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Studies on Natural *p*-Terphenyls: Total Syntheses of Vialinin A and Terrestrin B

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A powerful inhibitor of TNF-α production, vialinin A, was synthesized from sesamol through a series of reactions involving double Suzuki-Miyaura coupling, 2,3-dichloro-5,6-dicyano-1,4-benzoquino (DDQ) mediated de-methoxymethylation and oxidative removal of methylene acetal by lead tetraacetate. The synthetic method also made it possible to prepare a related compound, terrestrin B.

Key words: TNF-α; terphenyl; vialinin A; terrestin B; Suzuki-Miyaura coupling

Terphenyls are aromatic hydrocarbons consisting of a chain of three benzene rings. These compounds can be structurally classified into three types in which the terminal rings are *ortho*-, *meta*-, or *para*-substituents of the central aromatic ring. Most natural terphenyls are *para* (*p*)-terphenyl derivatives with polyhydroxyl groups, and have been mainly found as the secondary metabolites from fungi. Among them, several compounds have been reported to exhibit significant biological activities such as potent immunosuppressive, neuroprotective, antithrombotic, anticoagulative, specific 5-lipoxygenase inhibitory, and cytotoxicity.[1)] In our search for new bioactive compounds from edible Chinese mushrooms, we isolated a new terphenyl, vialinin A (**1**), together with a known atromentin (**2**)[2–7)] and an inseparable mixture of ganbajunins D (**3**) E (**4**)[8)] from dry fruiting bodies of *Thelephora vialis*.[9)] Compound **1** had powerful DPPH free radical-scavenging activity with an EC_{50} value of 14 μM (cf. EC_{50} = 10 μM for BHT). Asakawa *et al.* have isolated **1** and butyryl analog **5** from *Thelephora terrestris* and named them terrestrin A and terrestrin B, respectively.[10)] We have recently found that **1** strongly inhibited tumor necrosis factor (TNF)-α production in rat basophilic leukemia (RBL-2H3) cells: IC_{50} = 90 pM *vs* IC_{50} = 0.25 nM for FK-506.[11)] Interestingly, positional isomers **3** and **4** showed no such activity, and atromentin (**2**) also proved to be ineffective toward the cells, although **2** has been reported to be an effective anticoagulative agent[12)] and had significant smooth muscle stimulatory activity.[13)] TNF-α is a potent multifunctional cytokine that mediates a variety of biological actions with a central role in the pathogenesis of many inflammatory diseases.[14–16)] Thus, inhibitors of TNF-α production in activated mast cells and basophiles are promising candidates for a new type of anti-allergic agent. In order to clarify the target molecule of **1** and develop a new anti-allergic drug, we have started synthetic studies on natural *p*-terphenyls. Described here are details of the total synthesis of vialinin A (**1**)[17)] and its related compound (**5**).

Results and Discussion

Construction of the *p*-terphenyl skeleton is the main challenge in the synthesis of these molecules. We have designed an efficient strategy based on the Suzuki-Miyaura coupling reaction,[18)] using highly functionalized aryl halide/aryl triflate **6** and boronic acids **7–9** as shown in Scheme 1. Another problem in this study was selective protection of the hydroxyl groups in the core. This could be solved by using a properly protected benzene for the starting material of the core.

Synthesis began with preparation of a symmetrical benzene carrying two different *O*-protecting groups corresponding to the core in **1** and **5** (Scheme 2).[19)] Considering the difficulty in selective acetalization of such a polyhydroxybenzene as **10**, we chose unsymmetrical phenols **11–13**[20–22)] as the starting materials. According to the method described in ref. 22, these compounds were, apart from **12**, transformed smoothly into catechols **16** and **17** *via* **14** and **15**,* respectively. After *O*-methoxymethylation, resulting MOM ethers **18** and **19** were each subjected to *bis*-hydroxylation. *Ortho*-lithiation (2.4 eq. of *n*-BuLi, TMEDA, −78–0 °C) of **18** and subsequent treatment with triisopropylborate and an oxidative work-up resulted in partial debenzylation,[24)] giving no hydroquinone derivative. On the other hand, the reaction with **19** under similar conditions proceeded smoothly to afford desired hydroquinone **20** in a high yield. TMEDA was unnecessary for this methylation. The use of 1.2 mol eq. of *n*-BuLi afforded the corresponding mono-phenol in a moderate yield. Upon

* Bromination[23)] of **14** or **15** met with failure.

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Abbreviations: Ac, acetyl; Bn, benzyl; DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquino; MOM, methyloxymethyl; TBS, *t*-butyldimethylsilyl; Tf, trifluoromethanesulfonyl

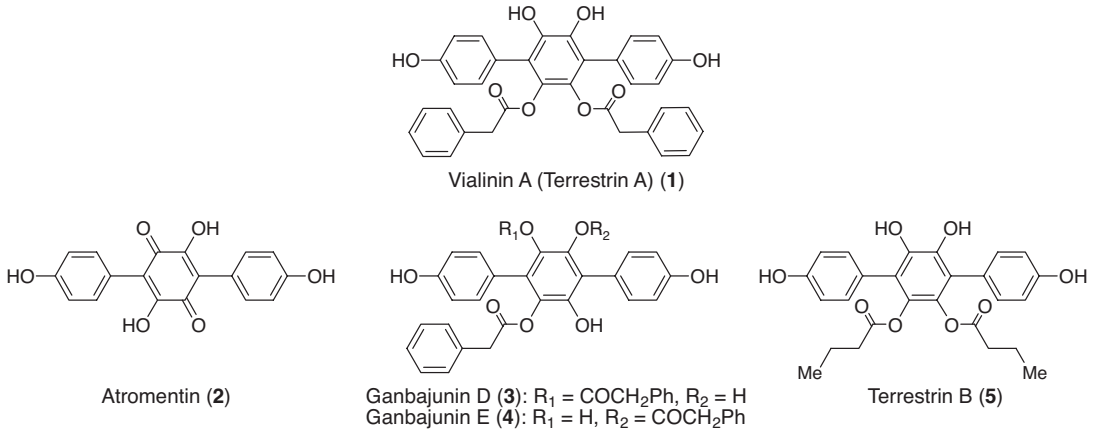
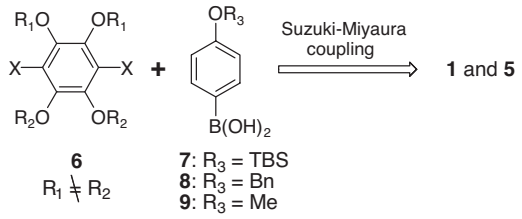


Fig. 1. Structures of Natural *p*-Terphenyls.



