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A Facile Transformation of Terminal Olefins to *vic*-Difluoro Olefins: Electro-optical Properties of Liquid Crystalline Materials Having a *vic*-Difluoro Olefinic Moiety

Kiyoshi Kanie,[#] Yoichiro Tanaka, Sadao Takehara,[†] and Tamejiro Hiyama[*,##]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503

†Dainippon Ink & Chemicals, Inc., 4472-1 Komuro, Ina-machi, Kita-adachi-gun, Saitama 362-8577

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A facile synthetic method of *vic*-difluoro olefins from the corresponding olefins is explored and applied to the synthesis of liquid crystals (LCs) having a terminal *vic*-difluoro olefinic moiety. The physical and electro-optical properties of these LCs are compared with those of the corresponding parent olefinic LCs.

Organofluorine compounds often demonstrate excellences in thermal and chemical stabilities, lipophilicity, viscosity, or biological activity, owing to the highest electronegativity among all elements, the steric similarity to hydrogen, the isoelectronic equivalent to oxygen, and the high energy of a carbon-fluorine bond.[1] Therefore, more attention has been directed to development of new functional materials and pharmaceuticals, taking advantage of the salient features of fluorine.[2]

Fluorine-containing liquid crystals (LCs) show properties appropriate to the materials for an LC display: wide mesophase range, low viscosity, reasonably high dielectric anisotropy ($\Delta\varepsilon$), high chemical and thermal stabilities, and high voltage holding ratio.[3] Furthermore, fluorine-containing LCs respond electro-optically at a relatively low threshold voltage (V_{th}) for low $\Delta\varepsilon$ as compared with cyano-substituted LCs. These features of fluorine-containing LCs are particularly suitable for the reduction of driving voltage of the display. Therefore, design and synthesis of novel LC materials having a fluorine substituent is a recent topic in synthetic organofluorine chemistry and material science.[4] For the future development of fluorinated functional materials, the fluorine effect needs to be well understood in comparison with non-fluorinated materials. For us to evaluate the fluorine effect precisely, properties of fluorinated materials should be compared with those of parent non-fluorinated ones. Accordingly, a method that allows us to introduce fluorine(s) into non-fluorinated materials is highly desirable.

Because LCs containing an ω-alkenyl side chain induce lower viscosity and V_{th} and higher voltage holding ratio than those with an alkyl side chain, the olefinic LCs are being utilized for the materials for current LC displays.[5] On the other hand, LCs having a *vic*-difluoro olefinic functionality in a mesogenic core were demonstrated to exhibit low viscosity and high polarity.[6] With these precedents, we envisaged that LCs having an ω-*vic*-difluoroalkenyl group would exhibit favorable properties and thus studied novel strategies for the fluorination of terminal olefins.[7,8]

Synthetic methods of *vic*-difluoro olefins can be classified into two categories, depending on the timing of fluorine introduction. The one involves C–C bond formation, using readily available partially fluorinated small molecules called fluorinated building blocks; the other consists of C–F bond formation with an electrophilic or nucleophilic fluorination reagent. Construction of *vic*-difluoro olefinic functionality using a fluorinated building block has been attained by: i) alkylation or arylation of (trifluorovinyl)silanes,[9] ii) palladium catalyzed cross-coupling reaction of 1,2-difluoroalkenyl (or alkenyl) zinc reagent with alkenyl (1,2-difluoroalkenyl) iodide,[10] iii) reaction of 1,2-difluoroalkenyllithium with carbonyl compounds or epoxides,[11] or iv) reaction of enolates with 1,2-difluoroacetylene generated from 1,1,2-trifluoroethylene and *t*-BuLi.[12] To control the configuration of the *vic*-difluoro olefins, *cis*- and *trans*- 1,2-difluoro olefinic precursors must be stereoselectively prepared.[13,14] Fluorination methods for *vic*-difluoro olefins[15] involve i) fluorination of β-keto esters with diethylaminosulfur trifluoride (DAST) to give 2,3-difluoro-2-alkanoate[16] and ii) dehydrofluorination of 1,2,2-trifluoroalkanes.[17] Furthermore, simultaneous use of the fluorinated building block method and the fluorination method leads to stereoselective preparation of *cis*- and *trans*-*vic*-difluoro olefins.[18] From the synthetic viewpoint of future functional materials, however, transformation of an olefinic moiety of the prevailing materials is favorable to the cor-

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Present address: Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

Present address: Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.

responding *vic*-difluoro olefinic ones with other functional groups being intact.

Herein we report experimental details of a facile method for the synthesis of LC materials having a *vic*-difluoro terminal olefinic moiety from the corresponding parent olefins.[7] We also disclose the phase transition behaviors and electro-optical properties of the difluoro olefinic LCs.

Results and Discussion

Transformation of Terminal Olefins to *vic*-Difluoro Olefins. In order to achieve the transformation of terminal olefins **1** to the corresponding *vic*-difluoro olefins **6**, we performed the following sequence of reactions: i) thio-fluorination of **1** to give β-fluoroalkyl phenyl sulfides **3**,[19] ii) fluoro-Pummerer rearrangement of **3** to give α,β-difluoroalkyl phenyl sulfides **4**,[20] iii) oxidation of **4** to sulfoxides **5**, and iv) thermolysis of **5**.[15,21,22] The route is shown in Scheme 1.

We chose LCs having an ω-alkenyl side chain for substrates that were used for LC displays. Initially, parent olefins **1** were converted into **3** by thio-fluorination[19] or alternatively by iodo-fluorination using tetrabutylammonium dihydrogentrifluoride (TBAH_2F_3) and *N*-iodosuccinimide (NIS)[23] followed by substitution of resulting iodo-fluorination products **2** with a phenythio nucleophile. Although the thio-fluorination reaction was straightforward, this was not applicable to vinylcyclohexanes **1a** and **1c**. Thus, the alternative route was applied to these olefins. The fluoro-Pummerer rearrangement of **3** using TBAH_2F_3 and 1,3-dibromo-5,5-dimethylhydantoin (DBH)[20a] gave **4** in high yields as 1 : 1 diastereomeric mixtures. The product ratios were assayed by ^{19}F NMR. Since **4** were not stable in neat liquid, these were immediately oxidized without isolation to give sulfoxides **5** by treatment with *m*-chloroperbenzoic acid (*m*CPBA). Finally, thermolysis of **5** at 170 °C in *o*-xylene (sealed tube) afforded a mixture of *cis*- and *trans*-difluoro olefins **6**. Each isomer was readily separated by flash column chromatography on silica gel. Isolation yields of intermediates **2**, **3**, **5**, and final products **6**, combined yields of **6**, and total yields of **6** from **1** are summarized in Table 1.

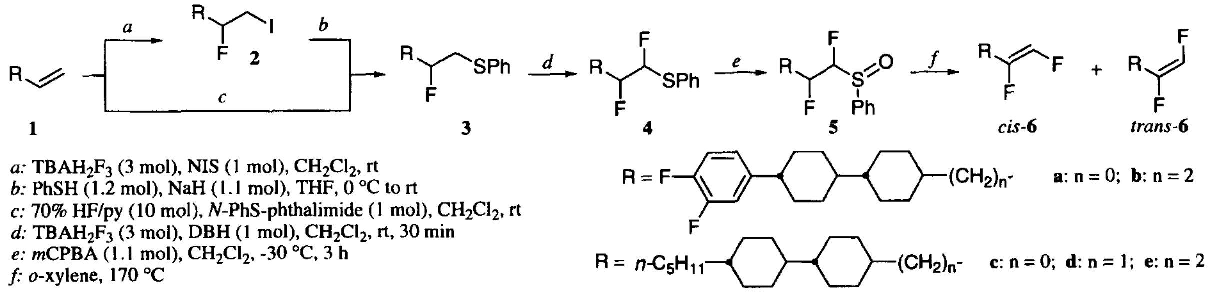
Isomerization of *vic*-Difluoro Olefins. In general, thermal elimination of phenyl sulfoxides proceeds in a *syn*-stereochemical course. Therefore, the ratio of *cis*-**6** and *trans*-**6** should reflect the diastereomeric ratio of fluoro-Pummerer products **4**.[24] However, *cis*-**6** were favored over *trans*-**6** as compared with the diastereomeric ratios in **4**, as summarized in Table 2.

Under the thermolytic conditions of **5** to give **6**, phenyl sulfenic acid is eliminated which is readily converted into diphenyl disulfide by dehydration and disproportionation.[25] Actually, the formation of diphenyl disulfide was detected by GC and TLC analyses. This suggests the isomerization of the *trans*-1,2-difluoro olefins to the corresponding *cis*-isomers may be assisted by diphenyl disulfide, because *trans*-1,2-difluoro(triethylsilyl)ethene is known to isomerize

Table 2. Diastereoselectivity of Fluoro-Pummerer Reaction of **3**

Compound	Diastereomeric ratio of **4**[a)]	*cis*-**6** : *trans*-**6**[b)]
4a	1.3 : 1	2.9 : 1
4b	1.4 : 1	1.5 : 1
4c	1.2 : 1	3.1 : 1
4d	1.0 : 1	1.6 : 1
4e	1.3 : 1	1.6 : 1

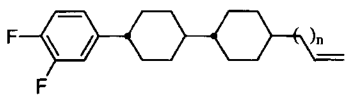
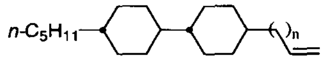
a) According to Eq. 1. Determined by integration ratios of ^{19}F NMR. b) Ratios of isolated yields of *cis*-**6** and *trans*-**6** according to Table 1.



a: TBAH_2F_3 (3 mol), NIS (1 mol), CH_2Cl_2, rt
b: PhSH (1.2 mol), NaH (1.1 mol), THF, 0 °C to rt
c: 70% HF/py (10 mol), *N*-PhS-phthalimide (1 mol), CH_2Cl_2, rt
d: TBAH_2F_3 (3 mol), DBH (1 mol), CH_2Cl_2, rt, 30 min
e: *m*CPBA (1.1 mol), CH_2Cl_2, -30 °C, 3 h
f: *o*-xylene, 170 °C

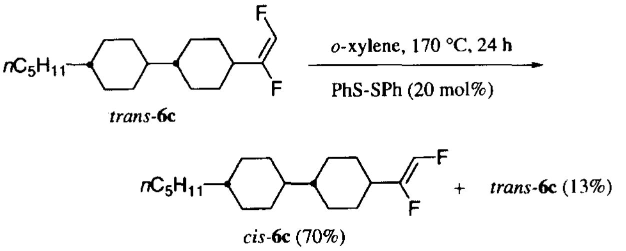
Scheme 1. Synthesis of *vic*-difluoro olefins **6**.

