Supporting Information 1

Tandem Cyclopropanation with Dibromomethane under Grignard Conditions

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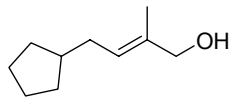
General. Reagents and solvents were purchased from commercial suppliers and used without further purification. Solvents for moisture-sensitive reactions contained < 0.1% water. Moisture-sensitive reactions were conducted under Argon and in oven-dried (130°C) glassware. The given temperatures refer to reaction thermometers. All reactions were carried out under stirring. The silica gel used for flash chromatography was Sorbsil, 0.04-0.063 mm. ^{1}H- and ^{13}C-NMR: all spectra were recorded at 400 MHz and in $CDCl_3$ or C_6D_6; δ in ppm rel. to $SiMe_4$; coupling constants *J* in Hz. ^{13}C-NMR peaks were assigned with q (CH_3), t (CH_2), d (CH) and s (C), in the case of deuterated C-atoms with triplet (1 D) and septet (3 D). GC/MS: relative intensities in % of the base peak. Nonpolar column: 5 % Diphenyl / 95% Dimethylpolysiloxan 30 x 250 x 0,2. Program: 50° / 3 min. 10°C / min to 60°C. 6°C / min to 240°C. 30°C / min to 270°C. Conditions: Injector: 240°C. Split 1:50. Flow: 1,0 ml/min. Transferline: 250°C. MS-Quadrupol: 106°C. MS- Source: 230°C. Carrier Gas: Helium. IR: ν~ in cm-1. Peak intensities assigned as strong (s), middle (m), weak (w) and broad (br). Samples were measured neat in ATR modus.

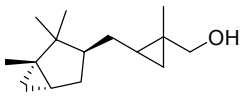
Table: Deprotonation, alkylation and cyclopropanation methods.

Method	Substrates	Deprotonation / alkylation (T)	Cyclopropanation	Products
A	allylic alcohols **1**	LiH (65°C)	Mg, CH_2Br_2 (Barbier)	**2a**, **2u'**
A1	allylic alcohols **1**, **3**	RLi (5°C)	Mg, CH_2Br_2 (Barbier)	**2a**, **2g**, **4b**
B	allyl alcohols **1**, conjugated aldehydes **5**	RMgX (5°C)	CH_2Br_2 / tBuMgCl (portionwise)	**2a-f**, **2r-s**,
B1	allylic alcohols **1**,**3** conjugated aldehydes **5**	RMgX (5°C)	CH_2Br_2 then dropwise tBuMgCl	**2g-l**, **2m-q**, **4a-b**
C	allylic alcohols **1**, **3**, conjugated ketones and esters **7**	RLi (5°C)	CH_2Br_2 / tBuMgCl (portionwise)	**2t-z**, **4b**, **8b-g**,
C1	conjugated ketone **7a**	RLi (-78°C - 0°C)	CH_2Br_2 then dropwise tBuMgCl	**8a**
C2	vinyl oxiranes **11**	RLi (-78°C)	CH_2Br_2 then dropwise tBuMgCl	**12a-c**
			Derivatives	
D	cyclopropyl carbinols **2**	NaH, EtI	ethyl ether	**17**,**22**,**23**
D1	cyclopropyl carbinols **2**	NaH, TBAJ, BnBr	benzyl ether	**20**,**24**,**26-28**
D2	cyclopropyl carbinols **2**	cat. DMAP, pyridine	camphanate	**9c**, **21**, **25**

Preparation of the Cyclopropyl carbinols



(*E*)-4-cyclopentyl-2-methylbut-2-en-1-ol (**1d**). According to a method described by Jung,[1] 2-methyl-2-vinyl oxirane (3 g, 34 mmol) is added dropwise to a suspension of CuBr (0.5 g, 3.4 mmol) in tetrahydrofuran (40 ml) at -30°C, followed by the dropwise addition of cyclopentyl magnesiumbromide 2 M in diethylether (22.5 ml, 45 mmol). After 1 h at -30°C the mixture is poured upon 2 M HCl. Extraction with *tert*-butyl methyl ether, washing of the combined organic phase with conc. $NaHCO_3$, conc. NaCl and water, drying over $MgSO_4$, filtration and evaporation of the solvents gives a residue, which is purified by bulb-to-bulb distillation at 70°C / 0.05 mbar giving 5.5g (87%) (*E*)-4-cyclopentyl-2-methylbut-2-en-1-ol (**1d**) as colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.1 – 1.9 (10 H), 1.65 (s, 3 H), 2.05 (m, 2 H), 4.0 (s, 2 H), 5.45 (dd, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 13.7 (q), 25.0 (t, 2C), 32.5 (t, 2C), 33.7 (t), 40.2 (d), 69.05 (t), 125.9 (d), 134.7 (s). MS (EI): m/z (%) 154 (M^+, 11), 136 ($[M - 18]^+$, 9), 121 (20), 107 (10), 94 (14), 81 (40), 68 (100), 55 (43). IR (film): 3313 (br, OH), 2947 (s), 2863 (s), 2863 (s), 1450 (m), 1010 (s). HRMS calcd for $C_{10}H_{18}O$: 154.13577. Found: 154.13546.



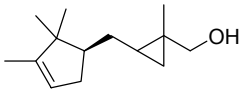
(1-methyl-2-(((1*S*,3*R*,5*R*)-1,2,2-trimethylbicyclo[3.1.0]hexan-3-yl)methyl)-cyclopropyl)methanol (Javanol^{TM}) (2a).

Method A. *Nor*-radjanol **1b** (200 g, 1 mol)[2] and lithium hydride (10 g, 1.24 mol) in tetrahydrofuran are heated under strong stirring and argon for 6 h at 65°C until hydrogen evolution ceases. Magnesium turnings (100 g, 4.1 mol) and 1900 ml tetrahydrofuran are added at 25°C. After addition of

dibromoethane (8.5 g, 50 mmol) the mixture is heated to 65°C and dibromomethane (280 ml, 4 mol) is added over 7 h. After another hour at 65°C the suspension is quenched with 2 M HCl under cooling. *Tert*-Butyl methyl ether extraction, washing of the organic phase with H_2O until pH 7, drying over $MgSO_4$ and concentration gives a crude (65% corr.) mono- and biscyclopropane mixture (**2a** / **2b** = 20 : 75), which after two further reaction cycles gives 95 g (43%) of pure Javanol **2a** after distillation (100°C / 0.05 Torr), whose analytical data (NMR, MS, IR, odor) are consistent with the ones described for this compound in the literature.[3]

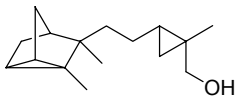
Method A1. Alternative deprotonation with *n*-butyl lithium 1.6 M in hexane (775 ml, 1.24 mol) under cooling followed by cyclopropanation under the above conditions (method A) gave similar yields.

Method B. Allyl alcohol **1a** (5 g, 24 mmol)[4] is added under cooling and stirring to methylmagnesium chloride 3 M in tetrahydrofuran (8 ml, 24 mmol) under nitrogen. This is followed by 3 additions of both dibromomethane (4.2 g) and *tert*-butylmagnesium chloride 2 M in diethylether (12 ml) in that order at 10°-20°C (making a total of 72 mmol each). Quench with conc. NH_4Cl, *tert*-Butyl methyl ether extraction, washing of the organic phase with H_2O until pH 7, drying over $MgSO_4$ and concentration gives 16.6 g of an an oily residue, which is bulb-to-bulb-distilled at 120°C / 0.07 Torr giving 4.7 g (89%) of Javanol **2a** (dr = 1:1), whose analytical data are consistent with the ones described for this compound in the literature.[3]

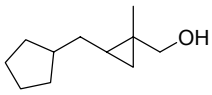


(*trans*)-(1-methyl-2-(((R)-2,2,3-trimethylcyclopent-3-enyl)methyl)cyclopropyl)methanol (**2b**): Prepared as described in method B from *nor*-radjanol **1b** (12.6 g, 65 mmol),[2] methylmagnesium chloride 3M in tetrahydrofuran (22 ml, 65 mmol), dibromomethane (3 x 10 g, 0.17 mol) and *tert*-butylmagnesium chloride 2 M in diethylether (3 x 28 ml, 0.17 mol). Work-up and bulb-to bulb

distillation at 110°C / 0.1 Torr gives 12.5g (93%) of **2b** as colorless oil (dr = 1:1), whose analytical data (NMR, MS, IR, odor) are consistent with the ones described for this compound in the literature.[2]



(*cis*)-{2-[2-(2,3-Dimethyl-tricyclo[2.2.1.0(2,6)]hept-3-yl)-ethyl]-1-methyl-cyclopropyl}-methanol (**2c**). Prepared according to method B from **1c** (5.3 g, 24 mmol),[5] methylmagnesium chloride 3 M in tetrahydrofuran (8 ml, 24 mmol), dibromomethane (2 x 6.3g, 72 mmol) and *tert*-butyl chloride 2 M in diethylether (2 x 18 ml, 72 mmol). Work-up after and bulb-to-bulb distillation gives 3.85 g of **2c** (68%). Odour: woody, creamy, weak. ^{1}H-NMR ($CDCl_3$): δ 0.08 (dd, 1 H), 0.45 (dd, 1 H), 0.6 (m, 1 H), 0.8 and 0.82 (2s, 3 H), 0.83 and 0.86 (2s, 3 H), 1.0 (s, 3 H), 1.05 (2 H), 1.1 – 1.45 (7 H), 1.5 – 1.6 (3 H), 3.5 – 3.6 (2d, 2 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 10.7 (2 q), 17.5 (2 t), 17.6 (2 q), 19.4 (2 d), 19.5 (2 d), 22.3 (2 s), 22.7 (2 q), 24.3 (2 t), 25.9 (2 d), 27.5 (2 s), 30.9 (2 t), 31.4 (2 t), 34.8 (2 t), 38.1 and 38.2 (2 d), 45.6 (2 s), 67.3 and 67.4 (2 t). MS (EI): m/z (%) 234 (M^+, 3), 219 ($[M - 15]^+$, 1), 203 ($[M - 18]^+$, 2), 161 (7), 121 (82), 107 (20), 93 (100), 91 (40), 79 (32), 77 (25), 55 (25), 41 (40). HRMS calcd for $C_{16}H_{26}O$: 234.1984. Found: 234.1982.

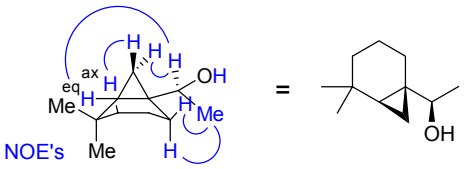


(*trans*)-(2-(cyclopentylmethyl)-1-methylcyclopropyl)methanol (**2d**). According to method B (*E*)-4-cyclopentyl-2-methylbut-2-en-1-ol **1d** (4 g, 21.5 mmol) is treated with methylmagnesium chloride 3 M in tetrahydrofuran (7 ml, 21.5 mmol), dibromomethane (4 x 4g, 86 mmol) and *tert*-butyl chloride 2 M in diethylether (4 x 11 ml, 86 mmol). Work-up after 20 h at 25°C and bulb-to-bulb distillation gives 3.1 g (88%) of a colorless oil. Odour: mushroomy, chemical, strong.

Alternatively (method C) prepared from camphanate **9c** (1.75 g, 5.3 mmol), methyl lithium 1.6 M in diethyl ether (4.6 ml, 7.5 mmol), followed by addition of dibromomethane (3 x 1.4 g, 24 mmol) and *t*BuMgCl (3 x 4 ml, 24 mmol). Work-up after 18 h and flash chromatography (hexane, tert-butyl methyl ether) gave 0.6 g of cyclopropyl carbinol **2d** (85%) and 0.55 g of compound **10** (60%).

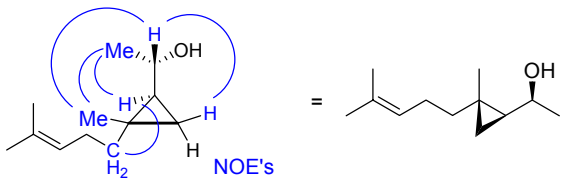
Analytical data of **2d**: ^{1}H-NMR ($CDCl_3$): δ 0 (m, 1 H), 0.55 (m, 1 H), 0.65 (m, 1 H), 1.15 (s, 3 H), 1.2 – 1.9 (12 H), 3.3 (s, 2 H). ^{13}C-NMR ($CDCl_3$): δ 15.4 (q), 16.8 (t), 21.8 (d), 22.05 (s), 25.0 and 25.1 (2 t), 32.5 and 32.7 (2 t), 35.0 (t), 40.85 (d), 72.7 (t). MS (EI): m/z (%)150 ($[M - 18]^+$, 1), 135 (7), 111 (26), 95 (82), 81 (54), 69 (45), 68 (30), 67 (100). IR (film): 3327 (br, OH), 2947 (s), 2864 (s), 1450 (m), 1383 (w), 1025 (s). HRMS calcd for $C_{11}H_{18}$ [M – 18]: 150.14085. Found: 150.13963. Anal. calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.78; H, 11.75.

Analytical data of compound **10**: vide infra.



