Total Synthesis of (+)-β-Himachalene

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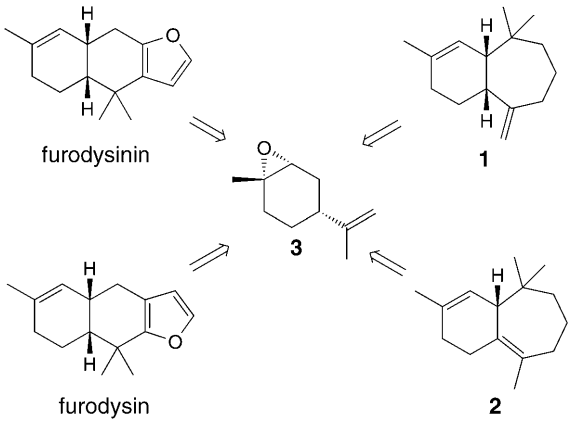
An enantioselective synthesis of (+)-β-himachalene (**2**) was accomplished starting from (1*S*,2*R*)-1,2-epoxy-*p*-menth-8-ene (**3**) in 15 or 16 steps with an overall yield of *ca.* 6% (*Schemes 3*, *5*, and *6*). Key transformations include an *Ireland–Claisen* rearrangement, a *Corey* oxidative 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 α-himachalene (**1**) and/or β-himachalene (**2**) may also be accessible from such an intermediate by a ring-expansion protocol (*Scheme 1*).

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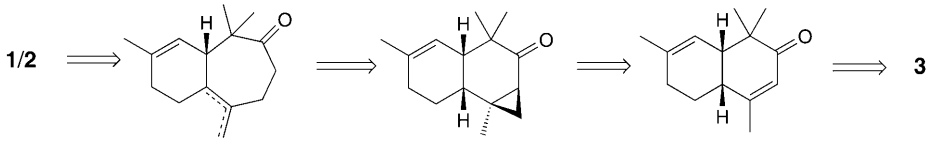
configurations of these bicyclic sesquiterpenes should be as shown in **1** and **2**. The chiral epoxymenthene **3** happens to possess the correct absolute configuration at the critical stereogenic centers for elaboration of the himachalenes.

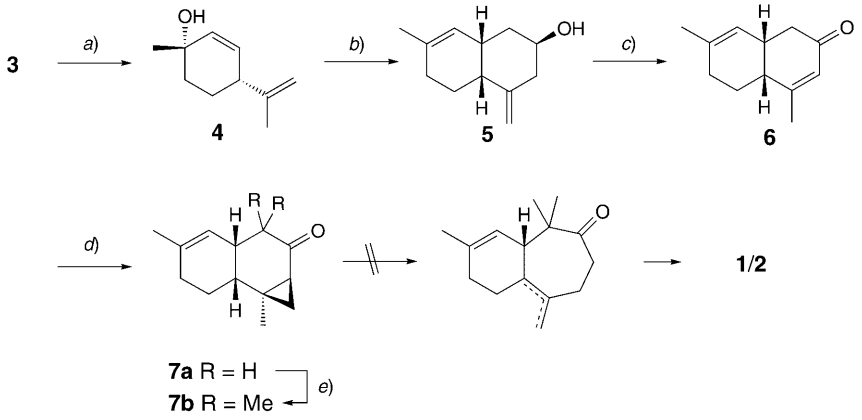
Several syntheses of the himachalenes have been completed, α-himachalene by using an intramolecular *Diels–Alder* reaction as the key step [7–9], β-himachalene based on a [2+2] photocycloaddition [10] or a homo-*Cope* rearrangement [11], and both isomers on an intramolecular *Diels–Alder* route [12]. 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 Me_2NH [13] or 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 MeCOMs [15], $Ac_2O/BF_3 \cdot OEt_2$ [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**



