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Highly Effective and Practical Stereoselective Synthesis of New Homoallylic Alcohols with (+)-Camphor and (-)-Fenchone Skeleton

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Dedicated to Professor Dr. Manfred Hesse on the occasion of his 60th birthday

Abstract: The new chiral nonracemic homoallylic *exo*-alcohols 6, 7, 10 with (1R)-(+)-camphor (1) and *endo*-alcohols 8, 9, 11 with (1R)-(-)-fenchone (2) skeleton were synthesized in high yields by the stereoselective addition of allyl and substituted allylic *Grignard* reagents 3-5 to 1 and 2, respectively. The addition of the 2-butenyl (crotyl) reagent 5 occurred with high selectivity leading exclusively to α -methylallyl alcohol 10 with ketone 1 and to (Z)-2-butenyl alcohol 11 with ketone 2. The absolute configurations of the homoallylic alcohols 6-11 were determined by NMR methods.

INTRODUCTION

The naturally occurring (1R)-(+)-camphor (1) and (1R)- (-)-fenchone^{1,2} (2), as well as related bicyclic ketones³ have been used as chiral sources for the construction of optically active organic molecules and for the investigation of stereoselectivity problems. Recently compounds possessing camphor and fenchone skeleton have been an object of increased interest, since *Noyori*⁴ has applied (-)-dimethylamino isoborneol as highly effective catalyst for the enantioselective addition of zinc alkyls to aldehydes. This finding led to the synthesis of some camphor and fenchone derived aminoalcohols^{4a,5} and recently also of diols⁶ for use as ligands⁷ in asymmetric reactions. The synthetic application of 1 and 2 for addition reactions with organometallic reagents has been studied in isolated cases², due to the low reactivity of these ketones towards some organometallic reagents has been shown to provide better results^{2,10}.

Related to our interest in synthetic applications based on 1 and 2, we now report a very effective synthesis of new optically active tertiary homoallylic alcohols *via* the addition of allylic *Grignard* reagents to these ketones. The stereoselectivities, remarkable particularly in the case of 2-butenylmagnesium bromide addition, were studied. The synthesized homoallylic alcohols are highly useful compounds for a number of further transformations, e.g. we have recently applied some of them for the synthesis of optically active 1,3-diols¹¹.

RESULTS AND DISCUSSION

The addition of the allylic *Grignard* compounds 3-5 to camphor (1) and fenchone (2) proceeded rapidly and quantitatively between -20°C and room temperature (*Scheme 1*). The reactions of reagents 3-5 with 1 and 2 were complete within 1 h at room temperature (in some protocols after 15 min). Contrary to the addition of alkyl, aryl and vinyl *Grignard* reagents¹⁰ the assistance of anhydrous CeCl₃ was not necessary¹². The homoallylic alcohols 6-11 were isolated on a multigramm scale in yields up to 97% after distillation. In reactions with 1 the attack of the reagents occurred exclusively from the *endo*-side with formation of the *exo*alcohols 6, 7 and 10. In the case of 2 an *exo*-attack was preferred, however, *endo*-attack was also observed. Our present investigations and recently reported results¹⁰ show that the unfavourable *endo*-attack to 2 depends on the entering group R, e.g. $R = vinyl (exo/endo = 91:9)^{10}$, allyl (8a/8b = 92:8). 2-methylallyl (9a/9b =82:18) and phenyl (*exo/endo* = 17:83)¹⁰. In previous reports^{8c,f} the addition of organometallic reagents to 2 has been described to proceed 100% from the *exo*-side. Actually, there are only two examples (addition of CH₃MgI and Me₂NCH₂CH₂CH₂CH₂Li)¹⁰ showing 100% *exo*-addition to ketone 2.

The observed selectivity allowed the absolute configuration to be defined as 1R, 2R-6, 1R, 2S-7 and 1R, 2S-10 for the campbor derived alcohols, and predominantly 1R, 2R-8, 1R, 2R-9, and 1R, 2R-11 for the fenchone derived alcohols, respectively.

