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Orthogonal Activation of Propargyl and *n*-Pentenyl Glycosides and 1,2-Orthoesters

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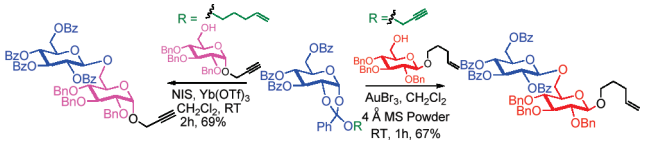

An orthogonal activation strategy with propargyl and *n*-pentenyl glycosides has been identified. According to this methodology, *n*-pentenyl glycosides can be selectively activated with NIS/TMSOTf in the presence of either armed or disarmed propargyl *O*-glycosides. In addition, we report herein that propargyl 1,2-orthoesters can be selectively activated with $AuBr_3$ in CH_2Cl_2 at room temperature in the presence of *n*-pentenyl glycosides. Similarly, pentenyl 1,2-orthoesters can be selectively activated with NIS/$Yb(OTf)_3$ in the presence of propargyl glycosides.

Glycoconjugates and oligosaccharides play significant roles in various extracellular and intracellular molecular recognition events.[1] Insufficient quantities of the glycoconjugates is one of the drawbacks in unraveling the importance of these glycoconjugates in the cellular context.[2] Chemical or enzymatic synthesis of oligosaccharides either in solution or on solid phase is a popular method to access sufficient quantity of glycoconjugates.[3] Glycoconjugates are often present as oligosaccharides coupled to a lipid, protein, steroid, etc. and the process of oligosaccharide synthesis breaks down to the systematic addition of sugar residues in either a convergent or a linear fashion by means of a glycosylation reaction.[4] A glycosylation reaction involves a glycosyl donor, usually a protected monosaccharide with an appendage at the anomeric position that can be activated to become a leaving group, and an aglycon bearing a lone hydroxyl group. In this context, several glycosyl donors that were developed over the past century can be classified into stable (e.g., *n*-pentenyl-,[5a] thio-,[5b−d] vinyl-,[5e] 2-carboxybenzyl-,[5f] etc.) and unstable (e.g., imidate-,[4a,5g] halo-,[2f,5h−j] etc.) glycosyl donors depending on the shelf life of the actual glycosyl donor.

Glycosylations with stable glycosyl donors are advantageous as the appendage at the anomeric position of the donor serves the dual role of a robust protecting group initially and later becomes a glycosyl donor upon addition of an appropriate promoter. The complete oligosaccharide synthesis often demands the use of more than one glycosyl donor to accomplish the target molecule.[4]

Ogawa popularized general orthogonal glycosylation strategy is an important milestone in the oligosaccharide synthesis.[6a] Orthogonal activation requires at least two glycosyl donors with appendages that can be activated independently and in the presence of the other thereby limiting the number of glycosyl donors eligible for this powerful technique. Earlier work by Ogawa's group demonstrated[6a] the orthogonal activation strategy using thioglycosides and glycosyl fluorides whereas Demchenko et al. have reported[6b] semiorthogonal glycosylation strategy exploiting thioethyl and *n*-pentenyl glycosides.

We recently reported that propargyl glycosides can become novel and stable glycosyl donors in the presence of a catalytic amount of $AuCl_3$ at 60 °C in acetonitrile.[7a] Furthermore, propargyl 1,2-orthoesters were found[7b] to give 1,2-*trans* stereoselective glycosides with $AuBr_3$ in CH_2Cl_2 at room temperature and subsequently temperature-controlled

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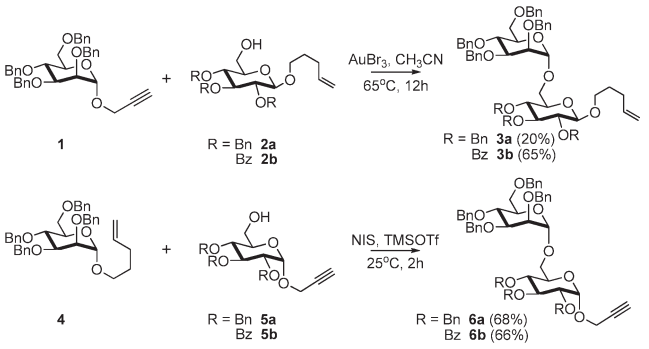
SCHEME 1. Orthogonal Activation of Propargyl and *n*-Pentenyl Glycosides



