Bryophyte Constituents, 9[◇]

Syntheses of Cyclic Bisbibenzyl Systems

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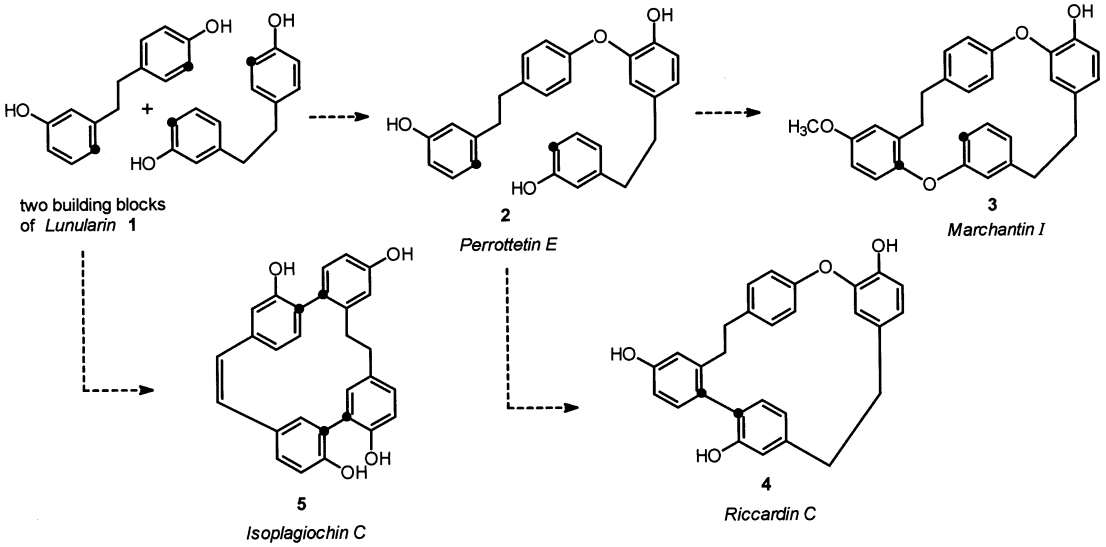
The cyclic bisbibenzyl systems *Marchantin I* (**3**), *Riccardin C* (**4**) and *Isoplagiochin C* (**5**) representing unique types of bryophyte constituents were prepared by a flexible, efficient and general synthetic approach involving the construction of biphenyl and bibenzyl units using Suzuki and Wittig protocols.

Introduction

Bisbibenzyl systems (*Perrottetins, Marchantins, Riccardins, Plagiochins*) are structurally simple phenolic natual products, which are found exclusively in bryophytes and exhibit remarkable biological activities[1][2][3]. They are constructed from two units of *Lunularin* (**1**), which can be combined by several modes (Scheme 1). O−C attachment leads to acyclic (*Perrottetins*, e.g. **2**) or cyclic systems (*Marchantins*, e.g. **3**) containing diphenyl ether units, O−C and C−Cattachment leads to macrocycles of the *Riccardin* (e.g. **4**) or *Plagiochin* type[4] containing diphenyl ether and biphenyl units; if only C−C attachment occurs systems of the *Isoplagiochin* type (e.g. **5**) containing two biphenyl units arise[5]. The syntheses of bisbibenzyls are reviewed in ref.[3]; except for the synthesis of *Perrottetins*[6], they in toto exhibit serious preparative disadvantages (e.g. ref.[7][8]).

We report on flexible, efficient and general synthetic approaches to the different types of cyclic bisbibenzyls, which are exemplified for syntheses of *Marchantin I* (**3**), *Riccardin C* (**4**) and *Isoplagiochin* C (**5**) providing the natural products on preparative scale[9]. In a convergent strategy, suitably substituted diphenyl ether or biphenyl building blocks are prepared, possessing free or acetal-protected aldehyde functions as well as ester or methyl groups transformable to a benzylphosphonium moiety. Formation of the bibenzyl bridges and cyclization is achieved by inter- and intramolecular Wittig reaction and subsequent hydrogenation, finally the phenolic protective groups have to be removed.

Scheme 1. Variants of bisbibenzylic bryophyte constituents



[◇] Part 8: T. Eicher, M. Wobido, A. Speicher, *J. Prakt. Chem.* **1996**, *338*, 706−710.

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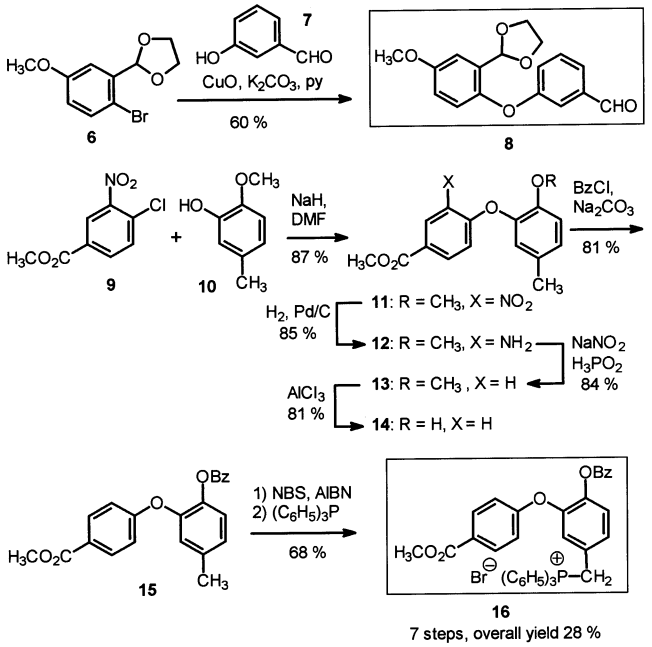
Results and Discussion

The synthesis of *Marchantin I* (**3**) starts with the Ullmann coupling of the protected 2-bromo-5-methoxybenzaldehyde **6**[10][11] with 3-hydroxybenzaldehyde (**7**) resulting in the formation of the diphenyl ether **8** (Scheme 2). As second diphenyl ether building block the phosphonium salt **16** is synthesized in a conventional sequence starting with S_{NAr} displacement at methyl 4-chloro-3-nitrobenzoate (**9**) by 2-methoxy-5-methylphenol (**10**) to give the diphenyl ether **11**, followed by catalytic reduction of the nitro group to the amine **12** and its reductive deamination by diazotation in H_3PO_2 to give **13**. Finally, exchange of the phenolic protective group by methoxy cleavage with $AlCl_3$ to give the phenol **14** and benzoylation to give **15**, followed by NBS bromination of **15** and reaction with triphenylphosphane afforded **16** in 7 steps and 28% overall yield.

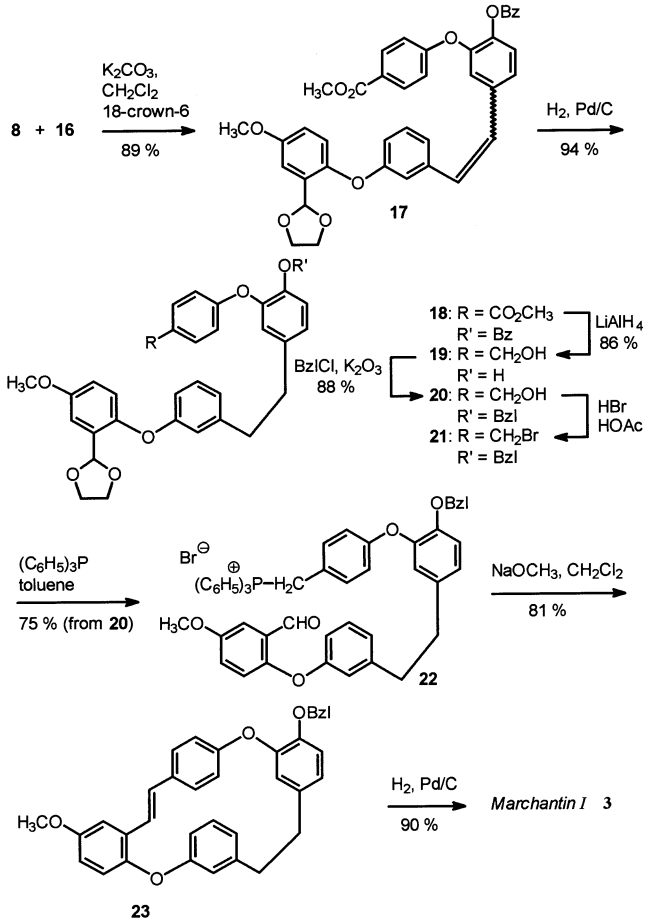
Scheme 2. Synthesis of the building block **16**



The building units **8** and **16** are combined by Wittig reaction in the presence of K_2CO_3/18-crown-6[12] and the stilbene **17** obtained as (*E*/*Z*) mixture is hydrogenated catalytically (Pd/C) to give the bibenzyl **18** (Scheme 3). Reaction of **18** with $LiAlH_4$ results in reduction of the carboxylic ester as well as removal of the benzoyl group and yields the benzyl alcohol **19**, in which the free phenolic OH group is protected by benzylation (→ **20**). When **20** is treated with HBr/acetic acid the dioxolane is cleaved and the benzyl bromide **21** is formed; triphenylphosphane gives rise to the benzyl phosphonium salt **22** bearing a free aldehyde function, the key intermediate of the synthesis. Cyclization of **22** by means of an intramolecular Wittig reaction is achieved with $NaOCH_3$ leading to the (*E*)-stilbene **23**, which by catalytic hydrogenation and concomitant hydrogenolytic debenzylation yields the natural product **3**.

Thus, *Marchantin I* (**3**) is obtained by convergence in 8 steps and 35% yield, from **10** in 15 steps and an overall yield of 10%[7].

Scheme 3. Synthesis of *Marchantin I* (**3**; Bzl = $C_6H_5-CH_2$)

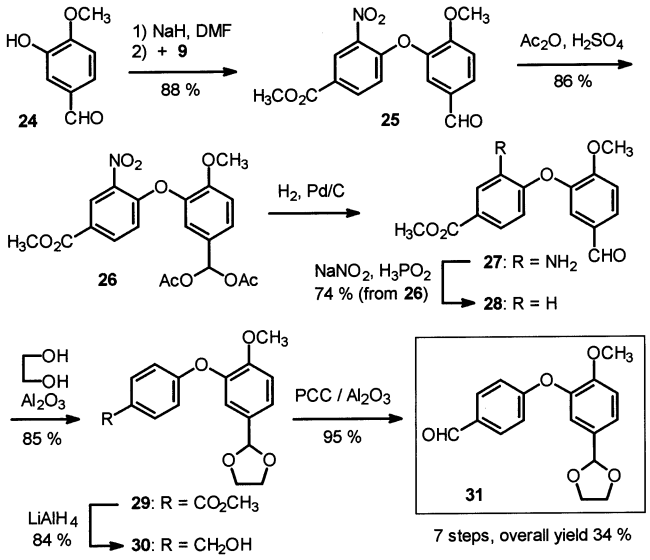


For the synthesis of *Riccardin C* (**4**) the diphenyl ether building block **31** and the biphenyl building block **37** are required. The diphenyl ether aldehyde **31** is obtained by S_{NAr} reaction of **9** with isovanilline (**24**) in a sequence **25** → **31** (Scheme 4) similar to the foregoing synthesis of **13** and additional transformation of the ester group into a free aldehyde function.

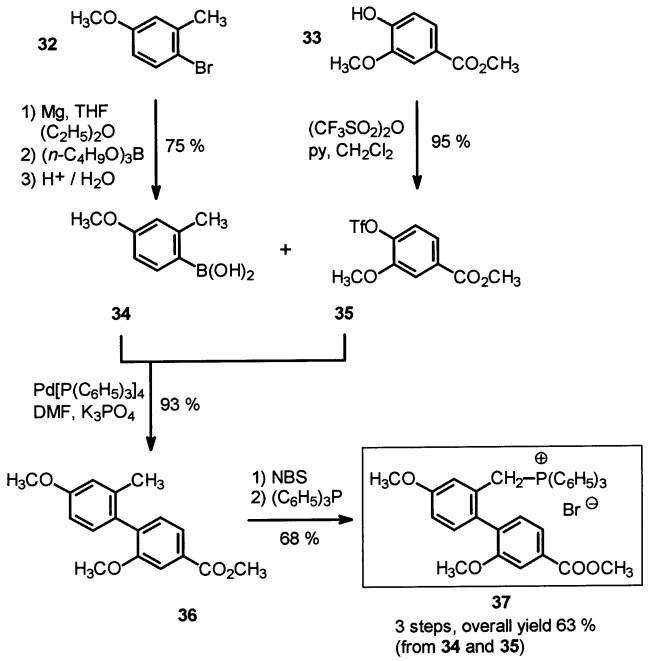
The biphenyl phosphonium salt **37** bearing an ester function is obtained by Suzuki reaction[13][14][15] of the triflate **35** derived from methyl 4-hydroxy-3-methoxybenzoate (**33**) with the boronic acid **34** derived from 4-bromo-3-methylanisol (**32**) catalyzed by Pd^0 to give **36**, NBS bromination of **36** and reaction with triphenylphosphane (Scheme 5).

