experiment on the resulting diene.

Diels–Alder Adducts. 10: ^{1}H NMR δ 0.0 (9 H, s), 1.0 (3 H, d, J = 7 Hz), 2.85 (1 H, m), 2.90 (2 H, s), 3.62 (6 H, s), 5.80 (1 H, br s); IR 1737, 1660, 1620 cm^{-1}; MS, m/z 282 (M^+), 267, 235. **12:** ^{1}H NMR δ 0.11 (9 H, s), 1.15 (6 H, s), 2.97 (2 H, s), 3.74 (3 H, s), 3.78 (3 H, s), 5.68 (1 H, br s); IR 1735, 1620 cm^{-1}; MS, m/z 296 (M^+), 281, 73. For **2a** with methyl propiolate, both GC and NMR show that two isomers were obtained, with a 5:1 ratio. From aromatization experiment, the major product was assigned as 2-carbomethoxy-3-methyl-5-(trimethylsilyl)-1,4-cyclohexadiene (**13a**): ^{1}H NMR δ 0.1 (9 H, s), 1.10 (3 H, d, J = 7 Hz), 2.8–3.0 (3 H, m), 3.72 (3 H, s), 6.0 (1 H, br s), 7.0 (1 H, br s); MS, m/z 224 (M^+), 209. Minor product, 1-carbomethoxy-3-methyl-5-(trimethylsilyl)-1,4-cyclohexadiene (**13b**): ^{1}H NMR δ 0.2 (9 H, s), 1.10 (3 H, d, J = 7 Hz), 2.8–3.0 (3 H, m), 3.72 (3 H, s), 5.84 (1 H, br s), 6.85 (1 H, br s); MS, 224 (M^+), 209. For **4a** with methyl propiolate, both GC and NMR show two isomers obtained with a 2:1 ratio. From aromatization experiment, the major product was assigned as 2-carbomethoxy-3-methyl-4-(trimethylsilyl)-1,4-cyclohexadiene (**11b**): ^{1}H NMR δ 0.09 (9 H, s), 1.06 (3 H, d, J = 7 Hz), 2.8–3.0 (3 H, m), 3.72 (3 H, s), 5.97 (1 H, br s), 6.97 (1 H, br s); IR 1737, 1660, 1620 cm^{-1}; MS, m/z 224 (M^+), 209. The minor product, 1-carbomethoxy-3-methyl-4-(trimethylsilyl)-1,4-cyclohexadiene (**11b**): ^{1}H NMR δ 0.08 (9 H, s), 1.06 (3 H, d, J = 7 Hz), 2.8–3.0 (3 H, m), 3.72 (3 H, s), 6.05 (1 H, br s), 6.92 (1 H, br s); IR 1735, 1660, 1620 cm^{-1}; MS, m/z 224 (M^+), 209. 7-(Trimethylsilyl)-1,2,3,4,5,6,4a,8a-octahydronaphthalene (**14**): GC shows two isomers with a 1:1 ratio; NMR shows two vinyl protons at δ 5.68 and 5.78 (total 1 H), 0.8–2.2 (14 H, m), 0.0 (9 H, s); MS, m/z 208 (M^+). 8-(Trimethylsilyl)-1,2,3,4,5,6,4a,8a-octahydronaphthalene (**15**): ^{1}H NMR δ 0.0 (9 H, s), 0.8–2.2 (14 H, m, three multiple bands, pattern identical with that of the trans 8-methyl analogue[15]), 5.92 (1 H, br s); MS, m/z 208 (M^+).

Acknowledgment. We thank Dr. T. S. Chou for useful discussions and the National Science Foundation of the Republic of China for financial support.

Registry No. **1**, 104692-94-6; **2a**, 104664-80-4; **2b**, 111379-20-5; **2c**, 111379-21-6; **2d**, 111379-22-7; **3a**, 111379-23-8; **3b**, 111379-24-9; **3c**, 111379-25-0; **3d**, 111379-26-1; **3e**, 111379-27-2; **4a**, 111379-28-3; **4b**, 111379-29-4; **4c**, 111379-32-9; **4d**, 111379-48-7; **5b**, 111379-30-7; **5c**, 111379-33-0; **5d**, 111379-35-2; **6b**, 111379-31-8; **6c**, 111379-34-1; **7a**, 111379-36-3; **7b**, 111379-37-4; **8**, 111379-46-5; **9**, 111379-47-6; **10**, 106212-32-2; **11a**, 111379-38-5; **11b**, 111379-39-6; **12**, 111379-40-9; **13a**, 111379-41-0; **13b**, 111379-42-1; *cis*-**14**, 111379-43-2; *trans*-**14**, 111379-44-3; **15**, 111379-45-4; MP, 922-67-8; DMAD, 762-42-5; MeI, 74-88-4; EtI, 75-03-6; BuI, 542-69-8; $C_6H_{11}I$, 626-62-0; $I(CH_2)_4I$, 628-21-7; $I(CH_2)_5I$, 628-77-3; (*E*)-BuCH=CHC(TMS)=CH_2, 111379-49-8; (*Z*)-CH_2=CHC(TMS)=CHBr, 111379-50-1; (*E*)-CH_2=CHC(TMS)=CHBu, 111379-51-2; (*E*,*E*)-BuCH=C(TMS)=CHBu, 111379-52-3; *i*-PrI, 75-30-9.

Total Syntheses of Marchantin A and Riccardin B, Cytotoxic Bis(bibenzyls) from Liverworts

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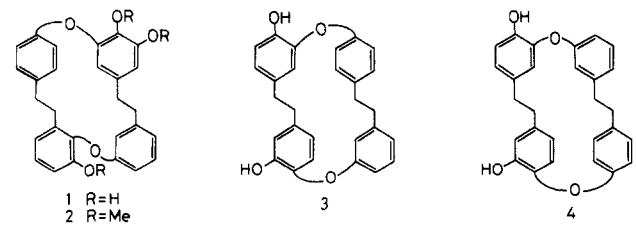
Marchantin A (**1**) and riccardin B (**3**) have been synthesized in twelve steps. The novel macrocyclic bis(bibenzyl) frameworks have been constructed by the intramolecular Wadsworth–Emmons olefination of the phosphonates **24** and **37**. The key intermediate **24** was prepared by the sequential connection of methyl 7-(4-formylphenoxy)-2,2-dimethyl-1,3-benzodioxole-5-carboxylate (**15**), diethyl [[2,3-bis(benzyloxy)phenyl]methyl]phosphonate (**16**), and *m*-bromobenzaldehyde, while **37** was synthesized from diethyl [4-[2-methoxy-5-(1,3-dioxan-2-yl)-phenoxy]benzyl]phosphonate (**32**) and methyl 3-methoxy-4-(3-formylphenoxy)benzoate (**33**). The synthesis established the structure of riccardin B as the formula **3**.

