Stereoselective Total Synthesis of Phenolic Nonadecanediol

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A simple and highly efficient synthetic route has been developed for synthesis of 1-(4-hydroxyphenyl)nonadecane-3,5-diol (**1**). The two stereogenic centers were generated by employing proline asymmetric α-hydroxylation (*MacMillan* α-hydroxylation), *Jacobsen*'s hydrolytic kinetic resolution (HKR), and, finally, *Yamaguchi* oxirane opening as key steps (*Scheme 2*).

Introduction. – Phenolic compounds are an important group of natural antioxidants with possible beneficial effects on human health, and they are widely distributed in the medicinal plants, spices, vegetables, fruits, grains, pulses, and other seeds. Their antioxidant activity [1] is based on their ability to donate H-atoms to free-radical scavengers by the formation of stable phenoxyl radicals. Moreover, phenolic compounds also have a broad spectrum of other biological features such as antimutagenic, antibacterial, antiviral, anticarcinogenic, anti-inflammation, antiallergic activities, as well as the ability to modify gene expression [2][3]. The resinous exudates of *Heliotropium sinuatum* possess very good antioxidant capacity due to the presence of phenolic compounds [4]. (3*S*,5*R*)-1-(4-Hydroxyphenyl)nonadecane-3,5-diol was isolated from *Heliotropium sinuatum* (family *Boraginaceae*) [5]. Recently, *Chen et al.* synthesized and determined the absolute configuration of both isomers of **1** on the basis of spectroscopic data and optical rotation [6]. Considering the structure as well as its activity, in continuation of our interest in the synthesis of biologically active natural products [7], herein we report a simple and facile route for the preparation of **1** using proline asymmetric α-hydroxylation (*MacMillan* α-hydroxylation), *Jacobsen's* hydrolytic kinetic resolution (HKR) as chirality-introducing steps, and, finally, *Yamaguchi* oxirane opening. The retrosynthesis of structure **1** is depicted in *Scheme 1* starting from 4-(2-hydroxyethyl)phenol (**2**).

Results and Discussion. – The synthesis of **1** started from commercially available 4-(2-hydroxyethyl)phenol **2**. The known intermediates **3**–**9** were prepared as follows [8]: selective protection of the phenolic OH group of **2** with BnBr afforded the corresponding benzyl ether **3** in 98% yield, which was oxidized with 2-iodoxybenzoic

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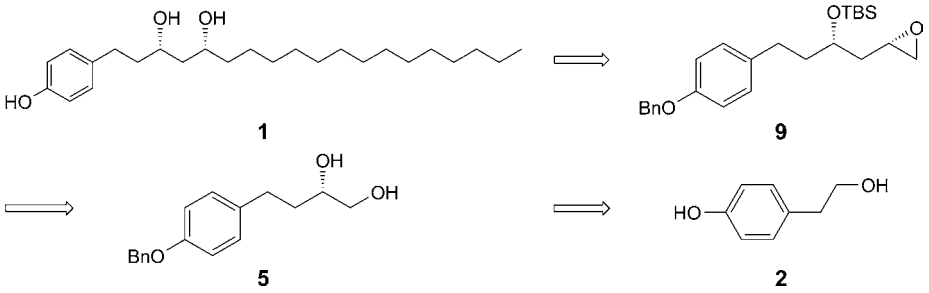
Scheme 1. *Retro synthetic Analysis*



