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Chiral Liquid Crystalline Compounds From D-(+)-Glucose[1a]

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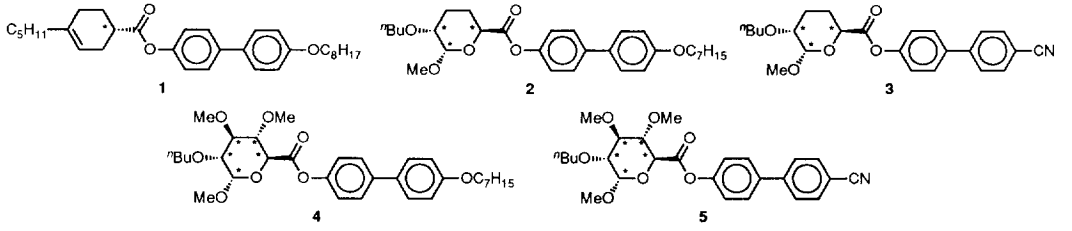
Abstract : D-(+)-Glucose was used as a starting material to prepare four potentially useful chiral liquid crystalline molecules **2**, **3**, **4** and **5** having multiple chiral centers in their rigid cores. It is clear that **2** indeed incorporates properties essential for ferroelectric liquid crystals, i.e., a chiral smectic C phase with an induced spontaneous polarization of about 23 nC/cm^2. Compound **3**, on the other hand, shows only a nematic phase, while **4** merely shows a sharp melting point and **5** is an oil.

INTRODUCTION

Optically active liquid crystalline compounds are widely applied in electronic devices, and indeed, such mesogenic molecules with a chiral smectic C (S_c*) phase have received particular attention due to their role in bi-stable, fast-switching surface stabilized ferroelectric liquid crystal (SSFLC) displays.[2] Many potentially useful compounds have been prepared in this research domain.[3-16] In this connection, the realization of liquid crystals containing a cyclohexene ring in their rigid core was reported recently by us.[17] Compound **1**, for example, has a very rich phase behavior, and there is a S_c* phase from 123.4 to 133°C.[17] However, the spontaneous polarization (P_s) of **1** was determined to be only -0.53 nC/cm^2. The reason for such a small P_s for **1** is likely due to the identical nature of the methylene groups immediately adjacent to its chiral center.



Carbohydrates are significant as a source of chiral mesogens, since practically every conversion of a carbohydrate moiety containing one or two alkyl attachment longer than C_7H_{14} has resulted in the observation of mesogenic properties.[18] The most straightforward alkoxy substitution are at C-1 or C-6 of a pyranose sugar or the termini of an acyclic sugar. Many other alternative sites are possible, for example, an alkyl chain can be substituted selectively at any one of the hydroxyl groups of the pyranose sugar.[18] Considering the fact that sugars are usually inexpensive and are from "renewable resources",[19] it is doubtless that the number of

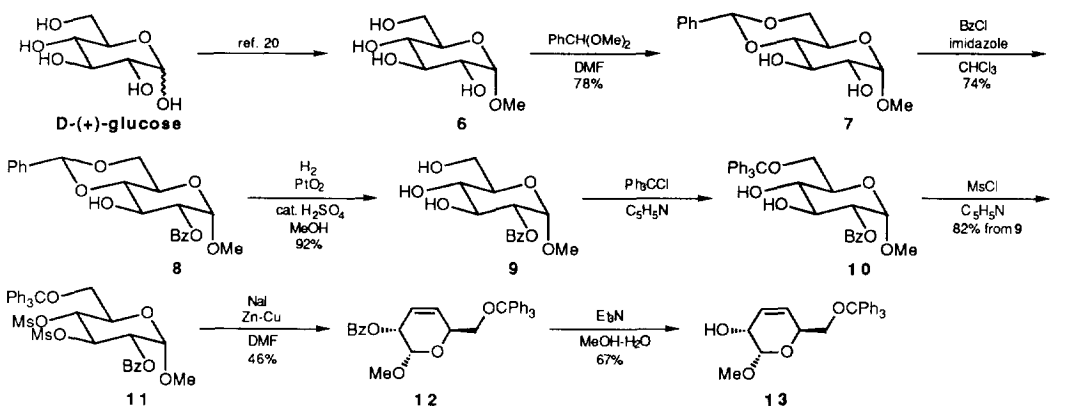
mesogens realized from carbohydrates will continue to increase.

In order to qualify a chiral liquid crystal as optical devices, it is necessary to maximize its mesophase chirality or magnetic polarizability. To achieve this goal, it is paramount to reduce the structural similarity of the two groups directly attached to the chiral carbon. In this paper, we wish to describe the synthesis of four potentially functional chiral liquid crystals **2**, **3**, **4** and **5**, utilizing D-(+)-glucose as a starting material. Despite their molecular similarity, we reason that the P_s of **2**, **3**, **4** and **5** should be higher than that of **1** because of the asymmetric nature of the two structural units next to their respective chiral centers. The carbon-oxygen bonds in these compounds would show a much larger dipole moment than that of the vicinal carbon-carbon bonds, and as a result would lead to a sizable overall dipole moment.

RESULTS AND DISCUSSION

(a) Synthesis of 4',4''-heptoxybiphenyl-(methyl 2-*O*-*n*-butyl-3,4-dideoxy-α-D-glucopyranosid)uronate (2) and 4',4''-cyanobiphenyl-(methyl 2-*O*-*n*-butyl-3,4-dideoxy-α-D-glucopyranosid)uronate (3).

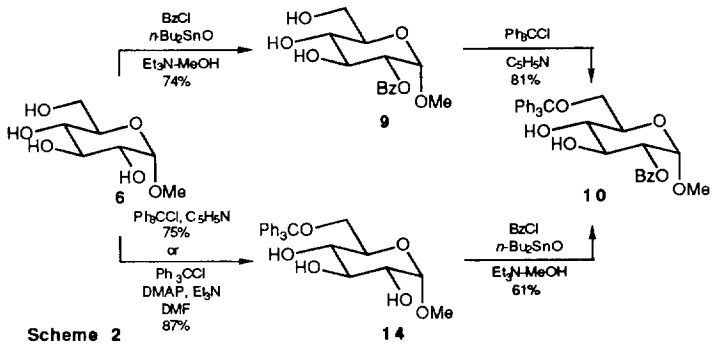
Our synthesis of **2** and **3** were elaborated from naturally occurring D-(+)-glucose. As depicted in Scheme 1, methyl α-D-glucopyranoside (**6**), which is available commercially, or can be obtained conveniently from D-(+)-glucose,[20] was converted to the 4,6-*O*-benzylidene **7** utilizing a procedure described by Evans.[21] The selective 2-*O*-benzoylation[22] of **7** developed by Carey and Hodgson[23] then paved the way to our key intermediate **8**, which, upon hydrogenolysis in the presence of Adams' catalyst and a few drops of sulfuric acid, was deprotected to yield **9**.[24] The primary hydroxyl group of **9** was again selectively protected to provide the trityl ether **10**.[24] An excess of mesyl chloride in pyridine then converted **10** to the bis-mesylate **11**,[24] which was subjected to elimination with NaI and Zn-Cu couple to give **12**, albeit in a rather disappointing yield.[24] Debenzoylation of **12** was effected with the MeOH-H_2O-Et_3N system and as a result furnished **13** as colorless crystals, whose structure is substantiated by its melting range, specific rotation and ^{1}H-NMR spectrometry, as compared with those reported in the literature.[24]



Scheme 1

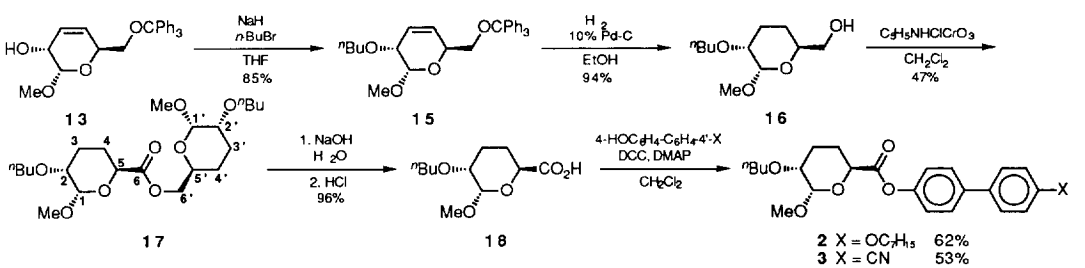
Other shorter pathways in which **11** could be obtained are outlined in Scheme 2. As can be seen, the acetal **6** was converted via a one step patent procedure[25] to furnish **9**. It is believed that by formation of a di-*n*-butylstannylene derivative, a regioselective activation of the C-2 secondary hydroxyl group was accomplished in the presence of other hydroxyl groups. Eventually, the primary hydroxyl group of **9** was selectively

protected as trityl ether **10**, and was used subsequently in our program for the synthesis of **2**, **3**, **4** and **5**. Alternatively, **6** could be protected as **14**, which was further transformed into **10** (Scheme 2).