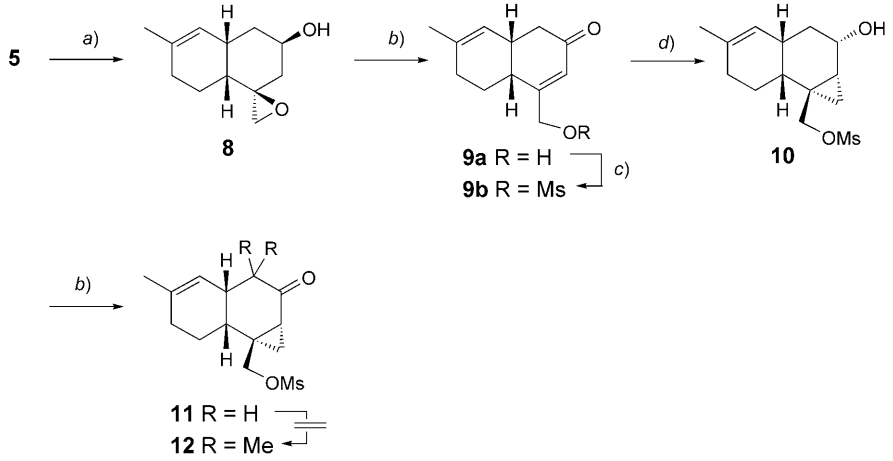
Scheme 3. *Attempted Cyclopropanation Route to* **1/2**



a) 1. Me_2NH, 159°, 18 h; 2. H_2O_2, 150–180°; 75%. *b*) 1. NaH, THF, 25°, 30 min; $PhSOCHCH_2$, KH(cat.), 25°, 3 h; 2. decalin, 200°, 12 h. *c*) *Swern oxidation*. d) $(Me_3SO)I$, NaH, DMSO, 25°, 5 h, 55°, 2 d. *e*) Me_3CCH_2ONa, THF, MeI, 60°, 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) [VO(acac)$_2$], ^{t}BuOOH, 0° → 25°, 13 h. *b*) *Dess–Martin oxidation.* *c*) MsCl, Et_3N, 0°, 3 h. *d*) 1. $NaBH_4$, MeOH, 25°, 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 $LiAlH_4$ reduction to **15**, pyridinium chlorochromate (PCC) oxidation, and treatment with 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 BF_3-catalyzed reaction with Me_3SiCHN_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 (+)-β-himachalene (**2**). Direct treatment of the product mixture **18a**/**18b** with Bu_4NF in MeCN gave **18a** in 58.5% yield. Subsequently, **18a** was reduced with $NaBH_4$, mesylated, and reduced with 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 (+)-β-himachalene. In the event, **18b** was subjected to borohydride reduction to afford a single product **19**. The bulky Me_3Si group provided stereocontrol for the reduction. The *cis*-α-silylcyloheptenol derivative **19** underwent *syn*-elimination on treatment with KH [19], and the resulting triene **20** was partially hydrogenated to afford **2** (*Scheme 6*).

In conclusion, we have achieved a total synthesis of (+)-β-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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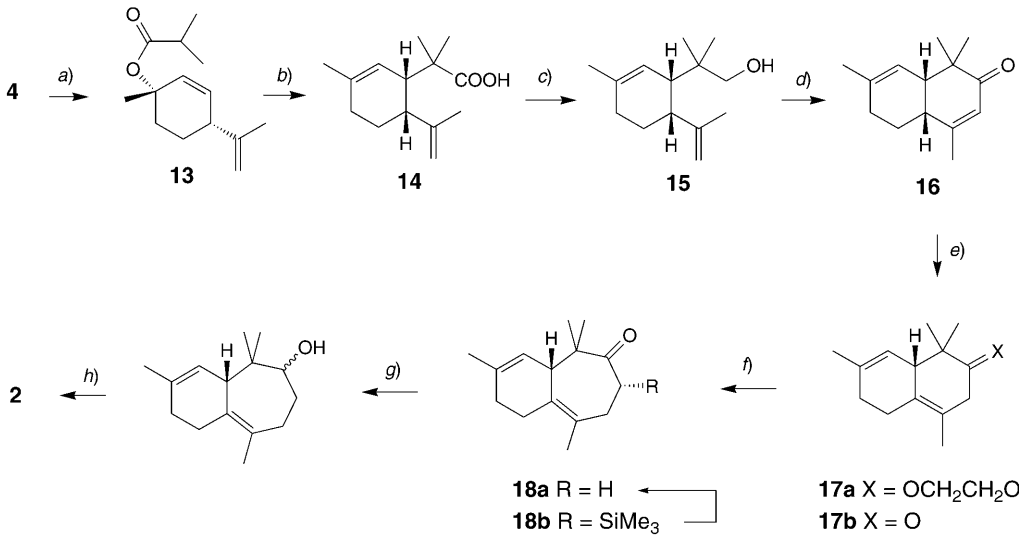
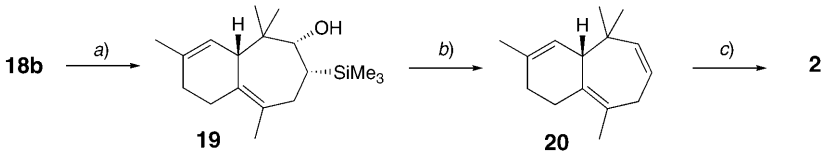
Scheme 5. *Total Synthesis of* **2**



