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A Facile Synthesis of Novel Liquid Crystalline Materials Having a Trifluoromethoxy Group and Their Electro-Optical Properties

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Novel liquid crystals (LCs) containing a trifluoromethoxy group connected to a cyclohexane mesogen or to an alkyl tail were prepared through an oxidative desulfurization–fluorination reaction of the corresponding dithiocarbonates. They were compared with LCs containing a methoxy group with respect to phase transition behavior and physical and electro-optical properties. Most of the CF_3O-substituted LCs exhibited in a wide range of temperatures LC phases depending on the type of a mesogenic structure. LCs with a trifluoromethoxycyclohexane mesogen were shown to be thermally more stable than the LCs with a trifluoromethoxybenzene mesogen. LCs having a trifluoromethoxyalkyl tail show physical and electro-optical properties favorable to materials for not only TN-LCDs but TFT-addressed TN-LCDs. Furthermore, 3-β-CF_3O-substituted cholestane was shown to be a potential chiral dopant for TFT-addressed TN-LCDs.

Because of the large bond energy and dipole moment of a C–F bond, organofluorine compounds show low viscosity and high polarity as well as high chemical and thermal stability. These features have attracted much attention in the development of new functional materials.[1] For example, liquid crystals (LCs) with a fluorinated aromatic mesogen exhibit properties appropriate to materials for liquid-crystalline displays (LCDs) such as broad mesophase range, low viscosity, reasonably high dielectric anisotropy ($\Delta\varepsilon$), fast response time (τ), and high voltage holding ratio.[2] These properties are particularly favorable to materials for thin film transistor (TFT)-addressed twisted nematic (TN) LCDs.[3] Owing to the increasing importance of TN-LCDs, the development of novel fluorinated LCs is an urgent problem in synthetic organofluorine chemistry and material science.[4] In particular, LC materials with a trifluoromethoxy-substituted aromatic mesogen show low viscosity and high voltage holding ratio and are utilized in TFT-addressed TN-LCDs.[5] Therefore, various types of trifluoromethoxy-substituted LCs have been synthesized and evaluated with respect to electro-optical properties.[6] However, trifluoromethoxybenzene derivatives as the starting substrates are expensive and thus not really available. Furthermore, introduction of a trifluoromethoxy moiety into an aromatic ring must be performed using highly toxic and/or explosive reagents such as liquid HF,[7] $SbF_3/SbCl_5$,[8] SF_4,[9] MoF_6,[10] or BrF_3[11] under special conditions. Because of these difficulties, exploitation of efficient, mild, and selective fluorination method has been desired for the exploration of novel fluorinated functional materials.

We have recently demonstrated that an oxidative desulfurization-fluorination reaction using an *N*-halo imide and a fluoride source is an effective and mild fluorination method.[12] According to this method, both aromatic and aliphatic trifluoromethyl ethers ($R–OCF_3$), for example, are readily prepared by the reaction of the corresponding dithiocarbonates ($R–OCS_2R'$).[13] This reaction is, to the best of our knowledge,[14] an exclusive method for the preparation of trifluoromethyl ethers from secondary aliphatic alcohols.[15] Accordingly, the oxidative desulfurization–fluorination reaction, leading to various types of trifluoromethyl ethers with many functional groups remaining intact, is a powerful synthetic tool for the development of a novel class of fluorinated functional materials.[6a,16]

Because LCs with a cyclohexane mesogen show lower viscosity and smaller birefringence (Δn) than those of with a benzene mesogen,[17] we envisaged that LCs with a trifluoromethoxycyclohexane mesogen would exhibit physical and electro-optical properties better than LCs with a trifluoromethoxybenzene mesogen. In addition, because LCs containing an ω-methoxyalkyl moiety show high $\Delta\varepsilon$, broad nematic mesophase, and low viscosity as well as high voltage holding ratio favorable for TFT-addressed TN-LCDs,[18] we envisaged that the use of a trifluoromethoxy group in lieu of a methoxy group would increase the chemical stability and the voltage holding ratio and would decrease the viscosity of parent LCs.[5,17b]

Herein we report experimental details of the synthesis of novel LCs containing i) a trifluoromethoxycyclohexane

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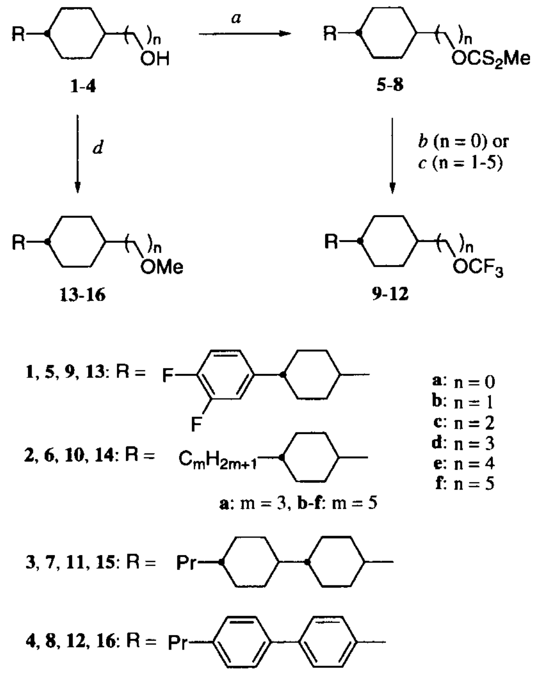
mesogen or ii) an ω-trifluoromethoxyalkyl tail through the oxidative desulfurization–fluorination. We also compare such LCs in respect to types of phase transition behavior and electro-optical properties with the corresponding LCs with a trifluoromethoxybenzene mesogen or an ω-methoxyalkyl tail.

Results and Discussion

Synthesis of Trifluoromethoxycyclohexane-LCs. Syntheses of LCs **9a**,[13a] **10a**, **11a**, and **12a**, all containing a trifluoromethoxycyclohexane mesogen, were carried out through the route shown in Scheme 1. Reduction of 4-substituted cyclohexanone with $LiAlH_4$, followed by separation by flash silica gel column chromatography and/or recrystallization, gave *trans*-cyclohexanols: **1a**, **2a**, **3a**, and **4a**. These were converted into the corresponding dithiocarbonates **5a**,[13a] **6a**, **7a**, and **8a** in high yields by treatment successively with NaH, CS_2, and MeI. For the synthesis of **7a**, NaH was replaced by *n*-BuLi to solubilize the alkoxide generated from **3a**. Treatment of **5a**, **6a**, **7a**, and **8a** with 50% hydrogen fluoride–pyridine (HF/py, 40 mol, prepared by neutralization of 70% HF/py[19] with pyridine) and *N*-bromosuccinimide (NBS, 5.0 mol) in CH_2Cl_2 at 0 °C afforded cyclohexyl trifluoromethyl ethers **9a**, **10a**, **11a**, and **12a** in moderate yields.[13a]

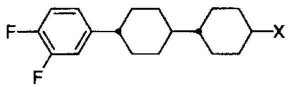
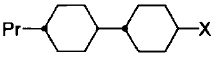
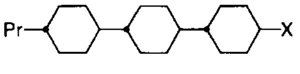
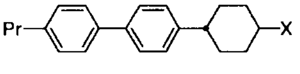
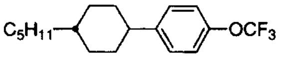
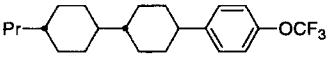
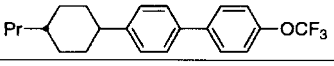
Phase Transition Behavior of Trifluoromethoxycyclohexane-LCs. Phase transition temperatures and LC phases of trifluoromethoxycyclohexanes **9a**, **10a**, **11a**, and **12a**, methoxycyclohexanes **13a**, **14a**, **15a**, and **16a**, and trifluoromethoxybenzenes **17**, **18**, and **19**[17] are summarized in Table 1. Although **9a** and **10a** showed only a melting point, trifluoromethyl ethers **11a** and **12a** exhibited nematic phase and smectic A phase, respectively, in a wide range of



a: i) NaH [or *n*-BuLi] (1.2 mol), ii) CS_2 (5.0 mol), iii) MeI (2.0 mol), THF.
b: 50% HF/py (40 mol), NBS (5.0 mol), CH_2Cl_2, 0 °C, 1 h.
c: i) 70% HF/py (40 or 60 mol), DBH (3.0 mol), CH_2Cl_2, −78; 0 °C, 1 h, ii) [*n*-BuLi (1.2 mol), THF, −78 °C, 10 min, then H_2O.]
d: i) NaH [or *n*-BuLi] (1.2 mol), ii) MeI (2.0 mol), THF.

Scheme 1. Synthesis of CF_3O-LCs **9**—**12** and CH_3O-LCs **13**—**16**.

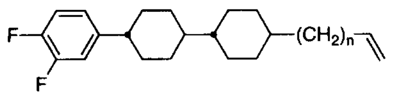
Table 1. Phase Transition Temperatures of CF_3O-LCs and CH_3O-LCs

Compound		Phase transition temp/°C [a)]
	**(9a)**	Cr 43 Iso[b)]
	(13a)	Cr 68 Iso[b)]
	**(10a)**	Cr 30 Iso
	(14a)	Cr 9 N 14 Iso
	**(11a)**	Cr 44 S_X 112 S_B 147 N 189 Iso
	(15a)	Cr 207 S_B 211 Iso
	**(12a)**	Cr 90 S_B 104 S_A 129 Iso
	(16a)	Cr 45 S_B 88 N 128 Iso
9a, **10a**, **11a**, **12a**: X = OCF_3;		**13a**, **14a**, **15a**, **16a**: X = OCH_3
	**(17)**	Cr 14 Iso
	**(18)**	Cr 38 S_B 69 N 153 Iso
	**(19)**	Cr 90 S_B 129 N 151 Iso

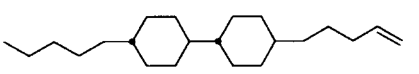
Cr: crystal, S_X: higher order smectic, S_B: smectic B, S_A: smectic A, N: nematic, Iso: isotropic liquid.
a) Measured by DSC on 2nd heating. b) Observed with an optical polarizing microscope.

temperatures. Differential scanning calorimetry (DSC) measurement of **11a** showed four endothermic peaks at 44, 112, 147, and 189 °C with enthalpy changes of 7.3, 2.7, 5.8, and 0.8 kJ mol^{-1}, respectively, on second heating. These peaks correspond to the phase transitions of Cr-to-S_X, S_X-to-S_B, S_B-to-N, and N-to-Iso, respectively. Trifluoromethyl ether **11a** exhibited nematic liquid-crystallinity much higher than the corresponding methyl ether **15a**, but such a CF_3-effect was not observed with **10a** and **12a**. Trifluoromethoxycyclohexane-LCs **10a**, **11a**, and **12a** were compared in respect to phase transition behavior with trifluoromethoxybenzene-LCs **17**, **18**, and **19**, and the effect of a mesogenic core was studied. The clearing temperature of **10a** was found to be much higher than that of the counter part **17**. Trifluoromethoxycyclohexane-LC **11a** showed a higher nematic-to-isotropic transition temperature (T_{NI}) than trifluoromethoxybenzene-LCs **18** and **19** did. These results indicate that a cyclohexane mesogen stabilizes a nematic phase more.

Electro-Optical Properties of Trifluoromethoxycyclohexane-LCs. We next studied the physical and electro-optical properties of trifluoromethoxycyclohexane-LCs **9a**, **10a**, **11a**, and **12a** as additives for nematic LCs and compared the properties found with those of **13a**, **14a**, **15a**, and **16a**, respectively, all having a methoxycyclohexane mesogen, and with **18** containing a trifluoromethoxybenzene mesogen. Each of these (20 wt%) was added to **host** (a 1 : 1 mixture of **20c** and **20e**) (Chart 1); then T_{NI}, $\Delta\varepsilon$, threshold voltage (V_{th}), Δn, and τ of the resulting mixture were measured in a TN cell. The data are summarized in Table 2. The T_{NI}'s of the resulting LC mixtures reflected the clearing temperatures of the additive. For example, T_{NI} of the mixture of **11a** was much higher than that of **18**. Extrapolation of $\Delta\varepsilon$ to 100% allowed us to estimate $\Delta\varepsilon'$. As $\Delta\varepsilon'$s of the mixtures containing trifluoromethoxycyclohexane-LCs **10a**, **11a**, and **12** are positive, these LC mixtures are proved to be p-type, whereas methoxycyclohexanes **14a**, **15a**, and **16a** are n-type ($\Delta\varepsilon' < 0$). In contrast, the opposite was observed between **9a** and **13a** that have a 3,4-difluorobenzene mesogen. The negative $\Delta\varepsilon'$ value of a **9a/host** mixture is apparently brought by compensation of dipole moment caused by F and CF_3O groups directing oppositely along the long axis of the molecule. In accord with the sign of $\Delta\varepsilon'$, trifluoromethoxycyclohexane-LCs **10a**, **11a**, and **12a** reduced the V_{th} of **host**, whereas **14a**, **15a**, and **16a** raised the V_{th} of **host**. Thus, a trifluoromethoxyl group connected to a cyclohexane mesogen contributes to the reduction of V_{th} of **host**. Each pair of **9a/13a**, **10a/14a**, **11a/15a**, and **12a/16a** showed similar low $\Delta n'$s, as estimated by extrapolation of Δn. Thus, Δn is governed by a mesogenic structure rather than a polar functional group. It is worth noting that **10a**, **11a**, and **12a** induced low Δn for relatively large $\Delta\varepsilon'$. Furthermore, V_{th} and $\Delta n'$ of **11a** were lower than those of **18**, in spite of the small $\Delta\varepsilon$ of **11a**. The features of **11a** are better than **18** in reducing driving voltage and also in controlling cell thickness[20] of TFT-addressed TN-LCDs. Trifluoromethoxycyclohexane-LCs **9a**, **10a**, **11a**, and **12a** are apparently thermally stable, since T_{NI} of a mixture of **10a** and **host** did not change at all after heating at 80 °C for 10 h.



20c: n = 0; **20e**: n = 2; **20f**: n = 3
host (**20c** : **20e** = 1 : 1 mixture)



21f

Chart 1.

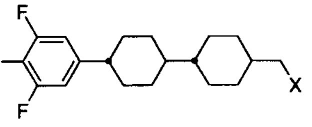
Synthesis of ω-Trifluoromethoxyalkyl-LCs. To examine the effect of tail length of LCs containing an ω-trifluoromethoxyalkyl group, we synthesized **9b**—**9f** and **10b**—**10f** having, respectively, *trans*-4-[*trans*-4-(3,4-difluorophenyl)-cyclohexyl]cyclohexane and *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexane mesogens. The corresponding methyl ethers **13b**—**13f** and **14b**—**14f** were also prepared to evaluate the fluorine substituent effect. The route is summarized in Scheme 1. Primary alcohols **1b**—**1f** and **2b**—**2f** were transformed to dithiocarbonates **5b**—**5f** and **6b**—**6f** in

Table 2. Physical and Electro-Optical Properties[a)] of Trifluoromethoxycyclohexanes **9a**—**12a** and the Corresponding Methyl Ethers **13a**—**16a** as Added by 20 wt% to **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)
9a	90.9	3.2	−3.2	2.18	0.085	0.082	35.1 (5.0)
10a	90.1	5.2	6.7	1.86	0.078	0.030	34.3 (4.3)
11a	130.2	4.7	4.3	2.10	0.084	0.060	37.0 (4.6)
12a	106.2	5.9	10.3	2.11	0.109	0.185	37.6 (4.8)
13a	107.4	4.0	0.8	2.12	0.087	0.075	33.8 (4.8)
14a	93.5	3.6	−1.2	2.20	0.077	0.025	36.3 (4.9)
15a	137.3	3.4	−2.2	2.43	0.084	0.060	44.1 (5.1)
16a	112.7	3.4	−2.2	2.45	0.105	0.165	31.2 (5.4)
18	122.4	5.1	6.5	2.19	0.089	0.087	—

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.

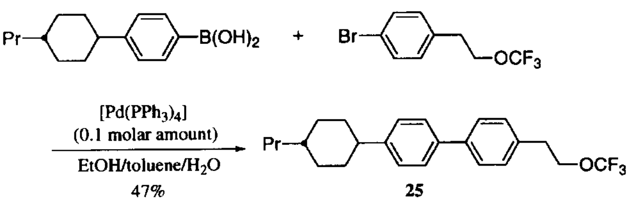
high yields by treatment with NaH (or *n*-BuLi), CS$_2$, and MeI. Trifluoromethoxylation of the dithiocarbonates was performed with 70% HF/py and 1,3-dibromo-5,5-dimethylhydantoin (DBH). For the substrates **5b**—**5f**, which have a difluorobenzene mesogen, trifluoromethoxylation leading to **9b**—**9f** was accompanied by bromination of the phenyl ring. The bromine functionality was removed by lithiation with *n*-BuLi, followed by protonation with H$_2$O to give the desired trifluoromethyl ethers in high yields. Trifluoromethyl ethers **10b**—**10f** were obtained directly from **6b**—**6f**. Methyl ethers **13b**—**13f** and **14b**—**14f** were prepared respectively from **1b**—**1f** and **2b**—**2f** as usual. To examine the effect of fluorine attached to a benzene mesogen, we additionally prepared trifluoromethyl ether **23** and methyl ether **24** and compared the results (Chart 2).



23: X = OCF$_3$; **24**: X = OCH$_3$

Chart 2.

Furthermore, in order to examine CF$_3$O and CF$_3$OCH$_2$CH$_2$ groups, we also prepared **25** and compared its results with those of **19**.



