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(54) Title: CHIRAL ALKOXY ALCOHOLS, CHIRAL 1,3-PHENYLENE-BIS[4-(4-ALKOXY) PHENYLIMINOMETHYL] BENZOATES AND PROCESSES FOR PREPARATION THEREOF

(57) Abstract: The present invention relates to chiral alkoxy alcohols, chiral 1,3-phenylene bts[4-(4-alkoxy)phenyl]tmnomethyl]benzoates, and the preparation methods of them. In particular, the chiral alkoxy alcohol of the present invention can be used for synthesizing chiral liquid crystal materials, pharmaceuticals, agricultural chemicals, and as intermediates for natural product synthesis. Since the chiral compound of 1,3-phenylene bts[4-(4-alkoxy)phenyl]tmnomethyl]benzoate has a lower phase transition temperature and exhibit ferroelectricity or antiferroelectricity depending on the length of chiral (alkoxy)alkyl terminal group, it can be used as an important component in the mixture of smectic liquid crystal.

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TITLE OF THE INVENTION

Chiral Alkoxy Alcohols, Chiral 1,3-Phenylene-bis[4-(4-alkoxy) phenyliminomethyl]
benzoates and Processes for Preparation Thereof

BACKGROUND OF THE INVENTION**5 (a) Field of the Invention**

The present invention relates to compounds of chiral primary alkoxyalcohols and chiral 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]benzoates, and the processes for their preparation.

(b) Description of the Related Art

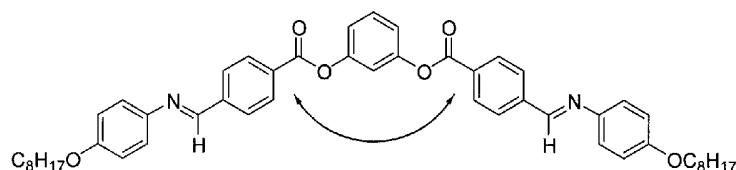
10 Chiral compounds have been widely used in fields of medicinal and agricultural chemical industry. Recently, chiral liquid crystal materials were found applicable to liquid crystal display.

In order to show a second-order nonlinear optical effects, organic materials should have an asymmetric center as a structure unit, and the ferroelectric liquid
15 crystal should be chiral [R. B. Meyer et al, *J. Physique Lett.* 1975, **36**, 69]. Attempts were made to synthesize optical active alcohols suitable for liquid crystal material. JP Laid-Open Publication Nos 1998-195004 and 1998-139706, and (KR Laid-Open Publication No. 1998-042071) disclose novel optically-active alcohols and alkoxy alcohols having trifluoromethyl groups at the asymmetric center.
20 However, these optically-active compounds are secondary alcohols having hydroxyl groups located right on the asymmetric center. It was not easy to prepare highly optically pure primary alcohols where the asymmetric carbon and a

hydroxyl group of the alcohols are at least one carbon unit apart.

In General, thermotropic liquid crystal materials employed in liquid crystal displays are mainly rod-like materials. Since Niori et al., (*J. Mater. Chem.*, 1996, **6**, 1231) discovered that achiral banana-shaped (bent-core) molecules possess
5 unusual and interesting properties, much attention has been paid for these materials. As a result of the bent shape, a polar order within the smectic layers can be induced and some phases exhibit ferroelectric and antiferroelectric properties although the molecules are a chiral.

An example of banana-shaped liquid crystal material known in the prior art
10 is 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]benzoate with an angle of about 120 °, which is represented by the following formula:



EP 1 215 195 A1 discloses a banana-shaped liquid crystal material having
a diverse skeleton and a different angle in addition to the bisbenzoate structure.
15 The banana-shaped liquid crystal materials having no asymmetric center were widely studied.

It was found that the interlayer steric interaction between the chiral alkyl groups in both ends of a banana-shaped liquid crystal plays a major role for the emergence of phase structures (Kumazawa et al., *J. Mater. Chem.*, 2004, **14**, 157-
20 164). Thus, by introducing an optically active group as a terminal group, diverse

materials with interesting mesophases can be obtained.

However, the banana-shaped liquid crystal material coming from primary alcohol, in which an asymmetric carbon with a methyl substituent is apart from a hydroxyl group of alcohol by one and more carbon unit, is quite rare. Since the
5 chiral primary alcohols are not readily available and they cannot be easily synthesized.

SUMMARY OF THE INVENTION

The present inventors have made extensive studies of techniques for easy and cost-effective synthesis of chiral primary alkoxy alcohols. The structure of
10 primary chiral alkoxy alcohols were made by replacing one methylene unit (CH_2) in the chiral primary alcohols with oxygen. It has been found that a novel chiral primary alkoxy alcohol with high optical purity where asymmetric carbon is apart from a hydroxyl group by a long carbon chain, could be synthesized in high yield.

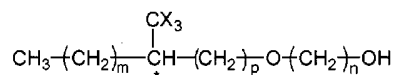
Moreover, in a similar way, novel chiral alkoxy alcohols with a
15 trifluoromethyl group at an asymmetric carbon instead of a methyl and a novel liquid crystal materials derived from them have been synthesized.

The object of the present invention is to provide the method of preparing a chiral alkoxy alcohol, and 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl] benzoates therefrom.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a chiral alkoxy alcohols represented by
20 Chemical Formula 1:

Chemical Formula 1



where, X is H or F,

m is an integer of 1 to 5,

5 n is an integer of 3 to 10,

p is an integer of 0 or 1, and

* is asymmetric carbon.

It is especially preferable when p is 0, m is an integer of 1 to 5 and n is 3;
and when p is 1, m is 1 and n is an integer of 3 to 10.

10 Representative examples of the compounds include, but are not limited to,
(S)-3-(2-butoxy)propan-1-ol, (S)-3-(2-pentyloxy)propan-1-ol, (S)-3-(2-hexyloxy)propan-1-ol, (S)-3-(2-heptyloxy)propan-1-ol, (S)-3-(2-octyloxy)propan-1-ol,
(S)-3-(1-trifluoromethyl-1-hexyloxy)propan-1-ol, (S)-3-(1-trifluoromethyl-1-heptyloxy)propan-1-ol, (S)-3-(2-methylbutoxy)propan-1-ol, (S)-4-(2-methyl
15 butoxy)butan-1-ol, (S)-5-(2-methylbutoxy)pentan-1-ol, (S)-6-(2-methylbutoxy)hexan-1-ol, and so on.

The chiral alkoxy alcohols of Chemical Formula 1 differ in terms of structure from the secondary alcohols which were suggested in JP Laid-Open publication. Nos. 1998-195004 and 1998-139706.

20 Namely, the chiral alkoxy alcohols of the present invention are primary alcohols bearing an asymmetric carbon bonded to a methyl or trifluoromethyl group, and hydroxyl group apart from the chiral center by a carbon chain including oxygen.

From now on, the preparation method of the chiral alkoxy alcohols of Chemical Formula 1 will be designated as compound of $p=0$ or $p=1$.

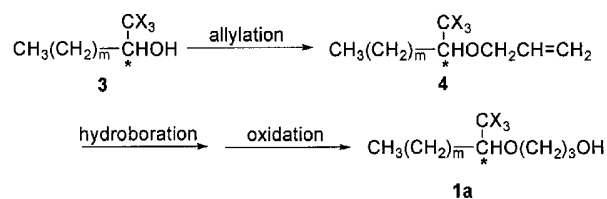
(1) Chemical Formula 1 where $p=0$

When p is 0, the compound of Chemical Formula 1 can be prepared according to Reaction Scheme 1, following the sequential steps of:

- a) reacting a secondary alcohol of Chemical Formula 3 with an alkylating agent to form an allyl ether compound of Chemical Formula 4, and
- b) reacting the allyl ethers compound of Chemical Formula 4 with a borane reagent followed by oxidation:

10

Reaction Scheme 1



(where, both X and m are the same as defined above.)

In step a), the secondary alcohol of Chemical Formula 3 is reacted in a solvent with an allylating agent in the presence of a base to prepare the allylether compound of Chemical Formula 4.

Among allylating agents, allylic halides are preferred.

As a solvent, ethers such as tetrahydrofuran, dioxane, 1,2-dimethoxyethane and dimethylformamide and alcohols such as methanol, ethanol, and isopropanol. Sometimes a mixture of these solvent can also be used.

In the allylation reaction, a base such as a metal hydride, a metal

hydroxide, a metal alkoxide, etc. can be used.

The alcohols of Chemical Formula 3 may be purchased or prepared. For example, the alcohol compound can be prepared by a racemic compound of 2-alkanol using the lipase Novozyme, as illustrated in JP Laid-Open Publication No. 1998-004998, or chiral 1-(trifluoromethyl)-1-alkanol can be prepared from a racemic mixture of 1-(trifluoromethyl)-1-alkanol using Novozyme.

In step b), the allylether compound of Chemical Formula 4 is then reacted with a borane compound in the presence of a solvent to perform hydroboration and oxidation to prepare the compound of Chemical Formula 1a.

Diborane or borane substituted with functional groups can be used for the hydroboration. Preferably a dialkylborane bearing a bulky alkyl group can be used to enhance regioselectivity. The solvents suitable for the present invention include ethers, or dimethylformamide, a mixed solvent. The reaction of step b) is performed at a temperature of ambient temperature to the boiling point of the solvent.

It is preferable to use m-chloroperbenzoic acid, hydrogen peroxide, or monoperoxyphthalic magnesium salt, as an oxidant.

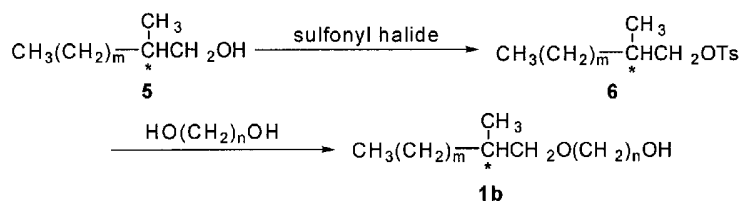
(2) Chemical Formula 1 where p is 1

When p is 1, the compounds of Chemical Formula 1b can be prepared according to the Reaction Scheme 2,

a) reacting a primary alcohol of Chemical Formula 5 with a sulfonyl halide to form a compound of Chemical Formula 6, and

b) reacting the compound of Chemical Formula 6 with a diol:

Reaction Scheme 2



(where, both m and n are the same as defined above, and Ts designates a

5 sulfonyl group.)