Liverworts have been shown to produce various types of natural products including terpenoids, phenolic compounds, lipids, and so on.[1] Among them, cyclic bis(bibenzyls) are particularly interesting because they constitute a new class of natural products and some of them exhibit cytotoxic activity against KB cell and P388 lymphocytic leukemia.[2] To date, more than 20 substances have been isolated from liverworts.[3,4] A representative compound of this family is marchanchin A (**1**) (Chart I), isolated as the major component of *Marchantia polymorpha* and related liverworts.[2] In this molecule, two unsymmetrically substituted bibenzyls are joined by two ether linkages forming a macrocyclic ionophor-like structure. The novel

Chart I

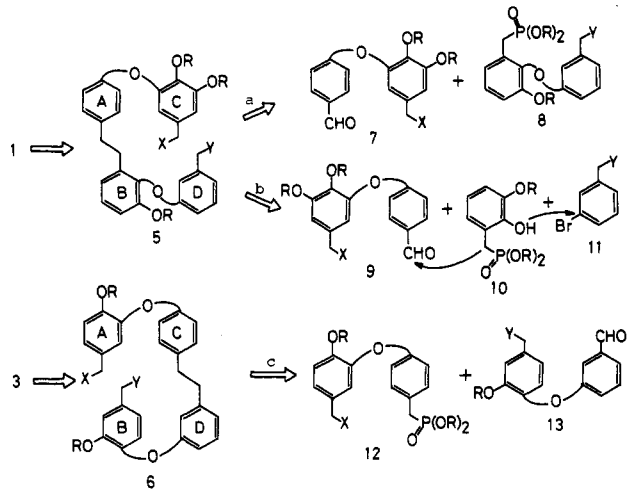


structure **1** was deduced on the basis of spectral analysis and chemical degradations and confirmed by X-ray crystallographic analysis of its trimethyl ether **2**. Riccardin B is another type of cyclic bis(bibenzyl) obtained from *Riccardia multifida*.[5] While the structure of this compound has been proposed by Asakawa et al.[5] as **3** on the basis of spectral analysis and biogenetic considerations, alternative structure **4** could not be fully excluded.

(1) Asakawa, Y. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer-Verlag: New York, 1982; Vol. 42.
(2) Asakawa, Y. *Rev. Latinoam. Quim.* **1984**, *14*(3), 109.
(3) Asakawa, Y.; Toyota, M.; Matsuda, R.; Takikawa, K.; Takemoto, T. *Phytochemistry* **1983**, *22*, 1413 and private communication from Prof. Y. Asakawa, Tokushima Bunri University.
(4) Tori, M.; Toyota, M.; Harrison, L. J.; Takikawa, K.; Asakawa, Y. *Tetrahedron Lett.* **1985**, *26*, 4735.
(5) Asakawa, Y.; Toyota, M.; Taira, Z.; Takemoto, T.; Kido, M. *J. Org. Chem.* **1983**, *48*, 2164.

0022-3263/88/1953-0072$01.50/0

Scheme I



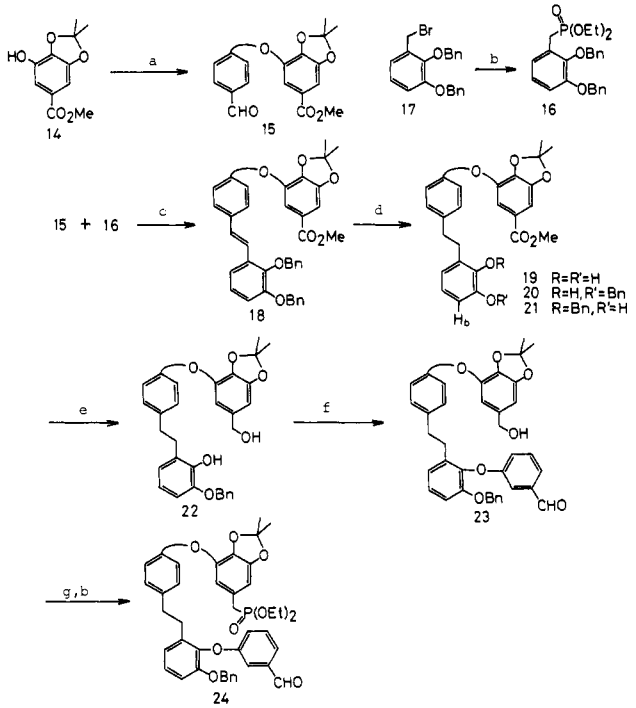
The fascinating structural features together with their biological activity stimulated our interest in this class of natural products, and we have recently achieved the total syntheses of **1** and **3**.[6,7] In this paper we disclose full details of our syntheses.

Naturally both compounds are expected to be synthesized by the cyclization of the seco compounds such as **5** and **6** as shown in Scheme I. For this final stage an intramolecular Wittig-type reaction seems to be most suitable because of its simple procedure and the wide applicability to this class of natural products. The key intermediates **5** and **6** should be prepared by the coupling of two properly functionalized diphenyl ethers (routes a and c in Scheme I), and indeed, this approach was found to be effective for the synthesis of riccardin B (**3**). However, in the case of **1**, some difficulties were encountered in the efficient synthesis of the B–D-ring segment **8** or equivalent compounds, and after some preliminary experiments, we were obliged to change the route to stepwise connection of B and D rings to the A–C-ring segment (route b).

Results

Synthesis of Marchantin A (1). According to the scheme described above, we started the synthesis from the preparation of the A–C-ring segment. The acetonide **14** of methyl gallate was coupled with *p*-bromobenzaldehyde in the presence of anhydrous potassium carbonate and cupric oxide (Scheme II). After the mixture was refluxed in pyridine for 12 h, the diphenyl ether **15** was obtained in 68% yield. The D-ring segment **16** was readily prepared in 74% yield by heating the known 2,3-bis(benzyloxy)-benzyl bromide[8] (**17**) with triethyl phosphite. Thus obtained **15** and **16** were combined by Wadsworth–Emmons olefination using potassium *tert*-butoxide in dry DMF at room temperature. The product **18** formed in 71% yield was then subjected to catalytic hydrogenation (10% Pd–C), thereby yielding the catechol derivative **19** in high yield. For the connection of the D ring, the C-3 hydroxyl group on the B ring of **19** is required to be protected. However, an attempted selective protection using potassium carbonate and a limited amount of benzyl bromide yielded always two monobenzyl ethers **20** and **21**, favoring the desired **20**. These were readily separated by column chromatography. The position of the protective group in **20** was evidenced by the observation of an NOE between H_b (6.81 ppm) and the methylene protons (5.09 ppm) of the benzyloxy group. The ester group of **20** was then reduced with lithium aluminum hydride to give the alcohol **22**. Coupling of **22** with *m*-bromobenzaldehyde required rather higher temperature and prolonged reaction time, and in pyridine–quinoline at 170 °C, the yield of the ether **23** was still limited to 42%. Reaction of **23** with thionyl bromide followed by treatment with triethyl phosphite afforded the key intermediate **24** in 60% yield.

Scheme II[a]



[a] (a) *p*-Bromobenzaldehyde–K_2CO_3, CuO, pyridine; (b) $P(OEt)_3$; (c) *t*-BuOK, DMF; (d) H_2/Pd–C; (e) $LiAlH_4$; (f) *m*-bromobenzaldehyde–K_2CO_3, CuO, pyridine–quinoline, 170 °C; (g) $SOBr_2$.

