Enantioselective Access to (−)-*Ambrox*® Starting from *β*-Farnesene[1])

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Dedicated to the memory of Dr. *G. Bernardinelli* (University of Geneva)

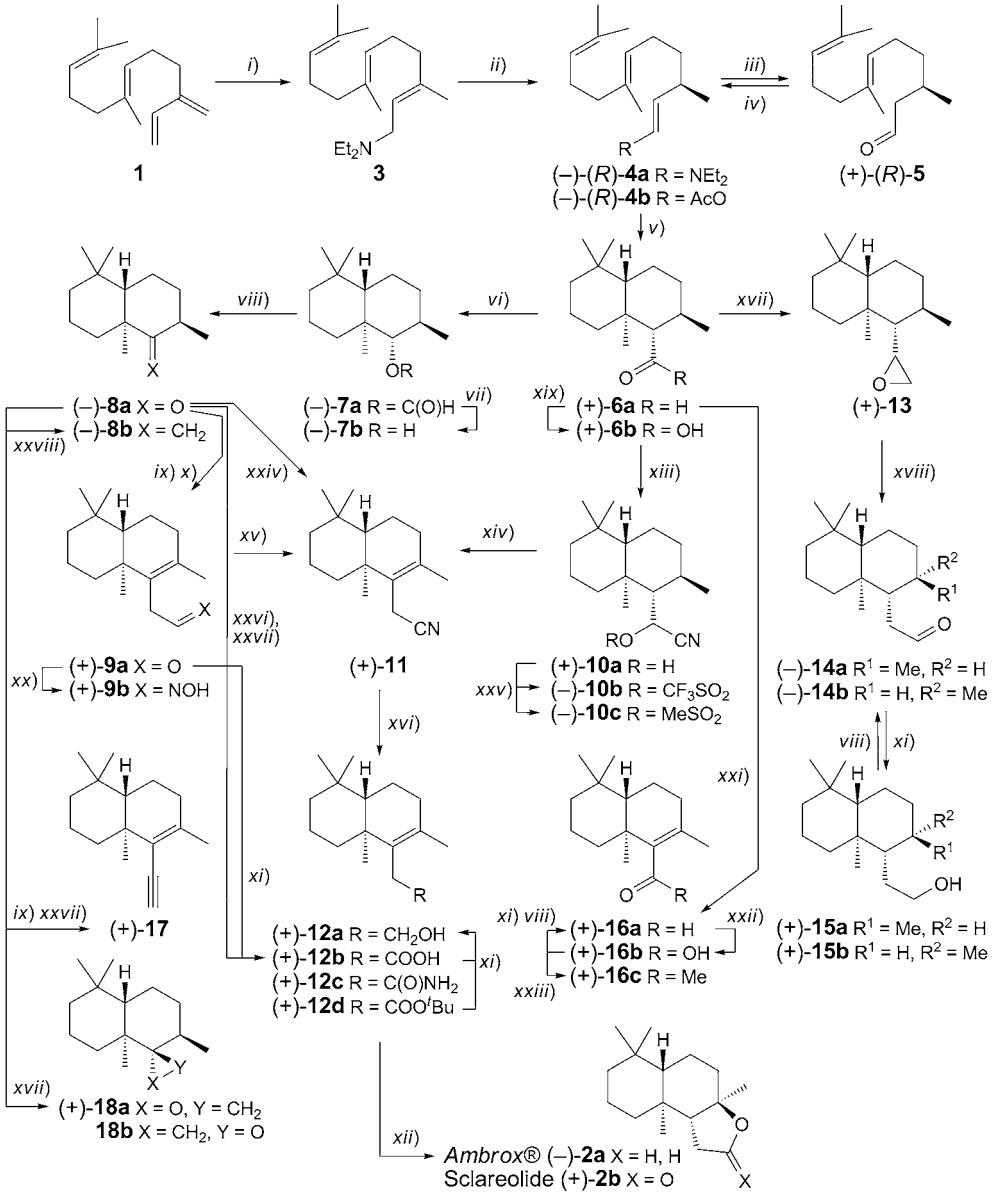
Starting from inexpensive (*E*)-*β*-farnesene (**1**), an eight-step enantioselective synthesis of the olfactively precious *Ambrox*® ((−)-**2a**) has been performed. The crucial step is the catalytic asymmetric isomerization of (2*E*,6*E*)-*N*,*N*-diethylfarnesylamine (**3**) to the corresponding enamine (−)-(*R*,*E*)-**4a**, applying *Takasago*'s well-known industrial methodology. The resulting dihydrofarnesal ((+)-(*R*)-**5**) (90% yield, 96% ee), obtained after *in situ* hydrolysis (AcOH, H_2O), was then cyclized under catalytic $SnCl_4$ conditions, *via* its corresponding unreported enol acetate (−)-(*R*)-**4b**, to afford *trans*-decalenic aldehyde (+)-**6a**. Subsequent transformations furnished bicyclic ketone (−)-**8a** and unsaturated nitrile (+)-**11**, both reported as intermediates to access to (−)-**2a**.

Introduction. – (*E*)-*β*-Farnesene (**1**), a precursor of farnesane biodiesel [1], is readily obtained by biotechnology from Brazilian sugar cane syrop [2] and has recently received particular attention as an extremely inexpensive starting material [3]. In a previous work, we succeeded in circumventing the patented BINAP/Rh^I *Takasago* industrial asymmetric isomerization process to access to optically active (+)-(*R*)-citronellal and (−)-isopulegol, and thus (−)-*l*-menthol, from myrcene [4]. In analogy, farnesene **1** was submitted to our modified conditions [5a], with *Ambrox*® ((−)-**2a**) as the potential target (*Scheme*).

Results and Discussion. – By analogy to myrcene [6], neat (*E*)-*β*-farnesene (**1**) was treated at 50° with Et_2NH in the presence of either metallic Li (75% yield) or BuLi (87% yield) to afford (2*E*,6*E*)-*N*,*N*-diethylfarnesylamine (**3**) stereoselectively [7]. Further treatment with 0.01 mol-equiv. of both $[Rh(COD)_2]CF_3SO_3$ (COD = cycloocta-1,5-diene) and (*S*,*R*)-(*t*Bu)josiphos (= di(tert-butyl){(*R*)-1-[(*S*)-2-diphenylphosphinoferrocenyl]ethyl}phosphine) in refluxing THF for 18 h readily furnished the so far unreported (1*E*)-enamine (−)-(*R*)-**4a**, which was hydrolyzed *in situ* (AcOH/

[1]) Work presented at the University of Geneva (12th June and 18th September 2012, as well as 12th June 2013, course 14C031 Perfume and Flavor Chemistry), and discussed at the IChOPAN Warsaw (6th September 2012).

Scheme



i) $HNEt_2$, Li, 75%, or $HNEt_2$, BuLi, 87%. *ii*) $[Rh(COD)_2]CF_3SO_3$, THF, 66°, (*S*,*R*)-(ᵗBu)josiphos; 90% yield, 92% ee; or (*S*)-BINAP; 93% yield, 96% ee. *iii*) AcOH, H_2O, 66°, >98%. *iv*) Ac_2O, AcOK, Et_3N; 87%, 7:3 ((1*E*)/(1*Z*)). *v*) 0.6 mol-equiv. $SnCl_4$, CH_2Cl_2, 20°, 52%. *vi*) *m*CPBA, CH_2Cl_2; 71%. *vii*) KOH, MeOH, H_2O, 65°; 88%. *viii*) PCC, CH_2Cl_2, 84–86%. *ix*) $HC{\equiv}CLi(H_2NCH_2)_2$, THF, −20° to 25°, 84%. *x*) $[V_2O_6SiPh_2]_n$, xylene, 145°; 85%; or $SOCl_2$, py, −40° to 20°; 78%, then ᵗBuOK, ᵗBuOH, 82°; 94%. *xi*) $LiAlH_4$, THF; >98% for (+)-**12a**; $CrO_3 \cdot H_2SO_4$, acetone, 60% for (+)-**12b**. *xii*) $FeCl_3$, $ClCH_2CH_2Cl$, 25°, 77%; or TsOH, $MeNO_2$, 100°; 36% from (+)-**12a**; *Amberlyst-15*, toluene, 110°, or HI, $CHCl_3$;

73–75% from (+)-**12b**. *xiii*) NaCN, $NaHSO_3$, THF, H_2O; 36%. *xiv*) P_2O_5, xylene, 140°; or Li_3PO_4 290–340°; 4–16% from (+)-**10a**; or toluylboronic acid, $Pd(OAc)_2$; 8–10% from (−)-**10b** or (−)-**10c**. *xv*) $H_2NOH \cdot HCl$, EtOH, $Pr_3P_3O_6$, 84% from (+)-**9a**; or $H_2NOH \cdot HCl$, EtOH, py, then Ac_2O, 100°; 75% *via* (+)-**9b**. *xvi*) DIBAL-H, toluene, −78°, then $NaBH_4$, ^{i}PrOH, 20°, (+)-**12a**; 78%; or excess KOH, ethylene glycol, 150° 4 h, (+)-**12c**, or 12 h, (+)-**12b**; 14–82%; or glycerol, 200°, 5 h, (+)-**12b**; 82–83%. *xvii*) Me_2S, Me_2SO, Me_2SO_4, NaOH; 70–78%. *xviii*) $Al(O^iPr)_3$, $AlCl_3$, toluene 110°; 25%. *xix*) HIO_3, DMSO, 46%. *xx*) $H_2NOH \cdot HCl$, EtOH, py; >98%. *xxi*) SO_2Cl_2, CH_2Cl_2, 40°, then LiCl, DMF, 150°; 3–6%. *xxii*) O_2, Et_2O; 60%. *xxiii*) MeLi, Et_2O, −78° to 25°; 91%. *xxiv*) $(EtO)_2P(O)CH_2CN$, ^{t}BuOK, THF, 82°; 98%. *xxv*) $(CF_3SO_2)_2O$, 2,6-lutidine, CH_2Cl_2; 94%; or $MeSO_2Cl$, Et_3N, CH_2Cl_2; 97%. *xxvi*) LDA, HMPA, $MeCOO^tBu$, −78°; 89%. *xxvii*) $SOCl_2$, DMAP, pyridine, −40° to 20°; 40–97%. *xxviii*) $Ph_3(Me)PI$, NaH, DMSO, 40–185°; 39%.

H_2O) to give the known dihydrofarnesal ((+)-(*R*)-**5**) [8a] in 90% yield and 92% ee[2]). When performed under the same conditions, but with (*S*)-BINAP (BINAP = (1,1′-binaphthalene-2,2′-diyl)bis(diphenylphosphine)) as ligand, (+)-(*R*)-**5** was isolated in 93% yield and 96% ee. Aldehyde (+)-(*R*)-**5** was then converted quantitatively to the so far unreported corresponding (1*E*)/(1*Z*)-enol acetate (−)-(*R*)-**4b** (Ac_2O, AcOK, Et_3N [11][[12]]). We were particularly interested in submitting this acyclic intermediate to the catalytic $SnCl_4$ cyclization conditions that we had earlier reported for the corresponding monocyclic analog [12], and were gratified to isolate the *trans*-decalenic aldehyde (+)-(1*S*,2*R*,4a*S*,8a*S*)-**6a** as a 75:25 (1*S*)/(1*R*) mixture in 52% yield[3]). This aldehyde mixture could be quantitatively epimerized (0.01 mol-equiv. EtONa, EtOH, 78°) to a 95:5 (1*S*)/(1*R*) mixture. Recognizing (+)-**6a** as a possible intermediate for access to the olfactively precious (−)-**2a**[4]), we decided to synthesize, *via* different routes, known precursors. The first route involved a *Baeyer–Villiger* oxidation, performed according to the conditions reported by *Margot et al.* on cyclocitronellal (*m*CPBA (*meta*-chloroperbenzoic acid), CH_2Cl_2, [17]), and delivered the so far unreported formate (−)-**7a** in 71% yield. Either simple saponification (KOH, MeOH, H_2O, 88% yield) or reduction ($LiAlH_4$, Et_2O, 98% yield) afforded the secondary bicyclic alcohol (−)-**7b**[5]). Further oxidation (PCC (= pyridinium chlorochromate), CH_2Cl_2, 84% yield) gave the corresponding ketone (−)-**8a** [13d][19], earlier used by *Fehr*, *via* Li acetylide addition of the ethylenediamine complex[6]) and *Meyer–Schuster* rearrangement to (+)-**9a**[7]), towards the synthesis of *Ambrox*® ((−)-**2a**) [24]. A second

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[2]) For *rac*-**5**, see [8b–8d]. Under our previously reported asymmetric hydrogenation conditions ((+)-(*R*,*R*)-chiraphos, (=(+)-(2*R*,3*R*)-2,3-bis(diphenylphosphino)butane), 0.01 mol-equiv. $Rh_4(CO)_{12}$, H_2, [5]), recently developed and exploited on an industrial scale by *BASF* chemists to access to (−)-*l*-menthol [9], *via* continuous dynamic distillation of neral from citral, resulting from the elegant cascade *Claisen–Cope* methodology, earlier reported by *Thomas* and *Ozainne* [10], (−)-(*S*)-**5** was also obtained from (2*E*,6*E*)-farnesal [10c], in 96% yield and 41% ee.

[3]) For *rac*-**6a**, see [12][13].

[4]) For reviews, and recent syntheses of *Ambrox*® ((−)-**2a**) and analogs, see [14][15] and [16], respectively.

[5]) For *rac*-**7b**, see [18].

[6]) For Li acetylide addition to (−)-**8a** under non-chelated conditions (55% yield), see [20].