Table 1. Yields of **2**, **3**, **5**, and **6** in Scheme 1

Compound	*n*	Isolated yield/%						
		2	3	5[a)]	*cis*-6	*trans*-6	*cis*-6 + *trans*-6	Total yields of 6[b)]
	0 (**1a**)	82 (**2a**)	91 (**3a**)	95 (**5a**)	46 (*cis*-**6a**)	16 (*trans*-**6a**)	62	44
	2 (**1b**)		77 (**3b**)	94 (**5b**)	33 (*cis*-**6b**)	22 (*trans*-**6b**)	55	40
	0 (**1c**)	68 (**2c**)	95 (**3c**)	88 (**5c**)	55 (*cis*-**6c**)	18 (*trans*-**6c**)	73	41
	1 (**1d**)		81 (**3d**)	93 (**5d**)	45 (*cis*-**6d**)	29 (*trans*-**6d**)	74	56
	2 (**1e**)		78 (**3e**)	87 (**5e**)	39 (*cis*-**6e**)	25 (*trans*-**6e**)	64	43

a) Yields for 2 steps from **3** are shown. b) Total yield from **1**.

to the corresponding *cis*-isomer in the presence of a catalytic amount of diphenyl disulfide under UV irradition of 254 nm.[13] Indeed, pure *trans*-**6c** isomerized to a 70 : 13 mixture of *cis*-**6c** and *trans*-**6c** in the presence of 20 mol% of diphenyl disulfide as shown in Eq. 1. In the absence of diphenyl disulfide, the isomerization did not occur at all, and *trans*-**6c** was recovered quantitatively. A plausible pathway is suggested in Scheme 2.



(1)

Phase Transition Behavior of *vic*-Difluoro Olefinic LCs. Phase transition temperatures and enthalpies of *cis*-**6**, *trans*-**6**, and **1** as well as LC phases are summarized in Table 3. While *trans*-**6a** and *trans*-**6b** showed a nematic phase in temperature ranges narrower than those of parent olefins **1a** and **1b**, *cis*-**6a** and *cis*-**6b** exhibited a nematic phase in similar ranges but at lower temperatures (Fig. 1). The LCs having a *trans*-4-pentylcyclohexylcyclohexane mesogen are summarized in Fig. 2. LC *cis*-**6c** exhibited a nematic temperature range much wider than **1c** or *trans*-**6c**, whereas those with a longer alkyl group diminished or lost the nematic phase. Among *trans*-difluoro olefins, *trans*-**6c** showed little liquid crystallinity; *trans*-**6d** and *trans*-**6e** exhibited an S_B phase in parallel with **1d** and **1e**. Thus, the fluorine effect was most striking in **6c**.

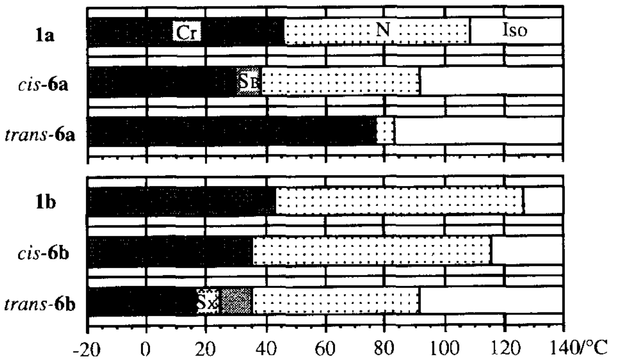


Fig. 1. Phase transition behaviors of **6a** and **6b** on 2nd heating.

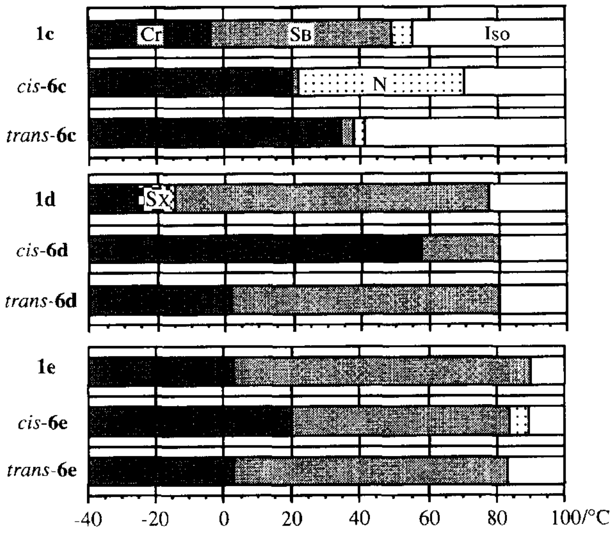
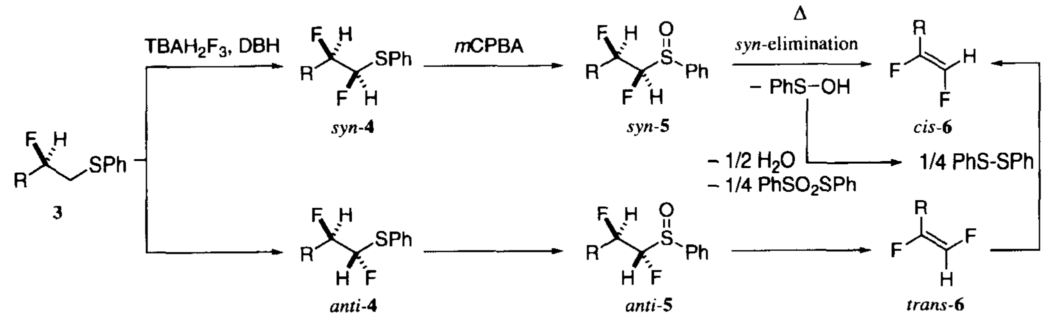


Fig. 2. Phase transition behaviors of **6c**, **6d**, and **6e** on 2nd heating.

Electro-Optical Properties of *vic*-Difluoro Olefins. To examine the electro-optical properties of difluoro olefinic LCs, we mixed each *cis*- and *trans*-isomer of **6a**—**6e** and parent olefinic LCs **1c**—**1e** by 20 wt% with **host**, a 1 : 1 mixture of **1a** and **1b**, and measured the dielectric anisotropy ($\Delta\varepsilon$), threshold voltage (V_{th}), birefringence (Δn), and response time (τ) of the resulting mixtures. These data are summarized in Table 4. The values of $\Delta\varepsilon$ and Δn were extrapolated to 100% to examine the dielectric anisotropy ($\Delta\varepsilon'$) and birefringence ($\Delta n'$) of pure samples of **6**. These values also are listed in Table 4.

In the case of **6a** and **6b** with a 3,4-difluorophenyl moiety in a mesogenic core, $\Delta\varepsilon$s of the resulting mixtures were lower as compared with that of **host**. The effect of *cis*-isomers was more striking than that of *trans*-ones owing probably to the cancelled dipole moment of C–F bonds in difluorophenyl and *cis*-difluoro olefinic moieties. Negative $\Delta\varepsilon'$ of *cis*-**6a** also suggests the reduced dipole moment along the molecular long axis of **6a**. To examine the effect of the *vic*-difluoro olefinic moiety more precisely, we next measured properties of LCs **6c**—**e**. All *trans*-**6c**—**e** exhibited $\Delta\varepsilon$s similar to parent olefins **1c**—**e**, probably because the dipole moments of the two C–F bonds compensate each other, whereas *cis*-**6c**—**e** showed varying $\Delta\varepsilon$s depending on the kind of side



Scheme 2. Isomerization of *vic*-difluoro olefins.

Table 3. Phase Transition Temperatures and Enthalpies of Compounds **1** and **6**

Entry	Compound	Phase transition temperature/°C$^{a,b)}$															
		DSC (on 1st cooling)							DSC (on 2nd heating)								
1	**1a**	Cr	24 (2.7)	$\mathrm{S_B}$	34 (9.4)	N	107 (0.67)	Iso					Cr	43 (13)	N	109 (0.70)	Iso
2	*cis*-**6a**			Cr	−3 (13)	N	92 (0.34)	Iso			Cr	30 (12)	$\mathrm{S_B}$	38 (13)	N	92 (0.51)	Iso
3	*trans*-**6a**	Cr	52 (6.5)	$\mathrm{S_B}$	61 (13)	N	83 (0.65)	Iso					Cr	77 (29)	N	83 (0.72)	Iso
4	**1b**			Cr	35 (12)	N	126 (1.1)	Iso					Cr	42 (13)	N	127 (0.99)	Iso
5	*cis*-**6b**			Cr	0 (19)	N	116 (0.49)	Iso					Cr	35 (22)	N	116 (0.48)	Iso
6	*trans*-**6b**	Cr	12 (0.66)	$\mathrm{S_B}$	18 (11)	N	92 (0.70)	Iso	Cr	16 (5.8)	$\mathrm{S_X}$	25 (7.0)	$\mathrm{S_B}$	35 (14)	N	92 (0.66)	Iso
7	**1c**	Cr	−4 (0.03)	$\mathrm{S_B}$	44 (2.9)	N	53 (0.63)	Iso			Cr	−4 (0.08)	$\mathrm{S_B}$	49 (3.5)	N	55 (1.0)	Iso
8	*cis*-**6c**	Cr	−14 (16)	$\mathrm{S_B}$	17 (3.1)	N	70 (0.75)	Iso			Cr	20 (3.0)	$\mathrm{S_B}$	22 (18)	N	0 (0.75)	Iso
9	*trans*-**6c**	Cr	−4 (19)	$\mathrm{S_B}$	37 (3.3)	N	41 (0.48)	Iso			Cr	34 (21)	$\mathrm{S_B}$	38 (3.3)	N	41 (0.42)	Iso
10	**1d**			Cr	−31 (9.4)	$\mathrm{S_B}$	77 (7.5)	Iso	Cr	−25 (7.5)	$\mathrm{S_{X1}}$	−18	$\mathrm{S_{X2}}$	14 (9.4)	$\mathrm{S_B}$	77 (7.6)	Iso
11	*cis*-**6d**			Cr	36 (23)	$\mathrm{S_B}$	79 (11)	Iso					Cr	57 (25)	$\mathrm{S_B}$	80 (11)	Iso
12	*trans*-**6d**			Cr	−12 (8.2)	$\mathrm{S_B}$	78 (8.0)	Iso					Cr	2 (9.7)	$\mathrm{S_B}$	80 (8.2)	Iso
13	**1e**			Cr	−2 (18)	$\mathrm{S_B}$	89 (8.5)	Iso					Cr	3 (23)	$\mathrm{S_B}$	90 (9.3)	Iso
14	*cis*-**6e**	Cr	−14 (24)	$\mathrm{S_B}$	84 (6.3)	N	89 (1.0)	Iso			Cr	20 (30)	$\mathrm{S_B}$	84 (6.4)	N	89 (0.82)	Iso
15	*trans*-**6e**			Cr	−20 (23)	$\mathrm{S_B}$	81 (7.3)	Iso					Cr	3 (27)	$\mathrm{S_B}$	83 (7.9)	Iso

a) Cr: Crystal. N: Nematic phase. $\mathrm{S_B}$: Smectic B phase. $\mathrm{S_X}$: Higher order smectic phases. b) Enthalpies of phase transitions in parentheses (kJ mol^{-1}).