(*RS*)-1-((1*RS*,6*SR*)-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)ethanol (**2e**). Prepared as described in method B from 1-(3,3-dimethylcyclohex-1-enyl)ethanol **1e** (3.7 g, 24 mmol)[5], methylmagnesium chloride 3 M in tetrahydrofuran (8 ml, 24 mmol), dibromomethane (2 x 6.3g, 72 mmol) and *tert*-butyl chloride 2 M in diethylether (2 x 18 ml, 72 mmol). Work-up after 20 h at 25°C and bulb-to-bulb distillation gives 3.2 g (82%) product (*syn* / *anti* = 97 : 3). Odour: Agrestic, strong. ^{1}H-NMR ($CDCl_3$): δ 0.18 (dd, 1 H), 0.44 (2 H), 0.85 – 1.5 (6 H), 0.95 (s, 3 H), 1.05 (s, 3 H), 1.19 (d, 3 H), 1.95 (1 H), 3.02 (m, 1 H). ^{13}C-NMR: ($CDCl_3$): δ 15.8 (t), 18.9 (t), 19.4 (q), 23.2 (t), 26.1 (s), 27.8 (s), 28.4 (d), 30.9 (q), 30.5 (q), 35.2 (t), 76.4 (d). Relative configuration tentatively assigned by COSY, HMBC, HSQC, NOESY of the above alcohol and its benzylether **19**, and further confirmed by X-ray-analysis of its

camphanate **20** (see SI 2). MS (EI): m/z (%) 168 (M^+, 1), 150 ($[M - 18]^+$, 20), 135 (30), 121 (25), 109 (50), 107 (65), 93 (50), 82 (50), 81 (55), 79 (56), 69 (65), 59 (65), 55 (55), 43 (100). IR (film): 3344 (br, OH), 2952 (s), 2928 (s), 2863 (m), 1467 (m), 1456 (m), 1362 (m), 1293 (w), 1024 (w), 1104 (m), 1079 (s), 1023 (m), 933 (m), 922 (m). R_T = 14.7 (*anti*), 15.1 (*syn*) min. HRMS calcd for $C_{11}H_{20}O$: 168.15142. Found: 168.15272.



(*syn, trans*)-1-((*E*)-2-methyl-2-(4-methylpent-3-enyl)cyclopropyl)ethanol (**2f**). Prepared from

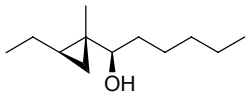
1f (3.6 g, 24 mmol)[6] and methylmagnesium chloride 3 M in THF (8 ml, 24 mmol) or

(*E*)-Citral **5f** (4 g, 24 mmol)[7] and methylmagnesium chloride 3 M in THF (8 ml, 24 mmol) or

9a (5 g, 24 mmol)[8] and methylmagnesium chloride 3 M in THF (19 ml, 60 mmol) or

9b (6 g, 24 mmol)[9] and methylmagnesium chloride 3 M in THF (25 ml, 60 mmol)

and subsequent cyclopropanation of the thus-prepared alcoholate by portionwise addition of dibromomethane (3 x 4.2 g, 72 mmol) and *tert*-butyl chloride 2 M in diethylether (3 x 12 ml, 72 mmol) according to method B. Work-up after 16 h at 25°C and bulb-to-bulb distillation gives 3.7 g (86%) of **2f**. Odour: citrus, weak. Analytical data identical with the ones reported for this compound.[10] *Syn*-configuration also confirmed by COSY, HSQC and NOESY in $CDCl_3$.

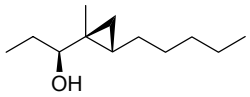


(*syn*, *trans*)-1-(2-ethyl-1-methylcyclopropyl)hexan-1-ol (**2g**).

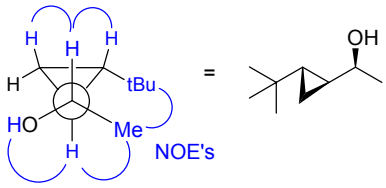
Method B1. (*E*)-4-Methyldec-3-en-5-ol **1g** (25 g, 0.15 mol)[11] is added under cooling and stirring to methylmagnesium chloride 3 M in tetrahydrofuran (49 ml, 0.15 mol) under nitrogen. Alternatively, the (*E*)-dec-3-en-5-olate magnesium halide is prepared from (*E*)-2-methylpent-2-enal (12.6 g, 0.15 mol) and pentane-magnesium bromide 2 M in diethyl ether (75 ml, 0.15 mol). Dibromomethane (77 g, 0.44 mol) is added to the the Grignard product followed by dropwise addition of *tert*-butylmagnesium chloride 2 M in diethylether (220 ml, 0.44 mol) at 10°-20°C. After 16 h at 25°C 2 M HCl is added. *Tert*-Butyl methyl ether extraction, washing of the organic phase with conc. $NaHCO_3$, H_2O and conc. NaCl, drying over $MgSO_4$, filtration and concentration gives 30.3 g of an an oily residue, which is distilled at 45°C / 0.03 Torr giving 24.4 g (90%) of **2g** as colorless oil, whose ^{1}H-NMR data are (within limits) identical to the ones described in ref.[12]

Alternatively (according to method A1) *n*-butyl lithium (11 ml, 17 mmol) is added dropwise and under cooling to (*E*)-4-methyldec-3-en-5-ol **1g** (3 g, 17 mmol)[11]. Magnesium powder (2.6 g, 0.1 mol) is added and the Barbier reaction started with a few drops of dibromomethane (18 g, 0.1 mol), which is then added at 60°C over 1 h. Work-up and bulb-to-bulb distillation at 55°C / 0.05 mbar gives 2.15 g (68% corr) of **2g** as colorless oil (*syn* / *anti* = 97:3).

Odour: green, fresh, spicy, chocolate. ^{1}H-NMR ($CDCl_3$): δ –0.05 (m, 1 H), 0.5 (2 H), 0.9 (t, 3 H), 0.99 (t, 3 H), 1.01 (s, 3 H), 1.25 – 1.35 and 1.35 – 1.6 (11 H), 2.7 (dd, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 11.6 (q), 14.0 (q), 14.3 (q), 17.8 (t), 22.0 (t), 22.6 (t), 24.0 (d), 24.9 (s), 26.0 (t), 32.0 (t), 33.9 (t), 80.9 (d). *syn*-configuration confirmed by NMR-analysis of the benzyl ether **25**. MS (EI): m/z (%) 166 ([M – 18]$^+$, 3) , 141 (5), 128 (15), 113 (10), 99 (32), 84 (35), 72 (85), 71 (100), 69 (60), 55 (70), 43 (75). IR (film): 3373 (br, OH), 2957 (s), 2930 (s), 2859 (m), 1456 (m), 1377 (w), 1310 (w), 1120 (w), 1060 (w), 1023 (s). Anal. calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.05; H, 13.04.

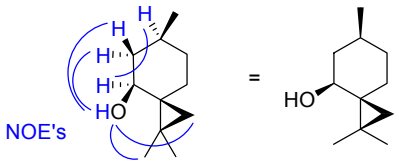


(*syn*, *trans*)-1-(1-methyl-2-pentylcyclopropyl)propan-1-ol (**2h**). Prepared as described in method B from (*E*)-4-methyldec-4-en-3-ol **1h** (20 g, 0.12 mol),[13] methylmagnesium chloride 3 M in tetrahydrofuran (39 ml, 0.12 mol), dibromomethane (3 x 21 g, 0.36 mol) and *tert*-butyl chloride 2 M in diethylether (3 x 59 ml, 0.36 mol). Work-up after 16 h at 25°C and distillation gives 20.7 g (96%) of **2h**. Odour: floral, fruity, weak. ^{1}H-NMR ($CDCl_3$): δ –0.05 (dd, 1 H), 0.5 (m, 1 H), 0.55 (m, 1 H) 0.9 (t, 3 H), 0.95 (t, 3 H), 1.0 (s, 3 H), 1.25 – 1.4 (8 H), 1.55 (2 H), 1.65 (br, OH), 2.6 (dd, 1 H) ppm. ^{13}C-NMR: δ 10.8 (q), 11.7 (q), 14.0 (q), 17.8 (t), 22.1 (d), 22.6 (t), 24.4 (s), 26.8 (t), 28.7 (t), 29.7 (t), 31.8 (t), 82.3 (d). *syn*-configuration confirmed by NMR-analysis of ethyl ether **21**. MS (EI): m/z (%) 166 ([M – 18]$^+$, 2), 155 ([M – C_2H_5]$^+$, 4) 126 (5), 99 (12), 94 (28), 86 (93), 84 (91), 71 (92), 69 (55), 57 (100), 55 (75), 43 (63), 41 (80). IR (film): 3364 (br, OH), 2958 (m), 2924 (s), 2855 (m), 1458 (m), 1378 (w), 1312 (w), 1232 (w), 1109 (w), 1080 (w), 1047 (w), 1012 (m), 965 (m), 943 (m), 897 (w), 725 (w). Anal. calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.13; H, 13.11.



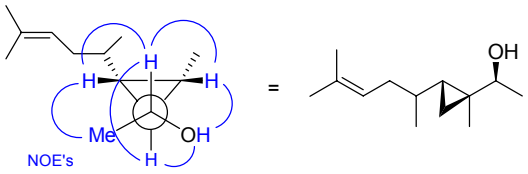
Method B3. (*syn, trans*)-1-(2-*Tert*-butylcyclopropyl)ethanol (**2i**). According to method B1 *tert*-butylmagnesium chloride 2M in diethylether (13 ml, 26 mmol) is added dropwise and at 10°-20°C to (E)-5,5-dimethylhex-3-en-2-ol **1i** (0.7 g, 5.3 mmol)[14] in dibromomethane (4.6g, 26 mmol). After 24 h at 25°C 2 M HCl is added. *Tert*-Butyl methyl ether extraction, washing of the organic phase with conc. $NaHCO_3$ and conc. NaCl, drying over $MgSO_4$, filtration and concentration gives 1.8 g of an an oily

residue, which is purified by flash chromatography over silicagel (hexane / *tert*-Butyl methyl ether gradient 95:5 to 80:20) giving 0.6 g (80%) of **2i** as colorless liquid (*syn* / *anti* = 81 : 19). ^{1}H-NMR ($CDCl_3$): δ 0.3 (m, 1 H), 0.45 (ddd, 1 H), 0.53 (ddd, 1 H), 0.8 (m, 1 H), 0.85 (s, 9 H), 1.27 (d, 3 H), 1.65 (br, OH), 3.07 (dq, 1 H) ppm. ^{13}C-NMR: δ 6.4 (t), 22.7 (q), 23.0 (d), 28.4 (3C, q), 28.6 (d), 29.1 (s), 73.1 (d). *syn*-configuration confirmed by HMBC, HMQC, COSY, NOESY in DMSO-D_6. MS (EI): m/z (%) 124 ([M – 18]$^+$, 4), 109 (11), 87 (7), 85 (5), 83 (6), 70 (100), 57 (16), 55 (53), 43 (24), 41 (25). R_T = 3.8 (*anti*), 4.0 (*syn*) min. IR (film): 3346 (br, OH), 3004 (w), 2954 (s), 2866 (m), 1467 (m), 1414 (w), 1364 (s), 1264 (m), 1208 (m), 1110 (s), 1078 (s), 1037 (m), 988 (m), 917 (w), 896 (m), 804 (w). HRMS calcd for C_9H_{16} [M – 18]: 124.12520. Found: 124.12616. HRMS calcd for C_5H_9O [M – *t*Bu]: 85.06534. Found: 85.06536.

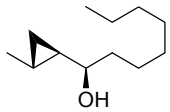


(3SR,4SR,6SR)-1,1,6-trimethylspiro[2.5]octan-4-ol (**2j**). Prepared as described in method B1 from *cis*-pulegol **1j** (10 g, 64 mmol)[15] and dibromomethane (45.5 g, 0.26 mol) in tetrahydrofuran (20 ml) by dropwise addition of *tert*-butylmagnesium chloride 2 M in diethylether (66 ml, 0.26 mol) at 10°-20°C. Work-up after 16 h at 25°C and flash chromatography over Silicagel (hexane / tert-butyl methyl ether 3 : 1) gave 4.4 g (39%) of **2j** as white solid (mp 56°-57°C). Odour: Minty, weak. ^{1}H-NMR ($CDCl_3$): δ 0.1 (d, 1 H), 0.45 (d, 1 H), 1.1 (d, 3 H), 1.12 (s, 3 H), 1.2 (s, 3 H), 1.15 – 1.3 (3 H), 1.4 (m, 1 H), 1.55 (m, 1 H), 1.7 – 1.85 (3 H), 3.7 (m, 3 H) ppm. ^{13}C-NMR: δ 20.2 (s), 21.5 (q), 22.0 (t), 22.1 (q), 22.7 (q), 25.6 (t), 28.55 (d), 30.9 (s), 32.3 (t), 41.0 (t), 71.4 (d). *syn*-configuration confirmed by COSY, HSQC, HMBC, NOESY in DMSO-D_6. MS (EI): m/z (%)150 ([M - 18]$^+$, 14), 135 (30), 112 (45), 110 (78), 107 (30), 97 (64), 95 (100), 93 (49), 70 (72), 67 (38), 59 (70), 55 (64), 41 (63). IR (film): 3362 (br, OH), 2950 (m), 2924 (s), 2903 (s), 2868 (m), 2843 (m), 1446 (m), 1371 (w), 1330 (w), 1120 (w), 1097 (m),

1048 (s), 1026 (s), 1005 (m), 968 (w), 954 (w), 912 (w), 879 (w), 840 (w). HRMS calcd for $C_{11}H_{18}O$ [M – 18]: 150.14085. Found: 150.14097.

