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"Dibutyltin diperchlorate" for activation of glycosyl fluoride

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ABSTRACT

The Bu_2SnCl_2–$2AgClO_4$ combination shows promise as an activator for glycosyl fluorides, as revealed by experiments with 2,3,4,6-tetra-*O*-benzyl-α-D-mannosyl fluoride as a model glycosyl donor in comparison with activators prepared in situ from five types of organotin chlorides (Bu_2SnCl_2, Me_2SnCl_2, Bu_3SnCl, Me_3SnCl, and Ph_3SnCl) in combination with silver perchlorate.

INTRODUCTION

Recent progress in cell biology has demonstrated significant roles played by glycoconjugates in cellular systems, and has made carbohydrate synthesis of major interest in synthetic organic chemistry. For construction of complex oligosaccharides, methods for *O*-glycosylation that are efficient in terms of reactivity and stereoselectivity, become more and more important.

A report in 1981 by Mukaiyama[1] provided an important lead: glycosyl fluorides, long thought to be poor glycosyl donors, may be efficiently activated by the combination of $SnCl_2$ and $AgClO_4$. This finding made glycosyl fluorides a useful new class of glycosyl donor, and they have enjoyed wide utility in oligosaccharide synthesis. Triggered by this pioneering work, various activators of glycosyl fluoride have subsequently appeared including SiF_4 or Me_3SiOTf (by Noyori[2]), $BF_3 \cdot OEt_2$ (by Nicolaou[3a] and by Kunz[3b]), TiF_4 (by Thiem[4]), Cp_2MCl_2–$AgClO_4$ (M = Zr, Hf: by us[5a]), and Me_2GaX (by Kobayashi[6]). Common to these activators[7] is the fluorophilicity of the center metals of the groups III, IV, and XIV.

Our metallocene-based system exhibits particularly high reactivity which is maintained for sterically hindered substrates, and is therefore, becoming of value for joining large oligosaccharide fragments (for examples, see ref 8). Furthermore,

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we have found that employment of Cp_2HfCl_2 and $AgClO_4$ in a 1:2 ratio offers enhancement of the reactivity. Our interpretation for this phenomenon is the generation of a dicationic species, namely $Cp_2Hf(ClO_4)_2$, whose reactivity far exceeds that of the corresponding monocationic complex[5b]. With this notion in mind, we were interested in generating a related species from diorganotin dichloride and exploring its potential utility as a new activator for glycosyl fluorides. This expectation rested on the fact that, even though tin is "softer" than silicon and its fluorophilicity is less evident, many organotin fluorides tend to precipitate out as polymeric aggregates through intermolecular fluorine-bridging[9]. Of interest was the relevance to, or difference from, Mukaiyama's method[1] with respect to the oxidation state of tin [Sn(II) or Sn(IV)], and the intriguing bonding properties of perchlorates of group XIV elements; the ionic or covalent character of organosilyl perchlorates has generated numerous discussions[10a], that have recently been extended to organotin perchlorate[10b].

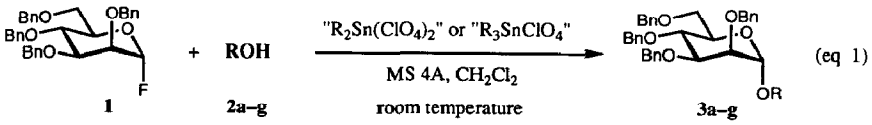
In this paper, we describe that the species generated from Bu_2SnCl_2 and two equivalents of $AgClO_4$ indeed exhibits high reactivity for the activation of glycosyl fluorides.

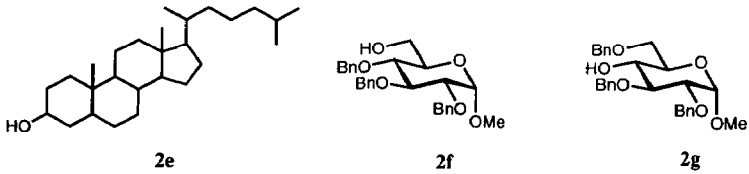
RESULTS AND DISCUSSION

As a model substrate, 2,3,4,6-tetra-*O*-benzyl-α-D-mannosyl fluoride[11] (**1**) was chosen, and its glycoside formation with 2,4-dimethyl-3-pentanol (**2a**) was tested (eq *1*). Five types of organotin chlorides (Bu_2SnCl_2, Me_2SnCl_2, Bu_3SnCl, Me_3SnCl, and Ph_3SnCl) were obtained from commercial sources and were used for this model study.