In step a), the primary alcohols of Chemical Formula 5 are reacted with alkanesulfonyl halide in the presence of a solvent and an organic base to prepare the compound of Chemical Formula 6.

An organic base such as triethylamine or pyridine is preferable.

10 The alkanesulfonyl ester, as a reagent for etherification, has good leaving group ability. *p*-Toluenesulfonyl halide, methanesulfonyl halide, etc. are used.

Suitable solvents include haloalkanes such as dichloromethane or ethers.

The alcohols of Chemical Formula 5 may be purchased or prepared following a known technique [J. Begmann, C. Lofstedt, V. D. Ivanov, W. Francke, 15 *European Journal of Organic Chemistry*, (16), 3175 - 3179 (2001); B. Guintchin, S. Bienz, *Tetrahedron*, 59 (38), 7527 - 7533 (2003)].

In step b), the compounds of Chemical Formula 6 are reacted with a diol in the presence of a solvent and base to prepare the chiral alkoxy alcohol compound of Chemical Formula 1b.

20 Preferably, the diol used may be at least one compound selected from the

group consisting of propandiol, butandiol, pentandiol, hexandiol, heptanediol, octanediol, nonandiol, and decanediol.

Bases such as an alkali metal or a metal hydride are preferable.

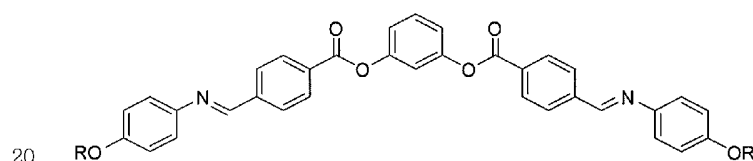
Suitable solvents include alcohols, ethers, dimethylformamide, and a
 5 mixture solvent. The reaction of step b) is performed at a temperature ranging from ambient to the boiling temperature of the solvent.

In accordance with the preparation method of the present invention, the chiral primary alkoxy alcohols can be prepared without affecting optical purity from secondary alcohol with high optical purity. The chiral primary alkoxy alcohols
 10 prepared by the present invention have a structure of a hydroxyl group and asymmetric carbon divided by an oxyalkyl chain.

The chiral alkoxyalcohols of Chemical Formula 1 can be used as valuable intermediates for medicinal and agricultural chemistry, and preferably for liquid crystal manufacture.

15 More specifically, banana-shaped liquid crystal materials of Chemical Formula 2 type can be prepared using the chiral alkoxy compound of Chemical Formula 1. The compound of Chemical Formula 2 is 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]benzoate:

Chemical Formula 2



(wherein, R is $\text{---}\overset{\zeta}{\underset{\zeta}{\text{C}}}(\text{CH}_2)_n\text{O}(\text{CH}_2)_p\text{---}\overset{\text{CX}_3}{\underset{*}{\text{CH}}}(\text{CH}_2)_m\text{CH}_3$, in which X is H or F, m is an integer from 1 to 5, n is an integer from 3 to 10, p is an integer of 0 or 1, and * is an asymmetric carbon.)

Preferably, the compounds of Chemical Formula 2 include 1,3-phenylene
 5 bis[4-{4-[(S)-3-(2-butoxy)-1-propoxy]]phenyliminomethyl]benzoate, 1,3-phenylene
 bis[4-{4-[(S)-3-(2-pentyloxy)-1-propoxy]]phenyliminomethyl]-benzoate, 1,3-
 phenylene bis[4-{4-[(S)-3-(2-hexyloxy)-1-propoxy]]-phenyliminomethyl]benzoate,
 1,3-phenylene bis[4-{4-[(S)-3-(2-heptyloxy)-1-
 propoxy]]phenyliminomethyl]benzoate, 1,3-phenylene bis[4-{4-[(S)-3-(1-trifluoro-
 10 methyl-1-heptyl oxy)]-1-propoxy]]phenyliminomethyl]benzoate, 1,3-phenylene
 bis[4-{4-[(S)-3-(2-methylbutoxy)-1-propoxy]]phenyliminomethyl]benzoate, 1,3-
 phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-1-butoxy]]phenyliminomethyl]-benzoate,
 1,3-phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-1-pentyloxy]]-
 phenyliminomethyl]benzoate, and 1,3-phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-
 15 1-hexyloxy]]phenyliminomethyl]benzoate.

The compound of Chemical Formula 2, 1,3-phenylene bis[4-(4-alkoxy)-phenyliminomethyl]benzoate, can be prepared following Reaction Scheme 3, by the steps of;

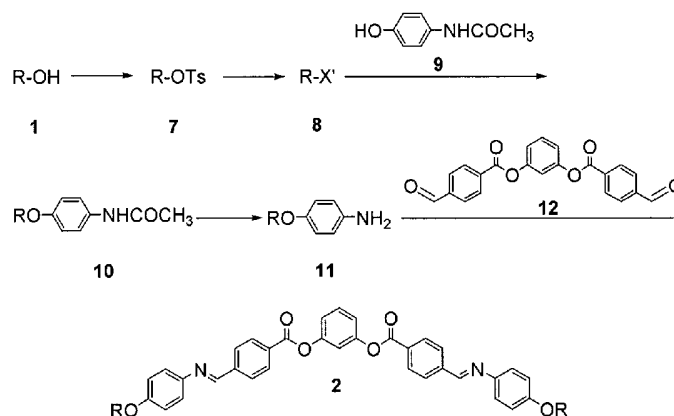
- a) reacting a chiral alkoxy alcohol of Chemical Formula 1 with a
 20 alkanesulfonyl halide to prepare a compound of Chemical Formula 7,
- b) halogenating the compound of Chemical Formula 7 to prepare a compound of Chemical Formula 8,

c) reacting the compound of Chemical Formula **8** with acetamidophenol of Chemical Formula **9** to prepare an alkoxyacetanilide compound of Chemical Formula **10**.

d) treating the compound of Chemical Formula 10 with an acid catalyst to
5 prepare an alkoxyaniline compound of Chemical Formula 11, and

e) reacting the alkoxyaniline compound of Chemical Formula 11 with a compound of Chemical Formula 12:

Reaction Scheme 3



10 (where, R is the same as described in the above Chemical Formula 2, and
X' is a halogen atom.)

In step a), the chiral alkoxy alcohol of Chemical Formula 1 is reacted with an alkanesulfonyl halide in the presence of a solvent and an organic base to prepare the compounds of Chemical Formula 7.

15 Organic base such as triethylamine or pyridine are preferred.

As a solvent, it is preferred to use one of the haloalkanes such as

dichloromethane or ethers.

A sulfonyl halide such as p-toluenesulfonyl halide, methanesulfonyl halide, etc. is used, of which esters acts as a reagent for etherification because of the good leaving group ability.

5 Then, the compounds of Chemical Formula 7 are reacted with a halogenating agent in the presence of a solvent to prepare the alkyl halides of Chemical Formula 8.

Suitable halogenating agents are alkali metal halides, preferably bromides.

Any water-miscible solvent such as acetone, methanol, and ethanol, or
10 acetonitrile may be used as a solvent.

Then, the compounds of Chemical Formula 8 are reacted with acetamidophenol of Chemical Formula 9 in the presence of a solvent and a base to prepare the alkoxyacetanilide compounds of Chemical Formula 10.

The acetamidophenol of Chemical Formula 9 may be either purchased or
15 prepared directly [Kumazawa *et al.*, *J. Mater. Chem.*, 2004, **14**, 157-164].

Inorganic bases such as potassium carbonate, potassium hydroxide, sodium carbonate etc. can be a suitable base. The reaction is performed in of water-miscible solvent.

Then, the alkoxyacetanilides of Chemical Formula 10 are treated with an
20 acid catalyst in the presence of a solvent to prepare an alkoxyanilines of Chemical Formula 11.

Among suitable acid catalysts are an inorganic acid such as hydrochloric

acid and sulfuric acid, or organic acid such as acetic acid.

Water and water miscible solvent combinations are preferred.

Then, the alkoxyanilines of Chemical Formula 11 are reacted with a bisaldehydes of Chemical Formula 12 in the presence of a haloalkane solvent to
5 prepare a compound of Chemical Formula 2.

The reaction in this step is described in a Ref: Kumazawa *et al.*, *J. Mater. Chem.*, 2004, **14**, 157-164.

Due to bearing a long of a chiral alkoxyalkyl chain, the 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]benzoates of Chemical Formula 2 have a liquid
10 crystal phase, as is the case of carbon derivatives in a Ref: Kumazawa *et al.*, *J. Mater. Chem.*, 2004, **14**, 157-164.

In addition, it can be used in the field of electronic optics as an important component of liquid crystal material, since the compound of the present invention has a low near-ambient phase-transition temperature. Moreover, the substitutions
15 of a methylene group with an ether linkage do not change the bonding angle, stereo-configuration, and torsional, as was disclosed in a Ref: (J. Dale, *Tetrahedron*, 1974, **30**, 1683). Therefore, the novel chiral alkoxy alcohols of the present invention can be used as substitutes of known chiral alcohols.

In addition, it can be used as carbon derivatives in fields of physiologically
20 active materials and other natural product synthesis.

The present invention is more specifically described by the following examples. However, it is clear that the present invention is not limited to these

examples in any manner.

Preparation Example 1

Preparation of chiral 2-alkanol

(S)-2-alkanol was prepared according to the method described in JP Laid-
5 Open Publication No. 1998-004998. To a racemic 2-alkanol, vinylpropionate in 2
eq. was added, and enantioselective esterification was carried out by lipase
Novozyme to prepare (R)-2-alkanol propionate and (S)-2-alkanol. By silica gel
chromatography (hexane : ether = 5 : 1), the (R)-2-alkanol propionate and (S)-2-
alkanol were separated. The (R)-2-alkanol was hydrolyzed in ethanol by KOH to
10 prepare (R)-2-alkanol. Both an (S)-isomer and an (R)-isomer can be used a chiral
alkoxy alcohol compound of the present invention. In all the examples of the
present invention, an (S)-isomer was used for convenience purposes.

Each prepared chiral alcohol was benzoylated using benzoyl chloride, and
the optical purity of benzoate was determined by performing chiral high
15 performance liquid chromatography [CHIRALCEL™ OB-H, IPA-0.05% TEA in
hexane] to identify the optical purity of over 99%ee.

