130. Syntheses of (±)- and Enantiomerically Pure (+)-Longifolene and of (±)- and Enantiomerically Pure (+)-Sativene by an Intramolecular *de Mayo* Reaction

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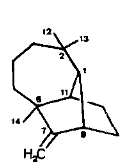
Summary

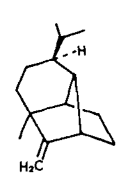
Starting from 2-cyclopentenoyl chloride ((*RS*)- or (*S*)-**8**), the racemic as well as the enantiomerically pure (+)-sesquiterpenes longifolene ((±)- and (+)-**1**, resp.) and sativene ((±)- and (+)-**2**, resp.) were synthesized efficiently by a sequence of nine and ten steps, respectively. The key sequence **10**→**16**→**3** is the first strategic application of an intramolecular photoaddition/*retro*-aldolization sequence (intramolecular *de Mayo* reaction) in organic synthesis.

Introduction. – (+)-Longifolene, known to occur in higher plants, mainly *Gymnospermae* [1][1]) has been assigned structure (+)-**1** on the basis of chemical [2] and X-ray [3] evidence. The less abundant sesquiterpene (+)-sativene, isolated from the turpentine of different *Abies species* exhibits the related structure (+)-**2** [6][2]). During the past 20 years, the intricate carbon network of longifolene has served as a challenging test case for synthetic methodology and planning [8]. More recently, sativene has received considerable attention in organic synthesis [8e] [9].

We wish to present here in detail the selective syntheses of both longifolene ((±)- and (+)-**1**) and sativene ((±)- and (+)-**2**), described previously in preliminary form[3]).



(+)-**1**



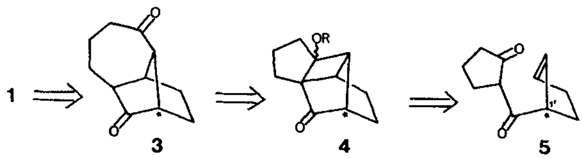
(+)-**2**

[1]) The antipode (−)-longifolene has been found in liverworts [4] and together with (−)-sativene in both *Helminthosporium sativum* and *H. victoriae* [5]. For the biosynthesis of longifolene and sativene see [5]. The numbering of **1** corresponds to [2] and is used in this discussion for all intermediates possessing the longifolene skeleton. The synthetic intermediates are named according to the IUPAC rules in the *Exper. Part.*

[2]) (−)-Sativene ((−)-**2**) was first isolated from *Helminthosporium sativum* and identified by conversion of (+)-longifolene to (+)-sativene [7].

[3]) Syntheses of: (±)-longifolene [8d], (+)-longifolene and (+)-sativene [8e] [11].

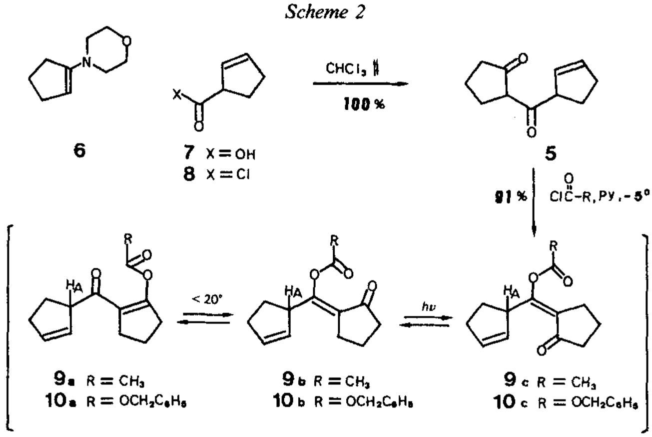
Scheme 1



Our underlying strategy *(Scheme 1)* centered on the photoaddition/*retro*-aldolization sequence[4]) **5**→**4**→**3**. This constitutes a formal annulating two-carbon ring expansion exploiting the as yet unrecognized potential of the intramolecular *de Mayo* reaction.

Preparation and *O*-Acylation of 1,3-Dione (±)-5 *(Scheme 2)*. – To implement this plan, enamine **6** was acylated with acyl chloride (±)-**8** under the usual conditions [12] to give, upon aqueous workup, 1,3-diketone (±)-**5** in virtually quantitative yield. Irradiation of (±)-**5** (125-W medium-pressure Hg-lamp, *Pyrex* filter, MeCN or cyclohexane for 12 to 100 h), however, did not yield the expected 1,5-dione (±)-**3** but rather unchanged (±)-**5** and/or intractable decomposition products[5]).

Scheme 2



In view of the former *de Mayo* reactions employing enol acetates derived from cyclic 1,3-diones [10], (±)-**5** was treated with AcCl/pyridine at 0° (thus avoiding *C*-acylation [14]). No attempt was made to establish rigorously the ratio of isomers (each racemic) resulting from *O*-acylation of the 'cyclic' (→**9a**) or 'acyclic' carbonyl group (→**9b**, **9c**) of **5**. This is of little relevance since rapid equilibration **9a**⇄**9b** is to be expected by thermal intramolecular [1,5]-acyl shift [15]. Indeed, IR absorptions at 1667 (minor) and 1722 cm^{-1} (major) indicate the presence of 'acyclic' (**9a**) and 'cyclic' (**9b**, **9c**)

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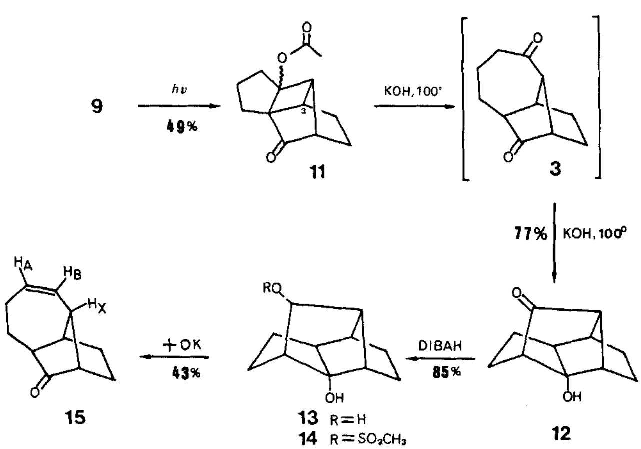
[4]) Reviews: bimolecular *de Mayo* reaction [10]; intramolecular photoaddition/cyclobutane-fragmentation sequence [11].

[5]) This lack of reactivity parallels the previous observation that only enol **ii** but not enol **iii** undergoes [2 + 2]-photoaddition to alkenes [13].

ketones [15c]. Moreover, the ^{1}H-NMR signals (assigned to H_A) at δ 4.05 and 3.66 ppm integrate for 0.38 H/0.62 H at +30° *vs.* 0.2 H/0.8 H at −50°, consistent with a displacement of the equilibrium **9a**⇄**9b** with change in temperature. No further attention was paid to the possible presence of the (*E*)-isomer **9c** since light-induced (*E*/*Z*)-isomerization **9c**⇄**9b** permits ready equilibration **9a**⇄**9b**⇄**9c** [15b, c]. Thus, on irradiation of the enol acetate mixture **9**, the photoaddition should involve selectively **9a** (leading to **11**) owing to the endocyclic nature of the conjugated olefinic bond and its favorable position with respect to the isolated double bond [11].

Construction of the Longifolene Skeleton 15 from Enol Acetates 9 *(Scheme 3)*. – Irradiation of the crude enol acetates **9** (racemic) in cyclohexane through *Pyrex* by means of a Hg high-pressure lamp afforded regioselectively **11** as a 3:1 mixture of racemic-epimers in 39% overall yield from dione (±)-**5**. The acetoxy/carbonyl disposi-

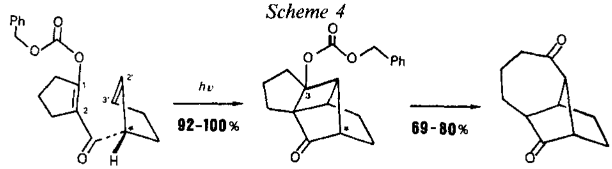
Scheme 3



tion in the separated (by chromatography) epimers **11** was tentatively assigned to be *cis* in the (less strained) major and *trans* in the minor product on the basis of their IR-carbonyl bands at 1735 and 1742 cm^{-1}, respectively [11]. Since subsequent ester cleavage/*retro*-aldolization **11**→(±)-**3** will destroy the chirality at C(3), the synthetic work was carried on with the unseparated mixture **11**. Saponification with 4% KOH in dioxane/H_2O 1:1 at 100° for 20 min, however, gave directly aldol **12** in 77% yield; presumably the desired dione (±)-**3** had been formed but underwent spontaneous cyclization to the stable aldol **12** under the basic saponification conditions. Restoration of the longifolene skeleton could be achieved in 37% yield by the sequence carbonyl reduction/regioselective *O*-mesylation/base-induced fragmentation **12**→**13**→**14**→**15**. Nevertheless, these additional transformations and the problem of achieving regioselective geminal dimethylation of olefin **15** would impose an unacceptable number of steps for the synthesis of (±)-longifolene ((±)-**1**).