Scheme 2

The synthetic route towards our target molecules **2** and **3** is summarized in Scheme 3. With **13** in hand, the butyl ether **15** was obtained in excellent yield by reaction of **13** with *n*-butyl bromide in the presence of sodium hydride.[17] In the ^{1}H-NMR of **15**, the proton absorptions of its *n*-butyl group appear at δ 0.91 (t, J = 7.4 Hz, 3H), 1.32-1.41 (m, 2H), 1.50-1.67 (m, 2H) and 3.50-3.60 (m, 2H). The molecular composition of **15** is also confirmed by FABMS which shows its M^+-1 at *m/e* 457, as well as by an elemental analysis. Catalytic hydrogenation of the double bond in **15**, and concomitant hydrogenolysis[26] of the trityl group afforded the saturated alcohol **16**, which was expected to undergo a smooth oxidation reaction to yield the corresponding acid. However, all attempts to oxidize **16** directly to an acid have so far been unsuccessful. After some experimentations, it was found that an ester **17** was instead formed when **16** was allowed to react with PCC[27] at room temperature for 18 hours.[28] The reason for this unexpected result is likely because of the condensation between the unreacted alcohol **16** and its corresponding aldehyde to deliver an acetal which was further oxidized *in situ* to form ester **17**. The ^{1}H-NMR spectrum of **17** is very complicated, showing the signal of H-5 as only a doublet at δ 4.20-4.35 (J_{aa} = 10.3 Hz, $J_{ae} \cong$ 0 Hz), and H-5' absorbs at δ 3.78-3.95 as an unresolvable multiplet. The structure of **17** is nevertheless verified by its ^{13}C-NMR spectrum which reveals 19 signals with an ester C-6 absorption at 170.91 ppm, as well as by its EIMS at *m/e* 431 (M^+-1) and its elemental analysis. Straightforward saponification of **17** generated in good yield our initial target acid **18**, together with alcohol **16**, which can be recycled. The structure of **18** was established by CIMS which gives M^+-1 at *m/e* 231, as well as by ^{1}H-NMR spectrometry which shows a doublet of doublets for H-5 at δ 4.30-4.40 (J_{ae} = 3.0 Hz, J_{aa} = 11.6 Hz), a doublet for H-1 at δ 4.90 (J_{ae} = 3.2 Hz) and a broad singlet for the carboxylic proton at δ 10.73.

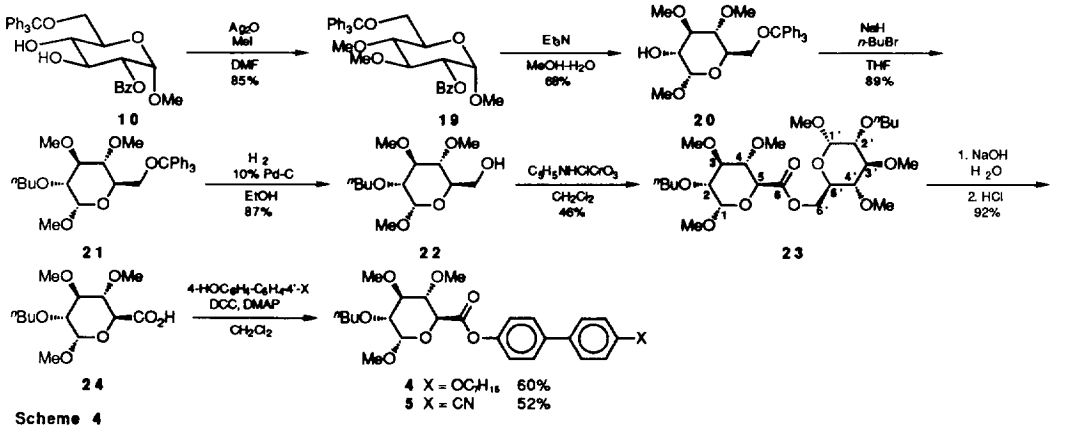


Scheme 3

Now we were left with the relatively easy task to convert acid **18** to the corresponding esters **2** and **3**. As shown in Scheme 3, by using a DMAP-catalyzed DCC dehydration method,[17] **16** and 4-hydroxy-4'-heptoxybiphenyl[29] gave the desired **2** as colorless microcrystalline solids. Using 4-hydroxy-4'-cyanobiphenyl, **3** was also obtained as needle-shaped crystals. The structures of **2** and **3** are supported by NMR spectrometric methods. In the ^{1}H-NMR spectrum of **2**, the doublet of doublets absorption at δ 4.52-4.61 is assigned to the axial proton at C-5 (J_{ae} = 2.7 Hz, J_{aa} = 11.5 Hz). The signal at δ 4.95 is due to the C-1 equatorial proton, which manifests a coupling constant of 2.7 Hz with the axial proton at C-2. The ^{13}C-NMR spectrum shows a quaternary C-6 signal at δ 170.69. The molecular formula of **2** is also confirmed by the EIMS, which reveals M^+ at *m/e* 498, as well as by an elemental analysis. The structure of **3** is substantiated likewise by ^{1}H-NMR and ^{13}C-NMR spectra, as well as by the EIMS which exhibits M^++1 at *m/e* 410.

(b) Synthesis of 4',4''-heptoxybiphenyl-(methyl 2-*O*-*n*-butyl-3,4-di-*O*-methyl-α-D-glucopyranosid)uronate (4) and 4',4''-cyanobiphenyl-(methyl 2-*O*-*n*-butyl-3,4-di-*O*-methyl-α-D-glucopyranosid)uronate (5).

The silver-assisted methylation[30] expectedly transformed diol **10** to methyl ether **19** as demonstrated in Scheme 4. The presence of the three methoxy groups in **19** is evident from the three 3-proton singlets (δ 3.31, 3.39 and 3.58) displayed in its ^{1}H-NMR spectrum. Additional structural proof of **19** was given by the FABMS, showing M^++1 at *m/e* 569 and M^++Na at *m/e* 591, as well as by an elemental analysis. A very mild debenzoylation of **19** with Et_3N in aqueous MeOH[22] provided alcohol **20**, from which the *n*-butyl ether **21** was prepared.[17] Deprotection of **21** by hydrogenolysis[26] in the presence of 10% Pd-C afforded the primary alcohol **22**. Similar to the oxidation of **16**, treatment of **22** with PCC[28] furnished ester **23**, whose molecular composition is certified by its CIMS (M^+-1 *m/e* 551) and its elemental analysis. The structure of **23** is also supported by a total number of 22 absorptions in the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum of **23** is rather complex, showing the C-5 axial proton absorption at δ 4.06 as a doublet (J_{aa} = 9.7 Hz), as well as the C-1 and C-1' equatorial proton absorptions at δ 4.74 and 4.79 as doublets with both J_{ae} equal to 3.5 Hz.



Scheme 4

The desired acid **24** was obtained through saponification of **23**, from which alcohol **22** was also generated for subsequent recycling. The doublet at δ 4.10 and its J_{aa} of 10.0 Hz in the ^{1}H-NMR spectrum of **24** is due to H-5, while the doublet at δ 4.84 with J_{ae} of 3.5 Hz and the broad signal at δ 7.41 are assigned to

H-1 and the carboxylic acid protons, respectively. Finally, by using the procedure described previoulsly,[17] acid **24** was converted to the target molecules **4** as colorless microcrystalline solids which melted between 60℃ and 62℃ without showing mesomorphic phases, and **5** was similarly obtained as a colorless oil. The structures of **4** and **5** are confirmed by ^{1}H-NMR and ^{13}C-NMR spectrometric methods, which include all the pertinent signals due to acid **24**, plus additional signals due to the biphenyl units. Further structural confirmation of **4** and **5** was provided by their EIMS, which display M^++1 at *m/e* 558 and 470, respectively.

(c) Mesomorphic phases and transition temperatures of chiral liquid crystals 2.

As mentioned in the last Section, molecules **4** and **5** do not exhibit liquid crystalline characters. Compound **3**, on the other hand, displays only a monotropic N* phase, and its characterization will be reported elsewhere. In this Section, only the mesomorphic phases and transition temperatures of **2** will be discussed.

1. Mesomorphic properties

The phase assignments and corresponding transition temperatures were determined both by thermal optical microscopy (Mettler FP5) and by differential scanning calorimetry (Perkin-Elmer DSC7). The liquid crystal transition temperatures and enthalpies for **2** are given below, where 1.1 J/g is the sum of the transition enthalpies of S_c*-TGB_c and TGB_c-N* and 1.8 J/g is the sum of the transition enthalpies of N*-BP and BP-I.

K	54	S_c*	77	TGB_c	77.2	N*	95.5	BP	96.5	I	(℃)
	30			1.1				1.8			(J/g)

On cooling from the isotropic phase of **2**, one could observe the blue phase with an iridescent platelet defect texture and on further cooling from this blue phase, the cholesteric phase appeared with focal conic or Grandjean plane textures. On further slow cooling from the cholesteric phase, the N*-TGB_c transition occurred and the TGB_c[31,32] phase was characterized by another Grandjean plane texture. At lower temperature, the S_c* phase was obtained with striated fan shaped texture or pseudohomeotropic texture.

