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An expedient one-step synthesis of polysubstituted guanidinoglucosides using HgO–4 Å molecular sieves as catalyst

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ABSTRACT

A novel one-step method of preparing polysubstituted guanidinoglucosides using peracetylated methyl 6-deoxy-6-thioureidoglucosides as starting materials and employing HgO in combination with molecular sieves as an efficient catalyst is reported. The structures of three methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-6-deoxy-α-D-glucopyranosides were unambiguously confirmed by X-ray crystallography. The methodology affords new compounds in good yields and also provides a promising route for the synthesis of carbamate-protected guanidines.

1. Introduction

Guanidino-containing sugars have a wide range of biologically important uses such as inhibition of the replication of HIV,[1] the inhibition of enzymes including thrombin,[2] glycosidases,[3–7] neuraminidase,[8] and nitric oxide synthases,[9] antibacterial activity,[10] antihypertensive activity,[11] the treatment of non-insulin-dependent diabetes,[12] and efficient recognition of anionic substrates such as carboxylate, phosphate, and nitronate functionalities.[13,14] Therefore, the synthesis of this class of guanidines has attracted continued research interests in recent years. In fact, the preparation protocols of guanidines have been intensively investigated in recent years,[15–22] and some new, efficient, synthetic methods and new guanidinylation reagents have been used for different classes of guanidine compounds. However, most of these synthetic methods are not favorable to guanidino-containing sugars which suffer from some disadvantages such as inconvenient preparation of the reagents, limited substrate scope, or incompatibility of sensitive groups to the reaction conditions.

Synthetic approaches to guanidinoglycosides grossly include two general strategies: a guanidinylation reaction or a guanylation reaction. In the former, a pre-formed guanidine, such as 3,5-dimethylpyrazoylformamidinium nitrate (DPFN),[2] dicyandiamide [$H_2NC(=NH)NHCN$],[12] 1*H*-pyrazolecarboxamidine hydrochloride,[23] or *N*,*N*′-diBoc-*N*″-triflylguanidine,[24] is reacted with amino sugars to give their guanidino derivatives, most of which are monosubstituted sugar guanidines. In the latter case, topically, a nucleophilic amine is reacted with a electrophilic carbodiimide to afford polysubstituded guanidines.[7,14,25] The carbodiimide precursors are obtained by either the desulfurization of thiourea or are employed in an iminophosphorescence-based approach.

In order to search for new polysubstituted sugar guanidines, our research group has continued work in the area of heavy-metal-promoted guanidinylation reaction of amines with sugar thioureas. Previously, we had described the one-step synthesis of guanidinoglucoside by the $HgCl_2$–Et_3N method.[26] Later, during the course of synthesizing peracetated methyl 6-deoxy-6-guanidinoglucosides, the reaction of peracetated methyl 6-deoxy-6-thioureidoglucosides with low-reactive aryl amines only led to low yields (32–56%) by the $HgCl_2$-promoted protocol. It was clear that there was a need for an improved, facile synthetic route for the study of diversity among guanidino-containing glycosides. Mercury(II) oxide, which is widely used in industry, is considered as a good inorganic thiophile.[27] To the best of our knowledge, only two examples of thiourea conversion into guanidine using HgO as the desulfurizing reagent have been described. One was to convert bis-Boc-thiourea to guanidine, where it was considered that HgO was much inferior to $HgCl_2$ and $CuCl_2$.[28] The other was to convert resin-bound thiourea to guanidine, where it was considered that HgO was superior to $AgNO_3$, $Hg(OAc)_2$, and the Mukaiyama reagent.[29] A heavy metal salt–4 Å molecular sieve complex has widely been applied in the synthesis of oligosaccharides as an effective catalytic system[30,31] in which molecular sieves were reported as an efficient dehydrating agent. In this paper, we employed HgO as the desulfurizing reagent and 4 Å molecular sieves

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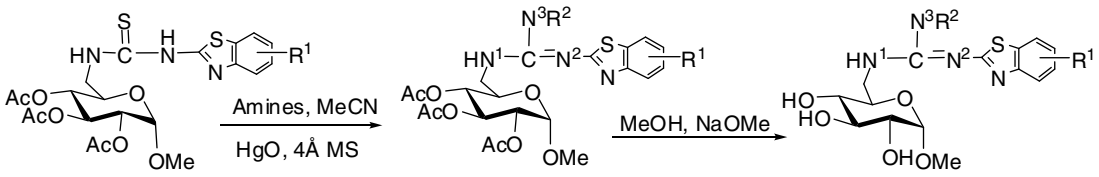

1a–1c **2a–2h, 3a–3h, 4a–4h** **5c–5h, 6c–6h, 7c–7h**

R^1: **1a**, **2**, **5**: H; **1b**, **3**, **6**: 6-OCH_3; **1c**, **4**, **7**: 6-CH_3;
R^2: **a**, $(CH_3)_2CH$–; **b**, C_6H_{11}–; **c**, $C_6H_5CH_2$–; **d**, *p*-$CH_3C_6H_4$–;
e, *p*-$CH_3OC_6H_4$–; **f**, *p*-ClC_6H_4–; **g**, $O(CH_2CH_2)_2$=; **h**, $C_2H_5O_2C$–

Scheme 1.

as the dehydrating agent and alkaline catalyst to synthesize a series of new trisubstituted guanidino-containing sugars in one-step (Scheme 1). HgO in combination with 4 **Å** molecular sieves showed much higher reactivity than the $HgCl_2$–EtN_3 protocol, being applicable to the guanidinylation reaction of low reactive sugar thioureas with low reactive amines. The method is economical, operationally simple, and allows the reaction to proceed under mild conditions.

2. Results and discussion

2.1. Optimization of guanidine formation

Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-thioureido-α-D-glucopyranosides **1a–c** were synthesized starting from methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-isothiocyanato-α-D-glucopyranoside and 2-aminobenzothiazole derivatives using a well-established method.[26] Methyl 2,3,4-tri-*O*-acetyl-6-[*N*-(benzothiazol-2-yl)]thioureido-6-deoxy-α-D-glucopyranoside (**1a**) and *p*-toluidine were chosen as test substrates to investigate various reaction conditions (Table 1). According to the method in Cunha's report,[32,33] the sugar thiourea was not desulfurized by $BiCl_3$ or $Bi(NO_3)_3{\cdot}5H_2O$, even after warming for several hours, and the solution became green-yellow. TLC showed that strongly polar compounds were formed. We speculated that Bi^{3+} as an efficient Lewis acid[34] preferentially catalyzes the deacetylation of the sugar. The desulfurization reaction of PbO[35] and $CuCl_2$ occurred very slowly, and several products tended to be formed as evidenced from TLC. However, the process of desulfurization was smooth and faster in the presence of Hg^{2+}. While $HgCl_2$ displayed moderate reactivity, use of HgO led to higher conversion and shorter reaction time in general. Moreover, the reaction rate could be significantly increased, and the reaction was complete within 12 h when the reaction was carried out in the presence of 4 **Å** molecular sieves (5 wt equiv to HgO). In the absence of molecular sieves, the reaction time was extended twofold, with yields of less than 19% along with some deacetylated guanidinoglucosides. As noted in entry 6 (Table 1), traces of the insoluble black mercuric sulfide that formed and molecular sieves could be efficiently removed by simple filtration of the cleavage solution over a thin pad of Celite. The filtrate was concentrated and purified by column chromatography to afford the target products (**2d**) in 65% yield. It is well known that the title compounds could be synthesized through a carbodiimide intermediate,[14] and here 4 **Å** molecular sieves act as a weak base and dehydrating agent to facilitate the formation of the carbodiimide.