Scheme 1. Synthetic Plan for Vialinin A (**1**) and Terrestrin B (**5**).

treatment with triflic anhydride-pyridine, **20** led to bis-triflate **21**.

Although many studies have been reported dealing with the synthesis of oligoarenes[25–28] by the Suzuki-Miyaura coupling, the synthetic examples have relied mainly on coupling simple arylhalides/aryltriflates with boronic acids. In our studies, the aryl triflate was highly oxgenated and electron-rich.[29–31] In order to confirm whether the coupling reaction using such a triflate with boronic acids would proceed without trouble or not, we examined Suzuki-Miyaura coupling of **21** with **7**–**9** under a variety of conditions (Scheme 3). The use of palladium acetate[32] in the presence of triphenylphosphine and sodium carbonate gave good results as shown in Table 1 (entries 2, 5, 8), although the TBS group was removed in one case (entry 2). In contrast, the TBS group was retained to provide *p*-terphenyl **22** in a good-high yield when tetrakis(triphenylphosphine)palladium was employed as a catalyst.[33] Interestingly, a small amount of tri-MOM derivatives **28** and **29** was also isolated by using a combination of the catalyst and cesium carbonate in toluene (entries 1 and 4). These compounds seemed to be produced through ligand exchange between intermediary Ar-Pd-OTf and TfO-Pd-OMOM generated from this by the elimination of a benzyne.[34] Among the three types of boronic acid used, benzyl derivative **8** proved to be unsuitable in this coupling reaction.

Compounds **22** and **25** were each obtained in a high yield and were employed in the remaining tasks. An approach from **25** was initially examined, because selective deprotection of the MOM groups seemed to be feasible. Hydrolysis of the MOM groups with HCl caused partial oxidation to provide a mixture of **30** and the corresponding *ortho*-quinone (Scheme 4). This mixture was, without separation, treated with sodium

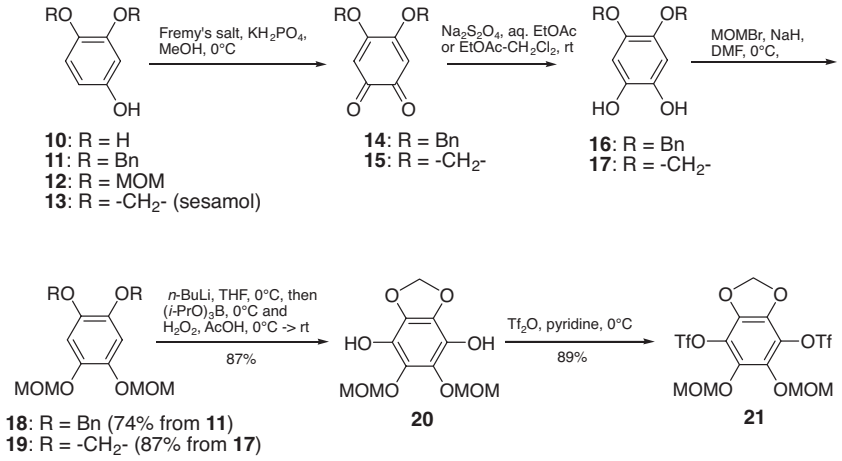
Table 1. Suzuki-Miyaura Coupling

Entry	Boronic acid (mol eq.)	Condition	Product yield (%)
1	**7** (4.0)	A	**22** (70), **28** (10)
2	**7** (2.3)	B	**23** (92)
3	**7** (4.0)	C[a]	**22** (96)
4	**8** (4.0)	A	**24** (62), **26** (22), **29** (7)
5	**8** (2.3)	B	**24** (76)
6	**8** (4.0)	C	**21** (59), **27** (9)
7	**9** (4.0)	A	**25** (78)
8	**9** (2.3)	B	**25** (91)
9	**9** (4.0)	C	**25** (82)

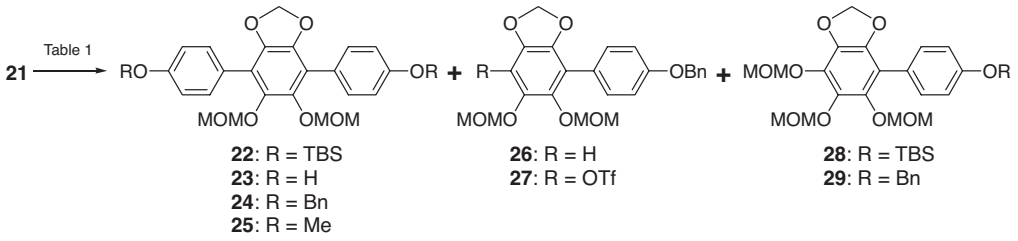
[a]The reaction time was 26 h for entry C.
Conditions: A: $Pd(PPh_3)_4$ (0.05 mol eq.), Cs_2CO_3 (4.0 mol eq.), toluene, 100 °C, 20 h; B: $Pd(OAc)_2$ (0.05 mol eq.), Ph_3P (0.15 mol eq.), Na_2CO_3(4.0 mol eq.), aq. propanol, 100 °C, 4 h; C: $Pd(PPh_3)_4$ (0.05 mol eq.), K_3PO_4 (4.0 mol eq.), KBr (2.1 mol eq.), dioxane, 100 °C, 20 h.

dithionite, converging into **30**. Since phenylacetylation of **30** by using pyridine-*N*,*N*-dimethylaminopyridine or triethylamine as a base gave unsatisfactory results, the catechol was successively treated with *n*-BuLi and then with phenylacetyl chloride, giving fully protected vialinin A **31** in a high overall yield. However, simultaneous deprotection of the methyl and methylene groups by using boron trichloride[35] or boron tribromide[36] resulted in a complex mixture because of the instability of the phenylacetyl groups toward the reaction conditions employed.

