Samarium Diiodide-Induced Couplings of Carbonyl Compounds with Methoxyallene Leading to 4-Hydroxy 1-Enol Ethers

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Experimental Conditions: All reactions were performed under argon atmosphere in flame dried flasks. Unless otherwise stated, materials were obtained from commercial suppliers and were used without further purification. Hexamethylphosphoramide was distilled and kept under argon. Tetrahydrofuran was freshly distilled from sodium/benzophenone under argon for each of the SmI_2 reactions.

General experimental procedure: Samarium (2.4 - 2.5 equiv) and 1,2-diiodoethane (2.2 equiv) were suspended in freshly distilled anhydrous THF (10 mL per mmol samarium) under an argon atmosphere and stirred for 2 h at room temperature. To the resulting dark blue solution HMPA (18 equiv) was added. Carbonyl compound **1** (1.0 equiv), methoxyallene (**6**) (2.0-3.0 equiv) and *tert*-butanol (2.0 equiv) were dissolved in anhydrous THF (15 mL per mmol **1**) and then added to the deep violet solution. After 16 h the mixture was quenched with saturated aqueous solution of sodium bicarbonate and water, the organic layer was separated and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed once with water and twice with brine, dried with anhydrous magnesium sulfate, filtered and evaporated. The resulting crude oil was purified by column chromatography on aluminum oxide (activity III) using hexane/ethyl acetate.

1-[(*Z*)-1-Benzyl(phenyl)ethenyl]cyclopentan-1-ol (5): According to the general procedure, the reaction was performed using diphenylallene **4** (0.192 g, 1.00 mmol) and cyclopentanone (**1a**) (0.076 g, 0.90 mmol). Chromatography on silica gel with hexane/ethyl acetate (95:5) gave **5** (0.173 g, 69%, dr > 97:3) as a colorless oil and a mixture of (*E*)- and (*Z*)-1,3-diphenylpropene (0.054 g, 28%, purity > 85%) as yellow oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.29-7.23, 7.20-7.16 (2 m, 8 H, 2 H, Ph), 7.02 (s, 1 H, 2'-H), 3.79 (s, 2 H, CH_2Ph), 1.88-1.78, 1.70-1.64 (2 m, 4 H, 4 H, 2-H, 3-H, 4-H, 5-H), 1.30 (br.s, 1 H, OH); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 144.0, 140.3, 137.5 (3 s, *i*-Ph, C-1'), 128.5, 128.4, 128.3, 126.7, 126.0 (5 d, Ph), 127.1 (d, C-2'), 85.6 (s, C-1), 39.9, 23.4 (2 t, C-2, C-3, C-4, C-5), 34.6 (t,

$\underline{C}H_2Ph$); IR (film): ν = 3420 cm^{-1} (O-H), 3080-3025 (=C-H), 2960-2870 (C-H), 1600-1495 (C=C); MS (EI, 80 eV, 40 °C) *m/z* (%) = 278 (M^+, 1), 260 (M^+ - H_2O, 4), 187 (M^+ - $CH_2C_6H_5$, 26), 170 (15), 169 (M^+ - $CH_2C_6H_5$ - H_2O, 100), 141 (42), 115 ($C_9H_7^+$, 20), 91 ($CH_2C_6H_5^+$, 50), 65 (10); $C_{20}H_{22}O$ (278.4) calcd. C 86.29, H 7.97; found C 86.51, H 7.81.

1-[(*E*)-3-Methoxyprop-2-enyl]cyclopentan-1-ol [(*E*)-7a] and 1-[(*Z*)-3-methoxyprop-2-enyl]cyclopentan-1-ol [(*Z*)-7a]: According to the general procedure, cyclopentanone (**1a**) (0.084 g, 1.00 mmol) and methoxyallene (**6**) (0.140 g, 2.00 mmol) were reacted with SmI_2. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (90:10 to 80:20) yielded a mixture of (*E*)-**7a** and (*Z*)-**7a** (0.133 g, 85%, *E*:*Z* = 60:40) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.38 (td, *J* = 1.1, 12.6 Hz, 1 H, 3'-H), 4.78 (td, *J* = 7.8, 12.6 Hz, 1 H, 2'-H), 3.55 (s, 3 H, OCH_3), 2.19 (dd, *J* = 1.1, 7.8 Hz, 2 H, 1'-H), 1.85-1.76, 1.67-1.53 (2 m, 3 H, 6 H, 2-H, 3-H, 4-H, 5-H, OH); (*Z*)-isomer: δ = 6.06 (td, *J* = 1.3, 6.3 Hz, 1 H, 3'-H), 4.48 (dt, *J* = 6.3, 7.7 Hz, 1 H, 2'-H), 3.60 (s, 3 H, OCH_3), 2.36 (dd, *J* = 1.3, 7.7 Hz, 2 H, 1'-H), 1.85-1.76, 1.67-1.53 (2 m, 3 H, 6 H, 2-H, 3-H, 4-H, 5-H, OH); ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 149.8 (d, C-3'), 97.8 (d, C-2'), 81.5 (s, C-1), 56.0 (q, OCH_3), 39.5 (t, C-1'); (*Z*)-isomer: δ = 148.3 (d, C-3'), 101.9 (d, C-2'), 82.0 (s, C-1), 59.5 (q, OCH_3), 35.6 (t, C-1'); the following signals could not be assigned to one of the isomers: δ = 39.2, 39.1, 23.9 (3 t, CH_2); IR (film): ν = 3425 cm^{-1} (O-H), 3060-3040 (=C-H), 2955-2830 (C-H), 1665 (C=C), 1655 (C=C); MS (EI, 80 eV, 30 °C) *m/z* (%) = 156 (M^+, 2), 85 ($C_5H_9O^+$, 46), 72 ($C_4H_8O^+$, 100), 71 (18), 67 (25), 57 ($C_3H_5O^+$, 12), 55 (11), 41 (18); HRMS (EI, 80 eV, 30 °C) calcd. for $C_9H_{16}O_2$ (M^+) 156.1150, found 156.1163.