Efficient Generation of the Dioxygenated Longifolene Skeleton (±)-3 *(Schemes 2 and 4)*. – Accordingly, we returned to our original plan. To avoide the undesired aldolization (±)-**3**→**12**, dione (±)-**5** was first *O*-acylated with benzyl chloroformate/py-

Scheme 4



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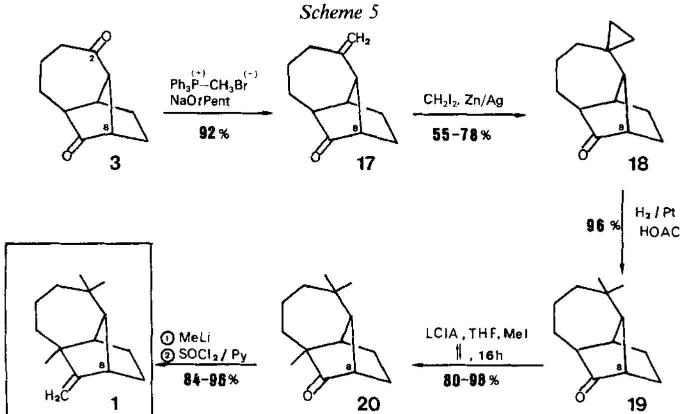
ridine to give, after crystallization, an enol carbonate (±)-**10**[6]), m.p. 60.5–62.5° in 76% yield.

The IR spectrum of the crystalline (±)-**10** (KBr) shows a strong band at 1720 cm^{-1} consistent with structure (±)-**10b** or (±)-**10c**, whereas in solution (CCl_4) the less intense band at 1720 cm^{-1} is accompanied by a new band at 1670 cm^{-1}. Thus, in analogy to the above-mentioned enol acetates, (±)-**10b** seems to equilibrate rapidly with (±)-**10a** in solution as indicated also by the *m* in the ^{1}H-NMR (H_A) at δ 3.63 and 4.06 ppm which integrate for 0.4 H/0.64 H at +30° and for 0.35 H/0.7 H at −50°, respectively.

On irradiating a solution of crystalline (±)-**10**[6]) in cyclohexane (*Pyrex*, Hg high-pressure lamp), the expected photoaddition was complete within 2 h giving a 3:2 mixture (±)-**16**[7]) of 3-epimers in 92% yield. Thus, the photoconversion (±)-**10**→(±)-**16**[7]) is by far superior to the analogous transformation **9**→**11** in terms of rate and efficiency. It is, furthermore, worth noting that the striking regioselectivity of the photoaddition (±)-**10**→(±)-**16** which joins exclusively C(2) with C(3′) agrees perfectly with the 'rule of five' [16]. The separated (by chromatography) epimers of (±)-**16**[7]) show IR bands at 1738 (major) and 1741 cm^{-1} (minor) in analogy to the acetates **11**. Hydrogenolysis (H_2, 10% Pd/C) of the non-separated mixture (±)-**16**[7]) in AcOH resulted in clean *retro*-aldol cleavage to give, after crystallization, the expected 1,5-dione (±)-**3** in 80% yield. Accordingly, the complex skeleton of longifolene has been assembled starting from acyl chloride (±)-**8** by a sequence of four steps in 56% overall yield.

Conversion of the 1,5-Diketone (±)-3 into (±)-Longifolene ((±)-**1**, *Scheme 5*). – The remaining task merely involves selective functionalizations of the sterically differ-

Scheme 5



LCIA = lithium cyclohexylisopropylamide

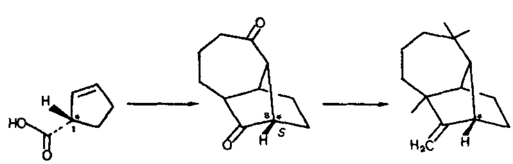
6) Enol carbonate (±)-**10** means the mixture of the possible isomers (±)-**10a**, (±)-**10b**, and (±)-**10c**; (−)-**10** is the mixture ([α] negative) of the corresponding antipodes.

7) Carbonate (±)-**16** means the 3:2 mixture of the racemic and (1*R*)-**16** of the optically active 3-epimers.

entiable CO-groups of (±)-**3**. First the less hindered C(2)-carbonyl was converted to a geminal dimethyl group as follows. Regioselective *Wittig* reaction of (±)-**3** with an excess of methyltriphenylphosphonium bromide/sodium *t*-pentylate in toluene [17] gave exclusively methylidene ketone (±)-**17** in 88% yield. Modified *Simmons-Smith* reaction of (±)-**17** using Zn/Ag and CH_2I_2 [18] furnished (±)-**18** (78% yield) which underwent regioselective cyclopropane hydrogenolysis [19] on stirring under H_2 (1 atm)/Pt in AcOH at room temperature. The resulting ketone (±)-**19** (96% yield) was identified by comparison with an authentic sample [8c]. The final transformations (±)-**19**→(±)-**1** rely on the procedure previously established in the laboratories of *Johnson* [8c] and *Corey* [8a]. Successive treatment of (±)-**19** with lithium cyclohexylisopropylamide at −78°→+60° and MeI in THF under reflux gave (±)-longicamphenylone ((±)-**20**) in 92% yield. Addition of an excess of MeLi to (±)-**20** followed by dehydration with $SOCl_2$/pyridine at 0° furnished (±)-longifolene ((±)-**1**) in 78% yield. Synthetic (±)-**1** shows IR, ^{1}H-NMR, ^{13}C-NMR, and MS identical to those of the naturally occurring (+)-longifolene.

Total Synthesis of (+)-Longifolene ((+)-**1**; *Schemes 2* and *4–6*). – After successful completion of the synthesis of (±)-longifolene, we envisaged the preparation of the enantiomerically pure sesquiterpene (+)-**1** based on the same strategic concept. The approach (−)-**7** (*S*)→(+)-**3** (8*S*)→(+)-**1** (8*S*) showed considerable promise because of the following features: 1) In the critical step **10**→**16**, one chiral center induces effi-

Scheme 6



(−)-**7** (*S*) (+)-**3** (+)-**1**

ciently the relative configuration of the other relevant centers. 2) This first center may be provided starting from (−)-**7** (*S*) previously obtained from (±)-**7** by crystallization of its (α-phenethyl)amine salt [20]. However, one potential problem concerns maintaining the configurational integrity of this particular center throughout the transformation (−)-**7**→(+)-**3** although the presumed crystallinity of (+)-**3** should facilitate its purification. Accordingly, epimerization was minimized by employing mild reaction conditions.

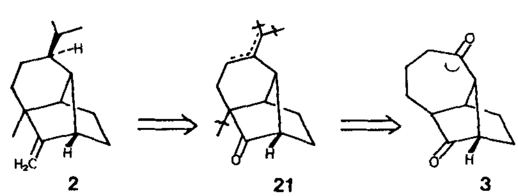
Enantiomerically enriched (95%) acid (−)-**7** (*S*) was treated with an excess of oxalyl chloride in CH_2Cl_2 at 0° to +25° to afford, after distillation, acyl chloride (*S*)-**8** (85% yield). Acylation of enamine **6** with (*S*)-**8** at 25° followed by hydrolysis furnished the dione (−)-**5** which was directly *O*-acylated to give the (*S*)-enol carbonate (−)-**10**[6]) in 91% yield. Following the above procedures, irradiation of (−)-**10** and subsequent hydrogenolysis of crude (1*R*)-**16**[7]) furnished, after chromatography, tricyclic dione (+)-**3** ($[\alpha]_D^{25}$ = +112°) in 96% yield from (−)-**10**; no impurity was visible in the ^{1}H-NMR spectrum. Successive recrystallizations until m.p. and optical rotation remained constant gave (+)-**3**, m.p. 59–60°, $[\alpha]_D^{25}$ = +133° (54% yield from (−)-**10**), which we presumed to be 100% enantiomerically pure. On this basis, we conclude that the enantiomeric purity (*e.e.*) of crude (+)-**3** amounts to 85% which indicates that only minor epimerization has occurred during the conversion (−)-**7** to (+)-**3**. Our assignment of high enantiomeric purity to the crystalline key intermediate (+)-**3** was confirmed by its conversion to crystalline (−)-longicamphenylone ((−)-**20**) *via* the oily intermediates (+)-**17**, (+)-**18** and (−)-**19**. Recrystallized (−)-**20**, m.p. 49–50°, obtained in 80% yield from (−)-**19** was proven to be identical with a sample obtained from natural (+)-longifolene (mixed m.p., optical rotation). Final conversion of the CO group in (−)-**20** furnished (+)-longifolene ((+)-**1**), indistinguishable from the naturally occurring sesquiterpene.

In summary, (±)-longifolene ((±)-**1**) has been obtained from (±)-**8** in 26% overall yield by a sequence of nine steps. Starting from the enantiomerically enriched acyl chloride (*S*)-**8** the synthesis of (+)-longifolene was achieved in 16% overall yield. These results compare very favorably with former syntheses of longifolene [8a, b, c].

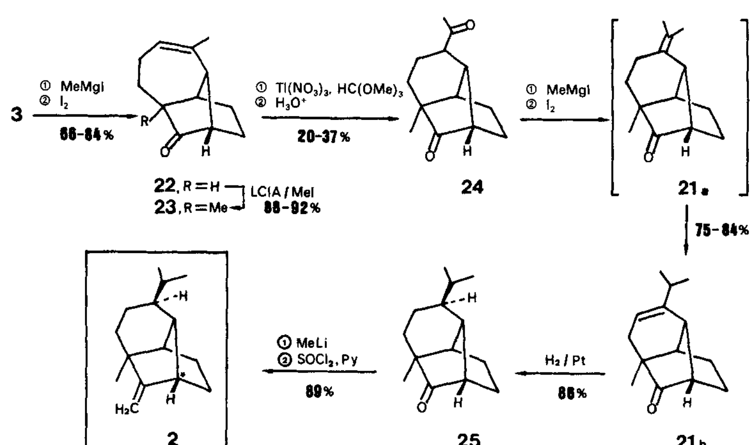
Syntheses of (±)- and Enantiomerically Pure (+)-Sativene. – We then considered the exploitation of the readily available, pure dione (+)-**3** as a key intermediate for the synthesis of (+)-sativene ((+)-**2**). This synthetic plan *(Scheme 7)* obviously requires a ring-contraction of the seven-membered ring, the introduction of three CH_3-groups (**3**→**21**), and hydrogenation of an exo- or endocyclic double bond. Hydrogen delivery from the convex face of the carbon skeleton of **21** should provide configurational control of the isopropyl-substituted center of **2**.

