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Supporting Information

Cyclic Ether Synthesis from Diols using Trimethyl Phosphate

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1. General information

All reactions were performed in oven-dried glassware under argon. Cyclopentyl methyl ether (CPME) was supplied by Zeon Corporation and used without further purification. Anhydrous THF, 1,4-dioxane, toluene were purchased from commercial sources and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63-210µm spherical, neutral). ¹H and ¹³C NMR spectra were recorded on a JEOL EX 400, AL400 or ECA 500 spectrometer at room temperature in CDCl₃ as a solvent and internal standard (¹H NMR: $\delta = 7.26$ for CDCl₃; ¹³C NMR: $\delta = 77.0$ for CDCl₃) with tetramethylsilane as an further internal standard. IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer and a JEOL JMS-T100TD Accu TOF TLC instrument. Optical rotation was measured by Jasco P-1020 Polarimeter. HPLC analysis was carried out on a Shimadzu FRC-10A instrument with auto sampler and multiple wavelength detectors. Substrate (1a) was prepared according to reference 1. Substrate (1b) was prepared according to reference 2. Substrate (1j) was prepared according to reference 3. Substrate (1k) was prepared according to reference 4. Substrate (11) was prepared according to reference 5. Substrate (10) was prepared according to reference 6. Substrate (1p) was prepared according to reference 7.

2. Preparation of diols Preparation of 1-(4'-chlorophenyl)butan-1,4-diol (1e)



To a suspension of ferric oxide (Fe₂O₃; 16.0 mg, 0.10 mmol) in THF (30 mL) was added dropwise 4-chlorophenylmagnesium bromide (10 mmol, 10 mL, 1.0 M in 2-methylTHF) at 0 °C under argon. After stirring for 48 h at room temperature, the reaction was quenched with saturated NH₄Cl aq. (20 mL) and extracted with EtOAc (30 mL x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 1/2 to 1/3) to give 1-(4'-chlorophenyl)butan-1,4-diol in 6% yield (124.6 mg, 0.62 mmol).

¹H NMR (500 MHz, CDCl₃): δ 7.33—7.28 (m, 4H), 4.73 (t, J = 6.3 Hz, 1H), 3.74—3.66 (m, 2H), 2.78 (brs, 1H), 2.01 (brs, 1H), 1.86—1.82 (m, 2H), 1.74—1.62 (m, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 8.

Preparation of dodecan-1,4-diol (1g)



To a solution of γ -dodecanolactone (2.1 mL, 10 mmol) in THF (30 mL) was added lithium aluminum hydride (1.1 g, 30 mmol) at 0 °C under argon. After stirring for 24 h at 0 °C to room temperature, H₂O and 15 % NaOH aq. were added to the reaction mixture at 0 °C. After further stirring for 2 h, the mixture was filtrated through celite pad with Et₂O (400 mL) and the filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (hex/EtOAc = 1/1 to EtOAc only) to give dodecan-1,4-diol (2.0 g, 10 mmol, quantitative yield).

Dodecan-1,4-diol (1g)



Colorless solid. M. p. 46—47 °C ¹H NMR (500 MHz, CDCl₃) δ : 3.72—3.62 (m, 3H), 2.02 (brs, 2H), 1.73—1.62 (m, 3H), 1.51—1.41 (m, 4H), 1.35—1.22 (m, 11H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ :71.8, 62.9, 37.6, 34.4, 31.8, 29.7, 29.6, 29.3, 29.1, 25.7, 22.6, 14.1. IR (ATR) cm⁻¹: 3195, 2955, 2916, 2869, 2847, 1464, 1434, 1421, 1375, 1345, 1327, 1301, 1286, 1253, 1231, 1171, 1131, 1108, 1073, 1060, 1051, 1038 ESI-HRMS m/z: 225.1814 ([M+Na]⁺); Calcd for C₁₂H₂₆O₂Na: 225.1825.

Preparationof1-(4'-methylphenyl)butan-1,4-diol(1d)and1,1-di(4'-methylphenyl)butan-1,4-diol (1h)



To a solution of γ -butyrolactone 430.5 mg, 5 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (585.2 mg, 6 mmol) and sodium methoxide (70.2 mg, 1.3 mmol) in THF was added dropwise 4-methylphenyl magnesium bromide (20 mmol, 20 mL, 1.0 M in THF) at 0 °C under argon. After stirring for 18 h at room temperature, 1N HCl aq. was added to the reaction mixture. After further stirring for 2 h, the reaction mixture was extracted with EtOAc (30 mL x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 2/1 to 1/1) to give the mixture of 1,1-di(4'-methylphenyl)butan-1,4-diol (ca. 0.90 mmol) and 4-hydroxy-1-(4'-methylphenyl)butan-1-one (ca. 1.13 mmol).

To a solution of the obtained mixture in MeOH was added sodium borohydride (85.6 mg, 2.26 mmol) at room temperature. After stirring for 6 days, the reaction was quenched with H₂O (5 mL) and extracted with EtOAc (30 mL x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 1/1 to 1/3) to give 1-(4'-methylphenyl)butan-1,4-diol in 21% yield (191.1 mg, 1.06 mmol) and 1,1-di(4'-methylphenyl)butan-1,4-diol in 28% yield (378.8 mg, 1.40 mmol)

1-(4'-Methylphenyl)butan-1,4-diol (1d)



¹H NMR (500 MHz, CDCl₃): δ 7.25 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.71 (t, J = 6.3 Hz, 1H), 3,73–3.65 (m, 2H), 2.34 (s, 3H), 1.96 (brs, 1H), 1.89–1.82 (m, 2H), 1.75–1.61 (m, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 9.

1,1-Di(4'-methylphenyl)butan-1,4-diol (1h)



¹H NMR (500 MHz, CDCl₃): δ 7.29 (d, J = 8.3 Hz, 4H), 7.11 (d, J = 8.3 Hz, 4H), 3.67 (td, J = 5.0, 6.0 Hz, 2H), 2.80 (brs, 1H), 2.39 (t, J = 7.5 Hz, 2H), 2.31 (s, 6H), 1.65 (brs, 1H), 1.62—1.56 (m, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 10.