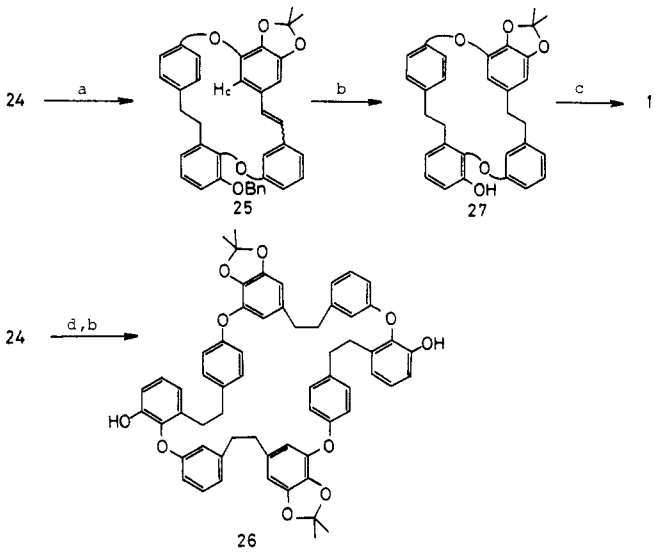
In a preliminary experiment, we observed that the intramolecular Wadsworth–Emmons olefination of **24** took place very rapidly. Therefore, the reaction was carried out simply by adding potassium *tert*-butoxide to the diluted solution (1.4 mM) of **24** in DMF at 0 °C, and the desired product **25** was obtained in 60% yield. When the reaction was carried out in 2.4 mM solution, a substantial amount of dimer was formed. The structure was determined on the basis of the ^1H NMR spectrum and mass spectrum (M^+, 960) of the hydrogenation product **26**. Although **25** was an inseparable mixture of two compounds, its ^1H NMR spectrum exhibited two aromatic proton signals at higher field (5.54 and 5.79 ppm, each doublet) in a ratio of 3:2. According to the recent analysis of the ^1H NMR spectrum of **2** by Tori et al.,[4] these signals are assignable to H_c (see structure **25**, Scheme III) shifted upfield due to the anisotropic effect of the other aromatic rings. These facts revealed both to be the cyclized product. Actually, when the mixture was catalytically hydrogenated (10% Pd–C), a single product **27** (marchantin A acetonide) was obtained in 87% yield. Thus, the above product **25** was confirmed to be a cis, trans mixture of double-bond isomers. Simple acid treatment of **27** afforded marchantin A (**1**). The identity was confirmed by comparison of TLC,

(6) Kodama, M.; Shiobara, Y.; Matsumura, K.; Sumitomo, H. *Tetrahedron Lett.* **1985**, *26*, 877.

(7) (a) Shiobara, Y.; Sumitomo, H.; Tsukamoto, M.; Harada, C.; Kodama, M. *Chem. Lett.* **1985**, 1587. (b) For another synthesis of riccardin B, see: Iyoda, M.; Sakaitani, M.; Otsuka, H.; Oda, M. *Tetrahedron Lett.* **1985**, *26*, 4777.

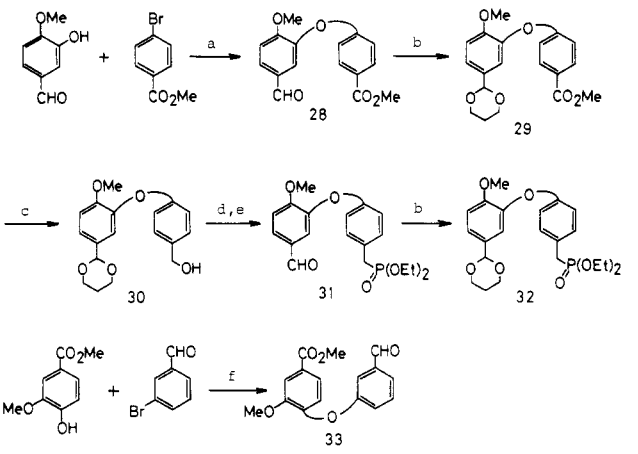
(8) Marchand, B.; Benezra, C. *J. Med. Chem.* **1982**, *25*, 650.

Scheme III[a]



[a] (a) *t*-BuOK, DMF, 1.4 mM; (b) H_2/Pd–C; (c) HCl; (d) *t*-BuOK, DMF, 2.8 mM.

Scheme IV[a]



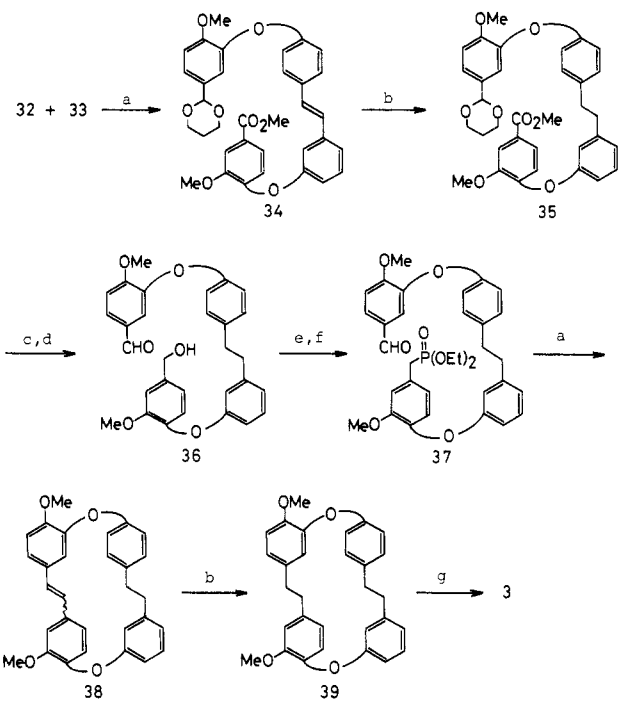
[a] (a) K_2CO_3, CuO, pyridine; (b) 1,3-propanediol, *p*-TsOH; (b) $LiAlH_4$; (d) $SOBr_2$; (e) $P(OEt)_3$; (f) K_2CO_3, CuO, pyridine–quinoline, 170 °C.

IR, and ^1H NMR spectra with those of an authentic specimen.

Synthesis of Riccardin B (3). Once the methodology has been established, the synthesis of other members of this class of bis(bibenzyls) is straightforward. The segments corresponding to **12** and **13** were readily prepared by a sequence of reactions similar to that described above. Thus, isovanillin was first allowed to react with methyl *p*-bromobenzoate in the presence of potassium carbonate and cupric oxide to give the diphenyl ether **28** in 79% yield (Scheme IV). Protection of the aldehyde group in **28** afforded the acetal **29**, which was reduced to the alcohol **30** in 75% yield. Bromination followed by the reaction with triethyl phosphite yielded the phosphonate **31** in 86% yield. Protection of the aldehyde group furnished the upper half segment **32**. The B–D-ring segment **33** was accessible by simple coupling of methyl 4-hydroxy-3-methoxybenzoate and *m*-bromobenzaldehyde (K_2CO_3–CuO in pyridine–quinoline at 170 °C).

Condensation of **32** and **33** was effected with potassium *tert*-butoxide in dry DMF (Scheme V). The product **34** obtained in 84% yield was hydrogenated over 5% Pd–C to the saturated compound **35**. Reduction of **35** with lithium aluminum hydride followed by treatment with acid

Scheme V[a]



[a] (a) *t*-BuOK, DMF; (b) H_2/PtO_2; (c) $LiAlH_4$; (d) HCl; (e) $SOBr_2$; (f) $P(OEt)_3$; (g) BBr_3.

yielded the alcohol **36**, which was converted to the diethyl phosphonate **37**. The overall yield in five steps was 62%.

The intramolecular Wadsworth–Emmons olefination was carried out in the same manner described above, and the desired product **38** was obtained in 89% yield. The ^1H NMR spectrum of **38** showed the presence of methoxy signals as two sets of two singlets in the ratio of 1:3 respectively, indicating **38** to be again a mixture of cis and trans isomers. In addition, two aromatic proton signals appeared at abnormally high field (5.28 and 5.59 ppm), which revealed that the cyclization took place as expected. Hydrogenation of **38** afforded riccardin B dimethyl ether (**39**). The methoxy groups in **39** were finally cleaved with boron tribromide to give riccardin B (**3**). The IR and ^1H NMR spectra of the synthetic material were identical with those of the natural product.

In conclusion, we have synthesized two novel macrocyclic bis(bibenzyls) by using an intramolecular Wadsworth–Emmons olefination as a key step. The present synthesis unequivocally established the structure of riccardin B.