2. Helical pitch measurements

The helical pitch has been measured by a method previously reported[31-35] on weak angle (< 0.25°) prismatic samples oriented in the Grandjean-Cano texture. A planar alignment is necessary in the cholesteric N* and TGB_c phases, whereas a coplanar (i.e. pseudohomeotropic) one is needed in the S_c* phase. The results are reported in Figure 1. The pitch variations in the N* and TGB_c phases are commented below.

In the N* phase the pitch is very short: lower than 0.2 μm at high temperature, giving selective reflexion of light in the UV range. It regularly augments on cooling: 0.24 μm at 85℃, it reaches 0.41 μm at 77.2℃, the reflected colors varying from violet to red. An important discontinuity of the pitch occurs then at the N*-TGB_c transition (from 0.41 μm to 0.78 μm). In the TGB_c phase, the pitch is rather large and diverges at the approach of the S_c* phase; the maximum value was measured to be 3.6 μm.

Such variations, especially the discontinuity, have been observed in other systems[34-36] and are characteristic of the phase sequences S_c*-TGB_c-N*. The photographs (Figure 2a,b,c) illustrate the main points. The short pitch of the N* phase gives narrow Grandjean-Cano steps (a); they break out at the N*-TGB_c transition because of the discontinuity of the pitch (b), a new system of large Grandjean-Cano steps is formed in the large pitch TGB_c phase (c).

3. Electrooptical studies

We have studied the electrooptical properties of **2** in the surface stabilized ferroelectric liquid crystal configuration[2] including the temperature dependence of the response time, polarization and tilt angle. The liquid crystal was confined between two ITO coated glass slides, the active area is 0.25 cm^2. To achieve a planar alignment the glasses were covered with a rubbed polyamide layer. the thickness of the cell used 5 μm

Figure 1 : Helical pitch variations versus temperature

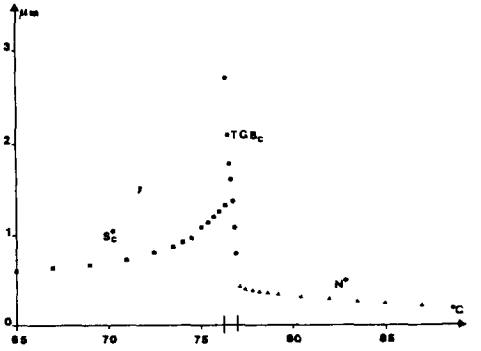


Figure 3 : Spontaneous Polarization versus temperature (V = 40 v; N = 100 Hz)

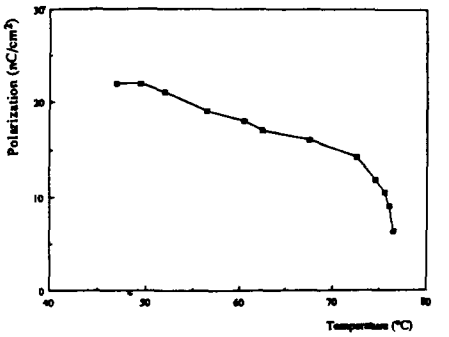


Figure 2 : Grandjean-Cano steps in planar prismatic samples : (a) N* phase, 77.4°C. (b) N*-TGB$_c$ transition, 77.2°C. (c) TGB$_c$ phase, 77°C

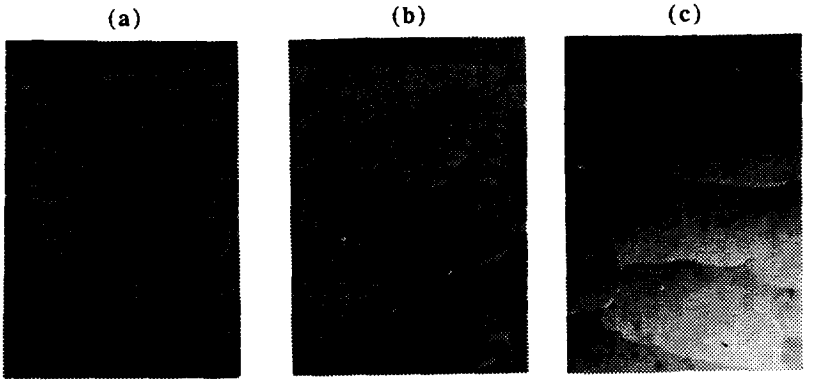


Figure 4 : Response time versus temperature (V = 40 v; N = 100 Hz)

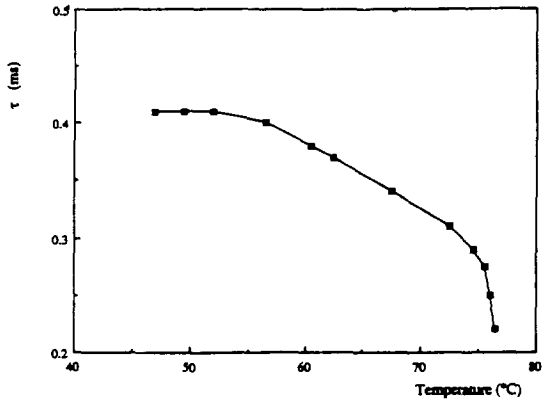
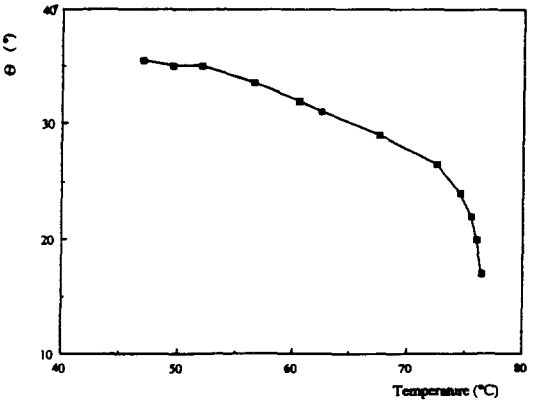


Figure 5 : Tilt angle versus temperature (V = 40 v; N = 0.2 Hz)



(purchased from Linkam L.T.D.). The alignment was improved by very slow cooling through the isotropic to N* transition. All measurements were achieved in the smectic C* phase range.

3.1 - Polarization at saturation versus temperature:

The spontaneous polarization is calculated by integration of switching current under a rectangular ac field at 100 Hz. The field value is 8 V/μm, such a field is sufficient to unwind the helical structure. Figure 3 shows a continuous variation of the polarization from 7 nC/cm^2 to the saturation at 23 nC/cm^2.

3.2 - Electric response time:

This time is defined as the time between field reversion and the maximum of the polarization peak. This measurement is realized at the same time as polarization determination. Obviously the electric response time decreases by increasing temperature from 0.22 to 0.31 ms (Figure 4).

3.3 - Tilt angle:

The apparent tilt angle Θ of molecules from the smectic layer normal was calculated from the difference between extinction positions of the sample between crossed polarizers under rectangular ac field (4 V/μm) at very low frequency (0.2 Hz). The accuracy of the measurement was estimated at ±1°. Figure 5 shows the variation of the tilt angle to the saturation at 34°.

EXPERIMENTAL SECTION

All reagents and solvents used were reagent grade. Further purification and drying by standard procedures[38] were employed when necessary. Optical rotations were taken on an ATAGO polarimeter with a 2-dm cell at 589 nm. NMR spectra were recorded on either a Bruker Cryospec WM 250 spectrometer or a Bruker ARX 500 spectrometer. ^{1}H-NMR (250.13 MHz or 500.13 MHz) and ^{13}C NMR (62.89 MHz or 125.76 MHz) chemical shifts are reported as parts per million (ppm) in δ units on the scale downfield from tetramethylsilane (TMS) or relative to the resonance of chloroform solvent (7.26 ppm in the ^{1}H mode, 77.00 ppm for the central line of the triplet in the ^{13}C mode, respectively). Coupling constants are reported in Hz. NMR spectrometric terms are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra (EIMS, CIMS, FABMS) were recorded on a HP5989A mass spectrometer and determined at an ionizing voltage of 70 eV, relevant data are tabulated as *m/e*. Both mass spectra and elemental analyses were carried out at Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, China. Unless stated otherwise, all reactions were carried out in oven-dried glassware. All solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using hexanes/EtOAc as the eluent unless specified otherwise. Merck silica gel (60 F_{254}) precoated on aluminum sheet was used for TLC studies and Merck silica gel (230-400 mesh) was used for column chromatography. Melting points were measured on a Reichert microscope apparatus and are uncorrected.

