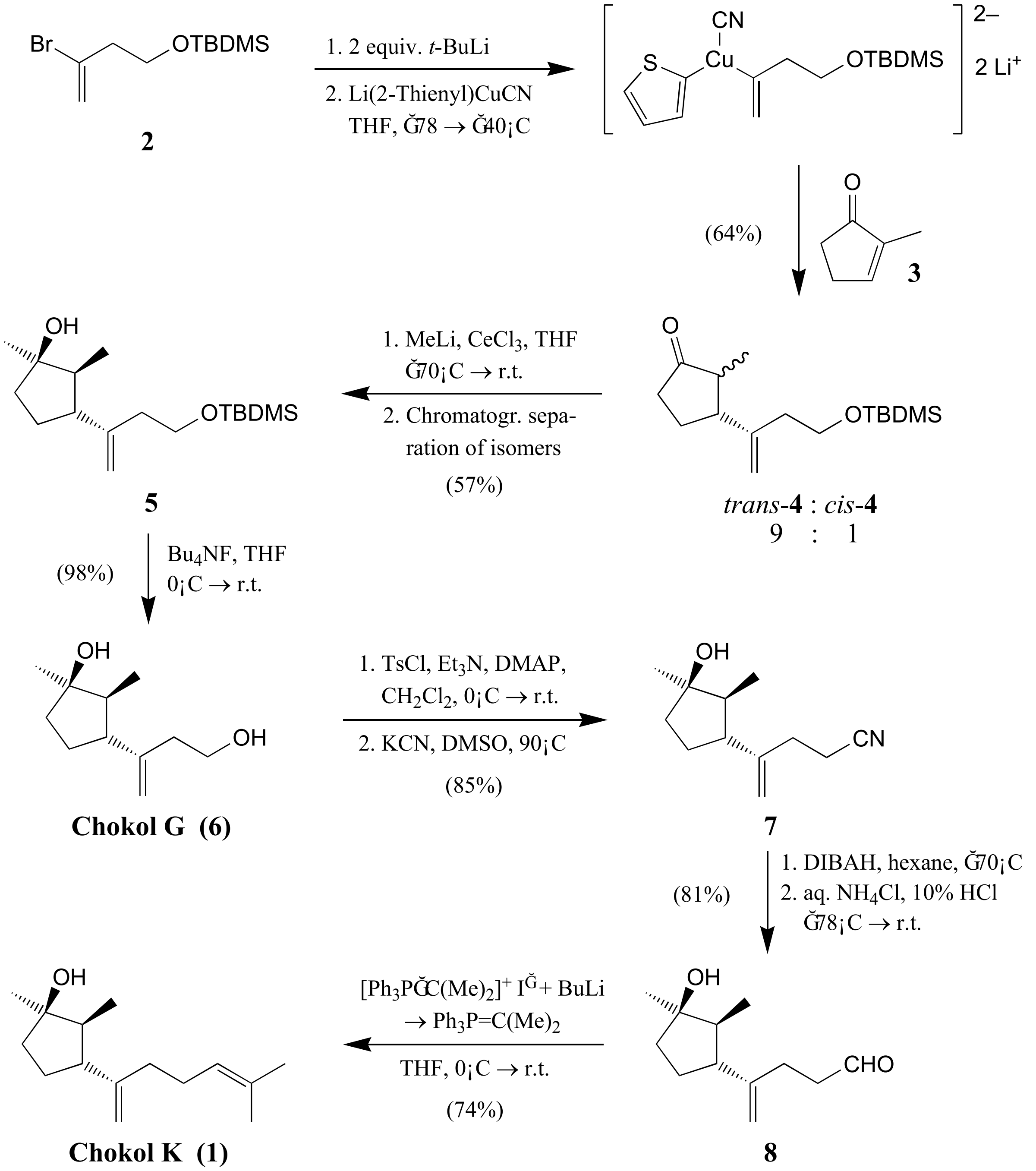
Electronic supplementary material:

The synthesis of (±)-chokol K ((1*R**,2*S**,3*R**)-1,2-dimethyl-3-(6-methylhepta-1,5-dien-2-yl)cyclopentanol) **1** is summarized in *Scheme 1*.