Table 4. Physical and Electro-Optical Properties$^{a)}$ of **1c**—**1e** and *cis*-and *trans*-**6a**—**6e** as Mixed by 20 wt% in **Host**

Compound	T_{NI}/°C	$\Delta\varepsilon$	$\Delta\varepsilon'$ $^{b)}$	V_{th}/V$^{c)}$	Δn	$\Delta n'$ $^{d)}$	τ/ms$^{c,e)}$(V)$^{f)}$
Host	116.7	4.8	—	2.14	0.090	—	25.3 (5.1)
cis-**6a**	116.0	3.2	−3.2	2.35	0.089	0.085	36.2 (5.5)
trans-**6a**	109.5	4.0	−0.8	2.01	0.090	0.090	33.2 (5.1)
cis-**6b**	117.4	3.6	−1.2	2.34	0.078	0.030	34.7 (5.2)
trans-**6b**	111.9	4.2	1.8	2.30	—	—	33.5 (5.0)
1c	102.8	3.6	−1.2	2.29	0.081	0.045	22.4 (5.3)
cis-**6c**	105.1	4.2	1.8	1.99	0.081	0.045	33.3 (4.3)
trans-**6c**	97.7	3.3	−2.7	2.16	0.081	0.045	31.2 (4.7)
1d	94.4	3.1	−3.7	2.08	0.077	0.025	32.6 (4.4)
cis-**6d**	87.4	3.0	−4.2	2.00	0.076	0.020	44.1 (4.2)
trans-**6d**	86.8	3.1	−3.7	2.04	0.075	0.025	43.1 (4.2)
1e	108.3	3.3	−2.7	2.29	0.082	0.050	26.9 (5.0)
cis-**6e**	108.3	4.0	0.8	2.15	0.083	0.055	29.4 (4.7)
trans-**6e**	101.6	3.2	−3.2	2.22	0.081	0.045	34.3 (4.7)

a) Measured at 20 °C. b) Extrapolated from $\Delta\varepsilon$. c) Corrected for 6.0 μm cell. d) Extrapolated from Δn. e) Responce time ($\tau_r = \tau_d$). f) Applied voltage/V.

chain; *cis*-**6c** and *cis*-**6e** were much larger in $\Delta\varepsilon$ than **1c** and **1e**, respectively; *cis*-**6d** had smaller $\Delta\varepsilon$ than **1d**. Since *cis*-**6d** has negative $\Delta\varepsilon'$, this is an *n*-type LC; both *cis*-**6c** and *cis*-**6e** shows positive $\Delta\varepsilon'$ and thus are *p*-type. All the *vic*-difluoro olefins lowered V_{th} of host LCs upon mixing by 20 wt% as compared with the parent olefins. In particular, the effect of *cis*-**6c**—**e** was remarkable in comparison with *trans*-**6c**—**e**. All the difluoro olefins had equally low Δn's as estimated by extrapolation, and thus mixing one of them in **host** results in lowering Δn of **host**. Accordingly, the difluoro olefins are a useful additive for reducing Δn of LC materials. Both *cis*- and *trans*-difluoro olefins are thermally stable, since no decomposition was observed by heating their xylene solutions at 170 °C for 24 h.

Conclusions. We have demonstrated that LCs having a *vic*-difluoro olefinic moiety are readily prepared from the corresponding parent olefinic LCs. Studies on the phase transition behavior of the newly prepared LCs reveal that the fluorine introduction effect is most striking with **6c**. The electro-optical properties of LCs having a $(CH_2)_nCF{=}CHF$ group change extensively depending on the configuration and the value of n. The difluoro olefinic LCs generally reduce V_{th} and Δn of host LCs upon mixing by 20 wt% more effectively than the corresponding parent olefins.

Experimental

General. Unless otherwise noted, reagents and solvents were purchased from Aldrich Chemical Co., Kanto Chemicals, Tokyo Kasei, or Wako Chemicals, Inc. and were used as received. All the reaction was carried out under an argon atmosphere in a dry, freshly distilled solvent unless otherwise noted. Tetrahydrofuran (THF), diethyl ether (Et_2O), benzene, toluene, and *o*-xylene were distilled from sodium/benzophenone, and *N*,*N*-dimethylformamide (DMF) from calcium hydride. Dichloromethane (CH_2Cl_2) was predried with P_2O_5 and distilled from calcium hydride. Yields refer to materials purified by column chromatography or recrystallization. Reactions were monitored by thin-layer chromatography using 0.25 mm E. Merck silica gel plates (Silica Gel F_{254}) with UV light as a visualizing device, by exposure to iodide, and/or by dipping the plates in an ethanolic phosphomolybdic acid or *p*-anisaldehyde solution and heating the plates. Silica gel from E. Merck (Kieselgel 60, 230—400 mesh) or Nacalai Tesque (Silica Gel 60, 150—325 mesh) was used for flash column chromatography. All NMR spectra were measured in a $CDCl_3$ solution. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer at 200 (^{1}H), 50.3 (^{13}C), and 188 (^{19}F) MHz, or on a Varian Mercury-300 spectrometer at 300 (^{1}H), 75.5 (^{13}C), and 282 (^{19}F) MHz, respectively. Chemical shifts of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR signals are quoted relative to internal standard Me_4Si ($\delta = 0.00$), $CDCl_3$ ($\delta = 77.00$) or $CFCl_3$ ($\delta = 0.00$), respectively, and expressed by chemical shift in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. IR spectra were recorded on a Shimadzu FTIR-8100A in neat unless otherwise noted. Mass spectra were recorded on a Shimadzu GC/MS QP-5000 or on a Hitachi H-80 double-focusing tandem GC-MS (70 eV) spectrometer. Melting points were measured with an Olympus BH-2 optical polarizing microscope equipped with a Mettler FP-900 hot-stage. The thermal characterization was conducted with a SII DSC-200C (scanning rate 1 °C min^{-1}) differential scanning calorimeter (DSC) system. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder. High-resolution mass spectra were obtained on a JEOL MStation. $TBAH_2F_3$ was prepared according to the literature procedure[26] and dried in vacuo at room temperature overnight right before use (CH_2Cl_2 solution of $TBAH_2F_3$ is commercially available from Acros Organics).[27]

Measurements. A sample for the measurement of dielectric anisotropy ($\Delta\varepsilon$), birefringence (Δn), threshold voltage (V_{th}), and response time (τ) was prepared by mixing a compound (20 wt%) with **host** (80%, Cr 11 N 117 Iso) made of equal amounts of **1a** and **1b**. The LC mixture was sealed in a polyimide rubbed cell of about 6 μm thickness. A rectangular electric field of 1 kHz was appled to the cell, and the intensity change of linearly polarized light transmitted through a pair of crossed polarizers was observed with a photodiode. Values of $\Delta\varepsilon$ were recorded on a YHP 4192A impedance analyzer by measuring electrical response. Values of Δn were obtained by an ATAGO 4T Abbe's refractometer. V_{th} was expressed as the voltage for 90% of maximum transmittance. Rising switching time (τ_r) and decay switching time (τ_d) were obtained respectively as electro-optical responses from 100 to 10% and from 0 to 90%. Values τ were estimated when τ_r became equal to τ_d at a properly applied voltage.

LCs Having *ω*-Alkenyl Side Chain. Compounds **1a**—**c** were commercially available from Dainippon Ink & Chemicals, Inc. Compounds **1d** and **1e** were prepared from **1c** as follows.

1-[*trans*-4-(2-Hydroxyethyl)cyclohexyl]-*trans*-4-pentylcyclohexane (7). In a two-necked flask were placed THF (200 mL) and 1-[*trans*-4-(ethenyl)cyclohexyl]-*trans*-4-pentylcyclohexane **1c** (24 g, 91 mmol). The flask was immersed in an ice-water bath. A borane THF solution (1.00 M, 46 mL, 1 M = 1 mol dm^{-3}) was added dropwise to the solution. The reaction mixture was stirred for 12 h at room temperature before quenching with H_2O (1 mL) at 0 °C. The mixture was treated with 3 M NaOH (22 mL) and 30% H_2O_2 (23 mL), and the resulting suspension was stirred for 6 h at room temperature before quenching with aq $NaHSO_3$. The organic phase was separated; the aqueous phase was extracted with Et_2O four times (400 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was recrystallized from hexane and purified by flash column chromatography (hexane : EtOAc = 5 : 1) to give **7** (22 g, 85% yield) as colorless needles, mp 152.0—152.9 °C, $R_f = 0.27$ (hexane : EtOAc = 5 : 1). IR (KBr) 3428, 2953, 2919, 2851, 1468, 1453, 1360, 1051, 1022, 963, 893 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.82$—1.34 (m, 24 H), 1.46 (dt, J = 7, 7 Hz, 2 H), 1.62—1.77 (m, 8 H), 3.68 (t, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.9 (s), 30.1 (s), 32.2 (s), 33.60 (s), 33.64 (s), 34.5 (s), 37.5 (s), 37.9 (s), 40.4 (s), 43.3 (s), 43.4 (s), 60.9 (s); MS *m/z* (rel intensity) 280 (M$^+$; 0.7), 263 (7), 262 (32), 233 (12), 191 (13), 151 (14), 137 (11), 124 (6), 109 (100), 97 (66), 96 (46), 95 (45), 83 (67), 81 (76), 79 (52), 69 (57), 67 (81). Found: C, 81.19; H, 13.04%. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94%.

