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Maura Belloni [a], M. Manickam [a], Zehn-He Wang [a] & Jon A. Preece [a]

[a] School of Chemical Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

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TOWARD BORONATE ESTER MESOGENIC STRUCTURES

*Maura Belloni, M. Manickam, Zehn-He Wang, and Jon A. Preece**
School of Chemical Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

This article describes efforts toward the development of a new core for calamitic mesogens based upon the introduction of an extended heteroaromatic boron-containing ring. A series of tri-catenar mesogenic boronate ester derivatives of the 2-phenyl-1,3,2-benzodioxaborole has been synthesized and characterized. The flat central core appeared to be a suitable feature for these derivatives to support anisotropic alignment. Additionally, these derivatives should possess an inherent dipole in the core. However, thermal analysis (polarized optical microscopy and differential scanning calorimetry) did not reveal any mesophases.

Keywords: boronate esters; 2-phenyl-1,3,2-benzodioxaborole; mesogenic

INTRODUCTION

The most important types of calamitic liquid crystals (LCs) commonly used in display devices are 4-alkyl-4′-cyanobiphenyls (nCBs) discovered by George Gray in 1973 [1]. Since the discovery of nCBs, research in the field of LCs has been driven by the development of new materials for display devices [2]. The modification of the parent structural motif of nCBs by entire or partial replacement of the phenyl rings, with heteroaromatic [3-8], cycloaliphatic [3,9,10], and cycloheteroaliphatic [5,6] moieties has been carried out to investigate the structural features that favor liquid crystallinity. In the 1980s the insertion of the boron atom in nonaromatic cores of thermotropic LCs was first achieved. Seto *et al.* [11–13] obtained *1,3,2-Dioxaborinane* liquid crystalline derivatives, which either had a wide nematic range

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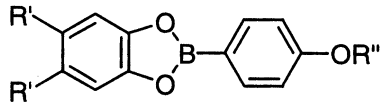
*Corresponding author. E-mail: j.a.preece@bham.ac.uk

or formed a chiral smectic C (S_{C*}) phase exhibiting ferroelectric behavior. Furthermore, other boron-containing LCs based on *cholesterylphenylboronic* acids [14] were synthesized as potential sugar receptors.

The objective of the research presented in this article was to incorporate the boron atom in the rigid core component of the pseudo-aromatic ring of the 2-phenyl-1,3,2-benzodioxaborole derivatives (Figure 1). The 2-phenyl-1,3,2-benzodioxaborole unit is much more planar [15] than the crystal structures of the classical 4-alkyl-4′-cyanobiphenyl LCs [16], in which there is a significant deviation from planarity of the two phenyl rings. X-ray studies of the 2-phenyl-1,3,2-benzodioxaborole have shown that the molecule in the crystalline state is nearly flat [15]. The length of the BO (boron-oxygen) bonds (1.39 Å) are intermediate between a single BO bond (1.43 Å) and a double BO bond (1.36 Å), suggesting aromatic-like conjugation in the five-membered ring [15]. Further evidence for the aromatic character [17] of the 2-phenyl-1,3,2-benzodioxaborole arises from IR [18] and UV [19] experiments. The length of the 2-phenyl-1,3,2-benzodioxaborole is ~8.85 Å, which is intermediate between the biphenyl (7.12 Å) [20,21] and terphenyl (11.54 Å) [22] cores. Additionally, the 2-phenyl-1,3,2-



Entry	R'	$C_xC_xBC_y$	R"
1	H	$C_0C_0BC_1$	CH_3
2	H	$C_0C_0BC_3$	C_3H_7
3	H	$C_0C_0BC_{11}$	$C_{11}H_{23}$
4	C_5H_{11}	$C_5C_5BC_1$	CH_3
5	C_5H_{11}	$C_5C_5BC_9$	C_9H_{19}
6	C_5H_{11}	$C_5C_5BC_{11}$	$C_{11}H_{23}$
7	C_6H_{13}	$C_6C_6BC_9$	C_9H_{19}
8	C_8H_{17}	$C_8C_8BC_3$	C_3H_7
9	C_8H_{17}	$C_8C_8BC_5$	C_5H_{11}
10	C_8H_{17}	$C_8C_8BC_9$	C_9H_{19}

FIGURE 1 Structure of the target boronate ester derivatives $C_xC_xBC_y$ **1–10**.

benzodioxaborole structure should be inherently dipolar, unlike the biphenyl and terphenyl, which have to be chemically modified by the introduction of cyano groups, for example. Therefore, it was our principal objective to design a core with structural similarities to the biphenyl and terphenyl system while having electronic properties that would make it attractive as a switching element in devices.

Thus, the research described in this article will focus on the synthesis of the 2-phenyl-1,3,2-benzodioxaborole derivatives **1–10** ($C_xC_xBC_y$ series) (Figure 1). These compounds are characterized by two features:

1. a boron atom incorporated into a pseudo-aromatic ring, and
2. a "Y" molecular shape distinctive of the polycatenar [23] and swallow-tailed [24] LCs.

RESULTS AND DISCUSSION

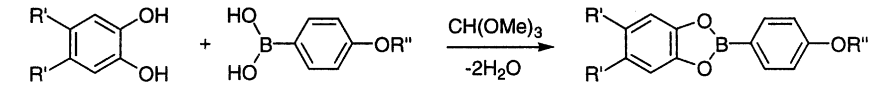
The 2-(4-alkyloxyphenyl)-5,6-dialkyl-benzo[1,3,2]dioxaboroles **1–10** were synthesized *via* the esterification of 4-alkyloxyphenylboronic acids **14–19** derivatives with 4,5-dialkylcatechol **11–13** derivatives (Scheme 1).

The two-step reaction to afford the desired boronic acids **14–19** (Scheme 2) required an initial standard *O*-alkylation [25–27] (with the appropriate alkyl halide under basic conditions) followed by a standard lithium/halogen exchange [28] (*n*-BuLi), followed by quenching with trimethyl borate and hydrolysis (aqueous HCl).

The 4-alkyloxyphenylboronic acids **14–19** were afforded as a mixture with their anhydrides **26–31** (Scheme 3). The acids trimerize to the anhydrides because of partial dehydration during isolation of the acids [29–32]. The presence of the boronic acid/anhydride mixture is shown by a twin set of signals in the ^{1}H NMR ($CDCl_3$) spectra of the isolated 4-alkyloxyphenylboronic acid **14–19** [32].*

A five-step protocol was followed to yield the 4,5-dialkylcatechols **11–13** (Scheme 4).

*Throughout the synthesis of the 4-alkyloxyphenylboronic acids **14–19**, clear evidence of partial formation of the corresponding anhydrides **26–31** was observed. These species are formed by trimerization of the acids with loss of three molecules of H_2O, to generate the trimers (triphenylboroxins). X-ray studies [31] of triphenylboroxin showed that the central unit, constituted by the conjugated system of the B_3O_3 ring, is nearly planar. Additionally, also the three-phenyl units were observed to be nearly coplanar with the central B_3O_3 ring, leading to a wide, flat, and rigid central core, which correctly functionalized might be suitable for the development of new discotic LCs. With this in mind, the anhydrides of the 4-alkyloxyphenylboronic acids **14–19** were observed under POM. However, they did not display any mesomorphic behavior, melting directly from the solid to the isotropic liquid.



