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Chiral Auxiliary-Directed Asymmetric Ortho-Lithiation of (Arene)tricarbonylchromium Complexes

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(π-Arene)tricarbonylchromium complexes play a very important role in stereoselective reactions, and some asymmetric syntheses are based on the use of optically pure chiral complexes. A number of groups have established particular utilities of optically active arene chromium complexes for a variety of synthetic applications.[1] However, the utilization of this chemistry by synthetic chemists has been hampered by the limited availability of enantiomerically enriched (arene)tricarbonylchromium complexes. Traditionally, optically active complexes have been obtained through resolution procedures,[2] diastereoselective complexation of arenes bearing chiral auxiliaries,[3] a chiral base-mediated asymmetric synthesis,[4] the external ligand-controlled enantioselective addition of organometallic reagents to prochiral molecules,[5] or others.[6]

We investigated whether sugars, which are easily obtained, could be used as directing groups in the synthesis of arene chromium complexes. In this note, we describe a new and easy method for the asymmetric synthesis of chiral benzaldehyde complexes modified by a sugar moiety, and a control of stereochemistry of chiral benzaldehyde complexes by changing the sugar portion. This is the first example of using a sugar moiety as an chiral auxiliary on the coordinated arene ring.

Ligand **1**, prepared by the methylation[7] of commercially available methyl (+)-4,6-*O*-benzylidene-α-D-glucopyranoside, was converted into its chromium tricarbonyl complex, **2**, by standard methods ($Cr(CO)_6/Bu_2O$ and THF(10/1)/reflux/2 days) quantitatively (Scheme 1).

Complex **2** could be deprotonated by *n*-BuLi at −78 °C and subsequently functionalized with several electrophiles. When 1.2 equiv of *n*-BuLi was added to a diethyl ether solution of **2** at −78 °C and the resulting anion quenched with 5 equiv of $SiMe_3Cl$, a diastereomer **3a** was formed as a sole product in 74% yield. There was only one chemical shift (δ 5.32) for hydrogen at the benzylic carbon in addition to one chemical shift (δ 0.39) for the hydrogens of the trimethylsilyl group in the ^1H NMR spectrum. The isolated yields for **3** were between 65% and 98%. In all cases **3** is formed as a single diastereomer (>98% de, judged by ^1H NMR analysis). The results are summarized in Table 1. Assignment of the direction of asymmetric induction was accomplished by the following ways. An X-ray structural analysis of the trimethylsilyl-substituted product **3a** (Figure 1) revealed a 1*R*,2*S* configuration at the chiral centers on the arene ring.[2a,8] The glucopyranoside moiety retains its chair conformation. Simple acid hydrolysis (THF/ 50% aqueous H_2SO_4) of **3a** and **3b** gave the known aldehyde complexes **4a** ($[\alpha]^{22}_{D} = -145°$, $c = 0.17$, $CHCl_3$) in >98% ee and 100% yield and **4b** ($[\alpha]^{22}_{D} = -665°$, $c = 0.10$, $CHCl_3$) in >98% ee and 100% yield, respectively.[9] To obtain high yields of aldehyde complexes, it was required to heat the reaction mixture at reflux for 2 h.[10] The presence of a minor enantiomer was not detectable using a chiral shift reagent $Eu(hfc)_3$.[11]

In the same way, methyl 2,3-di-*O*-methyl-4,6-*O*-(phenylmethylene)-α-D-galactopyranoside[12] was converted into its chromium tricarbonyl complex, **5** in 94% yield (Scheme 2).

Complex **5** was less stable than **2**. Complex **5** could be deprotonated by *n*-BuLi at −78 °C and subsequently functionalized with Me_3SiCl to yield **6**. Hydrolysis of **6** by refluxing 50% aqueous H_2SO_4 for 2 h gave the known aldehyde complex **7** ($[\alpha]^{28}_{D} = 167°$, $c = 0.15$, $CHCl_3$) in 98% ee (judged by ^1H NMR analysis using a chiral shift reagent $Eu(hfc)_3$) and 81% yield.[9,10] Therefore, either enantiomer of the (arene)tricarbonylchromium complex can be obtained by the judicious choice of the sugar moiety.

