Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

$ZnBr_2$-Catalyzed Direct C-Glycosylation of Glycosyl Acetates with Terminal Alkynes

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Table of Contents

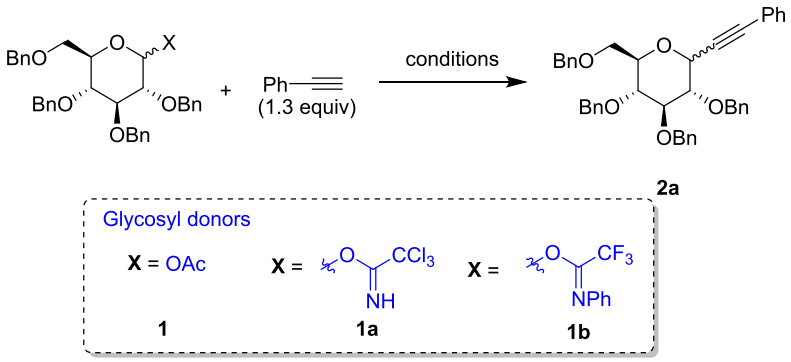
1 General Information

All reagents and chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Tetrahydrofuran (THF), Et_2O and 1,4-dioxane were distilled over sodium/benzophenone ketyl. Dichloromethane (DCM) and toluene were distilled over calcium hydride. Silica gel (200 - 300 mesh, Qingdao Marine Chemical Ltd., China), petroleum ether and ethyl acetate were used for product purification by flash column chromatography. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2 ± 0.03 mm using UV light as a visualizing agent and sulfuric acid in ethanol as a developing agent.

The ^{1}H and the ^{13}C NMR spectroscopic data were recorded on a Bruker Ascend 400 (400 MHz) and 800 (800MHz) spectrometers. Unless otherwise specified, the ^{1}H and the ^{13}C NMR spectroscopic data were recorded on a Bruker Ascend 400 (400 MHz) spectrometer (^{1}H and ^{13}C NMR at 400 and 100 MHz, respectively). All compounds were dissolved in $CDCl_3$. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS, The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet), coupling constant in Hz, and integration. HRMS determinations were recorded on a mass spectrometer (SHIMADZU UPLC-IT-TOF) with ESI ionization.

2 Optimization Studies

Table S1 Screening reaction conditions



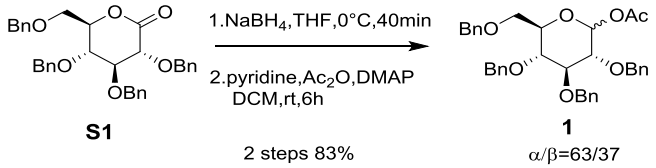
entry	donors[a]	conditions (equiv)	results
1	**1a**	[1]Ph_3PAuCl (0.3), AgOTf (0.2), DCE, 80 ℃, 6h	complex[b]
2	**1a**	[2]CuI (0.2), TMSOTf (1.2), DIPEA (1.3), toluene, reflux, 24h	NR[c]
3	**1a**	[3]$Cu(OTf)_2$ (0.1), ascorbic acid (0.1), CH_3CN, rt, 3h	complex[b]
4	**1a**	[4]$In(OTf)_3$ (0.2), DCE, 60 ℃, 24h	NR[c]
5	**1a**	[5]$ZnBr_2$ (0.2), BF_3 Et$_2$O (1.3), DIPEA (1.5), DCM. rt, 5h	trace[b]
6	**1b**	Ph_3PAuCl (0.3), AgOTf (0.2), DCE, 80 ℃, 6h	complex[b]
7	**1b**	$Cu(OTf)_2$ (0.1), ascorbic acid(0.1),CH_3CN,rt,24h	complex[b]
8	**1b**	$In(OTf)_3$ (0.2), DCE, 60 ℃, 24h	NR[c]
9	**1b**	$ZnBr_2$ (0.2), BF_3 Et$_2$O (1.3), DIPEA (1.5), DCM. rt, 3h	trace[b]
10	**1**	Ph_3PAuCl (0.3), AgOTf (0.2), DCE, 80 ℃, 24h	NR[c]
11	**1**	CuI (0.2), TMSOTf (1.2), DIPEA (1.3), DCM, rt, 24h	complex[b]
12	**1**	[6]$Cu(OTf)_2$ (0.2), DCM, rt, 24h	NR[c]
13	**1**	$Cu(OTf)_2$ (0.1), ascorbic acid (0.1),CH_3CN,rt,24h	NR[c]
14	**1**	$In(OTf)_3$ (0.2), DCE, 60 ℃, 24h	NR[c]
15	**1**	[7]TMSOTf (0.5), DCM, rt, 24h	NR[d]
16	**1**	TMSOTf (1.3),DIPEA (1.5), DCM, rt, 24h	NR[b]
17	**1**	$ZnBr_2$ (0.2), BF_3 Et$_2$O (1.3), DIPEA (1.5), DCM. rt, 20h	16%[e]
18	**1**	$ZnBr_2$ (0.2), BF_3 Et$_2$O (3.0), DIPEA (1.5), DCM. rt, **48h**	15%[e]
19	**1**	$ZnBr_2$ (0.5), BF_3 Et$_2$O (1.3), DIPEA (1.5), DCM. rt, **48h**	18%[e]
20	**1**	$ZnBr_2$ (0.2), DIPEA (1.5), DCM. rt, 24h	NR[c]
21	**1**	$ZnBr_2$ (1.0), DIPEA (1.5), DCM. rt, 24h	NR[c]

[a] **1,1a,1b** (0.2 mmol). [b] The donor was partially hydrolyzed. [c]No reaction. [d]The donor was completely hydrolyzed. [e]Isolated yield. DCE = 1,2-dichloroethane, DIPEA = *i*-Pr_2NEt.

3 Experimental Procedures

3.1. Synthesis of glycosyl acetate

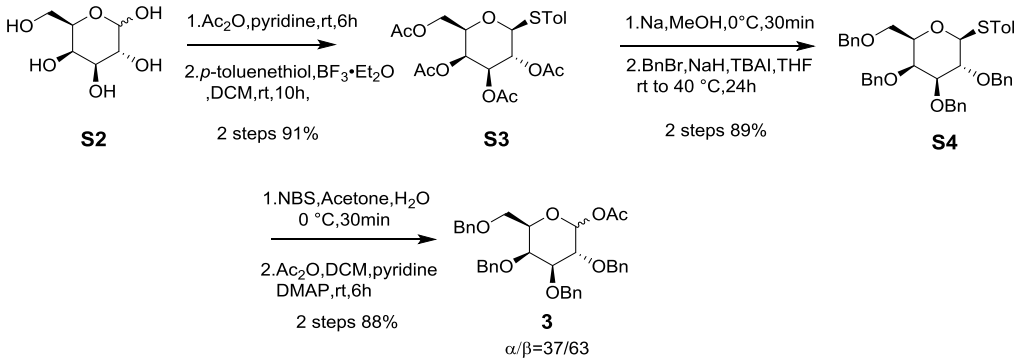
3.1.1 Synthesis of glucosyl acetate 1



To a solution of **S1** (3g, 5.58 mmol) in THF (20 ml) was slowly added $NaBH_4$ (318 mg, 8.37 mmol), and MeOH (1 ml) at 0 ℃, and the mixture was stirred vigorously for 40 min under Argon atmosphere. Then the reaction was quenched with H_2O, extracted with DCM. The combined organic phase was washed with brine, dried with Na_2SO_4, and evaporated *in vacuo* to afford crude product, which was used in the next step without further purification. To a solution of the crude product in DCM (28 ml) was added Ac_2O (1.6 ml, 16.7 mmol), pyridine (3 ml) and 4-dimethylaminopyridine (66mg, 0.54 mmol), and the mixture was stirred vigorously at rt for 6 h under Argon atmosphere. Then the solution was concentrated *in vacuo* and purification by flash chromatography (EtOAc/Petroleum ether =1/5) afforded **1** (2.7 g, 83%) as a colorless oil. Rf = 0.4 (Petroleum ether /EtOAc 6:1).

1 (α:β = 63:37): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (ddtd, *J* = 10.0, 7.1, 4.9, 2.7 Hz, 28H), 7.13 (dd, *J* = 6.4, 2.6 Hz, 4H), 6.36 (d, *J* = 3.5 Hz, 1H), 5.61 (d, *J* = 8.1 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.91 – 4.71 (m, 6H), 4.71 – 4.56 (m, 4H), 4.56 – 4.42 (m, 4H), 3.95 (t, *J* = 9.3 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.78 – 3.53 (m, 9H), 2.12 (s, 3H), 2.04 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.48, 169.33, 138.67, 138.40, 138.13, 138.04, 137.92, 137.83, 137.63, 128.52, 128.47, 128.45, 128.40, 128.17, 128.02, 128.00, 127.92, 127.90, 127.89, 127.86, 127.84, 127.82, 127.79, 127.75, 127.74, 127.69, 94.07, 90.03, 84.84, 81.70, 81.09, 78.90, 77.24, 76.96, 75.78, 75.73, 75.51, 75.34, 75.08, 75.06, 73.59, 73.55, 73.24, 72.85, 68.12, 21.17, 21.13. **HRMS** (ESI): m/z calcd for $C_{36}H_{38}O_7Na$ ($[M + Na]^+$): 605.2510, found: 605.2513.

3.1.2 Synthesis of galactosyl acetate 3 (General procedure)



S3: D-Galactose (1 g, 5.55 mmol) was dissolved in Ac_2O/ pyridine (5 ml/10 ml). The mixture was stirred at room temperature for 6h, then concentrated *in vacuo* to afford a yellow liquid (2.02 g, 100%), which was used in the next step without further purification. To a solution of this crude product, *p*-toluenethiol (1.5 g, 12.16 mmol) in DCM (30 ml) was add BF_3 Ɛt$_2$O (1.57 ml, 12.16 mmol) at 0 ℃ under argon atmosphere. The temperature was gradually raised to room temperature over 1 h, and the mixture was stirred overnight. Then it was quenched with saturated aqueous $NaHCO_3$, extracted with DCM, and washed with brine. The organic phase was dried by Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /4) afforded **S3** (2.3 g, 91%) as a white solid. mp 108–113 ℃, Rf = 0.38 (Petroleum ether /EtOAc 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 5.45 – 5.36 (m, 1H), 5.22 (t, J = 9.9 Hz, 1H), 5.04 (dd, J = 9.9, 3.4 Hz, 1H), 4.66 (d, J = 10.0 Hz, 1H), 4.23 – 4.04 (m, 2H), 3.98 – 3.84 (m, 1H), 2.35 (s, 3H), 2.11 (d, J = 6.3 Hz, 6H), 2.04 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.34, 170.17, 170.03, 169.40, 138.42, 133.11, 129.62, 128.61, 86.90, 77.42, 77.10, 76.78, 74.33, 72.01, 67.27, 67.21, 61.58, 21.15, 20.86, 20.67, 20.63, 20.58. **HRMS** (ESI): m/z calcd for $C_{21}H_{26}O_9SNa$ ($[M + Na]^+$): 477.1190, found: 477.1190.

S4: To a solution of **S3** (1 g, 2.2 mmol) in MeOH (10 ml) was added Na (10 mg, 0.44 mmol) at 0 ℃ under argon atmosphere. Then the mixture was stirred 30min and neutralized with HCl. The solvent was concentrated *in vacuo* to afford crude product as

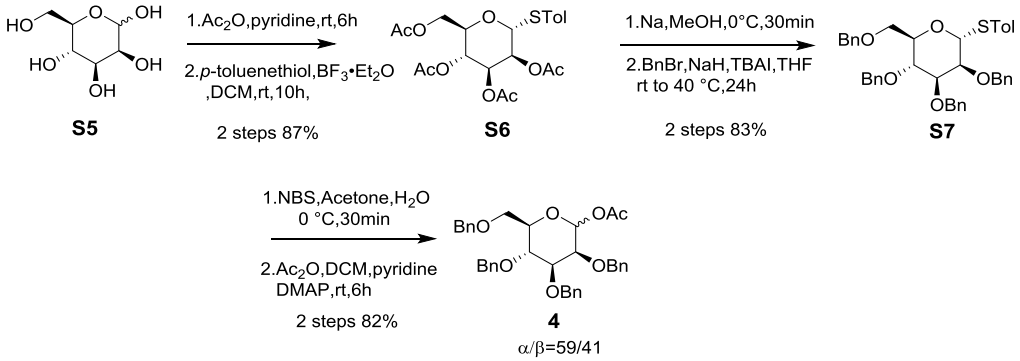
a yellow solid. This compound was suitable for the next step without purification. The crude product was dissolved in anhydrous THF (10 mL) and cooled to 0 ℃. NaH (528 mg, 13.2 mmol, 60% in mineral oil) was added and the solution was then stirred at rt for 1 h. Benzyl bromide (1.57 mL, 119.7 mmol) and tetrabutylammonium iodide (203 mg, 8.55 mmol) were added and the solution was then stirred at 35 ℃ for 23 h. The reaction was quenched with MeOH and the solution concentrated *in vacuo*. The obtained residue was dissolved in DCM and washed with H_2O. The aqueous phase was washed with DCM, the organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc 12:1) to afford **S4** as a white solid (1.26 g, 89%). mp 90–94 ℃, Rf = 0.7 (Petroleum ether /EtOAc 6:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 2H), 7.42 – 7.24 (m, 18H), 6.98 (d, J = 7.9 Hz, 2H), 4.96 (d, J = 11.5 Hz, 1H), 4.82 – 4.66 (m, 4H), 4.59 (dd, J = 10.6, 3.9 Hz, 2H), 4.49 – 4.34 (m, 2H), 3.97 (d, J = 2.7 Hz, 1H), 3.89 (t, J = 9.4 Hz, 1H), 3.69 – 3.52 (m, 4H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.82, 138.41, 138.30, 137.91, 137.22, 132.20, 130.23, 129.58, 128.45, 128.38, 128.36, 128.19, 127.96, 127.88, 127.82, 127.75, 127.70, 127.59, 127.46, 88.07, 84.25, 77.39, 77.35, 77.26, 77.07, 76.75, 75.66, 74.44, 73.60, 73.56, 72.74, 68.79, 21.15. **HRMS** (ESI): m/z calcd for $C_{41}H_{42}O_5SNa$ ($[M + Na]^+$): 669.2645, found: 669.2646.

3: To a solution of **S4** (616 mg, 1 mmol) in the mixed solvent acetone−water (9:1, 5 ml) was added N-Bromosuccinimide (534 mg, 3 mmol), and the mixture was stirred vigorously at 0 ℃ for 30 min. The reaction was quenched by the addition of a saturated solution of Na_2SO_3. After further stirring for 5 min, the resulting mixture was diluted with DCM. The organic phase was separated, and the remaining aqueous phase was extracted with DCM. The combined organic phase was washed with brine, dried with Na_2SO_4, and evaporated *in vacuo* to afford crude product, which was used in the next step without further purification. To a solution of the crude product in DCM (5 ml) was added Ac_2O (332 μl, 3 mmol), pyridine (232 μl) and 4-dimethylaminopyridine (12 mg,

0.1 mmol), and the mixture was stirred vigorously at rt for 6 h under Argon atmosphere. Then the solution was concentrated *in vacuo* and purification by flash chromatography (EtOAc/Petroleum ether =1/8) afforded **3** (510 mg, 88%) as a colorless oil. Rf = 0.4 (Petroleum ether /EtOAc 4:1).

3 (α:β = 37:63)**: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 32H), 6.39 (d, J = 3.7 Hz, 1H), 5.59 (d, J = 8.1 Hz, 1H), 4.94 (dd, J = 11.4, 6.0 Hz, 2H), 4.82 (dd, J = 11.6, 8.3 Hz, 2H), 4.76 – 4.54 (m, 7H), 4.40 (qd, J = 11.7, 6.7 Hz, 3H), 4.17 (dd, J = 10.1, 3.7 Hz, 1H), 4.04 – 3.84 (m, 4H), 3.73 – 3.64 (m, 1H), 3.64 – 3.42 (m, 4H), 2.07 (s, 2H), 1.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.66, 169.46, 138.74, 138.63, 138.61, 138.53, 138.33, 138.16, 137.91, 137.88, 128.56, 128.51, 128.48, 128.46, 128.40, 128.36, 128.29, 128.13, 128.10, 128.07, 127.99, 127.96, 127.86, 127.83, 127.79, 127.75, 127.68, 127.52, 94.41, 90.91, 82.50, 78.75, 78.28, 75.52, 75.42, 75.05, 74.82, 74.66, 74.18, 73.67, 73.60, 73.46, 73.20, 73.15, 72.94, 71.96, 68.52, 68.07, 60.48, 21.30, 21.16, 21.12, 14.35. **HRMS** (ESI): m/z calcd for $C_{36}H_{26}O_9Na$ ($[M + Na]^+$): 605.2510, found: 605.2512.

3.1.3 Synthesis of mannosyl acetate 4 (According to the general procedure of preparation of 3)



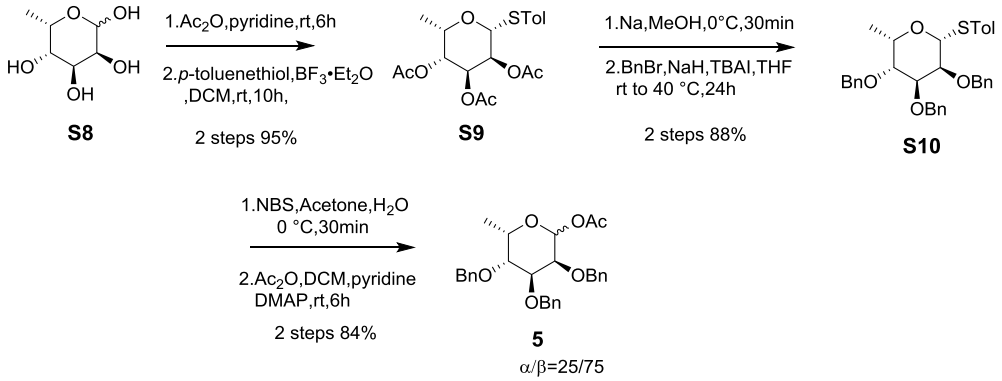
S6, colorless oil. Rf = 0.3 (Petroleum ether /EtOAc 2:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.50 (dd, J = 2.7, 1.5 Hz, 1H), 5.42 (d, J = 1.7 Hz, 1H), 5.37 – 5.29 (m, 2H), 4.62 – 4.51 (m, 1H), 4.30 (dd, J = 12.2, 5.9 Hz, 1H), 4.11 (dd, J = 12.2, 2.4 Hz, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 2.07 (d, J = 6.0 Hz, 6H), 2.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.50, 169.88, 169.77, 169.72, 138.42,

132.61, 132.58, 129.94, 129.82, 129.78, 128.75, 85.98, 70.83, 69.39, 69.35, 66.37, 62.47, 21.12, 20.86, 20.70, 20.68, 20.63. **HRMS** (ESI): m/z calcd for $C_{21}H_{26}O_9SNa$ ($[M + Na]^+$): 477.1190, found: 477.1191.

S7, light yellow oil, Rf = 0.5 (Petroleum ether /EtOAc 8:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 21H), 7.24 – 7.17 (m, 3H), 7.03 (d, J = 7.9 Hz, 2H), 5.55 (d, J = 1.7 Hz, 1H), 4.91 (d, J = 10.8 Hz, 1H), 4.75 – 4.45 (m, 8H), 4.30 (ddd, J = 9.9, 5.2, 1.9 Hz, 1H), 4.09 – 3.97 (m, 2H), 3.90 – 3.80 (m, 2H), 3.75 (dd, J = 10.9, 2.0 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.51, 138.46, 138.25, 137.98, 137.63, 132.23, 130.58, 129.82, 128.46, 128.41, 128.39, 128.34, 128.30, 128.02, 127.98, 127.88, 127.83, 127.80, 127.74, 127.72, 127.67, 127.65, 127.47, 86.04, 80.21, 76.18, 75.25, 75.09, 73.33, 72.75, 72.11, 71.86, 69.29, 21.18. **HRMS** (ESI): m/z calcd for $C_{41}H_{42}O_5SNa$ ($[M + Na]^+$): 669.2645, found: 669.2646.

4 (α:β = 59:41), colorless oil, Rf = 0.2 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (td, J = 7.8, 1.9 Hz, 3H), 7.36 – 7.24 (m, 26H), 7.16 (ddd, J = 9.7, 6.7, 2.5 Hz, 4H), 6.22 (d, J = 2.0 Hz, 1H), 5.59 (s, 1H), 4.92 – 4.83 (m, 4H), 4.75 (q, J = 12.4 Hz, 2H), 4.68 – 4.49 (m, 9H), 4.08 (t, J = 9.6 Hz, 1H), 4.03 – 3.92 (m, 2H), 3.85 (dd, J = 9.4, 3.3 Hz, 1H), 3.81 – 3.67 (m, 5H), 3.64 – 3.58 (m, 1H), 3.58 – 3.52 (m, 1H), 2.07 (s, 3H), 2.01 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.09, 169.02, 138.32, 138.25, 138.21, 138.18, 138.15, 137.98, 137.83, 128.49, 128.40, 128.37, 128.34, 128.32, 128.27, 128.25, 128.08, 128.03, 127.89, 127.79, 127.74, 127.72, 127.68, 127.63, 127.56, 93.31, 91.88, 82.28, 79.14, 77.39, 77.27, 77.07, 76.75, 76.48, 75.33, 75.17, 74.44, 74.30, 74.25, 74.15, 73.52, 73.47, 73.43, 73.35, 72.42, 72.21, 72.12, 68.93, 21.13, 21.08. **HRMS** (ESI): m/z calcd for $C_{36}H_{38}O_7Na$ ($[M + Na]^+$): 605.2510, found: 605.2510.

3.1.4 Synthesis of fucosyl acetate 5 (According to the general procedure of preparation of 3)



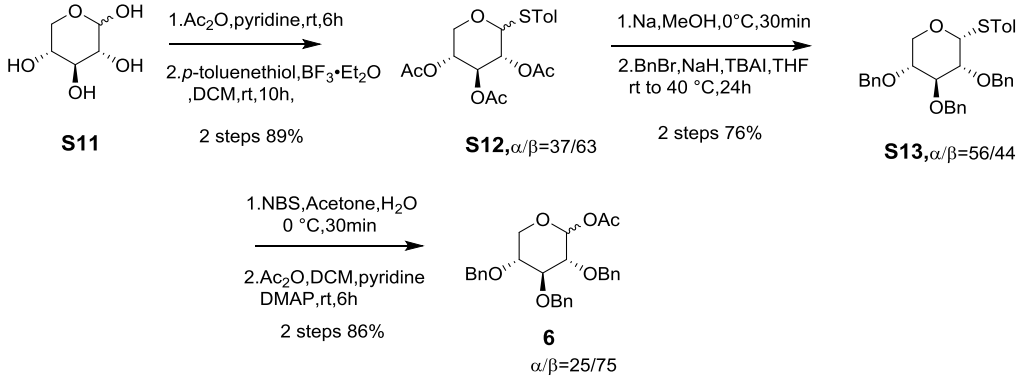
S9, white solid, mp 86–88 ℃. Rf = 0.46 (hexane/EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.29 – 5.14 (m, 2H), 5.04 (dd, J = 9.9, 3.4 Hz, 1H), 4.64 (d, J = 9.9 Hz, 1H), 3.86 – 3.76 (m, 1H), 2.34 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H), 1.23 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, CD Cl_3) δ 170.64, 170.16, 169.51, 138.22, 132.91, 129.73, 129.63, 129.07, 86.85, 73.11, 72.46, 70.35, 67.40, 21.16, 20.91, 20.68, 20.65, 16.48. **HRMS** (ESI): m/z calcd for $C_{19}H_{24}O_7SNa$ ($[M + Na]^+$): 419.1135, found: 419.1132.

S10, white solid, mp 94–97 ℃. Rf = 0.6 (Petroleum ether /EtOAc 8:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 2H), 7.33 (qd, J = 20.3, 19.8, 9.1 Hz, 15H), 7.01 (d, J = 7.8 Hz, 2H), 5.00 (d, J = 11.6 Hz, 1H), 4.86 – 4.61 (m, 5H), 4.55 (d, J = 9.8 Hz, 1H), 3.89 (t, J = 9.4 Hz, 1H), 3.67 – 3.54 (m, 2H), 3.50 (d, J = 6.4 Hz, 1H), 2.30 (s, 3H), 1.26 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.77, 138.47, 137.10, 132.19, 129.51, 128.44, 128.36, 128.33, 128.15, 127.96, 127.69, 127.58, 127.44, 87.88, 84.58, 77.35, 77.15, 77.03, 76.71, 76.59, 75.56, 74.56, 72.86, 21.13, 17.33. **HRMS** (ESI): m/z calcd for $C_{34}H_{36}O_4SNa$ ($[M + Na]^+$): 563.2227, found: 563.2225.

5 (α:β = 63:37), white solid, mp 64–66 ℃. Rf = 0.4 (Petroleum ether /EtOAc 4:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 18H), 5.56 (d, J = 8.1 Hz, 1H), 4.99 (d, J = 11.7 Hz, 1H), 4.85 (d, J = 11.4 Hz, 1H), 4.80 – 4.61 (m, 6H), 4.02 – 3.83 (m, 2H), 3.67

– 3.49 (m, 3H), 2.11 (s, 1H), 2.03 (s, 3H), 1.16 (dd, J = 13.1, 6.4 Hz, 4H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.68, 169.58, 138.76, 138.48, 138.40, 138.36, 138.30, 138.10, 128.52, 128.49, 128.43, 128.39, 128.38, 128.28, 128.25, 128.05, 127.88, 127.77, 127.73, 127.68, 127.63, 127.59, 127.42, 94.30, 90.91, 82.77, 79.02, 78.11, 77.42, 77.36, 77.10, 76.78, 75.93, 75.30, 74.99, 74.73, 73.32, 73.23, 73.14, 71.49, 69.12, 21.25, 21.12, 16.77. **HRMS** (ESI): m/z calcd for $C_{29}H_{32}O_6Na$ ([M + Na]$^+$): 499.2091, found: 499.2091.

3.1.5 Synthesis of xylosyl acetate 6 (According to the general procedure of preparation of 3)



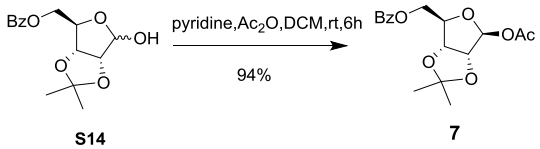
S12 (α:β = 37:63), light yellow solid, mp 91–96 ℃. Rf = 0.35 (Petroleum ether /EtOAc 4:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.1 Hz, 2H), 7.17 – 7.03 (m, 3H), 5.17 (t, J = 8.3 Hz, 1H), 4.91 (ddt, J = 8.3, 5.7, 2.3 Hz, 2H), 4.72 (d, J = 8.5 Hz, 1H), 4.25 (dd, J = 11.7, 5.0 Hz, 1H), 3.39 (dd, J = 11.7, 9.0 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 1H), 2.11 (s, 1H), 2.10 (s, 3H), 2.06 (s, 2H), 2.04 (d, J = 1.4 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.94, 169.76, 169.73, 169.31, 138.61, 138.02, 133.49, 132.38, 129.93, 129.78, 129.09, 128.05, 86.37, 85.77, 77.39, 77.27, 77.07, 76.75, 72.26, 70.79, 69.83, 69.53, 69.01, 68.46, 65.39, 59.88, 21.18, 21.12, 20.82, 20.79, 20.76, 20.73. **HRMS** (ESI): m/z calcd for $C_{18}H_{22}O_7Na$ ([M + Na]$^+$): 405.0978, found: 405.0978.

S13(α:β = 56:44), light yellow oil, Rf = 0.3 (Petroleum ether /EtOAc 10:1), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.25 (m, 30H), 7.10 (dd, *J* = 8.2, 2.2 Hz, 4H), 5.47

(d, *J* = 4.5 Hz, 1H), 4.97 – 4.81 (m, 5H), 4.80 – 4.57 (m, 8H), 4.12 – 4.00 (m, 2H), 3.84 – 3.74 (m, 2H), 3.71 – 3.53 (m, 4H), 3.45 – 3.35 (m, 1H), 3.26 – 3.15 (m, 1H), 2.32 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.78, 138.49, 138.31, 138.15, 138.10, 137.87, 137.83, 137.41, 132.67, 132.26, 130.59, 129.78, 129.75, 128.51, 128.47, 128.45, 128.43, 128.37, 128.22, 128.10, 128.08, 127.99, 127.91, 127.85, 127.82, 127.74, 127.64, 88.76, 87.78, 85.47, 81.67, 80.43, 79.53, 77.80, 77.69, 77.27, 75.79, 75.71, 75.47, 73.57, 73.26, 72.62, 67.54, 60.97, 21.16. **HRMS** (ESI): m/z calcd for $C_{33}H_{34}O_4SNa$ ($[M + Na]^+$): 549.2070, found: 549.2072.

6 (α:β = 25:75), colorless oil, Rf = 0.2 (Petroleum ether /EtOAc 12:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (q, J = 5.0 Hz, 15H), 5.55 (d, J = 7.8 Hz, 1H), 4.92 – 4.60 (m, 8H), 3.93 (dd, J = 11.8, 4.7 Hz, 1H), 3.69 – 3.57 (m, 3H), 3.49 (t, J = 8.1 Hz, 1H), 3.36 (dd, J = 11.7, 9.4 Hz, 1H), 2.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.37, 138.45, 138.18, 137.99, 128.54, 128.52, 128.45, 128.44, 128.01, 127.98, 127.97, 127.88, 127.82, 127.77, 94.66, 83.69, 80.46, 77.55, 75.65, 75.11, 73.37, 21.01. **HRMS** (ESI): m/z calcd for $C_{28}H_{30}O_6Na$ ($[M + Na]^+$): 485.1935, found: 485.1933.

3.1.6 Synthesis of ribofuranosyl acetate 7

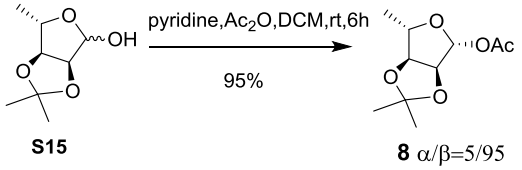


S14 **7**

To a solution of **S14**[8] (482 mg, 1.64 mmol) in DCM (8 ml) was added Ac_2O (462 μl, 4.9 mmol), pyridine (380 μl) and 4-dimethylaminopyridine (20 mg, 0.1 mmol), and the mixture was stirred vigorously at rt for 6 h under Argon atmosphere. Then the solution was concentrated *in vacuo* and purification by flash chromatography (EtOAc/Petroleum ether =1/8) afforded **7** (520 mg, 94%) as a colorless oil. Rf = 0.4 (Petroleum ether /EtOAc 6:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.2, 1.4 Hz, 2H), 7.60 – 7.51 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 6.24 (s, 1H), 4.88 – 4.81 (m, 1H), 4.78 (d, J = 5.9 Hz, 1H), 4.62 (t, J = 6.1 Hz, 1H), 4.38 (qd, J = 11.7, 6.2 Hz, 2H), 1.95

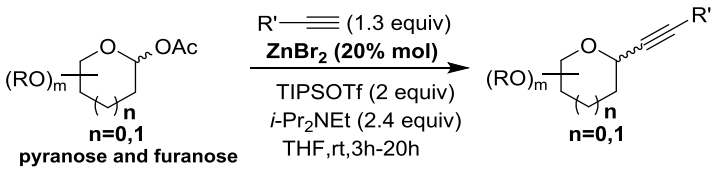
(s, 3H), 1.50 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.35, 165.98, 133.33, 129.72, 129.52, 128.47, 113.24, 102.35, 85.51, 85.28, 81.64, 77.42, 77.10, 76.78, 64.55, 26.48, 25.10, 21.09. **HRMS** (ESI): m/z calcd for $C_{17}H_{20}O_7Na$ ([M + Na]$^+$): 359.1101, found: 359.1103.

3.1.6 Synthesis of furanosyl acetate 8



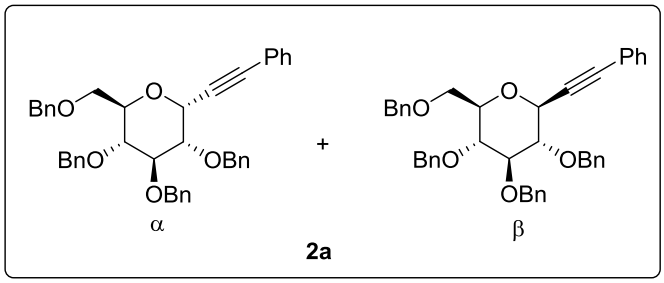
To a solution of **S15**[8] (170 mg, 0.97 mmol) in DCM (4 ml) was added Ac_2O (275 µl, 2.9 mmol), pyridine (250 µl) and 4-dimethylaminopyridine (12 mg, 0.1 mmol), and the mixture was stirred vigorously at rt for 6 h under Argon atmosphere. Then the solution was concentrated *in vacuo* and purification by flash chromatography (EtOAc/Petroleum ether =1/10) afforded **8** (200 mg, 95%) as a colorless oil. Rf = 0.4 (Petroleum ether /EtOAc 8:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.14 (s, 1H), 4.73 (d, J = 5.8 Hz, 1H), 4.53 (d, J = 5.8 Hz, 1H), 4.42 (q, J = 7.0 Hz, 1H), 2.03 (s, 3H), 1.46 (s, 3H), 1.29 (s, 4H), 1.26 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.55, 112.76, 102.63, 85.56, 84.93, 84.19, 26.44, 25.03, 21.28, 20.61. **HRMS** (ESI): m/z calcd for $C_{10}H_{16}O_5Na$ ([M + Na]$^+$): 239.0890, found: 239.0888.

3.2. Prepare of C-glycosides



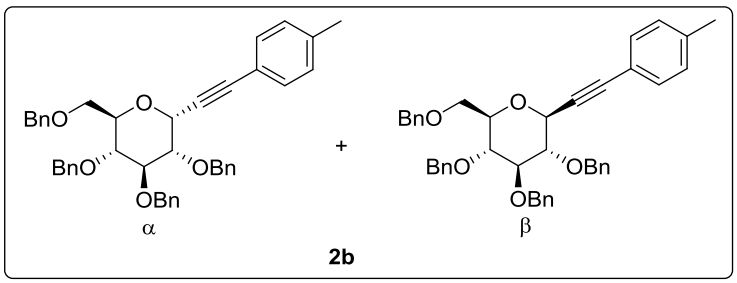
General Procedure: To a solution of glycosyl acetate (0.2 mmol) and $ZnBr_2$ (9 mg, 20 % mol) in dry THF (1 mL, 0.2 M) was added alkyne (0.26 mmol, 1.3 equiv) , *i*-Pr_2NEt (0.48 mmol, 80 µl, 2.4 equiv) and TIPSOTf (0.4 mmol, 107µl, 2 equiv) at rt (20 ℃ - 25 ℃) under Argon atmosphere. The reaction was stirred at rt for 20h, then silica gel (200 - 300 mesh, 500mg) was added and concentrated *in vacuo* to afford

yellow powder, which was purified by flash column chromatography on silica gel to give the pure desired product.



2a (α:β = 88:12)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/15) to give compound **2a**[8] (105 mg, 84%) as a colorless oil. Rf = 0.35 (Petroleum ether /EtOAc 10:1).

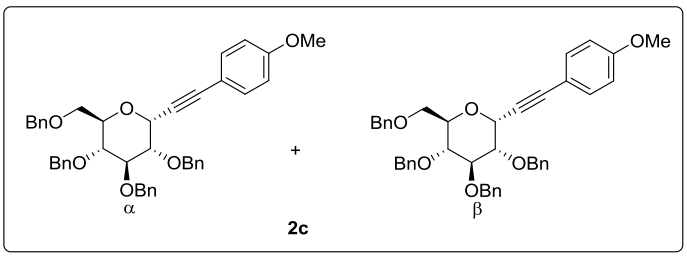
2a (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 6.9, 2.9 Hz, 2H), 7.32 (qd, J = 19.2, 16.3, 6.7 Hz, 20H), 7.18 – 7.07 (m, 3H), 5.04 – 4.97 (m, 2H), 4.84 (dt, J = 10.9, 2.9 Hz, 3H), 4.73 (s, 2H), 4.61 (d, J = 12.1 Hz, 1H), 4.50 (dd, J = 11.5, 6.1 Hz, 2H), 4.09 – 3.96 (m, 2H), 3.81 – 3.60 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.83, 138.25, 138.18, 137.94, 132.04, 131.85, 128.64, 128.46, 128.42, 128.41, 128.26, 128.07, 128.05, 127.91, 127.85, 127.77, 127.73, 127.62, 122.44, 89.42, 83.94, 83.14, 79.34, 77.55, 75.68, 75.29, 73.73, 73.57, 72.75, 68.67, 67.24. **HRMS** (ESI): m/z calcd for $C_{42}H_{40}O_5Na$ ($[M + Na]^+$): 647.2768, found: 647.2766.



2b (α:β = 83:17)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2b** (91 mg, 71%) as a colorless oil. Rf = 0.39 (Petroleum ether /EtOAc 10:1).

2b (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dddd, *J* = 23.8, 16.0, 10.4, 6.6 Hz, 23H), 7.18 – 7.06 (m, 5H), 5.05 – 4.97 (m, 2H), 4.84 (dd, *J* = 10.8, 2.9 Hz, 3H), 4.73 (s, 2H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.49 (dd, *J* = 11.4, 4.4 Hz, 2H), 4.10 – 3.97 (m, 2H), 3.81 – 3.63 (m, 5H), 2.34 (d, *J* = 3.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.83,

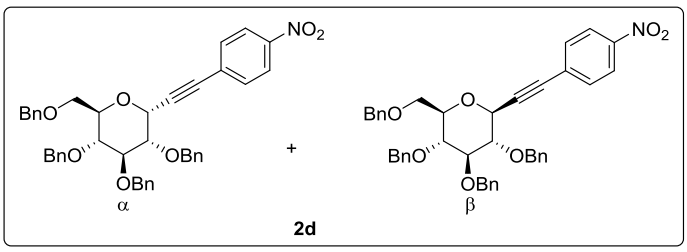
138.75, 138.24, 138.19, 137.93, 131.93, 131.74, 129.09, 129.00, 128.46, 128.44, 128.42, 128.40, 128.35, 128.08, 128.05, 127.97, 127.90, 127.85, 127.81, 127.76, 127.71, 127.61, 119.35, 89.56, 83.15, 83.12, 79.33, 77.54, 75.67, 75.28, 73.62, 73.55, 72.69, 68.63, 67.25, 21.56. **HRMS** (ESI): m/z calcd for $C_{43}H_{42}O_5Na$ ($[M + Na]^+$): 661.2924, found: 661.2923.



2c

2c (α:β = 79:21)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/10) to give compound **2c** (106 mg, 81%) as a colorless oil. Rf = 0.32 (Petroleum ether /EtOAc 8:1).

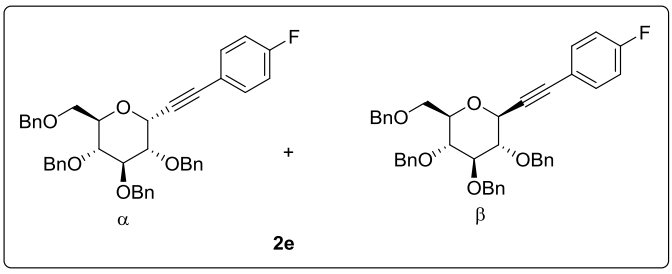
2c (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (ddd, *J* = 35.3, 16.1, 7.4 Hz, 26H), 7.14 (q, *J* = 5.5, 4.2 Hz, 3H), 6.83 (dd, *J* = 8.9, 3.0 Hz, 3H), 5.04 – 4.97 (m, 2H), 4.84 (d, *J* = 10.6 Hz, 3H), 4.73 (s, 2H), 4.66 – 4.58 (m, 1H), 4.49 (dd, *J* = 11.4, 4.1 Hz, 2H), 4.09 – 3.97 (m, 2H), 3.80 (d, *J* = 3.5 Hz, 4H), 3.77 – 3.63 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.83, 138.84, 138.23, 138.19, 137.93, 133.53, 133.34, 128.46, 128.43, 128.40, 128.35, 128.09, 128.05, 127.97, 127.91, 127.88, 127.86, 127.82, 127.77, 127.71, 127.61, 114.52, 113.96, 113.86, 89.37, 86.12, 83.13, 82.44, 79.33, 77.57, 75.66, 75.29, 73.57, 73.55, 72.68, 68.65, 67.27, 55.32, 55.30. **HRMS** (ESI): m/z calcd for $C_{43}H_{42}O_6Na$ ($[M + Na]^+$): 677.2874, found: 677.2872.



2d

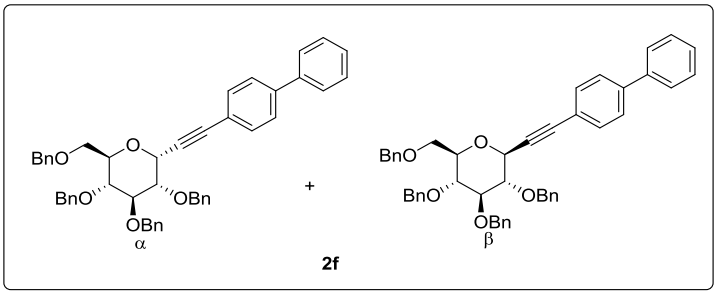
2d (α:β = 95:5)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/10) to give compound **2d** (74 mg, 55%) as a light yellow solid. mp 123–126 ℃, Rf = 0.31 (Petroleum ether /EtOAc 10:1).

2d (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.25 (m, 17H), 7.13 (dd, *J* = 6.8, 2.8 Hz, 2H), 5.07 – 4.96 (m, 2H), 4.85 (dd, *J* = 10.7, 4.0 Hz, 2H), 4.80 – 4.70 (m, 2H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.50 (dd, *J* = 11.4, 3.6 Hz, 2H), 4.04 – 3.91 (m, 2H), 3.81 – 3.62 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.34, 138.61, 137.97, 137.90, 137.76, 132.79, 129.16, 128.53, 128.48, 128.44, 128.13, 128.05, 128.03, 127.98, 127.93, 127.91, 127.82, 127.71, 123.54, 89.59, 87.31, 83.08, 79.08, 77.35, 75.71, 75.42, 74.13, 73.61, 73.05, 68.50, 67.24. **HRMS** (ESI): m/z calcd for $C_{42}H_{39}NO_7Na$ ([M + Na]$^+$): 692.2619, found: 692.2617.



2e (α:β = 92:8)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2e** (80 mg, 62%) as a light yellow solid. mp 60–64 ℃, Rf = 0.41 (Petroleum ether /EtOAc 8:1).

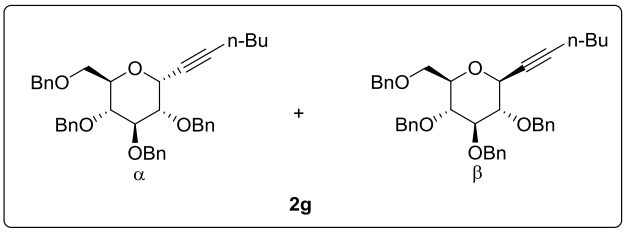
2e (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.41 – 7.25 (m, 20H), 7.14 (dd, *J* = 7.0, 2.7 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 5.04 – 4.96 (m, 2H), 4.84 (d, *J* = 10.8 Hz, 2H), 4.72 (d, *J* = 13.8 Hz, 2H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.56 – 4.46 (m, 2H), 4.06 – 3.96 (m, 2H), 3.80 – 3.61 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.94, 161.46, 138.75, 138.14, 138.09, 137.87, 134.01, 133.93, 128.46, 128.44, 128.41, 128.10, 128.04, 128.01, 127.96, 127.91, 127.88, 127.85, 127.81, 127.79, 127.74, 127.63, 118.48, 115.67, 115.45, 88.29, 83.66, 83.10, 79.22, 77.49, 75.67, 75.33, 73.74, 73.57, 72.80, 68.59, 67.18. **HRMS** (ESI): m/z calcd for $C_{42}H_{39}O_5FNa$ ([M + Na]$^+$): 665.2674, found: 665.2675.



2f

2f (α:β = 83:17)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2f** (65 mg, 46%) as a light yellow oil. Rf = 0.41 (Petroleum ether /EtOAc 8:1).

