A Concise Total Synthesis of Dactylol via Ring Closing Metathesis

Alois Fürstner* and Klaus Langemann

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany

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A straightforward total synthesis of the cyclooctenoid sesquiterpene dactylol (**1**) and of 3a-*epi*-dactylol (**13**) has been achieved in six synthetic operations. The unusual rearranged bicyclo[6.3.0]-undecane isoprenoid skeleton of these target molecules has been formed via an initial three-component coupling triggered by 1,4-addition of a methylcopper reagent (MeLi, CuI, Bu_3P) to cyclopentenone, followed by trapping of the enolate formed with 2,2-dimethyl-4-pentenal as the electrophile. The aldol **8** thus obtained was elaborated into the *trans*-disubstituted cyclopentanone derivative **10** which reacted with a methallylcerium reagent to afford a mixture of the tertiary alcohols **11a** and **12a**. Separation and O-silylation of these diastereoisomers, ring-closing metathesis (RCM) of the resulting dienes **11b** and **12b** to form the cyclooctene ring using Schrocks molybdenum carbene **5** as a precatalyst, and a final deprotection afforded the title compound and its epimer in excellent yields. This approach clearly surpasses previous ones in terms of efficiency, flexibility, accessibility of the substrates, number of steps, atom economy, and overall yield.

The synthesis of eight-membered ring systems remains a formidable challenge despite the progress which has been achieved in this area in recent years.[1] Unfavorable entropic and enthalpic factors impede their preparation; once they are formed, further functionalization is difficult due to their susceptibility to transannular reactions and the large number of low-energy conformations. These notions clearly emerge from many synthetic approaches *e.g.* to cyclooctanoid terpenes, a rapidly growing family of structurally diverse natural products. Among them, dactylol (**1**, Figure 1) has attracted particular attention because of its unusual rearranged *trans*-bicyclo[6.3.0]-undecane isoprenoid skeleton. This compound was first isolated from the Carribean sea hare *Aplysia dactylomela*[2] and was later found in the seaweed *Laurencia poitei*.[3] It seems likely that the mollusk concentrates this metabolite while grazing on *L. poitei* or related *Laurencia* species.[3]

Dactylol is biosynthetically derived from humulene (**4**) and structurally closely related to poitediol (**2**)[3] and precapnelladiene (**3**).[4] The known entries into this class of compounds, although they elegantly exploit either sigmatropic rearrangements[5,6] or cycloaddition strategies,[7,8] are rather lengthy with the overall yield being < 1% in all cases. This also holds true for a biomimetic approach to this challenging target.[9] In the following we disclose an unprecedentedly short and efficient total synthesis of dactylol (**1**) and its epimer **13** which is based on a three-component assembly followed by ring-closing metathesis (RCM) as the key steps.

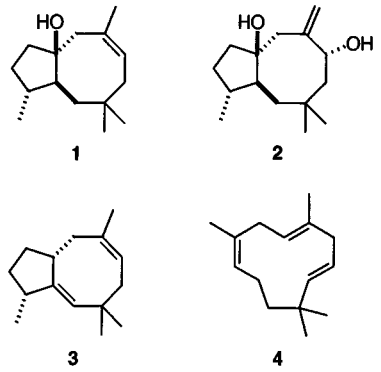

Figure 1.

The discovery of high-performance catalysts for RCM of functionalized 1,ω-dienes such as the molybdenum carbene **5** developed by Schrock et al. has substantially upgraded this valuable process in practical terms (Scheme 1).[10,11] Although most applications reported so far have focused on the formation of five-, six-, and seven-membered ring systems, some recent reports on successful cyclizations of rather strained medium-ring sized carbo- and heterocycles,[12] together with the excellent experiences which we have gained in RCM-based macrolide syntheses[13] prompted us to rely upon RCM in our approach to dactylol (Scheme 2).

Very reliable and efficient procedures for the consecutive introduction of two side chains to cyclopentenone derivatives have been explored in the context of prosta-

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(3) Fenical, W.; Schulte, G. R.; Finer, J.; Clardy, J. *J. Org. Chem.* **1978**, *43*, 3628−3630.

