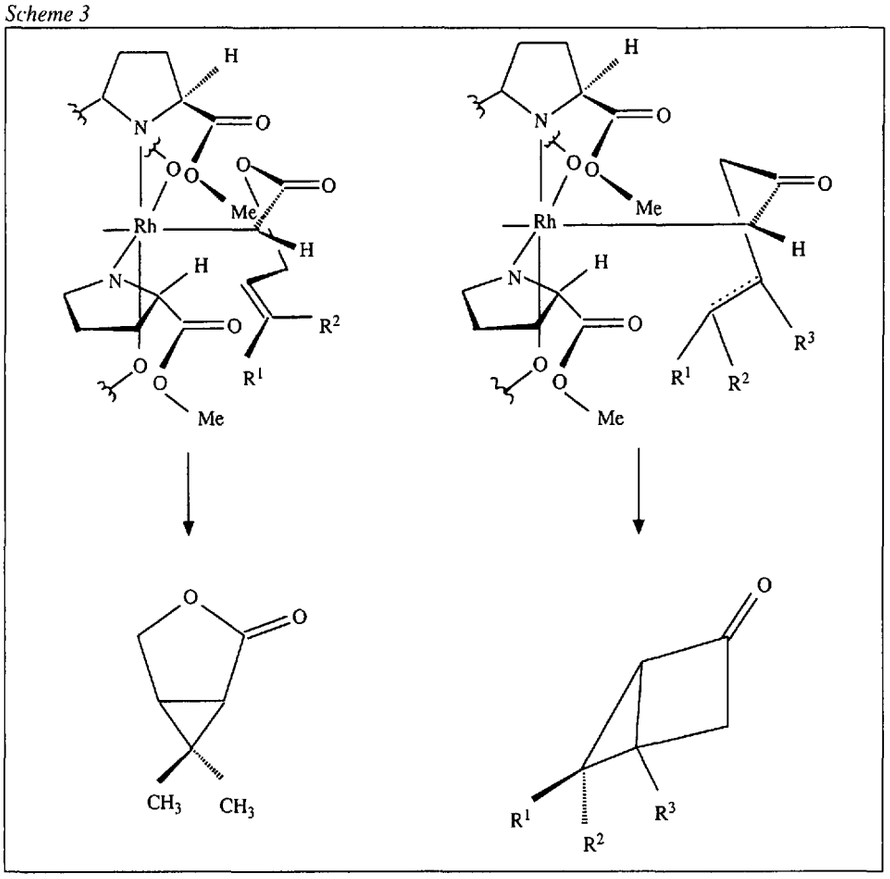
Scheme 3



control. At the same time, the distance between the carbene and the double bond decreases, and one might expect more influence by the olefinic substituents. This is, however, compensated, because the substituents move away from the carbenic centre owing to rehybridization of the olefinic C-atoms.

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Formal Synthesis of (±)-Coriolin by Diastereocontrolled Nickel(0)-Catalyzed 'Metallo-ene-type' Cyclization/Methoxycarbonylation

Wolfgang Oppolzer* and **Akira Ando**

Abstract. Bicyclooctanone (±)-**2**, an advanced intermediate for the synthesis of (±)-coriolin, has been synthesized in ten steps starting from 2,2-dimethylpent-4-enal (**7**). The key step **6** → **3** + **11** is a highly diastereoselective, Ni^0-catalyzed, tandem intramolecular alkene allylation/carbonylation reaction.

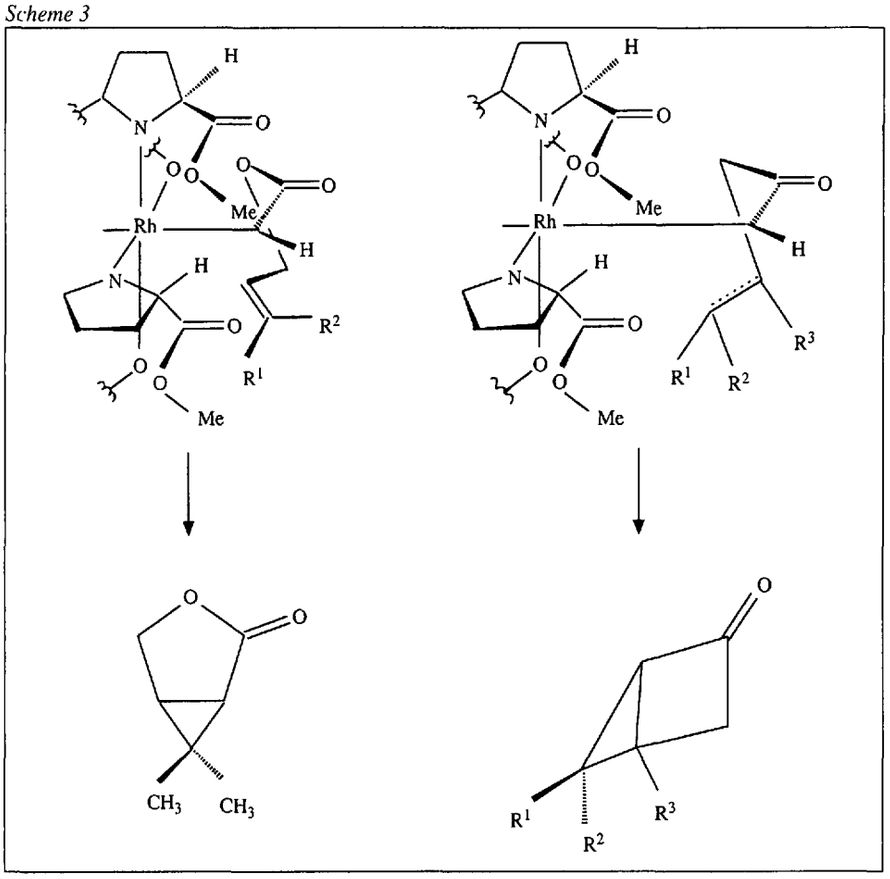
The development and creative application of transition-metal-catalyzed reactions is presently at the forefront of organic synthesis [1]. Thus, recently discovered Pd^0- and Ni^0-catalyzed intramolecular alkene (alkyne) allylations **I** → **II** show attractive perspectives for the stereocontrolled construction of various carbo- and heterocyclic systems (*Scheme 1*) [2].

