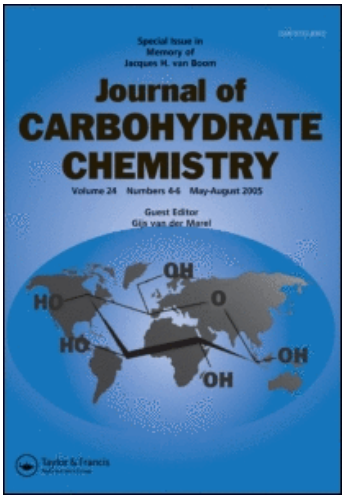

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C-GLYCOSYLATED ARYL TINS: VERSATILE BUILDING BLOCKS FOR ARYL *C*-GLYCOSIDE GLYCOMIMETICS

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ABSTRACT

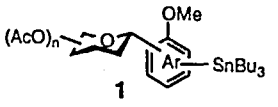
C-glycosylated aryl tins have been prepared as versatile building blocks of physiologically stable glycomimetics for glycoepitopes that have been recognized to serve biologically important roles in cell biochemistry.

INTRODUCTION

Glycoconjugates, also termed glycolipids, glycoproteins or proteoglycans, located on cell surfaces or extracellular matrices, have been recognized to be strongly involved in the basic phenomena governing multicellular society, such as cell differentiation and growth, recognition and adhesion, fertilization and implantation, growth of cancer cells, immunity, aging and so forth, and also in adhesion of bacteria and viruses through intercellular interaction.[1]

Some of these phenomena are thought to depend on specific small motifs of oligosaccharides in huge glycoconjugates. In a sialyl Lewis^x which mediates leukocytes rolling on endothelial cells and results in leukocyte migration to the inflamed tissue, the carboxylic acid in the sialic acid, and the galactose and the fucose moieties are necessary to

interact with selectins.[2] A pentasaccharide constitutes the active site on heparins for the antithrombin III binding activity.[3]



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In the course of our continuous effort to seek physiologically stable glycomimetics of those biologically important glycoepitopes, aryl *C*-glycosides have been proposed.[4]

We describe here the preparation of *C*-glycosylated aryl tins (**1**) that are versatile building blocks for aryl *C*-glycoside glycomimetics, coupled with palladium mediated C-C bond formation reactions. The palladium catalyzed cross-coupling reactions of organotin compounds with a variety of organic electrophiles were well documented[5] because of the mildness of the reactions and of their compatibility with a wide range of functional groups on either coupling partners.

RESULTS AND DISCUSSION

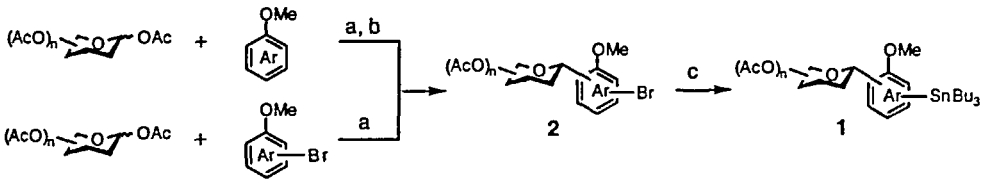
Although there are a couple of possible methods to introduce a stannyl group onto an aromatic ring,[6] the palladium-catalyzed substitution reaction of the corresponding aromatic halide is considered to be a general purpose method and tolerable by a wide range of functional groups.[6a,6d]

The general synthetic methods of the *C*-glycosylated aryl tins (**1**) are as follows (Scheme 1).

1. Peracetylated sugars were coupled with aromatics under $SnCl_4$-AgOTfa conditions to afford aryl *C*-glycosides (**3**).[4] The conventional bromination of the aryl *C*-glycosides (**3**) afforded the *C*-glycosylated aryl bromides (**2**). Brominated aromatics with peracetylated sugars using $SnCl_4$-AgOTfa also afforded the *C*-glycosylated aryl bromides (**2**). Each method was selected depending on the utility or the reactivity of aromatic rings.

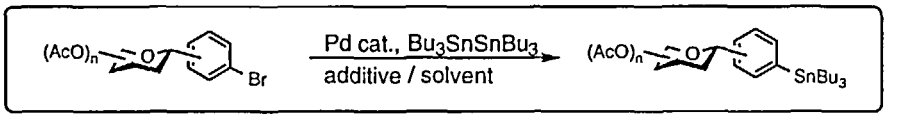
2. Subsequent stannylation of the *C*-glycosylated aryl bromides (**2**) was accomplished by *C*-glycosylated aryl bromides (**2**), bis(tributyltin), tetrakis(triphenylphosphine)palladium (0) and potassium carbonate (1 / 1.2 / 0.1 / 2) in refluxing toluene (condition A).[6a] As some of the products (**1**) are labile to silica gel and give destannyl-protonated products, a rapid, short column is recommended for purification.

In the Table, some of the selected examples are arranged in order of orientation of sugar parts and tins.

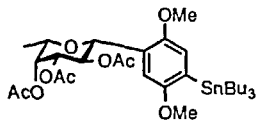


Scheme 1. General Synthetic Methods for *C*-Glycosylated Aryl Tins
a. $SnCl_4$, AgOTfa / CH_2Cl_2. b. Br_2 / CCl_4. c. $Bu_3SnSnBu_3$, $Pd(PPh_3)_4$, K_2CO_3 / toluene.