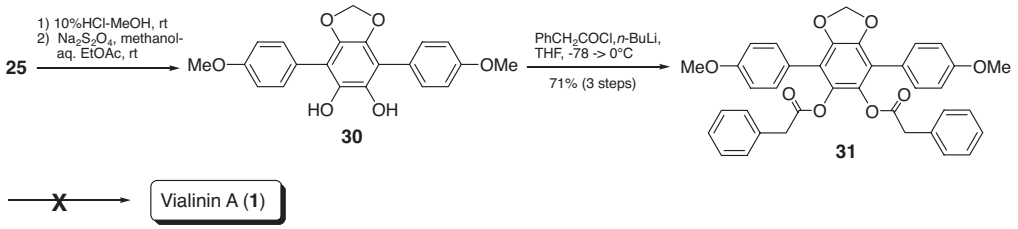
Selective removal of the MOM groups in **22** was also found to be difficult (Scheme 5). After several trials, we found that treating of **22** with DDQ in the presence of *p*-TsOH[37] in benzene at 50 °C afforded *ortho*-quinone **32** in a high yield. It is noteworthy that two TBS groups were retained under these reaction conditions. This key reaction would enable us to prepare many analogs of terphenyls. For example, **32** underwent hydrolysis under acidic conditions to give 4′,4″-dihydroxy-phlebiarubrone (**33**), have been isolated from a culture of *Punctularia atropurpurascens*.[38–40] The spectral and physical properties of **33** were identical to those of reported **33**. On the other hand, reduction of **32** gave corresponding catechol **34** which was immediately acylated to give **35**. Hydrolysis of the methylene acetal moiety in **35** was a troublesome step again. However, treatment of **35** with 2.5 equiv of lead tetraacetate[41] in benzene at 80 °C provided **36** in a high yield. Finally,



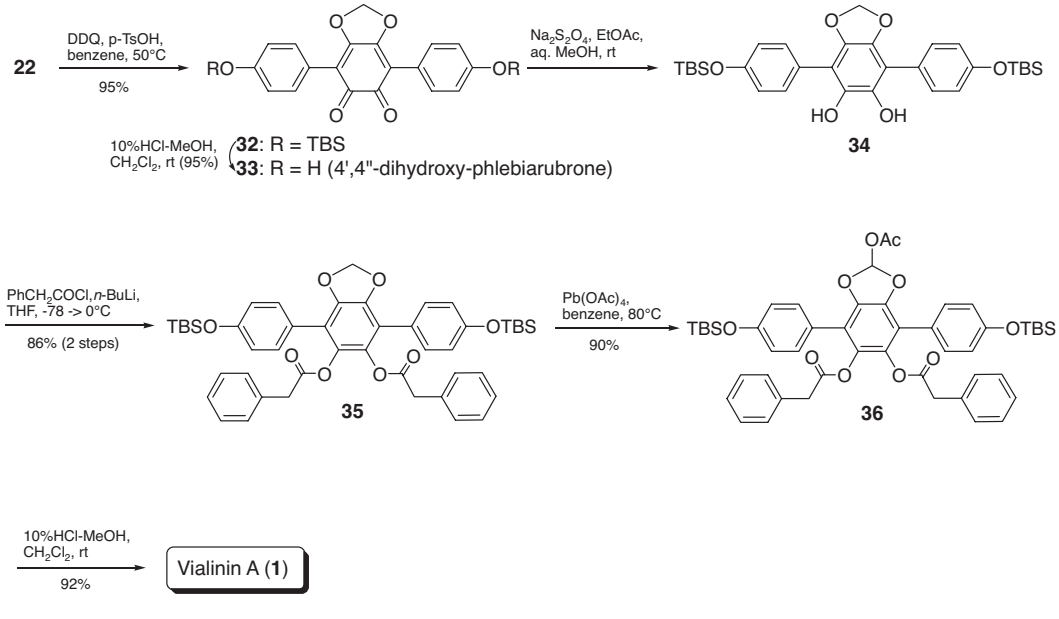
Scheme 2. Synthesis of the Central Ring **21**.



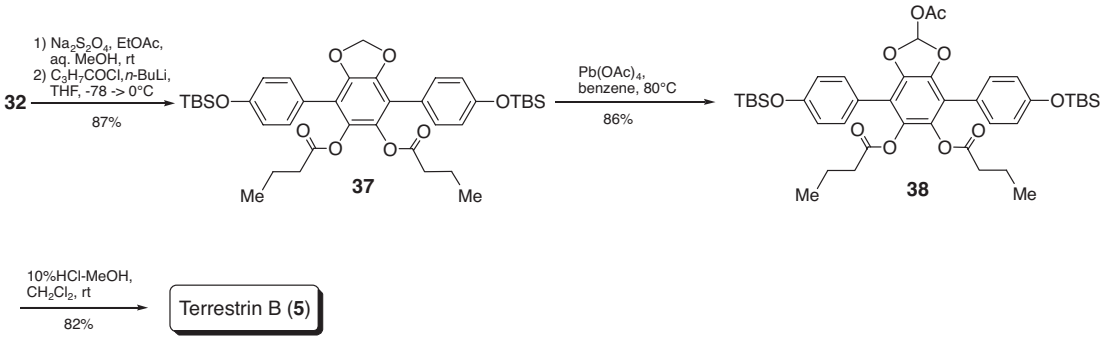
Scheme 3. Suzuki-Miyaura Coupling of **21** with Boronic Acids **7**–**9**.



Scheme 4. Synthetic Approach from **25** to Vialinin A (**1**).



Scheme 5. Total Synthesis of Vialinin A (**1**).



Scheme 6. Total Synthesis of Terrestrin B (**5**).

exposure of this to mildly acidic conditions led to the removal of two TBS groups concomitantly with hydrolysis of the orthoester, giving vialinin A (**1**). The spectral data for **1** were indistinguishable from those of the natural product.

Having completed the synthesis of vialinin A (**1**), we next turned our attention to terrestrin B (**5**), because its structure had not previously been established by a synthesis (Scheme 6). Reduction of **32** and subsequent acylation with butyryl chloride afforded **37** which underwent oxidation with lead tetraacetate to give **38** in a good overall yield. Finally, an acid treatment of **38** provided **5**. The ^{1}H- and ^{13}C- NMR data for the synthetic sample were identical with those reported[10] for the natural specimen, confirming the structure of the natural product.

In summary, we developed a short and efficient synthesis of vialinin A (**1**), based on Suzuki-Miyaura coupling as the key step. This synthesis required only nine steps and proceeded in a 44% overall yield from known catechol **17**. The usefulness of this synthetic method was also demonstrated by a total synthesis of terrestrin B (**5**). A bioassay of the synthetic samples is now underway.

