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Synthesis of Sugar Derivatives of Tervalent Phosphorus Compounds and Their Application to Homogeneous Asymmetric Hydrogenation

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Diphenylphosphine and diphenylphosphinite derivatives of sugars such as methyl 6-deoxy-4-*C*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-talopyranoside, methyl 4-*O*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside, methyl 4-*C*,4-*O*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-talopyranoside, 6-deoxy-6-*C*-(diphenylphosphino)-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose, and 6-*O*-(diphenylphosphino)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose were synthesized by the reaction of diphenylphosphine-sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA) and/or diphenylphosphinous chloride-triethylamine with sugar derivatives. Homogeneous asymmetric hydrogenations of several prochiral olefins (α-acetylaminocinnamic acid, methyl α-acetylaminocinnamate, α-benzoylaminocinnamic acid, itaconic acid, and tiglic acid) were carried out using rhodium(I) catalysts with the tervalent chiral phosphorus derivatives of sugars. The highest optical yield for all the five substrates was obtained when di-μ-chloro-bis(cyclooctadiene)dirhodium(I) and 6-*O*-(diphenylphosphino)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose were used. The advantages of this method are the simplicity in the synthesis of the chiral phosphorus compound and the comparatively high optical yield in the asymmetric hydrogenation of olefins.

Homogeneous catalytic hydrogenation of olefins had been widely investigated since Wilkinson's works on chlorotris(triphenylphosphine)rhodium(I) were published.[1] The chirality of phosphine ligands of the reported rhodium catalysts appeared either on a phosphorus atom or on a carbon atom of the ligands. Various diphosphine ligands were often used for the asymmetric hydrogenation and they gave efficient results.[2] Monophosphines such as neomenthyldiphenylphosphine were used as the ligand of catalysts for asymmetric hydrogenation; these results, especially for monophosphines having a chiral center on the carbon atom,[3,4] were not always satisfactory.

Monosaccharides have several chiral carbon atoms in their skeletons; their applications to homogeneous asymmetric hydrogenation of prochiral materials are found in only a few papers. Iwami reported the asymmetric hydrogenation of olefins by rhodium complex with the ligand of 6-deoxy-6-(diphenylphosphino) derivative of galactose and 2-deoxy-2-(diphenylphosphino) derivative of altrose giving reduction products in optical yields of 2—39%.[5] Cullen and Sugi obtained an enantiomeric excess of 60—91% in the enantioselective hydrogenation of α-acetylaminoacrylic acid by rhodium catalyst having 2,3-bis(diphosphinite) derivative of glucopyranoside.[6,7] Recent studies on the efficiency of various tervalent diphosphorus derivatives of glucose and idose revealed that the ligand afforded up to 56% of enantiomeric excess *N*-acetylphenylalanine with *R* configuration in the hydrogenation.[8]

Our work on syntheses of carbohydrates having a phosphorus atom in the hemiacetal ring[9,10] suggested that we investigate the utility of chirality in the phosphorus-sugar skeleton as a chiral ligand. This paper deals with the synthesis of carbohydrates having a phosphorus-carbon linkage and the efficient application for asymmetric hydrogenation of olefins as a ligand of rhodium catalysts.

Results and Discussion

Synthesis of Chiral Phosphorus Ligands from Carbohydrates. Methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**1**) was oxidized with phosphorus pentaoxide in dimethyl sulfoxide–pyridine to give methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (**2**) in 75% yield.[11] The reaction of glucosid-4-ulose **2** with diphenylphosphine in the presence of triethylamine under nitrogen atmosphere afforded methyl 6-deoxy-4-*C*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-talopyranoside (**3**) in 13% yield.[12] The analogous reaction of glycosid-4-ulose **2** with diphenylphosphine oxide gave the corresponding 4-*C*-(diphenylphosphinyl) derivative of α-L-talopyranoside **4** in quantitative yield.

The reaction of compound **1** with diphenylphosphinous chloride in the presence of triethylamine under nitrogen atmosphere gave methyl 4-*O*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**5**) in 97% yield. The analogous reaction of compound **3** with diphenylphosphinous chloride gave methyl 4-*C*,4-*O*-bis(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-talopyranoside (**6**) in 54% yield.

