Mesomorphic properties of monocyclic troponoids with a semi-fluorinated side group

Akira Mori[a]; Katsuyuki Uno[a]; Hitoshi Takeshita[a]; Shinji Takematsu[b]

[a] Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan [b] Graduate School of Engineering Sciences, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

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AKIRA MORI*†, KATSUYUKI UNO†, HITOSHI TAKESHITA† and SHINJI TAKEMATSU‡

†Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
‡Graduate School of Engineering Sciences, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

Eight types of monocyclic troponoids with alkoxy, acyloxy, and semi-fluorinated side chains were synthesized to investigate their thermal behaviour. They showed smectic A phases. The troponoids with a fluorinated side chain had higher transition temperatures than the corresponding non-fluorinated compounds.

1. Introduction

The introduction of fluorinated segments into conventional calamitic and discotic liquid crystals leads to a significant stabilization of smectic [1] and columnar phases [2] whereas nematic phase stability is reduced. It is known that the van der Waals radius of a fluorine atom is close to that of a hydrogen atom. Also it has a large electronegativity and dipole effect. In the research fields of drugs and liquid crystals, much attention has been paid to the effect of introducing fluorine atoms into the molecules. For example, the introduction of a trifluoromethyl group at the asymmetric centre induced ferroelectricity with a large spontaneous polarizability [3]. Furthermore, fluorine atoms were introduced in lateral positions to generate a lateral dipole, which provided a high dielectric biaxiality in ferroelectric mixtures [4].
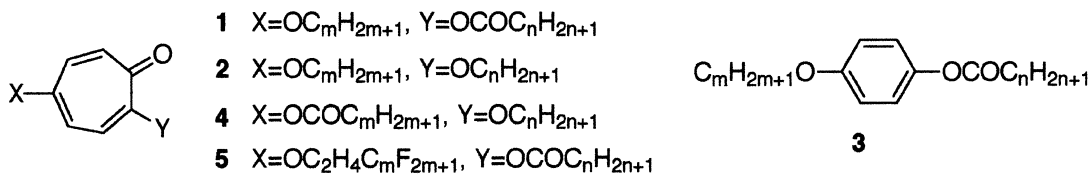
Normally, a single aromatic ring does not constitute a rigid mesogenic core. A fluorinated alkyl group has been introduced onto a single aromatic core to drive the induction of mesophases. In these cases, however, at least one polar substituent was required for mesophase formation [1(*c*),5]. Previously, we have reported that monocyclic 2-acyloxy-5-alkoxytropones (1) exhibit monotropic smectic A (SmA) phases [6, 7]; in this work we observed that the acyl group migrates between the oxygen atom at C-2 and the tropone carbonyl group in mesophases. This is referred to as a [1,9]-sigmatropic rearrangement. We suggested that the [1,9]-sigmatropy provided, on average a linear molecule that played a role in inducing mesomorphic states, because the corresponding non-[1,9]-sigmatropic 2,5-dialkoxytropones (2) [7] and benzenoids (3) [8] are not mesogenic. Later, we observed that non-[1,9]-sigmatropic 5-acyloxy-2-alkoxytropones (4) show virtual SmA phases with transition temperatures comparable to those of compounds 1 [9]. Hence, we concluded that the additional role of the tropone ring increased the polarity of the core, which gives rise to micro-segregation making layer structures feasible. Furthermore, we reported that the mesomorphic properties of monocyclic 2-acyloxy-5-(2-perfluoroalkylethoxy)tropones (5) [10], with a semi-fluorinated side chain at the C-5 position, showed enantiotropic SmA phases with higher thermal stability than the non-fluorinated molecules 1. A fluorinated group acted as a core enhancing the thermal stability of the monocyclic troponoid liquid crystals, and induced structural incompatibility into the molecules [1, 2]. In this paper we report the mesomorphic properties of monocyclic troponoid liquid crystals with a fluorinated side chain.

2. Synthesis

Compounds 5 were synthesized by reaction of 2-(*n*-perfluoroalkyl)ethanol with 2-acyloxy-5-hydroxytropones (6) in the presence of diethyl azodicarboxylate (DEAD) and triphenylphosphine (PPh₃). The ¹H NMR spectra of 5 revealed that the two tropone ring protons appeared as a broad signal due to the [1,9]-sigmatropic rearrangement, being similar to those of the corresponding non-fluorinated compounds [6, 7]. Compounds 7 with a 2-perfluorooctylpropanoyloxy group were synthesized by the reaction of 5-alkoxytropolones (8) with 3-(perfluorooctyl)propanoyl chloride. Compounds

*Corresponding author. Email: mori-a@cm.kyushu-u.ac.jp

1   $X=OC_mH_{2m+1}$, $Y=OCOC_nH_{2n+1}$

2   $X=OC_mH_{2m+1}$, $Y=OC_nH_{2n+1}$

4   $X=OCOC_mH_{2m+1}$, $Y=OC_nH_{2n+1}$

5   $X=OC_2H_4C_mF_{2m+1}$, $Y=OCOC_nH_{2n+1}$

$C_mH_{2m+1}O$—⟨ ⟩—$OCOC_nH_{2n+1}$

3

Structure 1.