Preparation	of	2-(2'-hydroxyphenyl)ethanol	(1m)	and
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2-(2'-hydroxymethylphenyl)ethanol (1n)



To a solution of 2-hydroxyphenylacetic acid (0.76 g, 5.0 mmol) or homophthalic acid (0.90 g, 5.0 mmol) in THF (25 mL) was added lithium aluminum hydride (0.57 g, 15 or 0.95 g, 25 mmol) at 0 °C under argon. After stirring for 24 h at 0 °C to room temperature, H₂O and 15 % NaOH aq. were added to the reaction mixture at 0 °C. After further stirring for 2 h, the mixture was filtrated through celite pad with Et₂O (400 mL) and the filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (hex/EtOAc = 3/1 or 1/2) to give 2-(2'-hydroxyphenyl)ethanol (160.3 mg, 1.2 mmol, 24% yield) or 2-(2'-hydroxymethylphenyl)ethanol (438.3 mg, 2.9 mmol, 58% yield), respectively.

2-(2'-Hydroxyphenyl)ethanol (1m)



¹H NMR (500 MHz, CDCl₃): δ 7.85 (brs, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 4.04—3.94 (m, 2H), 2.94—2.85 (m, 2H) 2.48 (brs, 1H). Spectroscopic data of ¹H NMR was identical to that of the reference 11.

2-(2'-Hydroxymethylphenyl)ethanol (1n)



¹H NMR (500 MHz, CDCl₃): δ 7.32—7.15 (m, 4H), 4.65 (s, 2H), 3.90 (t, *J* = 5.5 Hz, 2H), 2.96 (t, *J* = 5.5 Hz, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 12.

Preparation of (S)-1-phenylbutan-1,4-diol [(S)-1a)]



To a solution of 4-oxo-4-phenylbutyric acid (3.56 g, 20.0 mmol) in DMF (30 mL) were added NaHCO₃ (3.36 g, 40 mmol) and MeI (3.75 mL, 60 mmol) at room temperature under argon. After stirring 6 h at 60 °C, the reaction mixture was quenched with H₂O (20 mL) and extracted with hexane/EtOAc (4/1, 40 mL x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel chromatography (hex/EtOAc = 2/1) to give methyl 4-oxo-4-arylbutyrate in 99% yield (3.81 g, 19.8 mmol).

To a solution of (-)-diisopinocampheyl chloroborane (705.7 mg, 2.2 mmol) in THF (1.5 mL) was added obtained methyl 4-oxo-4-arylbutyric (384.4 mg, 2.0 mmol) in THF (0.7 mL) at -78 °C under argon. After stirring for 36 h at -78 to -10 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified by silica-gel column chromatography (hex/EtOAc = 5/1 to 3/1) to give mixture of (*S*)-methyl 4-hydroxy-4-phenylbutyrate and (*S*)-dihydro-5-phenyl-2(*3H*)-furanone (total 312.1 mg, 1.61 mmol).

To a solution of the mixture (ca. 1.61 mmol) in THF (8 mL) was added lithium aluminum hydride (152.9 mg, 4.03 mmol) at 0 °C under argon. After stirring for 1 h at 0 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified by silica-gel column chromatography (hex/EtOAc = 1/2 to 1/3) to obtain (*S*)-1-arylbutan-1,4-diol (187.4 mg, 1.13 mmol) in 57% yield (2 steps) and 97% ee.

(S)-1-Phenylbutan-1,4-diol [(S)-1a)]



¹H NMR (500 MHz, CDCl₃): δ 7.37—7.33 (m, 3H), 7.30—7.27 (m, 1H), 4.75 (t, *J* = 6.5 Hz, 1H), 3.74—3.67 (m, 2H), 2.40 (brs, 1H), 1.90—1.86 (m, 2H), 1.77—1.62 (m, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 13.

The enantiomeric ratio of (S)-1a was determined by HPLC analysis using Daicel Chiralcel

OD-H column: *n*-hexane : isopropanol = 95:5, flow rate 0.5 mL/min, λ = 210 nm: t₁ (minor) = 56.0 min, t₂ (major) = 61.7 min. Absolute configuration was determined by reference 14.



Preparation of (S)-1-arylbutan-1,4-diol

To a solution of succinic anhydride (1.00 g, 10.0 mmol) and anisole (1.30 mL, 12.0 mmol) in CH_2Cl_2 (10 mL) was added aluminum trichloride (2.00 g, 15.0 mmol) at 0 °C under argon. After stirring for 9 h at room temperature, the mixture was quenched with 1N HCl aq. (20 mL) and extracted with EtOAc (30 mL x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue (3.00 g) was used for next reaction without further purification.

To a solution of the residue (3.00 g) in DMF (15 mL) were added Na₂CO₃ (1.44 g, 20 mmol) and MeI (1.25 mL, 20 mmol) at room temperature under argon. After stirring 18 h at 60 °C, the reaction mixture was quenched with H₂O (20 mL) and extracted with hexane/EtOAc (4/1, 30 mL x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel chromatography (hex/EtOAc = 4/1 to 1/1) to give methyl 4-oxo-4-(4'-methoxyphenyl)butyrate in 69% yield (2 steps from first step, 1.54 g, 6.92 mmol).

To a solution of (-)-diisopinocampheyl chloroborane (705.7 mg, 2.20 mmol) in THF (4 mL) added obtained methyl 4-oxo-4-(4'-methoxyphenyl)butyrate (444.5 mg, 2.00 mmol) at -10 °C under argon. After stirring for 48 h at -10 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified silica-gel column chromatography (hex/EtOAc = 2/1 to 1/1) to give the mixture of (*S*)-methyl 4-hydroxy-4-(4'-methoxyphenyl)butyrate and (*S*)-dihydro-5-(4'-methoxyphenyl)-2(*3H*)-furanone (total 244.9 mg, 1.09 mmol).