Again, for convergence the building units **31** and **37** are subjected to a Wittig reaction in the presence of K_2CO_3/18-crown-6 and the resulting stilbene **38** obtained as (*E*/*Z*) mixture is hydrogenated to the bibenzyl **39** (Scheme 6). Reduction of the carboxylic ester function with $LiAlH_4$ gives rise to the benzyl alcohol **40**, treatment of **40** with HBr, followed by triphenylphosphane, transforms to the benzylphosphonium functionality and generates the free aldehyde group by acid cleavage of the dioxolane moiety. The bifunctional phosphonium salt **41** is readily cyclized in an intra-

Scheme 4. Synthesis of the building block **31**



Scheme 5. Synthesis of the building block **37** (Tf = $-SO_2CF_3$)

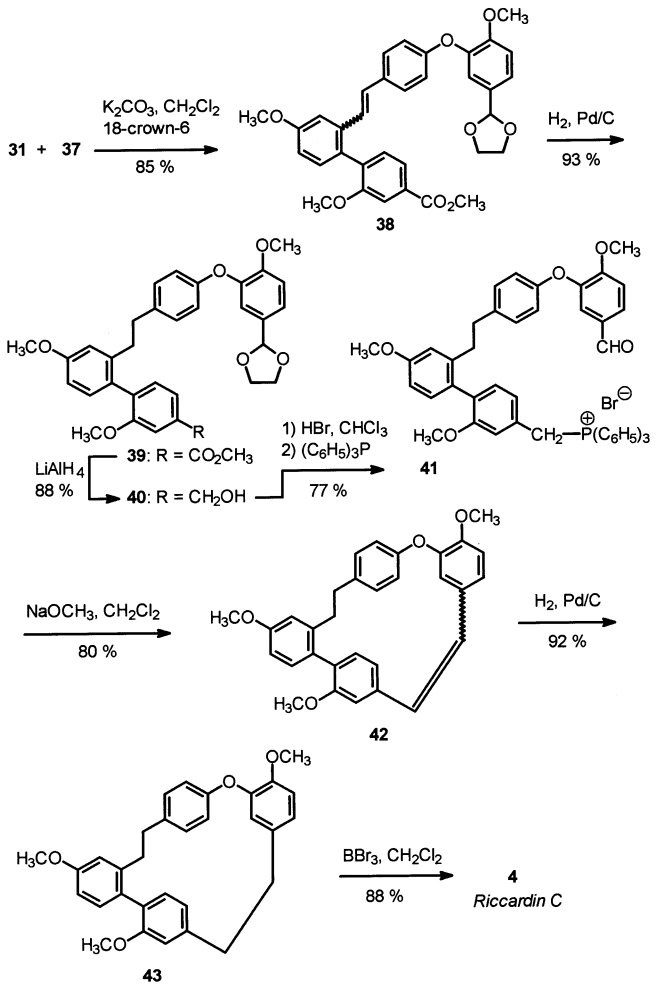


molecular carbonyl olefination reaction using $NaOCH_3$ to give the (*E*/*Z*)-stilbene **42**, which is hydrogenated to the trimethyl ether **43** of *Riccardin C*. Demethylation by means of BBr_3 yielded the natural product **4**.

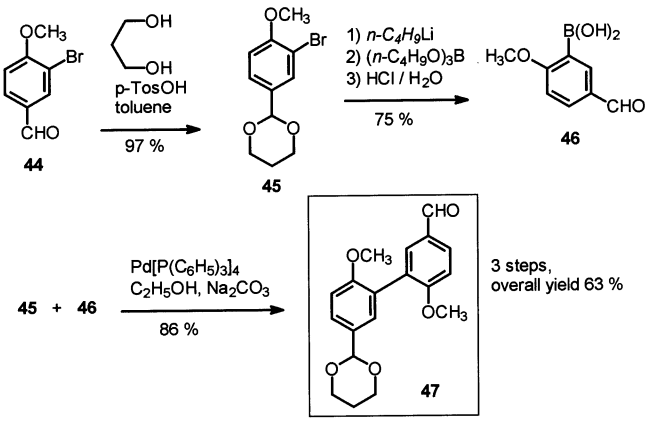
Thus, *Riccardin C* (**4**) is obtained by convergence in 8 steps and 35% yield, from **24** in 12 steps and an overall yield of 12%[8].

For the synthesis of *Isoplagiochin C* (**5**) a further biphenyl building block **47** was prepared by Suzuki reaction between the 1,3-dioxane **45** of 3-bromo-4-methoxybenzaldehyde **44** and the aldehyde-functionalized boronic acid **46** obtained from **45** (Scheme 7).

Scheme 6. Synthesis of *Riccardin C* (**4**)

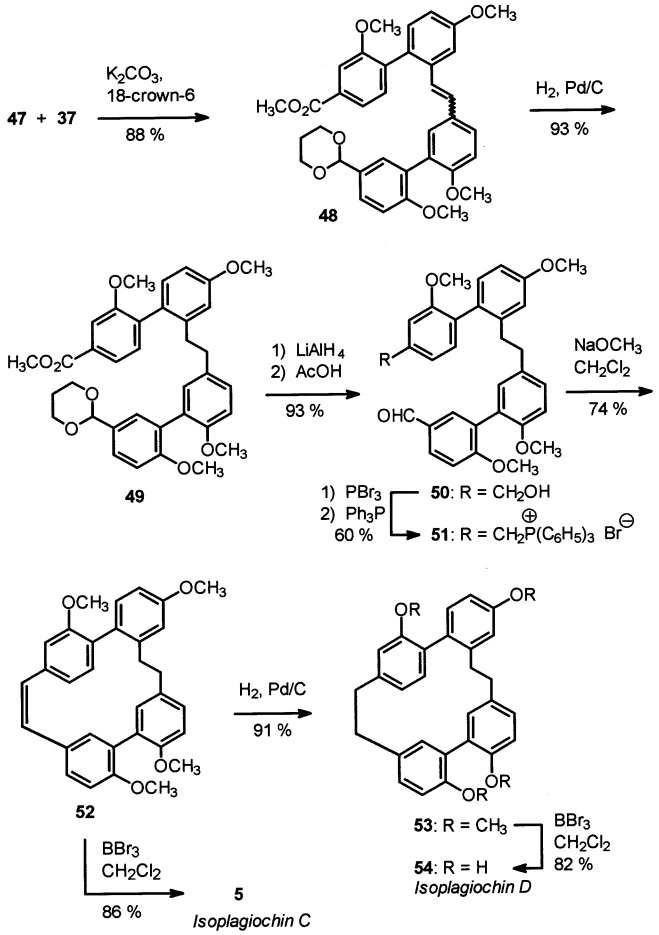


Scheme 7. Synthesis of the building block **47**



As in the syntheses before, the two building units **47** and **37** are linked by Wittig reaction (K_2CO_3/18-crown-6) yielding the stilbene **48** as (*E*/*Z*) mixture, followed by catalytic hydrogenation to the bisbibenzyl **49** (Scheme 8). The carboxylic ester group is reduced to the primary alcohol ($LiAlH_4$) with additional acidic cleavage of the 1,3-dioxane protective function (→ **50**) and transformed (PBr_3/triphenylphosphane) to the benzyl phosphonium moiety in

Scheme 8. Synthesis of *Isoplagiochin C* (**5**) and *Isoplagiochin D* **54**



51. Finally, the bifunctional aldehyde phosphonium salt **51** is cyclized by intramolecular Wittig reaction ($NaOCH_3$). The tetramethyl ether **52** of *Isoplagiochin C*, bearing exclusively *cis*-stilbene geometry, can be demethylated by means of BBr_3 to give the natural product **5** or hydrogenated (→ **53**), followed by demethylation to give the saturated system **54**, which also is found as a constituent of bryophytes called *Isoplagiochin D*[16].

The above sequence makes possible for the first time the synthesis of cyclic bisbibenzyls of the *isoplagiochin* type. *Isoplagiochin C* (**5**) is obtained from convergence in 8 steps and 29% yield, *Isoplagiochin D* (**54**) in 9 steps and 25% yield; the total yields from **44** over 11 (12) steps are 18% and 16%, respectively.

Experimental Section

General: IR: Beckmann Acculab 8. − UV: Varian DMS 80. − ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz): Bruker AM 400 (TMS as internal standard). − MS: Finnigan MAT 90 (CI 120 eV) or Varian MAT 311 (EI 70 eV). − Microanalyses: Leco CHNS-932. − Thin layer chromatography (TLC): Merck aluminium roll 0.2 mm (silica gel 60 F_{254} or alumina 60 F_{254} neutral type E). − Column chromatography (CC): Silica gel (J. T. Baker 63−200 μm); alumina (Fluka type 5016 A basic, activity I). − Flash chromatography: RP-18 (Macherey-Nagel Polygoprep 60−50 C18). − Catalytic hydrogenation: Parr Hydrogenation Apparatus. − Solvents were commonly dried and purified by conventional methods prior to use. All air- or moisture-sensitive reactions were carried out by inert gas techniques under nitrogen.

General Procedure 1 (GP 1) for the Catalytic Hydrogenation of Nitroarenes, Stilbenes and Benzyl Ethers

The nitroarene/stilbene/benzyl ether was dissolved in ethyl acetate or methanol (100−300 ml), palladium on activated carbon (5−10% Pd) was added (50 mg/mmol) and the hydrogenation performed at 3−5 bar hydrogen pressure. The catalyst was filtered off and the solvent removed in vacuo.

General Procedure 2 (GP 2) for the Preparation of Phosphonium Salts from Methylarenes, Benzyl Alcohols or Benzoic Esters

GP 2.1 for the Bromination of Methylarenes Using N-Bromosuccinimide: The methylarene in CCl_4 (5 ml/mmol) was heated to reflux for 2 h in presence of 1 equiv. NBS and a trace of AIBN. The mixture was cooled, the succinimide was filtered off and the solvent evaporated in vacuo.

GP 2.2 for the Reduction of Esters (e.g. Benzoic Esters to Benzyl Alcohols): To a suspension of an excess of $LiAlH_4$ in diethyl ether (10 ml/mmol) was added dropwise the ester to be reduced in diethyl ether (10 ml/mmol). The mixture was refluxed for 5 h and carefully hydrolysed with satd. NH_4Cl. The aqueous layer was extracted several times with diethyl ether and the combined organic layers dried ($MgSO_4$) and concentrated.

GP 2.3 for the Preparation of Phosphonium Salts from Benzyl Halides: The benzyl halide was dissolved in toluene or acetonitrile (5 ml/mmol) together with 1 equiv. of triphenylphosphane and heated to 100°C for 15 h. Usually, the phosphonium salt was filtered off, washed with petroleum ether and dried.

General Procedure 3 (GP 3) for the Wittig Reactions

GP 3.1 for Intermolecular Reaction Using K_2CO_3/18-Crown-6 in Dichloromethane: The aldehyde and the phosphonium salt (1.05 equiv.) were dissolved in CH_2Cl_2 (10 ml/mmol), anhydrous K_2CO_3 (1.05 equiv.) and a small amount of 18-crown-6 were added and the mixture refluxed for 24 h. The insoluble material was filtered off and the filtrate concentrated in vacuo. The crude material was purified by CC (normally SiO_2; CH_2Cl_2).

GP 3.2 for Intramolecular Reaction Using $NaOCH_3$ in Dichloromethane: To sodium methoxide (2 equiv.) in CH_2Cl_2 (50 ml/mmol) the phosphonium salt in CH_2Cl_2 (150 ml/mmol) was added dropwise (5 h/mmol). Stirring was continued for 15 h at 20°C and the mixture refluxed for 1 h. Insoluble material was filtered off, the solvent was removed in vacuo and the residue purified by CC (normally SiO_2; CH_2Cl_2).

General Procedure 4 (GP 4) for the Cleavage of Aryl Methyl Ethers

To the aryl methyl ether in CH_2Cl_2 (2 ml/mmol) was added dropwise BBr_3 (1 M solution in CH_2Cl_2, 2−3 equiv. per methyl ether to be cleaved) at −78°C or 0°C. Stirring was continued for 3 h at this temperature and the mixture allowed to warm up to 20°C within 15 h. Ice-cold water was added dropwise and the product isolated by filtration or extraction with a suitable solvent.

3-[2-(1,3-Dioxolan-2-yl)-4-methoxyphenoxy]benzaldehyde (**8**): A mixture of 10.4 g (40.0 mmol) of 4-bromo-3-(1,3-dioxolan-2-yl)-phenyl methyl ether (**6**), 6.10 g (50.0 mmol) of 3-hydroxybenzaldehyde (**7**), 6.90 g (50.0 mmol) of K_2CO_3 and 2.00 g (25.2 mmol)

of CuO in 40 ml of pyridine was heated to reflux for 24 h. The pyridine was distilled off in vacuo and the residue taken off in 200 ml of ethyl acetate discarding insoluble material. The crude material after evaporation of the solvent was purified by CC (alumina; diethyl ether/petroleum ether, 2:1); yield 7.21 g (60%) of a slightly yellow oil. − IR (film): $\tilde{\nu}$ = 2875, 1700 (CHO), 1585, 1495, 1475 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.90 (s, 1 H, CHO), 7.53 (dd, J_1 = 6.3 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 7.44 (t, J = 8.0 Hz, 1 H, Ar-H), 7.38 (d, J = 1.6 Hz, 1 H, Ar-H), 7.23−7.18 (not resolved, 2 H, Ar-H), 6.90 (m_c, 2 H, Ar-H), 5.99 (s, 1 H, OCHO), 4.11−3.93 (m, 4 H, OCH_2CH_2O), 3.82 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 191.57 (C=O), 159.64, 156.71, 147.32, 138.06, 131.20, 130.28, 123.90, 123.22, 121.91, 118.49, 117.08, 112.43, 99.28 (OCO), 65.37 (OCH_2CH_2O), 55.90 (OCH_3). − MS; *m/z* (%): 300 (22) [M^+], 256 (9), 169 (3), 135 (16), 97 (26), 86 (19), 84 (29), 51 (100), 49 (48). − $C_{17}H_{16}O_5$ (300.3): calcd. C 68.00, H 5.37; found C 67.90, H 5.29.

