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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 (1*R*)-(+)-camphor (**1**) and *endo*-alcohols **8**, **9**, **11** with (1*R*)-(-)-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 (1*R*)-(+)-camphor (**1**) and (1*R*)- (-)-fenchone[1,2] (**2**), as well as related bicyclic ketones[3] 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 diols[6] for use as ligands[7] in asymmetric reactions. The synthetic application of **1** and **2** for addition reactions with organometallic reagents has been studied in isolated cases[2], due to the low reactivity of these ketones towards some organometallic reagents[2,5c,8]. The use of the *Imamoto*'s[9] procedure for addition of *in situ* prepared organocerium 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-diols[11].

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* reagents[10] the assistance of anhydrous $CeCl_3$ was not necessary[12]. 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 results[10] 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 CH_3MgI and $Me_2NCH_2CH_2CH_2Li$)[10] showing 100% *exo*-addition to ketone **2**.

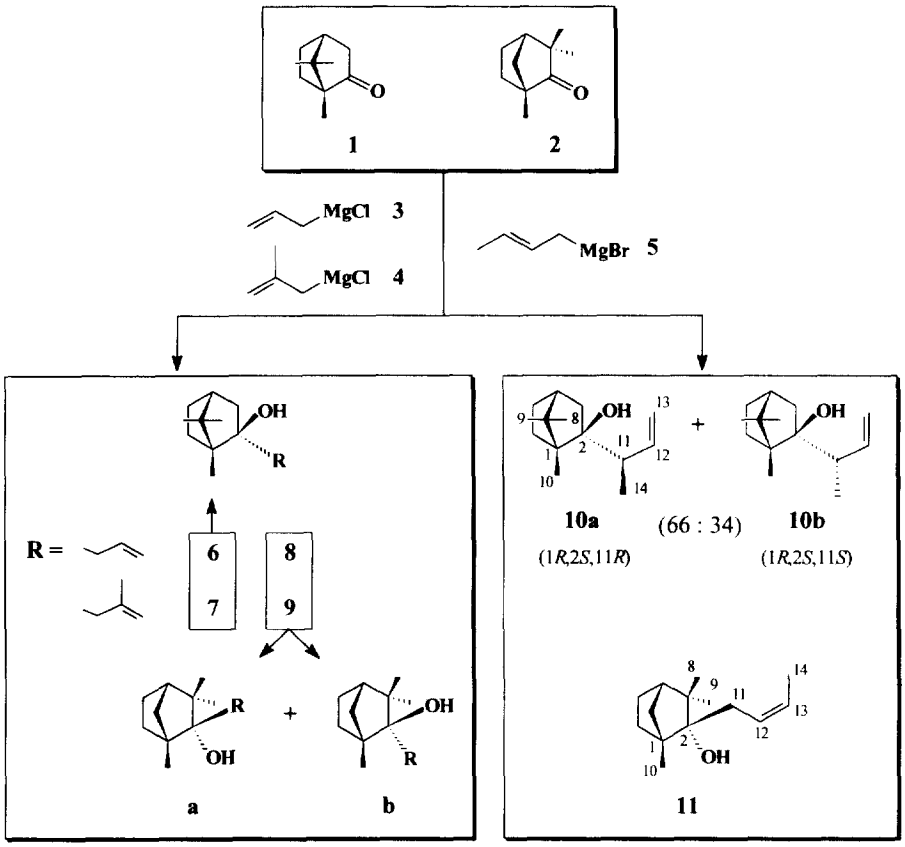
The observed selectivity allowed the absolute configuration to be defined as 1*R*,2*R*-**6**, 1*R*,2*S*-**7** and 1*R*, 2*S*-**10** for the camphor derived alcohols, and predominantly 1*R*,2*R*-**8**, 1*R*,2*R*-**9**, and 1*R*,2*R*-**11** for the fenchone derived alcohols, respectively.

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 reported[13] 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 solution[16]. 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 alcohols[17]. We prepared *in situ* (2-butenyl)$CeCl_2$ 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)$CeCl_2$ to **1** at -20°C, as well as after the reaction of $CeCl_3$-complexed ketone **1** with reagent **5** at room temperature.