acid (IBX) in DMSO to give the corresponding aldehyde. The crude aldehyde was subjected to C_2-homologation with methyl 2-(triphenylphosphorylidene)acetate to furnish an unsaturated ester ((*E*)/(*Z*) 85:15) in 92% yield. The latter was reduced by using $NiCl_2 \cdot 6\,H_2O/NaBH_4$ to the saturated ester **4** in 95% yield [8g]. Ester **4** was reduced with DIBAL in CH_2Cl_2 at $-78°$ to afford the corresponding aldehyde in 92% yield, which was subjected to proline-catalyzed α-hydroxylation (*MacMillan* α-hydroxylation) using D-proline and PhNO in DMSO at 0°, followed by *in situ* reduction of the resulting anilinoxy aldehyde with $NaBH_4$ in EtOH, and, subsequently, treatment with $CuSO_4 \cdot 5\,H_2O$ in MeOH at 0° provided the diol **5** in 65% yield [9][10]. The primary OH group in **5** was selectively tosylated with $TsCl/Et_3N/Bu_2SnO/CH_2Cl_2$ (88% yield). The intermediate tosylate was then transformed to the chiral epoxide **6** by treatment with K_2CO_3/MeOH in 90% yield. Opening of epoxide **6** with vinylmagnesium bromide furnished the homoallylic alcohol **7** in 85% yield. The resulting OH group in **7** was protected as its silyl ether **8** with TBSCl/1*H*-imidazole in 94% yield.

Compound **8** was subjected to epoxidation using *m*CPBA in CH_2Cl_2 to afford an inseparable diastereoisomer mixture of epoxides in 98% yield, which was subjected to *Jacobsen*'s hydrolytic kinetic resolution (HKR) using (*S*,*S*)-salen-Co(OAc) complex (0.5 mol-%) and H_2O (0.55 equiv.) at room temperature to afford pure epoxide **9** in 48% yield and diol **9a** in 48% yield [11]. Then, employing the *Yamaguchi* procedure [12], oxirane **9** was treated with the Li salt of tridec-1-ynate in dry THF at $-78°$ to furnish **10** in 95% yield. The TBS group in **10** was removed by using Bu_4NF in THF to give *syn*-1,3-diol **11** in 93% yield. Finally, hydrogenation of the C≡C bond and debenzylation of compound **11** by treatment with Pd/C (10 mol-%) afforded the natural phenolic nonadecanediol **1** in 65% yield.

In conclusion, we have achieved the asymmetric total synthesis of the phenolic diol **1** from the readily available starting material **2** in ten distinct steps with an overall yield of 8.75%. The synthesis involves proline-catalyzed α-hydroxylation (*MacMillan* α-hydroxylation), *Jacobsen*'s hydrolytic kinetic resolution, and finally, the Y*amaguchi* oxirane opening as key steps.

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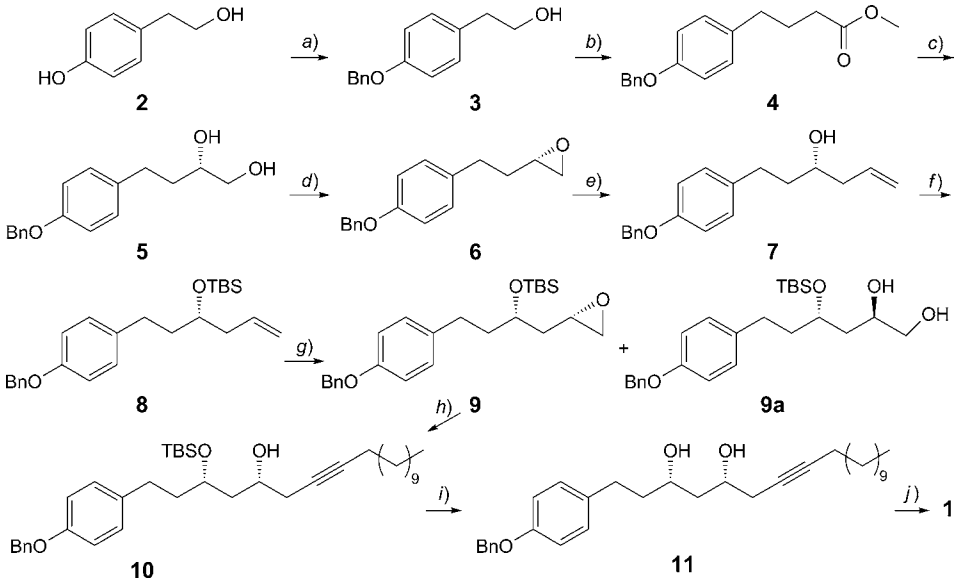
Scheme 2