Experimental Section

General. Nuclear magnetic resonance spectra (^1H NMR) were recorded on a JEOL GX-400 instrument in $CDCl_3$ solution with $(CH_3)_4Si$ as an internal standard. Infrared spectra (IR) were taken on a Shimadzu IR-27G spectrometer as a liquid film (neat) or as a suspension in Nujol on sodium chloride plates. Mass spectra (MS) were measured on a Shimadzu LKB-9000 spectrometer. High-resolution mass spectra (HRMS) were obtained on a JEOL HX-100 spectrometer. Melting points were determined on a Yanagimoto micro melting-point apparatus and are uncorrected. Thin-layer chromatography was performed on Merck Kieselgel $60F_{254}$ precoated silica gel plates, and spots were visualized by irradiation with ultraviolet light (254 nm) and/or by spraying with 2,4-dinitrophenylhydrazine–sulfuric acid followed by heating to 120 °C. Column chromatography was performed on silica gel (Merck SG-60, 70–230 mesh) or neutral alumina (Merck aluminum oxide 90, activity grade II–III).

Tetrahydrofuran (THF) and ether were distilled from lithium aluminum hydride ($LiAlH_4$) prior to use. Dimethylformamide (DMF) and pyridine were distilled from calcium hydride. Di-

chloromethane (CH_2Cl_2) was distilled from phosphorus pentoxide.

Methyl 7-(4-Formylphenoxy)-2,2-dimethyl-1,3-benzodioxole-5-carboxylate (15). To a solution of the acetonide **14** (11.3 g, 0.05 mol) and *p*-bromobenzaldehyde (14.0 g, 0.076 mol) in 100 mL of dry pyridine under argon were added anhydrous potassium carbonate (14.0 g, 0.10 mol) and cupric oxide (6.98 g, 0.08 mol). The mixture was heated under reflux for 12 h with vigorous stirring. After pyridine was evaporated in vacuo, 300 mL of ethyl acetate was added to the residue. The precipitate was filtered off and washed with ethyl acetate. The combined filtrates were washed with brine (50 mL), dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on 200 g of silica gel (CH_2Cl_2) to give 11.3 g (68%) of solid. Recrystallization from ethanol afforded **15** as colorless prisms: mp 93–94 °C; IR (Nujol) 1730, 1698 cm^{-1}; ^1H NMR δ 1.70 (s, 6 H), 3.87 (s, 3 H), 7.08 (d, J = 8.7 Hz, 2 H), 7.32 (d, J = 1.3 Hz, 1 H), 7.42 (d, J = 1.3 Hz, 1 H), 7.86 (d, J = 8.8 Hz, 2 H), 9.94 (s, 1 H); MS, m/z 328 (M^+), 313 (base peak (b.p.)). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.88. Found: C, 65.65; H, 4.86.

Diethyl [[2,3-Bis(benzyloxy)phenyl]methyl]phosphonate (16). A mixture of **17** (7.66 g, 0.02 mol) and triethyl phosphite (3.32 g, 0.02 mol) was heated at 80 °C with stirring for 3 h. The reaction mixture was directly chromatographed on 100 g of silica gel ($CHCl_3$) to afford **8** (6.48 g, 74%) as a colorless oil: IR (neat) 1586, 1270, 1050 cm^{-1}; ^1H NMR δ 1.23 (t, J = 7.6 Hz, 6 H), 3.22 (d, J = 22.4 Hz, 2 H), 4.02 (quintet, J = 7.6 Hz, 4 H), 5.12 (br s, 4 H), 6.91 (d, J = 7.8, 1 H), 6.99 (t, J = 7.8, 1 H), 7.02 (d, J = 7.8, 1 H), 7.30–7.46 (m, 10 H); MS, m/z 440 (M^+), 91 (b.p.); HRMS calcd for $C_{25}H_{29}O_5P$ m/z 440.1752, found 440.1736.

Methyl (*E*)-7-[4-[2-[2,3-Bis(benzyloxy)phenyl]ethenyl]-phenoxy]-2,2-dimethyl-1,3-benzodioxole-5-carboxylate (18). To an ice-cooled solution of **16** (13.0 g, 0.03 mol) in 130 mL of dry DMF under argon was added potassium *tert*-butoxide (4.31 g, 0.038 mol) in one portion. After 15 min at 0 °C, a solution of **15** (9.71 g, 0.03 mol) in 20 mL of dry DMF was added to the resulting yellow solution over 30 min. After being stirred at room temperature for 12 h, the reaction mixture was poured into 600 mL of ice–water, acidified to pH 4 with 2 N HCl, and extracted with ethyl acetate. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on 120 g of silica gel (1:1 hexane–CH_2Cl_2) to give **18** (12.9 g, 71%) as a viscous colorless oil: IR (neat) 1718, 1632, 1576 cm^{-1}; ^1H NMR δ 1.72 (s, 6 H), 3.84 (s, 3 H), 5.04 (s, 2 H), 5.15 (s, 2 H), 6.90–7.02 (m, 4 H), 7.04 (d, J = 16.6 Hz, 1 H), 7.23–7.48 (m, 16 H); MS, m/z 614 (M^+), 91 (b.p.); HRMS calcd for $C_{39}H_{34}O_7$ m/z 614.2304, found 614.2299.

Methyl 7-[4-[2-(2,3-Dihydroxyphenyl)ethyl]phenoxy]-2,2-dimethyl-1,3-benzodioxole-5-carboxylate (19). Benzyl ether **18** (6.09 g, 0.01 mol) in methanol–ethyl acetate (2:1, 60 mL) was hydrogenated over 10% Pd–C (0.6 g) under atmospheric pressure at room temperature. The catalyst was filtered off, and the filtrate was evaporated in vacuo to afford **19** (4.15 g, 96%) as colorless needles (methanol): mp 142–144 °C; IR (Nujol) 3480, 3390, 1696, 1600 cm^{-1}; ^1H NMR δ 1.73 (s, 6 H), 2.91 (br s, 4 H), 3.84 (s, 3 H), 6.66–6.74 (m, 3 H), 6.94 (d, J = 8.8 Hz, 2 H), 7.10 (d, J = 8.8 Hz, 2 H), 7.19 (s, 2 H); MS, m/z 436 (M^+), 313 (b.p.). Anal. Calcd for $C_{25}H_{24}O_7$: C, 68.81; H, 5.50. Found: C, 68.65; H, 5.53.

