

1 **Supplementary Material**

2 **Stereoisomeric Analysis of 6,10,14-Trimethylpentadecan-2-ol and the**  
3 **Corresponding Ketone in Wing Extracts from African *Bicyclus* Butterfly**  
4 **Species**

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## 2 **Experimental**

3 *General Procedures* Commercially available chemicals were used without further  
4 purification. (3*R*)-3,7-dimethyloct-6-enoic acid and other commercially available chemicals  
5 were obtained from Aldrich and analyzed by GC to be of > 99.9 % chemical purity. Amano  
6 PS was obtained from Amano Pharmaceutical Co. Ltd., Nagoya, Japan. The lipase was stored  
7 at 4 °C over silica gel. *Candida rugosa* lipase-type VII (CRL) was purchased from Sigma  
8 Aldrich. Lot: 056K1490, activity: 835 units / mg solid used in the immobilization. 2,2-  
9 Dimethyl-1-propanol was purchased from Sigma Aldrich and *iso*-octane was purchased from  
10 Fluka and used without further purification. Accurel EP 100 (200-350 µm) was a gift by  
11 Accurel systems, AKZO Faser AG, Obernburg, Germany. Dry Et<sub>2</sub>O was distilled from  
12 LiAlH<sub>4</sub>, and the alkyl halides were distilled prior to use and stored under argon. In the  
13 coupling reactions with organolithium reagents, the solvents were degassed by argon for  
14 about 1 h prior to use. Li metal was washed with *n*-heptane and was flattened by hammering  
15 and cut in very thin pieces prior to use. Preparative liquid chromatography (LC) was  
16 performed on normal phase silica gel (Merck 60, 230–400 mesh, 0.040–0.063 mm, Merck,  
17 Germany) employing an increasing concentration of distilled ethyl acetate in distilled  
18 cyclohexane (0 to 100%) as eluent. To monitor the progress of the reactions, thin layer  
19 chromatography (TLC) was performed on silica gel plates (Merck 60 F<sub>254</sub>, pre-coated  
20 aluminium foil) eluted with ethyl acetate (20 - 40% ethyl acetate in cyclohexane) and  
21 developed by spraying with vanillin in sulfuric acid and heated at 120 °C. NMR spectra were  
22 recorded on a Bruker DMX 250 (250 MHz <sup>1</sup>H and 62.9 MHz <sup>13</sup>C) and Bruker Avance 500  
23 (500 MHz <sup>1</sup>H, 125.8 MHz <sup>13</sup>C) spectrometer using CDCl<sub>3</sub> as solvent and TMS as internal  
24 reference. Optical rotations were measured on a Perkin Elmer 241 polarimeter using a 1-dm  
25 cell. Mass spectra were recorded on a Saturn 2000 instrument, operated in EI mode, coupled

1 to a Varian 3800 GC instrument with a 30 m × 0.25 mm I.D. capillary column coated with  
2 DB-1 (Durabond),  $d_f = 0.25 \mu\text{m}$ , carrier gas  $\text{N}_2$ , 12 psi, split ratio 1:50. Purity of products and  
3 in some cases conversions of reactions were monitored by a 30 m × 0.32 mm I.D. capillary  
4 column coated with EC-1 (Varian),  $d_f = 0.25 \mu\text{m}$ , carrier gas  $\text{N}_2$ , 12 psi, split ratio 1:50.  
5 Enantioselective GC analyses were carried out on a chiral  $\beta$ -dex225 column (30m x 0.25 mm,  
6  $d_f = 0.25$ ; Supelco) operated isothermally at 70 °C.

