Supporting Information

For

PHOTO-IRRADIATION-PROMOTED AMINOETHERIFICATION OF GLYCALS WITH *N*-ACYLIMINOIODINANE AND ALCOHOLS

Sota Masakado, Yusuke Kobayashi, and Yoshiji Takemoto*

Graduate School of Pharmaceutical Sciences, Kyoto University

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1. General information

Solvents and materials were obtained from commercial suppliers and used without further purification. Analytical thin-layer chromatography was performed using Silica gel 60 plates (Merck, Darmstadt, Germany). Silica gel column chromatography was performed using Kanto silica gel 60 (particle size 63–210 μm, Kanto, Tokyo, Japan) and Chromatorex BW-300 (Fuji silysia, Aichi, Japan). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on JNM-AL 400 (JEOL) at 400 MHz or Avance I 600 (Bruker Biospin AG, Switzerland) at 600 MHz. Chemical shifts were reported relative to Me_4Si (δ 0.00) in $CDCl_3$. Multiplicity was indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad); brs (broad singlet). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JNM-AL 400 at 100 MHz or on an Avance I 600 at 150 MHz. Chemical shifts were reported relative to $CDCl_3$ (δ 77.0). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a JNM-AL 400 at 376 MHz. Infrared spectra were recorded on a FT/IR-4100 Fourier-transform infrared spectrometer (JASCO, Tokyo, Japan) ATR (attenuated total reflectance). High resolution mass spectra were recorded on a LCMS-IT-TOF (Shimadzu, Kyoto, Japan) for ESI-MS. All melting points were measured on BÜCHI M-565 melting point apparatus and are uncorrected.

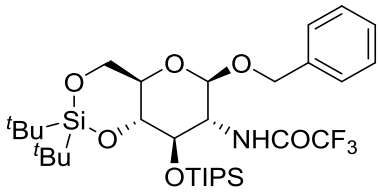
2. Preparation of *N*-acyliminoiodinane and substrate

N-acyliminoiodinane **1**[1)] and glycals **2**[1)] and **11**[2)] were prepared by following the literature.

3. Optimized general procedure for the photo-induced aminoetherification

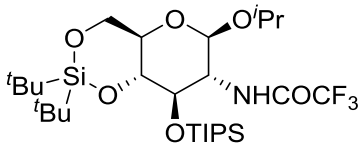
A mixture of glycal **2** or **11** (0.1 mmol, 44.3 mg), iminoiodinane **1** (0.2 mmol, 71.8 mg), and activated molecular sieves 5Å (MS 5Å, 50 mg) in dry dichloromethane (2.0 mL) was stirred at room temperature for 30 min. The reaction mixture was then cooled to 0℃ and stirred at the same temperature for 6 h under black light irradiation (λ = 365 nm), when the consumption of glycal was monitored by TLC. To the resulting mixture, was added alcohol (0.1 mmol or 0.3 mmol), and the whole mixture was stirred at room temperature for 30 min before the addition of TMSOTf (0.02 mmol, 3.6 μL). The reaction mixture was further stirred at room temperature overnight. After concentration of the solvent under reduced pressure, direct purification by flash column chromatography on silica gel gave the desired aminoconjugate **6** or **13**. The spectral data of 6a-c were reported in the preliminary communication.[1)]

Benzyl 2-deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranoside (13a)



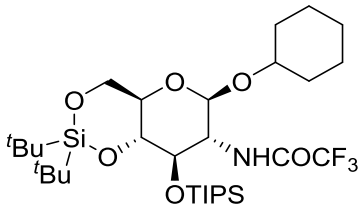
White solid; m. p. 137.9 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.37–7.26 (5H, m), 6.32 (1H, d, *J* = 8.2 Hz), 4.90 (1H, d, *J* = 8.8 Hz, H-1), 4.83 (1H, d, *J* = 11.5 Hz), 4.55 (1H, d, *J* = 11.5 Hz), 4.19 (1H, dd, *J* = 9.9, 4.9 Hz), 4.12 (1H, t, *J* = 9.1 Hz), 3.95 (1H, t, *J* = 10.2 Hz), 3.77 (1H, t, *J* = 8.8 Hz), 3.52 (1H, q, *J* = 8.8 Hz), 3.41 (1H, td, *J* = 9.9, 4.8 Hz), 1.12–1.08 (30H, m), 0.99 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.2 (q, *J* = 37.0 Hz), 136.7, 128.5, 128.1, 128.0, 115.6 (q, *J* = 288.7 Hz, CF_3), 98.2, 79.0, 74.6, 71.0, 70.3, 66.1, 59.7, 27.4, 26.9, 22.8, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –75.84; ESI-HRMS Calcd. for $C_{32}H_{53}F_3NO_6Si_2$ $[M–H]^-$ 660.3369; Found: 660.3370; IR (ATR) 3276, 1701 cm^{-1}; $[\alpha]_D^{25}$ –43.1 (*c* 1.21, $CHCl_3$).

Isopropyl 2-deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranoside (13b)



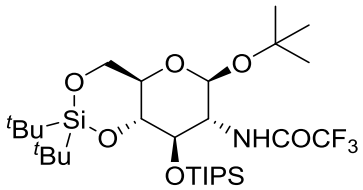
White solid; m. p. 200.5 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.45 (1H, d, *J* = 7.1 Hz), 5.04 (1H, d, *J* = 8.8 Hz, H-1), 4.28 (1H, t, *J* = 9.1 Hz), 4.14 (1H, dd, *J* = 10.4, 4.9 Hz), 3.93–3.90 (2H, m), 3.74 (1H, t, *J* = 8.8 Hz), 3.43 (1H, td, *J* = 9.9, 4.9 Hz), 3.25 (1H, q, *J* = 8.6 Hz), 1.19 (3H, d, *J* = 6.0 Hz), 1.16–1.04 (33H, m), 0.99 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.2 (q, *J* = 36.6 Hz), 115.6 (q, *J* = 288.7 Hz, *C*F_3), 97.4, 79.2, 74.2, 72.3, 70.2, 66.2, 60.7, 27.4, 27.0, 23.4, 22.8, 21.7, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –76.09; ESI-HRMS Calcd. for $C_{28}H_{53}F_3NO_6Si_2$ $[M-H]^-$ 612.3369; Found: 612.3365; IR (ATR) 3275, 1702 cm^{-1}; $[\alpha]_D^{25}$ −19.3 (*c* 0.69, $CHCl_3$).

Cyclopropyl 2-deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranoside (13c)



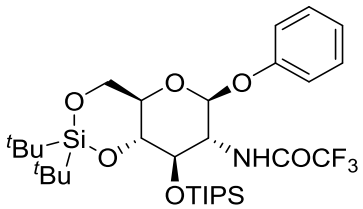
White solid; m. p. 193.9 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.44 (1H, d, *J* = 7.7 Hz), 5.06 (1H, d, *J* = 8.8 Hz, H-1), 4.27 (1H, t, *J* = 9.1 Hz), 4.14 (1H, dd, *J* = 10.4, 4.9 Hz), 3.92 (1H, t, *J* = 10.2 Hz), 3.74 (1H, t, *J* = 8.8 Hz), 3.60–3.57 (1H, m), 3.43 (1H, td, *J* = 9.9, 4.9 Hz), 3.29 (1H, q, *J* = 8.8 Hz), 1.85–1.84 (1H, m), 1.77–1.75 (1H, m), 1.70–1.67 (2H, m), 1.50–1.49 (1H, m), 1.37–1.33 (1H, m), 1.25–1.21 (2H, m), 1.14–1.12 (2H, m), 1.08–1.05 (30H, m), 0.99 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.2 (q, *J* = 36.6 Hz), 115.6 (q, *J* = 288.7 Hz, *C*F_3), 97.2, 79.1, 74.2, 70.2, 66.2, 60.7, 33.4, 31.6, 27.4, 27.0, 25.4, 22.8, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –76.03; ESI-HRMS Calcd. for $C_{31}H_{57}F_3NO_6Si_2$ $[M-H]^-$ 652.3682.; Found: 652.3669; IR (ATR) 3322, 1703 cm^{-1}; $[\alpha]_D^{25}$ −76.2 (*c* 0.09, $CHCl_3$).

***tert*-Butyl 2-deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranoside (13d)**



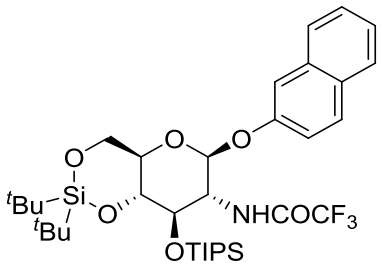
White solid; m. p. 168.5 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.47 (1H, d, *J* = 6.6 Hz), 5.13 (1H, d, *J* = 8.2 Hz, H-1), 4.35 (1H, t, *J* = 8.8 Hz), 4.08 (1H, dd, *J* = 10.4, 4.9 Hz), 3.92 (1H, t, *J* = 10.4 Hz), 3.73 (1H, t, *J* = 8.8 Hz), 3.42 (1H, td, *J* = 9.9, 5.1 Hz), 3.23 (1H, q, *J* = 8.6 Hz), 1.20 (9H, s), 1.08–1.05 (30H, m), 1.00 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.1 (q, *J* = 36.2 Hz), 115.6 (q, *J* = 288.7 Hz, *C*F_3), 93.5, 79.1, 76.5, 74.0, 69.9, 66.2, 61.1, 28.5, 27.4, 27.0, 22.8, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –76.06; ESI-HRMS Calcd. for $C_{29}H_{55}F_3NO_6Si_2$ $[M-H]^-$ 626.3526; Found: 626.3529; IR (ATR) 3307, 1704 cm^{-1}; $[\alpha]_D^{20}$ −12.5 (*c* 1.61, $CHCl_3$).

Phenyl 2-deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranoside (13e)



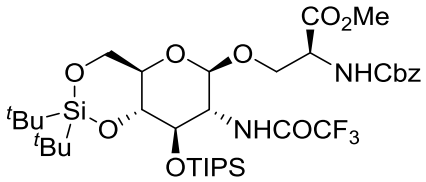
White solid; m. p. 213.2 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.28 (2H, t, *J* = 8.0 Hz), 7.06 (1H, t, *J* = 7.4 Hz), 6.96 (2H, d, *J* = 8.2 Hz), 6.44 (1H, d, *J* = 8.2 Hz), 5.41 (1H, d, *J* = 8.8 Hz, H-1), 4.23–4.20 (2H, m), 3.96 (1H, t, *J* = 10.2 Hz), 3.86 (1H, t, *J* = 8.8 Hz), 3.76 (1H, q, *J* = 8.8 Hz), 3.55 (1H, td, *J* = 9.7, 4.9 Hz), 1.19–1.06 (30H, m), 1.01 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.4 (*J* = 38.4 Hz), 157.0, 129.6, 123.4, 117.1, 115.6 (q, *J* = 288.7 Hz, *C*F_3), 98.2, 78.8, 74.6, 70.6, 66.1, 59.5, 27.4, 27.0, 22.8, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –75.87; ESI-HRMS Calcd. for $C_{31}H_{51}F_3NO_6Si_2$ $[M-H]^-$ 646.3213; Found: 646.3216; IR (ATR) 3256, 1704 cm^{-1}; $[\alpha]_D^{20}$ −25.1 (*c* 0.17, $CHCl_3$).

2-Naphthyl 2-deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranoside (13f)



White solid; m. p. 227.7 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.78–7.73 (3H, m), 7.45 (1H, t, *J* = 7.1 Hz), 7.38 (1H, t, *J* = 7.1 Hz), 7.31 (1H, d, *J* = 1.6 Hz), 7.14 (1H, dd, *J* = 9.1, 2.5 Hz), 6.54 (1H, d, *J* = 7.7 Hz), 5.56 (1H, d, *J* = 8.2 Hz, H-1), 4.28–4.23 (2H, m), 3.99 (1H, t, *J* = 10.2 Hz), 3.90 (1H, t, *J* = 8.8 Hz), 3.83 (1H, q, *J* = 8.8 Hz), 3.63 (1H, td, *J* = 9.9, 4.9 Hz), 1.11–1.08 (30H, m), 1.02 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.4 (q, *J* = 37.0 Hz), 154.7, 134.1, 130.2, 129.8, 127.7, 127.2, 126.6, 124.7, 118.7, 115.6 (q, *J* = 288.7 Hz, *C*F_3), 111.8, 98.3, 78.8, 74.6, 70.7, 66.1, 59.5, 27.4, 27.0, 22.8, 20.0, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –76.06; ESI-HRMS Calcd. for $C_{35}H_{53}F_3NO_6Si_2$ $[M-H]^-$ 696.3369.; Found: 696.3363; IR (ATR) 3360, 1706 cm^{-1}; $[\alpha]_D^{20}$ −3.6 (*c* 0.19, $CHCl_3$).

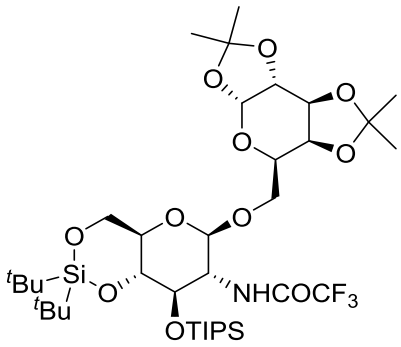
2-Deoxyl-2-trifluoroacetamido-3-*O*-triisopropylsilyl-4,6-*O*-(1,1-di-*tert*-butylsiloxane-1-yl)-β-D-glucopyranosyl-(1→*O*)-*N*-benzyloxycarbonyl-L-serine methyl ester (13g)



White solid; m. p. 178.9 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.36–7.30 (5H, m), 6.43 (1H, dd, *J* = 16.5, 7.7 Hz), 5.56 (1H, d, *J* = 7.7 Hz), 5.13 (1H, d, *J* = 12.6 Hz), 5.09 (1H, d, *J* = 12.6 Hz), 4.82 (1H, d, *J* = 8.8 Hz, H-1), 4.48–4.45 (1H, m), 4.14 (2H, td, *J* = 9.2, 4.0 Hz), 4.07 (1H, t, *J* = 9.1 Hz), 3.88 (1H, t, *J* = 10.4 Hz), 3.82 (1H, dd, *J* = 10.2, 3.0 Hz), 3.74 (3H, s), 3.72 (1H, d, *J* = 9.3 Hz), 3.46 (1H, q, *J* = 8.8 Hz), 3.38 (1H, td, *J* = 9.9, 4.9 Hz), 1.08–1.05 (30H, m), 0.98 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 170.1, 157.3 (*J* = 37.0 Hz), 156.0, 136.2, 128.5, 128.1, 128.0, 115.6 (*J* = 288.7 Hz, *C*F_3), 99.4, 78.8, 74.7, 70.5, 69.0, 67.1, 66.0, 59.1, 54.0, 52.7, 27.4, 26.9, 22.8, 19.9, 18.40, 18.2, 13.31; ^{19}F-NMR (376 MHz,

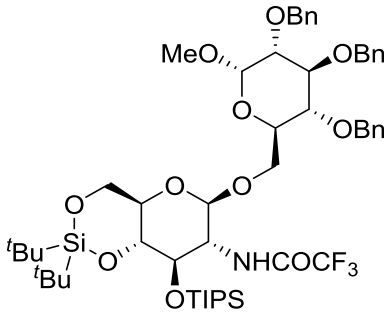
$CDCl_3$) δ: –75.71; ESI-HRMS Calcd. for $C_{31}H_{61}F_3N_2O_{10}Si_2Na$ $[M+Na]^+$ 829.3709; Found:829.3693; IR (ATR) 3318, 1709 cm^{-1}; $[\alpha]_D^{25}$ −10.8 (*c* 0.10, $CHCl_3$).

Disaccharide (13h)



White solid; m. p. 148.5 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.72 (1H, dd, *J* = 15.6, 8.5 Hz), 5.49 (1H, d, *J* = 4.9 Hz), 4.90 (1H, d, *J* = 8.2 Hz, H-1), 4.58 (1H, dd, *J* = 8.2, 2.2 Hz), 4.30 (1H, dd, *J* = 4.9, 2.2 Hz), 4.18–4.16 (3H, m), 3.94–3.88 (3H, m), 3.74 (1H, t, *J* = 8.8 Hz), 3.67 (1H, dd, *J* = 10.7, 6.9 Hz), 3.52 (1H, q, *J* = 8.8 Hz), 3.42 (1H, td, *J* = 9.9, 4.9 Hz), 1.49 (3H, s), 1.43 (3H, s), 1.32–1.32 (6H, m), 1.09–1.05 (30H, m), 0.99 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.4 (q, *J* = 37.0 Hz), 115.7 (q, *J* = 288.7 Hz, *C*F_3), 109.4, 109.4, 108.7, 108.7, 99.8, 96.3, 79.0, 74.5, 71.1, 70.7, 70.4, 70.3, 68.2, 67.2, 66.1, 59.1, 27.4, 27.0, 25.9, 25.8, 24.9, 24.4, 22.8, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –75.75; ESI-HRMS Calcd. for $C_{37}H_{65}F_3NO_{11}Si_2$ $[M-H]^-$ 812.4054.; Found: 812.4062; IR (ATR) 3312, 1714 cm^{-1}; $[\alpha]_D^{20}$ −48.1 (*c* 0.40, $CHCl_3$).

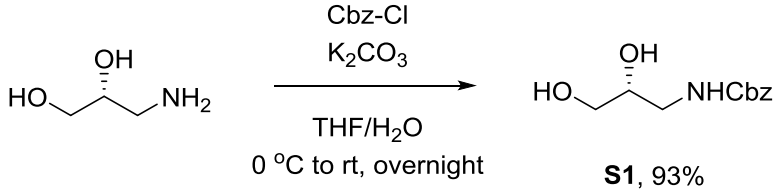
Disaccharide (13i)



White solid; m. p. 63.1 ˚C (decomp.); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.34–7.25 (15H, m), 6.34 (1H, d, *J* = 7.7 Hz), 4.97 (1H, d, *J* = 11.0 Hz), 4.84–4.76 (4H, m), 4.64 (1H, d, *J* = 12.1 Hz), 4.56 (1H, d, *J* = 3.8 Hz), 4.50 (1H, d, *J* = 11.0 Hz), 4.14–4.10 (2H, m), 4.00–3.95 (2H, m), 3.89 (1H, t, *J* = 10.2 Hz), 3.74–3.71 (2H, m), 3.58 (1H, dd, *J* = 10.7, 4.7 Hz), 3.49–3.46 (2H, m), 3.40–3.37 (2H, m), 3.33 (3H, s), 1.12–1.07 (30H, m), 0.99 (9H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.1 (q, *J* = 37.0 Hz), 138.8, 138.2, 138.1, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 115.6 (q, *J* = 288.7 Hz, *C*F_3), 99.2, 98.0, 81.9, 79.7, 78.9, 77.7, 75.6, 74.7, 74.5, 73.3, 70.3, 69.3, 67.8, 66.0, 59.6, 55.1, 27.3, 27.0, 22.8, 19.9, 18.4, 18.2, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –75.57; ESI-HRMS Calcd. for $C_{53}H_{78}F_3ClNO_{11}Si_2$ $[M+Cl]^+$ 1052.4760; Found: 1052.4719; IR (ATR) 3306, 1745 cm^{-1}; $[\alpha]_D^{15}$ −8.3 (*c* 0.07, $CHCl_3$).

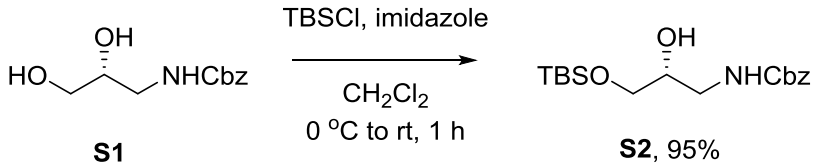
4. Synthesis of bioactive compound

Benzyl (*R*)-(2,3-dihydroxypropyl)carbamate (S1)



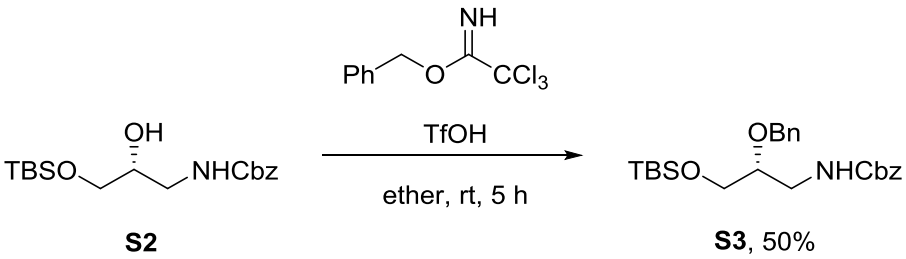
To a solution of commercially available (*R*)-3-amino-1,2-propandiol (1.0 g, 11 mmol) in THF (30 mL) was added potassium carbonate (4.6 g, 33 mmol) in water (15 mL). The reaction mixture was cooled to 0 ˚C, and benzyl chloroformate (1.6 g, 11 mmol) was added dropwise. The reaction mixture was then warmed up to room temperature and stirred at the same temperature for overnight. The reaction mixture was diluted with water and extracted with EtOAc (3 × 25 mL). Combined organic layer was washed with brine (25 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure to give analytically pure title compound as white solid (2.3 g, 93% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.35–7.34 (5H, m), 5.12 (3H, s), 3.80–3.77 (1H, m), 3.63–3.58 (2H, m), 3.38–3.33 (2H, m), 2.60 (1H, br s), 2.48 (1H, brs); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.6, 136.2, 128.6, 128.2, 128.1, 71.1, 67.1, 63.8, 43.3. The NMR spectra were consistent with literature data.[3)]

Benzyl (*R*)-(3-((*tert*-butyldimethylsilyl)oxy)-2-hydroxypropyl)carbamate (S2)



To a stirred solution of **S1** (2.3 g, 10.2 mmol) and imidazole (1.0 g, 15 mmol) in dichrolomethane (25 mL) was added a solution of TBSCl (1.6 g, 11 mmol) in dichloromethane (10 mL) at 0 ˚C dropwise. The reaction mixture was stirred at room temperature for 1 h, before being quenched with 1 M aqueous HCl (20 mL). The mixture was extracted with $CHCl_3$ (3 × 25 mL), and the combined organic phase was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give title compound as colorless oil (3.4 g, 95%), which was used for the next reaction without further purification; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.36–7.35 (4H, m), 7.32–7.31 (1H, m), 5.20 (1H, brs), 5.10 (2H, s), 3.76–3.75 (1H, m), 3.65 (1H, d, J = 9.9 Hz), 3.53 (1H, dd, J = 9.9, 6.0 Hz), 3.43–3.42 (1H, m), 3.21–3.17 (1H, m), 2.72 (1H, brs), 0.89 (9H, s), 0.07 (6H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.0, 136.5, 128.5, 128.1, 128.0, 70.9, 66.8, 64.7, 43.7, 25.8, 18.2, –5.5. The NMR spectra were consistent with literature data.[3)]

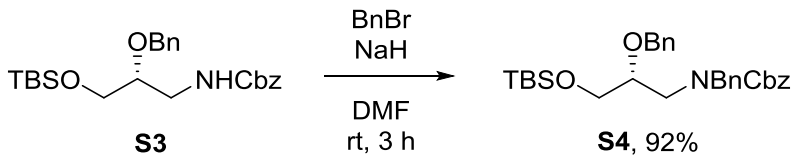
Benzyl (*R*)-(2-(benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)propyl)carbamate (S3)



To a stirred solution of **S2** (600 mg, 1.77 mmol) and benzyl 2,2,2-trichloroacetimidate (500 μL, 2.66 mmol) in ether (6.0

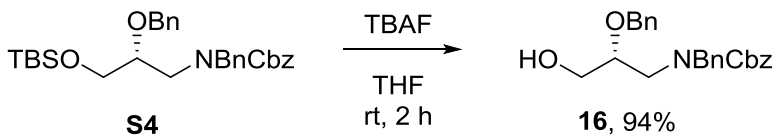
mL) was added trifluoromethanesulfonic acid (3 × 20 μL), and the reaction mixture was stirred at room temperature for 5 h before being quenched with Et_3N (500 μL). After the volatiles were removed under reduced pressure, the residue was directly purified by flash column chromatography on silica gel to give title compound as colorless oil (380 mg, 50%); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.35–7.32 (10H, m), 5.10–5.09 (3H, m), 4.66 (1H, d, *J* = 11.5 Hz), 4.57 (1H, d, *J* = 11.5 Hz), 3.72 (1H, dd, *J* = 10.7, 5.2 Hz), 3.65 (1H, dd, *J* = 10.7, 5.8 Hz), 3.58–3.57 (1H, m), 3.50 (1H, dt, *J* = 13.4, 5.4 Hz), 3.30–3.26 (1H, m), 0.89 (9H, s), 0.05 (6H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 156.3, 138.2, 136.6, 128.4, 128.3, 127.9, 127.9, 127.7, 127.6, 77.8, 71.9, 66.5, 63.5, 42.0, 25.7, 18.1, –5.6; ESI-HRMS Calcd. for $C_{24}H_{36}NO_4Si$ $[M+H]^+$ 430.2408; Found: 430.2408; IR (ATR) 3344, 1724 cm^{-1}; $[\alpha]_D^{15}$ +23.4 (*c* 0.48, $CHCl_3$).