a) K_2CO_3, BnBr, DMF, 0° to r.t., overnight; 98%. *b*) 1) 2-iodoxybenzoic acid, DMSO, CH_2Cl_2, 4 h. 2) $Ph_3PCHCOOMe$, CH_2Cl_2, r.t., 6 h; 92% (over two steps). 3) $NiCl_2 \cdot 6\ H_2O$, $NaBH_4$, MeOH, r.t., 1 min; 95%. *c*) 1) Diisobutylaluminium hydride (DIBAL), CH_2Cl_2, −78°, 1 h; 92%. 2) PhNO, D-proline, DMSO, 0°, 0.5 h, then $NaBH_4$, EtOH, 0°, 2 h, then $CuSO_4 \cdot 5\ H_2O$ in MeOH, r.t., overnight; 65%. *d*) 1) TsCl, Bu_2SnO, Et_3N, 0° to r.t., 4 h; 88%. 2) K_2CO_3, MeOH, 0° to r.t., 1 h; 90%. *e*) Vinylmagnesium bromide (1.0 M soln. in THF), THF, CuI, −20°, 1 h; 85%. *f*) (^{t}Bu)Me_2SiCl (TBSCl), 1*H*-Imidazole, dry CH_2Cl_2, 4 h; 94%. *g*) 1) *meta*-Chloroperbenzoic acid (*m*CPBA), CH_2Cl_2, r.t., 4 h, 98%. 2) (*S*,*S*)-(salen)-$Co^{II} \cdot OAc$ (0.5 mol-%), dist. H_2O (0.55 equiv), 0° to r.t., 16 h; 48% for **9**, 48% for **9a**. *h*) Tridec-1-yne, BuLi, $BF_3 \cdot Et_2O$, THF, −78°, 4 h; 95%. *i*) Bu_4NF (TBAF) (1.0 M soln. in THF), THF, r.t., 2 h; 93%. *j*) Pd/C (10 mol-%), H_2, AcOEt, r.t., overnight; 65%.

Experimental Part

General. All the reagents and solvents were of reagent grade and used without further purification unless otherwise stated. Technical-grade AcOEt and hexanes used for column chromatography (CC) were distilled before use. THF, when used as solvent for the reactions, was freshly distilled from Na benzophenone ketyl. All the reactions were performed under N_2 in flame or oven dried glassware with magnetic stirring. Column chromatography (CC): silica gel (SiO_2, 60–120 mesh). Optical rotations: *Anton Paar MLP 200* modular circular digital polarimeter by using a 2-ml cell with a path length of 1 dm. FT-IR Spectra: *PerkinElmer 683* IR spectrophotometer; neat or as thin films in KBr optics; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker-Avance 300* instrument (300 and 75 MHz resp.) at r.t.; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. Low-resolution (LR) MS: *Agilent Technologies LC-MSD* trap SL spectrometer; in *m*/*z*.

2-[4-(Benzyloxy)phenyl]ethanol (**3**). To a stirred soln. of **2** (5 g, 36.23 mmol) and K_2CO_3 (14.99 g, 108.6 mmol) in dry DMF (40 ml) was added BnBr (36.23 mmol, 4.3 ml) at 0° under N_2, the mixture was and stirred at r.t. for overnight. After completion of the reaction (TLC), the reaction was quenched with H_2O (50 ml) and the mixture was extracted with 50% AcOEt and hexane (3 × 30 ml), and the combined org. extract was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by CC (AcOEt/hexane 2 : 8) to afford pure **3** (8.09 g, 98%). White solid.

