O-Maltosylation of Heterocyclic Ketene Aminals

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The stereoselective synthesis of *O*-maltosides by reacting benzoyl-substituted heterocyclic ketene aminals 1 or 2 with acetylated maltosyl bromide 3 was investigated. Compounds 1 or 2 reacted with 3 in the presence of mercuric cyanide to give *O*-maltosides 4 or 5 with *E*-configuration. While 1 reacted with 3 in the presence of calcium hydride to give *O*-maltosides 6 with *Z*-configuration.

Keywords heterocyclic ketene aminal, maltosylation, stereoselective synthesis

Introduction

Heterocyclic ketene aminals are important intermediates for the synthesis of a wide variety of new heterocycles and fused heterocycles.[1,2] Some heterocyclic ketene aminals and their derivatives posses biological activities, therefore, the synthesis and reactions of heterocyclic ketene aminals have received much attention.[3-10] Heterocyclic ketene aminals are a kind of ambident nucleophiles. The *O*-glycosidation of benzoyl-substituted heterocyclic ketene aminals has been reported.[11-13]

In the past several decades, glycosidation has received much attention because a number of physiological activities of carbohydrates in biological systems have been recognized. The oligosaccharides and their derivatives also play important roles in living organisms.[14-16] The glycosidation of heterocyclic ketene aminals with oligosaccharides has been not reported yet. Herein we report the regioselective reaction between the benzoyl-substituted heterocyclic ketene aminals and acetylated maltosyl bromide.

Results and discussion

The benzoyl-substituted heterocyclic ketene aminals used were prepared from ketene dithioacetals with diamines by literature method.[17] Benzoyl-substituted heterocyclic ketene aminals **1** or **2** reacted with 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranosyl bromide (acetylated maltosyl bromide) (**3**) by using mercuric cyanide as catalyst in anhydrous acetonitrile to give product **4** or **5** in moderate yields (Scheme 1). The structures of **4** and **5** were determined by spectroscopic analysis and their constitutions were confirmed by HR-FAB MS or elemental analysis. In their IR spectra, there was a N—H stretching absorption appeared at *ca.* 3350—3400 cm^{-1} and a very strong carbonyl absorption for acetyl group at *ca.* 1750 cm^{-1}. Meanwhile, the carbonyl absorption of the aroyl group of the heterocyclic ketene aminals at *ca.* 1600 cm^{-1} disappeared. It was also found that the signals of two nitrogen protons of **4** and one nitrogen proton of **5** in the ^1H NMR spectra. Furthermore, the signal of one ethylenic proton was also found exists at δ 5.76—6.01. These data exclude either the *N*- or *C*-maltosylation of **1** and **2**. The appearance of a new carbon signal (*ca.* δ 155) instead of the carbonyl carbon signal (*ca.* δ 180) in the ^{13}C NMR spectra indicated that the products **4** and **5** were *O*-maltosides of **1** and **2**. The β linkage of the protected maltosyl moiety to the oxygen atom of heterocyclic ketene aminals in **4** and **5** was confirmed by the coupling constants ($J_{H_1\text{-}H_2}$ = ~ 8.0 Hz) of the glycopyranosyl ring in the ^1H NMR spectra. The β linkage formation is due to

