

Electronic Supplementary Information

Organo Photocatalytic Access to C-Glycosides: Multicomponent Coupling Reactions Using Glycosyl Bromides

Naoya Sawada,^a Ziyi Yu,^a Hiryu Takinami,^a Daichi Inoue,^a Titli Ghosh,^a Norihiko Sasaki,^{a,b}
Toshiki Nokami,^{*a,b} Tsuyoshi Taniguchi,^c Manabu Abe^{*d}, and Takashi Koike^e

^a*Department of Chemistry and Biotechnology, Tottori University, 4-101 Koyamachominami,
Tottori city, 680-8552 Tottori, Japan*

^b*Centre for Research on Green Sustainable Chemistry, Faculty of Engineering,
Tottori University, 4-101 Koyamachominami, Tottori city, 680-8552 Tottori, Japan*

^c*Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced
Industrial Science and Technology, 1-1-1 Higashi, Tsukuba city, Ibaraki, 305-8565, Japan*

^d*Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima
University, Higashi-Hiroshima city, Hiroshima, 739-8526, Japan*

^e*Department of Applied Chemistry, Faculty of Fundamental Engineering, Nippon Institute of
Technology, E24-315, 4-1 Gakuendai, Miyashiro-Machi, Minamisaitama-Gun, 345-8501
Saitama, Japan*

E-mail: tnokami@tottori-u.ac.jp, mabe@hiroshima-u.ac.jp

Contents

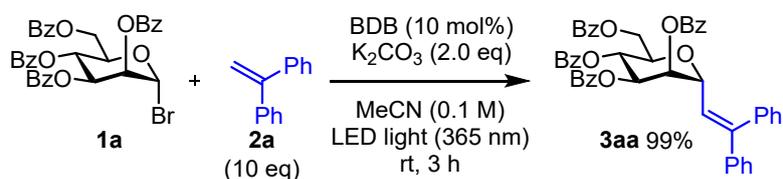
1. General	S2
2. Photochemical multi-components reactions	S2
3. Cyclic Voltammetry	S19
4. Stern-Volmer Plots	S20
5. Control experiment in the presence of TEMPO	S21
6. References	S22
7. ¹ H, ¹³ C, and ¹⁹ F NMR spectra	S23

1. General

The NMR spectra were recorded on Bruker AVANCE II. 600 (^1H NMR; 600 MHz, ^{13}C NMR; 150 MHz) and JEOL JNM-ECZ600 (^1H NMR; 600 MHz, ^{13}C NMR; 150 MHz, ^{19}F NMR; 565 MHz) at room temperature using chloroform- d as the deuterated solvent and chloroform as the internal standard for ^1H (7.26 ppm) and ^{13}C (77.0 ppm) and hexafluorobenzene as the internal standard for ^{19}F (0 ppm). NMR yields were based on 1,1,2,2-tetrachloroethane as an internal standard. Fourier transform mass spectrometry (ESI) was measured on Thermo Fisher SCIENTIFIC Exactive-Orbitrap MS1.1. Cyclic voltammetry and transient absorption spectra were recorded on UNISOKU picoTAS and BAS model 700E electrochemical analyzer, respectively. Silica gel (KANTO, spherical, neutral, 63-210 μm) was used for purification by column chromatography. 1,1-Diphenylethylene was washed with 0.5 M NaOH aqueous solution to remove a polymerization inhibitor, and other styrene derivatives were distilled under reduced pressure. Glycosyl bromides **1a-c**¹ and **2e**² were synthesized according to the reported procedure. Techno Sigma PER-AMP and LED ramps (365 nm, 507 mW) were used for photoirradiation.

2. Photochemical multi-components reactions

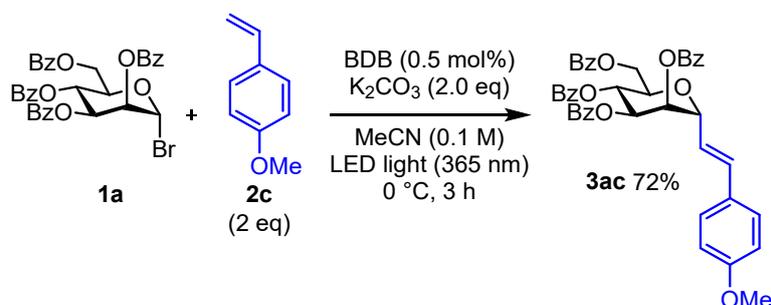
2-1-1. Two-component coupling reaction between **1a** and **2a**



Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL) and 1,1-diphenylethylene (**2a**) (2.0 mmol, 0.35 mL) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl_3 , concentrated under vacuum. Tetrachloroethane was added as an internal standard and ^1H NMR measurement was performed to determine NMR yield of **3aa** (99%). **3aa** was isolated by silica gel column (eluent: Hexane/EtOAc = 4:1) and preparative GPC (eluent: CHCl_3). **(2R,3R,4R,5R,6R)-2-((benzyloxy)methyl)-6-(2,2-diphenylvinyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (3aa)** TLC (Hexane/EtOAc 3:1): R_f = 0.43. ^1H NMR (CDCl_3 , 600 MHz) δ 8.10 (dd, J = 8.4, 1.2 Hz, 2 H), 7.99 (dd, J = 8.4, 1.2 Hz, 2 H), 7.97 (dd, J = 8.4, 1.2 Hz, 2 H), 7.81 (dd, J = 8.4, 1.2 Hz, 2 H), 7.58–7.51 (m, 3 H), 7.50–7.45 (m, 1 H), 7.43–7.27 (m, 18 H), 6.47 (d, J = 9.0 Hz, 1 H), 6.03 (*pseudo-t*, J = 7.2 Hz, 1 H), 5.99 (dd, J = 9.0, 3.0 Hz, 1 H), 5.82 (*pseudo-t*, J = 3.0 Hz, 1 H), 4.85 (dd, J = 9.0, 3.6 Hz, 1 H), 4.56–4.51 (m, 3 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.2, 165.6, 165.3,

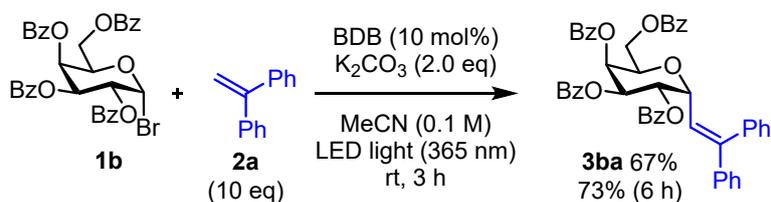
150.5, 141.6, 138.2, 133.4, 133.30, 133.26, 133.0, 129.73, 129.70, 129.4, 129.0, 128.9, 128.44, 128.42, 128.38, 128.31, 128.30, 128.1, 128.0, 120.2, 72.3, 71.5, 71.3, 70.1, 67.9, 63.0; HRMS (ESI) m/z calc for $C_{48}H_{38}KO_9$ $[M+K]^+$ 797.2147; found 797.2162.

2-1-2. Two-component coupling reaction between **1a** and **2c**



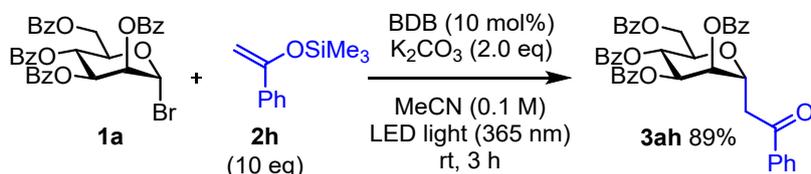
Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.001 mmol, 0.41 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL) and 4-methoxystyrene **2c** (0.4 mmol, 54 μ L) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with $CHCl_3$, concentrated under vacuum. Tetrachloroethane was added as an internal standard and 1H NMR measurement was performed to determine NMR yield of **3ac** (72%). **3ac** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:1) and preparative GPC (eluent: $CHCl_3$). **(2R,3R,4R,5R,6R)-2-((benzyloxy)methyl)-6-((E)-4-methoxystyryl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (3ac)** TLC (Hexane/EtOAc 3:1): R_f 0.32. 1H NMR ($CDCl_3$, 600 MHz) δ 8.13 (d, $J = 7.8$ Hz, 2 H), 8.08 (d, $J = 7.8$ Hz, 2 H), 7.97 (d, $J = 7.8$ Hz, 2 H), 7.87 (d, $J = 7.8$ Hz, 2 H), 7.59 (t, $J = 7.2$ Hz, 2 H), 7.51 (t, $J = 7.8$ Hz, 1 H), 7.48–7.38 (m, 7 H), 7.35 (t, $J = 7.8$ Hz, 2 H), 7.30 (t, $J = 7.8$ Hz, 2 H), 6.94–6.89 (m, 3 H), 6.29 (dd, $J = 16.2, 4.2$ Hz, 1 H), 6.17 (t, $J = 9.6$ Hz, 1 H), 5.99 (s, 1 H), 5.79 (dd, $J = 9.6, 2.4$ Hz, 1 H), 5.04–4.99 (m, 1 H), 4.73 (d, $J = 12.0$ Hz, 1 H), 4.54 (dd, $J = 12.0, 4.2$ Hz, 1 H), 4.49–4.44 (m, 1 H), 3.85 (s, 3 H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.5, 166.2, 165.6, 165.5, 165.4, 138.0, 133.9, 133.47, 133.41, 133.3, 133.1, 129.81, 129.79, 129.74, 129.65, 129.23, 129.16, 128.79, 128.76, 128.48, 128.47, 128.42, 128.35, 72.4, 71.6, 70.6, 70.3, 67.1, 63.1, 50.5, 34.2, 23.2; HRMS (ESI) m/z calc for $C_{44}H_{36}KNO_{10}$ $[M+K]^+$ 751.1940; found 751.1950.

2-1-3. Two-component coupling reaction between **1b** and **2a**



Glycosyl bromide **1b** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL) and 1,1-diphenylethylene (**2a**) (2.0 mmol, 0.35 mL) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **3ba** (67%). **3ba** was isolated by silica gel column (eluent: Hexane/EtOAc = 4:1) and preparative GPC (eluent: CHCl₃). **(2R,3S,4R,5S,6R)-2-((benzoyloxy)methyl)-6-(2,2-diphenylvinyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (3ba)** TLC (Hexane/EtOAc 3:1): R_f 0.39. ¹H NMR (CDCl₃, 600 MHz) δ 8.03 (t, *J* = 9.0 Hz, 4 H), 7.97 (d, *J* = 7.2 Hz, 2 H), 7.81 (d, *J* = 7.2 Hz, 2 H), 7.61–7.58 (m, 1 H), 7.56–7.51 (m, 2 H), 7.49–7.44 (m, 3 H), 7.42–7.37 (m, 4 H), 7.34–7.22 (m, 10 H), 7.17 (d, *J* = 6.6 Hz, 2 H), 6.53 (d, *J* = 9.0 Hz, 1 H), 6.08–6.03 (m, 2 H), 5.80 (dd, *J* = 9.0, 5.4 Hz, 1 H), 5.12 (dd, *J* = 9.6, 6.0 Hz, 1 H), 4.68 (*pseudo-t*, *J* = 6.0 Hz, 1 H), 4.60 (dd, *J* = 11.4, 7.2 Hz, 1 H), 4.33 (dd, *J* = 11.4, 7.2 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.0, 165.6, 165.5, 165.3, 151.5, 141.7, 138.3, 133.5, 133.4, 133.3, 133.1, 129.9, 129.7, 129.63, 129.61, 129.5, 129.12, 129.06, 128.9, 128.5, 128.4, 128.35, 128.29, 128.24, 128.19, 128.0, 127.9, 127.8, 70.7, 69.4, 69.2, 69.1, 68.7, 62.2; HRMS (ESI) *m/z* calc for C₄₉H₄₂KO₁₀ [M+K]⁺ 797.2147; found 797.2140.

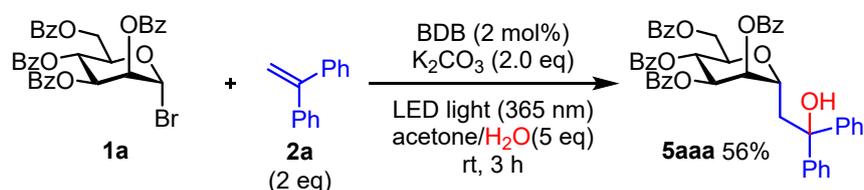
2-1-4. Two-component coupling reaction between **1a** and **2h**



Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL) and 1-Phenyl-1-trimethylsilyloxyethylene (**2h**) (2.0 mmol, 0.41 mL) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light

(wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **3ah** (89%). **3ah** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:2). **(2R,3R,4R,5S,6R)-2-((benzoyloxy)methyl)-6-(2-oxo-2-phenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (3ah)** TLC (Hexane/EtOAc 3:1): Rf 0.20. ¹H NMR (CDCl₃, 600 MHz) δ 8.04 (dd, *J* = 8.4, 1.2 Hz, 2 H), 8.02 (dd, *J* = 7.8, 1.8 Hz, 2 H), 8.01 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.95 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.59–7.53 (m, 4 H), 7.50 (t, *J* = 7.8 Hz, 4 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.43–7.38 (m, 6 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 5.93 (*pseudo-t*, *J* = 7.8 Hz, 1 H), 5.90 (dd, *J* = 8.4, 3.6 Hz, 1 H), 5.78 (dd, *J* = 4.2, 3.0 Hz, 1 H), 5.06 (dt, *J* = 9.0, 4.2 Hz, 1 H), 4.69 (dd, *J* = 12.0, 6.0 Hz, 1 H), 4.64 (dd, *J* = 12.0, 3.6 Hz, 1 H), 4.46 (td, *J* = 6.6, 3.6 Hz, 1H), 3.65 (dd, *J* = 16.2, 9.0 Hz, 1 H), 3.41 (dd, *J* = 16.2, 5.4 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 195.6, 166.1, 165.6, 165.4, 165.3, 136.3, 133.51, 133.49, 133.44, 133.40, 133.0, 129.8, 129.7, 129.3, 128.9, 128.8, 128.7, 128.48, 128.46, 128.44, 128.3, 128.2, 71.6, 70.9, 69.6, 67.8, 62.5, 38.5; HRMS (ESI) *m/z* calc for C₄₂H₃₄KO₁₀ [M+K]⁺ 737.1784; found 737.1746.

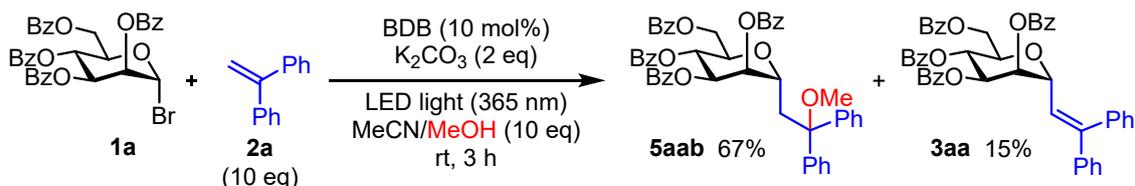
2-2-1. Three-component coupling reaction between **1a**, **2a** and water



Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.004 mmol, 1.7 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL), 1,1-diphenylethylene (**2a**) (0.4 mmol, 70 μl) and water (1.0 mmol, 18 μl) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **5aaa** (56%). **5aaa** was isolated by silica gel column (eluent: Hexane/EtOAc = 5:1) and preparative GPC (eluent: CHCl₃). **(2R,3R,4R,5R,6R)-2-((benzoyloxy)methyl)-6-(2-hydroxy-2,2-diphenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (5aaa)** TLC (Hexane/EtOAc 3:1): Rf 0.40. ¹H NMR (CDCl₃, 600 MHz) δ 8.17 (d, *J* = 7.2 Hz, 2 H), 8.01 (d, *J* = 7.2 Hz, 2 H), 7.95 (d, *J* = 7.8 Hz, 2 H), 7.79 (d, *J* = 7.8 Hz, 2 H), 7.62–7.54 (m, 3 H), 7.53–7.45 (m, 7 H), 7.44–7.37 (m, 4 H), 7.36–7.29 (m, 6 H), 7.27–7.20 (m, 2 H), 5.84–5.81 (m, 2 H), 5.68 (d, *J* = 2.4 Hz, 1 H), 4.63–4.59 (m, 1 H), 4.54–4.47

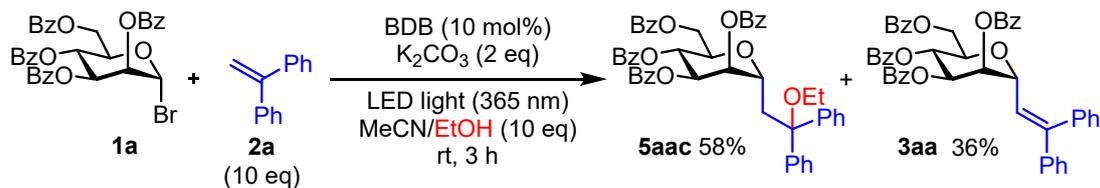
(m, 3 H), 4.29 (s, 1 H), 2.93 (dd, $J = 15.0, 10.8$ Hz, 1 H), 2.82 (dd, $J = 15.0, 1.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.1, 165.4, 165.3, 165.2, 146.6, 145.4, 133.6, 133.4, 133.2, 129.83, 129.81, 129.73, 129.67, 129.55, 129.2, 128.8, 128.5, 128.46, 128.3, 127.07, 127.05, 126.0, 125.5, 78.3, 72.5, 71.7, 71.3, 69.4, 67.7, 62.7, 39.3; HRMS (ESI) m/z calc for $\text{C}_{48}\text{H}_{40}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 815.2253; found 815.2209.

2-2-2. Three-component coupling reaction between **1a**, **2a** and methanol



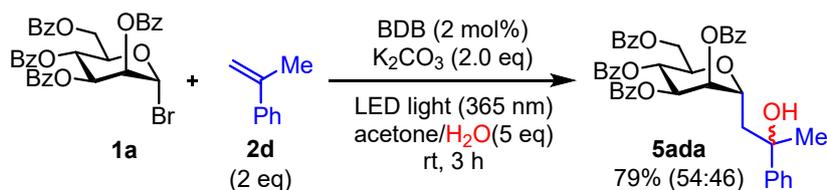
Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL), 1,1-diphenylethylene (**2a**) (0.4 mmol, 70 μl) and dry MeOH (2.0 mmol, 81 μL) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl_3 , concentrated under vacuum. Tetrachloroethane was added as an internal standard and ^1H NMR measurement was performed to determine NMR yield of **5aab** (67%). **5aab** was isolated by silica gel column (eluent: Hexane/EtOAc = 4:1) and preparative GPC (eluent: CHCl_3). **(2R,3R,4R,5R,6R)-2-((benzyloxy)methyl)-6-(2-methoxy-2,2-diphenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (5aab)** TLC (Hexane/EtOAc 3:1): $R_f = 0.50$. ^1H NMR (CDCl_3 , 600 MHz) δ 8.04 (d, $J = 7.8$ Hz, 2 H), 7.99 (d, $J = 7.2$ Hz, 2 H), 7.94 (d, $J = 7.8$ Hz, 2 H), 7.81 (d, $J = 7.8$ Hz, 2 H), 7.59–7.44 (m, 5 H), 7.42 (d, $J = 7.8$ Hz, 4 H), 7.39–7.23 (m, 12 H), 7.12 (t, $J = 7.2$ Hz, 1 H), 6.00 (*pseudo-t*, $J = 9.0$ Hz, 1 H), 5.82 (dd, $J = 9.0, 3.0$ Hz, 1 H), 5.49–5.47 (m, 1 H), 4.51–4.47 (m, 1 H), 4.23 (dd, $J = 12.0, 4.2$ Hz, 1 H), 4.06–4.02 (m, 2 H), 3.13 (s, 3 H), 3.03 (dd, $J = 15.0, 7.8$ Hz, 1 H), 2.85 (dd, $J = 15.0, 3.6$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.1, 165.7, 165.3, 165.2, 144.9, 144.1, 133.33, 133.26, 133.2, 132.9, 129.9, 129.8, 129.71, 129.67, 129.6, 129.0, 128.9, 128.42, 128.37, 128.34, 128.31, 128.30, 128.0, 127.3, 127.1, 126.8, 126.6, 81.3, 72.5, 71.7, 70.7, 70.3, 67.5, 62.7, 50.8, 34.0; HRMS (ESI) m/z calc for $\text{C}_{49}\text{H}_{42}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 829.2410; found 829.2383.

2-2-3. Three-component coupling reaction between **1a**, **2a**, and ethanol



Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL), 1,1-diphenylethylene (**2a**) (0.4 mmol, 70 μ l), and dry EtOH (2.0 mmol, 117 μ L) were added, and the mixture was stirred. The LED ramp was then attached to the Schrenk tube using a Teflon joint, and freeze degassing was performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photoirradiation, the reaction mixture was diluted with CHCl_3 and concentrated under vacuum. Tetrachloroethane was added as an internal standard and ^1H NMR measurement was performed to determine NMR yield of **5aac** (58%). **5aac** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:1). (**2R,3R,4R,5R,6R**)-2-((benzyloxy)methyl)-6-(2-ethoxy-2,2-diphenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (**5aac**) TLC (Hexane/EtOAc 3:1): R_f = 0.33. ^1H NMR (CDCl_3 , 600 MHz) δ 8.03 (dd, J = 8.4, 1.2 Hz, 2 H), 8.01 (dd, J = 8.4, 1.2 Hz, 2 H), 7.93 (dd, J = 8.4, 1.2 Hz, 2 H), 7.80 (dd, J = 8.4, 1.2 Hz, 2 H), 7.57 (*pseudo-t*, J = 7.8 Hz, 1 H), 7.54 (*pseudo-t*, J = 7.8 Hz, 1 H), 7.50 (*pseudo-t*, J = 7.2 Hz, 1 H), 7.45–7.43 (m, 5 H), 7.39–7.31 (m, 8 H), 7.30–7.27 (m, 4 H), 7.24 (*pseudo-t*, J = 7.2 Hz, 1 H), 7.19 (*pseudo-t*, J = 7.2 Hz, 1 H), 6.02 (*pseudo-t*, J = 9.0 Hz, 1 H), 5.82 (dd, J = 9.6, 3.0 Hz, 1 H), 5.46 (*pseudo-t*, J = 3.0 Hz, 1 H), 4.51–4.49 (m, 1 H), 4.18 (dd, J = 12.0, 3.6 Hz, 1 H), 4.02–3.97 (m, 2 H), 3.28–3.20 (m, 2 H), 3.01 (dd, J = 14.4, 1.2 Hz, 1 H), 2.86 (dd, J = 14.4, 4.2 Hz, 1 H), 1.20 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.1, 165.7, 165.28, 165.25, 145.2, 144.6, 133.3, 133.24, 133.19, 132.9, 129.9, 129.8, 129.72, 129.68, 129.6, 129.1, 128.9, 128.43, 128.37, 128.32, 128.30, 128.2, 128.0, 127.2, 127.0, 126.7, 126.6, 80.8, 72.6, 72.0, 70.5, 70.4, 67.5, 62.9, 58.2, 34.7, 15.3; HRMS (ESI) m/z calc for $\text{C}_{50}\text{H}_{44}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 843.2566; found 843.2537.

2-2-4. Three-component coupling reaction between **1a**, **2d** and water

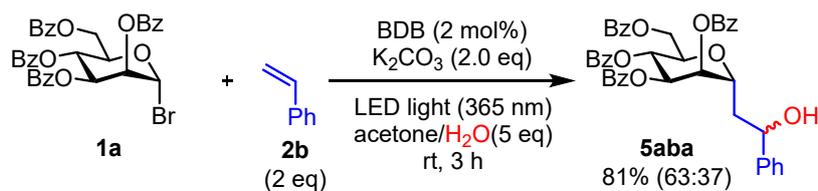


Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.004 mmol, 1.7 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry

MeCN (2.0 mL), α -methylstyrene (**2d**) (0.4 mmol, 52 μ L) and water (1.0 mmol, 18 μ l) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl_3 , concentrated under vacuum. Tetrachloroethane was added as an internal standard and ^1H NMR measurement was performed to determine NMR yield of **5ada** (79%, major/minor = 54:46). Isomers of **5ada** was isolated by silica gel column (eluent: Hexane/EtOAc = 4:1) and preparative TLC (eluent: Hexane/EtOAc = 2:1). **(2R,3R,4R,5R,6R)-2-((benzoyloxy)methyl)-6-(2-hydroxy-2-phenylpropyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (5ada)** major isomer: TLC (Hexane/EtOAc 3:1): $R_f = 0.33$. ^1H NMR (CDCl_3 , 600 MHz) δ 8.14 (d, $J = 7.8$ Hz, 2 H), 8.03 (d, $J = 8.4$ Hz, 2 H), 7.92 (d, $J = 7.8$ Hz, 2 H), 7.77 (d, $J = 7.8$ Hz, 2 H), 7.61–7.55 (m, 3 H), 7.52–7.46 (m, 3 H), 7.43–7.41 (m, 4 H), 7.38 (*pseudo-t*, $J = 7.8$ Hz, 2 H), 7.34–7.31 (m, 4 H), 7.27–7.25 (m, 1 H), 5.80 (dd, $J = 8.4, 3.0$ Hz, 1 H), 5.78 (*pseudo-t*, $J = 8.4$ Hz, 1 H), 5.57 (dd, $J = 4.2, 3.0$ Hz, 1 H), 4.59 (dd, $J = 10.8, 6.0$ Hz, 1 H), 4.52–4.47 (m, 2 H), 4.25 (dd, $J = 9.6, 3.0$ Hz, 1 H), 3.72 (s, 1 H), 2.58 (dd, $J = 15.0, 11.4$ Hz, 1 H), 2.32 (d, $J = 14.4$ Hz, 1 H), 1.60 (s, 3 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.1, 165.4, 165.27, 165.25, 146.8, 133.6, 133.4, 133.2, 129.9, 129.8, 129.73, 129.67, 129.6, 129.2, 128.82, 128.78, 128.53, 128.51, 128.48, 128.47, 126.8, 124.7, 75.1, 72.1, 71.7, 71.0, 69.2, 67.9, 62.8, 40.8, 31.6; HRMS (ESI) m/z calc for $\text{C}_{43}\text{H}_{38}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 753.2097; found 753.2086.

5ada minor isomer: TLC (Hexane/EtOAc 3:1): $R_f = 0.27$. ^1H NMR (CDCl_3 , 600 MHz) δ 8.11 (d, $J = 7.2$ Hz, 2H), 8.04 (d, $J = 7.8$ Hz, 2H), 7.96 (d, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.60–7.56 (m, 2H), 7.54–7.51 (m, 2H), 7.47–7.36 (m, 9H), 7.31–7.26 (m, 3H), 6.00 (*pseudo-t*, $J = 9.0$ Hz, 1H), 5.79 (dd, $J = 9.6, 3.6$ Hz, 1H), 5.68 (s, 1H), 4.61 (dt, $J = 9.6, 3.6$ Hz, 1H), 4.50–4.42 (m, 2H), 4.37 (ddd, $J = 9.0, 5.4, 3.0$ Hz, 1H), 3.01 (s, 1H), 2.60 (dd, $J = 15.0, 10.2$ Hz, 1H), 2.22 (dd, $J = 14.4, 3.0$ Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.2, 165.6, 165.3, 165.25, 147.3, 133.5, 133.4, 133.3, 133.1, 129.80, 129.78, 129.76, 129.71, 129.68, 129.4, 128.9, 128.5, 128.51, 128.44, 128.41, 128.37, 128.35, 126.9, 124.5, 73.7, 73.3, 72.4, 70.8, 69.9, 67.4, 63.0, 41.6, 29.8; HRMS (ESI) m/z calc for $\text{C}_{43}\text{H}_{38}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 753.2097; found 753.2082.

2-2-5. Three-component coupling reaction between **1a**, **2b** and water



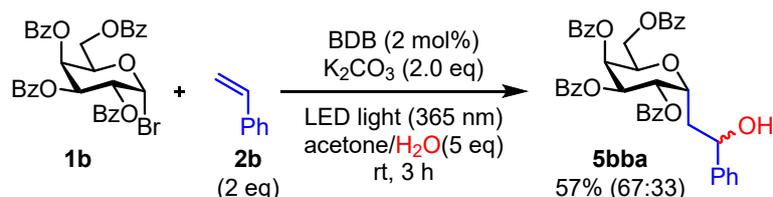
Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.004 mmol, 1.7 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry

MeCN (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μ L) and water (1.0 mmol, 18 μ L) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **5aba** (56%, major/minor = 63:37). **5aba** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:1) and preparative GPC (eluent: CHCl₃).

