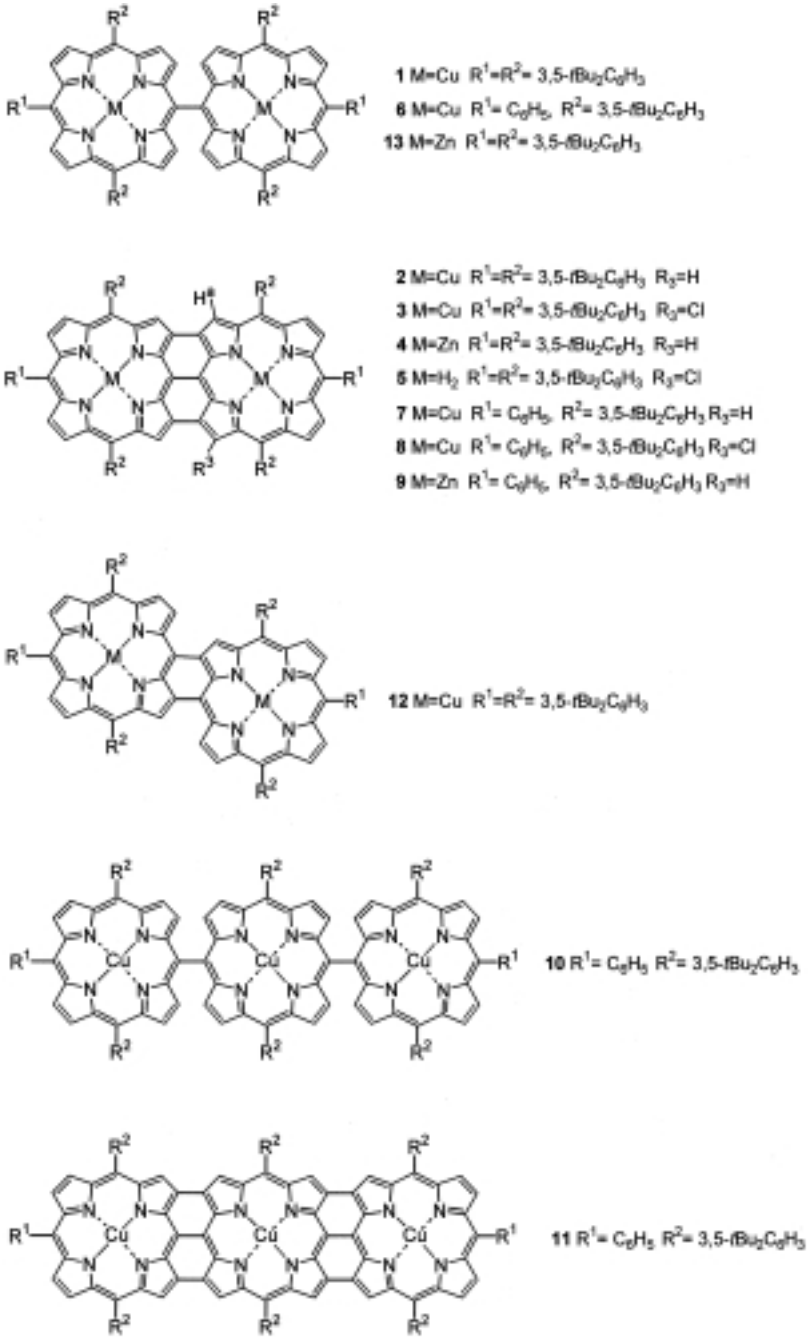
Completely Fused Diporphyrins and Triporphyrin**

Akihiko Tsuda, Hiroyuki Furuta, and Atsuhiro Osuka*

Recently, *meso*–*meso*-linked porphyrin arrays have emerged as potential photonic wires that is (capable of transmitting excitation energy over long distance) as a result of their favorable features, including a linear rodlike shape, ample electronic interactions for rapid incoherent energy hopping, and a lack of an energy sink that disrupts the energy flow along the array.[1–3] These properties originate from the orthogonal conformation of the arrays, which tends to minimize the electronic interaction between the neighboring porphyrins. If the arrays can be made planar and more electronically conjugated they will constitute a conductive electronic wire on a realistic molecular scale; the *meso*–*meso*-linked porphyrin arrays have now reached a discrete 128-mer with a molecular length of approximately 108 nm.[2]