Benzyl (*R*)-benzyl(2-(benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)propyl)carbamate (S4)



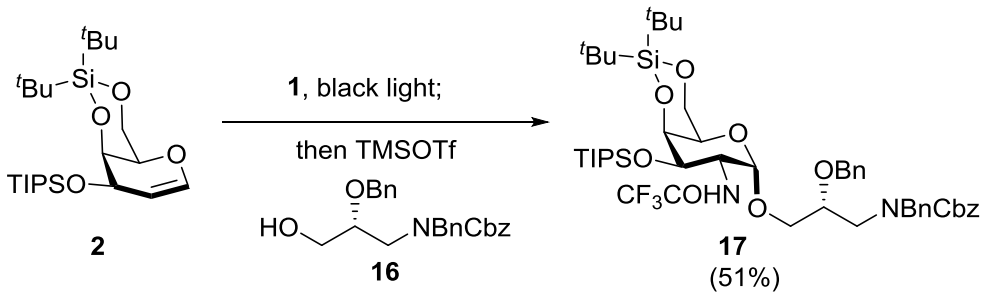
To a stirred solution of **S3** (380 mg, 0.88 mmol) in DMF (5.0 mL) was added NaH (60% oil suspension 53 mg, 1.33 mmol) at 0 ˚C, and the reaction mixture was stirred at room temperature for 30 min. BnBr (130 μL, 1.1 mmol) was then added dropwise at room temperature, and the reaction mixture was stirred at the same temperature for 3 h, before being quenched with water (10 mL). The whole mixture was extracted with *n*-hexane (3 × 10 mL), and the combined organic phase was concentrated under reduced pressure to give crude product, which was purified by flash column chromatography on silica gel to give title compound as colorless oil (420 mg, 92% yield); mixture of rotamers; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.30–7.24 (14H, m), 7.13 (1H, d, *J* = 7.1 Hz), 5.16–5.13 (2H, m), 4.68 (1H, t, *J* = 14.0 Hz), 4.59 (1H, d, *J* = 13.2 Hz), 4.54–4.47 (2H, m), 3.74 (2H, m), 3.61–3.55 (1H, m), 3.48–3.42 (1H, m), 3.28–3.22 (1H, m), 0.86 (9H, s), 0.01 (6H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 156.7, 156.3, 138.8, 138.5, 137.9, 137.9, 136.7, 128.5, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.3, 127.3, 127.1, 78.4, 78.3, 72.4, 67.3, 67.2, 63.9, 63.6, 51.6, 51.6, 48.4, 47.5, 25.9, 25.8, 18.2, –5.4; ESI-HRMS Calcd. for $C_{31}H_{42}NO_4Si$ $[M+H]^+$ 520.2878; Found: 520.2874; IR (ATR) 1701 cm^{-1}; $[\alpha]_D^{15}$ +53.0 (*c* 0.08, $CHCl_3$).

Benzyl (*R*)-benzyl(2-(benzyloxy)-3-hydroxypropyl)carbamate (16)



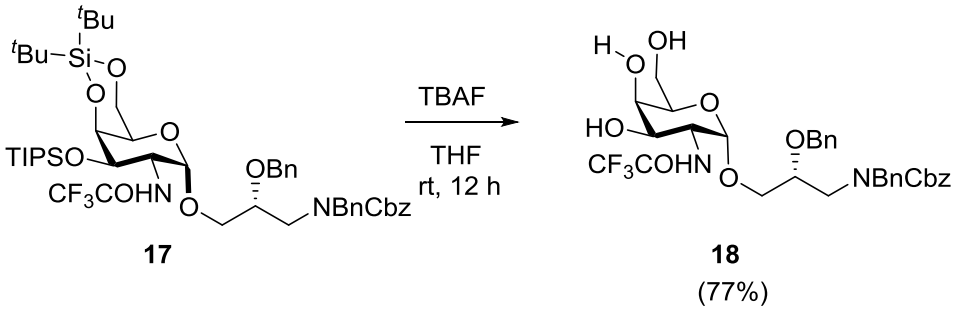
To a stirred solution of **S4** (420 mg, 0.81 mmol) in THF (10 mL) was added 1 M TBAF solution in THF (1.0 mL) and the reaction mixture was stirred at room temperature for 2 h. Concentration under reduced pressure gave crude product, which was directly purified by flash column chromatography on silica gel to give title compound as colorless oil (240 mg, 94% yiled); mixture of rotamers; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.28–7.19 (15H, m), 5.18 (2H, s), 4.62–4.53 (4H, m), 3.65–3.29 (6H, m); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.6, 138.1, 137.4, 136.3, 128.6, 128.5, 128.5, 128.1, 127.9, 127.8, 127.7, 127.4, 127.4, 78.0, 71.8, 67.7, 60.7, 51.8, 46.4; ESI-HRMS Calcd. for $C_{25}H_{27}NO_4Li$ $[M+Li]^+$ 412.2095; Found: 412.2100; IR (ATR) 3347, 1708 cm^{-1}; $[\alpha]_D^{15}$ +21.0 (*c* 0.22, $CHCl_3$).

Aminoglycoside (17)



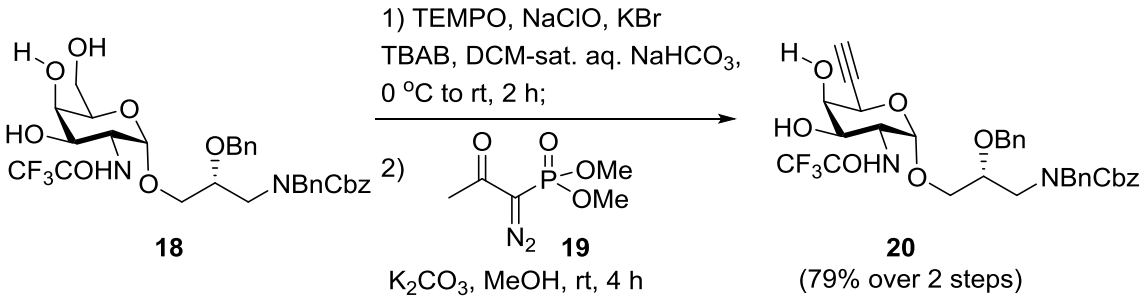
Following the optimized general procedure for the photo-induced aminoetherification of glycals using **2** (44.3 mg, 0.10 mmol) and **16** (31.5 mg, 0.10 mmol), the title compound was given as white solid (48.5 mg, 51% yield); mixture of rotamers; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.28–7.23 (13H, m), 7.09–7.08 (2H, m), 6.33 (1H, d, *J* = 7.7 Hz), 5.17 (1H, d, *J* = 12.1 Hz), 5.09 (1H, d, *J* = 12.6 Hz), 4.86 (1H, d, *J* = 3.3 Hz), 4.69–4.62 (2H, m), 4.53 (1H, d, *J* = 12.1 Hz), 4.46–4.34 (4H, m), 4.11–4.02 (3H, m), 3.75–3.70 (3H, m), 3.51–3.13 (2H, m), 1.07–1.05 (39H, m); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 157.5 (q, *J* = 37.3 Hz), 156.2, 137.9, 137.5, 136.5, 128.6, 128.5, 128.0, 127.8, 127.7, 127.4, 127.2, 115.9 (q, *J* = 284.9 Hz, *C*F_3), 97.7, 76.3, 74.0, 71.9, 70.1, 68.1, 67.3, 67.0, 66.3, 51.6, 50.3, 47.6, 27.4, 27.4, 23.4, 20.8, 18.1, 18.0, 12.8; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –75.23; ESI-HRMS Calcd. for $C_{50}H_{73}F_3N_2O_9Si_2Na$ $[M+Na]^+$ 981.4699; Found: 981.4691; IR (ATR) 1726, 1697 cm^{-1}; $[\alpha]_D^{15}$ +53.6 (*c* 0.25, $CHCl_3$).

Triol (18)



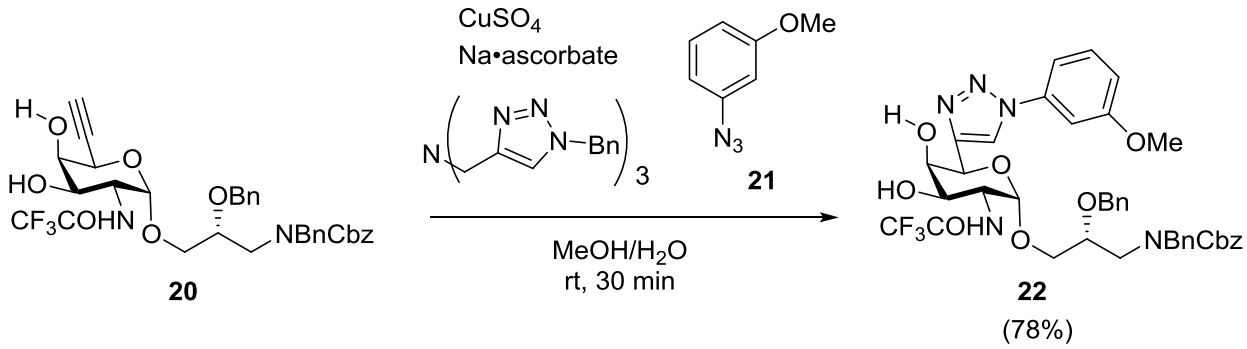
To a stirred solution of **17** (60 mg, 0.063 mmol) in THF (2.0 mL) was added 1 M TBAF solution in THF (320 μL), and the reaction mixture was stirred at room temperature for 12 h. After THF was removed under reduced pressure, the residue was directly purified by flash column chromatography on silica gel to give triol **18** as white solid (32 mg, 77% yield); mixture of rotamers; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.76–7.07 (15H, m), 6.68 (1H, brs), 5.14 (1H, d, *J* = 12.6 Hz), 5.10 (1H, d, *J* = 12.1 Hz), 4.85 (1H, d, *J* = 2.7 Hz), 4.58 (1H, d, *J* = 15.9 Hz), 4.53 (1H, d, *J* = 12.1 Hz), 4.44 (1H, d, *J* = 11.5 Hz), 4.38 (2H, m), 4.03 (1H, s), 3.95–3.69 (7H, m), 3.64–3.58 (1H, m), 3.39 (1H, dd, *J* = 10.4, 2.7 Hz), 3.31–3.12 (1H, m), 2.94 (1H, brs), 1.97 (1H, brs); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 158.8 (q, *J* = 37.0 Hz), 156.4, 137.7, 137.2, 136.3, 128.6, 128.5, 128.5, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 115.9 (q, *J* = 286.5 Hz, *C*F_3), 97.2, 75.6, 71.8, 70.1, 69.7, 69.2, 67.6, 66.1, 63.0, 51.5, 51.3, 47.4; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –74.85; ESI-HRMS Calcd. for $C_{33}H_{38}F_3N_2O_9$ $[M+H]^+$ 663.2524; Found: 663.2535; IR (ATR) 3424, 1719, 1696 cm^{-1}; $[\alpha]_D^{20}$ +61.9 (*c* 0.14, $CHCl_3$).

Alkyne (20)



To a mixture of **18** (8.3 mg, 0.013 mmol), TEMPO (0.1 mg, 0.63 μmol), KBr (0.1 mg, 1.3 μmol), and TBAB (0.2 mg, 0.63 μmol) in dichloromethane/saturated aqueous $NaHCO_3$ solution (1.0 mL/1.0 mL) was added NaClO in saturated aqueous $NaHCO_3$ solution (7.5 mM, 2.0 mL) dropwise at 0 ˚C, and the reaction mixture was stirred at room temperature for 30 min before being quenched with saturated aqueous $Na_2S_2O_3$/NaCl solution (3.0 mL). The mixture was extracted with EtOAc (3 × 2.0 mL), and the combined organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give crude aldehyde, which was used without further purification for the next reaction. The crude aldehyde was dissolved in MeOH (2.0 mL), and K_2CO_3 (3.5 mg, 0.025 mmol) and Ohira-Bestmann reagent **19** (2.25 μL, 0.015 mmol) were successively added. The reaction mixture was stirred at room temperature for 4 h. After MeOH was removed under reduced pressure, the resulting residue was directly purified by column chromatography on silica gel to afford title compound as white solid (6.5 mg, 79% overall yield); mixture of rotamers; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.80–7.09 (15H, m), 6.51 (1H, brs), 5.20 (1H, d, *J* = 12.6 Hz), 5.14 (1H, d, *J* = 12.6 Hz), 4.84 (1H, d, *J* = 2.7 Hz), 4.72 (1H, s), 4.62–4.58 (2H, m), 4.51–4.38 (3H, m), 4.01 (1H, s), 3.96–3.79 (3H, m), 3.59 (1H, d, *J* = 7.7 Hz), 3.43 (1H, dd, *J* = 10.7, 2.5 Hz), 3.15–3.08 (2H, m), 2.77 (1H, brs), 2.59 (1H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 159.0 (q, *J* = 38.4 Hz), 156.3, 137.6, 137.2, 136.3, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.8, 127.6, 127.3, 115.9 (q, *J* = 286.5 Hz, *C*F_3), 97.1, 78.7, 75.2, 75.0, 71.7, 70.7, 69.0, 67.6, 65.9, 62.6, 51.4, 50.9, 46.8; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –74.65; ESI-HRMS Calcd. for $C_{34}H_{36}F_3N_2O_8$ $[M+H]^+$ 657.2418; Found: 657.2411; IR (ATR) 3425, 3290, 2112, 1695 cm^{-1}; $[\alpha]_D^{18}$ +72.1 (*c* 0.09, $CHCl_3$).

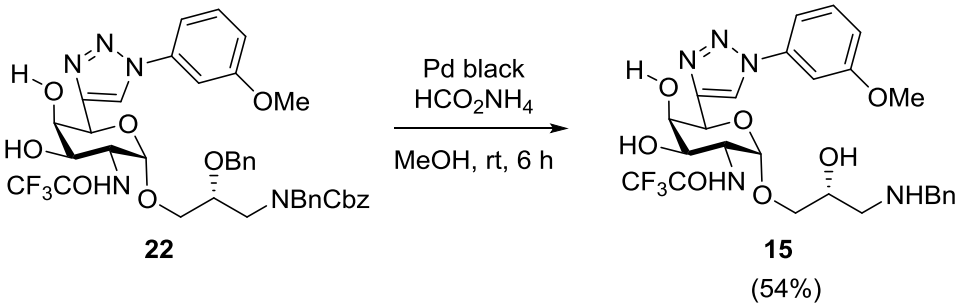
Triazole (22)



To a stirred mixture of **20** (25 mg, 38 μmol), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (2.0 mg, 3.8 μmol), azide **21**[4)] (9.4 mg, 76 μmol), and sodium ascorbate (1.5 mg, 7.6 μmol) in MeOH (2.0 mL) / H_2O (100 μL) was added $CuSO_4 \cdot 5H_2O$ (9.5 mg, 3.8 μmol), and the reaction mixture was stirred at room temperature for 30 min. After methanol was concentrated under reduced pressure, the residue was directly purified by flash column chromatography on silica gel to give triazole **22** (24 mg, 78% yield) as white solid; mixture of rotamers; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.09–6.93 (20H, m), 6.70 (1H, brs), 5.21 (1H, s), 5.15 (1H, d, *J* = 12.1 Hz), 5.10 (1H, d, *J* = 12.1 Hz), 4.94 (1H, d, *J* = 2.7 Hz), 4.63–4.37 (5H,

m), 4.28 (1H, s), 4.09 (1H, s), 3.89–3.81 (5H, m), 3.67 (1H, s), 3.58 (1H, brs), 3.46 (1H, dd, *J* = 10.4, 2.7 Hz), 3.36 (1H, brs), 3.20 (1H, dd, *J* = 14.0, 5.2 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 160.5, 158.7 (q, *J* = 37.0 Hz), 156.4, 145.4, 137.9, 137.8, 137.3, 136.3, 130.4, 128.6, 128.5, 128.1, 127.9, 127.8, 127.7, 127.5, 127.5, 127.3, 121.8, 115.9 (q, *J* = 286.9 Hz, *C*F_3), 114.7, 112.5, 106.3, 97.4, 75.4, 71.8, 70.3, 69.1, 67.5, 66.5, 66.1, 55.6, 51.5, 51.2, 47.2; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –74.76; ESI-HRMS Calcd. for $C_{41}H_{43}F_3N_5O_9$ $[M+H]^+$ 806.3007; Found: 806.3007; IR (ATR) 3439, 3276, 1697 cm^{-1}; $[\alpha]_D^{15}$ +55.0 (*c* 0.14, $CHCl_3$).

ASGPR ligand (15)



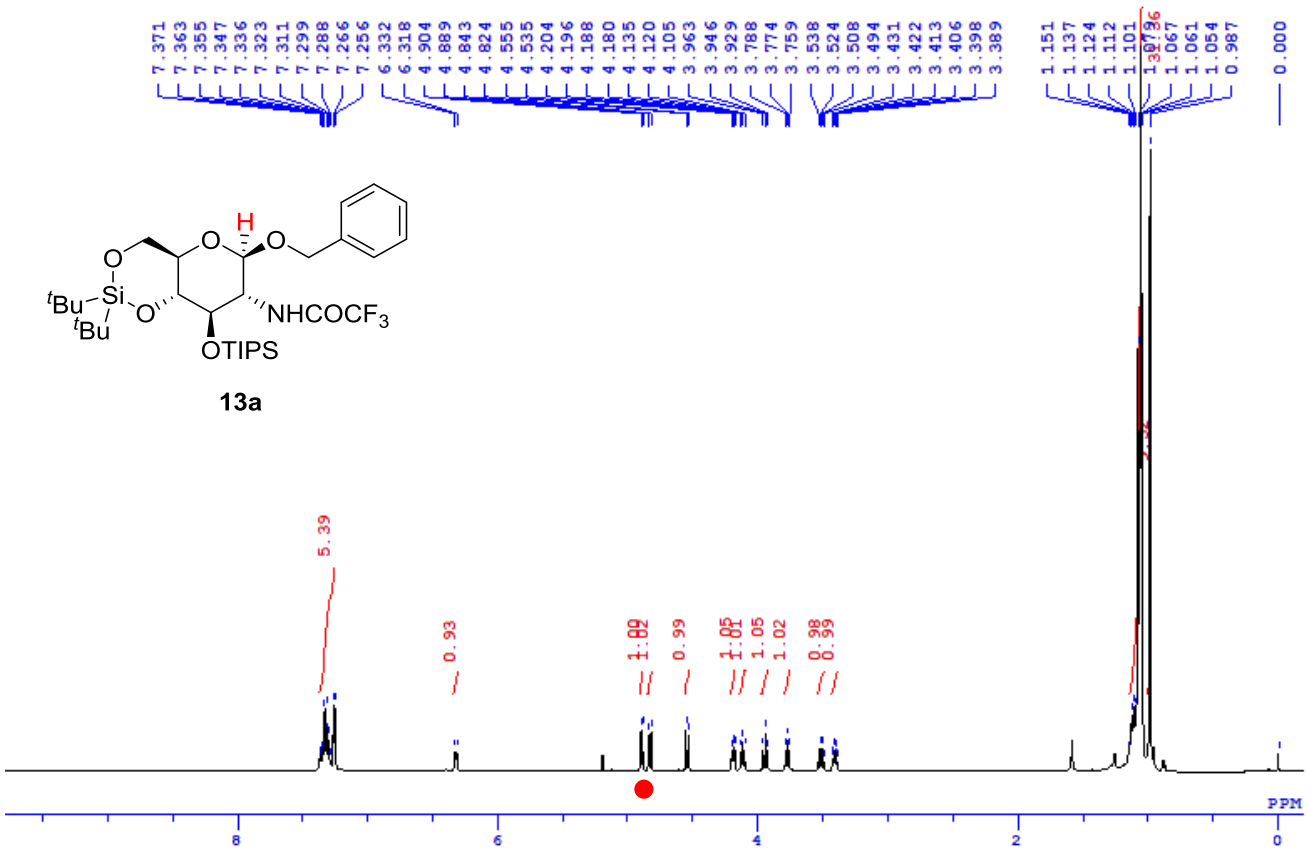
To a solution of **22** (24 mg, 30 μmol) and $HCOONH_4$ (100 mg, 1.6 mmol) in MeOH (2.0 mL) was added Pd black (50 mg, 0.47 mmol), and the reaction mixture was stirred at room temperature for 6 h. After MeOH was removed under reduced pressure, the reaction mixture was diluted with saturated aqueous NaCl solution (2.0 mL) and extracted with MeCN / EtOAc (3 × 1.0 mL/1.0 mL). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure to give the crude product, which was purified by preparative TLC on NH silica gel (EtOAc / MeOH 10:1) to obtain **15** as white solid (9.4 mg, 54% yield); ^{1}H-NMR (600 MHz, CD_3OD) δ: 8.39 (1H, s), 7.40 (1H, t, *J* = 8.2 Hz), 7.34–7.32 (2H, m), 7.27–7.20 (4H, m), 7.17 (1H, t, *J* = 7.1 Hz), 6.99 (1H, d, *J* = 8.2 Hz), 5.12 (1H, s), 4.98 (1H, d, *J* = 3.8 Hz), 4.60 (1H, d, *J* = 11.5 Hz), 4.50 (1H, d, *J* = 11.5 Hz), 4.37 (1H, dd, *J* = 11.3, 3.6 Hz), 4.08–4.07 (2H, m), 3.86 (1H, dd, *J* = 11.0, 3.8 Hz), 3.82 (3H, s), 3.60–3.57 (1H, m), 3.52 (1H, dd, *J* = 11.3, 4.1 Hz), 2.82–2.71 (2H, m) (three O-H protons and two N-H protons were not observed); ^{13}C-NMR (150 MHz, CD_3OD) δ: 162.3, 159.2 (q, *J* = 38.4 Hz), 139.4, 131.9, 129.4, 129.4, 129.1, 128.8, 123.4, 117.5 (q, *J* = 287.1 Hz, *C*F_3), 115.7, 113.5, 107.4, 99.0, 73.1, 72.0, 72.0, 68.5, 68.3, 56.2, 52.2, 43.3 (only major peaks are picked up, because the compound **15** was found to be decomposed in CD_3OD during ^{13}C-NMR measurement, possibly due to the methanolysis of the anomeric position); ^{19}F-NMR (376 MHz, CD_3OD) δ: –76.67; ESI-HRMS Calcd. for $C_{26}H_{31}F_3N_5O_7$ $[M+H]^+$ 582.2170; Found: 582.2169.