(1)

Phase Transition Behaviors of *ω*-Trifluoromethoxyalkylcyclohexane-LCs. Phase transition temperatures and LC phases of **9b**—**9f**, **10b**—**10f**, **13b**—**13f**, **14b**—**14f**, and **23**—**25** as well as trifluoromethoxycyclohexane-LCs **9a**, **10a**, **13a**, and **14a** are listed in Table 3. LCs **9** and **13** with a *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexane mesogen, **10** and **14** with a *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexane mesogen, and **25** with a *trans*-4-(*trans*-4-pentylcyclohexyl)biphenyl mesogen showed nematic, smectic B, and smectic A phases in a wide range of temperatures, respectively. Thus, the mesophase textures of trifluorometh-

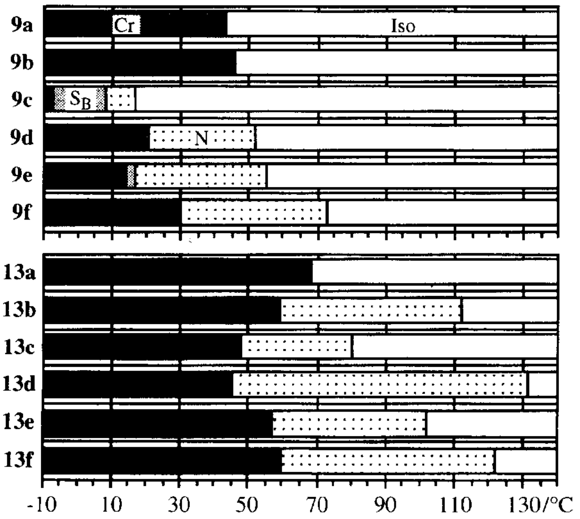
Table 3. Phase Transition Temperatures of **9**, **10**, **13**, and **14**

Compound	Phase transition temp/°C[a]													
	DSC (2nd heating)							DSC (1st cooling)						
9a					Cr	43	Iso[b]							
9b					Cr	46	Iso[b]							
9c	Cr	−7	$\mathrm{S_B}$	8	N	17	Iso			Cr	7	N	16	Iso
9d			Cr	21	N	52	Iso			Cr	−6	N	52	Iso
9e	Cr	14	$\mathrm{S_B}$	17	N	55	Iso			G	−1	N	54	Iso
9f			Cr	30	N	73	Iso	Cr	9	$\mathrm{S_B}$	13	N	73	Iso
13a					Cr	68	Iso[b]							
13b			Cr	59	N	111	Iso	Cr	6	$\mathrm{S_B}$	39	N	111	Iso
13c			Cr	48	N	80	Iso			Cr	2	N	79	Iso
13d			Cr	45	N	131	Iso	Cr	14	$\mathrm{S_B}$	35	N	130	Iso
13e			Cr	57	N	102	Iso			Cr	56	N	101	Iso
13f			Cr	60	N	122	Iso	Cr	2	$\mathrm{S_B}$	51	N	121	Iso
10a					Cr	30	Iso					Cr	13	Iso
10b	Cr	18	$\mathrm{S_X}$	26	$\mathrm{S_B}$	52	Iso	Cr	−6	$\mathrm{S_X}$	24	$\mathrm{S_B}$	50	Iso
10c			Cr	4	$\mathrm{S_B}$	53	Iso	Cr	−10	$\mathrm{S_X}$	−9	$\mathrm{S_B}$	52	Iso
10d			Cr	30	$\mathrm{S_B}$	96	Iso			Cr	24	$\mathrm{S_B}$	95	Iso
10e			Cr	4	$\mathrm{S_B}$	90	Iso			Cr	−12	$\mathrm{S_B}$	90	Iso
10f			Cr	22	$\mathrm{S_B}$	109	Iso			Cr	13	$\mathrm{S_B}$	109	Iso
14a			Cr	9	N	14	Iso	Cr	−2	$\mathrm{S_B}$	3	N	14	Iso
14b			Cr	−15	$\mathrm{S_B}$	73	Iso			Cr	−17	$\mathrm{S_B}$	71	Iso
14c			Cr	−12	$\mathrm{S_B}$	72	Iso			Cr	−19	$\mathrm{S_B}$	71	Iso
14d			Cr	30	$\mathrm{S_B}$	105	Iso			Cr	16	$\mathrm{S_B}$	105	Iso
14e			Cr	9	$\mathrm{S_B}$	97	Iso			Cr	−1	$\mathrm{S_B}$	96	Iso
14f			Cr	29	$\mathrm{S_B}$	113	Iso			Cr	9	$\mathrm{S_B}$	112	Iso
23					Cr	43	Iso[b]							
24			Cr	74	N	79	Iso			Cr	56	N	78	Iso
25			$\mathrm{S_B}$	132	$\mathrm{S_A}$	159	Iso			$\mathrm{S_B}$	130	$\mathrm{S_A}$	158	Iso

a) Iso: Isotropic liquid. N: Nematic phase. $\mathrm{S_A}$: Smectic A phase. $\mathrm{S_B}$: Smectic B phase. $\mathrm{S_X}$: Higher order smectic phases. Cr: Crystal. G: Glass state. b) Observed with an optical polarizing microscope on heating.

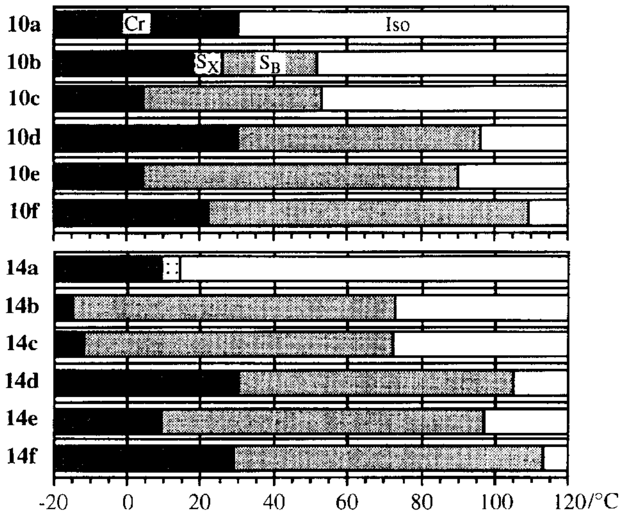
oxy-substituted LCs are dependent mainly on the structure of the mesogen. The phase transition behaviors of LCs **9** and **13** are shown in Fig. 1. Although LCs **9a** and **13a** with a *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexane mesogen exhibited only a melting point, LCs **9c**—**9f** and **13b**-**13f** having a methylene spacer between an ethereal oxygen and a mesogen exhibited nematic phase. A trifluoromethoxy group appears to lower clearing temperatures in comparison of **9** with **13**. With a longer alkyl chain (Fig. 1), trifluoromethyl ethers **9** tend to have higher $T_{\rm NI}$ temperatures and more stabilize nematic phases. In contrast, methyl ethers **13** have variable $T_{\rm NI}$ depending on the odd-even number of methylene units, and **13b**, **13d**, and **13f** exhibit a nematic temperature range much wider than that of **13c** or **13e**. The odd-even effect in crystal to nematic (or smectic) transition temperatures ($T_{\rm CN}$ or ($T_{\rm CS}$)) was only observed with **9**. Figure 2 illustrates temperature behaviors of **10** and **14** having a *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl mesogen. These LCs mainly exhibited smectic B phase in a wide range of temperatures, and their smectic-to-isotropic transition temperatures ($T_{\rm SI}$) and $T_{\rm CS}$ are influenced by the odd-even effect. A CF_3O group is shown to have a lower $T_{\rm SI}$ as compared with a CH_3O group.

Physical and Electro-Optical Properties of ω-Trifluoromethoxyalkylcyclohexane-LCs: Tail Length Effect. We mixed 20 wt% each of LCs **9b**—**9f**, **10b**—**10f**, **13b**—**13f**, **14b**—**14f**, **23**, and **25** with **host** (80 wt%) and measured the physical and electro-optical properties of the resulting mixtures. The data as well as those of **9a**, **10a**, **13a**, and **14a** are listed in Table 4. Among LCs with a *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexane mesogen, trifluoromethyl ethers **9b**—**9f** showed $\Delta\varepsilon$s lower than the corresponding methyl ethers **13b**—**13f**, owing probably to the effect discussed for **9a** and **13a**. LCs with the same mesogen exhibited almost uniform values in $\Delta\varepsilon$, $V_{\rm th}$, Δn, and τ, respectively, irrespective of the terminal structure of a tail. These values were found to be more dependent on the type of mesogen. In general, $V_{\rm th}$ of a LC mixture increases when $\Delta\varepsilon$ of the LC mixture is reduced, as was observed with **14**. In contrast, for small $\Delta\varepsilon$, $V_{\rm th}$ of the mixture of **9** or **10** was not large. Therefore, the trifluoromethyl ethers are apparently suitable for the purpose of reducing driving voltage of LCDs. The fact that $\Delta\varepsilon$ of trifluoromethyl ether **10b**, **10c**, **10d**, **10e**, or **10f** with a *trans*-4-(*trans*-4-pentylcyclohexyl)cyclo-hexylalkyl mesogen was only slightly higher than that of the corresponding methyl ether **14c**, **14d**, **14e**, or **14f**, respectively, suggests that the dipole moment induced by the trifluoromethoxy group in a tail of LCs is not striking. However, it is noteworthy that a trifluoromethoxy group connected directly to a cyclohexane mesogen raises $\Delta\varepsilon'$, as seen in **10a**, acting as a strong polar functional group. Accordingly, introduction of a trifluoromethoxy group into a cyclohexane mesogen of LCs is highly effective for induction of $\Delta\varepsilon$. Since **13b** and **14b**, which have a methoxymethyl substituent, did not form TN orientation in an LC cell, trifluoromethyl ethers **9b** and **10b** are favorable materials for TN-LCDs. Bulk viscosity (η_{20}) at 20 °C of **host** (η_{20} = 19.8) increased only slightly by a trifluoromethyl ether additive. For example, a mixture of **9b** and **host** (1 : 4 w/w) had η_{20} = 22.8; a mixture consisting of **23** and **host** (1 : 4 w/w) had η_{20} = 23.2.



Cr: crystal phase, S_B: smectic B phase,
N: nematic phase, Iso: isotropic liquid phase.

Fig. 1. Phase transition behaviors of **9** and **13**.



Cr: crystal phase, S_X: higher ordered smectic phase,
S_B: smectic B phase, Iso: isotropic liquid phase.

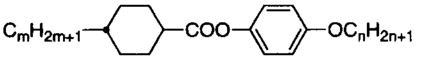
Fig. 2. Phase transition behaviors of **10** and **14**.

Trifluoromethoxy-LCs as Chiral Dopants for TN- and TFT-Addressed TN-LCDs. We next examined the possibility of LCs with a trifluoromethoxy group on a mesogen as a chiral dopant for TN-LCDs. As the chiral dopant for super-TN-LCDs, cholesteryl nonanoate (**26**) has been extensively utilized. We prepared 3β-trifluoromethoxycholestane (**27**)[13a] and 3β-methoxycholestane (**28**), mixed 1 wt% of each with **TN-host** consisting of 6-homologs (equal weight) of 4-alkoxyphenyl 4-alkylcyclohexane carboxylates, and measured the helical pitch of each mixture at 25 °C (Chart 3). All of the mixtures exhibited chiral nematic phase below 72 °C, with slight lowering of the clearing temperature of **TN-host**. Helical pitch of the mixture of **26**, **27**, or **28** was 15.9, 15.9,

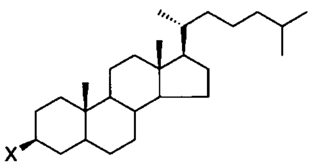
Table 4. Physical and Electro-Optical Properties[a] of **9**, **10**, and **13**, **14** as Added by 20 wt% to **host**

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)
9a	90.9	3.2	−3.2	2.18	0.082	0.050	45.3 (4.8)
9b	103.4	3.2	−3.2	2.26	0.085	0.065	35.1 (5.0)
9c	101.0	3.2	−3.2	2.16	0.084	0.060	36.6 (4.9)
9d	107.5	3.2	−3.2	2.18	0.086	0.070	44.1 (4.7)
9e	105.5	3.3	−2.7	2.10	0.083	0.055	39.7 (4.9)
9f	109.0	3.2	−3.2	2.19	0.083	0.055	43.4 (4.8)
13a	107.4	4.0	0.8	2.12	0.087	0.075	33.8 (4.8)
13b	—	—	—	—	—	—	—
13c	110.9	4.3	2.3	2.03	0.086	0.070	33.8 (4.3)
13d	120.7	4.8	4.8	2.12	0.091	0.095	33.4 (4.9)
13e	114.6	4.3	2.2	1.98	0.087	0.075	41.1 (4.3)
13f	118.3	4.6	3.6	2.08	0.088	0.080	38.5 (4.6)
10a	90.1	5.2	6.7	1.86	0.078	0.030	34.3 (4.3)
10b	94.7	3.6	−1.2	2.16	0.079	0.035	31.8 (4.2)
10c	94.1	3.6	−1.2	1.97	0.078	0.030	34.8 (4.2)
10d	99.9	3.4	−2.0	2.18	0.079	0.035	36.8 (4.4)
10e	99.4	3.5	−1.8	2.02	0.079	0.035	39.4 (4.7)
10f	101.9	3.3	−2.7	2.10	0.078	0.030	37.9 (4.5)
14a	93.5	3.6	−1.2	2.20	0.077	0.025	36.3 (4.9)
14b	—	—	—	—	—	—	—
14c	100.2	3.1	−3.7	2.22	0.077	0.025	31.0 (4.5)
14d	110.1	3.2	−3.2	2.31	0.081	0.045	32.3 (4.9)
14e	105.2	3.1	−3.7	2.21	0.079	0.035	40.3 (4.6)
14f	109.4	3.2	−3.2	2.33	0.079	0.035	35.8 (5.0)
23	98.9	3.5	−1.8	2.10	0.084	0.060	36.4 (4.6)
25	117.1	4.0	0.8	2.15	0.101	0.145	36.5 (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.



TN-host: a mixture of equal amounts of homologs (m, n) = (3, 2), (3, 4), (3, 5), (4, 2), (5, 1), (5, 2)
T_{NI} = 73.8 °C



27: X = OCF_3
28: X = OCH_3

Chart 3.

or 39.2 µm, respectively. The value for **27** was much smaller than that for **28**. Therefore, a trifluoromethoxy group in a chiral dopant is a polar functionality apparently better than a methoxy group. Furthermore, compound **27** induced helices of chiral nematic LCs to a degree comparable to **26** that is currently used for TN-LCDs. This means **27** may find applications as a chiral dopant for TFT-addressed TN-LC mixtures. Because LCs containing a cyano or alkoxycarbonyl group bring about a striking decrease in the voltage holding ratio, compound **26** is not suitable for TFT-addressed TN-LCDs. So, we next examined voltage holding ratio of a mixture of **27** (2 wt%) and **host** (98%) at 80 °C and were delighted to observe that it was 97.4%; that of **host** was 97.5%. A mixture of **28** and **host** (2 : 98 w/w) showed 97.0% of voltage holding ratio at 80 °C. The helical pitch of the mixture of **27/host** or **26/host** was 8.0 µm at 25 °C. Therefore, compound **27** is concluded to be an excellent chiral dopant not only for TN-LCDs but also for TFT-addressed TN-LCDs.

Trifluoromethoxycyclohexane-LCs as Materials for TFT-Addressed TN-LCDs. We further investigated the possibility of **11a** as an additive for TFT-addressed TN-LCDs. We prepared an LC mixture containing **11a** (20 wt%) in a TFT-host mixture that exhibited T_{NI} = 82.5 °C, $\Delta\varepsilon$ = 3.6, V_{th} = 1.71 V, Δn = 0.072, τ = 48.6 ms. The resulting mixture showed T_{NI} = 102.5 °C, $\Delta\varepsilon$ = 4.15, V_{th} = 1.88 V, Δn = 0.074, and τ = 44.1 ms. Thus, use of **11a** as an additive resulted in expansion of nematic phase range and improvement of response time of the TFT–host mixture without decrease of voltage holding ratio. Furthermore, T_{NI} of the **11a**/TFT–host mixture did not lower at all upon heating at 80 °C for 10 h or under UV irradiation. Accordingly, LCs having a trifluoromethoxycyclohexane mesogen are very stable against heat and UV light.

Conclusions

Novel LCs with a trifluoromethoxycyclohexane mesogen were prepared for the first time by the oxidative desulfurization–fluorination of dithiocarbonates derived from the corresponding cyclohexanols. LCs with an ω-trifluoromethoxyalkyl tail were also prepared in a similar way, starting with the corresponding primary alcohols. Most of the CF_3O-substituted LCs exhibited over a wide range of temperatures LC phases which depended on the type of mesogenic structure. The LCs with a trifluoromethoxycyclohexane mesogen were shown to be thermally more stable than the LCs with a trifluoromethoxybenzene mesogen. The LCs having a trifluoromethoxyalkyl tail, e.g. **11a**, show physical and electro-optical properties favorable to materials not only for TN-LCDs but also for TFT-addressed TN-LCDs. Furthermore, **27** was shown to be a potential chiral dopant for TFT-addressed TN-LCDs.