Chelation via a heteroatom in chiral auxiliaries has been well established.[13] Pyranosides coordinated to $Cr(CO)_3$ are quite similar to the ferrocenyl acetal system prepared by Kagan *et al.*[13a] from triol. Thus, pyranoside-

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(10) When the hydrolysis of **3** or **6** was carried out at room temperature, it took about 1 day to complete the reaction and the hydrolysis reaction was less successful due to the decomplexation of the tricarbonylchromium as in the ref 8a.

(11) When ^1H NMR spectra (500 MHz) of **4a** and **4b** were taken in 0.015 M $Eu(hfc)_3$ $CDCl_3$ solution, only one enantiomer was found for each case.

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S0022-3263(97)01276-0 CCC: $14.00

Scheme 1

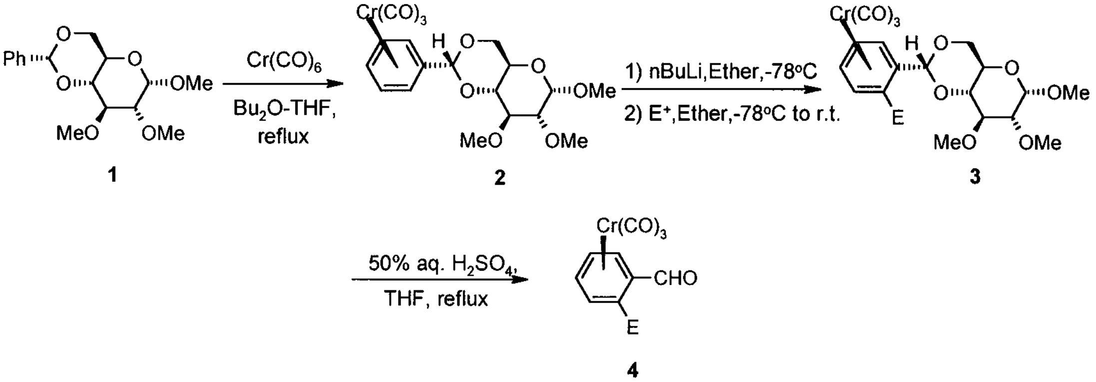
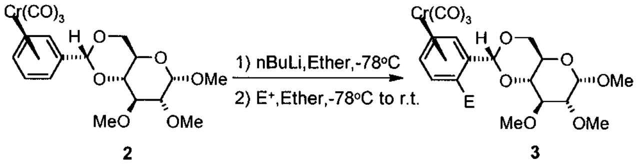


Table 1. Diastereoselective Lithiation/Alkylation Reations



electrophiles	E	compd	yield (%)[a]	de (%)[b]	[α]$_D$ (deg)[c]
Me_3SiCl	$SiMe_3$	**3a**	73	>98	73
MeI	Me	**3b**	65	>98	85
n-Bu_3SnCl	*n*-Bu_3Sn	**3c**	73	>98	37
PhCOPh	CPh_2OH	**3d**	98	>98	79
PhSSPh	SPh	**3e**	80	>98	389
Ph_2PCl	PPh_2	**3f**	74	>98	311
$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2$	**3g**	69	>98	127

[a] Yields of diastereomerically pure products. [b] Determined by ^{1}H NMR of a crude reaction product. [c] Measured in $CHCl_3$ at concentrations of 0.2–0.34 and temperatures of 22–24 °C.