9 were synthesized by acylation of 2-perfluoroalkylethoxy-5-hydroxytropones (**10**), which were obtained from hydrolysis of 5-pivaloyloxy-2-perfluoroalkylethoxytropones (**11**). Compounds **11** were prepared by the reaction of 3-(perfluoroalkyl)ethanol with 5-pivaloyloxytropolone (**12**) in the presence of DEAD and PPh₃. Compounds **13** and **14** were obtained by reactions of **8** with 3-(perfluoroalkyl)ethanol, and 2-alkoxy-5-hydroxytropones (**15**) with 3-(perfluoroalkyl)-ethanol, respectively.

3. Mesomorphic properties

3.1. *2-Acyloxy-5-(2-perfluoroalkylethoxy)tropones (5)*

The transition temperature of **5** was determined by differential scanning calorimetry (DSC). The thermal behaviour and microscopic textures were observed using a polarizing microscope equipped with a hot stage. The transition temperatures and enthalpies are summarized in table 1 together with those of compounds **1** [7].

Compounds **5** showed an enantiotropic SmA phase. Increasing the chain length of **5** increased both the melting and clearing points. By comparison, increasing the chain length at the C-2 position reduced the melting and clearing points, as shown in table 1. This behaviour was different from that of the non-fluorinated series; specifically compounds **1** showed that the longer the alkoxy chain, the higher the clearing and melting points [6]. On comparing the transition temperatures of **1** and **5**, it can be seen that the clearing points of **5** are higher by about 70–90°C and the melting points by 30–60°C. These data are in accord with results that semi-fluoroalkyl chains increase the transition temperatures [1 (*b*),11].

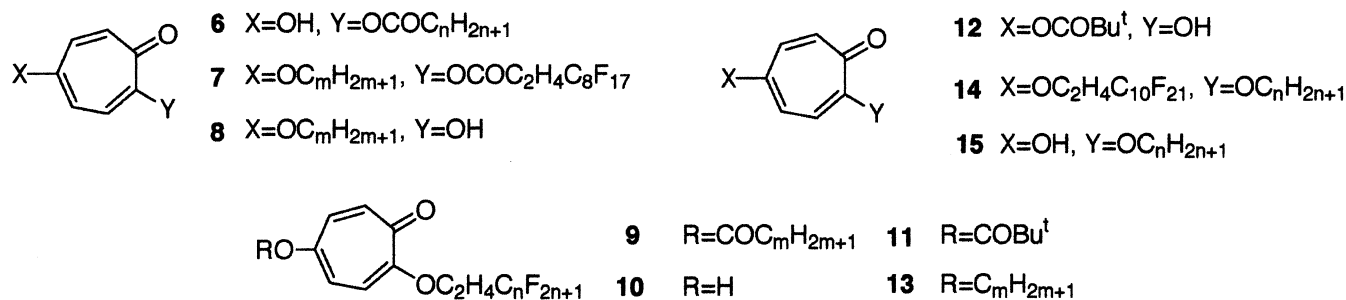### 3.2. *5-Alkoxy-2-[3-(perfluorooctyl)propanoyloxy]-tropones (7)*

Compounds **7** have higher transition temperatures than **1** by 50–60°C, as shown in table 2. As before, the perfluorooctylethyl chain raised the transition temperatures. On comparing the transition temperatures of **5** and **7**, compounds **5** have the higher transition temperatures. The semi-fluorinated segment in the substituent at the C-5 position was more effective in enhancing the thermal stability of the mesophases than that at the C-2 position.

3.3. *5-Acyloxy-2-[2-(perfluoroalkyl)ethoxy]-tropones (9)*

On comparing the transition temperatures of compounds **9** and the non-fluorinated analogues **4** [8, 9], compounds **9** have the higher transition temperatures, as shown in table 3. On comparing the transition temperatures of **9** and **5**, the latter have the higher transition temperatures because compounds **5** have a [1,9]-sigmatropic system.

3.4. *2-(Perfluoroalkylethoxy)-5-alkoxytropones (13) and 2-alkoxy-5-(perfluorodecylethoxy)tropones (14)*

We have reported that 2,5-dialkoxytropones (**2**) are not mesomorphic [7]. We introduced a fluoroalkyl group into compounds **2** to investigate their mesomorphic properties. Compounds **13** showed enantiotropoic SmA phases with lower transition temperatures than the other fluorinated compounds containing an ester group. The ester carbonyl group on the side chain increased the

6   $X=OH$, $Y=OCOC_nH_{2n+1}$

7   $X=OC_mH_{2m+1}$, $Y=OCOC_2H_4C_8F_{17}$

8   $X=OC_mH_{2m+1}$, $Y=OH$

12   $X=OCOBu^t$, $Y=OH$

14   $X=OC_2H_4C_{10}F_{21}$, $Y=OC_nH_{2n+1}$

15   $X=OH$, $Y=OC_nH_{2n+1}$

RO—⟨ ⟩=O, $OC_2H_4C_nF_{2n+1}$

9   $R=COC_mH_{2m+1}$ 11 $R=COBu^t$

10   $R=H$ 13 $R=C_mH_{2m+1}$

Structure 2.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in square brackets, for compounds **1** and **5**.

