

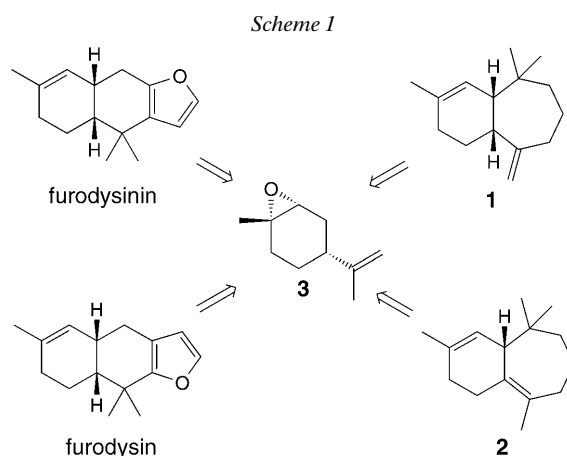
## Total Synthesis of (+)- $\beta$ -Himachalene

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An enantioselective synthesis of (+)- $\beta$ -himachalene (**2**) was accomplished starting from (1*S*,2*R*)-1,2-epoxy-*p*-menth-8-ene (**3**) in 15 or 16 steps with an overall yield of ca. 6% (Schemes 3, 5, and 6). Key transformations include an Ireland–Claisen rearrangement, a Corey oxidative cyclization, and a ring expansion.

We continue to hold an intense interest in the employment of abundant chiral monoterpenes as building blocks for synthesis [1]. When we investigated the synthesis of furodysin [2] and furodysinin [3] from (1*S*,2*R*)-1,2-epoxy-*p*-menth-8-ene (**3**) via a hexalone intermediate, we noticed that natural  $\alpha$ -himachalene (**1**) and/or  $\beta$ -himachalene (**2**) may also be accessible from such an intermediate by a ring-expansion protocol (Scheme 1).



The himachalenes are found in several cedar woods, *e.g.*, *Cedrus deodara* LOUD. [4], *Cedrus atlantica* [5], and *Cedrus libani* [5]. According to a biogenetic consideration [4][6] that correlates the himachalenes with a precursor of longifolene, the absolute

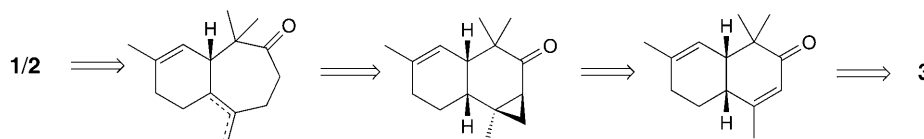
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configurations of these bicyclic sesquiterpenes should be as shown in **1** and **2**. The chiral epoxymenthene **3** happens to possess the correct absolute configuration at the critical stereogenic centers for elaboration of the himachalenes.

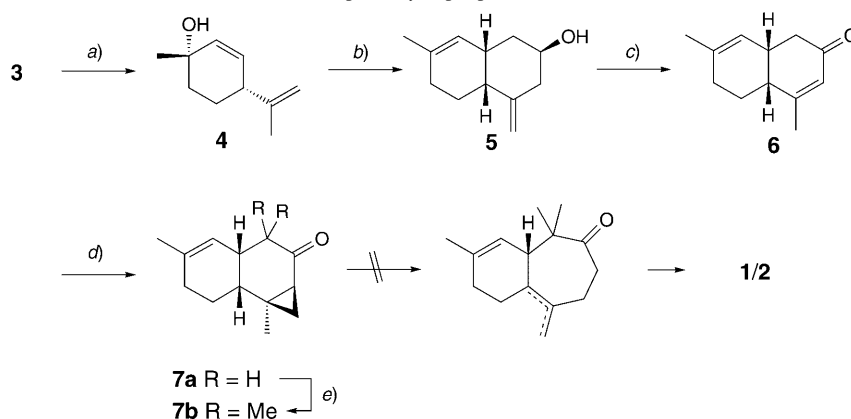
Several syntheses of the himachalenes have been completed,  $\alpha$ -himachalene by using an intramolecular *Diels–Alder* reaction as the key step [7–9],  $\beta$ -himachalene based on a [2+2] photocycloaddition [10] or a homo-*Cope* rearrangement [11], and both isomers on an intramolecular *Diels–Alder* route [12]. Except for the report of *Evans et al.*, all other syntheses led to racemic product(s). Our approach starting from a natural chiral terpene necessarily is enantioselective.

Our first retrosynthetic analysis is depicted in *Scheme 2* and an attempt of its realization is outlined in *Scheme 3*. Menthadienol **4** can be prepared from **3** by epoxide-ring opening either with  $\text{Me}_2\text{NH}$  [13] or  $\text{PhSeNa}$  [14], followed by oxidative elimination. After reaching **7b** via **5**, **6**, and **7a**, further progress was thwarted in its regioselective cleavage. Such reagents as  $\text{MeCOMs}$  [15],  $\text{Ac}_2\text{O}/\text{BF}_3 \cdot \text{OEt}_2$  [16] were totally ineffective. A modification starting from **5** via **8–10** (*Scheme 4*) that was directed toward **1**, relying on a fragmentation process, was also abandoned due to unsuccessful dimethylation of **11** to **12**.

Scheme 2. Retrosynthetic Analysis of **1** and **2**

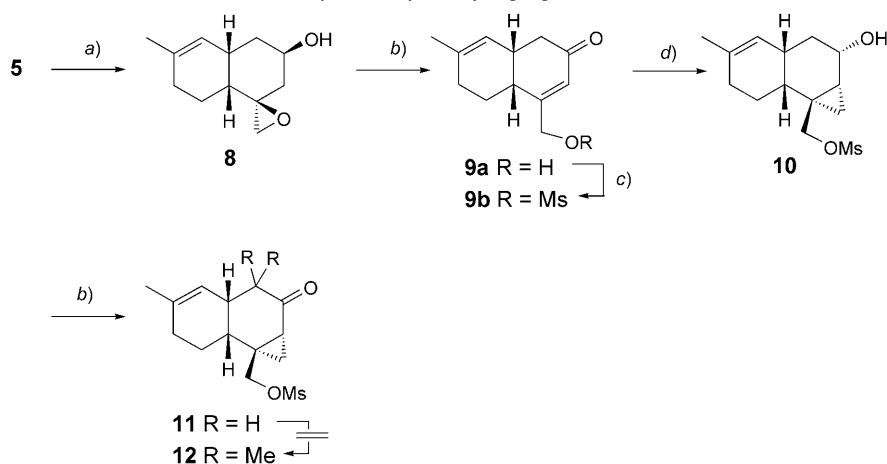


Scheme 3. Attempted Cyclopropanation Route to **1/2**



a) 1.  $\text{Me}_2\text{NH}$ ,  $159^\circ$ , 18 h; 2.  $\text{H}_2\text{O}_2$ ,  $150\text{--}180^\circ$ ; 75%. b) 1.  $\text{NaH}$ , THF,  $25^\circ$ , 30 min;  $\text{PhSOCH}_2\text{CH}_2$ ,  $\text{KH}(\text{cat.})$ ,  $25^\circ$ , 3 h; 2. decalin,  $200^\circ$ , 12 h. c) Swern oxidation. d)  $(\text{Me}_3\text{SO})\text{I}$ ,  $\text{NaH}$ , DMSO,  $25^\circ$ , 5 h,  $55^\circ$ , 2 d. e)  $\text{Me}_3\text{CCH}_2\text{ONa}$ , THF,  $\text{MeI}$ ,  $60^\circ$ , 12 h.

