SUPPORTING INFORMATION FOR

Total Stereoselective Synthesis of (+)-Goniothalesdiol

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Experimental Procedures

General: Melting points were obtained in open capillary tubes and are uncorrected. ^1H - and ^{13}C -NMR spectra were recorded in CDCl_3 at 300 and 75 MHz, respectively. All reactions were monitored by thin layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. Diisopropylamine was used freshly distilled over KOH. NaH was washed before use with several portions of hexane. CH_2Cl_2 was pre-dried over CaCl_2 , distilled over P_2O_5 and carefully kept under an argon atmosphere. Dry THF was distilled from sodium/benzophenone ketyl. All other reagent quality solvents were pre-dried over activated molecular sieves and kept under an argon atmosphere. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2 , and solvent drying with MgSO_4 .

(2*S*,3*S*)-Dimethyl-2,3-bis(benzyloxy)succinate (4**)**

Commercially available benzyl 2,2,2-trichloroacetimidate (5.5 mL, 29.0 mmol) was added dropwise to a solution of commercially available (–)-dimethyl-D-tartrate (2.0 g, 11.0 mmol) in a mixture of CH₂Cl₂ (12 mL) and cyclohexane (24 mL), followed by the carefully addition of trifluoromethanesulfonic acid (45 μL, 0.45 mmol). The reaction mixture was stirred for 12h, filtered and the solid washed with CH₂Cl₂-cyclohexane. The filtrate was washed with saturated aqueous sodium bicarbonate and brine, dried over magnesium sulphate, and concentrated to give 890 mg of an oil which was purified by flash chromatography (eluent cyclohexane/ethyl acetate 3:1), to afford compound **4** as a nearly colourless oil (2.7 g, 69% yield): *R*_f 0.32 (Cyclohexane/EtOAc 2:1); [α]_D²⁰ –131 (*c* 1.1, CHCl₃); ¹H NMR δ 3.66 (s, 6H), 4.39 (s, 2H), 4.43–4.88 (AB system, 4H, *J* = 12.0 Hz), 7.28–7.31 (m, 10H); ¹³C NMR δ 52.12 (2C), 73.25 (2C), 78.24 (2C), 128.05 (2C), 128.35 (2C), 128.39 (2C), 136.82 (2C), 169.54 (2C); MS (FAB+) *m/z* (%): 91 (100), 179 (18), 181 (38), 359 (*M*⁺ + 1, 15); HRMS (FAB+) calcd for C₂₀H₂₃O₆ (*M*⁺ + 1) 359.14946, found 359.14895.

(3*S*,4*S*,5*R*,*SR*)-5-[(*p*-tolylsulfinyl)methyl]-3,4-bis(benzyloxy)-dihydrofuran-2-one (**7**)**

A solution of *n*-BuLi 2.5M in hexanes (792 μ L, 1.90 mmol, 2.3 equiv) was added to a solution of dry diisopropylamine (280 μ L, 1.99 mmol, 2.2 equiv) in THF (2 mL) at 0 °C, under argon. The mixture was stirred for 30 min, cooled to –78 °C and a solution of (*SR*)-methyl-*p*-tolylsulfoxide¹ (268 mg, 0.87 mmol, 2 equiv) in THF (3 mL) was added dropwise. The reaction was allowed to reach –40 °C and stirred for 1 hour at this temperature. After cooling to –78 °C, the mixture was carefully added dropwise to a solution of compound **4** (310 mg, 0.87 mmol, 1 equiv) in THF (3 mL) at rigorous -78 °C and the resulting mixture was stirred at this temperature for 2 hours. The reaction was hydrolyzed with a saturated aqueous ammonium chloride solution (10 mL) and extracted with ethyl acetate. After workup, crude β -keto sulfoxide **5** was obtained as an orange syrup and used in the next step without further purification.

