General Procedure for Reaction with Bu_4NF. To a solution of each protected amino acid (0.2 mmol) was added the designated equivalent of Bu_4NF in the same solvent (total 2 mL), and the solution was stirred for 10–30 min (checked by TLC; $CHCl_3$:MeOH = 9:1) at rt. The reaction mixture was diluted with H_2O (2 mL) and benzene–EtOAc (1:1, 20 mL) and extracted with 5% $NaHCO_3$ (3 × 10 mL). The aqueous extract was acidified to pH 3–4 with saturated $KHSO_4$ and extracted with EtOAc (3 × 10 mL). In the case of Boc-Thr-OH (**8b**), the aqueous solution was saturated with NaCl prior to the EtOAc extraction. For Boc-Leu-Pro-OH (**10b**), alkaline extraction was omitted, but the organic layer was washed with 5% $KHSO_4$. The organic extract was washed with H_2O and saturated brine, dried (Na_2SO_4), and evaporated, and the residue was purified by LH-20 (entries 4–6, 12–14) or silica gel (entries 1–3) column chromatography and/or recrystallization (**1b**, **2b**, **4b–8b**). Compounds **1b**, **2b**, and **4b** were converted to their DCHA salts before recrystallization.

GC Analysis. The products (ca. 0.2 mg) obtained from entries 6 (**4b**), 8 (**6b**), 11 (**6b**), and 14 (**6b**) were deprotected by HBr–AcOH before recrystallization, as was **2b** (entry 4), by H_2–Pd/C followed by HCl–dioxane. Each deprotected amino acid was derivatized as its *N*-trifluoroacetyl isopropyl ester and analyzed on Chirasil Val III.[21]

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Abbreviations: All = allyl; Chx = cyclohexyl; DCHA = dicyclohexylamine; Fmoc = [(9-fluorenylmethyl)oxy]carbonyl; KHMDS = potassium hexamethyldisilazide; Nbn = 4-nitrobenzyl; Pac = phenacyl; Ppt = (diphenylphosphino)thioyl; Tce = 2,2,2-trichloroethyl; Teoc = 2-[(trimethylsilyl)ethoxy]carbonyl; Tmse = 2-(trimethylsilyl)ethyl.

Registry No. **1a**, 134757-73-6; **1b**·DCHA, 34404-29-0; **2a**, 42726-92-1; **2b**·DCHA, 13574-84-0; **3a**, 134757-74-7; **3b**, 132286-79-4; **4a**, 27486-72-2; **4b**·DCHA, 23632-70-4; **5a**, 134757-75-8; **5b**, 73821-95-1; **6a**, 10144-64-6; **6b**, 1142-20-7; **7a**, 77163-64-5; **7b**, 13139-15-6; **8a**, 77313-56-5; **8b**, 2592-18-9; **9a**, 67850-37-7; **10a**, 113317-89-8; **10b**, 64205-66-9; **11a**, 6530-41-2; TceOH, 115-20-8; Bu_4NF, 429-41-4; 4-$BrCH_2C_6H_4NO_2$, 100-11-8; $PhCOCH_2Br$, 70-11-1; BOC-Glu-ONbn·DNHC, 30924-92-6; H-Pro-OTce, 126134-58-5.

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C-Heteroarylation of Sugars by Indolylbromomagnesium Salts. Synthesis of 3-(Alditol-1-yl)indoles and Their Cyclization to Indole *C*-Nucleoside Analogues

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Carbon nucleosides as well as glycosides bearing carbon-linked nitrogen heterocycles have elicited numerous synthetic and biological studies[2] due to their potential antiviral and antitumor activities.[3] Recently, we introduced bromomagnesium salts of hydroxylated aromatic

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Table I. Synthesis of D-*manno*- and D-*glycero*-D-*talo*-Indolylalditols 4 and 5

run	indole	sugar	product	yield,[a] %
1	**1a**	**2**	**4a**	65
2	**1b**	**2**	**4b**	80
3	**1a**	**3**	**5**	70

[a] Based on pure isolated compound.