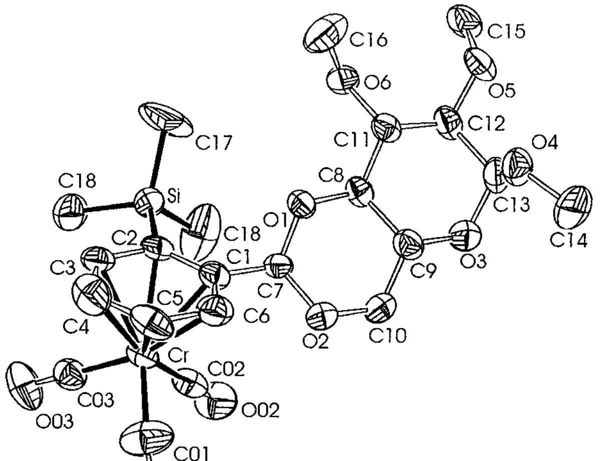


Figure 1. ORTEP drawing of **3a**.

directed metalation is presumed to occur via chelation of metal to the oxygen of the nearby methyl ether followed by selective delivery of base to one of the diastereotopic hydrogen atoms as in ferrocenyl acetal. We expect that at −78 °C the benzylic hydrogen atom preferentially occupies a site adjacent the $Cr(CO)_3$ moiety and the chelation of the lithium atom of *n*-BuLi to the methoxy group of the sugar moiety enhances the selective deprotonation of one of ortho protons on the arene ring to give an asymmetric metalation product. When we change the sugar moiety from glucose to galactose, the relative position of one of three methoxy groups on the sugar to the benzylic hydrogen becomes opposite. Thus, the origin of asymmetry operating in the metalation may come from the chelation through the methoxy group of the sugar moiety as shown in Scheme 3.

In conclusion, our preliminary results show that sugar can be employed as an efficient chiral auxiliary for the asymmetric formation of ortho-substituted (benzaldehyde)tricarbonylchromium complexes, and by choosing a proper sugar, one can obtain the proper plane chirality. From a practical standpoint, it is a particular note that the new method described is very efficient, uses a cheap, commercially available and easily removable chiral auxiliary, and gives products with predictable absolute configuration.

Experimental Section

All reactions were conducted under nitrogen using standard Schlenk type flask. Workup procedures were done in air. THF was freshly distilled from sodium benzophenone ketyl prior to use. Most organic compounds were purchased from Aldrich Chemical Co. and were used as received. ^{1}H or ^{13}C NMR spectra were obtained with a Bruker-300 or Bruker AMX-500 instrument. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer (spectra measured as films on NaCl by evaporation of the solvent). Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University. Mass spectra were recorded on a JEOL JMS AX 505 WA double focusing mass spectrometer. Optical rotations were measured by the JASCO DIP360 instrument. Compound **2** was prepared by the known procedures.[7] Compound **1** was synthesized by the published procedure.[14] Compounds **4a**, **4b**, and **7** were known compounds.[15,16]

Preparation of 2. Ligand **1** (3.0 g, 9.7 mmol) and $Cr(CO)_6$ (2.1 g, 9.7 mmol) were dissolved in a mixed solvent (110 mL) of THF and *n*-Bu_2O (v/v, 1/10). The solution was heated at 140 °C for 2 days. After cooling and chromatography on silica gel, **2** was obtained in 99% yield. ^{1}H NMR ($CDCl_3$) δ 5.56 (m, 2 H, Ph), 5.30–5.27 (m, 3 H, Ph), 5.26 (s, 1 H, benzylic), 4.82 (d, 3.7 Hz, 1 H), 4.24 (dd, 4.6, 10.1 Hz, 1 H), 3.72 (m, 1 H), 3.65 (dd, 10.3, 30.0 Hz, 2 H), 3.46 (t, 9.4 Hz, 1 H), 3.27 (dd, 3.8, 9.0 Hz, 1 H), 3.63 (s, 3 H, OCH_3), 3.55 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3); IR ν_{CO} 1960, 1880 cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_9Cr$: C, 51.13; H, 4.97. Found: C, 51.05; H, 4.63. $[\alpha]^{23}_D = +103°$ ($c = 0.2$, $CHCl_3$).

