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Supporting Information

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A Streamlined Strategy for Aglycone Assembly and Glycosylation**

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All reagents were used as received unless otherwise noted. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model # SPS-400-3 and PS-400-3). Bis(cyclooctadiene)nickel(0) ($Ni(COD)_2$), potassium *t*-butoxide (KO-*t*-Bu), titanium tetrafluoride (TiF_4), and silver tetrafluoroborate ($AgBF_4$) were stored and weighed in an inert atmosphere glovebox. *O*-3,4,6-Tri-*O*-benzyl β-D-glucosyl fluoride was prepared according to the method of Cumpstey et al.[1] 4-Formyl cyclohexanone was synthesized according to the method patented by Hoffman La Roche.[2] Aldehydes and alkynes were distilled or purified by flash column chromatography immediately before use. Chlorodimethylsilane (98% Aldrich, ($Me_2Si(H)Cl$) was distilled under N_2 and stored at 0 °C in a Schlenk flask prior to use. Powdered 3 Å molecular sieves were dried overnight before use at 175 °C at less than 1 torr, pellet (8 mesh) 3 Å molecular sieves were flame dried under vacuum immediately before use. All reactions were performed in flame-dried glassware under a nitrogen atmosphere. ^1H and ^{13}C spectra were obtained in $CDCl_3$ at rt, unless otherwise noted, on a Varian Mercury 400, Varian Unity 500, Varian vnmrs 500 or Varian vnmrs 700 MHz instrument. Chemical shifts of ^1H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm). NMR spectra are described using first order analysis. Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.16 ppm) on the δ scale. High resolution mass spectra (HRMS-ES (m/z)) were obtained via ESI on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory.

Preparation of Sugar Silane 1b

In a 25 mL round bottom flask, 3,4,6-tri-*O*-benzyl β-D-glucosyl fluoride (452 mg, 1.0 mmol) was dissolved in dry CH_2Cl_2 (5 mL, 0.2M) and cooled to 0 °C in an ice bath. Freshly distilled NEt_3 (280 μL, 2.0 mmol) was added and stirred for 5 min, $Me_2Si(H)Cl$ (166 μL, 1.5 mmol) was then added. This mixture was allowed to stir for 45 min, then volatiles were removed by rotary evaporation, and the resulting oil was extracted from ice cold $NaHCO_3$ (aq) with CH_2Cl_2. The combined organic extracts were dried quickly over $MgSO_4$, filtered, concentrated, and the resulting pale yellow oil was dried under high vacuum until complete removal of CH_2Cl_2 was observed by ^1H NMR. Suspension in benzene (~5 mL) and concentration by rotary evaporation facilitated removal of trace CH_2Cl_2.
Isolated yield 490 mg, 0.96 mmol, 96% yield.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36—7.25 (m, 13H), 7.14—7.10 (m, 2H), 5.06 (dd, *J* =52.9, 7.0 Hz, 1H), 4.89 (d, *J* =11.0 Hz, 1H), 4.82—4.74 (m, 3H), 4.63 (d, *J* =12.0 Hz, 1H), 4.54 (d, *J* =12.5 Hz, 1H), 4.51 (d, *J* =11.0 Hz, 1H), 3.77—3.63 (m, 4H), 3.59—2.54 (m, 2H), 0.26 (d, *J* =2.7 Hz, 3H), 0.25 (d, *J* =2.9 Hz, 3H);
^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.2, 137.81, 137.79, 128.40, 128.37, 127.91, 127.89, 127.83, 127.79, 127.72, 127.69, 109.4 (d, *J* =215 Hz), 84.5 (d, *J* =11.1 Hz), 76.8, 76.3 (d, *J* =21.8 Hz), 75.6, 75.0, 74.8 (*J* =5.2 Hz), 73.6, 68.2, -1.1, -1.2 (d, *J* = 2.0Hz)
IR (cm^{-1}) 1500, 1454, 1363, 1256, 1096, 1062, 899
HRMS-ES (m/z) [M+Na^+] calculated 533.2130 found: 533.2132

Preparation of IMCy ligand

Ligand IMCy was prepared according to the previously reported procedure by Montgomery,[3] but differed in the final purification. Following successful formation of the imidazolium salt, triethyl orthoformate was removed by concentration under high vacuum at room temperature. The crude residue was then purified by flash column chromatography using a gradient of 3.5:1 hexanes: EtOAc to 1:1 hexanes: EtOAc, yielding an oily, pale-yellow foam. This product was lyophilized from frozen benzene to yield a fluffy, white solid, which was dried at 45 °C under high vacuum overnight before being transferred to an inert atmosphere glove box for storage prior to use.

General procedure (1) for three-component coupling of an aldehyde, an alkyne and sugar silane 1b.

A solid mixture of $Ni(COD)_2$ (4.2 mg, 0.015 mmol), *R,R*-IMCy·HBF_4 (12.3 mg, 0.015 mmol), and KO*t*Bu (1.7 mg, 0.015 mmol) was dissolved in dry THF (0.75 mL) at rt under an inert atmosphere of N_2. The solution quickly turned a deep, brick red and was stirred for 30 – 45 min. The aldehyde (0.15 mmol, 1.0 equiv) was added directly to the catalyst solution via microsyringe. A solution of sugar silane (102 mg, 0.2 mmol, 1.3 equiv) and alkyne (0.15 mmol, 1.0 equiv) in THF (0.75 mL) was added to the catalyst solution over 50 min via a syringe drive. At the end of the syringe drive, a second aliquot of alkyne (0.15 mmol, 1.0 equiv) in 0.5 mL dry THF was added over 80 min. The reaction was stirred until disappearance of aldehyde was clearly observed by TLC or overnight, in the instance of incomplete conversion. The reaction mixture was diluted with an equal volume of hexane and filtered through a short plug of silica gel, which was washed with a mixture of EOtAc/hexanes. The solution was concentrated by rotary evaporation and the residue was purified via flash chromatography (SiO_2) to afford the desired product. Diastereomeric ratios were determined by ^{19}F-NMR analysis of the purified reaction mixtures.

General procedure (2) for intramolecular directed glycosylations of glucosyl fluorides.

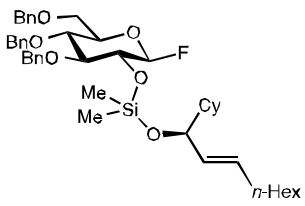
Prior to glycosylation, the tethered glucosyl fluoride was azeotropically dried by concentration in toluene and stored under high vacuum (at least 8 hrs) prior to use. The vial was charge with 3 Å molecular sieves (pellets, ~ 3 times the mass of sugar) and dry acetonitrile (0.03 M). The flask was then stirred for 45 min to 1 h.

Concurrently, a round bottom flask was charged with activated powdered 3 Å molecular sieves (75 mg/mL of final volume, TiF_4 (3 equiv), $AgBF_4$ (1.5 equiv) and a stir bar. The flask was covered in aluminum foil, placed under an inert atmosphere of N_2, and cooled to 0 °C in an ice bath. Dry acetonitrile was added (0.05 M with respect to sugar) and the mixture was stirred for 45 min to 1 h. The vial containing the sugar was cooled to 0 °C, and the sugar solution was transferred by cannula onto the heterogeneous catalyst solution at a steady drip. The reaction temperature was maintained between 0-4 °C for 5 h at which point completion of the reaction was confirmed by ^{19}F-NMR of an aliquot.

The reaction mixture was filtered over a pad of Celite onto ice cold $NaHCO_3$ (aq). Both the Celite and aqueous solution were washed with copious EtOAc. The mixture was filtered over celite a second time in the instance of an unbreakable emulsion. The combined organic layers were dried over $MgSO_4$ and concentrated. The oily residue containing the 2-*O*-$SiMe_2F$ analogue of the desired product was suspended in THF (0.05 M). Tetrabutylammonium fluoride (1.5 eq, 1.0 M in THF) was added and the reaction mixture was stirred until consumption of the intermediate was observed by TLC, typically less than 10 min. Prolonged exposure to TBAF

dramatically reduced yields. The solution was concentrated with silica gel and immediately purified by flash column chromatography (SiO_2) to afford the desired product as a mixture of diastereomers. Diastereomeric ratios were determined by ^{1}H-NMR analysis of the purified reaction mixtures.

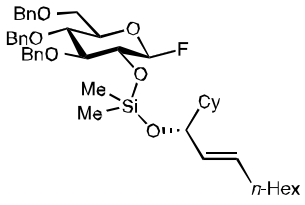
3-Component Reductive Couplings



2-*O*-[(((*E*)-1-cyclohexylnon-2-en-1-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6a)

According to the general procedure 1, freshly distilled cyclohexane carboxaldehyde (18 μL, 0.15 mmol), 1-octyne (2 aliquots of 23 μL, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) 1 were stirred for 13 h. The product was obtained by flash chromatography (7:1 hexanes: diethyl ether) as a colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 5.1: 1 (S:R allylic alcohol stereocenter) diastereomers (79 mg, 0.11 mmol, 72% yield).

^{1}H-NMR (700 MHz, $CDCl_3$) (major R,R Series) δ 7.36—7.30 (m, 8H), 7.29—7.25 (m, 5H), 7.11—7.10 (m, 2H), 5.46 (dt, *J* =15.4, 6.7 Hz, 1H), 5.36 (dd, *J* =15.4, 7.5 Hz, 1H), 5.10 (dd, J = 53.1 Hz, *J* =6.7 Hz), 4.96 (d, *J* =11.2 Hz, 1H), 4.78 (d, *J* =11.2 Hz, 1H), 4.77 (d, *J* =10.7 Hz, 1H), 4.62 (d, *J* =12.2 Hz, 1H), 4.54 (d, *J* =12.2 Hz, 1H), 4.51 (d, *J* =10.8 Hz, 1H), 3.88—3.82 (m, 2H), 3.75—2.69 (m, 2H), 3.67 (d, *J* =9.6 Hz, 1H), 3.62—3.57 (m, 2H), 2.01—1.95 (m, 2H), 1.81 (d, *J* =12.5 Hz, 1H), 1.71—1.67 (m, 2H), 1.65—1.61 (m, 2H), 1.36—1.22 (m, 9H), 1.19—1.05 (m, 3H), 0.91—0.85 (m, 5H), 0.142 (s, 3H), 0.138 (s, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) (major R,R series) δ 138.6, 138.1, 138.0, 132.2, 131.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 109.5 (d, *J* =215.3 Hz), 84.7 (d, *J* =10.2 Hz), 78.7, 75.3, 75.1, 74.9, 74.8, 74.7, 73.7, 68.6, 44.4, 31.8, 29.4, 29.1, 29.0, 28.9, 28.8, 26.8, 26.4, 26.3, 22.8, 14.2, -1.1, -1.3 (distinct minor) 132.1, 131.6, 78.7, 28.9, -1.0, -1.6;
^{19}F-NMR (377 MHz, $CDCl_3$) δ **(**minor, R,R series**) δ** -138.3 (*J* =53.1, 12.5 Hz); (major, R,R series) -138.5 *J* =53.5 Hz, 12.6 Hz;
IR (cm^{-1}) 1455, 1365, 1359, 1257, 1097, 1067, 873;
HRMS-ES (m/z) [M+NH_4^+] calculated: 750.4560; found: 750.4563.



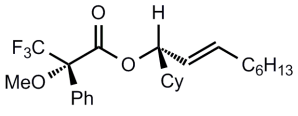
2-*O*-[(((*E*)-1-cyclohexylnon-2-en-1-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6b)

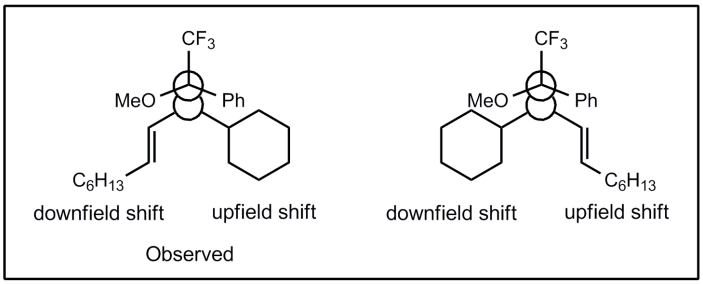
According to the general procedure 1 using *S,S* IMCy-HBF_4, freshly distilled cyclohexane carboxaldehyde (18 μL, 0.15 mmol), 1-octyne (2 aliquots of 23 μL, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) 1 were stirred for 11 h. The product was obtained by flash chromatography (7:1 hexanes: diethyl ether) as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 1:5.1 (S:R allylic alcohol stereocenter) diastereomers (75 mg, 0.10 mmol, 69% yield).

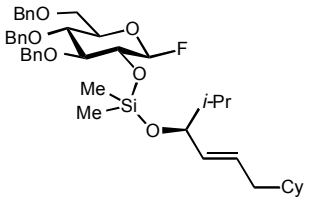
^{1}H-NMR (700 MHz, $CDCl_3$) (major SS series, minor RR series) δ 7.37—7.25 (m, 13H), 7.12—7.09 (m, 2H), 5.43 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.36 (dd, *J* = 15.4, 7.6 Hz, 1H), 5.11 (dd, *J* = 53.0, 6.8 Hz, 1H), 4.95 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 11.2 Hz, 1H), 4.77 (d, *J* = 10.7 Hz, 1H), 4.62 (d, *J* = 12.3 Hz, 1H), 4.54 (d, *J* = 12.3 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 3.89—3.81 (m, 2H), 3.76—3.69 (m, 2H), 3.67 (d, *J* = 9.5 Hz, 1H), 3.62—3.56 (m, 2H), 2.01—1.96 (m, 2H), 1.82 (d, *J* = 10.9 Hz, 1H), 1.71—1.66 (m, 2H), 1.65,1.58 (m, 2H), 1.36—1.21 (m, 12H), 1.18—1.04 (m, 3H), 0.91—0.84 (m, 5H), 0.14 (s, 3H), 0.12 (s, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) (major SS series, minor RR series) δ 138.7, 138.09, 138.06, 132.2, 131.7, 128.59, 128.57, 128.5, 128.12, 128.09, 128.0, 127.9, 127.8, 127.7, 109.5 (d, *J* = 215.8Hz), 84.8 (d, *J* = 10.2Hz), 84.75, 78.7, 75.4, 75.1, 75.0, 74.9, 74.8, 68.6, 44.4, 32.4, 31.9, 29.4, 29.12, 29.09, 28.9, 26.8, 26.40, 26.37, 22.8, 14.3, -0.9, -1.53;
^{19}F-NMR (470 MHz, $CDCl_3$) (major SS series) δ -138.3 (*J* =53.1, 12.5 Hz) (minor, SS series) -138.5 (*J* =53.5 Hz, 12.7 Hz);
IR (cm^{-1}) 1455, 1365, 1261, 1093, 1067, 977;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 750.4560 found: 750.4566.

Stereochemistry determination

The absolute stereochemistry of the allylic alcohol from **6a** was determined by preparing the (*S*)-Mosher's ester, which was synthesized from the corresponding alcohol and (*R*)-Mosher's acid chloride. Following Bu_4NF deprotection of **6a**, the resulting allylic alcohol (38 mg, 0.17 mmol) and 42 mg DMAP (0.34 mmol) were dissolved in 0.5 mL of tetrahydrofuran and stirred under nitrogen at 20 °C. A solution of (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (86 mg, 0.34 mmol) in 0.46 mL tetrahydrofuran was added dropwise, and the reaction mixture was stirred until TLC indicated complete consumption of the starting alcohol. The reaction mixture was filtered through a short silica plug with 15% ethyl acetate/85% hexanes and concentrated to yield the (*S*)-Mosher's ester product (67 mg, 89% yield). The observed downfield shift of the alkenyl protons in the major isomer indicates that it is has the (*S*) configuration, which is consistent with previous reports using the same catalyst.





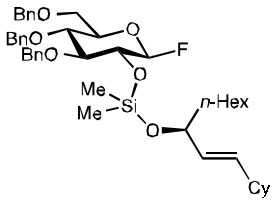


2-*O*-[(((*E*)-6-cyclohexyl-2-methylhex-4-en-3-yl)oxy) dimethylsilane]-3,4,6-tri-*O*-benzyl- β-D-glucopyranosyl fluoride (6c)

According to the general procedure 1, freshly distilled isobutyraldehyde (14 μL, 0.15 mmol), 3-cyclohexyl-1-propyne (2 aliquots of 22 μL, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) 1 were stirred for 11 h. The product was obtained by flash chromatography (7:1 hexanes: diethyl ether) as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture

indicated a ratio of 5.7: 1 (S:R allylic alcohol stereocenter) diastereomers (83 mg, 0.12 mmol, 78% yield).

^{1}H-NMR (700 MHz, $CDCl_3$) (major and minor) δ 7.37—7.30 (m, 8H), 7.28—7.25 (m, 5H), 7.12—7.10 (m, 2H), 5.48 (dt, *J* =15.3, 7.1 Hz, 1H), 5.35 (dd, *J* =15.3, 7.3 Hz, 1H), 5.11 ((minor) J_{HF} = 53.1 Hz, *J* =7.3 Hz), 5.09 ((major) J = 52.9 Hz, *J* =6.8 Hz), 4.95 (d, *J* =11.2 Hz, 1H), 4.78 (d, *J* =11.2 Hz, 1H), 4.77 (d, *J* =10.8 Hz, 1H), 4.61 (d, *J* =12.0 Hz, 1H), 4.53 (d, *J* =12.0 Hz, 1H), 4.50 (d, *J* =10.8 Hz, 1H), 3.90 (t, *J* =6.7 Hz, 1H), 3.84 (ddd, *J* =12.4, 8.3, 6.8 Hz, 1H), 3.74—3.66 (m, 3H), 3.60—3.46 (m, 2H), 1.94—1.84 (m, 2H), 1.70—1.60 (m, 6H), 1.29—1.09 (m, 4H), 0.92—0.77 (m, 8H), 0.15—0.14 (m, 6H);
^{13}C-NMR (175 MHz, $CDCl_3$) (major) δ 138.6, 138.1, 138.0, 132.2, 130.8, 128.5, 128.5, 128.4, 128.0, 127.9, 127.9, 127.8, 127.7, 109.6 (d, *J* =215.3 Hz), 84.8 (d, *J* =10.2 Hz), 79.1, 77.0, 75.3, 75.1, 75.0, 74.9, 74.8, 73.7, 68.6, 40.4, 38.1, 34.6, 33.3, 33.2, 26.7, 26.5, 18.5, 18.2, -1.2, -1.3 (distinct minor peaks) 132.2, 130.7, 79.1, 26.6, -1.1;
^{19}F-NMR (377 MHz, $CDCl_3$) (major) δ -138.4 (*J* =53.6, 12.5 Hz) **(minor)** -138.3 (*J* =53.6, 12.5 Hz);
IR (cm^{-1}) 1451, 1362, 1261, 1108, 1067, 884, 866;
HRMS-ES (m/z) [$M+NH_4^+$] calculated 722.4247: found: 722.4252.

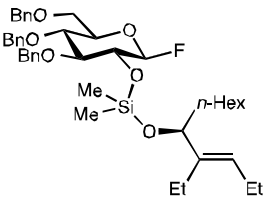


2-*O*-[(((*E*)-1-cyclohexylnon-1-en-3-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (6d)

According to the general procedure 1, freshly distilled heptanal (21 μL, 0.15 mmol), cyclohexyl acetylene (2 aliquots of 20 μL, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) 1 were stirred for 10 h. The product was obtained by flash chromatography (7:1 hexanes: diethyl ether) as colorless viscous oil of inseparable diastereomers and regioisomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a combined ratio of 8.5:1 of the 1,2 olefin to 1,1-substituted olefin (SI-1, not fully characterized). The diastereomeric ratio of the major regioisomer was 4.5:1 (S:R allylic alcohol stereocenter) (58 mg, 0.086 mmol, 58% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) (major and minor) δ 7.39—7.24 (m, 13H), 7.15—7.10 (m, 2H), 5.47 (dd, *J* =15.4, 6.6 Hz, 1H), 5.33 (dd, *J* =15.4, 7.2 Hz, 1H), 5.19—5.07 (m, 0.18 H, minor), 5.11 (dd, 0.82 H, major, J_{HF} = 53.1 Hz, *J* =6.6 Hz), 4.96 (d, *J* =11.2 Hz, 1H), 4.79 (d, *J* =11.1 Hz, 1H), 4.78 (d, *J* =10.8 Hz, 1H), 4.63 (d, *J* =12.2 Hz, 1H), 4.55 (d, *J* =12.2 Hz, 1H), 4.52 (d, *J* =11.0 Hz, 1H), 4.16 (q, *J* =7.2 Hz, 1H), 3.89—3.81 (m, 1H), 3.78—3.66 (m, 3H), 3.64—3.57 (m, 2H), 1.97—1.87 (m, 1H), 1.77—1.60 (m, 5H), 1.55—1.50 (m, 1H), 1.46—1.37 (m, 1H), 1.36—0.97 (m, 13H), 0.88 (t, *J* =7.0 Hz, 3H), 0.17 (s, 3H), 0.16 (s, 3H);
^{13}C-NMR (125 MHz, $CDCl_3$) (major) δ 138.6, 138.1, 138.0, 137.0, 130.6, 128.52, 128.51, 128.4, 128.1, 128.0, 127.93, 127.85, 127.8, 127.7, 109.5 (d, *J* =215.5 Hz), 84.8 (d, *J* =10.0 Hz), 77.0, 75.4, 75.1, 75.0, 74.9, 74.8, 74.3, 73.7, 68.6, 40.4, 38.4, 38.3, 33.1, 33.0, 32.0, 29.4, 26.3, 26.2, 25.5, 22.8, 14.3, -1.1, -1.2 (distinct minor peaks) 136.8, 38.2, 27.0, -1.1, -1.7;
^{19}F-NMR (470 MHz, $CDCl_3$) δ (major) -138.7 (dd, *J* = 47.2, 12.4 Hz)
(minor, 1,2 olefin) -138.6
(1,1- olefin containing products) -138.0 & -139.5 ;

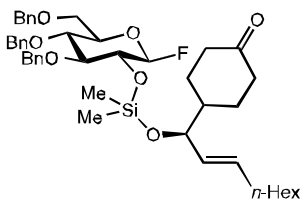
IR (cm^{-1}) 1459, 1350, 1096, 1067, 1031;
HRMS-ES (m/z) [M+Na^+] calculated: 755.4114 found: 755.4110.



2-*O*-[(((*E*)-4-ethylundec-3-en-5-y)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (6e)

A solid mixture of $Ni(COD)_2$ (4.2 mg, 0.015 mmol), *R,R*-IMCy·HBF_4 (12.3 mg, 0.015 mmol), and KO*t*Bu (1.7 mg, 0.015 mmol) was dissolved in dry THF (0.5 mL) at rt under an inert atmosphere of N_2. The solution quickly turned a deep brick red and was stirred for 45 min. The heptaldehyde (21 μL, 0.15 mmol, 1.0 equiv) was added directly to the catalyst solution via microsyringe. A solution of sugar silane (102 mg, 0.2 mmol, 1.3 equiv) and 3-hexyne (26 μL, 0.23 mmol, 1.5 equiv) in THF (1.0 mL) was added in a dropwise fashion via cannula transfer. The solution was stirred overnight. The reaction mixture was diluted with an equal volume of hexane and filtered through a short plug of silica gel, which was washed with a mixture of EOAc/hexanes. The filtrate was concentrated by rotary evaporation. The product was obtained by flash chromatography (7:1 hexanes: diethyl ether) as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 3.7:1 (S:R allylic alcohol stereocenter) diastereomers (68 mg, 0.096 mmol, 64% yield).

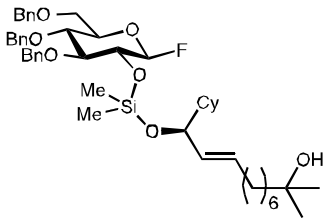
^{1}H-NMR (500 MHz, $CDCl_3$) (major and minor) δ 7.39—7.24 (m, 13H), 7.14—7.10 (m, 2H), 5.26 (t, *J* =7.0 Hz, 1H), 5.12 (dd, *J* = 53.1, 6.6 Hz, 0.21 H (minor)), 5.11 (dd, *J* = 53.1, 6.6 Hz, 0.79 H (major)), 4.97 (d, *J* =11.0 Hz, 1H), 4.79 (d, *J* =11.3 Hz, 1H), 4.78 (d, *J* =10.8 Hz, 1H), 4.63 (d, *J* =12.0 Hz, 1H), 4.55 (d, *J* =12.2 Hz, 1H), 4.52 (d, *J* =10.8 Hz, 1H), 4.12 (t, *J* =6.6 Hz, 1H), 3.89—3.81 (m, 1H), 3.78—3.66 (m, 3H), 3.64—3.57 (m, 2H), 2.08—1.96 (m, 4H), 1.54—1.45 (m, 2H), 1.33—1.13 (m, 8H), 0.99 (t, *J* =7.6 Hz, 3H), 0.95 (t, *J* =7.6 Hz, 3H), 0.88 (t, *J* =7.1 Hz, 3H), 0.14 (s, 6H);
^{13}C-NMR (125 MHz, $CDCl_3$) (major) δ 141.9, 138.6, 138.1, 138.0, 128.53, 128.52, 128.4, 128.06, 128.03, 127.9, 127.8, 127.76, 127.73, 127.6, 109.5 (d, *J* =215.5 Hz), 84.8 (d, *J* =10.5 Hz), 78.22, 77.0, 75.3, 75.1, 75.0, 74.8, 74.7, 73.7, 68.6, 36.8, 36.7, 29.4, 26.0, 22.8, 20.8, 19.7, 14.8, 14.5, 14.2, -1.2, -1.5 distinct minor peaks δ 78.2, 36.8, -1.0, -1.9;
^{19}F-NMR (470 MHz, $CDCl_3$) δ major: -138.6, (dd, *J* = 53, 13 Hz)
minor: -138.7,(dd, J = 53, 12 Hz);
IR (cm^{-1}) 1459,1369,1261,1112,1096,1063, 873;
HRMS-ES (m/z) [M+NH_4^+] calculated: 724.4403 found: 724.4405.



2-*O*-[4-((E)-1-((dimethylsilyl)oxy)non-2-en-1-yl)cyclohexanone]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6f)

According to the general procedure 1, freshly distilled 4-formyl cyclohexanone (19 mg, 0.15 mmol), 1-octyne (2 aliquots of 23 μL, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) were stirred for 15 h. The product was obtained by flash chromatography (4:1 hexanes: acetone) as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 3.5: 1 (S:R allylic alcohol stereocenter) diastereomers (61 mg, 0.082 mmol, 54% yield).

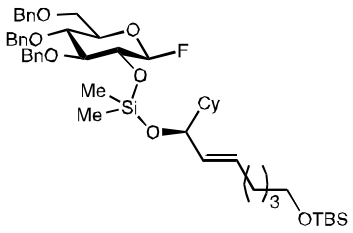
^{1}H-NMR (500 MHz, $CDCl_3$) (major and minor) δ 7.38—7.24 (m, 13H), 7.12—7.08 (m, 2H), 5.52 (dt, *J* = 15.2, 6.7 Hz, 1H), 5.37 (dd, *J* = 14.9, 7.1 Hz, 1H), 5.17—5.02 (m, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 12.5 Hz, 1H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.02 (apparent t, *J* = 6.8 Hz, 1H), 3.84—3.78 (m, 1H), 3.76—3.65 (m, 3H), 3.62—2.65 (m, 2H), 2.39—2.30 (m, 2H), 2.29—2.19 (m, 2H), 2.14—2.06 (m, 1H), 2.05—1.92 (m, 3H), 1.81—1.71 (m, 1H), 1.50—1.20 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.16 (s, 3H), 0.15 (s, 3H);
^{13}C-NMR (125 MHz, $CDCl_3$) (major) δ 212.6, 138.6, 138.0, 138.0, 133.4, 130.8, 128.6, 128.6, 128.6, 128.1, 128.1, 128.0, 128.0, 127.8, 127.6, 109.6 (d, *J* = 215.5 Hz), 84.7 (d, *J* = 10.5 Hz), 77.1, 77.1, 75.5, 75.2, 75.1, 75.1, 75.0, 74.9, 73.8, 68.5, 42.7, 40.9, 40.8, 32.4, 31.9, 29.4, 29.1, 28.6, 28.4, 22.8, 14.3, -1.1, -1.2, Peaks have been listed when C-F couplings cannot be unambiguously determined.
^{19}F-NMR (470 MHz, $CDCl_3$) δ (minor) -139.3 (dd, *J* = 54.5, 12.5 Hz)
(major) = -139.5 (dd, *J* = 52.9, 12.5 Hz);
IR (cm^{-1}) 1717, 1455, 1260, 1094, 1065, 1030;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 764.4352 found: 764.4352.



2-*O*-[(*E*)-11-((dimethylsilyl)oxy)-11-cyclohexyl-2-methylundec-9-en-2-ol]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6g)

According to the general procedure 1, freshly distilled cyclohexane carboxaldehyde (18 μL, 0.15 mmol), 2-methyl-9-decyn-2-ol (2 aliquots of 25 mg, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) were stirred for 13 h. The product was obtained by flash chromatography (6:1 hexanes: acetone) as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 5.1: 1 (S:R allylic alcohol stereocenter) diastereomers (74 mg, 0.093 mmol, 62% yield).

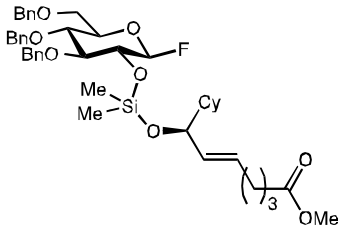
^{1}H-NMR (500 MHz, $CDCl_3$) (major and minor) 7.39—7.25 (m, 13H), 7.13—7.09 (m, 2H), 5.47 (dt, *J* =15.4, 6.6 Hz, 1H), 5.37 (dd, *J* =15.4, 7.6 Hz, 1H), 5.12 (dd, 0.15 H (minor), J_{HF} = 53 Hz, *J* =6.6 Hz), 5.10 (dd, 0.85 H (major), J_{HF} = 53.1 Hz, *J* =6.6 Hz), 4.97 (d, *J* =11.0 Hz, 1H), 4.79 (d, *J* =11.3 Hz, 1H), 4.77 (d, *J* =10.8 Hz, 1H), 4.62 (d, *J* =11.9 Hz, 1H), 4.55 (d, *J* =11.8 Hz, 1H), 4.52 (d, *J* =10.8 Hz, 1H), 3.90—3.82 (m, 2H), 3.77—3.66 (m, 3H), 3.64—3.57 (m, 2H), 2.04—1.95 (m, 2H), 1.82 (broad d, *J* =11.0 Hz, 1H), 1.74—1.48 (m, 4H), 1.47—1.42 (m, 3H), 1.38—1.26 (m, 9H), 1.24—1.02 (m, 9H), 0.96—0.83 (m, 2H), 0.15 (s, 3H), 0.145 (s, 3H);
^{13}C-NMR (125 MHz, $CDCl_3$) (major) δ 138.6, 138.1, 138.0, 132.0, 131.7, 128.52, 128.51, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 109.5 (d, *J* = 215.5 Hz), 84.7 (d, *J* = 10.5 Hz), 78.7, 77.0, 75.3, 75.0, 74.87, 74.91, 74.8, 71.1, 73.7, 68.6, 44.1, 32.3, 30.1, 29.4, 29.1, 28.8, 26.8, 26.4, 26.3, 24.5, -1.2, -1.3, Peaks have been listed when C-F coupling cannot be unambiguously determined; (distinct minor) 131.7, 78.6, 77.1, 44.0, 24.3;
^{19}F- NMR (470 MHz, $CDCl_3$) δ major: -138.4, (dd, *J* = 53, 13 Hz)
minor -138.3 (dd, J_{HF} = 53, 13 Hz);
IR (cm^{-1}) 1455, 1365, 1257, 1093, 1071, 877;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 808.4979 found: 808.4982.



