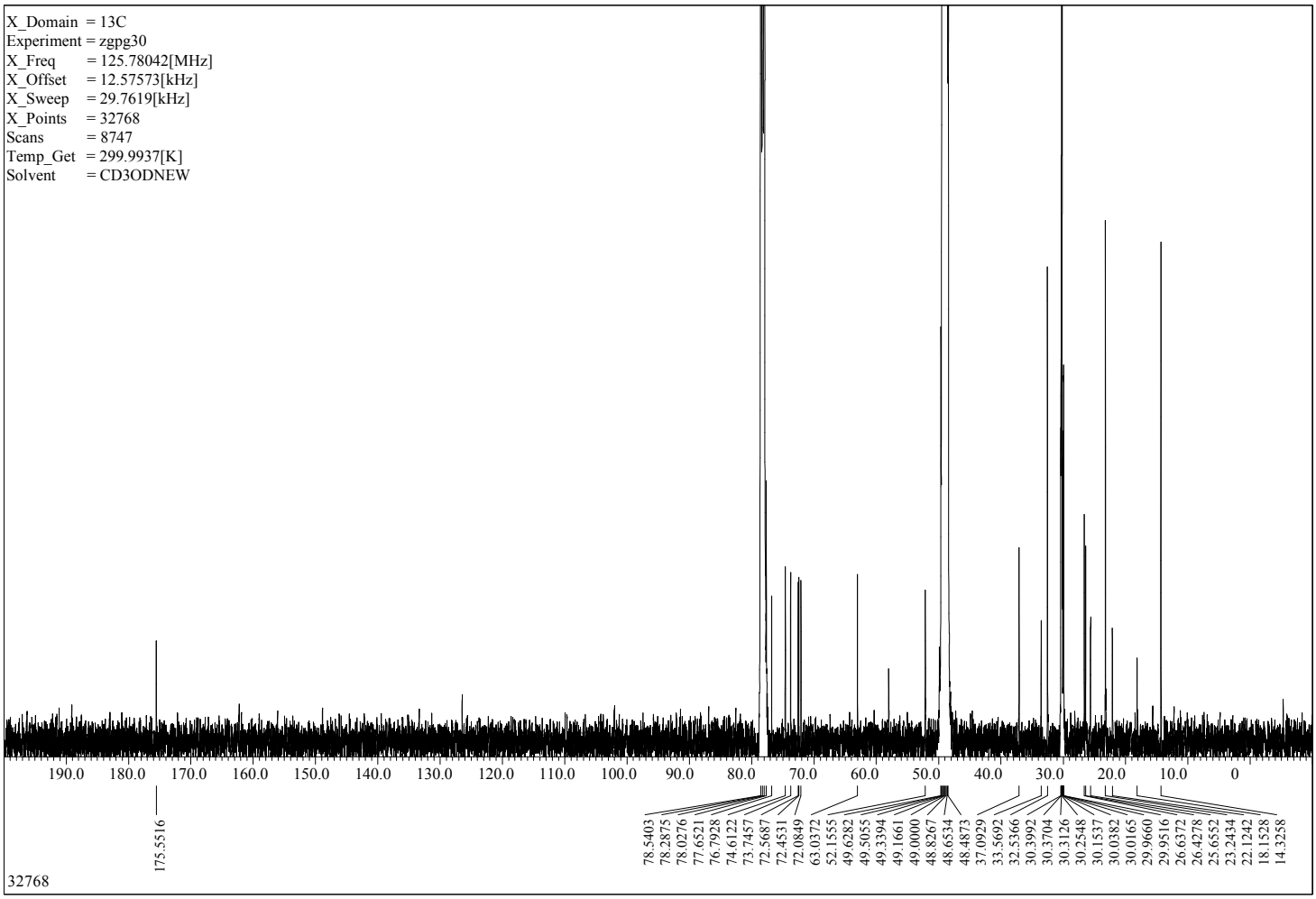
262144

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 1024
Temp_Get = 300.0103[K]
Solvent = CHLOROFORM-D

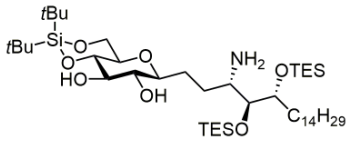


32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 512
Temp_Get = 299.9878[K]
Solvent = CD3ODNEW
19-α
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 8747
Temp_Get = 299.9937[K]
Solvent = CD3ODNEW
32768

