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Full Paper

Use of Flash Vacuum Thermolysis in a Stereocontrolled Synthesis of Optically Active Alkyl-substituted Cyclopentenones with Fragrant Properties

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The synthesis of four pairs of enantiopure antipodal substituted cyclopentenones is described. The synthetic sequences first comprise the preparation of a tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dienone system, a subsequent kinetic enzymatic resolution of the appropriately functionalized tricyclic system, followed by a series of chemical transformations to install the desired substituents, and finally a retro Diels–Alder reaction using flash vacuum thermolysis to give the target products in high chemical and optical yields. The strategy makes effective use of the concept of transient chirality involving complete stereochemical control over reactions with the chiral tricyclic systems before thermal removal of the cyclopentadiene.

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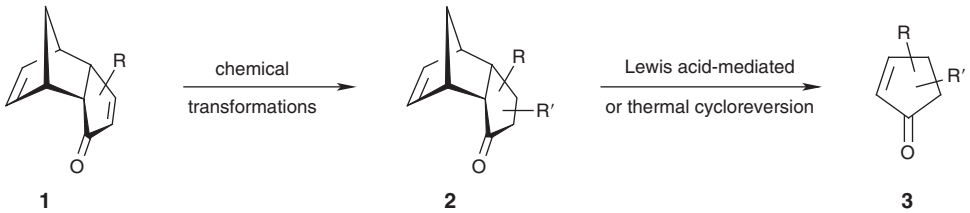
Introduction

The introduction of synthetic fragrance ingredients caused a revolution in the use of perfumes. Not until 100 years ago, perfumes were made entirely from natural products and as a consequence their use was restricted to wealthy people. Nowadays, fragrances are used in many consumer goods varying from personal products, such as soaps, shampoos, and deodorants, to household products such as detergents, cleaners, and bleaches. In 1996, the estimated world consumption of fragrance composites was valued at 2800 million dollars and that of synthetic fragrances was valued at 1400 million dollars.[1] The most significant turning point in the history of this industry was the introduction of the famous perfume Chanel No 5 in 1921. This was the first fine fragrance using synthetic organic compounds to produce unique fragrance aspects, and its immediate success led to growing interests in synthetic perfumes. The advantages of synthetic ingredients are low cost, availability, consistency, stability, originality, and additional functionality.

For the scent of a compound to be detected by humans, the compound needs to be volatile at ambient temperature. As a consequence, odorants are non-ionic compounds with molecular weights of less than 300 g mol^{-1}. They are usually hydrophobic organic compounds containing a limited number of functional groups. Olfactory research has long been challenged to investigate the structure–odour relationship,[2] and these studies often examine the molecular properties that determine the smell of a compound. Similar odours may be caused by compounds with completely different structures; conversely, compounds with similar structures may have very different odours.

The effect of chirality on odour is not always clear. The reported odour differences for enantiomers are sometimes so small that they are often associated with the presence of trace impurities, e.g. phosphine and sulfur-containing compounds. The most dramatic differences usually occur in rigid molecules[3] such as carvone.[4] Enantiomer *S*-(+)-carvone has a caraway-like odour whereas enantiomer *R*-(−)-carvone smells like spearmint. For the determination of relationships between odour and molecular structure, a collection of good, precise, and reproducible odour data are important.[5]

In recent years, it has been shown that the *endo*-tricyclo [5.2.1.$0^{2,6}$]decadienone system **1** is a useful synthon for the synthesis of a great variety of naturally occurring



1 **2** **3**

Scheme 1. Strategy for the synthesis of cyclopentenoids.

cyclopentenoids.[6,7] The synthetic strategy of cyclopentenones **3** using system **1** is outlined in Scheme 1. It usually involves stereoselective addition to the enone moiety of **1**, followed by further chemical transformations to introduce appropriate functionalities and then by thermal cycloreversion of the functionalized tricyclodecenones **2** using flash vacuum thermolysis (FVT). The availability of both antipodes of **1** in enantiopure form[6] completes this sequence for the enantioselective synthesis of a variety of cyclopentenoids. The concept of transient chirality has been extensively used,[6] whereby the stereocontrol of reactions with the bicyclic compounds **1** is of crucial importance.

Alkyl-substituted cyclopentenones are interesting compounds as many of them have a pleasant smell that makes them attractive targets for the perfume industry.[8] Notable examples are cyclopentenones **4**–**7** (Fig. 1). Racemic mixtures of these compounds are commercially used as fragrances. To gain further insight in the fundamentals of structure–odour relationship, it is desirable to study the fragrant properties of cyclopentenones and preferably those of its optical antipodes as well. These optically active alkyl-substituted cyclopentenoids are therefore ideal substrates for structure–odour relationship studies. All compounds contain similar substituents, but are quite different in molecular shape. Stereocontrolled synthesis of alkyl-substituted cyclopentenones is very difficult, but the combined use of the *endo*-tricyclo[5.2.1.$0^{2,6}$]decadienone system **1** with FVT is an attractive methodology for their synthesis (Scheme 1). Earlier, we reported the synthesis of a variety of substituted tricyclodecadienones **1** in a stereocontrolled and enantioselective manner that are suitable starting substrates in the approach depicted in Scheme 1. In this paper, the enantioselective synthesis of all possible stereoisomers of cyclopentenones **4**–**7** is reported.

Results and Discussion

Preparation of the Optically Active Tricyclodecadienone Precursors

The tricyclodecadienone system **1** is readily obtained in enantiopure form by two complimentary routes, both giving access to either antipode. The first route starts from the Herz ester (**10**)[9] that can be readily prepared by selective epoxidation of the enone moiety in Diels–Alder adduct **8** derived from cyclopentadiene and *p*-benzoquinone (Scheme 2), followed by a Favourskii ring contraction of the resulting tricyclic epoxide **9**.

Kinetic resolution of racemic tricyclic ester (+/−)-**10** with pig liver esterase (PLE) at room temperature in a 0.1 M phosphate buffer (pH 8) containing acetonitrile as co-solvent resulted in a slow hydrolysis reaction to give carboxylic acid (−)-**11** in excellent chemical yield and a high enantiopurity[10] (Scheme 3). The enantiopurity could be further improved by crystallization. The remaining ester (+)-**10** was obtained enantiopure after a repeated enzyme treatment. Alkaline hydrolysis of (+)-**10** resulted in the enantiopure antipode (+)-**11**.

The second synthetic route to preparing enantiopure tricyclodecadienone **1** starts from **12** (dimer of cyclopentadiene). Tricyclodecadienone **14** (**1**: R = H) was synthesized via two oxidation steps as depicted in Scheme 4. This sequence is in principle easier than that shown in Schemes 2 and 3, but product **14** lacks the functionality at the C_6 bridgehead position that is present in compound **10**. Enzymatic resolution was possible at the stage of *exo*-alcohol **13**[11], but was rather inefficient. The enzymatic resolution of the *endo*-alcohol **15** appeared to be a better choice[12] because purification could be carried out fast and the ultimate yields were higher despite the additional oxidation–reduction steps.

As shown in Scheme 5, treatment of racemic *endo*-alcohol (+/−)-**15** with Lipase PS (Amano) and vinyl acetate in *tert*-butyl methyl ether led to the enantioselective transesterification of (−)-**15** to acetate (−)-**16** in high optical yield. Acetate (−)-**16** could be easily separated from the remaining enantiopure alcohol (+)-**15**. Subsequent alkaline hydrolysis of (−)-**16** gave enantiopure alcohol (−)-**15**. Oxidation of antipodes (+)-**15** and (−)-**15** with manganese(IV) oxide in dichloromethane at room temperature yielded the enantiopure tricyclodecadienones (−)-**14** and (+)-**14**, respectively.