Methyl 4-(2-Methoxy-5-methylphenoxy)-3-nitrobenzoate (**11**): To a suspension of 2.40 g (0.10 mol) of NaH in 50 ml of DMF was added dropwise 13.8 g (0.10 mol) of 2-methoxy-5-methylphenol (**10**) in 100 ml of DMF. After stirring for 10 min at 20°C, 21.6 g (0.10 mol) of methyl 4-chloro-3-nitrobenzoate (**9**) in 100 ml of DMF was added dropwise with ice-cooling. The mixture was allowed to warm up to 20°C and stirred for additional 2 h. After evaporation of the solvent, the residue was taken up in 500 ml of $CHCl_3$, washed with each 300 ml of 2 M NaOH, 2 M HCl and H_2O, dried ($MgSO_4$) and concentrated. The crude material was purified by recrystallization from ethanol; yield 27.3 g (87%), slightly yellow needles, m.p. 65°C. − IR (KBr): $\tilde{\nu}$ = 2950, 2920, 1730 ($COOCH_3$), 1620, 1515 (NO_2), 1355 (NO_2) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.60 (d, J = 2.2 Hz, 1 H, Ar-H), 8.05 (dd, J_1 = 8.8 Hz, J_2 = 2.1 Hz, 1 H, Ar-H), 7.05 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 6.97 (d, J = 1.9 Hz, 1 H, Ar-H), 6.91 (d, J = 8.3 Hz, 1 H, Ar-H), 6.80 (d, J = 8.8 Hz, 1 H, Ar-H), 3.93 (s, 3 H, $COOCH_3$), 3.72 (s, 3 H, OCH_3), 2.31 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 164.90 (*C*$OOCH_3$), 155.33, 149.09, 142.01, 139.26, 134.76, 131.55, 127.50, 127.31, 123.88, 123.06, 117.14, 113.55, 56.21 (OCH_3), 52.46 (CO*O*CH_3), 20.43 (CH_3). − MS; *m/z* (%): 317 (32) [M^+], 286 (8) [$M^+ - OCH_3$], 137 (100), 109 (80), 107 (10), 94 (15), 91 (32), 81 (18), 79 (14), 77 (16), 66 (17), 65 (14). − $C_{16}H_{15}NO_6$ (317.3): calcd. C 60.57, H 4.77, N 4.41; found C 60.05, H 4.81, N 4.41.

Methyl 3-Amino-4-(2-methoxy-4-methylphenoxy)benzoate (**12**): 15.0 g (50.0 mmol) of the nitroarene **11** was hydrogenated according to GP 1 (5% Pd/C, ethyl acetate, 5 bar, 6 h). Recrystallization from ethanol yielded 12.2 g (85%) of compound **12** as colourless crystals, m.p. 101°C. − IR (film): $\tilde{\nu}$ = 3460, 3365 (NH_2), 1715 ($COOCH_3$), 1625, 1600 cm^{-1} . − ^1H NMR ($CDCl_3$): δ = 7.47 (d, J = 2.0 Hz, 1 H, Ar-H), 7.33 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 6.94 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1 H, Ar-H), 6.88 (d, J = 8.3 Hz, 1 H, Ar-H), 6.80 (d, J = 1.9 Hz, 1 H, Ar-H), 6.61 (d, J = 8.4 Hz, 1 H, Ar-H), 4.10−3.90 (br. s, 2 H, NH_2), 3.85 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, OCH_3), 2.25 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 167.04 (*C*$OOCH_3$), 147.17, 144.05, 137.04, 131.06, 125.61, 124.98, 123.90, 121.73, 120.43, 116.88, 115.58, 113.10, 56.16 (OCH_3), 51.81 (COO*C*H_3), 20.15 (CH_3). − MS; *m/z* (%): 287 (17) [M^+], 256 (27) [$M^+ - OCH_3$], 240 (18), 213 (51), 78 (12), 65 (11), 52 (11).

Methyl 4-(2-Methoxy-4-methylphenoxy)benzoate (**13**): To 14.4 g (50.0 mmol) of the aminoarene **12** dissolved in 100 g (75.0 mmol) of 50% aq. H_3PO_2 and 80 ml of H_2O was added dropwise 3.81 g (55.0 mmol) of $NaNO_2$ in 20 ml of H_2O at 0°C and stirring was continued for 2 h at 0°C and for 5 h at 20°C. The mixture was slightly alkalized using concd. NaOH and extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated to give the crude arene which was filtered through an SiO_2 pad eluting with CH_2Cl_2 and recrystallized from ethanol; yield 11.4 g (84%), colourless crystals, m.p. 90°C. − IR (KBr): $\tilde{\nu}$ = 2945, 1710 ($COOCH_3$), 1610, 1585 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.97−7.94 (m, 2 H, Ar-H), 6.98 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 6.92−6.87 (m, 4 H, Ar-H), 3.86 (s, 3 H, $COOCH_3$), 3.73 (s, 3 H, OCH_3), 2.27 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.66 (*C*$OOCH_3$), 162.43, 149.59, 143.27, 131.50, 131.15, 126.32, 123.89, 123.00, 155.80, 113.27, 56.07 (OCH_3), 51.78 (COO*C*H_3), 20.43 (CH_3). − MS; *m/z* (%): 272 (100) [M^+], 241 (30), 198 (46), 121 (10), 91 (7), 77 (7), 65 (7), 59 (10). − $C_{16}H_{16}O_4$ (272.3): calcd. C 70.58, H 5.92; found C 70.08, H 5.93.

Methyl 4-(2-Hydroxy-5-methylphenoxy)benzoate (**14**): To a solution of 10.6 g (36.7 mmol) of the methyl ether **13** in 200 ml of benzene was added batchwise 20.0 g (150 mmol) of anhydrous $AlCl_3$ and the slurry was refluxed for 15 h. After cooling, the mixture was poured into 350 g of crushed ice, extracted three times with 200 ml of diethyl ether, dried ($MgSO_4$) and concentrated in vacuo. The crude product was filtered through an SiO_2 pad eluting with diethyl ether/petroleum ether, 1:1, and recrystallized from toluene/petroleum ether, 1:1; yield 7.70 g (81%), colourless crystals, m.p. 102°C. − IR (film): $\tilde{\nu}$ = 3425 (OH), 2950, 1715 ($COOCH_3$), 1605, 1590 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.93−7.89 (m, 2 H, Ar-H), 6.96−6.87 (m, 4 H, Ar-H), 6.76 (d, J = 1.4 Hz, 1 H, Ar-H), 5.78 (br. s, 1 H, OH), 3.86 (s, 3 H, $COOCH_3$), 2.23 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.73 (*C*$OOCH_3$), 161.48, 145.68, 141.73, 131.75, 130.61, 128.49, 124.61, 123.87, 121.10, 166.76, 116.51, 52.05 (COO*C*H_3), 20.12 (CH_3). − MS; *m/z* (%): 258 (100) [M^+], 227 (59) [$M^+ - OCH_3$], 128 (10), 92 (8), 77 (13), 65 (10), 50 (9). − $C_{15}H_{14}O_4$ (258.3): calcd. C 69.76, H 5.46; found C 69.07, H 5.29.

Methyl 4-(2-Benzoyloxy-5-methylphenoxy)benzoate (**15**): 10.0 g (37.7 mmol) of the phenol **14** was dissolved in 150 ml of ethanol and combined with a solution of 12.7 g (90.0 mmol) of Na_2CO_3 in 150 ml of H_2O. 6.32 g (45.0 mmol) of benzoyl chloride was added dropwise at 20−25°C and the mixture was stirred for 5 h at 20°C and extracted three times with 200 ml of dichloromethane. The organic layer was washed with 200 ml of H_2O, dried ($MgSO_4$) and concentrated in vacuo. The crude product was filtered through an SiO_2 pad eluting with CH_2Cl_2 and recrystallized from methanol; yield 11.3 g (81%), colourless crystals, m.p. 62°C. − IR (KBr): $\tilde{\nu}$ = 1750, 1730 (C=O), 1605, 1510 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.94−7.91 (m, 4 H, Ar-H), 7.53−7.51 (m, 1 H, Ar-H), 7.37 (t, J = 7.8 Hz, 2 H, Ar-H), 7.20 (d, J = 8.2 Hz, 1 H, Ar-H), 7.06 (dd, J_1 = 8.2 Hz, J_2 = 1.7 Hz, 1 H, Ar-H), 6.96 − 6.93 (m, 3 H, Ar-H), 3.86 (s, 3 H, $COOCH_3$), 2.35 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.53 (*C*$OOCH_3$), 164.52 (C=O), 161.59, 146.60, 140.35, 137.42, 133.51, 131.58, 130.11, 129.06, 128.43, 126.04, 124.65, 123.93, 123.78, 122.43, 116.62, 51.89 (COO*C*H_3), 21.00 (CH_3). − MS; *m/z* (%): 362 (8) [M^+], 198 (2), 105 (100) [$PhCO^+$], 77 (26), 50 (7), 42 (10). − $C_{22}H_{18}O_5$ (362.4): calcd. C 72.92, H 5.01; found C 72.64, H 4.93.

[4-Benzoyloxy-3-(4-methoxycarbonylphenoxy)]benzyl Triphenylphosphonium Bromide (**16**): 5.00 g (13.8 mmol) of the methylarene **15** was brominated according to GP 2.1. From the crude benzyl bromide the phosphonium salt was prepared according to GP 2.3 (toluene); yield 6.45 g (68%), colourless salt, m.p. 244°C (acetonitrile). − IR (KBr): $\tilde{\nu}$ = 1735, 1720 (C=O), 1590 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.89 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 2 H, Ar-H), 7.82−7.75 (m, 11 H, Ar-H), 7.64−7.56 (m, 7 H, Ar-H), 7.38 (t, J = 7.9 Hz, 2 H, Ar-H), 7.23 (d, J = 8.3 Hz, 1 H, Ar-H), 7.02

(d, J = 8.1 Hz, 1 H, Ar-H), 6.86 (t, J = 2.2 Hz, 1 H, Ar-H), 6.68 (d, J = 1.7 Hz, 2 H, Ar-H), 5.58 (d, $J(^{31}P\text{-}^{1}H)$ = 14.5 Hz, 2 H, CH_2P), 3.88 (s, 3 H, $COOCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 166.39 (*C*$OOCH_3$), 164.33 (C=O), 160.58, 147.42, 142.59, 135.08, 134.58, 134.49, 133.80, 131.64, 130.34, 130.22, 130.11, 128.95, 128.90, 128.73, 128.56, 127.31, 127.23, 125.22, 124.19, 118.23, 117.28, 51.97 (COO*C*H_3), 30.48, 30.02 (CH_2P). − MS; *m/z* (%): 623 (1) [M^+ − Br], 525 (18), 445 (12), 381 (21), 367 (89), 262 (100) [PPh_3^+], 213 (3), 105 (4), 77 (1). − $C_{40}H_{32}BrO_5P$ (703.6): calcd. C 68.29, H 4.58; found C 68.37, H 4.51.

Methyl 4-{2-Benzoyloxy-5-[(E/Z)-2-{3-[2-(1,3-dioxolan-2-yl)-4-methoxyphenoxy]phenyl}-1-ethenyl]phenoxy}benzoate (**17**): Reaction between the aldehyde **8** (3.28 g, 10.9 mmol) and the phosphonium salt **16** (8.07 g, 11.5 mmol) according to GP 3.1, followed by CC (SiO_2; CH_2Cl_2) yielded 6.27 g (89%) of **17** as a colourless viscous oil. − IR (film): ṽ = 2940, 2875, 1745, 1720 (C=O), 1600, 1580 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.96−7.89 (m, 4 H, Ar-H), 7.38−6.74 (m, 16 H, Ar-H, CH=CH), 6.58 and 6.48 (d, J = 12.2 Hz, 1 H, CH=CH), 6.04 and 5.98 (s, 1 H, O−CH−O), 4.10−3.90 (m, 4 H, O−CH_2−CH_2−O), 3.84 and 3.83 (s, 3 H, $COOCH_3$), 3.78 and 3.76 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.36 (*C*$OOCH_3$), 164.20, 161.36, 161.09, 159.11, 158.71, 156.25, 156.13, 148.16, 148.02, 146.72, 141.42, 138.62, 138.35, 136.78, 136.34, 133.58, 131.58, 130.98, 130.75, 130.62, 130.08, 129.85, 129.65, 129.51, 129.15, 128.93, 128.44, 127.68, 125.83, 124.79, 124.36, 123.91, 123.59, 122.97, 122.02, 121.47, 120.97, 119.56, 117.57, 117.02, 116.88, 116.80, 116.70, 116.37, 115.40, 112.17, 99.26 (OCHO), 65.32 (OCH_2CH_2O), 55.86 (OCH_3), 51.83 (COO*C*H_3). − MS; *m/z* (%): 645 (25) [M^+], 331 (8), 300 (86), 277 (34), 256 (100), 241 (34), 225 (48), 197 (96), 149 (32), 121 (46), 105 (99), 83 (35). − $C_{39}H_{32}O_9$ (644.7): calcd. C 72.66, H 5.00; found C 72.72, H 5.04.

Methyl 4-(2-Benzoyloxy-5-{3-[2-(1,3-dioxolan-2-yl)-4-methoxyphenoxy]phenetyl}phenoxy)benzoate (**18**): 3.70 g (5.74 mmol) of the stilbene **17** was hydrogenated according to GP 1 (5% Pd/C, ethyl acetate, 5 bar, 12 h) in the presence of 7 ml of triethylamine. Filtering through an SiO_2 pad (eluent: CH_2Cl_2) yielded 3.49 g (94%) of a colourless oil. − IR (film): ṽ = 2950, 2890, 1750, 1725 (C=O), 1610, 1595 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.95−7.91 (m, 4 H, Ar-H), 7.55 (t, J = 8.0 Hz, 1 H, Ar-H), 7.38 (t, J = 7.8 Hz, 2 H, Ar-H), 7.23−7.15 (m, 3 H, Ar-H), 7.04 (dd, J_1 = 8.3 Hz, J_2 = 1.9 Hz, 1 H, Ar-H), 6.91−6.74 (m, 8 H, Ar-H), 6.02 (s, 1 H, OCHO), 4.14−3.95 (m, 4 H, OCH_2CH_2O), 3.87 (s, 3 H, $COOCH_3$), 3.81 (s, 3 H, OCH_3), 2.88 (s, 4 H, $ArCH_2CH_2Ar$). − ^{13}C NMR ($CDCl_3$): δ = 166.53 (*C*$OOCH_3$), 164.44 (C=O), 161.50, 158.74, 156.10, 148.40, 146.58, 142.93, 141.00, 140.71, 133.52, 131.61, 130.51, 130.11, 129.52, 129.04, 128.43, 125.43, 124.67, 123.88, 122.75, 121.94, 121.38, 117.60, 116.73, 116.45, 115.35, 112.00, 99.30 (OCHO), 65.40 (OCH_2CH_2O), 55.70 (OCH_3), 51.69 (COO*C*H_3), 37.40, 36.95 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 647 (3) [M^+], 479 (1), 285 (2), 225 (2), 194 (3), 149 (52), 125 (2), 111 (4), 105 (100) [$PhCO^+$], 97 (6), 91 (7), 77 (19), 71 (7), 61 (7), 57 (13). − $C_{39}H_{34}O_9$ (646.7): calcd. C 72.43, H 5.30; found C 72.39, H 5.25.