[7]) The chiroptical properties of this natural product, isolated by *Demole* and *Engist* from *Oriental* tobacco, were never reported [21][22]. For *rac*-**9a**, see [23a], for telescoped *Meyer–Schuster* and reduction conditions ($PhCO_2H$, $VO(OSiPh_3)_3$, xylene, 140°, then directly MeOH, $NaBH_4$), see [23b].

route comprised treatment of aldehyde (+)-**6a** with NaCN and $NaHSO_3$ in THF/H_2O [25], followed by dehydration (P_2O_5, xylene, 140°, 16% yield [26a]) of the resulting 56:44 cyanohydrin mixture (+)-**10a** to afford the unsaturated nitrile (+)-**11** [27][8]). Saponification under basic conditions (excess KOH, ethylene glycol, 150°, or glycerol, 200°, 5 h, 82–83% yield [30][31b]) furnished the corresponding acid (+)-**12b** [32a][9]), a known precursor of either (+)-sclareolide ((+)-**2b**) [31a][10]) or *β*-ambrol ((+)-**12a**) [24][11]). One synthetic step may be saved by performing the reported one-pot tandem DIBAL-H (=diisobutylaluminium hydride)/$NaBH_4$ reduction of (+)-**11** to (+)-**12a** [27], the final cyclization to (−)-**2a** having also been reported [24][35][12]). To avoid the linear approach *via* (−)-**8a**, we also searched for an alternative route from (+)-**6a**, which is based on a C_1 homologation, using a *Corey–Chaykovsky* reaction under the conditions we had reported earlier (Me_2S, Me_2SO, Me_2SO_4, NaOH, [36]). Accordingly, the equatorial epoxy derivative (+)-**13** could be cleanly isolated in 78% yield as a 56:44 mixture of stereoisomers[13]). It is noteworthy that, under these conditions, we could also start directly from the 75:25 (1*S*)/(1*R*) mixture of non-epimerized aldehyde[14]). Opening of the epoxy ring under basic conditions in order to access a positional isomer

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[8]) For other dehydration conditions, see [26b–26e]. Alternatively, pyrolysis (290°–340°, 4% yield), or *β*-elimination (toluylboronic acid, $Pd(OAc)_2$, 8–10% yield, [26f]) from the corresponding triflate (−)-**10b** (Tf_2O, 2,6-lutidine, CH_2Cl_2, 94% from **10a**), or methanesulfonate **10c** (MsCl, Et_3N, CH_2Cl_2, 97% from **10a**), were less efficient. Nitrile (+)-**11** was also obtained in a single step from (+)-**9a** ($H_2NOH \cdot HCl$, EtOH, $Pr_3P_3O_6$, 84% yield) by analogy to [28]. When this reaction was performed according to the usual two-step procedure ($H_2NOH \cdot HCl$, EtOH, py (=pyridine), then Ac_2O, 100°, 75% yield), the intermediate oxime (+)-**9b** was isolated quantitatively. A quantitative short cut from (−)-**8a** to (+)-**11** was performed by addition of an excess of $(EtO)_2P(O)CH_2CN$ and ^{t}BuOK in THF at 66° as described in [29]. It is noteworthy that the NMR analyses reported for **11** in [27] are incomplete and quite different, in addition to the erroneous chiroptical properties of the starting material used by the Spanish authors (see *Footnote 19*). We were unable to obtain a copy of their analyses.

[9]) For *rac*-**12b**, see [32b–32f]. Alternatively, by analogy to [32g], (+)-**12b** was also obtained in 60% yield by *Jones* oxidation of (+)-**9a**. For analytical purpose, we also isolated the intermediate acetamide (+)-**12c** after a few hours at 150°. The known and fully characterized ester (+)-**12d**, previously obtained from (−)-**8a** (LDA (=$LiN(^i Pr)_2$), HMPA (=hexamethylphosporamide), $MeCOO^t Bu$, −78°, 89%, then $SOCl_2$, DMAP, pyridine, 20°, 97%), was quantitatively reduced to (+)-**12a** ($LiAlH_4$, Et_2O) by *Hagiwara et al.* [34].

[10]) For *Amberlyst-15*, toluene, 110°, or HI, $CHCl_3$ lactonization conditions, see [31b][31c], respectively.

[11]) $[\alpha]_D^{20} = 83.3$ ($c = 0.2$, $CHCl_3$), [33]: $[\alpha]_D^{20} = 110$ ($c = 2.4$, $CHCl_3$); [34]: $[\alpha]_D^{20} = -41.8$ ($c = 1.0$, MeOH).

[12]) The TsOH, $MeNO_2$ cyclization conditions of (+)-**12a** to (−)-**2a** were initially discovered by Dr. *S. D. Escher* (*Firmenich SA*, unreported results, 1984).

[13]) For alternative oxiranylation conditions using either $ClCH_2Br$, CH_2Br_2; or CH_2I_2, with BuLi or metallic Li, see [37][38].

[14]) Under non-reversible conditions for the generation of the sulfur ylide (^{t}BuOK, ^{t}BuOH, Me_3SOI, 20% yield; or NaH, DMSO, Me_3SOI, 54% yield) [38a][39], the oxiranylation took place prior to epimerization, and the signals of the minor axial ethylene oxides were detectable at 3.05, 2.90, and 2.37 ppm in the ^{1}H-NMR spectrum. Furthermore, these conditions were less efficient, as heavier uncharacterized material, resulting from ylide double addition, was also observed.

of (+)-**12a** was unsuccessful under a variety of conditions, due to the extreme steric crowding of the axial H-atom at C(1)[15]. We eventually found that treatment of (+)-**13** with $Al(O^iPr)_3$ in refluxing toluene in the presence of $AlCl_3$ gave the so far unreported saturated aldehyde (−)-**14a** in 25% yield[16]. An oxidative elimination (SO_2Cl_2, CH_2Cl_2, 40°[17]), then LiCl, DMF, 100° [42f][43d]) allowed us to access again to intermediate (+)-**9a**, albeit in a miserable 3% yield. Additionally, reduction of aldehyde (−)-**14a**[18]) ($LiAlH_4$, THF, 94% yield) occurred readily to give the corresponding alcohol (+)-**15a**. Finally, the oxidation of aldehyde (+)-**6a** to *β*-bicyclofarnesal ((+)-**16a**), a natural compound first isolated by *Demole* and *Engist* from *Oriental* tobacco [21], then by *Toyota et al.* from liverwort *Diplophyllum serrulatum* [45], was also performed with SO_2Cl_2, CH_2Cl_2, 40°, then LiCl, DMF at 150° in 6% yield[19]). Further autoxidation (O_2, Et_2O, [36], 60% yield) afforded the known acid (+)-**16b**[20]) [46a]. Finally, treatement with MeLi in Et_2O from −78° to 25°, as reported for the fully characterized racemate [52], allowed us to determine the

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[15]) Epoxide (+)-**13** remained unchanged when treated with either LDA, ^{t}BuOK, or $NaNH_2$ in refluxing THF, toluene, or xylene, even in the presence of additional $LiBF_4$ or $LiClO_4$. A similar inertness was observed, either with ^{t}BuOK in refluxing ^{t}BuOH, even in the presence of the same Li salts, or with $Li/(H_2NCH_2)_2$ at 115 °. For alternative non-attempted conditions *via* pyrolysis on Li_3PO_4, see [40].

[16]) Besides (+)-**15a** (18% yield). For stereoisomers of **15**, see [41].

[17]) MS of the intermediate *α*-chloroaldehyde: 270 (5, M^+), 257 (12), 255 (30), 221 (10), 192 (28), 177 (25), 137 (12), 123 (100), 121 (15), 109 (37), 107 (20), 97 (12), 95 (43), 93 (18), 81 (40), 79 (17), 69 (50), 67 (22), 55 (28), 41 (28), 32 (18), 28 (31).

[18]) Identical reduction of the reported aldehyde (−)-**14b** [13b–13d] ($[\alpha]_D^{20} = -11.2$ ($c = 1.2$, $CHCl_3$)) afforded in 95% yield the corresponding weakly amber-like alcohol (+)-**15b**, earlier delivered to our perfumers by Mr. *C. Vial* (*Firmenich SA*, 1980, unpublished results), who obtained it by using an independent approach. The reverse oxidation of (+)-**15b** to (−)-**14b** was performed in 86% yield with PCC in CH_2Cl_2. The potential C_1 homologation of (+)-**6a** *via Wittig*/epoxidation was not attempted [44].

[19]) Enal (+)-**16a** (0.37%) was also isolated by *B. Maurer* from longoza concrete, extracted from *Hedychium flavum* (Zingiberaceae), a flower growing in Madagascar (*Firmenich SA*, unpublished results, 1987). The chiroptical properties of the natural product were not reported in the original papers, but astonishingly, *β*-drimenal (4a*S*,8a*S*)-**16a** was reported as exhibiting either dextrorotatory [46] or laevorotatory [27][47] chiroptical properties. For a report, in which laevorotatory properties were mentioned in the discussion and dextrorotatory properties in the experimental part, see [48]. For the enantiomer, see [46f]. The chemical yield of the intermediate *α*-chloroaldehyde (20%) was 66% based on the recovered pure unreacted stereoisomer (+)-**6a**. Addition/elimination of Br_2 in dioxane according to [42] was unsuccessful on diastereoisomerically pure (+)-**6a**, while treatment with HIO_3 in DMSO [49] afforded the saturated acid (+)-**6b** in 46% yield. Attempted addition of $MeNO_2$ to (−)-**8a** failed (either NaOH, EtOH, 25°–80°; or DBU (=1,8-diazabicyclo[5.4.0]undec-7-ene), 20°–100°; or $(H_2NCH_2)_2$, 0.15–1.0 mol-equiv., 100°) [50]. Treatments of (−)-**8a** with either $(EtO)_2P(O)CH_2NO_2$ [51], ^{t}BuOK, THF, 66°; or MeCN, deprotonated with either $(Me_3Si)_2NLi$, $CeCl_3$, or ^{s}BuLi, in THF, −78°, were not attempted.

[20]) Also found in *Oriental* tobacco, although not reported in [21].

chiroptical properties of the methyl ketone (+)-**16c** (90% yield)[21]). Alternatively, the key intermediate ketone (−)-**8a** was also submitted to the *Corey–Chaykovsky* oxiranylation conditions (Me_2S, Me_2SO, Me_2SO_4, NaOH, 70% yield [36]) to afford a 85:15 mixture of epoxides (+)-**18a**/**18b**[22]).

Conclusions. – We have described, *via* (+)-**10a** and (+)-**11**, an eight-step enantioselective access to *Ambrox*® ((−)-**2a**) from the inexpensive and industrially available *β*-farnesene (**1**), comprising the *in situ* hydrolysis of (−)-(*R*)-**4a**[23]). This methodology, based on *Takasago*'s industrial process, may also give access to other members of the labdane/podocarpane family[24]), starting from either intermediates (+)-**6a** and (−)-**14a**, or the natural products (+)-**9a** and (+)-**16a**, all possessing an aldehyde functionality for suitable chemical modifications.

I am indebted to my apprentices *Mayeul Crétignier* and *Tim Vernet* for their experimental skills.

Experimental Part

General. See [5a].

*(2*E*,6*E*)*-N,N-*Diethyl-3,7,11-trimethyldodeca-2,6,10-trien-1-amine* ((2*E*,6*E*)-**3**). In a *Schlenk* flask with a magnetic bar were placed *(*E*)-β-farnesene* (**1**; 2.04 g, 9.98 mmol), Et_2NH (1.39 g, 18.97 mmol), and Li (25 mg, 3.60 mmol) under N_2. The sealed *Schlenk* flask was heated to 50° and was stirred for 5 h. The cold mixture was poured into ice-water, the upper org. layer was separated, and the aq. layer was extracted with Et_2O. The combined org. layer was washed with brine, dried (Na_2SO_4), and concentrated. Bulb-to-bulb distillation afforded the desired material in 75% yield. When BuLi (18.97 mmol) was used instead of Li, (2*E*,6*E*)-**3** was isolated in 87% yield. B.p. 135°/0.2. IR: 2967, 2922, 1668, 1447, 1381, 1288,

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21) For an alternative direct conversion or analogous addition of MeLi to an enal, followed by *Dess–Martin* oxidation, see [53]. Alternatively, the *Rupe* rearrangement of a 56:44 mixture of (1*R*/*S*,2*R*,4a*S*,8a*S*)-1-ethynylperhydro-2,5,5,8a-tetramethyl-4a*H*-naphthalenol [20][24] (HCO_2H [54], 79% yield) also afforded (+)-**16c**. The inverse sequence (+)-**16c** → (+)-**16b** → (+)-**16a** may eventually be performed by analogy to [54b], followed by $LiAlH_4$/THF [55], then MnO_2/CH_2Cl_2 [55] or PCC/CH_2Cl_2 treatment [47], since the haloform oxidative degradation (NaOH, Br_2, 1,4-dioxane, 20°, or NaOH, NaOCl, 1,4-dioxane, 50°) was totally inefficient. Dehydration of the intermediate mixture of propargyl alcohols ($CuSO_4$, toluene 110°, or xylene 140°) was unsuccessful, while ($SOCl_2$, py, −40° [19i][20][34], 40% yield) furnished the so far unreported (+)-**17**. Further direct one-pot reduction *via* hydroboration/$NaBH_4$ reduction, using either 9-borabicyclo[3.3.1]nonane [56], or the less hindered $BH_3 \cdot THF$ complex [34], THF, from −10° to 20°, then K_2CO_3, 3% H_2O_2, and then H_2O, MeOH, $NaBH_4$ was inefficient.

