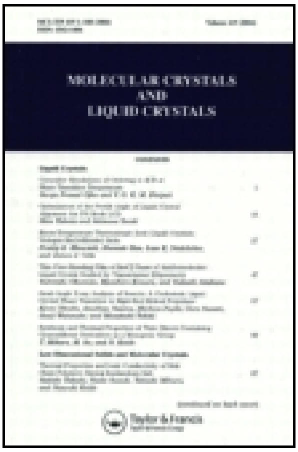

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Synthesis and Some Physical Properties of Bicyclohexanes Having Fluoro Substituted Alkyl Moiety

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SYNTHESIS AND SOME PHYSICAL PROPERTIES OF BICYCLOHEXANES HAVING FLUORO SUBSTITUTED ALKYL MOIETY

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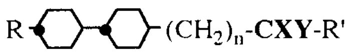
Abstract The influence of introducing fluorine atoms into alkyl chains of dialkylbicyclohexanes on their physical properties has been investigated. Wide mesophase ranges of the bicyclohexanes were induced by the fluorine atoms. Their viscosity changed depending on the position of fluorine atoms on the alkyl chains and some of the fluorinated bicyclohexanes showed low viscosity. Also dielectric anisotropy and birefringence increased by introducing fluorine atoms. By using the fluorinated compounds mixtures for TFT and STN applications having attractive properties; a wide mesophase range, lower viscosity and higher specific resistivity could be obtained.

INTRODUCTION

Dialkylbicyclohexanes **3** are very useful as base liquid crystals because of their low viscosity. However derivatives of **3** have not been investigated. In this report, to clarify the influence of introducing fluorine atoms on the properties of this homologue, we have synthesized gem-difluorinated compounds **1** and monofluorinated compounds **2** and investigated some of their physical properties.

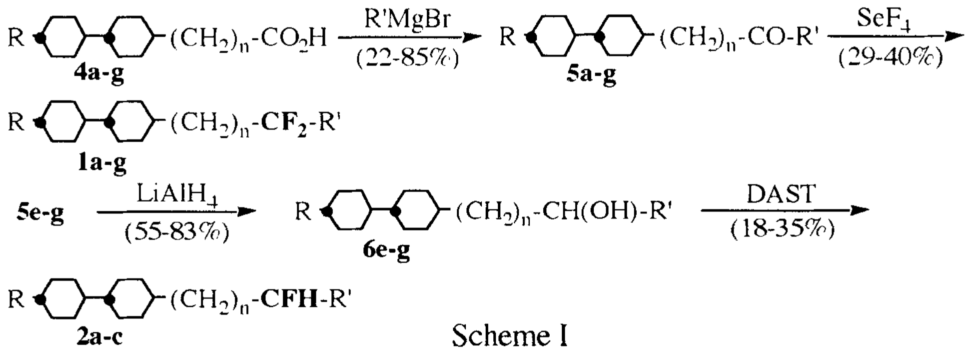


1 : X=F, Y=F
2 : X=F, X=H
3 : X=Y=H

In particular, the influence of the number and the position of fluorine atoms and the length of the terminal alkyl chain R' on the physical properties, i.e., mesophases, viscosity, dielectric anisotropy ($\Delta\varepsilon$) and birefringence (Δn) have been investigated.

SYNTHESIS

Chemically stable **1** and **2** have been synthesized through scheme I. Purities of all synthesized compounds were checked by GLC analysis and found to be more than 99.9%. Reduction by lithium aluminum hydride of the ketones **5**, that were obtained from the carboxylic acids **4** and the Grignard reagents in the presence of a catalyst, gave the alcohols **6** [1]. Fluorination of **5** using SeF_4 [2], and of **6** using diethylaminosulfur trifluoride (DAST) [3] gave **1** and **2**, respectively.