4-{3-[2-(1,3-Dioxolan-2-yl)-4-methoxyphenoxy]phenetyl}-2-[4-(hydroxymethyl)phenoxy]phenol (**19**): 3.50 g (5.41 mmol) of the diester **18** was reduced according to GP 2.2 (5.95 mmol of $LiAlH_4$). Purification by CC (SiO_2; diethyl ether) yielded 2.40 g (86%), colourless oil. − IR (film): ṽ = 3380 (OH), 1595 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.24 (d, J = 8.6 Hz, 2 H, Ar-H), 7.14−7.11 (m, 2 H, Ar-H, 6.91−6.72 (m, 8 H, Ar-H), 6.65 (s, 1 H, Ar-H), 6.58 (d, J = 2.0 Hz, 1 H, Ar-H), 5.97 (s, 2 H, OCHO, OH), 4.95 (s, 2 H, C*H*$_2$OH), 4.10−3.90 (m, 4 H, OCH_2CH_2O), 3.78 (s, 3 H, OCH_3), 2.76−2.74 (m, 4 H, $ArCH_2CH_2Ar$), 2.42 (s, 1 H, CH_2O*H*). − ^{13}C NMR ($CDCl_3$): δ = 158.49, 156.54, 155.98, 148.50, 145.79, 143.31, 143.07, 136.03, 133.08, 130.33, 129.38, 128.69, 124.84, 123.47, 122.88, 121.21, 120.69, 119.37, 117.98, 117.02, 116.67, 116.42, 116.29, 115.23, 112.07, 99.28 (O-CH-O), 65.35 (OCH_2CH_2O), 64.65 (CH_2OH), 55.42 (OCH_3), 37.73, 36.72 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 514 (6) [M^+], 453 (11), 211 (21), 149 (21), 91 (17), 87 (22), 79 (9), 73 (17), 63 (43), 59 (25), 57 (27), 45 (100). − $C_{31}H_{30}O_7$ (514.6): calcd. C 72.34, H 5.88; found C 72.02, H 5.79.

[4-(2-Benzyloxy-5-{3-[2-(1,3-dioxolan-2-yl)-4-methoxyphenoxy]phenethyl}phenoxy)phenyl]methanol (**20**): 2.00 g (3.89 mmol) of the phenol **19**, 0.49 g (3.89 mmol) of benzyl chloride and 0.54 g (3.89 mmol) of K_2CO_3 in 40 ml of DMF were stirred for 2 h at 120°C. The mixture was poured into 200 ml of H_2O and extracted with CH_2Cl_2 (4 × 100 ml). The organic layers were dried ($MgSO_4$) and concentrated and the residue purified by CC (SiO_2; diethyl ether); yield 2.07 g (88%), colourless oil. − IR (film): ṽ = 3440 (OH), 2930, 2880, 1585 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.27−7.13 (m, 9 H, Ar-H), 6.90−6.71 (m, 10 H, Ar-H), 5.99 (s, 1 H, OCHO), 5.02 (s, 2 H, CH_2Ph), 4.59 (s, 2 H, C*H*$_2$OH), 4.11−3.91 (m, 4 H, OCH_2CH_2O), 3.77 (s, 3 H, OCH_3), 2.80 (s, 4 H, $ArCH_2$-CH_2Ar), 2.02 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 158.55, 158.00, 156.01, 148.76, 148.48, 145.23, 143.31, 137.69, 135.39, 134.87, 130.37, 129.39, 128.47, 128.32, 127.68, 127.11, 124.79, 122.83, 122.07, 121.24, 117.74, 116.67, 116.39, 115.75, 115.23, 112.02, 99.26 (OCHO), 71.36 (OCH_2Ph), 65.36 (OCH_2CH_2O), 64.93 (CH_2OH), 55.69 (OCH_3), 37.61, 36.64 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 605 (8) [M^+], 561 (10), 344 (10), 302 (51), 279 (14), 258 (100), 240 (68), 225 (28), 211 (35), 167 (25), 149 (30), 124 (13), 111 (13), 91 (66), 71 (26), 43 (19). − $C_{38}H_{36}O_7$ (604.7): calcd. C 75.48, H 6.00; found C 74.93, H 5.86.

2-(3-{4-Benzyloxy-3-[4-(bromomethyl)phenoxy]phenethyl}-phenoxy)-5-methoxybenzaldehyde (**21**): 0.55 g (0.91 mmol) of the benzyl alcohol **20** in diethyl ether was treated with 1 ml of 33% HBr in acetic acid and stirred for 2 h at 20°C. The organic layer was washed sufficiently with satd. $NaHCO_3$, dried ($MgSO_4$) and concentrated. The resulting benzyl bromide was very sensitive and converted directly .− IR (film): ṽ = 2940, 2865, 1695 (CHO), 1615, 1590 cm^{-1}.

2-[3-(4-Benzyloxy-3-{4-[(1,1,1-triphenylphosphonio)methyl]-phenoxy}phenethyl)phenoxy]-5-methoxybenzaldehyde Bromide (**22**): From the crude benzyl bromide **21** (0.91 mmol) the phosphonium salt was prepared according to GP 2.3 (10 ml of toluene). The supernatant toluene was decanted and the viscous residue washed with 10 ml of toluene. Concentration in vacuo yielded 0.60 g (75% from **20**) of a beige salt, m.p. 175°C. − IR (KBr): ṽ = 2855, 1690 (CHO), 1610, 1585 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 10.33 (s, 1 H, CHO), 7.75−7.67 (m, 10 H, Ar-H), 7.60−7.56 (m, 6 H, Ar-H), 7.11 (dd, J_1 = 8.9 Hz, J_2 = 3.1 Hz, 1 H, Ar-H), 7.01 (dd, J_1 = 8.8 Hz, J_2 = 2.5 Hz, 2 H, Ar-H), 6.91−6.71 (m, 6 H, Ar-H), 6.66 (d, J = 2.0 Hz, 2 H, Ar-H), 5.31 (d, $J(^{31}P\text{-}^{1}H)$ = 13.9 Hz, 2 H, CH_2P), 5.02 (s, 2 H, CH_2Ph), 3.81 (s, 3 H, OCH_3), 2.81 (s, 4 H, $ArCH_2$-CH_2Ar). − ^{13}C NMR ($CDCl_3$): δ = 189.16 (CHO), 158.63, 157.81, 155.90, 153.54, 148.80, 144.47, 143.79, 136.95, 135.22, 134.98, 134.49, 134.39, 132.71, 130.29, 130.11, 129.92, 128.49, 127.84, 127.02, 125.28, 123.87, 123.60, 122.16, 121.47, 118.37, 118.26, 117.52, 116.98, 115.76, 115.52, 110.13, 71.12 (OCH_2Ph), 55.90 (OCH_3), 37.56, 36.63 ($ArCH_2CH_2Ar$), 30.50, 30.04 (CH_2P). − $C_{54}H_{46}BrO_5P$ (885.8): calcd. C 73.22, H 5.23; found C 72.95, H 5.01.

Benzyl Ether of (E)-Dehydromarchantin I (**23**): 0.50 g (0.56 mmol) of the phosphonium salt **22** was subjected to a Wittig reaction according to GP 3.2; yield 0.24 g (81%), colourless crystals,

m.p. 164°C. – IR (KBr): $\tilde{\nu}$ = 3025, 2925, 1610, 1585 cm^{-1}. – UV (acetonitrile): λ_{max} (log ε) = 275 (3.87), 218 (4.19) nm. – ^1H NMR ($CDCl_3$): δ = 7.51–6.09 (m, 20 H, Ar-H, CH=CH), 5.69 (d, *J* = 2.0 Hz, 1 H, Ar-H), 5.23 (s, 2 H, CH_2Ph), 3.87 (s, 3 H, OCH_3), 2.95–2.85 (m, 4 H, $ArCH_2CH_2Ar$). – ^{13}C NMR ($CDCl_3$): δ = 159.28, 157.03, 155.59, 151.31, 146.51, 146.02, 142.93, 137.53, 137.27, 135.95, 132.04, 131.79, 128.57, 127.86, 127.45, 126.99, 123.23, 122.80, 122.01, 119.31, 116.71, 115.27, 113.88, 112.90, 111.28, 71.86 (CH_2Ph), 55.73 (OCH_3), 34.09, 30.87 ($ArCH_2$-CH_2Ar). – MS; *m/z* (%): 527 (8) [M^+], 526 (16), 435 (8), 237 (12), 225 (6), 211 (49), 181 (7), 165 (6), 105 (12), 91 (100), 77 (11), 65 (14), 57 (17), 55 (11), 42 (17). – $C_{36}H_{30}O_4$ (526.6): calcd. C 82.10, H 5.74; found C 81.91, H 5.80.

Marchantin I (**3**): 0.20 g (0.38 mmol) of the (*E*)-stilbene **23** was hydrogenated according to GP 1 (10% Pd/C, methanol, 5 bar, 15 h). Purification by CC (SiO_2; CH_2Cl_2) yielded 150 mg (90%), colourless crystals, m.p. 135°C. – IR (KBr): $\tilde{\nu}$ = 3450 (OH), 2935, 2865, 1740, 1615, 1515, 1455, 1370, 1275, 1245, 1215, 1120, 1040, 920, 820, 785, 740, 705 cm^{-1}. – UV (ethanol): λ_{max} (log ε): 273 (1.64), 217 (4.14) nm. – ^1H NMR ($CDCl_3$): δ = 7.04 (t, *J* = 7.5 Hz, 1 H, Ar-H), 7.00 (d, *J* = 8.3 Hz, 1 H, Ar-H), 6.92 (d, *J* = 3.0 Hz, 2 H, Ar-H), 6.85 (d, *J* = 8.1 Hz, 1 H, Ar-H), 6.78 (d, *J* = 8.9 Hz, 1 H, Ar-H), 6.72 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1 H, Ar-H), 6.69 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 6.65 (dd, J_1 = 8.9 Hz, J_2 = 3.0 Hz, 1 H, Ar-H), 6.63 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.54 (d, *J* = 7.3 Hz, 1 H, Ar-H), 6.53 (s, 1 H, Ar-H), 5.87 (d, *J* = 1.8 Hz, 1 H, Ar-H), 5.54 (s, 1 H, OH), 3.81 (s, 3 H, OCH_3), 3.08 – 2.98 (m, 4 H, $ArCH_2CH_2Ar$), 2.89 – 2.76 (m, 4 H, $ArCH_2$-CH_2Ar). – ^{13}C NMR ($CDCl_3$): δ = 157.09, 155.30, 153.53, 148.07, 145.56, 144.06, 142.78, 137.93, 133.60, 133.14, 129.88, 128.38, 123.84, 120.43, 118.64, 117.77, 116.18, 116.13, 115.31, 114.97, 111.89, 55.61 (OCH_3), 36.77, 35.70, 34.38, 30.33 ($ArCH_2CH_2Ar$). – MS; *m/z* (%): 439 (36) [M^+], 438 (81), 225 (37), 211 (100), 199 (11), 182 (9), 165 (12), 149 (14), 120 (11), 117 (71), 105 (27), 91 (42), 77 (29), 65 (12), 55 (13), 51 (10), 42 (13). – $C_{29}H_{26}O_4$ (438.5): calcd. C 79.94, H 5.98; found C 79.79, H 5.88. – The ^1H-NMR and MS data were coincidental with those in ref.[7][17].

Methyl 4-(5-Formyl-2-methoxyphenoxy)-3-nitrobenzoate (**25**): To a suspension of 4.80 g (0.20 mol) of NaH in 100 ml of DMF was added dropwise 30.4 g (0.20 mol) of isovanilline (**24**) in 200 ml of DMF. After stirring for 20 min at 20°C for hydrogen evolution, 43.1 g (0.20 mol) of methyl 4-chloro-3-nitrobenzoate (**9**) in 200 ml of DMF was added dropwise with ice-cooling. The mixture was allowed to warm up to 20°C and stirred for additional 2 h. After evaporation of the solvent, the residue was taken up in 500 ml of $CHCl_3$, washed with each 300 ml of 2 M NaOH, 2 M HCl and H_2O, dried ($MgSO_4$) and concentrated. The crude material was purified by filtration through an SiO_2 pad eluting with $CHCl_3$ followed by recrystallization from ethanol/chloroform, 1:2; yield 58.5 g (88%), slightly yellow crystals, m.p. 114°C. – IR (KBr): $\tilde{\nu}$ = 3075, 3040, 3010, 2940, 2850 ($COOCH_3$), 1685 (CHO), 1625, 1610, 1580, 1540 (NO) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.89 (s, 1 H, CHO), 8.63 (d, *J* = 2.1 Hz, 1 H, Ar-H), 8.10 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.83 (dd, J_1 = 8.5 Hz, J_2 = 1.9 Hz, 1 H, Ar-H), 7.68 (d, *J* = 1.9 Hz, 1 H, Ar-H, 7.18 (d, *J* = 8.5 Hz, 1 H, Ar-H), 6.84 (d, *J* = 8.8 Hz, 1 H, Ar-H), 3.94 (s, 3 H, $COOCH_3$), 3.88 (s, 3 H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 189.66 (CHO), 164.66 (*C*O-OCH_3), 156.28, 154.29, 143.11, 139.67, 134.98, 130.60, 130.18, 127.50, 124.94, 122.16, 117.49, 112.92, 56.42 (OCH_3), 52.60 (CO-O*C*H_3). – MS; *m/z* (%): 331 (13) [M^+], 300 (5) [$M^+ - OCH_3$], 284 (5), 225 (4), 180 (4), 151 (100) [ether cleavage], 139 (5), 119 (4), 95 (53), 85 (41), 83 (64), 77 (23), 67 (9), 50 (10), 46 (18). – $C_{16}H_{13}NO_7$ (331.3): calcd. C 58.01, H 3.96, N 4.23; found C 58.24, H 3.83, N 4.66.

