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SUPPLEMENTARY INFORMATION

Photo-induced glycosylation using a diaryldisulfide as an organo-Lewis photoacid catalyst

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General experimental methods

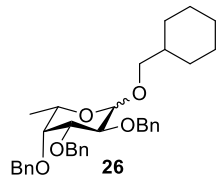
Melting points were determined on a micro hot-stage (Yanako MP-S3). Optical rotations were measured on a JASCO P-2200 polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL ECA-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) spectrometer, a JEOL ECS-400 (400 MHz for ^{1}H) spectrometer or a JEOL ECZ-400S (400 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. ^{1}H-NMR data are reported as follows; chemical shift in parts par million (ppm) downfield or upfield from tetramethylsilane (δ 0.00), $CDCl_3$ (δ 7.26), integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet and m = multiplet) and coupling constants (Hz). ^{13}C-NMR chemical shifts are reported in ppm downfield or upfield from $CDCl_3$ (δ 77.0). ESI-TOF Mass spectra were measured on a Waters LCT premier XE. Silica gel TLC and column chromatography were performed on Merck TLC 60F-254 (0.25 mm) and Silica Gel 60 N (spherical, neutral, 40-50 μm) (Kanto Chemical Co., Inc.), respectively.

General procedure for photo-induced glycosylations with trichloroacetimidate donors using disulfide catalysts

To a mixture of glycosyl donor (30.0 mg, 1.0 equiv.), glycosyl acceptor (2.0 equiv.) and MS 5Å (30.0 mg, 100 wt% to the glycosyl donor) was added a solution of disulfide **6a-c** or **7** (0.05 equiv.) in toluene (0.8 M to the glycosyl donor). After stirring for 2 h under the photoirradiation using a UV lamp (365 nm, 7 mW/cm^2) at 35 ºC, the mixture was concentrated in *vacuo*. The purification of the residue by flash column chromatography gave the corresponding glycoside.

The spectral data of the known glycosides **9**,[1] **18**,[1] **19**,[1] **20**,[1] **21**,[1] **22**,[1] **23**,[1] **24**,[2] **25**,[1] **27**,[3] **28**[1] and **29**[4] was identical with the literature data.

The spectral data of the new compounds **26**, **31** and **32** was shown below.



Molecular Weight: 530.71

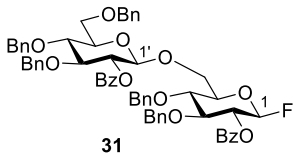
Cyclohexylmethyl 2,3,4-tri-*O*-benzyl-L-fucopyranoside (26)

To a mixture of glycosyl donor **1cα**[5] (30.0 mg, 51.8 μmol, 1.0 equiv.), glycosyl acceptor **8** (12.8 μL, 104 μmol, 2.0 equiv.) and MS 5Å (30.0 mg, 100 wt% to **1cα**) was added a solution of disulfide **6c** (0.7 mg, 2.6 μmol, 0.05 equiv.) in toluene (64.8 μL, 0.8 M to **1cα**). After stirring for 2 h under the photoirradiation using a UV lamp (365 nm, 7 mW/cm^2) at 35 ºC, the mixture was concentrated

in vacuo. The purification of the residue by flash column chromatography (6.6 g, 9/1 *n*-hexane/EtOAc) gave **26** (25.7 mg, 48.4 μmol, 93% yield, α/β = 10/90).

Data for **26α**: Colorless syrup; R_f 0.39 (15/1 *n*-hexane/EtOAc containing 4% NEt_3); $[\alpha]^{21}_D$ −39.9° (*c* 0.63, $CHCl_3$); mp 98.0-99.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (15H, m, ArH), 4.98 and 4.65 (2H, Abq, *J* = 11.6 Hz, $ArCH_2$), 4.88 and 4.74 (2H, ABq, *J* = 11.6 Hz, $ArCH_2$), 4.80 and 4.66 (2H, ABq, 12.4 Hz, $ArCH_2$), 4.76 (1H, d, *J* = 4.4 Hz), 4.02 (1H, dd, *J* = 4.0 and 10.0 Hz), 3.94 (1H, dd, *J* = 2.8 and 10.0 Hz), 3.86 (1H, q, *J* = 6.4 Hz), 3.66 (1H,d, *J* = 2.8 Hz), 3.37 (1H, dd, *J* = 7.2 and 9.2 Hz), 3.22 (1H, dd, *J* = 6.0 and 9.6 Hz), 1.83-1.62 (6H, m), 1.3-1.12 (3H, m), 1.10 (3H, d, *J* = 6.8 Hz), 0.97-0.84 (2H, m); ^{13}C-NMR (500 MHz, $CDCl_3$) δ 139.2, 139.0, 138.8, 128.4, 128.3, 128.2, 128.3, 128.1, 127.9, 127.5, 127.4×2, 97.6, 79.4, 77.8, 74.8, 73.8, 73.3, 73.1, 66.0, 37.6, 30.3, 30.0, 26.6, 25.9, 25.7, 16.7; HRMS (ESI-TOF) *m/z* 553.2952 (553.2930 calcd for $C_{34}H_{42}O_5Na$ $[M+Na]^+$).