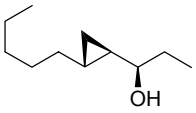


(*syn, trans*)-1-(1-methyl-2-(5-methylhex-4-en-2-yl)cyclopropyl)ethanol (**2k**). Prepared as described in method B1 from methyl magnesiumchloride 3 M in tetrahydrofuran (21 ml, 63 mmol), (*E*)-2,4,7-trimethylocta-2,6-dienal **5k** (10 g, 58 mmol),[16] dibromomethane (4 x 10 g, 0.23 mol) and *tert*-butylmagnesium chloride 2 M in diethylether (4 x 29 ml, 0.23 mol) at 0°-10°C. Work-up and bulb-to-bulb distillation at 65°C / 0.04 mbar gave 10.3 g (81%) of **2k** as colorless oil (dr = 1 :1). ^{1}H-NMR ($CDCl_3$): δ 0.0 and 0.1 (2 m, 1 H), 0.3 – 0.4 (2 m, 1 H), 0.55 (1 H), 0.95 and 1.0 (2 d, 3 H), 1.05 (d, 1 H), 1.17 (2 d, 3 H), 1.5 (br, 1 H), 1.6 (s, 3 H), 1.7 (s, 3 H), 1.8 – 2.2 (2 H), 2.95 (1 H), 5.2 (1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 11.4 and 12.1 (2 q), 17.5 and 17.8 (2 t), 17.7 (q), 19.07 and 19.13 (2 q), 19.9 and 20.2 (2 q), 25.3 and 26.2 (2 s), 25.8 (q), 28.8 and 29.0 (2 d), 33.85 and 34.25 (2 d), 35.5 and 35.9 (2 t), 76.2 and 76.4 (2 d), 123.0 and 123.1 (2 d), 131.87 and 131.95 (2 s). *syn*-configuration tentatively assigned by COSY, HMBC, HSQC, NOESY in $CDCl_3$. MS (EI): m/z (%) 178 ($[M - H_2O]^+$, 1), 163 (3), 149 (2), 127 (10), 109 (13), 95 (25), 83 (25), 69 (26), 55 (62), 43 (100). IR (film): 3350 (br, OH), 2962 (s), 2924 (s), 2870 (m), 1450 (s), 1374 (s), 1302 (m), 1271 (m), 1246 (m), 1173 (w), 1103 (s), 1072 (s), 1046 (m), 927 (s), 901 (m), 840 (w). HRMS calcd for $C_{13}H_{22}$ [M – 18]: 178.17215. Found: 178.17322.



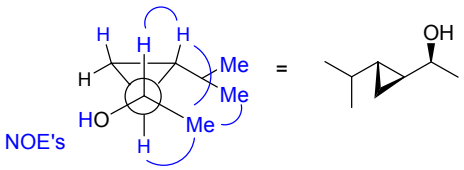
(*syn*)-1-(2-Methyl-cyclopropyl)-octan-1-ol (**2l**). Prepared as described in method B1 from heptyl magnesiumbromide (prepared from heptyl bromide (26 g, 0.14 mol) and magnesium (3.43g, 0.14 mol) in tetrahydrofuran (68 ml) at 70°C), *E*-croton aldehyde **5l** (8.4 g, 0.12 mol), dibromomethane (62.5 g, 0.36 mol) and of *tert*-butylmagnesium chloride 2M in diethylether (3 x 60 ml, 0.36 mol) at 10°-20°C. Work-up and distillation at 60°C / 0.04 Torr gave 24.4 g (86%) of **2l** (*trans*-isomer) as colorless oil. Odour: green, earthy, substantive.

Alternatively, this compound was prepared by Grignard reaction of octanal (18g, 0.14 mol) with *E*/*Z*-1-propenyl magnesiumbromide (prepared from magnesium (3.8 g, 0.14 mol), 1-bromopropene (17 g, 0.14 mol) in tetrahydrofuran (60 ml) at 60°C) followed by tandem cyclopropanation and work-up as described above giving 23.5 g (83%) of **2l** (*cis*/*trans* = 1:1). ^{1}H-NMR ($CDCl_3$) (*trans*-isomer): δ 0.25 (m, 1 H), 0.4 (m, 1 H), 0.6 (2 H), 0.9 (t, 3 H), 1.05 (d, 3 H), 1.2 – 1.45 (10 H), 1.5 – 1.55 (3 H), 2.88 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$) (*trans*-isomer): δ 10.7 (t), 11.15 (d), 14.1 (q), 18.3 (q), 22.6 (t), 25.7 (t), 26.9 (d), 29.3 (t), 29.7 (t), 31.8 (t), 37.4 (t), 76.4 (d). *syn*-configuration confirmed by NMR-analysis of benzyl ether **26**. MS (EI): m/z (%) 166 ([M – 18]$^+$, 2), 85 (100), 67 (32), 57 (50), 55 (30), 43 (42), 41 (45). IR (film): 3355 (br, OH), 2924 (s), 2855 (s), 1455 (m), 1417 (w), 1269 (w), 1075 (w), 1046 (m), 1021 (m), 894 (w), 866 (w), 788 (w), 722 (w). Anal. calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.13; H, 13.02.

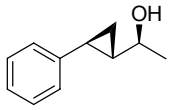


(*syn*,*trans*)-1-(2-Methyl-cyclopropyl)-octan-1-ol (**2m**). Prepared as described in method B1 from ethyl magnesiumbromide 1 M in tetrahydrofuran (200 ml, 0.2 mol), *E*-2-octenal **5m** (25 g, 0.2 mol), dibromomethane (103 g, 0.6 mol) followed by dropwise addition of *tert*-butylmagnesium chloride 2 M

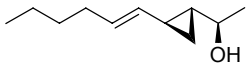
in diethylether (300 ml, 0.6 mol) at 10°-20°C. Work-up and distillation at 45°C / 0.04 Torr gave 12 g (36%) product as colorless oil (*syn* / *anti* = 98 : 2). Odour: fruity, pear, green, powdery, banana, strong. ^{1}H-NMR ($CDCl_3$): δ 0.25 (m, 1 H), 0.4 (m, 1 H), 0.6 (m, 2 H), 0.9 (t, 3 H), 1.0 (t, 3 H), 1.2 – 1.4 (8 H), 1.5 (br, OH), 1.6 (m, 2 H), 2.8 (ddd, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 9.7 (t), 10.0 (q), 14.0 (q), 17.1 (d), 22.6 (t), 25.4 (d), 29.1 (t), 30.0 (t), 31.7 (t), 33.7 (t), 77.7 (d). Relative configuration assigned by NMR-analysis of the benzyl ether **27**. MS (EI): m/z (%) 141 ([M – ethyl]$^+$, 15), 123 (13), 95 (6), 85 (17), 83 (24), 81 (50), 72 (34), 70 (29), 67 (32), 59 (22), 57 (100), 55 (44), 43 (32), 41 (43). R_T = 15.6 (*anti*), 15.7 (*syn*) min. HRMS calcd for $C_{11}H_{20}$ [M – 18]: 152.15650. Found: 152.15564. HRMS calcd for $C_9H_{17}O$ [M – C_2H_5]: 141.12794. Found: 141.12720.



(*syn*,*trans*)-2-isopropylcyclopropyl)ethanol (**2n**). Prepared as described in method B1 from methyl magnesiumchloride 2M in tetrahydrofuran (3.7 ml, 11 mmol), *E*-4-methyl-2-pentenal **5n** (1 g, 10 mmol), dibromomethane (5.2 g, 30 mmol) followed by dropwise addition of *tert*-butylmagnesium chloride 2M in diethylether (15 ml, 30 mmol) at 0°-10°C. Work-up after 20 h at 25°C and bulb-to-bulb distillation at 0.1 mbar gave 1.1 g (85%) of **2n** as colorless oil (*syn* / *anti* = 79:21). ^{1}H-NMR ($CDCl_3$): δ 0.3 – 0.45 (3 m, 3 H), 0.7 (m, 1 H), 1.0 (2d, 6 H), 1.25 (m, 1 H), 1.65 (br, OH), 3.1 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$) *syn*-isomer: δ 9.6 (t), 22.0 (2 q), 22.6 (q), 25.0 (d), 26.3 (d), 32.5 (d), 72.6 (d). ^{13}C-NMR ($CDCl_3$) *anti*-isomer: δ 8.5 (t), 21.9 (q), 23.5 (q), 25.5 (d), 26.1 (d), 32.4 (d), 72.1 (d). *syn*-configuration determined by COSY, HMBC, HSQC, NOESY in DMSO-D_6 of **2n** and NMR-analysis of ethyl ether **22**. MS (EI): m/z (%) 110 ([M – H_2O]$^+$, 1), 95 (47), 71 (30), 58 (44), 57 (50), 56 (100), 55 (68). R_T = 3.1 (*anti*), 3.3 (*syn*) min. Anal. calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.79; H, 12.50.



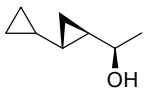
(*syn*,*trans*)-1-(2-Phenyl-cyclopropyl)-ethanol (**2o**). Prepared as described in method B1 from *E*-cinnamon aldehyde **5o** (3.2 g, 24 mmol), methylmagnesium chloride 3 M in tetrahydrofuran (8 ml, 24 mmol), dibromomethane (2 x 6.3 g, 72 mmol) and *tert*-butyl chloride 2 M in diethylether (2 x 18 ml, 72 mmol). Work-up after 18 h at 25°C and bulb-to-bulb distillation gives 3.3 g (83%) of **2o** as colorless oil (*syn* / *anti* = 82 : 18), whose analytical data are identical to the ones described for this compound in the literature.[17] R_T = 18.7 (*anti*), 18.8 (*syn*).



(*RS*)-1-((*1RS,2SR*)-2-((*E*)-hex-1-enyl)cyclopropyl)ethanol (**2p**). Prepared as described in method B1 from methyl magnesiumchloride 3 M in tetrahydrofuran (7.3 ml, 21 mmol), (2*E*,4*E*)-nona-2,4-dienal **5p** (3 g, 21 mmol), dibromomethane (15 g, 87 mmol) followed by dropwise addition of *tert*-butyl-magnesium chloride 2 M in diethylether (43 ml, 87 mmol) at 0°-10°C. Work-up after 18 h and bulb-to-bulb distillation at 80°C / 0.05 mbar gave 3.1 g (77%) of **2p** as colorless oil (*syn* / *anti* = 83 : 17). Odour: fruity, pear, green. ^{1}H-NMR ($CDCl_3$): δ 0.5 (m, 1 H), 0.7 (m, 1 H), 0.8 - 1 (2 H), 0.9 (t, 3 H), 1.2 – 1.4 (6 H), 1.8 – 2.0 (3 H), 3.2 (m, 1 H), 5.0 (m, 1 H), 5.5 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$) *syn*-isomer: δ 11.5 (t), 13.9 (q), 18.8 (d), 22.2 (t), 22.5 (q), 28.1 (d), 31.7 (t), 32.1 (t), 71.5 (d), 128.9 (d), 131.7 (d). ^{13}C-NMR ($CDCl_3$) *anti*-isomer: δ 10.8 (t), 14.0 (q), 19.6 (d), 22.2 (t), 22.5 (q), 28.3 (d), 31.7 (t), 32.1 (t), 72.0 (d), 128.7 (d), 132.0 (d). *syn*-configuration assigned by derivatization to **18** and NMR-comparison. MS (EI): m/z (%) 168 ($[M]^+$, 1), 150 ($[M - H_2O]^+$, 7), 113 (48), 95 (47), 82 (33), 81 (80), 68 (72), 67 (100), 57 (43), 55 (45), 54 (80), 45 (75), 43 (56), 41 (64). R_T (nonpolar column) = 6.35 (*syn and anti*). R_T (polar column) = 24.66 (*anti*), 24.83 (*syn*). IR (film): 3340 (br, OH), 2958 (m), 2925 (m),

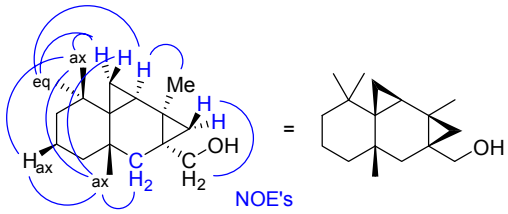
2871 (m), 2858 (m), 1455 (m), 1414 (w), 1366 (m), 1290 (w), 1180 (w), 1103 (m), 1076 (m), 1029 (m), 959 (s), 897 (m). HRMS calcd for $C_{11}H_{20}O$: 168.15142. Found: 168.15082.

(*syn*)-1-(2-((E)-prop-1-enyl)cyclopropyl)ethanol (**2q**). Prepared as described in method B1 from methyl magnesiumchloride 3M in tetrahydrofuran (3.5 ml, 10 mmol), (2*E*,4*E*)-hexadienal **5q** (1 g, 10 mmol), dibromomethane (2.9 ml, 40 mmol) followed by dropwise addition of *tert*-butylmagnesium chloride 2M in diethylether (21 ml, 40 mmol) at 0°-10°C. Work-up after 18 h and bulb-to-bulb distillation at 110°C / 17 mbar gave 0.7 g (55%) of **2q** as colorless oil (syn / anti = 88 : 12). ^{1}H-NMR ($CDCl_3$): δ 0.55 (m, 1 H), 0.7 (m, 1 H), 0.8 – 1.0 (2 H), 1.3 (d, 3 H), 1.65 (d, 3 H), 3.2 (m, 1 H), 5.05 (m, 1 H), 5.5 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$) *syn*-isomer: δ 11.4 (t), 17.7 (q), 18.8 (d), 22.5 (q), 28.0 (d), 71.7 (d), 123.2 (d), 133.0 (d). *syn*-configuration assigned by derivatization to **18** and NMR-comparison. MS (EI): m/z (%) 126 ($[M]^+$, 3), 108 ($[M - H_2O]^+$, 5), 82 (20), 71 (52), 68 (55), 67 (100), 45 (70). R_T (nonpolar column) = 6.35 (*syn and anti*). R_T = 3.97 (*syn*), 3.99 (*anti*). IR (film): 3355 (br, OH), 2965 (m), 2932 (m), 2871 (m), 2858 (m), 1712 (w), 1451 (w), 1366 (m), 1103 (m), 1073 (s), 1028 (m), 970 (s), 893 (m). HRMS calcd for $C_8H_{14}O$: 126.10447. Found: 126.10513. HRMS calcd for $C_7H_{11}O$ [M – 15]: 111.08099. Found: 111.08065.