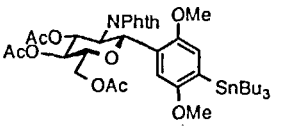
TABLE. Versatile *C*-Glycosylated Aryl Tins



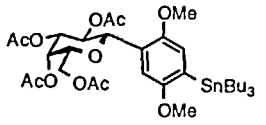
1,4-Oriented *C*-glycosylated aryl tins



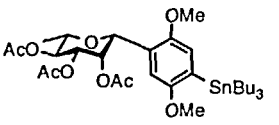
1a: 77%[a]



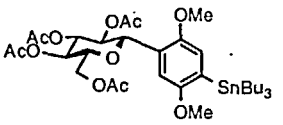
1d: 58%[b]



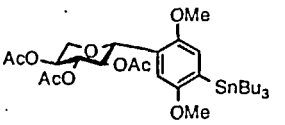
1b: 66%[a]



1e: 56%[b]

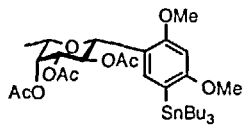


1c: 67%[b]

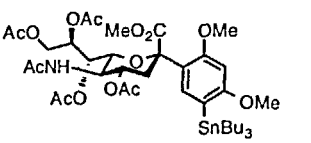


1f: 54%[b]

1,3-Oriented *C*-glycosylated aryl tins



1g: 57%[a]



1h: 38%[c]

a. Condition A; *C*-Glycosylated aryl bromide : $Bu_3SnSnBu_3$: $Pd(PPh_3)_4$: K_2CO_3 = 1 : 1.2 : 0.1 : 2 in refluxing toluene. b. Condition B; same as condition A but 1.6 eq of $Bu_3SnSnBu_3$ was used. c. Condition C; *C*-glycosylated aryl bromide : $Bu_3SnSnBu_3$: $Pd(OAc)_2$: $P(nBu)_3$: K_2CO_3 = 1 : 1.2 : 0.1 : 2 in refluxing 1,4-dioxane.

Although condition A was effective for the preparation of *C*-fucosylated or *C*-galactosylated aryl tins, it failed to afford good yields in cases such as glucose-, glucosamine-, rhamnose- and xylose-derived aryl bromides. The addition of a slight excess bis(tributyltin) (1.6 eq) was found to afford a fairly good yield for each of the above cases (condition B).

Noteworthy is the attainment of a *C*-sialylated aryl tin (**1h**), which will be a promising building block to provide the glycomimetics of sialylated epitopes that are considered to play a key role in cell communications. However, the synthesis of the *C*-sialylated aryl tin (**1h**) using either condition led to some problems in purification. After several trials to find a condition that would provide the pure *C*-sialylated aryl tin (**1h**) in good yield, palladium acetate (II) (0.1 eq), tri-*n*-butylphosphine (0.2 eq) and potassium carbonate (2 eq) in refluxing 1,4-dioxane was found to afford the pure product (**1h**) in 38% yield (condition C).

The protective group was readily converted from the acetyl group to the benzyl group by the conventional methods without any problems (Scheme 2). The feasibility of the protective group conversion will expand the use of these building blocks.

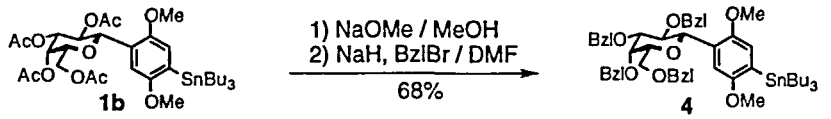
The palladium coupling of *C*-glycosylated aryl tins with a wide range of electrophiles like aryl halides, benzyl halides, vinyl halides, allyl halides, acid halides and so forth will be reported elsewhere.

EXPERIMENTAL

General methods. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Column chromatography was conducted using silica gel 60 (E. Merck 9385, 230-400 mesh). Melting points were measured with a Yanaco MP-500D and were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT-IR-8900 spectrometer. ^{1}H NMR spectra were measured on a JEOL-JNM-EX-270 (270 MHz) or a JEOL JNM-GX-270 (270 MHz) spectrometer. Chemical shifts from ^{1}H NMR spectra are reported relative to tetramethylsilane (δ 0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were recorded with a JEOL HX-100, a SX-102A or a JMS-AX-505H mass spectrometer. Optical rotation was measured on a Perkins-Elmer 241 polarimeter. All experiments were carried out under a nitrogen atmosphere. In experiments requiring dry solvents, dry CH_2Cl_2 and toluene were purchased from Kanto Chemica. 1M $SnCl_4$ CH_2Cl_2 solution was purchased from Aldrich. Other chemicals were used as purchased.

Procedure for aryl *C*-glycosidation of sugar acetates and *p*-dimethoxybenzene.

1,4-Dimethoxy-2-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)benzene (3a). To a mixture of L-fucose tetraacetate (10 g, 30 mmol), *p*-dimethoxybenzene (6.2 g, 45



Scheme 2. Benzyl Protected *C*-Glycosylated Aryl Tins

mmol) and AgOTfa (9.9 g, 45 mmol) in CH_2Cl_2 (150 mL) at 0 °C was added $SnCl_4$ 1M CH_2Cl_2 solution (1.5 mL, 1.5 mmol) dropwise. After the reaction mixture was stirred for 2 h at 0 °C, 1N HCl aqueous solution (20 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 3:1) to provide the product (6.7 g, 16 mmol) in 54% yield: TLC R_f 0.50 (hexane/EtOAc 3:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.06 (s, 1H, Ar), 6.80 (s, 2H, Ar), 5.45 (d, 1H, J = 3.3 Hz, H_4), 5.21 (dd, 1H, J = 9.9 Hz and 3.3 Hz, H_3), 4.91 (d, 1H, J = 9.9 Hz, H_1), 3.96 (q, 1H, J = 6.3 Hz, H_5), 3.79 (s, 3H, OMe), 3.78 (s, 3H, OMe), 2.23 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.79 (s, 3H, OAc), 1.21 (d, 3H, J = 6.3 Hz, H_6); IR (KBr pellet) 2987, 2941, 2910, 2838, 1751, 1505 cm^{-1}; FABHRMS *m/z* 410.1574 (410.1577 Calcd for $C_{20}H_{26}O_9$ $[M]^+$); $[\alpha]_D^{23}$ +6.1° (*c* 0.833 CH_2Cl_2).