1-[*trans*-4-(Formylmethyl)cyclohexyl]-*trans*-4-pentylcyclohexane (8). To a solution of **7** (8.5 g, 30 mmol) in CH_2Cl_2 (200 mL) was added pyridinium chlorochromate (PCC, 9.7 g, 45 mmol) in one portion at room temperature. The reaction mixture was stirred for 3 h at the same temperature, followed by the addition of Celite. The mixture was filtered through a pad of Celite by suction funnel; the filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (hexane : EtOAc = 5 : 1) to give **8** (7.2 g, 85% yield) as colorless solids. Phase transition temperature/°C: S_X 93 Iso; $R_f = 0.61$ (hexane : EtOAc = 5 : 1). IR 2915, 2849, 2716, 2361, 1723, 1468, 1447, 1408, 1379, 1352, 1291, 1217, 1024, 895 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.35 (m, 20 H), 0.88 (t, J = 7 Hz, 3 H), 1.64—1.84 (m, 8 H), 2.27 (dd, J = 2, 7 Hz, 2 H), 9.75 (t, J = 2 Hz, 1 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.7 (s), 30.0 (s), 32.2 (s), 33.0 (s), 33.5 (s), 33.6 (s), 37.5 (s), 37.9 (s), 42.9 (s), 43.3 (s), 51.4 (s), 203.1 (s); MS *m/z* (rel intensity) 280 (M$^+$+2; 5), 278 (M$^+$; 14), 234 (37), 149 (27), 137 (19), 135 (14), 125 (22), 115 (20), 108 (25), 97 (58), 95 (67), 81 (92), 69 (100). Found: *m*/*z* 278.2623. Calcd for $C_{19}H_{34}O$: M, 278.2610.

1-[*trans*-4-(2-Propenyl)cyclohexyl]-*trans*-4-pentylcyclohexane (1d). A solution of *n*-BuLi in hexane (1.60 M, 9.5 mL, 15.2 mmol) was added to methyltriphenylphosphonium bromide (5.7 g, 16 mmol) suspended in Et_2O (60 mL) at room temperature and the resulting mixture was stirred for 4 h at room temperature. Then an ethereal solution (18 mL) of **8** (4.1 g, 15 mmol) was added dropwise at room temperature. The resulting mixture was stirred for 4 h at the same temperature before being quenched with aq NH_4Cl. The organic phase was separated; the aq phase was extracted with Et_2O three times (300 mL). The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to give **1d** (2.9 g, 72% yield). Phase transition temp/°C: Cr-25 S_{X1} -18 S_{X2} -14 S_B 77 Iso (DSC on 2nd heating); $R_f = 0.89$ (hexane). IR 3077, 2915, 2849, 1642, 1447, 1215, 994, 911, 895 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.77$—1.34 (m, 23 H), 1.64—1.80 (m, 8 H), 1.93 (t, $J = 7$ Hz, 2 H), 3.68 (t, $J = 7$ Hz, 2 H), 4.90—4.93 (m, 1 H), 4.95—5.30 (m, 1 H), 5.65—5.90 (m, 1 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 30.0 (s), 30.1 (s), 32.3 (s), 33.3 (s), 33.7 (s), 37.5 (s), 37.95 (s), 37.97 (s), 41.9 (s), 43.4 (s), 43.5 (s), 115.1 (s), 137.8 (s); MS *m*/*z* (rel intensity) 277 (M^++1; 1), 276 (M^+; 5), 234 (11), 219 (14), 206 (3), 192 (3), 179 (4), 165 (5), 151 (10), 137 (18), 123 (40), 109 (36), 97 (76), 95 (47), 83 (100), 81 (85), 69 (79), 67 (78). Found: *m*/*z* 276.2823. Calcd for $C_{20}H_{36}$: M, 276.2817.

1-[*trans*-4-(2-Iodoethyl)cyclohexyl]-*trans*-4-pentylcyclohexane (9). To a THF solution of borane (1.00 M, 80 mL) cooled at 0 °C was added dropwise 2-methyl-2-butene (12.8 mL, 120 mmol) over 10 min, and the resulting mixture was stirred for 3 h at 0 °C. To the reagent solution, a solution of **1c** (11.5 g, 44 mmol) in THF (20 mL) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 11 h before quenching with methanol (1 mL) and iodine (34 g, 132 mmol). Then a methanol (40 mL) solution of sodium hydroxide (5.3 g) was added dropwise to the mixture. The whole mixture was stirred for 5 h at room temperature before treatment with aq NaOH (3 M, 20 mL) and 30% H_2O_2 solution (10 mL). The mixture was stirred for an additional period of 8 h at room temperature. The excess hydrogen peroxide was decomposed by careful portionwise addition of $NaHSO_3$, and the aqueous phase was extracted with Et_2O three times (500 mL). The combined organic extracts were washed by sat. aq NaCl solution and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (hexane) afforded **9** (12.9 g, 75% yield) as a colorless powder, mp 132.3—134.4 °C, $R_f = 0.81$ (hexane). IR (KBr) 2923, 2851, 1468, 1441, 1289, 1219, 1184, 1159, 953, 897, 723 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.84$—1.34 (m, 23 H), 1.67—1.78 (m, 10 H), 3.21 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 5.2$ (s), 14.1 (s), 22.7 (s), 26.7 (s), 29.7 (s), 30.1 (s), 32.2 (s), 32.7 (s), 33.6 (s), 37.5 (s), 37.9 (s), 38.8 (s), 41.2 (s), 43.3 (s), 43.4 (s); MS *m*/*z* (rel intensity) 391 (M^++1; 0.1), 390 (M^+; 0.5), 263 (19), 207 (3), 181 (9), 179 (8), 167 (13), 165 (12), 139 (19), 137 (19), 125 (26), 123 (24), 111 (64), 109 (53), 97 (100), 95 (48), 83 (94), 81 (73), 69 (85), 67 (86). Found: C, 58.50; H, 8.82%. Calcd for $C_{19}H_{35}I$: C, 58.46; H, 9.04%.

1-[*trans*-4-(3-Butenyl)cyclohexyl]-*trans*-4-pentylcyclohexane (1e). Vinylmagnesium bromide (1.0 M THF solution, 75 mL, 75 mmol) was added dropwise to a mixture of copper(I) iodide (7.1 g, 38 mmol) and **9** (12.1 g, 31 mmol) suspended in THF (150 mL) at −30 °C. The reaction mixture was then allowed to warm to 0 °C and stirred at 0 °C for 3 h before quenching with aq 1.0 M HCl. The organic phase was separated; the aqueous phase was extracted with Et_2O three times (300 mL). The combined organic extracts were washed with sat. aq NaCl solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to give **1e** (8.2 g, 90% yield) as a colorless mesomorphic oil. Phase transition temperature/°C: Cr 3 S_B 90 Iso (DSC on 2nd heating); $R_f = 0.81$ (hexane). IR 2927, 2849, 1642, 1468, 1447, 1379, 1219, 994, 909 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.36 (m, 22 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.64—1.80 (m, 8 H), 2.00—2.10 (m, 2 H), 4.88—5.40 (m, 2 H), 5.74—5.88 (m, 1 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 30.0 (s), 30.1 (s), 31.3 (s), 32.3 (s), 33.5 (s), 33.7 (s), 36.7 (s), 37.4 (s), 37.5 (s), 37.9 (s), 43.46 (s), 43.49 (s), 113.9 (s), 139.5 (s); MS *m*/*z* (rel intensity) 291 (M^++1; 3), 290 (M^+; 12), 248 (3), 233 (4), 219 (7), 192 (3), 151 (11), 137 (33), 123 (14), 109 (17), 97 (54), 83 (61), 81 (100), 69 (59), 67 (83). Found: *m*/*z* 290.2967. Calcd for $C_{21}H_{38}$: M, 290.2974.

1-{*trans*-4-[3-Fluoro-4-(phenylthio)butyl]cyclohexyl}-*trans*-4-(3,4-difluorophenyl)cyclohexane (3a). A 100 mL, dried, Teflon® bottle was charged with a solution of 1-[*trans*-4-(3-butenyl)cyclohexyl]-*trans*-4-(3,4-difluorophenyl)cyclohexane (**1a**) (3.3 g, 10.0 mmol), *N*-(phenylthio)phthalimide (2.68 g, 10.5 mmol) in CH_2Cl_2 (40 mL). To the reaction mixture stirred vigorously at room temperature, HF/py (70 wt% HF, 2.5 mL, 100 mmol) was added dropwise through a disposable polypropylene/polyethylene syringe. The mixture was stirred for 53 h at room temperature before quenching with aq $NaHSO_3$/$NaHCO_3$/NaOH (pH 10). The organic phase was separated; the aqueous phase was extracted with Et_2O three times (150 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : benzene = 6 : 1) to give **3a** (3.6 g, 77% yield) as a colorless powder, mp 69.3—69.8 °C, $R_f = 0.41$ (hexane : benzene = 5 : 1). IR (KBr) 2917, 2847, 1607, 1582, 1522, 1482, 1441, 1273, 1204, 1109, 1090, 945, 872, 820, 772, 741, 702, 691, 619, 581 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.84$—1.45 (m, 13 H), 1.61—1.92 (m, 10 H), 2.40 (tm, $J = 12$ Hz, 1 H), 2.96—3.29 (m, 2 H), 4.58 (dm, $J = 48$ Hz, 1 H), 6.85—7.41 (m, 8 H); ^{19}F NMR (188 MHz) $\delta = -139.23$ (ddd, $J = 9$, 12, 22 Hz, 1 F), −142.12 (dddd, $J = 5$, 8, 10, 22 Hz, 1 F), −176.73—−177.43 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 29.9$ (d, $J = 1$ Hz), 30.1 (s), 31.7 (d, $J = 21$ Hz), 32.3 (d, $J = 4$ Hz), 33.3 (d, $J = 13$ Hz), 34.5 (s), 37.6 (s), 38.5 (d, $J = 24$ Hz), 42.7 (s), 43.2 (s), 43.8 (s), 92.3 (d, $J = 173$ Hz), 115.4 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.5 (dd, $J = 4$, 6 Hz), 126.5 (s), 129.0 (s), 129.8 (s), 135.7 (s), 144.8 (dd, $J = 4$, 5 Hz), 148.5 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 12$, 147 Hz); MS *m*/*z* (rel intensity) 461 (M^++1; 5), 440 (9), 330 (12), 179 (10), 153 (18), 135 (45), 127 (71), 123 (38), 110 (100), 95 (27), 81 (55), 67 (55). Found: C, 72.97; H, 7.80%. Calcd for $C_{28}H_{35}F_3S$: C, 73.01; H, 7.66%.