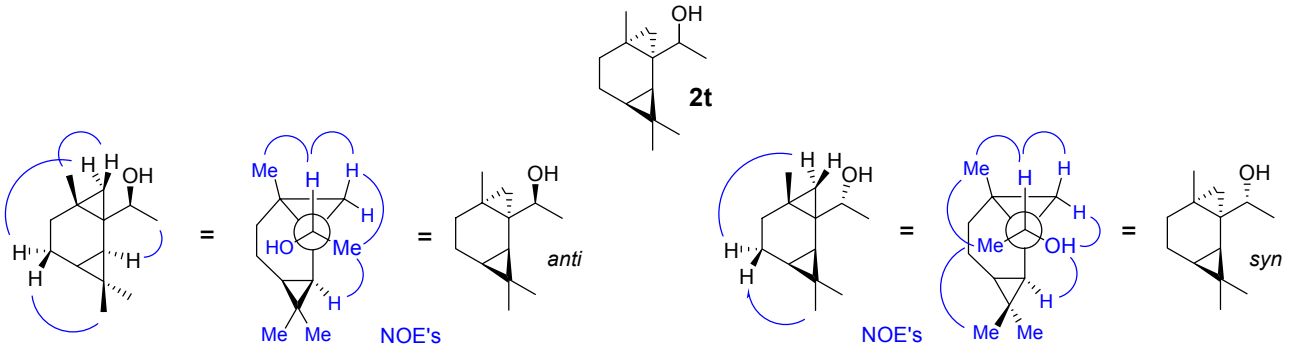
(*syn*)-1-((bi(cyclopropan)-2-yl)ethanol (**2r**). Prepared as described in method B from (*E*)-3-cyclopropylacrylaldehyde **1r** (0.5 g, 5.2 mmol),[18] methylmagnesium chloride 3M in tetrahydrofuran (1.7 ml, 5.2 mmol), dibromomethane (5 x 0.9 g, 26 mmol) and *tert*-butylmagnesium chloride 2 M in diethylether (5 x 2.6 ml, 26 mmol). Quench on conc. NH_4Cl (!), extraction and flash chromatography (hexane / *tert*-butyl methyl ether 98:2 → 95:5) gives 0.16 g (24%) of **2r** as colorless oil (*syn* / *anti* = 75 :

25). ^{1}H-NMR ($CDCl_3$): δ 0.0 (2 H), 0.3 (4 H), 0.6 (2 H), 0.8 (1 H), 1.2 (d, 3 H), 2.3 (d, 1 OH), 3.05 (q, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 2.9 (t), 3.0 (t), 8.5 (t), 11.6 (d), 18.3 (d), 22.5 (q), 24.95 (d), 72.2 (d). *syn*-configuration determined by NMR-analysis of benzylether **30**. MS (EI): m/z (%) 111 ([M – 15]$^+$, 1), 108 (2), 93 (14), 91 (8), 81 (10), 79 (22), 77 (12), 71 (100), 67 (78), 45 (60), 43 (83). R_T = 4.0 (*anti*), 4.1 (*syn*) min. IR (film): 3347 (br, OH), 3078 (w), 3000 (m), 2965 (m), 2925 (m), 2871 (m), 2857 (m), 1465 (m), 1368 (m), 1289 (m), 1102 (m), 1076 (s), 1015 (s), (w), 973 (s). HRMS calcd for $C_7H_{11}O$ [M – 15]: 111.08099. Found: 111.08088.



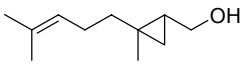
((11*S*,5*aS*,6*aR*,7*aR*,7*bS*)-2,2,5a,7a-tetramethyldecahydro-1H-dicyclopropa[b,d]naphthalen-6a-yl)methanol (**2s**). Prepared as described in method B from **1s** (1 g, 4.4 mmol)[19] dibromomethane (5 x 0.75 g, 21 mmol) and *tert*-butyl chloride 2 M in diethylether (5 x 2.1 ml, 21 mmol). Work-up after 18 h and flash chromatography (hexane / *tert*-butyl methyl ether 9:1 → 1:1) over Silicagel gives 0.75 g (70%) of **2s** (mp 93°C, from hexane). ^{1}H-NMR ($CDCl_3$): δ –0.01 (dd, 1 H), 0.15 (2 m, 2 H), 0.3 (d, 1 H), 0.6 (s, 3 H), 1.0 (s, 3 H), 1.04 (s, 3 H), 1.1 – 1.2 (m, 2 H), 1.2 – 1.3 (m, 2 H), 1.33 (s, 3 H), 1.4 – 1.6 (4 H), 1.7 – 1.85 (m, 1 H), 3.33 (d, 1 H), 3.6 (d, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 7.15 (t), 19.5 (t), 19.7 (s), 21.7 (s), 22.7 (q), 23.7 (t), 24.8 (d), 26.9 (q), 28.0 (q), 29.2 (q), 31.8 (s), 33.6 (s), 34.4 (s), 37.1 (t), 40.9 (t), 42.9 (t), 69.7 (t). Relative configuration confirmed by COSY, HSQC, HMBC, NOESY in C_6D_6. MS (EI): m/z (%) 248 [M]$^+$, 6), 233 ([M – 15]$^+$, 4), 217 (17), 178 (17), 177 (100), 161 (15), 159 (20), 147 (19), 145 (27), 123 (48), 121 (65), 119 (49), 109 (66), 107 (65), 105 (68), 95 (69), 93 (74), 91 (66), 69 (48), 67 (28), 55 (54), 41 (58). IR (film): 3310 (br, OH), 2900 (m), 1483 (w), 1454 (w), 1438 (w),

1371 (w), 1320 (w), 1104 (w), 1061 (w), 1015 (s), 969 (w), 907 (w), 728 (w). HRMS calcd for $C_{17}H_{28}O$: 248.21402. Found: 248.21522. HRMS calcd for $C_{16}H_{25}O$ [M – 15]: 233.19054. Found: 233.19038.

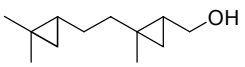


(1*RS*,2*SR*,4*RS*,7*SR*)-1-(Tricyclo[5.1.0.0^{2,4}]octane-4,8,8-trimeth-2-yl)-ethanol (**2t**). Prepared according to method C from **1t** (0.5 g, 3 mmol)[20] in tetrahydrofuran (5 ml) and methyl lithium 1.6 M in diethyl ether (2.3 ml, 3.8 mmol) followed by addition of dibromomethane (6 x 0.5 g, 17.4 mmol) and *t*BuMgCl 2 M in diethyl ether (6 x 1.4 ml, 17.4 mmol). Work-up and bulb-to-bulb distillation at 80°C / 0.05 mbar gave 0.3 2g (57%) of **2t** (*syn* / *anti* = 44:56) as an oily gel. The diastereomers were separated by flash chromatography over silicagel (hexane / *tert*-butyl methyl ether 98:2 → 95:5) with the *anti*-isomer eluting first. ^{1}H-NMR (C_6D_6) *anti*-isomer: δ –0.01 (d, 1 H), 0.4 (m, 1 H), 0.45 (d, 1 H), 0.8 (d, 1 H), 0.95 (s, 3 H), 1.05 (s, 3 H), 1.15 (s, 3 H), 1. 3 (d, 3 H), 1.4 (2 H), 1.65 (2 H), 3.45 (q, 1 H) ppm. ^{1}H-NMR (C_6D_6) *syn*-isomer: δ 0.05 (d, 1 H), 0.4 (m, 1 H), 0.45 (d, 1 H), 0.85 (s, 3 H), 1.0 (2 s, 6 H), 1.1 (d, 1 H), 1.2 (d, 3 H), 1. 25 (m, 1 H), 1.35 (m, 1 H), 1.5 (m, 1 H), 1.6 (m, 1 H), 3.4 (q, 1 H) ppm. ^{13}C-NMR (C_6D_6) *anti*-isomer: δ 17.5 (t), 18.3 (q), 19.2 (t), 19.7 (s), 20.8 (q), 21.0 (d), 21.9 (q), 22.3 (d), 22.5 (s), 28.6 (s), 28.9 (t), 30.0 (q), 71.3 (d). ^{13}C-NMR (C_6D_6) *syn*-isomer: δ 17.6 (t), 18.3 (q), 19.3 (t), 19.4 (s), 20.5 (d), 21.1 (q), 21.7 (q), 22.1 (d), 22.2 (s), 29.0 (t), 29.8 (q), 29.9 (s), 71.4 (d). Relative configurations confirmed by COSY, HSQC, HMBC, NOESY in C_6D_6 and DMSO-D_6. GC/MS (EI) *anti*-isomer: m/z (%) 194 $[M]^+$, 2), 179 ($[M - 15]^+$, 4), 176 (14), 161 (22), 133 (27), 123 (28), 121 (29), 119 (27), 109 (27), 107 (60), 105 (51), 95 (42), 93 (52), 91 (50), 81 (30), 79 (38), 77 (25), 69 (30), 67

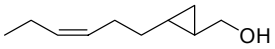
(25), 57 (12), 55 (35), 53 (19), 43 (100), 41 (54). GC/MS (EI) *syn*-isomer: m/z (%) 194 $[M]^+$, 4), 179 ($[M - 15]^+$, 6), 176 (15), 161 (27), 151 (14), 147 (13), 133 (42), 123 (27), 121 (32), 119 (42), 109 (27), 107 (61), 105 (73), 95 (40), 93 (58), 91 (63), 81 (29), 79 (46), 77 (29), 67 (30), 65 (29), 55 (42), 53 (23), 45 (23), 43 (100), 41 (60). R_T = 6.8 (*anti*), 7.2 (*syn*) min. IR (film): 3433 (br, OH), 2975 (m), 2862 (s), 1452 (m), 1372 (m), 1076 (m), 1016 (m), 925 (m), 894 (w), 844 (w), 781 (w). HRMS calcd for $C_{13}H_{22}O$: 194.16707. Found: 194.16683. HRMS calcd for $C_{12}H_{19}O$ [M – 15]: 179.14359. Found: 149.14335.



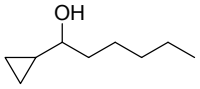
(*trans*)-(2-methyl-2-(4-methylpent-3-enyl)cyclopropyl)methanol (**2u**). Prepared according to method C from geraniol **1u** (5 g, 32.5 mmol), butyl lithium 1.6 M in hexane (28.4 ml, 42 mmol), followed by addition of dibromomethane (4 x 5.7 g, 130 mmol) and tBuMgCl 2 M in diethyl ether (4 x 16 ml, 130 mmol). Work-up and bulb-to-bulb distillation gave 4 g (73%) of cyclopropyl carbinol **2u**, whose analytical data are consistent with the ones from the literature.[21]



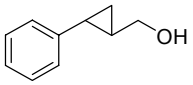
(*trans*)-(2-(2-(2,2-dimethylcyclopropyl)ethyl)-2-methylcyclopropyl)methanol (**2u'**). Prepared according to method A but in 3 reaction cycles from geraniol **1 u** (50g, 0.32 mol), lithium hydride (3 x 3.4g, 3 x 0.4 mol) in tetrahydrofuran (350 ml), magnesium powder (3 x 31.5 g, 3 x 1.3 mol) and dibromomethane (3 x 225 g, 3 x 1.3 mol). Work-up and bulb-to-bulb distillation gave 15 g (25%) of **2u'** as colorless oil, whose analytical data are consistent with the ones described in the literature. **2u** / **2u'** = 17 : 83.[21]



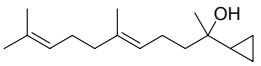
(*Z*, *trans*)-(2-(hex-3-enyl)cyclopropyl)methanol (**2v**). Prepared according to method C from (2*E*,6*Z*)-nona-2,6-dien-1-ol **1v** (2 g, 14 mmol), butyl lithium 1.6 M in hexane (12.5 ml, 19 mmol), followed by addition of dibromomethane (5 x 2.5 ml, 71 mmol) and *t*BuMgCl 2 M in diethyl ether (5 x 7.1 ml, 71 mmol). Work-up and bulb-to-bulb distillation at 45°C / 0.05 mbar gave 2.15 g (94%) of cyclopropyl carbinol **2v**, whose analytical data are consistent with the ones from the literature.[22]



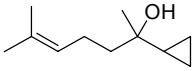
1-cyclopropylhexan-1-ol (**2w**). Prepared according to method C from oct-1-en-3-ol **1w** (2 g, 16 mmol), butyl lithium 1.6 M in hexane (13.6 ml, 21 mmol), followed by addition of dibromomethane (5 x 2.7 ml, 80 mmol) and *t*BuMgCl 2 M in diethyl ether (5 x 7.8 ml, 80 mmol). Work-up and bulb-to-bulb distillation at 50°C / 0.05 mbar gave 2.16 g (98%) of cyclopropyl carbinol **2w**, whose analytical data are consistent with the ones from the literature.[23]



(2-Phenylcyclopropyl)methanol (**2x**). Prepared according to method C from cinnamon alcohol **1x** (2 g, 15 mmol), butyl lithium 1.6 M in hexane (13 ml, 20 mmol), followed by addition of dibromomethane (5 x 2.6 ml, 70 mmol) and *t*BuMgCl 2 M in diethyl ether (5 x 7.5 ml, 70 mmol). Work-up and bulb-to-bulb distillation at 70°C / 0.05 mbar gave 1.2 g (54%) of cyclopropyl carbinol **2x**, whose analytical data are consistent with the ones from the literature.[24]

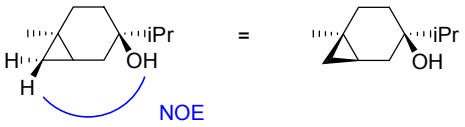


(*E*)-2-cyclopropyl-6,10-dimethylundeca-5,9-dien-2-ol (**2y**). Prepared according to method C from nerolidol **1y** (2 g, 9 mmol), butyl lithium 1.6 M in hexane (8 ml, 12 mmol), followed by addition of dibromomethane (5 x 0.62 ml, 50 mmol) and *t*BuMgCl 2 M in diethyl ether (5 x 4.5 ml, 50 mmol). Work-up and bulb-to-bulb distillation at 100°C / 0.05 mbar gave 1.7 g (80%) of cyclopropyl carbinol **2y**, whose analytical data are consistent with the ones from the literature.[25]