Preparation of 3. Complex **2** (0.20 g, 0.45 mmol) was dissolved in 20 mL of Et_2O at −78 °C. To the solution *n*-BuLi (0.54 mmol) was added dropwise for 30 s. The resulting solution was stirred for 1 h at −78 °C and treated with 5 equiv of electrophile at −78 °C. After stirring for an additional 1 h at

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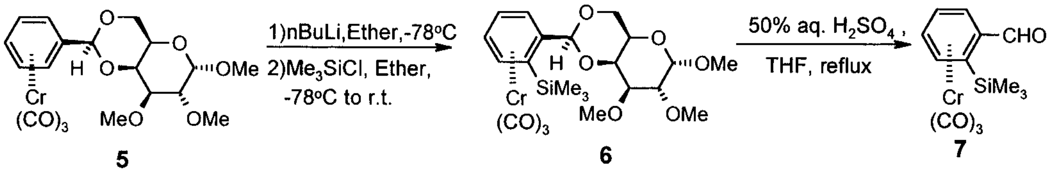
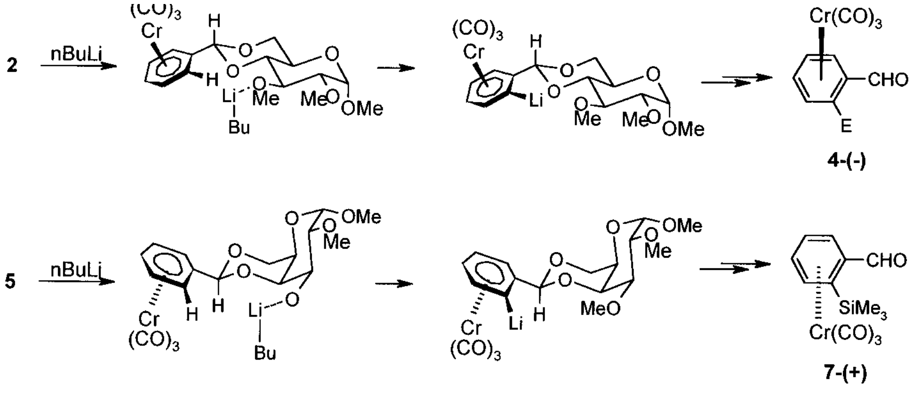
Scheme 2



Scheme 3



−78 °C, the solution was allowed to warm to room temperature. After quenching with 1 N aqueous NaOH, the organic layer was separated and chromatographed (hexane:Et$_2$O = 2:1) to yield **3**.

Compound **3a** (E = SiMe$_3$): ^{1}H NMR (CDCl$_3$) δ 5.63 (d, 6.5 Hz, 1 H, Ph), 5.57 (t, 6.5 Hz, 1 H, Ph), 5.41 (d, 6.5 Hz, 1 H, Ph), 5.32 (s, 1 H, benzylic), 5.17 (t, 6.0 Hz, 1 H, Ph), 4.84 (d, 3.5 Hz, 1 H), 4.27 (dd, 5.0, 10.5 Hz, 1 H), 3.71−3.52 (m, 3 H), 3.53 (s, 6 H, OCH$_3$), 3.45 (s, 3 H, OCH$_3$), 3.41 (m, 1 H), 3.29 (m, 1 H), 0.39 (s, 9 H, SiMe$_3$); IR ν_{CO} 1955, 1874 cm^{-1}. Anal. Calcd for C$_{22}$H$_{30}$O$_9$CrSi: C, 50.96; H, 5.83. Found: C, 51.15; H, 5.56. $[\alpha]^{22}_{D}$ = +73° (c = 0.2, CHCl$_3$).