These organotin chlorides were treated with silver perchlorate with the intention of generating two types of perchlorate species, $R_2Sn(ClO_4)_2$ (type A) and R_3SnClO_4 (type B), which were used without isolation as activators for the reaction of **1** and **2a**. Experimentally, the substrate–reagent ratio was set as follows: Based on fluoride **1** (1.0 equiv), **2a** (2.0 equiv) was used. The type A promoter was generated in situ from the dialkyltin dichloride (0.5 equiv for **1**) and $AgClO_4$ (1.0 equiv), and the reactions were conducted at room temperature. As for type B promoters, trialkyltin chlorides (1.0 equiv for **1**) and $AgClO_4$ (1.0 equiv) were used; the other reaction parameters were the same as before. Although neither the extent of ligand exchange (chloride → perchlorate) nor the exact composition of the species generated under these reaction conditions has been determined, nevertheless, it soon became clear that type A promoters are far more reactive than type B (Table I).

We can assess the relative reactivity of the promoters by comparing the reaction times in the table, namely the approximate times needed for complete consumption of the starting material. As shown in entries 1 and 2, the type A promoters, generated from R_2SnCl_2 and 2 equiv of $AgClO_4$, exhibited high reactivity and the reactions were complete very rapidly at room temperature. By contrast, the type B





promoters, generated from R_3SnCl and $AgClO_4$, were far less reactive, although the final product yields were excellent. It is notable that variation of the alkyl ligands of tin, for instance methyl or *n*-butyl, caused a marked difference in the α/β-selectivity (entries 3 and 4). Triphenyltin chloride, even though a type B promoter, showed a fairly high reactivity. The result employing Cp_2HfCl_2–$AgClO_4$ (ratio 1 : 2) is shown in entry 6 for comparison.

Our working hypothesis for this activation parallels that of the metallocene-based one[5b]. By changing the ligand from chloride to perchlorate, the organotin species acquires the ability for activating glycosyl fluorides. The fact that, for a type A promoter, 0.5 equiv of R_2SnCl_2 suffices for activating one mole of glycosyl fluoride is explained as follows. Double ligand-exchange generates the diperchlorate species **A**, which is highly electrophilic (eq 2). Upon activating the first equivalent of glycosyl fluoride, species **A** would be converted into mono-fluoro species **B**, which

TABLE I

Reaction of glycosyl fluoride **1** with alcohol **2a** employing various "organotin perchlorates"

Entry	Promoter	Reaction time (min)	Yield (%)	α/β
1	Bu_2SnCl_2–$2AgClO_4$	10	95	96/4
2	Me_2SnCl_2–$2AgClO_4$	10	94	97/3
3	Bu_3SnCl–$AgClO_4$	50	99	91/9
4	Me_3SnCl–$AgClO_4$	150	99	66/34
5	Ph_3SnCl–$AgClO_4$	10	99	96/4
6	Cp_2HfCl_2–$2AgClO_4$	10	92	97/3

TABLE II

Reaction of glycosyl fluoride **1** with alcohol **2b**

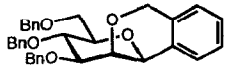
Entry	Promoter	Reaction time (min)	Yield (%)	α/β
1	Bu_2SnCl_2–$2AgClO_4$	30	91	98/2
2	Me_2SnCl_2–$2AgClO_4$	35	55	98/2
3	Ph_3SnCl–$AgClO_4$	45	91	53/47
4	Cp_2HfCl_2–$2AgClO_4$	30	86	97/3

may be assumed to have the potential for activating another equivalent of glycosyl fluoride, because of the highly electron-withdrawing nature of fluoride.

$$\underset{\mathbf{A}}{R_2Sn(ClO_4)_2} \longrightarrow \underset{\mathbf{B}}{R_2SnF(ClO_4)} \longrightarrow \underset{\mathbf{C}}{R_2SnF_2} \quad \text{(eq 2)}$$

For the next step of the reactivity evaluation the glycosyl acceptor employed was *tert*-butyl alcohol (**2b**) and the reaction was performed in a similar manner (Table II). Although the reason is not obvious, $Me_2Sn(ClO_4)_2$ proved to be less reactive than its dibutyl counterpart (entries 1 and 2). The triphenyltin system was reactive but the α/β selectivity was poor.