Data for **26β**: White solid; R_f 0.49 (15/1 *n*-hexane/EtOAc containing 4% NEt_3); $[\alpha]^{22}_D$ +13.9° (*c* 1.0, $CHCl_3$); mp 69.0-70.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.24 (15H, m, ArH), 4.98 and 4.72 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.95 and 4.76 (2H, ABq, *J* = 10.8 Hz, $ArCH_2$), 4.79 and 4.70 (2H, ABq, *J* = 12.0 Hz, $ArCH_2$), 4.28 (1H, d, *J* = 8.0 Hz), 3.80 (1H, dd, *J* = 8.0 and 9.6 Hz), 3.76 (1H, dd, *J* = 6.0 and 9.6 Hz), 3.54 (1H, d, *J* = 2.4 Hz), 3.50 (1H, dd, *J* = 2.8 and 9.6 Hz), 3.42 (1H, q, *J* = 6.4 Hz), 3.25 (1H, dd, *J* = 7.2 and 9.6 Hz), 1.87-1.56 (6H, m), 1.29-1.11 (3H, m), 1.17 (3H, *J* = 6.4 Hz), 1.02-0.91 (2H, m); ^{13}C-NMR (500 MHz, $CDCl_3$) δ 138.8, 138.7, 138.6, 128.5, 128.3, 128.2, 128.1, 127.5×2, 104.1, 82.6, 79.5, 76.7, 76.3, 75.5, 75.1, 74.5, 73.2, 70.2, 38.1, 30.2, 29.9, 26.6, 25.9, 25.8, 16.9; HRMS (ESI-TOF) *m/z* 553.2940 (553.2930 calcd for $C_{34}H_{42}O_5Na$ $[M+Na]^+$).



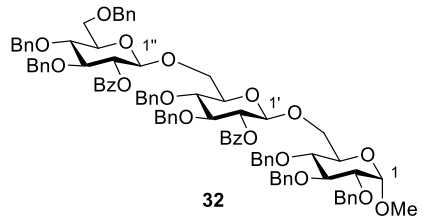
31

2-*O*-Benzoyl-3,4-di-*O*-benzyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoyl)-β-D-glucopyranosyl fluoride (31)

To a mixture of glycosyl donor **1eα**[6] (30.0 mg, 42.9 μmol, 3.0 equiv.), glycosyl acceptor **30**[7] (6.7 mg, 14.3 μmol, 1.0 equiv.) and MS 5Å (30 mg, 100 wt% to **1eα**) was added a solution of disulfide **6c** (0.7 mg, 2.1 μmol, 0.15 equiv.) in toluene/CH_2Cl_2 (1:1, v/v, 108 μL, 0.4 M to **1eα**). After stirring for 8 h under the photoirradiation using a UV lamp (365 nm, 7 mW/cm^2) at 25 °C, the mixture was concentrated *in vacuo*. The purification of the residue by flash column chromatography (3/1 *n*-hexane/EtOAc) gave **31** (12.2 mg, 12.2 μmol, 85% yield, β only).