The carboxylic acid (+)-**11** is a convenient precursor for the modified Barton decarboxylation[13] en route to preparing 6-bromo-*endo*-tricyclo[5.2.1.$0^{2,6}$]decadienone (+)-(**18**).[14] This

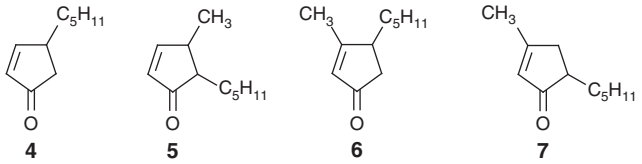
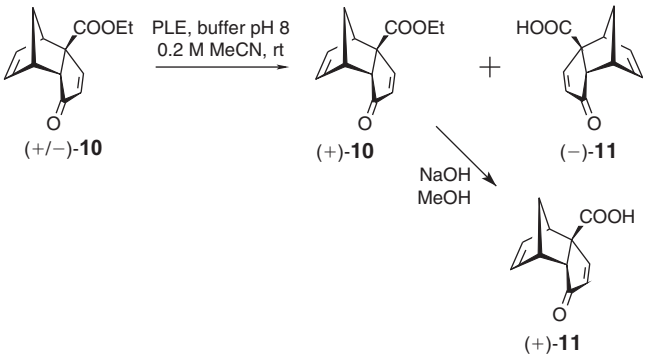
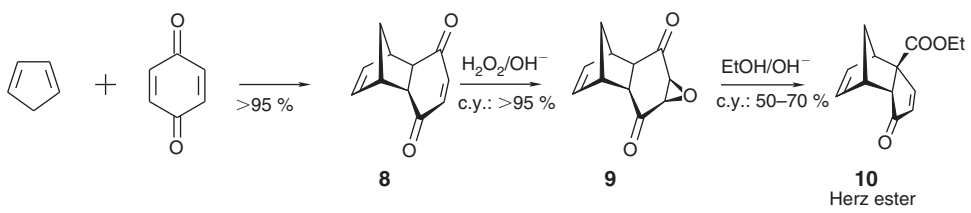


Fig. 1. Examples of cyclopentenones with fragrant properties.

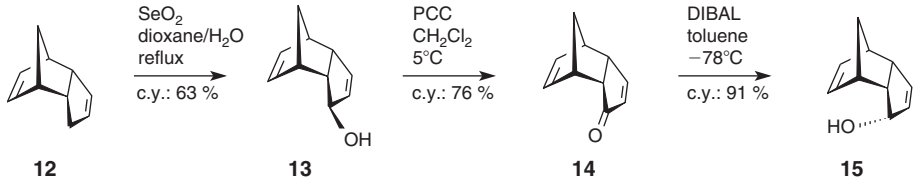


Scheme 3. Kinetic enzymatic resolution of the Herz ester.

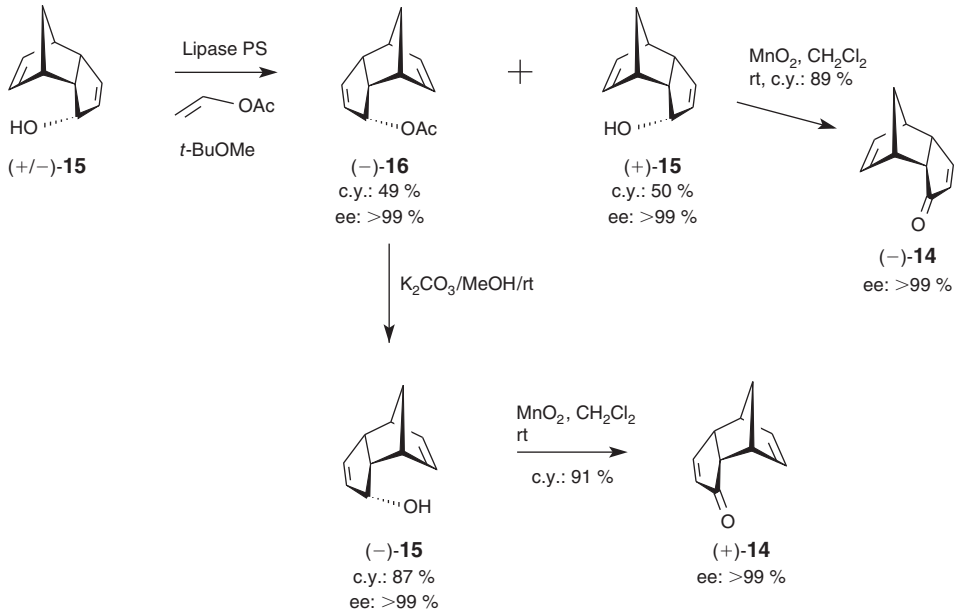


Scheme 2. Synthesis of the Herz ester.

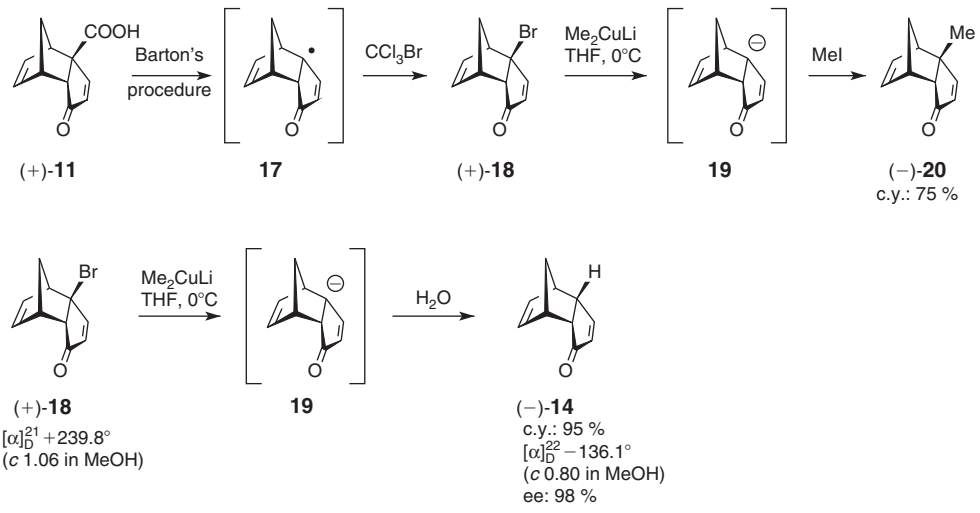
bromide can be either converted into the 6-methyl compound (−)-**20** or the parent ketone (−)-**14**. Treatment of enantiopure (+)-6-bromo-*endo*-tricyclo[5.2.1.$0^{2,6}$]decadienone (**18**) with lithium dimethylcuprate in THF led to bromine/metal exchange and formation of carbanion **19**. Quenching of **19** with methyl iodide afforded the methyl-substituted product **20**. The replacement of bromine in **18** was successfully observed for both antipodes, thus giving (+)- and (−)-**20**. Quenching of anion **19** with water gave tricyclodecadienone (−)-**14** (Scheme 6), which had the same optical rotation as (−)-**14** obtained via the route depicted in Scheme 5. The latter reaction connects both sets of synthetic routes (Schemes 2 and 3, and Schemes 4 and 5), thereby ensuring the correctness of the structures involved.



Scheme 4. Preparation of the *endo*-alcohol **15**.



Scheme 5. Kinetic resolution of the *endo*-alcohol (+/−)-**15**.



Scheme 6. Use of the Barton decarboxylation for the modification of the substituent at C_6.

The two antipodes of each respective compound **11**, **14**, and **20** are suitable starting materials for the preparation of the FVT precursor required for the synthesis of the cyclopentenones targets.