(2R,3R,4R,5R,6R)-2-((benzyloxy)methyl)-6-(2-hydroxy-2-phenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (5aba**)** major isomer: TLC (Hexane/EtOAc 3:1): R_f = 0.23. ¹H NMR (CDCl₃, 600 MHz) δ 8.11 (dd, *J* = 8.4, 1.2 Hz, 2 H), 8.02–8.00 (m, 4 H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.60–7.49 (m, 4 H), 7.45–7.38 (m, 6 H), 7.37–7.32 (m, 6 H), 7.31–7.26 (m, 1 H), 5.86 (*pseudo-t*, *J* = 7.2 Hz, 1 H), 5.82 (dd, *J* = 7.8 Hz, 1 H), 5.69 (dd, *J* = 10.2, 3.0 Hz, 1 H), 4.95–4.91 (m, 2 H), 4.72 (dt, *J* = 10.8, 4.2 Hz, 1 H), 4.52 (dd, *J* = 12.0, 3.0 Hz, 1 H), 4.41 (td, *J* = 6.6, 3.0 Hz, 1 H), 2.79 (d, *J* = 3.6 Hz, 1 H), 2.28 (ddd, *J* = 13.2, 10.8, 2.4 Hz, 1 H), 2.17 (ddd, *J* = 14.4, 9.6, 3.6 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.6, 165.5, 165.43, 165.38, 143.9, 133.6, 133.42, 133.35, 133.3, 129.9, 129.81, 129.75, 129.73, 129.6, 129.4, 128.9, 128.6, 128.5, 127.7, 125.6, 72.0, 71.3, 70.8, 69.9, 69.4, 68.2, 62.6, 38.8; HRMS (ESI) *m/z* calc for C₄₂H₃₆KO₁₀ [M+K]⁺ 739.1940; found 739.1935.

5aba minor isomer: TLC (Hexane/EtOAc 3:1): R_f = 0.17. ¹H NMR (CDCl₃, 600 MHz) δ 8.12 (dd, *J* = 8.4, 1.2 Hz, 2 H), 8.01 (dd, *J* = 8.4, 1.2 Hz, 2 H), 8.00 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.60–7.53 (m, 3 H), 7.49–7.47 (m, 1 H), 7.44–7.36 (m, 10 H), 7.33–7.29 (m, 3 H), 5.96 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 5.81 (dd, *J* = 9.0, 3.0 Hz, 1 H), 5.66 (*pseudo-t*, *J* = 3.0 Hz, 1 H), 5.05–5.02 (m, 1 H), 4.69 (dd, *J* = 12.0, 6.0 Hz, 1 H), 4.63 (dd, *J* = 12.0, 2.4 Hz, 1 H), 4.55 (ddd, *J* = 9.0, 6.6, 3.0 Hz, 1 H), 4.50 (dt, *J* = 10.8, 3.6 Hz, 1 H), 2.94 (d, *J* = 1.8 Hz, 1 H), 2.56 (ddd, *J* = 14.4, 4.8, 2.4 Hz, 1 H), 2.14 (dt, *J* = 14.4, 4.2 Hz, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.3, 165.54, 165.51, 165.37, 143.21, 133.6, 133.43, 133.38, 133.17, 129.83, 129.79, 129.74, 129.72, 129.6, 129.3, 128.8, 128.6, 128.53, 128.50, 128.48, 128.42, 127.9, 125.8, 74.4, 73.0, 71.5, 71.2, 69.7, 67.6, 63.0, 37.9; HRMS (ESI) *m/z* calc for C₄₂H₃₆KO₁₀ [M+K]⁺ 739.1940; found 739.1949.

2-2-6. Three-component coupling reaction between **1b**, **2b** and water

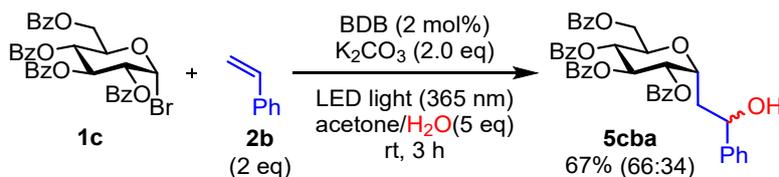


potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry acetone (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μ L) and water (1.0 mmol, 18 μ L) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl_3 , concentrated under vacuum. Tetrachloroethane was added as an internal standard and ^1H NMR measurement was performed to determine NMR yield of **5bba** (57%, major/minor = 67:33). **5bba** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:1) and preparative GPC (eluent: CHCl_3).

(2R,3S,4R,5S,6R)-2-((benzyloxy)methyl)-6-(2-hydroxy-2-phenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (5bba) major isomer : TLC (Hexane/EtOAc 3:1): $R_f = 0.27$. ^1H NMR (CDCl_3 , 600 MHz) δ 8.09 (dd, $J = 8.4, 1.2$ Hz, 2 H), 8.04–7.96 (m, 6 H), 7.61–7.54 (m, 4 H), 7.46–7.39 (m, 8 H), 7.31–7.28 (m, 4 H), 7.25–7.22 (m, 1 H), 5.96 (*pseudo-t*, $J = 4.2$ Hz, 1 H), 5.80 (dd, $J = 7.2, 3.6$ Hz, 1 H), 5.69 (dd, $J = 6.6, 3.6$ Hz, 1 H), 5.28 (s, 1 H), 4.93 (dt, $J = 10.8, 2.4$ Hz, 1 H), 4.88–4.83 (m, 1 H), 4.70–4.65 (m, 1 H), 4.36 (dd, $J = 12.0, 3.0$ Hz, 1 H), 3.19 (s, 1 H), 2.17 (ddd, $J = 13.8, 10.8, 2.4$ Hz, 1 H), 1.99–1.93 (m, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 167.0, 165.3, 165.23, 165.20, 144.1, 133.6, 133.5, 133.46, 129.84, 129.83, 129.75, 129.73, 129.4, 128.94, 128.91, 128.59, 128.57, 128.54, 128.5, 128.48, 127.43, 125.5, 70.9, 70.1, 69.6, 68.5, 67.8, 67.4, 61.5, 37.5; HRMS (ESI) m/z calc for $\text{C}_{42}\text{H}_{36}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 739.1940; found 739.1915.

5bba minor isomer : TLC (Hexane/EtOAc 3:1): $R_f = 0.22$. ^1H NMR (CDCl_3 , 600 MHz) δ 8.09 (d, $J = 7.2$ Hz, 2 H), 8.01 (d, $J = 7.2$ Hz, 2 H), 7.99 (d, $J = 7.8$ Hz, 2 H), 7.78 (d, $J = 7.8$ Hz, 2 H), 7.60 (t, $J = 7.8$ Hz, 1 H), 7.55 (d, $J = 7.8$ Hz, 2 H), 7.51 (t, $J = 7.2$ Hz, 1 H), 7.47–7.39 (m, 6 H), 7.36–7.25 (m, 7 H), 6.00 (m, 1 H), 5.81 (dd, $J = 8.0, 3.4$ Hz, 1 H), 5.74 (dd, $J = 8.0, 4.8$ Hz, 1 H), 4.97 (*pseudo-t*, $J = 6.0$ Hz, 1 H), 4.90–4.84 (m, 1 H), 4.80–4.75 (m, 1 H), 4.68 (dd, $J = 11.4, 3.6$ Hz, 1 H), 4.48 (dd, $J = 12.0, 3.6$ Hz, 1 H), 2.95 (s, 1 H), 2.49–2.42 (m, 1 H), 1.99 (dd, $J = 15.0, 3.0$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.4, 165.4, 165.53, 165.33, 165.32, 143.37, 133.61, 133.59, 133.4, 133.3, 129.9, 129.8, 128.92, 128.88, 128.83, 128.61, 128.55, 128.49, 128.46, 127.8, 125.8, 73.1, 71.5, 69.9, 69.3, 68.6, 68.1, 62.2, 35.9; HRMS (ESI) m/z calc for $\text{C}_{42}\text{H}_{36}\text{KO}_{10}$ $[\text{M}+\text{K}]^+$ 739.1940; found 739.1920.

2-2-7. Three-component coupling reaction between **1c**, **2b** and water

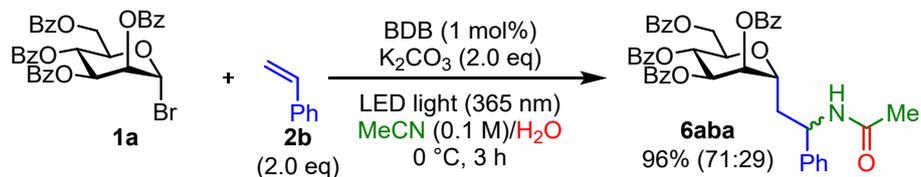


Glycosyl bromide **1c** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry

MeCN (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μ L) and water (1.0 mmol, 18 μ l) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in water bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **5cba** (67%, major/minor = 66:34). **5cba** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:1) and preparative GPC (eluent: CHCl₃). **(2R,3R,4R,5S,6R)-2-((benzoyloxy)methyl)-6-(2-hydroxy-2-phenylethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (5cba)** major isomer: TLC (Hexane/EtOAc 3:1): R_f = 0.25. ¹H NMR (CDCl₃, 600 MHz) δ 8.09 (d, *J* = 7.8 Hz, 2 H), 8.02 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 7.2 Hz, 2 H), 7.90 (d, *J* = 7.8 Hz, 2 H), 7.59–7.51 (m, 3 H), 7.48 (t, *J* = 7.2 Hz, 1 H), 7.45–7.36 (m, 6 H), 7.33–7.28 (m, 4 H), 7.27–7.24 (m, 3 H), 5.84 (*pseudo-t*, *J* = 6.6 Hz, 1 H), 5.48–5.44 (m, 2 H), 4.98 (dd, *J* = 12.0, 7.8 Hz, 1 H), 4.90–4.85 (m, 2 H), 4.50–4.46 (m, 1 H), 4.44 (dd, *J* = 12.0, 3.0 Hz, 1 H), 2.81 (d, *J* = 3.0 Hz, 1 H), 2.34–2.28 (m, 1 H), 2.04–1.97 (m, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.7, 165.4, 165.3, 165.1, 144.1, 133.5, 133.4, 129.93, 129.85, 129.93, 129.85, 129.76, 129.73, 129.4, 129.1, 128.81, 128.78, 128.54, 128.51, 128.4, 128.3, 127.6, 125.6, 71.8, 70.1, 69.6, 69.2, 68.5, 67.8, 62.4, 37.2; HRMS (ESI) *m/z* calc for C₄₂H₃₆KO₁₀ [M+K]⁺ 739.1940; found 739.1925.

5cba minor isomer: TLC (Hexane/EtOAc 3:1): R_f = 0.20. ¹H NMR (CDCl₃, 600 MHz) δ 8.10 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 7.93 (d, *J* = 8.4 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.56–7.47 (m, 4 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.40–7.29 (m, 10 H), 7.28–7.24 (m, 1 H), 5.92 (*pseudo-t*, *J* = 7.8 Hz, 1 H), 5.53 (*pseudo-t*, *J* = 7.2 Hz, 1 H), 5.45 (dd, *J* = 7.8, 4.8 Hz, 1 H), 4.96 (dd, *J* = 7.8, 5.4 Hz, 1 H), 4.69 (dd, *J* = 12.0, 7.2 Hz, 1 H), 4.66–4.55 (m, 3 H), 2.91 (s, 1 H), 2.59–2.51 (m, 1 H), 2.03–1.98 (m, 1 H); ¹³C NMR (CDCl₃, 150 MHz) δ 166.3, 165.4, 165.3, 165.25, 143.4, 133.54, 133.48, 133.4, 133.2, 129.9, 129.8, 129.5, 128.82, 128.78, 128.6, 128.51, 128.47, 128.44, 128.39, 127.8, 125.8, 73.2, 71.7, 70.8, 70.3, 69.7, 68.9, 62.9, 35.9; HRMS (ESI) *m/z* calc for C₄₂H₃₆KO₁₀ [M+K]⁺ 739.1940; found 739.1920.

2-3-1. Four-component coupling reaction between **1a**, **2b**, acetonitrile, and water

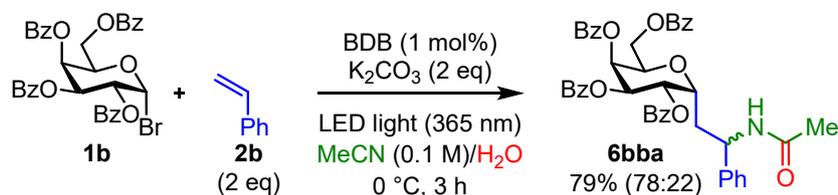


Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μ L) and water (1.0 mmol, 18 μ l) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were

performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6aba** (96%, major/minor = 71:29). **6aba** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:1 → 2:1 → 3:2) and preparative GPC (eluent: CHCl₃). **(2R,3R,4R,5R,6R)-2-(2-acetamido-2-phenylethyl)-6-((benzoyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (6aba)** major isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.36; ¹H NMR (CDCl₃, 600 MHz) δ 8.13 (d, *J* = 7.2 Hz, 2 H), 7.99 (dd, *J* = 8.4, 1.8 Hz, 2 H), 7.95 (d, *J* = 7.2 Hz, 2 H), 7.79 (d, *J* = 7.8 Hz, 2 H), 7.59–7.55 (m, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.40–7.27 (m, 11 H), 6.41 (br, 1 H), 5.90 (t, *J* = 7.2 Hz, 1 H), 5.76 (dd, *J* = 8.4, 3.0 Hz, 1 H), 5.64–5.62 (m, 1 H), 5.38–5.33 (m, 1 H), 5.38–5.33 (m, 1 H), 4.58–4.51 (m, 2 H), 4.40–4.32 (m, 2 H), 2.52–2.46 (m, 1 H), 2.29 (ddd, *J* = 14.4, 7.2, 3.0 Hz, 1 H), 1.96 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.6, 166.1, 165.4, 165.3, 165.2, 141.3, 133.4, 133.33, 133.30, 133.1, 129.65, 129.58, 129.56, 129.1, 128.73, 128.69, 128.41, 128.40, 128.3, 127.4, 126.2, 71.9, 71.2, 69.6, 67.6, 62.7, 50.7, 34.6, 23.2; HRMS (ESI) *m/z* calc for C₄₄H₃₉KNO₁₀ [M+K]⁺ 780.2206; found 780.2179.

6aba minor isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.30; ¹H NMR (CDCl₃, 600 MHz) δ 8.18 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 7.8 Hz, 2 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.59–7.49 (m, 3 H), 7.46–7.40 (m, 3 H), 7.40–7.24 (m, 11 H), 6.06 (t, *J* = 9.0 Hz, 1 H), 6.00–5.94 (m, 1 H), 5.81 (dd, *J* = 9.6, 3.0 Hz, 1 H), 5.60 (s, 1 H), 5.23–5.17 (m, 1 H), 4.75–4.67 (m, 2 H), 4.62 (dd, *J* = 12.0, 5.4 Hz, 1 H), 3.93 (d, *J* = 12.0 Hz, 1 H), 2.94 (td, *J* = 14.4, 4.2 Hz, 1 H), 2.11–2.04 (m, 1 H), 2.01 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.5, 166.2, 165.6, 165.5, 165.4, 139.3, 133.4, 133.3, 133.2, 133.0, 129.9, 129.81, 129.79, 129.73, 129.65, 129.3, 129.1, 128.9, 128.42, 128.37, 128.3, 128.2, 127.1, 72.7, 71.8, 70.44, 70.38, 67.1, 63.2, 51.1, 34.1, 23.3; HRMS (ESI) *m/z* calc for C₄₄H₃₉KNO₁₀ [M+K]⁺ 780.2206; found 780.2183.

2-3-2. Four-component coupling reaction between **1b**, **2b**, acetonitrile, and water



performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6bba** (79%, major/minor = 78:22). **6bba** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:2 → 5:4) and preparative GPC (eluent: CHCl₃). **(2R,3S,4R,5S,6R)-2-(2-acetamido-2-phenylethyl)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (6bba)** major isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.27; ¹H NMR (CDCl₃, 600 MHz) δ 8.09 (d, *J* = 7.8 Hz, 2 H), 8.05 (d, *J* = 7.8 Hz, 2 H), 7.92 (d, *J* = 7.8 Hz, 2 H), 7.81 (d, *J* = 7.8 Hz, 2 H), 7.62–7.56 (m, 3 H), 7.54 (t, *J* = 7.8 Hz, 1 H), 7.49–7.40 (m, 6 H), 7.37 (t, *J* = 7.8 Hz, 2 H), 7.31–7.21 (m, 5 H), 6.67 (d, *J* = 6.6 Hz, 1 H), 5.95 (s, 1 H), 5.72 (dd, *J* = 7.2, 3.0 Hz, 1 H), 5.55–5.48 (m, 1 H), 5.40–5.34 (m, 1 H), 4.73–4.66 (m, 2 H), 4.49 (d, *J* = 10.2 Hz, 1 H), 4.47–4.42 (m, 1 H), 2.38–2.31 (m, 1 H), 2.11 (dd, *J* = 15.0, 6.6 Hz, 1 H), 1.92 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.2, 166.2, 165.3, 165.2, 165.0, 141.0, 133.6, 133.5, 133.4, 133.3, 129.8, 129.7, 129.57, 129.56, 129.3, 128.70, 128.69, 128.66, 128.6, 128.50, 128.46, 128.4, 127.2, 125.9, 70.6, 70.1, 68.6, 68.4, 67.5, 50.4, 33.4, 23.2; HRMS (ESI) *m/z* calc for C₄₄H₃₉KNO₁₀ [M+K]⁺ 780.2206; found 780.2190.

6bba (minor): TLC (Hexane/EtOAc 1:1): R_f = 0.20; ¹H NMR (CDCl₃, 600 MHz) δ 8.13 (d, *J* = 7.8 Hz, 2 H), 8.00 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 7.8 Hz, 2 H), 7.81 (d, *J* = 7.8 Hz, 2 H), 7.60–7.52 (m, 3 H), 7.49–7.39 (m, 7 H), 7.31–7.25 (m, 5 H), 7.21–7.17 (m, 2 H), 6.00 (s, 1 H), 5.89–5.82 (m, 2 H), 5.73 (dd, *J* = 9.0, 5.4 Hz, 1 H), 5.21–5.14 (m, 1 H), 4.90–4.84 (m, 1 H), 4.80 (dd, *J* = 11.4, 7.8 Hz, 1 H), 4.39 (dd, *J* = 11.4, 4.8 Hz, 1 H), 4.32–4.25 (m, 1 H), 2.75–2.65 (m, 1 H), 2.03–1.94 (m, 4 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.2, 166.3, 165.43, 165.36, 165.3, 139.8, 133.50, 133.49, 133.3, 133.1, 129.87, 129.86, 129.8, 129.7, 129.6, 129.04, 128.96, 128.6, 128.5, 128.4, 128.3, 128.1, 126.9, 69.7, 69.3, 69.2, 68.8, 68.6, 62.6, 51.2, 32.0, 23.3; HRMS (ESI) *m/z* calc for C₄₄H₃₉KNO₁₀ [M+K]⁺ 780.2206; found 780.2191.

2-3-3. Four-component coupling reaction between **1c**, **2b**, acetonitrile, and water

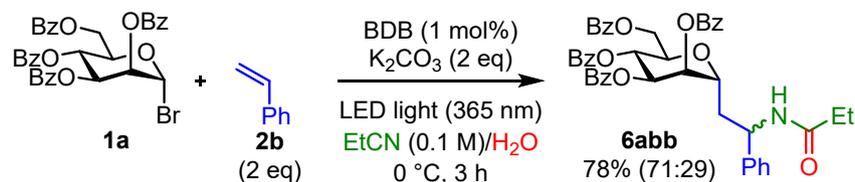


Glycosyl bromide **1c** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μL) and water (1.0 mmol, 18 μL) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were

performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6cba** (66%, major/minor = 76:24). **6cba** was isolated by silica gel column (eluent: Hexane/EtOAc = 7:4) (**2R,3S,4R,5R,6R**)-2-(2-acetamido-2-phenylethyl)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (**6cba**) major isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.23; ¹H NMR (CDCl₃, 600 MHz) δ 8.10 (dd, *J* = 8.4, 1.2 Hz, 2 H), 8.03 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.90 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.83 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.58 (dd, *J* = 13.8, 7.8 Hz, 2 H), 7.49 (dd, *J* = 13.8, 7.2 Hz, 2 H), 7.46–7.41 (m, 4 H), 7.35 (*pseudo-t*, *J* = 7.8 Hz, 2 H), 7.28–7.21 (m, 7 H), 6.45 (d, *J* = 8.4 Hz, 1 H), 5.79 (*pseudo-t*, *J* = 7.2 Hz, 1 H), 5.30 (dd, *J* = 7.2, 4.2 Hz, 1 H), 5.37 (td, *J* = 7.8, 3.6 Hz, 1 H), 5.48 (*pseudo-t*, *J* = 6.6 Hz, 1 H), 4.55–4.52 (m, 2 H), 4.48 (ddd, *J* = 11.4, 5.4 Hz, 1 H), 4.44 (dd, *J* = 11.4, 5.4 Hz, 1 H), 2.48 (ddd, *J* = 14.4, 10.2, 3.6 Hz, 1 H), 2.31 (ddd, *J* = 15.0, 7.2, 1.6 Hz, 1 H), 1.94 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.3, 166.3, 165.3, 165.2, 165.1, 141.0, 133.6, 133.5, 133.4, 133.3, 129.94, 129.86, 129.75, 129.69, 129.5, 128.9, 128.8, 128.7, 128.6, 128.51, 128.46, 128.3, 127.4, 126.1, 71.4, 70.4, 69.3, 68.7, 68.5, 62.6, 50.4, 33.3, 23.4; HRMS (ESI) *m/z* calc for C₄₄H₃₉KNO₁₀ [M+K]⁺ 780.2206; found 780.2208.

6cba minor isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.23; ¹H NMR (CDCl₃, 600 MHz) δ 8.14 (d, *J* = 9.0 Hz, 2 H), 7.96–7.94 (m, 4 H), 7.87 (d, *J* = 9.0 Hz, 2 H), 7.59–7.27 (m, 15 H), 7.23–7.20 (m, 2 H), 5.98 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 5.81 (d, *J* = 7.2 Hz, 1 H), 5.59 (*pseudo-t*, *J* = 9.0 Hz, 1 H), 5.41 (dd, *J* = 9.6, 5.4 Hz, 1 H), 5.18 (ddd, *J* = 11.4, 7.2, 4.8 Hz, 1 H), 4.73 (ddd, *J* = 9.0, 6.0, 3.0 Hz, 1 H), 4.64 (dd, *J* = 12.0, 6.0 Hz, 1 H), 4.57 (dd, *J* = 12.0, 6.0 Hz, 1 H), 4.42 (ddd, *J* = 12.0, 6.0, 3.0 Hz, 1 H), 2.82 (ddd, *J* = 14.4, 12.0, 4.8 Hz, 1 H), 2.07–2.04 (m, 1 H), 2.02 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.4, 166.3, 165.7, 165.3, 165.1, 139.5, 133.45, 133.37, 133.2, 133.0, 129.91, 129.85, 129.80, 129.75, 129.67, 129.1, 128.9, 128.7, 128.6, 128.5, 128.37, 128.33, 128.31, 128.1, 127.0, 126.0, 70.9, 70.5, 69.9, 69.8, 69.2, 63.2, 51.0, 31.8, 29.7, 23.3; HRMS (ESI) *m/z* calc for C₄₄H₃₉KNO₁₀ [M+K]⁺ 780.2206; found 780.2182.

2-3-4. Four-component coupling reaction between **1a**, **2b**, propionitrile, and water

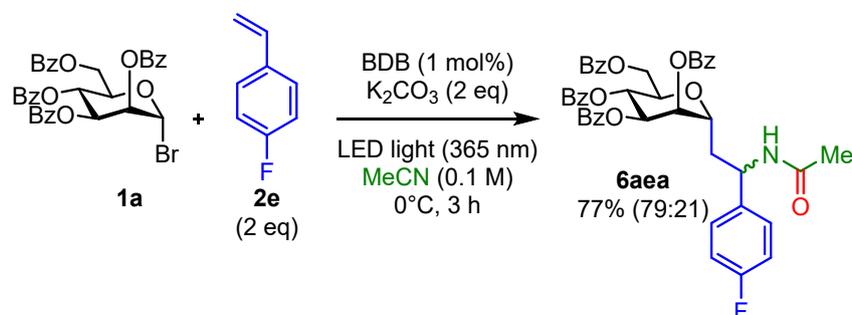


Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry propionitrile (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μL) and water (1.0 mmol, 18 μL) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing

were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6abb** (78%, major/minor = 71:29). **6abb** was isolated by silica gel column (eluent: Hexane/EtOAc = 1:1) and preparative GPC (eluent: CHCl₃). **(2R,3R,4R,5R,6R)-2-((benzyloxy)methyl)-6-(2-phenyl-2-propionamidoethyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (6abb)** major isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.43; ¹H NMR (CDCl₃, 600 MHz) δ 8.12 (d, *J* = 7.2 Hz, 2 H), 7.99 (d, *J* = 7.2 Hz, 2 H), 7.95 (d, *J* = 7.8 Hz, 2 H), 7.80 (d, *J* = 7.2 Hz, 2 H), 7.61–7.52 (m, 3 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 7.46–7.27 (m, 13 H), 6.30 (d, *J* = 7.2 Hz, 1 H), 5.90 (t, *J* = 7.8 Hz, 1 H), 5.76 (dd, *J* = 8.4, 3.0 Hz, 1 H), 5.64–5.60 (m, 1 H), 5.39–5.33 (m, 1 H), 4.56 (dd, *J* = 12.0, 5.4 Hz, 1 H), 4.51 (dd, *J* = 12.0, 2.4 Hz, 1 H), 4.40–4.31 (m, 2 H), 2.53–2.45 (m, 1 H), 2.29 (ddd, *J* = 14.4, 7.2, 2.4 Hz, 1 H), 2.26–2.14 (m, 2 H), 1.11 (t, *J* = 7.8 Hz, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 173.1, 166.2, 165.42, 165.37, 165.3, 141.2, 133.6, 133.4, 133.2, 129.82, 129.75, 129.73, 129.67, 129.2, 128.84, 128.78, 128.5, 128.4, 127.6, 126.3, 71.6, 71.0, 69.5, 67.8, 62.6, 50.7, 34.9, 29.7, 9.7; HRMS (ESI) *m/z* calc for C₄₅H₄₁KNO₁₀ [M+K]⁺ 794.2362; found 780.2376.

6abb minor isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.42; ¹H NMR (CDCl₃, 600 MHz) δ 8.18 (d, *J* = 7.8 Hz, 2 H), 7.99 (d, *J* = 7.8 Hz 2 H), 7.97 (d, *J* = 7.8 Hz 2 H), 7.81 (d, *J* = 7.2 Hz, 2 H), 7.59–7.51 (m, 3 H), 7.45–7.27 (m, 14 H), 6.06 (*pseudo-t*, *J* = 9.6 Hz, 1 H), 5.81–5.79 (m, 2 H), 5.59 (*pseudo-t*, *J* = 3.0 Hz, 1 H), 5.20 (ddd, *J* = 10.8, 6.6, 4.2 Hz, 1 H), 4.72 (ddd, *J* = 9.6, 5.4, 3.0 Hz, 1 H), 4.69 (dd, *J* = 12.0 Hz, 2.4 Hz 1 H), 4.62 (dd, *J* = 12.0 Hz, 5.4 Hz 1 H), 3.92–3.89 (dt, *J* = 11.4, 3.0 Hz, 1 H), 3.00–2.95 (m, 1 H), 2.23–2.21 (m, 2 H), 2.06 (ddd, *J* = 12.6, 10.8, 3.0 Hz, 1 H), 1.20 (t, *J* = 7.8 Hz, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 173.1, 166.3, 165.7, 165.53, 165.46, 139.4, 129.91, 129.87, 129.8, 129.7, 129.4, 129.2, 128.9, 128.46, 128.42, 128.39, 128.3, 127.2, 72.9, 71.9, 70.52, 70.50, 67.1, 63.3, 51.2, 34.1. 29.7, 9.7; HRMS (ESI) *m/z* calc for C₄₅H₄₁KNO₁₀ [M+K]⁺ 794.2362; found 794.2340.