Applications of this reagent system for various glycosyl acceptors is summarized in Table III. This table shows the wide applicability of the present activation method for various substrates. The following points are worthy of note: (*1*) The α/β selectivity depends heavily on the steric demand of the glycosyl acceptor; almost no α/β selectivity was observed for cyclohexylmethanol (entry 3), whereas high α-selectivities were observed for sugar-derived acceptors (entries 6 and 7). (*2*) The activation level is quite high and allows the glycosylation of a wide range of acceptors. However, the yield decreased significantly for glycosylation of the 4-hydroxyl group of the glucose derivative **2g** (entry 7), and a side product arising from the internal Friedel–Crafts reaction was obtained[5b].



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The present study clearly shows the promising reactivity of $Bu_2Sn(ClO_4)_2$, generated from Bu_2SnCl_2 and 2 equiv of $AgClO_4$, for the activation of glycosyl fluorides, which should find utility in glycoside synthesis.

EXPERIMENTAL

General methods.—Infrared (IR) spectra were recorded on a Jasco A-202 spectrometer. ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were

TABLE III

Reaction of glycosyl fluoride 1 and various acceptors employing $Bu_2Sn(ClO_4)_2$

Entry	ROH	Time (min)	Product	Yield (%)	α/β
1	**2a**	10	**3a**	95	96/4
2	**2b**	30	**3b**	91	98/2
3	**2c**	10	**3c**	93	52/48
4	**2d**	10	**3d**	96	84/16
5	**2e**	10	**3e**	quant	80/20
6	**2f**	10	**3f**	92	96/4
7	**2g**	10	**3g**	68	99/1

measured on a JNM GX-400 spectrometer. Chemical shifts are expressed in parts per million downfield from internal Me_4Si ($\delta = 0$). For ^{13}C NMR spectra, only the peaks at fields above 110 ppm are shown and the data for the anomeric carbons are summarized in Table IV. All experiments dealing with air- and moisture-sensitive compounds were carried out under an atmosphere of dry Ar. For thin layer chromatographic (TLC) analysis, Merck precoated plates (Silica Gel 60 GF_{254}, 0.25 mm) were used. Preparative TLC was performed on Merck Kieselgel 60 PF_{254} (No. 7747). For HPLC analysis, a Shimadzu liquid chromatograph (LC-6A) was used. Dichloromethane was distilled successively from P_2O_5 and CaH_2, and stored over 4A molecular sieves.

General procedure for glycosidation of **1** *employing* Bu_2SnCl_2–$AgClO_4$ *as the promoter.*—A mixture of alcohol **2** (1.5 mmol), Bu_2SnCl_2 (0.5 mmol), $AgClO_4$ (1

TABLE IV

^{13}C NMR and HPLC data for glycosides[12] **3a–3g**

	α or β	^{13}C NMR ($CDCl_3$)		HPLC [a]	
		δ (ppm)	$J_{C\text{-}1,H\text{-}1}$	t_R (min)	Eluent [b]
3a	α	100.8	166.7	11.7	*A*
	β	102.7	151.2	10.0	
3b	α	92.5	165.2	14.2	*A*
	β	96.1	151.2	18.8	
3c	α	98.0	168.1	11.5	*A*
	β	102.0	152.6	14.6	
3d	α	95.7	168.8	13.0	*A*
	β	99.5	155.4	16.3	
3e	α	95.8	164.5	18.5	*A*
	β	99.3	152.6	19.5	
3f	α	98.9	170.2	16.6	*B*
	β	[c]	[c]	15.6	
3g	α	100.5	170.9	9.5	*B*
	β	[c]	[c]	12.0	