This holds particularly for the tandem allylation/carbonylation **I** → **II** → **III** as illustrated by the syntheses of pentalenolactone E methyl ester [3], (+)-3-isoraunitricine [4], and, most recently, [5.5.5.5]fenestranes [5]. We present here a rational application of this process in a synthesis of the triquinane terpenoid coriolin which features the topological bias of a preexisting stereocenter over developing stereocenters in the carbometalation step **I** → **II**. Coriolin, a metabolite from the Basidiomycete *Coriolus consors* has been assigned structure **1** (*Scheme 2*) [6].

Reports of antibiotic and antitumor activity contributed to the popularity of **1** as a test case for cyclopentenone-annulation methodology [7]. The synthesis of (±)-**1**, reported by *Exon* and *Magnus* thus proceeds *via* the bicyclo[3.3.0]octanone **2**, in turn assembled by means of a stereoselective intramolecular *Pauson-Khand* process [7e].

**Correspondence*: Prof. W. Oppolzer
Département de Chimie Organique
Université de Genève
CH-1211 Genève 4

Scheme 3



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Wolfgang Oppolzer* and **Akira Ando**

Abstract. Bicyclooctanone (±)-**2**, an advanced intermediate for the synthesis of (±)-coriolin, has been synthesized in ten steps starting from 2,2-dimethylpent-4-enal (**7**). The key step **6** → **3** + **11** is a highly diastereoselective, Ni^0-catalyzed, tandem intramolecular alkene allylation/carbonylation reaction.

The development and creative application of transition-metal-catalyzed reactions is presently at the forefront of organic synthesis [1]. Thus, recently discovered Pd^0- and Ni^0-catalyzed intramolecular alkene (alkyne) allylations **I** → **II** show attractive perspectives for the stereocontrolled construction of various carbo- and heterocyclic systems (*Scheme 1*) [2].

This holds particularly for the tandem allylation/carbonylation **I** → **II** → **III** as illustrated by the syntheses of pentalenolactone E methyl ester [3], (+)-3-isoraunitricine [4], and, most recently, [5.5.5.5]fenestranes [5]. We present here a rational application of this process in a synthesis of the triquinane terpenoid coriolin which features the topological bias of a preexisting stereocenter over developing stereocenters in the carbometalation step **I** → **II**. Coriolin, a metabolite from the Basidiomycete *Coriolus consors* has been assigned structure **1** (*Scheme 2*) [6].

Reports of antibiotic and antitumor activity contributed to the popularity of **1** as a test case for cyclopentenone-annulation methodology [7]. The synthesis of (±)-**1**, reported by *Exon* and *Magnus* thus proceeds *via* the bicyclo[3.3.0]octanone **2**, in turn assembled by means of a stereoselective intramolecular *Pauson-Khand* process [7e].

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Département de Chimie Organique
Université de Genève
CH-1211 Genève 4

Our approach to the key intermediate **2** is summarized by the disconnective analysis depicted in *Scheme 2*. Hence, formation of the C(2)–C(9) bond (**6** → **5** → **4**), coupled with CO insertion between C(3) and C(8) and at C(12) would generate rings B and C of coriolin in a single operation. In view of model studies, we expected to achieve excellent induction by the resident center C(1) when employing Ni^0 catalysis [8].

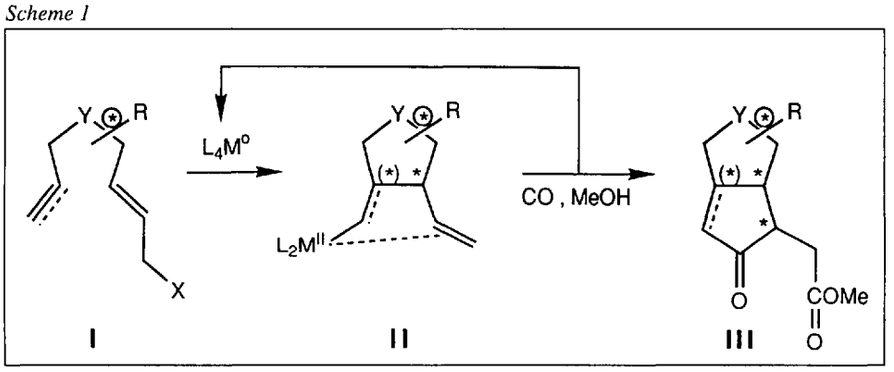
Putting this plan into practice (*Scheme 3*) aldehyde **7** was successively treated with lithiated 1-[(tetrahydropyran-2-yl)-oxy]prop-2-yne ($LiC{\equiv}CCH_2OTHP$), (*t*-butyl)dimethylsilyl chloride (TBDMSCl), and pyridinium *p*-toluenesulfonate (PPTS), which gave enynol **8** in 70% overall yield.