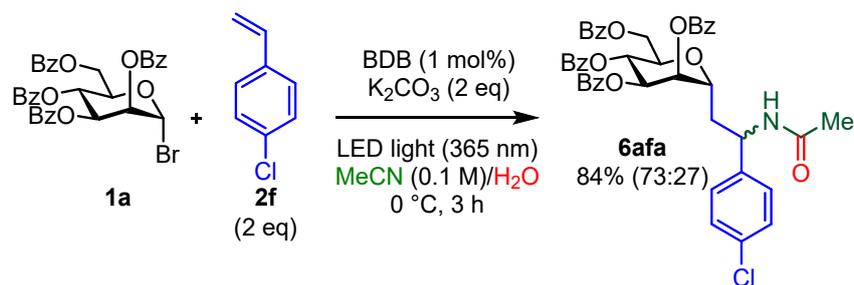
2-3-5. Four-component coupling reaction between **1a**, **2e**, acetonitrile, and water



Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry

MeCN (2.0 mL) and 4-fluorostyrene (**2e**) (0.4 mmol, 48 μ L) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6aea** (77%, major/minor = 79:21). **6aea** was isolated by silica gel column (eluent: Hexane/EtOAc = 2:1 \rightarrow 3:2 \rightarrow 1:1) and preparative GPC (eluent: CHCl₃). **(2R,3R,4R,5R,6R)-2-(2-acetamido-2-(4-fluorophenyl)ethyl)-6-((benzoyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (6aea)** major isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.33. ¹H NMR (CDCl₃, 600 MHz) δ 8.12 (d, J = 7.2 Hz, 2 H), 8.01 (d, J = 7.2 Hz, 2 H), 7.93 (d, J = 7.2 Hz, 2 H), 7.61–7.53 (m, 3 H), 7.51 (t, J = 7.2 Hz, 1 H), 7.46–7.32 (m, 8 H), 7.02 (t, J = 8.4 Hz, 1 H), 6.45–6.38 (m, 1 H), 5.86 (t, J = 7.2 Hz, 1 H), 5.77 (dd, J = 7.8, 3.0 Hz, 1 H), 5.63–5.58 (m, 1 H), 5.36–5.30 (m, 1 H), 4.64 (dd, J = 12.0, 6.0 Hz, 1 H), 4.57 (dd, J = 12.0, 3.0 Hz, 1 H), 4.42–4.37 (m, 1 H), 4.36–4.31 (m, 1 H), 2.48–2.40 (m, 1 H), 2.25 (ddd, J = 15.0, 7.8, 3.0 Hz, 1 H), 1.95 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.6, 166.2, 165.4, 165.2, 162.0 (d, J = 246.0 Hz), 137.1, 133.49 (d, J = 10.5 Hz), 133.47, 133.3, 129.74, 129.69, 129.67, 129.59, 129.55, 129.1, 128.8, 128.7, 128.5, 128.4, 115.6 (d, J = 21.0 Hz), 71.6, 71.4, 71.0, 69.5, 67.8, 62.7, 50.1, 34.8, 23.2; ¹⁹F NMR (CDCl₃, 565 MHz) δ 46.9 (tt, J = 8.5, 5.1 Hz); HRMS (ESI) m/z calc for C₄₄H₃₈FKNO₁₀ [M+K]⁺ 798.2111; found 798.2099. **6aea** minor isomer: TLC (Hexane/EtOAc 1:1): R_f = 0.23. ¹H NMR (CDCl₃, 600 MHz) δ 8.17 (d, J = 7.8 Hz, 2 H), 7.99 (d, J = 7.8 Hz, 2 H), 7.97 (d, J = 7.8 Hz, 2 H), 7.83 (d, J = 7.2 Hz, 2 H), 7.60–7.50 (m, 3 H), 7.48–7.41 (m, 3 H), 7.40–7.35 (m, 4 H), 7.31–7.25 (m, 4 H), 7.01 (t, J = 8.4 Hz, 2 H), 6.04 (t, J = 9.0 Hz, 1 H), 5.91–5.87 (br, 1 H), 5.79 (dd, J = 9.6, 3.0 Hz, 1 H), 5.60–5.57 (m, 1 H), 5.21–5.16 (m, 1 H), 4.71–4.61 (m, 3 H), 3.93 (d, J = 11.4 Hz, 1 H), 2.94 (td, J = 14.4, 4.8 Hz, 1 H), 2.08–2.01 (m, 4 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.5, 166.2, 165.6, 165.5, 165.4, 162.3 (d, J = 246.0 Hz), 135.25, 133.4 (d, J = 9.0 Hz), 133.3, 133.0, 129.87, 129.83, 129.80, 129.74, 129.66, 129.2, 128.85, 128.83, 128.80, 128.5, 128.4, 128.3, 116.0 (d, J = 22.5 Hz), 72.5, 71.7, 70.6, 70.32, 67.2, 63.2, 50.5, 34.3, 23.3; ¹⁹F NMR (CDCl₃, 565 MHz) δ 48.2 (tt, J = 8.5, 5.1 Hz); HRMS (ESI) m/z calc for C₄₄H₃₈FKNO₁₀ [M+K]⁺ 798.2111; found 798.2096.

2-3-6. Four-component coupling reaction between **1a**, **2f**, acetonitrile, and water

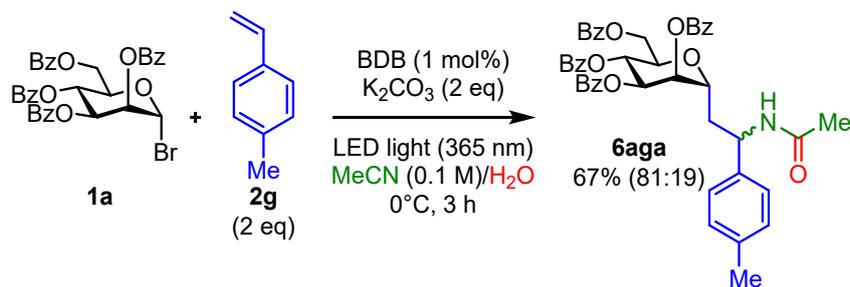


Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry acetonitrile (2.0 mL), 4-chlorostyrene (**2f**) (0.4 mmol, 51 μ L) and water (1.0 mmol, 18 μ L) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6afa** (84%, major/minor = 73:27). **6afa** was isolated by silica gel column (eluent: Hexane/EtOAc = 2:1→3:2→1:1) and preparative GPC (eluent: CHCl₃).

(2R,3R,4R,5R,6R)-2-(2-(2-acetamido-2-(4-chlorophenyl)ethyl)-6-(benzoyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (6afa) major isomer: TLC (Hexane/EtOAc 1:1) R_f = 0.28. ¹H NMR (CDCl₃, 600 MHz) δ 8.12 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 7.2 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 7.8 Hz, 2 H), 7.61–7.49 (m, 4 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.42–7.33 (m, 6 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.58–6.52 (m, 1 H), 5.86 (t, *J* = 7.2 Hz, 1 H), 5.79–5.74 (m, 1 H), 5.62–5.88 (br, 1 H), 5.34–5.28 (m, 1 H), 4.65 (dd, *J* = 12.6, 6.6 Hz, 1 H), 4.57 (dd, *J* = 12.0 Hz, 1 H), 4.43–4.38 (m, 1 H), 4.37–4.31 (m, 1 H), 2.48–2.40 (m, 1 H), 2.24 (ddd, *J* = 15.0, 7.8, 2.4 Hz, 1 H), 1.93 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.7, 166.1, 165.39, 165.35, 165.2, 140.0, 133.5, 133.44, 133.42, 133.2, 133.1, 129.67, 129.64, 129.61, 129.52, 129.47, 129.0, 128.76, 128.66, 128.57, 128.45, 128.42, 128.37, 127.6, 71.4, 70.9, 69.5, 67.7, 62.6, 50.0, 34.5, 23.1; HRMS (ESI) *m/z* calc for C₄₄H₃₈ClKNO₁₀ [M+K]⁺ 814.1816; found 814.1797.

6afa minor isomer: TLC (Hexane/EtOAc 1:1) R_f = 0.16. ¹H NMR (CDCl₃, 600 MHz) δ 8.16 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 7.8 Hz, 2 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 7.8 Hz, 2 H), 7.60–7.54 (m, 2 H), 7.45 (t, *J* = 7.8 Hz, 1 H), 7.48–7.42 (m, 3 H), 7.40–7.35 (m, 4 H), 7.32–7.27 (m, 4 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 6.03 (t, *J* = 9.0 Hz, 1 H), 5.99 (d, *J* = 6.6 Hz, 1 H), 5.80 (dd, *J* = 9.6, 3.0 Hz, 1 H), 5.59 (s, 1 H), 5.21–5.15 (m, 1 H), 4.71–4.63 (m, 3 H), 3.95 (d, *J* = 11.4 Hz, 1 H), 2.86 (td, *J* = 14.4, 4.2 Hz, 1 H), 2.08–1.99 (m, 4 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.5, 166.2, 165.6, 165.5, 165.4, 138.0, 133.9, 133.47, 133.41, 133.3, 133.1, 129.81, 129.79, 129.74, 129.65, 129.23, 129.16, 128.79, 128.76, 128.48, 128.47, 128.42, 128.35, 72.4, 71.6, 70.6, 70.3, 67.1, 63.1, 50.5, 34.2, 23.2; HRMS (ESI) *m/z* calc for C₄₄H₃₈ClKNO₁₀ [M+K]⁺ 814.1816; found 814.1774.

2-3-7. Four-component coupling reaction between **1a**, **2g**, acetonitrile, and water

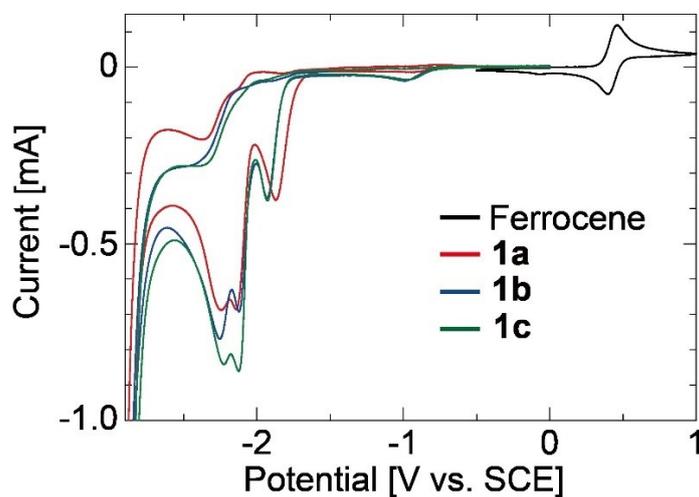


Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry acetonitrile (2.0 mL), 4-methylstyrene (**2g**) (0.4 mmol, 54 μ L) and water (1.0 mmol, 18 μ L) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with CHCl₃, concentrated under vacuum. Tetrachloroethane was added as an internal standard and ¹H NMR measurement was performed to determine NMR yield of **6aga** (67%, major/minor = 81:19). **6aga** was isolated by silica gel column (eluent: Hexane/EtOAc = 3:2→1:1) and preparative GPC (eluent: CHCl₃). **(2R,3R,4R,5R,6R)-2-(2-acetamido-2-(p-tolyl)ethyl)-6-((benzoyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (6aga)** major isomer: TLC (Hexane/EtOAc 1:1) R_f = 0.32. ¹H NMR (CDCl₃, 600 MHz) δ 8.12 (d, *J* = 7.8 Hz, 2 H), 8.00–7.94 (m, 4 H), 7.81 (d, *J* = 7.8 Hz, 2 H), 7.60–7.55 (m, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.41–7.36 (m, 4 H), 7.31 (t, *J* = 7.8 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 6.28 (d, *J* = 7.8 Hz, 1 H), 5.93 (t, *J* = 7.8 Hz, 1 H), 5.76 (dd, *J* = 8.4, 2.4 Hz, 1 H), 5.66–5.62 (m, 1 H), 5.35–5.29 (m, 1 H), 4.58–4.50 (m, 2 H), 4.40–4.35 (m, 1 H), 4.35–4.30 (m, 1 H), 2.54–2.46 (m, 1 H), 2.33 (s, 3 H), 2.28 (ddd, *J* = 14.4, 7.2, 3.0 Hz, 1 H), 1.96 (s, 3 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.5, 166.1, 165.41, 165.36, 165.2, 138.3, 137.1, 133.4, 133.31, 133.27, 133.0, 129.7, 129.61, 129.58, 129.4, 129.2, 128.8, 128.7, 128.41, 128.39, 128.33, 128.30, 126.2, 72.2, 71.3, 71.0, 69.7, 67.6, 62.8, 50.4, 34.6, 23.2, 21.0; HRMS (ESI) *m/z* calc for C₄₅H₄₁KNO₁₀ [M+K]⁺ 794.2362; found 794.2350.

6aga minor isomer: TLC (Hexane/EtOAc 1:1) R_f = 0.19. ¹H NMR (CDCl₃, 600 MHz) δ 8.18 (d, *J* = 7.8 Hz, 2 H), 7.98 (t, *J* = 8.4 Hz, 4 H), 7.82 (d, *J* = 7.2 Hz, 2 H), 7.59–7.53 (m, 2 H), 7.51 (t, *J* = 7.2 Hz, 1 H), 7.46–7.41 (m, 3 H), 7.37 (dd, *J* = 17.4, 8.4 Hz, 4 H), 7.29–7.24 (m, 2 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 6.07 (t, *J* = 9.6 Hz, 1 H), 5.88 (br, 1 H), 5.80 (dd, *J* = 10.2, 3.0 Hz, 1 H), 5.60 (s, 1 H), 5.20–5.12 (m, 1 H), 4.77–4.67 (m, 2 H), 4.62 (dd, *J* = 12.0, 4.8 Hz, 1 H), 3.92 (d, *J* = 12.0 Hz, 1 H), 3.01–2.91 (m, 1 H), 2.30 (s, 3 H), 2.08–1.98 (m, 4 H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.4, 166.2, 165.7, 165.5, 165.4, 138.1, 136.2, 133.4, 133.3, 133.2, 132.9, 130.0, 129.9, 129.83, 129.76, 129.7, 129.4, 128.9, 128.43, 128.39, 128.37, 128.3, 127.1, 72.9, 71.9, 70.5, 70.3, 67.1, 63.3, 50.9, 33.9, 23.4, 21.1; HRMS (ESI) *m/z* calc for C₄₅H₄₁KNO₁₀ [M+K]⁺ 794.2362; found 794.2353.

3. Cyclic Voltammetry

Cyclic voltammetry was measured in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ under argon atmosphere at room temperature (ca 25 °C) using glassy carbon (GC) working electrode, platinum wire counter electrode, and standard calomel electrode (SCE) as a reference electrode. Concentrations of glycosyl bromides



1a-c were 10 mM. Reduction potentials (E_{red}) of **1a-c** were determined from the first reduction peaks (**1a**: -1.87 V vs. SCE, **1b**: -1.93 V vs. SCE, **1c**: -1.93 V vs. SCE). Redox potential of ferrocene was obtained using the same electrolyte (0.43 V vs. SCE) and E_{red} of **1a-c** were corrected ($E_{\text{red}}(\text{Fc}/\text{Fc}^+) = E_{\text{red}}(\text{SCE}) - 0.43$).

Figure S1. Cyclic voltammetry of glycosyl bromides.

4. Stern-Volmer Plots

BDB (4.5 mg, 0.011 mmol) was dissolved in dry acetone (10 mL). Transient absorption spectra were recorded at variable concentrations of glycosyl bromides **1** (0.02-0.01 mM for **1a**, 0.03-0.075 mM for **1b** and **1c**). Quenching rate constants of glycosyl bromides **1** were calculated as follows (mannosyl bromide **1a**: $3.23 \times 10^{10} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$, galactosyl bromide **1b**: $2.38 \times 10^{10} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$, glucosyl bromide **1c**: $1.0 \times 10^{10} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$).

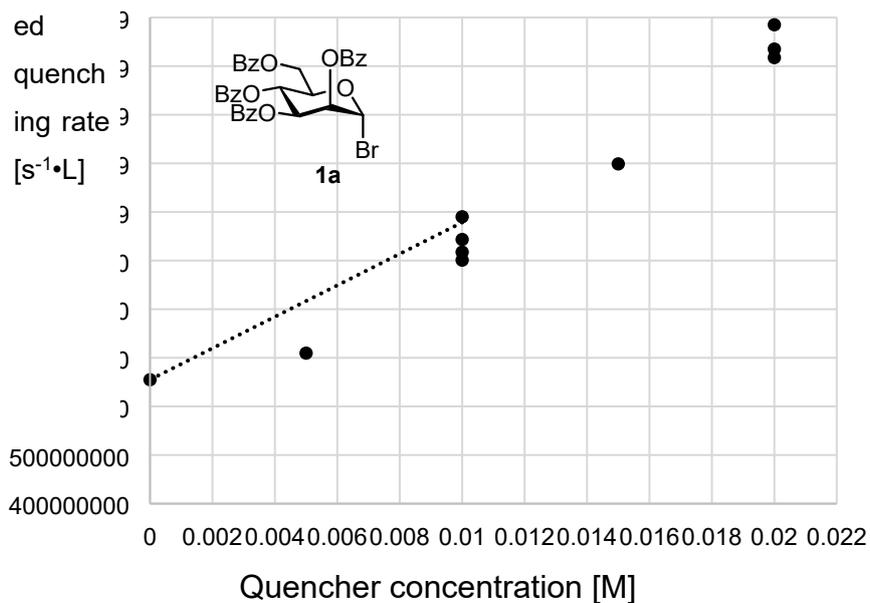


Figure S2. Stern-Volmer plot of variable concentrations of mannosyl bromide **1a**.

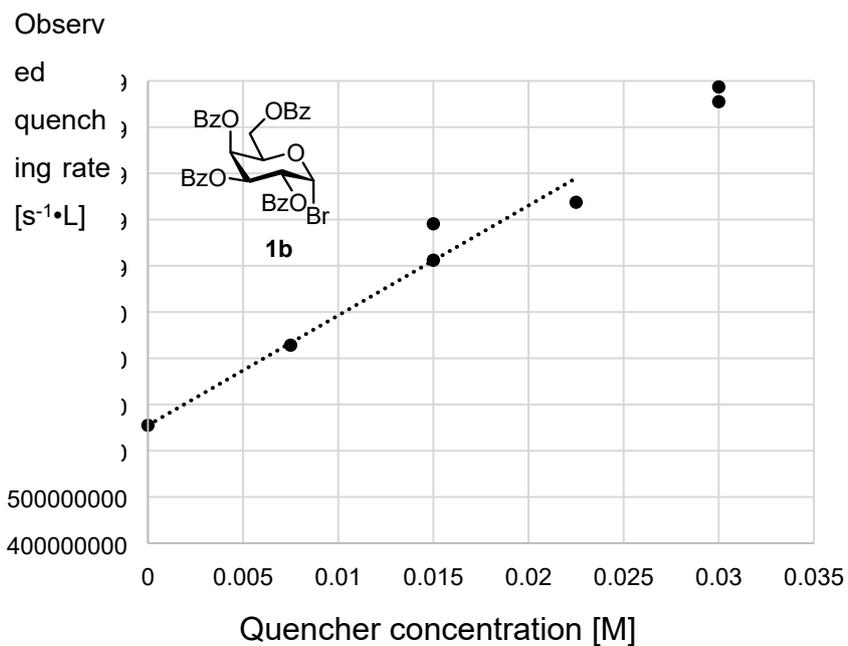


Figure S3. Stern-Volmer plot of variable concentrations of galactosyl bromide **1b**.

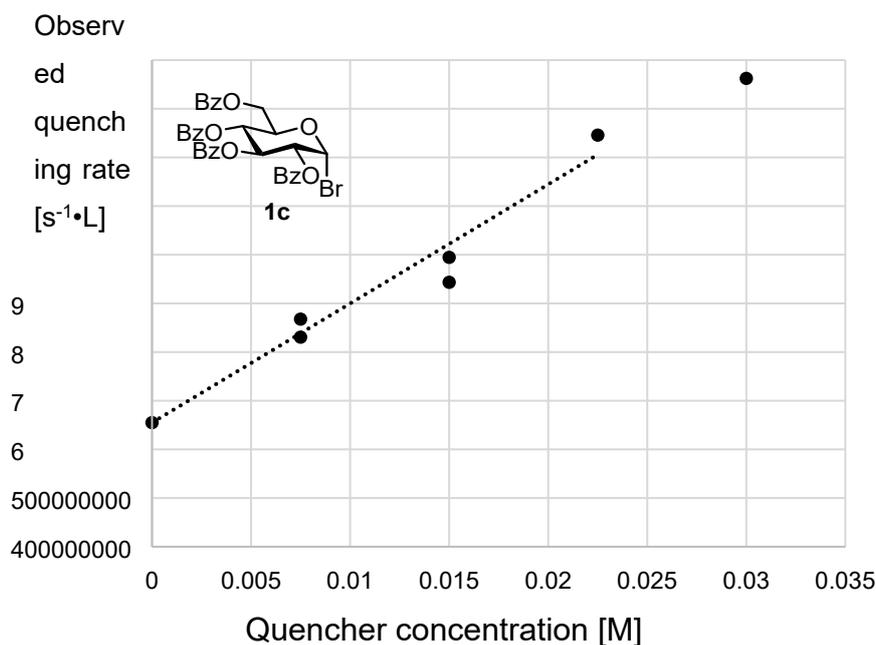
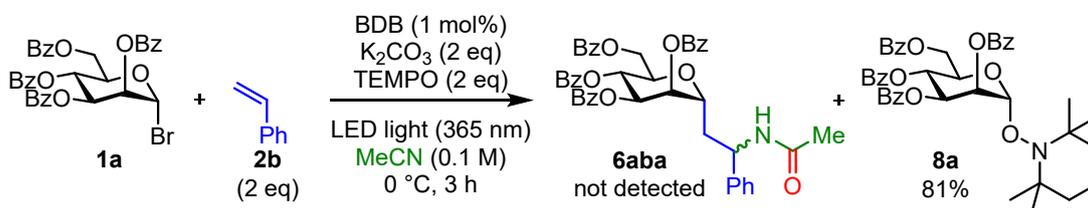


Figure S4. Stern-Volmer plot of variable concentrations of glucosyl bromide **1c**.

5. Control experiment in the presence of TEMPO



Glycosyl bromide **1a** (0.20 mmol, 132 mg), organic photocatalytic BDB (0.02 mmol, 8.3 mg), and potassium carbonate (0.40 mmol, 55.3 mg) were added to the dried Schrenk tube under argon. Dry MeCN (2.0 mL), styrene (**2b**) (0.4 mmol, 46 μ L), and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (0.4 mmol, 63 mg) were added and stirred. Then the LED ramp was attached to the Schrenk tube using a Teflon joint, and freeze degassing were performed using liquid nitrogen. The reaction was performed by irradiating LED light (wavelength: 365 nm) for 3 h in ice bath. After photo irradiation the reaction mixture was diluted with $CHCl_3$, concentrated under vacuum. Tetrachloroethane was added as an internal standard and 1H NMR measurement was performed to determine NMR yield of **8a** (81%). **8a** was isolated by silica gel column (eluent: Hexane/EtOAc = 5:1). **(2R,3R,4S,5S,6R)-2-((benzyloxy)methyl)-6-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (8a)** TLC (Hexane/EtOAc 3:1) R_f = 0.52; 1H NMR ($CDCl_3$, 600 MHz) δ 8.09 (d, J = 7.8 Hz, 2 H), 8.07 (d, J = 7.8 Hz, 2 H), 8.00 (d, J = 7.8 Hz, 2 H), 7.88 (d, J = 7.8 Hz, 2 H), 7.61–7.54

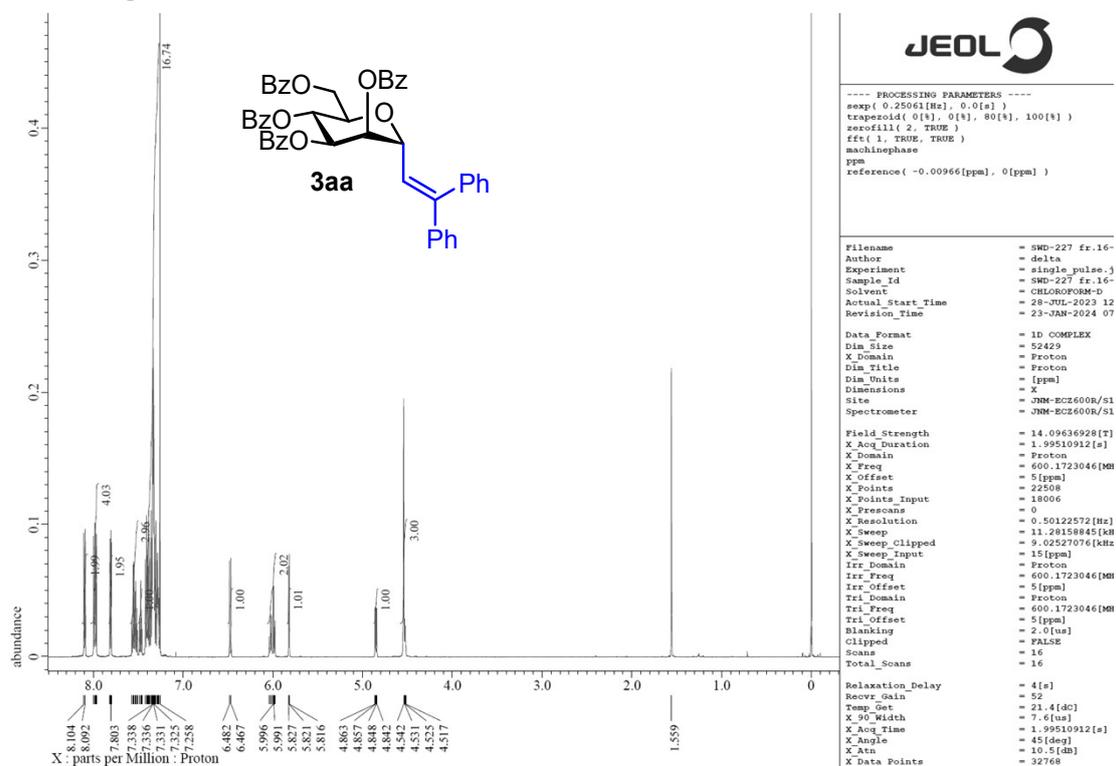
(m, 2 H), 7.51 (t, $J = 7.2$ Hz, 1 H), 7.44 (t, $J = 7.8$ Hz, 1 H), 7.42–7.36 (m, 6 H), 7.29 (t, $J = 7.8$ Hz, 2 H), 6.20 (t, $J = 10.2$ Hz, 1 H), 5.99 (s, 1 H), 5.86 (dd, $J = 10.2, 3.0$ Hz, 1 H), 5.44 (s, 1 H), 4.72–4.67 (m, 1 H), 4.59–4.54 (m, 1 H), 4.49 (dd, $J = 12.0, 4.8$ Hz, 1 H), 1.67–1.45 (m, 5H), 1.40–1.21 (m, 13 H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 166.2, 165.7, 165.5, 165.4, 133.4, 133.3, 133.2, 133.0, 129.84, 129.80, 129.74, 129.72, 129.1, 129.0, 128.52, 128.39, 128.30, 128.29, 103.2, 70.4, 69.9, 69.7, 66.6, 61.0, 59.8, 40.5, 40.2, 33.67, 33.53, 20.9, 20.3, 17.0; HRMS (ESI) m/z calc for $\text{C}_{44}\text{H}_{45}\text{KNO}_{10}$ $[\text{M}+\text{K}]^+$ 774.2675; found, 774.2659.

6. References

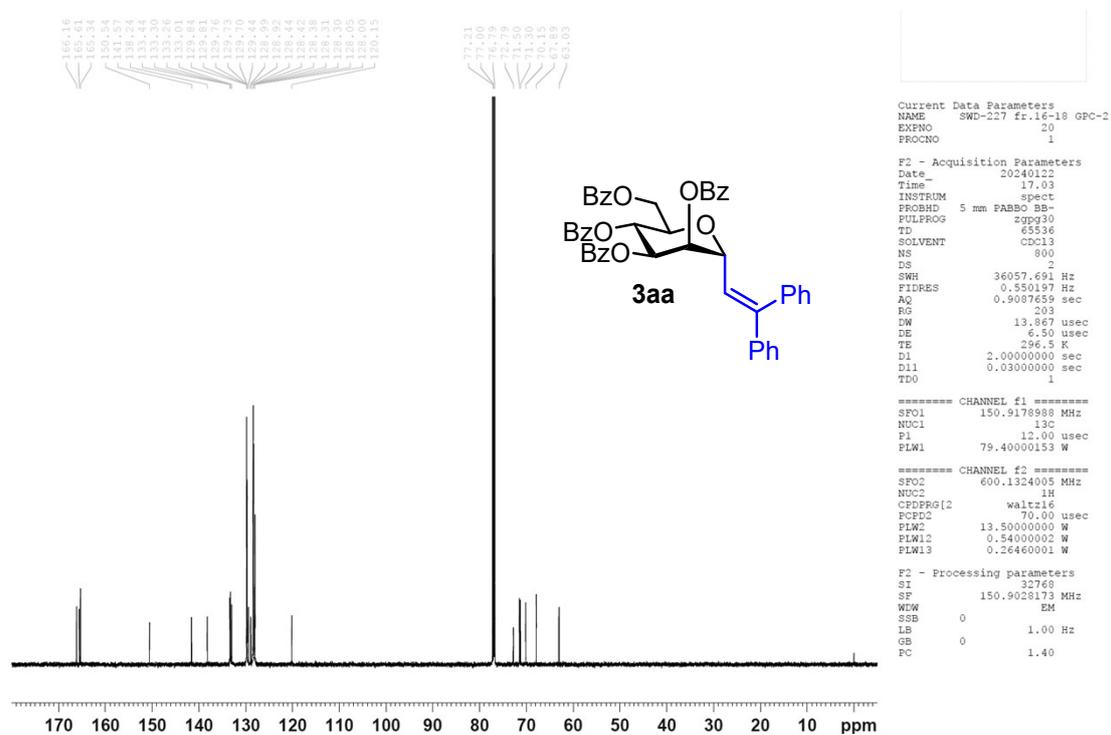
1. L. M. Doyle, S. O'Sullivan, C. Di Sarvo, M. McKinney, P. McArdle, P. V. Murphy, *Org. Lett.* **2017**, *19*, 5802.
2. S. Alazet, F. Le Vaillant, S. Nicolai, T. Courant, J. Waser, *Chem. Eur. J.* **2017**, *40*, 9501.