2-cyclopropyl-6-methylhept-5-en-2-ol (**2z**). Prepared according to method C from linalool **1z** (2 g, 12.5 mmol), butyl lithium 1.6 M in hexane (11 ml, 17 mmol), followed by addition of dibromomethane (5 x 0.9 ml, 63 mmol) and *t*BuMgCl 2 M in diethyl ether (5 x 6.3 ml, 63 mmol). Work-up and bulb-to-bulb distillation at 80°C / 0.05 mbar gave 1.8 g (850%) of cyclopropyl carbinol **2z**, whose analytical data are consistent with the ones from the literature.[26]

Preparation of Cyclopropane Alcohols 4



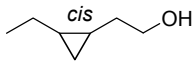
(*cis*)-3-isopropyl-6-methylbicyclo[4.1.0]heptan-3-ol (**4a**). Prepared as described in method B1 from terpinen-4-ol **3a** (2 g, 13 mmol) and dibromomethane (9.15 g, 52 mmol) in diethylether by dropwise addition of *tert*-butylmagnesium chloride 2M in diethylether (26 ml, 52 mmol) at 10°-20°C. Work-up after 16 h at 25°C and bulb-to-bulb distillation gave 2.1 g (85%) of **4a** as colorless oil. Odour: Agrestic. ^{1}H-NMR ($CDCl_3$): δ 0.3 (dd, 1 H), 0.43 (dd, 1 H), 0.6 (dddd, 1H), 0.89 (d, 3 H), 0.91 (d, 3 H), 1.03 (s, 3 H), 1.1 – 1.2 (m, 2 H), 1.2 – 1.3 (m, 1 H), 1.5 – 1.7 (2 m, 2 H), 1.75 – 1.9 (2 H), 2.2 (m, 2 H) ppm. ^{13}C-NMR: δ 14.4 (s), 16.2 (q), 16.4 (q), 17.7 (d), 19.9 (t), 27.2 (q), 28.1 (t), 31.6 (t), 31.9 (d), 35.7 (t), 72.8 (s). *syn*-configuration confirmed by COSY, HSQC, HMBC, NOESY in $CDCl_3$. MS (EI): m/z (%) 168 $[M]^+$, 3), 150 ($[M - 18]^+$, 8), 125 (32), 107 (65), 86 (38), 71 (80), 43 (100). IR (film): 3419 (br), 2936 (m), 2863 (m), 1458 (m), 1379 (w), 1302 (w), 1225 (w), 1133 (m), 1049 (w), 992 (s), 957 (w), 906 (w), 863 (w). HRMS calcd for $C_{11}H_{20}O$: 168.15142. Found: 168.15131. HRMS calcd for $C_{11}H_{18}$ [M – 18]: 150.14085. Found: 150.13919.

(*cis,syn*)-1-(-2-ethylcyclopropyl)propan-2-ol (**4b**). Prepared as described in method B1 but in 2 reaction cycles from (*Z*)-hept-4-en-2-ol **3b** (4 g, 35 mmol)[27] and dibromomethane (2 x 18.2 g, 0.2 mol) in diethylether by dropwise addition of *tert*-butylmagnesium chloride 2M in diethylether (2 x 52 ml, 0.2 mol) at 10°-20°C. Work-up after 18 h at 25°C gave 5.7 g of a crude oil which was distilled at 45°C / 12 mbar, giving 2.5 g (55%) of **4b** as colorless oil (97% purity, *syn* / *anti* = 83:17).

Alternatively prepared as described in method A1 from (*Z*)-hept-4-en-2-ol **3b** (3 g, 26 mmol),[17] *n*-Butyl lithium (16.5 ml, 26 mmol), magnesium powder (3.8 g, 0.16 mol) and dibromomethane (27 g, 0.16 mol). After 18h at 60°C work- up and bulb-to-bulb distillation at 45°C / 12 mbar gives 2.1 g (57% corr) of **4b** (*syn* / *anti* = 73:27).

Method C. Alternatively prepared by dropwise addition of n-butyl lithium 1.6 M in hexane (15.4 ml, 24 mmol) to (*Z*)-hept-4-en-2-ol **3b** (2 g, 18 mmol)[17] in 10 ml tetrahydrofuran under cooling. This is followed by 5 additions of both dibromomethane (1.25 ml) and *tert*-butylmagnesium chloride 2 M in diethylether (8.8 ml) at 10°-20°C (making a total of 90 mmol each). Work-up and distillation as above gives 2.2g (98%) of **4b** as colorless oil.

^{1}H-NMR ($CDCl_3$): δ –0.2 (m, 1 H), 0.6 – 0.8 (2 m, 2 H), 1.0 (t, 3H), 1.2 (d, 3 H), 1.2 – 1.4 (3 H), 1.6 (1 H), 2.3 (br, OH), 3.9 (m, 1 H) ppm. ^{13}C-NMR (*syn*-isomer): δ 10.5 (t), 12.4 (d), 14.2 (q), 16.6 (d), 22.0 (t), 23.0 (q), 37.8 (t), 68.8 d). ^{13}C-NMR (*anti*-isomer): δ 10.5 (t), 12.3 (d), 14.2 (q), 17.3 (d), 22.1 (t), 23.1 (q), 37.9 (t), 68.6 d).*syn*-configuration confirmed by X-ray analysis of camphanate **24** (see SI 2). MS (EI): m/z (%) 113 ([M – 15], 1), 110 ([M – 18]$^+$, 3), 95 (12), 84 (11), 81 (20), 68 (23), 55 (50), 45 (100). R_T = 5.82 (*syn*), 5.86 (*anti*) min. IR (film): 3340 (br), 2961 (s), 2929 (m), 2872 (m), 1456 (m), 1374 (m), 1308 (w), 1120 (m), 1084 (m), 1063 (m), 1022 (m), 994 (w), 940 (m), 927 (m), 855 (w), 815 (w), 739 (w). HRMS calcd for $C_7H_{13}O$ [M – 15]: 113.09664. Found: 113.09541. HRMS calcd for C_8H_{14} [M – 18]: 110.10955. Found: 110.10905.

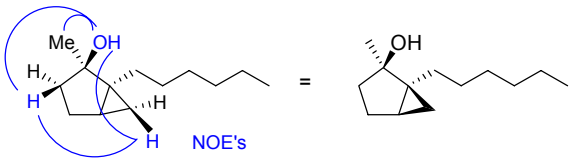


(*cis*)-2-(2-ethylcyclopropyl)ethanol 4e. Prepared according to method C from (*Z*)-hex-3-en-1-ol **3e** (30 g, 0.3 mol), butyl lithium 1.6 M in hexane (262 ml, 0.4 mol), followed by addition of dibromomethane (6 x 21 ml, 1.8 mol) and *t*BuMgCl 2 M in diethyl ether (6 x 150 ml, 1.8 mol). Work-up and distillation gave 43 g (59%) of **4e**, whose analytical data are consistent with the ones from the literature.[28]

Preparation of α,α-disubstituted cyclopropyl carbinols 8

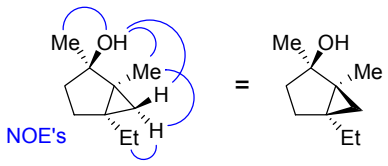
(*cis*)-5-isopropyl-2-methylbicyclo[3.1.0]hexan-2-ol (**8a**).

Method C1. Prepared from 3-isopropylcyclopent-2-enone **7a** (0.5 g, 4 mmol),[29] methyllithium 1.6 M in diethylether (2.8 ml, 4.5 mmol) at -78°C and dibromomethane (2.8 g, 16 mmol) at 5°C, followed by dropwise addition of *tert*-butylmagnesium chloride 2 M in diethylether (8 ml, 16 mmol) at 0°-5°C. Work-up after 6 h and flash chromatography over silicagel (hexane / tert-butyl methyl ether 3 : 1) gave 0.23 g (45%) of a colorless oil, whose analytical data are identical with the ones described for *cis*-Sabinene Hydrate **8a** in the literature.[30] MS (EI): m/z (%) 196 (M^+, 5), 139 ($[M - 15]^+$, 14), 136 ($[M - 18]^+$, 29), 121 (38), 107 (12), 93 (100), 71 (60), 55 (34), 43 (85).

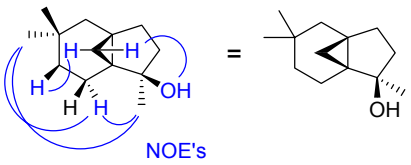


(*cis*)-1-hexyl-2-methylbicyclo[3.1.0]hexan-2-ol (**8b**). Prepared as described in method C1 from Isojasmone B11 **7b** (1 g, 6 mmol),[31] methyllithium 1.6 M in diethylether (4 ml, 7 mmol) at -78°C, CH_2Br_2 (3 x 0.6 ml, 24 mmol) and *tert*-butyl chloride 2M in diethylether (3 x 4 ml, 24 mmol). Work-up after 18 h at 25°C and bulb-to-bulb distillation gives 0.7 g (60%) of **8b** as colorless oil (*cis* / *trans* = 93:7). ^{1}H-NMR ($CDCl_3$): δ 0.3 (m, 1 H), 0.7 (m, 1 H), 0.9 (t, 3 H), 1.05 (m, 1 H), 1.2 – 2 (15 H), 1.3 (s, 3 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 11.0 (t), 14.0 (q), 22.6 (t), 23.4 (d), 24.7 (t), 25.15 (q), 27.5 (t), 29.9 (t), 31.2 (t), 31.8 (t), 34.3 (s), 37.9 (t), 81.05 (s). *cis*-configuration assigned by COSY, HMBC, HSQC,

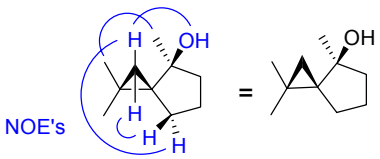
NOESY in DMSO-D_6. MS (EI): m/z (%) 196 (M^+, 2), 181 ([M – 15]$^+$, 14), 155 (24), 138 (15), 135 (27), 125 (32), 110 (34), 107 (38), 93 (92), 79 (50), 57 (14), 43 (100). R_T = 7.38 (*trans*), 7.42 (*cis*). IR (film): 3387 (br, OH), 2955 (m), 2926 (s), 2858 (m), 1693 (w), 1457 (m), 1363 (m), 1294 (w), 1245 (w), 1185 (m), 1158 (w), 1116 (m), 1023 (w), 990 (m), 932 (m), 724 (w), 673 (w). HRMS calcd for $C_{13}H_{24}O$: 196.18272. Found: 196.18199. HRMS calcd for $C_{12}H_{21}O$ [M - 15]: 181.15924. Found: 181.15922.



(*cis*)-5-Ethyl-1,2-dimethylbicyclo[3.1.0]hexan-2-ol (**8c**). Prepared as described in method C1 from **7c** (4 g, 32 mmol),[32] methyllithium 1.6 M in diethylether (28 ml, 45 mmol) at -20°C, dibromomethane (2 x 8.4 g, 97 mmol) and *tert*-butyl chloride 2M in diethylether (2 x 24.3 ml, 97 mmol). Work-up after 18 h at 25°C and bulb-to-bulb distillation gives 2.5 g (50%) of **8c** as colorless oil. ^{1}H-NMR ($CDCl_3$): δ –0.1 (d, 1 H), 0.75 (d, 1 H), 0.95 (t, 3 H), 1.1 (s, 3 H), 1.25 (s, 3 H), 1.3 (1 H), 1.4 (2 H), 1.55 (2 H), 1.8 (1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 11.4 (q), 12.7 (q), 18.4 (t), 24.9 (q), 25.8 (t), 28.5 (t), 32.35 (s), 34.6 (s), 36.5 (t), 81.3 (s). *cis*-configuration assigned by COSY, HMBC, HSQC, NOESY in DMSO-D_6. MS (EI): m/z (%) 154 (M^+, 1), 139 ([M – 15]$^+$, 36), 136 (55), 125 (34), 121 (27), 107 (85), 96 (58), 81 (100), 67 (30), 57 (42), 55 (36), 43 (84). IR (film): 3297 (br, OH), 2959 (s), 2933 (m), 2859 (m), 1453 (s), 1365 (s), 1300 (w), 1200 (m), 1115 (s), 993 (s), 938 (s), 926 (s). HRMS calcd for $C_9H_{15}O$ [M – 15]: 139.11229. Found: 139.11031.

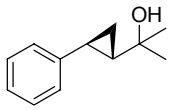


(1*RS*, 3a*SR*,7a*SR*)-Hexahydro-5,5-dimethyl-3a,7a-methano-1-methyl-inden-1-ol (**8d**). Prepared as described in method C1 from **7d** (4 g, 24 mmol),[33] methyllithium 1.6 M in diethylether (21.5 ml, 34 mmol) at 0°C, dibromomethane (2 x 6.4 g, 73 mmol) and *tert*-butyl chloride 2M in diethylether (2 x 18.3 ml, 73 mmol). Work-up after 18 h at 25°C and bulb-to-bulb distillation gives 3 g (65%) of **8d** as colorless oil. ^{1}H-NMR ($CDCl_3$): δ 0.1 (d, 1 H), 0.7 (d, 1 H), 0.8 (s, 6 H), 1.0 (m, 1 H), 1.2 (m, 1 H), 1.35 (m, 1 H), 1.4 (s, 3 H), 1.45 (s, 1 H), 1.5 (m, 1 H), 1.6 (2 H), 1.7 (m, 1 H), 1.85 (m, 1 H), 1.9 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 14.9 (t), 17.8 (t), 25.0 (q), 25.8 (q), 27.0 (s), 28.7 (s), 31.8 (q), 32.8 (t), 32.9 (s), 33.4 (t), 37.8 (t), 43.0 (t), 81.5 (s). Δ-*cis*-configuration assigned by COSY, HMBC, HSQC, NOESY in DMSO-D_6. MS (EI): m/z (%) 194 (M^+, 27), 179 ($[M - 15]^+$, 60), 176 (55), 161 (50), 136 (33), 121 (75), 120 (66), 107 (50), 105 (100), 95 (44), 93 (60), 91 (98), 81 (25), 79 (45), 77 (40), 67 (22), 55 (28), 43 (67), 41 (50). IR (film): 3285 (br, OH), 2945 (m), 2928 (m), 2897 (m), 2856 (m), 1453 (m), 1382 (w), 1306 (m), 1138 (s), 1098 (m), 982 (s), 924 (s). HRMS calcd for $C_{13}H_{22}O$: 194.16707. Found: 194.16601. HRMS calcd for $C_{12}H_{19}O$ [M – 15]: 179.14359. Found: 179.14421.