5. References

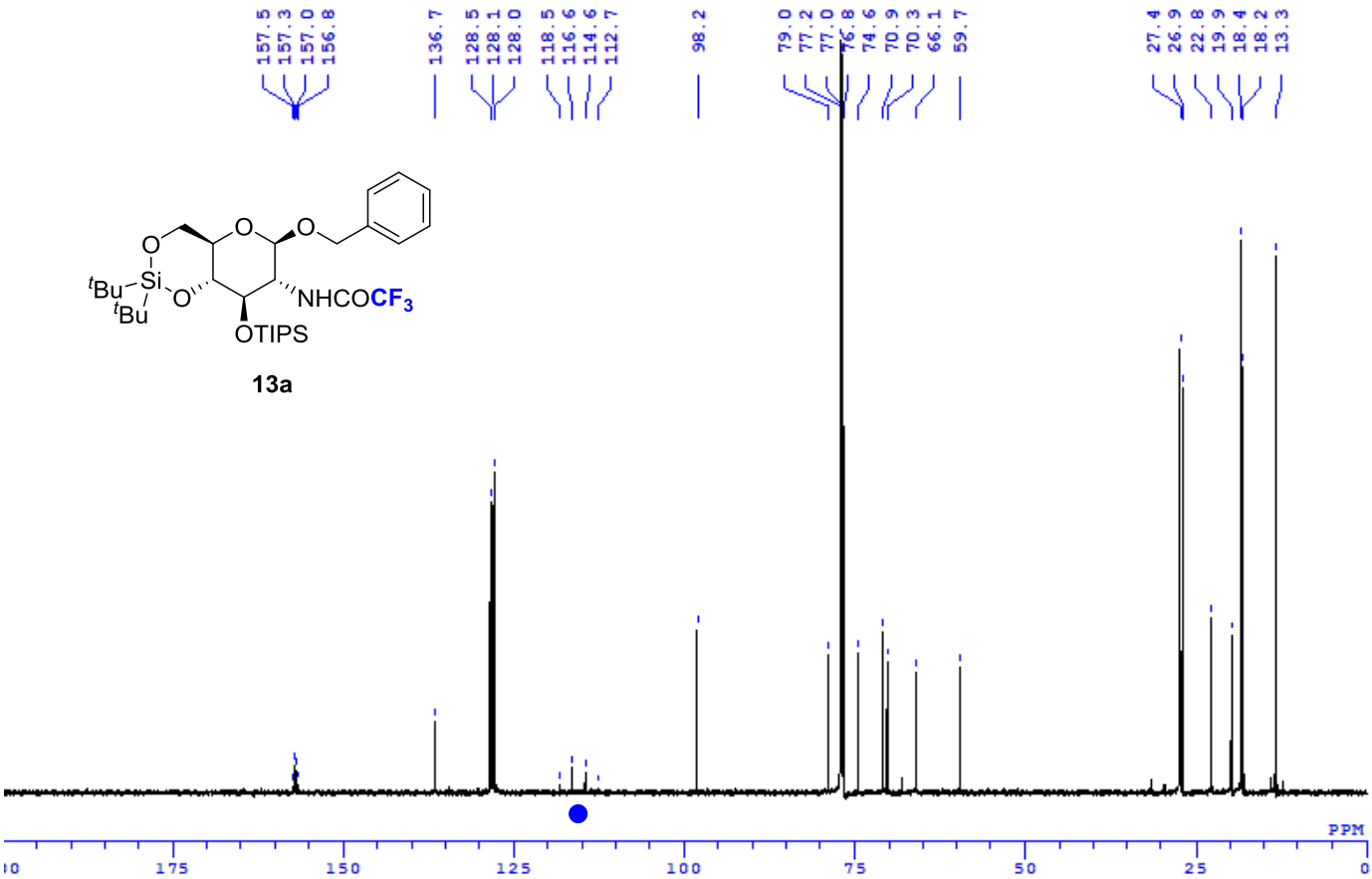
1) Y. Kobayashi, S. Masakado, Y. Takemoto, *Angew. Chem. Int. Ed.*, **2018**, *57*, 693.
2) E. I. Balmond, D. Benito-Alifonso, D. M. Coe, R. W. Alder, E. M. McGarrigle, M. C. Galan, *Angew. Chem. Int. Ed.*, **2014**, *53*, 8190.
3) T. James, I. Simpson, J. A. Grant, V. Sridharan, A. Nelson, *Org. Lett.*, **2013**, *15*, 6094.
4) S. K. Mamidyala, S. Dutta, B. A. Chrunyk, C. Prville, H. Wang, J. M. Withka, A. McColl, T. A. Subashi, S. J. Hawrylik, M. C. Griffor, S. Kim, J. A. Pfefferkorn, D. A. Price, E. MenhajiKlotz, V. Mascitti, M. G. Finn, *J. Am. Chem. Soc.*, **2012**, *134*, 1978.

6. Copies of ^{1}H and ^{13}C NMR charts

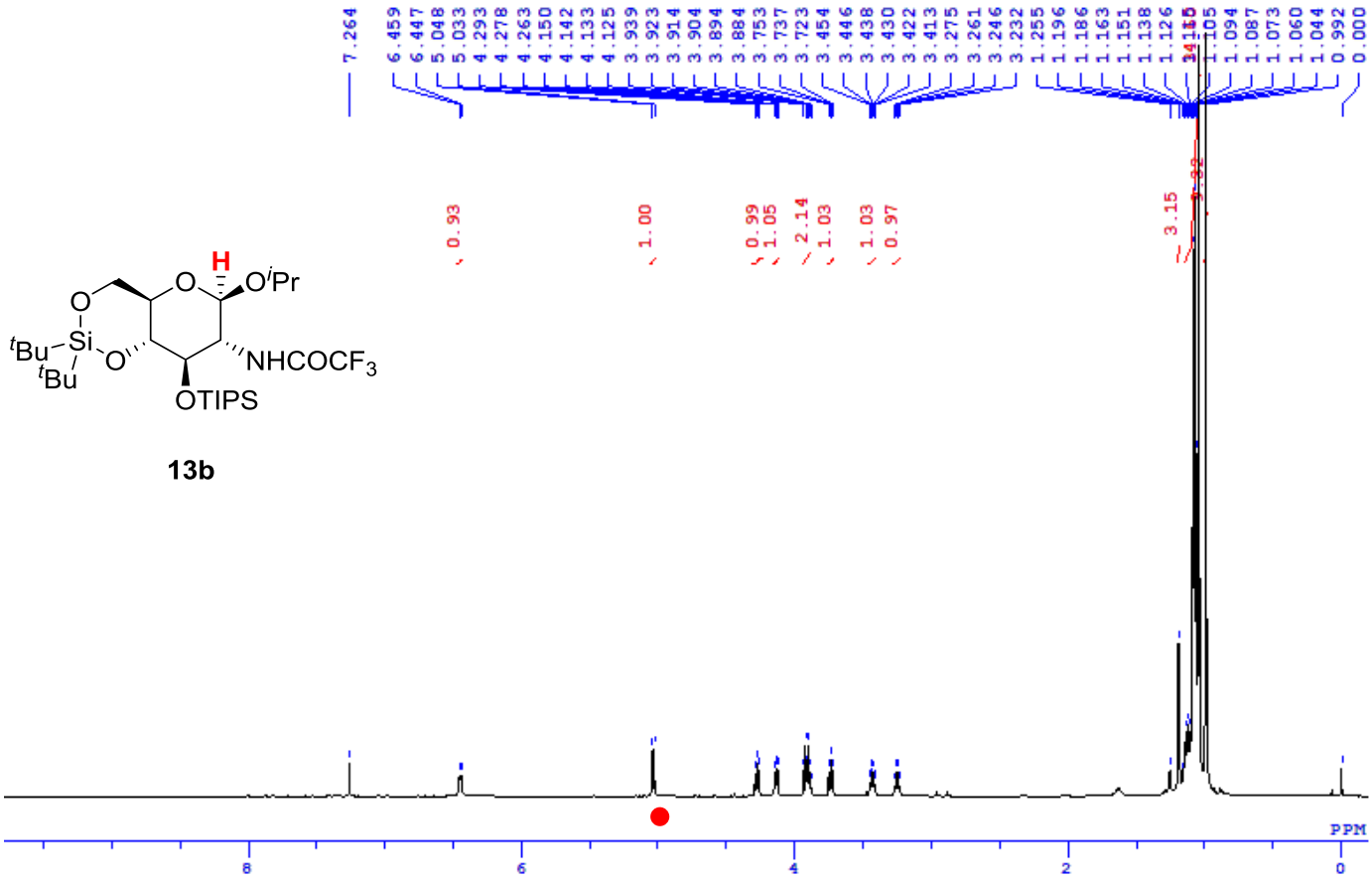
Compound **13a**, ^{1}H-NMR (600 MHz, $CDCl_3$)



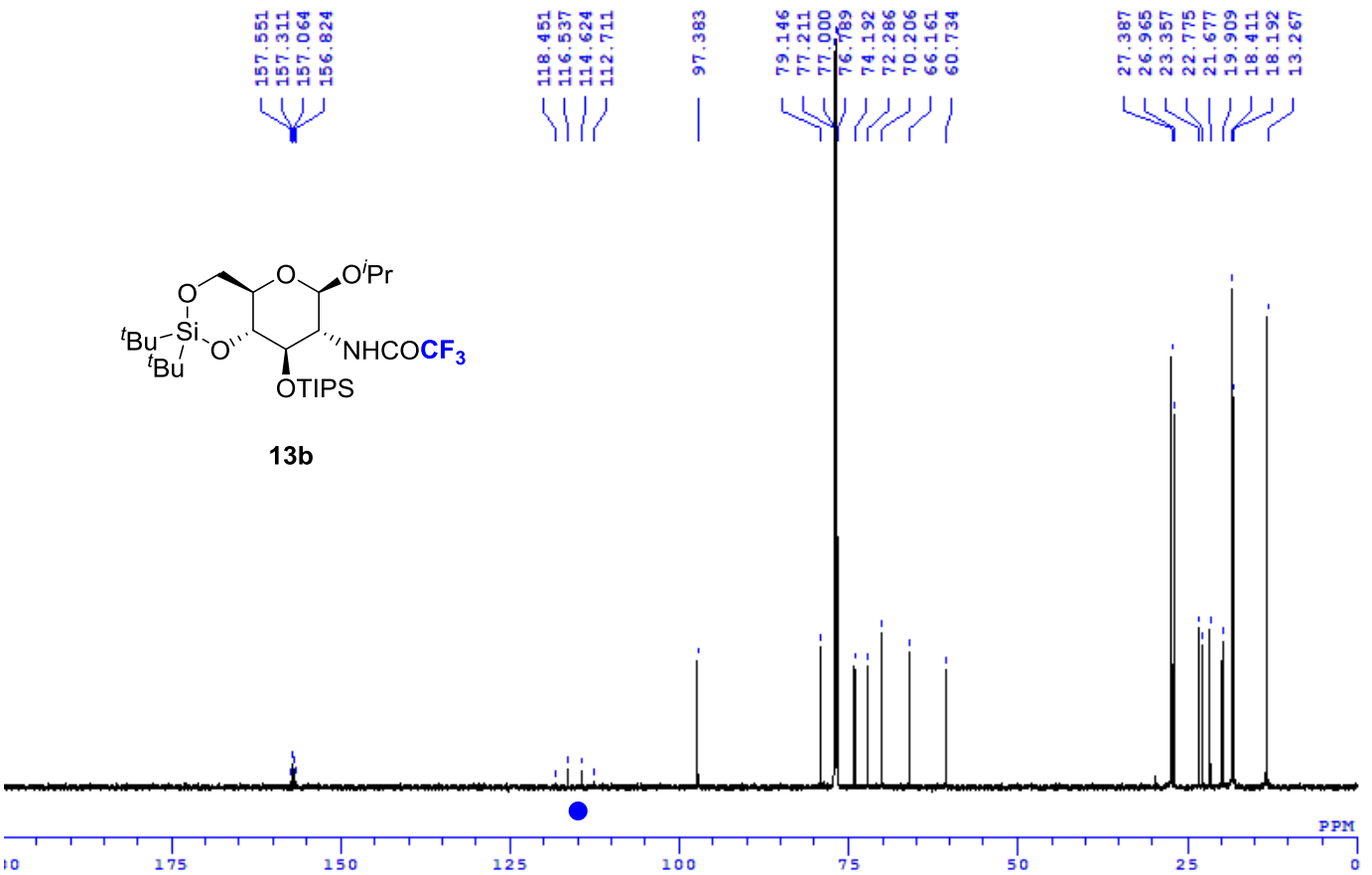
Compound **13a**, ^{13}C-NMR (150 MHz, $CDCl_3$)



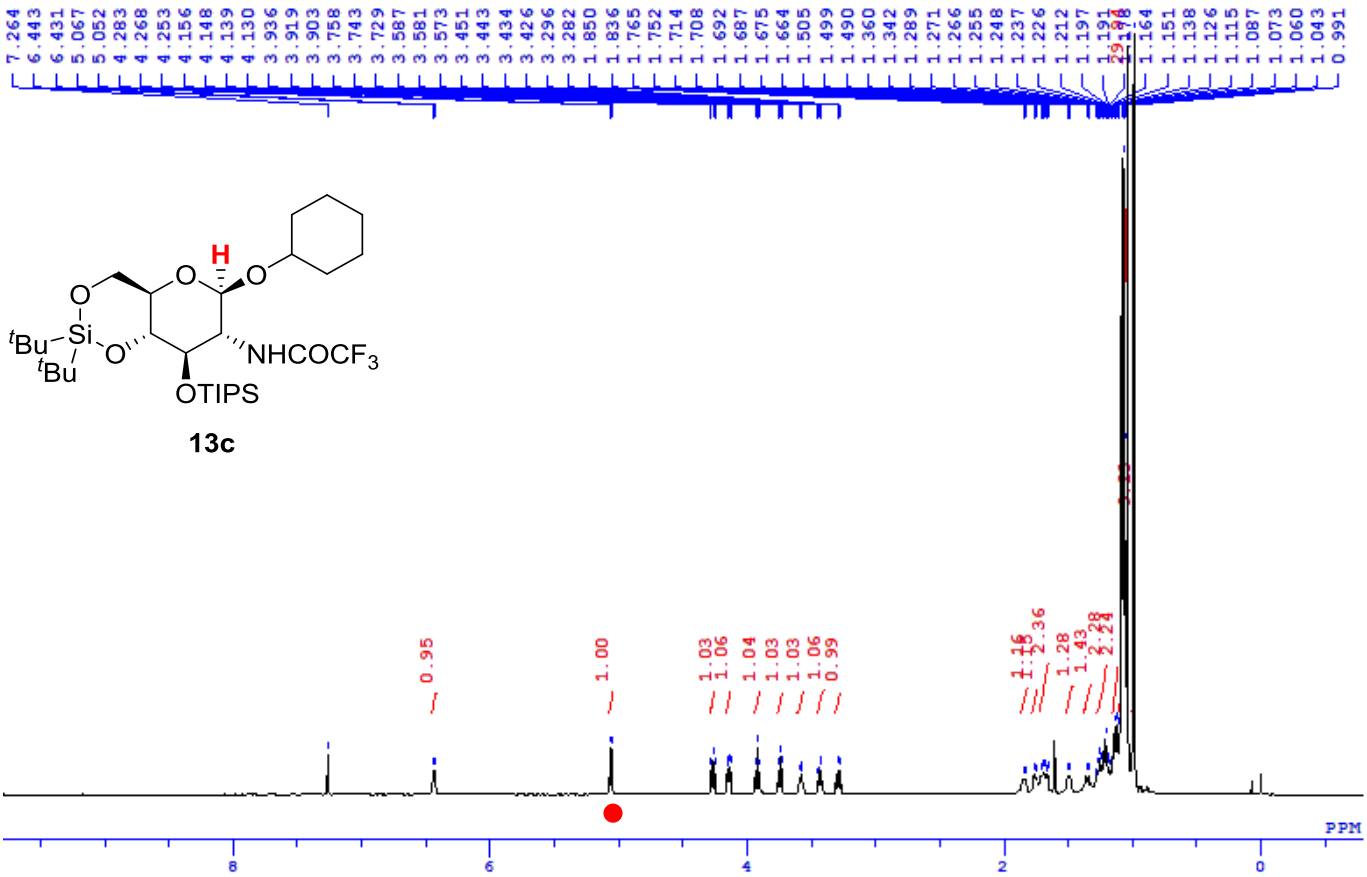
Compound **13b**, ^{1}H-NMR (600 MHz, $CDCl_3$)



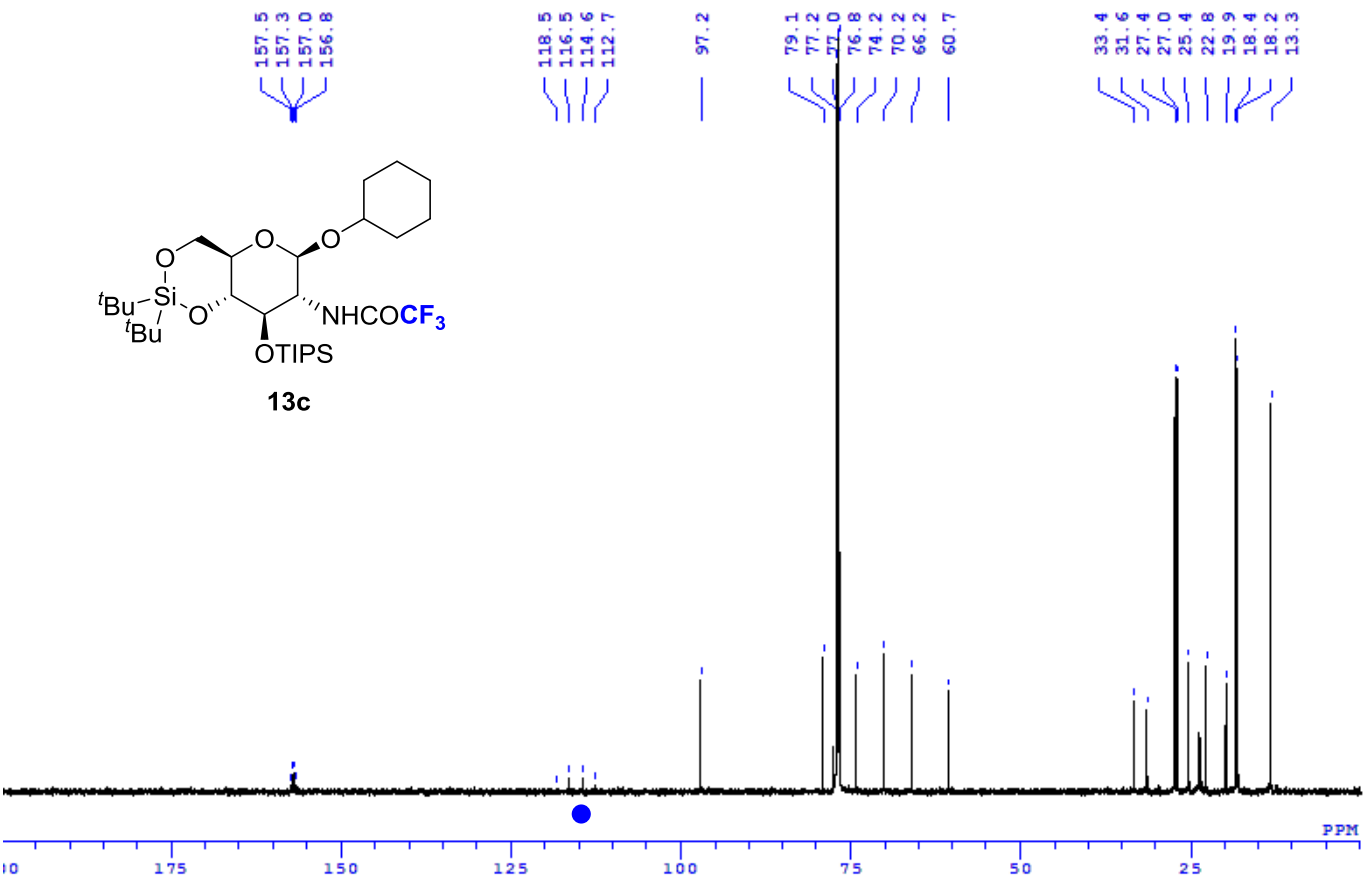
Compound **1ba**, ^{13}C-NMR (150 MHz, $CDCl_3$)



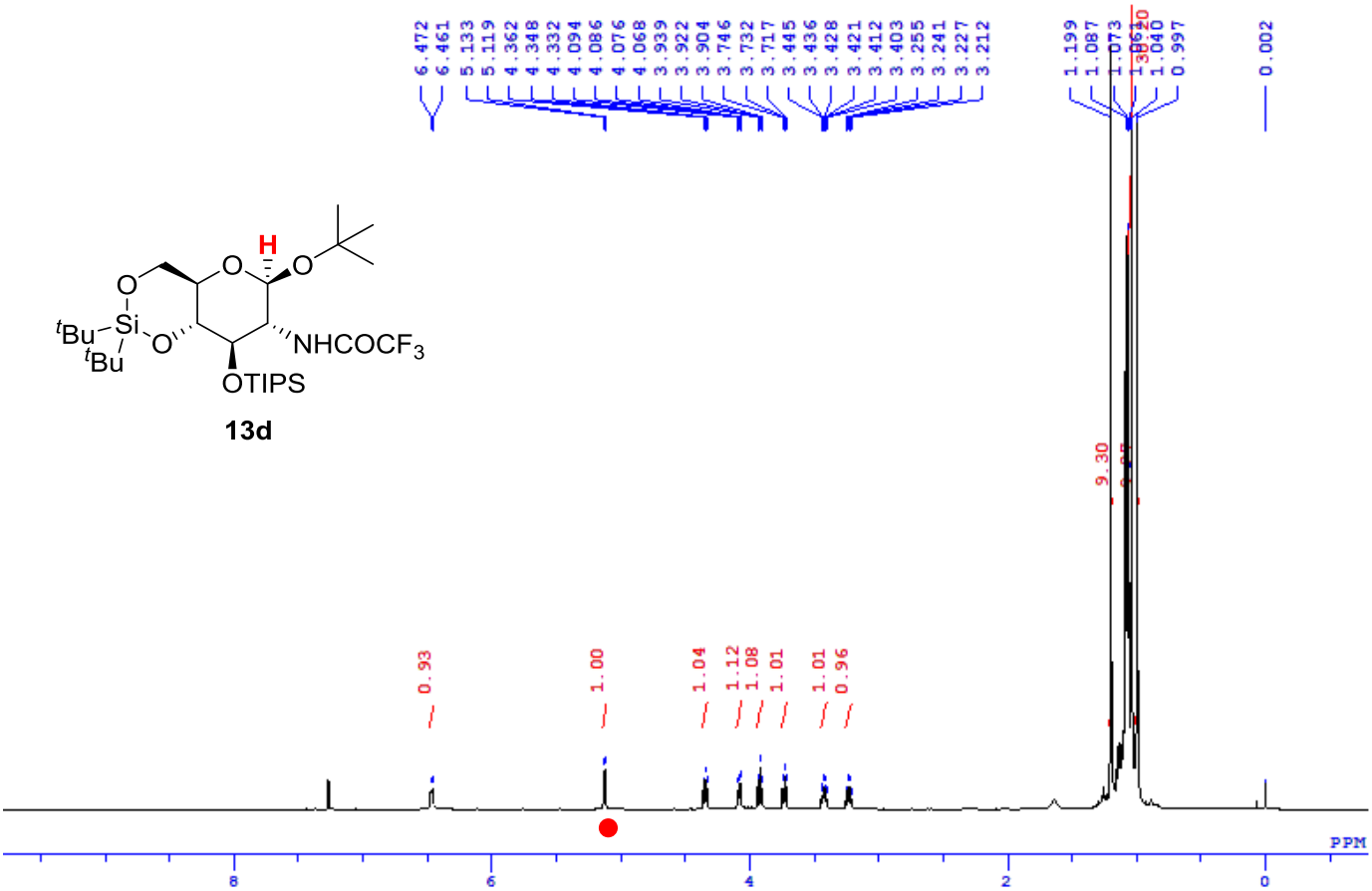
Compound **13c**, ^{1}H-NMR (600 MHz, $CDCl_3$)