Interestingly the addition of 2-butenylmagnesium bromide (5) to ketone 1 afforded only *endo*- α -methylallyl alcohol 10 (10a/10b = 66:34 by NMR), whereas to ketone 2 - only the linear (crotyl) alcohol 11, being to our knowledge, the first example of exclusively (Z)-2-butenyl product obtained by a *Grignard* addition to a ketone. An *endo*-attack to 2 was not observed in this case (based on NMR spectra of the crude product). The only example for the exclusive formation of a crotyl product, however with Z/E-ratio = 61:39, has been reported¹³ in the reaction of 2-butenyl *Grignard* reagent with di-t-butyl ketone. It has been previously found for the regioselectivity with respect to the allylic moiety, that the addition of 2-butenylmagnesium reagents to unhindered ketones provides α -methylallyl (*syn* and *anti*) products, whereas that to sterically hindered ketones - predominantly crotyl (*cis* and *trans*) products^{14,15}, which is due to the structure of allylic magnesium compounds in solution¹⁶. Therefore during the addition of 5, ketone 1 reacts as a sterically unhindered, whereas ketone 2 - as a sterically hindered one.

To investigate whether it is possible to obtain crotyl product with ketone 1, we added 2-butenylcerium reagent to 1, since it has been shown that unsymmetrically substituted allylcerium reagents react at -78° C even with aldehydes at the less substituted allylic terminus giving linear homoallyl alcohols¹⁷. We prepared *in situ* (2-butenyl)CeCl₂ at -78° C and allowed it to react with ketone 1 at this temperature. After hydrolysis and workup, only the branched alcohol 10 was isolated without change of the ratio 10a/10b. The same results were obtained after addition of (2-butenyl)CeCl₂ to 1 at -20° C, as well as after the reaction of CeCl₃-complexed ketone 1 with reagent 5 at room temperature.

The diastereoisomers 10a and 10b were separated by column chromatography and studied by NMR. NOE difference proved the absolute configuration of the newly formed chiral centre as 11R and 11S in 10a and 10b, respectively, taking into account the known 1R,2S-configuration. After irradiation of the C-10 methyl protons, nuclear Overhauser enhancements in 10a were observed for the C-14 protons, whereas in 10b - for the C-12 protons (see *Scheme 1*). Force field calculations show that in both diastereoisomers a single conformer predominates, in which the proton at C-11 (as sterically least demanding) is directed to the camphor

ring. These observations allowed the faster eluting diastereoisomer to be determine as 1R, 2S, 11R-10a (see Experimental Section). For the homoallylic alcohol 11, the highly shielded C-11 and C-14 proved the (Z)-configuration of the crotyl group (*Table 1*).





In connection with the regioselectivity reported above, it was interesting to check reaction of the highly hindered bis(1-norbornyl)ketone¹⁸ (12) with reagent 5. Surprisingly 12 did not react with 5 even with extended reaction time (10h) at room temperature. Applying our procedure¹⁰ for activation of 12 with stoichiometric amount of CeCl₃ at room temperature, a quantitative addition of 5 was achieved within 3h (*Scheme 2*). However, the reaction did not proceed selectively resulting the *Z*- and *E*-crotyl alcohols 13a and 13b, as well as the α -methylallyl product 13c, in contrast to the crotyl selectivity with the related di-t-butyl ketone¹³. The attempts to achieve the activation of ketone 12 with catalytic amounts (5 mol %) of CeCl₃ afforded only 64% conversion of 12, however, the ratio being in this case 13a/13b/13c = 3.5:1:2. It is difficult to discuss these results, since the reaction with 5 mol % CeCl₃ obviously occurs *via* the catalytic mediation of *in situ* formed alkoxycerium(III) species¹⁰, the mode of the addition being probably different from the case when stoichiometric amounts of CeCl₃ are used.



Scheme 2

For compounds 6-11 and 13 unambiguous assignment of the proton and carbon-13 spectra (*Table 1*) was made on the basis of COSY, DEPT and C-H correlation experiments. Most of the protons from the camphor and fenchone moiety of the molecules resonated in a close range of chemical shifts (± 0.1 ppm) irrespectively of the substituents as follows: $\delta = 1.95$ (H-3_{exo}), 1.70 (H-5_{exo}, H-4), 1.35 (H-6), 1.00 (H-5_{endo}) for *exo*-OH camphor derivatives; $\delta = 2.00$ (H-6_{endo}), 1.65 (H-5_{endo}, H-4, H-7_{syn}), 1.40 (H-5_{exo}), 1.10 (H-7_{anti}), 1.00 (H-6_{exo}) for *endo*-OH fenchone derivatives. The specific assignments for the other protons are given in the experimental section.