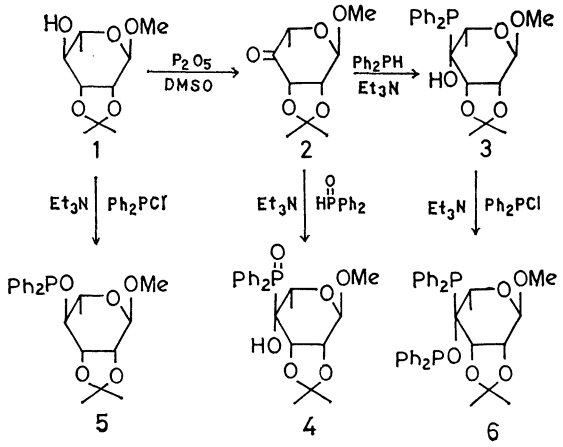
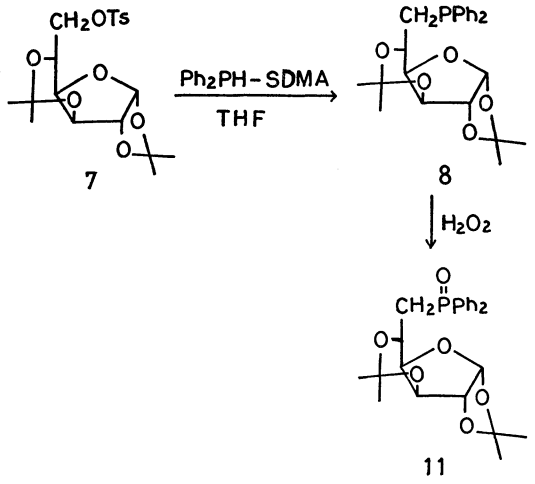


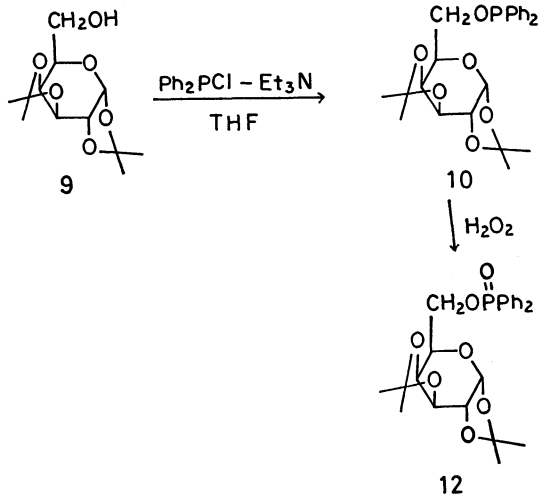
Table 1. Hydrogenation of olefins with $RhCl(C_8H_{14})_2$-compound **3**

Substrate[a]	Ratio of substrate to Rh (I)	Solvent[b]	Temp °C	Time h	H_2 Pressure atm
α-Acetamidocinnamic acid	40[c]	EtOH	r. t.	48	1
	40[c]	EtOH	50	120	1
	100[d]	Benzene–EtOH (1:1)	50	12	50
Itaconic acid	100[d]	MeOH	50	120	1

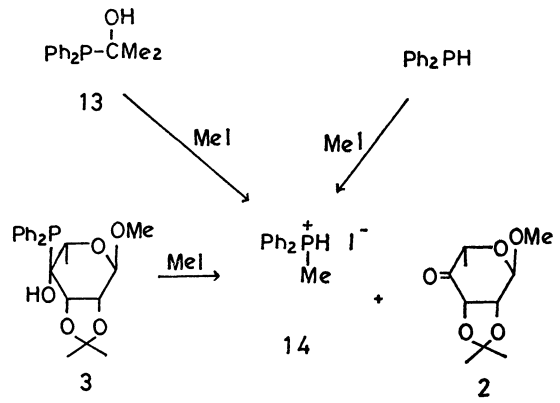
a) 10 mmol of the substrate was used. b) 15 ml of the solvent was used. c) 1 mmol of compound **3** and 1.5 mmol of triethylamine was used. d) 0.5 mmol of compound **3** and 0.6 mmol of triethylamine was used.