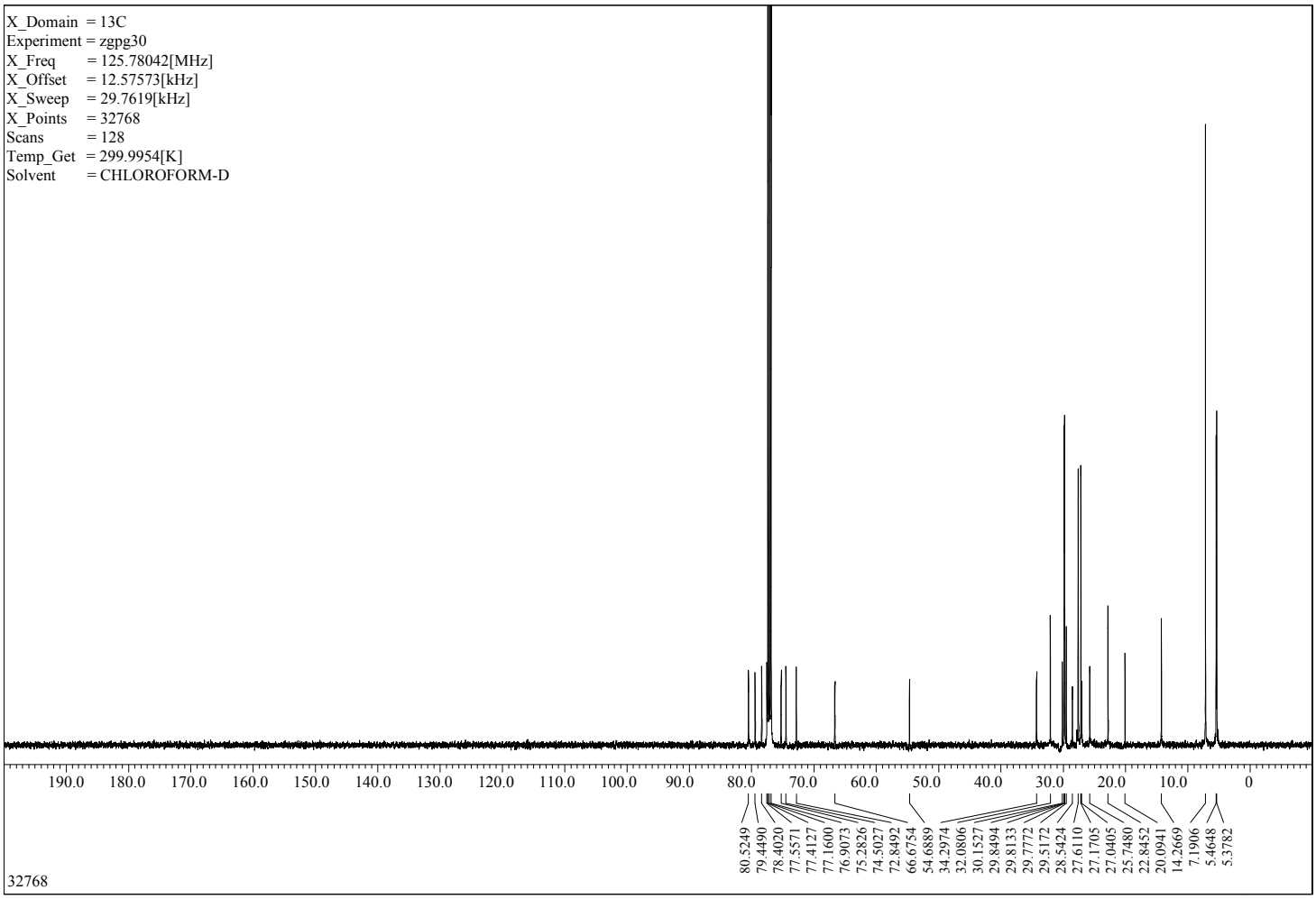
X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9874[K]
Solvent = CHLOROFORM-D



17bg-β

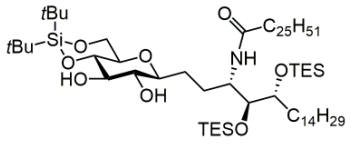
262144

X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 299.9954[K]
Solvent = CHLOROFORM-D