In conclusion, we have demonstrated an effective stereoselective synthesis of optically active homoallylic alcohols in high yields in a multigramm scale, which are of practical interest for further transformations¹¹.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in flame-dried *Schlenk* flasks under argon atmosphere. The solvent THF was dried and freshly distilled from sodium/benzophenone. Thin layer chromatography (TLC): aluminium sheets precoated with silica gel 60 F_{254} (Merck). Column chromatography: at normal pressure silica gel 60 (0.040-0.063 mm, Merck). $[\alpha]_D^{20}$: Perkin-Elmer 241 polarimeter. Mass spectra (MS): Jeol-JMS-D-300 spectrometer; fragment ions in *m/z* with relative intensities (%) in parentheses. NMR spectra: Bruker AVANCE DRX-250 (¹H at 250.1 MHz; ¹³C at 62.9 MHz; TMS as internal standard); standard BRUKER library programs (cosy45, dept135, dept90, hxdepttp and noemul) were used; the samples for the NOE difference experiments were prepared by blowing argon through the CDCl₃ solution for 10 minutes; the individual lines in the multiplet were irradiated for 0.1s maintaining the whole irradiation time to be 5s; the irradiation power was adjusted to suppress approximately 80% of the multiplet intensity. Elemental analyses were performed by the Microanalytical Service Laboratory of the Institute of Organic Chemistry.

Starting Materials. The following starting materials (commercially available or prepared according to the literature) were used: (1R)-(+)-camphor (Fluka AG), (1R)-(-)-fenchone (Fluka AG), bis(1-norbornyl)ketone¹⁸, allylmagnesium chloride¹⁹ (3) 1.36 M in THF, (2-methyl)-allylmagnesium chloride¹⁹ (4) 0.95 M in THF, 2-butenylmagnesium bromide¹⁹ (5) 0.33 M in THF, anhydrous CeCl₃¹⁰.

| lable 1. | ¹³ C NMR chemical shifts of compounds 6-11 and 13 (CDCl ₃ , 300K, δ in <i>ppm</i> from TMS); assignments marked with |
|----------|--|
| | asterisks are tentative. For the numbering of the C-atoms, see Scheme 1. |

| 13c | 58.70 | 31.72* | 31.15* | 34.80 | 30.89* | 31.29* | 41.52 | 77.64 | 49.50 | 115.52 | 143.42 | 18.52 | | | |
|------------------|-------|--------|--------|-------|--------|--------|-------|-------|-------|--------|--------|--------|--------|-------|----------------|
| 13b ^a | 58.75 | 32.72* | 30.30* | 34.77 | 30.21* | 32.65* | 41.68 | 75.25 | 39.11 | 128.58 | 129.38 | 18.19 | , | • | 2 nnm |
| 13a ^a | 58.91 | 31.96* | 31.10* | 34.97 | 30.90* | 31.37* | 41.39 | 76.20 | 33.39 | 127.10 | 127.64 | 13.21 | | 1 | ances up to () |
| 11 | 52.18 | 80.03 | 44.03 | 49.84 | 24.93 | 30.39 | 40.79 | 27.41 | 20.50 | 17.80 | 33.26 | 127.03 | 127.45 | 12.90 | chift differ |
| 10b ^b | 52.69 | 81.98 | 45.96 | 44.44 | 27.45 | 29.29 | 50.07 | 21.35 | 21.00 | 11.92 | 46.25 | 141.37 | 114.14 | 15.47 | le chemical |
| 10ab | 52.33 | 80.76 | 47.23 | 44.60 | 27.58 | 29.63 | 50.25 | 21.37 | 20.92 | 12.18 | 46.93 | 141.31 | 115.86 | 14.70 | omnoo l |
| 9ba | 53.38 | 80.77 | 45.73 | 49.08 | 25.74 | 30.30 | 41.63 | 24.41 | 25.38 | 16.70 | 39.51 | 144.07 | 114.60 | 25.57 | e individua |
| 9a ^a | 53.38 | 81.28 | 44.15 | 50.38 | 25.08 | 30.10 | 40.61 | 27.65 | 22.65 | 17.79 | 43.07 | 144.58 | 112.51 | 25.74 | shifts for th |
| 8b ^a | 52.68 | n.o. | 45.28 | 49.13 | 25.74 | 30.55 | 41.50 | 24.03 | 25.95 | 16.83 | 37.02 | 135.23 | 118.78 | T | bChemical |
| 8aa | 52.24 | 79.34 | 44.32 | 49.99 | 24.97 | 30.55 | 40.95 | 27.67 | 22.56 | 18.01 | 40.64 | 135.79 | 119.26 | • | ric mixmre |
| 7 | 52.89 | 78.17 | 47.14 | 45.41 | 27.08 | 29.92 | 48.55 | 21.42 | 20.90 | 10.20 | 47.25 | 143.68 | 115.66 | 24.17 | r the isome |
| 6 | 52.44 | 79.93 | 46.27 | 45.33 | 27.30 | 30.81 | 49.65 | 21.66 | 21.21 | 11.17 | 44.80 | 135.24 | 119.09 | T | cal shifts fo |
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | C-11 | C-12 | C-13 | C-14 | aChemi |