Methyl 4,6-*O*-Benzylidene-α-D-glucopyranoside (7).[21,24] A solution of methyl α-D-glucopyranoside (**6**)[20] (97 g, 0.5 mol), α,α-dimethoxytoluene (76 mL, 0.5 mol) and *p*-toluenesulfonic acid (10 g, 52.6 mmol) in dry DMF (400 mL) was refluxed on a steam bath under water-aspirator produced vacuum for 1 h. The solvent was removed from the reaction mixture and the final traces of DMF were evaporated under reduced pressure. The colorless crystalline residue was heated with sat. aq. $NaHCO_3$ solution (450 mL) at 90°C until the product was finely dispersed. The mixture was cooled to r.t. and the solids filtered off, washed thoroughly with water (8 x 140 mL), hexanes (3 x 100 mL). The solids were dried at normal pressure for 12 h, and then under high vacuum at 70°C for 16 h to give **7** as colorless crystalline solids (110 g, 78%), mp 164-165°C (lit.[21] mp 168-169°C); $[\alpha]_D^{23}$ +107° (*c* 2.1, EtOAc) {lit.[21] $[\alpha]_D$ +105° (*c* 1.1, $CHCl_3$)}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.48 (br. s, 1H, OH), 3.02 (br. s, 1H, OH), 3.47 (m, 4H, OCH_3 and H_{3a}), 3.55-3.68 (br. s, 1H, H_{5a}), 3.68-3.98 (m, 2H, H_6), 3.90 (t, *J* = 9.2 Hz, 1H, H_{4a}), 4.28 (dd, J = 3.5, 9.0 Hz, 1H, H_{2a}), 4.76 (d,

J = 3.5 Hz, 1H, H_{1e}), 5.51 (s, 1H, CHAr), 7.30-7.42 (m, 3H, ArH), 7.42-7.55 (m, 2H, ArH).

Methyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (8).[23] To a solution of imidazole (13.6 g, 0.2 mol) in $CHCl_3$ (150 mL) was added slowly benzoyl chloride (14.1 g, 12 mL, 0.1 mol) at 0℃. The suspension was stirred for a further 15 min at r.t. and filtered. The filtrate was added dropwise to a solution of **7** (28.7 g, 0.1 mol) in $CHCl_3$ (200 mL) at 0℃. After heating at reflux for 16 h, the reaction mixture was washed with sat. aq. $NaHCO_3$ solution (50 mL), brine (2 x 50 mL), dried over $MgSO_4$ and evaporated under reduced pressure to give solids which were recrystallized from acetone-water (3.3:1) to give **8** (28.6 g, 74%) as colorless needles, mp 170-171℃ (lit.[23] mp 169-170℃); $[\alpha]_D^{28}$ +104° (*c* 13, $CHCl_3$) {lit.[39] $[\alpha]_D^{26}$ +94° (*c* 1.5, $CHCl_3$)}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.86 (br. s, 1H, OH), 3.38 (s, 3H, OCH_3), 3.55-3.65 (t, J = 9.6 Hz, 1H, H_{4a}), 3.71-3.84 (t, J = 9.6 Hz, 1H, H_{3a}), 3.84-3.98 (td, J = 4.3, 9.9 Hz, 1H, H_{5a}), 4.26-4.40 (m, 2H, H_6), 5.00-5.11 (m, 1H, H_{2a}), 5.08 (d, J = 3.8 Hz, 1H, H_{1e}), 5.55 (s, 1H, CHAr), 7.32-7.65 (m, 8H, ArH), 8.11 (dd, J = 1.2, 8.3 Hz, 2H, ArH); ^{13}C-NMR (62.89 MHz, $CDCl_3$) δ 55.18, 61.97, 68.54, 68.61, 74.03, 81.28, 97.65, 101.67, 126.20, 128.02, 128.17, 128.91, 129.50, 129.73, 133.00, 137.06, 166.02.

Methyl 2-*O*-Benzoyl-α-D-glucopyranoside (9).

(a) From 8:[24] Compound **8** (53.4 g, 0.14 mol) was deprotected by hydrogenolysis at atmospheric pressure in MeOH (1.8 L) containing conc. H_2SO_4 (1 mL), with PtO_2 (0.8 g, 3.52 mmol) being the catalyst. After stirring at r.t. for 5 h, Na_2CO_3 (1 g) was added and the mixture was stirred for a further 1 h. The reaction mixture was filtered and the solvent removed. The residue obtained after evaporation under reduced pressure was chromatographed on a silica gel column (150 g, EtOAc) to give **9** as colorless microcrystalline solids (38.3 g, 92%), mp 182-183℃ (lit.[24] mp 181-182℃); $[\alpha]_D^{25}$ +156° (*c* 2.9, EtOAc) {lit.[24] $[\alpha]_D^{23}$ +152.3° (*c* 1, EtOH)}; ^{1}H-NMR (250 MHz, CD_3COCD_3) δ 3.36 (s, 3H, OCH_3), 3.50-3.65 (m, 2H, H_6), 3.65-3.72 (d, J = 5.8 Hz, 1H, OH), 3.72-3.82 (m, 1H, H_{5a}), 3.84-3.94 (m, 1H, H_{4a}), 4.00-4.12 (m, 1H, H_{3a}), 4.42 (d, J = 4.4 Hz, 1H, OH), 4.64 (d, J = 4.8 Hz, 1H, OH), 4.84 (dd, J = 3.7, 9.9 Hz, 1H, H_{2a}), 4.97 (d, J = 3.7 Hz, 1H, H_{1e}), 7.48-7.60 (m, 2H, ArH), 7.60-7.70 (m, 1H, ArH), 8.00-8.15 (dd, J = 1.4, 8.3 Hz, 2H, ArH); ^{13}C-NMR (62.89 MHz, CD_3COCD_3) δ 55.23, 62.79, 72.36, 73.17, 75.37, 98.16, 129.30, 130.48, 133.95, 166.71, 205.99.

(b) From 6:[25] A solution of **6** (19.4 g, 0.1 mol) and di-*n*-butyltin oxide (25 g, 0.1 mol) in dry MeOH (450 mL) was heated at reflux under N_2 for 3 h. The mixture was cooled to 10℃ and Et_3N (50 g, 70 mL, 0.5 mol) was addded in one portion, and was followed by benzoyl chloride (71 g, 59 mL, 0.5 mol) dropwise over a period of 7 h. After stirring for a further 1 h at 10℃, the mixture was allowed to warm to r.t. and stirring was continued overnight. the resulting precipitate was filtered, washed with EtOAc (2 x 100 mL) and the combined organic solution was evaporated under reduced pressure to dryness. The solids obtained were chromatographed on a silica gel column (500 g, EtOAc) to give **9** (22 g, 74%) as colorless microcrystalline solids. The physical and spectrometric data are identical with an authentic sample prepared previously.

Methyl 6-*O*-Trityl-α-D-glucopyranoside (14).[40]

(a) A solution of **6**[20] (1 g, 5 mmol), trityl chloride (1.5 g, 5.5 mmol), Et_3N (1.3 mL) and DMAP (31 mg) in dry DMF (10 mL) was stirred overnight at r.t. under N_2. After stirring for 19 h, the cloudy yellow solution was poured into an ice-water mixture (500 mL) and was then extracted with CH_2Cl_2 (4 x 20 mL). The combined organic extract was washed with sat. aq. NH_4Cl solution (2 x 15 mL), water (2 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by chromatography on a silica gel column (50 g, EtOAc) to give solids which were recrystallized from absolute EtOH to give **14** as colorless needles (2 g, 87%), mp 156-157℃ (lit.[40] mp 154.5-155.5℃); $[\alpha]_D^{26}$ +83° (*c* 2.1, EtOAc) {lit.[41] $[\alpha]_D^{16}$

+86°}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.02-3.12 (br. s, 1H, OH), 3.12-3.22 (br. s, 1H, H_{4a}), 3.39 (s, 3H, OCH_3), 3.22-3.55 (m, 4H, H_{3a}, H_{5a} and H_6), 3.63 (br. s, 1H, OH), 3.67 (br. s, 1H, OH), 3.85 (br. s, 1H, H_{2a}), 4.73 (d, J = 3.7 Hz, 1H, H_{1e}), 7.15-7.35 (m, 9H, ArH), 7.40-7.50 (m, 6H, ArH).

(b) A solution of **6** (0.97 g, 5 mmol), trityl chloride (1.4 g, 5 mmol) in pyridine (5 mL) was heated at 75-85°C for 6 h. The reaction mixture was then poured into an ice-water mixture (50 mL). The solution was acidified with aq. HCl (1.5N) to *p*H 4 and was then extracted with CH_2Cl_2 (5 x 20 mL). The combined extract was washed with sat. aq. $NaHCO_3$ solution (2 x 20 mL), brine (20 mL), dried with $MgSO_4$ and evaporated under reduced pressure to give a residue which was crystallized from EtOH to give **14** as colorless needles (1.64 g, 75%). The physical and spectrometric data are identical to an authentic sample prepared previously.

Methyl 2-*O*-Benzoyl-6-*O*-triyl-α-D-glucopyranoside (10).