### 7 **Synthesis of (2R)-6-Methoxy-2-methylheptyl-sulfonylbenzene as building block 2**

8 *6-Methylhept-5-en-2-ol* 6-Methylhept-5-en-2-one (11.7 ml, 92.8 mmol) in  $\text{Et}_2\text{O}$  (100 ml) was  
9 added dropwise to a suspension of  $\text{LiAlH}_4$  (1.39 g, 37.6 mmol) in  $\text{Et}_2\text{O}$  (500 ml) at 0 °C and  
10 the reaction was stirred for 3 h.  $\text{H}_2\text{O}$  (10 ml) and  $\text{HCl}$  (2M, 30 ml) were added to quench the  
11 reaction. The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (4 × 25 ml) and the combined organic  
12 phases were washed with  $\text{HCl}$  (2M, 2 × 20 ml) and brine (sat.aq., 20 mL), dried over  $\text{MgSO}_4$   
13 (anhydr.), and the solvent was removed under reduced pressure, which resulted in 12.6 g  
14 (quantitative yield, 99.4 % pure).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 5.13 (tt, 1H,  $J = 1.5$  and 7 Hz), 3.81 (m,  
15 1H), 2.07 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 1.51-1.64 (m, 2H), 1.19 (d, 3H,  $J = 6.3$  Hz).  
16 Analytical data were similar to data in Charlton et al (1980).

17 *6-Methoxy-2-methylhept-2-ene* 6-Methylhept-5-en-2-ol (0.5 g, 3.9 mmol) was added  
18 dropwise to a suspension of  $\text{NaH}$  (0.43 g, 18 mmol) in THF (12 ml) at 0 °C. After 1.5 h,  
19 methyl iodide (3.4 g, 24 mmol) was added dropwise during 30 min at 0 °C, and the mixture  
20 was stirred for 4 h. Methanol (5 ml) and  $\text{Et}_2\text{O}$  (15 ml) were added, followed by  $\text{HCl}$  (0.1M)  
21 until pH 6 was reached.  $\text{Et}_2\text{O}$  (50 ml) was added and the organic phase was separated from the  
22 aqueous phase. The organic layer was washed with  $\text{H}_2\text{O}$  (3 × 15 ml), dried over  $\text{MgSO}_4$   
23 (anhydr.), and the solvent was removed under reduced pressure resulting in 0.61 g of the  
24 product (quantitative yield, >99 % pure).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 5.10 (tt, 1H,  $J = 1.5, 7$  Hz), 3.31

1 (s, 3H), 3.28 (q, 2H,  $J = 6$  Hz), 2.03 (m, 2H), 1.61 (s, 3H), 1.59-1.36 (m, 1H), 1.13 (d, 3H,  $J =$   
2 5 Hz). Analytical data were similar to data in Masaki et al (1985).

3 (*E*)-6-Methoxy-2-methylhept-2-en-1-ol 6-Methoxy-2-methylhept-2-ene (12.06 g, 76.3 mmol)  
4 was added dropwise to a mixture of *tert*-butyl hydroperoxide (81 ml, 590 mmol, 70 %  
5 solution), SeO<sub>2</sub> (0.37 g, 3.33 mmol), salicylic acid (2.3 g, 16.65 mmol) in DCM (70 ml), and  
6 after 24 h additional *tert*-butyl hydroperoxide (81 ml, 590 mmol, 70 % solution) was added.  
7 After 24 h of stirring, the reaction was quenched by addition of MeOH (100 ml) and NaBH<sub>4</sub>  
8 (10 g) in NaOH (0.2 M, 100 ml). After 1.5 h, Et<sub>2</sub>O (150 ml) and H<sub>2</sub>O (150 ml) were added,  
9 and the aqueous phase was extracted with Et<sub>2</sub>O (2 × 400 ml) and the combined organic layer  
10 was washed with brine (sat.aq., 2 × 200 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent was  
11 removed. LC purification resulted in 10.49 g of the title compound 99% pure with a yield of  
12 87 %. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 5.41 (tt, 1H,  $J = 1.5, 7$  Hz), 4.01 (s, 2H), 3.31 (s, 3H), 3.30 (m, 1H),  
13 2.10 (m, 2H), 1.68 (m, 3H), 1.64-1.55 (m, 3H), 1.48-1.42 (m, 2H), 1.14 (d, 3H,  $J = 6.5$  Hz).

14 6-Methoxy-2-methylheptan-1-ol Ra-Ni (3 Pasteur pipettes) was added to (*E*)-6-methoxy-2-  
15 methylhept-2-en-1-ol (10.8 g, 68 mmol) in ethanol (150 ml), and the system was evacuated  
16 twice and stirred overnight under H<sub>2</sub> (g) at 1 atm. The reaction mixture was filtered through  
17 Celite. The solvent was removed under reduced pressure, and the crude product was diluted  
18 with Et<sub>2</sub>O (100 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent was removed under reduced  
19 pressure giving 11.59 g of the saturated alcohol (quantitative yield, > 99 % pure). The identity  
20 of the title compound was confirmed by <sup>1</sup>H-NMR and used in the next step without further  
21 analysis.