1-{*trans*-4-[2-Fluoro-3-(phenylthio)propyl]cyclohexyl}-*trans*-4-pentylcyclohexane (3d). In a similar manner as described for **3a**, **3d** (2.9 g, 81% yield) was prepared as a colorless powder from **1d** (2.4 g, 8.8 mmol). Mp 85.1—85.4 °C; $R_f = 0.47$ (hexane : benzene = 5 : 1). IR (KBr) 2953, 2923, 2907, 2890, 2847, 1586, 1482, 1439, 1094, 1069, 1051, 986, 961, 843, 820, 733, 702, 689 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.83$—1.43 (m, 23 H), 1.59—1.83 (m, 10 H), 2.92—3.28 (m, 2 H), 4.70 (dm, $J = 49$ Hz, 1 H), 7.15—7.41 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -176.04$—−176.78 (m); ^{13}C NMR (50.3 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.8 (d, $J = 12$ Hz), 30.1 (s), 32.2 (s), 33.0 (s), 33.6 (s), 34.1 (s), 34.3 (d, $J = 3$ Hz), 37.5 (s), 37.9 (s), 39.1 (d, $J = 24$ Hz), 41.9 (d, $J = 20$ Hz), 43.3 (d, $J = 13$

Hz), 90.8 (d, $J = 172$ Hz), 126.5 (s), 129.0 (s), 129.9 (s), 135.8 (s); MS m/z (rel intensity) 406 (M$^+$+ 2; 7), 405 (M$^+$+ 1; 25), 404 (M$^+$; 88), 384 (12), 275 (9), 274 (34), 149 (14), 135 (17), 123 (81), 110 (90), 109 (56), 97 (43), 83 (57), 81 (86), 79 (59), 69 (65), 67 (100). Found: C, 77.01; H, 10.02%. Calcd for $C_{26}H_{41}FS$: C, 77.17; H, 10.21%.

1-{*trans*-4-[3-Fluoro-4-(phenylthio)butyl]cyclohexyl}-*trans*-4-pentylcyclohexane (3e). This compound (6.6 g, 78% yield) was prepared as a colorless powder from **1e** (5.8 g, 20 mmol). Phase transition temperature/°C: S_B 63 Iso; $R_f = 0.38$ (hexane : benzene = 5 : 1). IR (KBr) 3060, 2924, 2851, 2361, 1586, 1482, 1468, 1379, 1217, 1090, 1069, 1024, 895, 737, 691 cm^{-1}. ^{1}H NMR (200 MHz) $\delta = 0.79$—1.43 (m, 25 H), 1.60—1.84 (m, 10 H), 2.93—3.27 (m, 2 H), 4.56 (ttd, $J = 6$, 6, 48 Hz, 1 H), 7.14—7.40 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -176.69$—-177.40 (m); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.9 (s), 30.1 (s), 31.7 (d, $J = 21$ Hz), 32.2 (s), 32.3 (d, $J = 3$ Hz), 33.4 (d, $J = 13$ Hz), 33.6 (s), 37.5 (s), 37.6 (s), 37.9 (s), 38.5 (d, $J = 24$ Hz), 43.3 (s), 43.4 (s), 92.8 (d, $J = 173$ Hz), 126.4 (s), 129.0 (s), 129.8 (s), 135.7 (s); MS m/z (rel intensity) 420 (M$^+$+ 2; 5), 419 (M$^+$+ 1; 18), 418 (M$^+$; 61), 288 (15), 183 (11), 136 (14), 135 (55), 123 (49), 111 (17), 110 (100), 109 (28), 97 (30), 95 (35), 83 (42), 81 (49), 79 (23), 69 (45), 67 (54). Found: m/z 418.3076. Calcd for $C_{27}H_{43}FS$: M, 418.3070.

1-[*trans*-4-(1-Fluoro-2-iodoethyl)cyclohexyl]-*trans*-4-(3,4-difluorophenyl)cyclo-hexane (2b). A solution of olefin **1b** (0.91 g, 3.0 mmol) in CH_2Cl_2 (4.0 mL) was added dropwise over 30 min to a mixture of $TBAH_2F_3$ (1.4 g, 4.6 mmol), NIS (3.4 g, 15 mmol), and CH_2Cl_2 (6.0 mL) placed in a 50 mL two-necked flask at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 23 h before quenching with aq $NaHCO_3$ and solid $NaHSO_3$. The organic phase was separated; the aq phase was extracted with hexane four times (200 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to give **2b** (1.10 g, 82% yield) as colorless needles. Phase transition temperature/°C: Cr 81 S_X 85 N 104 Iso; $R_f = 0.25$ (hexane). IR (KBr) 2923, 2853, 1605, 1516, 1451, 1269, 1211, 1186, 1117, 955, 939, 826, 772, 625, 581 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 1.00$—1.46 (m, 10 H), 1.59—2.45 (m, 9 H), 2.41 (tt, $J = 4$,12 Hz, 1 H), 3.30 (ddd, $J = 6$, 11, 22 Hz, 1 H), 3.40 (ddd, $J = 4$, 11, 23 Hz, 1 H), 4.16 (dddd, $J = 4$, 6, 6, 47 Hz, 1 H), 6.85—7.11 (m, 3 H); ^{19}F NMR (188 MHz) $\delta = -139.17$ (ddd, $J = 9$, 12, 21 Hz, 1 F), -143.03 (dddd, $J = 4$, 8, 10, 21 Hz, 1 F), -178.10 (dddd, $J = 15$, 22, 23, 47 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 5.9$ (d, $J = 25$ Hz), 27.3 (d, $J = 5$ Hz), 28.5 (d, $J = 5$ Hz), 29.1 (d, $J = 18$ Hz), 30.1 (s), 34.5 (s), 42.1 (d, $J = 19$ Hz), 42.6 (d, $J = 15$ Hz), 43.8 (s), 95.7 (d, $J = 177$ Hz), 115.4 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 2$, 6 Hz), 144.7 (dd, $J = 4$, 4 Hz), 148.5 (dd, $J = 13$, 245 Hz), 150.9 (dd, $J = 13$, 247 Hz); MS m/z (rel intensity) 450 (M$^+$; 19), 323 (7), 320 (6), 303 (7), 302 (7), 241 (10), 215 (6), 195 (14), 165 (10), 153 (21), 140 (44), 127 (100), 95 (24), 91 (40), 67 (38). Found: C, 53.35; H, 6.04%. Calcd for $C_{20}H_{26}F_3I$: C, 53.34; H, 5.82%.

1-[*trans*-4-(1-Fluoro-2-iodoethyl)cyclohexyl]-*trans*-4-pentylcyclohexane (2c). In a similar manner, **2c** (0.55 g, 68% yield) was prepared as a colorless powder from **1c** (0.53 g, 2.0 mmol). Phase transition temperature/°C: Cr 67 N 71 Iso; $R_f = 0.40$ (hexane). IR (KBr) 2923, 2849, 1445, 1414, 1190, 965, 920, 899, 801, 590 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.77$—1.35 (m, 22 H), 1.59—1.97 (m, 9 H), 3.29 (ddd, $J = 7$, 11, 22 Hz, 1 H), 3.39 (ddd, $J = 4$, 11, 23 Hz, 1 H), 4.13 (dddd, $J = 4$, 6, 7, 47 Hz, 1 H); ^{19}F NMR (188 MHz) $\delta = -178.06$ (dddd, $J = 16$, 22, 23, 47 Hz); ^{13}C NMR (75.5 MHz) $\delta = 6.0$ (d, $J = 25$ Hz), 14.1 (s), 22.7 (s), 26.7 (s), 27.4 (d, $J = 5$ Hz), 28.5 (d, $J = 5$ Hz), 29.1 (d, $J = 18$ Hz), 30.0 (s), 32.2 (s), 33.6 (s), 37.4 (s), 37.9 (s), 42.1 (d, $J = 19$ Hz), 43.1 (d, $J = 25$ Hz), 95.8 (d, $J = 177$ Hz); MS m/z (rel intensity) 409 (M$^+$+ 1; 0.96), 408 (M$^+$; 5), 317 (0.97), 281 (2), 261 (15), 235 (32), 221 (5), 205 (2), 179 (5), 165 (8), 153 (14), 139 (19), 123 (14), 109 (30), 97 (98), 83 (100), 67 (79). Found: m/z 408.1695. Calcd for $C_{19}H_{34}FI$: M, 408.1689.

1-{*trans*-4-[1-Fluoro-2-(phenylthio)ethyl]cyclohexyl}-*trans*-4-(3,4-difluorophenyl)cyclohexane (3b). A flame dried, two-necked, 30 mL flask was charged with sodium hydride (132 mg, 5.5 mmol) and THF (5.0 mL). To the suspension cooled at 0 °C, benzenethiol (0.62 mL, 6.0 mmol) was added dropwise. The mixture was stirred for 30 min at room temperature. The benzenethiolate reagent was added via cannula to a solution of **2b** (2.3 g, 5.0 mmol) in THF (5.0 mL) placed in a two-necked 50 mL flask and cooled at 0 °C. The reagent flask was washed with THF (10 mL). This also was added to the **2b** solution. The resulting mixture was allowed to warm to room temperature and stirred for 5 h before quenching with aq NH_4Cl. The organic phase was separated; the aq phase was extracted with Et_2O three times (50 mL). The combined organic phase was washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : benzene = 5 : 1) to give **3b** (1.98 g, 91% yield) as needles, mp 95.6—95.9 °C, $R_f = 0.32$ (hexane : benzene = 5 : 1). IR (KBr) 2923, 2853, 1607, 1582, 1516, 1480, 1273, 1211, 1117, 1090, 1053, 1024, 939, 741, 691 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.95$—1.45 (m, 10 H), 1.65—1.98 (m, 9 H), 2.41 (tt, $J = 3$, 9 Hz, 1 H), 3.10—3.23 (m, 2 H), 4.39 (ddt, $J = 6$, 48, 6 Hz, 1 H), 6.84—7.41 (m, 8 H); ^{19}F NMR (188 MHz) $\delta = -139.19$ (ddd, $J = 8$, 12, 21 Hz, 1 F), -143.06 (dddd, $J = 5$, 8, 10, 21 Hz, 1 F), -184.54 (ddt, $J = 20$, 48, 22 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 27.1$ (d, $J = 5$ Hz), 28.8 (d, $J = 5$ Hz), 29.3 (d, $J = 18$ Hz), 30.1 (s), 34.5 (s), 36.4 (d, $J = 24$ Hz), 41.2 (d, $J = 20$ Hz), 42.6 (d, $J = 20$ Hz), 43.8 (s), 95.8 (d, $J = 175$ Hz), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 4$, 6 Hz), 126.4 (s), 128.9 (s), 129.7 (s), 135.9 (s), 144.7 (dd, $J = 4$, 5 Hz), 148.5 (dd, $J = 13$, 246 Hz), 150.1 (dd, $J = 12$, 247 Hz); MS m/z (rel intensity) 433 (M$^+$+ 1; 7), 432 (M$^+$; 25), 412 (18), 303 (13), 302 (33), 221 (5), 193 (10), 179 (16), 165 (8), 153 (24), 140 (18), 127 (94), 123 (94), 110 (100), 109 (61), 95 (38), 79 (62), 67 (68). Found: C, 72.13; H, 7.44%. Calcd for $C_{26}H_{31}F_3S$: C, 72.19; H, 7.22%.