7. ¹H, ¹³C, and ¹⁹F NMR spectra

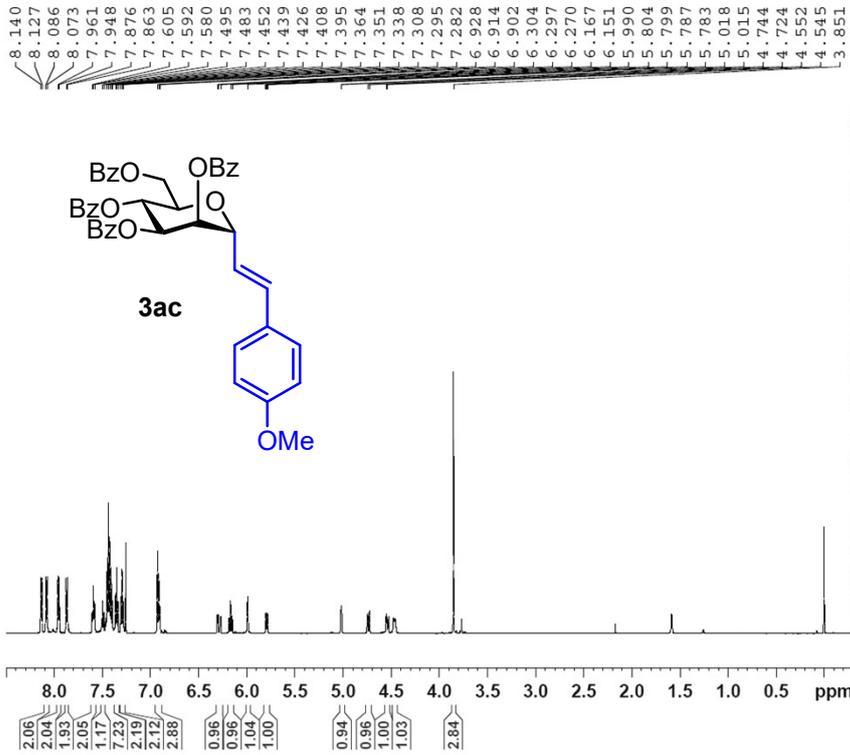
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¹³C NMR spectra 3aa



¹H NMR spectra 3ac



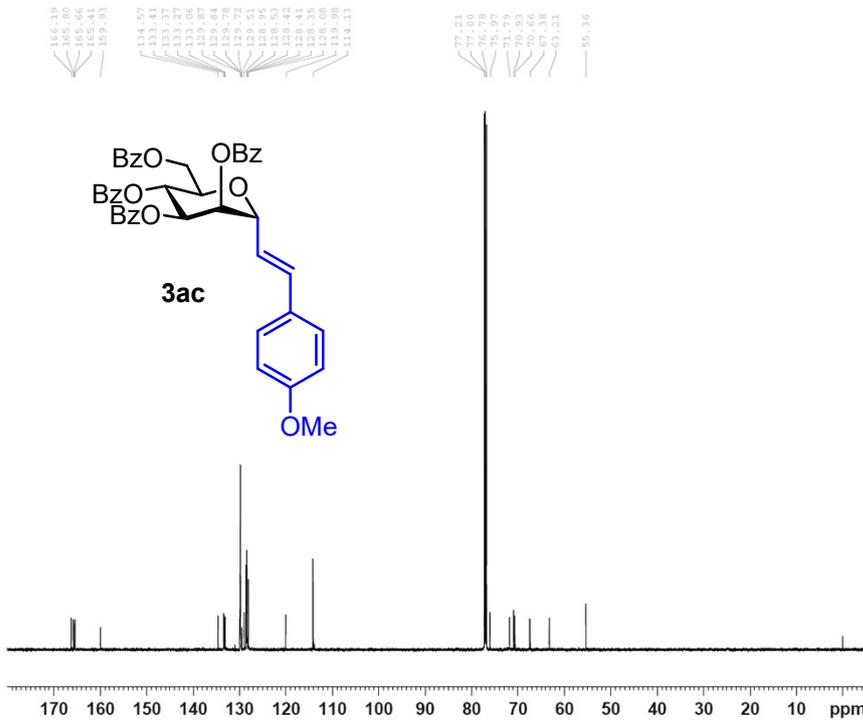
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¹³C NMR spectra 3ac



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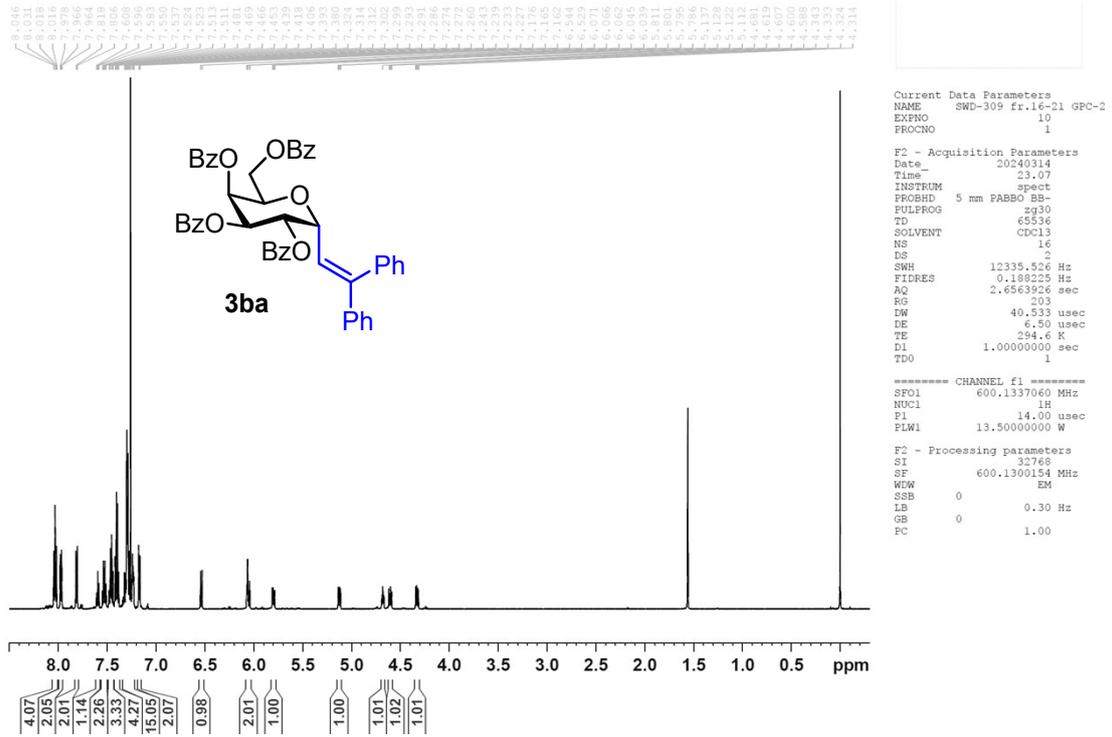
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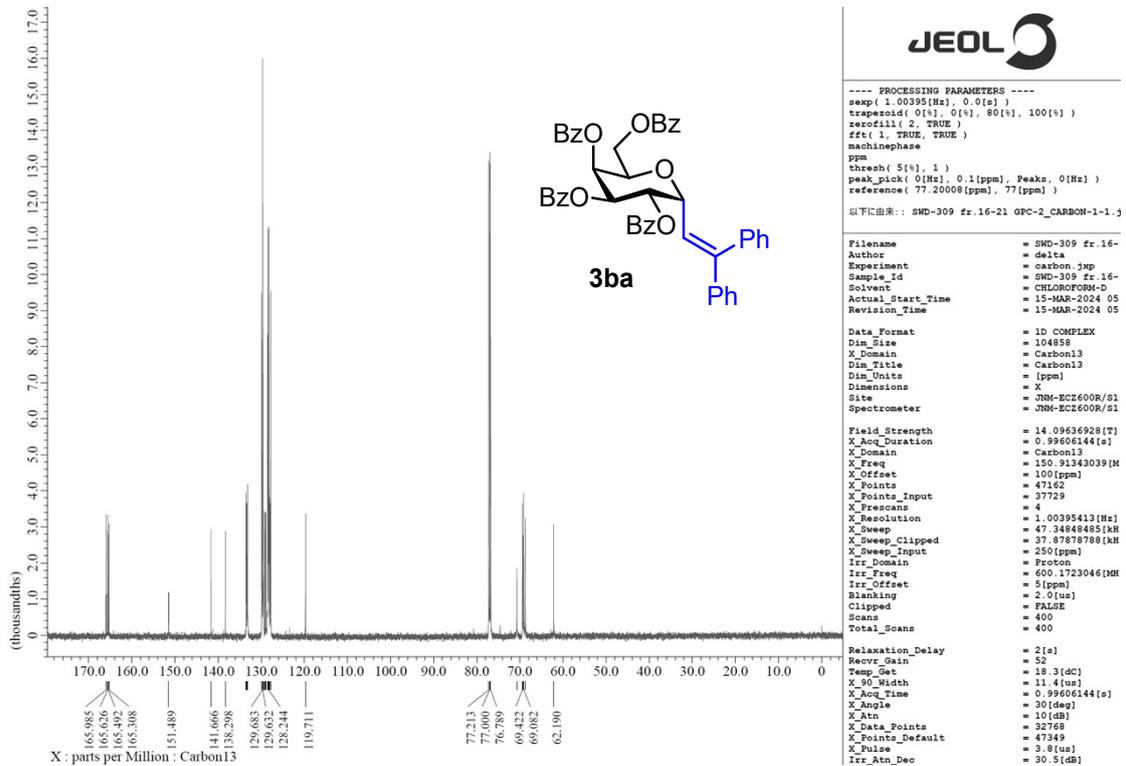
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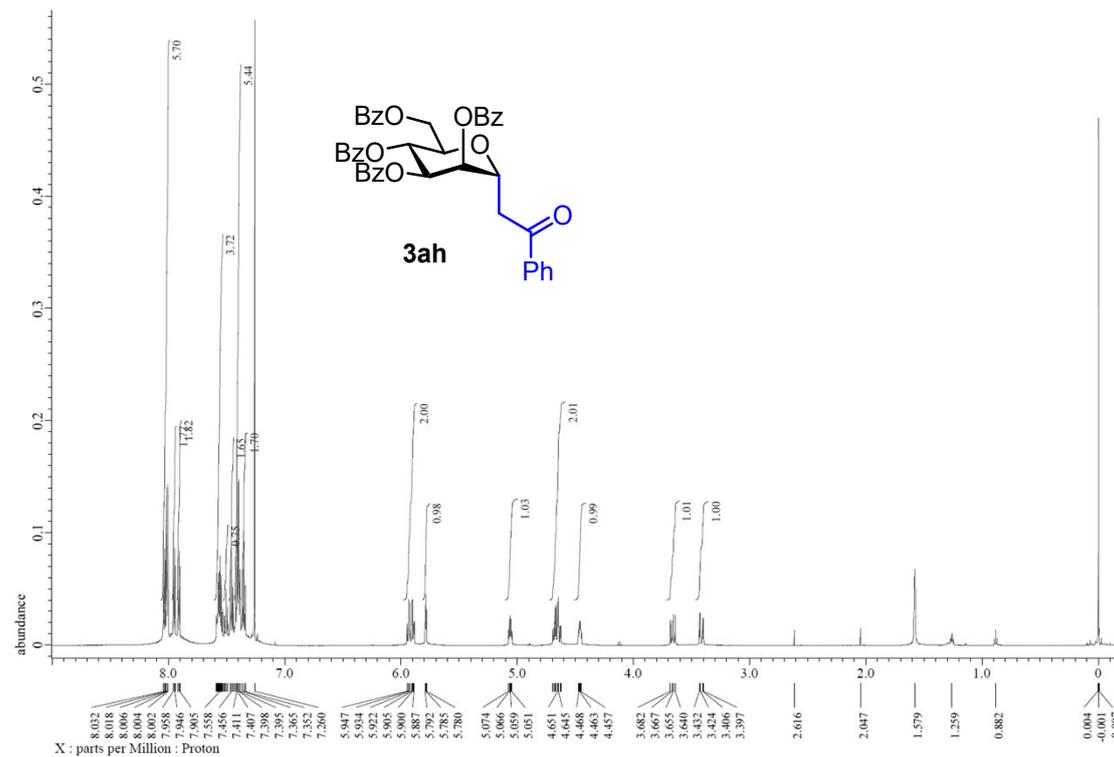
¹H NMR spectra 3ba



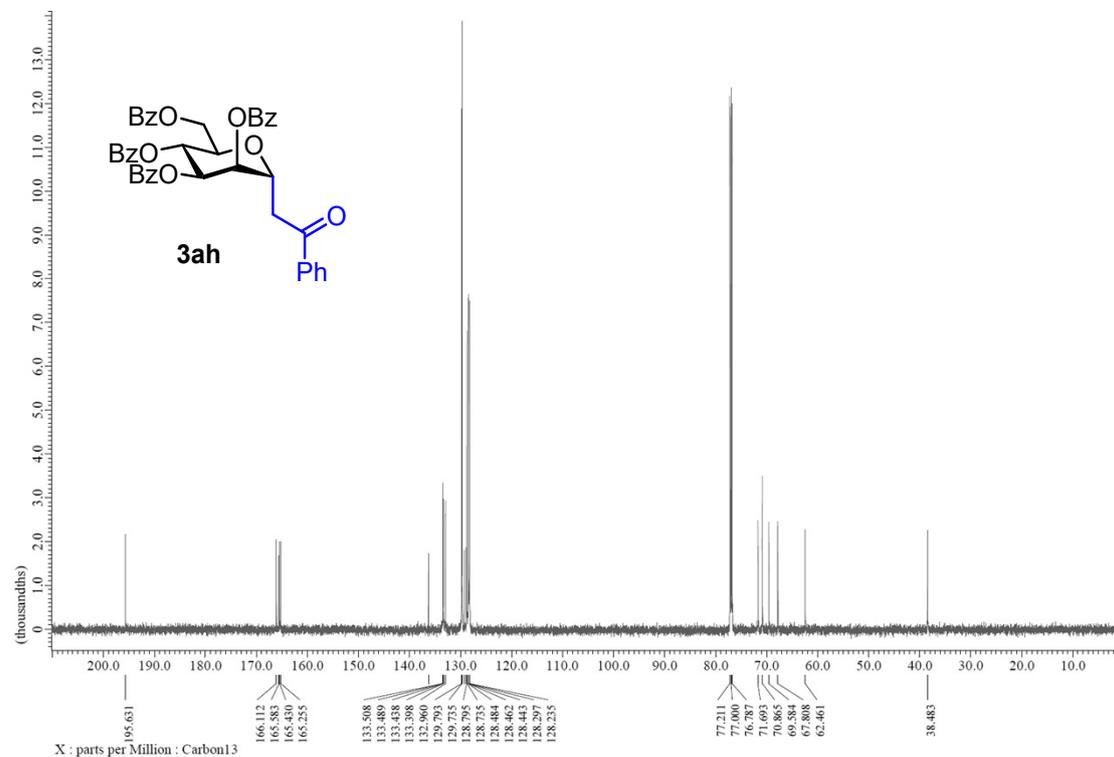
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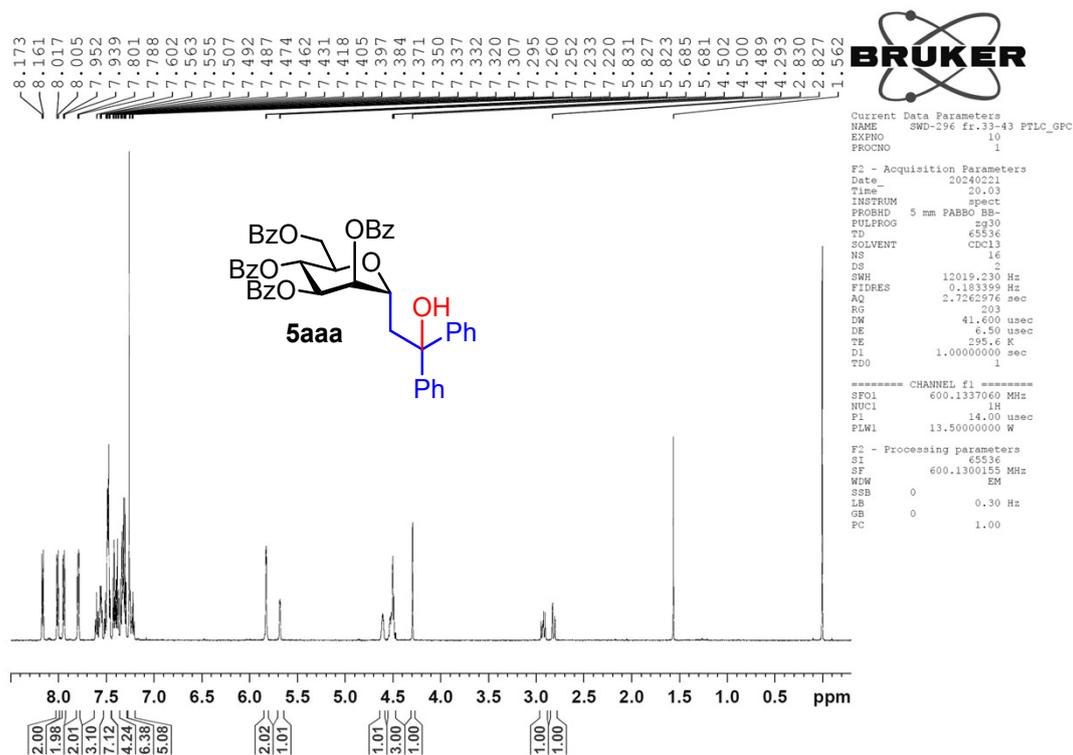
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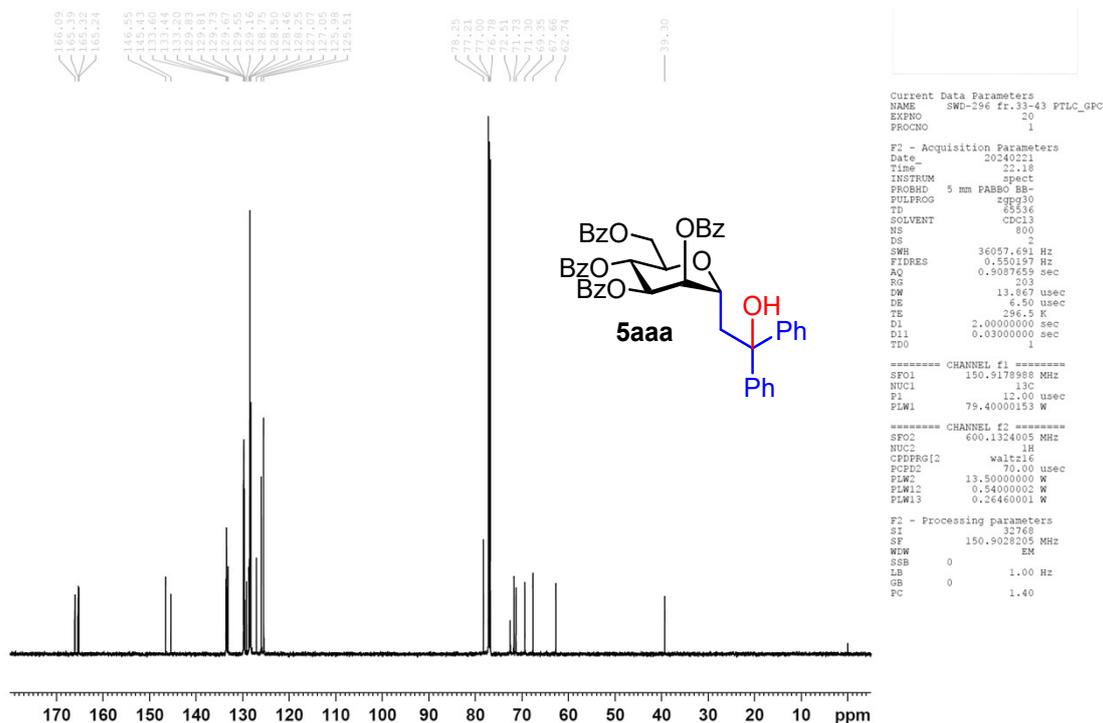
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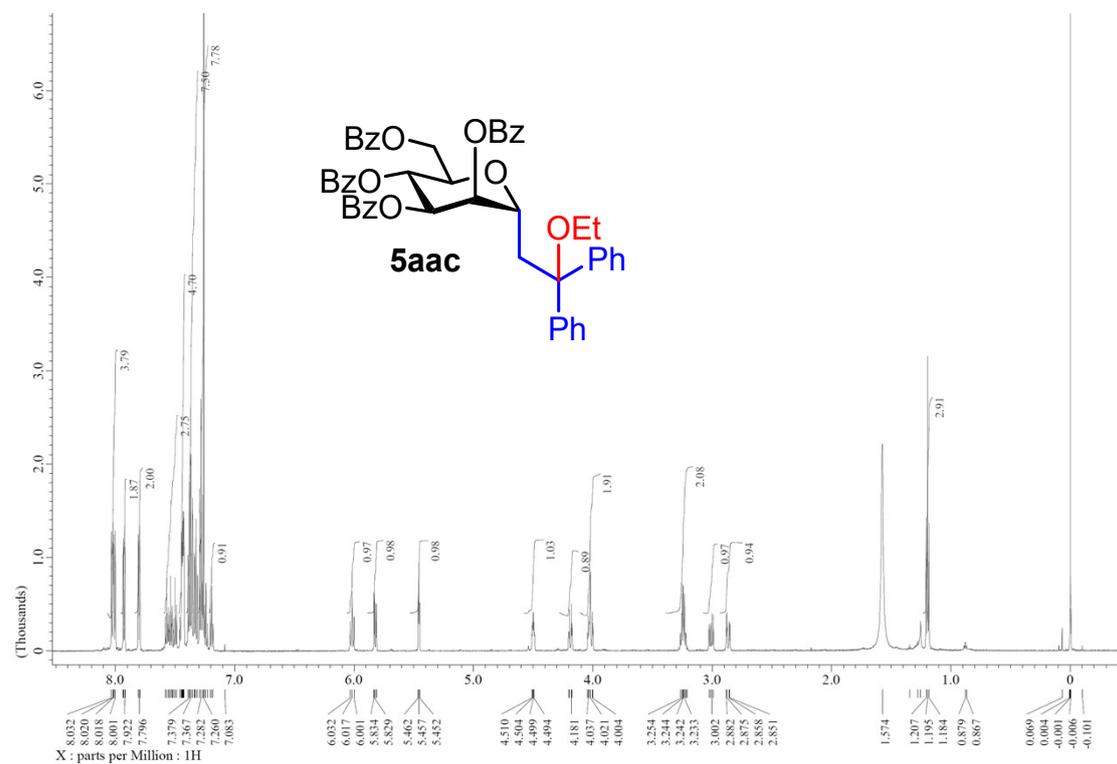
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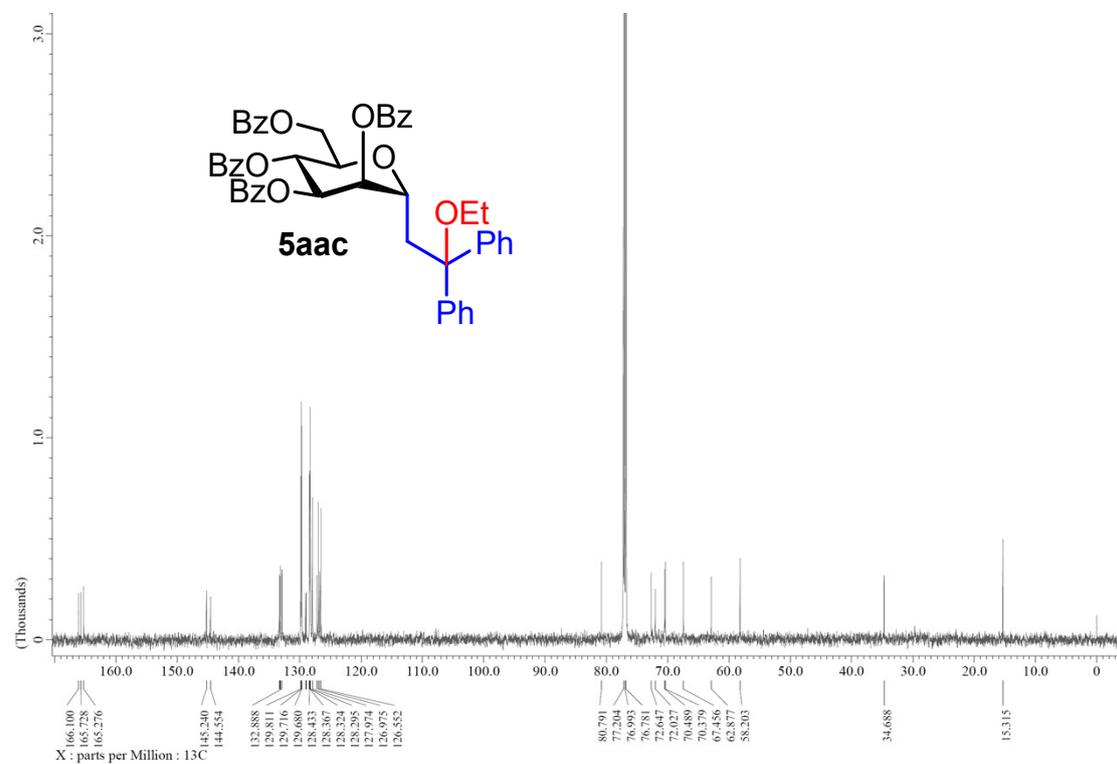
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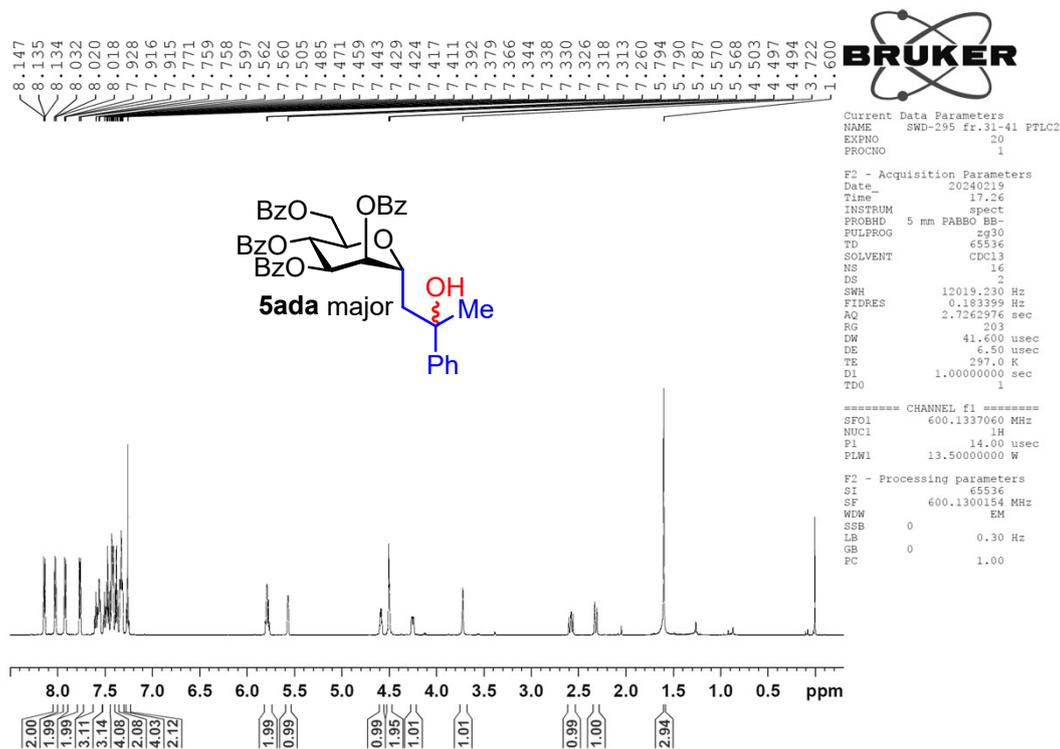
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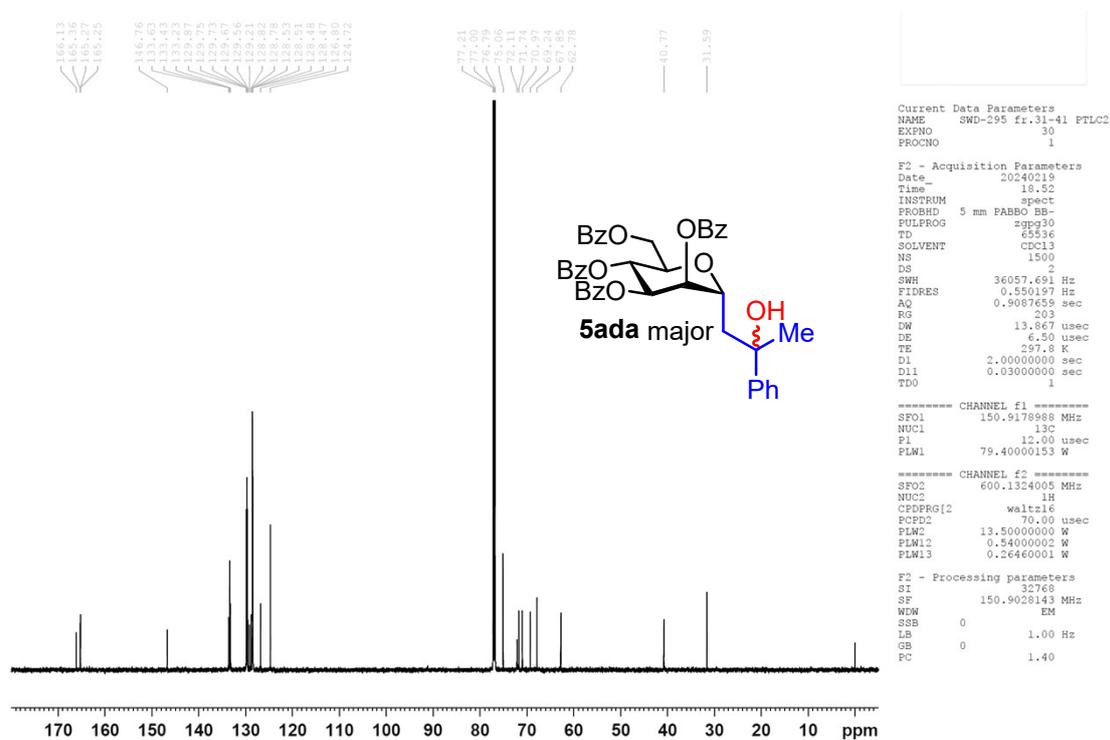
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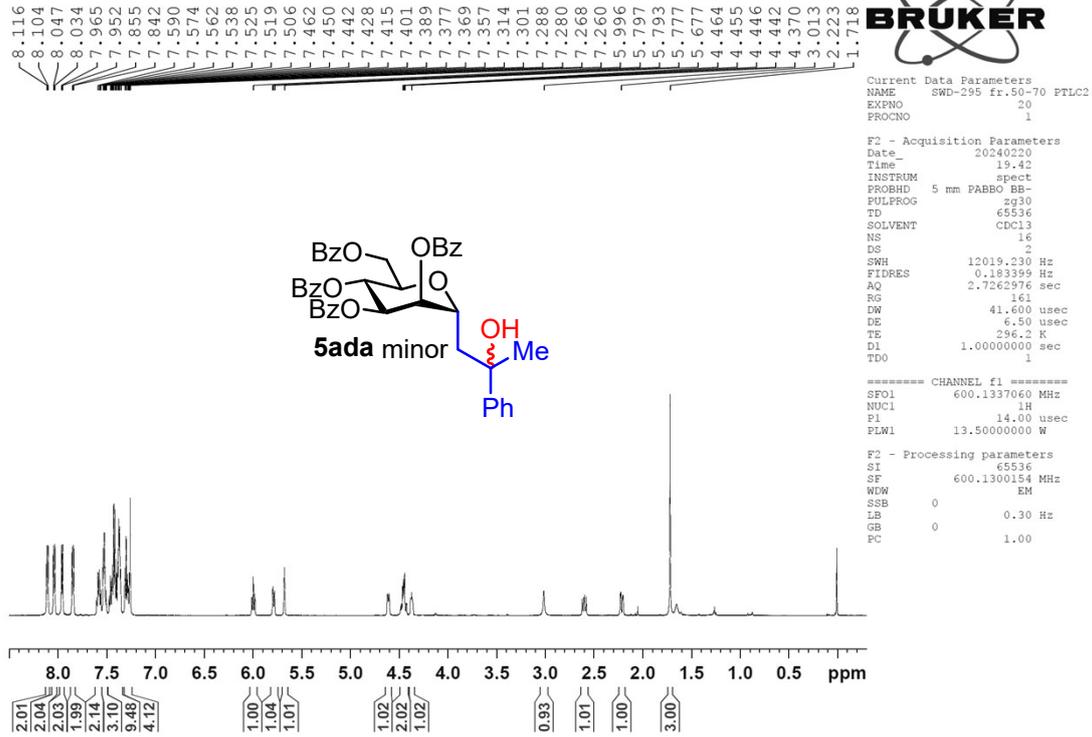
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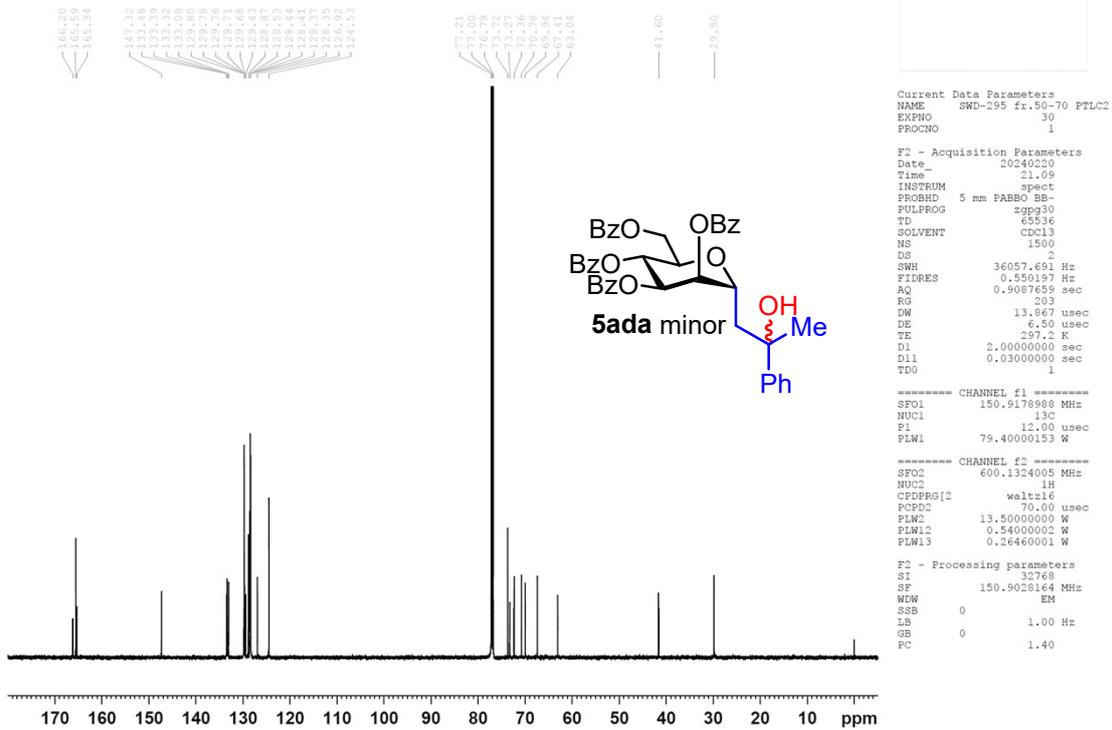
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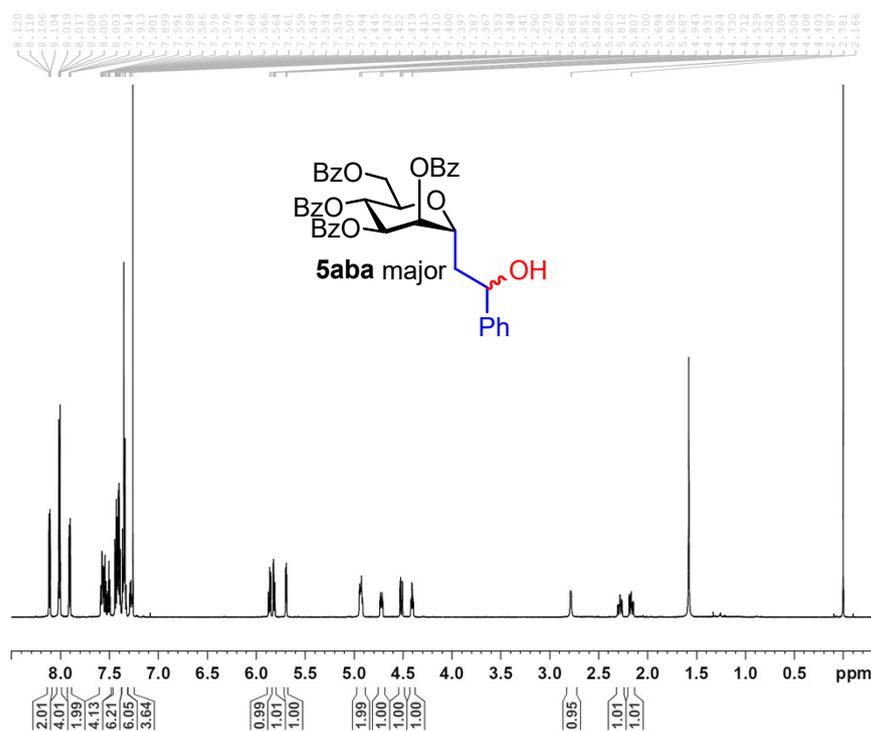
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¹³C NMR spectra **5ada minor**