Table 1
Optimization of guanidine formation

Entry	Reaction conditions	Convn (yield, %)	Reference
1	$CuCl_2$, DMF, Et_3N, 36 h	34	28
2	$BiCl_3$, DMF, Et_3N, 50 °C, 24 h	nr	32
3	$Bi(NO_3)_3{\cdot}5H_2O$, DMF, Et_3N, 24 h	nr	33
4	$HgCl_2$, DMF, Et_3N, 36 h	54	26
5	HgO, MeCN, 50 °C, 24 h	62	
6	HgO, MeCN, 50 °C, 12 h, 4 Å MS	65	
7	PbO, EtOH, 60 °C, 24 h 4 Å MS	48	35

2.2. The synthesis of guanidinoglucosides

With the optimal conditions in hand, amines of varying reactivity were investigated in order to gauge the scope of the reaction. The synthetic yields and reaction conditions for this series of reactions of sugar thioureas with amines are shown in Table 2. Isopropylamine and cyclohexylamine gave high yields of peracetylated guanidinoglucosides (Table 2, entries 1 and 2) within 6 h or less at 20–30 °C, while deacetylated guanidinoglucosides (**5a** and **5b**) were major products obtained in 38–45% yields, and compounds **2a** and **2b** were only obtained in 12–16% yields under warm conditions. Although the electronic nature of *p*-chloroaniline reduces the efficiency of the reaction of this amine to form a guanidine, aromatic amines also give the guanidinoglycosides in good to excellent yields under warm conditions (Table 2, entries 4–6). The results indicated that the strongly alkaline aliphatic amines [pK_a 9–11 (H_2O, 25 °C)] could lead the sugar to deacetylate easily under the conditions of heating, while the relatively weakly alkaline aromatic amines [pK_a 4–5 (H_2O, 25 °C)] could not do so. The secondary amine, morphiline, reacted with thioureidoglucosides **1a–c** to give the corresponding guanidinoglucosides **2g–4g** in 67–72% yields, the structures of which were unambiguously confirmed by X-ray crystallography (Figs. 1–3). Most noticeably, an attempt to increase the diversity of the products by incorporation of ethyl carbamate in this method succeeded, which gives rise to another route to synthesize carbamate-protected guanidines,[36,37] albeit in

Table 2
The reaction conditions and yields of guanidines **2a–h**, **3a–h**, and **4a–h**

Entry	Amine	Yield (%)[a]		
		R^1: H	R^1: 6-OCH3	R^1: 6-CH3
1	Isopropylamine	85	/	/
2	Cyclohexyl amine	81	/	/
3	Benzylamine	57	65	61
4	*p*-Methylphenylamine	65	69	63
5	*p*-Methoxyphenylamine	64	64	62
6	*p*-Chlorophenylamine	43	49	45
7	Morpholine	67	72	71
8	Ethyl carbamate	41	45	44

[a] In HgO–4 Å MS–MeCN, reaction conditions: entries 1 and 2, 25 °C, 6 h; entries 3–8, 50 °C, 12 h.

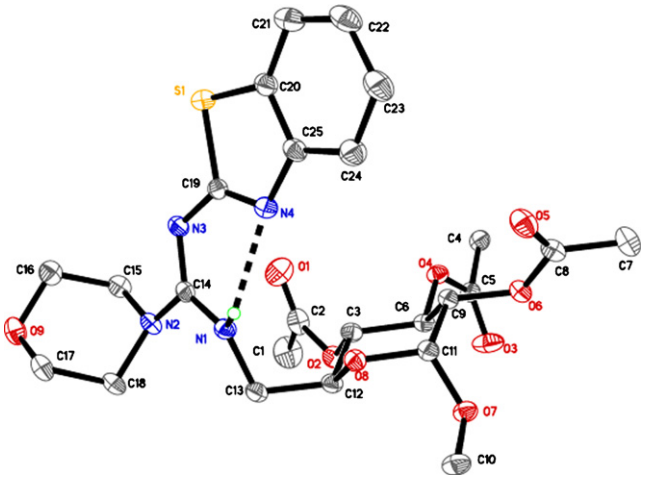

Figure. 1. X-ray crystallographic structure of compound **2g** with 30% thermal ellipsoids.

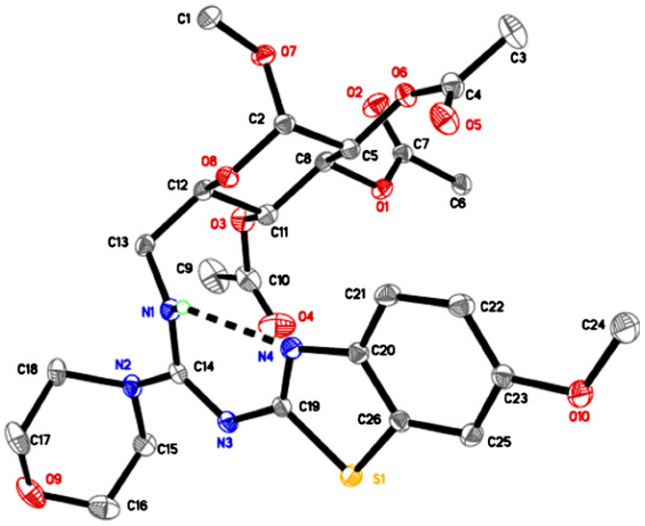

Figure. 2. X-ray crystallographic structure of compound **3g** with 30% thermal ellipsoids.

lower yields than with aromatic amines. All new guanidinoglucosides (**2**–**4**) were further deacetylated in methanol under standard NaOMe-catalyzed conditions to provide methyl 6-deoxy-6-guanidinoglucosides **5–7** in good yields.

The structures of new compounds were established by elemental analyses and by IR, ^{1}H, and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra of the peracetylated guanidinoglucosides, a broad signal around 9–12 ppm was detectable related to one N–H proton, suggesting the participation of one intramolecular hydrogen bond. As noted in Figure 1 of **2g**, Figure 2 of **3g** and Figure 3 of **4g**, strong hydrogen- bonding occurs between the benzothiazolyl nitrogen and the guanidino NH group (intermolecular hydrogen bonds: N1–H···N4 [2.670(3) Å], N1–H···N4 [2.6317(16) Å], and N1–H···N3 [2.636(2) Å]) providing a pseudo six-membered ring, which conjugates with the benzothiazol-ring to contribute to the planarity of the conjugated moiety of **2g**, **3g,** and **4g**.

In summary, we have demonstrated a simple and efficient method for the one-step synthesis of trisubstituted guanidinoglucosides employing HgO as the desulfurizing reagent and 4 **Å** molecular sieves as an efficient dehydrating agent. This protocol could also be used to synthesize a variety of carbomate-protected guanidinoglycosides.

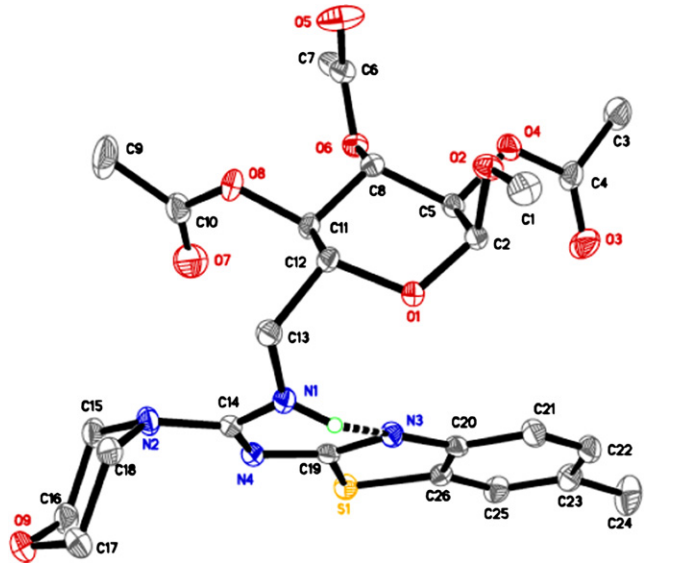

Figure. 3. X-ray crystallographic structure of compound **4g** with 30% thermal ellipsoids.