1-{*trans*-4-[1-Fluoro-2-(phenylthio)ethyl]cyclohexyl}-*trans*-4-pentylcyclohexane (3c). In a similar way, **3c** (2.0 g, 95% yield) was obtained from **2c** (2.3 g, 5.5 mmol) as colorless needles, mp 59.8—60.7 °C; $R_f = 0.50$ (hexane : benzene = 5 : 1). IR (KBr) 3058, 2923, 2845, 1586, 1482, 1439, 1422, 1090, 1024, 968, 903, 830, 735, 702, 687 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.84$—1.34 (m, 22 H), 1.66—1.92 (m, 9 H), 3.08—3.22 (m, 2 H), 4.37 (dtd, $J = 6$, 6, 48 Hz, 1 H), 7.15—7.40 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -184.47$ (dtd, $J = 19$, 22, 48 Hz); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 27.2 (d, $J = 5$ Hz), 28.9 (d, $J = 5$ Hz), 29.3 (d, $J = 18$ Hz), 30.0 (s), 32.2 (s), 33.6 (s), 36.5 (d, $J = 24$ Hz), 37.4 (s), 37.9 (s), 41.3 (d, $J = 19$ Hz), 43.1 (d, $J = 21$ Hz), 95.9 (d, $J = 175$ Hz), 126.3 (s), 128.9 (s), 129.7 (s), 136.0 (s); MS m/z (rel intensity) 391 (M$^+$+ 1; 6), 390 (M$^+$; 26), 370 (11), 261 (6), 260 (19), 189 (11), 165 (6), 163 (6), 135 (17), 123 (78), 110 (100), 109 (52), 95 (48), 81 (53), 79 (58), 69 (58), 67 (70). Calcd for $C_{25}H_{39}FS$: C, 76.87; H, 10.06%. Found: C, 76.88; H, 10.16%.

***trans*-1-(3,4-Difluorophenyl)-4-[*trans*-4-(3,4-difluoro-4-phenylsulfinylbutyl)cyclohexyl]cyclohexane (5a).** A mixture of $TBAH_2F_3$ (2.7 g, 9.0 mmol), **3a** (1.38 g, 3.0 mmol), CH_2Cl_2 (10 mL), and DBH (0.87 g, 3.0 mmol) placed in a flame dried, two-necked, 30 mL flask was stirred for 30 min at room temperature before quenching with aq $NaHCO_3$ and solid $NaHSO_3$ under vigorous agitation. The organic phase was separated; the aq phase was separated and extracted with Et_2O three times (200 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was transferred to a 100 mL round-bottomed flask dissolved in CH_2Cl_2 (10 mL) and cooled at −30 °C. To the mixture was added *m*CPBA (0.57 g, 3.3 mmol) in one portion; the whole was stirred for 3 h at −30 °C before quenching with solid $NaHSO_3$. The mixture was treated with water and then with 10% aq NaOH. The organic phase was separated; the aq phase was extracted with Et_2O three times (totally 200 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : EtOAc = 5 : 1) to give **5a** (1.39 g, 94% yield) as colorless solids. Phase transition temperature/°C: S_X 45 S_B 93 Iso; $R_f = 0.21$, 0.35 (hexane : EtOAc = 5 : 1, diastereomeric mixtures). IR (KBr) 2920, 2848, 1605, 1518, 1446, 1428, 1272, 1214, 1118, 1091, 1048, 1023, 938, 817, 749, 686 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.85$—1.98 (m, 23 H), 2.40 (tm, $J = 10$ Hz, 1 H), 4.47—5.46 (m, 2 H), 6.85—7.10 (m, 3 H), 7.55—7.78 (m, 5 H); ^{19}F NMR (188 MHz) as diastereomeric mixtures; $\delta = -139.12$—−139.33 (m), −143.06—−143.17 (m), −189.49—−189.84 (m), −192.06—−192.56 (m), −192.79—−192.90 (m), −193.73—−194.02 (m), −196.58—−196.65 (m), −197.82—−198.23 (m), −198.43—−198.50 (m), −201.22—−201.88 (m); MS *m*/*z* (rel intensity) 495 (M^++1; 0.7), 494 (M^+; 2), 479 (1), 478 (5), 477 (12), 459 (1), 458 (3), 195 (4), 179 (5), 167 (4), 153 (14), 140 (11), 127 (64), 126 (100), 125 (22), 109 (11), 95 (12), 81 (26), 79 (11), 78 (12), 77 (10), 69 (12), 67 (28). Found: *m*/*z* 494.2268. Calcd for $C_{28}H_{34}F_4OS$: M, 494.2266.

***trans*-1-(3,4-Difluorophenyl)-4-[*trans*-4-(1,2-difluoro-2-phenylsulfinylethyl)cyclohexyl]cyclohexane (5b).** This compound (1.31 g, 95% yield) was obtained from **3b** (1.3 g, 3.0 mmol) as a viscous oil by a procedure similar to the procedure for **5a**. $R_f = 0.15$ and 0.24 (hexane : EtOAc = 5 : 1, diastereomeric mixtures). IR (KBr) 2923, 2855, 1607, 1518, 1446, 1430, 1275, 1208, 1116, 1086, 1050, 999, 955, 863, 748, 689 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.98$—1.45 (m, 11 H), 1.63—2.04 (m, 8 H), 2.32—2.46 (m, 1 H), 4.41—5.36 (m, 2 H), 6.85—7.11 (m, 3H), 7.55—7.78 (m, 5 H); ^{19}F NMR (188 MHz) as diastereomeric mixtures; $\delta = -139.17$—−139.22 (m), −143.03—−143.20 (m), −188.44—−188.76 (m), −196.22—−196.70 (m), −197.51—−197.92 (m), −198.29—−198.68 (m), −201.89—−202.04 (m), −203.60—−203.87 (m); MS *m*/*z* (rel intensity) 467 (M^++1; 2), 466 (M^+; 4), 452 (1), 450 (4), 449 (8), 431 (4), 430 (9), 321 (3), 195 (11), 181 (6), 179 (9), 167 (4), 153 (16), 141 (13), 140 (15), 128 (10), 127 (88), 126 (100), 125 (16), 110 (16), 109 (14), 97 (12), 95 (11), 83 (27), 81 (30), 79 (15), 77 (12), 67 (29). Found: *m*/*z* 466.1949. Calcd for $C_{26}H_{30}F_4OS$: M, 466.1953.

1-[*trans*-4-(1,2-Difluoro-2-phenylsulfinylethyl)cyclohexyl]-*trans*-4-pentylcyclohexane (5c). Similarly, compound **5c** (1.13 g, 88% yield) was prepared from **3c** (1.18 g, 3.0 mmol) as a colorless powder. Phase transition temperature/°C: S_B 107 Iso; $R_f = 0.27$ and 0.39 (hexane : EtOAc = 5 : 1, diastereomeric mixtures). IR (KBr) 2922, 2850, 1445, 1378, 1341, 1084, 1044, 1000, 964, 748, 688 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.85$—1.41 (m, 22 H), 1.59—1.99 (m, 9 H), 4.66—5.32 (m, 2 H), 7.56—7.76 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -185.23$—−185.79 (m), −188.46—−188.87 (m), −196.31—−196.72 (m), −197.57—−198.02 (m), −198.32—−198.67 (m), −201.34—−202.14 (m), −203.36—−203.78 (m); MS *m*/*z* (rel intensity) 425 (M^++1; 1), 424 (M^+; 3), 409 (2), 408 (7), 407 (10), 388 (7), 259 (4), 177 (2), 165 (4), 153 (6), 151 (7), 139 (8), 137 (11), 127 (12), 126 (100), 125 (21), 123 (17), 111 (19), 110 (26), 109 (29), 97 (66), 95 (28), 93 (14), 83 (83), 81 (46), 79 (22), 77 (17), 71 (15), 69 (55), 67 (46). Found: *m*/*z* 424.2566. Calcd for $C_{25}H_{38}F_2OS$: M, 424.2611.

1-[*trans*-4-(2,3-Difluoro-3-phenylsulfinylpropyl)cyclohexyl]-*trans*-4-pentylcyclohexane (5d). Compound **5d** (1.63 g) was isolated in 93% yield from **3d** (1.62 g, 4.0 mmol) as a colorless powder by a procedure similar to that for the preparation of **5a**. Phase transition temperature/°C: Cr 93 S_B 142 Iso; $R_f = 0.22$ and 0.28 (hexane : EtOAc = 5 : 1, diastereomeric mixtures). IR (KBr) 2918, 2849, 1445, 1377, 1305, 1084, 1044, 999, 968, 744, 689 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.84$—1.53 (m, 23 H), 1.60—1.97 (m, 10 H), 4.43—5.47 (m, 2 H), 7.54—7.77 (m, 5 H); ^{19}F NMR (188 MHz) as diastereomeric mixtures; $\delta = -189.39$—−189.84 (m), −190.87—−191.08 (m), −193.54—−194.22 (m), −196.40—−196.86 (m), −197.40—−197.84 (m), −198.70—−199.44 (m), −200.52—−200.90 (m); MS *m*/*z* (rel intensity) 439 (M^++1; 2), 438 (M^+; 4), 422 (16), 421 (42), 141 (12), 127 (23), 126 (100), 125 (79), 111 (33), 110 (15), 109 (45), 97 (79), 83 (69), 81 (58), 69 (63), 67 (65); Found: *m*/*z* 438.2775. Calcd for $C_{26}H_{40}F_2OS$: M, 438.2768.