To a solution of the mixture (244.9 mg, 1.09 mmol) in THF (5.5 mL) was added lithium aluminum hydride (103.6 mg, 2.73 mmol) at 0 °C under argon. After stirring for 1 h at 0 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified by silica-gel column chromatography (hex/EtOAc = 1/3 to 1/5) to give (S)-1-(4'-methoxyphenyl)butan-1,4-diol in 44% yield (2 steps from third step, 204.1 mg, 1.04 mmol) and 77% ee.

(S)-1-(4'-Methoxyphenyl)butan-1,4-diol [(S)-1c)]



¹H NMR (500 MHz, CDCl₃): δ 7.28 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.69 (dd, J = 5.5, 7.5 Hz, 1H), 3.81 (s, 3H), 3.72—3.66 (m, 2H), 2.36 (brs, 1H), 2.05 (brs, 1H), 1.91—1.80 (m, 2H), 1.74—1.60 (m, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 8.

The enantiomeric ratio of (*S*)-**1c** was determined by HPLC analysis using Daicel Chiralcel AD-H column: *n*-hexane : isopropanol = 95:5, flow rate 1.0 mL/min, $\lambda = 210$ nm: t₁ (major) = 42.4 min, t₂ (minor) = 45.2 min. $[\alpha]_{D}^{28} = -27.4$ (c = 1.20 in benzene). Absolute configuration was determined by reference 8.

To a solution of succinic anhydride (1.00 g, 10.0 mmol) and fluorobenzene (1.12 mL, 12.0 mmol) in CH_2Cl_2 (10 mL) was added aluminum trichloride (2.00 g, 15.0 mmol) at 0 °C under argon. After stirring for 9 h at room temperature, the mixture was quenched with 1N HCl aq. (20 mL) and extracted with EtOAc (30 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue (1.44 g) was used for next reaction without further purification.

To a solution of the residue (1.44 g) in DMF (15 mL) were added Na_2CO_3 (1.44 g, 20 mmol) and MeI (1.25 mL, 20 mmol) at room temperature under argon. After stirring 18 h at 60 °C, the reaction mixture was quenched with H₂O (20 mL) and extracted with hexane/EtOAc (4/1, 30 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel chromatography (hex/EtOAc = 5/1 to 3/1) to give methyl 4-oxo-4-(4'-fluorophenyl)butyrate in 39% yield (2steps from first step, 0.828 g, 3.94 mmol).

To a solution of (-)-diisopinocampheyl chloroborane (1.39 g, 4.30 mmol) in THF (6 mL) added obtained methyl 4-oxo-4-(4'-fluorophenyl)butyrate (0.828 g, 3.94 mmol) at -10 °C under argon. After stirring for 48 h at -10 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified silica-gel column chromatography (hex/EtOAc = 3/1 to 1/1) to give the mixture of (*S*)-methyl 4-hydroxy-4-(4'-fluorophenyl)butyrate and

(S)-dihydro-5-(4'-fluorophenyl)-2(3H)-furanone (total 502.1 mg, 2.37 mmol).

To a solution of the mixture (502.1 mg, 2.37 mmol) in THF (12 mL) was added lithium aluminum hydride (225.0 mg, 5.93 mmol) at 0 °C under argon. After stirring for 1 h at 0 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified by silica-gel column chromatography (hex/EtOAc = 1/3 to 1/5) to give (*S*)-1-arylbutan-1,4-diol (2 steps from third step, 320.5 mg, 1.74 mmol) in 44% yield and 94% ee.

(S)-1-(4'-Fluorophenyl)butan-1,4-diol [(S)-1f]



¹H NMR (500 MHz, CDCl₃): δ 7.34—7.32 (m, 2H), 7.06—7.01 (m, 2H), 4.73 (d, J = 6.5 Hz, 1H), 3.75—3.66 (m, 2H), 2.60 (brs, 1H) 1.93 (brs, 1H), 1.87—1.83 (m, 2H), 1.75—1.61 (m, 2H). Spectroscopic data of ¹H NMR was identical to that of the reference 15.

The enantiomeric ratio of (*S*)-**1f** was determined by HPLC analysis using Daicel Chiralcel AD-H column: *n*-hexane : isopropanol = 95:5, flow rate 1.0 mL/min, λ = 210 nm: t₁ (major) = 25.6 min, t₂ (minor) = 27.2 min. Absolute configuration was determined by reference 14.

Preparation of Racemic 1-(4'-methoxyphenyl)butan-1,4-diol (1c) and 1-(4'-fluorophenyl)butan-1,4-diol (1f)



To a solution of 3-(4'-methylbenzoyl)propionic acid (292.5 mg, 1.40 mmol) in THF (7 mL) was added lithium aluminum hydride (212.5 mg, 5.60 mmol) at 0 °C under argon. After stirring for 1 h at 0 °C, a small amount of H₂O was added to the reaction mixture. The mixture was directly purified by silica-gel column chromatography (hex/EtOAc = 1/3 to 1/5) to give 1-(4'-methoxyphenyl)butan-1,4-diol (**1c**; 203.6 mg, 1.04 mmol) in 74% yield.

To a solution of 3-(4'-fluorobenzoyl)propionic acid (815.4 mg, 4.16 mmol) in THF (25 mL) was added lithium aluminum hydride (759.0 mg, 20.0 mmol) at 0 °C under argon. After stirring for 1 h at 0 °C to room temperature, H₂O and 15 % NaOH aq. were added to the reaction mixture at 0 °C. After further stirring for 1 h, the mixture was filtrated through celite pad with Et₂O (250 mL) and the filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (hex/EtOAc = 1/2 to 1/5) to give 1-(4'-fluorophenyl)butan-1,4-diol (**1f**;

386.8 mg, 2.10 mmol) in 50% yield.

3. Typical procedure of cyclic ether synthesis from diols

$$\begin{array}{c}
\mathsf{R} & \mathsf{NaH} (2 \text{ equiv.}) \\
\mathsf{OH} & \frac{\mathsf{PO}(\mathsf{OMe})_2 (2.5 \text{ equiv.})}{\mathsf{CPME}, \text{ rt}, 24 \text{ h}} & \mathsf{R} \\
\end{array}$$

To a solution of a diol derivative (0.200 mmol) in CPME (1 mL) was added NaH (0.400 mmol, 60% oil suspension) at room temperature under argon. After stirring for 10 min, trimethyl phosphate (0.500 mmol) was added. After further stirring for 24 h, the mixture was quenched with H_2O and extracted with Et_2O (20 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give a cyclic ether product.