An analytical sample of **(2*S*,3*S*,*SR*)-methyl 5-(*p*-tolylsulfinyl)-2,3-bis(benzyloxy)-4-oxopentanoate (5)** could be obtained after flash chromatography (eluent: ethyl ether/cyclohexane 1:2) as a colorless oil: R_f 0.35 (hexane/EtOAc 1:1); $[\alpha]_D^{20}$ +28 (c 0.3, CHCl_3); ^1H NMR δ 2.42 (s, 3H), 3.66 (s, 3H), 3.91 and 3.97 (AB system, 2H, J = 14.7 Hz), 4.27 (d, 1H, J = 3.4 Hz), 4.33 (d, 1H, J = 3.4 Hz), 4.39 and 4.62 (AB system, 2H, J = 11.7 Hz), 4.42 and 4.78 (AB system, 2H, J = 11.5 Hz), 7.23-7.34 (m, 12H), 7.46 (d, 2H, J = 8.2 Hz); ^{13}C NMR δ 21.4, 52.2, 66.4, 73.5, 74.3, 78.3, 84.9, 124.2, 128.3, 128.4, 128.5, 128.5, 128.5, 128.7, 130.0, 136.2, 136.3, 140.6, 142.0, 169.4, 202.1; MS (FAB+) m/z (%): 91 (100), 136 (21), 154 (20), 181 (11), 481 ($M^+ + 1$, 40); HRMS (FAB+) calcd for $\text{C}_{27}\text{H}_{29}\text{O}_6\text{S}$ ($M^+ + 1$) 481.16848, found 481.17041.

A solution of the crude β -ketosulfoxide **5** (534 mg), obtained as above, and dry zinc bromide (970 mg, 4.3 mmol, 5 equiv) in THF (6 mL) was stirred for 1h at room temperature, under argon, and then, added dropwise to a pre-cooled (–78 °C) solution of DIBAL-H 1.5 M solution in toluene (1.3 mL, 1.9 mmol, 2.2 equiv) in THF (5 mL). The resulting mixture was stirred at –78 °C for 1.5 h and quenched with a saturated aqueous solution of potassium sodium tartrate. The solution was allowed to reach room temperature and an additional saturated aqueous solution of sodium potassium tartrate (40 mL) in a

(1) Solladié, G.; Hutt, J.; Girardin, A. *Synthesis* **1987**, 173-175.

10:1 mixture of EtOAc/H₂O (40 mL) was added. Magnetic stirring was kept until aluminium salts were solved (2-6 h), the organic layer was separated and the aqueous phase was extracted with EtOAc. After workup, crude β -hydroxysulfoxide **6** was obtained and used in the next step without further purification.

An analytical sample of **(2S,3R,4R,SR)-methyl 5-(p-tolylsulfinyl)-2,3-bis(benzyloxy)-4-hydroxypentanoate (6)** could be obtained after flash chromatography (SiO₂ previously treated with HCl/H₂O) (eluent cyclohexane/EtOAc 1:1) as a colourless oil: R_f 0.36 (cyclohexane/EtOAc 1:4); [α]_D²⁰ +29 (*c* 0.2, CHCl₃); ¹H NMR δ 2.42 (s, 3H), 2.85-3.10 (AB part of ABX system, 2H, *J*_{AB} = 13.4, *J*_{AX} = 8.9, *J*_{BX} = 2.9 Hz, $\Delta\nu$ = 33.1 Hz), 3.67 (s, 3H), 3.70 (d, 1H, *J* = 2.7 Hz), 3.96 (broad t, 1H, *J* = 4.0 Hz), 4.32 (d, 1H, *J* = 3.8 Hz), 4.35 and 4.74 (AB system, 2H, *J* = 11.3 Hz), 4.36-4.44 (m, 1H), 4.58 and 4.70 (AB system, 2H, *J* = 11.7 Hz), 7.21-7.43 (m, 14H); ¹³C NMR δ 21.4, 52.0, 58.9, 68.0, 73.2, 73.9, 77.6, 79.9, 123.9, 127.9, 128.1, 128.3, 128.4, 128.5, 129.9, 136.7, 137.4, 140.4, 141.7, 171.1; MS (FAB+) *m/z* (%): 57 (70), 91 (100), 279 (12), 391 (37), 451 (20), 483 (*M*⁺ + 1, 41); HRMS (FAB+) calcd for C₂₇H₃₁O₆S (*M*⁺ + 1) 483.18413, found 483.18440.