*Synthesis of the Two Antipodes of Enantiopure Cyclopentenones **4**–**7***

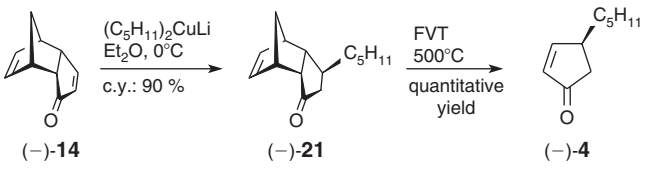
Retrosynthetically, the synthesis of γ-*n*-pentylcyclopentenone (**4**) requires 5-*n*-pentyltricyclodecadienone (**21**) as precursor (Scheme 7). The 5-alkylated tricyclic ketone was obtained, featuring complete *exo*-stereoselectivity by 1,4-addition of freshly prepared lithium di-*n*-pentylcuprate in diethyl ether to **14**. The observed *exo*-stereoselectivity of this addition reaction is entirely consistent with that observed for other lithium dialkyl cuprate additions to **14**.[15]

Thermal cycloreversion of **21** was carried out using FVT. Complete conversion was achieved at 500°C, giving the desired cyclopentenone **4** in quantitative yield (Scheme 7). The two antipodes of **4** were obtained in this way from enantiopure tricyclodecenones (−) and (+)-**21,** respectively. The level of stereochemical purity was maintained. Both antipodes of **4** had a penetrating but pleasant smell.

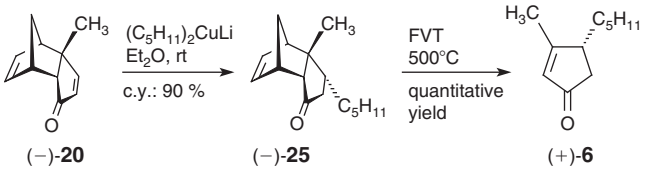
The synthetic sequence to preparing two of the four possible stereoisomers of cyclopentenone **5** is depicted in Scheme 8. Efforts to synthesize (−)-**23** from (−)-**14** in a three-component coupling process were unsuccessful in contrast to our expectations.[16] The sequence involving independent reaction steps is superior to the one-pot three-component version.

The required *exo*-5-methyltricyclodecenone (**22**) was readily prepared by addition of lithium dimethylcuprate to enone **14**. The precursor required for preparing *cis*-4-methyl-5-*n*-pentylcyclopentenone (**5a**) is *cis*-5-methyl-4-*n*-pentyltricyclodecenone (**23**). Its synthesis is not trivial as α-alkylation at the C_4 position from the *exo*-face in **22** may be sterically hampered by the adjacent 5-methyl group to such an extent that *endo*-alkylation is also feasible. Moreover, the use of a strong base to accomplish initial enolization at C_4 in **22** may lead to considerable epimerization at this position in *cis*-**23** on quenching with water during workup because *cis*-**23** is thermodynamically less stable than its epimer *trans*-dialkylated **24**. Fortunately, treatment of **22** with lithium dimethyl amide (LDA), followed by addition of *n*-pentyl iodide resulted in *cis*-4-*n*-pentyl-5-methyltricyclodecenone (**23**) in 55 % yield together with some dialkylated product and starting material (Scheme 8). No *trans* product was obtained at all. This finding shows that *cis*-alkylation of 5-*exo*-substituted tricyclodecenones, such as **22**, is quite possible despite enhanced steric hindrance from the *exo*-face of the cyclopentanone moiety. Also, the epimerization process is apparently too slow to disturb isolation of the *cis*-compound under normal workup conditions. Epimerization of *cis*-substituted (−)-**23** to (−)-**24** was readily accomplished by treatment with sodium methoxide in methanol at room temperature. The structures of both (−)-**23** and (−)-**24** were unambiguously established by 2D NMR analysis. *Cis*-disubstituted cyclopentenone (−)-**5a** was obtained by FVT of (−)-**23**. Both (−)-**23** and (−)-**5a** are sensitive to epimerization that would have occurred under acid-catalyzed retro Diels–Alder reactions, but is completely absent under FVT conditions. Thermolysis of (−)-**24** led to the *trans* compound (−)-**5b** as expected (Scheme 8).

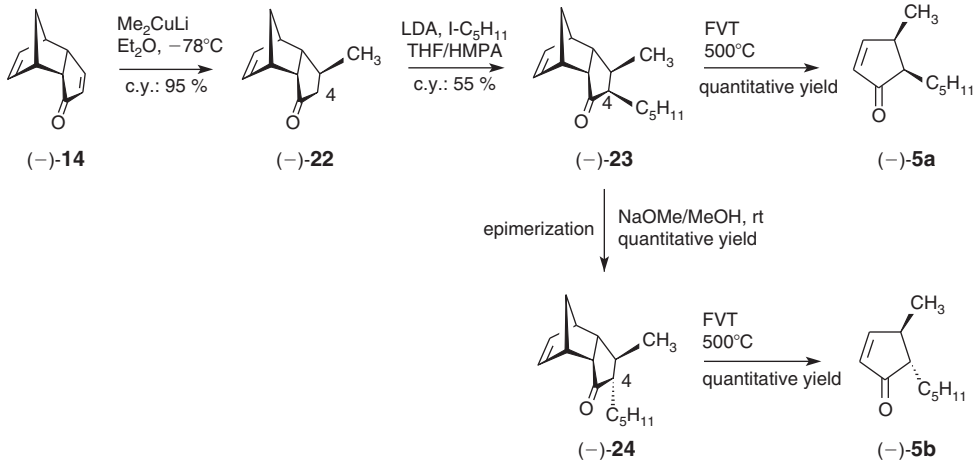
In contrast to the *exo*-face lithium dipentylcuprate addition to (−)-**14** (see Scheme 8), pentyl addition to **20** occurred exclusively at the *endo*-face (Scheme 9). In a different study,[17] we observed an *exo/endo* ratio of 1 : 1 for the addition reaction of dimethylcuprate to **20**. Thus, the complete *endo*-stereoselectivity observed in the present case is mainly caused by increased steric interactions between the larger di-*n*-pentylcuprate reagent and the 6-methyl substituent. Pyrolysis of (−)-**25** using FVT gave cyclopentenone (+)-**6** in quantitative yield (Scheme 9).



Scheme 7. Synthesis of γ-*n*-pentylcyclopentenone **4**.



Scheme 9. Synthesis of 3,4-disubstituted cyclopentenone **6**.



Scheme 8. Stepwise synthesis of 4,5-disustituted cyclopentenones **5**.

To accomplish the synthesis of cyclopentenone **7**, selective 1,4-reduction of 5-methyltricyclodecadienone (**20**) was required. However, this reduction proved to be impossible using standard procedures.[6,17–20] Attempted reduction of (−)-**20** with zinc in acetic acid under a variety of conditions did not result in the desired ketone (−)-**26** in contrast[19] to the fast zinc reduction of parent tricyclodecadienone **14**. Instead, similar issues to those of the 1,4-reduction with ester **10** were encountered. It seems that for the zinc/acetic acid 1,4-reduction, no functionality is allowed at the C_6 position in the tricyclodecadienone system. The reason for this is not clear. Treatment of (−)-**20** at low temperatures with $LiAlH_4$ gave only the 1,2-reduced product in contrast to the $LiAlH_4$ reduction of the Herz ester **10** that mainly led to the 1,4-reduction.[18] Improved results were obtained when calcium in ammonia was used. Consequently, the desired ketone (−)-**26** was isolated in good yields (Scheme 10).

Treatment of (−)-**26** with LDA, followed by quenching with *n*-pentyl iodide exclusively led to *exo*-substituted tricyclodecenone (−)-**27**. Cyclopentenone (−)-**7** was obtained in quantitative yields after FVT of (−)-**27** (Scheme 10).

Conclusion

Effective, stereocontrolled, and enantioselective syntheses of all possible stereoisomers and enantiomers of four cyclopentenones **4**–**7** were successfully performed. The fragrance properties of these optically pure cyclopentenones are very interesting and will be further explored in structure–odour relationship studies.