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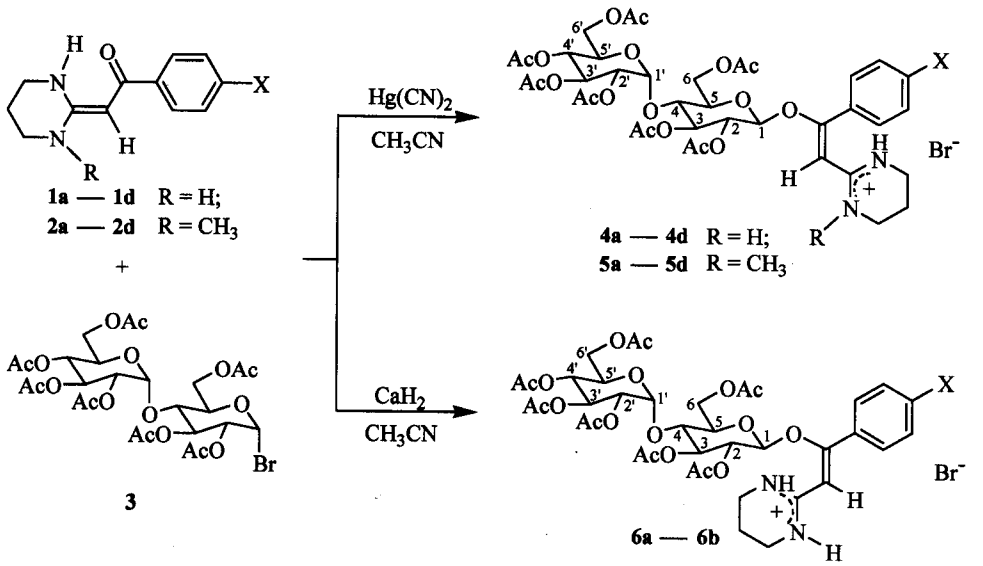
Scheme 1



participation of the neighboring acetyl group. The assignments of proton chemical shift of acetylated maltose residue are determined by ^{1}H-^{1}H COSY spectra. The *E*-configurations of **4** and **5** were determined by the NOE technique.[12]

Heterocyclic ketene aminals **1** reacted with **3** in the presence of calcium hydride in acetonitrile to give **6** (Scheme 1). Their spectral data are similar to those of **4** and **5** and also proved that they are *O*-maltosides of **1**. The *Z*-configuration of **6** was determined by the demonstrated NOE between the benzene ring and the ethylenic proton.[12] The glycopyranosyl ring $H_{1\text{-}2}$ coupling constants (*ca.* 8.0 Hz) indicated also a β linkage between the protected maltosyl group and the oxygen atom of heterocyclic ketene aminals.

Experimental

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 300 spectrometer. IR spectra were recorded on a Perkin-Elmer 782 spectrometer. HR-FAB MS spectra were recorded on an APEXII-FT-ICRMS instrument. Elemental analysis was carried out by the Analytical Laboratory of the Institute.

General procedure for synthesis of **4** *and* **5**

A mixture of benzoyl-substituted heterocyclic ketene aminals **1** or **2** (1 mmol), acetylated maltosyl bromide (**3**, 1 mmol) and mercuric cyanide (200 mg) in dried acetonitrile (25 mL) was stirred at room temperature for 8—10 h. The mixture was filtered and washed with CH_2Cl_2 (10 mL). After removal of solvent, the crude product was purified by column chromatograph on silica gel using the eluent ($CHCl_3$-CH_3OH, 100:1—25:1) to give **4** or **5**.

2-{(*E*)-2-*Phenyl*-2-[2,3,6-*tri*-*O*-*acetyl*-4-*O*-(2′, 3′, 4′, 6′-*tetra*-*O*-*acetyl*-α-*D*-*glucopyranosyl*)-α-*D*-*glucopyranosyloxy*]*vinyl*}*hexahydropyrimidinium bromide* (**4a**) Yield 62%, m.p. 125.5—127 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.18 (s, 2H, 2NH), 7.44—7.48 (m, 5H, ArH), 5.76 (s, 1H, C=CH), 5.29 (d, J = 4.2 Hz, 1H, 1′-H), 5.22 (t, J = 8.9 Hz, 1H, 3′-H), 5.19 (t, J = 8.6 Hz, 1H, 3-H), 5.06 (t, J = 8.0 Hz, 1H, 2-H), 4.97 (t, J = 9.8 Hz, 1H, 4′-H), 4.85 (d, J = 8.0 Hz, 1H, 1-H), 4.77 (dd, J = 10.5, 4.0 Hz, 1H, 2′-H), 4.32 (dd, J = 10.7, 2.0 Hz, 1H, 6-H), 4.08—4.24 (m, 2H, 6-H, 6′-H), 3.94—4.02 (m, 2H, 4-H, 6′-H), 3.86 (dt, 1H, J = 9.5, 2.2 Hz, 5′-H), 3.55—3.62 (m, 4H, $2NCH_2$), 3.25—3.35 (m, 1H, 5-H), 2.13, 2.12, 2.09, 2.05, 2.00, 1.97, 1.96 (s, 21H, $7COCH_3$), 1.99 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.9, 170.4, 170.4, 170.1, 169.5, 169.3, 162.8, 155.4, 131.4, 130.2, 129.0, 128.0, 101.3, 96.6, 95.6, 73.8, 73.1, 72.3, 71.5, 69.8, 68.8, 68.7, 67.7, 62.1, 61.3,