1-[(*E*)-3-Methoxyprop-2-enyl]cyclohexan-1-ol [(*E*)-7b] and 1-[(*Z*)-3-methoxyprop-2-enyl]cyclohexan-1-ol [(*Z*)-7b]: Cyclohexanone (**1b**) (0.098 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol) were reacted with SmI_2 under the described conditions. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (90:10 to 75:25) afforded a mixture of (*E*)-**7b** and (*Z*)-**7b** (0.134 g, 79%, *E*:*Z* = 60:40) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.32 (td, *J* = 1.2, 12.6 Hz, 1 H, 3'-H), 4.76 (td, *J* = 7.9, 12.6 Hz, 1 H, 2'-H), 3.54 (s, 3 H, OCH_3), 2.05 (dd, *J* = 1.2, 7.8 Hz, 2 H, 1'-H), 1.65 (br.s, 1 H, OH), 1.61-1.33, 1.28-1.20 (2 m, 9 H, 1 H, 2-H, 3-H, 4-H, 5-H, 6-H); (*Z*)-isomer: δ = 6.06 (td, *J* = 1.3, 6.3 Hz, 1 H, 3'-H), 4.45 (dt, *J* = 6.3, 7.9 Hz, 1 H, 2'-H), 3.59 (s, 3 H, OCH_3), 2.23 (dd, *J* = 1.3, 7.9 Hz, 2 H, 1'-H), 1.69 (br.s, 1 H, OH), 1.61-1.33, 1.28-1.20 (2 m, 9 H, 1 H, 2-H, 3-H, 4-H, 5-H, 6-H); ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 149.7 (d, C-3'), 96.8 (d, C-2'), 70.8 (s, C-1), 56.0 (q, OCH_3), 40.4 (t, C-1'); (*Z*)-isomer: δ = 148.4 (d, C-3'), 101.1 (d, C-2'), 71.7 (s, C-1), 59.5 (q, OCH_3), 36.3 (t, C-1'); the following signals could not be assigned to one of the isomers: δ = 37.4, 37.2, 25.8, 25.8, 22.4, 22.2 (6 t, CH_2); IR (film): ν = 3435 cm^{-1} (O-H), 3060-3040 (=C-H), 3000-2855 (C-H), 1665 (C=C), 1655 (C=C); MS (EI, 80 eV, 30 °C) *m/z* (%) = 170 (M^+, 2), 99 ($C_6H_{11}O^+$, 38), 81 ($C_6H_9^+$, 37), 72 ($C_4H_8O^+$, 100), 71 ($C_4H_7O^+$, 12), 55 (14), 43 (10), 41 (12); HRMS (EI, 80 eV, 30 °C) calcd. for $C_{10}H_{18}O_2$ (M^+) 170.1307, found 170.1315; $C_{10}H_{18}O_2$ (170.3) calcd. C 70.55, H 10.66; found C 69.82, H 9.85.

***trans*-4-(*tert*-Butyl)-1-[(*E*)-3-methoxyprop-2-enyl]cyclohexan-1-ol [(*E*)-7c] and *trans*-4-(*tert*-butyl)-1-[(*Z*)-3-methoxyprop-2-enyl]cyclohexan-1-ol [(*Z*)-7c]:** According to the general procedure, 4-*tert*-butylcyclohexanone (**1c**) (0.463 g, 3.00 mmol) and **6** (0.630 g, 8.99 mmol) were reacted with SmI_2. The resulting crude oil was purified by column chromatography on aluminium oxide (activity III) using hexane/ethyl acetate (90:10 to 70:30) to furnish **1c** (0.188 g, 41%) and a mixture of (*E*)-**7c** and (*Z*)-**7c** (0.397 g, 58%, *E*:*Z* = 60:40, dr > 97:3) as colorless solid (mp: 49-50 °C).

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.34 (td, *J* = 1.1, 12.6 Hz, 1 H, 3'-H), 4.74 (td, *J* = 7.9, 12.6 Hz, 1 H, 2'-H), 3.55 (s, 3 H, OCH_3), 2.14 (dd, *J* = 1.1, 7.9 Hz, 2 H, 1'-H), 1.61 (br.s, 1 H, OH), 1.81-1.75, 1.70-1.66, 1.42-1.34, 1.13-1.02 (4 m, 2 H, 2 H, 2 H, 3 H, 2-H, 3-H, 4-H, 5-H, 6-H), 0.86 [s, 9 H, $C(CH_3)_3$]; (*Z*)-isomer: δ = 6.08 (td, *J* = 1.3, 6.3 Hz, 1 H, 3'-H), 4.45 (dt, *J* = 6.3, 7.9 Hz, 1 H, 2'-H), 3.59 (s, 3 H, OCH_3), 2.31 (dd, *J* = 1.3, 7.9 Hz, 2 H, 1'-H), 1.91 (br.s, 1 H, OH), 1.81-1.75, 1.70-1.66, 1.42-1.34, 1.13-1.02 (4 m, 2 H, 2 H, 2 H, 3 H, 2-H, 3-H, 4-H, 5-H, 6-H), 0.86 [s, 9 H, $C(CH_3)_3$]; ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 149.8 (d, C-3'), 96.7 (d, C-2'), 71.4 (s, C-1), 56.0 (q, OCH_3), 47.5 (d, C-4), 38.5, 38.2, 24.5, 24.3 (4 t, C-2, C-3, C-5, C-6), 34.8 (t, C-1'), 32.2, 27.6 [s, q, $C(CH_3)_3$]; (*Z*)-isomer: δ = 148.6 (d, C-3'), 101.1 (d, C-2'), 72.5 (s, C-1), 59.5 (q, OCH_3), 47.6 (d, C-4), 38.5, 38.2, 24.5, 24.3 (4 t, C-2, C-3, C-5, C-6), 36.1, 27.6 [s, q, $C(CH_3)_3$], 31.1 (t, C-1'); IR (KBr): ν = 3410 cm^{-1} (O-H), 3060-3040 (=C-H), 2940-2865 (C-H), 1655 (C=C) cm^{-1}; MS (EI, 80 eV, 30 °C) *m/z* (%) = 226 (M^+, 1), 155 (M^+ - C_4H_7O, 26), 95 (11), 81 (21), 72 ($C_4H_8O^+$, 100), 71 ($C_4H_7O^+$, 18), 69 (10), 67 (11), 57 [$C(CH_3)_3^+$, 44], 55 (10), 41 (19); HRMS (EI, 80 eV, 30 °C) calcd. for $C_{14}H_{26}O_2$ (M^+) 226.1933, found 226.1956; $C_{14}H_{26}O_2$ (226.4) calcd. C 74.29, H 11.58; found C 74.04, H 11.12.

