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A comparison of smectic phase induction in a series of isostructural two-ring esters by tail fluorination and tail elongation

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The effectiveness of smectic phase induction in a series of isostructural two-ring nematic esters **1** by chain extension (**2**) or partial fluorination (**3**) of the pentyloxy group was investigated. Results show that the introduction of five fluorine atoms to **1** is more effective than the chain length doubling in suppressing nematic phases in favour of smectic phases in bicyclo[2.2.2]octane (**1B**), cyclohexane (**1C**) and benzene (**1D**) derivatives. Surprisingly, these structural transformations were ineffective in induction of smectic behaviour in the carborane ester **1A**. Both chain modifications, i.e. tail fluorination and chain length doubling, increased the clearing point only for the benzene derivative **1D**.

Keywords: smectic phase induction; two-ring esters; tail fluorination; tail elongation

1. Introduction

Induction of smectic phases (*1, 2*) in nematic mesogens is often accomplished by extending the length of the terminal alkyl chain or by its partial fluorination (*3, 4*). Whereas these methods work well for carbocyclic liquid crystals (*5*) extension of the alkyl chain is completely ineffective for induction of smectic phases in carborane-containing mesogens (*6–9*). Our interest in smectogenic carborane derivatives (*10*) prompted us to explore tail fluorination as means to induce lamellar behaviour in carborane mesogens. Recently, we demonstrated that partial fluorination of the octyloxy chain induced a broad range enantiotropic smectic A (SmA) and monotropic smectic C (SmC) phases in a three-ring carborane derivative (*11*). In another compound, a cholesteric phase was replaced with a monotropic chiral smectic A (SmA*) phase (*10*).

In this paper, we contrast the effectiveness of alkyl chain extension with its partial fluorination in induction of smectic behaviour in series of isostructural derivatives of carborane (**A**) and its carbocyclic analogues **B**–**D** (Figure 1). We focused on the known (*9, 12*) series **1** as convenient models for the study of the effect of structural modifications of the pentyloxy group by alkyl chain length doubling (series **2**) and partial fluorination (series **3**) on mesogenic properties.

Here we describe detailed synthesis, and thermal and optical properties of three series of isostructural mesogens **1**–**3**, and discuss the effectiveness of each method in induction of smectic behaviour as a function of ring *A*.

2. Results and discussion

Synthesis

Compounds **1** and **2** were prepared by esterification of 4-alkoxyphenols with the corresponding carboxylic acid **4** in the presence of DCC and DMAP (Scheme 1). The preparation of esters **3** involved alkylation of phenols **5** with 4,4,5,5,5-pentafluoropentanol under Mitsunobu reaction conditions (Scheme 2). Phenols **5** were prepared from benzyl ethers **6** by reductive removal of the benzyl protecting group (Scheme 2).

Thermal analysis

The transition temperatures and associated enthalpies for compounds in series **1**–**3** are presented in Table 1 and mesogenic properties of intermediates **5** and **6** are shown in Table 2. Phase structures were assigned by comparison of the observed textures with those published for reference compounds and established trends in thermodynamic stability (*13–15*).

All esters **1**–**3** exhibit mesogenic behaviour. The pentyloxyphenyl esters **1** display only nematic phases except for the cyclohexane ester **1C**, which also shows a narrow range SmA phase (*16*). Elongation of the alkoxy chain in **1** by five carbon atoms (alkyl chain length doubling) did not eliminate the nematic behaviour in series **2**, and esters **2A** and **2D** still exhibited exclusively nematic phases. However, the SmA phase of **1C** was significantly enhanced and a smectic B (SmB) phase was induced in **2C**. In the bicyclo[2.2.2]octane-1-carboxylate ester **1B** chain length doubling induced two smectic phases in **2B**, a SmA phase and a monotropic SmC phase.