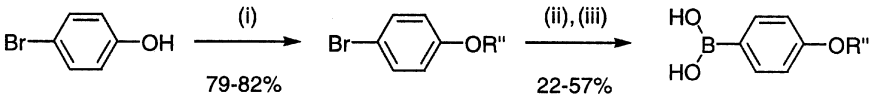
Entry	R'
11	C_5H_{11}
12	C_6H_{13}
13	C_8H_{17}

Entry	R"
14	CH_3
15	C_3H_7
16	C_5H_{11}
17	C_7H_{15}
18	C_9H_{19}
19	$C_{11}H_{23}$

1-10
10-92%

SCHEME 1 Formation of the 2-phenyl-1,3,2-benzodioxaborole derivatives **1–10** by esterification between 4,5-dialkylcatechols **11–13** and 4-alkyloxyphenylboronic acids **14–19**, with loss of two molecules of H_2O.

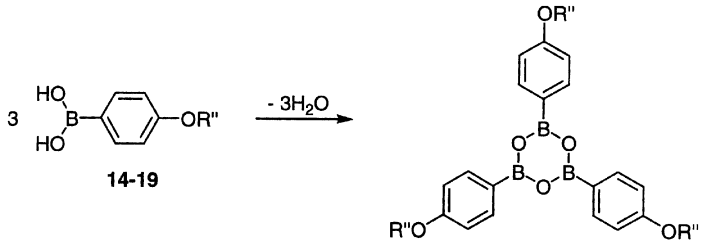
Commercially available 1,2-methylenedioxy-benzene was chosen as a convenient starting material because the bridging methylene unit (OCH_2O) protects both phenolic moieties, and can be removed in the final step. The first step (Scheme 4) involved the acid-catalyzed bromomethylation [33] of 1,2-methylenedioxy-benzene at the 4 and 5 positions of the phenyl ring, using paraformaldehyde and HBr in AcOH to afford **32**. In the second step **32** was converted to the bis-phosphonium salt **33** with an excellent yield [35,36]. The bis-phosphonium salt **33** was used in a Wittig [34,35] reaction (EtOLi, EtOH [36,37]) with the appropriate aldehyde, to form the mixture



14-19

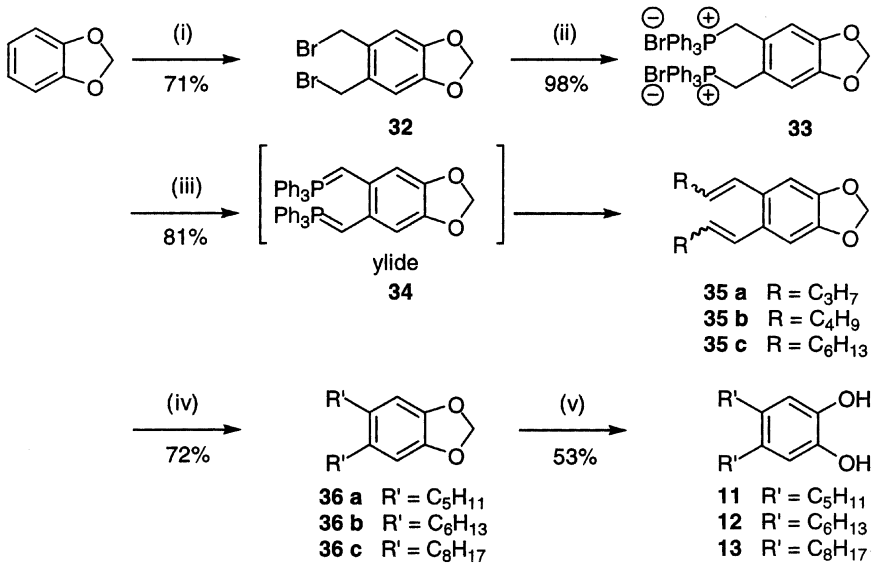
Entry	R"
20	CH_3
21	C_3H_7
22	C_5H_{11}
23	C_7H_{15}
24	C_9H_{19}
25	$C_{11}H_{23}$

SCHEME 2 Reagents and conditions: (i) 1.0 eq CH_3I or RBr, 10.0 eq K_2CO_3, CH_3CN, reflux, 24 h; (ii) 1.05 eq n-BuLi, −78°C, anhydrous THF, N_2 atmosphere, 45 min; 1.05 eq $B(OMe)_3$, −78°C, N_2 atmosphere, 1 h; (iii) 10% HCl, rt, 1 h.



Entry	R"
26	CH_3
27	C_3H_7
28	C_5H_{11}
29	C_7H_{15}
30	C_9H_{19}
31	$C_{11}H_{23}$

SCHEME 3 Dehydration and trimerization of boronic acids **14–19** to anhydrides **26–31**, with loss of three molecules of H_2O.



SCHEME 4 Reagents and conditions: (i) 4.7 eq $(CH_2O)_n$, 5.5 eq HBr/AcOH, rt, 3 h; (ii) 2.0 eq PPh_3, DMF, reflux, 3 h; (iii) 6.0 eq butyraldehyde, 1.0–2.5 eq EtOLi, EtOH, reflux, 24 h; (iv) H_2, Pd/C (10%), MeOH/$CHCl_3$, rt, 48 h; (v) 3.0 eq $AlBr_3$, EtSH, 0°C; then rt, 24 h, H_2O for quenching.

of diastereoisomeric dienes **35a–35c**. Although the dienes were obtained as a mixture of the *cis*,*cis*, *cis*,*trans*, and *trans*,*trans* stereoisomers, which were observed as three spots by TLC (hexane/EtOAc), separation of the three isomers was not necessary for the synthetic purposes, as they were hydrogenated (H_2, Pd/C [38]) to the saturated derivatives **36a–36c** in the next step. The hydroxyl functionalities were generated using aluminium tribromide ($AlBr_3$) and ethyl mercaptan (EtSH), a system [39–41] that cleaves the methylenedioxy group and reveals the catechol moieties in compounds **11–13** (Scheme 1). The final step (Scheme 1) was the esterification reaction to afford the boronate ester derivatives **1–10** ($C_xC_xBC_y$) with elimination of H_2O. In order to obtain an efficient removal of H_2O, the esterification was performed using trimethyl orthoformate, $CH(OMe)_3$ [42,43] as the solvent which acted as a dehydrating agent.

Compounds **1**, **2**, **3**, **4**, and **5** were crystalline at room temperature and easily isolated by recrystallization. However, the other homologous **6–10** were waxy materials at room temperature, and purification by recrystallization or column chromatography or solvent extraction was not successful.* Thus, among the series, only compounds **1–5** were obtained in an analytically pure form. However, we include compounds **6–10** in this article to illustrate the range of materials that were prepared and highlight the difficulties in their purification.

THERMAL ANALYSIS AND PHASE BEHAVIOR

Thermal behavior of these materials $C_xC_xBC_y$ (**1–10**) was investigated using polarized optical microscopy (POM) and differential scanning calorimetry (DSC). From the POM observations, compounds **1–4** melted directly from solid to the isotropic liquid at 115, 92, 75, and 73°C, respectively. Compound **4** underwent two polymorphic transitions at 28°C

*Attempts at purification methods carried out on $C_xC_xBC_y$:

I. Chromatography on silica gel (eluent: 60% EtOAc in hexane) or preparative TLC on silica plate (eluent: 30% EtOAc in $CHCl_3$) were unsuccessful, due to hydrolysis of the products by the acidic silica. In fact, generally boronate esters are easily hydrolyzed in acid conditions [19].