2-*O*-[((E)-7-(((*t*-butyldimethylsilyl)oxy)-1-cyclohexylhept-2-en-1-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6h)

According to the general procedure 1, freshly distilled cyclohexane carboxaldehyde (18 μL, 0.15 mmol), *O*-*t*-butyldimethylsilyl-5-hexyn-1-ol (2 aliquots of 32 mg, 0.15 mmol each) and sugar silane (102 mg, 0.20 mmol) were stirred overnight. The product was obtained by flash chromatography (7:1 hexanes: diethyl ether) as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 5.3: 1 (S:R allylic alcohol stereocenter) diastereomers (101 mg, 0.12 mmol, 81% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) (major and minor) δ 7.39—7.24 (m, 13H), 7.14—7.10 (m, 2H), 5.48 (dt, J = 15.4, 6.5 Hz, 1H), 5.38 (dd, J =15.4, 7.6 Hz), 5.19—5.02 (m, 1H), 4.98 (d, *J* =11.0 Hz, 1H), 4.79 (d, *J* =11.3 Hz, 1H), 4.78 (d, *J* =11.0 Hz, 1H), 4.63 (d, *J* =12.3 Hz, 1H), 4.55 (d, *J* =12.5 Hz, 1H), 4.52 (d, *J* =10.8 Hz, 1H), 3.91—3.82 (m, 2h), 3.77—3.67 (m, 3H) 3.64—3.56 (m, 4H) 2.07—1.96 (m, 2H), 1.83—1.81(m, 1H), 1.74—1.60 (m, 4H), 1.56—1.48 (m, 3H), 1.43—1.26 (m, 3H), 1.23—1.08(m, 3H), 0.98—0.89 (m, 10H), 0.16 (s, 3H), 0.15 (s, 3H), (0.06, s 6H);
^{13}C-NMR (125 MHz, $CDCl_3$) (major) δ 138.6, 138.1, 138.0, 131.9, 131.8, 128.53, 128.51, 128.4, 128.05, 128.03, 127.9, 127.84, 127.79, 127.7, 127.6, 109.5 (d, JCF = 215.2 Hz), 84.7 (d, JCF = 9.8 Hz), 78.6, 77.0, 75.3, 75.0, 74.93, 74.86, 74.3, 71.7, 73.7, 68.6, 63.2, 44.4, 32.6, 32.1, 29.1, 28.8, 26.8, 26.4, 26.3, 26.1, 25.7, 18.5, -1.1, -1.3, -5.1, Peaks have been listed when C-F coupling cannot be unambiguously determined.
^{19}F NMR (500 MHz, $CDCl_3$) δ major: -138.4 (dd, *J* = 53, 12 Hz)
minor -138.3;
IR (cm^{-1}) 1459, 1358, 1261, 1101, 1060, 839;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 852.5061; found: 852.5064.

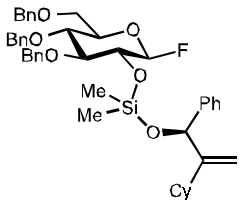


2-*O*-[(E)-methyl-7-((dimethylsilyl)oxy)-7-cyclohexylhept-5-enoate]- 3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6i)

Compound 6i was synthesized in a manner similar to the general procedure but utilized higher catalyst loadings. A solid mixture of $Ni(COD)_2$ (4.2 mg, 0.015 mmol), *R,R*-IMCy·HBF_4 (12.3 mg, 0.015 mmol), and KO*t*Bu (1.7 mg, 0.015 mmol) was dissolved in dry THF (0.75 mL) at rt under an inert atmosphere of N_2. The solution quickly turned a deep brick red and was stirred for 30 – 45 min. Cyclohexanecarboxaldehyde (18 μL, 0.15 mmol, 1.0 equiv) was added directly to the catalyst solution via microsyringe. A solution of sugar silane (102 mg, 0.2 mmol, 1.3 equiv) and methyl 5-hexynoate (19 mg, 0.15 mmol, 1.0 equiv) in THF (0.75 mL) was added to the catalyst solution over 50 min via a syringe drive. At the end of the syringe drive, a solution of $Ni(COD)_2$ (4.2 mg, 0.015 mmol), *R,R*-IMCy·HBF_4 (12.3 mg, 0.015 mmol), and KO*t*Bu (1.7 mg, 0.015 mmol) in 0.4 mL dry THF was added to the reaction mixture via cannula transfer. Subsequently, a second aliquot of alkyne (19 mg, 0.15 mmol, 1.0 equiv) in 0.5 mL dry

THF was added over 90 min. The reaction was stirred overnight. The reaction mixture was diluted with an equal volume of hexane and filtered through a short plug of silica gel, which was washed with a mixture of EOtAc/hexanes. The solution was concentrated by rotary evaporation and the residue was purified via flash chromatography (7:1 hexanes: EtOAc) to afford the desired product as colorless viscous oil of inseparable diastereomers. ^{19}F-NMR analysis of the purified reaction mixture indicated a ratio of 5.0: 1 (S:R allylic alcohol stereocenter) diastereomers (82 mg, 0.11 mmol, 73% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) (major and minor) δ 7.39—7.25 (m, 13H), 7.15—7.10 (m, 2H), 5.50—5.38 (m, 2H), 5.18—5.06 (m, 0.21 H, minor), 5.12 (dd, *J* = 53.8, 6.8 Hz, 0.79 H, (major)), 4.97 (d, *J* =11.2 Hz, 1H), 4.80 (d, *J* =11.0 Hz, 1H), 4.78 (d, *J* =11.2 Hz, 1H), 4.63 (d, *J* =12.2 Hz, 1H), 4.55 (d, *J* =12.4 Hz, 1H), 4.53 (d, *J* =11.0 Hz, 1H), 3.90 (t, *J* =6.0 Hz, 1H), 3.87—3.80 (m, 1H), 3.79—3.65 (m, 6H), 3.54—3.56 (m, 2H), 2.30 (t, *J* =7.6 Hz, 2H), 2.07—2.01 (m, 2H), 1.81 (br d, *J* =12.2 Hz, 1H), 1.76—1.60 (m, 6H), 1.40—1.29 (m, 1H), 1.22—1.06 (m, 3H), 0.98—0.83 (m, 2H), 0.16 (s, 3H), 0.15 (s, 3H);
^{13}C-NMR (125 MHz, $CDCl_3$) (major) δ 174.1, 138.6, 138.04, 138.00, 132.8, 130.5, 128.51, 128.49, 128.4, 128.02, 128.01, 127.9, 127.8, 127.7, 127.6, 109.5 (d, *J* =215.2 Hz), 84.7 (d, *J* =10.3 Hz), 78.4, 77.0, 75.3, 75.02, 74.99, 74.91, 74.87, 74.80, 73.7, 68.5, 51.6, 44.3, 33.5, 31.6, 29.0, 28.8, 26.7, 26.33, 26.29, 24.6, -1.30, -1.31,
(distinct minor peaks) 128.5, 128.4, 127.8, 127.7, 78.3, 28.8, -1.1, -1.6;
^{19}F-NMR (470 MHz, $CDCl_3$) major δ – 138.8 (dd, *J* =53, 13 Hz)
minor δ – 138. 6 (dd, *J* =53 Hz, 12 Hz);
IR (cm^{-1}) 1738, 1455, 1365, 1257, 1097, 1054, 873;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 766. 4145 found: 766.4151.



2-*O*-[(2-cyclohexyl-1-phenylallyl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (6j)

A solid mixture of $Ni(COD)_2$ (5.5 mg, 0.020 mmol), ±DPIPr·HBF_4 (12.6 mg, 0.020 mmol), and KO*t*Bu (2.2 mg, 0.020 mmol) was dissolved in dry THF (0.75 mL) at rt under an inert atmosphere of N_2. The solution was stirred for 30 min. Benzaldehyde (21 μL, 0.20 mmol, 1.0 equiv) was added directly to the catalyst solution via microsyringe. A solution of sugar silane (102 mg, 0.2 mmol, 1.3 equiv) and cyclohexylacetylene (40 μL, 0.30 mmol, 1.5 equiv) in THF (0.75 mL) was added to the catalyst solution over 30 min via a syringe drive. The reaction was stirred for 5 h after completion of the syringe drive addition. The reaction mixture was diluted with an equal volume of hexane and filtered through a short plug of silica gel, which was washed with a mixture of EOAc/hexanes. The filtrate was concentrated by rotary evaporation and the residue was purified via flash chromatography (SiO_2,7:1 hexanes: diethyl ether) to yield a colorless oil (123 mg, 0.17 mmol, 85% yield, 1:1 ratio of diastereomers by ^{19}F-NMR).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38—7.18 (m, 18H), 7.13—7.08 (m, 2H), 5.30 (s, 0.5H), 5.29 (s, 0.5H), 5.24 (s, 0.5H), 5.22 (s, 0.5H), 5.07 (dd, *J* =53.1, 6.8 Hz, 0.5H), 5.03 (dd, *J* =53.1, 6.8 Hz, 0.5H), 4.92 (s, 1H), 4.89 (d, *J* =11.0 Hz, 0.5H), 4.83 (d, *J* =11.3 Hz, 0.5H), 4.78 (d, *J* =11.3 Hz, 0.5H), 4.76 (d, *J* =10.8 Hz, 0.5H), 4.75 (d, *J* =10.8 Hz, 0.5H), 4.72 (d, *J* =11.3 Hz, 0.5H),

4.623 (d, *J* =12.2 Hz, 0.5H), 4.619 (d, *J* =12.2 Hz, 0.5H), 4.54 (d, *J* =12.0 Hz, 1H), 4.51 (d, *J* =10.8 Hz, 0.5H), 4.50 (d, *J* =10.8 Hz, 0.5H), 3.84—8.77 (m, 1H), 3.74—3.69 (m, 2H), 3.67—3.51 (m, 3H), 1.77—1.49 (m, 6H), 1.21—0.96 (m, 5H), 0.15 (s, 1.5H), 0.14 (s, 1.5H), 0.12 (s, 1.5H), 0.09 (s, 1.5H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 156.9, 156.8, 142.89, 142.87, 138.62, 138.60, 138.10, 138.08, 128.6, 128.54, 128.50, 128.15, 128.14, 128.11, 128.09, 128.02, 127.9, 127.78, 127.75, 127.72 127.33, 127.30, 127.2, 127.1, 109.5, (*J* = 215.2 Hz),108.6, 108.5, 84.7, 84.63, 84.57, 77.4, 77.1, 75.44, 75.36, 75.14, 75.11, 75.0, 74.8, 73.8, 68.6, 39.7, 39.7, 34.4, 33.4, 33.3, 27.1, 27.0, 26.5, -1.3, -1.4, -1.6, -1.8, Peaks have been listed when C-F coupling cannot be unambiguously determined.

^{19}F-NMR (470 MHz, $CDCl_3$) δ Diastereomer 1: -138.7 (J= 53 Hz, 13 Hz), Diastereomer 2 -138.8 (J= 53 Hz, 13 Hz);

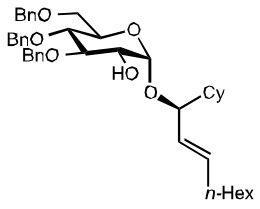
IR (cm^{-1})1496, 1459, 1373, 2137, 1101, 1067, 1033;

HRMS-ES (m/z) [$M+NH_4^+$] calculated: 742.3934 found: 742.3937.

Intramolecular Directed Glycosylations

((*E*)-1-cyclohexylnon-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7a) was synthesized according to general procedure 2**.** 2-*O*-[(((*E*)-1-cyclohexylnon-2-en-1-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride **6a** (60 mg, 0.082 mmol, 5.1:1 S:R), titanium tetrafluoride (31 mg, 0.25 mmol) and silver tetrafluoroborate (24 mg, 0.12 mmol) were stirred for 5h. Purification by flash chromatography (7:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H-NMR analysis revealed a diastereomeric ratio of 4.5:1 of **7a**:**7b** (42 mg, 0.064 mmol, 78 %).

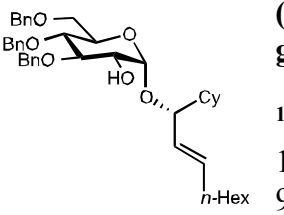
((*E*)-1-cyclohexylnon-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7b) was synthesized according to general procedure 2**.** 2-*O*-[(((*E*)-1-cyclohexylnon-2-en-1-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride **6b** (72 mg, 0.10 mmol, 1:5.1 S:R), titanium tetrafluoride (37 mg, 0.30 mmol) and silver tetrafluoroborate (29 mg, 0.15 mmol) were stirred for 5 h. Purification by flash chromatography (7:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H NMR analysis revealed a diastereomeric ratio of 1:5.8 of **7a**:**7b** (42 mg, 0.064 mmol, 64 %).



((*S*,*E*)-1-cyclohexylnon-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7a)

^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (d, *J* =7.4 Hz, 2H), 7.34—7.25 (m, 11H), 7.16—7.12 (m, 2H), 5.55 (dt, *J* =15.3, 6.7 Hz, 1H), 5.36 (ddt, *J* =15.4, 8.6, 1.3 Hz, 1H), 4.97 (d, *J* =3.8 Hz, 1H), 4.97 (d, *J* =11.2 Hz, 1H), 4.84 (d, *J* =11.2 Hz, 1H), 4.81 (d, *J* =10.5 Hz, 1H), 4.63 (d, *J* =12.0 Hz, 1H), 4.48 (d, *J* =10.6 Hz, 1H), 4.46 (d, *J* =12.0 Hz, 1H), 3.82 (dt, *J* =9.9, 2.5 Hz, 1H), 3.74 (dd, *J* =10.5, 3.3 Hz, 1H), 3.73—3.66 (m, 4H), 3.54 (dd, *J* =10.6, 2.0 Hz, 1H), 2.03—1.93 (m, 3H), 1.80 (d, *J* =11.2 Hz, 1H), 1.73 (apparent t, *J* =13.7 Hz, 2H), 1.67—1.62 (m, 2H), 1.52—1.49 (m, 1H), 1.37—1.08 (m, 11H), 1.00—0.90 (m, 2H), 0.89 (t, *J* =7.0 Hz, 3H);

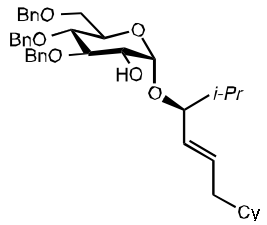
^{13}C-NMR (700 MHz, $CDCl_3$) δ 139.0, 138.4, 138.2, 134.0, 129.1, 128.51, 128.48, 128.2, 128.1, 128.0, 127.84, 127.79, 127.7, 98.7, 85.4, 83.9, 77.5, 75.4, 75.2, 73.73, 73.67, 70.7, 68.3, 32.4, 31.8, 29.33, 29.30, 29.1, 28.7, 26.7, 26.2, 22.8, 14.2;
IR (cm^{-1}) 1459, 1365, 1135, 1063, 1030;
HRMS-ES (m/z) [M+Na^+] calculated: 679.3969 found 679.3972.



((*R*,*E*)-1-cyclohexylnon-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7b)

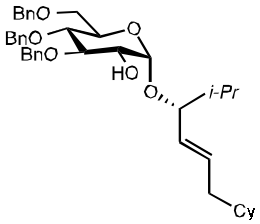
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (d, *J* =7.2 Hz, 2H), 7.35—7.26 (m, 11H), 7.16—7.14 (m, 2H), 5.61 (dt, *J* =15.3, 6.9 Hz, 1H), 5.17 (dd, *J* =15.5, 9.1 Hz, 1H), 5.00 (d, *J* =3.3 Hz, 1H), 4.98 (d, *J* =11.0 Hz, 1H), 4.84 (d, *J* =10.8 Hz, 1H), 4.82 (d, *J* =10.5 Hz, 1H), 4.65 (d, *J* =12.0 Hz, 1H), 4.52 (d, *J* =12.2 Hz, 1H), 4.50 (d, *J* =10.7 Hz, 1H), 3.82 (ddd, *J* =10.0, 3.5, 1.8 Hz, 1H), 3.77 (dd, *J* =15.5, 9.1 Hz, 1H), 3.73—3.70 (m, 3H), 3.67 (dd, *J* =10.6, 1.8 Hz, 1H), 3.63—3.61 (m, 1H), 2.06—2.03 (m, 2H), 1.99 (d, *J* =9.4 Hz, 1H), 1.90 (d, *J* =11.3 Hz, 1H), 1.71 (apparent t, *J* =13.2 Hz, 2H), 1.67—1.62 (m, 2H), 1.49—1.43 (m, 1H), 1.39—1.33 (m, 2H), 1.32—1.10 (m, 9H), 0.96—0.85 (m, 5H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.1, 138.4, 138.2, 137.8, 128.6, 128.54, 128.52, 128.3, 128.14, 128.06, 127.9, 127.8, 127.7, 127.5, 94.2, 84.2, 81.8, 77.6, 75.5, 75.3, 73.6, 73.2, 70.9, 68.7, 42.3, 32.5, 31.8, 29.7, 29.3, 29.0, 26.7, 26.2, 26.1, 22.8, 14.2;
IR (cm^{-1}) 1459, 1354, 1130, 1071, 1000;
HRMS-ES (m/z) [M+NH_4^+] calculated: 679.3969, found 679. 3979.

2-((*E*)-6-cyclohexyl-2-methylhex-4-en-3-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7c) was synthesized according to general procedure. 2-*O*-[(((*E*)-6-Cyclohexyl-2-methylhex-4-en-3-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (63 mg, 0.089 mmol, 5.7:1, S:R), titanium tetrafluoride (33 mg, 0.27 mmol) and silver tetrafluoroborate (26 mg, 0.13 mmol) were stirred for 5 h. Purification by flash chromatography (7:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H-NMR analysis revealed a diastereomeric ratio of 6.8:1 (S:R) (35 mg, 0.056 mmol, 63 %).



2-((*S*,*E*)-6-cyclohexyl-2-methylhex-4-en-3-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7c, entry 1, major diastereomer)

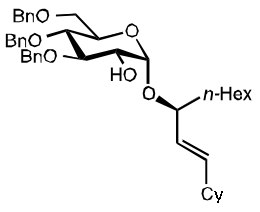
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.38 (apparent d, *J* =7.2 Hz, 2H), 7.33—7.25 (m, 11H), 7.25—7.13 (m, 2H), 5.54 (dt, *J* =15.3, 7.2 Hz, 1H), 5.34 (dd, *J* =15.3, 8.4 Hz, 1H), 4.97 (d, *J* =3.6 Hz, 1H), 4.95 (d, *J* =11.2 Hz, 1H), 4.83 (d, *J* =11.2 Hz, 1H), 4.81 (d, *J* =10.7 Hz, 1H), 4.63 (d, *J* =12.2 Hz, 1H), 4.48 (d, *J* =10.7 Hz, 1H), 4.46 (d, *J* =10.7 Hz, 1H), 3.81 (dt, *J* =9.9, 2.5 Hz, 1H), 3.75—3.65 (m, 5H), 3.54 (dd, *J* =10.6, 2.0 Hz, 1H), 1.98 (d, *J* =9.5 Hz, 1H), 1.92—1.89 (m, 1H), 1.86—1.79 (m, 2H), 1.67—1.61 (m, 5H), 1.27—1.08 (m, 4H), 0.92—0.82 (m, 8H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.0, 138.4, 138.2, 132.8, 129.5, 128.52, 128.50, 128.49, 128.1, 128.06, 128.04, 127.82, 127.80, 127.73, 98.53, 85.7, 83.9, 77.5, 75.4, 75.2, 73.7, 73.6, 70.7, 68.4, 40.6, 38.0, 33.4, 33.2, 32.5, 26.7, 26.5, 26.4, 18.8, 18.1;
IR (cm^{-1}) 1459, 1362, 1142, 1060, 1026**;**
HRMS-ES (m/z) [M+Na^+] calculated: 651. 3656 found 651.3662.



((*R*,*E*)-6-cyclohexyl-2-methylhex-4-en-3-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (entry 1 - minor diastereomer)

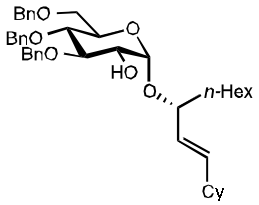
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (apparent d, *J* =6.9 Hz, 2H), 7.35—7.30 (m, 6H), 7.30—7.26 (m, 5H), 7.15—7.14 (m, 2H), 5.61 (dt, *J* =15.4, 6.9 Hz, 1H), 5.21 (dd, *J* =15.4, 9.0 Hz, 1H), 4.99 (d, *J* =3.1 Hz, 1H), 4.97 (d, *J* =11.0 Hz, 1H), 4.84 (d, *J* =11.2 Hz, 1H), 4.82 (d, *J* =10.8 Hz, 1H), 4.65 (d, *J* =12.1 Hz, 1H), 4.50 (d, *J* =11.9 Hz, 1H), 4.49 (d, *J* =10.6 Hz, 1H), 3.83 (ddd, *J* =10.0, 3.4, 2.1 Hz, 1H), 3.78 (dd, *J* =10.6, 3.7 Hz, 1H), 3.73—7.69 (m, 3H), 3.67 (dd, *J* =10.5, 1.9 Hz, 1H), 3.65—3.61 (m, 3H), 2.10—2.06 (m, 3H), 1.91 (d, *J* =12.5 Hz, 1H), 1.72 (apparent t, *J* =13.6 Hz, 2H), 1.64 (apparent t, *J* =11.9 Hz, 2H), 1.59—1.55 (m, 2H), 1.49—1.40 (m, 4H), 1.23—1.11 (m, 3H), 0.94—0.86 (m, 2H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.0, 138.4, 138.1, 136.3, 128.5, 128.49, 128.15, 128.08, 128.06, 128.03, 127.9, 127.8, 127.7, 94.4, 84.1, 82.6, 77.0, 75.5, 75.2, 73.6, 73.2, 70.9, 68.6, 40.6, 37.9, 33.3, 33.2, 32.8, 26.6, 26.4, 19.3, 18.8;
IR (cm^{-1})1459, 1358, 1134, 1074, 1033;
HRMS-ES (m/z) [M+Na^+] calculated: 651.3656 found 651.3660.

((*E*)-1-cyclohexylnon-1-en-3-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7d)
glucopyranoside was synthesized according to general procedure. 2-*O*-[(((*E*)-1-cyclohexylnon-1-en-3-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (43 mg, 0.059 mmol, 5.1:1 S:R), titanium tetrafluoride (22 mg, 0.17 mmol) and silver tetrafluoroborate (16 mg, 0.088 mmol) were stirred for 5 h. Purification by flash chromatography (7:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H NMR analysis revealed a regiomeric ratio of 12.5:1 (1,2 olefin to 1,1 olefin). ^{1}H NMR analysis revealed a diastereomeric ratio of 3.2:1 (S:R) of the major regioisomer (22 mg, 0.034 mmol, 57 %).



((*S*,*E*)-1-cyclohexylnon-1-en-3-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7d, entry 2, major diastereomer)

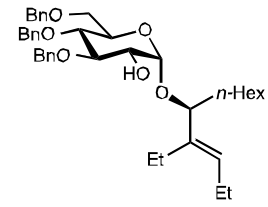
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* =7.4 Hz, 2H), 7.34—7.26 (m, 11H), 7.16—7.14 (m, 2H), 5.53 (dd, *J* =15.6, 6.5 Hz, 1H), 5.32 (ddd, *J* =15.5, 8.1, 1.2 Hz, 1H), 4.99 (d, *J* =3.8 Hz, 1H), 4.96 (d, *J* =11.2 Hz, 1H), 4.84 (d, *J* =11.2 Hz, 1H), 4.82 (d, *J* =10.7 Hz, 1H), 4.63 (d, *J* =12.2 Hz, 1H), 4.51 (d, *J* =10.7 Hz, 1H), 4.49 (d, *J* =12.2 Hz, 1H), 3.95 (apparent q, *J* =7.0 Hz, 1H), 3.82 (dt, *J* =9.9, 2.5 Hz, 1H), 3.75—3.65 (m, 4H), 3.57 (dd, *J* =10.6, 2.0 Hz, 1H), 2.02 (d, *J* =9.3 Hz, 1H), 1.92—1.87 (m, 1H), 1.72—1.62 (m, 6H), 1.49—1.42 (m, 1H), 1.31—1.19 (m, 10H), 1.17—1.10 (m, 1H), 1.08—0.98 (m, 2H), 0.88 (t, *J* =7.0 Hz, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.0, 138.9, 138.4, 138.2, 128.52, 128.50, 128.2, 128.1, 128.0, 127.84, 127.80, 127.7, 98.0, 83.9, 80.7, 77.5, 75.4, 75.2, 73.7, 73.5, 70.6, 68.4, 40.4, 35.3, 32.91, 32.89, 31.9, 29.4, 26.3, 26.14, 26.12, 25.3, 22.7, 14.2;
IR (cm^{-1}) 1459, 1365, 1127, 1071, 1033, 966;
HRMS-ES (m/z) [M+Na^+] calculated: 679.3969 found 679.3976.



((*R*,*E*)-1-cyclohexylnon-1-en-3-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (entry 2, minor diastereomer)

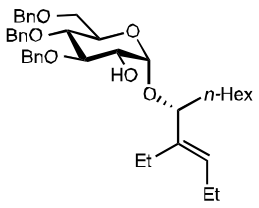
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* =7.2 Hz, 2H), 7.34—7.25 (m, 11H), 7.15—7.14 (m, 2H), 5.60 (dd, *J* =15.6, 6.7 Hz, 1H), 5.14 (ddd, *J* =15.5, 8.7, 0.9 Hz, 1H), 4.98 (d, *J* =4.1 Hz, 1H), 4.97 (d, *J* =11.3 Hz, 1H), 4.83 (d, *J* =11.2 Hz, 1H), 4.82 (d, *J* =10.6 Hz, 1H), 4.65 (d, *J* =12.0 Hz, 1H), 4.50 (d, *J* =12.0 Hz, 1H), 4.49 (d, *J* =10.7 Hz, 1H), 3.97 (app q, *J* =7.3 Hz, 1H), 3.82—3.80 (m, 1H), 3.78—3.61 (m, 5H), 2.01 (d, *J* =9.1 Hz, 1H), 1.99—1.93 (m, 1H), 1.73—1.68 (m, 4H), 1.65—1.59 (m, 2H), 1.50—1.44 (m, 1H), 1.33—1.23 (m, 10H), 1.18—1.12 (m, 1H), 1.09—1.03 (m, 2H), 0.87 (t, *J* =7.0 Hz, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 142.4, 139.0, 138.4, 138.2, 128.56, 128.54, 128.1, 128.0, 127.9, 127.85, 127.81, 127.7, 126.5, 94.5, 84.1, 77.6, 75.5, 75.2, 73.6, 73.1, 70.8, 68.7, 40.6, 35.7, 33.0, 31.9, 29.3, 26.2, 26.1, 25.7, 22.8, 14.3;
IR (cm^{-1})1459, 1354, 1130, 1071, 1000;
HRMS-ES (m/z) [$M+Na^+$] calculated: 679.3969; found : 679.3974.

((*E*)-4-ethylundec-3-en-5-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7e) was synthesized according to general procedure 2-*O*-[(((*E*)-4-ethylundec-3-en-5-y)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (63 mg, 0.089 mmol), titanium tetrafluoride (33 mg, 0.27 mmol) and silver tetrafluoroborate (26 mg, 0.14 mmol) were stirred for 3 h. Purification by flash chromatography (7:1 hexanes: acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H NMR analysis revealed a diastereomeric ratio of 2.8:1 (S:R) (23 mg, 0.036 mmol, 41 %).



((*S*,*E*)-4-ethylundec-3-en-5-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7e, entry 3, major diastereomer)

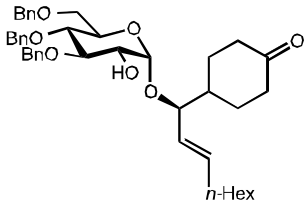
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* =4.5 Hz, 2H), 7.34—7.23 (m, 11H), 7.16—7.13 (m, 2H), 5.31 (t, *J* =7.2 Hz, 1H), 4.96 (d, *J* =3.6 Hz, 1H), 4.95 (d, *J* =11.2 Hz, 1H), 4.83 (d, *J* =11.2 Hz, 1H), 4.81 (d, *J* =10.9 Hz, 1H), 4.62 (d, *J* =12.3 Hz, 1H), 4.48 (d, *J* =10.7 Hz, 1H), 4.46 (d, *J* =12.1 Hz, 1H), 3.90 (t, *J* =6.9 Hz, 1H), 3.77—3.62 (m, 5H), 3.55—3.52 (m, 1H), 2.07—1.97 (m, 5H), 1.67—1.61 (m, 1H), 1.54—1.49 (m, 1H), 1.31—1.17 (m, 8H), 0.98 (t, *J* =7.6 Hz, 3H), 0.94 (t, *J* =7.5 Hz, 3H), 0.88 (t, *J* =7.2 Hz, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.7, 139.0, 138.5, 138.1, 130.7, 128.52, 128.49, 128.47, 128.09, 128.08, 128.04, 127.81, 127.79, 127.7, 98.0, 84.6, 83.9, 77.5, 75.4, 75.1, 73.6, 73.5, 70.9, 68.4, 33.5, 31.9, 29.4, 25.8, 22.8, 20.9, 20.2, 14.7, 14.5, 14.2;
IR (cm^{-1}) 1503, 1455, 1369, 1130, 1071, 1062, 1033, 914;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 648.4259 found: 648.4258.