Scheme I

MEASUREMENT

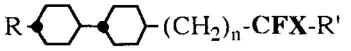
Phase transition temperatures were determined using a RIGAKU DSC-8230 differential scanning calorimeter and by a NIKON OPTIPHOT polarization microscope with a METTLER FP52 hot stage. Viscosity was measured at 20°C using a LAUDA VISCOBOY viscometer with a SCHOTT GERATE ubbelohde tube. Bulk viscosity was measured at 25°C using a TOKIMEC ELD-R rotational viscosimeter. Density was measured at 19.8°C using a PAAR DMA-60SI digital densimeter. Δn was measured with an ATAGO 4T & 2T Abbe refractometer. $\Delta\varepsilon$ was measured by a HEWLETT PACKARD 4284A LCR meter. Threshold voltage was measured using a HEWLETT PACKARD 3478A detector and a WAVETEK model 75 generator. Resistivity was measured by a TAKEDA RIKEN TR8601 ohm meter.

RESULTS AND DISCUSSION

Mesophases

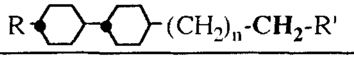
The transition temperatures of difluorinated **1a-1g** and monofluorinated **2a-2c** compounds are shown in TABLE 1. All the compounds showed a smectic B phase (S_B). The clearing points of the fluorinated compounds are more than 10°C higher than those of non-fluorinated compounds **3a-3d** [4] (TABLE 2). Also as shown in FIG.1 the clearing points are influenced by the position of F atoms on the alkyl chains (**1d**: 94.6°C, **1e**: 105.9°C, **1f**: 114.4°C). We attempted to explain the difference of the transition temperatures, especially the clearing points with their length-to-breadth ratios (l/d) [5]. Since there is a reasonable correlation between the clearing points and l/d calculated using the molecular orbital method MOPAC ver.6 / PM3 [6] (TABLE 3), it is clear that F atoms induced changes in the conformations of **1d-1f**, **2a** and **3d**, which influence the difference of their clearing points.

TABLE 1 Transition temperatures of fluorinated dialkylbicyclohexanes.



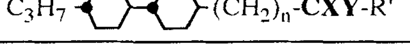
Compound	R	$-(CH_2)_n-\mathbf{CFX}-R'$	Transition temperature(°C) C		S_X		S_B		I
1a	C_3H_7	$-\mathbf{CF_2}-CH_3$	•	5.1	•	68.9	•	77.1	•
1b	C_3H_7	$-\mathbf{CF_2}-C_2H_5$	•	23.0			•	91.4	•
1c	C_3H_7	$-\mathbf{CF_2}-(CH_2)_2CH_3$	•	21.9			•	98.8	•
1d	C_3H_7	$-\mathbf{CF_2}-(CH_2)_3CH_3$	•	33.9			•	94.6	•
1e	C_3H_7	$-CH_2-\mathbf{CF_2}-(CH_2)_2CH_3$	•	22.1			•	105.9	•
1f	C_3H_7	$-(CH_2)_2-\mathbf{CF_2}-C_2H_5$	•	17.5			•	114.4	•
1g	C_5H_{11}	$-CH_2-\mathbf{CF_2}-C_2H_5$	•	2.3			•	118.1	•
2a	C_3H_7	$-CH_2-\mathbf{CFH}-(CH_2)_2CH_3$	•	41.5			•	110.2	•
2b	C_3H_7	$-(CH_2)_2-\mathbf{CFH}-C_2H_5$	•	33.5			•	107.1	•
2c	C_5H_{11}	$-CH_2-\mathbf{CFH}-C_2H_5$	•	10.4			•	120.1	•

TABLE 2 Transition temperatures of dialkylbicyclohexanes.



Compound	R	$-(CH_2)_n-\mathbf{CH_2}-R'$	Transition temperature(°C) C		S_X		S_B		I
3a	C_3H_7	$-C_2H_5$	•	−10.9			•	66.8	•
3b	C_3H_7	$-(CH_2)_2CH_3$	•	64.3			•	81.6	•
3c	C_3H_7	$-(CH_2)_3CH_3$	•	− 8.3			•	95.2	•
3d	C_3H_7	$-(CH_2)_4CH_3$	•	15.6			•	95.6	•

TABLE 3 Transition temperatures and length-to-breadth ratios (l/d) [a].