4. Optimization for usage of base and phosphate

$$\begin{array}{c} R & \begin{array}{c} \text{NaH} (X \text{ equiv.}) \\ PO(OMe)_2 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} R \\ OH \end{array} \\ \begin{array}{c} PO(OMe)_2 (Y \text{ equiv.}) \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array} \\ \begin{array}{c} PO(OMe)_1 (Y \text{ equiv.}) \\ \end{array} \\ \end{array}$$
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entry	(X eq.)	(Y eq.)	temperature	time (h)	yield ^a	
					SM	product
1	3.0	3.0	rt	24	3%	75%
2	1.0	3.0	rt	24	33%	51%
3	2.0	1.0	rt	16	65%	34%
4	2.0	2.0	rt	24	11%	71%
5	2.0	2.0	80 °C	24	7	68
6	2.0	2.5	rt	24	0	88% (86%) ^b
7	2.0	3.0	rt	24	0%	83%

a) The yield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

b) Isolated yield.

5. Spectroscopic data of products

When using a substrate (**1a**: 33.2 mg, 0.200 mmol) in Table 1, entry 1 and Table 2, entry 1 according to typical procedure, 3-phenyltetrahydrofuran (**2a**: 25.6 mg, 0.173 mmol) was obtained in 86% yield after the purification by silica-gel column chromatography (hex/Et₂O = 10/1). Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.34—7.31 (m, 2H), 7.27—7.21 (m, 3H), 4.15 (t, J = 8.0 Hz, 1H), 4.08 (td, J = 4.0, 8.0 Hz, 1H), 3.93 (q, J = 8.0 Hz, 1H), 3.73 (t, J = 8.0 Hz, 1H), 3.41 (quint, J = 8.0 Hz, 1H), 2.40—2.34 (m, 1H), 2.06—1.98 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 142.6, 128.6, 127.2, 126.5, 74.7, 68.5, 45.0, 34.6. Spectroscopic data of ¹H NMR and ¹³C NMR were identical to those of the reference 16.

2-Phenyltetrahydrofuran (2b)



When using a substrate (**1b**: 33.2 mg, 0.200 mmol) in Table 2, entry 2 according to typical procedure, 2-phenyltetrahydrofuran (**2b**: 26.8 mg, 0.181 mmol) was obtained in 91% yield after the purification by silica-gel column chromatography (pentane/Et₂O = 50/1).

Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.34—7.31 (m, 4H), 7.27—7.23 (m, 1H), 4.90 (t, J = 7.0 Hz, 1H), 4.10 (dd, J = 7.0, 15.0 Hz, 1H), 3.94 (dd, J = 8.0, 14.0 Hz. 1H), 2.36—2.30 (m, 1H), 2.07—1.95 (m, 2H), 1.85—1.77 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 143.4, 128.3, 127.1, 125.6, 80.7, 68.7, 34.6, 26.0. Spectroscopic data of ¹H NMR and ¹³C NMR were identical to those of the reference 17.

(S)-2-Phenyltetrahydrofuran [(S)-2b]



When using a substrate [(*S*)-**1b**: 33.2 mg, 0.200 mmol] in Table 3, entry 1 according to typical procedure, 2-phenyltetrahydrofuran [(*S*)-**2b**: 26.8 mg, 0.161 mmol] was obtained in 81% yield and 96% ee after the purification by silica-gel column chromatography (pentane/Et₂O = 20/1). The enantiomeric ratio of (*S*)-**2b** was determined by HPLC analysis using Daicel Chiralcel AD-H column: *n*-hexane : isopropanol = 79.9 : 0.1, flow rate 0.8 mL/min, λ = 210 nm: t₁ (major) = 13.6 min, t₂ (minor) = 15.3 min. Absolute configuration was determined by reference 14.

2-(4'-Methoxyphenyl)tetrahydrofuran (2c)



When using a substrate (1c: 39.2 mg, 0.200 mmol) in Table 2, entry 3 according to typical pro-

cedure, 2-(4'-methoxyphenyl)tetrahydrofuran (**2c**: 27.6 mg, 0.155 mmol) was obtained in 78% yield after the purification by silica-gel column chromatography (hex/EtOAc = 10/1).

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.27—7.25 (m, 2H), 6.89—6.86 (m, 2H), 4.83 (t, J = 7.5 Hz, 1H), 4.08 (dd, J = 7.5, 14.5 Hz, 1H), 3.94—3.88 (m, 1H), 3.80 (s, 3H), 2.29—2.24 (m, 1H), 2.07—1.95 (m, 2H), 1.83—1.77 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 158.8, 135.3, 126.9, 113.6, 80.4, 68.5, 55.3, 34.5, 26.0. Spectroscopic data of ¹H NMR and ¹³C NMR were identical to those of the reference 17.

(S)-2-(4'-Methoxyphenyl)tetrahydrofuran [(S)-2c]



When using a substrate [(*S*)-**1c**: 39.2 mg, 0.200 mmol] in Table 3, entry 3 according to typical procedure, (*S*)-2-(4'-methoxyphenyl)tetrahydrofuran [(*S*)-**2c**: 21.8 mg, 0.122 mmol] was obtained in 61% yield and 71% ee after the purification by silica-gel column chromatography (pentane/Et₂O = 50/1).

The enantiomeric ratio of (*S*)-2c was determined by HPLC analysis using Daicel Chiralcel OD-H column: *n*-hexane : isopropanol = 90:10, flow rate 1.0 mL/min, $\lambda = 210$ nm: t₁ (minor) = 6.2 min, t₂ (major) = 6.8 min. $[\alpha]_{D}^{28} = -21.9$ (c = 0.85 in CH₃Cl). Absolute configuration was determined by reference 18.