Chart I

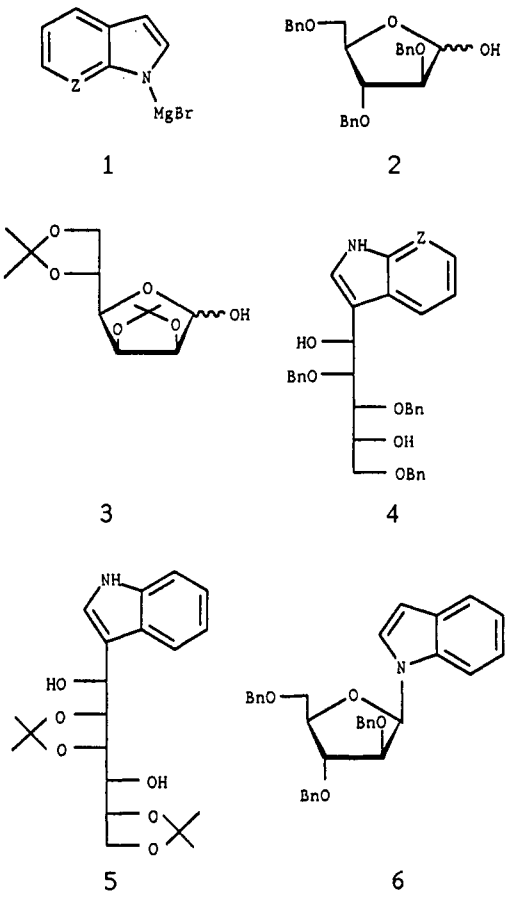

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Table II. Synthesis of α- and β-Indole *C*-Nucleosides 7–10

run	alditol	product	yield,[a] %
1	4a	7a	62
		8a	14
2	4b	7b	87
		8b	12
3	5	9	90
		10	10

[a] Based on pure isolated compound.

compounds as useful arylation reactants in *C*-arylglycoside synthesis and exploited key techniques to introduce a wide range of hydroxylated aromatic aglycons into diverse sugar matrices.[4]

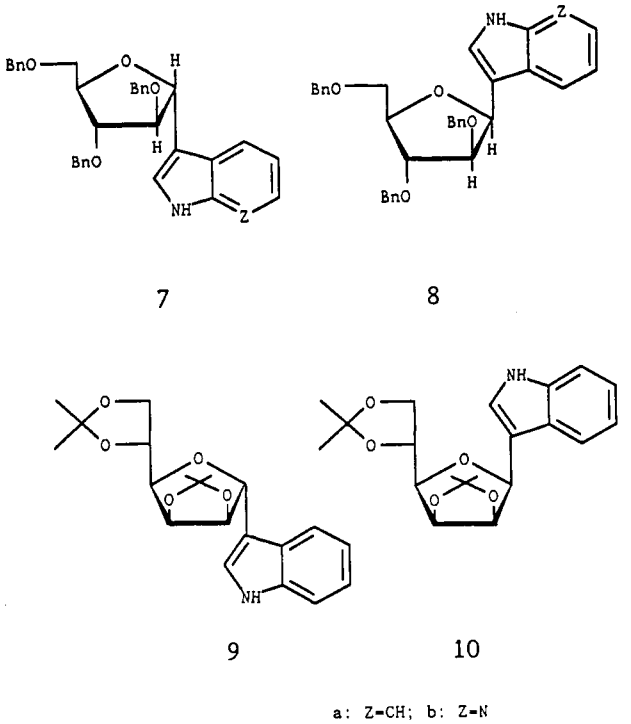
We envisioned that, adapting those findings to heteroaromatics having a free NH function, a novel route to certain *C*-nucleoside analogues could be designed. Herein we describe the synthesis of open-chain 3-(alditol-1-yl)-indole derivatives by starting with indolylbromomagnesium salts and protected furanoses, as well as their acid-catalyzed cyclization into the corresponding *C*-glycosylfuranosides.

The reaction between the bromomagnesium salt of indole **1a**[5] and 2,3,5-tri-*O*-benzyl-D-arabinofuranose **2**[6] was first investigated under varied reaction conditions. The effect of the reaction medium was crucial in determining the regioselectivity of N- vs C(3)-alkylation and the product distribution.[7] While predominant N-alkylation occurred using THF at ambient temperature (**6** to **4a** ratio, 86:14; 75% combined yield), C-alkylation became almost exclusive with CH_2Cl_2,[8] resulting in clean formation of 3-(2,3,5-tri-*O*-benzyl-D-*manno*-pentitol-1-yl)indole (**4a**, 65% yield). Application of the same protocol to 7-azaindole salt **1b**[9] was equally successful, as was the extension to isopropylidene-blocked mannofuranose **3**.[10] Table I summarizes the synthetic results.