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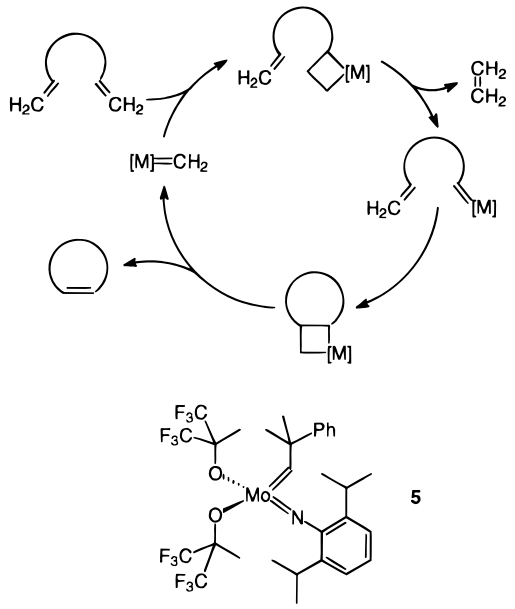
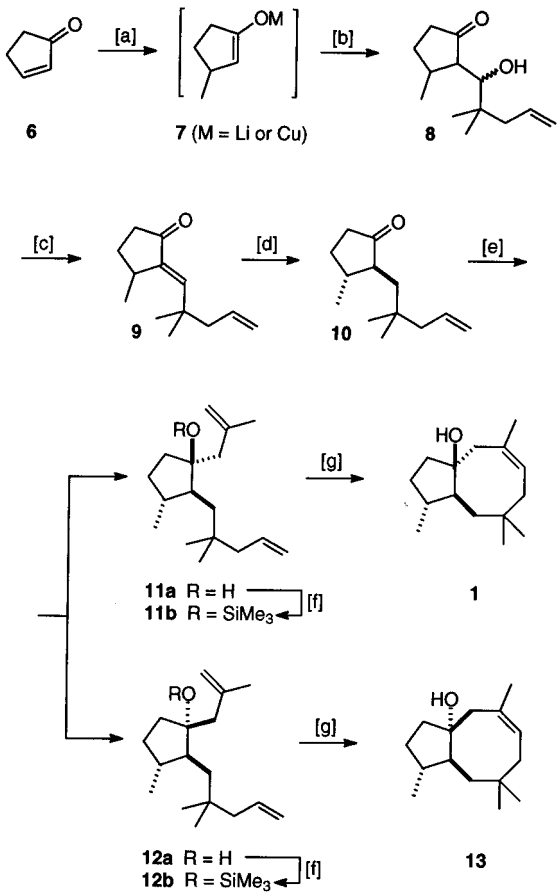
Scheme 1



5

glandin synthesis.[14] We made use of such a one-pot "three component coupling process" developed by Noyori et al.[15] for the expeditious assembly of the carbon skeleton of **1** from cyclopentenone **6** as the starting material. Specifically, reaction of **6** with the organocopper reagent formed *in situ* from MeLi, CuI, and Bu_3P at low temperature, followed by addition of commercially available 2,2-dimethyl-4-pentenal in order to trap the kinetically defined, nonequilibrating enolate **7**, gave compound **8** in 77% yield. Its dehydration afforded enone **9** as a single isomer which underwent chemo- and diastereoselective hydrogenation on treatment with Bu_3SnH in the presence of $ZnCl_2$ and catalytic amounts of $Pd(PPh_3)_4$.[16] The 1,2-*trans* arrangement in ketone **10** thus formed clearly emerged from the analysis of the ^{13}C NMR spectrum of this compound by comparison with literature data.[17] Thus, the stage was set for the formation of the tertiary alcohol group bearing a methallyl side chain. Best results were obtained upon reaction of the readily enolizable ketone **10** with a highly nucleophilic but only weakly basic organocerium reagent.[18] Hence, methallylbromide was first converted into the corresponding Grignard reagent without Wurtz coupling interfering on treatment with highly activated Mg–graphite in THF.[19] Its transmetalation with anhydrous

Scheme 2[a]