1,4-Dimethoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-benzene (3b). 82% yield; mp 76-78 °C; TLC R_f 0.56 (CH_2Cl_2/ether 5:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.04 (d, 1H, J = 2.4 Hz, Ar), 6.81 (d, 1H, J = 2.4 Hz, Ar), 6.81 (s, 1H, Ar), 5.52 (d, 1H, J = 3.5 Hz, H_4), 5.46 (t, 1H, J = 9.9 Hz, H_2), 5.21 (dd, 1H, J = 9.9 Hz and 3.5 Hz, H_3), 4.91 (d, 1H, J = 9.9 Hz, H_1), 4.21-4.04 (m, 3H, H_5 and H_6), 3.80 (s, 3H, OMe), 3.78 (s, 3H, OMe), 2.21 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.80 (s, 3H, OAc); IR (KBr pellet) 2940, 2800, 1752, 1505 cm^{-1}; EIHRMS *m/z* 468.1634 (468.1631 Calcd for $C_{22}H_{28}O_{11}$ $[M]^+$); $[\alpha]_D^{23}$ -2.2° (*c* 1.04 CH_2Cl_2).

1,4-Dimethoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)benzene (3c). 52% yield; TLC R_f 0.59 (hexane/EtOAc 3:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.95 (d, 1H, J =1.9 Hz, Ar), 6.82-6.80 (m, 2H, Ar), 5.37 (t, 1H, J = 9.0 Hz, H_3), 5.29 (t, 1H, J = 9.0 Hz, H_4), 5.23 (t, 1H, J = 9.0 Hz, H_2), 4.92 (d, 1H, J = 9.0 Hz, H_1), 4.27 (dd, 1H, J = 12.3 Hz and 4.7 Hz, H_6), 4.14 (dd, 1H, J = 12.3 Hz and 2.2 Hz, H_6), 3.89-3.80 (m, 1H, H_5), 3.79 (s, 3H, OMe), 3.77 (s, 3H, OMe), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.78 (s, 3H, OAc); IR (KBr pellet) 2999, 2949, 2838, 1754 cm^{-1}; FABHRMS *m/z* 468.1638 (468.1631 Calcd for $C_{22}H_{28}O_{11}$ $[M]^+$); $[\alpha]_D^{23}$ -11.4° (*c* 0.355 $CHCl_3$).

1,4-Dimethoxy-2-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)benzene (3d). 58% yield; TLC R_f 0.34 (hexane/EtOAc 3:2); ^{1}H NMR

(270 MHz, $CDCl_3$) δ 7.88-7.60 (m, 4H, Ar), 7.06 (d, 1H, J = 3.0 Hz, Ar), 6.71 (dd, 1H, J = 8.9 Hz and 3.0 Hz, Ar), 6.52 (d, 1H, J = 8.9 Hz, Ar), 6.17 (t, 1H, J = 10.0 Hz, H_3), 5.64 (d, 1H, J = 10.0 Hz, H_1), 5.28 (t, 1H, J = 10.0 Hz, H_4), 4.57 (t, 1H, J = 10.0 Hz, H_2), 4.35 (dd, 1H, J = 12.1 Hz and 4.7 Hz, H_6), 4.20 (dd, 1H, J = 12.1 Hz and 2.3 Hz, H_6), 4.09-4.00 (m, 1H, H_5), 3.77 (s, 3H, OMe), 3.36 (s, 3H, OMe), 2.11 (s, 3H, OAc), 2.07 (s, 3H, OAc), 1.88 (s, 3H, OAc); IR (KBr pellet) 2941, 2912, 2838, 1750, 1720 cm^{-1}; FABHRMS *m/z* 555.1752 (555.1741 Calcd for $C_{28}H_{29}O_{11}N$ $[M]^+$); $[\alpha]_D^{23}$ -60.1° (*c* 0.32 $CHCl_3$).

1,4-Dimethoxy-2-(2,3,4-tri-*O*-acetyl-β-L-rhamnopyranosyl)benzene (3e). 58% yield; TLC R_f 0.72 (hexane/EtOAc 3:1); ^1H NMR (270 MHz, $CDCl_3$) δ 7.06 (d, 1H, J = 2.8 Hz, Ar), 6.77, (dd, 1H, J = 8.9 Hz and 2.8 Hz, Ar), 6.72 (d, 1H, J = 8.9 Hz, Ar), 5.58 (dd, 1H, J = 3.4 Hz and 1.2 Hz, H_2), 5.27 (dd, 1H, J = 10.1 Hz and 3.4 Hz, H_3), 5.14 (t, 1H, J = 10.1 Hz, H_4), 5.01 (s, 1H, H_1), 3.78 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.68 (dq, 1H, J = 10.1 Hz and 6.2 Hz, H_5), 2.08 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.90 (s, 3H, OAc), 1.32 (d, 3H, J = 6.2 Hz, H_6); IR (KBr pellet) 2984, 2941, 2839, 1748 cm^{-1}. FABHRMS *m/z* 410.1575 (410.1573 Calcd for $C_{20}H_{26}O_9$ $[M]^+$); $[\alpha]_D^{23}$ +2.9° (*c* 1.00 $CHCl_3$).