Heteroarylalditols **4** and **5** were obtained in all the events as single enantiomerically pure diastereoisomers as ascertained by ^1H and ^{13}C NMR and reverse-phase HPLC. The erythro stereodisposition of the hydroxyl substituents at C1′ and C2′ was evinced by the characterstic $^3J_{1',2'} = 6$ Hz,[11] in line with the preferential anti-selective mechanistic behavior displayed during the opening of α-substituted lactols by aryl and alkyl organometallics.[12]

Having alditols **4** and **5**, we next considered their cyclization into the corresponding indolyl furanosides.[13] The

Chart II



objective was simply reached using a mild protocol consisting of treatment with 1.75 M HCl in CH_2Cl_2 at ambient temperature.[14] Formal dehydration of **4** and **5** was complete within a few minutes, resulting in formation of an anomeric mixture of furanosides, where α-anomers **7** and **9** always predominanted over the β-counterparts **8** and **10**.[15] Table II summarizes the results.

C-Nucleosides **7–10**, obtained in a pure state by flash chromatography over silica gel, were easily distinguished by ^1H NMR spectroscopy, where the H1′ doublet was proven particularly diagnostic. For the given series, α-anomers **7** and **9** invariably displayed a $^3J_{1',2'} > 6$ Hz, compared with a $^3J_{1',2'} < 4$ Hz for β-anomers **8** and **10**. The assignment was further corroborated by 2D NOE experiments at 500 MHz; at this field all signals were well separated and unambiguously assigned. In agreement with analogous observations,[16] the anomeric proton in the α-D-anomers **7** and **9** (1′,2′-trans relationship) correlates to H2′ (<4%) and H5′ while NOEs between H1′ and H2′ (>10%) and between H1′ and H4′ indicate that **8** and **10** are β-D configured (1′,2′-cis).

Experimental Section

General directions and routine apparatus are reported in our previous papers on this and related subjects.[4] 2,3,5-Tri-*O*-benzyl-β-D-arabinofuranose[6] and 2,3:5,6-di-*O*-propylidene-α-D-

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(13) Direct C-ribosylation of nitrogen heterocyclies as 7-deazaguanine and 9-deazaguanine in CH_3NO_2 in the presence of $SnCl_4$ gave rise to β-anomers (1′,2′-trans) exclusively: Girgis, N. S.; Michael, M. A.; Smee, D. F.; Alaghamandan, H. A.; Robins, R. K.; Cottam, H. B. *J. Med. Chem.* **1990**, *33*, 2750.

(14) Trifluoroacetic acid catalyzed cyclization of D-galacto-pentitolylpyrazoles led to D-lyxofuransyl derivatives with strong preference for the α-anomers (1′,2′-trans): Gòmez-Guillén, M.; Hans, F.; Lassaletta, J. M.; Martin, E. *Carbohydr. Res.* **1990**, *201*, 233.

(15) ^1H NMR experiments on pure **7a** show that α/β anomerization do not occur under the reaction conditions (HCl in CD_2Cl_2), while carbinol **4a** is rapidly transormed into cyclization products **7a** and **8a** under the same conditions. The **7a**:**8a** ratio do not change as a function of time.

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mannofuranose[10] were commercial products (Sigma). All sonicated reactions were performed by using a ELMA TRANSONIC-460/H Model ultrasonic cleaner with the reaction vessel completely submerged.

General Procedure for Reaction of Indolylmagnesium Bromides 1 with Furanoses 2 and 3. Synthesis of 3-(Alditol-1-yl)indole Derivatives 4 and 5. To a solution of EtMgBr (6 mmol) in diethyl ether (20 mL) a solution of the appropriate indole (6 mmol) in diethyl ether was added with stirring under nitrogen at room temperature. The ether was removed under vacuum, and then anhydrous methylene chloride (50 mL) was added. The reaction vessel was placed in a sonication bath, and a solution of furanose 2 and 3 (1 mmol) in CH_2Cl_2 (20 mL) was added. After being stirred for 48 h at room temperature, the mixture was quenched with saturated aqueous ammonium chloride solution and extracted with diethyl ether (3 × 30 mL). The combined extracts were dried and concentrated under reduced pressure, and the products were purified by chromatography on silica gel using a hexane/acetone (75:25) mixture. The following compounds were obtained.