¹H NMR spectra **5aba major**



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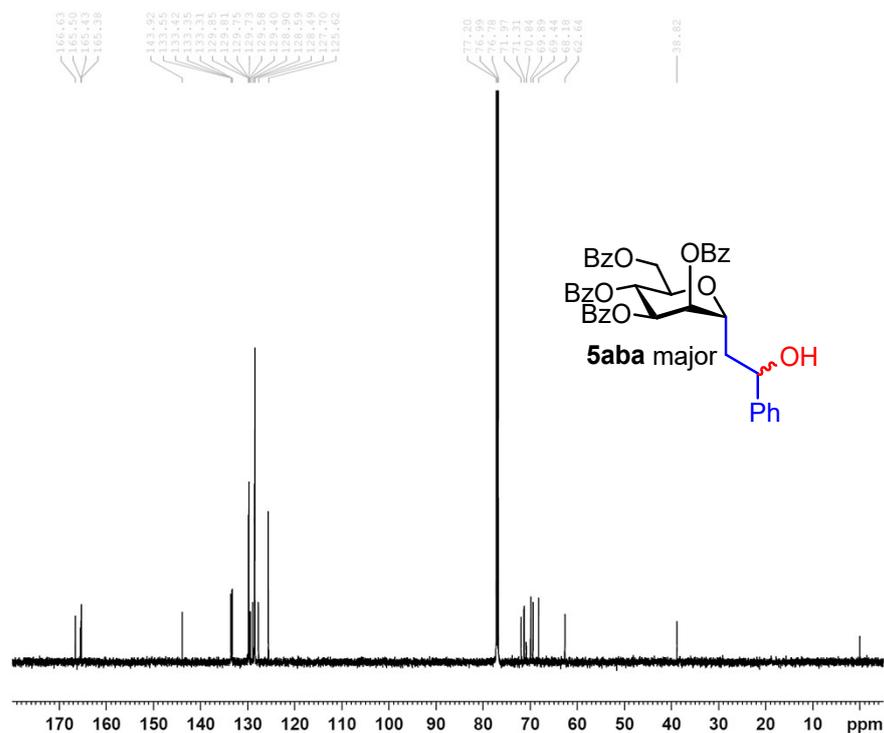
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¹³C NMR spectra **5aba major**



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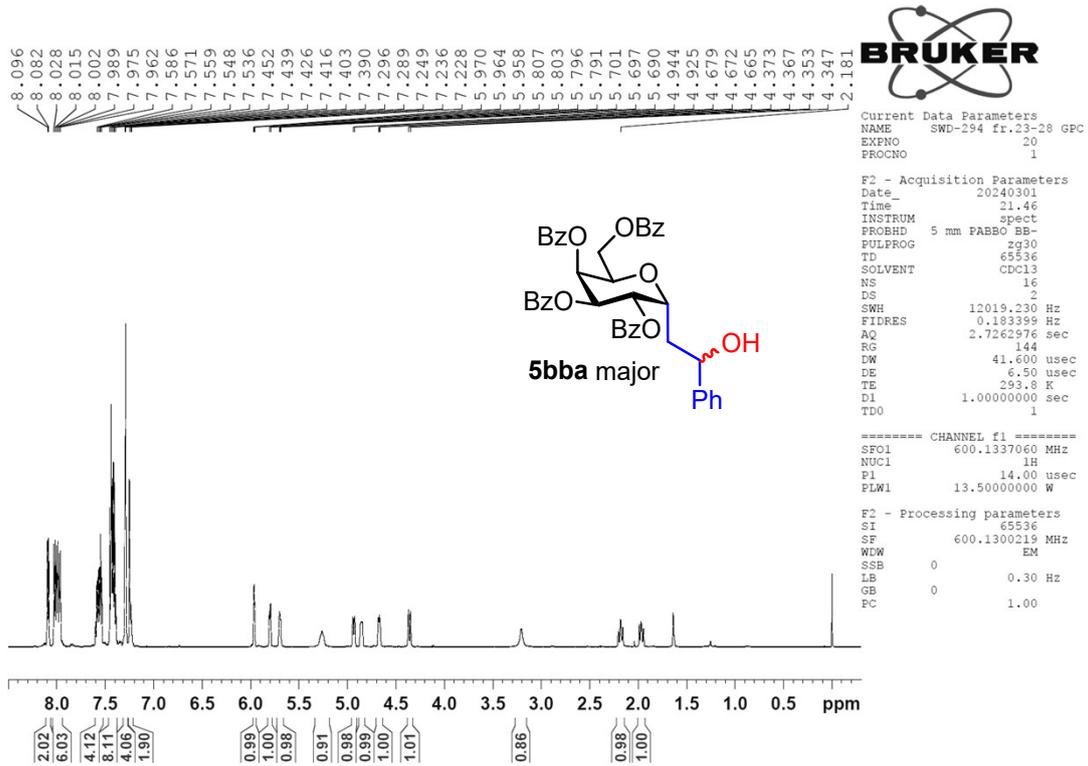
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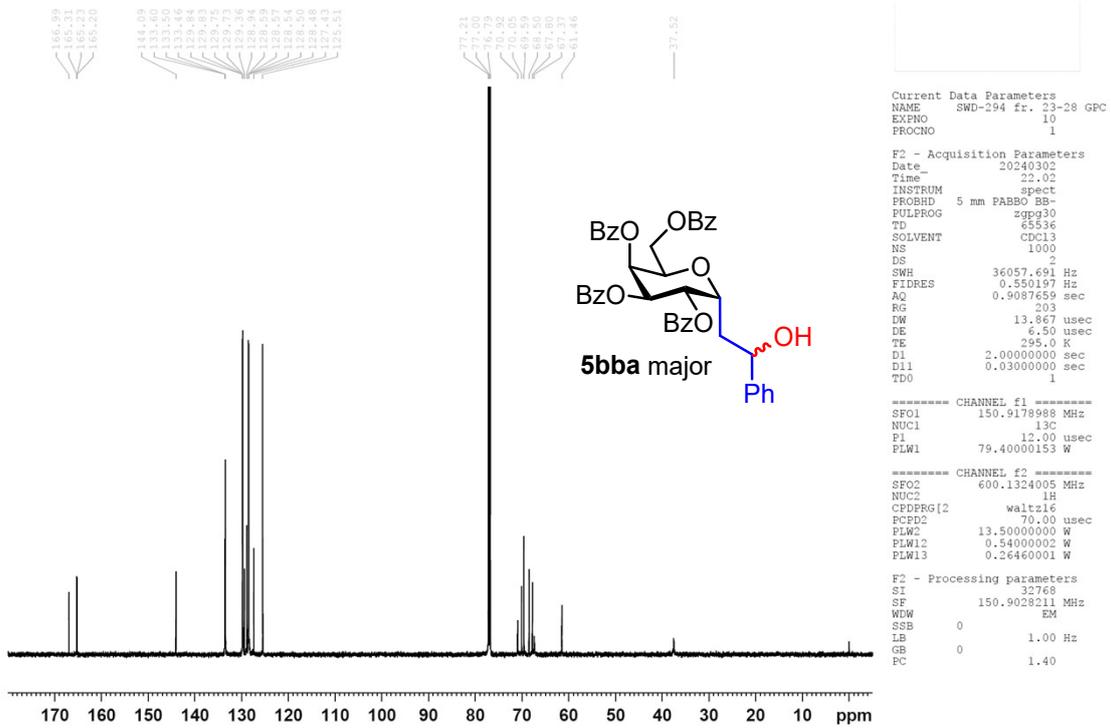
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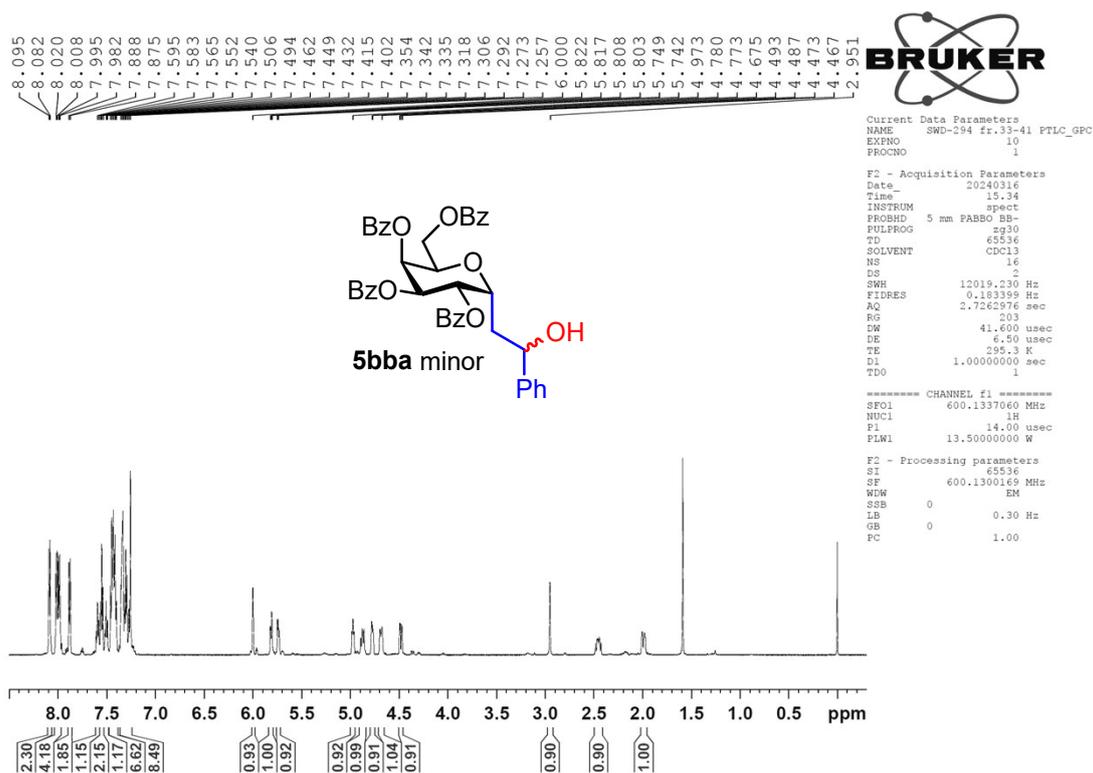

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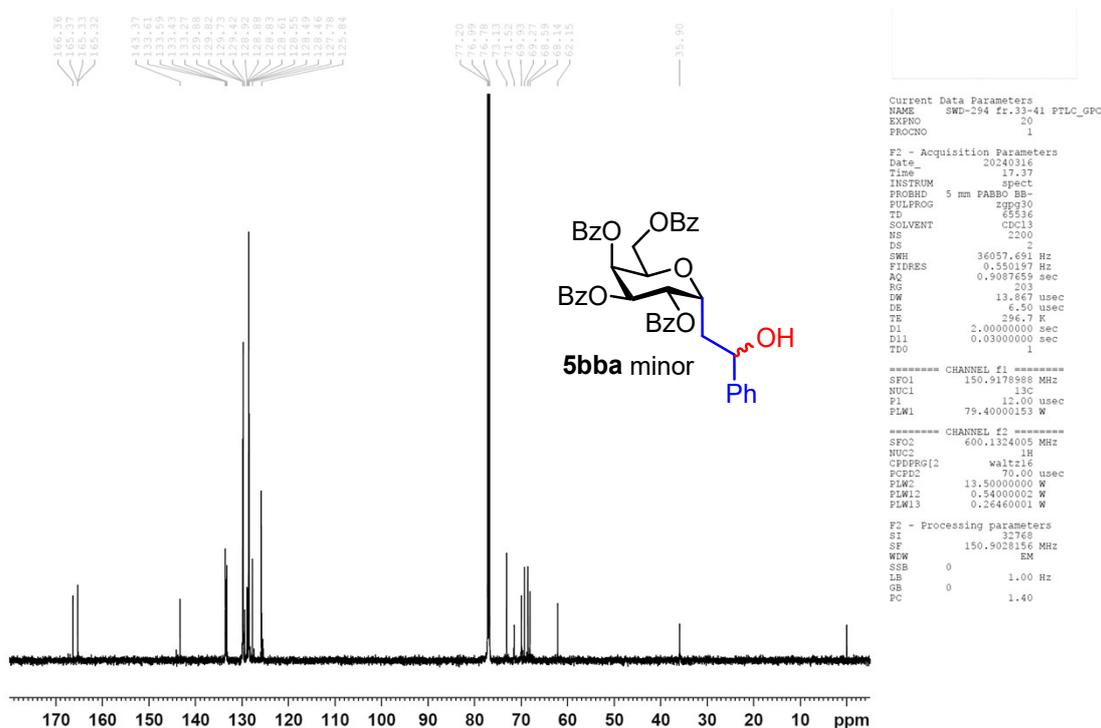
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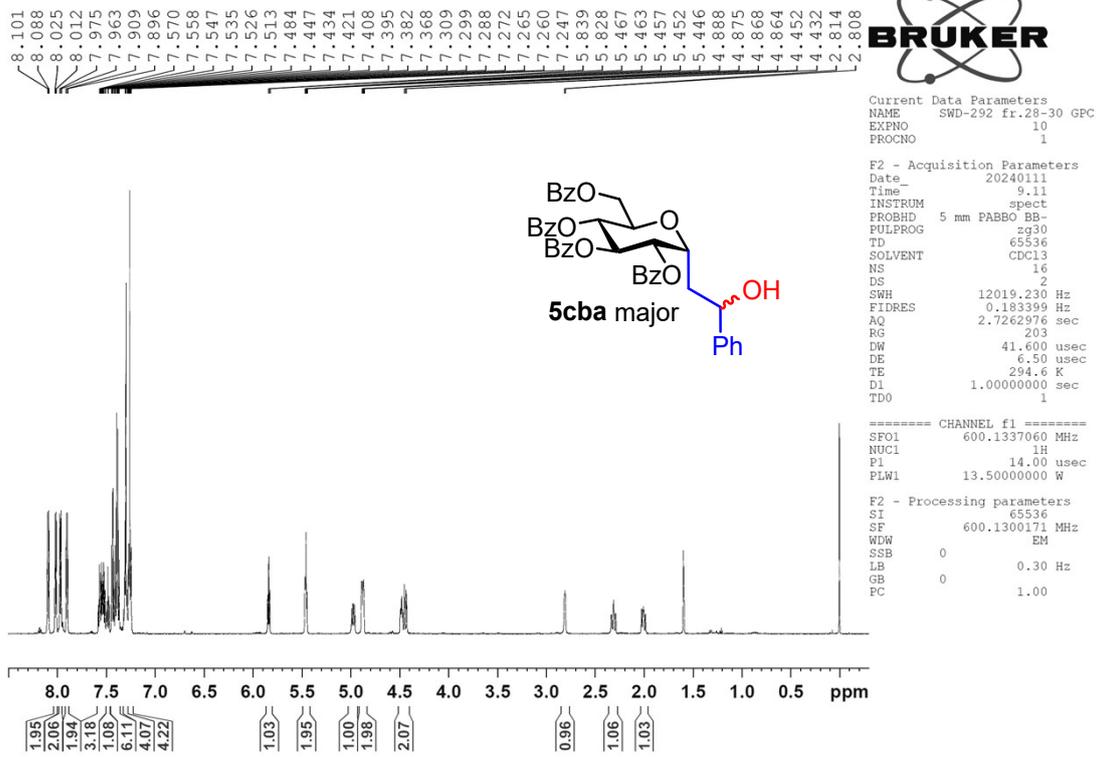
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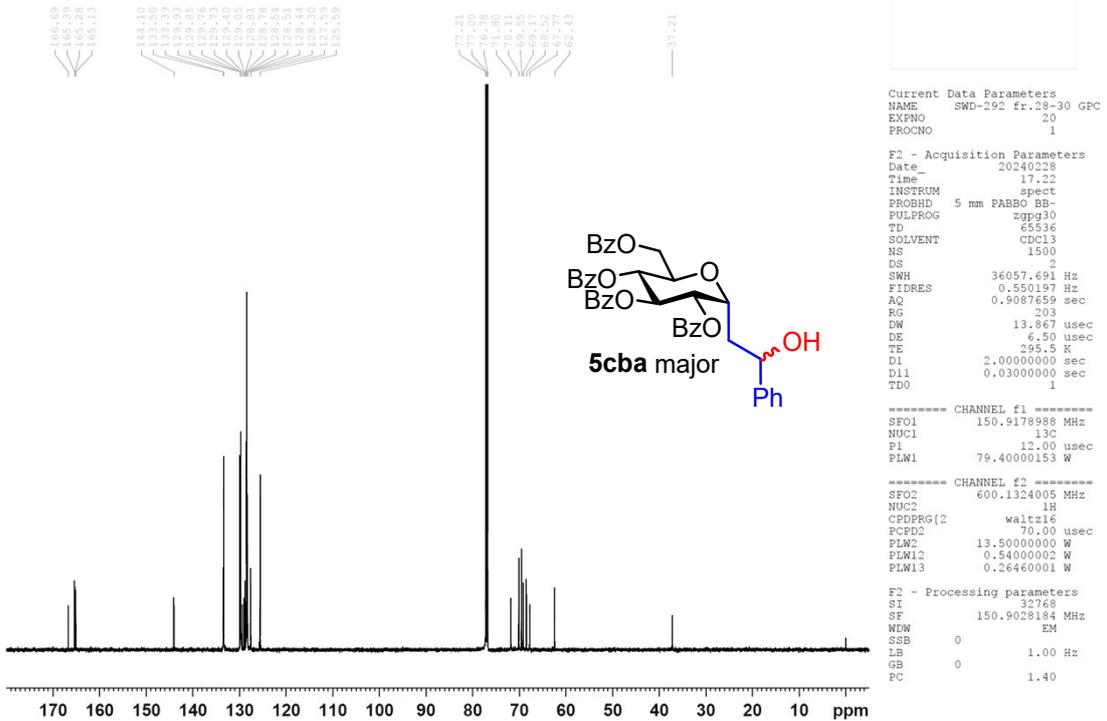
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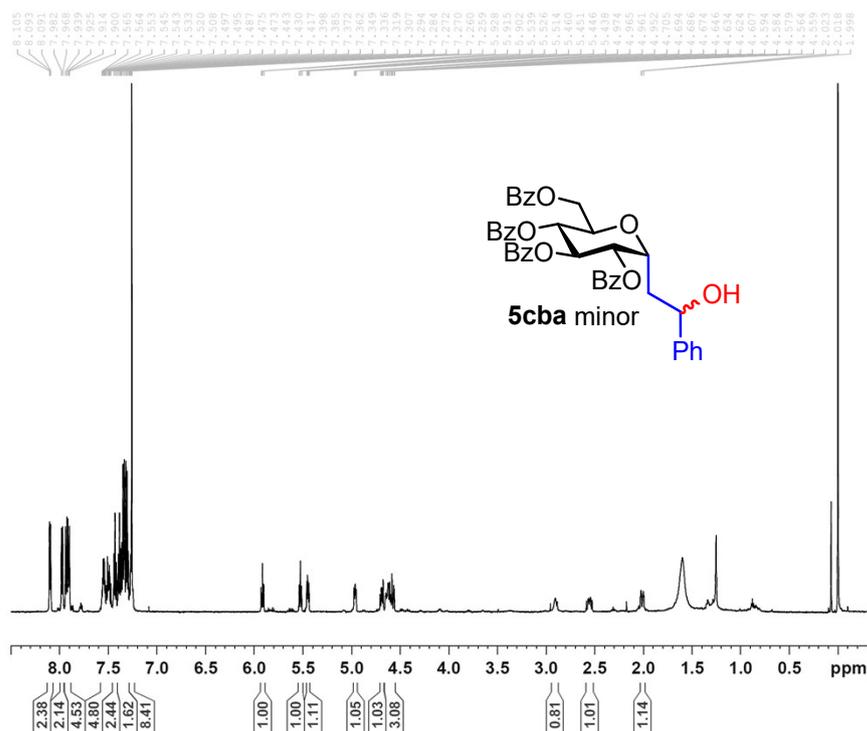
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¹³C NMR spectra **5cba** major