vidual compounds; chemical shift differences up to 0.3 ppm Ę 3 CITIC ł 5 Chemical shifts for the isometic mixture. were observed for the isomeric mixture. General Procedure (GP): Addition of allylmagnesium halides 3-5 to (1R)-(+)-camphor (1) and (1R)-(-)-fenchone (2): The pure ketone 1 or 2 was added to a stirred solution in THF of the corresponding allylmagnesium halide at -20°C. The mixture was allowed to warm to room temperature within ca. 30 min and was stirred at this temperature for 1 h. After hydrolysis with 2 N HCl was extracted with petroleum ether, the combined org. phases were washed with 5% NaHCO₃, and then with water, dried over MgSO₄, and evaporated. The crude product was distilled.

(1*R*,2*R*)-2-exo-Hydroxy-2-endo-allyl-1,7,7-trimethylbicyclo[2.2.1]heptane (6). Following *GP*, 6 was prepared from 87.65 ml (119.20 mmol) 1.36 M solution of 3 in THF and 17.24 g (113.27 mmol) of 1. Yield after distillation (b.p. 50°C/1 Torr) 21.41 g (97%) of 6 as colourless liquid. $[\alpha]_D^{20}$ +4.1 (c 3.95, CHCl₃), $[\alpha]_D^{20}$ -17.7 (4.00, EtOH). Anal. calc. for C₁₃H₂₂O (194.3): C, 80.35; H, 11.41; found: C, 80.15; H, 11.52. MS (70 eV) *m*/z (rel. int.): 194 (M⁺,7), 153 (40), 135 (8), 109 (29), 95 (100), 81 (7), 69 (32), 55 (18), 41 (42). ¹H NMR (CDCl₃, 300K): δ = 5.94 (m, 1H, H-12), 5.16 (d, 1H, H-13, J = 10.5 Hz), 5.14 (d, 1H, H-13, J = 17.0 Hz), 2.36-2.22 (m, 2H, H-11), 1.41 (d, 1H, H-3_{endo}) 1.10 (s, 3H, H-8), 0.86 (s, 3H, H-9), 0.85 (s, 3H, H-10).

(1*R*,2*S*)-2-*exo*-Hydroxy-2-*endo*-(2-methylallyl)-1,7,7-trimethylbicyclo[2.2.1]heptane (7). Following *GP*, 7 was prepared from 53.80 ml (51.10 mmol) 0.95 M solution of 4 in THF and 7.39 g (48.55 mmol) of 1. Yield after distillation (b.p. 54°/1 Torr) 9.80 g (97%) of 7 as colourless liquid. $[\alpha]_D^{20}$ +24.2 (c 4.16, CHCl₃), $[\alpha]_D^{20}$ +11.1 (c 4.10, EtOH). Anal. calc. for C₁₄H₂₄O (208.3): C, 80.71; H, 11.61; found: C, 80.58; H 11.53. MS (70 eV) *m*/*z* (rel. int.): 208 (M⁺, 13), 193 (20), 153 (100), 109 (40), 95 (80), 81 (40), 69 (83), 55 (34), 41 (68). ¹H NMR (CDCl₃, 300K): δ = 4.95 (br s, 1H, H-13), 4.79 (br s, 1H, H-13), 1.83 (s, 3H, H-14), 1.58 (d, 1H, H-3_{*endo*}) 1.10 (s, 3H, H-8), 0.86 (s, 3H H-9), 0.84 (s, 3H, H-10).