1-[*trans*-4-(3,4-Difluoro-4-phenylsulfinylbutyl)cyclohexyl]-*trans*-4-pentylcyclohexane (5e). In a similar manner as above, compound **5e** (1.20 g) was prepared in 87% yield from **3e** (1.3 g, 3.0 mmol) as a colorless powder. Phase transition temperature/°C: S_B 98 Iso; $R_f = 0.24$ and 0.36 (hexane : EtOAc = 5 : 1, diastereomeric mixtures). IR (KBr) 2920, 2850, 1445, 1378, 1320, 1090, 1050, 962, 897, 747, 688 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.84$—1.50 (m, 25 H), 1.58—2.01 (m, 10 H), 4.47—5.39 (m, 2 H), 7.54—7.76 (m, 5 H); ^{19}F NMR (188 MHz) as diastereomeric mixtures; $\delta = -189.52$—−189.97 (m), −191.71—−192.33 (m), −192.56—−193.25 (m), −193.43—−194.13 (m), −196.45—−196.92 (m), −197.71—−198.76 (m), −200.92—−201.33 (m); MS *m*/*z* (rel intensity) 453 (M^++1; 0.5), 452 (M^+; 0.8), 435 (14), 127 (10), 126 (100), 125 (33), 111 (11), 109 (18), 97 (39), 95 (19), 83 (34), 81 (30), 77 (15), 69 (44), 67 (47); Found: *m*/*z* 452.2933. Calcd for $C_{27}H_{42}F_2OS$: M, 452.2924.

1-{*trans*-4-[(*Z*)-3,4-Difluoro-3-butenyl]cyclohexyl}-*trans*-4-(3,4-difluorophenyl)cyclohexane (*cis*-6a) and 1-{*trans*-4-[(*E*)-3,4-Difluoro-3-butenyl]cyclohexyl}-*trans*-4-(3,4-difluorophenyl)cyclohexane (*trans*-6a). A solution of compound **5a** (1.39 g, 2.8 mmol) in *o*-xylene (15 mL) was placed in a thick-walled Pyrex pressure tube, and heated at 170 °C for 16 h under an argon atmosphere. The reaction mixture was cooled and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (10 mL) and treated with *m*CPBA (0.53 g, 3.1 mmol) in one portion at −30 °C to oxidize diphenyldisulfide. The whole was stirred for 6 h at −30 °C before quenching the excess peroxide with solid $NaHSO_3$ at −30 °C. The mixture was diluted with water and made alkaline with 10% aq NaOH. The organic phase was separated; the aq phase was extracted with Et_2O three times (200 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to give *cis*-**6a** (0.34 g, 33% yield) and *trans*-**6a** (0.23 g, 22% yield) both as mesomorphic oils.

***cis*-6a:** Phase transition temperature/°C: Cr 35 N 116 Iso (DSC on 2nd heating); $R_f = 0.38$ (hexane). IR (KBr) 2928, 2855, 1727, 1607, 1516, 1453, 1271, 1202, 1140, 1088, 884, 866, 822, 779, 750, 631 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.81$—1.44 (m, 13 H), 1.74—1.92 (m, 8 H), 2.00—2.20 (m, 2 H), 2.41 (tt, $J = 3$, 12 Hz, 1

H), 6.23 (tdd, J = 1, 18, 74 Hz, 1 H), 6.86—7.11 (m, 3 H); ^{19}F NMR (188 MHz) δ = −135.80 (ddt, J = 11, 18, 19 Hz, 1 F), −139.21 (ddd, J = 8, 12, 21 Hz, 1 F), −143.10 (dddd, J = 4, 8, 10, 21 Hz, 1 F), −167.70 (tdd, J = 5, 11, 74 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 24.8 (d, J = 22 Hz), 29.8 (s), 30.1 (s), 33.0 (d, J = 3 Hz), 33.2 (s), 34.5 (s), 37.0 (s), 42.7 (s), 43.1 (s), 43.8 (s), 115.4 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 132.4 (dd, J = 14, 250 Hz), 144.8 (dd, J = 4, 5 Hz), 148.5 (dd, J = 13, 245 Hz), 149.8 (dd, J = 6, 253 Hz), 150.1 (dd, J = 12, 247 Hz); MS *m/z* (rel intensity) 369 (M$^+$+1; 5), 368 (M$^+$; 21), 290 (18), 193 (14), 179 (27), 166 (8), 153 (27), 141 (13), 140 (79), 127 (100), 111 (11), 95 (36), 81 (42), 79(24), 67 (54). Calcd for $C_{22}H_{28}F_4$: C, 71.72; H, 7.66%. Found: C, 71.63; H, 7.68%.

***trans*-6a:** Phase transition temperature/°C: Cr 16 S_X 25 S_B 35 N 92 Iso (DSC on 2nd heating); R_f = 0.56 (hexane). IR (KBr) 2923, 2853, 1609, 1518, 1497, 1451, 1433, 1285, 1208, 1138, 1119, 1094, 939, 870, 818, 770, 627 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.88—1.51 (m, 13 H), 1.73—1.93 (m, 8 H), 2.28—2.49 (m, 3 H), 6.85—7.26 (m, 4 H); ^{19}F NMR (188 MHz) δ = −139.23(ddd, J = 8, 12, 21 Hz, 1 F), −143.12 (dddd, J = 5, 8, 10, 21 Hz, 1 F), −160.63 (tdd, J = 3, 23, 127 Hz, 1 F), −184.20 (tdd, J = 5, 77, 127 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 23.6 (d, J = 24 Hz), 29.9 (s), 30.2 (s), 32.8 (d, J = 2 Hz), 33.2 (s), 34.6 (s), 37.2 (s), 42.8 (s), 43.2 (s), 43.9 (s), 115.4 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 139.2 (dd, J = 68, 237 Hz), 144.8 (dd, J = 4, 5 Hz), 148.5 (dd, J = 13, 245 Hz), 150.2 (dd, J = 12, 247 Hz), 156.4 (dd, J = 40, 239 Hz); MS *m/z* (rel intensity) 369 (M$^+$+1; 6), 368 (M$^+$; 26), 290 (7), 193 (11), 179 (24), 173 (8), 153 (35), 140 (82), 127 (100), 111 (14), 95 (37), 81 (42), 79 (28), 69 (22), 67 (62). Calcd for $C_{22}H_{28}F_4$: C, 71.72; H, 7.66%. Found: C, 71.61; H, 7.83%.

1-{*trans*-4-[(Z)-1,2-Difluoroethenyl]cyclohexyl}-*trans*-4-(3,4-difluorophenyl)cyclohexane (*cis*-6b) and 1-{*trans*-4-[(*E*)-1,2-Difluoroethenyl]cyclohexyl}-*trans*-4-(3,4-difluorophenyl)cyclohexane (*trans*-6b). In a similar manner as for **6a**, *cis*-**6b** (0.44 g, 40% yield) and *trans*-**6b** (155 mg, 16% yield) were prepared both as mesomorphic oils from **5b** (1.31 g, 2.8 mmol).

***cis*-6b Showed:** Phase transition temperature/°C: Cr 30 S_B 38 N 92 Iso (DSC on 2nd heating); R_f = 0.41 (hexane). IR (KBr) 2923, 1715, 1605, 1514, 1451, 1429, 1275, 1215, 1179, 1161, 1138, 1115, 997, 965, 864, 752, 722, 583 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.88—1.53 (m, 10 H), 1.75—2.10 (m, 9 H), 2.41 (tt, J = 3,12 Hz, 1 H), 6.23 (dd, J = 18, 74 Hz, 1 H), 6.84—7.11 (m, 3 H); ^{19}F NMR (188 MHz) δ = −139.15 (ddd, J = 8, 12, 21 Hz, 1 F), −140.38 (ddd, J = 11, 17, 18 Hz, 1 F), −143.00 (dddd, J = 5, 8, 10, 21 Hz, 1 F), −171.32 (ddd, J = 4, 11, 74 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 29.2 (s), 29.7 (s), 30.0 (s), 34.4 (s), 37.1 (d, J = 21 Hz), 42.48 (s), 42.51 (s), 43.8 (s), 115.3 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 132.1 (dd, J = 14, 249 Hz), 144.7 (dd, J = 4, 5 Hz), 148.5 (dd, J = 13, 245 Hz), 150.1 (dd, J = 13, 247 Hz), 153.4 (dd, J = 6, 245 Hz); MS *m/z* (rel intensity) 341 (M$^+$+1; 2), 340 (M$^+$; 11), 320 (8), 193 (18), 179 (34), 166 (18), 153 (25), 140 (66), 127 (100), 111 (8), 97 (11), 81 (25), 79 (23), 77 (16), 67 (30). Calcd for $C_{20}H_{24}F_4$: C, 70.57; H, 7.11%. Found: C, 70.55; H, 7.32%.

***trans*-6b Showed:** Phase transition temperature/°C: Cr 77 N 83 Iso (DSC on 2nd heating); R_f = 0.59 (hexane). IR (KBr) 2917, 2857, 1607, 1516, 1491, 1451, 1433, 1345, 1283, 1215, 1111, 943, 864, 833, 816, 801, 779, 750, 631 cm^{-1}; ^{1}H NMR (200 MHz) δ = 1.05—1.66 (m, 10 H), 1.75—1.94 (m, 8 H), 2.34—2.69 (m, 2 H), 6.98 (dd, J = 4,78 Hz, 1 H), 6.84—7.11 (m, 3 H); ^{19}F NMR (188 MHz) δ = −139.16 (ddd, J = 9, 12, 21 Hz, 1 F), −143.02 (dddd, J = 5, 8, 10, 21 Hz, 1 F), −169.43 (ddd, J = 4, 29, 127 Hz, 1 F), −184.97 (ddd, J = 5, 78, 127 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 28.7 (d, J = 3 Hz), 29.4 (s), 30.1 (s), 34.5 (s), 35.8 (dd, J = 2, 22 Hz), 42.3 (s), 42.7 (s), 43.8 (d, J = 1 Hz), 115.4 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 138.3 (dd, J = 69, 237 Hz), 144.7 (dd, J = 4, 5 Hz), 148.5 (dd, J = 13, 245 Hz), 150.1 (dd, J = 12, 247 Hz), 159.2 (dd, J = 39, 241 Hz); MS *m/z* (rel intensity) 340 (M$^+$; 8), 320 (6), 193 (15), 179 (31), 166 (16), 153 (24), 140 (69), 127 (100), 111 (7), 97 (12), 81 (25), 80 (8), 79 (23), 77 (17), 67 (31). Found: *m/z* 340.1811. Calcd for $C_{20}H_{24}F_4$: M, 340.1814.