It is evident that a way to overcome the obstacle is to introduce the geminal-dimethyl at an earlier stage. Accordingly, we pursued a route involving an *Ireland–Claisen* rearrangement of **13** (*Scheme 5*). The acid **14** was homologated in 4 steps to

Scheme 4. Modification of the Cyclopropanation Route to **1**

a)  $[\text{VO}(\text{acac})_2]$ ,  $t\text{-BuOOH}$ ,  $0^\circ \rightarrow 25^\circ$ , 13 h. b) Dess–Martin oxidation. c)  $\text{MsCl}$ ,  $\text{Et}_3\text{N}$ ,  $0^\circ$ , 3 h. d) 1.  $\text{NaBH}_4$ ,  $\text{MeOH}$ ,  $25^\circ$ , 2 h; 2. Simmons–Smith reaction.

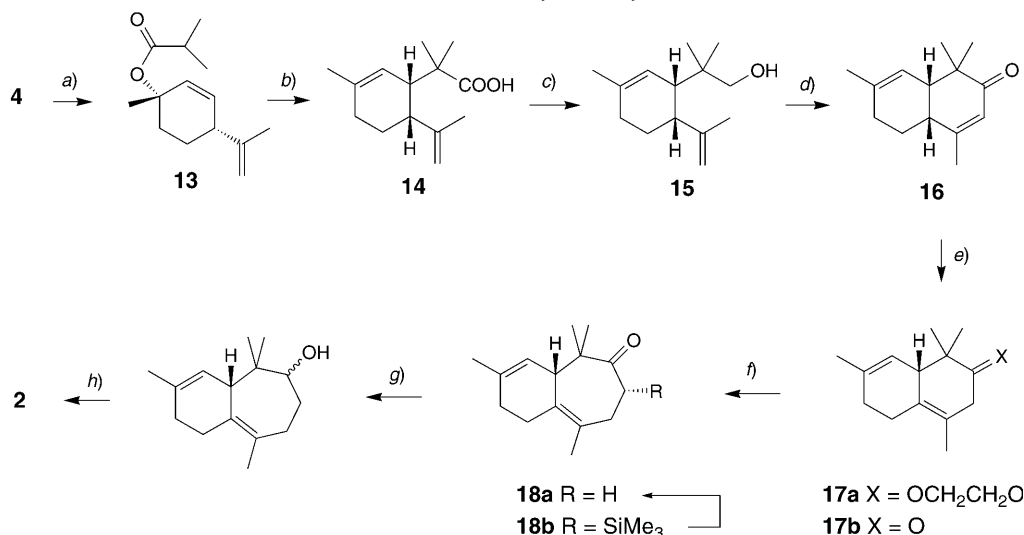
afford an aldehyde, with a plan to close the seven-membered ring by an intramolecular ene reaction. However, a disappointing result emerged, as products with a hydrindene skeleton were generated.

To push the synthesis forward, we converted **14** to **16** by a reaction sequence involving  $\text{LiAlH}_4$  reduction to **15**, pyridinium chlorochromate (PCC) oxidation, and treatment with  $\text{TsOH}$  in refluxing benzene [17]. While a selective cyclopropanation also was found to be problematic, we were forced to abandon the effort of synthesizing **1**. The change of target to **2** involved a different operation that involved deconjugation of **16** and a ring expansion of **17b**, the latter by a  $\text{BF}_3$ -catalyzed reaction with  $\text{Me}_3\text{-SiCHN}_2$  [18]. This last step was surprisingly regioselective, providing products solely from migration of the methylene group. With **18a** and **18b** in hand and a combined 65.3% yield (17.2% + 48.1%), we could complete a synthesis of (+)- $\beta$ -himachalene (**2**). Direct treatment of the product mixture **18a/18b** with  $\text{Bu}_4\text{NF}$  in  $\text{MeCN}$  gave **18a** in 58.5% yield. Subsequently, **18a** was reduced with  $\text{NaBH}_4$ , mesylated, and reduced with  $\text{Li}$  in liquid ammonia to furnish **2**.

The nonstereoselective borohydride reduction of **18a** prompted us to develop an alternative method to transform the major product **18b** of the ring expansion to (+)- $\beta$ -himachalene. In the event, **18b** was subjected to borohydride reduction to afford a single product **19**. The bulky  $\text{Me}_3\text{Si}$  group provided stereocontrol for the reduction. The *cis*- $\alpha$ -silylcycloheptenol derivative **19** underwent *syn*-elimination on treatment with  $\text{KH}$  [19], and the resulting triene **20** was partially hydrogenated to afford **2** (Scheme 6).

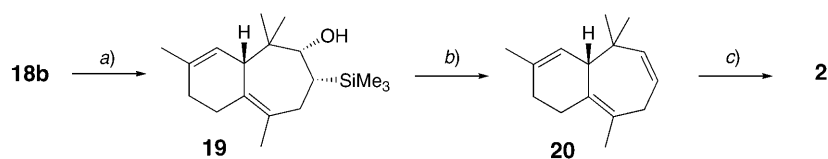
In conclusion, we have achieved a total synthesis of (+)- $\beta$ -himachalene (**2**) from (1*S*,2*R*)-1,2-epoxy-*p*-menth-8-ene (**3**) in 15 or 16 steps and *ca.* 6% overall yield.

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Scheme 5. Total Synthesis of **2**

a) Isobutyric anhydride, Et<sub>3</sub>N, *N,N*-dimethylpyridin-4-amine (DMAP; cat.), CH<sub>2</sub>Cl<sub>2</sub>, 25°, 2 d; 99%. b) Lithium diisopropylamide (LDA), THF, –78°, 1 h, –40°, 30 min; Me<sub>3</sub>SiCl, –78° → 25°; PhMe, reflux, 36 h; 68%. c) LiAlH<sub>4</sub>, THF, reflux, 5 h; 90%. d) pyridinium chlorochromate (PCC), CH<sub>2</sub>Cl<sub>2</sub>, r.t., 24 h; TsOH, benzene, reflux, 1.5 h, 44.1%. e) 1. Ethylene glycol, TsOH(cat.), *Dean-Stark*, reflux, 24 h, 92.1% of **17a**; 2. 35% CF<sub>3</sub>COOH/H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, 10–20°, 2 d, 98.8% of **17b**. f) Me<sub>2</sub>SiCHN<sub>2</sub>, BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, –40°, 2.5 h; 65.3%. g) Bu<sub>4</sub>NF, MeCN, r.t., 3 h, 58.5%. h) 1. NaBH<sub>4</sub>, MeOH, 0°, 1 h. 2. MsCl, pyridine, DMAP(cat.), 0° → 25°, 6 h; 3. Li, NH<sub>3</sub>(l), –78°, 1 h, 44.9% (3 steps).

Scheme 6



a) NaBH<sub>4</sub>, EtOH, 25°, 1.5 d; 86.9%. b) KH, THF, 25°, 24 h; 72.3%. c) CoCl<sub>2</sub>·6H<sub>2</sub>O, NaBH<sub>4</sub>, EtOH, 25°, 24 h; 72.6%.