Methyl 4-[4-(Benzyloxy)phenyl]butanoate (**4**). To a stirred soln. of 2-iodoxybenzoic acid (11.15 g, 39.82 mmol) in dry DMSO (8 ml) was added a soln. of **3** (6 gm, 26.54 mmol) in dry CH_2Cl_2 (50 ml) at r.t., and the mixture was stirred for 4 h. After completion of the reaction (TLC), the mixture was filtered through *Celite* and diluted with H_2O (25 ml) and extracted into CH_2Cl_2 (2×30 ml). The combined org. layer was washed with brine (20 ml), dried (Na_2SO_4), and concentrated to give crude aldehyde, which was used directly for the next step. To a stirred soln. of the aldehyde (4 g, 17.69 mmol) in dry CH_2Cl_2 (50 ml) was added $Ph_3PCHCOOMe$ (8.86 g, 26.54 mmol) at r.t., and the mixture was stirred for 6 h. After completion of the reaction (TLC), the mixture was diluted with H_2O (40 ml) and extracted with CH_2Cl_2 (3×25 ml). The combined org. extract was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by CC (AcOEt/hexane 1:9) to afford an (*E*)/(*Z*)-mixture (85:15; 4.59 g, 92%) as a colorless solid. To a cooled (0°) soln. of the unsat. esters (3 g, 10.63 mmol) and $NiCl_2 \cdot 6\,H_2O$ (0.25 g, 1.063 mmol) in MeOH was added $NaBH_4$ (0.4 g, 10.63 mmol) portionwise in open air (color changed from turbid white to black), immediately checked by TLC. The reaction was complete within a 1 min and was quenched by addition of crushed ice, MeOH was evaporated *in vacuo*, and the residue was extracted with AcOEt (2×15 ml). The combined org. extract was washed with brine, dried (Na_2SO_4) and concentrated, and the residue was purified by CC (hexane/AcOEt 8:2) to afford pure **4** (2.87 g, 95%). Colorless solid. IR (neat): 2935, 2851, 1733, 1609, 1510, 1219, 1016. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.49–7.30 (*m*, 5 H); 7.12 (*d*, $J = 8.3$, 2 H); 6.93 (*d*, $J = 8.3$, 2 H); 5.06 (*s*, 2 H); 3.68 (*s*, 3 H); 2.62 (*t*, $J = 7.5$, 2 H); 2.35 (*t*, $J = 7.5$, 2 H); 2.02–1.88 (*m*, 2 H).^{13}C-NMR (75 MHz, $CDCl_3$): 173.8; 157.0; 137.1; 133.6; 129.2; 128.4; 127.7; 127.3; 114.6; 69.9; 51.3; 34.1; 33.2; 26.5. ESI-MS: 285 ($[M+1]^+$).

(2S)-4-[4-(Benzyloxy)phenyl]butane-1,2-diol (**5**). To a cooled (−78°) soln. of **4** (2 g, 7.04 mmol) in dry CH_2Cl_2 (20 ml) was added slowly DIBAL (25% in toluene, 4 ml, 7.04 mmol) for 10 min., and the soln. was stirred for 1 h at the same temp. After completion of the reaction (TLC), the reaction was quenched with sodium potassium tartrate soln. (10 ml) at −78° and diluted with CH_2Cl_2, and the mixture was stirred for 0.5 h. Then, the separated org. layer was concentrated under reduced pressure, and the residue was purified by CC (hexane/AcOEt 8:2) to afford pure aldehyde (1.64 g, 92%) as colorless liquid. To a cooled (0°) soln. of PhNO (0.42 g, 3.93 mmol) and D-proline (0.18 g, 1.57 mmol) in dry DMSO (10 ml) was added the aldehyde (1 g, 3.93 mmol) in dry DMSO (15 ml). The mixture was stirred at r.t. for 0.5 h, followed by the addition of EtOH (20 ml) and $NaBH_4$ (0.59 g, 15.72 mmol) at r.t., and the mixture was stirred for 2 h. After completion (TLC), the reaction was quenched with crushed ice, EtOH was evaporated, and the resulting mixture was extracted with Et_2O (3×10 ml). The combined org. phases were dried (Na_2SO_4) and concentrated to give the crude aminooxy alcohol, which was directly used for the next step without purification. To a cooled (0°) soln. of the crude aminooxy alcohol in MeOH (15 ml) was added $CuSO_4 \cdot 5\,H_2O$ (0.29 g, 1.17 mmol), and the mixture was stirred at r.t. for overnight. After completion of the reaction (TLC), MeOH was evaporated *in vacuo*, and then the mixture was filtered through *Celite* and concentrated. The residue was purified by CC (hexane/AcOEt 7:3) gave **5** (0.696 g, 65%). Light-gray semisolid.