22 6-Methoxy-2-methylheptanoic acid Jones reagent (63 ml) was added dropwise to a solution of  
23 6-methoxy-2-methylheptan-1-ol (11.59 g, 65 mmol) in acetone (500 ml) at 0 °C. After 2 h,  
24 *iso*-PrOH (20 ml) was added, and the solvent was removed under reduced pressure. The crude

1 product was dissolved in Et<sub>2</sub>O (50 ml), and the organic phase was washed with H<sub>2</sub>O (2 × 10  
2 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent was removed under reduced pressure. The  
3 crude product was purified with LC and resulted in 8.84 g (78 % yield, >99 % pure). <sup>1</sup>H-NMR  
4 (CDCl<sub>3</sub>): 3.31 (s, 3H), 3.30 (m, 1H), 2.46 (m, 1H), 1.58-1.32 (m, 6H), 1.19 (d, 3H, *J* = 7 Hz),  
5 1.12 (d, 3H, *J* = 6 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 181.8, 76.64, 55.9, 39.2, 36.1, 33.6, 23.0, 19.0,  
6 16.9.

7 *(2R)*-6-Methoxy-2-methylheptanoic acid To 6-methoxy-2-methylheptanoic acid (8.53 g, 48.5  
8 mmol), 2,2-dimethyl-1-propanol (4.31 g, 48.5 mmol) and dodecane (1.97 g, 11.4 mmol) as  
9 internal standard in *iso*-octane (280 ml) was added the salt pair Na<sub>2</sub>SO<sub>4</sub> (8.8 g, 62.1 mmol)  
10 and Na<sub>2</sub>SO<sub>4</sub> × 10H<sub>2</sub>O (10.0 g, 31.1 mmol) to maintain a water activity (*a<sub>w</sub>*) of 0.76. The  
11 enantioselective esterification was started by addition of 3.95 g of CRL according to Sabbani  
12 et al (2006). After stirring at 20 °C, the reactions were stopped at 30% conversion by filtering  
13 off with Celite and washing the enzyme/Celite with several portions of Et<sub>2</sub>O. The remaining  
14 substrate acid was separated from the product ester via extraction with Na<sub>2</sub>CO<sub>3</sub> (4 × 10 ml).  
15 The water phase was acidified with HCl, and the acid extracted into Et<sub>2</sub>O (3 × 15 ml) and  
16 dried with MgSO<sub>4</sub> (anhydr.). This yielded 5.86 g of pure remaining *(2R)*-6-methoxy-2-  
17 methylheptanoic acid used below in the next step below after confirming the identity by <sup>1</sup>H-  
18 NMR and the optical activity (neat  $[\alpha]_{58920} = -5.9^\circ$ ). The enantioselective esterification also  
19 gave 5.99 g of the *(S)*-ester isolated from the remaining Et<sub>2</sub>O phase after drying with MgSO<sub>4</sub>  
20 (anhydr.). The ester was not analyzed further and not used in the rest of the synthesis.

21 *(2R)*-6-Methoxy-2-methylheptan-1-ol LiAlH<sub>4</sub> (0.55 g, 14.67 mmol) was added to *(2R)*-6-  
22 methoxy-2-methylheptanoic acid (5.8 g, 35.3 mmol) at 0 °C and stirred for 2 h. H<sub>2</sub>O (20 ml)  
23 and HCl (2M, 60 ml) were added, and the aqueous phase was extracted with Et<sub>2</sub>O (2 × 100  
24 ml). The combined organic layer was dried over MgSO<sub>4</sub> (anhydr.), and the solvent was  
25 removed under reduced pressure resulting in 4.44 g (yield of 78.6 %, 99.5 % pure). <sup>1</sup>H-NMR

1 (CDCl<sub>3</sub>): 3.45 (m, 2H), 3.31 (s, 3H), 1.60-1.40 (m, 2H), 1.13 (d, 3H,  $J = 6.5$  Hz), 0.92 (d, 3H,  
2  $J = 6.8$  Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 77.2, 68.7, 56.3, 36.9, 36.2, 33.6, 23.2, 19.4, 16.9.  
3  $\alpha = +3.2^\circ$ . GC Analysis on the chiral  $\beta$ -dex225 column showed the (2*R*)-isomers (75 %  
4 relative area) at 282.01 and 292.14 min, and the (2*S*)-isomers (25% relative area) at 303.95  
5 and 311.62 min.

