Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online Publication Date: 01 July 2008

To cite this Article Nagamine, Takashi, Januszko, Adam, Ohta, Kiminori, Kaszynski, Piotr and Endo, Yasuyuki(2008)'The effect of the linking group on mesogenic properties of three-ring derivatives of p-carborane and biphenyl',Liquid Crystals,35:7,865 — 884
To link to this Article: DOI: 10.1080/02678290802245450
URL: http://dx.doi.org/10.1080/02678290802245450

Liquid Crystals,
Vol. 35, No. 7, July 2008, 865–884

The effect of the linking group on mesogenic properties of three-ring derivatives of *p*-carborane and biphenyl

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(Received 5 May 2008; final form 3 June 2008)

Four series of mesogenic derivatives of *p*-carborane (series **A[0]** and **A[1]**) and their benzene analogues (series **B[0]** and **B[1]**) with variable linking groups $\mathcal{L}$ were prepared and investigated for phase behaviour. The data allowed a comparison of the effect of the group $\mathcal{L}$ on the mesophase stability as a function of the adjacent ring (carborane or benzene), the variable central ring (carborane or benzene), and the presence of an oxygen atom in the terminal chain. The results showed that substitution of carborane for a benzene ring in **B[m]** depresses the clearing point by 50 K to 208 K and eliminates all smectic behaviour in **A[m]**. The carborane derivatives **A[m]** are weakly dependent (effectiveness of $\mathcal{L}$: –CH=CHCOO–~–COO–~–CH=CH–>–CH=N–~–CH_2CH_2–>–CONH–), whereas the benzene analogues **B[m]** are strongly dependent (effectiveness of $\mathcal{L}$: –CONH–>–CH=CH–>–CH=N–~–CH=CHCOO–>–COO–>–CH_2CH_2–) on the structure of the linking group $\mathcal{L}$. The difference in the effectiveness of the amide group on mesophase stability (ΔT_I=208 K) has been attributed to the stabilizing intermolecular H-bonding in **B[m]**, which is prevented in **A[m]** by steric and electronic effects of the carborane cage on the carbonyl group.

Keywords: carborane mesogens; synthesis; structure–property analysis

1. Introduction

The structure of a classical mesogen consists of two or more rings connected by a linking group $\mathcal{L}$ and substituted with terminal alkyl chains (*1–3*) (Figure 1). The linking group typically is a small fragment that has a significant impact on mesogenic properties of the compound through its conformational properties, rigidity, polarity, electronic structure and ability to form H-bonds. These effects are moderated by the nature of the rings connected by the linking group, especially by their electronic and steric properties.

Previous comparative studies for two-ring benzene derivatives (*3–5*) considered the effect of up to eight different linking groups $\mathcal{L}$, whereas for the cyclohexane-benzene (*3*) and cyclohexane-cyclohexane derivatives (*6*) the variety of the $\mathcal{L}$ group was smaller. It was concluded that aromatic rings typically prefer unsaturated linking groups that allow for the extension of electronic conjugation, whereas the saturated cyclohexane rings are more compatible with the saturated dimethylene linker and the ester group.

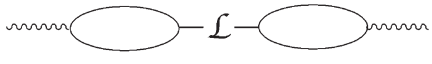

Figure 1. A schematic structure of a typical calamitic mesogen.

p-Carborane (**A**, Figure 2) is a relatively large nearly spherical σ-aromatic inorganic cluster with fivefold rotational axes (*7*). Our interest in understanding the structure–property relationships in liquid crystalline derivatives of *p*-carborane (*8–20*) led us to investigate the impact of the linking group $\mathcal{L}$ connected directly to the carborane fragment on mesogenic behaviour. Therefore, we focused on a series of three-ring derivatives of *p*-carborane **1A–7A** and their benzene structural analogues **1B–7B**.

In this paper, the synthesis and characterisation are reported of two series of mesogenic derivatives of *p*-carborane (**A[0]** and **A[1]**) and two series of their benzene analogues (**B[0]** and **B[1]**, Figure 2). Each

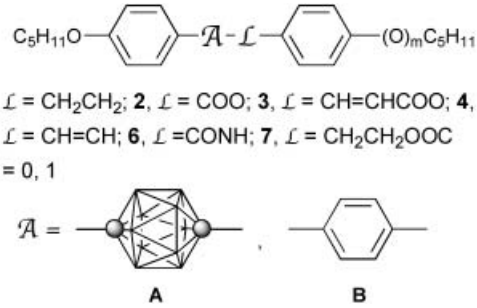

Figure 2. Molecular structures of mesogens **1–7** and structural units $\mathcal{A}$ and $\mathcal{L}$. In the structure **A** (*p*-carborane) each vertex represents a BH fragment and each sphere is a carbon atom.

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290802245450
http://www.informaworld.com

series consists of seven compounds containing different linking group $\mathcal{L}$. Analysis of the data allows for the comparison of the effectiveness of the linking group $\mathcal{L}$ in the mesophase stabilisation in the carborane (**A[m]**) and benzene (**B[m]**) series, effectiveness of the carborane in promoting mesogenic behaviour relative to the benzene analogues and the effect of incorporation of oxygen between the terminal chain and the benzene ring in both series of mesogens **A** and **B**.

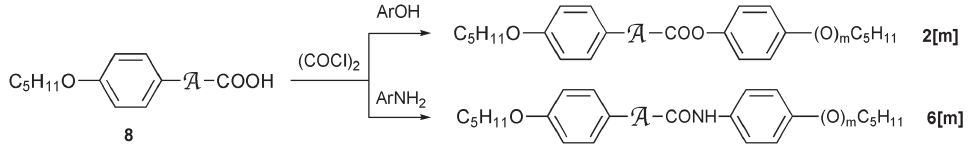
2. Results

Synthesis

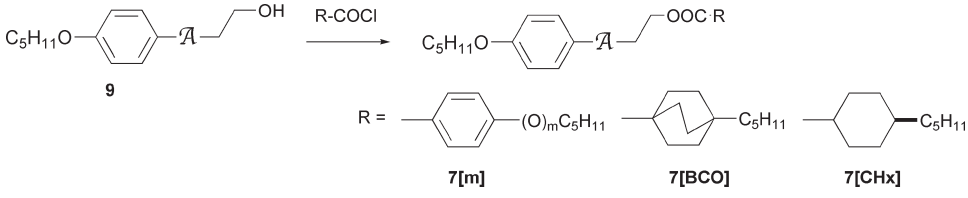
The synthesis of liquid crystalline derivatives **1–7** is shown in Schemes 1–5. Esters **2[1]** were obtained from carboxylic acids **8A** (*17*) and **8B** following the procedure described earlier for the synthesis of esters **2[0]** (*17*). Reaction of acid chlorides derived from **8** with 4-pentylanilline or 4-pentyloxyaniline gave the corresponding amides **6[0]** and **6[1]**, respectively (Scheme 1).

Esters **7[m]** were obtained from alcohols **9** (Scheme 2). In addition to the benzoates **7[m]**, alcohol **9A** was esterified with 4-pentylbicyclo[2.2.2]octane-1-carboxylic and 4-pentylcyclohexanecarboxylic acids to give the corresponding esters **7A[BCO]** and **7A[CHx]**.

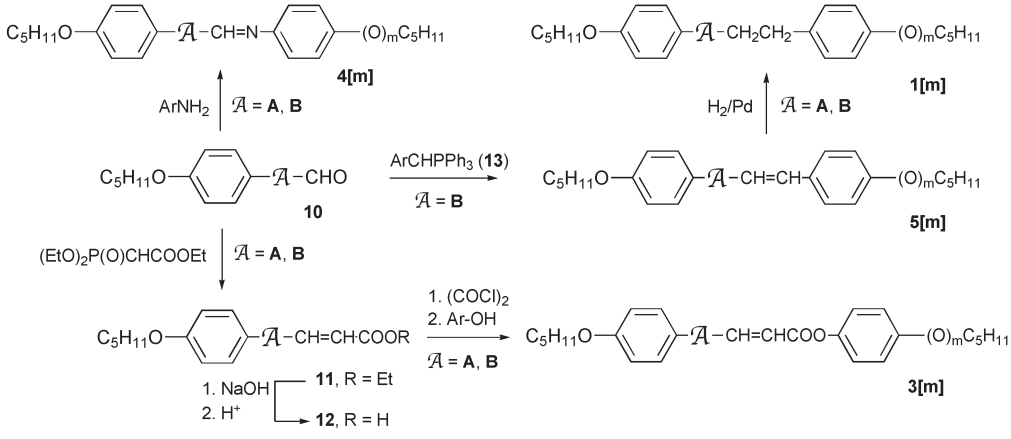
The remaining compounds in the series were prepared from aldehydes **10A** and **10B** using typical procedures shown in Scheme 3. Thus, condensation of aldehyde **10** with appropriate anilines gave Schiff bases **4[m]**. A Horner–Emmons (*21*) reaction of aldehyde **10** gave a good yield of the corresponding ethyl *E*-propenoate **11**, which was hydrolysed to the corresponding acid **12**. The acid was converted to the corresponding acid chloride and reacted with 4-pentylphenol and 4-pentyloxyphenol to give the corresponding esters **3[0]** and **3[1]**, respectively. The Wittig reaction of aldehyde **10B** with phosphorane **13[m]**, derived from the corresponding phosphonium salt **14[m]**, gave a mixture of *E* and *Z* isomers in approximately 1:1 ratio. The desired *trans* isomer **5B[m]** was isolated from the mixture by chromatography and crystallisation. Hydrogenation of **5[m]** gave derivatives **1[m]** in nearly quantitative yields.



Scheme 1. Synthesis of esters **2[m]** and the corresponding amides **6[m]**.

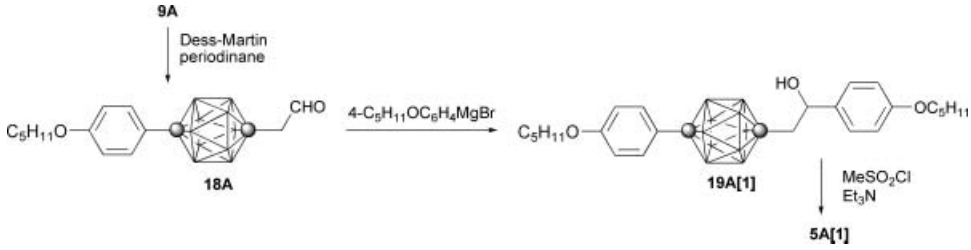


Scheme 2. Synthesis of esters **7[m]**, **7A[BCO]** and **7A[CHx]**.

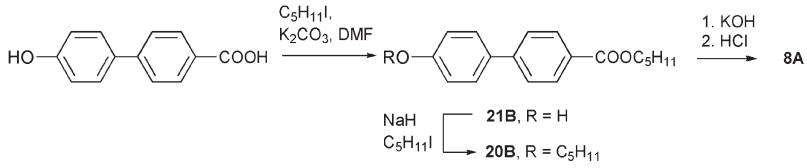


Scheme 3. Synthesis of Schiff bases **4[m]**, esters **3[m]** and derivatives **1[m]**.

Scheme 4. Synthesis of olefin **5A[0]**.



Scheme 5. Synthesis of olefin **5A[1]**.



Scheme 6. Synthesis of of carboxylic acid **8A**.

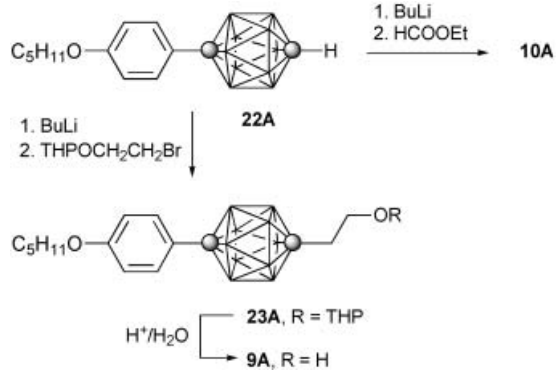
Olefin **5A[m]** could not be prepared from aldehyde **10A** and phosphorane **13[m]**; under the Witting reaction conditions the aldehyde was decarbonylated. Therefore, **5A[0]** was prepared in a three-step procedure starting with addition of a Grignard reagent derived from benzyl bromide **15[0]** to aldehyde **10A** (Scheme 4). The resulting alcohol **16A[0]** was converted to methanesulfonate **17A[0]**, which was treated with a base (DBU) to form olefin **5A[0]** in an overall yield of 35%.

A similar approach to the preparation of olefin **5A[1]** using a Grignard reagent derived from **15[1]** did not work well. Therefore, the preparation of olefin **5A[1]** was accomplished by addition of a Grignard reagent prepared from 1-bromo-4-pentyloxybenzene to aldehyde **18A**, which was prepared by Dess–Martin oxidation (*22*) of alcohol **9A** (Scheme 5). The resulting alcohol **19A[1]** was converted to **5A[1]** by treatment with $MeSO_2Cl$ in the presence of a base.

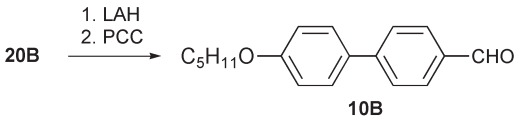
The preparation of carboxylic acid **8A** was reported recently (*17*). The known acid **8B** (*23*) was obtained by alkylation of 4′-hydroxybiphenyl-4-carboxylic acid and subsequent hydrolysis of the resulting pentyl ester **20B** (Scheme 6). Initial alkylation of the hydroxy acid in DMF using K_2CO_3 as a base gave mostly the hydroxy ester **21B** and the desired ester **20B** was formed as a minor product. Therefore, **21B** was separated and alkylated in the presence of NaH giving a good overall yield of ester **20B**.

Aldehyde **10A** was obtained directly from carborane derivative **22A** (*17*) by reacting its lithium salt with ethyl formate (Scheme 7). Biphenyl aldehyde **10B** was prepared from ester **20B** by reduction with LAH followed by oxidation with PCC (Scheme 8).

The preparation of 2-substituted ethanol **9A** was accomplished starting from carborane **22A**, which was alkylated with THP-protected 2-bromoethanol (Scheme 7). The resulting derivative **23A** was deprotected under mild acidic conditions to give the



Scheme 7. Synthesis of aldehyde **10A**, 2-substituted ethanol **9A** and derivative **23A**.



Scheme 8. Synthesis of biphenyl aldehyde **10B**.

substituted ethanol in 32% overall yield. The biphenyl analogue **9B** was obtained from the known bromobiphenyl **24B**, which was first converted into the more reactive iodide **25B**. The iodide was reacted with diethyl malonate under Buchwald conditions (*24*), under which the initially formed arylmalonate ester underwent decarboxylation to form the acetate **26B**, which was isolated in 54% overall yield (Scheme 9). Reduction of **26B** gave the desired alcohol **9B**.