Experimental

General

Fourier transform infrared (FTIR) spectra were recorded on a Biorad WIN-IR FTS-25 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM-400, a Bruker AC-300, and a Bruker AC-100 at 298 K unless stated otherwise. Chemical shifts are reported relative to TMS. Mass spectrometry (MS) analyses were performed on a double focussing VG Analytical 7070E mass spectrometer. Gas chromatography mass spectrometry (GC–MS) analyses were performed using a Varian Saturn II GC-MS ion trap system, equipped with a Varian 8100 autosampler. Separation was carried out on a fused silica HP-1 capillary column (DB-5, 30 m × 0.25 mm). Helium was used as a carrier gas and electron impact (EI) was used as ionization mode. Optical rotations were measured on a Perkin–Elmer 241 polarimetre. Melting points were determined with a Reichert Thermopan microscope and are uncorrected. GC analyses were performed on a Hewlett Packard HP5890A or a Hewlett Packard HP5890II gas chromatograph (flame ionization detector, FID) using a capillary column (HP-1, 25 m × 0.32 mm × 0.17 µm) and nitrogen at 2 mL min^{-1} (0.5 atm) as the carrier gas. The GC temperature programs employed involved heating at either from 50°C (5 min isothermal) to 250°C at 15°C min^{-1} followed by 2 min at 250°C (isothermal) or from 100°C to 250°C at 15°C min^{-1} followed by 10 min at 250°C (isothermal). Analytical HPLC was performed with a Chiralcel OD (10 µm) cellulose carbamate column (Baker, 250 × 4.6 mm) using either isopropanol (^{i}PrOH) or ethanol and hexane mixtures as eluent. Column chromatography was carried out at ambient pressure on a Merck Kieselgel 60. Thin layer chromatography (TLC) was carried out on a Merck pre-coated silica gel 60 F254 plates (0.25 mm) using appropriate eluents. Spots were visualized under UV following reaction with I_2 or molybdate spray. Solvents were dried using the following methods: dichloromethane and hexane were distilled from calcium hydride, diethyl ether was distilled from sodium hydride, ethyl acetate was distilled from potassium carbonate, and toluene was distilled from sodium. THF was first distilled from calcium hydride and then from sodium with benzophenone as indicator under argon, directly before use. All other solvents were of analytical grade.

All experiments were routinely conducted in conjunction with GC and chiral HPLC to ensure chemical and optical purity of the compounds, respectively. In all cases the optical purity was ≥98 %.

*(1R,2R,6R,7S)-5-Oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-2-carboxylic acid (+)-(**11**)*

Compound (+)-**11** (8 g) was synthesized according to literature procedures[10] and its spectral data were in agreement with those reported. $[\alpha]_D^{21}$ +83.6° (*c* 1.03 in methanol (MeOH)); lit[10] $[\alpha]_D^{25}$ +85°, ee 98 %.

*(1S,2S,6S,7R)-5-Oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-2-carboxylic acid (−)-(**11**)*

Compound (−)-**11** (8 g) was synthesized according to literature procedures[10] and its spectral data were in agreement with those reported. $[\alpha]_D^{21}$ −82.5° (*c* 1.55 in MeOH); lit[10] $[\alpha]_D^{25}$ −83°, ee 99 %.

*(1S,2R,6S,7R)-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (−)-(**14**)*

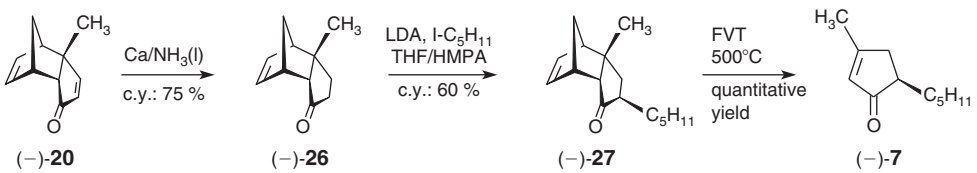
Compound (−)-**14** (10 g) was synthesized according to literature procedures[12] and its spectral data were in agreement with those reported. $[\alpha]_D^{21}$ −138.9° (*c* 1.86 in MeOH); lit[14] $[\alpha]_D^{25}$ −138.4°, ee >99 %.

*(1R,2S,6R,7S)-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (+)-(**14**)*

Compound (+)-**14** (10 g) was synthesized according to literature procedures[12] and its spectral data were in agreement with those reported. $[\alpha]_D^{21}$ +138.6° (*c* 0.99 in MeOH); lit[19] $[\alpha]_D^{25}$ +138.4°, ee >99 %.

*(1S,2S,6R,7R)-6-Bromotricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (+)-(**18**)*

Compound (+)-**18** (7 g) was synthesized according to literature procedures[15] and its spectral data were in agreement with those reported. mp >80°C (dec.). $[\alpha]_D^{21}$ +239.8° (*c* 1.06 in MeOH).



Scheme 10. Synthesis of 3,5-disubstituted cyclopentenones **7**.

*(1R,2R,6S,7S)-6-Bromotricyclo[5.2.1.0^{2,6}] deca-4,8-dien-3-one (−)-(**18**)*

Compound (−)-**18** was synthesized according to literature procedures[15] and its spectral data were in agreement with those reported. mp >80°C (dec.). $[\alpha]_D^{21}$ −232.4° (*c* 1.00 in MeOH); lit[15] $[\alpha]_D^{25}$ −222.4° (*c* 0.69 in MeOH).

*(1S,2R,6S,7R)-Tricyclo[5.2.1.0^{2,6}] deca-4,8-dien-3-one (−)-(**14**)*

The following experiment was carried out in dry THF under inert atmosphere. Lithium dimethylcuprate was prepared at 0°C by adding 1.6 M MeLi (1.5 mL, 2.4 mmol) to a suspension of CuI (0.230 g, 1.2 mmol) in THF (10 mL). After stirring for 15 min, (1*S*,2*S*,6*R*,7*R*)-6-bromotricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (+)-(**18**) {($[\alpha]_D^{21}$ +239.8° (*c* 1.06 in MeOH); 0.225 g, 1.0 mmol)} in THF (1 mL) was added slowly and the reaction mixture was then quenched with water (0.5 mL). After aqueous workup using standard procedures, the crude product was purified by column chromatography (ethyl acetate (EtOAc)/hexane 1 : 6). Finally, tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (−)-(**14**) (0.139 g, 0.95 mmol) was obtained as a white solid in 95 % yield and its spectral data were in agreement with those reported.[19] $[\alpha]_D^{22}$ −136.1° (*c* 0.80 in MeOH); lit[19] $[\alpha]_D^{25}$ −138.4°, ee 98 %.

*(1S,2R,6S,7R)-6-Methyltricyclo[5.2.1.0^{2,6}] deca-4,8-dien-3-one (−)-(**20**)*

Lithium dimethylcuprate was prepared at 0°C by adding 1.6 M MeLi (4.5 mL, 7.2 mmol) to a suspension of CuI (0.685 g, 3.6 mmol) in dry THF (30 mL) in an inert atmosphere. After stirring for 15 min, bromotricyclodecadienone (+)-**18** (0.675 g, 3.6 mmol) in THF (1 mL) was added slowly and the reaction mixture was then quenched with methyl iodide (2.1 mL, 30 mmol). After aqueous workup, using standard procedures, the crude product was purified by column chromatography (EtOAc/hexane = 1 : 6). Methyltricyclodecadienone (−)-**20** (0.365 g, 2.3 mmol) was obtained as a colourless oil (75 % yield). $[\alpha]_D^{20}$ −26.2° (*c* 0.98 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2967 (C–H), 2930 (C–H), 2870 (C–H), 1708 (C=O). δ_H ($CDCl_3$, 400 MHz) 7.24 (1H, d, $^3J_{5,4}$ 5.6, H_5), 5.95 (1H, br s, H_8), 5.90 (1H, br s, H_9), 5.84 (1H, d, $^3J_{4,5}$ 5.6, H_4), 3.22 (1H, br s, H_1), 2.57 (1H, brs, H_7), 2.44 (1H, d, $^3J_{2,1}$ 4.4, H_2), 1.92 (1H, d, $^2J_{10a,10s}$ 8.8, H_{10a}), 1.75 (1H, d, $^2J_{10s,10a}$ 8.8, H_{10s}), 1.45 (3H, s, CH_3). δ_C (H-dec, $CDCl_3$, 100 MHz) 210.7 (quat.), 169.1, 135.3, 134.4, 132.2, 58.0 (tert.), 53.8 (quat.), 51.0 (sec.), 50.0, 46.6 (tert.), 23.6 (prim.). *m/z* (EI) 160 (14 %, M^+), 145 (13 %, M^+–CH_3), 132 (37 %, M^+–CO), 117 (63 %, $C_9H_9^+$), 66 (100 %, $C_5H_6^+$). *m/z* 160.08878. HRMS Anal. Calc. for $C_{11}H_{12}O$ (M^+) 160.08882. *m/z* 117.07028. HRMS Anal. Calc. for $C_9H_9^+$ 117.07043.