38.7, 30.0, 20.7, 20.7, 20.7, 20.6, 20.4, 18.0; IR (KBr) ν: 3390 (NH), 1752 (CO), 1668, 1627 cm^{-1}; FA MS m/z: 821 $(M-Br)^+$. Anal. calcd for $C_{38}H_{49}BrN_2O_{18}$: C 50.61, H 5.84, N 3.11; found C 50.87, H 5.88, N 3.40.

2-{(*E*)-2-(*p-Methylphenyl*)-2-[2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-α-D-glucopyranosyl*)-*α*-*D-glucopyranosyloxy*]*vinyl*} *hexahydropyrimidinium bromide* (**4b**) Yield 62%, m.p. 123—125 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.65 (s, 2H, 2NH), 7.38 (d, J = 8.0 Hz, 2H, ArH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 6.09 (s, 1H, C=CH), 5.32 (d, J = 4.0 Hz, 1H, 1′-H), 5.25 (t, J = 10.0 Hz, 1H, 3′-H), 5.21 (t, J = 9.6 Hz, 1H, 3-H), 5.04 (t, J = 9.0 Hz, 1H, 2-H), 5.01 (t, J = 9.8 Hz, 1H, 4′-H), 4.89 (d, J = 8.1 Hz, 1H, 1-H), 4.79 (dd, J = 10.5, 4.0 Hz, 1H, 2′-H), 4.32 (dd, J = 11.3, 2.0 Hz, 1H, 6-H), 4.20 (dd, J = 12.6, 3.8 Hz, 1H, 6-H), 4.16 (dd, J = 12.7, 5.3 Hz, 1H, 6′-H), 4.04 (dd, J = 12.5, 1.8 Hz, 1H, 6′-H), 3.97 (t, J = 9.2 Hz, 1H, 4-H), 3.88 (dt, J = 10.0, 1.8 Hz, 1H, 5′-H), 3.55—3.62 (m, 4H, $2NCH_2$), 3.30—3.40 (m, 1H, 5-H), 2.40 (s, 3H, $ArCH_3$), 2.17, 2.14, 2.09, 2.02, 2.00, 1.99, 1.97 (s, 21H, $7COCH_3$), 1.91 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.9, 170.5, 170.3, 169.8, 169.7, 169.4, 163.4, 155.6, 141.9, 129.7, 128.3, 127.5, 100.9, 96.8, 95.6, 74.0, 73.1, 72.4, 71.4, 69.8, 69.0, 68.7, 67.8, 62.2, 61.4, 39.1, 29.6, 21.5, 20.9, 20.9, 20.7, 20.7, 20.5, 18.0; IR (KBr) ν: 3376 (NH), 1753 (CO), 1665, 1627 cm^{-1}. HRMS calcd for $C_{39}H_{51}N_2O_{18}$ $(M-Br)^+$ 835.3169, found 835.3120.