Experimental

All reactions were carried out in an argon atmosphere, unless otherwise noted. Melting point (mp) data are uncorrected. IR spectra were recorded with a Jasco Valor-III spectrophotometer by the ATR method, and UV spectra were measured with a Hitachi U-1500 spectrophotometer. Proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained with a Jeol JNM-A400 (400 MHz), JNM-ECA600 (600 MHz) or Varian NMR System 500 (500 MHz) spectrometer as solutions in $CDCl_3$, unless otherwise noted. Chemical shifts are reported in ppm downfield from tetramethylsilane, with the solvent resonance as the internal standard (δ_H 7.26 ppm or δ_C 77.0 ppm). Column chromatography was performed on Kanto silica gel 60N (spherical, neutral; 40–100 μm). Merck precoated silica gel 60 F_{254} plates of 0.25 mm thickness were used for analytical thin-layer chromatography. The solvent extracts were dried with magnesium sulfate, and the solutions were evaporated under reduced pressure at 35–40 °C.

4,5-Bis(benzyloxy)cyclohexa-3,5-diene-1,2-dione (14). To a stirred solution of Fremy's salt (60–75% assay, 10.81 g, *ca.* 26.2 mmol) and potassium dihydrogen phosphate (5.12 g, 37.6 mmol) in water (500 ml) was added dropwise a solution of **11** (3.49 g, 7.4 mmol) in methanol (40 ml). The mixture was vigorously stirred at 0 °C for 2.5 h and then extracted with dichloromethane. The extract was successively washed with water and brine, dried, and concentrated. The residue was treated with ether to give **14** (3.31 g) as a powder, this being employed for the next step without further purification; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.43–7.38 (10H, s), 5.84 (2H, s), 5.12 (4H, s).

4,5-Bis(benzyloxy)benzene-1,2-diol (16). To a stirred solution of **14** (3.31 g) in ethyl acetate-dichloromethane (15:8, 230 ml) was added dropwise a solution of sodium dithionite (7.19 g, 41.3 mmol) in water (25 ml) at rt. The resulting mixture was stirred for 30 min and then extracted with ethyl acetate. The extract was successively washed with cold aqueous HCl, water and brine, dried, and concentrated to give **16** (3.19 g), this being employed for the next step without further purification; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.40 (4H, d, $J = 6.8$ Hz), 7.37–7.28 (6H, m), 6.56 (2H, s), 5.05 (4H, s), 4.79 (2H, brs).

1,2-Dibenzyloxy-4,5-bis(methoxymethyoxy)benzene (18). To a stirred solution of **16** (3.19 g) in *N*,*N*-dimethylformamide (24 ml) was added sodium hydride (a 60% suspension in mineral oil, 0.91 g, 22.3 mmol) at 0 °C in portions. Bromomethyl methyl ether (1.9 ml, 24.0 mmol) was added dropwise after 1.5 h, and the resulting mixture was stirred at 0 °C → rt for 14 h. After adding saturated aqueous NH_4Cl, the resulting mixture was extracted with ether. The extract was successively washed with water and brine, dried and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 100 : 1 → 40 : 1) to give **18** (3.46 g, 74% from **11**) as colorless needles; mp 57.5–58 °C (*n*-hexane-ethyl acetate); IR υ_{max} (ZnSe) cm^{-1}: 2897, 2826, 1150, 1001, 960, 914; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.44–7.28 (10H, m), 6.87 (2H, s), 5.09 (8H, s), 3.47 (6H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 144.3, 141.7, 137.3, 128.4, 127.8, 127.6, 107.7, 96.4, 72.3, 56.1; HRMS (ESI) *m*/*z*: calcd. for $C_{24}H_{26}O_6Na$ $[M + Na]^+$, 433.1627; found, 433.1644. *Anal*. Found: C, 70.19; H, 6.42%. Calcd. for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38%.

5,6-Bis(methoxymethoxy)benzo[1,3]dioxole (19). Treatment of **17** (191 mg, 1.24 mmol) as described for the preparation of **18** yielded **19** (261 mg, 87%) as colorless needles; mp 46–46.5 °C (methanol); IR υ_{max} (ZnSe) cm^{-1}: 1496, 1479, 1206, 1172, 1143, 1033, 1004, 972; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.76 (2H, s), 5.87 (2H, s), 5.08 (4H, s), 3.50 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 142.4, 141.8, 101.3, 100.7, 96.7, 56.2. *Anal*. Found: C, 54.42; H, 5.79%. Calcd. for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83%.

5,6-Bis(methoxymethoxy)benzo[1,3]dioxole-4,7-diol (20). To a stirred solution of **19** (1.12 g, 4.63 mmol) in THF (18 ml) was added dropwise 1.52 M of *n*-BuLi (7.62 ml, 11.6 mmol) in *n*-hexane at 0 °C over 25 min. After 1.5 h, triisopropyl borate (2.66 ml, 11.6 mmol) was added dropwise, and the resulting mixture was stirred at 0 °C for 50 min. Acetic acid (1.31 ml, 23.2 mmol) was then added at 0 °C, before adding of 7% hydrogen peroxide (9.68 ml, 23.2 mmol). The resulting mixture was stirred at 0 °C → rt for 16 h, successively treated with saturated aqueous Na_2SO_3 and saturated aqueous $(NH_4)_2SO_4$, and then extracted with ethyl acetate. The extract was successively washed with water and brine, dried and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 50 : 1 → 10 : 1 → 4 : 1 → 1 : 1) to give **20** (1.10 g, 87%) as a white solid; mp 133.5–135 °C (methanol); IR υ_{max} (ZnSe) cm^{-1}: 3389, 1495, 1294, 1274, 1255, 1151, 1004, 987; ^{1}H-NMR (400 MHz, acetone-d_6) δ: 7.53 (2H, s), 5.86 (2H, s), 5.05 (4H, s), 3.54 (6H, s); ^{13}C-NMR (100 MHz, acetone-d_6) δ: 135.5, 133.1, 128.8, 102.1, 99.9, 57.4. *Anal*. Found: C, 47.95; H, 5.10%. Calcd. for $C_{11}H_{14}O_8$: C, 48.18; H, 5.15%.

5,6-Bis(methoxymethoxy)benzo[1,3]dioxole-4,7-diyl bis(trifluoromethanesulfonate) (21). To a stirred solution of **20** (1.09 g, 3.97 mmol) in pyridine (40 ml) was added dropwise triflic anhydride (1.47 ml, 8.74 mmol) at 0 °C and the mixture was stirred at the same temperature for 2.5 h. After adding ice-cooled water, the resulting mixture was stirred for 1 h and then extracted with ether. The extract was successively washed with cold aqueous HCl, water, saturated aqueous $NaHCO_3$, water and brine, dried and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 50 : 1) to give **21** (1.89 g, 89%) as a white solid; mp 58.5–59.0 °C (methanol); IR υ_{max} (ZnSe) cm^{-1}: 3013, 1474, 1422, 1200, 1132, 1037, 995, 969; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.14 (2H, s), 5.14 (4H, s), 3.60 (6H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 138.3, 137.6, 126.4, 118.5 (q, J_{CF} = 320.9 Hz), 104.5, 100.1, 58.1; HRMS (ESI) *m/z*: calcd. for $C_{13}H_{12}F_6NaO_{12}S_2$ $[M + Na]^+$, 560.9572; found, 560.9573.