((*R*,*E*)-4-ethylundec-3-en-5-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (entry 3, minor diastereomer)

^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* =7.1 Hz, 2H), 7.35—7.25 (m, 11H), 7.17—7.14 (m, 2H), 5.36 (t, *J* =7.2 Hz, 1H), 4.97 (d, *J* =11.1 Hz, 1H), 4.89 (d, *J* =3.9 Hz, 1H), 4.84 (d, *J* =11.1 Hz, 1H), 4.82 (d, *J* =10.7 Hz, 1H), 4.65 (d, *J* =12.1 Hz, 1H), 4.51 (d, *J* =12.1 Hz, 1H), 4.50 (d, *J* =10.7 Hz, 1H), 3.96 (t, *J* =7.0 Hz, 1H), 3.82—3.79 (m, 1H), 3.78—3.60 (m, 5H), 2.11—2.03 (m, 3H), 2.00—1.92 (m, 2H), 1.66—1.61 (m, 1H), 1.57—1.50 (m, 1H), 1.35—1.18 (m, 8H), 1.01 (t, *J* =7.7 Hz, 3H), 0.98 (t, *J* =7.5 Hz, 3H), 0.87 (t, *J* =7.1 Hz, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.0, 138.4, 138.2, 137.6, 133.5, 128.52, 128.48, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 94.4, 84.2, 81.7, 77.6, 75.5, 75.2, 73.6, 73.3, 70.8, 68.7, 34.3, 31.9, 29.3, 26.2, 22.8, 21.0, 19.5, 14.52, 14.50, 14.2;
IR (cm^{-1}) 1503, 1455,1362, 1134, 1026;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 648.4259 found: 648.4262.

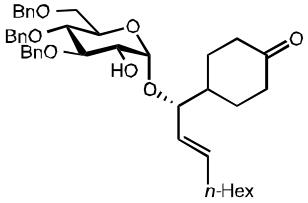
4-((E)-non-2-en-1-yl)cyclohexanone-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7f) was synthesized according to general procedure 2-*O*-[4-((E)-1-((dimethylsilyl)oxy)non-2-en-1-yl)cyclohexanone]-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (51 mg, 0.067 mmol), titanium tetrafluoride (25 mg, 0.20 mmol) and silver tetrafluoroborate (20 mg, 0.10 mmol) were stirred for 5 h. Purification by flash chromatography (6:1 to 1:1 hexanes: ethyl acetate) yielded the desired product as separate diastereomers (7 mg, 0.010 mmol, minor diastereomer) and (21 mg, 0.31 mmol, major diastereomer) for a combined yield of 60% with a diastereomeric ratio of 3:1.



4-((S,E)-non-2-en-1-yl)cyclohexanone-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7f, entry 4, major diastereomer)

^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.36—7.25 (m, 11H), 7.16—7.14 (m, 2H), 5.61 (dt, *J* =15.3, 6.8 Hz, 1H), 5.39 (dd, *J* =15.3, 8.7 Hz, 1H), 4.99 (d, *J* =3.7 Hz, 1H), 4.91 (A of AB, *J* = 11.2 Hz, 1H), 4.88 (B of AB, *J* =11.2 Hz, 1H), 4.81 (d, *J* =10.6 Hz, 1H), 4.64 (d, *J* =12.1 Hz, 1H), 4.49 (d, *J* = 10.9 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 3.86—3.80 (m, 2H), 3.76—3.65 (m, 4H), 3.54 (dd, *J* =10.5, 2.0 Hz, 1H), 2.43—2.37 (m, 2H), 2.34—2.27 (m, 2H), 2.18—2.12 (m, 1H), 2.02—1.91 (m, 5H), 1.48—1.40 (m, 2H), 1.36—1.21 (m, 8H), 0.88 (t, *J* =7.1 Hz, 3H),

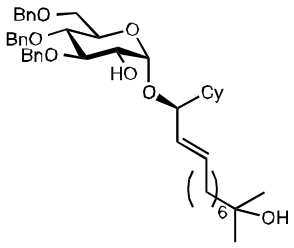
^{13}C-NMR (175 MHz, $CDCl_3$) δ 211.8, 138.8, 138.3, 138.1, 135.2, 128.7, 128.64, 128.58, 128.3, 128.2, 128.14, 128.12, 128.0, 127.9, 98.7, 84.1, 83.4, 77.8, 75.5, 75.3, 73.8, 73.4, 71.0, 68.3, 41.0, 40.7, 32.5, 31.9, 29.3, 29.1, 28.8, 28.3, 22.8, 14.3;
IR (cm^{-1}) 1716, 1455, 1130, 1074, 1052, 1033;
HRMS-ES (m/z) [$M+Na^+$] calculated: 693.3762, found 693.3759.



4-((R,E)-non-2-en-1-yl)cyclohexanone-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (entry 4, minor diastereomer)

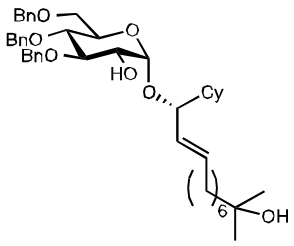
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.34—7.25 (m, 11H), 7.16—7.13 (m, 2H), 5.69 (dt, *J* = 15.2, 6.9 Hz, 1H), 5.22 (dd, *J* = 15.5, 9.0 Hz, 1H), 5.02 (d, *J* = 3.4 Hz, 1H), 4.95 (d, *J* = 11.1 Hz, 1H), 4.86 (d, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 10.6 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 10.6 Hz, 1H), 3.86 (apparent t, *J* = 8.3 Hz, 1H), 3.78—3.70 (m, 4H), 3.66 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.63—3.60 (m, 1H), 2.44—2.35 (m, 2H), 2.33—2.27 (m, 2H), 2.26—2.20 (m, 1H), 2.09—1.90 (m, 5H), 1.48—1.33 (m, 4H), 1.32—1.23 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 211.9, 138.93, 138.91, 138.2, 138.1, 128.67, 128.65, 128.62, 128.3, 128.12, 128.10, 127.98, 127.98, 127.91, 126.7, 94.4, 83.9, 80.4, 77.6, 75.6, 75.4, 73.8, 73.0, 71.3, 68.7, 40.7, 40.64, 40.57, 32.6, 31.8, 29.34, 29.28, 29.1, 29.0, 22.8, 14.3;
IR (cm^{-1}) 1717, 1456, 1132, 1068, 1029;
HRMS-ES (m/z) [M+Na^+] calculated: 693.3762; found 693.3757.

((*E*)-1-cyclohexyl-10-hydroxy-10-methylundec-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7g) was synthesized according to general procedure. 2-*O*-[(*E*)-11-((dimethylsilyl)oxy)-11-cyclohexyl-2-methylundec-9-en-2-ol]-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (63 mg, 0.080 mmol), titanium tetrafluoride (30 mg, 0.24 mmol) and silver tetrafluoroborate (24 mg, 0.12 mmol) were stirred for 13 h. Rough purification by flash chromatography (3:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers contaminated with 3,4,6-tri-*O*-benzyl α-D-glucosyl fluoride. ^{1}H NMR analysis revealed a diastereomeric ratio of 5.6:1 (S:R). HPLC purification on a ZorbaxRx-Sil column (1.6% iPrOH in hexanes) yielded the minor diastereomer (3.7 mg, 0.005 mmol) and the major diastereomer contaminated with 22% 3,4,6-tri-*O*-benzyl α-D-glucosyl fluoride (21 mg, 0.029 mmol) for a combined yield of 43%.



((*S*,*E*)-1-cyclohexyl-10-hydroxy-10-methylundec-2-en-1-yl)- 3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (7g, entry 5, major diastereomer)

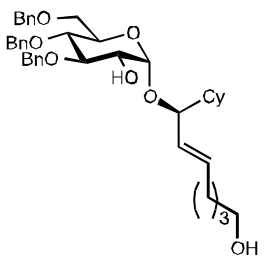
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 (d, *J* =7.4 Hz, 2H), 7.35—7.24 (m, 11H), 7.13 (d, *J* =7.0 Hz, 2H), 5.53 (dt, *J* =15.3, 6.7 Hz, 1H), 5.35 (dd, *J* =15.3, 8.4 Hz, 1H), 4.96 (d, *J* =3.6 Hz, 1H), 4.95 (d, *J* =11.1 Hz, 1H), 4.83 (d, *J* =11.1 Hz, 1H), 4.80 (d, *J* =10.6 Hz, 1H), 4.63 (d, *J* =12.3 Hz, 1H), 4.47—4.45 (m, 2H), 3.80 (d, *J* =9.9 Hz, 1H), 3.74—3.62 (m, 5H), 3.53 (d, *J* =10.4 Hz, 1H), 2.02—1.92 (m, 3H), 1.78 (d, *J* =12.9 Hz, 1H), 1.71 (t, *J* =14.1 Hz, 2H), 1.67—1.61 (m, 2H), 1.49—1.41 (m, 3H), 1.36—1.24 (m, 10H), 1.19 (s, 6H), 1.15—1.07 (m, 1H), 0.98—0.81 (m, 3H);
^{13}C NMR (175 MHz, $CDCl_3$) δ 139.0, 138.4, 138.1, 133.9, 129.2, 128.54, 128.53, 128.5, 128.2, 128.07, 128.03, 127.9, 127.81, 127.75, 98.6, 85.5, 83.9, 77.54, 75.45, 75.2, 73.72, 73.66, 71.2, 70.6, 68.4, 44.1, 42.5, 32.4, 30.1, 29.4, 29.34, 29.30, 28.7, 26.7, 26.2, 24.5 **IR (cm^{-1})** 1503, 1459, 1369, 1130, 1074, 1030. 1000. 910;
HRMS-ES (m/z) [M+Na^+] calculated: 737.4388, found 737.4393.



((*R*,*E*)-1-cyclohexyl-10-hydroxy-10-methylundec-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (entry 5, minor diastereomer)

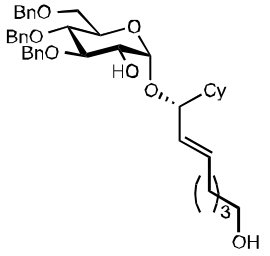
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* =7.3 Hz, 2H), 7.35—7.24 (m, 11H), 7.15 (d, *J* =7.8 Hz, 2H), 5.60 (dt, *J* =15.3, 6.7 Hz, 1H), 5.18 (dd, *J* =15.5, 9.0 Hz, 1H), 4.99 (d, *J* =3.4 Hz, 1H), 4.97 (d, *J* =11.0 Hz, 1H), 4.84 (d, *J* =10.9 Hz, 1H), 4.82 (d, *J* =10.6 Hz, 1H), 4.65 (d, *J* =12.1 Hz, 1H), 4.50 (d, *J* =12.1 Hz, 1H), 4.49 (d, *J* =10.7 Hz, 1H), 3.85—3.81 (m, 1H), 3.77 (dd, *J* =10.6, 3.8 Hz, 1H), 3.74—3.70 (m, 3H), 3.67 (dd, *J* =10.6, 1.8 Hz, 1H), 3.62 (t, *J* =9.3 Hz, 1H), 2.19 (d, *J* =9.0 Hz, 1H), 2.05 (q, *J* =6.8 Hz, 2H), 1.91 (d, *J* =12.6 Hz, 1H), 1.71 (apparent t, *J* =13.5 Hz, 2H), 1.66—1.61 (m, 2H), 1.58—1.55 (m, 1H), 1.50—1.43 (m, 3H), 1.40—1.24 (m, 10H), 1.2 (s, 6H), 1.16—1.08 (m, 1H), 0.95—0.87 (m, 2H);
^{13}C NMR (175 MHz, $CDCl_3$) δ 139.0, 138.4, 138.1, 133.9, 129.2, 128.53, 128.53, 128.49, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 98.6, 85.5, 83.9, 77.5, 75.4, 75.2, 73.71, 73.65, 71.1, 70.6, 68.3, 44.1, 42.5, 32.4, 29.9, 29.7, 29.4, 29.31, 29.29, 29.10, 29.08, 26.7, 26.2, 24.5;
IR (cm^{-1}) 1500, 1455, 1373, 1093, 1045, 880;
HRMS-ES (m/z) [M+Na^+] calculated: 737.4388, found: 737.4396.

((*E*)-1-cyclohexyl-7-hydroxyhept-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7h) was synthesized according to general procedure. 2-*O*-[((E)-7-(((*t*-butyldimethylsilyl)oxy)-1-cyclohexylhept-2-en-1-yl)oxy)dimethylsilane]-3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (81 mg, 0.097 mmol), titanium tetrafluoride (36 mg, 0.29 mmol) and silver tetrafluoroborate (28 mg, 0.14 mmol) were stirred for 5 h. Purification by flash chromatography (2:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H-NMR analysis revealed a diastereomeric ratio of 4.3:1 (S:R) (35 mg, 0.055 mmol, 57 %).



((*S*,*E*)-1-cyclohexyl-7-hydroxyhept-2-en-1-yl) - 3,4,6-tri-*O*-benzyl- α - D-glucopyranoside (7h, entry 6, major diastereomer)

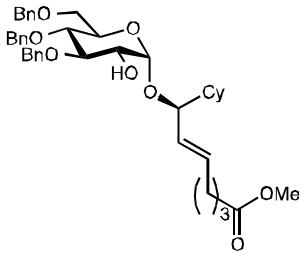
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (apparent d, *J* =7.4 Hz, 2H), 7.34—7.25 (m, 11H), 7.15—7.14 (m, 2H), 5.54 (dt, *J* =15.3, 6.8 Hz, 1H), 5.38 (dd, *J* =15.5, 8.6 Hz, 1H), 4.967 (d, *J* =3.8 Hz, 1H), 4.965 (d, *J* =11.0 Hz, 1H), 4.85 (d, *J* =11.2 Hz, 1H), 4.81 (d, *J* =10.5 Hz, 1H), 4.63 (d, *J* =12.2 Hz, 1H), 4.48 (d, *J* =10.5 Hz, 1H), 4.47 (d, *J* =12.2 Hz, 1H), 3.82 (dt, *J* =9.9, 2.5 Hz, 1H), 3.74—7.64 (m, 5H), 3.59 (apparent t, *J* =5.8 Hz, 2H), 3.55 (dd, *J* =10.7, 1.9 Hz, 1H), 2.02—1.98 (m, 3H), 1.79 (d, *J* =12.6 Hz, 1H), 1.75—1.71 (m, 2H), 1.65 (apparent t, *J* =11.7 Hz, 2H), 1.55—1.46 (m, 3H), 1.43—1.39 (m, 2H), 1.34 (t, *J* =5.4 Hz, 1H), 1.23—1.10 (m, 3H), 0.98—0.87 (m, 2H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 138.9, 138.3, 138.1, 133.6, 129.6, 128.49, 128.54, 128.50, 128.2, 128.08, 128.05 127.9, 127.8, 127.7, 98.4, 85.3, 83.8, 77.5, 75.4, 75.3, 73.7, 73.6, 70.7, 68.4, 62.9, 42.4, 32.4, 32.1, 29.3, 28.7, 26.6, 26.2, 25.3;
IR (cm^{-1}) 1500, 1459, 1362, 1216, 1138, 1056, 1030, 996, 918;
HRMS-ES (m/z) [M+Na^+] calculated: 667.3605, found 667.3610.



((*R*,*E*)-1-cyclohexyl-7-hydroxyhept-2-en-1-yl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (entry 6, minor diastereomer)

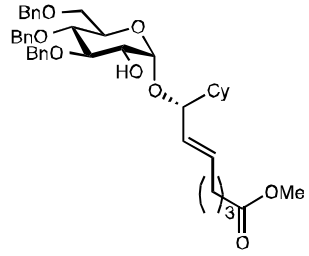
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (apparent d, *J* =6.9 Hz, 2H), 7.35—7.30 (m, 6H), 7.30—7.26 (m, 5H), 7.15—7.14 (m, 2H), 5.61 (dt, *J* =15.4, 6.9 Hz, 1H), 5.21 (dd, *J* =15.4, 9.0 Hz, 1H), 4.99 (d, *J* =3.1 Hz, 1H), 4.97 (d, *J* =11.0 Hz, 1H), 4.84 (d, *J* =11.2 Hz, 1H), 4.82 (d, *J* =10.8 Hz, 1H), 4.65 (d, *J* =12.1 Hz, 1H), 4.50 (d, *J* =11.9 Hz, 1H), 4.49 (d, *J* =10.6 Hz, 1H), 3.83 (ddd, *J* =10.0, 3.4, 2.1 Hz, 1H), 3.78 (dd, *J* =10.6, 3.7 Hz, 1H), 3.73—7.69 (m, 3H), 3.67 (dd, *J* =10.5, 1.9 Hz, 1H), 3.65—3.61 (m, 3H), 2.10—2.06 (m, 3H), 1.91 (d, *J* =12.5 Hz, 1H), 1.72 (apparent t, *J* =13.6 Hz, 2H), 1.64 (apparent t, *J* =11.9 Hz, 2H), 1.59—1.55 (m, 2H), 1.49—1.40 (m, 4H), 1.23—1.11 (m, 3H), 0.94—0.86 (m, 2H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 139.0, 138.3, 138.1, 137.0, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 94.3, 84.0, 81.9, 77.5, 75.5, 75.3, 73.6, 73.2, 70.9, 68.6, 62.8, 42.2, 32.2, 32.1, 29.7, 29.3, 26.6, 26.2, 26.0, 25.3;
IR (cm^{-1}) 1503, 1451, 1358, 1142, 1071, 1026, 888;
HRMS-ES (m/z) [M+Na^+] calculated: 667.3605; found 667.3606.

(*E*)-methyl-7-cyclohexylhept-5-enoate-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7i)
was synthesized according to general procedure 2. 2-*O*-[(E)-Methyl-7-((dimethylsilyl)oxy)-7-cyclohexylhept-5-enoate]- 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (70 mg, 0.094 mmol), titanium tetrafluoride (34 mg, 0.28 mmol) and silver tetrafluoroborate (27 mg, 0.14 mmol) were stirred for 5 h. Purification by flash chromatography (5:1 hexanes:acetone to 2:1 hexanes:acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H NMR analysis revealed a diastereomeric ratio of 4.2:1 (S:R) (32 mg, 0.049 mmol, 52 %).



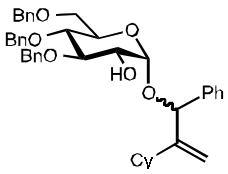
(*S*,*E*)-methyl-7-cyclohexylhept-5-enoate-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7i, entry 7, major diastereomer)

^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* =7.4 Hz, 2H), 7.34—7.25 (m, 11H), 7.15—7.14 (m, 2H), 5.52 (dt, *J* =15.3, 6.7 Hz, 1H), 5.40 (dd, *J* =15.4, 8.5 Hz, 1H), 4.96 (d, *J* =11.2 Hz, 1H), 4.95 (d, *J* =3.7 Hz, 1H), 4.85 (d, *J* =11.2 Hz, 1H), 4.81 (d, *J* =10.6 Hz, 1H), 4.63 (d, *J* =12.1 Hz, 1H), 4.48 (d, *J* =10.6 Hz, 1H), 4.47 (d, *J* =12.1 Hz, 1H), 3.80 (dt, *J* =10.0, 2.6 Hz, 1H), 3.75—3.54 (m, 8H), 3.55 (dd, *J* =10.6, 2.0 Hz, 1H), 2.29 (t, *J* =7.5 Hz, 2H), 2.05—1.96 (m, 3H), 1.79 (d, *J* =12.7 Hz, 1H), 1.75—1.62 (m, 6H), 1.52—1.51 (m, 1H), 1.26—1.09 (m, 3H), 0.99—9.88 (m, 2H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 174.1, 138.9, 138.4, 138.1, 132.5, 130.3, 128.52, 128.48, 128.2, 128.08, 128.05, 127.9, 127.8, 127.7, 98.6, 85.3, 83.8, 77.5, 75.4, 75.2, 73.6, 70.7, 68.4, 51.6, 42.4, 33.6, 31.7, 29.3, 28.7, 26.6, 26.2, 24.5;
IR (cm^{-1}) 1738, 1500, 1459, 1365, 1138, 1067, 1052;
HRMS-ES (m/z) [M+Na^+] calculated: 695.3554 found 695.3563.



(*R*,*E*)-methyl 7-cyclohexylhept-5-enoate - 3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (entry 7, minor diastereomer)

^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (d, *J* =7.2 Hz, 2H), 7.35—7.26 (m, 11H), 7.16—7.15 (m, 2H), 5.60 (dt, *J* =15.3, 6.8 Hz, 1H), 5.23 (dd, *J* =15.3, 8.9 Hz, 1H), 4.98 (d, *J* =11.2 Hz, 1H), 4.97 (d, *J* =3.4 Hz, 1H), 4.84 (d, *J* =11.2 Hz, 1H), 4.83 (d, *J* =10.6 Hz, 1H), 4.65 (d, *J* =12.1 Hz, 1H), 4.51 (d, *J* =12.1 Hz, 1H), 4.50 (d, *J* =10.6 Hz, 1H), 3.82 (ddd, *J* =10.0, 3.6, 2.0 Hz, 1H), 3.77 (dd, *J* =10.6, 3.9 Hz, 1H), 3.75—3.70 (m, 3H), 3.69—3.66 (m, 4H), 3.62 (t, *J* =9.7 Hz, 1H), 2.31 (t, *J* =7.5 Hz, 2H), 2.10 (q, *J* =7.0 Hz, 2H), 2.03 (d, *J* =9.2 Hz, 1H), 1.90 (d, *J* =12.8 Hz, 1H), 1.75—1.70 (m, 4H), 1.62 (apparent t, *J* =12.8 Hz, 2H), 1.50—1.44 (m, 1H), 1.26—1.10 (m, 3H), 0.96—0.88 (m, 2H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 174.0, 139.0, 138.3, 138.2, 136.0, 128.7, 128.53, 128.51, 128.49, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 94.3, 84.0, 81.6, 77.6, 75.5, 75.3, 73.6, 73.2, 71.0, 68.7, 51.7, 42.2, 33.5, 31.7, 29.7, 29.3, 26.6, 26.2, 26.0, 24.5;
IR (cm^{-1}) 1742, 1459, 1369, 1138, 1063, 1033, 996;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 695.3554 found 685.3560.



(2-cyclohexyl-1-phenylallyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7j)

Compound **7j** was synthesized according to general procedure. 2-*O*-[(E)-Methyl-7-((dimethylsilyl)oxy)-7-cyclohexylhept-5-enoate]- 3,4,6-tri-*O*-benzyl- β -D-glucopyranosyl fluoride (73 mg, 0.10 mmol), titanium tetrafluoride (37 mg, 0.30 mmol) and silver tetrafluoroborate (29 mg, 0.15 mmol) were stirred for 5 h. Purification by flash chromatography (7:1 hexanes: acetone to 4:1 hexanes acetone) yielded the desired product as a colorless oil as a mixture of separable diastereomers. ^{1}H-NMR analysis revealed a diastereomeric ratio of 1.1:1 (38 mg, 0.059 mmol, 59 %).

7j-1 (first eluting diastereomer):
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.40 (apparent d, *J* =7.2 Hz, 2H), 7.35—7.25 (m, 16H), 7.12—7.11 (m, 2H), 5.33 (s, 1H), 5.14 (s, 1H), 5.13 (s, 1H), 5.11 (d, *J* =3.3 Hz, 1H), 4.97 (d, *J* =11.0 Hz, 1H), 4.85 (d, *J* =11.1 Hz, 1H), 4.79 (d, *J* =10.5 Hz, 1H), 4.611 (d, 1H), 4.47—4.46 (m, 2H), 3.79—3.77 (m, 2H), 3.68—3.62 (m, 3H), 3.49 (d, *J* =8.8 Hz, 1H), 2.08 (d, *J* =9.1 Hz, 1H), 1.70—1.57 (m, 4H), 1.52 (d, *J* =14.1 Hz, 1H), 1.26—0.97 (m, 6H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 152.8, 140.0, 138.9, 138.2, 138.0, 128.6, 128.5, 128.49, 128.3, 128.24, 128.18, 128.05, 127.98, 127.96, 127.91, 127.81, 127.80, 127.5, 111.3, 96.5, 83.8, 80.6, 77.6, 75.6, 75.3, 73.5, 73.4, 70.8, 68.4, 40.2, 34.4, 32.7, 26.9, 26.8, 26.3;
IR (cm^{-1}) 1496, 1459, 1365, 1134, 1054, 1045, 1015, 918;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 666.3789; found 666.3790.

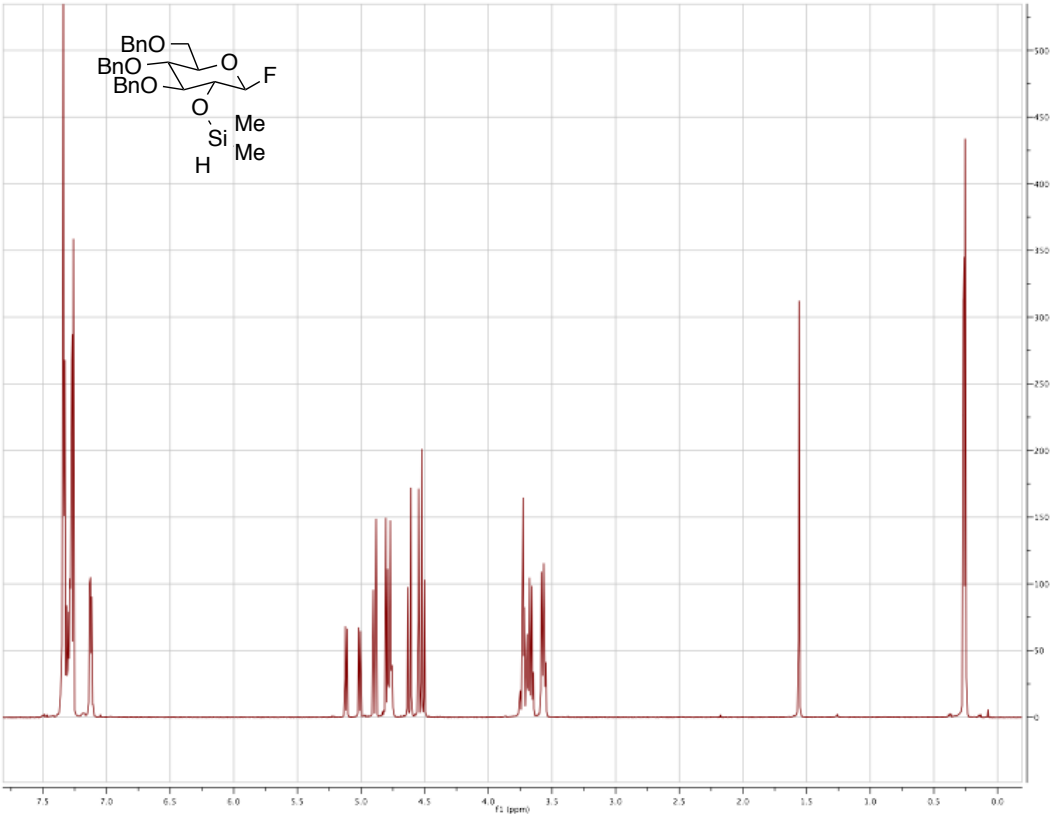
7j-2 (second eluting diastereomer):
^{1}H-NMR (700 MHz, $CDCl_3$) δ 7.39 (apparent d, *J* =7.2 Hz, 2H), 7.36—7.26 (m, 16H), 7.17—7.16 (m, 2H), 5.22 (s, 1H), 5.12 (s, 1H), 4.97 (d, *J* =11.2 Hz, 1H), 4.96 (s, 1H), 4.86 (d, *J* =11.2 Hz, 1H), 4.84 (d, *J* =10.8 Hz, 1H), 4.81 (d, *J* =4.1 Hz, 1H), 4.66 (d, *J* =12.0 Hz, 1H), 4.52 (d, *J*

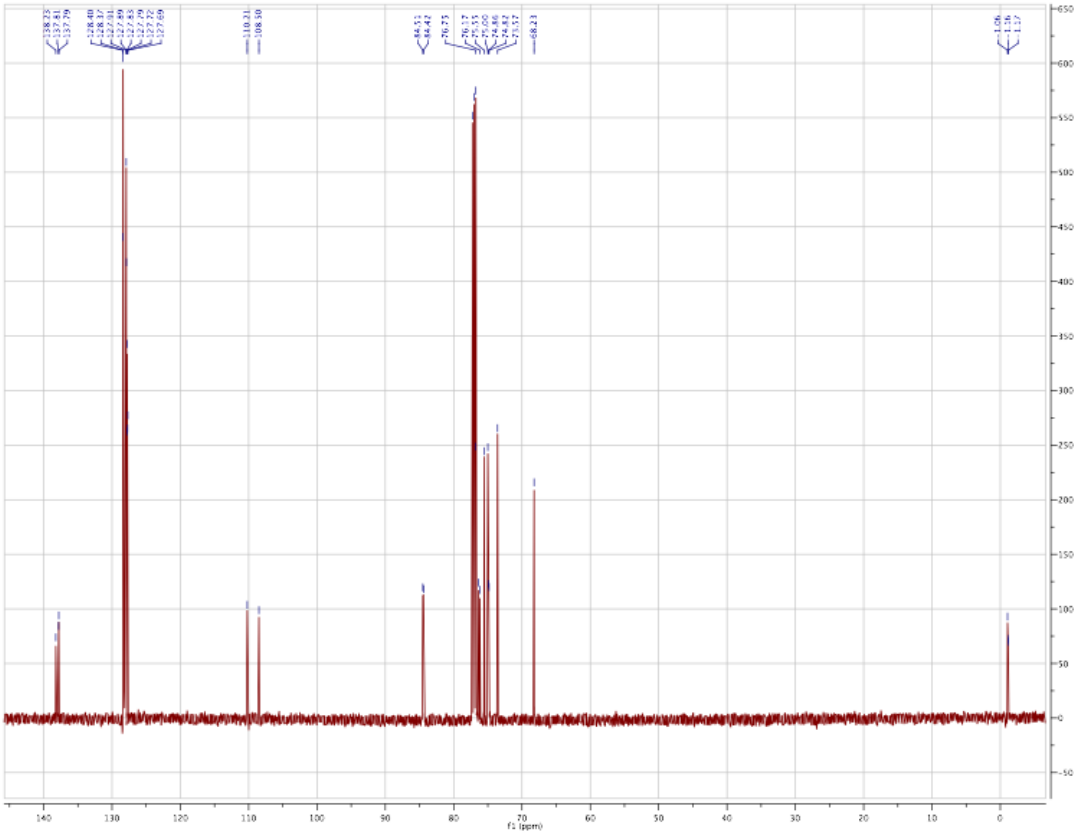
=12.0 Hz, 1H), 4.50 (d, *J* =10.7 Hz, 1H), 3.89 (ddd, *J* =10.1, 3.7, 1.9 Hz, 1H), 3.81 (t, *J* =9.2 Hz, 1H), 3.78 (dd, *J* =10.7, 4.0 Hz, 1H), 3.70 (dd, *J* =10.7, 1.9 Hz, 1H), 3.68—3.61 (m, 2H), 1.89 (d, *J* =9.5 Hz, 1H), 1.71—1.56 (m, 5H), 1.51 (d, *J* =12.9 Hz, 1H), 1.26—1.20 (m, 5H);
^{13}C-NMR (175 MHz, $CDCl_3$) δ 154.3, 139.1, 138.9, 138.3, 138.1, 128.6, 128.55, 128.51, 128.3, 128.20, 128.18, 128.1, 128.0, 127.9, 127.82, 127.80, 108.6, 95.5, 83.8, 79.1, 77.5, 75.5, 75.3, 73.6, 73.2, 71.2, 68.6, 40.8, 34.0, 32.5, 29.9, 26.9, 26.8;
IR (cm^{-1}) 1503, 1459, 1358, 1134, 1071, 1056, 1030, 903;
HRMS-ES (m/z) [$M+NH_4^+$] calculated: 666.3789. found 666.3790.

