SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 6, pp. 1125–1139, 2004

Synthesis of a Tetrasaccharide Related to the Repeating Unit of the Antigen from *Shigella dysenteriae* Type 9 in the Form of Its 2-(Trimethylsilyl)ethyl Glycoside

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ABSTRACT

Starting from D-mannose, D-galactose and D-glucosamine hydrochloride, two disaccharide blocks were synthesized. Schmidt's inverse addition technique for trichloroacetimidate was utilized for the construction of a disaccharide with a β-mannosidic linkage in good yield. The two disaccharides in the appropriate form were then allowed to react in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH) to give the tetrasaccharide derivative from which removal of protecting groups gave the desired tetrasaccharide in the form of its 2-(trimethylsilyl)ethyl glycoside.

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DOI: 10.1081/SCC-120028645 0039-7911 (Print); 1532-2432 (Online)

Key Words: Tetrasaccharide; *Shigella dysenteriae*; *N*-iodosuccinimide; Trifluoromethanesulfonic acid.

Shigella are facultative, non-motile, Gram-negative bacilli. They are pathogenic primarily due to their ability to invade intestinal epithelial cells. They are responsible for the intestinal diseases including dysentery and has the potential for causing catastrophic public health problem in developing countries.[1] They are much resistant to the anti-microbial drugs. It, therefore, necessitates the exploration of other medical approaches for control of diseases caused by these pathogens.[1] It has been suggested[2] that circulating antibodies to the O-specific polysaccharide of *Shigella* may protect the host against shigellosis and the conjugate vaccines consisting of the O-specific polysaccharide of *Shigella*, covalently attached to an immunogenic protein could, indeed, confer protective immunity to human against shigellosis. Recently, a glycoconjugate vaccine against *Shigella dysenteriae* type 1 was synthesized,[3] which was shown to have better antigenicity than the native antigen. It is, therefore, probable that the O-specific polysaccharide from *Shigella dysenteriae* type 9 (O-SP) may also play a protective role against bacillary dysentery and shigellosis in human. The O-SP have been reported to contain two β-D-galactoses, one *N*-acetyl-β-D-glucosamine and one β-D-mannose in its repeating unit (**I**). It also contains a pyruvic acid acetal at the 4,6-position of one D-galactose moiety and an acetyl group at the 2- or 3-position of the other galactose moiety. Immunochemical studies,[4] on *Shigella dysenteriae* type 9 showed that the presence of pyruvic acid acetal and the *O*-acetyl group in the related oligosaccharides make negligible contribution to the specificities in the immune precipitation.

We have already reported,[5] the synthesis of a blocked tetrasaccharide derivative related to the repeating unit **I** in the form of its methyl (*R*)-pyruvate ester and 2-(trimethylsilyl)ethyl glycoside. It is therefore deemed interesting to synthesize the tetrasaccharide analog related to the repeating unit of the *Shigella dysenteriae* type 9 as its 2-(trimethylsilyl)ethyl glycoside but without the pyruvate acetal. The blocked oligosaccharides can be easily transformed into the corresponding hemiacetal for the preparation of trichloroacetimidate donor and its transformation into a neoglycoconjugate.

D C B A

→3)-β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*-(1→4)-β-D-Man*p*-(1→4)-α-D-Gal*p*-(1→

4 6

CH_3 COOH

2/3OAc

I

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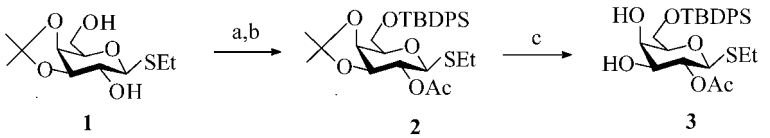
The basic strategy utilized in the synthesis of the tetrasaccharide related to the repeating unit of *Shigella dysenteriae* type 9 was first to synthesize the two disaccharide derivatives, convert them to a suitable disaccharide donor and a disaccharide acceptor and then allow them to react in the presence of an appropriate promoter to form the desired tetrasaccharide.

The known ethyl 3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside[6] (**1**) was treated with *tert*-butyldiphenylsilyl chloride (TBDPSCl)[7] followed by acetylation of the product to give **2** which on treatment with 80% acetic gave the acceptor **3** in 91% yield (Sch. 1). The structure of **3** was confirmed from its ^{1}H NMR spectrum.

The acceptor **3** with two hydroxyl groups of different reactivity was allowed to react with the known 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate[8] (**4**) in the presence of triethylsilyl-trifluoromethane sulfonate (TESOTf)[9,10] in dichloromethane to afford ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 $\rightarrow$ 3)-2-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio-β-D-galactopyranoside (**5**) in 69% yield. The formation of 1 $\rightarrow$ 3 linked disaccharide resulting from the better reactivity of the 3-OH compared to the 4-OH group of galactose. This was confirmed by the downfield shift of H-3^C proton which showed a double doublet at δ4.39. As expected, acetylation of **5** gave a product, which showed a downfield shift of the signal for H-4^C from δ4.15 to δ5.39 in its ^{1}H NMR spectrum. The β-anomeric configuration of the disaccharide was confirmed from the high coupling constant ($J_{1,2} = 8.4$ Hz) of the signal for H-1^D. Compound **5** has characteristic signals for phthalimido, 4 *O*-acetyl, TBDPS and C-2^D together with anomeric protons and carbons in the NMR spectra. Removal of TBDPS from **5** was effected with TBAF[11] in THF to afford **6** which was then stirred with α,α-dimethoxytoluene[12] and catalytic amount of 10-camphorsulphonic acid (CSA) to give the corresponding benzylidene derivative **7**. A sharp singlet at δ5.44 in the ^{1}H NMR spectrum confirmed the formation of benzylidene in the disaccharide. Dephthaloylation of the disaccharide **7** was performed with ethylenediamine in 1-butanol[13] to generate the free amine which was converted into the acetamido derivative **8** with acetic anhydride and pyridine (Sch. 2).