Preparation Example 2

Preparation of chiral 1-(trifluoromethyl)alkanol

A racemate of 1-(trifluoromethyl)alkanol was prepared by using Novozyme
20 according to Ref. [T. Ohtani, H. Nakatsukasa, M. Kamezawa, H. Tachibana, Y.
Naoshima, *J. Molecular Catalysis, B: Enzymatic* **4**, 1998, 53-60.]

To the solution of phosphate buffer solution, a racemic mixture of 1-

(trifluoromethyl)-1-alkyl acetate was hydrolyzed in the presence of a Novozyme catalyst. After stereo-selectivity hydrolysis, (*R*)-1-(trifluoromethyl)alkanol was prepared from (*R*)-acetate. (*S*)-Acetate was not hydrolyzed. The resulting (*R*)-alcohol and (*S*)-acetate mixture was separated by silica gel chromatography
 5 (hexane : ether = 8 : 1). The separated (*S*)-acetate in ethanol was hydrolyzed with KOH to obtain (*S*)-1-(trifluoromethyl)alkanol.

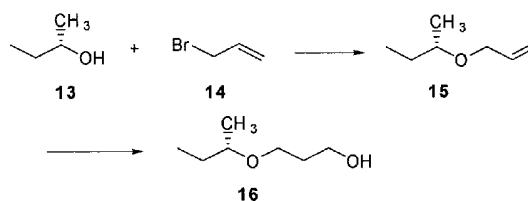
Both an (*S*)-isomer and an (*R*)-isomer can be used as chiral alkoxy alcohols of the present invention. In all the examples, an (*S*)-isomer was used for convenience purposes.

10 After preparing acetate derivatives from two chiral alcohols and racemic alcohol, the optical purity of benzoate was determined by performing chiral high performance liquid chromatography [CHIRALCEL™ OB-H, IPA-0.05% TEA in hexane] to identify the optical purity of over 99%ee.

Example 1

15 Preparation of (*S*)-3-(2-butoxy)propan-1-ol

The title compound was prepared following reaction scheme below.



Step 1) Preparation of allyl (*S*)-2-butyl ether (15)

NaH (60% dispersion in mineral oil, 2.95 g, 73.7 mmol) was washed with
 20 THF (20 ml × 2) and dimethylformamide (40 ml) was added. To the resulting

solution was slowly added (*S*)-2-butanol (**13**, 3.64 g, 49.1 mmol) at 0°C, and the mixture was stirred at room temperature for 1 hour. To the solution was added allylbromide (**14**, 5.95 g, 49.1 mmol) in dimethylformamide (25 ml). The resulting solution was refluxed at 60°C for 12 hours. The reaction was quenched by adding
5 1N HCl (25 ml). The product was extracted with ether (40 ml × 3), and washed with water (25 ml × 3), dried over anhydrous Na₂SO₄. Solvent was removed to obtain allyl (*S*)-2-butyl ether (**15**, 4.77 g, yield: 85%).

¹H-NMR δ 0.91 (t, 3H, J = 7.4 Hz), 1.14 (d, 3H, J = 6.2 Hz), 1.37 - 1.58 (m, 2H), 3.34 - 3.43 (m, 1H), 3.94 - 4.03 (m, 2H), 5.12 - 5.32 (m, 2H), 5.87 - 6.00 (m,
10 1H).

Step 2) Preparation of (*S*)-3-(2-butoxy)propan-1-ol (**16**)

To the solution of allyl (*S*)-2-butyl ether (4.70 g, 41.1 mmol) in THF (7 ml), 9-BBN (0.5 M THF solution, 82 ml, 41.1 mmol) was added, and the resulting solution was refluxed for 12 hours. Ethanol (30 ml), 4N NaOH (30 ml), and 30%
15 H₂O₂ (30 ml) were added thereto in sequence. The temperature was allowed to decrease to room temperature, and reaction was carried out for 2 hours and quenched by adding sat. aqueous NaHCO₃ (30 ml). The product was extracted with ether (40 ml × 3), and the combined extract was dried with Na₂SO₄ (anh.), and concentrated. The crude product was purified by column chromatography (silica
20 gel; hexane:ether = 3:1, R_f = 0.14) to obtain the compound (*S*)-3-(2-butoxy)propan-1-ol (**16**, 4.53 g, yield: 83%).

¹H-NMR δ 0.90 (t, 3H, J = 7.4 Hz), 1.13 (d, 3H, J = 6.2 Hz), 1.40 - 1.59 (m,

2H), 1.82 (quin, 2H, J = 5.6 Hz), 2.64 (br s, OH), 3.33 - 3.56 (m, 1H), 3.59 - 3.81 (m, 4H).

Example 2

Preparation of (S)-3-(2-pentyloxy)propan-1-ol

5 The title compound (3.20 g, yield: 57%) was prepared starting from (S)-2-pentanol (3.36 g, 38.1 mmol) in the same manner described in Example 1.

$^1\text{H-NMR}$ δ 0.91 (t, 3H, J = 6.6 Hz), 1.14 (d, 3H, J = 6.2 Hz), 1.21 - 1.56 (m, 4H), 1.82 (quin, 2H, J = 5.8 Hz), 2.59 (br s, OH), 3.36 - 3.45 (m, 1H), 3.50 - 3.81 (m, 4H).

10

Example 3

Preparation of (S)-3-(2-hexyloxy)propan-1-ol

The title compound (4.65 g, yield: 56%) was prepared starting from (S)-2-hexanol (5.39 g, 52.7 mmol) in the same manner described in Example 1.

$^1\text{H-NMR}$ δ 0.90 (t, 3H, J = 6.6 Hz), 1.14 (d, 3H, 6.2 Hz), 1.27 - 1.55 (m, 6H),
15 1.82 (quin, 2H, J = 5.6 Hz), 2.64 (br s, OH), 3.37 - 3.53 (m, 1H), 3.57 - 3.80 (m, 4H).

Example 4

Preparation of (S)-3-(2-heptyloxy)propan-1-ol

The title compound (1.63 g, yield: 51%) was prepared starting from (S)-2-heptanol (2.11 g, 18.6 mmol) in the same manner described in Example 1.

20 $^1\text{H-NMR}$ δ 0.90 (t, 3H, J = 6.4 Hz), 1.15 (d, 3H, J = 6.2 Hz), 1.22 - 1.54 (m, 8H), 1.83 (quin, 2H, J = 5.6 Hz), 2.38 (br s, OH), 3.31 - 3.44 (m, 1H), 3.48 - 3.82 (m, 4H).

Example 5**Preparation of (S)-3-(2-octyloxy)propan-1-ol**

The title compound (2.78 g, yield: 58%) was prepared starting from (S)-2-octanol (2.75 g, 21.1 mmol) in the same manner described in Example 1.

5 $^1\text{H-NMR}$ δ 0.90 (t, 3H, J = 6.2 Hz), 1.15 (d, 3H, J = 6.2 Hz), 1.20 - 1.54 (m, 10H), 1.83 (quin, 2H, J = 5.6 Hz), 2.23 (br s, OH), 3.36 - 3.51 (m, 1H), 3.54 - 3.82 (m, 4H).

Example 6**Preparation of (S)-3-(1-trifluoromethyl-1-hexyloxy)propan-1-ol**

10 The title compound (0.99 g, yield: 42%) was prepared starting from (S)-1-trifluoromethyl-1-hexanol (1.80 g, 9.7 mmol) in the same manner described in Example 1.

15 $^1\text{H-NMR}$ δ 0.90 (t, 3H, J = 6.8 Hz), 1.00 - 1.62 (m, 8H), 1.75 (br s, OH), 1.87 (quin, 2H, J = 6.0 Hz), 3.44 - 3.67 (m, 2H), 3.79 (t, 2H, J = 6.2 Hz), 3.77 - 3.86 (m, 1H).

Example 7**Preparation of (S)-3-(1-trifluoromethyl-1-heptyloxy)propan-1-ol**

20 The title compound (0.72 g, yield: 46%) was prepared starting from (S)-1-trifluoromethyl-1-heptanol (1.21 g, 6.54 mmol) in the same manner described in Example 1.

$^1\text{H-NMR}$ δ 0.90 (t, 3H, J = 6.6 Hz), 1.21 - 1.65 (m, 10H), 1.75 (br s, OH), 1.87 (quin, 2H, J = 5.8 Hz), 3.50 - 3.59 (m, 2H), 3.79 (t, 2H, J = 5.8 Hz), 3.89 - 3.99

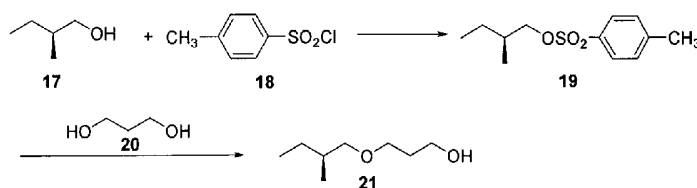
(m, 1H).

Example 8

Preparation of (S)-3-(2-methylbutoxy)propan-1-ol

The title compound was prepared according to the following reaction

5 scheme.



Step 1) Preparation of (S)-1-*p*-toluenesulfonyloxy-2-methylbutane (19)

The starting material, (S)-(-)-2-methyl-1-butanol (>99%ee) of Chemical
Formula 17, was purchased from Tokyo Kasei Kogyo Co., Ltd. and used as
10 received.

To a dichloromethane (35 ml) solution of (S)-(-)-2-methyl-1-butanol (5.00 g,
6.10 mmol) and triethylamine (1.48 g, 113.4 mmol), was added *p*-toluenesulfonyl
chloride (10.8 g, 56.7 mmol) in dichloromethane (25 ml). The reaction mixture
was stirred overnight at room temperature. To this was added saturated NaHCO₃
15 (30 ml), and the organic phase was separated and aqueous phase was extracted
with dichloromethane (10 ml × 3). The combined organic layers were dried
(Na₂SO₄), concentrated, and chromatographed on silical gel (hexanes:ether = 5:1,
R_f=0.42) to afford 13.2 g (96%) of (S)-1-*p*-toluenesulfonyloxy-2-methylbutane (19).

¹H-NMR δ 0.85 - 1.03 (m, 6H), 1.08 - 1.25 (m, 2H), 1.63 - 1.76 (m, 1H),

2.46 (s, 3H), 3.77 - 3.93 (m, 2H), 7.36 (d, 2H, J = 8.4 Hz), 7.80 (d, 2H, J = 8.4 Hz).