(2S)-2-{2-[4-(Benzyloxy)phenyl]ethyl}oxirane (**6**). To a cooled (0°) soln. of **5** (0.6 g, 2.20 mmol), a cat. amount of Bu_2SnO (5 mg), Et_3N (0.91 ml, 6.61 mmol) in CH_2Cl_2 (20 ml), and TsCl (0.42 g, 2.20 mmol) were added and the mixture was stirred at r.t. for 4 h. After completion of reaction (TLC), the mixture was diluted with H_2O and extracted with CH_2Cl_2 (3×5 ml). The org. layer was washed with brine and dried (Na_2SO_4), and the combined org. layer was concentrated. The residue was purified by CC (hexane/AcOEt 7:3) to afford the tosylated compound as a viscous liquid (0.82 g, 88%). To a soln. of this Ts compound (0.5 g, 1.17 mmol) in MeOH (10 ml) was added K_2CO_3 (0.34 g, 2.46 mmol) at r.t., and the mixture was stirred for 1 h. After completion of the reaction (TLC), MeOH was evaporated, diluted with H_2O, and the mixture was extracted with Et_2O (3×10 ml). The combined org. layer was dried (Na_2SO_4) and concentrated, and the residue was purified by CC (hexane/AcOEt 8:2) to give **6** (0.268 g, 90%). Colorless oil.

(3S)-1-[4-(Benzyloxy)phenyl]hex-5-en-3-ol (**7**). CuI (0.17 g, 0.94 mmol) was gently heated under vacuum and slowly cooled under N_2, then dry THF (10 ml) was added. The resulting suspension was cooled to −20° and vinyl magnesium bromide (1M in THF, 1.8 ml, 1.88 mmol) was added at the same temp. A soln. of **6** (0.24 g, 0.94 mmol) in dry THF (15 ml) was added, and the mixture was stirred at −20° for 1 h. After completion (TLC), the reaction was quenched with sat. aq. NH_4Cl at −20°, and the

mixture was extracted with AcOEt (3 × 5 ml). The combined org. layer was washed with brine, dried (Na_2SO_4) and concentrated, and the residue was purified by CC (hexane/AcOEt 8/2 (v/v)) to afford **7** (0.22 g, 85%). Colorless liquid.

*({(3*S*)-1-[4-(Benzyloxy)phenyl]hex-5-en-3-yl}oxy)(*tert*-butyl)(dimethyl)silane* (**8**). To a cooled (0°) soln. of **7** (0.2 g, 0.70 mmol) and 1*H*-imidazole (0.1 g, 1.48 mmol) in dry CH_2Cl_2 (5 ml) was added TBSCl (0.117 g, 0.78 mmol), and the mixture was stirred at r.t. for 4 h. After completion of the reaction (TLC), the mixture was diluted with H_2O (10 ml) and extracted with CH_2Cl_2 (3 × 5 ml). The combined org. layer was dried (Na_2SO_4) and concentrated, and the residue was purified by CC (hexane/AcOEt 9.5 : 0.5) to furnish pure **8** (0.26 g, 94%). $[\alpha]_D^{25} = -8.0$ ($c = 0.2$, $CHCl_3$). IR (neat): 2945, 2930, 1611, 1511, 1245, 1073, 773. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.45–7.29 (*m*, 5 H); 7.09 (*d*, *J* = 8.5, 2 H); 6.89 (*d*, *J* = 8.6, 2 H); 5.87–5.77 (*m*, 1 H); 5.08–5.01 (*m*, 4 H); 3.78–3.72 (*m*, 1 H); 2.69–2.61 (*m*, 1 H); 2.56–2.49 (*m*, 1 H); 2.26 (*t*, *J* = 7.0, 2 H); 1.79–1.65 (*m*, 2 H); 0.91 (*s*, 9 H); 0.06 (*s*, 3 H); 0.06 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.8; 137.1; 135.0; 134.9; 129.1; 128.4; 127.8; 127.4; 116.8; 114.6; 71.5; 69.9; 41.8; 38.8; 30.8; 25.8; 18.1; −4.33; −4.54. ESI-MS: 414 ($[M + NH_4]^+$).