### Experimental Part

*General.* For drying org. solns. during workup, Na<sub>2</sub>SO<sub>4</sub> was used. Column chromatography (CC): *Merck* silica gel (63–200 mesh). TLC: *Merck* silica gel 60 *F*<sub>254</sub> plates. M.p.: uncorrected; *Laboratory Devices*. [α]<sub>D</sub>: CHCl<sub>3</sub> soln. at 25°. IR Spectra: *Bio-Rad FTS 165*;  $\tilde{\nu}$  in cm<sup>–1</sup>. <sup>1</sup>H- and <sup>13</sup>C-NMR Spectra: *Varian Unity-300*; CDCl<sub>3</sub> unless otherwise indicated; δ in ppm, *J* in Hz. EI-MS: *Trio-2000* and *Jeol SX-102A*; ionization potential 70 eV; in *m/z*.

(*1S,4R*)-*p*-Mentha-2,8-dien-1-ol (= (*1S,4R*)-1-Methyl-4-(1-methylethenyl)cyclohex-2-en-1-ol; **4**). Limonene oxide (**3**; 5.0 g, 32.89 mmol) was mixed with 40% aq. Me<sub>2</sub>NH soln. (7.4 g, 164.44 mmol) in an autoclave and heated at 150° for 18 h. After removing excess Me<sub>2</sub>NH, the cooled mixture was stirred with 30% H<sub>2</sub>O<sub>2</sub> soln. (5 ml) at r.t. during 18 h. A trace of 5% Pd/C was used to decompose any remaining H<sub>2</sub>O<sub>2</sub>, and the liquid was filtered and placed in a distillation vessel. Gradual heating to 150° then 180° produced **4** which was purified by CC (silica gel): **4** (3.5 g, 75%). [α]<sub>D</sub> = +63.9 (*c* = 0.325, CHCl<sub>3</sub>). IR:

3650–3000, 2943, 2905, 2880. <sup>1</sup>H-NMR: 1.29 (s, 3 H); 1.40–1.65 (m, 4 H); 1.73 (s, 3 H); 1.82 (m, 1 H); 2.65 (m, 1 H); 4.73 (s, 1 H); 4.77 (s, 1 H); 5.66 (d, *J* = 10.0, 1 H); 5.68 (d, *J* = 10.0, 1 H). <sup>13</sup>C-NMR: 20.8 (q); 24.9 (t); 29.4 (q); 36.7 (t); 43.4 (d); 67.5 (s); 110.6 (t); 132.1 (t); 133.9 (t); 148.1 (s).

(2*R*,4*aR*,8*aS*)-1,2,3,4,4*a*,5,6,8*a*-Octahydro-7-methyl-4-methylenenaphthalen-2-ol (**5**). To a stirred suspension of NaH (1.06 g, 26.5 mmol) in dry THF (30 ml) were added a soln. of **4** (4.0 g, 26.3 mmol) in THF (30 ml), and after 30 min, phenyl vinyl sulfoxide (8.0 g, 52.6 mmol), followed by a small amount of KH. After 3 h, moist Et<sub>2</sub>O was introduced, and the mixture was washed with H<sub>2</sub>O and brine, dried, and evaporated. The residue was heated with NaHCO<sub>3</sub> in decalin at 200° for 20 h, cooled, and diluted with Et<sub>2</sub>O. After washing with H<sub>2</sub>O, drying, and evaporation, the residue was subjected to CC: **5** (2.52 g, 53.8%). M.p. 75°. [ $\alpha$ ]<sub>D</sub> = –10.39 (*c* = 1, CHCl<sub>3</sub>). IR: 3230, 3073, 2925, 1645, 1430, 1325, 1240, 1180, 1055, 1008, 935, 885, 849, 812, 711. <sup>1</sup>H-NMR: 1.34–1.45 (m, 3 H); 1.55 (s, 3 H); 1.62–1.66 (m, 1 H); 1.73–1.82 (m, 1 H); 1.88–1.95 (m, 1 H); 2.05–2.11 (m, 1 H); 2.15–2.17 (m, 1 H); 2.26–2.36 (m, 3 H); 3.88–3.90 (m, 1 H); 4.66 (s, 1 H); 4.82 (s, 1 H); 5.21 (br s 1 H). <sup>13</sup>C-NMR: 23.6 (q); 23.65 (t); 30.2 (t); 32.3 (d); 36.0 (t); 39.0 (t); 42.2 (d); 67.0 (d); 111.7 (t); 125.3 (d); 133.6 (s); 148.3 (s). EI-MS: 178 (100, *M*<sup>+</sup>), 162 (95), 145 (90). HR-MS: 178.1361 (*M*<sup>+</sup>, C<sub>12</sub>H<sub>18</sub>O<sup>+</sup>; calc. 178.1358).

(4*aR*,8*aS*)-4*a*,5,6,8*a*-Tetrahydro-4,7-dimethylnaphthalen-2(1*H*)-one (**6**). A soln. of **5** (450 mg, 2.52 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was added via a syringe into a stirred reagent prepared from oxalyl chloride (645 mg, 5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and DMSO (948 mg, 12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) at –78°. After 30 min, Et<sub>3</sub>N was added. The cooling bath was removed after 5 min., and the reaction was quenched with H<sub>2</sub>O. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the extract dried and evaporated, and the residue subjected to CC: **6** (410 mg, 92%). M.p. 75°. [ $\alpha$ ]<sub>D</sub> = +3.23 (*c* = 1, CHCl<sub>3</sub>). IR: 2929, 2724, 1668, 1627, 1432, 1379, 1302, 1262. <sup>1</sup>H-NMR: 1.63 (s, 3 H); 1.53–1.59 (m, 1 H); 1.77–1.92 (m, 1 H); 2.02 (s, 3 H); 2.07–2.21 (m, 3 H); 2.24–2.26 (m, 1 H); 2.30–2.32 (m, 1 H); 2.57–2.61 (m, 1 H); 5.21 (br s 1 H). <sup>13</sup>C-NMR: 22.5 (q); 22.6 (t); 23.4 (q); 30.6 (t); 34.7 (d); 39.6 (d); 40.1 (t); 123.9 (d); 126.4 (d); 134.4 (s); 164.4 (s); 198.6 (s). EI-MS: 176 (99.5, *M*<sup>+</sup>), 162 (100), 150 (70). HR-MS: 176.1205 (*M*<sup>+</sup>, C<sub>12</sub>H<sub>16</sub>O<sup>+</sup>; calc. 176.1201).