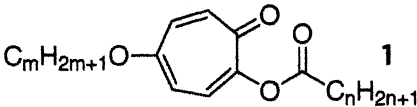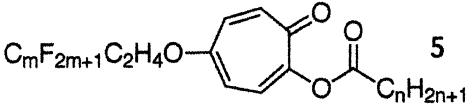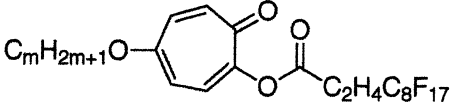| Compound	m	n	Phases

C$_m$H$_{2m+1}$O — **1** — C$_n$H$_{2n+1}$
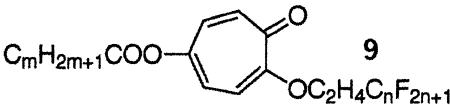
Compound	m	n	Phases
1a	12	9	Cr•48•(SmA•46•)I
1b	12	11	Cr•58•(SmA•45•)I
1c	12	13	Cr•63•(SmA•51•)I
1d	15	7	Cr•41•(SmA•39•)I
1e	15	9	Cr•48•(SmA•47•)I
1f	15	11	Cr•60•(SmA•52•)I
1g	15	13	Cr•67•I
1h	18	7	Cr•49•(SmA•39•)I
1i	18	9	Cr•53•(SmA•46•)I
1j	18	11	Cr•60•(SmA•52•)I
1k	18	13	Cr•72•I

C$_m$F$_{2m+1}$C$_2$H$_4$O — **5** — C$_n$H$_{2n+1}$

Compound	m	n	Phases
5a	6	9	Cr•80[27]•SmA•97[6]•I
5b	6	11	Cr•75[33]•SmA•89[7]•I
5c	8	7	Cr•101[36]•SmA•123[7]•I
5d	8	8	Cr•96[35]•SmA•120[8]•I
5e	8	9	Cr•99[40]•SmA•118[8]•I
5f	8	11	Cr•90[37]•SmA•113[8]•I
5g	10	9	Cr•109[37]•SmA•134[9]•I
5h	10	11	Cr•101[27]•SmA•127[7]•I
5i	10	13	Cr•94[34]•SmA•122[7]•I

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in square brackets, for compound **7**.

C$_m$H$_{2m+1}$O — **7** — C$_2$H$_4$C$_8$F$_{17}$

Compound	m	Phases
7a	8	Cr•107[43]•(SmA•103[7]•)I
7b	10	Cr•102[45]•(SmA•99[7]•)I
7c	12	Cr•95[44]•(SmA•92[9]•)I

melting point more than the clearing point. The transition temperatures of compounds **14** are summarized in table 4. On comparing the transition temperatures of **13** and **14**, those of **14** are higher. In compounds **14**, the semifluorinated part is located along the molecular long axis whereas the semifluorinated part

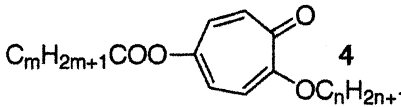Table 3. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in square brackets, for compounds **4** and **9**.

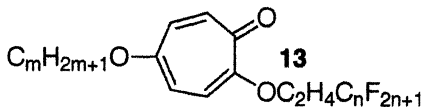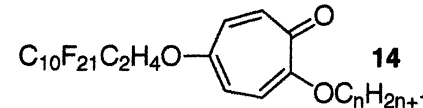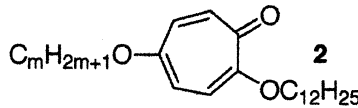| Compound	m	n	Phases

C$_m$H$_{2m+1}$COO — **4** — OC$_n$H$_{2n+1}$

Compound	m	n	Phases
4a	11	8	Cr•54•(SmA•38•)I
4b	11	10	Cr•59•(SmA•45•)I
4c	11	12	Cr•74•(SmA•50•)I
4d	11	14	Cr•80•(SmA•47•)I
4e	14	8	Cr•57•(SmA•36•)I
4f	14	10	Cr•66•(SmA•50•)I
4g	14	12	Cr•73•(SmA•54•)I
4h	17	8	Cr•49•(SmA•41•)I
4i	17	10	Cr•65•(SmA•53•)I
4j	17	12	Cr•75•(SmA•54•)I
4k	17	14	Cr•80•(SmA•57•)I