1 **2** **3**

Scheme 1. a. TBDPSCl, Pyr, 8 hr, 25°C, 78%; b. Ac_2O, Pyr, RT, 3 hr, 94%; c 80% acetic acid, 80°C, 2 hr, 91%.

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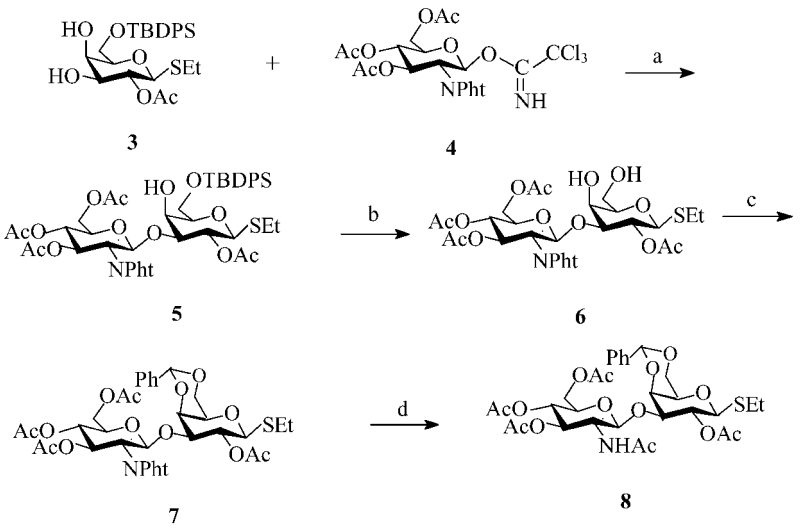
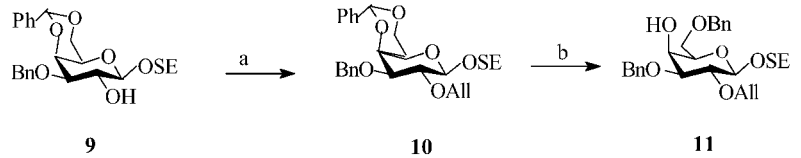


Scheme 2. a. TES-OTf, CH_2Cl_2, $-30^{\circ}C$, 30 min, 69%; b. TBAF, THF, $0^{\circ}C$, 6 hr, 76%; c. $PhCH(OCH_3)_2$, CSA, CH_3CN, RT, 16 hr, 89%; d. (i) 1-BuOH, $N_2NCH_2CH_2NH_2$, $90^{\circ}C$, 20 hr; (ii) Ac_2O, Pyr, RT, 24 hr, 85.3%.

In a separate experiment, allylation[15] of known 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-benzyl-β-D-galactopyranoside[14](**9**) afforded the 2-*O*-allyl compound **10**, the benzylidene ring of which was regioselectively opened[16] with $NaCNBH_3$ and HCl-OEt_2 giving 2-(trimethylsilyl)ethyl 2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (**11**) (Sch. 3).

Mannopyranosyl donor, 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate[5] (**12**) was allowed to react with the acceptor **11** in dichloromethane in the presence of TESOTf under inverse condition,[17] i.e the trichloroacetimidate donor being added to the mixture of acceptor and TESOTf, to afford the disaccharide 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1 $\rightarrow$ 4)-2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (**13**) in 89% yield with 2 : 7 ratio of α and β



Scheme 3. a. AllBr, NaH, DMF, RT, 6 hr; b. $NaCNBH_3$, $HCl.OEt_2$, MS 3 Å, $0^{\circ}C$, 45 min.

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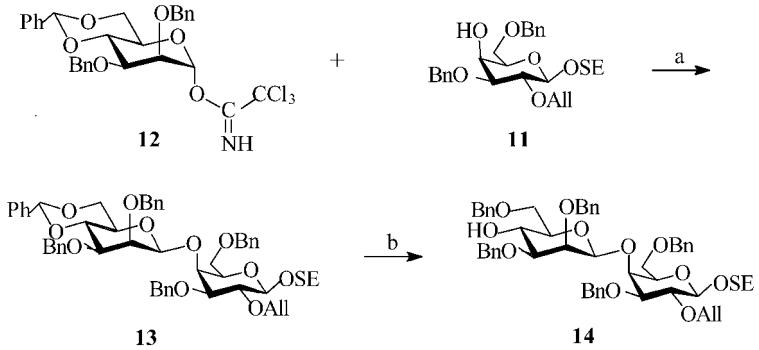

Scheme 4. a. TES-OTf, CH_2Cl_2, $-45^{\circ}C$, 45 min, 69%; b. $NaCNBH_3$; $HCl.OEt_2$, $0^{\circ}C$, 30 min, 68%.

anomers. The major amount of the β-product was probably due to the presence of 4,6-benzylidene ring in the mannose moiety. Regioselective opening[16] of the benzylidene ring of **13** using $NaCNBH_3$ and HCl-ether in THF afforded the disaccharide acceptor **14** (Sch. 4) in 70% yield together with a small amount ($\sim$5%) of the 6-hydroxy compound. The compound **14** was characterized from its signals in ^1H and ^{13}C NMR spectra.