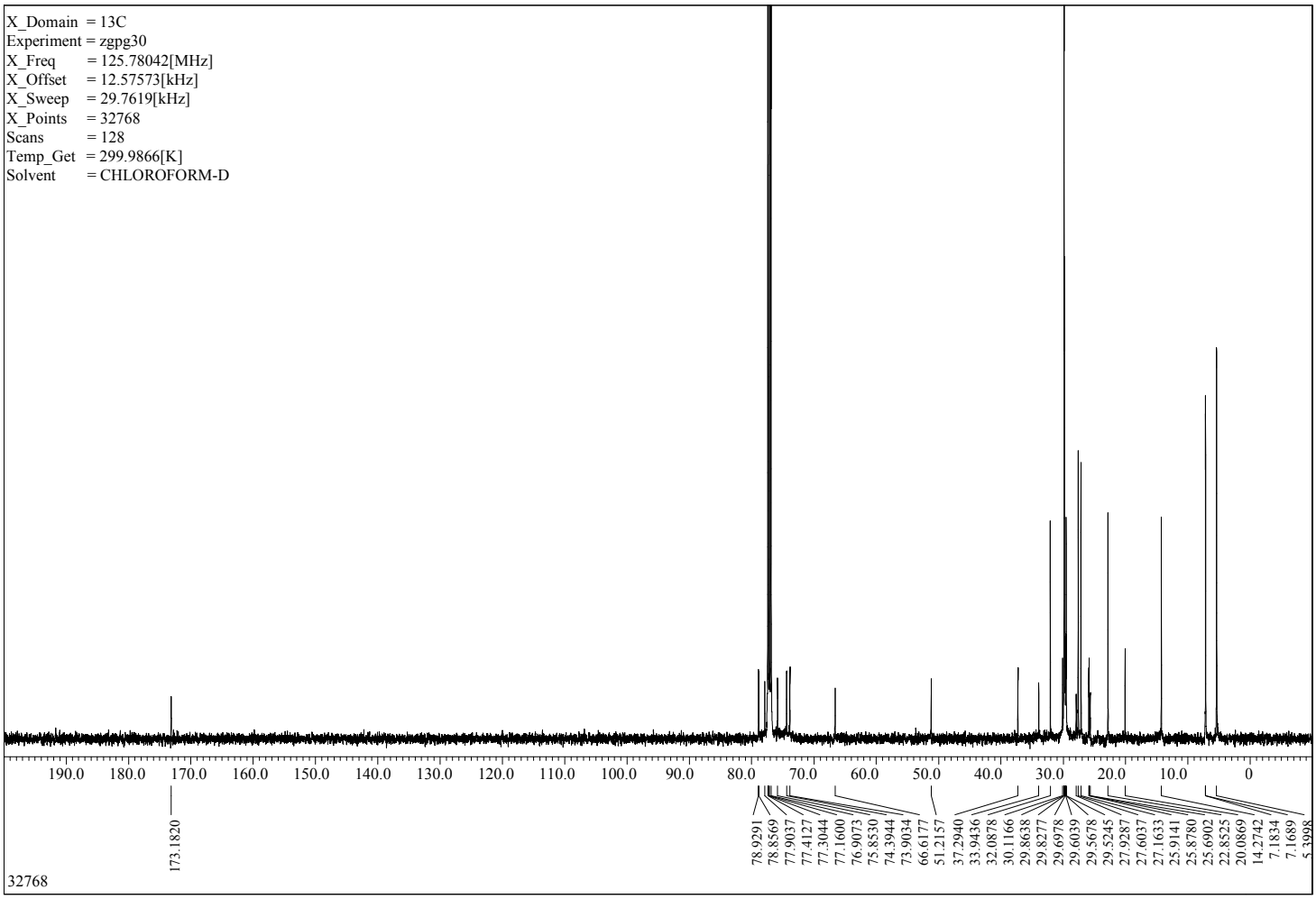
32768

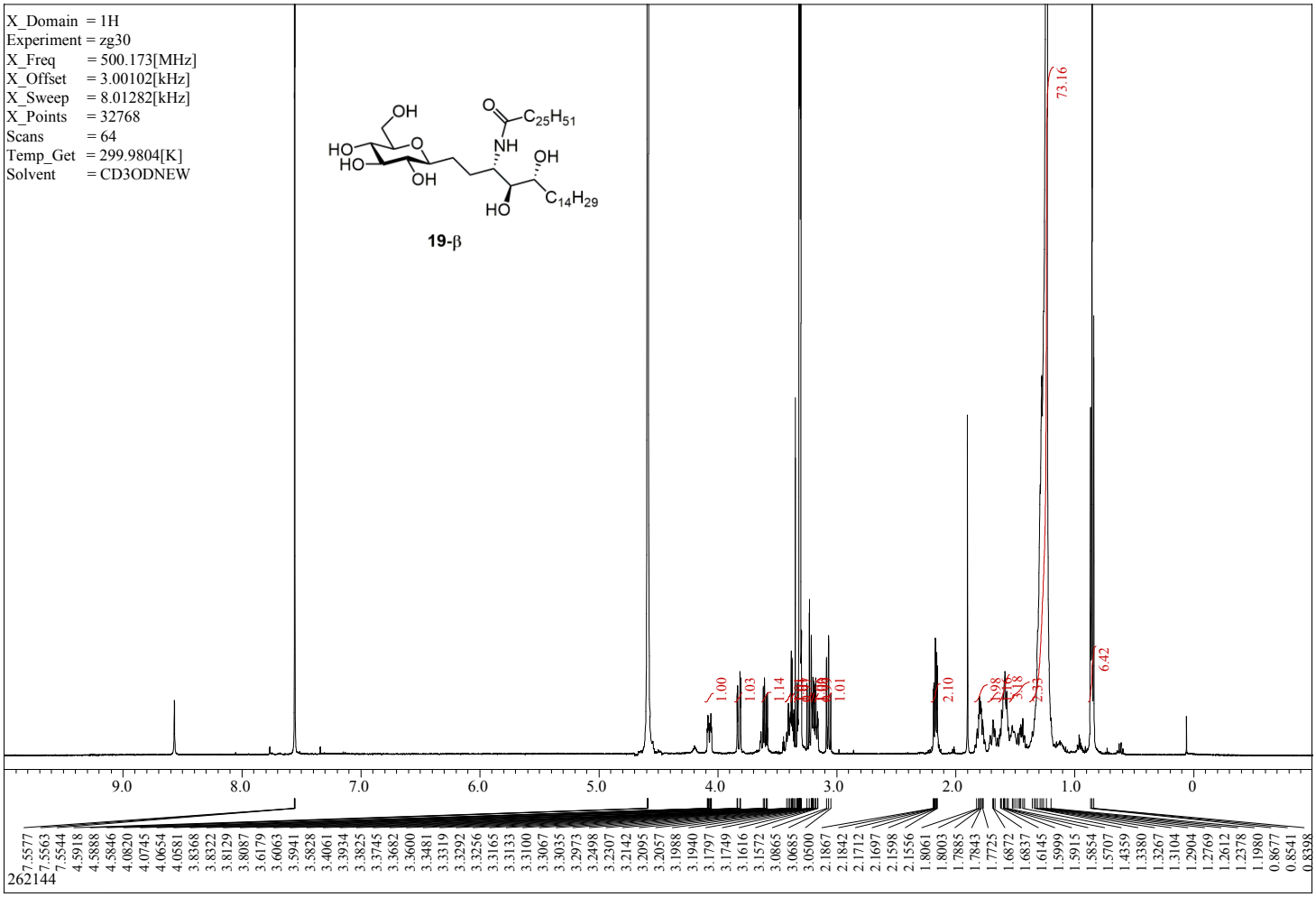
X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9902[K]
Solvent = CHLOROFORM-D