Here, we report an effective oxidative transformation of the *meso*–*meso*-linked diporphyrins into triply linked, fused diporphyrins, which exhibit properties associated with an extremely delocalized π-electronic system as a consequence of their planar structure that is enforced by a fused connection. Fused porphyrin arrays have also attracted considerable interest in light of their application as molecular wires as well as nonlinear optical (NLO) materials, but reported examples are rather limited.[4–7]

Meso–*meso*-linked Cu^{II}-diporphyrin **1** was treated with two equivalents of tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) in C_6F_6 at room temperature for two days to provide triply linked diporphyrins **2** and **3** in 62 and 6% yields, respectively. The structure of **2** has been suggested by its absorption spectrum ($\lambda_{max} = 411$, 576, and 996 nm), which is dramatically changed from that of **1**, and a parent molecular ion peak at m/z 1866 (calcd for $C_{124}H_{138}N_8Cu_2$: 1865) in its matrix-assisted laser-desorption/ionization time-of-flight (MALDI-TOF) mass spectrum, as well as by its transformation into Zn^{II}-diporphyrin **4**. The ^{1}H NMR spectrum of **4** is relatively simple (one set of mutually coupled two doublets at $\delta = 7.75$ and 7.70 for the β-protons, and a singlet at $\delta = 7.35$ for the β-protons (H^a)), which reflects its symmetric structure, and the MALDI-TOF mass spectrum shows a molecular ion at m/z 1868 in the spectrum (calcd for $C_{124}H_{138}N_8Zn_2$: 1867). Monochlorinated diporphyrin **3** exhibits a similar absorption spectrum ($\lambda_{max} = 409$, 573, and 990 nm) and has a parent peak at m/z 1900 in the MALDI-TOF mass spectrum (calcd for $C_{124}H_{137}ClCu_2N_8$: 1899).[8] The oxidation of **1** under similar



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conditions in $CHCl_3$ led to extensive β-chlorination with production of **2** (8%), **3** (29%), and dichlorinated diporphyrin[9] (34%). This result indicates that abstraction of chlorine atoms was involved in this oxidative ring-closure process and that C_6F_6 is a better solvent than $CHCl_3$ for suppressing the β-chlorination.

In order to confirm the X-ray structure of a parent triply linked fused diporphyrin, we converted *meso*–*meso*-Cu^{II}-diporphyrin **6** into triply linked diporphyrin **7** (*m*/*z* 1645, calcd for $C_{108}H_{106}N_8Cu_2$: 1641) and **8** (*m*/*z* 1677, calcd for $C_{108}H_{105}N_8Cu_2Cl$: 1675) in 76 and 6% yields, respectively. The X-ray structure of **7** (Figure 1)[10] shows the two porphyrin

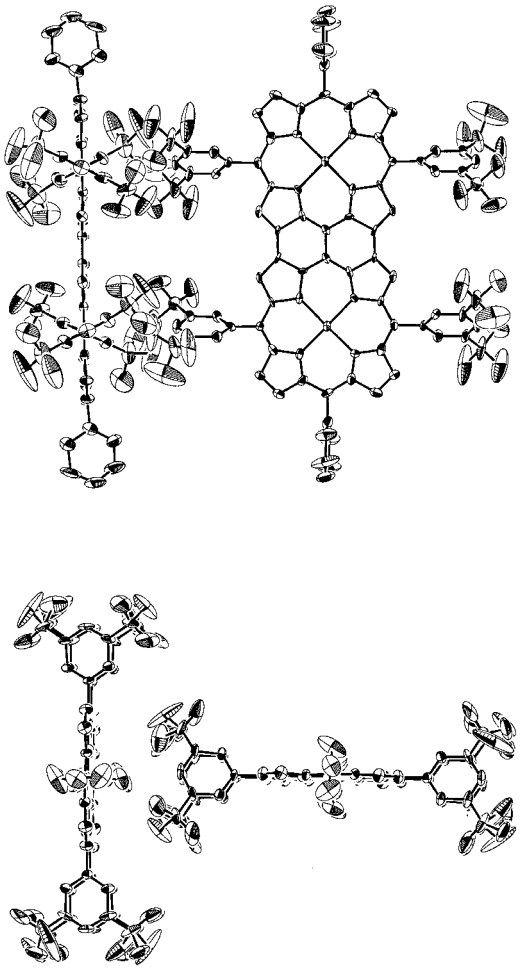

Figure 1. Molecular structure of **7**. Top: top view; bottom: side view. Hydrogen atoms and benzene molecules are omitted for clarity.