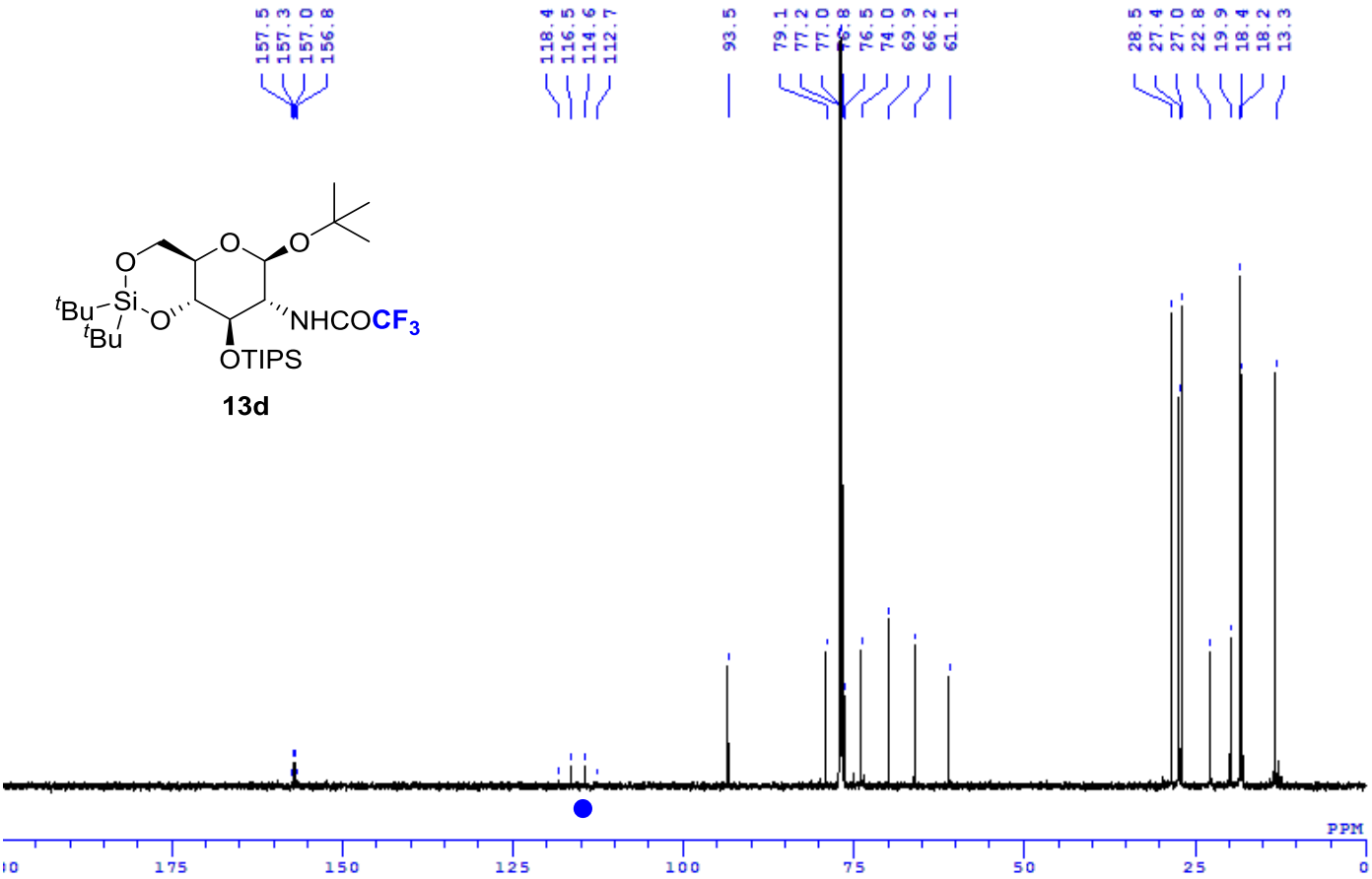
Compound **13c**, ^{13}C-NMR (150 MHz, $CDCl_3$)



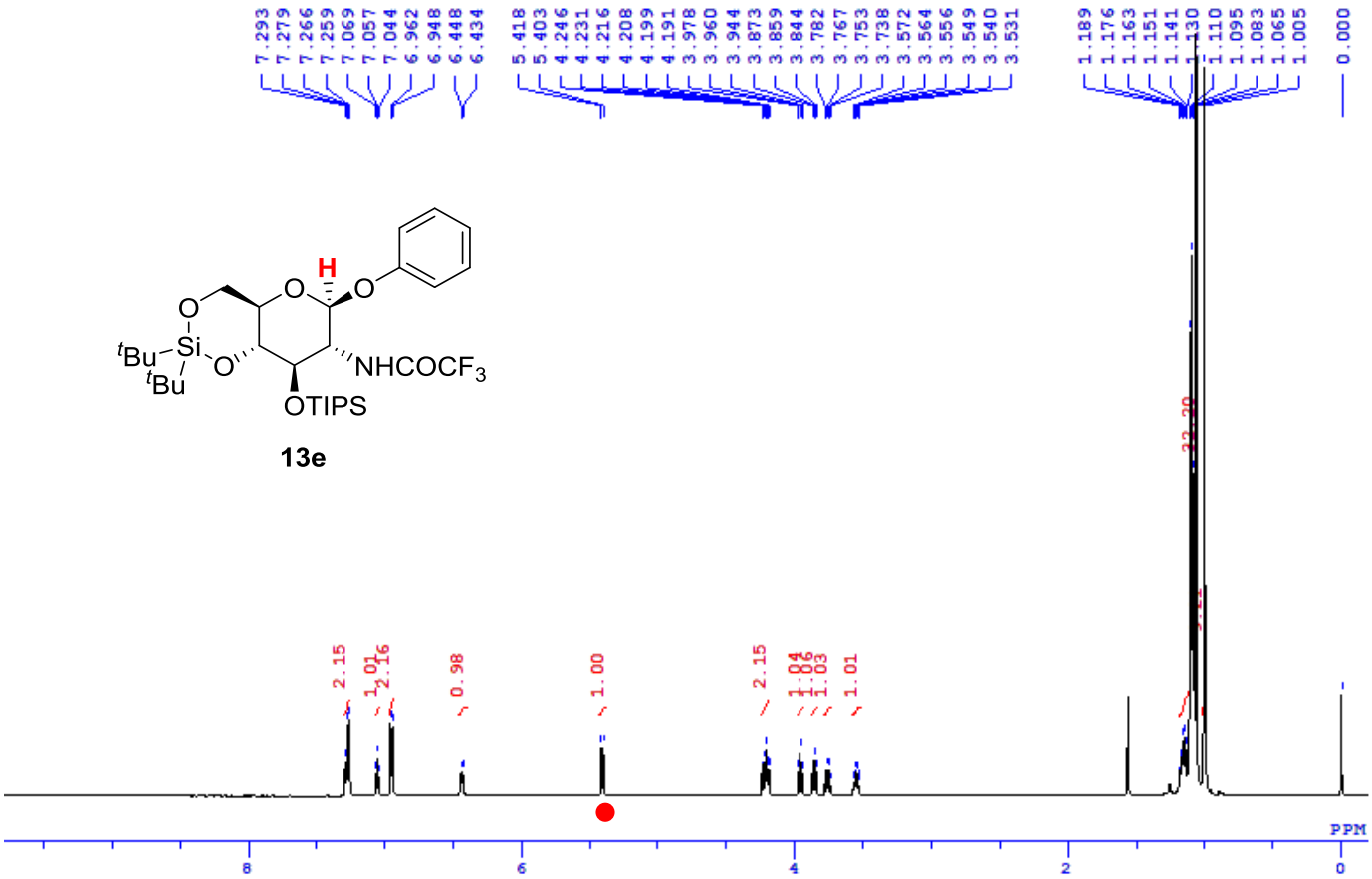
Compound **13d**, ^{1}H-NMR (600 MHz, $CDCl_3$)



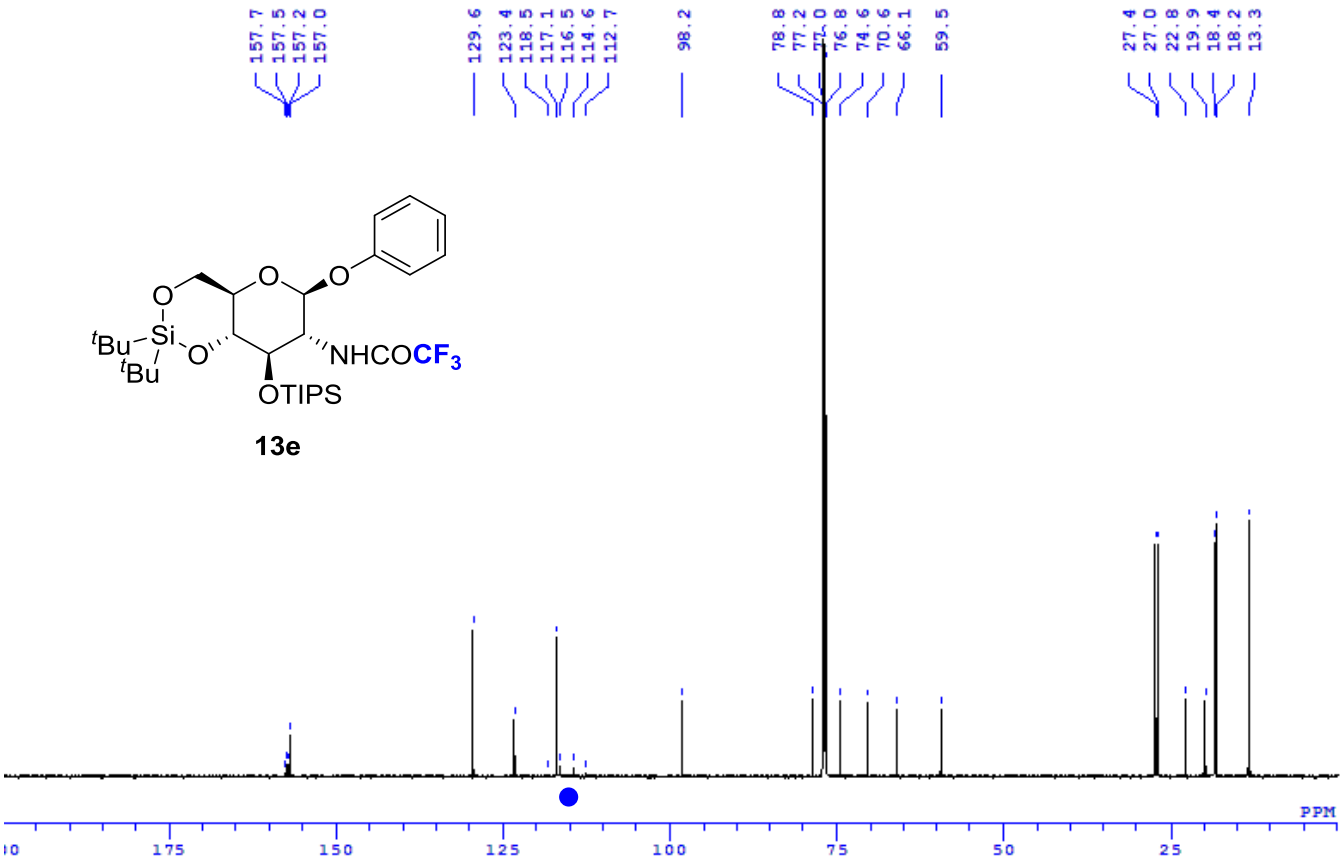
Compound **13d**, ^{13}C-NMR (150 MHz, $CDCl_3$)



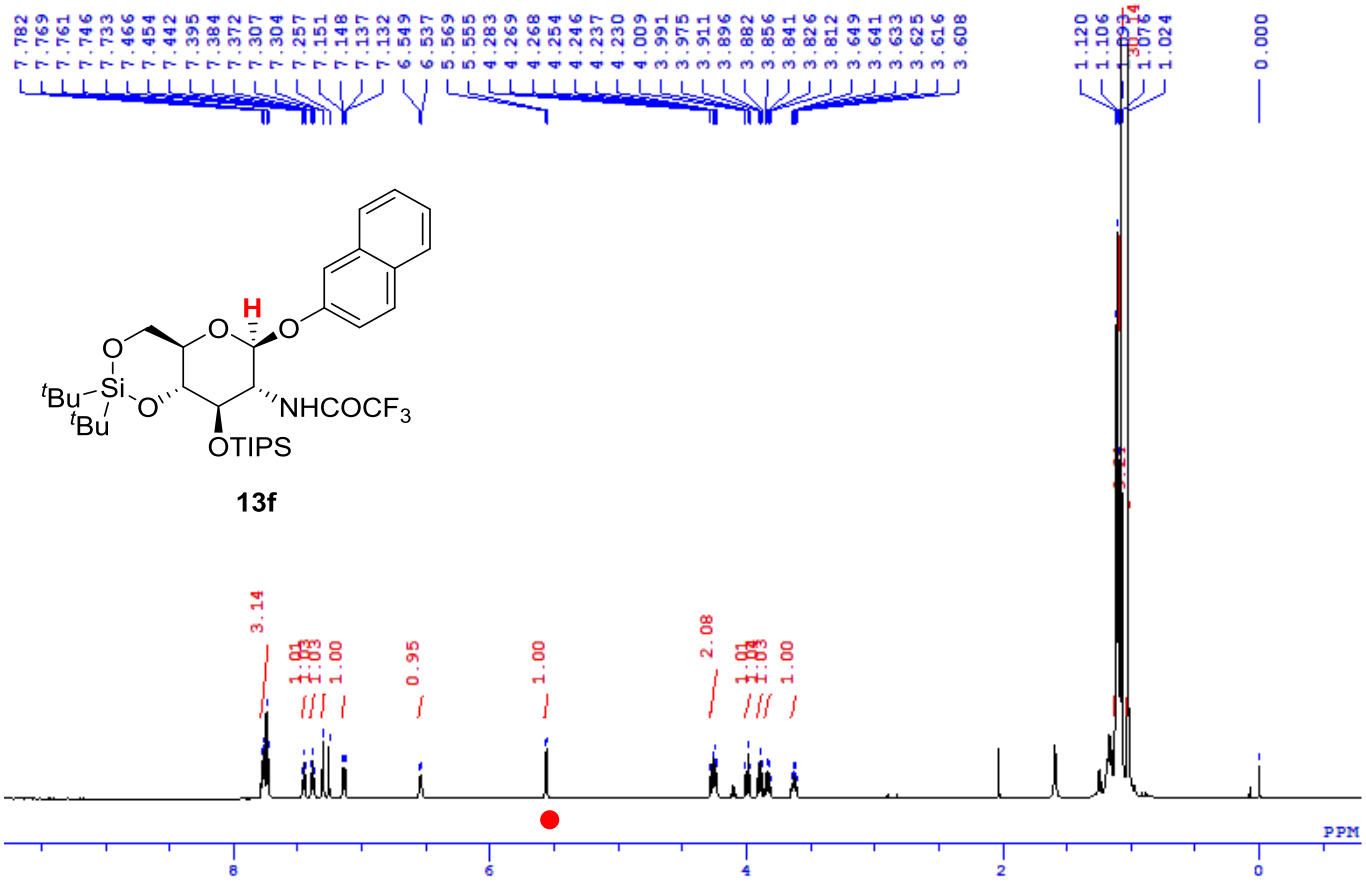
Compound **13e**, ^{1}H-NMR (600 MHz, $CDCl_3$)



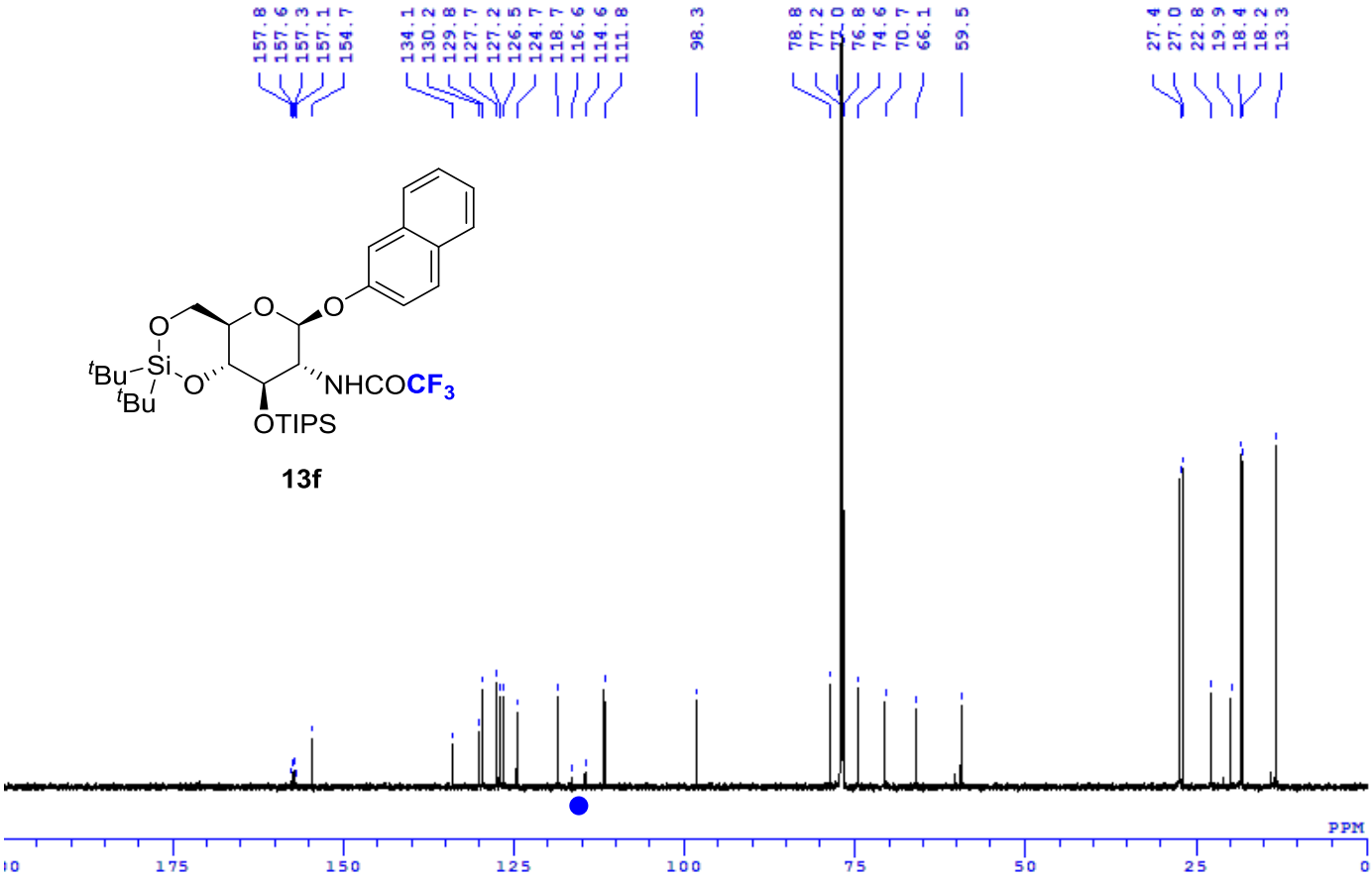
Compound **13e**, ^{13}C-NMR (150 MHz, $CDCl_3$)



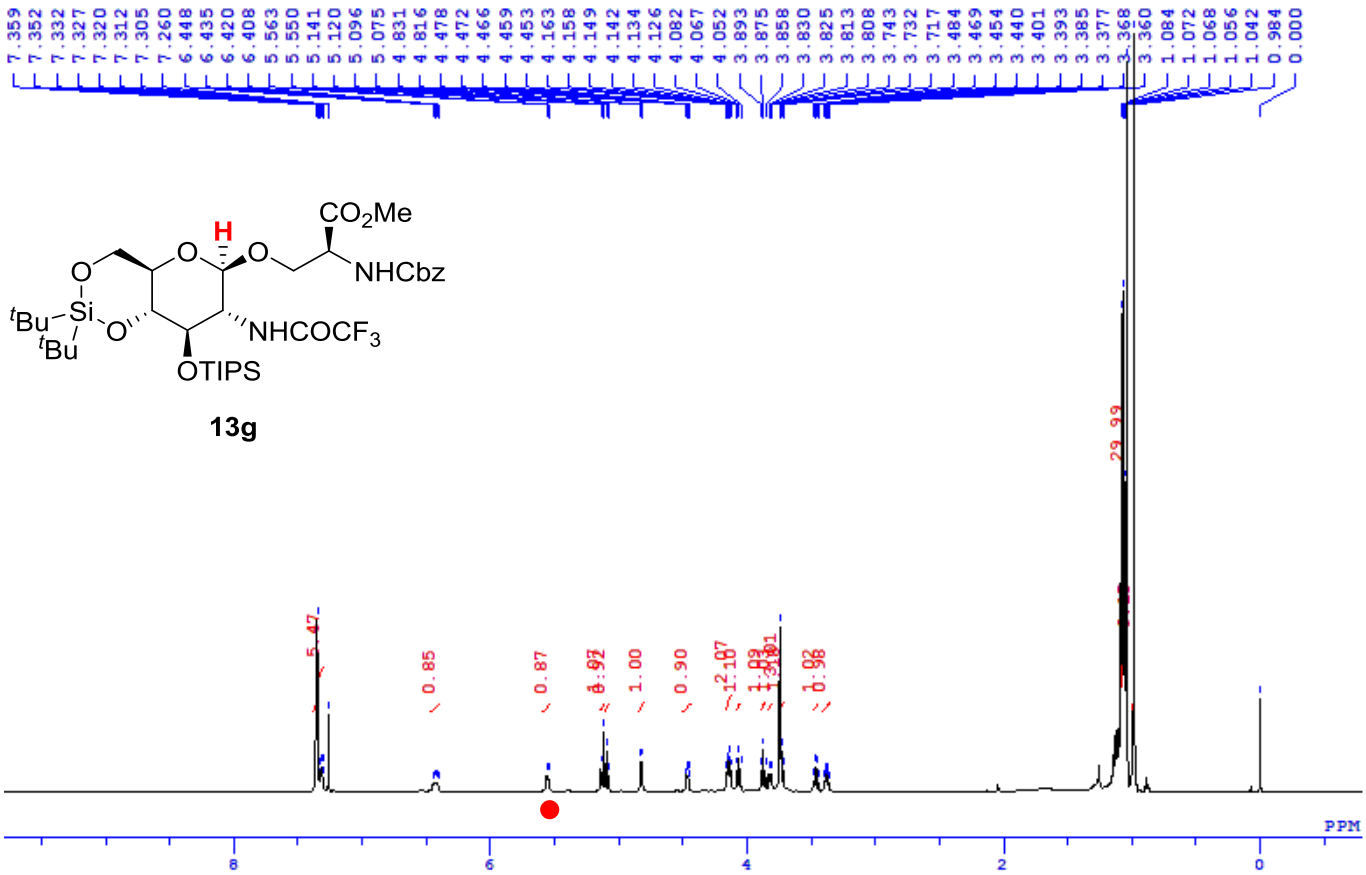
Compound **13f**, ^{1}H-NMR (600 MHz, $CDCl_3$)



