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# Syntheses of Macrocyclic Bis(bibenzyl) Compounds Derived from Perrottetin E

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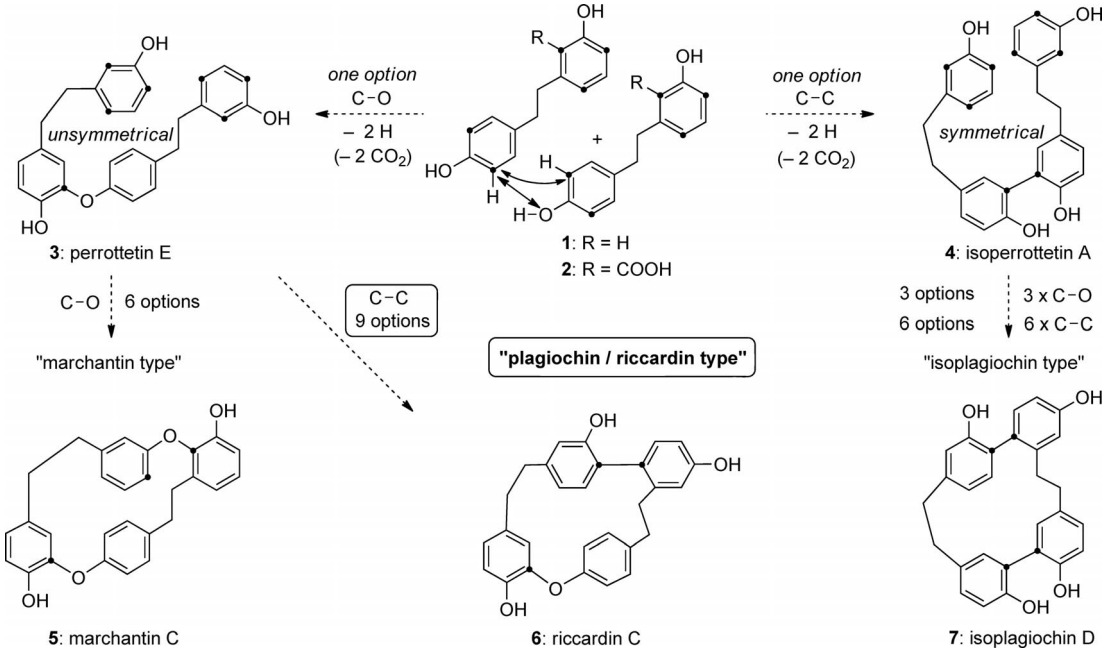
**Keywords:** Total synthesis / Natural products / Macrocycles / Bryophyte constituents

Macrocyclic bis(bibenzyl) compounds are natural products from liverworts and are of growing interest due to recent reports on new isolated compounds and on their remarkable biological activities. We report here on a flexible and general approach to the total set of nine bis(bibenzyl) compounds of the riccardin and plagiochin type derived from perrottetin E. The structures were confirmed through their spectroscopic data, which were compared carefully with those for the isolated products to exclude any errors in arene connection and substitution pattern.

## Introduction

Bis(bibenzyl)-type acyclic or cyclic phenolic natural products can be found exclusively in bryophytes.[1] Biosynthetically, they originate from the bibenzyl lunularin (**1**, Scheme 1)[2] or its precursor lunularic acid (**2**).[3] Two units of **1** or **2** can be combined by several modes of O–C and/or C–C attachment through phenol oxidation coupling to different subtypes (Scheme 1). From the acyclic precursors perrottetin E (**3**), with O–C connection, and isoperrottetin A (**4**), with C–C connection, are derived cyclic bis(bibenzyl) compounds of the plagiochin/riccardin type such as riccardin C (**6**), the marchantin-type-like marchantin C (**5**) or the isoplagiochin type such as isoplagiochin D (**7**), through a second O–C or C–C connection. Not all possible subtypes with all possible modes of connection have yet been isolated from bryophytes. The distribution of the cyclic bis(bibenzyl) compounds in liverworts, their structure elucidation and their total syntheses have been reviewed.[1,4] Unfortunately, the nomenclature for these compounds is not standardized (plant source, historical aspects). Furthermore, derivatives containing additional hydroxy groups or methyl ether functionalities have in some cases been isolated or the parent compound itself has not to date been isolated.




Scheme 1. Different subtypes of bis(bibenzylic) bryophyte constituents.

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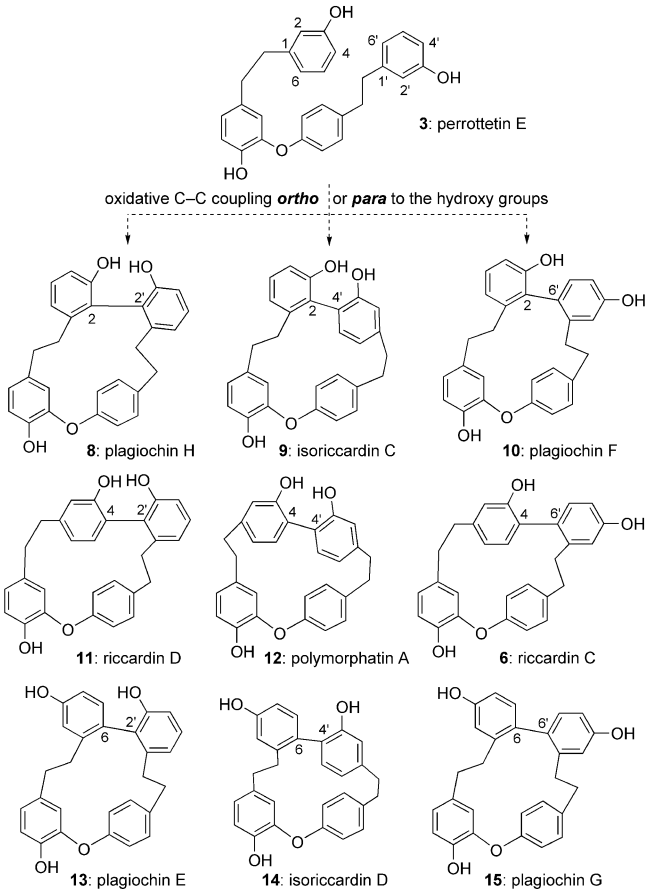
We have reported on the syntheses of riccardin C (**6**) and isoplagiochin D (**7**) and other demonstration model compounds[5] and recently on the highly bioactive marchantin C (**5**).[6] We have furthermore investigated the effects of axial chirality and ring strain in the macrocycles of the isoplagiochin type.[7,8]

Consideration of the *ortho*/*para* selectivity of the oxidative phenol coupling suggests that nine isomers of the plagiochin or riccardin type with different bis(bibenzyl) skeletons can in principle be deduced from the acyclic precursor perrottetin E (**3**, Scheme 2). The theoretical conformational strain in these compounds had been computed before[2] and several representatives were found in bryophytes (Table 1). Earlier reports were given on the isolation of riccardin C (**6**),[9] isoriccardin C (**9**)[10] and riccardin D (**11**).[11] In the case of the bis(bibenzyl)-type derived from **3** through coupling at the 6- and 6′-positions, only compounds with additional methylation and/or hydroxylation have been isolated, in the form of plagiochins A–D (structures not shown in Scheme 2).[12] The parent compound with only three free phenolic groups – we now call it plagiochin G (**15**) – has never been found in plant extracts. More recently, a compound named plagiochin E with the postulated structure **13** was isolated by a bioassay-guided separation from *Marchantia polymorpha*.[13,14] In the course of our attempts to synthesize **13**, however, we revised the structure of this isolated bis(bibenzyl) to that of riccardin D (**11**), which we synthesized together with the new skeleton of plagiochin F (**10**) for purposes of clear structure elucidation.[15] Very recently, isoriccardin D (**14**) and a compound named "polymorphatin A" (**12**) were also detected in *M. polymorpha* as minor bioactive substances.[16] Compounds **12** and **14** represent the first natural compounds with bis(bibenzyl) skeletons containing 4–4′ or 6–4′ substitution patterns. To the best of our knowledge, no bis(bibenzyl) compounds of the parent types **8** (2–2′ coupling), **10** (2–6′ coupling) and **13** (6–2′ coupling) or their derivatives have yet been isolated from natural sources.




Scheme 2. Bis(bibenzyl) compounds of the plagiochin or riccardin type derived from perrottetin E.

Table 1. Bis(bibenzyl) compounds of the plagiochin or riccardin type: natural sources, biological activities and syntheses.

| | Name | Isolation from liverworts[4] | Biological activities[17,18] | Total synthesis |
|---|---|---|---|---|
| **6** | riccardin C | *Reboulia hemisphaerica* (1982)[9] et al.[4]<br>*Ptagiochasm intermedlum* (2010)[19] | COX inhibition[4]<br>cytotoxic[20,21]<br>inhibitory activities against HIV-1 RT[21]<br>inhibition of NOS[22,23]<br>LXRα agonist but LXRβ antagonist[24,25]<br>antifungal[19]<br>apoptosis of human prostate cancer[26] | 1990[27]<br>1998[5]<br>2005[28]<br>2009[25] |
| **8** | plagiochin H | – | – | – |
| **9** | isoriccardin C | *Marchantia polymorpha, M. palmata* (1987)[10]<br>*Plagiochasma rupestre* (1999)[29] *Ptagiochasm intermedlum* (2010)[19] | COX inhibition[4] | – |
| **10** | plagiochin F | – | – | 2009[15] |
| **11** | riccardin D | *Monoclea forsteri* (1988)[11]<br>*Plagiochila cristata* (1997)[30] | antifungal[31][a] | 2009[15] |
| **12** | polymorphatin A | *Marchantia polymorpha* (2007)[16] | – | – |
| **13** | plagiochin E | – [compound from *Marchantia polymorpha* (2006)[13,14] and *Asterella angusta* (2007)[14] was revised to be **11**[15]] | antifungal,[13,14,32,33][a]<br>cancer chemotherapy,[34,35][a]<br>apoptosis of human prostate cancer[26] | 2009[15] |
| **14** | isoriccardin D | *Marchantia polymorpha* (2007)[16] | – | – |
| **15** | plagiochin G | –, derivatives only[12] | – | – |

[a] Biological activities published for plagiochin E (**13**) have to be reassigned to riccardin D (**11**).[15]

Macrocyclic bis(bibenzyl) compounds exhibit a broad spectrum of biological activities.[17,18] Specific effects of the compounds depicted in Scheme 2 are listed in Table 1.

In view of their attractiveness for numerous therapeutic approaches we now report flexible and efficient syntheses for the complete "library" of nine bis(bibenzyl) compounds derived from perrottetin E (**3**). Furthermore, with all parent compounds "to hand" it should now be possible to confirm or to revise structure elucidations given for the isolated products up to now and in the future.

## Results and Discussion

### Syntheses

For the syntheses of all subtypes (Scheme 2) we developed a construction unit synthesis based on arene units a to d (Figure 1). Because of the specific C–C coupling options, nine "northern" subunits b–d were prepared through Suzuki reactions. In a convergent manner, they were consecutively coupled, followed by ring closure with a common "southern" a–c subunit by inter- and intramolecular Wittig or McMurry reactions. The bis(bibenzyl) compounds were finally obtained by hydrogenation and deprotection of the phenolic groups. It is noteworthy that the syntheses of the highly *ortho*-substituted biaryls b–d as well the macrocyclization step are crucial in some cases due to steric hindrance as well as ring strain (Figure 1).

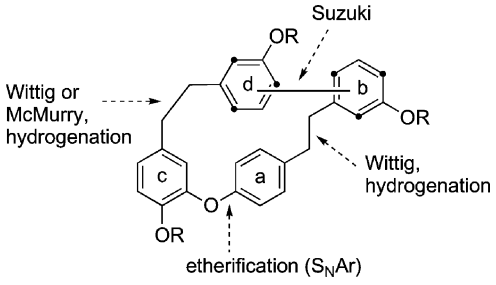
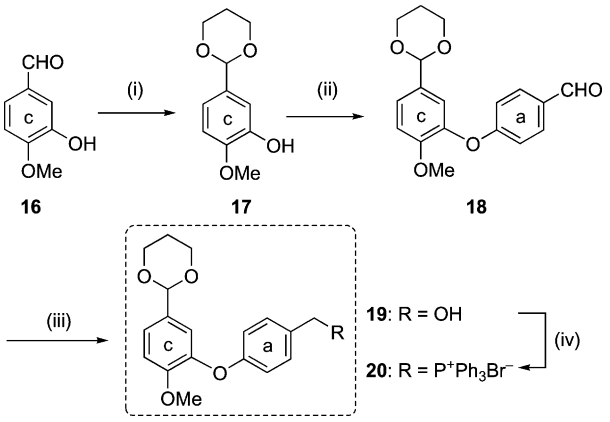


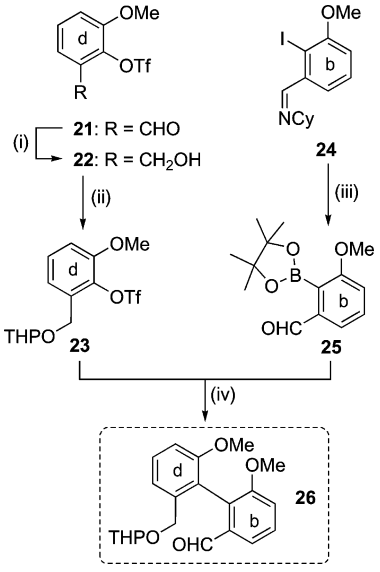

Figure 1. Construction unit system for the synthesis of cyclic bis(bibenzyl) compounds.

The common "southern" diaryl ether fragment was provided as the phosphonium salt **20** by an approach similar to that published for the synthesis of cavicularin[28] (Scheme 3).

The synthesis of the b–d subunit **26** (Scheme 4) for plagiochin H (**8**) started with the triflate **21** derived from *ortho*-vanillin. The aldehyde was reduced to the corresponding alcohol **22** with DIBAL-H, and **22** was protected as the THP ether **23**. The boronic ester **25** was obtained from the aryl iodide **24**[36] by a halogen/magnesium exchange and subsequent scavenging with trimethyl borate,[37] followed by treatment with pinacol. The building blocks **23** and **25** were coupled by a standard Suzuki protocol to afford the building block **26**.




Scheme 3. Synthesis of the common building block **20**. Reagents and conditions: i) propane-1,3-diol, $CH(OEt)_3$, tetrabutylammonium tribromide (TBATB), 65 °C, 6 h (97%); ii) 4-fluorobenzaldehyde, $K_2CO_3$, DMF, 160 °C, 20 h (93%); iii) $NaBH_4$, EtOH, 0 °C to r.t., 2 h (90%); iv) $PPh_3$·HBr, MeCN, reflux, 6 h, then propane-1,3-diol, $CH(OEt)_3$, TBATB, $CHCl_3$, 65 °C, 12 h.

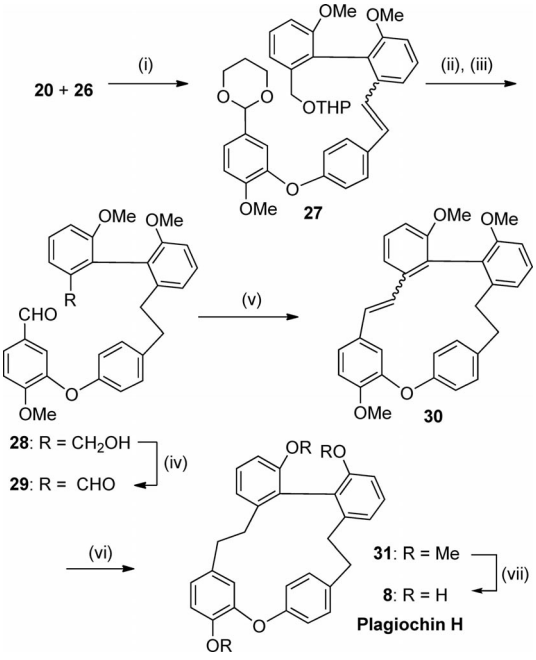



Scheme 4. Synthesis of subunit **26**. Reagents and conditions: i) DIBAL-H, $CH_2Cl_2$, –78 °C to r.t., 12 h (87%); ii) 3,4-dihydro-2*H*-pyran, *p*TosOH $CH_2Cl_2$, r.t., 16 h (85%); iii) *i*PrMgCl·LiCl, THF, –15 °C, 30 min, then $B(OMe)_3$ at –15 °C to r.t., then HCl (2 M), then pinacol, $MgSO_4$, r.t. 16 h (53%); iv) $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (30%).

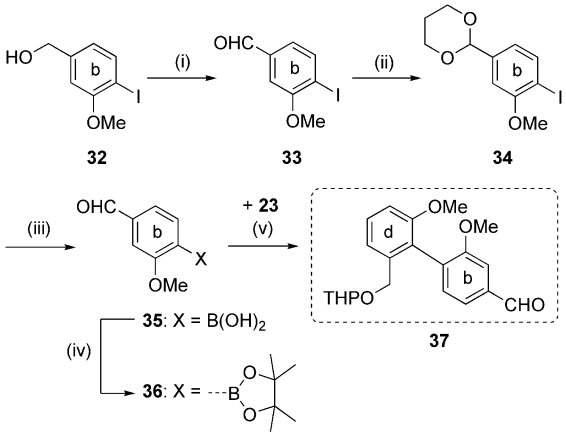
A Wittig reaction between the aldehyde **26** and the phosphonium salt **20** afforded the product **27** (Scheme 5) in good yield. After hydrogenation, acidic hydrolysis and oxidation with PCC the dialdehyde **29** was converted into the macrocycle stilbene **30** by means of an intramolecular McMurry reaction. Plagiochin H (**8**) was finally obtained after hydrogenation and subsequent methyl ether cleavage.

The synthesis of isoriccardin C (**9**) required the b–d subunit **37** (Scheme 6). The boronic ester **36** was synthesized from the iodo benzyl alcohol **32**[38] and Suzuki-coupled with the triflate **23**.

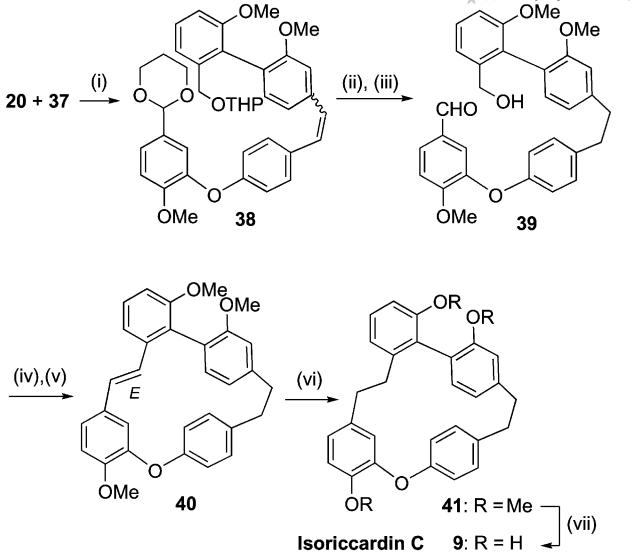



Scheme 5. Synthesis of plagiochin H (**8**). Reagents and conditions: i) **20** (1.3 equiv.) + **26**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (88%); ii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; iii) 2 M HCl/THF (1:1), r.t., 12 h (86% over two steps); iv) PCC/$Al_2O_3$, $CH_2Cl_2$ r.t., 16 h (95%); v) $TiCl_4$, Zn, THF, reflux, 24 h (27%); vi) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (97%); vii) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (75%).