Methyl 4-[5-(Diacetyloxymethyl)-2-methoxyphenoxy]-3-nitrobenzoate (**26**): 33.1 g (0.10 mol) of the aldehyde **25** in 350 ml of acetic anhydride together with some drops of concd. H_2SO_4 was stirred for 2 h at 20°C and the mixture was poured into crushed ice. The product precipitating within 10 h was filtered off, washed (H_2O), dried in vacuo and recrystallized from ethanol; yield 37.4 g (86%), yellow crystals, m.p. 107°C. – IR (KBr): $\tilde{\nu}$ = 3080, 3055, 3020, 2995, 2950, 2845, 1770 (CH_3COO), 1720 ($COOCH_3$), 1625, 1585, 1535 (NO) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.63 (d, *J* = 2.2 Hz, 1 H, Ar-H), 8.08 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.63 (s, 1 H, OCHO), 7.43 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1 H, Ar-H), 7.37 (d, *J* = 2.1 Hz, 1 H, Ar-H), 7.04 (d, *J* = 8.5 Hz, 1 H, Ar-H), 6.80 (d, *J* = 8.8 Hz, 1 H, Ar-H), 3.94 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, OCH_3), 2.13 (s, 6 H, CH_3COO). – ^{13}C NMR ($CDCl_3$): δ = 166.70 (CH_3COO), 164.80 ($COOCH_3$), 154.78, 152.29, 142.12, 139.27, 134.87, 129.21, 127.43, 125.92, 124.30, 120.95, 117.04, 113.09, 88.97 (O-CH-O), 56.16 (OCH_3), 52.55 (COO*C*H_3), 20.83 (*C*H_3COO). – MS; *m/z* (%): 433 (5) [M^+], 360 (9), 332 (24), 330 (18), 300 (13), 284 (5), 270 (5), 180 (7), 151 (35), 123 (5), 108 (8), 95 (14), 71 (10), 57 (13), 43 (100) [CH_3CO^+]. – $C_{20}H_{19}NO_{10}$ (433.4): calcd. C 55.43, H 4.42, N 3.23; found C 55.44, H 4.55, N 3.27.

Methyl 3-Amino-4-[5-(diacetyloxymethyl)-2-methoxyphenoxy]-benzoate (**27**): 34.70 g (80.0 mmol) of the nitroarene **26** was hydrogenated according to GP 1 (5% Pd/C, ethyl acetate, 5 bar, 4 h). The crude yellow amine **27** was very sensitive and converted directly. – IR (film): $\tilde{\nu}$ = 3470, 3370 (NH_2), 3060, 2980, 2945, 2835, 1765 (CH_3 COO), 1720 ($COOCH_3$), 1625, 1600 cm^{-1}.

Methyl 4-(5-Formyl-2-methoxyphenoxy)benzoate (**28**): To the crude aminoarene **27** in 120 ml of acetic acid and 65 ml of 15% HCl was added dropwise 6.40 g (92.8 mmol) of $NaNO_2$ in 15 ml of H_2O at 0°C. After additional stirring for 30 min, 160 ml of 30% H_3PO_2 was added and stirring was continued for 12 h at 0°C. The product was filtered off, washed (H_2O), dried (P_4O_{10}), filtered through an SiO_2 pad (eluting with CH_2Cl_2) and recrystallized from ethanol/H_2O, 10:1; yield 16.9 g (74% from **26**), colourless crystals, m.p. 117°C. – IR (KBr): $\tilde{\nu}$ = 3060, 2985, 2945, 2830, 2735, 1715 ($COOCH_3$), 1695 (CHO), 1610, 1585 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.86 (s, 1 H, CHO), 8.02–7.98 (m, 2 H, Ar-H), 7.75 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 7.59 (d, *J* = 2.0 Hz, 1 H, Ar-H), 7.14 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.95–6.92 (m, 2 H, Ar-H), 3.89 (s, 6 H, $COOCH_3$, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 189.96 (CHO), 166.51 (*C*$OOCH_3$), 161.39, 156.80, 144.40, 131.69, 130.48, 129.07, 124.76, 121.92, 116.27, 112.55, 56.25 (OCH_3), 51.96 (CO-O*C*H_3). – MS; *m/z* (%): 286 (92) [M^+], 255 (100) [$M^+ - OCH_3$], 240 (6), 212 (7), 183 (7), 155 (6), 149 (10), 127 (20), 119 (9), 92 (7), 79 (8), 76 (13), 63 (9), 59 (10), 50 (12). – $C_{16}H_{14}O_5$ (286.3): calcd. C 67.13, H 4.93; found C 67.56, H 4.98.

Methyl 4-[5-(1,3-Dioxolan-2-yl)-2-methoxyphenoxy]benzoate (**29**): 12.2 g (44.7 mmol) of the aldehyde **28** was dissolved in 250 ml of toluene together with 28.0 g (0.45 mol) of 1,2-dihydroxyethane. 20.0 g of alumina (acidic, dried at 100°C in vacuo) was added and the mixture refluxed for 24 h with vigorous stirring. After cooling, the alumina was filtered off and washed several times with CH_2Cl_2. The combined organic layers were washed (H_2O), dried ($MgSO_4$) and concentrated. The crude dioxolane crystallized with ethanol and was recrystallized from ethanol/H_2O, 5:1; yield 12.5 g (85%), colourless crystals, m.p. 74°C. – IR (KBr): $\tilde{\nu}$ = 2985, 2945, 2885, 1720 (C=O), 1620, 1605, 1585 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.97 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2 H, Ar-H), 7.32 (dd, J_1 =

8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 7.21 (d, J = 2.0 Hz, 1 H, Ar-H), 7.01 (d, J = 8.4 Hz, 1 H, Ar-H), 6.91 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2 H, Ar-H), 5.73 (s, 1 H, OCHO), 4.12−3.98 (m, 4 H, OCH_2CH_2O), 3.88 (s, 3 H, $COOCH_3$), 3.79 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.68 (*C*$OOCH_3$), 162.11, 152.41, 143.39, 131.55, 131.36, 124.33, 124.07, 120.55, 115.92, 112.77, 103.13 (OCHO), 65.29 (OCH_2CH_2O), 56.04 (OCH_3), 51.87 ($COOCH_3$). − MS; *m/z* (%): 330 (78) [M^+], 299 (20) [$M^+ - OCH_3$], 285 (29), 258 (100) [M^+ − dioxolane], 227 (25), 198 (6), 184 (8), 149 (29), 127 (21), 119 (20), 92 (9), 76 (13), 73 (32) dioxolane$^+$], 59 (12), 44 (23). − $C_{18}H_{18}O_6$ (330.3): calcd. C 65.45, H 5.49; found C 65.75, H 5.35.

{4-[5-(1,3-Dioxolan-2-yl)-2-methoxyphenoxy]phenyl}methanol (**30**): 11.5 g (34.8 mmol) of the methyl benzoate **29** was reduced according to GP 2.2 (32.0 mmol of $LiAlH_4$). The crude product was recrystallized from ethanol/H_2O, 2:1; yield 8.80 g (84%), colourless crystals, m.p. 80°C. − IR (KBr): $\tilde{\nu}$ = 3460 (OH), 2965, 2885, 2800, 1625, 1610, 1590 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.26−7.23 (m, 3 H, Ar-H), 7.09 (d, J = 2.0 Hz, 1 H, Ar-H), 6.98 (d, J = 8.4 Hz, 1 H, Ar-H), 6.93−6.89 (m, 2 H, Ar-H), 5.68 (s, 1 H, OCHO), 4.58 (d, J = 5.7 Hz, 2 H, C*H*$_2$OH), 4.07−3.93 (m, 4 H, OCH_2CH_2O), 3.81 (s, 3 H, OCH_3), 2.08 (s, 1 H, CH_2OH). − ^{13}C NMR ($CDCl_3$): δ = 157.35, 152.16, 144.92, 135.16, 131.01, 128.52, 123.15, 119.31, 117.25, 112.63, 103.24 (OCHO), 65.20 (OCH_2CH_2O), 64.82 (CH_2OH), 56.11 (OCH_3). − MS; *m/z* (%): 302 (100) [M^+], 257 (30), 243 (22), 230 (99) [M^+ − dioxolane], 213 (9), 149 (15), 128 (13), 124 (20), 119 (25), 107 (23), 89 (31), 79 (37), 77 (57), 73 (59) dioxolane$^+$], 65 (19), 50 (25), 44 (56). − $C_{17}H_{18}O_5$ (302.3): calcd. C 67.54, H 6.00; found C 67.23, H 6.05.

4-[5-(1,3-Dioxolan-2-yl)-2-methoxyphenoxy]benzaldehyde (**31**): To a solution of 8.60 g (28.4 mmol) of benzyl alcohol **30** in 250 ml of CH_2Cl_2 were added 25 ml of pyridine and 50.0 g (50 mmol) of pyridinium chlorochromate (PCC) on alumina. The mixture was stirred for 3 h at 20°C, filtered and the alumina washed several times with diethyl ether. The combined organic layers were washed (H_2O), dried ($MgSO_4$) and concentrated. The crude aldehyde was filtered through an alumina pad eluting with diethyl ether; yield 7.30 g (86%), colourless unstable oil. − IR (film): $\tilde{\nu}$ = 3060, 2955, 2885, 2835, 2735, 1700 (CHO), 1605, 1585 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 9.89 (s, 1 H; CHO), 7.82−7.79 (m, 2 H, Ar-H), 7.35 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1 H, Ar-H), 7.24 (d, J = 2.1 Hz, 1 H, Ar-H), 7.03 (d, J = 8.4 Hz, 1 H, Ar-H), 7.00−6.97 (m, 2 H, Ar-H), 5.74 (s, 1 H, OCHO), 4.13−4.00 (m, 4 H, OCH_2CH_2O), 3.79 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 190.71 (CHO), 163.41, 152.41, 142.92, 131.84, 131.46, 131.08, 124.73, 120.80, 116.34, 112.81, 103.07 (OCHO), 65.31 (OCH_2CH_2O), 56.04 (OCH_3).

4-Methoxy-2-methylphenylboronic Acid (**34**): To a solution of 80.6 g (0.35 mol) of tributyl borate in 150 ml of THF and 150 ml of diethyl ether was added at T < −60°C a Grignard solution,prepared from 70.4 g (0.35 mol) of 1-bromo-4-methoxy-2-methylbenzene (**32**) and 8.50 g (0.35 mol) of Mg in 250 ml of THF. The mixture was allowed to warm up to 20°C within about 12 h and hydrolysed by adding dropwise 300 ml of 10% HCl. Stirring was continued for 30 min and the mixture extracted three times with diethyl ether. The combined organic layers were extracted three times with 1 M NaOH and the alkaline solution acidified with concd. HCl. The product precipitated and was filtered off and dried; yield 43.3 g (75%); colourless crystals, m.p 191°C. − IR (KBr): $\tilde{\nu}$ = 3300 (OH), 3000, 2960, 2930, 1565 cm^{-1}. − ^{1}H NMR ([D_6]DMSO): δ = 7.73 (s, 2 H, OH), 7.45 (dd, J_1 = 5.0 Hz, J_2 = 3.9 Hz, 1 H, Ar-H), 6.69−6.67 (m, 2 H, Ar-H), 3.72 (s, 3 H, OCH_3), 2.41 (s, 3 H, CH_3). − ^{13}C NMR ([D_6]DMSO): δ = 159.97, 143.97, 135.42, 115.00, 109.79, 54.65 (OCH_3), 22.32 (CH_3).

Methyl 3-Methoxy-4-[(trifluoromethylsulfonyl)oxy]benzoate (**35**): To 9.10 g (50.0 mmol) of methyl 4-hydroxy-3-methoxybenzoate (methyl vanillinate, **33**) and 6.00 g (75.8 mmol) of pyridine in 150 ml of CH_2Cl_2 was added dropwise a solution of 15.0 g (53.2 mmol) of trifluoromethanesulfonic anhydride in 20 ml of CH_2Cl_2 at T < 0°C. Stirring was continued at 0°C for 30 min and the mixture poured into ice-cold water. The organic layer was washed with satd. $NaHCO_3$, dried ($MgSO_4$) and concentrated. The crude material was filtered through an SiO_2 pad eluting with CH_2Cl_2; yield 15.0 g (95%), colourless oil. − IR (film): $\tilde{\nu}$ = 3005, 2950, 2840, 1735 (C=O), 1610 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.72 (d, J = 1.9 Hz, 1 H, Ar-H), 7.67 (dd, J_1 = 8.4 Hz, J_2 = 1.9 Hz, 1 H, Ar-H), 7.28 (d, J = 8.4 Hz, 1 H, Ar-H), 3.97 (s, 3 H, $COOCH_3$), 3.93 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 165.48 (*C*$OOCH_3$), 151.29, 141.71, 131.08, 122.37, 120.25, 117.07, 114.15, 56.32 (OCH_3), 52.43 ($COOCH_3$). − MS; *m/z* (%): 314 (81) [M^+], 283 (16) [$M^+ - OCH_3$], 181 (100) [$M^+ - CF_3SO_2$], 149 (11), 125 (8), 121 (9), 94 (4), 79 (6), 59 (4). − $C_{10}H_9F_3O_6S$ (314.2): calcd. C 38.22, H 2.89; found C 38.37, H 2.74.