1-{*trans*-1-[(Z)-1,2-Difluoroethenyl)]cyclohexyl}-*trans*-4-pentylcyclohexane (*cis*-6c) and 1-{*trans*-1-[(*E*)-1,2-Difluoroethenyl)]cyclohexyl}-*trans*-4-pentylcyclohexane (*trans*-6c). A solution of compound **5c** (1.13 g, 2.7 mmol) in *o*-xylene (15 mL) was heated at 170 °C for 16 h. Concentration in vacuo followed by flash column chromatography (hexane) gave *cis*-**6c** (0.44 g, 55% yield) and *trans*-**6c** (143 mg, 18% yield).

***cis*-6c was characterized by:** Phase transition temperature/°C: Cr 20 S_B 22 N 70 Iso (DSC on 2nd heating); R_f = 0.32 (hexane). IR 3131, 2924, 2853, 2361, 1719, 1451, 1377, 1329, 1310, 1242, 1190, 1138, 1123, 1103, 980, 772, 733 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.84—1.34 (m, 22 H), 1.66—2.04 (m, 9 H), 6.22 (ddd, J = 1, 17, 74 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −140.26 (ddd, J = 11, 17, 17 Hz, 1 F), −171.52 (ddd, J = 4, 11, 74 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 22.7 (s), 26.7 (s), 29.3 (s), 29.4 (s), 30.0 (s), 32.2 (s), 33.6 (s), 37.2 (d, J = 21 Hz), 37.4 (s), 37.9 (s), 42.7 (s), 43.3 (s), 132.2 (dd, J = 14, 249 Hz), 153.5 (dd, J = 6, 255 Hz); MS *m/z* (rel intensity) 299 (M$^+$+1; 3), 298 (M$^+$; 13), 269 (2), 242 (2), 227 (11), 207 (3), 186 (8), 172 (8), 151 (18), 137 (14), 121 (7), 109 (21), 97 (79), 95 (46), 83 (91), 81 (87), 69 (81), 67 (100). Found: C, 76.18; H, 10.68%. Calcd for $C_{19}H_{32}F_2$: C, 76.46; H, 10.81%.

***trans*-6c Showed:** Phase transition temperature/°C: Cr 34 S_B 38 N 41 Iso (DSC on 2nd heating); R_f = 0.60 (hexane). IR (KBr) 2924, 2851, 1447, 1379, 1339, 1258, 1210, 1123, 795, 600 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.84—1.50 (m, 22 H), 1.67—1.81 (m, 8 H), 2.38—2.67 (m, 1 H), 6.97 (dd, J = 4,78 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −169.37 (ddd, J = 4, 29, 127 Hz, 1 F), −185.12 (ddd, J = 4, 78, 127 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 22.7 (s), 26.7 (s), 28.8 (d, J = 2 Hz), 29.5 (s), 30.0 (s), 32.3 (s), 33.6 (s), 35.8 (d, J = 22 Hz), 37.5 (s), 38.0 (s), 42.5 (s), 43.4 (s), 138.2 (dd, J = 69, 237 Hz), 159.3 (dd, J = 38, 241 Hz); MS *m/z* (rel intensity) 298 (M$^+$; 14), 242 (5), 207 (8), 191 (5), 173 (5), 151 (18), 149 (22), 137 (15), 121 (15), 109 (35), 97 (88), 95 (51), 83 (92), 81 (80), 71 (55), 69 (100), 67 (95). Found: *m/z* 298.2475. Calcd for $C_{19}H_{32}F_2$: M, 298.2472.

1-{*trans*-1-[(Z)-2,3-Difluoro-2-propenyl)]cyclohexyl}-*trans*-4-pentylcyclohexane (*cis*-6d) and 1-{*trans*-1-[(*E*)-2,3-Difluoro-2-propenyl)]cyclohexyl}-*trans*-4-pentylcyclohexane (*trans*-6d). Compounds *cis*-**6d** (0.36 g, 45% yield) and *trans*-**6d** (0.23 g, 29% yield) were isolated from **5d** (1.14 g, 2.60 mmol) and showed the following properties.

***cis*-6d:** Phase transition temperature/°C: Cr 57 S_B 80 Iso (DSC on 2nd heating); R_f = 0.71 (hexane). IR (KBr) 2951, 2907, 2847, 1727, 1441, 1325, 1223, 1200, 1148, 1113, 876, 797, 689, 586 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.80—1.52 (m, 23 H), 1.66—2.00 (m, 10 H), 6.18 (dd, J = 17, 74 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −134.80 (ddt, J = 10, 17, 23 Hz, 1 F), −166.17 (tdd, J = 4, 10, 74 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 22.7 (s), 26.7 (s), 29.7 (s), 30.1 (s), 32.3 (s), 33.0 (s), 33.6 (s), 34.6 (s), 34.9 (s), 37.5 (s), 37.9 (s), 43.1 (s), 43.3 (s), 132.9 (dd, J = 14, 251 Hz), 148.4 (dd, J = 6, 253 Hz); MS *m/z* (rel intensity) 313 (M$^+$+1; 0.2), 312 (M$^+$; 2), 241 (1), 160 (1), 153 (4), 151 (4), 139 (6), 123 (11), 111 (15), 109 (15), 97 (66), 95 (25), 83 (100), 81 (48), 79 (18), 71 (17), 69 (71), 67 (56). Found: *m/z* 312.2632. Calcd for $C_{20}H_{34}F_2$: M, 312.2629.

***trans*-6d:** Phase transition temperature/°C: Cr 2 S_B 80 Iso (DSC on 2nd heating); R_f = 0.83 (hexane). IR 2921, 2851, 1730, 1447, 1262, 1229, 1146, 1115, 895, 793 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.84—1.51 (m, 23 H), 1.66—1.81 (m, 8 H), 2.23 (ddd, J = 6, 6, 25 Hz, 2 H), 7.08 (dd, J = 4, 78 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −157.75 (dtd, J = 4, 25, 128 Hz, 1 F), −183.51 (tdd, J = 6, 78, 128 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 22.8 (s), 26.7 (s), 29.8 (s), 30.1 (s), 32.3 (s), 33.1 (s), 33.7 (s), 33.73 (dd, J = 2, 22 Hz), 34.9 (dd, J = 2, 2 Hz), 37.5 (s), 38.0 (s), 43.1 (s), 43.4 (s), 139.9 (dd, J = 67, 237 Hz), 155.2 (dd, J = 40, 240 Hz); MS *m/z* (rel intensity) 313 (M^++1; 3), 312 (M^+; 14), 235 (6), 179 (4), 165 (6), 151 (15), 139 (27), 123 (22), 109 (30), 97 (94), 95 (40), 83 (100), 81 (66), 69 (67), 67 (64). Found: *m/z* 312.2620. Calcd for $C_{20}H_{34}F_2$: M, 312.2629.

1-{*trans*-1-[(*Z*)-3,4-Difluoro-3-butenyl)]cyclohexyl}-*trans*-4-pentylcyclohexane (*cis*-6e) and 1-{*trans*-1-[(*E*)-3,4-Difluoro-3-butenyl)]cyclohexyl}-*trans*-4-pentylcyclo-hexane (*trans*-6e). Compounds *cis*-**6e** (0.34 g, 39% yield) and *trans*-**6e** (0.22 g, 25% yield) were obtained from **5e** (1.2 g, 2.7 mmol) by a procedure similar to that for the preparation of **6c**.

***cis*-6e showed:** Phase transition temperature/°C: Cr 20 S_B 84 N 89 Iso (DSC on 2nd heating); R_f = 0.69 (hexane). IR 2923, 2853, 1727, 1468, 1449, 1335, 1271, 1202, 1138, 1121, 885, 774 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.72—1.45 (m, 25 H), 1.57—1.85 (m, 8 H), 2.05—2.20 (m, 2 H), 6.20 (dd, J = 17, 74 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −135.71 (ddt, J = 11, 17, 19 Hz, 1 F), −167.74 (tdd, J = 5, 11, 74 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 22.7 (s), 24.8 (d, J = 22 Hz), 26.7 (s), 29.9 (s), 30.1 (s), 32.3 (s), 33.1 (d, J = 3 Hz), 33.2 (s), 33.6 (s), 37.1 (s), 37.5 (s), 37.9 (s), 43.3 (s), 43.4 (s), 132.3 (dd, J = 14, 250 Hz), 149.8 (dd, J = 6, 253 Hz); MS *m/z* (rel intensity) 327 (M^++1; 5), 326 (M^+; 11), 255 (7), 247 (16), 239 (13), 205 (11), 178 (15), 154 (21), 148 (13), 144 (17), 142 (13), 107 (39), 106 (35), 97 (100), 89 (19), 80 (22), 67 (50). Found: *m/z* 326.2783. Calcd for $C_{21}H_{36}F_2$: M, 326.2785.

***trans*-6e Exhibited:** Phase transition temperature/°C: Cr 3 S_B 83 Iso (DSC on 2nd heating); R_f = 0.80 (hexane). IR 2925, 2851, 1719, 1672, 1655, 1468, 1449, 1379, 1339, 1298, 1215, 1208, 1137, 1122, 895, 791 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.75—1.47 (m, 25 H), 1.63—1.85 (m, 8 H), 2.26—2.48 (m, 2 H), 7.03 (dd, J = 4, 78 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −160.58 (dtd, J = 4, 23, 128 Hz, 1 F), −184.22 (tdd, J = 6, 78, 128 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 22.8 (s), 23.6 (δ, J = 22 Hz), 26.7 (s), 29.9 (s), 30.1 (s), 32.3 (s), 32.8 (d, J = 1 Hz), 33.2 (s), 33.7 (s), 37.2 (s), 37.4 (s), 37.5 (s), 38.0 (s), 43.37 (s), 43.45 (s), 139.1 (dd, J = 68, 237 Hz), 156.4 (dd, J = 40, 239 Hz); MS *m/z* (rel intensity) 327 (M^++1; 2), 326 (M^+; 7), 306 (3), 248 (14), 233 (3), 192 (2), 172 (6), 152 (13), 137 (9), 123 (7), 111 (24), 97 (100), 83 (88), 81 (58), 69 (59), 67 (65). Found: *m/z* 326.2794. Calcd for $C_{21}H_{36}F_2$: M, 326.2785.

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