Step 2) Preparation of (S)-3-(2-methylbutoxy)propan-1-ol (21)

To a THF (25 ml) solution of 1,3-propanediol (**20**, 9.90 g, 132.0 mmol) was
5 added metallic sodium (1.14 g, 49.5 mmol) portionwise and stirred at room
temperature. When sodium was completely dissolved, tosylate (**19**, 8.00 g, 33.0
mmol) in THF was added. The reaction mixture was stirred overnight at 70-80°C
and cooled to room temperature. The solution was treated with water (70 ml) and
extracted with ether (50 ml × 3). The combined ether extracts were washed with
10 water, dried (Na₂SO₄), and concentrated to give (S)-3-(2-methylbutoxy)propan-1-ol
(**21**) (4.77 g, 99%).

¹H-NMR δ 0.84 - 0.96 (m, 6H), 1.09 - 1.68 (m, 3H), 1.83 (quin, 2H, J = 6.2
Hz), 2.56 (br s, OH), 3.16 - 3.34 (m, 2H), 3.60 (t, 2H, J = 5.6 Hz), 3.77 (t, 2H, J =
5.6 Hz).

15 **Example 9**

Preparation of (S)-4-(2-methylbutoxy)butan-1-ol

To a THF (17 ml) solution of 1,4-butanediol (7.61 g, 84.4 mmol) was added
metallic sodium (0.97 g, 42.2 mmol) portionwise and stirred at room temperature.
When sodium was completely dissolved, tosylate (3.41 g, 14.0 mmol) in THF was
20 added. The reaction mixture was stirred overnight at 70-80°C and cooled to room
temperature. The solution was treated with water (30 ml) and extracted with ether
(10 ml × 3). The combined ether extracts were washed with water, dried

(Na₂SO₄), and concentrated to give (S)-3-(2-methylbutoxy)-butane-1-ol (1.76 g, yield: 78%).

¹H-NMR δ 0.85 - 1.02 (m, 6H), 1.04 - 1.37 (m, 2H), 1.59 - 1.75 (m, 4H),
1.82 - 1.88(m, 1H), 2.47 (br s, OH), 3.16 - 3.34 (m, 2H), 3.45 (t, 2H, J = 5.8 Hz),
5 3.64 (t, 2H, J = 5.8 Hz).

Example 10

Preparation of (S)-5-(2-methylbutoxy)pentan-1-ol

To a THF (35 ml) solution of 1,5-pentanediol (13.82g, 132.6 mmol) was added metallic sodium (1.53 g, 66.3 mmol) portionwise and stirred at room
10 temperature. When sodium was completely dissolved, tosylate (5.36 g, 22.1 mmol) in THF was added. The reaction mixture was stirred overnight at 70-80°C and cooled to room temperature. The solution was treated with water (45 ml) and extracted with ether (15 ml × 3). The combined ether extracts were washed with water, dried (Na₂SO₄), and concentrated to give (S)-3-(2-methylbutoxy)-pentan-1-ol
15 (3.55 g, Yield: 85%).

¹H-NMR δ 0.84 - 0.92 (m, 6H), 1.07 - 1.24 (m, 2H), 1.37 - 1.50 (m, 2H),
1.53 - 1.67 (m, 4H), 1.81 - 1.88 (m, 1H), 2.02 (br s, OH), 3.12 - 3.25 (m, 2H), 3.40 (t,
2H, J = 6.2 Hz), 3.64 (t, 2H, J = 6.2 Hz).

Example 11

Preparation of (S)-6-(2-methylbutoxy)hexan-1-ol

To a THF (10 ml) solution of 1,6-hexanediol (3.90 g, 32.8 mmol) was added metallic sodium (0.29 g, 12.4 mmol) portionwise and stirred at room

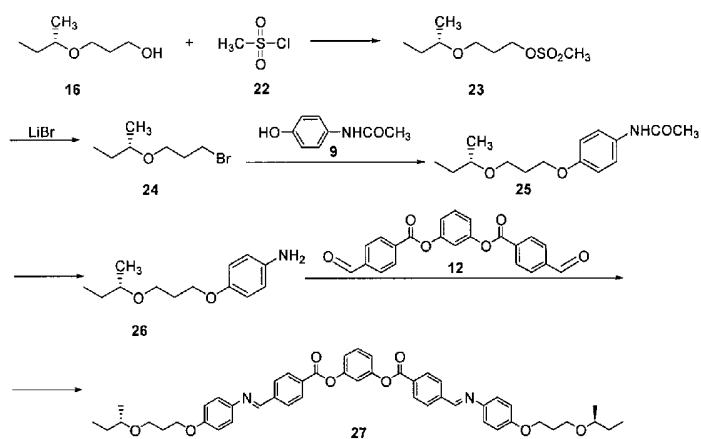
temperature. When sodium was completely dissolved, tosylate (2.00 g, 8.2 mmol) in THF was added. The reaction mixture was stirred overnight at 70-80°C and cooled to room temperature. The solution was treated with water (35 ml) and extracted with ether (15 ml × 3). The combined ether extracts were washed with
 5 water, dried (Na₂SO₄), and concentrated to give (S)-3-(2-methylbutoxy) hexan-1-ol (1.32 g, yield: 85%).

¹H-NMR δ 0.86 - 0.93 (m, 6H), 1.04 - 1.37 (m, 2H), 1.37 - 1.88 (m, 9H), 2.18 (br s, OH), 3.13 - 3.32 (m, 2H), 3.41 (t, 2H, J = 6.6 Hz), 3.66 (t, 2H, J = 6.6 Hz).

Example 12

10 Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-butoxy)-1-propoxy]]-phenyl-iminomethyl] benzoate

The title compound was prepared following reaction scheme shown below:



15

Step 1) Preparation of

(S)-1-methanesulfonyloxy-5-methyl-4-oxaheptane (23)

To an ether (150 ml) solution of the (S)-3-(2-butoxy)propan-1-ol (**16**, 4.31 g, 32.6 mmol) were added triethylamine (6.62 g, 60.2 mmol) and methanesulfonyl chloride (**22**, 7.46 g, 65.2 mmol) in ether (15 ml). The mixture was stirred
5 overnight at room temperature. To this solution was added water (100 ml) and the product was extracted with ether (30 ml × 3). The combined organic layers were dried (Na₂SO₄) and evaporated to give 5.60 g (82%) of mesylate **23**.

¹H-NMR δ 0.89 (t, 3H, J = 7.4 Hz), 1.11 (d, 3H, J = 6.4 Hz), 1.38 - 1.57 (m, 2H), 1.98 (quin, 2H, J = 6.2 Hz), 3.01 (s, 3H), 3.27 - 3.40 (m, 1H), 3.43 - 3.61 (m,
10 2H), 4.34 (t, 2H, J = 6.2 Hz).

Step 2) Preparation of (S)-1-bromo-5-methyl-4-oxaheptane (24)

A mixture of mesylate **23** (5.60 g, 26.6 mmol) and LiBr (7.00 g, 78.8 mmol) in acetone (100 ml) was heated to reflux for 12 h. The solvent was removed on a rotary evaporator until the volume of reaction mixture became about 25 ml. To
15 this was added water (50 ml) and the product was extracted with ether (30 ml × 3). The combined organic layers were washed with water, dried (Na₂SO₄), and concentrated to give 4.30 g (80%) of (S)-1-bromo-5-methyl-4-oxaheptane (**24**).

¹H-NMR δ 0.90 (t, 3H, J = 7.2 Hz), 1.19 (d, 3H, J = 6.2 Hz), 1.42 - 1.89 (m, 2H), 2.02 - 2.17 (m, 2H), 3.31 - 3.48 (m, 1H), 3.50 - 3.63 (m, 4H).

20 Step 3) Preparation of (S)-4-[3-(2-butoxy)-1-propoxy]acetanilide (25)

The mixture of 4-acetamidophenol (**9**, 3.33 g, 22.0 mmol), bromide **24** (4.30 g, 22.0 mmol), and potassium carbonate (9.13 g, 66.1 mmol) in 65 ml of acetone was

refluxed overnight. The solvent was removed on a rotary evaporator until the volume of the mixture became about 30 ml. To this solution was added water (30 ml) and the product was extracted with ether (20 ml × 3). The combined organic layers were dried (Na₂SO₄), concentrated, and chromatographed on silica gel
 5 (hexane:ether = 1:1, R_f = 0.48) to give 3.23 g (56%) of (S)-4-[3-(2-butoxy)-1-propoxy]acetanilide (**25**)

¹H-NMR δ 0.89 (t, 3H, J = 7.4 Hz), 1.13 (d, 3H, J = 5.8 Hz), 1.36 - 1.63 (m, 2H), 2.03 (quin, 2H, J = 6.2 Hz), 2.17 (s, 3H), 2.65 (br s, NH), 3.29 - 3.49 (m, 1H), 3.51 - 3.69 (m, 2H), 4.05 (t, 2H, J = 6.2 Hz), 6.87 (d, 2H, J = 9.2 Hz), 7.39 (d, 2H, J
 10 = 9.2 Hz).

Step 4) Preparation of (S)-4-[3-(2-butoxy)-1-propoxy]aniline (**26**)

An ethanol (75 ml) solution of acetanilide (**25**, 3.20 g, 12.0 mmol) and a catalytic amount of conc. HCl was stirred at 70°C. After 2 days, the solvent was evaporated *in vacuo*. To this was added saturated NaHCO₃ (20 ml) was added.
 15 The combined ether extracts (25 ml × 3) were dried (Na₂SO₄), concentrated, and chromatographed on silica gel (hexane:ether = 2:1, R_f = 0.24) to afford (S)-4-[3-(2-butoxy)-1-propoxy]aniline (**26**) (1.45 g, 53%).

¹H-NMR δ 0.90 (t, 3H, J = 7.2 Hz), 1.13 (d, 3H, J = 6.2 Hz), 1.36 - 1.53 (m, 2H), 2.01 (quin, 2H, J = 6.2 Hz), 3.31 - 3.60 (m, 5H, CH₂OCH₂, NH₂), 4.01 (t, 2H, J
 20 = 6.2 Hz), 6.68 (d, 2H, J = 9.2 Hz), 6.77 (d, 2H, 9.2 Hz).

Step 5) Preparation of 1,3-phenylene bis[4-{4-[(S)-3-2-butoxy)-1-propoxy]} phenyl iminomethyl]benzoate (**27**)

(5-1) Preparation of bisaldehyde compound (12)

To the dichloromethane (60 ml) solution of resorcinol (1.00 g, 9.0 mmol), 4-carboxybenzaldehyde (2.99 g, 19.8 mmol), N,N-dicyclohexylcarbodiimide (4.68 g, 22.7 mmol) and 4-dimethylaminopyridine (2.77 g, 22.7 mmol) were added, and the
5 resulting solution was stirred at room temperature for 2 days. The obtained product was concentrated to half of its volume and purified by column chromatography (silica gel) to give the compound of bisaldehyde (**12**, 2.20g, yield: 65%).