C$_m$H$_{2m+1}$COO — **9** — OC$_2$H$_4$C$_n$F$_{2n+1}$

Compound	m	n	Phases
9a	7	6	Cr•71•SmA•82•I
9b	9	6	Cr•67[29]•SmA•80[8]•I
9c	17	6	Cr•80•I
9d	7	8	Cr•94[28]•SmA•102[8]•I
9e	9	8	Cr•100[43]•(SmA•99[10]•)I
9f	10	8	Cr•91•SmA•100•I
9g	7	10	Cr•97•SmA•119•I
9h	9	10	Cr•113•SmA•116•I
9i	11	10	Cr•117•(SmA•114•)I
9j	13	10	Cr•108[30]•SmA•114[13]•I

of compounds **15** is off the long molecular axis. This is similar to the behaviour seen for compounds **5** and **7**.

4. Discussion

We have observed that the introduction of a semifluorinated alkyl segment makes it possible to obtain monocyclic liquid crystals with higher transition temperatures. We next synthesized three monocyclic troponoids (**16–18**) with an ester substituent having a perfluorooctylethyl group. When a semifluorinated segment was introduced on the ester group at the C-5 position of compound **4b**, the clearing and melting points of compound **16** were enhanced by 58 and 34°C, respectively. On the other hand, a semifluorinated segment introduced on the alkoxyl group at the C-2 position of compound **4b**, increased the clearing and melting points of compound **9f** by 55 and 32°C, respectively. Thus, the effect of the semifluorinated group on the transition temperatures changed very little in both non-[1,9]-sigmatropic cases.

Table 4. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in square brackets, for compounds **13**, **14** and **2**.

Compound	m	n	Phases

13a	10	8	Cr • 54[21] • SmA • 73[10] • I
13b	10	10	Cr • 49[21] • SmA • 74[10] • I
13c	12	10	Cr • 76 • SmA • 89 • I

14a		8	Cr • 88[32] • SmA • 110[5] • I
14b		10	Cr • 93[43] • SmA • 104[5] • I
14c		12	Cr • 103[53] • (SmA • 99[8] •)I

2a	12		Cr • 63 • I
2b	15		Cr • 63 • I
2c	18		Cr • 64 • I

When a perfluorooctylethoxyl group at the C-2 position of **9f** was replaced by a perfluorooctylpropanoyl group, the clearing point of **17** was increased by 15°C and the melting point decreased by 7°C. Similarly, the clearing point of compound **18** with an acyloxy group at the C-2 position was higher by 16°C and the melting point lower by 24°C than for **16**. This is explained by the effect of the [1,9]-sigmatropy. The introduction of a fluorinated segment into an acyloxy group is quite remarkable. Non-fluorinated 2,5-diacyloxytropones had clearing points around 50–70°C [8],
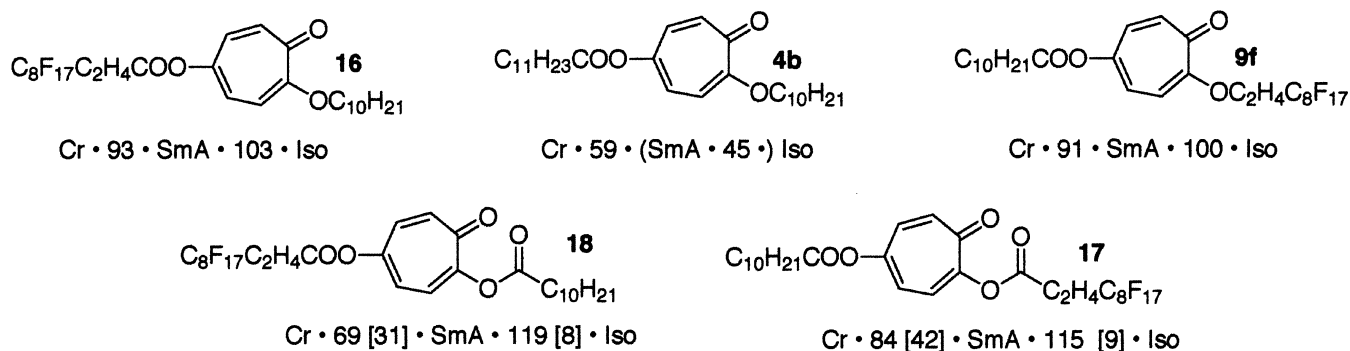
whereas the clearing points of **17** and **18** with a fluorinated segment were around 120°C. The fluorinated segments increased the thermal stability by 50–70°C. When comparing the thermal behaviours of the four sets of molecules **5** and **7**, **13** and **14**, **9f** and **16**, and **17** and **18**, the compounds (**5**, **14**, **16**, and **18**) with a fluorinated segment at the C-5 position had higher transition temperatures than the others (**7**, **13**, **9f**, and **17**). This may be because the fluorinated segment occupied the long molecular axis.