22) For analytical purposes, ketone (−)-**8a** was treated with Ph_3PCH_3I, NaH, DMSO, THF, 66° [57a], and the *Wittig* adduct (−)-**8b** [19b][57b] (39% yield) was epoxidized (AcO_2H, AcONa, CH_2Cl_2) to afford a 55:45 mixture of (+)-**18a**/**18b** in 91% yield. This mixture remained unchanged when treated with either LiN^iPr_2, or $LiNEt_2$, or $NaNH_2$, THF, −78° to 0°, in an unsuccessful attempt to obtain the desired allylic alcohol [27][46e], as a known precursor of (+)-**16a** [47]. Further additions of $MeNO_2$, 1,3-dithiane, or KCN to (+)-**18a**/**18b**, were not attempted.

23) Alternatively, a nine-step sequence, *via* (−)-**8a**, (+)-**12d**, and (+)-**12a**, comprising *in situ* saponification of (−)-**7a** to (−)-**7b**. The direct oxidation of (+)-**6a** to (−)-**8a** under the new conditions presented by *Baldovini et al.* (30% H_2O_2, DMSO, MeOH, KOH, 70°) at *Flavors & Fragrances 2013* (11–13 Sept., Leipzig) were not attempted.

24) We initially performed the beginning of this sequence in the enantiomeric series, using the first available optically active ligand we had.

1200, 1166, 1108, 1068, 1054, 984, 834, 763. ^{1}H-NMR: 5.27 (*qt*, *J* = 1.3, 6.8, 1 H); 5.11 (*qt*, *J* = 1.3, 6.8, 1 H); 5.09 (*qt*, *J* = 1.3, 7.1, 1 H); 3.06 (*d*, *J* = 7.1, 2 H); 2.51 (*q*, *J* = 7.1, 4 H); 2.14 – 1.95 (*m*, 8 H); 1.68 (br. *d*, *J* = 1.3, 3 H); 1.64 (*s*, 3 H); 1.60 (*s*, 6 H); 1.03 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR: 137.7 (*s*); 135.1 (*s*); 131.3 (*s*); 124.4 (*d*); 124.1 (*d*); 121.7 (*d*); 50.5 (*t*); 46.7 (2*t*); 39.8 (*t*); 39.7(*t*); 26.8 (*t*); 26.4 (*t*); 25.7 (*q*); 17.7 (*q*); 16.3 (*q*); 16.0 (*q*); 11.8 (2*q*). MS: 277 (9, M^+), 262 (7), 208 (39), 140 (78), 126 (54), 124 (16), 110 (15), 93 (14), 86 (58), 81 (48), 73 (36), 69 (98), 67 (22), 58 (100), 56 (17), 41 (53).

*(−)-(1*E*,3*R*,6*E*)*-N,N-*Diethyl-3,7,11-trimethyldodeca-1,6,10-trien-1-amine* ((−)-(3*R*)-**4a**). Isolated quantitatively by simple concentration and bulb-to-bulb distillation of the reaction mixture after isomerization of (2*E*,6*E*)-**3**, as described for (+)-(3*R*,6*E*)-**5**. B.p. 100°/0.07 mbar. $[\alpha]_D^{20} = -8.0$ (*c* = 3.5, $CHCl_3$). IR: 2965, 2917, 2853, 1650, 1449, 1375, 1244, 1197, 1095, 935, 834, 807, 783. ^{1}H-NMR: 5.80 (*d*, *J* = 13.8, 1 H); 5.06 – 5.14 (*m*, 2 H); 4.04 (*dd*, *J* = 8, 13.8, 1 H); 2.93 (*q*, *J* = 7, 4 H); 2.04 – 2.10 (*m*, 2 H); 1.95 – 2.01 (*m*, 4 H); 1.68 (*s*, 3 H); 1.60 (*s*, 3 H); 1.58 (*s*, 3 H); 1.18 – 1.36 (*m*, 3 H); 1.04 (*t*, *J* = 7, 6 H); 0.97 (*t*, *J* = 6.7, 3 H). ^{13}C-NMR: 135.8 (*d*); 134.4 (*s*); 131.2 (*s*); 125.8 (*d*); 124.5 (*d*); 105.1 (*d*); 44.5 (*t*); 39.8 (*t*); 38.9 (*t*); 35.0 (*d*); 26.8 (*t*); 26.0 (*t*); 25.7 (*q*); 22.8 (*q*); 17.7 (*q*); 16.0 (*q*); 12.2 (*q*). MS: 277 (4, M^+), 262 (4), 208 (57), 126 (100), 112 (5), 110 (6).

*(−)-(1*E*,3*R*,6*E*)-3,7,11-Trimethyldodeca-1,6,10-trien-1-yl Acetate* ((−)-(3*R*)-**4b**). *(+)-(3*R*,6*E*)-Dihydrofarnesal* (**5**; 17.65 g, 79 mmol) was added to a soln. of Et_3N (17.13g, 168 mmol) and AcOK (1.25 g, 12.61 mmol) in Ac_2O (125 ml). The soln. was heated at 120° for 5 h, cooled to 20°, poured into H_2O, and extracted with hexane. The org. phase was washed with sat. aq. $NaHCO_3$, brine, dried (Na_2SO_4), concentrated, and bulb-to-bulb distilled to afford the desired material in 87% yield as a 29 : 71 (1*Z*/1*E*) mixture. t_R (*Silicon DB1*, 100°, 1 min, then 10°/min to 220°, 0.32 μm, 50 m, He) 12.62 and 12.9 min, resp.[25]). B.p. 155°/0.1 mbar. $[\alpha]_D^{20} = -7.0$ (*c* = 2.4, $CHCl_3$). IR: 2961, 2917, 2870, 2855, 1756, 1672, 1452, 1369, 1216, 1104, 1087, 1043, 933. ^{1}H-NMR ((1*E*,3*R*,6*E*)-isomer): 7.06 (*dd*, *J* = 1, 12.5, 1 H); 5.30 (*dd*, *J* = 8.7, 12.5, 1 H); 5.10 – 5.06 (*m*, 2 H); 2.69 (*q*, *J* = 6.4, 1 H); 2.22 – 1.94 (*m*, 7 H); 1.68 (*s*, 3 H); 1.60 (*s*, 6 H); 1.37 – 1.23 (*m*, 4 H); 1.02 (*d*, *J* = 6.4, 3 H). ^{13}C-NMR: 168.3 (*s*); 135.2 (*s*); 134.6 (*d*); 131.3 (*s*); 124.4 (*d*); 124.2 (*d*); 120.6 (*d*); 39.8 (*t*); 37.2 (*t*); 32.0 (*d*); 26.7 (*t*); 25.7 (*q*); 25.6 (*t*); 20.9 (*q*); 20.7 (*q*); 17.7 (*q*); 16.0 (*q*). MS: 264 (0, M^+), 161 (13), 135 (19); 123 (11), 109 (40), 107 (23), 93 (23), 84 (19), 81 (17), 71 (32), 69 (92), 67 (18), 43 (100), 41 (47). Deduced from the mixture, ^{1}H-NMR ((1*Z*,3*R*,6*E*)-isomer): 6.99 (*dd*, *J* = 1, 6.4, 1 H); 5.10 – 5.06 (*m*, 2 H); 4.68 (*dd*, *J* = 6.4, 9.6, 1 H); 2.69 (*q*, *J* = 6.4, 1 H); 2.22 – 1.94 (*m*, 7 H); 2.13 (*s*, 3 H); 1.68 (*s*, 3 H); 1.58 (*s*, 6 H); 1.37 – 1.23 (*m*, 4 H); 0.99 (*d*, *J* = 6.4, 3 H). ^{13}C-NMR: 168.2 (*s*); 135.1 (*s*); 133.1 (*d*); 131.2 (*s*); 124.4 (*d*); 124.2 (*d*); 120.2 (*d*); 39.8 (*t*); 37.3 (*t*); 32.2 (*d*); 26.7 (*t*); 25.7 (*q*); 25.6 (*t*); 20.9 (*q*); 20.7 (*q*); 17.7 (*q*); 16.0 (*q*). MS: 264 (0, M^+), 161 (14), 135 (15), 123 (11), 109 (38), 107 (22), 93 (25), 84 (16), 81 (17), 71 (28), 69 (92), 67 (20), 43 (100), 41 (47).

*(+)-(3*R*,6*E*)-3,7,11-Trimethyldodeca-6,10-dienal* (= *(+)-(3*R*,6*E*)-Dihydrofarnesal*; **5**). In a glovebox, a soln. of $[Rh(cod)_2]CF_3SO_3$ in THF (0.01M; 2.5 ml, 0.025 mmol) was added to (*S*,*R*)-(*t*Bu)josiphos (13.6 mg, 0.025 mmol; 25 ml flask with a key stopper). After stirring for 1 h, (2*E*,6*E*)-**3** (1.0M/THF, 10 ml, 10 mmol) was added and the key stopper-closed flask, equipped with a condenser, was connected to a *Schlenk* line. The condenser was purged with Ar, then the key stopper was opened, and the clear soln. was refluxed for 20 h. To the soln. cooled to 0°, AcOH/H_2O 1 : 4 (5 ml) was added, and after 5 min at 0°, and then 30 min at 20°, the soln. was extracted with Et_2O, the extract was washed with H_2O (10 ml), 15% NaOH soln. (2 × 10 ml), H_2O to neutral, dried ($MgSO_4$), concentrated, and then bulb-to-bulb distilled

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[25]) For GC identification purpose, (6*Z*)-**5** [8d] was similarly transformed to (1*Z*,6*Z*)-**4b** (t_R (*Silicon DB1*): 12.2 min. MS: 264 (1, M^+), 189 (8), 161 (18), 148 (6), 135 (21), 122 (17), 113 (11), 109 (42), 107 (23), 95 (16), 93 (22), 84 (15), 81 (19), 79 (9), 71 (32), 69 (100), 67 (16), 43 (70), 41 (38)), and (1*E*,6*Z*)-**4b** (t_R (*Silicon DB1*): 12.5 min. MS: 264 (1, M^+), 204 (7), 189 (10), 161 (26), 135 (25), 126 (8), 123 (20), 113 (16), 109 (56), 107 (32), 105 (10), 97 (10), 95 (17), 93 (32), 84 (20), 81 (21), 71 (43), 69 (100), 67 (20), 55 (12), 53 (10), 43 (94), 41 (45)).

(110°/0.01 mbar): pure (+)-(3*R*,6*E*)-**5** (90% yield). $[\alpha]_D^{20} = +12.94$ ($c = 3.4$ $CHCl_3$), 92% ee; $[\alpha]_D^{20} +13.0$ ($c = 4.0$, $CHCl_3$), 93% yield, 96% ee using (*S*)-BINAP[26]). IR: 2957, 2923, 2871, 1725, 1453, 1377, 1107, 1080, 1019, 983, 870, 834, 741. ^{1}H-NMR: 9.75 (*t*, *J* = 2.4, 1 H); 5.12–5.06 (*m*, 2 H); 2.41 (*ddd*, *J* = 2.1, 5.7, 16, 1 H); 2.22 (*ddd*, *J* = 2.7, 7.8, 16, 1 H); 2.11–1.96 (*m*, 6 H); 1.68 (*d*, *J* = 1.0, 3 H); 1.60 (*s*, 6 H); 1.42–1.25 (*m*, 3 H); 0.97 (*d*, *J* = 6.6, 3 H). ^{13}C-NMR: 203.0 (*d*); 135.4 (*s*); 131.3 (*s*); 124.3 (*d*); 124.0 (*d*); 51.0 (*t*); 37.7 (*t*); 36.9 (*t*); 27.8 (*d*); 26.7 (*t*); 25.7 (*q*); 25.3 (*t*); 19.9 (*q*); 17.7 (*q*); 16.0 (*q*). MS: 222 (2, M^+), 179 (25), 161 (11), 123 (22), 109 (30), 93 (12), 81 (14), 69 (100), 67 (19), 41 (39). Tallow, burnt candle, waxy. The odor of the (−)-(3*S*,6*E*) enantiomer was aldehydic, watery, weak.