8-[(*E*)-3-Methoxyprop-2-enyl]-1,4-dioxaspiro[4.5]decan-8-ol [(*E*)-7d] and 8-[(*Z*)-3-methoxyprop-2-enyl]-1,4-dioxaspiro[4.5]decan-8-ol [(*Z*)-7d]: According to the general procedure, the reaction was performed using 1,4-dioxaspiro[4.5]decan-8-one (**1d**) (0.156 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol). Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (85:15 to 70:30 to 50:50) yielded a mixture of (*E*)-**7d** and (*Z*)-**7d** (0.124 g, 54%, *E*:*Z* = 55:45) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.31 (d, *J* = 12.6 Hz, 1 H, 3'-H), 4.72 (td, *J* = 7.9, 12.6 Hz, 1 H, 2'-H), 3.92 (m_c, 4 H, 2-H, 3-H), 3.52 (s, 3 H, OCH_3), 2.05 (dd, *J* = 1.1, 7.9 Hz, 2 H, 1'-H), 1.91-1.84, 1.64-1.55 (2 m, 2 H, 6 H, 6-H, 7-H, 9-H, 10-H), 1.41 (br.s, 1 H, OH); (*Z*)-isomer:

δ = 6.05 (td, *J* = 1.2, 6.3 Hz, 1 H, 3'-H), 4.42 (dt, *J* = 6.3, 8.0 Hz, 1 H, 2'-H), 3.92 (m_c, 4 H, 2-H, 3-H), 3.56 (s, 3 H, OCH_3), 2.23 (dd, *J* = 1.2, 8.0 Hz, 2 H, 1'-H), 1.91-1.84, 1.64-1.55 (2 m, 2 H, 6 H, 6-H, 7-H, 9-H, 10-H), 1.69 (br.s, 1 H, OH); ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 105.1 (d, C-3'), 108.9 (s, C-5), 96.5 (d, C-2'), 69.7 (s, C-8), 64.2, 64.1 (2 t, 2-H, 3-H), 56.1 (q, OCH_3), 40.6 (d, C-1'); (*Z*)-isomer: δ = 148.7 (d, C-3'), 108.9 (s, C-5), 100.7 (d, C-2'), 70.8 (s, C-8), 64.2, 64.1 (2 t, 2-H, 3-H), 59.5 (q, OCH_3), 36.5 (t, C-1'); the following signals could not be assigned to one of the isomers: δ = 34.6, 34.5, 30.6, 30.5 (4 t, CH_2); IR (film): *ν* = 3480 cm^{-1} (O-H), 3040-3020 (=C-H), 2935-2885 (C-H), 1655 (C=C); MS (EI, 80 eV, 30 °C) *m/z* (%) = 228 (M^+, 3), 197 (M^+ - OCH_3, 11), 168 (M^+ - $C_2H_4O_2$, 3), 157 (M^+ - C_4H_7O, 4), 129 (M^+ - $C_5H_7O_2$, 100), 101 (38), 100 (18), 99 ($C_5H_7O_2^+$, 53), 87 (11), 86 (26), 72 ($C_4H_8O^+$, 30); HRMS (EI, 80 eV, 30 °C) calcd. for $C_{12}H_{20}O_4$ (M^+) 228.1362, found 228.1383; $C_{12}H_{20}O_4$ (228.3) calcd. C 63.14, H 8.83; found C 62.65, H 8.56.

***N*-(*tert*-Butoxycarbonyl)-4-[(*E*)-3-methoxyprop-2-enyl]piperidin-4-ol [(*E*)-7e] and *N*-(*tert*-butoxycarbonyl)-4-[(*Z*)-3-methoxyprop-2-enyl]piperidin-4-ol [(*Z*)-7e]:** BOC-protected piperdinone **1e** (0.199 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol) were reacted with SmI_2 under the described conditions. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (70:30 to 50:50) gave piperidin-4-ol (0.023 g, 11%) and a mixture of (*E*)-**7e** and (*Z*)-**7e** (0.137 g, 51%, *E*:*Z* = 50:50) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.34 (d, *J* = 12.6 Hz, 1 H, 3'-H), 4.73 (td, *J* = 7.9, 12.6 Hz, 1 H, 2'-H), 3.55 (s, 3 H, OCH_3), 2.07 (dd, *J* = 1.1, 7.9 Hz, 2 H, 1'-H); (*Z*)-isomer: δ = 6.08 (td, *J* = 1.2, 6.2 Hz, 1 H, 3'-H), 4.43 (dt, *J* = 6.2, 8.0 Hz, 1 H, 2'-H), 3.60 (s, 3 H, OCH_3), 2.24 (dd, *J* = 1.2, 8.0 Hz, 2 H, 1'-H); the following signals could not be assigned to one of the isomers: δ = 3.79, 3.18 (m, 4 H, 4 H, (*E*)/(*Z*)-2-H, (*E*)/(*Z*)-6-H), 1.81, 1.78 (2 br.s, 1 H, 1 H, (*E*)/(*Z*)-OH), 1.59-1.48 (m, 8 H, (*E*)/(*Z*)-3-H, (*E*)/(*Z*)-5-H), 1.46, 1.45 [2 s, 9 H, 9 H, (*E*)/(*Z*)-$C(CH_3)_3$]; ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 154.8 (s, CO), 150.2 (d, C-3'), 95.8 (d, C-2'), 56.9 (q, OCH_3), 41.0 (t, C-1'); (*Z*)-isomer: δ = 154.8 (s, CO), 148.8 (d, C-3'), 99.9 (d, C-2'), 59.5 (q, OCH_3), 36.8 (t, C-1'); the following signals could not be assigned to one of the isomers: δ = 79.2, 79.1, 28.4, 28.4 [2 s, 2 q, (*E*)/(*Z*)-$C(CH_3)_3$], 69.9, 68.9 (2 s, (*E*)/(Z)-C-4), 39.8 (br.t, (*E*)/(Z)-C-2, (*E*)/(Z)-C-6), 36.5, 36.3 (2 t, (*E*)/(*Z*)-C-3, (*E*)/(*Z*)-C-5); IR (film): *ν* = 3445 cm^{-1} (O-H), 3040-2830 (=C-H, C-H), 1695, 1670 (C=O, C=C); MS (EI, 80 eV, 80 °C) *m/z* (%) = 271 (M^+, 4), 239 (M^+ - CH_3OH, 1), 215 (M^+ - C_4H_8, 3), 198 (M^+ - C_4H_9O, 11), 144 (M^+ - C_4H_8 - C_4H_7O, 42), 142 (18), 100 ($C_5H_8O_2^+$, 34), 98 (13), 72 ($C_4H_8O^+$, 77), 71 ($C_4H_7O^+$, 13), 57 [$C(CH_3)_3^+$, 100], 56 (10), 55 (10), 43 (42); HRMS (EI, 80 eV, 80 °C) calcd. for $C_{14}H_{25}NO_4$ (M^+) 271.1784, found 271.1765; $C_{14}H_{25}NO_4$ (271.4) calcd. C 61.97, H 9.29, N 5.16; found C 61.59, H 8.95, N 5.05.