rings are fused to form an almost completely coplanar conformation with a mean plane deviation of only 0.029 Å for the 25 core atoms above and below the mean plane, and with β–β bonds of 1.41 Å and a *meso*–*meso* bond of 1.44 Å. It is interesting to note that the nearest fused diporphyrin units take an almost orthogonal arrangement, with the 3,5-di-*tert*-butylphenyl groups pointing towards the Cu^{II}-diporphyrin plane. Such crystal packing, also observed for **5**, suggests an attractive CH–π interaction between the *tert*-butyl group and the π system of the diporphyrin,[11] which may be enhanced by the larger polarizability of the π-electronic system of the diporphyrin. This type of crystal packing has been observed in neither the corresponding metal complexes of tetrakis(3,5-di-*tert*-butylphenyl)porphyrin nor in doubly *meso*–β-linked fused Ni^{II}-diporphyrin.[4, 12] We have also succeeded in obtaining the X-ray structure of the triply linked Zn^{II}-diporphyrin **9**,[13] which displays a mean plane deviation of 0.23 Å, two β–β bonds of 1.44 Å, and a *meso*–*meso* bond of 1.51 Å (Figure 2).

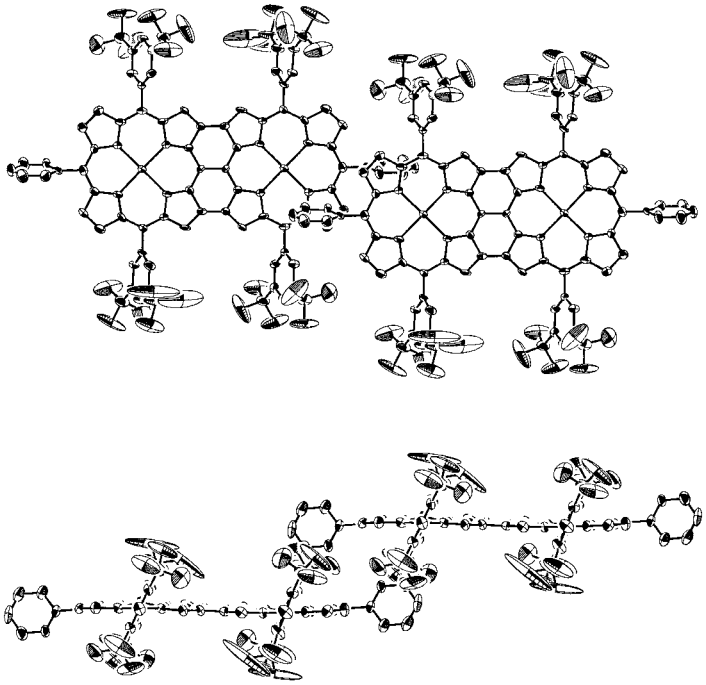

Figure 2. Molecular structure of **9**. Top: top view; bottom: side view. Hydrogen atoms, benzene, and ethanol molecules are omitted for clarity.

The crystal packing of **9** is like a parallel sheet with an interporphyrin separation of approximately 5.44 Å, which is common in porphyrin crystal structures but is entirely different from **7**. In this case, the central Zn^{II} ion is coordinated to ethanol and thus seems to be blocked from taking the orthogonal orientation found for **7**.

The *meso*–*meso*-linked Cu^{II}-triporphyrin **10** was oxidized with four equivalents of BAHA in C_6F_6 for three days to give triply linked triporphyrin **11** in 33% yield along with the recovery of **10** (30%). The fused triporphyrin **11** exhibits a parent molecular peak at *m*/*z* 2383 (calcd for $C_{156}H_{152}N_{12}Cu_3$: 2382) and an extremely red-shifted Q band at 1251 nm. Further characterization of **11** was hampered by its very poor solubility. However, this result encourages the extension of this oxidative ring-closure reaction to higher monodisperse and polymeric *meso*–*meso*-linked porphyrin arrays.[14]

It has been well established that the electronic interactions of multiply linked fused diporphyrins are strong and give rise to red-shifted intense Q bands and lower one-electron oxidation potentials.[4–6, 15] Figure 3 shows the absorption spectra of **1**, **2**, **4**, **10**, and **11**. The absorption spectrum of doubly *meso*–β-linked Cu^{II}-diporphyrin **12** is also shown for comparison. While the *meso*–*meso*-linked porphyrins **1** and **10** exhibit split Soret bands as reported previously,[1] the triply linked oligoporphyrins **2** and **11** show drastically altered absorption spectra with bands at 411, 576, and 996 nm and at