3-(2,3,5-Tri-*O*-benzyl-D-*manno*-pentitol-1-yl)indole (4a): colorless oil; $[\alpha]^{21}_D$ = +20.0° (*c* 0.1, $CHCl_3$); ^1H NMR (200 MHz, CD_3OD) δ 7.53 (1 H, d, $J_{6,7}$ = 7.59 Hz, H-7), 7.29 (1 H, d, $J_{4,5}$ = 8.18 Hz, H-4), 7.25–6.85 (17 H, m, CH_2Ph, H-5, and H-6), 5.25 (1 H, d, $J_{1',2'}$ = 6.66 Hz, H-1'), 4.61, 4.37, 4.30 (each 2 H, m, CH_2Ph), 4.23 (1 H, dd, $J_{1',2'}$ = 6.66, $J_{2',3'}$ = 3.50 Hz, H-2'), 3.98 (1 H, m, H-4'), 3.60 (1 H, dd, $J_{2',3'}$ = 3.50, $J_{3',4'}$ = 6.42 Hz, H-3'), 3.58 (1/2 AB quartet, $J_{4',5'a}$ = 6.72, $J_{5'a,5'b}$ = 9.75 Hz, H-5'a), 3.46 (1 H, 1/2 AB quartet, $J_{4',5'b}$ = 5.55, $J_{5',5'}$ = 9.75, H-5'b). Anal. Calcd for $C_{34}H_{35}O_5N$: C, 75.95; H, 6.56; N, 2.61. Found: C, 75.70; H, 6.39; N, 2.57.

3-(2,3,5-Tri-*O*-benzyl-D-*arabino*-pentitol-1-yl)-7-azaindole (4b): colorless oil; $[\alpha]^{21}_D$ = +16.8° (*c* 0.33, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 10.02 (1 H, bs, NH), 8.20 (1 H, dd, $J_{5,6}$ = 4.96, $J_{6,4}$ = 1.15 Hz, H-6), 7.86 (1 H, dd, $J_{4,5}$ = 7.88, $J_{5,6}$ = 4.69 Hz, H-4), 7.70–7.05 (15 H, m, CH_2Ph), 6.95 (1 H, dd, $J_{4,5}$ = 7.88, $J_{5,6}$ = 4.96 Hz, H-5), 6.86 (1 H, s, H-2), 5.25 (1 H, d, $J_{1',2'}$ = 5.85 Hz, H-1'), 4.95–4.40 (6 H, m, CH_2Ph), 4.20 (2 H, m, H-3' and H-4'), 3.75 (3 H, m, H-2' and H-5'), 3.35 (2 H, bs, OH). Anal. Calcd for $C_{33}H_{34}O_5N_2$: C, 73.58; H, 6.36; N, 5.20. Found: C, 73.46; H, 6.33; N, 5.24.

3-(2,3:5,6-Di-*O*-isopropylidene-D-*glycerol*-D-*talo*-hexitol-1-yl)indole (5): pale yellow oil; $[\alpha]^{21}_D$ = +15.5° (*c* 0.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 8.33 (1 H, s, NH), 7.68 (1 H, d, $J_{6,7}$ = 7.59 Hz, H-7), 7.45–7.05 (3 H, m, H-6, H-5, H-4), 7.02 (1 H, s, H-2), 5.43 (1 H, d, $J_{1',2'}$ = 7.00 Hz, H-1'), 4.71 (1 H, t, $J_{3',4'}$ = $J_{4',5'}$ = 6.71 Hz, H-4'), 4.37 (1 H, d, $J_{3',4'}$ = 6.71 Hz, H-3'), 4.06 (3 H, m, H-5' and H-6'), 4.00 (1 H, dd, $J_{1',2'}$ = 7.00, $J_{2',3'}$ = 6.71 Hz, H-2'), 3.45, 3.23 (each 1 H, 2 bs, OH), 1.48, 1.35, 1.32, 1.28 (each 3 H, 4 s, CH_3). Anal. Calcd for $C_{20}H_{27}O_6N$: C, 63.60; H, 7.21; N, 3.71. Found: C, 63.71, H, 7.18; N, 3.68.

General Cyclization Procedure. Synthesis of (*C*-Glycofuranosyl)indole Derivatives 7–10. To a solution of the appropriate alditol (1 mmol) in CH_2Cl_2 (5 mL) was added 200 μL of a 1.75 M solution of HCl in CH_2Cl_2 at room temperature. After 30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. After removal of the solvent, the anomeric furanosides were separated by silica gel chromatography using petroleum ether/acetone (5:1) or CH_2Cl_2 eluants. The following compounds were obtained.