*5,6-Bis(methoxymethoxy)-4,7-bis-(*p-*(t-butyldimethylsilyloxy)phenyl)-benzo[1,3]dioxole (22).* To a stirred mixture of **7** (1.93 g, 7.65 mmol), **21** (1.03 g, 1.91 mmol), potassium bromide (0.49 g, 4.11 mmol) and potassium phosphate (1.68 g, 7.91 mmol) in dioxane (12 ml) was added tetrakis(triphenylphosphine)palladium (110 mg, 0.10 mmol), and the mixture was stirred at 100 °C for 26 h, cooled, and then diluted with water. The resulting mixture was extracted with ether. The extract was successively washed with water and brine, dried, and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 200 : 1) to give **22** (1.20 g, 96%) as a white solid; mp 174.5–175.5 °C (ethanol); IR υ_{max} (ZnSe) cm^{-1}: 1515, 1438, 1250, 1169, 1044; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.47 (4H, d, J = 8.6 Hz), 6.90 (4H, d, J = 8.6 Hz), 5.93 (2H, s), 4.86 (4H, s), 3.02 (6H, s), 1.00 (18H, s), 0.21 (12H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.1, 141.9, 141.1, 131.5, 125.3, 119.7, 117.8, 101.0, 99.2, 57.1, 25.7, 18.2, −4.4. *Anal*. Found: C, 64.25; H, 7.75%. Calcd. for $C_{35}H_{50}O_8Si_2$: C, 64.19; H, 7.69%.

*5,6-Bis(methoxymethoxy)-4,7-bis-(*p-*hydroxyphenyl)benzo[1,3]dioxole (23).* A mixture of **7** (23.2 mg, 91.9 µmol) and **21** (21.5 mg, 39.9 µmol) in 1-propanol (1.0 ml) was stirred at rt for 30 min, allowing the solids to dissolve. The resulting solution was treated with palladium acetate (0.5 mg, 2.23 µmol), triphenylphosphine (1.6 mg, 6.10 µmol), 2 M sodium carbonate (0.06 ml, 0.12 mmol) and water (0.19 ml), heated at 100 °C while stirring for 4 h, and then cooled to rt. After adding water, the resulting mixture was stirred at rt for 1 h and then extracted with ethyl acetate. The extract was successively washed with water and brine, dried and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 50 : 1 → 10 : 1) to give **23** (15.7 mg, 92%) as a white solid; mp 198.5–199.5 °C (*n*-hexane-ethyl acetate); IR υ_{max} (ZnSe) cm^{-1}: 3391, 3296, 1518, 1400, 1270, 1204, 1170, 1041, 986, 951; ^{1}H-NMR (400 MHz, acetone-d_6) δ: 8.46 (2H, s), 7.45 (4H, d, J = 8.3 Hz), 6.92 (4H, d, J = 8.3 Hz), 5.95 (2H, s), 4.84 (4H, s), 3.05 (6H, s); ^{13}C-NMR (100 MHz, acetone-d_6) δ: 157.7, 142.9, 141.9, 132.5, 124.5, 118.4, 115.6, 101.6, 99.8, 57.1; HRMS (ESI) *m/z*: calcd. for $C_{23}H_{22}O_8Na$ $[M + Na]^+$, 449.1212; found, 449.1225. *Anal*. Found: C, 64.31; H, 5.25%. Calcd. for $C_{23}H_{22}O_8 \cdot 0.5H_2O$: C, 64.63; H, 5.42%.

*5,6-Bis(methoxymethoxy)-4,7-bis-(*p-*(benzyloxy)-phenyl)benzo[1,3]-dioxole (24).* Treatment of **8** (21.0 mg, 0.09 mmol) and **21** (21.5 mg, 0.04 mmol) as described for the preparation of **23** yielded **24** (18.5 mg, 76%) as colorless needles; mp 165–165.5 °C (ethanol); IR υ_{max} (ZnSe) cm^{-1}: 2904, 2826, 1436, 1246, 1051, 976, 956, 922, 828; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54 (4H, d, J = 8.8 Hz), 7.46–7.31 (10H, m), 7.05 (4H, d, J = 8.8 Hz), 5.92 (2H, s), 5.11 (4H, s), 4.86 (4H, s), 3.02 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 158.2, 142.0, 141.1, 136.9, 131.5, 128.6, 128.0, 127.5, 125.0, 117.7, 114.6, 101.0, 99.3, 70.0, 57.1; HRMS (ESI) *m/z*: calcd. for $C_{37}H_{34}O_8Na$ $[M + Na]^+$, 629.2151; found, 629.2162. *Anal*. Found: C, 73.15; H, 5.67%. Calcd. for $C_{37}H_{34}O_8$: C, 73.25; H, 5.65%.

*5,6-Bis(methoxymethoxy)-4,7-bis-(*p-*(methoxy)-phenyl)benzo[1,3]-dioxole (25).* Treatment of **9** (14.0 mg, 0.09 mmol) and **21** (21.5 mg, 0.04 mmol) as described for the preparation of **23** yielded **25** (16.6 mg, 91%) as a white solid; mp 145.5–147 °C (ethyl acetate); IR υ_{max} (ZnSe) cm^{-1}: 2934, 2836, 1517, 1434, 1288, 1251, 1156, 1049, 1029; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54 (4H, d, J = 8.5 Hz), 6.98 (4H, d, J = 8.5 Hz), 5.92 (2H, s), 4.87 (4H, s), 3.85 (6H, s), 3.06 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 159.0, 142.0, 141.2, 131.5, 124.7, 117.7, 113.6, 101.0, 99.3, 57.2, 55.3; HRMS (ESI) *m/z*: calcd. for $C_{25}H_{26}O_8Na$ $[M + Na]^+$, 477.1525; found, 477.1539. *Anal*. Found: C, 66.08; H, 5.82%. Calcd. for $C_{25}H_{26}O_8$: C, 66.07; H, 5.77%.