2-{(*E*)-2-(*p-Methoxyphenyl*)-2-[2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-α-D-glucopyranosyl*)-*α*-*D-glucopyranosyloxy*]*vinyl*} *hexahydropyrimidinium bromide* (**4c**) Yield 60%, m.p. 115—117.5 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.36 (s, 2H, 2NH), 7.52 (d, J = 8.6 Hz, 2H, ArH), 7.03 (d, J = 8.8 Hz, 2H, ArH), 5.92 (s, 1H, C=CH), 5.39 (d, J = 3.9 Hz, 1H, 1′-H), 5.32 (t, J = 9.7 Hz, 1H, 3′-H), 5.28 (t, J = 9.2 Hz, 1H, 3-H), 5.12 (t, J = 8.9 Hz, 1H, 2-H), 5.07 (t, J = 9.8 Hz, 1H, 4′-H), 4.98 (d, J = 8.2 Hz, 1H, 1-H), 4.86 (dd, J = 10.5, 3.9 Hz, 1H, 2′-H), 4.41 (dd, J = 11.2, 1.9 Hz, 1H, 6-H), 4.27 (dd, J = 11.9, 3.9 Hz, 1H, 6-H), 4.23 (dd, J = 11.7, 4.3 Hz, 1H, 6′-H), 4.11 (dd, J = 13.5, 1.5 Hz, 1H, 6′-H), 4.05 (t, J = 9.4 Hz, 1H, 4-H), 3.89—3.97 (m, 1H, 5′-H), 3.92 (s, 3H, $ArOCH_3$), 3.63—3.73 (m, 4H, $2NCH_2$), 3.20—3.25 (m, 1H, 5-H), 2.23, 2.21, 2.15, 2.09, 2.08, 2.07, 2.06 (s, 21H, $7COCH_3$), 2.03 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.6, 170.3, 170.0, 169.6, 169.5, 169.2, 162.8, 161.8, 155.5, 129.6, 122.3, 114.3, 100.2, 96.7, 95.4, 73.8, 73.0, 72.2, 71.3, 69.7, 68.8, 68.5, 67.6, 62.0, 61.2, 55.3, 38.6, 29.4, 20.7, 20.6, 20.5, 20.3, 17.9; IR (KBr) ν: 3355 (NH), 1753 (CO), 1661, 1603 cm^{-1}. HRMS calcd for $C_{39}H_{51}N_2O_{19}$ $(M-Br)^+$ 851.3086, found 851.3069.

1-*Methyl*-2-{(*E*)-2-(*p-methylphenyl*)-2-[2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-α-D-glucopyranosyl*)-*α*-*D-glucopyranosyloxy*]*vinyl*} *hexahydropyrimidinium bromide* (**5b**) Yield 60%, m.p. 115—117 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.59 (s, 1H, NH), 7.52 (d, J = 8.2 Hz, 2H, ArH), 7.26 (d, J = 8.0 Hz, 2H, ArH), 5.99 (s, 1H, C=CH), 5.34 (d, J = 4.0 Hz, 1H, 1′-H), 5.26 (t, J = 10.0 Hz, 1H, 3′-H), 5.17 (t, J = 9.1 Hz, 1H, 3-H), 5.04 (dd, J = 9.8, 3.0 Hz, 1H, 2-H), 5.02 (dd, J = 9.7, 4.8 Hz, 1H, 4′-H), 4.85 (d, J = 8.1 Hz, 1H, 1-H), 4.82 (dd, J = 10.5, 4.0 Hz, 1H, 2′-H), 4.43 (dd, J = 12.3, 2.3 Hz, 1H, 6-H), 4.23 (t, J = 4.0 Hz, 1H, 6-H), 4.19 (t, J = 3.9 Hz, 1H, 6′-H), 4.04 (dd, J = 12.6, 2.3 Hz, 1H, 6′-H), 4.00 (t, J = 9.3 Hz, 1H, 4-H), 3.89 (dd, J = 10.1, 2.3 Hz, 1H, 5′-H), 3.57—3.66 (m, 4H, $2NCH_2$), 3.45—3.47 (m, 1H, 5-H), 3.25 (s, 3H, NCH_3), 2.41 (s, 3H, $ArCH_3$), 2.19, 2.16, 2.09, 2.02, 2.01, 2.00, 1.98 (s, 21H, $7COCH_3$), 1.97 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.5, 170.3, 170.1, 169.8, 169.7, 169.3, 160.9, 156.4, 141.6, 129.6, 128.3, 127.8, 101.0, 96.8, 95.5, 74.8, 72.8, 72.2, 71.4, 69.8, 69.0, 68.5, 67.7, 62.2, 61.2, 48.4, 40.8, 38.8, 29.0, 21.4, 21.0, 20.7, 20.6, 20.5, 18.9; IR (KBr) ν: 3400 (NH), 1749 (CO), 1655, 1625 cm^{-1}. HRMS calcd for $C_{40}H_{53}N_2O_{18}$ $(M-Br)^+$ 849.3293, found 849.3276.