1,4-Dimethoxy-2-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)benzene (3f). 49% yield; TLC R_f 0.30 (hexane/EtOAc 3:2); ^1H NMR (270 MHz, $CDCl_3$) δ 6.92 (d, 1H, J = 2.3 Hz, Ar), 6.82 (dd, 1H, J = 9.1 Hz and 2.3 Hz, Ar), 6.79 (d, 1H, J = 9.1 Hz, Ar), 5.36 (t, 1H, J = 9.3 Hz, H_2), 5.27 (t, 1H, J = 9.3 Hz, H_3), 5.15 (dt, 1H, J = 9.3 Hz and 5.8 Hz, H_4), 4.81 (d, 1H, J = 9.3 Hz, H_1), 4.22 (dd, 1H, J = 11.2 Hz and 5.5 Hz, H_5), 3.80-3.71 (m, 1H, H_5), 3.79 (s, 3H, OMe), 3.76 (s, 3H, OMe), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.78 (s, 3H, OAc); IR (thin film) 2999, 2949, 2915, 2838, 1752 cm^{-1}; FABHRMS *m/z* 396.1415 (396.1421 Calcd for $C_{19}H_{24}O_9$ $[M]^+$); $[\alpha]_D^{23}$ -29.6° (*c* 0.395 $CHCl_3$).

Procedure for bromination of aryl *C*-glycosides (3).

1-Bromo-2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-benzene (2a). Br_2 (0.62 mL, 12 mmol) was added dropwise to a solution of 1,4-dimethoxy-2-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)benzene (**3a**) (4.1 g, 10 mmol) in CCl_4 (100 mL) at 0 °C. After the reaction mixture was stirred for 2 h at 0 °C, H_2O (30 mL) was added and then extracted with CH_2Cl_2 (100 mL). The CH_2Cl_2 solution was washed by aqueous $NaHCO_3$ solution, aqueous $Na_2S_2O_3$ solution, and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The remainder was purified by column chromatography on silica gel (hexane/EtOAc 4:1) to provide the product (3.32 g, 6.78 mmol) in 68% yield: mp 172-173 °C; TLC R_f 0.36 (hexane/EtOAc 3:2); ^1H NMR (270 MHz, $CDCl_3$) δ 7.07 (s, 1H, Ar), 7.03 (s, 1H, Ar), 5.48 (t, 1H, J = 10.1 Hz, H_2), 5.37 (d, 1H, J = 2.9 Hz, H_4), 5.21 (dd,

1H, J = 10.1 Hz and 2.9 Hz, H_3), 4.87 (d, 1H, J = 10.1 Hz, H_1), 3.97 (q, 1H, J = 6.6 Hz, H_5), 3.89 (s, 3H, OMe), 3.80 (s, 3H, OMe), 2.24 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.81 (s, 3H, OAc), 1.22 (d, 3H, J = 6.6 Hz, H_6); IR (KBr pellet) 2985, 2966, 2943, 2851, 1752 cm^{-1}; FABHRMS *m/z* 488.0684 (488.0682 Calcd for $C_{20}H_{25}BrO_9$, $[M]^+$); $[\alpha]_D^{23}$ +16.4° (*c* 1.00 CH_2Cl_2).

1-Bromo-2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)benzene (2b). 70% yield; TLC R_f 0.33 (hexane/EtOAc 3:2); ^1H NMR (270 MHz, $CDCl_3$) δ 7.08 (s, 1H, OAc), 7.01 (s, 1H, OAc), 5.52 (d, 1H, J = 3.4 Hz, H_4), 5.48 (t, 1H, J = 9.9 Hz, H_2), 5.21 (dd, 1H, J = 9.9 Hz and 3.4 Hz, H_3), 4.89 (d, 1H, J = 9.9 Hz, H_1), 4.19-4.05 (m, 3H, H_5 and H_6), 3.88 (s, 3H, OMe), 3.80 (s, 3H, OMe), 2.21 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.81 (s, 3H, OAc); IR (KBr pellet) 3479, 2964, 2943, 1751, 1495, 1370, 1219 cm^{-1}; FABHRMS *m/z* 547.0810 (547.0815 Calcd for $C_{22}H_{28}O_{11}{}^{79}Br$ $[M+H]^+$); $[\alpha]_D^{23}$ +22° (*c* 0.80 CH_2Cl_2).

1-Bromo-2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)benzene (2c). 74% yield; TLC R_f 0.46 (hexane/EtOAc 3:2); ^1H NMR (270 MHz, $CDCl_3$) δ 7.07 (s, 1H, Ar), 6.95 (s, 1H, Ar), 5.36 (t, 1H, J = 9.2Hz, H_3), 5.30 (t, 1H, J = 9.2 Hz, H_4), 5.23 (t, 1H, J = 9.2 Hz, H_2), 4.92 (d, 1H, J = 9.2 Hz, H_1), 4.27 (dd, 1H, J = 12.4 Hz and 4.9 Hz, H_6), 4.14 (dd, 1H, J = 12.4 Hz and 2.1 Hz, H_6), 3.87 (s, 3H, OMe), 3.87-3.77 (m, 1H, H_5), 3.80 (s, 3H, OMe), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.80 (s, 3H, OAc); IR (KBr pellet) 2947, 1754 cm^{-1}; FABHRMS *m/z* 546.0739 (546.0737 Calcd for $C_{22}H_{27}O_{11}{}^{79}Br$ $[M]^+$); $[\alpha]_D^{23}$ -18.7° (*c* 1.00 CH_2Cl_2).