Compound **3b** (E = Me): ^{1}H NMR (CDCl$_3$) δ 5.87 (d, 6.6 Hz, 1 H, Ph), 5.40 (t, 5.4 Hz, 1 H, Ph), 5.31 (s, 1 H, benzylic), 5.17 (t, 6.4 Hz, 1 H, Ph), 5.11 (d, 6.4 Hz, 1 H, Ph), 4.84 (d, 3.6 Hz, 1 H), 4.31 (dd, 3.9, 9.5 Hz, 1 H), 3.80−3.70 (m, 3 H), 3.60 (m, 1 H), 3.58 (s, 3 H, OCH$_3$), 3.55 (s, 3 H, OCH$_3$), 3.45 (s, 3 H, OCH$_3$), 3.25 (dd, 3.8, 12.9 Hz, 1 H), 2.26 (s, 3 H, Me) ppm; IR ν_{CO} 1955, 1869 cm^{-1}. Anal. Calcd for C$_{20}$H$_{24}$CrO$_9$: C, 52.18; H, 5.25. Found: C, 52.00; H, 4.80. $[\alpha]^{23}_{D}$ = +85° (c = 0.34, CHCl$_3$).

Compound **3c** (E = n-Bu$_3$Sn): ^{1}H NMR (CDCl$_3$): δ 5.52 (d, 6.3 Hz, 1 H, Ph), 5.47 (t, 5.9 Hz, 1 H, Ph), 5.31 (d, 5.8 Hz, 1 H, Ph), 5.18 (s, 1 H, benzylic), 5.16 (t, 1H, Ph), 4.84 (d, 2.9 Hz, 1 H), 4.24 (dd, 4.6, 9.9 Hz, 1 H), 3.75−3.62 (m, 3 H), 3.61 (s, 3 H, OCH$_3$), 3.59 (s, 3 H, OCH$_3$), 3.45 (s, 3 H, OCH$_3$), 3.40 (t, 9.5 Hz, 1 H), 3.27 9m, 1 H), 1.59−0.89 (m, 27 Hz, 3C$_4$H$_9$); ^{13}C NMR (CDCl$_3$): δ 232.9, 127.7, 125.6, 113.1, 99.9, 98.9, 97.9, 93.3, 91.0, 90.1, 81.3, 79.1, 68.3, 61.4, 60.7, 58.7, 28.6, 28.5, 26.9, 13.2, 11.2; IR ν_{CO} 1955, 1878 cm^{-1}; HRMS, m/z, (M$^+$) calcd 736.1725, obsd 736.1728. $[\alpha]^{23}_{D}$ = +37° (c = 0.1, CHCl$_3$).

Compound **3d** (E = −CPh$_2$OH): ^{1}H NMR (CDCl$_3$) δ 7.57−7.26 (m, 10 H, 2Ph), 5.65 (d, 6.4 Hz, 1 H, Ph), 5.44 (t, 6.2 Hz, 1 H, Ph), 5.08 (s, 1 H, benzylic), 5.02 (t, 6.3 Hz, 1 H, Ph), 5.00 (s, 1 H, OH), 4.83 (d, 6.6 Hz, 1 H, Ph), 4.76 (d, 3.2 Hz, 1 H), 4.15 (dd, 4.8, 10.2 Hz, 1 H), 3.62 (m, 1 H), 3.50 (m, 1 H), 3.48 (s, 3 H, OCH$_3$), 3.44 (s, 3 H, OCH$_3$), 3.41 (s, 3 H, OCH$_3$), 3.25 (m, 1 H), 3.13 (dd, 3.4, 9.1 Hz, 1 H), 2.87 (t, 9.5 Hz, 1 H); IR ν_{CO} 1962, 1862 cm^{-1}. Anal. Calcd for C$_{32}$H$_{32}$O$_{10}$Cr: C, 61.14; H, 5.13. Found: C, 60.96; H, 5.04. $[\alpha]^{24}_{D}$ = +79° (c = 0.2, CHCl$_3$).