(a) From 9: Compound **9** (0.9 g, 2.9 mmol) was treated with trityl chloride (1.2 g, 4.3 mmol) in dry pyridine (5 mL) at r.t. After stirring for 48 h, the reaction mixture was poured into an ice-water mixture (20 mL), acidified with aq. HCl (1.5N) to *p*H 4. The mixture was then extracted with CH_2Cl_2 (4 x 18 mL), and the combined extract was washed with brine (2 x 15 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (30 g, EtOAc/hexanes 1:2) to afford **10** as colorless microcrystalline solids (1.25 g, 81%), mp 92-94°C (lit.[25] 93-95°C); $[\alpha]_D^{25}$ +88° (*c* 1.7, EtOAc) {lit.[25] $[\alpha]_D$ +120°}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.82 (s, 1H, OH), 2.84 (s, 1H, OH), 3.30-3.48 (m, 2H, H_6), 3.37 (s, 3H, OCH_3), 3.62 (m, 1H, H_{5a}), 3.74 (t, J = 10.8 Hz, 1H, H_{4a}), 4.09 (t, J = 10.8 Hz, 1H, H_{3a}), 4.93 (dd, J = 3.7, 10.0 Hz, 1H, H_{2a}), 5.03 (d, J = 3.7 Hz, 1H, H_{1e}), 7.18-7.27 (m, 3H, ArH), 7.27-7.35 (m, 6H, ArH), 7.39-7.43 (m, 2H, ArH), 7.46-7.48 (m, 6H, ArH), 7.52-7.56 (m, 1H, ArH), 8.06-8.08 (t, J = 7.1 Hz, 2H, ArH); EIMS *m/e* 539 (M^+-1).

(b) From 14: A solution of **14** (2.2 g, 5 mmol) and di-*n*-butyltin oxide (1.3 g, 5 mmol) in dry MeOH (23 mL) was refluxed under N_2 for 3 h. the mixture was cooled to 10°C and Et_3N (2.5 g, 4 mL, 25 mmol) was added in one portion, and was followed by benzoyl chloride (3.6 g, 3 mL, 25 mmol) dropwise over a period of 7 h. After stirring for a further 1 h at 10°C, the mixture was allowed to warm to r.t. and stirring was continued at this temperature overnight. the resulting precipitate was filtered, and the filtrate was extracted with EtOAc (2 x 5 mL). The combined extract was evaporated under reduced pressure to dryness. The residue was chromatographed on a silica gel column (65 g, EtOAc/hexanes 1:2) to give **10** as colorless microcrystalline solids (1.9 g, 61%). The physical and spectrometric data are identical with an authentic sample prepared previously.

Methyl 2-*O*-Benzoyl-3,4-di-*O*-methanesulfonyl-6-*O*-trityl-α-D-glucopyranoside (11).[24]

(a) Directly from 9:[24] Compound **9** (13 g, 43.6 mmol) was treated with trityl chloride (21.7 g, 77.8 mmol) in dry pyridine (72 mL) at r.t. for 48 h. More pyridine (72 mL) was added, the solution was then cooled to -10°C, and MsCl (72 mL, 0.9 mol) was added. After stirring at -10°C for 2.5 h, the reaction mixture was poured into an ice-water mixture (1 L), acidified with aq. HCl (1.5N) to *p*H 4. It was then extracted with CH_2Cl_2 (4 x 150 mL), and the combined extract was washed with sat. aq. $NaHCO_3$ solution (150 mL), brine (150 mL) and dried over $MgSO_4$. After evaporation under reduced pressure, the oily residue was chromatographed on a silica gel column (700 g, EtOAc/hexanes, 1:2) to give **11** (25 g, 82%) as colorless microcrystalline solids, mp 176-177°C (lit.[24] mp 169-170°C); $[\alpha]_D^{25}$ +93° (*c* 3.7, EtOAc) {lit.[24] $[\alpha]_D^{23}$ +103.6° (*c* 5, $CHCl_3$)}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.68 (s, 3H, C_4-OSO_2CH_3), 3.04 (s, 3H, C_3-OSO_2CH_3), 3.30-3.40 (m, 1H, H_6), 3.47 (s, 3H, OCH_3), 3.51-3.57 (dd, J = 1.9, 11.0 Hz, 1H, H_6), 4.00-4.11 (m, 1H, H_{5a}), 4.77-4.86 (t, J = 9.6 Hz, 1H, H_{4a}), 5.20 (d, J = 3.6 Hz, 1H, H_{1e}), 5.13-5.25 (m, 1H, H_{3a}), 5.28-5.40 (m, 1H, H_{2a}), 7.20-7.36 (m, 9H, ArH), 7.42-7.50 (m, 8H, ArH), 7.50-7.65 (m, 1H, ArH), 8.12-8.22 (d, J = 7.9 Hz, 2H, ArH).

(b) From 10: A solution of **10** (210 mg, 0.39 mmol) in dry pyridine (1.8 mL) was cooled to -10℃, MsCl (1.5 g, 1 mL, 13 mmol) was added slowly. After stirring at -10℃ for 2 h, the reaction mixture was poured into an ice-water mixture (25 mL), acidified with aq. HCl (1.5N) to *p*H 4, and was extracted with CH_2Cl_2 (4 x 10 mL). The combined organic extract was washed with sat. aq. $NaHCO_3$ solution (10 mL), brine (10 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (10 g, EtOAc/hexanes 1:2) to afford **11** as colorless microcrystalline solids (230 mg, 85%). The physical and spectrometric data are identical with an authentic sample prepared previously.

Methyl 2-*O*-Benzoyl-3,4-dideoxy-6-*O*-trityl-α-D-erythro-hex-3-enopyranoside (12).[24] To a solution of **11** (25 g, 36 mmol) in dry DMF (180 mL) was added NaI (27.6 g, 180 mmol) and Zn-Cu couple (11.5 g, 180 mmol). The rapidly stirred solution was heated to reflux for 3 h, and was then poured into an ice-water mixture (600 mL). The resulting mixture was extracted with $CHCl_3$ (4 x 100 mL) and the combined organic extract was filtered through a bed of celite. The filtered cake was washed with a mixture of $CHCl_3$ and water (500 mL, 1:1). The $CHCl_3$ layer was separated and combined with the former $CHCl_3$ filtrate. The combined $CHCl_3$ solution was washed with dil. aq. $Na_2S_2O_3$ solution (2 x 200 mL), water (200 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (500 g, EtOAc/hexanes 1:6) to yield **12** (8.3 g, 46%) and **13** (3.5 g, 24%) as colorless microcrystalline solids. Compound **12**: mp 49-50℃; $[\alpha]_D^{24}$ +8° (*c* 3.1, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.19-3.27 (dd, *J* = 4.1, 9.3 Hz, 1H, H_6), 3.27-3.35 (dd, *J* = 6.1, 9.3 Hz, 1H, H_6), 3.48 (s, 3H, OCH_3), 4.32 (br. d, *J* = 2.3 Hz, 1H, H_5), 5.20-5.26 (d, *J* = 4.1 Hz, 1H, H_{1e}), 5.54-5.58 (d, *J* = 5.4 Hz, 1H, H_2), 5.76-5.86 (d, *J* = 10.5 Hz, 1H, H_4), 5.96-6.04 (d, *J* = 10.5 Hz, 1H, H_3), 7.16-7.35 (m, 9H, ArH), 7.38-7.44 (m, 2H, ArH), 7.44-7.51 (m, 6H, ArH), 7.51-7.59 (m, 1H, ArH), 8.08 (d, *J* = 7.5 Hz, 2H, ArH); CIMS *m/e* 507 (M^++1). Benzoate **12** was directly converted to alcohol **13** without further purification. Alcohol **13**: The physical and spectrometric data are identical with an authentic sample prepared below.

Methyl 3,4-Dideoxy-6-*O*-trityl-α-D-erythro-hex-3-enopyranoside (13).[24] A solution of **11** (5.8 g, 11.5 mmol) in MeOH-H_2O-Et_3N (5 mL, 3:1:1) was kept at 55℃ for 15 h. After removal of the solvents under reduced pressure, the residue was chromatographed on a silica gel column (8 g, EtOAc/hexanes 1:2) to give **13** as colorless microcrystalline solids (3.1 g, 67%), mp 120-121℃ (lit.[24] mp 122-123℃); $[\alpha]_D^{23}$ -8° (*c* 9, $CHCl_3$) {lit.[24] $[\alpha]_D^{23}$ -11° (*c* 6, $CHCl_3$)}; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.24 (d, *J* = 11.1 Hz, 1H, OH), 3.10-3.20 (dd, *J* = 5.5, 9.4 Hz, 1H, H_6), 3.20-3.30 (dd, *J* = 5.5, 9.4 Hz, 1H, H_6), 3.52 (s, 3H, OCH_3), 4.18-4.28 (br. m, 2H, H_2 and H_5), 4.89 (d, *J* = 4.2 Hz, 1H, H_{1e}), 5.68-5.77 (d, *J* = 10.6 Hz, 1H, H_4), 5.77-5.89 (d, *J* = 10.6 Hz, 1H, H_3), 7.19-7.38 (m, 9H, ArH), 7.39-7.50 (m, 6H, ArH).