The disaccharide donor **8** was allowed to react with the disaccharide acceptor **14** in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH)[18] to afford the tetrasaccharide derivative 2-(trimethylsilyl)ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 $\rightarrow$ 3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1 $\rightarrow$ 4)-2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (**15**) in 74% yield (Sch. 5). The formation of β-glycosidic linkage was confirmed from high coupling value of H-1 proton in ^1H NMR. The signals in ^{13}C also support the formation of β-glycosidic linkage. Compound **15** was deallylated,[19] debenzylated,[19] and deacetylated in succession to afford the desired tetrasaccharide **16**. Compound **16** has characteristic signals for $NHCOCH_3$, C-2^D,$OCH_2CH_2SiMe_3$ together with 4 anomeric protons and carbons in its NMR spectra.

EXPERIMENTAL

General

All reactions were monitored by TLC on Silica Gel G (E. Merck). Column chromatography was performed on 100–200 mesh Silica Gel (SRL,

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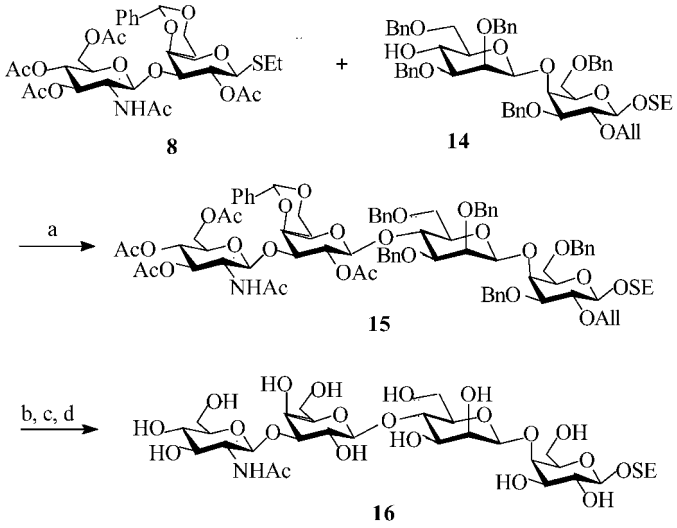

Scheme 5. a. NIS, TfOH, CH_2Cl_2, $-20^{\circ}C$, 1 hr, 74%; b. $PdCl_2$, MeOH; c. H_2, 10% Pd/C, EtOH; d. NaOMe, MeOH.

India) using 15–20 times (by weight) of the crude product. The organic extracts were dried over anhydrous Na_2SO_4. All solvents were distilled and/or dried before use and all evaporations were conducted at or below 40°C under reduced pressure unless stated otherwise. Optical rotations were measured at 24°C with a Perkin-Elmer 241 MC polarimeter. The ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard unless otherwise stated. Melting points were determined on a paraffin oil bath and are uncorrected.

Ethyl 2-*O*-Acetyl-6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (2)

To a solution of ethyl 3,4-*O*-isopropylidene-1-thio-*β*-D-galactopyranoside (**1**) (3 g, 11.34 mmol) in pyridine (15 mL) was added *tert*-butyldiphenylsilyl chloride (2.1 mL, 17.0 mmol). The mixture was stirred for 8 hr at 25°C and then concentrated under reduced pressure. Column chromatography of the residue in 1 : 1 toluene-EtOAc gave the pure TBDPS derivative (4.45 g, 78%) which was acetylated conventionally to afford pure **2** (4.3 g, 94%);

$[\alpha]_D^{25} + 21.4^\circ$ (*c* 0.7, $CHCl_3$); ^1H NMR: δ7.64–7.29 (m, 10H, aromatic protons), 4.93 (dd, 1H, $J_{2,3} = 7.5$ Hz, $J_{1,2} = 10.3$ Hz, H-2), 4.27 (dd, 1H, $J_{3,4} = 5.1$ Hz, $J_{4,5} = 2.0$ Hz, H-4), 4.25 (d, 1H, $J = 10.1$ Hz, H-1), 4.09 (dd, 1H, $J_{2,3} = 7.5$ Hz, $J_{3,4} = 5.3$ Hz, H-3), 3.88–3.77 (m, 3H, H-6, H-5), 2.58 (m, 2H, SCH_2CH_3), 2.02 (s, 3H, $OCOCH_3$), 1.46, 1.27 [2 s, 6H, $C(CH_3)_2$], 1.14 (t, 3H, $J = 7.3$ Hz, SCH_2CH_3), 0.98 [s, 9H, $Ph_2SiC(CH_3)_3$]; ^{13}C NMR: 170.2 ($OCOCH_3$), 136.1–125.7 (aromatic carbons), 110.7 [$C(CH_3)_2$], 83.0 (C-1), 77.9, 77.6, 73.9, 72.1, 63.1 (C-6), 28.2, 26.8 [$C(CH_3)_2$], 27.0 [$Ph_2SiC(CH_3)_3$], 24.2 (SCH_2CH_3), 21.5 ($OCOCH_3$), 19.6 [$Ph_2SiC(CH_3)_3$], 15.2 (SCH_2CH_3). Anal. Calcd for $C_{29}H_{40}O_6SiS$: C, 63.93; H, 7.40. Found: C, 63.77; H, 7.78.