Phosphonium salts **14[0]** (*25*) and **14[1]** were prepared from benzyl halides **15[0]** and **15[1]** and PPh_3 (Scheme 10). The halides were obtained from the corresponding benzyl alcohols **27[m]**, which were prepared from the analogous carboxylic acids by LAH reduction.

Mesogenic properties

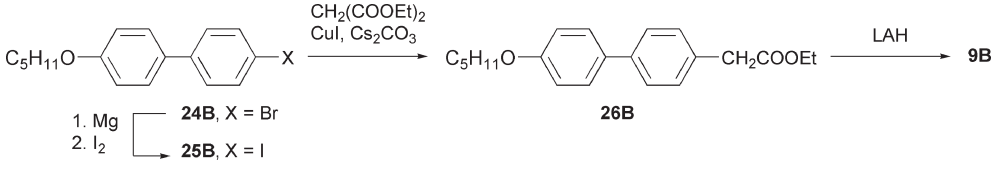
Phase transition temperatures and enthalpies for series **1–7** are shown in Table 1 and for selected intermediates in Table 2. The phase type was assigned by comparison of microscopic textures observed using a birefractive setup with those published for reference compounds and established trends in thermodynamic stability (*26–28*).

In general, carborane derivatives in both series exhibit exclusively a nematic phase. The only exceptions are the derivatives **7A** with the four-atom long linking group $\mathcal{L}$=–CH_2CH_2OOC–, which show no mesogenic behavior even upon supercooling by 30–50 K. In contrast, the biphenyl derivatives **1B–7B** exhibit nematic and smectic phases.

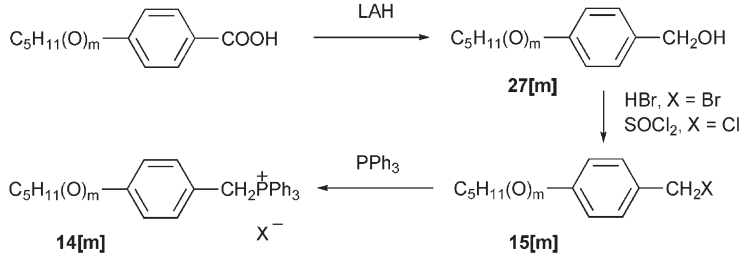
Derivatives **1B[0]** and **1B[1]** ($\mathcal{L}$=–CH_2CH_2–) exhibit only a soft crystalline phase E, amides **6B[0]** and **6B[1]** exclusively smectic A (SmA) phases and **7B[1]** ($\mathcal{L}$=–CH_2CH_2OOC–) has only a nematic phase. Other compounds exhibit rich smectic polymorphism in addition to nematic phases. Particularly interesting in this respect is Schiff base **4B[1]**. Thermal (Table 1, Figure 3) and optical analysis (Figure 4) revealed four smectic and one soft crystalline phases in addition to a nematic phase. The observed rare sequence of phases (G-F-I-C-A-N) is similar to that reported (*30*) for **28** (G-J-F-I-C-A-N, Figure 5), an analogue of **2B**. Similarly rich polymorphism was detected in ethene derivative **5B[1]** ($\mathcal{L}$=–CH=CH–), which shows several poorly resolved transitions clustered around 250°C.

Analysis of the data in Table 1 shows that the nematic–isotropic transition temperature, T_{NI}, for carborane derivatives **1A[m]–5A[m]** weakly depends on the structure of the linking group $\mathcal{L}$ and the average T_{NI} value for the m=0 series is 109±9°C and for m=1 is 132±8°C. This indicates that the insertion of an oxygen atom to the structure in series m=0 results in an average increase of the T_{NI} by 22±2 K in series m=1 (Figure 6). The amides **6A[0]** and **6A[1]** clearly stand out from this series. Their isotropic transitions are significantly lower than the average T_{NI} value (by 56 K for m=0 and 41 K for m=1) and the difference ΔT_{NI} between **6A[0]** and **6A[1]** is nearly twice bigger than for the remaining members of the series.

In contrast to carborane derivatives, isotropic transition temperatures, T_I, for all biphenyls **1B[m]–6B[m]** strongly depend on the structure of the linking group $\mathcal{L}$ (Figure 6). In the series m=0, the lowest T_I value of 158°C is observed for the ethane derivative

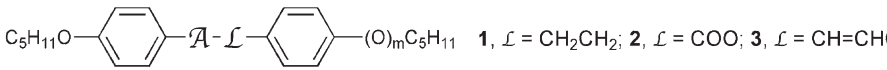


Scheme 9. Synthesis of biphenyl analogue **9B**.

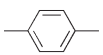
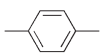


Scheme 10. Synthesis of phosphonium salts **14[m]**.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) for mesogens **1–7**).

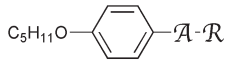


1, $\mathcal{L}$ = CH_2CH_2; **2**, $\mathcal{L}$ = COO; **3**, $\mathcal{L}$ = CH=CHCOO; **4**, $\mathcal{L}$ = CH=N; **5**, $\mathcal{L}$ = CH=CH; **6**, $\mathcal{L}$ =CONH; **7**, $\mathcal{L}$ = CH_2CH_2OOC

	m=0		m=1	
$\mathcal{A}$	 **A**	 **B**	 **A**	 **B**
1	Cr 80 N 102 I (25.2) (2.4)	Cr_1 49 Cr_2 81 E 158 I (1.3) (22.6) (19.9)	Cr_1 60 Cr_2 94 N 123 I (20.9) (30.6) (2.4)	Cr 118 E 173 I (26.6) (21.1)
2	Cr 60 N 117 I[a] (29.6) (1.7)	Cr 104 (SmB 95) SmA 188 N 203 I[a] (23.7) (2.1) (2.2) (1.3)	Cr 62 N 137 I (30.4) (1.6)	Cr 120 (SmB 111) SmC 124 SmA 201 N 220 I (32.7) (1.9) (0.3) (1.9) (1.4)
3	Cr 86 N 117 I (39.3) (2.1)	Cr 82 SmB 144 SmA 234 N 245 I (11.2) (3.2) (2.7) (1.6)	Cr 106 N 140 I (34.9) (2.3)	Cr 112 SmB 153 SmA 244 N 259 I (25.6) (3.6) (2.3) (1.8)
4	Cr 91 N 98 I (28.0) (2.3)	Cr 75 E 120 G 157 SmB 192 SmA 230 N 236 I (19.6) (0.9) (0.2) (5.0) (4.1) (1.6)	Cr 98 N 123 I (44.2) (2.3)	Cr[b] 163 G 173 SmF 182 SmI 203 SmC 216 SmA 242 N 254 I (23.3) (0.0) (0.1) (5.0) (0.1) (3.4) (1.7)
5	Cr 96 N 113 I (30.2) (2.2)	Cr_1 63 Cr_2 131 E 239 SmA 265 N 267 I (2.3) (10.8) (14.3) (5.7) (1.1)	Cr 124 N 135 I (54.3) (2.1)	Cr 72 X 209 G 254[c] SmC 258 SmA 281 N 285 I (7.7) (5.4) (11.8) (0.0) (4.4) (1.4)
6	Cr 93 (N 52)[d] I (45.4)	Cr 207 SmA 260 I (35.4) (10.3)	Cr 94 (N 91) I (46.7) (1.1)	Cr 211 SmA 277 I (35.9) (10.0)
7	Cr 106 I[e] (41.1)	Cr 87 (G 76 SmC 78) N 111 I (26.7) (2.0) (1.7) (6.0)	Cr 114 I[e] (48.5)	Cr 114 N 126 I[f] (40.3) (5.3)

[a]Lit. (*17*). [b]A crystal–crystal transition was observed at 79°C (11.5 kJ mol^{-1}). [c]On cooling, two additional transitions were observed at 253°C and 252°C. [d]Microscopic observations. [e]The isotropic phase supercools by about 50 K and crystallises. [f]The nematic phase supercools to 90°C and crystallises.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) for selected intermediates.



	$\mathcal{RA}$	A	B
8	COOH	Cr 197 I [a]	Cr 227.5 SmA 229.5 N 275 I [b]
11	CH=CHCOOEt	Cr 49 I [c]	Cr 68 E 167 SmA 183 I
12	CH=CHCOOH	Cr 196 (N 188) I	Cr 246 N 288 I (dec)
18	$COOC_5H_{11}$	[d]	Cr 76 SmA 86 I [e]

[a]Lit. (*17*). [b]Lit. (*23*). [c]No mesophase upon supercooling to −20°C. [d]Not investigated. [e]Lit. (*29*) Cr 77.0 SmA 86.7 I.

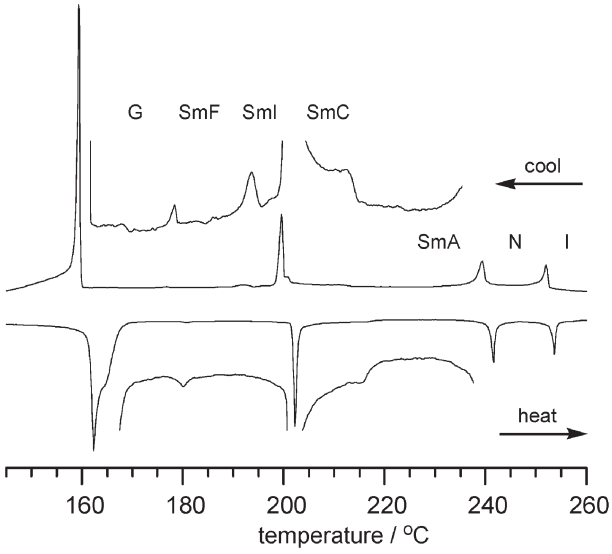
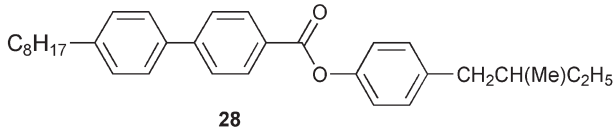


Figure 3. Partial heating (lower trace) and cooling (upper trace) DSC curves for **4B[1]** recorded at a scanning rate of 5 K min^{-1}.

1B[0], whereas the highest clearing point of 267°C is found for the ethene derivative **5B[0]**. The extension of the terminal pentyl group in the structure in series m=0 by an oxygen atom resulted in an average increase of T_I value by 16.5 ± 1.6°C in series m=1 (Figure 6).

A comparison of the clearing temperatures for pairs of isostructural derivatives shows that all carborane derivatives destabilize the mesophase relative to the benzene analogues, and that this destabilisation is greater by 6 ± 2 K (excluding **6[m]**) for series m=0 than for the oxygen-containing mesogens (m=1, Figure 7). Moreover, the degree of mesophase destabilisation strongly depends on the nature of the linking group $\mathcal{L}$. The smallest difference



28

Figure 5. Structure of compound **28**, an analogue of **2B**.

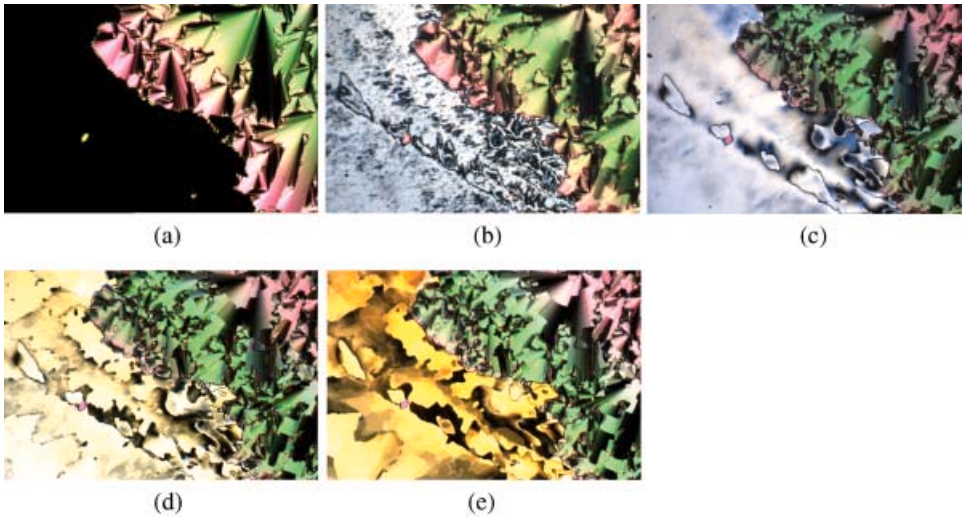


Figure 4. Natural textures observed in polarised light for **4B[1]** in the same sample region and identified as (a) SmA phase (230°C), (b) SmC phase (210°C), (c) SmI phase (190°C), (d) SmF phase (177°C) and (e) G phase (168°C). Magnification 60×.

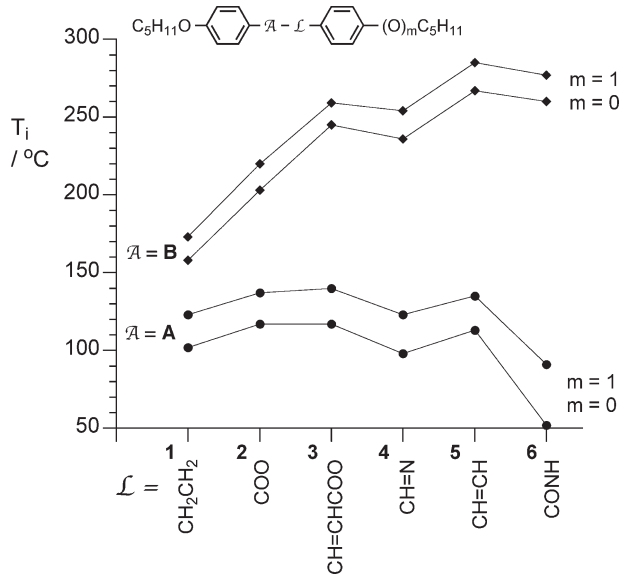


Figure 6. A plot of clearing temperatures T_I for two series of carborane mesogens **A[m]** (circles) and two series of biphenyl mesogens **B[m]** (diamonds). The lines are guides for the eye.

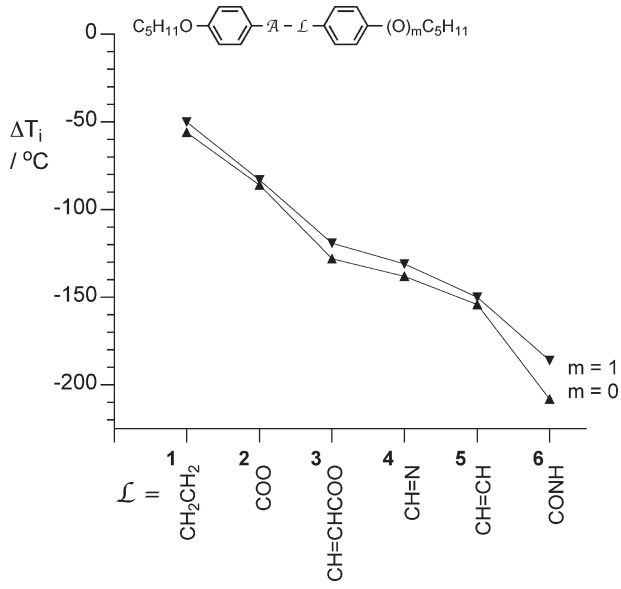


Figure 7. A plot of the difference between clearing temperatures for carborane mesogens and their benzene analogues [$\Delta T_I = T_I(A) - T_I(B)$]. The lines are guides for the eye.

in T_I of -50 K is observed for the dimethylene derivatives **1[1]** ($\mathcal{L}$=–CH_2CH_2–) and the largest of -208 K for the amides **6[0]** ($\mathcal{L}$=–CONH–).