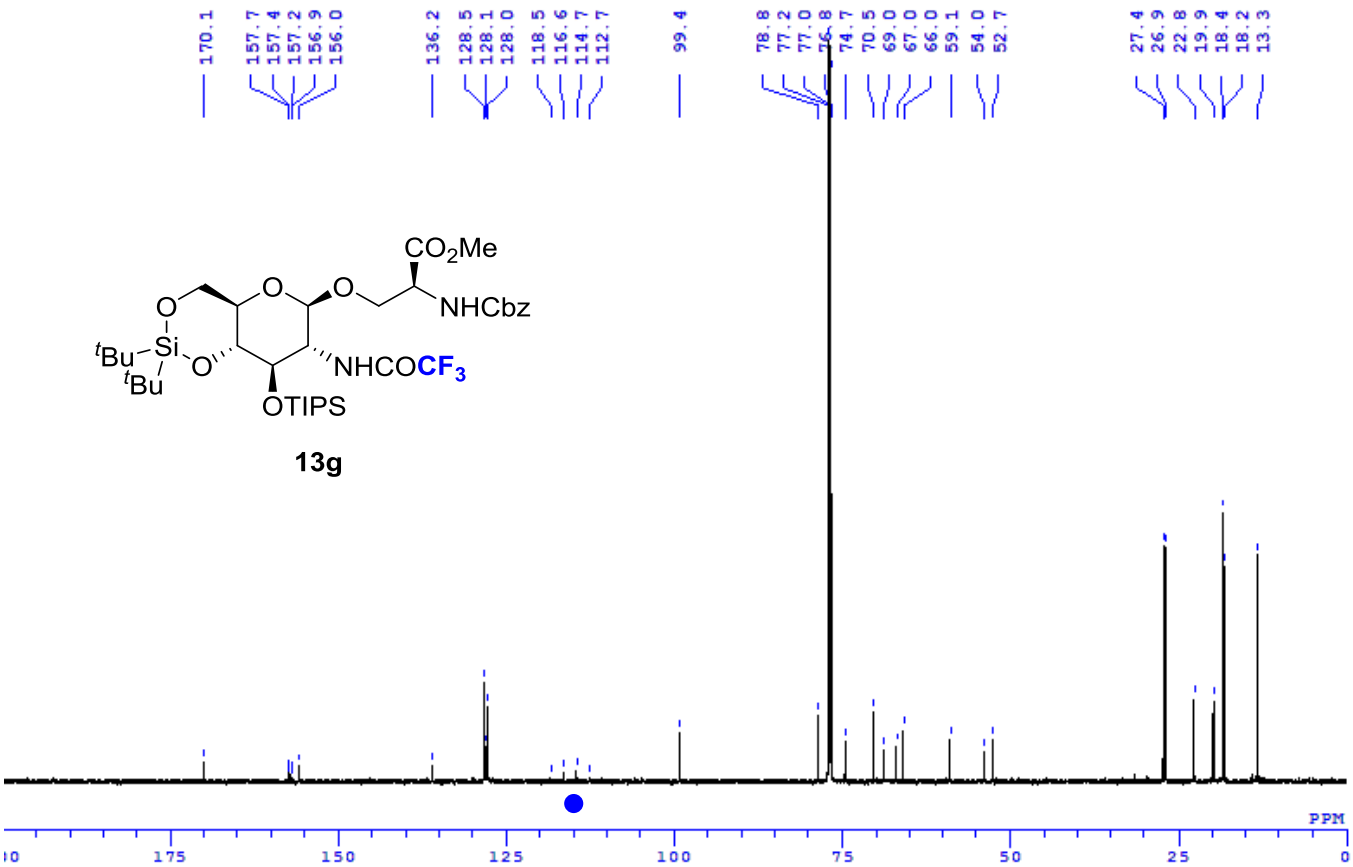
Compound **13f**, ^{13}C-NMR (150 MHz, $CDCl_3$)



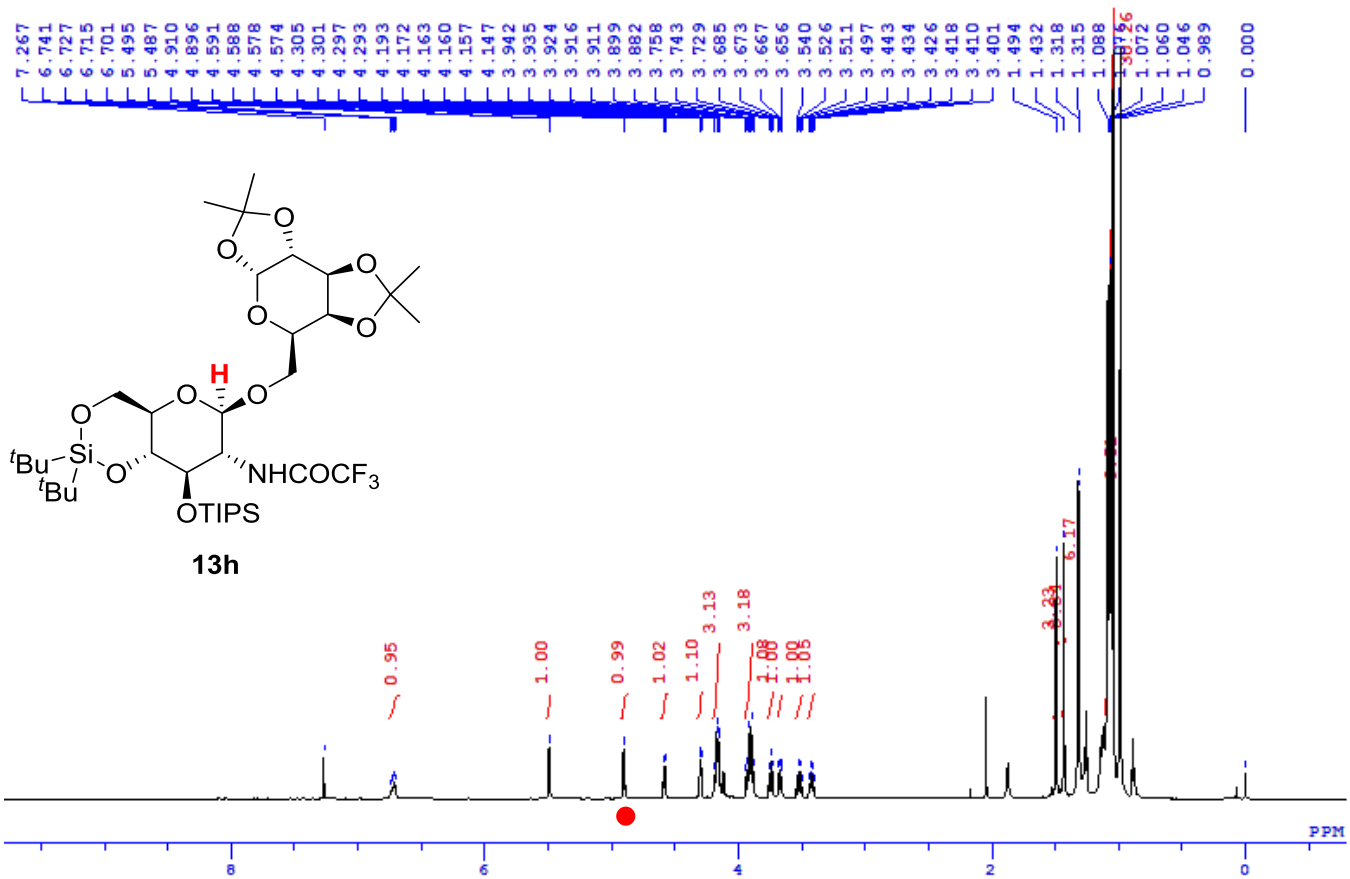
Compound **13g**, ^{1}H-NMR (600 MHz, $CDCl_3$)



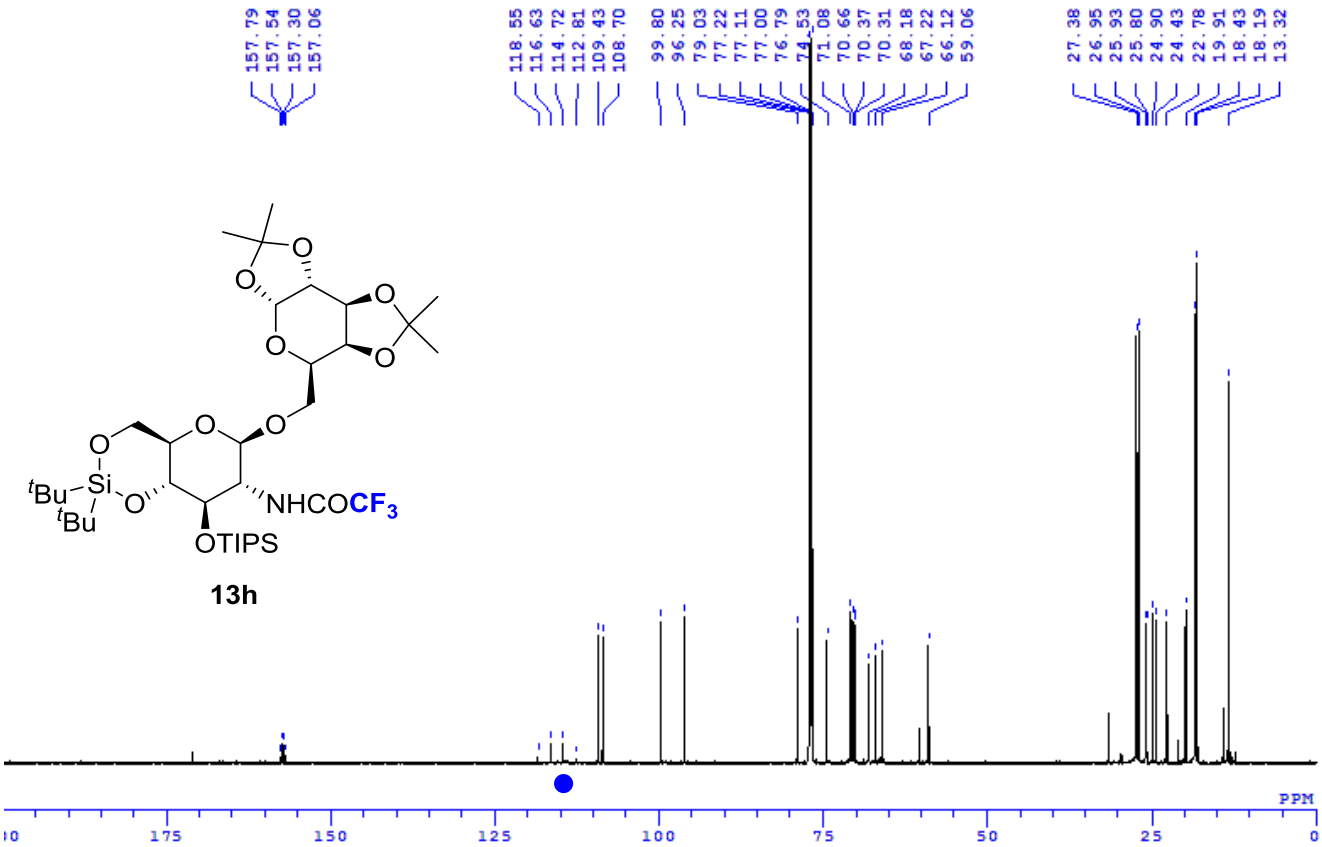
Compound **13g**, ^{13}C-NMR (150 MHz, $CDCl_3$)



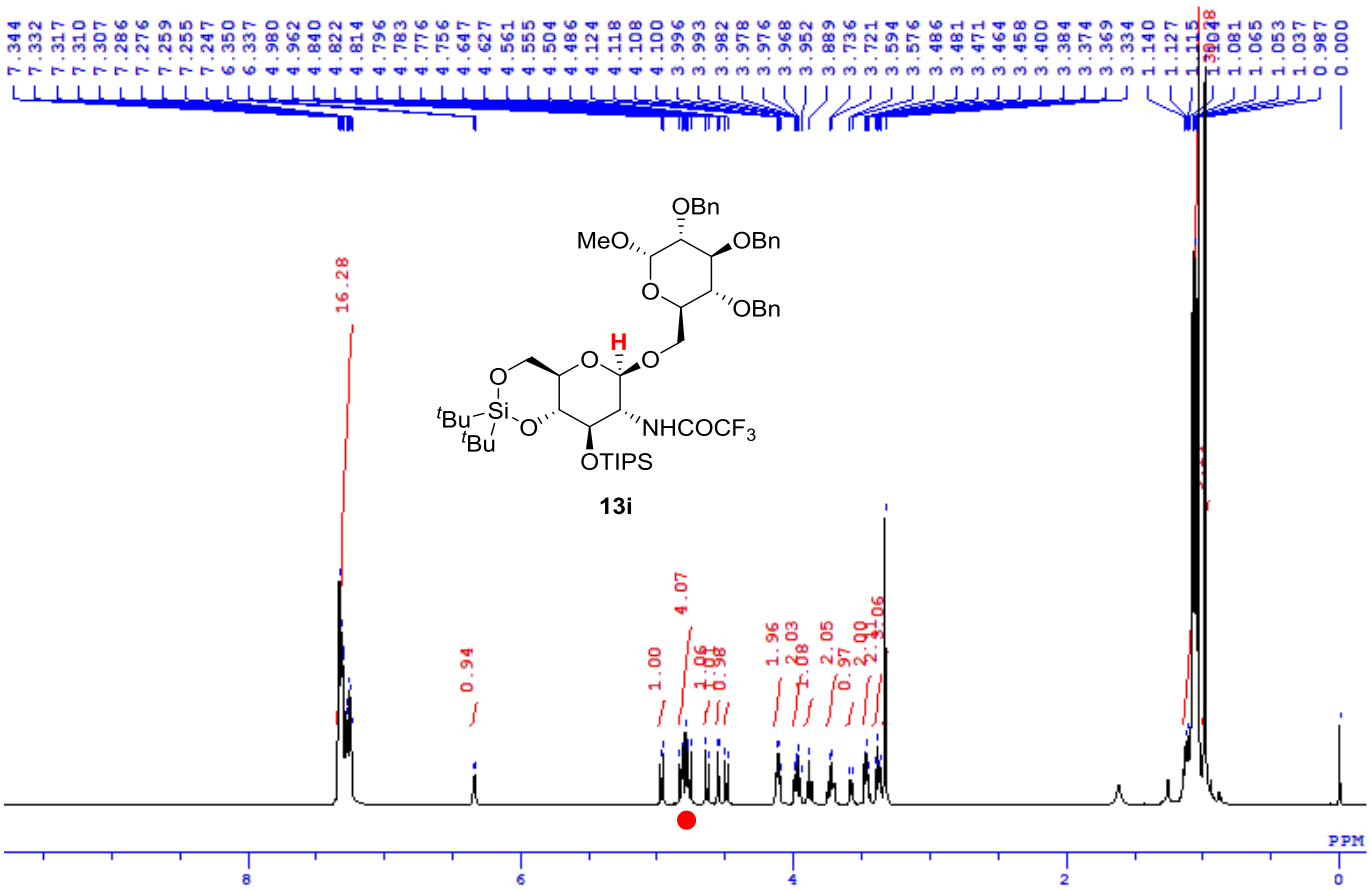
Compound **13h**, ^{1}H-NMR (600 MHz, $CDCl_3$)



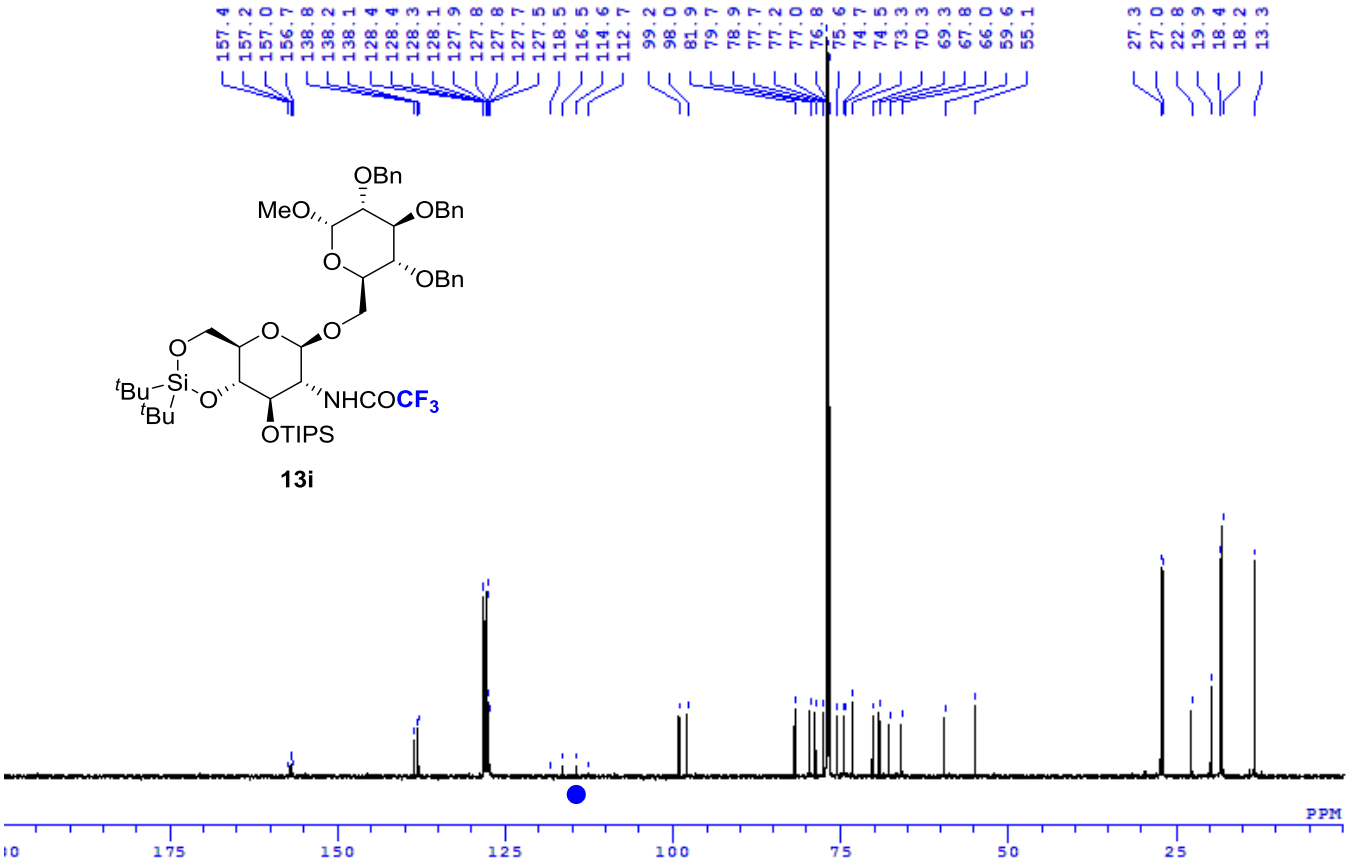
Compound **13h**, ^{13}C-NMR (150 MHz, $CDCl_3$)



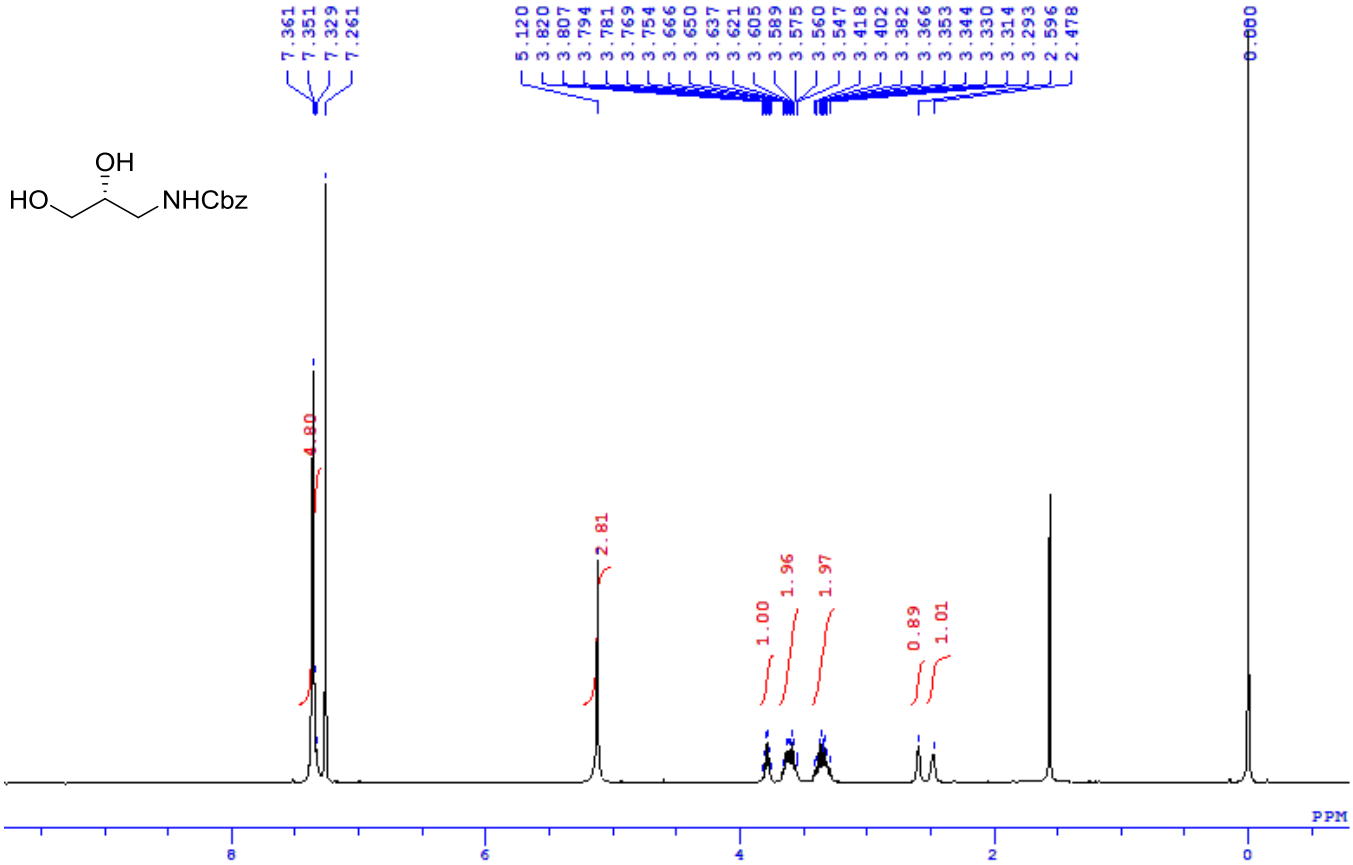
Compound **13i**, ^{1}H-NMR (600 MHz, $CDCl_3$)