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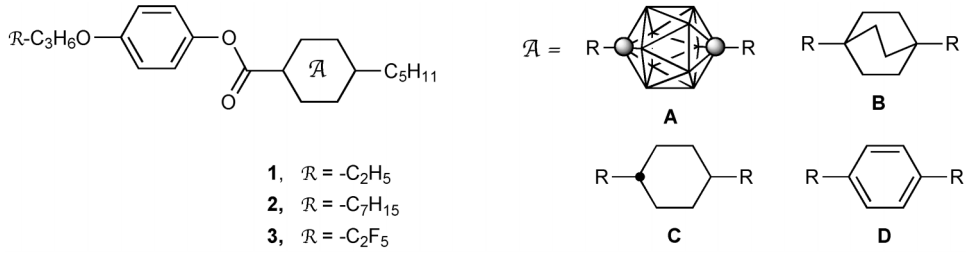


Figure 1. Isostructural derivatives with the four ring systems: 1,12-dicarba-*closo*-dodecaborane (*p*-carborane, **A**), bicyclo[2.2.2]octane (**B**), cyclohexane (**C**) and benzene (**D**). In **A**, each vertex represents a BH fragment and each sphere is a carbon atom.

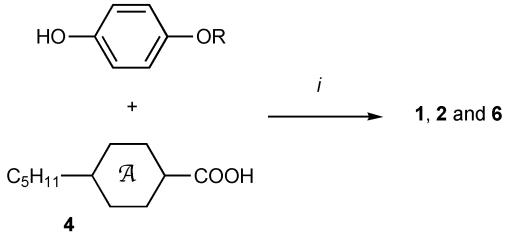
Introduction of five fluorine atoms to the pentyloxy chain in series **1** has a stronger effect on smectic phase induction in the esters than just doubling the chain length. In all three carbocyclic derivatives **1B**–**1D** the nematic phases were completely replaced with SmA phases in the partially fluorinated analogues **3B**–**3D**, and a SmB phase was induced in the cyclohexane derivative **3C**. In contrast, partial fluorination of the carborane derivative **1A** did not induce smectic behaviour in **3A**, and the nematic phase was significantly destabilised. No lamellar phase was found in **3A** even when the sample was supercooled to $-10^{\circ}C$.

Thermal analysis of intermediates **5** and **6** revealed that almost all carbocycles form liquid crystalline phases, while neither of the carborane derivatives, **5A** nor **6A**, display mesogenic behaviour (Table 2). Among the carbocyclic intermediates only phenol **5B** and the benzyloxy derivative **6C** exhibit enantiotropic nematic phases. Other compounds, except for **5D**, display monotropic nematic and also SmA (**6C**) and SmC (**6D**) phases.

3. Discussion and conclusions

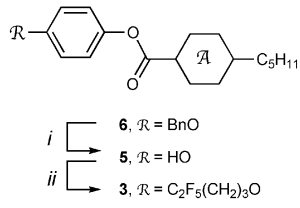
Data collected in Table 1 permit a comparison of the effect of chain fluorination on the structure and stability of the mesophase as a function of the core structure. These results, in turn, can be compared to those obtained for chain elongation (arbitrary chosen to be alkyl chain length doubling). Analysis of the data shows that fluorination is overall much more effective than chain elongation in suppressing nematic behaviour in the carbocyclic derivatives **1B**–**1D**. On the other hand, fluorination has a less favourable effect on the mesophase stability than chain elongation in **1A**–**1C** (Figure 2). Only for benzene derivative **1D** both modifications of the pentyloxy chain, fluorination and elongation, increase the clearing temperature by a few degrees. In cyclohexane **1C** chain doubling increases and in bicyclo[2.2.2]octane **1B** slightly decreases the mesophase stability, while chain fluorination decreases the T_{MI} for both compounds. Overall, the impact of both modifications of the pentyloxy chain on the mesophase stability follows the same trend **D**>**C**>**B**, and the change of the clearing temperature caused by chain doubling appears to be proportional to that resulting from chain fluorination.

The effects of structural changes on mesogenic properties in the carborane derivative **1A** do not follow the trends observed for the carbocyclic analogues **1B**–**1D**. Thus, neither transformation of the pentyloxy chain in **1A** induced smectic behavior. Moreover, while the effect of chain doubling on T_{MI} follows the order **A**~**D**>**C**>**B**, chain fluorination has the most destabilising effect in the series on mesophase stability of carborane **1A**, and the trend follows **D**>**C**>**B**>**A** (Figure 2). The former trend reflects the general tendency of the isotropic transition



i: DCC, DMAP, CH_2Cl_2.