Scheme 1

The vinyl bromide **2**, prepared by protection of the hydroxy group (t-BuMe$_2$SiCl, Et$_3$N, DMAP, CH$_2$Cl$_2$, 0°C → r.t., 95% yield) of commercially available 3-bromobut-3-en-1-ol (*Acros*) as its *t*-butyldimethylsilyl (TBDMS) ether, was converted to the higher-order mixed organocuprate species according to the protocol of Lipshutz (1987) and Lipshutz et al. (1993). Conjugate 1,4-addition of this mixed vinyl cyanocuprate reagent to 2-methylcyclohex-2-en-1-one **3** (Quinkert et al. 1988) generates the adduct **4** as an inseparable mixture of two diastereoisomers. The ^{1}H-NMR spectrum of this product mixture revealed a ratio of 9 : 1 in favor of the thermodynamically more stable *trans*-disubstituted diastereoisomer. The reaction of **4** with methylcerium dichloride (Imamoto 1984), according to the modified procedure of Dimitrov et al. (1994), afforded a mixture consisting of four diastereoisomeric alcohols from which the desired alcohol **5** was separated by repeated column chromatography (silica gel, hexane/*t*-BuOMe 20 : 1 → 10 : 1). Relative configurations at C(2), C(3), and C(4) for the major isomer **5** were established by means of 2D-NOE investigations. Cleavage of the silyl ether protecting group was accomplished by treatment of **5** with tetrabutylammonium fluoride in THF to provide the diol **6** ((±)-chokol G) as a colorless viscous oil. For the subsequent conversion of **6** into **1**, the four-step sequence established by Tanimori et al. (1994) was followed with some modification. After chromatographic purification (silica gel, pentane/Et$_2$O 1:1) and bulb-to-bulb distillation (55°C/10^{-2} Torr), **1** was obtained as a colorless oil. Spectroscopic data (IR, NMR, and MS[1])of the product were found to be in complete accordance with published data (Tanimori et al. 1994).

References

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[1] IR (*Perkin-Elmer* FT-IR spectrophotometer, model *Spectrum ONE*; film) $\nu_{\max}$ [cm^{-1}]: 3422*m*, 3079*w*, 2964*s*, 2930*s*, 2874*s*, 1640*m*, 1452*s*, 1376*s*, 1287*w*, 1194*m*, 1152*m*, 1103*m*, 1022*m*, 917*s*, 886*s*, 826*w*, 639*w*, 543*w*, 447*w*. ^{1}H-NMR (*Bruker DRX-500*, 500 MHz, CDCl$_3$) δ [ppm]: 5.13 (*tsept.* $^{3}J = 6.9$, $^{4}J = 1.4$ Hz, H–C(5')); 4.78, 4.76 (2 m_c, $H_2C(1')$); 2.39 (*dt,* $^{3}J = 11.3, 9.0$ Hz, H–C(3)); 2.14 (br. *q*, $^{3}J \approx 7.4$ Hz, $H_2C(4')$); 2.01–1.91 (*m*, $H_2C(3')$, H–C(4)); 1.75 (*t,* $^{3}J = 7.9$ Hz, $H_2C(5)$); 1.69 (*d,* $^{4}J = 0.9$ Hz, H_3C–C(6')); 1.62 (br. *s*, H_3C–C(6')); 1.55 (*dq*, $^{3}J = 11.3, 6.8$ Hz, H–C(2)); 1.43 (*dq*, $^{2}J = 13.0$ Hz, $^{3}J = 8.1$ Hz, H–C(4)); 1.28 (*s*, H_3C–C(1)); 1.14 (br. *s*, HO–C(1)); 0.87 (*d*, $^{3}J = 6.8$ Hz,

H_3C–C(2)). ^{13}C-NMR (*Bruker DRX-500*, 125.8 MHz, $CDCl_3$) δ [ppm]: 151.59 (*s*, C(2')); 131.53 (*s*, C(6')); 124.36 (*d*, C(5')); 108.09 (*t*, C(1')); 80.30 (*s*, C(1)); 51.98 (*d*, C(3)); 47.55 (*d*, C(2)); 39.99 (*t*, C(5)); 33.77 (*t*, C(3')); 28.63 (*t*, C(4)); 26.82 (*t*, C(4')); 26.60 (*q*, H_3C–C(1)); 25.69, 17.73 (2 *q*, $(H_3C)_2C(6')$); 10.66 (*q*, H_3C–C(2)); assignments *via* ^{1}H,^{13}C-correlation spectra. EI-MS (electron impact ionization, *MAT 95* spectrometer at 70 eV) *m/z* (%): 222 (5, $M^{+\bullet}$), 207 (4, $[M - CH_3]^+$), 204 (13, $[M - H_2O]^{+\bullet}$), 189 (7), 179 (7), 164 (12), 161 (52), 149 (6), 135 (25), 121 (28), 109 (48), 108 (17), 107 (16), 95 (25), 93 (17), 91 (10), 82 (10), 81 (12), 79 (14), 71 (12), 69 (100), 67 (20), 55 (15), 43 (30), 41 (45).