2-(4'-Methylphenyl)tetrahydrofuran (2d)



When using a substrate (**1d**: 36.0 mg, 0.200 mmol) in Table 2, entry 4 according to typical procedure, 2-(4'-methylphenyl)tetrahydrofuran (**2d**: 21.9 mg, 0.135 mmol) was obtained in 68% yield after the purification by silica-gel column chromatography (hex/EtOAc = 10/1).

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.23 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.86 (t, *J* = 6.5, 1H), 4.11—4.06 (m, 1H), 3.94—3.90 (m, 1H), 2.34 (s, 3H), 2.32—2.26 (m, 1H), 2.06—1.94 (m, 2H), 1.83—1.76(m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 140.3, 136.7, 128.9, 125.5, 80.5, 68.6, 34.6, 26.0, 21.1. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 17.

2-(4'-Chlorophenyl)tetrahydrofuran (2e)



When using a substrate (**1e**: 40.1 mg, 0.200 mmol) in Table 2, entry 5 according to typical procedure, 2-(4'-chlorophenyl)tetrahydrofuran (**2e**: 24.9 mg, 0.136 mmol) was obtained in 68% yield after the purification by silica-gel column chromatography (hex/EtOAc = 10/1). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.35—7.25 (m, 4H), 4.86 (t, *J* = 7.3 Hz, 1H), 4.11—4.06 (m, 1H), 3.95—3.91 (m, 1H), 2.35—2.29 (m, 1H), 2.03-1.98 (m, 2H), 1.78—1.73 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 142.0, 132.7, 128.4, 127.0, 80.0, 68.7, 34.7, 25.9. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 17.

2-(4'-Fluorophenyl)tetrahydrofuran (2f)



When using a substrate (**1f**: 36.8 mg, 0.25 mmol) in Table 2, entry 6 according to typical procedure, 2-(4'-fluorophenyl)tetrahydrofuran (**2f**: 17.6 mg, 0.106 mmol) was obtained in 53% yield after the purification by silica-gel column chromatography (pentane/Et₂O = 10/1).

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.34—7.28 (m, 2H), 7.03—7.00 (m, 2H), 4.85 (t, J = 7.0 Hz, 1H), 4.09 (dd, J = 7.0, 15.0 Hz, 1H), 3.97 (dd, J = 7.0, 15.0 Hz, 1H), 2.34—2.28 (m, 1H), 2.04—1.97 (m, 2H), 1.80—1.73 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 162.0 (d, J = 243.4 Hz), 139.0 (d, J = 3.5 Hz), 127.2 (d, J = 8.3 Hz), 115.0 (d, J = 21.5 Hz), 80.1, 68.6, 34.7, 26.0. Spectroscopic data of ¹H and ¹³C NMR were identical to that of the reference 19.

(S)-2-(4'-Fluorophenyl)tetrahydrofuran [(S)-2f)]



When using a substrate [(*S*)-**1f**: 36.8 mg, 0.200 mmol] in Table 3, entry 2 according to typical procedure, (*S*)-2-(4'-fluorophenyl)tetrahydrofuran [(*S*)-**2f**: 26.8 mg, 0.134 mmol] was obtained in 67% yield and 92% ee after the purification by silica-gel column chromatography (pentane/Et₂O = 10/1).

The enantiomeric ratio of (*S*)-**2f** was determined by HPLC analysis using Daicel Chiralcel OJ-H column: *n*-hexane : isopropanol = 80:20, flow rate 0.5 mL/min, λ = 210 nm: t₁ (minor) = 12.9

min, t_2 (major) = 14.7 min. $[\alpha]_{D}^{28} = -26.0$ (c = 0.59 in CH₂Cl₂). Absolute configuration was determined by reference 14.

2-Octyltetrahydrofuran (2g)

When using a substrate (**1g**: 40.5 mg, 0.200 mmol) in Table 2, entry 7 according to typical procedure, 2-octyltetrahydrofuran (**2g**: 28.9 mg, 0.157 mmol) was obtained in 79% yield after the purification by silica-gel column chromatography (hex/Et₂O = 30/1).

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 3.88—3.87 (m, 1H), 3.80—3.75 (m, 1H), 3.73—3.69 (m, 1H), 2.00—1.93 (m, 1H), 1.92—1.80 (m, 2H), 1.61—1.53 (m, 1H), 1.46—1.36 (m, 3H), 1.34—1.21 (m, 11H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ : 79.5, 67.6, 35.7, 31.9, 31.4, 29.8, 29.6, 29.3, 26.4, 25.7, 22.7, 14.1. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 20.

2,2-Di(4'-methylphenyl)tetrahydrofuran (2h)



When using a substrate (**1h**: 54.1 mg, 0.200 mmol) in Table 2, entry 8 according to typical procedure, 2,2-di(4'-methylphenyl)tetrahydrofuran (**2h**: 38.3 mg, 0.152 mmol) was obtained in 76% yield after the purification by silica-gel column chromatography (hex/EtOAc = 50/1). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.30 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.3 Hz, 4H), 4.02 (t, *J* = 7.0 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.96—1.90 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ :143.6, 136.1, 128.8, 125.7, 87.8, 67.3, 38.5, 25.4, 21.0. IR (ATR) cm⁻¹: 3022, 2974, 2920, 2872, 1900, 1612, 1509, 1454, 1407, 1377, 1312, 1245, 1210, 1182, 1121, 1050, 1020. ESI-HRMS m/z: 275.1409 ([M+Na]⁺); Calcd for C₁₈H₂₀ONa: 275.1406.

Phthalan (2i)



When using a substrate (**1i**: 27.6 mg, 0.200 mmol) in Table 2, entry 9 according to typical procedure, phthalan (**2i**: 16.1 mg, 0.134 mmol) was obtained in 67% yield after the purification by silica-gel column chromatography (pentane/ $Et_2O = 30/1$).

Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.28—7.23 (m, 4H), 5.12 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ : 139.0, 127.2, 120.9, 73.6. Spectroscopic data of ¹H NMR was identical to that of the reference 21. Spectroscopic data of ¹³C NMR were identical to those of the reference 22.