(3*S*,4*S*,4*aR*,8*aS*)-4*a*,5,6,8*a*-Tetrahydro-4,7-dimethyl-3,4-methylenenaphthalen-2(1*H*)-one (=1*aS*,3*aS*,7*aR*,7*bS*)-1,1*a*,3,3*a*,6,7,7*a*,7*b*-Octahydro-5,7*b*-dimethyl-2*H*-cyclopropa[*a*]naphthalen-2-one; **7a**). A soln. of **6** (50 mg, 0.28 mmol) in DMSO (5 ml) was added to the ylide derived from (Me<sub>3</sub>SO)I (300 mg, 1.36 mmol) and NaH (50 mg; 60% suspension degreased by hexane) in DMSO (5 ml). After stirring at r.t. for 10 h, the mixture was heated at 55° for 2 d. The cooled mixture was poured into ice/H<sub>2</sub>O (10 ml) and extracted with Et<sub>2</sub>O. The combined org. extract was washed with H<sub>2</sub>O, dried, and evaporated. CC gave **7a** (40 mg, 74%). [ $\alpha$ ]<sub>D</sub> = +82.04 (*c* = 1.78, CHCl<sub>3</sub>). IR: 2962, 2921, 2869, 2360, 1683, 1540, 1506, 1454, 1241. <sup>1</sup>H-NMR: 0.86 (q, *J* = 10.0, 1 H); 1.18 (s, 3 H); 1.16–1.19 (m, 1 H); 1.43 (t, *J* = 4.4, 1 H); 1.56–1.58 (m, 1 H); 1.60 (s, 3 H); 1.79–2.00 (m, 5 H); 1.98–2.33 (m, 2 H); 5.29 (d, *J* = 4.5, 1 H). <sup>13</sup>C-NMR: 18.9 (t); 21.2 (t); 22.7 (q); 23.4 (q); 27.7 (s); 30.0 (d); 30.7 (t); 33.5 (d); 35.8 (d); 39.7 (t); 124.5 (d); 133.5 (s); 208.6 (s). EI-MS: 190 (5, *M*<sup>+</sup>), 97 (45), 85 (70), 83 (55), 71 (100), 70 (44), 69 (63).

(1*R*,3*R*,4*aS*,8*aR*)-3,4,4*a*,7,8,8*a*-Hexahydro-6-methylspiro[naphthalene-1(2*H*)-2'-oxiran]-3-ol (**8**). To a soln. of **5** (500 mg, 2.80 mmol) and [VO(acac)<sub>2</sub>] (=bis(pentane-2,4-dionato- $\kappa$ O, $\kappa$ O')oxovanadium; 30 mg, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was slowly added 2.7*M* <sup>t</sup>BuOOH (in PhMe (3.0 ml, 8.10 mmol) at 0° under N<sub>2</sub> (green → dark red mixture). The soln. was allowed to warm to r.t. and stirred for 13 h. After addition of aq. Na<sub>2</sub>SO<sub>3</sub> soln., the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined extract washed with brine, dried, and evaporated, and the residue subjected to CC (AcOEt/hexane 1:9): **8** (450 mg, 82.6%). IR: 2926, 2888, 2831, 2719, 1645, 1426, 1307, 1185, 1010, 928, 770, 736. <sup>1</sup>H-NMR: 1.26–1.28 (m, 3 H); 1.39–1.61 (m, 3 H); 1.53 (s, 3 H); 1.75–1.92 (m, 3 H); 2.03 (dd, *J* = 15.0, 3.0, 1 H); 2.44 (s, 2 H); 2.58–2.72 (m, 1 H); 4.02 (d, *J* = 2.7, 1 H); 5.26 (d, *J* = 3.9, 1 H). <sup>13</sup>C-NMR: 21.2 (t); 23.3 (q); 28.3 (d); 30.2 (t); 34.7 (t); 34.8 (t); 40.7 (d); 50.1 (t); 59.8 (s); 66.8 (d); 125.0 (d); 133.0 (s). EI-MS: 194 (5, *M*<sup>+</sup>), 176 (48), 163 (56), 145 (98), 131 (46), 117 (38), 107 (32), 105 (67), 91 (77), 79 (56), 77 (42), 43 (80), 41 (100), 39 (73), 32 (56). HR-MS: 194.1310 (*M*<sup>+</sup>, C<sub>12</sub>H<sub>18</sub>O<sub>2</sub><sup>+</sup>; calc. 194.1308).

(4*aR*,8*aS*)-4*a*,5,6,8*a*-Tetrahydro-4-hydroxymethyl-7-methylnaphthalen-2(1*H*)-one (**9a**). A soln. of **8** (400 mg, 2.1 mmol) and Dess–Martin periodinane (1.30 g, 3.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was stirred at r.t. under N<sub>2</sub> for 12 h. The resulting mixture was poured into 1*N* NaOH and extracted with CH<sub>2</sub>Cl<sub>2</sub>, the extract washed with 1*N* NaOH, H<sub>2</sub>O, and brine, dried, and evaporated, and the residue subjected

to CC (AcOEt/hexane 1:4): **9a** (330 mg, 83.4 %). IR: 2964, 2929, 2878, 2381, 1660, 1447, 1380, 1362, 1301, 1261, 1194, 1131, 1078, 1044, 877, 826. <sup>1</sup>H-NMR: 1.63 (s, 3 H); 1.60–1.69 (m, 2 H); 1.92–2.04 (m, 2 H); 2.15–2.40 (m, 3 H); 2.60–2.65 (m, 1 H); 2.96 (br. s, 1 H); 4.28 (AA'BB', *J* = 17.1, 2 H); 5.31 (s, 1 H); 6.09 (s, 1 H). <sup>13</sup>C-NMR: 23.2 (t); 23.4 (q); 30.5 (t); 34.6 (d); 35.3 (d); 40.9 (t); 63.4 (t); 122.6 (d); 123.6 (d); 134.7 (s); 168.2 (s); 200.0 (s). EI-MS: 193 (15, [M + 1]<sup>+</sup>), 192 (77, M<sup>+</sup>), 174 (86), 164 (65), 159 (40), 146 (62), 133 (65), 132 (46), 131 (98), 117 (54), 105 (82), 91 (100), 79 (71), 77 (54), 55 (57). HR-MS: 192.1151 (M<sup>+</sup>, C<sub>12</sub>H<sub>16</sub>O<sub>2</sub><sup>+</sup>; calc. 192.1151).

(4aR,8aS)-4a,5,6,8a-Tetrahydro-7-methyl-4-[(methylsulfonyl)oxy]methyl)naphthalen-2(1H)-one (**9b**). A soln. of **9a** (300 mg, 1.6 mmol) and Et<sub>3</sub>N (400 mg, 4.0 mmol) in THF (10 ml) at 0° under N<sub>2</sub> was stirred for 20 min. Then MsCl (300 mg, 2.6 mmol) was added. After 2 h, the mixture was diluted with H<sub>2</sub>O and extracted with Et<sub>2</sub>O. The org. layer was washed with H<sub>2</sub>O and brine, dried, and evaporated: **9b** (400 mg, 94.8%). IR: 2924, 2858, 2360, 2324, 1456, 1339, 1265, 1087, 968. <sup>1</sup>H-NMR: 1.66 (s, 3 H); 1.82–1.85 (m, 2 H); 1.99–2.08 (m, 2 H); 2.24–2.29 (m, 1 H); 2.37–2.47 (m, 2 H); 2.65–2.69 (m, 1 H); 3.06 (s, 3 H); 4.83 (AA'BB', *J* = 14.4, 2 H); 5.34 (s, 1 H); 6.06 (s, 1 H). <sup>13</sup>C-NMR: 22.9 (t); 23.3 (q); 30.3 (t); 34.4 (d); 35.0 (d); 38.0 (q); 40.7 (t); 68.1 (t); 123.2 (d); 126.0 (d); 134.9 (s); 158.1 (s); 198.5 (s). EI-MS: 270 (0.5, M<sup>+</sup>), 174 (100), 159 (43), 146 (59), 133 (41), 132 (30), 131 (98), 117 (38), 105 (36), 91 (39). HR-MS: 270.0920 (M<sup>+</sup>, C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>S<sup>+</sup>; calc. 270.0927).