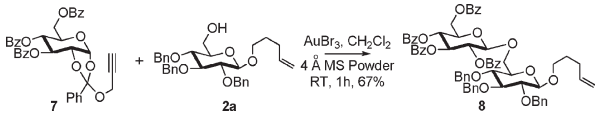
experiments were performed to show that propargyl 1,2-orthoesters can be selectively activated in the presence of propargyl *O*-glycosides.[7b] In continuation of this program on the development of novel strategies for the glycoconjugate synthesis, we became interested in the orthogonal activation of propargyl and *n*-pentenyl glycosides.

For an initial attempt to study the orthogonal activation, propargyl 2,3,4,6-tetra-*O*-benzyl mannopyranoside (**1**) and *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl mannopyranoside (**4**) were chosen as glycosyl donors mainly because of the possibility of expected 1,2-*trans* stereoselectivity in the products. Accordingly, propargyl glycosyl donor (**1**) was reacted with *n*-pentenyl glucoside as the glycosyl acceptor (**2a**) in the presence of 5 mol % of $AuBr_3$ in acetonitrile at 65 °C for 12 h to obtain 20% yield of the disaccharide **3a** and the yield could be improved to 65% by switching the protecting groups of the aglycon from armed benzyl ethers to disarmed benzoyl esters as in **2b** to obtain the corresponding disaccharide **3b** (Scheme 1).[8] Similarly, the *n*-pentenyl mannosyl donor **4** was reacted with propargyl-containing aglycons **5a** and **5b** to obtain the disaccharides **6a** and **6b** in 68% and 66% yield, respectively. The poor yield in the case of **1** + **2a** to give **3a** can be attributed to our recent observations that $AuBr_3$ also activates *n*-pentenyl glycosides at higher temperature.[9]

Thus we studied the utility of orthogonal activation strategy using propargyl 1,2-orthoesters as glycosyl donors and *n*-pentenyl glycosides as aglycons since propargyl 1,2-orthoesters would act as glycosyl donors at room temperature. Accordingly, a gold-catalyzed glycosylation reaction between propargyl orthoester **7** and aglycon **2a** was successfully carried out at room temperature in CH_2Cl_2 to obtain the disaccharide **8** as an *n*-pentenyl glycoside.[8] The protocol was then extended to various other aglycons (**11**, **13**, **15**) and glycosyl donors (**17**, **19**, **22**). Disaccharides (**12** and **14**) with an *n*-pentenyl group at the reducing end were obtained in good yields and the aglycon **15** fared slightly better to give the *n*-pentenyl disaccharide **16** in 75% yield (Table 1).[8] Similarly, propargyl orthoesters **17**, **19**, and **22** also resulted in the formation of corresponding pentenyl disaccharides (**18**, **20**, **21**) and trisaccharides (**23**,**24**, **25**), respectively. Furthermore, activation of *n*-pentenyl 1,2-orthoesters in the presence of a propargyl group containing aglycons was studied.

Accordingly, the reaction between *n*-pentenyl orthoester **9** and the propargyl glucoside **5a** in the presence of

TABLE 1. Activation of Propargyl Orthoesters in the Presence of *n*-Pentenyl Glycosides



Donor	Acceptor	Product	Time (h)	%Yield
7	11	12	2	65
	13	14	2	66
	15	16	2	75
17	2a	18	4	68
19	2a	20	1	65
	13	21	2	60
22	2a	23	2	70
	11	24	3	64
	15	25	3	70