(+)-(1S,2R,4aS,8aS)-Decahydro-2,5,5,8a-tetramethylnaphthalene-1-carbaldehyde ((+)-**6a**). $SnCl_4$ (1.0M in CH_2Cl_2, 3.6 ml, 3.6 mmol) was added to a stirred soln. of (−)-(3*R*)-**4b** (1.5 g, 5.67 mmol) in CH_2Cl_2 (20 ml) at 20°. After 18 h, the mixture was poured into H_2O and extracted with Et_2O. The org. phase was washed with sat. aq. $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated. CC (SiO_2; cyclohexane/AcOEt 97:3 to 95:5) and then bulb-to-bulb distillation afforded (+)-**6a** in 52% yield as a 3:1 mixture of *trans*/*cis* stereoisomers[27]). B.p. 150°/0.9 mbar. $[\alpha]_D^{20} = +15.3$ ($c = 0.83$, $CHCl_3$). IR: 2959, 2925, 2869, 2848, 1717, 1457, 1385, 1367, 1238, 1120, 1079, 1034, 975, 933, 784, 760. ^{1}H-NMR (main isomer): 9.69 (*d*, *J* = 4, 1 H); 2.08 (*m*, 1 H); 1.90 (*dq*, *J* = 13, 3, 1 H); 1.09 (*s*, 3 H); 0.86 (*s*, 3 H); 0.84 (*s*, 3 H); 0.78 (*d*, *J* = 7, 3 H). ^{13}C-NMR: 207.6 (*d*); 70.4 (*d*); 54.3 (*d*); 41.9 (*t*); 40.3 (*t*); 38.5 (*s*); 35.6 (*t*); 33.5 (*q*); 33.3 (*s*); 27.6 (*d*); 21.8 (*q*); 21.6 (*t*); 20.6 (*q*); 18.4 (*t*); 15.9 (*q*). MS: 222 (15, M^+), 207 (15), 189 (12), 152 (10), 138 (67), 123 (100), 109 (62), 107 (19), 97 (26), 95 (66), 93 (22), 91 (17), 84 (92), 81 (66), 79 (25), 77 (15), 71 (37), 69 (87), 67 (38), 55 (57), 41 (53). Deduced from the mixture with the minor unreported stereoisomer (1*R*,2*R*,4a*S*,8a*S*)-decahydro-2,5,5,8a-tetramethylnaphthalene-1-carbaldehyde: ^{1}H-NMR: 9.91 (*d*, *J* = 4, 1 H); 2.08 (*m*, 1 H); 1.90 (*dq*, *J* = 13, 3, 1 H); 1.13 (*s*, 3 H); 0.89 (*s*, 3 H); 0.86 (*s*, 3 H); 0.78 (*d*, *J* = 7, 3 H). ^{13}C-NMR: 206.5 (*d*); 67.0 (*d*); 49.4 (*d*); 42.2 (*t*); 39.7 (*s*); 38.2 (*t*); 37.4 (*t*); 33.5 (*q*); 33.0 (*s*); 30.1 (*t*); 29.1 (*d*); 24.2 (*q*); 22.3 (*q*); 18.0 (*t*); 15.9 (*q*). MS: 222 (3, M^+), 207 (7), 189 (6), 138 (64), 123 (74), 109 (37), 107 (14), 97 (17), 95 (48), 93 (19), 91 (17), 84 (100), 81 (48), 79 (21), 77 (12), 71 (27), 69 (58), 67 (28), 55 (38), 41 (43), 28 (48). Epimerization with 0.01 mol-equiv. EtONa in refluxing EtOH afforded quantitatively a 95:5 mixture. $[\alpha]_D^{20} = +33.9$ ($c = 1.6$, $CHCl_3$), 96% ee; $[\alpha]_D^{20} = +31.7$ ($c = 1.7$, $CHCl_3$), 92% ee [28]).

(+)-(1S,2R,4aS,8aS)-Decahydro-2,5,5,8a-tetramethylnaphthalene-1-carboxylic Acid ((+)-**6b**). In a flask protected from light, a soln. of HIO_3 (112 mg, 0.632 mmol) in DMSO (4 ml) was heated at 80° for 1.5 h, then a soln.of (+)-**6a** (47 mg, 0.21 mmol) in DMSO (4 ml) was added at 65°. After 24 h at 65°, the cold soln. was poured into 10% aq. HCl at 0° and then extracted with Et_2O. The org. phase was dried ($MgSO_4$), concentrated, and the residue was purified by CC (SiO_2; cyclohexane/AcOEt 95:5 to 9:1) to afford pure (+)-**6b** (46% yield). $[\alpha]_D^{20} = +13.9$ ($c = 0.6$, $CHCl_3$). IR: 2923, 2869, 2850, 1698, 1457, 1414, 1388, 1378, 1367, 1302, 1226, 1165, 1113, 1033, 979, 935, 693. ^{1}H-NMR: 11.40 (br. *s*, OH); 1.92–1.74 (*m*, 4 H); 1.60–0.95 (*m*, 9 H); 1.05 (*s*, 3 H); 0.87 (*d*, *J* = 7, 3 H); 0.86 (*s*, 3 H); 0.84 (*s*, 3 H). ^{13}C-NMR: 179.8 (*s*); 64.7 (*d*); 54.2 (*d*); 42.0 (*t*); 40.0 (*t*); 37.2 (*s*); 35.3 (*t*); 33.5 (*q*); 33.2 (*s*); 29.7 (*d*); 21.8 (*q*); 21.6 (*t*); 20.8 (*q*); 18.6 (*t*); 14.5 (*q*). MS: 238 (30, M^+), 223 (90), 182 (27), 137 (11), 123 (100), 109 (32), 95 (30), 87 (23), 81 (85), 69 (31), 67 (16), 55 (18), 41 (17).

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[26]) The optical purity is based on chiral GC analysis of (+)-(*R*)-**5**. *RGB-174* Column, 30 m/0.25 mm/0.25 μm; 90°, 60 min; 0.5°/min to 140°m 100 min; He, 1.5 ml/min. t_R (minor) 145.69 min, t_R (major) 146.35 min, baseline separated. Before to decide on these GC separation conditions, we also reduced (+)-(*R*)-**5** ($LiAlH_4$, Et_2O, 97% yield) to the nearly odorless naturally occurring (+)-(3*R*,6*E*)-dihydrofarnesol [8e], $[\alpha]_D^{20} = 4.0$ ($c = 3.9$, $CHCl_3$) [8h–8j], as intermediate for acylation to (+)-(3*R*,6*E*)-3,7,11-trimethyldodeca-6,10-dienyl acetate (Ac_2O, py, 94%), another natural product earlier isolated from *Cyperus serotinus* ROTTB. [8k]; $[\alpha]_D^{20} = 3.0$ ($c = 3.2$, $CHCl_3$). ^{13}C-NMR: 171.2 (*s*); 135.0 (*s*); 131.3 (*s*); 124.5 (*d*); 124.4 (*d*); 63.0 (*t*); 39.8 (*t*); 37.0 (*t*); 35.4 (*t*); 29.5 (*d*); 26.7 (*t*); 25.7 (*q*); 25.3 (*t*); 21.0 (*q*); 19.4 (*q*); 17.7 (*q*); 16.0 (*q*).

[27]) The reaction time could be reduced to 5 h by using an equimolar amount of $SnCl_4$.

[28]) The optical purity is based on chiral GC analysis of (+)-**6a**. *RGB-174* Column, 30 m/0.25 mm/0.25 μm; 90°, 60 min; 0.5°/min to 140°, 100 min; He, 1.5 ml/min. t_R (minor) 130.06 min, t_R (major) 131.65 min, baseline separated.

(−)-(1S,2R,4aS,8aS)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl Formate ((−)-**7a**). A soln. of (+)-**6a** (0.62g, 2.79 mmol) in CH_2Cl_2 (15 ml) was treated with *m*CPBA (70% pure, 1035 mg, 4.2 mmol) at 20° for 4 d. Upon complete conversion, the mixture was poured into H_2O. The aq. phase was extracted with CH_2Cl_2 (3 × 10 ml), and the combined org. phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by CC (SiO_2; cyclohexane/AcOEt 97:3 to 85:15) to afford pure (−)-**7a** (71% yield[29])). $[\alpha]_D^{20} = -30.1$ ($c = 1.6$, $CHCl_3$). IR: 2994, 2957, 2932, 2919, 2868, 1711, 1462, 1447, 1387, 1379, 1354, 1189, 1175, 1158, 1120, 1091, 1053, 975, 950, 912, 888, 633. ^{1}H-NMR: 8.23 (*s*, 1 H); 4.57 (*s*, 1 H); 2.01–1.94 (*m*, 1 H); 1.67–1.12 (*m*, 11 H); 1.00 (*s*, 3 H); 0.88 (*s*, 3 H); 0.81 (*s*, 3 H); 0.80 (*d*, $J = 6.7$, 3 H). ^{13}C-NMR: 161.2 (*d*); 82.7 (*d*); 45.6 (*d*); 42.1 (*t*); 38.5 (*s*); 35.3 (*t*); 33.0 (*s*); 33.0 (*q*); 30.4 (*d*); 30.1 (*t*); 21.8 (*q*); 21.5 (*t*); 19.2 (*q*); 18.4 (*t*); 18.4 (*q*). MS: 238 (4, M^+), 223 (58), 192 (28), 177 (100), 149 (11), 136 (28), 123 (80), 121 (40), 109 (32), 107 (40), 95 (41), 93 (28), 81 (45), 79 (21), 69 (37), 67 (24), 55 (35), 43 (16), 41 (41). Medicinal, pungent, weakly woody, rooty.

(−)-(1S,2R,4aS,8aS)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-ol ((−)-**7b**). A soln. of (−)-**7a** (358 mg, 1.5 mmol) in MeOH (5 ml) was heated under reflux in the presence of KOH (0.25 g, 4.5 mmol) in H_2O (0.76 ml) for 1 h to complete conversion. The mixture was cooled to 20°, extracted with Et_2O (3 × 10 ml), and the aq. phase extracted twice with Et_2O (10 ml). The dried (Na_2SO_4) combined org. phase was concentrated and purified by CC (SiO_2; cyclohexane/AcOEt 95:5 to 80:20) to afford (−)-**7b** (88% yield[30])). $[\alpha]_D^{20} = -10.8$ ($c = 2.6$, $CHCl_3$). IR: 3342, 2995, 2956, 2937, 2920, 2904, 2865, 1457, 1442, 1386, 1378, 1340, 1308, 1295, 1182, 1134, 1095, 1057, 1046, 1009, 980, 943, 919, 654. ^{1}H-NMR: 2.92 (*d*, $J = 2$, 1 H); 1.90–1.84 (*m*, 1 H); 1.73–1.07 (*m*, 12 H); 0.92 (*d*, $J = 6$, 3 H); 0.90 (*s*, 3 H); 0.87 (*s*, 3 H); 0.81 (*s*, 3 H). ^{13}C-NMR: 81.5 (*d*); 44.6 (*d*); 42.3 (*t*); 39.1 (*s*); 35.3 (*t*); 33.0 (*s*); 33.0 (*q*); 31.0 (*d*); 29.2 (*t*); 21.9 (*q*); 21.6 (*t*); 19.5 (*q*); 18.9 (*q*); 18.6 (*t*). MS: 210 (8, M^+), 195 (23), 192 (30), 177 (100), 149 (12), 136 (20), 125 (22), 123 (82), 121 (29), 109 (36), 107 (32), 95 (43), 93 (20), 81 (50), 79 (21), 69 (42), 67 (30), 55 (40), 41 (43). Woody, amber-like, weak.

(−)-(2R,4aS,8aS)-Octahydro-2,5,5,8a-tetramethylnaphthalen-1(2H)-one ((−)-**8a**). A soln. of (−)-**7b** (210 mg, 1.0 mmol) in CH_2Cl_2 (10 ml) was oxidized with PCC (260 mg, 1.2 mmol). After full conversion, the mixture was diluted with Et_2O, filtered over a short path of SiO_2, concentrated, and purified by bulb-to-bulb distillation to afford (−)-**8a** (84% yield). $[\alpha]_D^{20} = -30$ (neat); $[\alpha]_D^{20} = -30.5$ ($c = 1.2$, $CHCl_3$). IR: 2981, 2957, 2927, 2896, 2869, 1690, 1460, 1447, 1383, 1372, 1361, 1158, 1134, 1000, 987, 979, 963, 858, 848, 808, 754, 731, 693. ^{1}H-NMR: 2.68 (*sept.*, $J = 7$, 1 H); 2.13 (*m*, 1 H); 1.76–1.65 (*m*, 2 H); 1.57–1.51 (*m*, 4 H); 1.42–1.36 (*m*, 1 H); 1.26–1.09 (*m*, 3 H); 1.14 (*s*, 3 H); 0.97 (*d*, $J = 7$, 3 H); 0.93 (*s*, 3 H); 0.88 (*s*, 3 H). ^{13}C-NMR: 216.8 (*s*); 54.2 (*d*); 48.8 (*s*); 41.6 (*t*); 39.9 (*d*); 35.8 (*t*); 34.2 (*s*); 33.2 (*t*); 33.1 (*q*); 22.1 (*q*); 21.4 (*t*); 18.8 (*q*); 18.2 (*t*); 15.1 (*q*). MS: 208 (59, M^+), 193 (30), 175 (27), 165 (22), 150 (55), 138 (22), 135 (31), 125 (42), 123 (100), 109 (58), 98 (21), 95 (87), 81 (64), 79 (30), 69 (70), 67 (71), 55 (63), 41 (90). Ambery, woody, slightly liquorice and camphoraceous.

(−)-(4aS,6R,8aS)-Decahydro-1,1,4a,6-tetramethyl-5-methylidenenaphthalene ((−)-**8b**). A suspension of NaH (503 mg, 55% in mineral oil, 11.52 mmol, washed 3 × with pentane) in DMSO (2 ml) was heated at 40° for 3 h, then a soln. of $Ph_3(Me)PI$ (4.16 g, 10.3 mmol) in DMSO (6 ml) was added, followed, after 2 h at 40°, by a soln. of (−)-**8a** (300 mg, 1.44 mmol) in THF (1 ml). After 3 h at 185°, the cold mixture was diluted with H_2O (100 ml) and extracted with Et_2O (3 × 40 ml). The org. phase was washed with H_2O (2 × 100 ml), and then dried ($MgSO_4$) and concentrated. The residue was crystallized in pentane, and the filtrate was concentrated and then purified by CC (SiO_2; cyclohexane/AcOEt 99:1) to afford pure (−)-**8b** (39% yield). $[\alpha]_D^{20} = -50.1$ ($c = 0.8$, $CHCl_3$). IR: 2923, 2868, 2849, 1633, 1461, 1387, 1373, 1051, 986, 974, 893, 882, 861, 708, 650. ^{1}H-NMR: 4.63 (br. *s*, 1 H); 4.50 (br. *s*, 1 H); 2.33 (*dsept.*, $J = 1.6, 6.4$, 1 H); 1.87 (*dq*, $J = 4.1, 12.4$, 1 H); 1.66 (*tt*, $J = 3.3, 13.4$, 2 H); 1.59 (*dsext.*, $J = 1.9, 12.4$, 1 H); 1.55–1.42 (*m*, 5 H); 1.40 (*dsext.*, $J = 1.9, 13.4$, 1 H); 1.16 (*dt*, $J = 3.9, 13.4$, 1 H); 1.04 (*s*, 3 H); 1.00 (*d*, $J = 6.4$, 3 H); 0.86 (*s*, 3 H); 0.84 (*s*, 3 H). ^{13}C-NMR: 164.6 (*s*); 99.7 (*t*); 54.2 (*d*); 42.4 (*t*); 40.3 (*s*); 37.9 (*t*); 37.6 (*t*); 33.8 (*s*); 33.3 (*d*); 33.3 (*q*); 22.4 (*t*); 21.9 (*q*); 20.7 (*q*); 19.4 (*q*); 19.2 (*t*). MS: 206 (30, M^+), 191 (44), 163 (18), 149 (12), 136

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[29]) When a 75:25 mixture with the stereoisomer **6a** was used as starting material, an $[\alpha]_D^{20}$ value of −12.4 ($c = 1.94$, $CHCl_3$) was obtained for the corresponding mixture of **7a**.