1-*Methyl*-2-{(*E*)-2-(*p-methoxyphenyl*)-2-[2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-α-D-glucopyranosyl*)-*α*-*D-glucopyranosyloxy*]*vinyl*} *hexahydropyrimidinium bromide* (**5c**) Yield 60%, m.p. 113—115.5 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.87 (s, 1H, NH), 7.51 (d, J = 8.5 Hz, 2H, ArH), 7.00 (d, J = 8.6 Hz, 2H, ArH), 5.87 (s, 1H, C=CH), 5.35 (d, J = 3.8 Hz, 1H, 1′-H), 5.27 (t, J = 10.0

Hz, 1H, 3′-H), 5.21 (t, J = 9.0 Hz, 1H, 3-H), 5.08 (t, J = 8.8 Hz, 1H, 2-H), 5.03 (t, J = 9.8 Hz, 1H, 4′-H), 4.92 (d, J = 8.0 Hz, 1H, 1-H), 4.82 (dd, J = 10.5, 3.9 Hz, 1H, 2′-H), 4.45 (dd, J = 11.9, 2.0 Hz, 1H, 6-H), 4.26 (t, J = 5.2 Hz, 1H, 6-H), 4.22 (t, J = 4.0 Hz, 1H, 6′-H), 4.07 (t, J = 9.5 Hz, 1H, 6′-H), 4.04 (t, J = 8.7 Hz, 1H, 4-H), 3.90—3.94 (m, 1H, 5′-H), 3.88 (s, 3H, $ArOCH_3$), 3.55—3.70 (m, 4H, $2NCH_2$), 3.45—3.50 (m, 1H, 5-H), 3.29 (s, 3H, NCH_3), 2.19, 2.16, 2.10, 2.03, 2.02, 2.01, 2.00 (s, 21H, $7COCH_3$), 1.98 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.3, 170.2, 169.9, 169.8, 169.6, 169.2, 161.9, 161.5, 155.9, 129.8, 122.5, 114.4, 100.2, 96.8, 95.4, 74.5, 72.9, 72.1, 71.3, 69.7, 68.9, 68.4, 67.6, 61.9, 61.1, 55.4, 48.5, 40.7, 38.9, 29.4, 20.8, 20.7, 20.6, 20.5, 20.4, 18.9; IR (KBr) ν: 3350 (NH), 1751 (CO), 1656, 1600 cm^{-1}. HRMS calcd for $C_{40}H_{53}N_2O_{19}(M-Br)^+$ 865.3243, found 865.3251.