(1*R*,2*R*)-2-endo-Hydroxy-2-exo-allyl-1,3,3-trimethylbicyclo[2.2.1]heptane (8). Following *GP*, 8 was prepared from 10.96 ml (14.90 mmol) 1.36 M solution of 3 in THF and 2.15 g (14.13 mmol) of 2. Yield after distillation (b.p. 58°/1 Torr) 2.50 g (91%) of 8 as colourless liquid. $[\alpha]_D^{20}$ -32.8 (c 4.03, CHCl₃). Anal. calc. for C₁₃H₂₂O (194.3): C, 80.35; H, 11.41; found: C, 80.40; H, 11.32. MS (70 eV) *m/z* (rel. int.): 194 (M⁺, 18), 179 (4), 153 (39), 135 (40), 112 (24), 109 (18), 95 (22), 81 (89), 69 (100), 55 (33), 41 (63). ¹H NMR (CDCl₃, 300K): $\delta = 6.02$ (m, 1H, H-12), 5.16 (br. d, 1H, H-13, J = 11.3 Hz), 5.15 (br. d, 1H, H-13, J = 16.1 Hz), 2.43 (dd, 1H, H-11, J = 14.0, 6.1 Hz), 2.22 (dd, 1H, H-11, J = 14.0, 8.0 Hz), 1.09 (s, 3H, H-8), 1.02 (s, 3H, H-10), 0.92 (s, 3H, H-9).

(1*R*,2*R*)-2-endo-Hydroxy-2-exo-(2-methylallyl)-1,3,3-trimethylbicyclo[2.2.1]heptane (9). Following *GP*, 9 was prepared from 161.05 ml (153.00 mmol) 0.95 M solution of 4 in THF and 21.18 g (139.16 mmol) of 2. Yield after distillation (b.p. 72°/1 Torr) 26.61 g (92%) of 9 as colourless liquid. $[\alpha]_D^{20}$ -9.1 (c 3.96, CHCl₃). Anal. calc. for C₁₄H₂₄O (208.3): C, 80.71; H, 11.61; found: C, 80.83; H, 11.50. MS (70 eV) *m/z* (rel. int.): 208 (M⁺, 4), 193 (3), 153 (23), 125 (24), 109 (17), 95 (15), 81 (100), 69 (73), 55 (30), 41 (33). ¹H NMR (CDCl₃, 300K) for **9a/9b = 82**:18: **9a**: δ = 5.04 (br. s, 1H, H-13), 4.86 (br. s, 1H, H-13), 1.80 (s, 3H, 30).

¹H NMR (CDCl₃, 300K) for **9a/9b** = 82:18: **9a**: δ = 5.04 (br. s,1H, H-13), 4.86 (br. s, 1H, H-13), 1.80 (s, 3H, H-14), 1.08 (s, 3H, H-8), 1.01 (s, 6H, H-9, H-10). **9b** δ = 4.91 (br. s, 1H, H-13), 4.86 (br. s, 1H, H-13), 1.84 (s, 3H, H-14), 1.12 (s, 3H, H-8), 1.04 (s, 6H, H-9, H-10).

2-exo-Hydroxy-2-endo-(1-methylallyl)-1,7,7-trimethylbicyclo[2.2.1]heptane (10). Following *GP*, 10 was prepared from 87.88 ml (29.00 mmol) 0.33 M solution of **5** in THF and 3.39 g (22.27 mmol) of **1**. Yield after distillation (b.p. 58°/1 Torr) 4.04 g (87%) of **10** as colourless liquid (1R,2S,11R-10a/1R,2S,11S-10b = 66:34 by ¹H NMR). Anal. calc. for C₁₄H₂₄O (208.3): C, 80.71; H, 11.61; found: C, 80.90; H, 11.58. MS (70 eV) *m/z* (rel. int.): 208 (M⁺, 9), 153 (100), 135 (10), 125 (9), 109 (28), 95 (48), 81 (10), 69 (32), 55 (21), 42 (23), 41 (17). Separation by column chromatography (Ø 32 mm, 175 g silica gel, hexane/Et₂O = 30:1); from 2.10 g crude **10** were obtained 0.93 g **10a**, 0.53 g mixed fractions and 0.31 g **10b** (corresponding to 91% overall yield of **10** when isolated by chromatography).