The reaction of 1,2:3,5-di-*O*-isopropylidene-6-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose (**7**) with diphenylphosphine in the presence of SDMA gave 6-deoxy-6-*C*-(diphenylphosphino)-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**8**) in 90% yield. The reaction of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**9**) with diphenylphosphinous chloride in the presence of triethylamine in tetrahydrofuran gave the corresponding phosphinite, 6-*O*-(diphenylphosphino)-1,2:3,4-di-*O*-isopropyridene-α-D-galactopyranose (**10**), in 46% yield. Oxidation of compounds **8** and **10** with hydrogen peroxide gave the oxides **11** and **12**. These tervalent phosphorus compounds were used as chiral ligands of rhodium catalysts.





Asymmetric Hydrogenation of Prochiral Olefins. Asymmetric hydrogenations of α-acetylaminocinnamic acid and itaconic acid were carried out using compound **3** as a chiral ligand for chlorobis(cyclooctene)-rhodium(I) complex. The hydrogenation under the conditions shown in Table 1 afforded almost none of the corresponding products. This result shows that the ligand cannot contribute to the hydrogenation. The hydrogenation of α-acetylaminocinnamic acid in benzene–ethanol (1:1) under 50 atm. of hydrogen by chlorobis(cyclooctene)rhodium(I) and (1-hydroxy-1-methylethyl)diphenylphosphine (**13**) catalyst was also unsuccessful. The reaction of compound **3** with methyl iodide gave methyldiphenylphosphonium iodide (**14**) and glycosid-4-ulose **2**, instead of the methiodide of compound **3**. The same result was observed when compound **13** was treated with methyl iodide; the reaction product was compound **14**.



These findings suggest that the adducts of diphenylphosphine, *i.e.*, compounds **3** and **13**, are not so stable as to make complexes with the rhodium compound.

The asymmetric hydrogenation of α-acetylaminocinnamic acid by chlorobis(cyclooctene)rhodium(I) in the presence of compound **5** or **6** as a chiral ligand gave *N*-acetylphenylalanine with *R* configuration as a major product (Table 2). The dissociation of diphenylphosphine observed in adduct **3** should be depressed in making a rhodium complex with compound **6**.

The asymmetric hydrogenation of prochiral olefins in the presence of di-μ-chloro-bis(cyclooctadiene)dirhodium(I) and compound **8** gave the results summarized in Table 3. The same procedure using the rhodium complex and compound **10** for the prochiral olefins gave good results, as shown in Table 4. Table 5 summarizes the observed optical yield given by di-

Table 2. Asymmetric hydrogenation of α-acetamidicinnamic acid[a] with $RhCl(C_8H_{14})_2$-compound **5** or **6**

Phosphorus compound[b]	Ratio of substrate to Rh (I)	Temp °C	Time h	Conversion %	Optical yield/% (Configuration)
5	100	r. t.	24	100	13 (*R*)
6	100	r. t.	48	100	4.7(*R*)

a) 10 mmol of the acid, 40 ml of benzene-ethanol (1:1), and 0.6 mmol of triethylamine were used. b) 0.4 mmol of compound **5** and 0.1 mmol of compound **6** were used.

Table 3. Asymmetric hydrogenation of prochiral olefins with $Rh_2Cl_2(C_8H_{12})_2$-compound **8**[a]

Substrate	Reaction time h	Product	Chemical yield/%	$[\alpha]_D^{14}$/° (Solvent)	Optical yield/% (Configuration)
α-Acetylamino-cinnamic acid	24	*N*-Acetylphenylalanine ethyl ester	99	−1.3 (*c* 1.3, EtOH)	9 (*R*)
Methyl α-acetyl-aminocinnamate	24	*N*-Acetylphenylalanine methyl ester	99	−0.4 (*c* 1.0, MeOH)	2 (*R*)
α-Benzoylamino-cinnamic acid	24	*N*-Benzoylphenylalanine ethyl ester	72	−0.8 (*c* 1.0, MeOH)	2 (*S*)
Itaconic acid	24	Methylsuccinic acid	96	+2.4 (*c* 1.3, EtOH)	14 (*R*)
Tiglic acid	24	2-Methylbutyric acid	98	−0.3 (*c* 2.0, EtOH)	2 (*R*)

a) The ratios of substrate to Rh(I) complex and of compound **8** to Rh(I) complex were 25:1 and 4:1, respectively. All hydrogenations were carried out in 10 ml of benzene-ethanol (1:1) in the presence of 0.2 ml of triethylamine at room temperature under atmospheric pressure of hydrogen.