1-[(*E*)-3-Methoxyprop-2-enyl]cycloheptan-1-ol [(*E*)-7f] and 1-[(*Z*)-3-methoxy-prop-2-enyl]cycloheptan-1-ol [(*Z*)-7f] and 7-(methoxymethyl)bicyclo[4.2.1]nonan-1-ol (12f): According to the general procedure, cycloheptanone (**1f**) (0.112 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol) were reacted with SmI_2. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (90:10 to 75:25 to 50:50) yielded a mixture of (*E*)-**7f** and (*Z*)-**7f** (0.054 g, 29%, *E*:*Z* = 60:40) and **12f** (0.062 g, 34%, dr > 97:3) as colorless oils.

Analytical data of **7f**: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.33 (td, *J* = 1.2, 12.6 Hz, 1 H, 3'-H), 4.76 (td, *J* = 7.9, 12.6 Hz, 1 H, 2'-H), 3.55 (s, 3 H, OCH_3), 2.07 (dd, *J* = 1.2, 7.9 Hz, 2 H, 1'-H), 1.69-1.35 (m, 13 H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, OH); (*Z*)-isomer: δ = 6.06 (td, *J* = 1.3, 6.3 Hz, 1 H, 3'-H), 4.46 (dt, *J* = 6.3, 7.8 Hz, 1 H, 2'-H), 3.59 (s, 3 H, OCH_3), 2.24 (dd, *J* = 1.3, 7.8 Hz, 2 H, 1'-H), 1.69-1.35 (m, 13 H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, OH); ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 149.8 (d, C-3'), 97.2 (d, C-2'), 74.8 (s, C-1), 56.0 (q, OCH_3), 41.5 (t, C-1'); (*Z*)-isomer: δ = 148.4 (d, C-3'), 101.4 (d, C-2'), 75.7 (s, C-1), 59.5 (q, OCH_3), 37.5 (t, C-1'); the following signals could not be assigned to one of the isomers: δ = 40.9, 40.8, 29.8, 29.8, 22.4, 22.4 (6 t, CH_2); IR (film): ν = 3435 cm^{-1} (O-H), 3060-3040 (=C-H), 2995-2855 (C-H), 1655 (C=C); MS (EI, 80 eV, 30 °C) *m/z* (%) = 184 (M^+, 1), 113 (M^+ - C_4H_7O, 53), 95 (M^+ - $C_4H_9O_2$, 37), 72 ($C_4H_8O^+$, 100), 71 ($C_4H_7O^+$, 15), 69 (11), 55 (14), 43 ($C_2H_3O^+$, 10), 41 (20); HRMS (EI, 80 eV, 30 °C) calcd. for $C_{11}H_{20}O_2$ (M^+) 184.1463, found 184.1483; $C_{10}H_{18}O_2$ (184.3) calcd. C 71.70, H 10.94; found C 71.37, H 10.48.

Analytical data of **12f**: ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 3.30 (s, 3 H, OCH_3), AB part of ABX-system (δ_A = 3.24, δ_B = 3.19, J_{AB} = 8.9 Hz, J_{AX} = 7.5 Hz, J_{BX} = 6.5 Hz, each 1 H, 7-CH_2O), 2.07-2.04, 1.96-1.86, 1.83-1.75, 1.73-1.52, 1.48-1.32 (5 m, 1 H, 2 H, 3 H, 5 H, 4 H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, OH); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 82.3 (s, C-1), 78.4 (t, 7-CH_2O), 58.6 (q, OCH_3), 46.5 (d, C-6), 37.6 (d, C-7), 43.8, 43.6, 41.2, 34.2, 24.9, 23.0 (6 t, C-2, C-3, C-4, C-5, C-8, C-9); IR (film): ν = 3395 cm^{-1} (O-H), 2920-2735 (C-H); MS (EI, 80 eV, 60-80 °C) *m/z* (%) = 184 (M^+, 3), 166 (M^+ - H_2O, 3), 152 (M^+ - C_2H_5OH, 19), 139 (M^+ - CH_2OCH_3, 74), 127 (98), 111 (100), 95 (57), 83 (16), 67 (23), 55 (42), 45 (34), 43 (20), 41 (33); HRMS (EI, 80 eV, 70 °C) calcd. for $C_{11}H_{20}O_2$ (M^+) 184.1463, found 184.1473; $C_{10}H_{18}O_2$ (184.3) calcd. C 71.70, H 10.94; found C 70.87, H 10.74.