a) Isobutyric anhydride, Et_3N, *N*,*N*-dimethylpyridin-4-amine (DMAP; cat.), CH_2Cl_2, 25°, 2 d; 99%. *b*) Lithium diisopropylamide (LDA), THF, −78°, 1 h, −40°, 30 min; Me_3SiCl, −78° →25°; PhMe, reflux, 36 h; 68%. *c*) $LiAlH_4$, THF, reflux, 5 h; 90%. *d*) pyridinium chlorochromate (PCC), CH_2Cl_2, 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_3COOH/H_2O, CH_2Cl_2, 10–20°, 2 d, 98.8% of **17b**. *f*) Me_2SiCHN_2, $BF_3 \cdot OEt_2$, CH_2Cl_2, −40°, 2.5 h; 65.3%. *g*) Bu_4NF, MeCN, r.t., 3 h, 58.5%. *h*) 1. $NaBH_4$, MeOH, 0°, 1 h. 2. MsCl, pyridine, DMAP(cat.), 0° →25°, 6 h; 3. Li, NH_3(l), −78°, 1 h, 44.9% (3 steps).

Scheme 6



a) $NaBH_4$, EtOH, 25°, 1.5 d; 86.9%. *b*) KH, THF, 25°, 24 h; 72.3%. *c*) $CoCl_2 \cdot 6H_2O$, $NaBH_4$, EtOH, 25°, 24 h; 72.6%.

Experimental Part

General. For drying org. solns. during workup, Na_2SO_4 was used. Column chromatography (CC): *Merck* silica gel (63–200 mesh). TLC: *Merck* silica gel *60* F_{254} plates. M.p.: uncorrected; *Laboratory Devices*. $[\alpha]_D$: $CHCl_3$ soln. at 25°. IR Spectra: *Bio-Rad FTS 165*; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Varian Unity-300*; $CDCl_3$ 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_2NH soln. (7.4 g, 164.44 mmol) in an autoclave and heated at 150° for 18 h. After removing excess Me_2NH, the cooled mixture was stirred with 30% H_2O_2 soln. (5 ml) at r.t. during 18 h. A trace of 5% Pd/C was used to decompose any remaining H_2O_2, 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%). $[\alpha]_D = +63.9$ ($c = 0.325$, $CHCl_3$). IR:

3650–3000, 2943, 2905, 2880. ^{1}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). ^{13}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*,4a*R*,8a*S*)-1,2,3,4,4a,5,6,8a-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_2O was introduced, and the mixture was washed with H_2O and brine, dried, and evaporated. The residue was heated with $NaHCO_3$ in decalin at 200° for 20 h, cooled, and diluted with Et_2O. After washing with H_2O, drying, and evaporation, the residue was subjected to CC: **5** (2.52 g, 53.8%). M.p. 75°. $[\alpha]_D = -10.39$ (*c* = 1, $CHCl_3$). IR: 3230, 3073, 2925, 1645, 1430, 1325, 1240, 1180, 1055, 1008, 935, 885, 849, 812, 711. ^{1}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)). ^{13}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, $M^{+\bullet}$), 162 (95), 145 (90). HR-MS: 178.1361 (M^+, $C_{12}H_{18}O^{+\bullet}$; calc. 178.1358).