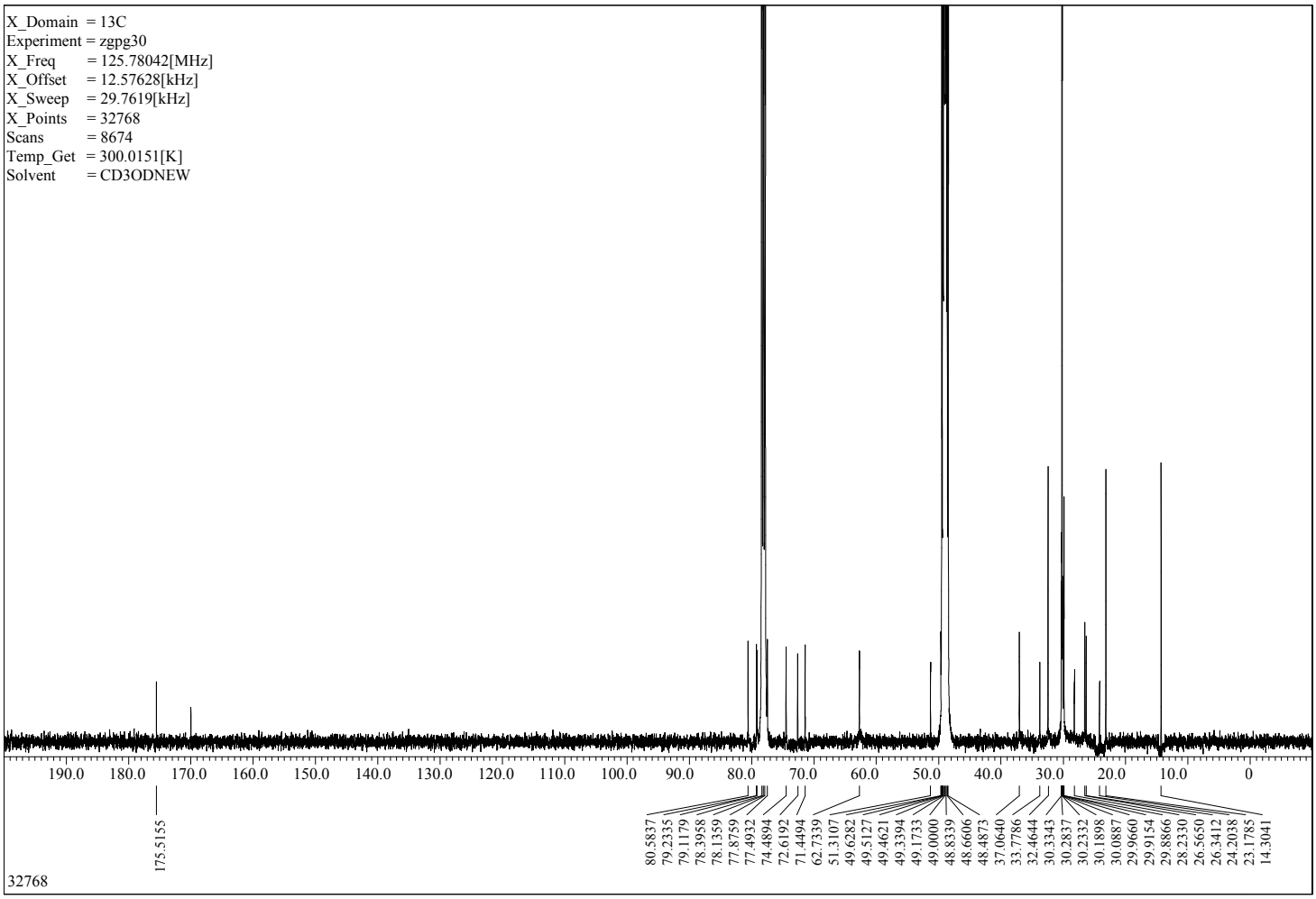


18bg-β

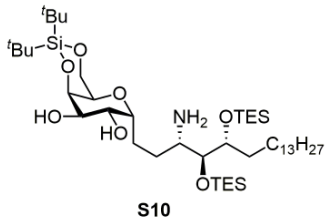
X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 299.9866[K]
Solvent = CHLOROFORM-D




X_Domain = 1H
Experiment = zg30
X_Freq = 500.173[MHz]
X_Offset = 3.00102[kHz]
X_Sweep = 8.01282[kHz]
X_Points = 32768
Scans = 64
Temp_Get = 299.9804[K]
Solvent = CD3ODNEW
19-β
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57628[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 8674
Temp_Get = 300.0151[K]
Solvent = CD3ODNEW
32768