Along these lines a suitable reaction sequence *(Scheme 8)* was elaborated starting with dione (±)-**3**. Addition of MeMgI to the less hindered CO-group and subsequent

Scheme 7



Scheme 8



LCIA = lithium cyclohexylisopropylamide

I_2-catalyzed dehydration gave enone (±)-**22** (84% yield) which was α-methylated using lithium cyclohexyldiisopropylamide/MeI in THF affording (±)-**23** in 92% yield. Ring contraction of (±)-**23** using thallium trinitrate in the presence of trimethyl orthoformate [21] was disappointingly unsuccessful. However, when using $Tl(NO_3)_3$ supported on the montmorillonit clay *K-10* [22] and after acidic hydrolysis, we obtained the ring-contracted dione (±)-**24** in 37% yield as 3:1 epimer mixture. To convert this mixture into isomerically pure sativene, the missing CH_3-group was introduced by a *Grignard* addition. Dehydration of the resulting alcohol and concomitant olefin isomerization with I_2 in toluene at 110° led in 84% yield to a 6:92 mixture (±)-**21a**/(±)-**21b**. Hydrogenation of this mixture proceeded stereoselectively from the convex side to furnish the known isopropylketone (±)-**25** [9b] in 86% yield. Successive treatment of (±)-**25** with MeLi and $SOCl_2$/pyridine [9a] afforded pure (±)-sativene ((±)-**2**) in 89% yield (18% overall from (±)-**3**).

Starting from recrystallized (+)-**3**, the same reaction sequence provided optically pure (+)-sativene ((+)-**2**), identified by chiroptic and spectral (IR, ^{1}H-NMR, ^{13}C-NMR, MS) comparison with naturally occurring (−)-sativene. Given the fact that the synthetic intermediates as well as (+)-**2** are oils, no enantiomeric enrichment has been possible, and it thus follows that the key precursor (+)-**3**, $[\alpha]_D^{25} = +133°$, is virtually 100% enantiomerically pure as initially assumed.

Conclusion. – The expedient construction of the structurally complex sesquiterpenes (+)-longifolene ((+)-**1**) and (+)-sativene ((+)-**2**) with virtually complete control over several chiral centers exemplifies the synthetic potential of the tandem intramolecular photoaddition/cyclobutane fragmentation. It is felt that such processes and related ones will play an increasing role in organic synthesis[8]).

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Experimental Part

General. All reactions were carried out under Ar with magnetic stirring. Solvents were dried by distillation from drying agents: Et_2O (NaH), THF (K), toluene (Na), $CHCl_3$ (P_2O_5); pyridine was kept over molecular sieves (4 Å). The organolithium reagents were analyzed by *Gilman*'s titration [24]. Irradiations were carried out in cyclohexane *(Merck, Uvasol)* using a 250-ml *Pyrex* reaction vessel at 15° surrounding a medium-pressure mercury lamp *(Philips HPK 125)*. Workup denotes extraction with an org. solvent, washing of the org. phase with sat. aq. NaCl, drying over anh. $MgSO_4$, and removal of solvent by distillation *in vacuo* using a rotatory evaporator. Column chromatography was carried out on SiO_2 (*Merck*, Kieselgel *60*). GC: *Carlo-Erba-Fractovap* 2101, 1 atm N_2; glass columns (3 mm i.d. × 3 m), stationary phases on *Chromosorb W* (acid washed, 80/100 mesh); *a*: 5% *SE 30*; *b*: 10% *OV 225*; *c*: 3% *SP2330*; *d*: 3% *Apiezon L*; retention time in min (area-%). Melting points (m.p.) were determined on a *Kofler* hot stage and are uncorrected. UV spectra: λ_{max} in nm (log ε). IR spectra: CCl_4, unless otherwise specified, $\tilde{\nu}_{max}$ in cm^{-1}. NMR spectra in $CDCl_3$; ^{1}H-NMR at 100 MHz, unless otherwise specified; ^{13}C-NMR at 25.2 MHz; standard tetramethylsilane δ [ppm] = 0; abbreviations: *s* singlet, *d* doublet, *t* triplet, *q* quadruplett, *m* multiplet, *J* spin-spin coupling constant [Hz]. Mass spectra

[8]) Review: [11]. For more récent examples see [23].

(MS): signals are given in *m/z* (rel.-%). The enantiomerically pure compounds reported here show GC, IR, NMR, and MS identical with those described for the corresponding racemates. Optical rotations [α] were measured using a *Perkin-Elmer-141* polarimeter; in $CHCl_3$, unless otherwise specified.

Preparation of 1,5-Diketones (±)- and (+)-3. – *(RS)-2-Cyclopentenecarboxylic Acid ((+)-7)* [25]. A solution of 3-chlorocyclopentene (113.55 g, 1.11 mol) in THF (150 ml) was added to a suspension of Mg turnings (27 g, 1.11 mol) in THF (300 ml), cooled to −10° by an external cooling bath (−15°), at such a rate that the temp. of the mixture remained between −10 and −12°. Then, the mixture was stirred at −10° for 1 h and carbonated at −60° by addition to solid CO_2 (excess). The mixture was allowed to warm up to r.t., filtered, and evaporated. Shaking of the residue with aq. $NaHCO_3/Et_2O$, acidification (HCl) of the separated aq. phase, subsequent extraction with Et_2O, workup and distillation furnished (±)-**7** (61 g, 68%), oil, b.p. 101°/11 Torr. IR (film): 3700–2300, 1710, 1420, 1230, 920. ^{1}H-NMR (60 MHz): 1.9–2.6 (4H); 3.4–3.8 (1H); 5.6–6.05 (2H); 11.25 (*s*, 1H).

(S)-2-Cyclopentenecarboxylic Acid ((−)-7) [20]. A solution of (±)-**7** (47.33 g, 422.1 mmol) in Et_2O (200 ml) was added to a mechanically stirred solution of (−)-(*S*)-(α-phenylethyl)amine (51.17 g, 422.1 mmol) in Et_2O (500 ml). After 1 h, the precipitated salt was filtered, dried, and recrystallized (5 ×) from acetone, until m.p. and [α] remained unchanged on further crystallization, to give a colorless salt (15.35 g), m.p. 100° (dec.), $[\alpha]^{25}_{578} = -141°$ (c = 0.5, MeOH) ([20]: m.p. 118.5–119.5°; $[\alpha]^{25}_{578} = -156.5°$ (c = 0.4, MeOH)). This salt (4.67 g, 20 mmol) was shaken with 1N aq. NaOH (21 ml)/Et_2O. Acidification (conc. aq. HCl, 1.75 ml) of the separated aq. phase followed by extraction (Et_2O), workup, and distillation furnished (−)-**7** (oil; 2.186 g, 98%), b.p. 105°/13 Torr. $[\alpha]^{25}_D = -248°$; $[\alpha]^{25}_{578} = -260°$; $[\alpha]^{25}_{546} = -299°$; $[\alpha]^{25}_{436} = -539°$; $[\alpha]^{25}_{365} = -910°$ (c = 0.5) ([20]: $[\alpha]^{25}_D = -262°$; $[\alpha]^{25}_{578} = -273.9°$ (c = 35.3)).

(RS)-2-Cyclopentenecarbonyl Chloride ((±)-**8**) [25]. Acid (±)-**7** (18.24 g, 162.7 mmol) was added dropwise to refluxing $SOCl_2$ (23.4 ml, 325.5 mmol). Addition of CCl_4 (5 ml), heating of the mixture at reflux for 1 h, concentration *in vacuo*, and distillation of the residue provided (±)-**8** (19.1 g, 90%), b.p. 68°/30 Torr. IR (film): 3080, 2960, 2870, 1800, 1460, 1065, 1040, 980, 760. ^{1}H-NMR (60 MHz, CCl_4): 1.9–2.7 (4H); 3.7–4.15 (1H); 5.65–6.15 (2H).

(S)-2-Cyclopentenecarbonyl Chloride ((S)-8). Oxalyl chloride (5 ml, 58.5 mmol) was added dropwise to a solution of (−)-**7** (2.186 g, 19.5 mmol) in CH_2Cl_2 (20 ml) at 0°. Keeping the mixture at r.t. for 3 h, evaporation and distillation as described above furnished (*S*)-**8** (2.16 g, 85%) which was reacted with enamine **6** as described below.

2-((RS)-2-Cyclopentenecarbonyl)cyclopentanone ((±)-5). Chloride (±)-**8** (10.25 g, 78.5 mmol) in $CHCl_3$ (30 ml) was added dropwise to a solution of enamine **6** [12] (26.5 g, 173 mmol) in $CHCl_3$ (100 ml). Heating of the mixture at reflux for 6 h, followed by addition of 3.5N aq. HCl (42 ml) and further heating at reflux for 6 h gave, on workup and distillation (using a 15-cm *Vigreux* column), (±)-**5** (9.1 g, 65%), b.p. 54–56°/0.01 Torr. GC (*a*, 150°): 4.47 (97%). UV ($CHCl_3$): 291 (3.87). UV (hexane): 286 (3.90). IR (film): 3060, 2960, 2860, 1740, 1702, 1640, 1605, 1380, 1240. ^{1}H-NMR: 1.7–2.9 (10H); 3.45–3.75 (1.2H); 3.85–4.15 (0.4H); 5.6–6.1 (2H); 9.0–11.0 (0.4H). MS: 178 (13, $C_{11}H_{14}O_2^{+}$), 111 (100), 94 (17), 84 (26), 83 (15), 67 (71), 55 (34), 41 (30).