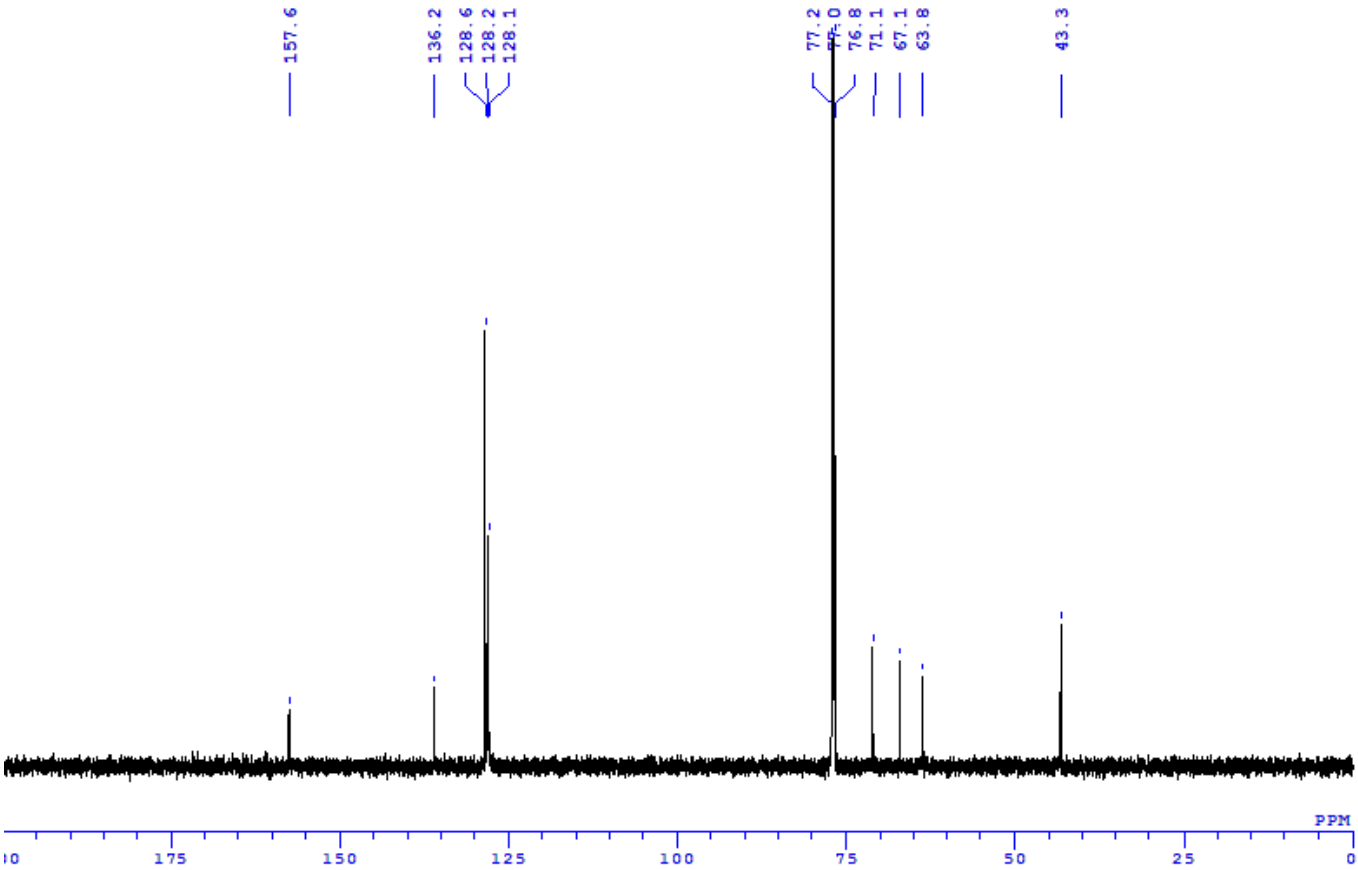
Compound **13i**, ^{13}C-NMR (150 MHz, $CDCl_3$)



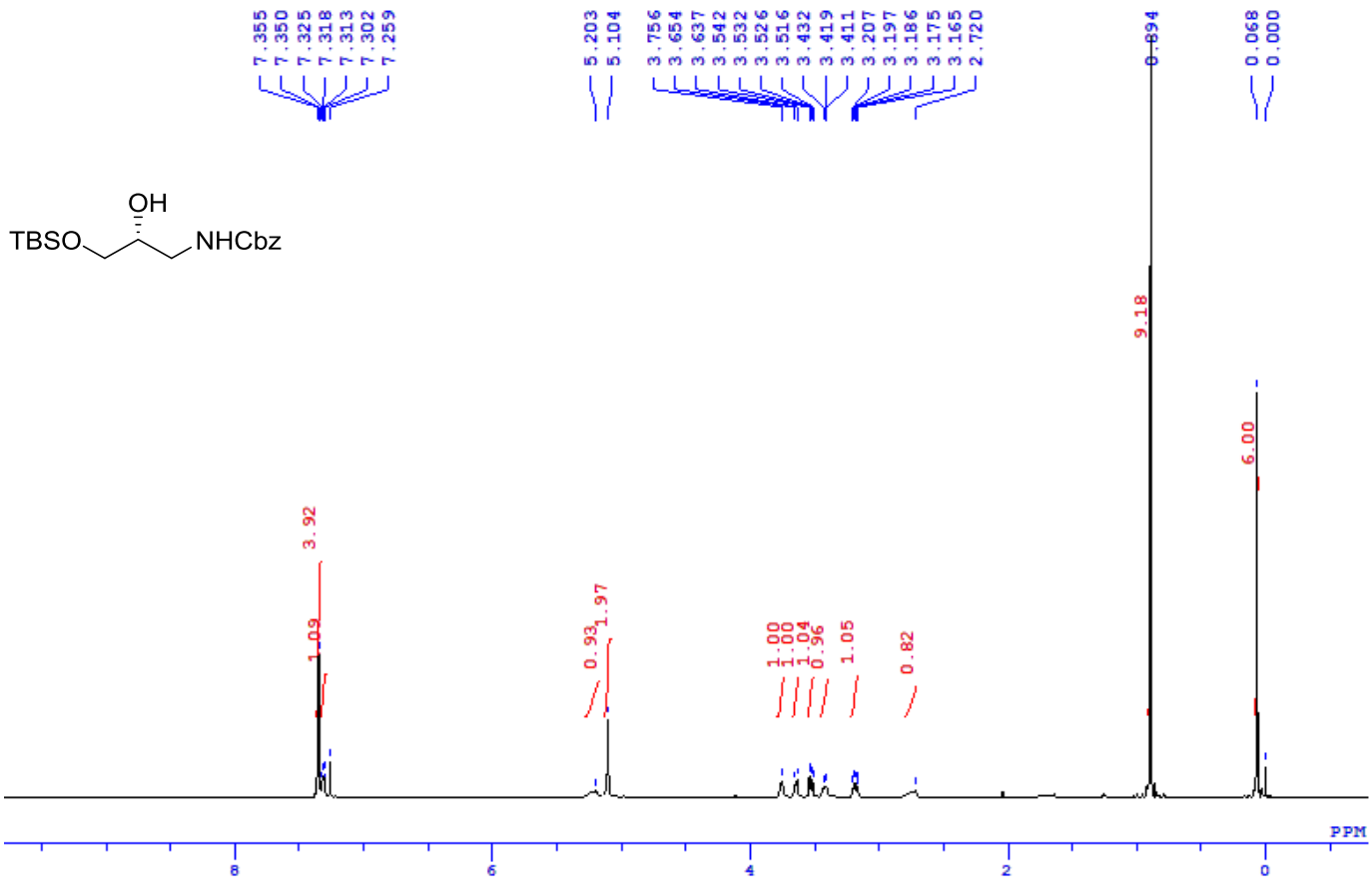
Compound **S1**, ^{1}H-NMR (400 MHz, $CDCl_3$)



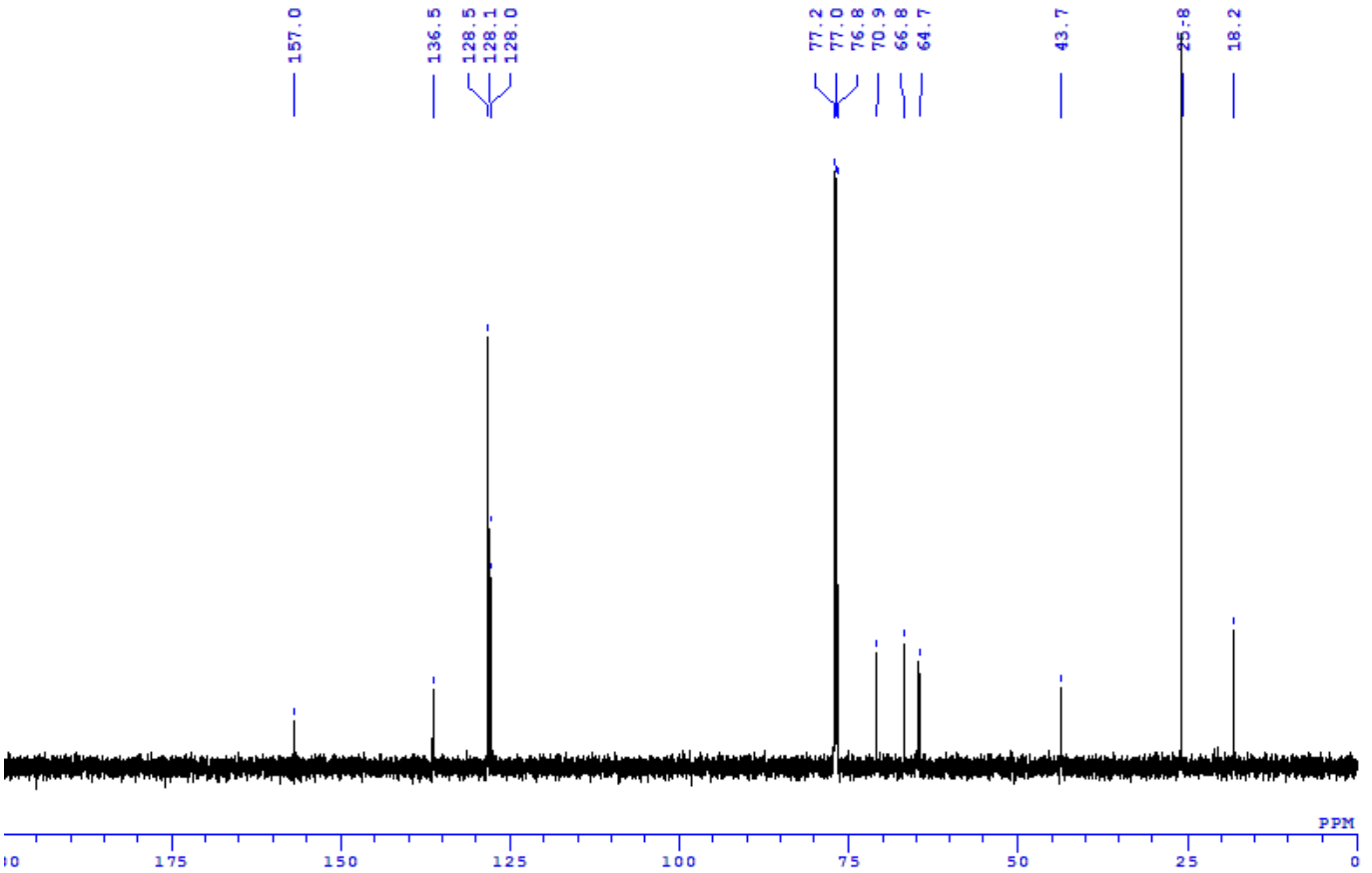
Compound **S1**, ^{13}C-NMR (150 MHz, $CDCl_3$)



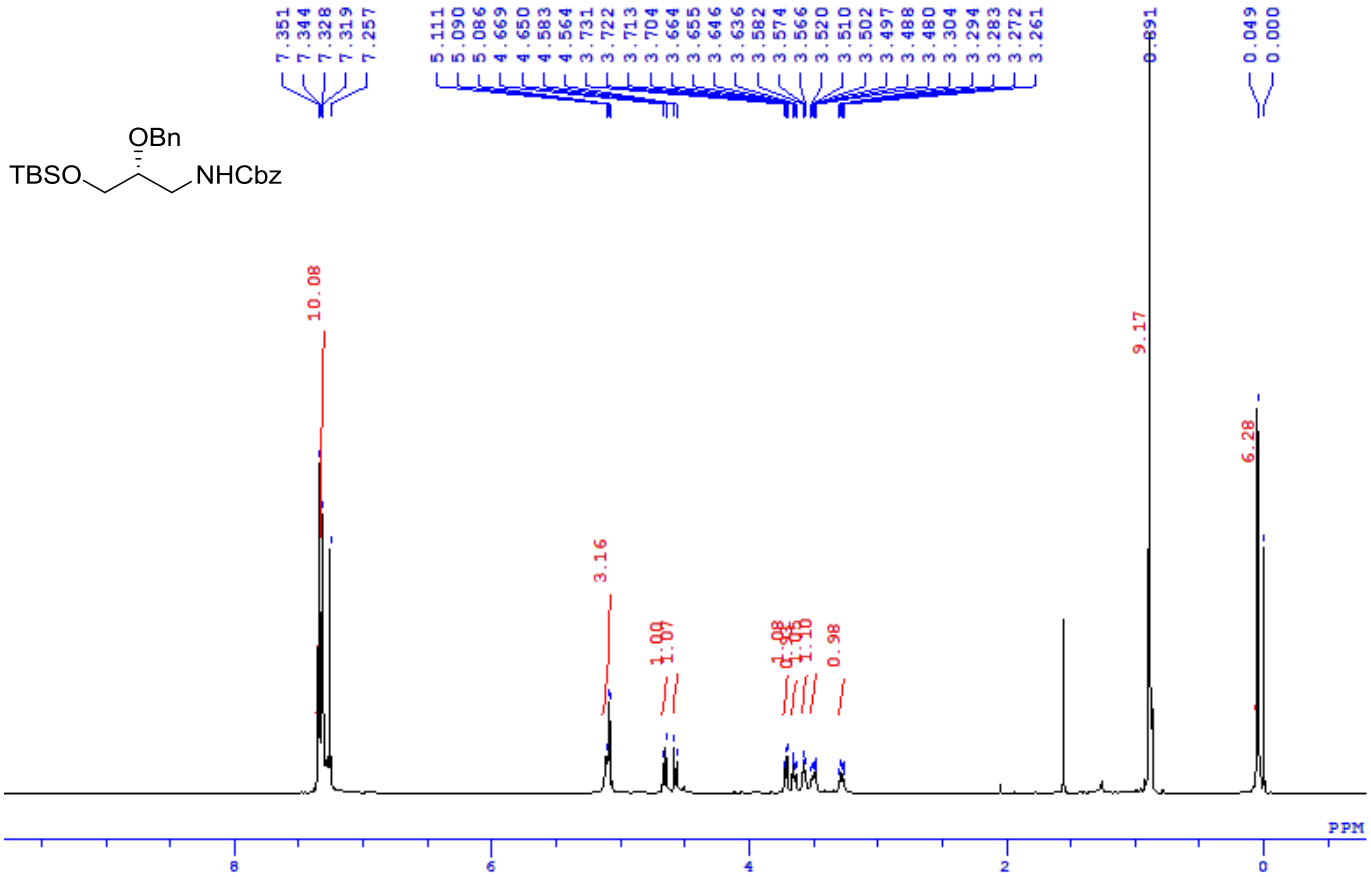
Compound **S2**, ^{1}H-NMR (600 MHz, $CDCl_3$)



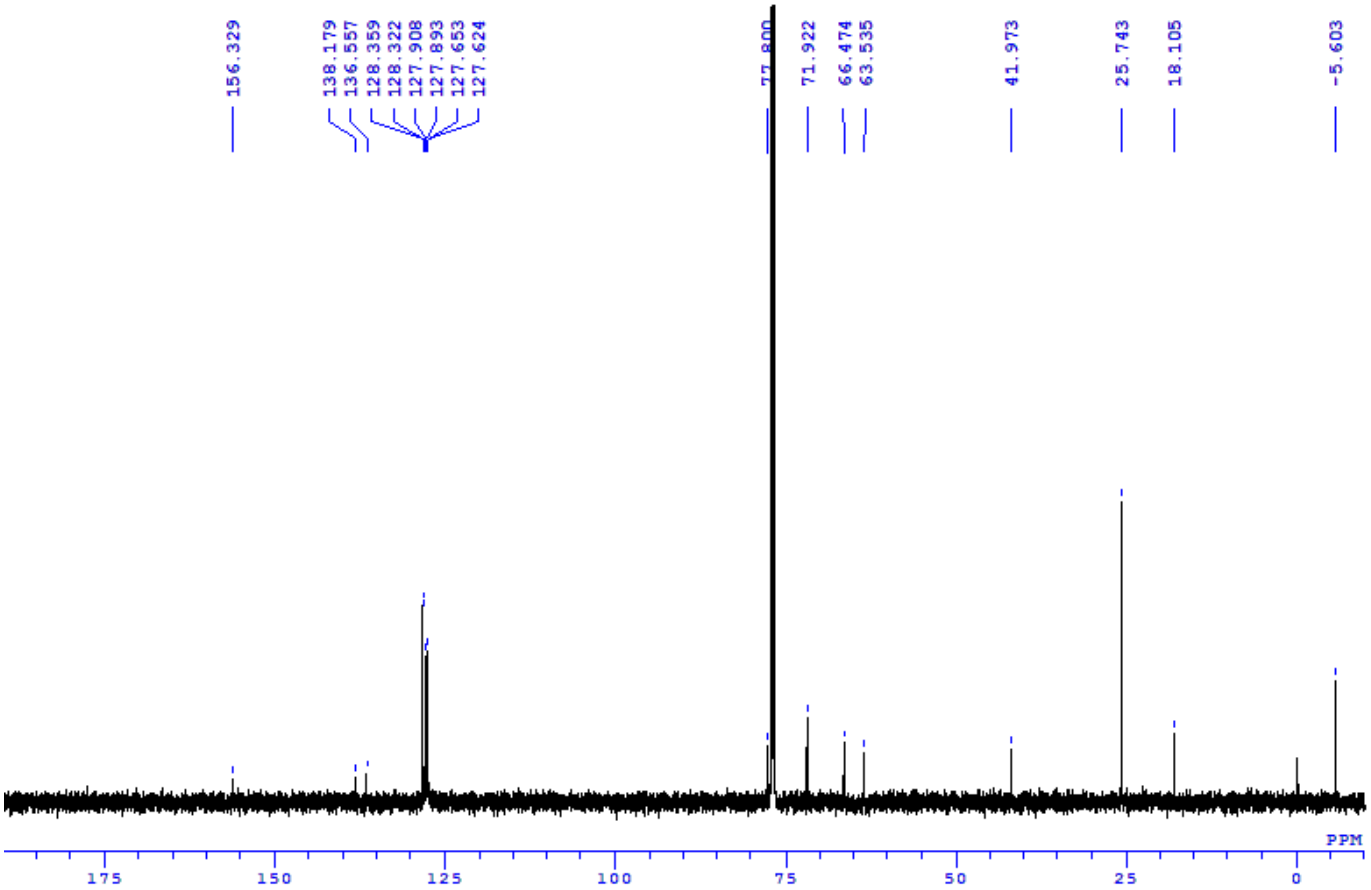
Compound **S2**, ^{13}C-NMR (150 MHz, $CDCl_3$)



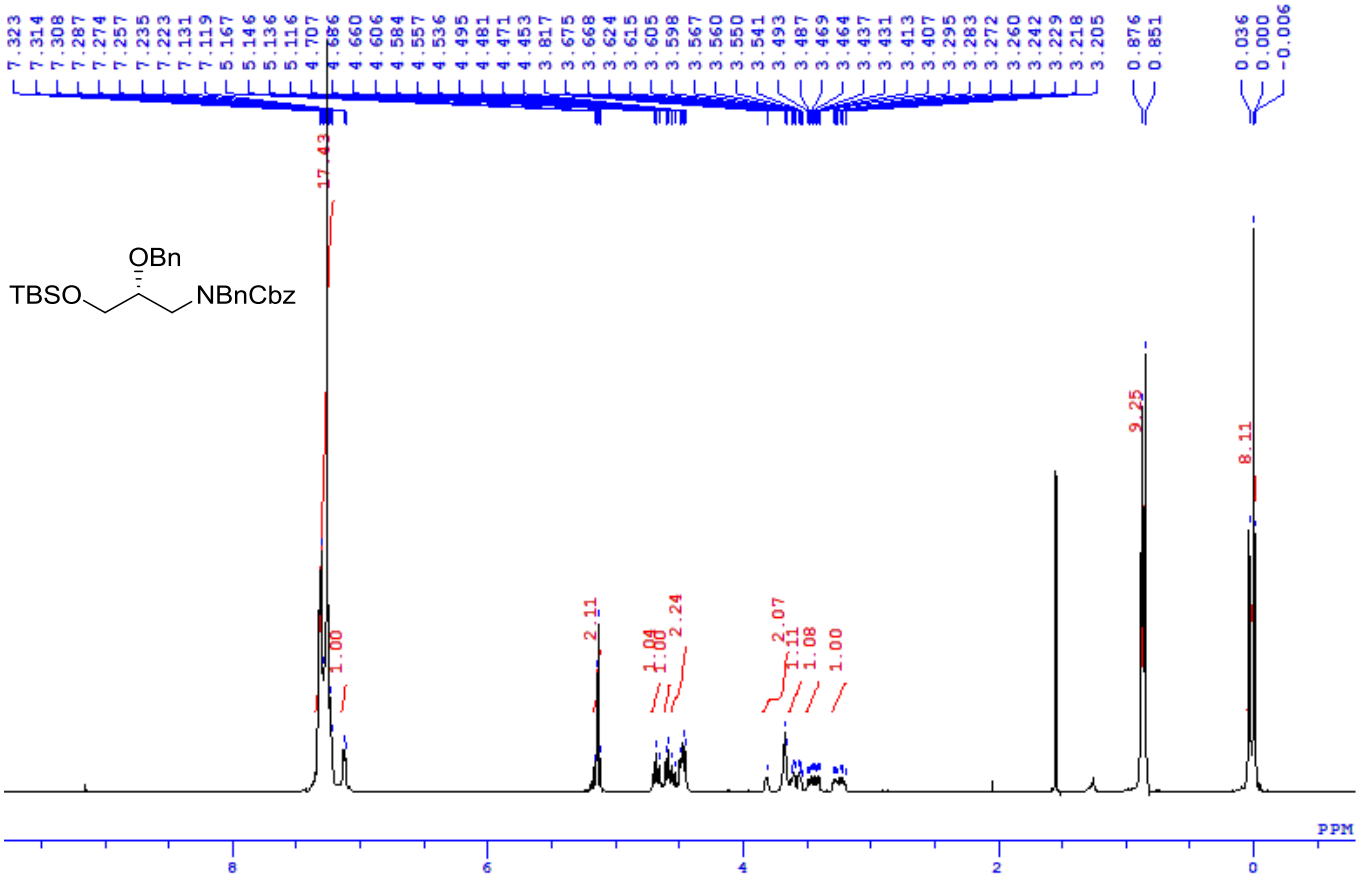
Compound **S3**, ^{1}H-NMR (600 MHz, $CDCl_3$)



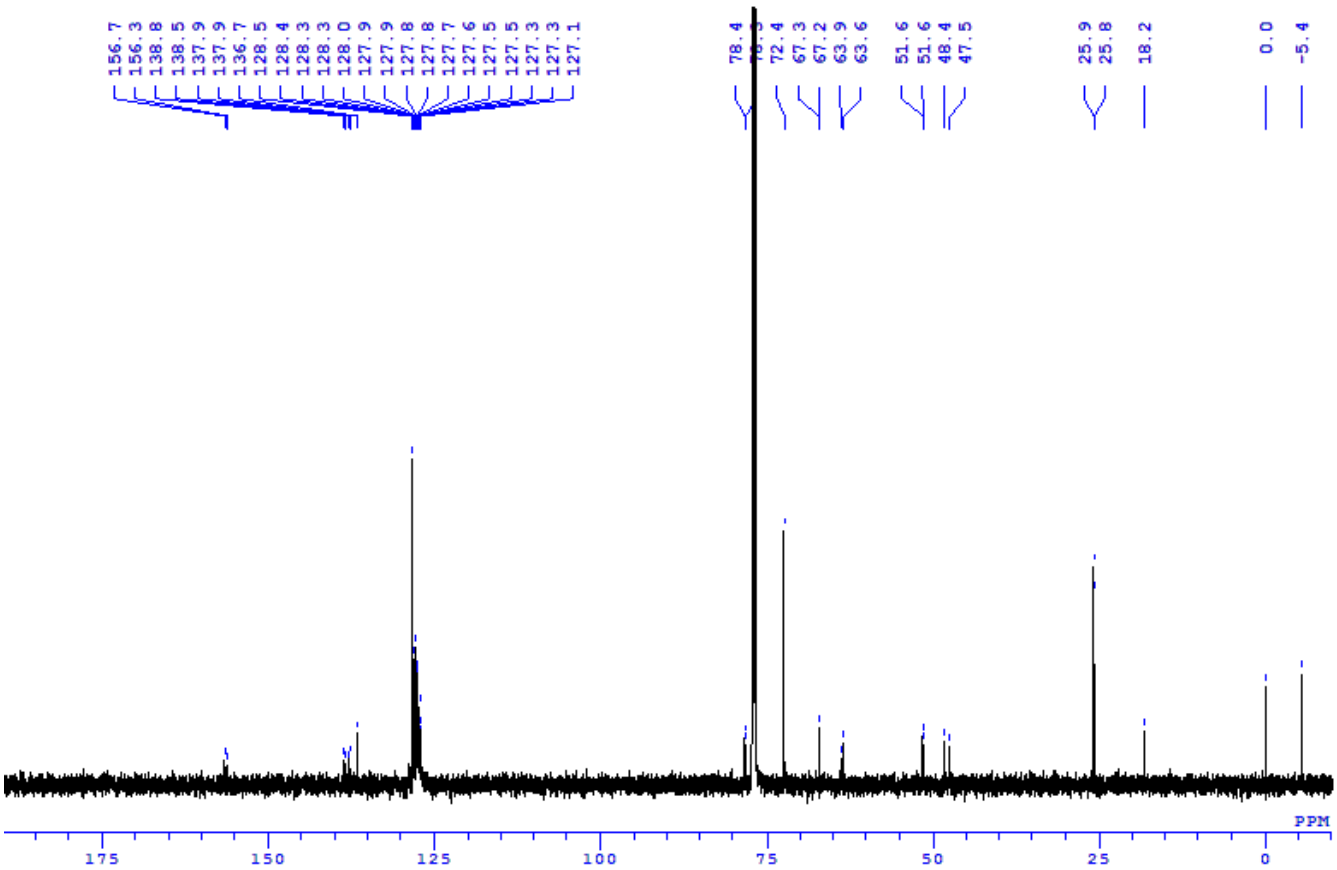
Compound **S3**, ^{13}C-NMR (150 MHz, $CDCl_3$)