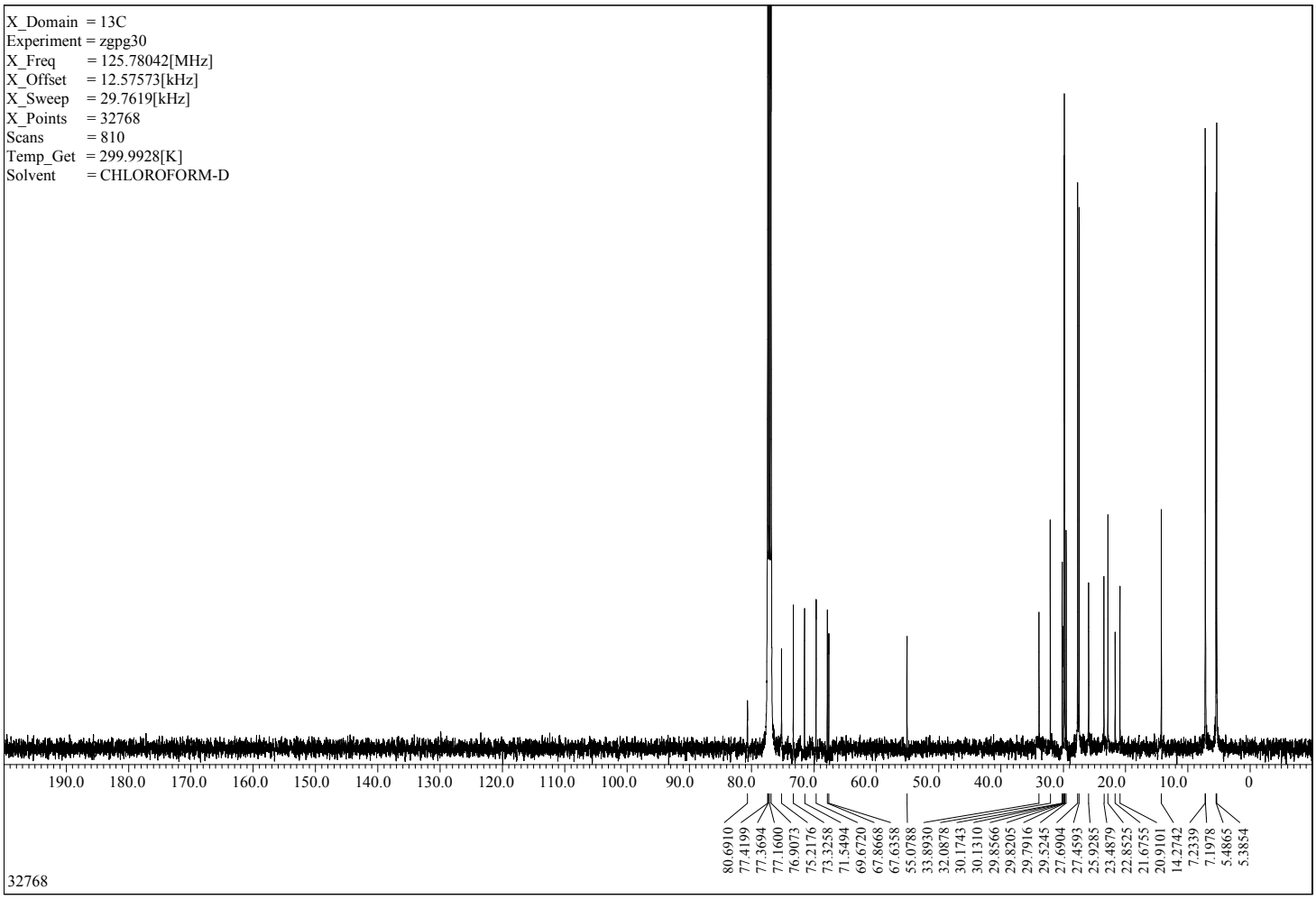
X_Domain = 1H
Experiment = zg30
X_Freq = 500.173[MHz]
X_Offset = 3.00102[kHz]
X_Sweep = 8.01282[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 299.9941[K]
Solvent = CHLOROFORM-D