1-Methyl-2-{(E)-2-(p-chlorophenyl)-2-[2,3,6-tri-O-acetyl-4-O-(2′, 3′, 4′, 6′-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyranosyloxy]vinyl} hexahydropyrimidinium bromide (**5d**) Yield 62%, m.p. 125—129 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.17 (s, 1H, NH), 7.56 (d, J = 8.2 Hz, 2H, ArH), 7.45 (d, J = 8.3 Hz, 2H, ArH), 6.01 (s, 1H, C=CH), 5.33 (d, J = 3.8 Hz, 1H, 1′-H), 5.26 (t, J = 10.0 Hz, 1H, 3′-H), 5.18 (t, J = 9.0 Hz, 1H, 3-H), 5.04 (t, J = 8.5 Hz, 1H, 2-H), 5.02 (t, J = 9.7 Hz, 1H, 4′-H), 4.83 (d, J = 8.1 Hz, 1H, 1-H), 4.79 (dd, J = 10.0, 3.9 Hz, 1H, 2′-H), 4.45 (dd, J = 11.8, 2.0 Hz, 1H, 6-H), 4.24 (t, J = 4.1 Hz, 1H, 6-H), 4.19 (t, J = 4.0 Hz, 1H, 6′-H), 4.05 (dd, J = 13.0, 2.0 Hz, 1H, 6′-H), 3.99 (t, J = 9.3 Hz, 1H, 4-H), 3.89 (dt, J = 10.0, 2.0 Hz, 1H, 5′-H), 3.52—3.61 (m, 4H, $2NCH_2$), 3.45—3.50 (m, 1H, 5-H), 3.24 (s, 3H, NCH_3), 2.19, 2.18, 2.13, 2.08, 2.00, 1.98, 1.96 (s, 21H, $7COCH_3$), 1.97 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.3, 170.1, 170.0, 169.7, 169.6, 169.2, 159.7, 156.1, 137.4, 129.8, 129.2, 128.9, 102.2, 96.8, 95.4, 74.6, 72.9, 72.0, 71.3, 69.7, 68.9, 68.4, 67.6, 62.0, 61.1, 48.3, 40.7, 38.8, 29.5, 20.8, 20.8, 20.6, 20.5, 20.4, 20.3, 18.8; IR (KBr) ν: 3379 (NH), 1754 (CO), 1659, 1584 cm^{-1}. HRMS calcd for $C_{39}H_{50}ClN_2O_{18}(M-Br)^+$ 869.2747, found 869.2755.

General procedure for synthesis of **6**

A mixture of **1** (1 mmol), **3** (1 mmol) and calcium hydride (200 mg) in dried acetonitrile (25 mL) was stirred at room temperature for 8—10 h. The reaction mixture was worked-up as above to give **6**.

2-{(Z)-2-Phenyl-2-[2,3,6-tri-O-acetyl-4-O-(2′, 3′, 4′, 6′-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyranosyloxy]vinyl} hexahydropyrimidinium bromide (**6a**) Yield 57%, m.p. 125.5—127 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 9.25 (s, 2H, 2NH), 7.40—7.46 (m, 5H, ArH), 6.29 (s, 1H, C=CH), 5.29 (d, J = 4.0 Hz, 1H, 1′-H), 5.20 (t, J = 10.6 Hz, 2H, 3-H, 3′-H), 4.98 (t, J = 8.9 Hz, 1H, 2-H), 4.97 (t, J = 9.9 Hz, 1H, 4′-H), 4.85 (d, J = 8.0 Hz, 1H, 1-H), 4.75 (dd, J = 10.5, 4.0 Hz, 1H, 2′-H), 4.24 (dd, J = 11.4, 1.7 Hz, 1H, 6-H), 4.14 (t, J = 10.9 Hz, 1H, 6-H), 4.12 (t, J = 11.8 Hz, 2H, 6′-H), 4.01 (dd, J = 12.5, 1.8 Hz, 1H, 6′-H), 3.93 (t, J = 9.2 Hz, 1H, 4-H), 3.83 (dt, J = 10.1, 2.1 Hz, 1H, 5′-H), 3.52—3.60 (m, 4H, $2NCH_2$), 3.33—3.37 (m, 1H, 5-H), 2.12, 2.11, 2.05, 1.99, 1.96, 1.95, 1.93 (s, 21H, $7COCH_3$), 1.97 (quin, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 170.9, 170.5, 170.2, 169.7, 169.6, 169.3, 162.9, 155.4, 131.4, 130.3, 129.1, 128.1, 101.1, 96.7, 95.6, 73.8, 73.2, 72.4, 71.5, 69.8, 68.9, 68.7, 67.8, 62.2, 61.4, 38.8, 29.9, 20.8, 20.8, 20.7, 20.7, 20.5, 18.0; IR (KBr) ν: 3389 (NH), 1753 (CO), 1667, 1627 cm^{-1}. HRMS calcd for $C_{38}H_{49}N_2O_{18}(M-Br)^+$ 821.2980, found 821.2979.