2-(S)-2-Cyclopentenecarbonyl)cyclopentanone ((−)-5). The chloride (*S*)-**8** (1.31 g, 10.03 mmol) was added to a solution of enamine **6** (3.23 g, 21.06 mmol) in $CHCl_3$ (20 ml). To minimize racemization, the mixture was stirred at r.t. for 15 h. Hydrolysis (as described above), workup, and bulb-to-bulb distillation furnished (−)-**5** (1.784 g, 100%), which was directly converted to (−)-**10**. $[\alpha]^{25}_D = -143$; $[\alpha]^{25}_{578} = -151°$; $[\alpha]^{25}_{546} = -175.5°$; $[\alpha]^{25}_{436} = -341.2$ (c = 0.5).

O-Acetylation of (±)-5: 2-(2-Cyclopentenecarbonyl)-1-cyclopentenyl Acetate (**9a**) *and (2-Cyclopentenyl)(2-oxocyclopentylidene)methyl Acetate* (**9b**(/**9c**)). AcCl (3.77 g, 48 mmol) was added slowly to a solution of (±)-**5** (5.73 g, 32.15 mmol) in pyridine (16 ml) at −5°. Stirring the mixture at 0° for 4 h, acidification with aq. 2N HCl, extraction with Et_2O, washing of the org. phase successively with 2N aq. HCl and sat. aq. $NaHCO_3$ and workup afforded crude **9** (5.69 g, 80%) that was directly subjected to the following photocycloaddition. A sample of **9** was chromatographed (toluene/EtOAc 9:1). UV ($CHCl_3$): 256 (4.08) UV (hexane): 243 (4.05). IR: 3080, 2980, 2860, 1775, 1722, 1667, 1640, 1366, 1212, 1188, 1173, 1163, 1096, 1015. ^{1}H-NMR (+30°): 1.75–3.0 (10H); 2.24 (*m*, 3H); 3.66 (*m*, 0.62H); 4.05 (*m*, 0.38H); 5.65 (*m*, 1H); 5.95 (*m*, 1H); at −50° the signals at 3.66 and 4.05 integrate for 0.8 and 0.2H, resp. MS: 220 (0.5, $C_{13}H_{16}O_3^{+}$), 194 (5.5), 178 (5.5), 153 (29), 111 (100), 99 (8), 67 (37).

8-Oxotetracyclo[5.4.0.0^{2,9}.0^{3,7}]undec-3-yl Acetate (**11**; *racemic 3-epimers*). A solution of crude **9** (5.69 g, 25.9 mmol) in cyclohexane (220 ml) was irradiated for 24 h. ^{1}H-NMR analysis indicated the presence of two isomers **11** (ratio 3:1). Medium-pressure chromatography (SiO_2, *Woelm*, 0.032–0.063 mm, toluene/EtOAc

19:1→3:1, 300 psi) gave the pure isomers **11** (2.7474 g, 39% from (±)-**5**) which were recrystallized (hexane/Et_2O) separately. Major, less polar isomer: m.p. 57–58°. IR: 2980, 2940, 2865, 1760, 1735, 1452, 1375, 1265, 1250, 1218, 1180, 1145, 1125, 1105, 1085, 1030, 1005. ^{1}H-NMR: 1.1–2.3 (10H), 2.1 (*s*, 3H); 2.78 (*m*, 1H); 3.41 (*m*, 2H). ^{13}C-NMR: 212.4 (*s*), 170.2 (*s*), 92.7 (*s*), 78.7 (*s*), 53.4 (*d*), 51.4 (*d*), 49.9 (*d*), 32.7 (*t*), 29.8 (*t*), 25.6 (*t*), 23.5 (*t*), 21.5 (*q*), 19.0 (*t*). MS: 220 (1.6, $C_{13}H_{16}O_3^{+}$), 178 (96), 160 (11), 153 (26), 150 (11), 133 (14), 123 (12), 122 (12), 117 (11), 111 (100), 91 (11), 43 (18). Minor, more polar isomer: m.p. 90°. IR: 2975, 2945, 2865, 1764, 1742, 1445, 1368, 1250, 1235, 1205, 1180, 1150, 1128, 1107, 1073, 1052, 960. ^{1}H-NMR: 1.3–2.4 (10H); 2.0 (*s*, 3H); 2.50 (*m*, 1H); 2.85 (*m*, 1H); 3.38 (*m*, 1H). ^{13}C-NMR: 207.3 (*s*), 169.6 (*s*), 93.0 (*s*), 82.9 (*s*), 58.3 (*d*), 50.5 (2 *d*), 32.2 (*t*), 31.2 (*t*), 29.8 (*t*), 23.9 (*t*), 21.0 (*q*), 20.1 (*t*). MS: 220 (15, $C_{13}H_{16}O_3^{+}$), 178 (100), 161 (10), 160 (11), 150 (25), 149 (10), 132 (28), 111 (22), 91 (28), 84 (39), 67 (20), 43 (43).

8-Hydroxytetracyclo[5.4.0.0^{2,9}.0^{4,8}]undecan-3-one (**12**). A solution of mixture **11** (1.265 g, 5.74 mmol) in 4% KOH (5 ml) in dioxane/H_2O 1:1 was heated at 100° for 20 min, then poured into 2N aq. HCl. Extraction with CH_2Cl_2, washing of the extracts with sat. aq. $NaHCO_3$, workup, and bulb-to-bulb distillation furnished **12** (786 mg, 77%), b.p. 130°/0.3 Torr. IR: 3595, 3420 (br.), 2940, 2900, 2860, 1748, 1732, 1310, 1282, 1267, 1175. ^{1}H-NMR: 1.3 (*m*, 1H); 1.5–2.3 (9H); 2.3 (*m*, 3H, add. of D_2O→2H); 2.61 (*m*, 1H). ^{13}C-NMR: 183.6 (*s*), 90.9 (*s*), 58.9 (*d*), 57.6 (*d*), 51.4 (*d*), 48.7 (*d*), 47.7 (*d*), 32.7 (*t*), 29.1 (*t*), 26.1 (*t*), 21.0 (*t*). MS: 178 (35, $C_{11}H_{14}O_2^{+}$), 150 (54), 108 (15), 84 (100), 83 (61), 82 (49), 67 (86).

Tetracyclo[5.4.0.0.^{2,9}.0^{4,8}]undecan-3,8-diol (**13**). A solution of 1N diisobutylaluminium hydride in toluene (6 ml, 6 mmol) was added dropwise at −78° to a solution of **12** (786 mg, 4.41 mmol) in toluene (10 ml). The mixture was stirred at r.t. for 3 h, then poured into sat. aq. sodium potassium tartrate. Extraction with EtOAc, workup, and crystallization (EtOAc) afforded **13** (675 mg, 85%), m.p. 145°. IR (KBr): 3300 (br.), 2940, 2870, 1321, 1292, 1119, 1074, 1038, 1012, 917. ^{1}H-NMR (60 MHz): 0.9–2.8 (16H). MS: 180 (23, $C_{11}H_{16}O_2^{+}$), 162 (66), 147 (9), 134 (15), 133 (13), 120 (12), 117 (16), 96 (34), 95 (31), 84 (100), 83 (50), 79 (36), 67 (81), 55 (31), metastable peak at 145.8.

3-Tricyclo[5.4.0.0^{2,9}]undecen-8-one (**15**). Methanesulfonyl chloride (85.4 µl, 1.1 mmol) was added slowly to a mixture of **13** (180 mg, 1 mmol) and Et_3N (0.21 ml, 1.5 mmol) in THF (3 ml) at 0°. The mixture was stirred at +5° for 15 h, poured into sat. aq. $CuSO_4$. Extraction with Et_2O and workup gave crude methanesulfonate **14**. *t*-BuOK (112 mg, 1 mmol) was added to the solution of crude **14** in *t*-BuOH (3 ml). Then, the mixture was stirred at 35° for 1 h and at reflux for 2.5 h, poured into 2N aq. HCl to give, after workup, chromatography (toluene/EtOAc 3:1), and bulb-to-bulb distillation, apart from unchanged **13** (36 mg), **15** (70 mg, 43%), b.p. 140° (bath)/1 Torr. IR: 3015, 2960, 2875, 1754, 1095. ^{1}H-NMR: 1.2–2.7 (9H); 2.52 (*m*, 2H); 3.04 (*m*, 1H); 5.45 (*m*, 1H, irradiation at 2.02→*dd*, *J* = 4, 11); 5.70 (*m*, 1H, irradiation at 2.02→*d*, *J* = 11). ^{13}C-NMR: 220.0, 129.0, 128.3, 56.2, 51.3, 50.2, 40.4, 29.3, 27.8, 23.0, 22.5. MS: 162 (40, $C_{11}H_{14}O^{+}$), 147 (8), 133 (12), 120 (19), 107 (21), 105 (15), 96 (100), 95 (60), 94 (28), 91 (48), 79 (41), 67 (32), 55 (20), metastable peak at 89.