Methyl 3-Methoxy-4-(4-methoxy-2-methylphenyl)benzoate (**36**): To 11.8 g (71.1 mmol) of the boronic acid **34** and 20.0 g (63.6 mmol) of the triflate **35** together with 2.30 g (2.00 mmol) of $Pd^0(PPh_3)_4$ in 350 ml of DMF was added 22.0 g (95.5 mmol) of $K_3PO_4 \cdot H_2O$ and the mixture heated to 100°C for 2 h with vigorous stirring. The batch was cooled to 20°C, poured into 300 ml of diethyl ether, filtered and washed with H_2O. The organic layer was dried ($MgSO_4$), concentrated and filtered through an alumina pad (eluting with CH_2Cl_2) for removal of the remaining catalyst. The crude product was recrystallized from methanol/H_2O, 10:1; yield 16.9 g (93%), colourless crystals, m.p. 64°C. − IR (KBr): $\tilde{\nu}$ = 3000, 2945, 2830, 1725 (C=O), 1610, 1565 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.69 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1 H, Ar-H), 7.62 (s, 1 H, Ar-H), 7.19 (d, J = 7.8 Hz, 1 H, Ar-H), 7.08 (d, J = 8.3 Hz, 1 H, Ar-H), 6.82−6.77 (m, 2 H, Ar-H), 3.94 (s, 3 H, $COOCH_3$), 3.82 (s, 6 H, OCH_3), 2.10 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 167.06 (*C*$OOCH_3$), 159.15, 156.88, 138.02, 135.65, 131.35, 130.72, 130.31, 130.13, 121.96, 115.34, 111.44, 110.93, 55.63, 55.17 (OCH_3), 52.17 ($COOCH_3$), 20.14 (CH_3). − MS; *m/z* (%): 286 (100) [M^+], 255 (15) [$M^+ - OCH_3$], 239 (7), 212 (22), 197 (10), 169 (5), 152 (7), 141 (8), 128 (9), 115 (7), 104 (3), 92 (4), 59 (9). − $C_{17}H_{18}O_4$ (286.3): calcd. C 71.31, H 6.34; found C 71.05, H 6.60.

{5-Methoxy-2-[2-methoxy-4-(methoxycarbonyl)phenyl]-benzyl}triphenylphosphonium Bromide (**37**): From 8.00 g (27.9 mmol) of the methylarene **36** the crude benzyl bromide was obtained according to GP 2.1 and the corresponding phosphonium salt using GP 2.3 (acetonitrile, reflux 2 h). After evaporation of the solvent, the phosphonium salt precipitated on digesting with hot toluene; yield 11.4 g (68%), colourless crystals, m.p. 212°C. − IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2950, 2830, 1720 (C=O), 1610, 1570, 1545 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.79−7.75 (m, 3 H, Ar-H), 7.57−7.54 (m, 7 H, Ar-H), 7.39−7.34 (m, 7 H, Ar-H), 7.00 (d, J = 8.4 Hz, 1 H, Ar-H), 6.92−6.86 (m, 2 H, Ar-H), 6.35 (d, J = 7.7 Hz, 1 H, Ar-H), 5.42 and 4.60 (t, $J(^{31}P\text{-}^1H)$ = 14.3 Hz, each 1 H, CH_2P), 3.97 (s, 3 H; $COOCH_3$), 3.74 and 3.54 (s, each 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 166.62 (*C*$OOCH_3$), 159.44, 156.13, 134.99, 134.28, 134.18, 133.23, 132.41, 131.11, 131.03, 130.85, 130.28, 130.14, 127.59, 127.51, 123.96, 122.22, 118.06, 117.22, 116.43, 115.85, 111.91, 56.10, 55.82 (OCH_3), 29.73, 29.26 (CH_2P). − MS; *m/z* (%): 531 (45) [$M^+ - Br - CH_3$], 515 (13) [$M^+ - Br - OCH_3$], 445 (26), 370 (7), 284 (22) [$M^+ - Br - PPh_3$], 269 (73), 262 (100) [PPh_3^+], 239 (33), 183 (38), 139 (13), 108 (11). − $C_{35}H_{32}BrO_4P$ (627.5): calcd. C 66.99, H 5.14; found C 67.11, H 5.15.

Methyl 4-{2-[(E/Z)-2-{4-[5-(1,3-Dioxolan-2-yl)-2-methoxyphenoxy]phenyl}-1-ethenyl]-4-methoxyphenyl}-3-methoxybenzoate (**38**): Reaction between 7.30 g (24.3 mmol) of the aldehyde **31** and 16.8 g (26.8 mmol) of the phosphonium salt **37** according to GP 3.1, followed by filtration through an Al_2O_3 pad (eluent: CH_2Cl_2) resulted in a yellow oil which was purified by CC (Al_2O_3; diethyl ether/petroleum ether, 3:1); yield 11.8 g (85%), colourless viscous oil. − IR (film): $\tilde{\nu}$ = 2990, 2945, 2885, 2830, 1725 (C=O), 1605, 1565 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.71−6.17 (m, 15 H, Ar-H, CH=CH), 5.70 and 5.69 (s, 1 H, OCHO), 4.08−3.96 (m, 4 H, OCH_2CH_2O), 3.94−3.81 (s not resolved, 12 H, $COOCH_3$, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 167.00 (*C*$OOCH_3$), 159.40, 158.85, 157.61, 157.00, 156.88, 152.24, 144.84, 144.64, 138.20, 137.25, 135.07, 134.69, 132.01, 131.58, 131.41, 131.26, 131.12, 130.57, 130.25, 129.76, 129.50, 129.35, 128,78, 127,71, 126.03, 123.83, 123.32, 123.12, 121.93, 121.79, 119.62, 119.35, 117.18, 116.79, 114.02, 113.47, 113.15, 112.84, 111.79, 109.89, 103.23 (OCHO), 65.23 (OCH_2CH_2O), 56.12, 55.81, 55.46, 55.34, 55.18 (OCH_3), 53.40, 52.14 (COO*C*H_3). − MS; *m/z* (%): 569 (100) [M^+], 524 (12), 496 (5) [M^+ − dioxolane], 466 (3), 340 (11), 315 (7), 285 (17), 253 (8), 239 (8), 145 (5), 73 (17) dioxolane$^+$], 59 (12), 44 (17), 42 (20). − $C_{34}H_{32}O_8$ (568.6): calcd. C 71.82, H 5.67; found C 71.38, H 5.89.

Methyl 4-(2-{4-[5-(1,3-Dioxolan-2-yl)-2-methoxyphenoxy]phenetyl}-4-methoxyphenyl)-3-methoxybenzoate (**39**): 11.8 g (20.8 mmol) of the (*E*/*Z*)-stilbene **38** was hydrogenated according to GP 1 (5% Pd/C, ethyl acetate, 5 bar, 18 h) in presence of 30 ml of triethylamine. Filtering through an Al_2O_3 pad (eluent: CH_2Cl_2) yielded 11.0 g (93%) of a colourless oil. − IR (film): $\tilde{\nu}$ = 2990, 2975, 2830, 1720 (C=O), 1610, 1570 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.68 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 7.62 (d, *J* = 1.4 Hz, 1 H, Ar-H), 7.22 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 7.13 (d, *J* = 7.7 Hz, 1 H, Ar-H), 7.07 (s, 1 H, Ar-H), 7.05 (d, *J* = 1.6 Hz, 1 H, Ar-H), 6.97 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.84−6.76 (m, 6 H, Ar-H), 5.68 (s, 1 H, OCHO), 4.07−3.95 (m, 4 H, OCH_2CH_2O), 3.94 (s, 3 H, $COOCH_3$), 3.82, 3.81, 3.80 (s, each 3 H, OCH_3), 2.65 (br. s, 4 H, $ArCH_2CH_2Ar$). − ^{13}C NMR ($CDCl_3$): δ = 166.98 (*C*$OOCH_3$), 159.20, 156.86, 155.87, 152.09, 145.22, 141.46, 135.92, 135.45, 131.55, 130.95, 130.40, 129.85, 129.30, 122.77, 121.91, 119.08, 117.13, 114.56, 112.52, 111.42, 111.22, 103.25 (OCHO), 65.19 (OCH_2CH_2O), 56.10, 55.64, 55.17 (OCH_3), 52.14 (COO*C*H_3), 36.30, 35.85 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 570 (20) [M^+], 285 (100) benzyl cleavage], 241 (21), 213 (21), 205 (9), 167 (8), 149 (30), 91 (18), 83 (16), 73 (23) dioxolane$^+$], 71 (26), 69 (15), 57 (35), 55 (24), 42 (58). − $C_{34}H_{34}O_8$ (570.6): calcd. C 71.56, H 6.01; found C 71.08, H 6.18.

[4-(2-{4-[5-(1,3-Dioxolan-2-yl)-2-methoxyphenoxy]phenethyl}-4-methoxyphenyl)-3-methoxyphenyl]methanol (**40**): 11.0 g (19.3 mmol) of the methyl benzoate **39** was reduced according to GP 2.2 (18.0 mmol of $LiAlH_4$). The crude product was purified by filtration through an Al_2O_3 pad (eluent: diethyl ether); yield 9.20 g (88%), colourless oil. IR (film): $\tilde{\nu}$ = 3470 (OH), 2990, 2930, 2885, 2830, 1610, 1575 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.22 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 7.07−7.04 (m, 3 H, Ar-H), 6.96 (d, *J* = 8.6 Hz, 1 H, Ar-H), 6.93 (s, 1 H, Ar-H), 6.85 (d, *J* = 8.6 Hz, 1 H, Ar-H), 6.81−6.76 (m, 6 H, Ar-H), 5.67 (s, 1 H, OCHO), 4.71 (d, *J* = 5.5 Hz, 2 H, C*H*$_2$OH), 4.07−3.93 (m, 4 H, OCH_2CH_2O), 3.81, 3.80, 3.75 (s, each 3 H, OCH_3), 2.67 (br. s, 4 H, $ArCH_2CH_2Ar$), 2.01 (t, *J* = 5.5 Hz, 1 H, CH_2OH). − ^{13}C NMR ($CDCl_3$): δ = 158.88, 157.06, 155.78, 152.11, 145.27, 141.72, 141.60, 136.23, 131.64, 131.32, 130.87, 130.57, 129.64, 129.33, 122,77, 119.07, 118.75, 117.11, 114.43, 112.52, 111.11, 109.28, 103.27 (O-CH-O), 65.31 (CH_2OH), 65.19 (OCH_2CH_2O), 56.11, 55.46, 55.16 (OCH_3), 36.25, 35.82 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 542 (24) [M^+], 526 (4), 285 (100) benzyl cleavage], 258 (18), 241 (19), 227 (15), 213 (11), 196 (6), 152 (5), 91 (9), 73 (11) dioxolane$^+$], 57 (15), 42 (43), 31 (90) [OCH_3^+]. − $C_{33}H_{34}O_7$ (542.6): calcd. C 73.04, H 6.32; found C 73.00, H 6.45.

4-Methoxy-3-[4-(5-methoxy-2-{2-methoxy-4-[(1,1,1-triphenylphosphonio)methyl]phenyl}phenethyl)phenoxy]benzaldehyde Bromide (**41**): Gaseous HBr was passed with vigorous stirring into a solution of 9.20 g (17.0 mmol) of benzyl alcohol **40** in 300 ml of $CHCl_3$ for 15 min at 20°C and stirring was continued for 2 h. The solution was washed with satd. $NaHCO_3$, followed by H_2O and dried ($MgSO_4$). From the crude benzyl bromide obtained after evaporation of the solvent the phosphonium salt was prepared according to GP 2.3 (toluene); yield 10.8 g (77%), colourless crystals, m.p. 209°C. − IR (KBr): $\tilde{\nu}$ = 3045, 2995, 2950, 2890, 2775, 1690 (CHO), 1605, 1575 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.75 (s, 1 H, CHO), 7.78−7.70 (m, 10 H, Ar-H), 7.63 (dd, J_1 = 8.4 Hz, J_2 = 1.9 Hz, 1 H, Ar-H), 7.57−7.52 (m, 6 H, Ar-H), 7.31 (d, *J* = 1.9 Hz, 1 H, Ar-H), 7.12 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.98−6.90 (m, 3 H, Ar-H), 6.85−6.70 (m, 6 H, Ar-H), 5.42 (br. s, 2 H, CH_2P), 3.92, 3.79, 3.40 (s, each 3 H, OCH_3), 2.68 (br. s, 4 H, $ArCH_2CH_2Ar$). − ^{13}C NMR ($CDCl_3$): δ = 190.22 (CHO), 159.14, 157.01, 156.41, 155.06, 146.75, 141.23, 137.13, 134.97, 134.61, 134.53, 131.57, 131.29, 130.30, 130.17, 130.05, 129.56, 129.05, 128.35, 127.74, 127.65, 123.95, 123.02, 122.98, 118.85, 118.47, 118.05, 117.63, 114.92, 114.42, 112.40, 111.27, 56.43, 55.90, 55.26 (OCH_3), 36.08, 35.48 ($ArCH_2CH_2Ar$), 31.02, 30.56 (CH_2P). − MS; *m/z* (%): 557 (100), 524 (8), 479 (26), 463 (15), 445 (4), (13), 329 (4), 279 (25), 263 (26), 262 (39) [PPh_3^+]. − $C_{49}H_{44}BrO_5P$ (823.8): calcd. C 71.44, H 5.38; found C 71.27, H 5.23.

Trimethyl Ether of (E/Z)-Dehydroriccardin C (**42**): 3.00 g (3.64 mmol) of the phosphonium salt **41** was subjected to a Wittig cyclization according to GP 3.2. The residue was purified by CC (SiO_2; diethyl ether/petroleum ether, 2:1); yield 1.35 g (80%), colourless crystals, m.p. 166−170°C (ethanol/$CHCl_3$, 3:1). − IR (KBr): $\tilde{\nu}$ = 3000, 2930, 2825, 1610, 1570, 1550 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.36−6.15 (m, 15 H, Ar-H, CH=CH), 3.96−3.64 (s, not resolved, 9 H, OCH_3), 3.13−2.59 (m, 4 H, $ArCH_2CH_2Ar$). − ^{13}C NMR ($CDCl_3$): δ = 159.28, 159.11, 158.53, 155.78, 154.52, 152.48, 148.80, 148.39, 147.58, 142.80, 141.20, 139.32, 136.70, 135.91, 134.41, 132.53, 131.87, 131.50, 130.97, 130.85, 129.88, 129.68, 129.19, 129.01, 128.76, 128.49, 127.88, 124.05, 123.87, 123.65, 122.74, 122.46, 122.07, 121.73, 120.41, 119.59, 115.46, 113.59, 111.82, 111.59, 111.35, 110.86, 110.40, 56.30, 56.00, 55.75, 55.23, 55.16 (OCH_3), 36.54, 35.81, 35.33, 34.15 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 464 (100) [M^+], 449 (3), 358 (6), 343 (3), 311 (3), 232 (6), 216 (5), 152 (3), 107 (2), 91 (3), 77 (3), 43 (4). − $C_{31}H_{28}O_4$ (464.6): calcd. C 80.15, H 6.08; found C 79.95, H 6.40.