3. Discussion and conclusions

Experimental data collected in Tables 1–2 show that the substitution of *p*-carborane for a benzene ring in the rigid core destabilises mesophases and eliminates smectic phases. This is consistent with results of our other studies of isostructural series of mesogens (*8–20*), and has been ascribed to the difference in the rotational symmetry of the two rings (fivefold for **A** vs. twofold for **B**) and consequently in conformational flexibility of their derivatives.

In agreement with our previous results (*13, 15*) a larger increase in mesophase stability for *p*-carborane derivatives as compared to the benzene analogues is observed upon replacement of the terminal alkyl with an alkoxy chain. The origin of this additional stabilization is not clear, but it may be related to the stronger quadrupolar intermolecular interactions between the carborane cage and the alkoxyphenyl ring as compared to that of the alkylphenyl ring.

The data in Table 1 and in Figure 6 demonstrate qualitative (order) and quantitative (magnitude) differences between the effectiveness of the linking groups $\mathcal{L}$ in mesophase stabilisation in the carborane derivatives **A[m]** and their biphenyl analogues **B[m]**. In the latter series, the order of the effectiveness (–CH=CH–>–CONH–>–CH=N–~–CH=CHCOO–>–COO–>–CH_2CH_2–>–CH_2CH_2OCO–) is in general agreement with results for simple two-ring benzene derivatives **I** and **II** (*3–5*) (Figure 8), and the clearing temperatures T_I span about 150 K. This order reflects the importance of rigidity and the

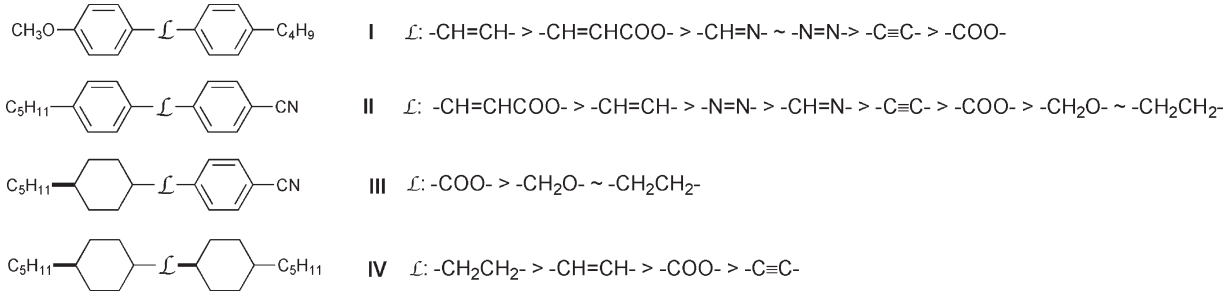
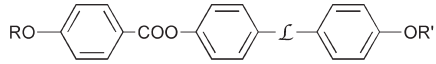


Figure 8. A comparison of the linking group $\mathcal{L}$ effectiveness on mesophase stability in four series of mesogens: **I** (*5, 31*), **II** (*3, 32*), **III** (*3*) and **IV** (*6*).

electronic interactions of the linking group with aromatic rings. In contrast, in the carborane series **A[m]** the order of the group $\mathcal{L}$ effectiveness is different (–CH=CHCOO–~–COO–~–CH=CH–>–CH=N–~–CH_2CH_2–>–CONH–>–CH_2CH_2OCO–), and the range of temperatures T_I in the series is much smaller, about one-third of that found in biphenyls **B[m]**. This indicates that the strong steric and electronic interactions present in the biphenyl mesogens are largely absent, and that the choice of the linking group $\mathcal{L}$ is much less critical for the mesophase stability in the carborane derivatives than in the benzene mesogens. The weakest Ar–$\mathcal{L}$ electronic interactions exist for the saturated linking groups $\mathcal{L}$ such as –CH_2CH_2– and –CH_2O– and these compounds typically have low stability mesophases. In contrast, for saturated and weakly interacting rings, these two linking groups and also –COO– give rise to relatively stable mesophases, as evident from a comparison in cyclohexane–benzene and cyclohexane–cyclohexane derivatives **III** and **IV** (*3, 6*) (Figure 8).

The original analysis (*3–5*) of series **I** and **II** included only four out of seven groups $\mathcal{L}$ used in the present studies. A literature search showed that the acrylate group, $\mathcal{L}$=–CH=CHCOO–, is very effective in stabilisation of the nematic phase in series **I** (*31*) and **II** (*32*), whereas in series **B[m]** its effectiveness is moderate and comparable to that of the azomethine group. This can be ascribed to the relatively large contribution of the acrylate group to the molecular anisometry in the two ring compounds **I** and **II**, whereas in the biphenyls **B[m]** this contribution is relatively smaller. The significance of the linking group rigidity and extended electronic interactions are clearly apparent from a comparison of the two groups $\mathcal{L}$ –CH=CHCOO– and –CH_2CH_2OCO–. Reduction of the double bond in the acrylate increases the molecular flexibility, which in turn results in the depression of the clearing temperature by over 130 K. Evidence for this increased flexibility is provided by the unusually high enthalpy of over 5 kJ mol^{-1} measured for the N–I transition in derivatives **7B[m]**. This enthalpy, which is nearly four times higher than a typical value, corresponds to a large entropy change and can be rationalised by large conformational changes at the phase transition due to excessive molecular flexibility of the derivatives.

The amido group, $\mathcal{L}$=–CONH–, is unique among the linking groups. Its geometry is similar to that of an ester group, but unlike it the amido group is a H-bond donor and capable of forming strong hydrogen bonds. Scant literature data (*33*) allows for limited comparison of the two linking groups. A series of 17 pairs of diesters **29** (*34*) and amido esters **30** (*35, 36*) (Figure 9), and also several other pairs of compounds



29, $\mathcal{L}$ = OCO
30, $\mathcal{L}$ = NHCO

Figure 9. Structure of diesters **29** (*34*) and amido esters **30** (*35, 36*).

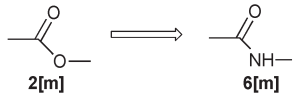
(*37*) demonstrate that the amido group increases both the melting and clearing points and preferentially stabilizes the smectic phases of the mesogen relative to the corresponding esters. Recent FTIR and X-ray diffraction investigation revealed the existence of intermolecular H-bonding in smectic phases of mesogenic amides that stabilise the lamellar-type molecular arrangements (*38*).

Similar behaviour is observed in the series **B[m]**. The replacement of the ester group in **2B** with the amido group in **6B** increases the melting point by about 100 K and the T_I by 57 K, and eliminates the nematic phase in favour of smectic behavior (Table 3). In contrast, the same replacement of the linking groups in the carborane series has completely opposite effect: whereas the melting point is higher by a modest 30 K, the T_I is dramatically depressed by 46 K (m=1) and 65 K (m=0) and no smectic phases are induced.

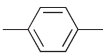
This counterintuitive result can be attributed to the inability of the carborane derivatives **6A** to form effective intermolecular H-bonds due to steric and electronic effects of the carborane on the carbonyl group. Thus, it can postulated that the steric bulk of the carborane prevents the close approach of the two molecules, and the moderate electron withdrawing character of the carborane group (σ_p=0.14) (*39*) lowers the nucleophilicity (H-bond accepting ability) of the carbonyl group. For a better understanding of these effects, we performed comparative computational studies of two anilides **31A** and **31B** as models for amides **6A** and **6B**, respectively (*40, 41*).

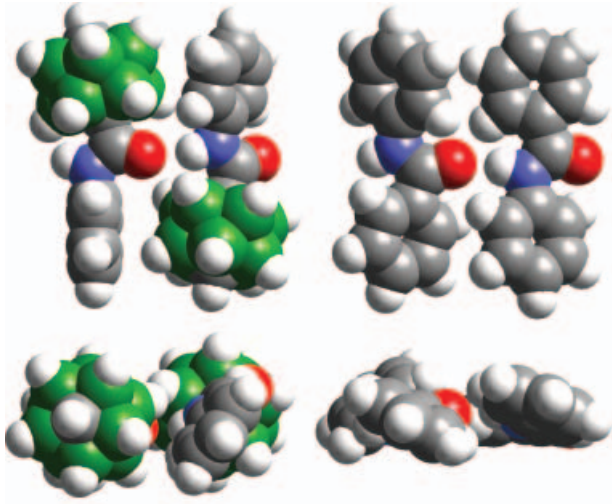
Ab initio calculations for two molecules constrained at the antiparallel orientation demonstrated that the formation of H-bonded dimer is moderately

Table 3. Change of clearing temperature upon linking group replacement.



2[m] ⟹ **6[m]**

$\mathcal{A}$/ΔT_I	m=0	m=1
A 	+57 K	+57 K
B 	−65 K	−46 K



	31A	31B
ΔSCF	–1.4 kcal/mol	–9.7 kcal/mol
$d_{H\cdots O}$	2.282 Å	2.197 Å
$d_{N\cdots O}$	3.212 Å	3.158 Å
μ	7.7 D	9.1 D

Figure 10. Two views (top and bottom) of molecular models for dimers of *N*-phenylcarborane-1-carboxamide (**31A**) and benzanilide (**31B**) obtained by geometry optimisation at the HF/3-21(d) level of theory. The relative orientation of the molecules in the dimers is constrained at antiparallel (the angle defined by **C**–**C**(=O)···**C**(=O)–**C** is set at 180°). The dimerisation energy is calculated as the ΔSCF.

exothermic by 9.3 kcal mol^{-1} for benzanilide (**31B**), whereas for the carborane derivative **31A** the dimerisation is only weakly favorable (Figure 10). The calculated lower stability of about 8 kcal mol^{-1} is accompanied by about 0.08 Å longer H···O distances in the carborane dimer **31A** than in the benzanilide dimer. In both dimers, the closest non-bonding separations correspond to the sum of van der Waals radii (*42*).

Removing the constraint for the antiparallel alignment allows for the full geometry optimization of the dimers and the formation of tighter hydrogen bonds. The molecules are rotated by 74° and 60° in the free dimers of **31A** and **31B**, respectively, and the H···O distance falls by 0.13 Å for the former and 0.16 Å for benzanilide. This geometry change results in stabilisation of the dimers **31A** and **31B** by 7.5 kcal mol^{-1} and 3.8 kcal mol^{-1}, respectively.

Overall, the computational results confirm the lower tendency toward the H-bond formation in the carborane amides than in benzanilides. The separation of the NH and O=C groups of the neighbouring molecules is nearly 0.1 Å larger and the stabilisation energy at least 4.5 kcal mol^{-1} lower for the carborane anilide than for the benzene analogue. This, in part, is a consequence of the large size of the carborane cluster, and, in part, the lower nucleophilicity of the carbonyl group. Calculations demonstrate that the van der Waals radius of the carborane is about 3.7 Å, whereas the "half-thickness" of the benzene ring is 1.75 Å. At the same time the charge density on the carbonyl oxygen atom is slightly lower ($q=-0.61$) in the isolated molecules of carborane amide **31A** than in benzanilide ($q=-0.64$).

The computed structures for the benzanilide dimer are consistent with solid-state structures for **31B** (*43*) and some of its simple derivatives (*44, 45*) in which molecules form infinite H-bonded chains. In some crystallographic modifications molecules are nearly parallel in the crystal lattice, and in some others long molecular axes form a substantial angle. Calculations demonstrate that these molecular arrangements should be relatively close in energy and hence benzanilides can achieve molecular alignments that are compatible with liquid crystalline phases. In contrast, significant stability in the carborane anilide dimer is gained only for nearly orthogonal arrangement of the molecules, which is incompatible with molecular alignments in typical liquid crystalline phases. These differences in molecular interactions and arrangement in the two amides are presumably the reason for the opposite effects of the substitution of the amido group for an ester group in **2**, as shown in Table 3. Whereas the exchange of the groups in the benzene derivatives **2B[m]** leads to phase stabilisation, presumably due to the formation of nearly parallel H-bonded chains, the strong driving force for angular arrangements of molecules in the carborane anilides destabilizes the mesophase. Incorporation of an oxygen atom to the terminal chain in **6A[1]** provides an alternative more sterically accessible H acceptor and partially alleviates the negative effect of the amido group.

Overall, the experimental data demonstrates that *p*-carborane is a bulky structural unit, which interacts with the linking groups in a similar way to a saturated system such as cyclohexane. As a consequence, the choice of the linking group $\mathcal{L}$ has a relatively small impact on mesogenic properties of the compound. However, the bulk of the *p*-carborane strongly affects the effectiveness of the amido group in stabilisation of the mesophases by discouraging the formation of the H-bonds.

4. Experimental section

Materials and characterisation

^{1}H NMR: spectra were obtained at 270 MHz in $CDCl_3$ and referenced to TMS, unless stated otherwise. ^{13}C NMR: spectra were obtained at 67.8 MHz in $CDCl_3$.

Elemental analysis was provided by Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University or at Atlantic Microlab, GA. *p*-Carborane was purchased from Katchem s.r.o. (Prague, Czech Republic).

Optical microscopy and 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 heating rate of 5 K min^{-1} under a flow of nitrogen gas. For DSC and microscopic analyses, each compound was additionally purified by filtration of CH_2Cl_2 solutions to remove particles. The solutions were subsequently evaporated and the products were recrystallised from isooctane or toluene/isooctane mixture. The resulting crystals were dried in vacuum overnight at ambient temperature.

Transition temperatures for compounds **1–7** and some of their mesogenic intermediates are given in Tables 1 and 2. Melting points for other compounds are listed in the synthesis section.