*O-Benzyloxycarbonylation of (±)-**5**: Benzyl 2-(2-Cyclopentenecarbonyl)-1-cyclopentenyl Carbonate ((±)-**10a**) and Benzyl (2-Cyclopentenyl)(2-oxocyclopentylidene)methyl Carbonate ((±)-**10b**/(±)-**10c**)).* Benzyl chloroformate (4.44 g, 22.4 mmol) was added slowly at −8° to a vigorously stirred solution of (±)-**5** (2.61 g, 14.6 mmol) and pyridine (8.8 ml, 109 mmol) in THF (20 ml). After stirring the mixture at 0° for 4 h, another portion of benzyl chloroformate (2.9 g, 14.6 mmol) was added. The mixture was stirred at +5° for 15 h, then poured into 2N aq. HCl (50 ml). Extraction with Et_2O, washing of the extracts with sat. aq. $CuSO_4$ and 0.5N aq. HCl, workup, chromatography (hexane/Et_2O 3:1→1:1) and crystallization (hexane/Et_2O) furnished (±)-**10**[6]) (3.46 g, 76%), m.p. 60.5–62.5°. UV ($CHCl_3$): 252 (3.95). UV (hexane): 242 (3.94). UV (cyclohexane): 241 (4.1); 329 (1.9). IR (KBr): 2965, 2940, 2885, 2845, 1769, 1720, 1638, 1456, 1384, 1285, 1235, 1215, 1160, 1005, 965, 944, 920, 831, 764, 741, 706. IR (CCl_4): 2975, 1772, 1725, 1670, 1645, 1382, 1235, 1210, 1172. ^{1}H-NMR: 1.75–2.95 (10H); 3.63 (*m*, 0.64H); 4.06 (*m*, 0.4H); 5.25 (*m*, 2H); 5.61 (*m*, 1H); 5.89 (*m*, 1H), 7.39 (*s*, 5H); at −50° the signals at 3.63 and 4.06 integrate for 0.7 and 0.35H, resp. MS: $C_{19}H_{20}O_4^{+}$ not found, 245 (2), 201 (24), 177 (21), 155 (15), 111 (21), 92 (26), 91 (100), 67 (41).

*O-Benzyloxycarbonylation of (−)-**5***. Following the above procedure, (−)-**5** (2.61 g, 14.6 mmol) was acylated to give, after chromatography, (−)-**10**[6]) (4.142 g, 91%). $[\alpha]_D^{25} = -95°$, $[\alpha]_{578}^{25} = -99.5°$, $[\alpha]_{546}^{25} = -113.5°$, $[\alpha]_{436}^{25} = -216$ (c = 0.65).

Benzyl 8-Oxotetracyclo[5.4.0.0^{2,9}.0^{3,7}]undec-3-yl Carbonate ((±)-**16**[7])). A solution of crystalline (±)-**10**[6]) (4.25 g, 13.6 mmol) in cyclohexane (220 ml) was irradiated for 2 h. Flash chromatography (toluene/EtOAc 9:1) furnished a crude 3:2 (^{1}H-NMR) mixture (±)-**16**[7]) (3.9 g, 92%) which was directly converted to (±)-**3** as described below. For its characterization, the mixture was chromatographed (hexane/Et_2O 3:1), and the separated isomers were crystallized (hexane/Et_2O). Major, less polar isomer: m.p. 108–110°. IR (KBr): 2980, 2960, 1759, 1738, 1390, 1285, 1268, 1245, 1208, 1171, 1133, 1062, 1027, 906, 863, 749, 697. ^{1}H-NMR: 1.1–2.3 (10H);

2.78 (*m*, 1H); 3.44 (*m*, 2H); 5.21 (*s*, 2H); 7.42 (*s*, 5H). ^{13}C-NMR: 212.1, 154.0, 135.1, 128.4, 128.1, 94.8, 78.8, 69.4, 53.5, 51.1, 50.0, 32.7, 29.7, 25.5, 23.4, 18.8. MS: $C_{19}H_{20}O_4^{+}$ not found, 268 (0.2), 177 (3), 160 (2), 149 (1.3), 131 (4.5), 117 (2), 105 (3.5), 92 (9.5), 91 (100). Minor, more polar isomer: m.p. 98–100°. IR (KBr): 2970, 1757, 1741, 1382, 1280, 1215, 1198, 953, 864, 745, 699. ^{1}H-NMR: 1.4–2.55 (11H); 2.9 (*m*, 1H); 3.38 (*m*, 1H); 5.14 (*s*, 2H); 7.37 (*s*, 5H). ^{13}C-NMR: 206.7, 153.2, 135.1, 128.4, 128.3, 127.9, 94.5, 82.9, 69.3, 58.1, 50.1, 49.8, 32.0, 31.3, 29.6, 23.6, 20.0. MS: 312 (0.08, $C_{19}H_{20}O_4^{+}$), 268 (0.7), 221 (0.5), 220 (0.3), 177 (4), 161 (2.5), 160 (2.6), 131 (6), 92 (8), 91 (100).

*Benzyl (1R)-8-Oxotetracyclo[5.4.0.0^{2,9}.0^{3,7}]undec-3-yl Carbonate ((1R)-**16**[7]).* Following the above procedure (–)-**10**[6] (4.142 g, 13.26 mmol) gave on irradiation (1*R*)-**16**[7]) (4.154 g, 100%) which was directly converted to (+)-**3**.

(±)-Tricyclo[5.4.0.0^{2,9}]undecan-3,8-dione ((±)-**3**). A solution of (±)-**16**[7]) (3.038 g, 9.727 mmol) in AcOH (15 ml) was stirred with 10% Pd/C (456 mg) under 1 atm H_2 at r.t. for 3.5 h. Filtration of the mixture, evaporation of the filtrate, chromatography (toluene/EtOAc 9:1), and crystallization (hexane/Et_2O) furnished (±)-**3** (1.388 g, 80%), m.p. 58–59°. IR (KBr): 2995, 2965, 2940, 2925, 2910, 2860, 1738, 1687, 1447, 1140, 1119, 1105, 1053, 783. ^{1}H-NMR: 1.45–2.9 (14H). ^{13}C-NMR: 218.5 (*s*), 211.3 (*s*), 61.8 (*d*), 54.6 (*d*), 51.8 (*d*), 42.9 (*t*), 41.2 (*d*), 28.9 (*t*), 28.2 (*t*), 23.7 (*t*), 20.7 (*t*). MS: 178 (75, $C_{11}H_{14}O_2^{+}$), 150 (18), 135 (7), 131 (9), 122 (16), 121 (9), 108 (8), 107 (15), 106 (12), 104 (10), 95 (16), 94 (36), 93 (26), 91 (23), 84 (100), 80 (44), 79 (53), 67 (60), 55 (34), metastable peak at 126.4.

*(+)-(1S,2R,7S,9S)-Tricyclo[5.4.0.0^{2,9}]undecan-3,8-dione ((+)-**3**).* Following the above procedure, (1*R*)-**16**[7]) (4.154 g, 13.3 mmol) was hydrogenolyzed to give, after chromatography, (+)-**3** (1.627 g, 69%). ^{1}H-NMR: no impurities. $[\alpha]_D^{25} = +112°$, $[\alpha]_{578}^{25} = +117°$, $[\alpha]_{546}^{25} = +136°$, $[\alpha]_{436}^{25} = +267°$, $[\alpha]_{365}^{25} = +536$ ($c = 0.5$). Successive recrystallizations (hexane/Et_2O) until m.p. and [α] remained constant gave 1.266 g (54%) of (+)-**3**, m.p. 59–60°. $[\alpha]_D^{23} = +133°$, $[\alpha]_{578}^{23} = +138°$, $[\alpha]_{546}^{23} = +161°$, $[\alpha]_{436}^{23} = +315°$, $[\alpha]_{365}^{23} = +636°$ ($c = 0.5$); accordingly, the chromatographed (+)-**3** is 85% optically pure. IR (KBr): 2980, 2968, 2918, 2875, 1745, 1695, 1463, 1445, 1320, 1288, 1145, 1122, 1098, 1047, 783.

Total Synthesis of (±)- and (+)-Longifolene ((±)- and (+)-1, resp.). – *(±)-3-Methylidenetricyclo[5.4.0.0^{2,9}]undecan-8-one* ((±)-**17**). A suspension of methyltriphenylphosphonium bromide (440 mg, 1.23 mmol) in toluene (5 ml) was added to 0.224N sodium *t*-pentylate in toluene (5 ml, 1.12 mmol). After 1 h at r.t., (±)-**3** (37.5 mg, 0.211 mmol) in toluene (3 ml) was added to the yellow solution of the ylide. The mixture was stirred for 1.5 h at r.t., then poured into 2N aq. HCl, worked up, chromatographed (toluene/EtOAc 9:1), and bulb-to-bulb distilled to give (±)-**17** (oil; 32.7 mg, 88%), b.p. 90° (bath)/0.01 Torr. GC (*b*, 180°): 13.2 (99.7%). IR: 2940, 2920, 2870, 2850, 1745, 1633, 1450, 1093, 895. ^{1}H-NMR: 1.35–2.43 (11H); 2.43–2.65 (2H); 2.75 (*m*, 1H); 4.78 (*s*, 2H). ^{13}C-NMR: 221.2 (*s*), 149.5 (*s*), 113.7 (*t*), 56.4 (*d*), 55.7 (*d*), 51.6 (*d*), 42.3 (*d*), 34.4 (*t*), 29.2 (*t*), 28.7 (*t*), 25.8 (*t*), 23.7 (*t*). MS: 176 (31, $C_{12}H_{16}O^{+}$), 158 (6), 148 (8), 147 (6), 134 (12), 133 (30), 132 (10), 120 (10), 119 (21), 118 (15), 106 (15), 105 (26), 92 (28), 91 (59), 81 (48), 80ß (21), 79 (45), 77 (22), 67 (100), 66 (27).