(*E*)- and (*Z*)-5-Methoxy-2-methylpent-4-en-2-ol [(*E*)-7g] and [(*Z*)-7g]: According to the general procedure, acetone (**1g**) (0.058 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol) were reacted with SmI_2. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (90:10 to 70:30) yielded a mixture of (*E*)-**7g** and (*Z*)-**7g** (0.034 g, 26%, *E*:*Z* = 65:35) as yellow oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.32 (td, *J* = 1.2, 12.6 Hz, 1 H, 5-H), 4.77 (td, *J* = 7.9, 12.6 Hz, 1 H, 4-H), 3.55 (s, 3 H, OCH_3), 2.07 (dd, *J* = 1.2, 7.9 Hz, 2 H, 3-H), 1.53

(br.s, 1 H, OH), 1.20 (s, 6 H, 1-H, 2-CH_3); (*Z*)-isomer: δ = 6.04 (td, *J* = 1.3, 6.3 Hz, 1 H, 5-H), 4.45 (dt, *J* = 6.3, 7.9 Hz, 1 H, 4-H), 3.59 (s, 3 H, OCH_3), 2.25 (dd, *J* = 1.3, 7.9 Hz, 2 H, 3-H), 1.75 (br.s, 1 H, OH), 1.21 (s, 6 H, 1-H, 2-CH_3); ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 149.8 (d, C-5), 97.7 (d, C-4), 70.2 (s, C-2), 56.1 (q, OCH_3), 41.9 (t, C-3), 28.8 (q, C-1, 2-CH_3); (*Z*)-isomer: δ = 149.3 (d, C-5), 101.8 (d, C-4), 71.0 (s, C-2), 59.5 (q, OCH_3), 38.1 (t, C-3), 28.9 (q, C-1, 2-CH_3); IR (film): ν = 3430 cm^{-1} (O-H), 2995-2915 (=C-H, C-H), 1655 (C=C); MS (EI, 80 eV, 30 °C) *m/z* (%) = 130 (M^+, 2), 115 (M^+ - CH_3, 11), 72 ($C_4H_8O^+$, 95), 71 ($C_4H_7O^+$, 22), 59 ($C_3H_7O^+$, 100), 57 (12), 45 (12), 43 ($C_2H_3O^+$, 33), 41 (30), 31 (OCH_3^+, 15); HRMS (EI, 80 eV, 30 °C) calcd. for $C_7H_{14}O_2$ (M^+) 130.0994, found 130.0986.

(*E*)- and (*Z*)-6-Methoxy-3-ethylhex-5-en-3-ol [(*E*)-7h] and [(*Z*)-7h]: Diethylketone (**1h**) (0.086 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol) were reacted with SmI_2 under the described conditions. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (100:0 to 80:20) afforded a mixture of **7h** (*E*:*Z* = 55:45) and 1-ethyl-3-(methoxymethyl)cyclopentan-1-ol (**12h**) (dr > 97:3) in a ratio of 85:15 (0.082 g, 52%, purity > 90 %) as colorless oil.

Analytical data of **7h**: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.30 (td, *J* = 1.0, 12.6 Hz, 1 H, 6-H), 4.69 (td, *J* = 7.9, 12.6 Hz, 1 H, 5-H), 3.52 (s, 3 H, OCH_3), 2.02 (dd, *J* = 1.0, 7.9 Hz, 2 H, 4-H), 1.48-1.41 (m, 4 H, CH_2), 1.31 (br.s, 1 H, OH), 0.85 (t, *J* = 7.5 Hz, 6 H, CH_3); (*Z*)-isomer: δ = 6.01 (td, *J* = 1.3, 6.3 Hz, 1 H, 6-H), 4.38 (dt, *J* = 6.3, 7.8 Hz, 1 H, 5-H), 3.57 (s, 3 H, OCH_3), 2.19 (dd, *J* = 1.3, 7.8 Hz, 2 H, 4-H), 1.60 (br.s, 1 H, OH), 1.48-1.41 (m, 4 H, CH_2), 0.85 (t, *J* = 7.5 Hz, 6 H, CH_3); ^{13}C-NMR ($CDCl_3$, 126 MHz) (*E*)-isomer: δ = 149.6 (d, C-6), 97.2 (d, C-5), 74.0 (s, C-3), 56.1 (q, OCH_3), 36.7 (t, C-4); (*Z*)-isomer: δ = 148.2 (d, C-6), 101.4 (d, C-5), 75.0 (s, C-3), 59.5 (q, OCH_3), 33.0 (t, C-4); the following signals could not be assigned to one of the isomers: δ = 30.8, 30.6 [2 t, (*E*)/(*Z*)-$\underline{C}H_2$], 7.9, 7.8 [2 q, (*E*)/(*Z*)-$\underline{C}H_3$]; IR (film): ν = 3460 cm^{-1} (O-H), 3060-3040 (=C-H), 2965-2830 (C-H), 1665-1655 (C=C); MS (EI, 80 eV, 40 °C) *m/z* (%) = 158 (M^+, 1), 129 (M^+ - C_2H_5, 3), 97 (16), 87 (M^+ - C_4H_7O, 57), 72 ($C_4H_8O^+$, 100), 71 ($C_4H_7O^+$, 22), 69 (25), 57 ($C_4H_9^+$, 53), 45 ($C_2H_5O^+$, 53), 43 ($C_2H_3O^+$, 15), 41 (27), 29 ($C_2H_5^+$, 25); HRMS (EI, 80 eV, 40 °C) calcd. for $C_9H_{18}O_2$ (M^+) 158.1307, found 158.1318.

The following signals in the proton-NMR of the mixture can be assigned to compound **12h**: δ = 3.40 (s, 3 H, OCH_3), 3.39 (m_c, 2 H, $C\underline{H}_2OCH_3$), 3.07 (br.s, 1 H, OH), 0.99 (t, *J* = 7.5 Hz, 3 H, CH_3).

(*E*)- and (*Z*)-6-Methoxy-2,2,3-trimethylhex-5-en-3-ol [(*E*)-7i] and [(*Z*)-7i] and 4-methoxymethyl-1,2,2-trimethylcyclopentan-1-ol (12i): According to the general procedure, pinacolone (**1i**) (0.088 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol) were reacted with SmI_2. Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (85:15 to 70:30) gave a mixture of **7i** (*E*:*Z* = 50:40) and 4-methoxymethyl-1,2,2-trimethylcyclopentan-1-ol (**12i**) (dr > 97:3) in a ratio of 20:80 (0.039 g, 22%) as colorless oil.