3. Experimental

3.1. Materials and general methods

Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. The IR spectra were recorded as KBr pellets on a Bruker FTIR Equinox 55 instrument. The ^{1}H and ^{13}C NMR spectra were recorded on an Inova 400 (using TMS as the internal standard, with chemical shifts expressed in δ-units (ppm) in $CDCl_3$ or DMSO-d_6 as solvent). The mass spectra were recorded on a Hewlett–Packard I000 LC–MS spectrometer (ESI). Elemental analyses were performed on a Thermo Flash EA-1112 elemental analyzer. Analytical thin-layer chromatography (TLC) was performed on silica gel GF_{254} (Qingdao, China) with EtOAc and light petroleum (fraction boiling in the range of 60–90 °C) and detection by UV light or iodine vapor. Column chromatography was performed on silica gel (100–200 mesh). All reagents were commercial products of analytical grade and were used directly without processing unless otherwise specified. The 4 **Å** molecular sieves were purchased in a powder form, crushed, sieved at 100 mesh screen and then activated at 200 °C for 4 h. Pyridine was dried over KOH and distilled prior to use. DMF and MeCN were dried over 4 **Å** molecular sieves. MeOH and EtOH were dried over magnesium and distilled prior to use.

Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-thioureido-α-D-glucopyranosides **1a–c** were synthesized starting from methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-isothiocyanato-α-D-glucopyranoside and 2-aminobenzothiazole derivatives using a well-established method.[26] Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-isothiocyanato-α-D-glucopyranoside was obtained from the reaction of the corresponding methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside with PPh_3 and CS_2 as reported.[38] 2-Aminobenzothiazole derivatives were prepared according to the reported method.[39]

3.2. General procedure for the reaction of sugar thioureas 1a–c with aliphatic amines

Sugar thiourea (1.0 mmol), 4 **Å** molecular sieves (1.0 g), and HgO (1.2 mmol) were added to 10 mL of MeCN and stirred under reflux for 30 min. Formation of carbodiimide was invariably completed. The solution was cooled to 25 °C, and a solution of

isopropylamine or cyclohexylamine (1.2 mmol) in MeCN (5 mL) was added to the reaction mixture, and the mixture was stirred at 25 °C until the reaction was completed (TLC, 1:1 EtOAc–petroleum ether). The reaction mixture was diluted with EtOAc and filtered through Celite, and the Celite cake was washed with additional EtOAc. The filtrate, together with the combined washings, was concentrated under reduced pressure to afford the desired guanidines (**2a** and **2b**).

3.2.1. Preparation of methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-isopropyl]guanidino-6-deoxy-α-D-glucopyranoside (2a)

White solid; yield 455 mg (85%); mp 85–86 °C. The product was analyzed by IR and ^{1}H NMR spectroscopy and used without further purification. The ^{1}H and ^{13}C NMR data were in full agreement with those reported in the literature.[26]

3.2.2. Preparation of methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-cyclohexyl] guanidino-6-deoxy-α-D-glucopyranoside (2b)

White solid; yield 466 mg (81%); mp 88–89 °C. The ^{1}H and ^{13}C NMR data were in full agreement with those reported in the literature.[26]

3.3. General procedure for the reaction of sugar thioureas 1a–c with aromatic amines

Sugar thiourea (1.0 mmol), 4 **Å** molecular sieves (1.0 g), and HgO (1.2 mmol) were added to 10 mL of MeCN and stirred under reflux for 30 min. Formation of the carbodiimide was invariably complete by this time. An aromatic amine (1.3 mmol) was added to the reaction mixture, and the mixture was stirred at 50 °C until the reaction was complete (TLC, 1:2–1:1 EtOAc–petroleum ether). The reaction mixture was diluted with EtOAc and filtered through Celite, and the Celite cake was washed with additional EtOAc. The filtrate, together with the combined washings, was concentrated under reduced pressure to afford the desired guanidine. The residue that remained after removal of solvent under reduced pressure was purified by silica column chromatography (eluent: 1:4–1:1 EtOAc–petroleum ether) to afford the guanidines **2**–**4**.

3.3.1. Methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-benzyl]guanidino-6-deoxy-α-D-glucopyranoside (2c)

White solid; yield 333 mg (57%); mp 83–84 °C; IR (KBr): 3374, 1752, 1601, 1587, 1465, 1225, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.05, and 2.09 (3s, each 3H, 3MeCO), 3.23 (s, 3H, OMe), 3.47–3.58 (br s, 2H, CH_2), 3.81–3.95 (m, 1H, H-6a), 4.47–4.61 (m, 2H, H-6b, H-5), 4.61–4.70 (br s, 1H, H-4), 4.71–4.84 (m, 2H, H-2, H-1), 5.42 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 6.86–7.63 (m, 9H, ArH), 10.00–10.86 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 170.7, 170.5, 170.2, 153.8, 145.4, 130.6, 128.9, 127.9, 127.4, 122.4, 121.3, 103.9, 96.7, 70.7, 69.8, 69.0, 55.4, 45.3, 41.5, 20.9, 20.8, 20.7; ESIMS: *m/z* 585 (100%, $[M+H]^+$), 607 (30%, $[M+Na]^+$). Anal. Calcd for $C_{28}H_{32}N_4O_8S$: C, 57.52; H, 5.52; N, 9.58. Found: C, 57.38; H, 5.49; N, 9.50.

3.3.2. Methyl 2,3,4-tri-*O*-acetyl-6-[N^3-benzyl-N^2-(6-methoxybenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (3c)

White solid; yield 398 mg (65%); mp 87–88 °C; IR (KBr): 3375, 1752, 1601, 1588, 1465, 1227, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99, 2.07, and 2.08 (3s, each 3H, 3MeCO), 3.23 (s, 3H, OMe), 3.47–3.57 (br s, 2H, CH_2), 3.83 (s, 3H, OMe), 3.83–3.97 (br s, 1H, H-6a), 4.49–4.61 (m, 2H, H-6b, H-5), 4.61–4.70 (br s, 1H, H-4), 4.71–4.85 (m, 2H, H-2, H-1), 5.41 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 6.85–7.67 (m, 8H, ArH), 10.00–10.88 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 170.2, 170.1, 169.8, 155.5, 145.9, 132.5, 129.0, 127.9, 127.2, 119.6, 113.3, 104.7, 96.5, 70.7, 69.8, 69.1, 55.8, 55.4, 45.3, 41.2, 20.8, 20.7; ESIMS: *m/z* 615 (100%, $[M+H]^+$), 637 (24%, $[M+Na]^+$). Anal. Calcd for $C_{29}H_{34}N_4O_9S$: C, 56.67; H, 5.58; N, 9.11. Found: C, 56.59; H, 5.55; N, 9.01.

3.3.3. Methyl 2,3,4-tri-*O*-acetyl-6-[N^3-benzyl-N^2-(6-methylbenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (4c)

White solid; yield 364 mg (61%); mp 97–98 °C; IR (KBr): 3369, 1754, 1602, 1590, 1468, 1227, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.06, and 2.09 (3s, each 3H, 3MeCO), 2.40 (s, 3H, Me), 3.23 (s, 3H, OMe), 3.46–3.58 (br s, 2H, CH_2), 3.83 (s, 3H, OMe), 3.83–3.96 (br s, 1H, H-6a), 4.47–4.60 (m, 2H, H-6b, H-5), 4.60–4.70 (br s, 1H, H-4), 4.70–4.87 (m, 2H, H-2, H-1), 5.42 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 6.85–7.60 (m, 8H, ArH), 10.02–10.85 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 170.7, 170.5, 170.2, 155.3, 145.2, 131.6, 128.4, 126.4, 126.3, 121.6, 113.5, 96.7, 70.8, 70.2, 69.9, 55.4, 45.2, 41.0, 23.5, 21.0, 20.9; ESIMS: *m/z* 598 (100%, $[M+H]^+$), 620 (30%, $[M+Na]^+$). Anal. Calcd for $C_{29}H_{34}N_4O_8S$: C, 58.18; H, 5.72; N, 9.36. Found: C, 58.07; H, 5.68; N, 9.27.