In order to establish the role of the tropone ring, the thermal behaviours of 4-octyloxyphenyl ω-hydroperfluorononanoate (**19**) [12] and compound **7a** were compared, although we note that the fluorinated side chains are not the same. The former is not mesomorphic while the latter has a SmA phase. This is clearly due to the contribution of the tropone ring.
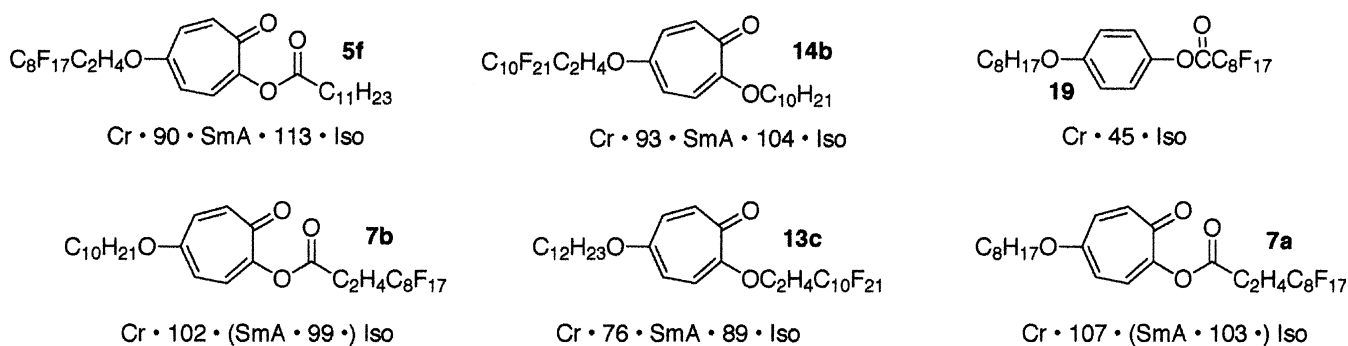
5. Conclusion

We synthesized eight types of monocyclic troponoids with a semifluorinated segment. The introduction of a fluorinated group enhanced the thermal stability of the mesophases, which may be explained by the fact that the fluorinated alkyl groups are rigid and act effectively as cores [1 (*b*)]. We observed that the fluorinated group on the C-5 position was more effective in enhancing the thermal stability of the phases than that on the C-2 position. The former substitution, with the fluorinated alkyl group lying along the long molecular axis promotes a linear molecular shape.

It has been reported that the monocyclic benzenoid **20** [1 (*e*)] with a fluorinated alkyl group on the alkoxy group has a monotropic SmA phase whereas compound **21** shows no mesophase [12]. Comparison of the thermal behaviour between the troponoid and benzenoid with a fluorinated segment illustrates that the presence of the troponoid ring is essential for the induction of mesophases in the monocyclic systems.

Cr • 93 • SmA • 103 • Iso

Cr • 59 • (SmA • 45 •) Iso

Cr • 91 • SmA • 100 • Iso

Cr • 69 [31] • SmA • 119 [8] • Iso

Cr • 84 [42] • SmA • 115 [9] • Iso

Structure 3.

C8F17C2H4O— (tropone ring) —O—C(=O)C11H23 **5f**

Cr • 90 • SmA • 113 • Iso

C10F21C2H4O— (tropone ring) —OC10H21 **14b**

Cr • 93 • SmA • 104 • Iso

C8H17O— (benzene ring) —O—C(=O)C8F17 **19**

Cr • 45 • Iso

C10H21O— (tropone ring) —O—C(=O)C2H4C8F17 **7b**

Cr • 102 • (SmA • 99 •) Iso

C12H23O— (tropone ring) —OC2H4C10F21 **13c**

Cr • 76 • SmA • 89 • Iso

C8H17O— (tropone ring) —O—C(=O)C2H4C8F17 **7a**

Cr • 107 • (SmA • 103 •) Iso

Structure 4.

C8F17C2H4O— (benzene ring) —C(=O)OC12H25 **20**

Cr • 61 • (SmA • 58 •) Iso

C10H21O— (benzene ring) —C(=O)OC2H4C10F21 **21**

Cr • 77 • Iso

Structure 5.

6. Experimental

The melting points and transition temperatures were determined using a differential scanning calorimeter (Seiko DSC 200); the mesomorphic phases were observed by a polarizing microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600 RMS). NMR spectra were measured on Jeol GSX 270H, LA 400, and LA 600 spectrometers in CDCl₃; the chemical shifts are expressed in δ units. The mass spectra were measured with Jeol 01SG-2 and JMS-700 spectrometers. The IR spectra were recorded on a Jasco IR-A102 spectrometer with KBr disks. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

6.1. 2-Acyloxy-5-(2-perfluoroalkylethoxy)tropones (5)