[30]) Alternatively, reduction of **7a** (65:35 mixture of stereoisomers at C(1)) with $LiAlH_4$ in THF at 20° afforded quantitatively a mixture of **7b**.

(100), 135 (31), 123 (29), 121 (50), 109 (51), 107 (40), 105 (12), 95 (55), 93 (37), 91 (24), 82 (41), 81 (41), 80 (40), 79 (26), 77 (16), 69 (28), 67 (28), 55 (27), 53 (13), 41 (28).

(+)-[(4aS,8aS)-3,4,4a,5,6,7,8,8a-Octahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]acetaldehyde ((+)-**9a**). A soln. of (4a*R*,6*R*,8a*S*)-5-[(*E*)-2-chloroethenyl]decahydro-1,1,4a,6-tetramethylnaphthalene (3:1 mixture of stereoisomers; see *Exper. Part* for (+)-**17**; 120 mg, 0.475 mmol) in ^{t}BuOH (5 ml) was added to a soln. of ^{t}BuOK (107 mg, 0.949 mmol) in ^{t}BuOH (5 ml). After 4 h at 82°, the cold mixture was diluted with H_2O (25 ml) and then extracted with Et_2O (3 × 40 ml). The org. phase was washed with H_2O and brine, dried (Na_2SO_4), concentrated, and purified by bulb-to-bulb distillation to afford pure (+)-**9a** (94% yield). B.p. 100°/0.01 mbar. $[\alpha]_D^{20} = +128.4$ ($c = 3.7$, $CHCl_3$). IR: 2925, 2866, 2847, 1721, 1458, 1387, 1374, 1366, 1239, 1190, 1116, 1091, 1062, 1048, 991, 949, 914, 824. For NMR and MS data, see [22b][24].

N-*Hydroxy-2-[(4aS,8aS)-3,4,4a,5,6,7,8,8a-octahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]ethanimine* ((+)-**9b**). Pyridine (3.4 ml) was added to a soln. of (+)-**9a** (950 mg, 3.97 mmol) and $NH_2OH \cdot HCl$ (800 mg, 10.37 mmol) in EtOH (3.4 ml), then the mixture was heated to 90° for 2 h. The cold mixture was diluted with Et_2O (5 ml) and H_2O (5 ml). The org. phase was washed with H_2O, then brine, dried (Na_2SO_4), and concentrated to afford quantitatively pure (+)-**9b** as a 2:1 (*E*)/(*Z*)-mixture after bulb-to-bulb distillation. $[\alpha]_D^{20} = +99.3$ ($c = 4.3$, $CHCl_3$). IR: 3220, 3080, 2924, 2865, 2847, 1592, 1457, 1440, 1387, 1374, 1032, 973, 932, 901, 753, 701, 665. Deduced from the mixture: ^{1}H-NMR ((*E*)-isomer): 7.32 (*t*, *J* = 4.1, 1 H); 7.30 (*m*, OH); 3.09 (*t*, *J* = 4.1, 2 H); 2.07–1.97 (*m*, 2 H); 1.80–1.61 (*m*, 3 H); 1.54 (*s*, 3 H); 1.51–1.38 (*m*, 4 H); 1.18–1.01 (*m*, 4 H); 0.96 (*s*, 3 H); 0.90 (*s*, 3 H); 0.83 (*s*, 3 H). ^{1}H-NMR ((*Z*)-isomer): 7.69 (*m*, OH); 6.54 (*t*, *J* = 5.1, 1 H); 2.98, 2.85 (2*dd*, *J* = 5.1, 15.1, each 1 H); 2.07–1.97 (*m*, 2 H); 1.80–1.61 (*m*, 3 H); 1.58 (*s*, 3 H); 1.51–1.38 (*m*, 4 H); 1.18–1.01 (*m*, 4 H); 0.96 (*s*, 3 H); 0.89 (*s*, 3 H); 0.83 (*s*, 3 H). ^{13}C-NMR ((*E*)-isomer): 153.1 (*d*); 136.3 (*s*); 128.8 (*s*); 52.0 (*d*); 41.7 (*t*); 38.8 (*s*); 36.7 (*t*); 33.8 (*t*); 33.3 (*s*); 33.3 (*q*); 28.1 (*t*); 24.0 (*t*); 21.6 (*q*); 19.7 (*q*); 19.5 (*q*); 19.0 (*t*). ^{13}C-NMR ((*Z*)-isomer): 151.7 (*d*); 134.9 (*s*); 129.6 (*s*); 51.7 (*d*); 41.6 (*t*); 38.8 (*s*); 37.1 (*t*); 33.8 (*t*); 33.3 (*s*); 33.3 (*q*); 28.1 (*t*); 24.0 (*t*); 21.6 (*q*); 19.9 (*q*); 19.5 (*q*); 19.0 (*t*). MS ((*E*)-isomer): 249 (18, M^+), 234 (32), 216 (38), 191 (96), 175 (18), 164 (26), 146 (100), 138 (22), 134 (35), 123 (97), 120 (53), 109 (40), 107 (37), 105 (54), 95 (52), 93 (40), 91 (55), 81 (33), 79 (35), 69 (52), 67 (20), 55 (28), 41 (37). MS ((*Z*)-isomer): 249 (2, M^+), 233 (13), 217 (41), 191 (40), 175 (30), 160 (12), 146 (100), 138 (8), 134 (32), 123 (94), 120 (43), 109 (24), 107 (27), 105 (50), 95 (30), 93 (33), 91 (40), 81 (23), 79 (25), 69 (45), 67 (14), 55 (22), 41 (30).

(+)-2-[(1S,2R,4aS,8aS)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]-2-hydroxyacetonitrile ((+)-**10a**). A soln. of (+)-**6a** (250 mg, 0.787 mmol) in THF (3 ml) was added to a soln. of $NaHSO_3$ (300 mg, 2.87 mmol) in H_2O (10 ml) at 0°. After 40 min at 0°, NaCN (159 mg, 3.15 mmol) was added. After 24 h at 20°, the mixture was treated with 10% HCl (under strong ventilation), then extracted with Et_2O. The org phase was washed with $NaHCO_3$, then with brine to neutrality, dried (Na_2SO_4), and concentrated. For anal. purposes, the residue was purified by CC (SiO_2; cyclohexane/AcOEt 99:1 to 8:2) to afford pure (+)-**10a** as a 56:44 mixture of stereoisomers (36% yield). $[\alpha]_D^{20} = +13.6$ ($c = 1.0$, $CHCl_3$). IR: 3440, 2924, 2869, 2850, 2239, 1450, 1388, 1369, 1221, 1118, 1089, 1072, 1052, 977, 934, 896, 861, 819. ^{1}H-NMR (major isomer): 4.90 (*s*, 1 H); 2.4 (br. *s*, OH); 2.0–1.2 (*m*, 13 H); 1.20 (*d*, *J* = 6.3, 3 H); 0.95 (*s*, 3 H); 0.86 (*s*, 3 H); 0.82 (*s*, 3 H). ^{13}C-NMR (major isomer): 121.9 (*s*); 61.1 (*d*); 57.7 (*d*); 57.1 (*d*); 41.7 (*t*); 39.9 (*t*); 38.3 (*s*); 36.5 (*t*); 33.6 (*q*); 33.3 (*s*); 27.8 (*d*); 24.3 (*q*); 21.7 (*q*); 21.7 (*t*); 18.7 (*t*); 15.2 (*q*). MS (major isomer): 249 (0, M^+), 222 (27), 207 (25), 189 (20), 152 (12), 138 (70), 123 (100), 109 (61), 107 (22), 97 (21), 95 (61); 93 (23), 91 (19), 84 (54), 81 (61), 79 (27), 71 (21), 69 (55), 67 (36), 55 (41), 41 (40). Minor stereoisomer deduced from the mixture: ^{1}H-NMR: 5.0 (*d*, *J* = 1, 1 H); 2.12 (br. *s*, OH); 2.0–1.2 (*m*, 13 H); 1.23 (*d*, *J* = 7.5, 3 H); 1.13 (*s*, 3 H); 0.86 (*s*, 3 H); 0.83 (*s*, 3 H). ^{13}C-NMR: 121.2 (*s*); 64.5 (*d*); 54.7 (*d*); 48.8 (*d*); 42.1 (*t*); 38.3 (*t*); 38.0 (*s*); 37.8 (*s*); 31.8 (*t*); 33.5 (*q*); 29.7 (*d*); 24.6 (*q*); 22.2 (*q*); 18.7 (*t*); 17.6 (*t*); 15.2 (*q*). MS: 249 (0, M^+), 222 (8), 207 (14), 189 (15), 152 (18), 138 (85), 123 (100), 109 (51), 107 (22), 97 (16), 95 (60), 93 (23), 91 (21), 84 (88), 81 (59), 79 (27), 71 (21), 69 (50), 67 (34), 55 (37), 41 (41).

(−)-Cyano[(1S,2R,4aS,8aS)-decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]methyl Trifluoromethanesulfonate ((−)-**10b**). Trifluoromethanesulfonic anhydride (217 mg, 0.77 mmol) was added dropwise at −50° to a soln. of **10a** (160 mg, 0.64 mmol) and 2,6-lutidine (84 mg, 0.77 mmol) in CH_2Cl_2 (3 ml). After 3 h at 0°, the mixture was diluted with CH_2Cl_2 (7 ml), washed with H_2O, dried (Na_2SO_4), and concentrated to afford a 1:1 mixture **10a**/**10b**. Purification by CC (SiO_2; cyclohexane/AcOEt 98:2) afforded **10b** as a main diastereoisomer (94% yield based on recovered **10a**). $[\alpha]_D^{20} = -2.9$ ($c = 0.7$,

$CHCl_3$). IR: 2928, 2872, 2851, 1741, 1459, 1422, 1390, 1369, 1244, 1208, 1139, 976, 924, 907, 849, 817. ^{1}H-NMR: 5.71 (*s*, 1 H); 2.31–2.26 (*m*, 1 H); 2.08–2.00 (*m*, 1 H); 1.94–1.87 (*m*, 1 H); 1.83–1.79 (*m*, 1 H); 1.68–1.55 (*m*, 3 H); 1.47–1.13 (*m*, 6 H); 1.08 (*d*, $J = 7$, 3 H); 1.00 (*s*, 3 H); 0.89 (*s*, 3 H); 0.84 (*s*, 3 H). ^{13}C-NMR: 171.2 (*s*); 113.9 (*s*); 73.2 (*d*); 61.1 (*d*); 54.6 (*d*); 41.4 (*t*); 39.2 (*t*); 38.3 (*s*); 36.0 (*t*); 33.5 (*d*); 33.4 (*s*); 30.7 (*q*); 21.8 (*q*); 21.4 (*t*); 21.2 (*q*); 18.6 (*t*); 15.6 (*q*). MS: 381 (4, M^+), 366 (18), 233 (13), 218 (100), 216 (17), 190 (9), 176 (13), 162 (13), 160 (11), 150 (15), 134 (10), 123 (98), 121 (25), 109 (38), 107 (17), 105 (11), 95 (35), 81 (34), 79 (20), 69 (57), 67 (21), 55 (28), 41 (25), 28 (32).