1-Bromo-2,5-dimethoxy-4-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)benzene (2d). 96% yield; TLC R_f 0.37 (hexane/EtOAc 3:2); ^1H NMR (270 MHz, $CDCl_3$) δ 7.88-7.65 (m, 4H, Ar), 7.04 (s, 1H, Ar), 6.82 (s, 1H, Ar), 6.13 (t, 1H, J = 10.0 Hz, H_3), 5.64 (d, 1H, J = 10.0 Hz, H_1), 5.29 (t, 1H, J = 10.0 Hz, H_4), 4.59 (t, 1H, J = 10.0 Hz, H_2), 4.35 (dd, 1H, J = 12.3 Hz and 4.9 Hz, H_6), 4.20 (dd, 1H, J = 12.3 Hz and 2.2 Hz, H_6), 4.10-4.00 (m, 1H, H_5), 3.88 (s, 3H, OMe), 3.41 (s, 3H, OMe), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.87 (s, 3H, OAc); IR (KBr pellet) 2936, 1751, 1721 cm^{-1}; FABHRMS *m/z* 633.0845 (633.0846 Calcd for $C_{28}H_{28}O_{11}N^{79}Br$ $[M]^+$); $[\alpha]_D^{23}$ -75.1° (*c* 0.23 CH_2Cl_2).

1-Bromo-2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-L-rhamnopyranosyl)-benzene (2e). 96% yield; TLC R_f 0.46 (hexane/EtOAc 1:1); ^1H NMR (270 MHz, $CDCl_3$) δ 7.07 (s, 1H, Ar), 7.00 (s, 1H, Ar), 5.57 (dd, 1H, J = 3.3 Hz and 1.1 Hz, H_2), 5.25 (dd, 1H, J = 9.9 Hz and 3.3 Hz, H_3), 5.14 (t, 1H, J = 9.9 Hz, H_4), 4.97 (s, 1H, H_1), 3.87 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.75-3.62 (m, 1H, H_5), 2.08 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.91 (s, 3H, OAc), 1.34 (d, 3H, J = 6.1 Hz, H_6); IR (KBr pellet) 2983, 2940, 2851, 1750 cm^{-1}; FABHRMS *m/z* 488.0680 (488.0682 Calcd for $C_{20}H_{25}O_9{}^{79}Br$ $[M]^+$); $[\alpha]_D^{23}$ +33.9° (*c* 1.00 CH_2Cl_2).

1-Bromo-2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)benzene (2f). 72% yield; TLC R_f 0.40 (hexane/EtOAc 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.27 (s, 1H, Ar), 7.06 (s, 1H, Ar), 5.35 (t, 1H, J = 9.4 Hz, H_2), 5.27 (t, 1H, J = 9.4 Hz, H_3), 5.22-4.97 (m, 1H, H_4), 4.81 (d, 1H, J = 9.4 Hz, H_1), 4.21 (dd, 1H, J = 11.0 Hz and 5.5 Hz, H_5), 3.86 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.46 (t, 1H, J = 11.0 Hz, H_5), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.80 (s, 3H, OAc); IR (thin film) 3014, 2947, 2852, 1755 cm^{-1}; FABHRMS *m/z* 474.0523 (474.0526 Calcd for $C_{19}H_{23}O_9{}^{79}Br$ $[M]^+$); $[\alpha]_D{}^{23}$ -28.6° (*c* 0.860 CH_2Cl_2).

Procedure for aryl *C*-glycosidation of sugar acetates and 1-bromo-2,4-dimethoxybenzene.

1-Bromo-2,4-dimethoxy-5-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-benzene (2g). A 1M $SnCl_4$ CH_2Cl_2 solution (75 mL, 75 mmol) was added to a mixture of L-fucose tetraacetate (16.6 g, 50 mmol), 1-bromo-2,4-dimethoxybenzene (15.2 g, 70 mmol) and AgOTfa (16.6 g, 75 mmol) in CH_2Cl_2 (75 mL) at 0 °C under N_2 atmosphere. After the reaction mixture was stirred for 4 h at 0 °C, aqueous $NaHCO_3$ solution was added and stirred for 20 min. The inorganic material was filtered off over a Celite^R pad and the filtrate was extracted several times with CH_2Cl_2. The combined CH_2Cl_2 solution was washed with brine, and dried over anhydrous $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide the product (8.2 g, 17 mmol) in 34% yield: mp 172-173 °C; TLC R_f 0.23 (hexane/EtOAc 2:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.59 (s, 1H, Ar), 6.41 (s, 1H, Ar), 5.41 (t, 1H, J = 10.0 Hz, H_2), 5.34 (d, 1H, J = 4.3 Hz, H_4), 5.18 (dd, 1H, J = 10.0 Hz and 4.3 Hz, H_3), 4.77 (d, 1H, J = 10.0 Hz, H_1), 3.92 (q, 1H, J = 6.6 Hz, H_5), 3.89 (s, 3H, OMe), 3.85 (s, 3H, OMe), 2.25 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.80 (s, 3H, OAc), 1.21 (d, 3H, J = 6.6 Hz, H_6); IR (KBr pellet) 3468, 2983, 2943, 2851, 1749, 1605, 1505 cm^{-1}; FABHRMS *m/z* 489.0755 (489.0760 calcd for $C_{20}H_{26}O_9{}^{79}Br$ $[M+H]^+$); $[\alpha]_D{}^{23}$ +23.3° (*c* 0.56 CH_2Cl_2).