2f (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 12.1 Hz, 7H), 7.46 – 7.23 (m, 25H), 7.18 – 7.10 (m, 3H), 5.06 – 4.98 (m, 2H), 4.85 (d, *J* = 10.7 Hz, 3H), 4.75 (s, 2H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.50 (dd, *J* = 11.4, 3.9 Hz, 2H), 4.12 – 3.98 (m, 2H), 3.85 – 3.61 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.37, 140.33, 138.82, 138.23, 138.18, 138.00, 137.92, 132.47, 132.27, 128.90, 128.50, 128.48, 128.44, 128.42, 128.09, 128.07, 127.93, 127.87, 127.79, 127.75, 127.73, 127.64, 127.09, 126.95, 121.30, 89.28, 84.60, 83.16, 79.34, 77.54, 75.71, 75.32, 73.75, 73.58, 72.77, 68.65, 67.30. **HRMS** (ESI): m/z calcd for $C_{48}H_{44}O_5Na$ ($[M + Na]^+$): 723.3081, found: 723.3080.

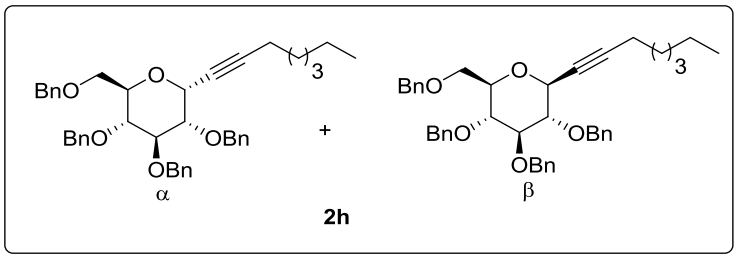


2g

2g (α:β = 94:6)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2g**[8] (90 mg, 75%) as a colorless oil. Rf = 0.36 (Petroleum ether /EtOAc 10:1).

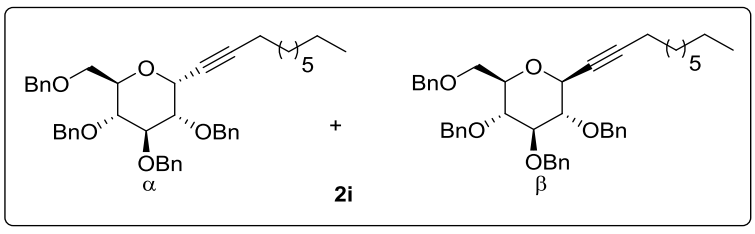
2g (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 18H), 7.14 (dd, *J* = 7.2, 2.5 Hz, 2H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.86 – 4.76 (m, 3H), 4.69 (s, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 2H), 4.03 – 3.90 (m, 2H), 3.74 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.63 (ddd, *J* = 20.0, 10.4, 3.7 Hz, 3H), 2.26 (td, *J* = 7.0, 2.3 Hz, 2H), 1.57 – 1.38

(m, 5H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.86, 138.28, 138.18, 137.97, 128.41, 128.39, 128.37, 128.04, 128.00, 127.95, 127.88, 127.77, 127.74, 127.67, 127.58, 90.44, 83.10, 79.30, 77.59, 75.63, 75.21, 74.53, 73.49, 73.20, 72.62, 68.66, 66.83, 30.71, 22.00, 18.71, 13.66. **HRMS** (ESI): m/z calcd for $C_{40}H_{44}O_5Na$ ([M + Na]$^+$): 627.3081, found: 627.3082.



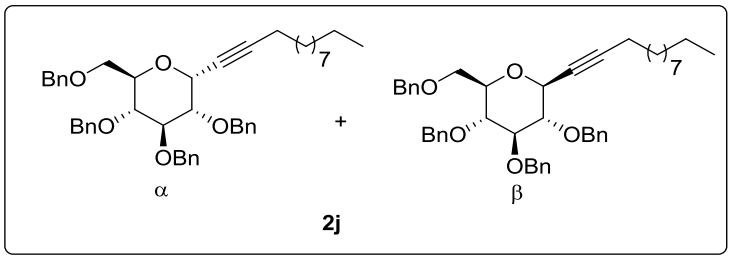
2h (α:β = 94:6)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2h** (87 mg, 69%) as a colorless oil. Rf = 0.41 (Petroleum ether /EtOAc 10:1).

2h (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 18H), 7.13 (dd, *J* = 6.9, 2.6 Hz, 2H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.86 – 4.75 (m, 3H), 4.69 (s, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 2H), 4.02 – 3.90 (m, 2H), 3.74 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.63 (qd, *J* = 10.1, 9.4, 3.0 Hz, 3H), 2.26 (td, *J* = 7.0, 2.2 Hz, 2H), 1.60 – 1.47 (m, 2H), 1.46 – 1.34 (m, 2H), 1.28 (dt, *J* = 7.7, 3.8 Hz, 4H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.88, 138.30, 138.18, 137.97, 128.40, 128.37, 128.04, 128.02, 127.99, 127.96, 127.90, 127.85, 127.79, 127.73, 127.68, 127.66, 127.59, 90.50, 83.15, 79.30, 77.59, 75.66, 75.21, 74.56, 73.51, 73.21, 72.63, 68.66, 66.85, 31.38, 28.60, 22.60, 19.03, 14.11. **HRMS** (ESI): m/z calcd for $C_{42}H_{48}O_5Na$ ([M + Na]$^+$): 655.3394, found: 655.3391.



2i (α:β = 94:6)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2i** (92 mg, 72%) as a colorless oil. Rf = 0.41 (Petroleum ether /EtOAc 10:1).

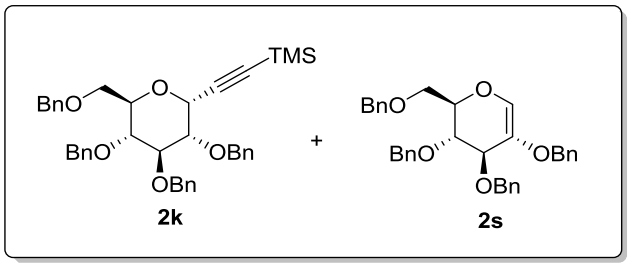
2i (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 18H), 7.17 – 7.09 (m, 2H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.86 – 4.76 (m, 3H), 4.69 (s, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 12.3 Hz, 2H), 4.01 – 3.89 (m, 2H), 3.74 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.63 (qd, *J* = 9.9, 9.3, 2.9 Hz, 3H), 2.25 (td, *J* = 7.1, 2.2 Hz, 2H), 1.59 – 1.47 (m, 2H), 1.40 (t, *J* = 7.6 Hz, 2H), 1.26 (q, *J* = 7.8, 7.1 Hz, 8H), 0.90 – 0.81 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.88, 138.30, 138.18, 137.97, 128.40, 128.39, 128.37, 128.04, 128.02, 127.99, 127.96, 127.90, 127.79, 127.74, 127.68, 127.58, 90.51, 83.15, 79.30, 77.59, 75.66, 75.22, 74.56, 73.51, 73.20, 72.63, 68.65, 66.85, 31.89, 29.27, 29.17, 28.95, 28.65, 22.69, 19.02, 14.15. **HRMS** (ESI): m/z calcd for $C_{44}H_{52}O_5Na$ ($[M + Na]^+$): 683.3707, found: 683.3709.



2j (α:β = 95:5)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compound **2j** (92 mg, 67%) as a colorless oil. Rf = 0.41 (Petroleum ether /EtOAc 10:1).

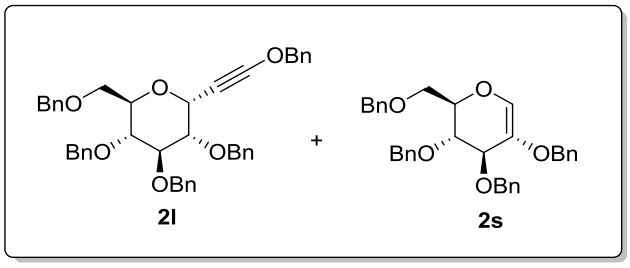
2j (α-anomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 18H), 7.13 (dd, *J* = 7.0, 2.5 Hz, 2H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.85 – 4.77 (m, 3H), 4.69 (s, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 12.5 Hz, 2H), 4.01 – 3.90 (m, 2H), 3.74 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.63 (qd, *J* = 10.0, 9.3, 2.9 Hz, 3H), 2.25 (td, *J* = 7.1, 2.2 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.40 (t, *J* = 7.5 Hz, 2H), 1.24 (d, *J* = 6.0 Hz, 12H), 0.86 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.87, 138.30, 138.19, 137.98, 128.44, 128.41, 128.39, 128.38, 128.04, 128.02, 128.00, 127.96, 127.90, 127.84, 127.79, 127.74, 127.69,

127.66, 127.59, 90.52, 83.16, 79.31, 77.59, 75.67, 75.22, 74.56, 73.51, 73.21, 72.63, 68.66, 66.85, 31.95, 29.67, 29.63, 29.39, 29.24, 28.96, 28.67, 22.73, 19.03, 14.17. **HRMS** (ESI): m/z calcd for $C_{46}H_{56}O_5Na$ ([M + Na]$^+$): 711.4020, found: 711.4021.



2k and **2s**: Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compounds **2k**[8] (43 mg, 35%) as a colorless oil and **2S** (17 mg, 17%) as a colorless oil, which solidified upon standing (NMR data, see next page).

2k: Rf = 0.38 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 18H), 7.24 – 7.16 (m, 2H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.91 – 4.83 (m, 3H), 4.74 (s, 2H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.54 (dd, *J* = 11.4, 4.7 Hz, 2H), 4.05 – 3.94 (m, 2H), 3.81 (dd, *J* = 10.8, 3.5 Hz, 1H), 3.75 – 3.64 (m, 3H), 0.26 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.80, 138.26, 137.94, 128.43, 128.39, 128.36, 128.11, 128.07, 128.03, 127.79, 127.74, 127.73, 127.71, 127.59, 100.14, 94.84, 82.79, 79.09, 77.41, 75.52, 75.26, 73.49, 72.46, 68.55, 67.03, 0.00. **HRMS** (ESI): m/z calcd for $C_{39}H_{44}O_5SiNa$ ([M + Na]$^+$): 643.2850, found: 643.2854.

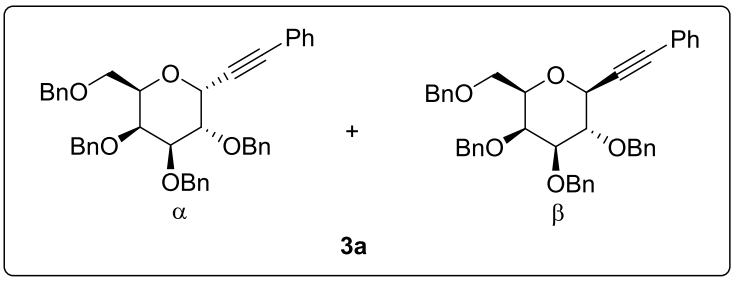


2l and **2s**: Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether = 1/12) to give compounds **2l** (55 mg,

42%) as a colorless oil and **2S** (15mg, 15%) as a colorless oil, which solidified upon standing.

2l, Rf = 0.29 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 23H), 7.13 (dd, *J* = 6.7, 2.7 Hz, 2H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.88 – 4.77 (m, 3H), 4.71 (s, 2H), 4.65 – 4.57 (m, 3H), 4.51 – 4.44 (m, 2H), 4.25 (t, *J* = 2.3 Hz, 2H), 4.03 – 3.91 (m, 2H), 3.74 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.70 – 3.59 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.73, 138.21, 137.95, 137.88, 137.33, 128.50, 128.45, 128.42, 128.41, 128.26, 128.02, 128.00, 127.97, 127.93, 127.89, 127.77, 127.74, 127.65, 85.49, 83.17, 81.42, 79.09, 77.45, 75.73, 75.24, 73.69, 73.55, 72.95, 71.42, 68.56, 66.79, 57.38. **HRMS** (ESI): m/z calcd for $C_{44}H_{44}O_6Na$ ($[M + Na]^+$): 691.3030, found: 691.3034.

2s: mp 60–63 ℃, Rf = 0.40 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 20H), 6.32 (s, 1H), 4.78 – 4.68 (m, 4H), 4.65 – 4.54 (m, 4H), 4.27 (d, *J* = 4.7 Hz, 1H), 4.10 (q, *J* = 2.9 Hz, 1H), 3.91 (dd, *J* = 6.7, 4.6 Hz, 1H), 3.79 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.70 (dd, *J* = 10.7, 3.5 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.91, 138.38, 138.04, 137.92, 137.17, 128.45, 128.43, 128.38, 128.34, 127.94, 127.92, 127.85, 127.83, 127.78, 127.70, 127.64, 127.62, 127.58, 76.23, 75.56, 74.24, 73.44, 72.87, 72.29, 71.01, 68.27. **HRMS** (ESI): m/z calcd for $C_{34}H_{34}O_5Na$ ($[M + Na]^+$): 545.2298, found: 545.2298.

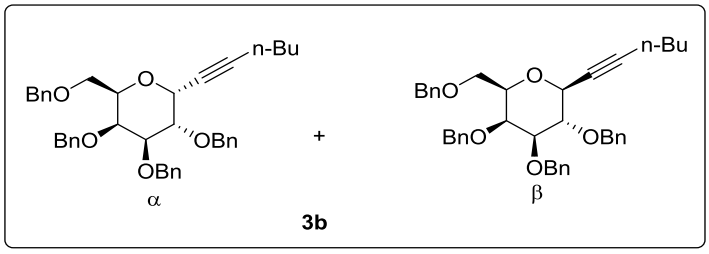


3a

3a (α:β = 96:4)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/12) to give compounds **3a** α-anomer[8] (108 mg, 86%) as a white solid and **3a** β-anomer (5 mg, 5%) as a colorless oil. **3a** (α-anomer), mp 104–110 ℃, Rf = 0.35 (Petroleum ether /EtOAc 10:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 16.0, 5.7 Hz, 6H), 7.33 (td, *J* = 10.7, 8.9, 4.6 Hz,

19H), 5.10 (d, *J* = 5.7 Hz, 1H), 5.00 (d, *J* = 11.4 Hz, 1H), 4.92 – 4.85 (m, 1H), 4.84 – 4.76 (m, 3H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.23 (dt, *J* = 15.0, 6.1 Hz, 2H), 4.08 – 3.97 (m, 2H), 3.61 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.76, 138.65, 138.57, 137.94, 132.05, 128.56, 128.44, 128.38, 128.35, 128.28, 128.26, 128.01, 127.78, 127.64, 127.62, 127.53, 122.59, 88.27, 84.38, 79.87, 75.73, 74.94, 74.90, 73.55, 73.07, 72.88, 72.72, 68.77, 67.90. **HRMS** (ESI): m/z calcd for $C_{42}H_{40}O_5Na$ ($[M + Na]^+$): 647.2768, found: 647.2773.

3a (β-anomer), Rf = 0.33 (Petroleum ether /EtOAc 10:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 25H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.97 (d, *J* = 11.6 Hz, 2H), 4.90 (d, *J* = 10.4 Hz, 2H), 4.75 (s, 2H), 4.64 (d, *J* = 11.6 Hz, 2H), 4.47 (d, *J* = 11.8 Hz, 2H), 4.41 (d, *J* = 11.8 Hz, 2H), 4.24 (d, *J* = 9.6 Hz, 2H), 4.10 (t, *J* = 9.5 Hz, 2H), 3.98 (d, *J* = 2.8 Hz, 1H), 3.64 – 3.55 (m, 4H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 138.57, 138.36, 138.20, 137.75, 131.82, 128.45, 128.40, 128.34, 128.33, 128.26, 128.20, 128.00, 127.80, 127.72, 127.62, 127.58, 127.49, 122.51, 86.46, 85.44, 83.43, 79.17, 75.83, 74.66, 73.74, 73.55, 72.75, 70.85, 68.57.



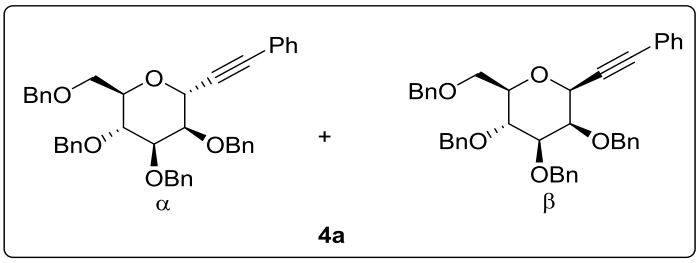
3b

3b (α:β = 98:2)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/12) to give compounds **3b** α-anomer (80 mg, 67%) as a colorless oil and **3b** β-anomer (1.8mg, 1.5%) as a colorless oil.

3b (α-anomer), Rf = 0.38 (Petroleum ether /EtOAc 10:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 20H), 4.93 (d, *J* = 11.4 Hz, 1H), 4.87 – 4.79 (m, 2H), 4.74 (dd, *J* = 11.9, 6.5 Hz, 3H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.39 (d, *J* = 11.8 Hz, 1H), 4.16 – 4.04 (m, 2H), 3.95 (d, *J* = 2.7 Hz, 1H), 3.87 (dd, *J* = 9.8, 2.9 Hz, 1H),

3.53 (d, *J* = 6.4 Hz, 2H), 2.25 (td, *J* = 6.9, 2.1 Hz, 2H), 1.54 – 1.35 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.86, 138.69, 138.60, 138.02, 128.42, 128.35, 128.29, 128.24, 127.95, 127.76, 127.59, 127.56, 127.54, 127.48, 89.15, 80.01, 75.73, 74.98, 74.87, 73.48, 73.11, 72.78, 72.23, 68.85, 67.55, 30.74, 22.00, 18.66, 13.68. **HRMS** (ESI): m/z calcd for $C_{40}H_{44}O_5Na$ ($[M + Na]^+$): 627.3081, found: 627.3083.

3b (β-anomer), Rf = 0.36 (Petroleum ether /EtOAc 10:1): ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 20H), 4.95 (dd, *J* = 11.1, 5.4 Hz, 2H), 4.86 (d, *J* = 10.5 Hz, 1H), 4.72 (s, 2H), 4.61 (d, *J* = 11.6 Hz, 2H), 4.44 (d, *J* = 11.7 Hz, 2H), 4.39 (d, *J* = 11.8 Hz, 2H), 3.99 (t, *J* = 2.0 Hz, 2H), 3.97 – 3.92 (m, 2H), 3.58 (t, *J* = 6.2 Hz, 2H), 3.53 – 3.46 (m, 3H), 3.42 (s, 1H), 2.25 – 2.21 (m, 2H), 1.49 (dd, *J* = 8.5, 6.6 Hz, 3H), 1.41 – 1.36 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 138.68, 138.44, 137.78, 128.38, 128.36, 128.27, 128.18, 128.15, 127.99, 127.56, 127.49, 127.47, 86.45, 83.40, 79.43, 75.63, 74.59, 73.71, 73.51, 72.66, 70.59, 68.50, 30.46, 22.02, 18.61, 13.56.



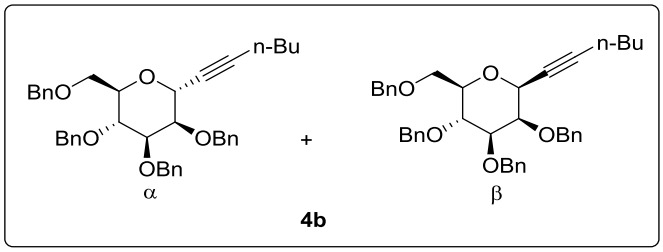
4a

4a (α:β = 95:5)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/12) to give compounds **4a** α-anomer[8] (93 mg, 75%) as a colorless oil and **4a** β-anomer (5 mg, 4%) as a colorless oil.

4a (α-anomer), Rf = 0.38 (Petroleum ether /EtOAc 9:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.40 – 7.23 (m, 21H), 7.21 – 7.13 (m, 2H), 5.04 (s, 1H), 4.91 (d, *J* = 10.6 Hz, 1H), 4.80 (d, *J* = 12.6 Hz, 1H), 4.75 – 4.61 (m, 4H), 4.55 (dd, *J* = 11.4, 5.8 Hz, 2H), 4.08 (dd, *J* = 27.5, 5.9 Hz, 3H), 3.91 (d, *J* = 2.7 Hz, 1H), 3.86 – 3.71 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.40, 138.36, 138.28, 138.08, 131.83, 128.82, 128.43, 128.40, 128.33, 128.31, 128.20, 127.96, 127.92, 127.73, 127.71, 127.52, 121.91, 89.05, 83.83, 80.02, 76.56, 75.43, 75.02, 74.88, 73.46, 72.06, 71.87, 69.28,

66.66. **HRMS** (ESI): m/z calcd for $C_{42}H_{40}O_5Na$ ([M + Na]$^+$): 647.2768, found: 647.2769.

4a (β-anomer), Rf = 0.36 (Petroleum ether /EtOAc 9:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.43 – 7.38 (m, 2H), 7.36 – 7.28 (m, 10H), 7.26 – 7.22 (m, 6H), 7.16 (dd, *J* = 7.3, 2.2 Hz, 2H), 5.05 (d, *J* = 2.6 Hz, 2H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.67 – 4.58 (m, 4H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.38 (d, *J* = 1.1 Hz, 1H), 4.06 (dd, *J* = 3.0, 1.1 Hz, 1H), 3.94 (t, *J* = 9.6 Hz, 1H), 3.79 (dd, *J* = 11.0, 1.9 Hz, 1H), 3.74 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.61 – 3.57 (m, 1H), 3.52 (ddd, *J* = 9.8, 5.8, 1.9 Hz, 1H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 138.44, 138.24, 138.18, 138.11, 131.78, 128.53, 128.41, 128.32, 128.27, 128.22, 128.11, 128.04, 127.68, 127.65, 127.56, 127.49, 127.46, 122.43, 85.72, 85.66, 83.59, 79.90, 77.20, 76.83, 75.82, 75.27, 74.69, 74.55, 73.47, 72.03, 69.86, 69.42.



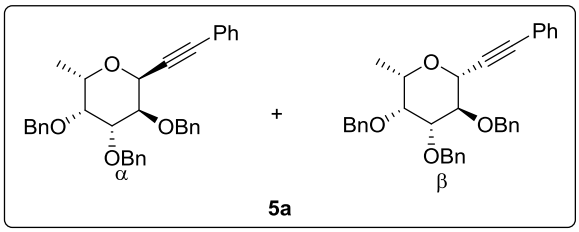
4b

4b (α:β = 92:8)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/12) to give compounds **4b** α-anomer[8] (75 mg, 62%) as a colorless oil and **4b** β-anomer (5 mg, 5%) as a colorless oil.

4b (α-anomer), Rf = 0.46 (Petroleum ether /EtOAc 9:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.24 (m, 18H), 7.17 (dd, *J* = 7.2, 2.4 Hz, 2H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.82 (q, *J* = 2.3 Hz, 1H), 4.76 (d, *J* = 12.6 Hz, 1H), 4.70 – 4.64 (m, 2H), 4.60 (s, 2H), 4.54 (dd, *J* = 11.4, 9.6 Hz, 2H), 4.07 – 3.94 (m, 3H), 3.79 (q, *J* = 3.7, 3.2 Hz, 2H), 3.73 (d, *J* = 10.7 Hz, 1H), 2.14 (td, *J* = 7.0, 2.1 Hz, 2H), 1.38 (dtd, *J* = 29.0, 9.9, 8.8, 4.8 Hz, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.49, 138.43, 138.40, 138.20, 128.36, 128.29, 128.14, 127.91, 127.84, 127.82, 127.64, 127.62, 127.60, 127.46, 90.11, 80.21, 76.66, 75.32, 75.07, 74.77, 74.37, 73.39, 71.93, 71.69, 69.32, 66.35, 30.52, 22.03,

18.48, 13.61. **HRMS** (ESI): m/z calcd for $C_{40}H_{44}O_5Na$ ($[M + Na]^+$): 627.3081, found: 627.3081.

4b (β-anomer), Rf = 0.44 (Petroleum ether /EtOAc 9:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 3H), 7.36 – 7.26 (m, 14H), 7.25 (d, *J* = 1.6 Hz, 3H), 7.18 – 7.09 (m, 2H), 5.00 (d, *J* = 1.7 Hz, 2H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.70 (s, 2H), 4.62 – 4.50 (m, 5H), 4.13 (td, *J* = 2.0, 1.0 Hz, 1H), 3.94 (dd, *J* = 3.0, 1.0 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.80 – 3.67 (m, 3H), 3.54 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.46 – 3.40 (m, 1H), 2.22 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.51 – 1.43 (m, 2H), 1.41 – 1.35 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 128.41, 128.39, 128.37, 128.34, 128.29, 128.24, 128.11, 128.04, 128.01, 127.91, 127.88, 127.75, 127.61, 127.58, 127.53, 127.43, 127.37, 86.82, 83.57, 79.68, 76.05, 75.22, 74.72, 74.48, 73.41, 71.88, 69.49, 69.48, 30.37, 22.04, 18.60, 13.58.

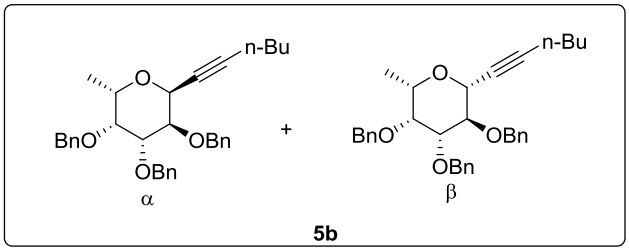


5a

5a (α:β = 97:3)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/10) to give compounds **5a** α-anomer[9] (93 mg, 90%) as a white solid and **5a** β-anomer (3 mg, 3%) as a colorless oil.

5a (α-anomer), mp 79–83 ℃. Rf = 0.42 (Petroleum ether /EtOAc 8:1): **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.24 (m, 20H), 5.03 (d, *J* = 5.7 Hz, 1H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.88 (d, *J* = 11.9 Hz, 1H), 4.81 – 4.71 (m, 3H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.14 (dq, *J* = 28.5, 6.0 Hz, 2H), 3.96 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.67 (d, *J* = 2.6 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.87, 138.60, 138.56, 131.98, 128.57, 128.49, 128.39, 128.33, 128.26, 128.25, 127.78, 127.66, 127.60, 127.53, 122.68, 87.87, 84.83, 80.17, 77.58, 75.62, 74.96, 73.22, 72.77, 69.90, 67.62, 16.97. **HRMS** (ESI): m/z calcd for $C_{35}H_{34}O_4Na$ ($[M + Na]^+$): 541.2349, found: 541.2346.

5a (β-anomer), Rf = 0.40 (Petroleum ether /EtOAc 8:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.38 (ddd, *J* = 7.5, 4.9, 2.0 Hz, 5H), 7.36 – 7.26 (m, 11H), 5.02 (t, *J* = 11.5 Hz, 2H), 4.91 (d, *J* = 10.5 Hz, 1H), 4.81 (d, *J* = 11.8 Hz, 1H), 4.75 (dd, *J* = 22.4, 11.7 Hz, 2H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.10 (t, *J* = 9.5 Hz, 1H), 3.64 (dd, *J* = 2.9, 1.0 Hz, 1H), 3.56 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.53 (dd, *J* = 6.4, 1.1 Hz, 1H), 1.22 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 138.44, 138.26, 131.82, 128.50, 128.42, 128.40, 128.34, 128.32, 128.18, 127.71, 127.65, 127.64, 127.53, 122.58, 86.65, 85.27, 83.79, 79.06, 76.56, 75.75, 74.77, 74.71, 72.96, 70.69, 17.28.



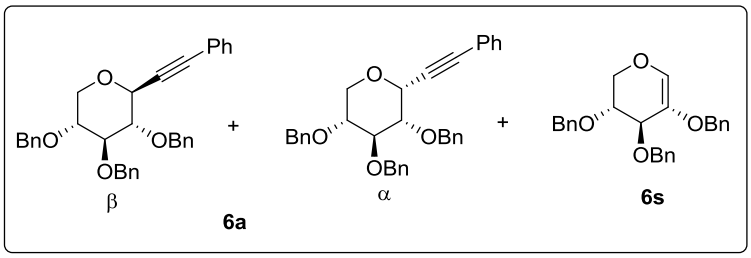
5b

5b (α:β = 97:3)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/10) to give compounds **5b** α-anomer (90 mg, 91%) as a white solid and **5b** β-anomer (3 mg, 3%) as a colorless oil.

5b (α-anomer), mp 70–73 ℃, Rf = 0.43 (Petroleum ether /EtOAc 8:1)**: ^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.33 (dddd, *J* = 29.4, 16.1, 7.3, 3.3 Hz, 15H), 4.97 (d, *J* = 11.6 Hz, 1H), 4.87 (d, *J* = 11.9 Hz, 1H), 4.81 (d, *J* = 5.7 Hz, 1H), 4.77 – 4.70 (m, 3H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.10 – 3.99 (m, 2H), 3.86 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.63 (d, *J* = 2.7 Hz, 1H), 2.25 (td, *J* = 6.9, 2.1 Hz, 2H), 1.45 (dtd, *J* = 32.4, 9.9, 8.8, 4.7 Hz, 4H), 1.13 (d, *J* = 6.4 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.99, 138.63, 138.61, 128.56, 128.35, 128.27, 128.20, 127.76, 127.61, 127.54, 127.48, 88.66, 80.31, 77.64, 75.61, 75.26, 74.87, 73.25, 72.67, 69.33, 67.25, 30.76, 21.97, 18.62, 16.93, 13.65. **HRMS** (ESI): m/z calcd for $C_{33}H_{38}O_4Na$ ($[M + Na]^+$): 521.2662, found: 521.2669.

5b (β-anomer), Rf = 0.40 (Petroleum ether /EtOAc 8:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 14H), 5.01 – 4.93 (m, 2H), 4.87 (d, *J* = 10.5 Hz, 1H), 4.81 – 4.68 (m,

3H), 4.00 – 3.91 (m, 2H), 3.60 (dd, *J* = 3.0, 1.0 Hz, 1H), 3.52 – 3.42 (m, 2H), 2.27 – 2.19 (m, 2H), 1.51 – 1.44 (m, 2H), 1.43 – 1.35 (m, 2H), 1.19 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 138.51, 128.43, 128.39, 128.27, 128.16, 128.14, 127.62, 127.59, 127.55, 127.50, 86.24, 83.77, 79.32, 76.60, 75.55, 74.62, 74.47, 72.89, 70.41, 30.47, 22.05, 18.64, 17.30, 13.57.

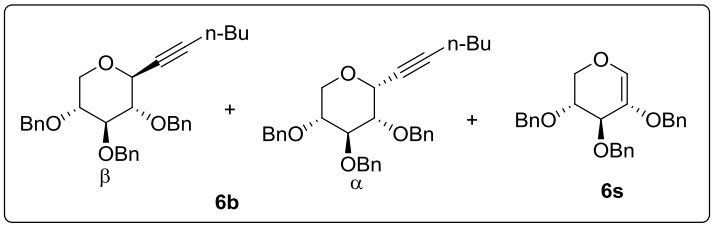


6a (α/β = 20/80)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/15) to give compounds **6a** (81 mg, 81%) as a colorless oil and **6s** (5 mg, 10%) as a colorless oil.

6a (α/β = 20/80), Rf = 0.39 (Petroleum ether /EtOAc 12:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 5.1 Hz, 1H), 7.46 – 7.24 (m, 28H), 5.03 (d, *J* = 10.5 Hz, 1H), 4.90 (dt, *J* = 9.7, 4.4 Hz, 4H), 4.85 (d, *J* = 3.2 Hz, 1H), 4.74 (dd, *J* = 6.9, 4.7 Hz, 3H), 4.64 (d, *J* = 11.6 Hz, 2H), 4.20 (d, *J* = 8.5 Hz, 1H), 4.02 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.91 (d, *J* = 9.0 Hz, 1H), 3.87 – 3.77 (m, 1H), 3.63 (dt, *J* = 14.5, 7.3 Hz, 4H), 3.25 (t, *J* = 10.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.82, 138.63, 138.26, 138.21, 138.07, 138.04, 132.02, 131.77, 128.72, 128.63, 128.52, 128.49, 128.45, 128.43, 128.37, 128.36, 128.27, 128.25, 128.09, 127.98, 127.95, 127.91, 127.88, 127.86, 127.81, 127.71, 127.62, 122.43, 122.19, 89.18, 86.19, 85.93, 85.22, 83.78, 82.17, 82.12, 78.93, 77.88, 77.75, 77.39, 75.78, 75.72, 75.66, 73.63, 73.52, 72.91, 70.94, 68.18, 67.54, 63.60. **HRMS** (ESI): m/z calcd for $C_{34}H_{32}O_4Na$ ($[M + Na]^+$): 527.2193, found: 527.2197.

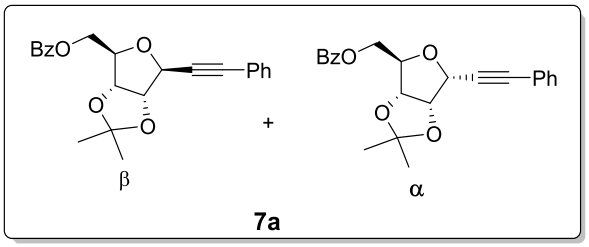
6s, Rf = 0.36 (Petroleum ether /EtOAc 12:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 15H), 6.41 (s, 1H), 4.74 – 4.63 (m, 5H), 4.59 (d, *J* = 11.1 Hz, 3H), 4.08 (dt, *J* = 11.7, 2.1 Hz, 1H), 3.96 (t, *J* = 1.9 Hz, 1H), 3.79 (dd, *J* = 11.7, 1.5 Hz, 1H), 3.64 (q, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.49, 138.31, 137.79, 137.32, 129.18,

128.52, 128.40, 128.38, 127.92, 127.88, 127.81, 127.79, 127.69, 127.58, 72.44, 71.78, 71.07, 70.98, 70.84, 63.41. **HRMS** (ESI): m/z calcd for $C_{26}H_{26}O_4Na$ ($[M + Na]^+$): 425.1723, found: 425.1725.



6b (α/β = 31/69)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/15) to give compounds **6b** (61 mg, 63%) as a colorless oil and **6s** (16 mg, 20%) as a colorless oil.

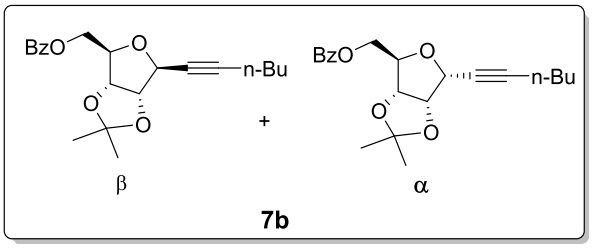
6b (α/β = 31/69), Rf = 0.42 (Petroleum ether /EtOAc 12:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (tq, *J* = 12.6, 7.9 Hz, 20H), 4.95 (t, *J* = 10.0 Hz, 1H), 4.91 – 4.78 (m, 4H), 4.78 – 4.54 (m, 5H), 3.96 (dd, *J* = 11.5, 6.2 Hz, 2H), 3.83 (d, *J* = 9.0 Hz, 1H), 3.80 – 3.69 (m, 1H), 3.61 (td, *J* = 9.5, 5.2 Hz, 1H), 3.57 – 3.43 (m, 3H), 3.18 (t, *J* = 10.9 Hz, 1H), 2.32 – 2.20 (m, 3H), 1.46 (ddq, *J* = 36.2, 21.9, 7.3, 6.8 Hz, 7H), 0.89 (dt, *J* = 20.7, 7.2 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.67, 138.24, 138.10, 128.49, 128.47, 128.39, 128.35, 128.11, 128.05, 127.96, 127.89, 127.88, 127.85, 127.79, 127.76, 127.65, 127.59, 86.95, 85.22, 82.42, 82.19, 78.97, 77.92, 77.24, 76.74, 75.64, 75.53, 74.35, 73.59, 73.44, 72.81, 70.68, 67.98, 67.15, 63.10, 30.72, 30.49, 22.01, 18.68, 18.49, 13.66, 13.59. **HRMS** (ESI): m/z calcd for $C_{32}H_{36}O_4Na$ ($[M + Na]^+$): 507.2506, found: 507.2506.



7a (α:β = 34:66)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/10) to give compounds **7a** β-anomer[8] (34 mg, 45%) as a colorless oil and **7a** α-anomer (16 mg, 21%) as a colorless oil.

7a (β-anomer), Rf = 0.45 (Petroleum ether /EtOAc 6:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 3H), 7.29 (d, *J* = 7.4 Hz, 2H), 4.99 (p, *J* = 2.7 Hz, 1H), 4.91 – 4.84 (m, 1H), 4.62 (dd, *J* = 11.2, 6.0 Hz, 1H), 4.58 – 4.46 (m, 2H), 1.57 (s, 2H), 1.38 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.23, 133.16, 131.65, 129.78, 129.69, 128.72, 128.39, 128.29, 121.99, 113.95, 87.29, 86.54, 86.23, 83.69, 82.98, 75.41, 64.32, 26.94, 25.37. **HRMS** (ESI): m/z calcd for $C_{23}H_{22}O_5Na$ ($[M + Na]^+$): 401.1359, found: 401.1356.

7a (α-anomer), Rf = 0.25 (Petroleum ether /EtOAc 6:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.27 (m, 7H), 5.09 (d, *J* = 4.7 Hz, 1H), 4.93 (dd, *J* = 6.1, 4.7 Hz, 1H), 4.85 (dd, *J* = 6.1, 1.5 Hz, 1H), 4.59 – 4.46 (m, 2H), 4.40 (dd, *J* = 11.9, 4.2 Hz, 1H), 1.64 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.15, 133.40, 131.95, 129.64, 129.46, 128.61, 128.58, 128.20, 122.43, 114.05, 88.59, 82.99, 82.76, 82.03, 81.63, 73.65, 64.69, 26.51, 25.55. **HRMS** (ESI): m/z calcd for $C_{23}H_{22}O_5Na$ ($[M + Na]^+$): 401.1359, found: 401.1358.

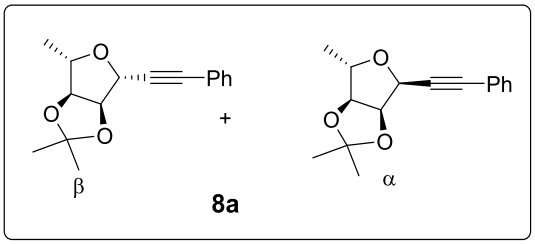


7b

7b (α:β = 31:69)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/10) to give compounds **7b** β-anomer (28 mg, 39%) as a colorless oil and **7b** α-anomer (12 mg, 17%) as a colorless oil.

7b (β-anomer), Rf = 0.38 (Petroleum ether /EtOAc 9:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.61 – 7.51 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.81 (qd, *J* = 6.2, 2.2 Hz, 2H), 4.74 (q, *J* = 2.2 Hz, 1H), 4.55 (dd, *J* = 11.4, 6.2 Hz, 1H), 4.51 – 4.38 (m, 2H), 2.16 (td, *J* = 7.0, 2.1 Hz, 2H), 1.54 (s, 3H), 1.48 – 1.36 (m, 4H), 1.35 (s, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.20, 133.13, 129.78, 128.38, 113.81, 88.43, 86.66, 83.42, 82.95, 77.43, 75.07, 64.40, 30.35, 26.91, 25.35, 21.95, 18.44, 13.55. **HRMS** (ESI): m/z calcd for $C_{21}H_{26}O_5Na$ ($[M + Na]^+$): 381.1672, found: 381.1672.

7b (α-anomer), Rf = 0.28 (Petroleum ether /EtOAc 9:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.82 (ddt, *J* = 11.7, 7.6, 3.9 Hz, 3H), 4.51 – 4.29 (m, 3H), 2.29 (td, *J* = 7.1, 1.8 Hz, 2H), 1.59 (s, 3H), 1.56 – 1.48 (m, 2H), 1.47 – 1.41 (m, 2H), 1.39 (s, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.14, 133.35, 129.63, 129.47, 128.54, 113.70, 89.75, 82.72, 81.93, 81.44, 77.22, 73.69, 73.30, 64.64, 30.54, 26.43, 25.43, 21.92, 18.69, 13.61. **HRMS** (ESI): m/z calcd for $C_{21}H_{26}O_5Na$ ($[M + Na]^+$): 381.1672, found: 381.1670.

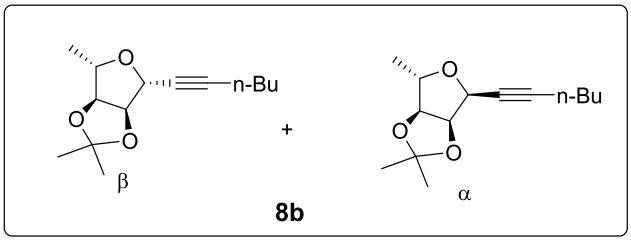


8a

8a (α:β = 7:93)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/40) to give compound **8a** β-anomer[8] (43 mg, 83%) as a colorless oil and **8a** α-anomer (3 mg, 6%) as a colorless oil.

8a (β-anomer), Rf = 0.45 (Petroleum ether /EtOAc 16:1): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.3, 2.4 Hz, 2H), 7.30 (dd, *J* = 5.5, 1.9 Hz, 3H), 4.91 (dd, *J* = 6.5, 3.2 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 4.51 (dd, *J* = 6.5, 3.0 Hz, 1H), 4.20 (dd, *J* = 6.7, 3.0 Hz, 1H), 1.42 (d, *J* = 6.7 Hz, 3H), 1.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.64, 128.59, 128.27, 122.33, 114.19, 86.87, 86.78, 86.64, 86.31, 81.89, 74.45, 26.97, 25.33, 19.33. **HRMS** (ESI): m/z calcd for $C_{16}H_{18}O_3Na$ ($[M + Na]^+$): 281.1148, found: 281.1149.

8a (α-anomer)**,** Rf = 0.21 (Petroleum ether /EtOAc 16:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.33 – 7.27 (m, 3H), 4.88 – 4.82 (m, 2H), 4.49 (dd, *J* = 6.2, 1.8 Hz, 1H), 4.35 (dd, *J* = 6.9, 1.8 Hz, 1H), 1.62 – 1.59 (m, 3H), 1.39 – 1.37 (m, 3H), 1.22 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 131.90, 128.43, 128.13, 122.61, 114.04, 88.27, 86.10, 83.36, 81.76, 79.38, 71.31, 26.44, 25.48, 16.93.



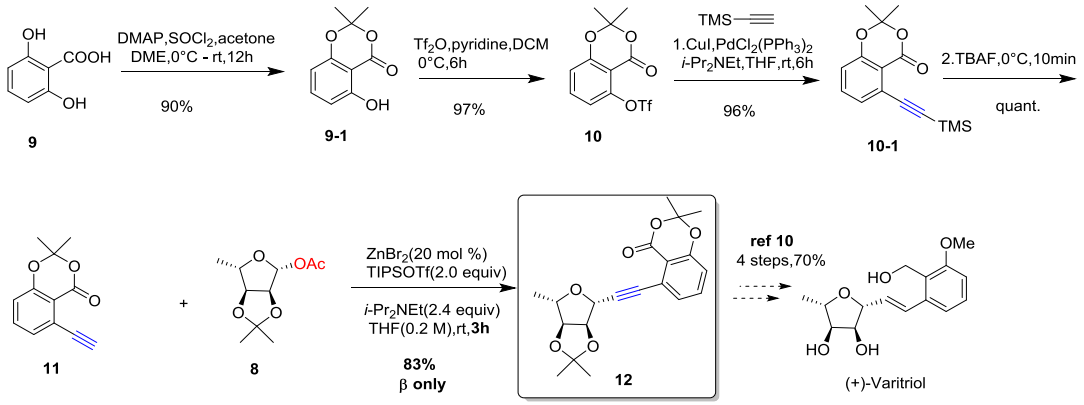
8b

8b (α:β = 8:92)**:** Prepared via General Procedure. The crude material was purified by silica gel chromatography (EtOAc/Petroleum ether =1/40) to give compound **8b** β-anomer (39 mg, 82%) as a colorless oil and **8b** α-anomer (3 mg, 6%) as a colorless oil.

8b (β-anomer), Rf = 0.5 (Petroleum ether /EtOAc 18:1) : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.74 (dd, *J* = 6.6, 3.5 Hz, 1H), 4.53 (dt, *J* = 4.0, 2.2 Hz, 1H), 4.43 (dd, *J* = 6.6, 3.3 Hz, 1H), 4.08 (dd, *J* = 6.7, 3.3 Hz, 1H), 2.21 (td, *J* = 7.0, 2.1 Hz, 2H), 1.52 (s, 3H), 1.49 – 1.43 (m, 2H), 1.41 (d, *J* = 7.2 Hz, 2H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 114.23, 87.70, 86.88, 86.25, 81.45, 77.73, 74.16, 30.46, 27.00, 25.34, 21.94, 19.26, 18.48, 13.58. **HRMS** (ESI): m/z calcd for $C_{14}H_{22}O_3Na$ ($[M + Na]^+$): 261.1461, found: 261.1462.