Data of (1*R***,2***S***,11***R***)-10a: [\alpha]_D^{20} + 9.85 (c 4.18, CHCl₃). ¹H NMR (CDCl₃, 300K): \delta = 6.06 (ddd, 1H, H-12, J = 17.3, 10.6, 6.7 Hz), 5.15 (m, 1H, H-13), 5.09 (m, 1H, H-13), 2. 38 (q, 1H, H-11, J = 6.8 Hz), 1.55 (d, 1H, H-3_{endo}, J = 13.0 Hz) 1.07 (s, 3H, H-8), 1.07 (d, 3H, H-14, J = 6.8 Hz), 0.95 (s, 3H, H-10), 0.83 (s, 3H, H-9). Data of (1***R***,2***S***,11***S***)-10b: [\alpha]_D^{20} -14.01 (c 4.23, CHCl₃). ¹H NMR (CDCl₃, 300K): \delta = 6.00 (m, 1H, H-12), 5.08-5.00 (m, 2H, H-13), 2.41 (q, 1H, H-11, J = 6.9 Hz), 1.43 (d, 1H, H-3_{endo}, J = 13.2 Hz) 1.06 (s, 3H, H-8), 1.05 (d, 3H, H-14, J = 6.9 Hz), 0.87 (s, 3H, H-10), 0.82 (s, 3H, H-9).**

(1*R*,2*R*)-2-endo-Hydroxy-2-exo-((Z)-2-butenyl)-1,3,3-trimethylbicyclo[2.2.1]heptane (11). Following *GP*, 11 was prepared from 55.15 ml (18.20 mmol) 0.33 M solution of **5** in THF and 2.65 g (17.41 mmol) of **2**. Yield after distillation (b.p. 62°/1 Torr) 2.70 g (74%) of 11 as colourless liquid. $[\alpha]_D^{20}$ -18.4 (c 4.01, CHCl₃). Anal. calc. for C₁₄H₂₄O (208.3): C, 80.71; H, 11.61; found: C, 80.95; H, 11.48. MS (70 eV) *m/z* (rel. int.): 208 (M⁺, 63), 193 (4), 153 (100), 135 (12), 125 (70), 109 (19), 95 (17), 81 (62), 69 (68), 55 (29), 42 (32), 41 (30). ¹H NMR (CDCl₃, 300K): δ = 5.80-5.50 (m, 2H, H-12, H-13), 2.40-2.22 (m, 2H, H-11), 1.64 (d, 3H, H-14, J = 6.0 Hz), 1.07 (s, 3H, H-8), 1.02 (s, 3H, H-10), 0.94 (s, 3H, H-9).

Butenyl-bis(bicyclo[2.2.1]hept-1-yl)methanol (isomer mixture 13). To 0.020 g (0.81 mmol) anhydrous CeCl₃ placed in a *Schlenk* flask was added 0.17 g (0.78 mmol) of ketone 12 in 7 ml THF and the mixture was stirred for 40 min at room temperature. The reagent 5, 2.70 ml (0.89 mmol) 0.33 M solution in THF was added at room temperature and then stirred for 3h. The mixture was quenched with 2 N HCl and extracted with petroleum ether. The combined org. phases were washed with 5% NaHCO₃ and then with water, dried over MgSO₄, and evaporated. The crude product was chromatographed (flash, Ø 13 mm, 15 g silica gel, hexane/Et₂O = 50:1); from 0.23 g crude 13 were obtained 0.047 g fraction (13b/13c = 1:1.7), 0.100 g fraction (13a/13b/13c = 2.3:1.5:1), 0.020 g fraction (13a/13b/13c = 5:1:1) and 0.025 g of pure 13a (corresponding to 90% overall yield of 13). Anal. calc. for C₁₉H₃₀O (274.5): C, 83.15; H, 11.02; found: C, 83.42; H, 10.92. MS (70 eV) *m/z* (rel. int.): 274 (M⁺, 1), 219 (100), 123 (32), 95 (55), 81 (10), 67 (17), 55 (14), 41 (11). ¹H NMR (CDCl₃, 300K): 13a: $\delta = 5.67-5.61$ (m, 2H, H-10, H-11), 2.54-2.52 (m, 2H, H-9), 1.66 (d, 3H, H-12, J = 6.0 Hz). 13b: $\delta = 5.55-5.45$ (m, 2H, H-10, H-11), 2.46 (d, 2H, H-9, J = 6.5 Hz). 13c: $\delta = 6.16-6.02$ (m, 1H, H-10), 5.06-5.00 (m, 2H, H-11), 2.81 (q, 1H, H-9, J = 7.6 Hz), 1.26 (d, 3H, H-12, J = 7.0 Hz).

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