*(−)-(*RS*)-Cyano[(1*S*,2*R*,4a*S*,8a*S*)-decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]methyl Methanesulfonate* ((−)-**10c**). MsCl (88 mg, 0.77 mmol) was added dropwise at 0° to a soln. of **10a** (160 mg, 0.64 mmol) and Et_3N (139 mg, 1.28 mmol) in CH_2Cl_2 (2 ml). After 2 h at 20°, the mixture was diluted with CH_2Cl_2 (8 ml), washed with H_2O, dried (Na_2SO_4), and concentrated to afford **10c** as a 1:1 mixture of diastereoisomers (97%). The crude material was used as such, or purified by CC (SiO_2; cyclohexane/AcOEt 95:5) for anal. purposes. $[\alpha]_D^{20} = -1.6$ ($c = 0.6$, $CHCl_3$). IR: 2926, 2869, 2853, 2175, 1703, 1515, 1459, 1374, 1334, 1261, 1222, 1180, 1085, 1020, 950, 905, 837, 815, 800, 720. Deduced from a 2:1 enriched mixture. ^{1}H-NMR: 5.58 (*s*, 1 H); 3.17 (*s*, 3 H); 2.15–2.10 (*m*, 1 H); 2.05–1.97 (*m*, 1 H); 1.90–1.83 (*m*, 1 H); 1.65–1.52 (*m*, 3 H); 1.44–1.41 (*m*, 1 H); 1.34–1.25 (*m*, 3 H); 1.21–1.11 (*m*, 3 H); 1.08 (*d*, $J = 7$, 3 H); 0.98 (*s*, 3 H); 0.87 (*s*, 3 H); 0.83 (*s*, 3 H). ^{13}C-NMR: 115.5 (*s*); 67.3 (*d*); 60.5 (*d*); 54.6 (*d*); 41.4 (*t*); 39.3 (*q*); 39.2 (*t*); 38.2 (*s*); 36.2 (*t*); 33.5 (*q*); 33.4 (*s*); 30.9 (*d*); 21.8 (*q*); 21.5 (*t*); 21.3 (*q*); 18.6 (*t*); 15.5 (*q*). MS: 327 (4, M^+), 312 (51), 248 (5), 232 (20), 218 (40), 216 (19), 190 (5), 176 (12), 162 (10), 160 (13), 150 (22), 137 (10), 123 (100), 121 (13), 109 (30), 107 (18), 95 (32), 91 (15), 81 (33), 79 (28), 69 (59), 67 (22), 55 (27), 41 (24), 32 (28), 28 (60). ^{1}H-NMR: 5.60 (*s*, 1 H); 3.20 (*s*, 3 H); 2.15–2.10 (*m*, 1 H); 2.05–1.97 (*m*, 1 H); 1.90–1.83 (*m*, 1 H); 1.65–1.52 (*m*, 3 H); 1.44–1.41 (*m*, 1 H); 1.34–1.25 (*m*, 3 H); 1.21–1.11 (*m*, 3 H); 1.18 (*d*, $J = 7$, 3 H); 0.97 (*s*, 3 H); 0.87 (*s*, 3 H); 0.83 (*s*, 3 H). ^{13}C-NMR: 117.5 (*s*); 63.7 (*d*); 60.7 (*d*); 54.9 (*d*); 41.5 (*t*); 39.9 (*t*); 39.2 (*q*); 37.9 (*s*); 36.4 (*t*); 33.5 (*q*); 31.0 (*s*); 28.5 (*d*); 21.7 (*q*); 21.5 (*t*); 21.3 (*q*); 18.6 (*t*); 14.7 (*q*). MS: 327 (10, M^+), 312 (76), 248 (4), 232 (18), 218 (28), 216 (12), 176 (11), 162 (8), 160 (9), 150 (19), 137 (8), 123 (100), 121 (10), 109 (21), 107 (16), 95 (27), 93 (14), 81 (29), 79 (27), 69 (55), 67 (20), 55 (27), 41 (22), 28 (15).

*(+)-2-[(4a*S*,8a*S*)-3,4,4a,5,6,7,8,8a-Octahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]acetonitrile* ((+)-**11**). Propane-1-phosphonic acid cyclic anhydride (50%/AcOEt, 1400 mg, 2.20 mmol) was added at 20° to a soln. of (+)-**9a** (500 mg, 2.00 mmol), $H_2NOH \cdot HCl$ (153 mg, 2.20 mmol) and Et_3N (225 mg, 2.20 mmol) in DMF (2 ml). After 1.25 h at 100°, the cold soln. was poured into aq. sat. $NaHCO_3$ and then extracted with AcOEt. The org. phase was washed with H_2O and brine, dried (Na_2SO_4), and concentrated, to afford (+)-**11** in 84% yield after bulb-to-bulb distillation. Alternatively, a soln. of (+)-**9b** (250 mg, 1.0 mmol) in Ac_2O (1 ml) was heated at 100° for 1 h. The cold mixture was diluted with Et_2O (20 ml) and H_2O (10 ml). The org. phase was washed with H_2O and sat. aq. $NaHCO_3$, dried (Na_2SO_4), concentrated, and purified by CC (SiO_2; cyclohexane/AcOEt 97:3) to afford (+)-**11** (75% yield). Alternatively, a mixture of diethyl cyanomethylphosphonate (1116 mg, 6.05 mmol), ^{t}BuOK (577 mg, 5.04 mmol), and (−)-**8a** (210 mg, 1.01 mmol) in THF (5 ml) was heated at 66° for 72 h. The cold mixture was diluted with H_2O and then extracted with Et_2O. The org. phase was washed with brine, dried (Na_2SO_4), concentrated, and bulb-to-bulb distilled to afford quantitatively (+)-**11**, contaminated with 7% of a 6:1 (*E*)/(*Z*)-mixture of the corresponding intermediate conjugated nitriles[31]). Alternatively, crude (+)-**10a** was treated with 2.0 mol-equiv. of P_2O_5 in refluxing xylene to afford (+)-**11** in 16% yield. B.p. 130°/0.1 mbar. $[\alpha]_D^{20} = +144.0$ ($c = 4.1$, $CHCl_3$). IR: 2925, 2866, 2243, 1458, 1441, 1428, 1388, 1377, 1367, 1240, 1198, 1130, 1042, 1018, 990, 974, 954, 937, 718. ^{1}H-NMR: 3.02 (*d*, $J = 17.9$, 1 H); 2.90 (*d*, $J = 17.9$ 1 H); 2.10–2.04 (*m*, 2 H); 1.75 (*dt*, $J = 3, 7$, 2 H); 1.68 (*s*, 3 H); 1.71–1.52 (*m*, 3 H); 1.45–1.26 (*m*, 2 H); 1.21–1.13 (*m*, 2 H); 0.96 (*s*, 3 H); 0.90 (*s*, 3 H); 0.84 (*s*, 3 H). ^{13}C-NMR: 132.3 (*s*); 130.6 (*s*); 119.2 (*s*); 51.6

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[31]) The intermediate major conjugated isomer, tentatively attributed to the thermodynamically more stable (*E*)-nitrile, exhibited the following MS data: 231 (6, M^+), 216 (7), 191 (4), 160 (5), 146 (14), 134 (7), 124 (59), 109 (100), 105 (11), 93 (9), 91 (14), 81 (13), 79 (10), 69 (14), 55 (10), 41 (14), 32 (38), 28 (68). ^{1}H-NMR: olefinic signal at 5.19. MS (minor conjugated (*Z*)-isomer): 231 (8, M^+), 216 (20), 189 (6), 174 (8), 160 (6), 135 (10), 123 (20), 121 (10), 109 (33), 95 (16), 91 (13), 81 (18), 69 (13), 67 (10), 55 (8), 44 (6), 41 (11), 32 (64), 28 (100), ^{1}H-NMR: 5.05.

(*d*); 41.3 (*t*); 38.7 (*s*); 36.7 (*t*); 33.8 (*t*); 33.2 (*s*); 33.1 (*q*); 21.5 (*q*); 19.8 (*q*); 19.5 (*q*); 18.8 (*t*); 18.7 (*t*); 15.2 (*t*). MS: 231 (12, M^+), 216 (34), 191 (33), 160 (10), 146 (100), 134 (28), 123 (90), 120 (40), 105 (22), 91 (26), 81 (14), 79 (15), 77 (12), 69 (32), 67 (9), 55 (11), 41 (18).

*(+)-2-[(4a*S*,8a*S*)-3,4,4a,5,6,7,8,8a-Octahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]acetic Acid* ((+)-**12b**). A mixture of (+)-**11** (200 mg, 0.864 mmol) and KOH (85%, 1.15 g, 17.4 mmol) in ethylene glycol (10 ml) was heated at 150° for 12 h. The cold mixture was extracted with toluene, the org. phase was discarded, and the aq. phase was acidified to pH 1 with conc. HCl at 0°, then, after 30 min at 20°, extracted with toluene. This org. phase was dried (Na_2SO_4) and concentrated to afford pure (+)-**12b**. The reaction time could be reduced to 5 h in glycerol at 200° (82–83% yield). Alternatively, a soln. of aldehyde (+)-**9a** (510 mg, 2.176 mmol) in acetone (20 ml) at 0° was treated with $CrO_3 \cdot H_2SO_4$ (2.7M, 1.6 ml, 4.352 mmol). After 1.5 h at 0°, the mixture was poured into H_2O and then extracted with Et_2O. The org. phase was washed with 5% aq. NaOH (2 × 25 ml). This aq. phase was acidified with 10% aq. HCl and then extracted with Et_2O. This org. phase was washed with H_2O and brine, dried (Na_2SO_4), concentrated, and purified by CC (SiO_2; cyclohexane/AcOEt 85:15) to afford (+)-**12b** (60% yield). $[\alpha]_D^{20} = +112.0$ ($c = 3.4$, $CHCl_3$); $[\alpha]_D^{20} = +134.5$ ($c = 8.93$, benzene [32a]). IR: 3200, 2925, 2865, 1703, 1458, 1441, 1407, 1387, 1376, 1324, 1281, 1241, 1217, 1206, 1194, 1169, 1120, 1042, 1019, 974, 935, 842, 786, 762, 735, 683, 635. ^{1}H-NMR: 11.0 (br. *s*, 1 H); 3.14 (*d*, *J* = 17, 1 H); 3.01 (*d*, *J* = 17, 1 H); 2.18–2.09 (*m*, 1 H); 2.02 (*dd*, *J* = 6.2, 17, 1 H); 1.72–1.65 (*m*, 2 H); 1.58 (*s*, 3 H); 1.60–1.37 (*m*, 4 H); 1.26–1.12 (*m*, 3 H); 0.94 (*s*, 3 H); 0.89 (*s*, 3 H); 0.84 (*s*, 3 H)[32]). ^{13}C-NMR: 179.2 (*s*); 133.4 (*s*); 130.7 (*s*); 51.4 (*d*); 41.5 (*t*); 38.6 (*s*); 36.3 (*t*); 33.6 (*t*); 33.3 (*s*); 33.1 (*q*); 33.0 (*t*); 21.6 (*q*); 20.1 (*q*); 19.7 (*q*); 18.9 (2*t*). MS: 250 (34, M^+), 235 (71), 204 (10), 190 (100), 175 (86), 165 (82), 163 (27), 161 (20), 153 (24), 147 (20), 139 (69), 135 (20), 133 (39), 123 (49), 121 (64), 119 (76), 109 (38), 107 (53), 105 (75), 97 (12), 95 (37), 93 (50), 91 (60), 83 (11), 81 (38), 79 (34), 77 (30), 69 (51), 67 (22), 65 (13), 55 (37), 53 (15), 43 (22), 41 (47), 39 (11), 32 (40), 28 (78). Vague odor.

*(+)-2-[(4a*S*,8a*S*)-3,4,4a,5,6,7,8,8a-Octahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]acetamide* ((+)-**12c**). Isolated after 4 h at 150° during the preparation of (+)-**12b** (<15% yield). $[\alpha]_D^{20} = +34.3$ (c = 2.5, $CHCl_3$). IR: 3500, 3347, 2922, 2853, 1670, 1458, 1375, 1215, 1042, 755. ^{1}H-NMR: 5.84 (br. *s*, 2 H); 3.08 (*d*, *J* = 17, 1 H); 2.90 (*d*, *J* = 17, 1 H); 2.10 (*dt*, *J* = 6.4, 17, 2 H); 1.78–1.09 (*m*, 9 H); 1.63 (*s*, 3 H); 0.96 (*s*, 3 H); 0.90 (*s*, 3 H); 0.85 (*s*, 3 H). ^{13}C-NMR: 175.0 (*s*); 136.3 (*s*); 131.1 (*s*); 52.1 (*d*); 41.6 (*t*); 38.9 (*s*); 36.1 (*t*); 35.7 (*t*); 33.6 (*t*); 33.4 (*s*); 33.2 (*q*); 21.6 (*q*); 20.2 (*q*); 19.9 (*q*); 18.8 (2*t*). MS: 249 (18, M^+), 234 (17), 190 (84), 175 (100), 163 (50), 147 (17), 138 (14), 133 (17), 123 (17), 121 (34), 119 (36), 109 (21), 107 (24), 105 (57), 95 (20), 91 (30), 81 (14), 79 (18), 77 (16), 69 (20), 60 (19), 55 (18), 41 (24).

