# Anionically Induced Domino Reactions − Synthesis of a Norpatchoulenol-Type Terpene

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*Dedicated to Professor Henning Hopf on the occasion of his 60th birthday*

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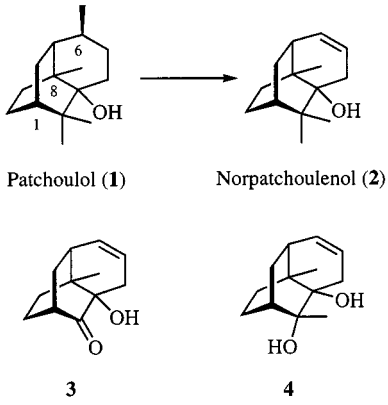
The tricyclic terpenoid compounds **3** and **4** were made from the functionalized bicyclo[2.2.2]octane **7**. The final ring was closed by an olefin metathesis reaction.

Patchoulol (**1**) is a major constituent of patchouli oil. Its regioselective microbial degradation gives norpatchoulenol (**2**), which was also found as a minor component in this essential oil. For olfactory reasons however, compound **2** is more interesting than compound **1** (Scheme 1).[1]




Patchoulol (**1**) Norpatchoulenol (**2**)

**3** **4**

Scheme 1

There are several very elegant and convergent syntheses published for both **1**[2] and **2**.[3−6] We considered an anionically induced domino reaction[7−9]as a key step in the synthesis of the tricyclic compounds **3** and **4**, which are structural analogues of norpatchoulenol (**2**).

The starting bicyclo[2.2.2]octanone **7** (Scheme 2), obtained from Li-**5** (kinetic controlled deprotonation of enone **5** with LDA/THF) and methyl acrylate (**6**)[10,11] was deprotonated with LDA and alkylated with allyl iodide in the presence of DMPU to give the allyl ketone **11** in moderate yield (55%). Allylation occurs exclusively from the *exo* face as indicated by a $^4J$ = 2.2 Hz coupling between 6-H and 4-H in the $^1$H NMR spectrum. Reduction (LAH in diethyl ether) of both of the carbonyls of **11** gave the diol **10** (95%, 70:30 mixture of epimers). Separation of the isomers at this stage seems to be unnecessary for the following steps. Oxidation of diol **10** with PCC in dichloromethane gave the sensitive aldehyde **9** which was immediately reacted with the ylide $Ph_3PCH_2$ (from methyltriphenylphophonium bromide and potassium *tert*-butoxide in THF[12]) to yield the olefin **8** (67% for two steps). The configuration at C-6 of compounds **8**−**11** remained unchanged during these synthetic steps (allyl sidechain *endo*, the attempted metathesis cyclization of di-olefin **8** failed, as expected). In order to introduce the *tertiary* hydroxyl group in the *endo* position at C-6, the intermediate enolate of ketone **8** (LDA, THF at −78 °C) was oxidized with Davis reagent[13] and oxygen.[14] Both reagents, however, gave mixtures of C-6 epimeric alcohols, so we turned to the bulkier reagent MoOPH in THF at −20 °C and obtained the alcohol **12** (62%) as a single isomer.[15] We could not handle the less toxic MoOPD[16] due to its thermally unstable character. Oxidation with this reagent occurred from the β side of the enolate Li-**8**. The configuration of C-6 was determinate by NOESY experiments which gave cross peaks of 3-H with one of the allylic methylene protons (1′-H's). Unfortunately, the cyclization of di-olefin **12** using Grubbs catalyst $[\{(Cy)_3P\}_2RuCl_2CHPh]$[17,18] failed (yield <5%) to form the tricyclic compound **3** due to de-oxygenation of the substrate (formation of **8**).[19] The alcohol **12** was easily silylated with TMS-imidazole to the TMS derivative **13** (97%) which was cyclized to give the tricyclic compound **14**. The protecting TMS group was sufficiently stable under the olefin metathesis reaction conditions (boiling benzene, argon, 12 h). Purification of tricyclic **14** turned out to be inconvenient, therefore we cleaved the TMS-protected **14** with TFA in aqueous THF to obtain **3** (78% for two steps). The addition of methyllithium (5 equiv. of 1.6 M MeLi in diethyl ether) to the tricyclic ketone **3** at 0 °C gives the diol **4** (75%) as a single compound. NOESY measurements (cross peaks for one 4-H and the methyl group at C-2) prove the β position of the methyl group.