Scheme 1. Synthesis of compounds **1** and **2**.



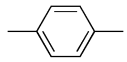
i: H_2/Pt; *ii*: $C_2F_5(CH_2)_3OH$, MeOOCN=NCOOMe, PPh_3, THF.

Scheme 2. Synthesis of compounds **3**.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) for compounds **1**–**3** determined by differential scanning calorimetry (DSC) on heating at 5 K min^{-1} (Cr=crystal; Sm=smectic; N=nematic; I=isotropic).


A

B

C

D

$\mathcal{A}$				
1	Cr 34.1 N 36.1 I[a]	Cr 49.5 N 93.5 I[a]	Cr 34.4 SmA 35.5 N 73.9 I[b] (26.7)[c] (0.5)	Cr 42.8 N 51.8 I[d] (19.3) (0.7)
2	Cr 29.2 N 42.9 I[a] (24.7) (0.8)	Cr 58.4 (SmC 30.5)[e] SmA 71 N 92.5 I[a] (22.2) (0.1) (1.4)	Cr 39.1 SmB 59 SmA 70.6 N 77.5 I (28.0) (3.9) (1.3) (1.6)	Cr 44.2 N 59.4 I[f] (43.1) (1.6)
3	Cr 32.5 (N 11)[e,g] I (16.8)	Cr 45.9 SmA 75.8 I (16.7) (2.8)	Cr 46.5 SmB 51.6 SmA 70.8 I (23.4) (1.9) (4.2)	Cr 40.0 SmA 57.1 I (24.3) (3.7)

[a]Ref. (*9*); [b]Lit. (*16*) Cr 34 SmA 36 N 75 I; Lit. (*12*) Cr 28 N 70 I.; [c]Combined enthalpy of Cr–SmA and SmA–N transitions; [d]Lit. (*17*) Cr 43 N 52 I; [e]Monotropic transition; [f]Lit. (*17*) Cr 49 N 60 I; [g]Microscopic observation.

temperature for asymptotic approach to the limit of about 70°C in long homologous series. The latter trend, however, incidentally is exactly opposite to that of the effective size of ring A (*18*).

Trends observed for 2-ring esters **1** are not general, however. Our recent results obtained for 3-ring mesogens **7** (*11*) and **8** (*10*) (Figure 3) show that, whereas in series **7** the introduction of 13 fluorine atoms to the octyloxy chain stabilises the mesophase in the order **B**~**D**>**A**, chain fluorination in compounds **8** increases the mesophase stability significantly more for the carborane derivative **8A** (71 K) than for the benzene analogue **8D** (55 K). Nevertheless, the findings for series **1** are consistent: induction of smectic phases is less effective in the carborane derivative **7A** than in the biphenyl **7D** upon chain fluorination and the former still exhibits a narrow range nematic phase above the SmA phase (*11*).

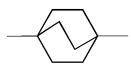
Overall, our results demonstrate that the effect of chain modification on mesogenic properties depends on the core structure and the identity of ring $\mathcal{A}$. Among the four isostructural two-ring derivatives **1A**–**1D**, only the benzene derivative **1D** has increased mesophase stability by both types of chain transformations. Additional examples of isostructural series of mesogens will provide a better understanding of the effect of tail fluorination on mesogenic properties, especially those of carborane derivatives.

4. Experimental section

General procedures

^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz and referenced to the solvent. Elemental analysis was provided by Atlantic Microlab, Norcross, Georgia. Optical microscopy for phase identification was performed using a PZO 'Biolar' polarised microscope equipped with a HCS402 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (1–2 mg) and a typical heating rate of 5 K min^{-1} under a flow of nitrogen gas. For DSC and microscopic analyses, each compound was additionally purified by dissolving in CH_2Cl_2, filtering, and recrystallisation. The resulting crystals were dried in vacuum overnight at ambient temperature.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) for intermediates **5** and **6** determined by DSC on heating at 5 K min^{-1} (Cr=crystal; Sm=smectic; N=nematic; I=isotropic).