8b (α-anomer)**,** Rf = 0.22 (Petroleum ether /EtOAc 18:1): **^{1}H NMR** (800 MHz, $CDCl_3$) δ 4.72 (dd, *J* = 6.2, 4.6 Hz, 1H), 4.62 (ddd, *J* = 4.1, 2.1, 1.4 Hz, 1H), 4.44 (dd, *J* = 6.2, 1.6 Hz, 1H), 4.30 – 4.25 (m, 1H), 2.27 (dd, *J* = 7.2, 2.1 Hz, 2H), 1.57 – 1.56 (m, 3H), 1.54 – 1.49 (m, 2H), 1.42 (dt, *J* = 8.2, 7.2 Hz, 2H), 1.36 – 1.35 (m, 3H), 1.16 (d, *J* = 6.9 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (200 MHz, $CDCl_3$) δ 113.58, 89.28, 86.07, 86.07, 81.65, 79.16, 70.86, 30.57, 26.35, 25.34, 21.90, 18.67, 16.79, 13.59.

3.3 Formal Synthesis of (+)-Varitriol



9-1: A solution of thionyl chloride (1.87 mL, 26 mmol) in dimethoxyethane (3 mL) was added dropwise to a stirred solution of 2,6-dihydoxybenzoic acid (3.08 g, 20 mmol), DMAP (122 mg, 1 mmol) and acetone (1.85 mL, 26 mmol) in dimethoxyethane (12 mL) at 0 ℃ under Argon atmosphere. After the addition, the temperature was increased to rt and stirred overnight. The solvents were removed in vacuo and the remaining residue was dissolved in saturated aqueous $NaHCO_3$, extracted with EtOAc, and washed with brine. The organic phase was dried by Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography (EtOAc/Petroleum ether = 1/10) afforded **9-1**[10] (3.5 g, 90%) as a white solid. mp 61–63 ℃, Rf = 0.7 (Petroleum ether /EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.39 (t, *J* = 8.3 Hz, 1H), 6.64 – 6.55 (m, 1H), 6.45 – 6.38 (m, 1H), 1.73 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.47, 161.39, 155.56, 137.93, 110.79, 107.25, 107.13, 99.34, 25.64.

10: Anhydrous pyridine (1.25 mL) and trifluoromethansulfonic anhydride (1.05 mL, 6.18 mmol) were successively added to a solution of **9-1** (1 g, 5.15 mmol) in dichloromethane (10 mL). The mixture was allowed to stir at 0 ℃ for 6h. The solvents were removed in vacuo and the remaining residue was dissolved in EtOAc, and washed with 1 N HCl. and the combined organic layers were washed with brine, dried and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc:hexane = 1:6) to afford **10**[10] as a white solid (1.63 g, 97%). mp 110–113 ℃, Rf = 0.5 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.62 (t, *J* = 8.3 Hz, 1H), 7.12 – 7.04 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 1.77 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.43, 157.10, 148.63, 136.26, 120.34, 117.89, 117.15, 116.55, 108.31, 106.88, 25.51.

10-1: To a solution of **10** (500 mg, 1.53 mmol) in anhydrous THF (5 ml) was added CuI (15 mg, 0.075 mmol), $PdCl_2(PPh_3)_2$ (55 mg, 0.075 mmol), *i*-Pr_2NEt (1.21 ml, 7.3 mmol) and trimethylsilylacetylene (0.44 ml, 3.06 mmol) at rt, and the mixture was stirred vigorously for 24h under Argon atmosphere. The reaction mixture was quenched with saturated aq. NH_4Cl, extracted with EtOAc, and washed with brine. The organic phase was dried by Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography (EtOAc/Petroleum ether = 1/20) afforded **10-1**[11] (400 mg, 96%) as a light yellow oil. Rf = 0.6 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.73 (dd, *J* = 8.2, 1.1 Hz, 1H), 1.52 (s, 6H), 0.10 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.59, 156.41, 134.77, 129.22, 124.96, 117.51, 114.30, 105.57, 102.39, 102.27, 25.69, -0.28.

11:To a solution of **10-1** (100 mg, 0.36 mmol) in anhydrous THF (2 ml) was added tetrabutylammonium fluoride (1 M in THF, 0.47 ml, 0.47 mmol) at 0 ℃ under Argon atmosphere. The mixture is stirred for 10 min and the solvents were removed in vacuo. Purification by flash chromatography (EtOAc/Petroleum ether = 1/10) afforded **11**[11] (72 mg, quant) as a white solid. mp 81–83 ℃, Rf = 0.5 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.97 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.53 (s, 1H), 1.73 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.81, 156.56, 135.01, 129.70, 124.05, 118.05, 114.55, 105.85, 84.15, 81.13, 25.69. **HRMS** (ESI): m/z calcd for $C_{12}H_{10}O_3Na$ ($[M + Na]^+$): 225.0522, found: 225.0525.

12: To a solution of L-furanossly acetate **8** (43 mg, 0.2 mmol) and $ZnBr_2$ (9 mg, 20 % mol) in dry THF (1 mL, 0.2 M) was added alkyne **11** (52 mg, 0.26 mmol), *i*-Pr_2NEt (0.48 mmol, 80 µl, 2.4 equiv) and TIPSOTf (0.4 mmol, 107µl, 2 equiv) at rt (20 ℃ -

25 ℃) under Argon atmosphere. The reaction was stirred at rt for 3 h, then silica gel (200 - 300 mesh, 500mg) was added and concentrated *in vacuo* to afford yellow powder, which was purified by flash column chromatography (EtOAc/Petroleum ether = 1/10) afforded **12**[8] (59 mg, 83%) as a colorless oil. Rf = 0.35 (Petroleum ether /EtOAc 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.15 (m, 1H), 6.96 – 6.88 (m, 1H), 5.07 (dd, *J* = 6.3, 2.4 Hz, 1H), 4.89 (d, *J* = 2.4 Hz, 1H), 4.57 (dd, *J* = 6.3, 2.4 Hz, 1H), 4.25 (dd, *J* = 6.8, 2.4 Hz, 1H), 1.69 (s, 6H), 1.51 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.68, 156.53, 134.95, 128.71, 124.37, 117.74, 114.15, 113.57, 105.73, 94.02, 86.65, 86.40, 84.16, 82.53, 74.66, 26.86, 25.76, 25.63, 25.25, 19.39. **HRMS** (ESI): m/z calcd for $C_{20}H_{22}O_6Na$ ($[M + Na]^+$): 381.1309, found: 381.1308.

4 References

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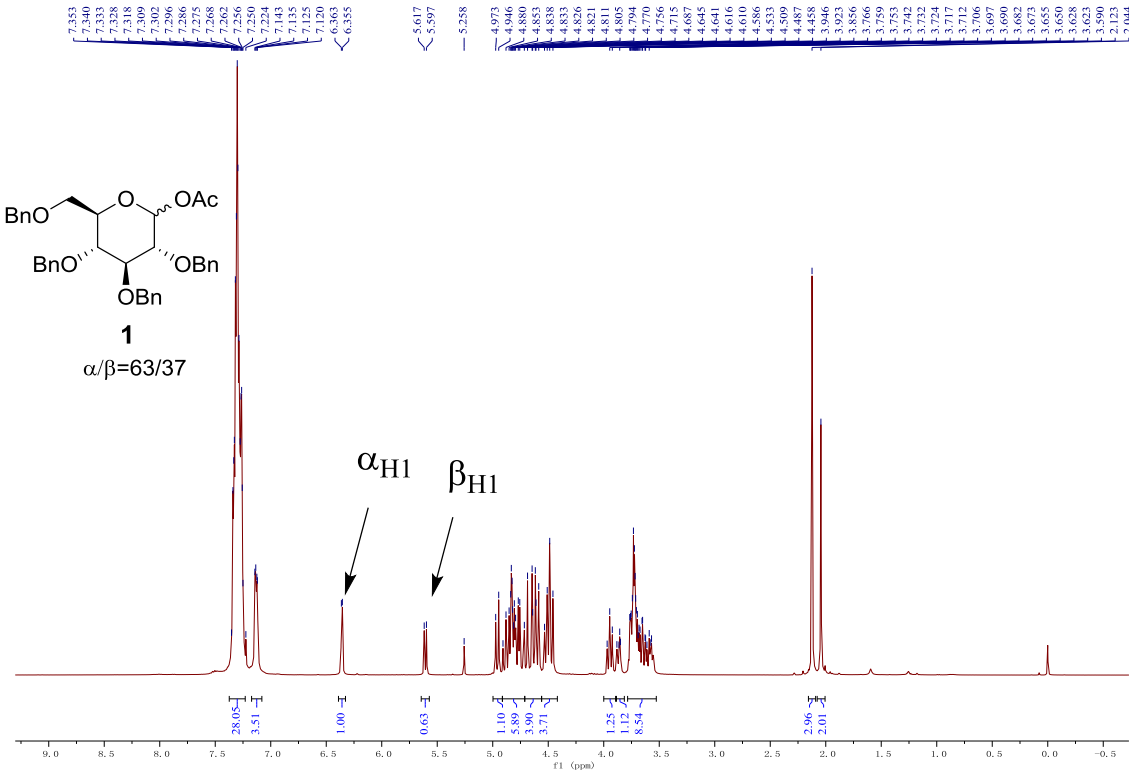
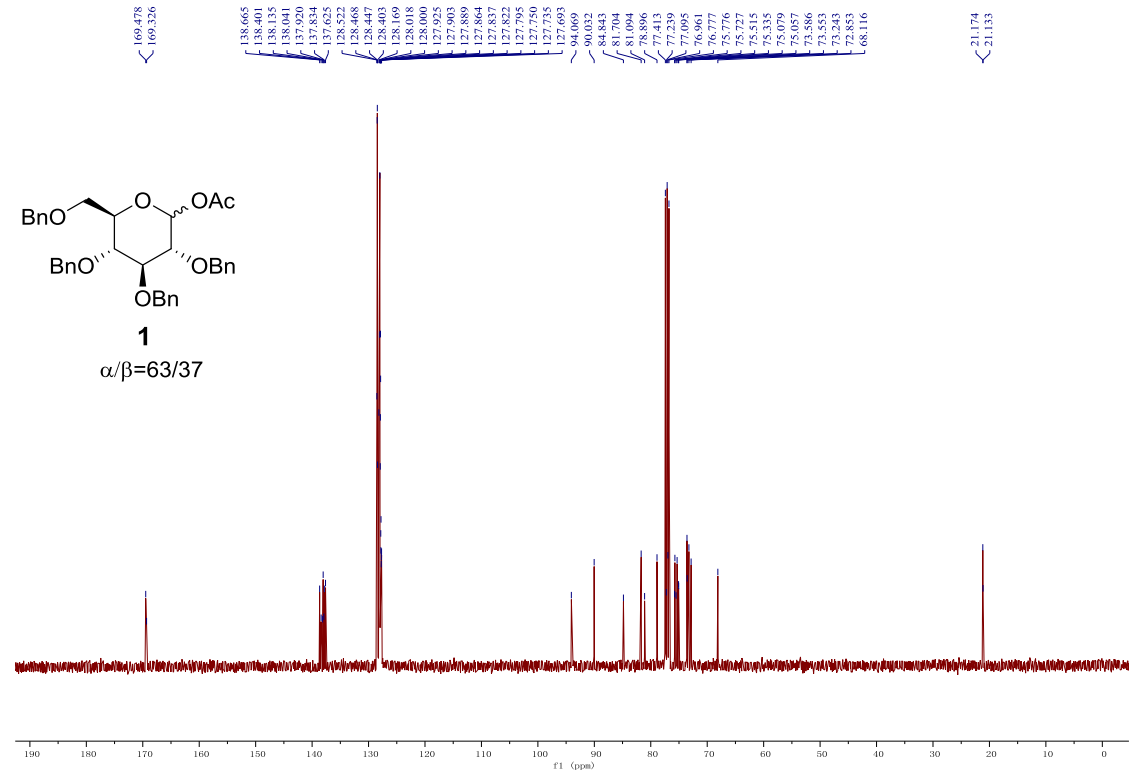
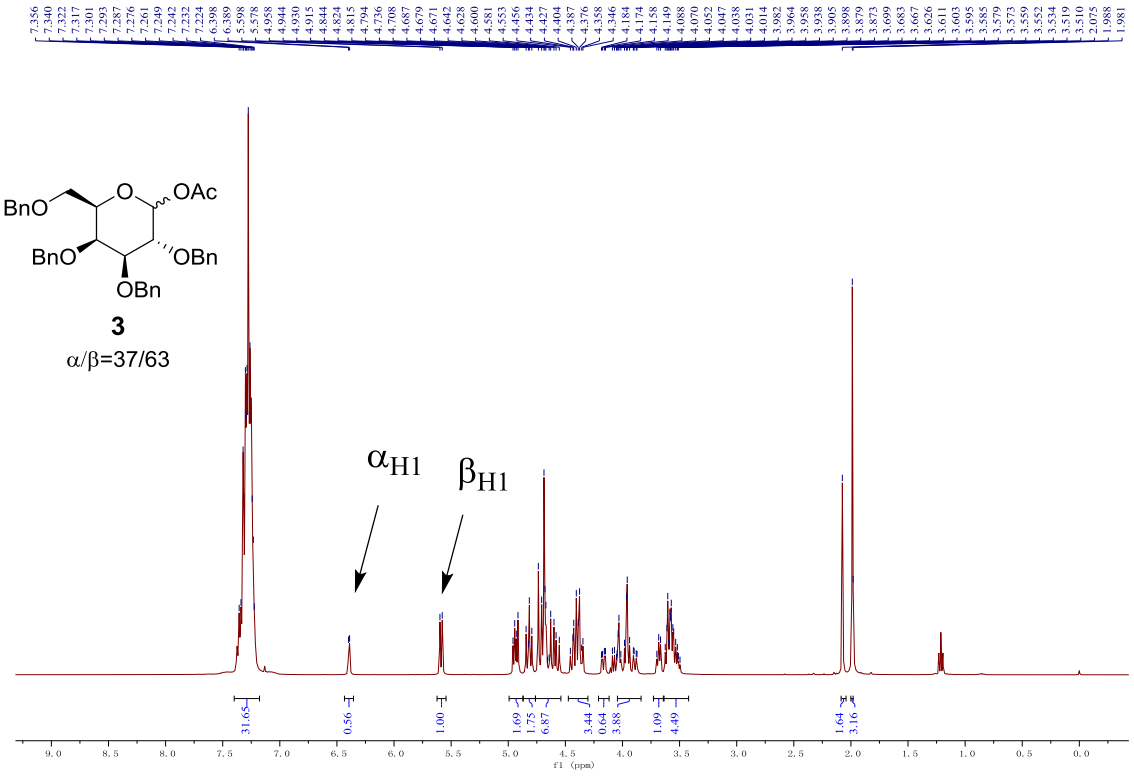
5 NMR Spectra of Products



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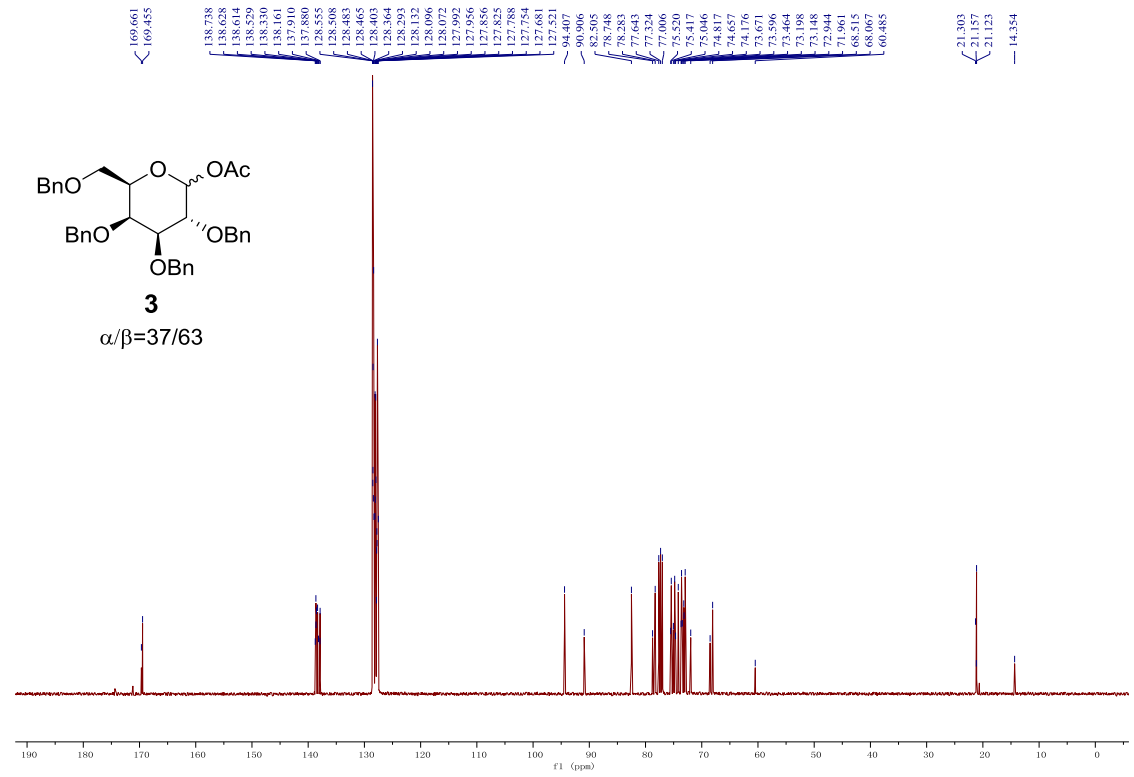
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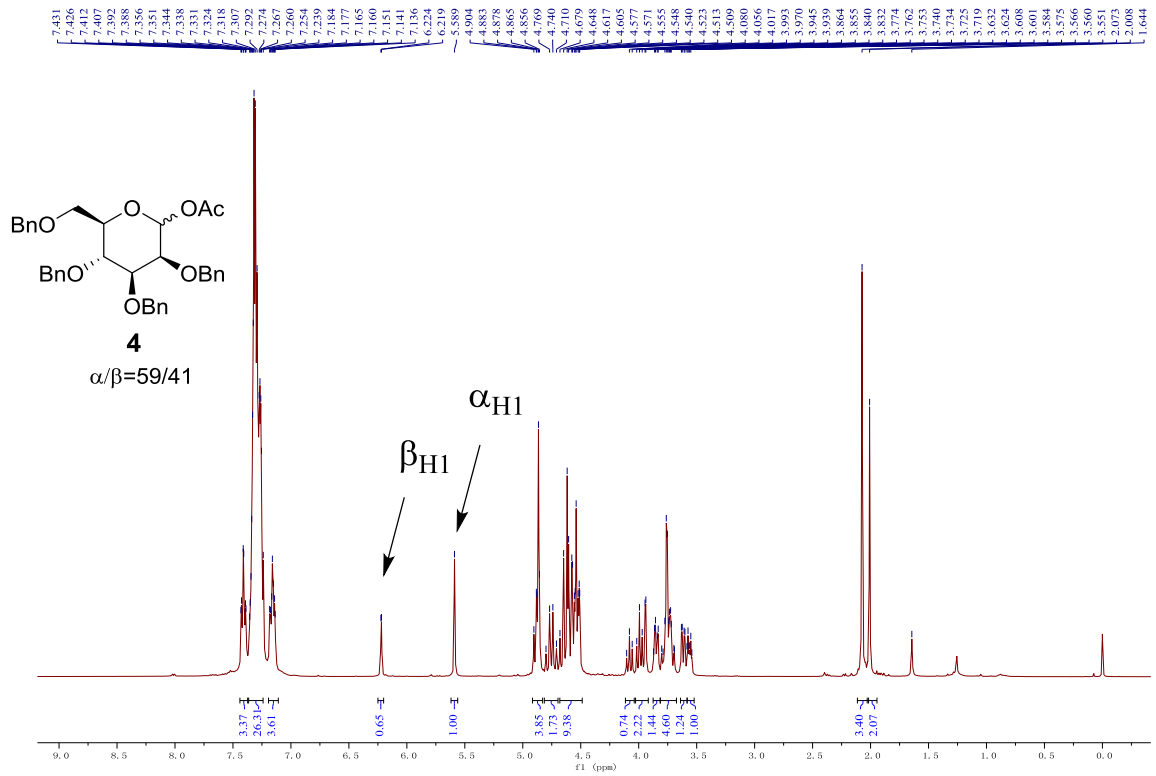
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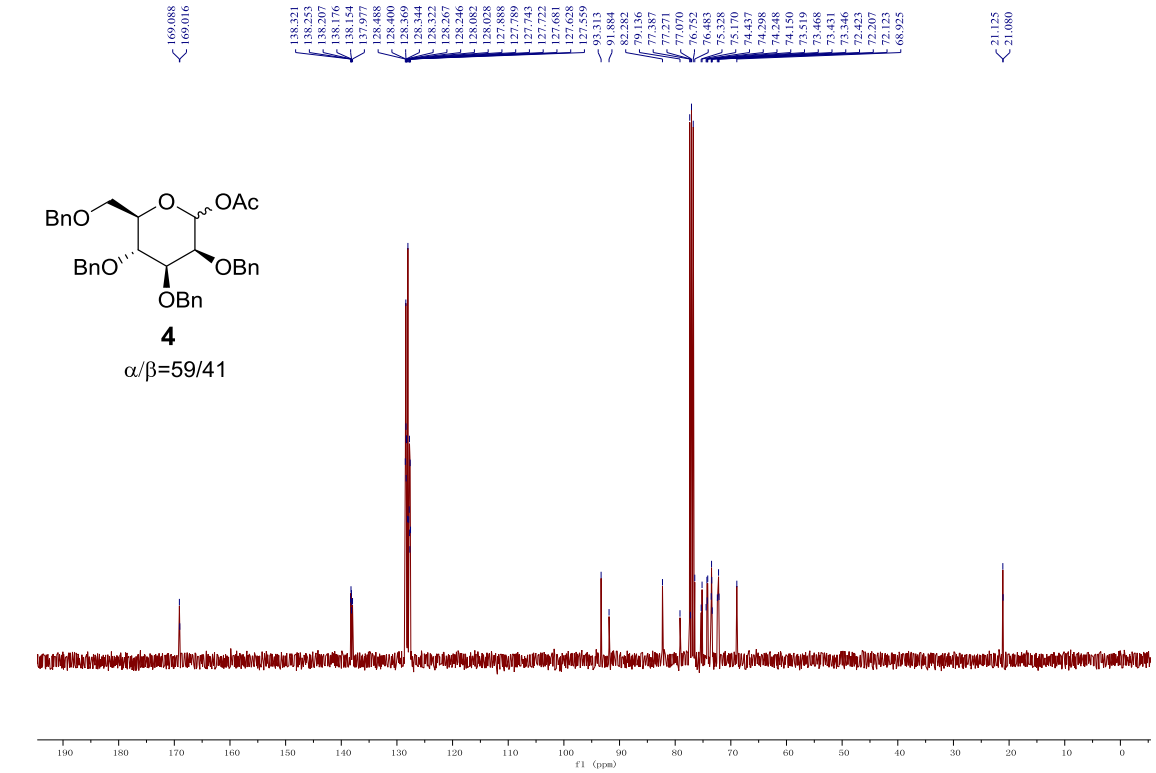
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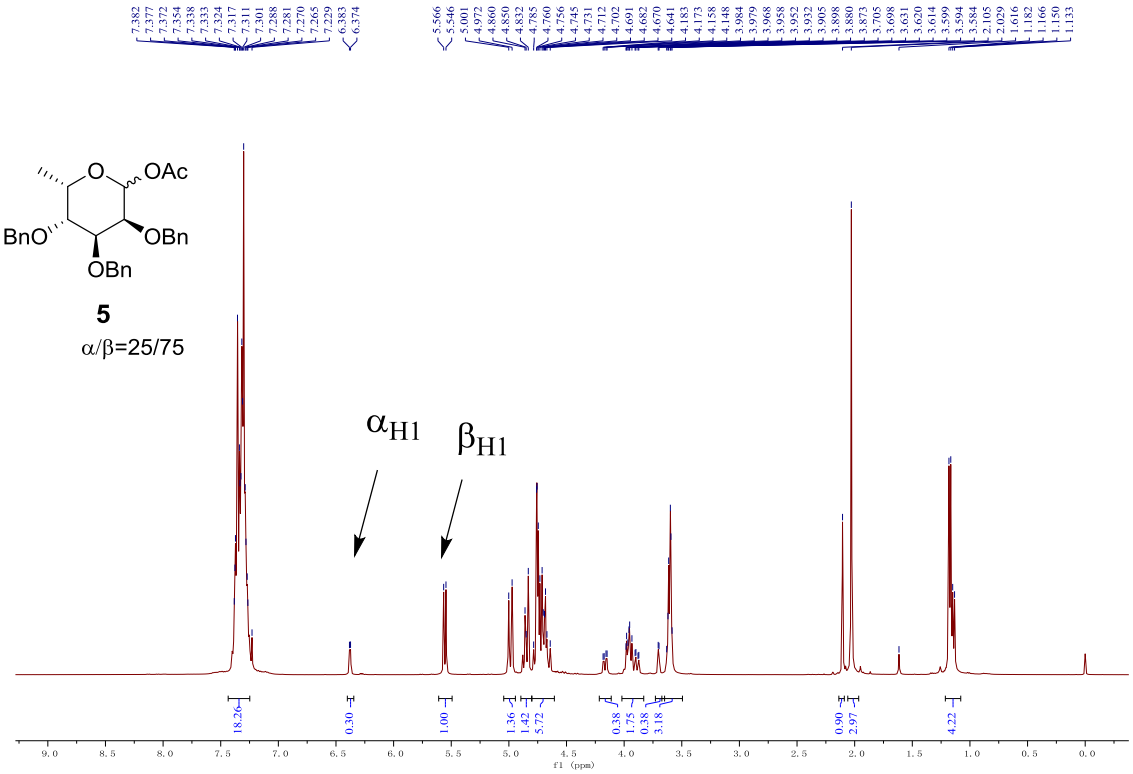
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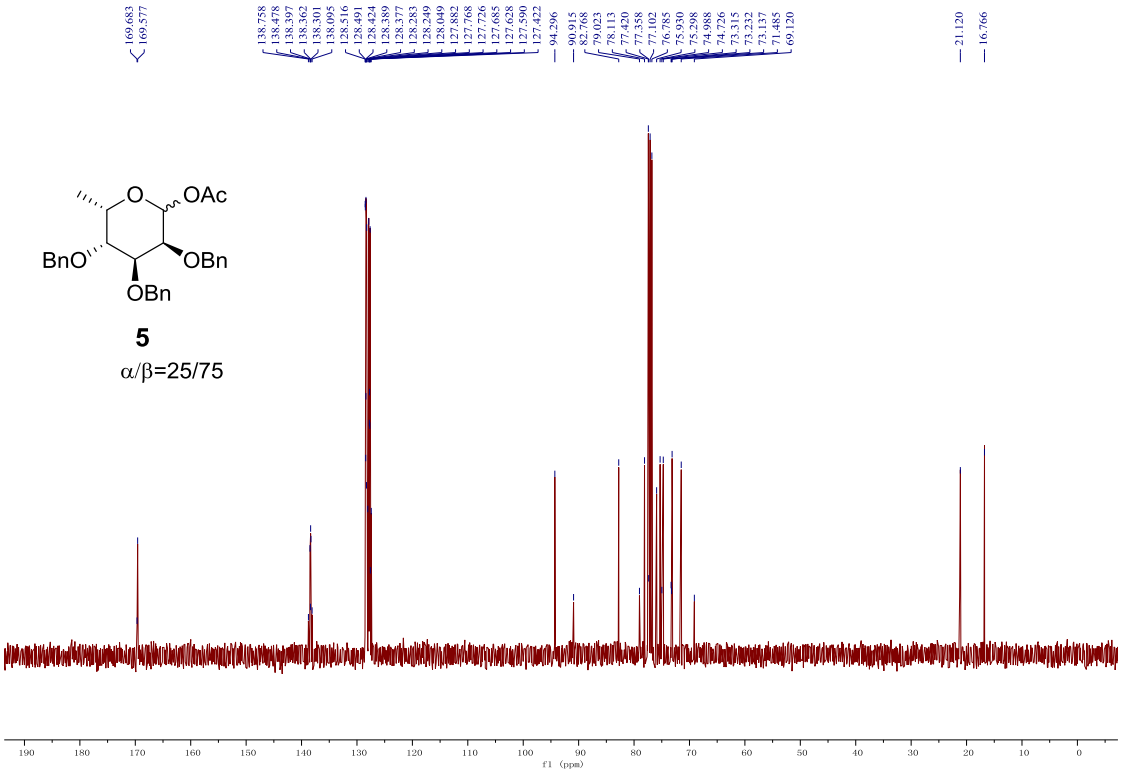
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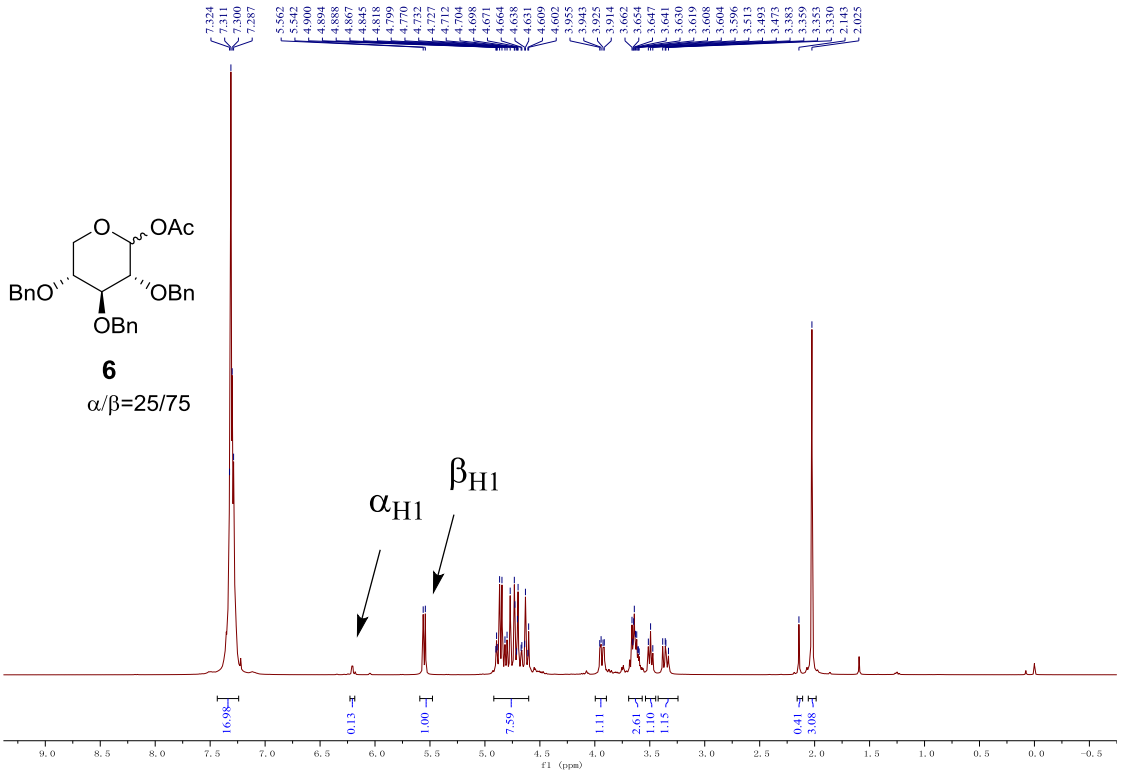
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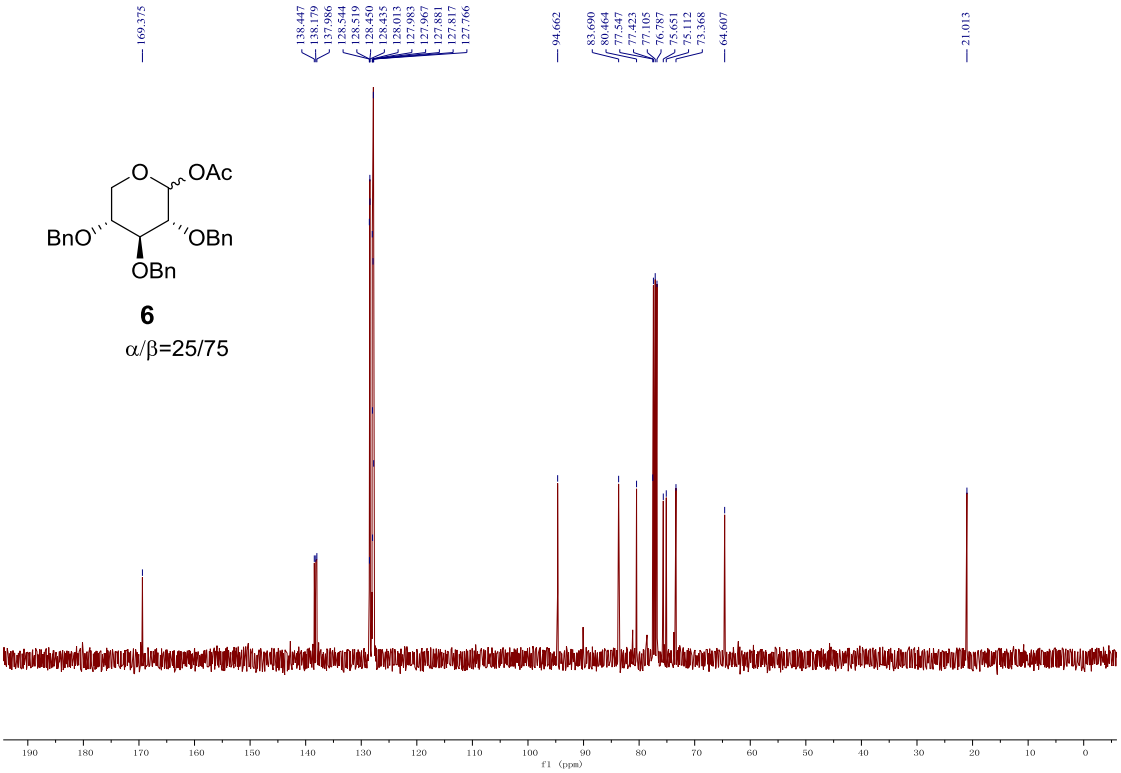
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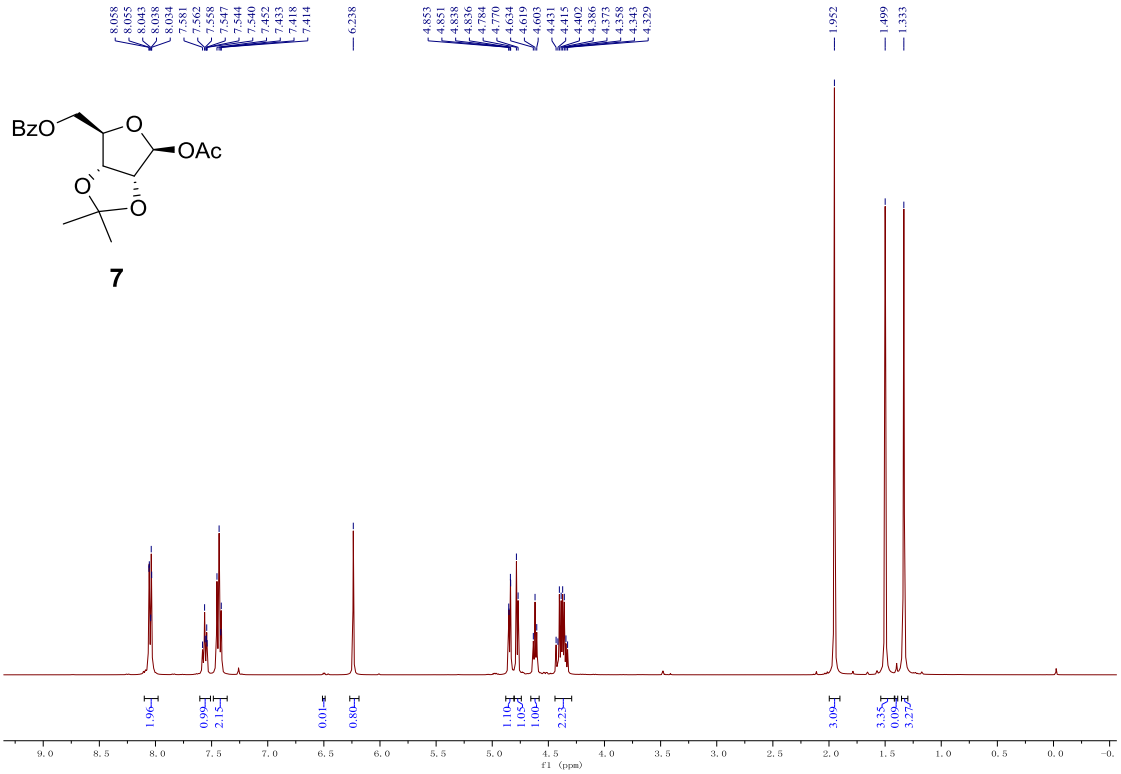
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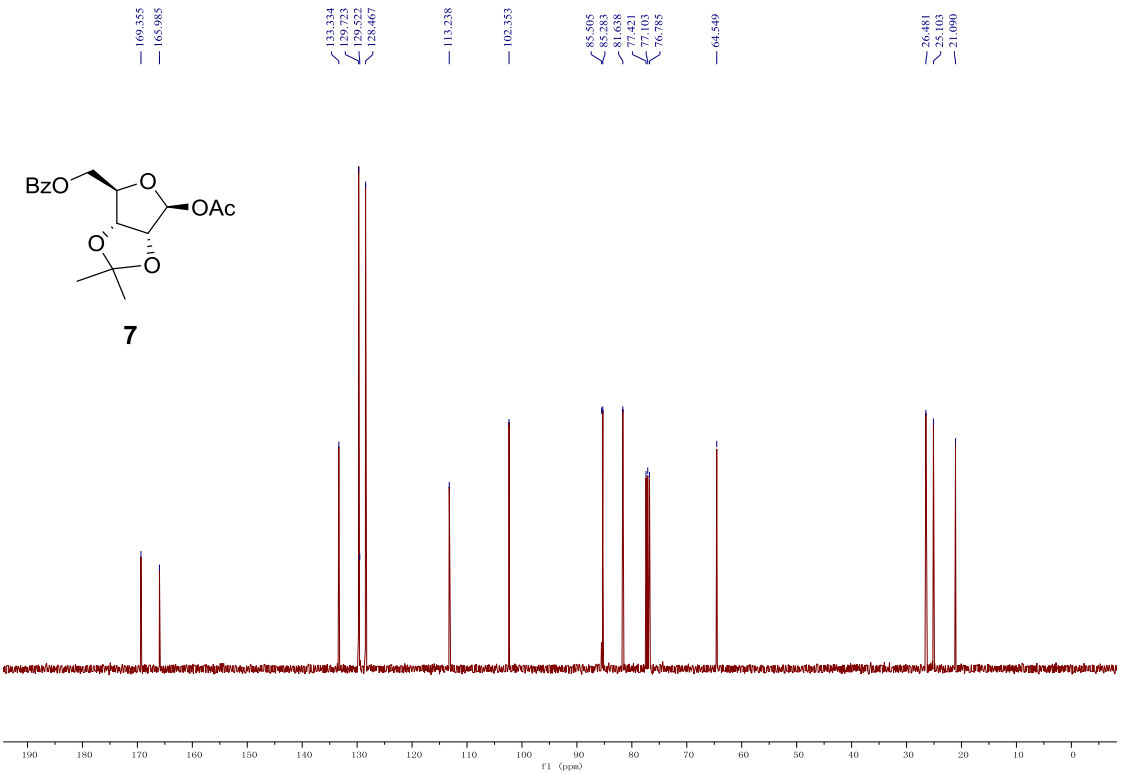
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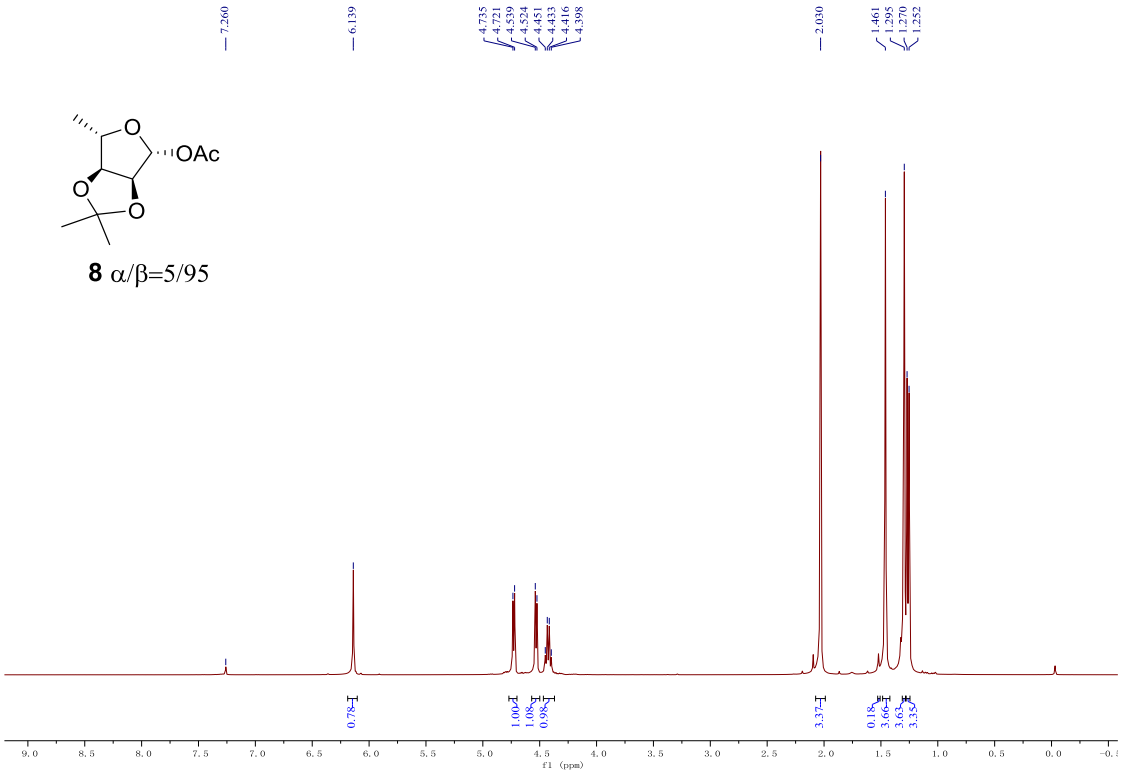
f1 (ppm)



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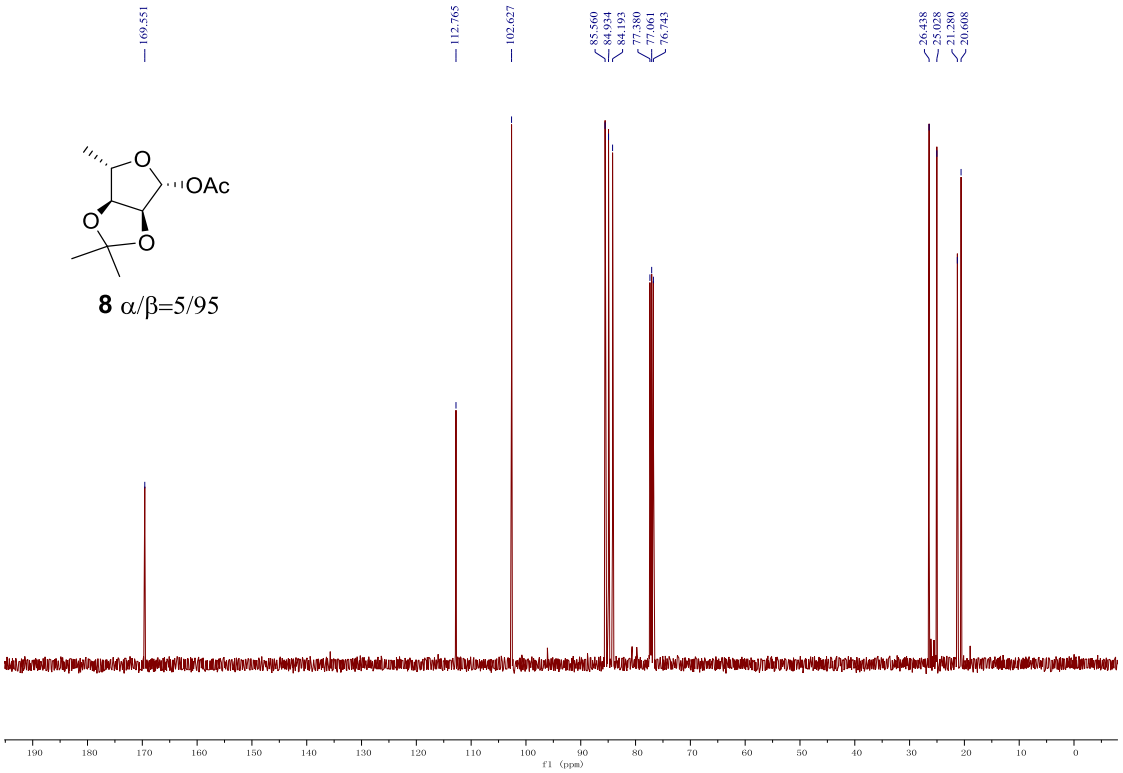