Data for **31**: White solid; R_f 0.57 (3/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +40.5° (*c* 1.0, $CHCl_3$); mp 160-

162 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (4H, m, ArH), 7.58 (1H, t, J = 7.6 Hz, ArH), 7.48-7.41 (3H, m, ArH), 7.37-7.25 (16H, m, ArH), 7.20-7.09 (14H, m, ArH), 5.35 (1H, dd, J = 8.4 Hz and 9.6 Hz), 5.29 (1H, m), 5.13 (1H, dd, J = 52.8 Hz and 5.6 Hz), 4.82 (1H, ABq, J = 11.2 Hz, $ArCH_2$), 4.74 (1H, ABq, J = 10.8 Hz, $ArCH_2$), 4.68-4.63 (4H, m, $ArCH_2$), 4.64 (1H, d, J = 9.6 Hz), 4.59-4.56 (3H, m, $ArCH_2$), 4.45 (1H, ABq, J = 12.0 Hz, $ArCH_2$), 4.19 (1H, d, J = 11.2 Hz), 3.84 (1H, dd, J = 9.2 Hz and 9.2 Hz), 3.80-3.68 (7H, m), 3.57 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.1, 164.9, 138.1, 137.5, 137.4, 133.4, 132.9, 129.8×2, 129.7, 129.2, 128.4, 128.3, 128.2×2, 127.9×2, 127.8, 127.7, 127.6, 106.6 (d, J = 217.5 Hz), 101.6, 82.6, 81.0, 80.9, 75.3, 75.0, 74.9, 74.5, 74.1, 73.6, 73.5, 72.9, 72.6, 68.7, 68.3; HRMS (ESI-TOF) *m/z* 1025.3923 (1025.3888 calcd for $C_{61}H_{59}O_{12}F_1Na$ $[M+Na]^+$).



32

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-{2-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoyl)-β-D-glucopyranoyl}-α-D-glucopyranoside (32)

To a solution of glycosyl donor **31** (8.0 mg, 8.0 μmol, 1.0 equiv.) and glycosyl acceptor **16**[8] (7.4 mg, 16.0 μmol, 2.0 equiv.) in toluene (296 μL) was added MS 5Å (8.0 mg, 100 wt% to **31**) at room temperature under Ar atmosphere. After stirring for 1 h, the resulting mixture was cooled to -40 °C. A solution of $Cp_2Hf(OTf)_2$ in toluene (104 μL), which was prepared from Cp_2HfCl_2 (7.6 mg, 20.0 μmol, 2.5 equiv.), AgOTf (10.3 mg, 40.0 μmol, 5.0 equiv.) and MS 5Å (72 mg, 900 wt% to **31**), was added to the reaction mixture. After stirring at the same temperature for 2 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was concentrated in *vacuo*, and the residue was chromatographed on silica gel (2/1 *n*-hexane/EtOAc) gave the glycoside **32** (9.8 mg, 6.8 μmol, 85% yield, β only).

Data for **32**: Colorless foam; R_f 0.52 (2/1 *n*-hexane/EtOAc); $[\alpha]^{28}_D$ +25.1° (*c* 0.40, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 8.4Hz, ArH), 7.87 (2H, d, J = 8.8 Hz, ArH), 7.47-6.92 (50H, m, ArH), 5.32-5.23 (2H, m), 4.84 (1H, ABq, J = 11.2 Hz, $ArCH_2$), 4.79 (1H, ABq, J = 11.2 Hz, $ArCH_2$), 4.71 (1H, ABq, J = 11.2 Hz, $ArCH_2$), 4.69 (1H, ABq, J = 12.0 Hz, $ArCH_2$), 4.67 (1H, d, J = 7.6 Hz), 4.65-4.61 (5H, m, $ArCH_2$), 4.58-4.53 (4H, m, $ArCH_2$), 4.47 (1H, ABq, J = 11.2 Hz, $ArCH_2$), 4.47 (1H, d, J = 3.2 Hz), 4.33 (1H, d, J = 7.6 Hz), 4.30 (1H, ABq, J = 11.6 Hz, $ArCH_2$), 4.14-4.10 (2H, m), 3.88 (1H, d, J = 7.2 Hz), 3.83-3.74 (4H, m), 3.71-3.67 (2H, m), 3.52-3.42 (4H, m), 3.38 (1H, dd, J = 9.6 Hz and 3.2 Hz), 3.32 (1H, dd, J = 9.6 Hz and 9.6 Hz), 3.17 (3H, s, OMe); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.9, 164.8, 138.9, 138.2, 138.1×2, 137.9, 137.7,

137.6, 133.0, 132.9, 129.9, 129.6×2, 128.3, 128.2×2, 128.1, 127.9, 127.8×2, 127.6, 127.4, 127.3, 101.1, 100.7, 98.0, 82.8, 82.6, 81.8, 79.6, 77.9, 77.7, 75.4, 75.3, 75.2, 74.9, 74.8, 74.5, 73.8, 73.5, 73.4, 69.3, 68.6, 67.8, 67.2, 55.2; HRMS (ESI-TOF) *m/z* 1469.6080 (1469.6025 calcd for $C_{89}H_{90}O_{18}Na$ $[M+Na]^+$).