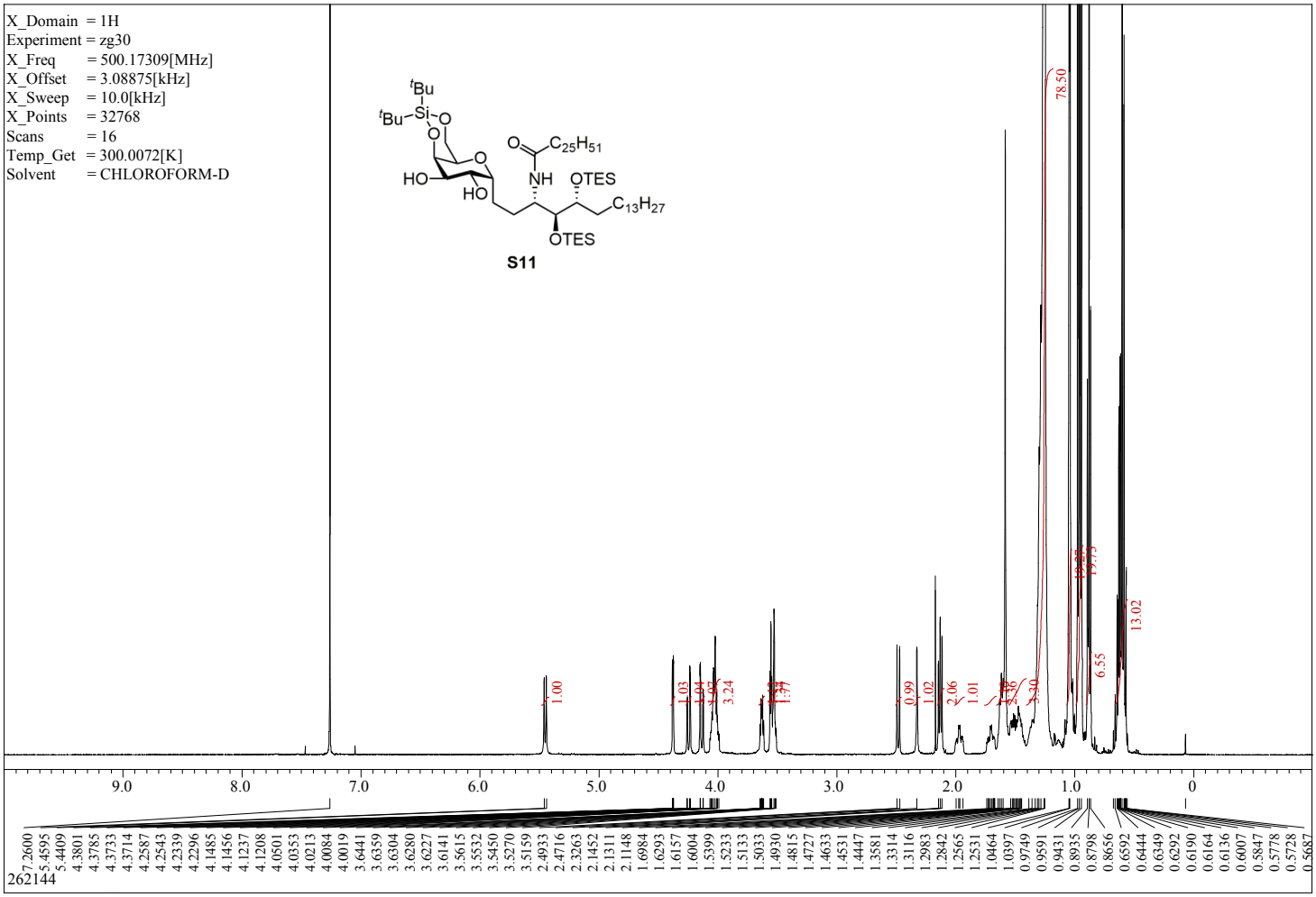
S10

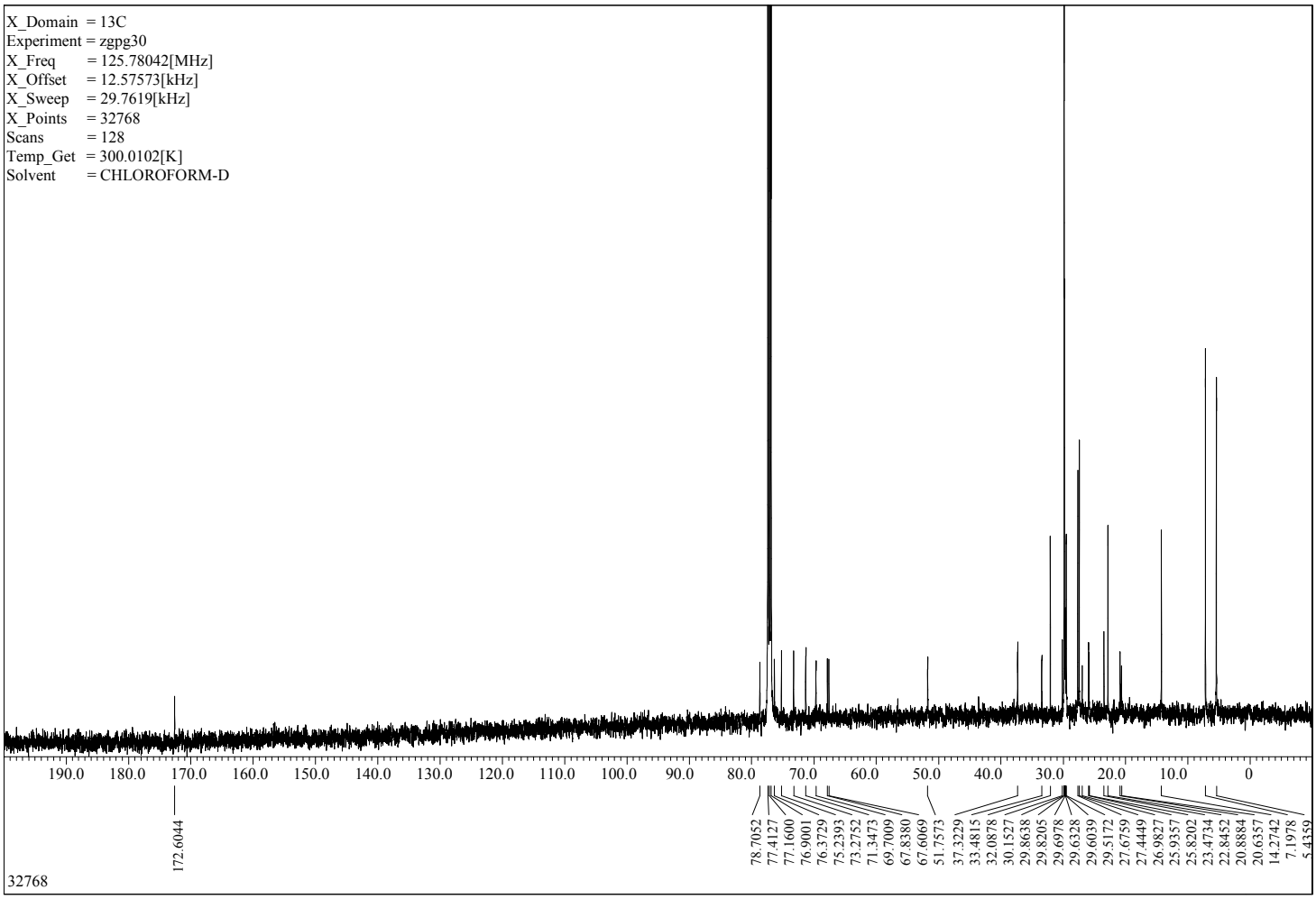
262144

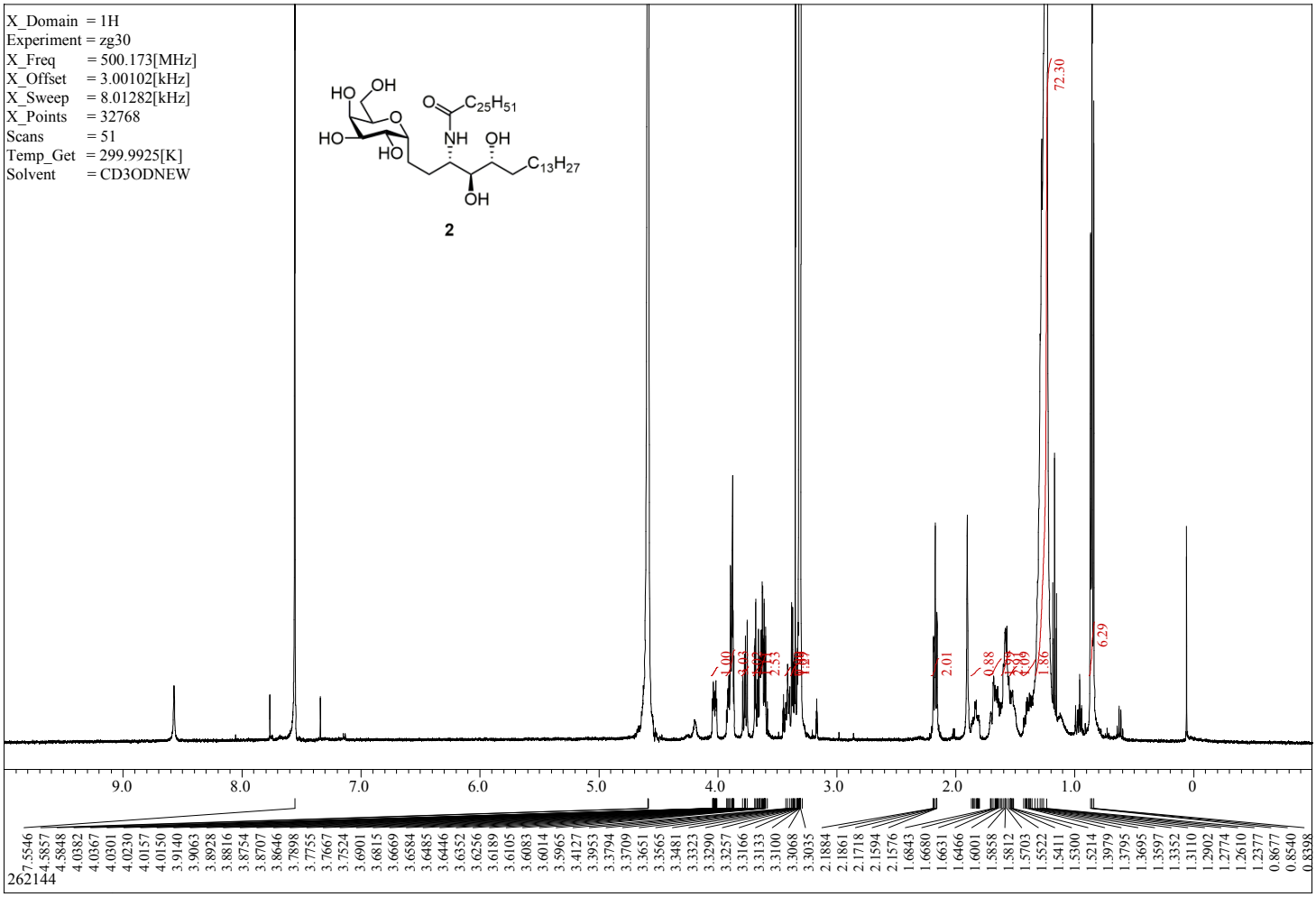
X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 810
Temp_Get = 299.9928[K]
Solvent = CHLOROFORM-D