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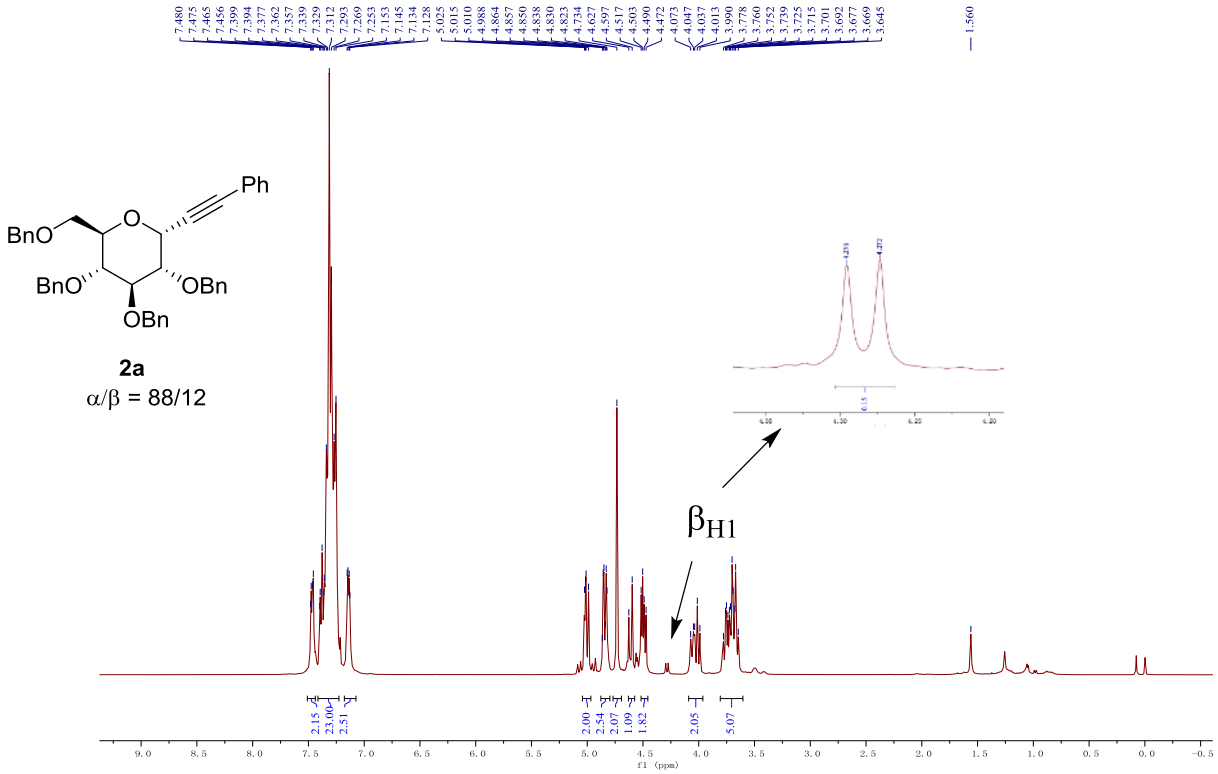
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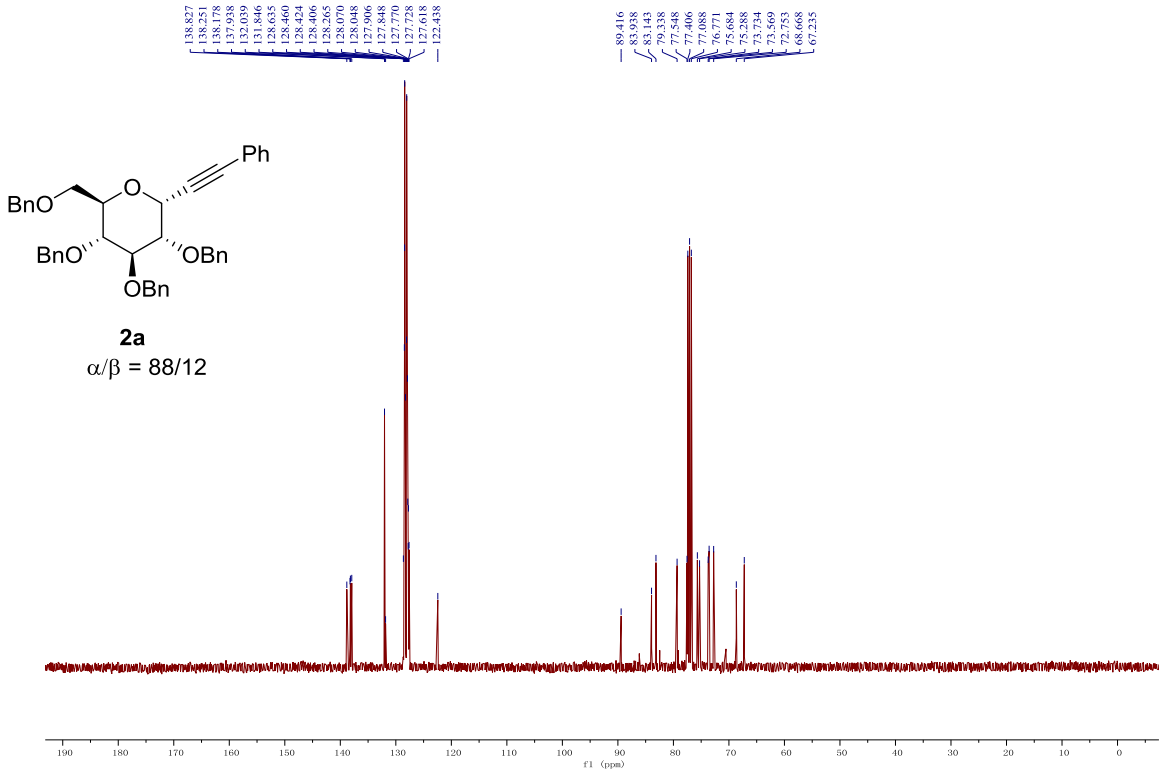
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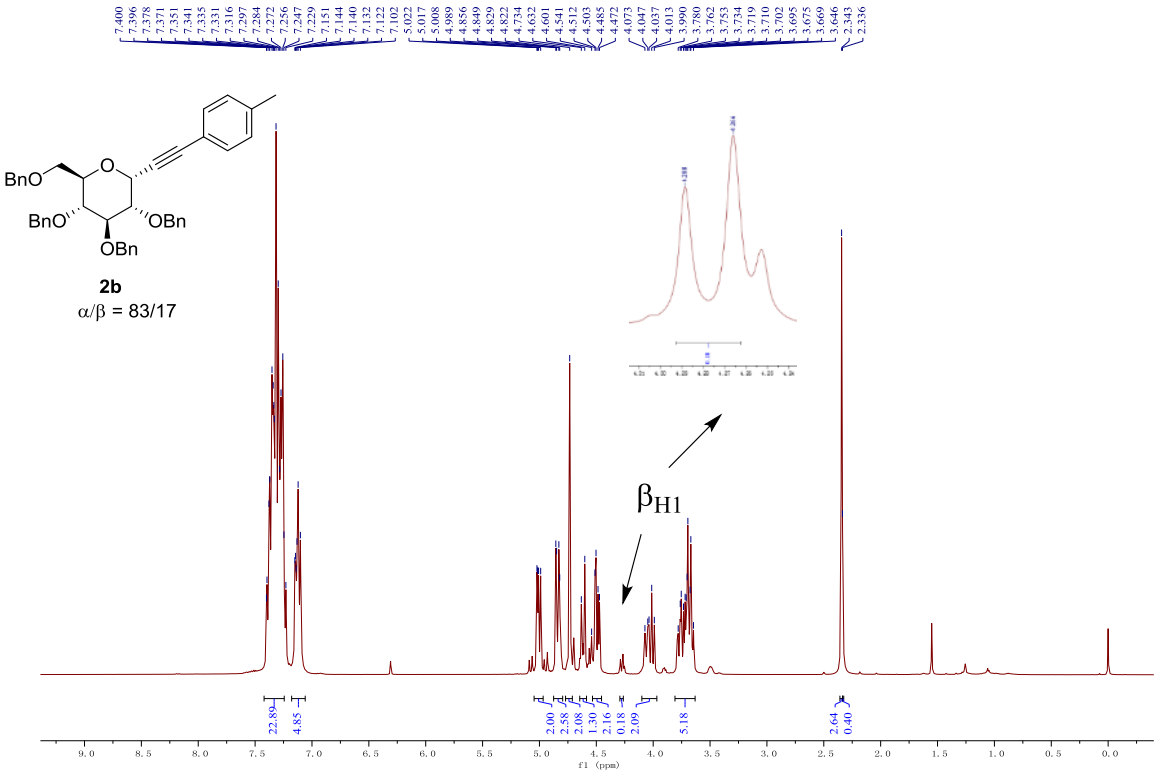
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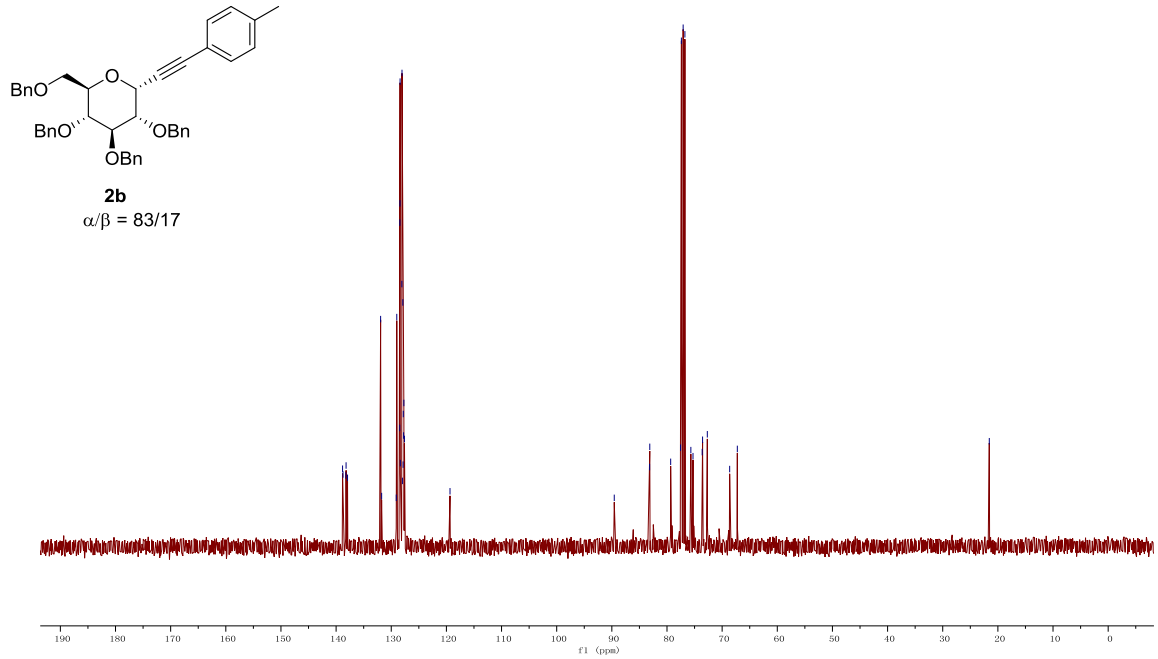
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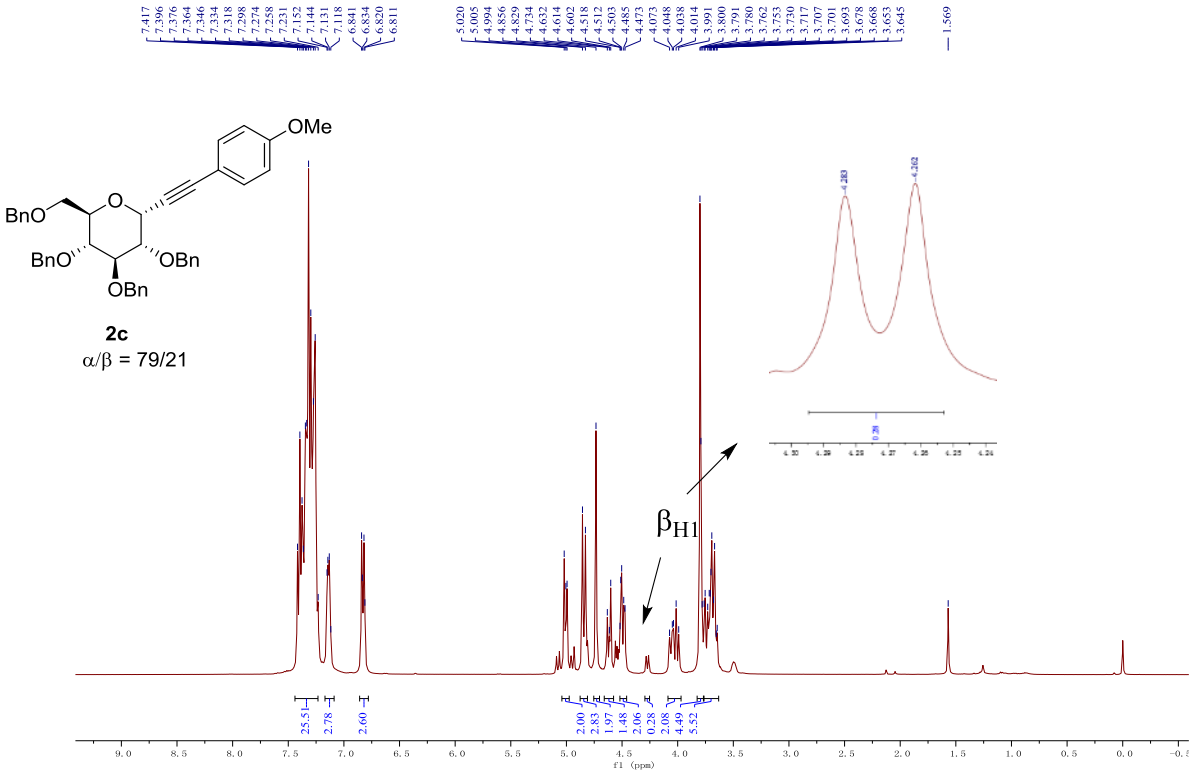
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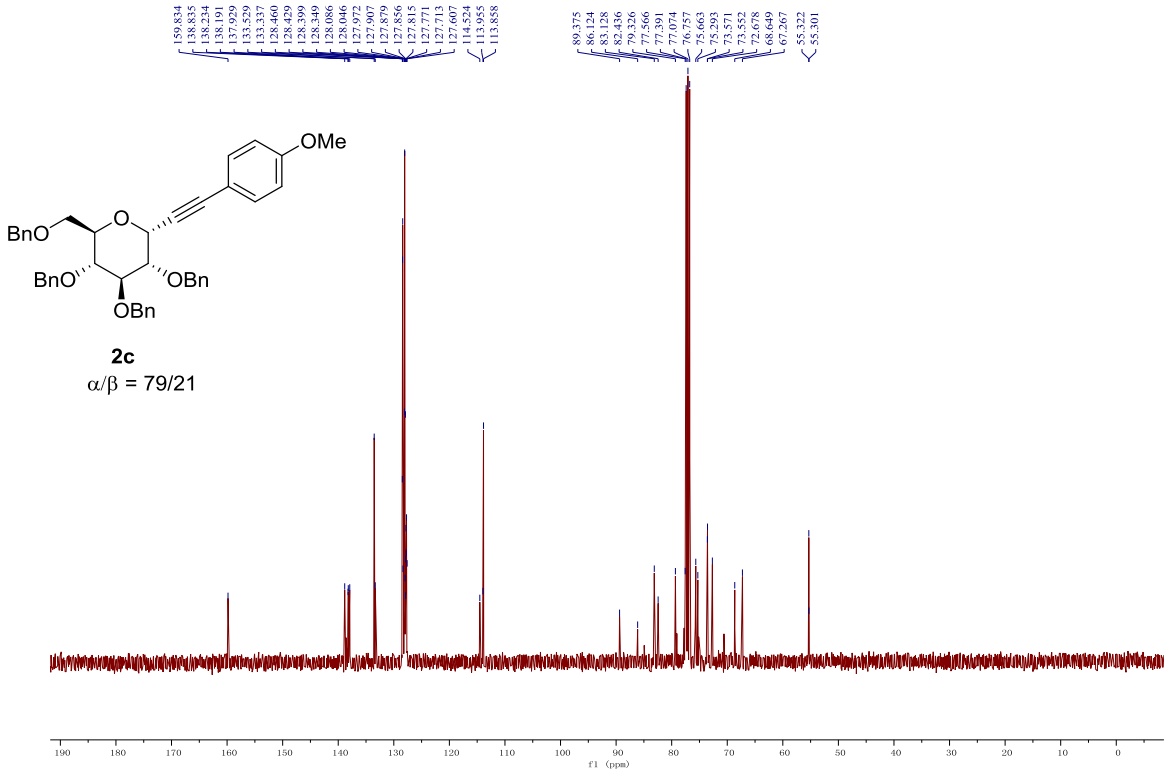
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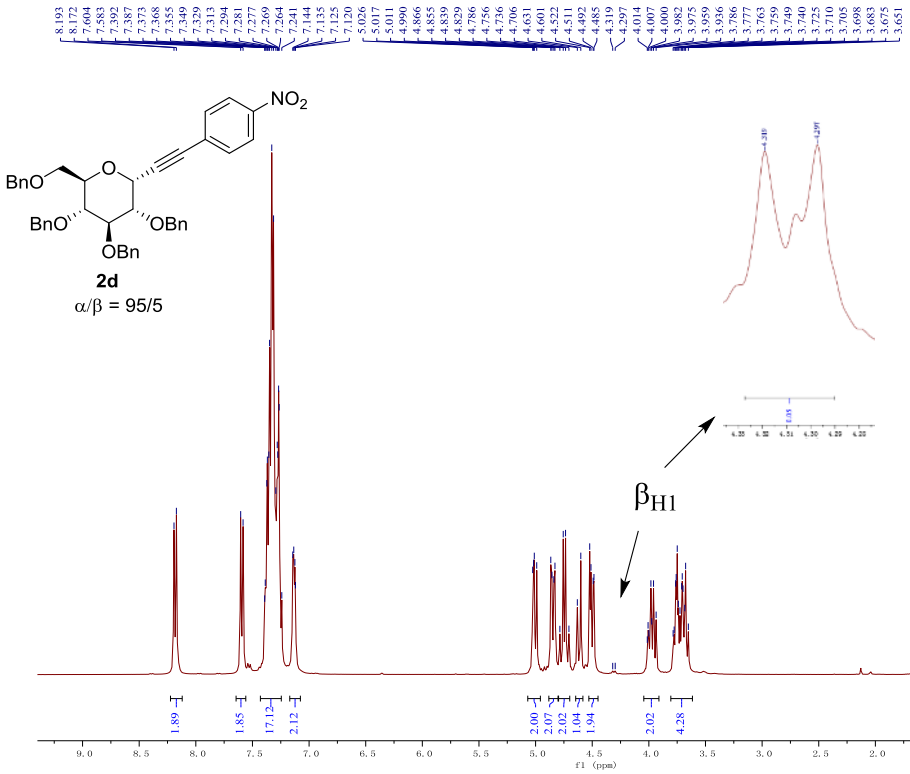
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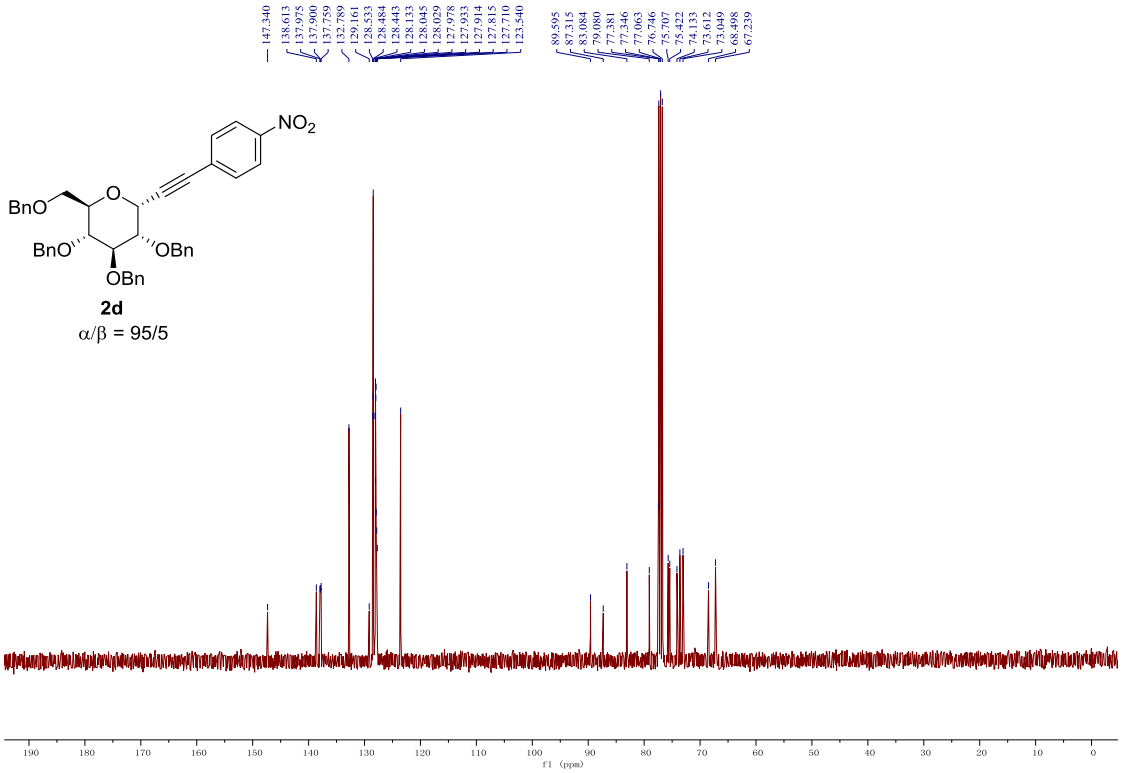
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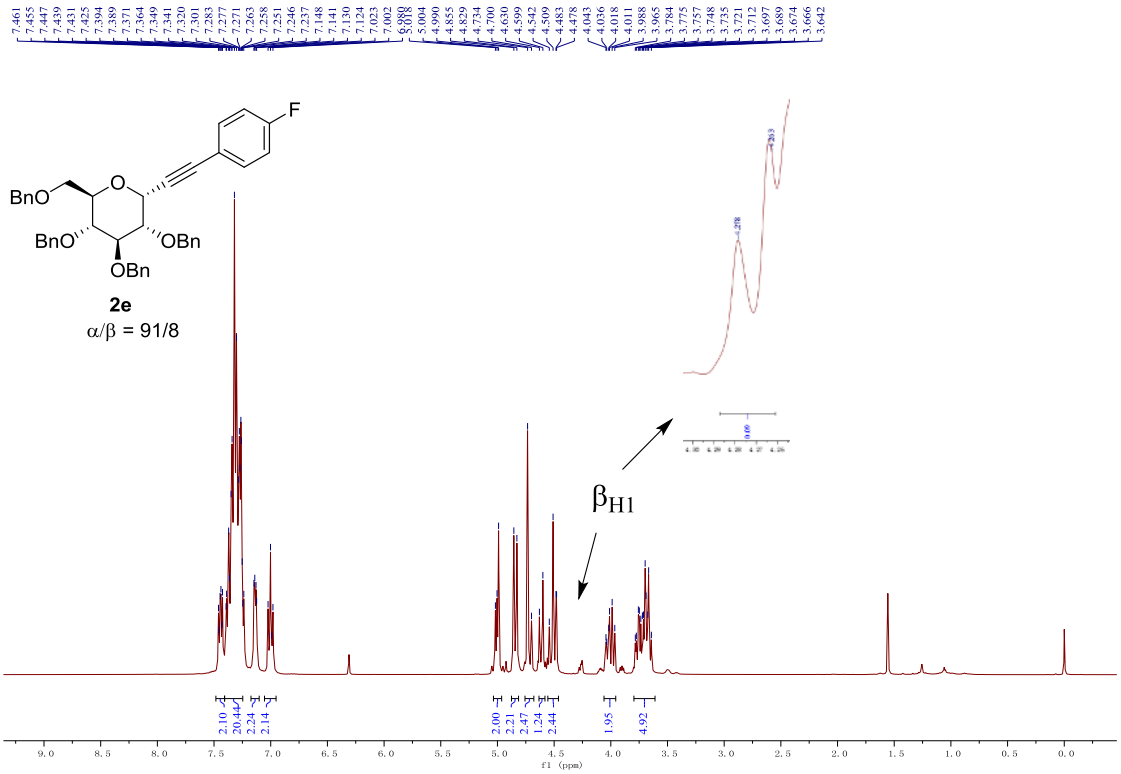
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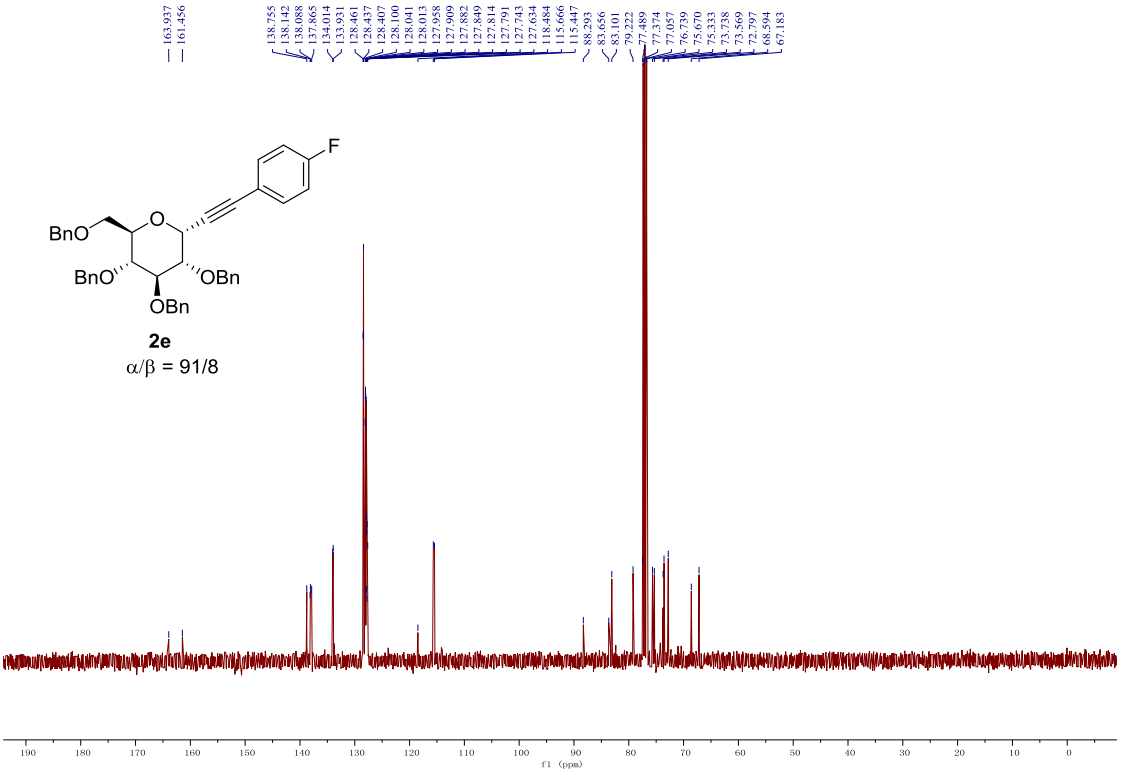
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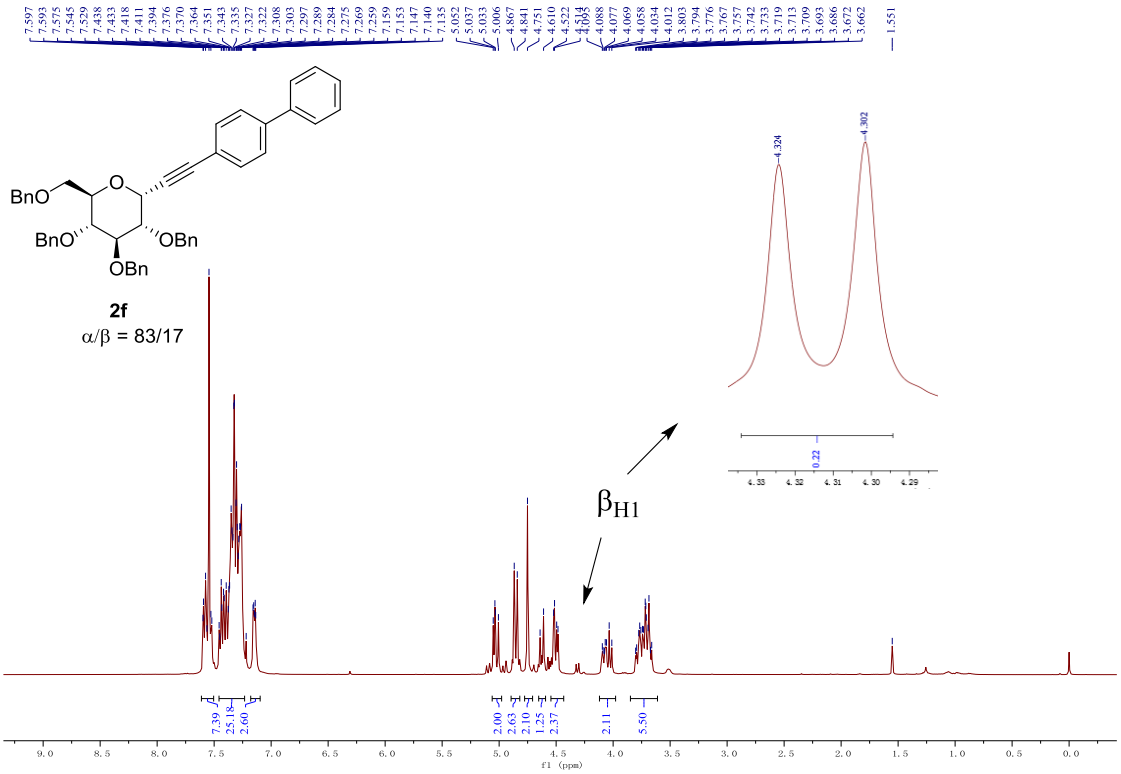
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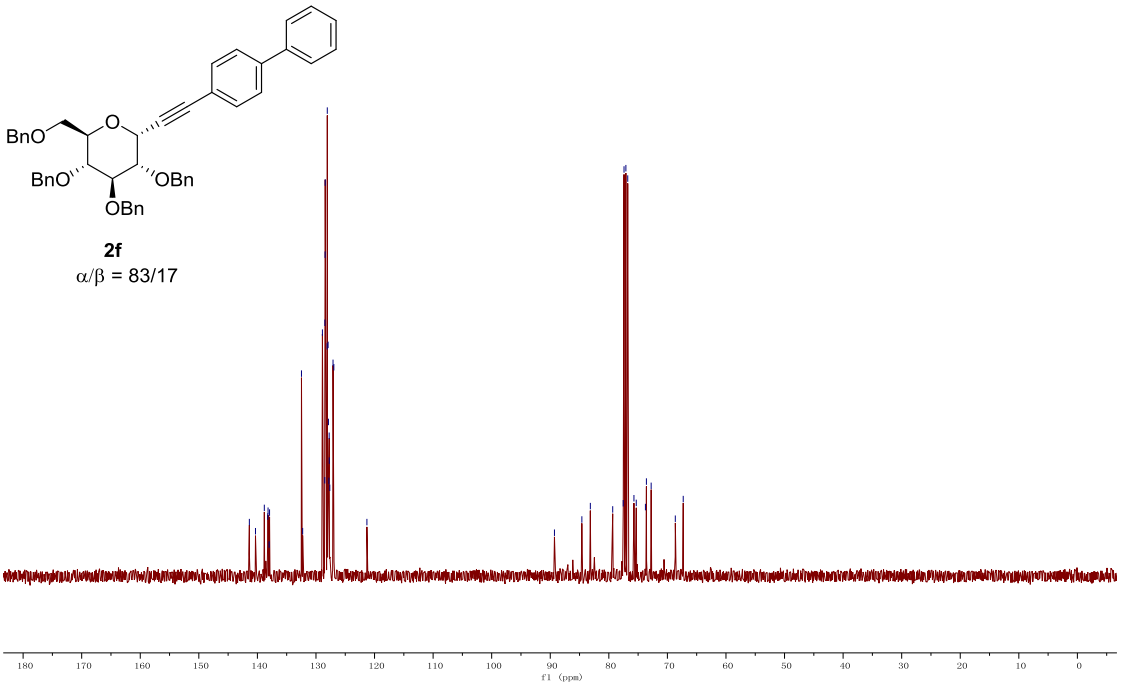
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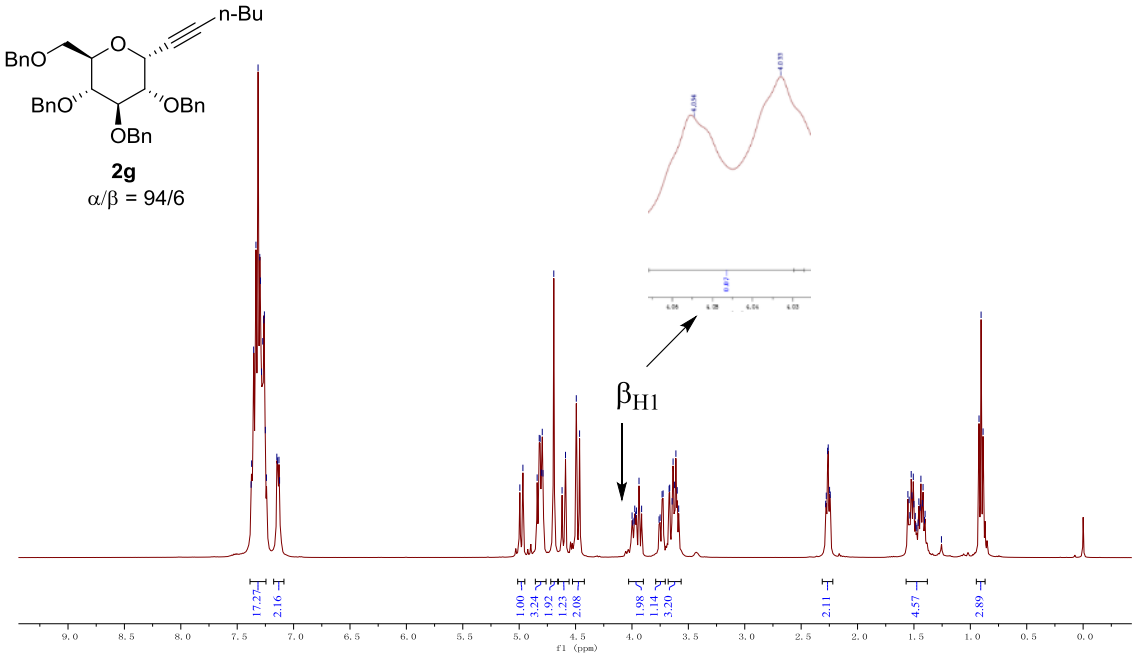
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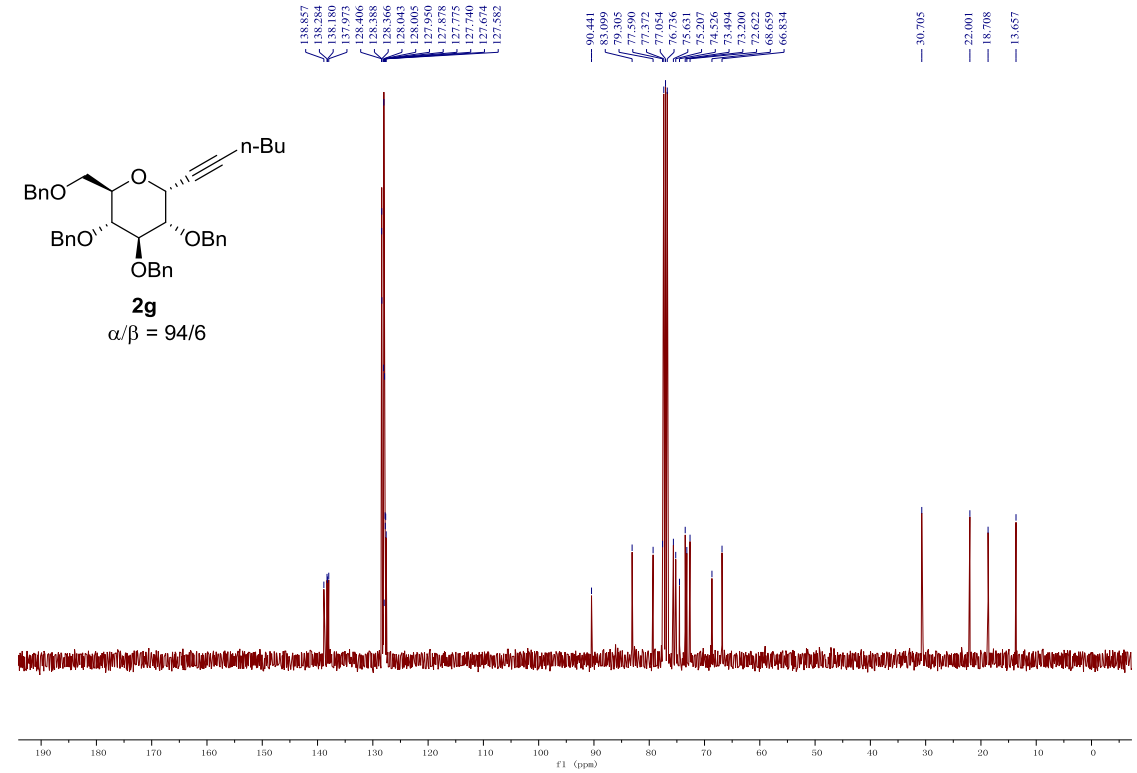
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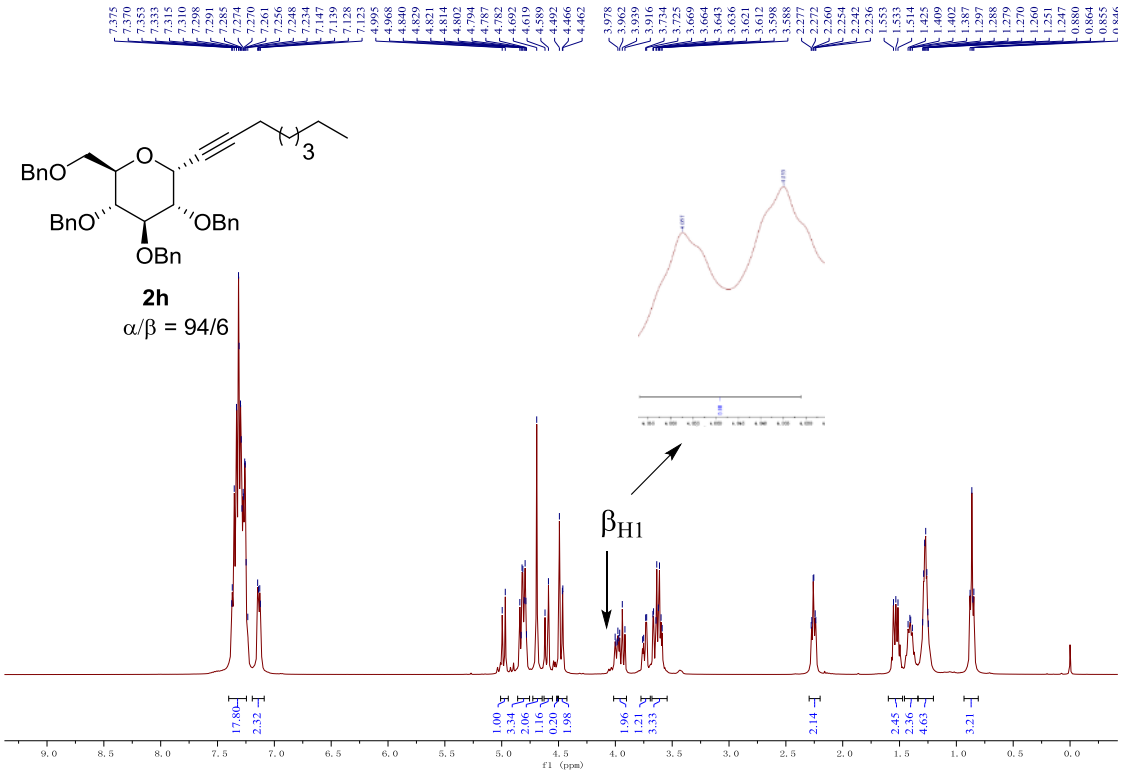
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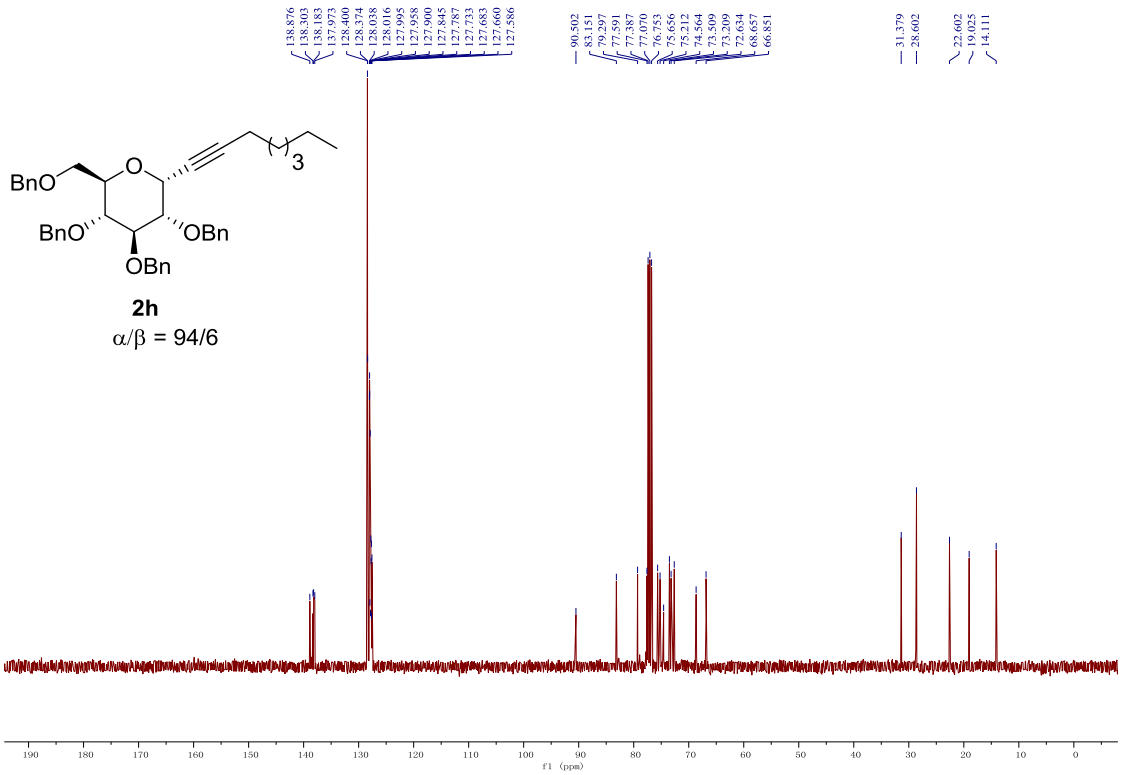
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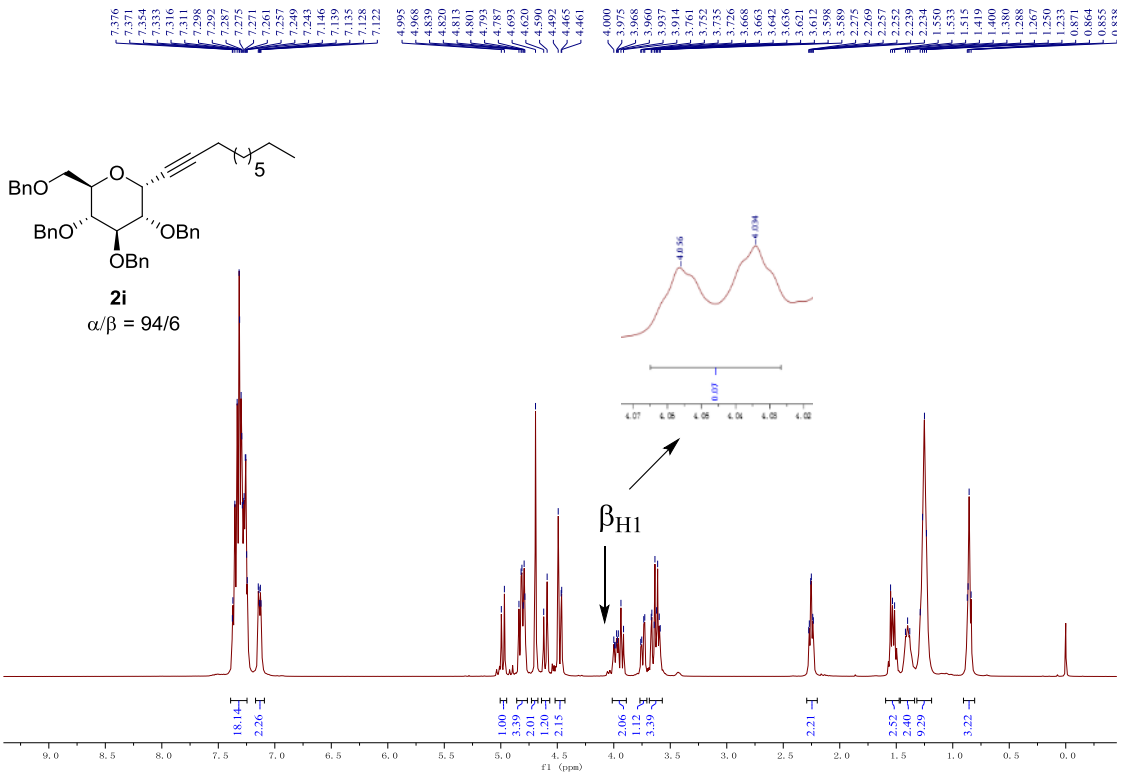
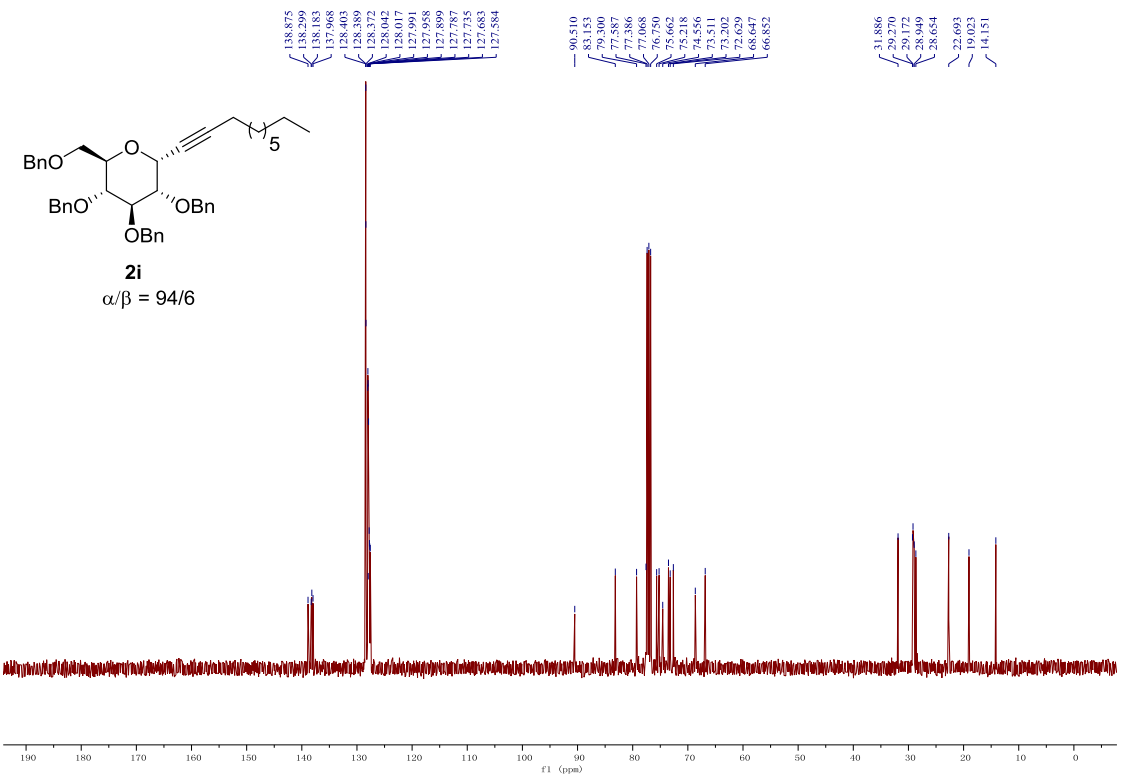
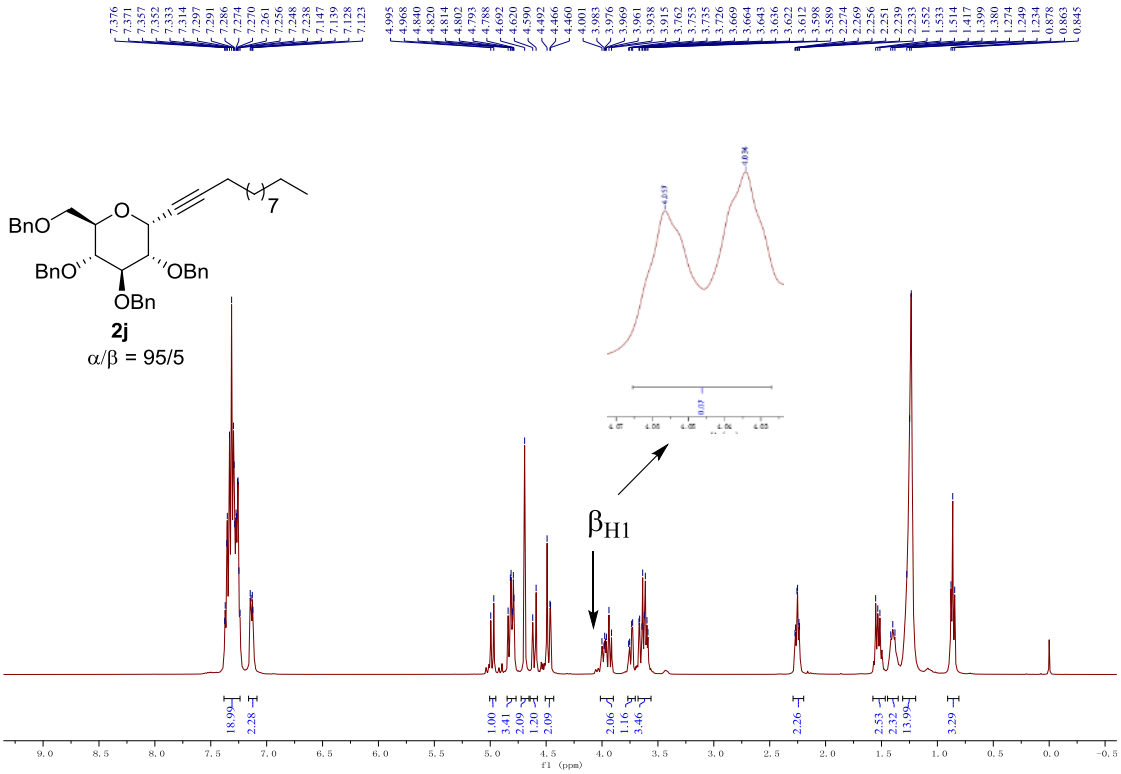
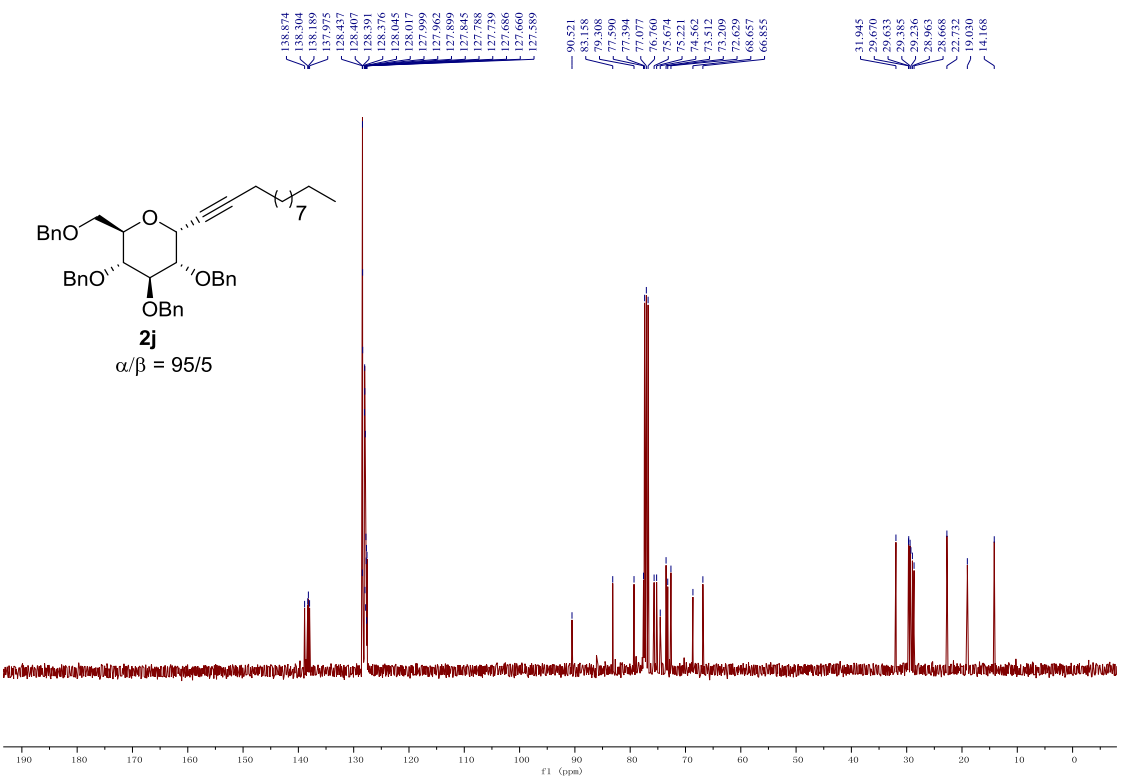
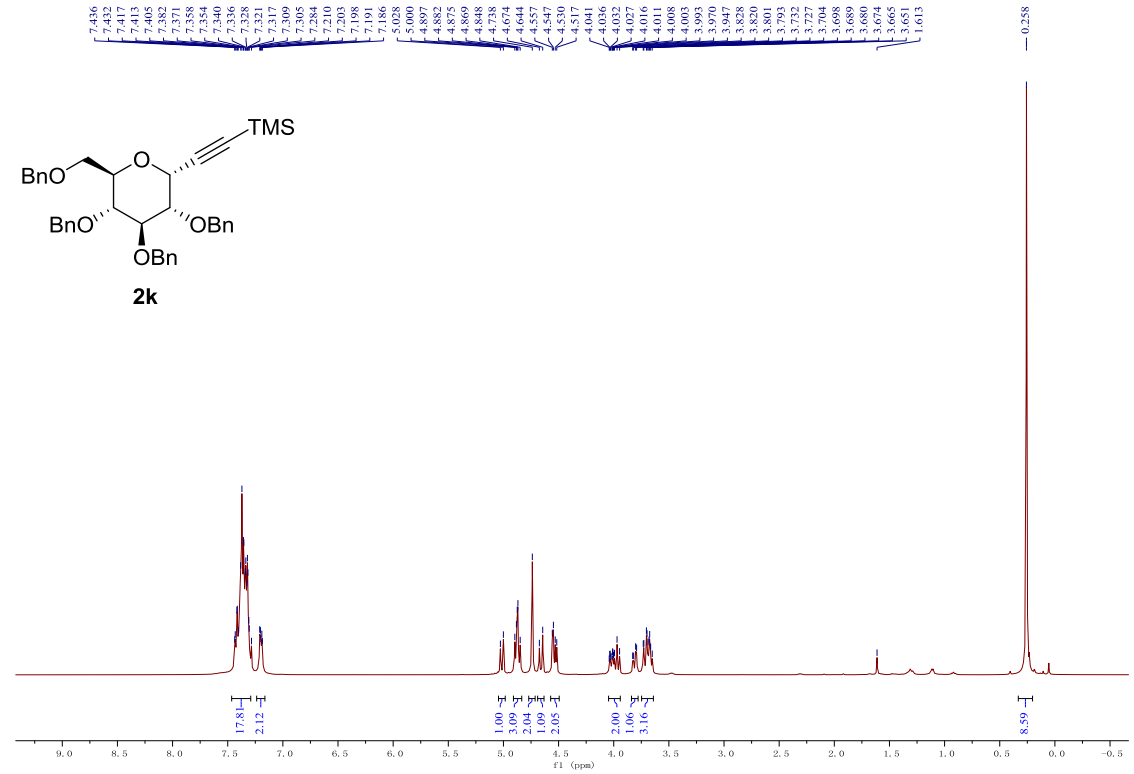
2h
α/β = 94/6