*(1R,2S,6R,7S)-6-Methyltricyclo[5.2.1.0^{2,6}] deca-4,8-dien-3-one (+)-(**20**)*

The same procedure as that employed for the synthesis of (−)-**20** was used. Starting from bromotricyclodecadienone (−)-**18**, methyltricyclodecadienone (+)-**20** (0.370 g, 2.3 mmol) was obtained as a colourless oil (75 % yield). $[\alpha]_D^{21}$ +25.8° (*c* 1.00 in $CDCl_3$). Other physical data are identical to those of its antipode (−)-**20**.

*(1R,2S,6R,7S)-6-Methyltricyclo[5.2.1.0^{2,6}] dec-8-en-3-one (−)-(**26**)*

Calcium (0.500 g, 12.5 mat) was added to condensed NH_3 (25 mL) under an inert atmosphere at −50°C and stirred for 30 min. A solution of 6-methyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (−)-(**20**) (0.200 g, 1.25 mmol) in diethyl ether (1 mL) was slowly added to the reaction mixture. After 45 min, the reaction was complete and carefully quenched with saturated NH_4Cl(aq) (5 mL). Then, diethyl ether (10 mL) was added and the reaction mixture was allowed to reach room temperature while NH_3 evaporated. After aqueous workup using standard procedures the crude product was purified by column chromatography (EtOAc/hexane = 1 : 6). Methyltricyclodecenone (−)-**26** (0.152 g, 0.94 mmol) was obtained as a colourless oil (75 % yield). $[\alpha]_D^{23}$ −170.9° (*c* 0.94 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2963 (C–H), 2927 (C–H), 2876 (C–H), 1735 (C=O). δ_H ($CDCl_3$, 400 MHz) 6.32 (1H, dd, $^3J_{8,9}$ 5.7, $^3J_{8,7}$ 3.1, H_8), 6.12 (1H, dd, $^3J_{9,8}$ 5.7, $^3J_{9,1}$ 2.9, H_9), 3.16 (1H, br s, H_1), 2.64 (1H, br s, H_7), 2.40 (1H, d, $^3J_{2,1}$ 4.1, H_2), 2.27 (2H, m, H_4), 2.04 (2H, m, H_5), 1.72 (1H, d, $^2J_{10a,10s}$ 8.6, H_{10a}), 1.60 (1H, d, $^2J_{10s,10a}$ 8.6, H_{10s}), 1.39 (3H, s, CH_3). δ_C (H-dec, $CDCl_3$, 100 MHz) 222.0 (quat.), 137.4, 135.5, 62.5, 53.7 (tert.), 50.8 (sec.), 47.7 (quat.), 47.4 (tert.), 41.5 (sec.), 31.6 (sec.), 29.7 (prim.). *m/z* (EI) 162 (<1 %, M^+), 97 (100 %, M^+–C_5H_5), 66 (82 %, $C_5H_6^+$). *m/z* 162.10445. HRMS Anal. Calc. for $C_{11}H_{14}O$ (M^+) 162.10447.

*(1S,2R,6S,7R)-6-Methyltricyclo[5.2.1.0^{2,6}] dec-8-en-3-one (+)-(**26**)*

The same procedure as that used for the synthesis of enantiomer (−)-**26** was used. Starting from methyltricyclodecadienone (+)-**20**, methyltricyclodecenone (+)-**26** (0.155 g, 0.96 mmol) was obtained as a colourless oil (75 % yield). $[\alpha]_D^{21}$ +170.8° (*c* 0.86 in $CDCl_3$). Other physical data are identical to those of its antipode (−)-**26**.

*(1R,2S,5S,6R,7S)-5-*n*-Pentyltricyclo[5.2.1.0^{2,6}] dec-8-en-3-one (+)-(**21**)*

n-Pentyllithium (1.0 M) was prepared by dropwise addition of *n*-pentyl bromide (6.2 mL, 50 mmol) to diethyl ether (50 mL) containing Li metal (0.385 g, 55 mat) at room temperature under an inert atmosphere. Lithium di-*n*-pentylcuprate was prepared at 0°C by adding pentyllithium (3.6 mL, 3.6 mmol) to a suspension of CuI (0.342 g, 1.8 mmol) in diethyl ether (15 mL). After stirring for 15 min, the temperature was lowered to −78°C and tricyclodecadienone (+)-**14** (0.220 g, 1.5 mmol) in diethyl ether (1 mL) was added slowly. The reaction mixture was stirred for 30 min followed by quenching with water. After aqueous workup using standard procedures the crude product was purified by column chromatography (EtOAc/hexane 1 : 10). *n*-Pentyltricyclodecenone (+)-**21** (0.295 g, 1.35 mmol) was obtained as a colourless oil (90 % yield). $[\alpha]_D^{21}$ +125.1° (*c* 0.96 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2963 (C–H), 2927 (C–H), 2860 (C–H), 1734 (C=O). δ_H ($CDCl_3$, 400 MHz) 6.14 (2H, br s, H_8 + H_9), 3.16 (1H, br s, H_1), 3.02 (1H, br s, H_7), 2.92 (1H, m, H_2), 2.61 (1H, m, H_6), 2.21 (1H, dd, $^2J_{4n,4x}$ 18.5, $^3J_{4n,5n}$ 9.0, H_{4n}), 1.93 (1H, ddd, $^2J_{4x,4n}$ 18.5, $^3J_{4x,5n}$ 7.0, *J* 1.9, H_{4x}), 1.68 (1H, br s, H_{5n}), 1.55 (1H, d, $^2J_{10s,10a}$ 8.2, H_{10s}), 1.42 (1H, d, $^2J_{10a,10s}$ 8.2, H_{10a}), 1.28 (8H, br s, $C_4H_8CH_3$), 0.89 (3H, t, ^3J 7.0, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 221.0 (quat.), 136.1, 135.3, 54.8 (tert.), 52.3 (sec.), 48.8 (tert.), 48.3 (sec.), 47.1, 46.1 (tert.), 37.9 (sec.), 36.7 (tert.), 31.9, 27.2, 22.6 (sec.), 14.0 (prim.). *m/z* (EI) 218 (<1 %, M^+), 153 (100 %, M^+–C_5H_5), 66 (55 %, $C_5H_6^+$). *m/z* 218.1673. HRMS Anal. Calc. for $C_{15}H_{22}O$ (M^+) 218.1671.

*(1S,2R,5R,6S,7R)-5-*n*-Pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (−)-(**21**)*

The same procedure as that applied for the synthesis of enantiomer (+)-**21** was used. Starting from tricyclodecadienone (−)-**14**, *n*-pentyltricyclodecenone (−)-**21** (0.290 g, 1.33 mmol) was obtained as a colourless oil (90 % yield). $[\alpha]_D^{22}$ −126.0° (*c* 0.95 in $CDCl_3$). Other physical data were identical to those of its antipode (+)-**21**.