6  
7 (2*R*)-6-Methoxy-2-methylheptyl 4-methylbenzenesulfonate *p*-Toluenesulfonyl chloride (2.38  
8 g, 12.5 mmol) was added in small portions to (2*R*)-6-methoxy-2-methylheptan-1-ol (1 g, 6.25  
9 mmol) and pyridine (1.48 g, 18.75 mmol) in DCM (20 ml) at 0 °C. The reaction was stirred  
10 overnight, and H<sub>2</sub>O (10 ml) and Et<sub>2</sub>O (40 ml) were then added. The organic phase was  
11 washed with 10% Na<sub>2</sub>CO<sub>3</sub> (10% aq., 3 × 10 ml), and brine (sat.aq., 10 ml), dried over MgSO<sub>4</sub>  
12 (anhydr.), and the solvent removed under reduced pressure. The product was purified with LC  
13 and Kügelrohr distillation resulting in 1.715 g of the sulfonate (quantitative yield, 95% pure).  
14 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.79 (d, 2H,  $J = 8.3$  Hz), 7.34 (d, 2H,  $J = 8.5$  Hz), 3.83 (m, 2H), 3.33-3.20  
15 (m, 1H), 3.31 (s, 3H), 2.45 (s, 3H), 1.78 (m, 1H), 1.50-1.10 (m, 1H), 1.09 (d, 3H,  $J = 6.3$  Hz),  
16 0.89 (d, 3H,  $J = 6.8$  Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 144.5, 129.9, 127.9, 75.2 55.9, 36.4, 32.6, 22.5,  
17 21.6, 19.1, 16.4.

18 (2*R*)-1-Iodo-6-methoxy-2-methylheptane (2*R*)-6-Methoxy-2-methylheptyl 4-methylbenzene-  
19 sulfonate (0.440 g, 1.42 mmol) was added to NaI (1.02 g, 6.82 mmol) in DMF (5 ml), and the  
20 reaction mixture was refluxed for 1.5 h. H<sub>2</sub>O (3 ml) was added, and the aqueous phase was  
21 extracted with Et<sub>2</sub>O (3 × 15 ml). The combined organic phase was washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
22 (10% aq., 2 × 3 ml) and brine (sat.aq., 2 × 3 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent  
23 was removed under reduced pressure. The product was purified with LC and Kügelrohr  
24 distillation resulting in 0.139 g (36.5 % yield) of product that was used in the next step after  
25 confirming the structure by <sup>1</sup>H-NMR.

1 *{[(2R)-6-Methoxy-2-methylheptyl]sulfonyl}benzene* NaSO<sub>2</sub>Ph (0.41 g, 2.49 mmol) was added  
2 to (2R)-1-iodo-6-methoxy-2-methylheptane (0.48 g, 1.78 mmol) in DMF (10 ml), and the  
3 reaction mixture was stirred for 2 d. The reaction mixture was poured into brine and extracted  
4 with Et<sub>2</sub>O (3 × 20 ml). The combined organic layer was washed with H<sub>2</sub>O (10 ml) and brine  
5 (sat.aq., 10 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent was removed under reduced  
6 pressure. The product was purified by LC and Kügelrohr distillation resulting in 0.364 g (81  
7 % yield) of the pure title compound. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.93 (d, 2H, *J* = 9.7 Hz), 7.65 (t, 1H, *J*  
8 = 7.5 Hz), 7.56 (t, 2H, *J* = 8.5 Hz), 3.28 (s, 3H), 3.08 (dd, 1H, *J* = 6, 18 Hz), 2.93 (dd, 1H, *J* =  
9 9.5, 19 Hz), 2.10 (m, 1H), 1.64 (s, 1H), 1.47-1.20 (m, 6H), 1.08 (m, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  
10 140.2, 133.5, 129.3, 127.9, 62.5, 56.9, 36.8, 36.2, 28.6, 22.2, 19.8, 18.9.