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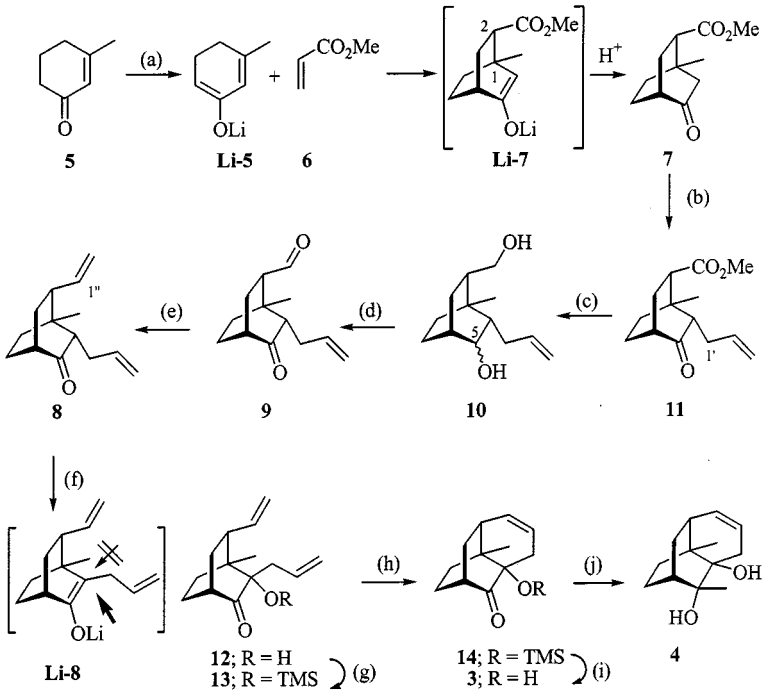


Scheme 2. (a) LDA, THF, Ar, −78 °C to 25 °C, 52%; (b) 1. LDA, THF, Ar, −78 °C, 2. DMPU (3 equiv.), 3. allyl iodide, −78 °C to 25 °C, 55%; (c) LAH, diethyl ether, 25 °C, Ar, 95%; (d) PCC, Ar, dichloromethane; (e) $Ph_3PCH_2$ (from $Ph_3PCH_3Br$ and KO*t*Bu), THF, Ar, 25 °C, 67%, [(d)+(e)]; (f) 1. LDA, THF, Ar, −78 °C, 2. MoOPH, THF,Ar, −20 °C, 62%; (g) TMS-imidazole, Ar, 100 °C, 97%; (h) Grubbs Ru catalyst, benzene, reflux, Ar, 12 h; (i) TFA/water/THF, Ar, 25 °C, 78% [(h)+(i)]; (j) 5 equiv. MeLi, THF, 0 °C, 1 h, 75%

## Experimental Section

**General Remarks:** THF was dried with benzophenone/sodium and distilled prior to use. Diisopropylamine was dried with calcium hydride and distilled. *n*-Butyllithium in *n*-hexane was titrated twice prior to use. − All reactions were performed under argon. − $^1$H NMR and $^{13}$C NMR: Varian $^{Unity}$INOVA-300, at 300 and 75.42 MHz, respectively − IR: Philips Infrared Spectrophotometer PU9516. − MS: Varian MAT 311 A, EI, 70 eV, low and high resolution. − GC: GC 8000 Series, Fisons Instruments, fused silica capillary column: DB 1, 10 m, methylsilicon rubber, nitrogen as carrier gas. − Melting points (not corrected): Büchi-SMP-20. − TLC: DC-aluminum foil, silica gel 60 $F_{254}$, Merck, Darmstadt. − Column chromatography: silica gel 60, 0.063−0.200 mm (70−220 mesh ASTM), Merck, Darmstadt. − Short path distillation: kugelrohr apparatus GKR-50, Fa. Büchi, Buchs, Switzerland. Temperatures are path temperatures. − Elemental analyses: Mikroanalytisches Laboratorium, Universität Stuttgart.