*5,6-Bis(methoxymethoxy)-4-(*p-*(benzyloxy)phenyl)benzo[1,3]dioxole (26) and 4,5,6-tris(methoxymethoxy)-7-(*p-*(benzyloxy)phenyl)benzo[1,3]-dioxole (29).* Tetrakis(triphenylphosphine)palladium (2.3 mg, 1.9 µmol) was added to a stirred mixture of **8** (36.5 mg, 0.16 mmol), **21** (21.5 mg, 0.04 mmol), and cesium carbonate (52.1 mg, 0.16 mmol) in toluene (1.5 ml), and the mixture was stirred at 100 °C for 20 h. The treatment described for the preparation of **22** yielded **24** (15.1 mg, 62%), **26** (3.8 mg, 22%), and **29** (1.4 mg, 7%).

26. Light yellow solid; IR υ_{max} (ZnSe) cm^{-1}: 2923, 1451, 1239, 1154, 1039, 984, 947; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.47 (2H, d, J = 8.6 Hz), 7.45–7.31 (5H, m), 7.06 (1H, s), 7.02 (2H, d, J = 8.6 Hz), 5.95 (2H, s), 5.12 (2H, s), 5.11 (2H, s), 4.72 (2H, s), 3.65 (3H, s), 3.11 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 158.0, 142.5, 141.4, 137.0, 135.6, 133.4, 131.4, 131.1, 128.6, 128.0, 127.5, 124.9, 114.6, 110.6, 101.5, 100.4, 99.3, 70.0, 57.4, 57.1; HRMS (ESI) *m/z*: calcd. for $C_{24}H_{24}O_7Na$ $[M + Na]^+$, 463.1369; found, 463.1354.

29. Light yellow solid; IR υ_{max} (ZnSe) cm^{-1}: 2920, 1609, 1435, 1236, 1156, 1088, 1058, 1037, 923, 888; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.47 (2H, d, J = 8.5 Hz), 7.44 (2H, d, J = 7.4 Hz), 7.38 (2H, dd, J = 7.4, 7.4 Hz), 7.32 (1H, t, J = 7.4 Hz), 7.02 (2H, d, J = 8.5 Hz), 5.91 (2H, s), 5.26 (2H, s), 5.13 (2H, s), 5.09 (2H, s), 4.78 (2H, s), 3.64 (3H, s), 3.59 (3H, s), 3.00 (3H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 158.1, 142.5, 142.1, 137.6, 136.9, 134.9, 133.3, 131.5, 128.6, 128.0, 127.5, 124.8, 114.6, 114.1, 101.3, 99.4, 99.3, 97.5, 70.0, 57.5, 57.1, 57.0; HRMS (ESI) *m/z*: calcd. for $C_{26}H_{28}O_9Na$ $[M + Na]^+$, 507.1631; found, 507.1630.

*5,6-Bis(methoxymethoxy)-4-(*p-*(benzyloxy)phenyl)benzo[1,3]dioxole-7-yl trifluoromethanesulfonate (27).* Treatment of **8** (36.5 mg, 0.16 mmol) and **21** (21.5 mg, 0.04 mmol) as described for the preparation of **22** yielded **21** (12.7 mg, 59%) and **27** (2.0 mg, 9%) as a syrup; IR υ_{max} (ZnSe) cm^{-1}: 2908, 2831, 1426, 1375, 1206, 1136, 1052, 1023, 976; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.50 (2H, d, J = 8.8 Hz), 7.45–7.32 (5H, m), 7.05 (2H, d, J = 8.8 Hz), 6.01 (2H, s), 5.20 (2H, s), 5.11 (2H, s), 4.77 (2H, s), 3.65 (3H, s), 3.02 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 158.6, 142.6, 142.1, 137.9, 136.7, 136.0, 131.4, 128.6, 128.0, 127.4, 125.5, 123.5, 119.1, 118.6 (q, J_{CF} = 320.5 Hz), 114.7, 102.6, 99.7, 99.4, 70.0, 57.9, 57.3; HRMS (ESI) *m/z*: calcd. for $C_{25}H_{23}F_3O_{10}NaS$ $[M + Na]^+$, 595.0862; found, 595.0862.

*4,5,6-Tris(methoxymethoxy)-7-(*p-*(t-butyldimethylsilyloxy)phenyl)-benzo[1,3]dioxole (28).* Treatment of **7** (40.4 mg, 0.16 mmol) and **21** (21.5 mg, 0.04 mmol) as described for the preparation of **26** yielded **22** (18.2 mg, 70%) and **28** (2.1 mg, 10%) as an amorphous solid; IR υ_{max} (ZnSe) cm^{-1}: 2927, 1607, 1514, 1434, 1252, 1157, 1057, 1035, 909; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.40 (2H, d, J = 8.5 Hz), 6.87 (2H, d, J = 8.5 Hz), 5.91 (2H, s), 5.26 (2H, s), 5.13 (2H, s), 4.77 (2H, s), 3.63 (3H, s), 3.59 (3H, s), 3.00 (3H, s), 0.99 (9H, s), 0.20 (6H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 155.0, 142.5, 142.1, 137.6, 135.0, 133.2, 131.4, 125.1, 119.7, 114.3, 101.3, 99.4, 99.3, 97.5, 57.5, 57.1, 57.0, 25.7, 18.2, −4.4; HRMS (ESI) *m/z*: calcd. for $C_{25}H_{36}O_9SiNa$ $[M + Na]^+$, 531.2026; found, 531.2024.

*5,6-Bis(phenylacetoxy)-4,7-bis-(*p-*(methoxy)phenyl)benzo[1,3]dioxole (31).* To a stirred solution of **25** (137 mg, 0.30 mmol) in dichloromethane (2.0 ml) was added a 10% HCl solution in methanol (2.0 ml), and the mixture was stirred at rt for 11 h and then concentrated. The residue was passed through a short column of silica gel (*n*-hexane-ethyl acetate = 50 : 1 → dichloromethane) to give a syrup (93 mg) which was treated with sodium dithionite (177 mg, 1.02 mmol) in ethyl acetate-methanol-water (4:1:1; 6.0 ml) at rt for 1 h. The resulting mixture was extracted with ethyl acetate. The extract was successively washed with cold aqueous HCl, water and brine, dried, concentrated and co-evaporated with dry benzene (×5) to give **30** as an amorphous solid which was employed for the next step without further