Synthesis

*1-(4-Pentyloxyphenyl)-12-[2-(4-pentylphenyl)ethyl]-p-carborane (**1A[0]**).*

Olefin **5A[0]** was hydrogenated at room temperature in a EtOH/AcOEt mixture in the presence of 10%Pd–C. After 12 h the mixture was filtrated through a Celite pad. The filtrate was concentrated to give crude product, which was purified by silica gel column chromatography (hexane). The resulting solid was recrystallised ($EtOH/CH_2Cl_2$) to give 71% yield of **1A[0]** as colourless needles. ^{1}H NMR: δ 0.87 (t, *J*=6.9 Hz, 3H), 0.91 (t, *J*=7.2 Hz, 3H), 1.20–1.45 (m, 8H), 1.50–3.75 (br m, 10H), 1.56 (quint, *J*=7.0 Hz, 2H), 1.73 (quint, *J*=6.8 Hz, 2H), 1.89–1.96 (m, 2H), 2.34–2.46 (m, 2H), 2.53 (t, *J*=7.7 Hz, 2H), 3.87 (t, *J*=6.5 Hz, 2H), 6.66 (d, *J*=8.9 Hz, 2H), 6.94 (d, *J*=8.1 Hz, 2H), 7.05 (d, *J*=8.4 Hz, 2H), 7.10 (d, *J*=8.9 Hz, 2H). ^{13}C NMR: δ 14.11, 14.16, 22.5, 22.6, 28.2, 28.9, 31.3, 31.6, 35.4, 35.5, 39.7, 67.9, 79.9, 81.2, 113.6, 127.9, 128.2, 128.4, 137.1, 140.7, 159.0. MS: *m/z* 480 (M^+), 161 (100%). HRMS: *m/z* calculated for $C_{26}H_{44}B_{10}O$, 480.4395; found 480.4391. Elemental analysis: calculated for $C_{26}H_{44}B_{10}O$, C 64.96, H 9.23; found, C 65.02, H 9.14%.

*1-(4-Pentyloxyphenyl)-12-[2-(4-pentyloxyphenyl)-ethyl]-p-carborane (**1A[1]**).*

It was obtained from **5A[1]** in 96% yield as colourless needles ($EtOH/CH_2Cl_2$) following the procedure for **1A[0]**. ^{1}H NMR: δ 0.91 (t, *J*=7.1 Hz, 3H), 0.92 (t, *J*=7.1 Hz, 3H), 1.25–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.73 (quint, *J*=6.8 Hz, 2H), 1.75 (quint, *J*=6.9 Hz, 2H), 1.86–1.94 (m, 2H), 2.36–2.40 (m, 2H), 3.87 (t, *J*=6.6 Hz, 2H), 3.89 (t, *J*=6.6 Hz, 2H), 6.66 (d, *J*=9.0 Hz, 2H), 6.77 (d, *J*=8.7 Hz, 2H), 6.94 (d, *J*=8.7 Hz, 2H), 7.10 (d, *J*=8.9 Hz, 2H). ^{13}C NMR: δ 13.97, 13.99, 22.39, 22.44, 28.1, 28.2, 28.8, 29.0, 34.8, 39.8, 67.95, 68.14, 79.8, 81.2, 113.7, 114.5, 128.3, 128.5, 129.0, 132.0, 157.6, 159.1. MS: *m/z* 496 (M^+), 107 (100%). Elemental analysis: calculated for $C_{26}H_{44}B_{10}O_2$, C 62.87, H 8.93; found, C 62.71, H 8.86%.

*4-Pentyloxy-4′-[2-(4-pentylphenyl)ethyl]biphenyl (**1B[0]**).*

It was obtained from **5B[0]** in a quantitative yield as a colourless solid after purification by silica gel column chromatography (hexane/AcOEt, 50/1) as described for **1A[0]**. ^{1}H NMR: δ 0.89 (t, *J*=6.8 Hz, 3H), 0.94 (t, *J*=7.0 Hz, 3H), 1.24–1.52 (m, 8H), 1.58 (quint, *J*=7.5 Hz, 2H), 1.81 (quint, *J*=6.9 Hz, 2H), 2.58 (t, *J*=7.7 Hz, 2H), 2.92 (s, 4H), 3.99 (t, *J*=6.6 Hz, 2H), 6.95 (d, *J*=8.9 Hz, 2H), 7.08–7.16 (m, 4H), 7.24 (d, *J*=8.6 Hz, 2H), 7.47 (d, *J*=8.1 Hz, 2H), 7.50 (d, *J*=8.9 Hz, 2H). ^{13}C NMR: δ 14.0, 22.5, 22.6, 28.2, 29.0, 31.3, 31.5, 35.5, 37.5, 37.6, 68.0, 114.7, 126.6, 127.9, 128.3, 128.4, 128.8, 133.4, 138.5, 138.9, 140.4, 140.5, 158.5. MS: *m/z* 414 (M^+), 253 (100 %). Elemental analysis: calculated for $C_{30}H_{38}O$, C 86.90, H 9.24; found, C 86.64, H 9.05%.

*4-Pentyloxy-4′-[2-(4-pentyloxyphenyl)ethyl]biphenyl (**1B[1]**).*

It was obtained from **5B[1]** in 95% yield as a colourless solid after purification by silica gel column chromatography (hexane/AcOEt, 50/1) as described for **1A[0]**. ^{1}H NMR: δ 0.93 (t, *J*=7.0 Hz, 3H), 0.94 (t, *J*=7.2 Hz, 3H), 1.30–1.52 (m, 8H), 1.78 (quint, *J*=7.3 Hz, 2H), 1.81 (quint, *J*=7.4 Hz, 2H), 2.90 (s, 4H), 3.93 (t, *J*=6.6 Hz, 2H), 3.99 (t, *J*=6.5 Hz, 2H), 6.82 (d, *J*=8.4 Hz, 2H), 6.96 (d, *J*=8.6 Hz, 2H), 7.10 (d, *J*=8.1 Hz, 2H), 7.22 (d, *J*=8.1 Hz, 2H), 7.47 (d, *J*=9.2 Hz, 2H), 7.50 (d, *J*=8.6 Hz, 2H). MS: *m/z* 430 (M^+), 107 (100 %). Elemental analysis: calculated for $C_{30}H_{38}O_2$, C 83.67, H 8.89; found, C 84.02, H 8.97%.

*4-Pentyloxyphenyl 12-(4-pentyloxyphenyl)-p-carborane-1-carboxylate (**2A[1]**).*

Carboxylic acid **8A** (0.5 mmol) was dissolved in CH_2Cl_2 (2 ml) and treated with oxalyl chloride (5.0 mmol) and a catalytic amount of DMF for 2 h at rt. Solvents were removed under reduced pressure. 4-Pentyloxyphenol (108 mg, 0.6 mmol), pyridine (2 ml)

and a catalytic amount of DMAP were added and the mixture was stirred for 12 h at room temperature (RT). Aqueous 10% HCl was added, and the mixture was extracted with AcOEt. The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated. The pure product was isolated by column chromatography (SiO_2, hexane/AcOEt, 20:1) and recrystallised (hexane) to give 82% yield of **2A[1]** as colourless cubes. ^{1}H NMR: δ 0.91 (t, J=7.0 Hz, 3H), 0.92 (t, J=7.0 Hz, 3H), 1.30–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.74 (quint, J=7.0 Hz, 2H), 1.76 (quint, J=7.0 Hz, 2H), 3.88 (t, J=6.8 Hz, 2H), 3.90 (t, J=6.6 Hz, 2H), 6.67 (d, J=8.9 Hz, 2H), 6.82 (d, J=8.9 Hz, 2H), 6.88 (d, J=8.9 Hz, 2H), 7.09 (d, J=8.9 Hz, 2H). ^{13}C NMR: δ 14.1, 22.5, 22.7, 28.2, 28.9, 29.0, 68.0, 68.4, 75.2, 85.8, 113.8, 114.9, 121.4, 127.9, 128.2, 143.6, 157.1, 159.3, 161.5. MS: *m/z* 512 (M^+, 100%). HRMS: *m/z* calculated for $C_{25}H_{40}B_{10}O_4$, 512.3929; found 512.3947. Elemental analysis: calculated for $C_{25}H_{40}B_{10}O_4$, C 58.57, H 7.86; found, C 58.66, H 7.93.

*4-Pentyloxyphenyl 4′-pentyloxybiphenyl-4-carboxylate (**2B[1]**).*

The ester was obtained from acid **8B** in quantitative yield as a colourless solid according to procedure for **2A[1]**. ^{1}H NMR: δ 0.94 (t, J=7.2 Hz, 3H), 0.95 (t, J=7.2 Hz, 3H), 1.30–1.55 (m, 8H), 1.80 (quint, J=6.8 Hz, 2H), 1.83 (quint, J=6.9 Hz, 2H), 3.97 (t, J=6.9 Hz, 2H), 4.02 (t, J=6.6 Hz, 2H), 6.94 (d, J=9.2 Hz, 2H), 7.00 (d, J=8.9 Hz, 2H), 7.13 (d, J=9.2 Hz, 2H), 7.59 (d, J=8.9 Hz, 2H), 7.68 (d, J=8.9 Hz, 2H), 8.22 (d, J=8.4 Hz, 2H). MS: *m/z* 446 (M^+), 266 (100). Elemental analysis: calculated for $C_{29}H_{34}O_4$, C 78.00, H 7.67; found, C 77.81, H 7.58%.

*4-Pentylphenyl (2E)-[12-(4-pentyloxyphenyl)-p-carboran-1-yl]propenoate (**3A[0]**).*

The ester was obtained from acid **12A** in quantitative yield as a colourless solid according to procedure for **2A[1]**. ^{1}H NMR: δ 0.89 (t, J=6.8 Hz, 3H), 0.91 (t, J=7.0 Hz, 3H), 1.23–1.43 (m, 8H), 1.50–3.75 (br m, 10H), 1.60 (quint, J=7.0 Hz, 2H), 1.74 (quint, J=6.9 Hz, 2H), 2.58 (t, J=7.7 Hz, 2H), 3.88 (t, J=6.5 Hz, 2H), 5.99 (d, J=15.7 Hz, 1H), 6.67 (d, J=8.9 Hz, 2H), 6.71 (d, J=15.1 Hz, 1H), 6.96 (d, J=8.4 Hz, 2H), 7.08 (d, J=8.9 Hz, 2H), 7.16 (d, J=8.4 Hz, 2H). Elemental analysis: calculated for $C_{27}H_{42}B_{10}O_3$, C 62.02, H 8.10; found, C 62.10, H 8.08%.

*4-Pentyloxyphenyl (2E)-[12-(4-pentyloxyphenyl)-p-carboran-1-yl] propenoate (**3A[1]**).*

The ester was obtained from acid **12A** in 97% yield as a colourless solid according to procedure for **2A[1]**. ^{1}H NMR: δ 0.90 (t, J=7.2 Hz, 3H), 0.93 (t, J=7.1 Hz, 3H), 1.34–1.46 (m, 8H), 1.50–3.75 (br m, 10H), 1.69–1.82 (m, 4H), 3.88 (t, J=6.8 Hz, 2H), 3.92 (t, J=6.5 Hz, 2H), 5.98 (d, J=15.4 Hz, 1H), 6.67 (d, J=8.9 Hz, 2H), 6.70 (d, J=15.7 Hz, 1H), 6.86 (d, J=9.2 Hz, 2H), 6.97 (d, J=9.2 Hz, 2H), 7.08 (d, J=8.9 Hz, 2H). Elemental analysis: calculated for $C_{27}H_{42}B_{10}O_4$, C 60.20, H 7.86; found, C 60.07, H 7.87%.

*4-Pentylphenyl (2E)-[4′-pentyloxybiphenyl-4-yl]propenoate (**3B[0]**).*

The ester was obtained from acid **12B** in 91% yield as a colourless solid according to procedure for **2A[1]**. ^{1}H NMR: δ 0.90 (t, J=6.8 Hz, 3H), 0.95 (t, J=7.2 Hz, 3H), 1.25–1.55 (m, 8H), 1.63 (quint, J=7.4 Hz, 2H), 1.82 (quint, J=7.0 Hz, 2H), 2.61 (t, J=7.7 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 6.64 (d, J=15.9 Hz, 1H), 6.98 (d, J=8.9 Hz, 2H), 7.08 (d, J=8.4 Hz, 2H), 7.21 (d, J=8.6 Hz, 2H), 7.56 (d, J=8.9 Hz, 2H), 7.62 (s, 4H), 7.88 (d, J=15.9 Hz, 1H). ^{13}C NMR: δ 14.0, 22.45, 22.51, 28.2, 28.9, 31.1, 31.5, 35.3, 68.1, 114.9, 116.8, 121.2, 127.0, 128.1, 128.8, 129.3, 132.2, 132.4, 140.4, 143.1, 146.0, 148.7, 159.3, 165.7. MS: *m/z* 456 (M^+), 293 (100 %). Elemental analysis: calculated for $C_{31}H_{36}O_3$, C 81.54, H 7.96; found, C 81.47, H 8.17%.

*4-Pentyloxyphenyl (2E)-[4′-pentyloxybiphenyl-4-yl]propenoate (**3B[1]**).*

The ester was obtained in 72% yield as a colourless solid according to procedure for **2A[1]**. ^{1}H NMR: δ 0.94 (t, J=7.0 Hz, 3H), 0.95 (t, J=7.0 Hz, 3H), 1.30–1.55 (m, 8H), 1.80 (quint, J=7.0 Hz, 2H), 1.82 (quint, J=7.0 Hz, 2H), 3.96 (t, J=6.6 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 6.63 (d, J=15.9 Hz, 1H), 6.91 (d, J=9.2 Hz, 2H), 6.99 (d, J=8.6 Hz, 2H), 7.08 (d, J=9.2 Hz, 2H), 7.56 (d, J=8.6 Hz, 2H), 7.62 (s, 4H), 7.88 (d, J=15.9 Hz, 1H). ^{13}C NMR: δ 14.1, 22.5, 28.2, 29.0, 68.1, 68.4, 114.9, 115.0, 116.7, 122.3, 127.0, 128.1, 128.8, 132.2, 132.5, 143.1, 144.1, 146.0, 156.8, 159.3, 165.9. MS: *m/z* 472 (M^+), 293 (100 %). Elemental analysis: calculated for $C_{31}H_{36}O_4$, C 78.78, H 7.68; found, C 78.62, H 8.01%.

*1-(4-Pentyloxyphenyl)-12-(4-pentylphenyliminomethyl)-p-carborane (**4A[0]**).*

A solution of aldehyde **10A** (200 mg, 0.6 mmol), 4-pentylaniline (118 mg, 0.72 mmol) and a catalytic amount of TsOH in dry toluene (5 ml) was refluxed under the Dean–Stark water trap for 12 h. Then the mixture was poured into saturated aqueous solution of $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$), and

concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 10:1) to give 268 mg (93% yield) of a solid, which was recrystallised (CH_2Cl_2/MeOH) yielding **4A[0]** as colourless rods. ^{1}H NMR: δ 0.87 (t, J=6.9 Hz, 3H), 0.91 (t, J=7.1 Hz, 3H), 1.20–1.45 (m, 8H), 1.50–3.75 (br m, 10H), 1.58 (quint, J=7.4 Hz, 2H), 1.74 (quint, J=6.9 Hz, 2H), 2.56 (t, J=7.6 Hz, 2H), 3.88 (t, J=6.5 Hz, 2H), 6.67 (d, J=8.9 Hz, 2H), 6.89 (d, J=8.2 Hz, 2H), 7.12 (d, J=8.9 Hz, 4H), 7.34 (s, 1H). ^{13}C NMR: δ 13.98, 13.99, 22.4, 22.5, 28.1, 28.8, 31.1, 31.4, 35.4, 68.0, 78.7, 84.5, 113.8, 120.6, 128.2, 128.6, 129.0, 141.9, 147.1, 154.9, 159.3. MS: *m/z* 479 (M^+, 100%). HRMS: *m/z* calculated for $C_{25}H_{41}B_{10}NO$, 479.4191; found 479.4228. Elemental analysis: calculated for $C_{25}H_{41}B_{10}NO$, C 62.59, H 8.61; found, C 62.39; H 8.68%.