*(+)-2-[(1*S*,2*R*,4a*S*,8a*S*)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]oxirane* ((+)-**13**). Under strong mechanical stirring (900 rpm) were added successively, in the reactor, DMSO (30 ml), Me_2S (0.5 ml, 6.74 mmol), and Me_2SO_4 (0.58 ml, 6.05 mmol). After 30 min at 20°, NaOH (small beads, diameter 1–2 mm, 1.6 g, 40 mmol) was added, followed by a soln. of (+)-**6** (1.6 g, 4.53 mmol) in DMSO (5 ml). After 5 d, the mixture was poured onto ice and then extracted twice with AcOEt. The org. phase was washed with brine to neutrality, dried (Na_2SO_4), concentrated, and then purified by CC (SiO_2; cyclohexane/AcOEt 99:1) to afford (+)-**13** in 78% yield, as a 44:56 mixture of stereoisomers[33]). $[\alpha]_D^{20} = +4.9$ ($c = 1.83$, $CHCl_3$). IR: 3038, 2921, 2868, 2850, 1456, 1385, 1365, 1262, 1204, 1181, 1135, 1035, 976, 961, 947, 935, 889, 868, 857, 827, 818. ^{1}H-NMR (major isomer): 2.98 (*ddd*, *J* = 3, 4, 9.3, 1 H); 2.85 (*dd*, *J* = 4, 5, 1 H); 2.55 (*dd*, *J* = 4, 5, 1 H); 1.13 (*d*, *J* = 7.5, 3 H); 1.06 (*s*, 3 H); 0.85 (*s*, 3 H); 0.84 (*s*, 3 H); 2.2–0.74 (*m*, 13 H). ^{1}H-NMR (minor isomer): 2.73 (*dd*, *J* = 4, 5, 1 H); 2.67 (*dd*, *J* = 3, 4, 8.7, 1 H); 2.55 (*dd*, *J* = 4, 5, 1 H); 1.02 (*d*, *J* = 6.7, 3 H); 1.00 (*s*, 3 H); 0.84 (*s*, 3 H); 0.83 (*s*, 3 H); 2.2–0.74 (*m*, 13 H). ^{13}C-NMR (major isomer): 56.8 (*d*); 56.2 (*d*); 51.6 (*d*); 50.0 (*t*); 42.1 (*t*); 40.5 (*t*); 38.0 (*s*); 34.2 (*t*); 33.5 (*q*); 33.2 (*s*); 30.1 (*d*); 21.7 (*q*); 18.3 (*t*); 17.3 (*t*); 17.2 (*q*); 16.4 (*q*). ^{13}C-NMR (minor isomer): 60.1 (*d*); 54.6 (*d*); 53.2 (*d*); 46.8 (*t*); 42.1 (*t*); 40.7 (*t*); 38.4 (*s*); 36.8 (*t*); 33.6 (*q*); 33.3 (*s*); 32.9 (*d*); 22.1 (*t*); 21.9 (*q*); 21.1 (*q*); 18.8 (*t*); 15.9 (*q*). MS (minor isomer): 236 (8, M^+), 221 (21), 177 (9), 149 (12), 135 (13), 123 (100), 121 (22), 109 (46), 95

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[32]) For the 60-MHz ^{1}H-NMR analysis of a mixture of three isomers, see [32b].

[33]) A chromatographically enriched 75:25 mixture of stereoisomers exhibited $[\alpha]_D^{20} = -0.67$ ($c = 1.93$, $CHCl_3$).

(51), 81 (44), 69 (50), 67 (29), 55 (30), 41 (28). MS (major isomer): 236 (3, M^+), 221 (22), 177 (11), 149 (15), 136 (21), 123 (100), 121 (32), 109 (65), 95 (62), 81 (57), 69 (59), 67 (37), 55 (35), 41 (32).

*(−)-2-[(1*S*,2*R*,4a*S*,8a*R*)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]acetaldehyde* ((−)-**14a**). Epoxide (+)-**13** (80 mg, 0.315 mmol) in toluene (1 ml) was added to a mixture of $Al(O^iPr)_3$ (64.3 mg, 0.315 mmol) and $AlCl_3$ (42 mg, 0.31 mmol) in refluxing toluene (5 ml). After 3 h, the cold soln. was hydrolyzed with H_2O. Extraction afforded after drying (Na_2SO_4), concentration, and CC (SiO_2; cyclohexane/AcOEt 99:1 to 9:1) pure (−)-**14a** (25% yield). $[\alpha]_D^{20} = -4.03$ ($c = 0.1$, $CHCl_3$). IR: 2922, 2868, 2849, 1726, 1459, 1377, 1203, 1084, 1029, 975, 747, 699. ^{1}H-NMR: 9.77 (*t*, *J* = 1, 1 H); 1.79–0.92 (*m*, 15 H); 0.87 (*s*, 3 H); 0.85 (*d*, *J* = 7, 3 H); 0.82 (*s*, 3 H); 0.80 (*s*, 3 H). ^{13}C-NMR: 203.4 (*d*); 54.9 (*d*); 51.3 (*d*); 44.0 (*t*); 41.9 (*t*); 39.4 (*t*); 37.6 (*s*); 36.5 (*t*); 33.6 (*d*); 33.4 (*q*); 33.3 (*s*); 21.8 (*t*); 21.7 (*q*); 21.2 (*q*); 18.7 (*t*); 14.5 (*q*). MS: 236 (12, M^+), 221 (33), 203 (9), 192 (29), 177 (15), 137 (8), 123 (100), 109 (25), 107 (13), 95 (33), 93 (12), 81 (31), 69 (31), 67 (21), 55 (29), 41 (28). Vaguely woody, cedar.

*(+)-2-[(1*S*,2*R*,4a*S*,8a*R*)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]ethanol* ((+)-**15a**). Isolated in 18% yield during the purification of (−)-**14a**. Also obtained in 94% yield by reduction of (−)-**14a** with $LiAlH_4$ (1.0 mol-equiv.) in THF. $[\alpha]_D^{20} = +6.83$ ($c = 0.31$, $CHCl_3$). IR: 3323, 2921, 2852, 1457, 1384, 1198, 1048, 1038, 1016, 814, 721, 704, 626. ^{1}H-NMR: 3.65–3.60 (*m*, 1 H); 3.52–3.47 (*m*, 1 H); 2.32 (br. *s*, OH); 1.77–0.93 (*m*, 15 H); 0.86 (*d*, *J* = 7, 3 H); 0.84 (*s*, 3 H); 0.81 (*s*, 3 H); 0.79 (*s*, 3 H). ^{13}C-NMR: 64.6 (*t*); 55.2 (*d*); 53.9 (*d*); 42.2 (*t*); 39.0 (*t*); 38.0 (*s*); 36.8 (*t*); 34.2 (*d*); 33.4 (*q*); 33.3 (*s*); 32.4 (*t*); 21.8 (*t*); 21.8 (*q*); 21.1 (*q*); 18.7 (*t*); 14.2 (*q*). MS: 238 (19, M^+), 223 (21), 138 (9), 123 (100), 109 (29), 95 (30), 81 (29), 69 (28), 67 (19), 55 (22), 41 (20).

*(+)-2-[(1*S*,2*S*,4a*S*,8a*R*)-Decahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]ethanol* ((+)-**15b**). Obtained in 95% yield from (−)-**14b** [13], according to the $LiAlH_4$ procedure used for (+)-**15a**. $[\alpha]_D^{20} = +28.6$ ($c = 1.2$, $CHCl_3$). IR: 3235, 2991, 2926, 2901, 2867, 2843, 1454, 1439, 1383, 1366, 1193, 1052, 1023, 1000, 962, 934, 916, 861. ^{1}H-NMR: 3.72–3.62 (*m*, 1 H); 3.59–3.51 (*m*, 1 H); 1.85–1.79 (*m*, 1 H); 1.72–1.32 (*m*, 13 H); 1.25–1.19 (*m*, 1 H); 1.14 (*dt*, *J* = 4.4, 14.2, 1 H); 0.93 (*d*, *J* = 7, 3 H); 0.85 (*s*, 6 H); 8.81 (*s*, 3 H). ^{13}C-NMR: 62.3 (*t*); 56.7 (*d*); 49.8 (*d*); 42.1 (*t*); 39.5 (*t*); 38.1 (*s*); 34.7 (*t*); 33.5 (*q*); 33.3 (*s*); 30.3 (*d*); 29.3 (*t*); 21.6 (*q*); 18.4 (*t*); 17.4 (*t*); 16.5 (*q*); 15.6 (*q*). MS: 238 (22, M^+), 223 (27), 138 (10), 123 (100), 109 (34), 95 (33), 81 (29), 69 (25), 67 (19), 55 (17), 41 (15).

*(+)-(4a*S*,8a*S*)-3,4,4a,5,6,7,8,8a-Octahydro-2,5,5,8a-tetramethylnaphthalene-1-carbaldehyde* ((+)-**16a**). A soln. of SO_2Cl_2 (138 mg, 1.007 mmol) in CH_2Cl_2 (2.5 ml) was added dropwise to a soln. of (+)-**6a** (75:25 (1*S*)/(1*R*) mixture; 260 mg, 0.959 mmol) in CH_2Cl_2 (2.5 ml) at 0°. The mixture was then heated at 40° for 2 h. Since only the minor stereoisomer reacted, the cold mixture was poured into H_2O (20 ml) and extracted with CH_2Cl_2. The org. phase was washed with sat. aq. $NaHCO_3$ and then brine, dried (Na_2SO_4), and concentrated. The residue[34]) (320 mg) was dissolved in DMF (5 ml) and heated at 150° for 58 h in the presence of LiCl (53 mg, 1.25 mmol). The cold mixture was diluted with H_2O (20 ml) and then extracted with AcOEt. The org. phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by CC (SiO_2; cyclohexane/AcOEt 99:1) to afford pure (+)-**16a** (6% yield). $[\alpha]_D^{20} = +52.0$ ($c = 1.0$, $CHCl_3$). For data, see [13c][21][27][45][46c][47].

*(+)-1-[(4a*S*,8a*S*)-3,4,4a,5,6,7,8,8a-Octahydro-2,5,5,8a-tetramethylnaphthalen-1-yl]ethanone* ((+)-**16c**). Obtained in 90% yield according to the procedure reported for the racemate [50]. Alternatively, a soln. of (2*R*,4a*S*,8a*S*)-1-ethynyldecahydro-2,5,5,8a-tetramethylnaphthalen-1-ol [20][24] (56:44 mix-

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[34]) A purified (CC (SiO_2)) sample of the intermediate single α-chloroaldehyde of undetermined configuration exhibited the following anal. data. $[\alpha]_D^{20} = -31.6$ ($c = 0.9$, $CHCl_3$). IR: 2955, 2938, 2882, 1742, 1464, 1392, 1210, 1120, 1032, 986, 823, 750. ^{1}H-NMR: 9.41 (*s*, 1 H); 2.49 (*quint.*, *J* = 6.5, 1 H); 2.17 (*tt*, *J* = 5.7, 13, 1 H); 1.85 (*dt*, *J* = 3.3, 12.1, 1 H); 1.75 (*dt*, *J* = 3.3, 13, 1 H); 1.68–1.35 (*m*, 7 H); 1.30–1.22 (*m*, 2 H); 1.20 (*s*, 3 H); 1.19 (*d*, *J* = 8, 3 H); 0.91 (*s*, 3 H); 0.85 (*s*, 3 H). ^{13}C-NMR: 192.2 (*d*); 87.9 (*s*); 47.2 (*d*); 42.0 (*s*); 41.3 (*t*); 37.1 (*d*); 35.0 (*t*); 33.6 (*q*); 33.3 (*s*); 28.3 (*t*); 21.4 (*q*); 18.9 (2*q*); 18.0 (*t*); 17.2 (*t*). MS: 256 (5, M^+), 241 (9), 220 (7), 205 (6), 191 (27), 177 (7), 151 (9), 149 (9), 138 (17), 135 (14), 123 (100), 121 (19), 109 (40), 107 (23), 105 (22), 95 (57), 93 (18), 91 (19), 81 (37), 69 (60), 67 (19), 55 (24), 41 (27); 20% yield, 66% yield based on recovered (+)-**6a**.

ture, 1.5 g, 6.44 mmol)[35]) in 99% HCOOH (11.07 ml, 290 mmol) was heated at 110° for 0.5 h. The cold mixture was poured onto ice and then extracted with Et_2O (3 × 80 ml). The org. phase was washed with sat. aq. $NaHCO_3$ and brine, dried (Na_2SO_4), concentrated, and then purified by CC (SiO_2; cyclohexane/AcOEt 99:1) to afford (+)-**16c** (79% yield), contaminated with 4% of the deconjugated isomer [51b]. $[\alpha]_D^{20} = 74.6$ ($c = 1.1$, $CHCl_3$). IR: 2924, 2866, 2847, 1687, 1457, 1442, 1428, 1388, 1376, 1366, 1348, 1251, 1195, 1167, 1060, 1050, 976, 946, 860, 692, 610. ^{1}H-NMR: 2.26 (*s*, 3 H); 2.05 (*dd*, *J* = 4.4, 8.8, 2 H); 1.73–1.57 (*m*, 2 H); 1.54 (*s*, 3 H); 1.53–1.41 (*m*, 5 H); 1.32–1.19 (*m*, 2 H); 1.18 (*s*, 3 H); 0.90 (*s*, 3 H); 0.85 (*s*, 3 H). ^{13}C-NMR: 209.9 (*s*); 147.1 (*s*); 127.2 (*s*); 50.6 (*d*); 41.7 (*t*); 37.4 (*t*); 37.2 (*s*); 34.0 (*q*); 33.3 (*q*); 33.2 (*s*); 32.1 (*t*); 21.5 (*q*); 20.6 (*q*); 20.3 (*q*); 18.7 (*t*); 18.6 (*t*). MS: 234 (4, M^+), 219 (15), 191 (100), 149 (22), 147 (10), 137 (10), 135 (16), 123 (15), 121 (50), 109 (29), 107 (15), 105 (10), 95 (47), 93 (10), 91 (15), 79 (10), 69 (15), 55 (10), 43 (31), 41 (12). Woody, dry, paper, weak.