3-(2,3,5-Tri-*O*-benzyl-α-D-arabinofuranosyl)indole (7a): colorless oil; $[\alpha]^{21}_D$ = −27.0° (*c* 0.5, $CHCl_3$); ^1H NMR (270 MHz, CD_3OD) δ 7.67 (1 H, d, $J_{7,6}$ = 7.02 Hz, H-7), 7.38 (1 H, d, $J_{4,5}$ = 7.83 Hz, H-4), 7.35–7.15 (16 H, m, CH_2Ar and H-2), 7.12 (1 H, dd, $J_{5,6}$ = 7.56 Hz, $J_{4,5}$ = 7.83 Hz, H-5), 6.99 (1 H, t, $J_{5,6}$ = $J_{6,7}$ = 7.83 Hz, H-6), 5.23 (1 H, d, $J_{1',2'}$ = 6.73 Hz, H-1') 4.58 (4 H, m, CH_2Ar), 4.50 (1 H, dd, $J_{1',2'}$ = 6.73, $J_{2',3'}$ = 4.05 Hz, H-2'), 4.40 (2 H, m, CH_2Ar), 4.28 (1 H, dd, $J_{3',4'}$ = 4.86, $J_{4',5'}$ = 5.40 Hz, H-4'), 4.21 (1 H, t, $J_{2',3'}$ = $J_{3',4'}$ = 4.86 Hz, H-3'), 3.67 (2 H, m, H-5'); ^{13}C NMR (25.4 MHz, CD_3OD), DEPT sequence, CH_2 δ 71.17, 72.68, 72.94, 74.27, CH δ 80.19, 82.37, 86.22, 89.04, 112.48, 120.15, 120.40, 122.74, 124.62, Cq δ 112.16, 138.45, 139.32. Anal. Calcd for $C_{34}H_{33}O_4N$: C, 78.59; H, 6.40; N, 2.70. Found: C, 78.61; H, 6.38; N, 2.72.

3-(2,3,5-Tri-*O*-benzyl-β-D-arabinofuranosyl)indole (8a): colorless oil; $[\alpha]^{23}_D$ = +14.2° (*c* 0.1, $CHCl_3$); ^1H NMR (270 MHz, CD_3OD) δ 7.62 (1 H, d, $J_{7,6}$ = 7.56 Hz, H-7), 7.34 (1 H, d, $J_{4,5}$ = 8.37 Hz, H-4), 7.32–7.15 (16 H, m, CH_2Ph and H-2), 7.14 (1 H, m, H-5), 6.97 (1 H, t, J = 7.02, H-6), 5.36 (1 H, d, $J_{1',2'}$ = 3.78 Hz, H-1') 4.56 (4 H, m, CH_2Ph), 4.52 (2 H, m, CH_2Ph), 4.12 (1 H, m, H-4'), 4.06 (2 H, m, H-2' and H-3'), 3.72 (1 H, 33, $J_{4',5'a}$ = 6.48, $J_{5'a,5'b}$ = 10.77 Hz, H-5'a), 3.65 (1 H, dd, $J_{4',5'b}$ = 5.86, $J_{5'a,5'b}$ = 10.77 Hz, H-5'b); ^{13}C NMR (25.4 MHz, CD_3OD) DEPT sequence, CH_2 δ 71.59, 72.57, 72.90, 74.32, CH δ 79.42, 83.16, 85.15, 86.22, 114.69, 120.75, 122.39, 125.48, Cq 111.22, 139.14, 139.48. Anal. Calcd for $C_{34}H_{33}O_4N$: C, 78.59; H, 6.40; N, 2.70. Found: C, 78.49; H, 6.43; N, 2.63.

3-(2,3,5-Tri-*O*-benzyl-α-D-arabinofuranosyl)-7-azaindole (7b): colorless oil; $[\alpha]^{23}_D$ = +60.3° (*c* 0.1, MeOH); ^1H NMR (200 MHz, CD_3OD) δ 8.07 (1 H, dd, $J_{5,6}$ = 7.90, $J_{4,6}$ = 1.46 Hz, H-6), 7.7–6.7 (18 H, m, CH_2Ph and 3 H arom), 5.18 (1 H, d, $J_{1',2'}$ = 5.84 Hz, H-1'), 4.63 (4 H, m, CH_2Ph), 4.54 (1 H, dd, $J_{1',2'}$ = 5.84, $J_{2',3'}$ = 3.63 Hz, H-2'), 4.35 (3 H, m, CH_2Ph), 4.23 (1 H, dd, $J_{2',3'}$ = 3.63, $J_{3',4'}$ = 6.72 Hz, H-3'), 3.67 (2 H, m, H-5'). Anal. Calcd for $C_{33}H_{32}O_4N_2$: C, 76.13; H, 6.20; N, 5.38. Found: C, 76.16; H, 6.16; N, 5.41.