Methyl 2-*O*-*n*-Butyl-3,4-dideoxy-6-*O*-trityl-α-D-erythro-hex-3-enopyranoside (15). To a stirred slurry of NaH (0.7 g, 27.5 mmol, 80% dispersion in oil) in dry THF (9 mL) at 45℃ udner N_2 was added a solution of *n*-butyl bromide (2.5 g, 2 mL, 18 mmol) in dry THF (3 mL). After heating to reflux for a further 10 h, the reaction mixture was cooled and sufficient amount of water was added to dissolve the precipitate. The mixture was extracted with Et_2O (3 x 15 mL). The combined ethereal extract was washed with brine (10 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (50 g, EtOAc/hexanes 1:6) to afford **15** as a pale yellow oil (1.8 g, 85%). $[\alpha]_D^{23}$ +50° (*c* 0.5, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.4 Hz, 3H, CH_3), 1.32-1.48 (m, 2H, CH_2), 1.50-1.67 (m, 2H, CH_2), 3.10-3.18 (dd, *J* = 5.5, 9.1 Hz, 1H, H_6), 3.18-3.28 (dd, *J* = 6.3, 9.1 Hz, 1H, H_6), 3.50 (s, 3H, OCH_3), 3.50-3.60 (m, 2H, OCH_2), 4.03 (s, 1H, H_5), 4.25 (s, 1H, H_2), 4.98 (d, *J* = 3.6 Hz, 1H, H_{1e}), 5.74 (d, *J* = 10.8 Hz, 1H, H_4), 5.81 (d, *J* = 10.8 Hz, 1H, H_3), 7.15-7.24 (m, 3H, ArH), 7.24-7.35 (m, 6H, ArH), 7.42-7.50 (m, 6H, ArH); FABMS *m/e* 457 (M^+-1), 481 (M^++Na). Anal. Calcd. for

$C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.68; H, 7.94.

Methyl 2-*O*-*n*-Butyl-3,4-dideoxy-α-D-glucopyranoside (16). A solution of **15** (80 mg, 0.2 mmol) in absolute EtOH (25 mL) was hydrogenated at 2.5 atm. over 10% Pd-C (5 mg) at 25℃ for 6 h. After removal of the catalyst by filtration and evaporation of the solvent under reduced pressure, the residue was purified by chromatography on a silica gel column (5 g, EtOAc/hexanes 1:1) to give **16** as a pale-yellow oil (36 mg, 94%). $[\alpha]_D^{23}$ +82° (*c* 5.5, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.3 Hz, 3H, CH_3), 1.30-1.41 (m, 2H, CH_2), 1.43-1.52 (m, 1H, H_{4a}), 1.52-1.60 (m, 2H, CH_2), 1.60-1.66 (m, 1H, H_{4e}), 1.74-1.92 (m, 2H, H_3), 2.06-2.22 (br. t, *J* = 5.3 Hz, 1H, OH), 3.33-3.42 (m, 1H, H_{5a}), 3.42-3.45 (s, 3H, OCH_3), 3.45-3.55 (m, 3H, OCH_2 and H_6), 3.56-3.57 (m, 1H, H_6), 3.76-3.84 (td, *J* = 3.2, 6.9 Hz, 1H, H_{2a}), 4.78 (d, *J* = 3.2 Hz, 1H, H_{1e}); ^{13}C-NMR (62.89 MHz, $CDCl_3$) δ 13.61, 19.04, 23.36, 26.10, 31.85, 54.65, 65.27, 68.66, 75.97, 97.99; EIMS *m/e* 217 (M^+-1, 3.66), 218 (M^+, 0.53), 219 (M^++1, 0.24). Anal. Calcd. for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.56; H, 10.55.

6-(Methyl 2-*O*-*n*-Butyl-3,4-dideoxy-α-D-glucopyranoside)-carbinyl-(methyl 2-*O*-*n*-butyl-3,4-dideoxy-α-D-glucopyranosid)uronate (17). To a solution of **16** (2 g, 9.4 mmol) in dry CH_2Cl_2 (20 mL) was added PCC (4 g, 18.8 mmol). The reaction mixture was stirred at r.t. for 17 h, and was then diluted with Et_2O (20 mL). The mixture was filtered through a bed of celite and the filtered cake was washed with CH_2Cl_2 (3 x 10 mL). the filtrate was washed with sat. $NaHCO_3$ solution (10 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (90 g, EtOAc/hexanes 2:5) to afford **17** as a pale yellow oil (1.9 g, 47%). $[\alpha]_D^{23}$ +86° (*c* 2.6, EtOAc); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.3 Hz, 6H, CH_3), 1.20-1.38 (m, 4H, CH_2), 1.38-1.56 (m, 4H, CH_2), 1.56-1.90 (m, 7H, H_3, $H_{3'}$, H_{4e}, $H_{4'}$), 1.90-2.10 (d, *J* = 12.5 Hz, 1H, H_{4a}), 3.20-3.50 (m, 12H, OCH_3, OCH_2 and $H_{6'}$), 3.78-3.95 (m, 1H, $H_{5'a}$), 3.95-4.20 (m, 2H, H_{2a} and $H_{2'a}$), 4.20-4.35 (d, *J* = 10.3 Hz, 1H, H_{5a}), 4.68 (s, 1H, $H_{1'e}$), 4.79 (s, 1H, H_{1e}); ^{13}C-NMR (62.89 MHz, $CDCl_3$) δ 13.60, 18.97, 23.36, 23.56, 26.53, 27.77, 31.77, 54.58, 55.18, 65.82, 66.60, 67.20, 68.68, 68.74, 75.00, 75.56, 97.82, 98.21, 170.91; EIMS *m/e* 431 (M^+-1). Anal. Calcd. for $C_{22}H_{40}O_8$: C, 61.09; H, 9.32. Found: C, 60.51; H, 9.46.

Methyl 2-*O*-*n*-Butyl-3,4-dideoxy-α-D-glucopyranosiduronic Acid (18). To a solution of **17** (170 mg, 0.4 mmol) in THF (1 mL) was added an aq. KOH solution (15 mL, 1.5N). After heating at 60℃ for 30 min, the solution was acidified with aq. HCl (1 mL, 1.5N) to *p*H 4. The resulting mixture was extracted with CH_2Cl_2 (5 x 10 mL) and the combined extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (5 g, EtOAc) to give alcohol **16** (83 mg, 97%). Further elution (EtOAc/HOAc 20:1) afforded acid **18** as light golden yellow needles (87 %, 96%). The physical and spectrometric data of **16** are identical to an authentic sample prepared previously. Acid **18**: mp 102-104℃; $[\alpha]_D^{23}$ +188° (*c* 0.4, EtOAc); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.4 Hz, 3H, CH_3), 1.25-1.43 (m, 2H, CH_2), 1.43-1.61 (m, 2H, CH_2), 1.61-1.81 (m, 1H, H_{4e}), 1.81-2.00 (td, *J* = 3.7, 8.8 Hz, 2H, H_3), 2.09-2.20 (m, 1H, H_{4a}), 3.30-3.60 (m, 3H, H_{2a} and OCH_2), 3.44 (s, 3H, OCH_3), 4.30-4.40 (dd, *J* = 3.0, 11.6 Hz, 1H, H_{5a}), 4.90 (d, *J* = 3.2 Hz, 1H, H_{1e}), 10.73 (br. s, 1H, CO_2H); CIMS *m/e* 231 (M^+-1). Anal. Calcd. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.40; H, 8.70.

4',4''-Heptoxybiphenyl-(methyl 2-*O*-*n*-butyl-3,4-dideoxy-α-D-glucopyranosid)uronate (2). A solution of **18** (100 mg, 0.4 mmol), 4-hydroxy-4'-heptoxybiphenyl[29] (141 mg, 0.4 mmol) and DCC (177 mg, 0.9 mmol) in dry CH_2Cl_2 (10 mL) containing a catalytic amount of DMAP was heated to reflux for 3 days. The reaction mixture was filtered. The filtrate was washed with sat. aq. $NaHCO_3$ solution (4 mL), dried with $MgSO_4$ and evaporated under reduced pressure. Flash column chromatography of the residue on a silica gel column (6 g, $CHCl_3$) afforded **2** as colorless microcrystalline solids (133 mg, 62%), melting range K 54 S_c*

77 TGB_c 77.2 N* 95.5 BP 96.5℃ I; $[\alpha]_D^{24}$ +91° (*c* 0.27, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86-0.94 (m, 6H, CH_3), 1.25-1.42 (m, 8H, CH_2), 1.42-1.52 (m, 2H, CH_2), 1.52-1.63 (m, 2H, CH_2), 1.75-1.84 (m, 2H, CH_2), 1.84-1.94 (m, 1H, H_{4e}), 1.94-2.05 (m, 2H, H_3), 2.23-2.32 (m, 1H, H_{4a}), 3.45 -3.60 (m, 3H, H_{2a} and OCH_2), 3.54 (s, 3H, OCH_3), 3.95-4.03 (t, *J* = 6.5 Hz, 2H, OCH_2), 4.52-4.61 (dd, *J* = 2.7, 11.5 Hz, 1H, H_{5a}), 4.95 (d, *J* = 2.7 Hz, 1H, H_{1e}), 6.96 (d, *J* = 8.5 Hz, 2H, ArH), 7.15 (d, *J* = 8.4 Hz, 2H, ArH), 7.48 (d, *J* = 8.6 Hz, 2H, ArH), 7.54 (d, *J* = 8.5 Hz, 2H, ArH); ^{13}C-NMR (125.76 MHz, $CDCl_3$) δ 14.56, 14.77, 19.87, 23.30, 24.43, 26.71, 28.75, 29.76, 31.60, 32.48, 32.62, 56.37, 68.20, 68.79, 69.75, 75.79, 99.16, 115.50, 122.19, 128.39, 128.76, 133.21, 139.65, 149.84, 159.52, 170.69; EIMS *m/e* 498 (M^+, 4.73). Anal. Calcd. for $C_{30}H_{42}O_6$: C, 72.26; H, 8.49. Found: C, 72.01; H, 8.99.