*1-(4-Pentyloxyphenyl)-12-(4-pentyloxyphenyliminomethyl)-p-carborane (**4A[1]**).*

The compound was obtained in 97% yield as a colourless leaflets according to the procedure for **4A[0]**. ^{1}H NMR: δ 0.87 (t, J=6.9 Hz, 3H), 0.91 (t, J=7.1 Hz, 3H), 1.20–1.45 (m, 8H), 1.50–3.75 (br m, 10H), 1.50–1.58 (m, 2H), 1.74 (quint, J=6.8 Hz, 2H), 2.56 (t, J=7.6 Hz, 2H), 3.88 (t, J=6.6 Hz, 2H), 6.67 (d, J=9.1 Hz, 2H), 6.89 (d, J=8.9 Hz, 2H), 7.11 (d, J=8.4 Hz, 4H), 7.34 (s, 1H). ^{13}C NMR: δ 14.1, 14.2, 22.5, 22.7, 28.2, 28.9, 29.2, 31.5, 31.9, 35.5, 68.0, 113.6, 113.7, 120.5, 128.1, 128.5, 128.9, 141.8, 147.0, 154.7, 159.1. MS: *m/z* 495 (M^+), 43 (100%). HRMS: *m/z* calculated for $C_{25}H_{41}B_{10}NO_2$, 495.4141; found 495.4166. Elemental analysis: calculated for $C_{25}H_{41}B_{10}NO_2$, C 60.57, H 8.34, N 2.83; found, C 60.60; H 8.25; N 2.79%.

*4-Pentyloxy-4′-(4-pentylphenyliminomethyl)biphenyl (**4B[0]**).*

The compound was obtained according to the procedure for **4A[0]**. The crude product was recrystallised (*n*-hexane containing some CH_2Cl_2) to give 77% yield of imine **4B[0]** as yellowish leaflets. ^{1}H NMR: δ 0.90 (t, J=6.6 Hz, 3H), 0.95 (t, J=6.9 Hz, 3H), 1.30–1.53 (m, 8H), 1.64 (quint, J=7.4 Hz, 2H), 1.82 (quint, J=6.9 Hz, 2H), 2.63 (t, J=7.7 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 6.99 (d, J=8.9 Hz, 2H), 7.17 (d, J=8.6 Hz, 2H), 7.22 (d, J=8.9 Hz, 2H), 7.58 (d, J=8.6 Hz, 2H), 7.66 (d, J=8.4 Hz, 2H), 7.93 (d, J=8.4 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR: δ 14.0, 22.45, 22.53, 28.2, 28.9, 31.2, 31.5, 35.5, 68.1, 114.9, 120.1, 126.8, 128.1, 129.07, 129.14, 132.5, 134.7, 140.8, 143.5, 149.7, 159.1, 159.2. MS: *m/z* 413 (M^+, 100 %). Elemental analysis: calculated for $C_{29}H_{35}NO$, C 84.22, H 8.53, N 3.39; found, C 84.02, H 8.59, N 3.34%.

*4-Pentyloxy-4′-(4-pentyloxyphenyliminomethyl)biphenyl (**4B[1]**).*

The compound was obtained according to the procedure for **4A[0]**. The crude product was recrystallised (*n*-hexane containing some CH_2Cl_2) to give 86% yield of imine **4B[1]** as a yellowish solid. ^{1}H NMR: δ 0.94 (t, J=6.9 Hz, 3H), 0.95 (t, J=6.9 Hz, 3H), 1.30–1.55 (m, 8H), 1.75–1.88 (m, 4H), 3.98 (t, J=6.8 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 6.93 (d, J=8.9 Hz, 2H), 6.99 (d, J=8.6 Hz, 2H), 7.24 (d, J=8.9 Hz, 2H), 7.58 (d, J=8.6 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H), 7.93 (d, J=8.4 Hz, 2H), 8.51 (s, 1H). ^{13}C NMR: δ 13.9, 22.5, 28.3, 29.0, 29.1, 68.3, 68.5, 115.1, 115.2, 122.2, 126.8, 128.2, 129.1, 132.8, 135.1, 143.5, 145.1, 157.7, 158.0, 159.4. MS: *m/z* 429 (M^+, 100 %). Elemental analysis: calculated for $C_{29}H_{35}NO_2$, C 81.08, H 8.21, N 3.26; found, C 81.17, H 8.41, N 3.24%.

*1-(4-Pentyloxyphenyl)-12-[2-(4-pentylphenyl)ethenyl]-p-carborane (**5A[0]**).*

A solution of methanesulfonyl derivative **17A[0]** (634 mg, 1.1 mmol) and DBU (0.33 ml, 2.2 mmol) in anhydrous toluene (6 ml) was refluxed for 20 h. The mixture was poured into 10% HCl and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by silica gel column chromatography (hexane/AcOEt, 20:1) to give 499 mg (94% yield) of **5A[0]** as a colourless needles (EtOH/CH_2Cl_2). ^{1}H NMR: δ 0.87 (t, J=6.9 Hz, 3H), 0.91 (t, J=7.2 Hz, 3H), 1.22–1.46 (m, 8H), 1.50–3.75 (br m, 10H), 1.57 (quint, J=7.3 Hz, 2H), 1.73 (quint, J=6.9 Hz, 2H), 2.53 (t, J=7.6 Hz, 2H), 3.87 (t, J=6.6 Hz, 2H), 5.90 (d, J=15.7 Hz, 1H), 6.37 (d, J=15.7 Hz, 1H), 6.67 (d, J=9.2 Hz, 2H), 7.08 (d, J=8.1 Hz, 2H), 7.10 (d, J=8.9 Hz, 2H), 7.15 (d, J=8.4 Hz, 2H). ^{13}C NMR: δ 14.1, 22.5, 22.6, 28.2, 28.9, 31.1, 31.5, 35.7, 67.9, 79.2, 81.6, 113.7, 125.1, 126.4, 128.1, 128.5, 128.6, 132.6, 133.0, 143.3, 159.0. MS: *m/z* 478 (M^+), 135 (100%). HRMS: *m/z* calculated for $C_{26}H_{42}B_{10}O$, 478.4239; found 478.4258. Elemental analysis: calculated for $C_{26}H_{42}B_{10}O$, C 65.23, H 8.84; found, C 65.26, H 8.73%.

*1-(4-Pentyloxyphenyl)-12-[2-(4-pentyloxyphenyl)ethenyl]-p-carborane (**5A[1]**).*

A mixture of alcohol **19A[1]** (500 mg, 0.977 mmol), $MeSO_2Cl$ (0.09 ml, 1.17 mmol) and Et_3N (0.41 ml, 2.93 mmol) was stirred at RT for 8 h. Then the mixture was poured into 10% HCl and the whole was extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product purified by column chromatography (SiO_2, *n*-hexane/AcOEt, 15:1) to give 423 mg (88%

yield) of **5A[1]** as colourless cubes (*n*-hexane). ^{1}H NMR: δ 0.91 (t, *J*=7.0 Hz, 3H), 0.92 (t, *J*=7.1 Hz, 3H), 1.30–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.74 (quint, *J*=6.9 Hz, 2H), 1.76 (quint, *J*=7.1 Hz, 2H), 3.87 (t, *J*=6.7 Hz, 2H), 3.93 (t, *J*=6.8 Hz, 2H), 5.80 (d, *J*=15.7 Hz, 1H), 6.33 (d, *J*=15.7 Hz, 1H), 6.67 (d, *J*=8.9 Hz, 2H), 6.79 (d, *J*=8.7 Hz, 2H), 7.11 (d, *J*=9.1 Hz, 2H), 7.21 (d, *J*=8.7 Hz, 2H). ^{13}C NMR: δ 14.0, 22.39, 22.43, 28.1, 28.8, 28.9, 67.95, 68.03, 79.5, 81.4, 113.8, 114.6, 123.8, 127.8, 127.9, 128.2, 128.6, 132.7, 159.2, 159.4. MS: *m/z* 494 (M^+, 100%). HRMS: *m/z* calculated for $C_{26}H_{42}B_{10}O_2$, 494.4188; found 494.4161. Elemental analysis: calculated for $C_{26}H_{42}B_{10}O_2$, C 63.12, H 8.56; found, C 62.87, H 8.56%.

*4-Pentyloxy-4′-[(1E)-2-(4-pentylphenyl)ethenyl]biphenyl (**5B[0]**).*

To a solution of 4-pentylbenzyltriphenylphosphonium bromide (554 mg, 1.34 mmol) in anhydrous DMF was added NaH (1.34 mmol) portionwise at 0°C and the reaction mixture was stirred at 0°C for 20 min. Then aldehyde **10B** (301 mg, 1.12 mmol) was added to the reaction mixture at 0°C and the mixture was stirred at RT for 3 h. Then 10% HCl was added at 0°C and the precipitate was filter off, washed with *n*-hexane and dried in *vacuo* to give 194 mg (35% yield) of **5B[0]** as a colourless solid. ^{1}H NMR: (600 MHz) δ 0.84 (t, *J*=7.1 Hz, 3H), 0.90 (t, *J*=7.0 Hz, 3H), 1.28–1.49 (m, 8H), 1.63 (quint, *J*=7.5 Hz, 2H), 1.81 (quint, *J*=7.0 Hz, 2H), 2.61 (t, *J*=7.9 Hz, 2H), 4.00 (t, *J*=6.6 Hz, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.09 (d, *J*=16.4 Hz, 1H), 7.12 (d, *J*=16.1 Hz, 1H), 7.18 (d, *J*=8.1 Hz, 2H), 7.45 (d, *J*=8.0 Hz, 2H), 7.52–7.55 (m, 6H). ^{13}C NMR: δ 14.0, 22.5, 22.6, 28.2, 29.0, 31.1, 31.5, 35.7, 68.1, 114.8, 126.4, 126.79, 126.82, 127.3, 127.8, 128.4, 128.8, 133.0, 134.8, 135.9, 139.8, 142.6, 158.8. MS: *m/z* 412 (M^+, 100). Elemental analysis: calculated for $C_{30}H_{36}O$, C 87.33, H 8.79. Found; C, 87.16, H 9.02%.

*4-Pentyloxy-4′-[(1Z)-2-(4-pentylphenyl)ethenyl]biphenyl (**5B[0]-Z**).*

The filtrate from the preparation of **5B[0]** was extracted with CH_2Cl_2. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt, 50/1) to give 227 mg (41% yield) of the *Z*-alkene **5B[0]-Z**. ^{1}H NMR (600 MHz): δ 0.83 (t, *J*=7.3 Hz, 3H), 0.89 (t, *J*=6.8 Hz, 3H), 1.20–1.48 (m, 8H), 1.60 (quint, *J*=7.6 Hz, 2H), 1.81 (quint. *J*=7.1 Hz, 2H), 2.57 (t, *J*=7.7 Hz, 2H), 3.99 (t, *J*=6.6 Hz, 2H), 6.55 (d, *J*=12.1 Hz, 1H), 6.58 (d, *J*=12.4 Hz, 1H), 6.95 (d, *J*=8.8 Hz, 2H), 7.05 (d, *J*=8.0 Hz, 2H), 7.22 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=8.4 Hz, 2H), 7.42 (d, *J*=8.0 Hz, 2H), 7.51 (d, *J*=8.8 Hz, 2H).

*4-Pentyloxy-4′-[(1E)-2-(4-pentyloxyphenyl)ethenyl]biphenyl (**5B[1]**).*

The compound was obtained in 38% yield according to the procedure for **5B[0]**. ^{1}H NMR (600 MHz): δ 0.94 (t, *J*=7.1 Hz, 3H), 0.95 (t, *J*=7.3 Hz, 3H), 1.35–1.0 (m, 8H), 1.80 (quint, *J*=7.2 Hz, 2H), 1.81 (quint, *J*=7.2 Hz, 2H), 3.98 (t, *J*=6.6 Hz, 2H), 4.00 (t, *J*=6.6 Hz, 2H), 6.90 (d, *J*=8.8 Hz, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.00 (d, *J*=16.5 Hz, 1H), 7.09 (d, *J*=16.4 Hz, 1H), 7.46 (d, *J*=8.0 Hz, 2H), 7.51–7.58 (m, 6H). MS: *m/z* 428 (M^+, 100). Elemental analysis: calculated for $C_{30}H_{36}O_2$, C 84.07, H 8.47; found, C, 84.12, H 8.50%.

*N-(4-Pentylphenyl)-12-(4-pentyloxyphenyl)-p-carborane-1-carboxamide (**6A[0]**).*

Carboxylic acid **8A** (700 mg, 2.0 mmol) was dissolved in CH_2Cl_2 (3 ml) and treated with oxalyl chloride (0.87 ml, 10 mmol) and a catalytic amount of DMF for 1 h at RT. Solvents were removed under reduced pressure. 4-Pentylaniline (392 mg, 2.4 mmol) and pyridine (3 ml) were added and the mixture was stirred for 3 h at RT. Aqueous 10% HCl was added, and the mixture was extracted with AcOEt. The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated. The pure product was isolated by column chromatography (SiO_2, hexane/AcOEt, 20:1) and recrystallised (hexane) to give 764 mg (77% yield) of **6A[0]** as a colourless solid. ^{1}H NMR: δ 0.87 (t, *J*=6.8 Hz, 3H), 0.91 (t, *J*=7.2 Hz, 3H), 1.20–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.74 (quint, *J*=7.0 Hz, 2H), 1.56 (quint, *J*=7.4 Hz, 2H), 2.54 (t, *J*=7.6 Hz, 2H), 3.88 (t, *J*=6.6 Hz, 2H), 6.68 (d, *J*=8.9 Hz, 2H), 7.09 (d, *J*=8.6 Hz, 2H), 7.10 (d, *J*=8.6 Hz, 2H), 7.23 (br s, 1H), 7.28 (d, *J*=8.6 Hz, 2H). ^{13}C NMR: δ 14.0, 22.4, 22.5, 28.1, 28.8, 31.1, 31.3, 35.3, 68.0, 79.1, 84.9, 113.9, 119.9, 128.0, 128.1, 128.9, 134.3, 140.2, 158.6, 159.5. Elemental analysis: calculated for $C_{25}H_{41}B_{10}NO_2$, C 60.57, H 8.34; found, C 60.62, H 8.29%.