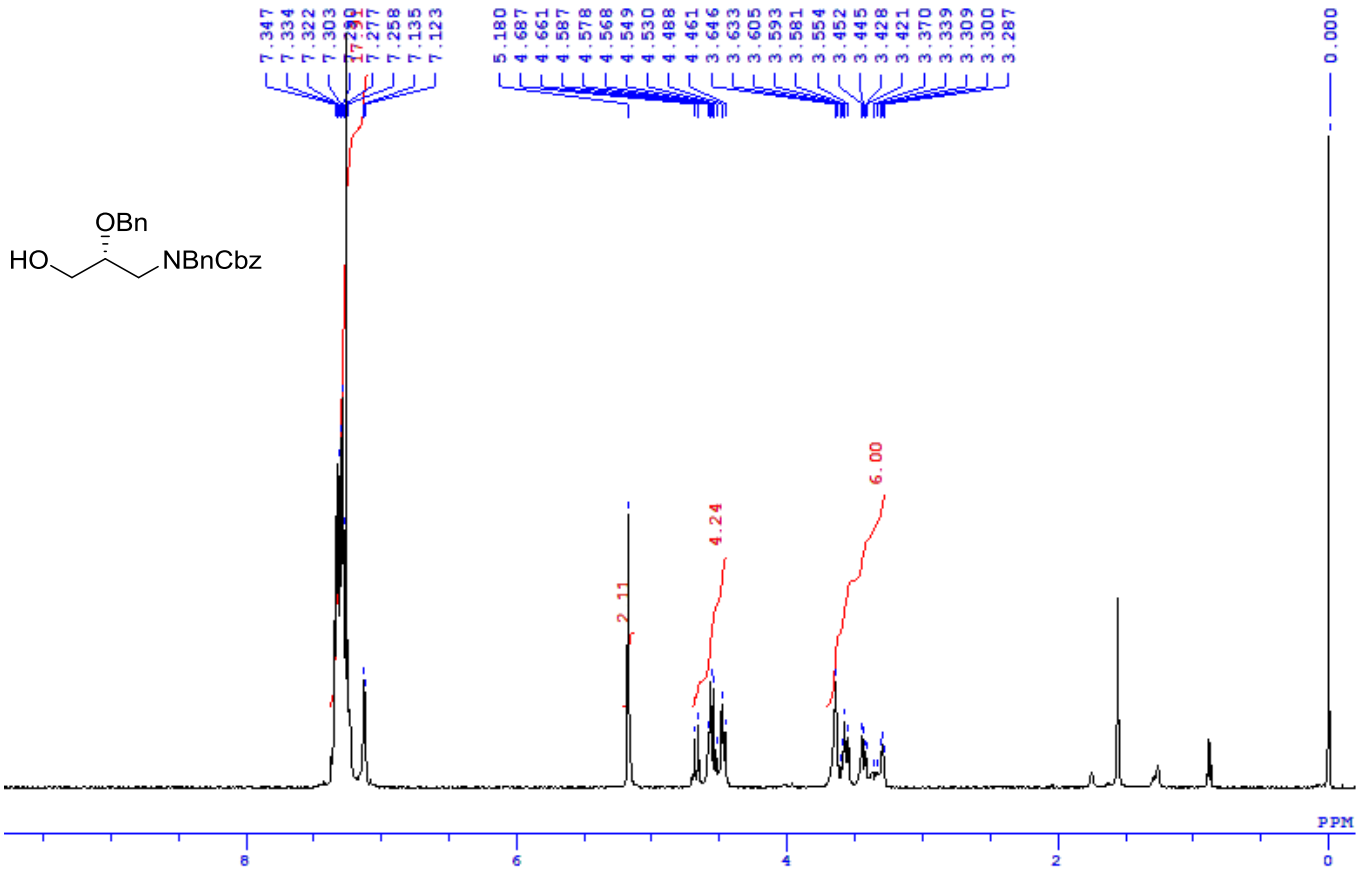
Compound **S4**, ^{1}H-NMR (600 MHz, $CDCl_3$)



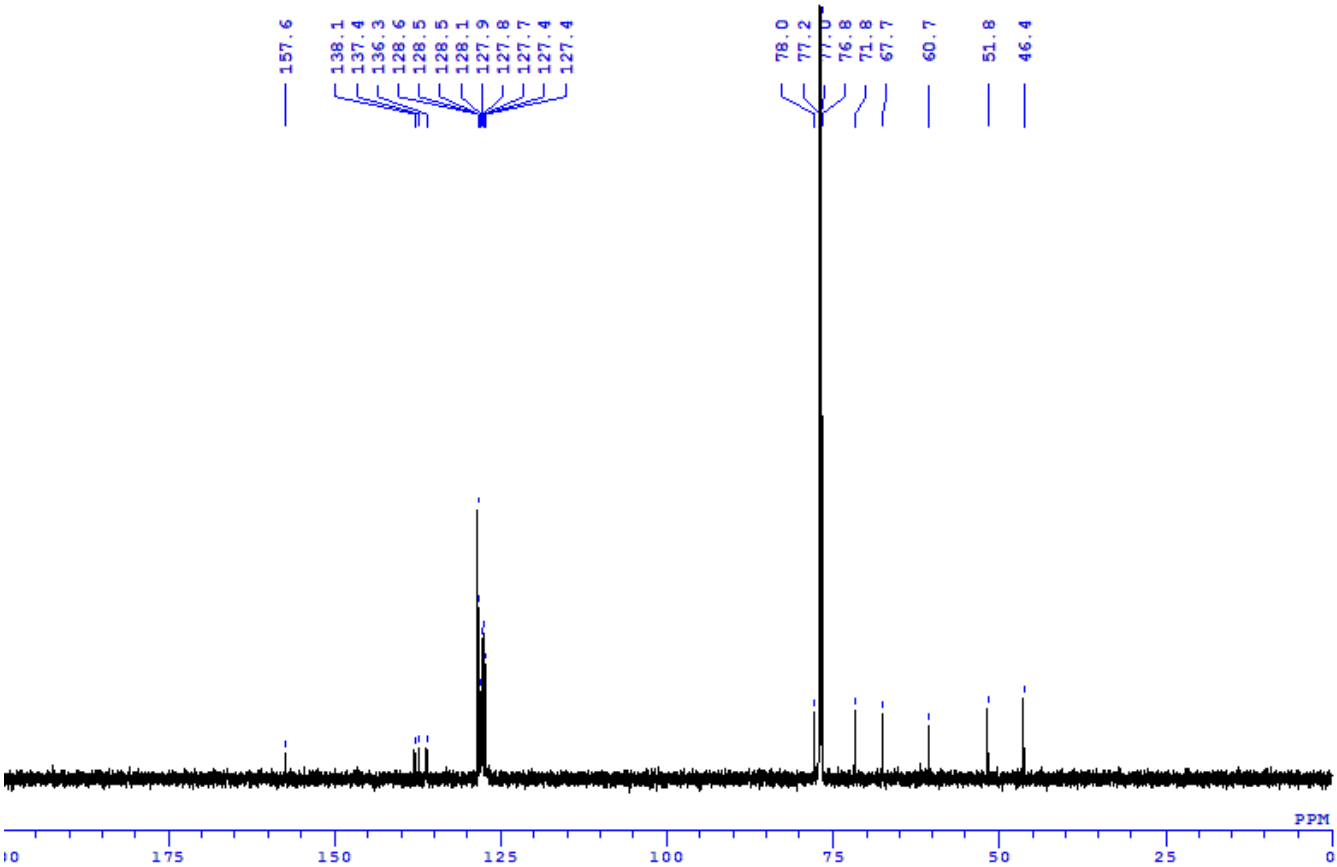
Compound **S4**, ^{13}C-NMR (150 MHz, $CDCl_3$)



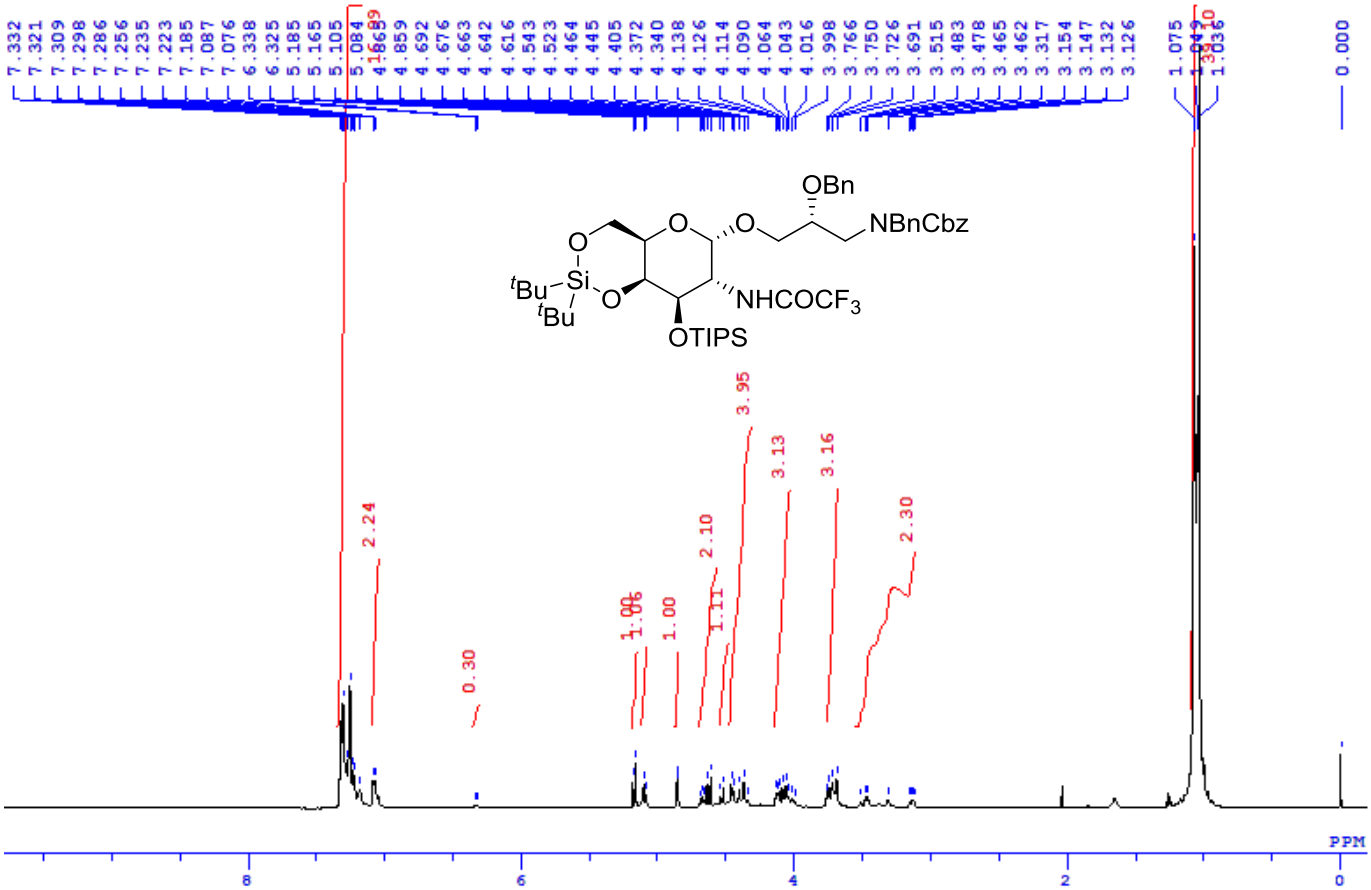
Compound **16**, ^{1}H-NMR (600 MHz, $CDCl_3$)



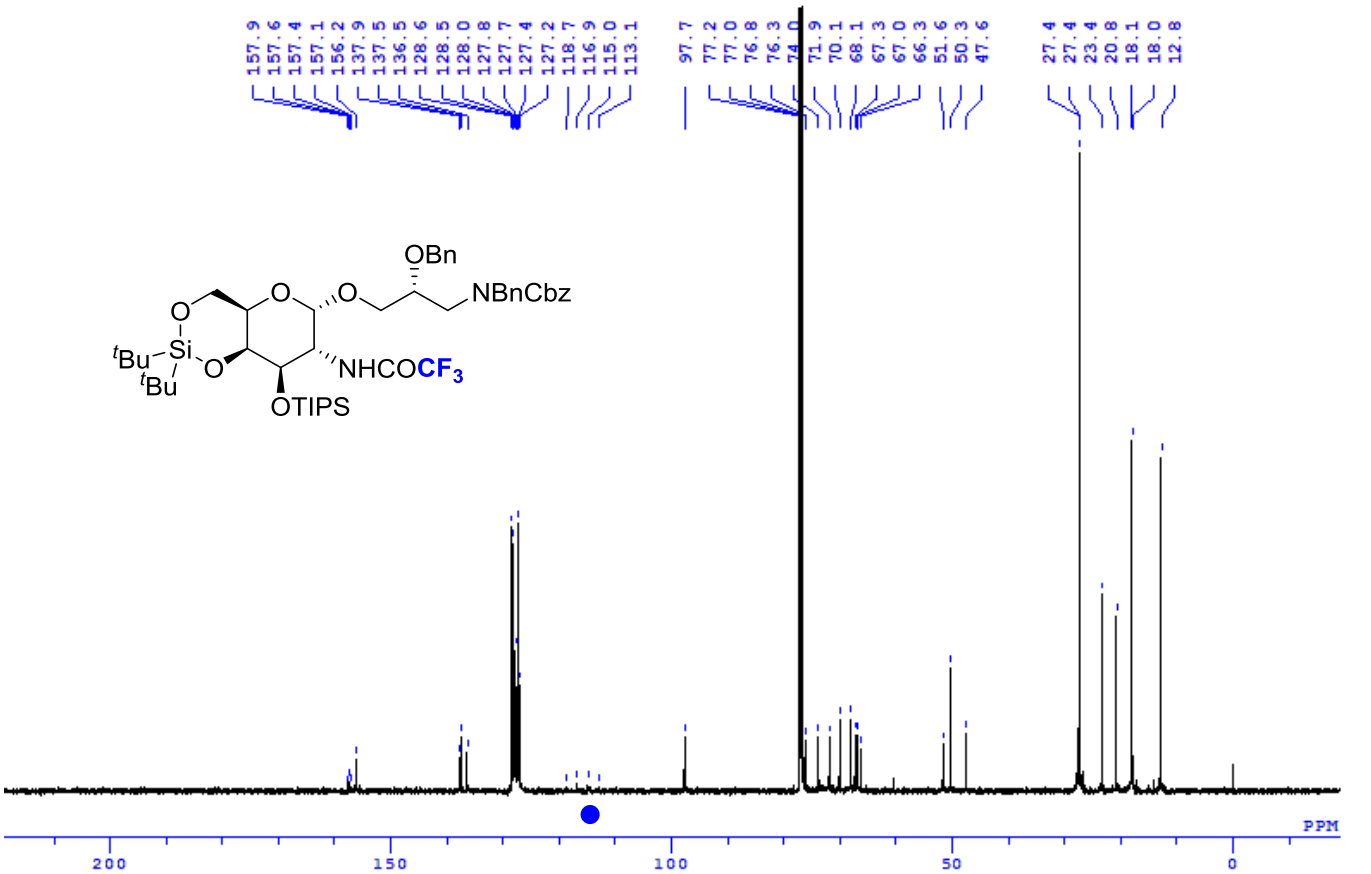
Compound **16**, ^{13}C-NMR (600 MHz, $CDCl_3$)



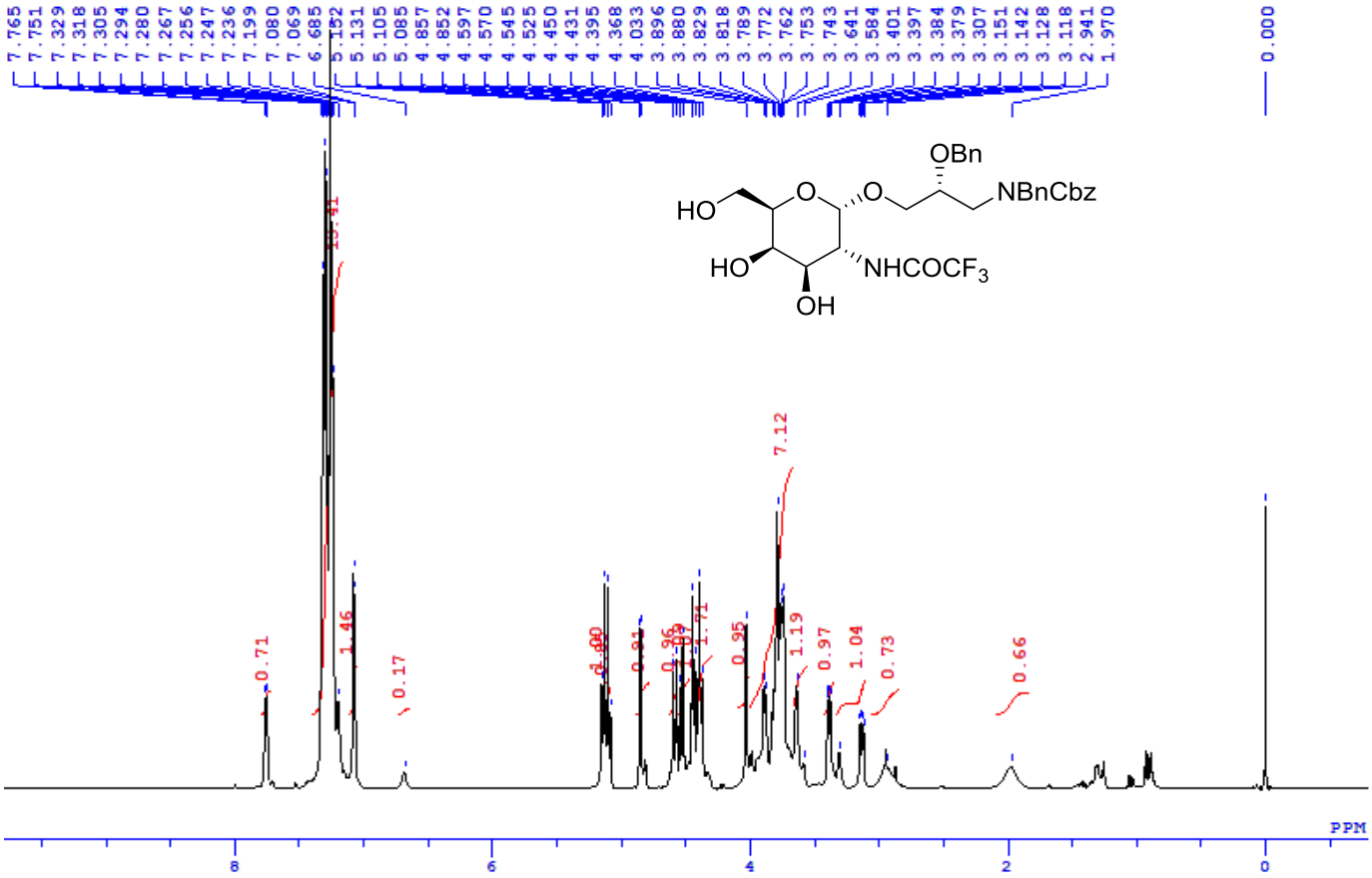
Compound **17**, ^{1}H-NMR (600 MHz, $CDCl_3$)



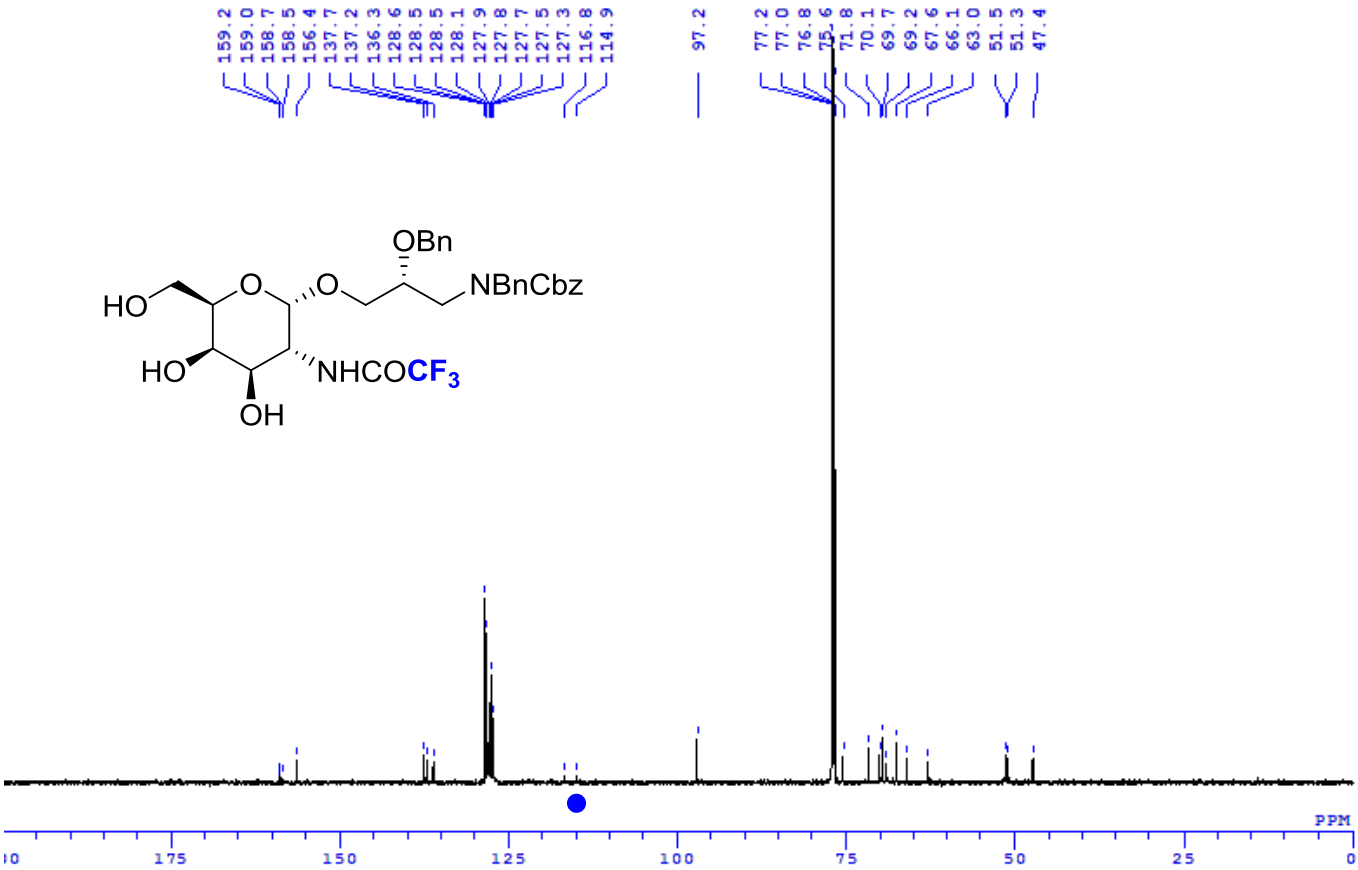
Compound **17**, ^{13}C-NMR (150 MHz, $CDCl_3$)