Compound	$-(CH_2)_n-\mathbf{CXY}-R'$	Transition temperature(°C) C		S_B		I	l/d
1d	$-\mathbf{CF_2}-(CH_2)_3CH_3$	•	33.9	•	94.6	•	2.659
1e	$-CH_2-\mathbf{CF_2}-(CH_2)_2CH_3$	•	22.1	•	105.9	•	3.474
1f	$-(CH_2)_2-\mathbf{CF_2}-CH_2CH_3$	•	17.5	•	114.4	•	3.482
2a	$-CH_2-\mathbf{CFH}-(CH_2)_2CH_3$	•	41.5	•	110.2	•	3.478
3d	$-(CH_2)_4CH_3$	•	15.6	•	95.6	•	3.439

a) calculated with MOPAC ver. 6.

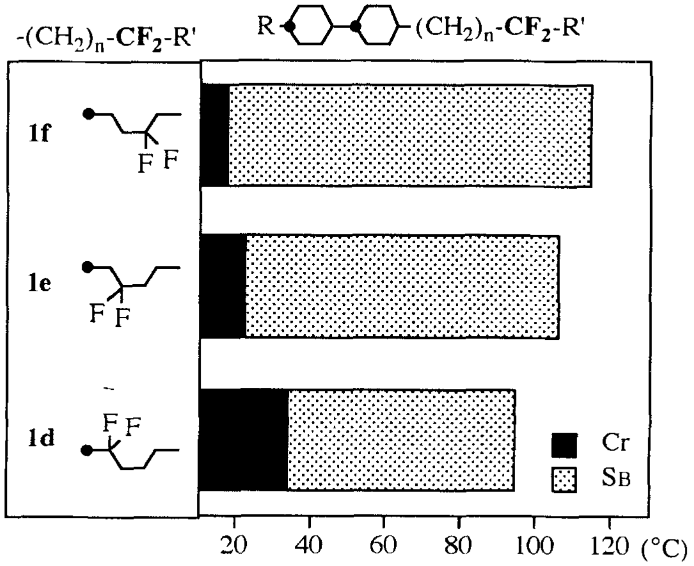


FIG. 1 Mesophase of **1d-1f**.

For **1a-1d** that all have F atoms on the nearest carbons from the cyclohexane rings (position-1) on their alkyl chains the clearing points strongly depend on the lengths of the terminal alkyl chains R' (FIG. 2), and when R' is propyl the compound **1c** shows the highest clearing point. On the other hand, the clearing points of **3a-3d** rise as the length of their R' increases (**3a**: 66.8°C, **3b**: 81.6°C, **3c**: 95.2°C, **3d**: 95.6°C). Therefore it is

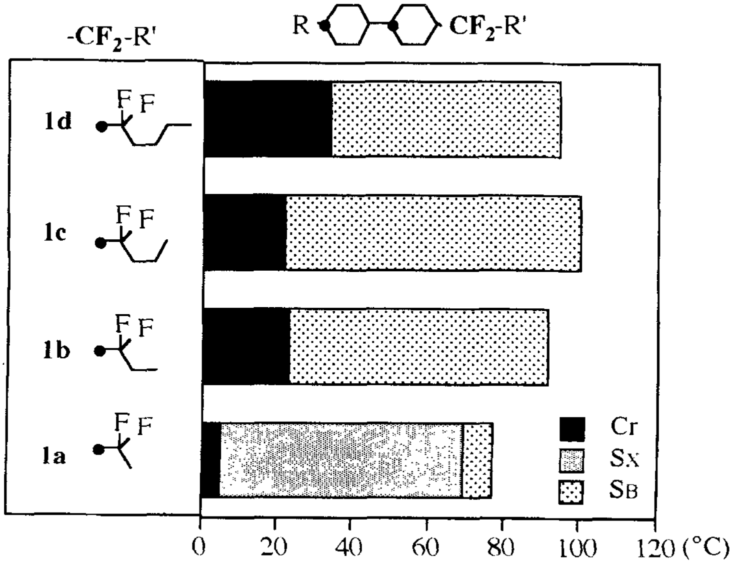


FIG. 2 Mesophases of **1a-1d**.

obvious that the rise in the clearing points among the homologues (**1a-1d**) does not depend on the introduction of F atoms but only on the increase of l/d corresponding with the increase in the length of the alkyl chains.