Experimental

General. Reagents and solvents of the highest commercial quality were purchased from Aldrich Chemical Co., Kanto Chemicals, Tokyo Kasei, or Wako Chemicals, Inc. and were used without further purification unless otherwise noted. All the reaction was carried out under an argon atmosphere in a dry, freshly distilled solvent unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium/benzophenone. *N*,*N*-Dimethylformamide (DMF) was distilled 2 times from calcium hydride under reduced pressure. Dichloromethane (CH_2Cl_2) was predried with P_2O_5 and distilled from calcium hydride. Pyridine was distilled from KOH and stored over solid KOH at room temperature. Unless otherwise stated, yields refer to materials purified by flash column chromatography or recrystallization. Most of the synthetic 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 iodine, and/or by dipping the plates in an ethanolic phosphomolybdic acid or *p*-anisaldehyde solution followed by heating. 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. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer at 200 (^1H), 50.3 (^{13}C), and 188 (^{19}F) MHz, or on a Varian Mercury-300 spectrometer at 300 (^1H), 75.5 (^{13}C), and 282 (^{19}F) MHz, respectively. Chemical shifts of ^1H 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. MS were recorded on a Shimadzu GC/MS QP-5000 or on a Hitachi H-80 double-focusing tandem gas chromatography mass spectrometer (70 eV). Mps were measured with an Olympus BH-2 optical polarizing microscope equipped with a Mettler FP-900 hot-stage. The thermal characterization was conducted with an SII DSC-200C (scanning rate 1.0 $^\circ C\,min^{-1}$) differential scanning calorimeter system. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder. HRMS were obtained on a JEOL MStation. The following chemicals were kindly donated by Dainippon Ink & Chemicals, Inc: 4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexanone, 4-(*trans*-4-propylcyclohexyl)cyclohexanone, 4-[*trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl]cyclohexanone, 4-(4′-propylbiphenyl-4-yl)cyclohexanone, 4-[*trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl]phenol, *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexanecarbaldehyde, *trans*-4-[*trans*-4-(3,4,5-trifluorophenyl)cyclohexyl]cyclohexanemethanol, *trans*-1-pentyl-4-(*trans*-4-vinylcyclohexyl)cyclohexane (**21c**), *trans*-1-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]-4-vinylcyclohexane (**20c**), and *trans*-1-[*trans*-4-(3-butenyl)cyclohexyl]-4-(3,4-difluorophenyl)cyclohexane (**20e**).

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) consisting of equal amounts of **20c** and **20e**. The LC mixture was sealed in a polyimide-rubbed-cell of about 6 μm thickness. A rectangular electric field of 1 kHz was applied 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 the 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 response from 100% to 10% and 0% to 90%. Values τ were estimated when τ_r became equal to τ_d at a properly applied voltage.

General Procedure for the Synthesis of Alcohols. Method A: Reduction of Cyclohexanones. To a stirred suspension of lithium aluminum hydride (45 mmol) in THF (60 mL) was added a solution of a 4-substituted cyclohexanone (30 mmol) in THF (40 mL) at 0 °C over a period of 5 min. The mixture was stirred at 0 °C for 10 min, quenched by slow addition of H_2O (1.7 mL) at 0 °C, and treated with 30% aq NaOH. The resulting mixture was stirred at room temperature for 30 min before mixing with Celite, $MgSO_4$, and Et_2O (100 mL) under vigorous stirring at room temperature for 1 h. The insoluble material was filtered off through a pad of Celite by suction funnel and washed with Et_2O (300 mL) and CH_2Cl_2 (50 mL). The filtrate was concentrated under reduced pressure, and the residue was recrystallized from hexane/EtOAc to give *trans*-4-substituted cyclohexanol. In some cases, the mother liquid was concentrated, and *cis*-4-substituted cyclohexanol was isolated by flash column chromatography.

Method B: Reduction of Phenols. A suspension of a 4-substituted phenol (14 mmol) and 10% Pd/C (1.9 g) in EtOAc (100 mL) was stirred vigorously under an H_2 atmosphere (20 atm) at 70 °C for 1 d. The insoluble material was filtered through a pad of Celite by vacuum filtration and washed with a 100 mL portion of CH_2Cl_2 (totally 1 L). The filtrate was concentrated under reduced pressure; the residue was chromatographed to give *trans*- and *cis*-4-cyclohexanol.

Method C: Hydroboration-Oxidation of Terminal Olefins. In a two-necked flask were placed THF (200 mL) and a terminal olefin (91 mmol). To this solution was added dropwise a solution of borane in THF (BH_3, 1.0 M, 46 mmol) (1 M = 1 mol dm^{-3}) at 0 °C. The reaction mixture was stirred for 12 h at room temperature before slow addition of H_2O (1.0 mL), 3 M NaOH (22 mL) and then 30% aq H_2O_2 (23 mL) at 0 °C. The resultant was stirred for 6 h at room temperature, and the excess peroxide was quenched with aq $NaHSO_3$. The organic phase was separated; the aq phase was extracted with Et_2O four times. The combined organic extracts were washed with sat. aq NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was recrystallized from hexane. The mother liquid was concentrated in vacuo and purified by flash column chromatography to give the desired alcohol.

Method D: Oxidative Cleavage of Terminal Olefins. To a mixture of formic acid (29 mL, 0.77 mol), 30% H_2O_2 (5.0 mL), and CH_2Cl_2 (2.0 mL), a terminal olefin (50 mmol) was added portionwise at 0 °C. The resulting mixture was stirred for 15 h at room temperature before quenching with 5% NaOH and aq $Na_2S_2O_3$. The whole was diluted with CH_2Cl_2 (100 mL); the combined organic phase was separated; the aq phase was extracted with CH_2Cl_2 eight times (totally 500 mL). The combined organic extracts were washed with sat. aq NaCl, dried over Na_2SO_4, filtered, and concentrated in vacuo to give a 1,2-diol. To the diol dissolved in Et_2O (200 mL) was added an aq solution of $NaIO_4$ (17.0 g) in H_2O (50 mL) at room temperature. The resulting mixture was stirred for 6 h; the organic phase was separated; the aq phase was extracted with Et_2O four times (totally 500 mL). The organic extracts were washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a crude aldehyde, which was reduced to the corresponding alcohol by the procedure for the preparation of compound **1b** as described above. Methods, yields, and spectral properties of alcohols are as follows.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexanol (1a).** Method A, 86% yield. Colorless needles, mp 146.2—147.0 °C; R_f = 0.28 (hexane : EtOAc = 5 : 1). IR (KBr) 3438, 2980, 2851, 1605, 1520, 1454, 1282, 1212, 1116, 1060, 938, 822, 781, 627 cm^{-1}; ^1H NMR (200 MHz) δ = 0.98—1.49 (m, 11 H), 1.66—2.11 (m, 8 H), 2.41 (tt, J = 3, 12 Hz, 1 H), 3.54 (tt, J = 4, 10 Hz, 1 H), 6.82—7.11 (m, 3 H); ^{19}F NMR (188 MHz) δ = −139.2 (ddd, J = 8, 12, 21 Hz, 1 F), −143.0 (dddd, J = 5, 8, 10, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 28.1 (s), 30.2 (s), 34.4 (s), 35.8 (s), 43.7 (d, J = 1 Hz), 71.1 (s), 115.3 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 4, 6 Hz), 144.7 (dd, J = 4, 5 Hz), 148.5 (dd, J = 13, 245 Hz), 150.1 (dd, J = 13, 247 Hz); MS m/z (rel intensity) 294 (M^+; 7), 276 (23), 194 (11), 193 (23), 179 (35), 140 (57), 127 (84), 121 (24), 82 (15), 81 (100), 79 (31), 67 (38). Found: C, 73.14; H, 8.19%. Calcd for $C_{18}H_{24}F_2O$: C, 73.44; H, 8.22%.

***trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexanol (2a) and *cis*-4-(*trans*-4-Propylcyclohexyl)cyclohexanol (2a′).** Alcohols **2a** and **2a′** were prepared in 63 and 16% yields, respectively, by Method A.

2a: Colorless needles, mp 125.3—126.7 °C; R_f = 0.24 (hexane : EtOAc = 5 : 1). IR (KBr) 3414, 3355, 2959, 2855, 1464, 1454, 1356, 1345, 1059, 943, 891 cm^{-1}; ^1H NMR (200 MHz) δ = 0.79—1.38 (m, 18 H), 1.61—1.84 (m, 7 H), 1.91—2.08 (m, 2 H), 3.51 (tt, J = 5, 10 Hz, 1 H); ^{13}C NMR (75.5 MHz) δ = 14.4 (s), 20.0 (s), 28.1 (s), 30.2 (s), 33.5 (s), 35.9 (s), 37.5 (s), 39.8 (s), 42.3 (s), 42.8 (s), 71.2 (s); MS m/z (rel intensity) 224 (M^+; 0.2), 123 (0.4), 206 (83), 177 (12), 164 (13), 163 (46), 135 (11), 124 (36), 123 (56), 122 (36), 109 (53), 95 (53), 83 (89), 82 (91), 81 (100), 69 (87), 67 (87). Found: C, 80.09; H, 12.38%. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58%.

2a′: Colorless needles, mp 100.2—101.0 °C; R_f = 0.39 (hexane : EtOAc = 5 : 1). IR (KBr) 3347, 2935, 2848, 1444, 1264, 1150, 1040, 977, 957, 763 cm^{-1}; ^1H NMR (200 MHz) δ = 0.79—1.21 (m, 12 H), 1.24—1.58 (m, 9 H), 1.68—1.80 (m, 6 H), 3.95—4.01 (m, 1 H); ^{13}C NMR (75.5 MHz) δ = 14.4 (s), 20.0 (s), 23.9 (s), 30.1 (s), 32.8 (s), 33.5 (s), 37.5 (s), 39.8 (s), 42.26 (s), 42.30 (s), 66.9 (s); MS m/z (rel intensity) 224 (M^+; 0.08), 206 (20), 163 (17), 123 (14), 109 (11), 96 (7), 95 (14), 83 (55), 82 (76), 81 (93), 79 (31), 69 (100), 67 (97). Found: m/z 224.2144. Calcd for $C_{15}H_{28}O$: M, 224.2140.

***trans*-4-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]cyclohexanol (3a) and *cis*-4-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]cyclohexanol (3a′).** Alcohols **3a** and **3a′** were obtained in 36 and 11% yields, respectively, by Method A. According to Method B, **3a** and **3a′** were prepared in 32 and 56% yields, respectively.

3a: Colorless needles. Phase transition temperature/°C: Cr 152 S_B 225 Iso; R_f = 0.20 (hexane : EtOAc = 5 : 1). IR 3341, 2953, 2849, 1444, 1432, 1372, 1057, 1051, 967, 903 cm^{-1}; ^1H NMR (200 MHz) δ = 0.79—1.41 (m, 23 H), 0.86 (t, J = 7.1 Hz, 3 H), 1.57—1.85 (m, 9 H), 1.87—2.05 (m, 2 H), 3.46—3.54 (m, 1 H); ^{13}C NMR (75.5 MHz) δ = 14.4 (s), 20.0 (s), 28.1 (s), 30.1 (s), 30.3 (s), 30.5 (s), 33.6 (s), 35.90 (s), 35.91 (s), 37.6 (s), 39.8 (s), 42.3 (s), 42.9 (s), 43.4 (s), 71.3 (s); MS m/z (rel intensity) 307 (M^++1; 0.2), 288 (30), 205 (10), 164 (13), 163 (16), 149 (11), 135 (8), 123 (15), 109 (20), 97 (10), 95 (30), 83 (41), 82 (39), 81 (100), 79 (27), 69 (71), 67 (72). Found: m/z 306.2920. Calcd for $C_{21}H_{38}O$: M, 306.2923

3a′: A colorless powder. Phase transition temperature/°C: Cr 137 S_B 222 Iso; R_f = 0.30 (hexane : EtOAc = 5 : 1). IR (KBr) 3344, 2980, 9850, 1444, 1363, 1264, 1040, 980, 960, 898, 763 cm^{-1}; ^1H NMR (200 MHz) δ = 0.79—1.85 (m, 34 H), 0.87 (t, J = 7.2 Hz, 3 H), 3.98 (brs, 1 H); ^{13}C NMR (75.5 MHz) δ = 14.4 (s), 20.0 (s), 23.9 (s), 30.1 (s), 30.3 (s), 30.4 (s), 32.8 (s), 33.6 (s), 37.6 (s), 39.8 (s), 42.3 (br s), 43.4 (s), 67.0 (s); MS m/z (rel intensity) 307 (M^++1; 1.5), 288 (29), 164 (11), 163 (18), 123 (13), 121 (14), 109 (18), 95 (27), 92 (15), 83 (48), 82 (37), 81 (100), 79 (38), 69 (67), 67 (85). Found: C, 82.06; H, 12.30%. Calcd for $C_{21}H_{38}O$: C, 82.29; H, 12.50%.

***trans*-4-(4′-Propylbiphenyl-4-yl)cyclohexanol (4a).** Method A, 65% yield. Colorless needles, mp 175.3—176.6 °C; R_f = 0.50 (CH_2Cl_2 : MeOH = 10 : 1). IR 3420, 2930, 2855, 1497, 1453, 1356, 1061, 1005, 804 cm^{-1}; ^1H NMR (200 MHz) δ = 0.97 (t, J = 7 Hz, 3 H), 1.33—1.78 (m, 7 H), 1.88—2.19 (m, 4 H), 2.42—2.70 (m, 3 H), 3.58—3.79 (m, 1 H), 7.20—7.27 (m, 4 H), 7.43—7.53 (m, 4 H); ^{13}C NMR (75.5 MHz) δ = 13.9 (s), 24.5 (s), 32.4 (s), 35.8 (s), 37.6 (s), 43.0 (s), 70.5 (s), 126.7 (s), 126.8 (s), 127.1 (s), 128.8 (s), 138.3 (s), 138.9 (s), 141.5 (s), 145.2 (s); MS m/z (rel intensity) 295 (M^++1; 15), 294 (M^+; 69), 276 (100), 261 (22), 147 (49), 222 (52), 205 (20), 193 (96), 178 (33), 165 (31), 91 (18). Found: C, 85.63; H, 9.21%. Calcd for $C_{21}H_{38}O$: C, 85.67; H, 8.90%.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexanemethanol (1b).** Sodium borohydride (0.98 g, 26 mmol) was added portionwise to a solution of *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexanecarbaldehyde (7.3 g, 24 mmol) in methanol (20 mL) and THF (20 mL) at room temperature under stirring. The resulting mixture was stirred at room temperature for 4 h, and the methanol solvent was removed under reduced pressure. The white solid residue was partitioned in sat. aq. $NaHCO_3$ and Et_2O (200 mL), and the organic phase was separated. The aq phase was extracted with Et_2O three times (totally 500 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by recrystallization to give **1b** (5.2 g) in 71% yield as colorless needles. Mp 97.7—99.1 °C; R_f = 0.15 (hexane : EtOAc = 5 : 1). IR (KBr) 3320, 2923, 2851, 1607, 1518, 1449, 1429, 1277, 1204, 1038, 812, 770 cm^{-1}; ^1H NMR (200 MHz) δ = 0.80—1.58 (m, 11 H), 1.68—2.00 (m, 8 H), 2.28—2.68 (m, 1 H), 2.39 (tm, J = 12 Hz, 1 H), 3.42 (d, J = 6 Hz, 2 H), 6.86—7.04 (m, 3 H); ^{19}F NMR (282 MHz) δ = −139.09 (dd, J = 8, 12, 21 Hz, 1 F), −142.98 (dddd, J = 8, 11, 14, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 29.3 (s), 29.6 (s), 29.9 (s), 34.3 (s), 40.4 (s), 42.5 (s), 43.0 (s), 43.6 (s), 68.1 (s), 115.0 (d, $J = 17$ Hz), 116.5 (d, $J = 17$ Hz), 122.2 (dd, $J = 3$, 6 Hz), 144.6 (dd, $J = 4$, 4 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.0 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 309 (M^++1; 8), 308 (M^+; 100), 275 (9), 269 (4), 208 (19), 207 (13), 196 (14), 194 (40), 193 (49), 192 (28), 191 (19), 190 (15), 180 (18), 179 (93), 165 (23), 132 (4). Found: *m/z* 308.1949. Calcd for $C_{19}H_{26}F_2O$: M, 308.1952.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexaneethanol (1c).** Method C, 76% yield. A colorless powder. Phase transition temperature/°C: Cr 101 N 129 Iso; $R_f = 0.29$ (hexane : EtOAc = 5 : 1). IR (KBr) 3434, 2944, 2921, 2888, 2849, 1605, 1518, 1453, 1429, 1358, 1279, 1213, 1115, 1051, 1019, 862, 822, 781 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.40 (m, 8 H), 1.45—1.55 (m, 6 H), 1.70—1.95 (m, 8 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.69 (t, $J = 7$ Hz, 2 H), 6.84—7.09 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.0$—-139.2 (m, 1 F), -142.9—-143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 29.9$ (s), 30.1 (s), 33.5 (s), 34.4 (s), 34.5 (s), 40.3 (s), 42.7 (s), 43.1 (s), 43.8 (s), 60.9 (s), 115.3 (d, $J = 17$ Hz), 116.1 (d, $J = 17$ Hz), 122.4 (d, $J = 3$, 6 Hz), 144.8 (d, $J = 5$, 5 Hz), 148.4 (d, $J = 13$, 245 Hz), 150.1 (d, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 324 (M^++2; 1), 323 (M^++1; 9), 322 (M^+; 41), 275 (10), 194 (13), 193 (18), 179 (39), 166 (11), 153 (22), 140 (72), 127 (100), 109 (93), 95 (27), 81 (63), 67 (86). Found: *m/z* 322.2114. Calcd for $C_{20}H_{28}F_2O$: M, 322.2108.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexanepropanol (1d).** Method D, 37% yield. Colorless needles. Phase transition temperature/°C: Cr 89 N 159 Iso; $R_f = 0.19$ (hexane : EtOAc = 5 : 1). IR (KBr) 3320, 2924, 2851, 1607, 1516, 1449, 1429, 1279, 1211, 1117, 1053, 1009, 943, 862, 818, 770 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.44 (m, 12 H), 1.46—1.68 (m, 3 H), 1.70—1.95 (m, 9 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.62 (t, $J = 7$ Hz, 2 H), 6.86—7.05 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.0$—-139.2 (m, 1 F), -142.8—-143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 30.0$ (s), 30.1 (s), 30.2 (s), 33.3 (s), 33.5 (s), 34.5 (s), 37.7 (s), 42.7 (s), 43.2 (s), 43.8 (s), 63.4 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 5$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 338 (M^++2; 0.9), 337 (M^++1; 6), 336 (M^+; 27), 179 (24), 153 (15), 140 (49), 127 (71), 123 (26), 95 (33), 81 (100), 67 (87). Found: *m/z* 336.2263. Calcd for $C_{21}H_{30}F_2O$: M, 336.2265.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexanebutanol (1e).** Method C, 88% yield. Colorless needles. Phase transition temperature/°C: Cr 97 N 152 Iso; $R_f = 0.18$ (hexane : EtOAc = 5 : 1). IR (KBr) 3434, 2919, 2849, 1609, 1518, 1495, 1451, 1435, 1289, 1211, 1115, 1045, 1021, 947, 817, 770 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.80$—1.46 (m, 15 H), 1.48—1.62 (m, 2 H), 1.68—1.96 (m, 8 H), 2.06 (brs, 1 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.65 (t, $J = 7$ Hz, 2 H), 6.86—7.06 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.1$ (ddd, $J = 8$, 12, 21 Hz, 1 F), -143.0 (dddd, $J = 8$, 11, 14, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 23.1$ (s), 30.0 (s), 30.1 (s), 33.0 (s), 33.5 (s), 34.5 (s), 37.2 (s), 37.8 (s), 42.7 (s), 43.2 (s), 43.8 (s), 63.1 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.6 (dd, $J = 4$, 4 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.2 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 351 (M^++1; 2), 350 (M^+; 6), 279 (12), 194 (12), 192(14), 178 (14), 167 (31), 149 (100), 137 (50), 128 (11), 119 (13), 105 (18). Found: *m/z* 350.2421. Calcd for $C_{22}H_{32}F_2O$: M, 350.2421.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexanepentanol (1f).** Method C, 86% yield. Colorless needles. Phase transition temperature/°C: Cr 93 N 158 Iso; $R_f = 0.31$ (hexane : EtOAc : CH_2Cl_2 = 4 : 1 : 1). IR (KBr) 3310, 2924, 2849, 1607, 1518, 1429, 1275, 1210, 1115, 1057, 951, 939, 862, 816, 772 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.64 (m, 19 H), 1.68—1.94 (m, 9 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.64 (t, $J = 7$ Hz, 2 H), 6.87—7.06 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.1$—-139.2 (m, 1 F), -142.9—-143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 26.1$ (s), 26.8 (s), 30.0 (s), 30.2 (s), 32.8 (s), 33.6 (s), 34.6 (s), 37.4 (s), 37.8 (s), 42.8 (s), 43.3 (s), 43.8 (s), 63.1 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.6 (dd, $J = 5$, 5 Hz), 148.5 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 366 (M^++2; 0.4), 365 (M^++1; 4), 364 (M^+; 15), 193 (12), 179 (28), 153 (16), 151 (20), 140 (47), 127 (75), 109 (30), 95 (77), 81 (71), 67 (100). Found: *m/z* 364.2563. Calcd for $C_{23}H_{34}F_2O$: M, 364.2578.

***trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexanemethanol (2b).** Method D, 80% yield. A colorless solid, mp 129.3—131.0 °C. $R_f = 0.20$ (hexane : EtOAc = 10 : 1). IR (KBr) 3250, 2944, 2909, 1453, 1379, 1339, 1289, 1044, 895 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.48 (m, 21 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.64—1.86 (m, 8 H), 3.40—3.44 (m, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.4 (s), 29.8 (s), 30.1 (s), 32.2 (s), 33.6 (s), 37.5 (s), 37.9 (s), 40.7 (s), 43.4 (s), 68.8 (s); MS *m/z* (rel intensity) 266 (M^+; 0.3), 248 (32), 219 (28), 177 (13), 151 (13), 137 (14), 123 (12), 113 (22), 109 (22), 97 (79), 95 (100), 83 (73), 81 (80), 79 (61), 69 (70), 67 (81). Found: *m/z* 266.2615. Calcd for $C_{18}H_{34}O$: M, 266.2610.

***trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexaneethanol (2c).** Method C, 85% yield. 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%.

***trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexanepropanol (2d).** Method C, 84% yield. A colorless solid. Mp 155.3—156.9 °C; $R_f = 0.36$ (hexane : EtOAcCH_2Cl_2 = 5 : 1 : 1). IR (KBr) 3340, 2923, 2849, 1509, 1468, 1443, 1378, 1339, 1217, 1057, 959, 899, 723 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.45 (m, 23 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.48—2.00 (m, 10 H), 3.60 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 30.0 (s), 30.1 (s), 30.2 (s), 32.2 (s), 33.4 (s), 33.6 (s), 33.7 (s), 37.5 (s), 37.7 (s), 37.9 (s), 43.4 (s), 43.5 (s), 63.4 (s); MS *m/z* (rel intensity) 295 (M^++1; 3), 276 (21), 248 (17), 124 (16), 123 (41), 122 (19), 11 (15), 109 (13), 97 (61), 96 (48), 83 (54), 80 (100), 67 (63). Found: *m/z* 294.2928. Calcd for $C_{20}H_{38}O$: M, 294.2923.

***trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexanebutanol (2e).** Method C, 67% yield. A colorless solid. Mp 160.4—161.2 °C; $R_f = 0.24$ (hexane : EtOAc = 5 : 1). IR (KBr) 3428, 3374, 2953, 2917, 2851, 1462, 1453, 1377, 1356, 1049, 1019, 992, 961, 893 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.42 (m, 24 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.53 (q, $J = 7$ Hz, 2 H), 1.62—1.82 (m, 9 H), 3.63 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 23.1 (s), 26.7 (s), 30.06 (s), 30.10 (s), 32.2 (s), 33.1 (s), 33.6 (s), 33.7 (s), 37.2 (s), 37.5 (s), 37.88 (s), 37.94 (s), 43.48 (s), 43.49 (s), 63.1 (s); MS *m/z* (rel intensity) 309 (M^++1; 8), 275 (18), 221 (12), 195 (15), 193 (29), 180 (17), 166 (45), 153 (26), 140 (56), 135 (36), 127 (100), 109 (45), 66 (32). Found: *m/z* 308.3070. Calcd for $C_{21}H_{40}O$: M, 308.3079.

***trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexanepentanol (2f).** Method C, 55% yield. A colorless solid. Mp 158.9—160.4 °C;

$R_f = 0.17$ (hexane : EtOAc = 5 : 1). IR (KBr) 3350, 2920, 2849, 1466, 1443, 1375, 1339, 1051, 988, 897, 725 cm^{-1}; ^1H NMR (300 MHz) $\delta = 0.75$—1.45 (m, 28 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.50—1.80 (m, 8 H), 3.05 (brs, 1 H), 3.65 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.0 (s), 26.7 (s), 26.8 (s), 30.06 (s), 30.09 (s), 32.3 (s), 32.6 (s), 33.6 (s), 33.7 (s), 37.4 (s), 37.5 (s), 37.85 (s), 37.93 (s), 43.5 (s), 63.1 (s); MS m/z (rel intensity) 322 (M^+; 3), 305 (18), 304 (78), 233 (24), 194 (16), 152 (49), 150 (43), 137 (40), 123 (30), 121 (34), 109 (100). Found: m/z 322.3237. Calcd for $C_{22}H_{42}O$: M, 322.3236.

***trans*-1-[*trans*-4-(4-Penten-1-yl)cyclohexyl]-4-pentylcyclohexane (21f).** A flask was charged with THF (150 mL), copper(I) iodide (4.8 g, 25 mmol), and 1-[*trans*-4-(2-iodoethyl)cyclohexyl]-*trans*-4-pentylcyclohexane[4e] (7.8 g, 20 mmol) and cooled at −78 °C. Allylmagnesium chloride (25 mL of 2.0 M THF solution, 50 mmol) was added dropwise to the mixture at −78 °C. After the addition was completed, the reaction mixture was allowed to warm to 0 °C over 4 h and stirred at room temperature for 2 h before quenching with aq HCl (1.0 M). The organic phase was separated; the aq phase was extracted with Et_2O three times (totally 300 mL). The combined organic extracts were washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to give **21f** (5.7 g) in 94% yield as a colorless mesomorphic oil. Phase transition temperature/°C: Cr −17 S_X 11 S_B 103 Iso (DSC 2nd heating); $R_f = 0.88$ (hexane). IR 2917, 2849, 1823, 1642, 1447, 1416, 1379, 1341, 1291, 1217, 989, 911, 895, 725 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.75$—1.04 (m, 10 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.06—1.42 (m, 14 H), 1.64—1.80 (m, 8 H), 2.01 (q, $J = 7$ Hz, 2 H), 4.90—5.02 (m, 2 H), 5.74—5.88 (m, 1 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.4 (s), 26.7 (s), 30.10 (s), 30.13 (s), 32.3 (s), 33.65 (s), 33.70 (s), 34.2 (s), 37.0 (s), 37.5 (s), 37.9 (s), 38.0 (s), 43.50 (s), 43.53 (s), 114.1 (s), 139.3 (s); MS m/z (rel intensity) 304 (M^+; 12), 166 (9), 149 (17), 140 (22), 127 (27), 125 (11), 122 (16), 111 (19), 99 (12), 95 (59), 83 (49), 81 (87), 67 (100). Found: m/z 304.3142. Calcd for $C_{22}H_{40}$: M, 304.3130.

***trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexanebutanal.** Pyridinium chlorochromate (5.8 g, 27 mmol) was added in one portion to a solution of **1e** (6.3 g, 18 mmol) in CH_2Cl_2 (200 mL) at room temperature. The reaction mixture was stirred for 3 h at room temperature before addition of Celite. The insoluble material was filtered off; the filtrate was concentrated in vacuo; the residue was purified by flash column chromatography (hexane : EtOAc = 20 : 1) to give the title aldehyde (5.4 g) in 86% yield as a colorless solid. Phase transition temperature/°C: S_X 82 N 139 Iso; $R_f = 0.57$ (hexane : EtOAc = 5 : 1). IR (KBr) 2919, 2847, 1724, 1717, 1607, 1518, 1449, 1285, 1210, 1198, 1115, 945, 862, 816 cm^{-1}; ^1H NMR (300 MHz) $\delta = 0.80$—1.46 (m, 13 H), 1.58—1.94 (m, 10 H), 2.34—2.48 (m, 3 H), 6.83—7.08 (m, 3 H), 9.74—9.77 (m, 1 H); ^{19}F NMR (282 MHz) $\delta = -139.0$—-139.2 (m, 1 F), -142.9—-143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 19.5$ (s), 29.9 (s), 30.1 (s), 33.3 (s), 34.5 (s), 36.8 (s), 37.6 (s), 42.7 (s), 43.2 (s), 43.8 (s), 44.2 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 5$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 12$, 246 Hz), 203.0 (s); MS m/z (rel intensity) 349 ($M^+ + 1$; 8), 348 (M^+; 17), 179 (26), 153 (26), 140 (50), 135 (75), 133 (17), 127 (100), 121 (18), 109 (25), 107 (21), 95 (34), 93 (37), 81 (59), 69 (32), 67 (98). Found: m/z 348.2251. Calcd for $C_{22}H_{30}F_2O$: M, 348.2265.

***trans*-1-(3,4-Difluorophenyl)-4-[*trans*-4-(4-penten-1-yl)cyclohexyl]cyclohexane (20f).** To triphenyl(methyl)phosphonium bromide (5.7 g, 16 mmol) suspended in Et_2O (100 mL) was added dropwise *n*-BuLi in hexane (1.6 M, 10 mL) at room temperature, and the mixture was stirred for 4 h at room temperature. To this ylide solution was added dropwise a solution of *trans*-4-[*trans*-4-(3,4-difluorophenyl)cyclohexyl]cyclohexanebutanal (14.1 g, 4.9 mmol) in Et_2O (100 mL) at room temperature; the resulting mixture was stirred for 10 h at room temperature before quenching with aq NH_4Cl. The organic phase was separated; the aq phase was extracted with Et_2O three times (300 mL). The combined organic extracts were washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to give **20f** (3.8 g) in 78% yield as a mesomorphic oil. Phase transition temperature/°C: Cr 17 N 88 Iso (DSC 2nd heating); $R_f = 0.54$ (hexane). IR 2923, 2851, 1607, 1518, 1449, 1431, 1279, 1211, 1117, 990, 911, 816 cm^{-1}; ^1H NMR (300 MHz) $\delta = 0.78$—1.48 (m, 15 H), 1.70—1.94 (m, 8 H), 2.02 (q, $J = 7$ Hz, 2 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 4.90—5.02 (m, 2 H), 5.74—5.88 (m, 1 H), 6.86—7.08 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.0$—-139.2 (m, 1 F), -142.9—-143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 26.3$ (s), 30.1 (s), 30.2 (s), 33.6 (s), 34.1 (s), 34.6 (s), 37.0 (s), 37.8 (s), 42.8 (s), 43.3 (s), 43.9 (s), 114.1 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 139.2 (s), 144.8 (dd, $J = 5$, 5 Hz), 148.5 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 13$, 247 Hz); MS m/z (rel intensity) 348 ($M^+ + 2$; 1), 347 ($M^+ + 1$; 4), 346 (M^+; 21), 194 (11), 193 (17), 179 (37), 153 (15), 140 (37), 127 (69), 109 (27), 95 (49), 81 (67), 67 (100). Found: m/z 346.2472. Calcd for $C_{23}H_{32}F_2$: M, 346.2472.

Preparation of Dithiocarbonates: General Procedure.

Method A: An oven-dried, 1-L, three-necked, round-bottomed flask, equipped with an argon inlet and a Teflon®-coated magnetic stirring bar, and fitted with a rubber septum, was flushed with argon, charged with alcohol **1**—**4** (50 mmol) and THF (200 mL), and was cooled at 0 °C using an ice-water bath. To the solution was added portionwise NaH (2.4 g, 60 mmol, 60% dispersion in mineral oil) over 5 min at 0 °C under purging with argon via the inlet. The ice-water bath was removed, the resulting white suspension was allowed to warm to room temperature and stirred for 60 min. The mixture was recooled at 0 °C, and carbon disulfide (0.25 mol, 15 mL) was added dropwise to the mixture via a syringe over 10 min. The resulting pale yellow suspension was allowed to warm to room temperature and stirred until all the substrate was consumed. The resulting yellow solution was recooled to 0 °C, and methyl iodide (6.2 mL, 0.10 mol) was added dropwise via a syringe over 10 min. The pale yellow creamy mixture was allowed to warm to room temperature, stirred for several hours, then quenched by careful addition of 50% aq NH_4Cl (100 mL) at 0 °C. The organic phase was separated; the aq phase was extracted three times with portions of Et_2O (totally 500 mL). The combined organic phase was washed with sat. aq NaCl (100 mL) containing 1 g of $NaHSO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. A yellow residue was flash column chromatographed or/and recrystallized to give dithiocarbonate **5**—**8**.

Method B: In the procedure for Method A, NaH (60 mmol) was replaced by *n*-BuLi (75 mmol).

***S*-Methyl *O*-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl] Dithiocarbonate (6a).** Method A, 79% yield. Pale yellow needles. Phase transition temperature/°C: Cr 61 N 75 Iso; $R_f = 0.68$ (hexane : EtOAc = 10 : 1). IR (KBr) 2950, 2907, 2856, 1702, 1464, 1442, 1237, 1215, 1050, 1018, 982, 918, 902, 733 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.73$—1.55 (m, 16 H), 1.62—1.93 (m, 8 H), 2.20—2.35 (m, 2 H), 2.53 (s, 3 H), 5.43 (tt, $J = 5$, 11 Hz, 1 H); ^{13}C NMR (50.3 MHz) $\delta = 14.4$ (s), 18.7 (s), 20.0 (s), 27.8 (s), 30.1 (s), 31.2 (s), 33.4 (s), 37.5 (s), 39.7 (s), 42.1 (s), 42.6 (s), 83.5 (s), 215.1 (s);

MS *m/z* (rel intensity) 314 (M^+; 0.4), 206 (37), 125 (12), 123 (16), 111 (22), 109 (29), 97 (126), 95 (29), 91 (17), 83 (63), 82 (25), 81 (62), 79 (24), 69 (100), 67 (68). Found: C, 64.65; H, 9.77%. Calcd for $C_{17}H_{30}OS_2$: C, 64.92; H, 9.61%.