References

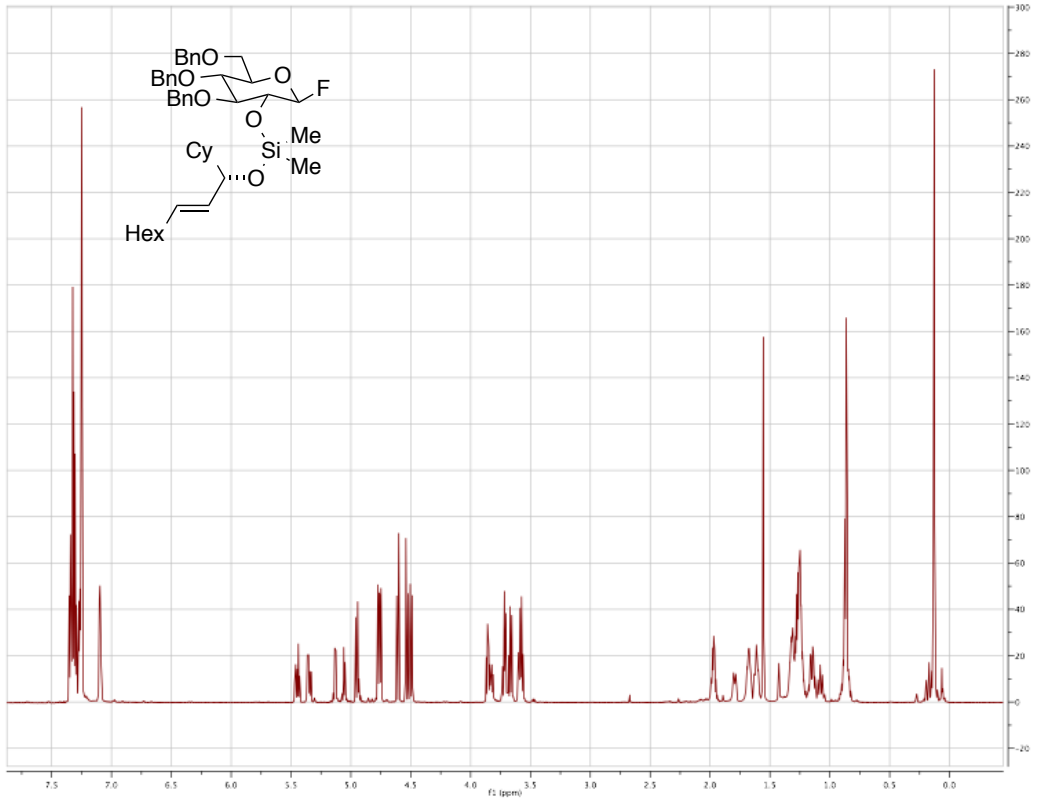
[1] Cumpstey, I., Fairbanks, A.J., Redgrave, Alison. J. *Mont. Fur Chemie* **2002**, *133*, 449-466.
[2] Petrzilka, M.; Schadt, M. (Hoffman La Roche Inc.) US Patent 5,238,602, May 26, 1987.
[3] Chaulagain, M. R.; Sormunen, G.; Montgomery, J. *J. Am. Chem. Soc.* **2007**, *129*, 9568-9569.

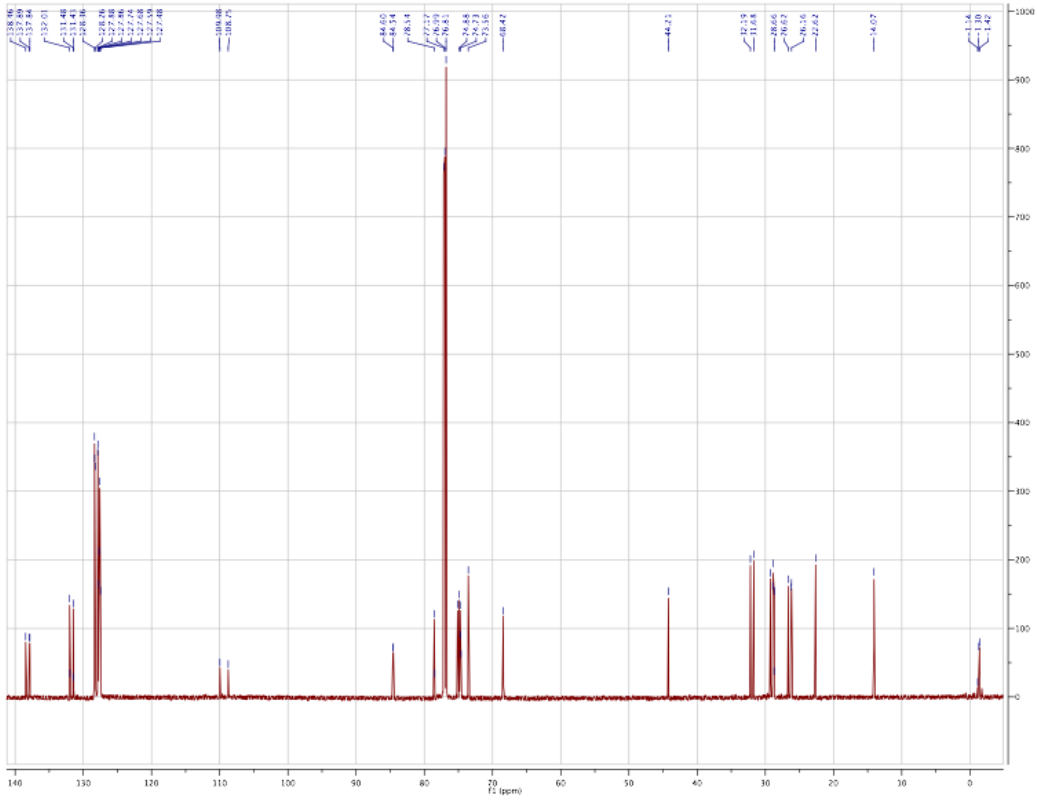
Fluorosilane **1b**



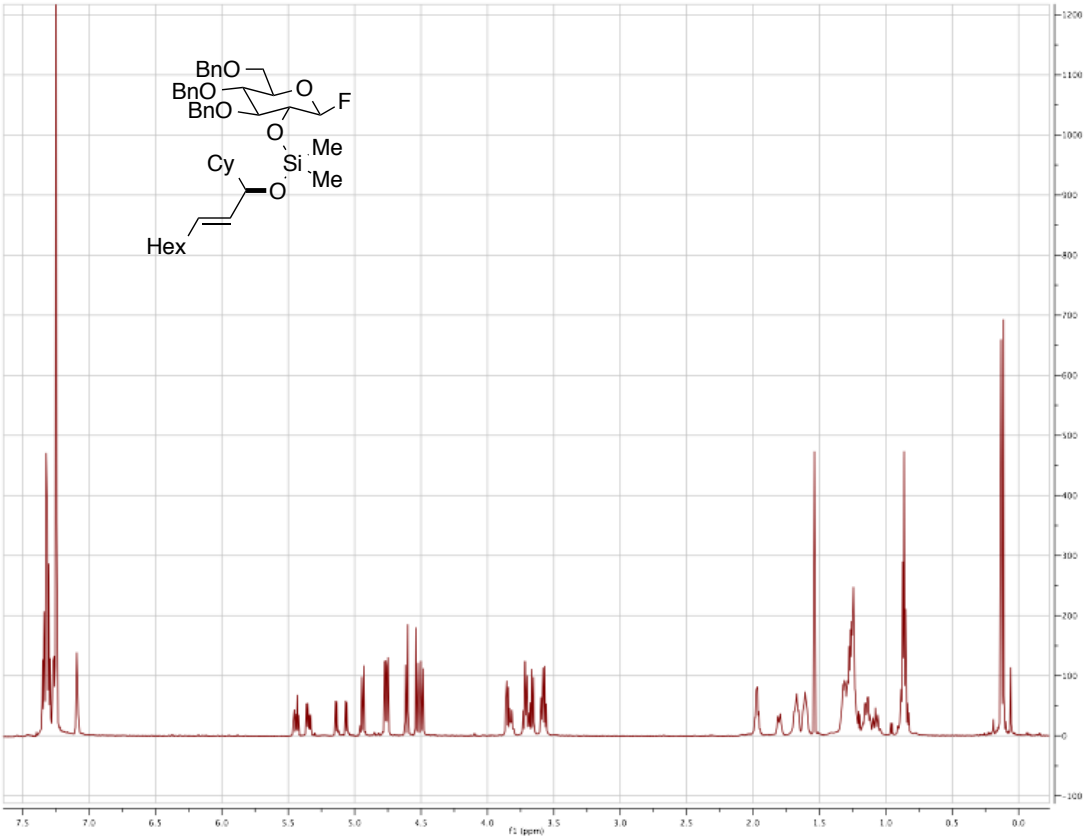


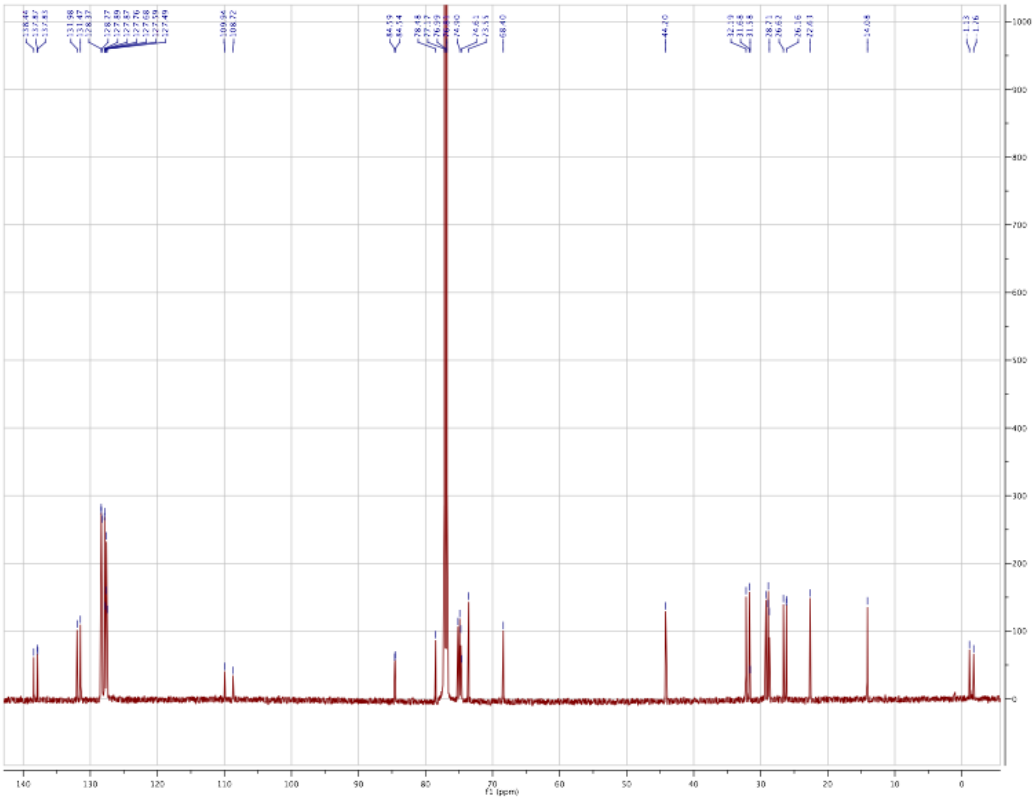
Compound **6a** (silane from RR-**5**)



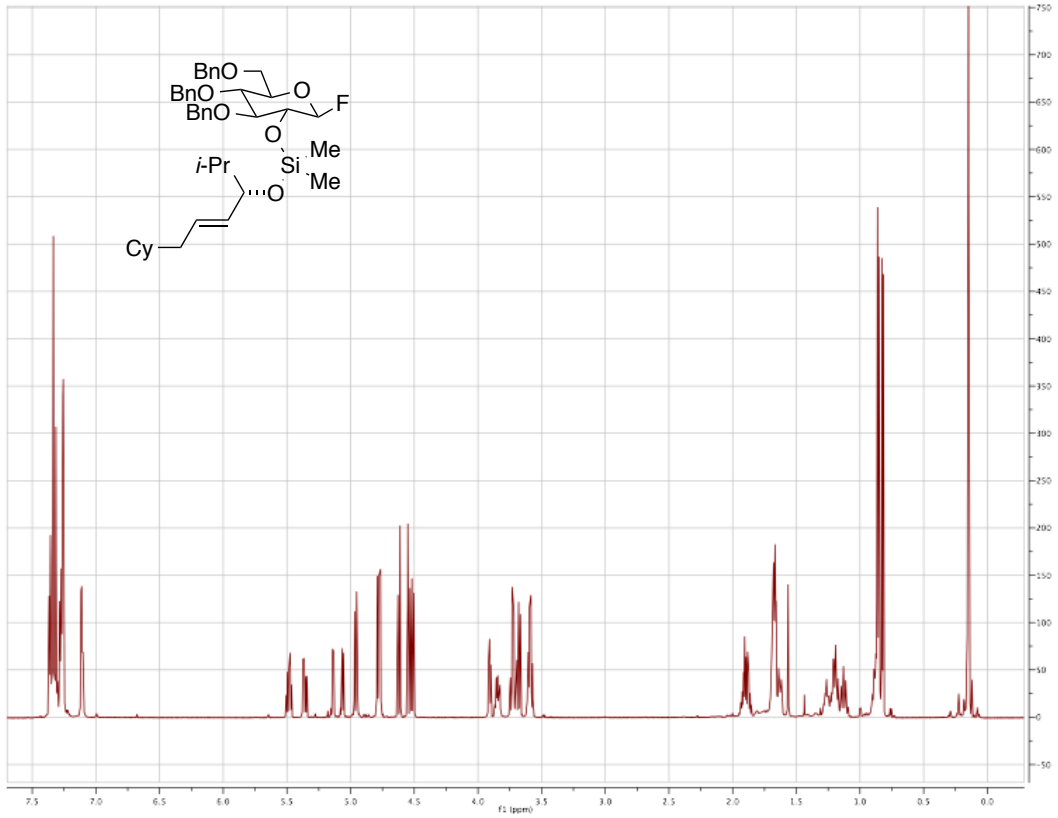


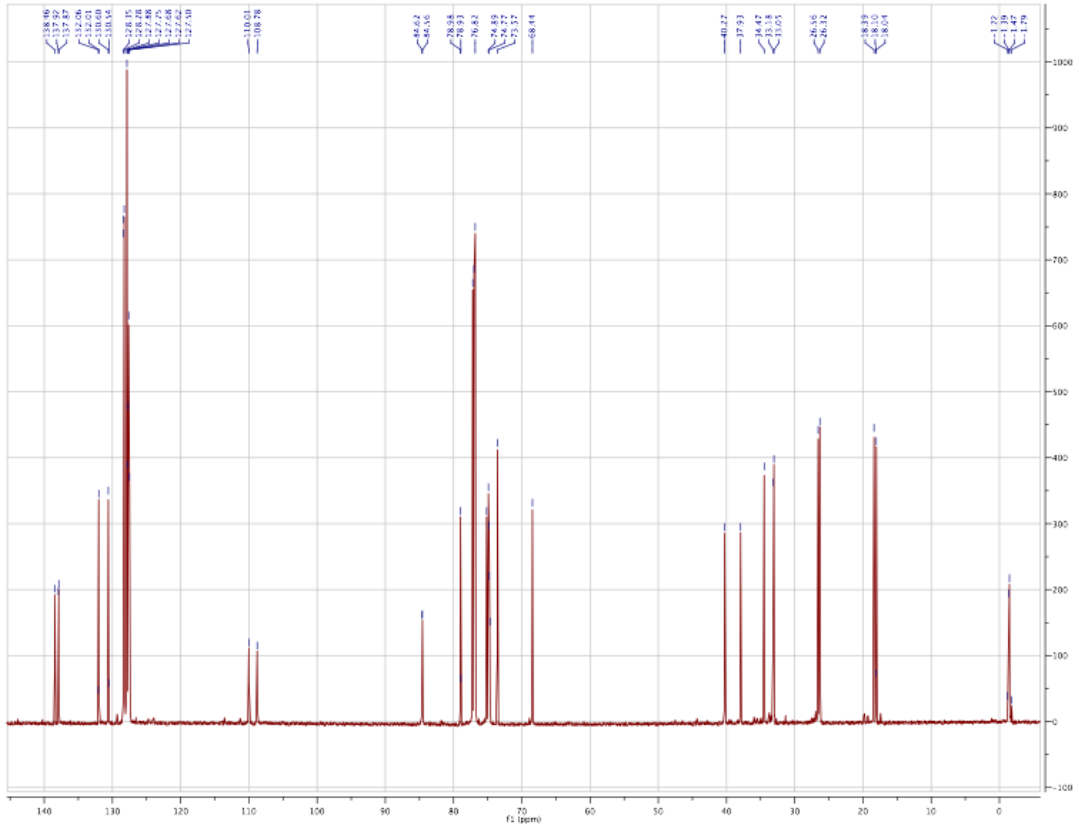
compound **6b** (silane from SS-**5**)