[a] Total synthesis of (±)-dactylol (**1**) and its 3a-epimer **13**. Only one antipode of the racemates is depicted: [a] MeLi (1 equiv), CuI (1 equiv), Bu_3P (2.2 equiv), Et_2O, −78 °C (1 h) → −40 °C (2.5 h); [b] 2,2-dimethyl-4-pentenal, −78 °C → rt, 77%; [c] methanesulfonyl chloride, DMAP, CH_2Cl_2, 35 °C, 18 h, 85%; [d] Bu_3SnH (1.2 equiv), $ZnCl_2$ (1.5 equiv), $Pd(PPh_3)_4$ (1.6 mol %), THF, rt, 20 min, 83%; [e] (i) methallyl bromide, Mg–graphite (4.3 equiv), THF, 65 °C, 30 min; (ii) $CeCl_3$, −78 °C, 2 h, 80% combined yield, **11a**:**12a** = 1:1.2; [f] $(Me_3Si)_2NH$ (1.25 equiv), acetyl chloride (1.25 equiv), DMAP (1.33 equiv), 93% (**11a** → **11b**), 95% (**12a** → **12b**); [g] (i) molybdenum carbene **5** (3 mol %), hexane, 55 °C, 3 h; (ii) aqueous TBAF, THF, 50 °C, 3 h, 92% (**11b** → **1**), 85% (**12b** → **13**).

$CeCl_3$ followed by addition of **10** gave alcohols **11a** and **12a** in a 1:1.2 ratio. These compounds can be readily separated by flash chromatography and were processed independently.

Attempted cyclization of these alcohols by RCM with the Schrock carbene **5** as the precatalyst[11] completely failed and led to quantitative recovery of the starting

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(15) Suzuki, M.; Kawagishi, T.; Suzuki, T.; Noyori, R. *Tetrahedron Lett.* **1982**, 4057–4060.

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(17) The C_α-atoms of substituents in *trans*-disubstituted cyclopentanes resonate at significantly lower field than that in the corresponding *cis*-disubstituted ones, *cf.*: Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR Spektroskopie*; Thieme: Stuttgart, 1984.

(18) (a) Imamoto, T.; Takiyama, N.; Nakamura, K. *Tetrahedron Lett.* **1985**, 4763–4766. (b) Review: Molander, G. A. *Chem. Rev.* **1992**, *92*, 29–68. (c) Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: New York, 1994. (d) A better diastereoselectivity was obtained with a titanium ate complex formed *in situ* from methallylmagnesium bromide and $Ti(O\text{-}iPr)_4$ (**11a**:**12a** = 2.3:1), *cf.*: Reetz, M. T.; Westermann, J.; Steinbach, R.; Wenderoth, B.; Peter, R.; Ostarek, R.; Maus, S. *Chem. Ber.* **1985**, *118*, 1421–1440; however, the conversion was low and the products formed were difficult to separate from the unreacted starting material.

(19) (a) For the preparation of Mg–graphite and applications in pinacol coupling reactions, see: Fürstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1729–1734. (b) Reviews on activated metal systems: Fürstner, A. *Angew. Chem.* **1993**, *105*, 171–197; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 164–189. (c) *Active Metals. Preparation, Characterization, Applications;* Fürstner, A., Ed.; VCH: Weinheim, 1996. (d) The solution of anhydrous $MgCl_2$ in THF was prepared from Mg and dichloroethane according to: Nützel, K. in *Houben-Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme: Stuttgart, 1973; Vol. XIII/2a, p 176.

material. Although such carbene species were reported to tolerate unprotected −OH groups in the substrates,[10] we reasoned that an interaction of this functionality with the electrophilic metal center might inhibit the desired metathetic conversion. Therefore these compounds were O-silylated using *N*,*O*-bis(trimethylsilyl)acetamide[20] formed *in situ* from $(Me_3Si)_2NH$, acetyl chloride, and DMAP. Analysis (^{13}C NMR, NOESY) of the fairly stable silyl ethers **11b** and **12b** formed clearly established the mutual *trans* relationship of the carbon side chains in the former compound. Most gratifyingly, however, both dienes cyclized smoothly to the corresponding cyclooctene derivatives in 0.03 M hexane solution in the presence of the molybdenum carbene **5** (3 mol %).[11] The crude products formed were desilylated by means of TBAF. Thus, dactylol (**1**) and 3a-*epi*-dactylol (**13**) were obtained in 92% and 85% isolated yield, respectively. The spectroscopic and analytical data of **1** are in full accordance with those reported in the literature.[2,5−8] The ^{13}C NMR spectrum of its epimer **13** features a characteristic broadening of the signals of the cyclooctene ring, indicating a slow equilibration of different conformers of this *cis*-fused [6.3.0] framework, which is considerably more strained than that of the natural product **1**.[21]