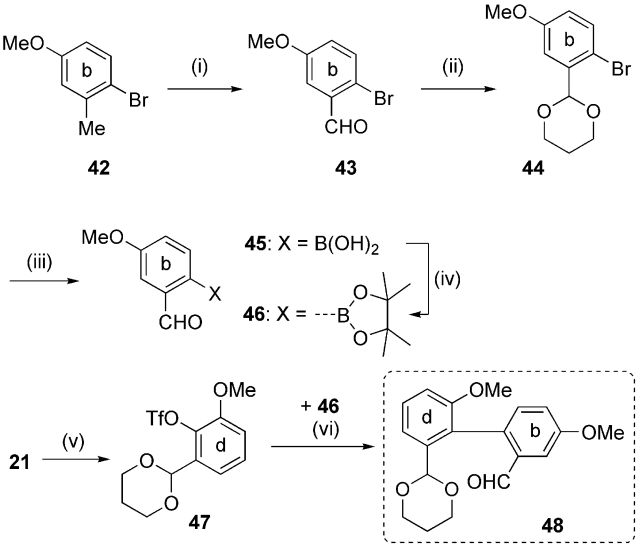

Scheme 6. Synthesis of the subunit **37**. Reagents and conditions: i) PCC/$Al_2O_3$, $CH_2Cl_2$, r.t., 16 h (92%); ii) $CH(OEt)_3$, TBATB, propane-1,3-diol, 65 °C, 12 h (99%); iii) *n*BuLi, THF, –78 °C, 30 min, then $B(OMe)_3$, –78 °C to r.t., then 2 M HCl (55%); iv) pinacol, $MgSO_4$, $CH_2Cl_2$, r.t., 12 h (86%); v) + **23**, $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (32%).

A subsequent Wittig reaction between **37** and **20**, hydrogenation and deprotection resulted in compound **39** with a free aldehyde and alcohol function (Scheme 7). This was converted into the corresponding benzylphosphonium salt as precursor for the following cyclization step. After an intramolecular Wittig reaction followed by catalytic hydrogenation and demethylation the natural product **9** was obtained.



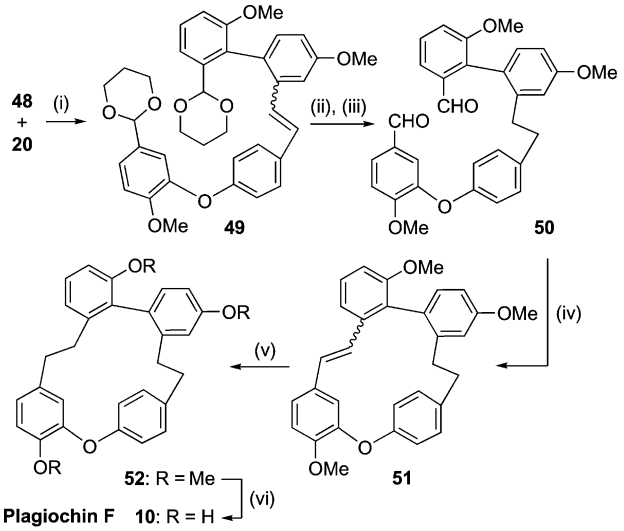

Scheme 7. Synthesis of isoriccardin C (**9**). Reagents and conditions: i) **20** (1.3 equiv.) + **37**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (76%); ii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; iii) 2 M HCl/THF (1:1), r.t., 12 h (96% over two steps); iv) $PPh_3$·HBr, MeCN, reflux, 12 h; v) NaOMe, $CH_2Cl_2$, 24 h, (44% over two steps); vi) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (99%); vii) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (86%).

The syntheses of plagiochin F (**10**) and riccardin D (**11**) have been reported previously[15] but should be summarized with full experimental data for completeness. The synthesis of **10** proceeds from the aldehyde **48** as the b–d subunit (Scheme 8); the macrocyclization after coupling with the a–c subunit was accomplished through an intramolecular McMurry reaction (Scheme 9).



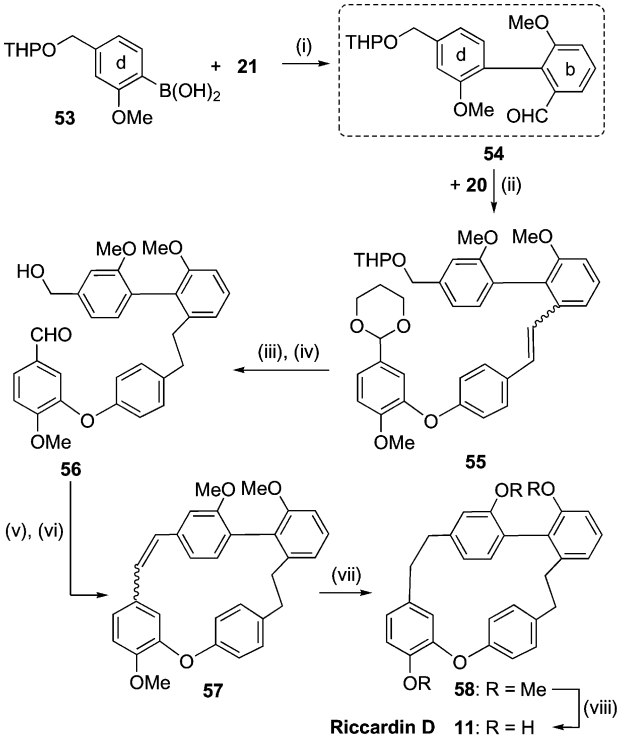

Scheme 8. Synthesis of the subunit **48**. Reagents and conditions: i) NBS (2 equiv.), AIBN, $CCl_4$, hν, reflux, 24 h, then aq. $CaCO_3$, reflux, 18 h (72%); ii) $CH(OEt)_3$, TBATB, propane-1,3-diol, 65 °C, 12 h (93%); iii) *n*BuLi, THF, –78 °C, 30 min, then $B(OMe)_3$, –78 °C to r.t., then 2 M HCl (52%); iv) pinacol, $MgSO_4$, $CH_2Cl_2$, r.t., 12 h (80%); v) $CH(OEt)_3$, TBATB, propane-1,3-diol, 65 °C, 12 h (98%); vi) + **46**, $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (67%).



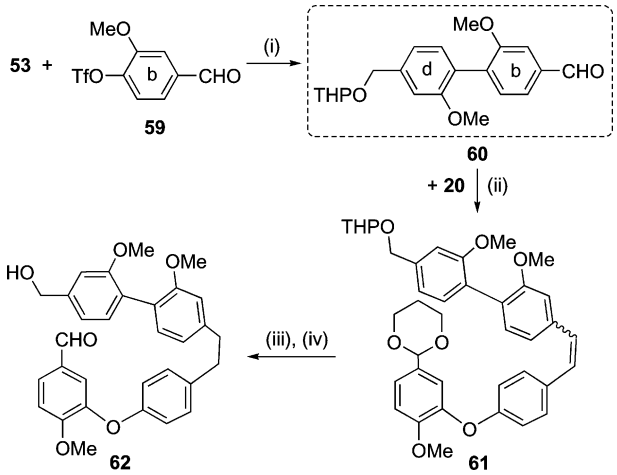

Scheme 9. Synthesis of plagiochin F (**10**). Reagents and conditions: i) **20** (1.3 equiv.) + **48**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (93%); ii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; iii) 2 M HCl/THF (1:1), r.t., 12 h (93% over two steps); iv) $TiCl_4$, Zn, THF, reflux, 24 h (29%); v) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (99%); vi) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (66%).

Riccardin D (**11**) was obtained by employing an intramolecular Wittig reaction as the key step. The aldehyde **54** (b–d unit) was prepared from the boronic acid **53**[38] and the triflate **21** (Scheme 10).

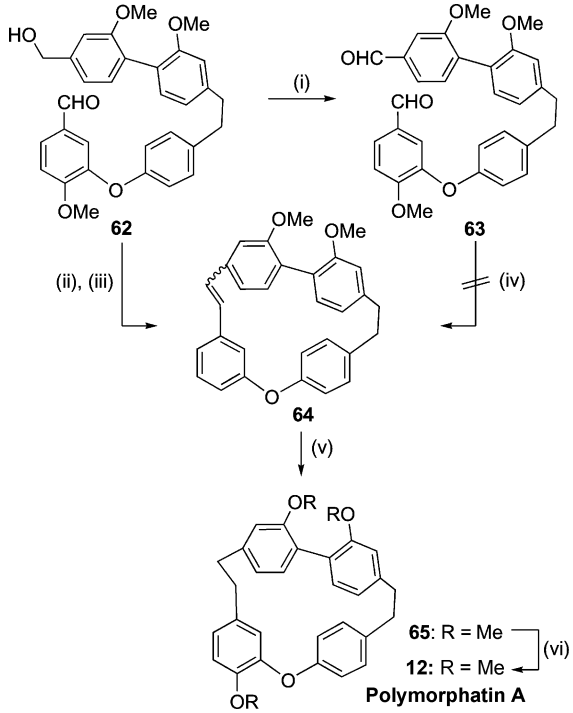



Scheme 10. Synthesis of riccardin D (**11**). Reagents and conditions: i) $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (69%), ii) **20** (1.3 equiv.) + **54** $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (94%); iii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; iv) 2 M HCl/THF (1:1), r.t., 12 h (96% over two steps); v) $PPh_3$·HBr, MeCN, reflux, 12 h; vi) NaOMe, $CH_2Cl_2$, 24 h (68% over two steps); vii) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (95%); viii) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (71%).

For the synthesis of polymorphatin A (**12**) the "northern" building block **60** containing a protected alcohol and an aldehyde group *para* to the biaryl axis was required (Scheme 11). For this, vanillin triflate (**59**) and the boronic acid **53** were Suzuki-coupled. In the subsequent steps compound **62** was generated to enable cyclization through an intramolecular Wittig reaction. Unfortunately, this cyclization only proceeded in low yield, whereas the alternative ring closure through a McMurry reaction failed (Scheme 12).



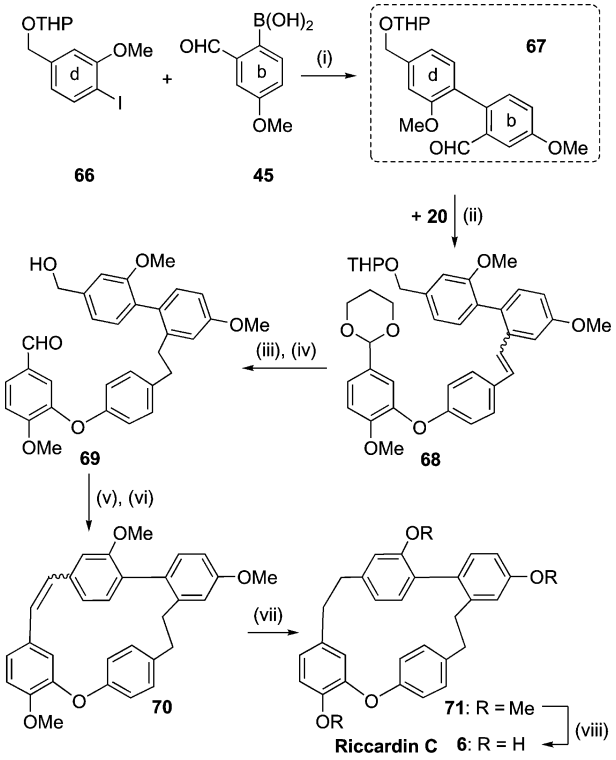

Scheme 11. Synthesis of the precursor **62**. Reagents and conditions: i) $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (79%); ii) **20** (1.3 equiv.) + **60**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (79%); iii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h (94%); iv) 2 M HCl/THF (1:1), r.t., 12 h (87% over two steps).




Scheme 12. Synthesis of polymorphatin A (**12**). Reagents and conditions: i) PCC/$Al_2O_3$, $CH_2Cl_2$ r.t., 16 h (96%); ii) $PPh_3$·HBr, MeCN, reflux, 12 h; iii) NaOMe, $CH_2Cl_2$, 24 h, (12% over two steps); iv) $TiCl_4$, Zn, THF, reflux, 24 h; v) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (95%); vi) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (89%).

For riccardin C (**6**) several synthetic routes have been published.[5,25,27,28] We now present a new approach through our improved strategy based on coupling of **20** and the aldehyde **67** as the b–d unit (obtained from the THP-protected iodorarene **66**[38] and the boronic acid **45**) and subsequent Wittig macrocyclization (Scheme 13).



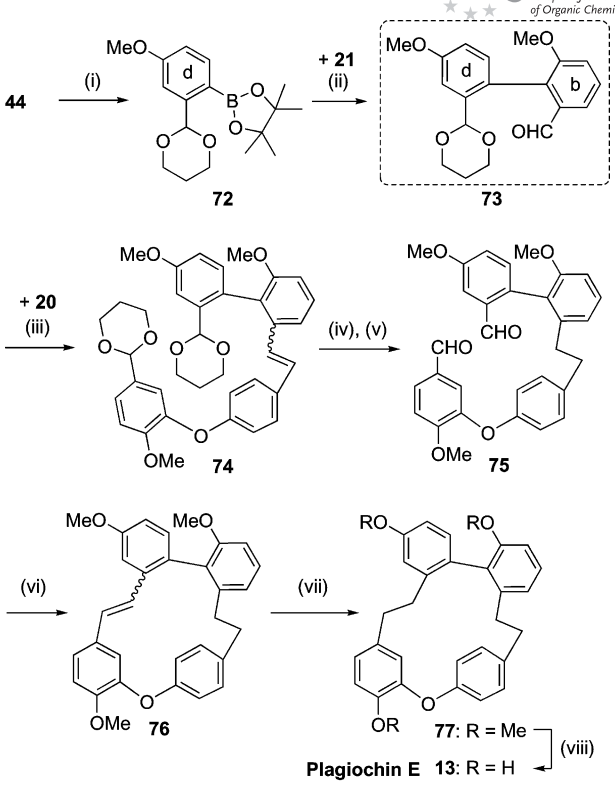

Scheme 13. Synthesis of riccardin C (**6**). Reagents and conditions: i) $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (91%); ii) **20** (1.3 equiv.) + **67**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (95%); iii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; iv) 2 M HCl/THF (1:1), r.t., 12 h (94% over two steps); v) $PPh_3$·HBr, MeCN, reflux, 12 h; vi) NaOMe, $CH_2Cl_2$, 24 h (38%); vii) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (95%); viii) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (85%).

Our synthesis of plagiochin E (**13**) was published recently;[15] the full experimental details are given below. The synthesis is summarized in Scheme 14.

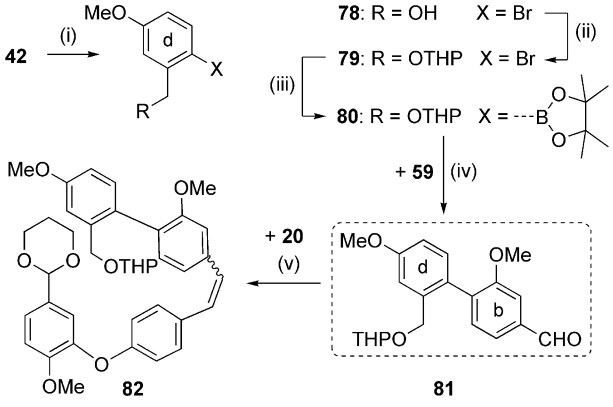
The synthesis of isoriccardin D (**14**) started with **42** (Scheme 15), which was converted into the benzyl alcohol **78** by NBS bromination followed by hydrolysis under basic conditions. After protection of the hydroxy group as the THP acetal the bromoarene **79** was functionalized to the boronic ester **80**. A Suzuki reaction with the triflate **59** yielded the aldehyde **81**, which was Wittig-coupled with the phosphonium salt **20** (Scheme 15).

Hydrogenation of **82** followed by hydrolysis afforded the precursor **83** for the Wittig cyclization. The natural product isoriccardin D (**14**) was obtained by the now improved protocols (Scheme 16).

The synthesis of plagiochin G (**15**) started with formation of the aldehyde **86** (Scheme 17) as the b–d unit, through a Suzuki coupling between the boronic acid **46** and

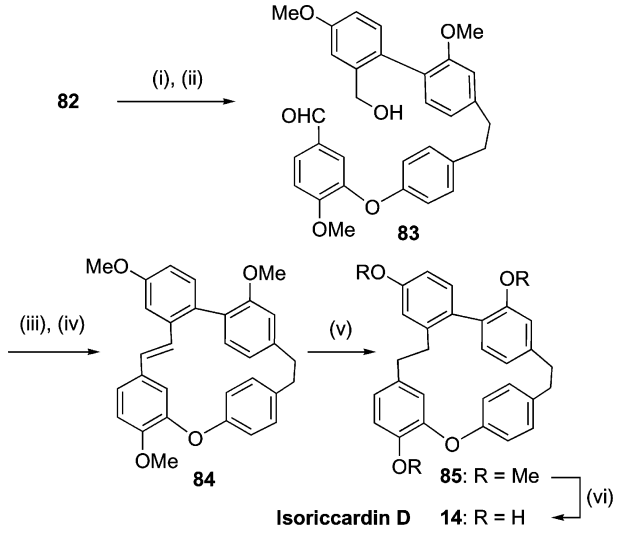



Scheme 14. Synthesis of plagiochin E (**13**). Reagents and conditions: i) *n*BuLi, THF, –78 °C, 30 min, then $B(OMe)_3$ at –78 °C to r.t., then pinacol, $MgSO_4$, $CH_2Cl_2$, r.t., 12 h (70%); ii) + **21**, $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (91%). iii) **20** (1.3 equiv.) + **73**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (87%); iv) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; v) 2 M HCl/THF (1:1), r.t., 12 h (89% over two steps), vi) $TiCl_4$, Zn, THF, reflux, 24 h (35%); vii) Pd/C (5%), 10 bar $H_2$, EtOAc, r.t., 24 h (98%); viii) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (68%).

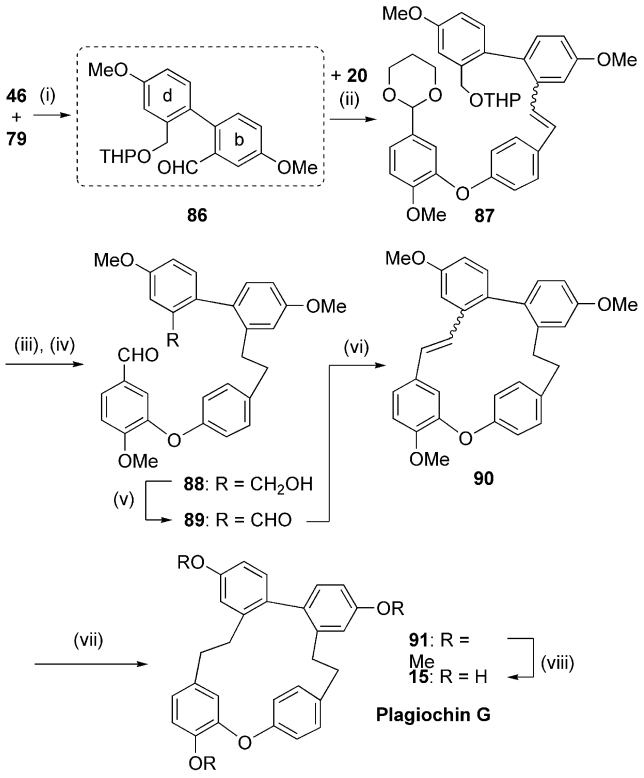



Scheme 15. Synthesis of the precursor **82**. Reagents and conditions: i) NBS (1.0 equiv.), AIBN, $CCl_4$, hv, reflux, 24 h, then aq. $CaCO_3$, reflux, 18 h (60%); ii) 3,4-dihydro-2*H*-pyran, *p*TosOH $CH_2Cl_2$, r.t., 16 h (93%); iii) *n*BuLi, THF, –78 °C, 30 min, then $B(OMe)_3$ –78 °C to r.t., then satd $KH_2PO_4$, then pinacol, $MgSO_4$, $CH_2Cl_2$, r.t., 12 h (75%); iv) + **59**, $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (74%); v) **20** (1.3 equiv.) + **81**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (95%).