**Keto Ester 7:** This ester was prepared from 3-cyclohexenone (**5**) and methyl acrylate (**6**) as described previously. Yield 52%.

**Allyl Keto Ester 11:** A solution of keto ester **7** (7.00 g, 35.7 mmol) in anhydrous THF (20 mL) was added dropwise to a cold (−78 °C) solution of LDA (35.7 mmol) in THF (250 mL) [prepared from diisopropylamine (4.00 g, 35.7 mmol) and 2.1 M *n*-butyllithium (18.7 mL, 35.7 mmol) at −78 °C]; DMPU (10.0 mL, 39.3 mmol) was added after 20 min. Stirring was continued for a further 20 min at −78 °C and allyl iodide (3.6 mL, 6.60 g, 39.3 mmol) was added slowly. The stirred mixture was allowed to warm to room temp. overnight. The reaction mixture was diluted with diethyl ether (200 mL) and washed with saturated aqueous ammonium chloride solution and brine. The organic phase was dried ($MgSO_4$). Concentration gave an oily residue which was distilled (250 °C, 0.1 Torr, kugelrohr). The distillate was purified by column chromatography (silica gel, petroleum ether/ether, 2:1). Yield: 4.58 g (55%) **11** as a colorless oil. − IR (film): $\tilde{\nu}$ = 3084 cm$^{-1}$, 2945, 2870 (CH), 1720 (C=O), 1634 (C=C), 1453, 1431, 1365, 1210, 1168, 915. − $^1$H NMR ($CDCl_3$): δ = 0.88 (s, 3 H, C$H_3$), 1.24 (m, 1 H, 7-H), 1.65 (m, 3 H, 7-H, 8-H), 1.93 (m, 2 H, 7-H), 2.25 (m, 3 H, 1′-H, 4-H), 2.48 (dd, *J* = 10.2 Hz, *J* = 7.5 Hz, 1 H, 2-H), 2.66 (dt, *J* = 5.9 Hz, *J* = 2.2 Hz, 1 H, 6-H), 4.84 (dq, *J* = 10.1 Hz, *J* = 1.6 Hz, 1 H, 3′-H), 4.93 (dq, *J* = 17.1 Hz, *J* = 1.6 Hz, 1 H, 3′-H), 5.78 (ddt, *J* = 17.1 Hz, *J* = 10.1 Hz, *J* = 6.3 Hz, 1 H, 2′-H). − $^{13}$C NMR ($CDCl_3$): δ = 22.6 (q, $CH_3$), 23.5 (t, C-8), 23.6 (t, C-3), 26.6 (t, C-7), 29.8 (t, C-1′), 38.6 (s, C-1), 41.6 (d, C-4), 47.4 (d, C-2), 50.2 (d, C-6), 51.3 (q, $OCH_3$), 115.2 (d, C-2′), 137.6 (t, C-3′), 175.2 (s, ester), 216.8 (s, C-5). − MS (70 eV); *m*/*z* (%) = 236 (10) [$M^+$], 204 (10) [$M^+ - OCH_3$], 176 (8), 150 (100). − $C_{14}H_{20}O_3$ (236.3): calcd. C 71.16, H 8.53; found C 71.03, H 8.62.

**Diol 10:** A solution of keto ester **11** (2.00 g, 8.5 mmol) in diethyl ether (20 mL) was added drop wise at room temp. to a suspension of LAH (0.65 g, 17.0 mmol) in diethyl ether (100 mL) with stirring. After 2 h the excess of LAH was destroyed with ethyl acetate, followed by 15% aqueous solution of sodium hydroxide (5 mL). The resulting slurry was filtered, the filtrate concentrated, and the residue distilled. Yield 1.70 g (95%) of **10** (70:30 mixture of epimers) as a colorless oil. − IR (film): $\tilde{\nu}$ = 3320 cm$^{-1}$ (OH), 3038, 2925, 2870 (CH), 1638 (C=C),1468, 1380, 1040, 918. − **10-(α-OH)** $^1$H NMR ($CDCl_3$): δ = 0.88 (s, 3H, C$H_3$), 1.07 (m, 1 H, 3-H), 1.39−1.65 (m, 6 H, 7-H, 8-H, 3-H, 2-H, 6-H), 1.74 (m, 2 H, 4-H, 7-H or 8-H), 1.82 (m, 1 H, 1′′-H), 2.27 (m, 1 H, 1′′-H), 3.78 (m, 1 H, 5-H), 3.73 (m, 2 H, 1′-H), 5.09 (d, *J* = 10.1 Hz, 1 H, 3′′-H),