5,6-Dimethoxyphthalan (2j)



When using a substrate (**1j**: 39.6 mg, 0.200 mmol) in Table 2, entry 10 according to typical procedure, 5,6-dimethoxyphthalan (**2j**: 16.5 mg, 0.092 mmol) was obtained in 46% yield after the purification by silica-gel column chromatography (hex/EtOAc = 10/1).

Colorless solid. M.p. 106-107 °C. ¹H NMR (500 MHz, CDCl₃) δ : 6.77 (s, 2H), 5.08 (s, 4H), 3.88 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ : 148.8, 130.4, 104.0, 73.8, 56.1. IR (ATR) cm⁻¹: 3010, 2957, 2905, 2854, 2835, 1755, 1659, 1612, 1504, 1465, 1417, 1364, 1328, 1307, 1279, 1249, 1219, 1189, 1174, 1101, 1044. ESI-HRMS m/z: 181..0859 ([M+H]⁺); Calcd for C₁₀H₁₃O₃: 181.0859.

5,6-Dichlorophthalan (2k)



When using a substrate (**1k**: 41.4 mg, 0.200 mmol) in Table 2, entry 11 according to typical procedure, 5,6-dichlorophthalan (**2k**: 19.0 mg, 0.101 mmol) was obtained in 50% yield after the purification by silica-gel column chromatography (hex/EtOAc = 20/1).

Colorless solid. ¹H NMR (500 MHz, CDCl₃) δ : 7.33 (s, 2H), 5.05 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ : 139.4, 131.3, 122.9, 72.9, 56.1. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 4.

2,9-Dimethylphthalan (*cis/trans* = 64/36) (2l)



When using a substrate (**11**: 33.2 mg, 0.200 mmol, dr = 69/31) in Table 2, entry 12 according to typical procedure, 2,9-dimethylphthalan (**21**: 11.6 mg, 0.078 mmol) was obtained in 39% yield after the purification by silica-gel column chromatography (hex/Et₂O = 10/1).

Inseperable diastereomer mixture was obtained. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.30—7.26 (m, 2H), 7.17—7.13 (m, 2H), 5.40 (q, *J* = 6.0 Hz, 0.72H), 5.23 (q, *J* = 5.8 Hz, 1.28H), 1.53 (d, *J* = 5.8 Hz, 3.84H), 1.47 (d, *J* = 6.0 Hz, 2.16H). ¹³C NMR (125 MHz, CDCl₃) δ : 143.7, 143.2, 127.4, 127.3, 120.9, 120.8, 78.7, 78.6, 22.3, 22.1. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 23.

2,3-Dihydrobenzofuran (2m)



When using a substrate (**1m**: 27.6 mg, 0.200 mmol) in Table 2, entry 13 according to typical procedure, 2,3-dihydrobenzofuran (**2m**: 22.0 mg, 0.180 mmol) was obtained in 90% yield after the purification by silica-gel column chromatography (pentane/Et₂O = 30/1).

Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.20 (d, *J* = 7.3 Hz, 1H), 7.11 (dd, *J* = 7.3, 7.5 Hz, 1H), 6.84 (dd, *J* = 7.3, 7.5 Hz, 1H), 6.79 (dd, *J* = 7.3, 7.5 Hz, 1H), 4.56 (t, *J* = 8.5 Hz, 2H), 3.21 (t, *J* = 8.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ : 160.0, 127.9, 126.8, 124.9, 120.3, 109.3, 71.0, 29.7. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 24.

Isochroman (2n)



When using a substrate (**1n**: 30.4 mg, 0.200 mmol) in Table 2, entry 14 according to typical procedure, isochroman (**2n**: 11.9 mg, 0.089 mmol) was obtained in 45% yield after the purification by silica-gel column chromatography (hex/EtOAc = 50/1).

Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.17—7.15 (m, 3H), 6.99—6.97 (m, 1H), 4.78 (s, 2H), 3.98 (t, *J* = 5.5 Hz, 2H), 2.87 (t, *J* = 5.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ : 134.9, 133.2, 128.9, 126.3, 126.0, 124.4, 67.9, 65.4, 28.3. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 25.

2-Phenyltetrahydropyran (20)



When using a substrate (**1o**: 36.0 mg, 0.200 mmol) in Table 2, entry 15 according to typical procedure, 2-phenyltetrahydropyran (**2o**: 8.4 mg, 0.053 mmol) was obtained in 26% yield after

the purification by silica-gel column chromatography (hex/Et₂O = 50/1).

Pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ : 7.36—7.24 (m, 5H), 4.34—4.31 (m, 1H), 4.16—4.13 (m, 1H), 3.65—3.60 (m, 1H), 1.96—1.93 (m, 1H), 1.85—1.82 (m, 1H), 1.73—1.57 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ : 143.3, 128.3, 127.3, 125.8, 80.1, 69.0, 34.0, 25.9, 24.0. Spectroscopic data of ¹H and ¹³C NMR were identical to those of the reference 19.

6,7-Dihydro-5*H*-dibenz[*c*, *e*]oxepine (2p)



When using a substrate (**1p**: 42.9 mg, 0.200 mmol) in Table 2, entry 16 according to typical procedure, 6,7-dihydro-5*H*-dibenz[*c*,*e*]oxepine (**2p**: 29.9 mg, 0.152 mmol) was obtained in 76% yield after the purification by silica-gel column chromatography (hex/EtOAc = 10/1). Colorless solid. ¹H NMR (500 MHz, CDCl₃) δ : 7.58—7.56 (m, 2H), 7.53—7.50 (m, 2H), 7.46—7.41 (m, 4H), 4.37 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ : 141.2, 135.1, 129.7, 128.9, 128.2, 127.5, 67.5. Spectroscopic data of ¹H NMR and ¹³C NMR were identical to those of the reference 26.