*(1S,2R,4R,5S,6R,7R)-5-Methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (−)-(**23**)*

Lithium dimethylcuprate was prepared by adding 1.6 M MeLi (4.5 mL, 7.2 mmol) to a suspension of CuI (0.690 g, 3.6 mmol) in diethyl ether (30 mL) at 0°C under an inert atmosphere. After stirring for 15 min, tricyclodecadienone (−)-**14** (0.435 g, 3.0 mmoL) in diethyl ether (2 mL) was added slowly and the reaction mixture was stirred for 30 min followed by quenching with water. After aqueous workup using standard procedures, the crude product was purified by column chromatography (EtOAc/hexane = 1 : 10). Methyltricyclodecenone (−)-**22** (0.450 g, 2.8 mmol) was obtained as a colourless oil (95 % yield). $[\alpha]_D^{21}$ −71.4° (*c* 1.26 in $CDCl_3$). Then, (−)-**22** (0.450 g, 2.8 mmol) was added to freshly prepared LDA (3 mmol) in THF (30 mL) with hexamethylphosphoramide (HMPA; 4 mL) as co-solvent at 0°C. After 30 min, excess *n*-pentyl iodide (3.65 mL, 28 mmol) was added and the reaction mixture was allowed to reach room temperature and stirred for 1 h. After aqueous workup using standard procedures, the crude product was purified by column chromatography (EtOAc/hexane = 1 : 10). Methyl-*n*-pentyltricyclodecenone (−)-**23** (0.360 g, 1.55 mmol) was obtained as a colourless oil (55 % yield). Methyltricyclodecenone (−)-**22** (35 %) and dialkylated product (10 %) were recovered. $[\alpha]_D^{21}$ −193.4° (*c* 1.28 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2962 (C–H), 2934 (C–H), 2871 (C–H), 1729 (C=O). δ_H ($CDCl_3$, 400 MHz) 6.21 (1H, dd, $^3J_{8,9}$ 5.7, $^3J_{8,7}$ 3.1, H_8), 6.14 (1H, dd, $^3J_{9,8}$ 5.7, $^3J_{9,1}$ 3.0, H_9), 3.18 (1H, br s, H_1), 3.04 (1H, br s, H_7), 2.91 (1H, dd, *J* 9.3, *J* 4.7, H_2), 2.45 (1H, dt, $^3J_{6,5}$ 9.3, $^4J_{6,CH3}$ 2.7, H_6), 2.02 (1H, m, H_{4n}), 1.98 (1H, m, H_{5n}), 1.52 (1H, d, $^2J_{10s,10a}$ 8.1, H_{10s}), 1.38 (1H, d, $^2J_{10a,10s}$ 8.1, H_{10a}), 1.23 (8H, br s, $C_4H_8CH_3$), 0.92 (3H, d, ^3J 7.0, CH_3), 0.87 (3H, t, ^3J 7.1, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 221.5 (quat.), 136.2, 135.1, 55.7, 53.1 (tert.), 52.6 (sec.), 48.4, 47.1, 46.7, 33.5 (tert.), 31.9, 27.4, 25.0, 22.5 (sec.), 18.1, 14.0 (prim.). *m*/*z* (EI) 232 (<1 %, M^+), 167 (100 %, M^+–C_5H_5), 97 (36 %, $C_6H_9O^+$), 96 (86 %, $C_6H_8O^+$), 66 (98 %, $C_5H_6^+$). *m*/*z* 232.18283. HRMS Anal. Calc. for $C_{16}H_{24}O$ (M^+) 232.18272.

*(1R,2S,4S,5R,6S,7S)-5-Methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (+)-(**23**)*

The same procedure as that applied for the synthesis of enantiomer (−)-**23** was used. Starting from tricyclodecadienone (+)-**14**, methyl-*n*-pentyltricyclodecenone (+)-**23** (0.360 g, 1.55 mmol) was obtained as a colourless oil (55 % yield). Methyltricyclodecenone (+)-**22** (35 %, $[\alpha]_D^{21}$ +171.0° (*c* 1.24 in $CDCl_3$)) and dialkylated product (10 %) were also recovered. (+)-**23**: $[\alpha]_D^{22}$ +197.4° (*c* 0.99 in $CDCl_3$). Other physical data were identical to those of its antipode (−)-**23**.

*(1R,2S,4R,5R,6S,7S)-5-Methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (+)-(**24**)*

To a solution of sodium (0.50 g, 22 mat) in methanol (25 mL) was added methyl-*n*-pentyltricyclodecenone (+)-**23** (0.175 g, 0.75 mmol), and resulting mixture was stirred overnight at room temperature. After aqueous workup using standard procedures epimerized product (+)-**24** (0.171 g, 0.74 mmol) was obtained as a colourless oil in quantitative yield. $[\alpha]_D^{22}$ +77.0° (*c* 0.79 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2959 (C–H), 2930 (C–H), 2867 (C–H), 1734 (C=O). δ_H ($CDCl_3$, 400 MHz) 6.14 (1H, dd, $^3J_{9,8}$ 5.7, $^3J_{9,1}$ 3.0, H_9), 6.02 (1H, dd, $^3J_{8,9}$ 5.7, $^3J_{8,7}$ 3.0, H_8), 3.13 (1H, br s, H_1), 3.03 (1H, br s, H_7), 3.03 (1H, br s, H_2), 2.49 (1H, m, H_6), 1.90 (1H, m, H_{4x}), 1.60 (1H, d, $^2J_{10s,10a}$ 8.3, H_{10s}), 1.45 (1H, d, $^2J_{10a,10s}$ 8.3, H_{10a}), 1.35 (1H, br s, H_{5n}), 1.30 (8H, br s, $C_4H_8CH_3$), 1.18 (3H, d, ^3J 6.6, CH_3), 0.86 (3H, t, ^3J 7.2, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 219.5 (quat.), 137.0, 135.6, 60.1, 55.2 (tert.), 52.5 (sec.), 48.2, 45.3, 44.4, 38.5 (tert.), 32.1, 27.1, 26.8, 22.5 (sec.), 21.4, 14.0 (prim.). *m*/*z* (EI) 232 (<1 %, M^+), 167 (99 %, M^+–C_5H_5), 97 (28 %, $C_6H_9O^+$), 96 (22 %, $C_6H_8O^+$), 66 (100 %, $C_5H_6^+$). *m*/*z* 232.18260. HRMS Anal. Calc. for $C_{16}H_{24}O$ (M^+) 232.18272.

*(1S,2R,4S,5S,6R,7R)-5-Methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (−)-(**24**)*

The same procedure as that applied for the synthesis of enantiomer (+)-**24** was used. Starting from methyl-*n*-pentyltricyclodecenone (−)-**23**, the epimerized product (−)-**24** (0.170 g, 0.73 mmol) was obtained as a colourless oil in quantitative yield. $[\alpha]_D^{21}$ −76.5° (*c* 1.09 in $CDCl_3$). Other physical data were identical to those of its antipode (+)-**24**.

*(1R,2S,5S,6R,7S)-6-Methyl-5-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (+)-(**25**)*

The same procedure as that applied for the synthesis of (+)-**21** was used. Starting from methyltricyclodecadienone (+)-**20** (0.240 g, 1.5 mmol),) (+)-**25** (0.315 g, 1.36 mmol) was obtained as a colourless oil (90 % yield). $[\alpha]_D^{21}$ +218.4° (*c* 0.80 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2964 (C–H), 2930 (C–H), 2860 (C–H), 1734 (C=O). δ_H ($CDCl_3$, 400 MHz) 6.35 (1H, dd, $^3J_{8,9}$ 5.7, $^3J_{8,7}$ 3.0, H_8), 6.03 (1H, dd, $^3J_{9,8}$ 5.7, $^3J_{9,1}$ 3.0, H_9), 3.12 (1H, br s, H_1), 2.64 (1H, br s, H_7), 2.47 (1H, d, $^3J_{2,1}$ 4.9, H_2), 2.23 (1H, dd, $^2J_{4n,4x}$ 18.0, $^3J_{4n,5x}$ 8.7, H_{4n}), 1.90 (1H, m, $^2J_{4x,4n}$ 18.0, $^3J_{4x,5x}$ 8.9, *J* 3.5, H_{4x}), 1.72 (1H, d, $^2J_{10a,10s}$ 8.5, H_{10a}), 1.63 (1H, br s, H_{5x}), 1.53 (1H, d, $^2J_{10s,10a}$ 8.5, H_{10s}), 1.36 (3H, s, CH_3), 1.30 (8H, br s, $C_4H_8CH_3$), 0.89 (3H, t, ^3J 6.8, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 221.3 (quat.), 137.6, 135.6, 63.0, 51.7 (tert.), 51.1 (sec.), 50.6 (quat.), 47.8 (sec.), 47.4, 45.3 (tert.), 32.1, 30.7 (sec.), 29.7 (prim.), 29.1, 22.6 (sec.), 14.0 (prim.). *m*/*z* (EI) 232 (<1 %, M^+), 167 (100 %, M^+–C_5H_5), 96 (10 %, $C_6H_8O^+$), 95 (10 %, $C_6H_7O^+$), 66 (37 %, $C_5H_6^+$). *m*/*z* 232.1828. HRMS Anal. Calc. for $C_{16}H_{24}O$ (M^+) 232.1827.