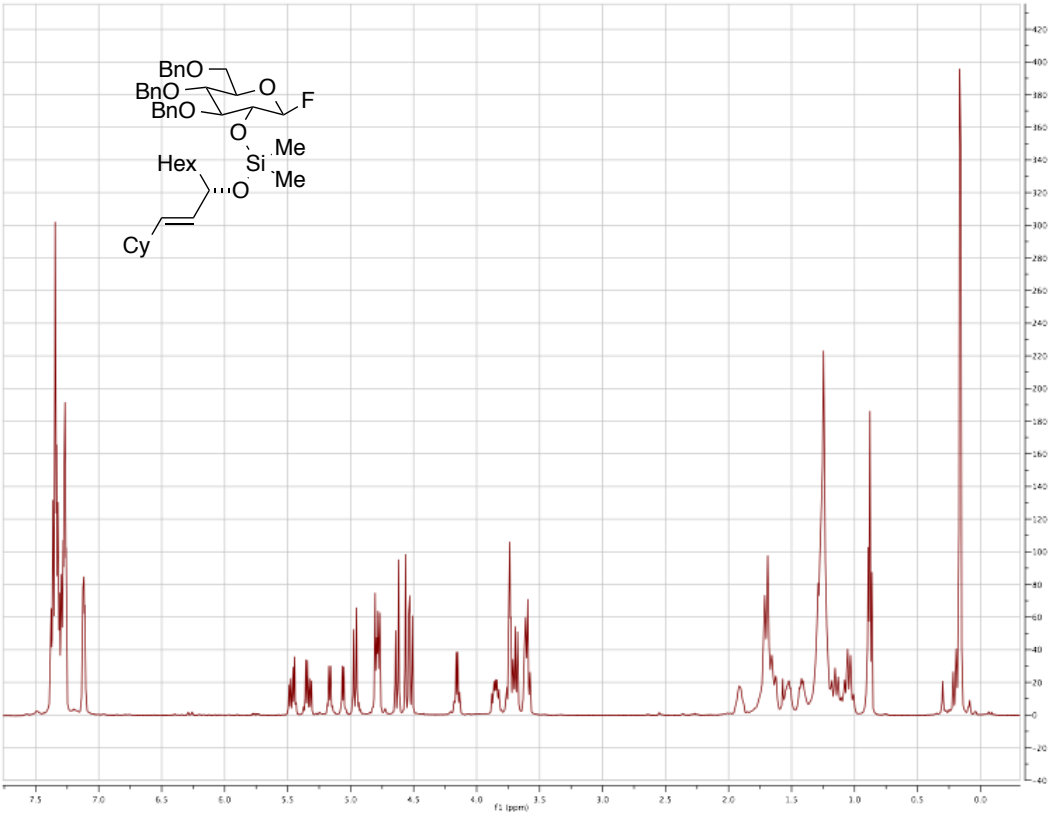


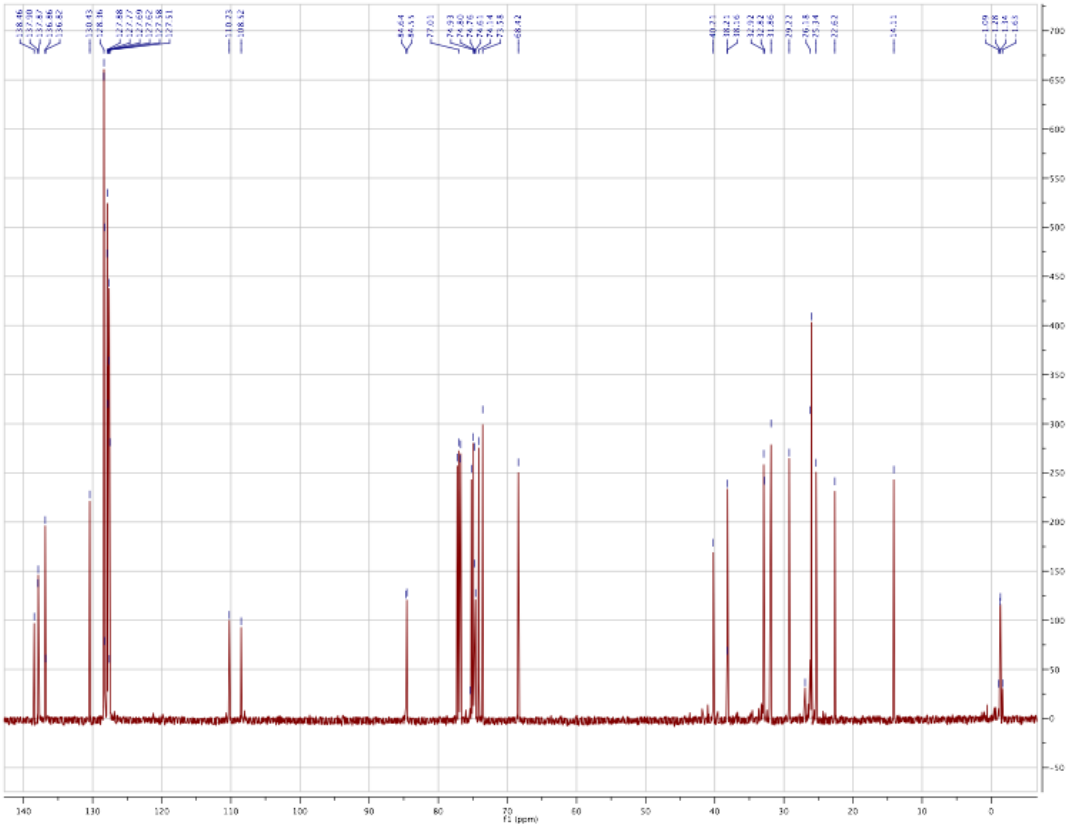
compound **6c**



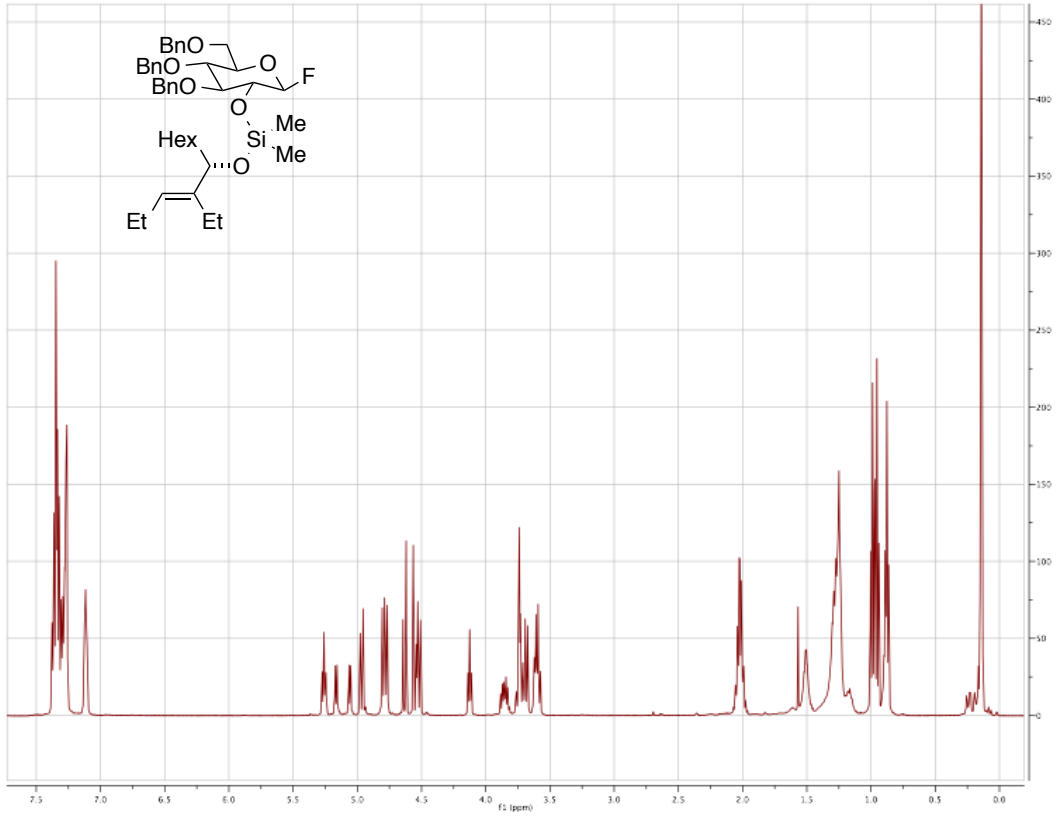


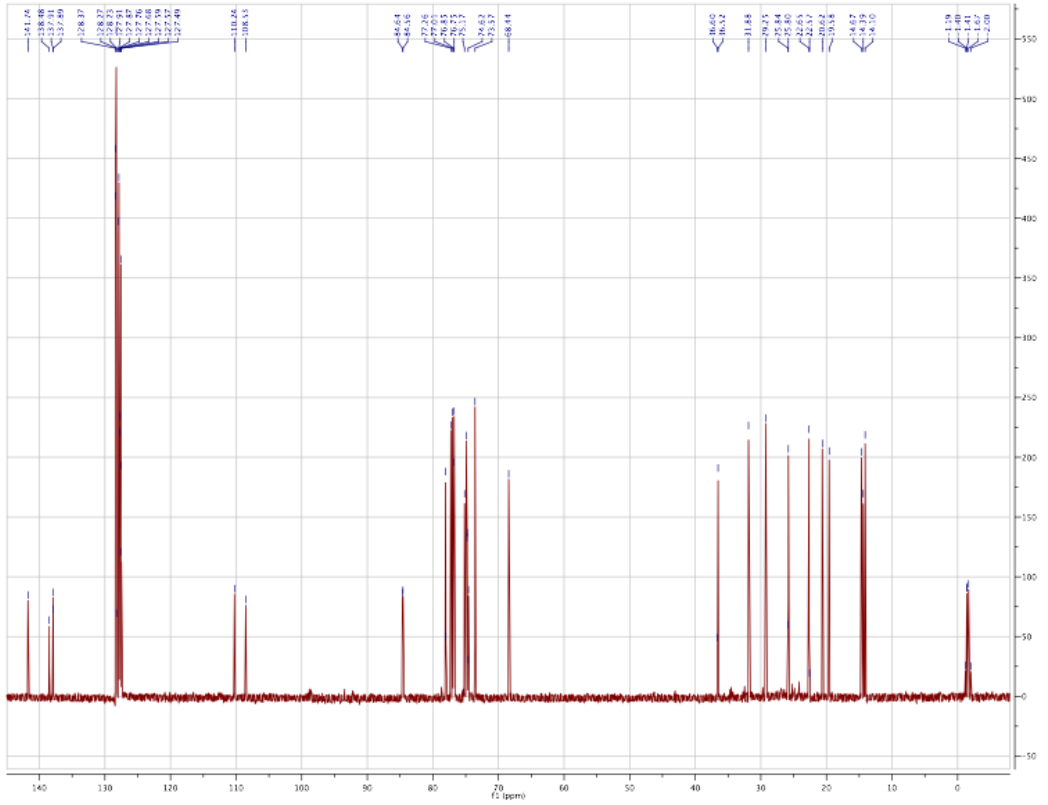
compound **6d**



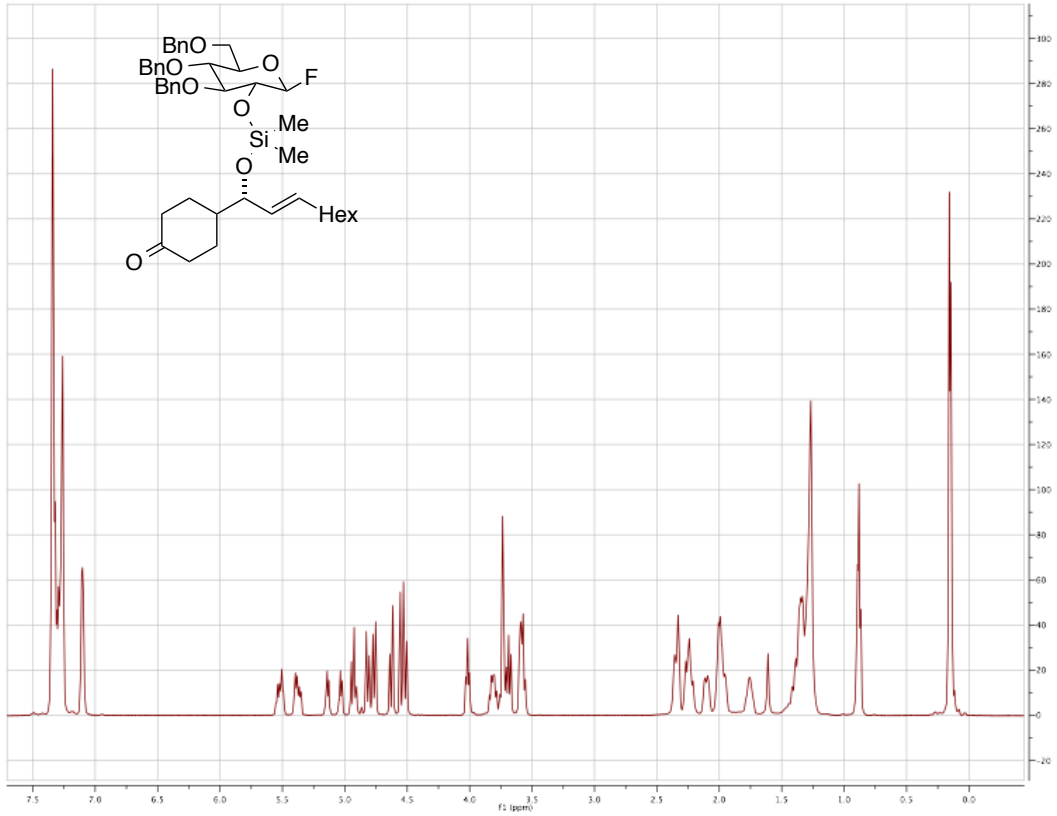


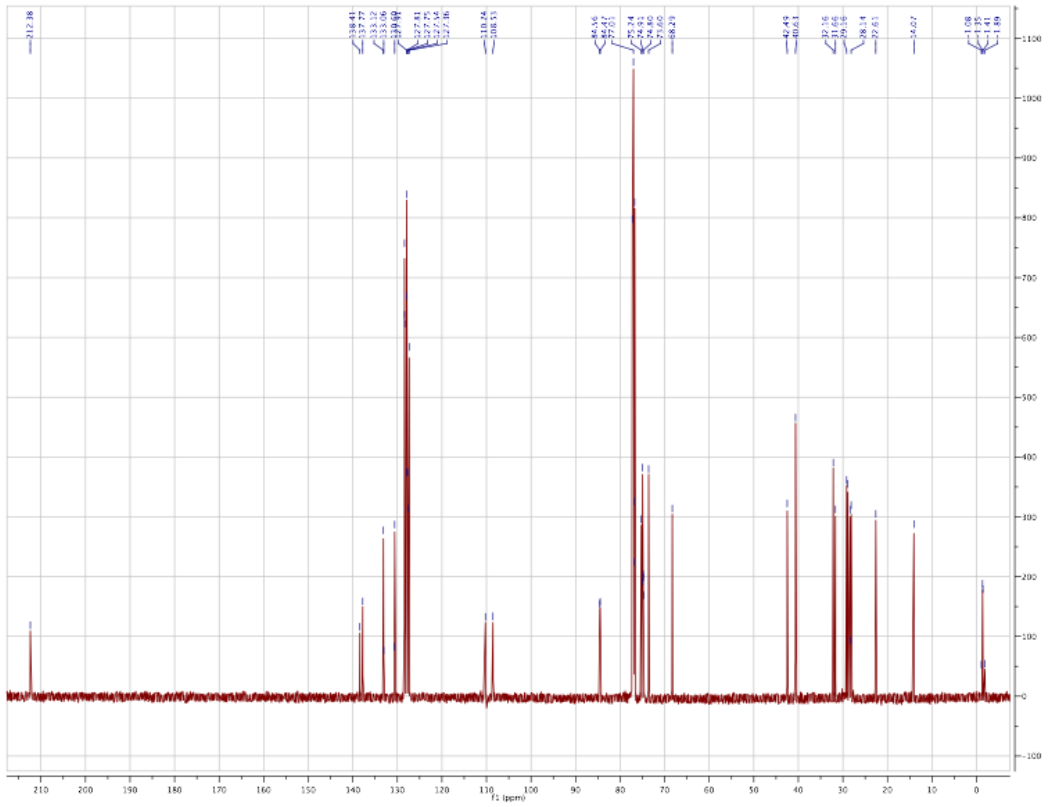
compound **6e**



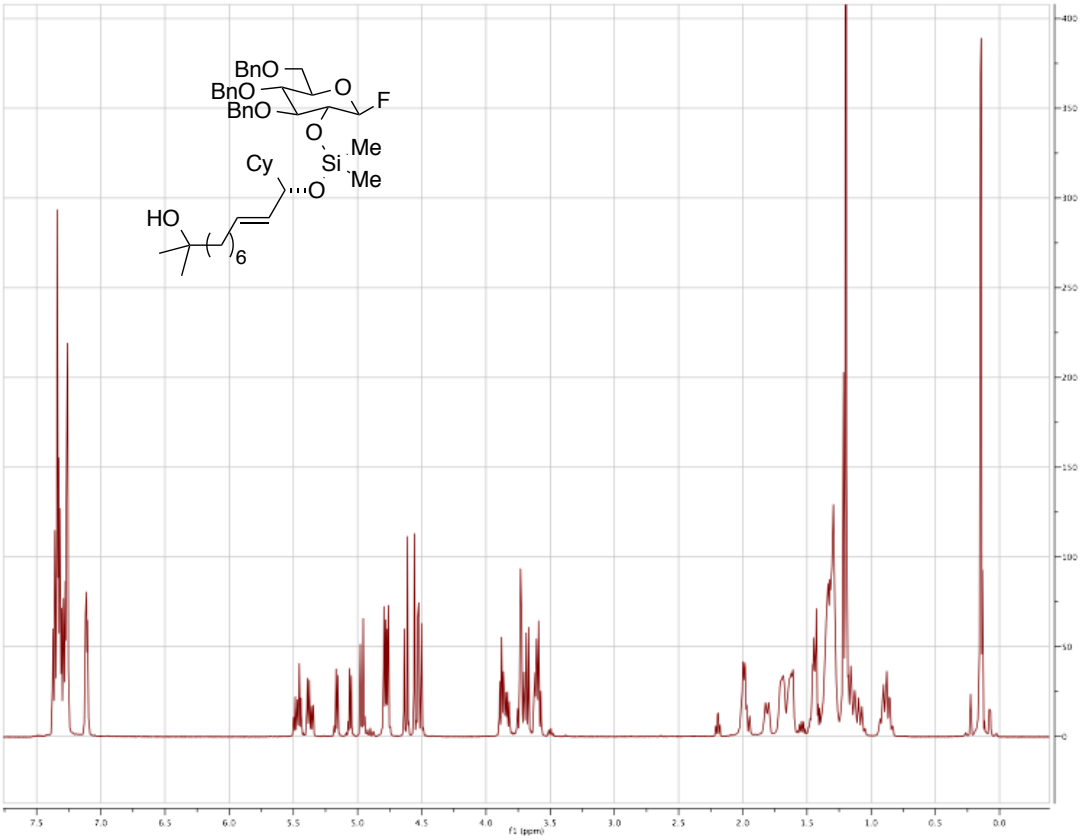


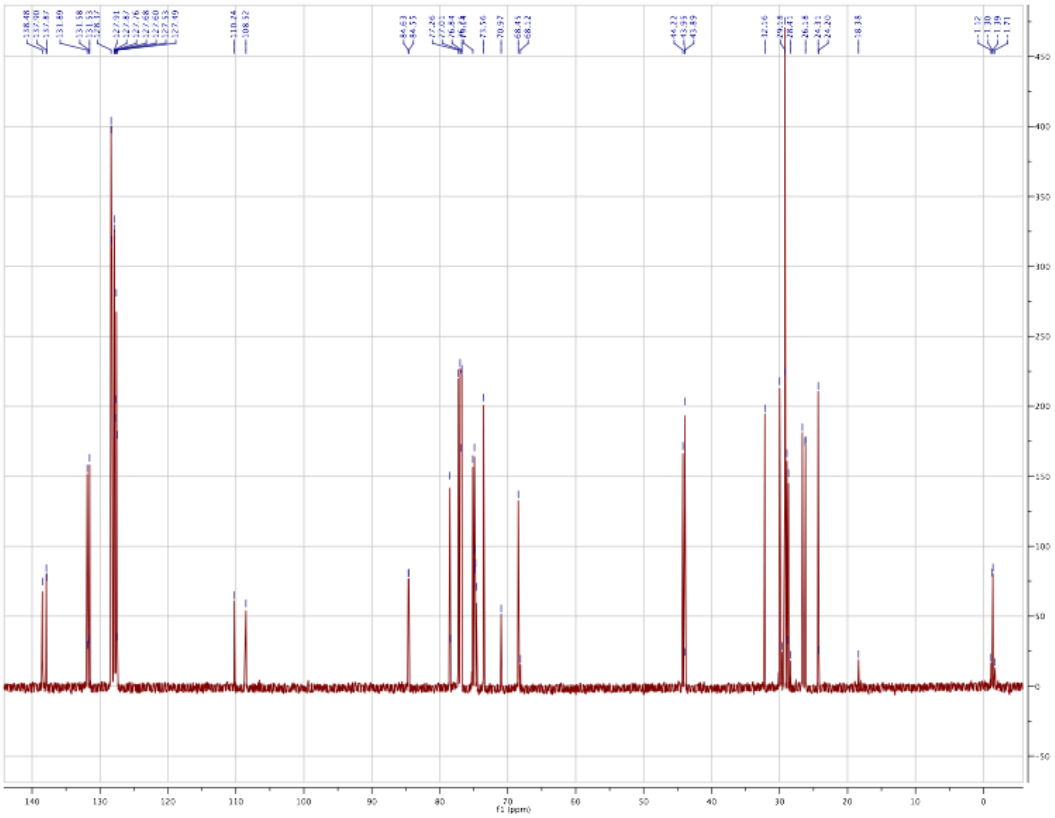
compound **6f**



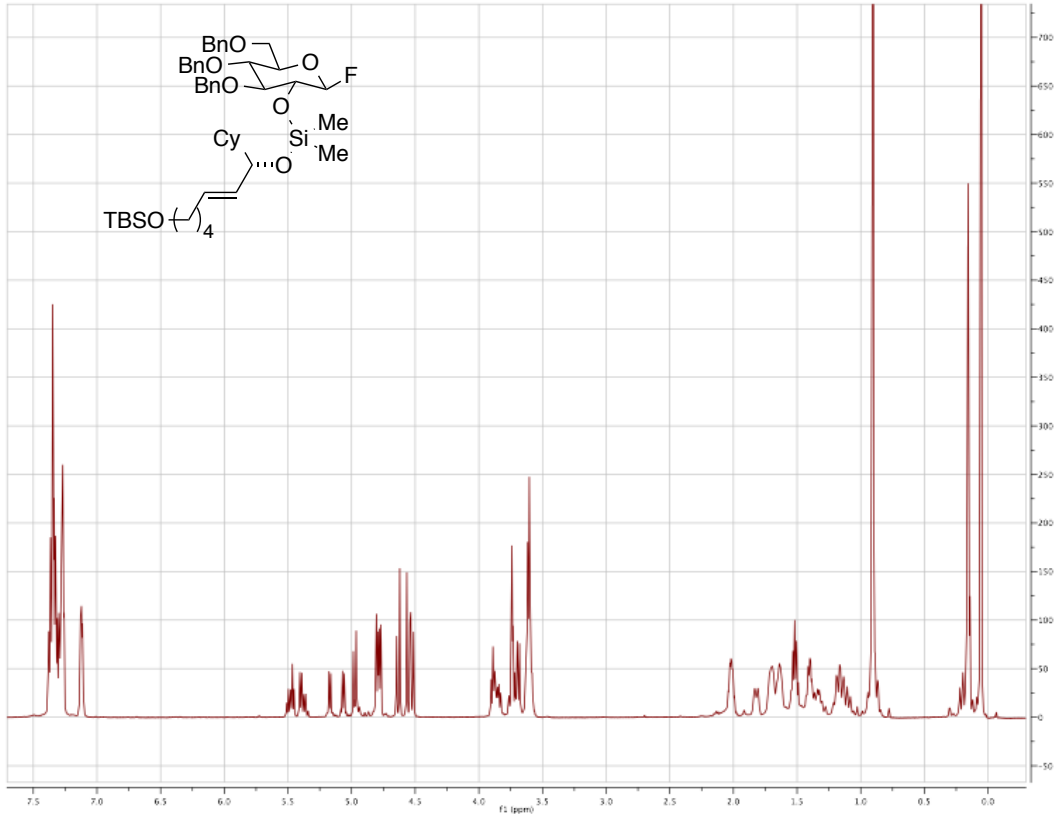


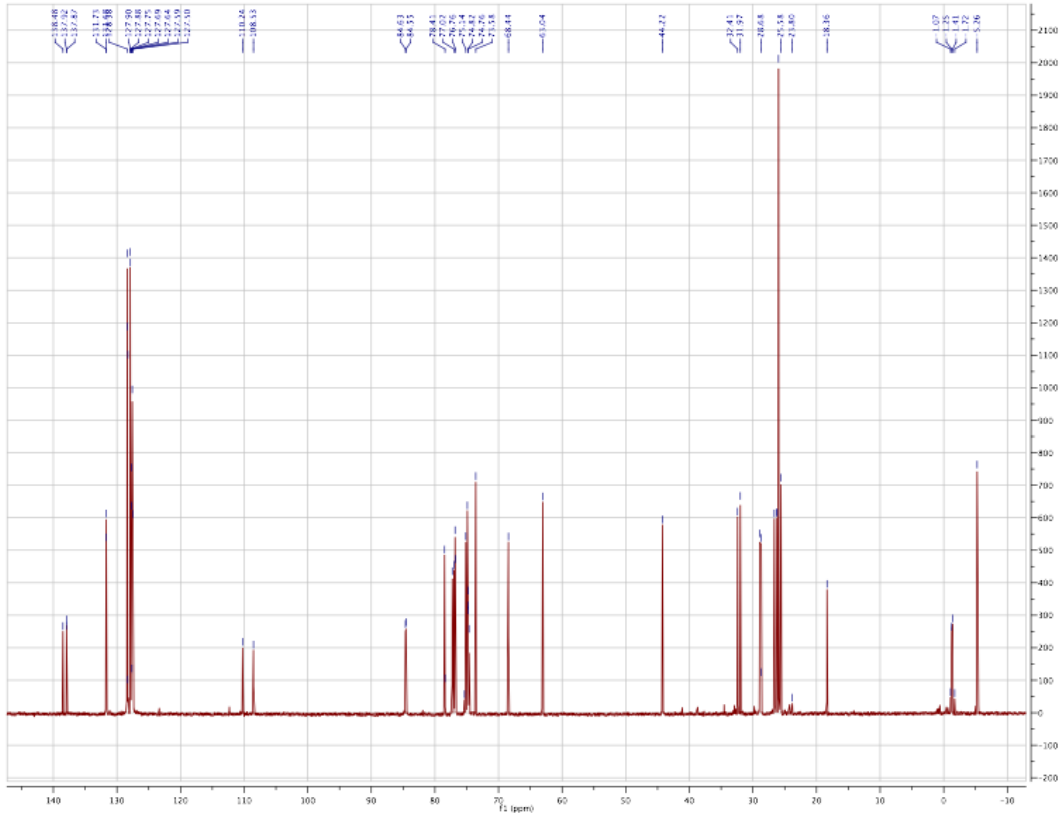
compound **6g**



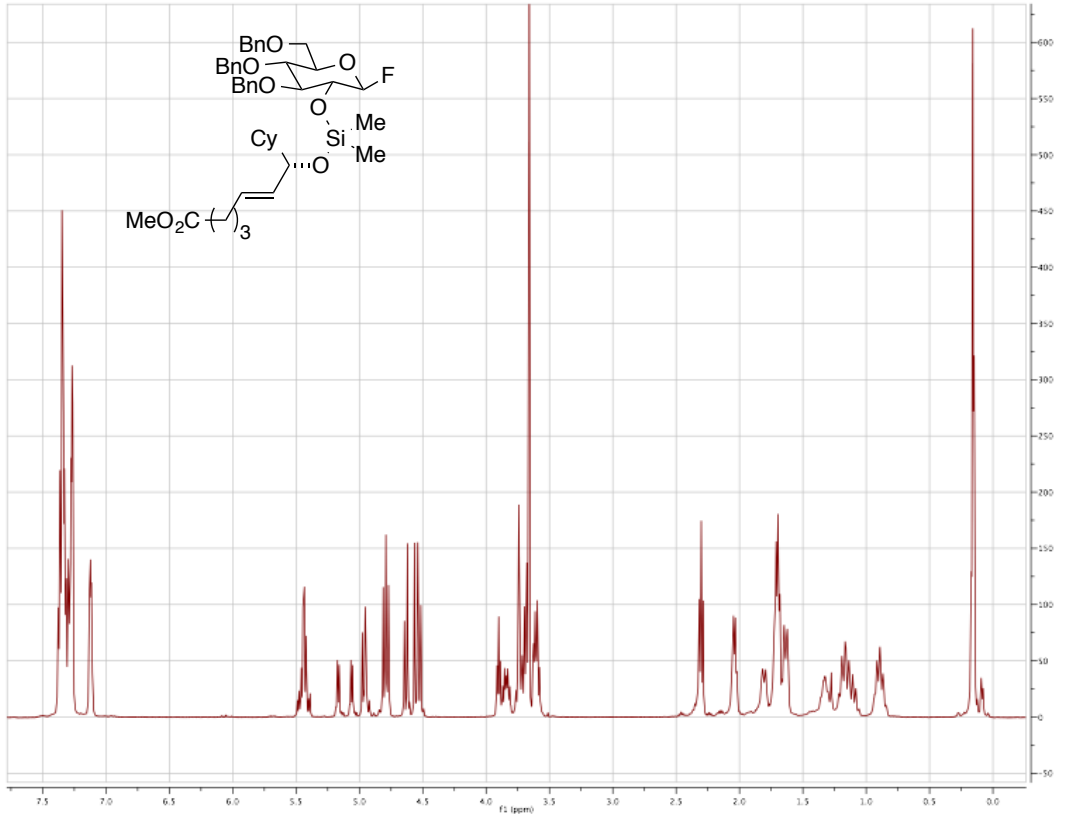


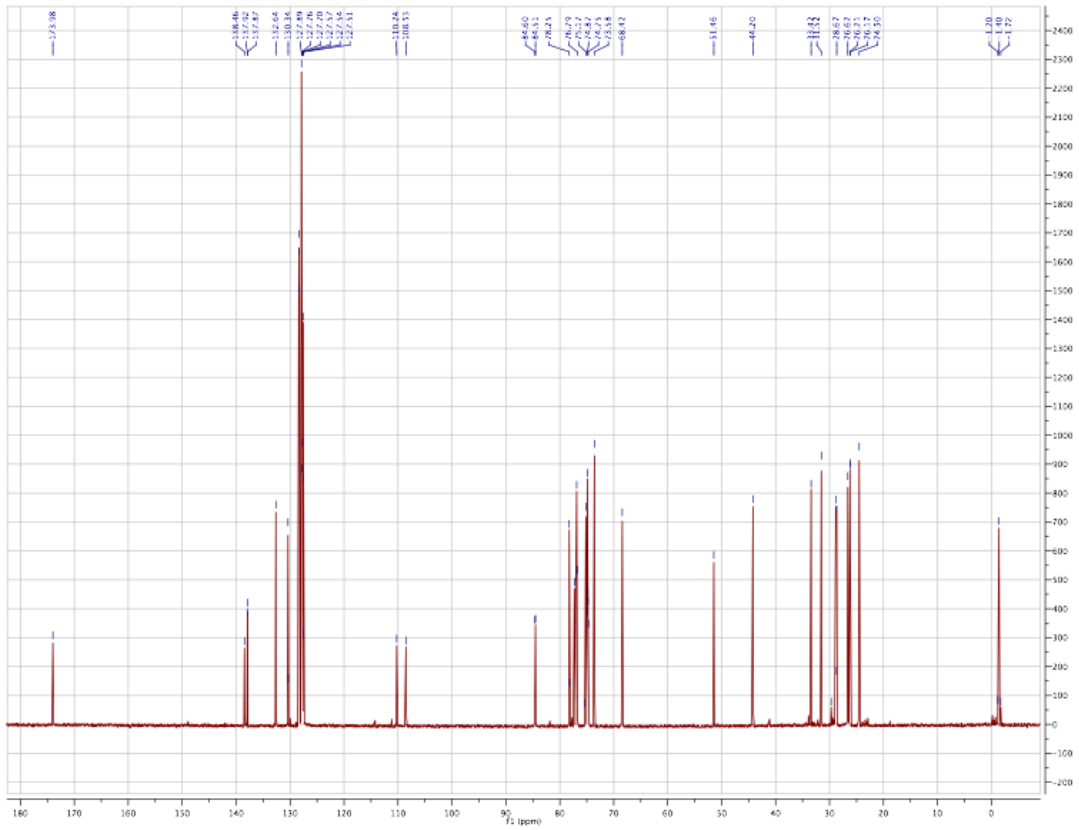
compound **6h**



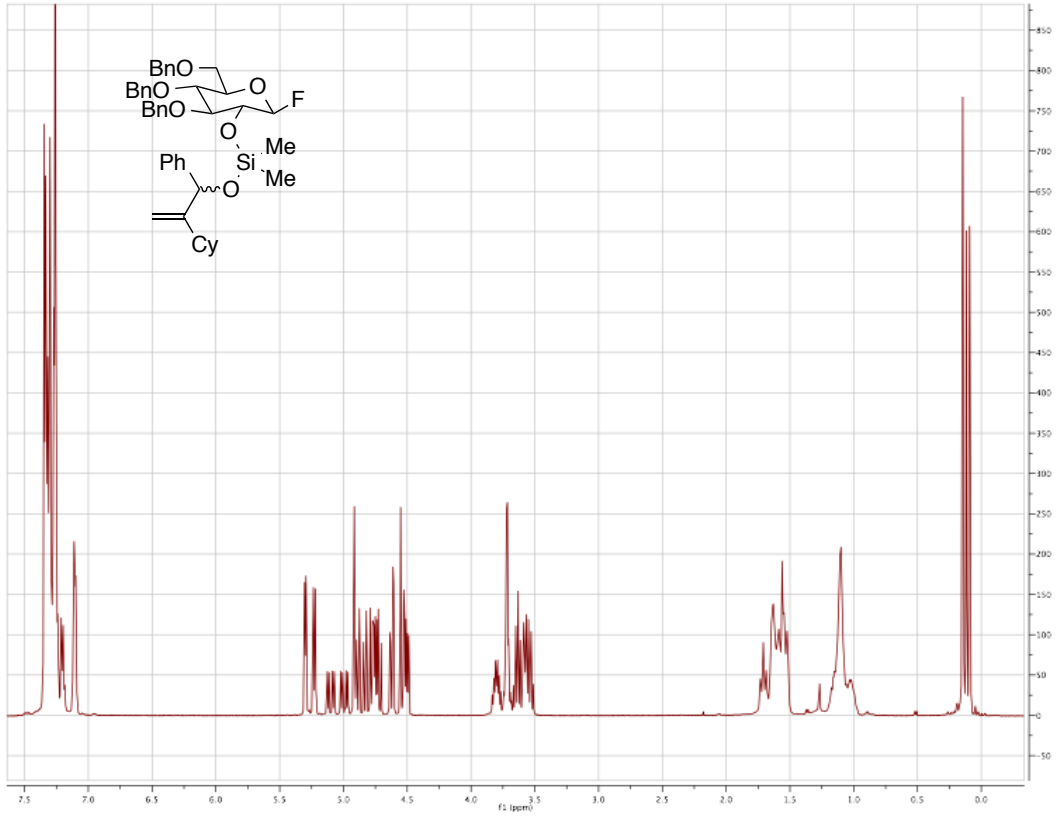


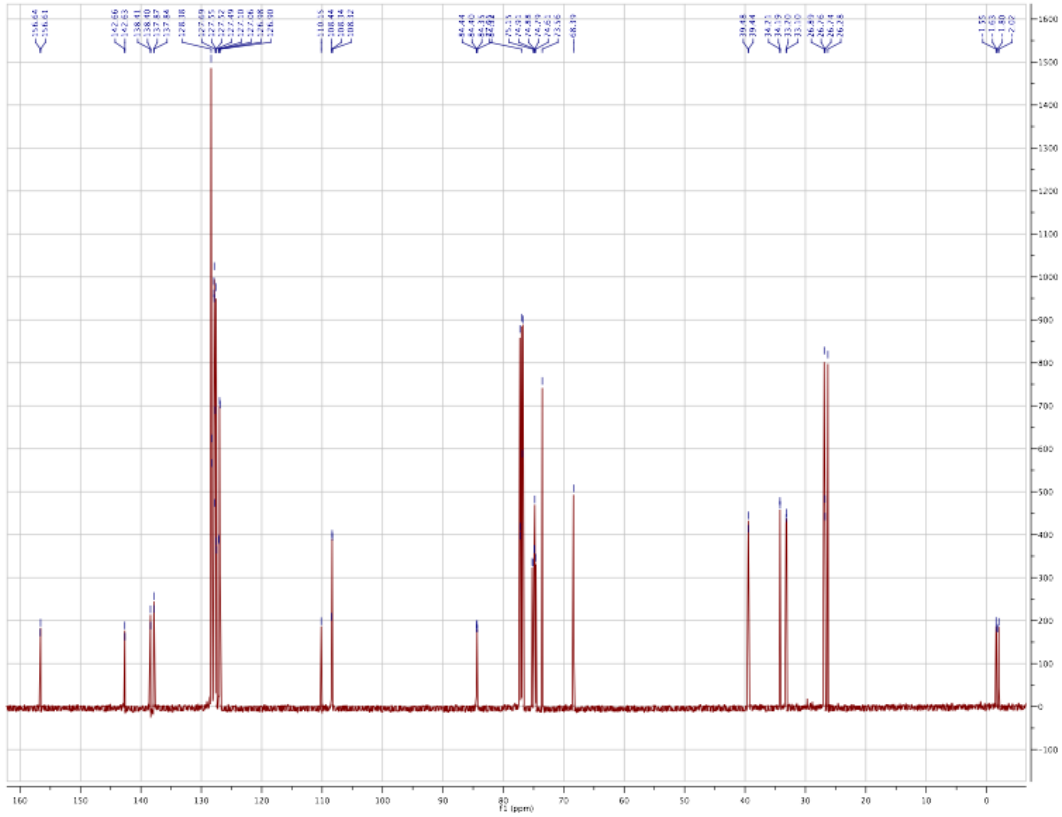
compound **6i**