5.12 (d, $J$ = 17.1 Hz, 1 H, 3′′-H), 5.91 (dddd, $J$ = 17.1 Hz, $J$ = 10.1 Hz, $J$ = 8.6 Hz, $J$ = 5.7 Hz, 1 H, 2′′-H). − $^{13}$C NMR ($CDCl_3$): δ = 23.1 (q, $CH_3$), 23.7 and 24.0 (t, C-7 and C-8), 30.0 (t, C-3), 32.9 (d, C-4), 33.4 (s, C-1), 34.8 (t, C-1′′), 44.7 (d, C-2), 46.3 (d, C-6), 64.2 (t, C-1′), 75.4 (d, C-5), 116.4 (t, C-3′′), 137.8 (d, C-2′′). − **10-(β-OH)** $^1$H NMR ($CDCl_3$): δ = 0.88 (s, 3 H, C$H_3$), 1.18 and 1.38 (m, 1 H, 7-H and 8-H), 1.64 (m, 2 H, 3-H, 6-H), 1.89 (m, 4 H, 2-H, 4-H, 7-H, 8-H), 2.08 (m, 1 H, 1′′-H), 2.80 (m, 1 H, 1′′-H), 3.80 (m, 2 H, 1′-H), 4.03 (m, 1 H, 5-H), 5.20 (m, 2 H, 3′′-H), 6.00 (m, 1 H, 2′′-H). − $^{13}$C NMR ($CDCl_3$): δ = 19.4 and 28.4 (t, C-7 and C-8), 23.1 (q, $CH_3$), 28.7 (t, C-1′′), 30.0 (t, C-3), 31.1 (d, C-4), 32.3 (s, C-1), 39.9 (d, C-2), 43.5 (d, C-6), 64.6 (t, C-1′), 70.2 (d, C-5), 115.6 (t, C-3′′), 140.6 (d, C-2′′). − MS (70 eV); $m/z$ (%) = 210 (2) [$M^+$], 192 (45) [$M^+ - H_2O$], 174 (9) [$M^+ - 2\ H_2O$], 161 (11), 151 (22), 150 (20), 134 (70), 133 (50). − $C_{13}H_{22}O_2$ (210.3): HRMS calcd. 210.1620; found 210.1630.

**Aldehyde 9:** A solution of diol **10** (0.41 g, 2.0 mmol) in dichloromethane (10 mL) was added under stirring at room temp. to a suspension of pyridinium chlorochromate (PCC) (1.26 g, 5.9 mmol) in dichloromethane (10 mL). Stirring continued for 2 h. Diethyl ether (20 mL) was added to the black reaction mixture. The heterogeneous mixture was filtered through a pad of silica gel, the remaining cake washed with diethyl ether (3 × 20 mL), and the filtrate was concentrated to a yellow oil which was used directly in the next reaction.