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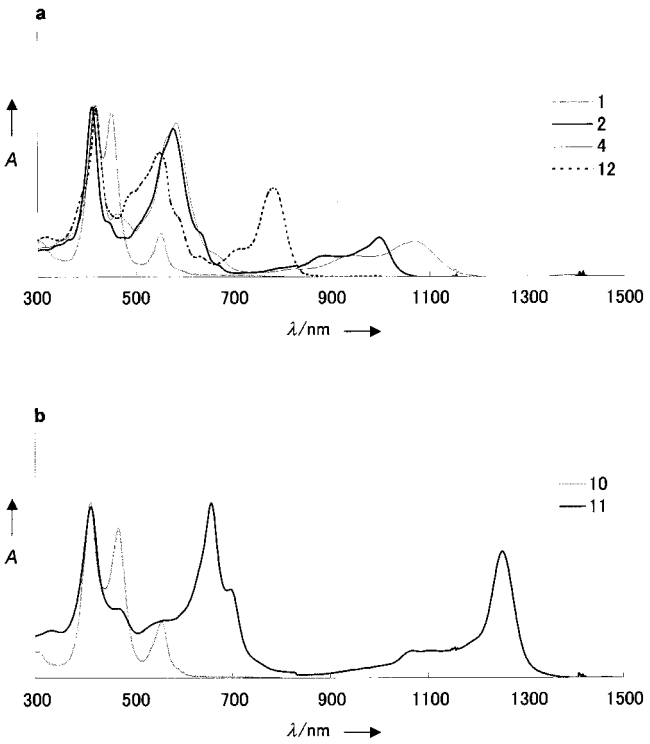

Figure 3. Absorption spectra taken in $CHCl_3$.

413, 657, and 1251 nm, respectively. Although the assignment of these absorption bands has not been done yet, it is probable that the fused connection causes a significant perturbation that breaks down the degeneracy of the e_g orbitals, and gives rise to intensified and red-shifted Q bands. The one-electron oxidation potentials were 0.69 V for **1**, 0.47 V for **12**, and 0.39 V for **2**.[16] Therefore it may be concluded that the electronic interaction in the triply linked diporphyrin **2** is much stronger than those in the fused diporphyrins (including **12**) reported before.[4–6] The effect of the central metal was preliminary examined by comparing Cu^{II}-diporphyrin **2** and Zn^{II}-diporphyrin **4**. The most red-shifted Q band is observed at 1068 nm in **4**, being red-shifted by 72 nm more than **2**, and the one-electron oxidation potential of *meso*–*meso*-linked Zn^{II}-diporphyrin **13** (0.54 V) is decreased to 0.11 V in **4** and thus the potential shift is larger in the Zn^{II} complex.

In light of the extremely strong electronic interactions, which are evidenced from the low one-electron oxidation potentials and the red-shifted intense absorption bands, the triply linked porphyrin arrays must be very promising for use as a component of an electronic molecular wire. Extension of this synthetic strategy to higher oligomeric and polymeric porphyrin arrays is a fascinating next project that is actively in progress in our laboratory. The electronic interaction in the triply-linked diporphyrins depends on the central metal and thus the incorporation of a variety of metals into this diporphyrin ligand is also an interesting project.

Experimental Section

A 50-mL round-bottomed flask was charged with a suspension of **6** (16 mg, 10 μmol) in C_6F_6 (20 mL). The reaction vessel was covered with foil and then BAHA (18 mg, 22 μmol) added in one portion. After the mixture had been stirred for 2 d at room temperature, the mixture was diluted with methanol and THF. The solvent was removed on a rotary evaporator and the residue was precipitated by treatment with benzene/methanol. The product was finally separated by flash chromatography on silica gel (Wakogel C-400). Elution with hexane/CH_2Cl_2 (95/5) gave recovered **6** (2 mg, 13 %) as the first fraction, monochlorinated **8** (1.0 mg, 6 %) as the second fraction, and **7** (12.2 mg, 76 %) as the third fraction. The triply linked Cu^{II}-diporphyrin **7** was transformed into the corresponding Zn^{II}-diporphyrin **9** in 80 % by demetalation with a mixture of conc. H_2SO_4 and TFA and the subsequent insertion of the Zn^{II} ions.