Reduction of the C≡C bond in **8** by sodium bis(methoxyethoxy)aluminum hydride (Red-Al) in Et_2O [9], conversion of the alcohol **9** to the primary bromide **10** (with CBr_4, PPh_3), and *Finkelstein* reaction provided (*E*)-iododiene **6** (69% from **8**).

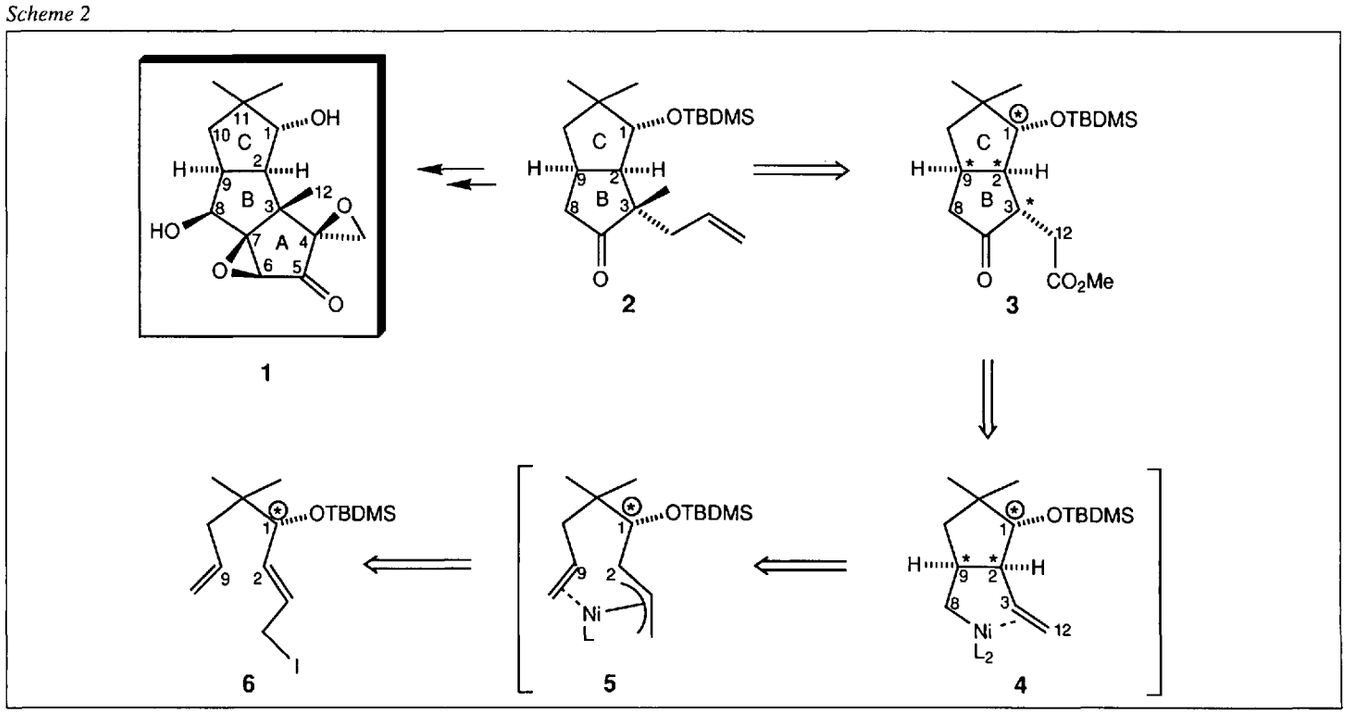
We then proceeded to the key reaction: stirring acyclic diene **6** with $Ni(COD)_2$ (COD = cyclooctadienyl; 0.25 mol-equiv.) and 1,4-diphenylphosphinobutane (dppb, 0.125 mol-equiv.) in THF-MeOH (4:1) under carbon monoxide (1 atm) at 60° for 16 h gave a 3:2 mixture of expected bicyclic ketoester **3** and isomeric lactone **11** in 63% yield. On raising the amount of $Ni(COD)_2$ to 0.5 mol-equiv. the combined yield of **3** + **11** increased to 70%. No other stereoisomer could be isolated from the reaction mixture. Each one of the separated (chromatography) cyclization products furnished the same oxo-acid **12** (98%) on mild saponification with LiOH. It, thus, follows that the cyclization **6** → **3** + **11** is completely stereoselective within experimental error, and that the synthesis of **1** can be pursued with the non-separated mixture **3/11**. Precedence from previous model experiments allowed a tentative assignment of the depicted relative configuration of the new stereocenters C(9), C(2), and C(3) in **3** and **11** [8]. The critical *cis*-disposition of the C(1)–OSi group with the angular H-atoms at C(2) and C(9) was confirmed by the following two step conversion of oxo-acid **12** to *Magnus*' coriolin precursor **2**. Reductive *Barton*-type decarboxylation [11] of **12** by esterification with *N*-hydroxy-2-thiopyridone/dicyclohexylcarbodiimide (DCC)/4-(dimethylamino)pyridine (DMAP) and photolysis of the resulting crude ester in the presence of *t*-BuSH, chromatography over *Florisil*, and extraction of *t*-butyl 2'-pyridyl disulfide with 15% aq. HCl (from Et_2O) provided nor-compound 13 in 58% yield. Stereoselective C(3)-allylation of **13** by successive treatment with NaH and allyl bromide in DME gave the key intermediate (±)-**2** in 46% yield (79% from a 4:1 C(3)-epimer mixture of **13** [7e]). Thus obtained (±)-**2**, identified by comparison (IR, ^{1}H-NMR) with previously prepared (±)-**2** [7e], showed in the ^{1}H-NMR spectrum the characteristic C(1)-*doublet* [7e][7g] at $\delta = 3.65$ ppm ($J = 7.5$ Hz).