Benzylation of 19. To a mixture of **19** (4.15 g, 9.52 mol) and anhydrous potassium carbonate (1.32 g, 9.56 mmol) in 80 mL of dry acetone was added benzyl bromide (1.13 mL, 9.52 mmol) under argon. After being refluxed with vigorous stirring overnight, the mixture was filtered and the filtrate was concentrated in vacuo. The residue was taken up in 200 mL of ethyl acetate, and the solution was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 120 g of silica gel. Elution with hexane–CH_2Cl_2 (1:1) yielded **20** (3.35 g, 67%) as colorless prisms (hexane–ethyl acetate): mp 101–102 °C. Further elution with hexane–CH_2Cl_2 (1:2) yielded **21** (0.99 g, 20%) as a colorless oil. **20**: IR (neat) 3540, 1719, 1633, 1610 cm^{-1}; ^1H NMR δ 1.72 (s, 6 H), 2.92 (m, 4 H), 3.81 (s, 3 H), 5.09 (s, 2 H), 5.82 (s, OH), 6.71 (dd, J = 7.3, 2.0 Hz, 1 H), 6.74 (t, J = 7.3 Hz, 1 H), 6.81 (dd, J = 7.3, 2.0 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.15 (d, J = 8.8 Hz, 2 H), 7.21 (d, J = 1.5 Hz, 1 H), 7.26 (d, J = 1.5 Hz, 1 H), 7.37–7.46 (m, 5 H); MS, m/z 526 (M^+), 91 (b.p.). Anal. Calcd for $C_{32}H_{30}O_7$: C, 72.72; H, 5.68. Found: C, 72.52; H, 5.79. **21**: IR (neat) 3450, 1720, 1630, 1605 cm^{-1}; ^1H NMR δ 1.71 (s, 6 H), 2.92 (br s, 4 H), 3.81 (s, 3 H), 4.85 (s, 2 H), 6.75 (dd, J = 8.0, 2.0 Hz, 1 H), 6.82 (dd, J = 8.0, 2.0 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 6.96 (t, J = 8.0 Hz, 1 H), 7.06 (d, J = 8.8 Hz, 2 H), 7.21 (d, J = 1.8 Hz, 1 H), 7.26 (d, J = 1.8 Hz, 1 H), 7.35–7.42 (m, 5 H); MS, m/z 526 (M^+), 91 (b.p.); HRMS calcd for $C_{32}H_{30}O_7$ m/z 526.1992, found 526.1977.

7-[4-[2-[2-Hydroxy-3-(benzyloxy)phenyl]ethyl]phenoxy]-2,2-dimethyl-1,3-benzodioxole-5-methanol (22). To an ice-cooled suspension of $LiAlH_4$ (242 mg, 6.37 mmol) in dry THF (100 mL) under argon was added **20** (3.35 g, 6.37 mmol) in 10 mL of dry THF over 15 min with stirring. After being stirred overnight at room temperature, the mixture was poured into 400 mL of ice–water, acidified with 2 N HCl, and then extracted with ethyl acetate. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 30 g of silica gel (CH_2Cl_2) to afford **22** (2.98 g, 94%) as a viscous colorless oil: IR (neat) 3540, 3400, 1632, 1608 cm^{-1}; ^1H NMR δ 1.65 (br s, OH), 1.69 (s, 6 H), 2.91 (m, 4 H), 4.48 (br s, 2 H), 5.09 (s, 2 H), 5.80 (br s, OH), 6.45 (br s, 1 H), 6.58 (br s, 1 H), 6.70 (dd, J = 7.8, 2.4 Hz, 1 H), 6.74 (t, J = 7.8 Hz, 1 H), 6.81 (dd, J = 7.8, 2.4 Hz, 1 H), 6.93 (d, J = 8.3 Hz, 2 H), 7.14 (d, J = 8.3 Hz, 2 H), 7.30–7.48 (m, 5 H); MS, m/z 480 ($M^+ - H_2O$), 91 (b.p.); HRMS calcd for $C_{31}H_{28}O_5$ m/z 480.9663, found 480.9696.

Coupling of 22 with *m*-Bromobenzaldehyde. To a solution of **22** (2.98 g, 5.98 mmol) and *m*-bromobenzaldehyde (1.44 g, 7.78 mmol) in a mixture of dry pyridine (20 mL) and dry quinoline (10 mL) under argon were added anhydrous potassium carbonate (1.66 g, 12.0 mmol) and cupric oxide (0.83 g, 10.4 mmol). The mixture was vigorously stirred at 170 °C for 6 h. The crude product obtained by the same workup as described in the preparation of **15** was chromatographed on 40 g of silica gel (CH_2Cl_2) to give **23** (1.56 g, 42%) as a viscous colorless oil: IR (neat) 3430, 1698, 1632, 1606 cm^{-1}; ^1H NMR δ 1.67 (s, 6 H), 1.80 (br s, OH), 2.84 (m, 4 H), 4.48 (s, 2 H), 4.98 (s, 2 H), 6.44 (br s, 1 H), 6.59 (br s, 1 H), 6.85–6.92 (m, 4 H), 7.00–7.05 (m, 3 H), 7.10 (t, J = 7.8 Hz, 1 H), 7.16–7.23 (m, 5 H), 7.28 (br s, 1 H), 7.43 (t, J = 7.8 Hz, 1 H), 7.51 (d, J = 7.8 Hz, 1 H), 9.90 (s, 1 H); MS, m/z 602 (M^+), 91 (b.p.); HRMS calcd for $C_{38}H_{34}O_7$ m/z 602.2314, found 602.2289.

Diethyl [[7-[4-[2-[3-(Benzyloxy)-2-(3-formylphenoxy)-phenyl]ethyl]phenoxy]-2,2-dimethyl-1,3-benzodioxol-5-yl]-methyl]phosphonate (24). To an ice-cooled solution of **23** (1.30 g, 2.16 mmol) in 40 mL of dry benzene was added thionyl bromide (0.18 mL, 2.32 mmol). After being stirred for 1 h, the reaction mixture was poured into ice–water and extracted with benzene. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent in vacuo afforded the crude bromide, which was used for the next step without purification. A mixture of the bromide (1.310 g, 1.97 mmol) and triethyl phosphite (358 mg, 2.16 mmol) was heated at 80 °C for 2.5 h. The reaction mixture was directly chromatographed on 30 g of silica gel ($CHCl_3$) to afford **24** (0.93 g, 60% from **23**) as a viscous colorless oil: IR (neat) 1700, 1635, 1610, 1245, 1050, 1028 cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.6 Hz, 6 H), 1.66 (s, 6 H), 2.84 (br s, 4 H), 2.97 (d, J = 20.8 Hz, 2 H), 4.01 (quintet, J = 7.6 Hz, 4 H), 4.97 (s, 2 H), 6.35 (br s, 1 H), 6.53 (br s, 1 H), 6.84–6.90 (m, 3 H), 6.91 (br d, J = 7.8 Hz, 1 H), 7.00–7.05 (m, 3 H), 7.11 (t, J = 7.8 Hz, 1 H), 7.16–7.24 (m, 5 H), 7.29 (br s, 1 H), 7.44 (t, J = 7.8 Hz, 1 H), 7.52 (br d, J = 7.8 Hz, 1 H), 9.90 (s, 1 H); MS, m/z 722 (M^+), 91 (b.p.); HRMS calcd for $C_{42}H_{43}O_9P$ m/z 722.2644, found 722.2678.

Intramolecular Wadsworth–Emmons Olefination of 24. To an ice-cooled solution of **24** (100 mg, 0.14 mmol) in 100 mL of dry DMF (1.4 mM solution) under argon was added potassium *tert*-butoxide (18.6 mg, 0.17 mmol) in one portion. After being stirred at room temperature for 30 min, the reaction mixture was poured into ice–water (350 mL) and extracted with ethyl acetate. The combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 10 g of silica gel (1:1 hexane–CH_2Cl_2) to afford the cyclized product **25** (47 mg, 60%) as a viscous colorless oil: ^1H NMR δ 1.74 and 1.75 (s, 3 H), 4.99 and 4.96 (s, 3 H), 5.79 and 5.54 (br s, 1 H) (each ca. 3:2 ratio); MS, m/z 568 (M^+), 420, 419, 255, 107, 92, 91 (b.p.), 65.