Analytical data of **12i**: ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 3.33 (s, 3 H, OCH_3), AB-part of ABX-system (δ_A = 3.29, δ_B = 3.27, J_{AB} = 8.6 Hz, J_{AX} = 3.9 Hz, J_{BX} = 3.7 Hz, each 1 H, 4-CH_2), 3.05 (br.s, 1 H, OH), 2.31-2.23 (m, 1 H, 4-H), 2.11 (dd, *J* = 11.4, 14.2 Hz, 1 H, 5-H), 1.65 (dd, *J* = 8.8, 12.8 Hz, 1 H, 3-H), 1.53 (dd, *J* = 3.2, 14.2 Hz, 1 H, 5-H), 1.48 (dd, *J* = 9.0, 12.8 Hz, 1 H, 3-H), 1.08, 0.94, 0.83 (3 s, each 3 H, 1-CH_3, 2-CH_3, 2-CH_3); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 81.0 (s, C-1), 76.1 (t, 4-CH_2), 58.9 (q, OCH_3), 46.2 (s, C-2), 42.6 (t, C-5), 41.2 (t, C-3), 33.7 (d, C-4), 25.9, 21.1, 20.4 (3 q, 1-CH_3, 2-CH_3, 2-CH_3); IR (film): *ν* = 3475 cm^{-1} (O-H), 2940-2870 (C-H); MS (EI, 80 eV, 60 °C) *m/z* (%) = 172 (M^+, 6), 154 (M^+ - H_2O, 2), 139 (M^+ - CH_3 - H_2O, 3), 127 (M^+ - CH_2OCH_3, 71), 83 (27), 75 (14), 72 ($C_4H_8O^+$, 12), 71 ($C_4H_7O^+$, 66), 56 (16), 55 (19), 45 ($C_2H_5O^+$, 16), 43 ($C_2H_3O^+$, 100), 41 (21); HRMS (EI, 80 eV, 60 °C) calcd. for $C_{10}H_{20}O_2$ (M^+) 172.1463, found 172.1482.

The following signals in the proton-NMR of the mixture can be assigned to compound **7i**: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.27 (d, *J* = 12.4 Hz, 1 H, 6-H), 4.76 (td, *J* = 7.9, 12.4 Hz, 1 H, 5-H), 3.52 (s, 3 H, OCH_3); (*Z*)-isomer: δ = 6.03 (d, *J* = 6.4 Hz, 1 H, 6-H), 4.46 (dt, *J* = 6.4, 7.6 Hz, 1 H, 5-H), 3.55 (s, 3 H, OCH_3); the following signals could not be assigned to one of the isomers: δ = 1.06, 1.05 (2 s, each 3 H, (*E*)/(*Z*)-3-CH_3), 0.92, 0.91 [2 s, each 9 H, (*E*)/(*Z*)-$C(CH_3)_3$].

(*E*)- and (*Z*)-1-Methoxydec-1-en-4-ol [(*E*)-7j] and [(*Z*)-7j]: In accordance with the general procedure, the reaction was performed with heptanal (**1j**) (0.114 g, 1.00 mmol) and **6** (0.140 g, 2.00 mmol). Chromatography on aluminum oxide (activity III) using hexane/ethyl acetate (90:10 to 80:20) yielded a mixture of (*E*)-**7j** and (*Z*)-**7j** (0.081 g, 43%, *E*:*Z* = 55:45) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) (*E*)-isomer: δ = 6.33 (d, *J* = 12.6 Hz, 1 H, 1-H), 4.68 (ddd, *J* = 7.0, 8.2, 12.6 Hz, 1 H, 2-H), 3.52-3.47 (m, 1 H, 4-H), 3.51 (s, 3 H, OCH_3), 2.14 (dddd, *J* = 1.2, 4.2, 7.0, 14.0 Hz, 1 H, 3-H), 1.95 (dddd, *J* = 0.7, 7.7, 8.2 14.0 Hz, 1 H, 3-H), 1.69 (d, *J* = 3.7 Hz, 1 H, OH), 1.45-1.23 (m, 10 H, 5-H, 6-H, 7-H, 8-H, 9-H), 0.86 (t, *J* = 6.9 Hz, 3 H, 10-H); (*Z*)-isomer: δ = 6.00 (td, *J* = 1.3, 6.3 Hz, 1 H, 1-H), 4.39 (dt, *J* = 6.3, 7.5 Hz, 1 H, 2-H), 3.61-3.56 (m, 1 H, 4-H), 3.57 (s, 3 H, OCH_3), 2.22-2.18 (m, 2 H, 3-H), 1.84 (d, *J* = 4.0 Hz, 1 H, OH), 1.45-1.23 (m, 10 H, 5-H, 6-H, 7-H, 8-H, 9-H), 0.86 (t, *J* = 6.9 Hz, 3 H, 10-H); ^{13}C-NMR ($CDCl_3$, 125 MHz) (*E*)-isomer: δ = 149.4 (d, C-1), 98.2 (d, C-2), 71.4 (d, C-4), 56.0 (q, OCH_3), 35.7 (t, C-3), 14.0 (q, C-10); (*Z*)-isomer: δ = 148.2 (d, C-1), 102.1 (d, C-2), 71.7 (d, C-4), 60.0 (q, OCH_3), 31.8 (t, C.3), 14.0 (q, C-10); the following signals could not be assigned to one of the isomers: δ = 36.9, 36.5, 32.0, 31.8, 29.3, 29.3, 25.7, 25.6, 22.6 (9 t, C-5, C-6, C-7, C-8, C-9); IR (film): *ν* = 3440 cm^{-1} (O-H), 3040 (=C-H), 2960-2830 (C-H), 1655 (C=C); MS (EI, 80 eV, 30 °C) *m/z* (%) = 186 (M^+, 1), 185 (M^+ - H, 2), 155 (M^+ - OCH_3, 14), 137 (M^+ - H_2O, 2), 101 (M^+ - $C_5H_9O_2^+$, 100), 72 ($C_4H_8O^+$, 28), 69 (34), 55 (14), 43 (11), 41 (17); HRMS (EI, 80 eV, 30 °C) calcd. for $C_{10}H_{19}O$ (M^+ - OCH_3) 155.1436, found 155.1453; $C_{11}H_{22}O_2$ (186.3) calcd. C 70.92, H 11.90; found C 70.94, H 11.65.