Table 4. Asymmetric hydrogenation of prochiral olefins with $Rh_2Cl_2(C_8H_{12})_2$-compound **10**[a]

Substrate	Reaction time h	Product	Chemical yield/%	$[\alpha]_D^{14}$/° (Solvent)	Optical yield/% (Configuration)
α-Acetylamino-cinnamic acid	24	*N*-Acetylphenylalanine ethyl ester	99	−8.9 (*c* 1.2, EtOH)	67 (*R*)
Methyl α-acetyl-aminocinnamate	24	*N*-Acetylphenylalanine methyl ester	99	−6.6 (*c* 2.2, MeOH)	29 (*R*)
α-Benzoylamino-cinnamic acid	24	*N*-Benzoylphenylalanine ethyl ester	85	−12.8 (*c* 1.0, MeOH)	32 (*S*)
Itaconic acid	24	Methylsuccinic acid	99	−8.4 (*c* 1.0, EtOH)	49 (*S*)
Tiglic acid	24	2-Methylbutyric acid	99	−11.9 (*c* 2.8, EtOH)	62 (*R*)

a) The ratios of substate to Rh(I) complex and of compound **10** to Rh(I) complex were 25:1 and 4:1, respectively. All hydrogenations were carried out in 10 ml of benzene-ethanol (1:1) in the presence of 0.2 ml of triethylamine at room temperature under atmospheric pressure of hydrogen.

μ-chloro-bis(cyclooctadiene)dirhodium(I) and chloro-bis(cyclooctene)rhodium(I) with compound **10** as the ligand.

These results indicate that efficiency of chiral phosphinite **10** is good enough for the asymmetric hydrogenation of prochiral olefins, since the reported enantiomeric excess of *N*-acetylphenylalanine is up to 56% in the homogeneous asymmetric hydrogenation of α-acetylaminocinnamic acid by a rhodium catalyst using chiral ligands of 5,6-bis(diphenylphosphino) derivatives of glucose and idose.[8] This procedure seems to be a simple and efficient way for the asymmetric hydrogenation of prochiral olefins, compared with the other methods reported in the literature,[8,13] owing to the convenience in the ligand synthesis and to comparably high optical yields.

Experimental

Measurements. Melting and boiling points were uncorrected. ^{1}H-NMR spectra were measured on Hitachi-Perkin-Elmer R-24 (60 MHz) spectrometer with tetramethylsilane as an internal standard, and IR spectra on a Japan Spectroscopic Co. Ltd. A-3 infrared spectrophotometer. Optical rotations were measured on Japan Spectroscopic Co. Ltd. DIP-4 digital polarimeter.

Materials. The following materials were synthesized according to reported methods: α-acetylaminocinnamic acid,[14] α-benzoylaminocinnamic acid,[15] methyl α-acetylam-

TABLE 5. ASYMMETRIC HYDROGENATION OF PROCHIRAL OLEFINS WITH $Rh_2Cl_2(C_8H_{12})_2$- OR $RhCl(C_8H_{14})_2$-COMPOUND **10**[a]

Rh(I) Complex	Substrate	Reaction time / h	Product	Chemical yield/%	$[\alpha]_D^{17}$/° (Solvent)	Optical yield/% (Configuration)
$Rh_2Cl_2(C_8H_{12})_2$	α-Acetylamino-cinnamic acid	96	*N*-Acetylphenyl-alanine ethyl ester	78	−3.3 (*c* 0.9, EtOH)	25 (*R*)
	Itaconic acid	96	Methylsuccinic acid	100	−3.8 (*c* 1.8, EtOH)	22 (*S*)
	Tiglic acid	120	2-Methylbutyric acid	100	−2.8 (*c* 1.6, EtOH)	15 (*R*)
$RhCl(C_8H_{14})_2$	α-Acetylamino-cinnamic acid	216	*N*-Acetylphenyl-alanine ethyl ester	88	−0.7 (*c* 1.1, EtOH)	6 (*R*)
	Itaconic acid	216	Methylsuccinic acid	100	−2.3 (*c* 1.6, EtOH)	14 (*S*)
	Tiglic acid	216	2-Methylbutyric acid	100	−1.0 (*c* 1.4, EtOH)	5 (*R*)

a) The ratios of substrate to Rh(I) complex and of compound **10** to Rh(I) complex were 100:1 and 4:1, respectively. All hydrogenations were carried out in 10 ml of benzene-ethanol (1:1) in the presence of 0.2 ml of triethylamine at room temperature under under atmospheric pressure of hydrogene.