2-{(Z)-2-(p-Methylphenyl)-2-[2,3,6-tri-O-acetyl-4-O-(2′, 3′, 4′, 6′-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyranosyloxy]vinyl} hexahydropyrimidinium bromide (**6b**) Yield 60%, m.p. 123—125 ℃, ^1H NMR ($CDCl_3$, 300 MHz) δ: 9.34 (s, 2H, 2NH), 7.33 (d, J = 7.9 Hz, 2H, ArH), 7.24 (d, J = 8.0 Hz, 2H, ArH), 6.37 (s, 1H, C=CH), 5.31 (d, J = 3.9 Hz, 1H, 1′-H), 5.24 (t, J = 10.0 Hz, 1H, 3′-H), 5.22 (t, J = 9.0 Hz, 1H, 3-H), 5.00 (t, J = 9.7 Hz, 1H, 2-H), 5.01 (t, J = 9.8 Hz, 1H, 4′-H), 4.89 (d, J = 8.1 Hz, 1H, 1-H), 4.78 (dd, J = 10.5, 3.9 Hz, 1H, 2′-H), 4.28 (dd, J = 11.3, 1.7 Hz, 1H, 6-H), 4.17 (t, J = 10.5 Hz, 1H, 6-H), 4.16 (t, J = 12.0 Hz, 1H, 6′-H), 4.06 (dd, J = 12.3, 2.0 Hz, 1H, 6′-H), 3.95 (t, J = 9.2 Hz, 1H, 4-H), 3.86 (dt, J = 9.9, 2.0 Hz, 1H, 5′-H), 3.51—3.56 (m, 4H,

2NCH$_2$), 3.42—3.46 (m, 1H, 5-H), 2.40 (s, 3H, ArCH$_3$), 2.16, 2.14, 2.09, 2.02, 2.00, 1.99, 1.96 (s, 21H, 7COCH$_3$), 1.97 (quin, 2H, CH$_2$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ: 170.9, 170.5, 170.2, 169.8, 169.6, 169.3, 163.2, 155.6, 142.0, 129.7, 128.0, 127.4, 100.9, 96.6, 95.6, 73.9, 73.1, 72.3, 71.5, 69.8, 68.9, 68.7, 67.7, 62.2, 61.3, 38.7, 29.9, 21.5, 20.8, 20.8, 20.7, 20.7, 20.5, 18.0; IR (KBr) ν: 3401 (NH), 1753 (CO), 1666, 1626 cm^{-1}. HRMS calcd for $C_{39}H_{51}N_2O_{18}(M-Br)^+$ 835.3137, found 835.3128.