*({(2*S*)-4-[4-(Benzyloxy)phenyl]-1-[(2*S*)-oxiran-2-yl]butan-2-yl}oxy)(*tert*-butyl)dimethylsilane* (**9**). To a cooled (0°) soln. of **8** (0.2 g, 0.50 mmol) in CH_2Cl_2 (5 ml) was added *m*CPBA (70%) (0.10 g, 0.60 mmol) and the mixture was stirred at r.t. for 4 h. The reaction was quenched by addition of sat. Na_2SO_3 soln., and the mixture was extracted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln., and dried (Na_2SO_4). The org. phase was concentrated, and the residue was purified by CC (hexane/AcOEt 8 : 2) to give a recemic epoxide as an inseparable mixture (0.20 g, 98%). Colorless liquid. A mixture of (*S*,*S*)-(salen)-Co^{II} (0.004 g, 0.0072 mmol) and AcOH (0.012 ml, 0.001 mmol) in toluene (1 ml) was stirred in open air at r.t. for 1 h. The solvent was removed under reduced pressure, and the brown residue was dried in high vacuum. The racemic epoxide (0.15 g, 0.36 mmol) was added in one portion to the above residue at 0° and H_2O (0.03 ml, 0.20 mmol) was slowly added, and the mixture was stirred at r.t. for 16 h. After completion of the reaction (TLC), the mixture was concentrated, and the residue was purified by CC to afford **9** (0.072 g, 48%) and **9a** (0.078 mg, 48%). Colorless liquids.

*(3*S*,5*R*)-1-[4-(Benzyloxy)phenyl]-3-{[(*tert*-butyl)(dimethyl)silyl]oxy}nonadec-7-yn-5-ol* (**10**). To a cooled (−78°) soln. of **9** (0.05 g, 0.12 mmol) in dry THF (5 ml) was added $BF_3 \cdot Et_2O$ (0.03 ml, 0.26 mmol) dropwise, and the mixture was stirred for 0.5 h, followed by addition of BuLi in hexane (2.5 M, 0.06 ml, 0.18 mmol) at −78° and stirring for 4 h at same temp. After completion (TLC), the reaction was quenched at −78° by addition of sat. aq. NH_4Cl soln., and the mixture was extracted with Et_2O (3 × 3 ml). The combined org. extract was washed with brine, dried ($MgSO_4$), and concentrated, and the residue was purified by CC (AcOEt/hexane 2 : 8) to provide pure **10** (0.068 g, 95%). Colorless liquid. $[\alpha]_D^{25} = -25.0$ ($c = 0.4$, $CHCl_3$). IR (neat): 3467, 3032, 2928, 2856, 1611, 1511, 1244, 1078. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46–7.28 (*m*, 5 H); 7.08 (*d*, *J* = 8.3, 2 H); 6.89 (*d*, *J* = 8.6, 2 H); 5.04 (*s*, 2 H); 4.10–3.99 (*m*, 1 H); 3.99–3.91 (*m*, 1 H); 2.64–2.49 (*m*, 2 H); 2.39–2.28 (*m*, 2 H); 2.21–2.10 (*m*, 2 H); 1.86–1.46 (*m*, 4 H); 1.45–1.09 (*m*, 18 H); 0.97–0.82 (*m*, 12 H); 0.08 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.0; 137.1; 134.4; 129.1; 128.5; 127.9; 127.4; 114.8; 82.9; 82.7; 70.0; 69.4; 67.4; 41.8; 40.6; 31.9; 31.0; 30.2; 29.3; 29.2; 29.0; 27.9; 27.7; 25.8; 22.7; 18.7; 17.9; 14.1; −4.0; −4.6. ESI-MS: 594 ($[M + 1]^+$).