*(1S,2R,5R,6S,7R)-6-Methyl-5-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (−)-(**25**)*

The same procedure as that applied for the synthesis of enantiomer (+)-**25** was used. Starting from methyltricyclodecadienone (−)-**20**, (−)-**25** (0.313 g, 1.35 mmol) was obtained as a colourless oil (90 % yield). $[\alpha]_D^{21}$ −224.0° (*c* 1.04 in $CDCl_3$). Other physical data were identical to those of its antipode (+)-**25**.

*(1R,2S,4S,6R,7S)-6-Methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (+)-(**27**)*

To a freshly prepared reaction mixture of LDA (1 mmol) in THF (10 mL) and HMPA (1 mL) as co-solvent was added methyltricyclodecenone (+)-**26** (0.150 g, 0.93 mmol) at 0°C. After

30 min, excess *n*-pentyl iodide (1.3 ml, 10 mmol) was added, the reaction mixture was allowed to reach room temperature and stirred for 30 min. After aqueous workup using standard procedures, the crude product was purified by column chromatography (EtOAc/hexane = 1 : 10). Methyl-*n*-pentyltricyclodecenone (+)-**27** (0.130 g, 0.56 mmol) was obtained as a colourless oil in 60 % yield. Starting material (+)-**26** (10 %) and dialkylated product (30 %) were obtained as well. $[\alpha]_D^{21}$ +143.3° (*c* 0.55 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2960 (C–H), 2930 (C–H), 2859 (C–H), 1730 (C=O). δ_H ($CDCl_3$, 400 MHz) 6.35 (1H, dd, $^3J_{8,9}$ 5.7, $^3J_{8,7}$ 3.2, H_8), 6.07 (1H, dd, $^3J_{9,8}$ 5.7, $^3J_{9,1}$ 2.9, H_9), 3.16 (1H, br s, H_1), 2.61 (1H, br s, H_7), 2.42 (1H, d, $^3J_{2,1}$ 4.6, H_2), 2.02 (1H, m, H_{5n}), 1.96 (1H, m, H_{5x}), 1.68 (1H, d, $^2J_{10a,10s}$ 8.5, H_{10a}), 1.64 (1H, m, H_{4n}), 1.54 (1H, d, $^2J_{10s,10a}$ 8.5, H_{10s}), 1.33 (3H, s, CH_3), 1.21 (8H, br s, $C_4H_8CH_3$), 0.86 (3H, t, ^3J 7.2, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 223.3 (quat.), 137.2, 135.7, 63.0, 53.9, 52.1 (tert.), 50.6 (sec.), 48.3 (tert.), 45.1 (quat.), 39.4, 31.8, 31.1 (sec.), 30.5 (prim.), 27.1, 22.5 (sec.), 14.0 (prim.). *m/z* (EI) 232 (<1 %, M^+), 167 (100 %, M^+–C_5H_5), 96 (22 %, $C_6H_8O^+$), 66 (55 %, $C_5H_6^+$). *m/z* 232.18283. HRMS Anal. Calc. for $C_{16}H_{24}O$ (M^+) 232.18272.

*(1S,2R,4R,6S,7R)-6-Methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}] dec-8-en-3-one (−)-(**27**)*

The same procedure as that applied for the synthesis of enantiomer (+)-**27** was employed. Starting from methyltricyclodecadienone (−)-**26**, (−)-**27** (0.125 g, 0.54 mmol) was obtained as a colourless oil in 60 % yield. Starting material (−)-**26** (10 %) and dialkylated product (30 %) were obtained as well. $[\alpha]_D^{21}$ −145.1° (*c* 0.43 in $CDCl_3$). Other physical data were identical to those of its antipode (+)-**27**.

*(4S)-4-*n*-Pentyl-2-cyclopenten-1-one (−)-(**4**)*

FVT of (1*S*,2*R*,5*R*,6*S*,7*R*)-5*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (−)-(**21**) (0.220 g, 1.01 mmol) was carried out using the conventional methodology[16] (sublimation oven: 120°C, FVT oven: 500°C). Pure (4*S*)-4-*n*-pentyl-2-cyclopenten-1-one (−)-(**4**) (0.151 g, 0.99 mmol) was obtained as a colourless oil in quantitative yield. $[\alpha]_D^{21}$ −162.0° (*c* 2.33 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2960 (C–H), 2929 (C–H), 2858 (C–H), 1707 (C=O). δ_H ($CDCl_3$, 400 MHz) 7.64 (1H, dd, $^3J_{3,2}$ 5.6, $^3J_{3,4}$ 2.4, H_3), 6.14 (1H, dd, $^3J_{2,3}$ 5.6, $^4J_{2,4}$ 2.0, H_2), 2,92 (1H, br s, H_4), 2,52 (1H, dd, $^2J_{5,5}$ 18.8, $^3J_{5,4}$ 6.3, H_5), 2.10 (1H, dd, $^2J_{5,5}$ 18.8, $^3J_{5,4}$ 2.1, H_5), 1.57 (1H, br s, $C_4H_8CH_3$), 1.35 (7H, br s, $C_4H_8CH_3$), 0.90 (3H, t, ^3J 6.8, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 210.1 (quat.), 168.6, 133.6, 41.5 (tert.), 41.1, 34.7, 31.8, 27.3, 22.5 (sec.), 14.0 (prim.). *m/z* (EI) 153 (100 %, M^++H), 152 (11 %, M^+), 81 (4 %, M^+–C_5H_{11}). *m/z* 152.120114. HRMS Anal. Calc. for $C_{10}H_{16}O$ (M^+) 152.120130.

*(4R)-4-*n*-Pentyl-2-cyclopenten-1-one (+)-(**4**)*

Cyclopentenoid (+)-**4** was prepared in quantitative yield, using the same procedure as that described for (−)-**4**. $[\alpha]_D^{21}$ +158.7° (*c* 1.34 in $CDCl_3$). Other physical data were identical to those of its antipode (−)-**4**.

*(4R,5R)-4-Methyl-5-*n*-pentyl-2-cyclopenten-1-one (−)-(**5a**)*

FVT (sublimation oven: 120°C, FVT oven: 500°C) of (1*S*,2*R*,4*R*,5*S*,6*R*,7*R*)-5-methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}] dec-8-en-3-one (−)-(**23**) (0.162 g, 0.70 mmol) gave pure (−)-**5a** (0.115 g, 0.69 mmol) as a colourless oil in quantitative yield. $[\alpha]_D^{22}$ −147.8° (*c* 1.50 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2961 (C–H), 2933 (C–H), 2873 (C–H), 2860 (C–H), 1699 (C=O). δ_H ($CDCl_3$, 400 MHz) 7.60 (1H, dd, $^3J_{3,2}$ 5.7, $^3J_{3,4}$ 2.8, H_3), 6.11 (1H, dd, $^3J_{2,3}$ 5.7, $^4J_{2,4}$ 1.7, H_2), 3.10 (1H, m, H_4), 2.31 (1H, m, H_5), 1.75 (1H, br s, $C_4H_8CH_3$), 1.33 (7H, br s, $C_4H_8CH_3$), 1.08 (3H, d, ^3J 7.3, CH_3), 0.90 (3H, t, ^3J 6.8, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 211.9 (quat.), 168.5, 131.8, 49.5, 39.0 (tert.), 32.0, 28.1, 25.6, 22.5 (sec.), 15.8, 14.0 (prim.). *m/z* (EI) 167 (100 %, M^++H), 166 (8 %, M^+), 109 (8 %, M^+–C_4H_9), 96 (10 %, M^+–C_5H_{10}), 95 (8, M^+–C_5H_{11}). *m/z* 166.135790. HRMS Anal. Calc. for $C_{11}H_{18}O$ (M^+) 166.135764.