3.3.4. Methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-(*p*-methylphenyl)]guanidino-6-deoxy-α-D-glucopyranoside (2d)

White solid; yield 379 mg (65%); mp 133–134 °C; IR (KBr): 3380, 1750, 1603, 1592, 1464, 1230, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.07, and 2.10 (3s, each 3H, 3MeCO), 2.36 (s, 3H, Me), 3.29 (s, 3H, OMe), 3.50–3.63 (m, 1H, H-6a), 3.64–3.75 (m, 1H, H-6b), 3.85–4.00 (m, 1H, H-5), 4.79 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz,1H, H-2), 4.81–4.86 (m, 1H, H-4), 4.89 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.44 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 6.96–7.55 (m, 8H, ArH), 11.43–11.76 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 170.4, 170.3, 170.0, 153.6, 150.1, 135.8, 130.9, 129.7, 129.4, 126.7, 125.9, 125.4, 121.4, 116.6, 96.5, 70.9, 69.9, 69.5, 69.4, 55.2, 41.3, 29.7, 21.0, 20.9, 20.7; ESIMS: *m/z* 585 (100%, $[M+H]^+$), 607 (26%, $[M+Na]^+$). Anal. Calcd for $C_{28}H_{32}N_4O_8S$: C, 57.52; H, 5.52; N, 9.58. Found: C, 57.44; H, 5.46; N, 9.47.

3.3.5. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-[N^2-(6-methoxybenzothiazol-2-yl)-N^3-(*p*-methylphenyl)]guanidino-α-D-glucopyranoside (3d)

White solid; yield 423 mg (69%); mp 147–148 °C; IR (KBr): 3365, 1751, 1601, 1595, 1463, 1227, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.07, and 2.09 (3s, each 3H, 3MeCO), 2.37 (s, 3H, Me), 3.29 (s, 3H, OMe), 3.51–3.62 (m, 1H, H-6a), 3.63–3.76 (m, 1H, H-6b), 3.83 (s, 3H, OMe), 3.86–3.97 (m, 1H, H-5), 4.78 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.80–4.85 (m, 1H, H-4), 4.88 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.45 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 7.00–7.56 (m, 7H, ArH), 11.46–11.78 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 170.2, 170.1, 169.8, 155.5, 150.0, 136.9, 133.8, 132.2, 131.5, 129.9, 126.5, 125.2, 120.8, 118.3, 116.5, 96.7, 70.8, 69.9, 69.8, 68.0, 55.7, 55.4, 41.3, 29.8, 21.1, 20.9, 20.8, 20.7; ESIMS: *m/z* 615 (100%, $[M+H]^+$), 637 (35%, $[M+Na]^+$). Anal. Calcd for $C_{29}H_{34}N_4O_9S$: C, 56.67; H, 5.58; N, 9.11. Found: C, 56.59; H, 5.53; N, 9.05.

3.3.6. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-[N^2-(6-methylbenzothiazol-2-yl)-N^3-(*p*-methylphenyl)]guanidino-α-D-glucopyranoside (4d)

White solid; yield 376 mg (63%); mp 153–154 °C; IR (KBr): 3373, 1753, 1601, 1597, 1470, 1227, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.10, and 2.12 (3s, each 3H, 3MeCO), 2.39 (s, 3H, Me), 2.41 (s, 3H, Me), 3.29 (s, 3H, OMe), 3.49–3.61 (m, 1H, H-6a), 3.65–3.78 (m, 1H, H-6b), 3.87–3.95 (m, 1H, H-5), 4.78 (dd, 1H, $J_{1,2}$ 4.0 Hz, $J_{2,3}$ 9.6 Hz, H-2), 4.81–4.87 (m, 1H, H-4), 4.89 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 5.45 (t, 1H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3),

7.02–7.54 (m, 7H, ArH), 11.47–11.74 (br, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 170.3, 170.1, 169.9, 153.5, 149.5, 137.0, 133.6, 132.0, 131.4, 130.6, 126.6, 126.2, 120.8, 118.9, 96.5, 70.9, 69.9, 69.6, 68.0, 55.2, 41.1, 29.7, 21.4, 21.0, 20.8, 20.7; ESIMS: *m/z* 599 (100%, $[M+H]^+$), 621 (30%, $[M+Na]^+$). Anal. Calcd for $C_{29}H_{34}N_4O_8S$: C, 58.18; H, 5.72; N, 9.36. Found: C, 58.09; H, 5.68; N, 9.25.

3.3.7. Methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-(*p*-chlorophenyl)]guanidino-6-deoxy-α-D-glucopyranoside (2f)

White solid; yield 259 mg (43%); mp 163–164 °C; IR (KBr): 3379, 1752, 1602, 1595, 1463, 1225, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.08, and 2.11 (3s, each 3H, 3MeCO), 3.33 (s, 3H, OMe), 3.54–3.63 (m, 1H, H-6a), 3.63–3.78 (m, 1H, H-6b), 3.86–4.03 (m, 1H, H-5), 4.78 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.84–5.00 (m, 2H, H-4, H-1), 5.48 (t, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, 1H, H-3), 7.12–7.67 (m, 8H, ArH), 11.49–11.96 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 170.2, 170.1, 169.9, 153.1, 151.3, 135.4, 132.8, 131.4, 130.0, 127.2, 125.4, 122.5, 120.9, 119.4, 96.6, 71.1, 70.8, 69.8, 69.4, 68.0, 55.4, 41.2, 29.7, 22.7, 20.8, 20.7; ESIMS: *m/z* 605 (100%, $[M+H]^+$), 627 (32%, $[M+Na]^+$). Anal. Calcd for $C_{27}H_{29}ClN_4O_8S$: C, 53.60; H, 4.83; N, 9.26. Found: C, 53.48; H, 4.76; N, 9.19.

3.3.8. Methyl 2,3,4-tri-*O*-acetyl-6-[N^3-(*p*-chlorophenyl)-N^2-(6-methoxybenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (3f)

White solid; yield 310 mg (49%); mp 147–148 °C; IR (KBr): 3370, 1753, 1601, 1589, 1475, 1225, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01, 2.06, and 2.11 (3s, each 3H, 3MeCO), 3.32 (s, 3H, OMe), 3.52–3.64 (br s, 1H, H-6a), 3.64–3.82 (br s, 1H, H-6b), 3.86 (s, 3H, OMe), 3.84–4.03 (m, 1H, H-5), 4.79 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.83–4.96 (m, 1H, H-4), 4.89 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.46 (t, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, 1H, H-3), 7.10–7.66 (m, 7H, ArH), 11.47–11.98 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 170.7, 170.3, 170.2, 155.4, 151.4, 149.6, 135.6, 132,5, 130.2, 127.4, 127.3, 122.4, 119.3, 117.6, 103.9, 96.5, 70.9, 70.2, 69.9, 68.0, 55.7, 55.4, 41.3, 29.3, 21.0, 20.9, 20.7; ESIMS: *m/z* 634 (100%, $[M+H]^+$), 656 (23%, $[M+Na]^+$). Anal. Calcd for $C_{28}H_{31}ClN_4O_9S$: C, 52.95; H, 4.92; N, 8.82. Found: C, 52.87; H, 4.89; N, 8.76.

3.3.9. Methyl 2,3,4-tri-*O*-acetyl-6-[N^3-(*p*-chlorophenyl)-N^2-(6-methylbenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (4f)

White solid; yield 278 mg (45%); mp 155–156 °C; IR (KBr): 3371, 1751, 1603, 1587, 1465, 1226, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01, 2.07, and 2.10 (3s, each 3H, 3MeCO), 2.42 (s, 3H, Me), 3.32 (s, 3H, OMe), 3.49–3.62 (br s, 1H, H-6a), 3.62-3.82 (br s, 1H, H-6b), 3.84–4.03 (m, 1H, H-5), 4.79 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.81–4.96 (m, 1H, H-4), 4.89 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.45 (t, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, 1H, H-3), 7.09–7.68 (m, 7H, ArH), 11.50–11.97 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 170.6, 170.5, 170.0, 153.8, 152.4, 150.0, 145.3, 133.6, 130.5, 128.4, 128.3, 126.4, 119.3, 117.6, 103.9, 96.5, 70.9, 69.9, 69.5, 68.0, 55.4, 41.3, 29.7, 22.7, 20.9, 20.8; ESIMS: *m/z* 619 (100%, $[M+H]^+$), 641 (26%, $[M+Na]^+$). Anal. Calcd for $C_{28}H_{31}ClN_4O_8S$: C, 54.32; H, 5.05; N, 9.05. Found: C, 54.20; H, 5.01; N, 8.95.