1-Bromo-2,5-dimethoxy-4-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-glycero-D-galacto-2-neuropyranosinate)benzene (2h). 70% yield; TLC R_f 0.53 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (s, 1H, Ar), 6.42 (s, 1H, Ar), 5.52 (dd, 1H, J = 10.9 Hz and 5.2 Hz, H_4), 5.47-5.41 (m, 1H, amide NH), 5.35 (dd, 1H, J = 5.8 Hz and 2.0 Hz, H_7), 5.28 (dt, 1H, J = 5.8 Hz and 3.0 Hz, H_8), 4.41 (dd, 1H, J = 12.4 Hz and 3.0 Hz, H_6), 4.23-4.10 (m, 2H, H_5 and H_9), 3.93-3.80 (m, 1H, H_9), 3.90 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.71 (s, 3H, OMe), 2.94 (dd, 1H, J = 13.3 Hz and 5.2 Hz, H_3), 2.18 (s, 3H, NAc), 2.10 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.90 (s, 3H, OAc), 1.85 (t, 1H, J = 13.3 Hz, H_3); IR (KBr pellet) 3377, 2956, 1746 cm^{-1}; FABHRMS m/z 690.1382 (690.1398 Calcd for $C_{28}H_{37}O_{14}N^{79}Br$ $[M+H]^+$); $[\alpha]_D{}^{23}$ -4.6° (*c* 0.72 CH_2Cl_2).

Procedure for stannylation (Condition A and B).

Tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-phenyl]stannane (1a). A suspended solution of 1-bromo-2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)benzene (**2a**) (6.9 g, 14.1 mmol), tetrakis(triphenylphosphine)palladium (810 mg, 0.7 mmol), potassium carbonate (1.98 g, 15 mmol) and bis(tributyltin) (9.28 g, 16 mmol) in toluene (150 mL) was refluxed for 10 h under a nitrogen atomosphere. After diluting the resulting mixture with EtOAc (150 mL), the organic solution was washed by aqueous KF solution, aqueous $NaHCO_3$ solution, and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The remainder was purified by column chromatography on silica gel (hexane/EtOAc 9:1) to provide the product (7.60 g, 10.9 mmol) in 77% yield: TLC R_f 0.63 (hexane/EtOAc 2:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.88 (s, 1H, Ar), 6.87 (s, 1H, Ar), 5.56 (t, 1H, J = 9.9 Hz, H_2), 5.37 (d, 1H, J = 3.2 Hz, H_4), 5.21 (dd, 1H, J = 9.9 Hz and 3.2 Hz, H_3), 4.90 (d, 1H, J = 9.9 Hz, H_1), 3.98 (q, 1H, J = 6.6 Hz, H_5), 3.81 (s, 3H, OMe), 3.75 (s, 3H, OMe), 2.24 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.78 (s, 3H, OAc), 1.6-0.8 (m, 27H, Bu), 1.22 (d, 3H, J = 6.6 Hz, H_6); IR (KBr pellet) 2956, 2928, 2872, 2852, 1752 cm^{-1}; FABHRMS *m/z* 719.2527 (719.2526 Calcd for $C_{32}H_{52}O_9Na^{116}Sn$ [M+Na]$^+$); $[\alpha]_D^{23}$ +15.3° (*c* 0.91 CH_2Cl_2).

Tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl)phenyl]stannane (1b). 60% yield; TLC R_f 0.67 (hexane/EtOAc 3:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.88 (s, 1H, Ar), 6.84 (s, 1H, Ar), 5.55 (t, 1H, J = 10.0 Hz, H_2), 5.51 (d, 1H, J = 3.4 Hz, H_4), 5.20 (dd, 1H, J = 10.0 Hz and 3.4 Hz, H_3), 4.91 (d, 1H, J = 10.0 Hz, H_1), 4.22-4.10 (m, 3H, H_5 and H_6), 3.80 (s, 3H, OMe), 3.73 (s, 3H, OMe), 2.20 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.76 (s, 3H, OAc), 1.59-1.46 (m, 6H, CH_2), 1.38-1.22 (m, 6H, CH_2), 1.04-0.98 (m, 6H, CH_2), 0.86 (t, 9H, J = 7.2 Hz, CH_3); IR (liquid film) 2956, 2928, 2872, 2851, 1754 cm^{-1}; FABHRMS *m/z* 777.2585 (777.2581 Calcd for $C_{34}H_{54}O_{11}Na^{116}Sn$ [M+Na]$^+$; $[\alpha]_D^{23}$ -6.1° (*c* 1.15 CH_2Cl_2).

Tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyrano-syl)phenyl]stannane (1c). 67% yield; TLC R_f 0.71 (hexane/EtOAc 3:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.88 (s, 1H, Ar), 6.79 (s, 1H, Ar), 5.44-5.19 (m, 3H, H_3, H_4 and H_2), 4.95 (d, 1H, J = 9.7 Hz, H_1), 4.27 (dd, 1H, J = 12.3 Hz and 4.7 Hz, H_6), 4.14 (dd, 1H, J = 12.3 Hz and 2.2 Hz, H_6), 3.90-3.80 (m, 1H, H_5), 3.81 (s, 3H, OMe), 3.73 (s, 3H, OMe), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.78 (s, 3H, OAc), 1.59-1.42 (m, 6H, CH_2), 1.31(m, 6H, CH_2), 1.02 (t, 6H, J = 7.4 Hz, CH_2), 0.87 (t, 9H, J = 7.4 Hz, CH_3); IR (KBr pellet) 2956, 2927, 2872, 2851, 1755 cm^{-1}; FABHRMS *m/z* 777.2585 (777.2581 Calcd for $C_{34}H_{54}O_{11}Na^{116}Sn$ [M+Na]$^+$); $[\alpha]_D^{23}$ -53.1° (*c* 0.85 CH_2Cl_2).