¹H NMR spectra **5cba** minor



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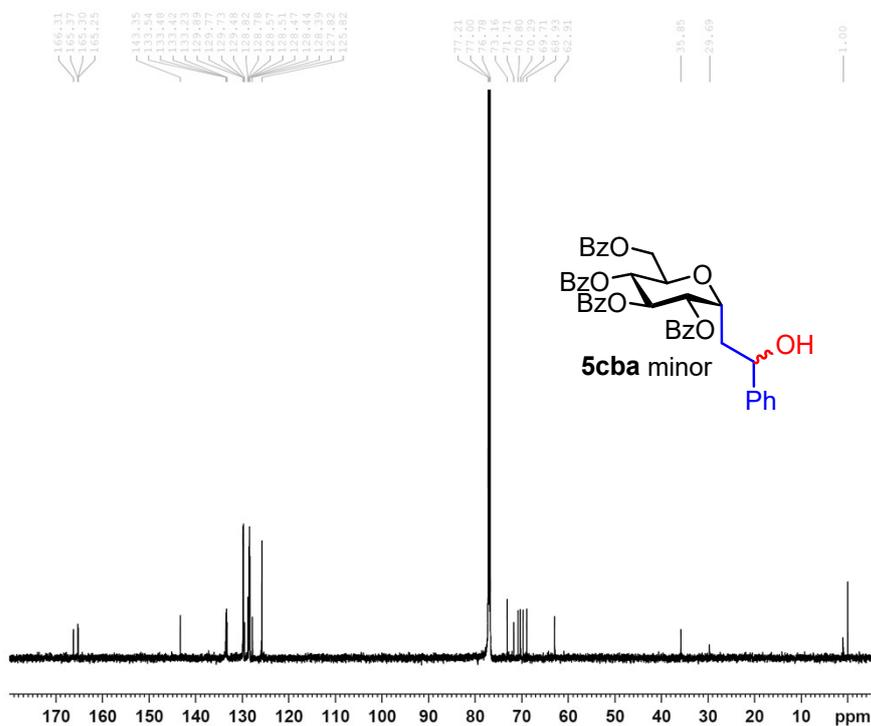
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TE 294.6 K
D1 1.00000000 sec
TD0 1

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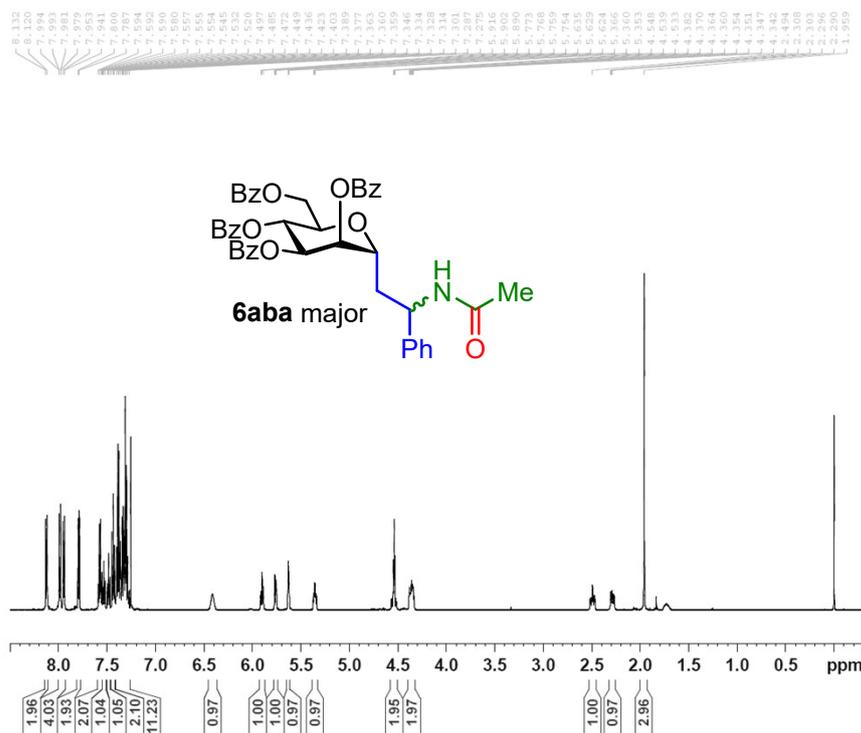
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PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 10000
DS 2
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9087659 sec
RG 203
DW 13.867 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 150.9178988 MHz
NUC1 13C
P1 12.00 usec
PLW1 79.40000153 W

===== CHANNEL f2 =====
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 70.00 usec
PLW2 13.50000000 W
PLW12 0.54000002 W
PLW13 0.26460001 W

F2 - Processing parameters
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SF 150.9028132 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
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¹H NMR spectra **6aba-major**



```

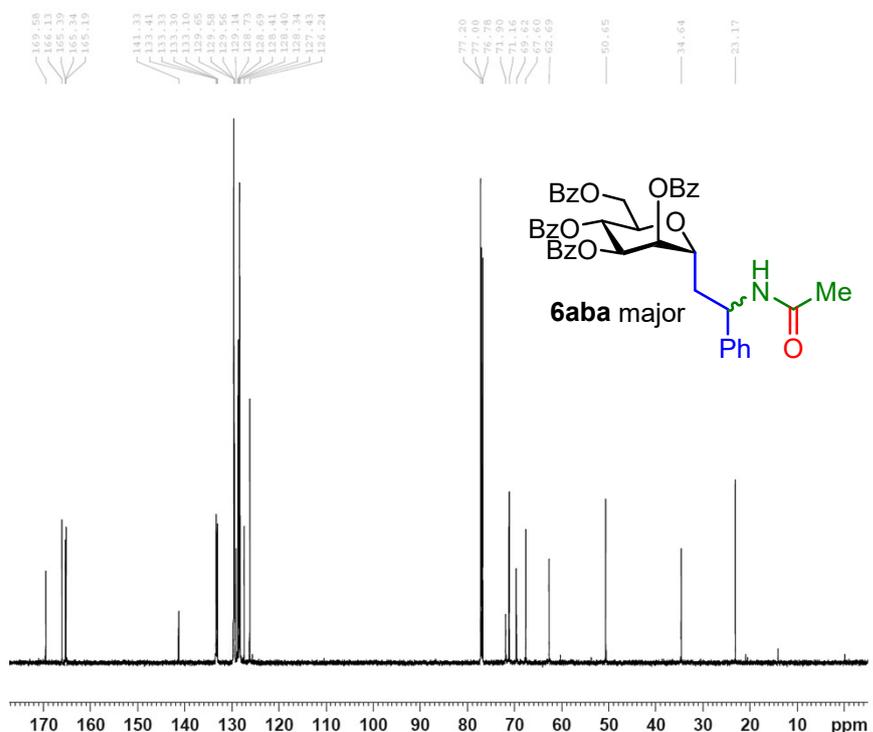
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NAME      HIT-38 major GPC
EXPNO    30
PROCNO   1

F2 - Acquisition Parameters
Date_    20240122
Time     9.03
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      12335.526 Hz
FIDRES   0.188225 Hz
AQ       2.6563926 sec
RG       203
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TD0      1

----- CHANNEL f1 -----
SFO1    600.1337060 MHz
NUC1     1H
P1       14.00 usec
PLW1     13.50000000 W

F2 - Processing parameters
SI       32768
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SSB      0
LB       0.30 Hz
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¹³C NMR spectra **6aba-major**



```

Current Data Parameters
NAME      HIT-38 major GPC
EXPNO    20
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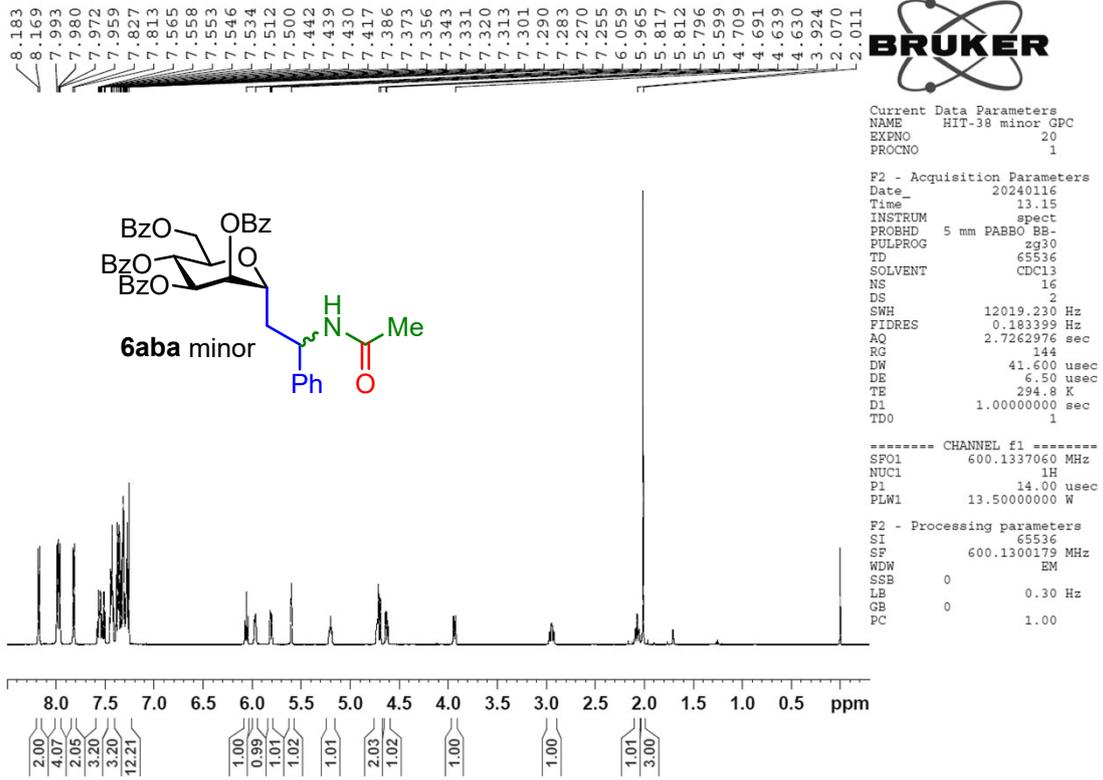
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Time     13.21
INSTRUM  spect
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PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       400
DS       2
SWH      36057.691 Hz
FIDRES   0.550197 Hz
AQ       0.9087659 sec
RG       203
DW       13.867 usec
DE       6.50 usec
TE       296.1 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0      1

----- CHANNEL f1 -----
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NUC1     13C
P1       12.00 usec
PLW1     79.40000153 W

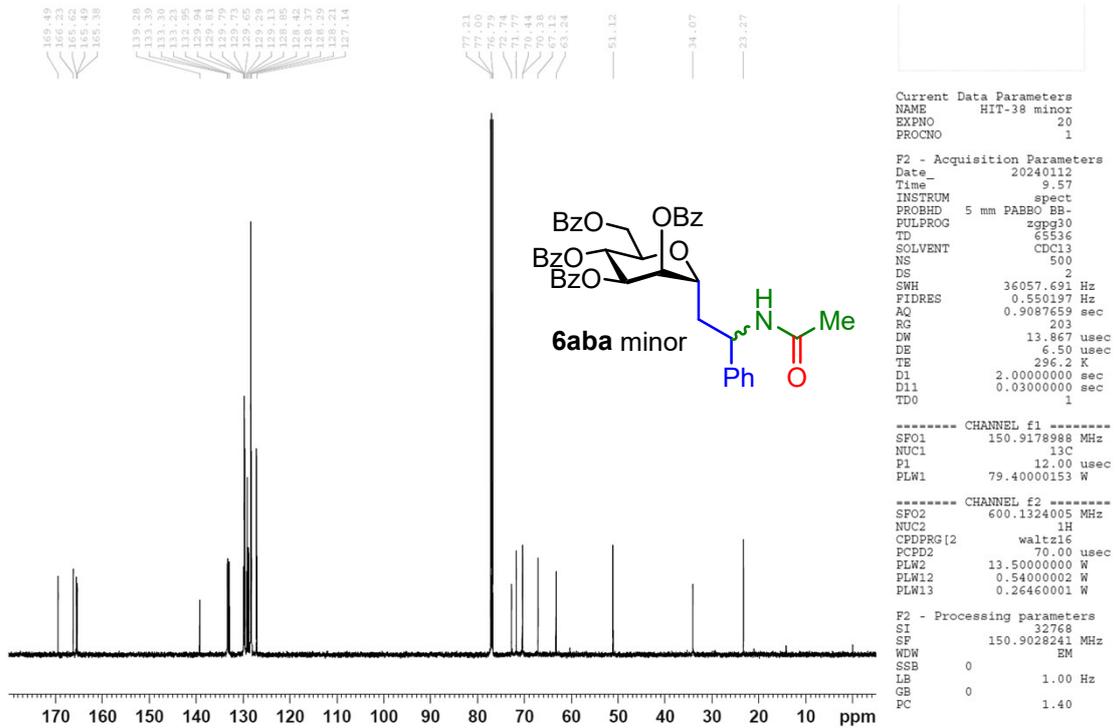
----- CHANNEL f2 -----
SFO2    600.1324005 MHz
NUC2     1H
CPDPRG2  waltz16
PCPD2    70.00 usec
PLW2     13.50000000 W
PLW12    0.54000002 W
PLW13    0.26460001 W

F2 - Processing parameters
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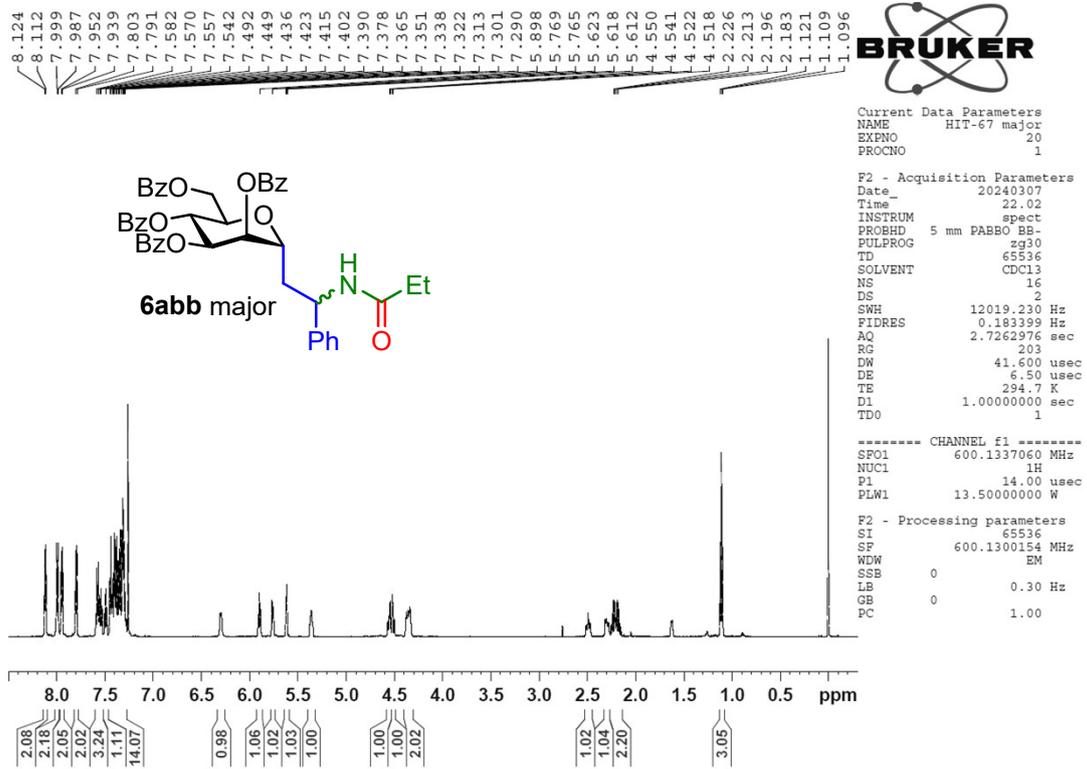
¹H NMR spectra **6aba-minor**



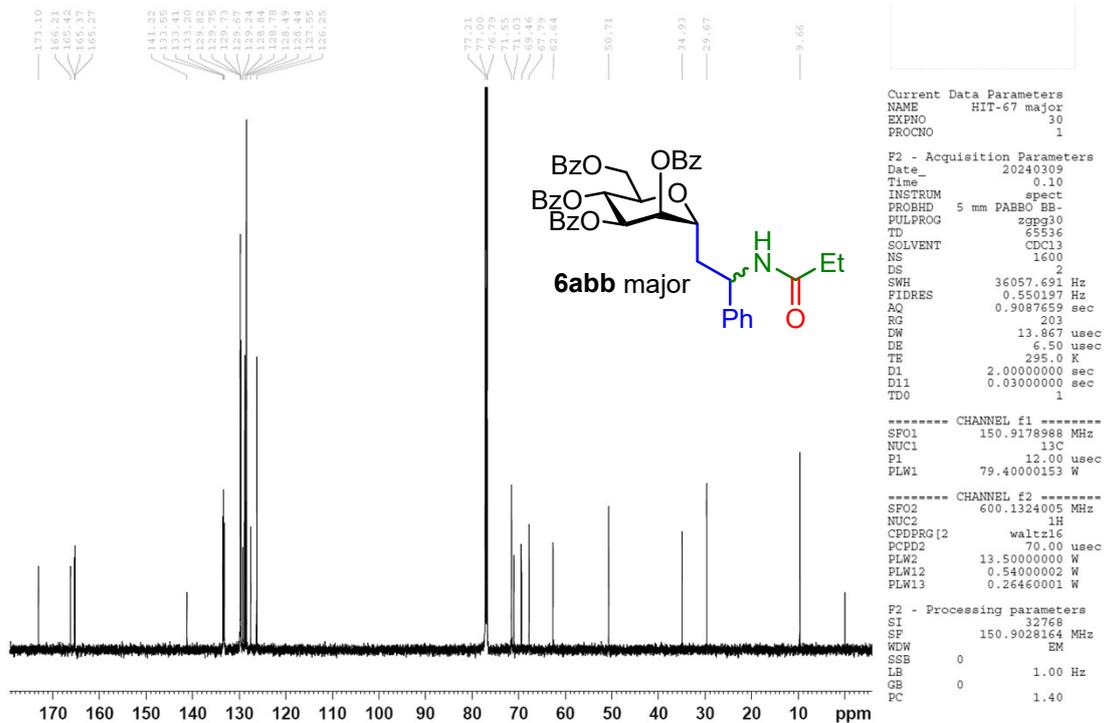
¹³C NMR spectra **6aba-minor**



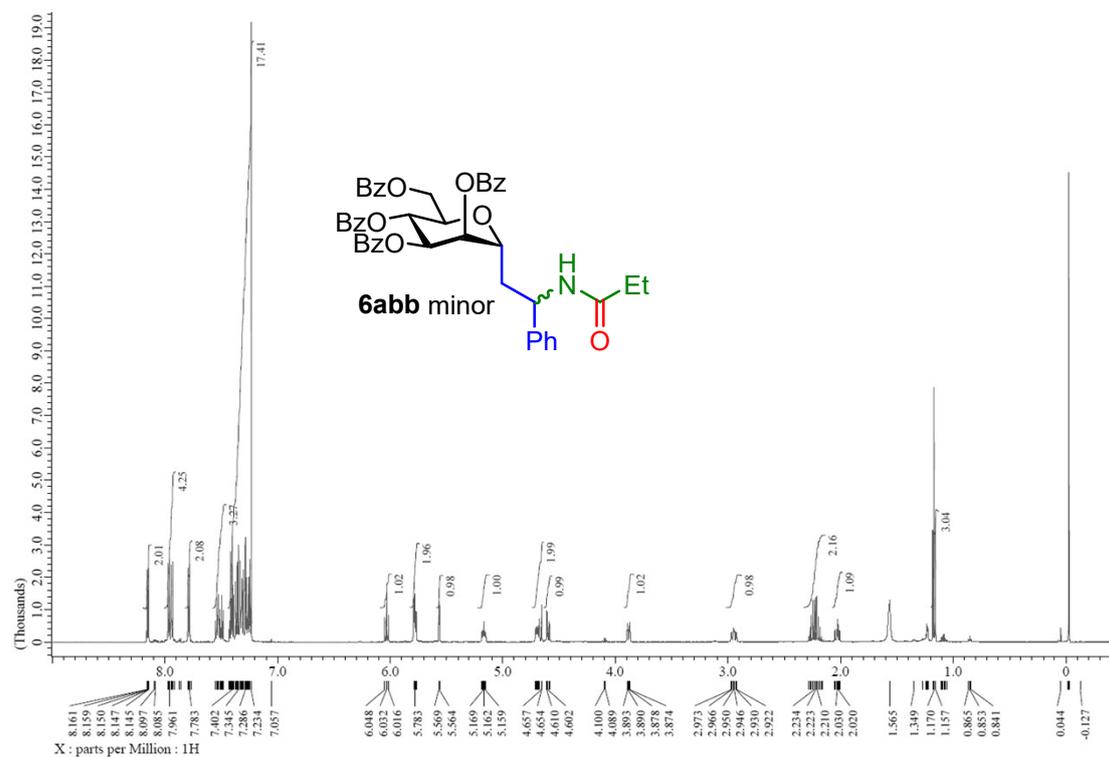
¹H NMR spectra **6abb major**



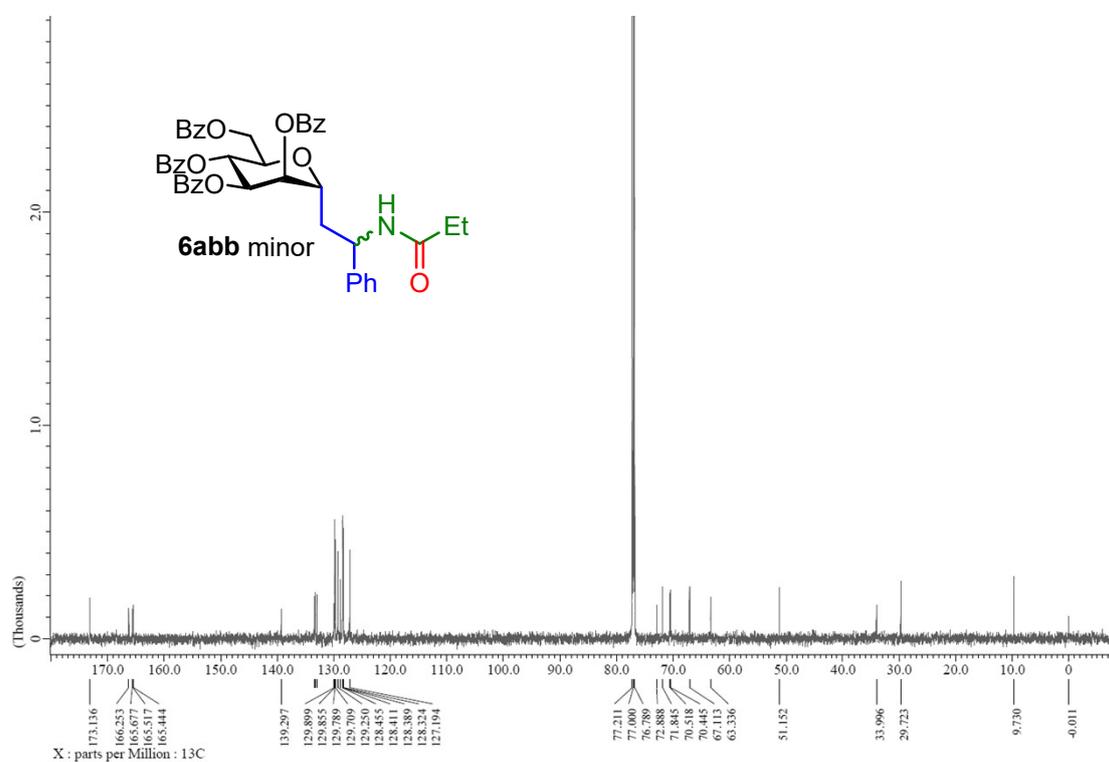
¹³C NMR spectra **6abb major**



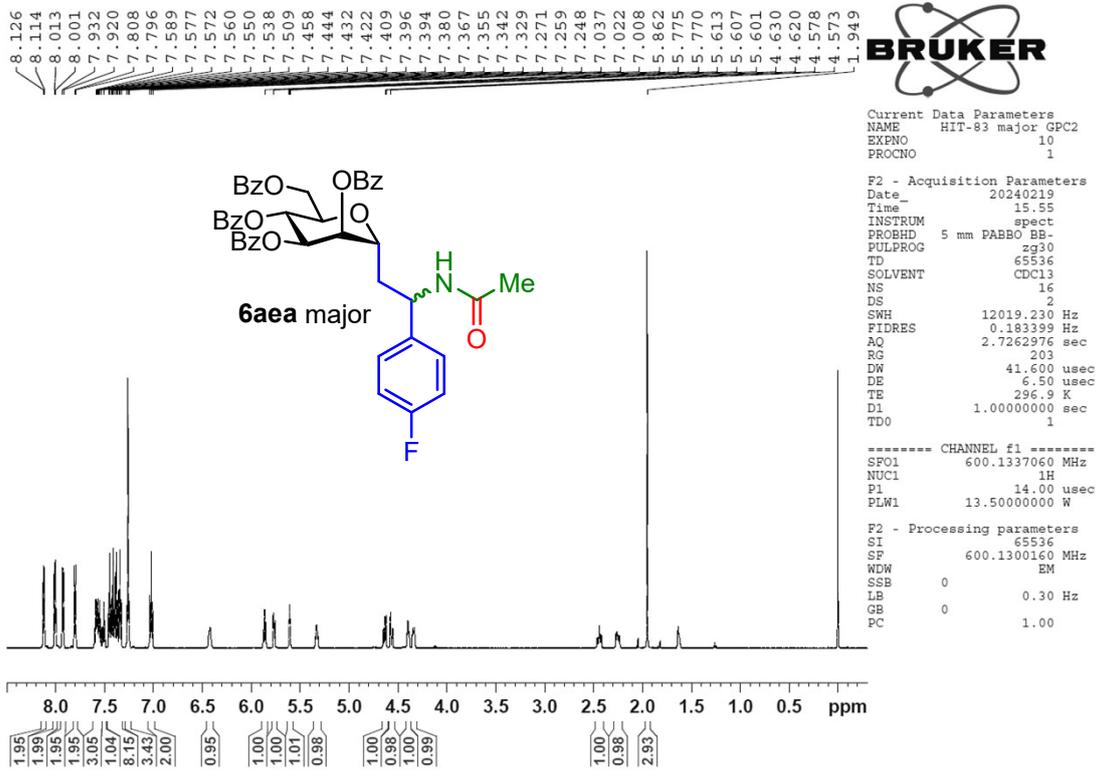
¹H NMR spectra **6abb** minor



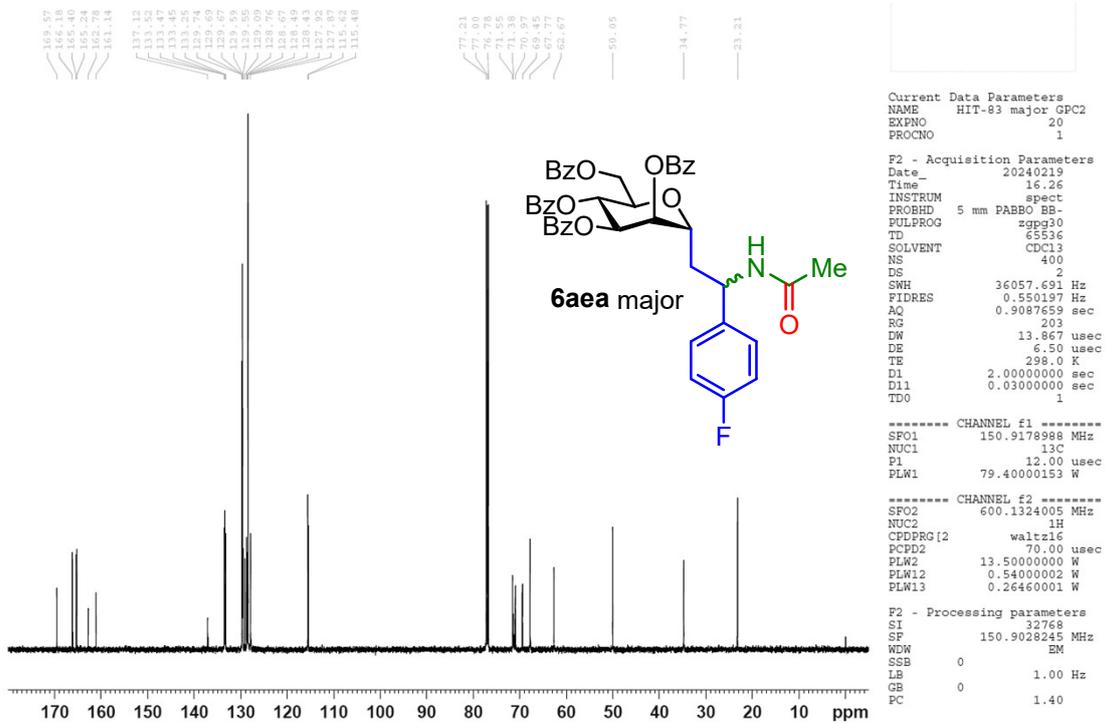
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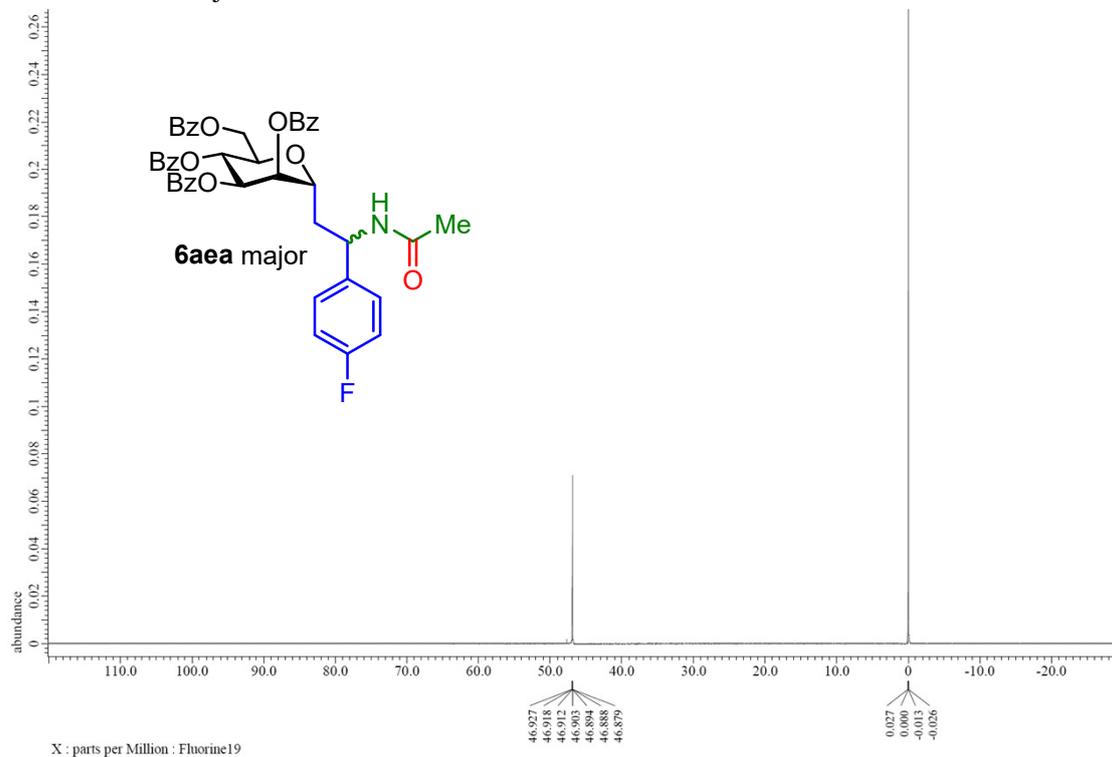
¹H NMR spectra **6aea major**