**Olefin 8:** A solution of the crude aldehyde **9** (0.31 g, 1.5 mmol) in THF (5 mL) was added under stirring to solution of ylide $Ph_3PCH_2$ (1.7 mmol) [prepared from methyltriphenylphosphonium bromide (0.61 g, 1.7 mmol) and potassium *tert*-butoxide (0.18 g, 1.6 mmol) in THF (30 mL), under reflux for 30 min] at room temp. Stirring was continued overnight. The mixture was diluted with petroleum ether (100 mL) and the turbid mixture was washed with water. The organic phase was concentrated and the residue purified on silica gel (petroleum ether ether/diethyl ether, 9+1). Yield 0.27 g (67%, two steps) as a colorless oil. − IR (Film): $\tilde{\nu}$ = 3088 $cm^{-1}$, 2945, 2875 (CH), 1728 (C=O), 1628 (C=C), 1472, 1455, 1005, 920. − $^1$H NMR ($CDCl_3$): δ = 0.94 (s, 3 H, C$H_3$), 1.38 (m, 1 H, 3-H), 1.65 (m, 1 H, 7-H or 8-H), 1.7−1.9 (m, 3 H, 7-H, 8-H), 2.08 (ddd, $J$ = 13.9 Hz, $J$ = 10.9 Hz, $J$ = 3.0 Hz, 1 H, 7-H or 8-H), 2.23 (m, 2 H, 6-H, 2-H), 2.33 (m, 1 H, 4-H), 2.38 (pseudo-t, 2 H, 1′′-H), 4.98−5.14 (m, 4 H, 3′′-H), 5.75 (dt, $J$ = 16.7 Hz, $J$ = 9.6 Hz, 1 H, 1′-H), 5.96 (ddt, $J$ = 17.0 Hz, $J$ = 10.0 Hz, $J$ = 7.1 Hz, 1 H, 2′′-H). − $^{13}$C NMR ($CDCl_3$): 23.3 (q, $CH_3$), 23.8 (t, C-3), 29.7 and 30.0 (t, C-7, C-8), 30.6 (t, C-1′′), 38.2 (s, C-1), 42.6 (d, C-4), 47.2 (d, C-6), 51.5 (d, C-2), 115.4 and 116.0 (t, C-2′, C-3′′), 138.0 (d, C-1′), 139.3 (d, C-2′′), 218.5 (s, C-5). − MS (70 eV); $m/z$ (%) = 204 (50) [$M^+$], 163 (90) [$M^+ - C_3H_5$], 149 (100), 93 (50), 81 (45). − $C_{14}H_{20}O$ (204.3): calcd. C 82.29, H 9.87; found C 82.06, H 9.87.

**Alcohol 12:** To a solution of LDA (2.7 mmol) at −78 °C [prepared from diisopropylamine (0.27 g, 2.7 mmol) and 1.8 M *n*-butyllithium (1.5 mL, 2.7 mmol) at −78 °C] in THF (5 mL) was added a solution of **8** (0.44 g, 2.0 mmol) in THF (3 mL) under stirring. The reaction mixture was allowed to warm to −20 °C and after 30 min solid MoOPh (1.20 g, 3.1 mmol) was added. The blue reaction mixture was stirred for a further 30 min at room temp. after which a saturated aqueous solution of sodium sulfite (5 mL) was added under stirring. The mixture was extracted with diethyl ether (3× 50 mL), the organic phases were washed twice with water, saturated aqueous ammonium chloride and brine, dried ($MgSO_4$), and concentrated to yield an oily residue which was purified on silica gel (petroleum ether ether/diethyl ether, 9+1). Yield 0.28 g (62%) as a colorless oil. − IR (film): $\tilde{\nu}$ = 3500 $cm^{-1}$ (OH), 3080, 2950, 2890 (CH), 1720 (C=O), 1618 (C=C), 1445, 1425, 1380, 1125, 1090, 1003, 923. − $^1$H NMR ($CDCl_3$): δ = 1.04 (s, 3 H, C$H_3$), 1.26 (m, 1 H, 7-H or 8-H), 1.90 (m, 3 H, 7-H or 8-H, 3-H), 2.0−2.2 (m, 2 H, 7-H or 8-H, 3-H), 2.38 (m, 2 H, 1′′-H), 2.50 (m, 2 H, 2-H, 4-H), 5.08−5.26 (m, 4 H, 2′-H, 3′′-H), 5.89 (m, 1 H, 2′′-H), 6.07 (m, 1 H, 1′-H). − $^{13}$C NMR ($CDCl_3$): δ = 13.3 (q, $CH_3$), 25.6 and 31.1 (t, C-7 and C-8), 28.1 (t, C-3), 39.2 (t, C-1′′), 41.7 (d, C-4), 42.5 (s, C-1), 44.5 (d, C-2), 78.4 (C-6), 115.8 and 119.7 (t, C-3′′ and C-2′), 132.0 (d, C-2′′), 140.1 (d, C-1′), 219.4 (s, C-5). − MS (70 eV); $m/z$ (%) = 220 (10) [$M^+$], 192 (5) [$M^+ - CO$], 179 (66) [$M^+ - C_3H_5$], 151 (62), 123 (70). − $C_{14}H_{20}O_2$ (220.3): HRMS calcd. 220.1463; found 220.1456.