Tri-*n*-butyl[2,5-dimethoxy-4-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)phenyl]stannane (1d). 58% yield; TLC R_f 0.35

(hexane/EtOAc 2:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87-7.56 (m, 4H, Ar), 6.89 (s, 1H, Ar), 6.62 (s, 1H, Ar), 6.13 (t, 1H, J = 10.0 Hz, H_3), 5.68 (d, 1H, J = 10.0 Hz, H_1), 5.30 (t, 1H, J = 10.0 Hz, H_4), 4.65 (t, 1H, J = 10.0 Hz, H_2), 4.34 (dd, 1H, J = 12.2 Hz and 4.7 Hz, H_6), 4.21 (dd, 1H, J = 12.2 Hz and 2.1 Hz, H_6), 4.10-3.98 (m, 1H, H_5), 3.74 (s, 3H, OMe), 3.45 (s, 3H, OMe), 2.10 (s, 3H, OAc), 2.07 (s, 3H, OAc), 1.87 (s, 3H, OAc), 1.50-1.35 (m, 6H, CH_2), 1.35-1.18 (m, 6H, CH_2), 0.95 (t, 6H, J = 7.1 Hz, CH_2), 0.83 (t, 9H, J = 7.2 Hz, CH_3); IR (liquid film) 2956, 2928, 2871, 2852, 1752, 1722 cm^{-1}; FABHRMS *m/z* 880.2441 (880.2453 Calcd for $C_{40}H_{55}O_{11}K^{116}Sn$ $[M+K]^+$); $[\alpha]_D^{23}$ -58.4° (*c* 0.55 CH_2Cl_2).

Tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-L-rhamnopyranosyl)phenyl]stannane (1e). 56% yield; TLC R_f 0.76 (hexane/EtOAc 2:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.94 (s, 1H, Ar), 6.79 (s, 1H, Ar), 5.56 (d, 1H, J = 3.3 Hz, H_2), 5.27 (dd, 1H, J = 9.9 Hz and 3.3 Hz, H_4), 5.15 (t, 1H, J = 9.9 Hz, H_3), 5.03 (s, 1H, H_1), 3.79 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.75-3.62 (m, 1H, H_5), 2.08 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.89 (s, 3H, OAc), 1.58-1.40 (m, 6H, CH_2), 1.40-1.20 (m, 6H, CH_2), 1.00 (t, 6H, J = 8.1 Hz, CH_2), 0.87 (t, 9H, J = 7.2 Hz, CH_3); IR (KBr pellet) 2953, 2928, 2869, 2854, 1750 cm^{-1}; FABHRMS *m/z* 735.2246 (735.2266 Calcd for $C_{32}H_{52}O_9K^{116}Sn$ $[M+K]^+$); $[\alpha]_D^{23}$ +32.6° (*c* 0.99 CH_2Cl_2).

Tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)phenyl]stannane (1f). 54% yield; TLC R_f 0.76 (hexane/EtOAc 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.87 (s, 1H, Ar), 6.78 (s, 1H, Ar), 5.36 (t, 1H, J = 9.3 Hz, H_2), 5.31 (t, 1H, J = 9.3 Hz, H_3), 5.23-5.09 (m, 1H, H_4), 4.84 (d, 1H, J = 9.3 Hz, H_1), 4.21 (dd, 1H, J = 11.0 Hz and 5.8 Hz, H_5), 3.81 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.48 (t, 1H, J = 11.0 Hz, H_5), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.78 (s, 3H, OAc), 1.57-1.42 (m, 6H, CH_2), 1.42-1.23 (m, 6H, CH_2), 1.02 (t, 6H, J = 8.0 Hz, CH_2), 0.87 (t, 9H, J = 7.3 Hz, CH_3); IR (liquid film) 2956, 2927, 2871, 2853, 1758 cm^{-1}; FABHRMS *m/z* 721.2078 (721.2109 Calcd for $C_{31}H_{50}O_9K^{116}Sn$ $[M+K]^+$); $[\alpha]_D^{23}$ -30.3° (*c* 0. 73 CH_2Cl_2).

Tri-*n*-butyl[2,4-dimethoxy-5-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)phenyl]stannane (1g). 57% yield; TLC R_f 0.77 (hexane/EtOAc 2:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.30 (s, 1H, Ar), 6.35 (s, 1H, Ar), 5.60 (t, 1H, J = 10.0 Hz, H_2), 5.34 (d, 1H, J = 2.3 Hz, H_4), 5.18 (dd, 1H, J = 10.0 Hz and 2.3 Hz, H_3), 4.74 (d, 1H, J = 10.0 Hz, H_1), 3.93 (q, 1H, J = 6.3 Hz, H_5), 3.86 (s, 3H, OMe), 3.75 (s, 3H, OMe), 2.22 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.75 (s, 3H, OAc), 1.70-0.80 (m, 27H, Bu), 1.20 (d, 3H, J = 6.3 Hz, H_6); IR (liquid film) 2956, 2930, 2872, 2852, 1753, 1593, 1579 cm^{-1}; FABHRMS *m/z* 723.2527 (723.2531 Calcd for $C_{32}H_{52}O_9Na^{120}Sn$ $[M+Na]^+$); $[\alpha]_D^{23}$ +22° (*c* 0.80 CH_2Cl_2).