A

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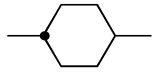
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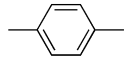

D

$\mathcal{A}$	R				
5	H	Cr 118 I (29.1)	Cr[a] 126 N 137 I (16.1) (2.3)	Cr 115 (N 103)[b] I (32.3) (1.5)	Cr 106 I (31.2)
6	$PhCH_2$	Cr 92 I (35.2)	Cr 120 (N 117)[b] I (43.8) (0.8)	Cr 89 (SmA 74)[b] N 97 I (40.3) (0.2) (0.9)	Cr 98 (SmC 66 N 71)[b] I (41.4) (1.1) (0.7)

[a]Crystalline polymorphs Cr_1 119 Cr_2 (13.5 kJ mol^{-1}); [b]Monotropic transition.

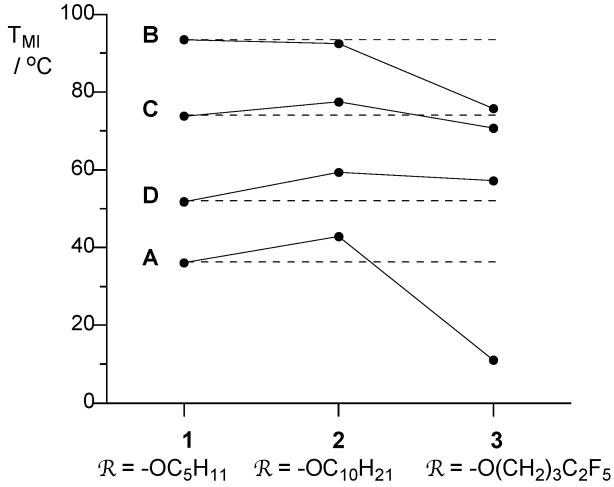


Figure 2. Clearing temperature, T_{MI}, as a function of the structure of the alkoxy chain R. The lines are a guide for the eye.

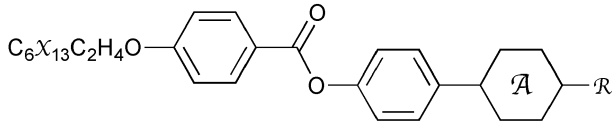
Synthesis

General procedures.

For the preparation of esters **1**, **2** and **6**, a solution of carboxylic acid **1** (1.5 mmol), appropriate 4-substituted phenol (1.5 mmol), DMAP (1.3 mg, 0.06 mmol) and DCC (305 mg, 1.5 mmol) in dry CH_2Cl_2 (20 ml) was stirred in a room temperature for 3 h. The solvent was evaporated and the crude product was passed through a silica gel plug with CH_2Cl_2 (**1** and **2**) or hexane/CH_2Cl_2 (1:1 ratio, **6A**). The crude products were purified by recrystallisation giving the esters in yield >85% as white crystals.

For preparation of esters **3**, a solution of phenol **5** (0.25 mmol), 4,4,5,5,5-pentafluoropentanol (53 mg, 0.25 mmol), PPh_3 (79 mg, 0.30 mmol) and dimethyl azodicarboxylate (44 mg, 0.30 mmol) in dry THF was stirred at room temperature for 24 h and the solvent was evaporated. The product was isolated by column chromatography (hexane/CH_2Cl_2, 1:1) and recrystallisation from iso-octane follow by MeCN to give ester **3** in yields >85% as colourless needles.

For preparation of phenols **5**, benzyloxy derivative **6** was dissolved in ethyl acetate, 5% Pd/charcoal was added and the mixture was stirred under hydrogen atmosphere for 24 h at room temperature.



7, $\mathcal{R}$ = C_5H_{11}

8, $\mathcal{R}$ = $COOCH(CH_3)C_6H_{13}$ $\mathcal{X}$ = H, F; $\mathcal{A}$ = **A**, **B**, **D**

Figure 3. Structure of three-ring analogues **7** and **8**.

The catalyst was filtered off, solvent was evaporated and the crude products were passed through a silica gel plug (CH_2Cl_2,) and recrystallised to give pure phenols **5** in yields >90%.