In summary, key intermediate **2** for the synthesis of (±)-coriolin (**1**) has been prepared from the simple aldehyde **7** *via* a sequence of ten steps in 9% overall yield. The strategic allylation/carbonylation step forms four C,C bonds in a single operation with virtually 100% stereoselectivity. This scheme also lends itself to a synthesis of (–)-coriolin from (*R*)-**6** , which in turn should be readily accessible *via* asymmetric addition of an (1-alkenyl)zinc reagent to aldehyde **7** [12].

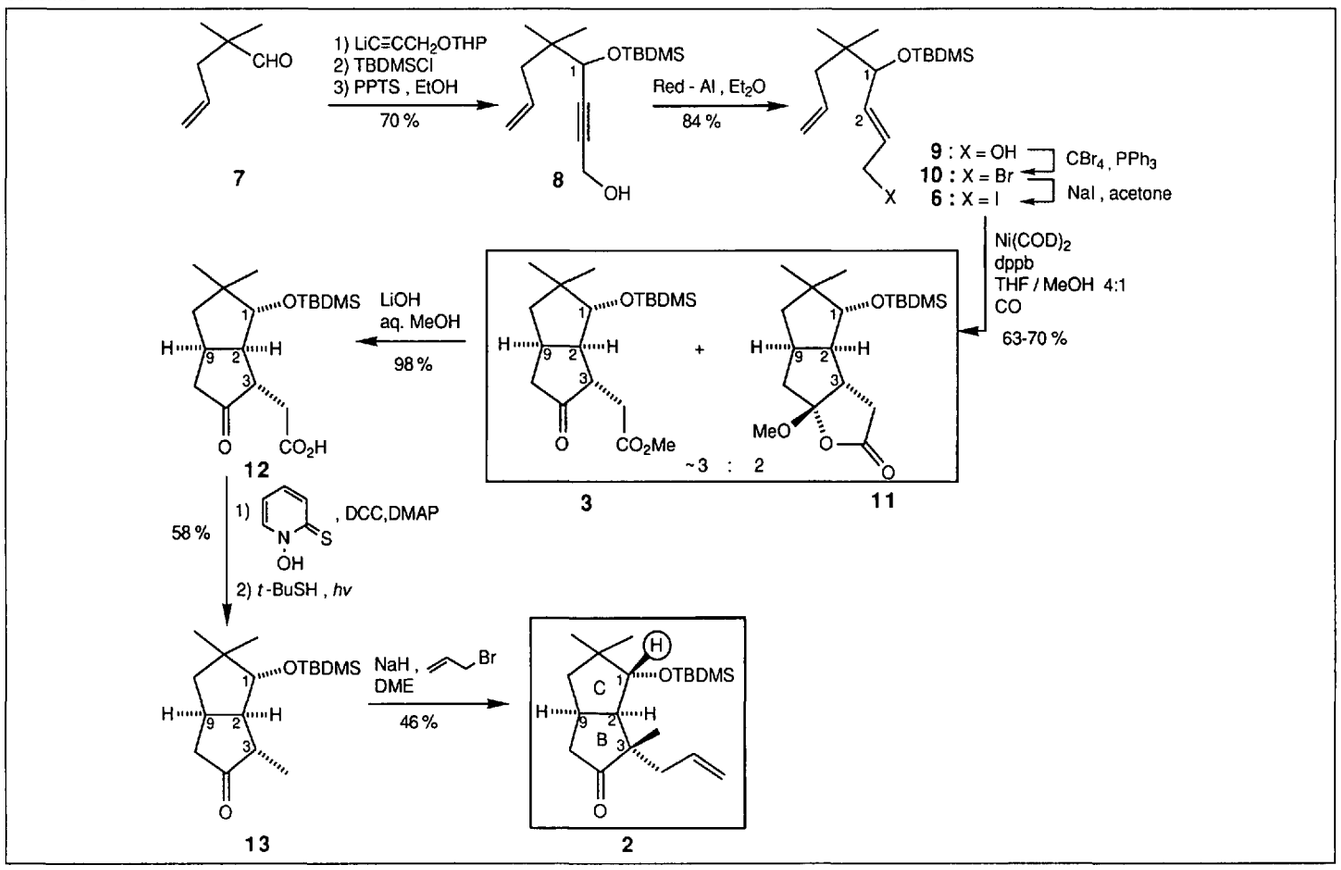
Scheme 1



Scheme 2



Scheme 3



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Experimental

All reactions were carried out under Ar unless otherwise specified. All solvents and solns. that were used in Ni-catalyzed reactions were rigorously degassed before use. Solvents were dried by distillation from drying agents as follows: THF (Na), Et_2O (Na), toluene (Na), DME (Na), CH_2Cl_2 (CaH_2), benzene (CaH_2), MeOH (Mg), EtOH (Mg). 'Workup' denotes extraction with Et_2O, washing of the org. phase with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation *in vacuo*. Silica gel *60* (*Merck 9385*) was used for flash chromatography (FC). Column chromatography on *Florisil* (*Fluka*). IR: *Polaris/Matteson*, in CH_2Cl_2 unless otherwise noted. NMR: ^1H at 400 MHz, ^{13}C at 100 MHz in $CDCl_3$, standard $CHCl_3$ ($\delta = 7.27$ ppm), J in Hz. MS: *m/z* (rel. %).