Nanosecond laser flash photolysis

Nanoseecond teansient absorption measurements were carried out using Unisoku TSP-2000 flash spectrometer. Surelite-I Nd-YAG (Q-switched) laser was employed for the flash photo-irradiation. A 150 W Xenon arc and halogen lamps were used as the monitor light source. The measurements were performed in toluene at room temperature, and excitation wavelength was 355 nm (thrid-harmonic generation (THG) wavelength of Nd-YAG laser).

References

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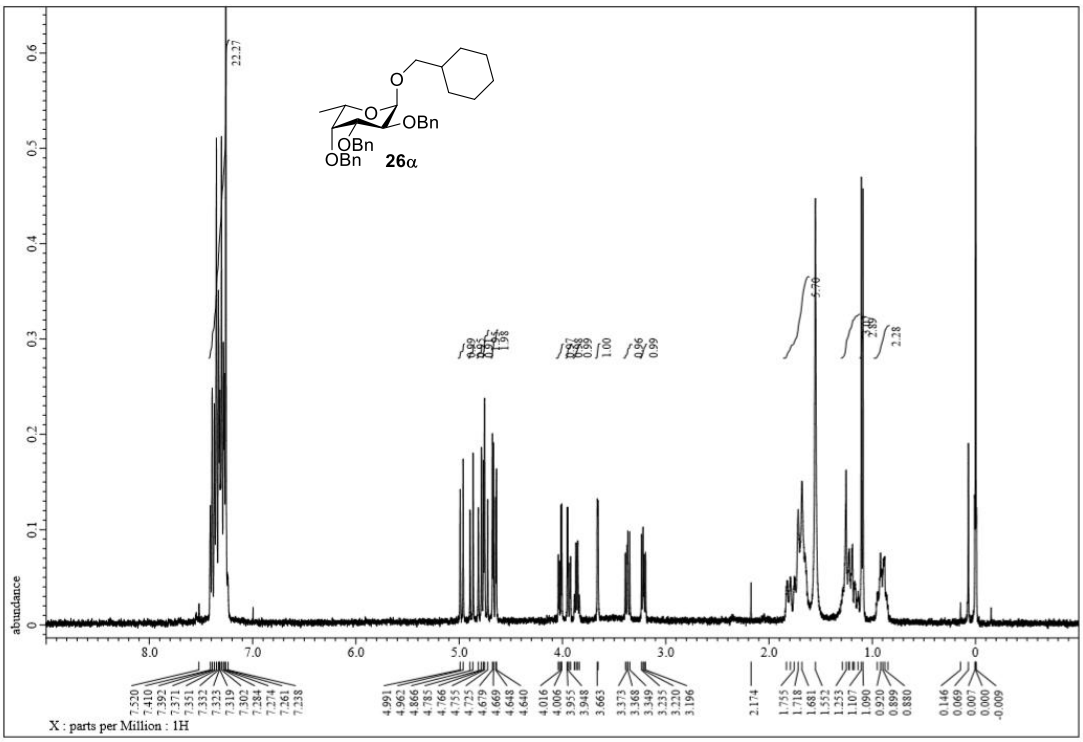
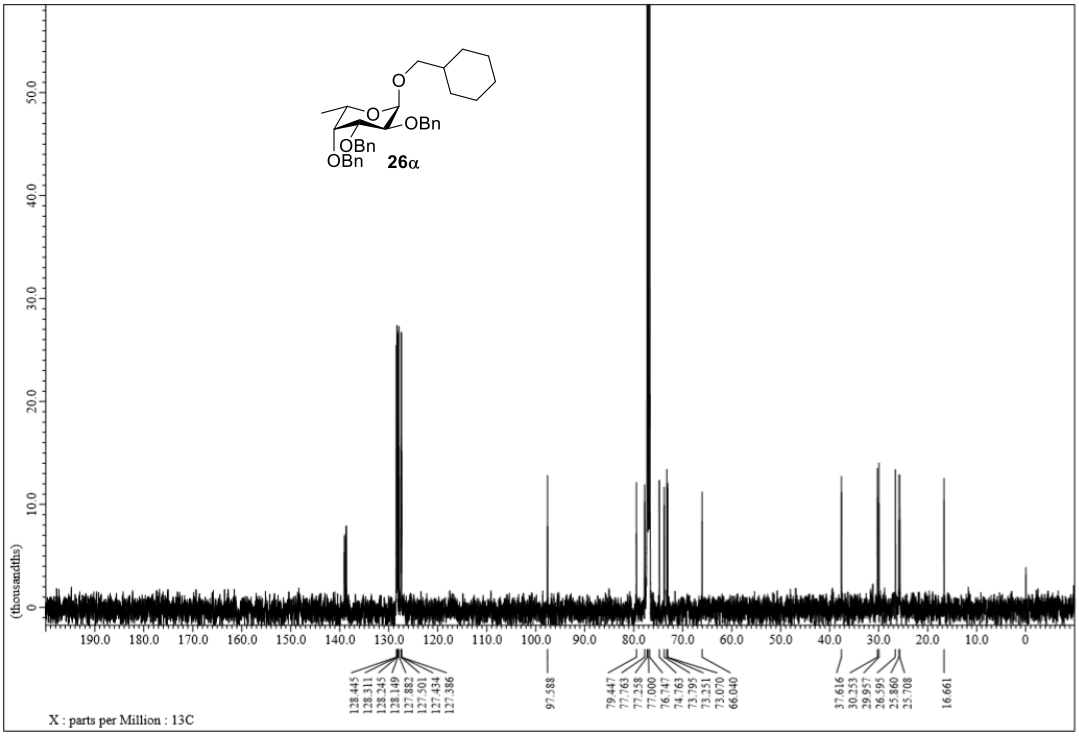
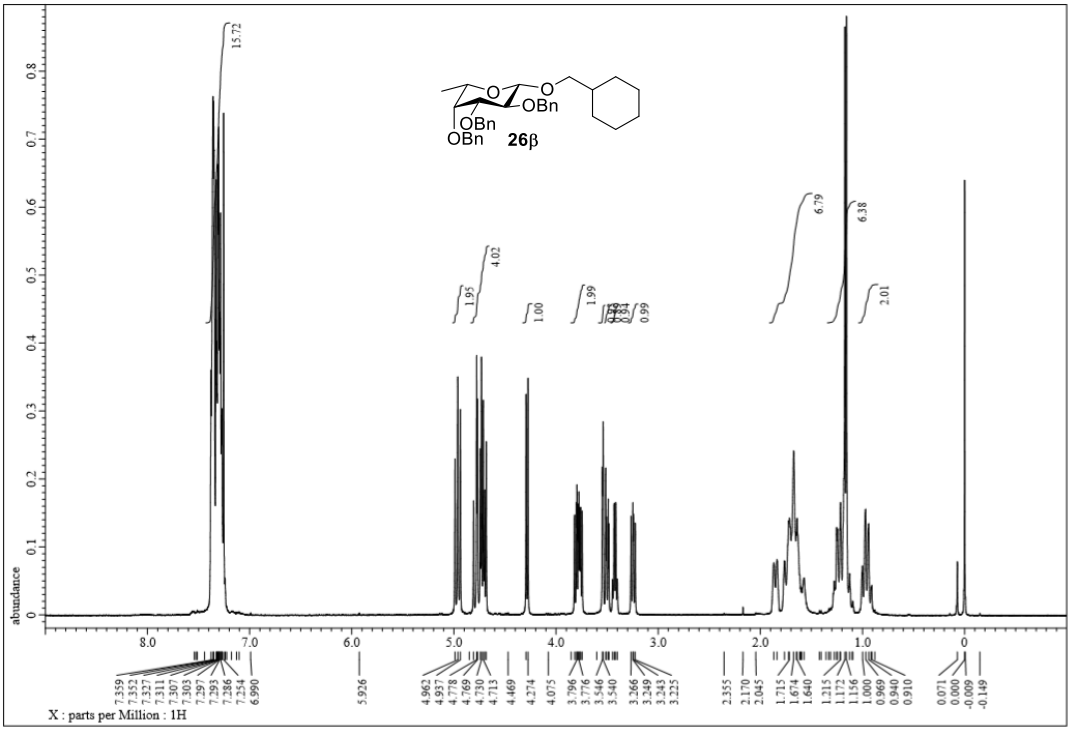
^{1}H- and ^{13}C-NMR spectral charts