3.3.10. Methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-6-deoxy-α-D-glucopyranoside (2g)

Transparent colorless crystals were obtained by slow evaporation over several days from ethanol solution. Yield 377 mg (67%); mp 178–179 °C; IR (KBr): 3209, 1745, 1598, 1579, 1476, 1443, 1222, 1043, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98, 2.03, and 2.06 (3s, each 3H, 3MeCO), 3.18 (s, 3H, OMe), 3.35–3.44 (m, 5H, $2CH_2$, H-6a), 3.44–3.54 (m, 1H, H-6b), 3.60–3.82 (m, 4H, $2CH_2$), 3.82–3.91 (m, 1H, H-5), 4.78 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.94 (t, $J_{3,4}$ = $J_{4,5}$ 9.8 Hz, 1H, H-4), 4.98 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.46 (t, $J_{2,3}$ = $J_{3,4}$ 9.8 Hz, 1H, H-3), 7.12–7.68 (m, 4H, ArH), 9.60–9.80 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 170.1, 170.0, 169.7, 160.1, 149.3, 132.3, 126.8, 126.5, 120.9, 119.8, 96.6, 70.9, 70.0, 69.4, 68.5, 66.7, 55.3, 48.5, 45.6, 21.4, 20.7, 20.6; ESIMS: *m/z* 565 (100%, $[M+H]^+$), 587 (35%, $[M+Na]^+$). Anal. Calcd for $C_{25}H_{32}N_4O_9S$: C, 53.18; H, 5.71; N, 9.92. Found: C, 53.10; H, 5.68; N, 9.86.

3.3.11. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-[N^2-(6-methoxybenzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-α-D-glucopyranoside (3g)

Transparent colorless crystals were obtained by slow evaporation over several days from ethanol solution. Yield 430 mg (72%); mp 152–153 °C; IR (KBr): 3212, 1743, 1598, 1576, 1475, 1446, 1225, 1041, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.02, and 2.06 (3s, each 3H, 3MeCO), 3.18 (s, 3H, OMe), 3.34–3.45 (m, 5H, $2CH_2$, H-6a), 3.45–3.55 (m, 1H, H-6b), 3.60–3.83 (m, 4H, $2CH_2$), 3.84 (s, 3H, OMe), 3.83–3.89 (m, 1H, H-5), 4.78 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.95 (t, $J_{3,4}$ = $J_{4,5}$ 9.8 Hz, 1H, H-4), 4.97 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.46 (t, $J_{2,3}$ = $J_{3,4}$ 9.8 Hz, 1H, H-3), 7.10–7.64 (m, 3H, ArH), 9.62–9.84 (br s, 1H, NH);^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 170.2, 170.0, 169.7, 160.1, 155.4, 149.3, 132.5, 120.9, 119.5, 108.1, 96.6, 70.9, 70.0, 69.4, 68.8, 66.6, 55.7, 55.4, 48.6, 45.5, 21.4, 20.8, 20.7; ESIMS: *m/z* 595 (100%, $[M+H]^+$), 617 (30%, $[M+Na]^+$). Anal. Calcd for $C_{26}H_{34}N_4O_{10}S$: C, 52.52; H, 5.76; N, 9.42. Found: C, 52.44; H, 5.73; N, 9.34.

3.3.12. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-[N^2-(6-methylbenzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-α-D-glucopyranoside (4g)

Transparent colorless crystals were obtained by slow evaporation over several days from ethanol solution. Yield 410 mg (71%); mp 186–187 °C; IR (KBr): 3210, 1742, 1600, 1581, 1477, 1441, 1224, 1041, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00, 2.03, and 2.08 (3s, each 3H, 3MeCO), 2.40 (s, 1H, Me), 3.18 (s, 3H, OMe), 3.33–3.45 (m, 5H, $2CH_2$, H-6a), 3.45–3.56 (m, 1H, H-6b), 3.60–3.84 (m, 4H, $2CH_2$), 3.87 (m, 1H, H-5), 4.78 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.96 (t, $J_{3,4}$ = $J_{4,5}$ 9.8 Hz, 1H, H-4), 4.97 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.46 (t, $J_{2,3}$ = $J_{3,4}$ 9.8 Hz, 1H, H-3), 7.08–7.65 (m, 3H, ArH), 9.60–9.82 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 170.1, 170.0, 169.6, 160.1, 149.3, 132.5, 132.3, 126.8, 120.9, 119.5, 96.6, 70.9, 70.1, 69.5, 68.5, 66.6, 55.3, 48.5, 45.6, 21.4, 20.7, 20.6; ESIMS: *m/z* 579 (100%, $[M+H]^+$), 610 (28%, $[M+Na]^+$). Anal. Calcd for $C_{26}H_{34}N_4O_9S$: C, 53.97; H, 5.92; N, 9.68. Found: C, 53.84; H, 5.89; N, 9.59.

3.3.13. Methyl 2,3,4-tri-*O*-acetyl-6-[N^2-(benzothiazol-2-yl-N^3-(ethoxycarbonyl))]guanidino-6-deoxy-α-D-glucopyranoside (2h)

White solid; yield 231 mg (41%); mp 145–146 °C; IR (KBr): 3469, 3240, 1754, 1611, 1496, 1440, 1218, 1066, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, *J* 7.2 Hz, 3H, Me), 2.02, 2.05, and 2.09 (3s, each 3H, 3MeCO), 3.36–3.46 (m, 4H, H-6b, OMe), 3.58–3.64 (m, 1H, H-6a), 3.93–4.00 (m, 1H, H-5), 4.40 (q, *J* 7.2 Hz, 2H, CH_2), 4.89 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.97 (t, $J_{3,4}$ = $J_{4,5}$ 9.6 Hz, 1H, H-4), 5.02 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.51 (t, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, 1H, H-3), 7.14–7.68 (m, 4H, ArH), 10.02–10.06 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 170.2, 170.1, 169.9, 157.3, 151,4, 150.0, 132.0, 125.5, 122.8, 121.0, 119.8, 96.5, 70.9, 70.5, 69.9, 67.8, 63.7, 55.4, 41.8, 20.8, 20.7, 14.5; ESIMS: *m/z* 567 (100%, $[M+H]^+$), 589 (16%, $[M+Na]^+$). Anal. Calcd for $C_{24}H_{30}N_4O_{10}S$: C, 50.88; H, 5.34; N, 8.95. Found: C, 50.76; H, 5.29; N, 9.02.

3.3.14. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-[N^3-(ethoxycarbonyl)-N^2-(6-methoxybenzothiazol-2-yl)]guanidino-α-D-glucopyranoside (3h)

White solid; yield 268 mg (45%); mp 146–147 °C; IR (KBr): 3468, 3245, 1753, 1611, 1499, 1441, 1217, 1067, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, J 7.2 Hz, 3H, Me), 2.01, 2.06, and 2.09 (3s, each 3H, 3MeCO), 3.34–3.45 (m, 4H, H-6b, OMe), 3.59–3.65 (m, 1H, H-6a), 3.85 (s, 3H, OMe), 3.91–3.96 (m, 1H, H-5), 4.41 (q, J 7.2 Hz, 2H, CH_2), 4.89 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.96 (t, $J_{3,4} = J_{4,5}$ 9.6 Hz, 1H, H-4), 5.02 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.52 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 7.12–7.67 (m, 4H, ArH), 10.00–10.06 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 170.3, 170.1, 170.0, 157.3, 154.6, 151,4, 150.0, 132.0, 125.5, 121.0, 115.8, 96.5, 70.9, 70.5, 69.8, 67.9, 63.7, 55.7, 55.3, 41.6, 20.7, 14.5; ESIMS: m/z 597 (100%, $[M+H]^+$), 619 (18%, $[M+Na]^+$). Anal. Calcd for $C_{25}H_{32}N_4O_{11}S$: C, 50.33; H, 5.41; N, 9.39. Found: C, 50.25; H,5.38; N, 9.27.