To a THF solution (20 ml) of 2-decanoyloxy-5-hydroxytropone [13] (146 mg, 0.5 mmol), 2-(*n*-perfluoro-hexyl)ethanol (219 mg, 0.6 mmol), and PPh₃ (197 mg, 0.75 mmol) was slowly added a THF solution (2 ml) of DEAD (131 mg, 0.75 mmol). The reaction mixture was stirred at room temperature overnight; it was then poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with water and satd NaCl solution, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give **5a** (75 mg, 24%). **5a:** ^{1}H NMR δ 0.88 (3H, t, *J*=7.5 Hz), 1.27–1.52 (8H, m), 1.76 (2H, m), 2.60 (2H, t, *J*=7.5 Hz), 2.67 (2H, m), 4.24 (2H, t, *J*=6.6 Hz), 6.70 (2H, br s) and 7.15 (2H, d,

J=11.7 Hz); IR (KBr) *v* 2932, 2860, 1758, 1586, 1537, 1390, 1243, 1210, 1185, 1141, 870, 700, and 652 cm^{-1}; calcd for C₂₅H₂₇O₄F₁₃, C 47.03, H 4.26; found, C 46.70, H 4.32%. **5b:** yield 14%; calcd for C₂₇H₃₁O₄F₁₃, C 48.66, H 4.69; found, C 48.64, H 4.76%. **5c:** yield 22%; calcd for C₂₅H₂₃O₄F₁₇, C 42.27, H 3.26; found, C 42.67, H 3.11%. **5d:** yield 28%; calcd for C₂₆H₂₅O₄F₁₇, C 43.11, H 3.48; found, C 43.11, H 3.23%. **5e:** yield 27%; calcd for C₂₇H₂₇O₄F₁₇, C 43.91, H 3.69; found, C 44.05, H 3.76%. **5f:** yield 25%; calcd for C₂₉H₃₁O₄F₁₇, C 45.44, H 4.07; found, C 45.36, H 4.11%. **5g:** yield 25%; calcd for C₂₉H₂₇O₄F₂₁, C 41.54, H 3.25; found, C 41.42, H 3.37%. **5h:** yield 28%; calcd for C₃₁H₃₁O₄F₂₁, C 42.97, H 3.61; found, C 43.04, H 3.17%. **5i:** yield 31%; calcd for C₃₃H₃₅O₄F₂₁, C 44.31, H 3.94; found, C 44.13, H 3.81%.

6.2. 5-Alkoxy-2-[3-(perfluorooctyl)propanoyloxy]-tropones (7)

The potassium salt of 3-(perfluorooctyl)propionic acid (160 mg, 0.3 mmol) was dissolved in 5 ml of water. The solution was acidified with 2M HCl solution and stirred at room temperature for 20 min. The reaction mixture was extracted with AcOEt; the organic layer was washed with water and sat. NaCl solution, then dried over Na₂SO₄ and evaporated under reduced pressure. Thionyl chloride was added to the residue and the reaction mixture heated under reflux for 3 h. Excess thionyl chloride was evaporated under reduced pressure. The prepared acid chloride was added to a THF solution (10 ml) of 5-octyloxytropolone (50 mg,

0.2 mmol) and the reaction mixture was stirred at room temperature overnight. It was poured into 2M HCl solution and extracted with AcOEt; the organic layer was washed with water and satd. NaCl solution, then dried on Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give **7a** (20 mg, 14%). **7a**: ^{1}H NMR δ 0.89 (3H, t, $J=6.8$ Hz), 1.29–1.49 (8H, m), 1.81 (2H, m), 2.61 (2H, t, $J=7.5$ Hz), 2.94 (2H, m), 3.93 (2H, t, $J=6.4$ Hz), 6.70 (2H, br s) and 7.18 (2H, d, $J=12.1$ Hz); calcd for $C_{26}H_{25}O_4F_{17}$, C 44.69, H 3.88; found, C 44.47, H 3.82%. **7b**: yield 29%; calcd for $C_{28}H_{29}O_4F_{17}$, C 43.11, H 3.48; found, C 42.80, H 3.60%. **7c**: yield 30%; calcd for $C_{30}H_{33}O_4F_{17}$, C 46.16, H 4.26; found, C 46.11, H 4.56%.

6.3. 5-Acyloxy-2-[2-(perfluoroalkyl)ethoxy]tropones (9)