$^1\text{H-NMR}$ δ 7.20 - 7.28 (m, 3H), 7.54 (t, 1H, J = 8.4 Hz), 8.03 - 8.07 (m, 4H),
10 8.36 - 8.40 (m, 4H), 10.17 (s, 2H).

(5-2) Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-butoxy)-1-propoxy]}-phenyliminomethyl] benzoate (27)

A solution of (S)-4-[3-(2-butoxy)propoxy]aniline (**26**, 1.43 g, 6.4 mmol) and bisaldehyde **12** (1.20 g, 3.2 mmol) in chloroform (100 ml) was refluxed for 4 h.
15 The reaction mixture was concentrated and recrystallized from chloroform-ethanol to give 1,3-phenylene bis[4-{4-[(S)-3-(2-butoxy)-1-propoxy]}-phenyliminomethyl] benzoate (**27**, 1.88 g, yield: 78%) as a yellow crystal.

$^1\text{H-NMR}$ δ 0.90 (t, 6H, J = 7.6 Hz), 1.14 (d, 6H, J = 6.2 Hz), 1.27 - 1.55 (m, 4H), 2.06 (quin, 4H, J = 6.2 Hz), 3.30 - 3.56 (m, 2H), 3.59 - 3.90 (m, 4H), 4.12 (t, 4H, J = 6.2 Hz), 6.98 (d, 4H, J = 8.8 Hz), 7.20 - 7.33 (m, 7H), 7.52 (t, 1H, J = 8.8 Hz), 8.04 (d, 4H, J = 8.4 Hz), 8.30 (d, 4H, J=8.4 Hz), 8.60 (s, 2H).

Example 13

Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-pentyloxy)-1-propoxy]}phenyliminomethyl]benzoate

A solution of (S)-4-{3-(2-pentyloxy)-1-propoxy}aniline (1.37 g, 5.8 mmol) and bisaldehyde **12** (1.1 g, 2.9 mmol) in chloroform (100 ml) was refluxed for 4 h.

5 The reaction mixture was concentrated and recrystallized from chloroform-ethanol to give 1,3-phenylene bis[4-{4-[(S)-3-(2-pentyloxy)-1-propoxy]}phenyliminomethyl]benzoate (1.88 g, yield: 78%) as a yellow crystal.

¹H-NMR δ 0.90 (t, 6H, J = 6.6 Hz), 1.14 (d, 6H, J = 6.2 Hz), 1.27 - 1.55 (m, 8H), 2.06 (quin, 4H, J = 6.2 Hz), 3.38 - 3.75 (m, 6H), 4.11 (t, 4H, J = 6.2 Hz), 6.97
10 (d, 4H, J = 8.8 Hz), 7.20 - 7.33 (m, 7H), 7.52 (t, 1H, J = 8.8 Hz), 8.04 (d, 4H, J = 8.4 Hz), 8.30 (d, 4H, J=8.4 Hz), 8.59 (s, 2H).

Example 14

Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-hexyloxy)-1-propoxy]}phenyliminomethyl]benzoate

15 A solution of (S)-4-{3-(2-hexyloxy)-1-propoxy}aniline (1.74 g, 6.9 mmol) and bisaldehyde **12** (1.29 g, 3.4 mmol) in chloroform (110 ml) was refluxed for 4 h. The reaction mixture was concentrated and recrystallized from chloroform-ethanol to give 1,3-phenylene bis[4-{4-[(S)-3-(2-hexyloxy)-1-propoxy]}phenyliminomethyl]benzoate (2.05 g, yield: 72%) as a yellow crystal.

20 ¹H-NMR δ 0.88 (t, 6H, J = 6.6 Hz), 1.14 (d, 6H, J = 6.2 Hz), 1.29 - 1.53 (m, 12H), 2.06 (quin, 4H, J = 5.8 Hz), 3.31 - 3.48 (m, 2H), 3.49 - 3.76 (m, 4H), 4.12 (t, 4H, J = 6.2 Hz), 6.97 (d, 4H, J = 8.8 Hz), 7.21 - 7.39 (m, 3H), 7.31 (d, 4H, J = 8.8

Hz), 7.52 (t, 1H, J = 8.8 Hz), 8.04 (d, 4H, J = 8.4 Hz), 8.30 (d, 4H, J = 8.4 Hz), 8.59 (s, 2H).

Example 15

Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-heptyloxy)-1-propoxy]}-phenyliminomethyl]benzoate

A solution of (S)-4-{3-(2-heptyloxy)-1-propoxy}aniline (0.63 g, 2.2 mmol) and bisaldehyde **12** (0.44 g, 1.1 mmol) in chloroform (100 ml) was refluxed for 4 h. The reaction mixture was concentrated and recrystallized from chloroform-ethanol to give 1,3-phenylene bis[4-{4-[(S)-3-(2-heptyloxy)-1-propoxy]}-phenyliminomethyl]benzoate (0.76 g, yield: 80%) as a yellow crystal.

¹H-NMR δ 0.88 (t, 6H, J = 6.6 Hz), 1.15 (d, 6H, J = 6.2 Hz), 1.22 - 1.68 (m, 16H), 2.06 (quin, 4H, J = 6.2 Hz), 3.36 - 3.45 (m, 2H), 3.51 - 3.79 (m, 4H), 4.12 (t, 4H, J = 6.2 Hz), 6.98 (d, 4H, J = 8.8 Hz), 7.20 - 7.33 (m, 3H), 7.32 (d, 4H, J = 8.8 Hz), 7.53 (t, 1H, J = 8.8 Hz), 8.05 (d, 4H, J = 8.4 Hz), 8.31 (d, 4H, J = 8.4 Hz), 8.60 (s, 2H).

Example 16

Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(1-trifluoromethyl)-1-heptyloxy]-1-propoxy}]phenyliminomethyl]benzoate

A solution of (S)-4-[3-(1-trifluoromethyl-1-heptyl)-1-propoxy]aniline (0.84 g, 1.4 mmol) and bisaldehyde **12** (0.27 g, 0.7 mmol) in chloroform (95 ml) was refluxed for 4 h. The reaction mixture was concentrated and recrystallized from chloroform-ethanol to give 1,3-phenylene bis[4-{4-[(S)-3-(1-trifluoromethyl)-1-

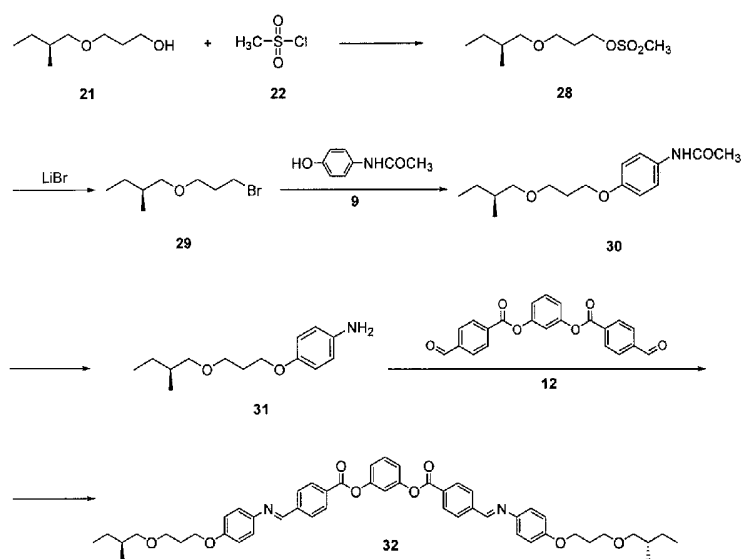
heptyloxy)-1-propoxy]]phenyliminomethyl]benzoate (0.45 g, yield: 62%) as a yellow crystal.

$^1\text{H-NMR}$ δ 0.88 (t, 6H, J = 6.2 Hz), 1.01 - 1.65 (m, 20H), 2.11 (quin, 4H, J = 6.2 Hz), 3.53 - 3.83 (m, 4H), 3.95 - 4.17 (m, 6H), 6.97 (d, 4H, J = 8.8 Hz), 7.22 - 7.41 (m, 3H), 7.32 (d, 4H, J = 8.8 Hz), 7.50 (t, 1H, J = 8.0 Hz), 8.05 (d, 4H, J = 8.4 Hz), 8.31 (d, 4H, J = 8.4 Hz), 8.60 (s, 2H).

Example 17

Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-1-propoxy]]-phenyliminomethyl]benzoate

The title compound was prepared following reaction scheme described below.



Step 1) Preparation of (S)-1-methanesulfonyloxy-6-methyl-4-octane (28)

To an ether (130 ml) solution of (S)-3-(2-methylbutoxy)propan-1-ol (**21**, 4.32 g, 29.5 mmol) were added triethylamine (5.98 g, 59.0 mmol) and methanesulfonyl chloride (**22**, 6.76 g, 59.0 mmol) in ether (13 ml). The mixture was stirred overnight at room temperature. To this solution was added water (100 ml) and the mixture was extracted with ether (30 ml × 3). The combined organic layer was dried (Na₂SO₄) and evaporated to give 6.62 g (99%) of (S)-1-methanesulfonyloxy-6-methyl-4-oxaoctane (**28**).

¹H-NMR δ 0.85 - 0.92 (m, 6H), 1.30 - 1.70 (m, 3H), 2.00 (quin, 2H, J = 6.2 Hz), 3.01 (s, 3H), 3.18 - 3.29 (m, 2H), 3.43 - 3.56 (m, 2H), 4.35 (t, 2H, J = 6.2 Hz).

10 Step 2) Preparation of (S)-1-bromo-6-methyl-4-oxaoctane (**29**)

A mixture of mesylate **28** (7.69g, 29.5 mmol) in acetone (95 ml) and LiBr (7.69 g, 88.6 mmol) in acetone (95 ml) was refluxed overnight. The solvent was removed on a rotary evaporator. Water (32 ml) was added and the mixture was extracted with ether (30 ml × 3). The combined organic extracts were washed with water, dried (Na₂SO₄), and concentrated to afford 5.02 g (70%) of (S)-1-bromo-6-methyl-4-oxaoctane (**29**).