II. Chromatography on alumina gel (eluent: CH_3CN) revealed that boronate esters were decomposed. This result was confirmed by ^{1}H-NMR data, which revealed that the different bands collected from the preparative TLC on alumina were neither the boronate esters nor the starting materials.

III. Continuous extraction was performed in CH_3CN and hexane using a liquid-liquid continuous extractor. The hexane (top layer) has been chosen as the extracting solvent, to remove the impurities, while the products preferentially remained in CH_3CN (bottom layer). This method, performed for three hours under reflux, was partially successful. Only compounds $C_6C_6BC_9$ **7** and $C_8C_8BC_5$ **9** were obtained with a satisfactory degree of purity (judged by ^{1}H-NMR).

and 43°C before reaching the isotropic liquid state at 62°C. On cooling it passed directly to the solid state at 22°C. The DSC analysis (Figure 2) suggested that compound **5** did not form any mesophase. In fact, only one peak on both the heating (41°C) and cooling (9.4°C) stages can be observed. Therefore, it has been concluded that this derivative was not liquid crystalline.

The POM observations on the other compounds **6–10** showed that they did not melt directly to the isotropic liquid, but became fluid-like, maintaining the same texture, which was not easily identifiable. The DSC phase transitions are listed in Table 1 (DSC data).

As previously mentioned, compounds **6–10** were not pure, therefore the interpretation of thermal analysis results cannot be conclusive. However, the results obtained on the pure derivative **5**, which did not exhibit mesomorphic behavior, lead to the conclusion that the whole $C_xC_xBC_y$ series of materials are not liquid crystalline.

CONCLUSIONS

A new series of mesogenic molecular structures $C_xC_xBC_y$ has been synthesized with the purpose of extending general investigations upon the molecular structures capable of displaying mesophase. In the $C_xC_xBC_y$ series of boronate ester derivatives, the attractive molecular aspect is represented by the planarity of the core and the inherent dipole due to the presence of the boron atom adjacent to two oxygen atoms. Ten $C_xC_xBC_y$ compounds were synthesized by esterification of a series of 4-alkyloxyphenylboronic acids **14–19** ($OCH_3OC_{11}H_{23}$) with 4,5-dialkylcatechol **11–13** in trimethyl orthoformate. These 2-phenyl-1,3,2-benzodioxaborole derivatives **1–10** differ in the length of the flexible peripheral chains attached to the central rigid core, so that the thermal properties could be

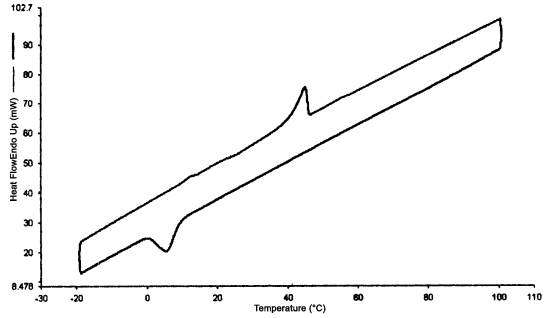


FIGURE 2 DSC trace of the pure compound **5** ($C_5C_5BC_9$).

TABLE 1 Transition Temperatures (°C) of **5–10** Recorded on Second Heating by DSC Analysis (T Onset Reported Values)

Sample	Sol		X		Y		Z		I
$C_5C_5BC_9$	•	–	–	–	–	–	–	41.0	•
5								(13.7)	
$C_5C_5BC_{11}$	•	−16.1	•	−0.8	•	–	–	18.2	•
6		(−10.8)		(0.1)				(11.3)	
$C_6C_6BC_9$[a]	•	−27.7	•	6.3	•	25.0	•	41.9	•
7		(−3.6)		(0.08)		(6.9)		(0.2)	
$C_8C_8BC_3$	•	−10.2[b]	•	22.8	•	–	–	45.2	•
8		(0.5)		(−1.8)				(1.6)	
$C_8C_8BC_5$[a]	•	−9.7[b]	•	−6.1	•	–	–	12.9	•
9		(0.07)		(0.03)				(13.7)	
$C_8C_8BC_9$	•	−10.4[b]	•	25.4	•	44.6	•	52.2	•
10		(0.2)		(14.0)		(0.1)		(0.03)	

[a]pure by ^{1}H NMR.

[b]peak values.

The enthalpy changes ΔH (kJ mol^{-1}) for the transitions observed are reported in brackets.

Sol represents either the solid or waxy state. **X**, **Y**, and **Z** represent undefined intermediate physical states.

investigated extensively over a range of homologues. Unfortunately, these derivatives were difficult to purify and easily susceptible to hydrolysis and degradation with time. Thermal analysis by POM and DSC revealed that compounds $C_xC_xBC_y$ melted to an isotropic liquid and failed to display any mesophases.*

The obvious question is why do these materials not exhibit mesophases, since we designed them to have similar steric (planarity and length) and electronic (16 π-electron) core requirements as the biphenyl and terphenyl derivatives? The following thoughts may, retrospectively, shed some light on this question. Firstly, the 2-phenyl-1,3,2-benzodioxaborole is a much more planar species than the biphenyl or terphenyl species, which have a torsional twist around the CC bonds joining the phenyl rings. There is no such torsional twist around the BC bond in the 2-phenyl-1,3,2-benzodioxaborole. Secondly, the two phenylene rings in 2-phenyl-1,3,2-benzodioxaborole are probably electron deficient as a result of the electron-deficient boron atom pulling electron density out of both phenylene rings, via resonance effects in the ring the boron is directly attached to and inductive

*The rigid core might need to be extended with at least an extra ring, as well as introducing a linking group such as an ester functionality, in order to build up flexibility in the molecular structure and show mesogeneity.

effects on the other ring. Thus, taking these two points together there are probably strong π-π interactions between adjacent 2-phenyl-1,3,2-benzodioxaboroles, resulting in materials that upon heating are unable to display anisotropic liquid phases.

The next obvious question to ask is how then might these materials be modified to induce mesophase behavior? One avenue to pursue is the replacement of the catechol moieties with 1,2-diamino moieties to afford more stable boronate amides derivatives, and allow access to a wider range of materials, as the purification process should be easier. However, it would be more interesting to investigate further the ideas discussed in the previous paragraph about the stereoelectronics. Thus, one can envisage the introduction of a Me substituent on the disubstituted phenylene ring *ortho* to the CB bond, in order to break the planar nature of the 2-phenyl-1,3,2-benzodioxaborole unit and hence reduce the strong tendency for anisotropic alignment. Additionally, the R′ groups, instead of being weak inductive +I groups, could be replaced with alkoxy groups which would considerably increase the π-electron density on the tetrasubstituted aromatic ring, and hence reduce the π-π stacking interactions.