*4-[(*tert*-Butyl)dimethylsilyloxy]-5,5-dimethyloct-7-en-2-yn-1-ol* (8). A 1.6M soln. of BuLi (hexane, 16.2 ml, 26 mmol) was added dropwise to a soln. of 1-[(tetrahydropyran-2-yl)oxy]prop-2-yne (3.64 g, 26 mmol) in THF (20 ml) at –78° and the mixture was stirred for 1 h. Slow addition of a soln. of 2,2-dimethylpent-4-enal (7) (2.26 g, 20 mmol) in THF (6 ml), stirring of the mixture at –78° for 1 h, adding a soln. of (*t*-Bu)Me_2SiCl (3.92 g, 26 mmol) in THF (10 ml), heating the mixture for 24 h under reflux, addition of sat. aq. NH_4Cl, workup and FC (hexane/Et_2O 20:1 and 40:1) gave 4-[(*t*-butyl)dimethylsilyloxy)-5,5-dimethyl-1-[(tetrahydropyran-2-yl)oxy]oct-7-en-2-yne as a colorless oil (5.37 g, 78%). A soln. of this derivative (1.77 g, 4.82 mmol) and pyridinium *p*-toluenesulfonate (61 mg, 0.24 mmol) in EtOH (25 ml) was heated at 50° for 41 h. Cooling to r.t., addition of solid $NaHCO_3$, workup and FC (hexane/Et_2O 5:1) gave alcohol **8** (1.25 g, 70% from 7) as a colorless oil. IR: 3605, 2960, 2935, 2860, 1640, 1475, 1390, 1365, 1250, 1130, 1080, 1010, 925, 855, 780. ^1H-NMR: 0.09 (*s*, 3 H); 0.15 (*s*, 3 H); 0.92 (*s*), 0.93 (*s*) (15 H); 1.73 (br. *t*, *J* = 6, 1 H); 2.07 (br. *dd*, *J* = 14, 7, 1 H); 2.13 (br. *dd*, *J* = 14, 7, 1 H); 4.06 (*t*, *J* = 2, 1 H); 4.30 (*dd*, *J* = 6, 2, 2 H); 5.00–5.06 (2 H); 5.76–5.86 (1 H). ^{13}C-NMR: –5.24 (*q*); –4.24 (*q*); 18.18 (*s*); 22.54 (*q*); 22.66 (*q*); 25.79 (*q*); 39.14 (*s*); 42.54 (*t*); 51.19 (*t*); 70.53 (*d*); 83.54 (*s*); 86.15 (*s*); 117.24 (*t*); 135.13 (*d*). MS: 225 (3.5, $[C_{16}H_{30}O_2Si–C_4H_9]^+$), 199 (8.2), 143 (2.5), 133 (8.6), 105 (13), 91 (10), 83 (14), 75 (100), 73 (56), 55 (30). Anal. calc. for $C_{16}H_{30}O_2Si$: C 68.03, H 10.70; found: C 67.97, H 10.65.

*(E)-4-[(*tert*-Butyl)dimethylsilyloxy]-5,5-dimethylocta-2,7-dien-1-ol* (**9**). A soln. of **8** (153 mg, 0.54 mmol) in Et_2O (1.5 ml) was added slowly at 0° to a 0.7M soln. of sodium bis(2-methoxyethoxy)aluminum hydride in toluene/Et_2O (1:4, 1.26 ml, 0.88 mmol). Stirring of the mixture at 0° for 10 min, then at r.t. for 2 h, addition of sat. aq. NH_4Cl at 0°, addition of 0.1N aq. HCl, workup, and FC (hexane/Et_2O 7:1) furnished **9** (129 mg, 84%). IR: 3610, 2960, 2930, 2860, 1640, 1470, 1380, 1360, 1250, 1090, 1065, 1010, 980, 920, 860, 840, 750. ^1H-NMR: –0.01 (*s*, 3 H); 0.04 (*s*, 3 H); 0.81 (*s*, 3 H); 0.84 (*s*, 3 H); 0.90 (*s*, 9 H); 1.32 (br. *s*, 1 H); 1.96 (*dd*, *J* = 14, 7, 1 H); 2.06 (*dd*, *J* = 14, 7, 1 H); 3.77 (*d*, *J* = 6, 1 H); 4.16 (br. *s*, 2 H); 4.97–5.04 (2 H); 5.66–5.76 (2 H); 5.82 (*ddt*, *J* = 17, 10, 7, 1 H). ^{13}C-NMR: –4.94 (*q*); –3.57 (*q*); 18.18 (*s*); 22.89 (*q*); 25.91 (*q*); 38.48 (*s*); 42.99 (*t*); 63.29 (*t*); 79.96 (*d*); 116.85 (*t*); 130.82 (*d*); 132.22 (*d*); 135.58 (*d*). MS: 227 (0.8, $[C_{16}H_{32}O_2Si–C_4H_9]^+$), 201 (15), 145 (10), 135 (3.3), 131 (11), 93 (7.7), 83 (46), 75 (80), 73 (100), 55 (62). Anal. calc. for $C_{16}H_{32}O_2Si$: C 67.55, H 11.34; found: C 67.30, H 11.28.