^{1}H-NMR spectrum of **26α**



^{13}C-NMR spectrum of **26α**



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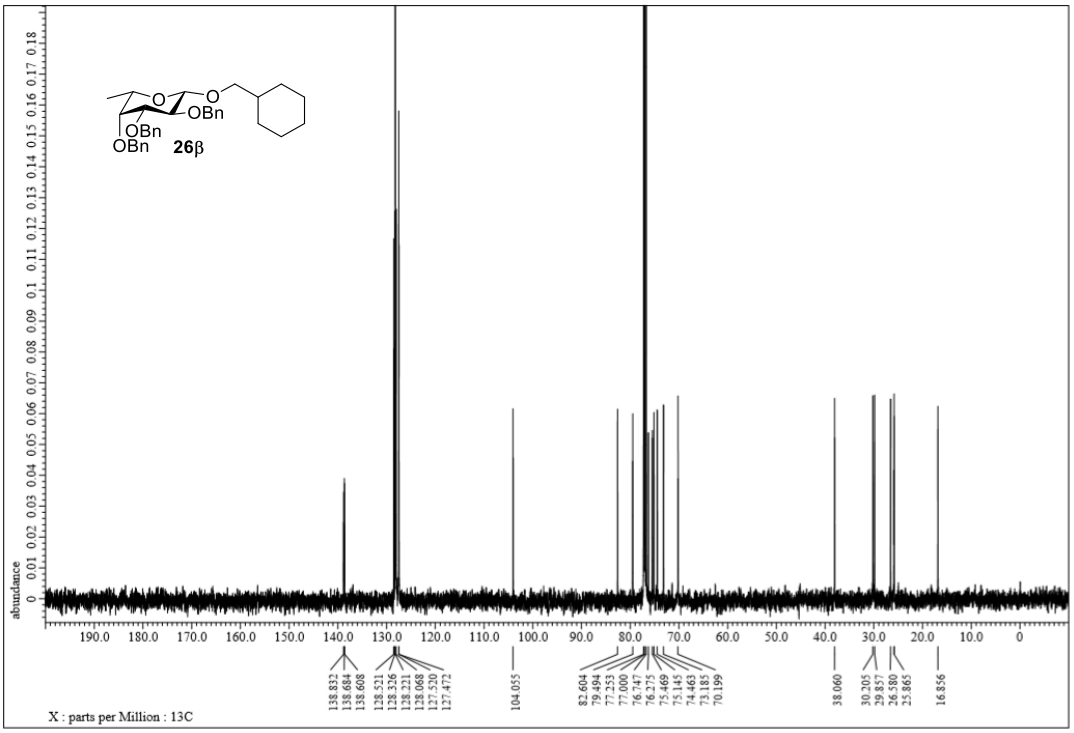

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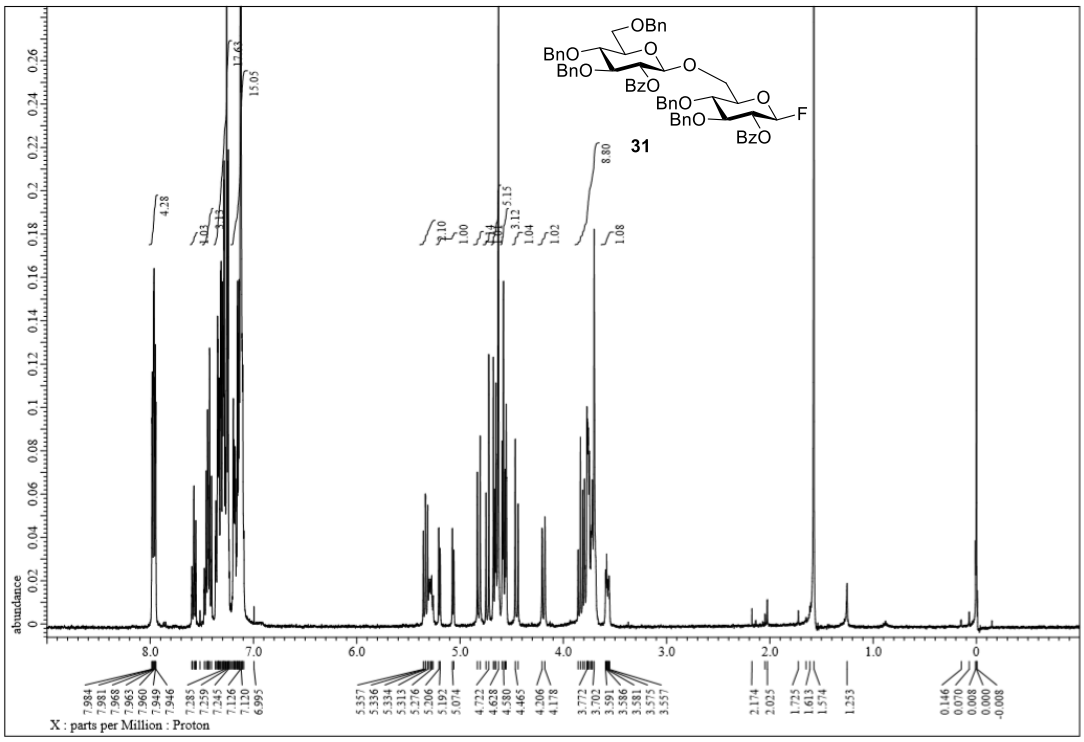