(3S,4aS,8aR)-3,4,4a,7,8,8a-Hexahydro-3-hydroxy-6-methylnaphthalene-1-methanol *α*-Methanesulfonate. To a stirred soln. of **9b** (100 mg, 0.37 mmol) in MeOH (1 ml) at 0° was added NaBH<sub>4</sub> (50 mg, 1.32 mmol) in 3 portions. After 10 min, the mixture was allowed to warm to r.t. for 1 h, quenched with H<sub>2</sub>O, extracted with Et<sub>2</sub>O, dried, and evaporated: reduction product of **9b** (80 mg, 79.4%). IR: 3424, 2929, 2863, 1673, 1455, 1377, 1193, 1105, 1041. <sup>1</sup>H-NMR: 1.18–1.32 (m, 2 H); 1.55 (s, 3 H); 1.70–1.84 (m, 3 H); 1.89–1.96 (m, 1 H); 2.01–2.10 (m, 2 H); 2.97 (br. s, 1 H); 3.18 (s, 3 H); 3.63 (d, *J* = 12.0, 1 H); 3.97 (d, *J* = 12.0, 1 H); 4.12–4.16 (m, 1 H); 5.21 (s, 1 H); 5.59 (s, 1 H). <sup>13</sup>C-NMR: 23.3 (q); 23.7 (t); 30.6 (t); 33.3 (d); 34.0 (d); 35.3 (t); 57.4 (q); 67.2 (d); 74.3 (t); 124.8 (d); 129.4 (d); 133.9 (s); 139.6 (s). EI-MS: 177 (5, [M – Ms]<sup>+</sup>), 176 (32), 145 (68), 143 (77), 129 (60), 107 (49), 105 (64), 95 (28), 93 (51), 91 (100), 79 (71), 77 (61), 41 (37).

[(1aR,2S,3aS,7aR,7bS)-1,1a,2,3,3a,6,7,7a-Octahydro-2-hydroxy-5-methyl-7bH-cyclopropa]naphthalene-7b-methanol *α*-Methanesulfonate (**10**). To a stirred soln. of CH<sub>2</sub>I<sub>2</sub> (100 mg, 0.37 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 ml) at 0° under N<sub>2</sub>, 1M Et<sub>2</sub>Zn in hexane (0.37 ml, 0.37 mmol) was added dropwise via a syringe, and after 10 min, a soln. of the above reduction product of **9b** (100 mg, 0.37 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 ml) was added. After stirring at r.t. for 2 h, the mixture was cooled to 0° again, quenched with sat. NH<sub>4</sub>Cl soln., and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was washed with 1N brine, dried, and evaporated and the residue subjected to CC (AcOEt/hexane 1:2): **10** (60 mg, 57.1%). <sup>1</sup>H-NMR: 0.21–0.26 (m, 1 H); 0.49 (t, *J* = 5.4, 1 H); 0.70–0.82 (m, 1 H); 1.16–1.28 (m, 3 H); 1.47–1.52 (m, 1 H); 1.57 (s, 3 H); 1.82–1.87 (m, 2 H); 1.96–2.04 (m, 3 H); 2.80 (d, *J* = 9.9, 1 H); 3.26 (s, 3 H); 3.36 (d, *J* = 9.9, 1 H); 4.11–4.15 (m, 1 H); 5.10 (s, 1 H). <sup>13</sup>C-NMR: 7.1 (t); 23.2 (t); 23.6 (q); 24.8 (d); 28.6 (s); 30.8 (t); 30.8 (d); 32.4 (t); 34.9 (d); 58.5 (d); 68.6 (d); 80.6 (t); 124.5 (d); 134.2 (s).

(1aR,3aS,7aR,7bS)-1,1a,3,3a,6,7,7a,7b-Octahydro-5-methyl-7b-[(methylsulfonyl)oxy]methyl]-2H-cyclopropa]naphthalene-2-one (**11**). A soln. of **10** (40 mg, 0.14 mmol) and Dess–Martin periodinane (100 mg, 0.23 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was stirred at r.t. under N<sub>2</sub> for 24 h. Then the mixture was poured into 1N NaOH and extracted with CH<sub>2</sub>Cl<sub>2</sub>, the extract washed with 1N NaOH, H<sub>2</sub>O, and brine, dried, and evaporated, and the residue subjected to CC (AcOEt/hexane 1:2): **11** (35 mg, 88.1%). <sup>1</sup>H-NMR: 0.94–0.99 (m, 1 H); 1.13 (t, *J* = 4.8, 1 H); 1.19–1.27 (m, 1 H); 1.40–1.50 (m, 1 H); 1.59 (s, 3 H); 1.65–1.70 (m, 1 H); 1.86–2.02 (m, 4 H); 2.18–2.26 (m, 1 H); 2.38–2.43 (m, 1 H); 2.96 (d, *J* = 10.5, 1 H); 3.26 (s, 3 H); 3.36 (d, *J* = 10.5, 1 H); 5.09 (s, 1 H). <sup>13</sup>C-NMR: 17.4 (t); 23.2 (t); 23.4 (q); 30.6 (t); 31.2 (d); 31.6 (d); 36.1 (s); 38.9 (d); 39.2 (t); 58.7 (d); 78.8 (t); 123.3 (d); 135.5 (s); 209.8 (s).

(1S,4R)-4-Isopropenyl-1-methylcyclohex-2-en-1-yl 2-Methylpropanoate (**13**). Et<sub>3</sub>N (20 ml), DMAP (0.20 g, 1.64 mmol), and isobutyric anhydride (15.6g, 98.60 mmol) were mixed with a soln. of **4** (5.0 g, 32.89 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) under N<sub>2</sub>. After stirring at r.t. for 2 d, the mixture was poured into sat. NaHCO<sub>3</sub> soln., and washed in sequence with 1N aq. ethane-1,2-diamine (to facilitate removal of excess anhydride), 1N HCl, H<sub>2</sub>O, and brine. The org. soln. was dried and evaporated: **13** (7.23 g, 99%). [*α*]<sub>D</sub> = –41.9 (c = 0.25, CHCl<sub>3</sub>). IR: 3485, 3447, 2973, 2937, 2875, 1731, 1470, 1449, 1386, 1372, 1273,

1189, 1159, 1098, 1068, 893, 863, 847, 742. <sup>1</sup>H-NMR: 1.00 (s, 3 H); 1.02 (s, 3 H); 1.44 (s, 3 H); 1.59 (s, 3 H); 1.62–1.65 (m, 3 H); 2.00–2.05 (m, 1 H); 2.31–2.35 (m, 1 H); 2.61–2.63 (m, 1 H); 4.65 (s, 2 H); 5.57 (d, *J* = 10.2, 1 H); 6.12 (d, *J* = 10.2, 1 H). <sup>13</sup>C-NMR: 18.4 (q); 18.6 (q); 19.8 (q); 23.9 (t); 25.3 (q); 34.2 (d); 35.2 (t); 43.2 (d); 76.3 (s); 110.3 (t); 130.4 (d); 132.9 (d); 147.4 (s); 175.4 (s).