*4-Pentyloxyphenyl trans-4-pentylcyclohexane-1-carboxylate (12) (**1C**).*

The product (**1C**) was recrystallised from *iso*-PrOH and then iso-octane. ^{1}H NMR: δ 0.89 (t, J=6.7 Hz, 3H), 0.92 (t, J=6.9 Hz, 3H), 0.96–1.05 (m, 2H), 1.14–1.53 (m, 15H), 1.77 (quint, J=7.2 Hz, 2H), 1.86 (brd, J=12.5 Hz, 2H), 2.11 (brd, J=10.8 Hz, 2H), 2.44 (tt, J_1=12.2 Hz, J_2=3.6, 1H), 3.92 (t, J=6.6 Hz, 2H), 6.86 (d, J=9.1 Hz, 2H), 6.95 (d, J=9.0 Hz, 2H).

*4-Pentyloxyphenyl 4-pentylbenzoate (17) (**1D**).*

The product (**1D**) was recrystallised from iso-octane and then MeCN. ^{1}H NMR: δ 0.90 (t, J=6.7 Hz, 3H), 0.94 (t, J=7.0 Hz, 3H), 1.28–1.50 (m, 8H), 1.60–1.70 (m, 2H), 1.79 (quint, J=7.3 Hz, 2H), 2.69 (t, J=7.7 Hz, 2H), 3.96 (t, J=6.6 Hz, 2H), 6.92 (d, J=8.9 Hz, 2H), 7.10 (d, J=8.9 Hz, 2H), 7.32 (d, J=8.1 Hz, 2H), 8.10 (d, J=8.1 Hz, 2H).

*4-Decyloxyphenyl trans-4-pentylcyclohexane-1-carboxylate (**2C**).*

The product (**2C**) was recrystallised from MeCN. ^{1}H NMR: δ 0.88 (t, J=6.8 Hz, 3H), 0.89 (t, J=6.9 Hz, 3H), 0.93–1.03 (m, 2H), 1.15–1.53 (m, 25H), 1.76 (quint, J=7.0 Hz, 2H), 1.87 (brd, J=11.1 Hz, 2H), 2.11 (brd, J=10.8 Hz, 2H), 2.45 (tt, J_1=12.2 Hz, J_2=3.5 Hz, 1H), 3.92 (t, J=6.6 Hz, 2H), 6.86 (d, J=9.1 Hz, 2H), 6.95 (d, J=9.1 Hz, 2H). Elemental analysis: calculated for $C_{28}H_{46}O_3$, C 78.09, H 10.77; found, C 78.03, H 10.95%.

*4-Decyloxyphenyl 4-pentylbenzoate (17) (**2D**).*

The product (**2D**) was recrystallised from hexane and then from iso-octane. ^{1}H NMR: δ 0.89 (t, J=6.9 Hz, 3H), 0.90 (t, J=6.4 Hz, 3H), 1.22–1.50 (m, 18H), 1.66 (quint, J=7.4 Hz, 2H), 1.79 (quint, J=7.3 Hz, 2H), 2.69 (t, J=7.7 Hz, 2H), 3.95 (t, J=6.5 Hz, 2H), 6.92 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.7 Hz, 2H), 7.30 (d, J=8.1 Hz, 2H), 8.10 (d, J=8.0 Hz, 2H).

*4-(4,4,5,5,5-Pentafluoropentyloxy)phenyl 12-pentyl-p-carborane-1-carboxylate (**3A**).*

^{1}H NMR: δ 0.83 (t, J=7.1 Hz, 3H), 1.02–1.28 (m, 6H), 1.63 (pseudo t, J=8.1 Hz, 2H), 1.5–3.5 (brm, 10H), 2.00–2.10 (m, 2H), 2.15–2.35 (m, 2H), 3.98 (t, J=5.8 Hz, 2H), 6.81 (d, J=9.2 Hz, 2H), 6.88 (d,

J=9.2 Hz, 2H). Elemental analysis: calculated for $C_{19}H_{31}B_{10}F_5O_3$, C 44.70, H 6.12; found, C 44.96, H 6.24%.

*4-(4,4,5,5,5-Pentafluoropentyloxy)phenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**3B**).*

^{1}H NMR: δ 0.88 (t, J=7.0 Hz, 3H), 1.06–1.38 (m, 8H), 1.44 (pseudo t, J=7.9 Hz, 6H), 1.90 (pseudo t, J=8.0 Hz, 6H), 2.02-2.12 (m, 2H), 2.17–2.37 (m, 2H), 4.00 (t, J=5.9 Hz, 2H), 6.85 (d, J=9.1 Hz, 2H), 6.94 (d, J=9.1 Hz, 2H). Elemental analysis: calculated for $C_{25}H_{35}F_5O_3$, C 63.01, H 6.98; found, C 63.24, H 7.06%.