Ethyl 2-*O*-Acetyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside (3)

A solution of **2** (3.8 g, 6.98 mmol) in 80% acetic acid (20 mL) was stirred at 80°C for 2 hr when TLC showed complete conversion to the product. Solvents were then evaporated off. Column chromatography with 3 : 1 toluene-EtOAc gave pure **3** (3.20 g, 91%) as a glassy mass. $[\alpha]_D^{25}$-25.4° (*c* 0.5, $CHCl_3$); ^1H NMR: δ7.72–7.38 (m, 10H, aromatic protons), 5.09 (t, 1H, $J = 9.6$ Hz, H-2), 4.35 (d, 1H, $J = 9.9$ Hz, H-1), 4.16 (d, 1H, $J = 3.0$ Hz, H-4), 3.95–3.91 (m, 2H, H-6), 3.62 (dd, 1H, $J_{2,3} = 9.3$ Hz, $J_{3,4} = 3.2$ Hz, H-3), 3.51 (t, 1H, $J = 5.0$ Hz, H-5), 2.68 (m, 2H, SCH_2CH_3), 2.15 (s, 3H, $OCOCH_3$), 1.24 (t, 3H, $J = 7.5$ Hz, SCH_2CH_3), 1.06 [s, 9H, $Ph_2SiC(CH_3)_3$]; ^{13}C NMR: δ136.1–128.3 (aromatic carbons), 83.5 (C-1), 78.0, 74.2, 71.6, 70.3 64.1 (C-6), 27.2 [$Ph_2SiC(CH_3)_3$], 23.9 (SCH_2CH_3), 21.5 ($OCOCH_3$), 19.5 [$Ph_2SiC(CH_3)_3$], 15.3 (SCH_2CH_3). Anal. Calcd for $C_{26}H_{36}O_6SiS$: C, 61.87; H, 7.19. Found: C, 61.65; H, 7.07.

Ethyl 3,4,6-tri-*O*-Acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside (5)

To a solution of the acceptor **3** (1.01 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added 4Å molecular sieve (2.5 g) and stirred for 2 hr under N_2 at −30°C. To this cold solution, were added TESOTf (81.7 μL, 0.36 mmol) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl trichloroacetimidate (**4**) donor (1.4 g, 2.41 mmol) and the solution was allowed to stir for 30 min at that temperature. Then the solution was diluted with CH_2Cl_2 (25 mL) and washed successively with saturated $NaHCO_3$ solution and

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water. The organic phase was collected, dried (Na_2SO_4) and concentrated. Column chromatography of the residue with 10 : 1 toluene-EtOAc gave pure **5** (1.28 g, 69%); $[\alpha]_D^{25} + 7.2^\circ$ (*c* 0.7, $CHCl_3$); ^{1}H NMR: δ 7.87–7.73 [m, 4H, $N(CO)_2C_6H_4$], 7.69–7.27 (m, 10H, aromatic protons), 5.77 (dd, 1H, $J_{2,3} = 9.2$ Hz, $J_{3,4} = 10.8$ Hz, H-3^D), 5.55 (d, 1H, $J = 8.5$ Hz, H-1^D), 5.18 (t, 1H, $J = 9.6$ Hz, H-4^D), 5.09 (t, 1H, $J = 9.7$ Hz, H-2^C), 4.38 (dd, 1H, $J_{1,2} = 8.4$ Hz, $J_{2,3} = 10.7$ Hz, H-2^D), 4.27 (dd, 1H, $J_{5,6a} = 4.3$ Hz, $J_{6e,6a} = 12.5$ Hz, H-6$_a^D$), 4.21 (d, 1H, $J = 9.8$ Hz, H-1^C), 4.13 (dd, 1H, $J_{5,6e} = 2.2$ Hz, $J_{6a,6e} = 12.4$ Hz, H-6$_e^D$), 3.71 (dd, 1H, $J_{2,3} = 9.4$ Hz, $J_{3,4} = 3.1$ Hz, H-3^C), 3.55 (t, 1H, $J = 6.0$ Hz, H-5^C), 2.52 (m, 2H, SCH_2CH_3), 2.03, 2.03, 1.86, 1.57 (4s, 12H, $4OCOCH_3$), 1.12 (t, 3H, $J = 7.5$ Hz, SCH_2CH_3), 1.04 [s, 9H, $Ph_2SiC(CH_3)_3$]; ^{13}C NMR: δ 171.0, 170.6, 169.8, 169.6 (4 $COCH_3$), 136.0–128.1 (aromatic carbons), 98.8 (C-1^D), 83.4 (C-1^C), 82.0, 78.8, 72.5, 70.8, 69.1, 68.8, 68.5, 62.9, 62.0 (C-6^C, C-6^D), 54.8 (C-2^D), 27.2 [$Ph_2SiC(CH_3)_3$], 23.4 (SCH_2CH_3), 21.1, 21.0, 20.9, 20.8 (4 $COCH_3$), 19.6 [$Ph_2SiC(CH_3)_3$], 15.0 (SCH_2CH_3). Anal. Calcd for $C_{46}H_{55}O_{15}SiNS$: C, 59.91; H, 6.01; N, 1.51. Found: C, 59.85; H, 5.98; N, 1.40.

Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-1-thio-β-D-galactopyranoside (6)