3.3.15. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-[N^3-(ethoxycarbonyl)-N^2-(6-methylbenzothiazol-2-yl)]guanidino-α-D-glucopyranoside (4h)

White solid; yield 255 mg (44%); mp 204–205 °C; IR (KBr): 3240, 3152, 1756, 1612, 1497, 1439, 1218, 1062, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, J 7.2 Hz, 3H, Me), 2.02, 2.06, and 2.08 (3s, each 3H, 3MeCO), 2.43 (s, 3H, Me), 3.35–3.47 (m, 4H, H-6b, OMe), 3.60–3.64 (m, 1H, H-6a), 3.92–3.97 (m, 1H, H-5), 4.43 (q, J 7.2 Hz, 2H, CH_2), 4.90 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, 1H, H-2), 4.97 (t, $J_{3,4} = J_{4,5}$ 9.6 Hz, 1H, H-4), 5.01 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 5.53 (t, $J_{2,3} = J_{3,4}$ 9.6 Hz, 1H, H-3), 7.13–7.68 (m, 4H, ArH), 10.02–10.05 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 170.2, 170.1, 170.0, 157.4, 151,3, 150.2, 132.5, 132.3, 125.7, 121.3, 117.3, 96.6, 70.9, 70.4, 69.8, 68.0, 63.8, 55.3, 41.6, 22.6, 20.7, 20.6, 14.4; ESIMS: m/z 581 (100%, $[M+H]^+$), 603 (30%, $[M+Na]^+$). Anal. Calcd for $C_{25}H_{32}N_4O_{10}S$: C, 51.72; H, 5.56; N, 9.65. Found: C, 51.67; H, 5.52; N, 9.58.

3.4. General procedure for the preparation of methyl 6-deoxy-6-guanidino-α-D-glucopyranosides 5–7

To a solution of the corresponding guanidines **2**–**4** (0.05 mmol) in MeOH (5 mL) was added NaOMe (0.1 M, 0.2 mL), and the reaction mixture was stirred at room temperature for 0.5–5 h when TLC (9:1 CH_3Cl–MeOH) revealed complete consumption of the starting material. The reaction mixture either crystallized on standing at 4 °C or some water was added to induce crystallization. The solution was filtered and washed with water to give the crude product, which was recrystallized from 90% alcohol to give the deacetylated guanidines **5**–**7**.

3.4.1. Methyl 6-(N^2-(benzothiazol-2-yl)-N^3-benzyl)]guanidino-6-deoxy-α-D-glucopyranoside (5c)

White solid; mp 189–190 °C; IR (KBr): 3489, 3390, 3348, 1603, 1578, 1490, 1033 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.12 (br s, 2H, H-4, H-2), 3.34 (br s, 4H, H-6a, OMe), 3.54 (br s, 1H, H-5), 3.73 (br s, 1H, H-3), 4.32 (br s, 1H, H-6b), 4.55 (s, 2H, CH_2Ph), 4.61 (br s, 1H, H-1), 7.11–7.72 (m, 9H, ArH), 10.82 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 155.8, 145.6, 135.6, 127.4, 122.4, 117.6, 113.9, 99.7, 73.5, 72.6, 70.4, 55.4, 45.6, 43.8; ESIMS: m/z 459 (100%, $[M+H]^+$), 481 (35%, $[M+Na]^+$). Anal. Calcd for $C_{22}H_{26}N_4O_5S$: C, 57.63; H, 5.72; N, 12.22. Found: C, 57.50; H, 5.65; N, 12.14.

3.4.2. Methyl 6-[N^3-benzyl-N^2-(6-methoxybenzothiazol-2-yl)]-guanidino-6-deoxy-α-D-glucopyranoside (6c)

White solid; mp 214–215 °C; IR (KBr): 3433, 1590, 1559, 1470, 1028 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.13 (br s, 1H, H-4), 3.34 (br s, 2H, H-2, H-6a), 3.46 (br s, 4H, H-5, OMe), 3.53–3.65 (m, 2H, H-6b, H-3), 3.75 (s, 3H, OMe), 4.42–4.58 (m, 2H, CH_2Ph), 4.65 (br s, 1H, H-1), 6.79–7.38 (m, 8H, ArH), 8.24 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.1, 154.8, 153.7, 145.9, 135.6, 129.0, 127.8, 127.2, 119.6, 113.4, 99.9, 73.6, 72.6, 71.0, 70.5, 55.7, 55.2, 45.5, 43.8; ESIMS: m/z 489 (100%, $[M+H]^+$), 501 (30%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{28}N_4O_6S$: C, 56.54; H, 5.78; N, 11.47. Found: C, 56.40; H, 5.74; N, 11.39.

3.4.3. Methyl 6-[N^3-benzyl-N^2-(6-methylbenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (7c)

White solid; mp 232–234 °C; IR (KBr): 3471, 1602, 1556, 1494, 1037 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.34 (s, 3H, Me), 2.96 (br s, 1H, H-4), 3.14 (br s, 1H, H-2), 3.43 (br s, 4H, H-6a, OMe), 3.54 (br s, 1H, H-5), 3.56–3.64 (m, 2H, H-3, H-6b), 4.41–4.58 (m, 2H, CH_2Ph), 4.64 (br s, 1H, H-1), 6.70–7.40 (m, 9H, ArH), 10.80 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.2, 154.6, 149.4, 135.6, 131.6, 128.4, 126.4, 126.0, 121.6, 113.9, 100.0, 73.5, 72.4, 70.6, 55.1, 45.3, 43.7, 21.2; ESIMS: m/z 473 (100%, $[M+H]^+$), 595 (15%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{28}N_4O_5S$: C, 58.46; H, 5.97; N, 11.86. Found: C, 58.35; H, 5.92; N, 11.76.

3.4.4. Methyl 6-[N^2-(benzothiazol-2-yl)-N^2-(*p*-methylphenyl)-]guanidino-6-deoxy-α-D-glucopyranoside (5d)

White solid; mp 163–164 °C; IR (KBr): 3383, 1614, 1566, 1463, 1347, 1043 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.29 (s, 3H, Me), 3.11 (br s, 1H, H-4), 3.34 (br s, 1H, H-2), 3.36 (s, 3H, OMe), 3.40–3.54 (m, 2H, H-5, H-6a), 3.59 (br s, 1H, H-3), 3.71–3.89 (m, 1H, H-6b), 4.67 (br s, 1H, H-1), 4.88 (d, $J_{OH,H}$ 6.0 Hz, OH,), 4.94 (d, $J_{OH,H}$ 4.4 Hz, OH), 5.27 (d, $J_{OH,H}$ 5.2 Hz, 1H, OH), 7.04–7.60 (m, 8H, ArH), 8.58 (br s, 1H, NH), 10.01 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.1, 154.5, 149.6, 131.8, 129.2, 126.8, 122.9, 119.0, 114.5, 100.7, 73.6, 72.6, 70.5, 55.2, 43.7, 21.1; ESIMS: m/z 459 (100%, $[M+H]^+$), 581 (32%, $[M+Na]^+$). Anal. Calcd for $C_{22}H_{26}N_4O_5S$: C, 57.63; H, 5.72; N, 12.22. Found: C, 57.56; H, 5.69; N, 12.15.