6. Mechanistic studies

Equation 1

To a solution of 2-phenylbutan-1,4-diol (**1a**; 33.2 mg, 0.200 mmol) in CPME (1 mL) was added NaH (16.0 mg, 0.400 mmol, 60% oil suspension) at room temperature under argon. After stirring for 10 min, trimethyl phosphate (57 μ l, 0.500 mmol) was added to the reaction mixture. After further stirring for 6 h or 24 h at room temperature, the mixture was quenched with brine (5 mL) and extracted with Et₂O (20 ml x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was analyzed by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard. After 6 h, **2a** (13.9 mg, 0.094 mmol, 47%), trace amount of mono-phosphorylated 2-phenylbutan-1,4-diol (**3**), cyclic phosphate (**4**) and diphosphorylated 2-phenylbutan-1,4-diol (**5**), and the recovered starting material (**1a**; 2.3 mg, 0.014 mmol, 7%) were detected, respectively. After 24 h, **2a** (26.1 mg, 0.200 mmol, 88%), trace amount of **3**, **4** and **5** were detected, respectively.

Equation 2

Preparation of mono-phosporylated 2-phenylbutan-1,4-diol (3)



To a solution of 2-phenylbutan-1,4-diol (**1a**: 332.5 mg, 2.0 mmol) in CH₂Cl₂ (10 mL) were added triethylamine (430 μ L, 3.1 mmol), dimethyl chlorophosphate (260 μ L, 2.4 mmol) and *N*,*N*-dimethyl-4-aminopyridine (24.5 mg, 0.2 mmol) at room temperature under argon. After stirring for 1 week at room temperature, the mixture was quenched with H₂O (20 mL) and extracted with EtOAc (20 ml x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel chromatography (hex/EtOAc = 1/5 to EtOAc only) to give the regioisomer mixture of mono-phosphorylated 2-phenylbutan-1,4-diol (**3**) in 20% yield (108.1 mg, 0.4 mmol).

mono-phosphorylated 2-phenylbutan-1,4-diol (63:37 mixture of regioisomers) (3)

 OR^1 $R^1 = H, R^2 = PO(OMe)_2$ and Ph OR^2 $R^1 = PO(OMe)_2, R^2 = H$

Pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.36—7.31 (m, 2H), 7.27—7.22 (m, 3H), 4.22—4.17 (m, 1H), 4.08—4.02 (m, 1H), 3.96—3.89 (m, 1H), 3.81—3.60 (m, 6.6H), 3.55—3.50 (m, 0.4H), 3.20—3.14 (m, 0.4H), 3.02—2.97 (m, 0.6H), 2.23—2.16 (m, 0.6H), 2.12—2.05 (m, 0.4H), 2.01—1.93 (m, 0.6H), 1.91—1.84 (m, 0.4H). ¹³C NMR (125 MHz, CDCl₃) δ : 140.9, 140.6, 128.8, 128.7, 128.0, 128.0, 127.1, 127.1, 71.3 (d, *J* = 5.9 Hz), 61.1, 65.9 (d, *J* = 6.0 Hz), 60.3, 54.3 (d, *J* = 5.9 Hz), 54.2 (d, *J* = 5.9 Hz), 44.6, 42.9 (d, *J* = 5.9 Hz), 34.6, 32.6 (d, *J* = 7.1 Hz). ³¹P NMR (213 MHz, CDCl₃, triphenyl phosphine as an external standard; -6.0 ppm): δ 2.0, 1.8. IR (ATR) cm⁻¹: 3409, 2956, 1602, 1494, 1453, 1254, 1185, 1015. ESI-HRMS m/z: 297.0872 ([M+Na]⁺); Calcd for C₁₂H₁₉O₅PNa: 297.0862.

Reaction of 3 (equation 2)

To a solution of **3** (41.1 mg, 0.150 mmol) in CPME (0.75 mL) was added NaH (6.0 mg, 0.150 mmol, 60% oil suspension) at room temperature under argon. After stirring for 6 h or 0.5 h, the mixture was quenched with brine and extracted with Et_2O (20 ml x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was analyzed by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard. For 6 h, **2a** (14.2 mg, 0.096 mmol, 47%), trace amount of cyclic phosphate (**4**) and recovered starting material (**3**; 2.3 mg, 0.014 mmol, 7%) were detected. For 0.5 h, **2a** (8.9 mg, 0.069 mmol, 40%) and **4** (20.8 mg, 0.086 mmol, 57%) were detected.

Cyclic phosphate (4)

Colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 7.36—7.31 (m, 2H), 7.30—7.27 (m, 1H), 7.20—7.18 (m, 2H), 4.45—4.39 (m, 1H), 4.30—4.08 (m, 3H), 3.87 (d, *J* = 11.5 Hz, 3H), 3.18—3.12 (m, 1H), 2.36—2.28 (m, 1H), 2.12—2.07 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 139.7, 129.0, 127.5, 127.2, 70.2 (d, *J* = 3.5 Hz), 67.2 (d, *J* = 7.1 Hz), 54.5 (d, *J* = 6.0 Hz), 46.5, 36.8. ³¹P NMR (213 MHz, CDCl₃, triphenyl phosphine as an external standard; -6.0 ppm): δ -0.2. IR (ATR) cm⁻¹: 3483, 2956, 2919, 2854, 1602, 1494, 1453, 1264, 1186, 1103, 1052, 1011. ESI-HRMS m/z: 265.0609 ([M+Na]⁺); Calcd for C₁₁H₁₅O₄PNa: 265.0600.

Equation 3

To a solution of **4** (24.2 mg, 0.100 mmol) and MeOH (12 μ L, 0.30 mmol) in CPME (0.5 mL) was added NaH (12.0 mg, 0.300 mmol, 60% oil suspension) at room temperature under argon. After stirring for 6 h at room temperature, the mixture was quenched with H₂O (5 mL) and extracted with EtOAc (30 ml x 3). The residue was analyzed by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard, **2a** (9.6 mg, 0.065 mmol, 65%) and **1a** (0.8 mg, 0.005 mmol, 5%) were detected.