**Trimethylsilyl Ether 13:** A mixture of alcohol **12** (0.33 g, 1.5 mmol) and TMS-imidazole (0.58 mL, 0.56 g, 4.0 mmol) was kept at 100 °C for 2 h, cooled to room temp. and diluted with petroleum ether (20 mL). The organic phase was washed with water (2× 20 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated. Yield 0.42 g (97%) as a colorless oil. − IR (film): $\tilde{\nu}$ = 3077 $cm^{-1}$ (CH), 2952, 2872, 1731 (C=O), 1634 (C=C), 1455, 1376, 1248, 1147, 1117, 1067, 911, 841. − $^1$H NMR ($CDCl_3$): δ = 0.17 [s, 9 H, Si(C$H_3$)$_3$], 0.99 (s, 3 H, C$H_3$), 1.19 (m, 1 H, 7-H or 8-H), 1.85 (m, 4 H, 3-H, 7-H, 8-H), 2.10 (m, 1 H, 7-H or 8-H), 2.40 (m, 4 H, 1′′-H,2-H, 4-H), 5.0−5.2 (m, 4 H, 2′-H,3′′-H), 5.9−6.2 (m, 2 H, 1′-H, 2′′-H). − $^{13}$C NMR ($CDCl_3$): δ = 1.9 [q, Si($CH_3$)], 19.5 (q, $CH_3$), 24.0 (t, C-7 or 8), 28.5 (t, C-3), 32.1 (t, C-7/8), 40.6 (t, C-1′′), 42.3 (d, C-4), 43.9 (s, C-1), 44.1(d, C-2), 82.3 (s, C-6), 115.26 and 116.28 (t, C-2′ and C-3′′), 134.6 (d, C-2′′), 140.6 (d, C-1′), 217.7 (C-5). − MS (70 eV); $m/z$ (%) = 292 (1) [$M^+$], 277 (4) [$M^+$ − CH3], 264 (8) [$M^+ - CO$], 251 (35) [$M^+ - C_3H_5$], 223 (10), 181 (15), 169 (18). − $C_{17}H_{28}O_2Si$ (292.5): HRMS calcd. 292.1859; found 292.1877.

**Tricyclo[5.3.1.0$^{8,3}$]undecanone 14 and Tricyclo[5.3.1.0$^{8,3}$]undecanone 3:** To a solution of trimethylsilyl ether **13** (0.32 g, 1.1 mmol) in anhydrous and oxygen-free benzene (2 mL), Grubbs catalyst {[(Cy)$_3$P]$_2$RuCl$_2$CHPh} (45.1 mg, 0.54 mmol) was added and the mixture was heated to reflux for 12 h. The catalyst was filtered off (silica gel), the filtrate mixed with water (0.5 mL), THF (0.5 mL), and TFA (0.2 mL), and the whole mixture was stirred at room temp. overnight. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$, the organic layer was separated, dried ($MgSO_4$) and concentrated. Chromatographic separation (silica gel, petroleum ether ether/diethyl ether, 5+1) gave 0.16 g (78%, two steps) **3** as colorless crystals, m.p. 105 °C. − IR (KBr): $\tilde{\nu}$ = 3426 $cm^{-1}$ (OH), 3026, 2955, 2936, 2867 (CH), 1710 (C=O), 1094, 966, 711. − $^1$H NMR ($CDCl_3$): δ = 0.90 (s, 3 H, C$H_3$), 1.38 (m, 1 H, 7-H or 8-H), 1.53 (dd, $J$ = 12.1 Hz, $J$ = 4.4 Hz, 1 H, 3-H), 1.85−2.04 (m, 3 H, 7-H, 8-H), 2.06 (m,1 H, 3-H), 2.12 (d, $J$ = 17.0 Hz, 1 H, 11-H), 2.30 (dd, $J$ = 16.3 Hz, $J$ = 5.6 Hz, 1 H, 2-H), 2.36 (m, 1 H, 4-H), 2.38 (dd, $J$ = 17.0 Hz, $J$ = 4.8 Hz, 1 H, 11-H), 5.35 (m, 1 H, 9-H), 5.54 (m, 1 H, 10-H). − $^{13}$C NMR ($CDCl_3$): δ = 18.7 (q, CH3), 24.7 and 26.5 (t, C-7, C-8), 31.7 (t, C-3), 33.1 (t, C-11), 36.4 (s, C-1), 39.8 (d, C-2), 40.6 (d, C-4), 75.5 (s, C-6), 122.4 (d, C-9), 131.6 (d, C-10), 220.4 (s, C=O). − MS (70 eV); $m/z$ (%) = 192 (85) [$M^+$], 174 (60) [$M^+ - H_2O$], 164 (90) [$M^+ - CO$], 131 (70), 121. − HRMS calcd. 192.1150; found 192.1136. − $C_{12}H_{16}O_2$ (192.3): calcd. C 74.97, H 8.39; found C 74.95, H 8.47.