*(+)-(1R,2R,7S,9S)-3-Methylidenetricyclo[5.4.0.0^{2,9}]undecan-8-one ((+)-**17**).* Following the above procedure, the recrystallized, enantiomerically pure (+)-**3** (462 mg, 2.59 mmol) was converted to (+)-**17** (oil; 421.6 mg, 92%). $[\alpha]_D^{25} = +110°$, $[\alpha]_{578}^{25} = +113°$, $[\alpha]_{546}^{25} = +129.5°$, $[\alpha]_{436}^{25} = +226.5$, $[\alpha]_{365}^{25} = +348°$ ($c = 0.6$).

*(Tricyclo[5.4.0.0^{2,9}]undecan-8-one)-3-spiro-1′-cyclopropane ((±)-**18**).* Activated (H_2SO_4) Zn turnings (1.67 g, 25.56 mmol) were added to a solution of AgOAc (9.8 mg, 0.06 mmol) in AcOH (10 ml). After 1 min, the cooled (0°) mixture was filtered and subsequently washed (5×) with Et_2O; after addition of Et_2O (15 ml) and some Ag cotton, CH_2I_2 (1.03 ml; 3.42 g, 12.78 mmol) was added to the mixture which was then stirred for 1 h at r.t.. Then, (±)-**17** (750 mg, 4.26 mmol) was added to the black solution. Heating at reflux for 60 h, addition of a solution of pyridine (1.3 ml, 17 mmol) in Et_2O (15 ml) at 0°, stirring of the suspension for 1 h at r.t., filtration *(Celite)*, washing of the filtrate successively with H_2O, sat. aq. $CuSO_4$, 1N aq. NaS_2O_3, workup, chromatography (toluene/EtOAc 9:1), and bulb-to-bulb distillation gave (±)-**18** (oil; 633.3 mg, 78%), b.p. 90° (bath)/0.01 Torr. GC (*b*, 180°): 19.2 (98.6%). IR: 3040, 2970, 2930, 2900, 2855, 2835, 1748, 1440, 1085, 1002. ^{1}H-NMR: 0.3 (*s*, 4H); 0.65 (*m*, 1H); 1.09 (*m*, 1H); 1.2–2.2 (10H); 2.54 (*m*, 2H). ^{13}C-NMR: 222.6 (*s*), 59.2 (*d*), 52.7 (*d*), 51.6 (*d*), 40.7 (*d*), 33.9 (*t*), 29.4 (*t*), 28.9 (*t*), 24.1 (*t*), 23.9 (*t*), 20.7 (*s*), 14.2 (*t*), 12.9 (*t*). MS: 190 (48, $C_{13}H_{18}O^{+}$), 186 (30), 162 (16), 161 (12), 148 (19), 147 (17), 143 (26), 133 (43), 129 (29), 119 (32), 105 (33), 95 (51), 94 (41), 93 (46), 92 (42), 91 (100), 80 (51), 79 (75), 67 (65), 55 (43), 44 (43), 41 (55).

*(+)-(1R,2R,7S,9S)-(Tricyclo[5.4.0.0^{2,9}]-undecan-8-one)-3-spiro-1′-cyclopropane ((+)-**18**).* Following the above procedure (+)-**17** (421.6 mg, 2.39 mmol) was converted to (+)-**18** which was purified by chromatography (SiO_2, 5% $AgNO_3$, toluene) and distillation (251.2 mg, 55%). $[\alpha]_D^{21} = +89°$, $[\alpha]_{578}^{21} = +93°$, $[\alpha]_{546}^{21} = +106.5°$, $[\alpha]_{436}^{21} = +186.5°$, $[\alpha]_{365}^{21} = +298.5°$ ($c = 0.4$).

*(±)-3,3-Dimethyltricyclo[5.4.0.0^{2,9}]undecan-8-one ((±)-**19**).* A solution of (±)-**17** (523.8 mg, 2.76 mmol) in AcOH (10 ml) was stirred, after addition of PtO_2 (100 mg), unter 1 atm H_2 at r.t. for 18 h. Then, the mixture was poured into 2N aq. K_2CO_3 to give, after workup and bulb-to-bulb distillation, (±)-**19** (oil; 509.4 mg, 96%), b.p. (bath) 90°/0.01 Torr. GC (*b*, 180°): 14.6 (99.4%). IR: 2950, 2870, 2855, 1740, 1472, 1455, 1369, 1092. ^{1}H-NMR: 0.94 (*s*, 3H); 1.04 (*s*, 3H); 0.9–2.2 (12H); 2.54 (*m*, 2H). ^{13}C-NMR: 222.2 (*s*), 60.7 (*d*), 51.1 (*d*), 50.2 (*d*), 38.6 (*d*), 37.1 (*t*), 33.4 (*s*), 30.7 (*q*), 29.6 (*t*), 29.0 (*t*), 28.8 (*q*), 24.1 (*t*), 20.2 (*t*). MS: 192 (100, $C_{13}H_{20}O^+$), 177 (34), 161 (12), 159 (18), 149 (62), 136 (12), 135 (21), 131 (13), 123 (28), 122 (23), 121 (53), 109 (69), 108 (55), 107 (53), 95 (69), 93 (72), 82 (97), 79 (76), 67 (95), 55 (74), 41 (93). ^{1}H-NMR comparison of (±)-**19** with an authentic sample (60 MHz) confirmed their identity.

*(−)-(1R,2R,7S,9S)-3,3-Dimethyltricyclo[5.4.0.0^{2,9}]undecan-8-one((−)-**19**).* Following the above procedure, (+)-**18** (251.2 mg, 1.32 mmol) was hydrogenolyzed to give enantiomerically pure (−)-**19** (245 mg, 96.5%). $[\alpha]_D^{20} = -3.6°$, $[\alpha]_{578}^{20} = -3.3°$, $[\alpha]_{546}^{20} = -3.0°$, $[\alpha]_{436}^{20} = +5.0°$, $[\alpha]_{365}^{20} = +40°$ ($c = 0.3$).

*(±)-3,3,7-Trimethyltricyclo[5.4.0.0^{2,9}]undecan-8-one(= (±)-Longicamphenylone; (±)-**20**).* A 1.36N solution of BuLi in hexane (1.7 ml, 2.3 mmol) was added to a solution of cyclohexylisopropylamine (0.42 ml, 2.5 mmol) in THF (10 ml) at −78°. After stirring the mixture at r.t. for 10 min, a solution of (±)-**19** (221 mg, 1.15 mmol) in THF (3 ml) was added slowly at −78°. The mixture was warmed up slowly and kept at +60° for 1.5 h and, after addition of MeI (355 mg, 2.5 mmol) at 0°, heated at reflux for 16 h. Pouring the mixture into 2N aq. HCl, workup, chromatography (hexane/Et_2O 9:1), and bulb-to-bulb distillation furnished (±)-**20** (218 mg, 92%), b.p. (bath) 100°/0.1 Torr. GC (*b*, 180°): 14.9 (97,8%). IR ($CHCl_3$): 2940, 2900, 2860, 1730, 1460, 1380. ^{1}H-NMR: 0.93 (*s*, 3H); 0.98 (*s*, 3H); 1.04 (*s*, 3H); 0.9–2.2 (11H); 2.4–2.62 (2H). ^{13}C-NMR: 224.6 (*s*), 60.6 (*d*), 51.0 (*d*), 48.2 (*s*), 43.0 (*d*), 40.1 (*t*), 36.7 (*t*), 33.5 (*s*), 30.9 (*q*), 29.1 (*q*), 25.2 (2 *t*, *q*), 20.2 (*t*). MS: 206 (100, $C_{14}H_{22}O^+$), 191 (27), 175 (37), 173 (37), 163 (38), 147 (46), 145 (64), 135 (45), 122 (26), 121 (33), 109 (75), 108 (53), 107 (78), 95 (50), 94 (44), 93 (67), 82 (53), 81 (67), 79 (47), 67 (69), 55 (67), 41 (94). GC properties (coinjection), IR, ^{1}H-NMR and MS of (±)-**20**: identical to those of authentic samples obtained from Prof. *W. S. Johnson* as well as by oxidative degradation of longifolene [26].

*(−)-Longicamphenylone ((−)-**20**).* Following the above procedure, (−)-**19** (119.5 mg, 0.621 mmol) was methylated to give, after crystallization (aq. EtOH), (−)-**20** (100 mg, 80%), m.p. 49–50°. $[\alpha]_D^{21} = -23°$, $[\alpha]_{578}^{21} = -24°$, $[\alpha]_{546}^{21} = -28°$, $[\alpha]_{436}^{21} = -51°$, $[\alpha]_{365}^{21} = -113°$ ($c = 0.35$). A comparison sample, obtained from natural (+)-longifolene ((+)-**1**) gave no depression of the m.p. on admixture to (−)-**20** and showed the following optical rotations: $[\alpha]_D^{21} = -23°$, $[\alpha]_{578}^{21} = -23.5$, $[\alpha]_{546}^{21} = -27°$, $[\alpha]_{436}^{21} = -50°$, $[\alpha]_{365}^{21} = -110°$ ($c = 0.35$).