Catalytic Hydrogenation of 25. Compound **25** (47 mg) in a mixture of methanol (2 mL) and ethyl acetate (2 mL) was

hydrogenated over 5% Pd–C (30 mg) under atmospheric pressure at room temperature. After the catalyst was filtered off, the filtrate was concentrated in vacuo. The residue was chromatographed on 10 g of silica gel (1:1 hexane–CH_2Cl_2) to give **27** (35 mg, 87%), which was crystallized from methanol to colorless needles: mp 201–202 °C; IR (neat) 3520, 1632, 1612, 1590 cm^{-1}; ^1H NMR δ 1.72 (s, 6 H), 2.76 (t-like, 2 H), 2.83 (t-like, 2 H), 3.00 (br s, 4 H), 5.14 (d, J = 1.5 Hz, 1 H), 6.31 (d, J = 1.5 Hz, 1 H), 6.43 (br d, J = 7.8 Hz, 1 H), 6.57 (br d, J = 7.8 Hz, 1 H), 6.58 (br s, 1 H), 6.63 (d, J = 8.8 Hz, 2 H), 6.86 (dd, J = 7.8, 1.5 Hz, 1 H), 6.91 (d, J = 8.8 Hz, 2 H), 7.01 (t, J = 7.8 Hz, 1 H), 7.02 (dd, J = 7.8, 1.5 Hz, 1 H), 7.15 (t, J = 7.8 Hz, 1 H); MS, m/z 480 (M^+, b.p.); HRMS calcd for $C_{31}H_{28}O_5$ m/z 480.1936, found 480.1929.

The Dimer 26. The phosphonate **24** (80 mg, 0.11 mmol) in 40 mL of dry DMF (2.8 mM) was similarly treated with potassium *tert*-butoxide (15 mg, 0.11 mmol). The reaction mixture was worked up as usual. The product (35 mg) which showed two major spots on TLC was hydrogenated over 5% Pd–C as described above and then chromatographed on 10 g of silica gel. Elution with hexane–CH_2Cl_2 (1:1) afforded **27** (19 mg, 36%) as colorless crystals. Further elution with CH_2Cl_2 afforded the dimer **26** (9 mg, 17%) as a viscous colorless oil: IR (neat) 3538, 1632, 1609 cm^{-1}; ^1H NMR δ 1.68 (s, 12 H), 2.66 (br s, 8 H), 2.73 (m, 8 H), 6.17 (d, J = 1.5 Hz, 2 H), 6.38 (d, J = 1.5 Hz, 2 H), 6.67 (br d, J = 7.8 Hz, 2 H), 6.74 (br s, 2 H), 6.78–6.83 (m, 8 H), 6.89 (d, J = 7.8 Hz, 4 H), 6.92 (dd, J = 7.8, 1.5 Hz, 2 H), 7.07 (t, J = 7.8 Hz, 2 H), 7.16 (t, J = 7.8 Hz, 2 H); MS, m/z 960 (M^+, b.p.), 480, 465, 315, 307, 269, 267, 255, 229, 227, 225, 215, 213, 212, 211, 210, 198, 163.

Marchantin A. To a solution of **27** (35 mg) in 2 mL of methanol was added 6 N HCl (2 mL), and the mixture was heated under reflux for 1 h under argon. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 10 g of silica gel to afford 25 mg (80%) of a colorless oil: IR (neat) 3400–3550 (br), 3030, 2930, 2865, 1605, 1519, 1468, 1448, 1213, 1026, 753 cm^{-1}; ^1H NMR δ 2.72–2.83 (m, 4 H), 2.96–3.04 (m, 4 H), 4.92 (s, OH), 5.12 (d, J = 2.0 Hz, 1 H), 5.39 (s, OH), 5.40 (s, OH), 6.41 (br d, J = 8.0 Hz, 1 H), 6.47 (d, J = 2.0 Hz, 1 H), 6.55 (br d, J = 8.0 Hz, 1 H), 6.58 (br s, 1 H), 6.59 (d, J = 8.2 Hz, 2 H), 6.87 (dd, J = 8.0, 1.5 Hz, 1 H), 6.93 (d, J = 8.2 Hz, 2 H), 6.99 (t, J = 8.0 Hz, 1 H), 7.01 (dd, J = 8.0, 1.5 Hz, 1 H), 7.15 (t, J = 8.0 Hz, 1 H). These spectral data were identical with those of natural marchantin A.

Methyl 4-(2-Methoxy-5-formylphenoxy)benzoate (28). To a solution of 3-hydroxy-4-methoxybenzaldehyde (9.1 g, 0.06 mol) and methyl *p*-bromobenzoate (10.8 g, 0.05 mol) in 100 mL of dry pyridine under argon were added anhydrous potassium carbonate (13.8 g, 0.1 mol) and cupric oxide (6.9 g, 0.087 mol). The mixture was heated under reflux for 16 h with vigorous stirring. The crude product obtained by the same workup as described in the preparation of **6** was chromatographed on 200 g of silica gel (CH_2Cl_2) to afford **28** (11.3 g, 79%). Recrystallization from hexane–ethyl acetate gave colorless needles: mp 87–89 °C; IR (Nujol) 1715, 1690, 1602, 1580, 1508 cm^{-1}; ^1H NMR δ 3.89 (s, 3 H), 3.90 (s, 3 H), 6.93 (d, J = 8.7 Hz, 2 H), 7.14 (d, J = 8.1 Hz, 1 H), 7.59 (d, J = 2.0 Hz, 1 H), 7.75 (dd, J = 8.1, 2.0 Hz, 1 H), 8.00 (d, J = 8.7 Hz, 2 H), 9.87 (s, 1 H); MS, m/z 286 (M^+, b.p.). Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.92. Found: C, 66.92; H, 4.85.

Methyl 4-[2-Methoxy-5-(1,3-dioxan-2-yl)phenoxy]benzoate (29). A solution of **28** (10.0 g, 0.035 mol), 1,3-propanediol (10 g, 0.13 mol) and *p*-toluenesulfonic acid (50 mg) was heated under reflux for 2 h, during which time water was removed by a Dean–Stark water separator. The reaction mixture was then washed with saturated $NaHCO_3$ solution. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to afford **29** (11.7 g, 97%) as a colorless oil: IR (neat) 1720, 1610, 1590, 1510 cm^{-1}; ^1H NMR δ 1.42 (m, 1 H), 2.20 (m, 1 H), 3.78 (s, 3 H), 3.88 (s, 3 H), 3.98 (m, 2 H), 4.23 (m, 2 H), 5.44 (s, 1 H), 6.91 (d, J = 9.0 Hz, 2 H), 7.00 (d, J = 8.5 Hz, 1 H), 7.22 (d, J = 2.0 Hz, 1 H), 7.33 (dd, J = 8.5, 2.0 Hz, 1 H), 7.96 (d, J = 9.0 Hz, 2 H); MS, m/z 344 (M^+, b.p.); HRMS calcd for $C_{19}H_{20}O_6$ m/z 344.9977, found 344.9954.

Reduction of 29 with Lithium Aluminum Hydride. To an ice-cooled suspension of $LiAlH_4$ (1.2 g, 0.032 mol) in 200 mL of dry ether was added **29** (11.6 g, 0.034 mol) in 10 mL of dry ether over 40 min with stirring. The mixture was stirred overnight at room temperature, and then excess reagent was decomposed by careful addition of water. The precipitate formed was dissolved by adding 1 N NaOH, and the solution was extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 300 g of alumina (CH_2Cl_2) to give **30** (8.16 g, 77%). Recrystallization from hexane–ethyl acetate afforded colorless needles: mp 83–86 °C; IR (neat) 3480, 1610, 1592, 1584, 1510 cm^{-1}; ^1H NMR δ 1.40 (m, 1 H), 2.18 (m, 1 H), 3.82 (s, 3 H), 3.95 (s, 3 H), 4.20 (m, 2 H), 4.61 (s, 2 H), 5.40 (s, 1 H), 6.92 (d, J = 8.6 Hz, 2 H), 6.98 (d, J = 8.6 Hz, 1 H), 7.11 (d, J = 1.8 Hz, 1 H), 7.25 (dd, J = 8.6, 1.8 Hz, 1 H), 7.27 (d, J = 8.6 Hz, 2 H); MS, m/z 316 (M^+, b.p.). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.35; H, 6.33. Found: C, 68.07; H, 6.37.