*(3*S*,5*R*)-1-[4-(Benzyloxy)phenyl]nonadec-7-yne-3,5-diol* (**11**). To a cooled (0°) soln. of **10** (0.06 g, 0.10 mmol) in THF (2 ml) was added Bu_4NF (0.03 ml, 0.15 mmol, 1.0 M soln. in THF) dropwise and the mixture was stirred at r.t. for 2 h. The reaction was quenched with sat. aq. NH_4Cl soln. (5 ml), and the mixture was extracted with AcOEt (2 × 5 ml). The combined org. layer was washed with brine (10 ml), dried (Na_2SO_4), and concentrated, and the residue was purified by CC (hexanes/AcOEt 70 : 30) to give pure **11** (0.044 g, 93%). Colorless white solid. $[\alpha]_D^{25} = -23.7$ ($c = 0.4$, $CHCl_3$). IR (KBr): 3379, 3072, 2952, 2931, 1612, 1513, 1249, 1092. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46–7.29 (*m*, 5 H); 7.12 (*d*, *J* = 8.3, 2 H); 6.90 (*d*, *J* = 8.6, 2 H); 5.04 (*s*, 2 H); 3.98–3.85 (*m*, 2 H); 2.76–2.59 (*m*, 4 H); 2.37–2.32 (*m*, 2 H); 2.16 (*t*, *J* = 7.1, 2 H); 1.85–1.68 (*m*, 3 H); 1.64–1.55 (*m*, 1 H); 1.52–1.44 (*m*, 2 H); 1.41–1.20 (*m*, 12 H); 0.89 (*t*, *J* = 6.8, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.9; 137.0; 134.2; 129.2; 128.4; 127.8; 127.4; 114.7; 83.5; 75.5; 71.6; 71.4; 69.9; 41.9; 39.7; 31.8; 30.7; 29.6; 29.5; 29.5; 29.3; 29.1; 28.9; 28.8; 28.2; 22.6; 18.6; 14.1. ESI-MS: 501 ($[M + Na]^+$).

*(3*S*,5*R*)-1-(4-Hydroxyphenyl)nonadecane-3,5-diol* (**1**). To a stirred soln. of **11** (0.02 g, 0.04 mmol) in dry AcOEt (5 ml) was added Pd/C (10 mol-%; 0.0004 g, 0.004 mmol) at r.t., and the mixture was stirred

overnight. After completion of the reaction (TLC), the mixture was filtered on *Celite*, the emulsion was concentrated, and the residue was purified by CC (AcOEt/hexane 6:4) to afford pure **1** (0.010 g, 65%). Colorless white solid. $[\alpha]_D^{25} = -4.8$ ($c = 0.25$, MeOH). IR (KBr): 3334, 2931, 2863, 1644, 1219, 1072. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.05 (*d*, $J = 7.5$, 2 H); 6.75 (*d*, $J = 8.3$, 2 H); 3.94–3.78 (*m*, 2 H); 2.76–2.57 (*m*, 2 H); 2.56–2.29 (br. *s*, 2 H); 1.85–1.67 (*m*, 2 H); 1.66–1.55 (*m*, 2 H); 1.54–1.40 (*m*, 2 H); 1.25 (*s*, 24 H); 0.87 (*t*, $J = 6.7$, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 153.8; 133.8; 129.4; 115.2; 73.3; 72.4; 42.8; 39.8; 38.3; 31.9; 30.7; 29.68; 29.64; 29.59; 29.3; 25.3; 22.6; 14.1. HR-EI-MS: 415.3342 ($[M + Na]^+$, $C_{25}H_{44}NaO_3^+$; calc. 415.3329).

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