EXPERIMENTAL

General Procedures

Commercially available chemicals were purchased from Aldrich and used as such without any purification unless otherwise stated. Anhydrous THF was distilled under a N_2 atmosphere over sodium/benzophenone. *n*-Butyllithium (*n*-B uLi) was titrated using diisopropylamine, 4-phenylbenzylidenebenzylamine (as the indicator) in anhydrous THF, and 2-butanol (1 M in xylene) as the titrating agent [44]. Thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F_{254} (Merck 5554). TLC plates were air-dried, revealed under UV lamp (254 nm) and developed in iodine vapor if needed. Column chromatographic separations were performed on silica gel 60 (Merck 9385, 230–400 mesh or ICN EchoChrom 32-63, 60 Å). ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on a Bruker AC300 (300.13 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC300 (75.5 MHz) spectrometer using the PENDANT pulse sequences. ^{31}P NMR spectra were recorded on a Bruker AC300 (121.5 MHz) spectrometer using ^{1}H decoupling. All chemical shifts are quoted in δ (ppm) to higher frequency from Me_4Si, using deuterated chloroform ($CDCl_3$), or acetone (acetone-d_6) as the lock and the residual solvent as the internal standard. The coupling constants J ($J = {}^3J_{vic}$, $J_o = {}^3J$ ortho, $J_m = {}^4J$ meta, $J_{P\text{-}H} = {}^3J$ coupling phosphorus-hydrogen, ${}^1J_{P\text{-}C}$, ${}^2J_{P\text{-}C}$, and ${}^3J_{P\text{-}C} = J$ coupling phosphorus-carbon) are

expressed in Hertz (Hz) with multiplicities abbreviated as follows: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, b = broad. Electron impact mass spectrometry (EIMS) was performed on a VG ProSpec and a Kratos Profile instrument. Liquid secondary ion mass spectrometry (LSIMS) was performed on a VG ZabSpec instrument equipped with a cesium ion source and using *m*-nitrobenzylalcohol (NOBA) as a matrix. Electrospray mass spectrometry (ESMS) was performed on a Micromass LCT time of flight (TOF) using methanol as the running solvent. High resolution mass spectrometry (HRMS) was performed on a Micromass ProSpec and Micromass ZabSpec instruments using perfluorokerosene (PFK) as calibrant for the EI and Cesium Iodide or Polyethylene glycol (PEG) for LSI. Elemental analysis was carried out on a Carlo Erba EA 1110 (C H N S) instrument. POM experiments were carried out using an Olympus BX40 optical microscope with crossed polarizers equipped with Linkam LT350 hot stage. DSC data was recorded on a Perkin-Elmer 7 Series thermal analysis system under a N_2 or He purge, using a cooling system of circling H_2O or liquid N_2, respectively. The software used in connection with the DSC instrument was Pyris I. All samples were heated and cooled in a double cycle, at the rate of 10.00°C/min. Melting points and boiling points were determined using an Electrothermal 9200 melting point apparatus and are uncorrected.

1-Bromo-4-alkyloxy-benzene derivatives (20–25) and 4-alkyloxyphenylboronic acid (14–19)

The general procedure for the synthesis of compounds **20–25** and **14–19** follows a slightly modified preparation reported in the literature [27]. However, details regarding the synthetic procedure and the full characterization of these compounds are thoroughly described in our previous publication [45].

1,2-Methylenedioxy-4,5-dibromomethylbenzene or 5,6-bis-bromomethyl-benzo[1,3]dioxole (32)

The preparation of compound **32** follows a literature procedure [46]. To a stirred suspension of formaldehyde (28.3 g, 0.94 mol) in 1,2-methylenedioxy-benzene (26.6 mL, 0.20 mol), HBr/AcOH (45%, 1.1 mol, 200 mL) was added at 0°C. The mixture was stirred for further 30 min at 0°C and then allowed to warm to room temperature and stirred overnight. H_2O was added until the product precipitated. The precipitate was filtered and dried in vacuo. The crude product was purified by silica gel column chromatography using $CHCl_3$ as eluent. The chromatographed material was further purified by recrystallization from hexane/toluene to yield the product as a

white solid [46] (43.9 g, 71%): m.p. 112.4–114.2°C; ν_{max}/cm^{-1} 1503, 1488, 1376, 1266, 1210, 1170, 1037, 931; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.58 (s, 4 H, BrC***H***$_2$), 5.98 (s, 2 H, OC***H***$_2$O), 6.81 (s, 2 H, Ar***H***); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 30.57 (2 C, Br***C***H$_2$), 101.85 (1 C, O***C***H$_2$O), 110.89 (2 C, Ar***C***H), 130.59 (2 C, Ar***C***), 148.33 (2 C, Ar***C***); ***m/z*** (EIMS) 308 (average M^+, 15%), 227 and 229 (M-Br^+, 75%), 148 (M-2Br^+, 100%). Elemental analysis: $C_9H_8Br_2O_2$ (M_m: 307.969: calc. C, 35.10; H, 2.62; found C, 35.14; H, 2.38).

1,2-Methylenedioxy-4,5-bis-(triphenyl)-methyl-benzene bis-phosphonium dibromo salt (33)

The procedure for the synthesis of compound **33** is described in the literature [34,35]. To a stirred solution of **32** (44.0 g, 0.14 mol) in DMF (300 mL), triphenylphosphine (75.3 g, 0.28 mol) was added. The reaction was heated under reflux under a N_2 atmosphere for 3 h and then cooled to room temperature. The resulting precipitate was filtered, washed with EtOAc, and then dried in vacuo at 280°C for 24 h, affording the product as a pale pink solid (114.0 g, 98%): m.p. 127°C (decomposition); ν_{max}/cm^{-1} 2797, 1483, 1435, 1263, 1110, 1037; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.91 (d, 4 H, ^{2}***J***$_{P\text{-}H}$ 14 MHz, PC***H***$_2$), 5.89 (s, 2 H, OC***H***$_2$O), 6.36 (s, 2 H, Ar***H***), 7.52–7.96 (m, 30 H, Ar***H***-Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 28.53 (2 C, d, ^{1}***J***$_{P\text{-}C}$ 49 MHz, P***C***H$_2$) [48], 103.64 (2 C, O***C***H$_2$O), 112.80 (2 C, s, Ar***C***H-3,6), 118.6 (6 C, d, ^{1}***J***$_{P\text{-}C}$ 86–82 MHz, Ar***C***) [48], 122.52 (2 C, t, ^{2}***J***$_{P\text{-}C}$ 9.9 MHz, Ar***C***) [49], 131.30 (12 C, t, ^{3}***J***$_{P\text{-}C}$ 6.4 MHz, Ar***C***H) [48], 135.44 (12 C, d, ^{2}***J***$_{P\text{-}C}$ 4.7 MHz, Ar***C***H) [48], 136.46 (6 C, s, Ar***C***H), 149.46 (2 C, Ar***C***); δ_P (121 MHz, CD_3CN) 20.17 (2 P); ***m/z*** (LSIMS) 855 (M+Na^+, 10%), 753 (MBr^+, 100%), 671 (MBrPh$^+$, 65%), 595 (MBr2Ph$^+$, 65%); HRMS (LSIMS) $C_{45}H_{40}Br_2O_2PBr$ calc. 753.1687; found 753.1682.