Diethyl [4-(2-Methoxy-5-formylphenoxy)benzyl]phosphonate (31). To an ice-cooled solution of **30** (7.34 g, 0.023 mol) in 200 mL of dry benzene was added thionyl bromide (1.8 mL, 0.023 mol) in one portion. After being stirred for 20 min, the reaction mixture was poured into ice–water (100 mL) and layers were separated. The benzene layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was used for the next reaction without purification. A mixture of the bromide (7.0 g, 0.022 mol) prepared above and triethyl phosphite (3.86 g, 0.023 mol) was heated at 90 °C for 1.5 h. The reaction mixture was directly chromatographed on 150 g of silica gel (CH_2Cl_2) to give **31** (7.55 g, 86%) as a colorless oil: IR (neat) 1682, 1605, 1510, 1220, 1050, 1020 cm^{-1}; ^1H NMR δ 1.25 (t, J = 7.1 Hz, 6 H), 3.12 (d, J = 21.5 Hz, 2 H), 3.94 (s, 3 H), 6.92 (d, J = 8.6 Hz, 2 H), 7.10 (d, J = 8.4 Hz, 1 H), 7.26 (dd, J = 8.6, 2.7 Hz, 2 H), 7.27 (d, J = 8.6 Hz, 2 H), 7.42 (d, J = 2.0 Hz, 1 H), 7.65 (dd, J = 8.4, 2.0 Hz, 1 H), 9.80 (s, 1 H); MS, m/z 378 (M^+), 241 (b.p.); HRMS calcd for $C_{19}H_{23}O_6P$ m/z 378.1256, found 378.1237.

Diethyl [4-[2-Methoxy-5-(1,3-dioxan-2-yl)phenoxy]benzyl]phosphonate (32). By the same procedure as described in the preparation of **29**, the aldehyde **31** (7.55 g) was converted into the acetal **32** in 95% yield as a colorless oil: IR (neat) 1605, 1582, 1505, 1220, 1040, 1020 cm^{-1}; ^1H NMR δ 1.24 (t, J = 6.6 Hz, 6 H), 2.1–2.2 (m, 1 H), 3.10 (d, J = 21.2 Hz, 2 H), 3.80 (s, 3 H), 5.40 (s, 1 H), 6.86 (d, J = 8.1 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 1 H), 7.11 (d, J = 1.5 Hz, 1 H), 7.20 (dd, J = 8.8, 2.7 Hz, 1 H), 7.25 (dd, J = 8.8, 1.5 Hz, 2 H); MS, m/z 436 (M^+), 241 (b.p.); HRMS calcd for $C_{22}H_{29}O_7P$ m/z 436.9823, found 436.9812.

Methyl 3-Methoxy-4-(3-formylphenoxy)benzoate (33). To a solution of methyl 4-hydroxy-3-methoxybenzoate (9.1 g, 0.05 mol) and *m*-bromobenzaldehyde (12.0 g, 0.065 mol) in a mixture of dry pyridine (70 mL) and dry quinoline (30 mL) under argon were added anhydrous potassium carbonate (13.8 g, 0.1 mol) and cupric oxide (6.9 g, 0.087 mol). The mixture was heated at 170 °C with vigorous stirring for 16 h. The product obtained by the same workup as described in the preparation of **23** was chromatographed on 200 g of silica gel (CH_2Cl_2) to afford **33** (7.0 g, 49%). Recrystallization from hexane–ethyl acetate gave colorless needles: mp 96–98 °C; IR (Nujol) 1722, 1695, 1588, 1502 cm^{-1}; ^1H NMR δ 3.88 (s, 3 H), 3.93 (s, 3 H), 7.00 (d, J = 8.4 Hz, 1 H), 7.26 (ddd, J = 7.7, 2.7, 1.3 Hz, 1 H), 7.42 (dd, J = 2.7, 1.3 Hz, 1 H), 7.50 (t, J = 7.7 Hz, 1 H), 7.61 (dt, J = 7.7, 1.3 Hz, 1 H), 7.66 (dd, J = 8.4, 2.0 Hz, 1 H), 7.71 (d, J = 2.0 Hz, 1 H), 9.95 (s, 1 H); MS, m/z 286 (M^+, b.p.); HRMS calcd for $C_{16}H_{14}O_5$ m/z 286.9887, found 286.9901.

Methyl 3-Methoxy-4-[3-[2-[4-[2-methoxy-5-(1,3-dioxan-2-yl)phenoxy]phenyl]ethenyl]phenoxy]benzoate (34). To an ice-cooled solution of **32** (3.98 g, 9.13 mmol) in 50 mL of dry DMF was added, under argon, potassium *tert*-butoxide (0.95 g, 8.5 mmol) in one portion. The resulting yellow solution was stirred at room temperature for 30 min, and then a solution of **33** (2.0 g, 6.99 mmol) in 5 mL of dry DMF was added slowly. After being stirred for an additional 1 h at the same temperature, the reaction mixture was poured into ice–water (250 mL) and extracted with ether. The combined ether layers were washed successively with brine and saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 200 g of alumina (1:1 benzene–CH_2Cl_2) to afford **34** (4.35 g, 84%) as a viscous colorless oil: IR (neat) 1715, 1602, 1590, 1580, 1504 cm^{-1}; ^1H NMR δ 1.40 (m, 1 H), 2.18 (m, 1 H), 3.81 (s, 3 H), 3.91 (s, 3 H), 3.93 (s, 3 H), 3.95 (m, 2 H), 4.21 (m, 2 H), 5.40 (s, 1 H), 6.88 (br d, J = 7.7 Hz, 1 H), 6.91 (d, J = 8.7 Hz, 2 H), 6.92 (d, J =

8.4 Hz, 1 H), 6.93 (d, J = 16.1 Hz, 1 H), 6.98 (d, J = 8.4 Hz, 1 H), 7.02 (d, J = 16.1 Hz, 1 H), 7.14 (br s, 1 H), 7.15 (d, J = 2.0 Hz, 1 H), 7.24 (br d, J = 7.7 Hz, 1 H), 7.27 (dd, J = 8.4, 2.0 Hz, 1 H), 7.30 (t, J = 7.7 Hz, 1 H), 7.39 (d, J = 8.7 Hz, 2 H), 7.62 (dd, J = 8.4, 2.0 Hz, 1 H), 7.68 (d, J = 2.0 Hz, 1 H); MS, m/z 568 (M^+, b.p.). Anal. Calcd for $C_{34}H_{32}O_8$: C, 71.82; H, 5.67. Found: C, 71.85; H, 5.63.