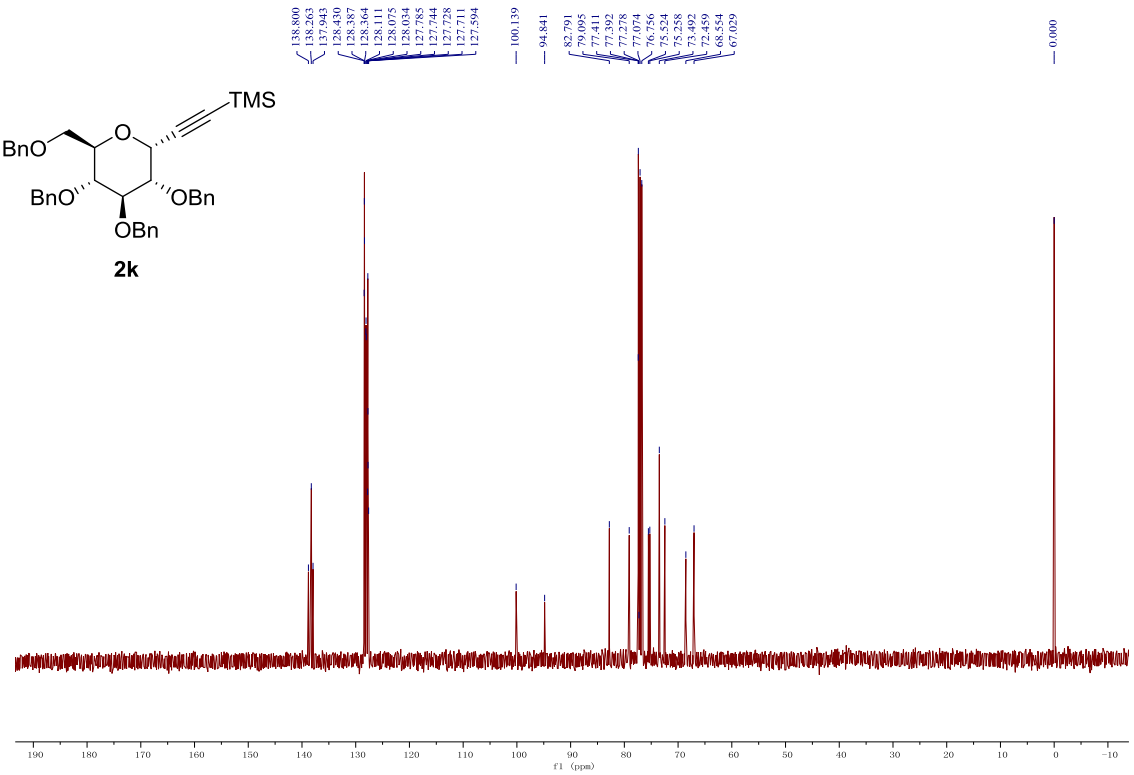

BnO
BnO
OBn
OBn
O
5
2i
α/β = 94/6
βH1

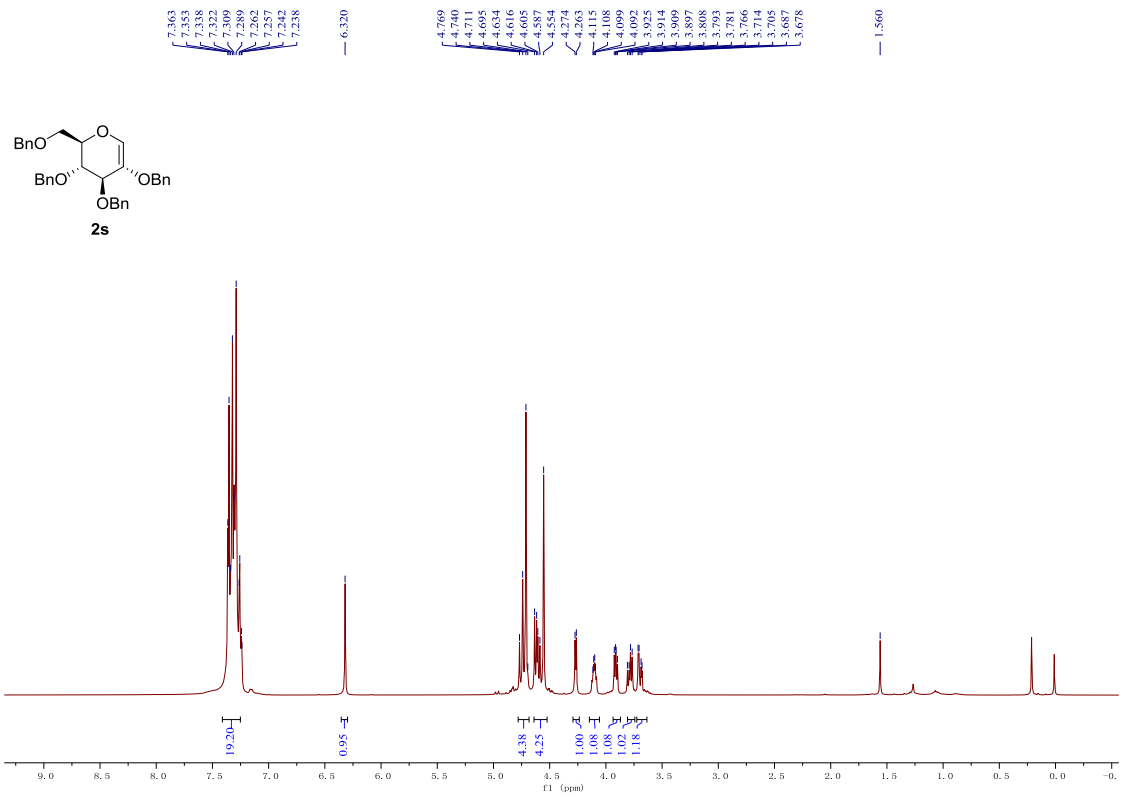

BnO
BnO
OBn
OBn
O
5
2i
α/β = 94/6

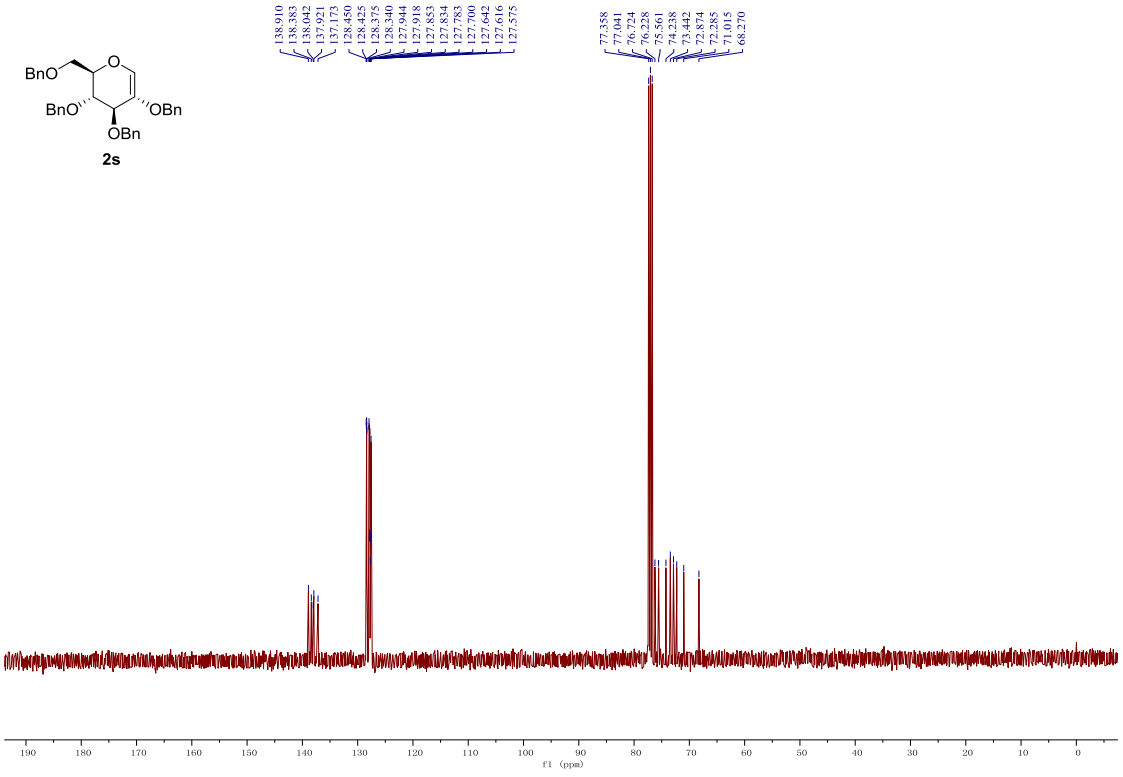

BnO
BnO
OBn
OBn
O
7
2j
α/β = 95/5
βH1

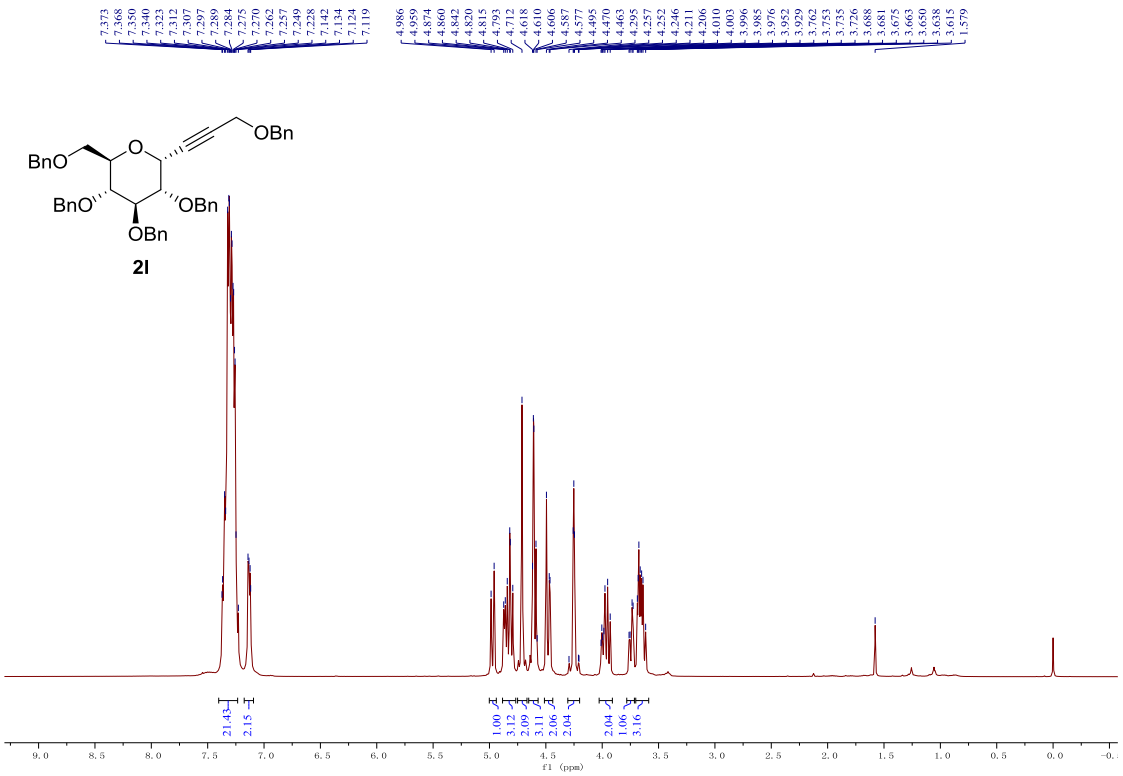

BnO
BnO
OBn
OBn
O
7
2j
α/β = 95/5

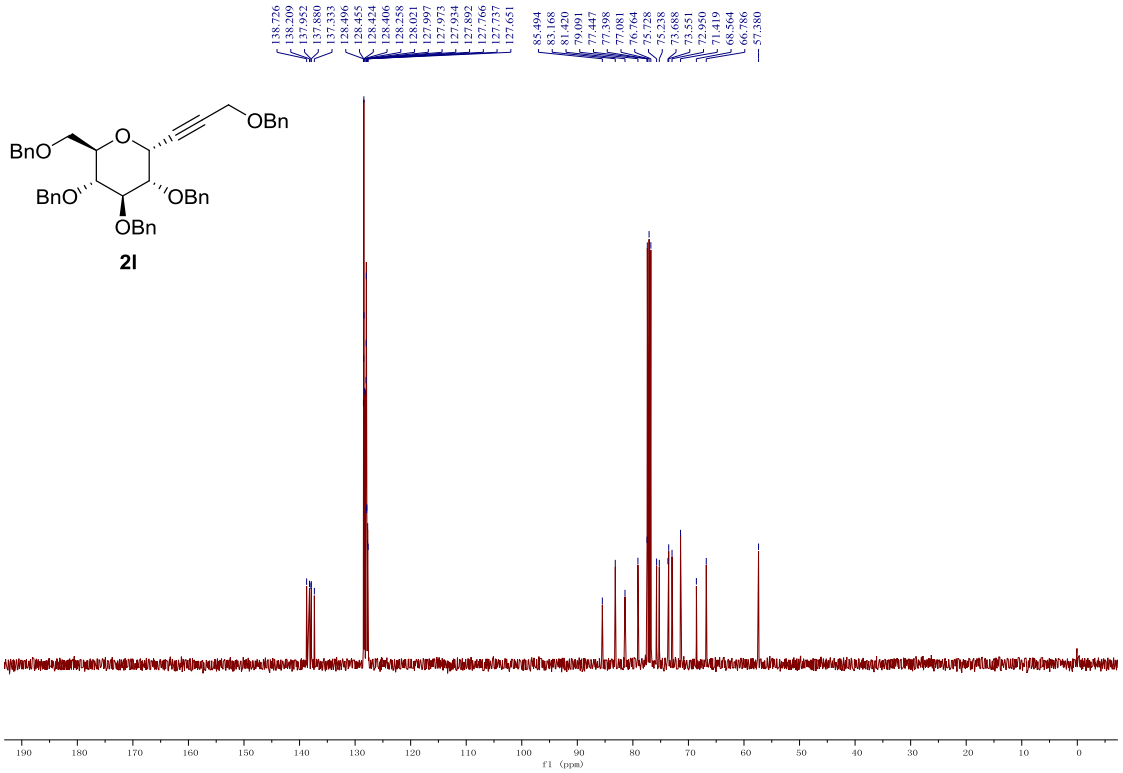

TMS
BnO
O
BnO
OBn
OBn
2k

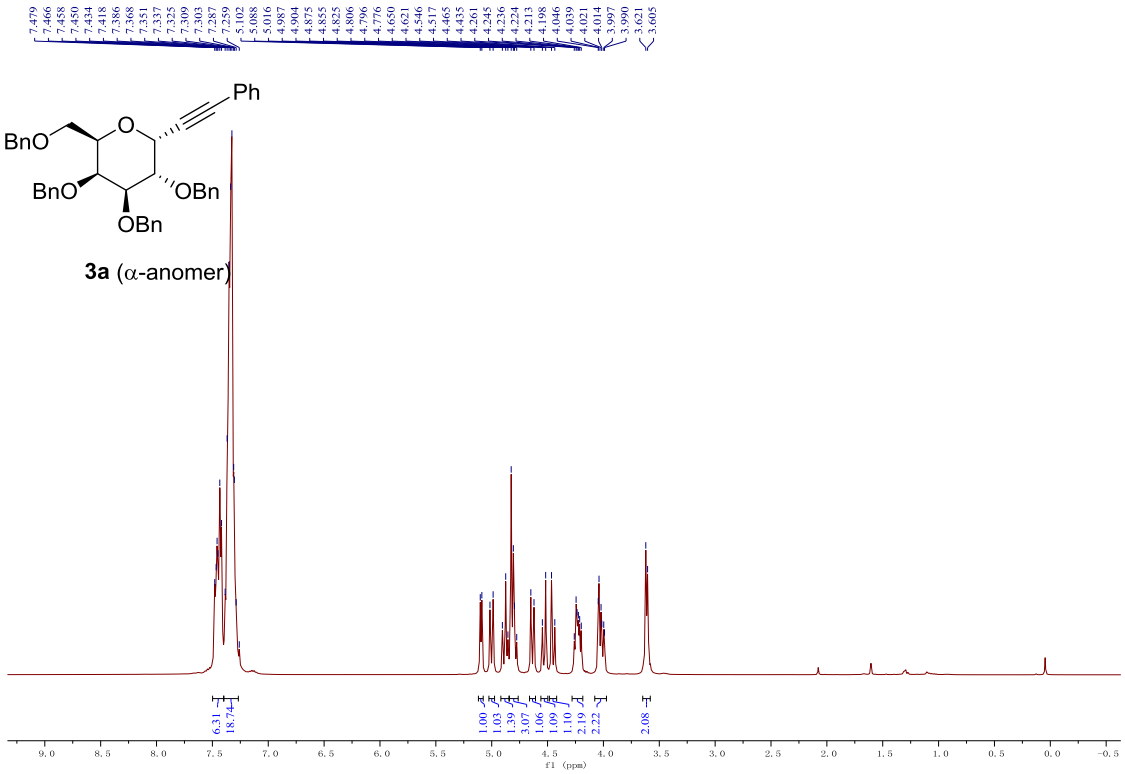

TMS
BnO
O
BnO
OBn
OBn
2k

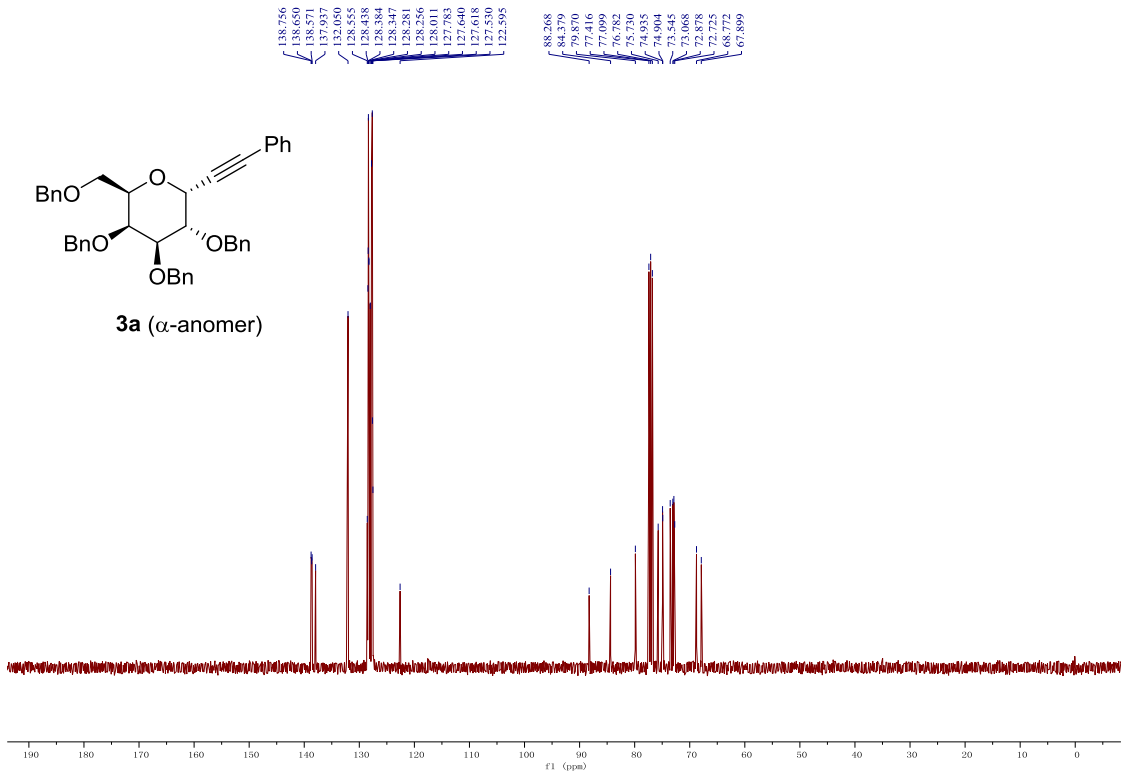

7.363
7.353
7.338
7.322
7.309
7.289
7.262
7.257
7.242
7.238
6.320
4.769
4.740
4.711
4.695
4.634
4.616
4.605
4.587
4.554
4.274
4.263
4.115
4.108
4.099
4.092
3.925
3.914
3.909
3.897
3.808
3.793
3.781
3.766
3.714
3.705
3.687
3.678
1.560
BnO
BnO
OBn
OBn
2s
19.20
0.95
4.38
4.25
1.00
1.08
1.08
1.02
1.18
f1 (ppm)

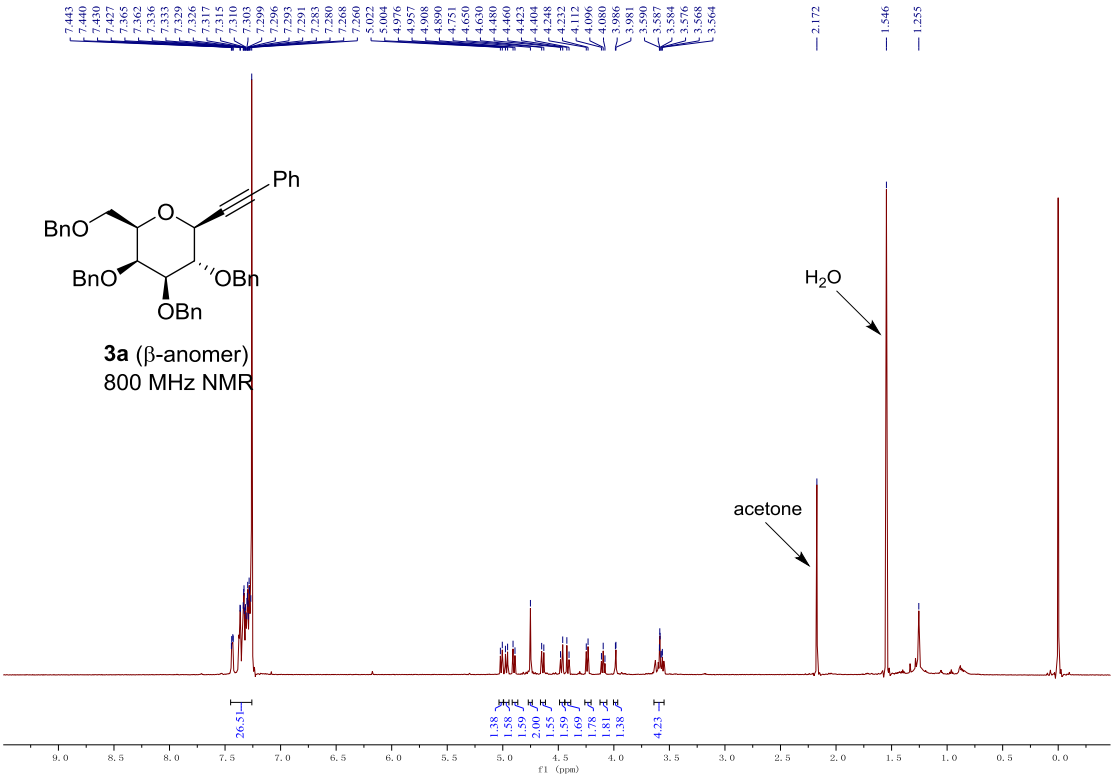

138.910
138.383
138.042
137.921
137.173
128.450
128.425
128.375
128.340
127.944
127.918
127.853
127.834
127.783
127.700
127.642
127.616
127.575
77.358
77.041
76.724
76.228
75.561
74.238
73.442
72.874
72.285
71.015
68.270
BnO
BnO
OBn
OBn
2s
f1 (ppm)

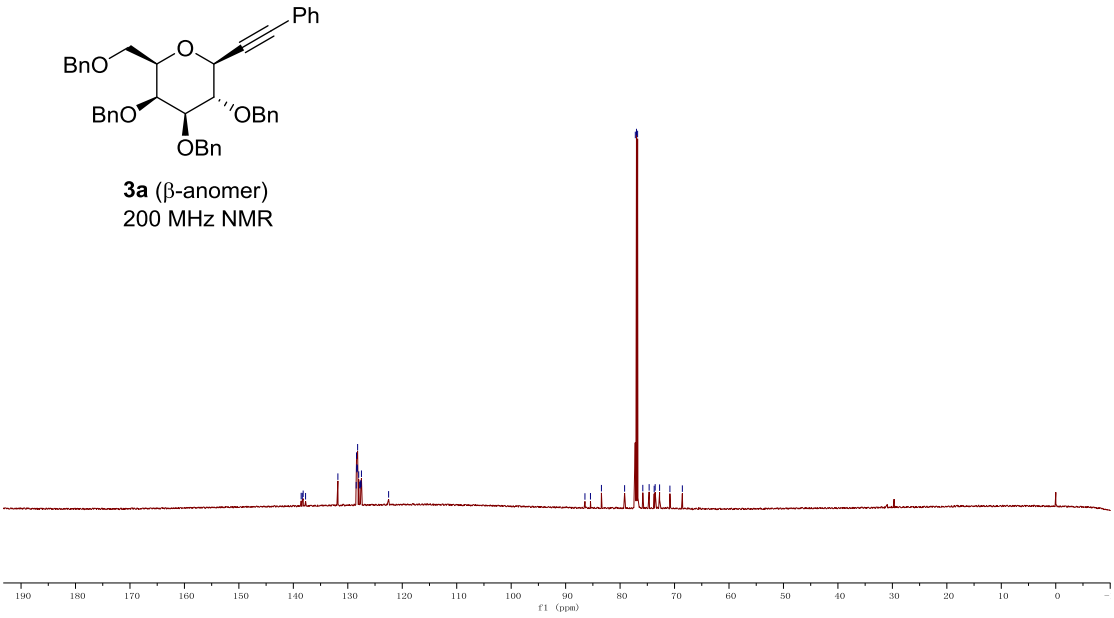

BnO
O
OBn
BnO
OBn
OBn
2l
f1 (ppm)

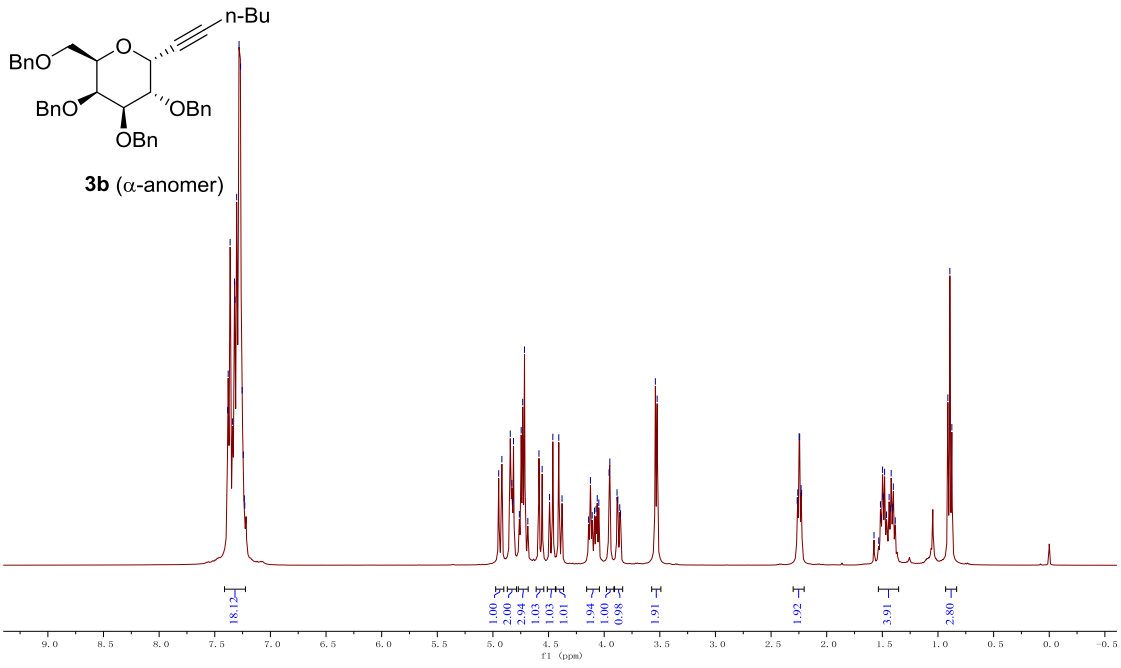

BnO
O
OBn
BnO
OBn
OBn
2l
f1 (ppm)

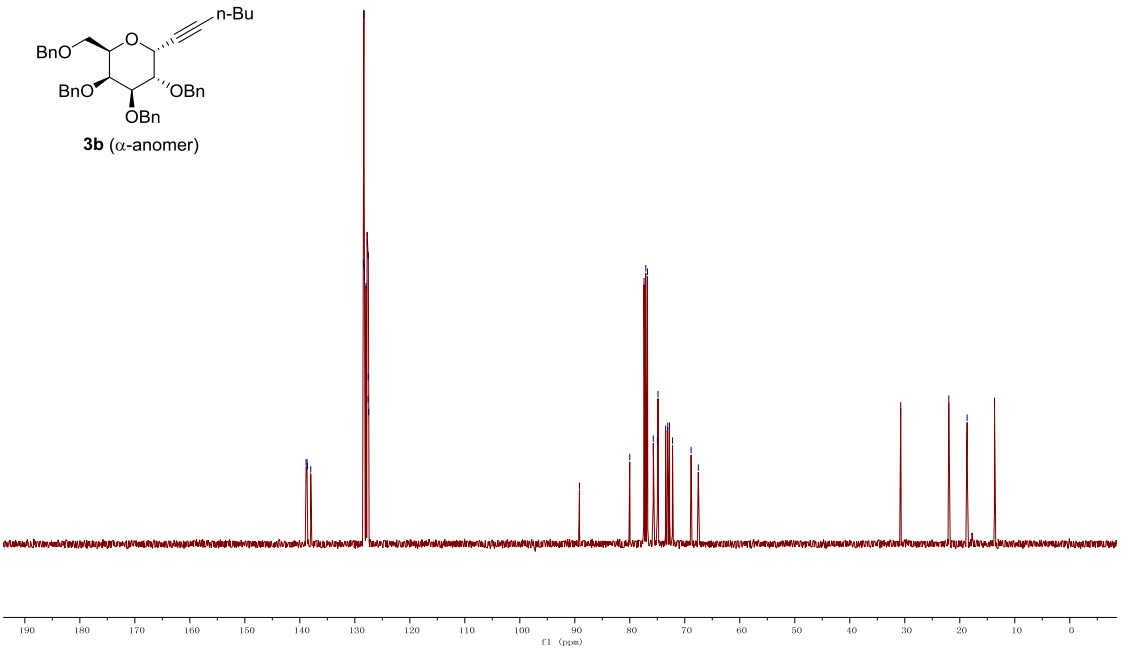

7.479
7.466
7.458
7.450
7.434
7.418
7.386
7.368
7.351
7.337
7.325
7.309
7.303
7.287
7.259
5.102
5.088
5.016
4.987
4.904
4.875
4.855
4.825
4.806
4.796
4.776
4.650
4.621
4.546
4.517
4.465
4.435
4.261
4.245
4.236
4.224
4.213
4.198
4.046
4.039
4.021
4.014
3.997
3.990
3.621
3.605
Ph
BnO
O
BnO
OBn
OBn
3a (α-anomer)
6.31
18.74
1.00
1.03
1.39
3.07
1.06
1.09
1.10
2.19
2.22
2.08
f1 (ppm)