$NIS/Yb(OTf)_3$ in CH_2Cl_2 showed the orthogonality to result in the isolation of disaccharide **10** as a propargyl glycoside in 69% yield. Subsequently, the orthogonal activation condition was tested with other orthoesters (**30**, **33**, **36**) and aglycons (**5a**, **26**, **28**). Glycosyl orthoesters (**9**, **30**, **33**, **36**) reacted with propargyl glycosides **5a**, **26**, and **28** to give corresponding disaccharides (**27**, **29**, **31**, **32**, **34**, **35**) and trisaccharides (**37**, **38**, **39**) as propargyl glycosides (Table 2).[8]

In conclusion, we studied the orthogonal activation strategy using propargyl and *n*-pentenyl glycosides. We observed that *n*-pentenyl glycosides can be activated to become glycosyl donors in the presence of propargyl glycosides as aglycons. In addition, propargyl 1,2-orthoesters were found to behave as glycosyl donors with *n*-pentenyl glycosides as aglycons. Similarly, *n*-pentenyl 1,2-orthoesters behaved as glycosyl donors with propargyl glycosides as aglycons. The resulting propargyl and *n*-pentenyl di- and trisaccharides can be used further for synthesizing higher oligosaccharides.[9,10]

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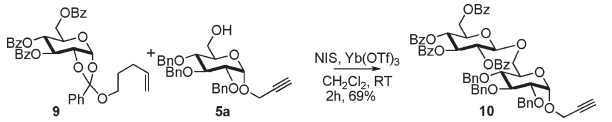
TABLE 2. Activation of *n*-Pentenyl Orthoesters in the Presence of Propargyl Glycosides



Donor	Acceptor	Product	Time (h)	%Yield
9	26	27	4	65
	28	29	6	63
30	5a	31	2.5	70
	26	32	4	67
33	5a	34	4	59
	26	35	6	55
36	5a	37	4	67
	26	38	12	65
	28	39	10	66

Application of the orthogonal activation to important immunogenic epitopes of infectious bacteria is currently underway.

Experimental Section

General Procedure for Glycosylations with Propargyl Glycosides as Glycosyl Donor. To a solution of glycosyl donor (0.1 mmol) and aglycon (0.12 mmol) in anhydrous acetonitrile (5 mL) was added a solution of 5 mol % of $AuBr_3$ in anhydrous acetonitrile (2 mL) under argon atmosphere at room temperature. The resulting mixture was heated to 65 °C and stirred until the completion of the reaction as judged by TLC analysis. The reaction mixture was concentrated in vacuo to obtain a crude residue, which was purified by conventional silica gel column chromatography with ethyl acetate−petroleum ether as the mobile phase.

General Procedure for Glycosylations with *n*-Pentenyl Glycosides as Glycosyl Donor. To a solution of glycosyl acceptor (0.1 mmol) in CH_2Cl_2 (5 mL) were added NIS (0.13 mmol) and TMSOTf(0.03 mmol) under argon atmosphere. The glycosyl donor (0.13 mmol) in 5 mL of CH_2Cl_2 was added at 0 °C and brought to room temperature, then stirred under argon atmosphere for a specified time. The reaction mixture was diluted with 15 mL of CH_2Cl_2 and washed with 10% aqueous sodium thiosulfate solution and saturated $NaHCO_3$. The organic layer was washed with brine solution and dried over anhydrous sodium sulfate. Dried CH_2Cl_2 solution was concentrated in vacuo and puried by silica gel column chromatography with ethyl acetate−petroleum ether as the mobile phase.

General Procedure for Glycosylations with *n*-Pentenyl 1,2-Orthoesters as Glycosyl Donor. To a CH_2Cl_2 solution of glycosyl donor (0.3 mmol) and glycosyl acceptor (0.1 mmol) at 0 °C was added *N*-iodosuccinimide (0.4 mmol) under argon atmosphere. After 5 min of stirring at 0 °C, a catalytic amount of $Yb(OTf)_3$ (0.033 mmol) was added with stirring at room temperature for a specified time. The reaction was quenched with 10% aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate, extracted with CH_2Cl_2, and purified by silica gel column chromatography with ethyl acetate−petroleum ether as the mobile phase.