*N-(4-Pentyloxyphenyl)-12-(4-pentyloxyphenyl)-p-carborane-1-carboxamide (**6A[1]**).*

The amide was obtained in 87% yield according to the procedure for **6A[0]**. ^{1}H NMR: δ 0.91 (t, *J*=7.0 Hz, 3H), 0.92 (t, *J*=7.2 Hz, 3H), 1.25–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.65–1.85 (m, 4H), 3.88 (t, *J*=6.5 Hz, 2H), 3.91 (t, *J*=6.8 Hz, 2H), 6.68 (d, *J*=8.9 Hz, 2H), 6.81 (d, *J*=8.9 Hz, 2H), 7.09 (d, *J*=8.9 Hz, 2H), 7.18 (br s, 1H), 7.26 (d, *J*=8.9 Hz, 2H). ^{13}C NMR: δ 14.0, 22.41,

22.44, 28.1, 28.8, 28.9, 68.0, 68.3, 79.1, 84.9, 113.9, 114.8, 121.7, 128.0, 128.1, 129.6, 156.6, 158.6, 159.5. Elemental analysis: calculated for $C_{25}H_{41}B_{10}NO_3$, C 58.68, H 8.08; found, C 58.63, H 8.25%.

*N-(4-Pentylphenyl)-4'-pentyloxybiphenyl-4-carboxamide (**6B[0]**).*

The amide was obtained in 81% according to the procedure for **6A[0]** and recrystallised from AcOEt/toluene. ^{1}H NMR: δ 0.90 (t, J=6.6 Hz, 3H), 0.95 (t, J=7.0 Hz, 3H), 1.27–1.53 (m, 8H), 1.62 (quint, J=7.4 Hz, 2H), 1.82 (quint, J=6.9 Hz, 2H), 2.60 (t, J=7.6 Hz, 2H), 4.02 (t, J=6.6 Hz, 2H), 6.98 (d, J=8.6 Hz, 2H), 7.17 (d, J=8.4 Hz, 2H), 7.56 (d, J=8.7 Hz, 2H), 7.57 (d, J=8.5 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 7.74 (br s, 1H), 7.89 (d, J=8.6 Hz, 2H). Elemental analysis: calculated for $C_{29}H_{35}NO_2$, C 81.08, H 8.21, N 3.26; found, C 80.92, H 8.31, N 3.21%.

*N-(4-Pentyloxyphenyl)-4'-pentyloxybiphenyl-4-carboxamide (**6B[1]**).*

The amide was obtained in 82% yield according to the procedure for **6A[0]** and recrystallised from AcOEt/toluene. ^{1}H NMR: δ 0.94 (t, J=7.0 Hz, 3H), 0.95 (t, J=7.2 Hz, 3H), 1.36–1.53 (m, 8H), 1.79 (quint, J=7.4 Hz, 2H), 1.82 (quint, J=7.3 Hz, 2H), 3.96 (t, J=6.8 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 6.90 (d, J=8.9 Hz, 2H), 6.98 (d, J=8.9 Hz, 2H), 7.53 (d, J=8.9 Hz, 2H), 7.55 (d, J=8.9 Hz, 2H), 7.65 (d, J=8.9 Hz, 2H), 7.66 (br s, 1H), 7.89 (d, J=8.4 Hz, 2H). Elemental analysis: calculated for $C_{29}H_{35}NO_3$, C 78.17, H 7.92, N 3.14; found, C 78.01, H 8.04, N 3.27%.

*2-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]ethyl 4-pentylbenzoate (**7A[0]**).*

4-Pentylbenzoyl chloride (0.14 ml, 0.69 mmol) was added to a solution of alcohol **9A** (200 mg, 0.57 mmol) and a catalytic amount of DMAP in pyridine (2 ml) and the mixture was stirred for 45 h at RT. The reaction mixture was poured into 10% aqueous HCl solution and extracted with AcOEt, washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 10:1) to give 299 mg (100% yield) of ester **7A[0]** as a colourless solid. ^{1}H NMR: δ 0.89 (t, J=6.9 Hz, 3H), 0.91 (t, J=7.1 Hz, 3H), 1.29–1.44 (m, 8H), 1.50–3.75 (br m, 10H), 1.63 (quint, J=7.5 Hz, 2H), 1.73 (quint, J=7.0 Hz, 2H), 2.15 (t, J=6.6 Hz, 2H), 2.65 (t, J=7.7 Hz, 2H), 3.87 (t, J=6.5 Hz, 2H), 4.11 (t, J=6.7 Hz, 2H), 6.55 (d, J=9.1 Hz, 2H), 7.08 (d, J=9.1 Hz, 2H), 7.24 (d, J=8.4 Hz, 2H), 7.91 (d, J=8.4 Hz, 2H). Elemental analysis: calculated for $C_{27}H_{44}B_{10}O_3$, C 61.80, H 8.45; found, C 61.54, H 8.40%.

*2-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]ethyl 4-pentyloxybenzoate (**7A[1]**).*

The ester was obtained in 92% yield as colourless rods according to the procedure for **7A[0]**. ^{1}H NMR: δ 0.91 (t, J=7.3 Hz, 3H), 0.94 (t, J=7.0 Hz, 3H), 1.30–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.73 (quint, J=6.9 Hz, 2H), 1.81 (quint, J=7.3 Hz, 2H), 2.14 (t, J=6.6 Hz, 2H), 3.87 (t, J=6.6 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 4.10 (t, J=6.8 Hz, 2H), 6.65 (d, J=8.9 Hz, 2H), 6.90 (d, J=8.9 Hz, 2H), 7.08 (d, J=8.9 Hz, 2H), 7.94 (d, J=8.9 Hz, 2H). MS: m/z 540 (M^+, 100%). HRMS: m/z calculated for $C_{27}H_{44}B_{10}O_4$, 540.4243; found 540.4266. Elemental analysis: calculated for $C_{27}H_{44}B_{10}O_4$, C 59.97, H 8.20; found, C 59.91, H 8.29%.

*(4'-Pentyloxybiphenyl-4-yl)ethyl 4-pentylbenzoate (**7B[0]**).*

The ester was obtained from alcohol **9B** in 85% yield as a colourless solid according to the procedure for **7A[0]**. ^{1}H NMR: δ 0.89 (t, J=6.9 Hz, 3H), 0.94 (t, J=7.3 Hz, 3H), 1.24–1.53 (m, 8H), 1.63 (quint, J=7.5 Hz, 2H), 1.81 (quint, J=7.0 Hz, 2H), 2.65 (t, J=7.7 Hz, 2H), 3.10 (t, J=6.9 Hz, 2H), 3.99 (t, J=6.5 Hz, 2H), 4.54 (t, J=7.0 Hz, 2H), 6.96 (d, J=8.9 Hz, 2H), 7.23 (d, J=8.4 Hz, 2H), 7.33 (d, J=7.8 Hz, 2H), 7.503 (d, J=8.9 Hz, 2H), 7.505 (d, J=7.8 Hz, 2H), 7.94 (d, J=8.4 Hz, 2H). ^{13}C NMR: δ 13.97, 14.01, 22.5, 28.2, 29.0, 30.8, 31.4, 34.9, 36.0, 65.3, 68.0, 114.7, 126.8, 127.7, 127.9, 128.4, 129.3, 129.6, 133.2, 136.3, 139.2, 148.5, 158.6, 166.6. MS: m/z 458 (M^+), 266 (100 %). Elemental analysis: calculated for $C_{31}H_{38}O_3$, C 81.18, H 8.35; found, C, 81.01, H 8.35%.

*2-(4'-Pentyloxybiphenyl-4-yl)ethyl 4-pentyloxybenzoate (**7B[1]**).*

The ester was obtained from alcohol **9B** in 92% yield as a colourless solid according to the procedure for **7A[0]**. ^{1}H NMR: δ 0.935 (t, J=7.0 Hz, 3H), 0.940 (t, J=7.3 Hz, 3H), 1.25–1.55 (m, 8H), 1.81 (quint, J=6.6 Hz, 4H), 3.09 (t, J=6.8 Hz, 2H), 3.99 (t, J=6.5 Hz, 2H), 4.00 (t, J=6.6 Hz, 2H), 4.52 (t, J=7.0 Hz, 2H), 6.90 (d, J=8.9 Hz, 2H), 6.96 (d, J=8.6 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 7.50 (d, J=8.4 Hz, 4H), 7.97 (d, J=8.9 Hz, 2H). ^{13}C NMR: δ 13.97, 14.00, 22.4, 22.5, 28.1, 28.2, 28.8, 29.0, 34.9, 65.1, 68.0, 68.2, 114.0, 114.7, 122.4, 126.8, 127.9, 129.3, 131.5, 133.2, 136.4, 139.1, 158.6, 163.0, 166.3. MS: m/z 474 (M^+), 266 (100 %). Elemental analysis: calculated for $C_{31}H_{38}O_4$, C 78.45, H 8.07; found, C, 78.16, H 8.30%.

*2-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]ethyl E-4-pentylcyclohexane-1-carboxylate (**7A[CHx]**).*

The ester was obtained from alcohol **9A** and *E*-4-pentylcyclohexane-1-carbonyl chloride as colourless leaflets according to the procedure for **7A[0]**. M.p. 82–84°C (DSC: 83°C, 43.5 kJ mol^{-1}). ^{1}H NMR: δ 0.88 (t, *J*=7.1 Hz, 3H), 0.90 (t, *J*=7.1 Hz, 3H), 1.18–1.45 (m, 17H), 1.50–3.60 (br m, 10H), 1.73 (quint, *J*=7.2 Hz, 2H), 1.80 (d, *J*=12.5 Hz, 2H), 1.93 (d, *J*=9.8 Hz, 2H), 2.00 (t, *J*=6.9 Hz, 2H), 2.17 (tt, J_1=12.2 Hz, J_2=3.5 Hz, 1H), 3.85 (t, *J*=6.8 Hz, 2H), 3.86 (t, *J*=6.5 Hz, 2H), 6.65 (d, *J*=8.9 Hz, 2H), 7.07 (d, *J*=8.9 Hz, 2H). Elemental analysis: calculated for $C_{27}H_{50}B_{10}O_3$, C 61.10, H 9.49; found, C 60.89, H 9.78%.

*2-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]ethyl 4-pentylbicyclo[2.2.2]octane-1-carboxylate (**7A[BCO]**).*

The ester was obtained from alcohol **9A** as colourless rods according to the procedure for **7A[0]**. The acid chloride was prepared from 4-pentylbicyclo[2.2.2] octane-1-carboxylic acid and $(COCl)_2$. M.p. 113–114°C (DSC: 112°C, 41.3 kJ mol^{-1}). ^{1}H NMR: δ 0.87 (t, *J*=7.0 Hz, 3H), 0.91 (t, *J*=7.2 Hz, 3H), 1.08–1.40 (m, 18H), 1.50–3.60 (br m, 10H), 1.69–1.75 (m, 8H), 1.98 (t, *J*=6.5 Hz, 2H), 3.83 (t, *J*=6.6 Hz, 2H), 3.87 (t, *J*=6.5 Hz, 2H), 6.65 (d, *J*=9.1 Hz, 2H), 7.07 (d, *J*=8.9 Hz, 2H). HRMS: *m/z* calculated for $C_{29}H_{52}B_{10}O_3$, 556.4928; found, 556.4919. Elemental analysis: calculated for $C_{29}H_{52}B_{10}O_3$, C 62.55, H 9.41; found, C 62.12, H 9.61%.

*4′-Pentyloxy-4-biphenylcarboxylic acid (**8B**) (23).*

Pentyl 4′-pentyloxy-4-biphenylcarboxylate (458 mg, 1.29 mmol) was dissolved in THF (5 ml), and 10% aqueous KOH (3 ml) was added at RT. The reaction mixture was refluxed for 5 h and poured into 10% HCl solution. The resulting precipitate was filtered off, washed with EtOH and dried to give 329 mg (90% yield) of acid **8B** as a colorless solid. ^{1}H NMR (DMSO-d_6): δ 0.89 (t, *J*=7.2 Hz, 3H), 1.29–1.44 (m, 4H), 1.73 (quint, *J*=6.8 Hz, 2H), 4.00 (t, *J*=6.5 Hz, 2H), 7.02 (d, *J*=8.9 Hz, 2H), 7.64 (d, *J*=8.4 Hz, 2H), 7.67 (d, *J*=7.6 Hz, 2H), 7.94 (d, *J*=8.4 Hz, 2H). MS: *m/z* 284 (M^+) 214 (100 %).

*2-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]ethanol (**9A**).*

A 1.56M solution of *n*-BuLi (6.0 ml, 9.36 mmol) in hexane was added dropwise to a solution of 1-(4-pentyloxyphenyl)-*p*-carborane (*17*) (**22A**, 2.39 g, 7.8 mmol) in a mixture of benzene (20 ml) and ether (10 ml) at 0°C under Ar. After stirring at room temperature for 30 min, the mixture was cooled to 0°C, and 2-bromo-1-(2-tetrahydropyranoxy)ethane (1.63 g, 7.8 mmol) was added. The resulting mixture was stirred for 12 h at RT, poured into water and organic products were extracted with AcOEt. The extracts were washed with brine, dried ($MgSO_4$) and solvents removed. The resulting residue was purified by column chromatography (SiO_2, AcOEt/hexane in 1:20 ratio) to give 2.27 g (67% yield) of 2-(4-pentyloxyphenyl)-12-(2-(2-tetrahydropyranoxy)ethyl)-*p*-carborane (**23A**) as a colourless oil. ^{1}H NMR: δ 0.90 (t, *J*=7.2 Hz, 3H), 1.31–1.68 (m, 10H), 1.50–4.00 (br m, 10H), 1.73 (quint, *J*=7.1 Hz, 2H), 1.98 (t, *J*=7.5 Hz, 2H), 3.17 (dt, J_1=7.6 Hz, J_2=10.1 Hz, 1H), 3.44–3.52 (m, 1H), 3.55 (dt, J_1=7.3 Hz, J_2=10.1 Hz, 1H), 3.75–3.82 (m, 1H), 3.86 (t, *J*=6.6 Hz, 2H), 4.48 (t, *J*=3.6 Hz, 1H), 6.65 (d, *J*=9.1 Hz, 2H), 7.08 (d, *J*=8.9 Hz, 2H)].

The protected alcohol **23A** (1.39 g, 3.2 mmol) was dissolved in MeOH (4 ml) containing a catalytic amount of *p*-toluenesulfonic acid monohydrate and the solution was stirred for 18 h at RT. After the solvent was removed under reduced pressure, the residue was dissolved in AcOEt, the solution was washed with saturated $NaHCO_3$ and brine and dried ($MgSO_4$). Solvents were removed under reduced pressure and the resulting residue was purified by column chromatography (SiO_2, AcOEt/hexane in 1:10 ratio) to give 0.653 g (58% yield) of alcohol **9A** as colourless cotton-like crystals (CH_2Cl_2/hexane). M.p. 61–62°C. ^{1}H NMR: δ 0.91 (t, *J*=7.2 Hz, 3H), 1.26–1.44 (m, 4H), 1.50–4.00 (br m, 10H), 1.73 (quint, *J*=6.9 Hz, 2H), 1.95 (t, *J*=6.9 Hz, 2H), 3.47 (d, *J*=6.7 Hz, 2H), 3.87 (t, J=6.6 Hz, 2H), 6.65 (d, *J*=8.9 Hz, 2H), 7.08 (d, *J*=8.9 Hz, 2H). HRMS *m/z* calculated for $C_{15}H_{30}B_{10}O_2$, 350.3249; found, 350.3278. Elemental analysis: calculated for $C_{15}H_{30}B_{10}O_2$, C 51.40, H 8.63; found, C 50.76, H 8.61%.