To a THF solution (25 ml) of 5-pivaloyloxytropolone [8] (**12**, 222 mg, 1 mmol), 2-(n-perfluorohexyl)ethanol (364 mg, 1 mmol) and PPh$_3$ (260 mg, 1 mmol) was slowly added a THF solution (1 ml) of DEAD (174 mg, 1 mmol) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into 2M HCl solution and extracted with AcOEt; the organic layer was washed with water and satd NaCl solution, then dried over Na_2SO_4, and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give **11**, which was heated under reflux in alkaline aqueous ethanol for 4 h. The reaction mixture was poured into a 2M HCl solution and extracted with ethyl acetate; the organic layer was washed with water and satd NaCl solution and dried with Na_2SO_4. After the solvent was evaporated under reduced pressure, the product was recrystallized with ethyl acetate to give pale yellow crystals of **10** (282 mg, 58%), which was reacted with octanoyl chloride at room temperature overnight. This reaction mixture was poured into a 2M HCl solution and extracted with ethyl acetate. The organic layer was washed with water and satd. NaCl solution and dried with Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue chromatographed on a silica gel column to give pale yellow crystals of **9a** (360 mg, 63%). **9a**: ^{1}H NMR δ 0.88 (3H, t, $J=6.8$ Hz), 1.30–1.52 (8H, m), 1.74 (2H, m), 2.54 (2H, t, $J=7.5$ Hz), 2.79 (2H, m), 4.34 (2H, t, $J=7.1$ Hz), 6.71 (1H, d, $J=10.6$ Hz), 6.77 (1H, dd, $J=10.6$, 2.2 Hz), 7.00 (1H, dd, $J=12.8$, 2.2 Hz) and 7.21 (1H, d, $J=12.8$ Hz); IR 2928, 2856, 1756, 1582, 1506, 1235, 1192, 1165, 858, 701 and 652 cm^{-1}; calcd for $C_{23}H_{23}O_4F_{13}$, C 45.26, H 3.80; found, C 45.57, H 3.81%. **9b**: yield 56%; calcd for $C_{25}H_{27}O_4F_{13}$, C 47.03, H 4.26; found, C 47.11, H 4.36%. **9c**: yield 63%; calcd for $C_{33}H_{43}O_4F_{13}$, C 52.80, H

5.77; found, C 53.14, H 5.66%. **9d**: yield 63%; calcd for $C_{25}H_{23}O_4F_{17}$, C 42.27, H 3.26; found, C 41.91, H 3.72%. **9e**: yield 76%; calcd for $C_{27}H_{27}O_4F_{17}$, C 43.91, H 3.69; found C 44.02, H 3.73%. **9f**: yield 80%; calcd for $C_{28}H_{29}O_4F_{17}$, C 44.69, H 3.88; found, C 44.98, H 4.12%. **9g**: yield 59%; calcd for $C_{29}H_{31}O_4F_{17}$, C 45.44, H 4.08; found, C 45.28, H 3.80%. **9h**: yield 53%; calcd for $C_{27}H_{23}O_4F_{21}$, C 40.02, H 2.86; found, C 39.71, H 2.79%. **9i**: yield 48%; calcd for $C_{29}H_{27}O_4F_{21}$, C 41.54, H 3.25; found, C 41.53, H 3.22%. **9j**: yield 75%; calcd for $C_{31}H_{31}O_4F_{21}$, C 42.97, H 3.61; found, C 43.25, H 3.56%. **9k**: yield 8%; calcd for $C_{33}H_{31}O_4F_{21}$, C 44.31, H 3.94; found, C 44.07, H 3.87%.

6.4. 2-(Perfluoroalkylethoxy)-5-alkoxytropones (13)

To a THF solution (15 ml) of 5-decyloxytropolone (139 mg, 0.5 mmol), 2-(n-perfluorooctyl)ethanol (278 mg, 0.6 mmol) and PPh$_3$ (197 mg, 0.75 mmol), was slowly added a THF solution (2 ml) of DEAD (130 mg, 0.75 mmol) and the reaction mixture was stirred at room temperature overnight. It was poured into 2M HCl solution and extracted with AcOEt; the organic layer was washed with water and satd. NaCl solution, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give **13a** (95 mg, 26%). **13a**: ^{1}H NMR δ 0.88 (3H, t, $J=6.6$ Hz), 1.28–1.53 (14H, m), 1.79 (2H, m), 2.72 (2H, m), 3.89 (2H, t, $J=6.4$ Hz), 4.32 (2H, t, $J=7.1$ Hz), 6.27 (1H, dd, $J=11.0$, 2.6 Hz), 6.89 (1H, d, $J=11.0$ Hz), 7.09 (1H, dd, $J=13.2$, 2.6 Hz) and 7.20 (1H, d, $J=13.2$ Hz); calcd for $C_{27}H_{29}O_3F_{17}$, C 44.76, H 4.03; found, C 44.51, H 4.03%; **13b**: yield 36%; calcd for $C_{29}H_{29}O_3F_{21}$, C 42.25, H 3.55; found, C 42.37, H 3.59%. **13c**: yield 37%; calcd for $C_{31}H_{33}O_3F_{21}$, C 43.67, H 3.90; found, C 43.51, H 3.85%.