*(±)-Longifolene ((±)-**1**).* A 1.58N solution of MeLi in Et_2O (6.7 ml, 10.6 mmol) was added at 0° to a solution of (±)-**20** (218 mg, 1.06 mmol) in THF (10 ml). The mixture was heated at 50° for 3 h, then quenched by addition of ice at 0°, and subjected to workup. The resulting crude alcohol was dissolved in pyridine (5 ml). After addition of $SOCl_2$ (0.77 ml, 10.56 mmol) at 0°, the mixture was stirred at 0° for 10 min, then quenched with ice, extracted with Et_2O, subjected to workup, chromatography (hexane), and bulb-to-bulb distillation to give (+)-**1** (168.2 mg, 78%), b.p. 140° (bath)/11 Torr. GC (*d*, 160°): 13.2 (95.5%). IR (20%): 3065, 2900–2850, 1659, 1480–1450, 1381, 1366, 1300, 1175, 1125, 1096, 984, 880, 688. ^{1}H-NMR: 0.92 (*s*, 3H); 0.97 (*s*, 3H); 1.01 (*s*, 3H); 0.8–1.95 (11H); 2.11 (*m*, 1H); 2.65 (br. *d*, $J = 4$, 1H); 4.53 (*s*, 1H); 4.78 (*s*, 1H). ^{13}C-NMR: 167.7 (*s*), 99.0 (*t*), 62.2 (*d*), 48.0 (*d*), 45.2 (*d*), 44.0 (*s*), 43.4 (*t*), 36.5 (*t*), 33.6 (*s*), 30.5 (2 *q*), 30.0 (*q*), 29.8 (*t*), 25.6 (*t*), 21.2 (*t*). MS: 204 (55, $C_{15}H_{24}^+$), 189 (55), 175 (19), 161 (100), 147 (31), 135 (45), 133 (45), 121 (38), 120 (29), 119 (47), 109 (50), 108 (45), 107 (66), 105 (60), 95 (61), 94 (87), 93 (65), 91 (63), 79 (51), 67 (32), 55 (48), 41 (71). The above spectra are identical to those of naturally occurring (+)-longifolene.

*(+)-Longifolene ((+)-**1**).* Following the above procedure, (−)-**20** (100 mg, 0.485 mmol) was converted into (+)-**1** (83.3 mg, 84%). $[\alpha]_D^{19} = +51.5°$, $[\alpha]_{578}^{19} = +54.5°$, $[\alpha]_{546}^{19} = +64°$, $[\alpha]_{436}^{19} = +130°$, $[\alpha]_{365}^{19} = +253°$ ($c = 0.35$). IR, ^{1}H- and ^{13}C-NMR, and MS: identical to those of naturally occurring (+)-longifolene which shows the following optical rotations: $[\alpha]_D^{19} = +51°$, $[\alpha]_{578}^{19} = +54°$, $[\alpha]_{546}^{19} = +63°$, $[\alpha]_{436}^{19} = +128.5°$, $[\alpha]_{365}^{19} = +248°$ ($c = 0.55$).

Total Syntheses of (±)- and (+)-Sativene ((±)- and (+)-2, resp.). – *(±)-3-Methyltricyclo[5.4.0.0^{2,9}]undec-3-en-8-one ((±)-**22**).* MeI (80 µl at once to start the reaction; then a solution of 7.2 g (50.8 mmol) in Et_2O (10 ml)) was added to a suspension of Mg turnings (1.123 g, 46.2 mmol) in Et_2O (5 ml) at such a rate that the mixture was maintained at gentle reflux. After stirring at r.t. for 30 min, a solution of (±)-**3** (1.6464 g, 9.238 mmol) in Et_2O (5 ml) was added slowly within 30 min. Stirring of the mixture at r.t. for 2 h, followed by addition of ice and 2N aq. HCl at 0° gave, after workup, a crude alcohol (1.848 g). Some crystals of I_2 were added to a solution of the crude alcohol (1.2136 g) in a few drops of toluene. Heating at 110° for 3 h, shaking with toluene/1N aq. $Na_2S_2O_3$, chromatography (SiO_2, 5% $AgNO_3$, toluene), and bulb-to-bulb distillation furnished (±)-**22** (oil; 905.2 mg, 84%), b.p., 90° (bath)/0.05 Torr. GC (*b*, 180°): 16.8. IR: 2970, 2940, 2880, 1755, 1450, 1318, 1152, 1093, 1028, 917, 852. ^{1}H-NMR: 0.9–2.8 (9H); 1.64 (*t*, *J* = 1.5, 3H); 2.42 (*m*, 1H); 2.68 (*m*, 1H); 3.13 (*m*, 1H); 5.44 (*m*, 1H). ^{13}C-NMR: 220.5 (*s*), 134.7 (*s*), 124.5 (*d*), 55.9 (*d*), 55.0 (*d*), 49.9 (*d*), 39.1 (*d*), 29.15 (*t*), 29.05 (*t*), 24.0 (*q*), 22.7 (*t*), 22.4 (*t*). MS: 176 (100, $C_{12}H_{16}O^+$), 161 (10), 149 (7), 147 (10), 134 (19), 121 (33), 110 (37), 105 (26), 95 (67), 93 (28), 91 (31), 84 (26), 79 (31), 49 (37).

*(−)-(1R,2R,7S,9S)-3-Methyltricyclo[5.4.0.0^{2,9}]undec-3-en-8-one ((−)-**22**).* Following the above procedure, (+)-**3** (372.5 mg, 2.09 mmol) was converted to the enantiomerically pure (−)-**22** (261.7 mg, 66%). $[\alpha]_D^{22} = -2.5°$, $[\alpha]_{578}^{22} = -2.0°$, $[\alpha]_{546}^{22} = -0.7°$, $[\alpha]_{436}^{22} = +14°$, $[\alpha]_{365}^{22} = +112°$ (*c* = 0.5).

*(±)-3,7-Dimethyltricyclo[5.4.0.0^{2,9}]undec-3-en-8-one ((±)-**23**).* A 2.18N solution of BuLi in hexane (0.66 ml, 1.43 mmol) was added to cyclohexylisopropylamine (222 mg, 1.57 mmol) in THF (3 ml) at −78°. After stirring at r.t. for 15 min, a solution of (±)-**22** (125.9 mg, 0.715 mmol) in THF (1 ml) was added slowly at −78°. Stirring of the mixture at r.t. for 1.5 h, then at 60° for 2 h, subsequent addition of MeI (500 mg, 3.57 mmol), stirring at 0° for 30 min, at r.t. for 1 h, and at 60° for 2 h, subsequent shaking with 2N aq. HCl/Et_2O, workup, chromatography (toluene/EtOAc 19:1), and bulb-to-bulb distillation furnished (±)-**23** (oil; 125.8 mg, 92%), b.p. 90°/0.05 Torr. GC (*c*, 180°): 7.3 (97.6%). IR: 2970, 2930, 2880, 2855, 1748, 1450, 1382, 1006, 842. ^{1}H-NMR: 1.0 (*s*, 3H); 1.3–2.8 (8H); 1.63 (*t*, *J* = 1.5, 3H); 2.43 (*m*, 1H); 2.66 (*m*, 1H); 3.02 (*m*, 1H); 5.46 (*dm*, *J* = 8, 1H). ^{13}C-NMR: 221.7 (*s*), 134.5 (*s*), 124.0 (*d*), 55.1 (2 *d*), 47.3 (*s*), 42.8 (*d*), 39.5 (*t*), 24.6 (*t*, *q*), 23.5 (*q*), 22.7 (2 *t*). MS: 190 (57, $C_{13}H_{18}O^+$), 175 (14), 161 (8), 147 (21), 134 (37), 124 (100), 121 (56), 119 (30), 109 (73), 107 (36), 105 (35), 97 (45), 95 (44), 94 (38), 93 (40), 91 (44), 79 (89), 67 (70), 55 (49), 41 (82).

*(−)-(1R,2R,7S,9S)-3,7-Dimethyltricyclo[5.4.0.0^{2,9}]undec-3-en-8-one ((−)-**23**).* Following the above procedure (−)-**22** (268.2 mg, 1.52 mmol) was methylated to give (−)-**23** (oil; 256.1 mg, 88%). $[\alpha]_D^{23} = -26.5°$, $[\alpha]_{578}^{23} = -30.5°$, $[\alpha]_{546}^{23} = -35°$, $[\alpha]_{436}^{23} = -57.5°$, $[\alpha]_{365}^{23} = -74.5°$ (*c* = 0.47).

*(+)-3-Acetyl-6-methyltricyclo[4.4.0.0^{2,8}]decan-7-one ((±)-**24**; 3:1 mixture).* Montmorrilonite clay *K-10* (*Süd-Chemie AG*, München; 11 g) was added to a solution of $Tl(NO_3)_3$ (4.9 g, 11 mmol) in $HC(OMe)_3$ (12.5 ml) /MeOH (10 ml). The mixture was stirred for 5 min, evaporated, and dried (0.1 Torr, 2 h). The thus obtained clay-supported $Tl(NO_3)_3$ (1.8 g, 1.1 mmol) was stirred together with (±)-**23** (176.9 mg, 0.927 mmol) in CH_2Cl_2 at r.t. for 45 min, then filtered. The concentrated filtrate was heated at reflux in MeOH/1N aq. H_2SO_4 (10 ml, 1:1) for 30 min, then saturated with solid NaCl, and extracted with Et_2O to give, after workup and chromatography (toluene/EtOAc 9:1), (±)-**24** (oil; 70.3 mg, 37%; 3:1 stereoisomeric mixture). GC (*c*, 200°): 13.5 (25.5%), 18.8 (73.2%). IR: 2965, 2930, 2880, 1745, 1715, 1645, 1455, 1383, 1355, 1283, 1213, 1154, 1043, 912. ^{1}H-NMR: 0.98 (*s*, 0.8H); 1.02 (*s*, 2.2H); 1.2–2.65 (11H); 2.17 (*s*, 2.2H); 2.23 (*s*, 0.8H); 2.95 (*m*, 1H).