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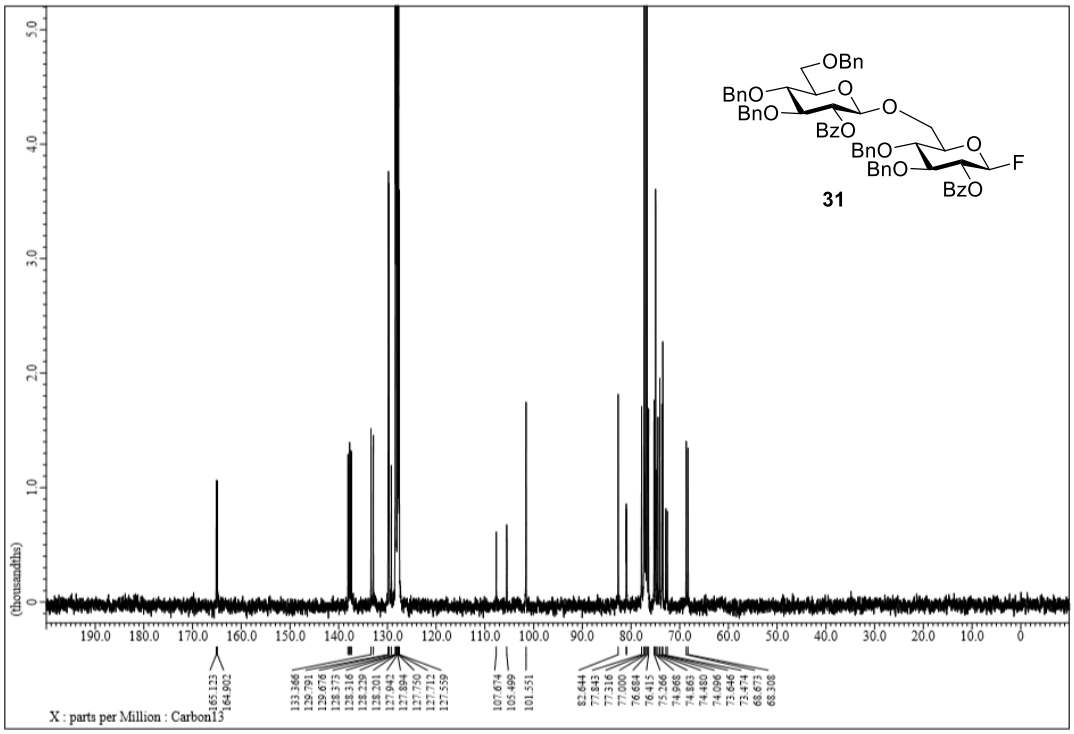