### 11 **Synthesis of (3R)-1-iodo-3,7-dimethyloctane as building block 3**

12 *(3R)-3,7-Dimethyloct-6-ene-1-ol* Following the approach used by Mori et al (1991), LiAlH<sub>4</sub>  
13 (3.70 g, 97.4 mmol) was added during 1 h to CoCl<sub>2</sub> (6.86 g, 51.2 mmol) in THF (250 ml) at  
14 -70 °C. (3R)-3,7-dimethyloct-6-enoic acid (3.0 g, 17.65 mmol) in THF (60 ml) were added  
15 dropwise to the above solution during 45 min, the reaction was stirred at -70 °C for an  
16 additional hour and left stirring overnight. Toluene (30 ml) was added, and the reaction  
17 mixture was stirred for 2 d and then H<sub>2</sub>O (60 ml) and HCl (1M, 60 ml) were added to quench  
18 the reaction. The aqueous phase was extracted with Et<sub>2</sub>O (6 × 100 ml), the combined organic  
19 layer was washed with brine (sat.aq., 3 × 20 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent  
20 was removed under reduced pressure. This resulted in 2.8 g of a crude mixture consisting of  
21 (3R)-3,7-dimethyloctan-1-ol (55 %) and (3R)-3,7-dimethyloct-6-en-1-ol (42 %). This mixture  
22 was used in the next step without further analysis and purification.

23 *(3R)-3,7-Dimethyloctan-1-ol*; Pd-C (a spatula end) was added to (3R)-3,7-dimethyloct-6-en-1-  
24 ol/(3R)-3,7-dimethyloct-6-en-1-ol (2.8 g, 17.4 mmol) diluted in EtOAc (20 mL). The system

1 was evacuated with H<sub>2</sub> (g) twice, and the reaction was stirred for 24 h. The reaction mixture  
2 was filtered and the collected filtrate was washed with Na<sub>2</sub>CO<sub>3</sub> (10% aq., 5 ml), dried over  
3 MgSO<sub>4</sub> (anhydr.), and the solvent was removed under reduced pressure resulting in 2.28 g (83  
4 % yield) of the saturated alcohol. Analytical data were similar to that in Mori et al (1991).

5 *(3R)-3,7-Dimethyloctyl 4-methylbenzenesulfonate* *p*-Toluenesulfonyl chloride (4.2 g, 22.03  
6 mmol) was added to a solution of *(3R)-3,7-dimethyloctan-1-ol* (2.28 g, 14.4 mmol) and  
7 pyridine (10 ml) in DCM (30 ml), and the mixture was stirred overnight. Et<sub>2</sub>O (50 ml) was  
8 added to dilute the reaction mixture, and the organic phase washed with HCl (1M, 3 × 10 ml),  
9 NaHCO<sub>3</sub> (10% aq., 2 × 5 ml) and brine (sat.aq., 5 ml), dried over MgSO<sub>4</sub> (anhydr.), and the  
10 solvent was removed under reduced pressure resulting in 3.14 g (70 % yield) of the title  
11 compound which was used without further purification. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.79 (d, 2H, *J* =  
12 8.3 Hz), 7.34 (d, 2H, *J* = 8.3 Hz), 4.06 (dt, 2H, *J* = 1, 6.25 Hz), 2.45 (s, 3H), 1.73-1.08 (m,  
13 11H), 0.85 (d, 6H, *J* = 6.5 Hz), 0.80 (d, 3H, *J* = 6.5 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 144.6, 129.8,  
14 127.9, 69.1, 39.1, 36.8, 35.7, 29.2, 27.9, 24.5, 22.6, 21.6, 19.2.