4',4''-Cyanobiphenyl-(methyl 2-*O*-*n*-butyl-3,4-dideoxy-α-D-glucopyranosid)uronate (3). A solution of **18** (65 mg, 0.3 mmol), 4'-hydroxy-4-biphenylcarbonitrile (55 mg, 0.3 mmol) and DCC (124 mg, 0.6 mmol) in dry CH_2Cl_2 (6 mL) containing a catalytic amount of DMAP was heated to reflux for 3 days. The reaction mixture was filtered. The filtrate was washed with sat. aq. $NaHCO_3$ solution (3 mL), dried over $MgSO_4$ and evaporated under reduced pressure. Flash chromatography of the residue on a silica gel column (6 g, $CHCl_3$) afforded colorless crystals which were purified by recrystallization (EtOAc/hexanes 1:9) to give **3** as colorless needles (61 mg, 53%), melting range K 88℃ (N* 61) I; $[\alpha]_D^{22}$ +298° (*c* 0.084, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H, CH_3), 1.31-1.45 (m, 2H, CH_2), 1.51-1.66 (m, 2H, CH_2), 1.85-2.05 (m, 3H, H_3 and H_{4e}), 2.30 (m, 1H, H_{4a}), 3.45-3.60 (m, 3H, H_{2a} and OCH_2), 3.55 (s, 3H, OCH_3), 4.60 (dd, *J* = 2.7, 11.6 Hz, 1H, H_{5a}), 4.96 (d, *J* = 2.7 Hz, 1H, H_{1e}), 7.24 (d, *J* = 8.5 Hz, 2H, ArH), 7.60 (d, *J* = 8.7 Hz, 2H, ArH), 7.66 (d, *J* = 8.3 Hz, 2H, ArH), 7.73 (d, *J* = 8.2 Hz, 2H, ArH); ^{13}C-NMR (62.89 MHz, $CDCl_3$) δ 13.80, 19.19, 23.75, 28.02, 31.98, 55.71, 67.59, 69.08, 75.17, 98.63, 111.27, 118.70, 122.08, 127.69, 128.37, 132.64, 137.15, 144.66, 150.84, 169.75. EIMS *m/e* 410 (M^++1, 2.90). Anal. Calcd. for $C_{24}H_{27}NO_5$: C, 70.40; H, 6.65; N, 3.42. Found: C, 70.47; H, 6.56; N, 3.47.

Methyl 2-*O*-Benzoyl-3,4-di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside (19) To a solution of **10** (175 mg, 0.3 mmol) in dry DMF (1 mL) were added MeI (276 mg, 1.9 mmol) and Ag_2O (300 mg, 1.3 mmol) at r.t. The mixture was stirred for 6 h and was then quenched by dilution with $CHCl_3$ (5 mL). The resulting mixture was filtered through a bet of celite. After removal of solvents under reduced pressure, the residue was chromatographed on a silica gel column (10 g, EtOAc/hexanes 1:4) to furnish **19** as colorless microcrystalline solids (157 mg, 85%), mp 67-68℃; $[\alpha]_D^{23}$ +112° (*c* 2.2, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.10-3.20 (m, 1H, H_{4a}), 3.31 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.39-3.50 (m, 2H, H_6), 3.58 (s, 3H, OCH_3), 3.66-3.79 (m, 2H, H_{3a} and H_{5a}), 5.02-5.10 (m, 2H, H_{1e} and H_{2a}), 7.20-7.26 (m, 3H, ArH), 7.26-7.34 (m, 6H, ArH), 7.42-7.50 (m, 2H, ArH), 7.50-7.54 (m, 6H, ArH), 7.54-7.62 (m, 1H, ArH), 8.13 (d, *J* = 7.6 Hz, 2H, ArH); FABMS *m/e* 569 (M^++1), 591 (M^++Na). Anal. Calcd. for $C_{35}H_{36}O_7$: C, 73.92; H, 6.38. Found: C, 73.78; H, 6.23.

Methyl 3,4-Di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside (20). A solution of **19** (157 mg, 0.3 mmol) in MeOH-H_2O-Et_3N mixture (12 mL, 3:1:1) was kept at 55℃ for 15 h. After removal of the solvents under reduced pressure, the residue was chromatographed on a silica gel column (9 g, EtOAc/hexanes 1:1) to give **20** as colorless microcrystalline solids (92 mg, 68%), mp 51-53℃; $[\alpha]_D^{26}$ +97° (*c* 2, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.19 (d, *J* = 8.2 Hz, 1H, OH), 3.09-3.16 (m, 1H, H_{4a}), 3.26 (s, 3H, OCH_3), 3.28-3.34 (m, 2H, H_6), 3.35-3.42 (m, 1H, H_{3a}), 3.46 (s, 3H, OCH_3), 3.64 (s, 3H), 3.58-3.68 (m, 2H, H_{2a} and H_{5a}), 4.83 (d, *J* = 3.9 Hz, 1H, H_{1e}), 7.18-7.26 (m, 3H, ArH), 7.26-7.32 (m, 6H, ArH), 7.47-7.51 (m, 6H, ArH); ^{13}C-NMR (125.76 MHz, $CDCl_3$) δ 55.71, 60.89, 61.72, 63.09, 71.17, 73.34, 84.64, 85.44, 86.99, 99.76, 127.64, 128.43, 129.46, 144.71; CIMS *m/e* 432 (M^+-MeOH); FABMS *m/e* 487 (M^++Na). Anal.

Calcd. for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.55; H, 6.44.

Methyl 2-*O*-*n*-Butyl-3,4-di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside (21). To a stirred slurry of NaH (72 mg, 2.4 mmol, 80% dispersion in oil) in dry THF (0.4 mL) at 45℃ under N_2 was added a solution of *n*-butyl bromide (248 mg, 0.2 mL, 1.8 mmol) in dry THF (0.1 mL), and was followed by dropwise addition of a solution of **20** (280 mg, 0.6 mmol) in dry THF (0.5 mL). After heating to reflux for 10 h, the reaction mixture was allowed to cool and sufficient water was added to dissolve all precipitate. The mixture was extracted with Et_2O (3 x 2 mL). The combined organic extract was washed with brine (1 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (10 g, EtOAc/hexanes 1:6) to afford **21** as a pale-yellow oil (278 mg, 89%); $[\alpha]_D^{26}$ +111°(*c* 0.68, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3H, CH_3), 1.35-1.50 (m, 2H, CH_2), 1.50-1.70 (m, 2H, CH_2), 3.09-3.15 (dd, *J* = 4.3, 10.0 Hz, 1H, H_{2a}), 3.26-3.32 (m, 1H, H_{5a}), 3.29 (s, 3H, OCH_3), 3.33-3.41 (t, *J* = 9.8 Hz, 2H, OCH_2), 3.43 (s, 3H, OCH_3), 3.44-3.51 (t, *J* = 9.2 Hz, 1H, H_{3a}), 3.58-3.71 (m, 3H, H_{4a} and H_6), 3.62 (s, 3H, OCH_3), 4.87 (d, *J* = 3.4 Hz, 1H, H_{1e}), 7.18-7.26 (m, 3H, ArH), 7.26-7.36 (m, 6H, ArH), 7.45-7.53 (m, 6H, ArH); CIMS *m/e* 519 (M^+-1). Anal. Calcd. for $C_{32}H_{40}O_6$: C, 73.82; H, 7.74. Found: C, 73.47; H, 7.94.

Methyl 2-*O*-*n*-Butyl-3,4-di-*O*-methyl-α-D-glucopyranoside (22). A solution of **21** (1.5 g, 2.9 mmol) in absolute EtOH (500 mL) was hydrogenated at 2.5 atm. over 10% Pd-C (45 mg) at 25℃ for 7 h. After removal of the catalyst by filtration and evaporation of the solvent under reduced pressure, the residue was chromatographed on a silical gel column (35 g, EtOAc/hexanes 1:1) to give **22** as a pale yellow oil (0.7 g, 87%); $[\alpha]_D^{25}$ +136°(*c* 3.7, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H, CH_3), 1.35-1.45 (m, 2H, CH_2), 1.52-1.64 (m, 2H, CH_2), 1.98 (br. s, 1H, OH), 3.08-3.18 (t, *J* = 9.4 Hz, 1H, H_{4a}), 3.20-3.27 (dd, *J* = 3.6, 9.6 Hz, 1H, H_{2a}), 3.40 (s, 3H, OCH_3), 3.48-3.67 (m, 4H, OCH_2, H_{3a} and H_{5a}), 3.58 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.70-3.77 (m, 1H, H_6), 3.77-3.87 (m, 1H, H_6), 4.76 (d, *J* = 3.6 Hz, 1H, H_{1e}); CIMS *m/e* 277 (M^+-1, 0.58); FABMS *m/e* 301 (M^++Na), 557 ($2M^+$+1). Anal. Calcd. for $C_{13}H_{26}O_6$: C, 56.10; H, 9.42. Found: C, 56.16; H, 9.61.