To a solution of the crude β -hydroxysulfoxide **6** (550 mg) obtained as above in CH₂Cl₂ (3 mL), trifluoroacetic acid (54 μ L, 0.7 mmol, 0.8 equiv) was added. The mixture was heated at 50 °C for 10h before being quenched with a saturated aqueous solution of NaHCO₃. After extraction with CH₂Cl₂, workup and flash chromatography on deactivated silica gel (pre-treated with a 1% solution of Et₃N) (eluent hexane/EtOAc 1:1), **(3S,4S,5R,SR)-5-[(p-tolylsulfinyl)methyl]-3,4-bis(benzyloxy)-dihydrofuran-2-one (7)** was obtained as a colorless oil (125 mg, 32% overall yield for three steps starting from compound **4**): R_f 0.51 (hexane/EtOAc 1:3); [α]_D²⁰ +2.0 (*c* 1.7, CHCl₃); ¹H NMR δ 2.41

(s, 3H), 3.18-3.32 (AB part of ABX system, $J_{AB} = 13.7$, $J_{AX} = 7.3$, $J_{BX} = 6.9$ Hz, $\Delta\nu = 27.5$ Hz), 4.08 (d, 1H, $J = 3.1$ Hz), 4.25 (dd, 1H, $J = 5.2$ and 3.1 Hz), 4.48 and 4.57 (AB system, 2H, $J = 11.7$ Hz), 4.66 and 4.87 (AB system, 2H, $J_{AB} = 11.7$ Hz), 4.91 (td, 1H, $J = 6.8$ and 5.1 Hz), 7.23-7.47 (m, 14H); ^{13}C NMR δ 21.4, 55.6, 72.3, 72.5, 75.1, 76.0, 79.0, 124.1, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 130.1, 136.3, 136.4, 139.5, 142.1, 171.7; MS (FAB+) m/z (%): 57 (49), 91 (38), 107 (20), 154 (58), 391 (100), 451 ($M^+ + 1$, 40); HRMS (FAB+) calcd for $\text{C}_{26}\text{H}_{27}\text{O}_5\text{S}$ ($M^+ + 1$) 451.15792, found 451.15742.

(2R,3S,4R,5R,SR)-3,4-Bis(benzyloxy)-5-phenyl-2-[(*p*-tolylsulfinyl)methyl]-tetrahydrofuran (10)

To a solution of lactone **7** (600 mg, 1.33 mmol, 1 equiv) in THF (22 mL), boron trifluoride etherate (422 μL , 3.33 mmol, 2.5 equiv) was added at -78°C under argon. After stirring for 1.5h, a solution of phenyl magnesium bromide (9.1 mL of a 1M solution in toluene, 6.65 mmol, 5 equiv), was added dropwise at rigorous -78°C . The resulting mixture was stirred for 2h at the same temperature and hydrolyzed with saturated aqueous solution of NH_4Cl (15 mL). After extraction with EtOAc, washing with brine and workup, the resulting colorless oil containing a 23:77 mixture of

(**2S,3R,4R,SR**)-2,3-bis-benzyloxy-4-hydroxy-1-phenyl-5-(*p*-tolylsulfinyl)-pentan-1-one (**8**) and hemiketal (**3S,4S,5R,SR**)-3,4-bis-benzyloxy-2-phenyl-5-[(*p*-tolylsulfinyl)methyl]-tetrahydrofuran-2-ol (**9**), as a mixture of diastereoisomers at C-2, was used in the next reaction without further purification.