Tetrabutylammonium fluoride (366 mg, 1.16 mmol) was added to a solution of **5** (800 mg, 0.86 mmol) in THF (3 mL) at 0°C, then the temperature was slowly raised to 25°C. After 6 hr the solution was concentrated. Column chromatography of the residue with 1 : 1 toluene-EtOAc gave pure **6** (450 mg, 76%); $[\alpha]_D^{25} - 16.6^\circ$ (*c* 0.6, $CHCl_3$); ^{1}H NMR: δ 7.86–7.73 [m, 4H, $N(CO)_2C_6H_4$], 5.75 (dd, 1H, $J_{2,3} = 9.3$ Hz, $J_{3,4} = 10.5$ Hz, H-3^D), 5.53 (d, 1H, $J = 8.4$ Hz, H-1^D), 5.13 (t, 1H, $J = 9.5$ Hz, H-4^D), 5.06 (t, 1H, $J = 9.5$ Hz, H-2^C), 4.34 (dd, 1H, $J_{1,2} = 8.4$, $J_{2,3} = 10.7$ Hz, H-2^D), 4.30–4.18 (m, 2H, H-6^D), 4.23 (d, 1H, $J = 10.0$ Hz, H-1^C), 4.15 (bs, 1H, H-4^C), 3.89 (m, 2H, H-6^C), 3.55 (bs, 1H, H-5^D), 2.54 (m, 2H, SCH_2CH_3) 2.10, 2.03, 1.83, 1.50 (4 s, 12 H, $OCOCH_3$), 1.14 (t, 3H, $J = 7.4$ Hz, SCH_2CH_3); ^{13}C NMR: δ 171.2, 170.5, 169.8, 169.6 (4 $COCH_3$), 134.9–124.1 (aromatic carbons), 98.8 (C-1^D), 83.6 (C-1^C), 81.9, 72.5, 70.7, 69.3, 69.1, 68.6, 62.5, 62.2 (C-6^C, C-6^D), 54.8 (C-2^D), 23.7 (SCH_2CH_3), 21.2, 21.1, 20.7, 20.6, (4 $COCH_3$), 15.1 (SCH_2CH_3). Anal. Calcd for $C_{30}H_{37}O_{15}SN$: C, 52.70; H, 5.45; N, 2.04. Found: C, 52.43; H, 5.26; N, 1.97.

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Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (7)

To a solution of **6** (350 mg, 0.51 mmol) in DMF (5 mL), α,α-dimethoxytoluene (115 μL, 0.76 mmol) and CSA (80 mg) were added. The mixture was stirred at r.t. for 16 hr. The reaction was quenched with Et_3N, concentrated and column chromatographed with 2 : 1 toluene-EtOAc to afford **7** (351 mg, 89%), $[\alpha]_D^{25}$ − 25° (c 0.5, $CHCl_3$); ^{1}H NMR: δ 7.76–7.63 [m, 4H, $N(CO)_2C_6H_4$], 7.42–7.27 (m, 5H, aromatic protons), 5.68 (dd, 1H, $J_{2,3} = 9.3$ Hz, $J_{3,4} = 10.8$ Hz, H-3^D), 5.49 (d, 1H, $J = 8.3$ Hz, H-1^D), 5.44 (bs, 1H, C*H*Ph), 5.12 (t, 1H, $J = 9.6$ Hz, H-4^D), 5.11 (t, 1H, $J = 9.6$ Hz, H-2^C), 4.32 (dd, 1H, $J_{4,5} = 2.2$ Hz, $J_{6e,6a} = 8.7$ Hz, H-3^C), 4.19 (d, 1H, $J = 9.4$ Hz, H-1^C), 4.17 (d, 1H, $J = 2.3$ Hz, H-4^C), 3.93 (d, 1H, $J = 12.3$ Hz, H-6aC), 3.77 (m, 2H, H-6^D), 3.37 (bs, 1H, H-5^C), 2.70–2.42 (m, 2H, SCH_2CH_3) 2.02, 1.96, 1.76, 1.62 (4 s, 12 H, $OCOCH_3$), 1.09 (t, 3H, $J = 7.4$ Hz, SCH_2CH_3); ^{13}C NMR: δ 171.0, 170.6, 169.8, 169.7 (4 $COCH_3$), 138.2–124.0 (aromatic carbons), 101.3 (*C*HPh), 99.2 (C-1^D), 83.2 (C-1^C), 79.3, 76.3, 72.4, 71.0,70.5, 69.5, 69.3, 68.2 (C-6^C), 62.1 (C-6^D), 54.8 (C-2^D), 22.9 (SCH_2CH_3), 21.9, 21.3, 21.1, 20.8, 20.4 (4 $COCH_3$), 15.1 (SCH_2CH_3). Anal. Calcd for $C_{37}H_{41}O_{15}SN$: C, 57.57; H, 5.35; N, 1.81. Found: C, 57.50; H, 5.26; N, 1.97.

Ethyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (8)

To compound **7** (300 mg, 0.43 mmol) dissolved in *n*-butanol (5 mL) ethylenediamine (1 mL) was added. The solution was stirred at 90°C for 20 hr. Solvents were then removed under reduced pressure and finally by co-evaporation twice with toluene to give yellow syrup. Acetic anhydride (3 mL) and pyridine (3 mL) were then added and stirring was continued. After 14 hr, the solution was concentrated to syrup which was purified by column chromatography using 1 : 1 toluene-EtOAc to give **8** (151.2 mg, 85.3%) as a thick glass, $[\alpha]_D^{25}$ + 18° (*c* 0.6, $CHCl_3$). ^{1}H NMR: δ 7.38–7.16 (m, 5H, aromatic protons), 5.90 (d, 1H, $J = 7.2$ Hz, N*H*$COCH_3$), 5.60 (dd, 1H, $J_{2,3} = 9.7$ Hz, $J_{3,4} = 9.9$ Hz, H-3^D), 5.36 (bs, 1H, C*H*Ph), 5.20 (t, 1H, $J = 9.3$ Hz, H-4^D), 5.19 (d, 1H, $J = 7.2$ Hz, H-1^D), 4.88 (t, 1H, $J = 9.5$ Hz, H-2^C), 4.11 (d, 1H, $J_{3,4} = 3.0$ Hz, H-4^C), 3.72 (dd, 1H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.8$ Hz, H-3^C), 3.30 (bs, 1H, H-5^C), 3.06 (m, 1H, H-5^D), 2.76–2.53 (m, 2H, SCH_2CH_3), 1.98, 1.95, 1.88, 1.86, 1.70 (5 s, 15H, $OCOCH_3$), 1.16 (t, 3H, $J = 7.4$ Hz, SCH_2CH_3); ^{13}C NMR: δ 171.3, 171.0, 170.6, 170.5, 170.1

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(5 $COCH_3$), 138.3–126.8 (aromatic carbons), 101.7 (*C*HPh), 100.0 (C-1^D), 83.3 (C-1^C), 78.3, 76.5, 72.0, 71.1, 70.5, 69.5, 69.4, 68.4 (C-6^C), 62.4 (C-6^D), 57.1 (C-2^D), 23.6 (SCH_2CH_3), 23.2 ($NHCOCH_3$), 21.7, 21.2, 21.1, 21.0 (4 $COCH_3$), 15.2 (SCH_2CH_3). Anal. Calcd for $C_{31}H_{41}O_{14}SN$: C, 54.45; H, 6.04; N, 2.04. Found: C, 54.50; H, 6.16; N, 2.10.