Procedure for stannylation (Condition C).

Tri-*n*-butyl[2,5-dimethoxy-4-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-glycero-D-galacto-2-neuropyranosinate)phenyl]-stannane (1h). A suspended solution of 1-bromo-2,5-dimethoxy-4-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-glycero-D-galacto-2-neuropyranosinate)benzene (**2h**) (172.7 mg, 0.251 mmol), palladium (II) acetate (6.2 mg, 0.0276 mmol), tributylphosphine (20 μL, 0.080 mmol), potassium carbonate (71.6 mg, 0.518 mmol) and bis(tributyltin) (170 μL, 0.336 mmol) in 1,4-dioxane (5 mL) was refluxed for 8 h under a nitrogen atmosphere. After diluting the resulting mixture with EtOAc (10 mL), the organic solution was washed by aqueous KF solution, aqueous $NaHCO_3$ solution, and brine, dried over $MgSO_4$ and, concentrated *in vacuo*. The remainder was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to provide the product (86.2 mg, 0.0967 mmol) in 38% yield: TLC R_f 0.59 (hexane/EtOAc 1:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (s, 1H, Ar), 6.33 (s, 1H, Ar), 5.52 (dd, 1H, J = 10.6 Hz and 5.1 Hz, H_4), 5.42-5.37 (m, 2H, H_7 and amide NH), 5.21 (dd, 1H, J = 6.4 Hz and 2.8 Hz, H_8), 4.45 (dd, 1H, J = 12.4 Hz and 3.0 Hz, H_6), 4.24-4.10 (m, 2H, H_5 and H_9), 3.81-3.72 (m, 1H, H_9), 3.77 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.71 (s, 3H, OMe), 2.89 (dd, 1H, J = 13.3 Hz and 5.1 Hz, H_3), 2.17 (s, 3H, NAc), 2.05 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.90 (s, 3H, OAc), 1.73 (dd, 1H, J = 13.3 Hz and 11.3 Hz, H_3), 1.60-1.48 (m, 6H, CH_2), 1.40-1.23 (m, 6H, CH_2), 1.07-1.01 (m, 6H, CH_2), 0.90 (t, 9H, J = 7.2 Hz, CH_3); IR (liquid film) 3263, 3219, 3075, 3057, 3022, 3012, 2992, 2956, 2927, 1747 cm^{-1}; FABHRMS *m/z* 920.3160 (920.3164 Calcd for $C_{40}H_{63}O_{14}Na^{116}Sn$ $[M+Na]^+$); $[\alpha]_D^{23}$ -0.5° (*c* 0.82 CH_2Cl_2).

Tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-benzyl-β-D-galacto-pyranosyl)phenyl]stannane (4). NaOMe (28% MeOH solution; 0.5 mL) at rt was added to a solution of tri-*n*-butyl[2,5-dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopy-ranosyl)phenyl]stannane (**1b**) (1.03 g, 1.36 mmol) in MeOH (80 mL). After 1 h, the mixture was neutralized by Amberlite^R CG-50. The insoluble materials were filtered, and solvent of the filterate was removed *in vacuo*. NaH (55% oil; 0.36 g, 8.25 mmol) was added to the residue in DMF (10 mL) at 0 °C, the mixture was stirred for 15 min at rt, and then benzyl chloride (1 mL, 7.2 mmol) was added. After 4 h, the mixture was diluted with EtOAc (10 mL), washed with aqueous HCl solution (1N; 5 mL) and brine (5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. A purification of the resulting residue by column chromatography with ethyl acetate/hexane (1:5) provided the compound (0.88 g, 0.93 mmol) in 68% yield: TLC R_f 0.61 (hexane/EtOAc 5:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40-7.25 (m, 15H, Ar), 7.15-7.12 (m, 3H, Ar), 6.90-6.85 (m, 4H, Ar), 5.06

(d, 1H, J = 11.5 Hz, Bn), 4.79 (s, 3H, H_1 and Bn), 4.65 (d, 1H, J = 11.5 Hz, Bn), 4.50 (d, 1H, J = 10.5 Hz, Bn), 4.46 (d, 1H, J = 12.5 Hz, Bn), 4.43 (d, 1H, J = 12.5 Hz, Bn), 4.10 (d, 2H, J = 2.5 Hz, H_2 and H_3), 4.00 (d, 1H, J = 10.5 Hz, Bn), 3.76-3.74 (m, 2H, H_4 and H_5), 3.72 (s, 3H, OMe), 3.69-3.65 (m, 1H, H_6), 3.67 (s, 3H, OMe), 3.59 (dd, 1H, J = 9.0 Hz and 5.5 Hz, H_6), 1.55-1.49 (m, 6H, Bu), 1.35-1.27 (m, 6H, Bu), 1.05-1.02 (m, 6H, Bu), 0.86 (t, 9H, J = 7.0 Hz, Bu); IR (liquid film) 2925 cm^{-1}; FABHRMS *m/z* 969.4008 (969.4037 Calcd for $C_{54}H_{70}O_7Na^{116}Sn$ $[M+Na]^+$; $[\alpha]_D^{23}$ -14° (*c* 0.51 CH_2Cl_2).

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