To a solution of the crude mixture of **8** and **9**, obtained as above, in CH_2Cl_2 (25 mL), triethylsilyl hydride (425 μL , 2.66 mmol, 2 equiv), followed by trimethylsilyl triflate (334 μL , 1.73 mmol, 1.3 equiv) were added dropwise at 0 °C, under argon. After stirring for 20 min at 0 °C, the reaction was hydrolyzed with water. After workup and flash chromatography (eluent $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 12:1), a non-separable 85:15 mixture of (**2R,3S,4R,5R,SR**)-3,4-bis(benzyloxy)-5-phenyl-2-[(*p*-tolylsulfinyl)methyl]-tetrahydrofuran (**10**) and (**2R,3S,4R,5S,SR**)-3,4-Bis(benzyloxy)-5-phenyl-2-[(*p*-tolylsulfinyl)methyl]-tetrahydrofuran (**11**) was obtained as a colorless oil (456 mg, 67% yield for the two last steps starting from lactone **7**).

The following data correspond to the mixture of **10** and **11**: R_f 0.5 (hexane/EtOAc 1:3); $[\alpha]_D^{20} +52$ (c 0.73, CHCl_3); ^1H NMR (major diastereoisomer **10**) δ 2.41 (s, 3H), 3.21-3.51 (AB part of ABX system, 2H, $J_{AB} = 12.8$, $J_{AX} = 6.7$, $J_{BX} = 7.1$ Hz, $\Delta\nu = 66.6$ Hz), 4.00 (dd, 1H, $J = 3.9$ and 1.0 Hz), 4.10 (dd, 1H, $J = 4.0$ and 1.0 Hz), 4.27 (td, 1H, $J = 6.8$ and 3.9 Hz), 4.41 and 4.53 (AB system, 2H, $J = 11.5$ Hz), 4.50 (s, 2H), 4.78 (d, 1H, $J = 3.9$ Hz), 7.20-7.53 (m, 19H); ^1H NMR (minor diastereoisomer **11**) δ 2.41 (s, 3H), 3.12-3.43 (AB part of ABX system, 2H, $J_{AB} = 12.9$, $J_{AX} = 6.9$, $J_{BX} = 7.2$ Hz, $\Delta\nu = 79.2$ Hz), 3.96 (broad d, 1H, $J = 4.2$ Hz), 4.14 (broad d, 1H, $J = 4.7$ Hz), 4.50 and 4.60 (AB system, 2H, $J = 11.7$ Hz), 5.18 (d, 1H, $J = 3.5$ Hz), 7.20-7.53 (m, 19H); ^{13}C NMR (major diastereoisomer **10**) δ 21.4, 56.4, 71.5, 72.0, 76.0, 83.3, 86.1, 89.2, 124.2, 126.3, 127.6, 127.8, 127.9, 128.4, 128.5, 129.9, 137.3 (2C), 140.0, 140.4, 141.5; MS (EI) m/z (%): 91 (100), 139 (8), 181 (5), 197 (5), 387 (1), 496 (4), 512 (M^+ , 0.4); HRMS (EI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_4\text{S}$ (M^+) 512.20213, found 512.20227.

Mixture of (*E*)- and (*Z*)-methyl-3-[(2*S*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-phenyl-tetrahydrofuran-2-yl]-acrylate (13** and **14**)**

To a solution of a 85:15 mixture of **10** and **11** (290 mg, 0.56 mmol, 1 equiv) and 2,6-lutidine (210 μL , 1.81 mmol, 3.2 equiv) in CH_3CN (8 mL), trifluoroacetic anhydride (244 μL , 1.73 mmol, 3.05 equiv) was added at 0°C , under nitrogen. After stirring at 0°C for 15 min, an aqueous solution (9 mL) of mercury (II) chloride (461 mg, 1.7 mmol) was added. The mixture was stirred at room temperature for 12h, extracted with ethyl ether and the organic layer washed with brine. After workup, a 85:15 mixture of (2*R*,3*S*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-phenyl-tetrahydrofuran-2-carbaldehyde (**12**) and its (5*S*) epimer was obtained as a colourless oil and used in the next step without further purification.