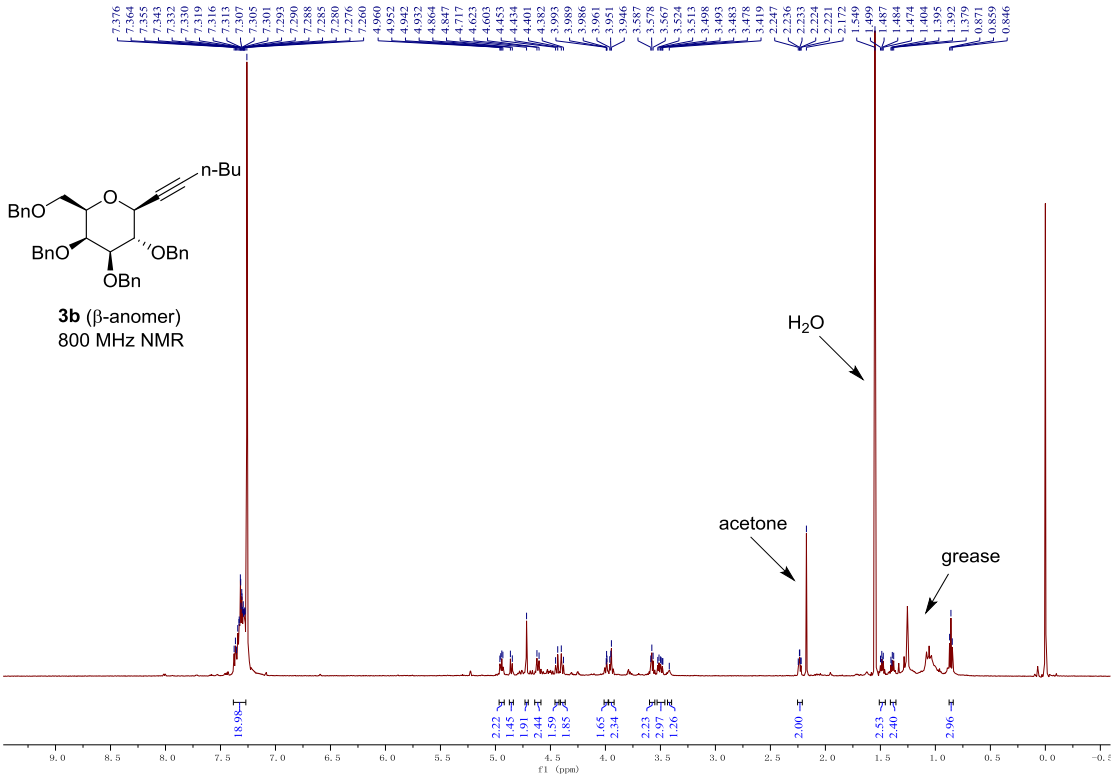

138.756
138.650
138.571
137.937
132.050
128.555
128.438
128.384
128.347
128.281
128.256
128.011
127.783
127.640
127.618
127.530
122.595
88.268
84.379
79.870
77.416
77.099
76.782
75.730
74.935
74.904
73.545
73.068
72.878
72.725
68.772
67.899
Ph
BnO
O
BnO
OBn
OBn
3a (α-anomer)
f1 (ppm)

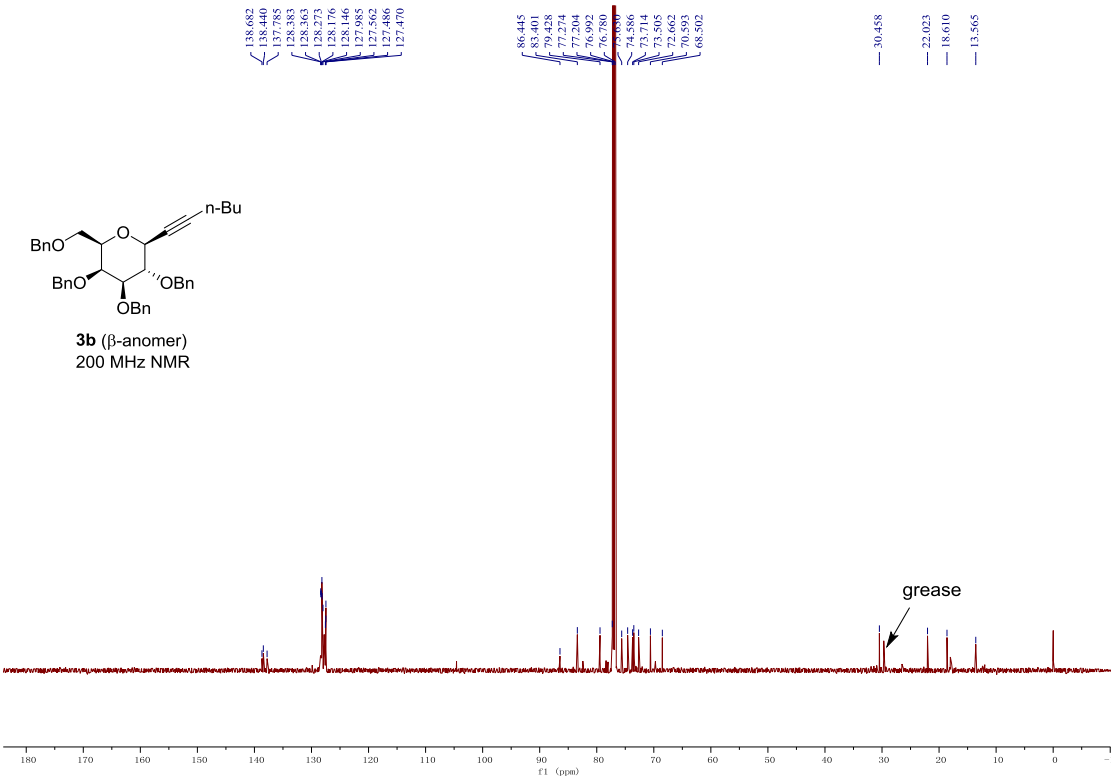

Ph
BnO
O
BnO
OBn
OBn
3a (β-anomer)
800 MHz NMR
H2O
acetone
f1 (ppm)

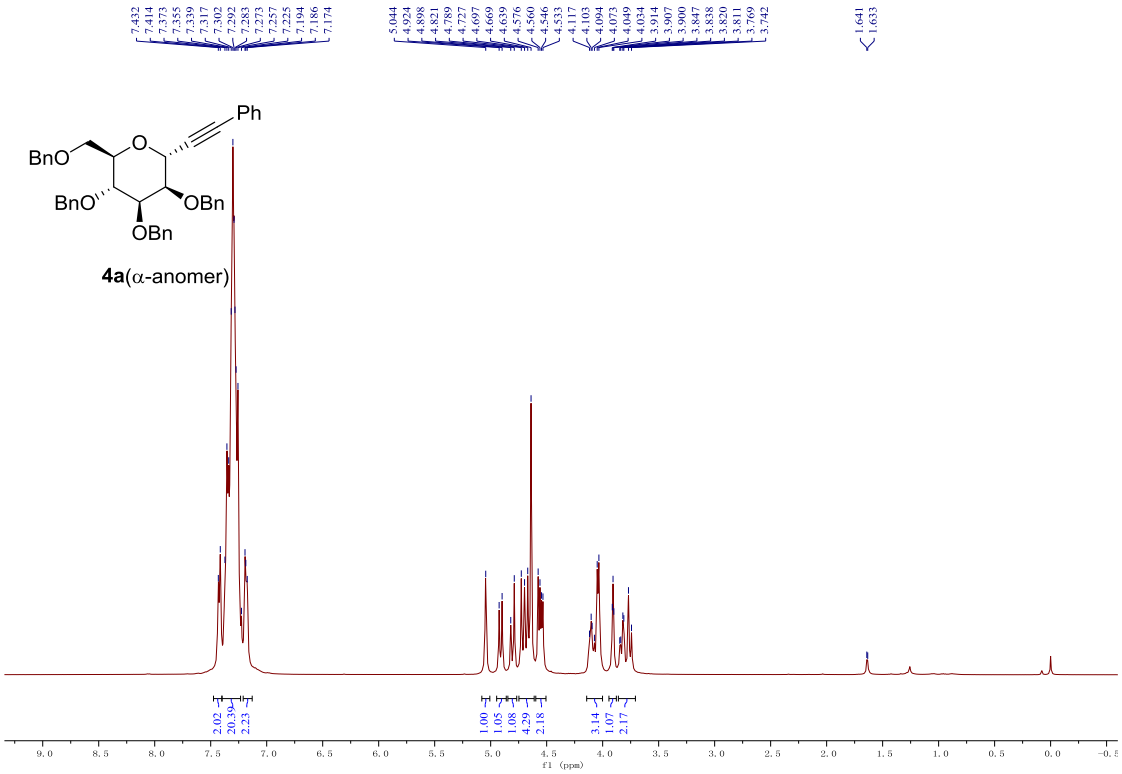

Ph
BnO
O
BnO
OBn
OBn
3a (β-anomer)
200 MHz NMR
f1 (ppm)

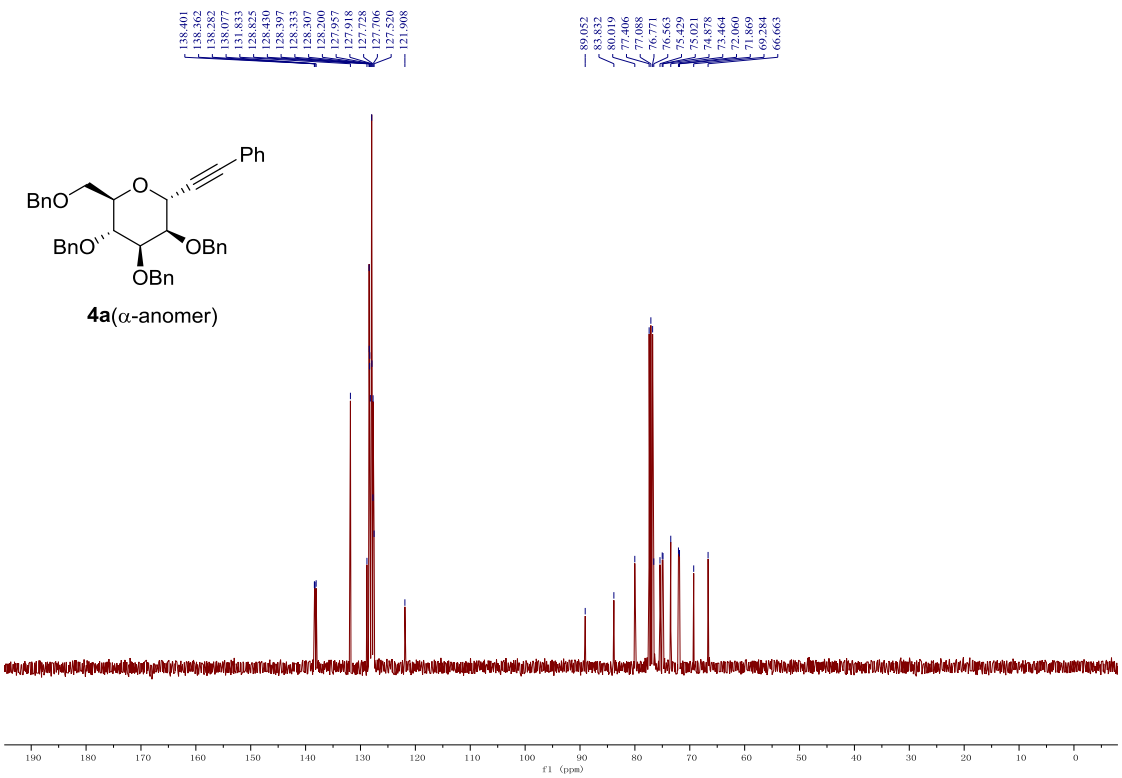

n-Bu
BnO
BnO
OBn
OBn
3b (α-anomer)

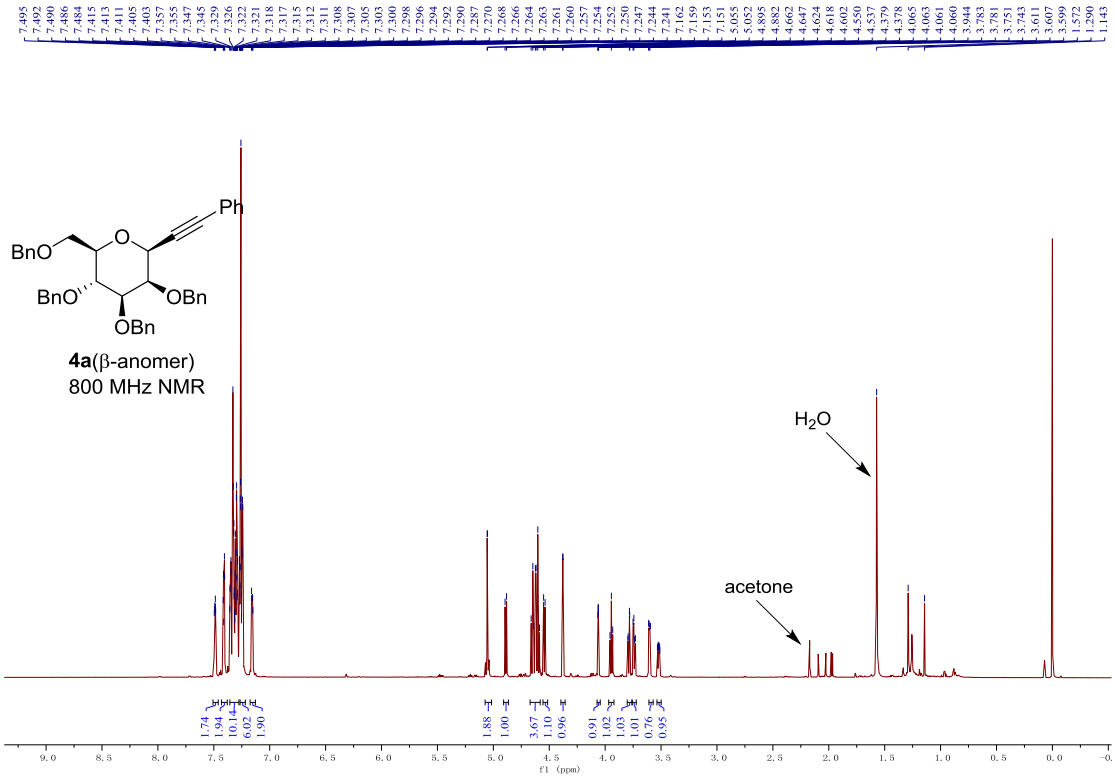

n-Bu
BnO
BnO
OBn
OBn
3b (α-anomer)

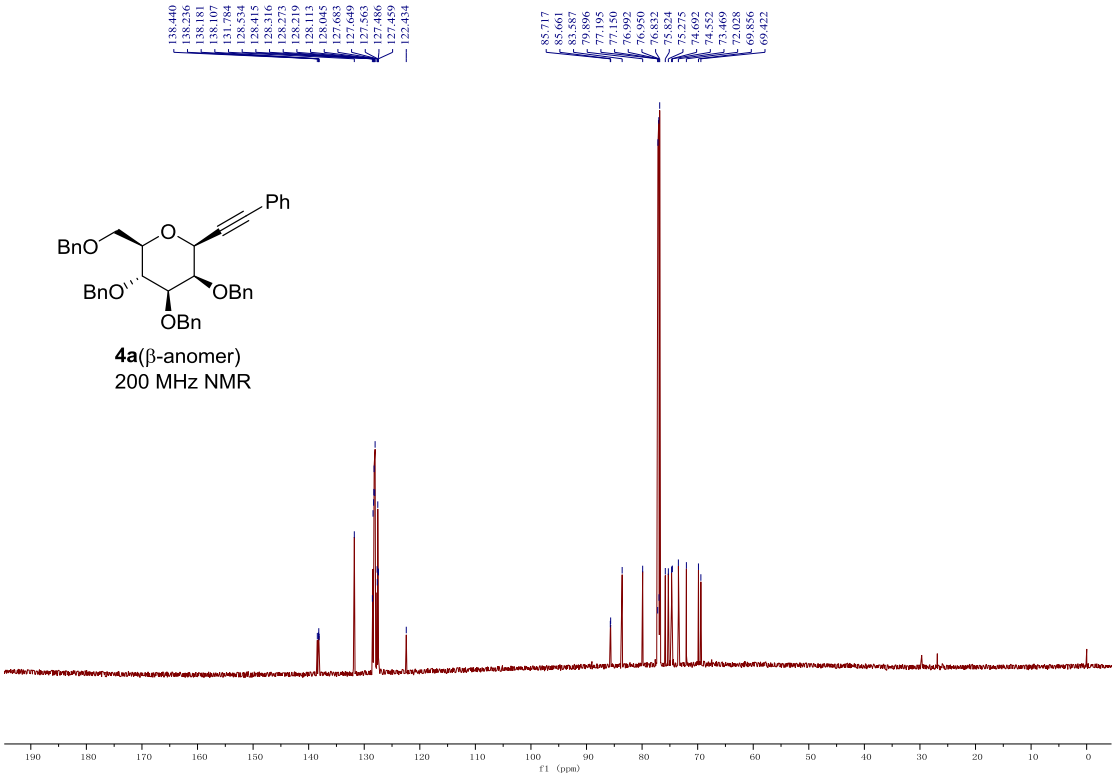

n-Bu
BnO
BnO
OBn
OBn
3b (β-anomer)
800 MHz NMR
H2O
acetone
grease
f1 (ppm)

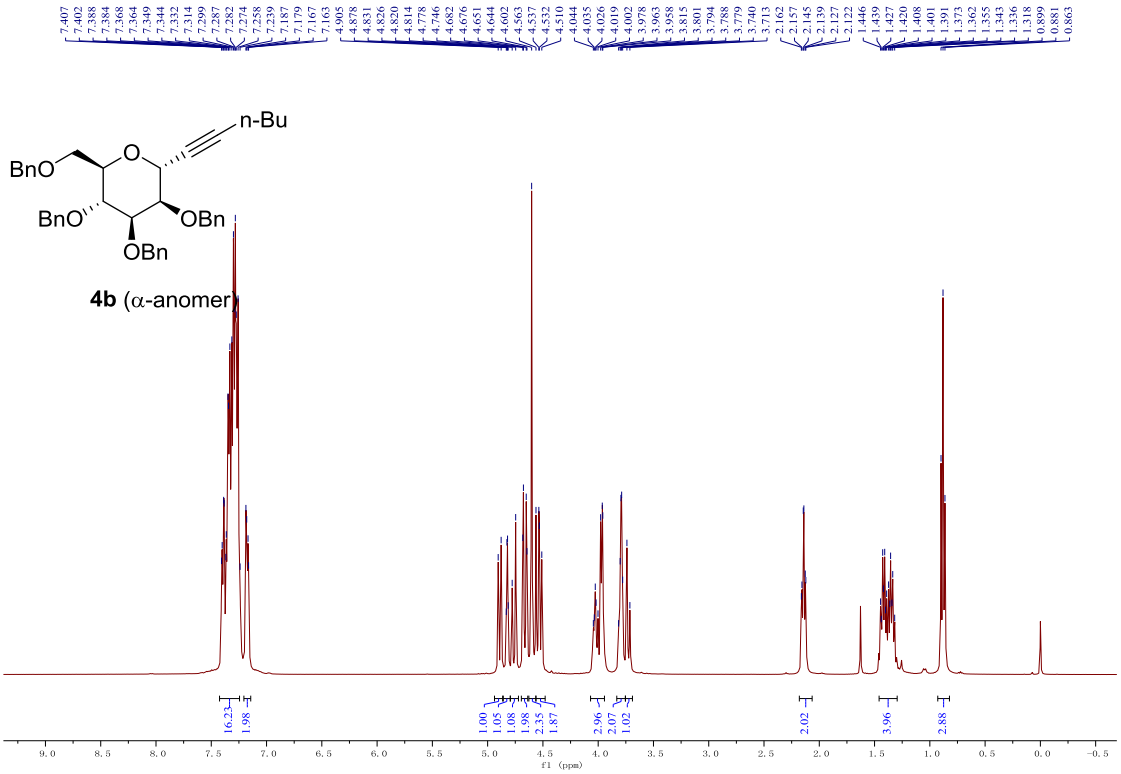

n-Bu
BnO
BnO
OBn
OBn
3b (β-anomer)
200 MHz NMR
grease
f1 (ppm)

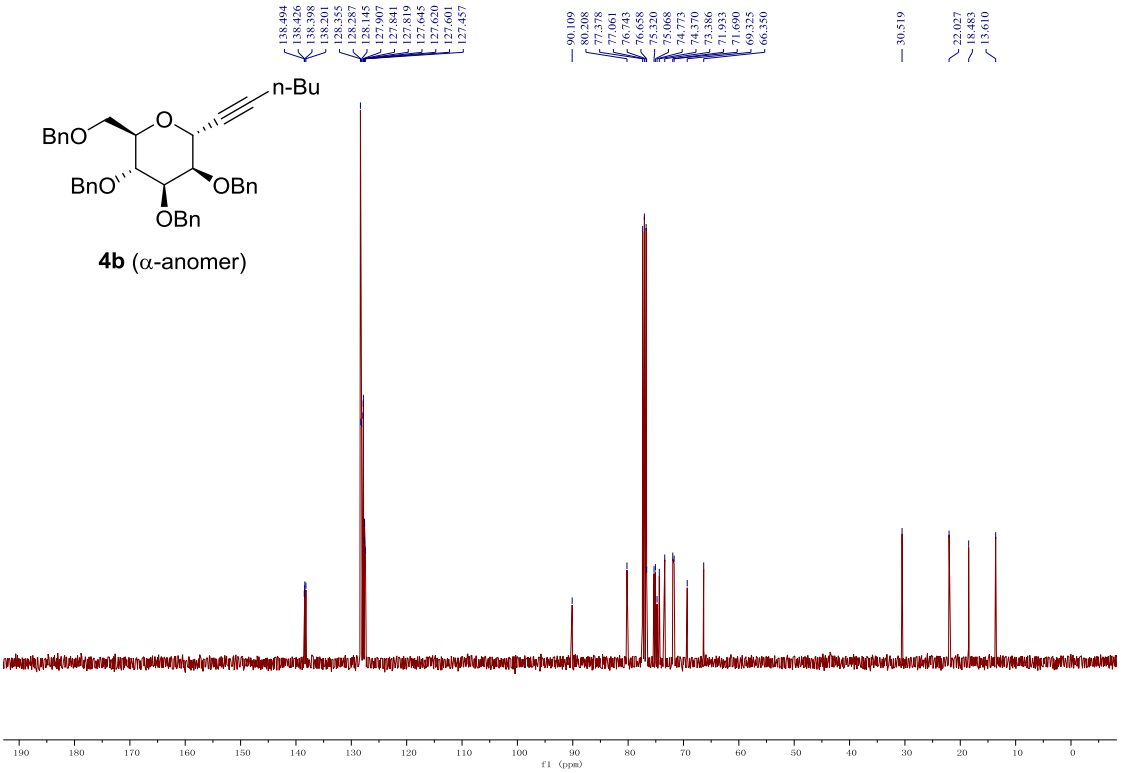

7.432
7.414
7.373
7.355
7.339
7.317
7.302
7.292
7.283
7.273
7.257
7.225
7.194
7.186
7.174
5.044
4.924
4.898
4.821
4.789
4.727
4.697
4.669
4.639
4.576
4.560
4.546
4.533
4.117
4.103
4.094
4.073
4.049
4.034
3.914
3.907
3.900
3.847
3.838
3.820
3.811
3.769
3.742
1.641
1.633
Ph
O
BnO
BnO
OBn
OBn
4a(α-anomer)
2.02
20.39
2.23
1.00
1.05
1.08
4.29
2.18
3.14
1.07
2.17
f1 (ppm)

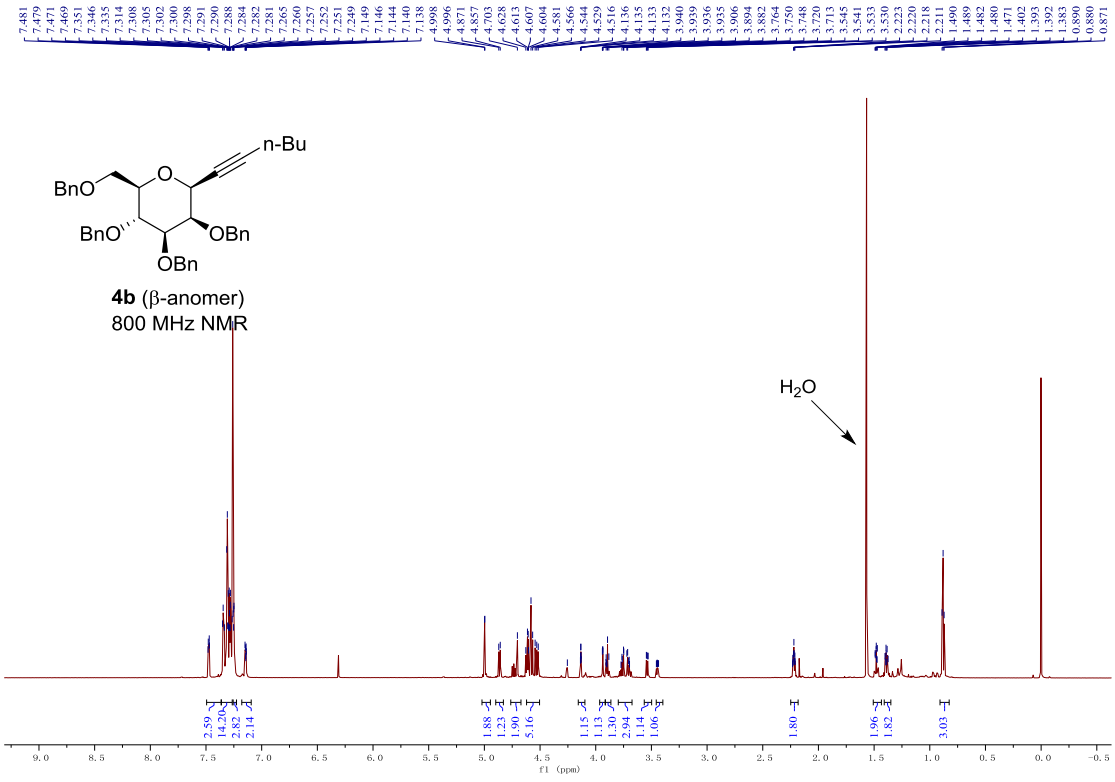

138.401
138.362
138.282
138.077
131.833
128.825
128.430
128.397
128.333
128.307
128.200
127.957
127.918
127.728
127.706
127.520
121.908
89.052
83.832
80.019
77.406
77.088
76.771
76.563
75.429
75.021
74.878
73.464
72.060
71.869
69.284
66.663
Ph
O
BnO
BnO
OBn
OBn
4a(α-anomer)
f1 (ppm)

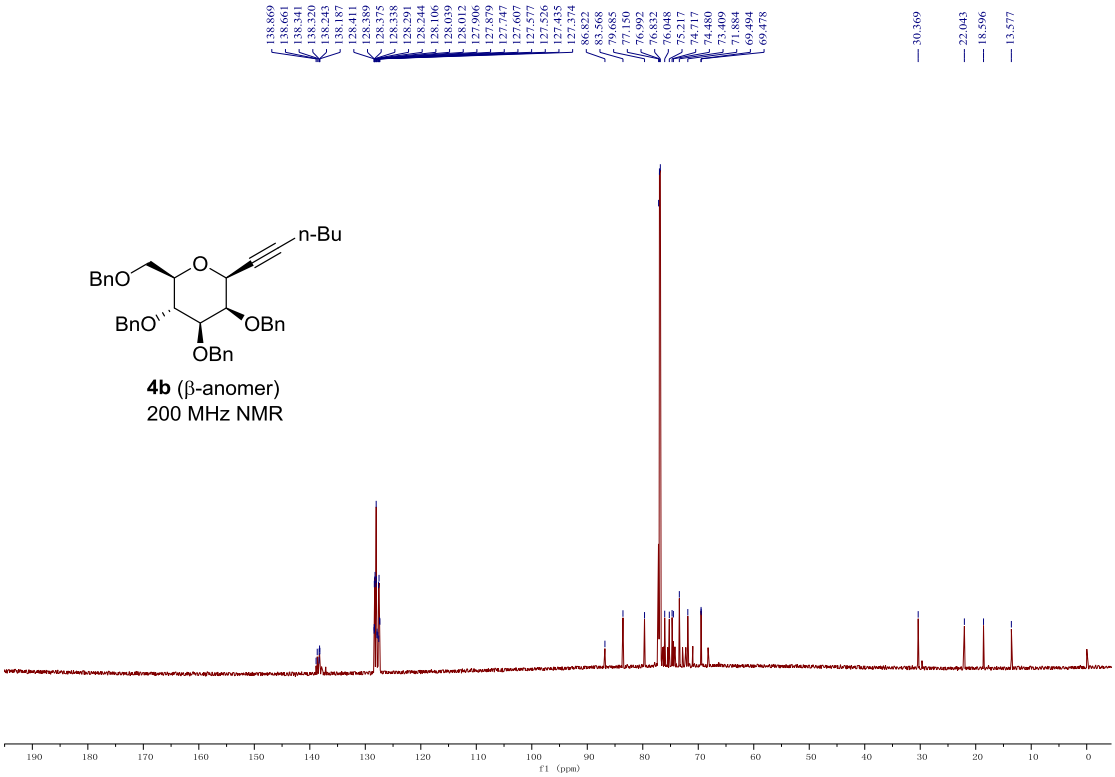

Ph
BnO
O
BnO
OBn
OBn
4a(β-anomer)
800 MHz NMR
H2O
acetone
f1 (ppm)

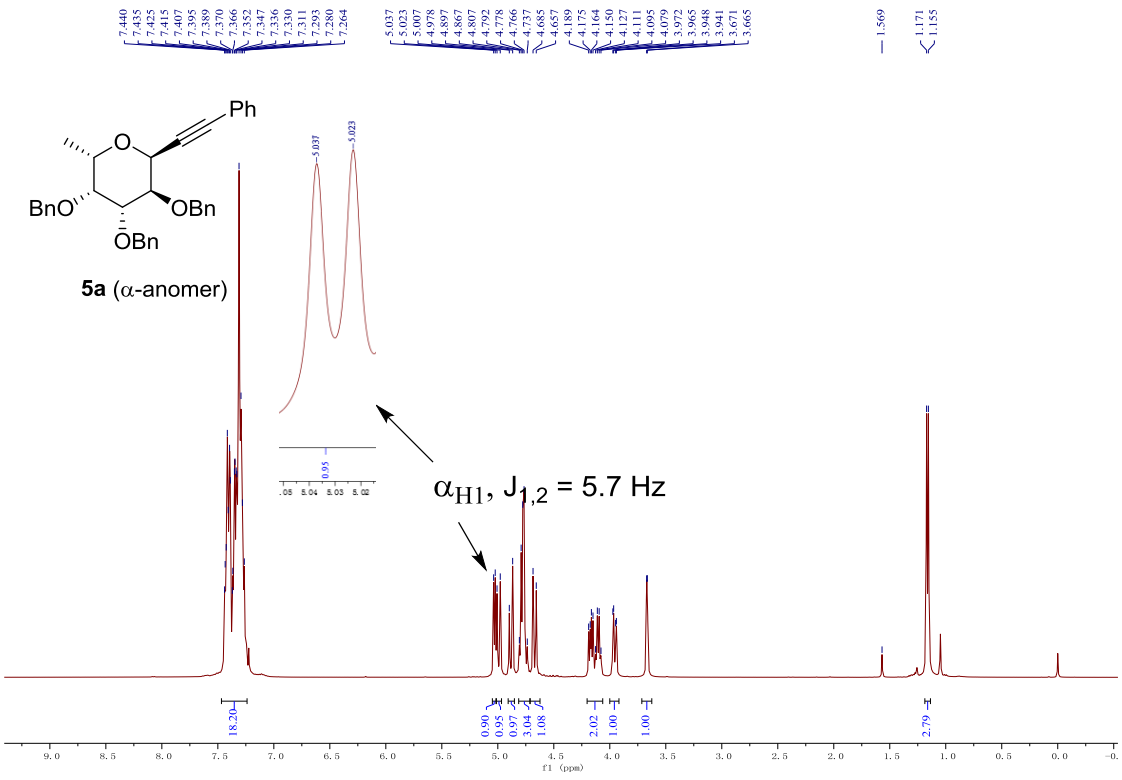

Ph
BnO
O
BnO
OBn
OBn
4a(β-anomer)
200 MHz NMR
f1 (ppm)

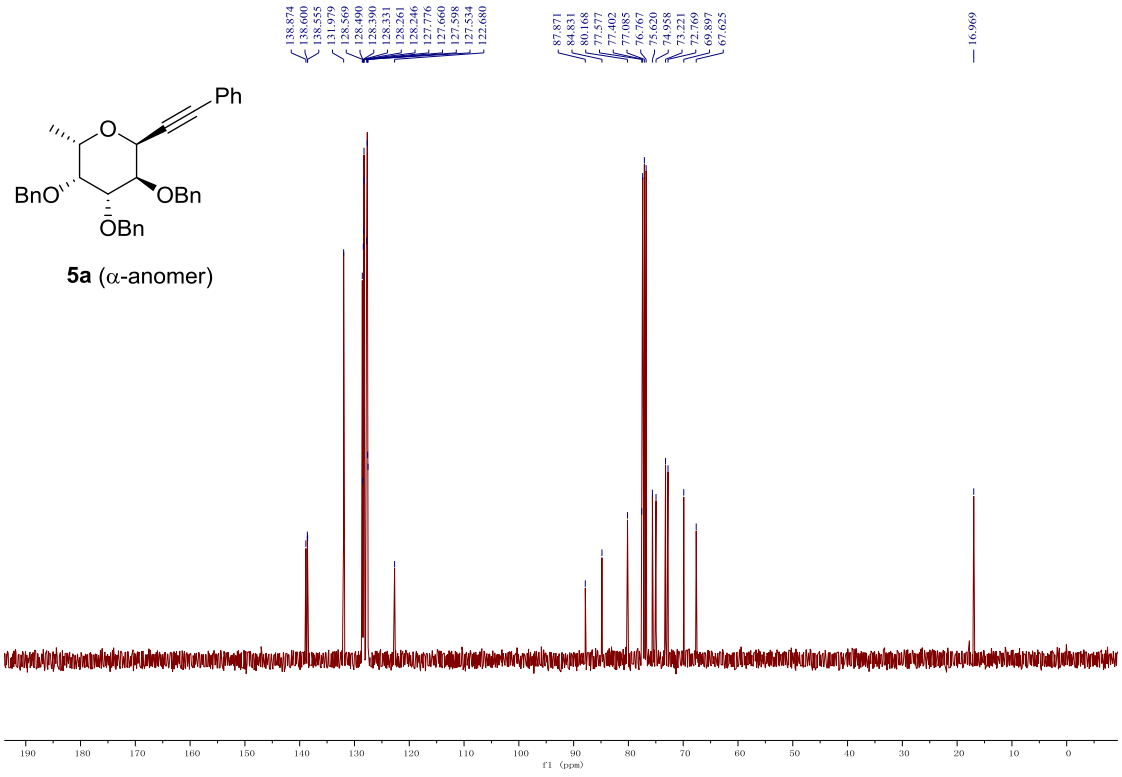

n-Bu
BnO
BnO
OBn
OBn
4b (α-anomer)
16.23
1.98
1.00
1.05
1.08
1.98
2.35
1.87
2.96
2.07
1.02
2.02
3.96
2.88
f1 (ppm)

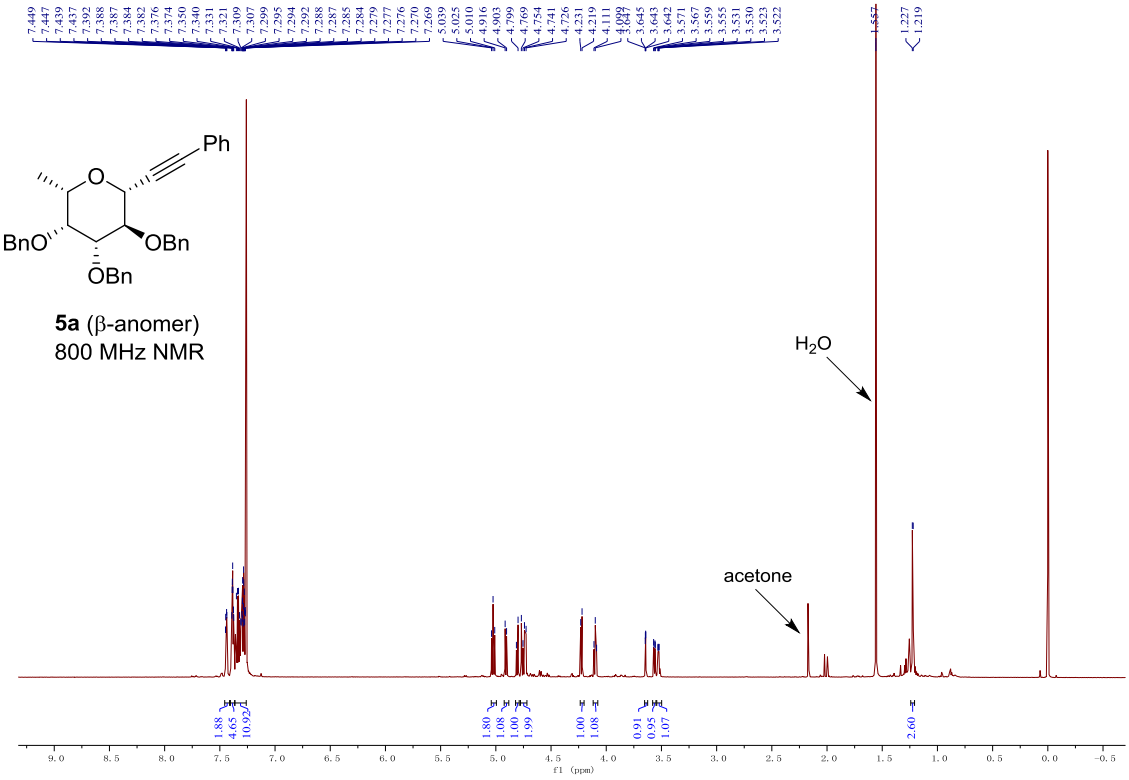

n-Bu
BnO
BnO
OBn
OBn
4b (α-anomer)
f1 (ppm)

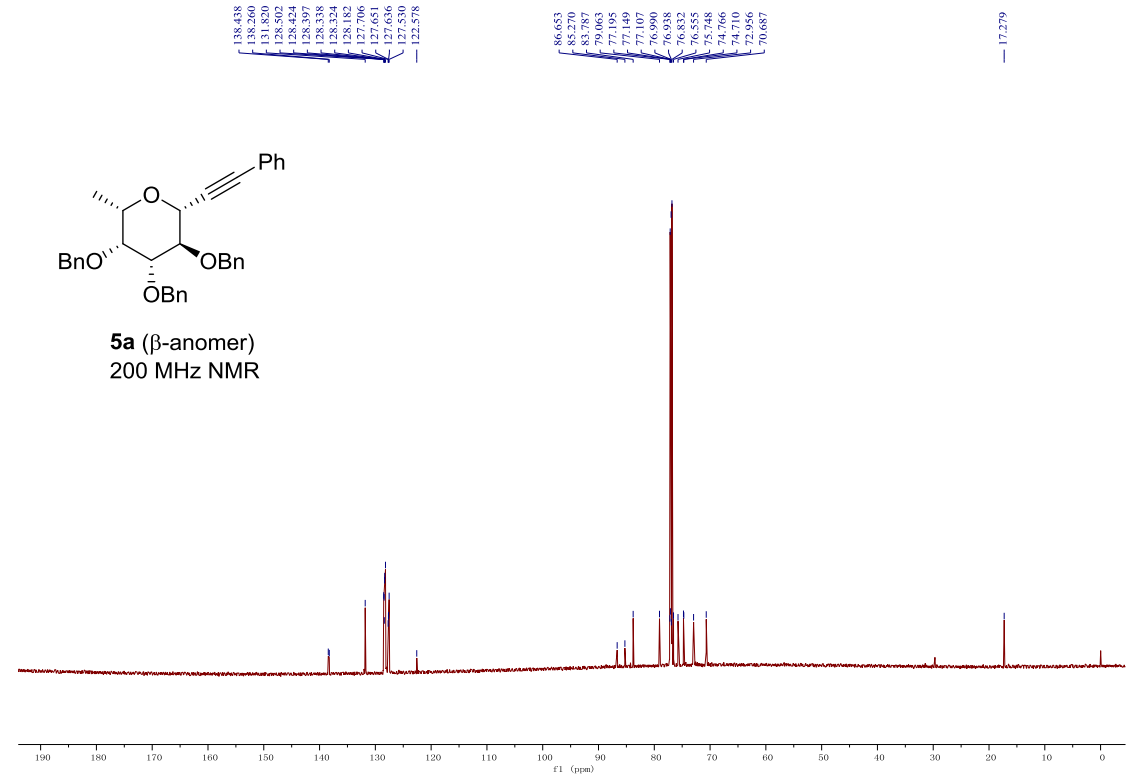

n-Bu
BnO
O
BnO
OBn
OBn
4b (β-anomer)
800 MHz NMR
H2O
f1 (ppm)

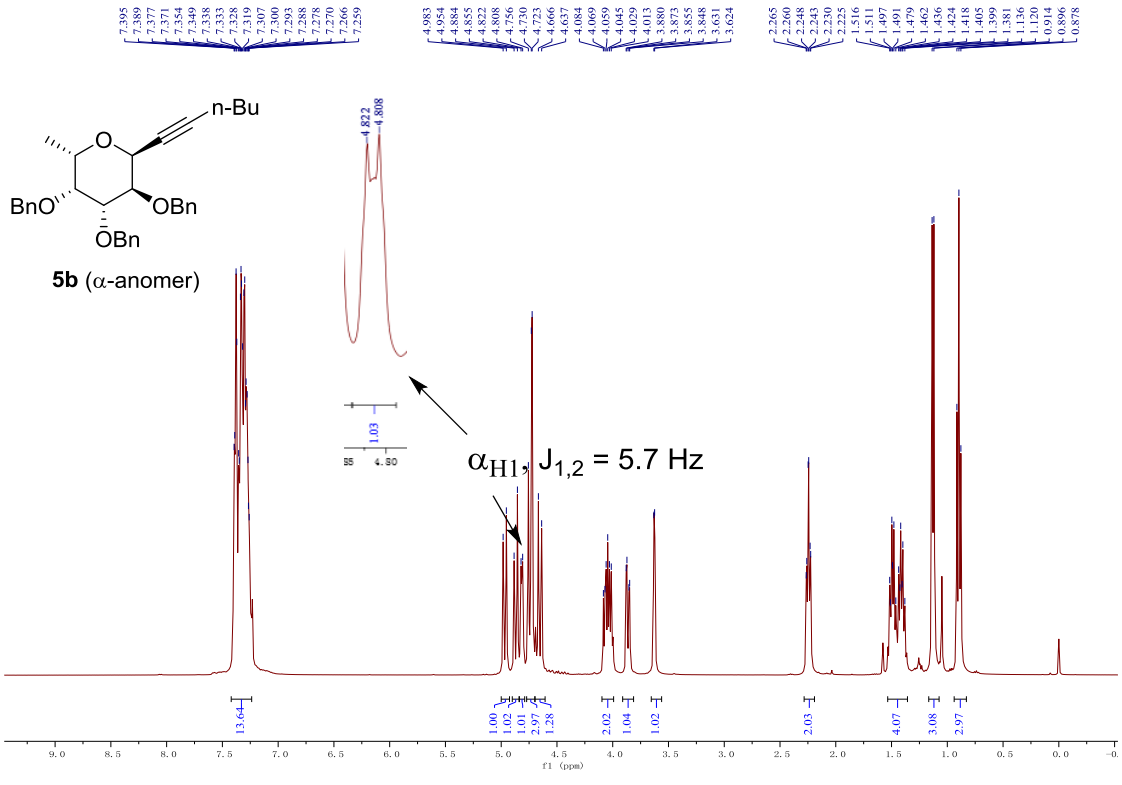

n-Bu
BnO
O
BnO
OBn
OBn
4b (β-anomer)
200 MHz NMR
f1 (ppm)