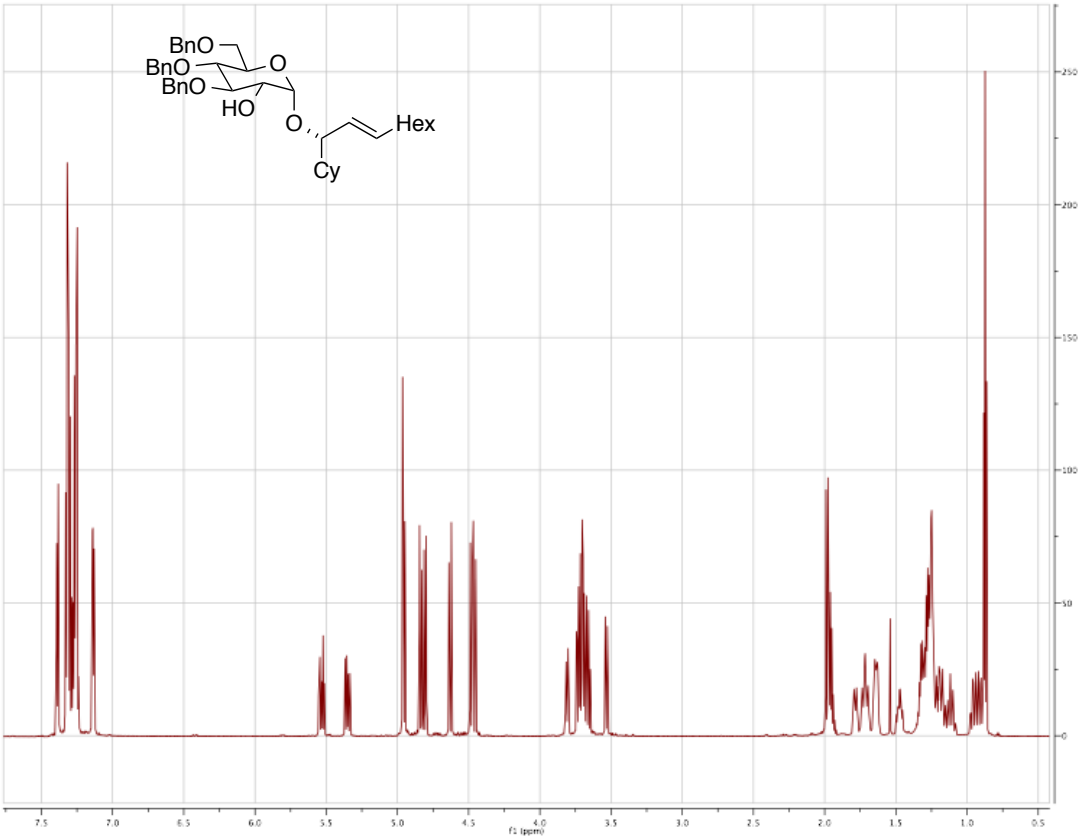


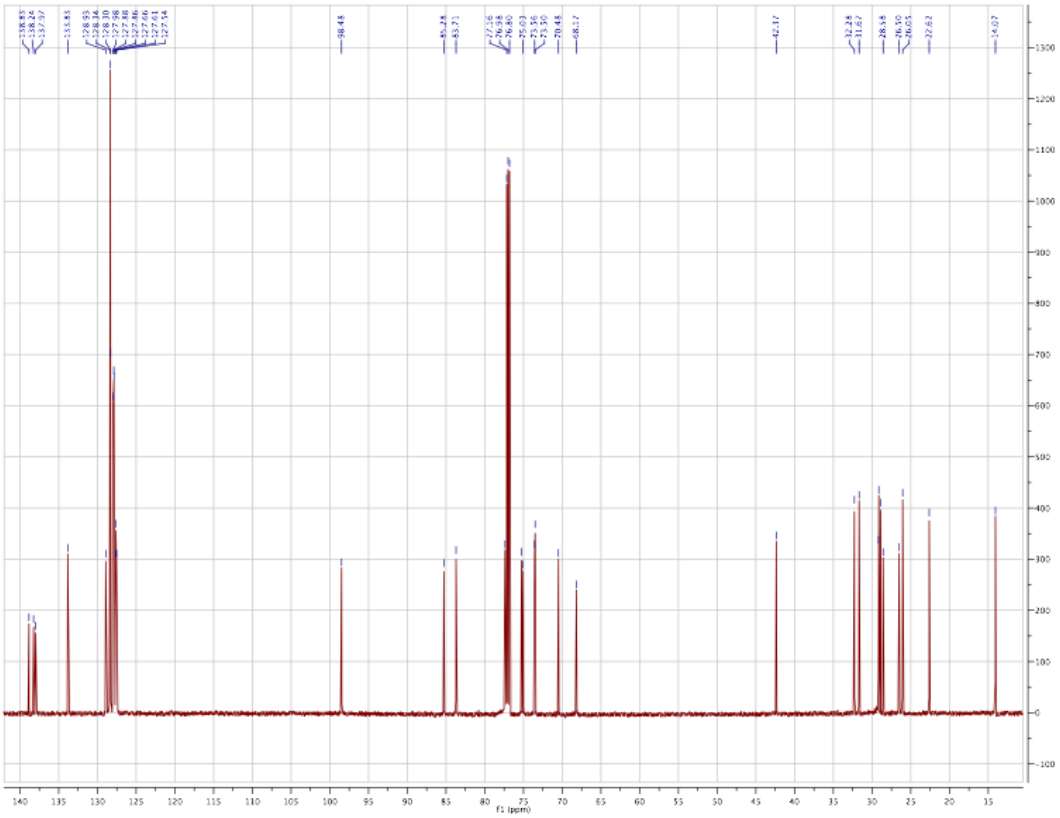
compound **6j**



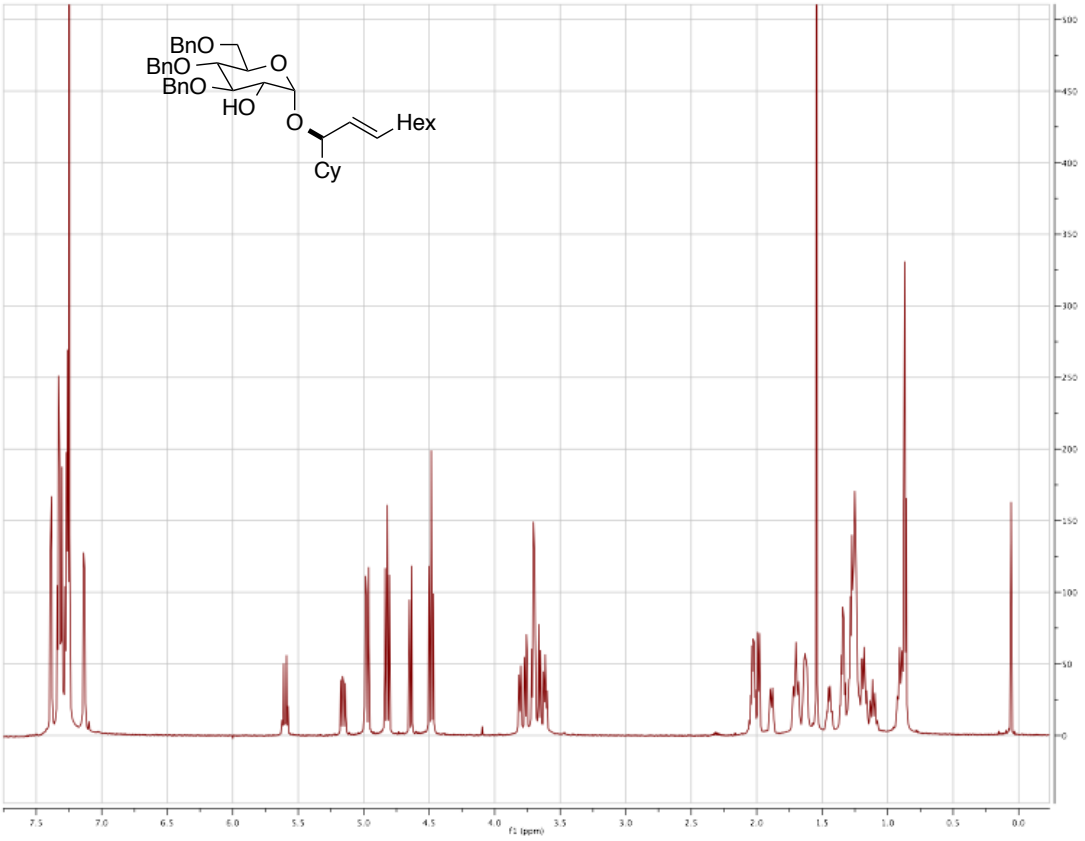


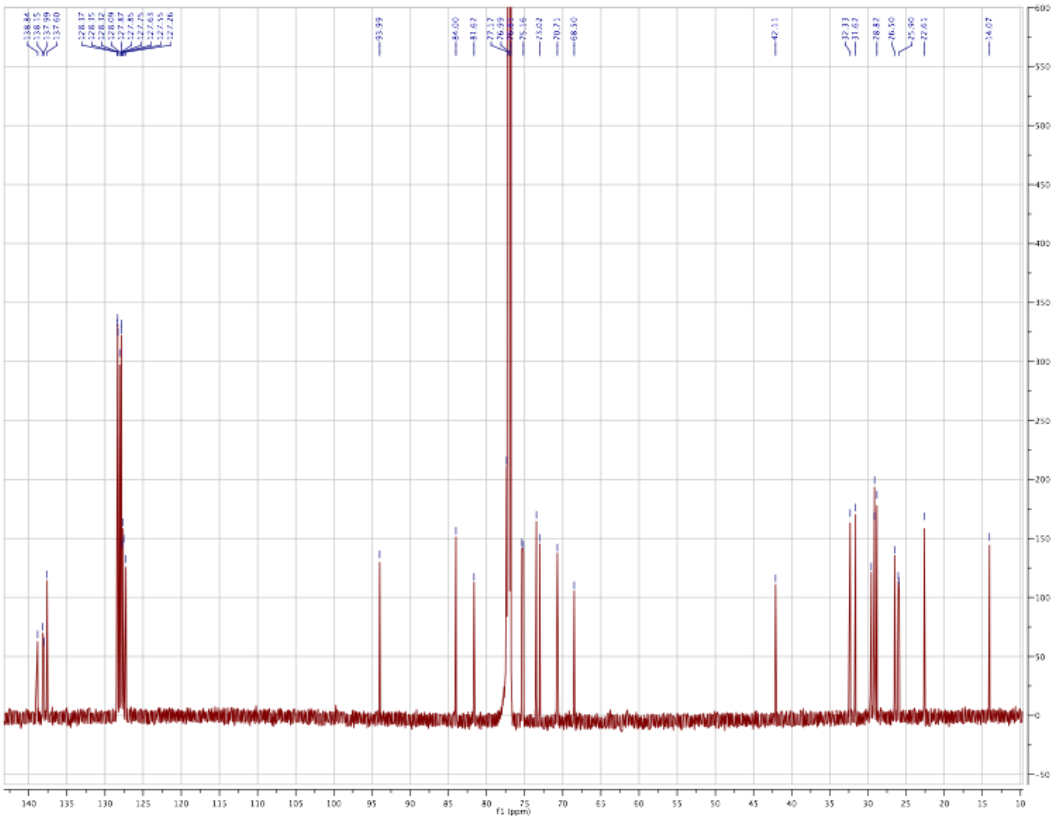
compound **7a** (glycoside from RR-**5**)



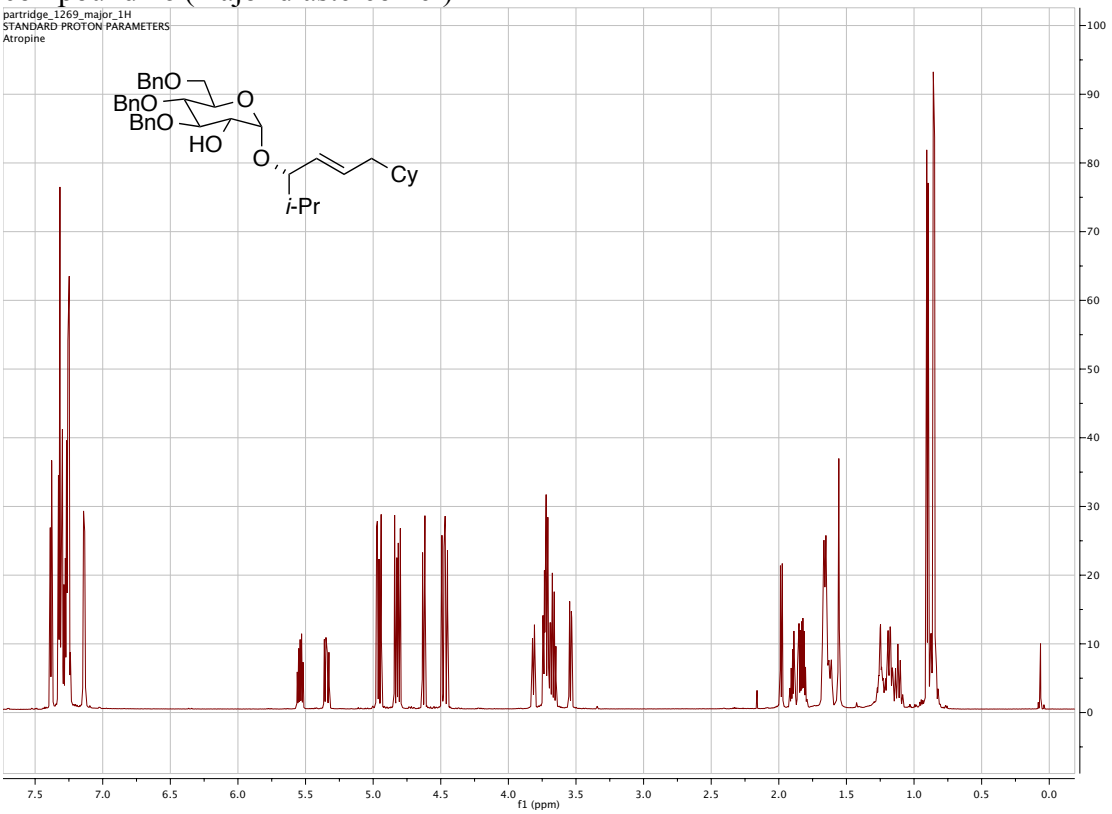


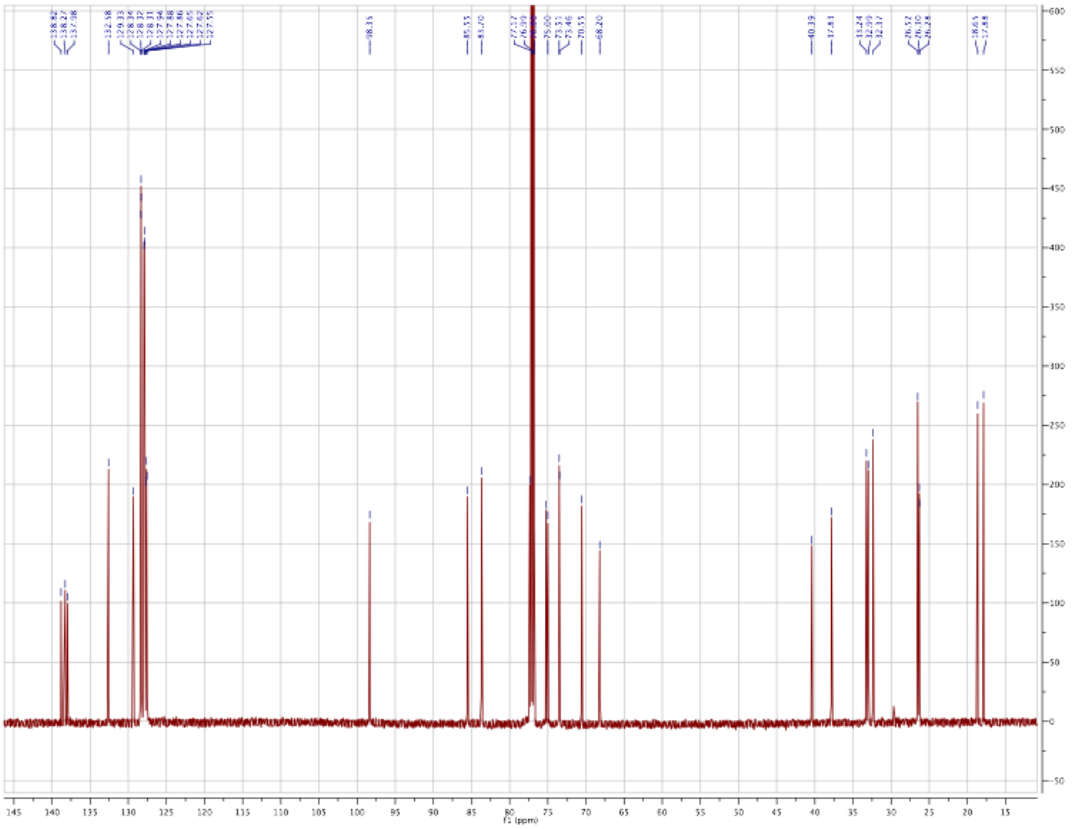
compound **7b** (glycoside from SS-**5**)



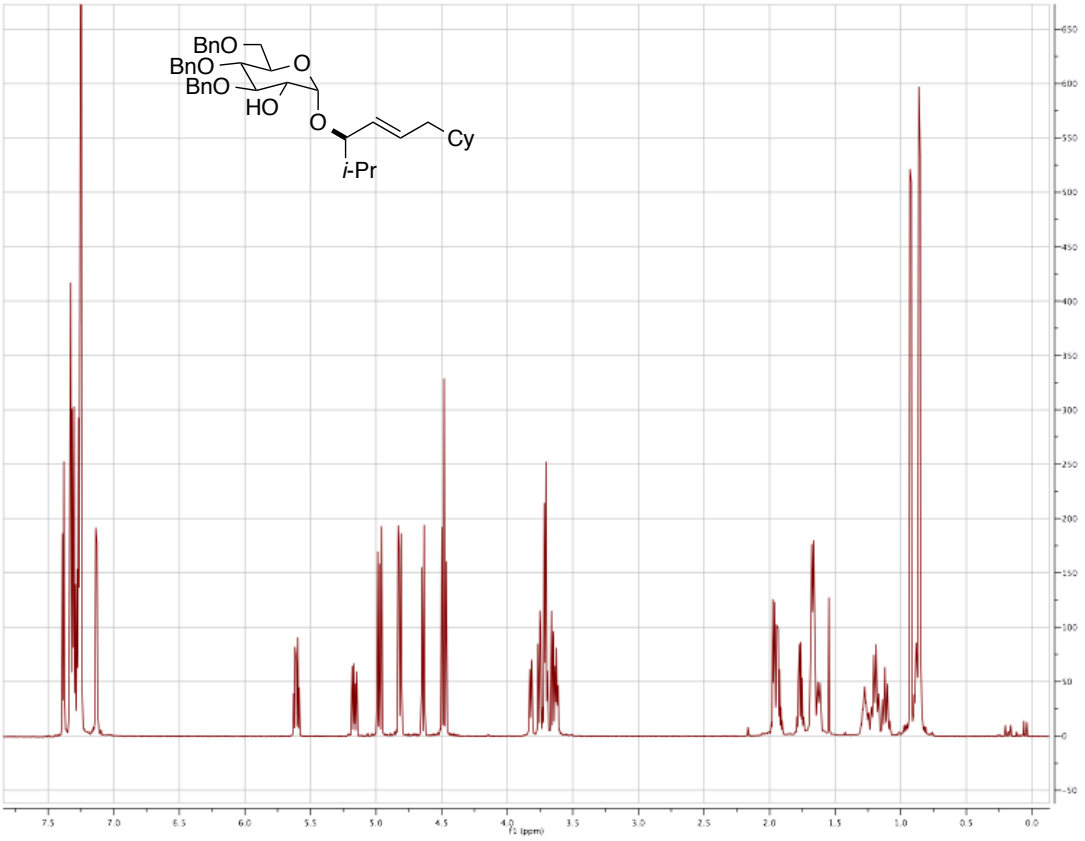


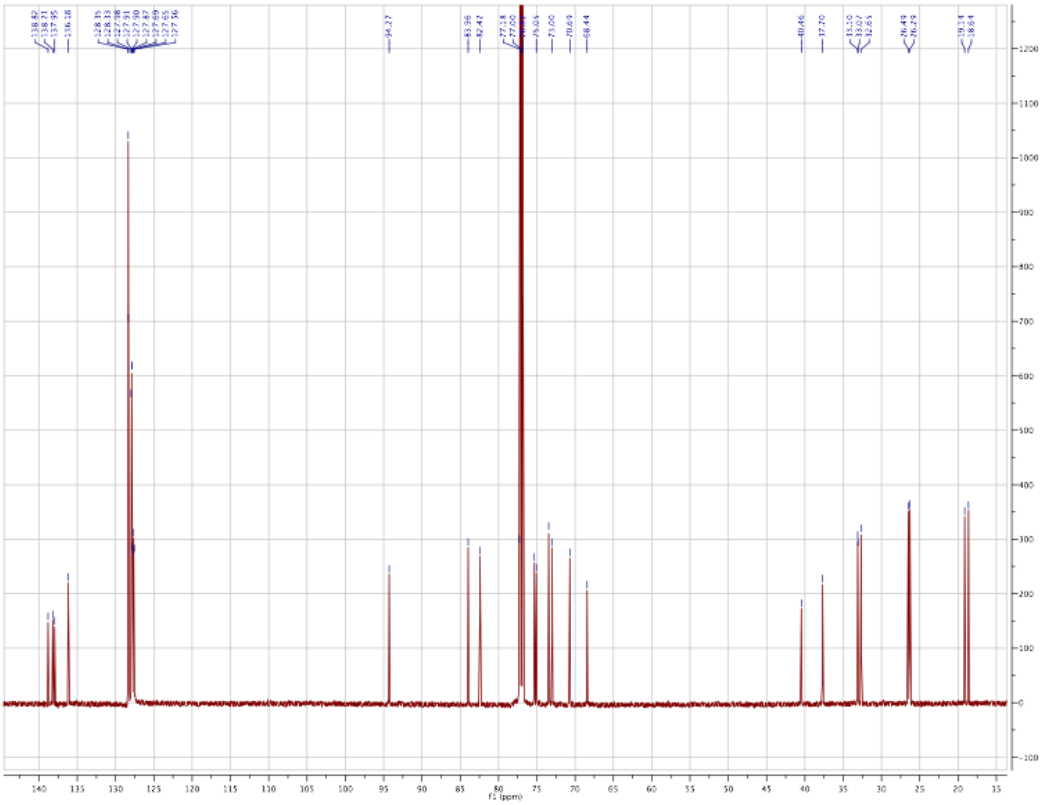
compound **7c** (major diastereomer)



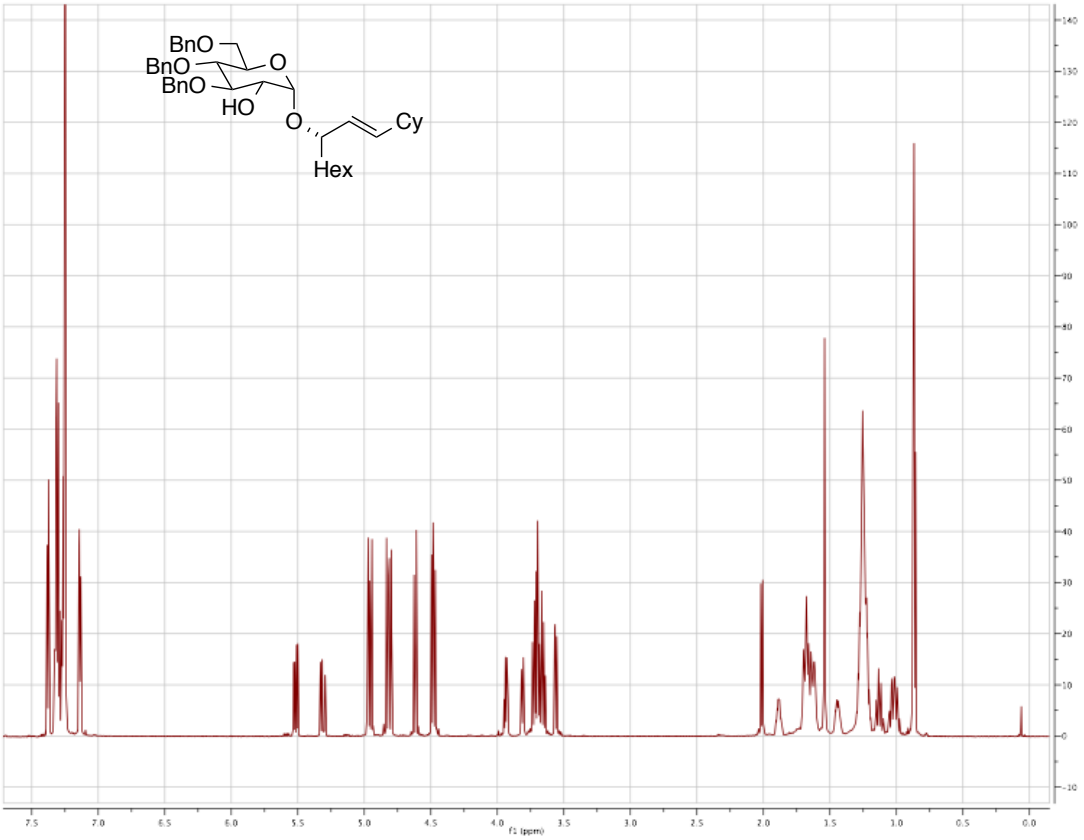


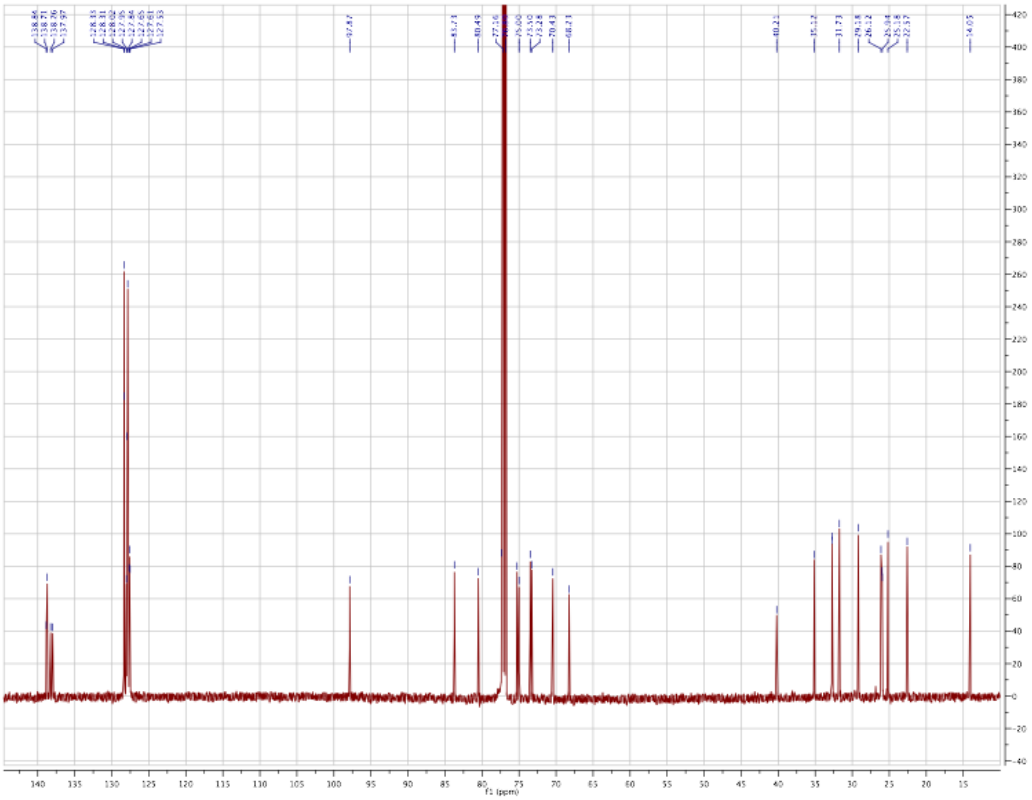
compound **7c** (minor diastereomer)



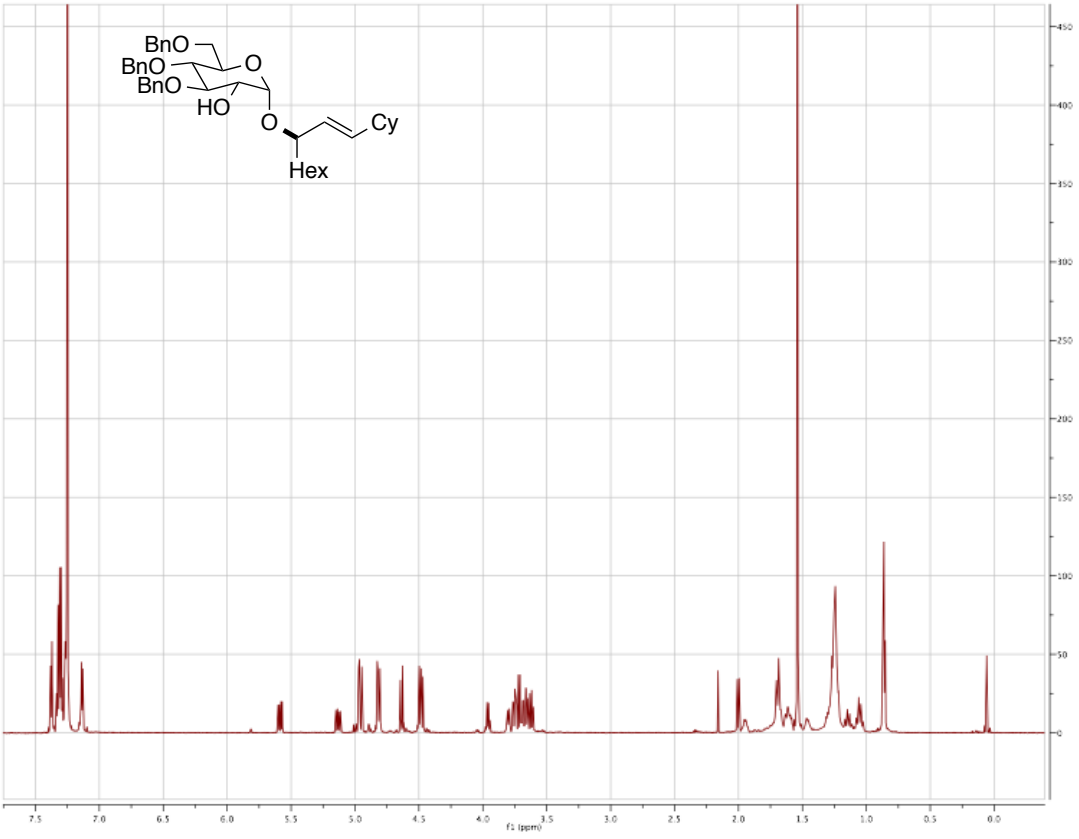


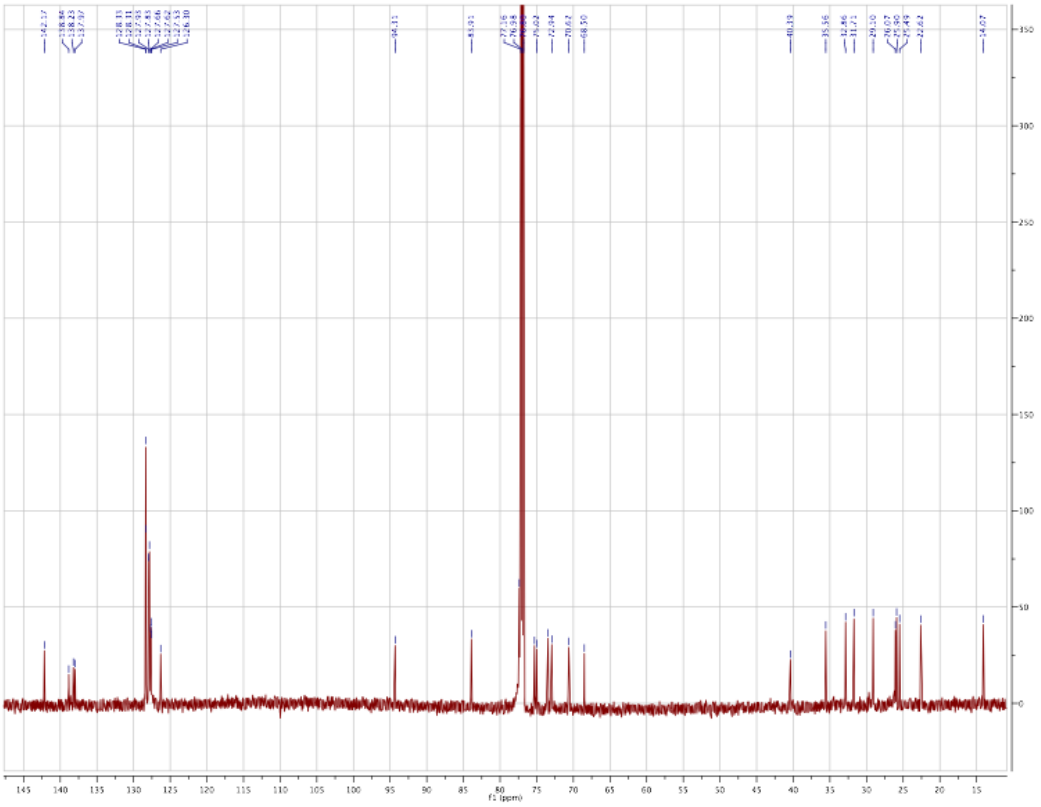
compound **7d** (major diastereomer)