[a] Column: Zolbax-sil (Du Pont), 4.6 mm i.d.×25 cm; Flow rate: 1.2 mL/min; Detection: 260 nm. [b] Eluent: *A*, 93:7 hexane–EtOAc; *B*, 4:1 hexane–EtOAc. [c] Not determined.

mmol), and powdered 4A molecular sieves (~300 mg) in CH_2Cl_2 (3 mL) was stirred for 10 min at room temperature. To the mixture was added dropwise glycosyl fluoride **1** (1 mmol) in CH_2Cl_2. The reaction was stopped by adding satd $NaHCO_3$ solution. The mixture was filtered through a Celite pad, and the filtrate was extracted with EtOAc, and the combined organic extract was washed with brine and dried (Na_2SO_4). After removal of the solvent, the residue was chromatographed on silica gel to give the glycoside as a mixture of anomers. The ratio of the anomers was determined by HPLC, and the pure α anomer isolated by preparative TLC. All new compounds gave satisfactory combustion analysis data ($\pm 0.4\%$).

2,4-Dimethylpentan-3-yl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**3a**-α).—The α anomer was isolated by preparative TLC (4:1 hexane–EtOAc, R_f 0.50; β anomer, R_f 0.44). **3a**-α; $[\alpha]_D^{26}$ +28° (*c* 0.84, $CHCl_3$); IR, ν_{max} 2930, 1950, 1880, 1810, 1740, 1600, 1495, 1450, 1380, 1360, 1200, 1080, 900, 840, 820, 790, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.15–7.40 (m, 20 H), 4.88 (d, 1 H, *J* 10.7 Hz), 4.83 (d, 1 H, $J_{1,2}$ 1.95 Hz, H-1), 4.48–4.75 (m, 7 H), 4.05 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.2$ Hz, H-4), 3.90–3.95 (m, 1 H, H-5), 3.92 (dd, 1 H, $J_{5,6a}$ 2.2, J_{gem} 10.2 Hz, H-6a), 3.81 (dd, 1 H, $J_{5,6b}$ 4.4, J_{gem} 10.2 Hz, H-6b), 3.76 (dd, 1 H, $J_{1,2}$ 1.95, $J_{2,3}$ 2.2 Hz, H-2), 3.68 (dd, 1 H, $J_{2,3}$ 2.2, $J_{3,4}$ 10.2 Hz, H-3), 3.01 (t, 1 H, *J* 4.9 Hz), 1.65–1.85 (m, 2H), 0.90 (d, 3 H, *J* 7.3 Hz), 0.86 (d, 3 H, *J* 6.8 Hz), 0.75 (d, 3 H, *J* 7.3 Hz), and 0.71 (d, 3 H, *J* 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 100.8, 91.1, 80.3, 75.4, 73.3, 72.4, 69.3, 30.6, 30.3, 20.6, 20.2, 18.2, and 17.9.

tert-*Butyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside* (**3b**-α).—The α anomer was isolated by preparative TLC (9:1 hexane–EtOAc, 4 times; R_f 0.34). **3b**-α; $[\alpha]_D^{26}$ +37° (*c* 1.4, $CHCl_3$); IR, ν_{max} 2950, 1960, 1880, 1820, 1750, 1605, 1500, 1450, 1395, 1370, 1250, 1200, 1080, 900, 845, 805, 740, 705 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.12–7.40 (m, 20 H), 5.11 (d, 1 H, $J_{1,2}$ 1.95 Hz, H-1), 4.88 (d, 1 H, *J* 10.7 Hz), 4.78 (d, 1 H, *J* 12.2 Hz), 4.59–4.72 (m, 4 H), 4.48–4.52 (m, 2 H), 4.01 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.2$ Hz, H-4), 3.90–3.96 (m, 2 H), 3.80 (dd, 1 H, $J_{5,6a}$ 4.4, J_{gem} 10.7 Hz, H-6a), 3.69 (dd, 1 H, $J_{2,3}$ 2.2, $J_{3,4}$ 10.2 Hz, H-3), 3.58 (dd, 1 H, $J_{1,2}$ 1.95, $J_{2,3}$ 2.2 Hz, H-2), and 1.15 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 92.5, 80.5, 76.1, 75.6, 73.3, 72.4, 69.4 and 28.5.

Cyclohexylmethyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**3c**-α).—The α anomer was isolated by preparative TLC (4:1 hexane–EtOAc, R_f 0.57). **3c**-α; $[\alpha]_D^{26}$ +24° (*c* 1.3, $CHCl_3$); IR, ν_{max} 2900, 1955, 1880, 1810, 1740, 1605, 1500, 1450, 1395, 1360, 1205, 1080, 900, 840, 790, 735, 695 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.15–7.38 (m, 20 H), 4.87 (d, 1 H, *J* 10.7 Hz), 4.82 (d, 1 H, $J_{1,2}$ 1.95 Hz, H-1), 4.76 (d, 1 H, *J* 12.7 Hz), 4.71 (d, 1 H, *J* 12.7 Hz), 4.60–4.68 (m, 3 H), 4.55 (d, 1 H, *J* 12.2 Hz), 4.51 (d, 1 H, *J* 10.7 Hz), 3.98 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 3.89 (dd, 1 H, $J_{5,6a}$ 2.4, J_{gem} 9.8 Hz, H-6a), 3.70–3.81 (m, 4 H), 3.45 (dd, 1 H, *J* 6.8 and 9.8 Hz), 3.15 (dd, 1 H, *J* 6.3 and 9.8 Hz), 1.40–1.80 (m, 5 H), 1.05–1.30 (m, 4 H), and 0.80–0.95 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 98.0, 80.3, 75.1, 73.3, 72.5, 71.8, 69.3, 37.8, 30.1, 29.9, 26.5, 25.8 and 25.7.

Cyclohexyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**3d-α**).—The anomers could not be separated by preparative TLC. IR, ν_{max} 2875, 1950, 1875, 1805, 1740, 1600, 1495, 1445, 1355, 1200, 1070, 900, 840, 790, 730, 690 cm^{-1}; ^1H NMR of **3d-α** ($CDCl_3$): δ 7.15–7.39 (m, 20 H), 5.00 (d, 1 H, $J_{1,2}$ 1.95 Hz, H-1), 4.88 (d, 1 H, *J* 10.7 Hz), 4.60–4.79 (m, 5 H), 4.43–4.58 (m, 2 H), 3.98 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.93 (dd, 1 H, $J_{5,6a}$ 2.9, J_{gem} 9.8 Hz, H-6a), 3.83–3.88 (m, 1 H, H-5), 3.79 (dd, 1 H, $J_{5,6b}$ 4.4, J_{gem} 9.8 Hz, H-6b), 3.73 (dd, 1 H, $J_{2,3}$ 2.2, $J_{3,4}$ 9.3 Hz, H-3), 3.72 (dd, 1 H, $J_{1,2}$ 1.95, $J_{2,3}$ 2.2 Hz, H-2), 3.54–3.61 (m, 1 H), and 1.13–1.84 (m, 10 H); ^{13}C NMR of **3d-α** ($CDCl_3$): δ 95.7, 80.4, 75.3, 74.8, 73.3, 72.2, 69.6, 33.3, 31.3, 25.7, 24.0 and 23.7.