***S*-Methyl *O*-{*trans*-4-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]cyclohexyl} Dithiocarbonate (7a).** Method B, 68% yield. Pale yellow needles. Phase transition temperature/°C: Cr 85 S_B 177 N 222 Iso; R_f = 0.29 (hexane). IR (KBr) 2951, 2934, 2888, 1464, 1443, 1234, 1208, 1092, 1049, 984 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.72—1.58 (m, 23 H), 0.86 (t, J = 7 Hz, 3 H), 1.60—1.88 (m, 8 H), 2.05—2.25 (m, 2 H), 2.53 (s, 3 H), 5.43 (tt, J = 5, 11 Hz, 1 H); ^{13}C NMR (50.3 MHz) δ = 14.4 (s), 20.0 (s), 27.8 (s), 27.9 (s), 30.1 (s), 30.2 (s), 30.4 (s), 31.2 (s), 31.9 (s), 33.6 (s), 37.6 (s), 39.8 (s), 42.0 (s), 42.7 (s), 43.4 (s), 83.6 (s), 215.1 (s); MS *m/z* (rel intensity) 396 (M^+; 2), 287 (3), 286 (20), 203 (2), 202 (4), 160 (13), 146 (16), 135 (11), 121 (26), 108 (31), 94 (42), 83 (67), 81 (98), 69 (94), 67 (100). Found: *m/z* 396.2532. Calcd for $C_{23}H_{40}OS_2$: M, 396.2520.

***S*-Methyl *O*-[*trans*-4-(4′-Propylbiphenyl-4-yl)cyclohexyl] Dithiocarbonate (8a).** Method A, 95% yield. Colorless needles. Phase transition temperature/°C: Cr 115 N 153 Iso; R_f = 0.45 (hexane : EtOAc = 10 : 1). IR (KBr) 3024, 2947, 2931, 2866, 1898, 1495, 1495, 1448, 1220, 1210, 1050, 997, 957, 803, 778, 518 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.96 (t, J = 7 Hz, 3 H), 1.59—1.80 (m, 6 H), 1.86—2.12 (m, 2 H), 2.24—2.42 (m, 2 H), 2.53 (s, 3 H), 2.50—2.64 (m, 2 H), 5.52—5.67 (m, 1 H), 7.19—7.24 (m, 4 H), 7.45—7.51 (m, 4 H); ^{13}C NMR (75.5 MHz) δ = 13.8 (s), 18.8 (s), 24.4 (s), 31.3 (s), 32.0 (s), 37.6 (s), 42.8 (s), 82.6 (s), 126.7 (s), 126.9 (s), 127.0 (s), 128.8 (s), 138.2 (s), 139.1 (s), 141.5 (s), 144.6 (s), 215.2 (s); MS *m/z* (rel intensity) 385 (M^++1; 1), 384 (M^+; 5), 277 (22), 276 (76), 223 (18), 222 (58), 193 (100), 180 (16), 165 (19), 91 (11), 81 (27). Found: *m/z* 384.1577. Calcd for $C_{23}H_{28}OS_2$: M, 384.1582.

***O*-*trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexylmethyl *S*-Methyl Dithiocarbonate (5b).** Method A, 92% yield. Pale yellow needles, mp 101.3—101.9 °C; R_f = 0.50 (hexane : EtOAc = 10 : 1). IR (KBr) 2920, 2892, 1605, 1516, 1449, 1426, 1291, 1227, 1216, 1073, 1059, 953, 938, 826, 774 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.95—1.25 (m, 8 H), 1.25—1.50 (m, 2 H), 1.70—1.95 (m, 9 H), 2.42 (tt, J = 3, 12 Hz, 1 H), 2.56 (s, 3 H), 4.41 (d, J = 6 Hz, 2 H), 6.85—7.08 (m, 3 H); ^{19}F NMR (282 MHz) δ = −138.9—−139.1 (m, 1 F), −142.8—−143.0 (m, 1 F); ^{13}C NMR (75.5 MHz) δ = 18.8 (s), 29.2 (s), 29.7 (s), 30.0 (s), 34.4 (s), 37.2 (s), 42.5 (s), 42.9 (s), 79.0 (s), 115.3 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 144.7 (dd, J = 5, 5 Hz), 148.4 (dd, J = 13, 245 Hz), 150.0 (dd, J = 13, 247 Hz), 215.8 (s); MS *m/z* (rel intensity) 399 (M^++1; 0.3), 398 (M^+; 0.3), 291 (9), 290 (40), 193 (14), 179 (24), 153 (20), 140 (37), 136 (10), 127 (100), 109 (10), 107 (8). Found: *m/z* 398.1558. Calcd for $C_{21}H_{28}F_2OS_2$: M, 398.1550.

***O*-2-{*trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexyl}ethyl *S*-Methyl Dithiocarbonate (5c).** Method A, 95% yield. A pale yellow powder, mp 73.4—74.6 °C; R_f = 0.75 (hexane : EtOAc = 10 : 1). IR (KBr) 2923, 2855, 1717, 1647, 1605, 1514, 1448, 1426, 1269, 1210, 1115, 1059, 968, 822, 777, 750 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.80—1.45 (m, 11 H), 1.65—1.90 (m, 10 H), 2.41 (tt, J = 3, 12 Hz, 1 H), 2.56 (s, 3 H), 4.64 (d, J = 6 Hz, 2 H), 6.85—7.07 (m, 3 H); ^{19}F NMR (282 MHz) δ = −139.0—−139.2 (m, 1 F), −142.9—−143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) δ = 18.9 (s), 29.8 (s), 30.1 (s), 33.3 (s), 34.5 (s), 34.8 (s), 35.5 (s), 42.6 (s), 43.0 (s), 43.8 (s), 72.6 (s), 115.3 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 144.7 (dd, J = 5, 5 Hz), 148.4 (dd, J = 13, 245 Hz), 150.1 (dd, J = 13, 247 Hz), 215.9 (s); MS *m/z* (rel intensity) 412 (M^+; 0.1), 379 (8), 305 (13), 304 (56), 193 (20), 179 (46), 166 (14), 153 (25), 141 (14), 140 (35), 127 (100), 111 (22), 109 (59), 97 (17), 95 (44), 81 (68), 69 (66), 67 (88). Found: *m/z* 412.1711. Calcd for $C_{22}H_{30}F_2OS_2$: M, 412.1706.

***O*-3-{*trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexyl}propyl *S*-Methyl Dithiocarbonate (5d).** Method A, 83% yield. Pale yellow needles, mp 76.6—78.0 °C; R_f = 0.64 (hexane : EtOAc = 10 : 1). IR (KBr) 2946, 2915, 2845, 1869, 1610, 1518, 1489, 1447, 1289, 1273, 1219, 1207, 1065, 1052, 963, 939, 816, 772 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.82—1.45 (m, 13 H), 1.68—1.98 (m, 10 H), 2.41 (tt, J = 3, 12 Hz, 1 H), 2.56 (s, 3 H), 4.58 (t, J = 7 Hz, 2 H), 6.80—7.09 (m, 3 H); ^{19}F NMR (282 MHz) δ = −139.0—−139.2 (m, 1 F), −142.9—−143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) δ = 18.9 (s), 25.7 (s), 29.9 (s), 30.1 (s), 33.4 (s), 33.4 (s), 34.5 (s), 37.5 (s), 42.7 (s), 43.2 (s), 43.8 (s), 74.6 (s), 115.3 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 144.8 (dd, J = 4, 4 Hz), 148.5 (dd, J = 13, 245 Hz), 150.1 (dd, J = 13, 247 Hz), 215.9 (s); MS *m/z* (rel intensity) 426 (M^+; 0.3), 393 (19), 319 (15), 318 (72), 276 (21), 195 (21), 193 (17), 179 (46), 140 (45), 127 (100), 123 (60), 109 (50), 95 (57), 81 (62), 69 (64), 67 (63). Found: *m/z* 426.1859. Calcd for $C_{23}H_{32}F_2OS_2$: M, 426.1863.

***O*-4-{*trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexyl}butyl *S*-Methyl Dithiocarbonate (5e).** Method A, 92% yield. A pale yellow powder. Phase transition temperature/°C: Cr 55 S_B 63 N 88 Iso; R_f = 0.41 (hexane). IR (KBr) 2924, 2851, 1869, 1522, 1509, 1459, 1217, 1090, 1051, 939, 806, 770 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.80—1.48 (m, 15 H), 1.68—1.94 (m, 10 H), 2.40 (tt, J = 3, 12 Hz, 1 H), 2.56 (s, 3 H), 4.59 (t, J = 7 Hz, 2 H), 6.80—7.09 (m, 3 H); ^{19}F NMR (188 MHz) δ = −139.0—−139.2 (m, 1 F), −142.9—−143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) δ = 18.9 (s), 23.3 (s), 28.5 (s), 30.0 (s), 30.1 (s), 33.4 (s), 34.5 (s), 36.9 (s), 37.7 (s), 42.7 (s), 43.2 (s), 43.8 (s), 74.3 (s), 115.4 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 144.8 (dd, J = 5, 5 Hz), 148.4 (dd, J = 13, 245 Hz), 150.1 (dd, J = 13, 247 Hz), 215.9 (s); MS *m/z* (rel intensity) 441 (M^++1; 0.3), 440 (M^+; 0.3), 407 (3), 333 (19), 332 (74), 193 (19), 179 (45), 153 (27), 139 (41), 127 (100), 109 (29), 95 (71), 81 (78), 69 (56). Found: *m/z* 440.2014. Calcd for $C_{24}H_{34}F_2OS_2$: M, 440.2019.

***O*-5-{*trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexyl}pentyl *S*-Methyl Dithiocarbonate (5f).** Method A, 86% yield. Pale yellow needles. Phase transition temperature/°C: Cr 71 S_B 77 N 81 Iso; R_f = 0.60 (hexane : EtOAc = 10 : 1). IR (KBr) 2944, 2917, 1869, 1522, 1221, 1208, 1069, 1053, 938, 868, 816, 772 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.79—1.45 (m, 17 H), 1.65—1.95 (m, 10 H), 2.40 (tt, J = 3, 12 Hz, 1 H), 2.56 (s, 3 H), 4.59 (t, J = 7 Hz, 2 H), 6.80—7.09 (m, 3 H); ^{19}F NMR (282 MHz) δ = −139.1—−139.2 (m, 1 F), −143.0—−143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) δ = 18.9 (s), 26.2 (s), 26.6 (s), 28.3 (s), 30.0 (s), 30.2 (s), 33.6 (s), 34.6 (s), 37.3 (s), 37.8 (s), 42.8 (s), 43.3 (s), 43.9 (s), 74.3 (s), 115.4 (d, J = 17 Hz), 116.7 (d, J = 17 Hz), 122.4 (dd, J = 3, 6 Hz), 144.8 (dd, J = 5, 5 Hz), 148.4 (dd, J = 13, 245 Hz), 150.1 (dd, J = 13, 247 Hz), 216.0 (s); MS *m/z* (rel intensity) 455 (M^++1; 0.3), 454 (M^+; 0.6), 347 (14), 346 (52), 275 (8), 206 (4), 194 (8), 193 (17), 179 (8), 153 (23), 151 (23), 140 (30), 137 (13), 127 (100), 109 (39), 95 (57), 81 (71), 67 (80). Found: *m/z* 454.2173. Calcd for $C_{25}H_{36}F_2OS_2$: M, 454.2176.

***S*-Methyl *O*-[*trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]methyl Dithiocarbonate (6b).** Method B, 96% yield. A pale yellow powder; mp 64.8—65.5 °C; R_f = 0.44 (hexane : EtOAc = 5 : 1). IR (KBr) 2919, 2851, 1456, 1238, 1165, 1061, 963, 895 cm^{-1};

^{1}H NMR (300 MHz) δ = 0.75—1.35 (m, 18 H), 0.88 (t, J = 7 Hz, 3 H), 1.63—1.80 (m, 10 H), 2.55 (s, 3 H), 4.39 (d, J = 6 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.8 (s), 22.7 (s), 26.6 (s), 29.2 (s), 29.8 (s), 30.0 (s), 32.2 (s), 33.6 (s), 37.2 (s), 37.4 (s), 37.9 (s), 43.1 (s), 43.3 (s), 79.2 (s), 215.9 (s); MS *m/z* (rel intensity) 356 (M^+; 2), 249 (11), 248 (29), 152 (13), 151 (21), 149 (19), 137 (30), 111 (31), 109 (21), 95 (80), 83 (83), 79 (39), 71 (38), 69 (85), 67 (100). Found: *m/z* 356.2212. Calcd for $C_{20}H_{36}OS_2$: M, 356.2208.

***S*-Methyl *O*-2-[*trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]ethyl Dithiocarbonate (6c).** Method B, 95% yield. A pale yellow powder; phase transition temperature/°C: Cr 30 N 41 Iso; R_f = 0.71 (hexane : EtOAc = 10 : 1). IR (KBr) 2920, 1559, 1509, 1466, 1443, 1375, 1225, 1086, 1055, 967, 897 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.75—1.40 (m, 20 H), 0.87 (t, J = 7 Hz, 3 H), 1.60—1.90 (m, 10 H), 2.53 (s, 3 H), 4.60 (t, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.9 (s), 22.9 (s), 26.7 (s), 29.8 (s), 30.0 (s), 32.2 (s), 33.4 (s), 33.6 (s), 34.9 (s), 35.5 (s), 37.4 (s), 37.9 (s), 43.2 (s), 43.4 (s), 72 6 (s), 215.8 (s); MS *m/z* (rel intensity) 371 (M^+; 3), 308 (20), 307 (100), 193 (24), 189 (10), 179 (13), 178 (14), 167 (26), 149 (43), 139 (14), 133 (15), 127 (12), 123 (16), 113 (24), 105 (22). Found: *m/z* 370.2366. Calcd for $C_{21}H_{38}OS_2$: M, 370.2364.

***S*-Methyl *O*-3-[*trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]propyl Dithiocarbonate (6d).** Method B, 96% yield. A pale yellow powder; mp 67.5—68.3 °C; R_f = 0.78 (hexane : EtOAc = 10 : 1). IR (KBr) 2951, 2923, 2849, 1717, 1445, 1420, 1217, 1061, 1052, 968, 899 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.75—1.05 (m, 10 H), 0.88 (t, J = 7 Hz, 3 H), 1.10—1.32 (m, 12 H), 1.65—1.85 (m, 10 H), 2.55 (s, 3 H), 4.57 (t, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.9 (s), 22.7 (s), 25.7 (s), 26.7 (s), 29.9 (s), 30.1 (s), 32.2 (s), 33.4 (s), 33.5 (s), 33.7 (s), 37.48 (s), 37.52 (s), 37.9 (s), 43.39 (s), 43.43 (s), 74.6 (s), 215.9 (s); MS *m/z* (rel intensity) 385 (M^++1; 3), 384 (M^+; 3), 276 (13), 207 (15), 153 (20), 140 (23), 137 (21), 135 (18), 127 (36), 123 (29), 109 (51), 97 (59), 81 (56), 69 (63), 67 (100). Found: *m/z* 384.2526. Calcd for $C_{22}H_{40}OS_2$: M, 384.2521.

***S*-Methyl *O*-4-[*trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]butyl Dithiocarbonate (6e).** Method B, 95% yield. A pale yellow powder; phase transition temperature/°C: Cr 59 N 65 Iso; R_f = 0.80 (hexane : EtOAc = 10 : 1). IR (KBr) 2847, 1709, 1655, 1446, 1450, 1220, 1152, 1086, 1055, 967, 899 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.75—1.04 (m, 10 H), 0.88 (t, J = 7 Hz, 3 H), 1.06—1.50 (m, 14 H), 1.64—1.82 (m, 10 H), 2.56 (s, 3 H), 4.58 (t, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.9 (s), 22.7 (s), 23.3 (s), 26.7 (s), 28.5 (s), 30.0 (s), 30.1 (s), 32.2 (s), 33.5 (s), 33.7 (s), 37.5 (s), 37.7 (s), 37.9 (s), 43.4 (s), 43.5 (s), 74.3 (s), 215.9 (s); MS *m/z* (rel intensity) 400 (M^++2; 0.9), 399 (M^++1; 0.9), 398 (M^+; 2), 336 (16), 335 (85), 262 (15), 136 (22), 82 (100), 75 (26), 71 (25). Found: *m/z* 398.2666. Calcd for $C_{23}H_{42}OS_2$: M, 398.2677.

***S*-Methyl *O*-5-[*trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]pentyl Dithiocarbonate (6f).** Method B, 91% yield. A pale yellow powder; mp 76.9—78.3 °C; R_f = 0.38 (hexane : EtOAc = 10 : 1). IR (KBr) 2924, 2849, 1734, 1717, 1684, 1559, 1541, 1509, 1458, 1223, 1090, 1053 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.75—1.04 (m, 10 H), 0.88 (t, J = 7 Hz, 3 H), 1.06—1.45 (m, 16 H), 1.64—1.84 (m, 10 H), 2.55 (s, 3 H), 4.58 (t, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.9 (s), 22.7 (s), 26.2 (s), 26.6 (s), 26.7 (s), 28.2 (s), 30.0 (s), 30.1 (s), 32.2 (s), 33.59 (s), 33.63 (s), 37.3 (s), 37.5 (s), 37.8 (s), 37.9 (s), 43.4 (s), 74.2 (s), 215.8 (s); MS *m/z* (rel intensity) 413 (M^++1; 0.3), 412 (M^+; 0.1), 379 (12), 365 (6), 305 (20), 304 (83), 233 (26), 178 (12), 152 (27), 151 (59), 137 (17), 123 (20), 109 (100). Found: *m/z* 412.2829. Calcd for $C_{24}H_{44}OS_2$: M, 412.2834.