*(4S,5S)-4-Methyl-5-*n*-pentyl-2-cyclopenten-1-one (+)-(**5a**)*

Cyclopentenoid (+)-**5a** was prepared in quantitative yield, using the same procedure as that described for (−)-**5a**. $[\alpha]_D^{22}$ +149.6° (*c* 1.15 in $CDCl_3$). Other physical data were identical to those of its antipode (−)-**5a**.

*(4R,5S)-4-Methyl-5-*n*-pentyl-2-cyclopenten-1-one (−)-(**5b**)*

FVT (sublimation oven: 120°C, FVT oven: 500°C) of (1*S*,2*R*,4*S*,5*S*,6*R*,7*R*)-5-methyl-4-*n*-pentyltricyclo[5.2.1.0^{2,6}] dec-8-en-3-one (−)-(**24**) (0.162 g, 0.70 mmol) gave pure (4*R*,5*S*)-4-methyl-5-*n*-pentyl-2-cyclopenten-1-one (−)-(**5b**) (0.115 g, 0.69 mmol) as a colourless oil in quantitative yield. $[\alpha]_D^{22}$ −86.9° (*c* 1.50 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2961 (C–H), 2931 (C–H), 2873 (C–H), 2859 (C–H), 1698 (C=O). δ_H ($CDCl_3$, 400 MHz) 7.52 (1H, dd, $^3J_{3,2}$ 5.7, $^3J_{3,4}$ 2.4, H_3), 6.09 (1H, dd, $^3J_{2,3}$ 5.7, $^4J_{2,4}$ 1.9, H_2), 2,66 (1H, m, H_4), 1,86 (1H, m, H_5), 1.78 (1H, br s, $C_4H_8CH_3$), 1.33 (7H, br s, $C_4H_8CH_3$), 1.23 (3H, d, ^3J 7.3, CH_3), 0.89 (3H, t, ^3J 5.4, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 212.3 (quat.), 168.3, 132.5, 53.6, 42.8 (tert.), 31.9, 30.6, 27.0, 22.5 (sec.), 19.7, 14.0 (prim.). *m/z* (EI) 167 (100 %, M^++H), 166 (14 %, M^+), 109 (2 %, M^+–C_4H_9), 95 (1 %, M^+–C_5H_{11}). *m/z* 166.135790. HRMS Anal. Calc. for $C_{11}H_{18}O$ (M^+) 166.135764.

*(4S,5R)-4-Methyl-5-*n*-pentyl-2-cyclopenten-1-one (+)-(**5b**)*

Cyclopentenoid (+)-**5b** was prepared in quantitative yield, using the same procedure as that described for (−)-**5b**. $[\alpha]_D^{22}$ +89.8° (*c* 0.88 in $CDCl_3$). Other physical data were identical to those of its antipode (−)-**5b**.

*(4S)-3-Methyl-4-*n*-pentyl-2-cyclopenten-1-one (−)-(**6**)*

FVT (sublimation oven: 120°C, FVT oven: 500°C) of (1*R*,2*S*,5*S*,6*R*,7*S*)-6-methyl-5-*n*-pentyltricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (+)-**25** (0.230 g, 0.99 mmol) afforded pure (−)-**6** (0.163 g, 0.98 mmol) as a colourless oil in quantitative yield. $[\alpha]_D^{21}$ −32.5° (*c* 1.72 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2959 (C–H), 2931 (C–H), 2860 (C–H), 1684 (C=O). δ_H ($CDCl_3$, 400 MHz) 5.90 (1H, s, H_2), 2,75 (1H, br s, H_5), 2,53 (1H, dd, $^2J_{4,4}$ 18.6, $^3J_{4,5}$ 6.5, H_4), 2.10 (1H, d, $^2J_{4,4}$ 18.6, H_4), 2.08 (3H, s, CH_3), 1.75 (1H, br s, $C_4H_8CH_3$), 1.22 (7H, br s, $C_4H_8CH_3$), 0.89 (3H, t, ^3J 6.4, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 209.1, 181.7 (quat.), 130.7, 44.3 (tert.), 41.7, 32.5, 31.8, 26.7, 22.5 (sec.), 17.3, 14.0 (prim.). *m/z* (EI) 167 (100 %, M^++H), 166 (4 %, M^+), 109 (13 %, M^+–C_4H_9), 96 (6 %, M^+–C_5H_{10}), 95 (9 %, M^+–C_5H_{11}). *m/z* 166.135790. HRMS Anal. Calc. for $C_{11}H_{18}O$ (M^+) 166.135764.

*(4R)-3-Methyl-4-*n*-pentyl-2-cyclopenten-1-one (+)-(**6**)*

Cyclopentenoid (+)-**6** was prepared in quantitative yield, using the same procedure as that described for (−)-**6**. $[\alpha]_D^{21}$ +33.8° (*c* 2.50 in $CDCl_3$). Other physical data were identical to those of its antipode (−)-**6**.

*(5S)-3-Methyl-5-*n*-pentyl-2-cyclopenten-1-one (+)-(**7**)*

FVT (sublimation oven: 120°C, FVT oven: 500°C) of (1*R*,2*S*,4*S*,6*R*,7*S*)-6-methyl-4-*n*-pentyltricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (+)-(**27**) (0.114 m, 0.49 mmol) afforded pure (+)-**7** (0.079 g, 0.48 mmol) as a colourless oil in quantitative yield. $[\alpha]_D^{20}$ +32.2° (*c* 0.45 in $CDCl_3$). ν_{max} (CCl_4)/cm^{-1} 2959 (C–H), 2931 (C–H), 2858 (C–H), 1689 (C=O). δ_H ($CDCl_3$, 400 MHz) 5.90 (1H, s, H_2), 2,73 (1H, dd, $^2J_{4,4}$ 18.6, $^3J_{4,5}$ 6.6, H_4), 2,39 (1H, br s, H_5), 2.25 (1H, d, $^2J_{4,4}$ 18.6, H_4), 2.12 (3H, s, CH_3), 1.78 (1H, br s, $C_4H_8CH_3$), 1.31 (7H, br s, $C_4H_8CH_3$), 0.88 (3H, t, ^3J 6.5, $C_4H_8CH_3$). δ_C (H-dec, $CDCl_3$, 100 MHz) 212.3, 177.2 (quat.), 130.0, 46.8 (tert.), 39.9, 31.8, 31.4, 27.0, 22.5 (sec.), 19.4, 14.0 (prim.). *m/z* (EI) 167 (23 %, M^++H), 166 (4 %, M^+), 109 (30 %, M^+–C_4H_9), 96 (100 %, M^+–C_5H_{10}), 95 (21 %, M^+–C_5H_{11}). *m/z* 166.135790. HRMS Anal. Calc. for $C_{11}H_{18}O$ (M^+) 166.135764.

*(5R)-3-Methyl-5-*n*-pentyl-2-cyclopenten-1-one (−)-(**7**)*

Cyclopentenoid (−)-**7** was prepared in quantitative yield, using the same procedure as that described for (+)-**7**. $[\alpha]_D^{20}$ −33.1° (*c* 0.73 in $CDCl_3$). Other physical data were identical to those of its antipode (+)-**7**.

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