6.5. 2-Alkoxy-5-(perfluorodecylethoxy)tropones (14)

To a THF solution (15 ml) of 2-octyloxy-5-hydroxy-tropone (125 mg, 0.5 mmol), 2-(n-perfluorodecyl)ethanol (310 mg, 0.55 mmol), and PPh$_3$ (170 mg, 0.65 mmol) was slowly added a THF solution (2 ml) of DEAD (130 mg, 0.75 mmol) and the reaction mixture was stirred at room temperature overnight. It was then poured into 2M HCl solution and extracted with AcOEt; the organic layer was washed with water and satd. NaCl solution, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give **14a** (30 mg, 8%). **14a**: ^{1}H NMR δ 0.88 (3H, t, $J=6.8$ Hz), 1.28–1.51 (10H, m), 1.88 (2H, m), 2.65 (2H, m), 3.99 (2H, t, $J=7.0$ Hz), 4.20 (2H, t, $J=6.6$ Hz), 6.33 (1H, dd, $J=10.6$, 2.9 Hz), 6.72 (1H, d, $J=10.6$ Hz), 7.05 (1H, dd, $J=13.2$, 2.9 Hz)

and 7.19 (1H, d, $J=13.2$ Hz); calcd for $C_{27}H_{25}O_3F_{21}$, C 40.72, H 3.16; found, C 40.75, H 3.14%. **14b**: yield 11%; calcd for $C_{29}H_{29}O_3F_{21}$, C 42.25, H 3.55; found, C 42.14, H 3.52%. **14c**: yield 11%; calcd for $C_{31}H_{33}O_3F_{21}$, C 43.67, H 3.90; found, C 43.96, H 3.99%.

6.6. *2-Alkoxy-5-[3-(perflurooctyl)propanoyloxy]-tropones (16)*

The potassium salt of 3-(perfluorooctyl)propionic acid (345 mg, 0.65 mmol) was dissolved in 5 ml of water; the solution was acidified with 2M HCl solution and stirred at room temperature for 20 min. The reaction mixture was extracted with AcOEt; the organic layer was washed with water and satd NaCl solution, dried over Na_2SO_4, and evaporated under reduced pressure. Thionyl chloride was added to the residue and the reaction mixture was heated under reflux for 3 h. Excess thionyl chloride was evaporated under reduced pressure. The prepared acid chloride was added to a THF solution (10 ml) of 2-decyloxy-5-hydroxytropone (139 mg, 0.5 mmol) and the reaction mixture was stirred at room temperature overnight. It was then poured into 2M HCl solution and extracted with AcOEt; the organic layer was washed with water and satd. NaCl solution, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give **16** (215 mg, 57%). **16**: ^{1}H NMR δ 0.88 (3H, t, $J=6.6$ Hz), 1.27–1.46 (14H, m), 1.91 (2H, m), 2.58 (2H, m) 2.89 (2H, t, $J=7.7$ Hz), 4.04 (2H, t, $J=6.8$ Hz), 6.62 (1H, d, $J=11.0$ Hz), 6.77 (1H, dd, $J=11.0, 2.6$ Hz), 6.97 (1H, dd, $J=12.8, 2.6$ Hz) and 7.19 (1H, d, $J=12.8$ Hz); calcd for $C_{28}H_{29}O_4F_{17}$, C 44.69, H 3.88; found, C 44.58, H 3.69%.

6.7. *2-[3-(Perflorooctyl)propanoyloxy]-5-undecanoyloxytropone (17)*

By analogy with the preparation of **16**, a THF solution of 5-undecanoyloxytropolone (306 mg, 1.05 mmol) and 3-(perfluorooctyl)propinoyl chloride, obtained from the potassium salt (690 mg, 1.3 mmol) of 3-(perfluorooctyl)propionic acid, was stirred at room temperature overnight. A work-up similar to that described above gave **17** (435 mg, 53%). **17**: ^{1}H NMR δ 0.88 (3H, t, $J=6.6$ Hz), 1.28–1.39 (14H, m), 1.74 (2H, m), 2.55 (2H, m), 2.61 (2H, m), 2.94–3.00 (2H, m), 6.91 (2H, d, $J=12.1$ Hz), 7.20 (2H, d, $J=12.1$ Hz); calcd for $C_{29}H_{29}O_5F_{17}$, C 44.63, H 3.75; found, C 44.63, H 3.77%.

6.8. *2-Undecanoyloxy-5-[3-(perflorooctyl)propanoyloxy]-tropone (18)*

By analogy with the preparation of **16**, a THF solution of 2-undecanoyloxy-5-hydroxytropone (306 mg, 1.05 mmol) and 3-(perfluorooctyl)propionoyl chloride, obtained from the potassium salt (690 mg, 1.3 mmol) of 3-(perfluorooctyl)propionic acid, was stirred at room temperature overnight. A similar work-up to that described above gave **18** (430 mg, 53%). **18**: ^{1}H NMR δ 0.88 (3H, t, $J=6.6$ Hz), 1.27–1.41 (14H, m), 1.76 (2H, m), 2.55 (2H, m), 2.61 (2H, t, $J=7.5$ Hz), 2.91 (2H, t, $J=7.5$ Hz), 6.88 (2H, d, $J=12.1$ Hz), 7.17 (2H, d, $J=12.1$ Hz); calcd for $C_{29}H_{29}O_5F_{17}$, C 44.63, H 3.75; found, C 44.19, H 3.71%.

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