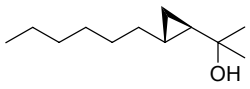


(3*SR*,4*SR*)-1,1,4-trimethylspiro[2.4]heptan-4-ol (**8e**). Prepared as described in method C from **7e** (1.8 g, 15 mmol),[34] methyllithium 1.6 M in diethylether (13.5 ml, 22 mmol) at -20°C, dibromomethane (4 x 2.5 g, 58 mmol) and *tert*-butyl chloride 2M in diethylether (4 x 7.3 ml, 58 mmol). Work-up after 18 h at 25°C and bulb-to-bulb distillation gave 1.2 g (53%) of a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 0.0 (d, 1 H), 0.65 (d, 1 H), 1.1 (s, 3 H), 1.2 (s, 3 H), 1.3 (s, 3 H), 1.4 (m, 1 H), 1.4 (s, 3 H), 1.55 (m, 1 H), 1.7 (m, 1

H), 1.8 (m, 2 H), 2.0 (m, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 18.6 (t), 18.7 (s), 20.8 (q), 23.8 (t), 24.3 (q), 24.8 (q), 31.6 (t), 37.1 (s), 43.95 (t), 78.3 (s). Δ-*cis*-configuration assigned by COSY, HMBC, HSQC, NOESY in DMSO-D_6. MS (EI): m/z (%) 154 (M^+, 2), 139 ($[M - 15]^+$, 12), 136 (20), 111 (48), 98 (48), 97 (51), 96 (80), 93 (36), 83 (64), 81 (96), 71 (18), 69 (35), 67 (24), 59 (35), 55 (46), 43 (100), 41 (44), 39 (23). IR (film): 3407 (br, OH), 2930 (s), 2868 (s), 1466 (m), 1449 (m), 1372 (s), 1302 (w), 1204 (m), 1186 (m), 1147(m), 1123 (m), 1105 (m), 1069 (m), 964 (m), 933 (m). HRMS calcd for $C_{10}H_{18}O$: 154.13577. Found: 154.13515. HRMS calcd for $C_9H_{15}O$ [M – 15]: 139.11229. Found: 139.11125.

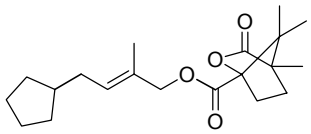


(*trans*)-2-(2-phenylcyclopropyl)propan-2-ol (**8f**). Methyl lithium 1.6 M in diethyl ether (27.5 ml, 44 mmol) is added dropwise to (*E*)-ethyl cinnamate **7f** (3 g, 19 mmol) in diethyl ether (15 ml) at -10°C. At 0°-5°C dibromomethane (3 x 4.5 g, 75 mmol) and *tert*-butyl magnesium chloride 2M in diethyl ether (3 x 13 ml, 75 mmol) are added portionwise according to method C. Work-up after 18 h at 25°C and bulb-to-bulb distillation under high vacuum gives 2.2g (65%) of **7f** as colorless oil, whose analytical data are consistent with the ones described for this compound in the literature.[35]



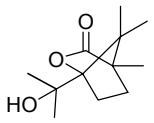
(*trans*)-2-(2-hexylcyclopropyl)propan-2-ol (**8g**). Prepared according to method C from methyl lithium 1.6 M in diethyl ether (7.4 ml, 12 mmol) and (*E*)-methyl non-2-enoate (Neofolione) **7g** (1 g, 6 mmol) in diethyl ether (10 ml) at -78°C, followed by dibromomethane (5 x 1 g, 30 mmol) and *tert*-butyl magnesium chloride 2M in diethyl ether (5 x 3 ml, 30 mmol) at 0°-5°C. Work-up after 18 h at 25°C and bulb-to-bulb distillation under high vacuum gives 0.8g (74%) of a colorless oil. ^{1}H-NMR ($CDCl_3$):

δ 0.15 (m, 1 H), 0.45 (m, 1 H), 0.7 (2 m, 2 H), 1.15 (s, 3 H), 1.2 (s, 3 H), 1.2 – 1.4 (7 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 8.1 (t), 14.1 (q), 15.1 (d), 22.6 (t), 28.4 (q), 28.9 (q), 29.2 (t), 29.4 (t), 30.3 (d), 31.9 (t), 34.1 (t), 69.7 (s). MS (EI): m/z (%) 169 ([M – 15]$^+$, 19), 151 (3), 123 (4), 110 (11), 109 (12), 97 (14), 95 (37), 72 (88), 71 (89), 43 (100). IR (film): 3377 (br, OH), 2960 (m), 2922 (s), 2853 (m), 1464 (m), 1367 (m), 1229 (w), 1145 (m), 944 (m), 915 (m). HRMS calcd for $C_{11}H_{21}O$ [M – 15]: 169.15924. Found: 169.15994. HRMS calcd for $C_{12}H_{22}$ [M – 18]: 166.17215. Found: 166.17197.



(1*R*,4*S*)-((E)-4-cyclopentyl-2-methylbut-2-enyl)-1,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-4-carboxylate (**9c**).

Method D2. Allylic alcohol **1d** (1.05g, 7 mmol), (-)-camphanic chloride (2.2 g, 10 mmol) and DMAP (0.1 g, 0.7 mmol) in pyridine (30 ml) are stirred for 18 h at 25°C. The mixture is poured upon ice / water and extracted with tert-butyl methyl ether. Washing of the organic phase with 2M HCl, 10% Na_2CO_3 and conc. NaCl, evaporation of the solvent under reduced pressure and filtration over silicagel gives 2g of **9c** (72%) as an oil. ^{1}H-NMR ($CDCl_3$): δ 0.95 (s, 3 H), 1.05 (s, 3 H), 1.05 - 1,2 (1 H), 1.15 (s, 3 H), 1.45-1.65 (4 H), 1. 7 (s, 3 H), 1.65-1.8 (4 H), 1.85 (m, 1 H), 1.95 (m, 1 H), 2.0-2.1 (3 H), 2.4 (m, 1 H), 4.6 (2 H), 5.55 (t, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 9.7 (q), 14.1 (q), 16.69 (q), 16.74 (q), 25.0 (t), 28.9 (t), 30.6 (t), 32.25 (t), 33.75 (t), 39.9 (d), 54.05 (s), 54.7 (s), 71.4 (t), 91.2 (s), 129.1 (s), 130.7 (d), 167.3 (s), 178.1 (s) . MS (EI): m/z (%) 266 ([M – cyclopentenyl]$^+$, 1), 252 (3), 199 (4), 181 (11), 153 (19), 136 (94), 121 (49), 109 (50), 83 (45), 81 (45), 69 (40), 68 (100), 67 (48), 41 (63). Anal. calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.95; H, 8.97.



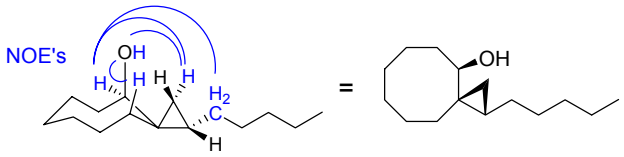
(1*R*,4*S*)-4-(2-hydroxypropan-2-yl)-1,7,7-trimethyl-2-oxabicyclo[2.2.1]heptan-3-one (**10**). Separated from **2d** by flash chromatography. White crystals (mp 78°C). $[\alpha]_D^{22}$ = -1.1 (c = 1, EtOH). ^{1}H-NMR ($CDCl_3$): δ 1.05 (s, 6 H), 1.1 (s, 3 H), 1.34 (s, 3 H), 1.35 (s, 3 H), 1.65 (m, 1 H), 1. 8-1.9 (2 H), 2.1 (1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 9.6 (q), 18.5 (q), 18.6 (q), 25.2 (q), 27.9 (q), 28.7 (2 t), 52.5 (s), 55.0 (s), 72.3 (s), 98.1 (s), 179.9 (s). MS (EI): m/z (%) 197 ($[M - 15]^+$, 1), 184 ($[M - CO]^+$, 13), 169 (5), 154 (11), 153 (12), 126 (20), 111 (34), 109 (43), 108 (37), 83 (18), 59 (100). IR (film): 3334 (br, OH), 2978 (m), 2964 (m), 2936 (m), 1767 (s), 1098 (m), 913 (m). HRMS calcd for $C_{11}H_{17}O_3$ [M – 15]: 197.11777. Found: 197.11674. HRMS calcd for $C_{11}H_{20}O_2$ [M – CO]: 184.14633. Found: 184.14615.

Cyclopropylcarbinols 12

((*cis*)-1-methyl-2-pentylcyclopropyl)methanol (**12a**).

Method C2. 2-Methyl-2-vinyl oxirane (1g, 11 mmol) is added dropwise to *n*-butyl lithium 1.6 M in hexane (7 ml, 11 mmol) in diethyl ether (20 ml) at -78°C. After 1 h at -78°C the solution is slowly warmed up to room temperature. Dibromomethane (7.7g, 45 mmol) is added followed by dropwise addition of tert-butyl magnesium chloride (23 ml, 45 mmol) at 10°-20°C. After 24 h at 25°C the mixture is poured upon 2M HCl. Extraction with tert-butyl methyl ether, washing of the organic phase with conc. $NaHCO_3$, conc. NaCl, drying over $MgSO_4$, filtration and evaporation of the solvents gives 2.3g of a residue, which is purified by bulb-to-bulb distillation at 50°C / 0.06 mbar giving 1.45g (83%) of **12a** as colorless oil (cis / trans = 85:15). ^{1}H-NMR ($CDCl_3$): δ 0.1 (m, 1 H), 0.45 (m, 1 H), 0.65 (m, 1 H), 0.9 (t, 3 H), 1.15 (s, 3 H), 1.2 – 1.5 (8 H), 3.5 – 3.6 (2 d, 2 H) ppm. ^{13}C-NMR ($CDCl_3$) *cis*-isomer: δ 14.0 (q), 17.6 (t), 22.0 (s), 22.6 (t), 22.7 (q), 25.1 (d), 29.2 (t), 29.9 (t), 31.7 (t), 67.5 (t). *cis*-configuration determined by ^{13}C-NMR ($\underline{C}H_2O$ shift). ^{13}C-NMR ($CDCl_3$) *trans*-isomer: δ 15.2 (q), 16.8 (t), 21.9 (s), 22.6 (t), 22.7 (q), 25.1 (d), 29.0 (t), 29.8 (t), 31.75 (t) 72.8 (t). MS (EI): m/z (%) 138 ([M – H_2O]$^+$, 1), 125 (1), 123 (1), 99 (33), 83 (47), 71 (42), 69 (44), 58 (98), 57 (87), 56 (68), 55 (100), 43 (51), 41 (63). IR (film): 3331 (br, OH), 2655 (m), 2924 (s), 2857 (m), 1465 (m), 1378 (w), 1198 (w), 1097 (w), 1028 (s), 966 (w), 920 (w), 973 (w), 725 (w). HRMS calcd for $C_{10}H_{18}$ [M – 18]: 138.14085. Found: 138.14266. HRMS calcd for $C_6H_{11}O$ [M – *n*Bu]: 99.08099. Found: 99.08108.

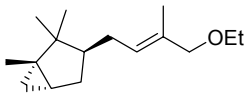
((cis)-2-isobutyl-1-methylcyclopropyl)methanol (**12b**). Prepared as described in method C2 from 2-methyl-2-vinyl oxirane (1g, 11 mmol), isopropyl lithium 0.7 M in pentane (16 ml, 11 mmol), dibromomethane (7.7g, 45 mmol) and tert-butyl magnesium chloride (23 ml, 45 mmol). Work-up and bulb-to-bulb distillation at 45°C / 0.06 mbar gave 1.3 g (84 %) of **12b** as colorless oil (*cis* / *trans* = 75:25). ^{1}H-NMR ($CDCl_3$): δ 0.0 and 0.1 (2 m, 1 H), 0.45 and 0.55 (2 m, 1 H), 0.65 (1 H), 0.9 (2 d, 6 H), 1.05 – 1.15 (1 H), 1.13 and 1.18 (2 s, 3 H), 1.45 (1 H), 1.65 (1 H), 3.5 – 3.6 (2 d, 2 H) ppm. ^{13}C-NMR ($CDCl_3$) *cis*-isomer: δ 18.0 (t), 21.7 (s), 22.6 and 22.7 (2 q), 23.4 (d), 26.95 (q), 29.1 (d) 38.2 (t), 67.5 (t). *cis*-configuration determined by ^{13}C-NMR ($\underline{C}H_2O$ shift). ^{13}C-NMR ($CDCl_3$) *trans*-isomer: δ 16.9 (t), 21.8 (s), 22.5 and 22.7 (2 q), 23.4 (d), 29.0 (d), 29.4 (q), 38.0 (t), 72.8 (t). MS (EI): m/z (%) 124 ([M – H_2O]$^+$, 3), 111 (7), 109 (19), 85 (39), 71 (30), 69 (90), 58 (100), 57 (97), 56 (65), 56 (68), 55 (99), 43 (100), 41 (93). IR (film): 3335 (br, OH), 2953 (s), 2928 (m), 2902 (m), 2869 (m), 1465 (m), 1382 (m), 1366 (m), 1029 (s), 970 (w), 877 (w). HRMS calcd for C_9H_{16} [M – 18]: 124.12520. Found: 124.12601. HRMS calcd for C_5H_9O [M – *i*Bu]: 85.06534. Found: 85.06538.