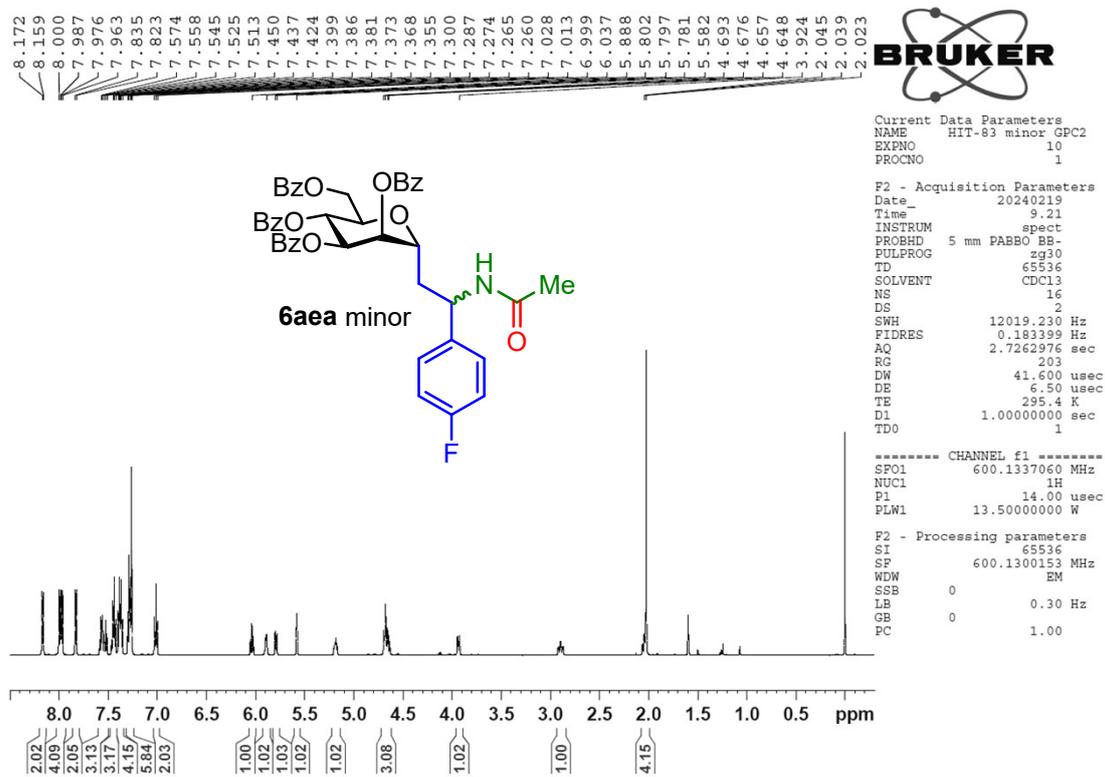
¹³C NMR spectra **6aea major**



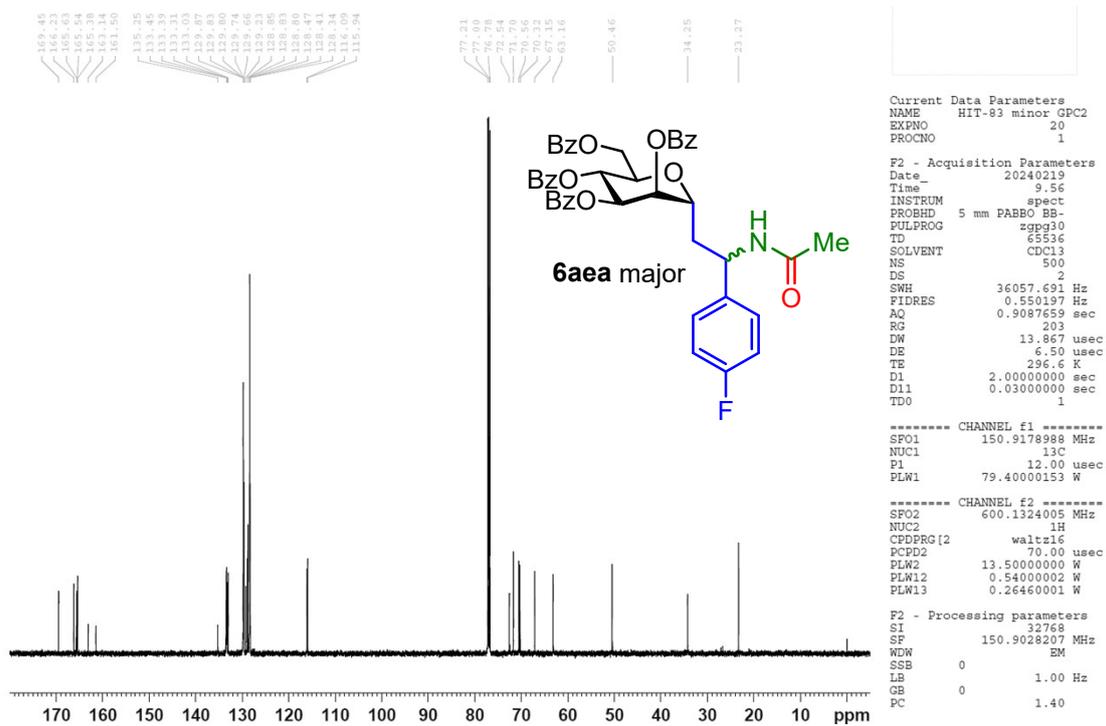
¹⁹F NMR 6aea major



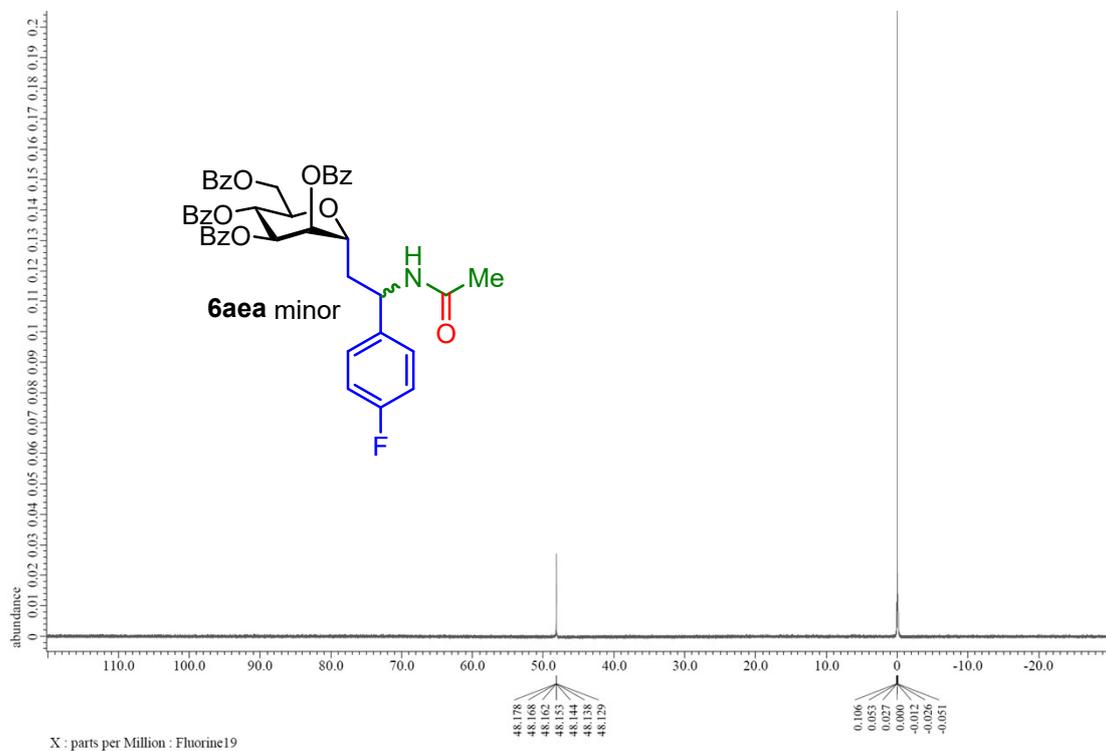
¹H NMR spectra 6aea minor



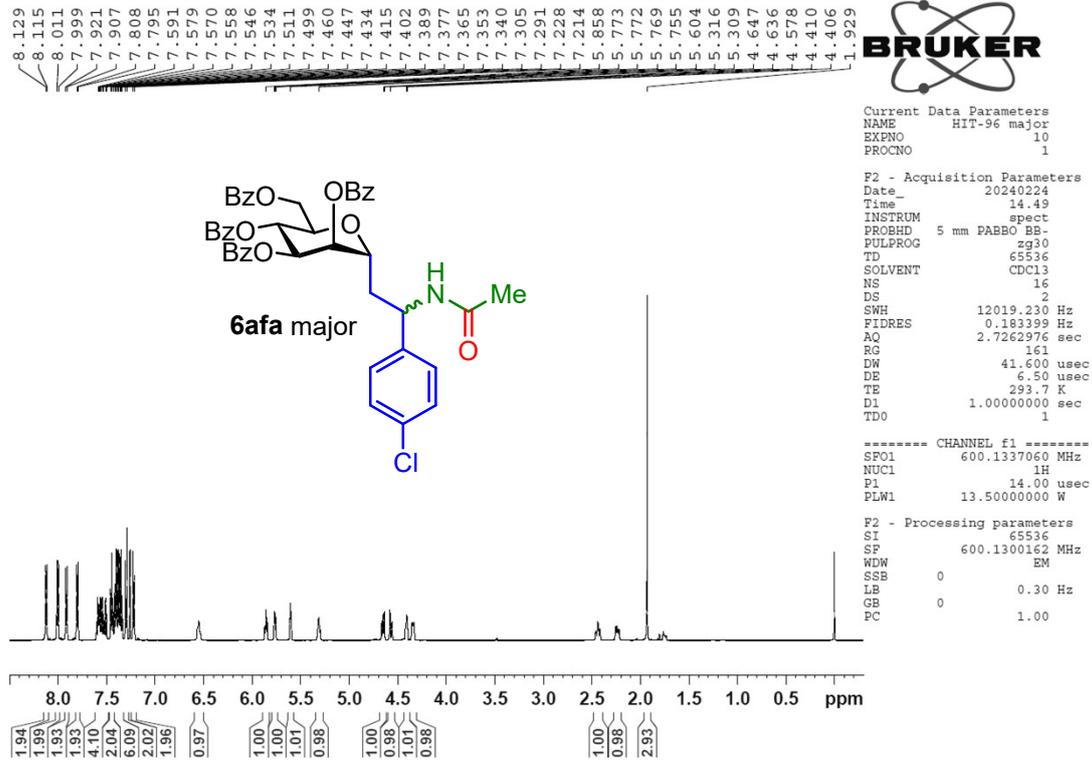
¹³C NMR spectra **6aea minor**



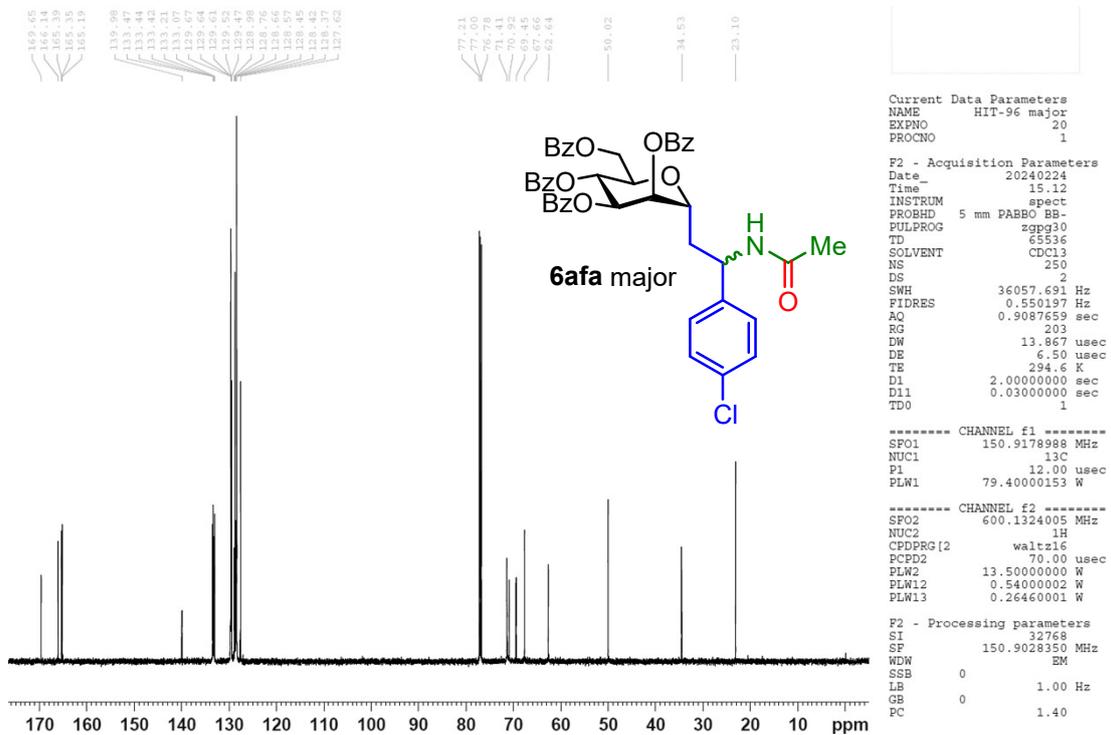
¹⁹F NMR **6aea minor**



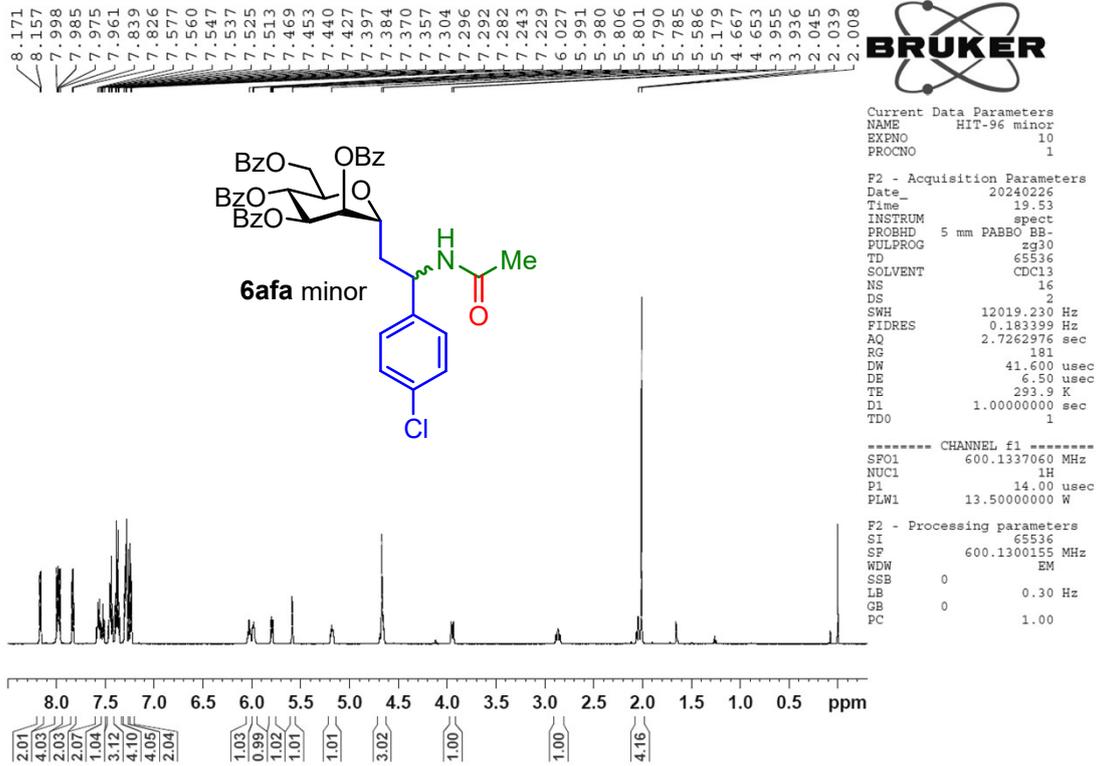
¹H NMR spectra **6afa** major



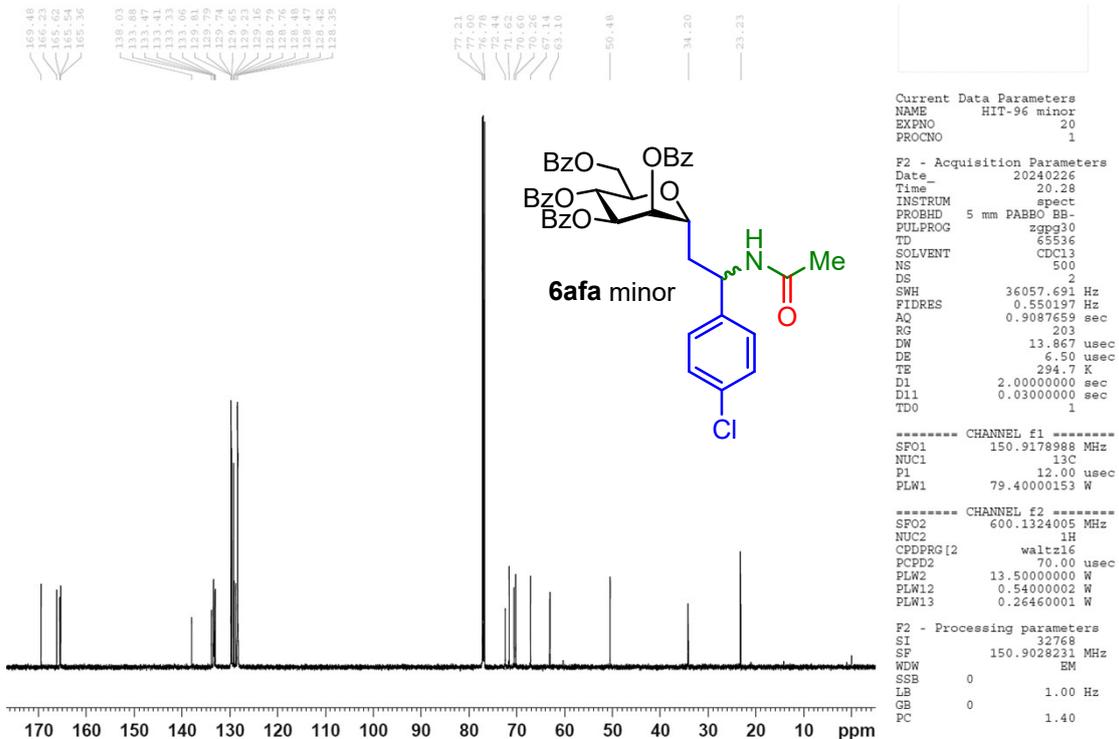
¹³C NMR spectra **6afa** major



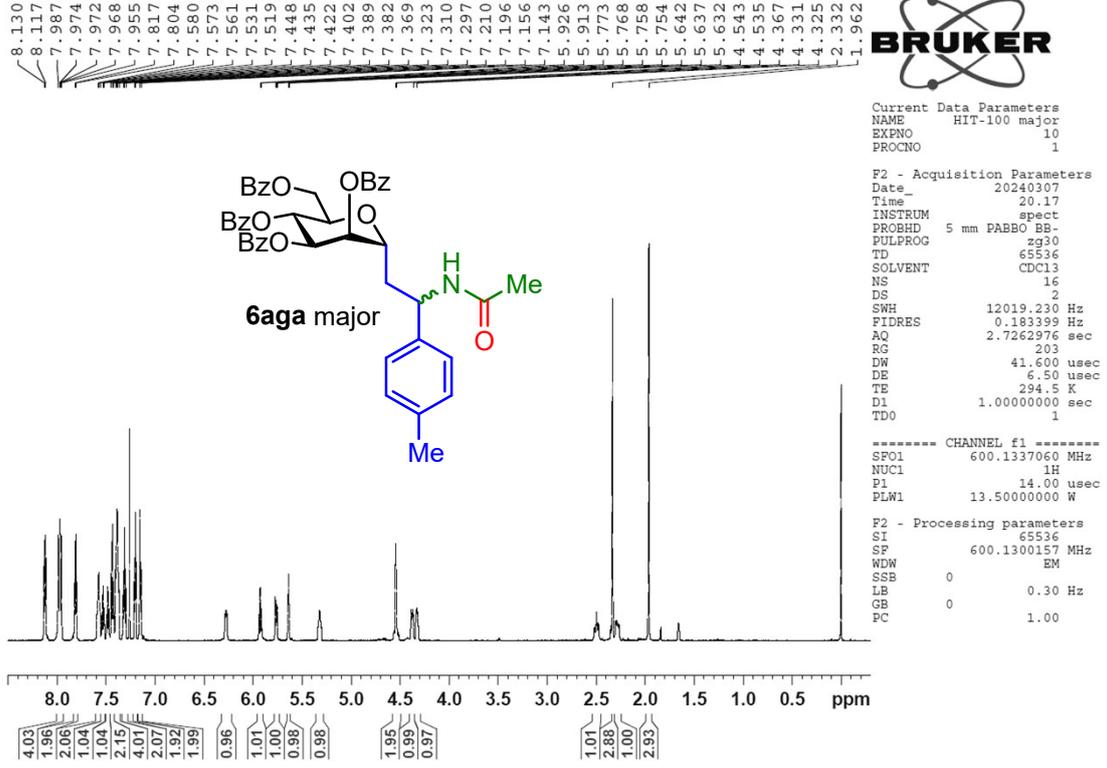
¹H NMR spectra **6afa** minor



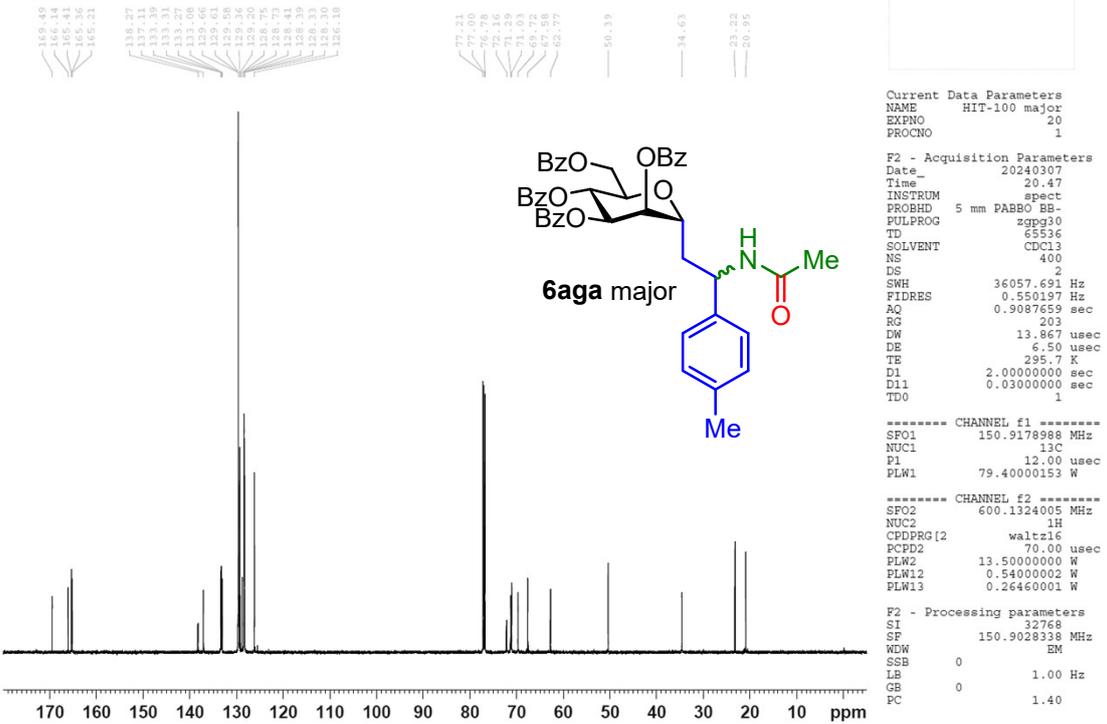
¹³C NMR spectra **6afa** minor



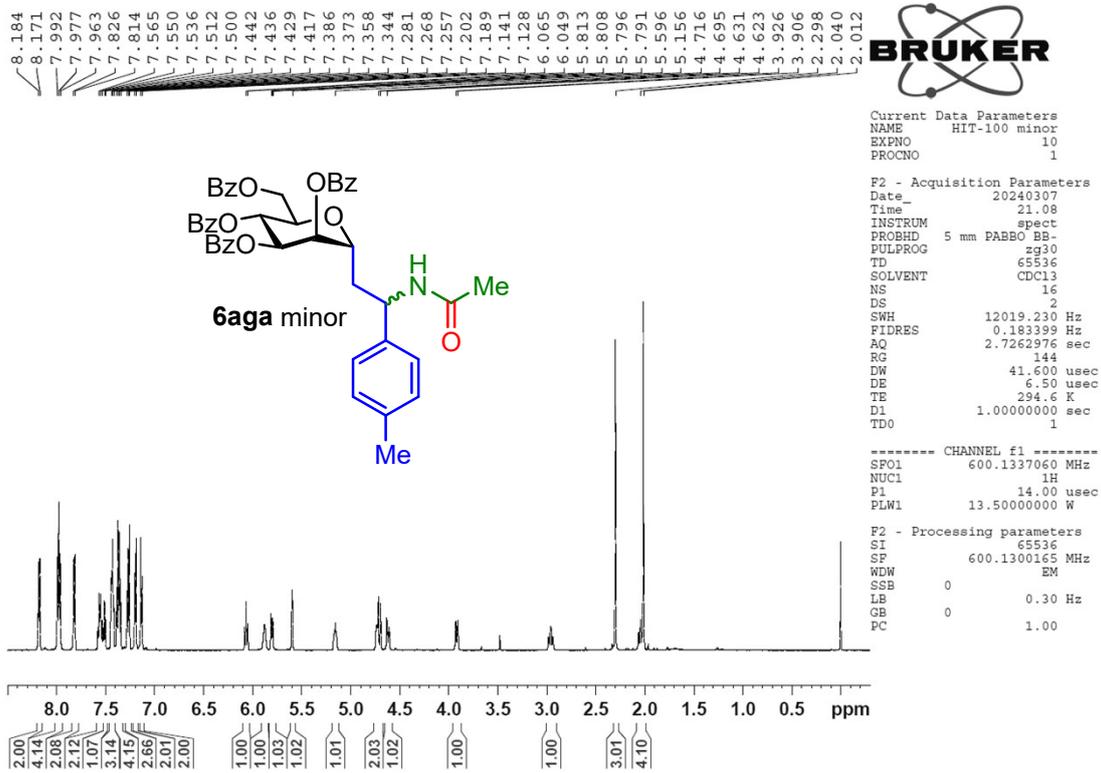
¹H NMR spectra **6aga major**



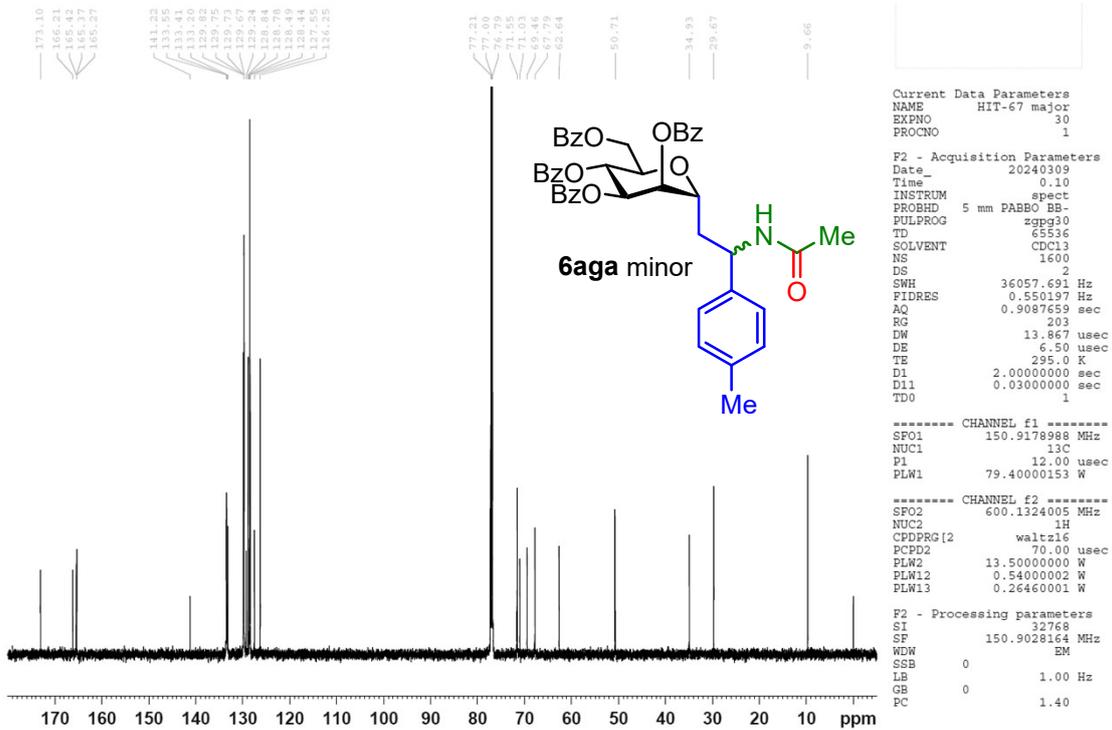
¹³C NMR spectra **6aga major**