***trans*-8-(*tert*-Butyl)-1-oxaspiro[4.5]decan-2-one (13):** A solution of enol ether **7c** (0.048 g, 0.21 mmol) in THF (5 mL) and 10 % sulfuric acid (0.5 mL) was stirred 18 hours at room temperature. Saturated aqueous sodium bicarbonate solution (2 mL) was added and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The organic layer was dried with sodium sulfate, filtered and evaporated to yield the corresponding lactol (0.040 g, quant) as colorless solid. The crude product was dissolved in dichloromethane (2 mL) under argon, 4 Å molecular sieves (0.050 g) and PCC (0.083 g, 0.38 mmol) were added and the mixture was stirred at room temperature overnight. The mixture was diluted with diethyl ether and filtered over Florisil. The solvents were removed in vacuo to afford crude **13** (0.040 g, quant). Chromatography on silica gel using hexane/ethyl acetate (60:40) gave **13** (0.037 g, 86 % over two steps, dr > 97:3) as colorless solid (mp. 95-97 °C, 97-98 °C in ref 12).

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 2.58 (t, J = 8.3 Hz, 2 H, 3-H), 2.06 (t, J = 8.3 Hz, 2 H, 4-H), 1.84-1.81, 1.77-1.71, 1.13-1.05 (3 m, 4 H, 2 H, 3 H, 6-H, 7-H, 8-H, 9-H, 10-H), 0.87 [s, 9 H, $C(CH_3)_3$]; ^{13}C-NMR ($CDCl_3$, 126 MHz) δ = 176.6 (s, C-2), 87.2 (s, C-5), 46.7 (t, C-3), 36.8 (d, C-8), 32.2, 27.5 [s, q, $C(CH_3)_3$], 30.2, 28.6, 24.1 (3 t, C-4, C-6, C-7, C-9, C-10).

***trans*-2-Allyl-8-(*tert*-butyl)-1-oxaspiro[4.5]decane (14):** A solution of enol ether **7c** (0.054 g, 0.24 mmol) in THF (5 mL) and 10 % sulfuric acid (0.5 mL) was stirred 10 hours at room temperature. Saturated aqueous sodium bicarbonate solution (2 mL) was added and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The organic layer was dried with sodium sulfate, filtered and evaporated to yield the corresponding lactol (0.050 g, quant) as colorless solid. The crude product was dissolved in dichloromethane (1 mL) under argon and cooled to -78 °C. Allyltrimethylsilane (0.042 mL, 0.030 g, 0.26 mmol) and boron trifluoride etherate (0.033 mL, 0.037 g, 0.26 mmol) were added and the mixture was stirred 45 min at -78 °C and then 5 h at room temperature. After addition of water (1 mL) the solution was extracted with dichloromethane (3 x 5 mL). The organic layer was dried with magnesium sulfate, filtered and the solvent was removed in vacuo. Chromatography on silica gel using hexane/ethyl acetate (100:0 to 94:6) yielded **14** (0.044 g, 79%, over two steps) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 5.80 (tdd, J = 7.0, 10.2, 17.1 Hz, 1 H, 2'-H), AB-part of ABXY-system (δ_A = 5.06, δ_B = 5.02, J_{AB} = 2.2 Hz, J_{AX} = 17.1 Hz, J_{BX} = 10.2 Hz, J_{AY} = J_{BY} = 1.3 Hz, each 1 H, 3'-H), 3.99 (m_c, 1 H, 2-H), 2.37 (tddd, J = 1.3, 5.6, 7.0, 13.7 Hz, 1 H, 1'-H), 2.19 (tddd, J = 1.3, 6.9, 7.0, 13.7 Hz, 1 H, 1'-H), 1.95 (dddd, J = 4.5, 5.9, 7.7, 12.2 Hz, 1 H, 3-H), 1.77-1.41, 1.05-0.96 (2 m, 9 H, 3 H, 3-H, 4-H, 6-H, 7-H, 8-H, 9-H, 10-H), 0.83 [s, 9 H, $C(CH_3)_3$]; ^{13}C-NMR ($CDCl_3$, 126 MHz): δ = 135.1 (d, C-2'), 116.6 (t, C-3'), 83.4 (s, C-5), 77.1 (d, C-2), 47.3 (d, C-8), 40.8

(t, C-1'), 38.7, 38.2, 33.8, 31.0, 25.8, 25.2 (6 t, C-3, C-4, C-6, C-7, C-9, C-10), 32.3, 27.7 [s, q, $C(CH_3)_3$]; IR (film): ν = 3075 cm^{-1} (=C-H), 2940-2860 (C-H), 1640 (C=C); MS (EI, 80 eV, 60 °C) *m/z* (%) = 236 (M^+, 1), 221 (M^+ - CH_3, 1), 196 (14), 195 (M^+ - C_3H_5, 100), 177 (M^+ - C_4H_{11}, 55), 137 (61), 121 (26), 107 (11), 95 (20), 93 (11), 83 (17), 81 (17), 69 (16), 67 (24), 57 ($C_4H_9^+$, 79), 55 (36), 43 (12), 41 ($C_3H_5^+$, 32); HRMS (EI, 80 eV, 60 °C) calcd. for $C_{16}H_{28}O$ (M^+) 236.2140, found 236.2178; $C_{16}H_{28}O$ (236.4) calcd. C 81.29, H 11.94; found C 81.28, H 12.09.