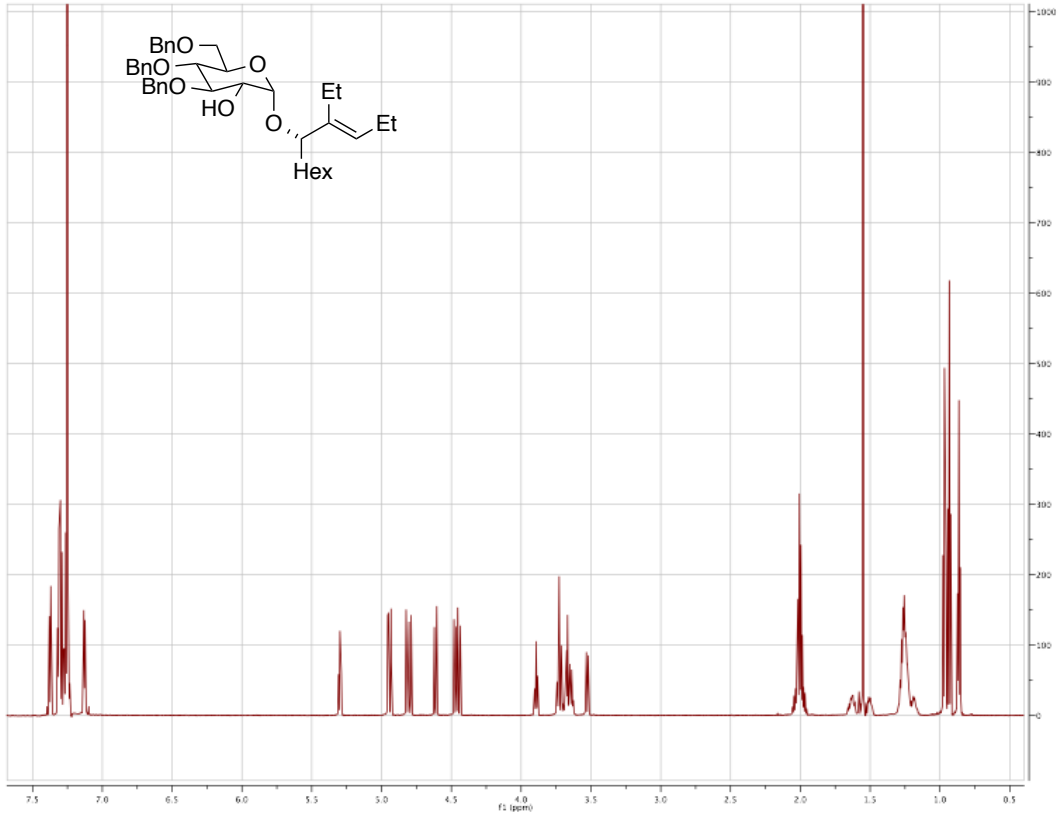


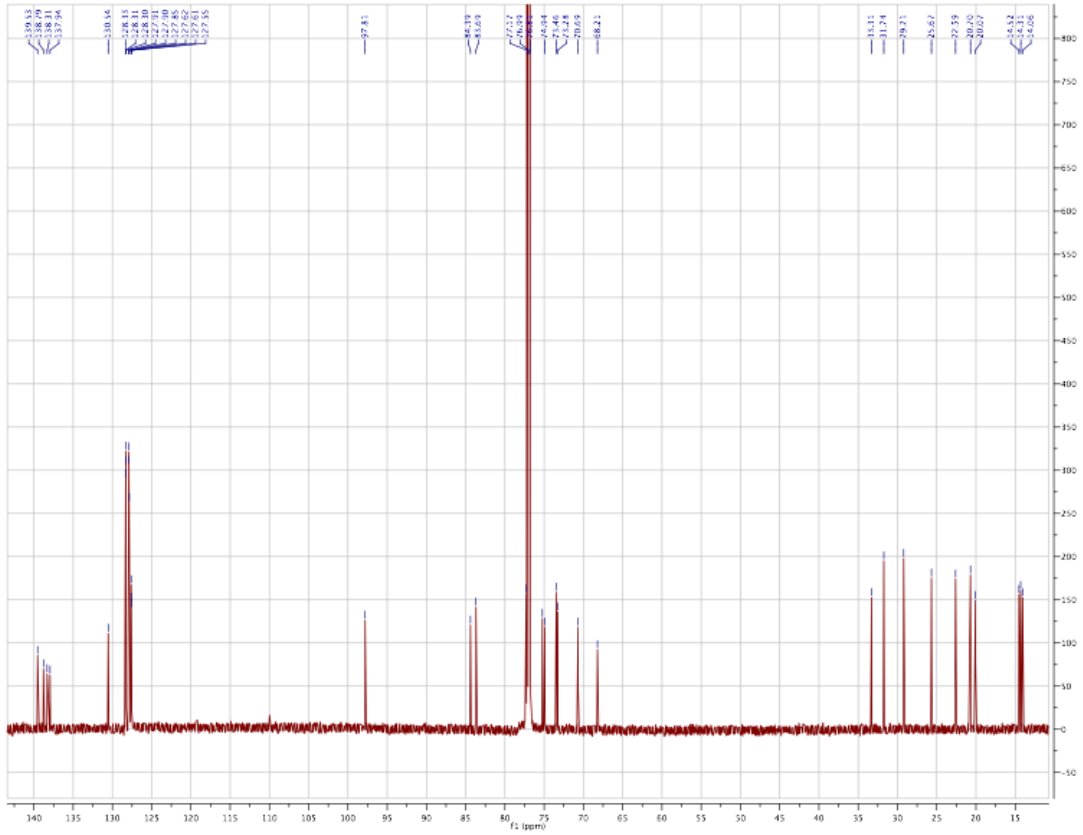
compound **7d** (minor diastereomer)



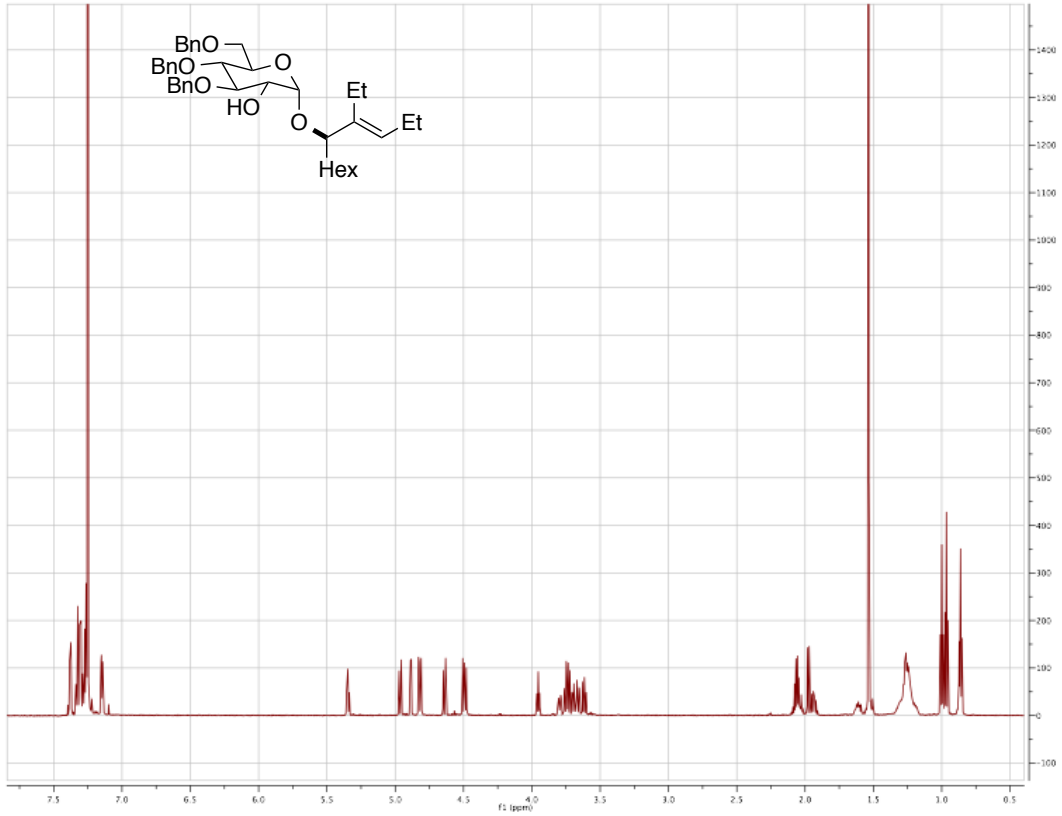


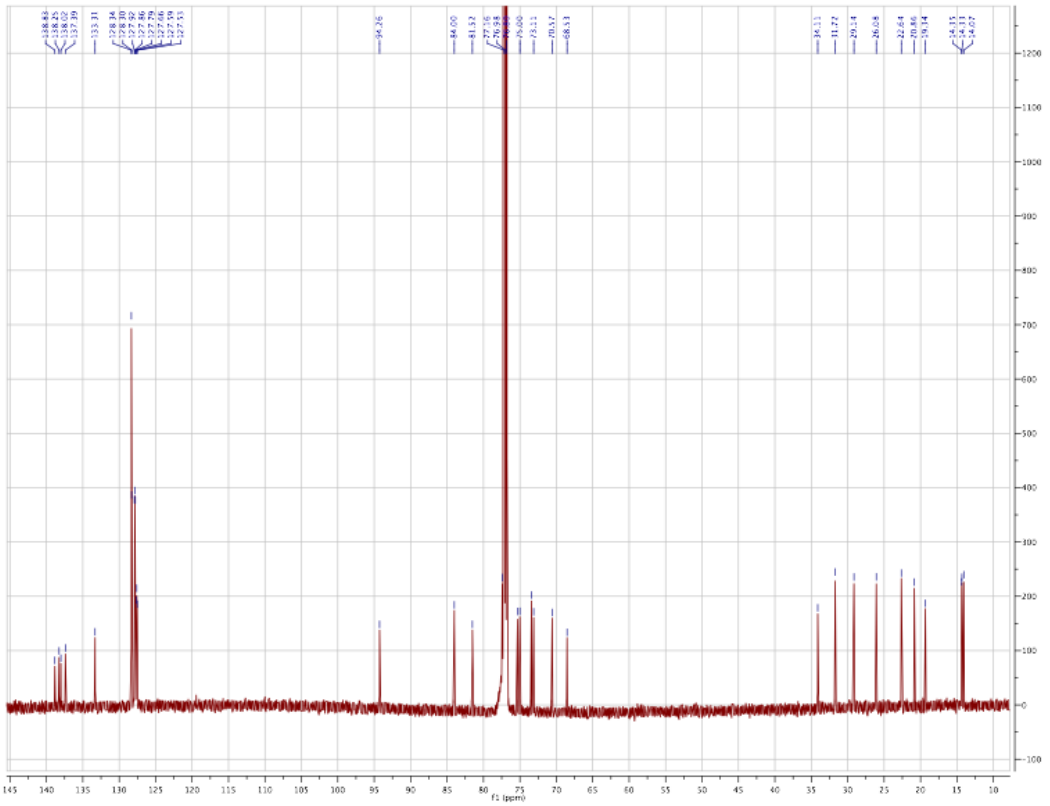
compound **7e** (major diastereomer)



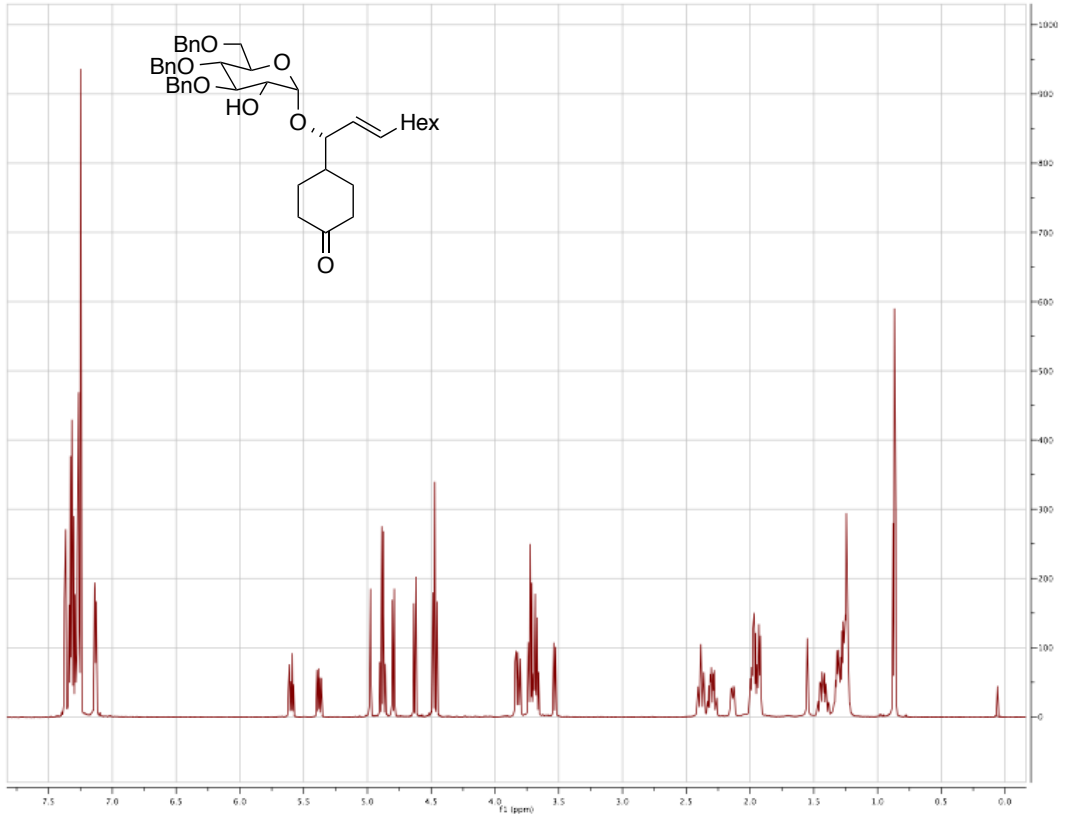


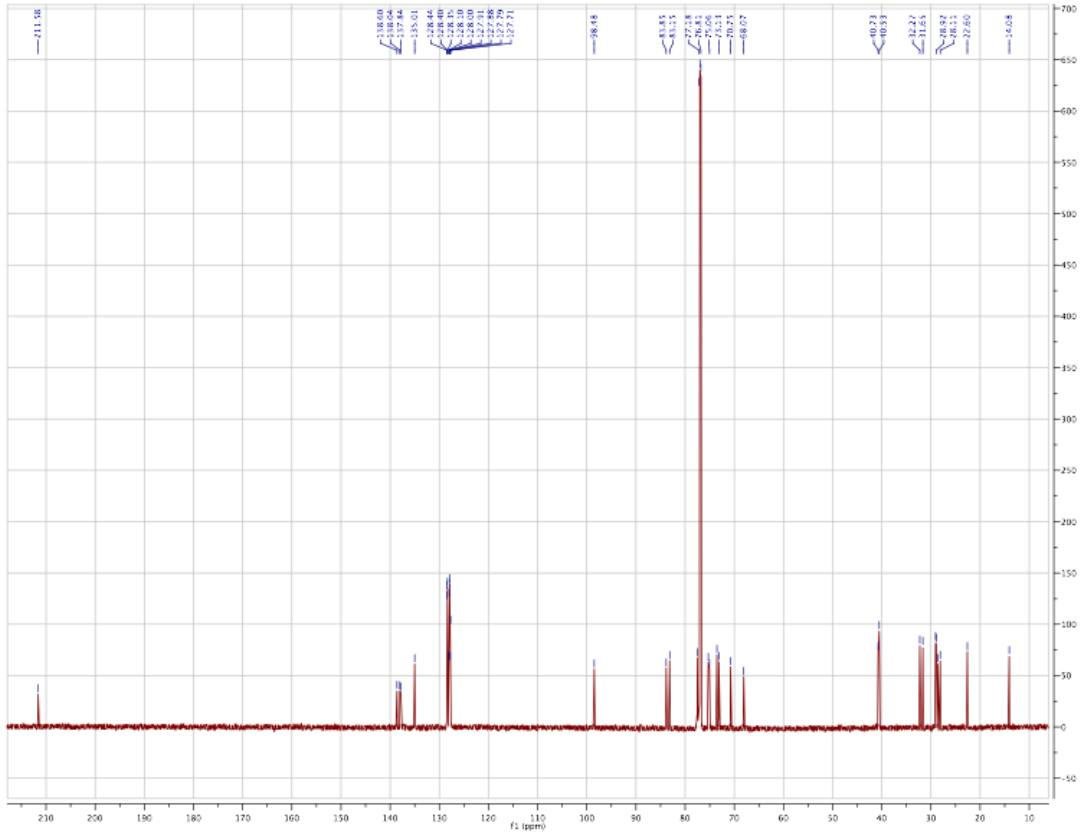
compound **7e** (minor diastereomer)



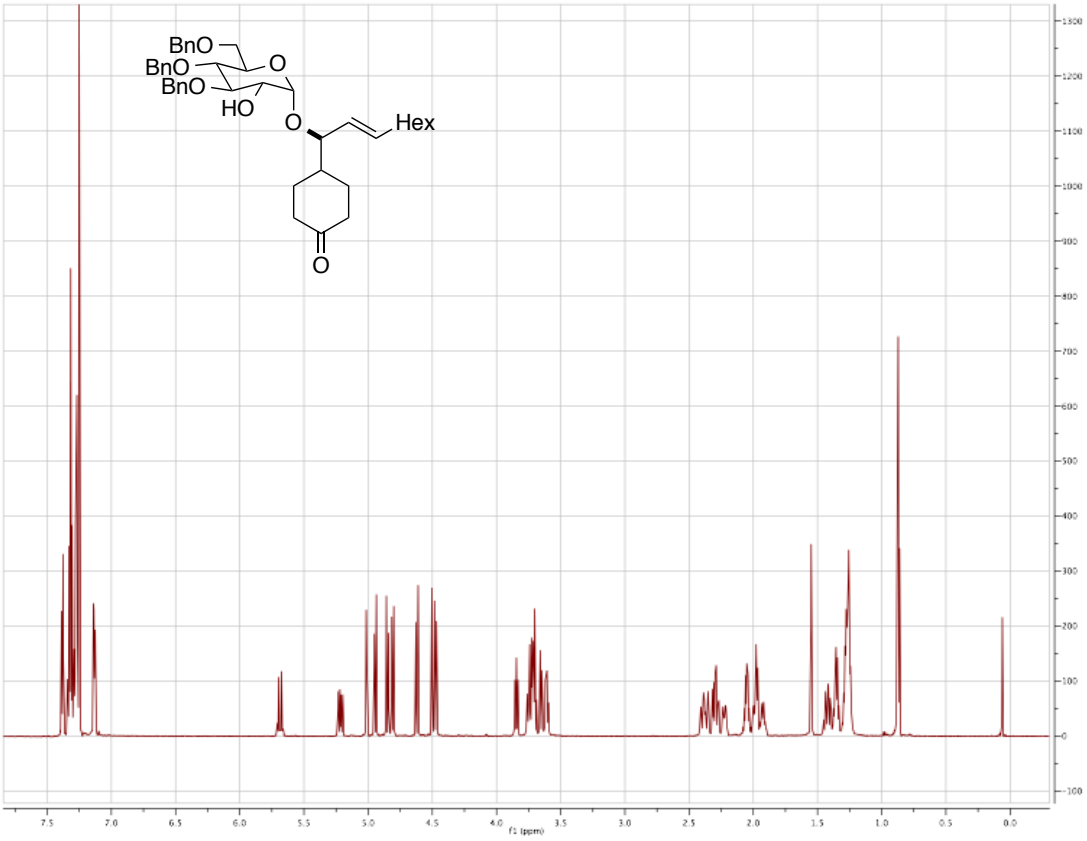


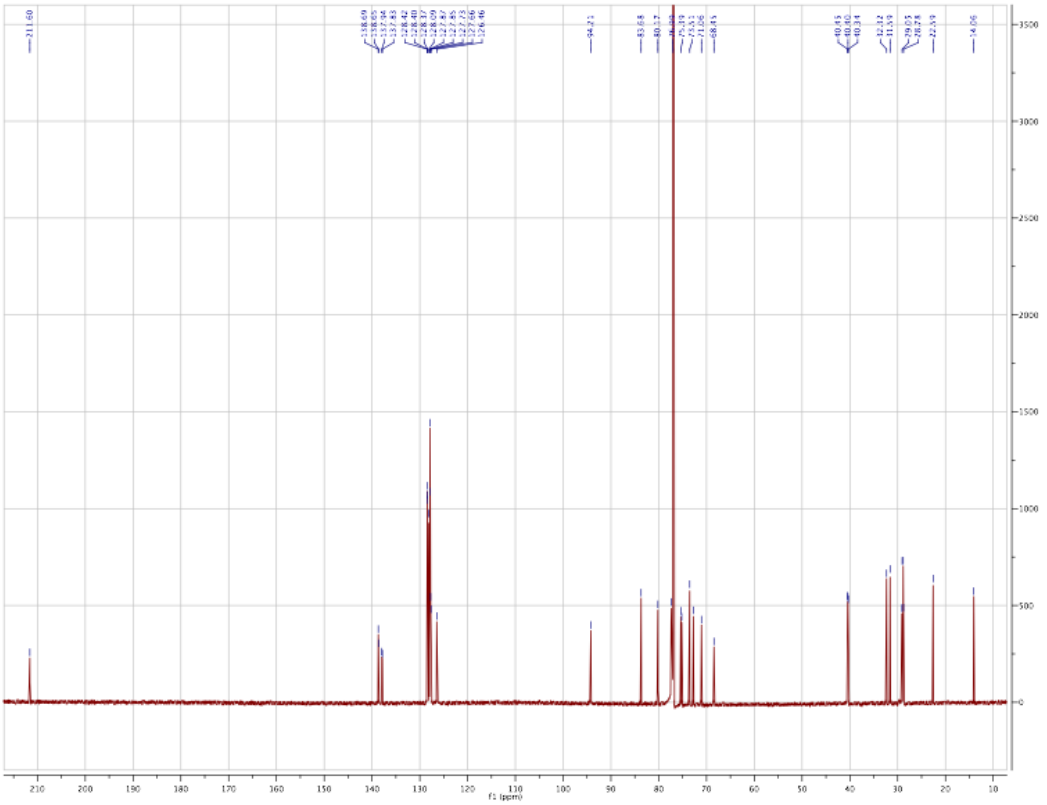
compound **7f** (major diastereomer)



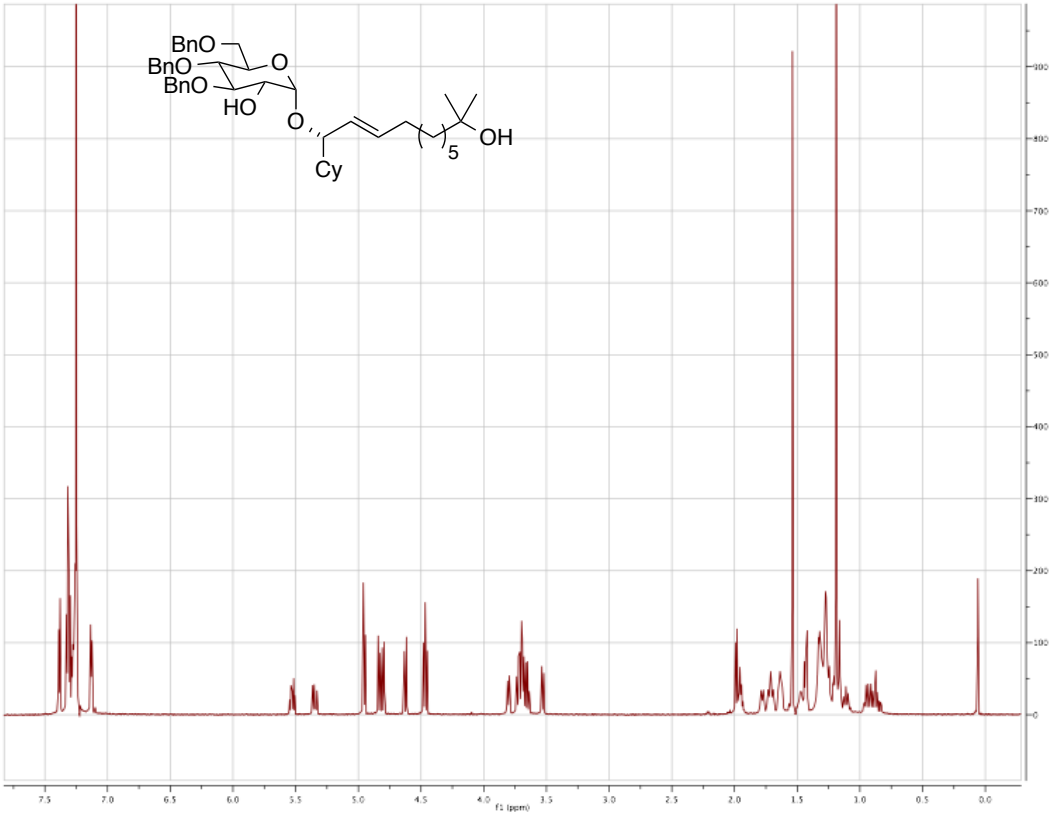


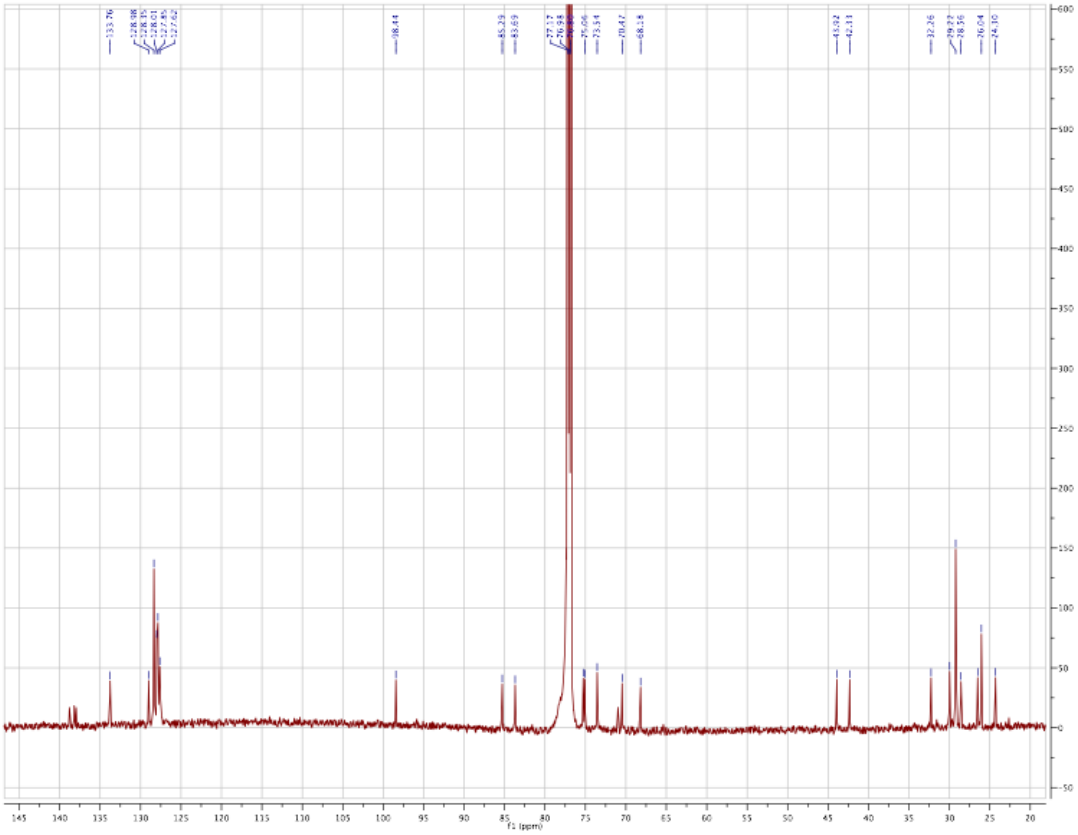
compound **7f** (minor diastereomer)



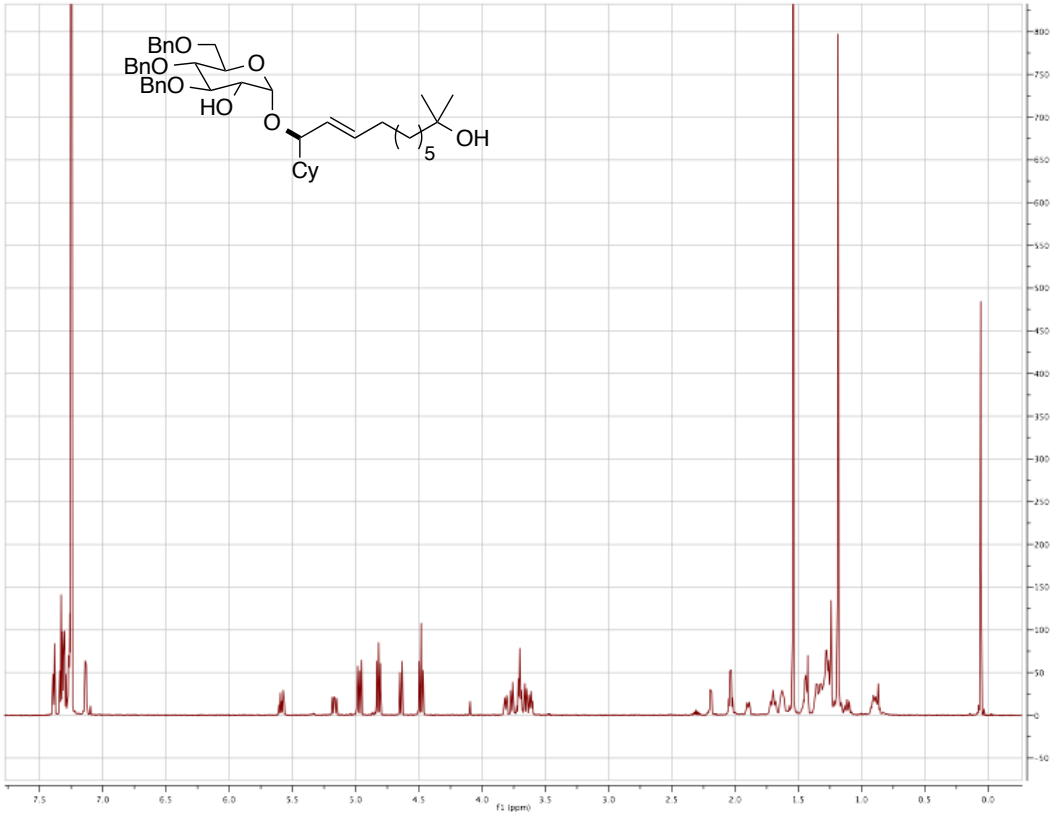


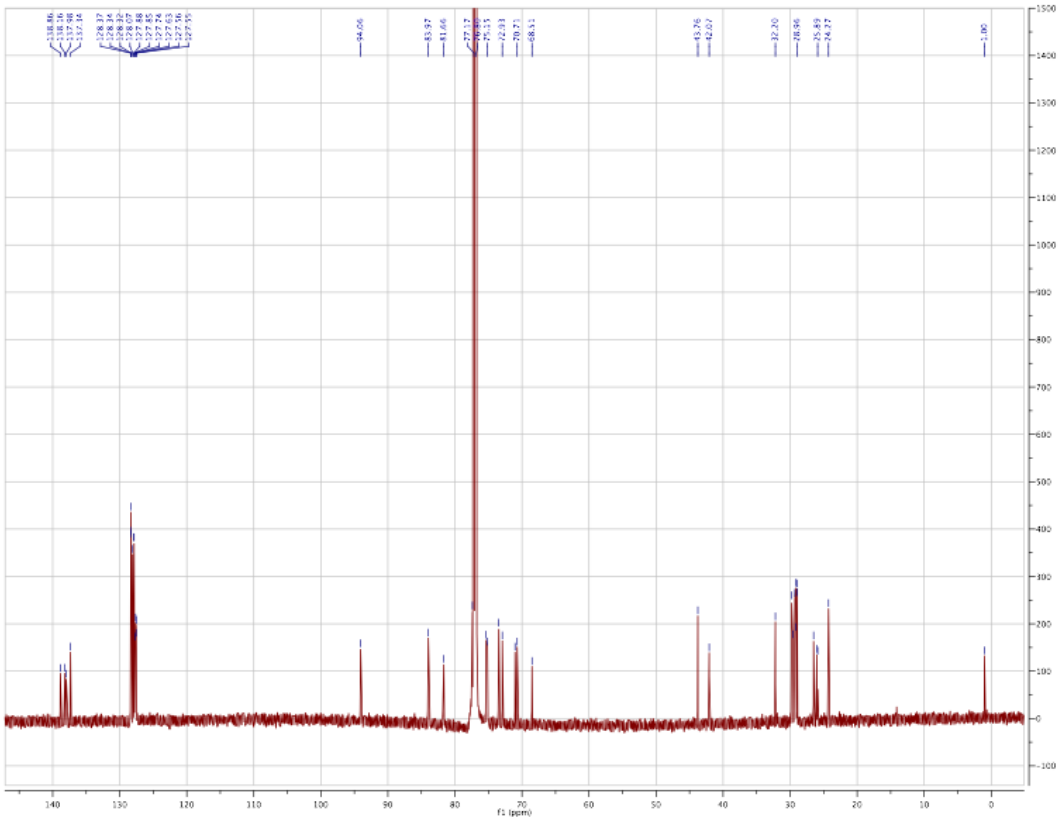
compound **7g** (major diastereomer)