1,2-Methylenedioxy-4,5-di-(alk-1-enyl)benzene or 5,6-di-alk-1-enyl-benzo[1,3]dioxole (35a–35c)

The conditions employed in order to perform the Wittig reaction were as reported in the literature [34,35]. To a stirred solution of compound **33** (1.0 eq) in EtOH (100–300 mL) the appropriate aldehyde (6.0 eq) and EtOLi (1.0–2.5 eq) were added under a N_2 atmosphere. The reaction was stirred at room temperature overnight. The reaction was then heated under reflux under a N_2 atmosphere for 8 h and then allowed to cool to room temperature. The mixture was extracted with Et_2O:EtOAc (150 mL:60 mL) and washed with H_2O (2 × 30 mL) and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed in vacuo. The product

TABLE 2 Quantities of Reagents Used to Synthesize Compounds **35a–35c** and Their Analytical Data: *m/z* (EIMS), ^{1}H NMR (ppm), ^{13}C NMR (ppm), Elemental Analysis (EA), or High Resolution Mass Spectrometry (HRMS)

Target	33	Aldehyde	EtOLi	Yield	m/z (EIMS) ^{1}H NMR (300 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$)	EA and/or HRMS
35a	18.1 g, 24 mmol	Butyraldehyde: 10.4 g, 144 mmol	3.2 g, 60 mmol	5.0 g, 81%	EIMS 258 (M^+, 35%), 215 ($MC_3H_6^+$, 65%), 173 ($M2C_3H_6^+$, 100%)	$C_{17}H_{22}O_2$ HRMS (EIMS) calc. 258.1620 found 258.1622
35b	7.25 g, 8.71 mmol	Pentanal: 2.2 g, 21.7 mmol	1.1 g, 21.7 mmol	4.3 g, 70%	EIMS 286 (M^+, 43%) ^{1}H NMR: 0.80–0.95 (m, 6 H), 1.19–1.48 (m, 10 H), 2.03–2.25 (m, 4 H), 5.61–6.98 (m, 6 H); ^{13}C NMR: 14.00, 22.40, 28.22, 31.73, 32.92, 56.44, 105.01, 109.30, 127.43, 127.53, 130.56, 133.32	
35c	7.25 g, 8.71 mmol	Heptanal: 2.8 g, 21.7 mmol	1.1 g, 21.7 mmol	5.6 g, 76%	EIMS 342 (M^+, 33%), 271 ($MC_5H_{11}^+$, 18%), 257 ($MC_6H_{13}^+$, 83%) ^{1}H NMR: 0.76–0.99 (m, 6 H), 1.02–1.67 (m, 20 H), 2.03–2.24 (m, 2 H), 5.44–6.98 (m, 6 H)	

TABLE 3 Quantities of Reagents Used to Synthesize Compounds **36a–36c** and Their Analytical Data: m/z (EIMS), ^{1}H NMR (ppm), ^{13}C NMR (ppm), IR

Target	35	Yield	m/z (EIMS) ^{1}H NMR (300 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$)	IR
36a	35a: 3.0 g, 11.6 mmol	2.16 g, 71.5%	EIMS 262 (M^+, 65%), 205 ($MC_4H_8^+$, 15%), 149 ($M2C_4H_8^+$, 100%) ^{1}H NMR: 0.91 (t, 6 H, *J* 6.8 MHz, C*H*$_3$), 1.27–1.37 (m, 8 H, C*H*$_2$), 1.49–1.57 (m, 4 H, C*H*$_2$), 2.51 (t, 4 H, *J* 7.9 MHz, Ph-C*H*$_2$), 5.89 (s, 2 H, OC*H*$_2$O), 6.67 (s, 2 H, Ar*H*); ^{13}C ;NMR: 14.11 (2 C, *C*H$_3$), 22.65 (2 C, *C*H$_2$), 31.33 (2 C, *C*H$_2$), 31.89 (2 C, *C*H$_2$), 32.63 (2 C, Ph-*C*H$_2$), 100.55 (1 C, O*C*H$_2$O), 109.25 (2 C, Ar*C*H), 133.65 (2 C, Ar*C*), 145.37 (2 C, Ar*C*)	ν_{max}/cm^{-1} 2956, 2927, 2870, 1503, 1485, 1245, 1161, 1042, 938
36b	35b: 4.9 g, 17 mmol	3.85 g, 78%	EIMS 290 ((M^+, 41%), 219 (M-$C_5H_{11}^+$, 5%), 149 (M-2$C_5H_{11}^+$, 100%) ^{1}H NMR: 0.89 (t, 6 H, *J* 6.6 MHz), 1.24–1.40 (m, 12 H), 1.40–1.56 (m, 4 H), 2.50 (t, 4 H, *J* 7.9 MHz), 5.87 (s, 2 H), 6.63 (s, 2 H); ^{13}C NMR: 14.30, 22.83, 29.51, 31.75, 31.95, 32.80, 56.70, 100.20, 109.37, 133.78, 145.47	
36c	35c: 5.8 g, 17 mmol	4.77 g, 81%	EIMS 346 ((M^+, 94%), 247 (M-$C_7H_{15}^+$, 10%), 149 (M-2$C_7H_{15}^+$, 100%) ^{1}H NMR: 0.88 (t, 6 H, *J* 6.6 MHz), 1.19–1.39 (m, 20 H), 1.39–1.57 (m, 4 H), 2.49 (t, 4 H, *J* 7.9 MHz), 5.87 (s, 2 H), 6.63 (s, 2 H) ^{13}C NMR: 14.03, 22.59, 29.20, 29.43, 29.56, 31.51, 31.81, 32.53, 56.80, 100.39, 109.10, 133.51, 145.91	

TABLE 4 Quantities of Reagents Used to Synthesize Compounds **11–13** and Their Analytical Data: m/z (EIMS), ^{1}H NMR (ppm), ^{13}C NMR (ppm), elemental analysis (EA), or High Resolution Mass Spectrometry (HRMS), IR

Target	36	$AlBr_3$	Yield	^{1}H NMR (300 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$)	m/z (EIMS)	EA and/or HRMS	IR
11	36a: 2.0 g, 3.8 mmol	3.06 g, 11.5 mmol	1.0 g, 53%	^{1}H NMR: 0.91 (t, 6 H, ***J*** 6.8 MHz, C***H***$_3$), 1.28–1.38 (m, 8 H, C***H***$_2$), 1.47–1.57 (m, 4 H, C***H***$_2$), 2.48 (t, 4 H, ***J*** 7.8 MHz, C***H***$_2$), 5.08 (bs, 2 H, O***H***), 6.76 (s, 2 H, ArC***H***); ^{13}C NMR: 14.10 (2 C, ***C***H$_3$), 22.65 (2 C, ***C***H$_2$), 31.18 (2 C, ***C***H$_2$), 31.91 (2 C, ***C***H$_2$), 32.03 (2 C, Ph-***C***H$_2$), 116.20 (2 C, Ar***C***H), 133.5 (2 C, Ar***C***), 141.07 (2 C, Ar***C***)	250 (M^+, 30%), 193 (M-$C_4H_8^+$, 10%), 137 (M-$2C_4H_8^+$, 100%)	$C_{16}H_{26}O_2$ HRMS (LSIMS) calc. 250.1928 found: 250.1928	ν_{max}/cm^{-1} 3359, 2956, 2928, 2859, 1606, 1516, 1454, 1290
12	36b: 0.9 g, 3.42 mmol	2.28 g, 8.55 mmol	714 mg, 75%	^{1}H NMR: 0.88 (t, 6 H, ***J*** 6.6 MHz), 1.24–1.39 (m, 12 H), 1.45–1.55 (m, 4 H), 2.46 (t, 4 H, ***J*** 7.7 MHz), 4.96 (s, 2 H), 6.65 (s, 2 H); ^{13}C NMR: 14.15, 22.67, 29.38, 31.45, 31.81, 32.07, 56.16, 116.14, 133.43, 141.07	278 (M^+, 41%), 207 (M-$C_5H_{11}^+$, 11%), 137 (M-$2C_5H_{11}^+$, 100%)	$C_{18}H_{30}O_2$ calc. C, 77.65; H, 10.86 found: C, 77.81; H, 10.89	