Catalytic Reduction of 34. The ester **34** (4.25 g) was hydrogenated over platinum(IV) oxide (0.2 g) in a mixture of methanol (30 mL) and ethyl acetate (10 mL) at atmospheric pressure. The catalyst was filtered off, and the filtrate was evaporated in vacuo to afford **35** (4.26 g, quantitative) as a viscous colorless oil: IR (neat) 1715, 1600, 1575, 1502 cm^{-1}; ^1H NMR δ 1.40 (m, 1 H), 2.05 (br s, OH), 2.18 (m, 1 H), 2.87 (br s, 4 H), 3.82 (s, 3 H), 3.91 (s, 3 H), 3.94 (s, 3 H), 3.96 (m, 2 H), 4.20 (m, 2 H), 6.82–6.89 (m, 5 H), 6.93 (br d, J = 7.8 Hz, 1 H), 6.98 (d, J = 8.0 Hz, 1 H), 7.05 (d, J = 7.8 Hz, 1 H), 7.06 (br d, J = 7.8 Hz, 1 H), 7.09 (d, J = 2.0 Hz, 1 H), 7.23 (t, J = 7.8 Hz, 1 H), 7.25 (dd, J = 7.8, 2.0 Hz, 1 H), 7.61 (dd, J = 8.0, 2.0 Hz, 1 H), 7.67 (d, J = 2.0 Hz, 1 H); MS, m/z 570 (M^+), 299 (b.p.); HRMS calcd for $C_{34}H_{34}O_8$ m/z 570.2254, found 570.2252.

Reduction of 35 with Lithium Aluminum Hydride to 36. To a suspension of $LiAlH_4$ (0.17 g, 4.5 mmol) in 50 mL of dry THF at 0 °C was added **35** (3.34 g, 5.96 mmol) in 10 mL of dry THF over 30 min with stirring. After the reaction mixture was stirred for an additional 1 h at room temperature, the excess reagent was decomposed by careful addition of water. The mixture was acidified with 2 N HCl to pH 2, diluted with excess water, and extracted with ether. The combined ether layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 75 g of silica gel (CH_2Cl_2) to yield **36** (2.32 g, 82%) as a viscous colorless oil: IR (neat) 3450, 1690, 1600, 1582, 1502 cm^{-1}; ^1H NMR δ 1.80 (br s, OH), 2.88 (s, 4 H), 3.85 (s, 3 H), 3.96 (s, 3 H), 4.68 (s, 2 H), 6.76 (br s, 1 H), 6.78 (br d, J = 7.6 Hz, 1 H), 6.85–6.91 (m, 5 H), 7.04 (br s, 1 H), 7.08–7.12 (m, 3 H), 7.20 (br t, J = 7.6 Hz, 1 H), 7.38 (d, J = 2.0 Hz, 1 H), 7.62 (dd, J = 8.2, 2.0 Hz, 1 H), 9.78 (s, 1 H); MS, m/z 484 (M^+), 241 (b.p.); HRMS calcd for $C_{30}H_{28}O_6$ m/z 484.1886, found 484.1900.

Diethyl [3-Methoxy-4-[3-[2-[4-(2-methoxy-5-formylphenoxy)phenyl]ethyl]phenoxy]benzyl]phosphonate (37). By the same procedure as described in the preparation of **32**, alcohol **36** (2.22 g) was converted into the phosphonate **37** (2.10 g), a viscous colorless oil, in 76% yield: IR (neat) 1692, 1600, 1582, 1508, 1240, 1050, 1020 cm^{-1}; ^1H NMR δ 1.26 (t, J = 7.1 Hz, 6 H), 2.87 (s, 4 H), 3.15 (d, J = 21.5 Hz, 2 H), 3.83 (s, 3 H), 3.93 (s, 3 H), 4.05 (m, 4 H), 6.75 (br d, J = 7.8 Hz, 1 H), 6.79 (br s, 1 H), 6.82–6.92 (m, 5 H), 7.00 (br s, 1 H), 7.07–7.13 (m, 3 H), 7.18 (t, J = 7.8 Hz, 1 H), 7.39 (d, J = 2.0 Hz, 1 H), 7.62 (dd, J = 8.2, 2.0 Hz, 1 H), 9.78 (s, 1 H); MS, m/z 604 (M^+), 241 (b.p.); HRMS calcd for $C_{34}H_{37}O_7P$ m/z 604.9633, found 604.9633.

Intramolecular Wadsworth–Emmons Olefination of 37. To an ice-cooled solution of **37** (193 mg, 0.32 mmol) in 160 mL of dry DMF was added potassium *tert*-butoxide (43 mg, 0.38 mmol) under argon. After being stirred for 1 h at room temperature, the reaction mixture was worked up as usual. The product thus obtained was chromatographed on 8 g of silica gel (benzene) to afford **38** (128 mg, 89%) as a colorless oil: IR (neat) 1600, 1582, 1502 cm^{-1}; ^1H NMR δ 3.77, 3.82 (1:3), 3.99, 3.83 (1:3) (OMe), 5.28, 5.59 (1:3, aromatic protons), 6.27, 6.90 (1:3, each d, J = 16.0 Hz); MS, m/z 450 (M^+, b.p.); HRMS calcd for $C_{30}H_{26}O_4$ m/z 450.1831, found 450.1858.

Riccardin B Dimethyl Ether (39). The compound **38** (128 mg) was hydrogenated in a mixture of methanol (15 mL) and THF (5 mL) over platinum(IV) oxide (20 mg) at atmospheric pressure overnight. The catalyst was filtered off, and the filtrate was evaporated in vacuo. The residue was chromatographed on 10 g of silica gel (benzene) to give **39** (116 mg, 90%). Recrystallization form petroleum ether gave colorless needles: mp 151–152 °C; IR (Nujol) 1607, 1585, 1509, 1267, 1211, 1120, 1030, 799, 690, 658 cm^{-1}; ^1H NMR δ 2.75–2.85 (m, 8 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 5.99 (m, 1 H), 6.00 (dd, J = 8.0, 2.0 Hz, 1 H), 6.02 (d, J = 2.0 Hz, 1 H), 6.17 (d, J = 8.0 Hz, 1 H), 6.59 (d, J = 8.6 Hz, 2 H), 6.66 (d, J = 2.0 Hz, 1 H), 6.71 (d, J = 8.6 Hz, 2 H), 6.94 (d, J = 8.3 Hz, 1 H), 6.95 (dd, J = 7.8, 1.5 Hz, 1 H), 7.01 (dd, J = 8.3, 2.0 Hz, 1 H), 7.05 (br d, J = 7.8 Hz, 1 H), 7.32 (t, J = 7.8 Hz, 1 H). Anal. Calcd for $C_{30}H_{28}O_4$: C, 79.65; H, 6.19. Found: C, 79.68; H, 6.19. These spectral data were identical with those of riccardin B dimethyl ether derived from natural **3**.

Riccardin B (3). A solution of **39** (65 mg, 0.144 mmol) in 5 mL of CH_2Cl_2 was chilled to −78 °C (dry ice–acetone), and boron tribromide (0.03 mL, 0.032 mmol) was added via syringe with stirring. After 10 min, the cooling bath was taken off and stirring was continued for 20 min. The reaction mixture was poured into water (20 mL) and extracted with chloroform. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on 10 g of silica gel (CH_2Cl_2) to afford **3** (56 mg, 92%) as a viscous colorless oil: IR (neat) 3550, 3030, 2940, 2870, 1596, 1503, 1435, 1335, 1264, 1207 cm^{-1}; ^1H NMR δ 2.68–2.76 (m, 4 H), 2.78–2.86 (m, 4 H), 5.45 (br s, OH), 5.60 (br s, OH), 6.00 (dd, J = 8.0, 2.0 Hz, 1 H), 6.02–6.06 (m, 2 H), 6.19 (d, J = 8.3 Hz, 1 H), 6.64 (d, J = 8.6 Hz, 2 H), 6.68 (d, J = 2.0 Hz, 1 H), 6.71 (d, J = 8.6 Hz, 2 H), 6.91 (dd, J = 8.3, 2.0 Hz, 1 H), 6.95 (br d, J = 7.8 Hz, 1 H), 6.96 (d, J = 8.0 Hz, 1 H), 7.07 (br d, J = 7.8 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 1 H). These spectral data were identical with those of natural riccardin B.

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