2-[(1*S*,6*R*)-6-Isopropenyl-3-methylcyclohex-2-en-1-yl]-2-methylpropanoic Acid (**14**). To a soln. of LDA, prepared from <sup>3</sup>Pr<sub>2</sub>NH (5.80 g, 57.32 mmol) and 1.6M BuLi (28 ml, 44.8 mmol) at 0° in anh. THF (40 ml), a soln. of **13** (5.0 g, 22.52 mmol) in THF (40 ml) was added during 15 min at –78° under N<sub>2</sub>. After 1 h, the temp. was raised and kept at –40° for 30 min. On recooling to –78°, Me<sub>3</sub>SiCl (4.3 ml, 33.88 mmol) was added, the resulting mixture allowed to attain r.t., and the solvent evaporated. The residue was heated to reflux in dry toluene (90 ml) under N<sub>2</sub> for 36 h, cooled, and poured into 5% HCl soln. The aq. phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined org. phase evaporated, and the residue dissolved in 1*N* NaOH and washed with Et<sub>2</sub>O. Acidification, extraction with CH<sub>2</sub>Cl<sub>2</sub>, drying, and evaporation gave **14** (3.40 g, 68%). [ $\alpha$ ]<sub>D</sub> = +59.9 (*c* = 0.125, CHCl<sub>3</sub>). IR: 2970, 2929, 2652, 2362, 1698, 1474, 1450, 1373, 1280, 1166, 940, 891, 740. <sup>1</sup>H-NMR: 1.18 (s, 3 H); 1.19 (s, 3 H); 1.67 (s, 3 H); 1.76 (s, 3 H); 1.81–2.02 (m, 4 H); 2.36 (m, 1 H); 2.81 (s, 1 H); 4.79 (s, 2 H); 5.45 (s, 1 H). <sup>13</sup>C-NMR: 21.9 (q); 23.7 (q); 24.3 (q); 25.7 (q); 26.0 (t); 29.3 (t); 42.8 (d); 43.1 (d); 45.7 (s); 112.6 (t); 121.2 (d); 135.9 (s); 142.7 (s); 185.1 (s). EI-MS: 222 (15, *M*<sup>+</sup>), 136 (72), 134 (100), 110 (55), 109 (51), 107 (96), 93 (89), 91 (50), 79 (47), 41 (63). HR-MS: 222.1617 (*M*<sup>+</sup>, C<sub>14</sub>H<sub>22</sub>O<sub>2</sub><sup>+</sup>; calc. 222.1621).

2-[(1*S*,6*R*)-6-Isopropenyl-3-methylcyclohex-2-en-1-yl]-2-methylpropan-1-ol (**15**). To a stirred suspension of LiAlH<sub>4</sub> (1.16 g, 30.53 mmol) in THF (30 ml) was added slowly a soln. of **14** (3.40 g, 15.32 mmol) in anh. THF (30 ml). The mixture was refluxed for 5 h, cooled, quenched with sat. NH<sub>4</sub>Cl soln., and extracted with Et<sub>2</sub>O. The org. layer was washed with brine, dried, and evaporated: **15** (2.87 g, 90%). [ $\alpha$ ]<sub>D</sub> = +49.0 (*c* = 0.25, CHCl<sub>3</sub>). IR: 3409, 2962, 2928, 1715, 1644, 1455, 1376, 1261, 1041, 889, 801, 742. <sup>1</sup>H-NMR: 0.87 (s, 3 H); 0.91 (s, 3 H); 1.61 (s, 3 H); 1.76 (s, 3 H); 1.81–2.01 (m, 4 H); 2.14 (s, 1 H); 2.38–2.41 (m, 2 H); 3.31–3.43 (m, 2 H); 4.77 (d, *J* = 1.8, 1 H); 4.79 (d, *J* = 1.8, 1 H); 5.45 (s, 1 H). <sup>13</sup>C-NMR: 22.9 (q); 23.1 (q); 23.7 (q); 24.2 (q); 27.6 (t); 28.2 (t); 39.0 (s); 41.6 (d); 43.8 (d); 70.7 (t); 112.1 (t); 122.5 (d); 134.8 (s); 148.6 (s). EI-MS: 208 (10, *M*<sup>+</sup>), 207 (100), 133 (56), 93 (42), 63 (56), 55 (47), 43 (68), 41 (50). HR-MS: 208.1826 (*M*<sup>+</sup>, C<sub>14</sub>H<sub>24</sub>O<sup>+</sup>; calc. 208.1828).

(4*aR*,8*aS*)-4*a*,5,6,8*a*-Tetrahydro-1,1,4,7-tetramethylnaphthalen-2(1*H*)-one (**16**). PCC (14.50 g, 67.28 mmol) was added to a stirred soln. of **15** (2.8 g, 12.61 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (100 ml) at r.t. After 24 h, the mixture was diluted with dry Et<sub>2</sub>O (150 ml) and the supernatant liquid was percolated through a short pad of Florisil, with Et<sub>2</sub>O to wash the residue. After evaporation, a soln. of the crude product and TsOH·H<sub>2</sub>O (0.30 g) in dry benzene (100 ml) was refluxed for 1.5 h. Extractive workup followed by CC (AcOEt/hexane 1:9) afforded **16** (1.21 g, 44.1%). [ $\alpha$ ]<sub>D</sub> = –8.0 (*c* = 0.25, CHCl<sub>3</sub>). IR: 2966, 2930, 2872, 1677, 1446, 1382, 1261, 1095, 1019, 866, 801, 737. <sup>1</sup>H-NMR: 1.02 (s, 3 H); 1.11 (s, 3 H); 1.59 (s, 3 H); 1.66–1.75 (m, 2 H); 1.88–1.95 (m, 2 H); 1.89 (s, 3 H); 2.39 (s, 1 H); 2.53 (s, 1 H); 5.27 (s, 1 H); 5.71 (s, 1 H). <sup>13</sup>C-NMR: 21.5 (q); 22.5 (q); 23.8 (q); 24.5 (q); 24.6 (t); 28.1 (t); 37.6 (s); 44.5 (d); 45.0 (d); 119.4 (d); 125.7 (d); 136.3 (s); 160.0 (s); 204.4 (s). EI-MS: 204 (81, *M*<sup>+</sup>), 189 (52), 95 (88), 91 (42), 43 (54), 41 (100), 39 (58). HR-MS: 204.1517 (*M*<sup>+</sup>, C<sub>14</sub>H<sub>20</sub>O<sup>+</sup>; calc. 204.1515).

(8*aS*)-3',5',6',8'*a*-Tetrahydro-1',1',4',7'-tetramethylspiro[1,3-dioxolane-2,2'(1*H*)-naphthalene] (**17a**). A mixture of **16** (1.0 g, 4.90 mmol), ethylene glycol (2.7 g, 43.55 mmol), and TsOH·H<sub>2</sub>O (30 mg) in benzene (30 ml) was refluxed under a Dean–Stark trap for 24 h. The mixture was cooled, poured into H<sub>2</sub>O, and extracted with Et<sub>2</sub>O. The combined extract was washed with 10% NaHCO<sub>3</sub> soln. and brine, dried, and evaporated: **17a** (1.12 g, 92.1%). [ $\alpha$ ]<sub>D</sub> = –12.1 (*c* = 0.25, CHCl<sub>3</sub>). IR: 2970, 2903, 2880, 2727, 1447, 1380, 1216, 1162, 1107, 1086, 1047, 976, 948, 847, 769. <sup>1</sup>H-NMR: 0.72 (s, 3 H); 0.93 (s, 3 H); 1.62 (s, 3 H); 1.67 (s, 3 H); 1.92–1.98 (m, 4 H); 2.24 (d, *J* = 18.3, 1 H); 2.64–2.68 (m, 1 H); 2.83 (s, 1 H); 3.83–4.00 (m, 4 H); 5.27 (s, 1 H); <sup>13</sup>C-NMR: 18.2 (q); 18.8 (q); 19.0 (q); 23.7 (q); 26.4 (t); 31.2 (t); 39.5 (t); 40.6 (s); 46.1 (d); 65.0 (t); 65.4 (t); 111.9 (s); 121.1 (s); 121.2 (d); 128.9 (s); 135.3 (s). EI-MS: 247 (2, [*M* – 1]<sup>+</sup>), 161 (28), 87 (30), 86 (51), 44 (58), 43 (100), 41 (35).