inocinnamate,[16] diphenylphosphine (bp 108.5—113 °C/2 mmHg[17]),[18] diphenylphosphinous chloride (bp 110 °C/0.5 mmHg),[19] chlorobis(cyclooctene)rhodium(I),[20] di-μ-chlorobis(cyclooctadiene)dirhodium(I),[21] methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**1**),[12] 1,2-*O*-isopropylidene-6-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose (**7**) (mp 108 °C),[22] 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**9**),[23] (1-hydroxy-1-methylethyl)diphenylphosphine (13) (mp 140 °C).[24]

Methyl 6-Deoxy-2,3-O-isopropylidene-α-L-lyxo-hexopyranosid-4-ulose (2). Compound **1** (8.2 g) in dimethyl sulfoxide (32.8 ml)-pyridine (8.2 ml) was oxidized with phosphorus pentaoxide (20.5 g) at room temperature for 4 d. The work-up, with addition of water and extraction with chloroform, gave compound **2** in 75% yield,[12] $[\alpha]_D^{15}$ −110° (*c* 0.7, EtOH). Mass spectrum, *m/e*, 216 (M^+).

Found: C, 55.08; H, 7.46%. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46%.

Addition of Diphenylphosphine to Compound 2. Addition of diphenylphosphine (0.30 g) to glycosid-4-ulose **2** (0.30 g) in the presence of triethylamine under nitrogen atmosphere at room temperature for 2 days gave methyl 6-deoxy-4-*C*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-talopyranoside (**3**) (0.080 g) in 13% yield, mp 100—101.5 °C, $[\alpha]_D^{16}$ −97° (*c* 0.71, EtOH). ^{1}H-NMR ($CDCl_3$) δ 0.98, 1.30 (2×s, 6H, CMe_2), 1.36 (d, *J*=6.6 Hz, C_5–Me), 3.35 (s, 3H, C_1–OMe), 4.0—4.9 (m, 5H, C_1–, C_2–, C_3–, C_4–OH), 7.05—8.0 (m, 10H, Ph); IR ν_{max}^{KBr} 3200 cm^{-1} (OH); mass spectrum, *m/e*, 402 (M^+). Oxidation of compound **3** gave the oxide (compound **4**).

Found: C, 62.80; H, 6.31%. Calcd for $C_{22}H_{27}O_6P$: C, 63.15; H, 6.50%.

Addition of Diphenylphosphine Oxide to Compound 2. Addition of diphenylphosphine oxide (0.10 g) to glycosid-4-ulose **2** (0.10 g) in the presence of triethylamine under nitrogen flow at room temperature for 3 h gave a crystalline adduct **4**. Recrystallization of the product from methanol-ether gave 0.18 g of pure methyl 6-deoxy-4-*C*-(diphenylphosphinyl)-2,3-*O*-isopropylidene-α-L-talopyranoside (**4**), mp 117—118.5 °C, $[\alpha]_D^{25}$ −132° (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 1.00 (d, *J*=12 Hz, 3H, C_5–Me), 1.05, 1.31 (2×s, 6H, CMe_2), 3.45 (s, 3H, C_1–OMe), 3.96—5.0 (m, 5H, C_1–, C_2–, C_3–, C_5–H, C_4–OH), 7.0—8.5 (m, 10H, Ph); IR ν_{max}^{KBr} 3150 cm^{-1} (OH); mass spectrum, *m/e*, 418 (M^+).

Found: C, 63.06; H, 6.76%. Calcd for $C_{22}H_{27}O_6P$: C, 63.15; H, 6.50%.

Methyl 4-O-(Diphenylphosphino)-2,3-O-isopropylidene-α-L-rhamnopyranoside (5). Reaction of compound **1** (0.10 g) with diphenylphosphinous chloride (0.10 g) in triethylamine (4 ml) under nitrogen atmosphere at room temperature for 24 h, followed by work-up by adding water and extraction with chloroform, gave compound **5** (0.189 g) in 97% yield, $[\alpha]_D^{20}$ −8.3° (*c* 2.0, EtOH). ^{1}H-NMR ($CDCl_3$) δ 1.25 (d, *J*=6.0 Hz, 3H, C_5–Me), 1.30, 1.50 (2×s, 6H, CMe_2), 3.35 (s, 3H, C_1–OMe), 3.50—4.90 (m, 5H, C_1–, C_2–, C_3–, C_4–, C_5–H), 7.0—8.0 (m, 10H, Ph); mass spectrum, *m/e*, 402 (M^+).