(1*SR*,3*RS*,4*RS*)-1-pentylspiro[2.7]decan-4-ol (**12c**). Prepared as described in method C2 from 1-vinyl-9-oxabicyclo[6.1.0]nonane (3g, 18 mmol),[36] n-butyl lithium 1.6 M in hexane (11 ml, 18 mmol), dibromomethane (12.5g, 72 mmol) and tert-butyl magnesium chloride (36 ml, 72 mmol). Work-up and bulb-to-bulb distillation at 98°C / 0.05 mbar gave 2.6 g (65 %) of **12c** as colorless oil (dr = 93:7). ^{1}H-NMR ($CDCl_3$): δ 0.3 (m, 1 H), 0.5 (m, 1 H), 0.8 (m, 1 H), 0.8 – 1.1 and 1.2 – 2.4 (22 H), 3.25 (1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 14.1 (q), 20.7 (t), 22.7 (t), 23.3 (t), 23.5 (t), 24.3 (d), 26.5 (t), 26.8 (t), 28.9

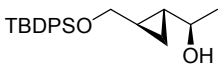
(t), 29.4 (s), 29.7 (t), 30.4 (t), 31.2 (t), 31.7 (t), 73.7 (d). *cis*-configuration assigned by COSY, HMBC, HSQC, NOESY in DMSO-D_6. MS (EI): m/z (%) 224 (M^+, 1), 206 ($[M - 18]^+$, 10), 178 (4), 163 (5), 149 (12), 135 (22), 126 (24), 109 (22), 107 (24), 98 (58), 97 (33), 96 (80), 95 (46), 93 (54), 69 (41), 68 (42), 67 (84), 55 (100), 41 (80). IR (film): 3362 (br, OH), 2919 (s), 2852 (m), 1456 (m), 1364 (w), 1106 (w), 1029 (m), 989 (m), 811 (w), 741 (w), 726 (w). HRMS calcd for $C_{11}H_{21}O$ [M – 15]: 169.15924. Found: 169.15994. HRMS calcd for $C_{15}H_{28}O$: 224.21402. Found: 224.21737. HRMS calcd for $C_{15}H_{26}$: 206.20345. Found: 206.20372.

Reference Compounds and Derivatives for Analysis.



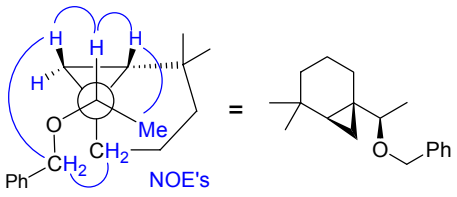
(trans)-3-((E)-4-ethoxy-3-methylbut-2-enyl)-1,2,2-trimethylbicyclo[3.1.0]hexane (**17**).

Method D. Sodium hydride 50% in mineral oil (1.6 g, 32 mmol) is added portionwise to alcohol **1a** (5 g, 24 mmol) in tetrahydrofuran (10 ml) at -50°C under nitrogen and stirring. The mixture is slowly warmed-up to 25°C overnight and poured upon water. *Tert*-butyl methyl ether extraction, washing of the organic phase with 4% oxalic acid, conc. $NaHCO_3$ and conc. NaCl until pH 7, drying over $MgSO_4$ and concentration gives 6.1g of an an oily residue, which is bulb-to-bulb-distilled at 85°C / 0.05 mbar giving 4.6 g (81%) of **17** as colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz): -0.5 (dd, 1 H), 0.35 (dd, 1 H), 0.75 (s, 3 H), 0.8 (m, 1 H), 0.85 (s, 3 H), 0.9 (m, 1 H), 0.95 (s, 3 H), 1.15 (m, 1 H), 1.2 (br, OH), 1.35 (m, 1 H), 1.55 (s, 3 H), 1.65 (m, 1 H), 1.7 (m, 1 H), 1.95 (m, 1 H), 3.75 (2 H), 5.3 (dd, 1 H) ppm. ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 13.8 (q), 13.9 (t), 15.2 (q), 17.4 (q), 19.7 (q), 22.5 (q), 22.9 (d), 28.25 (t), 31.4 (s), 32.5 (t), 41.2 (s), 44.7 (d), 64.8 (t), 76.8 (t), 127.8 (d), 132.0 (s). MS (EI): m/z (%) 236 (M^+, 2), 221 ($[M - 15]^+$, 3), 190 (7), 177 (20), 175 (30), 149 (12), 147 (11), 136 (12), 135 (23), 133 (18), 123 (67), 121 (90), 109 (43), 107 (80), 99 (32), 93 (46), 91 (37), 81 (94), 79 (34), 67 (41), 57 (44), 55 (62), 43 (100), 41 (70). IR (film): 3060 (w), 2952 (s), 2925 (s), 2856 (s), 1450 (m), 1378 (m), 1362 (m), 1348 (m), 1260 (w), 1206 (w), 1090 (s), 1013 (m), 970 (w), 872 (w), 834 (w), 816 (w). Anal. calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.33; H, 12.09.



(*syn*)-1-(2-((tert-butyldimethylsilyloxy)methyl)cyclopropyl)ethanol (**19**). Compound **2p** (1 g, 6 mmol) or **2q** (0.75 g, 6 mmol) in methanol (15 ml) and dichloromethane (5 ml) is ozonized at -70°C.

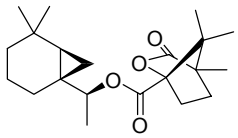
After appearance of a persistent green-blue color the ozone generator is switched of and oxygen is bubbled for a few minutes through the solution. $NaBH_4$ (0.5 g, 12 mmol) is added at -70°C. After warming to room temperature water is added. Extraction with ethyl acetate, drying over $MgSO_4$, filtration and evaporation of the solvents gives 0.5g of a crude oil, which is dissolved in tetrahydrofuran (10 ml). Sodium hydride 60% in mineral oil (0.14 g, 3.4 mmol) is added at -20°C, followed by tert-butyl diphenylsilyl chloride (0.95 g, 3.4 mmol). After 2 h at -20°C methanol (2 ml) is added and water (20 ml). Ethyl acetate extraction, washing of the combined organic phase with conc. NaCl, drying over $MgSO_4$, filtration and evaporation gives 1.1 g of a crude oil, which is purified by filtration over silicagel using first tert-butyl methyl ether then methanol as eluents. One obtains 0.31- 0.47g (17-26%) of **19** as colorless oil, whose analytical data are identical with the ones described in the literature for this compound.[37]



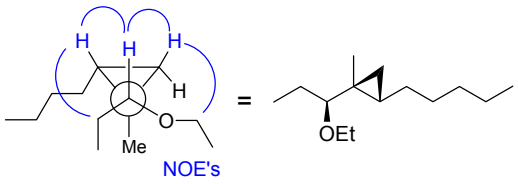
(1*RS*,6*SR*)-1-((*RS*)-1-(benzyloxy)ethyl)-5,5-dimethylbicyclo[4.1.0]heptane (**20**).

Method D1. Sodium hydride 50% in mineral oil (0.3 g, 7 mmol) and cyclopropyl carbinol **2e** (1 g, 6 mmol) in tetrahydrofuran (20 ml) are heated 7 h at 70°C under nitrogen and stirring. Tributylammonium iodide (20 mg, 0.06 mmol) are added followed by slow addition of benzyl bromide (1 g, 6 mmol). After 2 days at 25°C the mixture is quenched with 2 M HCl and extracted with *tert*-butyl methyl ether. After washing the organic phase with conc. $NaHCO_3$, drying over $MgSO_4$, filtration and concentration the residue is bulb-to-bulb distilled giving 1 g (64%) of benzylether **20** as colorless oil. ^{1}H-NMR ($CDCl_3$): δ 0.25 (dd, 1 H), 0.3 (dd, 1 H), 0.5 (dd, 1 H), 0.8 – 1.5 (6 H), 1.0 (s, 3 H), 1.05 (s, 3 H), 1.2 (d, 3 H), 2.05 (1 H), 2.7 (q, 1 H), 4.4 (d, 1 H), 4.7 (d, 1 H), 7.2 – 7.4 (5 H) ppm. ^{13}C-NMR: ($CDCl_3$): δ 18.5 (t), 18.6 (q), 19.1 (t), 23.0 (s), 23.2 (t), 26.6 (d), 27.8 (s), 29.8 (q), 30.7 (q), 35.2 (t), 70.1 (t), 82.5 (d), 127.2

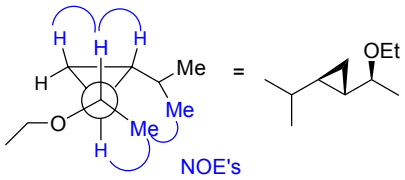
(d), 127.5 (2 d), 128.3 (2 d), 139.4 (s). Relative configuration tentatively assigned by HMBC, HSQC and NOESY in C_6D_6. MS (EI): m/z (%): 243 ($[M - 15]^+$, 1), 225 (1), 167 (2), 152 (6), 150 (6), 135 (7), 123 (10), 121 (6), 109 (8), 107 (11), 91 (100), 67 (10), 43 (14). IR (film): 2925 (s), 2859 (s), 1495 (w), 1454 (m), 1361 (m), 1203 (w), 1091 (s), 1027 (m), 933 (w), 732 (s), 696 (s). Anal. calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.65; H, 10.49.



(1*S*)-((*S*)-1-((1*S*,6*R*)-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)ethyl)4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (**21**). Prepared according to method D2 from cyclopropyl carbinol **2e** (1 g, 6 mmol), (-)-camphanic chloride (1.3 g, 6 mmol) and DMAP (72 mg, 0. 6 mmol) in pyridine (25 ml). The crude product is dissolved in *tert*-butyl methyl ether, filtered over Silicagel and concentrated. The residue is slowly crystallized from hexane giving **21** in form of white needles (mp117°C), whose relative configuration was determined by X-ray analysis (see SI 2). ^{1}H-NMR ($CDCl_3$): δ 0.2 (dd, 1 H), 0.5 (dd, 1 H), 0.6 (dd, 1 H), 0.9 – 1.0 (1 H) 0.95 (s, 3 H), 0.96 (s, 3 H), 1.0 – 1.1 (1 H), 1.06 (s, 3 H), 1.07 (s, 3 H), 1.12 (s, 3 H), 1.2 – 1.3 (1 H), 1.2 – 1.3 (1 H), 1.29 (d, 2 H), 1.3 - 1.4 (m, 1 H), 1.7 (1 H), 1.9 – 2.1 (4 H), 2.4 (m, 1 H), 4.4 (q, 1 H) ppm. ^{13}C-NMR: ($CDCl_3$): δ 9.7 (q), 16.6 (t), 16.7 (q), 16.8 (q), 17.3 (q), 18.7 (t), 23.95 (s), 24.0 (t), 27.8 (s), 28.9 (d), 29.0 (t), 29.9 (q), 30.4 (q), 30.45 (t), 34.9 (t), 53.9 (s), 54.7 (s), 80.4 (d), 91.3 (s), 166.9 (s), 178.4 (s). MS (EI): m/z (%): 306 (2), 291 (4), 199 (2), 181 (4), 164 (2), 150 (100),135 (100), 121 (30), 109 (24), 107 (40), 95 (24), 93 (28), 83 (26), 81 (17), 79 (19), 67 (20), 55 (32), 43 (11), 41 (25). IR (film): 2954 (m), 2932 (m), 2865 (m), 1790 (s), 1743 (s), 1726 (m), 1449 (m), 1372 (m), 1309 (m), 1260 (s), 1168 (m), 1103 (s), 1059 (s), 1017 (m), 992 (m), 957 (w), 932 (m), 896 (w), 864 (w), 794 (w), 741 (w), 627 (w). Anal. calcd for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.42; H, 9.39.

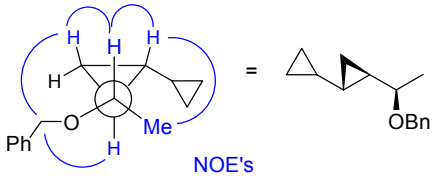


(*syn, trans*)-1-(1-ethoxypropyl)-1-methyl-2-pentylcyclopropane (**22**). Prepared according to method D from **2h** (2 g, 11 mmol), sodium hydride 60% in mineral oil (0.7 g, 17 mmol) and ethyl iodide (2.7 g, 17.4 mmol) in toluene (9 ml). Yield of **21** after bulb-to-bulb distillation (80°C / 0.2 Torr): 2.1 g (92%). ^{1}H-NMR ($CDCl_3$): δ 0.05 (dd, 1 H), 0.35 (m, 1 H), 0.6 (dd, 1 H) 0.9 (t, 3 H), 0.95 (t, 3 H), 1.0 (s, 3 H), 1.2 (t, 3 H), 1.25 – 1.6 (11 H), 2.25 (dd, 1 H), 3.3 (m, 1 H), 3.75 (m, 1 H) ppm. ^{13}C-NMR: δ 11.3 (q), 12.2 (q), 14.1 (q), 15.6 (q), 19.3 (d), 20.4 (t), 21.4 (s), 22.6 (t), 26.1 (t), 28.8 (t), 29.7 (t), 31.9 (t), 64.4 (t), 89.0 (d). *syn*-configuration confirmed by NMR-analysis of ethyl ether **22**. MS (EI): m/z (%) 183 ([M – C_2H_5]$^+$, 26), 166 ([M – EtOH]$^+$, 2), 129 (54), 114 (53), 99 (100), 87 (70), 83 (39), 81 (33), 71 (63), 59 (81), 57 (50), 55 (58), 43 (36), 41 (59). IR (film): 2958 (m), 2925 (s), 2855 (m), 1458 (m), 1381 (w), 1340 (w), 1212 (w), 1153 (w), 1111 (s), 1080 (m), 1025 (w), 979 (m), 883 (w), 725 (w). HRMS calcd for $C_{12}H_{23}O$ [M – C_2H_5]: 183.17489. Found: 183.17451. HRMS calcd for $C_{12}H_{22}$ [M – EtOH]: 166.17215. Found: 166.17225.