*(4a*R*,8a*S*)-4a,5,6,8a-Tetrahydro-4,7-dimethylnaphthalen-2(1*H*)-one* (**6**). A soln. of **5** (450 mg, 2.52 mmol) in CH_2Cl_2 (3 ml) was added *via* a syringe into a stirred reagent prepared from oxalyl chloride (645 mg, 5 mmol) in CH_2Cl_2 (10 ml) and DMSO (948 mg, 12 mmol) in CH_2Cl_2 (3 ml) at −78°. After 30 min, Et_3N was added. The cooling bath was removed after 5 min., and the reaction was quenched with H_2O. The product was extracted with CH_2Cl_2, the extract dried and evaporated, and the residue subjected to CC: **6** (410 mg, 92%). M.p. 75°. $[\alpha]_D = +3.23$ (*c* = 1, $CHCl_3$). IR: 2929, 2724, 1668, 1627, 1432, 1379, 1302, 1262. ^{1}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)). ^{13}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, $M^{+\bullet}$), 162 (100), 150 (70). HR-MS: 176.1205 (M^+, $C_{12}H_{16}O^{+\bullet}$; calc. 176.1201).

*(3*S*,4*S*,4a*R*,8a*S*)-4a,5,6,8a-Tetrahydro-4,7-dimethyl-3,4-methylenennaphthalen-2(1*H*)-one* (= *(1a*S*, 3a*S*,7a*R*,7b*S*)-1,1a,3,3a,6,7,7a,7b-Octahydro-5,7b-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 $(Me_3SO)I$ (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_2O (10 ml) and extracted with Et_2O. The combined org. extract was washed with H_2O, dried, and evaporated. CC gave **7a** (40 mg, 74%). $[\alpha]_D = +82.04$ (*c* = 1.78, $CHCl_3$). IR: 2962, 2921, 2869, 2360, 1683, 1540, 1506, 1454, 1241. ^{1}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). ^{13}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, $M^{+\bullet}$), 97 (45), 85 (70), 83 (55), 71 (100), 70 (44), 69 (63).

*(1*R*,3*R*,4a*S*,8a*R*)-3,4,4a,7,8,8a-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)$_2$] (= bis(pentane-2,4-dionato-*κO*,*κO′*)oxovanadium; 30 mg, 0.11 mmol) in CH_2Cl_2 (20 ml) was slowly added 2.7M ^{t}BuOOH (in PhMe (3.0 ml, 8.10 mmol) at 0° under N_2 (green → dark red mixture). The soln. was allowed to warm to r.t. and stirred for 13 h. After addition of aq. Na_2SO_3 soln., the mixture was extracted with CH_2Cl_2, 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. ^{1}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). ^{13}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, $M^{+\bullet}$), 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^+, $C_{12}H_{18}O_2^{+\bullet}$; calc. 194.1308).

*(4a*R*,8a*S*)-4a,5,6,8a-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_2Cl_2 (40 ml) was stirred at r.t. under N_2 for 12 h. The resulting mixture was poured into 1N NaOH and extracted with CH_2Cl_2, the extract washed with 1N NaOH, H_2O, 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. ^{1}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). ^{13}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, $[M+1]^+$), 192 (77, $M^{+\bullet}$), 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^+, $C_{12}H_{16}O_2^{+\bullet}$; calc. 192.1151).

*(4a*R*,8a*S*)-4a,5,6,8a-Tetrahydro-7-methyl-4-{[(methylsulfonyl)oxy]methyl}naphthalen-2(1*H*)-one* (**9b**). A soln. of **9a** (300 mg, 1.6 mmol) and Et_3N (400 mg, 4.0 mmol) in THF (10 ml) at 0° under N_2 was stirred for 20 min. Then MsCl (300 mg, 2.6 mmol) was added. After 2 h, the mixture was diluted with H_2O and extracted with Et_2O. The org. layer was washed with H_2O and brine, dried, and evaporated: **9b** (400 mg, 94.8%). IR: 2924, 2858, 2360, 2324, 1456, 1339, 1265, 1087, 968. ^{1}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). ^{13}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, $M^{+\bullet}$), 174 (100), 159 (43), 146 (59), 133 (41), 132 (30), 131 (98), 117 (38), 105 (36), 91 (39). HR-MS: 270.0920 (M^+, $C_{13}H_{18}O_4S^{+\bullet}$; calc. 270.0927).

*(3*S*,4a*S*,8a*R*)-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 $NaBH_4$ (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_2O, extracted with Et_2O , dried, and evaporated: reduction product of **9b** (80 mg, 79.4%). IR: 3424, 2929, 2863, 1673, 1455, 1377, 1193, 1105, 1041. ^{1}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). ^{13}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, $[M-Ms]^+$), 176 (32), 145 (68), 143 (77), 129 (60), 107 (49), 105 (64), 95 (28), 93 (51), 91 (100), 79 (71), 77 (61), 41 (37).