(8*aS*)-1,2,3,5,6,8*a*-Hexahydro-1,1,4,7-tetramethylnaphthalen-2(1*H*)-one (**17b**). A 35% aq. CF<sub>3</sub>COOH soln. (10 ml) was added to a vigorously stirred soln. of **17a** (1.12 g, mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) at 10–20°. After 48 h, the mixture was diluted with Et<sub>2</sub>O and poured into an ice-cooled NaHCO<sub>3</sub> soln. The org. phase was washed with brine, dried, and evaporated: **17b** (910 mg, 98.8%). [ $\alpha$ ]<sub>D</sub> = –70.4 (*c* = 0.25,

CHCl<sub>3</sub>). IR: 2969, 2871, 2840, 1715, 1446, 1382, 1264, 1188, 1128, 853, 724. <sup>1</sup>H-NMR: 0.89 (s, 3 H); 1.10 (s, 3 H); 1.67 (s, 3 H); 1.73 (s, 3 H); 1.92–1.97 (m, 3 H); 2.63–2.66 (m, 1 H); 2.67–2.70 (m, 1 H); 2.83 (s, 1 H); 2.97 (d, *J* = 6.8, 1 H); 5.24 (s, 1 H). <sup>13</sup>C-NMR: 17.9 (q); 19.8 (q); 20.5 (q); 23.9 (q); 26.2 (t); 30.3 (t); 44.0 (t); 47.3 (s); 47.4 (d); 119.4 (d); 121.3 (s); 129.0 (s); 137.8 (s); 214.7 (s). EI-MS: 204 (61, *M*<sup>+</sup>), 134 (100), 119 (65), 95 (69), 91 (47). HR-MS: 204.1510 (*M*<sup>+</sup>, C<sub>14</sub>H<sub>20</sub>O<sup>+</sup>; calc. 204.1515).

(4*aS*,7*R*)-1,2,4*a*,5,7,8-Hexahydro-3,5,5,9-tetramethyl-7-(trimethylsilyl)-6H-benzocyclohepten-6-one (**18b**). To a stirred soln. of **17** (0.60 g, 2.94 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.4 ml, 3.16 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added 2*M* Me<sub>3</sub>SiCHN<sub>2</sub> in toluene (1.6 ml, 3.2 mmol) at –40° under N<sub>2</sub>. After 2.5 h, H<sub>2</sub>O was added, the org. soln. washed with brine, dried, and evaporated, and the residue subjected to CC (AcOEt/hexane 1:30): **18b** (0.41 g, 48.1%) and **18a** (0.11 g, 17.2%). **18b**: [α]<sub>D</sub> = –97.4 (*c* = 0.15, CHCl<sub>3</sub>). IR: 2963, 2908, 2727, 1695, 1464, 1447, 1378, 1247, 1096, 1051, 1031, 864, 838, 693, 615. <sup>1</sup>H-NMR: 0.02 (s, 9 H); 0.84 (s, 3 H); 1.09 (s, 3 H); 1.56 (s, 3 H); 1.71 (s, 3 H); 1.78–1.91 (m, 3 H); 2.08 (dd, *J* = 16.5, 10.8, 1 H), 2.50–2.67 (m, 2 H); 2.94 (t, *J* = 9.9, 1 H); 3.58 (s, 1 H); 5.37 (s, 1 H). <sup>13</sup>C-NMR: –2.6 (q); 17.7 (q); 20.9 (q); 23.1 (q); 24.0 (q); 27.0 (t); 30.1 (t); 35.0 (t); 35.1 (d); 44.0 (d); 55.2 (s); 118.7 (d); 126.8 (s); 132.0 (s); 136.5 (s); 218.1 (s). EI-MS: 290 (5, *M*<sup>+</sup>), 185 (52), 170 (39), 143 (30), 73 (60), 43 (100), 41 (53), 32 (75). HR-MS: 290.2073 (*M*<sup>+</sup>, C<sub>18</sub>H<sub>30</sub>OSi<sup>+</sup>; calc. 290.2067).

(4*aS*)-2,4*a*,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-6H-benzocyclohepten-6-one (**18a**). A mixture of **18b** (0.25 g, 0.86 mmol) and 1*M* Bu<sub>4</sub>NF (1.7 ml, 1.7 mmol) in MeCN (10 ml) was stirred at r.t. for 3 h. After evaporation, the residue was subjected to CC (AcOEt/hexane 1:30): **18a** (0.11 g, 58.5%). [α]<sub>D</sub> = –86.1 (*c* = 0.10, CHCl<sub>3</sub>). IR: 2966, 2927, 2910, 2728, 1706, 1465, 1448, 1381, 1248, 1081, 851. <sup>1</sup>H-NMR: 0.88 (s, 3 H); 1.15 (s, 3 H); 1.63 (s, 3 H); 1.71 (s, 3 H); 1.84–2.00 (m, 3 H); 2.10–2.16 (m, 1 H); 2.22–2.30 (m, 1 H); 2.56–2.58 (m, 1 H); 2.64–2.68 (m, 1 H); 3.04–3.13 (m, 1 H); 3.33 (s, 1 H); 5.37 (s, 1 H). <sup>13</sup>C-NMR: 18.8 (q); 20.2 (q); 23.9 (q); 24.2 (q); 26.1 (t); 30.1 (t); 30.8 (t); 36.2 (t); 43.8 (d); 53.6 (s); 118.6 (d); 127.4 (s); 132.7 (s); 136.6 (s); 215.5 (s). EI-MS: 218 (3, *M*<sup>+</sup>), 119 (24), 105 (36), 91 (14), 55 (30), 43 (100), 41 (72), 39 (30), 32 (82). HR-MS: 218.1669 (*M*<sup>+</sup>, C<sub>15</sub>H<sub>22</sub>O<sup>+</sup>; calc. 218.1671).