2-(Trimethylsilyl)ethyl 2-*O*-Allyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galacto-pyranoside (10)

To a solution of **9**[14] (2.5 g, 5.45 mmol) in DMF (15 mL) was added NaH (654 mg, 13.6 mmol, 60% oil coated) at 0°C with stirring. After 30 min, allyl bromide (0.7 mL, 8.18 mmol) was added and stirring was continued at room temperature for 7 hr. Excess NaH was decomposed by the addition of MeOH (5 mL). The reaction mixture was then diluted with CH_2Cl_2 and filtered. The organic layer was washed with water, dried (Na_2SO_4) and concentrated. Column chromatography of the syrupy product with 5 : 1 toluene-EtOAc gave pure **10** (2.4 g, 92%); $[\alpha]_D^{25} + 7.7^\circ$ (*c* 0.8, $CHCl_3$); ^{1}H NMR: δ7.38–7.08 (m, 10H, aromatic protons), 5.80 (m, 1H, $CH_2CH{=}CH_2$), 5.31 (s, 1H, C*H*Ph), 5.16–4.97 (m, 2H, $CH_2CH{=}CH_2$), 4.52, 4.46 (2d, 2H, $J = 12.5$ Hz, CH_2Ph), 4.25 (dd, 1H, $J_{5,6} = 5.7$ Hz, $J_{6a,6e} = 12.3$ Hz, H-6_e), 4.16 (d, 1H, $J = 7.8$ Hz, H-1), 4.11 (dd, 1H, $J_{5,6a} = 5.9$ Hz, $J_{6e,6a} = 12.4$ Hz, H-6_a), 3.91 (d, 1H, $J = 3.4$ Hz, H-4), 3.53 (dd, 1H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 3.30 (dd, 1H, $J_{2,3} = 9.6$ Hz, $J_{3,4} = 3.6$ Hz, H-3), 3.12 (bs, 1H, H-5), 3.87–3.80 [m, 2H, $OCH_2CH_2Si(Me)_3$], 0.85 [m, 2H, $OCH_2CH_2Si(CH_3)_3$], −0.15 [s, 9H, $OCH_2CH_2Si(CH_3)_3$]; ^{13}C NMR: δ138.4–126.5 (aromatic carbons), 135.3 ($CH_2CH{=}CH_2$), 116.4 ($CH_2CH{=}CH_2$), 103.1 (C-1), 101.3 (*C*HPh), 78.9, 78.0, 74.1, 73.9, 72.0, 69.1, 67.2 [$OCH_2CH_2Si(CH_3)_3$], 66.2 (C-6), 18.2 [$OCH_2CH_2Si(CH_3)_3$], −1.5 [$OCH_2CH_2Si(CH_3)_3$]. Anal. Calcd for $C_{28}H_{38}O_6Si$: C, 67.44; H, 7.68. Found: C, 67.33; H, 7.56.

2-(Trimethylsilyl)ethyl 2-*O*-Allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (11)

To a solution of **10** (2 g, 4.01 mmol) in dry THF (20 mL) was added $NaCNBH_3$ (2.3 g, 36.1 mmol) at 0°C. A saturated solution of HCl in ethylether was added drop-wise with vigorous stirring till pH came down to about 2–3. The suspension was stirred for 45 min at 0°C, filtered through a Celite bed and washed with CH_2Cl_2. The combined filtrate and washings was washed with aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. Column chromatography of the syrupy product with 5 : 1 toluene-EtOAc gave **11** (1.4 g, 70%);

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$[\alpha]_D^{25}$ − 4.7° (*c* 0.5, $CHCl_3$); ^{1}H NMR: δ7.22–7.09 (m, 10H, aromatic protons), 5.86–5.74 (m, 1H, $CH_2CH{=}CH_2$), 5.16–4.97 (m, 2H, CH_2-$CH{=}CH_2$), 4.56 (s, 2H, CH_2Ph), 4.42 (s, 2H, CH_2Ph), 4.23 (dd, 1H, $J_{5,6e} = 5.7$ Hz, $J_{6a,6e} = 12.3$ Hz, H-6_e), 4.13 (d, 1H, J = 7.5 Hz, H-1), 4.13 (dd, 1H, $J_{5,6a} = 5.7$ Hz, $J_{6e,6a} = 12.3$ Hz, H-6_a), 3.86 (dd, 1H, $J_{1,2} = 7.5$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 3.83 (bs, 1H, H-4), 3.65–3.52 [m, 2H, OCH_2CH_2-$Si(Me)_3$], 3.38 (m, 1H, H-5), 3.27 (dd, 1H, $J_{2,3} = 9.3$ Hz, $J_{3,4} = 3.3$ Hz, H-3), 0.85 [m, 2H, $OCH_2CH_2Si(CH_3)_3$], −0.15 [s, 9H, $OCH_2CH_2Si(CH_3)_3$]; ^{13}C NMR: δ138.6–128.1 (aromatic carbons), 135.8 ($CH_2CH{=}CH_2$), 117.1 ($CH_2CH{=}CH_2$), 103.6 (C-1), 81.0, 79.1, 74.1, 74.4, 73.7, 72.9, 69.7 (C-6), 67.7, 67.4 [$OCH_2CH_2Si(CH_3)_3$], 18.8 [$OCH_2CH_2Si(CH_3)_3$], −0.9 [OCH_2-$CH_2Si(CH_3)_3$]. Anal. Calcd for $C_{28}H_{40}O_6Si$: C, 67.16; H, 8.05. Found: C, 67.33; H, 8.26.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1 → 4)-2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (13)