*2-(4′-Pentyloxybiphenyl-4-yl)ethanol (**9B**).*

To a solution of ethyl 4′-pentyloxy-4-biphenylacetate (**26B**, 474 mg, 1.45 mmol) in dry THF (5 ml) was added $LiAlH_4$ (110 mg, 2.9 mmol) in small portion at 0°C under Ar and the reaction mixture was stirred at RT for 6 h. The reaction mixture was poured into ice water and 10% HCl was added. The mixture was extracted with Et_2O and the organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 5/1) to give 339 mg (82% yield) of alcohol **9B** as a colourless solid. M.p. 132–134°C. ^{1}H NMR: δ 0.94 (t, *J*=7.0 Hz, 3H), 1.32–1.52 (m, 4H), 1.40 (t, *J*=5.9 Hz, 1H), 1.81 (quint, *J*=7.0 Hz, 2H), 2.91 (t, *J*=6.5 Hz, 2H), 3.91 (q, *J*=6.3 Hz, 2H), 3.99 (t,

J=6.6 Hz, 2H), 6.96 (d, J=8.9 Hz, 2H), 7.28 (d, J=9.2 Hz, 2H), 7.497 (d, J=8.6 Hz, 2H), 7.504 (d, J=8.1 Hz, 2H). ^{13}C NMR: δ 14.0, 22.4, 28.2, 28.9, 38.7, 63.6, 68.0, 114.7, 126.8, 127.9, 129.3, 133.2, 136.8, 139.1, 158.6. Elemental analysis: calculated for $C_{19}H_{24}O_2$, C 80.24, H 8.51. Found; C, 80.01, H 8.58%.

*12-(4-Pentyloxyphenyl)-p-carborane-1-carbaldehyde (**10A**).*

To a stirred solution of 1-(4-pentyloxyphenyl)-*p*-carborane (*17*) (**22A**, 1.00 g, 3.27 mmol) in anhydrous Et_2O (10 ml) was added dropwise 1.56M hexane solution of *n*-BuLi (2.51 ml, 3.92 mmol) at 0°C under Ar atmosphere and the reaction mixture was stirred at RT for 30 min. Then HCO_2Et (0.32 ml, 3.92 mmol) was added at −78°C and the reaction mixture was stirred at RT for 24 h. The mixture was poured into water and the whole was extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using 15:1 hexane/CH_2Cl_2 as the eluent to give 802 mg (74% yield) of aldehyde **10A** as a colourless solid, which was recrystallised from *n*-hexane. M.p. 59°C. ^{1}H NMR: δ 0.91 (t, J=7.1 Hz, 3H), 1.29–1.45 (m, 4H), 1.50–3.75 (br m, 10H), 1.74 (quint, J=6.9 Hz, 2H), 3.88 (t, J=6.5 Hz, 2H), 6.67 (d, J=9.1 Hz, 2H), 7.11 (d, J=8.9 Hz, 2H), 8.88 (s, 1H). Elemental analysis: calculated for $C_{14}H_{26}B_{10}O_2$, C 50.27, H 7.84; found, C 50.46, H 7.77%.

*4′-Pentyloxybiphenyl-4-carbaldehyde (**10B**).*

To a solution of pentyl 4′-pentyloxybiphenyl-4-carboxylate (**21B**, 1.65 g, 4.66 mmol) in dry THF (20 ml) was added $LiAlH_4$ (353 mg, 9.32 mmol) in small portion at 0°C under Ar and the reaction mixture was stirred at RT for 6 h. Then the reaction mixture was poured into ice water and added 10% HCl. The mixture was extracted with Et_2O and the organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt , 5/1) to give 1.13 g (90% yield) of 4′-pentyloxybiphenyl-4-methanol as a colourless solid. M.p. 147–149°C. ^{1}H NMR: δ 0.94 (t, J=7.0 Hz, 3H), 1.35–1.52 (m, 4H), 1.63 (t, J=6.2 Hz, 1H), 1.82 (quint, J=6.9 Hz, 2H), 4.00 (t, J=6.6 Hz, 2H), 4.73 (d, J=5.9 Hz, 2H), 6.97 (d, J=8.6 Hz, 2H), 7.42 (d, J=8.1 Hz, 2H) 7.51 (d, J=8.9 Hz, 2H), 7.55 (d, J=8.1 Hz, 2H). ^{13}C NMR: δ 14.0, 22.5, 28.2, 29.0, 65.2, 68.1, 114.8, 126.8, 127.5, 128.0, 133.1, 139.1, 140.3, 158.8. MS: *m/z* 270 (M^+), 200 (100 %).

Without further purification the alcohol (1.13 g, 4.19 mmol) was dissolved in anhydrous CH_2Cl_2 (30 ml), Celite (1.00 g) was added followed by pyridinium chlorochromate (4.51 g, 20.94 mmol) at 0°C. The mixture was stirred at RT for 6 h, filtered through a pad of Celite and the filtrate was concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt , 10/1) to give 1.06 g (94% yield) of aldehyde **10B** as a colourless solid. ^{1}H NMR: δ 0.95 (t, J=7.0 Hz, 3H), 1.33–1.53 (m, 4H), 1.82 (quint, J=7.0 Hz, 2H), 4.02 (t, J=6.5 Hz, 2H), 7.00 (d, J=8.9 Hz, 2H), 7.58 (d, J=8.9 Hz, 2H), 7.72 (d, J=8.6 Hz, 2H), 7.92 (d, J=8.6 Hz, 2H), 10.03 (s, 1H). MS: *m/z* 268 (M^+), 198 (100 %).

*Ethyl (2E)-3-[12-pentyloxyphenyl)-p-carboran-1-yl]-2-propenoate (**11A**).*

NaH (63 mg, 1.57 mmol) was added portionwise to a solution of ethyl diethylphosphonoacetate (0.31 ml, 1.57 mmol) in anhydrous DMF (1 ml) at 0°C and the mixture was stirred at RT for 30 min. Then a solution of aldehyde **10A** (350 mg, 1.1 mmol) in anhydrous DMF (10 ml) was added to a reaction mixture at 0°C. After stirring at RT for 30 min, the mixture was poured into ice water and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt , 20/1) to give 382 g (90% yield) of ester **11A** as colourless solid. M.p. 49°C. ^{1}H NMR: δ 0.91 (t, J=7.0 Hz, 3H), 1.26 (t, J=7.1 Hz, 3H), 1.34–1.45 (m, 4H), 1.50–3.75 (br m, 10H), 1.73 (quint, J=7.0 Hz, 2H), 3.89 (t, J=6.6 Hz, 2H), 4.15 (q, J=7.0 Hz, 2H), 5.79 (d, J=15.4 Hz, 1H), 6.53 (d, J=15.4 Hz, 1H), 6.66 (d, J=9.2 Hz, 2H), 7.07 (d, J=8.9 Hz, 2H). ^{13}C NMR: δ 14.0, 14.1, 22.4, 28.1, 28.8, 60.8, 67.9, 75.9, 83.3, 113.6, 124.3, 127.9, 128.1, 142.5, 159.0, 164.8. Elemental analysis: calculated for $C_{18}H_{32}B_{10}O_3$, C 53.44, H 7.97; found, C 53.62, H 8.08%.

*Ethyl (2E)-3-[4′-pentyloxybiphenyl-4-yl]-2-propenoate (**11B**).*

The ester was obtained from aldehyde **10B** (3.73 mmol) in 89% yield as a colourless solid according to the procedure for **11A**. M.p. 67°C. ^{1}H NMR: δ 0.94 (t, J=7.2 Hz, 3H), 1.35 (t, J=7.2 Hz, 3H), 1.37–1.53 (m, 4H), 1.82 (quint, J=6.9 Hz, 2H), 4.00 (t, J=6.6 Hz, 2H), 4.28 (q, J=7.1 Hz, 2H), 6.45 (d, J=15.9 Hz, 1H), 6.97 (d, J=8.9 Hz, 2H), 7.54 (d, J=8.6 Hz, 2H), 7.58 (s, 4H), 7.71 (d, J=15.9 Hz, 1H). ^{13}C NMR: δ 13.9, 14.2, 22.4, 28.1, 28.9, 60.3, 67.9, 114.8, 117.5, 126.8, 127.9, 128.4, 132.2, 132.6, 142.5, 144.1, 159.1, 166.9. MS: *m/z* 338 (M^+, 100 %).

Elemental analysis: calculated for $C_{22}H_{26}O_3$, C 78.07, H 7.74; found, C 77.93, H 7.82%.

*(2E)-3-[12-Pentyloxyphenyl-p-carboran-1-yl]-2-propenoic acid (**12A**).*

Aqueous NaOH (10%, 2 ml) was added to a stirred solution of ethyl ester **11A** (95 mg, 0.23 mmol) in EtOH (2 ml) at RT. The reaction mixture was stirred for 3 h, and the solvent removed. The residue was poured into 10% HCl and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated to give 86 mg (100% yield) of acid **12A** as a colourless solid. M.p. 197°C. ^{1}H NMR: δ 0.91 (t, J=7.1 Hz, 3H), 1.36–1.41 (m, 4H), 1.50–3.75 (m, 10H), 1.73 (quint, J=6.9 Hz, 2H), 3.87 (t, J=6.6 Hz, 2H), 5.80 (d, J=15.7 Hz, 1H), 6.61 (d, J=15.7 Hz, 1H), 6.66 (d, J=8.9 Hz, 2H), 7.07 (d, J=8.9 Hz, 2H). Elemental analysis: calculated for $C_{16}H_{28}B_{10}O_3$, C 51.04, H 7.50; found, C 51.18, H 7.46%.

*(2E)-3-[4′-Pentyloxybiphenyl-4-yl]-2-propenoic acid (**12B**).*

Ethyl ester **11B** (900 mg, 2.66 mmol) was dissolved with 5 ml of THF, and 3 ml of 10% KOH aqueous solution was added at room temperature. After being refluxed for 5 h, the reaction mixture was poured into 10% HCl aqueous solution. Then the precipitate was filtered off, washed with EtOH and dried to give 717 mg (87% yield) of acid **12B** as a colourless solid, which was recrystallliaed from AcOH. M.p. 247°C. ^{1}H NMR: δ 0.95 (t, J=6.9 Hz, 3H), 1.35–1.55 (m, 4H), 1.82 (quint, J=7.2 Hz, 2H), 4.01 (t, J=6.6 Hz, 2H), 6.46 (d, J=15.9 Hz, 1H), 6.97 (d, J=8.9 Hz, 2H), 7.54 (d, J=8.9 Hz, 2H), 7.59 (s, 4H), 7.79 (d, J=16.2 Hz, 1H). MS: m/z 310 (M^+) 240 (100 %). Elemental analysis: calculated for $C_{20}H_{22}O_3$, C 77.39, H 7.14; found, C 77.15, H 7.15%.

*(4-Pentylbenzyl)triphenylphosphonium bromide (**14[0]**) (25).*

A mixture of bromide **15[0]** and triphenylphosphine (1.1 equiv.) in anhydrous toluene was refluxed for 12 h. After cooling, the phosphonium salt was precipitated, filtered off, washed with anhydrous Et_2O and dried in vacuo to give 94% yield of phosphonium salt **14[0]** as a colourless solid. ^{1}H NMR: δ 0.87 (t, J=7.0 Hz, 3H), 1.15–1.37 (m, 4H), 1.52 (quint, J=7.5 Hz, 2H), 2.50 (t, J=6.8 Hz, 2H), 5.35 (d, J=14.0 Hz, 2H), 6.93 (d, J=8.1 Hz, 2H), 6.98 (dd, J_1=2.2 Hz, J_2=8.4 Hz, 2H), 7.58–7.81 (m, 15H). Elemental analysis: calculated for $C_{30}H_{32}BrP$, C 71.54, H 6.41; found, C 71.55, H 6.47%.

*(4-Pentyloxybenzyl)triphenylphosphonium chloride (**14[1]**).*

The salts was obtained in 78% yield as described for **14[0]**. ^{1}H NMR: δ 0.92 (t, J=7.0 Hz, 3H), 1.27–1.46 (m, 4H), 1.73 (quint, J=7.0 Hz, 2H), 3.85 (t, J=6.5 Hz, 2H), 5.44 (d, J=13.8 Hz, 2H), 6.64 (d, J=8.1 Hz, 2H), 7.01 (dd, J_1=2.4 Hz, J_1=8.1 Hz, 2H), 7.58–7.81 (m, 15H).

*4-Pentylbenzyl bromide (**15[0]**) (25).*

A mixture of 4-pentylbenzyl alcohol (*25*) (**27[0]**, 1.78 g, 10 mmol) and 47% aqueous HBr (8.6 ml, 50 mmol) in benzene (10 ml) was refluxed for 6 h. The mixture was cooled and the organic layer was separated. The organic layer was washed with saturated $NaHCO_3$ followed by brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane) to give 2.13 g (89% yield) of bromide **15[0]** as a colourless oil. ^{1}H NMR: δ 0.89 (t, J=6.9 Hz, 3H), 1.24–1.41 (m, 4H), 1.60 (quint, J=7.4 Hz, 2H), 2.59 (t, J=7.7 Hz, 2H), 4.49 (s, 2H), 7.14 (d, J=8.1 Hz, 2H), 7.30 (d, J=8.1 Hz, 2H). ^{13}C NMR: δ 14.1, 22.6, 31.1, 31.5, 33.9, 35.7, 128.7, 128.9, 134.9, 143.3. MS: m/z 240 (M^+), 161 (100 %). HRMS: m/z calculated for $C_{12}H_{17}Br$, 240.0514; found 240.0549.

*4-Pentyloxybenzyl chloride (**15[1]**) (46).*

Thionyl chloride (4 ml, 50 mmol) followed by a catalytic amount of DMF were added to a solution of 4-pentyloxybenzyl alcohol (*47*) (**27[1]**, 2.00 g, 10.3 mmol) in benzene (20 ml) at 0°C. The reaction mixture was stirred at 70°C for 6 h and solvents removed. The resulting residue was passed through a short silica gel column (hexane/AcOEt, 5:1) to give 1.92 g (88% yield) of chloride **15[1]** as a colourless oil. ^{1}H NMR: δ 0.93 (t, J=7.0 Hz, 3H), 1.31–1.53 (m, 4H), 1.78 (quint, J=7.0 Hz, 2H), 3.95 (t, J=6.6 Hz, 2H), 4.56 (s, 2H), 6.87 (d, J=8.6 Hz, 2H), 7.29 (d, J=8.6 Hz, 2H). MS: m/z 212 (M^+), 107 (100 %). HRMS: m/z calculated for $C_{12}H_{17}Cl$, 212.0968; found 212.0956.