Equation 4

Prearation of diphosphorylated 2-phenylbutan-1,4-diol (5)



To a solution of **1a** (498.7 mg, 3.0 mmol) in CPME (15 mL) was added NaH (240.0 mg, 6.0 mmol, 60% oil suspension) at room temperature under argon. After stirring for 10 min, dimethyl chlorophosphate (812 μ L, 7.5 mmol) was added. After further stirring for 24 h at room temperature, the mixture was quenched with H₂O (15 mL) and extracted with EtOAc (20 ml x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica-gel chromatography (EtOAc/MeOH = 30/1 to 10/1) to give diphosphorylated 2-phenylbutan-1,4-diol (**5**) in 14% yield (155.6 mg, 0.41 mmol).

Diphosphorylated 2-phenylbutan-1,4-diol (5)

Colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 7.34—7.19 (m, 5H), 4.22—4.12 (m, 2H), 4.05—3.99 (m, 1H), 3.91—3.85 (m, 1H), 3.75—3.70 (m, 6H), 3.68 (d, *J* = 11.0 Hz, 3H), 3.62 (d, *J* = 12.0 Hz, 3H), 3.19—3.13 (m, 1H), 2.29—2.22 (m, 1H), 2.01—1.95 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 139.5, 128.7, 128.0, 127.3, 71.0 (d, *J* = 6.0 Hz), 65.3 (d, *J* = 6.0 Hz), 54.2 (d, *J* = 3.8 Hz), 54.2 (d, *J* = 5.9 Hz), 42.4 (d, *J* = 7.1 Hz), 32.4 (d, *J* = 7.3 Hz). ³¹P NMR (213 MHz, CDCl₃, triphenyl phosphine as an external standard; -6.0 ppm): δ 0.7, 0.4. IR (ATR) cm⁻¹: 3473, 2956, 2854, 1495, 1454, 1265, 1185, 1012. ESI-HRMS m/z: 405.0834 ([M+Na]⁺); Calcd for C₁₄H₂₄O₈PNa: 405.0839.

Reaction of 5 (Equation 4)

To a solution of **5** (37.8 mg, 0.100 mmol) and MeOH (12 μ L, 0.300 mmol) in CPME (0.5 mL) was added NaH (12.0 mg, 0.300 mmol, 60% oil suspension) at room temperature under argon. After stirring for 2 h at room temperature, the mixture was quenched with H₂O (5 mL) and extracted with EtOAc (30 ml x 3). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was analyzed by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard, **2a** (12.0 mg, 0.081 mmol, 81%) was detected.

7. ¹H and ¹³C NMR spectra of newly synthesized substrate and products ¹H NMR of dodecan-1,4-diol (1g)



¹³C NMR of dodecan-1,4-diol (1g)



¹H NMR of 3-phenyltetrahydrofuran (2a)



¹³C NMR of 3-phenyltetrahydrofuran (2a)



¹H NMR of 2-phenyltetrahydrofuran (2b)



¹³C NMR of 2-phenyltetrahydrofuran (2b)





¹H NMR of 2-(4'-methoxyphenyl)tetrahydrofuran (2c)

¹³C NMR of 2-(4'-methoxyphenyl)tetrahydrofuran (2c)





¹H NMR of 2-(4'-methylphenyl)tetrahydrofuran (2d)

¹³C NMR of 2-(4'-methylphenyl)tetrahydrofuran (2d)





¹H NMR of 2-(4'-chlorophenyl)tetrahydrofuran (2e)

¹³C NMR of 2-(4'-chlorophenyl)tetrahydrofuran (2e)





¹H NMR of 2-(4'-fluorophenyl)tetrahydrofuran (2f)

¹³C NMR of 2-(4'-fluorophenyl)tetrahydrofuran (2f)



¹H NMR of 2-octyltetrahydrofuran (2g)



¹³C NMR of 2-octyltetrahydrofuran (2g)





¹H NMR of 2,2-di(4'-methylphenyl)tetrahydrofuran (2h)

¹³C NMR of 2,2-di(4'-methylphenyl)tetrahydrofuran (2h)



¹H NMR of phthalan (2i)



¹³C NMR of phthalan (2i)







¹³C NMR of 5,6-dimethoxyphthalan (2j)







¹³C NMR of 5,6-dichlorophthalan (2k)





¹H NMR of 2,9-dimethylphthalan (*cis/trans* = 64/36) (2l)

¹³C NMR of 2,9-dimethylphthalan (*cis/trans* = 64/36) (2l)



¹H NMR of 2,3-dihydrobenzofuran (2m)



¹³C NMR of 2,3-dihydrobenzofuran (2m)



¹H NMR of isochroman (2n)



¹³C NMR of isochroman (2n)



¹H NMR of 2-phenyltetrahydropyran (20)



¹H NMR of 2-phenyltetrahydropyran (20)





¹H NMR of 6,7-dihydro-5*H*-dibenz[*c*,*e*]oxepine (2p)

¹³C NMR of 6,7-dihydro-5*H*-dibenz[*c*,*e*]oxepine (2p)





¹H NMR of mono-phosporylated 2-phenylbutan-1,4-diol (3)







³¹P NMR of mono-phosporylated 2-phenylbutan-1,4-diol (3)

¹H NMR of Cyclic phosphate (4)



¹³C NMR of Cyclic phosphate (4)



³¹P NMR of Cyclic phosphate (4)





¹H NMR of diphosphorylated 2-phenylbutan-1,4-diol (5)

¹³C NMR of diphosphorylated 2-phenylbutan-1,4-diol (5)





³¹P NMR of diphosphorylated 2-phenylbutan-1,4-diol (5)

8. HPLC charts of chiral substrates and products



(S)-1-Phenylbutan-1,4-diol [(S)-1a]



(S)-1-(4'-Methoxyphenyl)butan-1,4-diol [(S)-1c]





(S)-1-(4'-Fluorophenyl)butan-1,4-diol [(S)-1f]







(S)-2-Phenyltetrahydrofuran [(S)-2b]





(S)-2-(4'-Methoxyphenyl)tetrahydrofuran [(S)-2c]

(S)-2-(4'-Fluorophenyl)tetrahydrofuran [(S)-2f)]

0-

ò

1 PDA Multi 1/210nm 4nm



S48

€ 12.853

15

20

min

10

5

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