In summary we have achieved a straightforward synthesis of the cyclooctenoid sesquiterpene dactylol (**1**) and its epimer **13** based on a three-component coupling for the functionalization of the cyclopentane entity followed by an efficient cyclization of the eight-membered ring via ring closing metathesis. This approach which affords these structurally demanding target molecules in 17% and 19% overall yield, respectively, in only six synthetic operations clearly surpasses previous ones in terms of efficiency and practicability. We now try to implement this flexible concept into the synthesis of related natural and nonnatural products.

Experimental Section

General. All reactions were carried out under Ar using Schlenk techniques. The Schrock carbene **5** was purchased from Strem Chemical Inc. and used as received.[11] Anhydrous $CeCl_3$: the commercially available $CeCl_3 \cdot 7H_2O$ (Aldrich, 99.9%) was flame-dried *in vacuo*; the crystals obtained were rapidly pulverized in a mortar and redried for 24 h at 150 °C at 10^{-2} Torr. The pyrophoric potassium−graphite laminate (C_8K) used for the preparation of activated Mg−graphite was prepared and handled as described in the literature.[19] Bu_3P and 2-cyclopentenone were distilled under Ar prior to use. All other commercially available substrates (Aldrich) were used as received. The solvents were dried by distillation over the following drying agents prior to use and were transferred under Ar: Et_2O (Na/K), CH_2Cl_2 (P_4O_{10}), THF (Mg−anthracene), and hexane (Na/K). Flash chromatography: For this procedure Merck silica gel 60 (230−400 mesh) was used with *n*-hexane/ethyl acetate in various proportions as eluents, unless stated otherwise. For the instrumentation used see the Supporting Information. Elemental analyses: Dornis & Kolbe, Mülheim.

2-(1-Hydroxy-2,2-dimethylpent-4-en-1-yl)-3-methylcyclopentanone (8). To a stirred suspension of CuI (1.651 g, 8.67 mmol) in Et_2O (60 mL) is added P(*n*-Bu)$_3$ (4.75 mL, 19.07 mmol) at ambient temperature. After stirring for 10 min the colorless solution is cooled to −78 °C and MeLi (1.14 M in diethyl ether, 7.61 mL, 8.67 mmol) is added, causing the formation of a white suspension. Stirring is continued for another 20 min at that temperature prior to the addition of 2-cyclopentenone (**6**, 677 mg, 691 μL, 8.25 mmol) in Et_2O (20 mL). The yellow suspension is stirred for 1 h at −78 °C and 2.5 h at −40 °C. After the suspension is recooled to −78 °C, 2,2-dimethyl-4-pentenal (923 mg, 1.119 mL, 8.23 mmol) is added via syringe. The reaction mixture is allowed to warm to rt and is quenched with saturated aqueous NH_4Cl (50 mL). The organic layer is separated, the aqueous phase is extracted twice with diethyl ether (30 mL each); the combined extracts are dried over Na_2SO_4, filtered, and evaporated to dryness. The residue is purified by column chromatography (hexane/ethyl acetate 30:1→2:1) to give **8** as a colorless liquid (1.328 g, 77%) which is admixed with ≈15% of the dehydration product **9**: R_f 0.62 (hexane/ethyl acetate 2:1); ^{1}H NMR (300 MHz) δ 5.92−5.65 (m, 1H), 5.09−4.99 (m, 2H), 3.36 (s, 1H), 2.52 (s, 1H), 2.38−2.12 (m, 5H), 2.04−1.92 (m, 2H), 1.47−1.41 (m, 1H), 1.16−1.13 (m, 3H), 0.91 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (75 MHz) δ 220.3, 135.2, 117.5, 77.8, 57.2, 43.4, 38.8, 38.6, 37.9, 29.3, 23.5, 22.8, 19.3; IR (neat) 3531, 3074, 2959, 2930, 2872, 1729, 1639, 1465, 1406, 1292, 1154, 1095, 1053, 997, 913 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 192 ([M$^+$ − H_2O], 2), 151 (28), 109 (41), 98 (27), 69 (48), 55 (100); MS (CI) 228 ([M + NH_4^+], 2).