Scheme 16. Synthesis of isoriccardin D (**14**). Reagents and conditions: i) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; ii) 2 M HCl/THF (1:1), r.t., 12 h (88% over two steps); iii) $PPh_3$·HBr, MeCN, reflux, 12 h; iv) NaOMe, $CH_2Cl_2$, 24 h (40% over two steps); v) Pd/C (5%), 3 bar $H_2$, EtOAc, r.t., 24 h (95%); vi) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (76%).

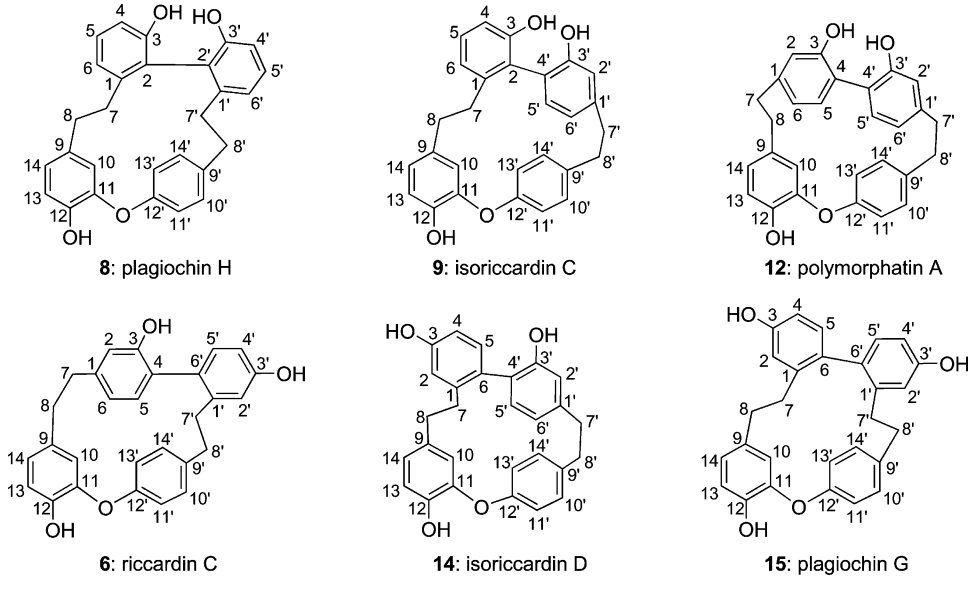



Scheme 17. Synthesis of plagiochin G (**15**). Reagents and conditions: i) $Pd(PPh_3)_4$, PhMe/EtOH/2 M $Na_2CO_3$, reflux, 16 h (77%); ii) **20** (1.3 equiv.) + **86**, $K_2CO_3$, 18-crown-6, $CH_2Cl_2$, reflux, 24 h (97%); iii) Pd/C (5%), 3 bar $H_2$, $NEt_3$, EtOAc, r.t., 24 h; iv) 2 M HCl/THF (1:1), r.t., 12 h (97% over two steps); v) PCC/$Al_2O_3$, $CH_2Cl_2$ r.t., 16 h (73%); vi) $TiCl_4$, Zn, THF, reflux, 24 h (39%); vii) Pd/C (5%), 10 bar $H_2$, EtOAc, r.t., 24 h (99%); viii) $BBr_3$ (10 equiv.), $CH_2Cl_2$, –78 °C to r.t. over 5 h, then 10 h at r.t. (85%).

the aryl bromide **79**. A poor yield for the macrocyclization by the Wittig protocol via the benzyl alcohol **88** prompted us to pursue the McMurry strategy via the dialdehyde **89**.

### Structure Verification and Total NMR Assignment

The structures of the synthesized compounds **6** and **8**–**15** (Scheme 18) were verified by NMR experiments (H,H COSY; C,H COSY; HMBC). The total assignment is listed in Tables 2, 3 and 4. The NMR spectroscopic data for compounds **10**, **11** and **13** have been published in full previously.[15] The spectroscopic data for synthetic **9**, **6** and **14** were coincident with those reported for the isolated compounds.




Scheme 18. Atom numbering for assignment of the NMR signals.

Table 2. $^1$H NMR spectroscopic data for the synthetic compounds **8**, **9** and **12** ($\delta$ in ppm, $J$ in Hz).[a]

| 400 MHz, [D$_6$]acetone | Plagiochin H (**8**) | Isoriccardin C (**9**) | Polymorphatin A (**12**) |
|---|---|---|---|
| H–C(2) | – | – | 6.59 (d, $J$ = 1.6) |
| HO–C(3) | 7.26 (br. s) | 7.32 (br. s) | 8.58 (br. s) |
| H–C(4) | 6.61 (dd, $J$ = 8.0, 0.8) | 6.72 (dd, $J$ = 7.8, 1.0) | – |
| H–C(5) | 6.90 (dd, $J$ = 8.0, 7.8) | 7.10 (dd, $J$ = 7.8, 7.8) | 7.17 (d, $J$ = 7.8) |
| H–C(6) | 6.45 (dd, $J$ = 7.8, 0.8) | 6.86 (dd, $J$ = 7.8, 1.0) | 6.67 (dd, $J$ = 7.8, 1.6) |
| CH$_2$(7) | 2.89–2.81 (m) + 1.80–1.72 (m) | 2.52–2.44 (m) | 2.92–2.86 (m) |
| CH$_2$(8) | 2.73–2.62 (m) + 2.59–2.52 (m) | 2.66–2.59 (m) | 2.94–2.89 (m) |
| H–C(10) | 5.17 (d, $J$ = 2.0) | 5.73 (d, $J$ = 2.0) | 6.37 (d, $J$ = 2.0) |
| HO–C(12) | 7.60 (br. s) | 7.69 (br. s) | 7.89 (br. s) |
| H–C(13) | 6.58 (d, $J$ = 8.0) | 6.75 (d, $J$ = 8.0) | 7.01 (d, $J$ = 8.3) |
| H–C(14) | 6.50 (dd, $J$ = 8.0, 2.0) | 6.67 (dd, $J$ = 8.0, 2.0) | 7.09 (dd, $J$ = 8.3, 2.0) |
| H–C(2′) | – | 6.64 (d, $J$ = 1.7) | 6.94 (d, $J$ = 1.6) |
| HO–C(3′) | 7.36 (br. s) | 7.32 (br. s) | 8.29 (br. s) |
| H–C(4′) | 6.61 (m) | – | – |
| H–C(5′) | 7.42 (dd, $J$ = 7.8, 7.8) | 6.79 (d, $J$ = 7.5) | 7.22 (d, $J$ = 7.9) |
| H–C(6′) | 7.16 (m) | 6.55 (dd, $J$ = 7.5, 1.7) | 6.90 (dd, $J$ = 7.9, 1.6) |
| CH$_2$(7′) | 3.03–2.97 (m) + 2.29–2.21 (m) | 3.07–3.01 (m) | 2.68 (m) |
| CH$_2$(8′) | 3.22–3.15 (m) + 2.89–2.81 (m) | 3.16–3.09 (m) | 2.68 (m) |
| H–C(10′)[b] | 7.01 (dd, $J$ = 8.3, 2.3) | 7.18–7.12 (m) | 7.02 (d, $J$ = 8.8) |
| H–C(11′)[b] | 6.54 (dd, $J$ = 8.3, 2.5) | 6.82–6.79 (m) | 6.56 (d, $J$ = 8.8) |
| H–C(13′)[b] | 6.70 (dd, $J$ = 8.3, 2.5) | 6.82–6.79 (m) | 6.56 (d, $J$ = 8.8) |
| H–C(14′)[b] | 6.93 (dd, $J$ = 8.3, 2.3) | 7.18–7.12 (m) | 7.02 (d, $J$ = 8.8) |

[a] The NMR spectroscopic data for compounds **10**, **11** and **13** have been published in full previously.[15] [b] Signals for H–C(10′)/H–C(14′) and H–C(11′)/H–C(13′) interchangeable.

Table 3. $^1$H NMR spectroscopic data for the synthetic compounds **6**, **14** and **15** ($\delta$ in ppm, $J$ in Hz).

| 400 MHz, [D$_6$]acetone | Riccardin C (**6**) | Isoriccardin D (**14**) | Plagiochin G (**15**) |
|---|---|---|---|
| H–C(2) | 6.35 (d, $J$ = 1.8) | 6.81 (d, $J$ = 2.6) | 6.59 (d, $J$ = 2.3) |
| HO–C(3) | 7.51 (br. s) | 8.14 (br. s) | 8.05 (br. s) |
| H–C(4) | – | 6.66 (d, $J$ = 8.4, 2.6) | 6.62 (dd, $J$ = 8.0, 2.3) |
| H–C(5) | 6.78 (d, $J$ = 7.8) | 6.89 (d, $J$ = 8.4) | 6.83 (d, $J$ = 8.0) |
| H–C(6) | 6.14 (dd, $J$ = 7.8, 1.8) | – | – |
| CH$_2$(7) | 2.65–2.56 (m) | 2.33–2.27 (m) | 3.05–2.97 (m) + 2.17–2.11 (m) |
| CH$_2$(8) | 2.69–2.60 (m) | 2.73–2.67 (m) + 2.52–2.46 (m) | 2.92–2.87 (m) + 2.85–2.80 (m) |
| H–C(10) | 5.36 (d, $J$ = 2.0) | 5.85 (d, $J$ = 1.9) | 5.34 (d, $J$ = 2.0) |
| HO–C(12) | 7.64 (br. s) | 7.71 (br. s) | 7.70 (br. s) |
| H–C(13) | 6.83 (d, $J$ = 8.0) | 6.75 (d, $J$ = 8.2) | 6.75 (d, $J$ = 8.0) |
| H–C(14) | 6.70 (dd, $J$ = 8.0, 2.0) | 6.89 (dd, $J$ = 8.2, 1.9) | 6.68 (d, $J$ = 8.0, 2.5) |
| H–C(2′) | 6.92 (d, $J$ = 2.6) | 6.54 (d, $J$ = 1.6) | 7.20 (d, $J$ = 2.5) |
| HO–C(3′) | 8.22 (br. s) | 7.32 (br. s) | 8.21 (br. s) |
| H–C(4′) | 6.73 (dd, $J$ = 8.4, 2.6) | – | 6.64 (dd, $J$ = 8.5, 2.5) |
| H–C(5′) | 6.95 (d, $J$ = 8.4) | 6.79 (d, $J$ = 7.9) | 6.98 (d, $J$ = 8.5) |
| H–C(6′) | – | 6.53 (dd, $J$ = 7.9, 1.6) | – |
| CH$_2$(7′) | 2.92–2.86 (m) | 3.09–3.07 (m) + 3.06–2.99 (m) | 3.04–2.97 (m) + 2.91–2.85 (m) |
| CH$_2$(8′) | 2.93–2.84 (m) | 3.12–3.05 (m) | 3.10–3.04 (m) |
| H–C(10′)[a] | 6.95–6.80 (br. m) | 7.16 (dd, $J$ = 8.2, 2.2) | 6.96 (m) |
| H–C(11′)[a] | 6.75–6.68 (br. m) | 6.83 (dd, $J$ = 8.2, 2.5) | 6.72–6.68 (m) |
| H–C(13′)[a] | 6.75–6.68 (br. m) | 6.76 (dd, $J$ = 8.2, 2.5) | 6.72–6.68 (m) |
| H–C(14′)[a] | 6.95–6.80 (br. m) | 7.06 (dd, $J$ = 8.2, 2.2) | 7.02 (m) |

[a] Signals for H–C(10′)/H–C(14′) and H–C(11′)/H–C(13′) interchangeable.

It should be mentioned that the NMR spectroscopic data for synthetic polymorphatin A (**12**) show significant deviations from those published for the isolated bis(bibenzyl) reported by Lou et al.[16] Furthermore, the spectroscopic data for isolated **12** are not concordant with the data for **6** and **15**, two related structures with a similar substitution pattern. With respect to the work of Lou et al. we advise further investigation with regard to the structure of the bis(bibenzyl) isolated from *Marchantia polymorpha* with the proposed structure **12**.

## Conformations of the Bis(bibenzyl) Compounds

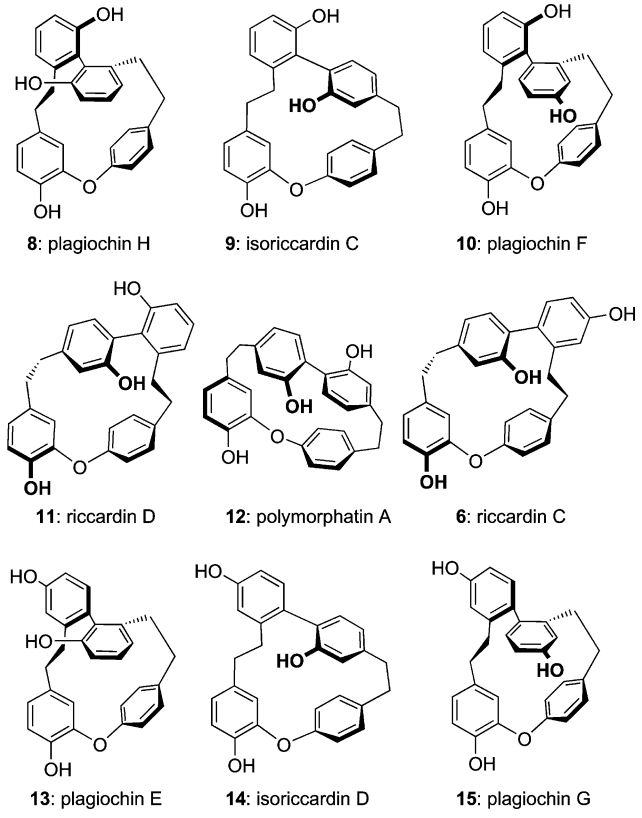
The conformers of the nine bis(bibenzyl) compounds of the plagiochin/riccardin type with the minimum strain energy were calculated by use of HyperChem Professional v. 7.52. The structures thus obtained are depicted in Scheme 19. It is remarkable that the carbon skeletons of plagiochins H (**8**), E (**13**), F (**10**) and G (**15**) are almost congruent; their structures mainly differ in the position of the hydroxy groups. The same analogy can be found for the

Table 4. $^{13}C$ NMR spectroscopic data for the synthetic compounds **8**, **9**, **12**, **6**, **14** and **15** ($\delta$ in ppm).[a]

| 100 MHz, [D$_6$]acetone | **8** | **9** | **12** | **6** | **14** | **15** |
|---|---|---|---|---|---|---|
| C(1) | 142.75 | 143.31 | 143.13 | 141.71 | 141.85 | 139.72 |
| C(2) | 123.23 | 125.31 | 118.69 | 116.96 | 115.17 | 113.49 |
| C(3) | 155.77 | 155.87 | 154.41 | 154.37 | 156.40 | 155.80 |
| C(4) | 113.56 | 113.67 | 124.95 | 126.70 | 112.48 | 111.08 |
| C(5) | 128.85 | 129.03 | 132.84 | 133.06 | 131.19 | 132.37 |
| C(6) | 117.90 | 121.10 | 122.83 | 121.44 | 128.51 | 130.34 |
| C(7) | 31.41 | 37.54 | 38.84 | 38.55 | 36.45 | 30.87 |
| C(8) | 30.67 | 38.54 | 37.42 | 37.89 | 37.02 | 29.42 |
| C(9) | 133.62 | 134.53 | 134.25 | 133.32 | 133.42 | 131.91 |
| C(10) | 117.00 | 116.24 | 124.36 | 117.69 | 115.31 | 114.81 |
| C(11) | 151.18 | 149.34 | 142.76 | 147.96 | 144.36 | 149.73 |
| C(12) | 144.41 | 145.51 | 148.46 | 145.25 | 147.94 | 143.44 |
| C(13) | 116.42 | 116.36 | 118.69 | 116.57 | 115.17 | 115.57 |
| C(14) | 121.92 | 122.40 | 126.41 | 122.72 | 121.32 | 121.24 |
| C(1′) | 141.30 | 138.04 | 144.33 | 144.28 | 140.29 | 139.39 |
| C(2′) | 124.43 | 117.49 | 117.97 | 117.41 | 116.04 | 115.63 |
| C(3′) | 155.85 | 155.45 | 155.09 | 157.78 | 153.78 | 155.74 |
| C(4′) | 113.79 | 121.29 | 125.36 | 113.99 | 125.29 | 112.00 |
| C(5′) | 128.57 | 131.84 | 133.01 | 133.46 | 130.14 | 131.93 |
| C(6′) | 120.16 | 121.58 | 121.89 | 130.39 | 119.88 | 131.53 |
| C(7′) | 35.84 | 36.73 | 38.92 | 35.95 | 35.57 | 34.78 |
| C(8′) | 33.29 | 35.31 | 37.82 | 38.77 | 35.44 | 34.41 |
| C(9′) | 141.50 | 142.01 | 136.74 | 140.80 | 136.73 | 139.74 |
| C(10′)[b] | 131.22 | 131.49 | 130.50 | 130.23 | 130.23 | 129.93 |
| C(11′)[b] | 124.90 | 122.07 | 117.08 | 122.92 | 120.70 | 123.43 |
| C(12′) | 156.75 | 154.84 | 157.60 | 154.06 | 153.67 | 154.97 |
| C(13′)[b] | 123.30 | 122.07 | 117.08 | 122.72 | 120.63 | 122.02 |
| C(14′)[b] | 130.79 | 131.39 | 130.50 | 130.23 | 130.23 | 129.80 |

[a] The NMR spectroscopic data for compounds **10**, **11** and **13** have been published in full previously.[15] [b] Signals for H–C(10′)/H–C(14′) and H–C(11′)/H–C(13′) interchangeable.




Scheme 19. Minimum-energy conformers of the bis(bibenzyl) compounds of the plagiochin/riccardin type.

isorricardins C (**9**) and D (**14**), as well as for the riccardins C (**6**) and D (**11**). The structure of polymorphatin A (**12**) is not comparable with the others and represents a unique skeleton of the bis(bibenzyl) family (Scheme 19).

## Conclusions

Cyclic bis(bibenzyl) compounds of the plagiochin and riccardin type derived from the open-chain precursor perrottettin E (**3**) are structurally interesting compounds.[15] Some of them have been isolated since 1982 as natural products from liverworts (bryophytes); others might be in the future. Structure elucidation has proved wrong in at least one case up to now, which is crucially important with respect to a growing interest in these compounds' considerable biological activities. We have synthesized the "library" of the nine bis(bibenzyl) compounds through the use of a construction unit system, followed by detailed and comparative spectroscopic characterization. With all bis(bibenzyl) types on hand, further and systematic investigations on structural aspects of axial chirality and biological activities will be performed.

## Experimental Section

**General:** $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker Avance 2 spectrometer (400 or 100 MHz) at ambient temperature with reference to TMS or solvent standard with the chemical shifts recorded as $\delta$ values in ppm units. Coupling constants ($J$) are given in Hz and signal patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet, br, broad signal. High-resolution mass spectrometry (HRMS) analyses were conducted with a Finnigan MAT 95 instrument. The melting points (m.p.) were determined with a Büchi melting point apparatus (Dr. Tottoli). Column chromatography was performed on silica gel 60 (63–260 μm) and flash chromatography on silica gel 60 (35–70 μm).