*1-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]-2-(4-pentylphenyl)ethanol (**16A[0]**).*

To a suspension of Mg (582 mg, 24 mmol) in anhydrous Et_2O (10 ml) was added dropwise a solution of *p*-pentylbenzyl bromide (**15[0],** 2.88 g, 12 mmol) in anhydrous Et_2O (4 ml) and the mixture was stirred at RT for 15 min. Then a solution of aldehyde **10A** (2.00 g, 6.0 mmol) in anhydrous Et_2O (4 ml) was added at 0°C and the mixture was stirred at RT for 12 h. Then the mixture was poured into saturated aqueous NH_4Cl

at 0°C and the mixture was extracted with Et_2O. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 20:1) to give 1.52 g (51% yield) of alcohol **16A[0]**, which was recrystallised (EtOH) to form colourless cubes. M.p. 95–96°C. ^{1}H NMR: δ 0.88 (t, J=6.9 Hz, 3H), 0.91 (t, J=7.3 Hz, 3H), 1.23–1.45 (m, 8H), 1.50–3.75 (br m, 10H), 1.57 (quint, J=7.4 Hz, 2H), 1.70 (d, J=4.3 Hz, 1H), 1.74 (quint, J=6.9 Hz, 2H), 2.32 (dd, J_1=11.1 Hz, J_2=13.8 Hz, 1H), 2.55 (t, J=7.7 Hz, 2H), 2.76 (dd, J_1=1.9 Hz, J_2=13.8 Hz, 1H), 3.64–3.70 (m, 1H), 3.87 (t, J=6.5 Hz, 2H), 6.67 (d, J=8.9 Hz, 2H), 7.02 (d, J=7.8 Hz, 2H), 7.09 (d, J=8.1 Hz, 2H), 7.11 (d, J=8.9 Hz, 2H). MS: *m/z* 496 (M^+), 162 (100%). HRMS: *m/z* calculated for $C_{26}H_{44}B_{10}O_2$, 496.4344; found 496.4365.

*1-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]-2-(4-pentylphenyl)ethyl methanesulfonate (**17A[0]**).*

To a solution of alcohol **16A[0]** (828 mg, 1.67 mmol) in anhydrous THF (8 ml) was added dropwise *n*-BuLi (1.59M solution in hexane, 1.26 ml, 2.0 mmol) at 0°C and the mixture was stirred at RT for 15 min. Then $MeSO_2Cl$ (0.15 ml, 2.0 mmol) was added at 0°C and the mixture was stirred at RT for 6 h. Then the mixture was poured into 10% HCl and was extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product purified by flash column chromatography (SiO_2, *n*-hexane/AcOEt, 15:1) to give 739 mg (77% yield) of sulfonate **17A[0]** as a colourless solid. ^{1}H NMR: δ 0.86 (t, J=6.9 Hz, 3H), 0.91 (t, J=6.6 Hz, 3H), 1.17–1.46 (m, 8H), 1.50–3.75 (br m, 10H), 1.53 (quint, J=7.6 Hz, 2H), 1.73 (quint, J=6.8 Hz, 2H), 1.85 (s, 3H), 2.54 (t, J=7.7 Hz, 2H), 2.58 (dd, J_1=11.9 Hz, J_2=14.6 Hz, 1H), 2.93 (dd, J_1=2.4 Hz, J_2=14.3 Hz, 1H), 3.87 (t, J=6.5 Hz, 2H), 4.74 (dd, J_1=2.7 Hz, J_2=11.6 Hz, 1H), 6.67 (d, J=8.9 Hz, 2H), 7.04 (d, J=8.1 Hz, 2H), 7.10 (d, J=8.4 Hz, 2H), 7.10 (d, J=8.9 Hz, 2H). MS: *m/z* 574 (M^+), 43 (100%). HRMS: *m/z* calculated for $C_{27}H_{46}B_{10}O_4S$, 574.4120; found: 574.4124.

*12-(4-Pentyloxyphenyl)-p-carborane-1-acetaldehyde (**18A**).*

Dess–Martin periodinate (1.817 g, 4.27 mmol) was added portionwise to a stirred solution of alcohol **9A** (1.50 g, 4.27 mmol) in anhydrous CH_2Cl_2 (15 ml). The mixture was stirred at RT for 5 h and filtrated through a pad of Celite. The filtrate was concentrated and the crude product was purified by a column chromatography (SiO_2, hexane/AcOEt, 10:1) to give 1.421 g (95% yield) of **18A** as a colourless solid (*n*-hexane). M.p. 61–63°C. ^{1}H NMR: δ 0.91 (t, J=7.0 Hz, 3H), 1.30–1.45 (m, 4H), 1.50–3.75 (br m, 10H), 1.73 (quint, J=7.0 Hz, 2H), 2.58 (d, J=2.7 Hz, 2H), 3.87 (t, J=6.6 Hz, 2H), 6.67 (d, J=9.2 Hz, 2H), 7.08 (d, J=9.2 Hz, 2H), 9.37 (t, J=2.8 Hz, 1H). ^{13}C NMR: δ 14.0, 22.4, 28.1, 28.8, 48.7, 68.0, 71.8, 83.0, 113.8, 128.0, 128.1, 159.3, 196.7. MS: *m/z* 348 (M^+), 279 (100%). HRMS: *m/z* calculated for $C_{15}H_{28}B_{10}O_2$, 348.3093; found 348.3096.

*2-[12-(4-Pentyloxyphenyl)-p-carboran-1-yl]-1-(4-pentyloxyphenyl)ethanol (**19A[1]**).*

To a suspension of Mg (63 mg, 2.62 mmol) in anhydrous THF (0.5 ml) was added dropwise a solution of *p*-bromopentyloxybenzene (578 mg, 2.38 mmol) in anhydrous THF (1 ml) and the mixture was stirred at RT for 1 h. The prepared Grignard reagent was added to a solution of aldehyde **18A** (415 mg, 1.19 mmol) in anhydrous THF (2 ml) at 0°C and the mixture was stirred at RT for 12 h. Then the mixture was poured into saturated aqueous NH_4Cl at 0°C and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 50:1) to give 338 mg (55% yield) of alcohol **19A[1]**, which was recrystallised (*n*-hexane) to form colourless cubes. M.p. 110–112°C. ^{1}H NMR: δ 0.92 (t, J=7.1 Hz, 6H), 1.20–1.50 (m, 8H), 1.50–3.75 (br m, 10H), 1.65–1.82 (m, 4H), 1.81 (d, J=2.8 Hz, 1H), 1.97 (dd, J_1=2.4 Hz, J_2=15.4 Hz, 1H), 2.12 (dd, J_1=9.2 Hz, J_2=15.3 Hz, 1H), 3.87 (t, J=6.6 Hz, 2H), 3.92 (t, J=6.6 Hz, 2H), 4.48 (dt, J_1=2.9 Hz, J_2=9.2 Hz, 1H), 6.66 (d, J=8.9 Hz, 2H), 6.82 (d, J=8.7 Hz, 2H), 7.09 (d, J=8.9 Hz, 2H), 7.12 (d, J=8.6 Hz, 2H). ^{13}C NMR: δ 13.98, 14.01, 22.4, 22.5, 28.15, 28.19, 28.85, 28.94, 47.0, 68.0, 68.1, 72.8, 77.8, 81.9, 113.8, 114.6, 126.9, 128.2, 128.4, 135.3, 158.9, 159.2. MS: *m/z* 494 (M^+–H_2O, 100%).

*Pentyl 4′-pentyloxy-4-biphenylcarboxylate (**20B**).*

A mixture of 4′-hydroxy-4-biphenylcarboxylic acid (2.50 g, 11.67 mmol), K_2CO_3 (4.03 g, 29.2 mmol) and 1-iodopentane (3.8 ml, 29.2 mmol) in DMF (30 ml) was stirred at 100°C for 24 h. The mixture was poured into ice water and the extracted with Et_2O. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, gradient from 10/1 to 1/1) to give a colourless solid of pentyl 4′-pentyloxy-4-biphenylcarboxylate (**20B**, 0.94 g, 23% yield) and a pale yellow solid of pentyl 4′-hydroxy-4-biphenylcarboxylate (**21B**, 2.41 g, 72% yield). ^{1}H NMR: δ 0.94 (t, J=7.0 Hz, 3H), 1.33–1.51 (m, 4H),

1.79 (t, J=7.0 Hz, 2H), 4.34 (t, J=7.2 Hz, 2H), 5.23 (s, 1 H), 6.94 (d, J=8.4 Hz, 2H), 7.53 (d, J=8.6 Hz, 2H) 7.61 (d, J=8.4 Hz, 2H), 8.08 (d, J=8.1 Hz, 2H).

Without further purification the hydroxy ester **21B** was converted to **20B** by treatment with NaH (1.3 eq) followed by *n*-$C_5H_{11}I$ (1.3. eq) in dry DMF. The pentyl ester **20B** was obtained in a combined yield of 83% of as a colourless solid. M.p. 76°C. ^{1}H NMR: δ 0.94 (t, J=7.3 Hz, 3H), 0.95 (t, J=7.0 Hz, 3H), 1.34–1.50 (m, 8H), 1.79 (quint, J=7.3 Hz, 2H), 1.82 (quint, J=7.3 Hz, 2H), 4.01 (t, J=6.5 Hz, 2H), 4.33 (t, J=6.5 Hz, 2H), 6.98 (d, J=8.9 Hz, 2H), 7.56 (d, J=8.4 Hz, 2H), 7.62 (d, J=8.1 Hz, 2H), 8.08 (d, J=8.1 Hz, 2H). ^{13}C NMR: δ 13.99, 14.01, 22.4, 22.5, 28.18, 28.21, 28.5, 28.9, 65.1, 68.1, 114.9, 126.4, 128.3, 128.5, 130.0, 132.2, 145.2, 159.4, 166.6. Elemental analysis: calculated for $C_{23}H_{30}O_3$, C 77.93, H 8.53; found, C 77.93, H 8.41%.

*4-Bromo-4′-pentyloxybiphenyl (**24B**) (48).*

NaH (60% in oil, 2.08 g, 52 mmol) was added portionwise to a solution of 4-bromo-4′-hydroxybiphenyl (10.0 g, 40 mmol) in anhydrous DMF (100 ml) at 0°C. After stirring for 30 min at RT, 1-iodopentane (6.78 ml, 52 mmol) was added at 0°C and the mixture was stirred for 6 h. The mixture was poured into ice water and extracted with Et_2O. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was recrystallised (hexane) to give 11.76 g (92% yield) of bromide **24B** as colourless crystals. M.p. 132°C [lit. (*48*) m.p. 133°C]. ^{1}H NMR: δ 0.94 (t, J=7.0 Hz, 3H), 1.30–1.52 (m, 4H), 1.81 (quint, J=7.0 Hz, 2H), 3.99 (t, J=6.5 Hz, 2H), 6.96 (d, J=8.9 Hz, 2H), 7.41 (d, J=8.4 Hz, 2H), 7.47 (d, J=8.9 Hz, 2H), 7.53 (d, J=8.9 Hz, 2H). ^{13}C NMR: δ 14.0, 22.5, 28.2, 29.0, 68.1, 114.9, 120.7, 127.9, 128.2, 131.7, 132.2, 139.8, 159.0. MS: *m/z* 318 and 320 (1:1, M^+), 248 (100 %). Elemental analysis: calculated for $C_{17}H_{19}BrO$, C 63.96, H 6.00; found, C 63.91, H 6.00%.

*4-Iodo-4′-pentyloxybiphenyl (**25B**).*

A solution of bromide **24B** (1.60 g, 5.02 mmol) in THF (16 ml) was added dropwise to a mixture of Mg (158 mg, 6.53 mmol) and THF (1 ml) at RT and the mixture was refluxed for 1 h. The reaction mixture was cooled and added to a stirring solution of I_2 (828 mg, 6.53 mmol) in THF (10 ml) at 0°C. The reaction mixture was stirred at RT for 1 h, 10% aqueous $NaHSO_3$ was added and the mixture extracted with Et_2O. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The crude product was purified by flash column chromatography (SiO_2, hexane) to give 939 mg (51% yield) of iodide **25B** as a colourless solid. M.p. 142–143°C. ^{1}H NMR: δ 0.94 (t, J=7.2 Hz, 3H), 1.30–1.53 (m, 4H), 1.81 (quint, J=7.0 Hz, 2H), 3.99 (t, J=6.5 Hz, 2H), 6.96 (d, J=8.9 Hz, 2H), 7.29 (d, J=8.1 Hz, 2H), 7.47 (d, J=8.6 Hz, 2H), 7.72 (d, J=8.6 Hz, 2H). ^{13}C NMR: δ 14.0, 22.5, 28.2, 28.9, 68.1, 92.0, 114.9, 127.9, 128.5, 132.2, 137.7, 140.4, 159.0. MS: *m/z* 366 (M^+), 296 (100 %). Elemental analysis: calculated for $C_{17}H_{19}IO$, C 55.75, H 5.23; found, C 55.90, H 5.13%.

*Ethyl 4′-pentyloxy-4-biphenylacetate (**26B**).*

The double neck flask was charged sequentially with iodide **25B** (1.00 g, 2.73 mmol), CuI (206 mg, 1.092 mmol), 2-phenylphenol (370 mg, 2.19 mmol) and Cs_2CO_3 (1.33 g, 4.1 mmol). The flask was evacuated and backfilled with Ar (3 times). Anhydrous 1,4-dioxane (15 ml) was added followed by diethyl malonate (0.82 ml, 5.46 mmol) and the reaction mixture was refluxed at 140°C for 12 h. The reaction mixture was cooled and filtrated through a pad of Celite. The filtrate was washed with saturate aqueous NH_4Cl followed by brine, dried ($MgSO_4$) and concentrated. The crude product purified by flash column chromatography (SiO_2, *n*-hexane/AcOEt, gradient from 30:1 to 10:1) to give 0.48 g (54% yield) of ester **26B** as a colourless solid. ^{1}H NMR: δ 0.94 (t, J=7.2 Hz, 3H), 1.27 (t, J=7.3 Hz, 3H), 1.32–1.52 (m, 4H), 1.81 (quint. J=7.0 Hz, 2H), 3.64 (s, 2H), 3.99 (t, J=6.6 Hz, 2H), 4.17 (q, J=7.1 Hz, 2H), 6.95 (d, J=8.9 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 7.50 (d, J=8.9 Hz, 2H), 7.51 (d, J=8.6 Hz, 2H).

Acknowledgements

This project was supported in part by Grant-in-Aid for Scientific Research (B) No. 13470468, the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by the NSF grant (DMR-0111657 and DMR-0606317).

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