2-(2,2-Dimethylpent-4-en-1-ylidene)-3-methylcyclopentanone (9). DMAP (580 mg, 4.75 mmol) and methanesulfonyl chloride (272 mg, 184 μL, 2.37 mmol) in CH_2Cl_2 (10 mL) are added to a stirred solution of **8** (200 mg, 0.95 mmol) in CH_2Cl_2 (10 mL). The mixture is refluxed for 18 h, cooled to rt, and filtered through a plug of silica, which is washed several times with CH_2Cl_2. The solvent is removed, and the resulting oil is purified by flash chromatography (hexane/ethyl acetate 5:1) to give **9** as a colorless syrup (155 mg, 85%): R_f 0.64 (hexane/ethyl acetate 2:1); ^{1}H NMR (300 MHz) δ 6.44 (d, 1H, *J* = 1.6), 5.79−5.65 (m, 1H), 5.06−5.00 (m, 2H), 3.39−3.34 (m, 1H), 2.38−2.15 (m, 4H), 1.98−1.87 (m, 1H), 1.77−1.74 (m, 1H), 1.17−1.15 (m, 9H); ^{13}C NMR (75 MHz) δ 208.4, 143.8, 140.2, 134.7, 117.7, 47.7, 37.1, 34.1, 32.9, 27.9, 27.4, 27.1, 21.6; UV λ_{max} (log ε) 238 (4.36), 359 (1.76), 345 (1.90), 332 (1.87); IR (neat) 3076, 2964, 2931, 2872, 1724, 1640, 1462, 1414, 1203, 1178, 997, 914, 799 cm^{-1}; MS *m*/*z* (rel intensity) 192 ([M$^+$], 3), 151 (69), 109 (100), 93 (9), 81 (14), 67 (29); HR-MS ($C_{13}H_{20}O$) calcd 192.1514, found 192.1512; $C_{13}H_{20}O$ (192.3) calcd C 81.20, H 10.48; found C 81.15, H 10.54.

***trans*-2-(2,2-Dimethylpent-4-en-1-yl)-3-methylcyclopentanone (10).** (*n*-Bu)$_3$SnH (716 mg, 662 μL, 2.46 mmol) is added within 5 min via syringe to a stirred mixture of enone **9** (394 mg, 2.05 mmol), Pd(PPh$_3$)$_4$ (46 mg, 0.004 mmol), and $ZnCl_2$ (409 mg, 3 mmol) in THF (5 mL) at ambient temperature. The yellow solution is stirred for an additional 20 min and then quenched with saturated aqueous NH_4Cl (10 mL). A standard extractive workup (Et_2O) followed by flash chromatography (hexane/ethyl acetate 20:1) affords the title compound as a single diastereomer (330 mg, 83%); R_f 0.63 (hexane/ethyl acetate 10:1); ^{1}H NMR (200 MHz) δ 5.86 (ddt, 1H, *J* = 16.3, 10.8, 7.4), 5.05−4.95 (m, 2H), 2.42−2.26 (m, 1H), 2.19−1.94 (m, 4H), 1.78-1.39 (m, 4H), 1.15−1.12 (m, 4H), 0.87 (s, 3H), 0.86 (s, 3 H); ^{13}C NMR (50 MHz) δ 220.9 (s), 135.6 (d), 116.9 (t), 53.1 (d), 47.3 (t), 40.4 (t), 39.4 (d), 37.1 (t), 33.4 (s), 29.3 (t), 26.7 (q), 26.6 (q), 19.4 (q); IR (neat) 3462, 3075, 3003, 2958, 2928, 2878, 1742, 1639, 1466, 1367, 1154, 995, 912, 806 cm^{-1}; MS *m*/*z* (rel intensity) 194 ([M$^+$], 18), 179 (31), 153 (100), 135 (36), 111 (39), 97 (57), 83 (50); $C_{13}H_{22}O$ (194.3) calcd C 80.35, H, 11.41, found C 80.19, H 11.26.