To a solution of the acceptor **11** (560 mg, 1.12 mmol) and TESOTf (45 μL, 0.20 mmol) in CH_2Cl_2 (5.0 mL) was added 4 Å molecular sieves (300 mg) and the mixture was stirred for 2 hr at −45°C. To this mixture 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α,β-D-mannopyranosyl trichloroacetimidate (**12**) (800 mg, 1.34 mmol) in CH_2Cl_2 (1.0 mL) was added drop-wise and the mixture was allowed to stir for 45 min at that temperature when TLC showed optimum amount of the product. The reaction was quenched with the addition of Et_3N, diluted with CH_2Cl_2 (50 mL), filtered and washed successively with water, sat. $NaHCO_3$ and water. The organic phase was collected, dried (Na_2SO_4) and concentrated. Column chromatography of the residue with 10 : 1 toluene-EtOAc gave pure disaccharide **13** (690 mg, 69%); $[\alpha]_D^{25}$ − 18° (*c* 0.7, $CHCl_3$); ^{1}H NMR: δ7.36–7.04 (m, 25H, aromatic protons), 5.84–5.73 (m, 1H, $CH_2CH{=}CH_2$), 5.42 (s, 1H, $CHPh$), 5.09–4.96 (m, 2H, $CH_2CH{=}CH_2$), 4.90, 4.74 (2d, 2H, CH_2Ph), 4.47 (bs, 1H, H-1^B), 4.37 (d, 1H, $J = 2.2$ Hz, H-4^A), 4.16 (d, 1H, $J = 4.7$ Hz, H-1^A), 3.71–3.64 [m, 2H, $OCH_2CH_2Si(Me)_3$], 3.01 (m, 1H, H-5^B), 0.86 [m, 2H, OCH_2CH_2-$Si(CH_3)_3$], −0.15 [s, 9H, $OCH_2CH_2Si(CH_3)_3$]; ^{13}C NMR: δ138.6–125.9 (aromatic carbons), 135.2 ($OCH_2CH{=}CH_2$), 116.4 ($OCH_2CH{=}CH_2$) 103.2 (C-1^A), 102.3 (C-1^B), 101.2 ($CHPh$), 81.5, 79.2, 78.3, 78.2, 74.3, 73.7, 73.3, 73.3, 71.9, 69.3, 67.5, 67.1 (C-6^A,C-6^B), 18.3 [$OCH_2CH_2Si(CH_3)_3$], −1.5 [$OCH_2CH_2Si(CH_3)_3$]. Anal. Calcd for: $C_{55}H_{66}O_{11}Si$: C, 70.93; H, 7.14; Found: C, 71.02; H, 6.97.

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2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-β-D-mannopyranosyl-(1 → 4)-2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (14)

The benzylidene ring of **13** (500 mg, 0.53 mmol) was regioselectively opened up (as described for compound **11**) to afford pure **14** (340.7 mg, 68%) as a thick syrup; $[\alpha]_D^{25}$ − 27.4° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.30–7.01 (m, 25H, aromatic protons), 5.86–5.76 (m, 1H, CH_2CH═CH_2), 5.16–4.97 (m, 2H, CH_2CH═CH_2), 4.63 (bs, 1H, H-1^B), 4.59 (bs, 2H, CH_2Ph), 4.43, 4.22 (2 d, 2H, CH_2Ph), 4.15 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^A), 3.96 (d, 1H, $J_{2,3}$ = 2.3 Hz, H-2^B), 3.78 (d, 1H, $J_{3,4}$ = 2.9 Hz, H-4^A), 3.80 [m, 2H, $OCH_2CH_2Si(Me)_3$], 3.29 (dd, 1H, $J_{5,6e}$ = 2.9 Hz, $J_{6e,6a}$ = 9.6 Hz, H-6$_e^B$), 3.14 (m, 1H, H-5^B), 2.94 (dd, 1H, $J_{5,6a}$ = 2.9 Hz, $J_{6e,6a}$ = 9.4 Hz, H-6$_a^B$), 2.43 (bs, 1H, 4-OH^B), 0.88 [m, 2H, $OCH_2CH_2Si(CH_3)_3$], −0.15 [s, 9H, $OCH_2CH_2Si(CH_3)_3$]; ^{13}C NMR: δ 139.0–127.4 (aromatic carbons), 135.2 (OCH_2CH═CH_2), 116.6 (OCH_2CH═CH_2), 103.4 (C-1^A), 102.0 (C-1^B), 82.0, 81.8, 79.6, 75.5, 74.0, 73.9, 73.8, 73.6, 73.3, 72.9, 71.2, 70.9, 70.3 (C-6^A), 68.0, 67.4 (C-6^B), 18.6 [$OCH_2CH_2Si(CH_3)_3$], −1.2 [$OCH_2CH_2Si(CH_3)_3$]. Anal. Calcd for: $C_{55}H_{68}O_{11}Si$: C, 70.78; H, 7.34. Found: C, 70.62; H, 7.49.