*4-(4,4,5,5,5-Pentafluoropentyloxy)phenyl trans-4-pentylcyclohexane-1-carboxylate (**3C**).*

^{1}H NMR: δ 0.89 (t, J=6.9 Hz, 3H), 0.92–1.02 (m, 2H), 1.13–1.38 (m, 11H), 1.87 (brd, J=12.6 Hz, 2H), 2.02–2.38 (m, 8H), 2.45 (tt, J_1=12.2 Hz, J_2=3.4 Hz, 1H), 4.00 (t, J=5.8 Hz, 2H), 6.86 (d, J=9.0 Hz, 2H), 6.97 (d, J=9.1 Hz, 2H). Elemental analysis: calculated for $C_{23}H_{31}F_5O_3$, C 61.32, H 6.94; found, C 61.16, H 6.96%.

*4-(4,4,5,5,5-Pentafluoropentyloxy)phenyl 4-pentylbenzoate (**3D**).*

^{1}H NMR: δ 0.90 (t, J=6.5 Hz, 3H), 1.30-1.38 (m, 4H), 1.66 (quint, J=7.4 Hz, 2H), 2.05–2.15 (m, 2H), 2.18–2.38 (m, 2H), 2.69 (t, J=7.6 Hz, 2H), 4.04 (t, J=5.8 Hz, 2H), 6.92 (d, J=8.1 Hz, 2H), 7.12 (d, J=8.1 Hz, 2H), 7.31 (d, J=7.9 Hz, 2H), 8.10 (d, J=7.4 Hz, 2H). Elemental analysis: calculated for $C_{23}H_{25}F_5O_3$, C 62.12, H 5.67; found, C 62.31, H 5.70%.

*4-Hydroxyphenyl 12-pentyl-p-carborane-1-carboxylate (**5A**).*

The product (**5A**) was recrystallised from iso-octane/toluene mixture and then from EtOH (needles). ^{1}H NMR: δ 0.83 (t, J=7.1 Hz, 3H), 1.00–1.25 (m, 6H), 1.5–3.5 (brm, 10H), 1.62 (pseudo t, J=7.1 Hz, 2H), 4.80 (s, 1H), 6.75 (d, J=9.1 Hz, 2H), 6.82 (d, J=8.9 Hz, 2H). Elemental analysis: calculated for $C_{14}H_{26}B_{10}O_3$, C 47.98, H 7.47; found, C 47.85, H 7.45%.

*4-Hydroxyphenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**5B**).*

The product (**5B**) was recrystallised from iso-octane/toluene mixture and EtOH (needles). ^{1}H NMR: δ 0.90 (t, J=7.0 Hz, 3H), 1.05–1.38 (m, 8H), 1.45 (pseudo t, J=7.9 Hz, 6H), 1.92 (pseudo t, J=7.9 Hz, 6H), 4.87 (s, 1H), 6.77 (d, J=9.0 Hz, 2H), 6.88 (d, J=9.0 Hz, 2H). Elemental analysis: calculated for $C_{20}H_{28}O_3$, C 75.91, H 8.92; found, C 75.80, H 8.96%.

*4-Hydroxyphenyl trans-4-pentylcyclohexane-1-carboxylate (**5C**).*

The product (**5C**) was recrystallised from iso-octane/toluene mixture (plates). ^{1}H NMR: δ 0.89 (t, J=6.7 Hz, 3H), 0.92–1.06 (m, 2H), 1.14–1.38 (m, 9H), 1.45–1.60 (m, 2H), 1.86 (brd, J=13.8 Hz, 2H), 2.11 (brd, J=13.8 Hz, 2H), 2.45 (tt, J_1=12.2 Hz, J_2=3.5 Hz, 1H), 4.96 (s, 1H), 6.76 (d, J=9.0 Hz, 2H), 6.89 (d, J=8.9 Hz, 2H). Elemental analysis: calculated for $C_{18}H_{26}O_3$, C 74.45, H 9.02; found, C 74.48, H 9.19%.