***S*-Methyl *O*-*trans*-4-[*trans*-4-(3,4,5-Trifluorophenyl)cyclohexyl]cyclohexylmethyl Dithiocarbonate (22).** This compound was prepared by Method A in 83% yield as a pale yellow powder from *trans*-4-[*trans*-4-(3,4,5-trifluorophenyl)cyclohexyl]cyclohexanemethanol. Mp 96.8—98.2 °C; R_f = 0.43 (hexane : EtOAc = 10 : 1). IR (KBr) 2930, 2855, 1707, 1611, 1530, 1443, 1345, 1231, 1211, 1059, 1034, 959, 845, 777 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.95—1.53 (m, 10 H), 1.65—2.04 (m, 9 H), 2.39 (tm, J = 12 Hz, 1 H), 2.55 (s, 3 H), 4.41 (d, J = 6 Hz, 2 H), 6.79 (dd, J = 7, 9 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −135.9 (dd, J = 9, 21 Hz, 2 F), −164.7 (tt, J = 7, 21 Hz, 1 F); ^{13}C NMR (50.3 MHz) δ = 18.8 (s), 29.2 (s), 29.7 (s), 29.9 (s), 34.2 (s), 37.2 (s), 42.5 (s), 42.8 (s), 43.8 (s), 79.0 (s), 110.4 (dd, J = 7, 13 Hz), 137.7 (td, J = 16, 248 Hz), 143.9 (dt, J = 7, 7 Hz), 150.9 (ddd, J = 4, 10, 248 Hz), 215.8 (s); MS *m/z* (rel intensity) 416 (M^+; 0.1), 309 (21), 308 (94), 211 (22), 197 (54), 183 (10), 171 (22), 158 (38), 145 (100), 121 (17), 109 (29), 97 (73), 95 (99), 83 (68), 81 (88), 67 (88). Found: *m/z* 416.1458. Calcd for $C_{21}H_{27}F_3OS_2$: M, 416.1455.

Preparation of Trifluoromethoxycyclohexane-LC: General Procedure. To a suspension of NBS (5.0 mmol) and CH_2Cl_2 (2.5 mL), placed in an oven-dried polypropylene round-bottom tube that was equipped with a rubber septum and a Teflon®-coated magnetic stirring bar, were added dropwise pyridine (0.46 mL) and subsequently 70% HF/py (1.0 mL, 40 mmol of HF) at −42 °C (cooled by a CCl_4/dry ice bath) under an argon atmosphere. The resulting mixture was stirred at room temperature for 5 min and then cooled at 0 °C. A solution of dithiocarbonate **5a**, **6a**, **7a**, or **8a** (1.0 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to the suspension at 0 °C to give a dark-red mixture. This was stirred at 0 °C for 1 h, diluted carefully with Et_2O (5.0 mL), and quenched with an ice-cold buffer solution (pH = 10, $NaHCO_3$, $NaHSO_3$, and NaOH). The pH of the mixture was adjusted to 10 by careful addition of ice-cold 10% NaOH aq solution. The whole was extracted with Et_2O; the aq phase was extracted with Et_2O three times. The combined organic phase was washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography (cyclohexane) afforded trifluoromethyl ether **9a**,[13a] **10a**, **11a**, or **12a**. Yields and spectral properties of products are as follows.

***trans*-1-(*trans*-4-Propylcyclohexyl)-4-trifluoromethoxycyclohexane (10a).** Obtained in 40% yield as colorless crystals, mp 30.8—31.1 °C; bp 160 °C/0.4 mmHg (1 mmHg = 133.322 Pa); R_f = 0.91 (hexane). IR 2980, 2850, 1452, 1442, 1366, 1305, 1130, 1024, 859, 673 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.75—1.92 (m, 19 H), 0.87 (t, J = 7 Hz, 3 H), 2.00—2.28 (m, 4 H), 4.07 (tt, J = 5, 11 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −58.0 (s, 3 F); MS *m/z* (rel intensity) 292 (M^+; 15), 263 (12), 220 (19), 194 (21), 182 (18), 164 (28), 149 (100), 135 (27), 121 (30), 104 (39). Found: *m/z* 292.2007. Calcd for $C_{16}H_{27}OF_3$: M, 292.2014.

***trans*-1-[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]-4-trifluoromethoxycyclohexane (11a).** Prepared in 34% yield as a colorless powder; phase transition temperature/°C: Cr 44 S_X 112 S_B 147 N 189 Iso (DSC on 2nd heating); R_f = 0.77 (hexane). IR (KBr) 2952, 2908, 2854, 1445, 1366, 1265, 1253, 1156, 1023, 857 cm^{-1}; ^{1}H NMR (200 MHz) δ = 0.77—1.58 (m, 23 H), 0.87 (t, J = 7 Hz, 3 H), 1.65—1.90 (m, 8 H), 2.05—2.18 (m, 2 H), 4.07 (tt, J = 5, 11 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −58.0 (s, 3 F); ^{13}C NMR (75.5 MHz) δ = 14.4 (s), 20.0 (s), 28.0 (s), 30.1 (s), 30.2 (s), 30.4 (s), 32.7 (s), 33.6 (s), 37.6 (s), 39.8 (s), 41.8 (s), 42.6 (s), 43.38 (s), 43.40 (s), 78.6 (q, J = 2 Hz), 121.7 (q, J = 254 Hz); MS *m/z* (rel intensity) 374 (M^+; 10), 288 (26), 245 (20), 183 (7), 123 (18), 95 (36), 83 (53), 82 (66), 81 (88), 79 (29), 69 (100), 67 (58). Found:

m/z 374.2795. Calcd for $C_{22}H_{37}OF_3$: M, 374.2796.

***trans*-1-(4′-Propylbiphenyl-4-yl)-4-trifluoromethoxycyclohexane (12a).** Isolated in 25% yield as a colorless powder; phase transition temperature/°C: Cr 90 S_X 104 S_A 129 Iso; $R_f = 0.21$ (hexane). IR (KBr) 2957, 1499, 1455, 1333, 1283, 1256, 1211, 1132, 1040, 982, 860, 806, 785 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.97$ (t, $J = 7$ Hz, 3 H), 1.42—1.80 (m, 6 H), 1.94—2.12 (m, 2 H), 2.18—2.32 (m, 2 H), 2.43—2.68 (m, 3 H), 4.24 (tt, $J = 5$, 11 Hz, 1 H), 7.22—7.25 (m, 4 H), 7.46—7.53 (m, 4 H); ^{13}C NMR (75.5 MHz) $\delta = 13.9$ (s), 24.6 (s), 32.0 (s), 32.8 (s), 37.7 (s), 42.4 (s), 77.7 (q, $J = 2$ Hz), 121.7 (q, $J = 255$ Hz), 126.8 (s), 127.00 (s), 127.02 (s), 128.8 (s), 138.2 (s), 139.2 (s), 141.7 (s), 144.4 (s); MS *m/z* (rel intensity) 363 ($M^+ + 1$; 24), 362 (M^+; 100), 333 (78), 235 (13), 194 (13), 193 (76), 178 (23), 165 (19), 69 (10). Found: *m/z* 362.1857. Calcd for $C_{22}H_{25}OF_3$: M, 362.1857.

ω-Trifluoromethoxyalkyl-LCs 10b—10f. An oven-dried Teflon®-vessel equipped with a rubber septum, a Teflon®-coated magnetic stirring bar, and an argon inlet, was flushed with argon and charged with DBH (5.2 g, 18.0 mmol) and CH_2Cl_2 (6.0 mL). The resulting suspension was stirred for 10 min at −78 °C. To the mixture was slowly added over 5 min under vigorous stirring 70% HF/py (40 mmol of HF/mL, 9.0 mL, 0.36 mol) using a polypropylene/polyethylene syringe under an argon atmosphere. To this mixture was added dropwise a solution of **6b**—**6f** (6.0 mmol) in CH_2Cl_2 (6.0 mL) at −78 °C via a cannula by applying positive argon pressure. The resulting red-brown mixture was stirred at 0 °C for 1 h, diluted with Et_2O (20 mL) carefully (*caution! during this operation, hydrogen fluoride is often released vigorously*), and quenched by careful addition of an ice-cold aq $NaHSO_3$/$NaHCO_3$/NaOH (pH 10) solution at 0 °C until the red-brownish color of the mixture disappeared. The pH value was readjusted to 10 by slow addition of ice-cooled 30% NaOH aq solution at 0 °C and diluted with Et_2O (200 mL). The organic phase was separated; the aq phase was extracted four times with Et_2O; the combined organic phase was washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Pyridine of the residue was removed by double toluene azeotrope under reduced pressure. The residue was purified by flash column chromatography (hexane) to give trifluoromethyl ethers **10b**—**10f**.

ω-Trifluoromethoxyalkyl-LCs 9b—9f. Fluorination of dithiocarbonate **5b**—**5f** (5.0 mmol) using 70% HF/py (5.0 mL, 0.20 mol) and DBH (4.3 g, 15.0 mmol) was carried out according to the procedure for **10b**—**10f**. Purification of the resulting crude mixture afforded a mixture of **9b**—**9f** and a bromination product, *trans*-1-[*trans*-4-(bromo-3,4-difluorophenyl)cyclohexyl]-4-(trifluoromethoxyalkyl)cyclohexane. The mixture dissolved in THF (10 mL) was treated with *n*-BuLi (1.6 M in hexane, 3.8 mL, 6.0 mmol) at −78 °C for 10 min before quenching with H_2O at −78 °C and extraction with Et_2O (three times, totally 200 mL). The combined organic extracts were washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated. Purification by flash column chromatography (hexane) gave **9b**—**9f**. Yields and spectral properties of products are as follows.

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-(trifluoromethoxymethyl)cyclohexane (9b).** Yield 82%. A colorless powder. Mp 45.5—46.4 °C; $R_f = 0.40$ (hexane). IR 2924, 2855, 1609, 1518, 1451, 1277, 1213, 1140, 1038, 951, 866, 818, 772 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.82$—1.50 (m, 10 H), 1.53—2.02 (m, 9 H), 2.41 (tm, $J = 12$ Hz, 1 H), 3.75 (d, $J = 6$ Hz, 2 H), 6.86—7.10 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -61.2$ (s, 3 F), −139.2 (ddd, $J = 8$, 12, 21 Hz, 1 F), −143.0 (dddd, $J = 4$, 8, 11, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 29.1$ (s), 29.4 (s), 30.1 (s), 34.5 (s), 37.3 (s), 42.6 (s), 43.0 (s), 43.81 (s), 43.83 (s), 72.4 (q, $J = 3$ Hz), 115.4 (d, $J = 17$ Hz), 116.8 (d, $J = 17$ Hz), 121.8 (q, $J = 258$ Hz), 122.5 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 4$, 5 Hz), 148.7 (dd, $J = 13$, 245 Hz), 150.3 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 377 ($M^+ + 1$; 13), 376 (M^+; 46), 207 (12), 205 (10), 195 (14), 153 (24), 149 (20), 140 (100), 127 (90), 121 (14), 109 (19), 95 (85), 91 (22), 83 (43), 81 (68), 71 (22), 69 (71). Found: *m/z* 376.1836. Calcd for $C_{20}H_{25}F_5O$: M, 376.1826.

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-(2-trifluoromethoxyethyl)cyclohexane (9c).** Yield 88%. A colorless oil. Phase transition temperature/°C: Cr −5 N 18 Iso (DSC on 2nd heating); $R_f = 0.56$ (hexane). IR 2923, 2853, 1609, 1518, 1449, 1431, 1410, 1297, 1138, 1028, 939, 866, 818, 772 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.88$—1.20 (m, 8 H), 1.25—1.45 (m, 3 H), 1.50—1.63 (m, 2 H), 1.70—1.95 (m, 8 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 4.00 (t, $J = 6$ Hz, 2 H), 6.88—7.08 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -61.15$ (s, 3 F), −139.1 (ddd, $J = 8$, 12, 21 Hz, 1 F), −143.0 (dddd, $J = 4$, 8, 11, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 29.8$ (s), 30.1 (s), 33.2 (s), 34.2 (s), 34.5 (s), 36.0 (s), 42.7 (s), 43.0 (s), 43.8 (s), 65.6 (s), 115.4 (d, $J = 16$ Hz), 116.8 (d, $J = 16$ Hz), 121.7 (q, $J = 254$ Hz), 122.4 (dd, $J = 3$, 3 Hz), 144.8 (m), 148.5 (dd, $J = 13$, 245 Hz), 150.2 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 392 ($M^+ + 2$; 2), 391 ($M^+ + 1$; 11), 390 (M^+; 42), 195 (11), 140 (100), 128 (13), 127 (98), 109 (61), 95 (23), 91 (10), 83 (23), 81 (46), 79 (18), 67 (82). Found: *m/z* 390.1984. Calcd for $C_{21}H_{27}F_5O$: M, 390.1982.

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-(3-trifluoromethoxypropyl)cyclohexane (9d).** Yield 89%. A mesomorphic oil. Phase transition temperature/°C: Cr 21 N 52 Iso (DSC on 2nd heating); $R_f = 0.42$ (hexane). IR 2923, 2853, 1607, 1518, 1451, 1431, 1408, 1275, 1225, 1140, 1057, 939, 864, 818, 772 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.45 (m, 13 H), 1.52—1.95 (m, 10 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.92 (t, $J = 6$ Hz, 2 H), 6.86—7.05 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -61.1$ (s, 3 F), −139.1 (ddd, $J = 8$, 12, 21 Hz, 1 F), −143.0 (dddd, $J = 4$, 8, 11, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 26.2$ (s), 29.9 (s), 30.2 (s), 33.0 (s), 33.4 (s), 34.6 (s), 37.5 (s), 42.7 (s), 43.2 (s), 43.9 (s), 67.9 (s), 115.3 (d, $J = 16$ Hz), 116.7 (d, $J = 16$ Hz), 121.7 (q, $J = 254$ Hz), 122.4 (dd, $J = 3$, 3 Hz), 144.8 (m), 148.5 (dd, $J = 13$, 245 Hz), 150.2 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 405 ($M^+ + 1$; 4), 404 (M^+; 16), 206 (10), 196 (13), 192 (15), 177 (10), 167 (24), 161 (10), 153 (14), 149 (100), 140 (39), 133 (14), 127 (48), 123 (35), 111 (29), 109 (31), 104 (12). Found: *m/z* 404.2139. Calcd for $C_{22}H_{29}F_5O$: M, 404.2139.

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-(4-trifluoromethoxybutyl)cyclohexane (9e).** Yield 88%. A mesomorphic oil. Phase transition temperature/°C: Cr 14 S_X 17 N 55 Iso (DSC on 2nd heating); $R_f = 0.40$ (hexane). IR 2923, 2853, 1609, 1518, 1449, 1410, 1275, 1215, 1140, 1038, 939, 864, 816, 772 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.49 (m, 15 H), 1.60—1.95 (m, 10 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.94 (t, $J = 6$ Hz, 2 H), 6.86—7.02 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -61.1$ (s, 3 F), −139.1 (ddd, $J = 8$, 12, 21 Hz, 1 F), −143.0 (dddd, $J = 4$, 8, 11, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 26.2$ (s), 29.0 (s), 30.0 (s), 30.2 (s), 33.5 (s), 34.6 (s), 36.8 (s), 37.7 (s), 42.8 (s), 43.3 (s), 43.9 (s), 67.5 (q, $J = 3$ Hz), 115.3 (d, $J = 16$ Hz), 116.7 (d, $J = 16$ Hz), 121.7 (q, $J = 254$ Hz), 122.4 (dd, $J = 3$, 3 Hz), 144.9 (dd, $J = 4$, 4 Hz), 148.5 (dd, $J = 13$, 245 Hz), 149.3 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 420 ($M^+ + 2$; 2), 419 ($M^+ + 1$; 14), 418 (M^+; 51), 195 (10), 167 (12), 153 (24), 140 (96), 137 (17), 127 (100), 109 (12), 97 (12), 96 (13), 95 (37), 83 (26), 81 (54), 79 (18), 69 (90), 67 (62). Found: *m/z* 418.2300. Calcd for $C_{23}H_{31}F_5O$: M, 418.2295.

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-(5-trifluoromethoxypentyl)cyclohexane (9f).** Yield 92%. A mesomorphic oil. Phase transition temperature/°C: Cr 32 N 74 Iso (DSC on 2nd heating); $R_f = 0.58$ (hexane). IR 2923, 2853, 1609, 1518, 1449, 1408, 1277, 1217, 1140, 939, 864, 817, 772 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.80$—1.45 (m, 17 H), 1.52—1.85 (m, 10 H), 2.39 (tt, $J = 3$, 12 Hz, 1 H), 3.93 (t, $J = 7$ Hz, 2 H), 6.80—7.15 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -61.1$ (s, 3 F), -138.9—-139.1 (m, 1 F), -142.8—-143.0 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 25.8$ (s), 26.5 (s), 28.8 (s), 30.0 (s), 30.2 (s), 33.6 (s), 34.6 (s), 37.3 (s), 37.8 (s), 42.8 (s), 43.3 (s), 43.9 (s), 67.5 (q, $J = 3$ Hz), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 121.7 (q, $J = 253$ Hz), 122.5 (dd, $J = 3$, 6 Hz), 144.9 (dd, $J = 5$, 5 Hz), 148.5 (dd, $J = 13$, 245 Hz), 150.2 (dd, $J = 12$, 247 Hz); MS *m/z* (rel intensity) 434 (M^++2; 2), 433 (M^++1; 18), 432 (M^+; 66), 196 (15), 195 (11), 181 (15), 153 (23), 149 (10), 141 (17), 140 (92), 127 (100), 109 (22). Found: *m/z* 432.2460. Calcd for $C_{24}H_{33}F_5O$: M, 432.2452.