purification. To a stirred solution of **30** (*ca.* 0.25 mmol) in THF (3.0 ml) was added dropwise 1.55 M of *n*-BuLi (0.36 ml, 0.56 mmol) in *n*-hexane at −78 °C. After 10 min, phenylacetyl chloride (60 µl, 0.66 mmol) was added, and the mixture was stirred at −78 °C for 20 min and then at 0 °C for 40 min. After adding ice-cooled water, the resulting mixture was stirred for 30 min and then extracted with ethyl acetate. The extract was successively washed with water, saturated aqueous $NaHCO_3$, water and brine, dried and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 100 : 1 → 50 : 1 → 10 : 1) to give **31** (129 mg, 71% from **25**) as a white solid; 135 °C (dec., ethyl acetate-methanol); IR υ_{max} (ZnSe) cm^{-1}: 3015, 2950, 2836, 1749, 1436, 1396, 1245, 1124, 1027; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.30 (4H, d, J = 8.8 Hz), 7.28–7.22 (6H, m), 7.10–7.07 (4H, m), 6.82 (4H, d, J = 8.8 Hz), 5.97 (2H, s), 3.82 (6H, s), 3.31 (4H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 168.8, 159.2, 143.0, 134.7, 132.9, 130.6, 129.3, 128.6, 127.2, 123.0, 116.8, 113.8, 101.6, 55.2, 40.5; HRMS (ESI) m/z: calcd. for $C_{37}H_{30}O_8Na$ $[M + Na]^+$, 625.1838; found, 625.1831.

*4,7-Bis-(*p-(t-*butyldimethylsilyloxy)phenyl)benzo[1,3]dioxole-5,6-dione (32).* To a stirred solution of **22** (269 mg, 0.41 mmol) in benzene (5.0 ml) were added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (283 mg, 1.23 mmol) and *p*-TsOH·H_2O (121 mg, 0.62 mmol). The mixture was stirred at 50 °C for 2.5 h, cooled, and then directly poured into a short column of silica gel (*n*-hexane). Elution with *n*-hexane-ethyl acetate (100 : 1 → 25 : 1) gave a syrup which was chromatographed on silica gel (*n*-hexane-ethyl acetate = 100 : 1 → 25 : 1) to give **32** (221 mg, 95%) as a dark red solid; mp 265–267 °C (methanol-ether); IR υ_{max} (ZnSe) cm^{-1}: 1636, 1600, 1508, 1335, 1295, 1249, 1168, 1058; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.55 (4H, d, J = 8.8 Hz), 6.88 (4H, d, J = 8.8 Hz), 6.10 (2H, s), 1.00 (18H, s), 0.23 (12H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 176.6, 155.9, 155.7, 130.9, 121.9, 119.8, 113.1, 102.5, 25.6, 18.2, −4.4. *Anal*. Found: C, 65.71; H, 7.16%. Calcd. for $C_{31}H_{40}O_6Si_2$: C, 65.92; H, 7.14%.

4′,4″-Dihydroxy-phlebiarubrone (33). To a stirred solution of **32** (10.4 mg, 0.02 mmol) in dichloromethane (0.5 ml) was added a 10% HCl solution in methanol (0.5 ml), and the mixture was stirred at rt for 12 h and then concentrated. The resulting residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 10 : 1 → pyridine) to give **33** (5.9 mg, 95%) as a dark red solid; mp >300 °C (methanol) {lit.[26] >300 °C}; IR υ_{max} (ZnSe) cm^{-1}: 3439, 1602, 1514, 1255, 1057; ^{1}H-NMR (400 MHz, acetone-d_6) δ: 8.59 (2H, s), 7.53 (4H, d, J = 8.6 Hz), 6.90 (4H, d, J = 8.6 Hz), 6.35 (2H, s); ^{13}C-NMR (100 MHz, pyridine-d_5) δ: 177.4, 159.2, 156.5, 131.9, 121.2, 116.1, 113.0, 103.7; HRMS (ESI) m/z: calcd. for $C_{19}H_{12}O_6Na$ $[M + Na]^+$, 359.0532; found, 359.0544.

*5,6-Bis(phenylacetoxy)-4,7-bis-(*p-(t-*butyldimethyl-silyloxy)phenyl)-benzo[1,3]dioxole (35).* To a stirred solution of **32** (72.4 mg, 0.13 mmol) in ethyl acetate-methanol (10:1; 22 ml) was added dropwise a solution of sodium dithionite (89.3 mg, 0.51 mmol) in water (2.0 ml) at rt. The resulting mixture was stirred for 4 h and then extracted with ethyl acetate. The extract was successively washed with cold aqueous HCl, water and brine, dried, concentrated and co-evaporated with dry benzene (×5) to give **34** as an amorphous solid (70.6 mg) which was employed for the next step without further purification. To a stirred solution of **34** (70.6 mg, *ca*. 0.13 mmol) in THF (2.0 ml) was added dropwise 1.57 M of *n*-BuLi (0.17 ml, 0.27 mmol) in *n*-hexane at −78 °C. After 20 min, phenylacetyl chloride (40 µl, 0.29 mmol) was added and the mixture was stirred at −78 °C for 30 min and then at 0 °C for 1 h. After adding ice-cooled water, the resulting mixture was stirred for 30 min and then extracted with ether. The extract was successively washed with water, saturated aqueous $NaHCO_3$, water and brine, dried and concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 100 : 1) to give **35** (88.8 mg, 86% from **32**) as a white solid; mp 135–137 °C (methanol); IR υ_{max} (ZnSe) cm^{-1}: 1776, 1607, 1517, 1456, 1431, 1388, 1252, 1229, 1215, 1050 ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.27 (4H, d, J = 8.4 Hz), 7.22–7.29 (6H, m), 7.08 (4H, dd, J = 7.9, 2.0 Hz), 6.76 (4H, d, J = 8.4 Hz), 5.97 (2H, s), 3.29 (4H, s), 1.00 (18H, s), 0.22 (12H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 168.8, 155.5, 142.9, 135.1, 133.0, 130.6, 129.4, 128.6, 127.2, 123.6, 119.8, 116.9, 101.6, 40.4, 25.7, 18.4, −4.4; HRMS (ESI) m/z: calcd. for $C_{47}H_{54}O_8Si_2Na$ $[M + Na]^+$, 825.3255; found, 825.3288. *Anal*. Found: C, 70.15; H, 6.79%. Calcd. for $C_{47}H_{54}O_8Si_2$: C, 70.29; H, 6.78%.