**5-(1,3-Dioxan-2-yl)-2-methoxyphenol (17):** Tetrabutylammonium tribromide (289 mg, 0.60 mmol) was added to a mixture of isovanillin (**16**, 15.2 g, 0.10 mol), triethyl orthoformate (11.1 g, 75.0 mmol) and propane-1,3-diol (18.2 g, 0.20 mol) and the solution was stirred for 6 h at 65 °C. The mixture was cooled to r.t. and diluted with EtOAc (100 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (3 × 50 mL) and saturated aqueous NaCl (1 × 50 mL), dried ($MgSO_4$) and concentrated. The dioxane **17** (20.4 g, 97%) was obtained as colourless crystals; m.p. 89 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.05 (d, $J$ = 2.0 Hz, 1 H), 6.97 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 6.82 (d, $J$ = 8.3 Hz, 1 H), 5.66 (s, 1 H, Ar-OH), 5.41 (s, 1 H, OCHO), 4.28–4.18 (m, 2 H, $OCH_2$), 4.00–3.90 (m, 2 H, $OCH_2$), 3.86 (s, 3 H, $OCH_3$), 2.27–2.11 (m, 1 H), 1.45–1.36 (m, 1 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 146.98, 145.52, 132.21, 117.77, 112.62, 110.34, 101.45 (OCHO), 67.34 ($OCH_2$), 56.01 ($OCH_3$), 25.75 ppm. HRMS: calcd. for $C_{11}H_{14}O_4$ 210.0892; found 210.0877.

**4-[5-(1,3-Dioxan-2-yl)-2-methoxyphenoxy]benzaldehyde (18):** A mixture of the phenol **17** (19.5 g, 92.8 mmol), 4-fluorobenzaldehyde (11.6 g, 93.6 mmol) and $K_2CO_3$ (11.7 g, 84.9 mmol) in anhydrous DMF (130 mL) was stirred for 20 h at 165 °C. After cooling to r.t. the reaction mixture was poured into ice/water and extracted with $Et_2O$ (3 × 200 mL). The combined organic layers were washed with

saturated aqueous NaCl (5 × 50 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The biaryl ether **18** (27.2 g, 93%) was obtained as a yellow resin. $^1$H NMR ($CDCl_3$): $\delta$ = 9.89 (s, 1 H, CHO), 7.80 (d, $J$ = 8.8 Hz, 2 H), 7.35 (dd, $J$ = 8.1, 2.1 Hz, 1 H), 7.26 (d, $J$ = 2.1 Hz, 1 H), 7.01 (d, $J$ = 8.1 Hz, 1 H), 6.98 (d, $J$ = 8.8 Hz, 2 H), 5.46 (s, 1 H, OCHO), 4.27–4.19 (m, 2 H, $OCH_2$), 4.00–3.91 (m, 2 H, $OCH_2$), 3.78 (s, 3 H, $OCH_3$), 2.25–2.13 (m, 1 H), 1.46–1.39 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.80 (CHO), 163.45, 151.93, 142.63, 132.42, 131.83, 130.92, 124.09, 120.49, 116.31, 112.58, 100.71 (OCHO), 67.34 ($OCH_2$), 56.00 ($OCH_3$), 25.66 ppm. HRMS: calcd. for $C_{18}H_{18}O_5$ 314.1154; found 314.1143.

**{4-[5-(1,3-Dioxan-2-yl)-2-methoxyphenoxy]phenyl}methanol (19):**[39] The aldehyde **18** (27.2 g, 86.5 mmol) was dissolved in THF (50 mL) and EtOH (250 mL). $NaBH_4$ (3.28 g, 86.7 mmol) was added at 0 °C and the mixture was stirred for 30 min. The mixture was allowed to warm to r.t. and stirring was continued for 2 h. Ice/water (230 mL) was added and the mixture was extracted with $Et_2O$ (3 × 100 mL). After drying ($MgSO_4$) and removal of the solvents the crude material was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/EtOAc 4:1). The alcohol **19** (24.5 g, 90%) was obtained as colourless crystals; m.p. 72 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.24 (dd, $J$ = 8.5, 2.0 Hz, 1 H), 7.22 (d, $J$ = 8.6 Hz, 2 H), 7.11 (d, $J$ = 2.0 Hz, 1 H), 6.96 (d, $J$ = 8.5 Hz, 1 H), 6.90 (d, $J$ = 8.6 Hz, 2 H), 5.38 (s, 1 H, OCHO), 4.54 (s, 2 H, $CH_2OH$), 4.20–4.16 (m, 2 H, $OCH_2$), 3.93–3.87 (m, 2 H, $OCH_2$), 3.79 (s, 3 H, $OCH_3$), 2.33 (br. s, 1 H, $CH_2OH$), 2.20–2.08 (m, 1 H), 1.40–1.36 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 157.30, 151.67, 144.67, 135.06, 132.03, 128.49, 122.52, 118.97, 117.23, 112.41, 100.96 (OCHO), 67.28 ($OCH_2$), 64.67 ($CH_2OH$), 56.05 ($OCH_3$), 25.61 ppm. HRMS: calcd. for $C_{18}H_{20}O_5$ 316.1311; found 316.1272.

**{4-[5-([1,3]Dioxan-2-yl)-2-methoxyphenoxy]benzyl}triphenylphosphonium Bromide (20):** The alcohol **19** (17.6 g, 55.3 mmol) and $PPh_3$·HBr (20.0 g, 58.4 mmol) were dissolved in MeCN (300 mL) and the system was heated at reflux for 6 h. The solvent was removed in vacuo and the residue was dissolved in $CHCl_3$ (150 mL). Propane-1,3-diol (40.0 g, 0.53 mol), triethyl orthoformate (23.0 g, 0.16 mol) and tetrabutylammonium tribromide (400 mg, 0.83 mmol) were added. The reaction mixture was heated under reflux for 12 h. After evaporation of the solvent the phosphonium salt, contaminated with propane-1,3-diol (81.6 g of crude product ca. 0.68 mmol g$^{-1}$) was obtained as a yellow oil. The crude phosphonium salt **20** was used in the following Wittig reactions without further purification.

**2-Formyl-6-methoxyphenyl Trifluoromethanesulfonate (Orthovanillin Triflate, 21):**[40] Orthovanillin (8.05 g, 52.9 mmol) and pyridine (8.38 g, 106 mmol) were dissolved in anhydrous $CH_2Cl_2$ (200 mL). $Tf_2O$ (19.9 g, 70.5 mmol) was added dropwise over 1 h at 0 °C. The reaction mixture was allowed to warm to r.t. and filtered through a short pad of $SiO_2$ with elution with $CH_2Cl_2$. After removal of the solvent the triflate **21** (14.3 g, 95%) was obtained as a colourless oil. $^1$H NMR ($CDCl_3$): $\delta$ = 10.23 (s, 1 H, CHO), 7.51 (dd, $J$ = 7.9, 1.9 Hz, 1 H), 7.47 (dd, $J$ = 7.9, 7.9 Hz, 1 H), 7.33 (dd, $J$ = 7.9, 1.9 Hz, 1 H), 3.96 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 186.89 (CHO), 151.81, 139.26, 129.66, 129.27, 121.41, 118.81, 118.80 (q, $J_{C,F}$ = 320.6 Hz, $CF_3$), 56.64 ($OCH_3$) ppm. HRMS: calcd. for $C_9H_7F_3O_5S$ 283.9966; found 283.9884.

**2-(Hydroxymethyl)-6-methoxyphenyl Trifluoromethanesulfonate (22):** A solution of DIBAL-H (1.5 M in toluene, 43.0 mL, 64.5 mmol) was added dropwise at –78 °C to a solution of **21** (14.2 g, 50.0 mmol) in anhydrous $CH_2Cl_2$ (120 mL). The mixture was allowed to warm to r.t. and stirred for 12 h, and HCl (2 M, 80 mL) was added at 0 °C. After separation of the layers the aqueous layer was extracted with $CH_2Cl_2$ (2 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 50 mL) and dried ($MgSO_4$). The solvents were removed in vacuo and the crude product was purified by column chromatography ($SiO_2$, $CH_2Cl_2$). The alcohol **22** (12.4 g, 87%) was obtained as a colourless oil. $^1$H NMR ($CDCl_3$): $\delta$ = 7.30 (dd, $J$ = 8.3, 8.0 Hz, 1 H), 7.13 (dd, $J$ = 8.0, 1.5 Hz, 1 H), 6.95 (dd, $J$ = 8.3, 1.5 Hz, 1 H), 4.73 (d, $J$ = 5.5 Hz, 2 H, $CH_2OH$), 3.88 (s, 3 H, $OCH_3$), 2.38 (br. t, $J$ = 5.5 Hz, 1 H, $CH_2OH$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 151.12, 136.10, 135.11, 128.99, 120.64, 118.78 (q, $J_{C,F}$ = 320.6 Hz, $CF_3$), 112.28, 59.42 ($CH_2OH$), 56.15 ($OCH_3$) ppm. HRMS: calcd. for $C_9H_9F_3O_5S$ 286.0123; found 286.0104.

**2-Methoxy-6-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]phenyl Trifluoromethanesulfonate (23):** The alcohol **22** (11.8 g, 41.2 mmol) was dissolved in anhydrous $CH_2Cl_2$. After addition of 3,4-dihydro-2*H*-pyran (10.2 g, 121 mmol) and *p*TosOH·$H_2O$ (300 mg, 1.60 mmol) the mixture was stirred for 16 h at r.t., filtered through a short pad of $SiO_2$ with elution with $CH_2Cl_2$ and concentrated. The crude material was purified by column chromatography ($SiO_2$, *n*-hexane/$CH_2Cl_2$ 1:1). Compound **23** (13.0 g, 85%) was obtained as a colourless oil. $^1$H NMR ($CDCl_3$): $\delta$ = 7.30 (dd, $J$ = 8.3, 7.9 Hz, 1 H), 7.14 (dd, $J$ = 7.9, 0.9 Hz, 1 H), 6.96 (dd, $J$ = 8.3, 0.9 Hz, 1 H), 4.83 (d, $J$ = 12.8 Hz, 1 H, Ar–$CH_2$O), 4.72 (t, $J$ = 3.5 Hz, 1 H, OCHO), 4.62 (d, $J$ = 12.8 Hz, 1 H, Ar–$CH_2$O), 3.89 (s, 3 H, $OCH_3$), 3.89 (m, 1 H, $CH_2$O), 3.56 (m, 1 H, $CH_2$O), 1.90–1.52 (m, 6 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 151.15, 136.77, 132.95, 128.64, 121.37, 118.79 (q, $J_{C,F}$ = 320.6 Hz, $CF_3$), 112.22, 98.29 (OCHO), 63.26, 62.18, 56.12 ($OCH_3$), 30.39, 25.43, 19.26 ppm. HRMS: calcd. for $C_{14}H_{17}F_3O_6S$ 370.0698; found 370.0600.

**3-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (25):** A solution of *i*PrMgCl (1.2 M in THF 10.9 mL, 13.1 mmol) was added over 15 min at –15 °C to a solution of the iodide **24**[36] (3.00 g, 8.74 mmol) in anhydrous THF (70 mL) and the mixture was stirred for an additional 2 h. Trimethyl borate (1.86 g, 17.9 mmol) was added in one portion at –15 °C and the mixture was allowed to warm to r.t. over 2 h. A solution of HCl (2 M, 20 mL) was added dropwise and the mixture was stirred for 30 min. After addition of saturated aqueous NaCl (20 mL) the reaction mixture was extracted with $CH_2Cl_2$ (3 × 50 mL). Pinacol (2.60 g, 22.0 mmol) and $MgSO_4$ (13.0 g, 0.11 mol) were added to the combined organic layers and the mixture was stirred for 12 h. The reaction mixture was filtered through a short pad of $SiO_2$ with elution with $CH_2Cl_2$ and the filtrate was concentrated under reduced pressure. The crude material was purified by column chromatography ($SiO_2$, *n*-hexane/EtOAc 4:1). The boronic ester **25** (1.20 g, 53%) was obtained as a yellow solid. $^1$H NMR ($CDCl_3$): $\delta$ = 9.94 (s, 1 H, CHO), 7.48 (dd, $J$ = 8.3, 7.5 Hz, 1 H), 7.10 (dd, $J$ = 8.3, 0.8 Hz, 1 H), 7.41 (dd, $J$ = 7.5, 0.8 Hz, 1 H), 3.88 (s, 3 H, $OCH_3$), 1.45 (s, 12 H, $CH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 193.09 (CHO), 163.14, 141.02, 130.93, 124.37, 115.98, 84.24 [$OC(CH_3)_2$], 55.95 ($OCH_3$), 24.81 ($CH_3$) ppm. HRMS: calcd. for $C_{14}H_{19}BO_4$ 262.1376; found 262.1358.

**2′,6-Dimethoxy-6′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-2-carbaldehyde (26):** The boronic ester **25** (0.86 g, 3.27 mmol) and the triflate **23** (1.57 g, 4.24 mmol) were dissolved in toluene (30 mL). EtOH (15 mL) and $Na_2CO_3$ (2 M, 15 mL) were added and the mixture was degassed with a stream of argon. $Pd(PPh_3)_4$ (485 mg, 0.42 mmol) was added and the mixture was heated for 16 h at 105 °C. After cooling to r.t. the mixture was filtered through a short pad of $SiO_2$ with elution with EtOAc. After evaporation of the solvents the residue was purified by flash

chromatography ($SiO_2$, *n*-hexane/EtOAc 3:1 → 2:1). The biaryl **26** was obtained as an inseparable mixture of diastereomers (0.34 g, 30%) and as a colourless oil. $^1H$ NMR ($CDCl_3$): $\delta$ = 9.58 + 9.57 (d, $J$ = 0.8 Hz, 2×0.5 H, CHO), 7.63 + 7.62 (dd, $J$ = 7.8, 1.3 Hz, 2×0.5 H), 7.46 (dd, $J$ = 7.8, 7.8 Hz, 2×0.5 H), 7.42 (dd, $J$ = 7.5, 7.5 Hz, 2×0.5 H), 7.20–7.18 (m, 1 H), 7.18 (m, 1 H), 6.95–6.93 (m, 1 H), 4.54 (t, $J$ = 2.5, 0.5 Hz, OCHO) + 4.17 (t, $J$ = 2.0 Hz, 0.5 H, OCHO), 4.51 + 3.99 (d, $J$ = 11.8 Hz, 2×0.5 H, Ar–$OCH_2$), 4.35 + 4.16 (d, $J$ = 12.0 Hz, 2×0.5 H, Ar–$OCH_2$), 3.76 (s, 1.5 H, $OCH_3$), 3.75 (s, 1.5 H, $OCH_3$), 3.69 (s, 1.5 H, $OCH_3$), 3.68 (s, 1.5 H, $OCH_3$), 3.74–3.70 (m, 0.5 H, $OCH_2$), 3.40–3.35 (m, 0.5 H, $OCH_2$), 3.28–3.25 (m, 1 H, $OCH_2$), 1.57–1.34 (m, 6 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 192.87 (CHO), 192.84 (CHO), 157.22, 157.19, 157.04, 157.00, 138.98, 138.91, 135.72, 135.52, 129.43, 128.88, 121.77, 121.52, 121.20, 121.01, 118.70, 118.57, 116.04, 115.93, 110.00, 109.94, 98.43 (OCHO), 97.74 (OCHO), 67.50 (Ar–$OCH_2$), 67.25 (Ar–$OCH_2$), 61.86 ($OCH_2$), 61.09 ($OCH_2$), 56.04 ($OCH_3$), 56.01 ($OCH_3$), 55.79 ($OCH_3$), 30.19, 30.12, 25.37, 25.30, 19.13, 18.64 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1622.

**Stilbene 27:** A mixture of the aldehyde **26** (0.87 g, 2.45 mmol), the phosphonium salt **20** (4.60 g, 3.13 mmol), $K_2CO_3$ (3.50 g, 25.3 mmol) and a catalytic amount of 18-crown-6 in anhydrous $CH_2Cl_2$ (120 mL) was heated under reflux for 24 h. After cooling to r.t. the mixture was filtered through a pad of $SiO_2$ with elution with EtOAc and concentrated. The crude material was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 3:1 → 2:1). The stilbene **27** (*E*/*Z* mixture, 1.41 g, 88%) was obtained as a colourless resin. Complex NMR spectroscopic data. HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2874.

**Bibenzyl 28:** The stilbene **27** (1.02 g, 1.60 mmol) was dissolved in EtOAc (200 mL) and $NEt_3$ (5 mL). After addition of Pd/C (5%, 1.00 g) the mixture was hydrogenated in a Parr apparatus at 3 bar $H_2$ for 24 h. The catalyst was filtered off and the solution was concentrated in vacuo. The residue was dissolved in THF (50 mL) and HCl (2 M, 50 mL). After stirring for 16 h at r.t. the mixture was diluted with EtOAc (150 mL) and saturated aqueous NaCl (50 mL). After separation the organic layer was washed with saturated aqueous $NaHCO_3$ (3×50 mL) followed by saturated aqueous NaCl (3×50 mL) and dried ($MgSO_4$). The solvents were evaporated under reduced pressure and the crude product was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 2:1). The bibenzyl **28** (0.69 g, 86%) was obtained as a colourless resin. $^1H$ NMR ($CDCl_3$): $\delta$ = 9.79 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.3, 1.9 Hz, 1 H), 7.43 (dd, $J$ = 8.3, 7.9 Hz, 1 H), 7.36 (d, $J$ = 1.9 Hz, 1 H), 7.33 (dd, $J$ = 8.0, 7.8 Hz, 1 H), 7.21 (dd, $J$ = 7.8, 1.0 Hz, 1 H), 7.09 (d, $J$ = 8.3 Hz, 1 H), 6.98 (dd, $J$ = 8.3, 1.0 Hz, 1 H), 6.95 (dd, $J$ = 7.8, 1.0 Hz, 1 H), 6.89 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 6.85 (d, $J$ = 8.8 Hz, 2 H), 6.81 (d, $J$ = 8.8 Hz, 2 H), 4.24 (d, $J$ = 12.1 Hz, 1 H, $CH_2OH$), 4.20 (d, $J$ = 12.1 Hz, 1 H, $CH_2OH$), 3.94 (s, 3 H, $OCH_3$), 3.72 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 2.68–2.48 (m, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 190.42 (CHO), 156.97, 156.84, 156.13, 154.59, 146.92, 142.00, 140.90, 137.44, 130.19, 129.66, 129.03, 128.64, 127.73, 124.70, 124.56, 122.12, 120.98, 118.86, 118.22, 111.94, 110.31, 109.27, 63.83 ($CH_2OH$), 56.28 ($OCH_3$), 56.01 ($OCH_3$), 55.71 ($OCH_3$), 35.90 ($CH_2CH_2$), 35.83 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2039.

**Bibenzyl Dialdehyde 29:** The benzyl alcohol **28** (0.65 g, 1.31 mmol) was dissolved in anhydrous $CH_2Cl_2$ (80 mL). PCC on $Al_2O_3$ (1 mmol $g^{-1}$) was added (2.80 g, 2.80 mmol) and the suspension was stirred for 16 h at r.t. The mixture was filtered through a short pad of $SiO_2$ with elution with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 1:1). The dialdehyde **29** (0.61 g, 95%) was obtained as a colourless resin. $^1H$ NMR ($CDCl_3$): $\delta$ = 9.80 (s, 1 H, CHO), 9.56 (d, $J$ = 0.8 Hz, 1 H, CHO), 7.66 (dd, $J$ = 7.8, 1.0 Hz, 1 H), 7.64 (dd, $J$ = 8.5, 2.0 Hz, 1 H), 7.49 (ddd, $J$ = 8.3, 7.8, 0.8 Hz, 1 H), 7.38 (d, $J$ = 2.0 Hz, 1 H), 7.32 (dd, $J$ = 8.3, 7.8 Hz, 1 H), 7.23 (dd, $J$ = 8.3, 1.0 Hz, 1 H), 7.08 (d, $J$ = 8.5 Hz, 1 H), 6.92 (dd, $J$ = 7.8, 0.8 Hz, 1 H), 6.86 (dd, $J$ = 8.3, 0.8 Hz, 1 H), 6.81 (d, $J$ = 9.0 Hz, 2 H), 6.81 (d, $J$ = 9.0 Hz, 2 H), 3.94 (s, 3 H, $OCH_3$), 3.78 (s, 3 H, $OCH_3$), 3.68 (s, 3 H, $OCH_3$), 2.65–2.52 (m, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 192.73 (CHO), 190.42 (CHO), 157.32, 157.28, 156.17, 154.73, 146.79, 142.32, 136.96, 135.46, 130.23, 130.20, 129.58, 129.28, 128.89, 127.66, 121.61, 121.52, 119.15, 118.92, 118.15, 116.18, 111.97, 108.36, 56.28 ($OCH_3$), 56.00 ($OCH_3$), 55.73 ($OCH_3$), 35.93 ($CH_2CH_2$), 35.78 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 496.1886; found 496.1850.