*[(1a*R*,2*S*,3a*S*,7a*R*,7b*S*)-1,1a,2,3,3a,6,7,7a-Octahydro-2-hydroxy-5-methyl-7b*H*-cyclopropa[*a*]naphthalene-7b-methanol α-Methanesulfonate* (**10**). To a stirred soln. of CH_2I_2 (100 mg, 0.37 mmol) in CH_2Cl_2 (1 ml) at 0° under N_2, 1M Et_2Zn 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_2Cl_2 (1 ml) was added. After stirring at r.t. for 2 h, the mixture was cooled to 0° again, quenched with sat. NH_4Cl soln., and extracted with CH_2Cl_2. 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%). ^{1}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). ^{13}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*).

*(1a*R*,3a*S*,7a*R*,7b*S*)-1,1a,3,3a,6,7,7a,7b-Octahydro-5-methyl-7b-{[(methylsulfonyl)oxy]methyl}-2*H*-cyclopropa[a]naphthalene-2-one* (**11**). A soln. of **10** (40 mg, 0.14 mmol) and *Dess–Martin* periodinane (100 mg, 0.23 mmol) in CH_2Cl_2 (5 ml) was stirred at r.t. under N_2 for 24 h. Then the mixture was poured into 1N NaOH and extracted with CH_2Cl_2, the extract washed with 1N NaOH, H_2O, and brine, dried, and evaporated, and the residue subjected to CC (AcOEt/hexane 1:2): **11** (35 mg, 88.1%). ^{1}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). ^{13}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*).

*(1*S*,4*R*)-4-Isopropenyl-1-methylcyclohex-2-en-1-yl 2-Methylpropanoate* (**13**). Et_3N (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_2Cl_2 (20 ml) under N_2. After stirring at r.t. for 2 d, the mixture was poured into sat. $NaHCO_3$ soln., and washed in sequence with 1N aq. ethane-1,2-diamine (to facilitate removal of excess anhydride), 1N HCl, H_2O, and brine. The org. soln. was dried and evaporated: **13** (7.23 g, 99%). $[\alpha]_D = -41.9$ (*c* = 0.25, $CHCl_3$). IR: 3485, 3447, 2973, 2937, 2875, 1731, 1470, 1449, 1386, 1372, 1273,

1189, 1159, 1098, 1068, 893, 863, 847, 742. ^{1}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). ^{13}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 ^{i}Pr$_2$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_2. After 1 h, the temp. was raised and kept at −40° for 30 min. On recooling to −78°, Me_3SiCl (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_2 for 36 h, cooled, and poured into 5% HCl soln. The aq. phase was extracted with CH_2Cl_2, the combined org. phase evaporeted, and the residue dissolved in 1N NaOH and washed with Et_2O. Acidification, extraction with CH_2Cl_2, drying, and evaporation gave **14** (3.40 g, 68%). $[\alpha]_D=+59.9$ ($c=0.125$, $CHCl_3$). IR: 2970, 2929, 2652, 2362, 1698, 1474, 1450, 1373, 1280, 1166, 940, 891, 740. ^{1}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). ^{13}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, $M^{+\bullet}$), 136 (72), 134 (100), 110 (55), 109 (51), 107 (96), 93 (89), 91 (50), 79 (47), 41 (63). HR-MS: 222.1617 (M^+, $C_{14}H_{22}O_2^{+\bullet}$; 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 $LiAlH_4$ (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_4Cl soln., and extracted with Et_2O. The org. layer was washed with brine, dried, and evaporated: **15** (2.87 g, 90%). $[\alpha]_D=+49.0$ ($c=0.25$, $CHCl_3$). IR: 3409, 2962, 2928, 1715, 1644, 1455, 1376, 1261, 1041, 889, 801, 742. ^{1}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). ^{13}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, $M^{+\bullet}$), 207 (100), 133 (56), 93 (42), 63 (56), 55 47), 43 (68), 41 (50). HR-MS: 208.1826 (M^+, $C_{14}H_{24}O^{+\bullet}$; calc. 208.1828).