General Procedure for Glycosylations with Propargyl 1,2-Orthoesters as Glycosyl Donor. To a solution of glycosyl donor (0.1 mmol), glycosyl acceptor (0.11 mmol), and activated 4 Å molecular sieves powder (50 mg) in anhydrous CH_2Cl_2 (5 mL) was added $AuBr_3$ (10 mol %) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the reaction mixture was filtered and the filtrate was concentrated in vacuo. The resulting residue was purified by silica gel column chromatography with ethyl acetate−petroleum ether as the mobile phase.

Compound Characterization Data for Disaccharide 3b. $[\alpha]^{25}_D$ +17.8 ($CHCl_3$, *c* 1.85); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.55(q, 2H, J = 6.4, 13.2 Hz), 1.93 (q, 2H, J = 6.4, 13.6 Hz), 3.36−3.98 (m, 10H), 4.35−4.96 (m, 7H), 4.39 (br s, 2H), 4.51 (ABq, 2H, J = 12.0 Hz), 4.67 (br s, 2H), 5.53 (m, 3H), 5.84 (t, 1H, J = 9.7 Hz), 7.08−7.53 (m, 29H), 7.75−8.03 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 28.5, 29.8, 66.5, 69.1, 69.4, 70.3, 71.8, 72.0, 72.1, 72.5, 72.9, 73.0, 73.3, 74.4, 74.7, 75.0, 80.0, 98.2, 101.2, 114.9, 127.4−130.0, 133.2, 133.2, 133.2, 133.3, 137.8, 138.4, 138.6, 138.7, 165.1, 165.2, 165.9; HRMS (MALDI-TOF) calcd for $C_{66}H_{66}O_{14}Na$ 1105.4350, found 1105.4356.

Compound Characterization Data for Disaccharide 6b. $[\alpha]^{25}_D$ +68.6 ($CHCl_3$, *c* 1.00); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 2.36(t, 1H, J = 2.3 Hz), 3.50−3.78 (m, 4H), 3.82−3.90 (m, 3H), 4.27 (d, 2H, J = 2.3 Hz), 4.32−4.95 (m, 11H), 5.28 (dd, 1H, J = 3.8, 10.2 Hz), 5.48 (d, 1H, J = 3.6 Hz), 5.60 (t, 1H, J = 9.8 Hz), 6.12 (t, 1H, J = 9.8 Hz), 7.12−7.58 (m,29H), 7.82−8.02 (m, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 55.5, 65.9, 68.7, 68.9, 69.6, 70.3, 71.6, 71.8, 72.1, 72.5, 73.1, 74.7, 74.7, 74.9, 75.4, 78.2, 79.8, 94.9, 98.2, 127.3−129.9, 133.1, 133.2, 133.3, 138.3, 138.4, 138.5, 138.6, 165.0, 165.7, 165.8; HRMS (MALDI-TOF) calcd for $C_{64}H_{60}O_{14}Na$ 1075.3881, found 1075.3817.

Compound Characterization Data for Disaccharide 8. $[\alpha]^{25}_D$ +9.5 ($CHCl_3$, *c* 0.9); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.63 (q, 2H, J = 6.9, 14.5 Hz), 2.08 (q, 2H, J = 6.9, 14.5 Hz), 3.34 (m, 4H), 3.53 (dd, 1H, J = 8.9, 17.3 Hz), 3.64−3.88 (m, 2H), 4.03−4.33 (m, 3H), 4.35−4.75 (m, 6H), 4.76−5.10 (m, 5H), 5.46−5.96 (m, 4H), 7.10−7.58 (m, 27H), 7.75−8.08 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 28.9, 30.3, 63.2, 68.5, 69.2, 69.7, 71.9, 72.2, 73.0, 74.6, 74.9, 74.9, 75.6, 77.8, 82.1, 84.6, 101.3, 103.5, 115.0, 127.6−129.9, 133.2, 133.2, 133.3, 133.5, 137.9, 138.2, 138.5, 138.6, 165.1, 165.2, 165.9, 166.2; HRMS (MALDI-TOF) calcd for $C_{66}H_{64}O_{15}Na$ 1119.4143, found 1119.4149.