*(E)-1-Bromo-4-[(*tert*-butyl)dimethylsilyloxy]-5,5-dimethylocta-2,7-diene* (**10**). CBr_4 (195 mg, 0.59 mmol) and PPh_3 (304 mg, 1.16 mmol) were added to a soln. of **9** (150 mg, 0.53 mmol) in Et_2O (2 ml), and the mixture was stirred at r.t. for 4.5 h. The precipitate was removed by filtration through *Celite* and washed with Et_2O. Evaporation of filtrates and FC (hexane) of the residue provided **10** (160 mg, 87%) as a colorless oil. IR: 2960, 2930, 2855, 1640, 1470, 1390, 1365, 1250, 1205, 1105, 1065, 1005, 970, 920, 860, 780. ^1H-NMR: 0.00 (*s*, 3 H); 0.03 (*s*, 3 H); 0.80 (*s*, 3 H); 0.84 (*s*, 3 H); 0.90 (*s*, 9 H); 1.94 (*dd*, *J* = 14, 8, 1 H); 2.04 (*dd*, *J* = 14, 7, 1 H); 3.75 (*d*, *J* = 6, 1 H); 3.97 (*d*, *J* = 7, 2 H); 4.97–5.05 (2 H); 5.71–5.86 (3 H). ^{13}C-NMR: –4.99 (*q*); –3.61 (*q*); 18.15 (*s*); 22.89 (*q*); 25.90 (*q*); 32.46 (*t*); 38.76 (*s*); 42.98 (*t*); 79.35 (*d*); 117.02 (*t*); 127.71 (*d*); 135.36 (*d*); 136.00 (*d*). MS: 291 (0.4, $[C_{16}H_{31}BrOSi–C_4H_9)^+$), 289 (0.4), 265 (7.0), 263 (6.7), 209 (3.5), 207 (3.3), 184 (6.1), 135 (7.3), 127 (18), 83 (92), 75 (56), 73 (100), 55 (92). Anal. calc. for $C_{16}H_{31}BrOSi$: C 55.32, H 8.99; found: C 55.12, H 8.82.

*(E)-4-[(*tert*-Butyl)dimethylsilyloxy]-1-iodo-5,5-dimethylocta-2,7-diene* (**6**). A mixture of **10** (671 mg, 1.93 mmol) and NaI (1.45 g, 9.67 mmol) in acetone (20 ml) was stirred in the dark at r.t. for 13 h. Evaporation of the mixture, trituration of

the residue with CH_2Cl_2, evaporation, and FC (hexane/Et_2O 20:1) gave iodide **6** (716 mg, 94%) as a pale brown oil. IR: 2960, 2930, 2860, 1640, 1475, 1385, 1365, 1255, 1150, 1105, 1060, 1010, 970, 915, 860, 840, 780. ^{1}H-NMR: 0.00 (*s*, 3 H); 0.02 (*s*, 3 H); 0.79 (*s*, 3 H); 0.83 (*s*, 3 H); 0.90 (*s*, 9 H); 1.93 (*ddt*, *J* = 13.5, 7.5, 1, 1 H); 2.03 (*ddt*, *J* = 13.5, 7.5, 1, 1 H); 3.71 (*d*, *J* = 7.5, 1 H); 3.89 (*d*, *J* = 8, 2 H); 4.70–5.04 (2 H); 5.68 (*dd*, *J* = 15, 7.5, 1 H); 5.74–5.86 (2 H). ^{13}C-NMR: –4.99 (*q*); –3.52 (*q*); 5.44 (*t*); 18.13 (*s*); 22.90 (*q*); 25.92 (*q*); 39.02 (*s*); 43.00 (*t*); 79.32 (*d*); 116.98 (*t*); 129.10 (*d*); 134.70 (*d*); 135.42 (*d*). MS: 337 (1.3,$[C_{16}H_{31}IOSi–C_4H_9]^+$), 311 (9.9), 267 (1.9), 255 (3.4), 184 (23), 135 (26), 127 (36), 95 (12), 83 (93), 75 (65), 73 (63), 55 (100).

*Methyl 8-[(*tert*-Butyl)dimethylsilyloxy]-7,7-dimethyl-3-oxobicyclo[3.3.0]octane-2-acetate* (**3**) *and 11-[(*tert*-Butyl)dimethylsilyloxy]-6-methoxy-10,10-dimethyl-5-oxatricyclo[6.3.0.0^{2,6}]undecan-4-one* (**11**). Using a glove box under N_2, a suspension of bis(cyclooctadienyl)nickel [10] (39 mg, 0.14 mmol) in degassed THF/MeOH (4:1, 1.5 ml) was stirred under CO (1 atm) for 30 min. Then the degassed soln. of 1,4-bis(diphenylphosphino)butane (30 mg, 0.07 mmol) in THF/MeOH (4:1, 1.5 ml) was added, and the mixture was stirred at r.t. for 30 min. Addition of **6** (219 mg, 0.56 mmol in THF/MeOH 4:1, 2 ml), heating of the mixture in the dark at 60° under a constant stream of CO for 16 h, addition of AcOEt, evaporation, and FC (hexane/AcOEt 15:1) furnished the less polar **11** (oil, 48 mg, 24%). IR: 2950, 2925, 2855, 1775, 1470, 1465, 1385, 1375, 1365, 1330, 1300, 1290, 1260, 1250, 1205, 1140, 1125, 1115, 1060, 1005, 910, 890, 840. ^{1}H-NMR: 0.03 (s, 3 H); 0.06 (*s*, 3 H); 0.84 (*s*, 3 H); 0.88 (*s*, 9 H); 0.96 (*s*, 3 H); 1.19 (*dd*, *J* = 13, 7, 1 H); 1.58 (*dd*, *J* = 18, 13, 1 H); 1.84 (*dd*, *J* = 13, 8, 1 H); 2.05–2.13 (1 H); 2.38 (*d*, *J* = 18, 1 H); 2.50 (*dd*, *J* = 8, 5, 1 H); 2.56–2.64 (2 H); 2.92 (*dd*, *J* = 18, 8, 1 H); 3.39 (*s*, 3 H); 3.55 (*d*, *J* = 9, 1 H). ^{13}C-NMR: –4.27 (*q*); –3.74 (*q*); 18.00 (*s*); 20.78 (*q*); 25.81 (*q*); 27.15 (*q*); 35.79 (*d*); 36.91 (*t*); 41.31 (*t*); 44.88 (*s*); 45.03 (*t*); 48.51 (*d*); 52.61 (*q*); 56.25 (*d*); 86.92 (*d*); 122.23 (*s*); 176.58 (*s*). MS: 354 (0.4, $[C_{19}H_{34}O_4Si]^+$), 339 (2.2), 323 (2.2), 297 (100), 265 (18), 237 (7.2), 191 (10), 163 (18), 121 (11), 95 (12), 89 (19), 75 (45), 73 (36). Anal. calc. for $C_{19}H_{34}O_4Si$: C 64.36, H 9.67; found: C 64.40, H 9.66.