*(4a*R*,8a*S*)-4a,5,6,8a-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_2Cl_2 (100 ml) at r.t. After 24 h, the mixture was diluted with dry Et_2O (150 ml) and the supernatant liquid was percolated through a short pad of *Florisil*, with Et_2O to wash the residue. After evaporation, a soln. of the crude product and $TsOH\cdot H_2O$ (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** (1.21g, 44.1%). $[\alpha]_D=-8.0$ ($c=0.25$, $CHCl_3$). IR: 2966, 2930, 2872, 1677, 1446, 1382, 1261, 1095, 1019, 866, 801, 737. ^{1}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). ^{13}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, $M^{+\bullet}$), 189 (52), 95 (88), 91 (42), 43 (54), 41 (100), 39 (58). HR-MS: 204.1517 (M^+, $C_{14}H_{20}O^{+\bullet}$; calc. 204.1515).

*(8′a*S*)-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 $TsOH\cdot H_2O$ (30 mg) in benzene (30 ml) was refluxed under a *Dean–Stark* trap for 24 h. The mixture was cooled, poured into H_2O, and extracted with Et_2O. The combined extract was washed with 10% $NaHCO_3$ soln. and brine, dried, and evaporated: **17a** (1.12 g, 92.1%). $[\alpha]_D=-12.1$ ($c=0.25$, $CHCl_3$). IR: 2970, 2903, 2880, 2727, 1447, 1380, 1216, 1162, 1107, 1086, 1047, 976, 948, 847, 769. ^{1}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); ^{13}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, $[M-1]^+$), 161 (28), 87 (30), 86 (51), 44 (58), 43 (100), 41 (35).

*(8a*S*)-1,2,3,5,6,8a-Hexahydro-1,1,4,7-tetramethylnaphthalen-2(1*H*)-one* (**17b**). A 35% aq. CF_3COOH soln. (10 ml) was added to a vigorously stirred soln. of **17a** (1.12 g, mmol) in CH_2Cl_2 (20 ml) at 10–20°. After 48 h, the mixture was diluted with Et_2O and poured into an ice-cooled $NaHCO_3$ soln. The org. phase was washed with brine, dried, and evaporated: **17b** (910 mg, 98.8%). $[\alpha]_D=-70.4$ ($c=0.25$,

$CHCl_3$). IR: 2969, 2871, 2840, 1715, 1446, 1382, 1264, 1188, 1128, 853, 724. ^{1}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). ^{13}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, $M^{+\bullet}$), 134 (100), 119 (65), 95 (69), 91 (47). HR-MS: 204.1510 (M^+, $C_{14}H_{20}O^{+\bullet}$; calc. 204.1515).

*(4a*S*,7*R*)-1,2,4a,5,7,8-Hexahydro-3,5,5,9-tetramethyl-7-(trimethylsilyl)-6*H*-benzocyclohepten-6-one* (**18b**). To a stirred soln. of **17** (0.60 g, 2.94 mmol) and $BF_3 \cdot OEt_2$ (0.4 ml, 3.16 mmol) in dry CH_2Cl_2 (15 ml) was added 2M Me_3SiCHN_2 in toluene (1.6 ml, 3.2 mmol) at $-40°$ under N_2. After 2.5 h, H_2O 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**: $[\alpha]_D = -97.4$ ($c = 0.15$, $CHCl_3$). IR: 2963, 2908, 2727, 1695, 1464, 1447, 1378, 1247, 1096, 1051, 1031, 864, 838, 693, 615. ^{1}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). ^{13}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, $M^{+\bullet}$), 185 (52), 170 (39), 143 (30), 73 (60), 43 (100), 41 (53), 32 (75). HR-MS: 290.2073 (M^+, $C_{18}H_{30}OSi^{+\bullet}$; calc. 290.2067).

*(4a*S*)-2,4a,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-6*H*-benzocyclohepten-6-one* (**18a**). A mixture of **18b** (0.25 g, 0.86 mmol) and 1M Bu_4NF (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%). $[\alpha]_D = -86.1$ ($c = 0.10$, $CHCl_3$). IR: 2966, 2927, 2910, 2728, 1706, 1465, 1448, 1381, 1248, 1081, 851. ^{1}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). ^{13}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, $M^{+\bullet}$), 119 (24), 105 (36), 91 (14), 55 (30), 43 (100), 41 (72), 39 (30), 32 (82). HR-MS: 218.1669 (M^+, $C_{15}H_{22}O^{+\bullet}$; calc. 218.1671).