**Dehydroplagiochin H Trimethyl Ether 30:** $TiCl_4$ (4.30 mL, 7.40 g, 39.0 mmol) was added dropwise with cooling in an ice/NaCl bath to a suspension of zinc dust (6.00 g, 91.8 mmol) in anhydrous THF (50 mL). The mixture was heated to reflux for 1 h. A solution of the dialdehyde **29** (690 mg, 1.38 mmol) in anhydrous THF (200 mL) was added dropwise over 4 h. The black mixture was heated to reflux for 24 h. After cooling to r.t. the reaction mixture was filtered through a short pad of $SiO_2$ with elution with EtOAc. The colourless filtrate was then concentrated and purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 4:1). The stilbene **30** (NMR: *E*/*Z* 1.1:1, 170 mg, 27%) was obtained as a colourless solid; m.p. 148 °C. Complex NMR spectroscopic data. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1970.

**Plagiochin H Trimethyl Ether (31):** The macrocyclic stilbene **30** (160 mg, 0.34 mmol) was dissolved in $CH_2Cl_2$ (150 mL). After addition of Pd/C (5%, 80 mg) the mixture was hydrogenated in a Parr apparatus at 3 bar $H_2$ for 24 h. The catalyst was filtered off and the solution was concentrated in vacuo. The residue was filtered through a short pad of $SiO_2$ with elution with $CH_2Cl_2$. After removal of the solvent the trimethyl ether **31** (155 mg, 97%) was obtained as a colourless solid; m.p. 186 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.35–7.31 (m, 2 H), 7.18 (dd, $J$ = 8.0, 8.0 Hz, 1 H), 7.07 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.95 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.83 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.78–6.73 (m, 3 H), 6.71–6.68 (m, 3 H), 5.23 (d, $J$ = 2.0 Hz, 1 H), 3.89 (s, 3 H, $OCH_3$), 3.65 (s, 3 H, $OCH_3$), 3.59 (s, 3 H, $OCH_3$), 3.25 (m, 1 H, $CH_2CH_2$), 3.03 (m, 1 H, $CH_2CH_2$), 2.96–2.73 (m, 4 H, $CH_2CH_2$), 2.28 (m, 1 H, $CH_2CH_2$), 1.94–1.85 (m, 1 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 156.97, 156.95, 155.35, 151.63, 146.14, 141.99, 140.38, 140.22, 133.96, 130.40, 129.81, 128.05, 127.56, 125.68, 124.69, 124.17, 122.74, 120.55, 120.22, 118.25, 116.02, 111.48, 108.32, 108.07, 56.14 ($OCH_3$), 55.53 ($OCH_3$), 55.39 ($OCH_3$), 34.95 ($CH_2CH_2$), 32.91 ($CH_2CH_2$), 30.23 ($CH_2CH_2$), 30.04 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2134.

**Plagiochin H (8):** The trimethyl ether **31** (150 mg, 0.32 mmol) was dissolved in anhydrous $CH_2Cl_2$. A solution of $BBr_3$ (1 M in $CH_2Cl_2$, 3.20 mL, 3.20 mmol) was added at –78 °C. The mixture was allowed to warm to r.t. over 6 h. Ice-cold water (20 mL) was added dropwise and the mixture was stirred for 10 min. The reaction mixture was diluted with EtOAc (40 mL), washed with saturated aqueous NaCl (3×20 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 3:1). Plagiochin H (**8**, 102 mg, 75%) was obtained as a colourless powder; m.p. 241 °C. NMR spectroscopic data; see Tables 2 and 4. HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1660.

**4-Iodo-3-methoxybenzaldehyde (33):** The benzyl alcohol **32**[36] (17.2 g, 65.1 mmol) was dissolved in anhydrous $CH_2Cl_2$ (200 mL). PCC on $Al_2O_3$ (1 mmol g$^{-1}$) was added (108 g, 108 mmol) and the suspension was stirred for 16 h at r.t. The mixture was filtered through a short pad of $SiO_2$ with elution with EtOAc. The solvents were removed under reduced pressure and the crude product was purified by flash chromatography ($SiO_2$, $CH_2Cl_2$). The aldehyde **33** (15.7 g, 92%) was obtained as a colourless solid; m.p. 83 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 9.95 (s, 1 H, CHO), 7.99 (d, $J$ = 7.8 Hz, 1 H), 7.29 (d, $J$ = 1.8 Hz, 1 H), 7.19 (dd, $J$ = 7.8, 1.8 Hz, 1 H), 3.96 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 191.32 (CHO), 158.87, 140.27, 137.82, 124.95, 108.62, 95.22 (C-I), 56.56 ($OCH_3$) ppm. HRMS: calcd. for $C_8H_7IO_2$ 261.9491; found 261.9463.

**2-(4-Iodo-3-methoxyphenyl)-1,3-dioxane (34):** The dioxane **34** was prepared from **33** (9.56 g, 36.5 mmol) in a procedure analogous to that used for the synthesis of **17** and was obtained as colourless crystals (11.6 g, 99%); m.p. 43 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.53 (d, $J$ = 8.0 Hz, 1 H), 6.98 (d, $J$ = 1.8 Hz, 1 H), 6.82 (dd, $J$ = 8.0, 1.8 Hz, 1 H), 5.44 (s, 1 H, OCHO), 4.25 (m, 2 H, $OCH_2$), 3.96 (m, 2 H, $OCH_2$), 3.89 (s, 3 H, $OCH_3$), 2.20 (m, 1 H), 1.44 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 158.01, 140.66, 139.09, 120.24, 108.55, 100.75 (OCHO), 86.21 (C-I), 67.32 ($OCH_2$), 56.30 ($OCH_3$), 25.64 ppm. HRMS: calcd. for $C_{11}H_{13}IO_3$ 319.9909; found 320.9985 ([M + H] 320.9988).

**4-Formyl-2-(methoxyphenyl)boronic Acid (35):**[41] A solution of *n*BuLi (2.5 M in *n*-hexane, 42.0 mL, 105 mmol) was added slowly at –78 °C to a solution of the iodide **34** (25.8 g, 80.6 mmol) in anhydrous THF (150 mL) and the mixture was stirred for an additional 60 min. Trimethyl borate (12.6 g, 121 mmol) was added in one portion at –78 °C and the mixture was allowed to warm to r.t. over 2 h. A solution of HCl (2 M, 100 mL) was added dropwise and the mixture was stirred for 30 min. The reaction mixture was extracted with $Et_2O$ (3 × 75 mL). The combined organic layers were washed with saturated aqueous NaCl (100 mL) and extracted with NaOH (1 M, 1 × 50 mL, 2 × 25 mL). The aqueous phase was neutralized with concentrated HCl (cooling in an ice bath). The precipitated solid was collected by filtration, washed with $H_2O$ (2 × 40 mL) and dried under reduced pressure over $CaCl_2$. The boronic acid **35** (7.93 g, 55%) was obtained as a colourless powder; m.p. 136 °C. $^1$H NMR ([D$_6$]DMSO): $\delta$ = 9.99 (s, 1 H, CHO), 8.01 [br s, 2 H, $B(OH)_2$], 7.67 (d, $J$ = 7.3 Hz, 1 H), 7.49 (dd, $J$ = 7.3, 1.0 Hz, 1 H), 7.40 (d, $J$ = 1.0 Hz, 1 H), 3.85 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 193.10 (CHO), 163.16, 138.48, 135.10, 122.50, 109.10, 55.43 ($OCH_3$) ppm. HRMS: calcd. for $C_8H_9BO_4$ 180.0594; found 180.0606.

**3-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (36):** The boronic acid **35** (4.00 g, 22.2 mmol) and pinacol (5.00 g, 42.3 mmol) were dissolved in $CH_2Cl_2$ (150 mL) and $MgSO_4$ (25.0 g, 0.21 mol) was added. The suspension was stirred for 16 h at r.t. The solid was filtered off, the filtrate was concentrated in vacuo, and the residue was purified by column chromatography ($SiO_2$, *n*-hexane/EtOAc 4:1). The boronic ester **36** (4.98 g, 86%) was obtained as a colourless oil. $^1$H NMR ($CDCl_3$): $\delta$ = 10.00 (s, 1 H, CHO), 7.81 (d, $J$ = 7.3 Hz, 1 H), 7.43 (dd, $J$ = 7.3, 1.2 Hz, 1 H), 7.35 (d, $J$ = 1.2 Hz, 1 H), 3.90 (s, 3 H, $OCH_3$), 1.37 (s, 12 H, $CH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.42 (CHO), 164.39, 139.60, 136.94, 123.28, 108.57, 84.05 [$OC(CH_3)_2$], 55.93 ($OCH_3$), 24.82 ($CH_3$) ppm. HRMS: calcd. for $C_{14}H_{19}BO_4$ 262.1376; found 262.1373.

**2,2′-Dimethoxy-6′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-4-carbaldehyde (37):** The biaryl **37** was prepared from **23** (3.67 g, 9.91 mmol) and **36** (2.00 g, 7.63 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a yellow oil (865 mg, 32%). $^1$H NMR ($CDCl_3$): $\delta$ = 10.0 (d, $J$ = 0.8 Hz, 1 H, CHO), 7.51 (ddd, $J$ = 7.5, 1.3, 0.8 Hz, 1 H), 7.48 + 7.48 (d, $J$ = 1.3 Hz, 1 H), 7.38 (dd, $J$ = 8.0, 7.8 Hz, 1 H), 7.33 + 7.32 (d, $J$ = 7.5 Hz, 1 H), 7.20 [dd (not resolved), 1 H], 6.93 [dd (not resolved), 1 H], 4.54 + 4.43 (d, $J$ = 12.3 Hz, 1 H, Ar–$OCH_2$), 4.49 + 4.40 (t, $J$ = 3.5 Hz, 1 H, OCHO), 4.18 + 4.07 (d, $J$ = 12.3 Hz, 1 H, Ar–$OCH_2$) 3.80 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 3.68–3.53 (m, 1 H, $CH_2O$), 3.40–3.32 (m, 1 H, $CH_2O$), 1.82–1.40 (m, 6 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.04 (CHO), 157.96, 157.82, 156.81, 138.14, 138.04, 137.14, 132.85, 132.36, 132.25, 129.03, 128.94, 125.69, 125.52, 124.02, 123.92, 120.74, 120.70, 120.59, 112.25, 110.31, 110.23, 109.20, 109.17, 98.05 (OCHO), 66.95 (Ar–$OCH_2$), 61.74 ($OCH_2$), 61.59 ($OCH_2$), 55.95 ($OCH_3$), 55.82 ($OCH_3$), 55.79 ($OCH_3$), 30.46, 30.45, 25.41, 19.16, 19.07 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1608.

**Stilbene 38:** The stilbene **38** was prepared from **37** (0.95 g, 2.67 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 1.30 g, 76%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2853.

**Bibenzyl 39:** The bibenzyl **39**, as a benzyl alcohol, was prepared from **38** (1.07 g, 1.68 mmol) in a procedure analogous to that used for the synthesis of **28** and was obtained as a colourless solid (0.80 g, 96%); m.p. 43 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 9.80 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.35 (dd, $J$ = 7.9, 7.9 Hz, 1 H), 7.17 (d, $J$ = 8.7 Hz, 2 H), 7.15 (dd, $J$ = 7.9, 1.0 Hz, 1 H), 7.10 (d, $J$ = 8.3 Hz, 1 H), 7.02 (d, $J$ = 7.8 Hz, 1 H), 6.93 (d, $J$ = 8.7 Hz, 2 H), 6.92 (dd, $J$ = 7.9, 1.0 Hz, 1 H), 6.87 (dd, $J$ = 7.8, 1.5 Hz, 1 H), 6.80 (d, $J$ = 7.8 Hz, 1 H), 4.33 (d, $J$ = 12.3 Hz, 1 H, $CH_2OH$), 4.30 (d, $J$ = 12.3 Hz, 1 H, $CH_2OH$), 3.96 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 3.70 (s, 3 H, $OCH_3$), 2.97 (s, 4 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.40 (CHO), 157.23, 156.65, 156.10, 154.74, 147.00, 142.69, 141.06, 137.16, 131.61, 130.20, 129.85, 128.71, 127.82, 126.24, 122.77, 120.93, 120.66, 118.64, 118.43, 111.96, 111.91, 110.51, 63.70 ($CH_2OH$), 56.28 ($OCH_3$), 55.95 ($OCH_3$), 55.80 ($OCH_3$), 38.14 ($CH_2CH_2$), 36.99 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2020.

**Dehydroisoriccardin C Trimethyl Ether (40):** A solution of the benzyl alcohol **39** (1.73 g, 3.46 mmol) and $PPh_3$·HBr (1.31 g, 3.81 mmol) in MeCN (50 mL) was heated at reflux for 12 h. The solvent was removed in vacuo and the crude phosphonium salt was dissolved in anhydrous $CH_2Cl_2$ (300 mL). This solution was added dropwise over 6 h to a mixture of NaOMe (0.75 g, 13.9 mmol) in anhydrous $CH_2Cl_2$ (200 mL) and stirring was continued for 12 h. After filtration and evaporation of the solvent the residue was purified by column chromatography ($SiO_2$, *n*-hexane/EtOAc 3:1) and **40** (NMR: *E* isomer only, 710 mg, 44%) was obtained as a colourless solid; m.p. 218 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.35 (dd, $J$ = 8.0, 0.8 Hz, 1 H), 7.26 (dd, $J$ = 8.0, 8.0 Hz, 1 H), 7.18 (m, 1 H), 7.12 (m, 1 H), 6.94 (m, 1 H), 6.92 (m, 1 H), 6.86 (d, $J$ = 7.5 Hz, 1 H), 6.84 (d, $J$ = 16.3 Hz, 1 H), 6.83 (d, $J$ = 8.30 Hz, 1 H), 6.82 (dd, $J$ = 8.0, 0.8 Hz, 1 H), 6.78 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 6.71 (dd, $J$ = 7.5, 1.4 Hz, 1 H), 6.64 (d, $J$ = 1.4 Hz, 1 H), 6.20 (d, $J$ = 2.0 Hz, 1 H), 6.12 (d, $J$ = 16.3 Hz, 1 H) 3.94 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 3.57 (s, 3 H, $OCH_3$), 3.20–3.11 (m, 4 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 157.50, 156.87, 152.73, 150.26, 148.40, 140.98, 137.20, 136.97, 131.66, 130.63, 130.46, 128.04, 126.75, 126.46, 125.79, 122.61, 122.26, 122.10, 121.94, 121.26, 116.17, 112.40, 111.44, 109.54, 109.48, 56.06 ($OCH_3$), 55.82 ($OCH_3$), 55.77 ($OCH_3$), 35.70 ($CH_2CH_2$), 34.81 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1945.

**Isoriccardin C Trimethyl Ether (41):** The stilbene **40** (630 mg, 1.36 mmol) was hydrogenated in a procedure analogous to that used for **31**. The trimethyl ether **41** (626 mg, 99%) was obtained as a colourless solid; m.p. 198 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.28 (dd, $J$ = 8.0, 7.8 Hz, 1 H), 7.13 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 7.03 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.97 (dd, $J$ = 7.8, 1.0 Hz, 1 H), 6.92 (dd, $J$ = 8.3, 2.4 Hz, 1 H), 6.87 (d, $J$ = 7.6 Hz, 1 H), 6.86 (dd, $J$ = 8.3, 2.4 Hz, 1 H), 6.81 (d, $J$ = 8.2 Hz, 1 H), 6.80 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 6.76 (dd, $J$ = 8.2, 2.0 Hz, 1 H), 6.66 (dd, $J$ = 7.6, 1.5 Hz, 1 H), 6.56 (d, $J$ = 1.5 Hz, 1 H), 5.73 (d, $J$ = 2.0 Hz, 1 H), 3.91 (s, 3 H, $OCH_3$), 3.66 (s, 3 H, $OCH_3$), 3.59 (s, 3 H, $OCH_3$), 3.16–3.05 (m, 6 H, $CH_2CH_2$), 2.64–2.49 (m, 2 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 157.39, 156.61, 153.57, 149.87, 147.02, 142.01, 140.79, 137.03, 134.82, 130.81, 130.53, 130.25, 128.14, 126.76, 123.14, 121.78, 121.59, 121.19, 121.16, 121.04, 115.21, 112.03, 111.38, 108.33, 56.08 ($OCH_3$), 55.83 ($OCH_3$), 55.46 ($OCH_3$), 37.67 ($CH_2CH_2$), 36.73 ($CH_2CH_2$), 36.11 ($CH_2CH_2$), 35.15 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2158.

**Isoriccardin C (9):** Isoriccardin C (**9**) was prepared from the trimethyl ether **41** (600 mg, 1.29 mmol) in a procedure analogous to that used for the synthesis of **8**. The crude product was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 2:1) and **9** was obtained as colourless crystals (472 mg, 86%); m.p. 208 °C. NMR spectroscopic data; see Tables 2 and 4. HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1677.

**2-Bromo-5-methoxybenzaldehyde (43):**[42] NBS (35.6 g, 0.20 mol) and a small amount of AIBN were added to a solution of 1-bromo-4-methoxy-2-methylbenzene (**42**,[43] 20.1 g, 0.10 mol) in $CCl_4$ (150 mL). The reaction mixture was heated to reflux for 6 h with additional irradiation (daylight, 300 W). The mixture was cooled to r.t. and the solid was filtered off and washed with $CCl_4$ (50 mL). The solvent was removed in vacuo and $CaCO_3$ (43.0 g, 0.43 mol) and $H_2O$ (200 mL) were added to the obtained benzyl dibromide. The suspension was heated to reflux for 16 h. The mixture was diluted with EtOAc (200 mL) and HCl (6 M) was added dropwise (cooling in an ice bath) until the solid was dissolved completely. After separation the aqueous layer was extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with saturated aqueous NaCl (3 × 100 mL), dried ($MgSO_4$) and concentrated. The crude material was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/*n*-hexane 1:1). The aldehyde **43** (15.5 g, 72%) was obtained as a colourless solid; m.p. 76 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 10.29 (s, 1 H, CHO), 7.50 (d, $J$ = 8.8 Hz, 1 H), 7.40 (d, $J$ = 3.3 Hz, 1 H), 7.02 (dd, $J$ = 8.8, 3.3 Hz, 1 H), 3.83 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 191.69 (CHO), 159.25, 134.54, 133.96, 123.04, 117.92, 112.71, 55.71 ($OCH_3$) ppm.

**2-(2-Bromo-5-methoxyphenyl)-1,3-dioxane (44):** The dioxane **44** was prepared from **43** (15.5 g, 72.1 mmol) in a procedure analogous to that used for the synthesis of **17** and was obtained as a yellow oil (18.3 g, 93%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.40 (d, $J$ = 8.8 Hz, 1 H), 7.25 (d, $J$ = 3.0 Hz, 1 H), 6.76 (dd, $J$ = 8.8, 3.0 Hz, 1 H), 5.71 (s, 1 H, OCHO), 4.26 (m, 2 H, $OCH_2$), 4.02 (m, 2 H, $OCH_2$), 3.80 (s, 3 H, $OCH_3$), 2.25 (m, 1 H), 1.45 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 159.14, 138.26, 133.22, 117.14, 112.72, 112.60 100.83 (OCHO), 67.57 ($OCH_2$), 55.53 ($OCH_3$), 25.68 ppm. HRMS: calcd. for $C_{11}H_{13}BrO_3$ 272.0048; found 272.0070.