(4*aS*,6*S*,7*R*)-2,4*a*,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-7-(trimethylsilyl)-1*H*-benzocyclohepten-6-ol (**19**). To a stirred soln. of **18b** (0.16 g, 0.55 mmol) in EtOH (2 ml) was added NaBH<sub>4</sub> (0.20 g, 5.28 mmol) in portions during 5 min. After 36 h at r.t., the reaction was quenched with H<sub>2</sub>O and the mixture extracted with Et<sub>2</sub>O. Drying, evaporation, and CC (AcOEt/hexane 1:30) gave **19** (0.14 g, 86.9%). [α]<sub>D</sub> = 62.2 (*c* = 0.15, CHCl<sub>3</sub>). IR: 3564, 2960, 2905, 1448, 1404, 1383, 1247, 1078, 1036, 995, 864, 834, 746. <sup>1</sup>H-NMR: 0.01 (s, 9 H); 0.89 (s, 3 H); 0.94 (s, 3 H); 1.41–1.44 (m, 1 H); 1.70 (s, 3 H); 1.72 (s, 3 H); 1.83–2.02 (m, 5 H); 2.61–2.78 (m, 2 H); 3.08 (s, 1 H); 3.47 (d, *J* = 12.0, 1 H); 5.34 (s, 1 H). <sup>13</sup>C-NMR: –2.59 (q); 20.3 (q); 21.1 (q); 24.0 (q); 24.9 (d); 26.3 (t); 27.8 (q); 30.3 (t); 30.9 (t); 41.9 (s); 44.7 (d); 80.9 (d); 121.4 (d); 128.7 (s); 134.6 (s); 135.1 (s). EI-MS: 292 (2, *M*<sup>+</sup>), 137 (67), 134 (38), 91 (43), 75 (38), 73 (100). HR-MS 292.2223 (*M*<sup>+</sup>, C<sub>18</sub>H<sub>32</sub>OSi<sup>+</sup>; calc. 292.2224).

(4*aR*)-2,4*a*,5,8-Tetrahydro-3,5,5,9-tetramethyl-1*H*-benzocycloheptene (**20**). A 30% suspension of KH in oil (100 mg, 0.87 mmol) was washed with hexane and suspended in THF (1 ml). A soln. of **19** (60 mg, 0.21 mmol) in THF (2 ml) was added. The resulting mixture was stirred for 24 h at r.t., quenched with sat. NH<sub>4</sub>Cl soln., and poured into H<sub>2</sub>O overlaid with Et<sub>2</sub>O. The org. layer was washed with H<sub>2</sub>O (2×), dried, and evaporated and the residue subjected to CC (hexane): **20** (30 mg, 72.3%). [α]<sub>D</sub> = +81.8 (*c* = 0.10, CHCl<sub>3</sub>). IR: 3002, 2962, 2927, 2908, 2835, 1467, 1439, 1375, 1355, 1156, 980, 853, 744, 697. <sup>1</sup>H-NMR: 0.82 (s, 3 H); 1.07 (s, 3 H); 1.72 (s, 3 H); 1.76 (s, 3 H); 1.95–2.00 (m, 3 H); 2.11 (q, *J* = 9.0, 1 H); 2.63–2.68 (m, 1 H); 3.27–3.33 (m, 2 H); 5.15 (dd, *J* = 11.4, 3.3, 1 H); 5.44–5.52 (m, 2 H). <sup>13</sup>C-NMR: 20.1 (q); 24.1 (q); 24.3 (q); 26.0 (t); 29.1 (q); 30.2 (t); 33.2 (t); 38.4 (s); 45.4 (d); 121.5 (d); 123.2 (d); 131.7 (s); 131.8 (s); 136.1 (s); 142.1 (d). EI-MS: 202 (3, *M*<sup>+</sup>), 104 (43), 103 (42), 91 (98), 77 (42), 44 (100). HR-MS: 202.1722 (*M*<sup>+</sup>, C<sub>15</sub>H<sub>22</sub><sup>+</sup>; calc. 202.1722).

(+)-β-Himachalene (= (4*aR*)-2,4*a*,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-1*H*-benzocycloheptene; **2**) from **18a**. To a stirred soln. of **18a** (100 mg, 0.46 mmol) in MeOH (1 ml) was added NaBH<sub>4</sub> (50 mg, 1.32 mmol) at 0°. After 1 h, H<sub>2</sub>O was added, the mixture extracted with Et<sub>2</sub>O, dried, and evaporated. The obtained crude alcohol was directly mixed with DMAP (5 mg) in pyridine (1 ml) under N<sub>2</sub>, cooled to 0°, and treated with MsCl (0.1 ml, 1.29 mmol). On removal of the ice-bath, stirring was continued for 6 h. Then the mixture was poured into ice-water and extracted with CH<sub>2</sub>Cl<sub>2</sub> and the org. layer washed twice with 10% HCl soln., sat. NaHCO<sub>3</sub>, and brine, dried, and evaporated: mesylate.



Li-Wire (80 mg, 11.53 mmol) was added to anh. liq.  $\text{NH}_3$  (15 ml) at  $-78^\circ$ , and the mixture was stirred until the Li metal was completely dissolved. A soln. of the mesylate (see above) in THF (3 ml) was added dropwise. The mixture was stirred for 1 h and then quenched by solid  $\text{NH}_4\text{Cl}$  (600 mg, 11.21 mmol). Upon evaporation of the  $\text{NH}_3$ , the mixture was partitioned between  $\text{H}_2\text{O}$  and  $\text{Et}_2\text{O}$ , the aq. layer extracted with  $\text{Et}_2\text{O}$ , the combined org. phase dried and evaporated, and the residue subjected to CC (hexane): **2** (42 mg, 44.9% over 3 steps).  $[\alpha]_{\text{D}}^{25} = +212.3$  ( $c = 0.05$ ,  $\text{CHCl}_3$ ). IR: 2962, 2911, 2853, 2726, 1646, 1447, 1376, 1361, 1187, 1155, 859, 814.  $^1\text{H-NMR}$ : 0.71 (s, 3 H); 0.95 (s, 3 H); 1.35–1.58 (m, 4 H); 1.65 (s, 3 H); 1.69 (s, 3 H); 1.83–1.95 (m, 4 H); 2.38–2.45 (m, 1 H); 2.60–2.62 (m, 1 H); 2.87 (s, 1 H); 5.40 (s, 1 H).  $^{13}\text{C-NMR}$ : 20.2 (q); 21.4 (t); 23.7 (q); 24.1 (q); 26.0 (t); 29.2 (q); 30.2 (t); 34.0 (t); 34.6 (s); 45.1 (t); 46.1 (d); 122.5 (d); 129.1 (s); 131.2 (s); 134.7 (s). EI-MS: 204 (38,  $M^+$ ), 133 (41), 121 (43), 119 (100), 105 (40), 93 (24), 91 (36), 55 (20), 41 (50). HR-MS: 204.1876 ( $M^+$ ,  $\text{C}_{15}\text{H}_{24}^+$ ; calc. 204.1879).

(+)- $\beta$ -Himachalene (**2**) from **20**. To a soln. of **20** (30 mg, 0.15 mol) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (36 mg, 0.15 mmol) in EtOH (1 ml) under  $\text{N}_2$  at  $0^\circ$  was added  $\text{NaBH}_4$  (6 mg, 0.15 mmol). The soln. immediately became dark with evolution of  $\text{H}_2$ . The mixture was stirred under  $\text{N}_2$  at r.t. for 24 h and poured into 3N HCl soln. The aq. soln. was extracted with  $\text{Et}_2\text{O}$ , the  $\text{Et}_2\text{O}$  layer was dried and evaporated, and the residue subjected to CC (hexane): **2** (22 mg, 72.6%).  $[\alpha]_{\text{D}}^{25} = +213$  ( $c = 0.05$ ,  $\text{CHCl}_3$ ) ( $[\alpha]_{\text{D}}^{25} = +224.7$  ( $\text{CHCl}_3$ );  $[\alpha]_{\text{D}}^{25} = +204$  ( $\text{CHCl}_3$ )).

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