***trans*-1-(*trans*-4-Pentylcyclohexyl)-4-trifluoromethoxymethylcyclohexane (10b).** Yield 89%. A mesomorphic oil. Phase transition temperature/°C: Cr 18 S_X 26 S_B 52 Iso (DSC on 2nd heating); $R_f = 0.76$ (hexane). IR 2917, 2851, 1470, 1447, 1410, 1379, 1260, 1140, 1078, 1038, 1022, 963, 895, 866, 725 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.36 (m, 18 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.54—1.86 (m, 10 H), 3.73 (d, $J = 6$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.2$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.1 (s), 29.4 (s), 30.1 (s), 32.3 (s), 33.6 (s), 37.3 (s), 37.5 (s), 37.9 (s), 43.1 (s), 43.3 (s), 72.5 (q, $J = 3$ Hz), 121.7 (q, $J = 253$ Hz); MS *m/z* (rel intensity) 335 (M^++1; 1), 334 (M^+; 11), 180 (22), 153 (15), 152 (17), 111 (19), 109 (12), 97 (100), 95 (50), 83 (89), 81 (56), 69 (72). Found: *m/z* 334.2491. Calcd for $C_{19}H_{33}F_3O$: M, 334.2483.

***trans*-1-(*trans*-4-Pentylcyclohexyl)-4-(2-trifluoromethoxyethyl)cyclohexane (10c).** Yield 100%. A mesomorphic oil. Phase transition temperature/°C: Cr 4 S_B 53 Iso (DSC on 2nd heating); $R_f = 0.85$ (hexane : EtOAc = 5 : 1). IR 2917, 2849, 1480, 1447, 1410, 1379, 1264, 1140, 1051, 1015, 895, 879, 855, 725 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.35 (m, 20 H), 0.87 (t, $J = 7$ Hz, 3 H), 1.50—1.57 (m, 2 H), 1.62—1.78 (m, 8 H), 3.96 (t, $J = 7$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -61.2$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.8 (s), 26.7 (s), 29.8 (s), 30.1 (s), 32.3 (s), 33.3 (s), 33.7 (s), 34.2 (s), 36.0 (s), 37.5 (s), 38.0 (s), 43.3 (s), 43.4 (s), 65.5 (q, $J = 3$ Hz), 121.7 (q, $J = 254$ Hz); MS *m/z* (rel intensity) 348 (M^+; 8), 221 (6), 194 (20), 181 (11), 167 (26), 163 (13), 152 (14), 150 (15), 149 (100), 139 (10), 129 (15), 127 (26), 121 (12), 119 (12), 113 (22), 109 (14). Found: *m/z* 348.2628. Calcd for $C_{20}H_{35}F_3O$: M, 348.2640.

***trans*-1-(*trans*-4-Pentylcyclohexyl)-4-(3-trifluoromethoxypropyl)cyclohexane (10d).** Yield 100%. A colorless oil. Phase transition temperature/°C: Cr 30 S_B 96 Iso (DSC on 2nd heating); $R_f = 0.89$ (hexane). IR (KBr) 2924, 2907, 2849, 1412, 1269, 1227, 1144, 1057, 862 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.38 (m, 22 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.62—1.80 (m, 10 H), 3.92 (t, $J = 7$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.2$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.8 (s), 26.3 (s), 26.8 (s), 30.0 (s), 30.1 (s), 32.3 (s), 33.1 (s), 33.5 (s), 33.7 (s), 37.5 (s), 37.6 (s), 38.0 (s), 43.4 (s), 43.5 (s), 67.8 (q, $J = 3$ Hz), 121.7 (q, $J = 254$ Hz); MS *m/z* (rel intensity) 363 (M^++1; 11), 362 (M^+; 49), 235 (9), 209 (16), 208 (89), 153 (55), 152 (100), 137 (11), 125 (15), 124 (28), 123 (81), 111 (78), 109 (62). Found: *m/z* 362.2803. Calcd for $C_{21}H_{37}F_3O$: M, 362.2796.

***trans*-1-(*trans*-4-Pentylcyclohexyl)-4-(4-trifluoromethoxybutyl)cyclohexane (10e).** Yield 94%. A mesomorphic oil. Phase transition temperature/°C: Cr 4 S_B 90 Iso (DSC on 2nd heating); $R_f = 0.84$ (hexane). IR 2915, 2849, 1509, 1449, 1267, 1140, 895 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.04 (m, 10 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.06—1.43 (m, 14 H), 1.62—1.78 (m, 10 H), 3.93 (t, $J = 7$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.2$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.8 (s), 22.9 (s), 26.8 (s), 29.1 (s), 30.1 (s), 30.2 (s), 32.3 (s), 33.6 (s), 33.8 (s), 36.9 (s), 37.6 (s), 37.8 (s), 38.0 (s), 43.50 (s), 43.53 (s), 67.5 (q, $J = 3$ Hz), 121.7 (q, $J = 253$ Hz); MS *m/z* (rel intensity) 377 (M^++1; 2), 376 (M^+; 7), 290 (5), 222 (16), 152 (24), 149 (16), 137 (24), 123 (12), 111 (18), 109 (18), 97 (90), 96 (80), 95 (57), 83 (99), 81 (95), 69 (100). Found: *m/z* 376.2959. Calcd for $C_{22}H_{39}F_3O$: M, 376.2953.

***trans*-1-(*trans*-4-Pentylcyclohexyl)-4-(5-trifluoromethoxypentyl)cyclohexane (10f).** Yield 81%. A mesomorphic oil. Phase transition temperature/°C: Cr 22 S_B 109 Iso (DSC on 2nd heating); $R_f = 0.84$ (hexane). IR 2917, 2849, 1445, 1266, 1140, 669 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.75$—1.04 (m, 8 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.06—1.40 (m, 16 H), 1.62—1.78 (m, 12 H), 3.93 (t, $J = 7$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.2$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.8 (s), 25.9 (s), 26.5 (s), 26.8 (s), 28.6 (S), 28.8 (s), 30.1 (s), 30.2 (s), 32.4 (s), 33.69 (s), 33.75 (s), 37.4 (s), 37.6 (s), 37.9 (s), 38.1 (s), 43.6 (s), 67.5 (q, $J = 3$ Hz), 121.7 (q, $J = 253$ Hz); MS *m/z* (rel intensity) 391 (M^++1; 2), 390 (M^+; 9), 236 (22), 153 (9), 152 (26), 111 (15), 97 (80), 96 (100), 83 (71), 81 (57). Found: *m/z* 390.3110. Calcd for $C_{23}H_{41}F_3O$: M, 390.3109.

***trans*-1-Trifluoromethoxymethyl-4-[*trans*-(3,4,5-trifluorophenyl)cyclohexyl]-cyclohexane (23).** Synthesis of this compound was performed by a procedure similar to the one for **10** in 89% yield as a colorless powder. Mp 42.6—43.6 °C; $R_f = 0.43$ (hexane). IR (KBr) 2923, 2855, 1717, 1684, 1617, 1534, 1509, 1264, 1237, 1215, 1154, 1036, 959, 847 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.88$—1.50 (m, 10 H), 1.53—2.08 (m, 9 H), 2.38 (tm, $J = 12$ Hz, 1 H), 3.75 (t, $J = 7$ Hz, 2 H), 6.78 (dd, $J = 7$, 9 Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -61.2$ (s, 3 F), -135.9 (dd, $J = 9$, 21 Hz, 2 F), -165.4 (tt, $J = 6$, 21 Hz, 1 F); ^{13}C NMR (50.3 MHz) $\delta = 29.1$ (s), 29.4 (s), 30.0 (s), 34.3 (s), 37.3 (s), 42.6 (s), 42.9 (s), 72.4 (q, $J = 3$ Hz), 110.5 (dd, $J = 7$, 13 Hz), 121.8 (q, $J = 253$ Hz), 137.8 (td, $J = 15$, 248 Hz), 144.0 (dt, $J = 7$, 7 Hz), 150.1 (ddd, $J = 4$, 10, 248 Hz); MS *m/z* (rel intensity) 395 (M^++1; 13), 394 (M^+; 33), 259 (11), 213 (13), 171 (22), 158 (75), 151 (12), 145 (86), 99 (11), 95 (100), 81 (61), 69 (42), 67 (77). Found: *m/z* 394.1738. Calcd for $C_{20}H_{24}F_6O$: M, 394.1731.

4-(*trans*-4-Propylcyclohexyl)-4′-(2-trifluoromethoxyethyl)biphenyl (25). A solution of 4-(*trans*-4-propylcyclohexyl)phenylboronic acid (2.2 g, 8.9 mmol) in EtOH (15 mL) was added to a stirred mixture of 1-bromo-4-(2-trifluoromethoxyethyl)benzene[13a] (1.61 g, 6.0 mmol), [Pd(PPh_3)$_4$] (70 mmol, 0.060 mmol) in toluene (30 mL) and aq K_2CO_3 (2.3 M, 30 mL) at room temperature under an argon atmosphere. The resulting mixture was heated under reflux for 18 h before quenching by addition of H_2O (100 mL) and toluene (100 mL). The organic phase was separated; the aq phase was extracted with toluene three times (300 mL). The combined organic extracts were washed with sat. aq NaCl, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane) and subsequent recrystallization from EtOH (four times) to give **25** in 47% yield as a colorless mesomorphic solid. Phase transition temperature/°C: S_B 132 S_A 159 Iso (DSC 2nd heating); $R_f = 0.20$ (hexane). IR (KBr) 2959, 2924, 2851, 1909, 1498, 1404, 1278, 1142, 1034, 811, 527 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.91$ (t, $J = 7$ Hz, 3 H), 0.96—1.14 (m, 2 H), 1.16—1.56 (m, 5 H), 1.82—1.96 (m, 4 H), 2.50 (tt, $J = 3$, 12 Hz), 3.01 (t, $J = 7$ Hz, 2 H), 4.16 (t, $J = 7$ Hz, 2 H), 7.25 (d,

$J = 8$ Hz, 2 H), 7.26 (d, $J = 8$ Hz, 2 H), 7.49 (d, $J = 8$ Hz, 2 H), 7.52 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.1$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.4$ (s), 20.0 (s), 35.6 (s), 34.3 (s), 34.9 (s), 37.0 (s), 39.7 (s), 44.3 (s), 67.7 (q, $J = 3$ Hz), 121.6 (q, $J = 255$ Hz), 126.9 (s), 127.2 (s), 129.2 (s), 135.1 (s), 138.2 (s), 138.7 (s), 139.9 (s), 147.0 (s); MS *m/z* (rel intensity) 392 (M^++2; 5), 391 (M^++1; 21), 390 (M^+; 67), 305 (23), 292 (33), 279 (22), 219 (37), 193 (56), 191 (27), 165 (20), 149 (100), 133 (15), 123 (14), 104 (14), 96 (20), 91 (24), 77 (28). Found: *m/z* 390.2168. Calcd for $C_{24}H_{29}F_3O$: M, 390.2170.

Preparation of Methyl Ethers: General Procedure. Method A: To a stirred solution of an alcohol **1**—**4** (6.6 mmol) in THF (6.0 mL), sodium hydride (NaH, 60% in oil, 7.4 mmol) was slowly added potionwise at 0 °C. After the mixture was stirred for 12 h at room temperature, MeI (9.6 mmol) was added dropwise to the reaction mixture at room temperature. The resulting mixture was stirred for 10 h at room temperature before quenching with aq NH_4Cl. The mixture was diluted with Et_2O (50 mL); the organic phase was separated; the aq phase was extracted with Et_2O three times (200 mL). The combined organic phase was washed with sat. aq NaCl, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography or recrystallization (EtOH) to give methyl ether **13**—**16**, **23**, or **24**.

Method B: Sodium hydride in Method A was replaced by *n*-BuLi (9.3 mmol).

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-methoxycyclohexane (13a).** Method A, 100% yield. Colorless needles, mp 68.7—69.2 °C. $R_f = 0.50$ (hexane : EtOAc = 5 : 1). IR (KBr) 3042, 2941, 2928, 2861, 1604, 1516, 1442, 1096, 940, 926, 777, 753 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.98$—1.49 (m, 10 H), 1.65—1.95 (m, 6 H), 2.00—2.18 (m, 2 H), 2.34 (tt, $J = 3$, 12 Hz, 1 H), 3.05 (tt, $J = 4$, 10 Hz, 1 H), 3.33 (s, 3 H), 6.82—7.13 (m, 3 H); ^{19}F NMR (188 MHz) $\delta = -138.8$—-139.2 (m, 1 F), -142.6—-143.0 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 27.9$ (s), 30.1 (s), 31.9 (s), 34.3 (s), 42.1 (s), 42.3 (s), 43.6 (d, $J = 1$ Hz), 79.6 (s), 115.2 (d, $J = 17$ Hz), 116.6 (d, $J = 17$ Hz), 122.3 (dd, $J = 3$, 6 Hz), 144.6 (dd, $J = 4$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.0 (dd, $J = 13$, 247 Hz); MS *m/z* (rel intensity) 308 (M^+; 10), 247 (17), 193 (31), 179 (36), 153 (32), 149 (24), 136 (19), 126 (27), 95 (21), 81 (72), 71 (100). Found: C, 74.03; H, 8.57%. Calcd for $C_{19}H_{26}F_2O$: C, 73.99; H, 8.50%.

***trans*-1-Methoxy-4-(*trans*-4-propylcyclohexyl)cyclohexane (14a).** Method B, 99% yield. Colorless oil, bp 145 °C/0.34 mmHg. $R_f = 0.44$ (hexane : EtOAc = 10 : 1). IR 2980, 2850, 2820, 1465, 1450, 1192, 1105, 929 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.75$—1.35 (m, 13 H), 0.87 (t, $J = 7$ Hz, 3 H), 1.62—1.83 (m, 6 H), 2.00—2.13 (m, 4 H), 3.04 (tt, $J = 4$, 10 Hz, 1 H), 3.33 (s, 3 H); ^{13}C NMR (50.3 MHz) $\delta = 14.3$ (s), 20.0 (s), 28.1 (s), 30.2 (s), 32.1 (s), 33.5 (s), 37.5 (s), 39.8 (s), 42.6 (s), 42.9 (s), 55.5 (s), 79.8 (s); MS *m/z* (rel intensity) 239 (M^++1; 0.2), 238 (M^+; 0.3), 206 (48), 176 (12), 163 (20), 124 (15), 123 (24), 109 (22), 93 (10), 83 (44), 82 (55), 81 (100), 79 (30), 71 (68), 67 (67). Found: C, 80.47; H, 12.75%. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68%.

***trans*-1-Methoxy-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]cyclohexane (15a).** Method B, 42% yield. A colorless powder. Phase transition temperature/°C: Cr 207 S_B 211 Iso (DSC on 2nd heating); $R_f = 0.53$ (hexane : EtOAc = 10 : 1); IR (KBr) 2930, 2855, 1495, 1451, 1372, 1098, 1005, 803 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.75$—1.40 (m, 21 H), 0.79 (t, $J = 7$ Hz, 3 H), 1.55—1.74 (m, 8 H), 1.94—2.14 (m, 4 H), 2.92—3.03 (m, 1 H), 3.27 (s, 3 H); ^{13}C NMR (75.5 MHz) $\delta = 14.4$ (s), 20.0 (s), 28.1 (s), 30.1 (s), 30.3 (s), 30.5 (s), 32.1 (s), 33.60 (s), 33.65 (s), 37.6 (s), 39.8 (s), 42.6 (s), 43.0 (s), 43.5 (s), 55.5 (s), 79.9 (s); MS *m/z* (rel intensity) 322 (M^++2; 4), 321 (M^++1; 22), 374 (M^+; 25), 289 (14), 288 (32), 207 (21), 205 (13), 193 (9), 165 (11), 149 (35), 127 (7), 125 (25), 124 (20), 123 (22), 109 (39), 97 (38), 83 (91), 71 (78), 69 ()100), 60 (41). Found: *m/z* 320.3083. Calcd for $C_{22}H_{40}O$: M, 320.3079.

***trans*-1-Methoxy-4-(4′-propylbiphenyl-4-yl)cyclohexane (16a).** Method A, 90% yield. A colorless powder. Phase transition temperature/°C: Cr 45 S_B 88 N 128 Iso (DSC on 2nd heating); $R_f = 0.44$ (hexane : EtOAc = 5 : 1). IR (KBr) 2930, 2855, 1495, 1451, 1372, 1098, 1005, 803 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.95$ (t, $J = 7$ Hz, 3 H), 1.22—1.61 (m, 4 H), 1.66 (sextet, $J = 7$ Hz, 2 H), 1.97 (dm, $J = 12$ Hz, 2 H), 2.19 (dm, $J = 11$ Hz, 2 H), 2.53 (tt, $J = 3$, 12 Hz, 1 H), 2.61 (t, $J = 7$ Hz, 2 H), 3.20 (tt, $J = 4$, 11 Hz, 1 H), 3.37 (s, 3 H), 7.19—7.25 (m, 4 H), 7.46—7.51 (m, 4 H); ^{13}C NMR (75.5 MHz) $\delta = 13.8$ (s), 24.5 (s), 32.2 (s), 32.4 (s), 37.6 (s), 43.3 (s), 55.6 (s), 79.1 (s), 126.7 (s), 126.8 (s), 127.0 (s), 128.8 (s), 138.3 (s), 138.9 (s), 141.5 (s), 145.4 (s); MS *m/z* (rel intensity) 309 (M^++1; 10), 308 (M^+; 33), 277 (24), 276 (100), 261 (21), 247 (46), 233 (10), 219 (12), 205 (21), 193 (46), 191 (17), 178 (23), 165 (21), 91 (11), 73 (14), 71 (16). Found: *m/z* 308.2139. Calcd for $C_{22}H_{28}O$: M, 308.2140.