6-(Methyl 2-*O*-*n*-Butyl-3,4-di-*O*-methyl-α-D-glucopyranoside)-carbinyl-(methyl 2-*O*-*n*-butyl-3,4-di-*O*-methyl-α-D-glucopyranosid)uronate (23). To a solution of **22** (210 mg, 0.8 mmol) in dry CH_2Cl_2, was added PCC (244 mg, 1.1 mmol). The mixture was stirred at r.t. for 17 h, and was then diluted with Et_2O (2 mL) and filtered through a bed of celite. The filtered cake was washed with CH_2Cl_2 (3 x 2 mL). the combined fitrate was washed with sat. aq. $NaHCO_3$ solution (2 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (6 g, EtOAc/hexanes 1:2) to afford **23** as a pale yellow oil (193 mg, 46%); $[\alpha]_D^{24}$ +223°(*c* 0.34, EtOAc); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 6H, CH_3), 1.20-1.48 (m, 4H, CH_2), 1.48-1.69 (m, 4H, CH_2), 3.08 (t, *J* = 9.6 Hz, 1H, H_{4a}), 3.35 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.62 (s, 6H, OCH_3), 3.17-3.80 (m, 10 H, OCH_2, H_{2a}, $H_{2'a}$, H_{3a}, $H_{3'a}$, $H_{4'a}$ and $H_{5'a}$), 4.06 (d, *J* = 9.7 Hz, 1H, H_{5a}), 4.40 (d, *J* = 3.7 Hz, 2H, $H_{6'}$) 4.74 (d, *J* = 3.5 Hz, 1H, H_{1e}), 4.79 (d, *J* = 3.5 Hz, 1H, $H_{1'e}$); ^{13}C-NMR (62.89 MHz, $CDCl_3$) δ 13.72, 19.13, 32.12, 55.09, 55.55, 60.27, 60.35, 60.86, 64.24, 68.56, 70.24, 71.22, 71.38, 79.74, 80.20, 80.67, 81.08, 82.85, 83.44, 97.93, 98.68, 169.60; CIMS *m/e* 551 (M^+-1, 2.42). Anal. Calcd. for $C_{26}H_{48}O_{12}$: C, 56.51; H, 8.75. Found: C, 56.32; H, 8.84.

Methyl 2-*O*-*n*-Butyl-3,4-di-*O*-methyl-α-D-glucopyranosiduronic Acid (24). To a solution of **23** (137 mg, 0.3 mmol) in THF was added an aq. KOH solution (12 mL, 1.5N). After heating at 60℃ for 30 min, the solution was acidified with aq HCl solution (1.5N) to *p*H 4. The resulting mixture was extracted with CH_2Cl_2 (5 x 8 mL) and the combined extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (5 g, EtOAc) to give alcohol **22** (64 mg, 92%).

Further elution (EtOAc/HOAc 20:1) afforded acid **24** as a pale yellow oil (67 mg, 92%). The physical and spectrometric data of **22** are identical with an authentic sample prepared previously. Acid **24**: $[\alpha]_D^{25}$ +124° (*c* 2, EtOAc); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.92 (t, *J* = 14.6 Hz, 3H, CH_3), 1.30-1.50 (m, 2H, CH_2), 1.50-1.70 (m, 2H, CH_2), 3.25-3.40 (m, 2H, H_{3a} and H_{4a}), 3.41 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.45-3.67 (m, 3H, OCH_2 and H_{2a}), 4.10 (d, *J* = 10.0 Hz, 1H, H_{5a}), 4.84 (d, *J* = 3.5 Hz, 1H, H_{1e}), 7.41 (br. s, 1H, CO_2H); ^{13}C-NMR (62.89 MHz, $CDCl_3$) δ 13.72, 19.10, 32.06, 55.74, 60.50, 60.95, 69.36, 71.40, 80.03, 81.05, 82.93, 98.57, 172.86; CIMS *m/e* 291 (M^+-1, 3.35). Anal. Calcd. for $C_{13}H_{24}O_7$: C, 53.41; H, 8.28. Found: C, 53.35; H, 8.42.

4',4''-Heptoxybiphenyl-(methyl 2-*O*-*n*-butyl-3,4-di-*O*-methyl-α-D-glucopyranosid)uronate (**4**). A solution of **24** (89 mg, 0.3 mmol), 4-hydroxy-4'-heptoxybiphenyl[29] (86 mg, 0.3 mmol) and DCC (186 mg, 0.9 mmol) in dry CH_2Cl_2 (8 mL) containing a catalytic amount of DMAP was heated to reflux for 3 days. The reaction mixture was then filtered. The filtrate was washed with sat. aq. $NaHCO_3$ solution (4 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (6 g, $CHCl_3$) to provide **4** as colorless microcrystalline solids (101 mg, 60%), mp 60-62℃; $[\alpha]_D^{23}$ +57° (*c* 0.22, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.88-0.92 (t, *J* = 7.1 Hz, 3H, CH_3), 0.92-0.96 (t, *J* = 7.4 Hz, 3H, CH_3), 1.26-1.54 (m, 10H, CH_2), 1.54-1.70 (br. s, 2H, CH_2), 1.70-1.86 (m, 2H, CH_2), 3.39 (d, *J* = 3.6 Hz, 1H, H_{2a}), 3.52 (s, 3H, OCH_3), 3.45-3.55 (m, 1H, H_{4a}), 3.60 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.55-3.70 (m, 3H, OCH_2 and H_{3a}), 3.99 (t, *J* = 6.6 Hz, 2H, OCH_2), 4.29 (d, *J* = 10.0 Hz, 1H, H_{5a}), 4.89 (d, *J* = 3.4 Hz, 1H, H_{1e}), 6.96 (d, *J* = 8.9 Hz, 2H, ArH), 7.19 (d, *J* = 8.6 Hz, 2H, ArH), 7.48 (d, *J* = 8.9 Hz, 2H, ArH), 7.55 (d, *J* = 8.6 Hz, 2H, ArH); ^{13}C-NMR (125.76 MHz, $CDCl_3$) δ 14.52, 14.77, 19.82, 23.30, 26.71, 29.76, 31.60, 32.48, 32.75, 56.51, 61.43, 61.85, 68.79, 70.91, 72.20, 80.75, 81.97, 83.58, 99.40, 115.51, 122.29, 128.43, 128.78, 133.21, 139.79, 149.96, 159.54, 169.13; EIMS *m/e* 558 (M^+, 11.43). Anal. Calcd. for $C_{32}H_{46}O_8$: C, 68.79; H, 8.30. Found: C, 68.84; H, 8.29.

4',4''-Cyanobiphenyl-(methyl 2-*O*-*n*-butyl-3,4-di-*O*-methyl-α-D-glucopyranosid)uronate (**5**). A solution of **24** (112 mg, 0.4 mmol), 4'-hydroxy-4-biphenylcarbonitrile (75 mg, 0.4 mmol) and DCC (158 mg, 0.8 mmol) in dry CH_2Cl_2 (8 mL) containing a catalytic amount of DMAP was heated to reflux for 3 days. The reaction mixture was filtered. The filtrate was washed with sat. aq. $NaHCO_3$ solution (4 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (7 g, $CHCl_3$) to afford **5** as a colorless oil (92 mg, 52%); $[\alpha]_D^{22}$ +250° (*c* 0.4, EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3H, CH_3), 1.34-1.47 (m, 2H, CH_2), 1.55-1.69 (m, 2H, CH_2), 3.34-3.44 (dd, *J* = 3.4, 9.6 Hz, 1H, H_{2a}), 3.45-3.55 (m, 1H, H_{4a}), 3.52 (s, 3H, OCH_3), 3.55-3.70 (m, 3H, OCH_2 and H_{3a}), 3.62 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 4.31 (d, *J* = 9.8 Hz, 1H, H_{5a}), 4.89 (d, *J* = 3.5 Hz, 1H, H_{1e}), 7.27 (d, *J* = 8.8 Hz, 2H, ArH), 7.61 (d, *J* = 8.4 Hz, 2H, ArH), 7.66 (d, *J* = 8.3 Hz, 2H, ArH), 7.73 (d, *J* = 8.2 Hz, 2H, ArH); ^{13}C-NMR (125.76 MHz, $CDCl_3$) δ 14.51, 19.81, 32.73, 56.54, 61.40, 61.85, 70.87, 72.21, 80.74, 81.86, 83.54, 99.44, 111.86, 119.47, 122.72, 128.39, 129.14, 133.35, 137.98, 145.29, 151.48, 168.97; EIMS *m/e* 470 (M^++1, 5.59). Anal. Calcd. for $C_{26}H_{31}NO_7$: C, 66.51; H, 6.65; N, 2.98. Found: C, 66.34; H, 6.64; N, 3.00.

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