3.4.5. Methyl 6-deoxy-6-[N^2-(6-methoxybenzothiazol-2-yl)-N^3-(*p*-methylphenyl)]guanidino-α-D-glucopyranoside (6d)

White solid; mp 149–150 °C; IR (KBr): 3365, 1611, 1576, 1484, 1364, 1047 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 2.28 (s, 3H, Me), 3.14 (br s, 1H, H-4), 3.33 (br s, 1H, H-2), 3.35 (s, 3H, OMe), 3.38–3.55 (m, 2H, H-5, H-6a), 3.60 (br s, 1H, H-3), 3.70–3.89 (m, 4H, H-6b, OMe), 4.67 (br s, 1H, H-1), 4.88 (d, $J_{OH,H}$ 6.0 Hz, OH), 4.93 (d, $J_{OH,H}$ 4.4 Hz, OH), 5.26 (d, $J_{OH,H}$ 4.4 Hz, 1H, OH), 7.05–7.62 (m, 7H, ArH), 8.39 (br s, 1H, NH), 10.04 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.0, 155.8, 153.2, 145.8, 133.4, 131.6, 129.6, 127.4, 113.1, 105.6, 100.4, 73.6, 72.5, 70.6, 55.7, 55.3, 43.9, 21.1; ESIMS: m/z 489 (100%, $[M+H]^+$), 581 (26%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{28}N_4O_6S$: C, 56.54; H, 5.78; N, 11.47. Found: C, 56.42; H, 5.72; N, 11.36.

3.4.6. Methyl 6-deoxy-6-[N^2-(6-methylbenzothiazol-2-yl)-N^3-(*p*-methylphenyl)]guanidino-α-D-glucopyranoside (7d)

White solid; mp 147–148 °C; IR (KBr): 3383, 1614, 1566, 1459, 1347, 1043 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 2.29 (s, 3H, Me), 2.34 (s, 3H, Me), 3.12 (br s, 1H, H-4), 3.20–3.39 (m, 4H, H-2, OMe), 3.40–3.54 (m, 2H, H-5, H-6a), 3.58 (br s, 1H, H-3), 3.69–3.86 (m, 1H, H-6b), 4.67 (br s, 1H, H-1), 4.88 (d, $J_{OH,H}$ 6.0 Hz, OH,), 4.94 (d, $J_{OH,H}$ 4.4 Hz, OH), 5.27 (d, $J_{OH,H}$ 5.2 Hz, 1H, OH), 7.02–7.57 (m, 7H, ArH), 8.59 (br s, 1H, NH), 9.95 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 172.9, 154.3, 149.9, 132.0, 131.3, 129.7, 127.3, 123.9, 121.5, 119.0, 100.7, 73.6, 72.5, 70.6, 55.2, 43.8, 21.5, 21.1; ESIMS: m/z 473 (100%, $[M+H]^+$), 595 (32%, $[M+Na]^+$). Anal. Calcd for $C_{23}H_{28}N_4O_5S$: C, 58.46; H, 5.97; N, 11.86. Found: C, 58.56; H, 5. 94; N, 11.80.

3.4.7. Methyl 6-[N^2-(benzothiazol-2-yl)-N^3-(*p*-chlorophenyl)]guanidino-6-deoxy-α-D-glucopyranoside (5f)

White solid; mp 232–233 °C; IR (KBr): 3314, 1603, 1569, 1487, 1365, 1050, 1031 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.08–3.19 (m, 1H, H-4), 3.21–3.38 (br s, 4H, H-2, OMe), 3.38–3.50 (m, 1H, H-5), 3.53 (dd, $J_{5,6}$ 2.0 Hz, $J_{6a,6b}$ 12.3 Hz, 1H, H-6a), 3.61 (t, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, 1H, H-3), 3.80 (d, $J_{6a,6b}$ 12.3 Hz, 1H, H-6b), 4.67 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 4.88 (d, $J_{OH,H}$ 6.0 Hz, OH,), 4.94 (d, $J_{OH,H}$ 4.4 Hz, OH), 5.27 (d, $J_{OH,H}$ 5.2 Hz, 1H, OH), 6.81–7.79 (m, 8H, ArH), 8.59 (br s, 1H, NH), 10.02 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.7, 154.5, 149.6, 131.8, 129.2, 126.8, 122.9, 121.5, 119.0, 114.5, 100.7, 73.6, 72.6, 70.5, 55.2, 43.7; ESIMS: *m/z* 479 (100%, $[M+H]^+$), 601 (18%, $[M+Na]^+$). Anal. Calcd for $C_{21}H_{23}ClN_4O_5S$: C, 52.66; H, 4.84; N, 11.70. Found: C, 52.48; H, 4.80; N, 11.65.

3.4.8. Methyl 6-[N^3-(*p*-chlorophenyl)-N^2-(6-methoxybenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (6f)

White solid; mp 206–207 °C; IR (KBr): 3435, 3354, 1608, 1562, 1470, 1361, 1049, 1028 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.08–3.19 (m, 1H, H-4), 3.21–3.38 (br s, 4H, H-2, OMe), 3.39–3.49 (m, 1H, H-5), 3.53 (dd, $J_{5,6}$ 2.0 Hz, $J_{6a,6b}$ 12.3 Hz, 1H, H-6a), 3.61 (t, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, 1H, H-3), 3.65–3.86 (m, 4H, H-6b, OMe), 4.70 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 4.91 (d, $J_{OH,H}$ 6.0 Hz, 1H, OH,), 4.96 (d, $J_{OH,H}$ 4.4 Hz, 1H, OH), 5.31 (d, $J_{OH,H}$ 5.2 Hz, 1H, OH), 6.79–7.70 (m, 7H, ArH), 8.77 (br s, 1H, NH), 9.90 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.7, 156.0, 153.7, 146.0, 132.4, 129.0, 124.6 122.9, 120.0, 114.3, 105.7, 100.7, 73.6, 72.5, 70.6, 56.2, 55.3, 43.9; ESIMS: *m/z* 509 (100%, $[M+H]^+$), 531 (32%, $[M+Na]^+$). Anal. Calcd for $C_{22}H_{25}ClN_4O_6S$: C, 51.92; H, 4.95; N, 11.01. Found: C, 51.84; H, 4.93; N, 10.96.

3.4.9. Methyl 6-[N^3-(*p*-chlorophenyl)-N^2-(6-methylbenzothiazol-2-yl)]guanidino-6-deoxy-α-D-glucopyranoside (7f)

White solid; mp 209–210 °C; IR (KBr): 3442, 3338, 1617, 1573, 1488, 1460, 1354, 1048, 1026 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.35 (s, 3H, Me), 3.15 (t, $J_{3,4}$ = $J_{4,5}$ 9.6 Hz, 1H, H-4), 3.30 (dd, $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz, 1H, H-2), 3.35 (s, 3H, OMe), 3.45 (t, $J_{2,3}$ = $J_{3,4}$ 9.60 Hz, 1H, H-3), 3.51 (br s, 4H, H-6a, OMe), 3.54–3.68 (m, 1H, H-5), 3.78 (dd, $J_{5,6}$ 2.0 Hz, $J_{6a,6b}$ 12.8 Hz, 1H, H-6a), 4.71 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1), 4.98 (d, $J_{OH,H}$ 6.0 Hz, OH), 5.02 (d, $J_{OH,H}$ 4.4 Hz, OH), 5.37 (d, $J_{OH,H}$ 5.2 Hz, 1H, OH), 7.10–7.60 (m, 7H, ArH), 8.30 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.6, 154.3, 149.8, 133.8, 131.1, 129.2, 126.8, 121.5, 119.0, 100.7, 73.5, 72.5, 70.7, 55.2, 43.9, 21.6; ESIMS: *m/z* 493 (100%, $[M+H]^+$), 515 (24%, $[M+Na]^+$). Anal. Calcd for $C_{22}H_{25}ClN_4O_5S$: C, 53.60; H, 5.11; N, 11.37. Found: C, 53.51; H, 5.09; N, 11.28.