***trans*-3-[4-(*tert*-Butyl)-1-(*tert*-butyldimethylsilyloxy)cyclohexyl]prop-2-enal (15):** Compound **7c** (0.300 g, 1.33 mmol) was dissolved in dry dichloromethane (3 mL) under argon and subsequently, triethylamine (0.24 mL, 0.175 g, 1.73 mmol), DMAP (0.010 g, 0.082 mmol) and TBSOTf (0.41 mL, 0.470 g, 1.8 mmol) were added. The mixture was stirred for 24 h at room temperature and then quenched with saturated aqueous ammonium chloride solution. The aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried with magnesium sulfate, filtered and the solvent was removed in vacuo. Chromatography on aluminium oxide (activity III) using pure hexane gave TBS-protected product (0.331 g, 73% , *E*:*Z* = 60:40) as colorless oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz): (*E*)-isomer: δ = 6.26 (d, *J* = 12.8 Hz, 1 H, 3'-H), 4.82 (td, *J* = 7.4 Hz, 12.8 Hz, 1 H, 2'-H), 3.52 (s, 3 H, OCH_3), 2.09 (dd, *J* = 0.7, 7.4 Hz, 2 H, 1'-H), 1.80-1.78, 1.63-1.59, 1.41-1.35, 1.16-1.07, 1.05-0.94 (5 m, 2 H, 2 H, 2 H, 1 H, 2 H, 2-H, 3-H, 4-H, 5-H, 6-H), 0.86 [s, 9 H, 4-$C(CH_3)_3$], 0.84 [s, 9 H, $SiC(CH_3)_3$], 0.07 [s, 6 H, $Si(CH_3)_2$]; (*Z*)-isomer: δ = 5.94 (td, *J* = 1.5, 6.3 Hz, 1 H, 3'-H), 4.52 (dt, *J* = 6.3, 7.1 Hz, 1 H, 2'-H), 3.55 (s, 3 H, OCH_3), 2.28 (dd, *J* = 1.3, 7.1 Hz, 2 H, 1'-H), 1.80-1.78, 1.63-1.59, 1.41-1.35, 1.16-1.07, 1.05-0.94 (5 m, 2 H, 2 H, 2 H, 1 H, 2 H, 2-H, 3-H, 4-H, 5-H, 6-H), 0.85 [s, 9 H, 4-$C(CH_3)_3$], 0.84 [s, 9 H, $SiC(CH_3)_3$], 0.06 [s, 6 H, $Si(CH_3)_2$]; ^{13}C-NMR ($CDCl_3$, 62.9 MHz) (*E*)-isomer: δ = 147.9 (d, C-3'), 98.9 (d, C-2'), 75.4 (s, C-1), 55.7 (q, OCH_3), 47.5 (d, C-4), 39.1, 38.7, 24.5, 24.5 (4 t, C-2, C-3, C-5, C-6), 35.6 (t, C-1'); (*Z*)-isomer: δ = 146.8 (d, C-3'), 103.3 (d, C-2'), 75.5 (s, C-1), 59.3 (q, OCH_3), 47.6 (d, C-4), 39.1, 38.7, 24.5, 24.5 (4 t, C-2, C-3, C-5, C-6), 32.3 (t, C-1'); the following signals could not be assigned to one of the isomers: δ = 35.5, 31.7, 27.6, 27.6 [2 s, 2 q, $C(CH_3)_3$], 25.9, 25.9, 18.2, 18.2 [2 q, 2 s, $SiC(CH_3)_3$], -1.7, -1.8 [2 q, $Si(CH_3)_2$]; IR (film) ν = 3065-3045 cm^{-1} (=C-H), 2950-2855 (C-H), 1655 (C=C); MS (EI, 80 eV, 40 °C) *m/z* (%) = 340 (M^+, 1), 325 (M^+ - CH_3, 1), 283 [M^+ - $C(CH_3)_3$, 2], 270 (23), 269 (M^+ - C_4H_7O, 100), 75 (C_2H_7O Si^+, 34), 73 ($C_4H_9O^+$, 38), 71 ($C_4H_7O^+$, 12), 57 [$C(CH_3)_3^+$, 11]; HRMS (EI, 80 eV, 40 °C) calcd. for $C_{19}H_{37}O_2Si$ (M^+ - CH_3) 325.2563, found 325.2561; $C_{20}H_{40}O_2Si$ (340.6) calcd. C 70.52, H 11.84; found C 70.77, H 11.50.

Palladium(II) acetate (0.013 g, 0.058 mmol) was dissolved in acetonitrile (0.5 mL) and susbsequently 5% aqueous sodium bicarbonate solution (0.04 mL) and cooper(II) acetate (0.024 g, 0.12 mmol) were added. The mixture was cooled to 0 °C, a solution of the TBS-protected product (0.040 g, 0.12 mmol) in acetonitrile (0.3 mL) was added dropwise and the mixture was stirred 1 h at 0 °C and then 1 h at room temperature. The mixture was poured into saturated aqueous ammonium chloride solution (2 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with magnesium sulfate, filtered and evaporated to afford crude **15** (0.030 g, 77%, purity > 85 %). Chromatography on silica gel using hexane/ethyl acetate (100:0 to 90:10) gave **15** (0.020 g, 51%, purity > 95 %) as a single diastereomer [(*E*)/(*Z*) > 97:3] as a yellow oil.

Analytical data: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ = 9.59 (d, *J* = 7.9 Hz, 1 H, 1-H), 7.00 (d, *J* = 15.6 Hz, 1 H, 3-H), 6.33 (dd, *J* = 7.9, 15.6 Hz, 1 H, 2-H), 1.96-1.93, 1.77-1.73, 1.70-1.65, 1.49-1.06 (4 m, 2 H, 2 H, 2 H, 3 H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H), 0.87, 0.85 [2 s, 9 H, 9 H, 4'-$C(CH_3)_3$, $SiC(CH_3)_3$], 0.08 [s, 6 H, $Si(CH_3)_2$]; ^{13}C-NMR ($CDCl_3$, 126 MHz) δ = 194.3 (d, C-1), 161.8 (d, C-3), 130.7 (d, C-2), 74.8 (s, C-1'), 47.5 (d, C-4'), 39.7, 24.7 (2 t, C-2', C-3', C-5', C-6'), 32.3, 27.6 [s, q, 4'-$C(CH_3)_3$], 25.8, 18.2 [q, s, $SiC(CH_3)_3$], -1.7 [s, $Si(CH_3)_2$]; IR (film) ν = 2955-2725 cm^{-1} (=C-H, C-H), 1695 (C=O), 1635 (C=C); MS (EI, 80 eV, 50 °C) *m/z* (%) = 324 (M^+, 2), 309 (M^+ - CH_3, 3), 295 (M^+ - CHO, 2), 269 (18), 268 (22), 267 [M^+ - $C(CH_3)_3$], 131 ($OSiC_6H_{15}^+$, 33), 129 (17), 75 ($OSiC_2H_7^+$, 61), 73 (30), 57 [$C(CH_3)_3^+$, 31], 41 (13); HRMS (EI, 80 eV, 50 °C) calcd. for $C_{19}H_{36}O_2Si$ (M^+) 324.2485, found 324.2456.