3-(2,3,5-Tri-*O*-benzyl-β-D-arabinofuranosyl)-7-azaindole (8b): colorless oil; $[\alpha]^{23}_D$ = +32.0° (*c* 0.1, MeOH); ^1H NMR (200 MHz, CD_3OD) δ 7.97 (1 H, dd, $J_{5,6}$ = 7.90, $J_{4,6}$ = 1.32 Hz, H-6), 7.5–6.5 (18 H, m, CH_2Ph and 3 H arom), 5.31 (1 H, d, $J_{1',2'}$ = 3.21 Hz, H-1'), 4.44 (4 H, m, CH_2Ph), 4.28 (2 H, m, CH_2Ph), 4.22 (1 H, m, H-4'), 4.15 (2 H, m, H-2' and H-3'), 3.62 (2 H, m, H-5'). Anal. Calcd for $C_{33}H_{32}O_4N_2$: C, 76.13; H, 6.20; N, 5.38. Found: C, 76.17; H, 6.26; N, 5.42.

3-(2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl)indole (9): colorless oil; $[\alpha]^{21}_D$ = +69.2° (*c* 0.2, MeOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.31 (1 H, bs, NH), 7.78 (1 H, d, $J_{6,7}$ = 7.88 Hz, H-7), 7.36 (1 H, d, $J_{4,5}$ = 7.88, H-4), 7.17 (2 H, m, H-5 and H-6), 7.04 (1 H, bs, H-2), 5.48 (1 H, d, $J_{1',2'}$ = 0.77 Hz, H-1'), 5.14 (1 H, dd, $J_{1',2'}$ = 0.77 Hz, $J_{2',3'}$ = 6.13 Hz, H-2'), 4.81 (1 H, dd, $J_{2',3'}$ = 6.13 Hz, $J_{3',4'}$ = 3.79 Hz, H-3'), 4.49 (1 H ddd, $J_{4',5'}$ = 6.13, $J_{5',6'a}$ = 4.96 Hz, $J_{5',6'b}$ = 8.46 Hz, H-5'), 4.11 (2 H, 2 AB quartets, $J_{6'a,6'b}$ = 9.63, $J_{5',6'a}$ = 4.96, $J_{5',6'b}$ = 8.46 Hz, H-6'), 3.86 (1 H, dd, $J_{3',4'}$ = 3.79, $J_{4',5'}$ = 6.13 Hz, H-4'); ^{13}C NMR (25.4 MHz, $CDCl_3$), DEPT sequence, CH_3 δ 24.80, 25.23, 26.23, 26.96, CH_2 67.19, CH δ 73.52, 80.76, 80.67, 81.21, 85.33 (5CH), 111.32, 119.72, 120.09, 121.23, 122.70, Cq 112.71, 113.75. Anal. Calcd for $C_{20}H_{25}O_5N$: C, 66.83; H, 7.01; N, 3.90. Found: C, 66.78; H, 7.09; N, 3.86.

3-(2,3:5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl)indole (10): colorless oil; $[\alpha]^{21}_D$ = +46.4° (*c* 0.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 8.16 (1 H, bs, NH), 7.66 (1 H, d, $J_{6,7}$ = 7.29 Hz, H-7), 7.45–7.00 (4 H, m, H-2, H-4, H-5, and H-6), 5.00–4.85 (3 H, H-1', H-2' and H-4'), 4.53 (1 H, m, H-5'), 4.14 (1 H, m, H-6'), 3.68 (1 H, dd, J = 3.21, J = 4.96 Hz, H-3'), 1.53, 1.48, 1.40, 1.34 (each 3 H, 4 s, CH_3); ^{13}C NMR (25.4 MHz, $CDCl_3$), DEPT sequence, CH_3 δ 24.40, 24.82, 25.37, 25.88, CH_2 67.29, CH 73.33, 77.90, 80.69, 81.54, 82.33, 111.22, 119.48, 119.80, 122.22, 124.27, Cq 109.21, 112.36, 135.90. Anal. Calcd for $C_{20}H_{25}NO_5$: C, 66.83; H, 7.01; N, 3.90. Found: C, 66.75; H, 6.98; N, 3.94.

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Synthesis of 2-Deoxy Sugars from Glycals†

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2-Deoxy sugars are present in numerous biologically active natural products such as compactin, olivimycin, mithramycin, daunomycin, calicheamicin, etc. The chemical synthesis of these natural products requires the ready

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