Compound Characterization Data for Disaccharide 10. $[\alpha]^{25}_D$ +30.5 ($CHCl_3$, *c* 1.0); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 2.38 (t, 1 H, J = 2.3 Hz), 3.21−3.52 (m, 2 H), 3.89 (t, 1 H, J = 9.2 Hz),

3.72−3.92 (m, 2 H), 4.10−4.32 (m, 5 H), 4.45−5.02 (m, 9 H), 5.58 (dd, 1 H, J = 8.0, 9.6 Hz), 5.67 (t, 1 H, J = 9.6 Hz), 5.90 (t, 1 H, J = 9.5 Hz), 7.00−7.57 (m, 27 H), 7.78−8.02 (m, 8 H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 54.3, 63.2, 68.1, 69.8, 70.1, 71.8, 72.2, 72.9, 72.9, 74.6, 74.7, 75.5, 77.2, 79.0, 79.3, 81.7, 95.0, 101.3, 127.4−129.7, 133.1, 133.1, 133.2, 133.4, 138.0, 138.2, 138.8, 165.0, 165.1, 165.2, 165.8; HRMS (MALDI-TOF) calcd for $C_{64}H_{58}O_{15}Na$ 1089.3673, found 1089.3605.

Compound Characterization Data for Trisaccharide 25. $[\alpha]^{25}_D$ +42.2 ($CHCl_3$, *c* 2.5); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.29 (m, 2H), 1.89 (m, 2H), 2.94 (m, 1H), 3.32 (m, 1H), 3.55−3.93 (m, 9H), 4.05−4.42 (m, 3H), 4.45−4.75 (m, 8H), 4.78−4.99 (m, 4H), 5.30−5.88 (m, 6H), 7.05−7.83 (m, 36H), 7.81−8.15 (m, 14H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 28.2, 30.2, 61.0, 62.3, 66.3, 67.5, 69.2, 69.8, 71.2, 71.3, 71.7, 71.9, 71.9, 72.4, 72.8, 72.9, 74.3, 74.9, 75.9, 77.2, 80.1, 97.4, 100.9, 101.4, 114.6, 127.3−129.9, 132.9, 133.0, 133.2, 133.3, 133.4, 133.5, 133.5, 138.1, 138.2, 138.2, 138.3, 164.7, 165.0, 165.1, 165.3, 165.4, 165.5, 165.8; HRMS (MALDI-TOF) calcd for $C_{93}H_{86}O_{23}Na$ 1594.5491, found 1594.5451.

Compound Characterization Data for Trisaccharide 39. $[\alpha]^{25}_D$ +51.1 ($CHCl_3$, *c* 1.0); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 2.35 (t, 1H, J = 2.3 Hz), 3.60−3.98 (m, 10H), 4.10−4.52 (m, 7H), 4.53−4.78 (m, 4H), 4.80−4.97 (m, 3H), 5.43 (dd, 1H, J = 3.2, 10.3 Hz), 5.59 (dd, 1H, J = 7.9, 10.0 Hz), 5.70−5.95 (m, 3H), 7.01−7.65 (m, 36H), 7.70−8.04 (m, 14H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 53.5, 60.9, 62.2, 67.3, 69.0, 69.7, 71.2, 71.6, 71.6, 71.6, 72.4, 72.7, 72.7, 73.8, 74.5, 74.6, 74.6, 74.7, 75.8, 78.5, 79.7, 95.6, 100.7, 101.3, 127.1−129.8, 132.8, 132.9, 133.1, 133.1, 133.2, 133.2, 133.3, 137.8, 138.0, 138.1, 164.6, 164.9, 165.0, 165.2, 165.2, 165.3, 165.6; HRMS (MALDI-TOF) calcd for $C_{91}H_{80}O_{23}Na$ 1564.5022, found 1564.5022.

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Supporting Information Available: ^{1}H, ^{13}C NMR, and MS spectral charts, other characterization data for all new compounds, and general experimental protocols. This material is available free of charge via the Internet at http://pubs.acs.org.