***trans*-1-[*trans*-(3,4-Difluorophenyl)cyclohexyl]-4-(methoxymethyl)cyclohexane (13b).** Yield 96% (Method A). A colorless powder. Phase transition temperature/°C: Cr 59 S_B 112 Iso (DSC on 2nd heating); $R_f = 0.41$ (hexane : EtOAc = 10 : 1). IR (KBr) 2920, 2851, 1869, 1605, 1516, 1458, 1298, 1211, 1107, 828 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.85$—1.20 (m, 8 H), 1.24—1.44 (m, 2 H), 1.45—1.60 (m, 1 H), 1.72—1.96 (m, 8 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.18 (d, $J = 6$ Hz, 2 H), 3.32 (s, 3 H), 6.86—7.08 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.0$—-139.3 (m, 1 F), -142.9—-143.2 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 29.5$ (s), 30.1 (s), 30.2 (s), 34.5 (s), 38.2 (s), 42.7 (s), 43.2 (s), 43.8 (s), 58.8 (s), 78.8 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 5$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 12$, 247 Hz); MS *m/z* (rel intensity) 323 (M^++1; 1), 322 (M^+; 8), 290 (10), 261 (21), 179 (17), 153 (11), 140 (26), 127 (58), 121 (14), 95 (100), 81 (33), 67 (41). Found: *m/z* 322.2092. Calcd for $C_{20}H_{28}F_2O$: M, 322.2108.

***trans*-1-[*trans*-(3,4-Difluorophenyl)cyclohexyl]-4-(2-methoxyethyl)cyclohexane (13c).** Yield 98% (Method A). A colorless powder. Phase transition temperature/°C: Cr 48 N 80 Iso; $R_f = 0.38$ (hexane : EtOAc = 10 : 1). IR (KBr) 2920, 2845, 1717, 1684, 1609, 1522, 1429, 1389, 1289, 1271, 1208, 1125, 1105, 1162, 936, 868, 822, 772 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.20 (m, 8 H), 1.24—1.46 (m, 5 H), 1.64—1.94 (m, 8 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.32 (s, 3 H), 3.40 (t, $J = 7$ Hz, 2 H), 6.86—7.07 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.0$—-139.3 (m, 1 F), -142.9—-143.2 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 29.9$ (s), 30.1 (s), 33.5 (s), 34.5 (s), 34.7 (s), 37.0 (s), 42.7 (s), 43.1 (s), 43.8 (s), 58.5 (s), 70.8 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 5$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 12$, 247 Hz); MS *m/z* (rel intensity) 336 (M^+; 9), 304 (14), 244 (11), 238 (18), 233 (20), 207 (18), 194 (23), 180 (20), 152 (22), 149 (100), 140 (29), 127 (32), 122 (20), 109 (38), 105 (38). Found: *m/z* 336.2273. Calcd for $C_{21}H_{30}F_2O$: M, 336.2265.

***trans*-1-[*trans*-(3,4-Difluorophenyl)cyclohexyl]-4-(3-methoxypropyl)cyclohexane (13d).** Yield 89% (Method A). A colorless oil. Phase transition temperature/°C: Cr 45 N 131 Iso; $R_f = 0.43$ (hexane : EtOAc = 10 : 1). IR (KBr) 2924, 2851, 1520, 1509, 1456, 1115, 939, 823 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.80$—1.22 (m, 11 H), 1.24—1.46 (m, 2 H), 1.52—1.64 (m, 2 H), 1.66—1.94 (m, 8 H), 2.40 (tt, $J = 3$, 12 Hz, 1 H), 3.33 (s, 3 H), 3.37 (t, $J = 7$ Hz, 2 H), 6.86—7.08 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -139.1$—-139.3 (m, 1 F), -142.9—-143.1 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 27.1$ (s), 30.0 (s), 30.2 (s), 33.5 (s), 33.7 (s), 34.6 (s), 37.8 (s), 42.8 (s), 43.2 (s), 43.8 (s), 58.5 (s), 73.3 (s), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 5$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 12$, 247 Hz); MS *m*/*z* (rel intensity) 351 (M$^+$+1; 3), 350 (M$^+$; 9), 318 (21), 193 (14), 179 (26), 140 (36), 127 (56), 123 (24), 121 (15), 95 (34), 81 (100), 79 (20), 67 (77). Found: *m*/*z* 350.2420. Calcd for $C_{22}H_{32}F_2O$: M, 350.2421.

***trans*-1-[*trans*-(3,4-Difluorophenyl)cyclohexyl]-4-(4-methoxybutyl)cyclohexane (13e).** Yield 97% (Method A). A colorless powder. Phase transition temperature/°C: Cr 57 N 102 Iso; $R_f = 0.55$ (hexane : EtOAc = 5 : 1). IR (KBr) 2930, 2847, 1607, 1522, 1509, 1458, 1289, 1210, 1192, 1117, 870, 820, 772 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.78$—1.44 (m, 15 H), 1.48—1.60 (m, 2 H), 1.65—1.93 (m, 8 H), 2.39 (tt, $J = 3$, 12 Hz, 1 H), 3.32 (s, 3 H), 3.35 (t, $J = 6$ Hz, 2 H), 6.82—7.06 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -138.9$—-139.1 (m, 1 F), -142.8—-143.0 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 23.5$ (s), 30.0 (s), 30.1 (s), 33.5 (s), 34.5 (s), 37.3 (s), 37.8 (s), 42.7 (s), 43.2 (s), 43.8 (s), 58.4 (s), 72.9 (s), 115.2 (d, $J = 17$ Hz), 116.6 (d, $J = 17$ Hz), 122.3 (dd, $J = 3$, 6 Hz), 144.7 (dd, $J = 4$, 4 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.0 (dd, $J = 12$, 247 Hz); MS *m*/*z* (rel intensity) 365 (M$^+$+1; 2), 364 (M$^+$; 6), 332 (28), 194 (11), 193 (17), 179 (32), 153 (12), 140 (36), 137 (23), 135 (16), 127 (75), 123 (18), 121 (13), 109 (20), 97 (11), 95 (52), 93 (13), 81 (100), 67 (82). Found: *m*/*z* 364.2585. Calcd for $C_{23}H_{34}F_2O$: M, 364.2578.

***trans*-1-[*trans*-(3,4-Difluorophenyl)cyclohexyl]-4-(5-methoxypentyl)cyclohexane (13f).** Yield 93% (Method A). A colorless powder. Phase transition temperature/°C: Cr 60 N 122 Iso; $R_f = 0.73$ (hexane : EtOAc = 5 : 1). IR (KBr) 2919, 2851, 1522, 1509, 1489, 1289, 1213, 1117, 945, 837 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.45 (m, 17 H), 1.50—1.62 (m, 2 H), 1.65—1.93 (m, 8 H), 2.39 (tt, $J = 3$, 12 Hz, 1 H), 3.32 (s, 3 H), 3.36 (t, $J = 7$ Hz, 2 H), 6.85—7.07 (m, 3 H); ^{19}F NMR (282 MHz) $\delta = -138.9$—-139.1 (m, 1 F), -142.8—-143.0 (m, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 26.5$ (s), 26.8 (s), 29.7 (s), 30.0 (s), 30.1 (s), 33.5 (s), 34.5 (s), 37.4 (s), 37.8 (s), 42.7 (s), 43.3 (s), 43.8 (s), 58.4 (s), 72.9 (s), 115.3 (d, $J = 17$ Hz), 116.6 (d, $J = 17$ Hz), 122.4 (dd, $J = 3$, 6 Hz), 144.8 (dd, $J = 5$, 5 Hz), 148.4 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 13$, 247 Hz); MS *m*/*z* (rel intensity) 379 (M$^+$+1; 3), 378 (M$^+$; 10), 346 (28), 194 (11), 193 (15), 179 (24), 153 (15), 140 (51), 127 (84), 121 (11), 109 (39), 95 (98), 81 (89), 67 (100). Found: *m*/*z* 378.2741. Calcd for $C_{24}H_{36}F_2O$: M, 378.2734.

***trans*-1-(Methoxymethyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane (14b).** Yield 100% (Method B). A mesomorphic oil. Phase transition temperature/°C: Cr 20 S$_B$ 73 Iso (DSC on 2nd heating); $R_f = 0.62$ (hexane : EtOAc = 10 : 1). IR 2917, 2849, 2737, 2681, 1447, 1379, 1369, 1219, 1140, 1103, 955, 895, 725 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.36 (m, 19 H), 0.88 (t, $J = 7$ Hz, 3 H), 1.42—1.58 (m, 1 H), 1.64—1.84 (m, 8 H), 3.16 (d, $J = 6$ Hz, 2 H), 3.31 (s, 3 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 29.5 (s), 30.1 (s), 30.3 (s), 32.2 (s), 33.6 (s), 37.5 (s), 37.9 (s), 38.3 (s), 43.4 (s), 43.5 (s), 58.8 (s), 78.9 (s); MS *m*/*z* (rel intensity) 280 (M$^+$; 0.5), 248 (28), 219 (18), 123 (10), 19 (11), 97 (30), 96 (27), 95 (100), 83 (34), 82 (17), 81 (49). Found: *m*/*z* 280.2776. Calcd for $C_{19}H_{36}O$: M, 280.2766.

***trans*-1-(2-Methoxyethyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane (14c).** Yield 95% (Method B). A mesomorphic oil; Phase transition temperature/°C: Cr -12 S$_B$ 72 Iso (DSC on 2nd heating); $R_f = 0.48$ (hexane : EtOAc = 10 : 1). IR 2925, 2734, 2681, 1482, 1447, 1387, 1379, 1291, 1273, 1219, 1192, 1117, 992, 970, 895, 725 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.08 (m, 12 H), 1.10—1.38 (m, 10 H), 1.45 (q, $J = 7$ Hz, 2 H), 1.60—1.82 (m, 9 H), 3.32 (s, 3 H), 3.40 (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), 34.8 (s), 37.1 (s), 37.5 (s), 37.9 (s), 43.3 (s), 43.4 (s), 58.5 (s), 70.9 (s); MS *m*/*z* (rel intensity) 294 (M$^+$; 0.3), 262 (38), 233 (5), 151 (13), 111 (18), 110 (26), 109 (77), 108 (19), 97 (36), 83 (36), 81 (40), 69 (43), 67 (100). Found: *m*/*z* 294.2930. Calcd for $C_{20}H_{38}O$: M, 294.2923.

***trans*-1-(3-Methoxypropyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane (14d).** Yield 89% (Method B). A colorless oil. Phase transition temperature/°C: Cr 30 S$_B$ 96 Iso (DSC on 2nd heating); $R_f = 0.61$ (hexane : EtOAc = 5 : 1). IR 2923, 2851, 1717, 1559, 1509, 1458, 1397, 1341, 1123 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.75$—1.36 (m, 22 H), 0.87 (t, $J = 7$ Hz, 3 H), 1.52—1.62 (m, 2 H), 1.64—1.80 (m, 8 H), 3.33 (s, 3 H), 3.34 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.7 (s), 27.1 (s), 30.0 (s), 30.1 (s), 32.2 (s), 33.6 (s), 33.7 (s), 33.8 (s), 37.5 (s), 37.8 (s), 37.9 (s), 43.4 (s), 43.5 (s), 58.5 (s), 73.3 (s); MS *m*/*z* (rel intensity) 308 (M$^+$; 1), 277 (6), 276 (28), 248 (16), 152 (15), 149 (14), 137 (12), 123 (30), 122 (28), 110 (13), 109 (19), 97 (49), 95 (42), 83 (41), 82 (38), 81 (100), 71 (31), 67 (90). Found: *m*/*z* 308.3078. Calcd for $C_{21}H_{40}O$: M, 308.3079.

***trans*-1-(4-Methoxybutyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane (14e).** Yield 82% (Method B). A mesomorphic oil. Phase transition temperature/°C: Cr 7 S$_X$ 9 S$_B$ 97 Iso (DSC on 2nd heating); $R_f = 0.61$ (hexane : EtOAc = 5 : 1). IR 2925, 2734, 1732, 1480, 1447, 1387, 1379, 1219, 1119, 959, 895, 725 cm^{-1}; ^{1}H NMR (200 MHz) $\delta = 0.77$—1.40 (m, 24 H), 0.89 (t, $J = 7$ Hz, 3 H), 1.48—1.59 (m, 2 H), 1.64—1.78 (m, 8 H), 3.33 (s, 3 H), 3.34 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 23.5 (s), 26.7 (s), 29.9 (s), 30.1 (s), 32.2 (s), 33.6 (s), 33.7 (s), 37.3 (s), 37.5 (s), 37.88 (s), 37.93 (s), 43.5 (s), 58.5 (s), 73.0 (s); MS *m*/*z* (rel intensity) 322 (M$^+$; 0.8), 290 (34), 178 (10), 137 (24), 136 (15), 123 (17), 121 (14), 111 (20), 109 (19), 97 (55), 96 (42), 95 (80), 83 (64), 81 (100), 69 (68). Found: *m*/*z* 322.3231. Calcd for $C_{22}H_{42}O$: M, 322.3236.

***trans*-1-(5-Methoxypentyl)-4-(*trans*-4-pentylcyclohexyl)cyclohexane (14f).** Yield 71% (Method B). A mesomorphic oil. Phase transition temperature/°C: Cr 60 S$_B$ 114 Iso (DSC on 2nd heating); $R_f = 0.56$ (hexane : EtOAc = 10 : 1). IR (KBr) 2925, 2735, 1464, 1447, 1393, 1379, 1217, 1192, 1123, 961, 949, 895, 727 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.80$—1.45 (m, 29 H), 1.55—1.80 (m, 12 H), 3.32 (s, 3 H), 3.35 (t, $J = 7$ Hz, 2 H); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s), 26.5 (s), 26.7 (s), 26.9 (s), 29.7 (s), 30.07 (s), 30.09 (s), 32.3 (s), 33.6 (s), 33.7 (s), 37.4 (s), 37.5 (s), 37.8 (s), 37.9 (s), 43.5 (s), 58.5 (s), 72.9 (s); MS *m*/*z* (rel intensity) 337 (M$^+$; 0.2), 305 (22), 304 (97), 234 (22), 233 (22), 194 (19), 178 (11), 151 (78), 150 (68), 137 (39), 123 (27), 121 (26), 109 (100), 108 (26). Found: *m*/*z* 336.3398. Calcd for $C_{23}H_{44}O$: M, 336.3392.

***trans*-1-(Methoxymethyl)-4-[*trans*-4-(3,4,5-trifluorophenyl)cyclohexyl]cyclohexane (24).** This compound was prepared by Method A from *trans*-4-[*trans*-4-(3,4,5-trifluorophenyl)cyclohexyl]cyclohexanemethanol in 93% yield as colorless needles. Phase transition temperature/°C: Cr 74 N 79 Iso (DSC on 2nd heating); $R_f = 0.15$ (hexane). IR (KBr) 2917, 2851, 1617, 1534, 1509, 1456, 1445, 1348, 1235, 1105, 1038, 850 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.86$—1.68 (m, 11 H), 1.72—1.96 (m, 8 H), 2.38 (tt, $J = 3$, 12 Hz, 1 H), 3.18 (d, $J = 6$ Hz, 2 H), 3.30 (s, 3 H), 6.78 (dd, $J = 7$, 9 Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -136.0$ (dd, $J = 9$, 20 Hz, 2 F), -165.4 (dd, $J = 7$, 20 Hz, 1 F); ^{13}C NMR (50.3 MHz) $\delta = 29.5$ (s), 30.0 (s), 30.2 (s), 34.3 (s), 38.2 (s), 42.6 (s), 43.2 (s), 43.9 (s), 58.8

(s), 72.4 (q, $J = 3$ Hz), 110.5 (dd, $J = 7$, 13 Hz), 137.7 (td, $J = 16$, 248 Hz), 144.0 (dt, $J = 7$, 7 Hz), 150.9 (ddd, $J = 4$, 10, 248 Hz); MS *m/z* (rel intensity) 341 ($M^+ + 1$; 1), 340 (M^+; 6), 308 (30), 280 (13), 279 (45), 151 (14), 149 (12), 145 (56), 137 (31), 135 (24), 125 (13), 123 (13), 197 (31), 158 (21), 121 (23), 109 (25), 83 (67), 81 (100), 67 (94). Found: *m/z* 340.2007. Calcd for $C_{20}H_{27}F_3O$: M, 340.2014.

3β-Methoxycholestane (28). Yield 75% (Method A). A colorless solid, mp 86.0—87.3 °C. $R_f = 0.43$ (hexane : EtOAc = 5 : 1). IR (KBr) 2930, 2850, 1472, 1374, 1173, 1106, 944, 929, 770 cm^{-1}; ^{1}H NMR (300 MHz) $\delta = 0.62$—1.99 (m, 46 H), 3.07—3.17 (m, 1 H), 3.34 (s, 3 H); ^{13}C NMR (75.5 MHz) $\delta = 12.1$ (s), 12.2 (s), 18.7 (s), 21.2 (s), 22.5 (s), 22.8 (s), 23.9 (s), 24.2 (s), 27.9 (s), 28.0 (s), 28.3 (s), 28.9 (s), 32.1 (s), 34.4 (s), 35.5 (s), 35.8 (s), 36.2 (s), 37.0 (s), 39.5 (s), 40.1 (s), 42.6 (s), 44.8 (s), 54.4 (s), 55.4 (s), 55.5 (s), 56.3 (s), 56.5 (s), 79.9 (s); MS *m/z* (rel intensity) 404 ($M^+ + 2$; 2), 403 ($M^+ + 1$; 10), 402 (M^+; 35), 387 (16), 355 (16), 262 (19), 248 (53), 216 (41), 215 (100), 201 (14), 179 (31), 161 (16), 149 (23), 147 (32), 138 (17), 135 (27), 121 (46), 107 (70). Found: C, 83.24; H, 12.58%. Calcd for $C_{28}H_{50}O$: C, 83.51; H, 12.51%.

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