Trimethyl Ether of Riccardin C (**43**): 1.30 g (2.80 mmol) of the *(E/Z)*-stilbene **42** was hydrogenated according to GP 1 (5% Pd/C, ethyl acetate, 5 bar, 15 h). Purification (CC: SiO_2; CH_2Cl_2) resulted in a viscous oil which crystallized on heating with ethanol; yield 1.20 g (92%), colourless crystals, m.p. 155°C. − IR (KBr): $\tilde{\nu}$ = 3020, 3000, 2925, 2850, 2825, 1610, 1585, 1575 cm^{-1}. − UV (ethanol): λ_{max} (log ε) = 280 (3.73), 220 (4.10) nm. − ^1H NMR ($CDCl_3$): δ = 7.05 (d, *J* = 8.5 Hz, 1 H, Ar-H), 6.96 (d, *J* = 2.7 Hz, 1 H, Ar-H), 6.87 (d, *J* = 8.2 Hz, 1 H, Ar-H), 6.83−6.68 (m, 7 H, Ar-H), 6.43 (d, *J* = 1.3 Hz, 1 H, Ar-H), 6.23 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1 H, Ar-H), 5.36 (d, *J* = 2.0 Hz, 1 H, Ar-H), 3.93, 3.87, 3.66 (s, each 3 H, OCH_3), 3.07, 2.92, 2.84, 2.62 (each m_c, total 8 H, $ArCH_2CH_2Ar$). − ^{13}C NMR ($CDCl_3$): δ = 159.20, 156.07, 152.88, 148.80, 147.03, 143.28, 141.23, 139.73, 133.89, 132.47, 132.43, 130.97, 129.37, 127.70, 123.84, 122.29, 121.70, 121.45, 116.79,

115.41, 112.07, 111.48, 111.30, 56.18 (OCH_3), 55.23 (OCH_3), 38.25, 38.08, 37.21, 35.64 ($ArCH_2CH_2Ar$). − MS; *m/z* (%): 466 (95) [M^+], 239 (100) benzyl cleavage], 233 (14), 227 (10), 225 (12), 211 (14), 209 (7), 165 (5), 153 (4), 121 (4), 105 (12), 90 (21), 77 (8). − $C_{31}H_{30}O_4$ (466.6): calcd. C 79.80, H 6.48; found C 79.70, H 6.65.

Riccardin C (**4**): 1.00 g (2.14 mmol) of the trimethyl ether **43** was cleaved according to GP 4 (20.0 mmol of BBr_3, 0°C → 20°C). The crude product was isolated by extraction with CH_2Cl_2 and purification by CC (SiO_2; diethyl ether) resulting in a foam which crystallized on heating with *n*-hexane; yield 0.80 g (88%), colourless crystals, m.p. 194°C. − IR (KBr): $\tilde{\nu}$ = 3600, 3400 (OH), 3015, 2960, 2915, 2845, 1605, 1580, 1565, 1505, 1435, 1340, 1275, 1225, 1190, 1160, 1105, 1015, 975, 930, 900, 850, 810, 720 cm^{-1}. − UV (ethanol): λ_{max} (log ε) = 280 (3.90), 225 (4.14) nm. − ^1H NMR ($CDCl_3$ / [D_6]DMSO): δ = 8.48 (s, 1 H, OH), 6.98 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.94 (d, *J* = 2.5 Hz, 1 H, Ar-H), 6.88 (d, *J* = 8.0 Hz, 1 H, Ar-H), 6.79 (d, *J* = 2.5 Hz, 1 H, Ar-H), 6.78−6.68 (m, 6 H, Ar-H), 6.70 (s, 1 H, OH), 6.36 (d, *J* = 1.3 Hz, 1 H, Ar-H), 6.24 (s, 1 H, OH), 6.16 (dd, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 1 H, Ar-H), 5.34 (d, *J* = 1.8 Hz, 1 H, Ar-H), 3.00, 2.88, 2.62 (each br. s, total 8 H, $ArCH_2CH_2Ar$). − ^{13}C NMR ($CDCl_3$/[D_6]DMSO): δ = 157.09, 152.78, 152.58, 146.72, 143.65, 143.38, 141.34, 139.98, 133.02, 132.53, 131.67, 129.33, 127.94, 125.22, 122.25, 122.02, 121.08, 117.40, 116.47, 116.10, 115.30, 114.19, 38.13, 37.76, 37.03, 35.07. − MS; *m/z* (%): 424 (88) [M^+], 225 (7), 212 (40), 211 (100) benzyl cleavage], 197 (9), 152 (4), 120 (7), 107 (24), 91 (19), 77 (10), 55 (5), 31 (12). The ^1H-NMR and MS data were coincidental with those reported in ref.[18].

2-(3-Bromo-4-methoxyphenyl)-1,3-dioxane (**45**): 4.30 g (20.0 mmol) of 3-bromo-4-methoxybenzaldehyde (**44**) and 1.60 ml (1.67 g, 22.0 mmol) of 1,3-propanediol together with 0.10 g of toluene-4-sulfonic acid in 50 ml of toluene were heated to reflux for 24 h in a Dean-Stark water separator. After cooling, the toluene layer was washed (1 M NaOH, satd. NaCl), dried ($MgSO_4$) and concentrated. The crude dioxane was purified by CC (SiO_2; ethyl acetate/hexane, 1:1) or distillation; yield 5.30 g (97%), colourless oil, solidifying; m.p. 66°C, b.p.$_{0.001}$ 116°C. − IR (film): $\tilde{\nu}$ = 2955, 2840 (OC−H), 1610 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.67 (d, *J* = 1.8 Hz, 1 H), 7.37 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 5.42 (s, 1 H, OCHO), 4.26−4.21 and 3.98−3.92 (m, each 2 H, OCH_2), 3.87 (s, 3 H, OCH_3), 2.25−2.13 and 1.45−1.40 (m , each 1 H, HCH). − ^{13}C NMR ($CDCl_3$): δ = 156.1, 132.7, 131.2, 126,3, 111.5, 100.5, 67.3, 56.3, 25.7. − MS; *m/z* (%): 273 (13) [M^+], 243 (18), 241 (11), 193 (90), 188 (24), 186 (19), 163 (13), 157 (12), 155 (17), 134 (22), 120 (14), 118 (12), 107 (25), 104 (32), 103 (16), 86 (27), 82 (17), 78 (14), 69 (22), 65 (41), 55 (41), 43 (100). − $C_{11}H_{13}BrO_3$ (273.1): calcd. C 48.37, H 4.80; found C 49.02, H 4.90.

5-Formyl-2-methoxyphenylboronic Acid (**46**): To 1.10 g (4.02 mmol) of the bromoarene **45** in 15 ml of diethyl ether was added 1.80 ml (4.50 mmol) of 2.5 M *n*BuLi in hexane at *T* < −70°C. After stirring for additional 4 h at −70°C, 1.40 ml (1.16 g, 5.04 mmol) of tributyl borate was added and the mixture was allowed to warm up to 20°C within about 12 h and hydrolysed by adding 8 ml of 2 M HCl. The product precipitated and was filtered off. A second fraction could be obtained by extracting the ethereal layer with 2 M NaOH and acidifying. The combined boronic acid was recrystallized from water and dried in vacuo (extensive drying over P_4O_{10} may result in formation of the anhydride); yield 0.54 g (75%), colourless crystals, m.p. 160°C. − IR (KBr): $\tilde{\nu}$ = 3235 (OH), 1685 (C=O), 1660, 1600, 1575 cm^{-1}. − ^1H NMR ([D_6]DMSO): δ = 9.88 (s, 1 H, CHO), 8.06 (d, *J* = 2.0 Hz, 1 H), 7.93 [m, 3 H, Ar-H, $B(OH)_2$], 7.17 (d, *J* = 8.6 Hz, 1 H), 3.90 (s, 3 H, OCH_3). − ^{13}C NMR ([D_6]DMSO): δ = 191.4, 167.8, 136.9, 133.6, 129.1, 110.7, 55.8.

3-[5-(1,3-Dioxan-2-yl)-2-methoxyphenyl]-4-methoxybenzaldehyde (**47**): 4.00 g (22.2 mmol) of the boronic acid **46** in 20 ml of ethanol was added to a mixture of 5.46 g (20.0 mmol) of bromoarene **45**, 40 ml of toluene, 0.70 g (0.61 mmol) of $Pd^0(PPh_3)_4$ and 20 ml of 2 M aq. Na_2CO_3. After heating to reflux for 24 h the mixture was cooled and water was added followed by extraction with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated. The crude biphenyl was purified by CC (alumina; CH_2Cl_2); yield 5.65 g (86%), colourless oil, solidifying, m.p. 105°C. − IR (film): $\tilde{\nu}$ = 2965, 2840, 2725, 1690 (C=O), 1605 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.89 (s, 1 H, CHO), 7.86 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.76 (d, *J* = 2.2 Hz, 1 H, Ar-H), 7.47 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.35 (d, *J* = 2.2 Hz, 1 H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.95 (d, *J* = 8.8 Hz, 1 H, Ar-H), 5.49 (s, 1 H, OCHO), 4.25−4.22 and 4.00−3.93 (m, each 2 H, OCH_2), 3.81 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 2.26−2.14 and 1.44−1.40 (m, each 1 H, HCH). − ^{13}C NMR ($CDCl_3$): δ = 190.9. 162.3, 157.5, 133.5, 131.2, 131.1, 129.6, 129.1, 128.7, 127.0, 126.4, 110.8, 101.5, 67.4, 55.9, 25.8. − MS; *m/z* (%): 328 (31) [M^+], 270 (100), 92 (11), 87 (18), 77 (30), 65 (12), 63 (15), 57 (23), 55 (12), 51 (14), 45 (18). − $C_{19}H_{20}O_5$ (328.4): calcd. C 69.50, H 6.14; found C 69.10, H 6.14.

Methyl 4-{2-[(E/Z)-2-{3-[5-(1,3-Dioxan-2-yl)-2-methoxyphenyl]-4-methoxyphenyl}-1-ethenyl]-4-methoxyphenyl}-3-methoxybenzoate (**48**): Reaction between 5.00 g (15.2 mmol) of the aldehyde **47** and 10.5 g (16.7 mmol) of the phosphonium bromide **37** according to GP 3.1, followed by filtration through an Al_2O_3 pad (CH_2Cl_2 as eluent) yielded 8.00 g (88%), colourless viscous oil. − IR (KBr): $\tilde{\nu}$ = 2945, 2830, 1720 (C=O), 1600 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.69−7.15 (m, 9 H, Ar-H), 6.97 (d, *J* = 16.2 Hz, 1 H, *E*-CH=CH), 6.95−6.73 (m, 3 H, Ar-H), 6.69 (d, *J* = 16.2 Hz, 1 H, *E*-CH=CH), 6.34 (d, *J* = 12.2 Hz, 1 H, *Z*-CH=CH), 6.15 (d, *J* = 12.2 Hz, 1 H, *Z*-CH=CH), 5.46 (s, 1 H, OCHO, *E*), 5.45 (s, 1 H, OCHO, *Z*), 4.23−4.19 and 3.97−3.94 (m, each 2 H, OCH_2), 3.93, 3.88, 3.78, 3.72, 3.70 (s, each 3 H, OCH_3), 2.22−2.12 and 1.40−1.37 (m, each 1 H, HCH). − ^{13}C NMR ($CDCl_3$): δ = 167.1, 159.5, 157.1, 156.9, 137.6, 134.9, 132.1, 131.7, 131.4, 131.1, 130.6, 130.2, 130.0, 129.8, 129.4, 129.3, 128.0, 127.6, 126.7, 126.4, 125.5, 122.0, 113.1, 111.9, 111.5, 110.8, 110.1, 101.7, 67.4, 55.9, 55.4, 52.2, 27.0. − MS; *m/z* (%): 597 (4) [M^+], 539 (18), 387 (100), 327 (49), 299 (15), 269 (26), 195 (11), 193 (29), 134 (11), 87 (28), 59 (11), 57 (15). − $C_{36}H_{36}O_8$ (596.6): calcd. C 72.46, H 6.08; found C 72.22, H 5.98.

Methyl 4-(2-{3-[5-(1,3-Dioxan-2-yl)-2-methoxyphenyl]-4-methoxyphenetyl}-4-methoxyphenyl)-3-methoxybenzoate (**49**): 8.00 g (13.4 mmol) of the (*E*/*Z*)-stilbene **48** was hydrogenated according to GP 1 (2.5 g 5%, Pd/C ethyl acetate, 3.5 bar, 24 h) in the presence of 25 ml of triethylamine. Filtering through an Al_2O_3 pad (eluting with CH_2Cl_2) yielded 7.50 g (93%) of a colourless oil. − IR (KBr): $\tilde{\nu}$ = 2935, 2830, 1720 (C=O), 1610, 1570 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.66 (dd, J_1 = 7.5 Hz, J_2 = 1.3 Hz, 1 H, Ar-H), 7.61 (d, *J* = 1.3 Hz, 1 H, Ar-H), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.24 (d, *J* = 2.2 Hz, 1 H, Ar-H), 7.15 (d, *J* = 7.5 Hz, 1 H, Ar-H), 7.05 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.91 (d, *J* = 8.8 Hz, 1 H, Ar-H), 6.86 (d, *J* = 2.2 Hz, 1 H, Ar-H), 6.83−6.78 (m, 3 H, Ar-H), 6.75 (d, *J* = 8.4 Hz, 1 H, Ar-H), 5.47 (s, 1 H, OCHO), 4.26−4.22 and 4.00−3.96 (m, each 2 H, OCH_2), 3.93, 3.80, 3.79, 3.72, 3.67 (s, each 3 H, OCH_3), 2.67 (br. s, 4 H, CH_2CH_2), 2.26−2.14 and 1.43−1.39 (m, each 1 H, HCH). − ^{13}C NMR ($CDCl_3$): δ = 167.0, 159.3, 157.5, 156.9, 155.5, 141.8, 135.6, 133.5,

131.6, 131.4, 131.0, 130.9, 130.4, 129.9, 129.3, 128.1, 127.9, 127.7, 126.2, 122.0, 114.4, 111.5, 111.4, 111.2, 110.8, 101.7, 67.3, 55.8, 55.7, 55.2, 52.1, 36.2, 35.8, 25.9. − MS; *m/z* (%): 599 (100) [M^+], 313 (35), 290 (10), 117 (19), 89 (82). − $C_{36}H_{38}O_8$ (598.7): calcd. C 72.22, H 6.40; found C 71.86, H 6.40.