Compound **3e** (E = SPh): ^{1}H NMR (CDCl$_3$) δ 7.56−7.38 (m, 5 H, Ph), 5.82 (d, 6.1 Hz, 1 H, Ph), 5.71 (s, 1 H, benzylic), 5.25−5.19 (m, 1 H, Ph), 4.98 (d, 6.4 Hz, 1 H, Ph), 4.84 (d, 3.7 Hz, 1 H), 4.32 (m, 1 H), 3.78−3.45 (m, 4 H), 3.53 (s, 3 H, OCH$_3$), 3.51 (s, 3 H, OCH$_3$), 3.46 (s, 3 H, OCH$_3$), 3.27 (dd, 3.6, 12.8 Hz, 1 H); IR ν_{CO} 1958, 1882 cm^{-1}. Anal. Calcd for C$_{25}$H$_{26}$O$_9$CrS: C, 54.15; H, 4.73; S, 5.78. Found: C, 54.09; H, 4.59; S, 5.85. $[\alpha]^{23}_{D}$ = +389° (c = 0.2, CHCl$_3$).

Compound **3f** (E = PPh$_2$): ^{1}H NMR (CDCl$_3$) δ 7.39−7.31 (m, 10 H, Ph), 6.10 (d, 5.7 Hz, 1 H, benzylic), 5.61 (m, 2 H, Ph), 5.06 (m, 2 H, Ph), 4.78 (d, 3.7 Hz, 1 H), 4.28 (dd, 4.6, 10.1 Hz, 1 H), 3.75 (t, 10.3 Hz, 1 H), 3.65 (m, 1 H), 3.44 (m, 1 H), 3.44 (s, 3 H, OCH$_3$), 3.42 (s, 3 H, O CH$_3$), 3.33 (t, 9.2 Hz, 1 H), 3.18 (dd, 3.7, 9.2 Hz, 1 H), 2.66 (s, 3 H, OCH$_3$); IR ν_{CO} 1961, 1888 cm^{-1}. Anal. Calcd for C$_{31}$H$_{31}$O$_9$CrP: C, 59.05; H, 4.96. Found: C, 59.30; H, 4.78. $[\alpha]^{23}_{D}$ = +311° (c = 0.2, CHCl$_3$).

Compound **3g** (E = CH$_2$=CHCH$_2$Br): ^{1}H NMR (CDCl$_3$) δ 5.95 (m, 1 H, vinyl), 5.83 (dd, 1.2, 6.7 Hz, 1 H), 5.39 (dt, 1.1, 6.2 Hz, 1 H), 5.37 (s, 1 H, benzylic), 5.25−5.09 (m, 4 H), 4.84 (d, 3.6 Hz, 1 H), 4.31 (m, 1 H), 3.72−3.70 (m, 2 H), 3.59 (s, 3H, OCH$_3$), 3.54 (s, 3 H, OCH$_3$), 3.46 (s, 3 H, OCH$_3$), 3.43−3.34 (m, 1 H), 3.27 (dd, 3.8, 9.5 Hz, 1 H), 3.20−3.12 (m, 1 H); IR ν_{CO} 1956, 1878 cm^{-1}. Anal. Calcd for C$_{31}$H$_{31}$O$_9$Cr: C, 54.32; H, 5.39. Found: C, 54.00; H, 5.13. $[\alpha]^{24}_{D}$ = 127° (c = 0.25, CHCl$_3$).

Hydrolysis of 3a. Compound **3a** (E = SiMe$_3$, 0.70 g, 0.13 mmol) was dissolved in 5 mL of THF. To the solution was added 0.5 mL of 50% aqueous H$_2$SO$_4$ solution. The resulting solution was refluxed for 2 h. After cooling and neutralization with aqueous NaHCO$_3$, the organic layer was separated and chromatographed (hexane:Et$_2$O = 20:1). Compound **4a** was obtained in 100% yield.

Compound **4a** (E = SiMe$_3$): ^{1}H NMR (CDCl$_3$) δ 9.74 (s, 1 H, CHO), 5.80 (d, 6.5 Hz, 1 H), 5.58 (t, 6.2 Hz, 1 H), 5.52 (t, 5.6 Hz, 1 H), 5.43 (d, 6.1 Hz, 1 H), 0.43 (s, 9 H, SiMe$_3$) ppm; IR ν_{CO} 1968, 1894 cm^{-1}; $[\alpha]^{22}_{D}$ = −145° (c = 0.17, CHCl$_3$). (lit. $[\alpha]^{18}_{D}$ = −154° (c = 1.14, CHCl$_3$) .