¹H-NMR δ 0.86 - 0.93 (m, 6H), 1.10 - 1.89 (m, 3H), 2.10 (quin, 2H, J = 6.2 Hz), 3.16 - 3.34 (m, 2H), 3.43 - 3.56 (m, 4H).

Step 3) Preparation of (S)-4-[3-(2-methylbutoxy)-1-propoxy]acetanilide (**30**)

20 The mixture of 4-acetamidophenol (**9**, 3.62 g, 24.0 mmol) and potassium carbonate (9.95 g, 72.0 mmol) in acetone (60 ml) was added (S)-1-bromo-6-methyl-4-oxaoctane (**29**, 5.02 g, 24.0 mmol) in acetone. The mixture was refluxed

overnight and the solvent was removed with rotary evaporator. To this solution was added water (20ml) and extracted with ether (20 ml $\times$ 3). The combined organic extracts were dried (Na_2SO_4), concentrated, and chromatographed on silica gel (hexane:ether = 1:1, R_f =0.48) to give 4.71 g (70%) of (S)-4-[3-(2-methylbutoxy)-1-propoxy]acetanilide (**30**).

$^1\text{H-NMR}$ δ 0.87 - 0.92 (m, 6H), 1.01 - 1.97 (m, 3H), 2.03 (quin, 2H, J = 6.2 Hz), 2.16 (s, 3H), 2.62 (br s, NH), 3.21 - 3.38 (m, 2H), 3.58 (t, 2H, J = 6.2 Hz), 4.01 (t, 2H, J = 6.2 Hz), 6.84 (d, 2H, J = 8.8 Hz), 7.38 (d, 2H, J = 8.8 Hz).

Step 4) Preparation of (S)-4-[3-(2-methylbutoxy)-1-propoxy]aniline (**31**)

10 An ethanol (110 ml) solution of (S)-4-[3-(2-methylbutoxy)-1-propoxy]acetanilide (**30**, 4.71 g, 16.8 mmol) and a catalytic amount of conc. HCl was stirred at 70°C. After 2 days, the solvent was evaporated *in vacuo*. To this was added saturated NaHCO_3 (20 ml) and the mixture was extracted with ether (20 ml $\times$ 3). The combined organic layers were dried (Na_2SO_4), concentrated, and
15 chromatographed on silica gel (hexane:ether = 2:1, R_f =0.24) to give 2.00 g (50%) of (S)-4-[3-(2-methylbutoxy)-1-propoxy]aniline (**31**).

$^1\text{H-NMR}$ δ 0.89 - 0.93 (m, 6H), 1.01 - 1.67 (m, 3H), 2.02 (quin, 2H, J = 6.2 Hz), 3.16 - 3.34 (m, 4H, CHCH_2O , NH_2), 3.58 (t, 2H, J = 6.2 Hz), 4.01 (t, 2H, J = 6.2 Hz), 6.66 (t, 2H, J = 8.8 Hz), 6.77 (t, 2H, J = 8.8 Hz).

20 Step 5) Preparation of 1,3-phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-1-propoxy]}phenyliminomethyl]benzoate (**32**)

A solution of bisaldehyde **12** (1.43 g, 3.80 mmol) and (S)-4-[3-(2-

methylbutoxy)-1-propoxy]aniline (**31**, 1.81 g, 7.60 mmol) in chloroform (100 ml) was refluxed for 4 h. The solvent was evaporated and the residual solid was recrystallized from chloroform-ethanol to give 1,3-phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-1-propoxy]]phenyliminomethyl]benzoate (**32**, 2.24 g, 72%) as a yellow crystal.

$^1\text{H-NMR}$ δ 0.86 - 0.93 (m, 12H), 1.07 - 1.68 (m, 6H), 2.08 (quin, 4H, $J = 6.2$ Hz), 3.18 - 3.36 (m, 4H), 3.61 (t, 4H, $J = 6.2$ Hz), 4.12 (t, 4H, $J = 6.2$ Hz), 6.97 (d, 4H, $J = 8.8$ Hz), 7.20 - 7.34 (m, 3H), 7.31 (d, 4H, $J = 8.8$ Hz), 7.53 (t, 1H, $J = 9.2$ Hz), 8.05 (d, 4H, $J = 8.4$ Hz), 8.30 (d, 4H, $J = 8.4$ Hz), 8.59 (s, 2H).

10

Example 18

Preparation of 1,3-phenylene bis[4-{4-[(S)-4-(2-methylbutoxy)-1-butoxy]]-phenyliminomethyl]benzoate

Step 1) Preparation of (S)-1-methanesulfonyloxy-7-methyl-5-oxanonane

The title compound of (S)-1-methanesulfonyloxy-7-methyl-5-oxanonane (5.30 g, yield: 99%) was prepared starting from (S)-3-(2-methylbutoxy)butan-1-ol (3.57 g, 22.2 mmol) in the same manner described in 1) of Example 17.

$^1\text{H-NMR}$ δ 0.85 - 1.80 (m, 12H), 1.82 - 1.88 (m, 1H), 3.01 (s, 3H), 3.16 - 3.34 (m, 2H), 3.43 (t, 2H, $J = 5.8$ Hz), 4.27 (t, 2H, $J = 6.2$ Hz).

Step 2) Preparation of (S)-1-bromo-7-methyl-5-oxanonane

The title compound of (S)-1-bromo-7-methyl-5-oxanonane (3.53 g, yield: 71%) was prepared starting from (S)-1-methanesulfonyloxy-7-methyl-5-oxanonane (5.30 g) in the same manner described in 2) of Example 17.

20

$^1\text{H-NMR}$ δ 0.85 - 0.93 (m, 6H), 1.17 - 1.25 (m, 2H), 1.61 - 2.16 (m, 5H),
3.17 - 3.49 (m, 6H).

Step 3) Preparation of (S)-4-[4-(2-methylbutoxy)-1-butoxy]acetanilide

The title compound of (S)-4-[4-(2-methylbutoxy)-1-butoxy]acetanilide (2.87
5 g, yield: 62%) was prepared starting from (S)-1-bromo-7-methyl-5-oxanonane (3.53
g, 15.8 mmol) in the same manner described in 3) of Example 16.

$^1\text{H-NMR}$ δ 0.86 - 0.93 (m, 6H), 1.17 - 1.25 (m, 2H), 1.62 - 2.16 (m, 5H), 2.15
(s, 3H), 2.62 (br s, NH), 3.19 - 3.28 (m, 2H), 3.47 (t, 2H, J = 6.2 Hz), 3.96 (t, 2H, J =
6.2 Hz), 6.84 (d, 2H, J = 8.8 Hz), 7.38 (d, 2H, J = 8.8 Hz).

10 Step 4) Preparation of (S)-4-[4-(2-methylbutoxy)-1-butoxy]aniline

The title compound of (S)-4-[4-(2-methylbutoxy)-1-butoxy]aniline (1.58 g,
yield: 64%) was prepared starting from (S)-4-[4-(2-methylbutoxy)-1-
butoxy]acetanilide (2.87 g, 9.7 mmol) in the same manner described in 4) of
Example 17.

15 $^1\text{H-NMR}$ δ 0.86 - 0.99 (m, 6H), 1.02 - 1.22 (m, 2H), 1.60 - 1.86 (m, 5H),
3.14 - 3.32 (m, 4H, CHCH_2O , NH_2), 3.46 (t, 2H, J = 6.2 Hz), 3.91 (t, 2H, 6.4 Hz),
6.65 (d, 2H, 8.8 Hz), 6.75 (d, 2H, 8.8 Hz).

Step 5) Preparation of 1,3-phenylene bis[4-[4-[(S)-4-(2-methylbutoxy)-1-
butoxy]]phenyliminomethyl]benzoate

20 To the dichloromethane (100ml) solution of bisaldehyde **12** (1.17 g, 3.1
mmol) and (S)-4-[4-(2-methylbutoxy)-1-butoxy]aniline (1.58 g, 6.2 mmol) was
refluxed for 4 hours. The reaction mixture was concentrated and recrystallized

from ethanol to give the title compound (2.84 g, yield: 74%).

$^1\text{H-NMR}$ δ 0.87 - 0.93 (m, 12H), 1.14 - 1.22 (m, 4H), 1.41 - 1.94 (m, 10H),
 3.20 - 3.34 (m, 4H), 3.49 (t, 2H, J = 6.2 Hz), 4.04 (t, 2H, J = 6.2 Hz), 6.96 (d, 4H, J
 = 8.8 Hz), 7.20 - 7.33 (m, 3H), 7.31 (d, 4H, J = 8.8 Hz), 7.53 (t, 1H, J = 9.2 Hz),
 5 8.04 (d, 4H, J = 8.4 Hz), 8.30 (d, 4H, J = 8.4 Hz), 8.59 (s, 2H).

Example 19

Preparation of 1,3-phenylene bis[4-{4-[(S)-5-(2-methylbutoxy)-1-pentyloxy]}phenyliminomethyl]benzoate

The title compound of (2.57 g) was prepared starting from (S)-5-(2-methylbutoxy)pentan-1-ol (3.55 g, 20.3 mmol) in the same manner described in of
 10 Example 18.

Step 1) Preparation of (S)-1-methanesulfonyloxy-8-methyl-6-oxadecane

Yield: 97%

$^1\text{H-NMR}$ δ 1.84 - 0.92 (m, 6H), 1.07 - 1.24 (m, 2H), 1.37 - 1.89 (m, 7H),
 15 3.00 (s, 3H), 3.16 - 3.25 (m, 2H), 3.40 (t, 2H, J = 6.2 Hz), 4.23 (t, 2H, J = 6.6 Hz).

Step 2) Preparation of (S)-1-bromo-8-methyl-6-oxadecane

Yield: 82%

$^1\text{H-NMR}$ δ 0.87 - 0.92 (m, 6H), 1.01 - 1.25 (m, 2H), 1.41 - 1.96 (m, 7H),
 3.16 - 3.38 (m, 2H), 3.40 - 3.53 (m, 4H).

Step 3) Preparation of (S)-4-[5-(2-methylbutoxy)-1-pentyloxy] acetanilide

Yield: 75%

$^1\text{H-NMR}$ δ 0.89 - 0.93 (m, 6H), 1.00 - 1.82 (m, 9H), 2.15 (s, 3H), 2.62 (br s,

NH), 3.14 - 3.33 (m, 2H), 3.43(t, 2H, J = 6.2 Hz), 3.90 (t, 2H, J = 6.2 Hz), 6.84 (d, 2H, J = 8.8 Hz), 7.38 (d, 2H, J = 8.8 Hz).