2-(2,2-Dimethylpent-4-en-1-yl)-3-methyl-1-(2-methyl-2-propen-1-yl)cyclopentanols (11a and 12a). A solution of $MgCl_2$ in THF (10.72 mL, 0.3844 M, 4.12 mmol)[19d] is added at rt to a stirred suspension of C_8K (1.114 g, 8.24 mmol) in THF (20 mL). The mixture is refluxed for 30 min and stirred at rt for another 2 h. 3-Bromo-2-methyl-1-propene (556 mg, 415 μL, 4.12 mmol) is then added dropwise, and stirring is continued for 2 h at that temperature. The Grignard solution is transferred via cannula to a cooled (−78 °C) suspension of anhydrous $CeCl_3$ (1.016 g, 4.12 mmol) in THF (20 mL). After the resulting yellow suspension was stirred for 2 h at −78 °C, a solution of **10** (186 mg, 0.96 mmol) in THF (10 mL) is added, and the reaction is allowed to warm to ambient temperature overnight. Treatment with 30 mL of aqueous saturated NH_4Cl followed by a standard extractive workup and a final flash

(20) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, **1991**; and literature cited.
(21) For details see the Supporting Information.

chromatography (hexane/diethyl ether 30:1) gives pure **11a** (86 mg, 36%) and pure **12a** (105 mg, 44%) as a colorless syrup each. Analytical data for **11a**: R_f 0.30 (hexane/diethyl ether 30:1), ^{1}H NMR (600 MHz, C_6D_6) δ 5.85 (ddt, 1H, J = 17.1, 10.0, 7.4), 5.06−5.01 (m, 2H), 4.85−4.84 (m, 1H), 4.75 (m, 1H), 2.36 (d, 1H, J = 13.0), 1.97−1.86 (m, 4H), 1.82 (d, 1H, J = 13.0), 1.76 (s, 3H), 1.70 (dd, 1H , J = 15.0, 3.2), 1.56 (ddd, 1H, J = 13.2, 9.4, 8.0), 1.47 (ddd, 1H, J = 13.2, 8.3, 4.0), 1.18 (dd, 1H, J = 15.0, 5.9), 1.18 (s, 1H), 1.11−1.05 (m, 1H), 0.99 (d, 3H, J = 6.7), 0.97 (ddd, 1H, J = 8.4, 5.9, 3.0), 0.86 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz) δ 143.3 (s), 135.8 (d), 116.8 (t), 114.5(t), 82.5 (s), 51.9 (d), 48.4 (t), 48.1 (t), 41.0 (t), 39.9 (d), 37.9 (t), 33.2 (s), 31.1 (t), 27.4 (q), 24.7 (q), 21.0 (q); MS m/z (rel intensity) 232 (1), 217 (2), 195 (4), 177 (28), 153 (31), 135 (30), 121 (18), 107 (28), 97 (41), 83 (39), 69 (37), 55 (100), 41 (58). Analytical data for **12a**: R_f 0.39 (hexane/diethyl ether 30:1); ^{1}H NMR (600 MHz, C_6D_6) δ 5.86 (ddt, 1H, J = 16.8, 10.3, 7.4), 5.07−5.02 (m, 2H), 4.87−4.86 (m, 1H), 4.74 (m, 1H), 2.26 (d, 1H, J = 13.4), 2.00 (dd, 2H, J = 7.4, 1.1), 1.91 (d, 1H, J = 13.4), 1.77 (s, 3H), 1.69−1.61 (m, 2H), 1.47 (dd, 1H, J = 14.3, 4.9), 1.44−1.40 (m, 3H), 1.30−1.24 (m, 2H), 1.05 (d, 3H, J = 6.4), 0.95 (dd, 1H, J = 14.3, 4.3), 0.93 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz) δ 143.5 (s), 135.9 (d), 116.7 (t), 114.6 (t), 82.3 (s), 53.9 (d), 47.8 (t), 44.6 (t), 41.6 (t), 40.3 (d), 38.2 (t), 33.5 (s), 30.8 (t), 27.4 (q), 27.3 (q), 24.9 (q), 21.5 (q); IR (neat) 3475, 3074, 2956, 2870, 1639, 1453, 1386, 1375, 1367, 1097, 1072, 1020, 912, 888 cm^{-1}; MS m/z (rel intensity) 232 (1), 217 (3), 191 (8), 177 (26), 153 (13), 135 (25), 121 (17), 107 (24), 97 (38), 83 (39), 69 (36), 55 (100), 41 (53).