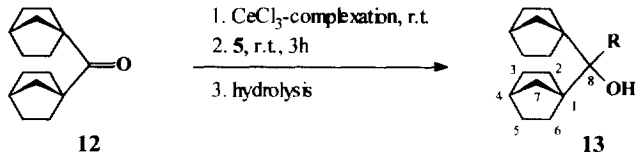
The diastereoisomers **10a** and **10b** were separated by column chromatography and studied by NMR. NOE difference proved the absolute configuration of the newly formed chiral centre as 11*R* and 11*S* in **10a** and **10b**, respectively, taking into account the known 1*R*,2*S*-configuration. After 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 1*R*,2*S*,11*R*-**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*).



Scheme 1

In connection with the regioselectivity reported above, it was interesting to check reaction of the highly hindered bis(1-norbornyl)ketone[18] (**12**) with reagent **5**. Surprisingly **12** did not react with **5** even with extended reaction time (10h) at room temperature. Applying our procedure[10] for activation of **12** with stoichiometric amount of $CeCl_3$ 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 ketone[13]. The attempts to achieve the activation of ketone **12** with catalytic amounts (5 mol %) of $CeCl_3$ 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 % $CeCl_3$ obviously occurs *via* the catalytic mediation of *in situ* formed alkoxycerium(III) species[10], the mode of the addition being probably different from the case when stoichiometric amounts of $CeCl_3$ are used.



12 **13**

Stoichiometry			Conversion	Product ratio[a] (**R** =)		
12	$CeCl_3$	**5**	of **12** → **13**	**13a**	**13b**	**13c**
1	1	1.1	100	1.5	1	1.2
1	0.05	1.1	64	3.5	1	2

[a] Ratio by NMR

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: δ = 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; δ = 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 transformations[11].

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; ^{13}C 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 $CDCl_3$ 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: (1*R*)-(+)-camphor (Fluka AG), (1*R*)-(-)-fenchone (Fluka AG), bis(1-norbornyl)ketone[18], allylmagnesium chloride[19] (**3**) 1.36 M in THF, (2-methyl)-allylmagnesium chloride[19] (**4**) 0.95 M in THF, 2-butenylmagnesium bromide[19] (**5**) 0.33 M in THF, anhydrous $CeCl_3$[10].

Table 1. ^{13}C NMR chemical shifts of compounds **6-11** and **13** ($CDCl_3$, 300K, δ in *ppm* from TMS); assignments marked with asterisks are tentative. For the numbering of the C-atoms, see *Scheme 1*.

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

[a]Chemical shifts for the isomeric mixture. [b]Chemical shifts for the individual compounds; chemical shift differences up to 0.3 ppm were observed for the isomeric mixture.

General Procedure (*GP*): Addition of allylmagnesium halides **3-5** to (1*R*)-(+)-camphor (**1**) and (1*R*)-(-)-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% $NaHCO_3$, and then with water, dried over $MgSO_4$, 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, $CHCl_3$), $[\alpha]_D^{20}$ -17.7 (4.00, EtOH). Anal. calc. for $C_{13}H_{22}O$ (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 ($CDCl_3$, 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, $CHCl_3$), $[\alpha]_D^{20}$ +11.1 (c 4.10, EtOH). Anal. calc. for $C_{14}H_{24}O$ (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 ($CDCl_3$, 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, $CHCl_3$). Anal. calc. for $C_{13}H_{22}O$ (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 ($CDCl_3$, 300K): δ = 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, $CHCl_3$). Anal. calc. for $C_{14}H_{24}O$ (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 ($CDCl_3$, 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 (1*R*,2*S*,11*R*-**10a**/1*R*,2*S*,11*S*-**10b** = 66:34 by ^1H NMR). Anal. calc. for $C_{14}H_{24}O$ (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/Et_2O = 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, $CHCl_3$). ^1H NMR ($CDCl_3$, 300K): δ = 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, $CHCl_3$). ^1H NMR ($CDCl_3$, 300K): δ = 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, $CHCl_3$). Anal. calc. for $C_{14}H_{24}O$ (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 ($CDCl_3$, 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 $CeCl_3$ 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% $NaHCO_3$ and then with water, dried over $MgSO_4$, and evaporated. The crude product was chromatographed (flash, Ø 13 mm, 15 g silica gel, hexane/Et_2O = 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 $C_{19}H_{30}O$ (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 ($CDCl_3$, 300K): **13a:** δ = 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:** δ = 5.55-5.45 (m, 2H, H-10, H-11), 2.46 (d, 2H, H-9, J = 6.5 Hz). **13c:** δ = 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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