**2-Formyl-4-methoxyphenylboronic Acid (45):**[44] A solution of *n*BuLi (2.5 M in *n*-hexane, 41.0 mL, 103 mmol) was added slowly at –78 °C to a solution of the bromoarene **44** (23.5 g, 86.0 mmol) in anhydrous THF (250 mL) and the mixture was stirred for an additional 60 min. Trimethyl borate (11.2 g, 108 mmol) was added in one portion at –78 °C and the mixture was allowed to warm to r.t. over 2 h. A solution of HCl (2 M, 100 mL) was added dropwise and the mixture was stirred for 30 min and then extracted with $Et_2O$ (1 × 150 mL, 2 × 75 mL). The combined organic layers were washed with saturated aqueous NaCl (100 mL) and extracted with NaOH (1 M, 3 × 50 mL). The aqueous phase was neutralized with concentrated HCl (cooling in an ice bath). The precipitated solid was collected by filtration, washed with $H_2O$ (2 × 40 mL) and dried under reduced pressure over $CaCl_2$. The boronic acid **45** (8.00 g, 52%) was obtained as a colourless powder; m.p. 151 °C. $^1$H NMR ([D$_6$]DMSO): $\delta$ = 10.23 (s, 1 H, CHO), 7.63 (d, $J$ = 8.1 Hz, 1 H), 7.39 (d, $J$ = 2.7 Hz, 1 H), 7.21 (dd, $J$ = 8.1, 2.7 Hz, 1 H), 3.83 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 194.21 (CHO), 159.98, 141.39, 135.57, 119.17, 112.39, 55.25 ($OCH_3$) ppm.

**5-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (46):** The boronic ester **46** was prepared from **45** (2.00 g, 11.1 mmol) in a procedure analogous to that used for the synthesis of **36** and was obtained as a colourless oil (2.32 g, 80%). $^1$H NMR ($CDCl_3$): $\delta$ = 10.68 (s, 1 H, CHO), 7.86 (d, $J$ = 8.3 Hz, 1 H), 7.51 (d, $J$ = 2.8 Hz, 1 H), 7.13 (dd, $J$ = 8.3, 2.8 Hz, 1 H), 3.88 (s, 3 H, $OCH_3$), 1.37 (s, 12 H, $CH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 194.76 (CHO), 161.96, 143.63, 137.96, 119.91, 110.32, 84.15 [$OC(CH_3)_2$], 55.37 ($OCH_3$), 24.86 ($CH_3$) ppm. HRMS: calcd. for $C_{14}H_{19}BO_4$ 262.1376; found 262.1383.

**2-(1,3-Dioxan-2-yl)-6-methoxyphenyl Trifluoromethanesulfonate (47):** The dioxane **47** was prepared from **21** (13.5 g, 47.5 mmol) in a procedure analogous to that used for the synthesis of **17** and was obtained as a yellow oil (16.0 g, 98%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.33 (dd, $J$ = 8.0, 7.0 Hz, 1 H), 7.31 (dd, $J$ = 8.0, 2.8 Hz, 1 H), 7.02 (dd, $J$ = 7.0, 2.8 Hz, 1 H), 5.72 (s, 1 H, OCHO), 4.25 (m, 2 H, $OCH_2$), 3.99 (m, 2 H, $OCH_2$), 3.88 (s, 3 H, $OCH_3$), 2.26 (m, 1 H), 1.45 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 150.95, 136.15, 133.02, 128.78, 119.16, 118.88 (q, $J_{C,F}$ = 320.6 Hz), 113.51, 96.85 (OCHO), 67.52 ($OCH_2$), 56.17 ($OCH_3$), 25.58 ppm. HRMS: calcd. for $C_{12}H_{13}F_3O_6S$ 342.0385; found 342.0351.

**2′-(1,3-Dioxan-2-yl)-4,6′-dimethoxybiphenyl-2-carbaldehyde (48):** The biaryl **48** was prepared from **46** (2.20 g, 8.39 mmol) and **47** (3.73 g, 9.91 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a colourless solid (1.85 g, 67%); m.p. 144 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 9.55 (s, 1 H, CHO), 7.54 (d, $J$ = 2.5 Hz, 1 H), 7.45 (dd, $J$ = 7.8, 7.5 Hz, 1 H), 7.41 (dd, $J$ = 7.8, 1.8 Hz, 1 H), 7.23 (d, $J$ = 8.5 Hz, 1 H), 7.19 (dd, $J$ = 8.5, 2.5 Hz, 1 H), 6.96 (dd, $J$ = 7.5, 1.8 Hz, 1 H), 4.97 (s, 1 H, OCHO), 4.13 (m, 1 H, $OCH_2$), 4.00 (m, 1 H, $OCH_2$), 3.92 (s, 3 H, $OCH_3$), 3.69 (s, 3 H, $OCH_3$), 3.65 (m, 1 H, $OCH_2$), 3.50 (m, 1 H, $OCH_2$), 2.12 (m, 1 H), 1.28 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.21 (CHO), 159.26, 156.78, 139.01, 135.65, 132.86, 132.05, 129.71, 124.85, 120.78, 118.41, 110.86, 109.09, 99.62 (OCHO), 67.20 ($OCH_2$), 67.10 ($OCH_2$), 55.77 ($OCH_3$), 55.51 ($OCH_3$), 25.49 ppm. HRMS: calcd. for $C_{19}H_{20}O_5$ 328.1311; found 328.1262.

**Stilbene 49:** The stilbene **49** was prepared from **48** (1.75 g, 5.33 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 3.04 g, 93%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{37}H_{38}O_8$ 610.2567; found 610.2536.

**Bibenzyl Dialdehyde 50:** The dialdehyde **50** was prepared from **49** (3.04 g, 4.83 mmol) in a procedure analogous to that used for the synthesis of **39** and was obtained as a colourless solid (2.30 g, 93%); m.p. 67 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 9.80 (s, 1 H, CHO), 9.61 (d, $J$ = 0.8 Hz, 1 H, CHO), 7.62 (dd, $J$ = 7.8, 1.0 Hz, 1 H), 7.62 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.47 (ddd, $J$ = 8.0, 7.8, 0.8 Hz, 1 H), 7.39 (d, $J$ = 2.0 Hz, 1 H), 7.21 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 7.08 (d, $J$ = 8.3 Hz, 1 H), 7.05 (d, $J$ = 8.0 Hz, 1 H), 6.86 (d, $J$ = 2.6 Hz, 1

H), 6.85 (d, $J$ = 8.8 Hz, 2 H), 6.83 (dd, $J$ = 8.0, 2.6 Hz, 1 H), 6.80 (d, $J$ = 8.8 Hz, 2 H), 3.93 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$), 2.73–2.57 (m, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 192.51 (CHO), 190.47 (CHO), 159.49, 157.36, 156.15, 154.77, 146.65, 142.17, 136.74, 135.77, 133.98, 132.22, 130.13, 129.58, 128.84, 127.75, 124.84, 119.14, 118.95, 118.12, 115.75, 114.84, 111.95, 111.20, 56.25 ($OCH_3$), 55.93 ($OCH_3$), 55.20 ($OCH_3$), 35.93 ($CH_2CH_2$), 35.90 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{28}O_6$ 496.1886; found 496.1870.

**Dehydroplagiochin F Trimethyl Ether (51):** The stilbene **51** was prepared from **50** (1.10 g, 2.22 mmol) in a procedure analogous to that used for the synthesis of **30** and was obtained as a colourless solid (NMR: *E*/*Z*, 1.3:1, 296 mg, 29%); m.p. 121 °C. Complex NMR spectroscopic data. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1960.

**Plagiochin F Trimethyl Ether (52):** The stilbene **51** (167 mg, 0.36 mmol) was hydrogenated in a procedure analogous to that used for **31**. The trimethyl ether **52** (166 mg, 99%) was obtained as a colourless powder; m.p. 120 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.22 (d, $J$ = 2.5 Hz, 1 H), 7.16 (dd, $J$ = 8.0, 8.0 Hz, 1 H), 7.03 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.98 (d, $J$ = 8.3 Hz, 1 H), 6.96 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.80 (dd, $J$ = 8.3, 2.3 Hz, 1 H), 6.78 (d, $J$ = 8.0 Hz, 1 H), 6.77 [dd (not resolved), 1 H], 6.74–6.69 (m, 4 H), 5.26 (d, $J$ = 2.0 Hz, 1 H), 3.91 (s, 3 H, $OCH_3$), 3.88 (s, 3 H, $OCH_3$), 3.70 (s, 3 H, $OCH_3$), 3.21–3.14 (m, 1 H, $CH_2CH_2$), 3.11–2.78 (m, 5 H, $CH_2CH_2$), 2.41–2.34 (m, 1 H, $CH_2CH_2$), 2.01–1.93 (m, 1 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 158.36, 156.92, 155.05, 151.45, 146.17, 140.96, 140.54, 139.86, 133.45, 131.84, 130.35, 129.80, 128.86, 128.37, 127.85, 123.98, 122.67, 120.66, 118.94, 115.60, 114.34, 111.57, 110.13, 108.02, 56.18 ($OCH_3$), 55.47 ($OCH_3$), 55.15 ($OCH_3$), 35.25 ($CH_2CH_2$), 33.78 ($CH_2CH_2$), 31.61 ($CH_2CH_2$), 30.27 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2147.

**Plagiochin F (10):** The free phenolic groups were liberated from **52** (150 mg, 0.32 mmol) in a procedure analogous to that used for the synthesis of **8**. Plagiochin F (**10**, 90 mg, 66%) was obtained as colourless crystals; m.p. 252 °C. NMR spectroscopic data; see ref.[15] HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1690.

**2′,6-Dimethoxy-4′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-2-carbaldehyde (54):** The biaryl **54** was prepared from **21** (6.00 g, 21.1 mmol) and **53**[36] (5.30 g, 19.9 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a yellow oil (4.86 g, 69%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.68 (s, 1 H, CHO), 7.62 (dd, $J$ = 7.8, 1.3 Hz, 1 H), 7.44 (dd, $J$ = 8.1, 7.8 Hz, 1 H), 7.20 (dd, $J$ = 8.1, 1.3 Hz, 1 H), 7.19 (d, $J$ = 7.5 Hz, 1 H), 7.04 (dd, $J$ = 7.5, 2.8 Hz, 1 H), 7.02 (d, $J$ = 2.8 Hz, 1 H), 4.86 (d, $J$ = 12.1 Hz, 1 H, Ar–$OCH_2$), 4.79 (m, 1 H, OCHO) 4.57 (d, $J$ = 12.1 Hz, 1 H, Ar–$OCH_2$), 3.99–3.93 (m, 1 H, $OCH_2$), 3.77 (s, 3 H, $OCH_3$), 3.73 (s, 3 H, $OCH_3$), 3.61–3.56 (m, 1 H, $OCH_2$), 1.94–1.56 (m, 6 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 192.84 (CHO), 157.36, 157.26, 157.22, 140.31, 135.40, 132.40, 131.09, 128.68, 121.09, 121.06, 119.65, 119.60, 118.72, 116.24, 110.17, 110.12, 98.01 (OCHO), 68.82 (Ar–$OCH_2$), 62.30 ($OCH_2$), 62.27 ($OCH_2$), 56.12 ($OCH_3$), 55.56 ($OCH_3$), 30.64, 25.50, 19.46, 19.45 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1614.

**Stilbene 55:** The stilbene **55** was prepared from **54** (4.76 g, 13.4 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 8.01 g, 94%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2890.

**Bibenzyl 56:** The bibenzyl **56**, as a benzyl alcohol, was prepared from **55** (8.90 g, 13.9 mmol) in a procedure analogous to that used for the synthesis of **29** and was obtained as a colourless resin (6.65 g, 96%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.77 (s, 1 H, CHO), 7.60 (dd, $J$ = 8.4, 2.0 Hz, 1 H), 7.35 (d, $J$ = 2.0 Hz, 1 H), 7.26 (dd, $J$ = 8.0, 8.0 Hz, 1 H), 7.07 (d, $J$ = 8.4 Hz, 1 H), 7.05 (d, $J$ = 7.5 Hz, 1 H), 7.04 (d, $J$ = 1.5 Hz, 1 H), 6.99 (dd, $J$ = 7.5, 1.5 Hz, 1 H), 6.88 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 6.87 (d, $J$ = 8.7 Hz, 2 H), 6.83 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 6.81 (d, $J$ = 8.7 Hz, 2 H), 4.73 (br. s, 2 H, $CH_2OH$), 3.92 (s, 3 H, $OCH_3$), 3.74 (s, 3 H, $OCH_3$), 3.69 (s, 3 H, $OCH_3$), 2.72–2.53 (m, 4 H, $CH_2CH_2$), 2.14 (br. s, 1 H, $CH_2OH$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 190.49 (CHO), 157.39, 157.37, 156.07, 154.47, 146.99, 141.76, 141.69, 137.60, 131.64, 130.12, 129.68, 128.23, 127.75, 126.99, 125.43, 121.48, 118.80, 118.62, 118.25, 111.92, 109.59, 108.75, 65.39 ($CH_2OH$), 56.24 ($OCH_3$), 55.87 ($OCH_3$), 55.58 ($OCH_3$), 36.34 ($CH_2CH_2$), 35.79 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2029.

**Dehydroriccardin D Trimethyl Ether (57):** The stilbene **57** was prepared from **56** (2.50 g, 5.03 mmol) in a procedure analogous to that used for the synthesis of **40**. The crude material was purified by column chromatography ($SiO_2$, $CH_2Cl_2$) and compound **57** (NMR: *E*/*Z* 1.1:1, 1.60 g, 68%) was obtained as a colourless solid; m.p. 101 °C. Complex NMR spectroscopic data. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1992.

**Riccardin D Trimethyl Ether (58):** The stilbene **57** (1.30 g, 2.80 mmol) was hydrogenated in a procedure analogous to that used for the synthesis of **31**. The riccardin D trimethyl ether (**58**, 1.24 g, 95%) was obtained as a colourless solid; m.p. 79 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.33 (dd, $J$ = 8.0, 7.8 Hz, 1 H), 7.06 (dd, $J$ = 7.8, 1.0 Hz, 1 H), 6.91–6.84 (br. m, 2 H), 6.88 (d, $J$ = 8.0 Hz, 1 H), 6.85 (d, $J$ = 7.5 Hz, 1 H), 6.81 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 6.80–6.72 (br. m, 2 H), 6.78 (dd, $J$ = 8.0, 2.0 Hz, 1 H), 6.40 (dd, $J$ = 7.5, 1.5 Hz, 1 H), 6.38 (d, $J$ = 1.5 Hz, 1 H), 5.48 (d, $J$ = 2.0 Hz, 1 H), 3.94 (s, 3 H, $OCH_3$), 3.66 (s, 3 H, $OCH_3$), 3.64 (s, 3 H, $OCH_3$), 2.97–2.62 (m, 8 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 157.34, 156.71, 152.91, 149.09, 146.89, 143.72, 141.56, 140.26, 134.28, 132.65, 129.39, 129.26, 128.40, 127.14, 122.67, 122.46, 122.30, 122.18, 121.42, 120.81, 116.63, 111.88, 111.79, 108.24, 56.12 ($OCH_3$), 55.80 ($OCH_3$), 55.31 ($OCH_3$), 38.10 ($CH_2CH_2$), 37.67 ($CH_2CH_2$), 36.91 ($CH_2CH_2$), 34.84 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2138.

**Riccardin D (11):** Riccardin D (**11**) was prepared from the trimethyl ether **58** (600 mg, 1.29 mmol) in a procedure analogous to that used for the synthesis of **8** and was obtained as a colourless solid (388 mg, 71%); m.p. 173 °C. NMR spectroscopic data; see ref.[15] HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1659.

**4-Formyl-2-methoxyphenyl Trifluoromethanesulfonate (Vanillin Triflate, 59):**[45] The triflate **59** was prepared from vanillin (6.85 g, 45.0 mmol) in a procedure analogous to that used for the synthesis of **21** and was obtained as a pale yellow oil (11.7 g, 91%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.99 (s, 1 H, CHO), 7.57 (d, $J$ = 1.8 Hz, 1 H), 7.52 (dd, $J$ = 8.1, 1.8 Hz, 1 H), 7.42 (d, $J$ = 8.1 Hz, 1 H), 4.00 (s, 3 H, $OCH_3$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 190.39 (CHO), 152.30, 142.79, 136.85, 124.13, 123.26, 118.74 (q, $J_{C,F}$ = 320.6 Hz, $CF_3$), 111.85, 56.55 ($OCH_3$) ppm.

**2,2′-Dimethoxy-4′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-4-carbaldehyde (60):** The biaryl **60** was prepared from **53** (4.75 g, 17.9 mmol) and **59** (5.83 g, 20.5 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a colourless oil (5.02 g, 79%). $^1H$ NMR ($CDCl_3$): $\delta$ = 10.01 (s, 1 H, CHO), 7.51 (dd, $J$ = 7.7, 1.3 Hz, 1 H), 7.49 (d, $J$ = 1.5 Hz, 1 H), 7.41 (d, $J$ = 7.7 Hz, 1 H), 7.21 (d, $J$ = 8.0 Hz, 1 H), 7.04 (dd, $J$ = 8.0, 1.5 Hz, 1 H), 7.02 (d, $J$ = 1.5 Hz, 1 H), 4.84 (d, $J$ = 12.0 Hz, 1 H, Ar–

$OCH_2$), 4.77 (t, $J$ = 3.6 Hz, 1 H, OCHO), 4.55 (d, $J$ = 12.0 Hz, 1 H, Ar–$CH_2$), 4.00–3.92 (m, 1 H, $OCH_2$), 3.84 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$), 3.62–3.55 (m, 1 H, $OCH_2$), 1.79–1.50 (m, 6 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 191.98 (CHO), 156.90, 155.77, 139.91, 136.87, 134.69, 132.09, 130.97, 125.74, 123.98, 119.77, 110.62, 109.38, 97.96 (OCHO), 68.85 (Ar–$OCH_2$), 62.28 ($OCH_2$), 55.84 ($OCH_3$), 55.72 ($OCH_3$), 30.63, 25.50, 19.45 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1638.

**Stilbene 61:** The stilbene **61** was prepared from **60** (4.70 g, 13.2 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 6.10 g, 79%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2867.

**Bibenzyl 62:** The bibenzyl **62**, as a benzyl alcohol, was prepared from **61** (4.00 g, 6.79 mmol) in a procedure analogous to that used for the synthesis of **28** and was obtained as a colourless resin (2.96 g, 87%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.81 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.41 (d, $J$ = 2.0 Hz, 1 H), 7.23 (d, $J$ = 7.5 Hz, 1 H), 7.20 (d, $J$ = 8.7 Hz, 2 H), 7.16 (d, $J$ = 7.6 Hz, 1 H), 7.10 (d, $J$ = 8.3, 2.0 Hz, 1 H), 7.02 (d, $J$ = 1.4 Hz, 1 H), 6.98 (dd, $J$ = 7.5, 1.4 Hz, 1 H), 6.94 (d, $J$ = 8.7 Hz, 2 H), 6.86 (dd, $J$ = 7.6, 1.5 Hz, 1 H), 6.79 (d, $J$ = 1.5 Hz, 1 H), 4.73 (d, $J$ = 5.8 Hz, 2 H, $CH_2OH$), 3.97 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$), 3.75 (s, 3 H, $OCH_3$), 2.97 (s, 4 H, $CH_2CH_2$), 1.74 (t, $J$ = 5.8 Hz, 1 H, $CH_2OH$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 190.42 (CHO), 157.33, 156.94, 156.11, 154.73, 147.02, 142.47, 141.46, 137.32, 131.68, 131.68, 130.32, 129.83, 127.74, 127.18, 125.13, 120.35, 118.77, 118.72, 118.46, 111.96, 111.51, 109.78, 65.54 ($CH_2OH$), 56.30 ($OCH_3$), 55.77 ($OCH_3$), 55.71 ($OCH_3$), 38.14 ($CH_2CH_2$), 37.05 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2027.