7: MALDI-TOF MS: m/z: 1645, calcd for $C_{108}H_{106}N_8Cu_2$: 1641; UV/Vis ($CHCl_3$): $\lambda_{max} = 411$ (Soret), 575 (Soret), and 994 nm.

9: ^{1}H NMR ($CDCl_3$): $\delta = ^1$H NMR ($CDCl_3$) 1.45 (s, 72 H, *t*Bu), 7.35 (s, 4 H, Por-β), 7.56 (d, $J = 4.9$ Hz, 4 H, Por-β), 7.62 (t, $J = 1.8$ Hz, 4 H, Ar-H), 7.66 (d, $J = 1.8$ Hz, 8 H, Ar-H), 7.69 (s, $J = 1.8$ Hz, 10 H, Ar-H), and 7.80 (d, $J = 4.9$ Hz, 4 H, Por-β); MALDI-TOF MS: m/z: 1646, calcd for $C_{108}H_{106}N_8Zn_2$: 1643; UV/Vis ($CHCl_3$): $\lambda_{max} = 418$ (Soret), 581 (Soret), and 1068 nm.

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[8] The structure of the metal-free diporphyrin **5** (m/z: 1778, calcd for $C_{124}H_{141}N_8$: 1777) including the chlorination site was confirmed by preliminary X-ray crystallography data (see the Supporting Information).

[9] The dichlorinated diporphyrin has been identified as a single product with a parent peak at m/z: 1936 (calcd for $C_{124}H_{136}Cl_2Cu_2N_8$: 1933) in the MALDI-TOF mass spectrum and an absorption spectrum ($\lambda_{max} =$ 408, 571, and 987 nm) similar to those of **2** and **3**, but the secondary chlorination site has not been determined yet.

[10] Data for the crystal structure of $\mathbf{7} \cdot 2C_6H_6$: $C_{120}H_{118}Cu_2N_8$, $M_r = 1796$, crystal obtained from C_6H_6/C_2H_5OH, crystal dimensions $0.3 \times 0.3 \times 0.1$ mm^3, space group $C2/c$, $a = 44.268(2)$, $b = 17.791(6)$, $c = 17.326(5)$ Å, $\alpha = 90$, $\beta = 98.365(2)$, $\gamma = 90°$, $V = 13500$ Å^3. $Z = 6$, $\rho_{calcd} = 1.21$ g cm^{-3}, $\mu_{Mo} = 5.26$ cm^{-1}, $\theta_{max} = 27.5°$, 15223 measured reflections, $R_1 = 0.096$ for 3555 data [$I > 3\sigma(I)$], $wR_2 = 0.137$ for all measured data. Diffraction data were collected on a RIGAKU-RAXIS imaging plate system diffractometer (296 K, $Mo_{K\alpha}$ radiation $\lambda = 0.7107$ Å). The structures were solved by direct methods and refined by F^2 with all observed reflections. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to calculated positions. The structure was solved using the SIR92 Program and refined by teXane for Windows.

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[13] Data for the crystal structure of $\mathbf{9} \cdot C_6H_6 \cdot 2C_2H_6O$: $C_{118}H_{124}N_8O_2Zn_2$, $M_r = 1817$, crystal obtained from C_6H_6/C_2H_5OH, crystal dimensions $0.3 \times 0.2 \times 0.1$ mm^3, space group $P\bar{1}$, $a = 17.428(7)$, $b = 20.324(2)$, $c =$

8.566(2) Å, $\alpha = 91.696(2)$, $\beta = 96.988(4)$, $\gamma = 99.278(4)^\circ$, $V = 2968$ Å^3, $Z = 1$, $\rho_{calcd} = 1.02$ g cm^{-3}, $\mu_{Mo} = 4.51$ cm^{-1}, $\theta_{max} = 27.5^\circ$, 11695 measured reflections, $R_1 = 0.098$ for 4134 data [$I > 3\sigma(I)$], $wR_2 = 0.119$ for all measured data.

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[16] Redox potentials versus $AgClO_4$/Ag were measured by cyclic voltammetry in $CHCl_3$.