The following data correspond to the 85:15 mixture of **12** and its (5*S*) epimer: R_f 0.5 (hexane/EtOAc 1:1); $[\alpha]_D^{20} +28$ (c 0.55, CHCl_3); ^1H NMR [major (5*R*) epimer **12**] δ 4.07 (dd, 1H, $J = 3.6$ Hz and $J = 1.4$ Hz), 4.46 (m, 5H), 4.56 (dd, 1H, $J = 4.6$ and 1.7 Hz), 5.01 (d, 1H, $J = 3.7$ Hz), 7.12-7.53 (m, 15H), 9.86 (d, 1H, $J = 1.8$ Hz). ^1H NMR [minor (5*S*) epimer] δ 3.96 (broad d, 1H, $J = 2.9$ Hz), 4.46 (m, 5H), 4.74 (dd, 1H, $J = 4.7$ and 1.8 Hz), 5.43 (d, 1H, $J = 3.1$ Hz), 7.12-7.53 (m, 15H), 9.76 (d, 1H, $J = 2.0$ Hz).

To a solution of the 85:15 crude mixture of **12** and its (5*S*) epimer, obtained as above, in CH₂Cl₂ (19 mL), commercially available methyl (triphenylphosphoranylidene)acetate (281 mg, 0.84 mmol, 1.5 equiv) was added at 0 °C. After stirring for 1h at 0 °C, the solvent was evaporated and the crude mixture was purified by flash chromatography (eluent hexane/EtOAc, 5:1) to afford a 55:45 mixture of the *E/Z* isomers of methyl-3-[(2*S*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-phenyl-tetrahydrofuran-2-yl]-acrylate (**13**) and (**14**) together with their corresponding (5*S*) epimers, as a colorless oil (204 mg, 82% overall yield for two steps starting from the 85:15 mixture of **10** and **11**).

An analytical sample of a 85:15 mixture of (*E*)-methyl-3-[(2*S*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-phenyltetrahydrofuran-2-yl]-acrylate (**13**) and its (5*S*) epimer could be obtained after flash chromatography (eluent hexane/EtOAc, 5:1): *R*_f 0.46 (hexane/EtOAc 1:2); [α]_D²⁰ +20 (*c* 1.3, CHCl₃), ¹H NMR [major (5*R*) epimer (*E*)-**13**] δ 3.76 (s, 3H), 4.02 (dd, 1H, *J* = 4.1 and 1.5 Hz), 4.08 (dd, 1H, *J* = 4.2 and 1.5 Hz), 4.43 and 4.52 (AB system, 2H, *J* = 12.2 Hz), 4.45 and 4.49 (AB system, 2H, *J* = 8.6 Hz), 4.75 (ddd, 1H, *J* = 5.4, 4.2 and 1.6 Hz), 4.89 (d, 1H, *J* = 4.1 Hz), 6.26 (dd, 1H, *J* = 15.8 and 1.6 Hz), 7.15 (dd, 1H, *J* = 15.8 and 5.4 Hz), 7.19-7.46 (m, 15H); ¹H NMR [minor (5*S*) epimer] δ 3.76 (s, 3H), 3.99 (broad d, 1H, *J* = 3.4 Hz), 4.13 (dd, 1H, *J* = 4.3 and 1.1 Hz), 4.41-4.57 (m, 4H), 5.01 (ddd, 1H, *J* = 5.4, 4.5 and 1.7 Hz), 5.29 (d, 1H, *J* = 3.5 Hz), 6.22 (dd, 1H, *J* = 15.7 and 1.7 Hz), 7.09 (dd, 1H, *J* = 15.6 and 5.2 Hz), 7.19-7.46 (m, 15H); ¹³C NMR [major (5*R*) epimer (*E*)-**13**] δ 51.6, 71.8, 72.1, 80.6, 84.3, 85.8, 89.7, 122.8, 126.5, 127.6, 127.7, 128.0, 128.4, 128.5, 137.4, 137.5, 140.0, 142.8, 166.6; MS (EI) *m/z* (%): 98 (91), 105 (43), 181 (31), 197 (100), 205 (41), 239 (32), 295 (18), 353 (10), 444 (M⁺, 0.2); HRMS (EI) calcd for C₂₈H₂₈O₅ (M⁺) 444.19367, found 444.19492.