*5,6-Bis(phenylacetoxy)-4,7-bis-(*p-(t-*butyldimethyl-silyloxy)phenyl)-benzo[1,3]dioxole-2-yl acetate (36).* A mixture of **35** (17.5 mg, 21.8 µmol) and lead tetraacetate (16.5 mg, 37.2 µmol) in benzene (0.5 ml) was stirred at 80 °C for 12 h. More lead tetraacetate (8.3 mg, 18.7 µmol) was then added, stirring was continued for a further 24 h. After being cooled to rt, the reaction mixture was directly poured into a column of silica gel (*n*-hexane-ethyl acetate = 100 : 1). Elution with *n*-hexane-ethyl acetate (100 : 1 → 50 : 1) gave **36** (16.8 mg, 90%) as an amorphous solid; mp 112–113 °C (*n*-hexane); IR υ_{max} (ZnSe) cm^{-1}: 1759, 1607, 1518, 1252, 1096, 1003, 963; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.72 (1H, s), 7.26 (4H, d, J = 8.3 Hz), 7.24–7.28 (6H, m), 7.09 (4H, dd, J = 7.8, 1.7 Hz), 6.77 (4H, d, J = 8.3 Hz), 3.31 (4H, s), 2.09 (3H, s), 1.00 (18H, s), 0.23 (12H, s); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ: 169.14, 169.08, 156.4, 140.7, 136.1, 133.4, 131.1, 129.8, 129.0, 127.7, 123.4, 120.4, 117.9, 113.5, 40.7, 25.8, 21.3, 18.5, −4.2; HRMS (ESI) m/z: calcd. for $C_{49}H_{56}O_{10}Si_2Na$ $[M + Na]^+$, 883.3310; found, 883.3327.

Vialinin A (1). To a stirred solution of **36** (6.0 mg, 7.0 µmol) in dichloromethane (0.5 ml) was added a 10% HCl solution in methanol (0.1 ml), and the mixture was stirred at rt for 30 h and then concentrated. The residue was chromatographed on silica gel (*n*-hexane-ethyl acetate = 100 : 1 → 10 : 1 → 5 : 1) to give **1** (3.6 mg, 92%) as a colorless solid; mp 213–214 °C (*n*-hexane-ethyl acetate) {lit.[5] 220–223 °C (methanol-water)}; IR υ_{max} (ZnSe) cm^{-1}: 3308, 1762, 1716, 1522, 1456, 1248, 1140; ^{1}H-NMR (400 MHz, acetone-d_6) δ: 8.43 (2H, s), 7.50 (2H, s), 7.22–7.28 (6H, m), 7.13 (4H, d, J = 8.3 Hz), 7.03 (4H, dd, J = 7.3, 1.5 Hz), 6.84 (4H, d, J = 8.3 Hz), 3.37 (4H, s); ^{13}C-NMR (100 MHz, acetone-d_6) δ: 169.6, 157.8, 141.7, 134.7, 134.6, 132.3, 130.2, 129.2, 127.7, 124.3, 123.1, 115.9, 40.6; HRMS (ESI) m/z: calcd. for $C_{34}H_{26}O_8Na$ $[M + Na]^+$, 585.1525; found, 585.1532.

*5,6-Bis(butyryloxy)-4,7-bis-(*p-(t-*butyldimethylsilyl-oxy)phenyl)benzo-[1,3]dioxole (37).* According to the method described for preparation of **35**, **32** (70.7 mg, 0.13 mmol) was transformed into **34** which was successively treated with *n*-BuLi (0.18 ml, 0.29 mmol) and butyryl chloride (0.03 ml, 0.29 mmol) in THF (3.0 ml) at −78 → 0 °C to afford, after purification, **37** (73.7 mg, 87%) as an amorphous solid; IR υ_{max} (ZnSe) cm^{-1}: 2930, 2857, 1751, 1609, 1518, 1432, 1249, 1177, 1051; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.37 (4H, d, J = 8.8 Hz), 6.88 (4H, d, J = 8.8 Hz), 5.99 (2H, s), 2.28 (4H, t, J = 7.3 Hz), 1.55 (4H, tq, J = 7.3, 7.3 Hz), 1.00 (18H, s), 0.84 (6H, t, J = 7.3 Hz), 0.23 (12H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.0, 155.5, 142.8, 134.9, 130.8, 123.9, 119.8, 116.9, 101.5, 35.6, 25.6, 18.2, 13.5, −4.4; HRMS (ESI) m/z: calcd. for $C_{39}H_{54}O_8Si_2Na$ $[M + Na]^+$, 729.3255; found, 729.3277.

*5,6-Bis(butyryloxy)-4,7-bis-(*p-(t-*butyldimethylsilyl-oxy)phenyl)-benzo[1,3]dioxole-2-yl acetate (38).* Treatment of **37** (60.0 mg, 0.09 mmol) with lead tetraacetate (78.4 mg, 0.18 mmol) in benzene (3.0 ml) as described for the preparation of **36** yielded **38** (58.0 mg, 86%) as an amorphous solid; IR υ_{max} (ZnSe) cm^{-1}: 2931, 2857, 1764, 1607, 1518, 1252, 1003, 963, 907; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.74 (1H, s), 7.37 (4H, d, J = 8.8 Hz), 6.88 (4H, d, J = 8.8 Hz), 2.29 (4H, t, J = 7.3 Hz), 2.16 (3H, s), 1.55 (4H, tq, J = 7.3, 7.4 Hz), 1.00 (18H, s), 0.84 (6H, t, J = 7.4 Hz), 0.23 (12H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.9, 168.7, 155.8, 140.2, 135.7, 130.8, 123.3, 119.9, 117.5, 112.9, 35.6, 30.9, 25.6, 21.1, 18.2, 13.5, −4.4; HRMS (ESI) m/z: calcd. for $C_{41}H_{56}O_{10}Si_2Na$ $[M + Na]^+$, 787.3310; found, 787.3288.

Terrestrin B (5). Treatment of **38** (40.0 mg, 0.05 mmol) as described for the preparation of **1** yielded **5** (20.1 mg, 82%) as faint yellow needles; mp 174–175 °C (*n*-hexane-ethyl acetate-ether); IR υ_{max} (ZnSe) cm^{-1}: 3426, 2967, 1733, 1611, 1525, 1453, 1265, 1150; ^{1}H-NMR (500 MHz, CD_3OD) δ: 7.16 (4H, d, J = 8.8 Hz), 6.83 (4H, d, J = 8.8 Hz), 2.17 (4H, t, J = 7.3 Hz), 1.44 (4H, tq, J = 7.3, 7.3 Hz), 0.77 (6H, t, J = 7.3 Hz); ^{13}C-NMR (125 MHz, CD_3OD) δ: 173.1, 158.1, 142.5, 134.8, 132.7, 125.0, 123.9, 116.0, 36.4, 19.2, 13.8; HRMS (ESI) m/z: calcd. for $C_{26}H_{26}O_8Na$ $[M + Na]^+$, 489.1525; found, 489.1541.

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