2-{(*Z*)-2-(*p-Methoxyphenyl*)-2-[2, 3, 6-*tri-O*-acetyl-4-*O*-(2′, 3′, 4′, 6′-*tetra-O-acetyl-α-D-glucopyranosyl*)-*α-D-glucopyranosyloxy*]*vinyl*} *hexahydropyrimidinium bromide* (**6c**) Yield 55%, m.p. 115—117 ℃, ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 9.14 (s, 2H, 2NH), 7.38 (d, J = 8.6 Hz, 2H, ArH), 6.90 (d, J = 8.8 Hz, 2H, ArH), 6.28 (s, 1H, C=CH), 5.28 (d, J = 3.9 Hz, 1H, 1′-H), 5.21 (t, J = 10.1 Hz, 1H, 3′-H), 5.19 (t, J = 8.9 Hz, 1H, 3-H), 5.00 (t, J = 8.7 Hz, 1H, 2-H), 4.96 (t, J = 9.7 Hz, 1H, 4′-H), 4.89 (d, J = 8.1 Hz, 1H, 1-H), 4.75 (dd, J = 10.5, 4.1 Hz, 1H, 2′-H), 4.27 (dd, J = 11.1, 2.1 Hz, 1H, 6-H), 4.15 (t, J = 8.0 Hz, 1H, 6-H), 4.13 (t, J = 7.5 Hz, 1H, 6′-H), 4.02 (dd, J = 13.5, 1.9 Hz, 1H, 6′-H), 3.94 (t, J = 9.2 Hz, 1H, 4-H), 3.82—3.88 (m, 1H, 5′-H), 3.81 (s, 3H, ArOCH$_3$), 3.47—3.53 (m, 4H, 2NCH$_2$), 3.32—3.38 (m, 1H, 5-H), 2.12, 2.10, 2.05, 1.98, 1.96, 1.95, 1.93 (s, 21H, 7COCH$_3$), 1.94 (quin, 2H, CH$_2$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ: 170.7, 170.5, 170.4, 170.2, 169.7, 169.3, 163.0, 162.0, 155.6, 129.8, 122.5, 114.5, 100.3, 96.5, 95.6, 74.0, 73.2, 72.4, 71.5, 69.9, 68.9, 68.7, 67.8, 62.2, 61.4, 55.5, 38.7, 29.6, 20.7, 20.6, 20.5, 18.1; IR (KBr) ν: 3398 (NH), 1751 (CO), 1664, 1627 cm^{-1}. HRMS calcd for $C_{39}H_{51}N_2O_{19}(M-Br)^+$ 851.3086, found 851.3070.

2-{(*Z*)-2-(*p-Chlorophenyl*)-2-[2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-α-D-glucopyranosyl*)-*α-D-glucopyranosyloxy*]*vinyl*} *hexahydropyrimidinium bromide* (**6d**) Yield 62%, m.p. 125—127 ℃, ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 9.29 (s, 2H, 2NH), 7.42 (s, 4H, ArH), 6.51 (s, 1H, C=CH), 5.31 (d, J = 4.0 Hz, 1H, 1′-H), 5.24 (t, J = 10.0 Hz, 1H, 3′-H), 5.22 (t, J = 9.1 Hz, 1H, 3-H), 4.99 (t, J = 9.4 Hz, 2H, 2-, 4′-H), 4.85 (d, J = 8.1 Hz, 1H, 1-H), 4.77 (dd, J = 10.5, 4.0 Hz, 1H, 2′-H), 4.29 (dd, J = 11.3, 1.8 Hz, 1H, 6-H), 4.16 (t, J = 11.2 Hz, 1H, 6-H), 4.15 (t, J = 12.7 Hz, 1H, 6′-H), 4.05 (dd, J = 12.5, 1.6 Hz, 1H, 6′-H), 3.94 (t, J = 9.2 Hz, 1H, 4-H), 3.87 (dt, J = 10.1, 2.0 Hz, 1H, 5′-H), 3.51—3.57 (m, 4H, 2NCH$_2$), 3.35—3.39 (m, 1H, 5-H), 2.14, 2.13, 2.07, 2.01, 1.99, 1.98, 1.95 (s, 21H, 7COCH$_3$), 1.96 (quin, 2H, CH$_2$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ: 170.9, 170.5, 170.4, 170.1, 169.7, 169.6, 169.3, 161.4, 155.4, 137.8, 129.4, 128.8, 102.0, 96.8, 95.6, 73.8, 73.3, 72.4, 71.5, 69.9, 68.9, 68.8, 67.8, 62.2, 61.4, 38.8, 29.6, 20.9, 20.8, 20.7, 20.6, 20.5, 18.0; IR (KBr) ν: 3389 (NH), 1753 (CO), 1668, 1628 cm^{-1}. HRMS calcd for $C_{38}H_{48}ClN_2O_{18}(M-Br)^+$ 855.2591, found 855.2572.

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