An analytical sample of a 85:15 mixture of (*Z*)-methyl-3-[(2*S*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-phenyltetrahydrofuran-2-yl]-acrylate (**14**) and its (5*S*) epimer could be obtained after flash chromatography (eluent hexane/EtOAc, 5:1): *R*_f 0.54 (hexane/EtOAc, 1:2); [α]_D²⁰ +154 (*c* 0.44, CHCl₃); ¹H NMR [major (5*R*) epimer (*Z*)-**14**] δ 3.64 (s, 3H), 3.94 (dd, 1H, *J* = 4.6 and 1.3 Hz), 4.33 (dd, 1H, *J* = 4.3 and 1.3 Hz), 4.33 and 4.40 (AB system, 2H, *J* = 12.2 Hz), 4.38 and 4.43 (AB system, 2H, *J* = 11.9 Hz), 4.75 (d, 1H, *J* = 4.6 Hz), 5.51 (ddd, 1H, *J* = 6.9, 4.3 and 1.6 Hz), 5.92 (dd, 1H, *J* = 11.8 and 1.6 Hz), 6.52 (dd, 1H, *J* = 11.8 and 6.9 Hz), 7.11-7.39 (m, 15H); ¹H NMR [minor (5*S*) epimer] δ 3.63 (s, 3H), 3.88 (broad d, 1H, *J* = 3.7 Hz), 4.01 and 4.13 (AB system, 2H, *J* = 12.5 Hz), 4.29-4.45 (m, 3H), 5.25 (d, 1H, *J* = 3.3 Hz), 5.78 (ddd, 1H, *J* = 6.4, 4.2 and 1.7 Hz), 5.88 (dd, 1H, *J* = 11.7 and 1.7 Hz), 6.44 (dd, 1H, *J* = 11.7 and 7.0 Hz), 7.11-7.39 (m, 15H); ¹³C NMR [major (5*R*) epimer (*Z*)-**14**] δ 52.4, 72.7, 72.9, 80.1, 85.9, 86.7, 91.3, 121.4, 127.5, 128.6, 128.7, 129.2, 129.3, 129.4, 138.6, 138.8, 141.2, 147.3, 167.1.

Methyl 3-[(2*S*,3*S*,4*S*,5*R*)-3,4-dihydroxy-5-phenyltetrahydrofuran-2-yl]propanoate (1**): (+)-Goniothalesdiol**

To a solution of the crude mixture of (*E*)-**13** and (*Z*)-**14** (52 mg, 0.11 mmol, 1 equiv), obtained as above, in methanol (4 mL) and formic acid (176 μ L), under argon, palladium black (14 mg, 0.13 mmol, 1.2 equiv) was added and the flask was flushed again with argon. The reaction mixture was stirred at 55 °C for 6h, cooled to room temperature and filtered over celite. After evaporation of the solvent and

flash chromatography (eluent CH₂Cl₂/ethyl ether 3:1), three compounds could be isolated: (+)-5-epi-Goniothalesdiol (**2**) as colorless oil (2.6 mg, 9% yield), (*S*)-dihydro-5-[(1*S*,2*R*)-1,2-dihydroxy-3-phenylpropyl]furan-2(3*H*)-one (**15**) as a white solid (9.0 mg, 35% yield), and (+)-Goniothalesdiol (**1**) as a colourless oil (12.0 mg, 41% yield).