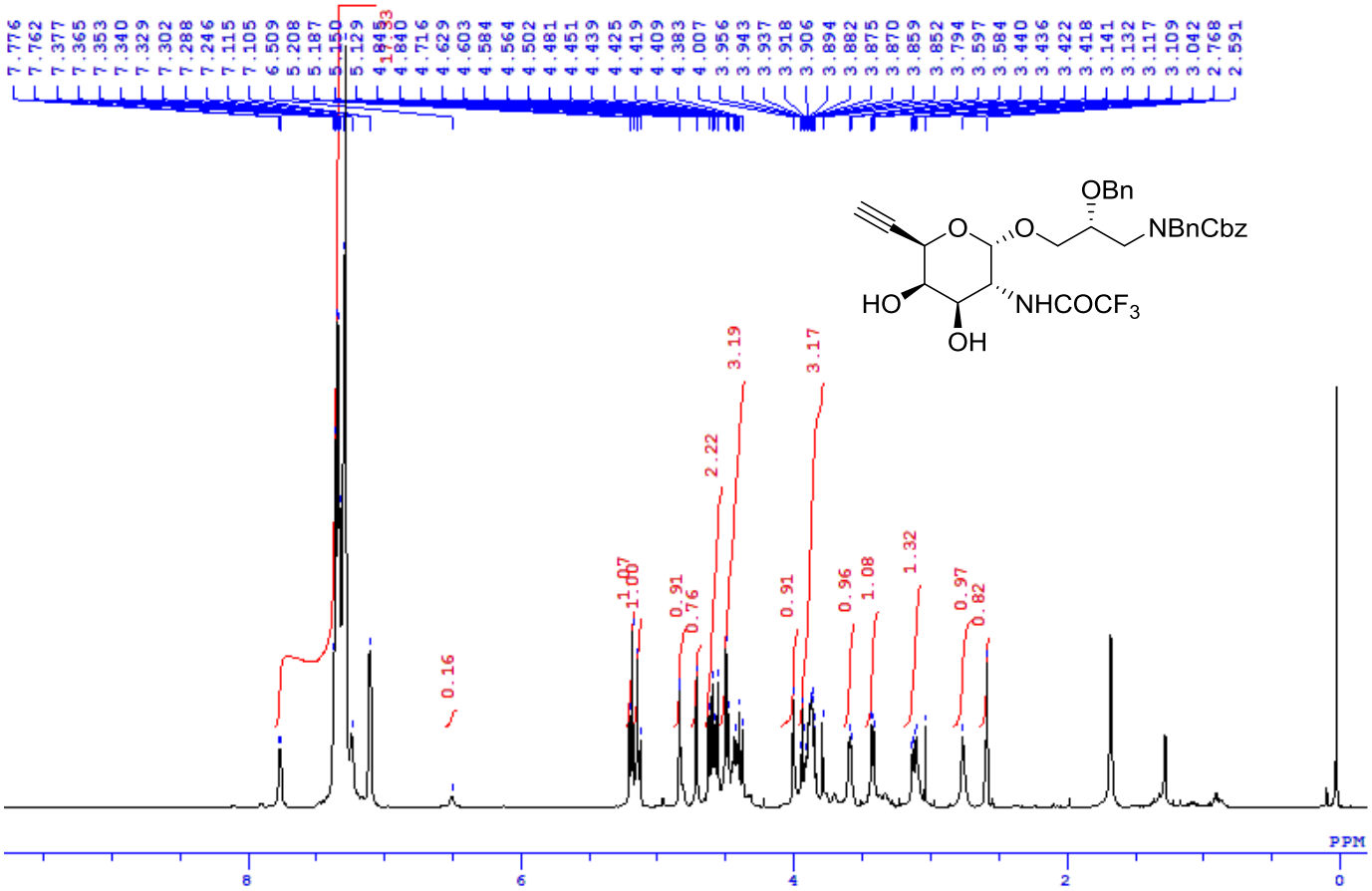
Compound **18**, ^{1}H-NMR (600 MHz, $CDCl_3$)



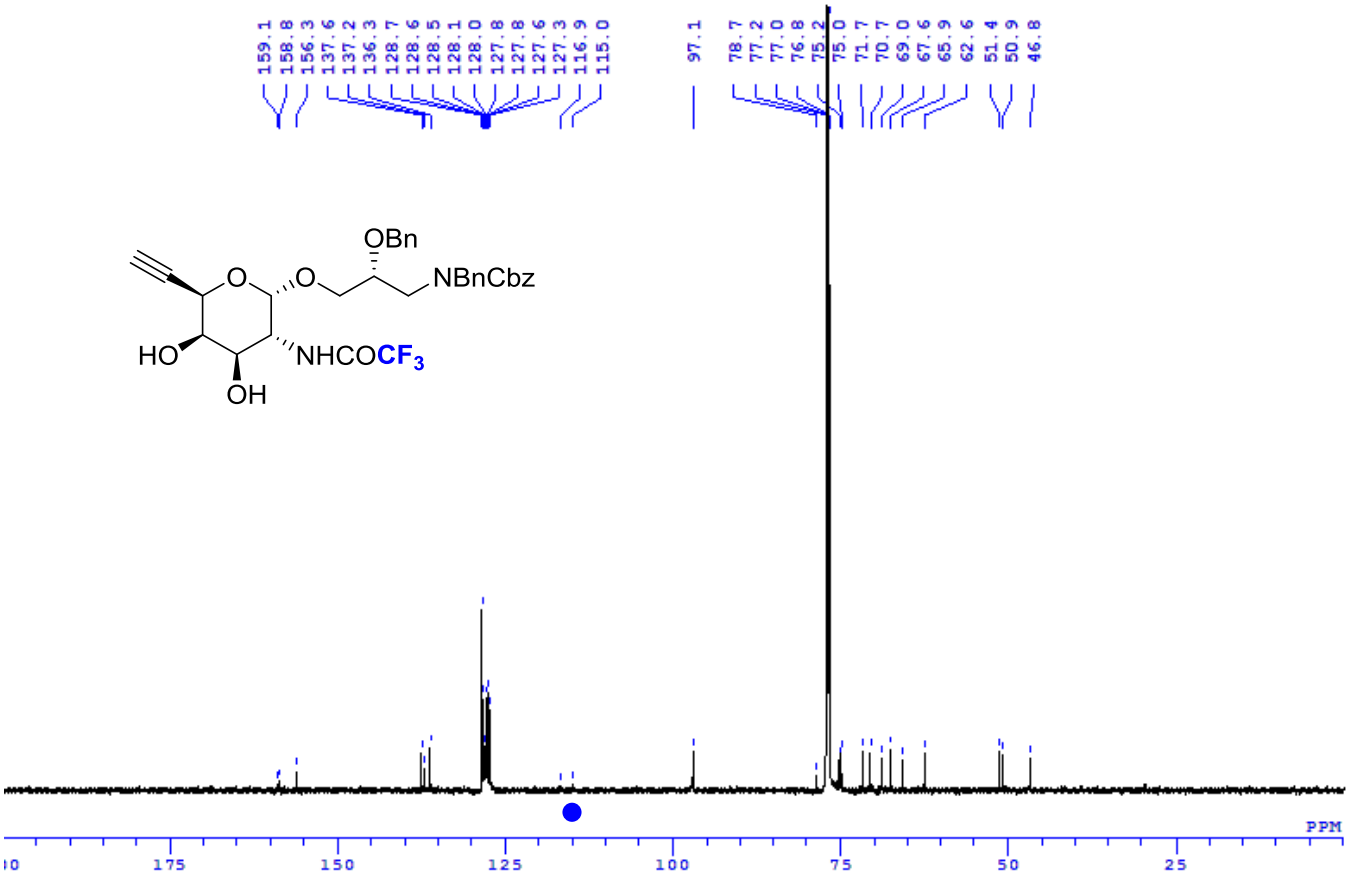
Compound **18**, ^{13}C-NMR (150 MHz, $CDCl_3$)



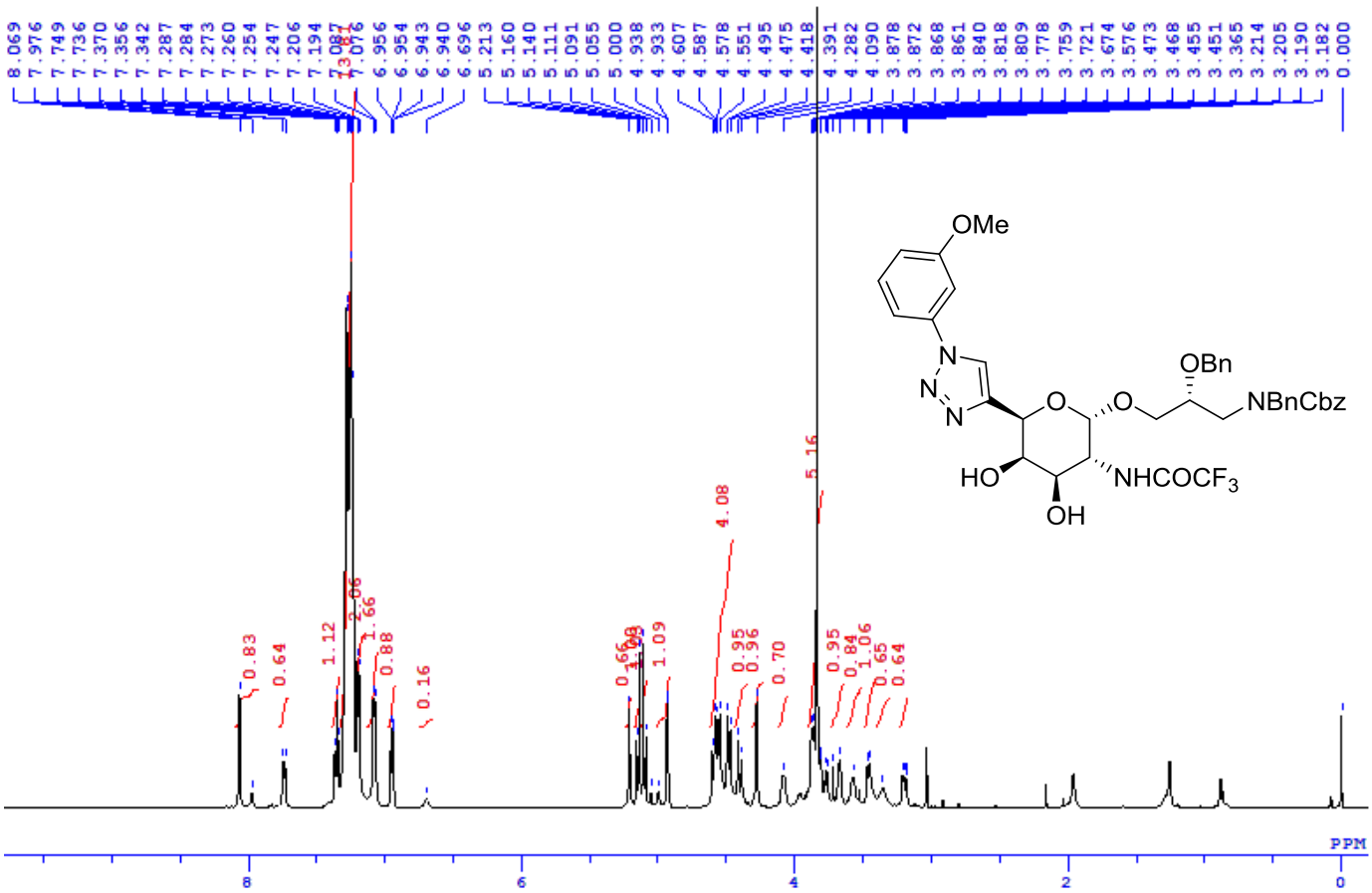
Compound **20**, ^{1}H-NMR (600 MHz, $CDCl_3$)



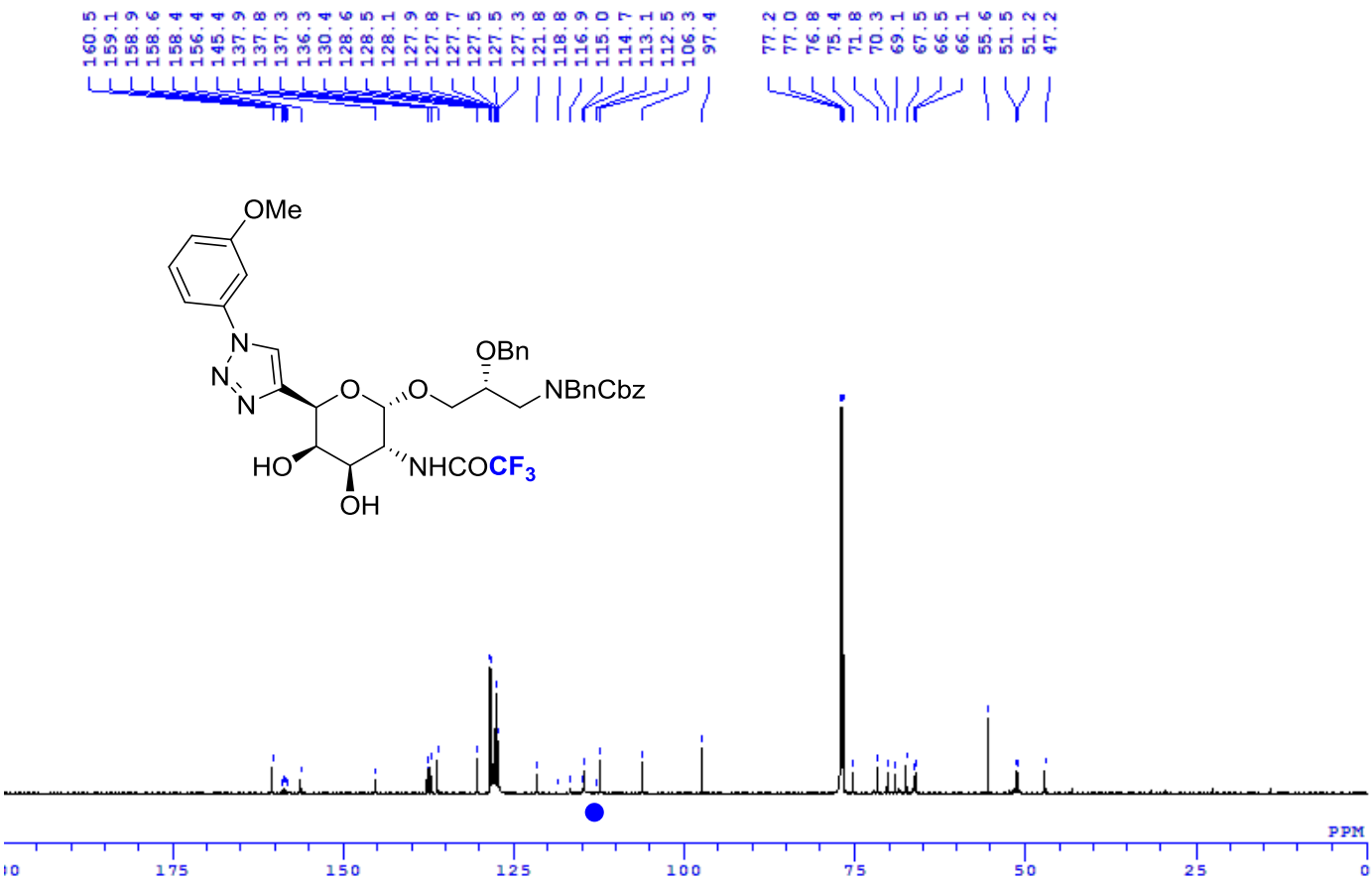
Compound **20**, ^{13}C-NMR (150 MHz, $CDCl_3$)



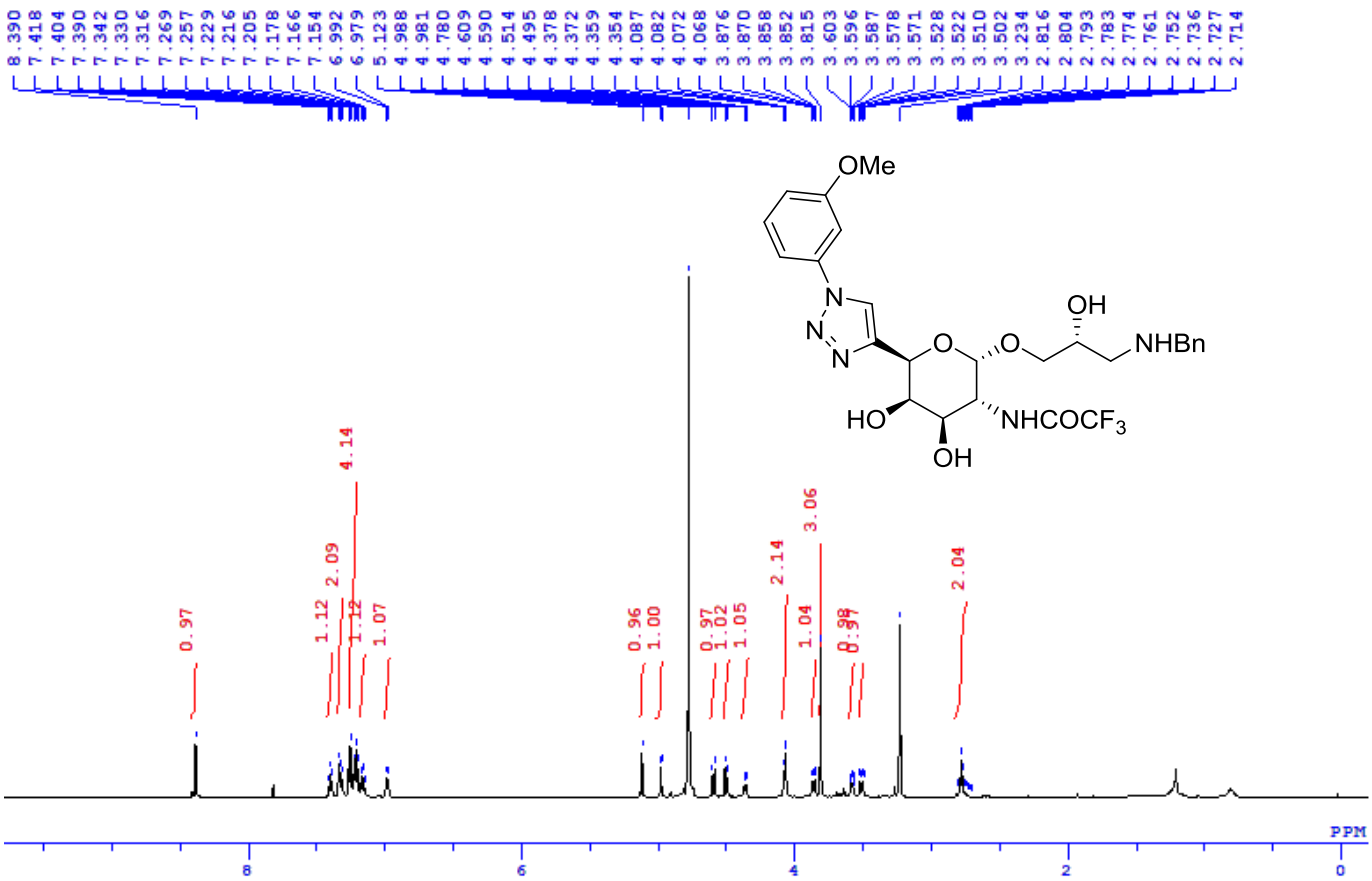
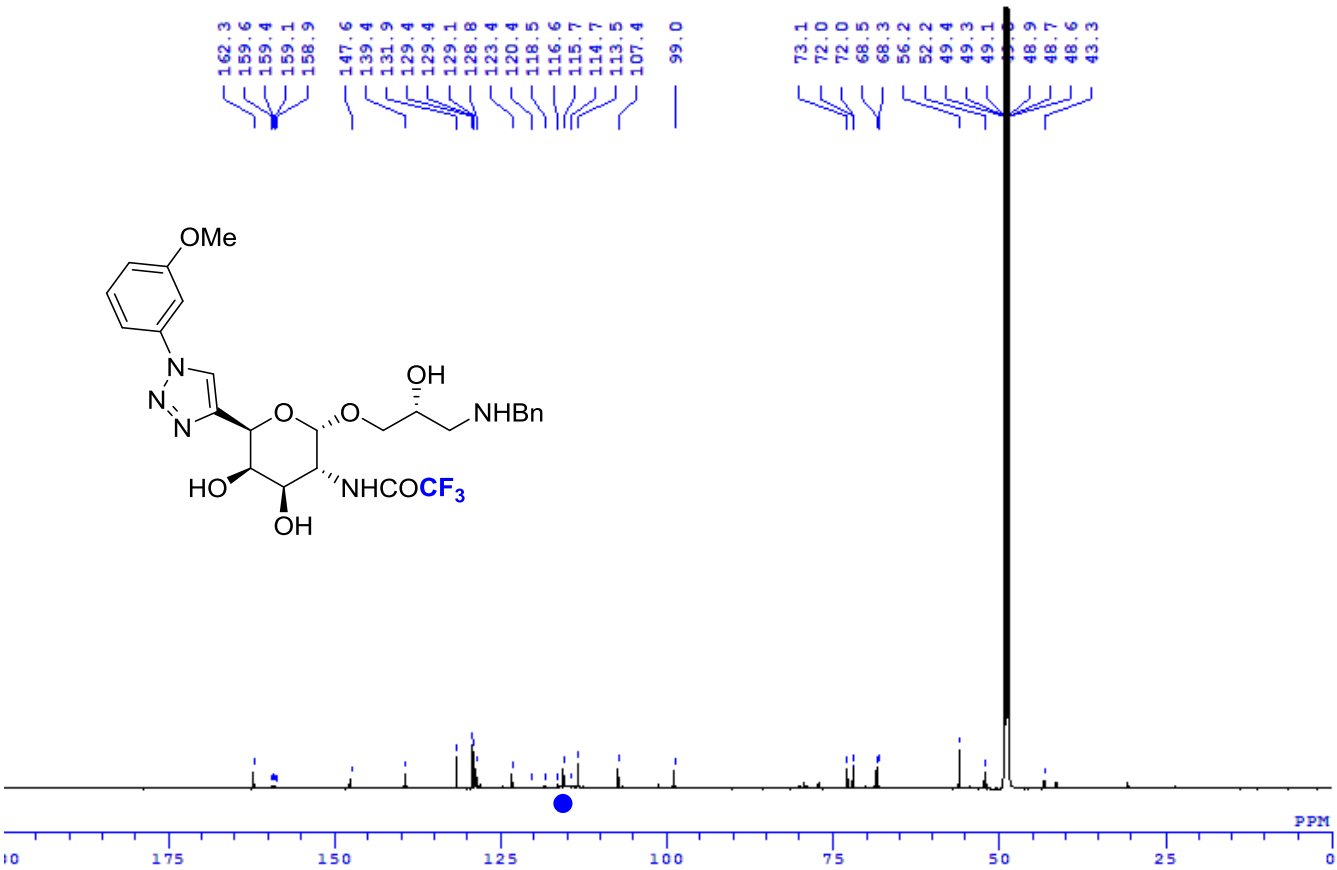
Compound **22**, ^{1}H-NMR (600 MHz, $CDCl_3$)



Compound **22**, ^{13}C-NMR (600 MHz, $CDCl_3$)



Compound **15**, ^{1}H-NMR (600 MHz, CD_3OD)



Compound **15**, ^{13}C-NMR (150 MHz, CD_3OD)