13	36c: 1.2 g, 3.42 mmol	2.28 g, 8.55 mmol	835 mg, 73%	^{1}H NMR: 0.88 (t, 6 H, J 6.6 MHz), 1.20–1.38 (m, 20 H), 1.45–1.55 (m, 4 H), 2.46 (t, 4 H, J 7.7 MHz), 4.93 (s, 2 H), 6.65 (s, 2 H); ^{13}C NMR: 14.16, 22.73, 29.33, 29.57, 29.72, 31.50, 31.95, 32.08, 56.68, 116.16, 133.46, 141.07	334 (M^{+}, 87%)	$C_{22}H_{38}O_2$ calc. C, 78.99; H, 11.45 found: C, 78.82; H, 11.27

TABLE 5 Quantities of Reagents Used to Synthesize Compounds **1–10**

Compound	Catechol derivative	Boronic acid derivative	Yield	Melting point[a]
1	Catechol: 165 mg, 1.5 mmol	**14** 210 mg, 1.5 mmol	30 mg, 30%	110°C
2	Catechol: 77 mg, 0.7 mmol	**15** 121 mg, 0.7 mmol	20 mg, 10%	92°C
3	Catechol: 660 mg, 6.0 mmol	**19** 1.7 g, 6.0 mmol	2.0 g, 92%	75°C
4	**11** 66 mg, 0.2 mmol	**14** 36 mg, 0.2 mmol	70 mg, 80%	73°C
5	**11** 130 mg, 0.5 mmol	**18** 137 mg, 0.5 mmol	130 mg, 52%	62°C
6	**11** 55 mg, 0.2 mmol	**19** 66 mg, 0.2 mmol	46 mg, 41%	27.5°C
7	**12** 66 mg, 0.2 mmol	**18** 63 mg, 0.2 mmol	44 mg, 44%	33.4°C
8	**13** 68 mg, 0.2 mmol	**15** 34 mg, 0.2 mmol	20 mg, 21%	52°C
9	**13** 67 mg, 0.2 mmol	**16** 38 mg, 0.2 mmol	63 mg, 62%	29.6°C
10	**13** 67 mg, 0.2 mmol	**18** 53 mg, 0.2 mmol	48 mg, 43%	37.4°C

[a]Melting point determined by POM during the second heating cycle.

was purified by silica gel column chromatography, using petroleum ether (60/80°C fraction) as the eluent, to afford **35a–35c** as pale yellow oils (70–81%), as a mixture of the *cis,cis, cis,trans*, and *trans,trans* diastereoisomers. In Table 2 are listed the quantities of reagents used to synthesize compounds **35a–35c** and their analytical data.

1,2-Methylenedioxy-4,5-dialkyl-benzene or 5,6-dialkyl-benzo[1,3]dioxole (36a–36c)

A general procedure to hydrogenate double bonds using H_2 gas in the presence of a metal catalyst was followed [38,48]. A catalytic amount of Pd/C (10%) was added to a stirred solution of diastereoisomeric mixture of dienes **35a–35c** in $CHCl_3$:MeOH (70 mL:70 mL). The reaction was stirred under a H_2 atmosphere for 48 h. The mixture was filtered to remove the Pd/C powder and concentrated in vacuo and purified by silica gel column chromatography, using hexane as the eluent, to yield **36a–36c** as light brown oils (71–81%). In Table 3 are listed the quantities of reagents used to synthesize compounds **36a–36c** and their analytical data.

TABLE 6 Analytical Data for Compounds **1–10**: ^{1}H NMR (ppm), ^{13}C NMR (ppm), *m/z* (EIMS), Elemental Analysis (EA), or High Resolution Mass Spectrometry (HRMS), IR

Compound	^{1}H NMR (300 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$)[a]	m/z (EIMS)	EA and/or HRMS	IR
1	^{1}H NMR: 3.88 (s, 3 H, OC***H***$_3$), 7.01 (d, 2 H, ***J*** 8.5 MHz, ArC***H***), 7.08–7.13 (m, 2 H, ArC***H***), 7.27–7.32 (m, 2 H, ArC***H***), 8.03 (d, 2 H, J_o 8.5 MHz, ArC***H***); ^{13}C NMR: 55.23 (1 C, O***C***H$_3$), 112.45 (2 C, Ar***C***H), 113.95 (2 C, Ar***C***H), 122.65 (2 C, Ar***C***H), 136.90 (2 C, Ar***C***H), 148.63 (2 C, Ar***C***), 163.05 (1 C, Ar***C***)	226 (M^+, 100%), 196 (M-OCH_3^+, 10%)	$C_{13}H_{11}BO_3$ calc. C, 69.08; H, 4.91 found: C, 69.20; H, 4.83	ν_{max}/cm^{-1} 2930, 2830, 1604, 1374, 1333, 1256, 1239
2	^{1}H NMR: 1.06 (t, 3 H, ***J*** 7.4 MHz, C***H***$_3$), 1.78–1.90 (m, 2 H, C***H***$_2$), 4.00 (t, 2 H, t, ***J*** 6.4 MHz, OC***H***$_2$), 7.00 (d, 2 H, J_o 8.5 MHz, Ar***H***), 7.07–7.13 (m, 2 H, Ar***H***), 7.28–7.31 (m, 2 H, Ar***H***), 8.02 (d, 2 H, J_o 8.5 MHz, Ar***H***); ^{13}C NMR: 10.74 (1 C, ***C***H$_3$), 22.74 (1 C, ***C***H$_2$), 69.59 (1 C, O***C***H$_2$), 112.60 (2 C, Ar***C***H), 114.61 (2 C, Ar***C***H), 122.79 (2 C, Ar***C***H), 137.05 (2 C, Ar***C***H), 148.82 (2 C, Ar***C***), 162.84 (1 C, Ar***C***)	254 (M^+, 30%), 212 (M-$C_3H_6^+$, 100%)	$C_{15}H_{15}BO_3$ calc. C, 70.90; H, 5.95 found: C, 70.87; H, 6.03	ν_{max}/cm^{-1} 2963, 2875, 1606, 1374, 1334, 1235
3	^{1}H NMR: (t, 3 H, J_o 6.6 MHz, C***H***$_3$), 1.26–1.51 (m, 16 H, C***H***$_2$), 1.75–1.84 (m, 2 H, C***H***$_2$), 4.01 (t, 2 H, ***J*** 6.6 MHz, OC***H***$_2$), 6.98 (d, 2 H, J_o 8.8 MHz, Ar***H***), 7.06–7.12 (m, 2 H, Ar***H***), 7.25–7.30 (m, 2 H, Ar***H***), 8.00 (d, 2 H, ***J*** 8.8 MHz, Ar***H***); ^{13}C NMR: 14.04 (1 C, ***C***H$_3$), 22.60 (1 C, ***C***H$_2$), 25.93 (1 C, ***C***H), 29.09 (1 C, ***C***H$_2$), 29.26 (1 C, ***C***H$_2$), 26.30 (1 C, ***C***H$_2$), 29.48 (1 C, ***C***H$_2$), 29.51 (1 C, ***C***H$_2$), 29.53 (1 C, ***C***H$_2$), 31.82 (1 C, ***C***H$_2$), 67.81 (1 C, O***C***H$_2$), 112.28 (2 C, Ar***C***H), 114.29 (2 C, Ar***C***H), 122.47 (2 C, Ar***C***H), 136.73 (2 C, Ar***C***H), 148.512 (2 C, Ar***C***), 162.53 (1 C, Ar***C***)	366 (M^+, 15%), 212 (M-$C_{11}H_{22}^+$, 45%)	$C_{23}H_{31}BO_3$ calc. C, 75.35; H, 8.40 found: C, 75.41; H, 8.53	ν_{max}/cm^{-1} 2918, 2848, 1607, 1374, 1330, 1265, 1236