Viscosity

Viscosity and density of mixtures containing 20wt% of **1a-1f**, **2a**, **2b**, **3a**, **3c** and **3d** in a base mixture A comprising three cyanophenylcyclohexane derivatives were measured. The relationship between the viscosity and the density of the compounds is shown in FIG.3. The viscosity and the density showed a good correlation, and there was a tendency for the higher viscosity and density to be induced through the introduction of F atoms. The viscosities of difluorinated (**1a-1f**), monofluorinated (**2a** and **2b**) and non-fluorinated (**3a**, **3c** and **3d**) compounds were approximately 22 cst, 20 cst and 16.8 cst respectively.

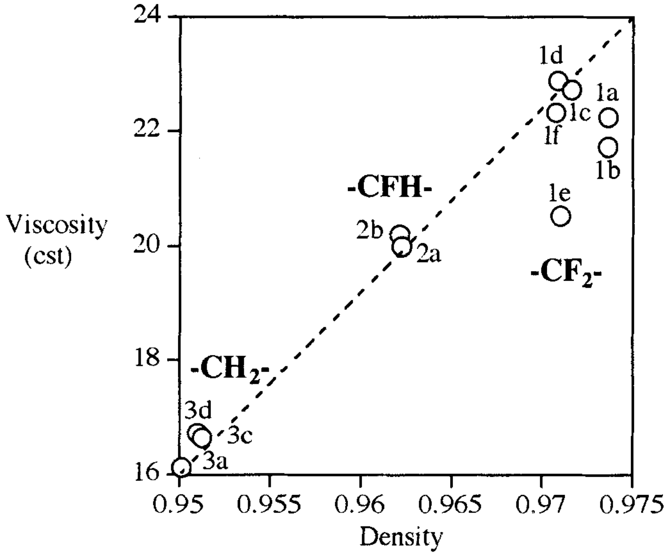


FIG. 3 Viscosity and density of mixtures containing 20wt% of dialkylbicyclohexanes in mixture A (clearing point; 52.3°C).

However, when we considered the difluorinated compounds in detail, though their density was almost at the same level (0.970-0.973), their viscosity was distributed across a broad range (**1e**: 20.50 cst - **1d**: 22.29 cst). It therefore seems that the position of F atoms affects intermolecular interactions. For the **1d-1f** series, the viscosity of **1e** having F atoms in the even position on the alkyl chain was rather lower than that of **1d** and **1f** having F atoms in the odd positions.

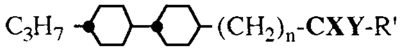
Dielectric anisotropy

The dielectric anisotropies of mixtures containing of **1a-1f**, **2a**, **2b** and **3a-3d** in a base mixture B comprising five phenylcyclohexanecarboxylates were measured at T_{NI} −30°C (TABLE 4). $|\Delta\varepsilon|$ increased in the order of non-fluorinated (−0.97 to −1.03) < monofluorinated (−1.25 and −1.31) < difluorinated (−1.26 to −1.36) compounds. The dipole anisotropies ($\Delta\mu$) of the compounds calculated with MOPAC ver.6 / PM3 and POLAR [7] defined by the equation

$$\Delta\mu = \mu_X{}^2 - (\mu_Y{}^2 + \mu_Z{}^2)$$

are listed in TABLE 4. Since there was a good correlation between $\Delta\varepsilon$ and $\Delta\mu$, it seems that the larger absolute value of $|\Delta\varepsilon|$ of the fluorinated compounds was induced by the increase of $|\Delta\mu|$ with the introduction of F atoms.

TABLE 4. Dielectric anisotropy of mixtures containing 20wt% of dialkylbicyclohexanes in mixture B (clearing point; 74.6°C, $\Delta\varepsilon$; −1.23) and calculated dipole anisotropy $\Delta\mu$ (A.U.) of dialkylbicyclohexanes.