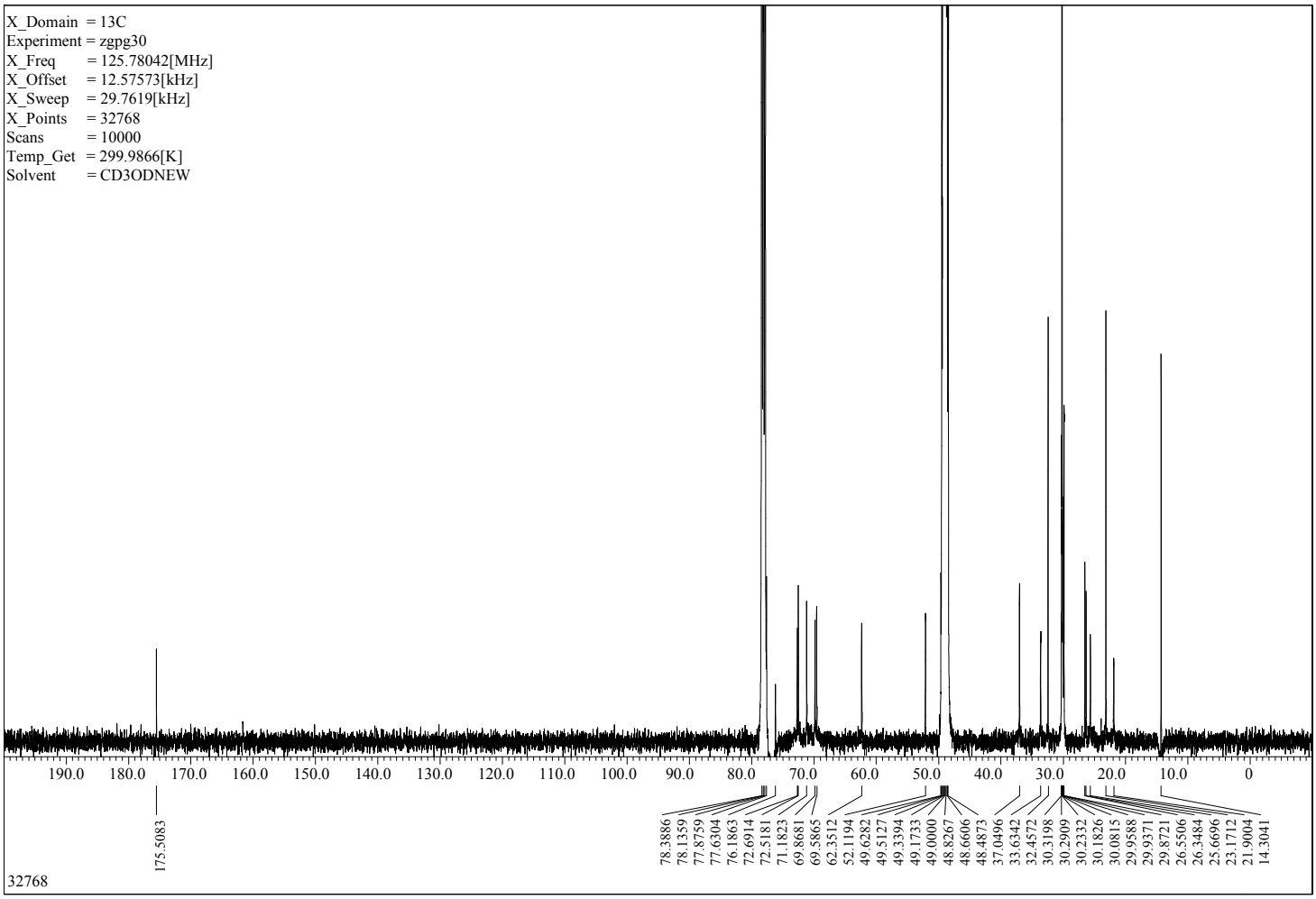


32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.17309[MHz]
X_Offset = 3.08875[kHz]
X_Sweep = 10.0[kHz]
X_Points = 32768
Scans = 16
Temp_Get = 300.0072[K]
Solvent = CHLOROFORM-D
S11
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 128
Temp_Get = 300.0102[K]
Solvent = CHLOROFORM-D
32768


X_Domain = 1H
Experiment = zg30
X_Freq = 500.173[MHz]
X_Offset = 3.00102[kHz]
X_Sweep = 8.01282[kHz]
X_Points = 32768
Scans = 51
Temp_Get = 299.9925[K]
Solvent = CD3ODNEW
2
72.30
6.29
2.01
1.86
0.88
1.00
262144


X_Domain = 13C
Experiment = zgpg30
X_Freq = 125.78042[MHz]
X_Offset = 12.57573[kHz]
X_Sweep = 29.7619[kHz]
X_Points = 32768
Scans = 10000
Temp_Get = 299.9866[K]
Solvent = CD3ODNEW
175.5083
78.3886
78.1359
77.8759
77.6304
76.1863
72.6914
72.5181
71.1823
69.8681
69.5865
62.3512
52.1194
49.6282
49.5127
49.3394
49.1733
49.0000
48.8267
48.6606
48.4873
37.0496
33.6342
32.4572
30.3198
30.2909
30.2332
30.1826
30.0815
29.9588
29.9371
29.8721
26.5506
26.3484
25.6696
23.1712
21.9004
14.3041
32768