(Continued)

TABLE 6 Continued

Compound	^{1}H NMR (300 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$)[a]	m/z (EIMS)	EA and/or HRMS	IR
4	^{1}H NMR: 0.89–0.92 (m, 6 H, C*H*$_3$), 1.34–1.38 (m, 8 H, CH_2), 1.55–1.60 (m, 4 H, C*H*$_2$), 2.61 (t, 4 H, , *J* 7.9 MHz, C*H*$_2$), 3.86 (m, 3 H, OC*H*$_3$), 6.99 (d, 2 H, *J* 8.5 MHz, Ar*H*), 7.06 (2 H, s, Ar*H*), 7.99 (2 H, d, *J* 8.5, Ar*H*); ^{13}C NMR: 14.05 (2 C, *C*H$_3$), 22.61 (2 C, *C*H$_2$), 31.19 (2 C, *C*H$_2$), 31.92 (2 C, *C*H$_2$), 32.73 (2 C, *C*H$_2$), 55.17 (1 C, O*C*H$_3$), 112.56 (2 C, Ar*C*H), 113.86 (2 C, Ar*C*H), 134.98 (2 C, Ar*C*H), 136.76 (2 C, Ar*C*H), 146.61 (2 C, Ar*C*), 162.88 (1 C, Ar*C*)	366 (M^+, 45%), 255 (M-2C_4H_8+H^+, 100%)	$C_{23}H_{31}BO_3$ calc. C, 75.41; H, 8.53 found: C, 75.39; H, 8.44	ν_{max}/cm^{-1} 2956, 2926, 2856, 1599, 1373, 1342, 1257, 1177, 1081
5	^{1}H NMR: 0.83–0.94 (m, 9 H, C*H*$_3$), 1.25–1.78 (m, 24 H, C*H*$_2$), 1.81–1.85 (m, 2 H, C*H*$_2$), 2.61 (t, 4 H, *J* 7.9 MHz, C*H*$_2$), 4.02 (t, 2 H, *J* 6.6 MHz, OC*H*$_2$), 6.98 (d, 2 H, d, J_o 8.5 MHz, Ar*H*), 7.06 (s, 2 H, Ar*H*), 7.98 (t, 2 H, J_o 8.5 MHz, Ar*H*); ^{13}C NMR: 14.11 (3 C, *C*H$_3$), 22.63 (3 C, *C*H$_2$), 26.05–31.90 (10 C, *C*H$_2$), 32.74 (2 C, *C*H$_2$), 67.90 (1 C, O*C*H$_2$), 112.55 (2 C, Ar*C*H′), 114.35 (2 C, Ar*C*H), 134.94 (2 C, Ar*C*), 136.74 (2 C, Ar*C*H), 146.61 (2 C, Ar*C*), 162.50 (1 C, Ar*C*)	478 (M^+, 100%), 365 (M-2C_4H_9+H^+, 43%), 239 (M-2C_4H_8-$C_9H_{19}^+$, 20%)	$C_{31}H_{47}BO_3$ calc. C, 77.81; H, 9.90)[b] found: C, 76.44; H, 10.18 HRMS (LSIMS) calc. 478.3733 found 478.3743	ν_{max}/cm^{-1} 2955, 2915, 2849, 1602, 1375, 1341, 1242, 1173
6	^{1}H NMR: 0.82–0.94 (m, 9 H, C*H*$_3$), 1.24–1.61 (m, 28 H, C*H*$_2$), 1.76–1.85 (m, 2 H, C*H*$_2$), 2.61 (t, 4 H, *J* 7.9 MHz, C*H*$_2$), 4.01 (t, 2 H, *J* 6.6 MHz, OC*H*$_2$), 6.98 (d, 2 H, J_o 8.5, Ar*H*), 7.06 (s, 2 H, Ar*H*), 7.99 (d, 2 H, J_o 8.5 MHz, Ar*H*); ^{13}C NMR: 14.01 (2 C, *C*H$_3$), 14.08 (1 C, *C*H$_3$), 22.56 and 22.65 (3 C, *C*H$_2$), 25.98–31.86 (12 C, *C*H$_2$), 32.67 (2 C, *C*H$_2$), 67.82 (1 C, O*C*H$_2$), 112.48 (2 C, Ar*C*H), 114.28 (2 C, Ar*C*H), 134.86 (2 C, Ar*C*), 136.66 (2 C, Ar*C*H), 146.54 (2 C, Ar*C*H), 162.42 (1 C, Ar*C*)	506 (M^+, 100%), 393 (M-2$C_4H_8^+$, 35%), 351 (M-$C_{11}H_{22}^+$, 5%), 239 (M-2C_4H_8-$C_{11}H_{22}^+$, 20%)		