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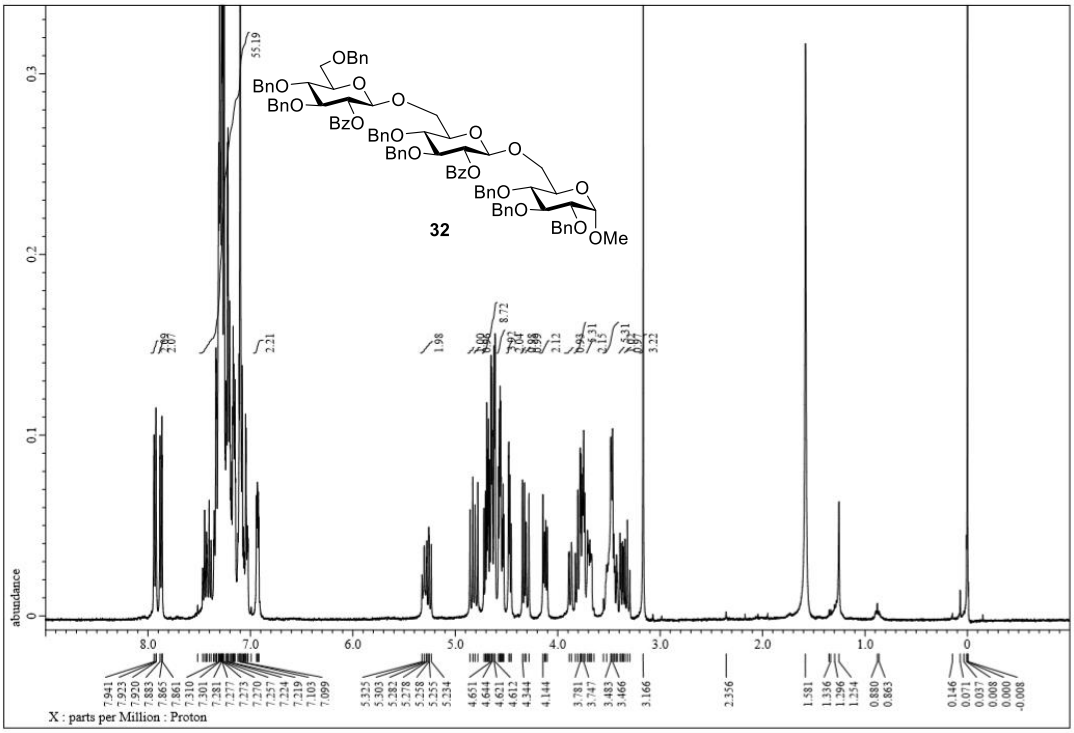

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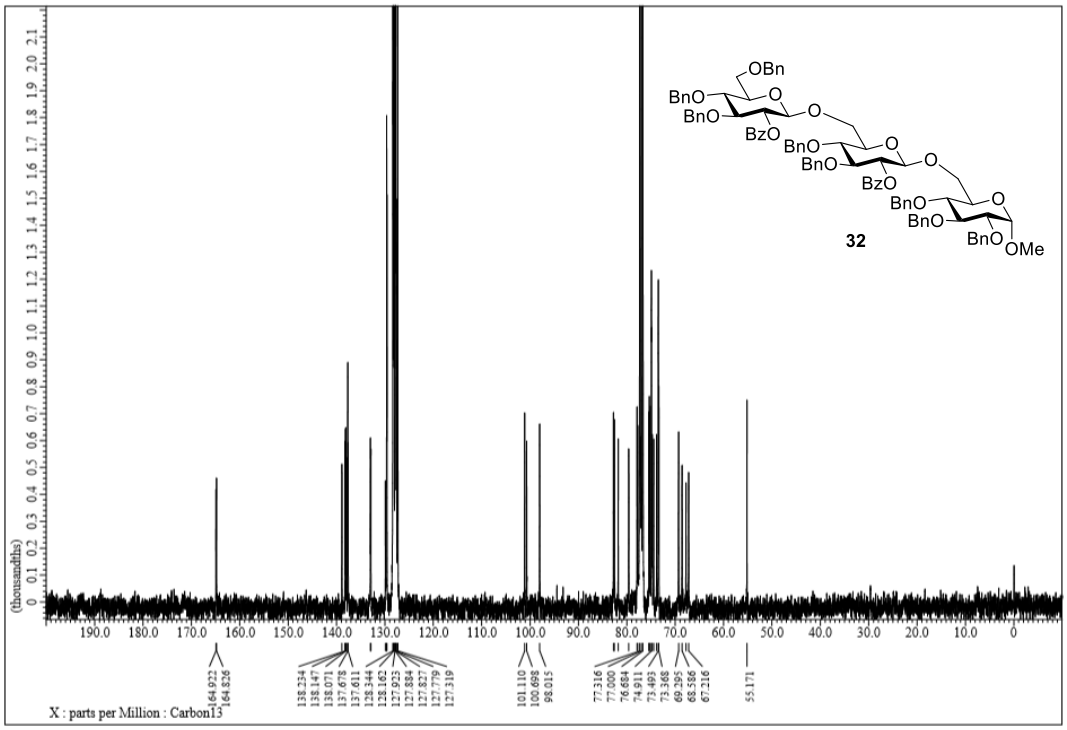

^{13}C-NMR spectrum of **32**