Cholestan-3-yl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (**3e-α**).—The α anomer was isolated by preparative TLC (4:1 hexane–EtOAc, R_f 0.69). **3e-α**; $[\alpha]_D^{24}$ +32° (*c* 1.1, $CHCl_3$); IR, ν_{max} 2900, 1950, 1875, 1810, 1735, 1605, 1500, 1450, 1380, 1360, 1210, 1060, 900, 840, 800, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.15–7.38 (m, 20 H), 5.02 (d, 1 H, $J_{1,2}$ 1.95 Hz, H-1), 4.88 (d, 1 H, *J* 10.7 Hz), 4.76 (d, 1 H, *J* 12.2 Hz), 4.71 (d, 1 H, *J* 12.2 Hz), 4.60–4.68 (m, 3 H), 4.53 (d, 1 H, *J* 12.2 Hz), 4.50 (d, 1 H, *J* 10.7 Hz), 3.97 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 3.92 (dd, 1 H, $J_{5,6a}$ 2.4, J_{gem} 9.8 Hz, H-6a), 3.83–3.88 (m, 1 H, H-5), 3.79 (dd, 1 H, $J_{5,6b}$ 4.4, J_{gem} 9.8 Hz, H-6b), 3.71–3.76 (m, 2 H), 3.49–3.58 (m, 1 H) and 0.64–1.97 (m, 46 H); ^{13}C NMR ($CDCl_3$): δ 95.8, 80.5, 76.1, 75.3, 73.3, 72.1, 69.6, 56.5, 56.4, 54.4, 45.0, 42.6, 40.1, 39.5, 36.9, 36.2, 35.8, 35.6, 34.6, 32.1, 30.7, 28.7, 28.6, 28.0, 27.5, 24.2, 23.9, 22.8, 22.6, 21.3, 18.7, 12.3, and 12.1.

Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α-mannopyranosyl)-α-D-glucopyranoside (**3f-α**).—The anomers could not be separated by preparative TLC. IR, ν_{max} 2900, 1950, 1870, 1810, 1740, 1600, 1495, 1450, 1390, 1360, 1205, 1090, 900, 840, 780, 730, 690 cm^{-1}; ^1H NMR of **3f-α** ($CDCl_3$): δ 7.11–7.39 (m, 35 H), 4.98 (d, 1 H, *J* 11.2 Hz), 4.97 (d, 1 H, $J_{1',2'}$ 1.95 Hz, H-1′), 4.88 (d, 1 H, *J* 11.2 Hz), 4.86 (d, 1 H, *J* 11.2 Hz), 4.55–4.81 (m, 9 H), 4.49 (d, 1 H, *J* 11.2 Hz), 4.48 (d, 1 H, *J* 11.2 Hz), 4.43 (d, 1 H, *J* 11.2 Hz), 3.99 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 3.97 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.8$ Hz, H-3), 3.81–3.87 (m, 2 H), 3.78 (dd, 1 H, $J_{1',2'}$ 1.95, $J_{2',3'}$ 2.2 Hz, H-2′), 3.57–3.72 (m, 5 H), 3.45 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 9.8 Hz, H-2), 3.39 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), and 3.30 (s, 3 H); ^{13}C NMR of **3f-α** ($CDCl_3$): δ 98.9, 97.2, 82.1, 80.0, 77.6, 75.8, 75.0, 74.6, 73.2, 72.4, 69.8, 65.8, and 55.1.

Methyl 2,3,6-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-α-D-glucopyranoside (**3g-α**).—The α anomer was isolated by preparative TLC (7:3 hexane–EtOAc, R_f 0.43). **3g-α**; $[\alpha]_D^{27}$ +13.5° (*c* 1.9, $CHCl_3$); IR, ν_{max} 2900, 1955, 1880, 1810, 1740, 1600, 1500, 1450, 1385, 1205, 1050, 900, 840, 780, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.11–7.35 (m, 35 H), 5.29 (d, 1 H, $J_{1',2'}$ 1.95 Hz, H-1′), 5.08 (d, 1 H, *J* 12.2 Hz), 4.84 (d, 1 H, *J* 10.7 Hz), 4.67 (d, 1 H, *J* 12.2 Hz), 4.46–4.62 (m, 9 H), 4.423 (d, 1 H, *J* 12.2 Hz), 4.417 (d, 1 H, *J* 12.2 Hz), 4.30 (d, 1 H, *J* 12.2 Hz), 4.21 (d, 1 H, *J* 12.2 Hz), 3.97 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 3.86 (dd, 1 H, *J* 2.4 and 9.8 Hz), 3.63–3.84 (m, 7 H), 3.54–3.59 (m, 1 H), 3.53 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$

9.8 Hz, H-2), and 3.39 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 100.5, 97.7, 81.5, 80.0, 77.7, 76.3, 75.0, 73.3, 73.1, 69.8, 69.4, and 55.2

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