Comp.	$-(CH_2)_n$-**CXY**-R'	$\varepsilon_\perp$ [a]	$\varepsilon_{//}$ [a]	$\Delta\varepsilon$	μ_x [b]	μ_y [b]	μ_z [b]	$\Delta\mu$ [b]
1a	**-CF$_2$**-CH$_3$	4.47	3.21	−1.26	0.47	0.63	0.46	−0.39
1b	**-CF$_2$**-CH$_2$CH$_3$	4.42	3.09	−1.33	0.41	0.63	0.45	−0.43
1c	**-CF$_2$**-(CH$_2$)$_2$CH$_3$	4.37	3.08	−1.29	0.36	0.67	0.43	−0.51
1d	**-CF$_2$**-(CH$_2$)$_3$CH$_3$	4.38	3.05	−1.33	0.34	0.67	0.43	−0.52
1e	-CH$_2$-**CF$_2$**-(CH$_2$)$_2$CH$_3$	4.34	3.01	−1.33	0.19	0.52	0.60	−0.59
1f	-(CH$_2$)$_2$-**CF$_2$**-CH$_2$CH$_3$	4.43	3.07	−1.36	0.31	0.54	0.58	−0.53
2a	-CH$_2$-**CFH**-(CH$_2$)$_2$CH$_3$	4.22	2.91	−1.31	0.26	0.55	0.03	−0.23
2b	-(CH$_2$)$_2$-**CFH**-CH$_2$CH$_3$	4.18	2.93	−1.25	0.27	0.55	0.04	−0.23
3a	-CH$_2$CH$_3$	3.80	2.77	−1.03	0.01	0.01	0.00	0.00
3b	-(CH$_2$)$_2$CH$_3$	- c)	- c)	- c)	0.00	0.00	0.00	0.00
3c	-(CH$_2$)$_3$CH$_3$	3.75	2.77	−0.98	0.00	0.00	0.00	0.00
3d	-(CH$_2$)$_4$CH$_3$	3.73	2.76	−0.97	0.00	0.00	0.00	0.00
Mixture B		4.21	2.98	−1.23				

a) $\varepsilon_\perp$ and $\varepsilon_{//}$ were measured at $T_{N\text{-}I}$ −30°C.

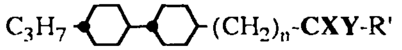
b) calculated with MOPAC ver.6 and POLAR.

c) crystallized.

The $\Delta\varepsilon$ of **1d**-**1f** having F atoms in different positions (position-1, 2 and 3) was not influenced by the position of F atoms (**1d**: −1.33, **1e**: −1.33, **1f**: −1.36). When we consider the conformations of the alkyl chains of the fluorinated compounds, it appears that the three compounds show almost the same Δε value because there are no other substituents having large dipole moments in the molecules.

The birefringences at T_{NI} -30°C of mixtures containing 20 wt% of the compounds **1a**-**1f**, **2a**, **2b** and **3a**-**3d** in the mixture A are listed in TABLE 5. Although the Δn of monofluorinated compounds **2a** and **2b** is almost the same as that of non-fluorinated compound **3d**, that of difluorinated compounds **1a**-**1f**, especially those having a shorter terminal alkyl chain R', was larger than that of the corresponding non-fluorinated compounds **3a**, **3c** and **3d**.

TABLE 5. Birefringence of mixtures containing 20wt% of dialkylbicyclohexanes in mixture B.



Compound	-$(CH_2)_n$-**CXY**-R'	Δn [a)]
1a	**-CF_2**-CH_3	0.1065
1b	**-CF_2**-CH_2CH_3	0.1053
1c	**-CF_2**-$(CH_2)_2CH_3$	0.1031
1d	**-CF_2**-$(CH_2)_3CH_3$	0.1029
1e	-CH_2-**CF_2**-$(CH_2)_2CH_3$	0.1045
1f	-$(CH_2)_2$-**CF_2**-CH_2CH_3	0.1020
2a	-CH_2-**CFH**-$(CH_2)_2CH_3$	0.1032
2b	-$(CH_2)_2$-**CFH**-CH_2CH_3	0.1031
3a	-CH_2CH_3	0.1010
3b	-$(CH_2)_2CH_3$	- b)
3c	-$(CH_2)_3CH_3$	0.1018
3d	-$(CH_2)_4CH_3$	0.1031
Mixture A		0.1200

a) Δn was measured at $T_{N\text{-}I}$ -30°C.
b) crystallized.