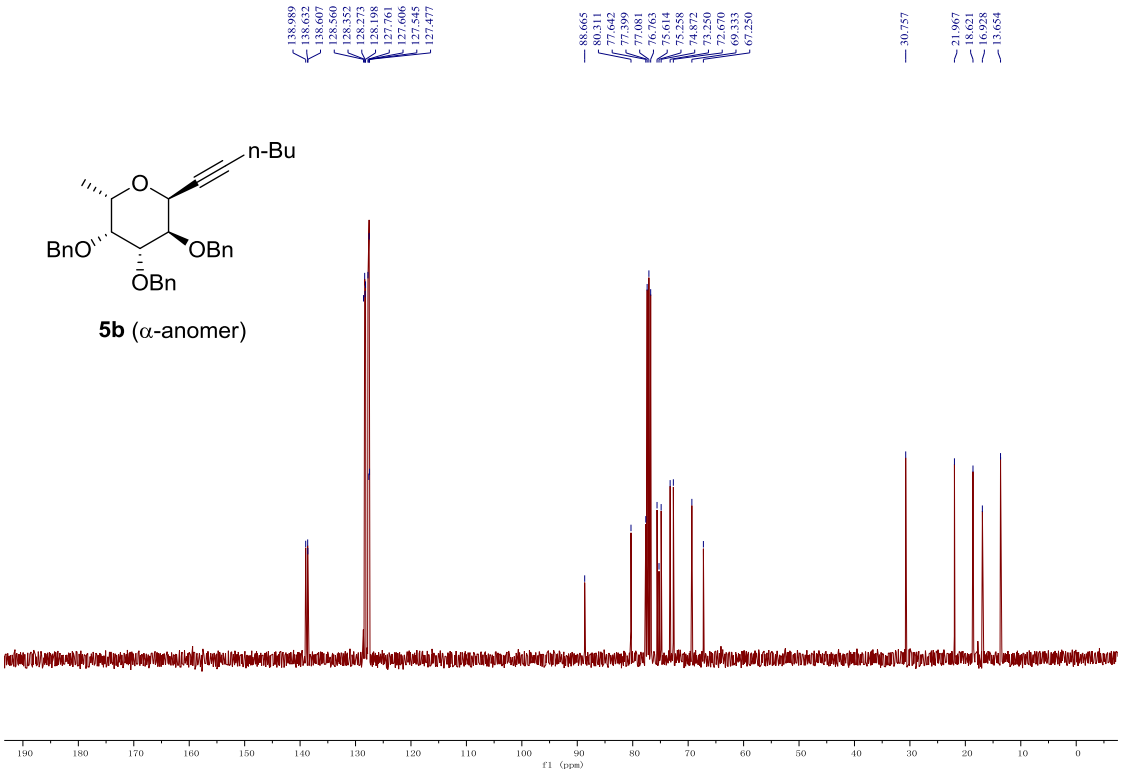

Ph
O
BnO
OBn
OBn
5a (α-anomer)
5.037
5.023
αH1, J1,2 = 5.7 Hz

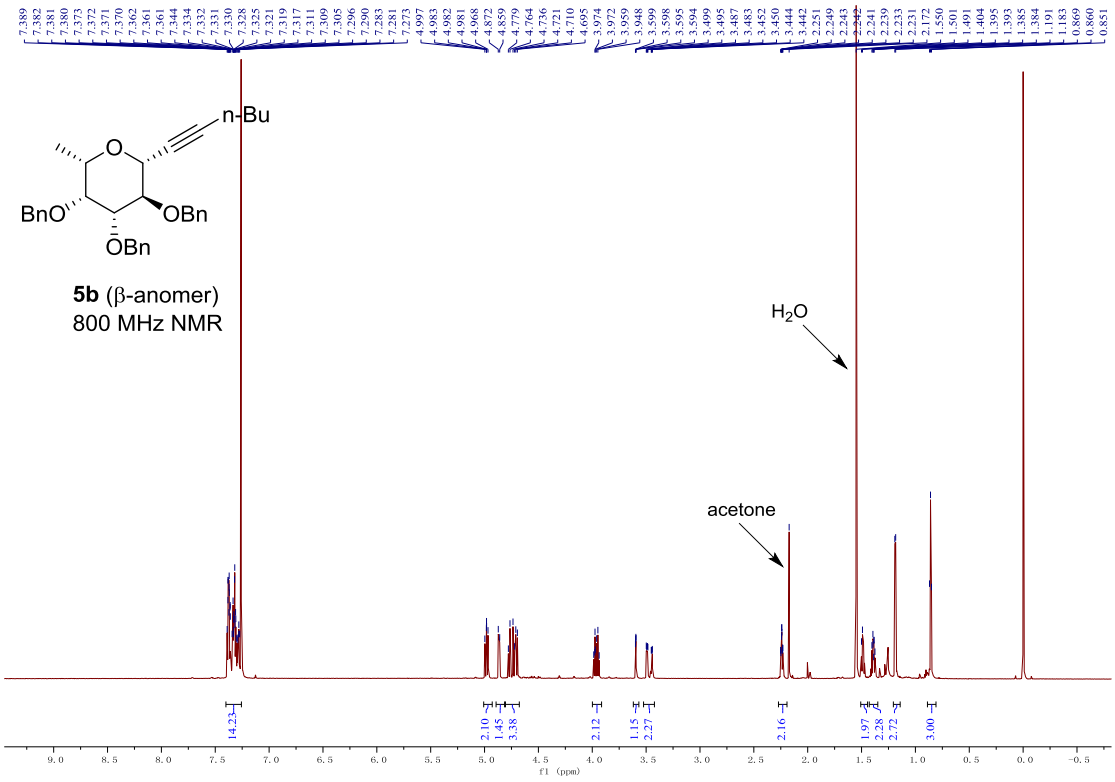

Ph
O
BnO
OBn
OBn
5a (α-anomer)


Ph
O
BnO
OBn
OBn
5a (β-anomer)
800 MHz NMR
H2O
acetone
f1 (ppm)

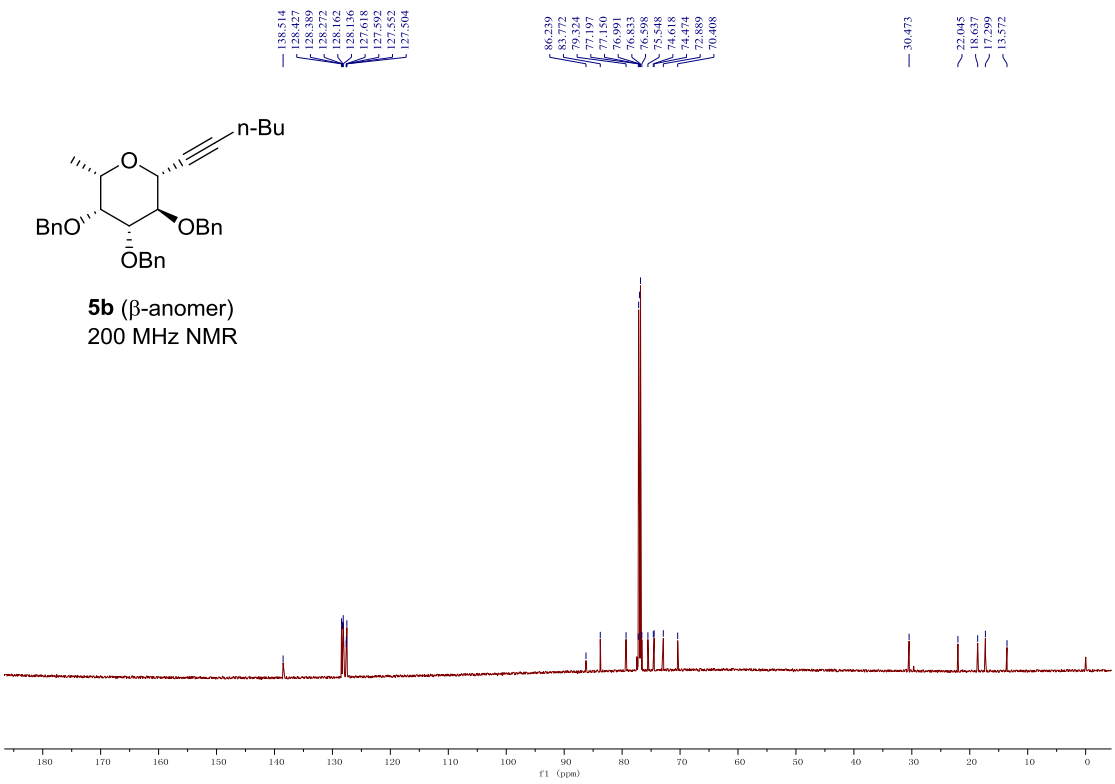

Ph
O
BnO
OBn
OBn
5a (β-anomer)
200 MHz NMR
f1 (ppm)


n-Bu
BnO
OBn
OBn
5b (α-anomer)
4.822
4.808
1.03
α_{H1}, $J_{1,2}$ = 5.7 Hz
13.64
1.00
1.02
1.01
2.97
1.28
2.02
1.04
1.02
2.03
4.07
3.08
2.97
f1 (ppm)

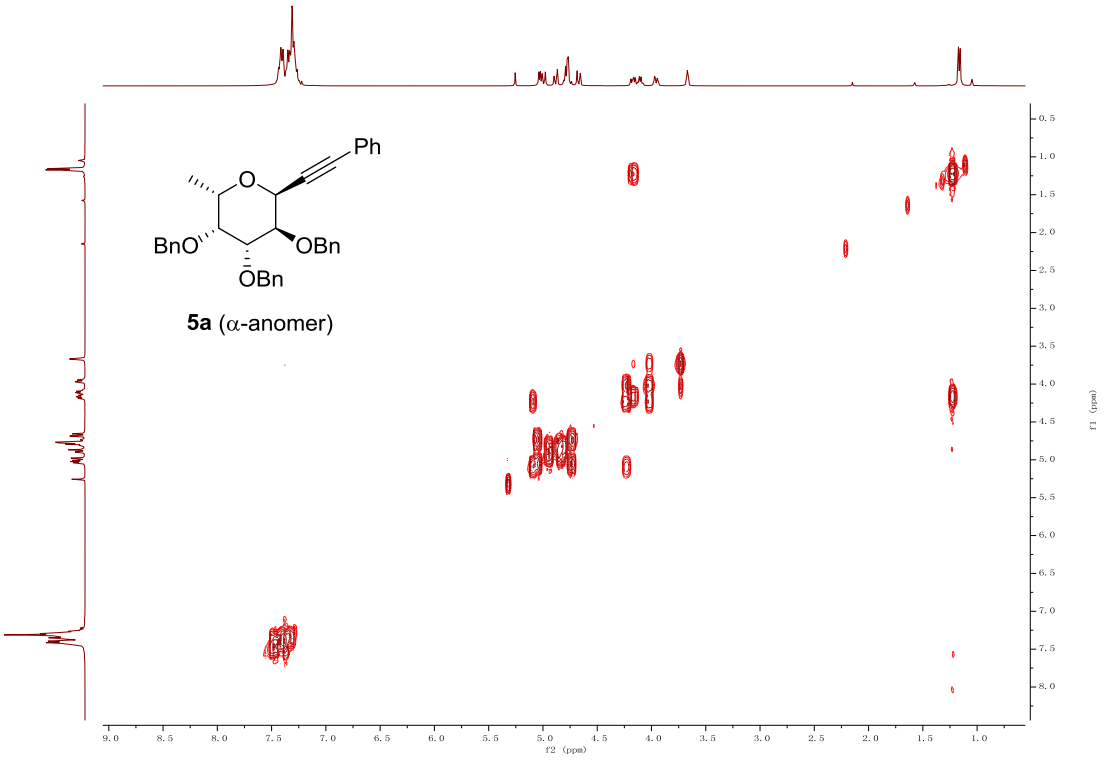

n-Bu
BnO
OBn
OBn
5b (α-anomer)
f1 (ppm)

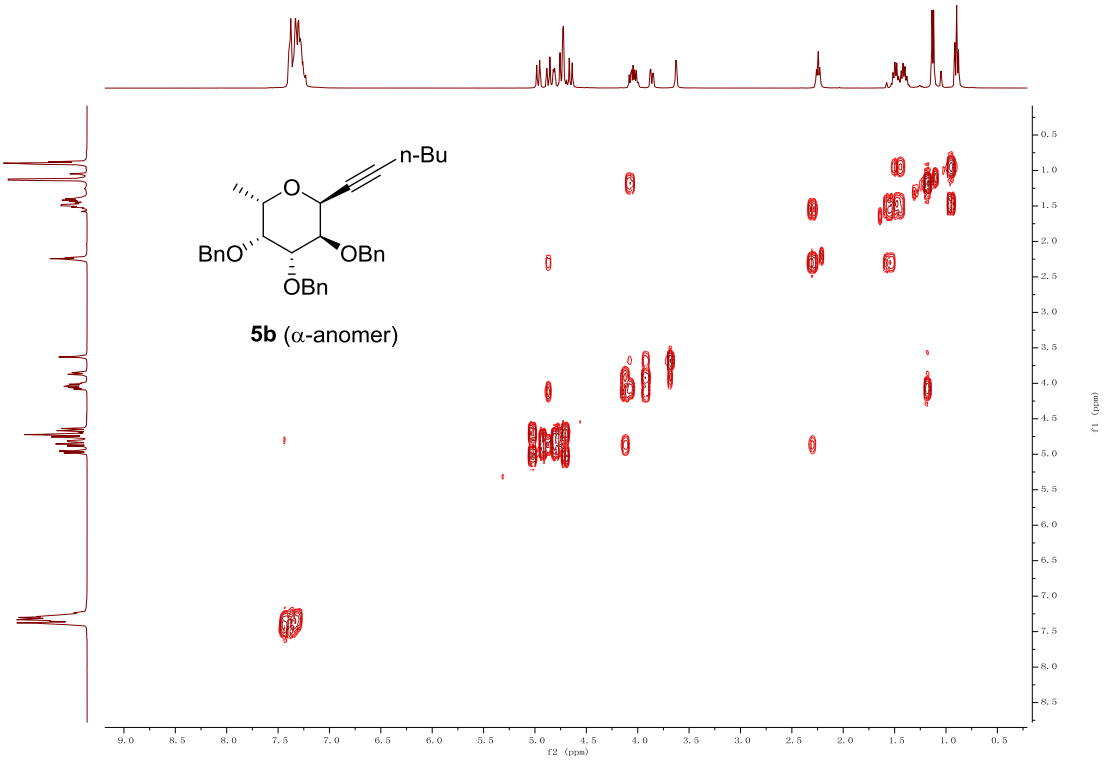


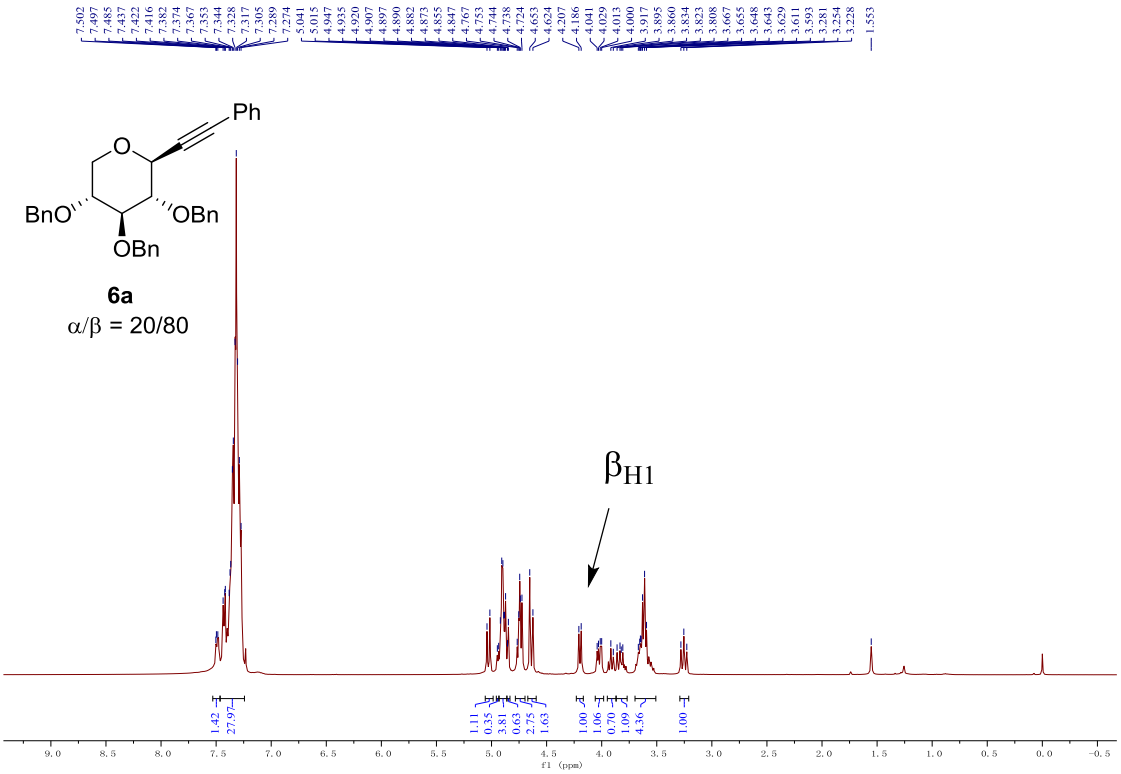
5b (β-anomer)
800 MHz NMR

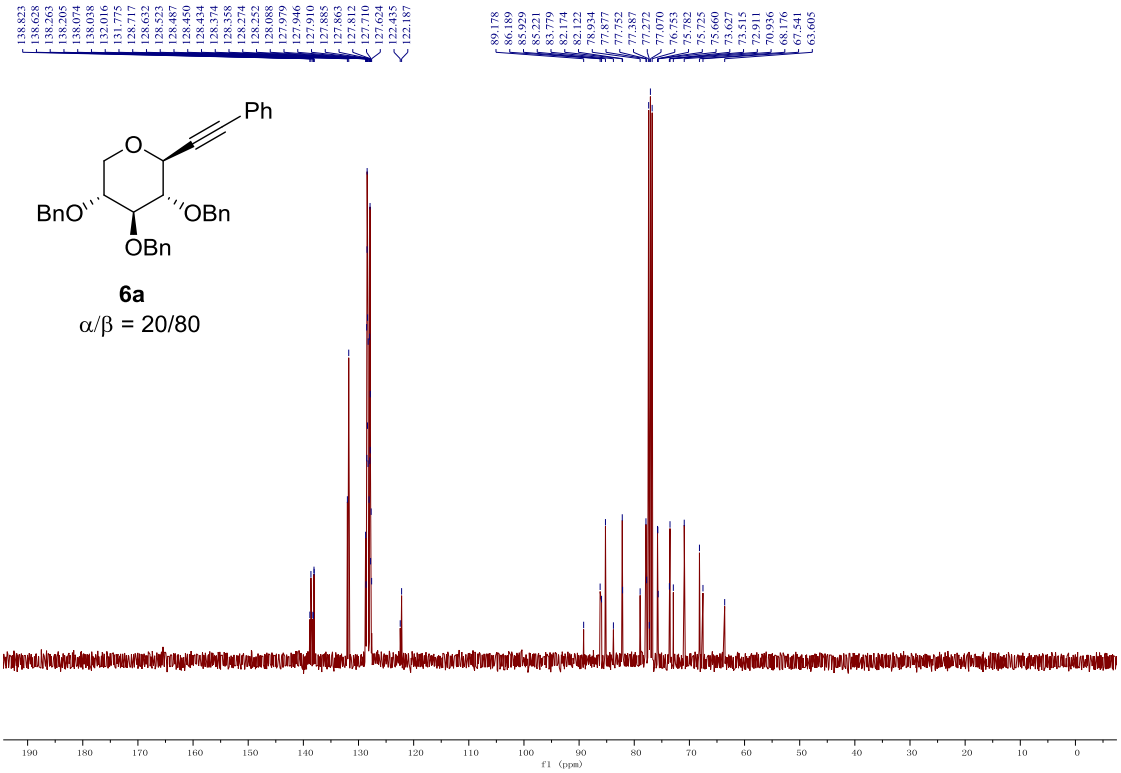


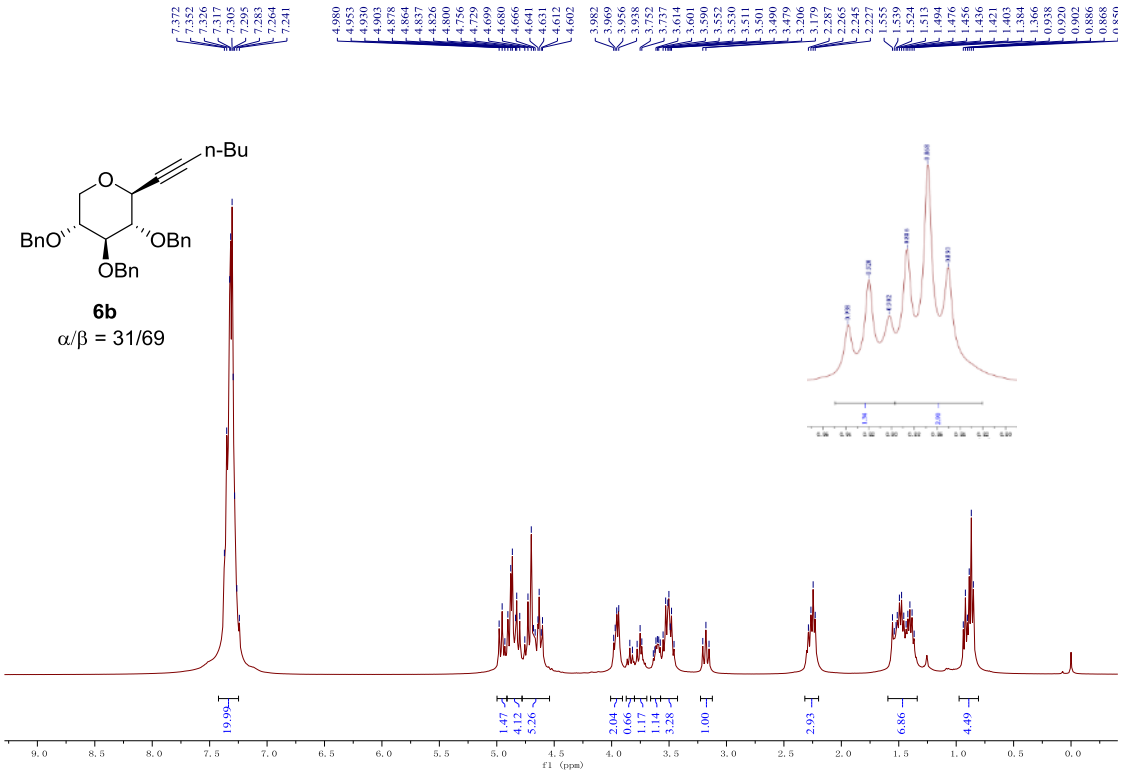
5b (β-anomer)
200 MHz NMR

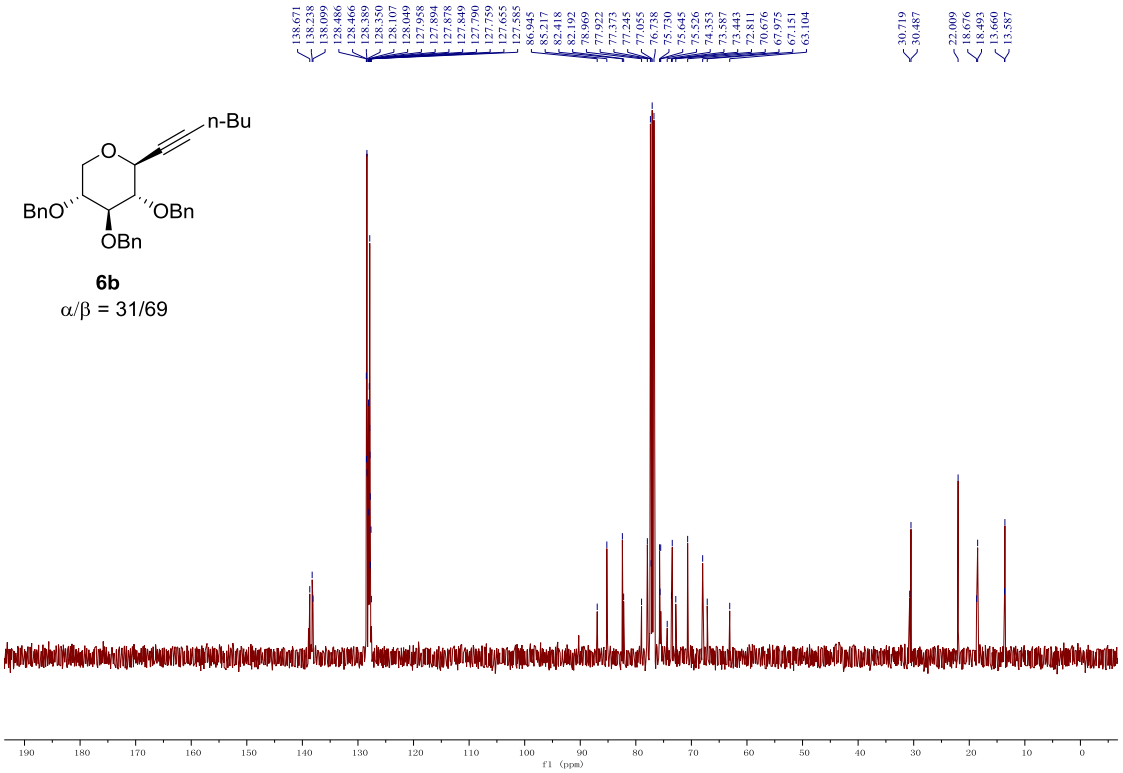

Ph
O
BnO
OBn
OBn
5a (α-anomer)
f2 (ppm)
f1 (ppm)

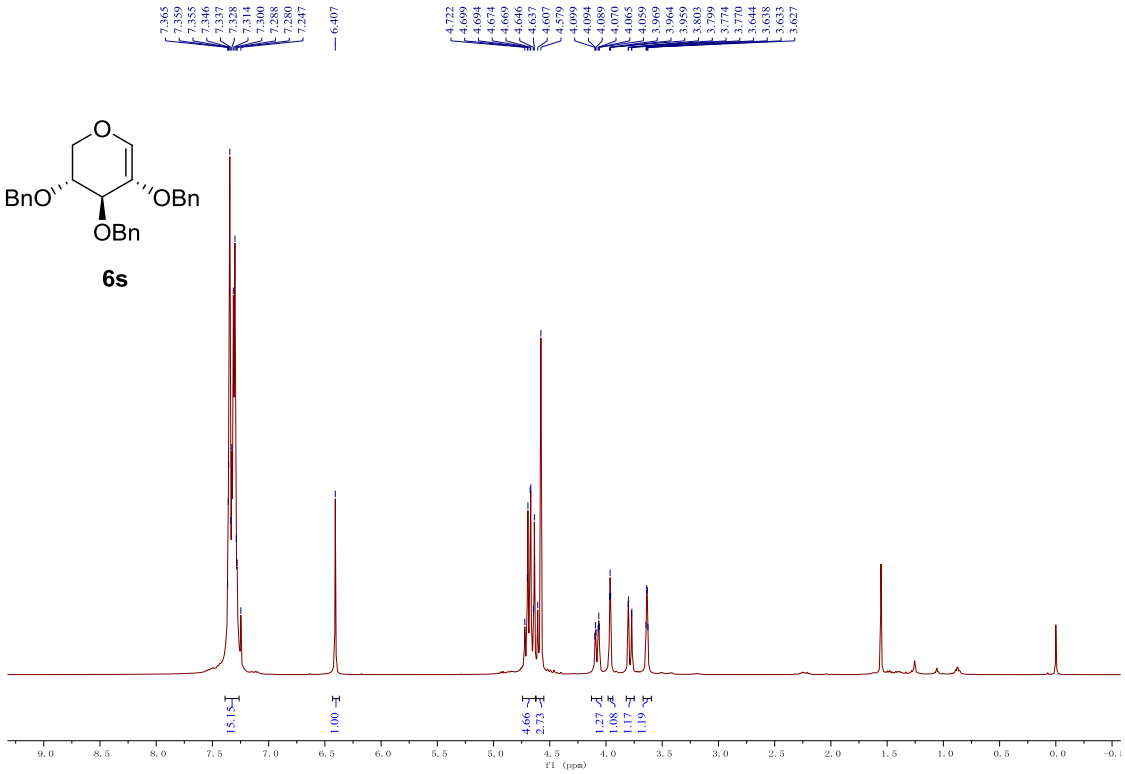

n-Bu
O
BnO
OBn
OBn
5b (α-anomer)
f2 (ppm)
f1 (ppm)

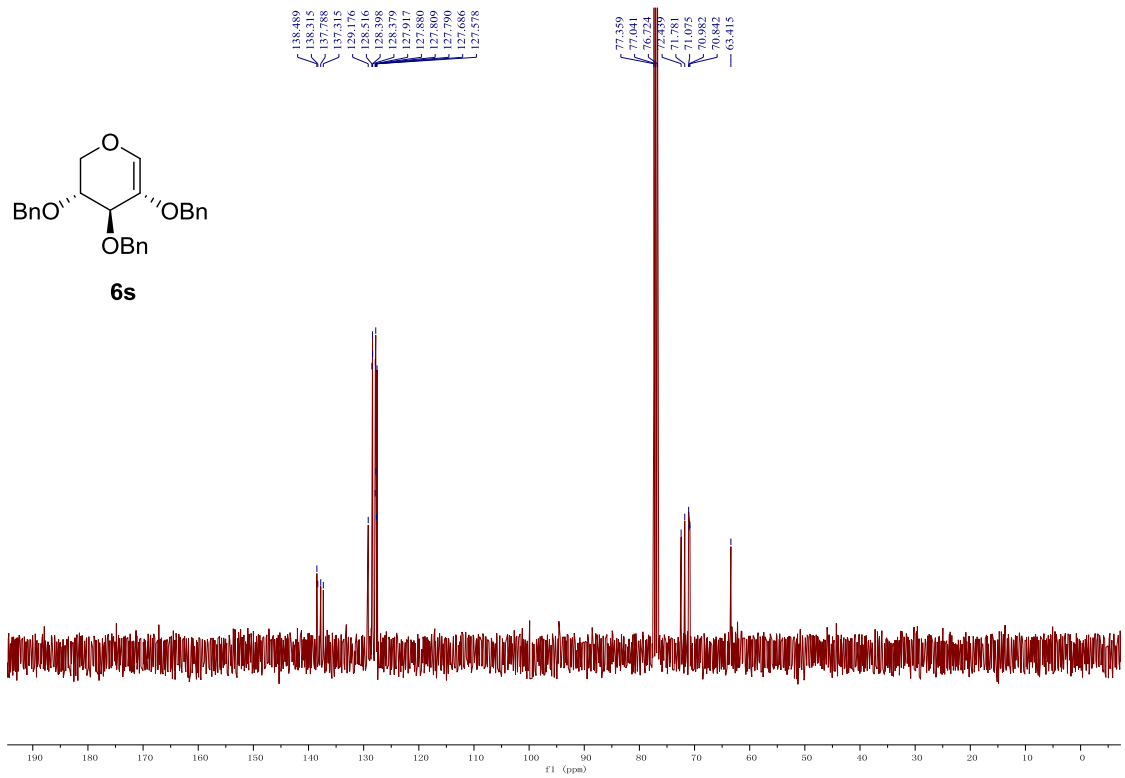

Ph
O
BnO
OBn
OBn
6a
α/β = 20/80
βH1

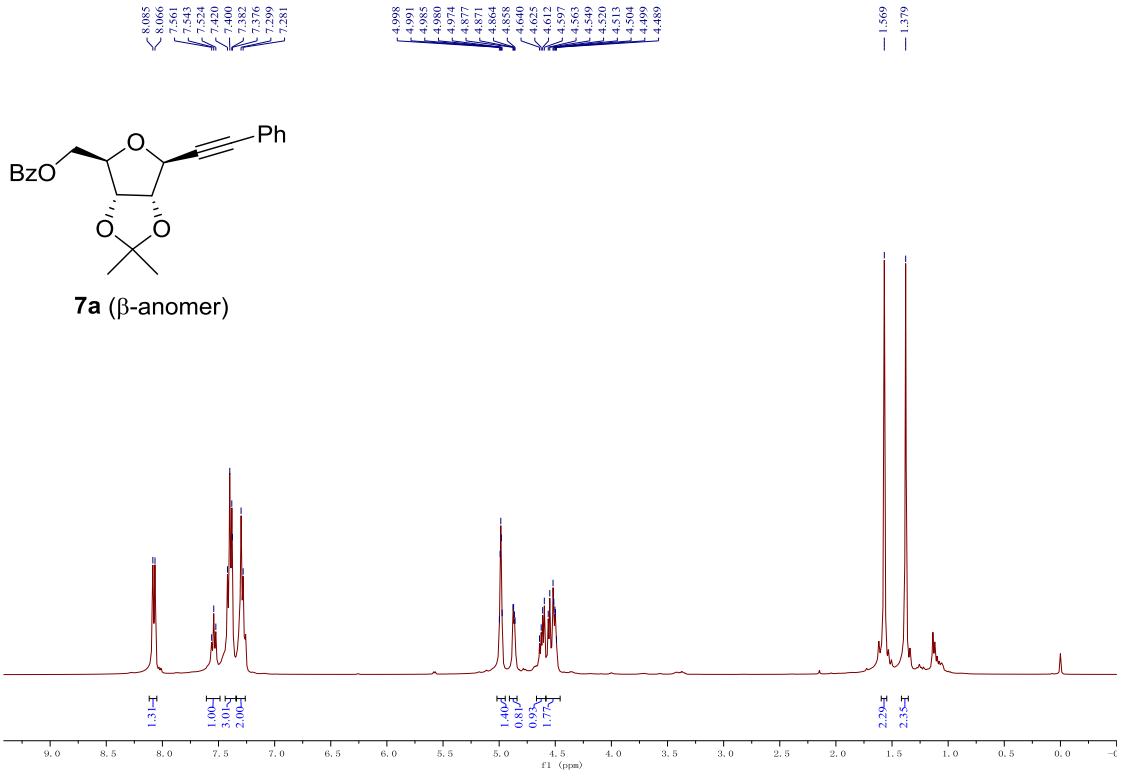

Ph
O
BnO
OBn
OBn
6a
α/β = 20/80


n-Bu
O
BnO
OBn
OBn
6b
α/β = 31/69
19.99
1.47
4.12
5.26
2.04
0.66
1.17
1.14
3.28
1.00
2.93
6.86
4.49
f1 (ppm)

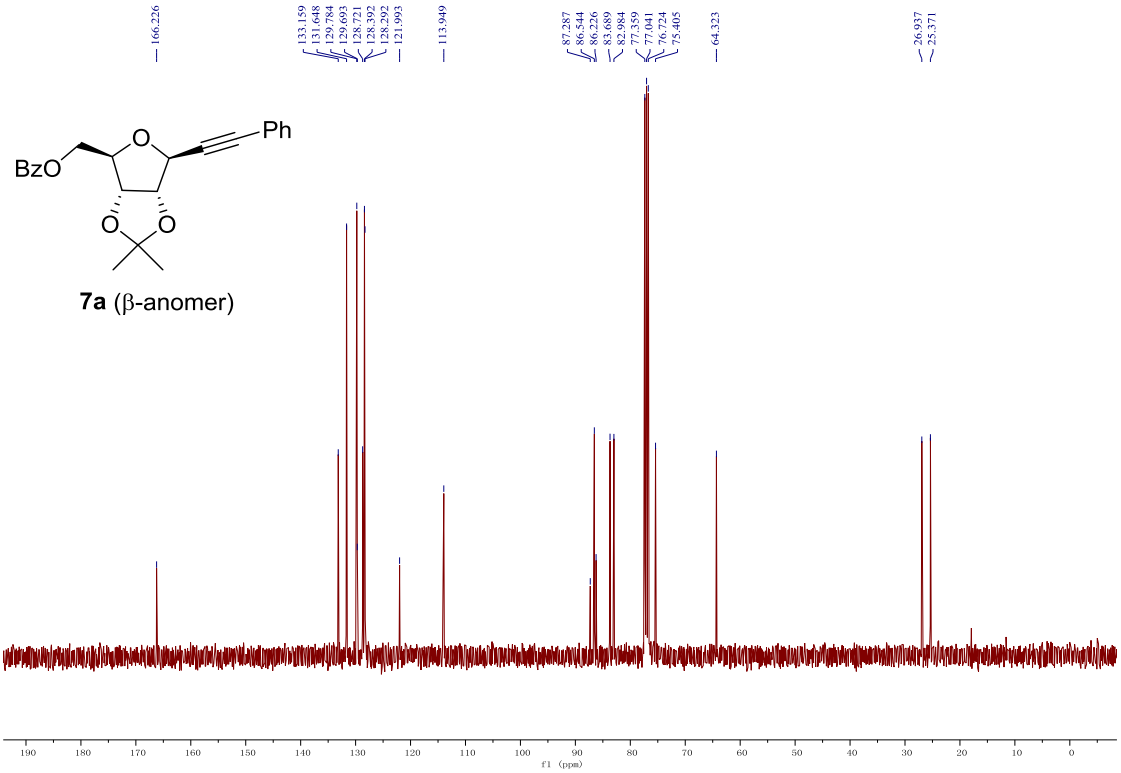

n-Bu
O
BnO
OBn
OBn
6b
α/β = 31/69
f1 (ppm)


7.365
7.359
7.355
7.346
7.337
7.328
7.314
7.300
7.288
7.280
7.247
6.407
4.722
4.699
4.694
4.674
4.669
4.646
4.637
4.607
4.579
4.099
4.094
4.089
4.070
4.065
4.059
3.969
3.964
3.959
3.803
3.799
3.774
3.770
3.644
3.638
3.633
3.627
BnO
OBn
OBn
6s
15.15
1.00
4.66
2.73
1.27
1.08
1.17
1.19
f1 (ppm)

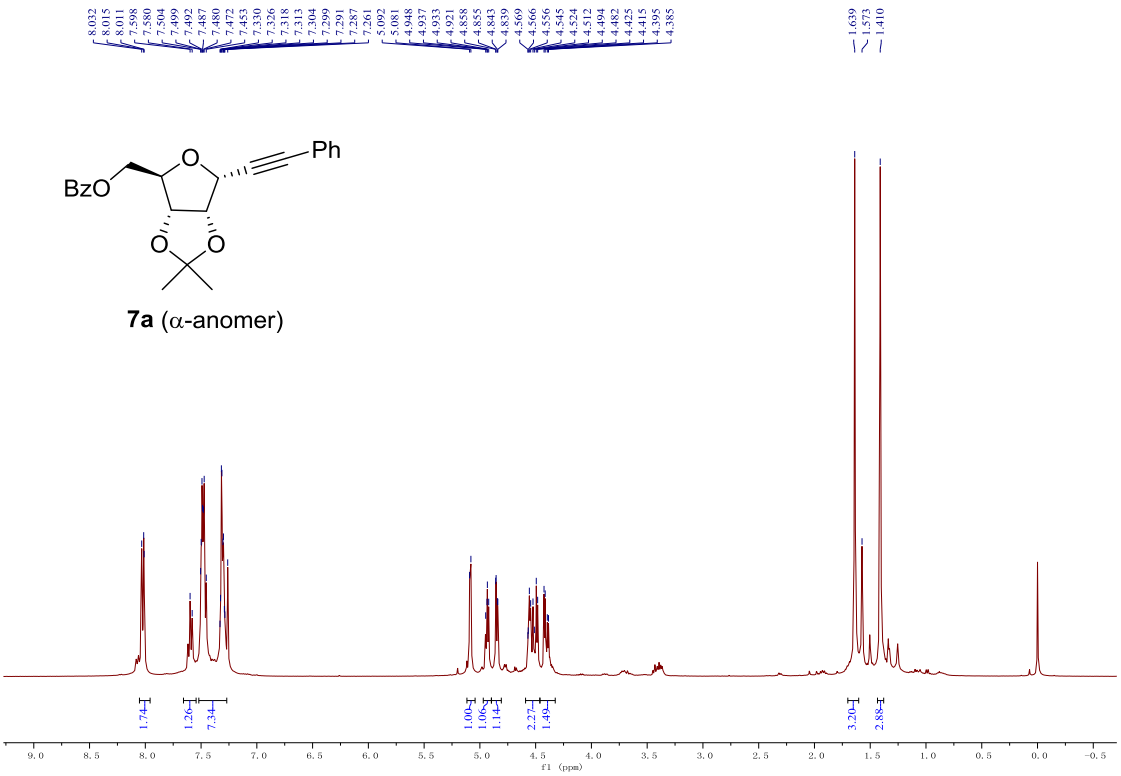

138.489
138.315
137.788
137.315
129.176
128.516
128.398
128.379
127.917
127.880
127.809
127.790
127.686
127.578
77.359
77.041
76.724
72.459
71.781
71.075
70.982
70.842
63.415
BnO
OBn
OBn
6s
f1 (ppm)



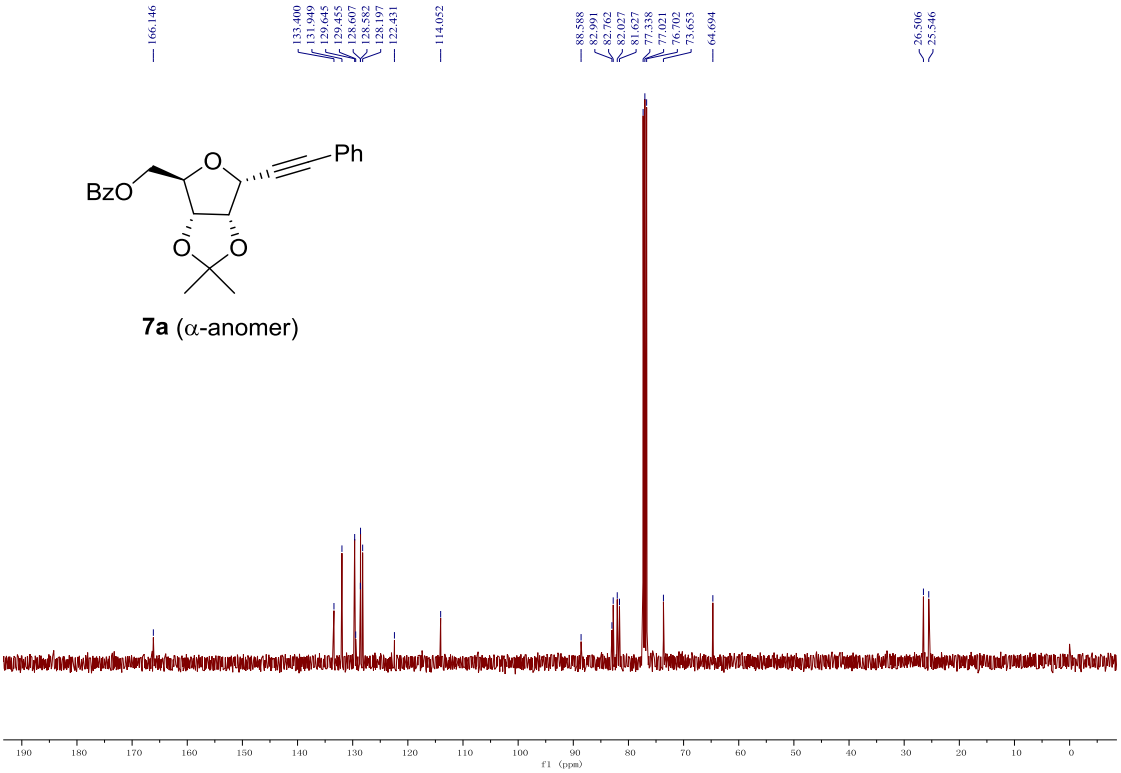
7a (β-anomer)



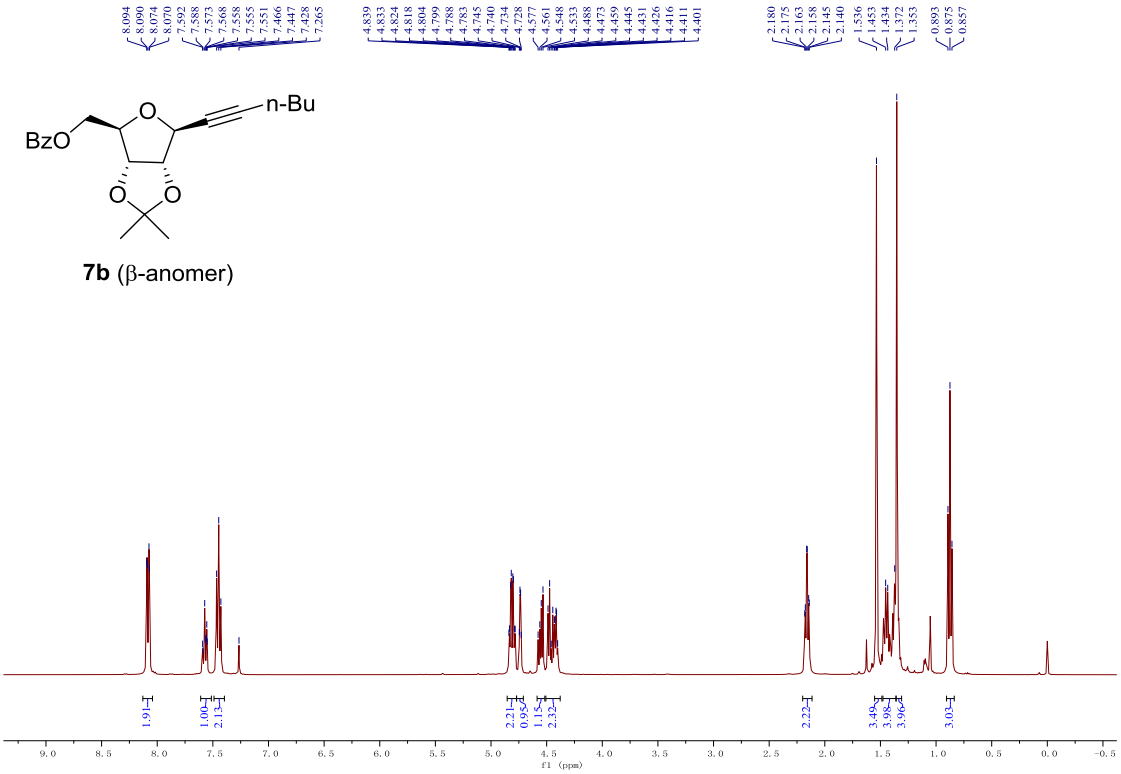
7a (β-anomer)