*(+)-(4a*S*,8a*S*)-8-Ethynyl-1,2,3,4,4a,5,6,8a-octahydro-4,4,7,8a-tetramethylnaphthalene* ((+)-**17**). $SOCl_2$ (65 µl, 106 mg, 0.894 mmol) was added dropwise to a soln. of (1*R*,2*R*,4a*S*,8a*S*)-1-ethynyldecahydro-2,5,5,8a-tetramethylnaphthalen-1-ol (56:44 mixture of diastereoisomers [20][24]; 190 mg, 0.813 mmol) in pyridine (3 ml) at −40°. After 30 min, H_2O and then Et_2O were added. The temp. was adjusted to 20°, and the mixture was extracted. The org. phase was washed with H_2O and brine, dried (Na_2SO_4), then concentrated. Purification by CC (SiO_2; cyclohexane/AcOEt 99:1 to 98:2) afforded (+)-**17** (40% yield[36])). $[\alpha]_D^{20} = +107.8$ ($c = 0.4$, $CHCl_3$). IR: 3310, 2923, 2865, 2851, 2086, 1457, 1441, 1426,

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[35]) (2*R*,4a*S*,8a*S*)-1-Ethynyldecahydro-2,5,5,8a-tetramethylnaphthalen-1-ol: ^{1}H-NMR: 2.53 (*s*, 1 H); 1.89–1.83 (*m*, 1 H); 1.74 (*dt*, *J* = 3.6, 12.3, 2 H); 1.65–1.16 (*m*, 10 H); 1.02 (*d*, *J* = 7, 3 H); 0.99 (*s*, 3 H); 0.87 (*s*, 3 H); 0.83 (*s*, 3 H). ^{13}C-NMR: 84.5 (*s*); 80.8 (*s*); 76.2 (*d*); 48.8 (*d*); 42.8 (*s*); 41.7 (*t*); 36.1 (*d*); 33.5 (*t*); 33.3 (*q*); 33.1 (*s*); 31.9 (*t*); 21.7 (*q*); 21.1 (*t*); 18.6 (*t*); 16.4 (*q*); 13.5 (*q*). MS: 234 (0, M^+), 219 (18), 201 (15), 191 (12), 177 (18), 163 (27), 159 (13), 151 (17), 149 (21), 145 (14), 137 (23), 135 (26), 123 (100), 121 (26), 119 (14), 109 (43), 107 (30), 105 (16), 97 (25), 95 (57), 93 (21), 91 (21), 82 (60), 79 28), 69 (40), 67 (33), 55 (42), 53 (27), 43 (22), 41 (41). (1*S*,2*R*,4a*S*,8a*S*)-1-Ethynyldecahydro-2,5,5,8a-tetramethylnaphthalen-1-ol: ^{1}H-NMR: 2.39 (*s*, 1 H); 1.94–1.86 (*m*, 1 H); 1.76 (*s*, OH); 1.63–1.46 (*m*, 7 H); 1.39–1.18 (*m*, 4 H); 1.11 (*s*, 3 H); 1.04 (*d*, *J* = 7, 3 H); 0.87 (*s*, 3 H); 0.82 (*s*, 3 H). ^{13}C-NMR: 86.2 (*s*); 78.1 (*s*); 73.3 (*d*); 44.1 (*d*); 42.0 (*s*); 41.9 (*t*); 35.6 (*d*); 33.3 (*q*); 33.2 (*s*); 32.7 (*t*); 29.7 (*t*); 21.8 (*q*); 21.1 (*t*); 18.6 (*t*); 17.3 (*q*); 16.9 (*q*). MS: 234 (2, M^+), 219 (17), 201 (19), 191 (12), 177 (20), 163 (30), 159 (14), 151 (19), 149 (14), 137 (13), 135 (13), 123 (100), 121 (27), 119 (16), 110 (32), 109 (43), 107 (29), 105 (20), 97 (27), 95 (56), 93 (14), 91 (14), 82 (60), 79 (30), 77 (19), 69 (42), 67 (34), 55 (44), 53 (27), 41 (42).

[36]) The isolated main side product (43% yield) was an inseparable 75:25 mixture of (4a*R*,6*R*,8a*S*)-5-[(*E*)-2-chloroethenyl]decahydro-1,1,4a,6-tetramethylnaphthalene. This compound became the unique reaction product (78% yield), when this transformation was performed at 20°. Anal. data deduced from the mixture of diastereoisomers: IR: 2926, 2869, 2848, 1946, 1454, 1388, 1376, 1365, 1334, 1229, 1204, 1191, 1127, 1103, 1050, 1027, 994, 979, 947, 927, 847, 814, 785, 754, 727, 693, 669, 658, 634. ^{1}H-NMR (major): 6.09 (*d*, *J* = 2.5, 1 H); 2.44–2.38 (*m*, 1 H); 1.97–1.92 (*m*, 1 H); 1.70–1.60 (*m*, 2 H); 1.55–1.38 (*m*, 8 H); 1.15 (*s*, 3 H); 0.96 (*d*, *J* = 6.3, 3 H); 0.85 (*s*, 6 H). ^{13}C-NMR: 194.4 (*s*); 132.8 (*s*); 90.3 (*d*); 53.8 (*d*); 42.1 (*t*); 38.9 (*s*); 38.7 (*t*); 36.6 (*t*); 33.8 (*s*); 33.1 (*q*); 31.0 (*d*); 21.8 (*t*); 21.7 (*q*); 20.3 (*q*); 19.7 (*q*); 18.8 (*t*). MS: 254 (7, M^+), 252 (20), 237 (11), 217 (31), 201 (20), 182 (16), 175 (16), 173 (10), 161 (21), 159 (13), 155 (14), 150 (38), 147 (38), 145 (24), 141 (22), 135 (100), 133 (23), 131 (30), 129 (13), 123 (53), 121 (33), 119 (44), 117 (23), 115 (22), 109 (28), 107 (38), 105 (62), 103 (11), 97 (20), 95 (33), 93 (31), 91 (62), 81 (32), 79 (33), 77 (39), 69 (59), 67 (25), 65 (21), 55 (37), 53 (15), 41 (43). ^{1}H-NMR (minor): 6.04 (*d*, *J* = 2.7, 1 H); 2.37–2.33 (*m*, 1 H); 2.16–2.12 (*m*, 1 H); 1.85–1.77 (*m*, 2 H); 1.55–1.38 (*m*, 8 H); 1.10 (*s*, 3 H); 0.97 (*d*, *J* = 6.3, 3 H); 0.89 (*s*, 3 H); 0.87 (*s*, 3 H). ^{13}C-NMR: 194.7 (*s*); 132.9 (*s*); 90.1 (*d*); 53.7 (*d*); 42.0 (*t*); 39.0 (*s*); 38.8 (*t*); 36.6 (*t*); 33.9 (*s*); 33.4 (*q*); 31.2 (*d*); 21.0 (*t*); 21.6 (*q*); 20.2 (*q*); 19.7 (*q*); 18.6 (*t*). MS: 254 (8, M^+), 252 (22), 237 (11), 217 (33), 201 (17), 182 (16), 175 (16), 173 (10), 161 (20), 159 (13), 155 (14), 150 (39), 147 (39), 145 (23), 141 (21), 135 (100), 133 (23), 131 (29), 129 (16), 123 (56), 121 (32), 119 (39), 117 (20), 115 (22), 109 (26), 107 (38), 105 (59), 103 (11), 97 (20), 95 (32), 93 (31), 91 (57), 81 (31), 79 (32), 77 (40), 69 (57), 67 (23), 65 (20), 55 (33), 53 (15), 41 (40). Further treatment (^{t}BuOK, ^{t}BuOH, 82° [58]; 94% yield) afforded (+)-**9a**.

1388, 1374, 1243, 1231, 1205, 1029, 1013, 975, 861, 836, 729, 630. ^{1}H-NMR: 3.04 (br. *s*, 1 H); 2.12 (*dt*, *J* = 6.5, 13.1, 1 H); 2.02 (*ddt*, *J* = 1.4, 3.1, 13.1, 1 H); 1.85 (*s*, 3 H); 1.69 (*ddt*, *J* = 1.9, 6.7, 13.1, 1 H); 1.61 (*tq*, *J* = 3.4, 13.7, 1 H); 1.56 (*s*, 1 H); 1.50 (*dquint.*, *J* = 3.4, 14, 1 H); 1.43 (*s*, 1 H); 1.44–1.39 (*m*, 2 H); 1.16 (*dt*, *J* = 4.0, 13.3, 1 H); 1.09 (*dd*, *J* = 2.0, 12.7, 1 H); 1.06 (*s*, 3 H); 0.89 (*s*, 3 H); 0.84 (*s*, 3 H). ^{13}C-NMR: 141.6 (*s*); 126.8 (*s*); 82.1 (*s*); 80.4 (*d*); 50.9 (*d*); 41.8 (*t*); 38.2 (*t*); 37.0 (*s*); 33.3 (*s*); 33.1 (*t*); 33.1 (*q*); 22.1 (*q*); 21.5 (*q*); 20.5 (*q*); 19.1 (*t*); 18.4 (*t*). MS: 216 (58, M^+), 201 (100), 173 (16), 159 (19), 145 (41), 131 (74), 129 (19), 128 (18), 119 (99), 117 (17), 115 (22), 109 (14), 107 (10), 105 (51), 103 (10), 91 (40), 81 (11), 79 (14), 77 (20), 69 (24), 55 (12), 41 (19).

*(+)-(1*S*,2*R*,4a*S*,8a*S*)-Octahydro-2,5,5,8a-tetramethyl-2*H*-spiro[naphthalene-1,2′-oxirane]* ((+)-**18a**). Obtained in 70% yield from (−)-**8a** as a 85:15 mixture (+)-**18a**/**18b** according to the procedure used for (+)-**13**. Anal. pure material was obtained in 27% yield after purification by CC (SiO_2; cyclohexane/AcOEt 99:1). $[\alpha]_D^{20} = +64.3$ (*c* = 1.1, $CHCl_3$). IR: 3054, 2933, 2868, 1460, 1387, 1378, 1364, 1346, 1232, 1212, 1186, 1149, 1098, 1047, 1024, 976, 969, 940, 911, 899, 881, 835, 822, 768, 731, 681, 604. ^{1}H-NMR: 2.67 (*d*, *J* = 4.2, 1 H); 2.58 (*d*, *J* = 4.2, 1 H); 2.21–2.16 (*m*, 1 H); 1.70–1.65 (*m*, 2 H); 1.57 (*tq*, *J* = 3.5, 13.7, 1 H); 1.48–1.40 (*m*, 2 H); 1.33–1.24 (*m*, 4 H); 1.14 (*dt*, *J* = 4, 13.7, 1 H); 1.08 (*s*, 3 H); 1.06 (*dt*, *J* = 4, 12.4, 1 H); 0.86 (*s*, 3 H); 0.82 (*s*, 3 H); 0.67 (*d*, *J* = 6.8, 3 H). ^{13}C-NMR: 66.9 (*s*); 50.0 (*d*); 45.8 (*t*); 41.5 (*t*); 38.0 (*s*); 33.4 (*s*); 33.4 (*t*); 32.8 (*q*); 31.2 (*t*); 29.7 (*d*); 22.1 (*t*); 21.7 (*q*); 19.6 (*q*); 18.3 (*t*); 15.0 (*q*). MS: 222 (40, M^+), 207 (100), 191 (27), 177 (66), 175 (38), 165 (20), 153 (59), 151 (38), 149 (21), 147 (35), 138 (32), 135 (30), 133 (19), 123 (90), 121 (58), 119 (30), 109 (44), 107 (57), 105 (35), 98 (30), 95 (54), 93 (45), 91 (40), 84 (38), 81 (66), 79 (40), 77 (26), 69 (48), 67 (40), 55 (48), 53 (20), 43 (22), 41 (54).

*(1*R*,2*R*,4a*S*,8a*S*)-Octahydro-2,5,5,8a-tetramethyl-2*H*-spiro[naphthalene-1,2′-oxirane]* (**18b**). AcOOH (39% in AcOH; 143 mg, 0.125 ml, 0.74 mmol) was added dropwise to a soln. of (−)-**8b** (101 mg, 0.49 mmol) and AcONa (19 mg, 0.233 mmol) in CH_2Cl_2 (5 ml) at 0°. After 20 min at 0°, and 1 h at 20°, the fully converted mixture was diluted with CH_2Cl_2 (10 ml), washed with sat. aq. $NaHCO_3$, brine, and H_2O, dried (Na_2SO_4), and concentrated to afford a 55:45 mixture (+)-**18a**/**18b** (91% yield). IR: 2921, 2852, 1460, 1378, 1364, 1346, 1232, 1212, 1186, 1048, 1025, 975, 940, 899, 823, 732, 683. Deduced from the mixture: ^{1}H-NMR: 2.89 (*d*, *J* = 3.8, 1 H); 2.59 (*d*, *J* = 4.0, 1 H); 1.88 (*dq*, *J* = 3.9, 13.0, 1 H); 1.70–1.65 (*m*, 2 H); 1.57 (*tq*, *J* = 3.5, 13.7, 1 H); 1.48–1.40 (*m*, 2 H); 1.33–1.24 (*m*, 4 H); 1.14 (*dt*, *J* = 4, 13.7, 1 H); 1.11 (*s*, 3 H); 1.06 (*dt*, *J* = 4, 12.4, 1 H); 0.87 (*s*, 3 H); 0.85 (*s*, 3 H); 0.68 (*d*, *J* = 6.1, 3 H). ^{13}C-NMR: 68.5 (*s*); 53.1 (*d*); 46.0 (*t*); 42.3 (*t*); 38.5 (*s*); 34.5 (*t*); 33.6 (*s*); 33.2 (*d*); 32.6 (*q*); 31.2 (*t*); 22.1 (*t*); 22.0 (*q*); 18.4 (*t*); 17.5 (*q*); 15.0 (*q*). MS: 222 (31, M^+), 207 (84), 204 (8), 190 (19), 177 (52), 175 (25), 165 (14), 161 (10), 153 (40), 151 (29), 149 (18), 147 (27), 138 (42), 135 (36), 133 (20), 123 (100), 122 (32), 121 (50), 119 (27), 109 (55), 107 (51), 105 (30), 98 (25), 95 (64), 93 (43), 91 (37), 84 (45), 81 (70), 79 (40), 77 (22), 69 (60), 67 (42), 55 (49), 43 (21), 41 (51), 39 (16). Woody, straw, dusty, earthy.

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