For **1d**-**1f** that all have the same length of alkyl chains, the Δn of the compounds was influenced by the position of F atoms. The Δn of **1e** having F atoms in the even position on the alkyl chain was larger than that of **1d** and **1f** having F atoms in the odd positions. However, in the case of monofluorinated compounds the Δn of **2a** (F atom in position-2) was not different from that of **2b** (F atom in position-3).

Miscibility and practical nematic liquid crystalline mixtures

D.Demus et.al. have shown that specific resistivity (ρ) was a function of an average of dielectric anisotropy ($\bar{\varepsilon}$) [8]. Mixtures containing the fluorinated compounds **1** and **2** having a small average of $\bar{\varepsilon}$ that are defined by the equation

$$(2\varepsilon_{\perp} + \varepsilon_{//}) / 3$$

show high ρ. Compounds **1** and **2** also show good miscibility at low temperatures. Therefore by using **1** and **2**, mixtures for TFT and STN applications having wide mesophase ranges, low viscosity and high specific resistivity can be obtained (TABLE 6).

TABLE 6. Nematic LC mixtures for TFT (C, D, E and F) and STN (G, H and I) applications using fluorinated dialkylbicyclohexanes.

Mixture	C	D	E	F	G	H	I
S-N (°C)	< -30	< -30	< -30	< -30	< -30	< -30	< -30
N-I (°C)	71.5	75.8	78.2	80.8	61.1	62.5	77.0
η[mPa•S] (20°C)	20.0	19.1	20.9	24.9	22.8	27.3	24.0
Δn (20°C)	0.0829	0.0815	0.0883	0.0689	0.1105	0.1315	0.1637
Δε (20°C)	4.0	2.9	3.7	4.7	11.1	7.7	4.6
ρ (Ωcm)	$>6.0\times10^{13}$	$>3.4\times10^{13}$	$>6.0\times10^{13}$	$>1.1\times10^{14}$	$>9.8\times10^{11}$	$>5.3\times10^{12}$	$>1.6\times10^{13}$
V_{10} (volt)	2.83	3.48	3.41	2.83	1.69	2.05	3.06
V_{50} (volt)	2.31	2.83	2.79	2.31	1.38	1.76	2.61
V_{90} (volt)	2.02	2.49	2.41	2.02	1.18	1.55	2.32
Cell width (μm)	8.7	8.8	8.7	8.7	8.6	8.7	8.7

CONCLUSION

The mesophase range of a dialkylbicyclohexane is expanded by introducing fluorine atoms into the alkyl chain. The viscosity of the dialkylbicyclohexane having two fluorine atoms in position-2 on the alkyl chain is relatively low, although viscosity is increased by introducing fluorine atoms. Introduction of fluorine atoms induces large negative $\Delta\varepsilon$ and large Δn. When a terminal alkyl chain is short or the fluorine atoms on the alkyl chain are in position-2, Δn is large. By introducing fluorine atoms into the alkyl chain, a liquid crystalline compound having large Δn, large negative $\Delta\varepsilon$ and a wide mesophase range can be obtained. By using the compound, mixtures for TFT and STN applications having attractive properties, can be obtained.

EXPERIMENT

The chemical structures of the compounds were determined by 90MHz and 400MHz ^{1}H, ^{13}C and ^{19}F-FT-NMR. Chemical purities were checked using a SHIMADZU 14A GLC with a capillary column (40m, CBP1-M50-025).