*(4a*S*,6*S*,7*R*)-2,4a,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-7-(trimethylsilyl)-1H-benzocyclohepten-6-ol* (**19**). To a stirred soln. of **18b** (0.16 g, 0.55 mmol) in EtOH (2 ml) was added $NaBH_4$ (0.20 g, 5.28 mmol) in portions during 5 min. After 36 h at r.t., the reaction was quenched with H_2O and the mixture extracted with Et_2O. Drying, evaporation, and CC (AcOEt/hexane 1:30) gave **19** (0.14 g, 86.9%). $[\alpha]_D = 62.2$ ($c = 0.15$, $CHCl_3$). IR: 3564, 2960, 2905, 1448, 1404, 1383, 1247, 1078, 1036, 995, 864, 834, 746. ^{1}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). ^{13}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, $M^{+\bullet}$), 137 (67), 134 (38), 91 (43), 75 (38), 73 (100). HR-MS 292.2223 (M^+, $C_{18}H_{32}OSi^{+\bullet}$; calc. 292.2224).

*(4a*R*)-2,4a,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_4Cl soln., and poured into H_2O overlaid with Et_2O. The org. layer was washed with H_2O (2×), dried, and evaporated and the residue subjected to CC (hexane): **20** (30 mg, 72.3%). $[\alpha]_D = +81.8$ ($c = 0.10$, $CHCl_3$). IR: 3002, 2962, 2927, 2908, 2835, 1467, 1439, 1375, 1355, 1156, 980, 853, 744, 697. ^{1}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). ^{13}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, $M^{+\bullet}$), 104 (43), 103 (42), 91 (98), 77 (42), 44 (100). HR-MS: 202.1722 (M^+, $C_{15}H_{22}^{+\bullet}$; calc. 202.1722).

(+)-β-Himachalene (= *(4a*R*)-2,4a,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 $NaBH_4$ (50 mg, 1.32 mmol) at 0°. After 1 h, H_2O was added, the mixture extracted with Et_2O, dried, and evaporated. The obtained crude alcohol was directly mixed with DMAP (5 mg) in pyridine (1 ml) under N_2, 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_2Cl_2 and the org. layer washed twice with 10% HCl soln., sat. $NaHCO_3$, and brine, dried, and evaporated: mesylate.

Li-Wire (80 mg, 11.53 mmol) was added to anh. liq. NH_3 (15 ml) at $-78°$, 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 NH_4Cl (600 mg, 11.21 mmol). Upon evaporation of the NH_3, the mixture was partitioned between H_2O and Et_2O, the aq. layer extracted with Et_2O, the combined org. phase dried and evaporated, and the residue subjected to CC (hexane): **2** (42 mg, 44.9% over 3 steps). $[\alpha]_D = +212.3$ ($c = 0.05$, $CHCl_3$). IR: 2962, 2911, 2853, 2726, 1646, 1447, 1376, 1361, 1187, 1155, 859, 814. ^{1}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}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, $M^{+\bullet}$), 133 (41), 121 (43), 119 (100), 105 (40), 93 (24), 91 (36), 55 (20), 41 (50). HR-MS: 204.1876 (M^+, $C_{15}H_{24}^{+\bullet}$; calc. 204.1879).

(+)-β-Himachalene (**2**) from **20**. To a soln. of **20** (30 mg, 0.15 mol) and $CoCl_2 \cdot 6H_2O$ (36 mg, 0.15 mmol) in EtOH (1 ml) under N_2 at 0° was added $NaBH_4$ (6 mg, 0.15 mmol). The soln. immediately became dark with evolution of H_2. The mixture was stirred under N_2 at r.t. for 24 h and poured into 3N HCl soln. The aq. soln. was extracted with Et_2O, the Et_2O layer was dried and evaporated, and the residue subjected to CC (hexane): **2** (22 mg, 72.6%). $[\alpha]_D = +213$ ($c = 0.05$ $CHCl_3$) ([4]:$[\alpha]_D = +224.7$ ($CHCl_3$); [5]: $[\alpha]_D = +204$ ($CHCl_3$)).

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