15 *(3R)-1-Iodo-3,7-dimethyloctane* *(3R)-3,7-Dimethyloctyl 4-methylbenzenesulfonate* (3.14 g,  
16 10.06 mmol) was added to NaI (6.6 g, 44 mmol) in DMF (55 ml) and refluxed overnight. H<sub>2</sub>O  
17 (20 ml) was added, and the aqueous phase was extracted with Et<sub>2</sub>O (5 × 10 ml). The  
18 combined organic layer was washed with HCl (1M, 10 ml), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10% aq., 2 × 10 ml) and  
19 brine (sat.aq., 10 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent was removed under  
20 reduced pressure. The product was purified with LC and Kügelrohr distillation and resulted in  
21 0.44 g (16 % yield, 99 % pure). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.27-3.23 (m, 1H), 3.19-3.15 (m, 1H),  
22 1.91-1.84 (m, 1H), 1.68-1.61 (m, 1H), 1.57-1.48 (m, 2H), 1.36-1.07 (m, 6H), 0.87 (d, 3H, *J* =  
23 6.5 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 41.0, 39.2, 33.9, 27.9, 24.5, 22.6, 18.7, 5.4. Analytical data  
24 similar to that in Chen et al (1996).



1 **Synthesis of (2R/S,6S,10R)-6,10,14-trimethylpentadecan-2-ol (1) by coupling of building**  
2 **block 2 and 3**

3 *(6R,10R)-2-Methoxy-6,10,14-trimethyl-7-pentadecanyl-sulfonylbenzene* A similar method to  
4 those described for different substrates in Nakamura and Mori (2000) and Shibata et al (2002)  
5 was used. BuLi (1.6 M in hexane, 0.45 ml, 0.72 mmol) was added slowly to (2R)-6-methoxy-  
6 2-methylheptyl-sulfonylbenzene (0.10 g, 0.35 mmol) and DMPU (0.6 ml) in THF (4 ml) at  
7  $-80\text{ }^{\circ}\text{C}$ . After addition, the reaction mixture was allowed to reach  $-40\text{ }^{\circ}\text{C}$  and was stirred at  
8 this temperature for 1 h. The reaction mixture was cooled to  $-80\text{ }^{\circ}\text{C}$  and (3R)-1-iodo-3,7-  
9 dimethyloctane (0.147 g, 0.55 mmol) in THF (1 ml) was added dropwise and the reaction was  
10 stirred overnight.  $\text{NH}_4\text{Cl}$  (sat. aq., 2 ml) was added, and the aqueous phase was extracted with  
11 EtOAc ( $5 \times 10$  ml). The combined organic layers were washed with brine (sat.aq., 5 ml),  
12 dried over  $\text{MgSO}_4$  (anhydr.), and the solvent was removed under reduced pressure. The  
13 product was purified by Kugelrohr distillation and resulted in 0.113 g (76 % yield) of product.  
14  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.93 (d, 2H,  $J = 8\text{ Hz}$ ), 7.66 (t, 1H,  $J = 8.5\text{ Hz}$ ), 7.58 (t, 2H,  $J = 7.5\text{ Hz}$ ),  
15 3.30 (s, 3H), 3.27-3.23 (m, 1H), 3.09 (dd, 1H,  $J = 4.5, 14\text{ Hz}$ ), 2.94 (dd, 1H,  $J = 7.5, 14\text{ Hz}$ ),  
16 1.91-1.84 (m, 1H), 1.68-1.61 (m, 1H), 1.57-1.48 (m, 2H), 1.09 (d, 3H,  $J = 6\text{ Hz}$ ), 1.08 (d, 3H,  
17  $J = 6.5\text{ Hz}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 140.2, 133.5, 129.3, 127.9, 76.5, 62.5, 55.9, 36.8, 36.2, 28.6,  
18 22.2, 19.9, 19.0.