(+)-5-Epi-Goniothalesdiol (2): R_f 0.41 (CH₂Cl₂/ethyl ether, 3:1); [α]_D²⁰ +55 (c 0.04, EtOH) {lit:² [α]_D²⁰ = +66.6 (c 0.74, EtOH), lit:³ [α]_D²⁰ = +70.3 (c 0.23, EtOH)}; ¹H NMR δ 1.82-2.07 (m, 2H), 2.31 (broad s, 1H), 2.35-2.64 (m, 2H), 2.99 (d, 1H, *J* = 3.7 Hz), 3.65 (s, 3H), 4.12 (broad s, 1H), 4.20 (broad s, 1H), 4.25 (m, 1H), 5.3 (d, 1H, *J* = 3.4 Hz), 7.30 (m, 5H)

(*S*)-Dihydro-5-[(1*S*,2*R*)-1,2-dihydroxy-3-phenylpropyl]furan-2(3*H*)-one (15): mp 104-106 °C; R_f 0.37 (EtOAc); [α]_D²⁰ +28.4 (c 0.31, EtOH); ¹H NMR δ 2.06-2.26 (m, 2H), 2.37-2.62 (m, 2H), 2.64 (d, 1H, *J* = 5.8 Hz), 2.77-2.99 (AB part of ABX system, 2H, *J*_{AB} = 13.3, *J*_{AX} = 6.5, *J*_{BX} = 7.7 Hz, Δ*v* = 24.5 Hz), 3.39-3.43 (ddd, 1H, *J* = 5.7, 4.0 and 3.2 Hz), 3.87-3.95 (m, 1H), 4.55 (td, 1H, *J* = 6.9 and 3.9 Hz), 7.16-7.29 (m, 5H); ¹³C NMR δ 23.9, 28.2, 40.0, 72.7, 73.6, 81.5, 126.8, 128.7, 129.4, 137.3, 176.8; MS (FAB+) *m/z* (%): 91 (49), 107 (35), 149 (62), 167 (19), 201 (31), 237 (*M*⁺ + 1, 35); HRMS (Electrospray) calcd for C₁₃H₁₆O₄ (*M*⁺ + Na) 259.0940, found 259.0941.

(+)-Goniothalesdiol (1): R_f 0.33 (CH₂Cl₂/ethyl ether, 3:1); [α]_D²⁰ +6.4 (c 0.36, EtOH) {lit:⁴ [α]_D²⁰ = +7.5 (c 0.23, EtOH), lit:^{3a} [α]_D²⁰ = +6.5 (c 0.6, EtOH), lit:^{3b} [α]_D²⁰ = +6.9 (c 0.38, MeOH), lit:⁵ [α]_D²⁰ = -7.1 (c 0.15, EtOH)}; ¹H NMR δ 2.04- 2.17 (m, 2H), 2.28 (broad s, 1H), 2.45-2.68 (m, 3H), 3.69 (s, 3H), 4.05-4.11 (m, 3H), 4.61 (d, 1H, *J* = 4.5 Hz), 7.28 (broad d, 1H, *J* = 7.0 Hz), 7.34 (broad t, 2H, *J* = 7.0 Hz), 7.42 (broad d, 2H, *J* = 7.0 Hz); ¹³C NMR δ 23.7, 30.6, 51.9, 79.1, 80.7, 85.4, 86.2, 126.1, 127.8, 128.5, 140.0, 174.6; MS (FAB+) *m/z* (%): 77 (17), 89 (17), 107 (22), 120 (13), 152 (9), 267 (*M*⁺ + 1, 16); HRMS (FAB+) calcd for C₁₄H₁₈O₅ (*M*⁺ + 1) 267.12325, found 267.12298.

(2) Yoda, H.; Shimajo, T.; Takabe, K. *Synlett* **1999**, 1969–1971.

(3) (a) Babjak, M.; Kapitán, P.; Gracza, T. *Tetrahedron Lett.* **2002**, *43*, 6983–6985. (b) Babjak, M.; Kapitán, P.; Gracza, T. *Tetrahedron* **2005**, *61*, 2471–2479.

(4) Cao, S.-G.; Wu, X.-H.; Sim, K.-Y.; Tan, B. K. H.; Pereira, J. T.; Gog, S.-H. *Tetrahedron* **1998**, *54*, 2143–2148.

(5) Yoda, H.; Nakaseko, Y.; Takabe, K. *Synlett* **2002**, 1532–1534.