*(1R,2S,6S,8S)-3-Acetyl-6-methyltricyclo[4.4.0.0^{2,8}]decan-7-ones ((1R)-**24**; mixture of 3-epimers).* Following the above procedure, (−)-**23** (207.9 mg, 1.09 mmol) was converted to (1*R*)-**24** (45.1 mg, 20%).

*(±)-3-Isopropylidene-6-methyltricyclo[4.4.0.0^{2,8}]decan-7-one ((±)-**21a**) and (±)-3-Isopropyl-6-methyltricyclo[4.4.0.0^{2,8}]dec-3-en-7-one ((±)-**21b**).* MeI (30 µl to start the reaction; then 609 mg (4.29 mmol) in Et_2O (10 ml)) was added to an externally cooled (ice bath) suspension of Mg turnings (94.8 mg, 3.9 mmol) in Et_2O (1 ml) at such a rate that the mixture was maintained at gentle reflux. Stirring the mixture at r.t. for 30 min, subsequent addition of a solution of (±)-**24** (80.5 mg, 0.39 mmol) in Et_2O (2 ml) at 0°, stirring at r.t. for 2 h, quenching at 0° with ice and 2N aq. HCl and workup afforded a crude alcohol which was heated with several drops of toluene and a few crystals of I_2 at 110° for 1.5 h. Shaking of the mixture with toluene/1N aq. $Na_2S_2O_3$, chromatography (toluene/EtOAc 19:1), and bulb-to-bulb distillation furnished (±)-**21a**/(±)-**21b** (6:92 by GC; 66.8 mg, 84%), b.p. 90° (bath)/0.01 Torr which were converted to (±)-**25** without separation. For their identification, the isomers were separated by extensive chromatography (hexane/EtOAc 9:1). GC (*c*, 180°) of minor isomer (±)-**21a**: 5.61. IR: 2970, 2940, 2880, 1745, 1455, 1378, 1055, 1028. ^{1}H-NMR: 1.02 (*s*, 3H); 1.2–2.3 (7H); 1.66 (*s*, 3H); 1.73 (*s*, 3H); 2.06 (*m*, 1H); 2.3–2.7 (2H); 3.04 (*m*, 1H). ^{13}C-NMR: 222.7, 128.2, 124.6, 55.6, 49.8, 49.6, 49.2, 36.4, 36.2, 26.2, 25.0, 24.3, 22.5, 20.5, 19.9, 17.5. MS: 204 (100, $C_{12}H_{20}O^+$), 189 (22), 176 (18), 161 (80), 149 (55), 147 (25), 138 (30), 134 (26), 133 (53), 119 (22), 107 (25), 105 (33), 93 (31), 91 (37), 79 (22), 77 (22), 67 (21), 55 (21), 41 (43). GC (*c*, 180°) of major isomer (±)-**21b**: 4.26. IR: 2960, 2875, 1749, 1465, 1450, 1062, 1013. ^{1}H-NMR: 1.01 (*d*, *J* = 7, 6H); 1.07 (*s*, 3H); 1.4–2.5 (9H); 2.7 (br. *d*, *J* = 3, 1H); 5.23 (br. *t*, *J* = 3, 1H). ^{13}C-NMR: 221.3 (*s*), 145.1 (*s*), 116.9 (*d*), 59.7 (*d*), 49.6 (*s*), 47.8 (*d*), 47.1 (*d*), 39.2 (*t*), 34.6 (*d*), 25.9 (*t*), 21.7 (*t*), 21.5 (*q*), 21.0 (*q*); 17.6 (*q*). MS: 204 (52, $C_{14}H_{20}O^+$), 189 (12), 176 (5), 161 (100), 147 (40), 133 (45), 119 (21), 105 (45), 93 (22), 91 (29), 79 (13), 77 (16), 55 (16), 41 (28).

*(1R,2R,6S,8S)-3-Isopropyl-6-methyltricyclo[4.4.0.0^{2,8}]dec-3-en-7-one ((1R)-**21b**).* Following the above procedure, (1*R*)-**24** (45.1 mg, 0.218 mmol) was converted to (1*R*)-**21b** (33.3 mg, 75%).

*(±)-3-Isopropyl-6-methyltricyclo[4.4.0.0^{2,8}]decan-7-one ((±)-**25**).* A solution of (±)-**21a**/(±)-**21b** (6:92; 66.8 mg, 0.327 mmol) in AcOH (5 ml) was stirred, after addition of PtO_2 (13 mg), under 1 atm H_2 at r.t. for

18 h. Evaporation followed by chromatography (toluene/EtOAc 19:1) and bulb-to-bulb distillation furnished (±)-**25** (oil; 60.6 mg, 86%), b.p. (bath) 120°/0.5 Torr. GC (c = 150°): 10.2 (96.3%). IR: 2985, 2935, 2880, 2850, 1745, 1479, 1468, 1453, 1392, 1378, 1373, 1097, 1057, 1038. ^{1}H-NMR: 0.88 (d, J = 6, 3H); 0.93 (d, J = 6, 3H); 1.0 (s, 3H); 1.1–2.0 (10H); 1.94 (m, 1H); 2.22 (m, 1H); 2.5 (br. d, J = 3, 1H). ^{13}C-NMR: 222.8, 51.4, 50.5, 49.9, 49.0, 42.9, 36.5, 32.7, 26.7, 25.4, 22.0, 21.1, 20.8, 16.9. MS: 206 (29, $C_{14}H_{22}O^+$), 188 (6), 173 (7), 163 (18), 145 (26), 135 (51), 124 (10), 121 (10), 108 (10), 107 (18), 93 (35), 81 (19), 79 (23), 67 (20), 59 (15), 55 (25), 45 (74), 44 (100), 43 (25), 41 (46); metastable peak at 171.5.

*(±)-(1R,2R,3S,6S,8S)-3-Isopropyl-6-methyltricyclo[4.4.0.0^{2,8}]decan-7-one ((±)-**25**).* Following the above procedure, (1R)-**21b** (33.3 mg, 0.163 mmol) was hydrogenated to give (+)-**25** (16.7 mg, 47%). $[\alpha]_D^{24}$ = +164°, $[\alpha]_{578}^{24}$ = +172°, $[\alpha]_{546}^{24}$ = +199°, $[\alpha]_{436}^{24}$ = +382°, $[\alpha]_{365}^{24}$ = +752.5° (c = 0.17).

*(±)-Sativene ((±)-**2**).* A 1.85N solution of MeLi in Et_2O (1.5 ml, 2.8 mmol) was added to a solution of (±)-**25** (60.6 mg, 0.294 mmol) in THF (5 ml) at 0°. Heating of the mixture at 50° for 3 h, quenching at 0° with ice/2N aq. HCl and workup furnished a crude alcohol which was dissolved in pyridine (2 ml). After addition of $SOCl_2$ (335.5 mg, 2.8 mmol) at 0°, the mixture was stirred at 0° for 15 min. Quenching with ice/2N aq. HCl, extraction with Et_2O, washing of the Et_2O phase with sat. aq. $CuSO_4$, workup, chromatography (hexane), and bulb-to-bulb distillation provided (±)-**2** (53.6 mg, 89%), b.p. 125° (bath)/10 Torr. GC (d, 160°): 10.9 (99.6%). IR (20%): 3060, 2980–2860, 2840, 1669, 1474, 1388, 1372, 1113, 1095, 878. ^{1}H-NMR: 0.87 (d, J = 6, 3H); 0.91 (d, J = 6, 3H); 1.04 (s, 3H); 1.1–1.8 (10H); 1.85 (m, 1H); 2.63 (m, 1H); 4.46 (s, 1H); 4.79 (s, 1H). ^{13}C-NMR: 163.3 (s), 98.8 (t), 51.7 (d), 49.4 (d), 47.3 (d), 45.2 (s), 43.3 (d), 40.1 (t), 33.1 (d), 32.6 (t), 25.5 (t), 22.3 (t), 21.2 (q), 21.0 (q), 20.9 (q). MS: 204 (12, $C_{15}H_{24}O^+$), 189 (6), 175 (2), 161 (35), 147 (10), 133 (25), 119 (25), 108 (100), 105 (45), 93 (47), 91 (61), 79 (39), 67 (29), 55 (23), 41 (28). GC properties, IR, ^{1}H- and ^{13}C-NMR, and MS of (±)-**2**: identical with those of (−)-sativene of natural origin.

*(+)-Sativene ((±)-**2**).* Following the above procedure, (+)-**25** (16.7 mg, 0.077 mmol) was converted into (+)-**2** (11.5 mg, 73%). $[\alpha]_D^{20}$ = +191°, $[\alpha]_{578}^{20}$ = +199°, $[\alpha]_{546}^{20}$ = +229°, $[\alpha]_{436}^{20}$ = +414°, $[\alpha]_{365}^{20}$ = +697.5° (c = 0.18). A sample of (−)-sativene shows the following optical rotations: $[\alpha]_D^{20}$ = −191°, $[\alpha]_{578}^{20}$ = −202°, $[\alpha]_{546}^{20}$ = −231.5°, $[\alpha]_{436}^{20}$ = −417.5°, $[\alpha]_{365}^{20}$ = −705.5° (c = 0.24). IR, ^{1}H- and ^{13}C-NMR, and MS of synthetic (+)-**2**: identical with those of naturally occurring (−)-sativene.

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