Further elution furnished the more polar **3** (oil, 77 mg, 39%). IR: 2950, 2925, 2860, 1740, 1475, 1465, 1435, 1405, 1380, 1365, 1255, 1200, 1165, 1115, 910, 880, 840. ^{1}H-NMR: 0.03 (*s*, 3 H); 0.06 (*s*, 3 H); 0.89 (*s*, 9 H); 0.91 (*s*, 3 H); 0.99 (*s*, 3 H); 1.20 (*dd*, *J* = 13, 9, 1 H); 1.96 (*dd*, *J* = 13, 8, 1 H); 2.05 (*dd*, *J* = 19, 6, 1 H); 2.32–2.39 (2 H); 2.58 (*dd*, *J* = 17, 5, 1 H); 2.68 (*dd*, *J* = 19, 10, 1 H); 2.75–2.84 (1 H); 2.89 (*dd*, *J* = 17, 4, 1 H); 3.53 (*d*, *J* = 7, 1 H); 3.66 (*s*, 3 H). ^{13}C-NMR: –4.07 (*q*); –3.94 (*q*); 18.05 (*s*); 21.04 (*q*); 25.88 (*q*); 27.45 (*q*); 32.36 (*d*); 35.86 (*t*); 43.73 (*s*); 45.71 (*t*); 46.82 (*t*); 49.09 (*d*); 51.79 (*q*); 52.60 (*d*); 88.30 (*d*); 172.20 (*s*); 221.08 (*s*). MS: 337 (8.9, $[C_{19}H_{34}O_4Si$ –17]$^+$), 323 (4.0), 297 (100), 265 (6.9), 237 (5.3), 201 (8.5), 163 (9.2), 95 (10), 89 (23), 75 (39), 73 (45), 59 (10), 55 (10). Anal. calc. for $C_{19}H_{34}O_4Si$: C 64.36, H 9.67; found: C 64.80, H 9.66.

Under analogous reaction conditions, but in the presence of 0.5 mol-equiv. of $Ni(COD)_2$ and 0.25 mol-equiv. of dppb, **6** (226 mg, 0.57 mmol) furnished **11** (56 mg, 28%) and **3** (85 mg 42%).

*8-[(*tert*-Butyl)dimethylsilyloxy]-7,7-dimethyl-3-oxobicyclo[3.3.0]octane-2-acetic Acid* (**12**). a) *From Oxo-ester* **3**. The mixture of **3** (83 mg, 0.23 mmol) and $LiOH/H_2O$ (59 mg, 1.41 mmol) in $MeOH/H_2O$ (3:1, 4 ml) was stirred at r.t. for 3 h. Addition of H_2O (10 ml), acidification to pH ~3 with 1N aq. HCl, addition of solid NaCl, extraction with Et_2O and evaporation of the dried extracts gave the crude acid **12** (77 mg, 98%) which was subjected to the decarboxylation without further purification. IR: 3490, 2960, 2930, 2860, 1735, 1710, 1470, 1465, 1405, 1385, 1250, 1120, 880, 835. ^{1}H-NMR: 0.04 (*s*, 3 H); 0.07 (*s*, 3 H); 0.90 (*s*, 9 H); 0.93 (*s*, 3 H); 0.99 (*s*, 3 H); 1.21 (*dd*, *J* = 13, 9, 1 H); 1.96 (*dd*, *J* = 13, 8, 1 H); 2.06 (*dd*, *J* = 19, 7, 1 H); 2.33–2.41 (2 H); 2.61 (*dd*, *J* = 18, 6, 1 H); 2.65 (*dd*, *J* = 19, 10, 1 H); 2.72–2.83 (1 H); 2.92 (*dd*, *J* = 18, 4, 1 H); 3.54 (*d*, *J* = 7, 1 H). ^{13}C-NMR: –4.07 (*q*); –3.94 (*q*); 18.00 (*s*); 21.00 (*q*); 25.84 (*q*); 27.39 (*q*); 32.23 (*d*); 35.70 (*t*); 43.42 (*s*); 45.57 (*t*); 46.74 (*t*); 48.83 (*d*); 52.37 (*d*); 88.27 (*d*); 177.41 (*s*); 221.01 (*s*).

b) *From* **11**. Following the above protocol, **11** (98 mg, 0.28 mmol) gave identical **12** (92 mg, 98%).