Step 4) Preparation of (S)-4-[5-(2-methylbutoxy)-1-pentyloxy]aniline

Yield: 87%

5 ¹H-NMR (200MHz, CDCl₃) δ 0.89 - 0.93 (m, 6H), 1.00 - 1.82 (m, 9H), 3.14 - 3.33 (m, 4H, CHCH₂O, NH₂), 3.43 (t, 2H, J = 6.2 Hz), 3.90 (t, 2H, J = 6.2 Hz), 6.65 (d, 2H, J = 8.8 Hz), 6.76 (d, 2H, J = 9.2 Hz).

Step 5) Preparation of 1,3-phenylene bis[4-[4-[5-(2-methylbutoxy)-1-pentyloxy]]phenyliminomethyl]benzoate

10 Yield: 69%

¹H-NMR δ 0.87 - 0.94 (m, 12H), 1.10 - 1.21 (m, 4H), 1.40 - 1.88 (m, 14H), 3.18 - 3.36 (m, 4H), 3.45 (t, 4H, J = 6.2 Hz), 4.01 (t, 4H, J = 6.2 Hz), 6.96 (d, 4H, J = 8.8 Hz), 7.11 - 7.33 (m, 3H), 7.31 (d, 4H, J = 8.8 Hz), 7.53 (t, 1H, J = 9.2 Hz), 8.05 (d, 4H, J = 8.4 Hz), 8.30 (d, 4H, J = 8.4 Hz), 8.59 (s, 2H)

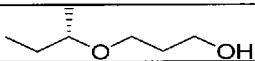
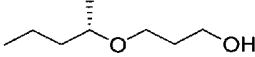
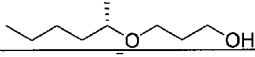
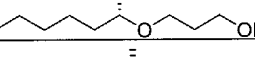
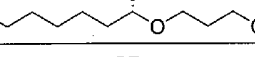
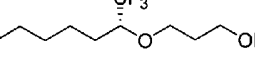
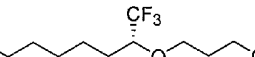
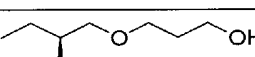
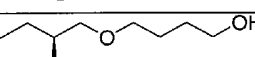
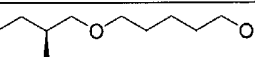
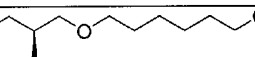
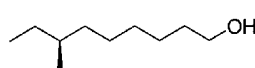
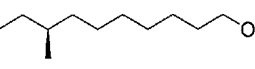
15 **Experimental Example 1**

Detection of optical rotation

Optical rotation for compounds of Examples 1-11 was measured with an autopolarimeter (Autopol IV, Rudolph Research Analytical). After adding chloroform to a cell (10 cm), the zero point was carefully adjusted. After washing
20 with a sample solution, a sample solution was added to the cell, and the value of optical rotation was recorded at a temperature range of 20 to 26 °C. The optical rotation was estimated to have a standard deviation of less than 5% over five times,

and the results are arranged in Table 1. Optical purity of each compound is the same as that of each starting material.

<Table 1>

Example	Chemical formula	Optical purity (%ee)	Optical rotation ($[\alpha]_D^{20}$) (c = g/100ml, CHCl ₃)
1		98	+ 14.7° (c 1.10)
2		99	+ 16.1° (c 0.11)
3		99	+ 14.7° (c 0.61)
4		97	+ 10.0° (c 0.03)
5		99	+ 8.0° (c 1.00)
6		99	+ 11.9° (c 1.06)
7		99	+ 18.2° (c 1.10)
8		98	+ 2.8° (c 0.67)
9		98	+ 2.4° (c 1.00)
10		98	+ 2.0° (c 1.04)
11		98	+ 1.7° (c 0.70)
Comparative compound 1**		-	+ 8.44° (c 1.05)
Comparative		-	+ 7.73° (c 0.88)

compound 2**			
* $[\alpha]_D^{26}$ ** Comparative compound 1, 2: K. Imaizumi, H. Terasima, K. Akasaka, and J. Ohri, <i>Analytical Sciences</i> , 19 , 1243 (2003).			

Experimental Example 2

Detection of phase transition temperature

Observations of the liquid crystal phases and the phase-transition temperature of chiral compounds of Examples 12-20 were performed using a polarization microscope and a differential scanning calorimeter (DSC).

The temperature of heating element in the polarization microscope was calibrated by a standard solution having N-bromosuccinimide (NBS) and benzoic acid, and a heating and cooling rate of 1-2 °C/min. was maintained. A sample between glass plates (20 mm × 20 mm × 0.01mm) was placed on the heater and the liquid crystal phase was monitored with a right angle polarizer and observer with the magnification rate of 500.

The temperature and transition energy of DSC (Perkin Elmer Co. Ltd, DSC-7 series) was calibrated with Indium (99.9%, 156.60 °C, 28.45 J/g), and the scanning range was determined by the above-observed phase-transition temperature. The sample size of 2 to 4 mg, and the rate of heating and cooling was 3 °C/min. The results from the polarization microscope and DSC showed that all compounds of 1,3-phenylene bis[4-(4-alkoxy)-phenyliminomethyl]benzoate of the present invention have a liquid crystal phase.

Table 2 shows the phase-transition temperature of each compound. The

nomenclature "Bn phases" (B1-B7) was suggested at the workshop on Banana-shaped Liquid Crystal: Chirality by Achiral Molecules, held in Berlin in 1997.

<Table 2>

Example	Phase Transition Temperature			
13	Cry	$\xrightleftharpoons[84.1\text{ }^{\circ}\text{C}]{91.9\text{ }^{\circ}\text{C}}$	B2	$\xrightleftharpoons[102.6\text{ }^{\circ}\text{C}]{108.0\text{ }^{\circ}\text{C}}$ Iso
14	Cry	$\xrightleftharpoons[79.9\text{ }^{\circ}\text{C}]{91.8\text{ }^{\circ}\text{C}}$	B2	$\xrightleftharpoons[100.4\text{ }^{\circ}\text{C}]{101.6\text{ }^{\circ}\text{C}}$ Iso
15	Cry	$\xrightleftharpoons[79.9\text{ }^{\circ}\text{C}]{92.7\text{ }^{\circ}\text{C}}$	B7	$\xrightleftharpoons[95.1\text{ }^{\circ}\text{C}]{96.4\text{ }^{\circ}\text{C}}$ Iso
17	Cry	$\xrightleftharpoons[118.0\text{ }^{\circ}\text{C}]{121.8\text{ }^{\circ}\text{C}}$	B2	$\xrightleftharpoons[120.3\text{ }^{\circ}\text{C}]{130.0\text{ }^{\circ}\text{C}}$ Iso
18	Cry	$\xrightleftharpoons[111.2\text{ }^{\circ}\text{C}]{116.5\text{ }^{\circ}\text{C}}$	B2	$\xrightleftharpoons[138.3\text{ }^{\circ}\text{C}]{144.5\text{ }^{\circ}\text{C}}$ Iso
19	Cry	$\xrightleftharpoons[110.8\text{ }^{\circ}\text{C}]{120.4\text{ }^{\circ}\text{C}}$	B2	$\xrightleftharpoons[128.3\text{ }^{\circ}\text{C}]{134.6\text{ }^{\circ}\text{C}}$ Iso
Iso: Isotropic liquid phase; Cry: Crystal phase; B2, B7: Liquid crystal phase				

The compounds of 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]-benzoate derived from chiral alkoxy alcohols show similar electronic optical properties as banana-shaped liquid crystal compounds from chiral alcohols. The odd-even behavior for the alternative appearance of ferroelectricity and antiferroelectricity was observed in two homologous series; the banana-shaped mesogen of our invention Example 17 and Example 19 and their carbon analogues (Chemical Formula 2, where R is (S)-6-methyloctyl and (S)-8-methyldecyl) where the length of n is even, exhibited ferroelectric phases. On the contrary, the mesogens Example 18 and carbon analogues (Chemical Formula 2 where R is

(S)-7-methylnonyl and (S)-5-methylheptyl) where n is odd, showed antiferroelectric phases. It is obvious that the phase behavior of two homologues is dependent upon the position (odd or even) of the chiral center from the chain end (methyl carbon) (Lee *et al.*, *J. Am. Chem. Soc.* 2005, **127**, 11085-11091). Two

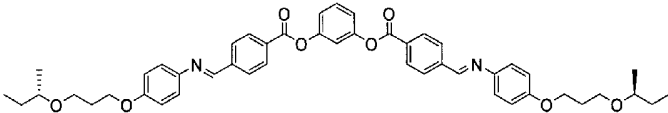
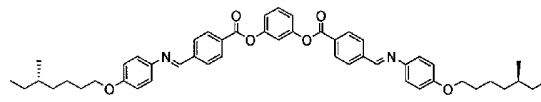
5 homologous banana-shaped liquid crystals bearing chiral alkyl and chiral (alkoxy)alkyl terminal groups exhibit the similar phase behavior. This implies that the alkoxy alcohols of the present invention can be a preferable substitute for alkyl

alcohols of carbon derivatives. In addition, the compounds of the present invention have much lower phase-transition temperature than that of known

10 banana-shaped compounds derived from alkyl alcohols.

The following Table 3 shows the phase-transition temperature of compound of Example 12 and a commonly known compound:

<Table 3>

Compound
Example 12  Phase transition temp. Iso $\xrightarrow{115.4\text{ }^{\circ}\text{C}}$ B2 $\xrightarrow{104.4\text{ }^{\circ}\text{C}}$ Cry
Comparative compound 12'  Phase transition temp.

Iso $\xrightarrow{158\text{ }^{\circ}\text{C}}$ B2 $\xrightarrow{120\text{ }^{\circ}\text{C}}$ Cry		
* Comparative compound 12: Kumazawa <i>et al.</i> , <i>J. Mater. Chem.</i> , 2004, 14 , 157-164		

The chiral alkoxy alcohols of the present invention have asymmetric carbon away from the alcoholic hydroxyl group by oxygen-containing carbon chain. These can be used for synthesis of chiral liquid crystal materials, pharmaceuticals, agricultural chemicals, and intermediates of natural product synthesis. Moreover,

5 the chiral compound, 1,3-phenylene bis[4-(4-alkoxy)- phenyliminomethyl]benzoate bearing an alkoxy alcohol group as an end group has the same or more satisfactory liquid crystal phase and electric optical property, and a low phase transition temperature, when compared with a known carbon derivative with a chiral alkyl group. The emergence of ferroelectricity and antiferroelectricity of

10 them depend on the length of chiral (alkoxy)alkyl terminal group, they can be used as important components in the mixture of smectic liquid crystal materials.