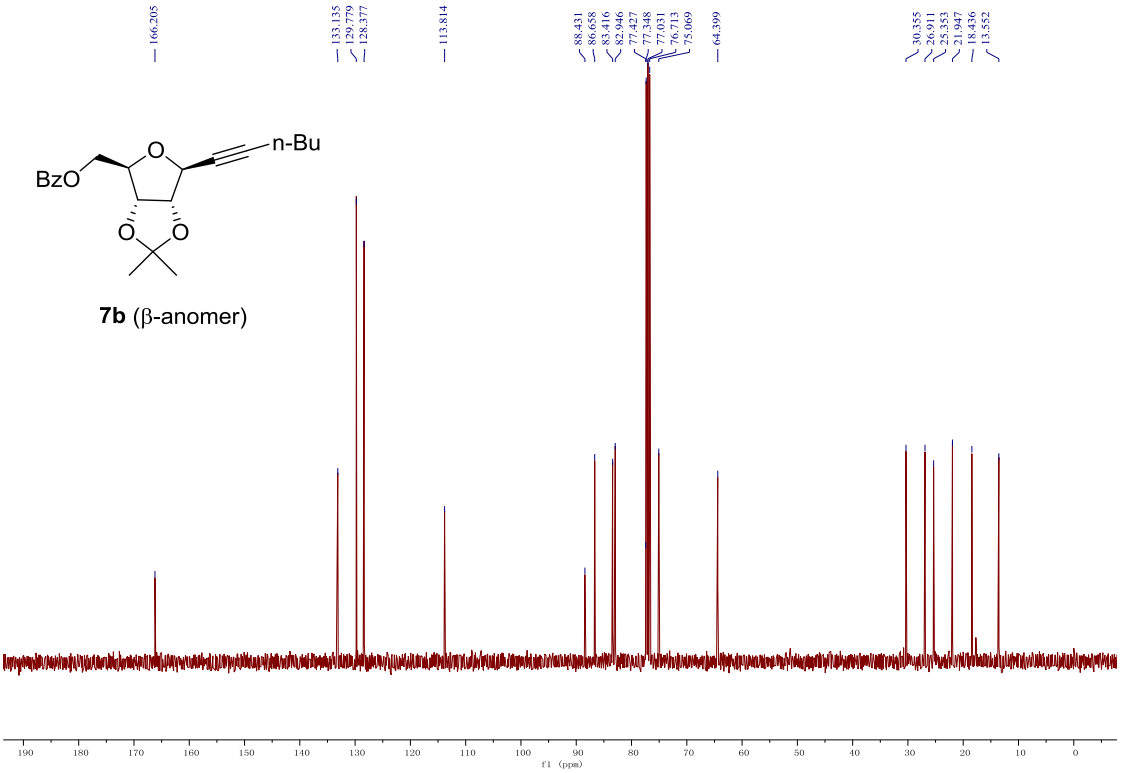
7a (α-anomer)



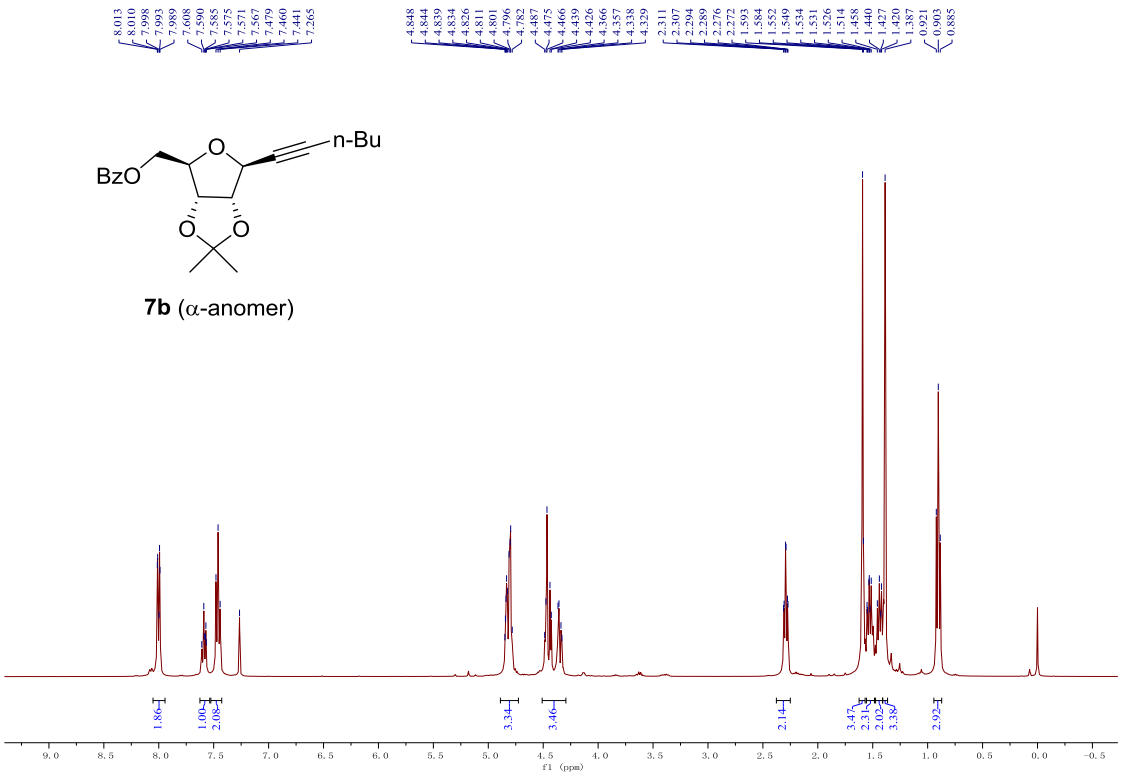
7a (α-anomer)

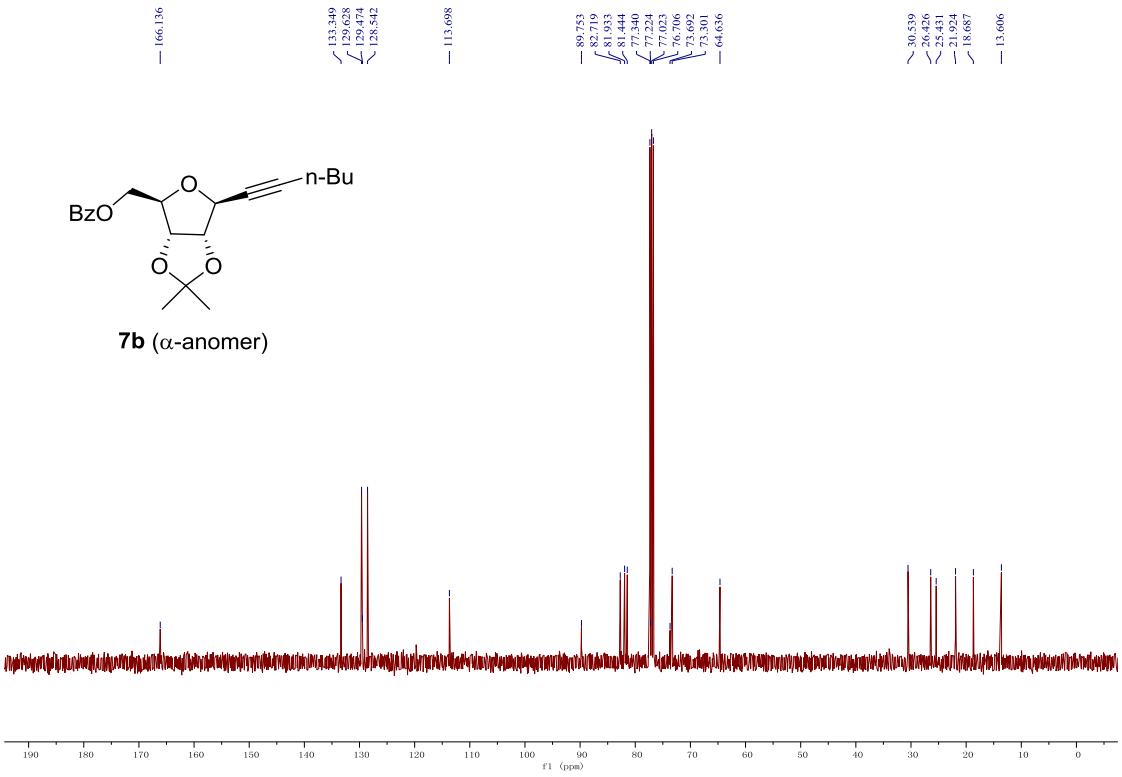


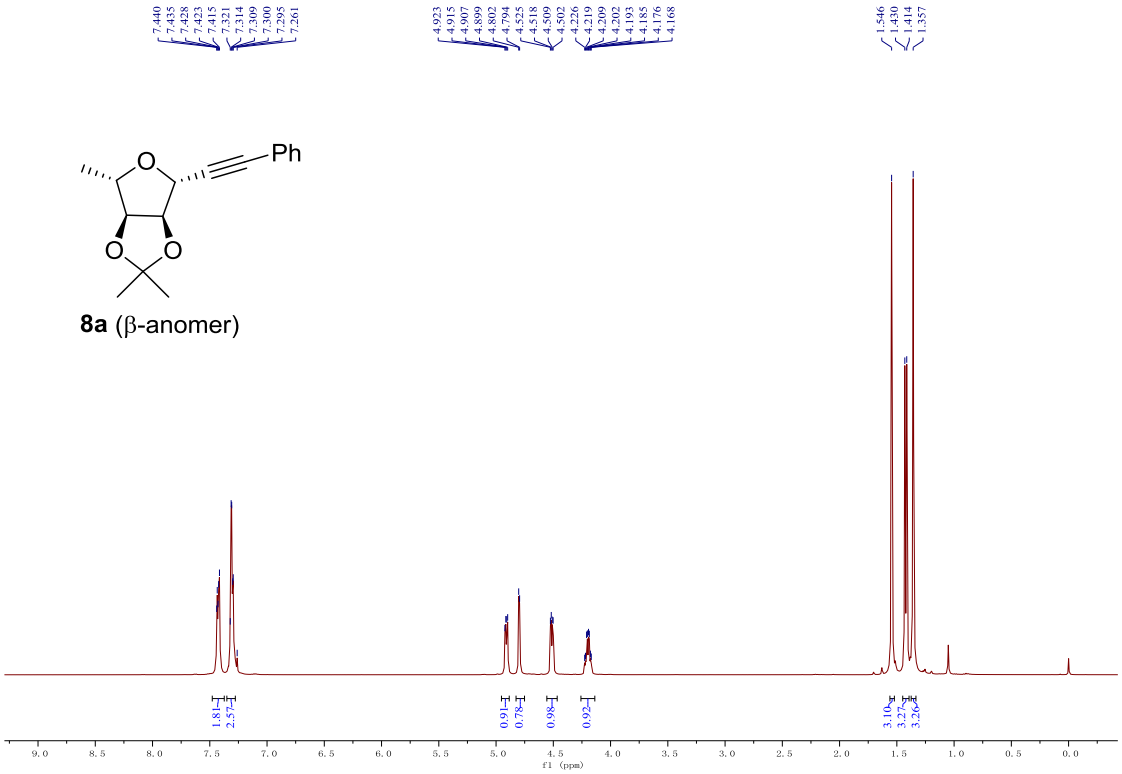
7b (β-anomer)

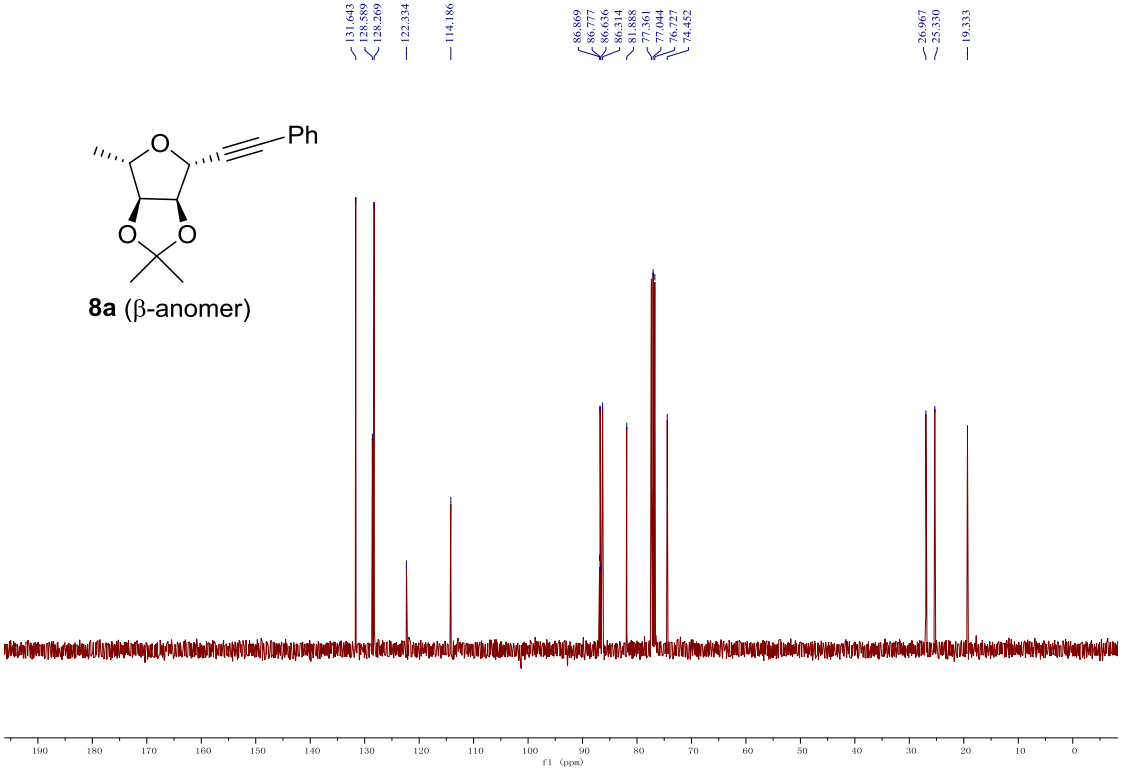


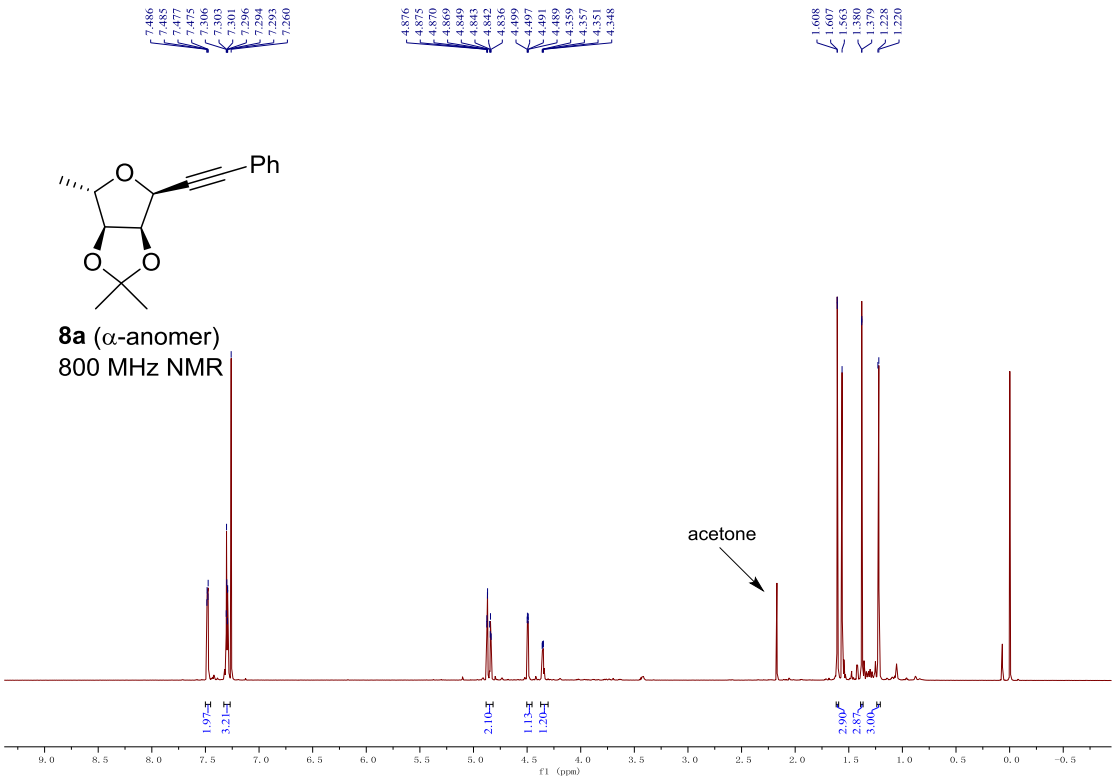
7b (β-anomer)

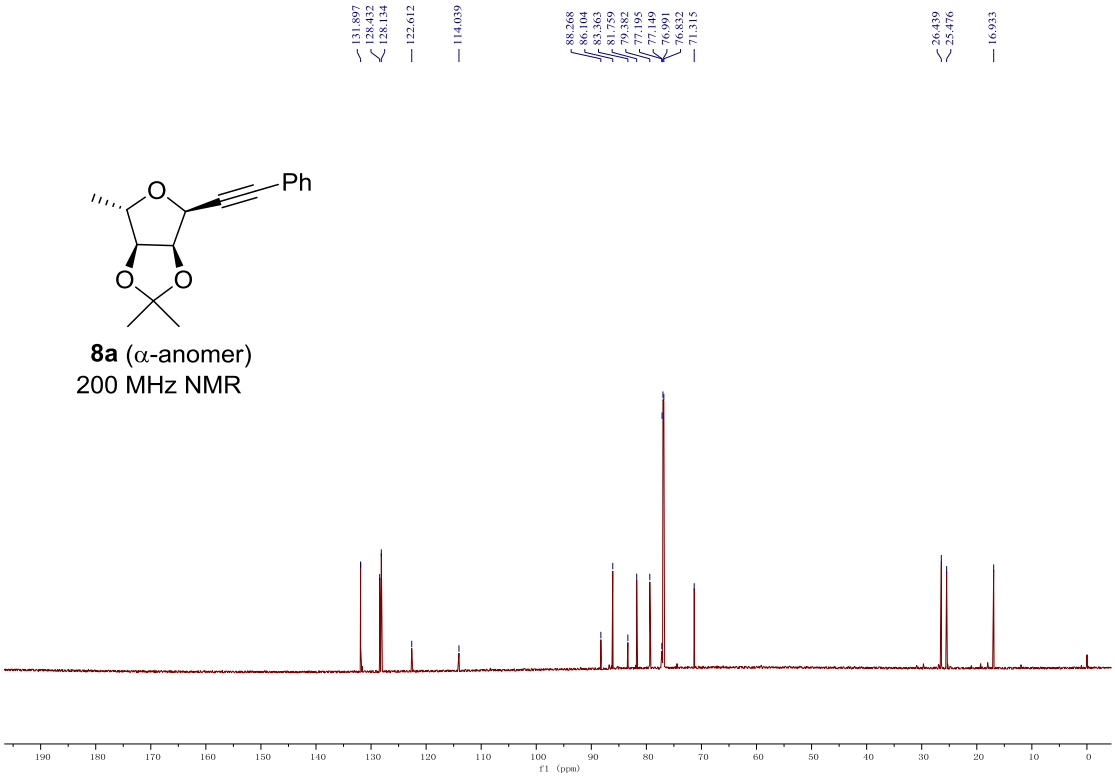

8.013
8.010
7.998
7.993
7.989
7.608
7.590
7.585
7.575
7.571
7.567
7.479
7.460
7.441
7.265
4.848
4.844
4.839
4.834
4.826
4.811
4.801
4.796
4.782
4.487
4.475
4.466
4.459
4.426
4.366
4.357
4.338
4.329
2.311
2.307
2.294
2.289
2.276
2.272
1.593
1.584
1.552
1.549
1.544
1.531
1.526
1.514
1.458
1.440
1.427
1.420
1.387
0.921
0.903
0.885
n-Bu
BzO
O
O
O
7b (α-anomer)
1.86
1.00
2.08
3.34
3.46
2.14
3.47
2.31
2.02
3.39
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

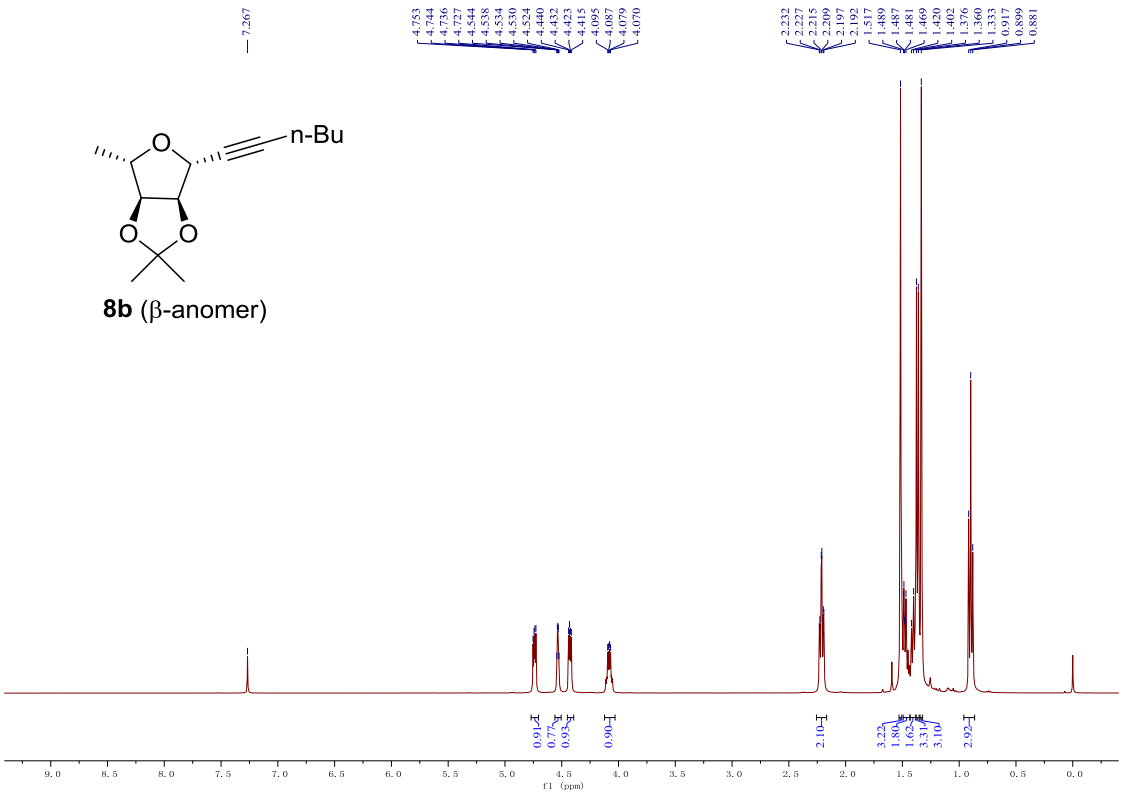

166.136
133.349
129.628
129.474
128.542
113.698
89.753
82.719
81.933
81.444
77.340
77.224
77.023
76.706
73.692
73.301
64.636
30.539
26.426
25.431
21.924
18.687
13.606
n-Bu
BzO
O
O
O
7b (α-anomer)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

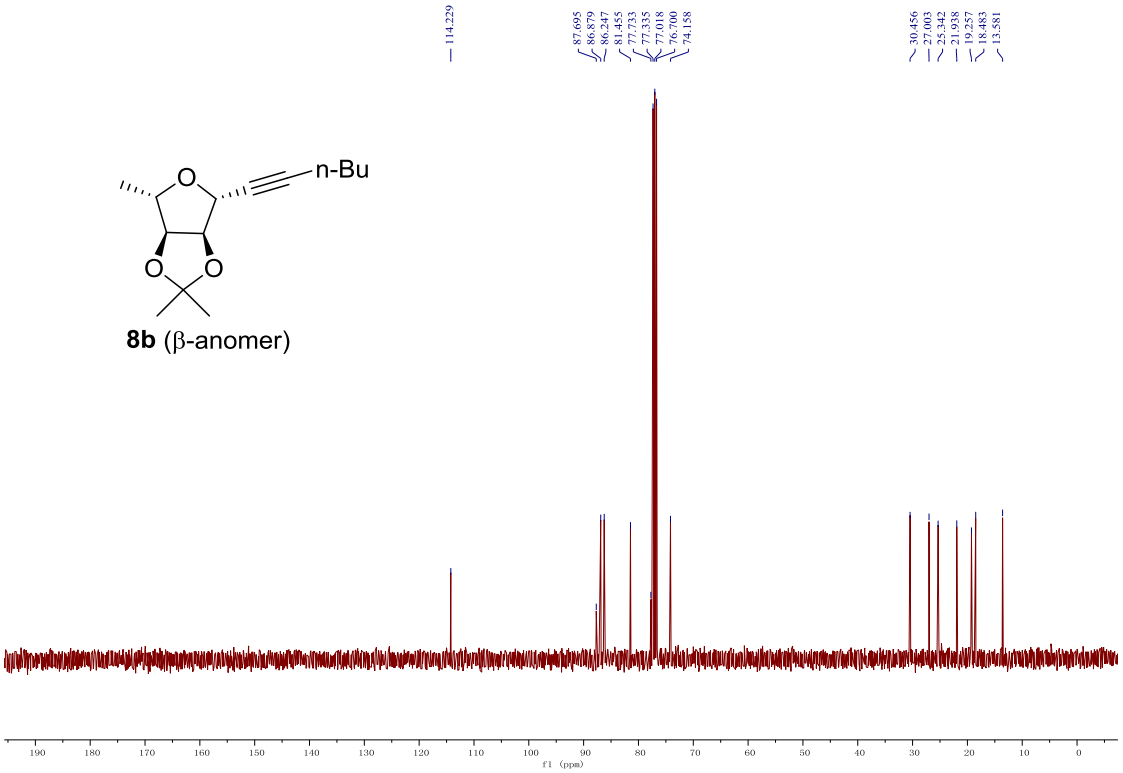

7.440
7.435
7.428
7.423
7.415
7.371
7.314
7.309
7.300
7.295
7.261
4.923
4.915
4.907
4.899
4.802
4.794
4.525
4.518
4.509
4.502
4.226
4.219
4.209
4.202
4.193
4.185
4.176
4.168
1.546
1.430
1.414
1.357
Ph
O
O
O
8a (β-anomer)
1.81
2.57
0.91
0.78
0.98
0.92
3.10
3.27
3.26
f1 (ppm)

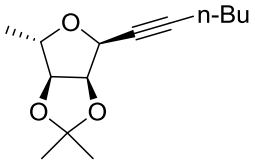

131.643
128.589
128.269
122.334
114.186
86.869
86.777
86.636
86.314
81.888
81.661
77.004
76.727
74.452
26.967
25.330
19.333
Ph
O
O
O
8a (β-anomer)
f1 (ppm)


7.486
7.485
7.477
7.475
7.306
7.303
7.301
7.296
7.294
7.293
7.260
4.876
4.875
4.870
4.869
4.849
4.843
4.842
4.836
4.499
4.497
4.491
4.489
4.359
4.357
4.351
4.348
1.608
1.607
1.563
1.380
1.379
1.228
1.220
Ph
O
O
O
8a (α-anomer)
800 MHz NMR
acetone
1.97
3.21
2.10
1.13
1.20
2.90
2.87
3.00
f1 (ppm)

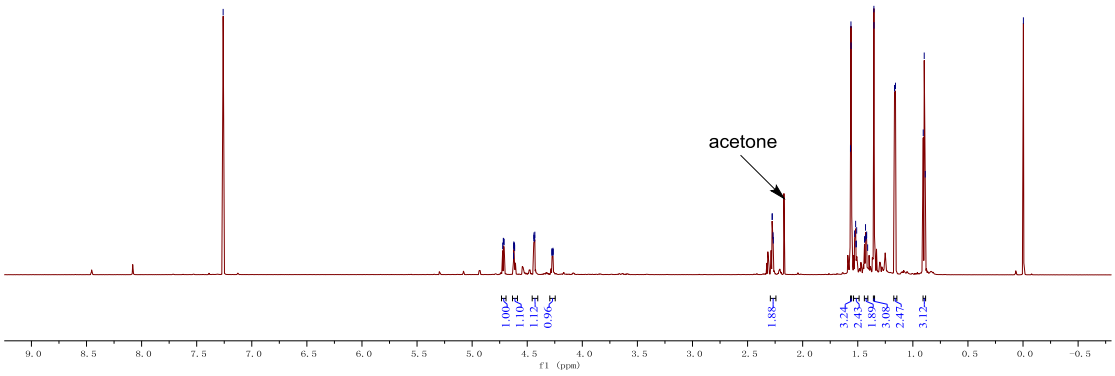

131.897
128.432
128.134
122.612
114.039
88.268
86.104
83.363
81.759
79.382
77.195
77.149
76.991
76.832
71.315
26.439
25.476
16.933
Ph
O
O
O
8a (α-anomer)
200 MHz NMR
f1 (ppm)

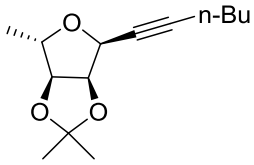

7.267
4.753
4.744
4.736
4.727
4.544
4.538
4.534
4.530
4.524
4.440
4.432
4.423
4.415
4.095
4.087
4.079
4.070
2.232
2.227
2.215
2.209
2.197
2.192
1.517
1.489
1.487
1.481
1.469
1.420
1.402
1.376
1.360
1.333
0.917
0.899
0.881
n-Bu
O
O
O
8b (β-anomer)
0.91
0.77
0.93
0.90
2.10
3.22
1.80
1.62
3.31
3.10
2.92
f1 (ppm)


114.229
87.695
86.879
86.247
81.455
77.733
77.335
77.018
76.700
74.158
30.456
27.003
25.342
21.938
19.257
18.483
13.581
n-Bu
O
O
O
8b (β-anomer)
f1 (ppm)

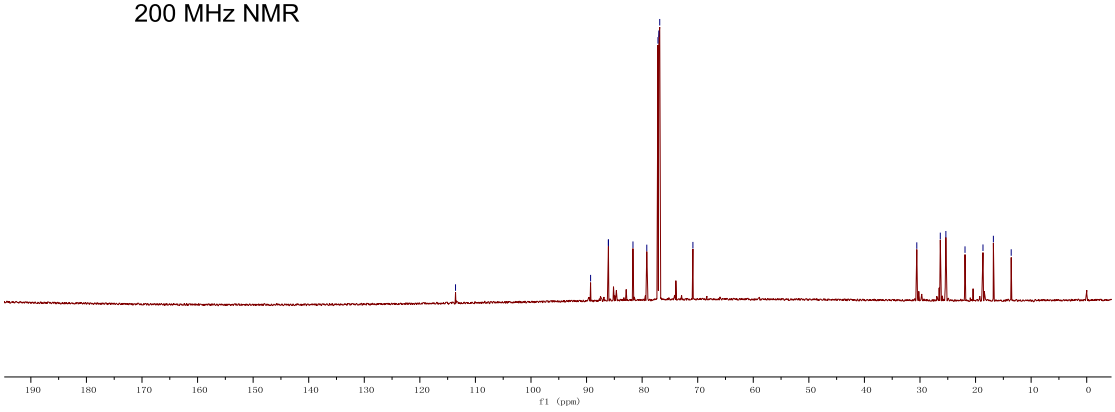


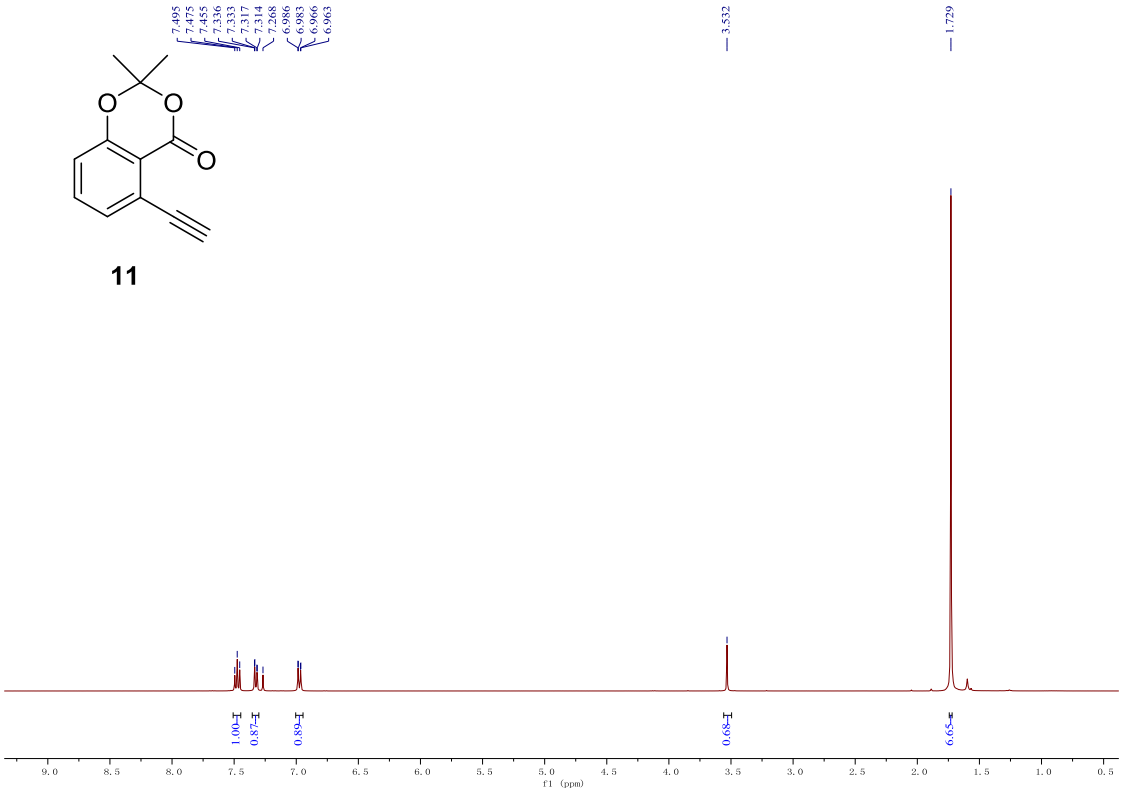
8b (α-anomer)
800 MHz NMR



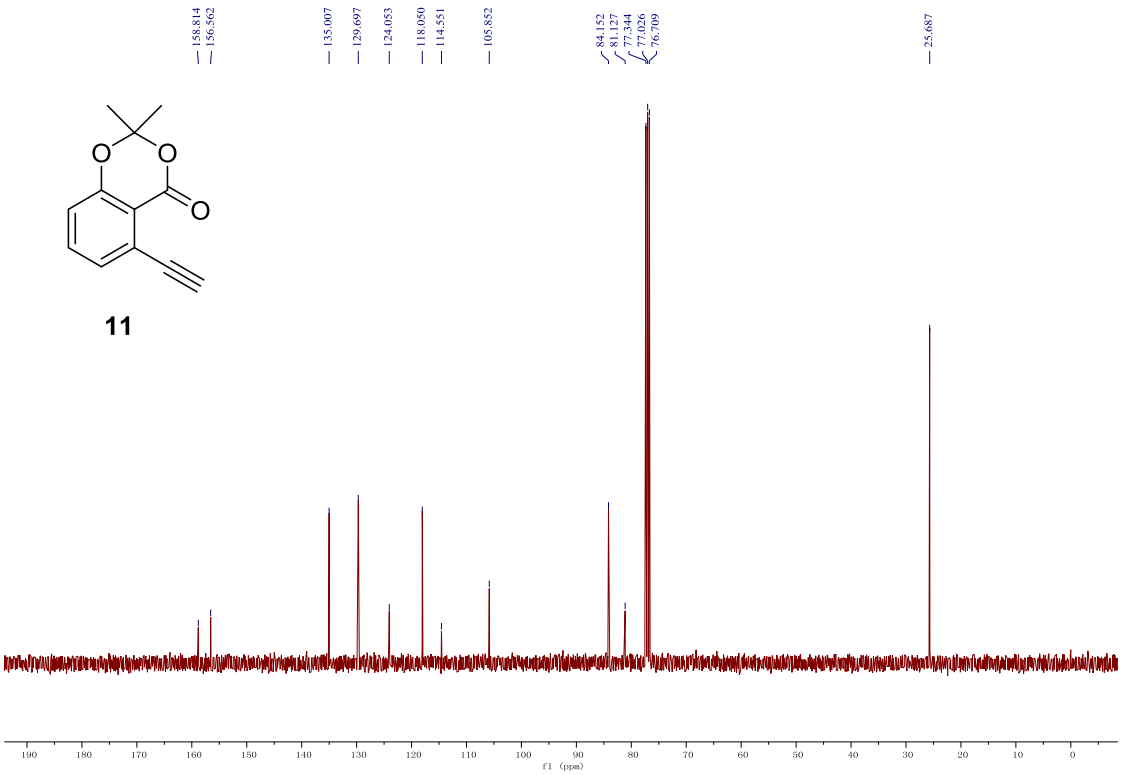


8b (α-anomer)
200 MHz NMR

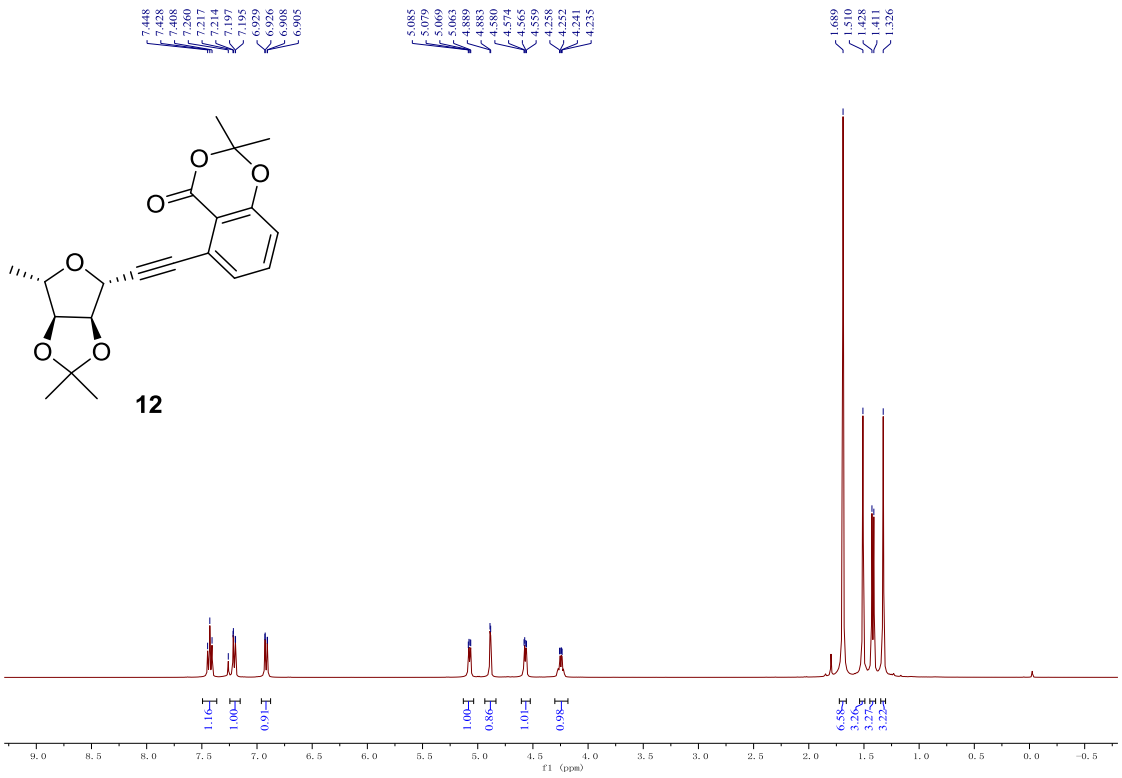


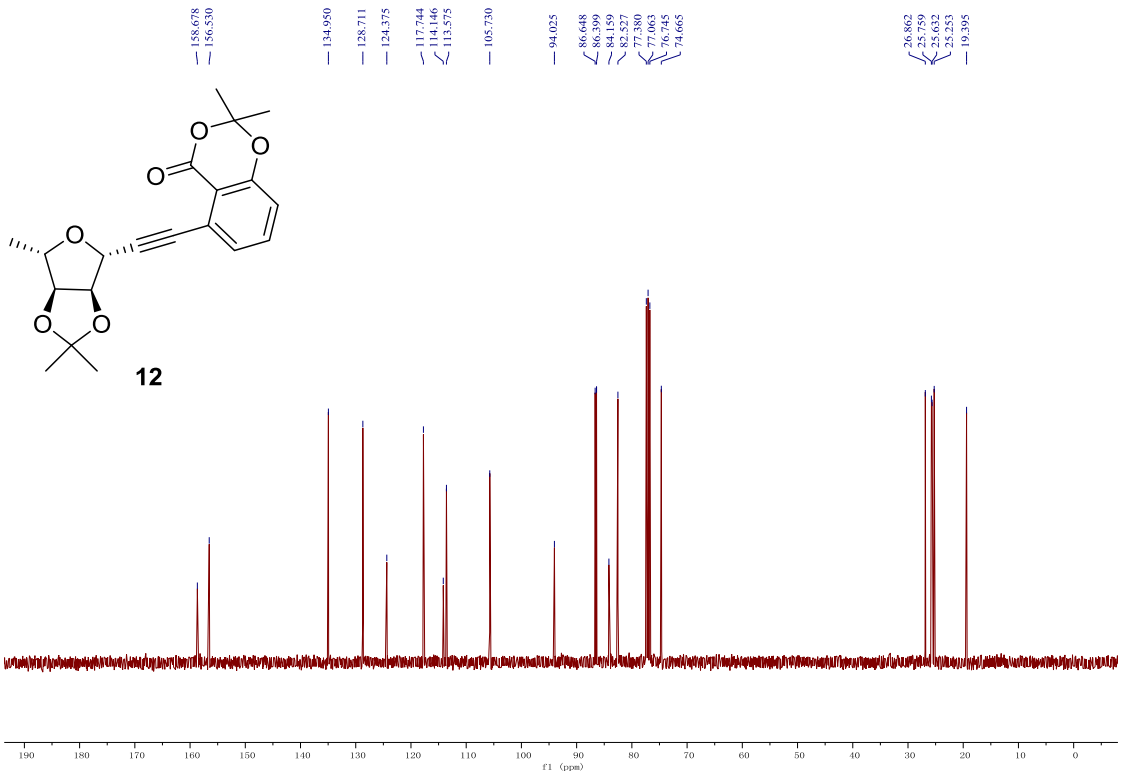

7.495
7.475
7.455
7.336
7.333
7.317
7.314
7.268
6.986
6.983
6.966
6.963
3.532
1.729
1.00
0.87
0.89
0.68
6.65
f1 (ppm)

11


158.814
156.562
135.007
129.697
124.053
118.050
114.551
105.852
84.152
81.127
77.344
77.026
76.709
25.687
f1 (ppm)

11


7.448
7.428
7.408
7.260
7.217
7.214
7.197
7.195
6.929
6.926
6.908
6.905
5.085
5.079
5.069
5.063
4.889
4.883
4.580
4.574
4.565
4.559
4.258
4.252
4.241
4.235
1.689
1.510
1.428
1.411
1.326
12
1.16
1.00
0.91
1.00
0.86
1.01
0.98
6.58
3.26
3.25
3.22
f1 (ppm)


158.678
156.530
134.950
128.711
124.375
117.744
114.146
113.575
105.730
94.025
86.648
86.399
84.159
82.527
77.380
77.063
76.745
74.665
26.862
25.759
25.632
25.253
19.395
12
f1 (ppm)