**Tricyclo[5.3.1.0$^{3,8}$]undecanole 4:** To a stirred solution of **3** (35.6 mg, 0.185 mmol) in THF (10 mL) at 0 °C was added a solution of 1.6 M of methyllithium in diethyl ether (1.2 mL, 1.85 mmol). Stirring was continued for 1 h. The reaction was quenched with sat. aqueous $NH_4Cl$ solution. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated. Chromatographic

separation (silica gel, petroleum ether/diethyl ether, 1:1) gave 28.8 mg (75%) as a colorless solid. – $^1$H NMR ($CDCl_3$): δ = 0.90 (s, 3 H, $CH_3$), 1.16 (pseudo dt, *J* = 12.9 Hz, *J* = 6.0 Hz, 1 H, 9-H or 10-H), 1.30 (m, 2 H, 9-H or 10-H, 11-H), 1.44 (s, 3 H, $CH_3$), 1.55 (m, 1 H, 1-H), 1.80 (t, *J* = 12.1 Hz, 1 H, 11-H), 1.88 (dt, *J* = 13.6 Hz, *J* = 2.8 Hz, 1 H, 9-H or 10-H), 2.02–2.18 (m, 2 H, 7-H, 9-H or 10-H), 2.16 (d, *J* = 18.2 Hz, 1 H, 4-H), 2.36 (dd, *J* = 18.2 Hz, *J* = 4.8 Hz, 1 H, 4-H), 5.55 (ddd, *J* = 9.7 Hz, *J* = 5.2 Hz, *J* = 2.2 Hz, 1 H, 5-H), 5.74 (m, 1 H, 6-H). – $^{13}$C NMR ($CDCl_3$): δ = 21.1 (t, C-9 or C-10), 21.4 (q, C*H*$_3$), 25.6 (q, C*H*$_3$), 27.3 (t, C-9 or C-10), 30.0 (t, C-11), 34.4 (t, C-4), 35.7 (s, C-8), 38.7 (d, C-1), 39.9 (d, C-4), 73.8 and 74.4 (d, C-5 and C-6). – MS (70 eV); *m*/*z* (%): 208 (5) [$M^+$], 190 (90) [$M^+ - H_2O$], 175 (50), 147 (62), 133 (42), 121 (62), 108 (85). – $C_{13}H_{20}O_2$ (208.3): HRMS calcd. 208.1463; found 208.1452.

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[18] This catalyst was a gift from BASF AG, Ludwigshafen (Rhein), Germany.
[19] The GC-MS shows several mono deoxygenated open chain products. We have no explanation for this unwanted reaction. The bulky TMS group, however, may have a beneficial conformational effect in the metathesis reaction (pre-organization of the substrate). We thank one of the referees for drawing our attention to this possibility.

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