Typical procedure

trans-4-(3-Oxopentyl)-trans-4'-propylbicyclohexane **5f**

A mixture of 3-(trans-4-(trans-4-propylcyclohexyl)cyclohexyl)propionic acid **4f** (0.53mmol) and thionyl chloride (1.68mol) was relfuxed for 3 hours. Removing excess thionyl chloride at a reduced pressure gave oily yellow 3-(trans-4-(trans-4-propylcyclohexyl)cyclohexyl)propionyl chloride (0.50mmol). To a mixture of the acid chloride, Fe(acac)$_3$ and toluene (2L), ethylmagnesium bromide (6M in THF, 0.90mol) was added dropwise at -45°C. After stirring at this temperature for 1 hour, the reaction mixture was poured into 6N HCl. The organic layer was washed with 6N HCl, aq. 2N NaOH and water, then dried over anhydrous MgSO$_4$. Purification by column chromatography (silica gel, toluene), a distillation (170°C, 1mmHg) and recrystallization from heptane (100ml) gave colorless crystals **5f** (0.36mol, 67%).

Mp. 67.4°C, $T_{S\text{-}I}$ 85.5°C. ^{1}H-NMR (CDCl$_3$) δ : 0.79-1.76 (m, 32H); 2.38 (t, 2H); 2.40 (t, 2H) ppm.

trans-4-(3-Hydroxypentyl)-trans-4'-propylbicyclohexane **6f**

To a suspension of LiAlH$_4$ (40.75mmol) and THF (15ml), a solution of **5f** (100mmol) in THF (210ml) was added dropwise at below 6°C. After stirring for 1 hour, the reaction mixture was poured into a mixture of 6N HCl and ethyl acetate. The organic layer was washed with sat. aqueous NaHCO$_3$, then dried over anhydrous MgSO$_4$. Recrystallization from heptane (100ml) gave colorless needles **6f** (55mmol, 55%).

Mp. 127.3-129.3°C. ^{1}H-NMR ($CDCl_3$) δ : 0.79-2.09 (m, 37H); 3.47 (brs, 1H) ppm.

trans-4-(3-Fluoropentyl)-trans-4'-propylbicyclohexane **2b**

To a mixture of **6f** (55mmol), dichloromethane (200ml) and THF (150ml), DAST (82.5mmol) was added at below 10°C for 1hour. The reaction mixture was poured into ice-cold water, and the organic layer was washed with sat. aqueous $NaHCO_3$ and water, and dried over anhydrous $MgSO_4$. Purification by column chromatography (silica gel, heptane) and recrystallization (benzene : ethanol (1 : 6), 65ml) gave colorless crystals **2b** (18mmol, 32%).

^{1}H-NMR ($CDCl_3$) δ : 0.79-1.69 (m, 36H); 4.34 (dt, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ : 9.21; 9.45; 14.40; 20.04; 27.56; 28.51; 30.04; 30.09; 31.68; 32.60; 32.78; 33.62; 37.76; 39.86; 43.46; 95.91 (t, J (C-F)=167.8Hz) ppm. ^{19}F-NMR ($CDCl_3$) δ : -181.71 (d) ppm.

trans-4-(3,3-Difluoropentyl)-trans-4'-propylbicyclohexane **1f**

A mixture of **5f** (66mmol), SeF_4 (66mmol) and 1,1,2-trichloro-1,2,2-trifluoroethane (60ml) was relfuxed for 2 hours. After quenching with water, the organic layer was washed with sat. aqueous $NaHCO_3$, then dried over anhydrous $MgSO_4$. Purification by column chromatography (silica gel, heptane) and recrystallization (heptane : ethanol (1:5)) gave **1f** (15.6mmol, 24%).

^{1}H-NMR ($CDCl_3$) δ : 0.75-2.05 (m, 36H) ppm. ^{13}C-NMR ($CDCl_3$) δ : 6.65; 14.41; 20.05; 28.23; 29.42; 29.60; 30.05; 30.58; 32.35; 33.39; 33.66; 34.61; 37.72; 39.87; 43.45; 125.84 (t, J (C-F)=240.3Hz) ppm. ^{19}F-NMR ($CDCl_3$) δ : -100.55 (t) ppm.

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