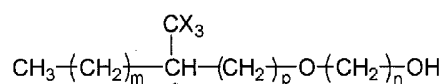
WHAT IS CLAIMED IS:

1. A chiral alkoxy alcohol compound represented by following Chemical

Formula 1:

5

Chemical Formula 1



where X is H or F,

m is an integer of 1 to 5,,

n is an integer of 3 to 10,

10

p is an integer of 0 or 1, and

* depicts an asymmetric carbon.

2. The chiral alkoxy alcohols of claim 1, wherein m is an integer of 1 to 5 and n is an integer of 3 to 5 when p is 0, or m is 1 and n is an integer of 3 to 10 when p is

15 1.

3. The chiral alkoxy alcohol compound of the claim 1, wherein the chiral alkoxy alcohol compound is a compound selected from the group consisting of:

(S)-3-(2-butoxy)propan-1-ol;

20

(S)-3-(2-pentyloxy)propan-1-ol;

(S)-3-(2-hexyloxy)propan-1-ol;

(S)-3-(2-heptyloxy)propan-1-ol;

(S)-3-(2-octyloxy)propan-1-ol;

(S)-3-(1-trifluoromethyl-1-hexyloxy)propan-1-ol;

(S)-3-(1-trifluoromethyl-1-heptyloxy)propan-1-ol;

5 (S)-3-(2-methylbutoxy)propan-1-ol;

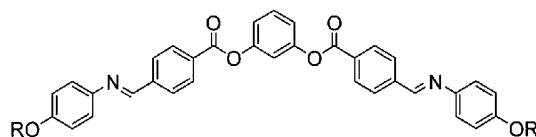
(S)-4-(2-methylbutoxy)butan-1-ol;

(S)-5-(2-methylbutoxy)pentan-1-ol; and

(S)-6-(2-methylbutoxy)hexan-1-ol.

- 10 4. A compound of 1,3-phenylene bis-[4-(4-alkoxy)phenyliminomethyl]-benzoate represented by following Chemical Formula 2:

Chemical Formula 2



wherein R is $\text{---}\frac{5}{3}\text{---}(\text{CH}_2)_n\text{O---}(\text{CH}_2)_p\text{---}\underset{*}{\text{CH}}(\text{CX}_3)\text{---}(\text{CH}_2)_m\text{CH}_3$, in which X is H or F,

- 15 m is an integer of 1 to 5, n is an integer of 3 to 10, p is an integer of 0 or 1, and * is an asymmetric carbon.

5. The compound of the claim 4, wherein m is an integer of 1 to 5 and n is an integer of 3 to 5 when p is 0, or m is 1 and n is an integer of 3 to 10 when p is 1.

20

6. The compound of the claim 4, wherein the 1,3-phenylene bis-[4-(4-

alkoxy)phenyliminomethyl]benzoate compound is a compound selected from the group consisting of:

1,3-phenylene bis[4-{4-[(S)-3-(2-butoxy)-1-propoxy]}phenyliminomethyl]-benzoate;

5 1,3-phenylene bis[4-{4-[(S)-3-(2-pentyloxy)-1-propoxy]}phenyliminomethyl]benzoate;

1,3-phenylenebis[4-{4-[(S)-3-(2-hexyloxy)-1-propoxy]}phenyliminomethyl]benzoate;

10 1,3-phenylene bis[4-{4-[(S)-3-(2-heptyloxy)-1-propoxy]}phenyliminomethyl]benzoate;

1,3-phenylene bis[4-{4-[(S)-3-(1-trifluoromethyl)-1-heptyloxy]}-1-propoxy]phenyliminomethyl] benzoate;

1,3-phenylene bis[4-{4-[(S)-3-(2-methylbutoxy)-1-propoxy]}phenyliminomethyl] benzoate;

15 1,3-phenylene bis[4-{4-[(S)-4-(2-methylbutoxy)-1-butoxy]}phenyliminomethyl] benzoate; and

1,3-phenylene bis[4-{4-[(S)-5-(2-methylbutoxy)-1-pentyloxy]}phenyliminomethyl] benzoate.

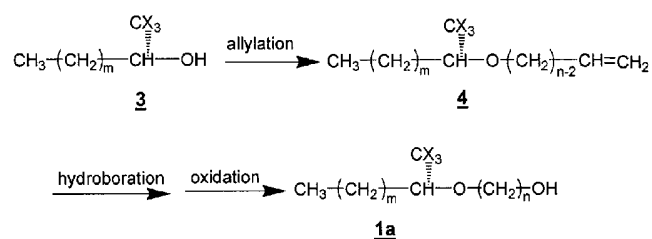
20 7. A method of preparing a chiral alkoxyalcohol compound of Chemical Formula 1a, represented by Reaction Scheme 1 comprising:

a) reacting a secondary alcohol of following Chemical Formula 3 with an

allylating agent to form an allylether compound of the following Chemical Formula 4, and

b) reacting the allylether compound of Chemical Formula 4 and oxidizing it:

Reaction Scheme 1



5

Wherein, X is H or F,

m is an integer of 1 to 5, and

n is an integer of 3 to 10.

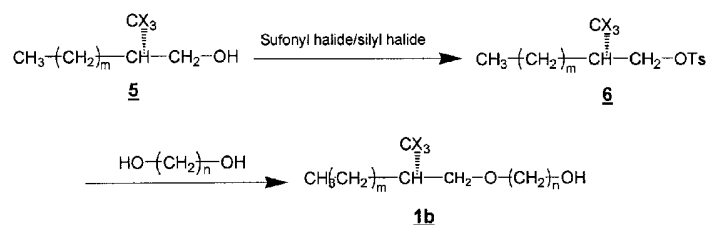
10 8. A method of preparing a compound of Chemical Formula 1b represented by Reaction Scheme 2, comprising:

a) reacting a primary alcohol of the following Chemical Formula 5 with a sulfonyl halide to form a compound of following Chemical Formula 6, and

b) reacting the compound of Chemical Formula 6 with a diol:

15

Reaction Scheme 2



wherein, X is H or F,

m is an integer of 1 to 5,

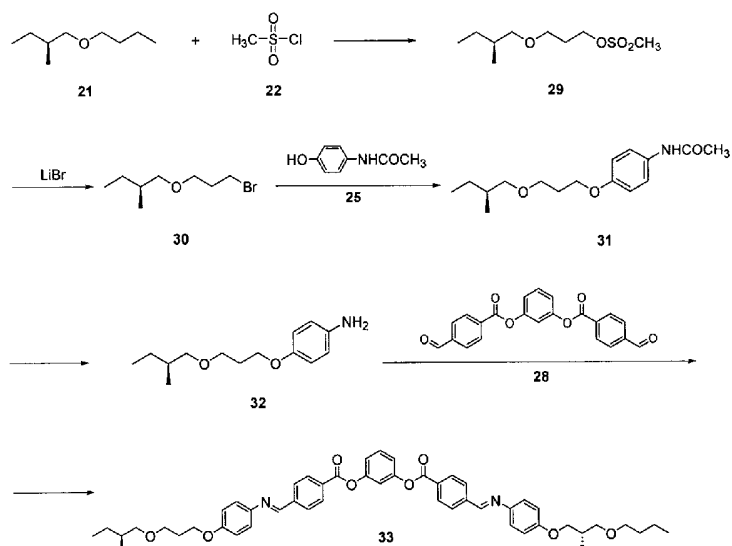
n is an integer of 3 to 10, and

5 Ts is a sulfonyl or silyl group.

9. A method of preparing the compound of Chemical Formula 2 represented by Reaction Scheme 3, comprising:

- a) reacting a chiral alkoxy alcohol of Chemical Formula 1 with a sulfonyl
- 10 halide to prepare a compound of Chemical Formula 7,
- b) halogenating the compound of Chemical Formula 7 to prepare a compound of Chemical Formula 8,
- c) reacting the compound of Chemical Formula 8 with acetamidophenol of Chemical Formula 9 to prepare an alkoxyacetanilide compound of Chemical
- 15 Formula 10,
- d) treating the compound of Chemical Formula 10 using an acid catalyst to prepare an alkoxyaniline compound of Chemical Formula 11, and
- e) reacting the alkoxyaniline compound of Chemical Formula 11 with a compound of Chemical Formula 12:

Reaction Scheme 3



wherein, R is $\text{---} \text{C}(\text{X})_3 \text{---} (\text{CH}_2)_n \text{---} \text{O} \text{---} (\text{CH}_2)_p \text{---} \text{CH} \text{---} (\text{CH}_2)_m \text{---} \text{CH}_3$, in which X is H or F,

m is an integer of 1 to 5, n is an integer of 3 to 10, p is an integer of 0 or 1, and * is an asymmetric carbon; and X' is a halogen atom.

10. An intermediate compound represented by Chemical Formula 1 for preparing 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]benzoate.

10 11. A liquid crystal material comprising the 1,3-phenylene bis[4-(4-alkoxy)phenyliminomethyl]benzoate of claim 4.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/002870

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C07C 43/13**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 69/76, 41/26, 43/10, C09K 19/12, 19/30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN International, e-Korean Intellectual Property Office Patent Search System, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6730371 B2(Mitsubishi Gas Chemical Company, Inc.) May 4, 2004 see the claim 1 and the example 10	1 - 11
A	US 5637256 A(University Research Corp.) June 10, 1997 see the whole document	1 - 11
A	EP 0937765 A1(Mitsubishi Gas Chemical Company, Inc.) August 25, 1999 see the abstract and the formula (1)	1 - 11
A	EP0994097 A2(Mitsubishi Gas Chemical Company, Inc.) April 19, 1999 see the abstract and the formula (1)	1 - 11
A	JP2002-322113 A(Mitsubishi Gas Chemical Company, Inc.) November 08, 2002 see the whole document	1 - 11
P, X	Lee, Seng Kue et al. 'Odd-even behavior of ferroelectricity and antiferroelectricity in two homologous series of bent-core mesogens'; Journal of the American Chemical Society, 2005, 127(31), 11085-11091, see the abstract and the chemical compounds with Registry No. 863989-56-4 and 863991-86-0	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Information on patent family members

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