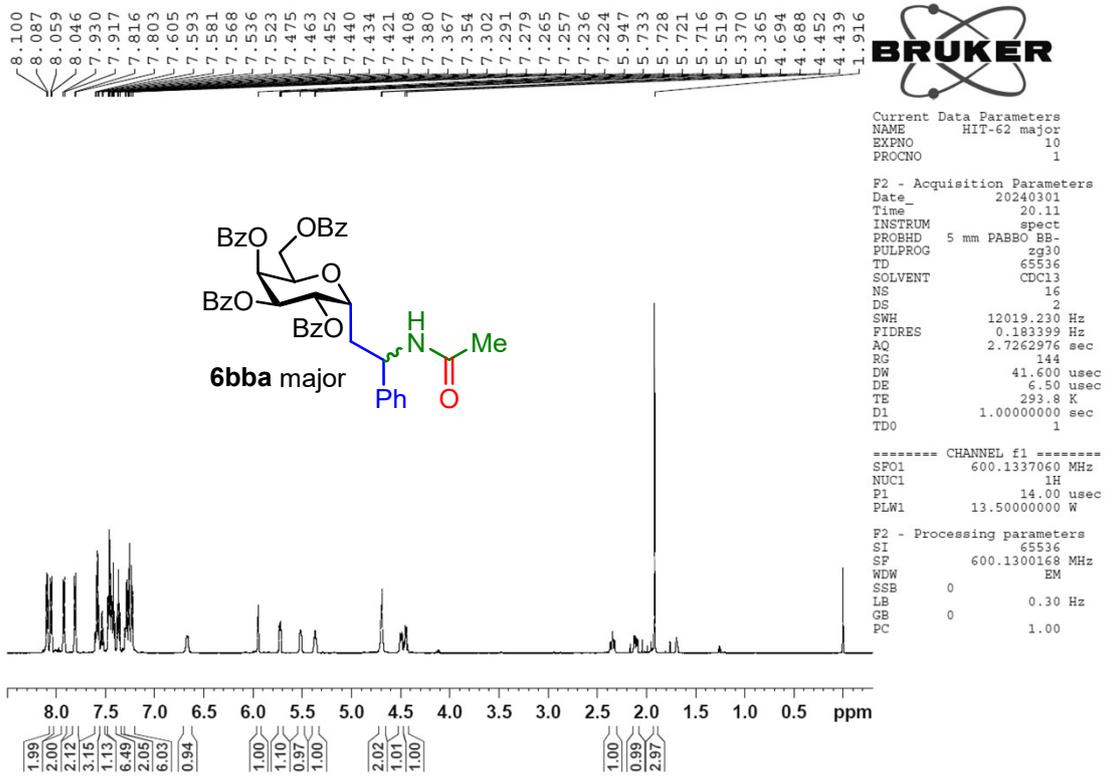
¹H NMR spectra **6aga minor**



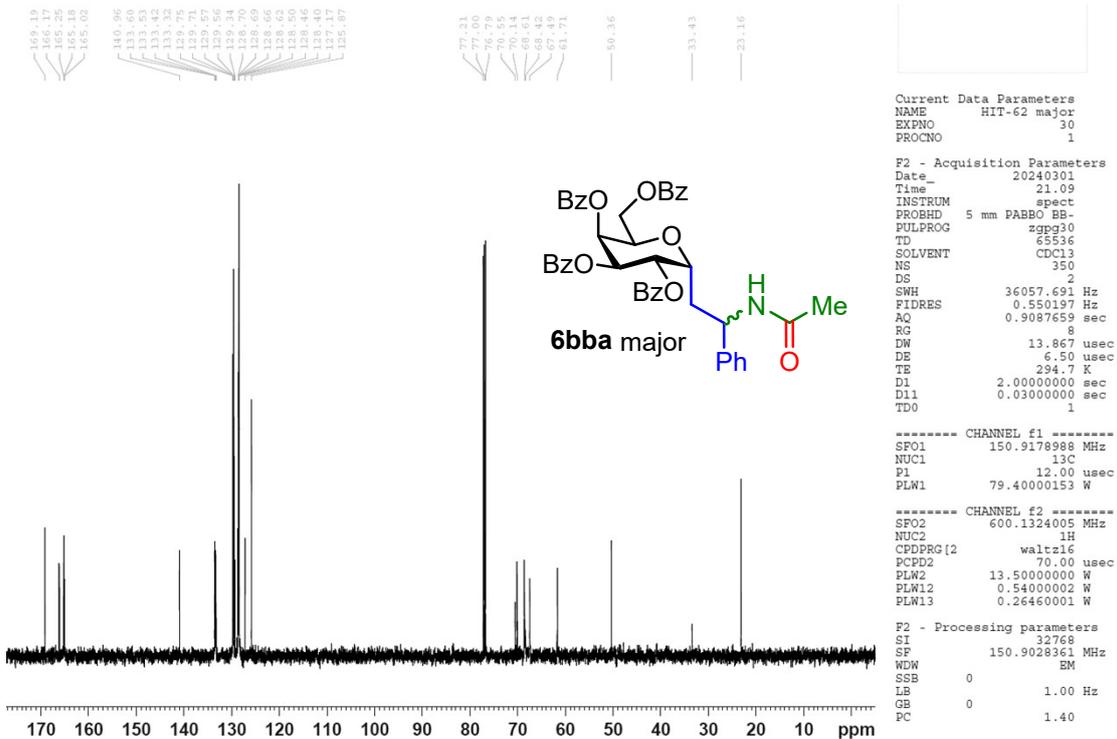
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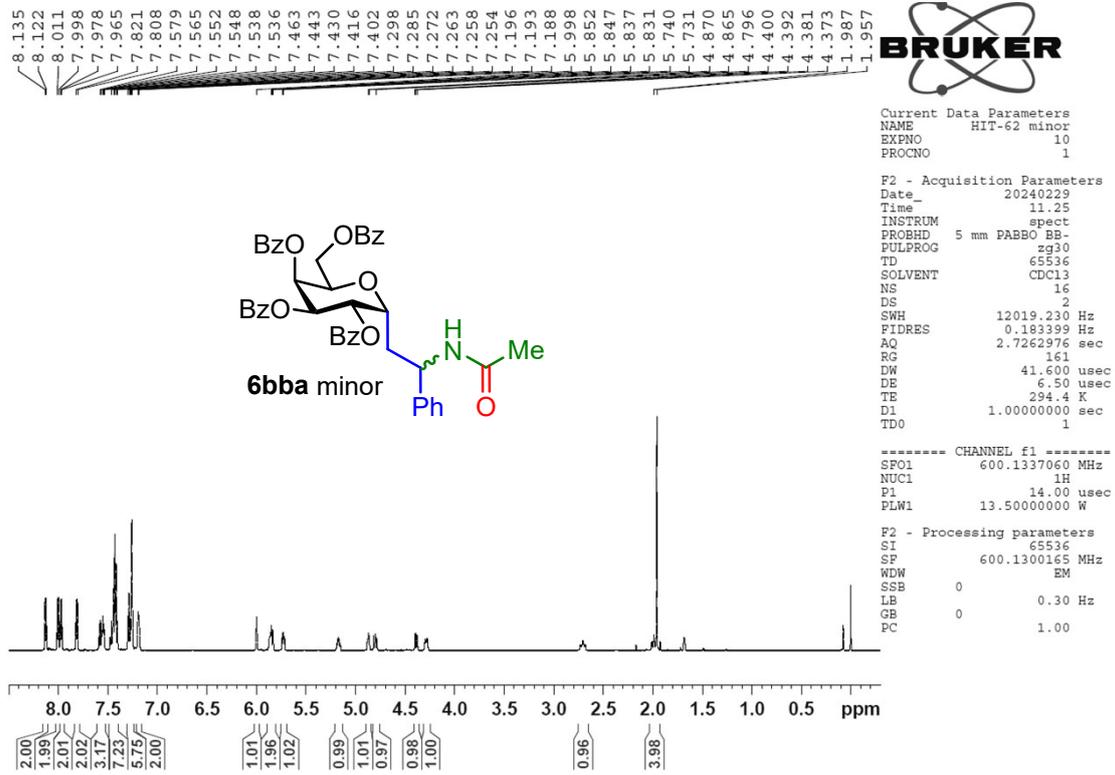
¹H NMR spectra **6bba** major



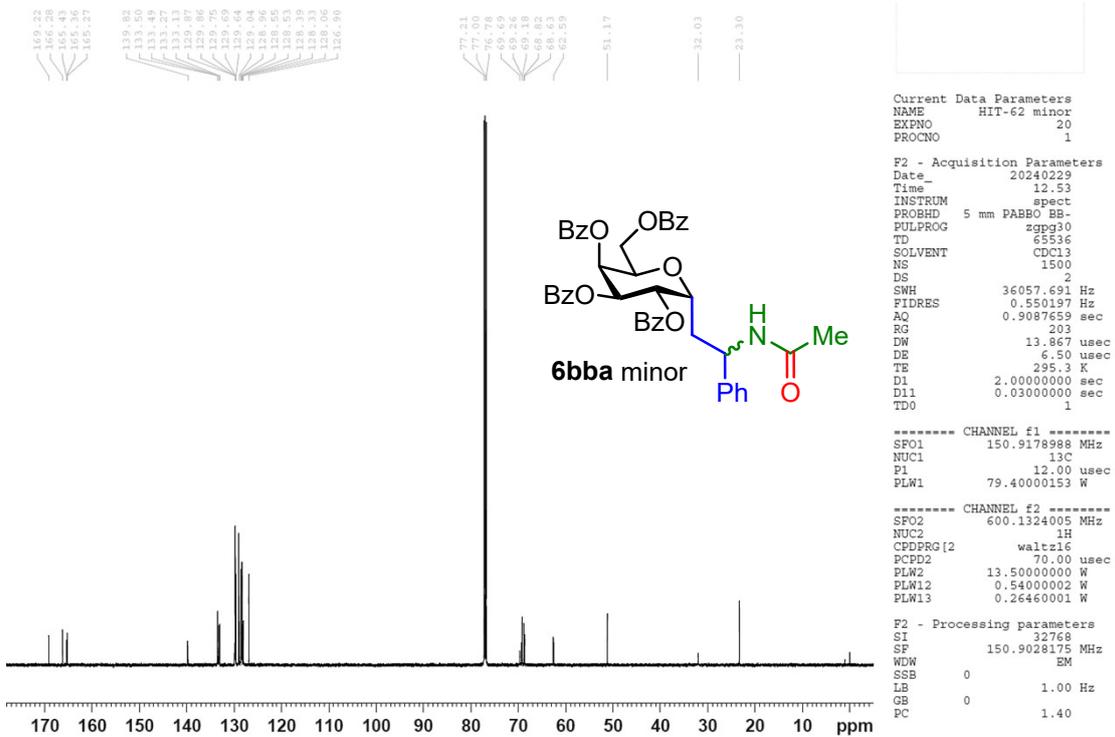
¹³C NMR spectra **6bba** major



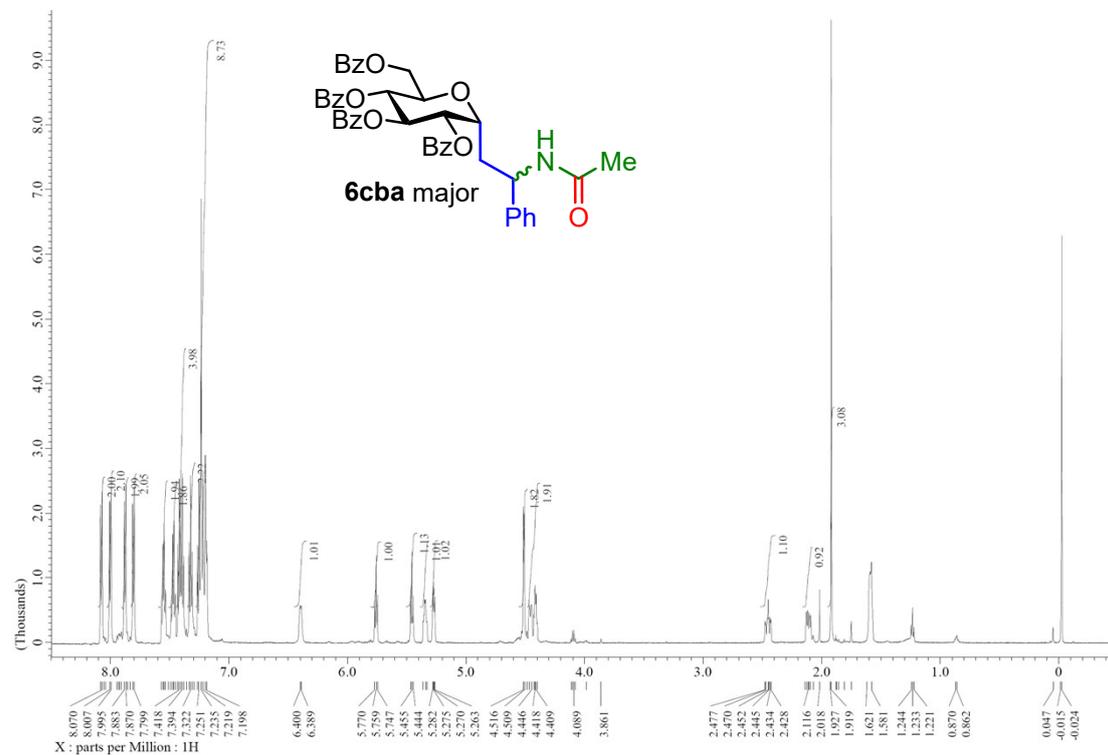
¹H NMR spectra **6bba** minor



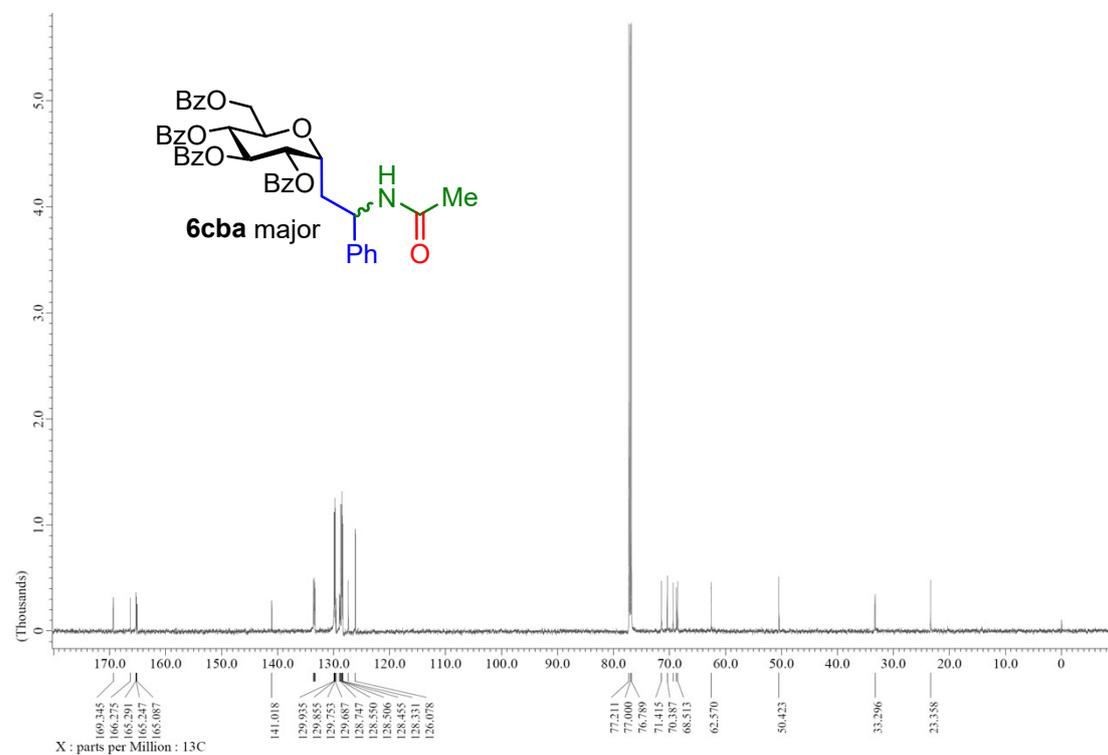
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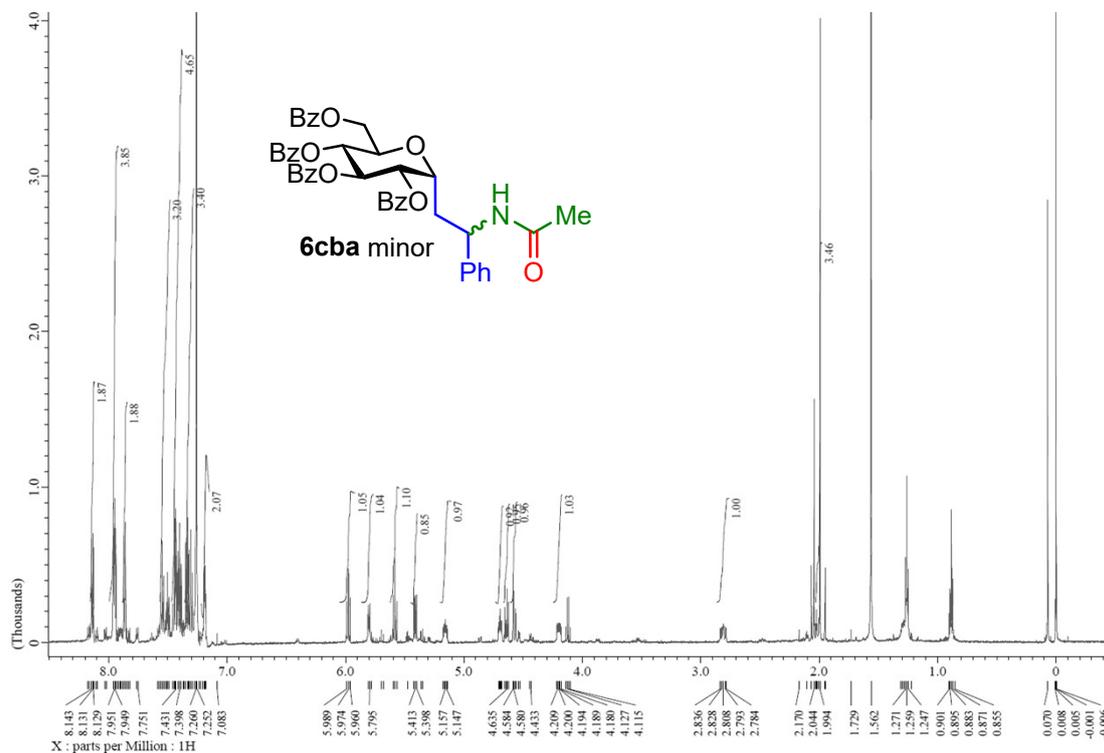
¹H NMR spectra **6cba** major



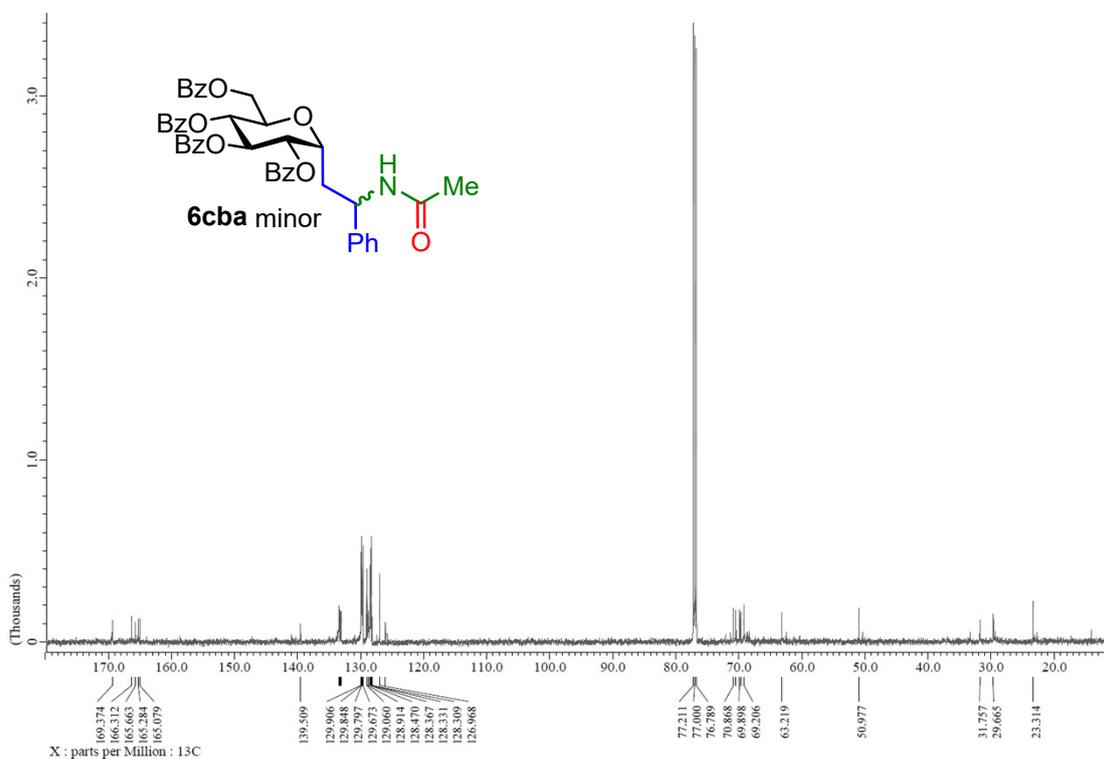
¹³C NMR spectra **6cba** major



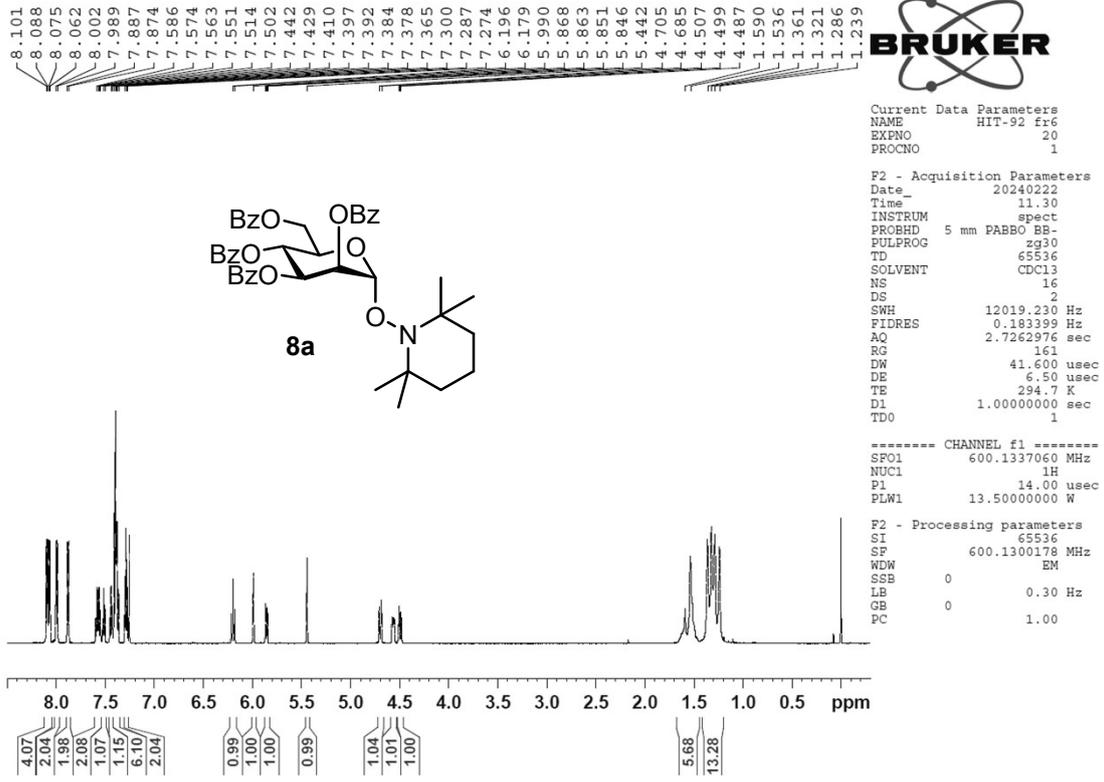
¹H NMR spectra **6cba** minor



¹³C NMR spectra **6cba** minor



¹H NMR spectra **8a**



¹³C NMR spectra **8a**