Compound 12b. DMAP (40 mg, 0.32 mmol) and acetyl chloride (24 mg, 21 μL, 0.30 mmol) are added to a stirred solution of **12a** (60 mg, 0.24 mmol) and hexamethyldisilazane (48 mg, 62 μL, 0.30 mmol) in CH_2Cl_2 (10 mL). The resulting solution is stirred at rt for 24 h until TLC shows complete conversion of the starting material. The mixture is filtered through a short pad of silica, which is washed several times with hexane. Evaporation of the solvent and flash chromatography (hexane) gives **12b** (74 mg, 95%) as a colorless syrup: R_f 0.95 (hexane/ethyl acetate 40:1); ^{1}H NMR (400 MHz) δ 5.85 (ddt, 1H, J = 16.7, 10.5, 7.4), 4.87−4.82 (m, 2H), 4.71−4.70 (m, 1H), 4.52−4.51 (m, 1H), 2.23 (d, 1H, J = 13.5), 2.01−1.98 (m, 2H), 1.91−1.86 (m, 2H), 1.78 (s, 3H), 1.69 (m, 1H), 1.66 (dt, 1H, J = 12.8, 3.4), 1.59−1.49 (m, 2H), 1.51−1.46 (m, 1H), 1.24 (m, 1H), 1.06 (m,1H), 1.02 (d, 3H, J = 6.6), 0.90 (s, 3H), 0.89 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (100 MHz) δ 144.0 (s), 133.3 (d), 116.4 (t), 113.6 (t), 85.8 (s), 54.7 (d), 47.8 (t), 43.1 (t), 41.1 (t), 38.0 (d), 35.4 (t), 33.4 (s), 30.0 (t), 27.7 (q), 24.9 (q), 22.1 (q), 2.5 (q); IR (neat) 3074, 2954, 2872, 1641, 1467, 1453, 1414, 1385, 1374, 1321, 1306, 1261, 1251, 1106, 1093, 1051, 1038, 961, 912, 888, 865, 839, 751 cm^{-1}; MS m/z (rel intensity) 322 ([M$^+$], 9), 307 (9), 267 (84), 183 (100), 177 (16), 170 (13), 155 (14), 135 (23), 121 (14), 95 (25), 73 (78), 55 (23); HR-MS ($C_{20}H_{38}OSi$) calcd 322.2692, found 322.2701.

Compound 11b. Prepared as described above in 93% isolated yield as a colorless syrup: R_f 0.70 (hexane); ^{1}H NMR (400 MHz) δ 5.84 (ddt, 1H, J = 16.9, 10.3, 7.4), 5.01−4.98 (m, 2H), 4.96−4.94 (m, 1H), 4.84−4.82 (m, 1H), 2.28 (d, 1H, J = 13.4), 2.09 (d, 1H, J = 13.4), 1.95 (d, 2H, J = 7.4), 1.89−1.80 (m, 2H), 1.78 (s, 3H), 1.74−1.61 (m, 3H), 1.26−1.22 (m, 1H), 1.13−1.02 (m, 1H), 0.99 (d, 3H, J = 6.8), 0.98−0.95 (m, 1H), 0.85 (s, 3H), 0.84 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (100 MHz) δ 143.4 (s), 136.2 (d), 116.4 (t), 114.4 (t), 86.8 (s), 51.1 (d), 49.4 (t), 48.6 (t), 42.6 (t), 40.4 (d), 37.7 (t), 33.4 (s), 31.7 (t), 27.7 (q), 27.4 (q), 25.1 (q), 21.1 (q), 2.5 (q); IR (KBr) 3075, 2955, 2870, 1932, 1829, 1793, 1640, 1466, 1385, 1375, 1366, 1310, 1260, 1250, 1114, 1071, 994, 963, 912, 890, 864, 838, 752, 685 cm^{-1}; MS m/z (rel intensity) 322 (M$^+$, 6), 307 (8), 267 (100), 191 (15), 183 (82), 177 (21), 170 (11), 155 (14), 135 (38), 121 (19), 107 (13), 95 (29), 73 (73), 55 (25); HR-MS ($C_{20}H_{38}OSi$) calcd 322.2692, found 322.2695.