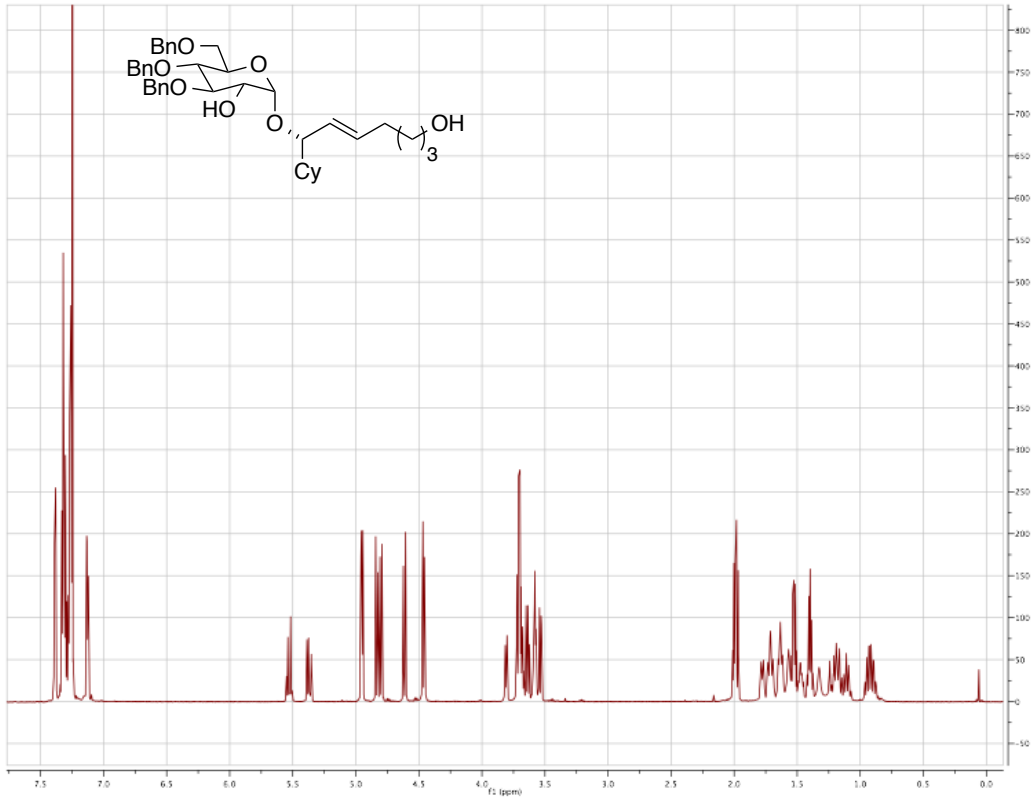


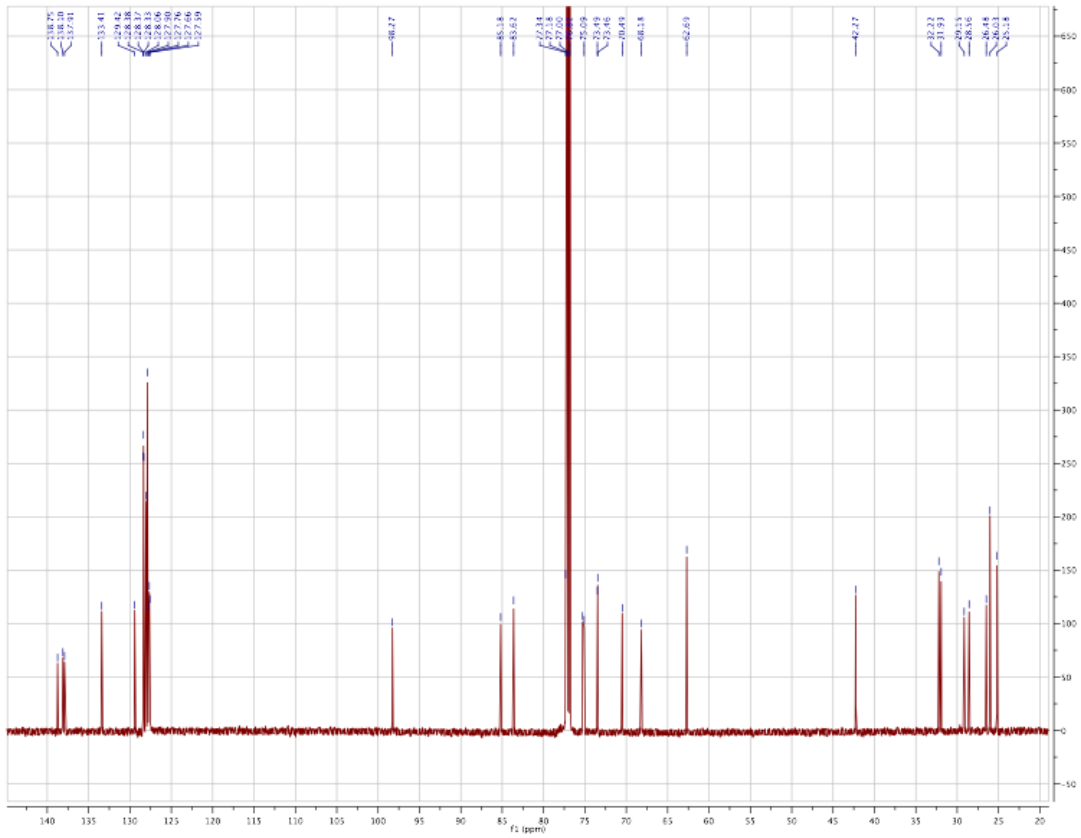
compound **7g** (minor diastereomer)



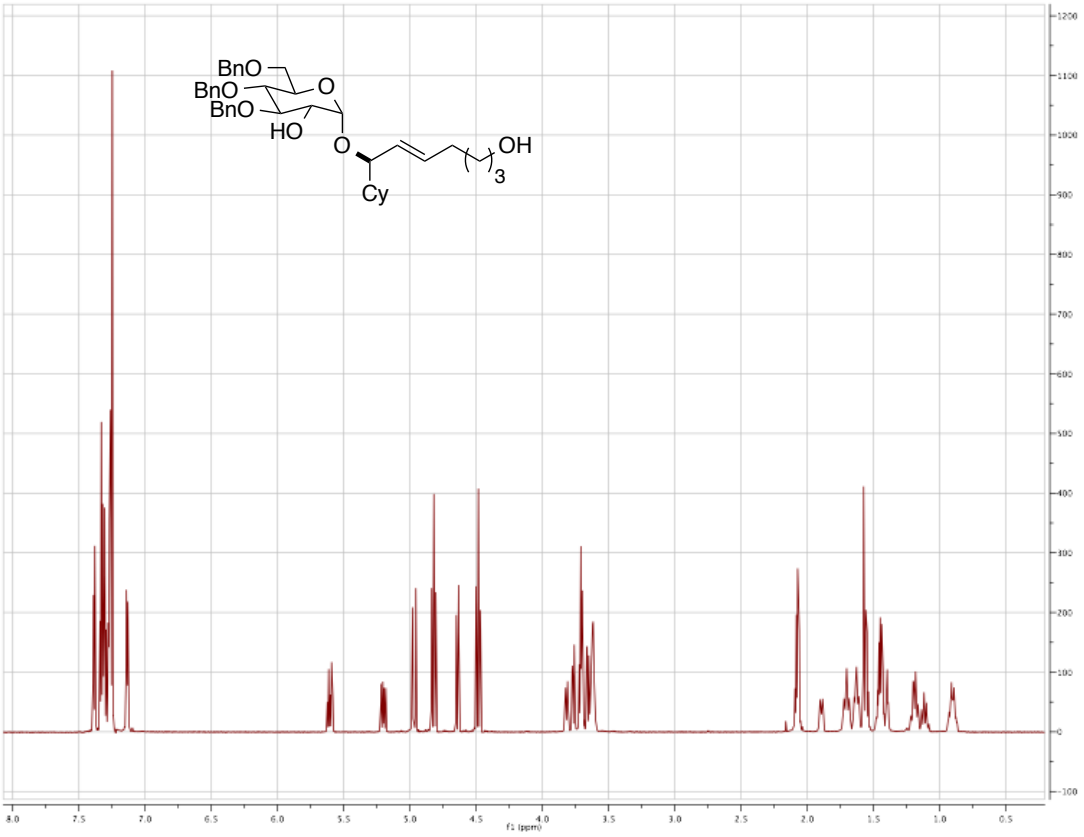


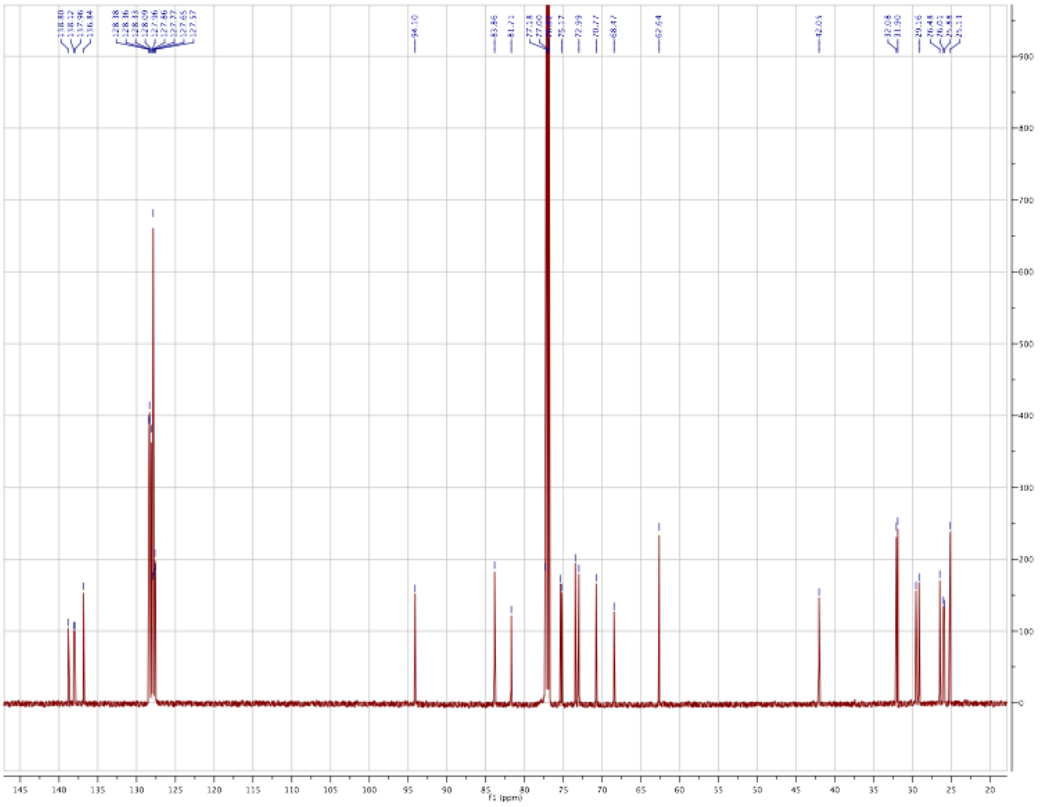
compound **7h** (major diastereomer)



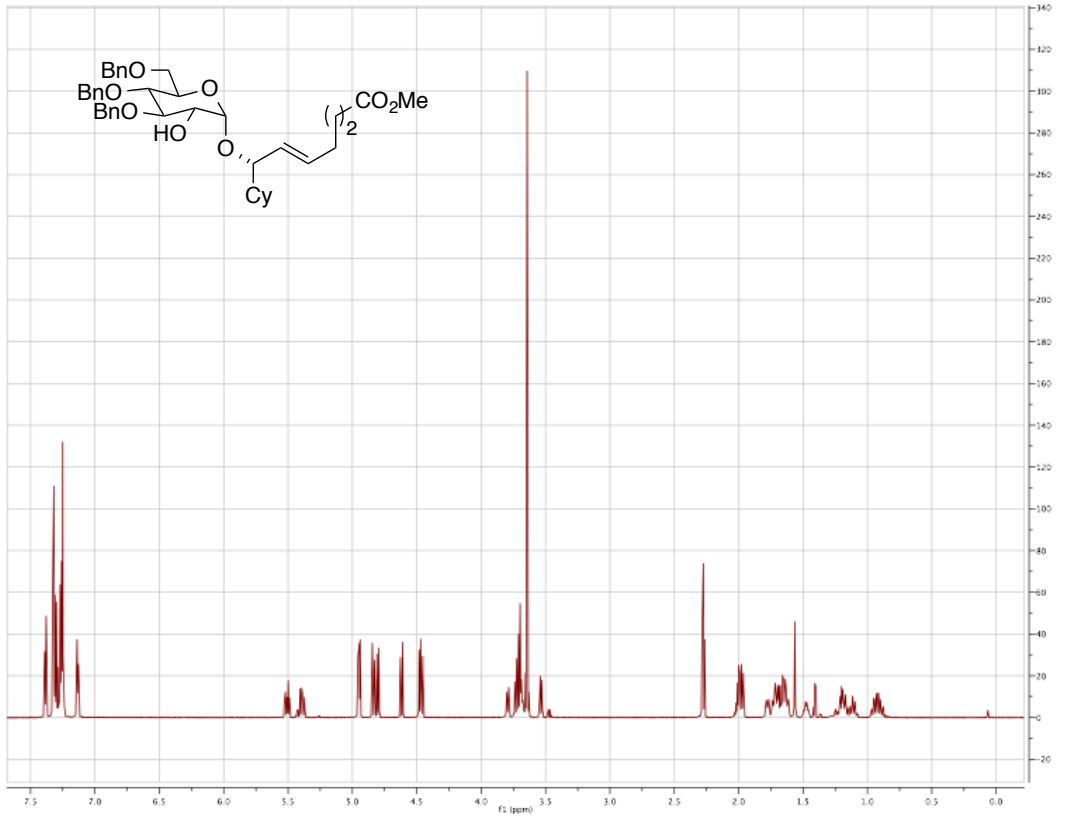


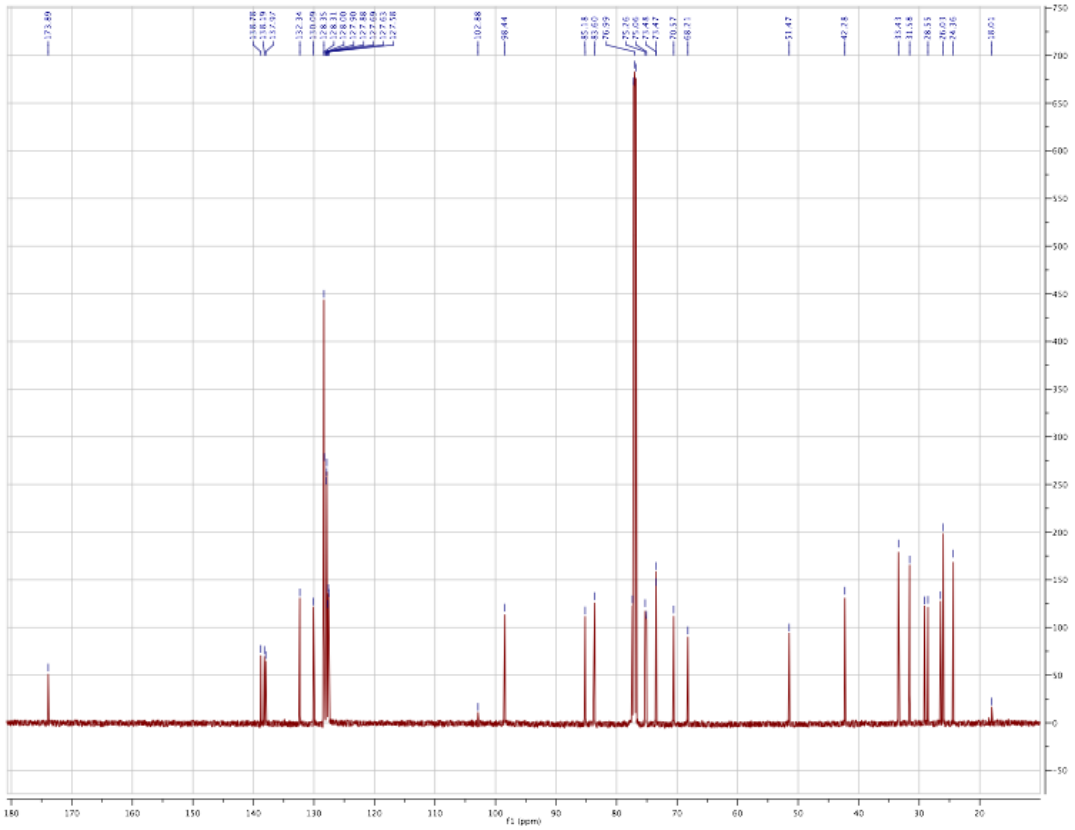
compound **7h** (minor diastereomer)



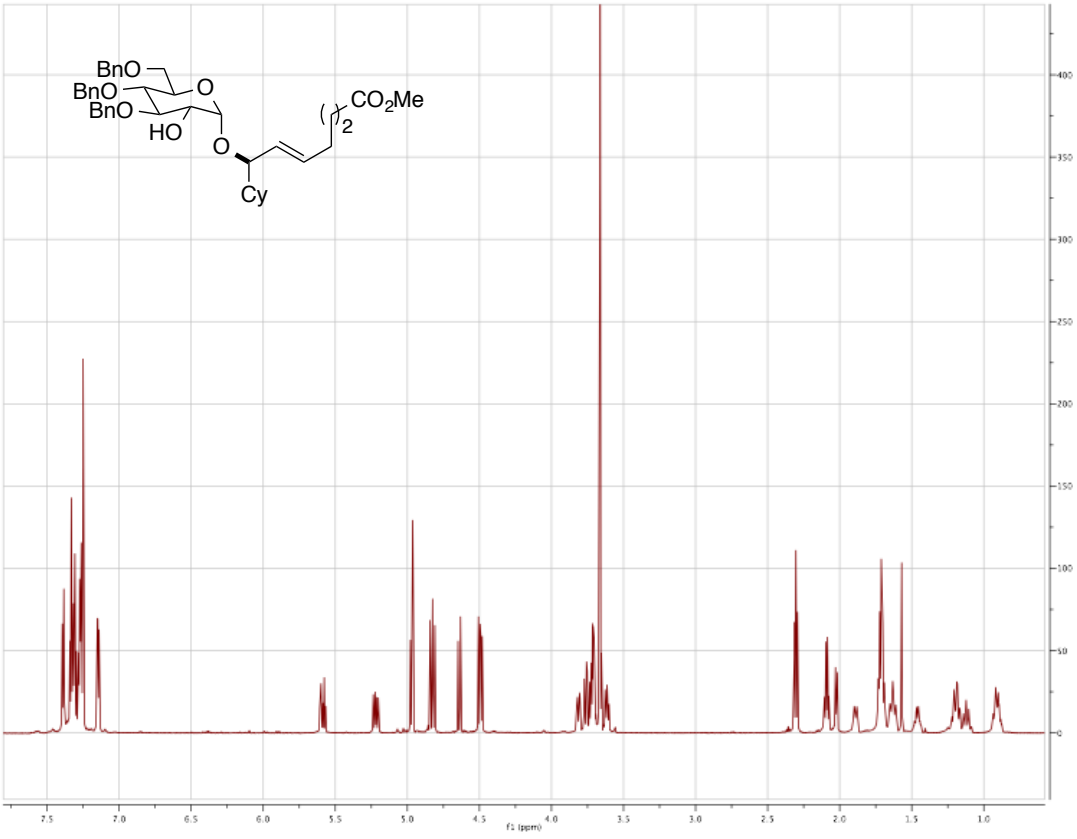


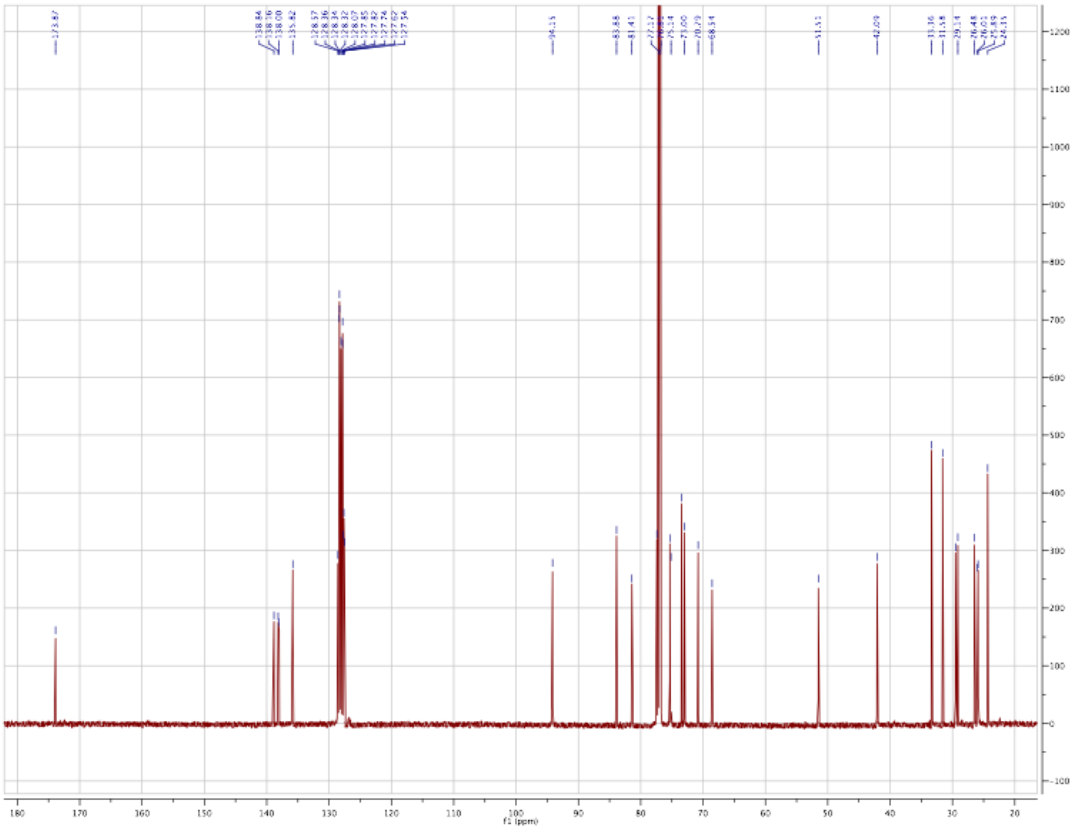
compound **7i** (major diastereomer)



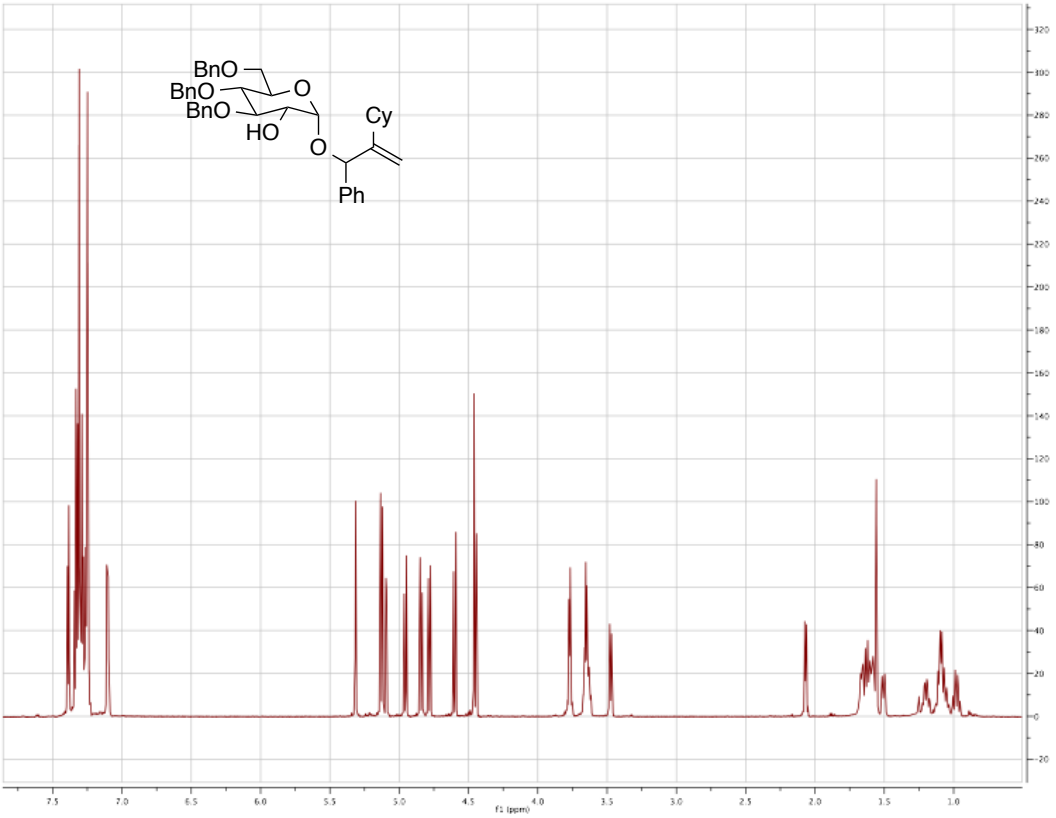


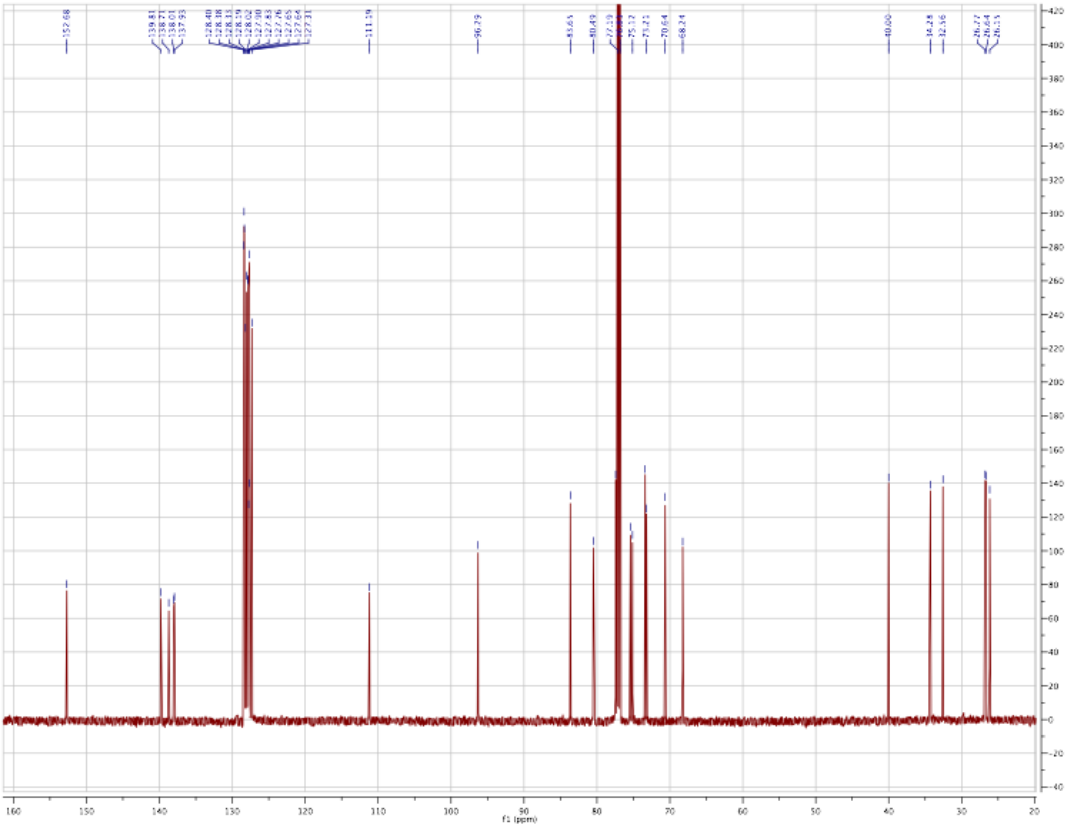
compound **7i** (minor diastereomer)





compound **7j** (1st to elute)





compound **7j** (2nd to elute)