2-(Trimethylsilyl)ethyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1 → 4)-2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (15)

To a solution of the donor **8** (80 mg, 0.11 mmol) and the acceptor **14** (91 mg, 0.09 mmol) in dry CH_2Cl_2 (3 mL) was added MS 4 Å (100 mg) stirred under N_2 for 2 hr. The mixture was then cooled to −20°C, NIS (34.2 mg, 0.15 mmol) and TfOH (1.5 μL, 0.016 mmol) were added and the mixture was allowed to stir for 1 hr at this temperature. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through a Celite bed. The filtrate was washed successively with 10% $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. Column chromatography of the resulting syrupy product with 3 : 1 toluene-EtOAc gave **15** (112.2 mg, 74%) as a foam, 0.63, $[\alpha]_D^{25}$ − 8.3° (*c* 0.6, $CHCl_3$). ^{1}H NMR: δ 7.27–7.04 (m, 30H, aromatic protons), 5.81 (m, 1H, CH_2CH═CH_2), 5.80 (d, 1H, *J* = 6.6 Hz, N*H*$COCH_3$), 5.47 (s, 1H, C*H*Ph), 5.35 (t, 1H, *J* = 9.7 Hz, H-3^D), 5.15–4.97 (m, 2H, CH_2CH═CH_2), 4.84 (t, 1H, *J* = 9.5 Hz, H-2^C), 4.40 (d, 1H, *J* = 8.9 Hz, H-1^C), 4.15 (d, 1H, *J* = 7.5 Hz, H-1^A), 3.97 (bs, 1H, H-4^C), 3.79 (d, 1H, *J* = 2.4 Hz, H-4^A), 3.29 (dd, 1H, $J_{3,4}$ = 2.6 Hz, $J_{2,3}$ = 9.4 Hz, H-3^A),

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3.17–3.08 (m, 1H, H-5^B), 2.01, 2.00, 1.87, 1.84, 1.78 (5 s, 15H, 5COCH_3), 0.86 [m, 2H, $OCH_2CH_2Si(CH_3)_3$], −0.15 [s, 9H, $OCH_2CH_2Si(CH_3)_3$]; ^{13}C NMR: δ 170.8 (NH*C*OCH_3), 170.5, 170.3, 169.8, 169.4 (4 O*C*OCH_3), 138.4–126.9 (aromatic carbons), 116.5, 103.1 (C-1^A), 101.7 (C-1^C), 101.2 (C*H*Ph), 100.5 (C-1^B), 99.8 (C-1^D), 81.3, 80.6, 79.3, 75.8, 74.4, 73.9, 73.7, 73.6, 73.5, 73.3, 73.3, 73.2, 71.7, 71.3, 71.1, 71.0, 70.2, 68.8, 67.1, 62.0, 61.8, 55.9 (C-2^D), 23.1 (NHCO*C*H_3), 21.0, 20.5, 20.5, 20.4 (4 CO*C*H_3), 18.3 [$OCH_2CH_2Si(CH_3)_3$], −1.5 [$OCH_2CH_2Si(CH_3)_3$]. Anal. Calcd for: $C_{84}H_{103}O_{25}NSi$: C, 64.89; H, 6.67; N, 0.90 Found: C, 64.73; H, 6.52; N, 0.93.

2-(Trimethylsilyl)ethyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-mannopyranosyl-(1 → 4)-β-D-galactopyranoside (16)

To a solution of **15** (106 mg, 0.068 mmol) in methanol (2 mL), $PdCl_2$ (9 mg, 0.05 mmol) was added and the mixture was stirred at rt for 3 hr. The solvent was removed and the product was purified by column chromatography with 1 : 1 toluene-EtOAc. To the purified product, dissolved in EtOH (7 mL), was added 10% Pd/C (100 mg) and the mixture was stirred under H_2 for 72 hr when TLC (EtOAc) showed a single spot. The mixture was then filtered through a Celite bed and the filtrate was concentrated to a thick glass. The product was treated with 0.05 *M* NaOMe in MeOH (3 mL) for 6 hr, decationized with Dowex 50W H^+ resin, filtered and concentrated to dryness to afford **16** (29 mg, 53% overall in 3 steps); $[\alpha]_D$ − 59° (c, 0.9, water). ^{1}H NMR (D_2O) δ 5.10 (d, 1 H, $J = 7$ Hz, H-1^D), 4.59 (bs, 1 H, H-1^B), 4.48 (d, 1 H, $J = 8.1$ Hz, H-1^C), 4.24 (d, 1 H, $J = 7.3$ Hz, H-1^A), 4.10 (H-4^A), 3.88 (1-H, H-2^B), 1.76 (NHCOCH_3), 0.84 (m, 2 H, $OCH_2CH_2SiMe_3$), −0.15 [s, 9 H, $OCH_2CH_2Si(CH_3)_3$]. ^{13}C NMR δ 170.0 (NH*C*OCH_3), 103.5 (C-1^A), 103.0 (C-1^D), 102.6 (C-1^C), 100.8 (C-1^B), 81.5, 80.8, 79.5, 78.1, 75.2, 74.6, 73.4, 73.1, 73.0, 72.6, 71.5, 70.1, 71.0, 68.4, 67.0, 64.0, 63.7, 62.1, 61.4, 56.1 (C-2^D), 21.2 (NHCO*C*H_3), 18.4 [$OCH_2CH_2Si(CH_3)_3$], −1.5 [$OCH_2CH_2Si(CH_3)_3$]. Anal. Calcd for $C_{31}H_{57}O_{21}NSi$: C, 46.09; H, 7.11; N, 1.73. Found: C, 46.25; H, 7.34; N, 1.82.

ACKNOWLEDGMENT

Financial support from the Department of Science and Technology, New Delhi, India (Project No. SP/S1/G14/95) is thankfully acknowledged.

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Received in India September 8, 2003

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