What Is the Structure of Glabrescol? Stereoselective Synthesis of Reported Glabrescol**

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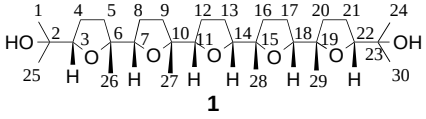
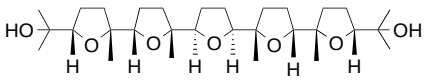
Glabrescol is a triterpene isolated as a minor constituent of the branches and trunk of *Spathelia glabrescens*. Based on extensive NMR spectra analysis, as well as the symmetrical nature of the molecule, Jacobs et al. proposed a *meso*-type structure **1** containing five continuously linked tetrahydrofuran rings.[1] The novel structural features prompted us to attempt the synthesis of glabrescol.[2, 3] Furthermore, we expected that the synthesis would make it possible to examine the biological activity, including the ionophore-like character which has not yet been reported on. Herein, we describe the stereoselective synthesis of **1** and one of its diastereomers **2**,



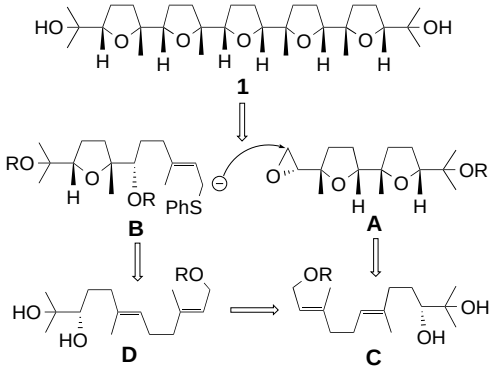
1



2

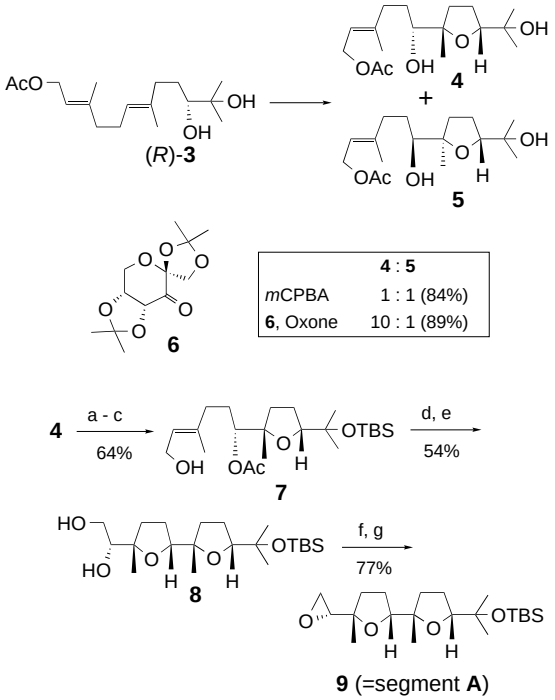
using a baker's yeast reduction as the chirality induction method.[4] Comparison of NMR spectra, however, revealed that neither compound was identical to the natural product.

The retrosynthetic analysis for **1** is illustrated in Scheme 1. Thus, compound **1** is constructed by coupling the 15-carbon segments **A** and **B**, followed by stereoselective oxygenation and tetrahydrofuran (THF) ring formation. Segments **A** and **B** can be prepared from the common (*R*)-diol **C**, obtained by baker's yeast reduction, through asymmetric oxidation.



Scheme 1. Retrosynthetic analysis of the reported glabrescol (**1**).

Segment **A** was synthesized according to Scheme 2. (*R*)-**3**[5] was first treated with *m*CPBA to yield diastereomeric THF derivatives **4** and **5** in a 1:1 ratio.[6] When the same transformation was performed using the epoxidation mediated by



9 (=segment **A**)

Scheme 2. Synthesis of segment **A**. a) Ac_2O, Et_3N, DMAP; b) TBSOTf, 2,6-lutidine; c) LiOH, MeOH; d) Ti(O*i*Pr)$_4$, (−)-DET, *t*BuOOH, 4 Å molecular sieves; e) 1M NaOH, MeOH; f) TsCl, Et_3N, DMAP; g) K_2CO_3, MeOH. *m*CPBA = *meta*-chloroperoxybenzoic acid, DMAP = 4-dimethylaminopyridine, TBS = *tert*-butyldimethylsilyl, Tf = triflate = trifluoromethanesulfonyl, (−)-DET = (−)-diethyl tartrate, Ts = tosyl = toluene-4-sulfonyl.

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