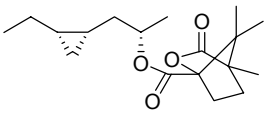


(*syn*, *trans*)-1-(1-ethoxyethyl)-2-isopropylcyclopropane (**23**). Prepared according to method D from **2n** (1 g, 5 mmol), sodium hydride 60% in mineral oil (0.3 g, 7 mmol) and ethyl iodide (1.1 g, 7 mmol) in toluene (9 ml) and purified by bulb-to-bulb distillation at reduced pressure giving 0.6 g (79%) of **23** as colorless oil. ^{1}H-NMR ($CDCl_3$) *syn*-isomer: δ 0.25 (m, 1 H), 0.4 (m, 1 H), 0.5 (m, 1 H), 0.6 (m, 1 H), 0.95 (2 d, 6 H), 1.2 (m, 1 H), 1.2 (t, 3 H), 1.25 (d, 3 H), 2.7 (m, 1 H), 3.4 (m, 1 H), 3.6 (m, 1 H) ppm.

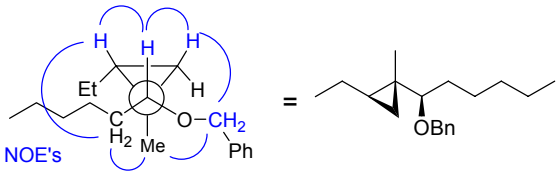
^{13}C-NMR ($CDCl_3$) *syn*-isomer: δ 11.3 (t), 15.7 (q), 20.6 (q), 21.9 (q), 22.1 (q), 23.6 (2 d), 32.6 (d), 63.5 (t), 79.4 (d). *syn*-configuration determined by COSY, HMBC, HSQC, NOESY in C_6D_6. MS (EI): m/z (%) 141 ([M – 15]$^+$, 22), 110 ([M – EtOH]$^+$, 27), 101 (40), 85 (90), 73 (44), 58 (86), 57 (82), 55 (100), 45 (79), 43 (60). HRMS calcd for $C_9H_{17}O$ [M – 15]: 141.12794. Found: 141.12787. HRMS calcd for C_8H_{14} [M – EtOH]: 110.10955. Found: 110.10990.



(*syn*, *trans*)-2-(1-(benzyloxy)ethyl)bi(cyclopropane) (**24**). Prepared according to method D1 from **2r** (20 mg, 0.16 mmol), sodium hydride 60% in mineral oil (10 mg, 0.23 mmol), TBAJ (1 mg, 0.003 mmol) and benzyl bromide (27 mg, 0.16 mmol) in THF (1 ml) to give after work-up and concentration under high vacuum 32 mg (98%) of crude **24**. ^{1}H-NMR ($CDCl_3$): δ 0.03 (m, 1 H), 0.35 (m, 2 H), 0.45 (m, 2 H), 0.6 (m, 1 H), 0.65 (m, 1 H), 0.85 (2 H), 1.25 (d, 3 H), 2.85 (q, 1 H), 4.5 (d, 1 H), 4.6 (d, 1 H), 7.35 (5 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 2.8 (t), 2.9 (t), 10.6 (t), 11.7 (d), 17.0 (d), 20.4 (q), 22.2 (d), 70.1 (t), 78.5 (d), 127.3 (d), 127.5 (2 d), 128.3 (2 d), 139.3 (s). *syn*-configuration tentatively confirmed by COSY, HMBC, HSQC and NOESY in C_6D_6. MS (EI): m/z (%) 162 ([M – BnOH]$^+$, 2), 161 (12), 129 (1), 118 (1), 117 (1), 108 (1), 107 (1), 105 (3), 104 (3), 93 (4), 92 (12), 91 (100), 81 (, bicyclopropyl$^+$, 5), 79 (7), 65 (10), 55 (9), 53 (3), 43 (11), 41 (7). R_T = 4.0 (*anti*), 4.1 (*syn*) min. IR (film): 3066 (w), 3000 (w), 2962 (m), 2925 (m), 2854 (m), 1719 (w), 1496 (w), 1454 (m), 1369 (m), 1202 (w), 1096 (s), 1058 (m), 1028 (m), 1016 (m), 966 (w), 902 (m), 819 (w), 733 (s), 696 (s). Anal. calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.21; H, 9.46.

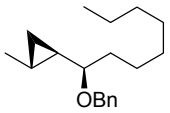


(S)-1-((1S,2S)-2-ethylcyclopropyl)propan-2-yl)-4,7,7-trimethyl-3-oxo-2-oxa-bicyclo[2.2.1]heptane-1-carboxylate (**25**). Prepared according to method D2 from **4b** (4 g, 31 mmol), (-)-camphanic chloride (6.8 g, 31 mmol) and pyridine (70 ml). Work-up, concentration and bulb-to-bulb distillation at 170°C / 0.05 Torr gives 7.9 g (83%) of **25**. Crystallization from hexane between 0° and -20°C gives white needles (mp 50 - 55°C), whose structure was determined by X-ray analysis (see SI 2). ^{1}H-NMR ($CDCl_3$): δ -0.15 (m, 1 H), 0.6 - 0.75 (3 H), 0.97 (s, 3 H), 0.99 (t, 3 H), 1.06 (s, 3 H), 1.12 (s, 3 H), 1.2 (m, 1 H), 1.35 (d, 3 H), 1.4 (m, 1 H), 1.5 (m, 1 H), 1.7 (2 H), 1.9 (m, 1 H), 2.0 (m, 1 H), 2.45 (m, 1 H), 5.15 (m, 1 H) ppm. ^{13}C-NMR: ($CDCl_3$): δ 9.7 (q), 10.4 (t), 12.0 (d), 14.3 (q), 16.7 (q), 16.8 (q), 17.0 (d), 20.0 (q), 22.0 (t), 28.9 (t), 30.5 (t), 34.6 (t), 53.9 (s), 54.8 (s), 73.5 (d), 91.1 (s), 167.0 (s), 178.2 (s). MS (EI): m/z (%): 308 (M^+, 1), 293 ($[M - 15]^+$, 1), 280 ($[M - CO]^+$, 1), 267 (2), 251 ($[M - CO - C_2H_5]^+$, 3), 199 (6), 181 (10), 155 (10), 153 (30), 137 (14), 125 (35), 110 (80), 109 (60), 97 (40), 95 (41), 83 (79), 81 (83), 69 (80), 68 (100), 67 (39), 55 (93), 41 (76). IR (film): 2961 (w), 2932 (w), 1789 (s), 1747 (m), 1725 (m), 1451 (w), 1379 (w), 1312 (w), 1266 (m), 1167 (m), 1126 (w), 1102 (m), 1060 (s), 1017 (m), 992 (w), 958 (w), 897 (w), 830 (w), 740 (w). Anal. calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.23; H, 9.15.

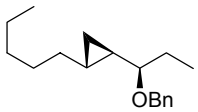


***cis, syn*-((-1-(2-ethyl-1-methylcyclopropyl)hexyloxy)methyl)benzene** (**26**). Prepared according to method D1 from **2g** (1.8 g, 9.8 mmol), sodium hydride 60% in mineral oil (0.3 g, 15 mmol), TBAJ (36 mg, 0.1 mmol) and benzyl bromide (2.1 g, 12 mmol) in THF (45 ml) to give after work-up and flash

chromatography over silicagel (hexan / *tert*-butyl methyl ether 50:1) 1.3 g (48%) of benzylether **26**. ^{1}H-NMR ($CDCl_3$): δ 0.15 (dd, 1 H), 0.3 (m 1 H), 0.7 (dd, 1 H), 0.9 (t, 3 H), 1.0 (t, 3 H), 1.15 (s, 3 H), 1.25 – 1.7 (11 H), 2.5 (dd, 1 H), 4.4 (d, 1 H), 4.75 (d, 1 H), 7.25 (1 H), 7.35 (4 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 12.0 (q), 14.1 (q), 14.4 (q), 20.8 (t), 21.0 (d), 21.5 (s), 22.0 (t), 22.7 (t), 26.4 (t), 32.0 (t), 33.3 (t), 70.6 (t), 86.65 (d), 127.2 (d), 127.2 (2 d), 128.2 (2 d), 139.5 (s). *syn*-configuration confirmed by COSY, HMBC, HSQC and NOESY in C_6D_6. MS (EI): m/z (%) 218 ($[M - C_4H_8]^+$,3), 203 ($[M - C_5H_{11}]^+$, 6), 91 (100), 55 (10). IR (film): 2957 (m), 2931 (m), 2858 (m), 1454 (m), 1378 (w), 1306 (w), 1093 (m), 1070 (s), 1028 (m), 949 (w), 926 (w), 732 (s), 695 (s). Anal. calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.24; H, 10.91.



***cis*, *syn*-((1-(2-methylcyclopropyl)octyloxy)methyl)benzene** (**27**). Prepared according to method D1 from **2l** (1.8 g, 9.8 mmol), sodium hydride 60% in mineral oil (0.35 g, 15 mmol), TBAJ (36 mg, 0.1 mmol) and benzyl bromide (2.1 g, 12 mmol) in THF (45 ml) to give after work-up and flash chromatography over silicagel (hexan / *tert*-butyl methyl ether 50:1) 1.45 g (53%) of benzylether **27**. ^{1}H-NMR ($CDCl_3$): δ 0.4 (m, 1 H), 0.45 (m), 0.55 (m, 2 H), 0.9 (t, 3 H), 1.05 (d, 3 H), 1.2 – 1.35 (8 H), 1.35 – 1.5 (2 H), 1.6 (1 H), 1.7 (1 H), 2.7 (m, 1 H), 4.5 (d, 1 H), 4.7 (d, 1 H), 7.25 (1 H), 7.3 (4 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 9.4 (d), 13.0 (t), 14.1 (q), 18.5 (q), 22.7 (t), 23.9 (d), 25.7 (t), 29.3 (t), 29.8 (t), 31.9 (t), 35.5 (t), 70.3 (t), 82.7 (d), 127.2 (d), 127.55 (2 d), 127.8 (2 d), 139.4 (s). *syn*-configuration confirmed by COSY, HMBC, HSQC and NOESY in C_6D_6. MS (EI): m/z (%) 175 ($[M - heptyl]^+$, 22), 91 (100), 55 (50). IR (film): 2925 (m), 2854 (m), 1496 (w), 1453 (m), 1379 (w), 1091 (m), 1068 (m), 1027 (m), 969 (w), 892 (w), 937 (s), 696 (s). HRMS calcd for $C_{12}H_{15}O$ [$M - C_7H_{15}$]: 175.11229. Found: 175.11300.



***cis*, *syn*-((1-(2-pentylcyclopropyl)propoxy)methyl)benzene** (**28**). Prepared according to method D1 from **2m** (1.7 g, 10 mmol), sodium hydride 60% in mineral oil (0.36 g, 15 mmol), TBAJ (37 mg, 0.1 mmol) and benzyl bromide (2.1 g, 12.5 mmol) in THF (45 ml) to give after work-up and flash chromatography over silicagel (hexan / *tert*-butyl methyl ether 50:1) 1.1 g (42%) of benzylether **28**. ^{1}H-NMR ($CDCl_3$): δ 0.4 (m, 1 H), 0.45 (m, 1 H), 0.5 (m, 1 H), 0.6 (m, 1 H), 0.9 (t, 3 H), 1.0 (t, 3 H), 1.2 – 1.4 (8 H), 1.7 (2 H), 2.65 (ddd, 1 H), 4.5 (d, 1 H), 4.7 (d, 1 H), 7.2 – 7.4 (5 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 10.1 (q), 11.9 (t), 14.1 (q), 15.3 (d), 22.3 (d), 22.7 (t), 28.0 (t), 29.1 (t), 31.75 (t), 33.8 (t), 70.3 (t), 83.9 (d), 127.2 (d), 127.5 (2 d), 127.7 (2 d), 139.4 (s). *syn*-configuration confirmed by COSY, HMBC, HSQC and NOESY in C_6D_6. MS (EI): m/z (%) 231 ([M – ethyl]$^+$, 12), 91 (100), 55 (7). IR (film): 2957 (m), 2923 (m), 2853 (m),1496 (m), 1377 (w), 1100 (m), 1067 (m), 1028 (m), 970 (w), 903 (w), 932 (s), 696 (s). HRMS calcd for $C_{16}H_{23}O$ [M – C_2H_5]: 231.17489. Found: 231.17504.

Abbreviations

Ac	acetyl
Anal.	Analysis
bp	boiling point
calcd	calculated
COSY	correlation spectroscopy
d	doublet (NMR)
dist	distilled
DMAP	4-dimethylamino pyridine
DMSO	dimethylsulfoxide
dr	diastereomer ratio
EI	electron induction (MS)
equiv	equivalents (molar)
Et	ethyl
FC	flash chromatography
GC	gas chromatography
gem	geminal
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple quantum coherence
HRMS	high resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
*i*Bu	isobutyl
*i*Pr	isopropyl
IR	infrared (spectrometry)
m	middle (IR)
m	multiplet (NMR)
M	metal
M	molecular mass (MS)
Me	methyl
MHz	mega Hertz
mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser enhancement spectroscopy
n	number of substituents R
*n*Pr	*n*-propyl
Ph	phenyl
ppm	parts per million (NMR)
q	quartet (NMR)
quant.	quantitative (yield)
R	organic rest
ref.	reference
r_T	retention time (GC)
RT	room temperature
s	singlet (NMR)
s	strong (IR)
SI	supporting information
t	triplet (NMR)
TBAJ	tetrabutylammonium iodide
TBDPS	*tert*-butyl diphenyl silyl
*t*Bu	*tert*-butyl
THF	tetrahydrofuran
*t*Pe	tert-pentyl
w	weak (IR)

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