3-(5-{2-[4-(Hydroxymethyl)-2-methoxyphenyl]-5-methoxyphenethyl}-2-methoxyphenyl)-4-methoxybenzaldehyde (**50**): 5.00 g (8.35 mmol) of the methyl benzoate **49** was reduced according to GP 2.2 (8.00 mmol of $LiAlH_4$). The crude benzyl alcohol still bearing a dioxane moiety was stirred in 40 ml of acetic acid/10 ml of H_2O for 2 h at 20°C. 300 ml of an ice-cold satd. Na_2CO_3 solution was added, followed by 250 ml of a satd. NaCl solution. The mixture was extracted exhaustively with diethyl ether and the organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified by CC (SiO_2; $CHCl_3$/ethyl acetate, 1:1); yield 4.00 g (93%), colourless oil. − IR (film): $\tilde{\nu}$ = 3445 (OH), 2930, 2830, 1690 (C=O), 1600, 1580 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.91 (s, 1 H, CHO), 7.86 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1 H, Ar-H), 7.68 (d, J = 2.2 Hz, 1 H, Ar-H), 7.08−7.06 (m, 2 H, Ar-H), 7.02 (d, J = 8.4 Hz, 1 H, Ar-H), 6.98 (d, J = 2.2 Hz, 1 H, Ar-H), 6.93−6.91 (m, 2 H, Ar-H), 6.83 (d, J = 2.2 Hz, 1 H, Ar-H), 6.80 (dd, J_1 = 8.0 Hz, J_2 = 2.6 Hz, 2 H, Ar-H), 6.74 (d, J = 2.2 Hz, 1 H, Ar-H), 4.66 (s, 2 H, CH_2OH), 3.83, 3.81, 3.74, 3.71 (s, each 3 H, OCH_3), 2.69 (br. s, 4 H, CH_2CH_2), 1.94 (br. s, 1 H, CH_2OH). − ^{13}C NMR ($CDCl_3$): δ = 191.1, 162.3, 159.0, 157.2, 155.3, 141.9, 141.8, 134.2, 132.8, 131.8, 131.7, 131.4, 131.2, 130.8, 129.7, 129.2, 128.9, 126.3, 118.7, 114.5, 111.2, 111.1, 110.9, 109.3, 65.3, 56.0, 55.9, 55.5, 55.2, 36.3, 36.1. − MS; *m/z* (%): 513 (5) [M^+], 330 (3), 272 (62), 258 (100), 255 (19), 241 (22), 227 (8), 213 (8), 152 (8), 89 (15), 83 (14), 61 (12), 57 (18), 45 (12). − $C_{32}H_{32}O_6$ (512.6): calcd. C 74.98, H 6.29; found C 74.75, H 6.32.

4-Methoxy-3-[2-methoxy-5-(5-methoxy-2-{2-methoxy-4-[(1,1,1-triphenylphosphonio)methyl]phenyl}phenethyl)phenyl]benzaldehyde Bromide (**51**): To a solution of 3.20 g (6.25 mmol) of benzyl alcohol **50** in 40 ml of CH_2Cl_2 was added 0.60 ml (1.70 g, 6.25 mmol) of PBr_3 and the mixture was stirred for 2 h at 20°C, washed with cold satd. $NaHCO_3$, dried ($MgSO_4$) and concentrated. The crude and unstable benzyl bromide was converted directly to the phosphonium salt according to GP 2.3 (toluene); yield 3.10 g (60%), colourless salt, m.p. 184°C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 2990, 2930, 2825, 1680 (C=O), 1600 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.84 (s, 1 H, CHO), 7.82−7.67 (m, 10 H, Ar-H), 7.57−7.51 (m, 8 H, Ar-H), 7.16−7.12 (m, 3 H, Ar-H), 6.97−6.90 (m, 2 H, Ar-H), 6.82−6.68 (m, 4 H, Ar-H), 5.35 (d, J = 14.1 Hz, 2 H, CH_2P), 3.87 (s, 3 H, OCH_3), 3.76 (s, 6 H, OCH_3) 3.69 (s, 3 H, OCH_3), 2.68 (br. s, 4 H, CH_2CH_2). − ^{13}C NMR ($CDCl_3$): δ = 191.0, 162.4, 159.1, 157.0, 155.4, 141.5, 139.5, 135.0, 134.6, 134.5, 133.9, 132.4, 132.1, 131.6, 131.1, 130.2, 130.1, 129.6, 129.2, 129.1, 128.9, 128.3, 127.7, 126.4, 125.3, 122.9, 121.5, 118.4, 117.5, 114.8, 111.3, 110.9, 56.1, 56.0, 55.9, 55.1, 35.9, 35.6, 30.6.

Isoplagiochin C Tetramethyl Ether (**52**): 2.50 g (3.00 mmol) of the phosphonium bromide **51** was subjected to a Wittig reaction according to GP 3.2. Purification by CC (SiO_2; CH_2Cl_2) afforded 1.07 g (74%), colourless viscous oil. − IR (film): $\tilde{\nu}$ = 2905, 1560, 1535 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.21−7.19 (m, 1 H, Ar-H), 7.14−7.11 (m, 2 H, Ar-H), 7.08−7.02 (m, 2 H, Ar-H), 6.98−6.96 (m, 1 H, Ar-H), 6.88−6.87 (m, 2 H, Ar-H), 6.83 (d, J = 8.4 Hz, 1 H, Ar-H), 6.79 (dd, J_1 = 8.4 Hz, J_2 = 2.7 Hz, 2 H, Ar-H), 6.73 (d, J = 8.0 Hz, 1 H, Ar-H), 6.66 and 6.60 (d, J = 11.9 Hz, each 1 H, CH=CH), 6.49 (d, J = 2.2 Hz, 1 H, Ar-H), 3.83, 3.79, 3.78, 3.74(s, each 3 H, OCH_3), 2.88−2.63 (m, 4 H, CH_2CH_2). − ^{13}C NMR ($CDCl_3$): δ = 159.0, 156.3, 155.3, 143.7, 140.1, 135.5, 133.7, 132.1, 131.4, 131.2, 131.0, 130.3, 129.6, 128.9, 127.2, 127.0, 120.8, 114.2, 113.9, 111.5, 111.0, 110.8, 110.6, 110.4, 55.8, 55.6, 55.5, 55.1, 37.9, 37.6. − MS; *m/z* (%): 478 (97) [M^+], 302 (19), 300 (24), 288 (36), 286 (41), 268 (35), 266 (28), 254 (59), 252 (55), 239 (18), 167 (16), 149 (26), 97 (12), 85 (68), 83 (100), 71 (21), 69 (16), 57 (33), 55 (16), 49 (11), 47 (26). − $C_{32}H_{30}O_4$ (478.6): calcd. C 80.31, H 6.32; found C 80.12, H 6.42.

Isoplagiochin C (**5**): 480 mg (1.00 mmol) of the tetramethyl ether **52** was cleaved according to GP 4 (8.00 mmol BBr_3, −78°C → 20°C). The crude product was isolated by extraction with CH_2Cl_2 and purified by flash chromatography on RP-18 using methanol/H_2O, 1:1; yield 363 mg (86%), colourless oil. − IR (film): $\tilde{\nu}$ = 3435 (OH), 2925, 1685, 1670, 1650, 1635, 1625, 1575, 1560, 1540, 1520, 1505, 1475, 1460, 1440, 1420, 1375, 1340, 1300, 1280, 1240, 1215, 1160, 1110, 1080, 1030, 980, 905, 820, 760 cm^{-1}. − ^1H NMR (CD_3OD): δ = 7.13 (d, J = 2.2 Hz, 1 H, Ar-H), 7.05 (dd, J_1 = 8.0 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.00 (d, J = 7.5 Hz, 1 H), 6.91 (d, J = 8.4 Hz, 1 H), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 2.6 Hz, 1 H, Ar-H), 6.76 (d, J = 8.0 Hz, 1 H, Ar-H), 6.74 (d, J = 1.8 Hz, 1 H, Ar-H), 6.71 (dd, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1 H, Ar-H), 6.68 (d, J = 2.6 Hz, 1 H, Ar-H), 6.64 (d, J = 8.4 Hz, 1 H, Ar-H), 6.59 (dd, J_1 = 8.0 Hz, J_2 2.2 Hz, 1 H, Ar-H), 6.55 (d, J = 12.0 Hz, 1 H, CH=CH), 6.48 (d, J = 2.2 Hz, 1 H, Ar-H), 6.46 (d, J = 12.0 Hz, 1 H, CH=CH), 2.60−2.51 (m, 4 H, CH_2CH_2). − ^{13}C NMR (CD_3OD): δ = 157.9, 156.2, 153.9, 152.2, 144.7, 141.1, 137.1, 134.5, 134.3, 133.4, 132.6, 131.4, 130.9, 130.7, 130.6, 129.9, 128.8, 128.6, 128.0, 127.3, 120.8, 117.7, 116.8, 113.8, 39.5, 38.6. − MS; *m/z* (%): 423 (4) [M^++1], 422 (2) [M^+], 421 (4), 255 (5), 178 (12), 165 (12), 98 (14), 95 (12), 91 (28), 89 (16), 87 (18), 83 (38), 81 (22), 78 (100), 73 (23), 71 (22), 69 (22), 57 (49), 55 (59), 51 (27), 45 (46). − $C_{28}H_{22}O_4$ (422.5): calcd. C 79.60, H 5.25; found C 79.77, H 5.32. − For reference data see ref.[16].

Isoplagiochin D Tetramethyl Ether (**53**): 480 mg (1.00 mmol) of the (*Z*)-stilbene **52** was hydrogenated according to GP 1 (ethyl acetate, 5% Pd/C, 3.5 bar, 24 h). The crude product was purified by CC (SiO_2; CH_2Cl_2); yield 438 mg (91%), colourless crystals, m.p. 134°C. − IR (KBr): $\tilde{\nu}$ = 2920, 2845, 1610, 1575 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.17−7.09 (m, 2 H, Ar-H), 7.05−7.00 (m, 2 H, Ar-H), 6.88−6.87 (m, 1 H, Ar-H), 6.85 (d, J = 8.4 Hz, 1 H, Ar-H), 6.78 (dd, J_1 = 8.4 Hz, J_2 = 2.6 Hz, 1 H, Ar-H), 6.71 (dd, J_1 = 8.4 Hz, J_2 = 2.6 Hz, 1 H, Ar-H), 6.38 (m, 1 H, Ar-H), 6.33−6.26 (m, 2 H, Ar-H), 6.21 (m, 1 H, Ar-H), 3.81, 3.77, 3.75, 3.73 (s, each 3 H, OCH_3), 2.88−2.66 (m, 4 H, CH_2CH_2), 2.54−2.45 (m, 4 H, CH_2CH_2). − ^{13}C NMR ($CDCl_3$): δ = 158.9, 156.7, 155.4, 143.6, 142.0, 135.6, 135.3, 134.4, 132.9, 131.7, 130.8, 131.4, 130.5, 129.1, 128.1, 126.8, 123.2, 120.7, 113.9, 111.2, 110.7, 110.2, 55.8, 55.7, 55.5, 55.1, 37.7, 36.9, 36.6, 36.0. − MS; *m/z* (%): 480 (100) [M^+], 241 (12), 239 (26), 225 (10), 121 (10), 111 (14), 97 (18), 95 (13), 85 (14), 83 (15), 81 (12), 71 (21), 69 (18), 57 (36), 55 (23). − $C_{32}H_{32}O_4$ (480.6): calcd. C 79.97, H 6.71; found C 79.81, H 6.83.

Isoplagiochin D (**54**): 240 mg (0.50 mmol) of the tetramethyl ether **53** was cleaved according to GP 4 (4.00 mmol BBr_3, −78°C → 20°C). The crude product was isolated by extraction with CH_2Cl_2 and purified by flash chromatography on RP-18 using methanol/H_2O, 1:1; yield 175 mg (82%), colourless viscous oil. − IR (film): $\tilde{\nu}$ = 3300 (OH), 2920, 2860, 1610, 1580, 1570, 1495, 1445, 1420, 1370, 1345, 1285, 1235, 1160, 1015, 960, 895, 865, 820, 730 cm^{-1}. − ^1H NMR (CD_3OD): δ = 7.04 (dd, J_1 = 8.0 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 7.00 (d, J = 7.5 Hz, 1 H, Ar-H), 6.96 (d, J = 8.0 Hz, 1 H, Ar-H), 6.91 (dd, J_1 = 8.0 Hz, J_2 = 2.2 Hz, 1 H, Ar-H), 6.79 (d, J = 8.4 Hz, 1 H, Ar-H), 6.78 (d, J = 2.6 Hz, 1 H, Ar-H), 6.70−6.67 (m, 3 H, Ar-H), 6.64 (d, J = 1.3 Hz, 1 H), 6.47 (d, J =

2.2 Hz, 1 H), 6.37 (d, J = 2.2 Hz, 1 H, Ar-H), 2.93−2.83 (m, 4 H, CH_2CH_2), 2.78−2.64 (m, 4 H, CH_2CH_2). − ^{13}C NMR (CD_3OD): δ = 157.7, 155.5, 153.3, 152.9, 144.8, 143.4, 136.3, 134.7, 134.3, 132.9, 132.7, 130.7, 129.7, 128.7, 128.0, 127.1, 122.1, 118.0, 117.5, 116.7, 116.5, 113.8, 39.8, 39.3, 38.8, 37.0. − MS; *m/z* (%): 424 (61) [M^+], 320 (12), 227 (14), 213 (100), 211 (81), 199 (15), 197 (15), 195 (19), 181 (11), 149 (12), 107 (70), 83 (12), 77 (11), 73 (10), 71 (15), 69 (17), 57 (36), 45 (10). − $C_{28}H_{24}O_4$ (424.5): calcd. C 79.23, H 5.70; found C 79.07, H 6.94. − For reference data see ref.[16].

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