**Bibenzyl Dialdehyde 63:** The dialdehyde **63** was prepared from **62** (1.85 g, 3.71 mmol) in a procedure analogous to that used for the synthesis of **29** and was obtained as a colourless resin (1.76 g, 96%). $^1H$ NMR ($CDCl_3$): $\delta$ = 10.00 (s, 1 H, CHO), 9.81 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.5, 2.0 Hz, 1 H), 7.50 (dd, $J$ = 7.5, 1.5 Hz, 1 H), 7.48 (d, $J$ = 1.5 Hz, 1 H), 7.43 (d, $J$ = 7.5 Hz, 1 H), 7.41 (d, $J$ = 2.0 Hz, 1 H), 7.20 (d, $J$ = 8.5 Hz, 2 H), 7.17 (d, $J$ = 7.6 Hz, 1 H), 7.11 (d, $J$ = 8.5 Hz, 1 H), 6.94 (d, $J$ = 8.5 Hz, 2 H), 6.88 (dd, $J$ = 7.6, 1.5 Hz, 1 H), 6.80 (d, $J$ = 1.5 Hz, 1 H), 3.97 (s, 3 H, $OCH_3$), 3.85 (s, 3 H, $OCH_3$), 3.75 (s, 3 H, $OCH_3$), 2.98 (s, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 192.01 (CHO), 190.40 (CHO), 157.77, 156.74, 156.10, 154.75, 147.03, 143.34, 137.15, 136.77, 134.83, 132.16, 130.94, 130.22, 129.84, 127.87, 124.20, 123.98, 120.46, 118.56, 118.51, 111.95, 111.57, 109.40, 56.30 ($OCH_3$), 55.86 ($OCH_3$), 55.70 ($OCH_3$), 38.14 ($CH_2CH_2$), 36.99 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{28}O_6$ 496.1886; found 496.1869.

**Polymorphatin A Trimethyl Ether (65):** A solution of **62** (4.00 g, 8.03 mmol) and $PPh_3$·HBr (3.02 g, 8.80 mmol) in MeCN (130 mL) was heated at reflux for 12 h. The solvent was removed in vacuo and the crude phosphonium salt was dissolved in anhydrous $CH_2Cl_2$ (400 mL). This solution was added dropwise over 6 h to a mixture of NaOMe (0.75 g, 13.9 mmol) in anhydrous $CH_2Cl_2$ (300 mL) and stirring was continued for 24 h. After filtration and evaporation of the solvent the residue (460 mg, 12%) was dissolved in $CH_2Cl_2$ (150 mL) and EtOAc (100 mL) and after addition of Pd/C (5%, 200 mg) the mixture was hydrogenated in a Parr apparatus at 3 bar $H_2$ for 24 h. The catalyst was filtered off and the solution was concentrated in vacuo. The residue was purified by flash chromatography ($SiO_2$, *n*-hexane/$CH_2Cl_2$/EtOAc 12:6:1) and **65** (440 mg, 12%) was obtained as a colourless solid; m.p. 213 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.11 (dd, $J$ = 8.4, 2.0 Hz, 1 H), 7.07 (d, $J$ = 7.7 Hz, 1 H), 7.04 (d, $J$ = 7.5 Hz, 1 H), 7.02 (d, $J$ = 8.5 Hz, 2 H), 7.01 (d, $J$ = 8.4 Hz, 1 H), 6.84 (dd, $J$ = 7.7, 1.5 Hz, 1 H), 6.80 (d, $J$ = 1.5 Hz, 1 H), 6.61 (d, $J$ = 8.5 Hz, 2 H), 6.55 (dd, $J$ = 7.5, 1.5 Hz, 1 H), 6.52 (d, $J$ = 1.5 Hz, 1 H), 6.48 (d, $J$ = 2.0 Hz, 1 H), 3.82 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 3.62 (s, 3 H, $OCH_3$), 2.98–2.81 (m, 8 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 157.00, 156.43, 156.43, 149.79, 143.47, 142.52, 141.23, 135.31, 134.39, 131.67, 131.22, 129.27, 125.43, 125.20, 124.78, 123.78, 120.94, 119.97, 115.95, 113.36, 111.79, 111.26, 56.29 ($OCH_3$), 55.60 ($OCH_3$), 55.46 ($OCH_3$), 38.41 ($CH_2CH_2$), 38.24 ($CH_2CH_2$), 36.90 ($CH_2CH_2$), 36.53 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2111.

**Polymorphatin A (12):** Polymorphatin A (**12**) was prepared from the trimethyl ether **65** (420 mg, 0.90 mmol) in a procedure analogous to that used for the synthesis of **8** and was obtained as a colourless solid (340 mg, 89%); m.p. >300 °C. NMR spectroscopic data; see Tables 2 and 4. HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1683.

**2′,4-Dimethoxy-4′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-2-carbaldehyde (67):** The biaryl **67** was prepared from **45** (2.70 g, 15.0 mmol) and **66**[38] (6.80 g, 19.5 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a colourless oil (4.67 g, 91%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.74 (s, 1 H, CHO), 7.49 (d, $J$ = 2.8 Hz, 1 H), 7.27 (d, $J$ = 8.5 Hz, 1 H), 7.23 (d, $J$ = 7.5 Hz, 1 H), 7.19 (dd, $J$ = 8.5, 2.8 Hz, 1 H), 7.07 (dd, $J$ = 7.5, 1.3 Hz, 1 H), 7.00 (d, $J$ = 1.3 Hz, 1 H), 4.85 (d, $J$ = 12.1 Hz, 1 H, Ar–$OCH_2$), 4.76 (t, $J$ = 3.5 Hz, 1 H, OCHO), 4.56 (d, $J$ = 12.1 Hz, 1 H, Ar–$OCH_2$), 3.98–3.93 (m, 1 H, $OCH_2$), 3.89 (s, 3 H, $OCH_3$), 3.75 (s, 3 H, $OCH_3$), 3.61–3.56 (m, 1 H, $OCH_2$), 1.93–1.55 (m, 6 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 192.46 (CHO), 159.16, 156.70, 140.34, 134.91, 134.49, 132.51, 131.53, 125.75, 121.20, 120.24, 110.05, 109.43, 98.05 (OCHO), 68.73 (Ar–$OCH_2$), 62.33 ($OCH_2$), 55.54 ($OCH_3$), 55.43 ($OCH_3$), 30.63, 25.48, 19.47 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1674.

**Stilbene 68:** The stilbene **68** was prepared from **67** (1.90 g, 5.33 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 3.24 g, 95%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2845.

**Bibenzyl 69:** The bibenzylic benzyl alcohol **69** was prepared from **68** (3.20 g, 5.01 mmol) in a procedure analogous to that used for the synthesis of **28** and was obtained as a colourless resin (2.35 g, 94%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.78 (s, 1 H, CHO), 7.61 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.36 (d, $J$ = 2.0 Hz, 1 H), 7.08 (d, $J$ = 8.2 Hz, 1 H), 7.07 (d, $J$ = 8.3 Hz, 1 H), 7.07 (d, $J$ = 7.5 Hz, 1 H), 7.0 (d, $J$ = 1.5 Hz, 1 H), 6.97 (dd, $J$ = 7.5, 1.5 Hz, 1 H), 6.90 (d, $J$ = 8.5 Hz, 2 H), 6.82 (d, $J$ = 8.5 Hz, 2 H), 6.81 (d, $J$ = 2.8 Hz, 1 H), 6.79 (dd, $J$ = 8.2, 2.8 Hz, 1 H), 4.73 (br. s, 2 H, $CH_2OH$), 3.93 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 3.76 (s, 3 H, $OCH_3$), 2.80–2.63 (m, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 190.48 (CHO), 158.87, 157.06, 156.11, 154.54, 146.96, 141.63, 137.48, 131.63, 131.37, 130.57, 130.14, 129.67, 129.56, 127.78, 118.78, 118.68, 118.25, 114.48, 111.95, 111.11, 109.28, 65.31 ($CH_2OH$), 56.26 ($OCH_3$), 55.48 ($OCH_3$), 55.17 ($OCH_3$), 36.28 ($CH_2CH_2$), 35.79 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2028.

**Dehydroriccardin C Trimethyl Ether (70):** The stilbene **70** was prepared from **69** (2.12 g, 4.25 mmol) in a procedure analogous to that used for the synthesis of **40** and was obtained as a colourless powder (NMR: *E*/*Z* 1:1, 750 mg, 38%); m.p. 108 °C. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1956.

**Riccardin C Trimethyl Ether (71):** The stilbene **70** (500 mg, 1.07 mmol) was hydrogenated in a procedure analogous to that used for the synthesis of **31** and was obtained as a colourless solid (487 mg, 97%); m.p. 84 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.06 (d, $J$ = 8.5 Hz, 1 H), 6.96 (d, $J$ = 2.8 Hz, 1 H), 6.90–6.85 (br. m, 1 H), 6.89 (d, $J$ = 8.3 Hz, 1 H), 6.82 (d, $J$ = 7.6 Hz, 1 H), 6.81 (dd, $J$ = 8.5, 2.8 Hz, 1 H), 6.79–6.70 (br. m, 2 H), 6.78 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 6.75–6.67 (br. m, 1 H), 6.44 (d, $J$ = 1.5 Hz, 1 H), 6.24 (dd, $J$ = 7.6, 1.5 Hz, 1 H), 5.37 (d, $J$ = 2.0 Hz, 1 H), 3.94 (s, 3 H, $OCH_3$), 3.88 (s, 3 H, $OCH_3$), 3.67 (s, 3 H, $OCH_3$), 3.14–2.58 (m, 8 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 159.12, 155.98, 152.73, 148.65, 146.90, 143.26, 141.22, 139.71, 133.78, 132.44, 132.41, 130.92, 129.53, 129.20, 127.58, 122.31, 121.70, 121.40, 116.66, 115.38, 111.79, 111.43, 111.14, 56.11 ($OCH_3$), 55.23 ($OCH_3$), 55.20 ($OCH_3$), 38.24 ($CH_2CH_2$), 38.09 ($CH_2CH_2$), 37.25 ($CH_2CH_2$), 35.59 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2117.

**Riccardin C (6):** Riccardin C (**6**) was prepared from its trimethyl ether **71** (225 mg, 0.48 mmol) in a procedure analogous to that used for the synthesis of **8** and was obtained as a colourless solid (174 mg, 85%); m.p. 164 °C. NMR spectroscopic data; see Tables 3 and 4. HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1693.

**2-[2-(1,3-Dioxan-2-yl)-4-methoxyphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (72):** A solution of *n*BuLi (2.5 M in *n*-hexane, 16.2 mL, 40.4 mmol) was added slowly at –78 °C to a solution of the bromide **44** (8.50 g, 31.1 mmol) in anhydrous THF (80 mL) and the mixture was stirred for an additional 60 min. Trimethyl borate (7.41 g, 71.3 mmol) was added in one portion at –78 °C and the mixture was allowed to warm to r.t. over 2 h. A solution of saturated aqueous $KH_2PO_4$ (100 mL) was added dropwise and the mixture was extracted with $CH_2Cl_2$ (1 × 80 mL, 2 × 40 mL). Pinacol (7.35 g, 62.2 mmol) and $MgSO_4$ (37.6 g, 0.31 mol) were added to the combined organic layers and the mixture was stirred for 12 h. The solid was filtered off and washed with $CH_2Cl_2$ (50 mL), and the filtrate was concentrated under reduced pressure. The crude material was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 4:1). The boronic ester **72** (6.94 g, 70%) was obtained as colourless crystals; m.p. 62 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.69 (d, $J$ = 8.3 Hz, 1 H), 7.27 (d, $J$ = 2.8 Hz, 1 H), 6.83 (dd, $J$ = 8.3, 2.8 Hz, 1 H), 6.07 (s, 1 H, OCHO), 4.23 (m, 2 H, $OCH_2$), 4.02 (s, 2 H, $OCH_2$), 3.83 (s, 3 H, $OCH_3$), 2.22 (m, 1 H), 1.41 (m, 1 H), 1.34 (s, 12 H, $CH_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 161.85, 146.21, 137.09, 114.10, 110.00, 100.18 (OCHO), 83.33 [$OC(CH_3)_2$], 67.42 ($OCH_2$), 55.18 ($OCH_3$), 25.93, 24.92 ($CH_3$) ppm. HRMS: calcd. for $C_{17}H_{25}BO_5$ 320.1795; found 320.1722.

**2′-(1,3-Dioxan-2-yl)-4′,6-dimethoxybiphenyl-2-carbaldehyde (73):** The biaryl **73** was prepared from **21** (4.62 g, 16.3 mmol) and **72** (4.00 g, 12.5 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a colourless solid (3.75 g, 91%); m.p. 102 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 9.54 (d, $J$ = 0.8 Hz, 1 H, CHO), 7.62 (dd, $J$ = 7.8, 1.3 Hz, 1 H), 7.46 (ddd, $J$ = 8.1, 7.8, 0.8 Hz, 1 H), 7.33 (d, $J$ = 2.8 Hz, 1 H), 7.17 (dd, $J$ = 8.1, 1.3 Hz, 1 H), 7.08 (d, $J$ = 8.4 Hz, 1 H), 6.95 (dd, $J$ = 8.4, 2.8 Hz, 1 H), 4.98 (s, 1 H, OCHO), 4.18–4.13 (m, 1 H, $OCH_2$), 3.93–3.88 (m, 1 H, $OCH_2$), 3.88 (s, 3 H, $OCH_3$), 3.75 (s, 3 H, $OCH_3$), 3.71–3.64 (m, 1 H, $OCH_2$), 3.42–3.36 (m, 1 H, $OCH_2$), 2.13–2.01 (m, 1 H), 1.26–1.22 (m, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.41 (CHO), 159.72, 157.34, 138.91, 136.19, 132.63, 131.87, 128.82, 124.10, 118.41, 115.50, 115.05, 110.50, 99.86 (OCHO), 67.26 ($OCH_2$), 66.95 ($OCH_2$), 56.08 ($OCH_3$), 55.38 ($OCH_3$), 25.45 ppm. HRMS: calcd. for $C_{19}H_{20}O_5$ 328.1311; found 328.1298.

**Stilbene 74:** The stilbene **71** was prepared from **73** (2.50 g, 7.61 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 4.05 g, 87%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{37}H_{38}O_8$ 610.2567; found 610.2532.

**Bibenzyl Dialdehyde 75:** The dialdehyde **75** was prepared from **74** (3.90 g, 6.39 mmol) in a procedure analogous to that used for the synthesis of **28** and was obtained as a colourless solid (2.83 g, 89%); m.p. 71 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 9.80 (s, 1 H, CHO), 9.58 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.4, 2.0 Hz, 1 H), 7.53 (d, $J$ = 2.8 Hz, 1 H), 7.39 (d, $J$ = 2.0 Hz, 1 H), 7.34 (dd, $J$ = 8.0, 8.0 Hz, 1 H), 7.22 (dd, 8.5, 2.8 Hz, 1 H), 7.10 (d, $J$ = 8.5 Hz, 1 H), 7.08 (d, $J$ = 8.4 Hz, 1 H), 6.97 (dd, $J$ = 8.0, 0.8 Hz, 1 H), 6.85 (d, $J$ = 8.8 Hz, 2 H), 6.82 (dd, $J$ = 8.0, 0.8 Hz, 1 H), 6.81 (d, $J$ = 8.8 Hz, 2 H), 3.94 (s, 3 H, $OCH_3$), 3.90 (s, 3 H, $OCH_3$), 3.67 (s, 3 H, $OCH_3$), 2.77–2.56 (m, 4 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.42 (CHO), 190.43 (CHO), 159.06, 157.26, 156.13, 154.78, 146.69, 141.90, 136.59, 135.24, 133.72, 132.65, 130.15, 129.63, 129.17, 127.72, 125.60, 121.84, 121.51, 119.11, 118.14, 111.94, 109.40, 108.13, 56.25 ($OCH_3$), 55.62 ($OCH_3$), 55.52 ($OCH_3$), 36.38 ($CH_2CH_2$), 35.44 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{28}O_6$ 496.1886; found 496.1839.

**Dehydroplagiochin E Trimethyl Ether (76):** The stilbene **76** was prepared from **75** (720 mg, 1.45 mmol) in a procedure analogous to that used for the synthesis of **30** and was obtained as a colourless powder (NMR: *E*/*Z* 3.5:1, 235 mg, 35%); m.p. 197 °C. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1971.

**Plagiochin E Trimethyl Ether (77):** The stilbene **76** (105 mg, 0.23 mmol) was hydrogenated in a procedure analogous to that used for the synthesis of **31** and was obtained as a colourless solid (103 mg, 98%); m.p. 213 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.35–7.30 (m, 2 H), 7.02–6.98 (m, 2 H), 6.88 (dd, $J$ = 9.0, 1.9 Hz, 1 H), 6.86 (d, $J$ = 8.3 Hz, 1 H), 6.74 (d, $J$ = 8.0 Hz, 1 H), 6.73–6.68 (m, 4 H), 6.67 (dd, $J$ = 9.0, 2.0 Hz, 1 H), 5.23 (d, $J$ = 1.8 Hz, 1 H), 3.90 (s, 3 H, $OCH_3$), 3.76 (s, 3 H, $OCH_3$), 3.61 (s, 3 H, $OCH_3$), 3.30–3.23 (m, 1 H, $CH_2CH_2$), 3.06–2.76 (m, 5 H, $CH_2CH_2$), 2.55–2.48 (m, 1 H, $CH_2CH_2$), 1.96–1.88 (m, 1 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 158.68, 157.37, 155.48, 151.66, 146.28, 142.67, 139.82, 139.27, 134.13, 131.73, 130.52, 130.03, 129.76, 128.44, 127.43, 124.28, 122.65, 120.84, 120.50, 116.43, 112.65, 111.38, 108.91, 107.92, 56.17, 55.31, 54.99, 35.44, 33.31, 31.06, 30.62 ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2141.

**Plagiochin E (13):** Plagiochin E (**13**) was prepared from the trimethyl ether **77** (150 mg, 0.32 mmol) in a procedure analogous to that used for the synthesis of **8** and was obtained as a colourless solid (93 mg, 68%); m.p. 181 °C. NMR spectroscopic data; see ref.[15] HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1687.

**(2-Bromo-5-methoxyphenyl)methanol (78):**[46] NBS (17.8 g, 0.10 mol) and a small amount of AIBN were added to a solution of the bromoarene **42**[43] (20.3 g, 0.10 mol) in $CCl_4$ (150 mL). The reaction mixture was heated to reflux for 6 h with additional irradiation (daylight, 300 W). The mixture was cooled to r.t. and the solid was filtered off and washed with $CCl_4$ (50 mL). The solvent was removed in vacuo and $CaCO_3$ (43.0 g, 0.43 mol) and $H_2O$ (200 mL) were added to the obtained benzyl bromide. The suspension was heated to reflux for 16 h. The mixture was diluted with EtOAc (200 mL) and HCl (6 M) was added dropwise (cooling in an ice bath) until the solid was dissolved completely. After separation the aqueous layer was extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with saturated aqueous NaCl (3 × 100 mL), dried ($MgSO_4$) and concentrated. The crude material was purified by column chromatography ($SiO_2$, $CH_2Cl_2$). The benzyl alcohol **78** was obtained as a colourless crystalline solid (13.1 g, 60%); m.p. 41 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.42 (d, $J$ =

8.7 Hz, 1 H), 7.06 (d, $J$ = 3.0 Hz, 1 H), 6.71 (dd, $J$ = 8.7, 3.0 Hz, 1 H), 4.69 (s, 2 H, $CH_2OH$), 3.80 (s, 3 H, $OCH_3$), 2.20 (br. s, 1 H, $CH_2OH$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 159.24, 140.76, 133.11, 114.74, 114.18, 112.47, 64.92 ($CH_2OH$), 55.50 ($OCH_3$) ppm. HRMS: calcd. for $C_8H_9BrO_2$ 215.9786; found 215.9814.