19 *(6S,10R)-2-Methoxy-6,10,14-trimethylpentadecane* Lithium (150 mg) was cut into pieces and  
20 added to  $\text{EtNH}_2$  (10 ml) at  $-80\text{ }^{\circ}\text{C}$  and was stirred for 45 min. (6R,10R)-2-Methoxy-6,10,14-  
21 trimethyl-7-pentadecan-sulfonyl}benzene (0.113 g) in THF (6 ml) was added dropwise at  $-80$   
22  $^{\circ}\text{C}$  to the solution above. After 2 h THF (10 ml) and  $\text{NH}_4\text{Cl}$  (sat.aq., 12 ml) were added. The  
23 aqueous phase was extracted with heptane ( $5 \times 10$  ml), the combined organic layers were  
24 washed with brine (sat.aq., 5 ml) and  $\text{H}_2\text{O}$  (5 ml), dried over  $\text{MgSO}_4$  (anhydr.), and the

1 solvent was removed under reduced pressure resulting in 72 mg (95 % yield, 80 % pure) that  
2 was used in the next step without further purification or analysis.

3 *(6S,10R)-6,10,14-Trimethylpentadecan-2-one* (6S,10R)-2-methoxy-6,10,14-  
4 trimethylpentadecane from above was diluted with acetonitrile (1.9 ml), H<sub>2</sub>O (2.8 ml), and  
5 CCl<sub>4</sub> (0.9 ml). NaIO<sub>4</sub> (1.0 g, 4.67 mmol) and RuCl<sub>3</sub> (spatula tip) were added and after 24 h  
6 additional NaIO<sub>4</sub> (0.5 g, 2.33 mmol), RuCl<sub>3</sub> (spatula tip) and acetonitrile (1 ml) were added.  
7 The reaction mixture was stirred for an additional 24 h when Et<sub>2</sub>O (10 ml) and H<sub>2</sub>O (10 ml)  
8 were added. The aqueous phase was extracted with Et<sub>2</sub>O (4 ×10 ml), the combined organic  
9 layer was washed with HCl (1M, 10 ml), dried over MgSO<sub>4</sub> (anhydr.), and the solvent was  
10 removed under reduced pressure. The product was purified with LC to give 63 mg of the  
11 product (quantitative yield) which was checked by <sup>1</sup>H-NMR and then used immediately in the  
12 next step without further purification or analysis. The analytical data were similar to data in  
13 Nam et al (2007) and Suga et al (1989).

14 *(2R/S,6S,10R)-6,10,14-Trimethylpentadecan-2-ol* (6S,10R)-6,10,14-Trimethylpentadecan-2-  
15 one from above was diluted in EtOAc (3 ml) and LiAlH<sub>4</sub> (40 mg, 1.05 mmol) was added. H<sub>2</sub>O  
16 (1 ml) and HCl (1M, 1 ml) was added after 1 h and the aqueous phase was extracted with  
17 Et<sub>2</sub>O (3 × 10 ml), the combined organic layer was washed with HCl (1M, 5 ml) and brine  
18 (sat.aq., 5 ml), dried over MgSO<sub>4</sub> (anhydr.) and the solvent was removed under reduced  
19 pressure resulting in 57 mg of the *(2R/S,6S,10R)-6,10,14-trimethylpentadecan-2-ol* (**1**) in >99  
20 % purity (99 % yield). This reference mixture **1** was analyzed and used as reference as  
21 described above. Analytical data were similar to data in Mori et al (1991); Nam et al (2007);  
22 and Suga et al (1989).

1 **Synthesis of (2*S*,6*R*/*S*,10*R*/*S*)-6,10,14-trimethylpentadecan-2-ol, (2*R*,6*R*/*S*,10*R*/*S*)-6,10,14-**  
2 **trimethylpentadecan-2-ol, (2*S*,6*R*,10*R*)-6,10,14-trimethylpentadecan-2-ol and**  
3 **(2*R*,6*R*,10*R*)-6,10,14-trimethylpentadecan-2ol**

4 (*2S,6R/S,10R/S*)- and (*2R,6R/S,10R/S*)-6,10,14-trimethylpentadecan-2-ol was synthesized  
5 from (*2E,7R/S,11R/S*)-3,7,11,15-tetramethyl-2-hexadecen-1-ol (phytol) following the  
6 protocol in Nieberding et al (2008).

7  
8 (*2S,6R,10R*)-6,10,14-trimethylpentadecan-2-ol and (*2R,6R,10R*)-6,10,14-trimethylpenta-  
9 decan-2ol were synthesized according to a published method from (*2E,7R,11R*)-phytol  
10 resulting in pure stereoisomers of the two title compounds (Nieberding et al. 2008).

11

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