Found: C, 65.52; H, 6.99%. Calcd for $C_{22}H_{27}O_5P$: C, 65.66; H, 6.76%.

Methyl 4-C,4-O-(Diphenylphosphino)-2,3-O-isopropylidene-α-L-talopyranoside (6). Reaction of compound **3** (0.080 g) with diphenylphosphinous chloride (0.050 g) in triethylamine (4 ml) at room temperature for 24 h, followed by purification by liquid chromatography, gave compound **6** (0.062 g) in 54% yield, $[\alpha]_D^{15}$ −28° (*c* 1.0, EtOH). ^{1}H-NMR ($CDCl_3$) δ 1.21 (d, *J*=13.6 Hz, 3H, C_5–Me), 1.21, 1.48 (2×s, 6H, CMe_2), 3.44 (s, 3H, C_1–OMe), 2.95—5.0 (m, 4H, C_1–, C_2–, C_3–, C_5–H), 7.0—8.5 (m, 20H, Ph); mass spectrum, *m/e*, 586.

The oxidation of compound **6** with hydrogen peroxide gave the dioxide, mp 104—106 °C, mass spectrum, *m/e*, 618 (M^+).

Found: C, 65.84; H, 6.33%. Calcd for $C_{34}H_{36}O_7P_2$: C, 66.01; H, 5.87%.

6-Deoxy-6-C-(diphenylphosphino)-1,2:3,5-di-O-isopropylidene-α-D-glucofuranose (8). Addition of compound **7** (1.5 g) in tetrahydrofuran (10 ml) to a mixture of diphenylphosphine (1.0 g) and SDMA (2.0 g) in tetrahydrofuran at room temperature, followed by refluxing for 4 h, gave compound **8**. Work-up by addition of water and neutralization, followed by filtration, concentration *in vacuo*, and isolation by liquid chromatography, gave 1.4 g of pure compound **8** (90% yield), $[\alpha]_D^{15}$ +2.1° (*c* 1.0, EtOH). ^{1}H-NMR ($CDCl_3$) δ 1.06, 1.26, 1.31, 1.45 (4×s, 12H, CMe_2), 2.02 (d, *J*=13.0 Hz, 2H, C_6–, $C_{6'}$–H), 3.3—5.0 (m, 4H, C_2–, C_3–, C_4–, C_5–H), 5.92 (d, 1H, *J*=4.0 Hz, C_1–H), 7.15—7.90 (m, 10H, Ph); mass spectrum, *m/e*, 428 (M^+).

Found: C, 67.35; H, 6.87%. Calcd for $C_{24}H_{29}O_5P$: C, 67.28; H, 6.82%.

*6-O-(Diphenylphosphino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**10**).* Reaction of compound **9** (5.4 g) with diphenylphosphinous chloride (6.8 g) in the presence of triethylamine (13 ml) at room temperature for 24 h under nitrogen atmosphere, followed by filtration, concentration, and purification by liquid chromatography, gave compound **10** (4.1 g, 46% yield), $[\alpha]_D^{16}$ +47.0° (*c* 1.18, EtOH). ^{1}H-NMR ($CDCl_3$) δ 1.32, 1.42, 1.46 (4×s, 12H, CMe_2), 3.76—4.76 (m, 6H, C_2–, C_3–, C_4–, C_5–, C_6–, $C_{6'}$–H), 5.56 (d, *J*=5.0 Hz, 1H, C_1–H), 7.16—7.72 (m, 10H, Ph); mass spectrum, *m/e*, 444 (M^+).

Found: C, 64.35; H, 6.70%. Calcd for $C_{24}H_{29}O_6P$: C, 64.86; H, 6.58%.