3.4.10. Methyl 6-[N^2-(benzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-6-deoxy-α-D-glucopyranoside (5g)

White solid; mp 178–179 °C; IR (KBr): 3465, 3346, 2898, 1588, 1576, 1476, 1370, 1043 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.21 (br s, 4H, H-4, OMe), 3.38–3.52 (m, 6H, CH_2NCH_2, H-2, H-6a), 3.58–3.70 (br s, 2H, H-3, H-6b), 3.70–3.84 (m, 5H, H-5, CH_2OCH_2), 4.66 (br s, 1H, H-1), 7.05–7.64 (m, 4H, ArH), 8.38 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 143.9, 125.8, 122.8, 121.1, 109.3, 99.5, 74.0, 72.1, 70.5, 66.2, 55.2, 47.9, 41.7; ESIMS: *m/z* 439 (100%, $[M+H]^+$), 461 (30%, $[M+Na]^+$). Anal. Calcd for $C_{19}H_{26}N_4O_6S$: C, 52.04; H, 5.98; N, 12.78. Found: C, 51.95; H, 5.96; N, 12.74.

3.4.11. Methyl 6-deoxy-6-[N^2-(6-methoxybenzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-α-D-glucopyranoside (6g)

White solid; mp 152–153 °C; IR (KBr): 3468, 3374, 2899, 1596, 1552, 1471, 1346, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.23 (br s, 1H, H-4), 3.29 (s, 3H, OMe), 3.36–3.53 (m, 6H, CH_2NCH_2, H-2, H-6a), 3.57–3.72 (br s, 2H, H-3, H-6b), 3.72–3.85 (m, 8H, H-5, CH_2OCH_2, OMe), 4.67 (br s, 1H, H-1), 7.04–7.65 (m, 3H, ArH), 8.40 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 157.1, 155.7, 145.5, 133.0, 120.2, 113.7, 104.8, 99.6, 74.1, 72.0, 70.5, 66.5, 55.7, 55.2, 47.8, 41,8; ESIMS: *m/z* 469 (100%, $[M+H]^+$), 491 (25%, $[M+Na]^+$). Anal. Calcd for $C_{20}H_{28}N_4O_7S$: C, 51.27; H, 6.02; N, 11.96. Found: C, 51.22; H, 5. 99; N, 11.89.

3.4.12. Methyl 6-deoxy-6-[N^2-(6-methylbenzothiazol-2-yl)-N^3-(oxydi-1,2-ethandiyl)]guanidino-α-D-glucopyranoside (7g)

White solid; mp 186–187 °C; IR (KBr): 3443, 3356, 1601, 1595, 1576, 1463, 1369, 1045 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, Me), 3.23 (br s, 4H, H-4, OMe), 3.39–3.58 (m, 6H, CH_2NCH_2, H-2, H-6a), 3.58–3.69 (br s, 2H, H-3, H-6b), 3.69–3.85 (m, 5H, H-5, CH_2OCH_2), 4.67 (br s, 1H, H-1), 7.03–7.65 (m, 3H, ArH), 8.36 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 154.9, 143.8, 133.8, 132.5, 122.5, 119.6, 109.7, 99.9, 74.2, 72.1, 70.7, 66.6, 55.4, 47.8, 41.7, 21.6; ESIMS: *m/z* 453 (, 100%, $[M+H]^+$), 475 (32%, $[M+Na]^+$). Anal. Calcd for $C_{20}H_{28}N_4O_6S$: C, 53.08; H, 6.24; N, 12.38. Found: C, 52.98; H, 6.21; N, 12.29.

3.4.13. Methyl 6-[N^2-(benzothiazol-2-yl)-N^3-(ethoxycarbonyl)]guanidino-6-deoxy-α-D-glucopyranoside (5h)

White solid; mp 145–146 °C; IR (KBr): 3463, 3354, 1751, 1613, 1469, 1218, 1066 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, *J* 7.0 Hz, 3H, Me), 3.05 (br s, 1H, H-4), 3.31–3.52 (m, 4H, H-2, OMe), 3.57 (d, $J_{5,6a}$ 5.6 Hz, 1H, H-6a), 3.65–3.83 (m, 2H, H-5, H-6b), 4.37 (q, *J* 7.0 Hz, 2H, CH_2), 4.81 (d, $J_{1,2}$ 3.2 Hz, 1H, H-1), 6.88–7.45 (m, 4H, ArH), 9.79 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 157.3, 143.5, 125.9, 122.6, 121.0, 109.6, 99.3, 74.6, 72.4, 71.5, 70.1, 63.4, 55.3, 42.2, 14.3; ESIMS: *m/z* 441 (100%, $[M+H]^+$), 463 (16%, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{24}N_4O_7S$: C, 49.08; H, 5.49; N, 12.72. Found: C, 49.01; H, 5.47; N, 12.68.

3.4.14. Methyl 6-deoxy-6-[N^3-(ethoxycarbonyl)-N^2-(6-methoxybenzothiazol-2-yl)]guanidino-α-D-glucopyranoside (6h)

White solid; mp 146–147 °C; IR (KBr): 3458, 3383, 1754, 1613, 1463, 1210, 1057 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, *J* 7.0 Hz, 3H, Me), 3.03 (br s, 1H, H-4), 3.34–3.50 (m, 4H, H-2, OMe), 3.56 (d, $J_{5,6a}$ 5.6 Hz, 1H, H-6a), 3.64–3.85 (m, 5H, H-5, H-6b, OMe), 4.37 (q, *J* 7.0 Hz, 2H, CH_2), 4.81 (d, $J_{1,2}$ 3.2 Hz, 1H, H-1), 6.85–7.44 (m, 3H, ArH), 9.78 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 157.2, 155.9, 145.5, 133.0, 120.1, 113.7, 104.6, 99.1, 74.6, 72.3, 71.6, 70.0, 63.5, 55.7, 55.4, 42.1, 14.5; ESIMS: *m/z* 471 (100%, $[M+H]^+$), 493 (15%, $[M+Na]^+$). Anal. Calcd for $C_{19}H_{26}N_4O_8S$: C, 48.50; H, 5.57; N, 11.91. Found: C, 48.38; H, 5.54; N, 11.84.

3.4.15. Methyl 6-deoxy-6-[N^3-(ethoxycarbonyl)-N^2-(6-methylbenzothiazol-2-yl)]guanidino-α-D-glucopyranoside (7h)

White solid; mp 204–205 °C; IR (KBr) 3452, 3368, 1753, 1612, 1469, 1223, 1066 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.34 (t, *J* 7.0 Hz, 3H, Me), 2.34 (s, 3H, Me), 3.03 (br s, 1H, H-4), 3.32–3.54 (m, 4H, H-2, OMe), 3.57 (d, $J_{5,6a}$ 5.6 Hz, 1H, H-6a), 3.64–3.76 (m, 1H, H-5), 3.89 (br s, 1H, H-6b), 4.37 (q, *J* 7.0 Hz, 2H, CH_2), 4.82 (d, $J_{1,2}$ 3.2 Hz, 1H, H-1), 6.84–7.45 (m, 3H, ArH), 9.76 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 157.3, 145.7, 133.2, 132.5, 122.1, 119.7, 109.6, 99.2, 74.5, 72.3, 71.5, 70.0, 63.5, 55.4, 42.1, 21.5, 14.5; ESIMS: *m/z* 455 (100%, $[M+H]^+$), 477 (22%, $[M+Na]^+$). Anal. Calcd for $C_{19}H_{26}N_4O_7S$: C, 50.21; H, 5.77; N, 12.33. Found: C, 50.14; H, 5.74; N, 12.26.

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Supplementary data

Complete crystallographic data for the structural analysis of compounds **2g**, **3g**, and **4g** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 673146, 675337, and 675338, respectively. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (tel.: +44-01223-762910, fax: +44-01223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: http://www.ccdc.cam.ac.uk). Tables containing selected bond lengths and bond angles for the compounds **2g, 3g,** and **4g** are available at http://www.ccdc.cam.ac.uk/deposit. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.07.016.

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