Compound **4b** (E = Me): ^{1}H NMR (CDCl$_3$) δ 9.80 (s, 1 H, CHO), 6.05 (d, 6.6 Hz, 1 H), 5.72 (t, 6.4 Hz, 1 H), 5.22 (t, 6.3 Hz, 1 H), 5.03 (d, 6.5 Hz, 1 H), 2.53 (s, 3 H, Me); IR ν_{CO} 1965, 1891 cm^{-1}; $[\alpha]_{D}$ = −665° (c = 0.1, CHCl$_3$, 20 °C) (lit. $[\alpha]^{20}_{D}$ = −664° (c = 0.26, CHCl$_3$)).

Preparation of 5. A typical procedure is the same as the synthesis of compound **2**, except using methyl 2,3-di-O-methyl-4,6-O-(phenylmethylene)-α-D-galactopyranoside instead of methyl 2,3-di-O-methyl-4,6-O-(phenylmethylene)-α-D-glucopyranoside. ^{1}H NMR (CDCl$_3$) δ 5.63 (m, 2 H), 5.32 (m, 3 H), 5.28 (s, 1 H, benzylic), 4.96 (d, 2.5 Hz, 1 H), 4.37−4.25 (m, 2 H), 4.04 (m, 1 H), 3.73−3.64 (m, 3 H), 3.52 (s, 3 H, OCH$_3$), 3.50 (s, 3 H, OCH$_3$), 3.45 (s, 3 H, OCH$_3$); IR ν_{CO} 1953, 1870 cm^{-1}. Anal. Calcd for C$_{19}$H$_{22}$CrO$_9$: C, 51.13; H, 4.97. Found: C, 51.05; H, 4.90; $[\alpha]^{20}_{D}$ = +127° (c = 0.2, CHCl$_3$).

Preparation of 6. A typical procedure was the same as the synthesis of **3**, except using **5** instead of **2**. Yield: 61%. ^{1}H NMR of major isomer (CDCl$_3$) δ 5.72 (d, 6.9 Hz, 1 H), 5.58 (t, 6.7 Hz, 1 H), 5.41 (d, 6.4 Hz, 1 H), 5.36 (s, 1 H, benzylic), 5.16 (t, 6.5 Hz, 1 H), 4.96 (d, 2.6 Hz, 1 H), 4.30−4.03 (m, 3 H), 3.70−3.62 (m, 3 H), 3.53 (s, 3 H, OCH$_3$), 3.50 (d, 3 H, OCH$_3$), 3.46 (s, 3 H, OCH$_3$), 0.40 (s, 9H, Si(CH$_3$)$_3$); IR ν_{CO} 1950, 1880 cm^{-1}. Due to the low stability, we failed to obtain the combustion data of **6**.

Preparation of 7. A typical procedure was the same as the synthesis of **3**, except using **6** instead of **3**. $[\alpha]^{28}_{D}$ = 168° (c = 0.15, CHCl$_3$) (lit. $[\alpha]^{20}_{D}$ = 146° (c = 0.1, CHCl$_3$)). Yield: 81%.

X-ray Crystal Determination of 3a. Crystals of **3a** were grown by slow evaporation of a solution of **3a** in hexane. Diffraction was measured by an Enraf-Nonius CAD4 diffractometer with a $\omega-2\theta$ scan method. Unit cells were determined by centering 25 reflections in the approximate 2θ range. Other relevant experimental details are in Supporting Information. The structure was solved by direct method using SHELXS-86 and refined by full-matrix least squares with SHELXL-93. All non hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were refined isotropically using riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

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Supporting Information Available: Spectroscopic data for new compounds and tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom positional and displacement parameters for **3a** (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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