*Asymmetric Hydrogenation of α-Acetylaminocinnamic Acid with Di-μ-chloro-bis(cyclooctadiene)dirhodium(I) and Compound **10**.* Asymmetric hydrogenation of α-acetylaminocinnamic acid (500 mg) in anhydrous benzene (5 ml)–absolute ethanol (5 ml) was carried out using di-μ-chloro-bis(cyclooctadiene)-dirhodium (I) (35 mg) and compound **10** (211 mg) as the catalyst in the presence of triethylamine (0.2 ml) under atmospheric pressure of hydrogen at room temperature for 24 h. Removal of the catalyst by passing a column peacked with ion exchange resine Dowex 50W (H^+), followed by decolorization with activated charcoal and removal of the solvent *in vacuo*, gave *N*-acetylphenylalanine ethyl ester (100% conversion). The identification of the product was performed by ^{1}H-NMR, whose spectrum was as follows: ($CDCl_3$) δ 1.21 (t, *J*=7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 1.95 (s, 3H, Ac), 3.09 (d, *J*=6.0 Hz, 2H, $C\underline{H}_2Ph$), 4.15 (q, *J*=7.5 Hz, 2H, $OC\underline{H}_2CH_3$), 4.85 (dd, *J*=6.0 Hz, 1H, CH), 6.46 (bd, *J*=7.5 Hz, NH), 7.05—7.40 (m, 5H, Ph). The product had $[\alpha]_D^{16}$ −8.82° (*c* 1.2, EtOH) which showed 67% optical yield of the *R* configuration.

The asymmetric hydrogenation of methyl α-acetylaminocinnamate, *N*-benzoylaminocinnamic acid, itaconic acid, and tiglic acid were performed in a similar fashion. The optical yields of the products were calculated based on the reported values of optical rotation for *N*-acetyl-(*S*)-phenylalanine,[25] *N*-acetyl-(*S*)-phenylalanine ethyl ester,[26] *N*-acetyl-(*S*)-phenylalanine methyl ester,[26] *N*-benzoyl-(*R*)-phenylalanine ethyl ester,[27] (*R*)-methylsuccinic acid,[5] and (*S*)-2-methylbutyric acid.[28]

*Reaction of 6-Deoxy-4-C-(diphenylphosphino)-2,3-O-isopropylidene-α-L-talopyranoside (**3**) with Methyl Iodide.* Reaction of compound **3** (0.10 g) with an excess amount of methyl iodide in anhydrous ether (10 ml) under nitrogen atmosphere gave methyldiphenylphosphonium iodide (**14**) and glycosid-4-ulose **2** in 80% yield.

*Oxidation of Compound **10** with Hydrogen Peroxide.* Oxidation of compound **10** with 38% hydrogen peroxide (0.11 g) at room temperature, followed by work-up by treatment with sodium thiosulfate and extraction with chloroform, gave 6-*O*-(diphenylphosphinyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**12**) in 75% yield, mp 115—116 °C, $[\alpha]_D^{15}$ −40° (*c* 0.6, EtOH). ^{1}H-NMR δ 1.26, 1.33, 1.50 (4×s, 12H, CMe_2), 3.8—4.9 (m, 6H, C_2–, C_3–, C_4–, C_5–, C_6–, $C_{6'}$–H), 5.60 (d, *J*=8.0 Hz, 1H, C_1–H), 7.2—8.1 (m, 10H, Ph); mass spectrum, *m/e*, 460 (M^+).

Found: C, 62.80; H, 6.45%. Calcd for $C_{24}H_{29}O_7P$: C, 62.60; H, 6.35%.

*Oxidation of Compound **8**.* Oxidation of compound **8** in a similar way as described above gave 6-deoxy-6-*C*-(diphenylphosphinyl)-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**11**), $[\alpha]_D^{16}$ +1.8° (*c* 1.2, EtOH), ^{1}H-NMR ($CDCl_3$) δ 1.16, 1.23, 1.40 (4×s, 12H, CMe_2), 2.02—2.75 (m, 2H, C_6–, $C_{6'}$–H), 3.25—4.46 (m, 3H, C_3–, C_4–, C_5–H), 4.50 (d, *J*=5.1 Hz, 1H, C_2–H), 5.89 (d, *J*=5.1 Hz, 1H, C_1–H), 6.80—7.93 (m, 10H, Ph); mass spectrum, *m/e*, 444 (M^+).

Found: C, 64.94; H, 6.40%. Calcd for $C_{24}H_{29}O_6P$: C, 64.86; H, 6.58%.

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