7	^{1}H NMR: 0.82–0.90 (m, 9 H, CH_3), 1.22–1.58 (m, 28 H, CH_2), 1.74–1.82 (m, 2 H, CH_2), 2.60 (t, 4 H, J 7.9 MHz, CH_2), 3.99 (t, 2 H, J 6.4 MHz, OCH_2), 6.96 (d, 2 H, J_o 8.5 MHz, ArH), 7.03 (s, 2 H, ArH), 7.96 (d, 2 H, J_o 8.5 MHz, ArH); ^{13}C NMR: 14.11 (3 C, CH$_3$), 22.64–31.87 (15 C, CH$_2$), 32.76 (2 C, CH$_2$), 67.87 (1 C, OCH$_2$), 112.52 (2 C, ArCH), 114.32 (2 C, ArCH), 134.93 (2 C, ArC), 136.71 (2 C, ArCH), 146.57 (2 C, ArCH), 162.46 (1 C, ArC)	506 (M^+, 100%), 365 (M-2$C_5H_{10}^+$, 27%), 238 (M-2C_5H_{10}-$C_9H_{18}^+$, 27%)	$C_{33}H_{52}BO_3$ HRMS (LSIMS) calc. 506.4046 found 506.4036	ν_{max}/cm^{-1} 2926, 2857, 1605, 1484, 1375, 1341, 1246, 1175
8	^{1}H NMR: 0.86–0.90 (m, 6 H, CH_3), 1.05 (t, 3 H, J 7.3 MHz, CH_3), 1.25–1.40 (m, 20 H, CH_2), 1.52–1.62 (m, H, CH_2), 1.78–1.89 (m, 2 H, CH_2), 2.59–2.63 (t, 4 H, J 7.7 MHz, CH_2), 3.98 (t, 2 H, J 6.6 MHz, OCH_2), 6.98 (d, 2 H, J_o 8.8 MHz, ArH), 7.06 (s, 2 H, ArH), 7.99 (d, 2 H, d, J_o 8.8 MHz, ArH) ^{13}C NMR: 10.56 (1 C, CH$_3$), 14.16 (2 C, CH$_3$), 22.73 (2 C, CH$_2$), 29.33–31.95 (9 C, CH$_2$), 32.81 (2 C, CH$_2$), 69.39 (2 C, OCH$_2$), 112.57 (2 C, ArCH), 114.37 (2 C, ArCH-3,6), 134.98 (2 C, ArC), 136.76 (2 C, ArCH-2′), 146.62 (2 C, ArCH), 162.50 (1 C, ArC)	478 (M^+, 82%), 281 (M-2C_7H_{15}+H^+, 100%), 238 (M-2C_7H_{15}-$C_3H_6^+$, 23%)	$C_{31}H_{48}BO_3$ HRMS (LSIMS) calc. for 478.3732 found 478.3755	ν_{max}/cm^{-1} 2957, 2922, 2847, 1603, 1340, 1232
9	^{1}H NMR: 0.86–0.96 (m, 9 H, CH_3), 1.23–1.48 (m, 24 H, CH_2), 1.52–1.60 (m, 4 H, CH_2), 1.76–1.85 (m, 2 H, CH_2), 2.60 (t, 4 H, J 7.7 MHz, CH_2), 4.01 (t, 2 H, J 6.6 MHz, OCH_2), 6.97 (d, 2 H, J_o 8.4 MHz, ArH), 7.05 (s, 2 H, ArH-), 7.98 (d, 2 H, J_o 8.4 MHz, ArH); ^{13}C NMR: 14.07 (1 C, CH$_3$), 14.17 (2 C, CH$_3$), 22.50 (1 C, CH$_2$), 22.74 (2 C, CH$_2$), 28.23 (2 C, CH$_2$), 28.93 (1 C, CH$_2$), 29.35–31.96 (9 C, CH$_2$), 32.82 (2 C, CH$_2$), 67.91 (1 C, OCH$_2$), 112.58 (2 C, ArCH), 114.37 (2 C, ArCH), 134.98 (2 C, ArC), 136.77 (2 C, ArCH), 146.63 (2 C, ArC), 162.52 (1 C, ArC)	506 (M^+, 100%), 309 (M-2C_7H_{15}+H^+, 90%), 238 (M-2C_7H_{15}-$C_5H_{10}^+$, 27%);	$C_{33}H_{52}BO_3$ HRMS (LSIMS) calc. for 506.4046 found 506.4029	ν_{max}/cm^{-1} 2953, 2924, 2845, 1605, 1370, 1340, 1253

(Continued)

TABLE 6 Continued

Compound	^{1}H NMR (300 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$)[a]	m/z (EIMS)	EA and/or HRMS	IR
10	^{1}H NMR: 0.86–0.89 (m, 9 H, C***H***$_3$), 1.25–1.37 (m, 32 H, C***H***$_2$), 1.52–1.62 (m, 4 H, C***H***$_2$), 1.76–1.85 (m, 2 H, C***H***$_2$), 2.61 (t, 4 H, ***J*** 7.9 MHz, C***H***$_2$), 4.01 (t, 2 H, ***J*** 6.6 MHz, OC***H***$_2$), 6.98 (d, 2 H, ***J***$_o$ 8.6 MHz, Ar***H***-), 7.05 (s, 2 H, Ar***H***), 7.98 (d, 2 H, ***J***$_o$ 8.6 MHz, Ar***H***); ^{13}C NMR: 14.12 (3 C, ***C***H$_3$), 22.68–31.92 (19 C, ***C***H$_2$), 32.79 (2 C, ***C***H$_2$), 67.90 (1 C, O***C***H$_2$), 112.54 (2 C, Ar***C***H), 114.34 (2 C, Ar***C***H), 134.95 (2 C, Ar***C***), 136.73 (2 C, Ar***C***H), 146.59 (2 C, Ar***C***H), 162.48 (1 C, Ar***C***)	562 (M^+, 100%), 435 (M-$C_9H_{19}^+$, 8%), 365 (M-2C_7H_{15}+H^+, 65%), 239 (M-2C_7H_{14}-$C_9H_{19}^+$, 30%)	$C_{37}H_{60}BO_3$ HRMS (LSIMS) calc. for 562.4672 found 562.4657	ν_{max}/cm^{-1} 2954, 2923, 2853, 1605, 1466, 1340, 1257, 1175

[a]The ^{13}C NMR δ (ppm) for the C-B signal of compounds **1–10** is never detected because the quadrupole effect of the boron atom tends to broaden the signal of the adjacent carbon.

[b]The pattern of the elemental analysis results (higher H, lower C) is typical in case of wet (H_2O) compounds.

4,5-Dialkyl-catechol or 5,6-dipentyl-benzene-1,2-diol (11–13)

A general procedure for deprotection of benzo[1,3]dioxole rings was followed [39–41]. A stirred solution of compound **36a–36c** (1.0 eq) in EtSH (2–3 mL) was cooled to 0°C. $AlBr_3$ (2.5–3.0 eq) was added and the reaction was stirred at room temperature overnight. The reaction was quenched with H_2O (10 mL). Extraction of the product was carried out using EtOAc (20 mL), H_2O (2×20 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$), filtered, and the solvent removed in vacuo. The crude product was purified by silica gel column chromatography, using $CHCl_3$ as eluent, to afford **11–13** [49] as light brown oils (53–75%). In Table 4 are listed the quantities of reagents used to synthesize compounds **1–10** and their analytical data.

4,5-Dialkyl-catechol-*B*-(4-alkyloxyphenyl)borane or 2-(4-alkyloxyphenyl)-5,6-dialkyl-benzo[1,3,2]dioxaborole (1–10)

The general procedure for the synthesis of compounds **1–10** is as follows: to a stirred solution of catechol or 4,5-dialkyl-catechol **11–13** (1.5 eq) in $CH(OMe)_3$ (15 mL) was added the appropriate 4-alkyloxyphenylboronic acid **14–19** (1.5 eq). The reaction was stirred at room temperature overnight. The reaction mixture was then concentrated in vacuo. The crude product was either recrystallized from toluene (**1–3**) or purified from the mixture of reaction with CH_3CN (**4–5**); otherwise the purification method used consisted in a continuous extraction (3 h) using CH_3CN (100 mL) and hexane (40 mL) to yield a waxy yellow product (**6–10**). In Table 5 are listed the quantities of reagents used to synthesize compounds **1–10** and in Table 6 their analytical data are reported.

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