**2-(2-Bromo-5-methoxybenzyloxy)tetrahydro-2*H*-pyran (79):** The THP ether **79** was prepared from the benzyl alcohol **78** (4.50 g, 20.7 mmol) in a procedure analogous to that used for the synthesis of **23** and was obtained as a colourless oil (5.80 g, 93%). $^1H$ NMR ($CDCl_3$): $\delta$ = 7.41 (d, $J$ = 8.8 Hz, 1 H), 7.10 (d, $J$ = 3.2 Hz, 1 H), 6.70 (dd, $J$ = 8.8, 3.2 Hz, 1 H), 4.78 (d, $J$ = 13.6 Hz, 1 H, Ar–$OCH_2$), 4.77 (t, $J$ = 3.5 Hz, 1 H, OCHO), 4.54 (d, $J$ = 13.6 Hz, 1 H, Ar–$OCH_2$), 3.93 (m, 1 H, $OCH_2$), 3.80 (s, 3 H, $OCH_3$), 3.58 (m, 1 H, $OCH_2$), 1.93–1.53 (m, 6 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 159.07, 138.92, 133.00, 114.66, 114.24, 112.81, 98.44 (OCHO), 68.47 (Ar–$OCH_2$), 62.22 ($OCH_2$), 55.47 ($OCH_3$), 30.55, 25.46, 19.37 ppm. HRMS: calcd. for $C_{13}H_{17}BrO_3$ 300.0361; found 300.0351.

**2-{4-Methoxy-2-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80):** A solution of *n*BuLi (2.5 M in *n*-hexane, 8.10 mL, 20.3 mmol) was added slowly at –78 °C to a solution of the bromoarene **79** (4.70 g, 15.6 mmol) in anhydrous THF (80 mL) and the mixture was stirred for an additional 60 min. Trimethyl borate (3.25 g, 31.3 mmol) was added in one portion at –78 °C and the mixture was allowed to warm to r.t. over 2 h. A solution of saturated aqueous $KH_2PO_4$ (100 mL) was added dropwise and the mixture was extracted with $CH_2Cl_2$ (1 × 80 mL, 2 × 40 mL). Pinacol (3.79 g, 31.2 mmol) and $MgSO_4$ (37.6 g, 0.31 mol) were added to the combined organic layers and the mixture was stirred for 12 h. The solid was filtered off and washed with $CH_2Cl_2$ (50 mL), and the filtrate was concentrated under reduced pressure. The crude material was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 4:1 → 3:1). The boronic ester **80** (4.08 g, 75%) was obtained as a colourless oil. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.76 (d, $J$ = 8.3 Hz, 1 H), 7.09 (d, $J$ = 2.5 Hz, 1 H), 6.79 (dd, $J$ = 8.3, 2.5 Hz, 1 H), 4.94 (d, $J$ = 12.8 Hz, 1 H, Ar–$OCH_3$), 4.85 (d, $J$ = 12.8 Hz, 1 H, Ar–$OCH_2$), 4.77 (m, 1 H, OCHO), 3.95 (m, 1 H, $OCH_2$), 3.83 (s, 3 H, $OCH_3$), 3.54 (m, 1 H, $OCH_2$), 1.91–1.51 (m, 6 H), 1.32 (s, 12 H, $CH_3$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 161.99, 147.30, 137.85, 113.43, 111.68, 98.32 (OCHO), 83.31 [$OC(CH_3)_2$], 68.48 (Ar–$OCH_2$), 62.08 ($OCH_2$), 55.09 ($OCH_3$), 30.73, 25.59, 24.90 ($CH_3$), 24.85 ($CH_3$), 19.51 ppm. HRMS: calcd. for $C_{19}H_{29}BO_5$ 348.2108; found 348.2148.

**2,4′-Dimethoxy-2′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-4-carbaldehyde (81):** The biaryl **81** was prepared from **59** (3.10 g, 10.9 mmol) and **80** (2.93 g, 8.41 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a yellow oil (2.23 g, 74%). $^1H$ NMR ($CDCl_3$): $\delta$ = 10.01 (s, 1 H, CHO), 7.49 (dd, $J$ = 7.5, 1.5 Hz, 1 H), 7.45 (d, $J$ = 1.5 Hz, 1 H), 7.35 (d, $J$ = 7.5 Hz, 1 H), 7.15 (d, $J$ = 2.8 Hz, 1 H), 7.12 (d, $J$ = 8.4 Hz, 1 H), 6.89 (dd, $J$ = 8.4, 2.8 Hz, 1 H), 4.73–4.49 (br. m, 1 H, Ar–$OCH_2$), 4.65–4.39 (br. m, 1 H, OCHO), 4.35–4.14 (br. m, 1 H, Ar–$OCH_2$), 3.86 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 3.80–3.59 (br. m, 1 H, $OCH_2$), 3.45–3.31 (br. m,1 H, $OCH_2$), 1.83–1.41 (m, 6 H) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 191.90 (CHO), 159.48, 157.52, 138.32, 136.98, 136.59, 132.02, 130.94, 128.79, 124.10, 113.54, 112.68, 108.99, 98.15 (OCHO), 66.99 (Ar–$OCH_2$), 61.88 ($OCH_2$), 55.71 ($OCH_3$), 55.29 ($OCH_3$), 30.51, 25.42, 19.22 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1578.

**Stilbene 82:** The stilbene **82** was prepared from **81** (2.10 g, 2.67 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 3.57 g, 95%). HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2878.

**Bibenzyl 83:** The bibenzyl **83**, as a benzyl alcohol, was prepared from **82** (3.80 g, 5.95 mmol) in a procedure analogous to that used for the synthesis of **28** and was obtained as a colourless resin (2.63 g, 88%). $^1H$ NMR ($CDCl_3$): $\delta$ = 9.81 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.41 (d, $J$ = 2.0 Hz, 1 H), 7.18 (d, $J$ = 8.8 Hz, 2 H), 7.12 (d, $J$ = 8.5 Hz, 1 H), 7.11 (d, $J$ = 2.8 Hz, 1 H), 7.10 (d, $J$ = 8.3 Hz, 1 H), 7.06 (d, $J$ = 7.8 Hz, 1 H), 6.94 (d, $J$ = 8.8 Hz, 2 H), 6.89 (dd, $J$ = 8.5, 2.8 Hz, 1 H), 6.86 (dd, $J$ = 7.8, 1.5 Hz, 1 H), 6.75 (d, $J$ = 1.5 Hz, 1 H), 4.40 (br. s, 2 H, $CH_2OH$), 3.97 (s, 3 H, $OCH_3$), 3.86 (s, 3 H, $OCH_3$), 3.72 (s, 3 H, $OCH_3$), 2.97 (s, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 190.42 (CHO), 159.26, 156.46, 156.10, 154.77, 147.02, 142.70, 140.78, 137.05, 131.48, 131.43, 130.21, 129.86, 129.68, 127.90, 127.21, 121.05, 118.56, 118.49, 113.44, 113.35, 111.96, 111.49, 63.87 ($CH_2OH$), 56.30 ($OCH_3$), 55.76 ($OCH_3$), 55.31 ($OCH_3$), 38.02 ($CH_2CH_2$), 37.08 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2057.

**Dehydroisoriccardin D Trimethyl Ether (84):** The stilbene **84** was prepared from **83** (2.00 g, 4.01 mmol) in a procedure analogous to that used for the synthesis of **40** and was obtained as a colourless solid (NMR: *E* isomer only, 750 mg, 40%); m.p. 186 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.22 (d, $J$ = 2.6 Hz, 1 H), 7.21 (dd, $J$ = 8.0, 2.4 Hz, 1 H), 7.16 (d, $J$ = 8.4 Hz, 1 H), 7.01 (dd, $J$ = 8.0, 2.4 Hz, 1 H), 6.99 (dd, $J$ = 8.0, 2.4 Hz, 1 H), 6.91 (d, $J$ = 7.8 Hz, 1 H), 6.90 (dd, $J$ = 8.0, 2.4 Hz, 1 H), 6.86–6.90 (m, 4 H), 6.70 (dd, $J$ = 7.8, 1.4 Hz, 1 H), 6.52 (d, $J$ = 1.4 Hz, 1 H), 6.32 (d, $J$ = 1.8 Hz, 1 H), 6.21 (d, $J$ = 16.3 Hz, 1 H), 3.95 (s, 3 H, $OCH_3$), 3.86 (s, 3 H, $OCH_3$), 3.55 (s, 3 H, $OCH_3$), 3.23–3.03 (m, 4 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 158.83, 156.44, 152.79, 150.07, 148.44, 141.08, 137.04, 136.42, 131.33, 131.18, 130.79, 130.74, 130.68, 130.29, 126.49, 126.43, 125.68, 122.19, 122.04, 121.78, 120.90, 113.08, 112.19, 111.52, 109.54, 108.50, 56.05 ($OCH_3$), 55.44 ($OCH_3$), 55.25 ($OCH_3$), 35.88 ($CH_2CH_2$), 35.43 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1992.

**Isoriccardin D Trimethyl Ether (85):** The stilbene **84** (470 mg, 1.01 mmol) was hydrogenated in a procedure analogous to that used for the synthesis of **31** and was obtained as a colourless solid (448 mg, 95%); m.p. 149 °C. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.16 (dd, $J$ = 8.2, 2.3 Hz, 1 H), 7.03 (d, $J$ = 8.5 Hz, 1 H), 6.97 (dd, $J$ = 8.2, 2.3 Hz, 1 H), 6.92 (d, $J$ = 7.6 Hz, 1 H), 6.89 (dd, $J$ = 8.2, 2.3 Hz, 1 H), 6.87 (d, $J$ = 2.6 Hz, 1 H), 6.81 (d, $J$ = 8.3 Hz, 1 H), 6.80 (dd, $J$ = 8.2, 2.3 Hz, 1 H), 6.77 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 6.76 (dd, $J$ = 8.5, 2.6 Hz, 1 H), 6.66 (dd, $J$ = 7.6, 1.4 Hz, 1 H), 6.41 (d, $J$ = 1.4 Hz, 1 H), 5.85 (d, $J$ = 2.0 Hz, 1 H), 3.91 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 3.56 (s, 3 H, $OCH_3$), 3.16 (m, 2 H, $CH_2CH_2$), 3.02 (m, 2 H, $CH_2CH_2$), 2.71 (m, 1 H, $CH_2CH_2$), 2.57 (m, 1 H, $CH_2CH_2$), 2.32 (m, 2 H, $CH_2CH_2$) ppm. $^{13}C$ NMR ($CDCl_3$): $\delta$ = 158.86, 156.27, 153.77, 149.75, 147.23, 141.77, 140.86, 136.78, 134.91, 131.31, 130.83, 130.67, 130.47, 130.16, 127.43, 121.61, 121.41, 121.22, 120.84, 115.37, 114.20, 111.83, 111.62, 111.06, 56.14 ($OCH_3$), 55.22 ($OCH_3$), 55.17 ($OCH_3$), 37.29 ($CH_2CH_2$), 36.66 ($CH_2CH_2$), 36.43 ($CH_2CH_2$), 35.46 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2159.

**Isoriccardin D (14):** Isoriccardin D (**14**) was prepared from its trimethyl ether **85** (480 mg, 1.03 mmol) in a procedure analogous to that used for the synthesis of **8** and was obtained as a colourless solid (332 mg, 76%); m.p. 285 °C. NMR spectroscopic data; see Tables 3 and 4. HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1684.

**4,4′-Dimethoxy-2′-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]biphenyl-2,6-dicarbaldehyde (86):** The biaryl **86** was prepared from **45** (2.32 g, 12.9 mmol) and **79** (5.03 g, 16.7 mmol) in a procedure analogous to that used for the synthesis of **26** and was obtained as a yellow oil (3.53 g, 77%). $^1$H NMR ($CDCl_3$): $\delta$ = 9.70 + 9.69 (s, 1 H, CHO), 7.49 + 7.48 (d, $J$ = 2.8 Hz, 1 H), 7.24 + 7.22 (d, $J$ = 8.3 Hz, 1 H), 7.16 + 7.16 (dd, $J$ = 8.3, 2.8 Hz, 1 H), 7.13–7.10 (m, 2 H), 6.99 (m, 1 H), 4.53 + 4.38 (t, $J$ = 3.4 Hz, 1 H, OCHO), 4.52 + 4.48 + 4.17 + 4.09 (d, $J$ = 11.8 Hz, 2 H, Ar–$OCH_2$), 3.90 + 3.90 (s, 3 H, $OCH_3$), 3.87 (s, 3 H, $OCH_3$), 3.71 + 3.53 + 3.44–3.34 (m, 2 H, $OCH_2$), 1.80–1.41 (m, 6 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.24 (CHO), 192.15 (CHO), 159.57, 159.22, 138.33, 138.31, 137.28, 137.17, 135.50, 135.39, 132.42, 132.08, 131.97, 129.39, 129.29, 121.16, 121.05, 114.58, 114.51, 112.72, 109.35, 98.44 (OCHO), 98.00 (OCHO), 67.47 (Ar–$OCH_2$), 67.21 (Ar–$OCH_2$), 61.95 ($OCH_2$), 61.63 ($OCH_2$), 55.60 ($OCH_3$), 55.38 ($OCH_3$), 30.33, 30.19, 25.38, 25.34, 19.17, 18.98 ppm. HRMS: calcd. for $C_{21}H_{24}O_5$ 356.1624; found 356.1589.

**Stilbene 87:** The stilbene **87** was prepared from **86** (2.90 g, 8.14 mmol) and **20** in a procedure analogous to that used for the synthesis of **27** and was obtained as a colourless resin (*E*/*Z* mixture, 5.03 g, 97%). Complex NMR spectroscopic data. HRMS: calcd. for $C_{39}H_{42}O_8$ 638.2880; found 638.2848.

**Bibenzyl 88:** The bibenzyl **88** as benzyl alcohol was prepared from **87** (5.50 g, 8.61 mmol) in a procedure analogous to that used for the synthesis of **28** and was obtained as a colourless resin (4.16 g, 97%). $^1$H NMR ($CDCl_3$): $\delta$ = 9.79 (s, 1 H, CHO), 7.62 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.37 (d, $J$ = 2.0 Hz, 1 H), 7.11 (d, $J$ = 2.5 Hz, 1 H), 7.08 (d, $J$ = 8.3 Hz, 1 H), 7.03 (d, $J$ = 8.3 Hz, 1 H), 7.00 (d, $J$ = 8.3 Hz, 1 H), 6.90–6.80 (m, 6 H), 6.77 (dd, $J$ = 8.3, 2.5 Hz, 1 H), 4.38 (d, $J$ = 13.1 Hz, 1 H, $CH_2OH$), 4.30 (d, $J$ = 13.1 Hz, 1 H, $CH_2OH$), 3.94 (s, 3 H, $OCH_3$), 3.86 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 2.72–2.56 (m, 4 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 190.45 (CHO), 159.09, 158.94, 156.15, 154.73, 146.81, 141.21, 140.49, 136.96, 131.98, 131.71, 131.39, 131.14, 130.17, 129.74, 127.78, 118.95, 118.17, 114.71, 112.68, 112.46, 111.99, 111.20, 63.12 ($CH_2OH$), 56.26 ($OCH_3$), 55.34 ($OCH_3$), 55.24 ($OCH_3$), 36.49 ($CH_2CH_2$), 35.63 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{30}O_6$ 498.2042; found 498.2070.

**Bibenzyl Dialdehyde 89:** The dialdehyde **89** was prepared from **88** (1.13 g, 2.27 mmol) in a procedure analogous to that used for the synthesis of **29**. The crude product was purified by flash chromatography ($SiO_2$, *n*-hexane/EtOAc 2:1) and **89** was obtained as a colourless resin (0.82 g, 73%). $^1$H NMR ($CDCl_3$): $\delta$ = 9.68 (s, 1 H, CHO), 7.63 (dd, $J$ = 8.3, 2.0 Hz, 1 H), 7.49 (d, $J$ = 2.5 Hz, 1 H), 7.39 (d, $J$ = 2.0 Hz, 1 H), 7.17 (dd, $J$ = 8.5, 2.5 Hz, 1 H), 7.14 (d, $J$ = 8.5 Hz, 1 H), 7.09 (d, $J$ = 8.3 Hz, 1 H), 7.07 (d, $J$ = 8.3 Hz, 1 H), 6.85 (d, $J$ = 2.5 Hz, 1 H), 6.84 (d, $J$ = 8.8 Hz, 2 H), 6.81 (dd, $J$ = 8.3, 2.5 Hz, 1 H), 6.80 (d, $J$ = 8.8 Hz, 2 H), 3.93 (s, 3 H, $OCH_3$), 3.90 (s, 3 H, $OCH_3$), 3.84 (s, 3 H, $OCH_3$), 2.78–2.64 (m, 4 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 192.23 (CHO), 190.37 (CHO), 159.49, 159.05, 156.21, 154.92, 146.64, 141.57, 137.98, 136.39, 135.18, 132.68, 132.15, 130.20, 129.64, 129.24, 127.74, 121.32, 119.28, 118.08, 114.86, 112.02, 111.22, 109.42, 56.25 ($OCH_3$), 55.58 ($OCH_3$), 55.31 ($OCH_3$), 36.33 ($CH_2CH_2$), 35.58 ($CH_2CH_2$) ppm. HRMS: calcd. for $C_{31}H_{28}O_6$ 496.1886; found 496.1848.

**Dehydroplagiochin G Trimethyl Ether (90):** The stilbene **90** was prepared from **89** (1.00 g, 2.01 mmol) in a procedure analogous to that used for the synthesis of **30** and was obtained as a colourless solid (NMR: *E*/*Z* 2.5:1, 365 mg, 39%); m.p. 92 °C. HRMS: calcd. for $C_{31}H_{28}O_4$ 464.1988; found 464.1976.

**Plagiochin G Trimethyl Ether (91):** The stilbene **90** (345 mg, 1.01 mmol) was hydrogenated in a procedure analogous to that used for the synthesis of **31** and was obtained as a colourless solid (347 mg, 99%); m.p. 70 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.20 (d, $J$ = 2.5 Hz, 1 H), 7.03 (d, $J$ = 8.5 Hz, 1 H), 6.95–6.91 (m, 3 H), 6.78–6.66 (m, 7 H), 5.29 [d (not resolved), 1 H], 3.90 (s, 3 H, $OCH_3$), 3.87 (s, 3 H, $OCH_3$), 3.73 (s, 3 H, $OCH_3$), 3.14–2.83 (m, 7 H, $CH_2CH_2$), 2.24–2.16 (m, 1 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 158.36, 158.17, 154.94, 151.33, 146.25, 140.29, 139.57, 139.22, 133.23, 132.78, 132.34, 132.09, 131.67, 130.18, 129.78, 123.91, 122.49, 120.76, 115.49, 115.03, 113.35, 111.63, 110.10, 108.98, 56.16, 55.22, 55.07, 34.96, 34.74, 31.53, 30.21 ppm. HRMS: calcd. for $C_{31}H_{30}O_4$ 466.2144; found 466.2165.

**Plagiochin G (15):** Plagiochin G (**15**) was prepared from its trimethyl ether **91** (330 mg, 0.71 mmol) in a procedure analogous to that used for the synthesis of **8** and was obtained as a colourless solid (255 mg, 85%); m.p. 222 °C. NMR spectroscopic data; see Tables 3 and 4. HRMS: calcd. for $C_{28}H_{24}O_4$ 424.1675; found 424.1691.

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