*4-Hydroxyphenyl 4-pentylbenzoate (**5D**).*

The product (**5D**) was recrystallised from iso-octane/toluene mixture (plates). ^{1}H NMR: δ 0.90 (t, J=6.7 Hz, 3H), 1.25–1.43 (m, 4H), 1.66 (quint, J=7.4 Hz, 2H), 2.70 (t, J=7.7 Hz, 2H), 5.01 (s, 1H), 6.83 (d, J=8.9 Hz, 2H), 7.05 (d, J=8.9 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H), 8.10 (d, J=8.3 Hz, 2H). Elemental analysis: calculated for $C_{18}H_{20}O_3$, C 76.03, H 7.09; found, C 76.19, H 7.06%.

*4-Benzyloxyphenyl 12-pentyl-p-carborane-1-carboxylate (**6A**).*

The product (**6A**) was recrystallised from MeCN. ^{1}H NMR: δ 0.81 (t, J=7.1 Hz, 3H), 1.00–1.28 (m, 6H), 1.5–3.5 (brm, 10H), 1.62 (pseudo t, J=7.9 Hz, 2H), 5.02 (s, 2H), 6.85–6.90 (m, 4H), 7.31–7.45 (m, 5H). Elemental analysis: calculated for $C_{21}H_{32}B_{10}O_3$, C 57.25, H 7.32; found, C 57.26, H 7.26%.

*4-Benzyloxyphenyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**6B**).*

A mixture of acid **4B** (577 mg, 3.0 mmol), PCl_5 (1.1 eq, 687 mg) and dry CCl_4 (10 ml) was refluxed for 3 h. The solvent and the volatiles were evaporated, the resulting crude acid chloride was dissolved in dry CCl_4 (10 ml), 4-benzyloxyphenol (600 mg, 3 mmol) was added and the mixture was refluxed for 3 h. The solvent was evaporated, the resulting crude product was passed through a SiO_2 plug (CH_2Cl_2) and purified by recrystallisation from hexane (2 ×) and then from iso-octane giving 780 mg (64% yield) of ester **6B** as white flakes. ^{1}H NMR: δ 0.88 (t, J=7.0 Hz, 3H), 1.06–1.38 (m, 8H), 1.43 (pseudo t, J=7.9 Hz, 6H), 1.90 (pseudo t, J=7.8 Hz, 6H), 5.04 (s, 2H), 6.94 (s, 4H), 7.30–7.46 (m, 5H). Elemental analysis: calculated for $C_{27}H_{34}O_3$, C 79.76, H 8.43; found, C 79.52, H 8.51%.

*4-Benzyloxyphenyl trans-4-pentylcyclohexane-1-carboxylate (**6C**).*

The product (**6C**) was recrystallised from MeCN (flakes). ^{1}H NMR: δ 0.89 (t, J=6.9 Hz, 3H), 0.92–1.06 (m, 2H), 1.15–1.38 (m, 9H), 1.46–1.63 (m, 2H), 1.89 (brd, J=13.4 Hz, 2H), 2.14 (brd, J=13.3 Hz, 2H), 2.47 (tt, J_1=12.2 Hz, J_2=3.5 Hz, 1H), 5.06 (s, 2H), 6.92–7.00 (m, 4H), 7.30–7.46 (m, 5H). Elemental analysis: calculated for $C_{25}H_{32}O_3$, C 78.91, H 8.48; found, C 79.19, H 8.51%.

*4-Benzyloxyphenyl 4-pentylbenzoate (**6D**).*

The product (**6D**) was recrystallised from iso-octane/toluene mixture (flakes). ^{1}H NMR: δ 0.90 (t, J=6.9 Hz, 3H), 1.30–1.48 (m, 4H), 1.66 (quint, J=7.5 Hz, 2H), 2.69 (t, J=7.7 Hz, 2H), 5.08 (s, 2H), 7.00 (d, J=9.0 Hz, 2H), 7.12 (d, J=9.0 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 7.32–7.48 (m, 5H), 8.10 (d, J=8.2 Hz, 2H). Elemental analysis: calculated for $C_{25}H_{26}O_3$, C 80.18, H 7.00; found, C 79.74, H 7.02%.

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