(1α,3aα,9aα)-1,2,3,4,7,8,9,9a-Octahydro-1,5,8,8-tetramethyl-3a*H*-cyclopentacycloocten-3*β*-ol (13). To a stirred solution of **12b** (80 mg, 0.25 mmol) in hexane (5 mL) at 55 °C is added the molybdenum carbene **5** (6 mg, 0.0076 mmol, 3 mol %) dissolved in hexane (2 mL) via cannula. The reddish mixture is stirred at that temperature for 2.5 h, cooled to rt, and aerated for 15 min. The solvent is evaporated and the residue is flashed through a pad of silica with hexane. The solvent is removed, and the remaining oil dissolved in THF (20 mL) and desilylated upon treatment with Bu_4NF (0.5 mL, 1 M solution in THF) at 50 °C for 4.5 h. Quenching with H_2O (20 mL) followed by a standard extractive workup and flash chromatography (hexane/ethyl acetate 20:1) affords product **13** as a colorless syrup (47 mg, 85%): R_f 0.27 (hexane/ethyl acetate 10:1); ^{1}H NMR (400 MHz) δ 5.44 (t, 1H, J = 6.1), 2.36 (d, 1H, J = 11.6), 2.13 (d, 1H, J = 11.6), 2.07 (bs, 1H), 1.79 (s, 3H), 1.70−1.57 (m, 4H), 1.45−1.32 (m, 5H), 1.05 (d, 1H, J = 9.0), 1.03 (d, 3H, J = 4.6), 0.87 (s, 6H); ^{13}C NMR (100 MHz) δ 136.0, 123.8, 85.7, 54.4, 46.8, 44.7, 43.1, 39.5, 36.2, 32.2, 31.3, 27.3, 26.2, 20.7; IR (KBr) 3466, 3039, 2951, 2868, 1669, 1459, 1364, 1374, 1285, 1264, 1203, 1121, 1002, 987, 882, 856, 840, 758 cm^{-1}; MS m/z (rel intensity) 222 ([M$^+$], 6), 204 (51), 189 (19), 161 (15), 153 (100), 148 (21), 135 (43), 111 (57), 97 (43), 81 (36), 69 (57), 55 (40), 41 (37). HR-MS ($C_{15}H_{26}O$) calcd 222.1984, found 222.1954.

Dactylol (1) is prepared according to the procedure described above using **11b** (60 mg, 0.19 mmol) and carbene **5** (5 mg, 0.0065 mmol, 3 mol %). Dactylol was obtained as colorless crystals (39 mg, 92%): R_f 0.33 (hexane/ethyl acetate 10:1); mp 48−50 °C (lit.[2] mp 50.3−51.5 °C); ^{1}H NMR (300 MHz) δ 5.53 (t, 1H, J = 8.6), 2.40 (d, 1H, J = 13.5), 2.18 (d, 1H, J = 13.5), 2.02 −1.86 (m, 2H), 1.84 (s, 3H), 1.76−1.70 (m, 3H), 1.59 (dd, 1H, J = 12.7, 6.3), 1.40 (dd, 2H, J = 14.4, 8.1), 1.22−1.07 (m, 2H), 0.96 (d, 3H, J = 6.6), 0.92 (s, 3H), 0.91 (s, 3H), 0.83 (d, 1H, J = 14.1); ^{13}C NMR (50 MHz) δ 135.3 (s), 124.9 (d), 83.2 (s), 52.8 (d), 42.8 (t), 39.9 (t), 39.1 (t), 36.4 (t), 35.1 (s), 29.2 (q), 28.7 (q), 27.7 (q), 19.0 (q); IR (neat) 3488, 3030, 2952, 2910, 2867, 1469, 1383, 1375, 1364, 1339, 1259, 1204, 1046, 1015, 859, 735 cm^{-1}; MS m/z (rel intensity) 222 ([M$^+$], 18), 207 (7), 153 (100), 135 (17), 110 (40), 97 (27), 81 (17), 69 (34), 55 (23), 41 (21); HR-MS ($C_{15}H_{26}O$) calcd 222.1984, found 222.1960.

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Supporting Information Available: Copies of the ^{1}H, ^{13}C, and 2D NMR spectra of all new compounds; compilation of the instrumentation used (31 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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