*8-[(*tert*-Butyl)dimethylsilyloxy]bicyclo-[3.3.0]octan-3-one* (**13**). 4-(Dimethyla-mino)pyridine (56 mg, 0.46 mmol), *N*-hydroxy-2-thiopyridone (46 mg, 0.36 mmol), and then a soln. of 1,3-dicyclohexylcarbodiimide (95 mg, 0.46 mmol) in THF (1.5 ml) were successively added to a soln. of **12** (103 mg, 0.30 mmol) in THF (2 ml). Stirring of the mixture in the dark at r.t. for 3 h, addition of *t*-BuSH (0.34 ml, 3.0 mmol), irradiation with a 500 W tungsten lamp for 20 min, evaporation, chromatography on *Florisil* (hexane/Et_2O 9:1), dissolving the evaporated eluate in Et_2O, washing with 15% aq. HCl (2x) and evaporation of the dried Et_2O soln. afforded the nor-compound **13** (52 mg, 58%) as a pale yellow oil. IR: 2960, 2930, 2860, 1730, 1475, 1465, 1410, 1385, 1370, 1365, 1250, 1175, 1125, 1110, 1010, 875, 835, 775. ^{1}H-NMR: 0.05 (*s*, 3 H); 0.06 (*s*, 3 H); 0.91 (*s*, 9 H); 0.92 (*s*, 3 H); 0.98 (*s*, 3 H); 1.15 (*d*, *J* = 7, 3 H); 1.16 (*dd*, *J* = 13, 8.5, 1 H); 1.92 (*dd*, *J* = 13, 8.5, 1 H); 1.99 (*dd*, *J* = 19, 5.5, 1 H); 2.15–2.23 (2 H); 2.58 (*dd*, *J* = 19, 10, 1 H); 2.69–2.79 (1 H); 3.48 (*d*, *J* = 7, 1 H). ^{13}C-NMR: –4.19 (*q*); –4.02 (*q*); 17.31 (*q*); 18.06 (*s*); 21.08 (*q*); 25.85 (*q*); 27.33 (*q*); 31.65 (*d*); 43.40 (*s*); 44.29 (*t*); 46.66 (*t*); 48.09 (*d*); 54.63 (*d*); 87.79 (*d*); 222.73 (*s*). MS: 297 (0.4, $[C_{17}H_{32}O_2Si+1]^+$), 281 (0.6), 239 (14), 197 (1.0), 169 (3.7), 147 (10), 121 (11), 75 (100), 73 (29), 57 (11), 55 (11). Anal. calc. for $C_{17}H_{32}O_2Si$: C 68.86, H 10.88; found: C 68.74, H 10.80.

*2-Allyl-8-[(*tert*-Butyl)dimethylsilyloxy]-2,7,7-trimethylbicyclo[3.3.0]octan-3-one* (**2**). A soln. of **13** (42 mg, 0.14 mmol) in dimethoxyethane (1 ml) was added to a suspension of NaH (60% suspension in mineral oil, 8.1 mg, 0.20 mmol) in dimethoxyethane (0.5 ml), and the mixture was stirred at r.t. for 3 h. Addition of allyl bromide (0.12 ml, 1.4 mmol), stirring for 4 h, workup, and chromatography on *Florisil* (hexane/Et_2O 15:1) provided **2** (22 mg, 46%) as a colorless oil. IR ($CHCl_3$): 2960, 2930, 2860, 1730, 1640, 1470, 1460, 1410, 1350, 1335, 1290, 1260, 1110, 1010, 925, 870, 835. ^{1}H-NMR: 0.08 (*s*, 3 H); 0.10 (*s*, 3 H); 0.91 (*s*, 9 H); 0.94 (*s*, 3 H); 0.99 (*s*, 3 H); 1.02 (*dd*, *J* = 13, 2, 1 H); 1.10 (*s*, 3 H); 1.89 (*dd*, *J* = 13, 8.5, 1 H); 1.94 (*dd*, *J* = 19, 4.5, 1 H); 2.11 (*ddt*, *J* = 13, 7.5, 1, 1 H); 2.19 (*ddt*, *J* = 13.5, 7.5, 1, 1 H); 2.53 (*dd*, *J* = 10.5, 7.5, 1 H); 2.57 (*dd*, *J* = 19, 10.5, 1 H); 2.66–2.77 (1 H); 3.65 (*d*, *J* = 7.5, 1 H); 5.01–5.10 (2 H); 5.67 (*ddt*, *J* = 17, 10, 7.5, 1 H). ^{13}C-NMR: –4.19 (*q*); –2.74 (*q*); 18.49 (*s*); 18.90 (*q*); 21.04 (*q*); 26.22 (*q*); 27.15 (*q*); 30.38 (*d*); 42.97 (*s*); 43.49 (*t*); 45.68 (*t*); 47.41 (*t*); 51.05 (*s*); 55.63 (*d*); 82.88 (*d*); 118.49 (*t*); 133.51 (*d*); 222.89 (*s*). MS: 319 (1.1, $[C_{17}H_{32}O_2Si$ –17]$^+$), 279 (12), 237 (4.4), 187 (5.0), 107 (16), 95 (14), 93 (13), 75 (100), 73 (54), 59 (13), 57 (17), 55 (15).

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